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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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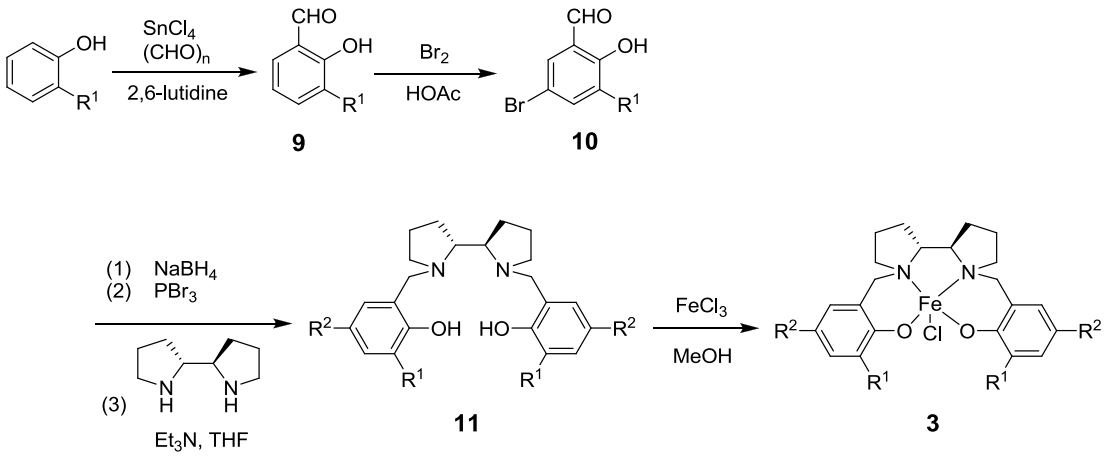
## General information

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, $Et_2O$, benzene, dioxane, cyclohexane), or calcium hydride (DCM, DCE, EA, MeCN) under an argon atmosphere and collected by distillation. $^1H$ and $^{13}C$ NMR spectra were recorded on a Varian Mercury 300 (300 MHz) or Bruker AM 400 (400 MHz) spectrometer. $^1H$ and $^{13}C$ NMR spectra were referenced internally to residual protio-solvent ($^1H$) or solvent ($^{13}C$) 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'-Bipyrrolidine[1,2] was synthesized according to the literature procedures. All other reagents were commercially available and used as received.

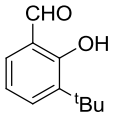
## I. Preparation of the iron complexes



Synthesis of salicylaldehyde **10**[3-4]

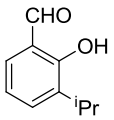
At room temperature, tin(IV) tetrachloride (0.4 mL) was added to a solution of phenol (33.3 mmol) and 2,6-lutidine (23.4 mmol) in freshly distilled toluene (30 mL) under a argon atmosphere. After the addition was complete, the mixture was stirred at room temperature for a further 30 min. Paraformaldehyde (2.2 g) was then introduced and the resulting yellowish solution was heated to 100 $^{o}$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.




**9c**

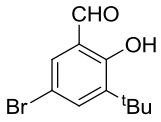
Yield: 73% (4.30 g); $^1$H NMR (300 MHz, $CDCl_3$): δ 11.80 (s, 1H), 9.88 (s, 1H), 7.54 (dd, *J* = 1.2, 7.4 Hz, 1H), 7.41 (dd, *J* = 1.2, 7.8 Hz, 1H), 6.95 (t, *J* = 7.8 Hz, 1H), 1.42 (s, 9H); MS (EI): *m/z* 178 ($M^+$), 164 (14.82), 163 (100.00), 135 (60.44), 115 (14.18), 107 (22.30), 91 (16.47), 77 (12.92).




**9d**

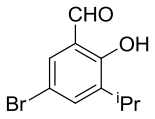
Yield: 65% (3.55 g); $^1$H NMR (300 MHz, $CDCl_3$): δ 11.38 (s, 1H), 9.89 (s, 1H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.40 (dd, *J* = 2.1, 7.8 Hz, 1H), 6.99 (t, *J* = 7.2 Hz, 1H), 3.35-3.41

(m, 1H), 1.25 (d, $J$ = 7.2 Hz, 6H); MS (ESI): *m/z* 165.0 $[M+1]^+$.




**10c**

Yield: 90% (21.3 g); $^1$H NMR (300 MHz, $CDCl_3$): δ 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).




**10d**

Yield: 84% (18.8 g); $^1$H NMR (300 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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, 1261, 1207, 973, 766, 720, 701 $cm^{-1}$.

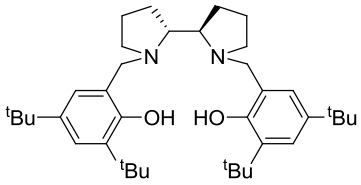
Synthesis of ligand **11**[5-6]

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 × 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 × 50 mL). The combined extracts

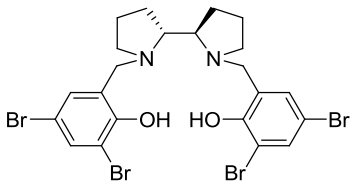
were dried over anhydrous $MgSO_4$, concentrated, and dried in vacuo to give a pale-yellow liquid, which was used without further purification.

$Et_3N$ (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 $Et_3N \cdot HBr$, 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.




**11a**

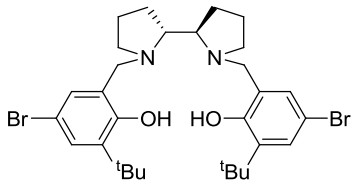
Yield: 67% (494 mg); $^1$H NMR (300 MHz, $CDCl_3$): δ 7.23 (d, *J* = 2.1 Hz, 2H), 6.81 (d, *J* = 2.1 Hz, 2H), 4.00 (d, *J* = 13.5 Hz, 2H), 3.38 (d, *J* = 13.5 Hz, 2H), 3.07-3.04 (m, 2H), 2.77-2.74 (m, 2H), 2.23-2.19 (m, 2H), 1.99 (m, 2H), 1.81-1.73(m, 6H), 1.41 (s, 18H) , 1.28 (s, 18H); MS (ESI): *m/z* 577.3 $[M+1]^+$.




**11b**

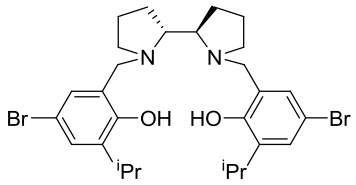
Yield: 55% (471 mg); m.p.($^o$C): 224-226; $^1$H NMR (300 MHz, $CDCl_3$): δ 7.56 (d, *J* = 1.9 Hz, 2H), 7.06 (d, *J* = 1.9 Hz, 2H), 4.24 (d, *J* = 14.1 Hz, 2H), 3.37 (d, *J* = 14.1 Hz, 2H), 3.10-3.05 (m, 2H), 2.99-2.95 (m, 2H), 2.28-2.23 (m, 2H), 2.13-2.08 (m, 2H), 1.91-1.80 (m, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ153.67, 134.08, 129.72, 124.68, 110.69, 64.60, 57.46, 54.81, 25.20, 23.57; IR (KBr): $\nu_{max}$3445, 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 $[C_{22}H_{25}N_2O_2Br_4^+]$ Calcl. 664.8644, Found: 664.8659; $[\alpha]^D_{25}$:+61.1(c= 1.02, solv:

$CHCl_3$).



**11c**

Yield: 70% (557 mg); m.p.($^oC$): 176-178; $^1H$ NMR (300 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ155.72, 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: $[C_{30}H_{43}N_2O_2Br_2^+]$ Calcl. 621.1686, Found: 621.1687; $[\alpha]^D_{25}$: +36.6 (c= 0.89, solv: $CHCl_3$).

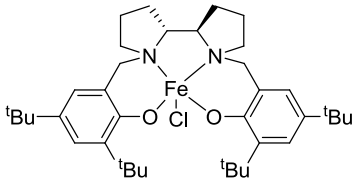


**11d**

Yield: 62% (472 mg); m.p.($^oC$): 170-172; $^1H$ NMR (300 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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 $[C28H39N2O2Br2]^+$ Calcl. 593.1373, Found: 593.1363; $[\alpha]^D_{20}$: +81.7 (c= 0.91, solv: $CHCl_3$).

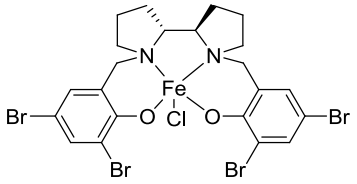
Synthesis of iron complex **3**

$FeCl_3$ (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 $Na_2SO_4$ and concentrated. The complex was obtained by recrystallization of the residue in DCM and hexane.



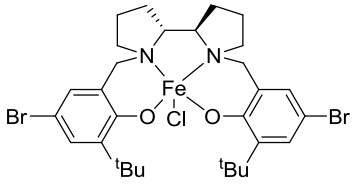

**3a**

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



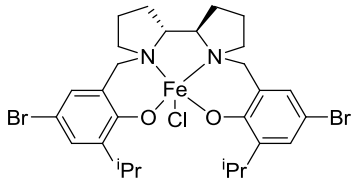

**3b**

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




**3c**

Yield: 78% (555 mg); IR (KBr): $\nu_{max}$ 3445, 2955, 1732, 1463, 1430, 1408, 1389, 1357, 1293, 1250, 1167, 870, 814, 733, 569, 496; MS (MALDI): *m/z* 674.1 $[M\text{-}Cl]^+$; HRMS (MALDI): For $[C30H40N2O2Br2^{54}Fe]^+$ $(M\text{-}Cl)^+$ Calcl. 672.0847, Found: 672.0841.



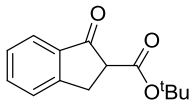

**3d**

Yield: 62% (424 mg); IR (KBr): $\nu_{max}$ 2958, 2867, 1434, 1337, 1291, 1251, 1220, 1002, 930, 868, 849, 757, 597; MS (MALDI): *m/z* 646.0 $[M\text{-}Cl]^+$; HRMS (MALDI): For $[C28H36N2O2Br2^{54}Fe]^+$ $(M\text{-}Cl)^+$ Calcl. 644.0534, Found: 644.0525.

## II. Synthesis of *β*-keto esters

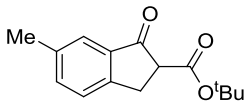
Synthesis of cyclic **4a-4g**, **4l**[7]

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 ($Na_2SO_4$) and concentrated. The residue was purified by flash silica gel chromatography.



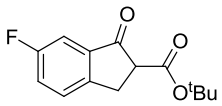

**4a**

Yield: 81% (940 mg); $^1$H NMR (300 MHz, $CDCl_3$): 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).



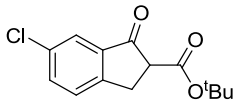

**4b**

Yield: 80% (985 mg); m.p.($^{o}$C): 59-61; $^{1}$H NMR (300 MHz, $CDCl_3$):δ 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, $CDCl_3$): δ 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): $\nu_{max}$ 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: $[C15H18O3]^+$ Calcl. 246.1256; Found: 246.1254.



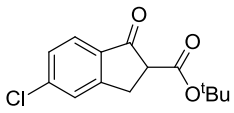

**4c**

Yield: 67% (838 mg); m.p.($^{o}$C): 65-67; $^{1}$H NMR (300 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ -114.11- -114.17 (m, 1F); IR (KBr): $\nu_{max}$ 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: $[C14H15O3F]^+$ Calcl. 250.1005; Found: 250.1009.



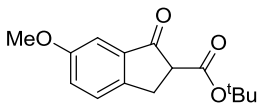

**4d**

Yield: 70% (933 mg); m.p.($^{o}$C): 88-90; $^{1}$H NMR (300 MHz, $CDCl_3$):δ7.72 (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, $CDCl_3$): δ 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): $\nu_{max}$ 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: $[C14H15O3Cl]^+$ Calcl. 266.0710; Found: 266.0713.



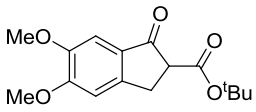

**4e**

Yield: 75% (1.00 g); $^{1}$H NMR (300 MHz, $CDCl_3$): δ 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).



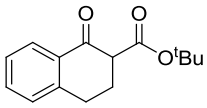

**4f**

Yield: 79% (1.04g); m.p.($^{o}$C): 84-86; $^{1}$H NMR (300 MHz, $CDCl_3$): δ7.38 (d, *J* = 8.4 Hz, 1H), 7.27-7.19 (m, 2H), 3.84 (s, 3H), 3.64 (dd, *J* = 3.9, 8.0 Hz, 1H), 3.38 (d, *J* = 3.9 Hz, 1H), 3.29 (d, *J* = 8.0 Hz, 1H), 1.49 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 197.46, 165.81, 156.99, 144.02, 134.01, 122.12, 122.09, 102.93, 79.39, 52.98, 52.51, 27.09, 25.43, 25.38; IR (KBr): $\nu_{max}$ 2983, 2929, 2842, 1721, 1698, 1615, 1493, 1438, 1430, 1371, 1330, 1300, 1278, 1229, 1150, 1031, 995, 862, 849, 827, 782, 765, 516; MS (EI): *m/z* 262 ($M^+$), 206 (36.32), 189 (30.72), 188 (18.75), 161 (34.30), 160 (100.00), 118 (9.64), 89 (11.73), 57 (21.75); HRMS (EI): For: $[C15H18O4]^+$ Calcl. 262.1205; Found: 262.1202.




**4g**

Yield: 82% (1.20 g); $^1$H NMR (300 MHz, $CDCl_3$): δ 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).

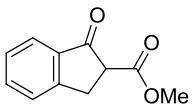



**4l**

Yield: 55% (677 mg); $^1$H NMR (300 MHz, $CDCl_3$): δ 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**[8]

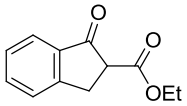
Following the reported procedure, a 100 mL two-neck flask was charged with a suspension of NaH (3.32 g, 60% in mineral oil, 83 mmol, 2.2 equiv.) in dimethyl carbonate (10 mL). 1-Indanone (5.0 g, 37.75 mmol, 1 equiv.) in dimethyl carbonate (35 mL) was added dropwise and the resulting mixture was refluxed at 80 ℃ for 2 h. After cooling to RT, 100 mL of water was added. The aqueous layer was separated and extracted with DCM (3 ×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.




**4h**

Yield: 70% (5.03g); $^1$H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.1 Hz, 1H), 7.64 (t, *J*

= 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).



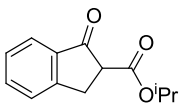

**4i**

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

Yield: 66% (5.09 g); $^1$H NMR (300 MHz, $CDCl_3$): 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**

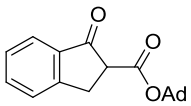
The methyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate with different substituent was prepared as **4h**. A solution of methyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (1.0 mmol), dibutyltin oxide (0.10 mmol) and iso-propyl alcohol or 1-adamantanol (10 mmol) in toluene (10 mL) was refluxed for 8 h. Evaporation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




**4j**

Yield: 61% (133 mg); $^1$H NMR (300 MHz, $CDCl_3$): 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

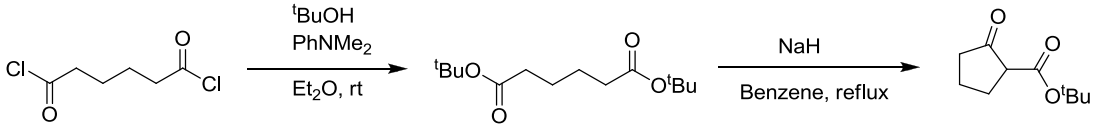
(25.80), 131 (46.10), 130 (100.00), 103 (26.94), 77 (27.09), 43 (21.71);




**4k**

Yield: 52% (162 mg); $^1$H NMR (300 MHz, $CDCl_3$): δ 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**[9]

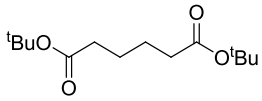



**12** **4m**

A solution of adipoyl chloride (9.0 g) in $Et_2O$ (10 mL) was added dropwise to a solution of $^t$BuOH (15 mL, 162 mmol) and *N*,*N*-dimethylaniline (20 mL, 157.0 mmol) in $Et_2O$ (10 mL) at 0 °C. The resultant mixture was allowed to warm slowly to RT and stirred for 24 h. The solution was diluted with $H_2O$ (50 mL) and the aqueous phase was separated. The organic portion was washed sequentially with 1 M HCl (3 × 50 mL), 2 M NaOH (aq, 2 × 50 mL) and brine (80 mL), then dried and concentrated in vacuo to give di-*tert*-butyl adipate (**12**) as a colourless oil.

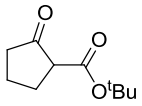
NaH (60% suspension in mineral oil, 2.7 g, 112.5 mmol) was suspended in benzene (25 mL). A solution of di-*tert*-butyladipate (0.3 g) in $^t$BuOH (0.15 mL) and benzene (25 mL) was added. After refluxed for 30 min, more di-*tert*-butyladipate (8.0 g) as a solution in benzene (15 mL) was added dropwise over 45 min. The resultant mixture was heated to reflux for 10 h, then allowed to cool to RT before being cooled to 0 °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).



**12**

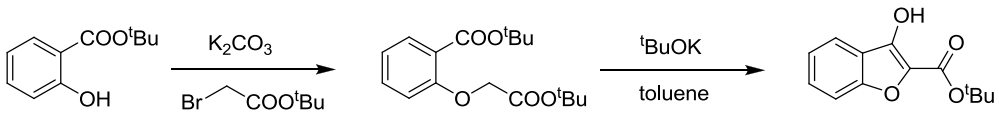
Yield: 88% (11.2 g); $^1$H NMR (300 MHz, $CDCl_3$): δ 2.26-2.20 (m, 4H), 1.65-1.58 (m, 4H), 1.44 (s, 18H); MS (EI): *m/z* 258 ($M^+$), 147 (17.64), 146 (28.10), 129 (94.67), 128 (14.98), 111 (18.99), 57 (100.00), 55 (18.76), 41 (23.54).



**4m**

Yield: 71% (4.20 g); $^1$H NMR (300 MHz, $CDCl_3$): δ 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]

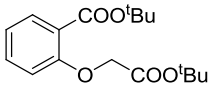


**13** **4n**

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 $Na_2SO_4$. Evaporation of the solvent and chromatography afforded the product as a white solid.

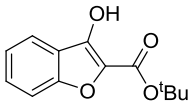
To a suspension of potassium *tert*-butoxide (218 mg, 1.95 mmol) in toluene (10 mL) was added *tert*-butyl 2-(2-*tert*-butoxy-2-oxoethyl) benzoate (300 mg, 0.974

mmol) and the mixture was stirred for 30 min at room temperature. The reaction was quenched with $NH_4Cl$ (aq.) and the whole mixture was extracted with EA. The organic layer was washed with brine and dried over $Na_2SO_4$. Evaporation and chromatography afforded the product as a grey solid.




**13**

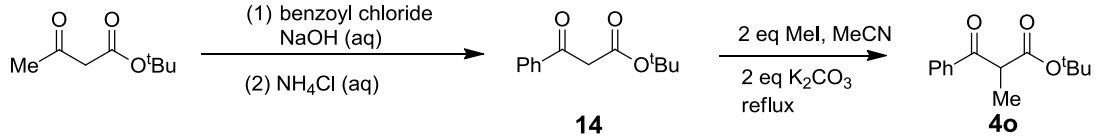
Yield: 86% (546 mg); $^1$H NMR (300 MHz, $CDCl_3$): δ 7.74 (dd, *J* = 0.6, 7.7 Hz, 1H), 7.42-7.36 (m, 1H), 7.01 (t, *J* = 7.7 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 1H), 4.59 (s, 2H), 1.59 (s, 9H), 1.47 (s, 9H); MS (EI): *m/z* 308 ($M^+$), 196 (22.91), 179 (24.36), 152 (22.63), 151 (22.77), 123 (21.34), 121 (19.05), 57 (100.00), 41 (21.49).




**4n**

Yield: 90% (205 mg); $^1$H NMR (300 MHz, $CDCl_3$): δ 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).

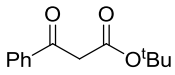
Synthesis of **4o**[11]




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 $H_2O$ (25 mL) at 0 ℃. 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 ℃. The mixture was then warmed to 35 ℃ for 30 min, before transferring to aseparating funnel. The aqueous layer was separated

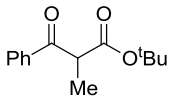
and returned to the flask, to which $NH_4Cl$ (4 g, 74.8mmol) was added. After stirring at RT for a further 18 h the solution was diluted with brine (20 mL) andextracted to $Et_2O$ (3 × 40 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated in vacuo. The crude product was purified by flash chromatography to afford the product **14**.

A mixture of **14** (11.6 mmol), MeI (1.45 mL, 23.2 mmol), $K_2CO_3$ (3.19 g, 23.2 mmol) and MeCN (40 mL) was refluxed for 18 h. The mixture was cooled, quenched with $H_2O$ (100 mL), and extracted with $Et_2O$ (2 × 80 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography to give the product **4o** as a colourless oil.




**14**

Yield: 78% (12.8 g); $^1$H NMR (300 MHz, $CDCl_3$): 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).



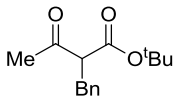

**4o**

Yield: 44% (1.20 g); $^1$H NMR (300 MHz, $CDCl_3$): δ 7.97 (dd, *J* = 1.2, 7.8 Hz, 2H), 7.60-7.55 (m, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 4,.25 (q, *J* = 7.2 Hz, 1H), 1.46 (d, *J* = 7.2 Hz, 3H), 1.34 (s, 9H); MS (EI): *m/z* 178 ($[M-C_4H_8]^+$), 106 (8.58), 105 (100.00), 77 (26.53), 57 (28.33), 56 (6.46), 51 (6.55), 41 (7.83).

Synthesis of **4p**[11]

NaH (60% suspension in mineral oil, 15.1mmol, 1.25 equiv.) was suspended in THF (25 mL). A solution of *tert*-butyl acetoacetate (1.10g, 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 $H_2O$ (35 mL) and extracted with $Et_2O$ (2 × 50 mL). The combined organic extracts were dried ($MgSO_4$)

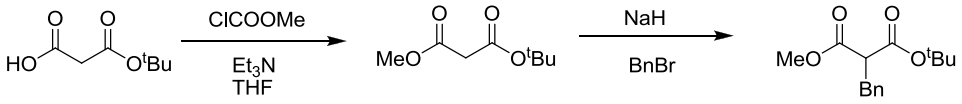
and concentrated. The residue was purified by column chromatography to give the product **4p** as a colourless oil.



**4p**

Yield: 51% (1.52 g); $^1$H NMR (300 MHz, $CDCl_3$): δ 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).

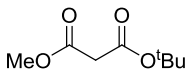
Synthesis of **4q**[11]



**15** **4q**

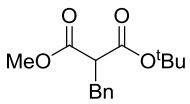
Mono-*tert*-butyl malonate (1 g, 6.25 mmol) and $NEt_3$ (0.871 mL, 6.25 mmol) were dissolved in THF (30 mL) and the solution cooled to 0 ℃. After dropwise addition of methyl choroformate, the mixture was stirred for 30 min and then filtered. The filtrate was concentrated in vacuo to give **15** as a yellow oil.

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



**15**

Yield: 74% (812 mg); $^1$H NMR (300 MHz, $CDCl_3$): δ 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).



**4q**

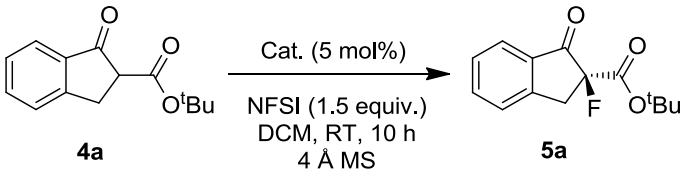
Yield: 57% (1.82 g); $^1$H NMR (300 MHz, $CDCl_3$): δ 7.28-7.19 (m, 5H), 3.70 (s, 3H),

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 ℃ 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.

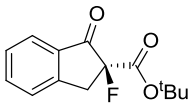
**Table S1** Catalyst screening for the fluorination reaction of **4a**[a]




**4a** **5a**

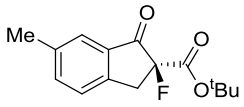
| Entry | Catalyst | Yield (%) | ee (%)[c] |
|---|---|---|---|
| 1 | **1a** | 84 | 58 |
| 2 | **1b** | 97 | 3 |
| 3 | **1c** | 81 | 36 |
| 4 | [d] | 45 | 38 |
| 5 | **2** | 61 | 8 |
| 6 | **3a** | 94 | 26 |
| 7 | **3b** | 95 | 57 |
| 8 | **3c** | 96 | 87 |
| 9 | **3d** | 94 | 8 |

[a] 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. [b] Isolated yield. [c]Determined by chiral HPLC. [d] 10 mol% $Co(acac)_2$ and 10 mol% Jacobsen's Salen ligand were used as catalyst.



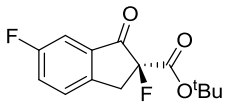
**5a**

Yield: 96% (64.1 mg); $^{1}$H NMR (300 MHz, $CDCl_3$): 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); $^{19}$F NMR(282 MHz, $CDCl_3$) 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/$^{i}$PrOH=99/1, 1.0 mL/min, 254 nm, tR(major)= 11.7 min, tR(minor)= 14.0 min (94% *ee*); $[\alpha]^{D}_{20}$: -1.2 (c= 1.04, solv: $CHCl_3$, 94% *ee*).



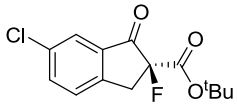
**5b**

Yield: 97% (68.2 mg); $^{1}$H NMR (300 MHz, $CDCl_3$): 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); $^{13}$C NMR (75 MHz, $CDCl_3$): 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; $^{19}$F NMR (282 MHz, $CDCl_3$) δ -164.16 (dd, *J* = 11.0, 23.4 Hz, 1F); IR (KBr): $\nu_{max}$ 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 ($[M-CH_3]^+$), 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 $[C14H14O3F]^+$ ($[M-CH_3]^+$) Calcl. 249.0927, Found: 249.0933; HPLC: Daicel Chiralpak AD-H, Hexane/$^{i}$PrOH=99/1, 1.0 mL/min, 254 nm, tR(major)= 11.9 min, tR(minor)= 20.2 min (97% *ee*); $[\alpha]^{D}_{20}$: +5.0 (c= 1.05, solv: $CHCl_3$, 97% *ee*).



