Supplementary Material (ESI) for Chemical Communications


– Electronic Supplementary Information (ESI) –

# Highly enantioselective hydrogenation of α-aryl-β-substituted acrylic acids catalyzed by Ir-SpinPHOX

Yi Zhang,[a,b] Zhaobin Han,[b] Fuying Li,[a] Kuiling Ding,[b,*] Ao Zhang[a,*]

[a] *Synthetic Organic & Medicinal Chemistry Laboratory, Shanghai Institute of Materia Medica (SIMM), Chinese Academy of Sciences, 555 Zuchongzhi Road, Shanghai 201203 (P.R. China).E-mail: aozhang@mail.shcnc.ac; Fax: (+86) 21 50806035*

[b] *State Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai, 200032 (P.R. China). E-mail: kding@mail.sioc.ac.cn; Fax: (+86) 21 64166128.*

**General.** All reactions and manipulations were performed using standard Schlenk techniques. Anhydrous THF and toluene were distilled from sodium benzophenone ketyl. Anhydrous DCE, $Et_3N$ and isopropyl alcohol were distilled form $CaH_2$ under an atmosphere of argon. Anhydrous MeOH and EtOH were distilled from magnesium under nitrogen atmosphere. Melting points were measured on a RY-I apparatus and uncorrected. $^1H$, $^{13}C$, $^{31}P$ and $^{19}F$ NMR spectra were recorded on Varian Mercury 300 MHz or 400 MHz spectrometers. Chemical shifts (δ values) were reported in ppm downfield from internal TMS ($^1H$ NMR) or $CDCl_3$ ($^{13}C$ NMR), external 85% $H_3PO_4$ ($^{31}P$ NMR) and external $CF_3CO_2H$ ($^{19}F$ NMR), respectively. Optical rotations were determined using a Perkin Elmer 341 MC polarimeter. EI (70 ev) and MALDI-TOF mass spectra were obtained on Agilent 5973N and MATRIX VOYAGR-DE STR spectrometers, respectively. HRMS(MALDI) were determined on IonSpect 4.7 TESLA FTMS spectrometers. HPLC analyses were performed on a JASCO 2089 or Techcomp N2000 liquid chromatograph.

**Materials.** (±)-Spiro[4,4]-1,6-nonane-diketone was prepared in >50% overall yield in hundreds-gram scale from industrially available diethyl adipate and ethyl 4-bromobutanoate by following a modified literature procedure.[S1] $[Ir(COD)Cl]_2$ was purchased from Stream Co. and used as received. $NaBAr_F$ was prepared according to the literature procedure.[S2] The ligand **2a-e** and their Ir(I) complexes were prepared according to our previous reported procedure.[S3] All acids were prepared according to the reported procedures.[S4] Acids **1b-d,f,i-k** and products **3b-e,i-j,l** are known compounds and their $^1H$ NMR data are consistent with those of the literatures.[S5~S10]

**Preparation and Analytical Data of Spiro Phosphino-Oxazoline Ligands.** The synthetic pathway of the ligands similar to our previous report is outlined as follow[S3]:

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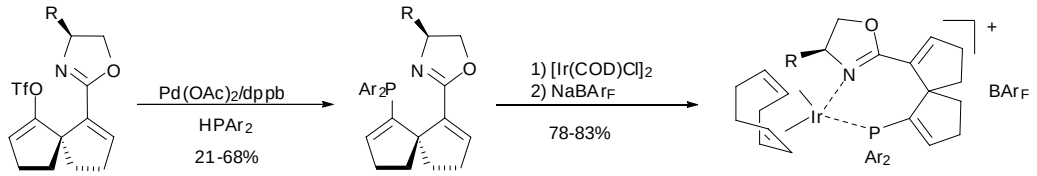
(S3) Z. Han, Z. Wang, X. Zhang and K. Ding, *Angew. Chem., Int. Ed.*, 2009, **48**, 5345.
(S4) P. H. Briner, M. C. T. Fyfe, J. P. Madeley, P. J. Murray, M. J. Procter and F. Spindler, *Int. Pat.*, WO 2006/016178, 2006.
(S5) G. Argouarch, O. Samuel and H. B. Kagan, *Eur. J. Org. Chem.*, 2000, **39**, 2885.
(S6) G. Sarakinos and E. J. Corey, *Org. Lett.*, 1999, **1**, 1741.
(S7) S. Li, S.-F. Zhu, C.-M. Zhang, S. Song and Q.-L. Zhou, *J. Am. Chem. Soc.*, 2008, **130**, 8584.
(S8) M. C. T. Fyfe, L. S. Gardner, M. Nawano, M. J. Procter, C. M. Rasamison, K. L. Schofield, V. K. Shah and K. Yasuda, *Int. Pat.*, WO 2004/072031, 2004.
(S9) G. R. Bebernitz and L. Kirman, *Int. Pat.*, WO 2007/041366, 2007.
(S10) S. Chen, P. T. W. Cheng and R. A. Smirk, *Int. Pat.*, WO 2008/005914, 2008.




(*R*,*S*)-**2f** R= *i*Bu, Ar = *o*-Tol
(*R*,*S*)-**2g** R= *i*Bu, Ar = 3,5-Xyl
(*R*,*S*)-**2h** R= Ph, Ar = *o*-Tol

Ir(I)/(*R*,*S*)-**2f** R= *i*Bu, Ar = *o*-Tol
Ir(I)/(*R*,*S*)-**2g** R= *i*Bu, Ar = 3,5-Xyl
Ir(I)/(*R*,*S*)-**2h** R= Ph, Ar = *o*-Tol

## Analytic data for ligand 2f-h

### (*R*,*S*)-2f (R = *i*Bu, Ar = *o*-Tol)

Colorless oil, yield 68%; $^1$H NMR (300 MHz, $CDCl_3$) δ = 7.26-7.00 (m, 8H), 6.43 (br s, 1H), 5.43 (d, *J* = 2.7 Hz, 1H), 3.96-3.91 (m, 2H), 3.81-3.74 (m, 1H), 2.82-2.69 (m, 2H), 2.56-2.23 (m, 10H), 1.91-1.81 (m, 2H), 1.56-1.49 (m, 2H), 1.18-1.11 (m, 1H), 0.91 (t, *J* = 6.6 Hz, 3H), 0.80 (d, *J* = 6.6 Hz, 3H) ppm; $^{31}$P NMR (121 MHz, $CDCl_3$) δ = -43.95 (s) ppm; ESI-MS m/z : 458.2 [M+H$^+$]; HRMS (MALDI) m/z: calcd. for $C_{30}H_{37}NOP$: 458.2607, Found: 458.2603 [M+H$^+$].

### (*R*,*S*)-2g (R = *i*Bu, Ar = 3,5-Xyl)

Colorless oil, yield 21%; $^1$H NMR (300 MHz, $CDCl_3$) δ = 7.03 (d, *J* = 6.3 Hz, 2H), 6.95-6.93 (m, 2H), 6.86 (s, 1H), 6.42 (s, 1H), 5.68 (t, *J* = 2.1 Hz, 1H), 4.03-3.97 (m, 2H), 3.82-3.78 (m, 1H), 2.70-2.63 (m, 1H), 2.54-2.36 (m, 3H), 2.33-2.30 (m, 1H), 2.28 (s, 6H), 2.24 (s, 6H), 2.13-2.06 (m, 1H), 1.92-1.82 (m, 2H), 1.55-1.47 (m, 2H), 1.18-1.48 (m, 1H), 0.92 (t, *J* = 2.7 Hz, 3H), 0.80 (d, *J* = 4.8 Hz, 3H) ppm; $^{31}$P NMR (121 MHz, $CDCl_3$) δ = -26.76 (s) ppm.

### (*R*,*S*)-2h (R = Ph, Ar = *o*-Tol)

Colorless oil, yield 41%; $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.32-7.08 (m, 13H), 6.58-6.57 (m, 1H), 5.46-5.44 (m, 1H), 5.15 (t, *J* = 9.2 Hz, 1H), 4.33 (dt, *J* = 8.0 Hz, 1H), 3.83 (t, *J* = 8.2 Hz, 1H), 2.91-2.84 (m, 1H), 2.80-2.74 (m, 1H), 2.61-2.56 (m, 1H), 2.45 (s, 3H), 2.37 (s, 3H), 2.36-2.29 (m, 3H), 1.97-1.88 (m, 2H) ppm; $^{31}$P NMR (162 MHz, $CDCl_3$) δ = -45.33 (s) ppm.

## Analytic data for Ir complex of 2f-h

### Ir(I)/(*R*,*S*)-2f (R = *i*Bu, Ar = *o*-Tol)

Red powder, yield 83%; M.p. = 180-183 °C; $[\alpha]_D^{20}$ = -16.1° (*c* 0.51, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ = 9.25 (q, *J* = 7.2 Hz, 1H), 7.72 (br s, 8H), 7.58-7.52 (m, 5H), 7.45-7.34 (m, 4H), 7.19-7.15 (m, 1H), 7.09-7.02 (m, 1H), 6.07-6.00 (m, 2H), 5.27 (br s, 1H), 4.54-4.49 (m, 1H), 4.38-4.35 (m, 2H), 4.24-4.19 (m, 1H), 2.82-2.79 (m, 1H), 2.69 (s, 3H), 2.57-2.29 (m, 5H), 2.13 (s, 3H), 2.09-1.69 (m, 9H), 1.42-1.20 (m, 6H), 0.98 (t, *J* = 7.2 Hz, 3H), 0.82 (d, *J* = 6.9 Hz, 3H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) δ = 117.6 (d, *J* = 1.8 Hz), 161.7 (q, *J* = 49.7 Hz), 144.4 (d, *J* = 3.7 Hz), 145.3, 143.1, 142.4, 142.1, 140.5, 140.4, 135.2, 134.8, 134.6, 133.1 (d, *J* = 6.7 Hz), 132.9 (d, *J* = 2.5 Hz), 132.6 (d, *J* = 6.1 Hz), 132.1 (d, *J* = 7.9 Hz), 131.7 (d, *J* = 2.5 Hz), 130.4, 130.0, 129.5 (m), 129.1 (m), 128.7 (m), 128.3 (m), 126.3, 126.1, 125.9, 125.7 (2 peak), 125.6, 123.7, 123.0, 122.7, 119.1, 117.6-117.3 (m), 89.7 (d, *J* = 7.9 Hz), 80.0 (d, *J* = 16.4 Hz), 73.4, 69.1, 68.9, 68.5, 68.0, 59.6, 42.5 (d, *J* = 6.0 Hz), 38.6, 35.8 (d, *J* = 4.9 Hz), 34.2, 33.8, 31.7, 31.2 (d, *J* =

12.1 Hz), 27.9, 26.4, 25.6, 24.6, 24.5, 23.0 (d, *J* = 3.7 Hz), 12.0, 11.6 ppm; $^{31}$P NMR (121 MHz, $CDCl_3$) δ = 2.52 (s) ppm; $^{19}$F NMR (282 MHz, $CDCl_3$) δ = -62.80 (s) ppm;
IR (film) ν 2972, 2840, 1671, 1592, 1507, 1458, 1387, 1352, 1275, 1167, 1128, 1030, 900, 886, 834, 776, 716, 681, 668 $cm^{-1}$;
MS (MALDI) m/z: 648.5 $[M\text{-}COD\text{-}BAr_F]^+$; HRMS (MALDI) m/z calcd. for $C_{38}H_{48}NOP^{191}Ir^+$ $[M\text{-}BAr_F]^+$: 756.3074, Found: 756.3073.

**Ir(I)/(*R,S*)-2g (R = *i*Bu, Ar = 3,5-Xyl)**
Red powder, yield 80%; M.p. = 124-125 °C; $[\alpha]_D^{20}$ = -10.0° (*c* 0.26, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ = 7.71 (s, 8H), 7.52 (s, 4H), 7.43 (d, *J* = 11.7 Hz, 2H), 7.18-7.09 (m, 4H), 6.24 (s, 1H), 6.16 (d, *J* = 7.8 Hz, 1H), 5.03 (br s, 1H), 4.47-4.22 (m, 4H), 3.31 (br s, 1H), 3.10-3.05 (m, 1H), 2.48-2.27 (m, 15H), 2.13-1.70 (m, 10H), 1.53-1.16 (m, 6H), 0.97 (t, *J* = 8.2 Hz, 3H), 0.80 (d, *J* = 8.2 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ = 169.3, 161.7 (q, *J* = 50.2 Hz), 146.7 (d, *J* = 2.6 Hz), 140.2, 138.9, 138.8, 138.7, 138.6 (2 peak), 138.1, 134.8, 133.6 (m), 133.1, 133.0, 130.9, 130.8, 130.0, 129.5 (m), 129.2 (m), 128.7 (m), 128.5, 128.3 (m), 126.9, 126.3, 126.2, 122.7, 119.1, 117.6 (m), 90.3 (d, *J* = 8.7 Hz), 82.1 (d, *J* = 16.0 Hz), 69.7 (d, *J* = 2.2 Hz), 69.3, 68.7, 68.5, 60.8, 40.5 (d, *J* = 6.6 Hz), 38.7, 35.8, 35.6 (d, *J* = 5.0 Hz), 33.3, 32.5, 31.5, 31.3, 29.7, 28.7, 26.3, 26.1, 21.4, 21.2, 12.8, 11.6; $^{31}$P NMR (121 MHz, $CDCl_3$) δ = 2.63 (s); $^{19}$F NMR (282 MHz, $CDCl_3$) δ = -62.83 (s);
IR (film) ν 2963, 1684, 1653, 1608, 1558, 1541, 1507, 1457, 1354, 1277, 1163, 1126, 887, 796, 714, 682, 670 $cm^{-1}$;
MS (MALDI) m/z: 784.3 $[M\text{-}BAr_F]^+$, 676.2 $[M\text{-}COD\text{-}BAr_F]^+$; HRMS (MALDI) m/z calcd. for $C_{40}H_{52}NOP^{191}Ir^+$ $[M\text{-}BAr_F]^+$: 784.3387, Found: 784.3366.

**Ir(I)/(*R,S*)-2h (R = Ph, Ar = *o*-Tol)**
Red powder, yield 78%; M.p.= 206-208 °C; $[\alpha]_D^{20}$ = -13.4° (*c* 1.2, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.29 (q, *J* = 6.8 Hz, 2H), 7.73 (s, 8H), 7.58-7.42 (m, 9H), 7.37-7.30 (m, 4H), 7.22-7.19 (m, 1H), 7.12-7.07 (m, 1H), 7.01-6.97 (m, 1H), 6.18 (s, 1H), 5.96 (d, *J* = 8 Hz, 1H), 5.59-5.55 (m, 1H), 5.47-5.40 (m, 1H), 4.88 (t, *J* = 9.2 Hz, 1H), 4.60-4.56 (m, 1H), 4.45-4.41 (m, 1H), 3.16-3.12 (m, 3H), 2.68-2.52 (m, 4H), 2.30-2.23 (m, 4H), 2.18 (s,3H), 2.12-1.94 (m, 2H), 1.91 (s, 3H), 1.68-1.52 (m, 2H), 1.39-1.21 (m, 3H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 171.5, 161.7 (q, *J* = 49.4 Hz), 145.3, 145.1, 143.2, 142.1 (d, *J* = 27.7 Hz), 140.9 (d, *J* = 10.9 Hz), 138.6, 134.8, 133.1 (d, *J* = 6.3 Hz), 132.8 (d *J* = 1.9 Hz), 132.4 (q, *J* = 5.8 Hz), 131.9 (d, *J* = 8.5 Hz), 131.4 (d, *J* = 1.2 Hz), 130.2, 129.9, 129.7, 129.1 (q, *J* = 2.9 Hz), 129.0 (q, *J* = 2.9 Hz), 128.7 (q, *J* = 2.8 Hz), 128.6, 128.5 (q, *J* = 2.8 Hz), 127.0, 126.0, 125.9, 125.4 (d, *J* = 8.1 Hz), 125.0, 124.6, 123.8, 123.2, 123.2, 120.4, 117.5-117.4 (m), 89.1 (d, *J* = 2.9 Hz), 78.4 (d, *J* = 18.5 Hz), 75.6, 73.8, 69.4, 69.1 (d, *J* = 13.6 Hz), 59.1, 42.9 (d, *J* = 6.8 Hz), 35.4 (d, *J* = 4.5 Hz), 34.2, 34.1, 31.8, 31.3, 31.1, 29.7, 27.9, 25.4, 24.1 (d, *J* = 9.7 Hz), 22.9 (d, *J* = 3.5 Hz) ppm; $^{31}$P NMR (162 MHz, $CDCl_3$) δ = -1.21 (s) ppm; $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -61.68 (s) ppm;
IR (film) ν 2921, 2849, 1668, 1594, 1458, 1386, 1354, 1278, 1161, 1127, 1031, 947, 888, 839, 805, 757, 744, 714, 682, 671, 595 $cm^{-1}$;
MS (MALDI) m/z: 778.3 $[M\text{-}BAr_F]^+$; HRMS (MALDI) m/z calcd. For $C_{40}H_{44}NOP^{191}Ir^+$ ($[M\text{-}BAr_F]^+$): 776.2761, Found: 776.2787.

## Spectral data for acids 1a-l

### (*E*)-2-Phenyl-3-(tetrahydro-2*H*-pyran-4-yl)acrylic acid (1a)

white solid, M.p. = 145-147 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ = 10.96 (br s, 1H), 7.39-7.33 (m, 3H), 7.17-7.14 (m, 2H), 6.94 (d, *J* = 10.0 Hz, 1H), 3.93-3.89 (m, 2H), 3.30-3.23 (m, 2H), 2.42-2.32 (m, 1H), 1.61-1.55 (m, 2H), 1.50-1.46 (m, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 172.0, 149.6, 134.6, 132.6, 129.4, 128.1, 127.7, 66.7, 35.5, 31.3 ppm; HRMS-EI (m/z) $M^+$ calcd. for $C_{14}H_{16}O_3$. 232.1099, found 232.1096.

### 2-Phenylacrylic acid (1b)[S5]

white solid, M.p. = 101-103 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ = 10.03 (br s, 1H), 7.44-7.30 (m, 5H), 6.54 (d, *J* = 0.8 Hz, 1H), 6.01 (d, *J* = 0.8 Hz, 1H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 172.2, 140.6, 136.0, 129.4, 128.4, 128.3, 128.1 ppm; HRMS-EI (m/z) $M^+$ calcd. for $C_9H_8O_2$. 148.0524 found 148.0526.

### (*E*)-2-Phenylbut-2-enoic acid (1c)[S6]

white solid, M.p. = 143-145 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ = 11.63 (br s, 1H), 7.38-7.27 (m, 4H), 7.19-7.16 (m, 2H), 1.76 (d, *J* = 7.2 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 172.6, 142.7, 134.3, 134.1, 129.7, 128.0, 127.5, 15.7 ppm; HRMS-EI (m/z) $M^+$ calcd. for $C_{10}H_{10}O_2$. 162.0681 found 162.0680.

### (*E*)-2,3-Diphenylacrylic acid (1d)[S7]

white solid, M.p. = 174-175 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ = 11.12 (br s, 1H), 7.95 (s, 1H), 7.40-7.32 (m, 3H), 7.24-7.13 (m, 5H), 7.07-7.04 (m, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 173.4, 142.4, 135.2, 134.2, 131.6, 130.8, 129.7, 129.4, 128.6, 128.2, 128.0 ppm; HRMS-EI (m/z) $M^+$ calcd. for $C_{15}H_{12}O_2$. 224.0837 found 224.0831.

### (*E*)-3-Cyclopentyl-2-phenylacrylic acid (1e)

white solid, M.p. = 104-106 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ = 11.10 (br s, 1H), 7.38-7.28 (m, 3H), 7.19-7.16 (m, 2H), 7.07 (d, *J* = 10.8 Hz, 1H), 2.54-2.43 (m, 1H), 1.77-1.64 (m, 4H), 1.56-1.35 (m, 4H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 172.8, 152.6, 135.0, 131.4, 129.8, 127.9, 127.4, 40.1, 33.4, 25.6 ppm; HRMS-EI (m/z) $M^+$ calcd. for $C_{14}H_{16}O_2$. 216.1150 found 216.1148.

### (*E*)-2-(4-Methoxyphenyl)-3-(tetrahydro-2*H*-pyran-4-yl)acrylic acid (1f)[S8]

white solid, M.p. = 112-114 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ = 9.60 (br s, 1H), 7.10 (td, *J* = 2.0 Hz, *J* = 8.4 Hz, 2H), 6.93-6.89 (m, 3H), 3.93-3.90 (m, 2H), 3.82 (s, 3H), 3.32-3.26 (m, 2H), 2.46-2.36 (m, 1H), 1.60-1.56 (m, 2H), 1.50-1.47 (m, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 172.3, 159.0, 149.5, 132.1, 130.5, 126.8, 113.6, 66.7, 55.1, 35.5, 31.4 ppm; HRMS-EI (m/z) $M^+$ calcd. for $C_{15}H_{18}O_4$. 262.1205 found 262.1208.

### (*E*)-2-(4-Fluorophenyl)-3-(tetrahydro-2*H*-pyran-4-yl)acrylic acid (1g)

white solid, M.p. = 172-173 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) δ = 10.58 (br s, 1H), 7.15-7.10 (m, 2H), 7.09-7.03 (m, 2H), 6.96 (d, *J* = 10.4 Hz, 1H), 3.95-3.91 (m, 2H), 3.32-3.25 (m, 2H), 2.40-2.30 (m, 1H), 1.65-1.54 (m, 2H), 1.49-1.45 (m, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 171.9, 161.7 (d, *J* = 245.6 Hz), 150.1, 131.6, 131.1 (d, *J* = 8.2 Hz), 130.4 (d, *J* = 3.1 Hz), 115.2 (d, *J* = 21.7 Hz), 66.6, 35.5, 31.2 ppm; $^{19}$F NMR

(376 MHz, $CDCl_3$) δ = -114.03 (s) ppm; HRMS-EI (m/z) $M^+$ calcd. for $C_{14}H_{15}O_3F$. 250.1005 found 250.1003.

**(*E*)-2-(4-Iodophenyl)-3-(tetrahydro-2*H*-pyran-4-yl)acrylic acid (1h)**
white solid, M.p. = 182-183 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ = 9.83 (br s, 1H), 7.71 (td, *J* = 2.0 Hz, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 10.4 Hz, 1H), 6.91 (td, *J* = 2.0 Hz, *J* = 8.4 Hz, 2H), 3.94-3.90 (m, 2H), 3.32-3.25 (m, 2H), 2.40-2.30 (m, 1H), 1.64-1.52 (m, 2H), 1.48-1.44 (m, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 171.5, 150.2, 137.3, 134.0, 131.5, 131.3, 93.7, 66.6, 35.6, 31.2 ppm; HRMS-EI (m/z) $M^+$ calcd. for $C_{14}H_{15}O_3I$. 358.0066 found 358.0065.

**(*E*)-2-(4-(Methylsulfonyl)phenyl)-3-(tetrahydro-2*H*-pyran-4-yl)acrylic acid (1i)**[S8]
white solid, M.p. = 254-256 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.97 (d, *J* = 8.4 Hz, 2H) , 7.38 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 10.4 Hz, 1H), 5.83 (br s, 1H), 3.97-3.91 (m, 2H), 3.31-3.23 (m, 2H), 3.29 (t, *J* = 11.2 Hz, 2H), 3.10 (s, 3H), 2.34-2.25 (m, 1H), 1.67-1.57 (m, 2H), 1.49-1.46 (m, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 170.5, 151.2, 140.5, 139.9, 130.9, 130.5, 127.3, 66.5, 44.3, 35.7, 31.1 ppm; HRMS-EI (m/z) $M^+$ calcd. for $C_{15}H_{18}O_5S$. 310.0875 found 310.0874.

**(*E*)-2-(4-(Cyclopropylsulfonyl)phenyl)-3-(tetrahydro-2*H*-pyran-4-yl)acrylic acid (1j)**[S8]
white solid, M.p. = 93-95 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.91 (d, *J* = 8.0 Hz, 2H) , 7.37 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 10.8 Hz, 1H), 3.95-3.91 (m, 2H), 3.32-3.26 (m, 2H), 2.55-2.47 (m, 1H), 2.35-2.25 (m, 1H), 1.67-1.56 (m, 2H), 1.50-1.46 (m, 2H), 1.40-1.30 (m, 2H), 1.10-1.03 (m, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 169.9, 150.5, 140.2, 139.9, 131.1, 130.3, 127.4, 66.4, 35.5, 32.6, 31.1, 5.9 ppm; HRMS-EI (m/z) $M^+$ calcd. for $C_{17}H_{20}O_5S$. 336.1031 found 336.1035.

