Supporting Information

Multifunctional Chiral Phosphines-Catalyzed Highly Diastereoselective and Enantioselective Substitution of Morita-Baylis-Hillman Adducts with Oxazolones

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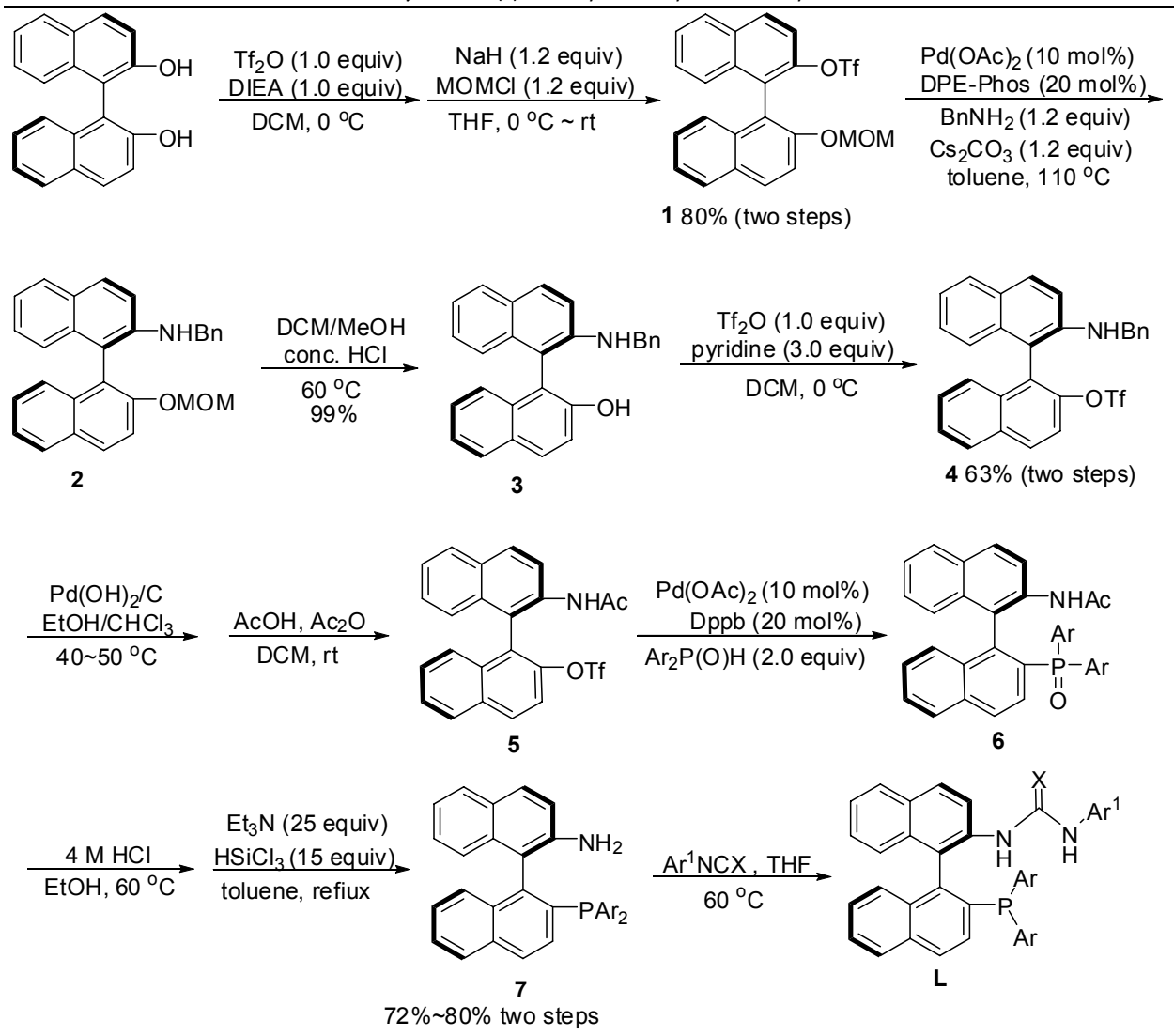
CONTENTS

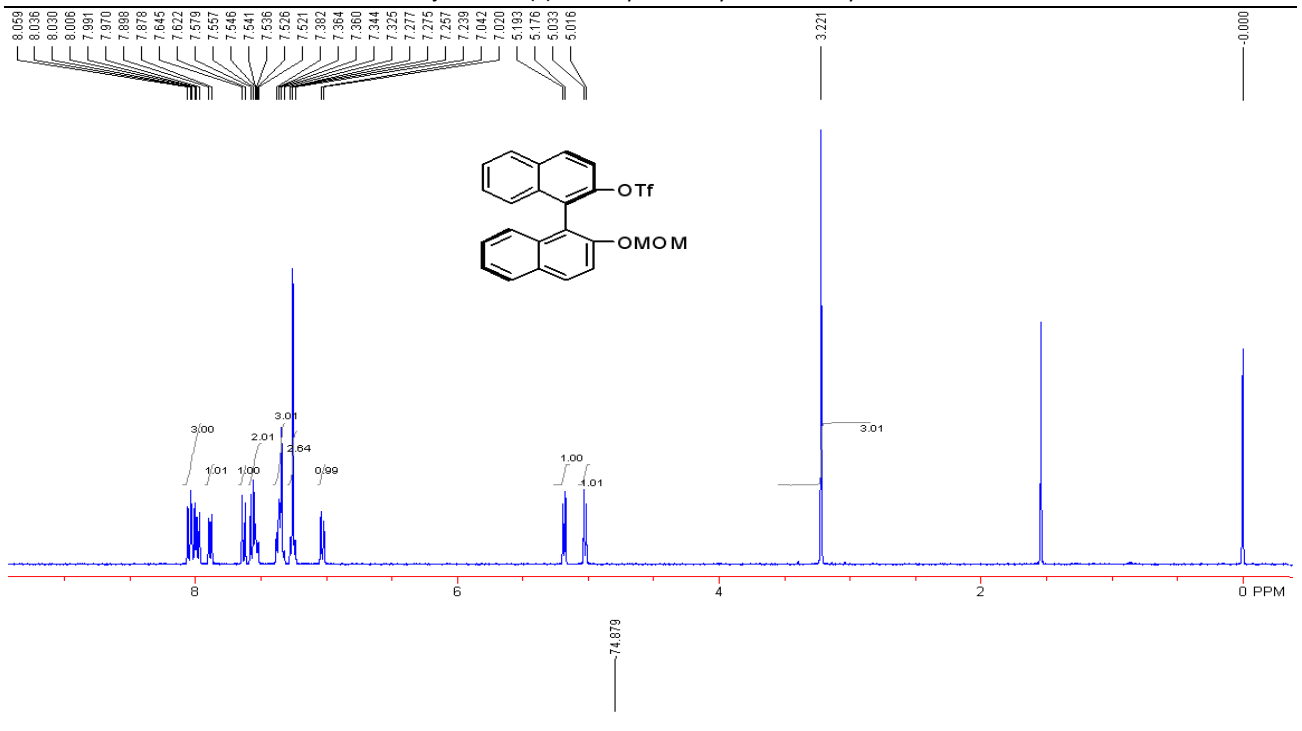
General Remarks: ^{1}H NMR spectra were recorded on a Bruker AM-300 or AM-400 spectrometer for solution in CDCl3 with tetramethylsilane (TMS) as internal standard; J-values are in Hz. Mass spectra were recorded with a HP-5989 instrument. All of the compounds reported in this paper gave satisfactory HRMS analytic data. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer-341 MC digital polarimeter; $[\alpha]_D$-values are given in unit of 10 deg^{-1} cm^2 g^{-1}. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Chiral HPLC was performed on a SHIMADZU SPD-10A vp series with chiral columns (Chiralpak AD-H, IC-H columns 4.6 × 250 mm, (Daicel Chemical Ind., Ltd.)). THF, toluene and Et_2O were distilled from sodium (Na) under argon (Ar) atmosphere. CH_3CN, 1,2-dichloroethane and dichloromethane were distilled from CaH_2 under argon (Ar) atmosphere.Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure. All the oxazolones were prepared according to the literature.[1]

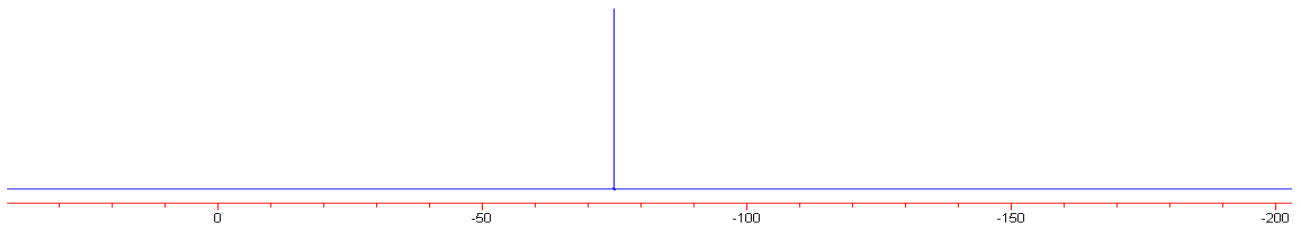
Reaction Procedure for the Preparation of Catalysts: Reaction procedure for the preparation of (*R*)-1-argio-3-(2'-(diargiophosphino)-1,1'-binaphthyl-2-yl)thiourea.



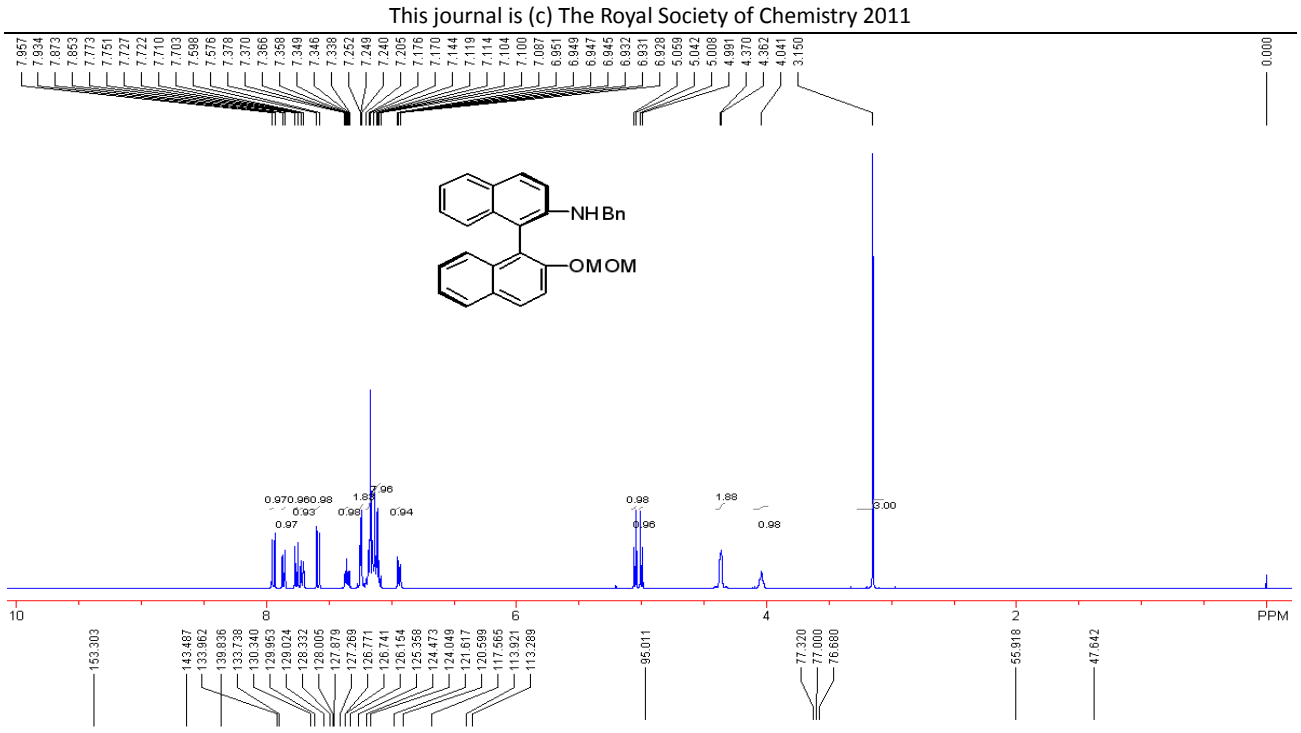
L1: X = S; Ar^1 = 3,5-$(CH_3)_2C_6H_3$; Ar = C_6H_5
L2: X = S; Ar^1 = 3,5-$(CH_3)_2C_6H_3$; Ar = $CH_2C_6H_5$
L3: X = O; Ar^1 = C_6H_5; Ar = C_6H_5
L4: X = S; Ar^1 = 3,5-$(CH_3)_2C_6H_3$; Ar = 3,5-$(CF_3)_2C_6H_3$
L6: X = S; Ar^1 = 3,5-$(CH_3O)_2C_6H_3$; Ar = $CH_2C_6H_5$