**5c**

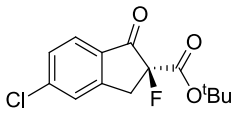
Yield: 95% (68.0 mg); $^{1}$H NMR (300 MHz, $CDCl_3$): δ 7.48-7.40 (m, 3H), 3.70 (dd, *J* = 10.5, 17.1 Hz, 1H), 3.34 (dd, *J* = 17.1, 21.8 Hz, 1H), 1.44 (s, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 194.82 (dd, *J* = 3.1, 18.6 Hz), 165.66 (d, *J* = 27.7 Hz), 162.47 (d, *J* = 248.6 Hz), 146.30 (dd, *J* = 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, $CDCl_3$) δ -112.65- -112.72 (m, 1F), -163.80 (dd, *J* = 10.5, 21.8 Hz, 1F); IR (KBr): $\nu_{max}$ 2982, 2936, 1763, 1733, 1615, 1489, 1441, 1396, 1372, 1297, 1286, 1228, 1210, 1156, 1077, 975, 865, 839, 805, 768 $cm^{-1}$; MS (EI): *m/z* 253 ($[M\text{-}CH_3]^+$), 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 (EI): For $[C13H11O3F2]^+$ ($[M\text{-}CH_3]^+$) Calcl. 253.0676, Found: 253.0682; HPLC: Phenomenex PC-2, Hexane/$^{i}$PrOH=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*).



**5d**

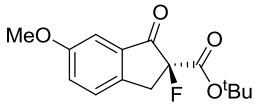
Yield: 98% (74.5 mg); $^{1}$H NMR (300 MHz, $CDCl_3$): δ 7.79 (d, *J* = 2.1 Hz, 1H), 7.64 (dd, *J* = 2.1, 8.1 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 3.70 (dd, *J* = 10.5, 17.7 Hz, 1H), 3.36 (dd, *J* = 17.7, 22.2 Hz, 1H), 1.44 (s, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 194.59 (d, *J* = 18.5 Hz), 165.72 (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, $CDCl_3$) δ -163.86 (dd, *J* = 10.5, 22.2 Hz, 1F); IR (KBr): $\nu_{max}$ 2981, 2935, 1763, 1732, 1602, 1471, 1428, 1371, 1293, 1258, 1204, 1187, 1155, 1118, 1075, 949, 839, 802, 731, 598, 515 $cm^{-1}$; MS (EI): *m/z* 269 ($[M\text{-}CH_3]^+$), 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 (EI): For $[C13H11O3FCl]^+$

([M-$CH_3$]$^+$) Calcl. 269.0381, Found: 269.0382; HPLC: Daicel Chiralpak IC, Hexane/$^i$PrOH=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*).




**5e**

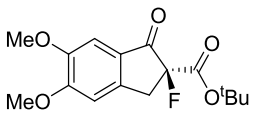
Yield: 93% (70.7 mg); $^1$H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.1 Hz, 1H), 7.50 (s, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 3.71 (dd, *J* = 10.5, 17.9 Hz, 1H), 3.38 (dd, *J* = 17.9, 22.4 Hz, 1H), 1.44 (s, 9H); $^{19}$F NMR (282 MHz, $CDCl_3$) δ -163.76 (dd, *J* = 10.5, 22.4 Hz, 1F); MS (EI): *m/z* 284 (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/$^i$PrOH=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*).




**5f**

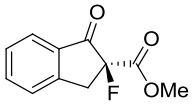
Yield: 99% (74.1 mg); $^1$H NMR (300 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.4 Hz, 1H), 7.29-7.24 (m, 2H), 3.86 (s, 3H), 3.65 (dd, *J* = 10.2, 17.3 Hz, 1H), 3.32 (dd, *J* = 17.3, 22.8 Hz, 1H), 1.44 (s, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 195.78 (d, *J* = 18.6 Hz), 166.24 (d, *J* = 27.7 Hz), 159.93, 143.91 (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, $CDCl_3$) δ -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 $[C15H17O4F]^+$ Calcl. 280.1111, Found: 280.1108; HPLC: Daicel Chiralpak AD-H, Hexane/$^i$PrOH=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,

solv: $CHCl_3$, 95% *ee*).



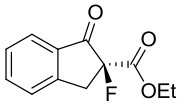

**5g**

Yield: 99% (82.0 mg); $^1$H NMR (300 MHz, $CDCl_3$): 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); $^{19}$F NMR (282 MHz, $CDCl_3$) 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/$^i$PrOH=85/15, 0.7 mL/min, 254 nm, tR(minor)= 10.8 min, tR(major)= 11.9 min (96% *ee*); $[\alpha]^D_{20}$: +59.9 (c= 1.09, solv: $CHCl_3$, 96% *ee*).




**5h**

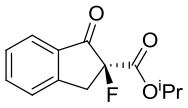
Yield: 99% (55.0 mg); $^1$H NMR (300 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.7 Hz, 1H), 7.72 (t, *J* = 7.2 Hz, 1H), 7.49 (dd, *J* = 7.5, 14.7 Hz, 2H), 3.81 (dd, *J* = 11.7, 17.7 Hz, 1H), 3.82 (s, 3H), 3.45 (dd, *J* = 17.7, 23.4 Hz, 1H); $^{19}$F NMR (282 MHz, $CDCl_3$) δ -164.96 (dd, *J* = 11.7, 23.4 Hz, 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/$^i$PrOH=85/15, 0.7 mL/min, 254 nm, tR(major)= 30.8 min, tR(minor)= 35.8 min (46% *ee*).




**5i**

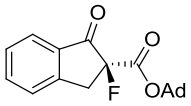
Yield: 99% (58.7 mg); $^1$H NMR (300 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.8 Hz, 1H), 7.71 (dt, *J* = 1.5, 7.7 Hz, 1H), 7.48 (dd, *J* = 7.8, 14.9 Hz, 2H), 4.29 (q, *J* = 7.5 Hz, 2H), 3.80 (dd, *J* = 11.7, 17.6 Hz, 1H), 3.43 (dd, *J* = 17.6, 23.2 Hz, 1H), 1.27 (t, *J* = 7.5 Hz, 6H); $^{19}$F NMR (282 MHz, $CDCl_3$) δ -164.87 (dd, *J* = 11.7, 23.2 Hz, 1F); MS (EI): *m/z*

222 ($M^+$), 202 (46.88), 158 (28.04), 149 (100.00), 130 (32.21), 129 (22.68), 102 (20.55), 101 (57.67), 75 (21.06); HPLC: Daicel Chiralpak IC, Hexane/$^i$PrOH=90/10, 0.7 mL/min, 254 nm, tR(major)= 35.6 min, tR(minor)= 42.0 min (59% *ee*).




**5j**

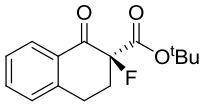
Yield: 98% (61.8 mg); $^1$H NMR (300 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.8 Hz, 1H), 7.70 (t, *J* = 7.8 Hz, 1H), 7.48 (dd, *J* = 8.1, 15.2 Hz, 2H), 5.17-5.12 (m, 1H), 3.77 (dd, *J* = 11.7, 17.4 Hz, 1H), 3.43 (dd, *J* = 17.4, 23.1 Hz, 1H), 1.25 (t, *J* = 6.6 Hz, 6H); $^{19}$F NMR (282 MHz, $CDCl_3$) δ -164.77 (dd, *J* = 11.7, 23.1 Hz, 1F); MS (EI): *m/z* 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*).




**5k**

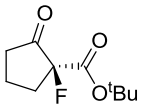
Yield: 99% (65.0 mg); $^1$H NMR (300 MHz, $CDCl_3$): δ 7.83 (d, *J* = 7.8 Hz, 1H), 7.68 (t, *J* = 7.8 Hz, 1H), 7.46 (q, *J* = 7.8 Hz, 2H), 3.73 (dd, *J* = 10.5, 17.4 Hz, 1H), 3.32 (dd, *J* = 17.4, 22.8 Hz, 1H), 2.05 (s, 9H), 1.62 (s, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 195.83 (d, *J* = 17.8 Hz), 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, $CDCl_3$) δ -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/z* 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/$^{i}$PrOH=99/1, 0.7 mL/min, 254 nm, tR(major)= 29.6 min, tR(minor)= 39.5 min (92% *ee*); $[\alpha]^{D}_{20}$: -0.7 (c= 0.90, solv: $CHCl_3$, 92% *ee*).



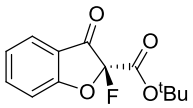
**5l**

Yield: 96% (67.7 mg); $^{1}$H NMR (300 MHz, $CDCl_3$): 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); $^{19}$F NMR (282 MHz, $CDCl_3$) δ -163.72 (dd, *J* = 11.0, 20.6 Hz, 1F); HPLC: Daicel Chiralpak AD-H, Hexane/$^{i}$PrOH=99/1, 1.0 mL/min, 254 nm, tR(minor)= 10.8 min, tR(major)= 12.2 min (69% *ee*); $[\alpha]^{D}_{20}$: -6.1 (c= 0.88, solv: $CHCl_3$, 69% *ee*).



**5m**

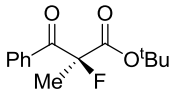
Yield: 88% (47.5 mg); $^{1}$H NMR (300 MHz, $CDCl_3$): δ 2.52-2.44 (m, 3H), 2.43-2.14 (m, 1H), 2.14-2.09 (m, 2H), 1.50 (s, 9H); $^{19}$F NMR (282 MHz, $CDCl_3$) δ -163.19 (dd, *J* = 16.6, 21.4 Hz, 1F); MS (EI): *m/z* 202 ($M^{+}$),146 (41.59), 129 (19.22), 118 (32.81), 101 (37.26), 73 (33.17), 59 (24.20), 57 (100.00), 41 (28.12); HPLC: REGIS (S, S)-Whelk-O1, Hexane/$^{i}$PrOH=98/2, 0.5 mL/min, 214 nm, tR(major)= 14.9 min, tR(minor)= 17.1 min (95% *ee*); $[\alpha]^{D}_{20}$: -56.7 (c= 1.01, solv: $CHCl_3$, 95% *ee*).



**5n**

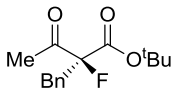
Yield: 91% (61.3 mg); $^{1}$H NMR (300 MHz, $CDCl_3$): δ 7.76-7.70 (m, 2H), 7.28-7.21 (m, 2H) , 1.50 (s, 9H); $^{19}$F NMR (282 MHz, $CDCl_3$) δ -127.99 (s, 1F); MS (EI): *m/z* 252 ($M^{+}$), 152 (27.43), 151 (41.78), 123 (9.65), 95 (13.96), 57 (100.00), 76 (14.36), 75 (6.84), 41 (19.54); HPLC: Phenomenex PC-2, Hexane/$^{i}$PrOH=90/10, 0.5 mL/min, 214 nm, tR(minor)= 8.9 min, tR(major)= 9.7 min (83% *ee*); $[\alpha]^{D}_{20}$: -47.6 (c= 1.02,

solv: $CHCl_3$, 83% *ee*).



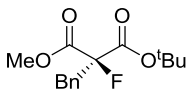
**5o**

Yield: 87% (43.9 mg); $^1$H NMR (300 MHz, $CDCl_3$): δ 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, $CDCl_3$) δ -151.27 (q, *J* = 22.5 Hz, 1F); MS (EI): *m/z* 196 ($[M-C_4H_8]^+$), 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/$^i$PrOH=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*).



**5p**

Yield: 96% (51.1 mg); $^1$H NMR (300 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$) δ -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 $[C15H19O3F]^+$ Calcl. 266.1318, Found: 266.1316; HPLC: Phenomenex PC-3, Hexane/$^i$PrOH=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*).



**5q**

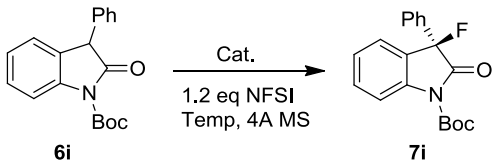
Yield: 72% (40.7 mg); $^1$H NMR (300 MHz, $CDCl_3$): δ 7.27 (s, 5H), 3.79 (s, 3H), 3.44

(d, $J$ = 25.8 Hz, 2H), 1.42 (s, 9H); $^{19}$F NMR (282 MHz, $CDCl_3$) δ -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/$^i$PrOH=95/5, 0.5 mL/min, 214 nm, tR(major)= 10.7 min, tR(minor)= 13.6 min (51% *ee*).

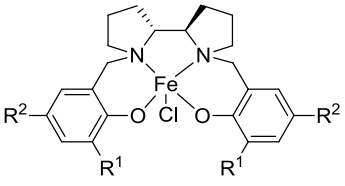
## IV. Optimization of reaction conditions for enantioselective fluoronation of oxindoles

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]




**6i** **7i**




**3**

**3a** $R^1 = R^2 = {}^t$Bu
**3b** $R^1 = R^2$ = Br
**3c** $R^1 = {}^t$Bu, $R^2$ = Br
**3d** $R^1 = {}^i$Pr, $R^2$ = Br

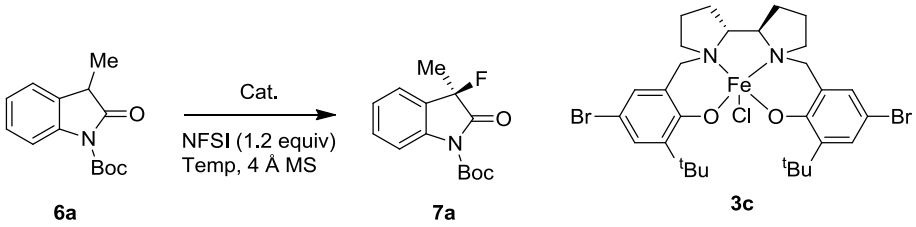
| Entry | Solvent | Cat. | Additives (5 mol%) | Temp. (°C) | Time (h) | Yield (%) | ee (%) |
|---|---|---|---|---|---|---|---|
| 1 | DCM | **3c** | - | 25 | 3 | 86 | 78 |
| 2 | MeCN | **3c** | - | 25 | 1.5 | 90 | 64 |
| 3 | toluene | **3c** | - | 25 | 3 | 85 | 81 |
| 4 | $Et_2O$ | **3c** | - | 25 | 1.5 | 91 | 80 |
| 5 | THF | **3c** | - | 25 | 3 | 92 | 70 |
| 6 | MeOH | **3c** | - | 25 | 1.5 | 94 | 59 |
| 7 | DCE | **3c** | - | 25 | 1.5 | 90 | 75 |
| 8 | Dioxane | **3c** | - | 25 | 4 | 79 | 77 |
| 9 | MTBE | **3c** | - | 25 | 3 | 92 | 80 |
| 10 | DME | **3c** | - | 25 | 1.5 | 83 | 76 |
| 11 | Acetone | **3c** | - | 25 | 1.5 | 86 | 70 |
| 12 | EA | **3c** | - | 25 | 2 | 94 | 76 |
| 13 | $Et_2O$ | **3a** | - | 25 | 1.5 | 91 | 75 |
| 14 | $Et_2O$ | **3b** | - | 25 | 4 | 63 | 79 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 15 | $Et_2O$ | **3d** | - | 25 | 6 | 88 | 82 |
| 16 | $Et_2O$ | **3d** | $AgClO_4$ | 25 | 0.5 | 92 | 80 |
| 17 | $Et_2O$ | **3d** | $AgClO_4$ | 0 | 3 | 93 | 85 |
| 18 | $Et_2O$ | **3d** | $AgClO_4$ | -20 | 16 | 90 | 84 |
| 19 | $Et_2O$ | **3d** | AgOAc | 25 | 1 | 88 | 79 |

[a]Reaction 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 atmostphere.

2. Optimization of the reaction conditions for 3-methyl oxindole

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

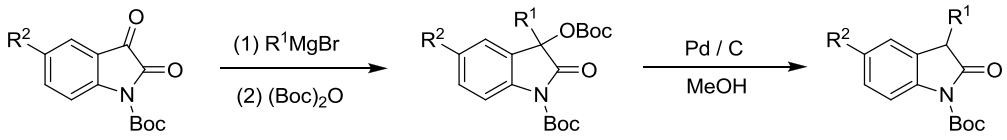



**6a** **7a** **3c**

| Entry | Additives | Solvent | Temp ($^oC$) | Time (h) | Yield (%) | ee (%) |
|---|---|---|---|---|---|---|
| 1 | - | DCM | 25 | 20 | 78 | 91 |
| 2 | - | $Et_2O$ | 25 | 6 | 93 | 93 |
| 3 | - | $Et_2O$ | 0 | 36 | 90 | 95 |
| 4 | $AgClO_4$ | $Et_2O$ | 25 | 0.5 | 96 | 94 |
| 5 | $AgClO_4$ | $Et_2O$ | 0 | 3 | 94 | 96 |

[a]Reaction 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 atmostphere.

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



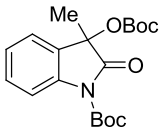

**16** **6**

Synthesis of **16**[12]

A solution of $R^1MgBr$ (13.6 mmol) was added to a stirred cold (-40 ℃) 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

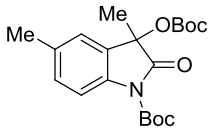
consumed. The reaction mixture was diluted with ether, cooled in an ice-bath, and then quenched with 1N HCl. The aqueous layer was extracted with ether, and the combined organic layers were washed with water and brine and then dried over $Na_2SO_4$. After the removal of solvent, the crude product can 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 $NH_4Cl$. The aqueous layer was extracted with ethyl acetate, and the combined organic layers were washed with water and brine and then dried over $Na_2SO_4$. After the removal of solvent, purification by flash column chromatography was carried out to give the product.




**16a**

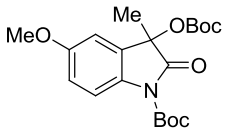
Yield: 65%; $^1$H NMR (300 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.4 Hz, 1H), 7.40-7.32 (m, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 1.66 (s, 12H), 1.35 (s, 9H); MS (EI): *m/z* 363 ($M^+$), 175 (54.42), 146 (35.34), 145 (15.15), 133 (89.11), 132 (31.59), 117(15.61), 57 (100.0), 41 (26.13).




**16b**

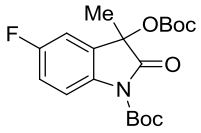
Yield: 70%; $^1$H NMR (300 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.1 Hz, 1H), 7.16 (d, *J* = 8.1 Hz, 1H), 7.13 (s, 1H), 2.35 (s, 3H), 1.65 (s, 9H), 1.63 (s, 3H), 1.35 (s, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 173.28, 150.59, 148.93, 136.57, 134.37, 130.24, 128.15, 122.38, 115.09, 84.25, 83.60, 77.89, 27.97, 27.38, 24.32, 20.87; IR (KBr): $\nu_{max}$ 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.



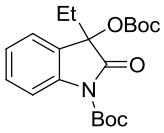

**16c**

Yield: 61%; $^1H$ NMR (300 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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): $\nu_{max}$ 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.



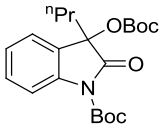

**16d**

Yield: 73%; $^1H$ NMR (300 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$)δ -117.48- -117.55 (m, 1F); IR (KBr): $\nu_{max}$ 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.



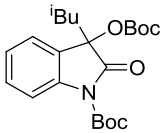

**16e**

Yield: 74%; $^{1}$H NMR (300 MHz, $CDCl_3$): δ 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).




**16f**

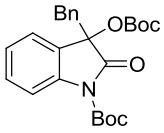
Yield: 68%; $^{1}$H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.1 Hz, 1H), 7.36 (td, *J* = 1.5, 8.1 Hz, 1H), 7.31-7.26 (m, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 2.00-1.94 (m, 2H), 1.65 (s, 9H), 1.34 (s, 9H), 1.35-1.18 (m, 2H), 0.85 (t, *J* = 7.5 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 172.94, 150.72, 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): $\nu_{max}$ 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 $[C21H29NO6]^+$ Calcl. 391.1995, Found: 391.1996.




**16g**

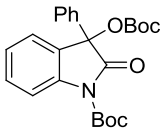
Yield: 60%; $^{1}$H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.1 Hz, 1H), 7.39 (t, *J* = 1.5 Hz, 1H), 7.35-7.26 (m, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 2.05-1.94 (m, 2H), 1.64 (s, 9H), 1.64-1.51 (m, 1H), 1.33 (s, 9H), 0.85 (d, *J* = 6.9 Hz, 3H), 0.73 (d, *J* = 6.9 Hz, 3H); MS (EI): *m/z* 405 ($M^+$), 193 (29.57), 187 (53.56), 180 (29.85), 149 (22.15), 146

(27.57), 145 (28. 40), 57 (100.00), 41 (23.41).



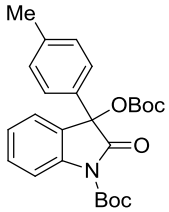

**16h**

Yield: 74%; $^1$H NMR (300 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.1 Hz, 1H), 7.31-7.25 (m, 1H), 7.16-7.05 (m, 5H), 6.84 (d, *J* = 6.9 Hz, 2H), 3.30 (q, *J* = 15.6 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).



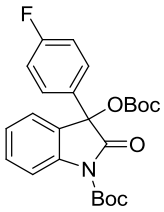

**16i**

Yield: 82%; $^1$H NMR (300 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.4 Hz, 1H), 7.43 (t, *J* = 6.9 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).




**16j**

Yield: 77%; $^1$H NMR (300 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.1 Hz, 1H), 7.45 (td, *J* = 1.5, 8.1 Hz, 1H), 7.32-7.19 (m, 4H), 7.12 (d, *J* = 8.1 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).

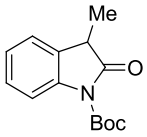



**16k**

Yield: 73%; $^{1}$H NMR (300 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ -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).

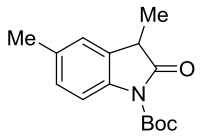
Synthesis of **6**[12]

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.



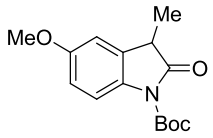

**6a**

Yield: 84%; $^{1}$H NMR (300 MHz, $CDCl_3$): δ 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).



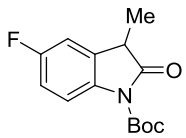

**6b**

Yield: 79%; $^{1}$H NMR (300 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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): $\nu_{max}$ 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.




**6c**

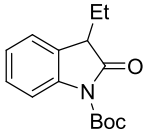
Yield: 83%; $^{1}$H NMR (300 MHz, $CDCl_3$): δ 7.73 (d, *J* = 9.6 Hz, 1H), 6.83-6.80 (m, 2H), 3.81 (s, 3H), 3.54 (q, *J* = 7.5 Hz, 1H), 1.64 (s, 9H), 1.51 (d, *J* = 7.5 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): δ 176.65, 156.63, 149.15, 132.81, 130.52, 115.63, 112.37, 109.68, 83.73, 55.37, 41.15, 27.90, 15.78; IR (KBr): $\nu_{max}$ 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.




**6d**

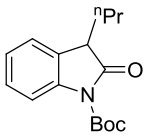
Yield: 81%; $^{1}$H NMR (300 MHz, $CDCl_3$): δ 7.80 (dd, *J* = 4.8, 8.7 Hz, 1H), 7.03-6.95 (m, 2H), 3.56 (q, *J* = 7.2 Hz, 1H), 1.64 (s, 9H), 1.52 (d, *J* = 7.2 Hz, 3H); $^{13}$C NMR (75

MHz, $CDCl_3$): δ 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, $CDCl_3$) δ -118.57- -118.64 (m, 1F); IR (KBr): $\nu_{max}$ 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 $[C14H16FNO3]^+$ Calcl. 265.1114, Found: 265.1117.



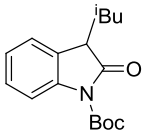

**6e**

Yield: 78%; $^1H$ NMR (300 MHz, $CDCl_3$): δ 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).



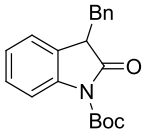

**6f**

Yield: 75%; $^1H$ NMR (300 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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): $\nu_{max}$ 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 $[C16H21NO3]^+$ Calcl. 275.1521, Found: 275.1519.



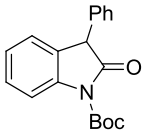

**6g**

Yield: 70%; $^1$H NMR (300 MHz, $CDCl_3$): δ 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).



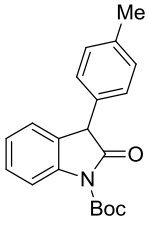

**6h**

Yield: 73%; $^1$H NMR (300 MHz, $CDCl_3$): δ 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).



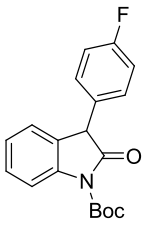

**6i**

Yield: 84%; $^1$H NMR (300 MHz, $CDCl_3$): δ 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).




**6j**

Yield: 81%; $^{1}$H NMR (300 MHz, $CDCl_3$): δ 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 ($M^+$), 224 (16.96), 223 (100.00), 222 (13.86), 208 (11.26), 194 (24.70), 180 (31.79), 57 (79.57), 41 (18.20).

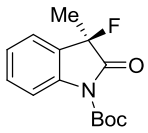



**6k**

Yield: 80%; $^{1}$H NMR (300 MHz, $CDCl_3$): δ 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); $^{19}$F NMR (282 MHz, $CDCl_3$): δ -114.74- -114.83 (m, 1F); MS (EI): *m/z* 327 ($M^+$), 228 (14.00), 227 (92.16), 226 (17.11), 223 (15.35), 198 (48.09), 180 (16.44), 57 (100.00), 41 (21.14).

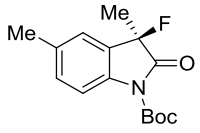
## VI. Enatioselective fluoronation of oxindoles

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 ℃). 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.



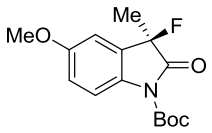

**7a**

Yield: 94% (49.9 mg); $^{1}$H NMR (300 MHz, $CDCl_3$): δ 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, $CDCl_3$) δ -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/$^{i}$PrOH=99/1, 0.4 mL/min, 214 nm, tR(minor)= 14.0 min, tR(major)= 15.5 min (96% *ee*); $[\alpha]^{D}_{20}$: +2.1 (c= 0.94, solv: $CHCl_3$, 96% *ee*).



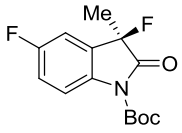

**7b**

Yield: 89% (49.7 mg); $^{1}$H NMR (300 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$) δ -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 $[C15H18NO3F]^+$ Calcl. 279.1271, Found: 279.1266; HPLC: Phenomenex PC-3, Hexane/$^{i}$PrOH=80/20, 0.7 mL/min, 214 nm, tR(minor)= 5.4 min, tR(major)= 5.9 min (94% *ee*); $[\alpha]^{D}_{20}$: +0.9 (c= 0.96, solv: $CHCl_3$, 94% *ee*).




**7c**

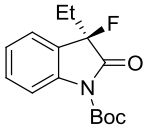
Yield: 82% (48.4 mg); $^{1}$H NMR (300 MHz, $CDCl_3$): δ 7.81 (dd, *J* = 1.2, 9.2 Hz, 1H), 7.01 (t, *J* = 2.4 Hz, 1H), 6.95 (td, *J* = 2.0, 9.2 Hz, 1H), 3.83 (s, 3H), 1.78 (d, *J* = 21.6 Hz, 3H), 1.64 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 171.22 (d, *J* = 21.7 Hz), 157.11 (d, *J* = 3.0 Hz), 148.73 (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, $CDCl_3$) δ -145.48 (q, *J* = 20.3 Hz, 1F); IR (KBr): $\nu_{max}$ 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 $[C15H18NO4F]^+$ Calcl. 295.1220, Found: 295.1224; HPLC: Phenomenex PC-3, Hexane/$^{i}$PrOH=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*).