**(*E*)-2-(4-(Methylthio)phenyl)-3-(tetrahydro-2*H*-pyran-4-yl)acrylic acid (1k)**[S8]
white solid, M.p. = 168-170 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ = 10.77 (br s, 1H), 7.24 (td, *J* = 2.0 Hz, *J* = 8.4 Hz, 2H), 7.09-7.07 (td, *J* = 2.0 Hz, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 10.4 Hz, 1H), 3.94-3.90 (m, 2H), 3.32-3.25 (m, 2H), 2.49 (s, 3H), 2.45-2.34 (m, 1H), 1.64-1.53 (m, 2H), 1.49-1.45 (m, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 171.9, 149.7, 138.1, 131.9, 131.1, 129.7, 125.8, 66.6, 35.4, 31.2, 15.4 ppm; HRMS-EI (m/z) $M^+$ calcd. for $C_{15}H_{18}O_3S$. 278.0977 found 278.0980.

**(*E*)-2-(4-(Cyclopropylthio)phenyl)-3-(tetrahydro-2*H*-pyran-4-yl)acrylic acid (1l)**
white solid, M.p. = 152-154 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ = 10.90 (br s, 1H), 7.36 (td, *J* = 2.0 Hz, *J* = 8.4 Hz, 2H) , 7.08 (td, *J* = 2.0 Hz, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 10.4 Hz, 1H), 3.94-3.90 (m, 2H), 3.32-3.27 (m, 2H), 2.47-2.37 (m, 1H), 2.21-2.15 (m, 1H), 1.64-1.54 (m, 2H), 1.50-1.46 (m, 2H), 1.12-1.02 (m, 2H), 0.73-0,69 (m, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 172.0, 149.7, 138.7, 132.0, 131.0, 129.7, 125.7, 66.6, 35.4, 31.3, 11.6, 8.4 ppm; HRMS-EI (m/z) $M^+$ calcd. for $C_{17}H_{20}O_3S$. 304.1133 found 304.1131.

**General procedure for asymmetric hydrogenation of acids 1 using iridium complexes of 2 as the catalysts.** To a test tube were charged with a stir bar, acid (0.1 mmol), the catalyst Ir(I)/**2** (0.001 mmol), base (0.1 mmol) and 1mL MeOH under Ar atmosphere. The test tube was placed in a Parr steel autoclave in a glove box, which was purged three times with hydrogen and finally pressurized to 10 or 30 atm. The reaction mixture was stirred for 20 h at 30-50°C. Then the hydrogen gas was released and the conversion was determined by $^1$H NMR. The reaction mixture was then treated with $CH_2N_2$ in ether for 2 h. After a flash column chromatography separation on silica gel with EtOAc as eluent, the desired methyl ester was obtained. The ee value of the product was determined by chiral HPLC using its methyl ester derivative.

**Characterization data for product corresponding derivatives 3a-l**

**(-)-Methyl 2-phenyl-3-(tetrahydro-2*H*-pyran-4-yl)propanoate (3a)**

pale yellow oil, 96% ee, $[\alpha]_D^{20}$ = -44.4° (*c* 1.16, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.34-7.24 (m, 5H), 3.93-3.90 (m, 2H), 3.70-3.65 (m, 4H), 3.29 (t, *J* = 11.2 Hz, 2H), 2.07-2.00 (m, 1H), 1.77-1.56 (m, 4H), 1.40-1.27 (m, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 174.4, 138.9, 128.6, 127.8, 127.2, 67.8, 67.7, 52.0, 48.2, 40.4, 32.9, 32.7, 32.6 ppm; HRMS-EI (m/z) $M^+$ calcd. for $C_{15}H_{20}O_3$. 248.1412 found 248.1409. HPLC condition for corresponding methyl ester: Chiralcel AD-H column (hexane : isopropanol = 99 : 1, flow rate = 1.0 mL/min, UV detection at λ = 230 nm) $t_R$ = 12.0 min (minor), $t_R$ = 15.8 min (major).

**(*R*)-Methyl 2-phenylpropanoate(3b)**[S5]

pale yellow oil, 88% ee, $[\alpha]_D^{20}$ = -15.2° (*c* 0.83, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.34-7.22 (m, 5H), 3.73 (q, *J* = 7.2 Hz, 1H), 3.65 (s, 3H), 1.50 (d, *J* = 7.2 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 174.9, 140.5, 128.6, 127.4, 127.1, 51.9, 45.3, 18.5 ppm; HRMS-EI (m/z) $M^+$ calcd. for $C_{10}H_{12}O_2$. 164.0837 found 164.0841. HPLC condition for corresponding methyl ester: Chiralcel OJ column (hexane : isopropanol = 99 : 1, flow rate = 1.0 mL/min, UV detection at λ = 230 nm) $t_R$ = 12.8 min (minor), $t_R$ = 16.1 min (major).

**(*R*)-Methyl 2-phenylbutanoate(3c)**[S6]

pale yellow oil, 94% ee, $[\alpha]_D^{20}$ = -38.8° (*c* 1.64, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.33-7.23 (m, 5H), 3.65 (s, 3H), 3.45(t, *J* = 7.6 Hz, 1H), 2.13-2.06 (m, 1H), 1.83-1.76 (m, 1H), 0.89 (t, *J* = 6.4 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 174.5, 139.0, 128.5, 127.9, 127.1, 53.3, 51.8, 26.7, 12.1 ppm; HRMS-EI (m/z) $M^+$ calcd. for $C_{11}H_{14}O_2$. 178.0994 found 178.0996. HPLC condition for corresponding methyl ester: Chiralcel OD-H column (hexane : isopropanol = 99 : 1, flow rate = 1.0 mL/min, UV detection at λ = 230 nm) $t_R$ = 5.3 min (major), $t_R$ = 5.9 min (minor).

**(*R*)-Methyl 2,3-diphenylpropanoate (3d)**[S7]

pale yellow oil, 94% ee, $[\alpha]_D^{20}$ = -53.3° (*c* 1.17, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ = 7. 30-7.10 (m, 10H), 3.87-3.81 (m, 1H), 3.59 (s, 3H), 3.44-3.38 (m, 1H), 3.02 (dd, *J* = 6.8 Hz, *J* = 13.6 Hz, 1H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 173.8, 139.0, 138.6, 128.8, 128.6, 128.3, 127.9, 127.3, 126.3, 53.5, 51.9, 39.7 ppm; HRMS-EI (m/z) $M^+$ calcd. for $C_{16}H_{16}O_2$. 240.1150 found 240.1153. HPLC condition for corresponding methyl ester:

Chiralcel OD-H column (hexane : isopropanol = 99 : 1, flow rate = 1.0 mL/min, UV detection at λ = 230 nm) $t_R$ = 7.0 min (major), $t_R$ = 7.9 min (minor).

**(-)-Methyl 3-cyclopentyl-2-phenylpropanoate (3e)**[S9]
pale yellow oil, 95% ee, $[\alpha]_D^{20}$ = -41.1° (*c* 1.23, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ = 7.32-7.25 (m, 5H), 3.64 (s, 3H), 3.60 (t, *J* = 10.4 Hz, 1H), 2.09-2.02 (m, 1H), 1.82-1.43 (m, 8H), 1.12-1.07 (m, 2H) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$) δ = 174.7, 139.3, 128.5, 127.9, 127.1, 51.9, 50.7, 39.8, 37.8, 32.6, 32.2, 25.0 ppm; HRMS-EI (m/z) $M^+$ calcd. for $C_{15}H_{20}O_2$. 232.1463 found 232.1461. HPLC condition for corresponding methyl ester: Chiralcel OJ-H column (hexane : isopropanol = 90 : 10, flow rate = 0.7 mL/min, UV detection at λ = 230 nm) $t_R$ = 8.4 min (major), $t_R$ = 8.8 min (minor).

**(-)-Methyl 2-(4-methoxyphenyl)-3-(tetrahydro-2*H*-pyran-4-yl)propanoate (3f)**
pale yellow oil, 95% ee, $[\alpha]_D^{20}$ = -43.0° (*c* 0.76, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ = 7.21 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 3.92-3.89 (m, 2H), 3.79 (s, 3H), 3.64-3.61 (m, 4H), 3.29 (t, *J* = 11.6 Hz, 2H), 2.03-1.96 (m, 1H), 1.74-1.55 (m, 4H), 1.41-1.25 (m, 2H) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$) δ = 174.7, 158.8, 130.9, 128.8, 114.0, 67.8, 67.7, 55.2, 51.9, 47.3, 40.4, 33.0, 32.6, 32.6 ppm; HRMS-EI (m/z) $M^+$ calcd. for $C_{16}H_{22}O_4$. 278.1518 found 278.1520. HPLC condition for corresponding methyl ester: Chiralcel AD-H column (hexane : isopropanol = 92 : 8, flow rate = 0.7 mL/min, UV detection at λ = 230 nm) $t_R$ = 9.8 min (minor), $t_R$ = 11.8 min (major).

**(-)-Methyl 2-(4-fluorophenyl)-3-(tetrahydro-2*H*-pyran-4-yl)propanoate (3g)**
pale yellow oil, 95% ee, $[\alpha]_D^{20}$ = -38.7° (*c* 0.62, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ = 7.28-7.25 (m, 2H), 7.01 (t, *J* = 8.4 Hz, 2H), 3.93-3.90 (m, 2H), 3.69-3.65 (m, 4H), 3.29 (t, *J* = 12.0 Hz, 2H), 2.05-1.97 (m, 1H), 1.73-1.55 (m, 4H), 1.41-1.24 (m, 2H) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$) δ = 174.3, 162.0 (d, *J* = 244.2 Hz), 134.6, 129.3 (d, *J* = 8.3 Hz), 115.5 (d, *J* = 21.2 Hz), 67.7, 67.7, 52.0, 47.5, 40.5, 32.9, 32.6 ppm; HRMS-EI (m/z) $M^+$ calcd. for $C_{15}H_{19}O_3F$. 266.1318 found 266.1319. HPLC condition for corresponding methyl ester: Chiralcel AD-H column (hexane : isopropanol = 99 : 1, flow rate = 1.0 mL/min, UV detection at λ = 230 nm) $t_R$ = 12.4 min (minor), $t_R$ = 15.9 min (major).

**(-)-Methyl 2-(4-iodophenyl)-3-(tetrahydro-2*H*-pyran-4-yl)propanoate (3h)**
yellow solid, M.p. = 61-63 °C; 91% ee, $[\alpha]_D^{20}$ = -39.5° (*c* 1.05, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ = 7.65 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 3.92-3.89 (m, 2H), 3.65-3.61 (m, 4H), 3.29 (t, *J* = 11.6 Hz, 2H), 2.03-1.96 (m, 1H), 1.73-1.54 (m, 4H), 1.43-1.25 (m, 2H) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$) δ = 173.9, 138.5, 137.7, 129.8, 92.8, 67.7, 67.7, 52.1, 47.8, 40.2, 32.9, 32.5 ppm; HRMS-EI (m/z) $M^+$ calcd. for $C_{15}H_{19}O_3I$. 374.0379 found 374.0375. HPLC condition for corresponding dehalogenated methyl ester: Chiralcel AD-H column (hexane : isopropanol = 99 : 1, flow rate = 1.0 mL/min, UV detection at λ = 230 nm) $t_R$ = 9.8 min (minor), $t_R$ = 12.0 min (major).

**(*R*)-Methyl 2-(4-(methylsulfonyl)phenyl)-3-(tetrahydro-2*H*-pyran-4-yl)propanoate (3i)**[S8]
white solid, M.p. = 143-145 °C; 91% ee, $[\alpha]_D^{20}$ = -41.1° (*c* 0.87, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ = 7.91 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 3.94-3.91 (m, 2H),

3.62-3.78 (m, 1H), 3.68 (s, 3H), 3.30 (t, $J$ = 11.2 Hz, 2H), 3.06 (s, 3H), 2.10-2.05 (m, 1H), 1.77-1.72 (m, 2H), 1.60-1.58 (m, 2H), 1.40-1.25 (m, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 173.3, 145.1, 139.5, 128.9, 127.8, 67.6, 67.6, 52.3, 48.2, 44.4, 40.3, 32.8, 32.6, 32.5 ppm; HRMS-EI (m/z) $M^+$ calcd. for $C_{16}H_{22}O_5S$. 326.1188 found 326.1186. HPLC condition for corresponding methyl ester: Chiralcel OD-H column (hexane : isopropanol = 80 : 20, flow rate = 1.0 mL/min, UV detection at λ = 230 nm) $t_R$ = 24.4 min (minor), $t_R$ = 27.8 min (major).

**(*R*)-Methyl 2-(4-(cyclopropylsulfonyl)phenyl)-3-(tetrahydro-2*H*-pyran-4-yl) propanoate (3j)**[S8]

yellow solid, M.p. = 54-56 °C; 89% ee, $[\alpha]_D^{20}$ = -28.1° (*c* 0.40, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.86 (d, $J$ = 8.0 Hz, 2H), 7.50 (d, $J$ = 8.0 Hz, 2H), 3.94-3.91 (m, 2H), 3.79 (t, $J$ = 8.0 Hz, 1H), 3.68 (s, 3H), 3.30 (t, $J$ = 12.6 Hz, 2H), 2.48-2.44 (m, 1H), 2.12-2.04 (m, 1H), 1.77-1.58 (m, 6H), 1.06-1.02 (m, 2H), 0.88-0.82 (m, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 173.4, 144.7, 139.7, 128.8, 128.0, 67.7, 67.6, 52.3, 48.2, 40.4, 32.8, 32.7, 32.6, 29.6, 5.9 ppm; HRMS-EI (m/z) $M^+$ calcd. for $C_{18}H_{24}O_5S$. 352.1344 found 352.1349. HPLC condition for corresponding methyl ester: Chiralcel OD-H column (hexane : isopropanol = 80 : 20, flow rate = 0.7 mL/min, UV detection at λ = 230 nm) $t_R$ = 32.8 min (minor), $t_R$ = 36.1 min (major).

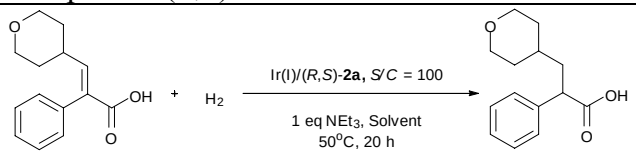
**(-)-Methyl 2-(4-(methylthio)phenyl)-3-(tetrahydro-2*H*-pyran-4-yl)propanoate (3k)**

yellow solid, M.p. = 79-81 °C; 94% ee, $[\alpha]_D^{20}$ = -32.4° (*c* 0.45, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.21 (s, 4H), 3.92-3.90 (m, 2H), 3.66-3.62 (m, 4H), 3.29 (t, $J$ = 11.6 Hz, 2H), 2.47 (s, 3H), 2.03-1.96 (m, 1H), 1.75-1.55 (m, 3H), 1.41-1.21 (m, 3H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 174.3, 137.4, 135.6, 128.3, 126.8, 67.8, 67.7, 52.0, 47.7, 40.3, 33.0, 32.6, 32.6, 15.7 ppm; HRMS-EI (m/z) $M^+$ calcd. for $C_{16}H_{22}O_3S$. 294.1290 found 294.1294. HPLC condition for corresponding sulfone methyl ester after oxidation with *m*CPBA: Chiralcel AD-H column (hexane : isopropanol = 80 : 20, flow rate = 1.0 mL/min, UV detection at λ = 230 nm) $t_R$ = 24.5 min (minor), $t_R$ = 28.1 min (major).

**(*R*)-Methyl 2-(4-(cyclopropylthio)phenyl)-3-(tetrahydro-2*H*-pyran-4-yl)propanoate (3l)**[S10]

pale yellow oil, 95% ee, $[\alpha]_D^{20}$ = -45.8° (*c* 0.52, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.31 (d, $J$ = 8.0 Hz, 2H), 7.21 (d, $J$ = 8.0 Hz, 2H), 3.93-3.90 (m, 2H), 3.65-3.62 (m, 4H), 3.30 (t, $J$ = 11.6 Hz, 2H), 2.19-2.14 (m, 1H), 2.04-1.97 (m, 1H), 1.75-1.68 (m, 1H), 1.60-1.56 (m, 2H), 1.43-1.25 (m, 3H), 1.08-1.05 (m, 2H), 0.69-0.67 (m, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 174.4 137.9, 135.5, 128.2, 126.6, 67.8, 67.7, 52.0, 47.7, 40.3, 32.9, 32.6, 32.6, 11.9, 8.4 ppm; HRMS-EI (m/z) $M^+$ calcd. for $C_{18}H_{24}O_3S$. 320.1439 found 320.1442. HPLC condition for corresponding sulfone methyl ester after oxidation with *m*CPBA: Chiralcel OD-H column (hexane : isopropanol = 80 : 20, flow rate = 0.7 mL/min, UV detection at λ = 230 nm) $t_R$ = 26.7 min (minor), $t_R$ = 29.0 min (major).

Table S1. Optimization of reaction conditions for the asymmetric hydrogenation of acid **1a** catalyzed by Ir(I) complex of (*R,S*)-**2a**[a]

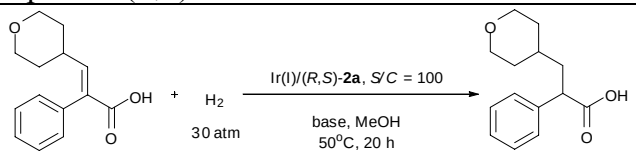



**1a** **3a**

| entry | Solvent | [sub] (M) | $PH_2$ (atm) | conv. (%)[b] | ee (%)[c] |
|---|---|---|---|---|---|
| 1 | Toluene | 0.1 | 30 | 43 | 71 (-) |
| 2 | DCE | 0.1 | 30 | 41 | 91 (-) |
| 3 | THF | 0.1 | 30 | 87 | 95 (-) |
| 4 | EA | 0.1 | 30 | 35 | 92 (-) |
| 5 | MeOH | 0.1 | 30 | 92 | 93 (-) |
| 6 | MeOH | 0.2 | 30 | 84 | 93 (-) |
| 7 | MeOH | 0.05 | 30 | 92 | 93 (-) |
| 8 | EtOH | 0.1 | 30 | 92 | 93 (-) |
| 9 | i-PrOH | 0.1 | 30 | 92 | 93 (-) |
| 10 | MeOH | 0.1 | 10 | 91 | 93 (-) |
| 11[d] | MeOH | 0.1 | 30 | 61 | 92 (-) |

[a] Reaction condition: 0.1 mmol scale, [substrate] = 0.1 mol $L^{-1}$ in solvent, s/c = 100.
[b] Determined by $^1H$ NMR. [c] Determined by chiral HPLC analysis of the corresponding methyl ester on Chiralcel AD-H column. [d] Reaction temperature is 30°C.

Table S2. Optimization of addatives for the asymmetric hydrogenation of acid **1a** catalyzed by Ir(I) complex of (*R,S*)-**2a**[a]



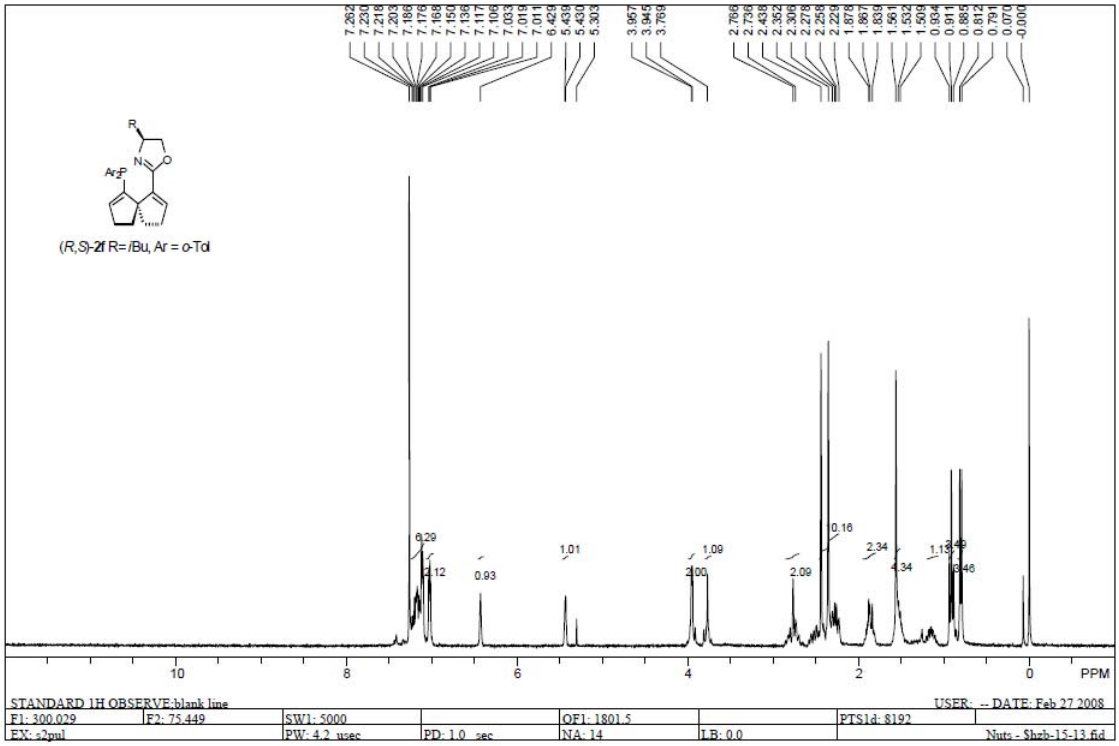

**1a** **3a**

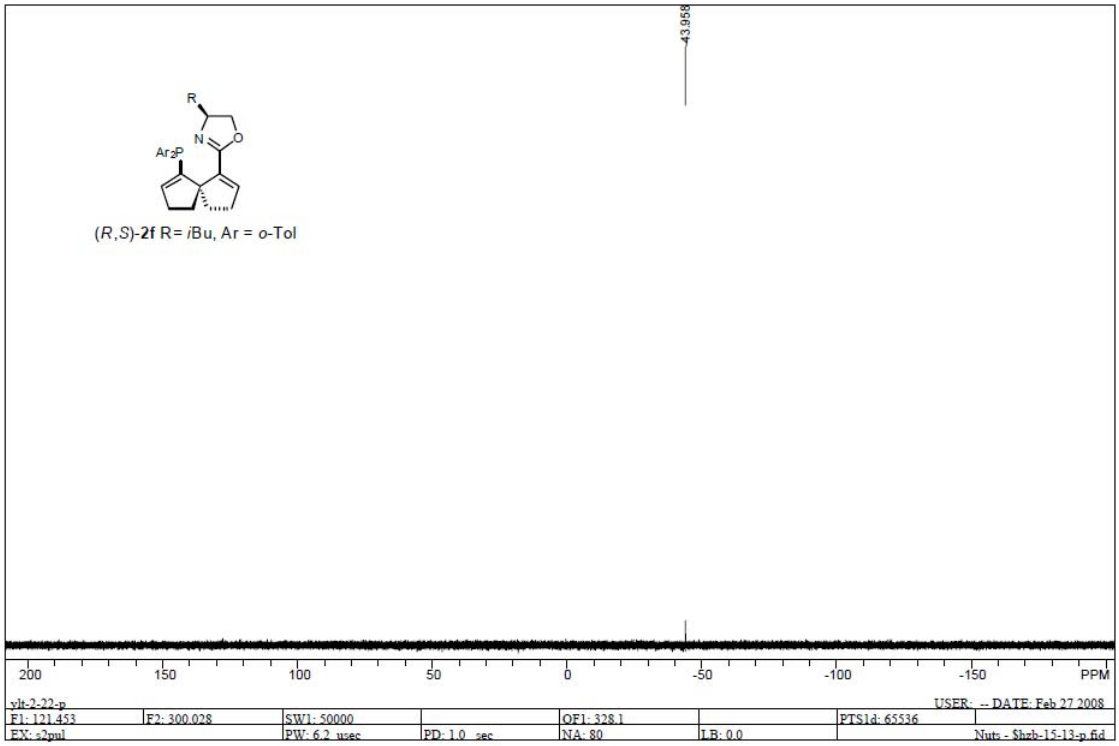
| entry | base | [base] (eq.) | conv. (%)[b] | ee (%)[c] |
|---|---|---|---|---|
| 1 | $Et_3N$ | 1 | 92 | 93 (-) |
| 2 | DIPEA | 1 | 74 | 93 (-) |
| 3 | Pyridine | 1 | trace | N.D. |
| 4 | $Me_3N$ | 1 | 75 | 93 (-) |
| 5 | $NaHCO_3$ | 1 | trace | N.D. |
| 6 | $K_2CO_3$ | 1 | trace | N.D. |
| 7 | $Cs_2CO_3$ | 1 | trace | N.D. |
| 8 | KOH | 1 | 63 | 92 (-) |
| 9 | $Et_3N$ | 0.5 | 90 | 93 (-) |
| 10 | $Et_3N$ | 2 | 40 | 92 (-) |

[a] Reaction condition: 0.1 mmol scale, [substrate] = 0.1 mol $L^{-1}$ in MeOH, s/c = 100.
[b] Determined by $^1H$ NMR. [c] Determined by chiral HPLC analysis of the corresponding methyl ester on Chiralcel AD-H column.