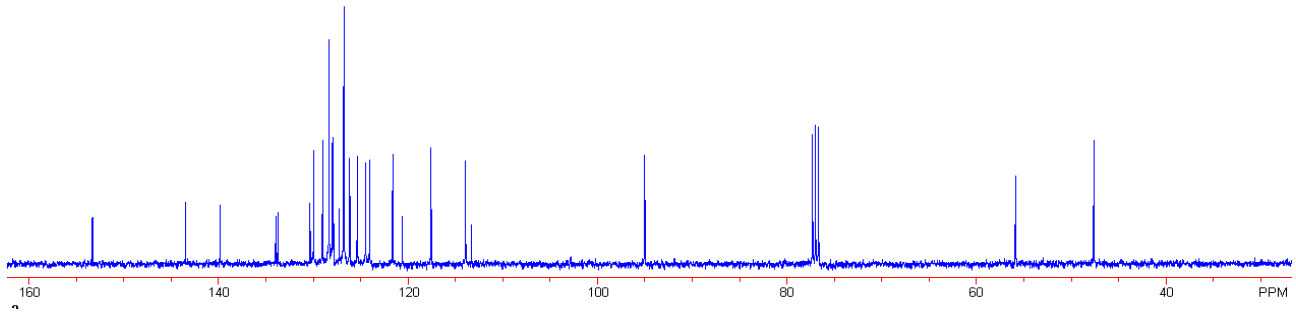
Compound 1: This is a known compound.[2] $[\alpha]^{20}_D$ = -33.0 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.97-8.06 (3H, m, Ar-H), 7.89 (1H, d, *J* = 8.0 Hz, Ar-H), 7.63 (1H, d, *J* = 8.8 Hz, Ar-H), 7.58-7.52 (2H, m, Ar-H), 7.38-7.34 (3H, m, Ar-H), 7.26-7.24 (1H, m, Ar-H), 7.03 (1H, d, *J* = 8.8 Hz, Ar-H), 5.18 (1H, d, *J* = 6.8 Hz, $ArOCH_2$), 5.03 (1H, d, *J* = 6.8 Hz, $ArOCH_2$), 3.22 (3H, s, OCH_3); ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -74.9.





Compound 2: This is a known compound.[2] $[\alpha]^{20}_{D}$ = +109.9 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.95 (1H, d, *J* = 9.2 Hz, Ar-H), 7.86 (1H, d, *J* = 8.0 Hz, Ar-H), 7.76 (1H, d, *J* = 9.2 Hz, Ar-H), 7.72 (1H, d, *J* = 9.6 Hz, Ar-H), 7.59 (1H, d, *J* = 8.8 Hz, Ar-H), 7.38-7.34 (1H, m, Ar-H), 7.24 (2H, d, *J* = 3.6 Hz, Ar-H), 7.20-7.08 (8H, m, Ar-H), 6.95-6.93 (1H, m, Ar-H), 5.05 (1H, d, *J* = 6.8 Hz, $ArOCH_2$), 5.00 (1H, d, *J* = 6.8 Hz, $ArOCH_2$), 4.37 (2H, d, *J* = 3.2 Hz CH_2Ph), 4.04 (1H, brs, ArNH), 3.15 (3H, s, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 153.3, 143.5, 139.8, 134.0, 133.7, 130.3, 129.9, 129.0, 128.3, 128.0, 127.9, 127.3, 126.8, 126.2, 125.4, 124.5, 124.0, 121.6, 120.6, 117.6, 113.9, 113.3, 95.0, 55.9, 47.6.

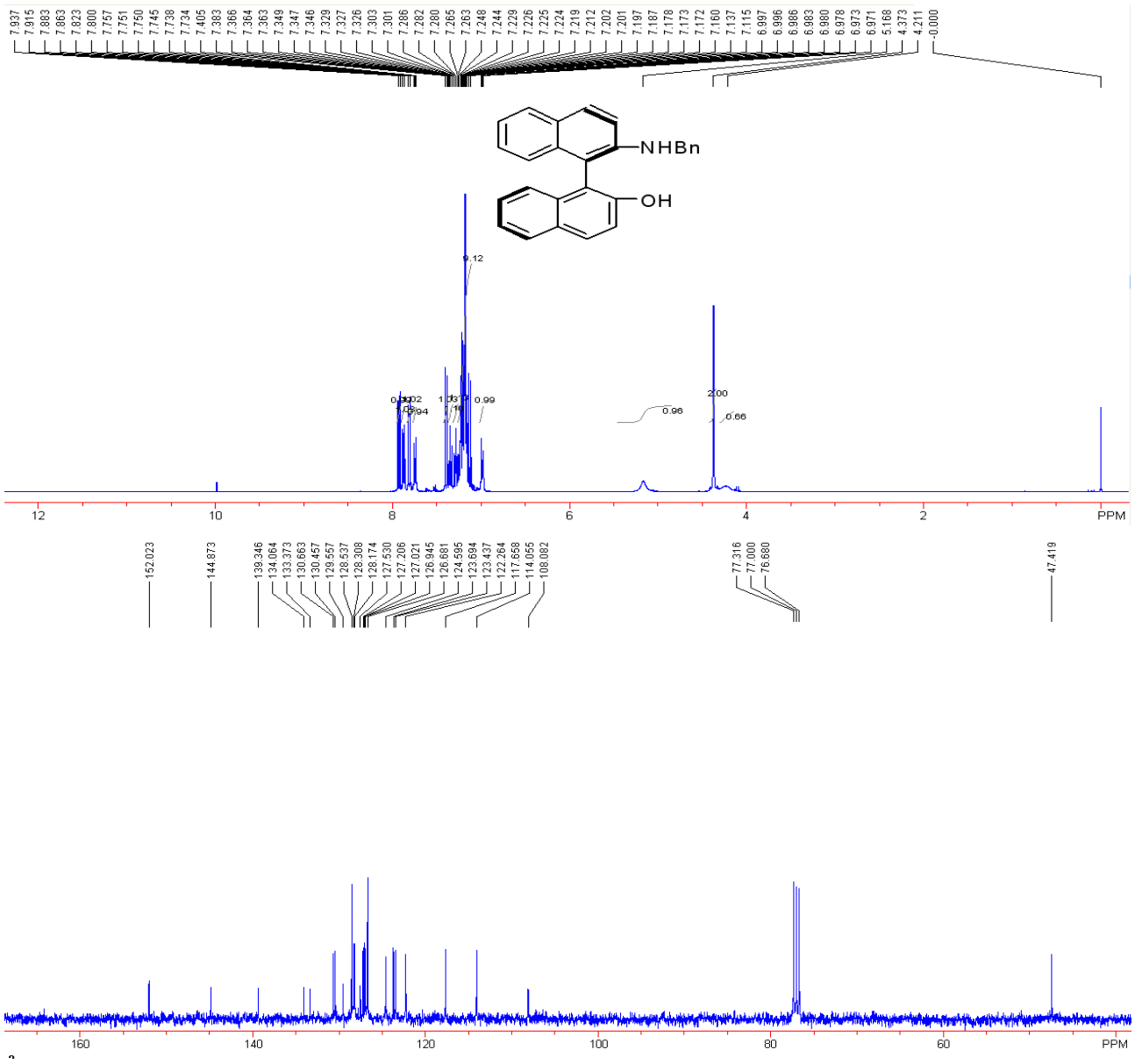




Compound 3: (*R*)-2'-(benzylamino)-1,1'-binaphthyl-2-ol

Compound **2** (1.79 g, 4.28 mmol) was dissolved into the mixed solvent of DCM/MeOH (15 mL/15 mL), and then 1.5 mL conc. HCl was added into the solution at room temperature. Then, the mixture was stirred for 8 hours at 60 ^{o}C. After being cooled to room temperature, the solution was poured into water and quenched by addition of saturated $NaHCO_3$ solution, extracted with CH_2Cl_2 twice, the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and residue was used for the next reaction without further purification, affording product **3** as white solid (1.60 g, 99% yield). m.p. 133-135 ^{o}C; $[\alpha]^{20}_{D}$ = +103.4 (c 1.0, $CHCl_3$). IR (CH_2Cl_2) ν 3418, 3071, 3051, 3017, 1699, 1616, 1596, 1495, 1427, 1339, 1295, 1178, 1144, 972, 812, 747 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.93 (1H, d, *J* = 8.8 Hz, Ar-H), 7.87 (1H, d, *J* = 8.0 Hz, Ar-H), 7.81 (1H, d, *J* = 9.2 Hz, Ar-H), 7.76-7.73 (1H, m, Ar-H), 7.39 (1H, d, *J* = 8.8 Hz, Ar-H), 7.37-7.33 (1H, m, Ar-H), 7.30-7.26 (1H, m, Ar-H), 7.25-7.11 (9H, m, Ar-H), 7.00-6.97 (1H, m, Ar-H), 5.16 (1H, bs, ArOH), 4.37 (2H, s, CH_2Ph), 4.21 (1H, bs, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 144.9, 139.3, 134.1, 133.4, 130.7, 130.5, 129.6, 128.5,

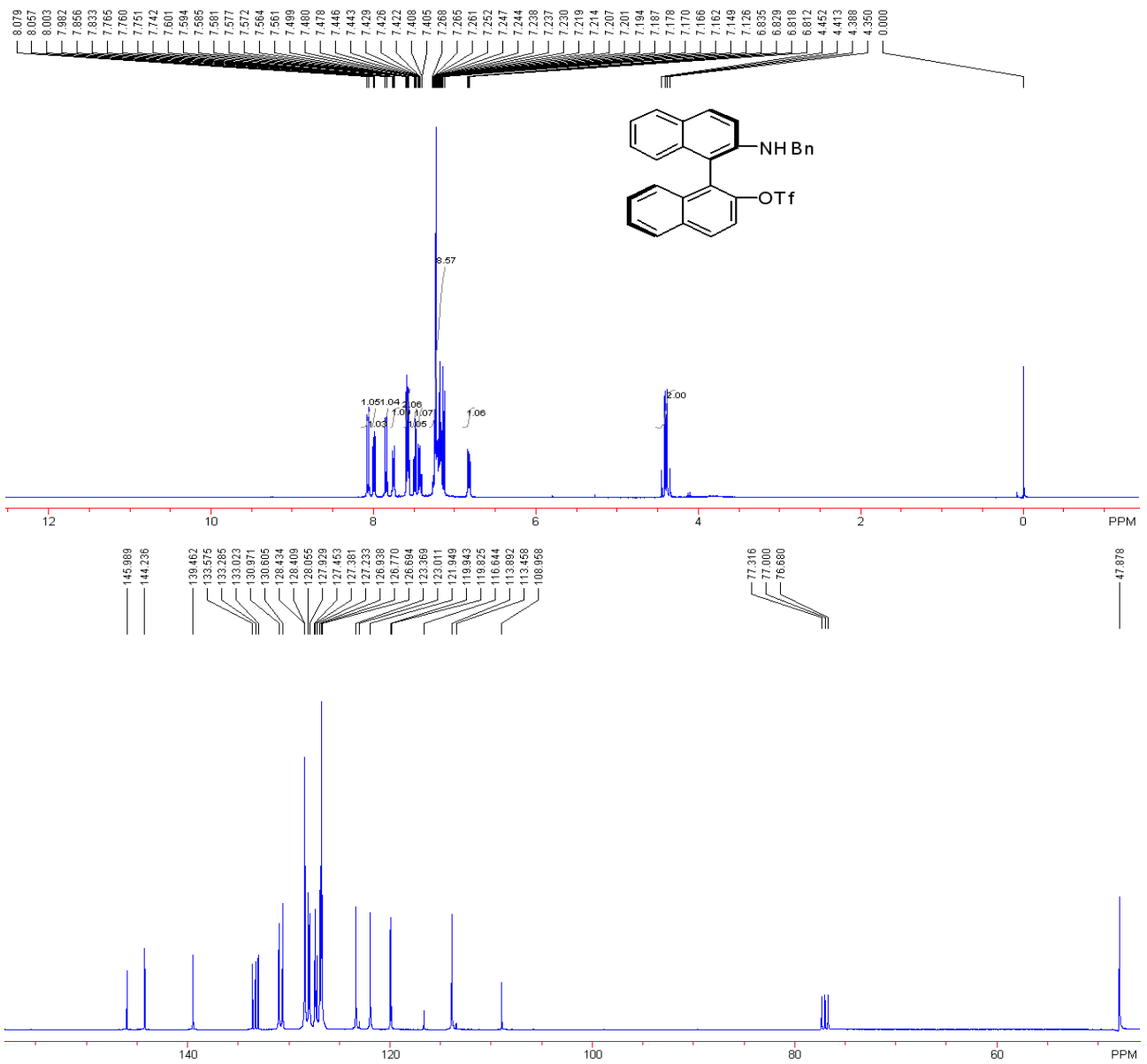
128.3, 128.2, 127.5, 127.2, 127.0, 126.9, 126.7, 124.6, 123.7, 123.4, 122.3, 117.7, 114.1, 108.1, 47.4; MS (EI) *m/z* (%) 375 (100) [M^+], 284 (45.71), 267 (25.33), 242 (18.00), 230 (6.70), 169 (6.50), 155 (9.21), 98 (25.11), 91 (41.75), 85 (56.27), 71 (61.10), 57 (67.71), 43 (55.74); HRMS (EI) Calcd for $C_{27}H_{21}NO$ [M^+] requires 375.1623, Found 375.1629.