**7d**

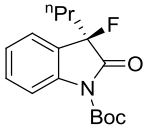
Yield: 84% (47.6 mg); $^{1}$H NMR (300 MHz, $CDCl_3$): 7.93-7.89 (m, 1H), 7.20-7.11 (m, 2H), 1.78 (d, *J* = 21.6 Hz, 3H), 1.64 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 170.66 (dd, *J* = 0.8, 21.6 Hz), 159.92 (dd, *J* = 3.1, 244.4 Hz), 148.62, 135.45 (dd, *J* = 2.7, 4.9 Hz), 127.63 (dd, *J* = 8.0, 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, $CDCl_3$) δ -116.47- -116.53 (m, 1F), -146.10 (q, *J* = 21.1 Hz, 1F); IR (KBr): $\nu_{max}$ 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 $[C14H15NO3F2]^+$ Calcl. 283.1020, Found:

283.1021; HPLC: Phenomenex PC-3, Hexane/$^{i}$PrOH=90/10, 0.7 mL/min, 214 nm, tR(minor)= 6.1 min, tR(major)= 7.1 min (93% *ee*); $[\alpha]^{D}_{20}$: +2.3 (c= 1.08, solv: $CHCl_3$, 93% *ee*).




**7e**

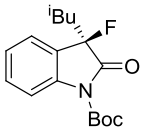
Yield: 94% (52.5 mg); $^{1}$H NMR (300 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.47-7.27 (m, 2H), 7.24 (t, *J* = 7.8 Hz, 1H), 2.26-2.16 (m, 1H), 1.65 (s, 9H), 0.85 (t, *J* = 7.8 Hz, 1H); $^{19}$F NMR (282 MHz, $CDCl_3$) δ -149.31 (t, *J* = 13.5 Hz, 1F); MS (EI): *m/z* 279 ($M^+$), 179 (55.83), 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/$^{i}$PrOH=99/1, 0.5 mL/min, 214 nm, tR(minor)= 12.5 min, tR(major)= 16.3 min (93% *ee*); $[\alpha]^{D}_{20}$: +12.2 (c= 1.05, solv: $CHCl_3$, 93% *ee*).




**7f**

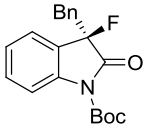
Yield: 84% (49.3 mg); $^{1}$H NMR (300 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.7 Hz, 1H), 7.46-7.40 (m, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 2.18-2.08 (m, 2H), 1.65 (s, 9H), 1.35-1.09 (m, 2H), 0.90 (t, *J* = 7.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 171.26 (d, *J* = 21.3 Hz), 148.69 (d, *J* = 0.7 Hz), 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; $^{19}$F NMR (282 MHz, $CDCl_3$) δ -148.30 (t, *J* = 13.5 Hz, 1F); IR (KBr): $\nu_{max}$ 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 $[C16H20NO3F]^+$ Calcl. 293.1427, Found: 293.1423; HPLC: Phenomenex PC-3, Hexane/$^{i}$PrOH=98/2, 0.4 mL/min, 214 nm, tR(minor)= 11.8 min, tR(major)= 12.8

min (91% *ee*); $[\alpha]^{D}_{20}$: +12.9 (c= 1.09, solv: $CHCl_3$, 91% *ee*).



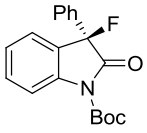

**7g**

Yield: 87% (53.5 mg); $^1$H NMR (300 MHz, $CDCl_3$): δ 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, $CDCl_3$) δ -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/$^i$PrOH=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*).




**7h**

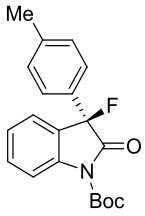
Yield: 88% (60.1 mg); $^1$H NMR (300 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.1 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.23-6.99 (m, 7H), 3.57 (dd, *J* = 9.6, 13.2 Hz, 1H), 3.24 (dd, *J* = 13.2, 22.2 Hz, 1H), 1.60 (s, 9H); $^{19}$F NMR (282 MHz, $CDCl_3$) δ -150.73 (dd, *J* = 9.3, 22.2 Hz, 1F); MS (EI): *m/z* 341 ($M^+$),245 (44.42), 244 (19.38), 241 (34.18), 216 (31.92), 91 (56.57), 57 (100.00), 43 (8.48), 41 (19.55); HPLC: Daicel Chiralcel OJ-H, Hexane/$^i$PrOH=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*).




**7i**

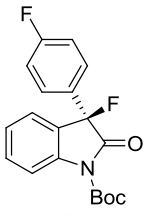
Yield: 93% (60.9 mg); $^1$H NMR (300 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.1 Hz, 1H), 7.49 (t, *J* = 8.1 Hz, 1H), 7.41-7.37 (m, 6H), 7.30-7.26 (m, 1H), 1.62 (s, 9H); $^{19}$F NMR (282 MHz, $CDCl_3$) δ -145.79 (s, 1F); MS (EI): *m/z* 327 ($M^+$), 228 (14.27), 227 (89.04), 226

(25.95), 199 (7.79), 198 (53.98), 197 (11.18), 57 (100.00), 41 (19.92); HPLC: Daicel Chiralcel OD-H, Hexane/$^{i}$PrOH=99/1, 0.25 mL/min, 254 nm, tR(major)= 23.4 min, tR(minor)= 26.2 min (85% *ee*); $[\alpha]^{D}_{20}$: -73.7 (c= 0.99, solv: $CHCl_3$, 85% *ee*).




**7j**

Yield: 88% (60.1 mg); $^{1}$H NMR (300 MHz, $CDCl_3$): 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); $^{19}$F NMR (282 MHz, $CDCl_3$) 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/$^{i}$PrOH=99/1, 0.7 mL/min, 214 nm, tR(major)= 6.8 min, tR(minor)= 8.0 min (82% *ee*); $[\alpha]^{D}_{20}$: -73.4 (c= 0.99, solv: $CHCl_3$, 82% *ee*).

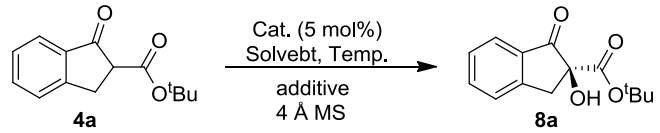


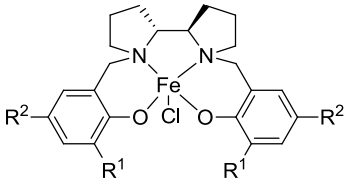

**7k**

Yield: 86% (60.9 mg); $^{1}$H NMR (300 MHz, $CDCl_3$): 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); $^{19}$F NMR (282 MHz, $CDCl_3$) 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/$^{i}$PrOH=99/1, 0.7 mL/min, 214 nm, tR(major)= 6.7 min, tR(minor)= 8.3 min (83% *ee*); $[\alpha]^{D}_{20}$: -91.6 (c= 1.05, solv: $CHCl_3$, 83% *ee*).

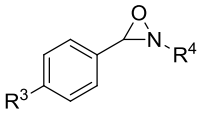
## VII. Optimization of reaction conditions for enatioselective hydroxylation of $\beta$-keto ester

**Table S4** Hydroxylation of $\beta$-keto ester **4a** catalysed by iron-salan complexes **3**[a]

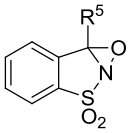


**3a** $R^1 = R^2 = {}^t$Bu
**3b** $R^1 = R^2$ = Br
**3c** $R^1 = {}^t$Bu, $R^2$ = Br
**3d** $R^1 = {}^i$Pr, $R^2$ = Br



**17** $R^3 = R^4$ = H
**18** $R^3 = NO_2$, $R^4 = SO_2Ph$
**19** $R^3 = NO_2$, $R^4$= Ts



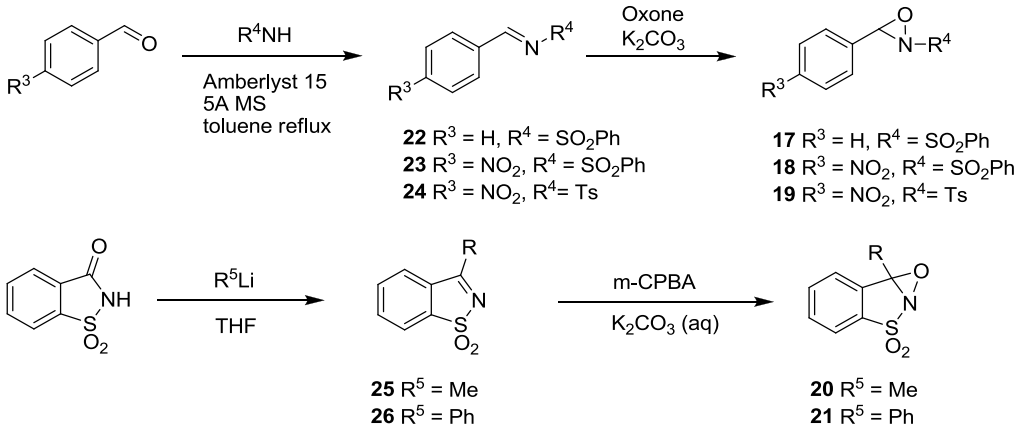
**20** $R^5$ = Me
**21** $R^5$ = Ph

| Entry | Oxidant | Cat. | Additives (x mol%) | Solvent | Temp. ($^o$C) | Time (h) | Yield (%) | ee (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | TBHP | **3c** | $AgClO_4$ (5) | DCM | RT | 24 | trace | - |
| 2 | *m*-CPBA | **3c** | $AgClO_4$ (5) | DCM | RT | 1 | 98 | 0 |
| 3 | **17** | **3c** | $AgClO_4$ (5) | DCM | RT | 6 | 90 | 76 |
| 4 | **18** | **3c** | $AgClO_4$ (5) | DCM | RT | 4 | 86 | 74 |
| 5 | **20** | **3c** | $AgClO_4$ (5) | DCM | RT | 6 | 83 | 51 |
| 6 | **21** | **3c** | $AgClO_4$ (5) | DCM | RT | 6 | 72 | 71 |
| 7 | **18** | **3c** | $AgClO_4$ (5) | MeCN | RT | 4 | 74 | 84 |
| 8 | **18** | **3c** | $AgClO_4$ (5) | DCE | RT | 4 | 67 | 88 |
| 9 | **18** | **3c** | $AgClO_4$ (5) | toluene | RT | 4 | 62 | 77 |
| 10 | **18** | **3c** | $AgClO_4$ (5) | $Et_2O$ | RT | 4 | 62 | 77 |
| 11 | **18** | **3c** | $AgClO_4$ (5) | THF | RT | 4 | 53 | 71 |
| 12 | **18** | **3c** | $AgClO_4$ (5) | MeOH | RT | 4 | 52 | 88 |
| 13 | **18** | **3a** | $AgClO_4$ (5) | DCM | RT | 6 | 93 | 64 |
| 14 | **18** | **3d** | $AgClO_4$ (5) | DCM | RT | 12 | 67 | 12 |
| 15 | **18** | **3d** | - | DCM | RT | 6 | 86 | 28 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 16 | **18** | **3c** | $AgClO_4$ (7.5) | DCM | RT | 3 | 88 | 77 |
| 17 | **18** | **3c** | AgOTf (7.5) | DCM | RT | 3 | 82 | 73 |
| 18 | **18** | **3c** | AgOAc (7.5) | DCM | RT | 3 | 87 | 66 |
| 19 | **18** | **3c** | NaBArF (7.5) | DCM | RT | 3 | 93 | 64 |
| 20 | **18** | **3c** | $AgClO_4$ (7.5) | DCM | 0 | 10 | 88 | 80 |
| 21 | **18** | **3c** | $AgClO_4$ (7.5) | DCM | -10 | 16 | 95 | 84 |
| 22 | **18** | **3c** | $AgClO_4$ (7.5) | DCM | -20 | 24 | 90 | 83 |
| 23 | **17** | **3c** | $AgClO_4$ (7.5) | DCM | -10 | 48 | 35 | 67 |
| 24 | **19** | **3c** | $AgClO_4$ (7.5) | DCM | -10 | 16 | 95 | 82 |

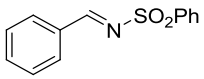
[a]Reaction conditions: substrate (0.15 mmol), cat. (5 mol%), oxidant (1.2 equiv.) and solvent (1.5 mL) and corresponding additive were stirred under Ar atmostphere.

## VIII. Synthesis of oxidants



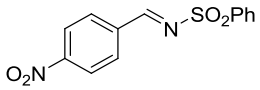

Synthesis of **22**, **23**, **24**[13]

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. Theresidue 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.



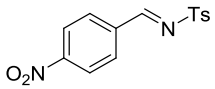
**22**

Yield: 55%; $^1$H NMR (300 MHz, $CDCl_3$): δ 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).



**23**

Yield: 64%; $^1$H NMR (300 MHz, $CDCl_3$): δ 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).

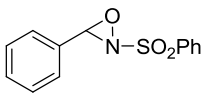


**24**

Yield: 63%; $^1$H NMR (300 MHz, $CDCl_3$): δ 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).

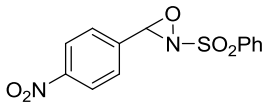
Synthesis of **17**, **18**, **19**[14]

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 $K_2CO_3$ (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.



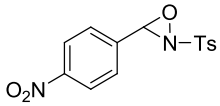
**17**

Yield: 84%; $^1$H NMR (300 MHz, $CDCl_3$): δ 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).



**18**

Yield: 87%; $^1$H NMR (300 MHz, $CDCl_3$): δ 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).



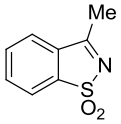
**19**

Yield: 84%; $^1$H NMR (300 MHz, $CDCl_3$): δ 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]

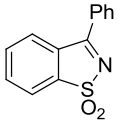
To a 250 mL Schlenck flask equipped with a condenser, septum and magnetic stirring bar was placed saccharin (1.83 g, 10.0 mmol) in THF (100 mL). The flask was cooled to –78 ℃ in a dry ice-acetone bath, and methyl lithium or phenyl lithium (21 mmol) was carefully added by syringe. The reaction was stirred at –78 ℃ for an additional 4 h; $H_2O$ (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% $NaHCO_3$ (2×60 mL), and $H_2O$ (100 mL) and dried over anhydrous $MgSO_4$. Removal of the solvent *in vacuo* gave a white solid, which was crystallized from absolute ethanol to give the product.




**25**

Yield: 71%; $^1$H NMR (300 MHz, $CDCl_3$): 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).



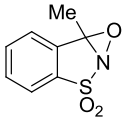

**26**

Yield: 76%; $^1$H NMR (300 MHz, $CDCl_3$): 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**, **21**[16]

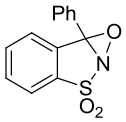
In a 100 mL three-necked flask, equipped with an addition funnel, were placed the appropriate 1,2-benzisothiazole-1,1-dioxide (2.0 mmol) in DCM (30 mL) and 30 mL of saturated solution of potassium carbonate. The reaction was stirred vigorously and a solution of mCPBA (0.56 g) in DCM (20 mL)was added 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 $MgSO_4$, 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.




**20**

Yield: 72%; $^1$H NMR (300 MHz, $CDCl_3$): δ 7.79-7.74 (m, 4H), 2.14 (s, 3H); MS (EI): *m/z* 197 ($M^+$), 167 (100.00), 103 (47.46), 77 (92.03), 76 (73.64), 64 (48.01), 63 (46.12), 50 (66.33), 43 (63.73).

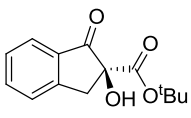



**21**

Yield: 77%; $^1$H NMR (300 MHz, $CDCl_3$): δ 7.88 (dd, *J* = 0.6, 6.6 Hz, 1H), 7.81-7.71 (m, 2H), 7.65-7.50 (m, 6H); MS (EI): *m/z* 259 ($M^+$), 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

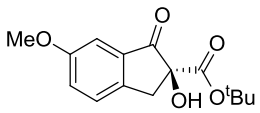
The β-ketoester (0.15 mmol) was dissolved in the indicated solvent (2.0 mL). To this solution was added the iron complex (5 mol%, 0.0075 mmol), and successively 3-(4-nitrophenyl)-2-(phenylsulfonyl)-1,2-oxaziridine (55.2 mg, 0.18 mmol) was added at the given temperature (-10 °C). The reaction mixture 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.




**8a**

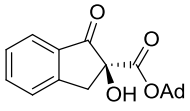
Yield: 95% (35.0 mg); $^1$H NMR (300 MHz, $CDCl_3$): δ 7.80 (d, *J* = 7.5 Hz, 1H), 7.66

(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/$^i$PrOH=90/10, 1.0 mL/min, 254 nm, tR(major)= 8.1 min, tR(minor)= 13.7 min (83% *ee*); $[\alpha]^D_{20}$: +36.9 (c= 1.03, solv: $CHCl_3$, 83% *ee*).




**8b**

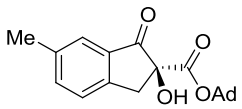
Yield: 95% (39.7 mg); $^1$H NMR (300 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.1 Hz, 1H), 7.27-7.21 (m, 2H), 4.03 (s, 1H), 3.85 (s, 3H), 3.57 (d, *J* = 16.8 Hz, 1H), 3.14 (d, *J* = 16.8 Hz, 1H), 1.37 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): δδ 201.32, 170.54, 159.55, 145.25, 134.92, 126.92, 125.19, 105.94, 83.82, 81.06, 55.52, 38.76, 27.60; IR (KBr): $\nu_{max}$ 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 $[C15H18O5]^+$ Calcl. 278.1154, Found: 278.1151; HPLC: Daicel Chiralpak IC, Hexane/$^i$PrOH=90/10, 1.0 mL/min, 254 nm, tR(major)= 22.1 min, tR(minor)= 28.2 min (80% *ee*); $[\alpha]^D_{20}$: +22.8 (c= 1.04, solv: $CHCl_3$, 80% *ee*).




**8c**

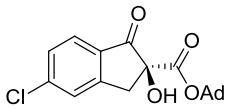
Yield: 97% (47.5 mg); $^1$H NMR (300 MHz, $CDCl_3$): δ 7.79 (d, *J* = 6.0 Hz, 1H), 7.65 (dt, *J* = 0.9, 5.7 Hz, 1H), 7.48 (d, *J* = 6.0 Hz, 1H), 7.42 (dt, *J* = 0.6, 5.7 Hz, 1H), 4.02 (s, 1H), 3.66 (d, *J* = 12.9 Hz, 1H), 3.22 (d, *J* = 12.9 Hz, 1H), 2.12 (s, 3H), 1.97-1.95 (m, 6H), 1.61-1.59 (m, 6H); 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/$^i$PrOH=90/10, 1.0 mL/min, 254 nm, tR(major)= 16.7 min, tR(minor)=

26.4 min (87% *ee*); $[\alpha]^{D}_{20}$: +29.8 (c= 1.07, solv: $CHCl_3$, 87% *ee*).



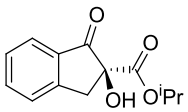

**8d**

Yield: 97% (49.5 mg); $^1$H NMR (300 MHz, $CDCl_3$): δ 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), 91 (5.80), 79 (12.30), 77 (8.25), 43 (5.85), 40 (34.92); HPLC: Daicel Chiralpak AD-H, Hexane/$^i$PrOH=85/15, 1.0 mL/min, 254 nm, tR(major)= 11.1 min, tR(minor)= 19.7 min (84% *ee*); $[\alpha]^{D}_{20}$: +17.7 (c= 1.06, solv: $CHCl_3$, 84% *ee*).




**8e**

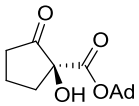
Yield: 92% (49.8 mg); $^1$H NMR (300 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.4 Hz, 1H), 7.48 (s, 1H), 7.40 (d, *J* = 8.1 Hz, 1H), 4.08 (s, 1H), 3.63 (d, *J* = 17.4 Hz, 1H), 3.20 (d, *J* = 17.4 Hz, 1H), 2.13 (s, 3H), 1.98-1.96 (m, 6H), 1.60-1.59 (m, 6H); MS (ESI): *m/z* 383.0 ($[M+Na]^+$), 743.0 ($[2M+Na]^+$); HPLC: Daicel Chiralpak AD-H, Hexane/$^i$PrOH=70/30, 0.7 mL/min, 214 nm, tR(major)= 13.9 min, tR(minor)= 23.1 min (63% *ee*); $[\alpha]^{D}_{20}$: +44.5 (c= 1.02, solv: $CHCl_3$, 63% *ee*).




**8f**

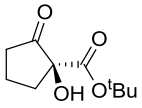
Yield: 89% (31.3 mg); $^1$H NMR (300 MHz, $CDCl_3$): δ 7.80 (d, *J* = 7.5 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.51-7.41, (m, 2H), 5.14-5.01 (m, 1H), 4.03 (s, 1H), 3.70 (d, *J* = 17.1 Hz, 1H), 3.24 (d, *J* = 17.1 Hz, 1H), 1.17 (dd, *J* = 6.3, 20.7 Hz, 6H); MS (EI): *m/z* 234 ($M^+$), 192 (87.67), 147 (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/$^i$PrOH=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, solv: $CHCl_3$, 69% *ee*).



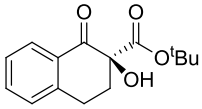

**8g**

Yield: 95% (39.7 mg); $^1$H NMR (300 MHz, $CDCl_3$): δ 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/$^i$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, solv: $CHCl_3$, 89% *ee*).




**8h**

Yield: 88% (26.4 mg); $^1$H NMR (300 MHz, $CDCl_3$): δ 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/$^i$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, solv: $CHCl_3$, 84% *ee*).




**8i**

Yield: 92% (36.2 mg); $^1$H NMR (300 MHz, $CDCl_3$): δ 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/$^i$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, solv: $CHCl_3$, 46% *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


1. A. Alexakis, A. Tomassini, C. Chouillet, S. Rolans, P. Mangeney and G. Bernardinelli, *Angew. Chem. Int. Ed.*, 2000, **39**, 4093.
2. X.-N. Song and Z.-J. Yao, *Tetrahedron*, 2010, **66**, 2589.
3. L. Canali, E. Cowan, H. Deleuze, C. L. Gibson and D. C. Sherrington, *J. Chem. Soc., Perkin Trans. 1*, 2000, 2055.
4. N. Gisch, J. Balzarini and C. Meier, *J. Med. Chem.*, 2007, **50**, 1658.
5. L. H. Tong, Y.-L.Wong, S. I. Pascu and J. R. Dilworth, *Dalton Trans.*, 2008, 4784.
6. E. Sergeeva, J. Kopilov, I. Goldberg and M. Kol, *Chem. Commun.*, 2009, 3053.
7. T. A. Moss, D. R. Fenwick and D. J. Dixon, *J. Am. Chem. Soc.*, 2008, **130**, 10076.
8. (*a*) E. Tanzer, W. B. Schweizer, M. Ebert and R. Gilmour, *Chem. Eur. J.*, 2012, **18**, 2006; (*b*) A. M. R. Smith, K.-K. Hii and D. Billen, *Chem. Commun.*, 2009, 3925.
9. E. Abraham, C. W. Bailey, T. D. W. Claridge, S. G. Davies, K. B. Ling, B. Odell, T. L. Rees, P. M. Roberts, A. J. Russell, A. D. Smith, H. R.Storr, M. J. Sweet, A. L. Thompson, J. E. Thomson, G. E. Tranter, D. J. Watkin and L. J. Smith, *Tetrahedron: Asymmetry*, 2010, **21**, 1797.
10. M. Nakajima, S. Yamamoto, Y. Yamaguchi, S. Nakamura and S. Hashimoto, *Tetrahedron*, 2003, **59**, 7307.
11. A. M. R. Smith, H. S. Rzepa, A. J. P. White, D. Billen and K. K. Hii, *J. Org. Chem.*, 2010, **75**, 3085.
12. Y. Hamashima, T. Suzuki, H. Takano, Y. Shimura and M. Sodeoka, *J. Am. Chem. Soc.*, 2005, **127**, 10164.
13. F. A. Davis, S. G. Lal and H. D. Durst, *J. Org. Chem.*, 1988, **53**, 5004.
14. F. A. Davis, S. Chattopadhyay, J. C. Towson, S. Lal and T. Reddy, *J. Org. Chem.*, 1988, **53**, 2087.
15. Q. Yang, G. Shang, W.-Z. Gao, J.-G. Deng and X.-M. Zhang, *Angew. Chem. Int. Ed.*, 2006, **45**, 3832.
16. F. A. Davis, J. C. Towson, D. B. Vashi, R. T. Reddy and J. P. McCauley, *J. Org. Chem.*, 1990, **55**, 1254.