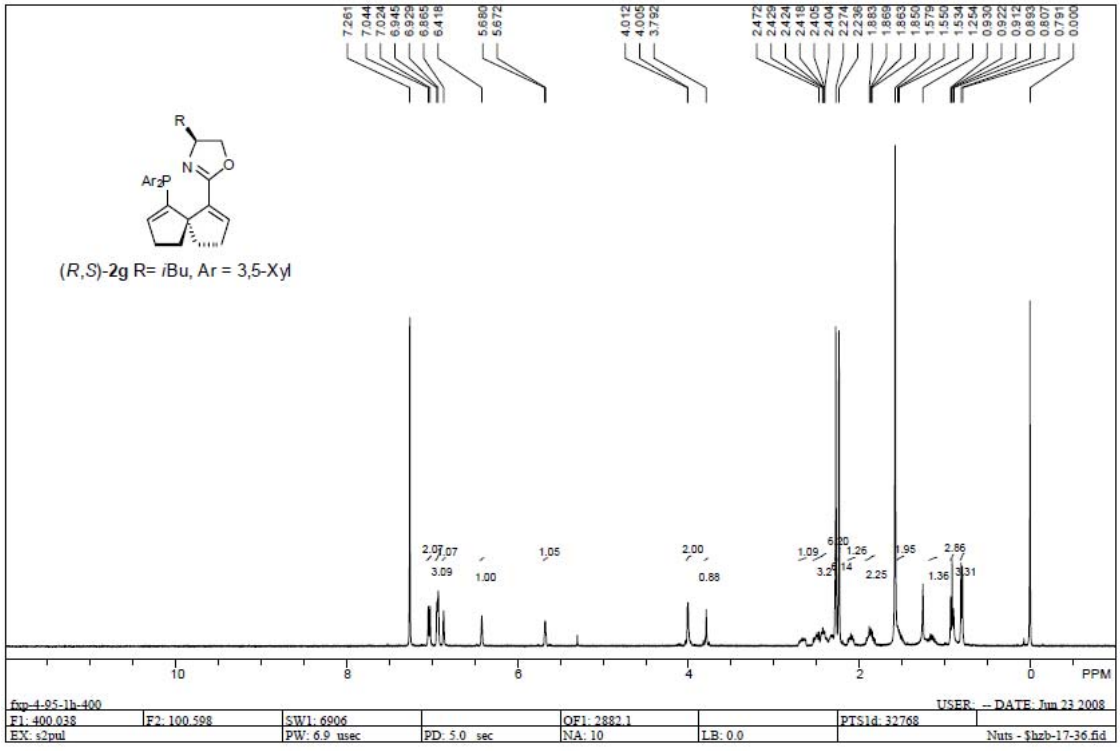
# NMR data for new compounds

## Ligand (*R*,*S*)-2f



## Ligand (*R*,*S*)-2g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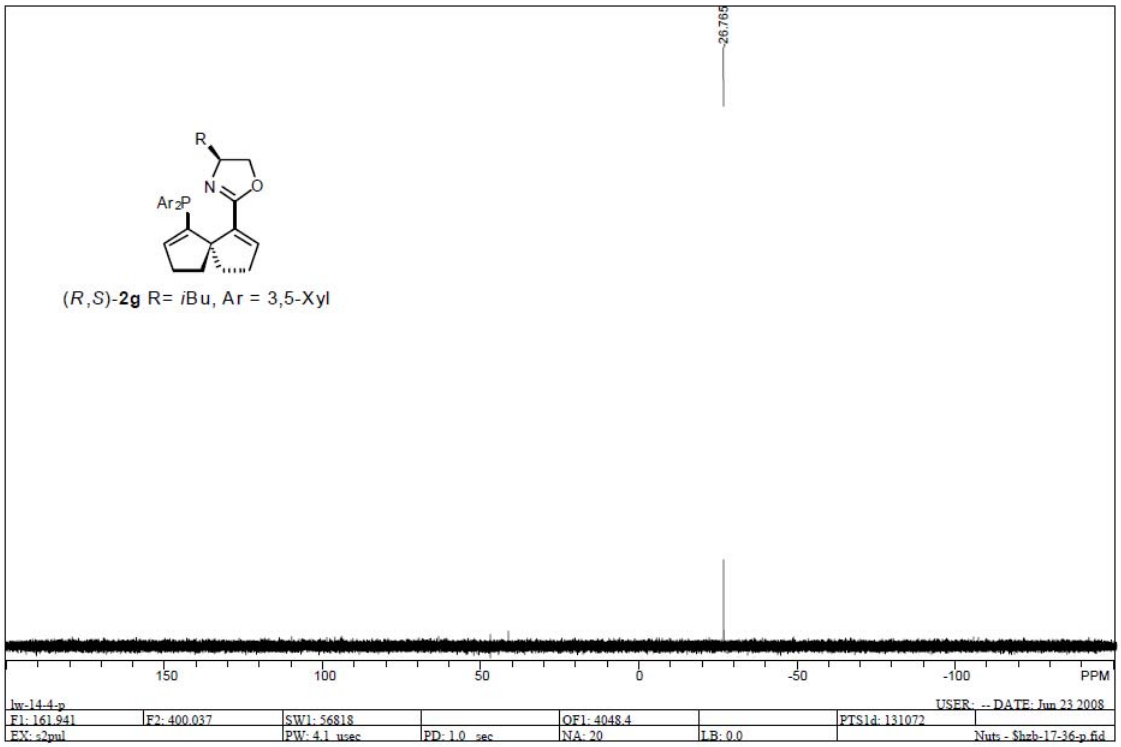
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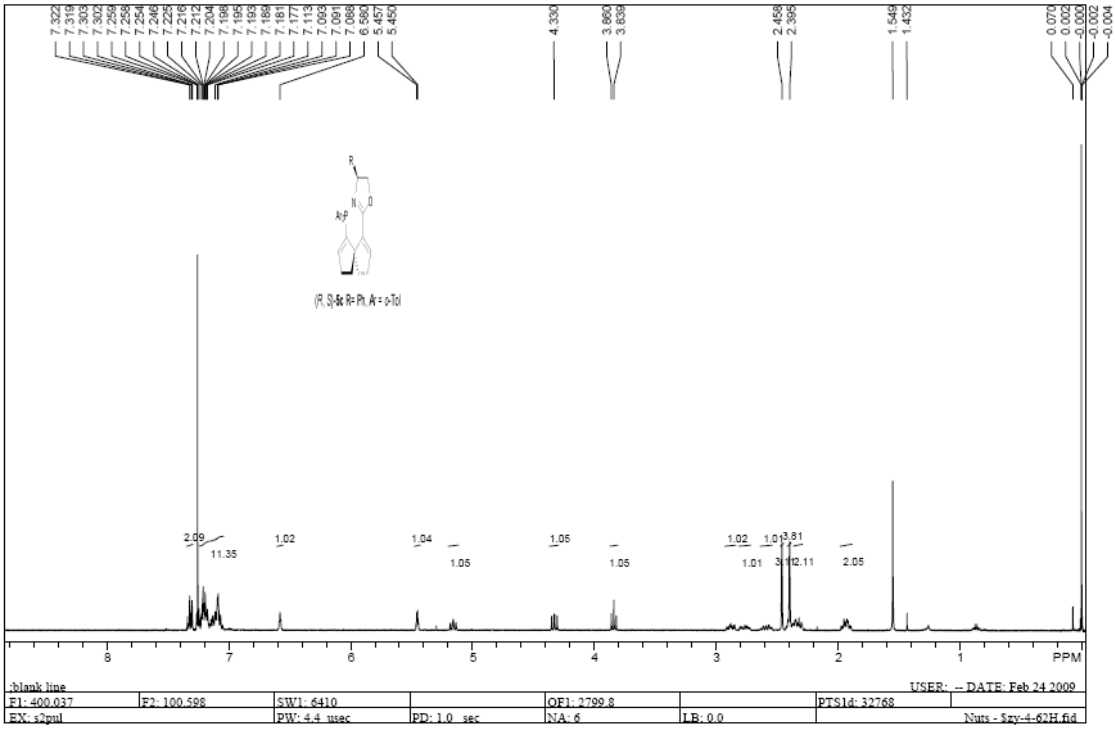
## Ligand (*R*,*S*)-2h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7.195
7.193
7.189
7.161
7.177
7.113
7.093
7.091
7.088
6.580
5.457
5.450
4.330
3.860
3.839
2.458
2.395
1.549
1.432
0.070
0.002
0.000
-0.002
-0.004
(R,S)-2h R= Ph, Ar = o-Tol
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11.35
1.02
1.04
1.05
1.05
1.05
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1.01
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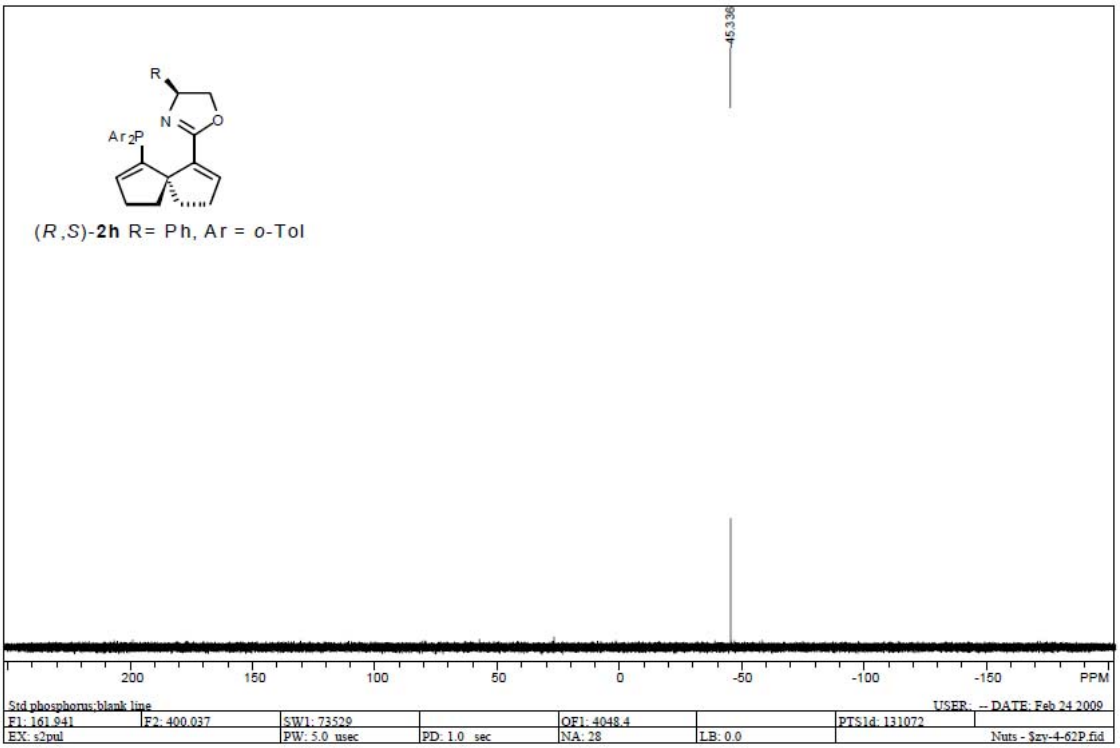
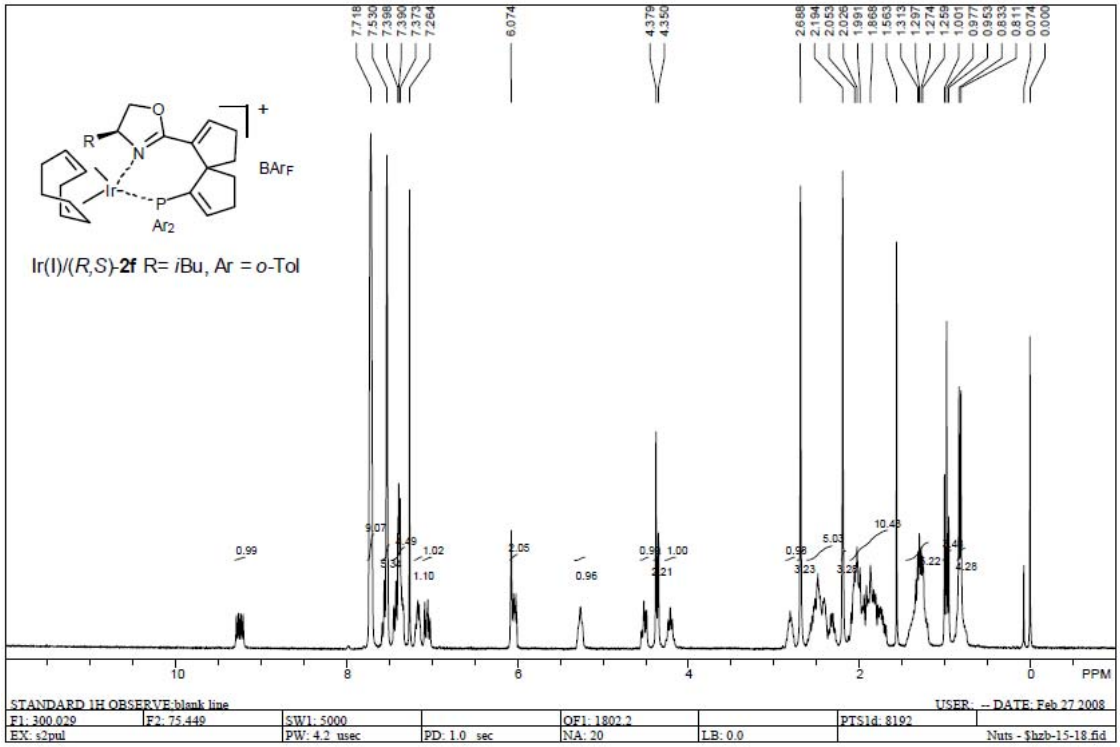
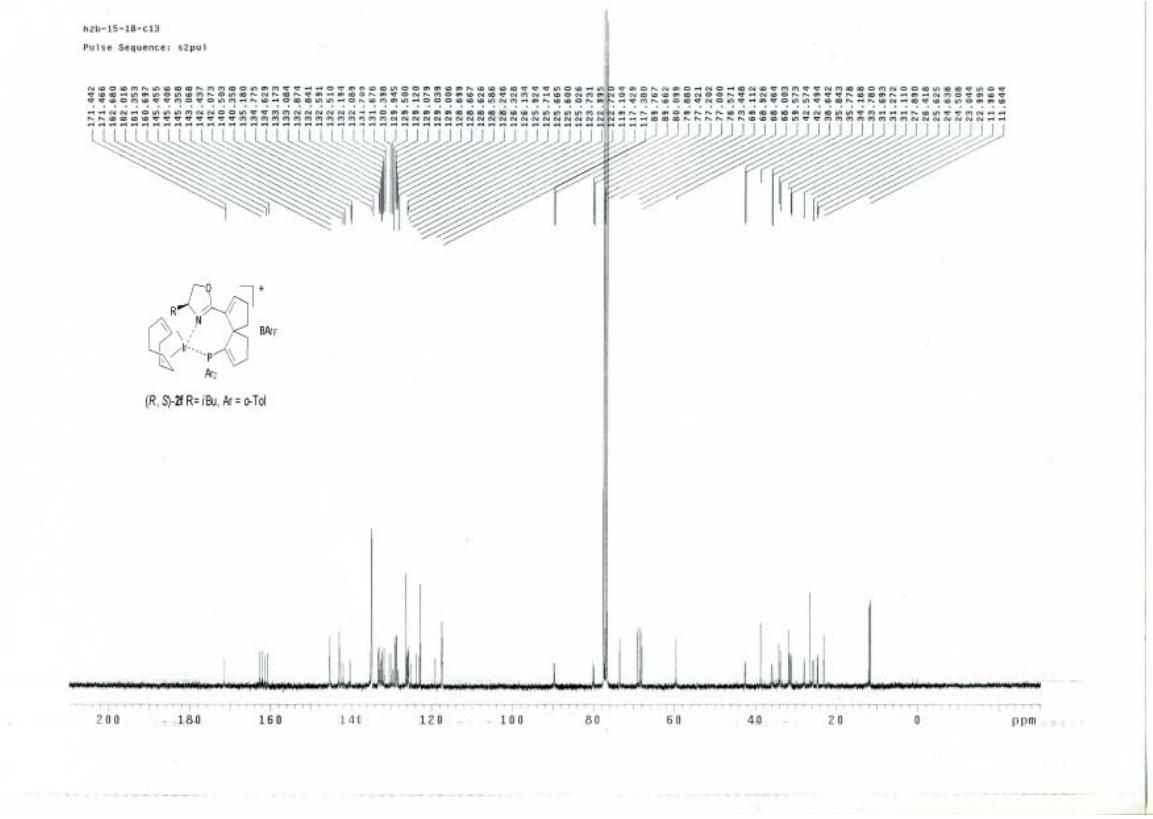
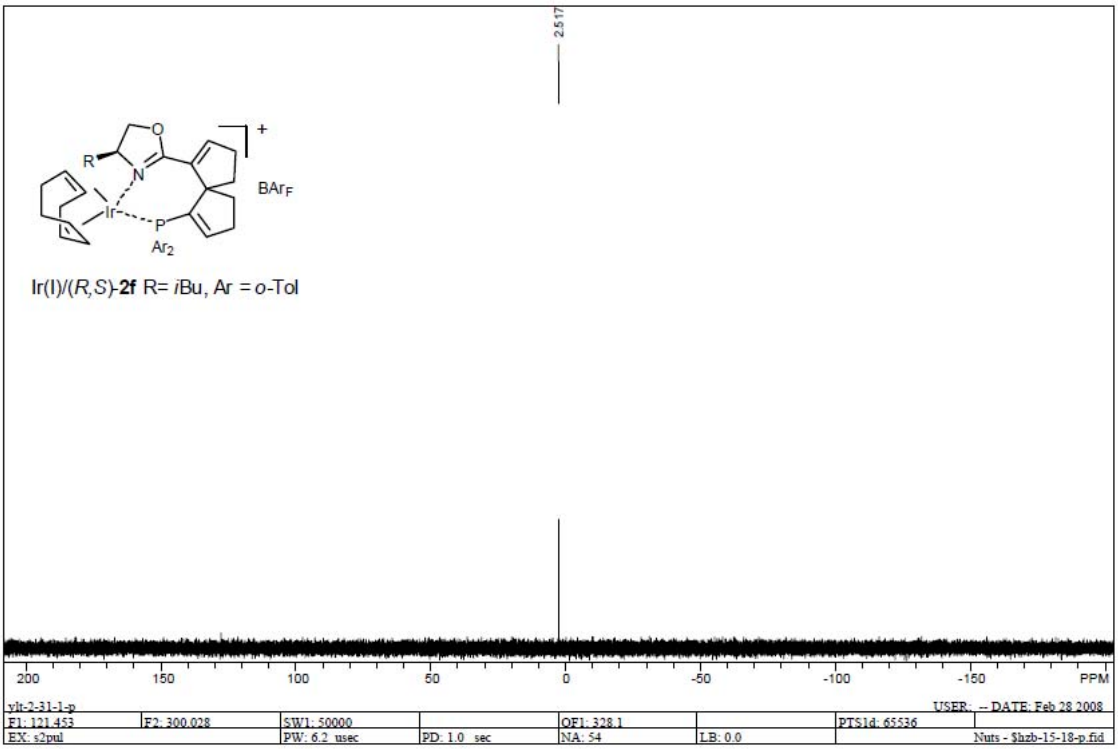
LB: 0.0
Nuts - $zy-4-62H.fid

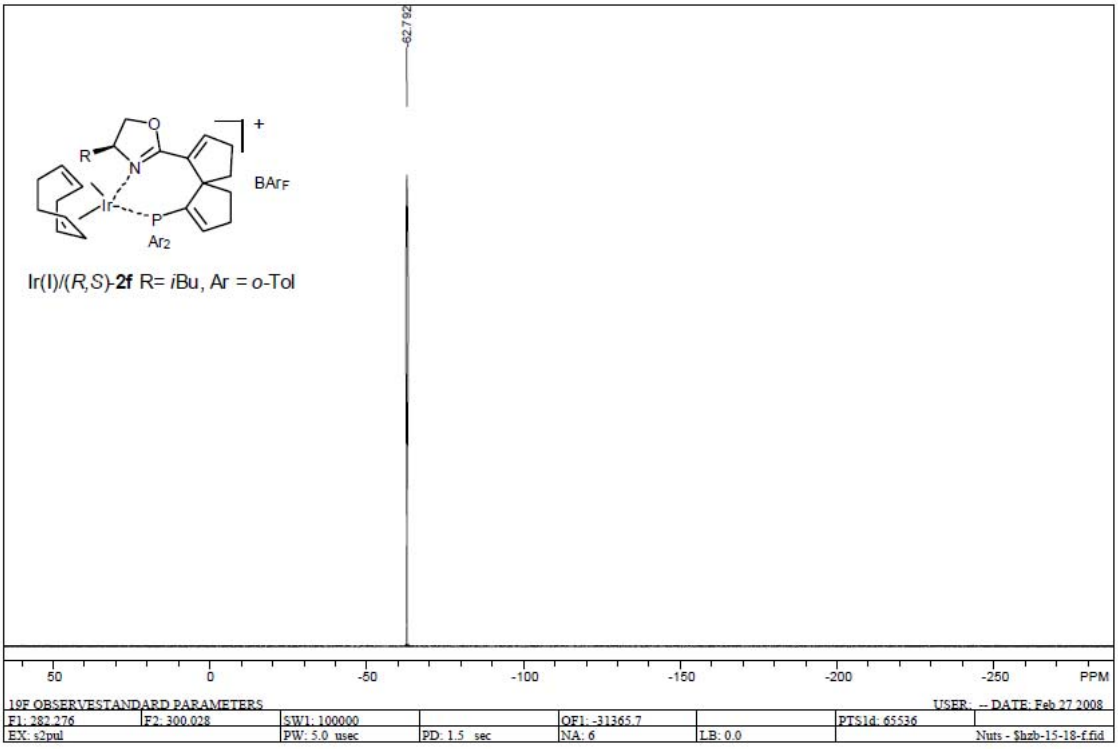

45.336
R
N
O
Ar2P
(R,S)-2h R= Ph, Ar = o-Tol
200
150
100
50
0
-50
-100
-150
PPM
Std phosphorus;blank line
USER: -- DATE: Feb 24 2009
F1: 161.941
F2: 400.037
SW1: 73529
OF1: 4048.4
PTS1d: 131072
EX: s2pul
PW: 5.0 usec
PD: 1.0 sec
NA: 28
LB: 0.0
Nuts - $zy-4-62P.fid