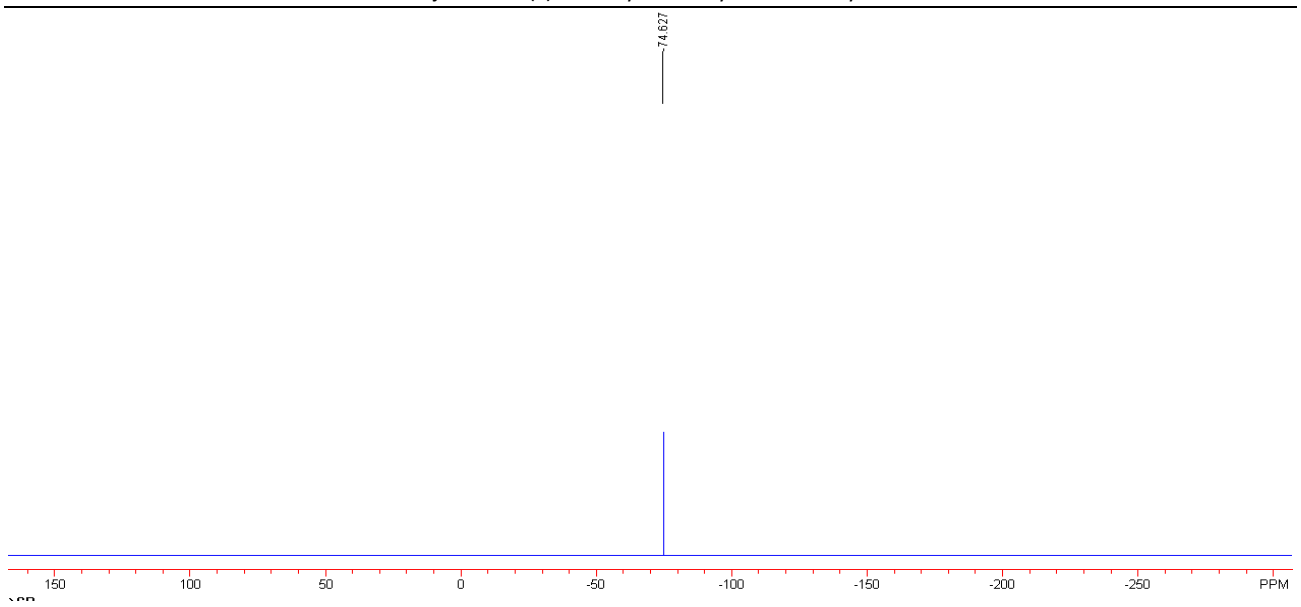


Compound 4: (*R*)-2'-(benzylamino)-1,1'-binaphthyl-2-yl trifluoromethanesulfonate

Procedure: Compound **3** (1.60 g, 4.27 mmol) was dissolved in 20 mL of CH_2Cl_2 and pyridine (12.81 mmol), and the mixture was cooled to 0 ^oC with ice-water bath, then Tf_2O (6.40 mmol) was added slowly. The resulting mixture was stirred at room temperature for 4 hours, and then the reaction was quenched by addition of 0.1 N HCl, and extracted with CH_2Cl_2, washed by water and brine, dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (EtOAc/PE = 1/16 as eluent) to furnish product **4** as white solid (1.38 g, 2.73 mmol, 64% yield). m.p. 143-146 ^oC; $[\alpha]^{20}_D$ = +49.7 (c 0.6, $CHCl_3$). IR (CH_2Cl_2) ν 3433, 3059, 1781, 1712, 1621, 1600, 1497, 1421, 1344, 1213, 1141, 957,

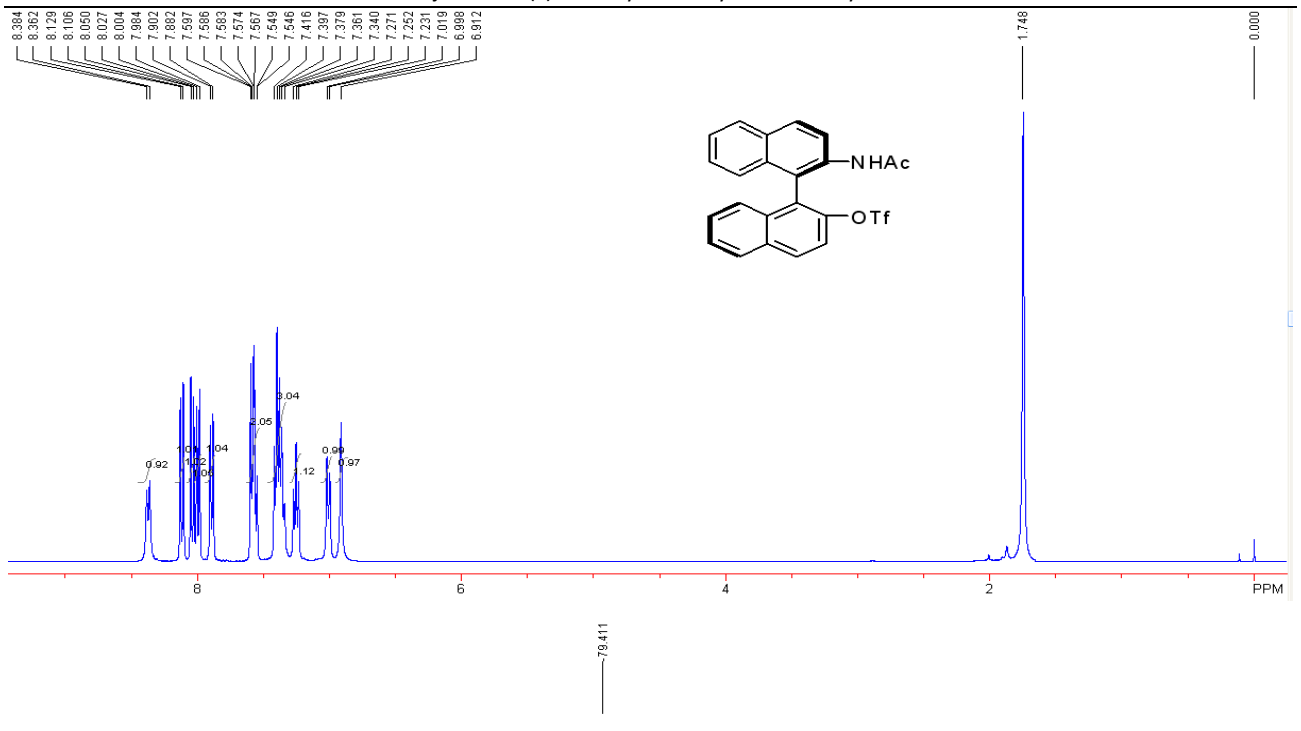
942, 835, 811, 745 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.07 (1H, d, *J* = 8.8 Hz, Ar-H), 7.99 (1H, d, *J* = 8.4 Hz, Ar-H), 7.84 (1H, d, *J* = 8.8 Hz, Ar-H), 7.77-7.74 (1H, m, Ar-H), 7.60-7.56 (2H, m, Ar-H), 7.49 (1H, d, *J* = 7.8 Hz, Ar-H), 7.45-7.40 (1H, m, Ar-H), 7.27-7.13 (8H, m, Ar-H), 6.84-6.81 (1H, m, Ar-H), 4.43 (1H, d, *J* = 15.6 Hz), 4.37 (1H, d, *J* = 15.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.0, 144.2, 139.5, 133.6, 133.3, 133.0, 131.0, 130.6, 128.4, 128.1, 127.9, 127.5, 127.4, 127.2, 126.9, 126.8, 126.7, 123.4, 121.9, 119.9, 118.2 (CF_3, q, $J_{C\text{-}F}$ = 318.6 Hz), 113.9, 109.0, 47.9; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -74.6; MS (EI) *m/z* (%) 507 (100) [M^+], 374 (93.19), 357 (19.40), 281 (10.40), 268 (19.03), 239 (15.07), 231 (30.76), 91 (57.40), 69(10.21); HRMS (EI) Calcd for $C_{28}H_{20}NO_3F_3S$ [M^+] requires 507.1116, Found 507.1119.





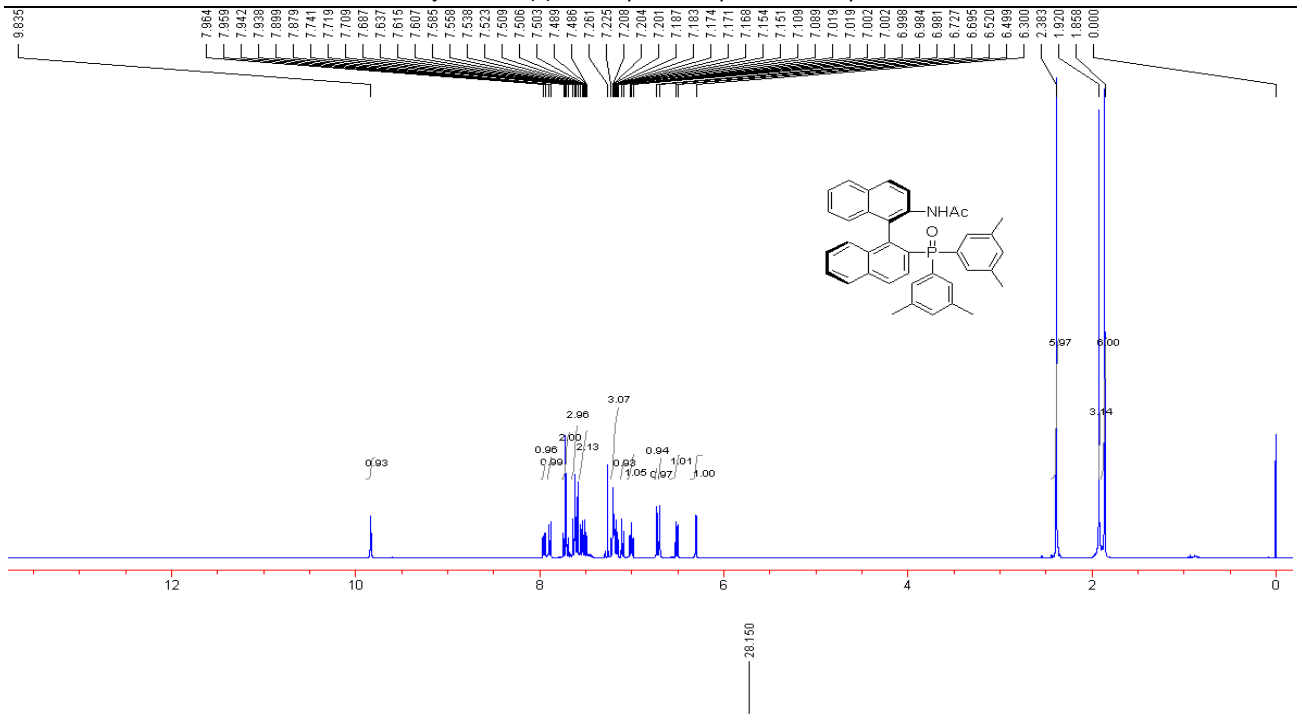
Compound 5: (*R*)-2'-(acetamino)-1,1'-binaphthyl-2-yl trifluoromethanesulfonate