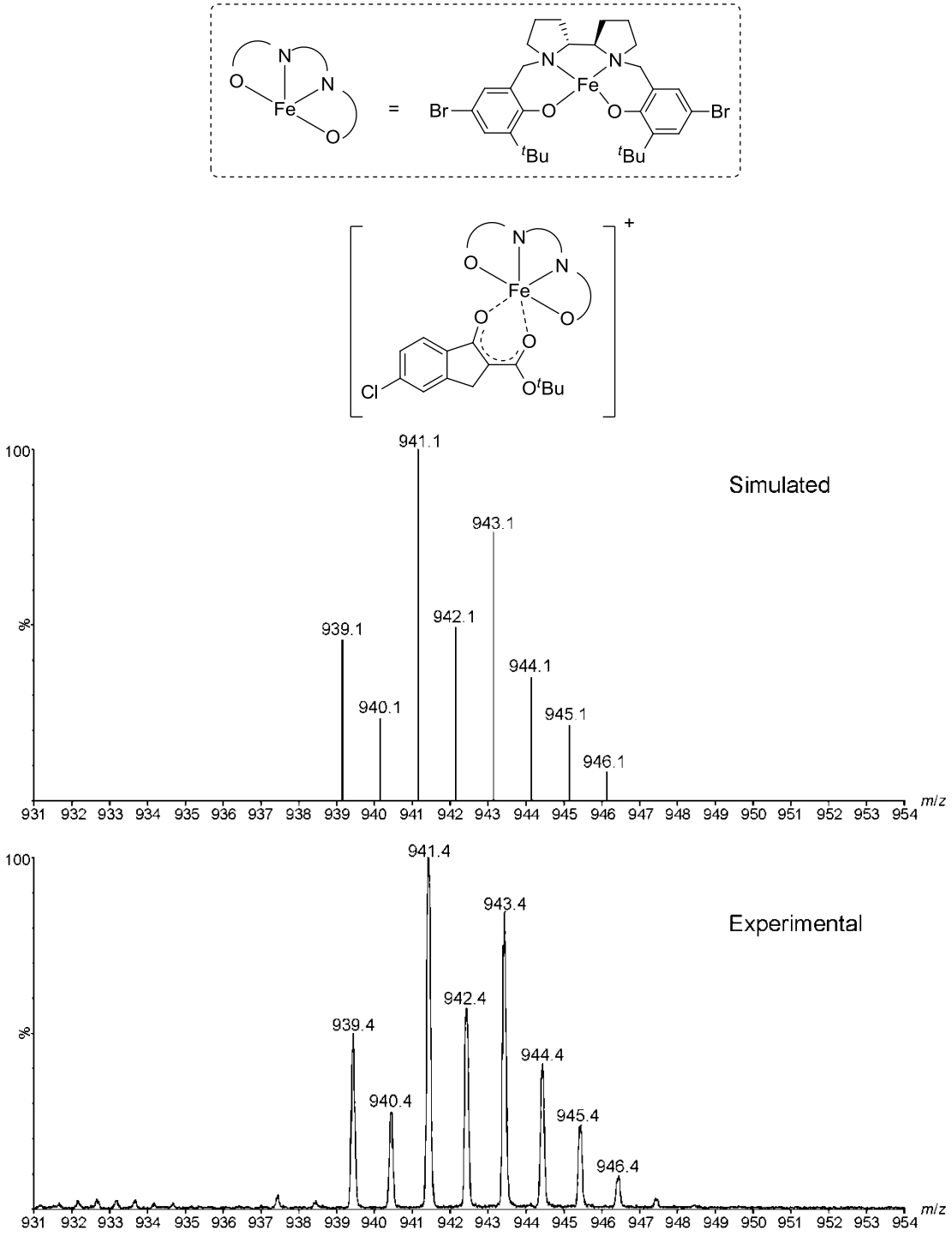
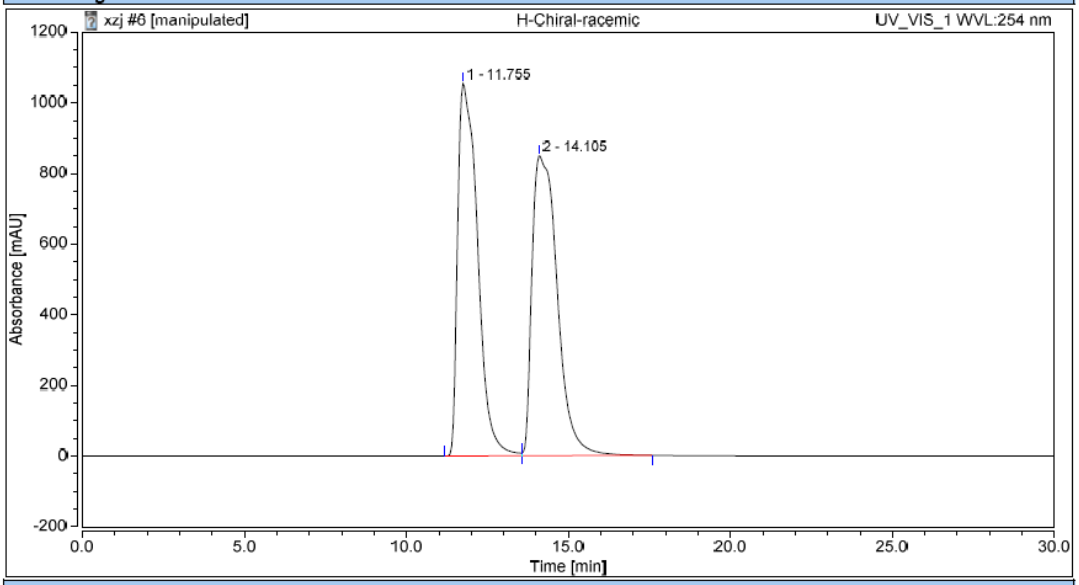



**Fig. S1** Upper: Simulated isotopic distribution pattern for the adduct formed between the deprotonated form of substrate **4e** with catalyst **3c** (with $ClO_4^-$ as counter anion). Lower: Observed isotopic distribution pattern for the peak at *m*/*z* 941.4 detected by high-resolution ESI-MS analysis of a reaction mixture of **4e** and **3c** in acetonitrile.

HPLC of **5a**

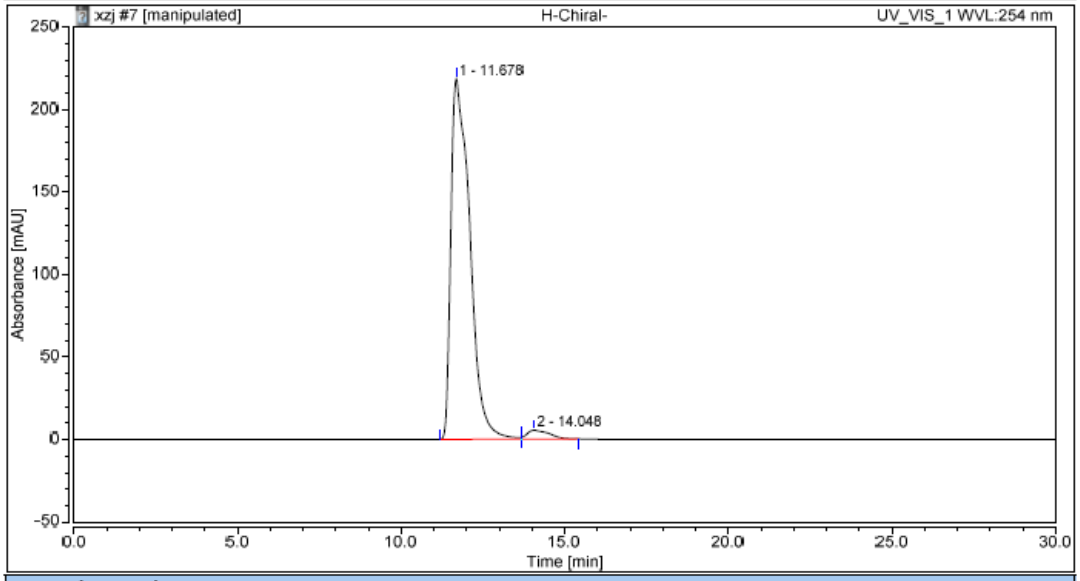
**Chromatogram**




**Integration Results**

| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | PhMe | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 11.755 | 748.794 | 1055.194 | 49.48 | 55.38 | n.a. |
| 2 | | 14.105 | 764.492 | 850.014 | 50.52 | 44.62 | n.a. |
| **Total:** | | | **1513.286** | **1905.208** | **100.00** | **100.00** | |

**Chromatogram**

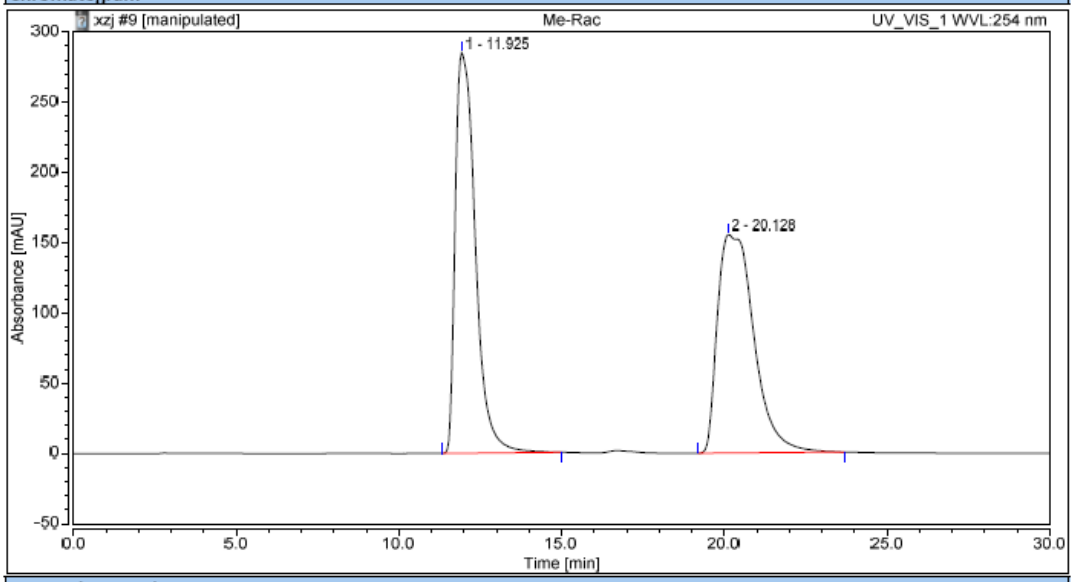



**Integration Results**

| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | PhMe | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 11.678 | 146.204 | 218.542 | 97.19 | 97.59 | n.a. |
| 2 | | 14.048 | 4.226 | 5.392 | 2.81 | 2.41 | n.a. |
| **Total:** | | | **150.430** | **223.933** | **100.00** | **100.00** | |

HPLC of **5b**

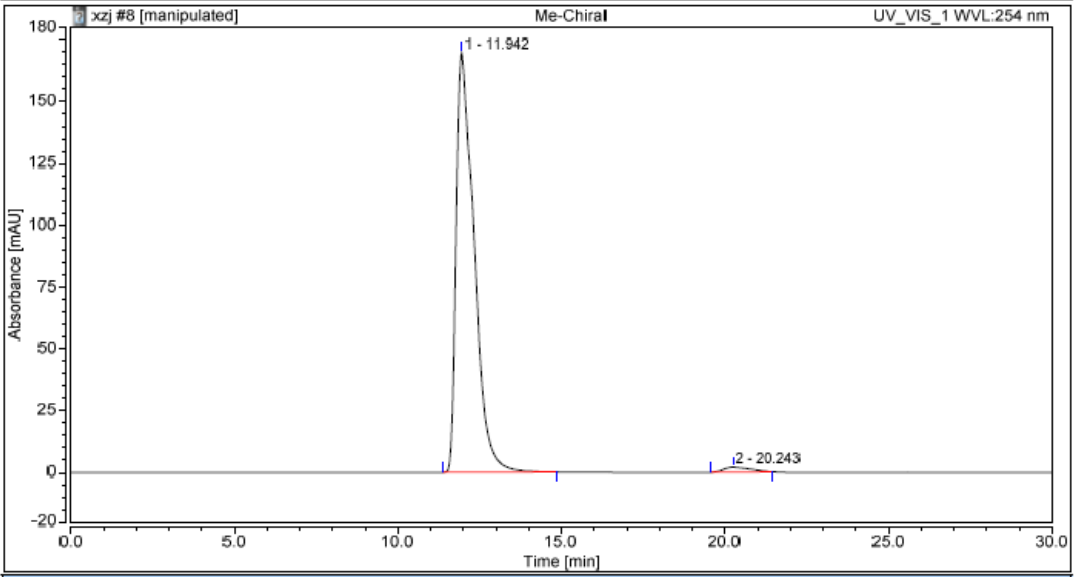
Chromatogram




Integration Results

| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | PhMe | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 11.925 | 203.764 | 285.175 | 50.24 | 64.72 | n.a. |
| 2 | | 20.128 | 201.828 | 155.468 | 49.76 | 35.28 | n.a. |
| **Total:** | | | **405.592** | **440.643** | **100.00** | **100.00** | |

Chromatogram




Integration Results

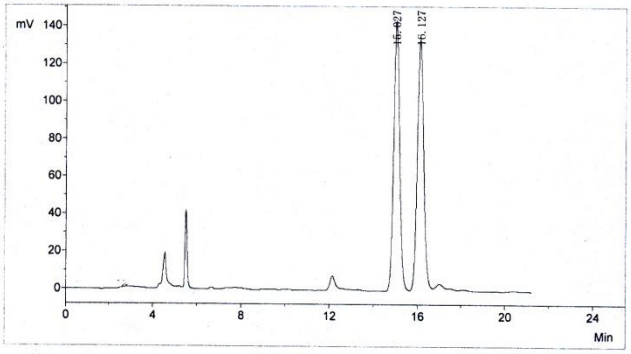
| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | PhMe | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 11.942 | 107.729 | 169.665 | 98.31 | 98.85 | n.a. |
| 2 | | 20.243 | 1.857 | 1.981 | 1.69 | 1.15 | n.a. |
| **Total:** | | | **109.586** | **171.645** | **100.00** | **100.00** | |

HPLC of **5c**

# 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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| 2 | 2 | | 16.127 | 131642.1 | 2654202.8 | 49.5742 |
| 合计: | | | | 275207.2 | 5353998.9 | 100.0000 |

# 色谱分析报告

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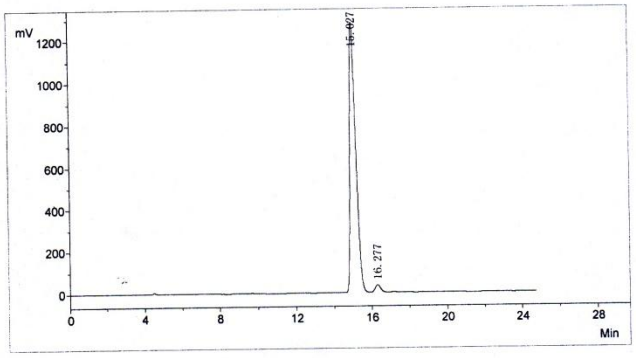
样品批号:
分析日期:2011-09-22

样品文件名:gx-6-90.che
分析者:
分析时间:09:27




| 序号 | 峰号 | 组份名 | 保留时间 | 峰高 | 峰面积 | 面积百分比(%) |
|---|---|---|---|---|---|---|
| 1 | 1 | | 15.027 | 1279952.0 | 28070431.1 | 97.5193 |
| 2 | 2 | | 16.277 | 34307.3 | 714050.8 | 2.4807 |
| 合计: | | | | 1314259.4 | 28784481.9 | 100.0000 |

HPLC of **5d**

Data File C:\HPCHEM\1\DATA\SIG16598.D Sample Name: gx-6-86

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

```
Injection Date  : 9/28/11 8:46:47 PM
Sample Name     : gx-6-86                          Location : Vial 1
Acq. Operator   : gx
Method          : C:\HPCHEM\1\METHODS\ZKAMINE.M
Last changed    : 9/28/11 8:23:16 PM by gx
                  (modified after loading)
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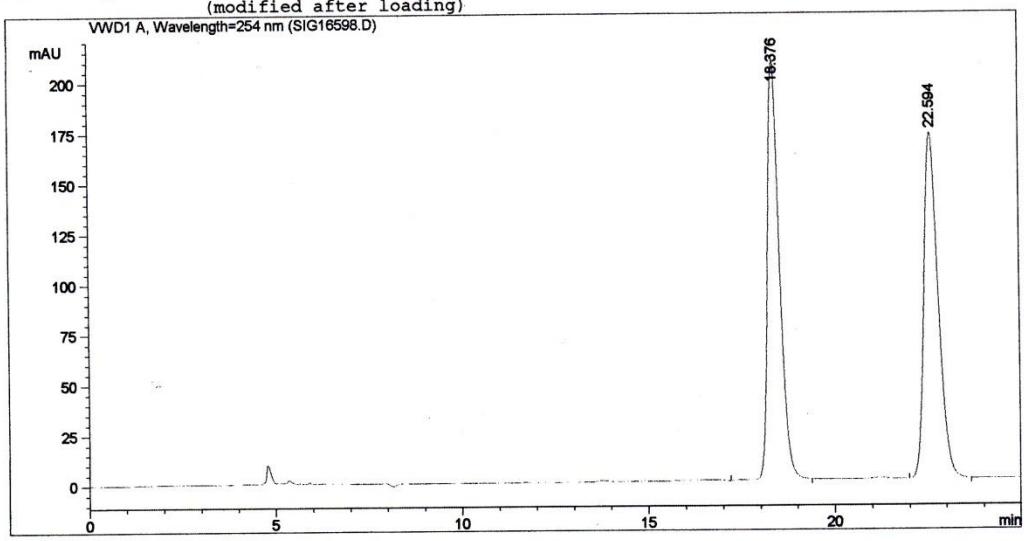


Area Percent Report

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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
```

Signal 1: VWD1 A, Wavelength=254 nm

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 18.376 | PB | 0.3422 | 4624.59326 | 208.11803 | 50.1494 |
| 2 | 22.594 | BB | 0.4168 | 4597.03125 | 171.09828 | 49.8506 |
| Totals : | | | | 9221.62451 | 379.21631 | |

Results obtained with enhanced integrator!

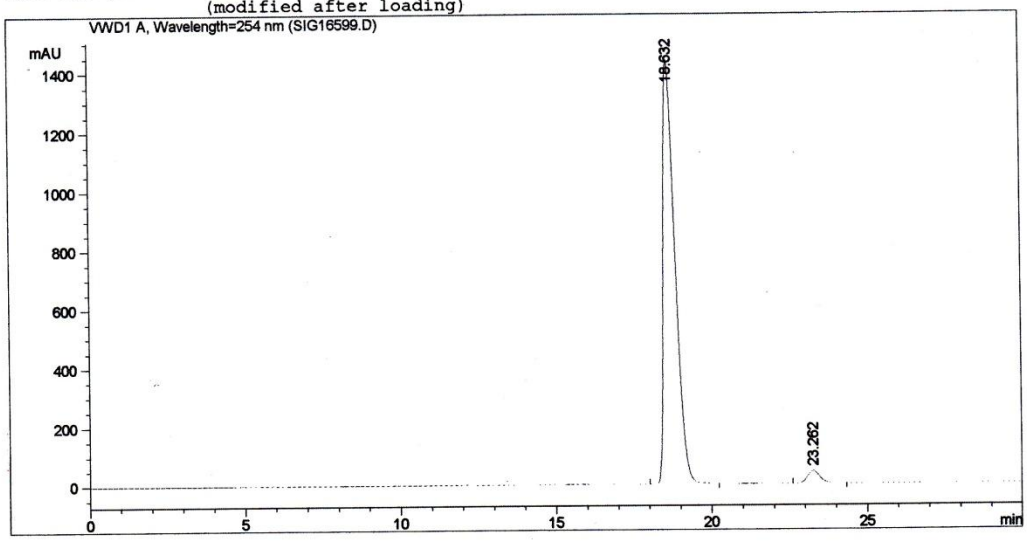
*** End of Report ***

Instrument 1 9/28/11 9:22:06 PM gx Page 1 of 1

Data File C:\HPCHEM\1\DATA\SIG16599.D Sample Name: gx-6-96

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

```
Injection Date  : 9/28/11 9:29:59 PM
Sample Name     : gx-6-96                    Location : Vial 1
Acq. Operator   : gx
Method          : C:\HPCHEM\1\METHODS\ZKAMINE.M
Last changed    : 9/28/11 9:29:52 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

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 18.632 | VB | 0.4117 | 3.79313e4 | 1435.12878 | 96.9912 |
| 2 | 23.262 | BB | 0.4220 | 1176.69836 | 42.89190 | 3.0088 |
| Totals : | | | | 3.91080e4 | 1478.02068 | |

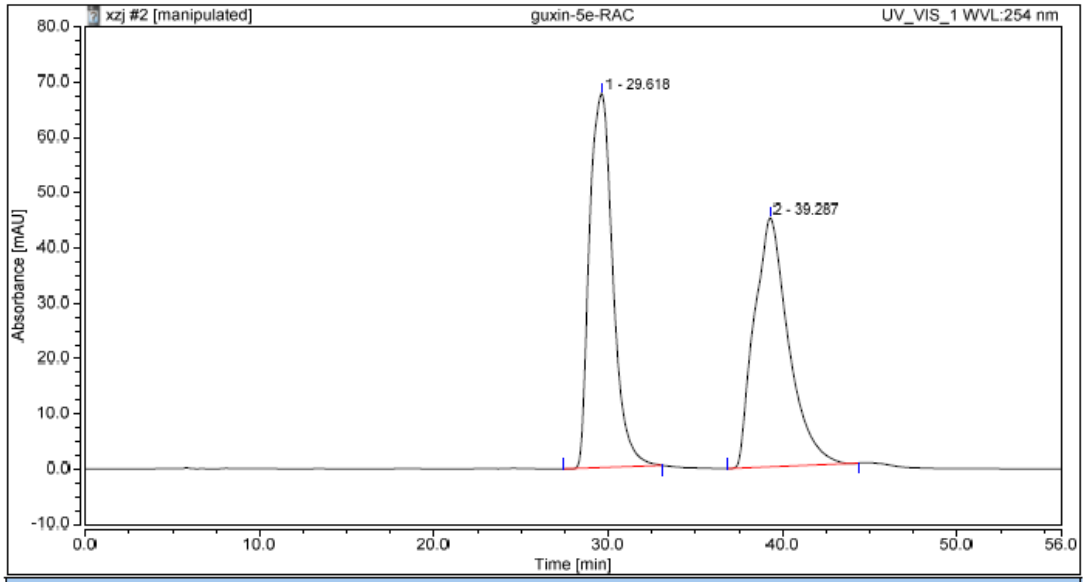
Results obtained with enhanced integrator!

*** End of Report ***

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

HPLC of **5e**

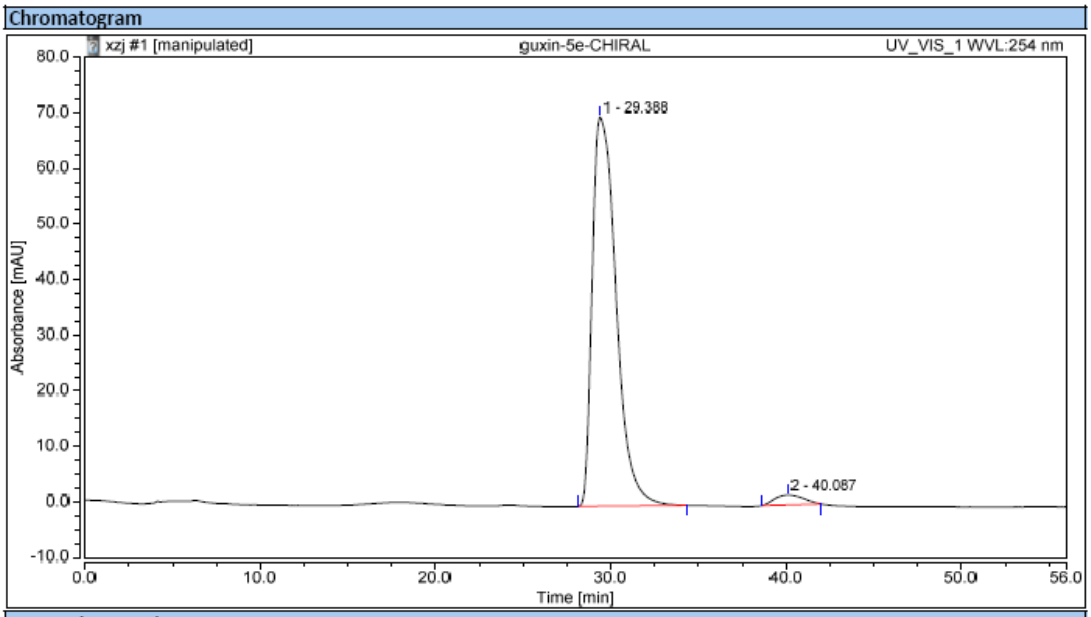
Chromatogram




Integration Results

| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | PhMe | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 29.618 | 104.993 | 67.703 | 50.62 | 60.08 | n.a. |
| 2 | | 39.287 | 102.430 | 44.988 | 49.38 | 39.92 | n.a. |
| **Total:** | | | **207.422** | **112.691** | **100.00** | **100.00** | |

Chromatogram

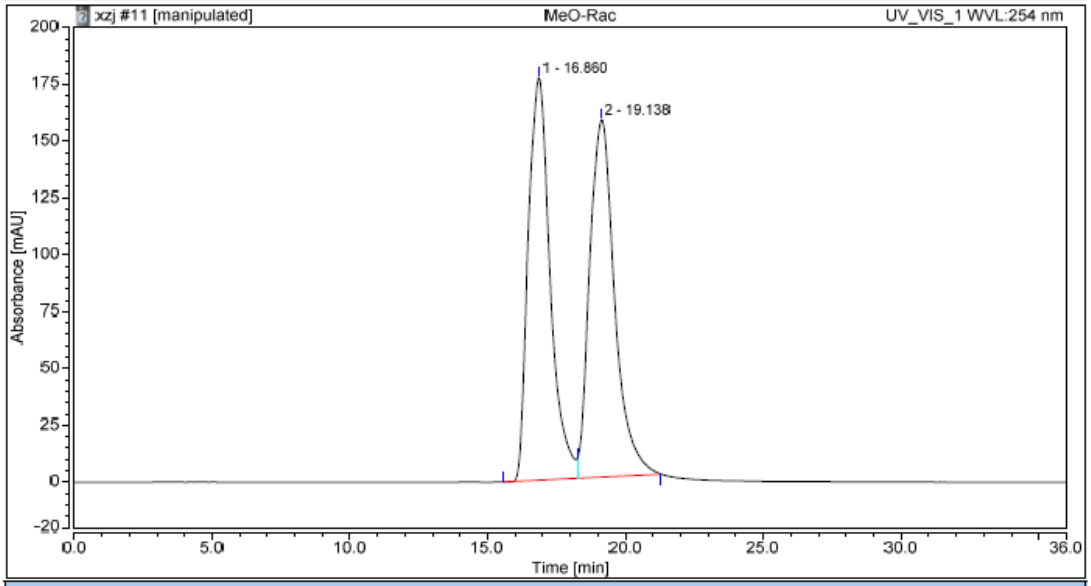



Integration Results

| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | PhMe | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 29.388 | 110.464 | 70.037 | 97.03 | 97.53 | n.a. |
| 2 | | 40.087 | 3.383 | 1.776 | 2.97 | 2.47 | n.a. |
| **Total:** | | | **113.847** | **71.812** | **100.00** | **100.00** | |

HPLC of **5f**

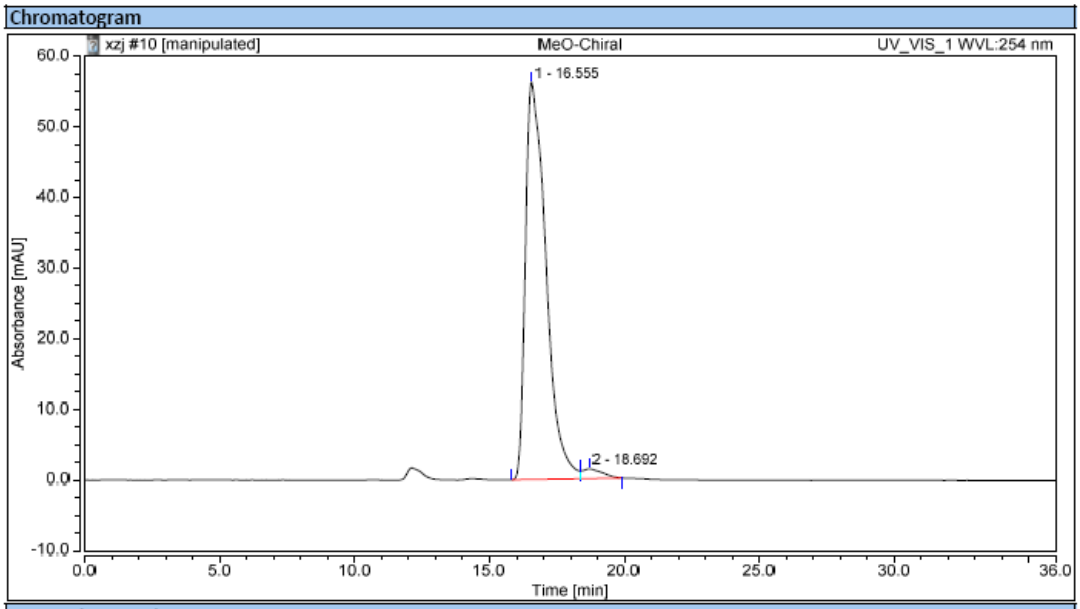
Chromatogram




Integration Results

| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | PhMe | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 16.860 | 163.062 | 177.195 | 49.64 | 52.97 | n.a. |
| 2 | | 19.138 | 165.399 | 157.346 | 50.36 | 47.03 | n.a. |
| **Total:** | | | **328.461** | **334.541** | **100.00** | **100.00** | |

Chromatogram




Integration Results

| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | PhMe | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 16.555 | 49.388 | 56.227 | 97.65 | 97.61 | n.a. |
| 2 | | 18.692 | 1.191 | 1.374 | 2.35 | 2.39 | n.a. |
| **Total:** | | | **50.579** | **57.601** | **100.00** | **100.00** | |

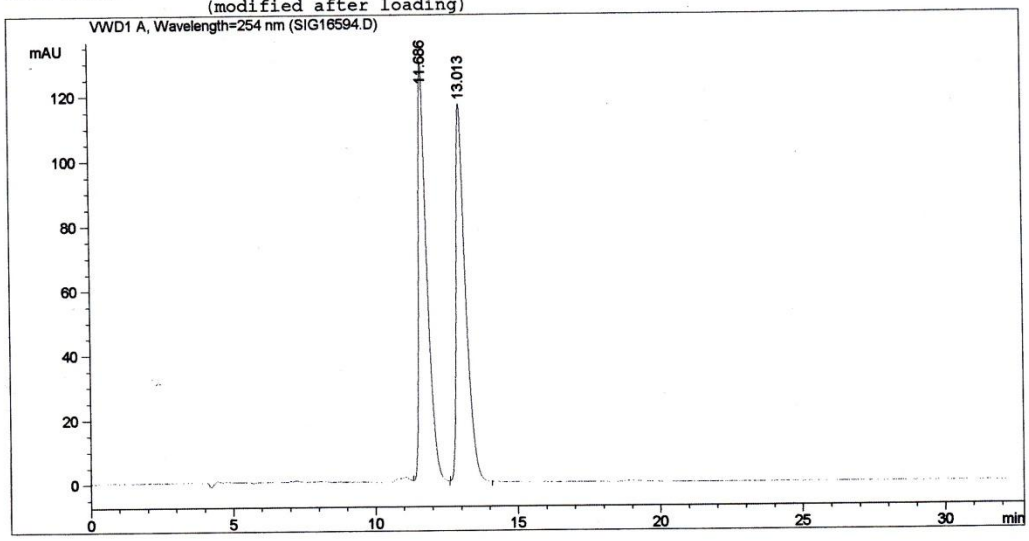
HPLC of **5g**

Data File C:\HPCHEM\1\DATA\SIG16594.D

Sample Name: gx-6-93

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