## Ir(I)/(*R*,*S*)-2f (R = *i*Bu, Ar = *o*-Tol)

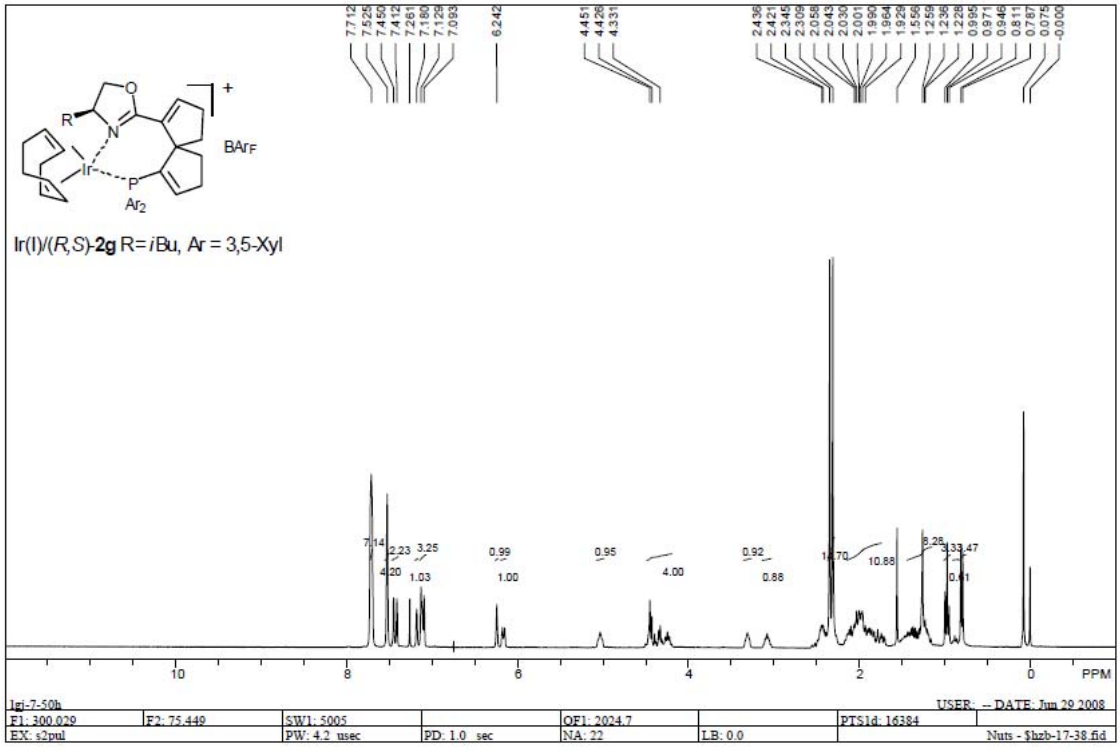


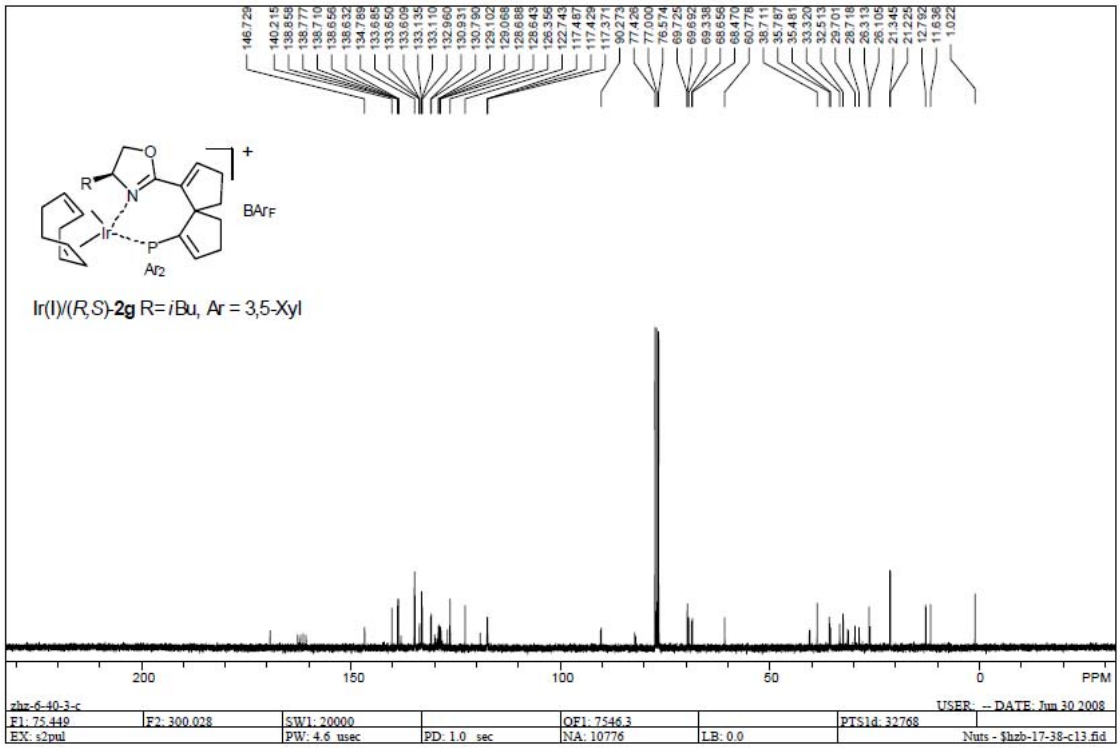



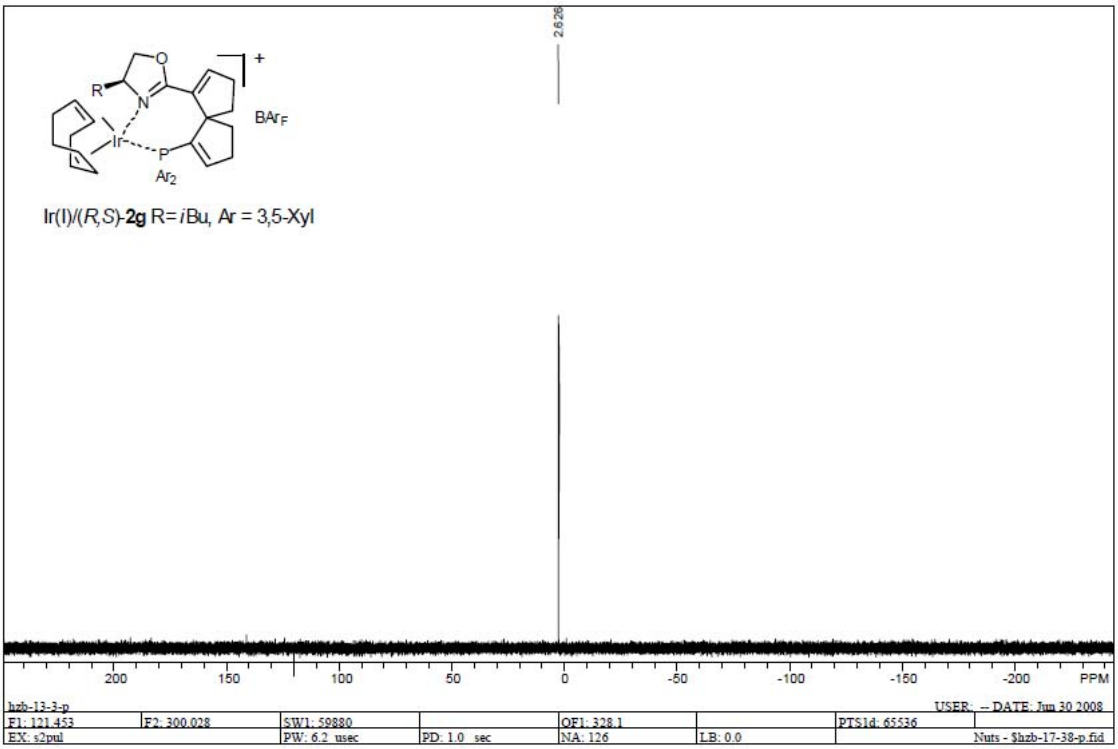

2.517
BAr$_F$
Ar$_2$
Ir(I)/(*R,S*)-**2f** R= *i*Bu, Ar = *o*-Tol
200
150
100
50
0
-50
-100
-150
PPM
ylt-2-31-1-p
USER: -- DATE: Feb 28 2008
F1: 121.453
F2: 300.028
SW1: 50000
OF1: 328.1
PTS1d: 65536
EX: s2pul
PW: 6.2 usec
PD: 1.0 sec
NA: 54
LB: 0.0
Nuts - $hzb-15-18-p.fid


-62.792
BAr$_F$
Ar$_2$
Ir(I)/(*R,S*)-**2f** R= *i*Bu, Ar = *o*-Tol
50
0
-50
-100
-150
-200
-250
PPM
19F OBSERVESTANDARD PARAMETERS
USER: -- DATE: Feb 27 2008
F1: 282.276
F2: 300.028
SW1: 100000
OF1: -31365.7
PTS1d: 65536
EX: s2pul
PW: 5.0 usec
PD: 1.5 sec
NA: 6
LB: 0.0
Nuts - $hzb-15-18-f.fid

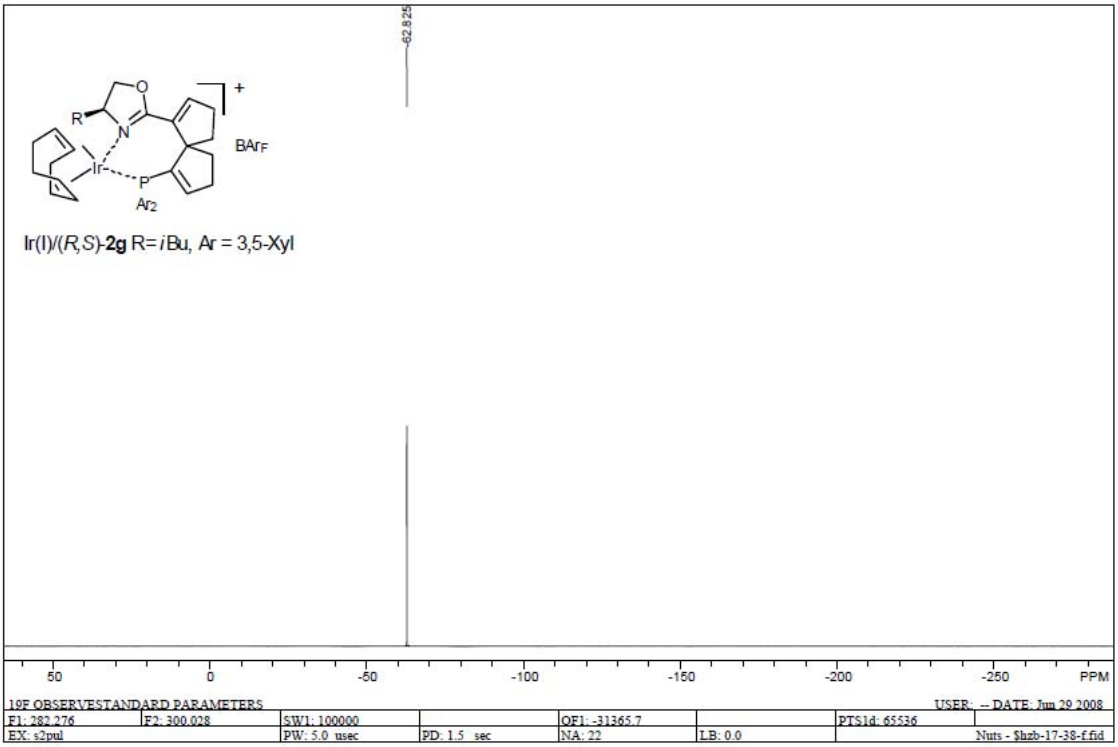
## Ir(I)/(*R*,*S*)-2g (R = *i*Bu, Ar = 3.5-Xyl)



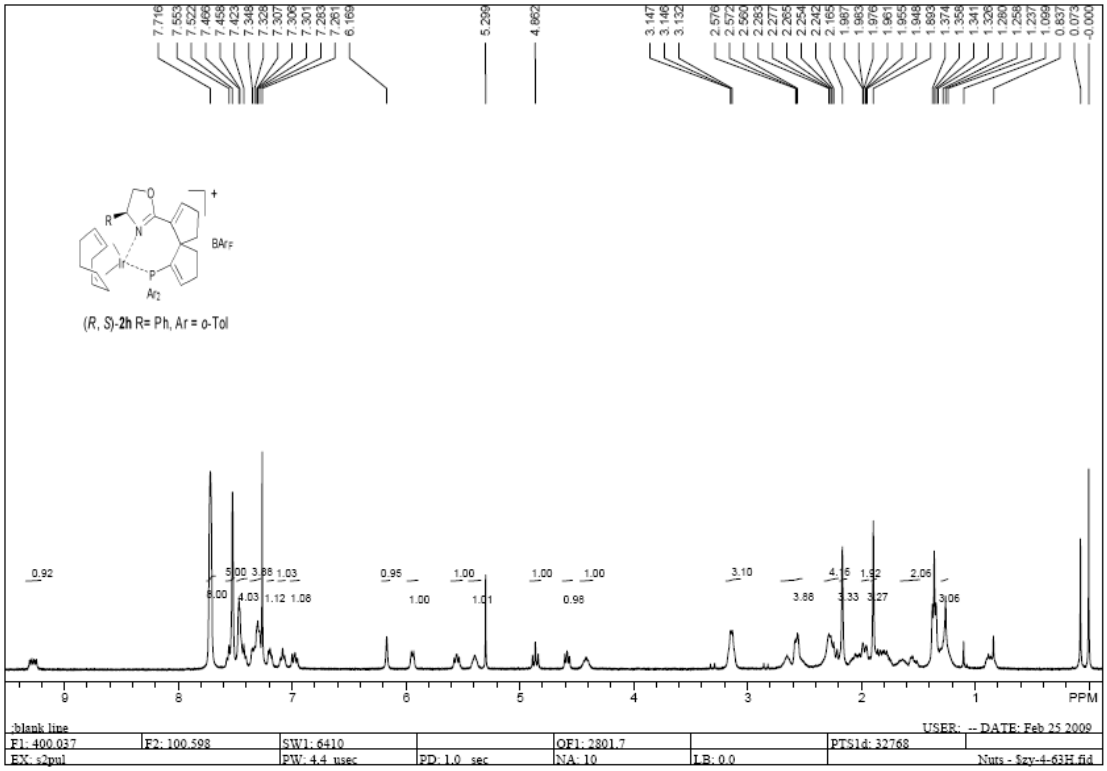


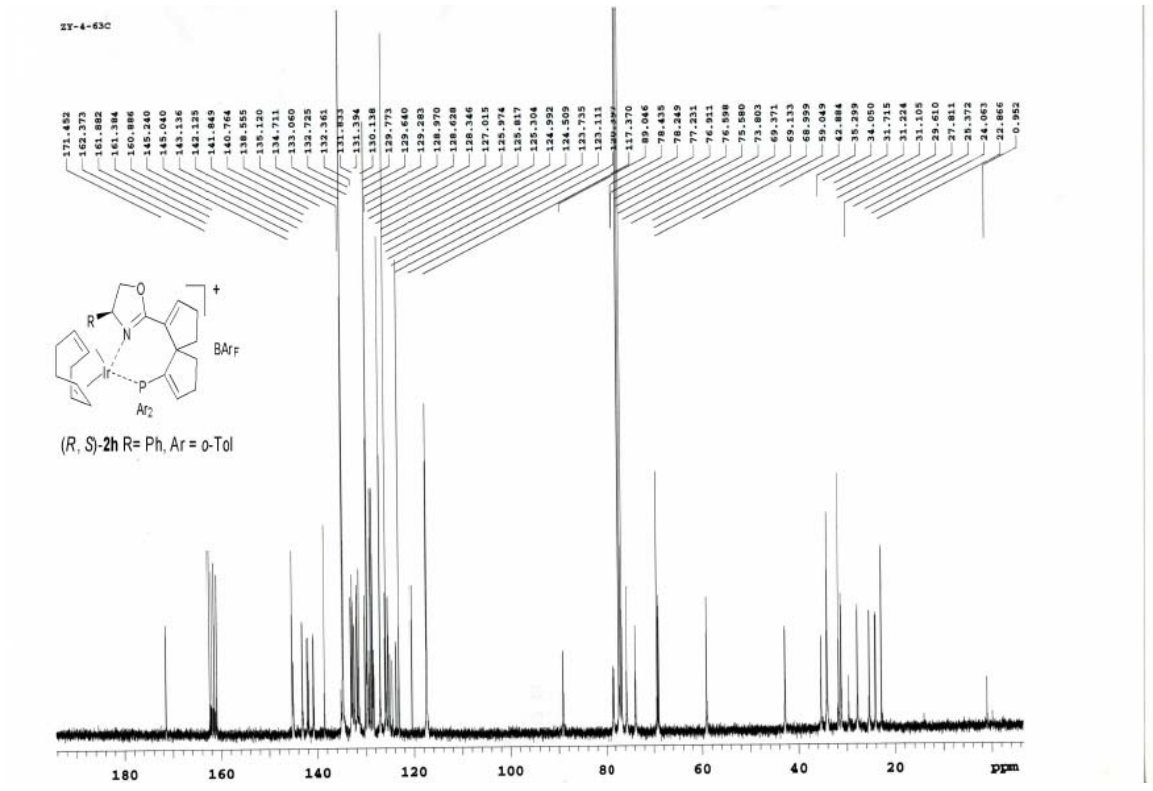

Ir(I)/(*R,S*)-**2g** R= *i*Bu, Ar = 3,5-Xyl

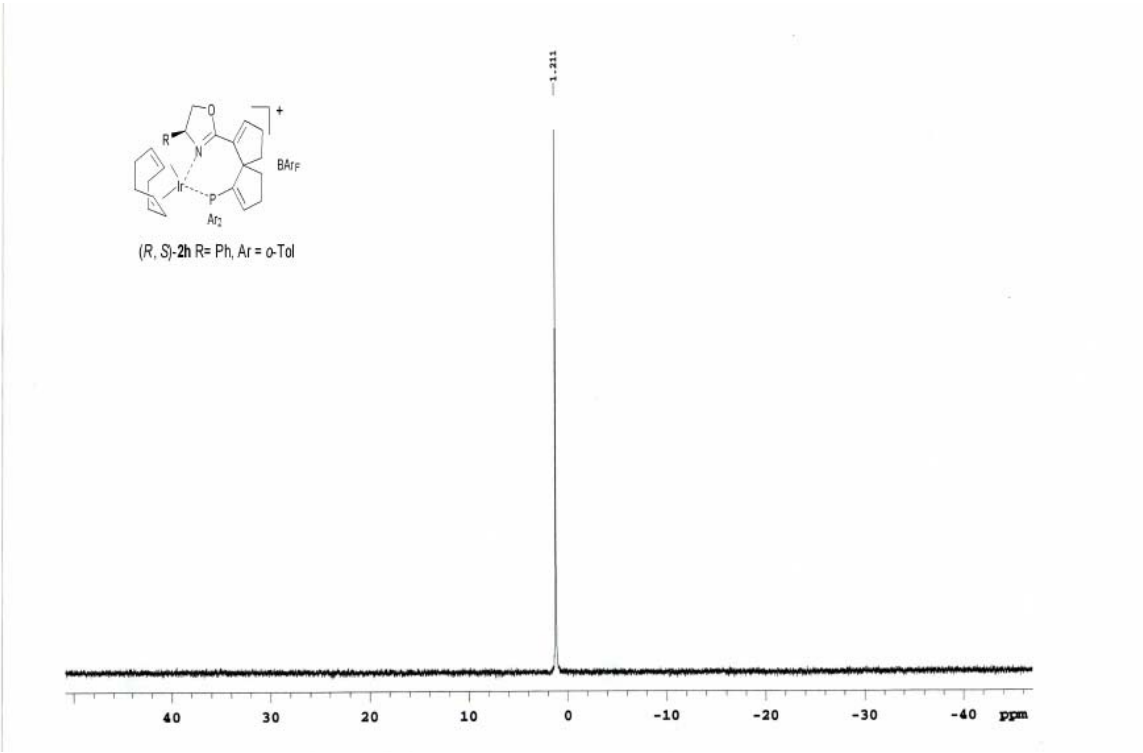



Ir(I)/(*R,S*)-**2g** R= *i*Bu, Ar = 3,5-Xyl

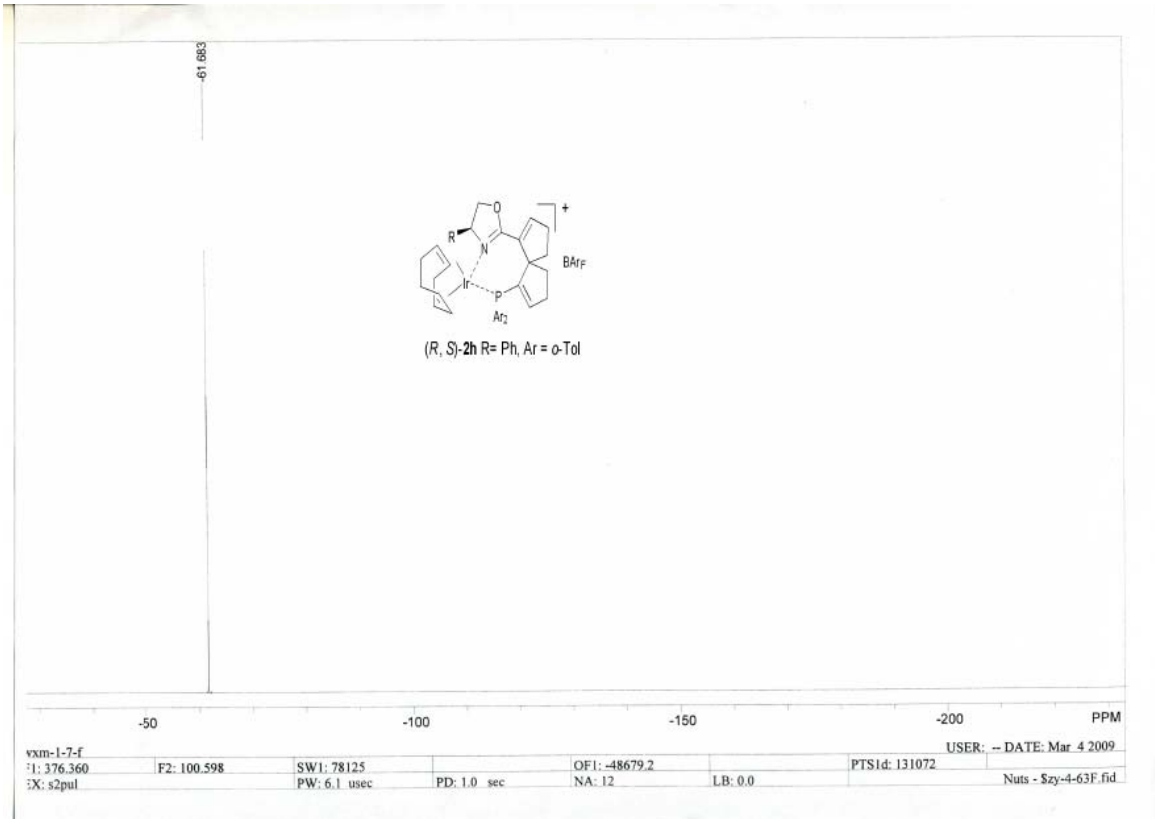
## Ir(I)/(*R*,*S*)-2h (R = Ph, Ar = *o*-Tol)