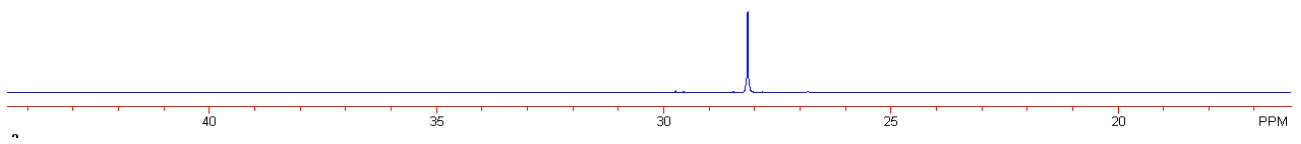
Procedure: Compound **4** (3.58 g, 7.07mmol) was dissolved in mixed solvent of EtOH/$CHCl_3$ (80 mL/20 mL), then 1.2 g of $Pd(OH)_2/C$ was added into the solution. The resulting mixture was heated to 40-50 ^oC for 8 hours. After the catalyst was filtered off, the solvent was removed under reduced pressure and the residue was purified by column chromatography on neutral Al_2O_3 (EtOAc/PE = 1/16 as eluent) to give the corresponding intermediate as white solid (2.60 g, 6.20 mmol, 87% yield). This white solid was dissolved in 10 mL of CH_2Cl_2 mixed with 1.5 mL AcOH and 3.0 mL Ac_2O and the resulting mixture was stirred at room temperature overnight. The reaction was quenched by addition of saturated $NaHCO_3$ solution, extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (EtOAc/PE = 1/4 as eluent) to furnish product **5** as off-white solid (2.80 g, 95% yield). This is a known compound. $[\alpha]^{20}_D$ = +72.8 (c 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 8.37 (1H, d, *J* = 8.8 Hz, Ar-H), 8.12 (1H, d, *J* = 9.2 Hz, Ar-H), 8.04 (1H, d, *J* = 9.2 Hz, Ar-H), 7.99 (1H, d, *J* = 8.8 Hz, Ar-H), 7.89 (1H, d, *J* = 8.0 Hz, Ar-H), 7.60-7.55 (2H, m, Ar-H), 7.42-7.34 (3H, m, Ar-H), 7.25 (1H, t, *J* = 8.4 Hz, Ar-H), 7.05 (1H, d, *J* = 8.4 Hz, Ar-H), 6.91 (1H, s, Ar-NH), 1.75 (3H, s, $COCH_3$); ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -79.4.



Compound 6: (*R*)-N-(2'-bis(3,5-dimethylphenyl)phosphoryl)-1,1'-binaphthyl-2-yl)acetamide.

This was prepared according to the previous literature.[3] A white solid. m.p. 110-113 ^{o}C; $[\alpha]^{20}_{D}$ = -171.7 (c 0.6, $CHCl_3$). IR (CH_2Cl_2) ν 3052, 3030, 2904, 1794, 1686, 1594, 1501, 1398, 1274, 1174, 1113, 877, 818, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 9.84 (1H, s, ArNH), 7.95 (1H, d, *J* = 8.0 Hz, Ar-H), 7.89 (1H, d, *J* = 8.0 Hz, Ar-H), 7.73 (1H, d, *J* = 8.8 Hz, Ar-H), 7.70 (1H, d, *J* = 8.8 Hz, Ar-H), 7.64-7.59 (3H, m, Ar-H), 7.56-7.49 (2H, m, Ar-H), 7.23-7.15 (3H, m, Ar-H), 7.10 (1H, d, *J* = 8.0 Hz, Ar-H), 7.00-6.98 (1H, m, Ar-H), 6.73 (1H, s, Ar-H), 6.70 (1H, s, Ar-H), 6.51 (1H, d, *J* = 8.4 Hz, Ar-H), 6.30 (1H, s, Ar-H), 2.38 (6H, s, $ArCH_3$), 1.92 (3H, s, $COCH_3$); 1.86 (6H, s, $ArCH_3$); ^{31}P NMR (162 MHz, $CDCl_3$, 85% H_3PO_4): δ 28.2; MS (EI) *m/z* (%) 567 (52.13) [M^+], 552 (27.86), 309 (93.79), 267 (100), 257 (40.23), 133 (16.68), 91 (18.90), 57 (29.76), 43 (69.01); HRMS (EI) Calcd for $C_{38}H_{34}NO_2P$ [M^+] requires 567.2327, Found 567.2330.

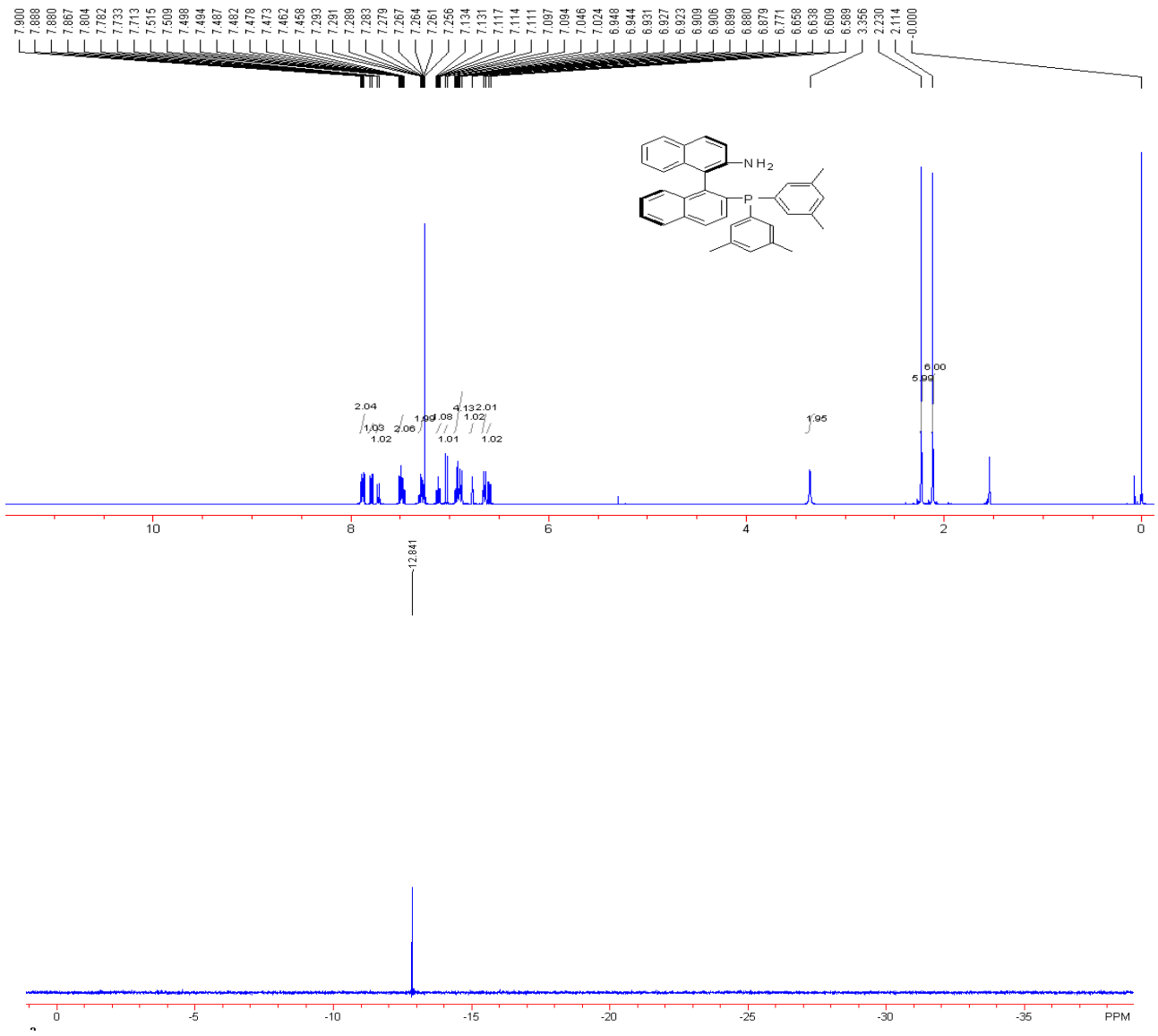




Compound 7: (*R*)-2'-bis(3,5-dimethylphenyl)phospino)-1,1'-binaphthyl-2-amine

Procedure: Compound **6** (1.0 mmol, 0.57 mg) was dissolved in 20 mL of EtOH, and then 4.0 N HCl solution was added into the mixture. The resulting solution was heated to 60 ^{o}C overnight and the reaction was quenched by addition of saturated $NaHCO_3$ solution, washed with water, extracted by CH_2Cl_2 twice, dried by anhydrous Na_2SO_4. The solution was concentrated for the next step without further purification (quantitative yield). Triethylamine (13.49 g, 25 mmol) in toluene (20 mL) was added into this product mixture (2.80 g, 5.33 mmol) and then trichlorosilane (8.31 g, 12 mmol) was added. The resulting mixture was heated at 110 ^{o}C for three days. After being cooled to room temperature, the product mixture was diluted with dichloromethane, quenched with a small amount of saturated $NaHCO_3$ solution. The resulting suspension was filtered through Celite, and washed with dichloromethane. The combined extracts were dried over anhydrous Na_2SO_4, and the residue was chromatographed on silica gel (PE/EA = 8:1 as eluent) to provide compound **7** as white solid (1.85 g, 70% yield). m.p. 119-121 ^{o}C ; $[\alpha]^{20}_{D}$ = -201.3 (c 1.0, $CHCl_3$). IR (CH_2Cl_2) ν 3461,

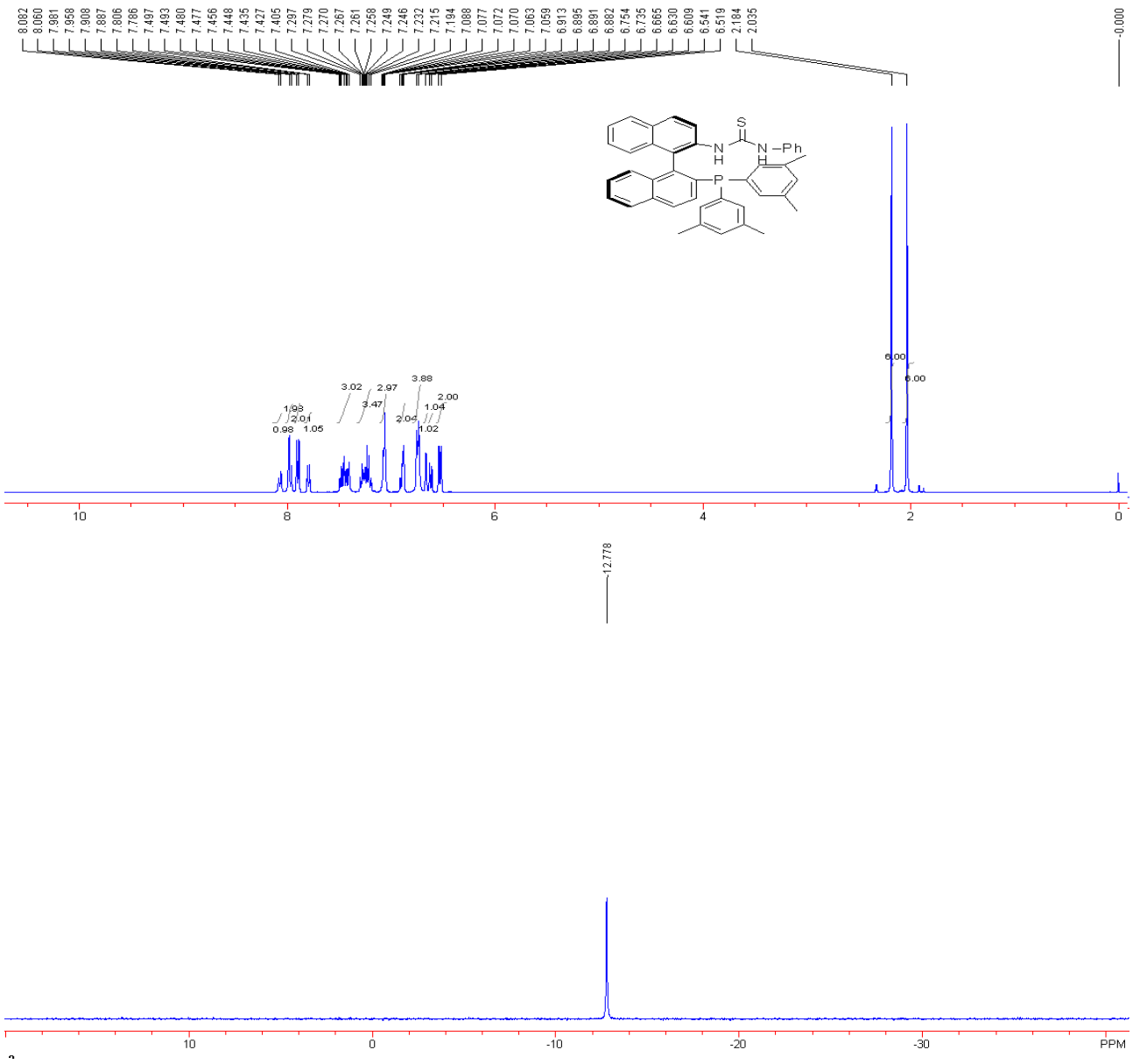
3328, 3215, 3052, 2917, 1712, 1619, 1600, 1513, 1433, 1358, 1271, 1182, 873, 818, 747, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.89 (1H, d, *J* = 4.8 Hz, Ar-H), 7.87 (1H, d, *J* = 5.2 Hz, Ar-H), 7.79 (1H, d, *J* = 8.8 Hz, Ar-H), 7.72 (1H, d, *J* = 8.0 Hz, Ar-H), 7.52-7.46 (2H, m, Ar-H), 7.29-7.26 (2H, m, Ar-H), 7.12-7.09 (1H, m, Ar-H), 7.03 (1H, d, *J* = 7.2 Hz, Ar-H), 6.94-6.88 (4H, m, Ar-H), 6.77 (1H, s, Ar-H), 6.65 (1H, d, *J* = 8.0 Hz, Ar-H), 6.60 (1H, d, *J* = 8.0 Hz, Ar-H), 3.36 (2H, s, NH_2), 2.23 (6H, s, $ArCH_3$), 2.11 (6H, s, $ArCH_3$); ^{31}P NMR (162 MHz, $CDCl_3$, 85% H_3PO_4): δ -12.9; MS (EI) *m/z* (%) 509 (0.91) [M^+], 525 (57.07), 267 (100), 266 (19.78), 239 (11.00), 133 (9.62), 99 (11.37), 85 (24.21), 71 (26.49), 57 (47.14), 43 (25.25); HRMS (EI) Calcd for $C_{36}H_{32}NP$ [M^+] requires 509.2272, Found 509.2271.