```
Injection Date  : 9/27/11 8:22:33 PM
Sample Name     : gx-6-93                          Location : Vial 1
Acq. Operator   : gx
Method          : C:\HPCHEM\1\METHODS\ZKAMINE.M
Last changed    : 9/27/11 8:55:02 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

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 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 ***

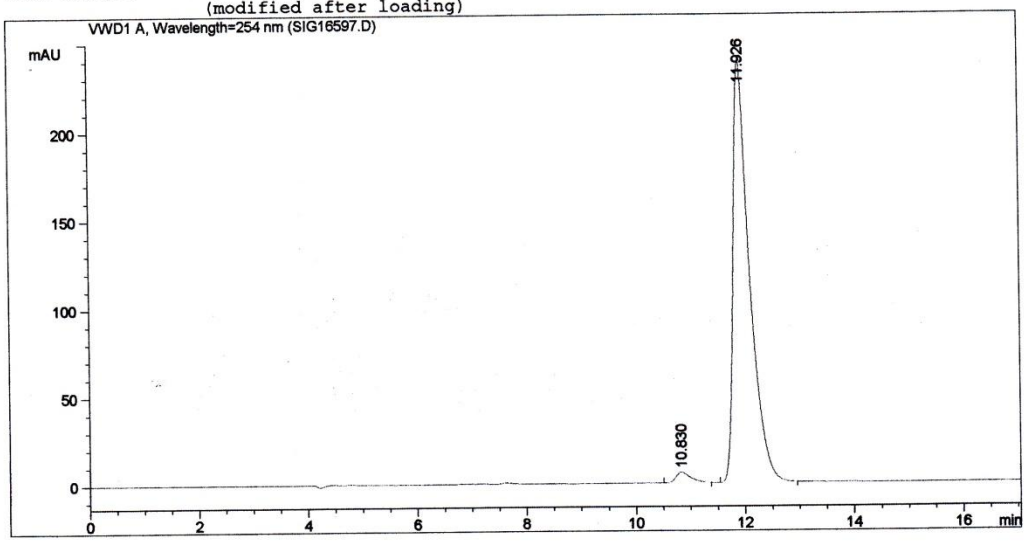
Instrument 1 9/27/11 8:55:07 PM gx

Page 1 of 1

Data File C:\HPCHEM\1\DATA\SIG16597.D Sample Name: gx-6-98

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

Injection Date : 9/28/11 7:54:10 PM
Sample Name : gx-6-98 Location : Vial 1
Acq. Operator : gx
Method : C:\HPCHEM\1\METHODS\ZKAMINE.M
Last changed : 9/28/11 8:10:54 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

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.830 | VB | 0.2704 | 110.68613 | 6.08534 | 2.1845 |
| 2 | 11.926 | PB | 0.3051 | 4956.20850 | 238.42421 | 97.8155 |
| Totals : | | | | 5066.89463 | 244.50955 | |

Results obtained with enhanced integrator!

*** End of Report ***

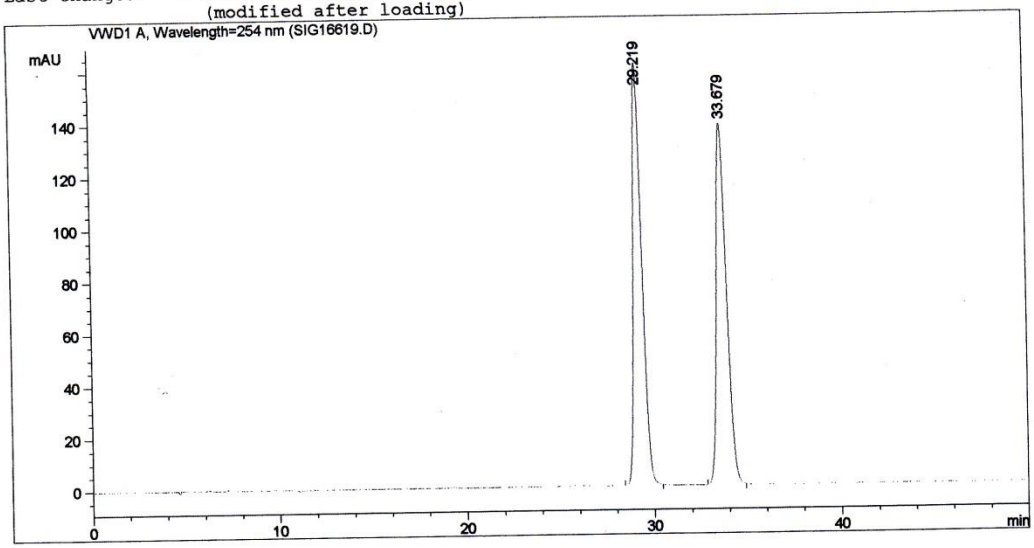
Instrument 1 9/28/11 8:10:58 PM gx Page 1 of 1

HPLC of **5h**

Data File C:\HPCHEM\1\DATA\SIG16619.D

IC, 85/15, 0.7 ml/min 254 nm

```
Injection Date  : 10/20/11 8:44:58 AM
Sample Name     : gx-7-14                    Location : Vial 1
Acq. Operator   : gx
Method          : C:\HPCHEM\1\METHODS\ZKAMINE.M
Last changed    : 10/20/11 9:28:07 AM by gx
                  (modified after loading)
```




Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
```

Signal 1: VWD1 A, Wavelength=254 nm

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 29.219 | BB | 0.5020 | 5216.41016 | 161.52530 | 50.0662 |
| 2 | 33.679 | BB | 0.5761 | 5202.62158 | 138.19688 | 49.9338 |
| Totals : | | | | 1.04190e4 | 299.72218 | |

Results obtained with enhanced integrator!

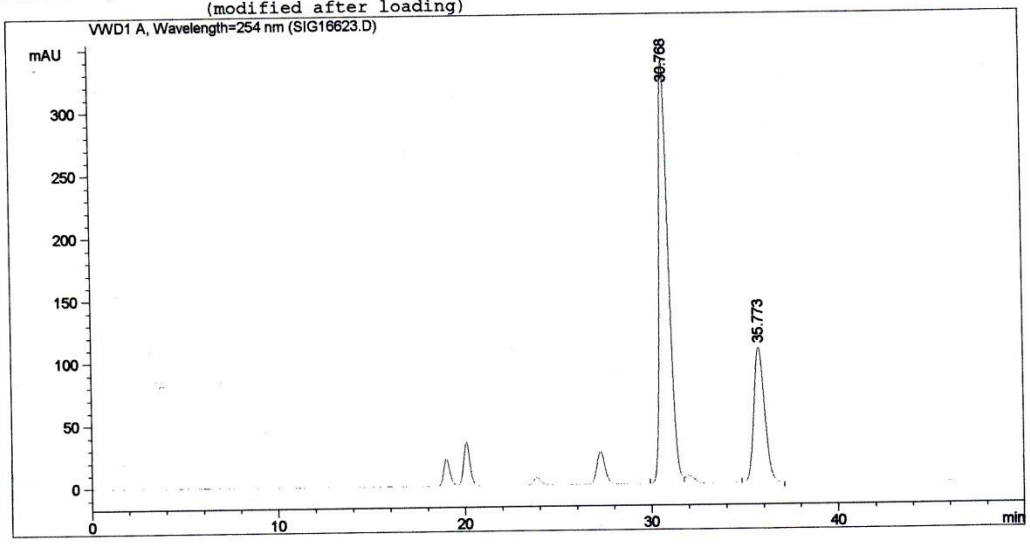
*** End of Report ***

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

Data File C:\HPCHEM\1\DATA\SIG16623.D

IC, 85/15, 0.7 ml/min 254 nm

Injection Date : 10/20/11 9:39:46 PM
Sample Name : gx-7-20 Location : Vial 1
Acq. Operator : gx
Method : C:\HPCHEM\1\METHODS\ZKAMINE.M
Last changed : 10/20/11 10:28:48 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

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 30.768 | BV | 0.5402 | 1.17215e4 | 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

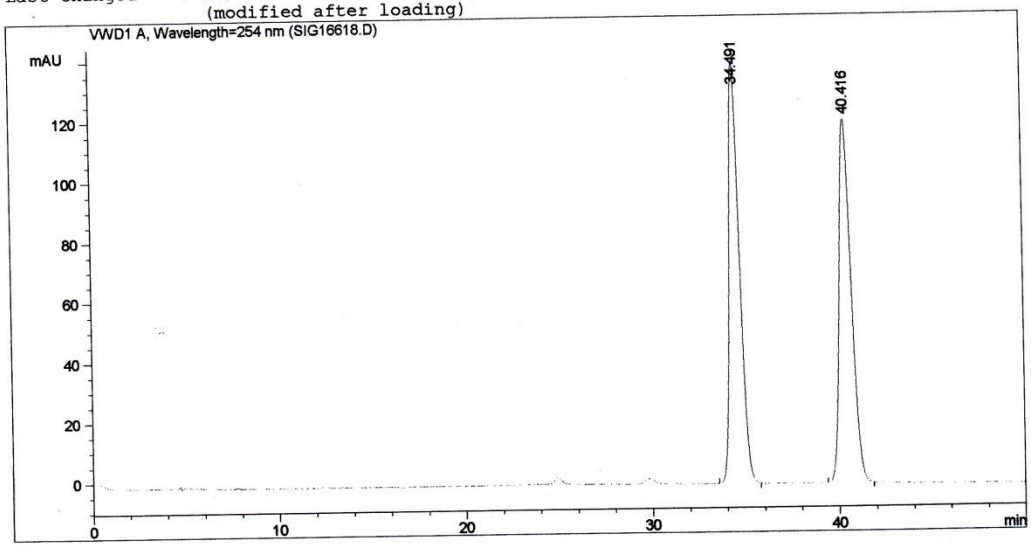
Page 1 of 1

HPLC of **5i**

Data File C:\HPCHEM\1\DATA\SIG16618.D

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

```
Injection Date  : 10/19/11 10:58:36 PM
Sample Name     : gx-7-16                          Location : Vial 1
Acq. Operator   : gx
Acq. Method     : C:\HPCHEM\1\METHODS\ZKAMINE.M
Last changed    : 10/19/11 10:41:13 PM by gx
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\ZKAMINE.M
Last changed    : 10/19/11 11:49:47 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

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  34.491 BB    0.5984 5393.06299  139.85783  50.0142
   2  40.416 BB    0.6942 5389.99316  120.70573  49.9858

Totals :                  1.07831e4   260.56357

 Results obtained with enhanced integrator!
```

*** End of Report ***

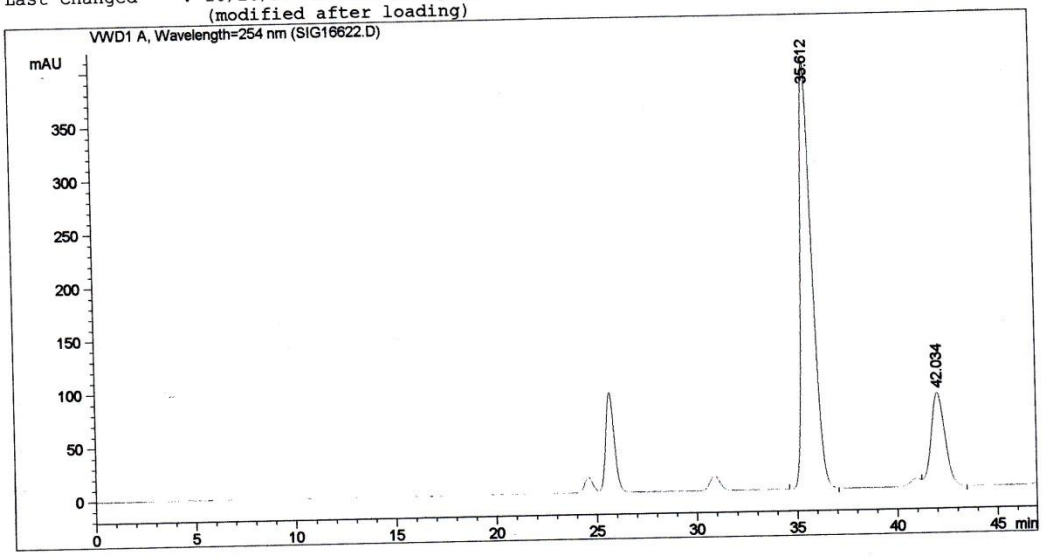
Instrument 1 10/19/11 11:50:00 PM gx

Page 1 of 1

Data File C:\HPCHEM\1\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 Location : Vial 1
Acq. Operator : gx
Method : C:\HPCHEM\1\METHODS\ZKAMINE.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

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 35.612 | VB | 0.6255 | 1.61238e4 | 399.28278 | 79.3263 |
| 2 | 42.034 | VB | 0.7355 | 4202.13184 | 87.42609 | 20.6737 |
| Totals : | | | | 2.03259e4 | 486.70886 | |

Results obtained with enhanced integrator!

*** End of Report ***

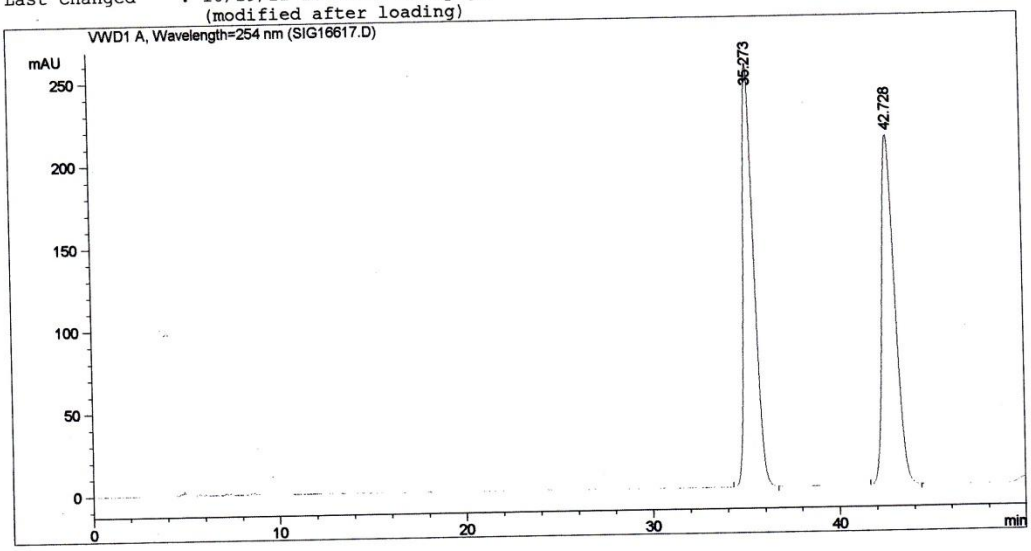
Instrument 1 10/20/11 9:10:24 PM gx

HPLC of **5j**

Data File C:\HPCHEM\1\DATA\SIG16617.D

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

```
Injection Date  : 10/19/11 9:42:45 PM                    Location : Vial 1
Sample Name     : gx-7-15
Acq. Operator   : gx
Acq. Method     : C:\HPCHEM\1\METHODS\ZKAMINE.M
Last changed    : 10/19/11 10:26:50 PM by gx
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\ZKAMINE.M
Last changed    : 10/19/11 10:41:13 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

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  35.273 BB    0.6093 1.01120e4   256.01620  49.9553
   2  42.728 BB    0.7405 1.01301e4   211.04936  50.0447

Totals :                  2.02420e4   467.06557

 Results obtained with enhanced integrator!
```

*** End of Report ***

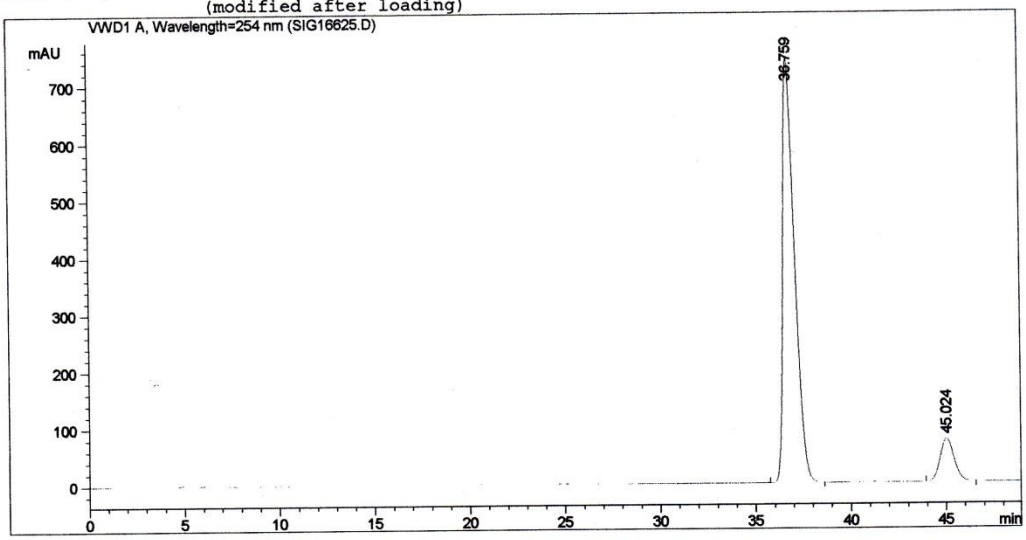
Instrument 1 10/19/11 10:41:28 PM gx

Page 1 of 1

Data File C:\HPCHEM\1\DATA\SIG16625.D Sample Name: gx-7-23

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\1\METHODS\ZKAMINE.M
Last changed : 10/22/11 12:01:15 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

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 36.759 | VB | 0.6736 | 3.22495e4 | 741.24268 | 89.4810 |
| 2 | 45.024 | BB | 0.7855 | 3791.12085 | 75.10535 | 10.5190 |
| Totals : | | | | 3.60406e4 | 816.34803 | |

Results obtained with enhanced integrator!

*** End of Report ***

Instrument 1 10/22/11 12:01:21 PM gx

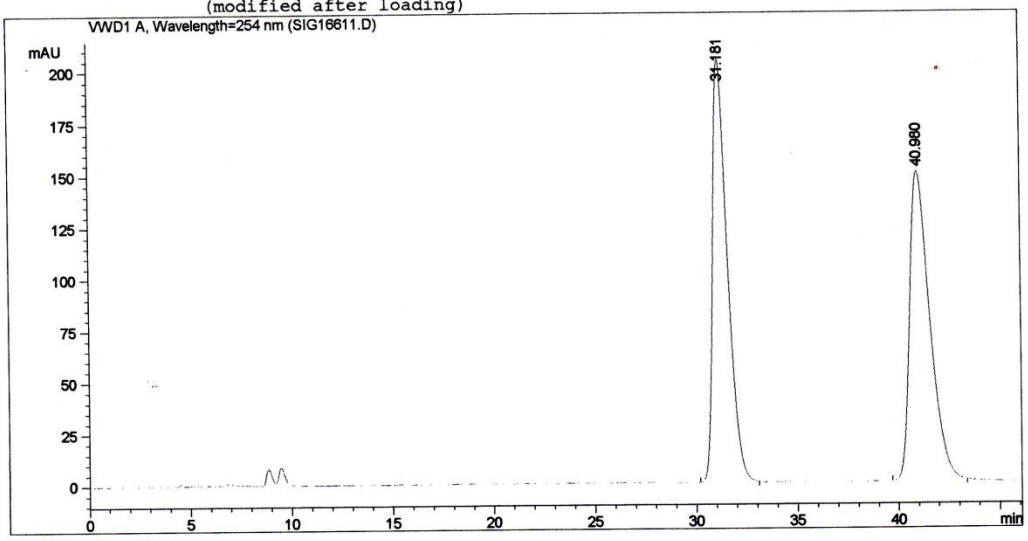
HPLC of **5k**

Data File C:\HPCHEM\1\DATA\SIG16611.D

Sample Name: gx-7-17

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

```
Injection Date  : 10/19/11 3:33:31 PM
Sample Name     : gx-7-17                          Location : Vial 1
Acq. Operator   : gx
Method          : C:\HPCHEM\1\METHODS\ZKAMINE.M
Last changed    : 10/19/11 4:19:14 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

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 31.181 | BB | 0.7693 | 1.03615e4 | 204.31961 | 50.0937 |
| 2 | 40.980 | BB | 1.0381 | 1.03227e4 | 149.03740 | 49.9063 |
| Totals : | | | | 2.06841e4 | 353.35701 | |

Results obtained with enhanced integrator!

*** End of Report ***

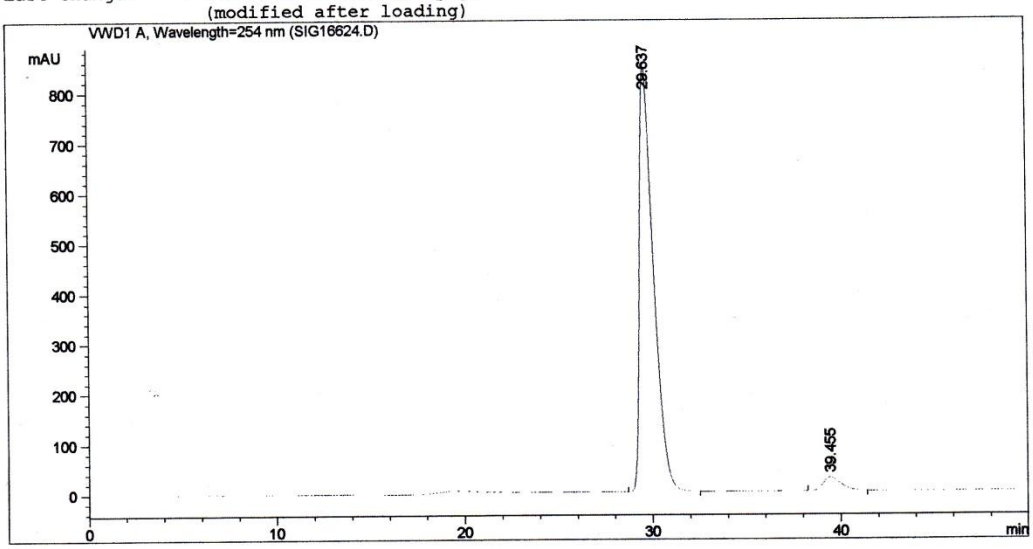
Instrument 1 10/19/11 4:19:39 PM gx

Page 1 of 1

Data File C:\HPCHEM\1\DATA\SIG16624.D Sample Name: gx-7-22

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

```
Injection Date  : 10/21/11 9:06:12 PM
Sample Name     : gx-7-22                          Location : Vial 1
Acq. Operator   : gx
Method          : C:\HPCHEM\1\METHODS\ZKAMINE.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 1: VWD1 A, Wavelength=254 nm

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 29.637 | BB | 0.7773 | 4.40646e4 | 845.02240 | 96.0209 |
| 2 | 39.455 | VB | 0.9223 | 1826.05176 | 27.58408 | 3.9791 |
| Totals : | | | | 4.58906e4 | 872.60648 | |

Results obtained with enhanced integrator!

*** End of Report ***

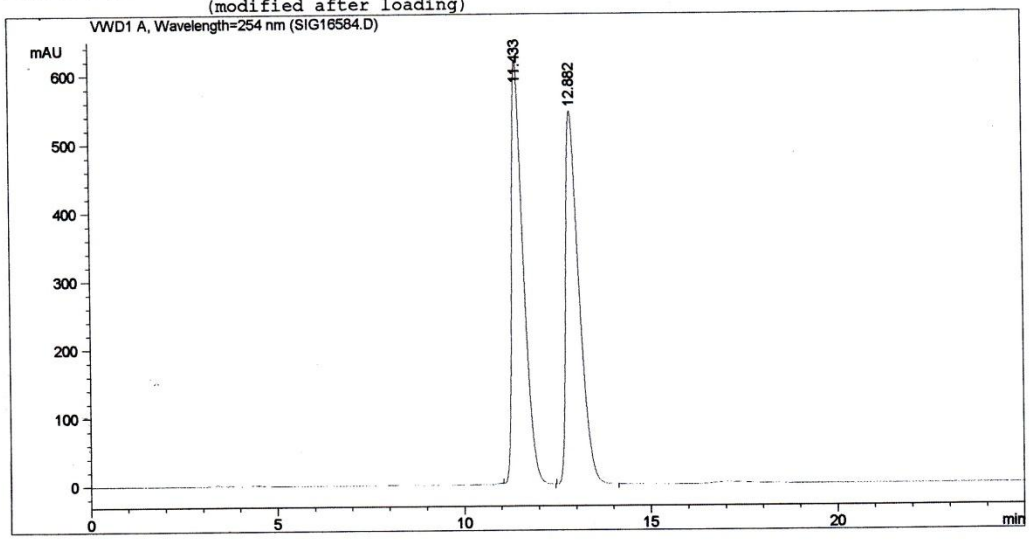
Instrument 1 10/21/11 9:56:17 PM gx Page 1 of 1

HPLC of **5l**

Data File C:\HPCHEM\1\DATA\SIG16584.D Sample Name: gx-6-88

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

```
Injection Date  : 9/22/11 1:29:21 PM
Sample Name     : gx-6-88                    Location : Vial 1
Acq. Operator   : gx
Method          : C:\HPCHEM\1\METHODS\ZKAMINE.M
Last changed    : 9/22/11 1:54:24 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

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.433 | VB | 0.3261 | 1.34263e4 | 618.46295 | 50.1074 |
| 2 | 12.882 | BB | 0.3710 | 1.33688e4 | 544.34467 | 49.8926 |
| Totals : | | | | 2.67951e4 | 1162.80762 | |

Results obtained with enhanced integrator!