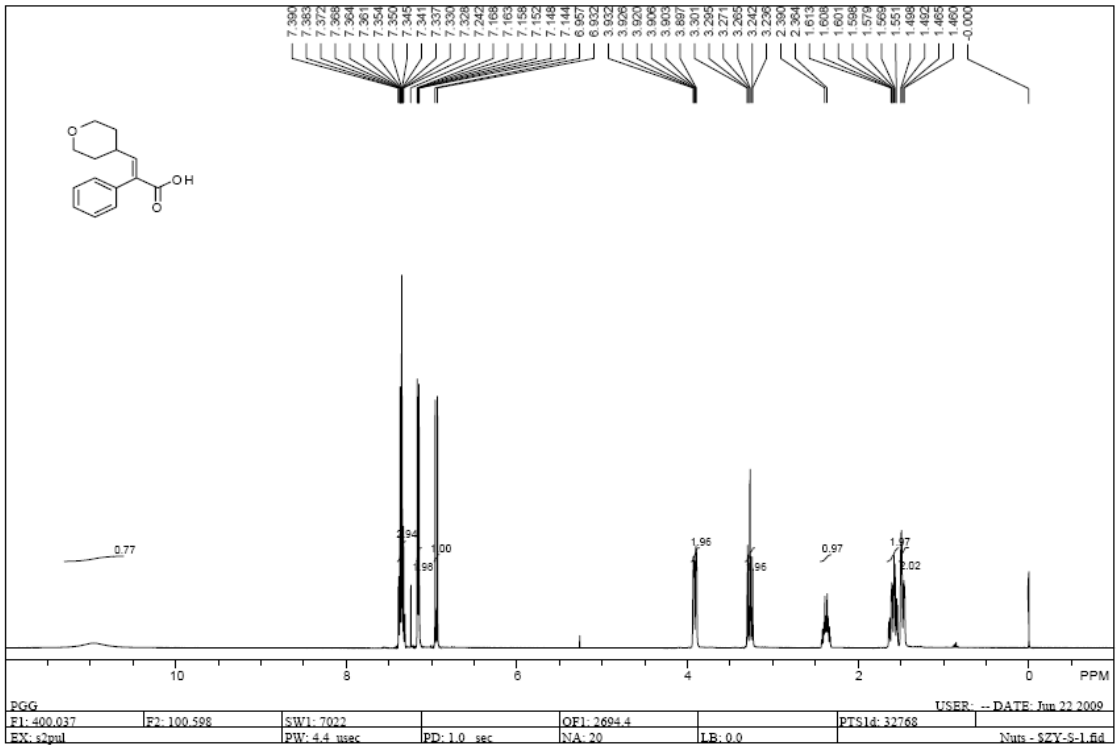


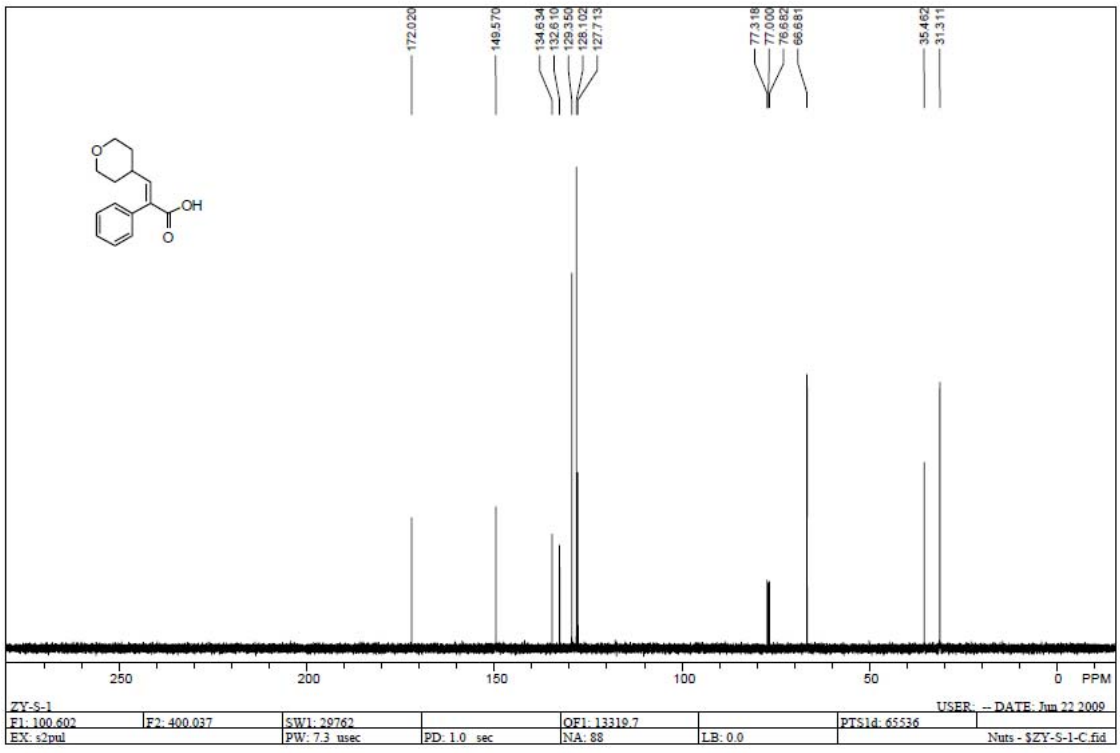

(*R*, *S*)-**2h** R= Ph, Ar = *o*-Tol



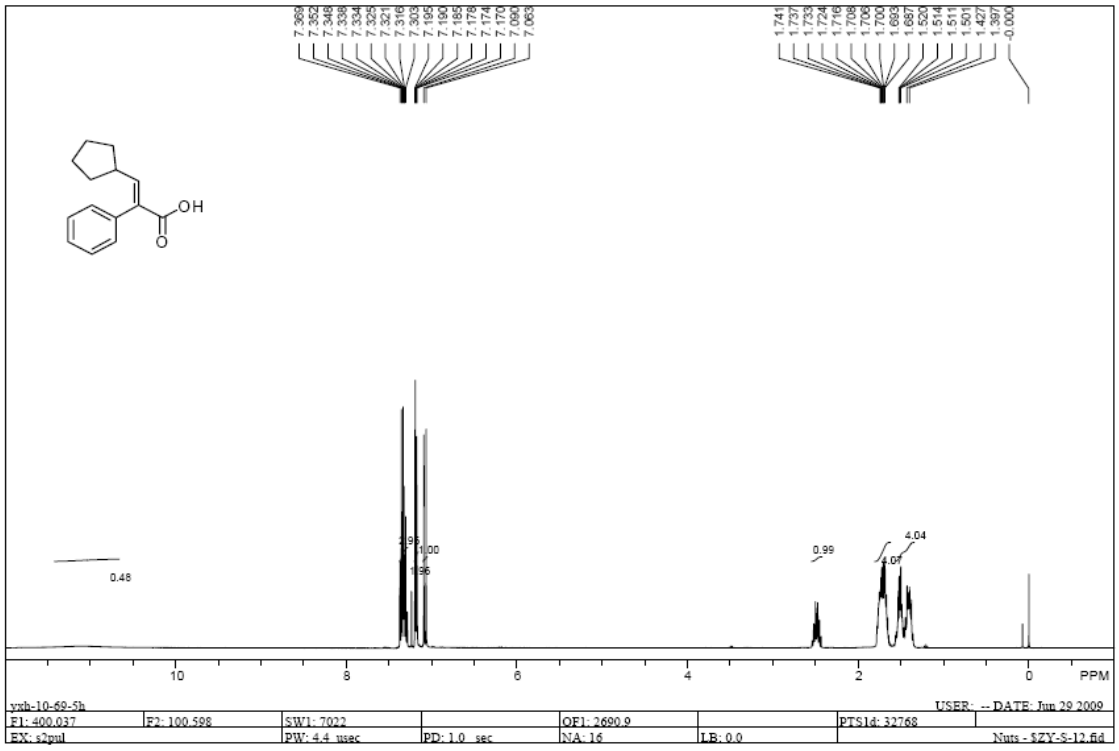

(*R*, *S*)-**2h** R= Ph, Ar = *o*-Tol

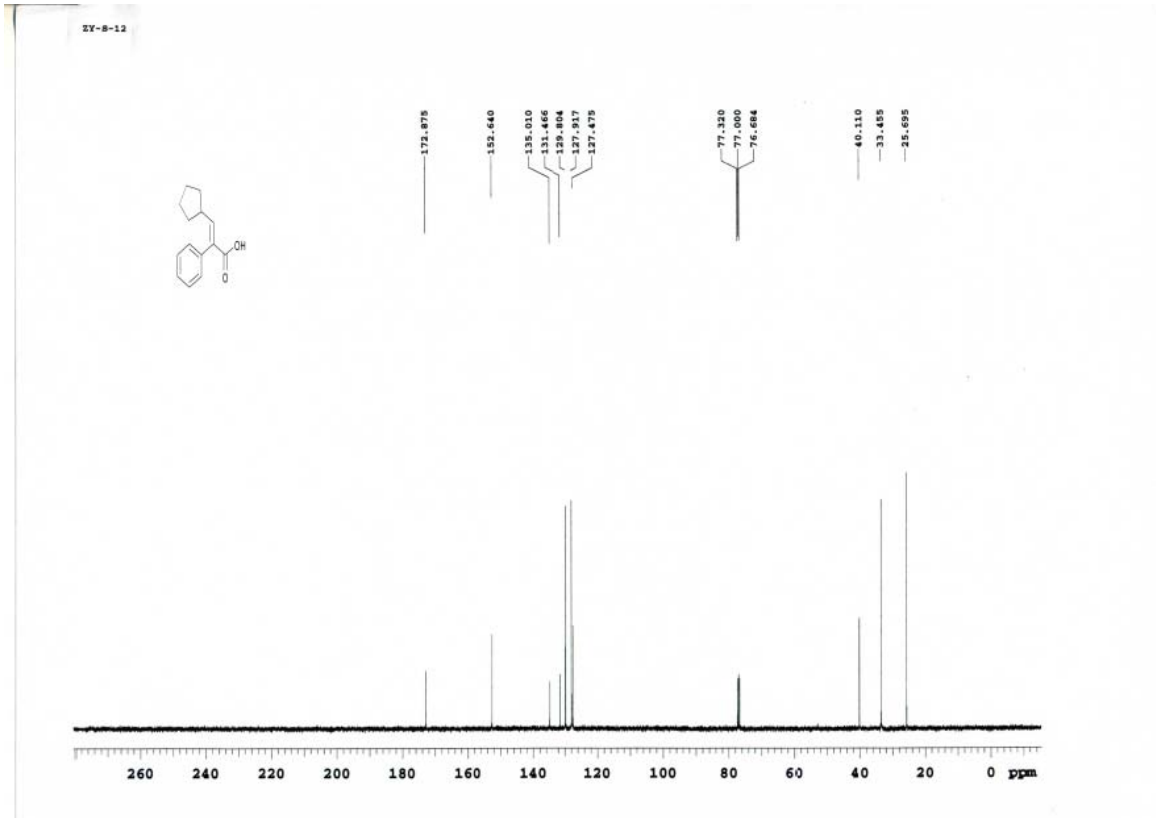
# Compound 1a


7.390
7.383
7.372
7.368
7.364
7.361
7.354
7.350
7.345
7.341
7.337
7.330
7.328
7.242
7.168
7.163
7.158
7.152
7.148
7.144
6.957
6.932
3.932
3.926
3.920
3.906
3.903
3.897
3.301
3.295
3.271
3.265
3.242
3.236
2.390
2.384
1.613
1.608
1.601
1.598
1.579
1.569
1.551
1.489
1.482
1.465
1.460
-0.000
OH
O
0.77
2.94
1.00
0.98
1.96
0.96
0.97
1.97
2.02
10
8
6
4
2
0
PPM
PGG
USER: -- DATE: Jun 22 2009
F1: 400.037
F2: 100.598
SW1: 7022
OF1: 2694.4
PTS1d: 32768
EX: s2pul
PW: 4.4 usec
PD: 1.0 sec
NA: 20
LB: 0.0
Nuts - $ZY-S-1.fid

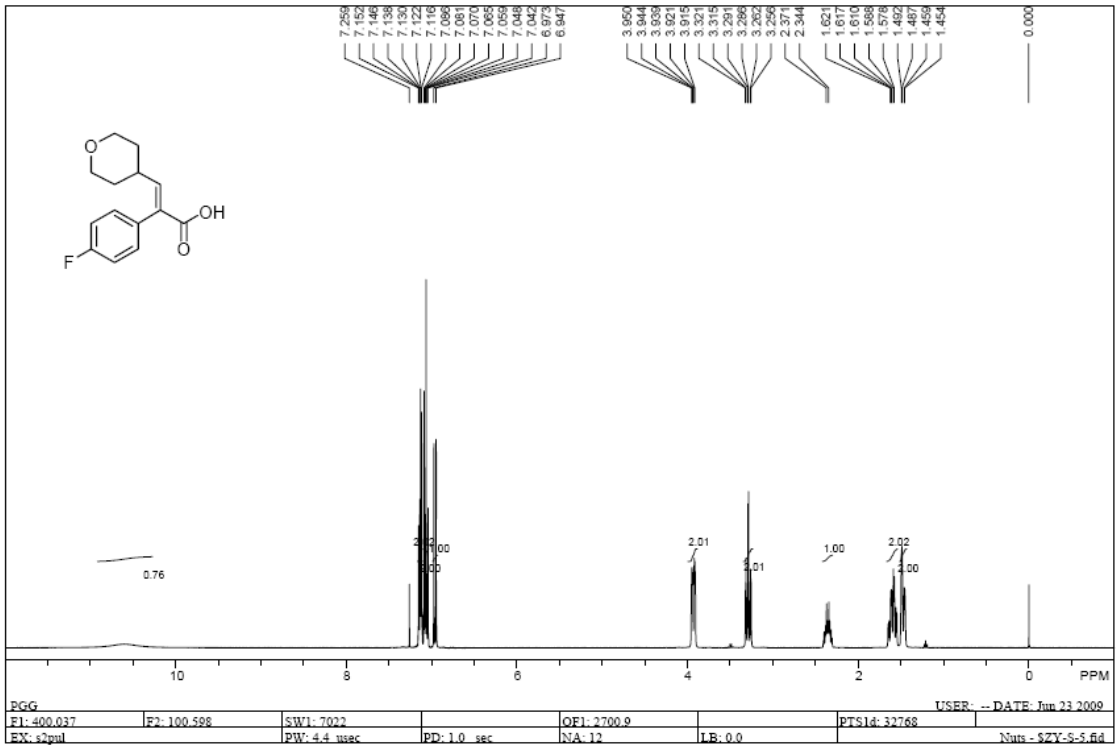

172.020
149.570
134.634
132.610
129.350
128.102
127.713
77.318
77.000
76.682
66.681
35.462
31.311
OH
O
250
200
150
100
50
0
PPM
ZY-S-1
USER: -- DATE: Jun 22 2009
F1: 100.602
F2: 400.037
SW1: 29762
OF1: 13319.7
PTS1d: 65536
EX: s2pul
PW: 7.3 usec
PD: 1.0 sec
NA: 88
LB: 0.0
Nuts - $ZY-S-1-C.fid

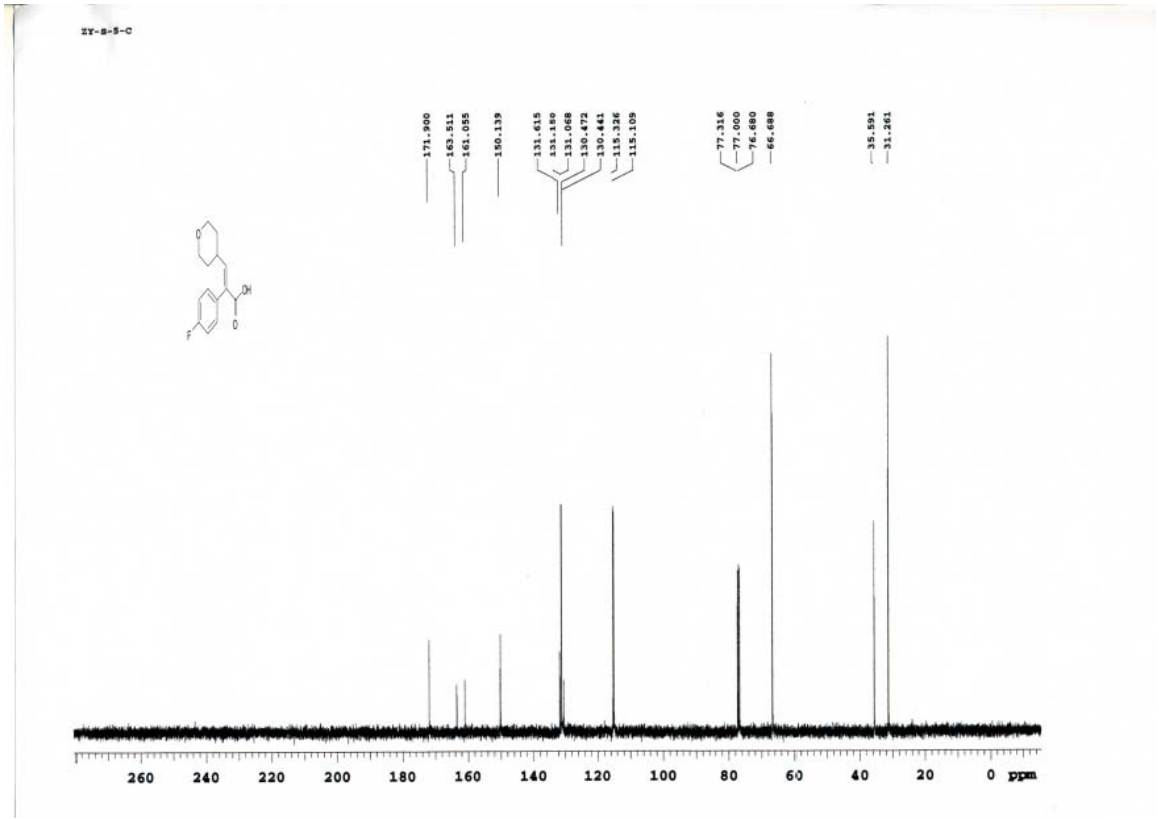
## Compound 1e

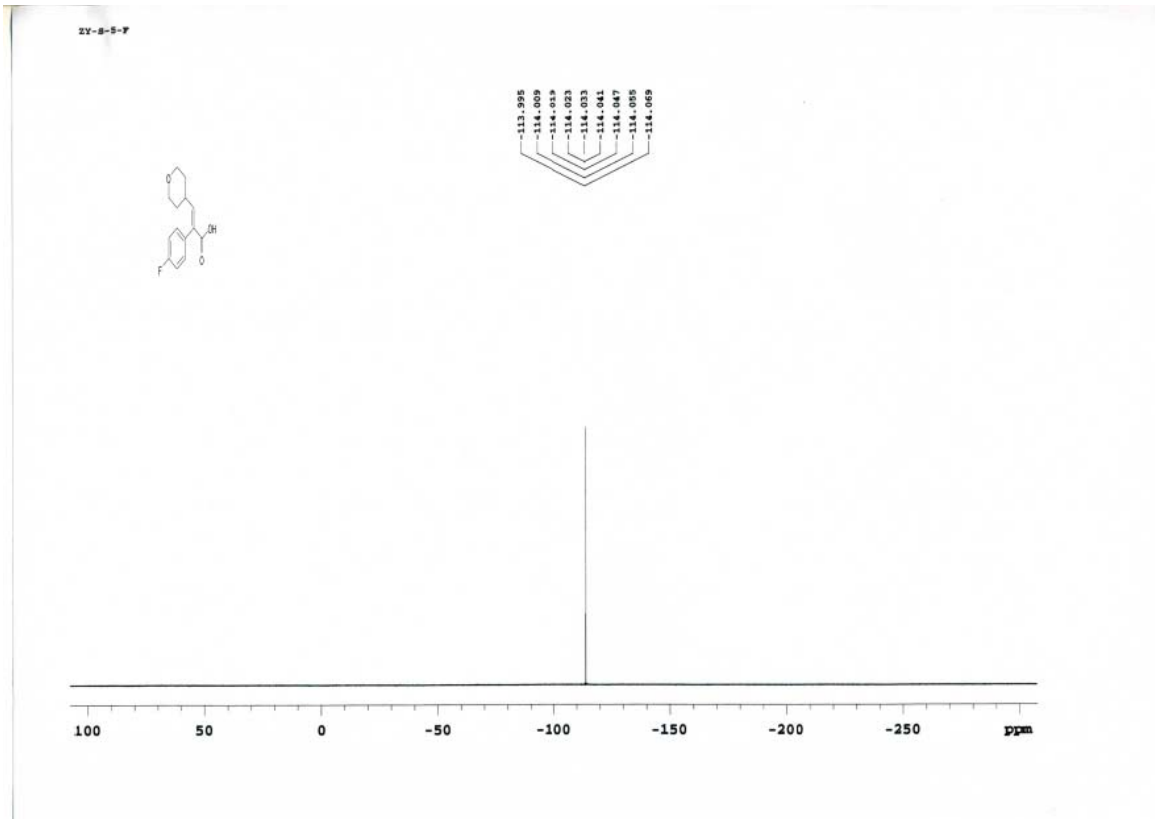

7.369
7.352
7.346
7.338
7.334
7.325
7.321
7.316
7.303
7.195
7.190
7.185
7.178
7.174
7.170
7.090
7.063
1.741
1.737
1.733
1.724
1.716
1.708
1.706
1.700
1.689
1.657
1.520
1.514
1.511
1.501
1.427
1.397
-0.000
OH
O
0.48
2.96
1.00
1.96
0.99
4.04
4.07
10
8
6
4
2
0
PPM
yxh-10-69-5h
USER: -- DATE: Jun 29 2009
F1: 400.037
F2: 100.598
SW1: 7022
OF1: 2690.9
PTS1d: 32768
EX: s2pul
PW: 4.4 usec
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - $ZY-S-12.fid


ZY-S-12
172.875
152.640
135.010
131.466
129.804
127.917
127.475
77.320
77.000
76.684
40.110
33.455
25.695
OH
O
260
240
220
200
180
160
140
120
100
80
60
40
20
0 ppm

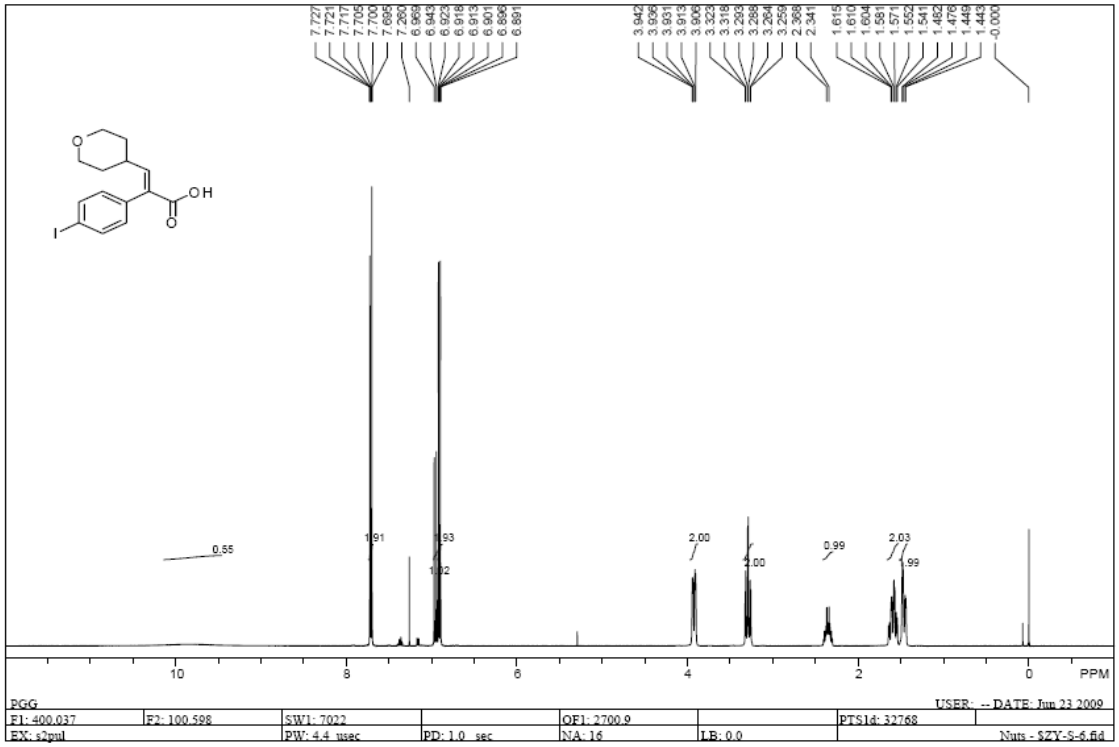
## Compound 1g

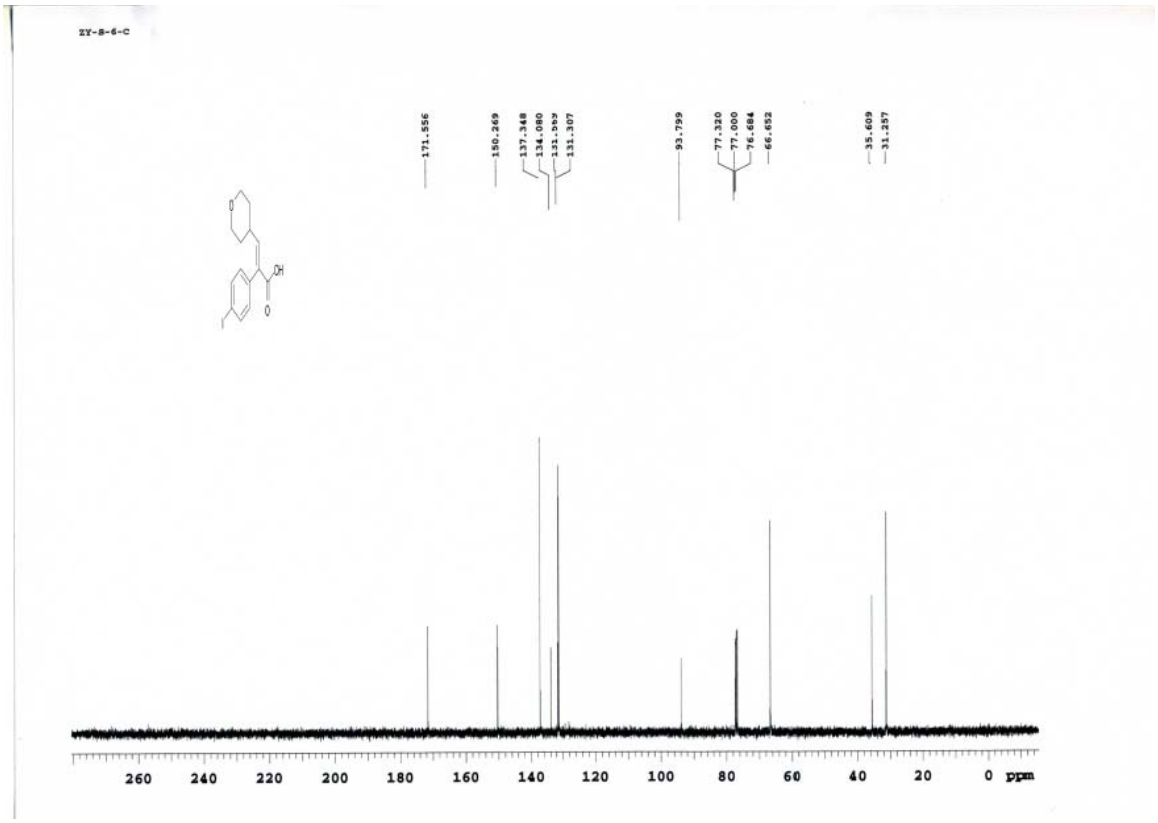

7.259
7.152
7.145
7.138
7.130
7.122
7.116
7.096
7.081
7.070
7.065
7.059
7.048
7.042
6.973
6.947
3.950
3.944
3.938
3.921
3.915
3.321
3.315
3.291
3.286
3.262
3.256
2.371
2.344
1.621
1.617
1.610
1.588
1.578
1.492
1.487
1.459
1.454
0.000
O
OH
O
F
0.76
2.01
1.01
1.00
2.02
2.00
10
8
6
4
2
0
PPM
PGG
USER: -- DATE: Jun 23 2009
F1: 400.037
F2: 100.598
SW1: 7022
OF1: 2700.9
PTS1d: 32768
EX: s2pul
PW: 4.4 usec
PD: 1.0 sec
NA: 12
LB: 0.0
Nuts - SZY-S-5.fid


ZY-S-5-C
171.900
163.511
161.055
150.139
131.615
131.180
131.068
130.472
130.441
115.326
115.109
77.316
77.000
76.680
66.688
35.591
31.261
260
240
220
200
180
160
140
120
100
80
60
40
20
0 ppm