L1: (*R*)-1-(2'-(bis(3,5-dimethylphenyl)phosphino)-1,1'-binaphthyl-2-yl)-3-phenylthiourea

Procedure: This compound was prepared according to the previous literature.[4] Compound **7** (800 mg, 1.57 mmol) was dissolved in 2.0 mL of dry THF, and then isothiocyanatobenzene (255 mg, 1.88 mmol) was added and the reaction mixture was heated to 60 ^oC under argon for 7 days. After cooling to room temperature, the solution was concentrated by vacuum and the residue was purified

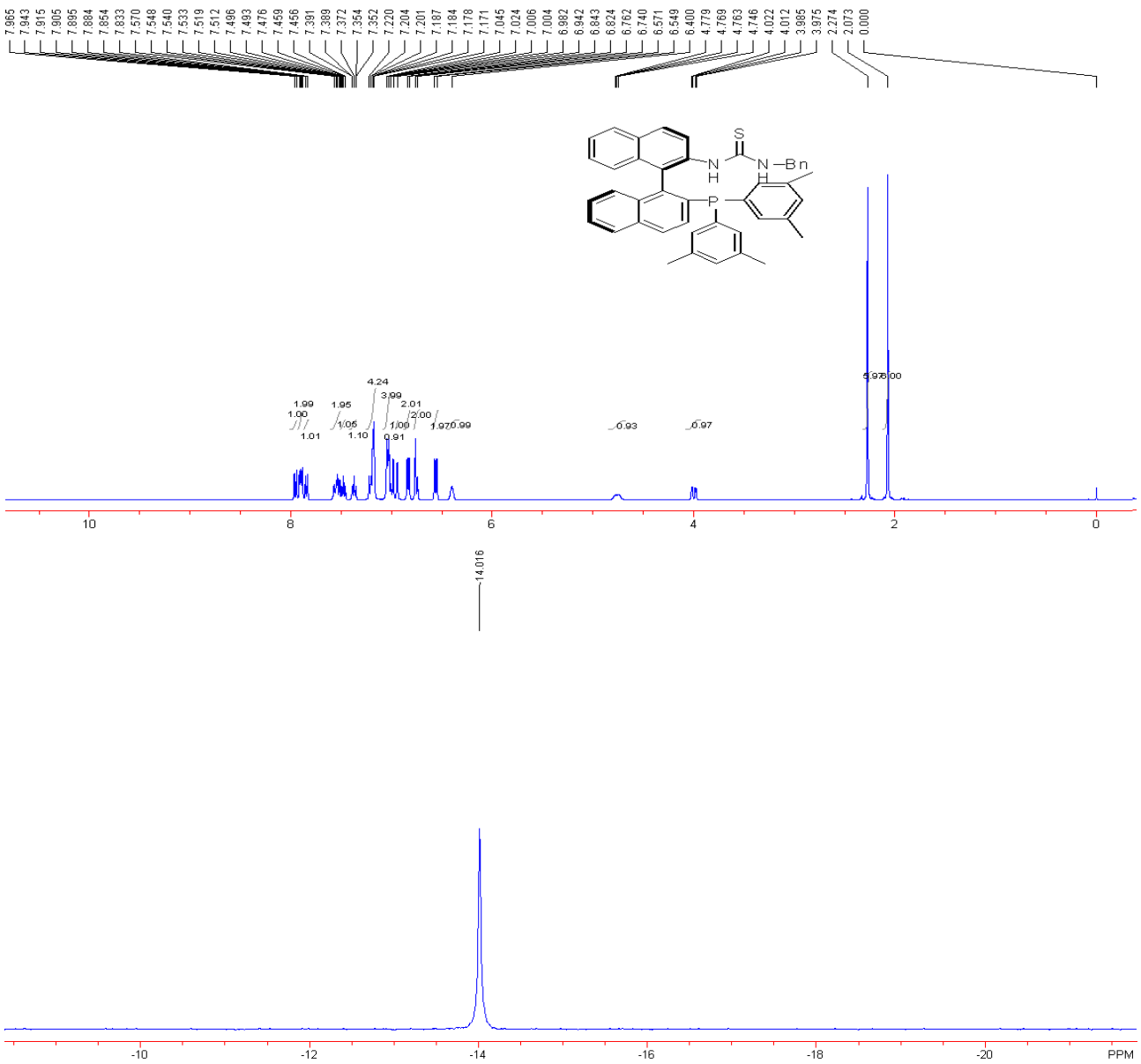
by column chromatography on silica gel (EtOAc/PE = 1/8 as eluent) to provide **L1** as white solid (620 mg, 61% yield). m.p. 112-115 ^{o}C; $[\alpha]^{20}_{D}$ = +158.2 (c 0.6, $CHCl_3$). IR (CH_2Cl_2) ν 3326, 3044, 2963, 1789, 1707, 1595, 1497, 1308, 1261, 1183, 1117, 840, 817, 748, 692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.07 (1H, d, *J* = 8.8 Hz), 7.97 (2H, d, *J* = 8.8 Hz), 7.90 (2H, d, *J* = 8.4 Hz), 7.80 (1H, d, *J* = 8.0 Hz), 7.50-7.41 (3H, m) 7.30-7.19 (3H, m), 7.09-7.06 (3H, m), 6.91-6.88 (2H, m), 6.74 (4H, d, *J* = 7.8 Hz), 6.67 (1H, s), 6.62 (1H, d, *J* = 8.4 Hz), 6.53 (2H, d, *J* = 8.8 Hz), 2.18 (6H, s, $ArCH_3$), 2.04 (6H, s, $ArCH_3$); ^{31}P NMR (162 MHz, $CDCl_3$, 85% H_3PO_4): δ -12.8; MS (ESI) *m/z* (%) 645.5 [M^++H]; HRMS (ESI) Calcd for $C_{43}H_{38}N_2PS$ [M^++H] requires 645.2488, Found 645.2483.



L2: (*R*)-1-benzyl-3-(2'-(bis(3,5-dimethylphenyl)phosphino)-1,1'-binaphthyl-2-yl)thiourea

Procedure: Compound **7** (800.0 mg, 1.57 mmol) was dissolved in 2.0 mL dry THF, and then (isothiocyanatomethyl)benzene (280.7 mg, 1.88 mmol) was added. The resulting mixture was heated to 60 ^{o}C under argon for 7 days, cooled to room temperature, concentrated by vacuum, and

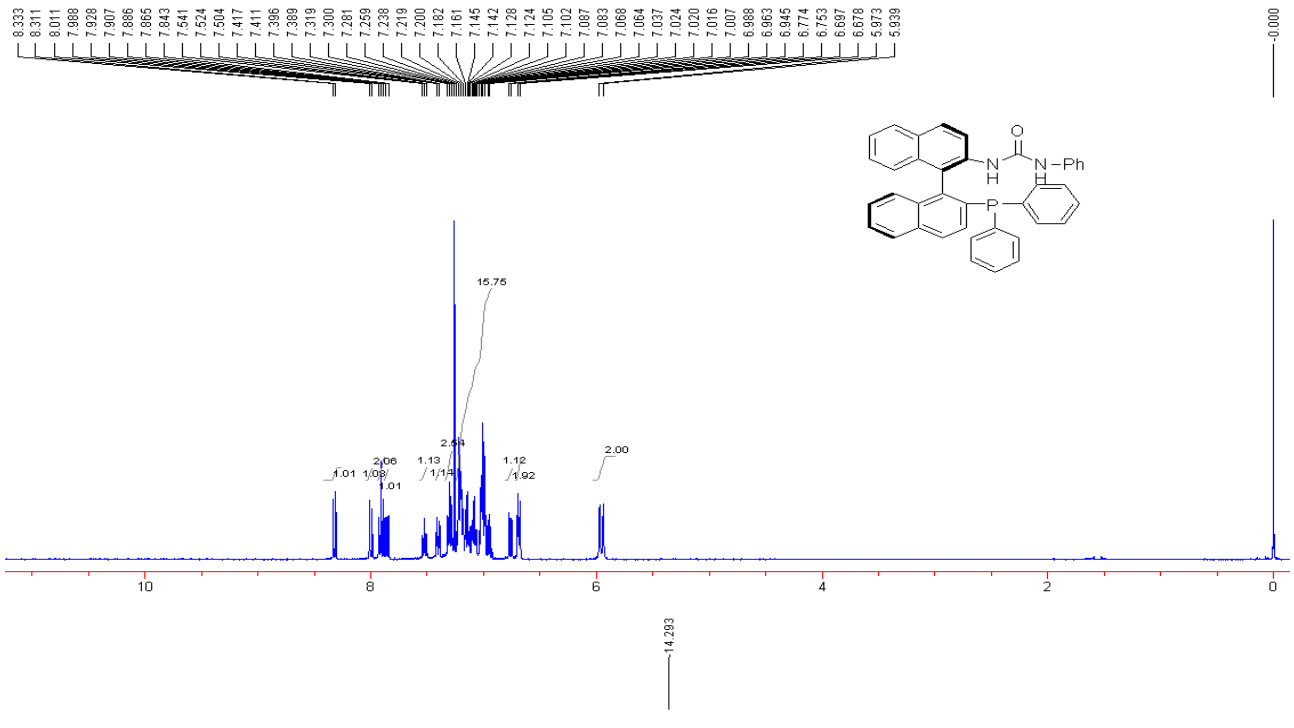
the residue was purified by column chromatography on silica gel (EtOAc/PE = 1/8 as eluent) to provide **L2** as white solid (580.0 mg, 56% yield). m.p. 116-119 ^{o}C; $[\alpha]^{20}_{D}$ = +190.5 (c 0.5, $CHCl_3$). IR (CH_2Cl_2) ν 3367, 3058, 2921, 1782, 1697, 1424, 1369, 1254, 1179, 1143, 1076, 848, 819, 747, 693 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.95 (1H, d, *J* = 8.8 Hz), 7.91-7.89 (2H, m), 7.84 (1H, d, *J* = 8.4 Hz), 7.55-7.46 (3H, m), 7.39-7.35 (1H, m), 7.22-7.17 (4H, m), 7.05-7.00 (4H, m), 6.98 (1H, s), 6.94 (1H, s), 6.83 (1H, d, *J* = 8.4 Hz), 6.75 (2H, d, *J* = 8.8 Hz), 6.56 (2H, d, *J* = 8.8 Hz), 6.40 (1H, brs), 4.77-4.74 (1H, m), 3.99 (1H, dd, J_1 = 14.8 Hz, J_2 = 4.0 Hz), 2.27 (6H, s, $ArCH_3$), 2.07 (6H, s, $ArCH_3$); ^{31}P NMR (162 MHz, $CDCl_3$, 85% H_3PO_4): δ -14.0; MS (ESI) *m/z* (%) 659.6 [M^++H]; HRMS (ESI) Calcd for $C_{44}H_{40}N_2PS$ [M^++H] requires 659.2644, Found 659.2651.