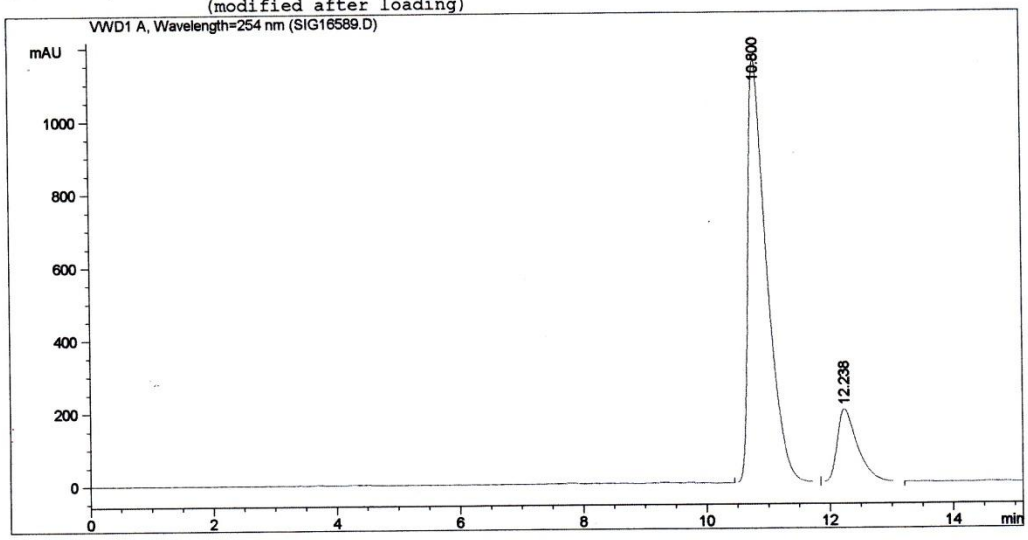
*** End of Report ***

Instrument 1 9/22/11 1:54:45 PM gx

Data File C:\HPCHEM\1\DATA\SIG16589.D Sample Name: gx-6-92

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

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




Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: VWD1 A, Wavelength=254 nm

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.800 | BV | 0.3115 | 2.42758e4 | 1158.21375 | 84.3408 |
| 2 | 12.238 | VB | 0.3343 | 4507.18848 | 198.87408 | 15.6592 |
| Totals : | | | | 2.87830e4 | 1357.08783 | |

Results obtained with enhanced integrator!

*** End of Report ***

Instrument 1 9/23/11 12:09:58 AM gx

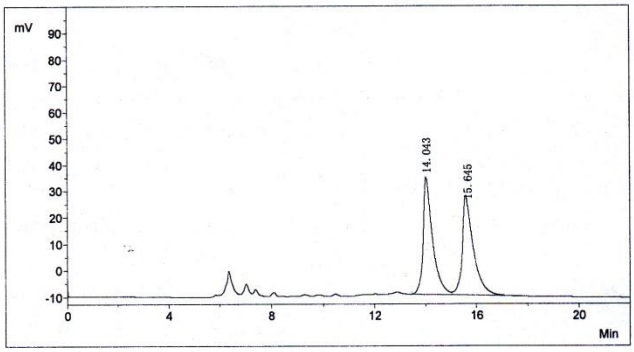
HPLC of **5m**

REGZS 98/2 0.5

# HPLC REPORT (S,S) whelk-01 214

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

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

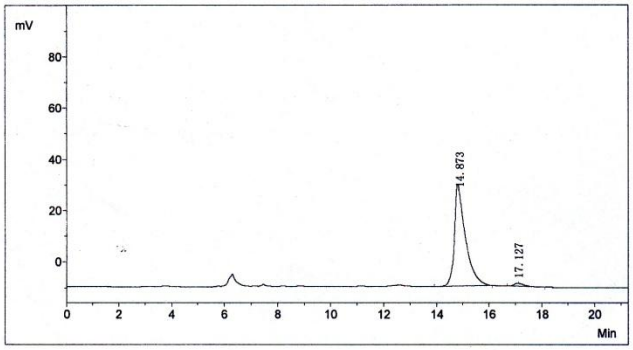



| No. | PeakNo | ID.Name | R.Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|---|
| 1 | 1 | Unknown | 14.043 | 43956.5 | 1130663.5 | 49.6815 |
| 2 | 2 | Unknown | 15.645 | 26368.5 | 1145158.9 | 50.3185 |
| Total | | | | 70325.0 | 2275822.4 | 100.0000 |

# HPLC REPORT

Sample Name:gx-7-65.che
Time:08:58
Column:
Wave Length:

Date:2011-12-05
Method:
Flow Rate:
Mobile Phase:



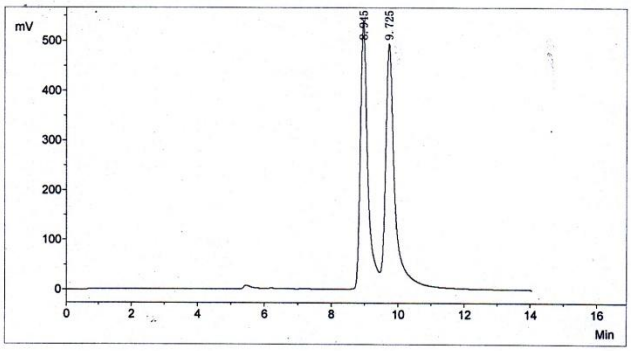

| No. | PeakNo | ID.Name | R.Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|---|
| 1 | 1 | Unknown | 14.873 | 32170.9 | 1150165.4 | 97.2868 |
| 2 | 2 | Unknown | 17.127 | 1260.2 | 32076.0 | 2.7132 |
| Total | | | | 33431.1 | 1182241.4 | 100.0000 |

HPLC of **5n**

# HPLC Report

Sample Name:
Operator:
Time:09:17

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

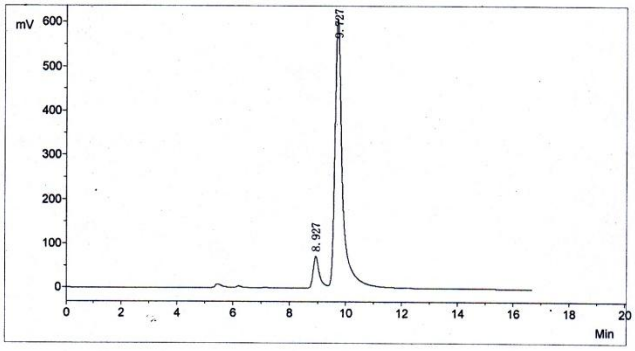



| No. | PeakNo | ID.Name | R.Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|---|
| 1 | 1 | | 8.945 | 518117.6 | 7254115.1 | 49.5291 |
| 2 | 2 | | 9.725 | 459403.8 | 7392042.7 | 50.4709 |
| Total | | | | 977521.4 | 14646157.8 | 100.0000 |

# HPLC Report

Sample Name:
Operator:
Time:09:50

Data File:GX-9-69.che
Date:2012-06-08



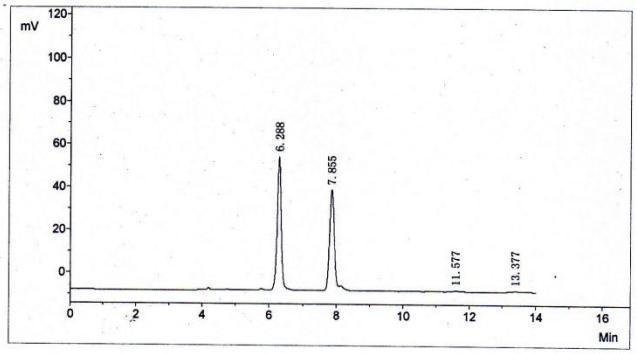

| No. | PeakNo | ID. Name | R. Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|---|
| 1 | 1 | | 8.927 | 71419.4 | 1108978.1 | 8.6959 |
| 2 | 2 | | 9.727 | 593664.1 | 11643856.4 | 91.3041 |
| Total | | | | 665083.5 | 12752834.5 | 100.0000 |

HPLC of **5o**

# HPLC Report

Sample Name:
Operator:
Time:10:58

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

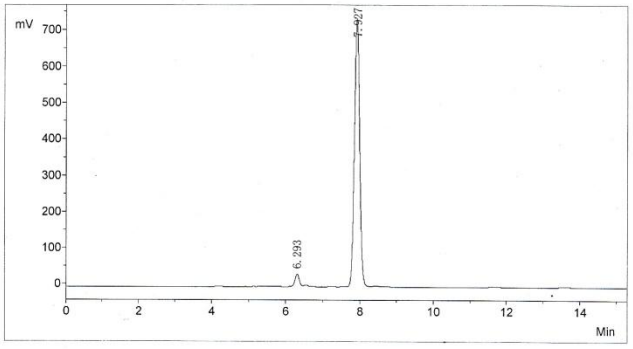



| No. | PeakNo | ID. Name | R. Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|---|
| 1 | 1 | | 6.288 | 61974.5 | 512200.4 | 53.3600 |
| 2 | 2 | | 7.855 | 45941.9 | 438115.8 | 45.6420 |
| 3 | 3 | | 11.577 | 344.2 | 5013.7 | 0.5223 |
| 4 | 4 | | 13.377 | 278.9 | 4565.9 | 0.4757 |
| Total | | | | 108539.6 | 959895.8 | 100.0000 |

# HPLC Report

Sample Name:
Operator:
Time:10:06

Data File:GX-10-75.che
Date:2012-09-27



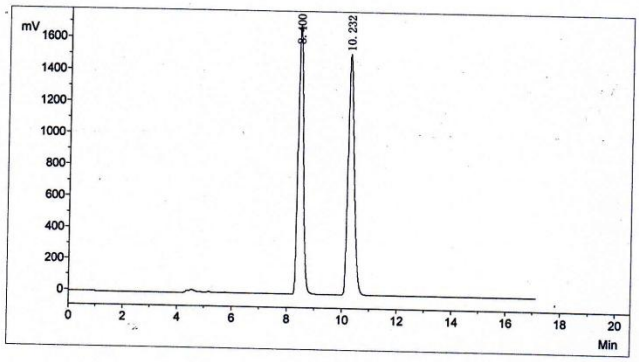

| No. | PeakNo | ID.Name | R.Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|---|
| 1 | 1 | | 6.293 | 32416.7 | 235866.1 | 3.1294 |
| 2 | 2 | | 7.927 | 732258.1 | 7301244.0 | 96.8706 |
| Total | | | | 764674.8 | 7537110.1 | 100.0000 |

HPLC of **5p**

# HPLC Report

Sample Name:
Operator:
Time:08:47

Data File:Gx-10-84+-PC-3910.7214.che
Date:2012-10-19

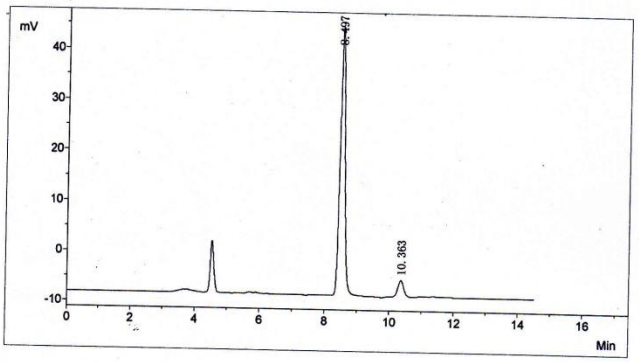



| No. | PeakNo | ID. Name | R. Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|---|
| 1 | 1 | | 8.400 | 1696693.4 | 22486997.1 | 48.8362 |
| 2 | 2 | | 10.232 | 1520980.8 | 23558761.0 | 51.1638 |
| Total | | | | 3217674.1 | 46045758.1 | 100.0000 |

# HPLC Report

Sample Name:
Operator:
Time:09:09

Data File:GX-10-93.che
Date:2012-10-19




| No. | PeakNo | ID. Name | R. Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|---|
| 1 | 1 | | 8.497 | 53174.6 | 564931.8 | 93.5189 |
| 2 | 2 | | 10.363 | 3222.5 | 39151.5 | 6.4811 |
| Total | | | | 56397.2 | 604083.3 | 100.0000 |

HPLC of **5q**

# HPLC Report

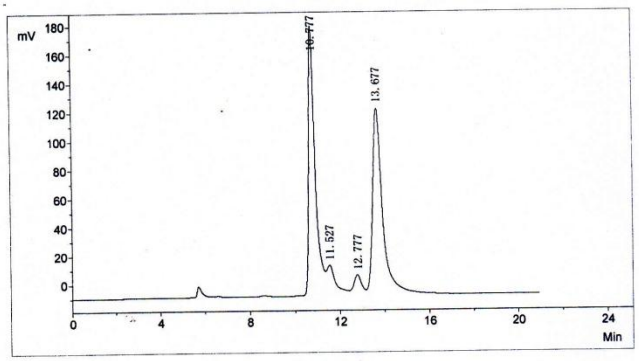
Sample Name:

Operator:

Time:10:41

Data File:GX-11-33+-PC-29550.5214.che

Date:2012-11-07




| No. | PeakNo | ID. Name | R. Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|---|
| 1 | 1 | | 10.777 | 187291.1 | 3783973.6 | 42.4920 |
| 2 | 2 | | 11.527 | 21332.8 | 646131.1 | 7.2557 |
| 3 | 3 | | 12.777 | 14244.6 | 361889.5 | 4.0638 |
| 4 | 4 | | 13.677 | 130038.5 | 4113158.4 | 46.1885 |
| Total | | | | 352907.0 | 8905152.6 | 100.0000 |

# HPLC Report

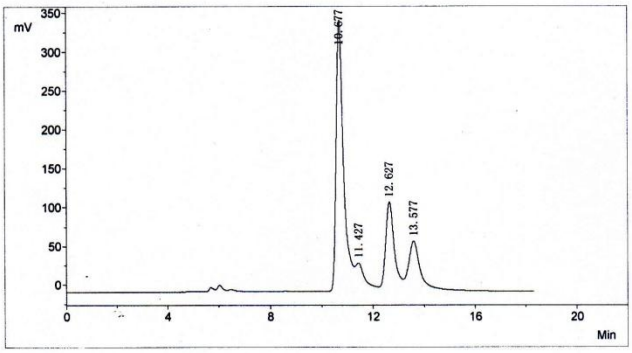
Sample Name:

Operator:

Time:11:38

Data File:GX-11-44.che

Date:2012-11-07




| No. | PeakNo | ID. Name | R. Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|---|
| 1 | 1 | | 10.677 | 343350.0 | 7114588.4 | 53.6153 |
| 2 | 2 | | 11.427 | 36925.5 | 1034827.2 | 7.7984 |
| 3 | 3 | | 12.627 | 114671.0 | 2790354.8 | 21.0280 |
| 4 | 4 | | 13.577 | 64828.6 | 2329916.0 | 17.5582 |
| Total | | | | 559775.1 | 13269686.3 | 100.0000 |

HPLC of **7a**

2012-4-20 14:41:09 1 / 1

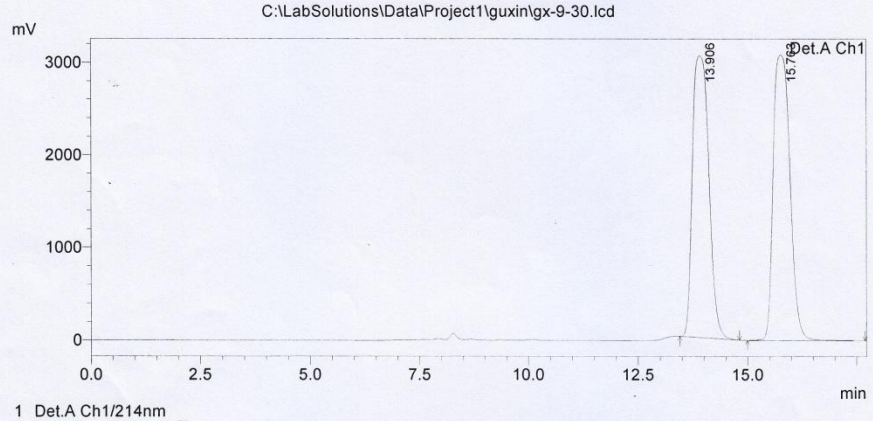
## ==== Shimadzu LCsolution Analysis Report ====

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

| | |
|---|---|
| Acquired by | : Admin |
| Sample Name | : gx-9-30 |
| method | :OD-H,99/1,0.4,214 |
| Injection Volume | : 10 uL |
| Data File Name | : gx-9-30.lcd |
| Method File Name | : 1.lcm |
| Report File Name | : 1.lcr |
| Data Acquired | : 2012-4-20 14:22:44 |
| Data Processed | : 2012-4-20 14:40:28 |

**<Chromatogram>**

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




1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

| Peak# | Ret. Time | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 13.906 | 79242150 | 3041583 | 48.955 |
| 2 | 15.763 | 82625968 | 3082210 | 51.045 |
| Total | | 161868118 | 6123793 | 100.000 |

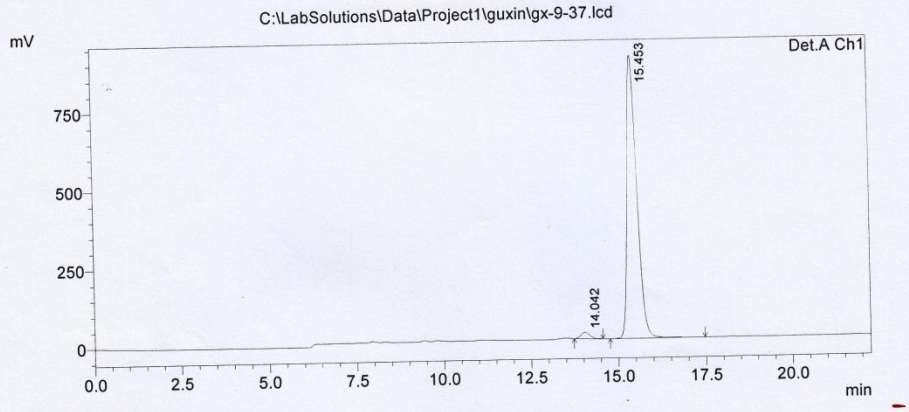
C:\LabSolutions\Data\Project1\guxin\gx-9-30.lcd

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

C:\LabSolutions\Data\Project1\guxin\gx-9-37.lcd

| | |
|---|---|
| Acquired by | : Admin |
| Sample Name | : gx-9-37 |
| method | :OD-H, 99\1, 1.0, 214 |
| Injection Volume | : 10 uL |
| Data File Name | : gx-9-37.lcd |
| Method File Name | : 1.lcm |
| Report File Name | : 1.lcr |
| Data Acquired | : 2012-5-10 19:15:18 |
| Data Processed | : 2012-5-10 19:37:33 |

**<Chromatogram>**




1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

| Peak# | Ret. Time | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 14.042 | 361301 | 20747 | 2.013 |
| 2 | 15.453 | 17590488 | 901693 | 97.987 |
| Total | | 17951788 | 922440 | 100.000 |

HPLC of **7b**

# HPLC Report

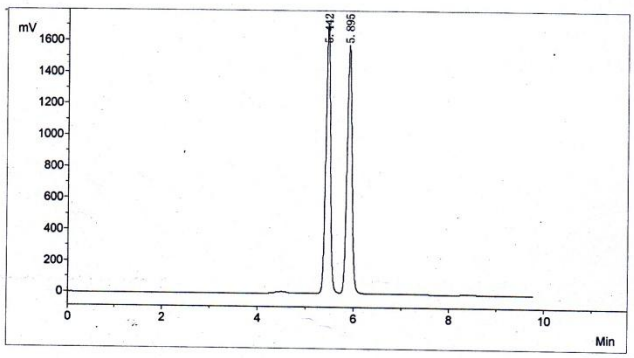
Sample Name:

Operator:

Time:10:16

Data File:GX-10-6+-PC-3820.7214.che

Date:2012-07-10

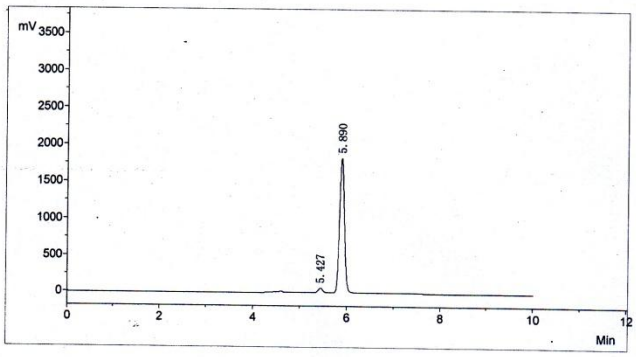



| No. | PeakNo | ID.Name | R.Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|---|
| 1 | 1 | | 5.442 | 1696870.0 | 11417450.0 | 50.1536 |
| 2 | 2 | | 5.895 | 1571499.3 | 11347515.2 | 49.8464 |
| Total | | | | 3268369.3 | 22764965.2 | 100.0000 |

# HPLC Report

Sample Name:
Operator:
Time:10:31

Data File:GX-10-7.che
Date:2012-07-10



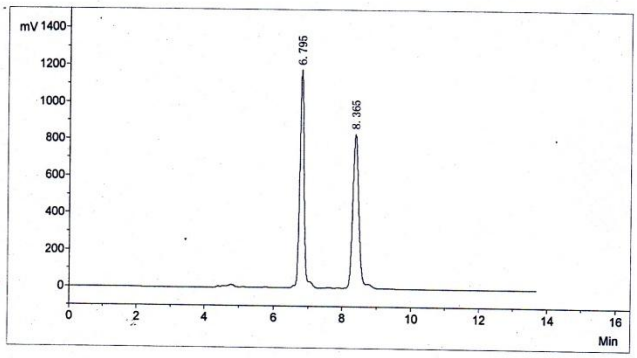

| No. | PeakNo | ID. Name | R. Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|---|
| 1 | 1 | | 5.427 | 56625.7 | 417213.3 | 3.0326 |
| 2 | 2 | | 5.890 | 1822668.2 | 13340465.5 | 96.9674 |
| Total | | | | 1879293.9 | 13757678.8 | 100.0000 |

HPLC of **7c**

# HPLC Report

Sample Name:
Operator:
Time:09:44

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

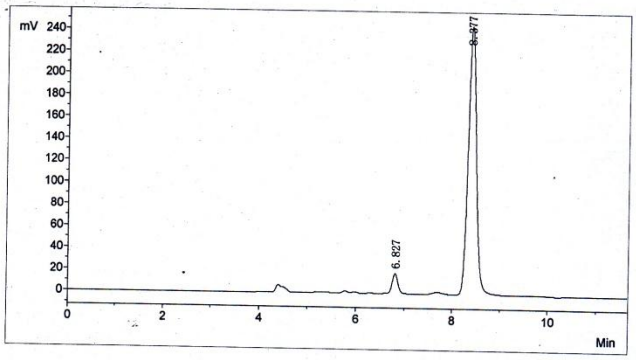



| No. | PeakNo | ID. Name | R. Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|---|
| 1 | 1 | | 6.795 | 1176611.7 | 10185918.1 | 50.0012 |
| 2 | 2 | | 8.365 | 820397.0 | 10185420.5 | 49.9988 |
| Total | | | | 1997008.7 | 20371338.7 | 100.0000 |

# HPLC Report

Sample Name:
Operator:
Time:10:02

Data File:Gx-10-9.che
Date:2012-07-10



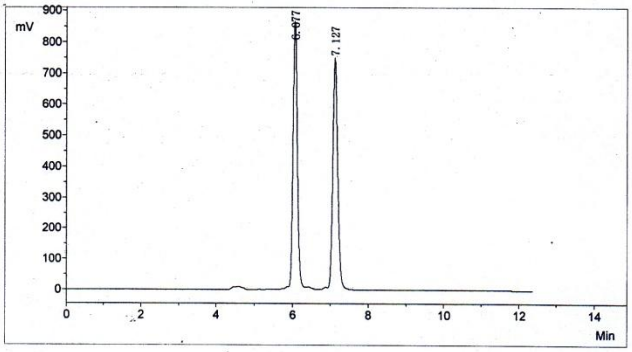

| No. | PeakNo | ID. Name | R. Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|---|
| 1 | 1 | | 6.827 | 18061.3 | 184280.3 | 5.9217 |
| 2 | 2 | | 8.377 | 243361.2 | 2927644.7 | 94.0783 |
| Total | | | | 261422.5 | 3111925.0 | 100.0000 |

HPLC of **7d**

# HPLC Report

Sample Name:
Operator:
Time:10:38

Data File:GX-10-10+-PC-3910.7214.che
Date:2012-07-11

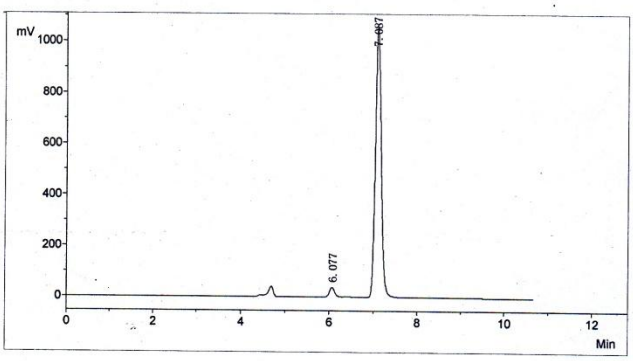



| No. | PeakNo | ID.Name | R.Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|---|
| 1 | 1 | | 6.077 | 831160.6 | 7126651.4 | 50.1245 |
| 2 | 2 | | 7.127 | 739604.5 | 7091235.5 | 49.8755 |
| Total | | | | 1570765.1 | 14217886.9 | 100.0000 |