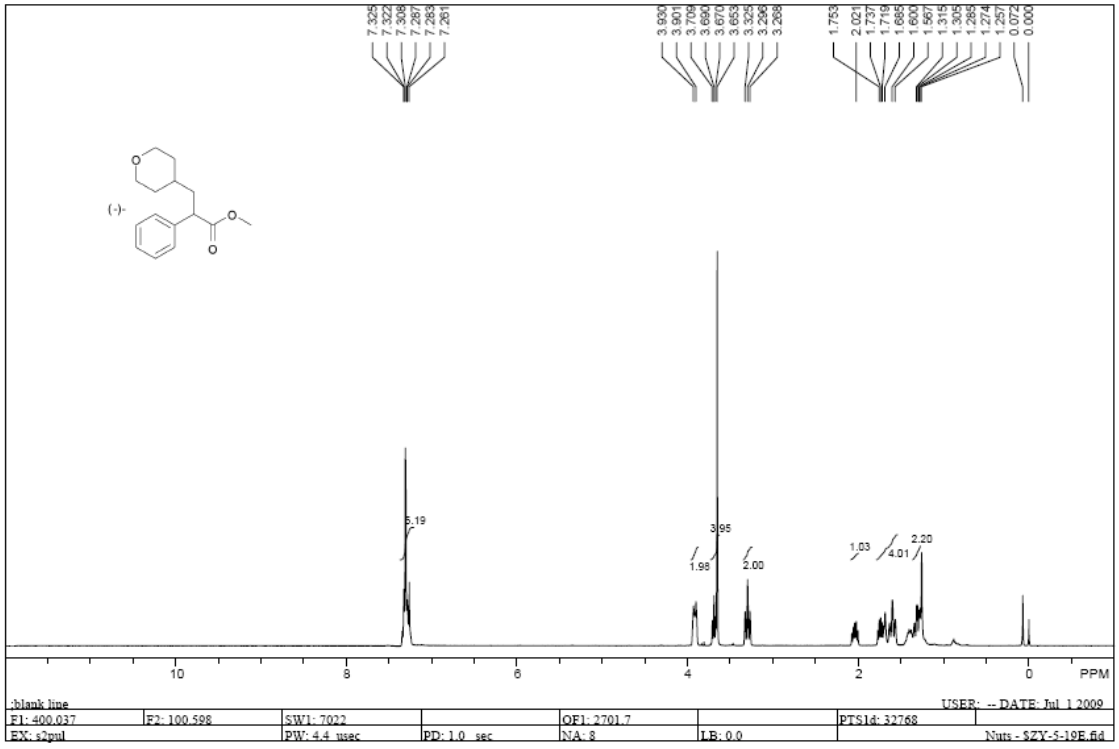

ZY-S-5-F
-113.995
-114.009
-114.019
-114.023
-114.033
-114.041
-114.047
-114.055
-114.069
100
50
0
-50
-100
-150
-200
-250
ppm

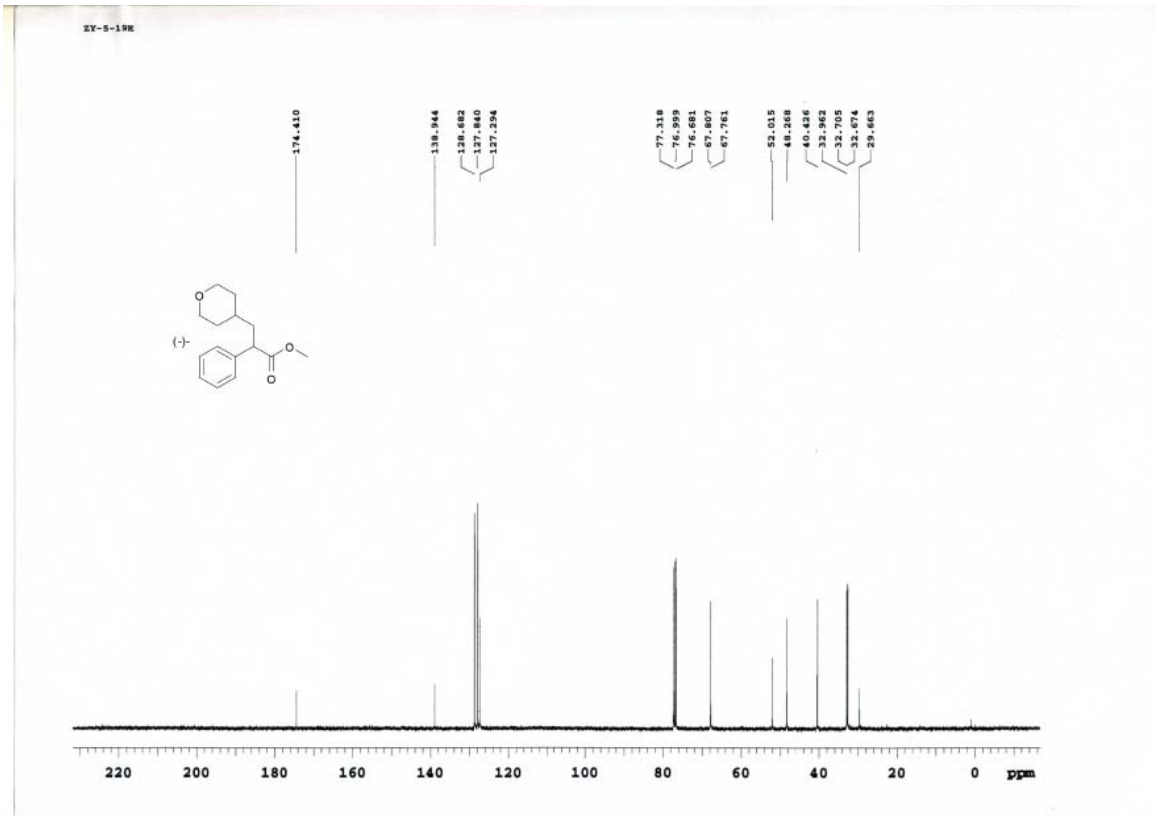
**Compound 1h**


7.727
7.721
7.717
7.705
7.700
7.695
7.260
6.969
6.943
6.923
6.918
6.913
6.901
6.896
6.891
3.942
3.936
3.931
3.913
3.906
3.323
3.318
3.293
3.288
3.264
3.259
3.238
2.341
1.615
1.610
1.604
1.581
1.571
1.562
1.541
1.482
1.476
1.449
1.443
-0.000
OH
O
I
0.55
1.91
1.93
1.02
2.00
2.00
0.99
2.03
1.99
10
8
6
4
2
0
PPM
PGG
USER: -- DATE: Jun 23 2009
F1: 400.037
F2: 100.598
SW1: 7022
OF1: 2700.9
PTS1d: 32768
EX: s2pul
PW: 4.4 usec
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - SZY-S-6.fid

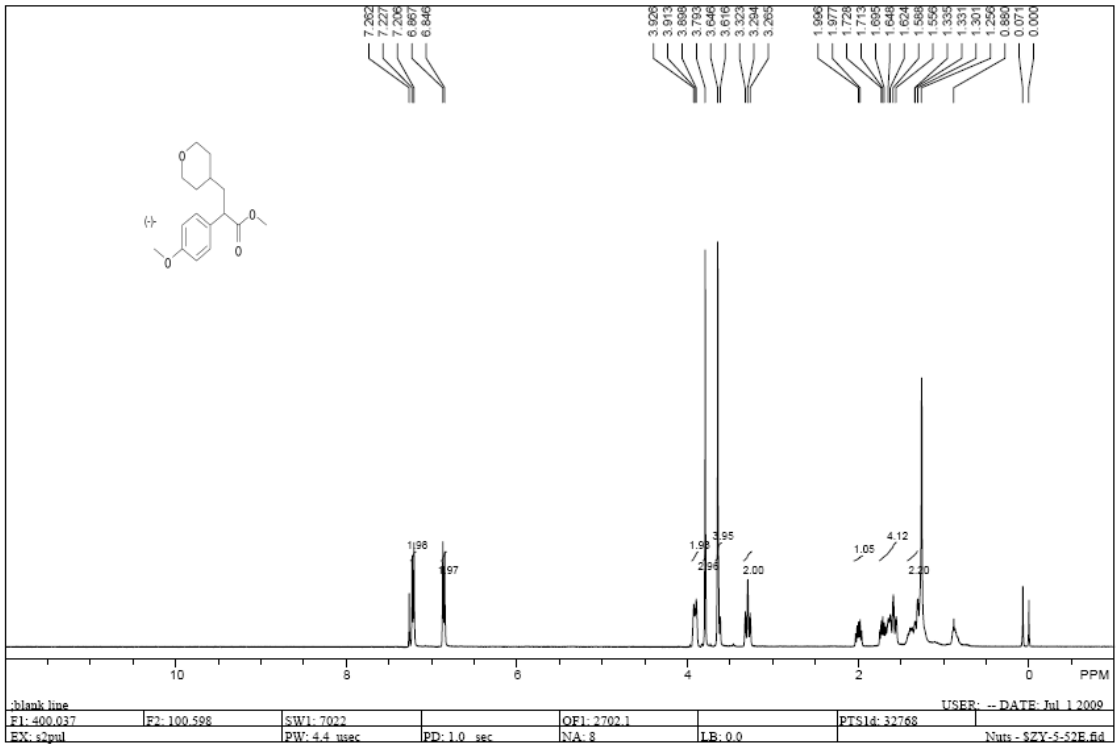

ZY-8-6-C
171.556
150.269
137.348
134.080
131.959
131.307
93.799
77.320
77.000
76.684
66.652
35.609
31.257
260
240
220
200
180
160
140
120
100
80
60
40
20
0 ppm

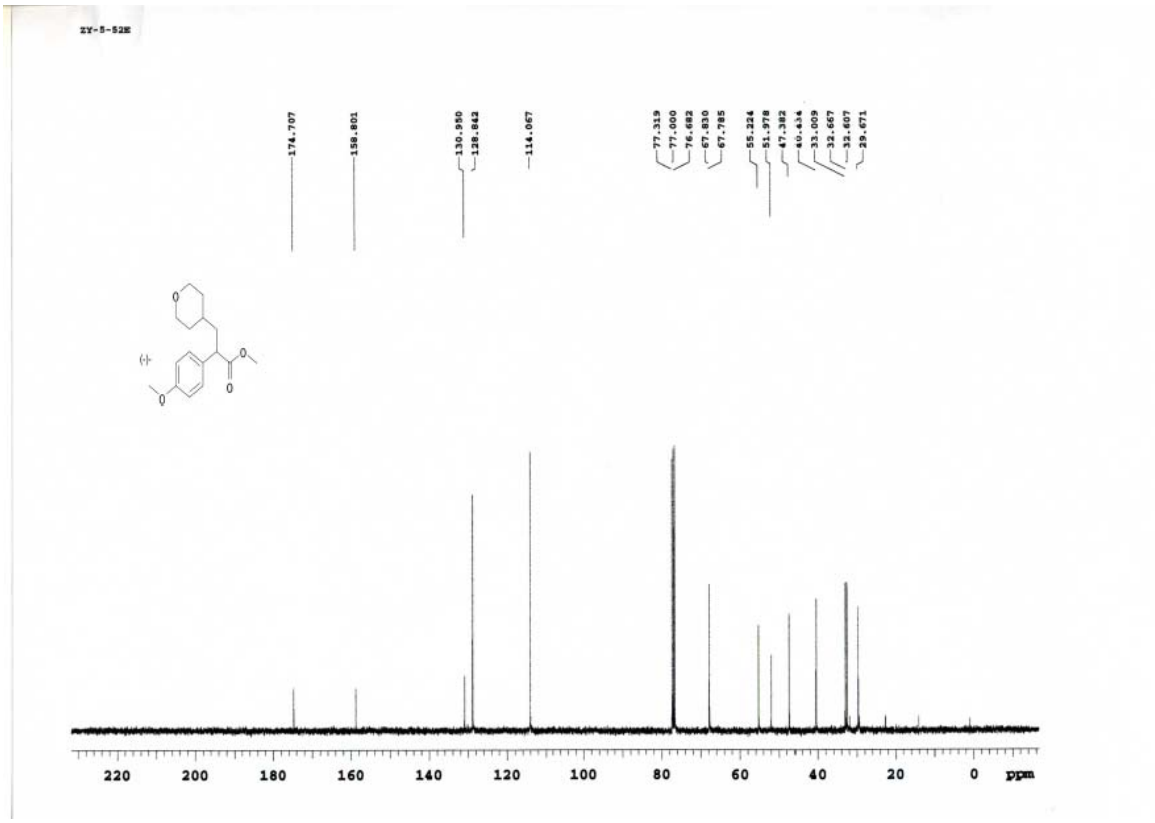
**Compound 3a**


7.325
7.322
7.308
7.287
7.283
7.261
3.930
3.901
3.709
3.690
3.670
3.653
3.325
3.296
3.268
1.753
2.021
1.737
1.719
1.685
1.600
1.567
1.315
1.305
1.285
1.274
1.257
0.072
0.000
(-)-
5.19
1.98
3.95
2.00
1.03
4.01
2.20
10
8
6
4
2
0
PPM
:blank line
USER: -- DATE: Jul 1 2009
F1: 400.037
F2: 100.598
SW1: 7022
OF1: 2701.7
PTS1d: 32768
EX: s2pul
PW: 4.4 usec
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - SZY-5-19E.fid

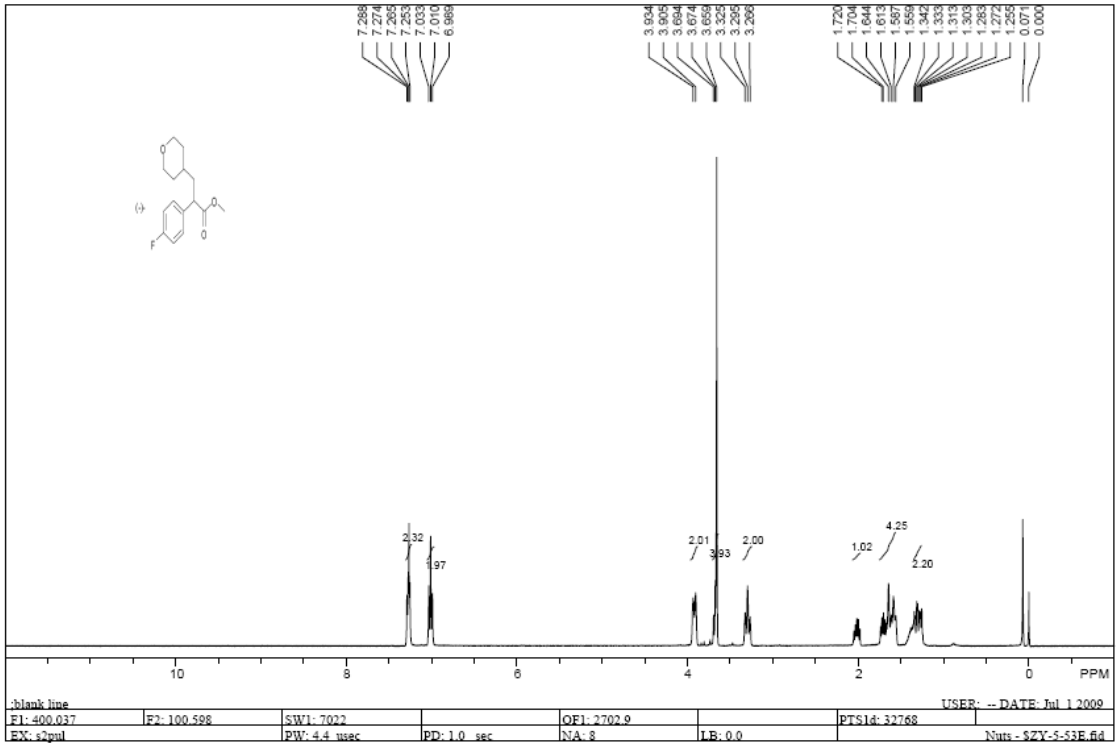

ZY-5-19E
174.410
138.944
128.682
127.840
127.294
77.318
76.999
76.681
67.807
67.761
52.015
48.268
40.426
32.962
32.705
32.674
29.663
(-)-
220
200
180
160
140
120
100
80
60
40
20
0
ppm

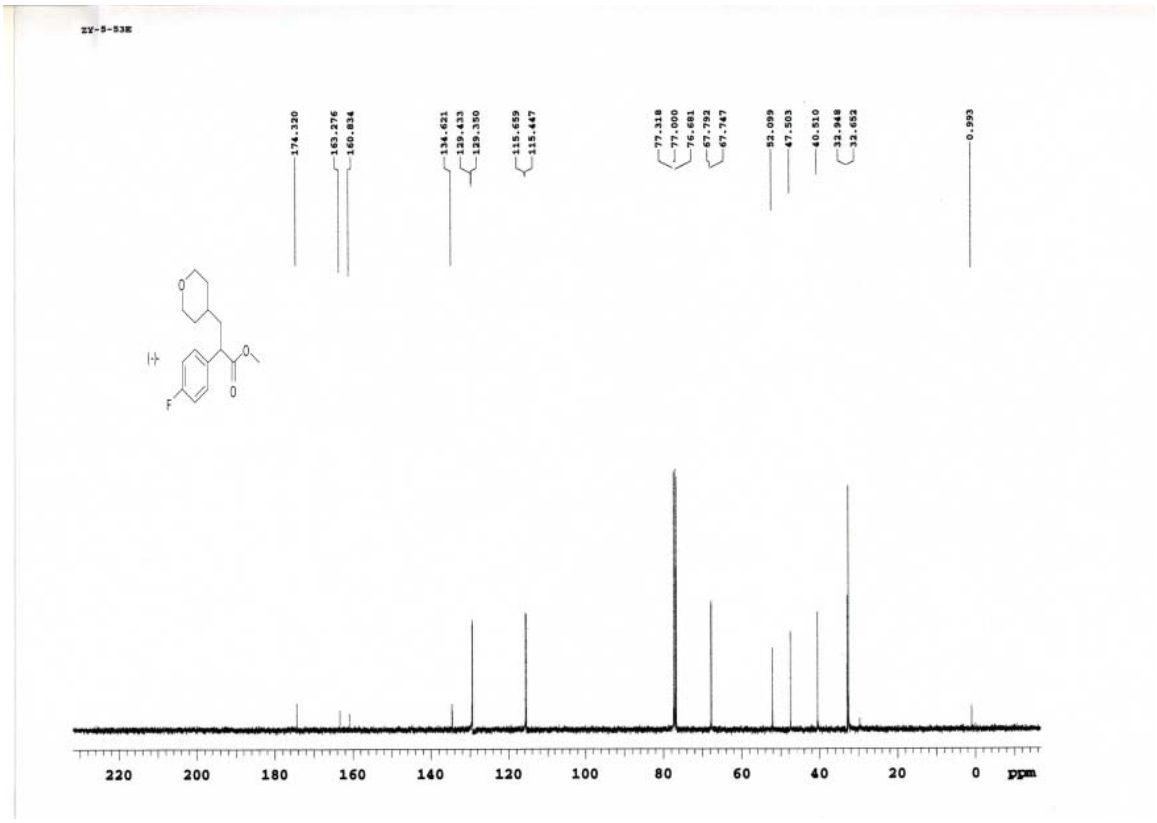
## Compound 3f

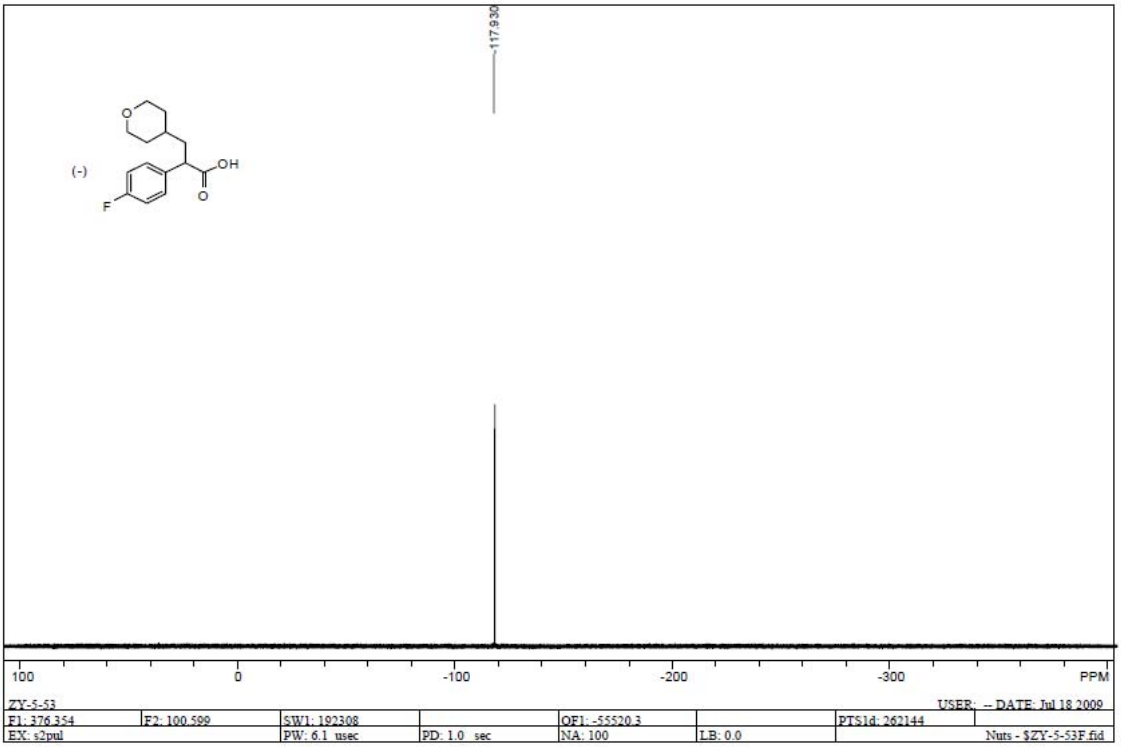

7.262
7.227
7.205
6.867
6.846
3.926
3.913
3.898
3.793
3.646
3.616
3.323
3.294
3.265
1.996
1.977
1.728
1.713
1.695
1.648
1.624
1.588
1.556
1.335
1.331
1.301
1.256
0.880
0.071
0.000
(-)-
1.96
1.97
1.98
2.96
3.95
2.00
1.05
4.12
2.20
10
8
6
4
2
0
PPM
:blank line
USER: -- DATE: Jul 1 2009
F1: 400.037
F2: 100.598
SW1: 7022
OF1: 2702.1
PTS1d: 32768
EX: s2pul
PW: 4.4 usec
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - SZY-5-52E.fid


ZY-5-52E
174.707
158.801
130.950
128.843
114.067
77.319
77.000
76.682
67.830
67.785
55.224
51.978
47.382
40.434
33.009
32.667
32.607
29.671
220
200
180
160
140
120
100
80
60
40
20
0
ppm