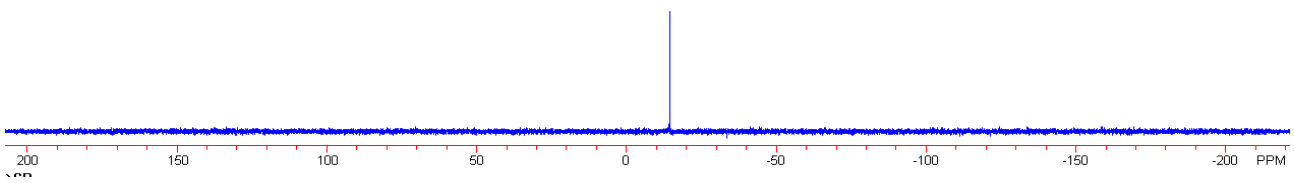


L3: (R)-1-(2'-(diphenylphosphino)-1,1'-binaphthyl-2-yl)-3-phenylurea

This is a known compound. $[\alpha]^{20}_{D}$ = +72.3 (c 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.32 (1H, d, *J* = 8.8 Hz), 8.00 (1H, d, *J* = 8.8 Hz), 7.91 (2H, t, *J* = 8.4 Hz), 7.85 (1H, d, *J* = 8.8 Hz), 7.52 (1H, t, *J* = 7.6 Hz), 7.40 (1H, dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz), 7.32-6.95 (17H, m), 6.76 (1H, d, *J*

= 8.8 Hz), 6.68 (2H, d, *J* = 7.6 Hz), 5.97 (1H, s), 5.94 (1H, s); ^{31}P NMR (162 MHz, $CDCl_3$, 85% H_3PO_4): δ -14.3.

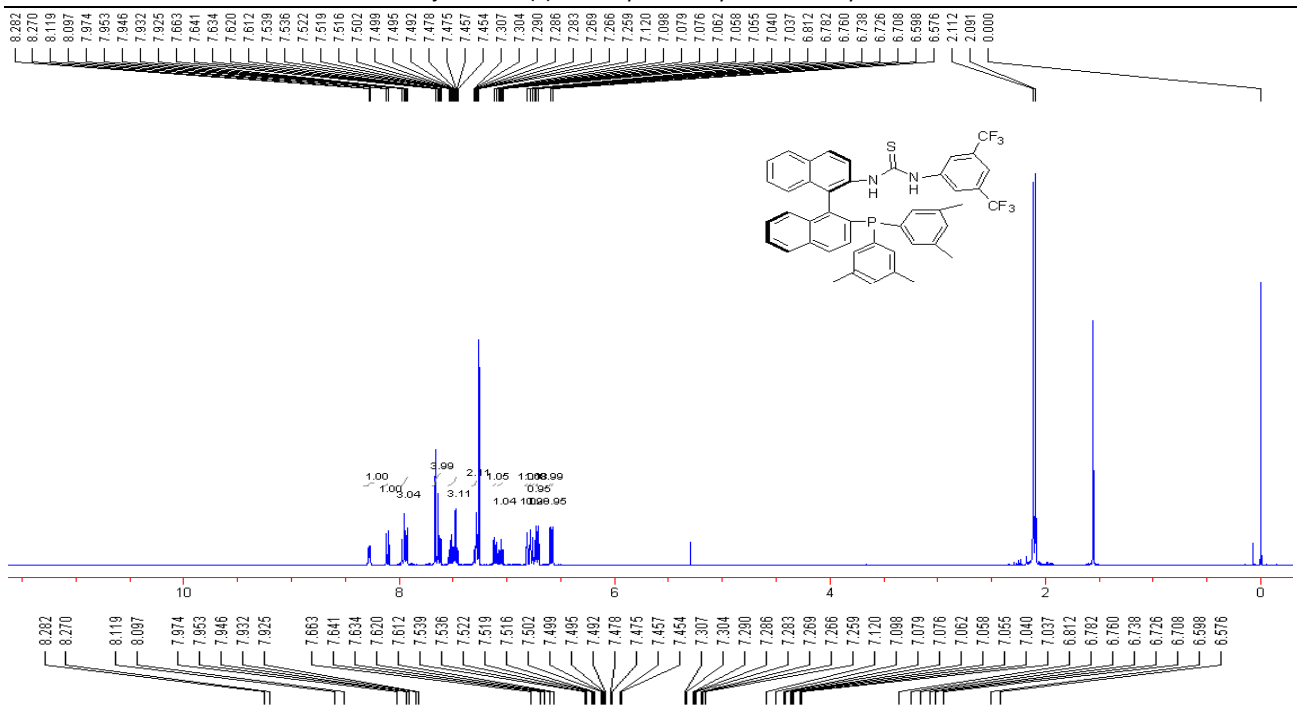




L4:

(*R*)-1-(2'-(bis(3,5-dimethylphenyl)phosphino)-1,1'-binaphthyl-2-yl)-3-(3,5-bis(trifluoromethyl) phenyl)thiourea

A white solid. yield: 77%. m.p. 118-122 ^{o}C; $[\alpha]^{20}_{D}$ = +348.3 (c 0.5, $CHCl_3$). IR (CH_2Cl_2) ν 3052, 2921, 1779, 1707, 1580, 1473, 1383, 1277, 1250, 1178, 1134, 992, 883, 847 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.28 (1H, d, *J* = 4.8 Hz), 8.11 (1H, d, *J* = 8.8 Hz), 7.97-7.93 (3H, m), 7.66-7.61 (4H, m), 7.54-7.46 (3H, m), 7.30-7.27 (2H, m), 7.11 (1H, d, *J* = 8.8 Hz), 7.08-7.04 (1H, m), 6.81 (1H, s), 6.78 (1H, s), 6.75 (1H, d, *J* = 8.8 Hz), 6.73 (1H, s), 6.71 (1H, s), 6.60 (1H, s), 6.58 (1H, s), 2.11 (6H, s, $ArCH_3$), 2.10 (6H, s, $ArCH_3$); ^{31}P NMR (162 MHz, $CDCl_3$, 85% H_3PO_4): δ -13.5; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -63.0; MS (ESI) *m/z* (%) 781.4 [M^++H]; HRMS (ESI) Calcd for $C_{45}H_{36}F_6N_2PS$ [M^++H] requires 781.2236, Found 781.2239.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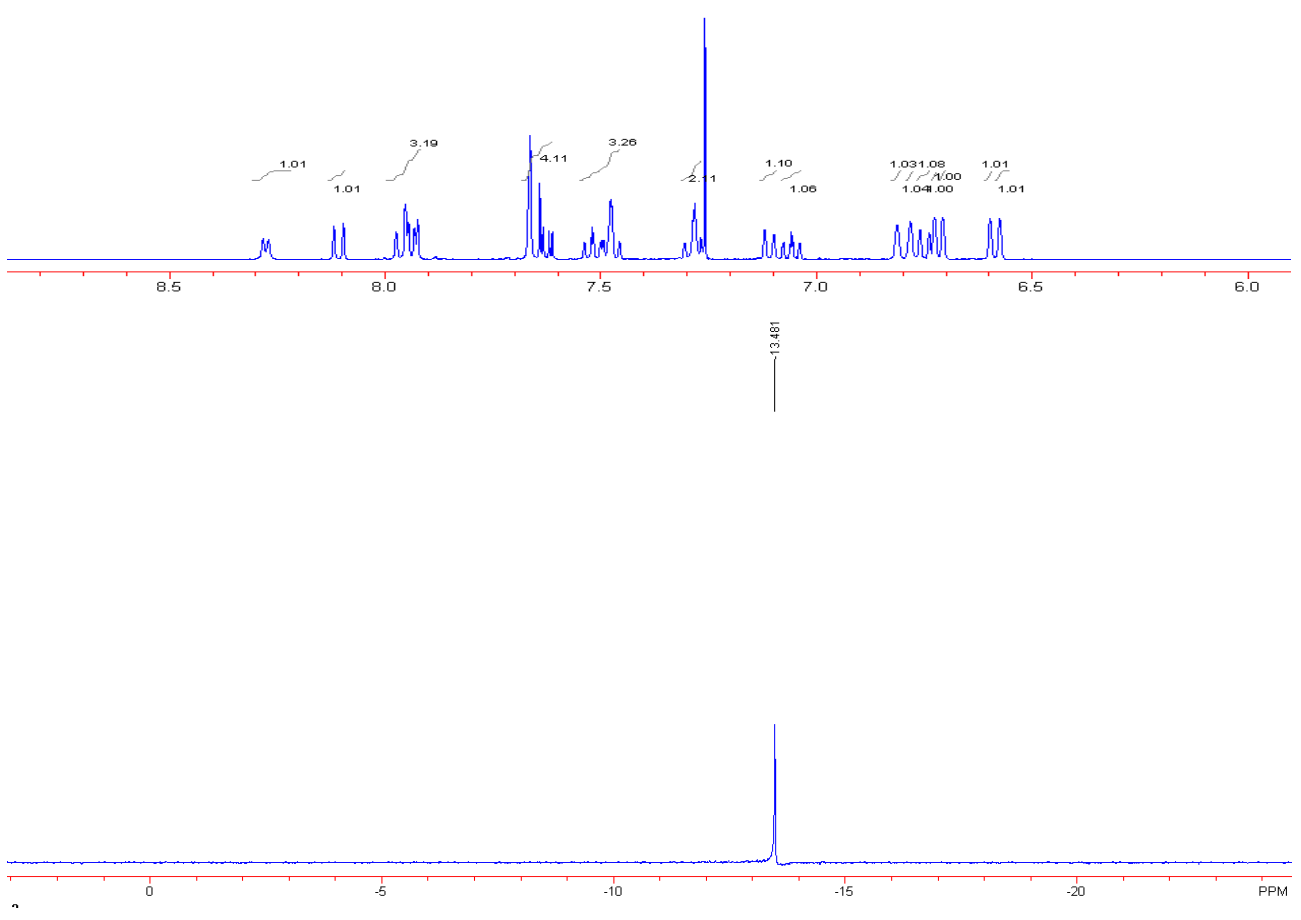
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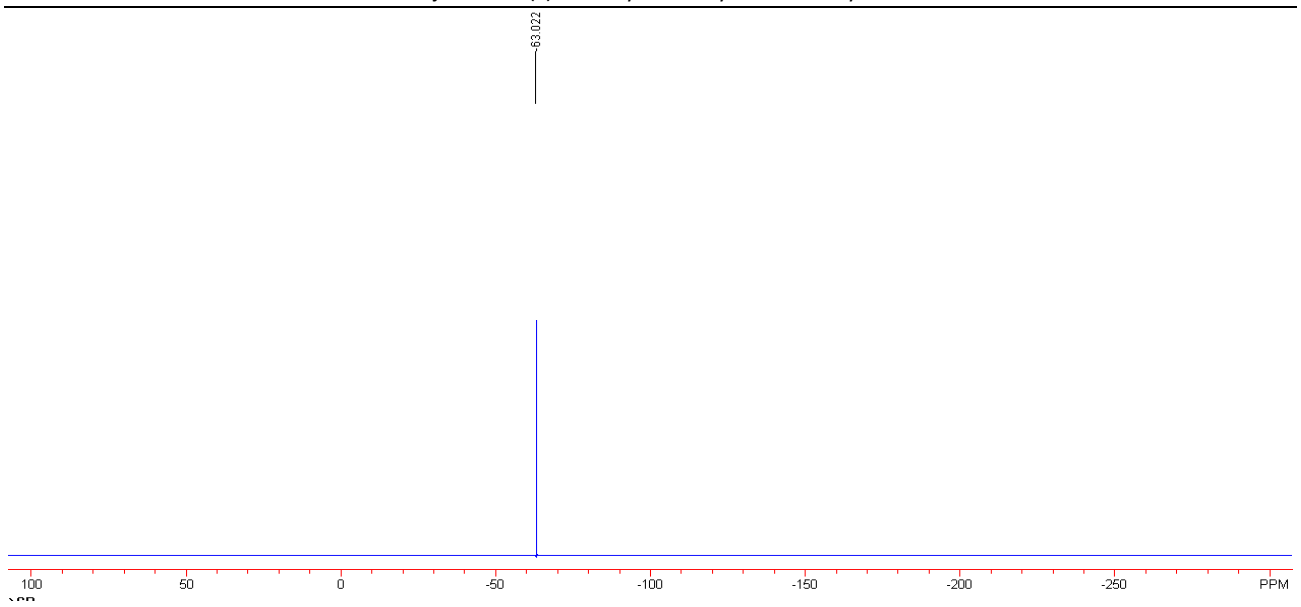
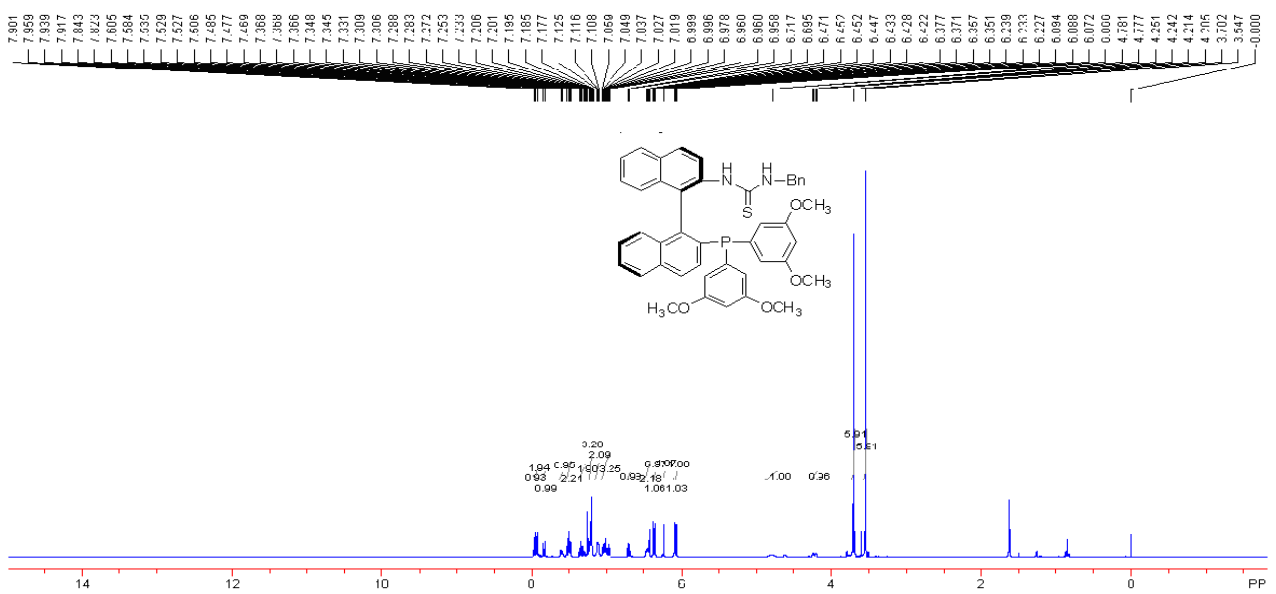
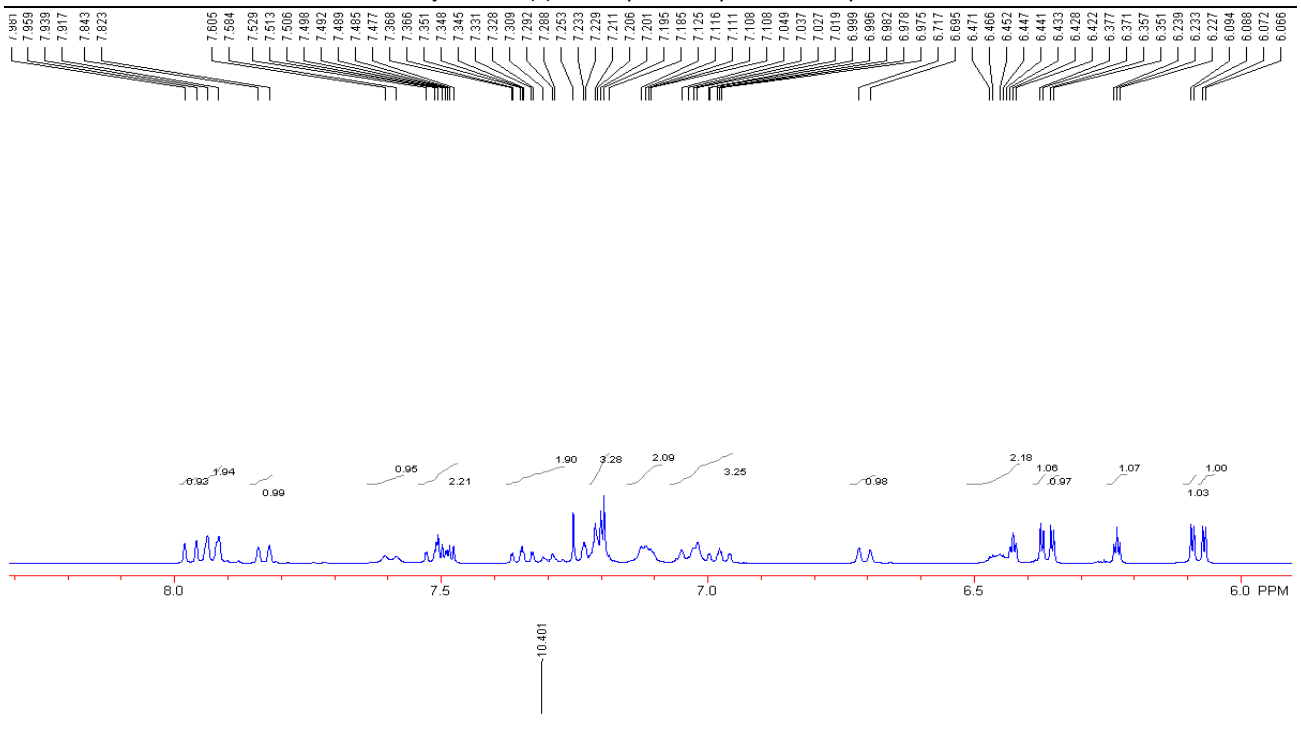
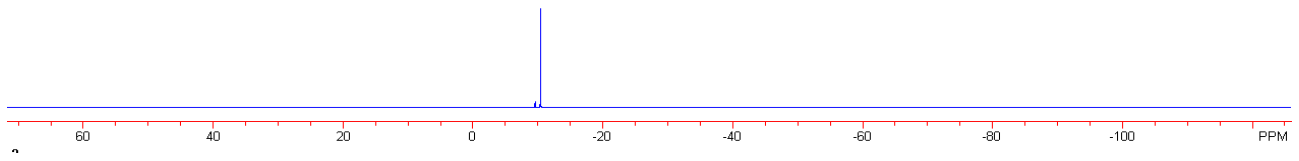