# HPLC Report

Sample Name:
Operator:
Time:10:53

Data File:GX-10-11.che
Date:2012-07-11




| No. | PeakNo | ID. Name | R. Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|---|
| 1 | 1 | | 6.077 | 36421.8 | 342600.7 | 3.4071 |
| 2 | 2 | | 7.087 | 1048461.6 | 9713008.1 | 96.5929 |
| Total | | | | 1084883.4 | 10055608.9 | 100.0000 |

HPLC of **7e**

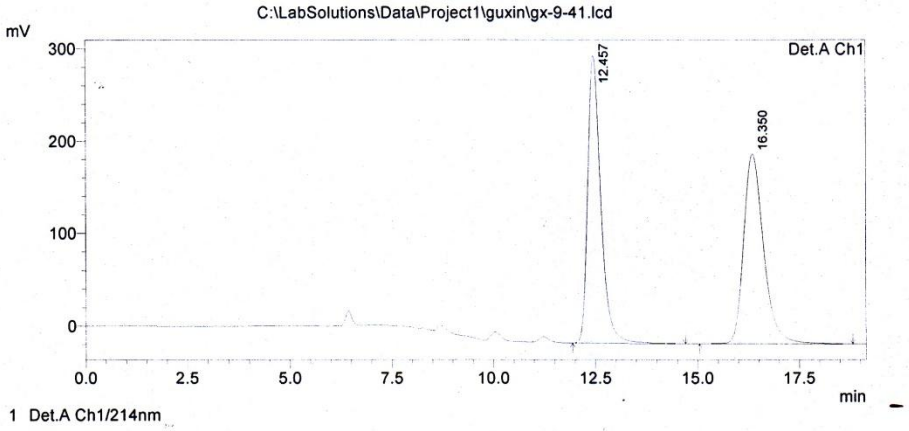
2012-5-19 17:21:38 1 / 1

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

C:\LabSolutions\Data\Project1\guxin\gx-9-41.lcd

| | |
|---|---|
| Acquired by | : Admin |
| Sample Name | : gx-9-41 |
| method | :OJ-H, 99/1, 0.5, 214 |
| Injection Volume | : 10 uL |
| 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>**




1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

| Peak# | Ret. Time | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 12.457 | 6974277 | 310358 | 49.909 |
| 2 | 16.350 | 6999722 | 204807 | 50.091 |
| Total | | 13973999 | 515165 | 100.000 |

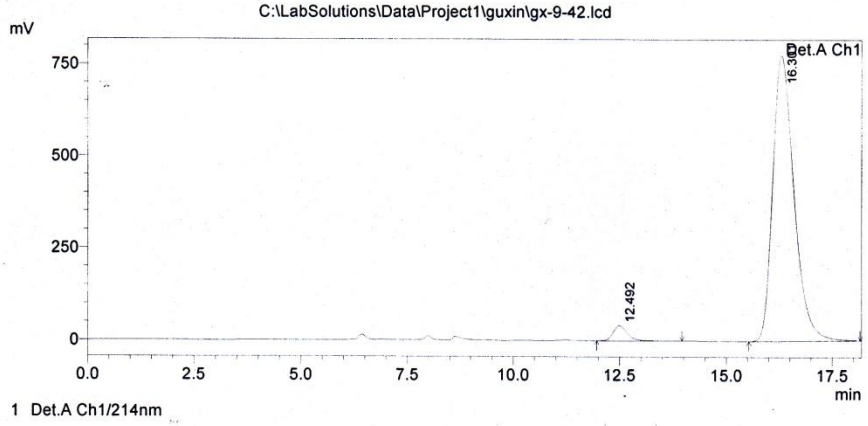
C:\LabSolutions\Data\Project1\guxin\gx-9-41.lcd

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

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

| | |
|---|---|
| Acquired by | : Admin |
| Sample Name | : gx-9-42 |
| method | :OJ-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.lcr |
| Data Acquired | : 2012-5-19 17:25:37 |
| Data Processed | : 2012-5-19 17:43:49 |

**<Chromatogram>**




1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

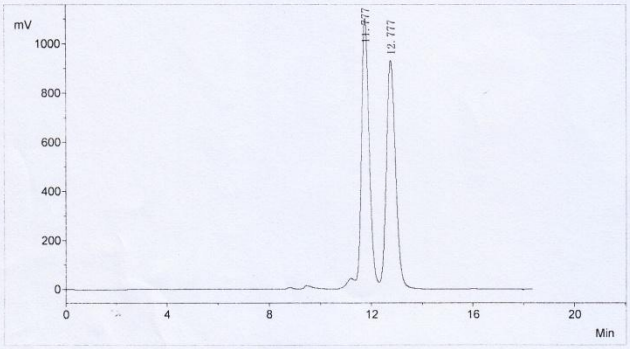
| Peak# | Ret. Time | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 12.492 | 964524 | 41301 | 3.427 |
| 2 | 16.301 | 27176381 | 774737 | 96.573 |
| Total | | 28140905 | 816038 | 100.000 |

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

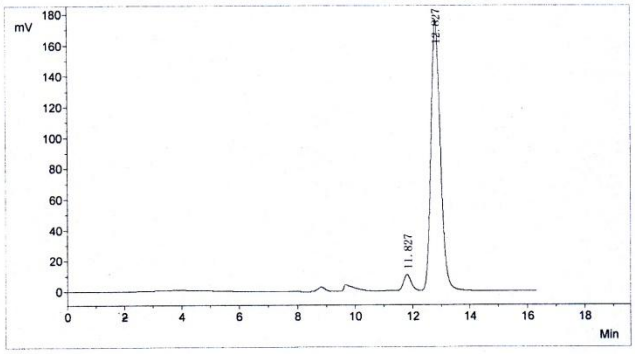



| No. | PeakNo | ID. Name | R. Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|---|
| 1 | 1 | | 11.777 | 1062711.8 | 21542694.1 | 50.0997 |
| 2 | 2 | | 12.777 | 907150.3 | 21456943.9 | 49.9003 |
| Total | | | | 1969862.1 | 42999638.0 | 100.0000 |

# HPLC Report

Sample Name:
Operator:
Time:14:13

Data File:Gx-9-72.che
Date:2012-06-08




| No. | PeakNo | ID. Name | R. Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|---|
| 1 | 1 | | 11.827 | 10319.2 | 193841.0 | 4.6009 |
| 2 | 2 | | 12.827 | 175451.8 | 4019240.6 | 95.3991 |
| Total | | | | 185771.0 | 4213081.7 | 100.0000 |

HPLC of **7g**

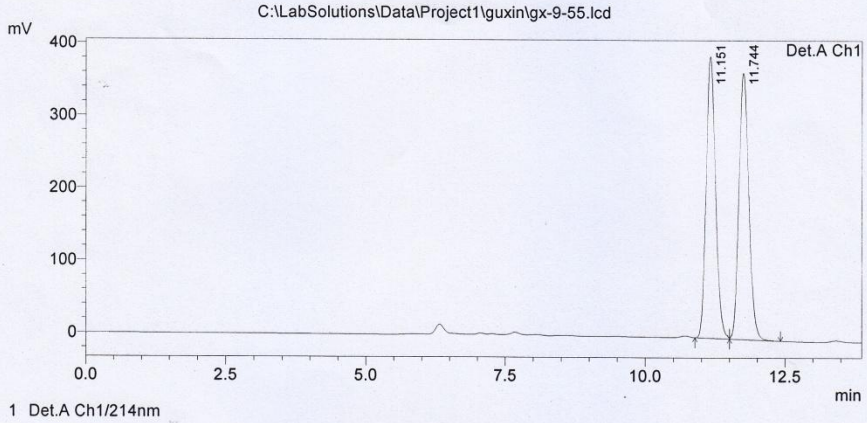
2012-5-29 10:33:07 1 / 1

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

C:\LabSolutions\Data\Project1\guxin\gx-9-55.lcd

| | |
|---|---|
| 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>**




1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

| Peak# | Ret. Time | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 11.151 | 4525130 | 388661 | 49.888 |
| 2 | 11.744 | 4545529 | 368245 | 50.112 |
| Total | | 9070659 | 756905 | 100.000 |

C:\LabSolutions\Data\Project1\guxin\gx-9-55.lcd

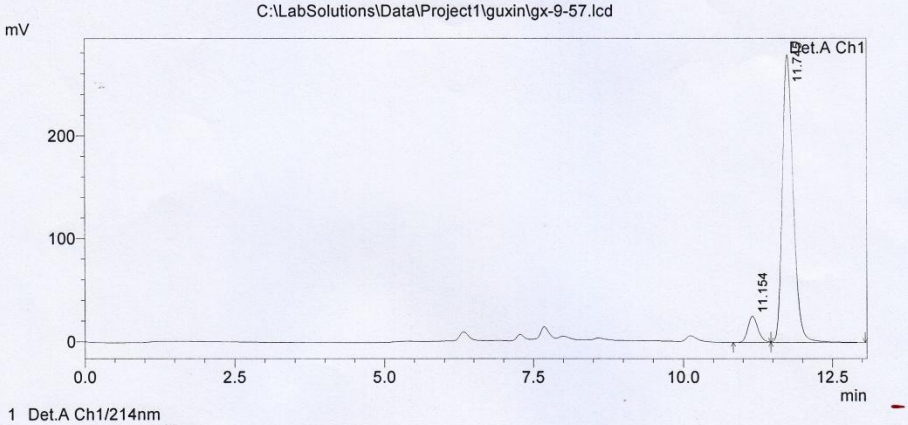
# ==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\guxin\gx-9-57.lcd

| | |
|---|---|
| Acquired by | : Admin |
| Sample Name | : gx-9-57 |
| method | :AD-H, 99.5/0.5, 0.5, 214 |
| Injection Volume | : 10 uL |
| Data File Name | : gx-9-57.lcd |
| Method File Name | : 1.lcm |
| Report File Name | : 1.lcr |
| Data Acquired | : 2012-5-29 10:33:41 |
| Data Processed | : 2012-5-29 10:46:47 |

**<Chromatogram>**

C:\LabSolutions\Data\Project1\guxin\gx-9-57.lcd




1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

| Peak# | Ret. Time | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 11.154 | 297588 | 25326 | 7.753 |
| 2 | 11.745 | 3540600 | 279023 | 92.247 |
| Total | | 3838187 | 304349 | 100.000 |

HPLC of **7h**

2012-6-9 10:52:13 1 / 1

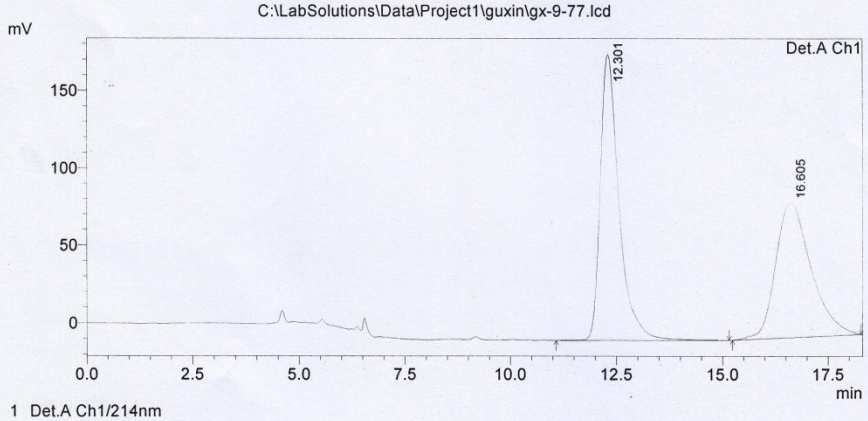
## ==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\guxin\gx-9-77.lcd

| | |
|---|---|
| Acquired by | : Admin |
| Sample Name | : gx-9-77 |
| method | :oj-h,99\1,0.70,214 |
| Injection Volume | : 10 uL |
| Data File Name | : gx-9-77.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\Project1\guxin\gx-9-77.lcd




1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

| Peak# | Ret. Time | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 12.301 | 5645674 | 184141 | 52.700 |
| 2 | 16.605 | 5067180 | 87069 | 47.300 |
| Total | | 10712853 | 271210 | 100.000 |

C:\LabSolutions\Data\Project1\guxin\gx-9-77.lcd

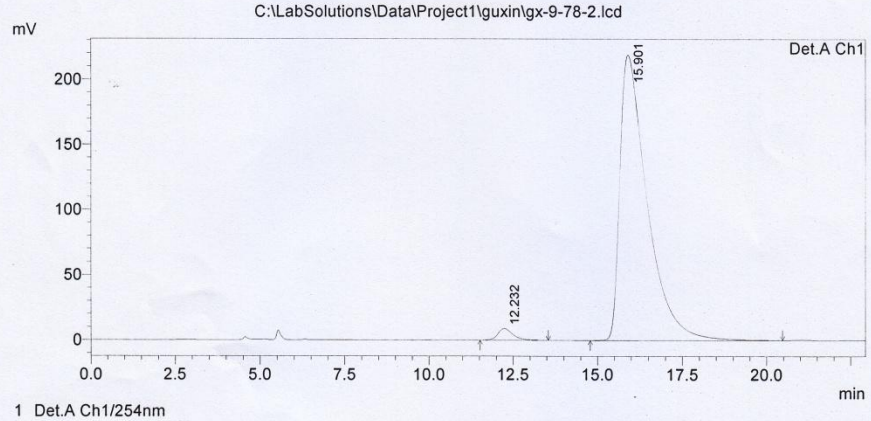
# ==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\guxin\gx-9-78-2.lcd

| | |
|---|---|
| Acquired by | : Admin |
| Sample Name | : gx-9-78-2 |
| method | :oj-h,99\1,0.70,214 |
| Injection Volume | : 10 uL |
| Data File Name | : gx-9-78-2.lcd |
| Method File Name | : 21.lcm |
| Report File Name | : 1.lcr |
| Data Acquired | : 2012-6-9 11:27:57 |
| Data Processed | : 2012-6-9 11:50:54 |

**<Chromatogram>**

C:\LabSolutions\Data\Project1\guxin\gx-9-78-2.lcd




1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 12.232 | 279346 | 8950 | 2.233 |
| 2 | 15.901 | 12231517 | 218787 | 97.767 |
| Total | | 12510864 | 227737 | 100.000 |

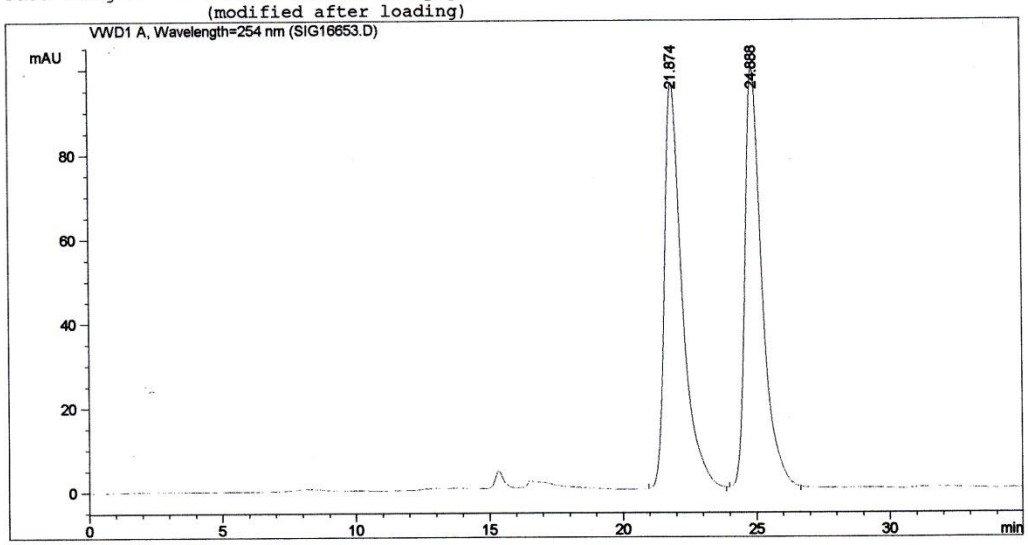
C:\LabSolutions\Data\Project1\guxin\gx-9-78-2.lcd

HPLC of **7i**

Data File C:\HPCHEM\1\DATA\SIG16653.D Sample Name: gx-7-35

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

```
Injection Date  : 11/4/11 8:57:40 AM
Sample Name     : gx-7-35                          Location : Vial 1
Acq. Operator   : gx
Method          : C:\HPCHEM\1\METHODS\ZKAMINE.M
Last changed    : 11/4/11 9:26:59 AM by gx
                  (modified after loading)
```




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
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  21.874 BB    0.6782 4409.16211   96.05463  50.2630
   2  24.888 BB    0.6590 4363.02197   99.42214  49.7370