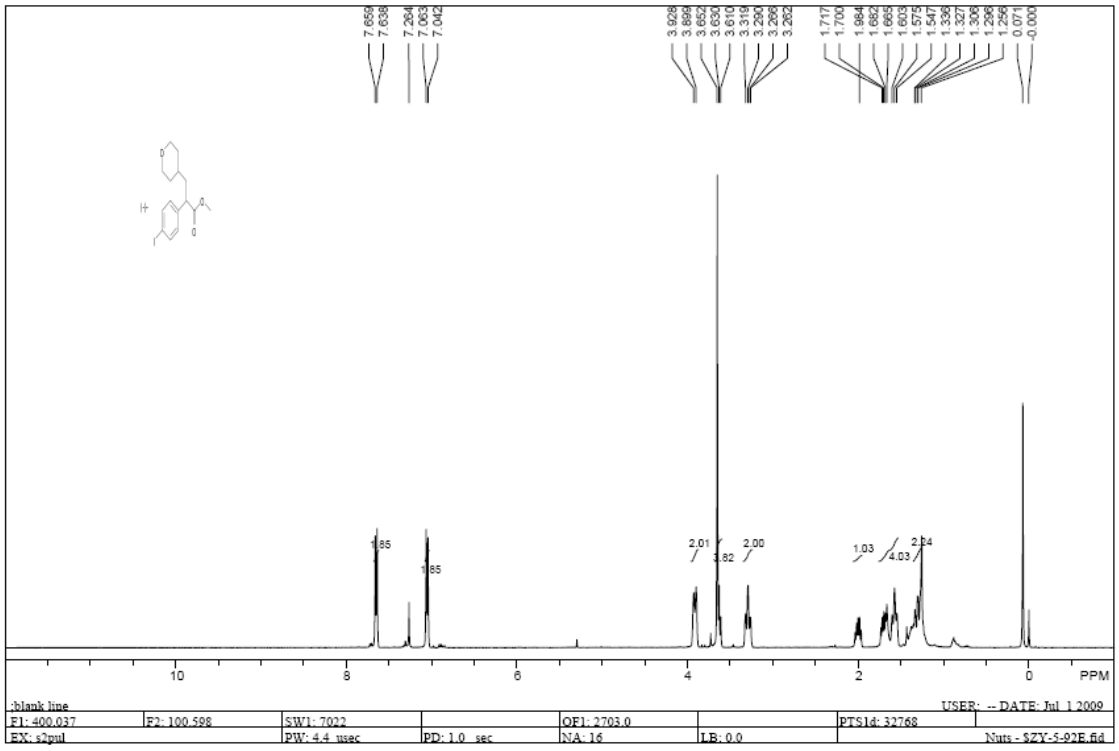
## Compound 3g

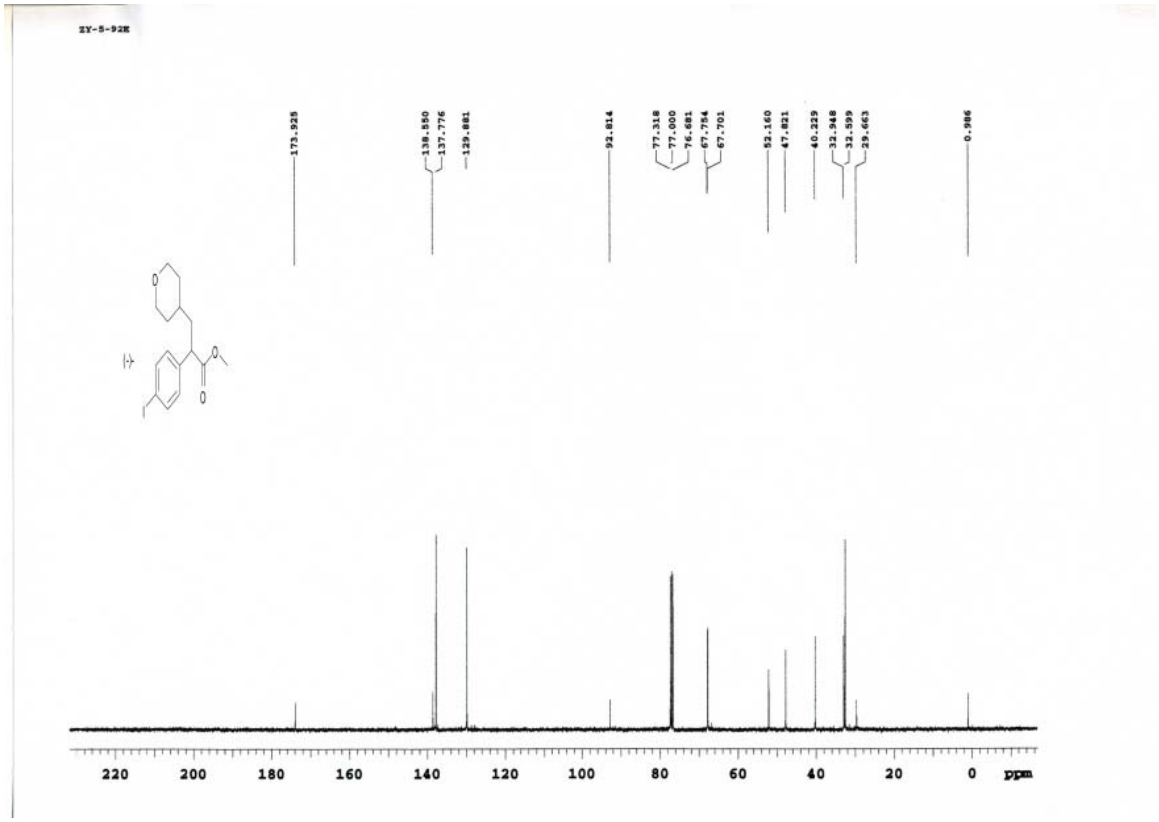

7.288
7.274
7.265
7.253
7.033
7.010
6.989
3.934
3.905
3.694
3.674
3.659
3.325
3.295
3.266
1.720
1.704
1.644
1.613
1.587
1.559
1.342
1.333
1.313
1.303
1.283
1.272
1.255
0.071
0.000
2.32
1.97
2.01
3.93
2.00
1.02
4.25
2.20
10
8
6
4
2
0
PPM
:blank line
USER: -- DATE: Jul 1 2009
F1: 400.037
F2: 100.598
SW1: 7022
OF1: 2702.9
PTS1d: 32768
EX: s2pul
PW: 4.4 usec
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - SZY-5-53E.fid


ZY-5-53E
174.320
163.276
160.034
134.621
130.433
129.350
115.659
115.447
77.318
77.000
76.681
67.792
67.747
52.099
47.503
40.510
32.948
32.652
0.993
(+)
F
O
O
O
220
200
180
160
140
120
100
80
60
40
20
0
ppm


117.930
(-)
F
OH
O
O
100
0
-100
-200
-300
PPM
ZY-5-53
USER: -- DATE: Jul 18 2009
F1: 376.354
F2: 100.599
SW1: 192308
OF1: -55520.3
PTS1d: 262144
EX: s2pul
PW: 6.1 usec
PD: 1.0 sec
NA: 100
LB: 0.0
Nuts - $ZY-5-53F.fid

## Compound 3h

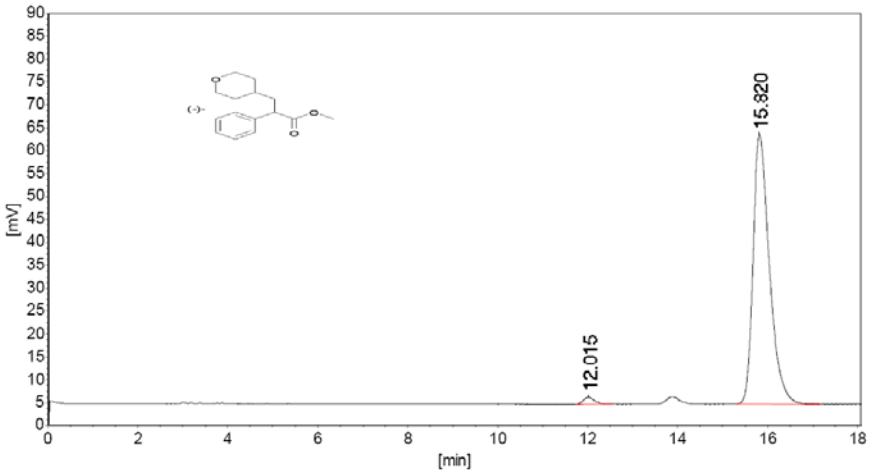

7.659
7.638
7.284
7.063
7.042
3.929
3.899
3.652
3.630
3.610
3.319
3.290
3.266
3.262
1.717
1.700
1.984
1.682
1.665
1.603
1.575
1.547
1.336
1.327
1.306
1.296
1.256
0.071
-0.000
1.85
1.85
2.01
3.82
2.00
1.03
4.03
2.24
10
8
6
4
2
0
PPM
blank line
USER: -- DATE: Jul 1 2009
F1: 400.037
F2: 100.598
SW1: 7022
OF1: 2703.0
PTS1d: 32768
EX: s2pul
PW: 4.4 usec
PD: 1.0 sec
NA: 16
LB: 0.0
Nuts - SZY-5-92E.fid


ZY-5-92E
173.925
139.550
137.776
129.881
92.614
77.318
77.000
76.681
67.754
67.701
52.160
47.821
40.229
32.948
32.599
29.663
0.986
220
200
180
160
140
120
100
80
60
40
20
0
ppm

# HPLC Chromatograms for the asymmetric hydrogenation reactions

## Reaction of 1a

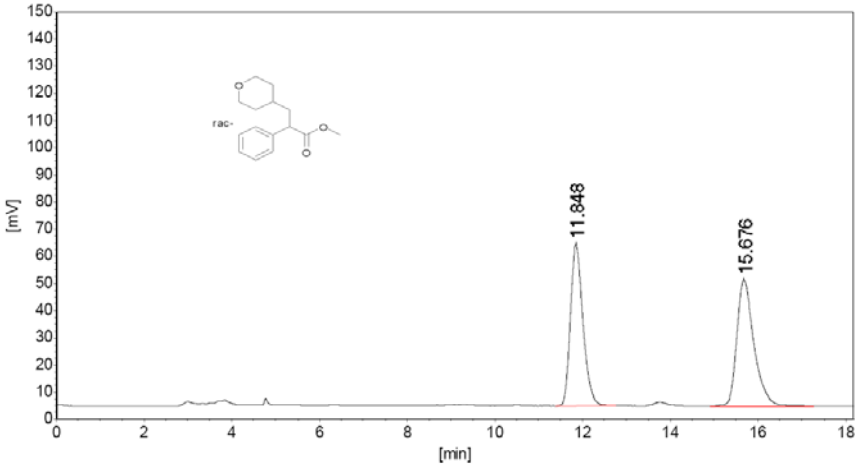
Notes:AD-H, 99:1, 1.0 mL/min, 230 nm




### General Results

| Nos. | Compound | R.Time | Height[uV] | Area[uV*S] | Area% | Conc. (%) | Type |
|---|---|---|---|---|---|---|---|
| 1 | | 12.015 | 1528 | 26514 | 1.75736 | 1.75736 | BB |
| 2 | | 15.820 | 58805 | 1482219 | 98.24264 | 98.24264 | BB |
| Total: | | | 60333 | 1508733 | 100.00000 | 100.00000 | |

Notes:AD-H, 99:1, 1.0 mL/min, 230 nm

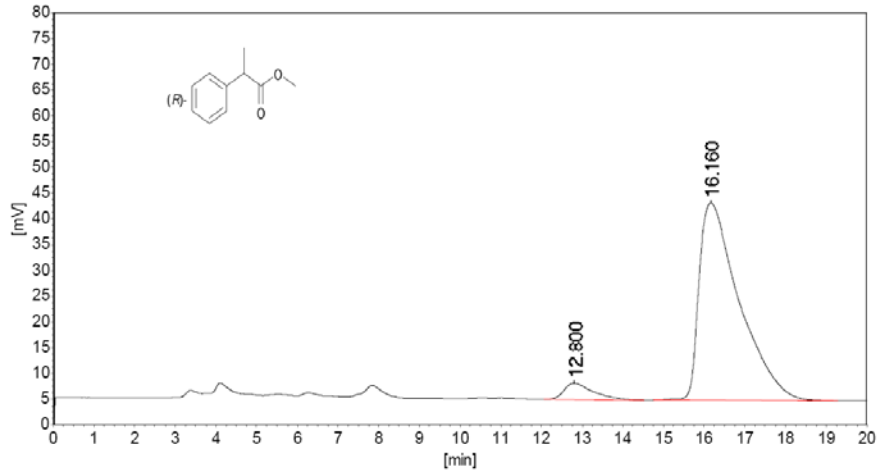



### General Results

| Nos. | Compound | R.Time | Height[uV] | Area[uV*S] | Area% | Conc. (%) | Type |
|---|---|---|---|---|---|---|---|
| 1 | | 11.848 | 59475 | 1197678 | 48.68448 | 48.68448 | BB |
| 2 | | 15.676 | 46377 | 1262403 | 51.31552 | 51.31552 | BB |
| Total: | | | 105852 | 2460081 | 100.00000 | 100.00000 | |

## Reaction of 1b

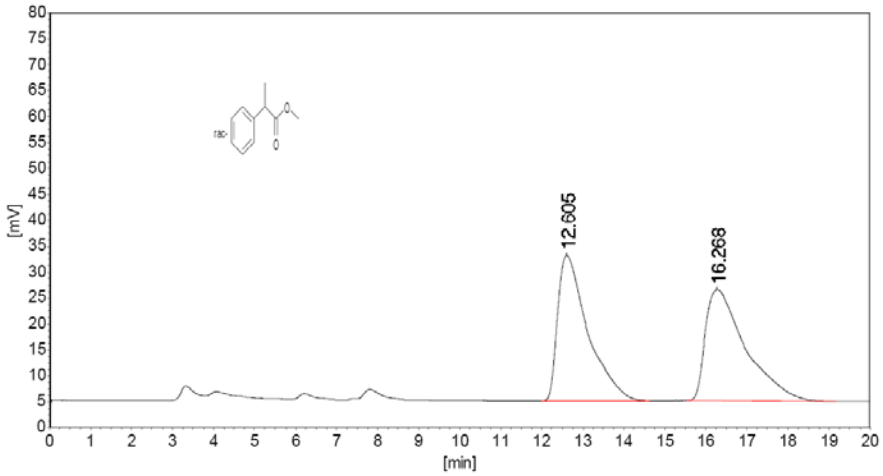
Notes:OJ, 99:1, 1.0 mL/min, 230 nm




**General Results**

| Nos. | Compound | R.Time | Height[uV] | Area[uV*S] | Area% | Type |
|---|---|---|---|---|---|---|
| 1 | | 12.800 | 3176 | 158492 | 5.69386 | BB |
| 2 | | 16.160 | 38230 | 2625064 | 94.30614 | BB |
| Total: | | | 41406 | 2783556 | 100.00000 | |

Notes:OJ, 99:1, 1.0 mL/min, 230 nm

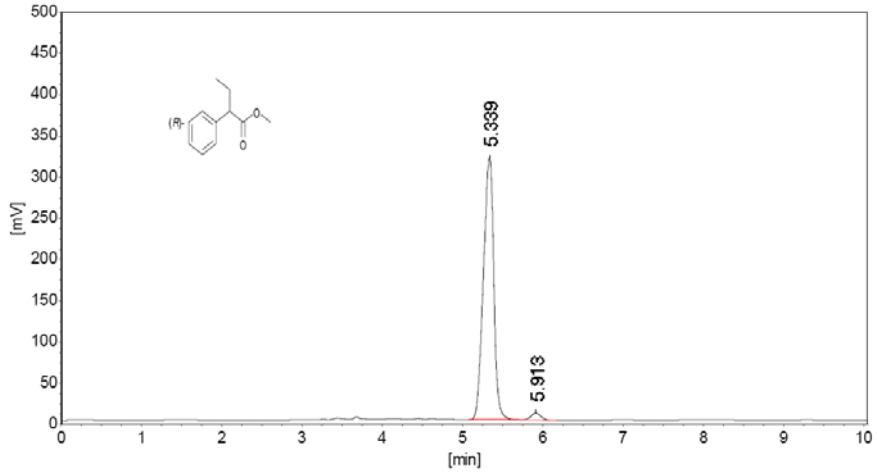



**General Results**

| Nos. | Compound | R.Time | Height[uV] | Area[uV*S] | Area% | Type |
|---|---|---|---|---|---|---|
| 1 | | 12.605 | 28013 | 1422835 | 49.55247 | BB |
| 2 | | 16.268 | 21362 | 1448536 | 50.44753 | BB |
| Total: | | | 49375 | 2871371 | 100.00000 | |

## Reaction of 1c

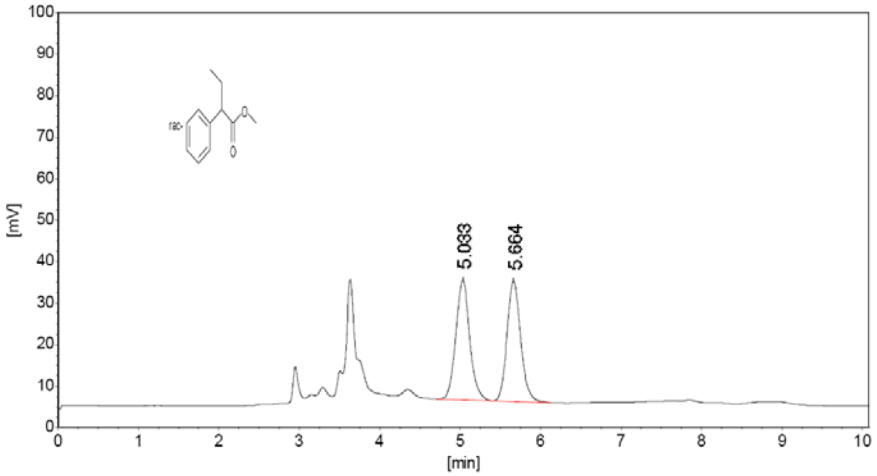
Notes:OD-H, 99:1, 1.0 mL/min, 230 nm




**General Results**

| Nos. | Compound | R.Time | Height[uV] | Area[uV*S] | Area% | Conc.(%) | Type |
|---|---|---|---|---|---|---|---|
| 1 | | 5.339 | 317946 | 2888718 | 97.41819 | 97.41819 | BB |
| 2 | | 5.913 | 8918 | 76558 | 2.58181 | 2.58181 | BB |
| Total: | | | 326864 | 2965276 | 100.00000 | 100.00000 | |

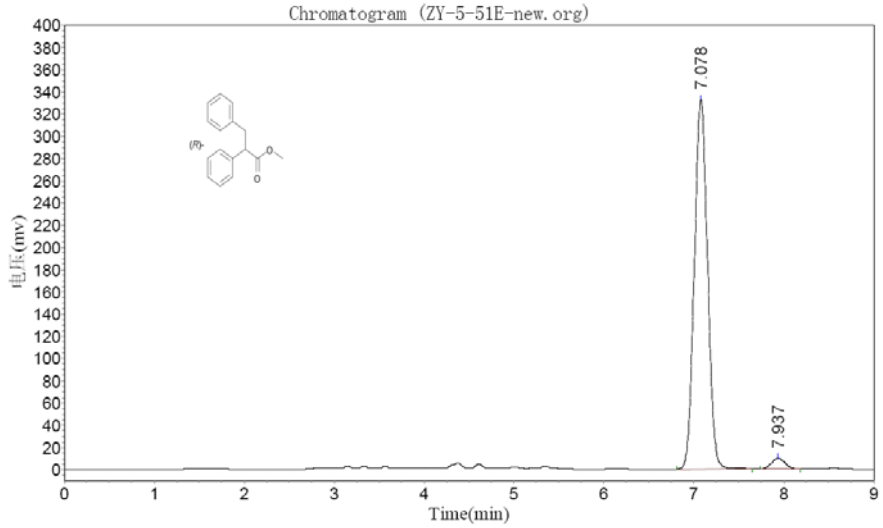
Notes:OD-H, 99:1, 1.0 mL/min, 230 nm




General Results

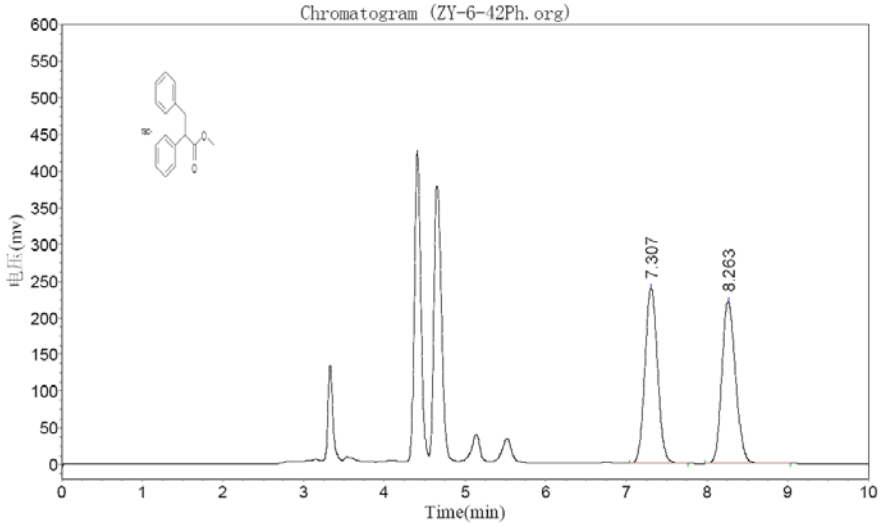
| Nos. | Compound | R.Time | Height[uV] | Area[uV*S] | Area% | Conc.(%) | Type |
|---|---|---|---|---|---|---|---|
| 1 | | 5.033 | 28800 | 346976 | 50.43784 | 50.43784 | BB |
| 2 | | 5.664 | 28979 | 340952 | 49.56216 | 49.56216 | BB |
| Total: | | | 57779 | 687928 | 100.00000 | 100.00000 | |

## Reaction of 1d




**Results**

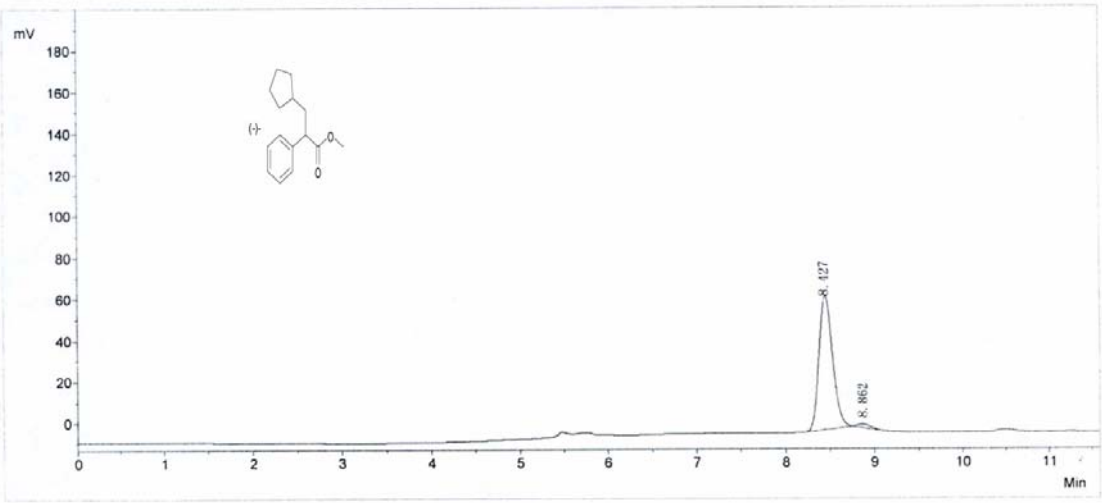
| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|---|---|---|---|---|---|
| 1 | | 7.078 | 332953.813 | 3402421.250 | 97.0954 |
| 2 | | 7.937 | 9867.821 | 101784.297 | 2.9046 |
| Total | | | 342821.634 | 3504205.547 | 100.0000 |



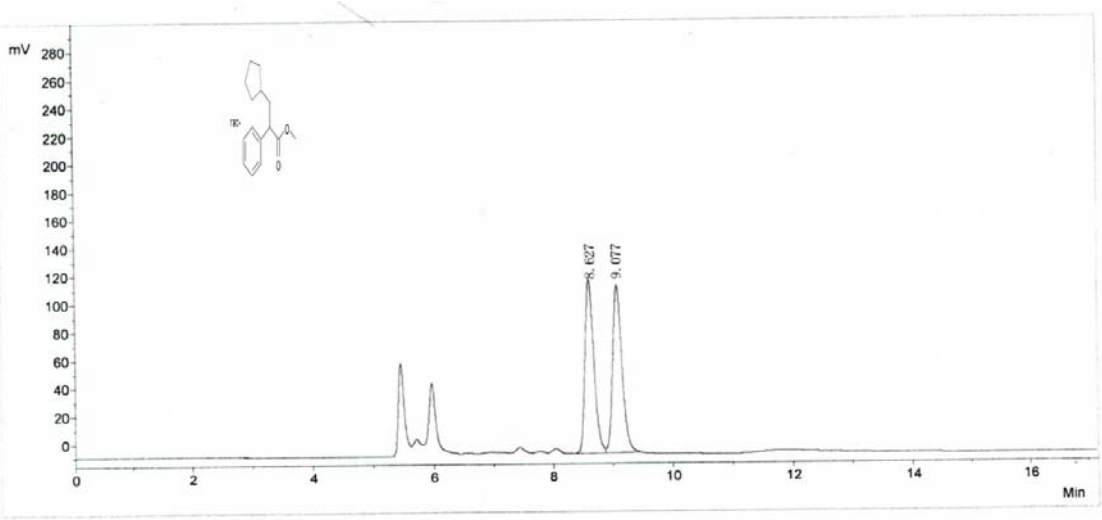

**Results**

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|---|---|---|---|---|---|
| 1 | | 7.307 | 239132.984 | 2610626.000 | 49.8525 |
| 2 | | 8.263 | 220567.641 | 2626079.250 | 50.1475 |
| Total | | | 459700.625 | 5236705.250 | 100.0000 |

## Reaction of 1e



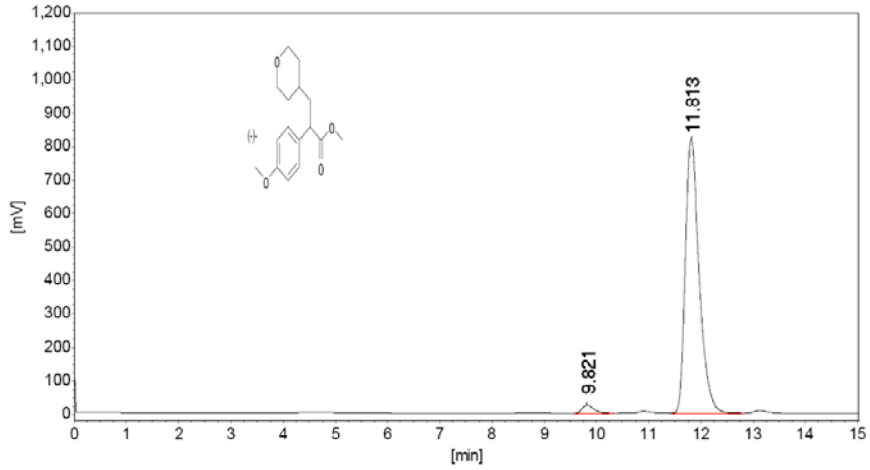

| No. | PeakNo | R.Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|
| 1 | 1 | 8.427 | 61734.6 | 688286.7 | 97.7256 |
| 2 | 2 | 8.862 | 1657.8 | 16018.7 | 2.2744 |
| Total | | | 63392.3 | 704305.4 | 100.0000 |




| No. | PeakNo | R.Time | PeakHeight | PeakArea | PerCent |
|---|---|---|---|---|---|
| 1 | 1 | 8.627 | 120107.0 | 1287527.6 | 49.8823 |
| 2 | 2 | 9.077 | 119461.8 | 1293604.0 | 50.1177 |
| Total | | | 239568.8 | 2581131.5 | 100.0000 |