L6: (*R*)-1-benzyl-3-(2'-(bis(3,5-dimethoxyphenyl)phosphino)-1,1'-binaphthyl-2-yl)thiourea

A white solid. yield: 58%. m.p. 103-105 ^{o}C; $[\alpha]^{20}_{D}$ = +123.8 (c 0.5, $CHCl_3$). IR (CH_2Cl_2) ν 2932, 1580, 1524, 1485, 1453, 1411, 1327, 1280, 1202, 1153, 1060, 1042, 817, 747 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.97 (1H, d, *J* = 8.8 Hz), 7.93 (2H, d, *J* = 8.8 Hz), 7.83 (1H, d, *J* = 8.0 Hz), 7.59 (1H, d, *J* = 8.4 Hz), 7.53-7.48 (2H, m), 7.37-7.28 (2H, m), 7.23-7.19 (3H, m), 7.13-7.11 (2H, m), 7.05-6.96 (3H, m), 6.71 (1H, d, *J* = 8.8 Hz), 6.47-6.42 (2H, m), 6.37 (1H, d, *J* = 2.4 Hz), 6.35 (1H, d, *J* = 2.4 Hz), 6.23 (1H, t, *J* = 2.4 Hz), 6.09 (1H, d, *J* = 2.4 Hz), 6.07 (1H, d, *J* = 2.4 Hz), 4.78 (1H, brs, CH_2Ph), 4.23 (1H, dd, J_1 = 12.8 Hz, J_2 = 3.6 Hz, CH_2Ph), 3.70 (6H, s, $ArOCH_3$), 3.55 (6H, s, $ArOCH_3$); ^{31}P NMR ($CDCl_3$, 162 MHz, 85% H_3PO_4): δ -10.4; MS (ESI) *m/z* (%) 723.4 [M^++H]; HRMS (ESI) Calcd for $C_{44}H_{40}O_4N_2PS$ [M^++H] requires 723.2448, Found 723.2441.







Reference:

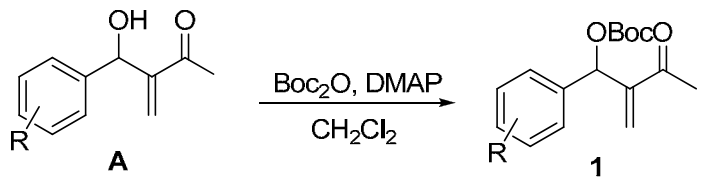
[1] a) Obrecht, D.; Altorfer, M.; Lehmann, C.; Schönholzer, P.; Müller, K. *J. Org. Chem*. **1996**, *61*, 4080. b) Chen, F. M. F.; Kuroda, K.; Benoiton, N. L. *Synthesis* **1979**, 230.

[2] Takashi, O.; Kohsuke, O.; Keiji, M. *J. Am. Chem. Soc.* **2007**, *129*, 2410.

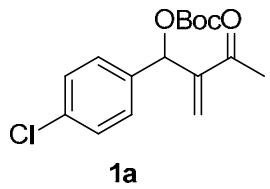
[3] Štěpán, V.; Martin, S.; Vladimír, H.; Miroslav, P.; Pavel, K. *J. Org. Chem*. **1998**, *63*, 7738.

[4] Shi, Y.-L.; Shi, M. *Adv. Synth. Catal.* **2007**, *349*, 2129.

Typical procedure for the preparation of Boc-protected Morita-Baylis-Hillman adducts.