Totals :                  8772.18408  195.47677

 Results obtained with enhanced integrator!
```

*** End of Report ***

Instrument 1 11/4/11 9:34:01 AM gx

Page 1 of 1

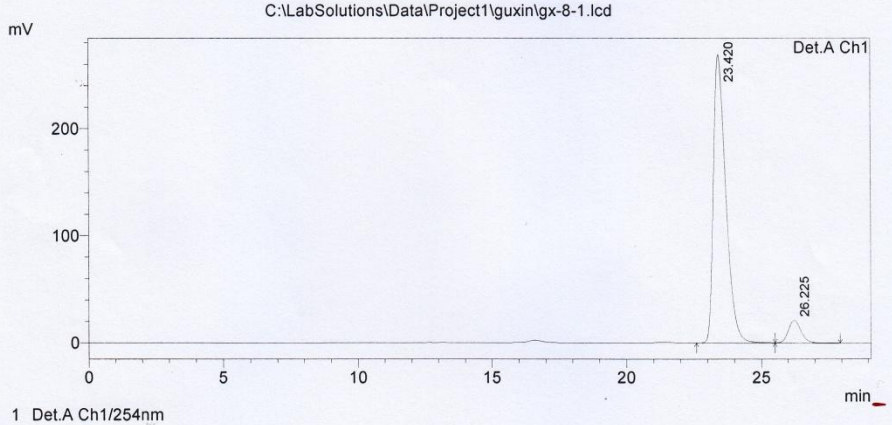
# ==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\guxin\gx-8-1.lcd

| | |
|---|---|
| Acquired by | : Admin |
| Sample Name | : gx-8-1 |
| method | :OD-H,99/1,0.25,254 |
| Injection Volume | : 10 uL |
| Data File Name | : gx-8-1.lcd |
| Method File Name | : 1.lcm |
| Report File Name | : 1.lcr |
| Data Acquired | : 2011-12-20 15:43:53 |
| Data Processed | : 2011-12-20 16:20:01 |

**<Chromatogram>**

C:\LabSolutions\Data\Project1\guxin\gx-8-1.lcd




1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 23.420 | 8649918 | 269159 | 92.569 |
| 2 | 26.225 | 694411 | 21148 | 7.431 |
| Total | | 9344330 | 290307 | 100.000 |

HPLC of **7j**

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

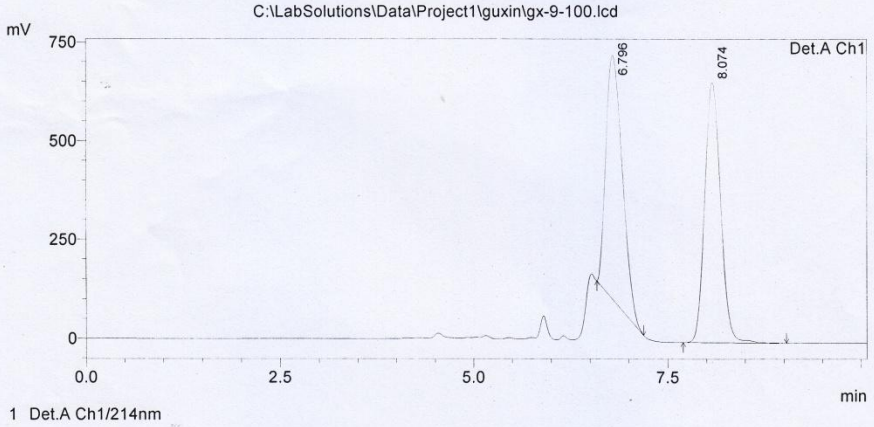
## ==== Shimadzu LCsolution Analysis Report ====

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

| | |
|---|---|
| Acquired by | : Admin |
| Sample Name | : gx-9-100 |
| method | :OD-H,99/1, 0.7, 214 |
| Injection Volume | : 10 uL |
| Data File Name | : gx-9-100.lcd |
| Method File Name | : 21.lcm |
| Report File Name | : 1.lcr |
| Data Acquired | : 2012-7-3 11:55:15 |
| Data Processed | : 2012-7-3 12:05:21 |

**<Chromatogram>**

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




1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

| Peak# | Ret. Time | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 6.796 | 9106836 | 617835 | 49.350 |
| 2 | 8.074 | 9346903 | 656605 | 50.650 |
| Total | | 18453739 | 1274440 | 100.000 |

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

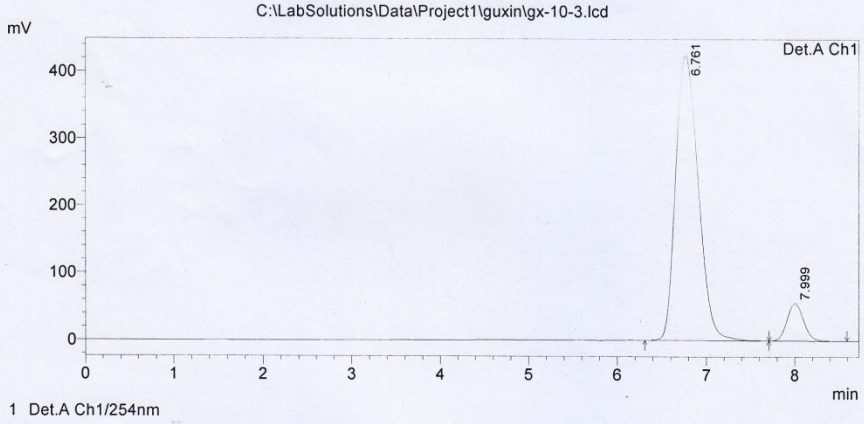
# ==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\guxin\gx-10-3.lcd

| | |
|---|---|
| Acquired by | : Admin |
| Sample Name | : gx-10-3 |
| method | :OD-H,99/1, 0.7, 214 |
| Injection Volume | : 10 uL |
| Data File Name | : gx-10-3.lcd |
| Method File Name | : 21.lcm |
| Report File Name | : 1.lcr |
| Data Acquired | : 2012-7-3 12:10:56 |
| Data Processed | : 2012-7-3 12:19:40 |

**<Chromatogram>**

C:\LabSolutions\Data\Project1\guxin\gx-10-3.lcd




1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 6.761 | 7477552 | 424319 | 91.100 |
| 2 | 7.999 | 730528 | 55838 | 8.900 |
| Total | | 8208081 | 480157 | 100.000 |

HPLC of **7k**

2012-7-3 12:35:30 1 / 1

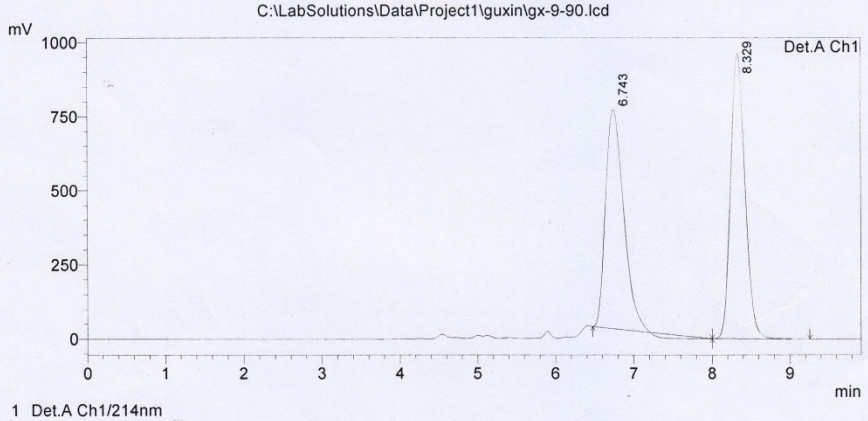
## ==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\guxin\gx-9-90.lcd

| | |
|---|---|
| Acquired by | : Admin |
| Sample Name | : gx-9-90 |
| method | :OD-H,99/1, 0.7, 214 |
| Injection Volume | : 10 uL |
| Data File Name | : gx-9-90.lcd |
| Method File Name | : 21.lcm |
| Report File Name | : 1.lcr |
| Data Acquired | : 2012-7-3 12:24:54 |
| Data Processed | : 2012-7-3 12:34:51 |

**<Chromatogram>**

C:\LabSolutions\Data\Project1\guxin\gx-9-90.lcd




1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

| Peak# | Ret. Time | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 6.743 | 11519065 | 737712 | 47.984 |
| 2 | 8.329 | 12486963 | 961191 | 52.016 |
| Total | | 24006028 | 1698903 | 100.000 |

C:\LabSolutions\Data\Project1\guxin\gx-9-90.lcd

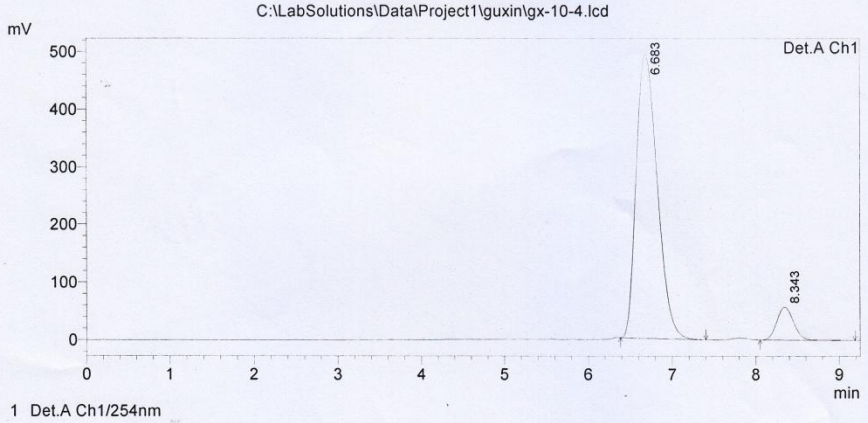
# ==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\guxin\gx-10-4.lcd

| | |
|---|---|
| Acquired by | : Admin |
| Sample Name | : gx-10-4 |
| method | :OD-H,99/1, 0.7, 214 |
| Injection Volume | : 10 uL |
| Data File Name | : gx-10-4.lcd |
| Method File Name | : 21.lcm |
| Report File Name | : 1.lcr |
| Data Acquired | : 2012-7-3 12:39:48 |
| Data Processed | : 2012-7-3 12:49:04 |

**<Chromatogram>**

C:\LabSolutions\Data\Project1\guxin\gx-10-4.lcd




1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 6.683 | 8570596 | 491601 | 91.427 |
| 2 | 8.343 | 803625 | 57114 | 8.573 |
| Total | | 9374222 | 548715 | 100.000 |

HPLC of **8a**

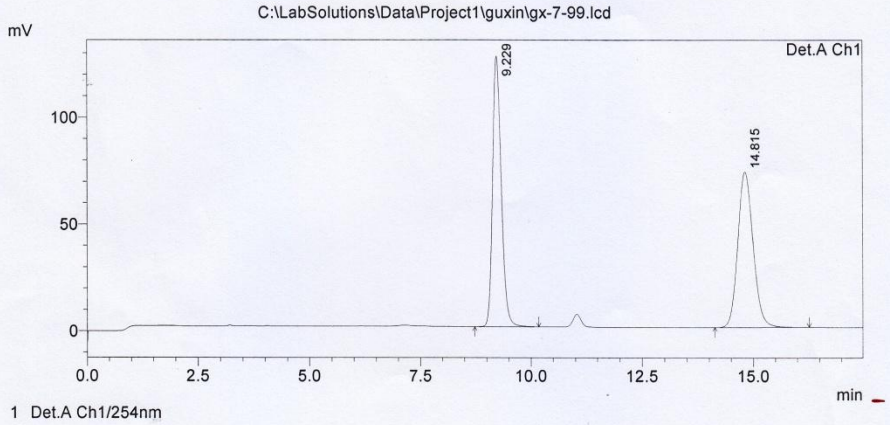
2011-12-17 23:20:20 1 / 1

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

C:\LabSolutions\Data\Project1\guxin\gx-7-99.lcd

| | |
|---|---|
| Acquired by | : Admin |
| Sample Name | : gx-7-99 |
| method | :OJ-H,90/10,1.0,254 |
| Injection Volume | : 10 uL |
| 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>**




1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 9.229 | 1733098 | 126508 | 49.801 |
| 2 | 14.815 | 1746951 | 72576 | 50.199 |
| Total | | 3480048 | 199084 | 100.000 |

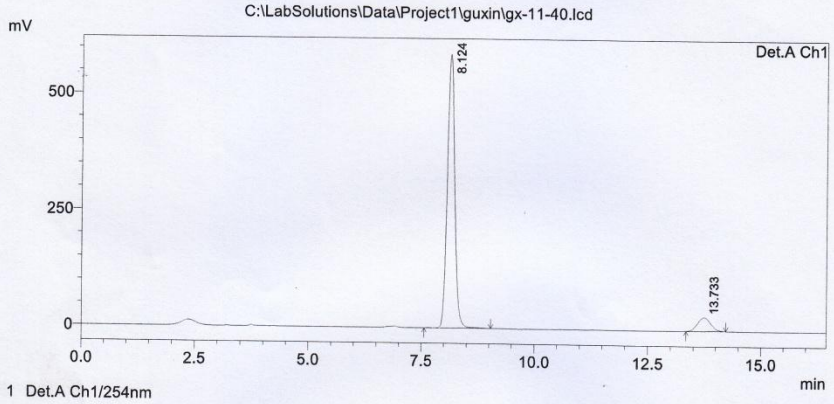
C:\LabSolutions\Data\Project1\guxin\gx-7-99.lcd

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

C:\LabSolutions\Data\Project1\guxin\gx-11-40.lcd

| | |
|---|---|
| Acquired by | : Admin |
| Sample Name | : gx-11-40 |
| method | :hydro |
| Injection Volume | : 5 uL |
| Data File Name | : gx-11-40.lcd |
| Method File Name | : 1.lcm |
| Report File Name | : 1.lcr |
| Data Acquired | : 2012-11-1 19:31:47 |
| Data Processed | : 2012-11-1 19:48:15 |

**<Chromatogram>**




1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 8.124 | 6738826 | 588784 | 91.673 |
| 2 | 13.733 | 612104 | 29913 | 8.327 |
| Total | | 7350930 | 618697 | 100.000 |

HPLC of **8b**

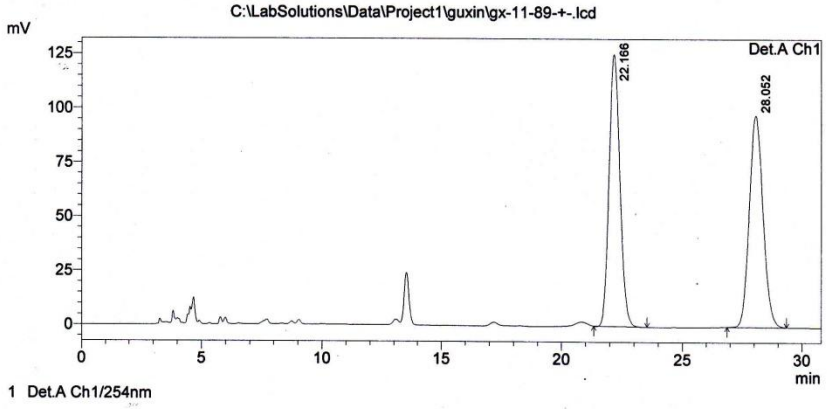


## ==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\guxin\gx-11-89-+-.lcd

| | |
|---|---|
| Acquired by | : Admin |
| Sample Name | : GX-11-89-+- |
| method | :IC, 9/1, 1.0, 254 |
| Injection Volume | : 5 uL |
| Data File Name | : gx-11-89-+-.lcd |
| Method File Name | : 1.lcm |
| Report File Name | : 1.lcr |
| Data Acquired | : 2012-11-29 22:31:50 |
| Data Processed | : 2012-11-29 23:02:39 |

**<Chromatogram>**




1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

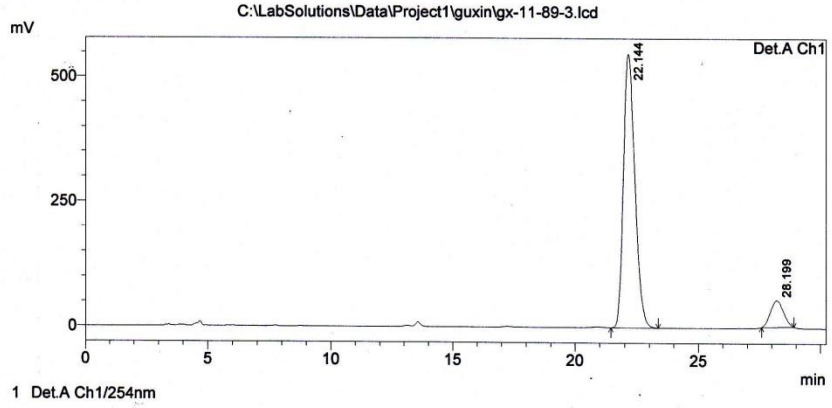
| Peak# | Ret. Time | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 22.166 | 3900233 | 125155 | 49.992 |
| 2 | 28.052 | 3901489 | 97248 | 50.008 |
| Total | | 7801722 | 222402 | 100.000 |

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

C:\LabSolutions\Data\Project1\guxin\gx-11-89-3.lcd

| | |
|---|---|
| Acquired by | : Admin |
| Sample Name | : GX-11-89-3 |
| method | :IC, 9/1, 1.0, 254 |
| Injection Volume | : 5 uL |
| Data File Name | : gx-11-89-3.lcd |
| Method File Name | : 1.lcm |
| Report File Name | : 1.lcr |
| Data Acquired | : 2012-11-29 23:07:04 |
| Data Processed | : 2012-11-29 23:37:18 |

**<Chromatogram>**




PeakTable

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 22.144 | 17628313 | 547925 | 89.872 |
| 2 | 28.199 | 1986661 | 53134 | 10.128 |
| Total | | 19614973 | 601059 | 100.000 |

HPLC of **8c**

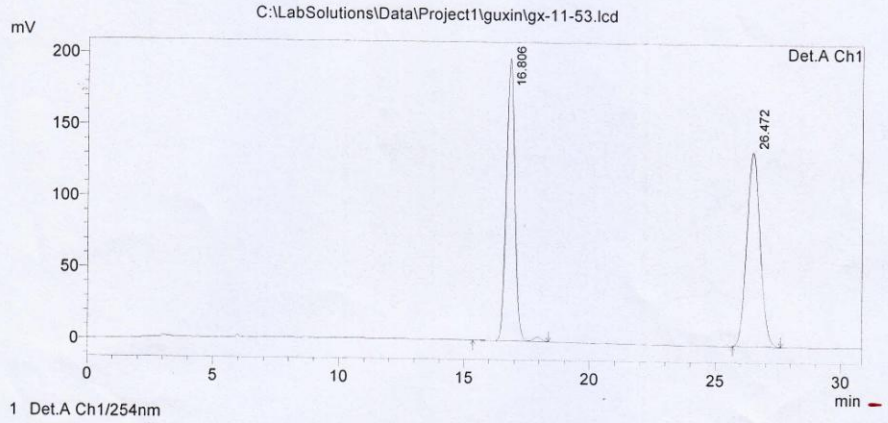
2012-11-9 18:48:36 1 / 1

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

C:\LabSolutions\Data\Project1\guxin\gx-11-53.lcd

| | |
|---|---|
| Acquired by | : Admin |
| Sample Name | : gx-11-53 |
| method | :AD-H, 90/10, 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>**




PeakTable

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 16.806 | 4679607 | 197313 | 48.110 |
| 2 | 26.472 | 5047253 | 135395 | 51.890 |
| Total | | 9726860 | 332708 | 100.000 |

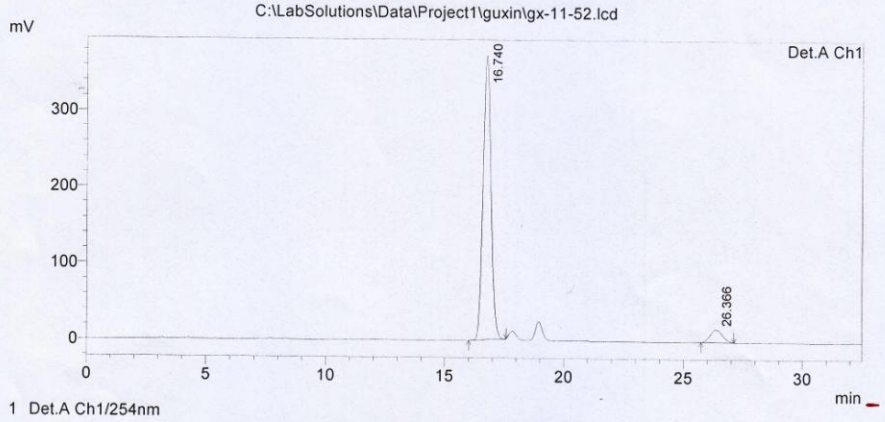
C:\LabSolutions\Data\Project1\guxin\gx-11-53.lcd

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

C:\LabSolutions\Data\Project1\guxin\gx-11-52.lcd

| | |
|---|---|
| Acquired by | : Admin |
| Sample Name | : gx-11-52 |
| method | :AD-H, 90/10, 1.0, 254 |
| Injection Volume | : 5 uL |
| Data File Name | : gx-11-52.lcd |
| Method File Name | : 1.lcm |
| Report File Name | : 1.lcr |
| Data Acquired | : 2012-11-9 18:28:59 |
| Data Processed | : 2012-11-9 19:01:30 |

**<Chromatogram>**




PeakTable

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 16.740 | 8660030 | 372112 | 93.576 |
| 2 | 26.366 | 594468 | 16701 | 6.424 |
| Total | | 9254499 | 388813 | 100.000 |

HPLC of **8d**

2012-11-20 15:06:10 1 / 1

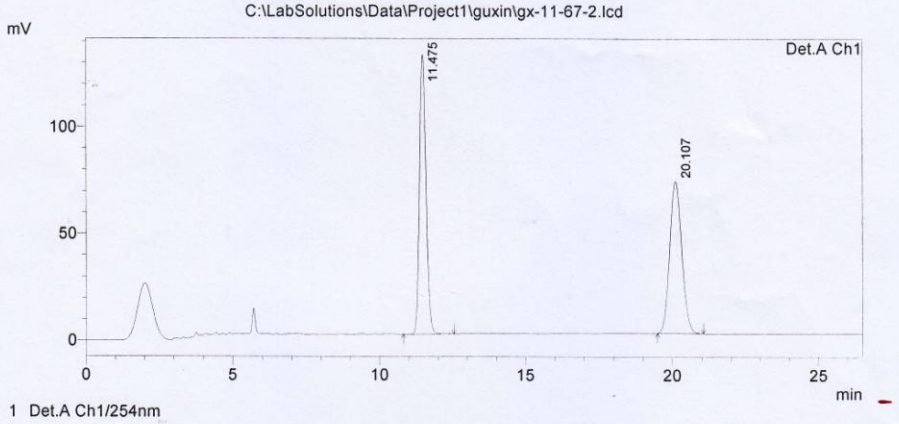
## ==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\guxin\gx-11-67-2.lcd

| | |
|---|---|
| Acquired by | : Admin |
| Sample Name | : gx-11-67-2 |
| method | : |
| Injection Volume | : 5 uL |
| Data File Name | : gx-11-67-2.lcd |
| Method File Name | : 1.lcm |
| Report File Name | : 1.lcr |
| Data Acquired | : 2012-11-20 14:38:48 |
| Data Processed | : 2012-11-20 15:05:20 |

**<Chromatogram>**

C:\LabSolutions\Data\Project1\guxin\gx-11-67-2.lcd




1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 11.475 | 2036846 | 130912 | 50.080 |
| 2 | 20.107 | 2030344 | 71066 | 49.920 |
| Total | | 4067190 | 201979 | 100.000 |

C:\LabSolutions\Data\Project1\guxin\gx-11-67-2.lcd

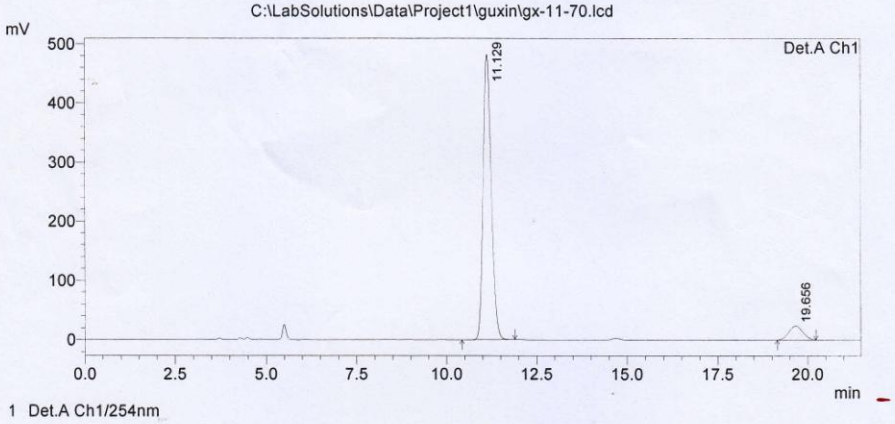
# ==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\guxin\gx-11-70.lcd

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

**<Chromatogram>**

C:\LabSolutions\Data\Project1\guxin\gx-11-70.lcd




1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

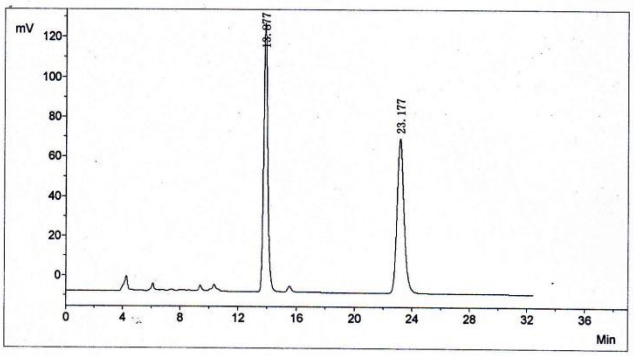
| Peak# | Ret. Time | Area | Height | Area % |
|---|---|---|---|---|
| 1 | 11.129 | 7572485 | 481921 | 92.144 |
| 2 | 19.656 | 645619 | 23580 | 7.856 |
| Total | | 8218104 | 505502 | 100.000 |

HPLD of **8e**

# HPLC Report

Sample Name:
Operator:
Time:13:28

Data File:GX-11-81RACAD-H730.7214.che
Date:2012-11-26

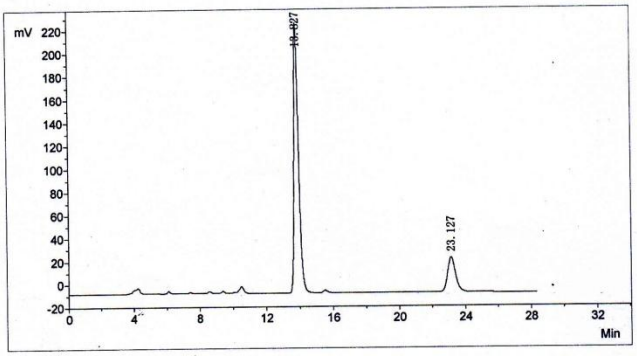



| No. | PeakNo | ID. Name | R. Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|---|
| 1 | 1 | | 13.877 | 133773.4 | 2617501.2 | 50.0524 |
| 2 | 2 | | 23.177 | 77693.4 | 2612020.1 | 49.9476 |
| Total | | | | 211466.7 | 5229521.2 | 100.0000 |

# HPLC Report

Sample Name:
Operator:
Time:14:04

Data File:GX-11-81.che
Date:2012-11-26



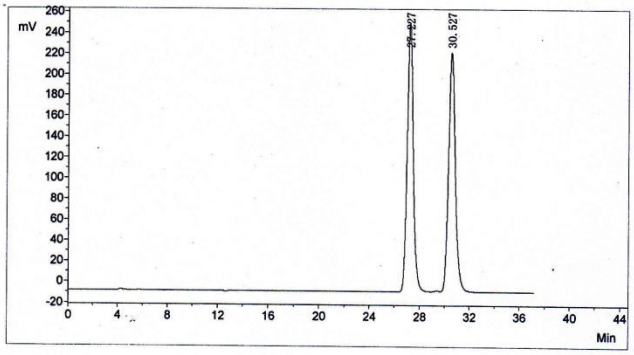

| No. | PeakNo | ID. Name | R. Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|---|
| 1 | 1 | | 13.827 | 230588.0 | 4491965.2 | 81.4694 |
| 2 | 2 | | 23.127 | 30328.7 | 1021717.7 | 18.5306 |
| Total | | | | 260916.6 | 5513682.9 | 100.0000 |

HPLC of **8f**

# HPLC Report

Sample Name:
Operator:
Time:08:27

Data File:GX-11-78RACAD-H910.7254.che
Date:2012-11-23

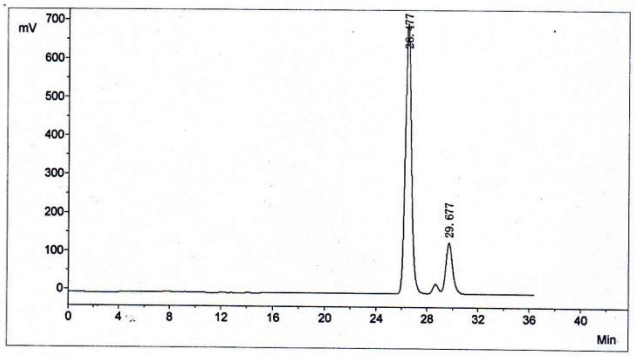



| No. | PeakNo | ID. Name | R. Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|---|
| 1 | 1 | | 27.227 | 257176.9 | 8809409.3 | 50.5467 |
| 2 | 2 | | 30.527 | 229916.4 | 8618839.7 | 49.4533 |
| Total | | | | 487093.3 | 17428248.9 | 100.0000 |

# HPLC Report

Sample Name:
Operator:
Time:09:07

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



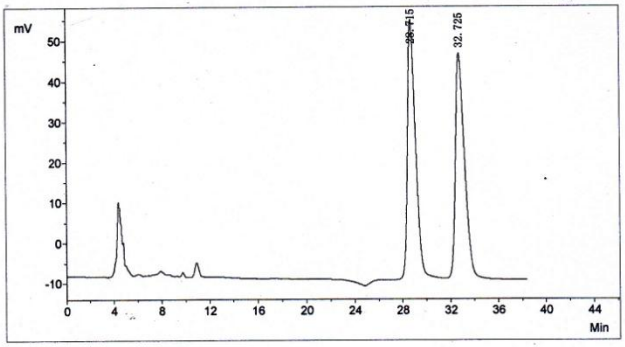

| No. | PeakNo | ID. Name | R. Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|---|
| 1 | 1 | | 26.477 | 698358.9 | 23195585.1 | 84.5323 |
| 2 | 2 | | 29.677 | 127538.5 | 4244315.4 | 15.4677 |
| Total | | | | 825897.3 | 27439900.5 | 100.0000 |

HPLC of **8g**

# HPLC Report

Sample Name:
Operator:
Time:09:58

Data File:GX-11-66+-PC-49552140.7.che
Date:2012-11-20

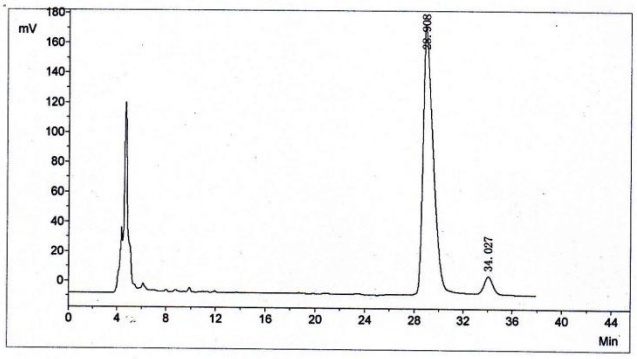



| No. | PeakNo | ID.Name | R.Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|---|
| 1 | 1 | | 28.715 | 63796.5 | 2915194.5 | 50.2350 |
| 2 | 2 | | 32.725 | 55403.0 | 2887923.5 | 49.7650 |
| Total | | | | 119199.6 | 5803118.0 | 100.0000 |

# HPLC Report

Sample Name:
Operator:
Time:09:15

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



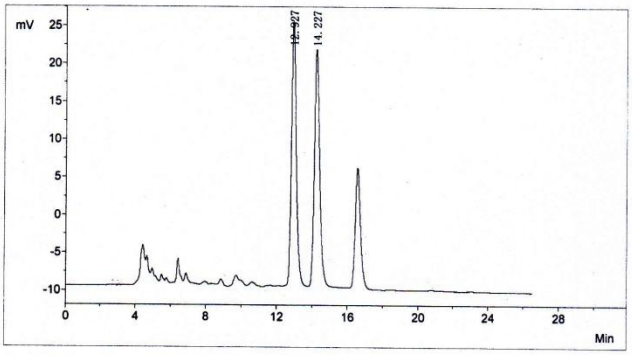

| No. | PeakNo | ID. Name | R. Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|---|
| 1 | 1 | | 28.908 | 179817.2 | 9960944.8 | 94.5498 |
| 2 | 2 | | 34.027 | 11878.1 | 574183.2 | 5.4502 |
| Total | | | | 191695.4 | 10535128.0 | 100.0000 |

HPLC of **8h**

# 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:GX-11-91+-IC820.7214.che
分析者:
分析时间:09:36

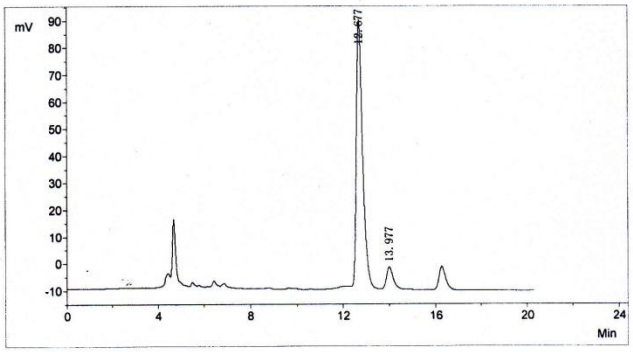



| 序号 | 峰号 | 组份名 | 保留时间 | 峰高 | 峰面积 | 面积百分比(%) |
|---|---|---|---|---|---|---|
| 1 | 1 | | 12.927 | 34341.6 | 663193.6 | 50.0739 |
| 2 | 2 | | 14.227 | 31105.7 | 661237.4 | 49.9261 |
| 合计: | | | | 65447.3 | 1324430.9 | 100.0000 |

# 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:GX-11-91-2.che
分析者:
分析时间:10:06



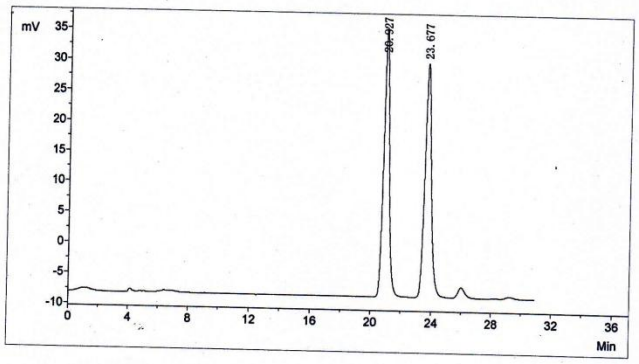

| 序号 | 峰号 | 组份名 | 保留时间 | 峰高 | 峰面积 | 面积百分比(%) |
|---|---|---|---|---|---|---|
| 1 | 1 | | 12.677 | 97804.3 | 1847251.2 | 91.9016 |
| 2 | 2 | | 13.977 | 8077.2 | 162779.9 | 8.0984 |
| 合计: | | | | 105881.5 | 2010031.2 | 100.0000 |

HPLC of **8i**

# HPLC Report

Sample Name:
Operator:
Time:09:49

Data File:GX-11-77RAC-AD-H910.7254.che
Date:2012-11-23

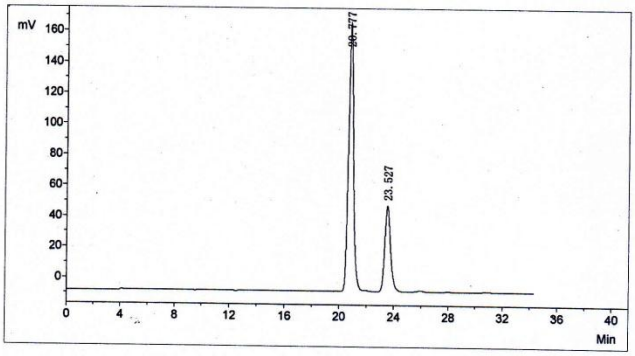



| No. | PeakNo | ID.Name | R.Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|---|
| 1 | 1 | | 20.927 | 43894.2 | 1149151.9 | 50.0376 |
| 2 | 2 | | 23.677 | 38061.3 | 1147424.7 | 49.9624 |
| Total | | | | 81955.6 | 2296576.5 | 100.0000 |

# HPLC Report

Sample Name:
Operator:
Time:10:24

Data File:GX-11-77-2.che
Date:2012-11-23




| No. | PeakNo | ID. Name | R. Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|---|
| 1 | 1 | | 20.777 | 174029.0 | 4437557.7 | 72.8071 |
| 2 | 2 | | 23.527 | 55880.7 | 1657394.7 | 27.1929 |
| Total | | | | 229909.6 | 6094952.4 | 100.0000 |