## Reaction of 1f

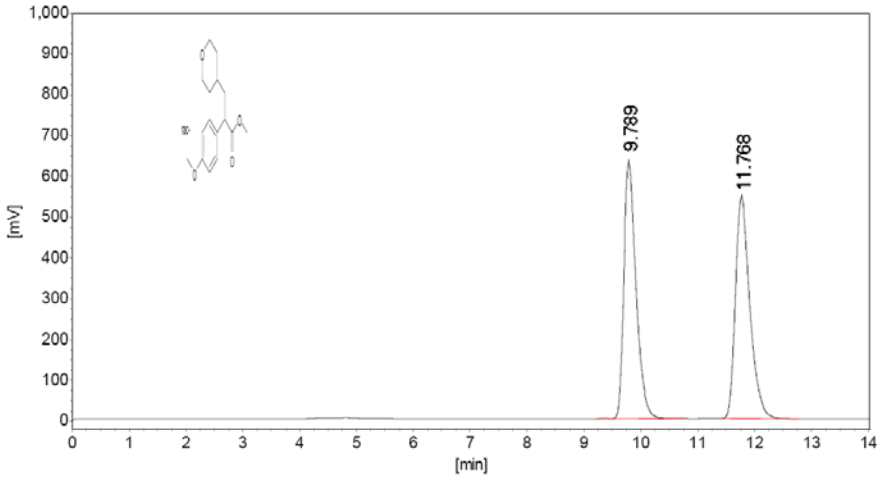
Notes:AD-H, 92:8, 0.7 mL/min, 230 nm




**General Results**

| Nos. | Compound | R.Time | Height[uV] | Area[uV*S] | Area% | Type |
|---|---|---|---|---|---|---|
| 1 | | 9.821 | 25241 | 363686 | 2.36019 | BB |
| 2 | | 11.813 | 819035 | 15045487 | 97.63981 | BB |
| Total: | | | 844276 | 15409173 | 100.00000 | |

Notes:AD-H, 92:8, 0.7 mL/min, 230 nm

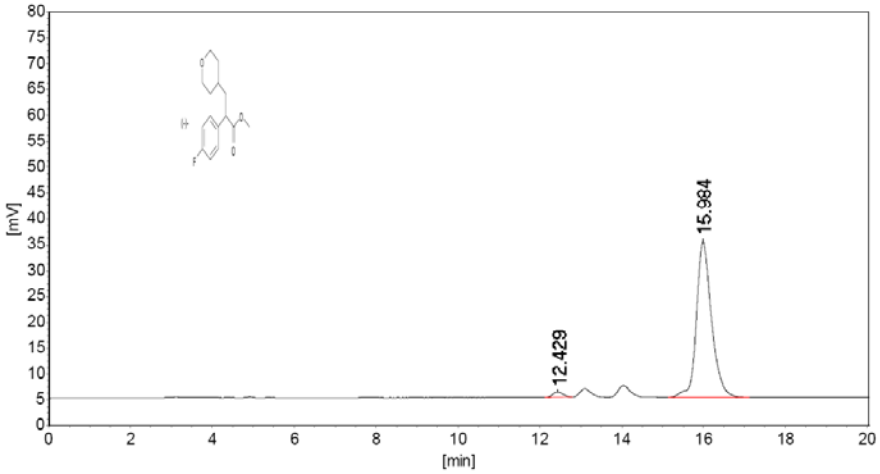



**General Results**

| Nos. | Compound | R.Time | Height[uV] | Area[uV*S] | Area% | Type |
|---|---|---|---|---|---|---|
| 1 | | 9.789 | 627888 | 9394519 | 49.26728 | BB |
| 2 | | 11.768 | 544496 | 9673955 | 50.73272 | BB |
| Total: | | | 1172384 | 19068474 | 100.00000 | |

## Reaction of 1g

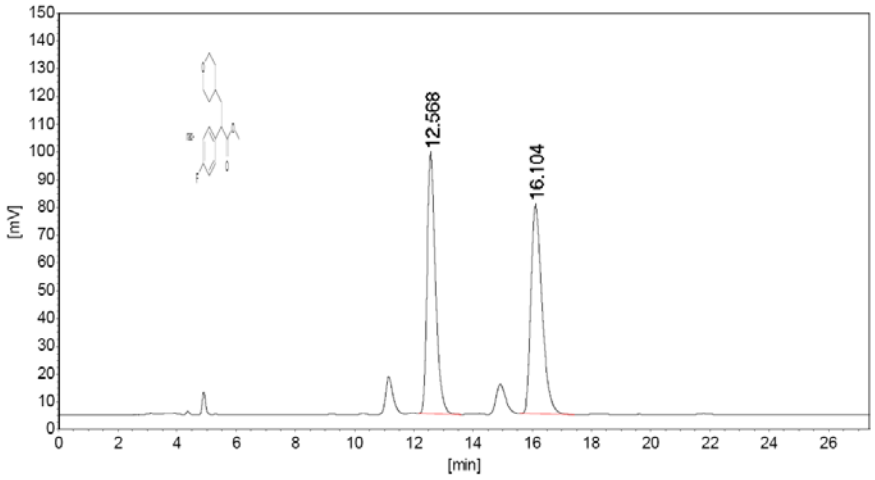
Notes:AD-H, 99:1, 1.0 mL/min, 230 nm




### General Results

| Nos. | Compound | R.Time | Height[uV] | Area[uV*S] | Area% | Type |
|---|---|---|---|---|---|---|
| 1 | | 12.429 | 1018 | 17583 | 2.22281 | BB |
| 2 | | 15.984 | 30181 | 773462 | 97.77719 | BB |
| Total: | | | 31199 | 791045 | 100.00000 | |

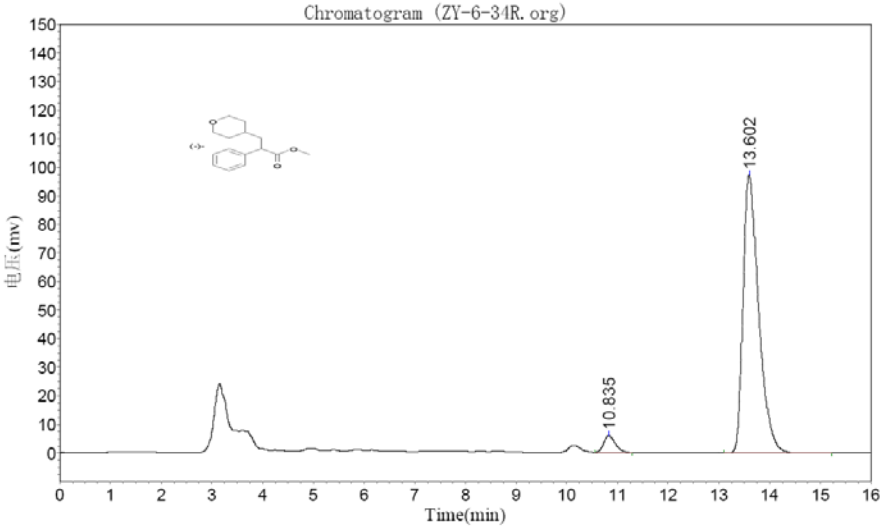
Notes:AD-H, 99:1, 1.0 mL/min, 230 nm




### General Results

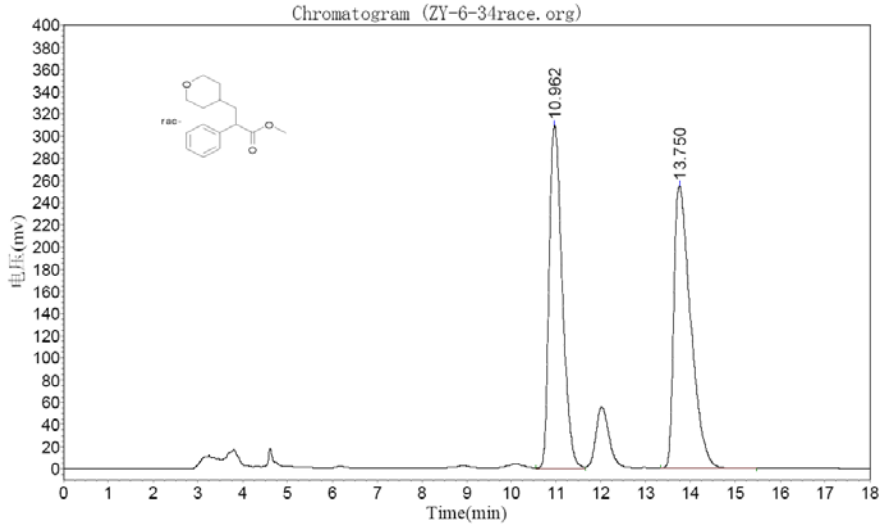
| Nos. | Compound | R.Time | Height[uV] | Area[uV*S] | Area% | Type |
|---|---|---|---|---|---|---|
| 1 | | 12.568 | 93315 | 1854932 | 48.93168 | BB |
| 2 | | 16.104 | 74691 | 1935930 | 51.06832 | BB |
| Total: | | | 168006 | 3790862 | 100.00000 | |

## Reaction of 1h




**Results**

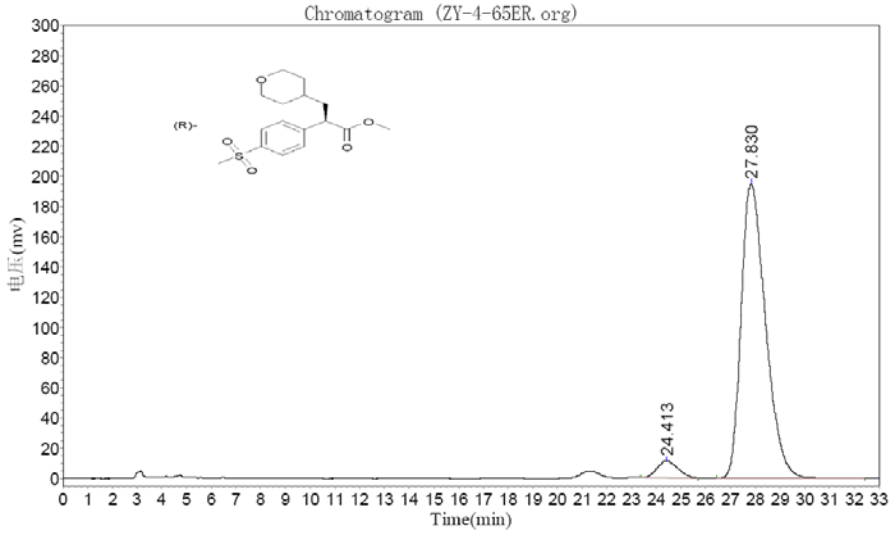
| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|---|---|---|---|---|---|
| 1 | | 10.835 | 5994.114 | 93924.797 | 4.3097 |
| 2 | | 13.602 | 97307.961 | 2085458.125 | 95.6903 |
| Total | | | 103302.075 | 2179382.922 | 100.0000 |




**Results**

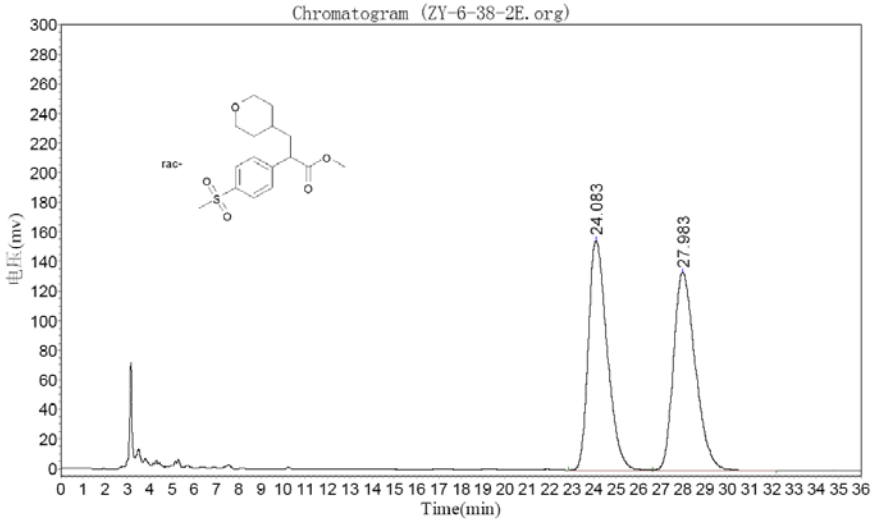
| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|---|---|---|---|---|---|
| 1 | | 10.962 | 309558.438 | 6258053.500 | 48.6340 |
| 2 | | 13.750 | 255178.297 | 6609609.500 | 51.3660 |
| Total | | | 564736.734 | 12867663.000 | 100.0000 |

## Reaction of 1i




**Results**

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|---|---|---|---|---|---|
| 1 | | 24.413 | 10977.248 | 625055.313 | 4.4857 |
| 2 | | 27.830 | 195013.750 | 13309214.000 | 95.5143 |
| Total | | | 205990.998 | 13934269.312 | 100.0000 |

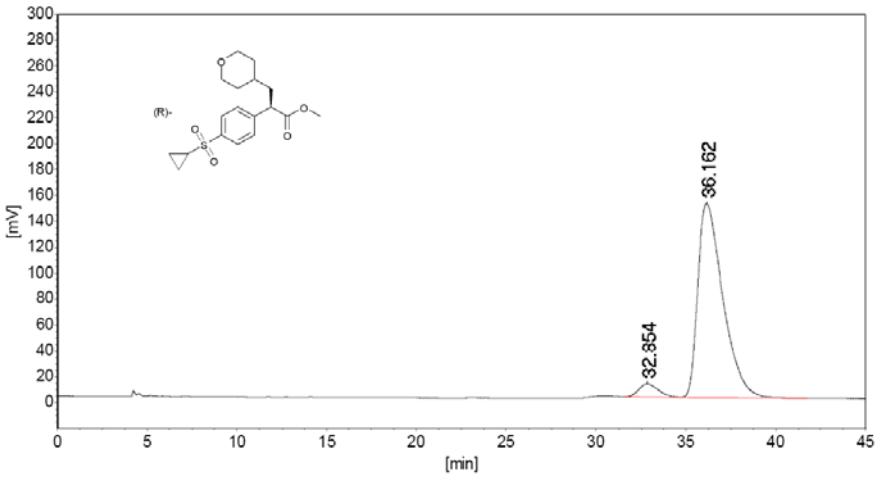



**Results**

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|---|---|---|---|---|---|
| 1 | | 24.083 | 155066.469 | 9099944.000 | 49.9911 |
| 2 | | 27.983 | 133297.188 | 9103187.000 | 50.0089 |
| Total | | | 288363.656 | 18203131.000 | 100.0000 |

## Reaction of 1j

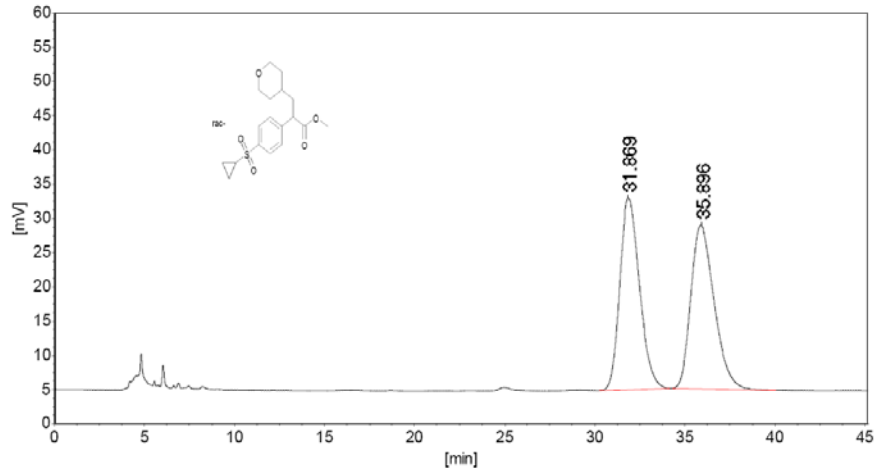
Notes:OD-H(New), 80:20, 0.7 mL/min, 230 nm




### General Results

| Nos. | Compound | R.Time | Height[uV] | Area[uV*S] | Area% | Conc.(%) | Type |
|---|---|---|---|---|---|---|---|
| 1 | | 32.854 | 10150 | 777317 | 5.08358 | 5.08358 | BB |
| 2 | | 36.162 | 149602 | 14513427 | 94.91642 | 94.91642 | BB |
| Total: | | | 159752 | 15290744 | 100.00000 | 100.00000 | |

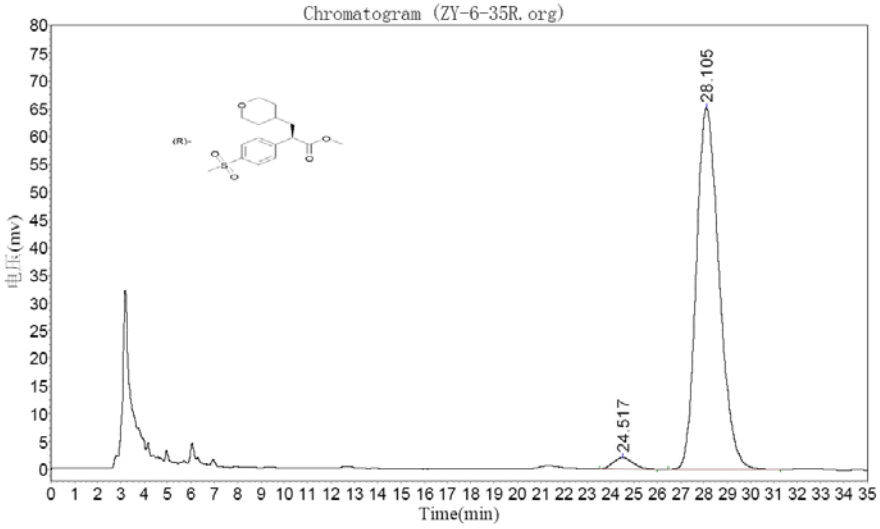
Notes:OD-H(New), 80:20, 0.7 mL/min, 230 nm




### General Results

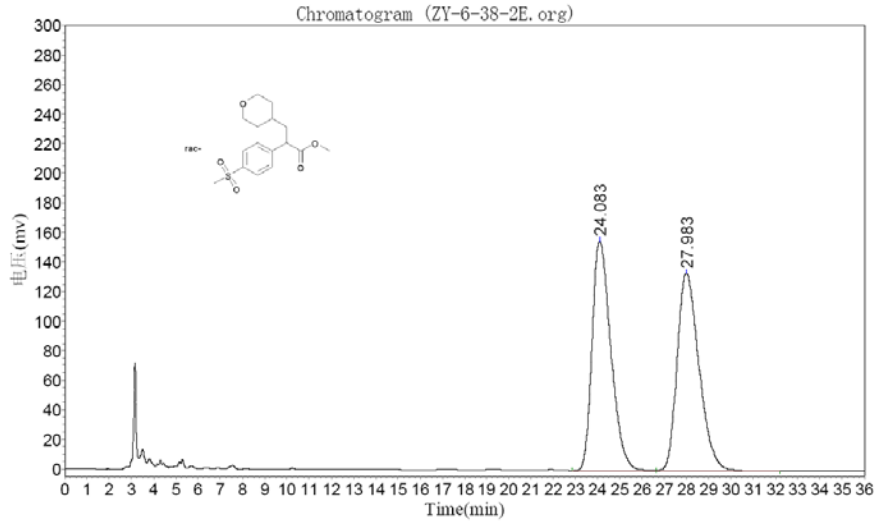
| Nos. | Compound | R.Time | Height[uV] | Area[uV*S] | Area% | Conc.(%) | Type |
|---|---|---|---|---|---|---|---|
| 1 | | 31.869 | 28013 | 2123052 | 49.65721 | 49.65721 | BB |
| 2 | | 35.896 | 23937 | 2152363 | 50.34279 | 50.34279 | BB |
| Total: | | | 51950 | 4275415 | 100.00000 | 100.00000 | |

## Reaction of 1k




**Results**

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|---|---|---|---|---|---|
| 1 | | 24.517 | 2097.542 | 122911.805 | 2.6956 |
| 2 | | 28.105 | 65150.445 | 4436835.500 | 97.3044 |
| Total | | | 67247.987 | 4559747.305 | 100.0000 |

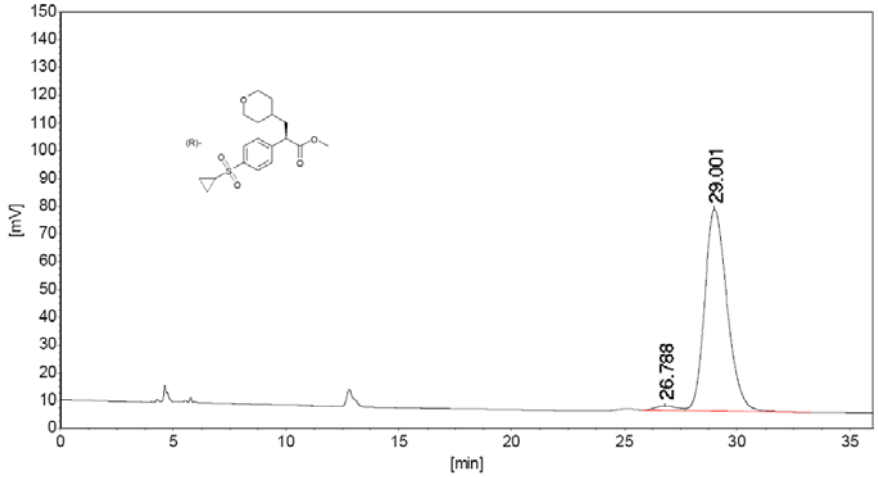



**Results**

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|---|---|---|---|---|---|
| 1 | | 24.083 | 155066.469 | 9099944.000 | 49.9911 |
| 2 | | 27.983 | 133297.188 | 9103187.000 | 50.0089 |
| Total | | | 288363.656 | 18203131.000 | 100.0000 |

## Reaction of 1l

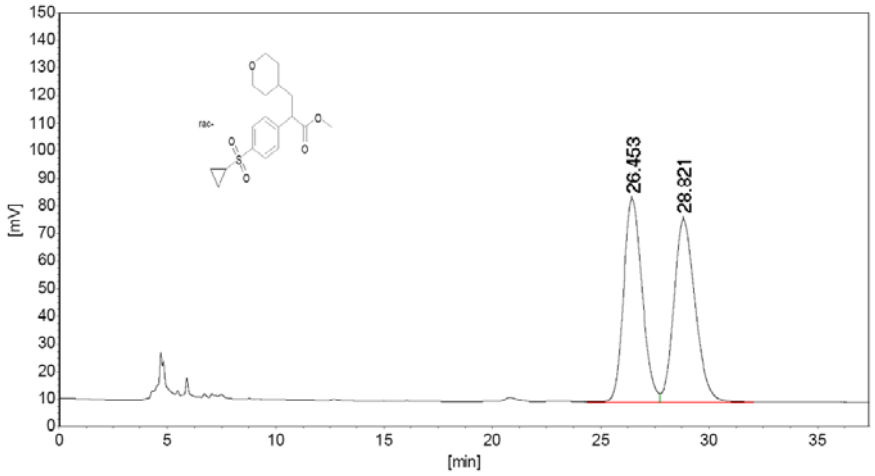
Notes:OD-H, 80:20, 0.7 mL/min, 230 nm




### General Results

| Nos. | Compound | R.Time | Height[uV] | Area[uV*S] | Area% | Type |
|---|---|---|---|---|---|---|
| 1 | | 26.788 | 1622 | 102639 | 2.01144 | BV |
| 2 | | 29.001 | 72449 | 5000111 | 97.98856 | VB |
| Total: | | | 74071 | 5102750 | 100.00000 | |

Notes:OD-H, 80:20, 0.7 mL/min, 230 nm




### General Results

| Nos. | Compound | R.Time | Height[uV] | Area[uV*S] | Area% | Type |
|---|---|---|---|---|---|---|
| 1 | | 26.453 | 73416 | 4350209 | 49.19520 | BV |
| 2 | | 28.821 | 66124 | 4492542 | 50.80480 | VB |
| Total: | | | 139540 | 8842751 | 100.00000 | |