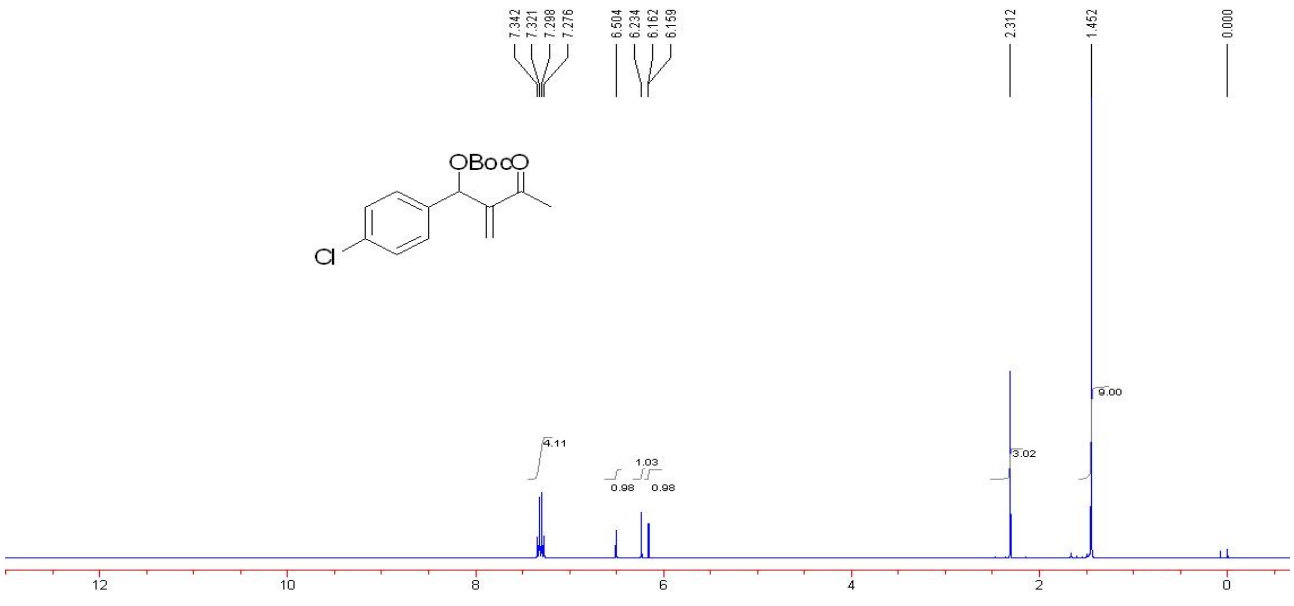


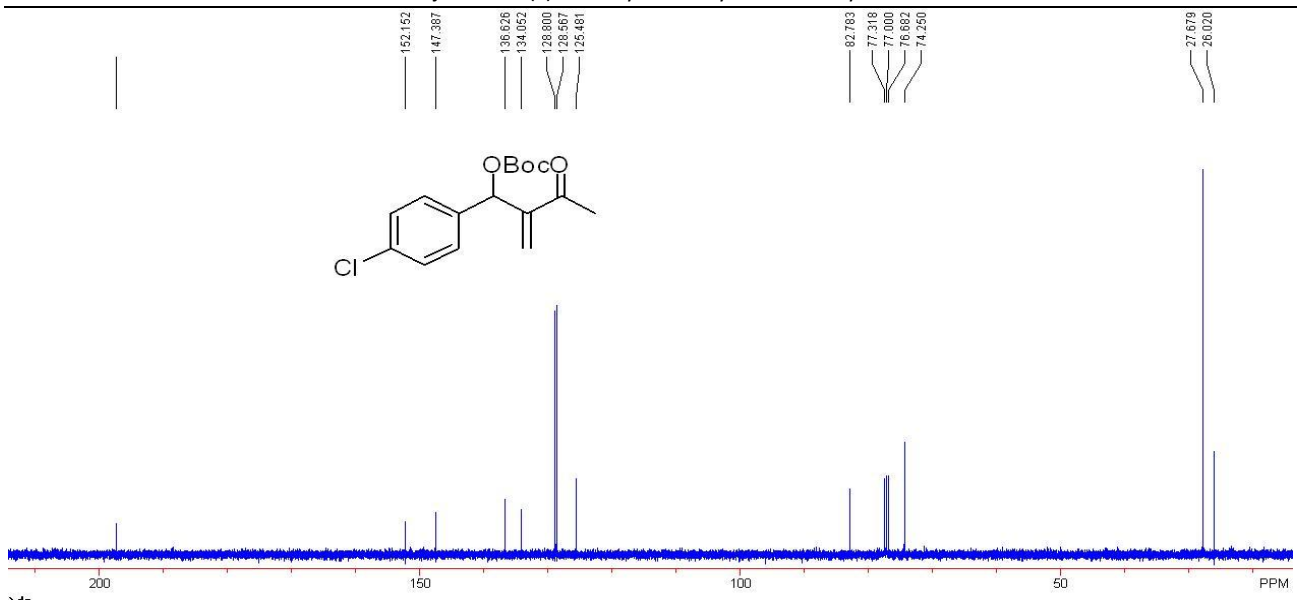
To an ice-water cooled solution of **A** (10.0 mmol) in dry CH_2Cl_2 (20.0 mL) was added Boc_2O (11.0 mmol) and DMAP (0.5 mmol) in dry CH_2Cl_2 (20.0 mL) over half an hour. The reaction mixture was stirred at room temperature overnight. The solution was washed with aqueous hydrochloric acid (15%, 20 mL), saturated sodium bicarbonate (20 mL), and brine (20 mL) sequentially, dried over anhydrous sodium sulfate, concentrated, and purified by column chromatography to get the product

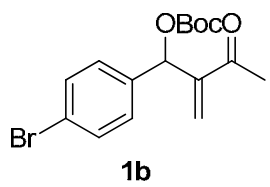


1a

tert-butyl 1-(4-chlorophenyl)-2-methylene-3-oxobutyl carbonate **1a**: a white solid; yield: 77%; m.p. 97-99 ^oC; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.34-7.27 (m, 4H), 6.50 (s, 1H), 6.23 (brs, 1H), 6.16 (d, J = 1.2 Hz, 1H), 2.31 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 152.4, 147.4, 136.9, 134.1, 128.8, 128.6, 125.5, 82.8, 74.3, 27.7, 26.0; IR (neat) ν 3065, 3034, 2981, 2934, 1745, 1681, 1370, 1277, 1159 cm^{-1}; MS (%) m/e 254 (M-C_4H_8, 19), 209 (71), 195 (24), 193 (30), 192 (40), 175 (70), 115 (56), 57 (100), 43 (81); HRMS (EI) for $C_{12}H_{10}O_4Cl$ (M-C_4H_8): 253.0268; Found: 253.0265.

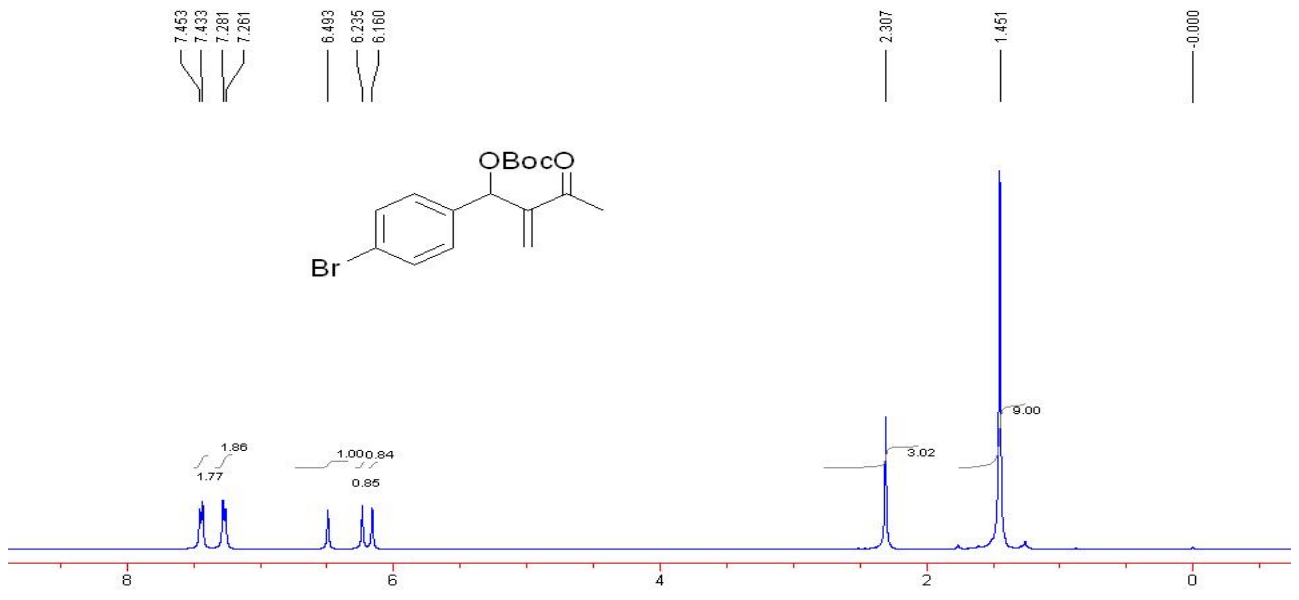


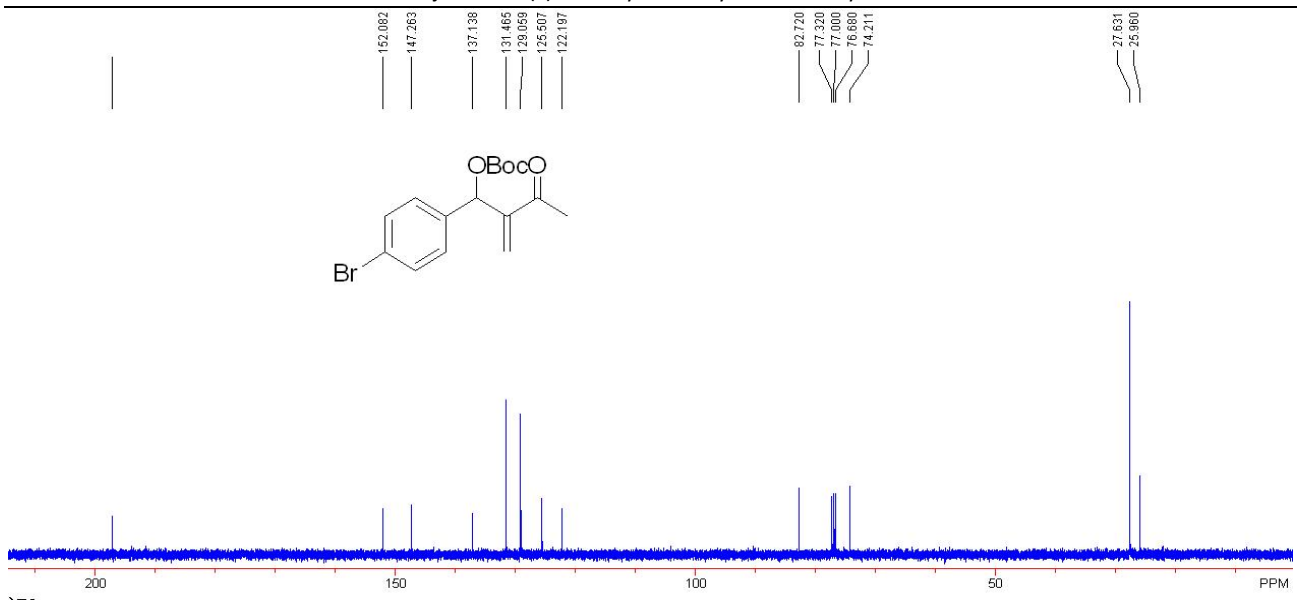


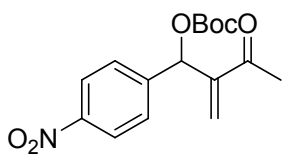


1b

tert-butyl 1-(4-bromophenyl)-2-methylene-3-oxobutyl tert-butyl carbonate **1b**: a white solid; yield: 67%; m.p. 101-103 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.45-7.43 (m, 2H), 7.28-7.25 (m, 2H), 6.50 (s, 1H), 6.24 (s, 1H), 6.16 (s, 1H), 2.31 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 152.1, 147.3, 137.4, 131.5, 129.1, 125.5, 122.2, 82.7, 74.2, 27.6, 26.0. IR (neat) ν 2981, 2934, 1746, 1681, 1370, 1488, 1370, 1280, 1157, 1084, 1073 cm^{-1}; MS (ESI) m/e 377 (M+Na); HRMS (ESI) for $C_{16}H_{19}BrNaO_4$ (M+Na): 377.0359; Found: 377.0359.

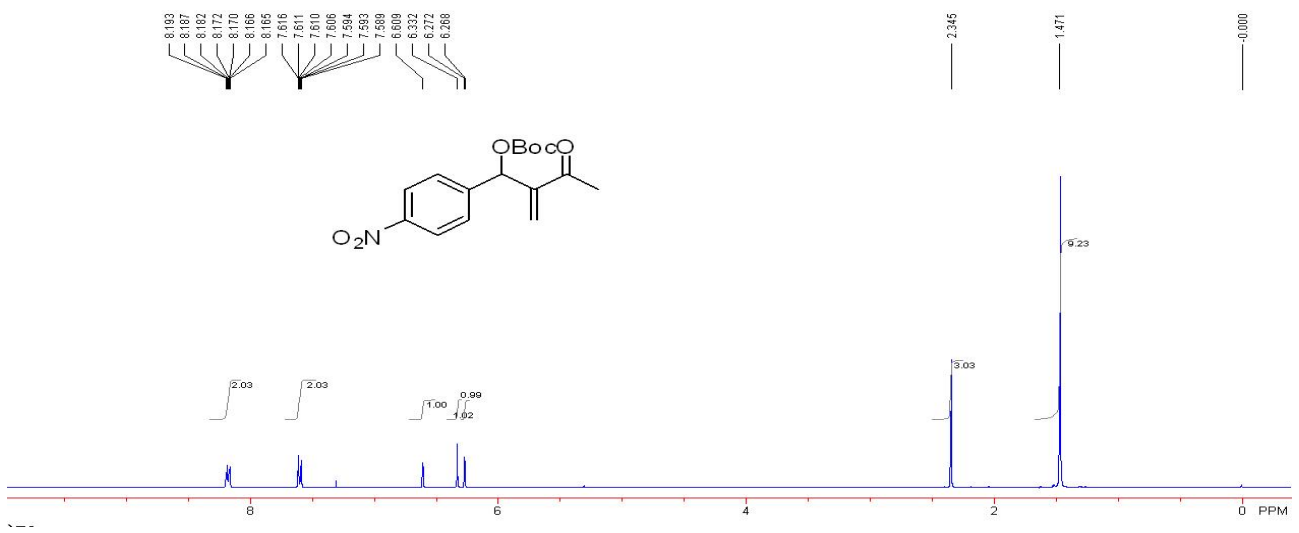


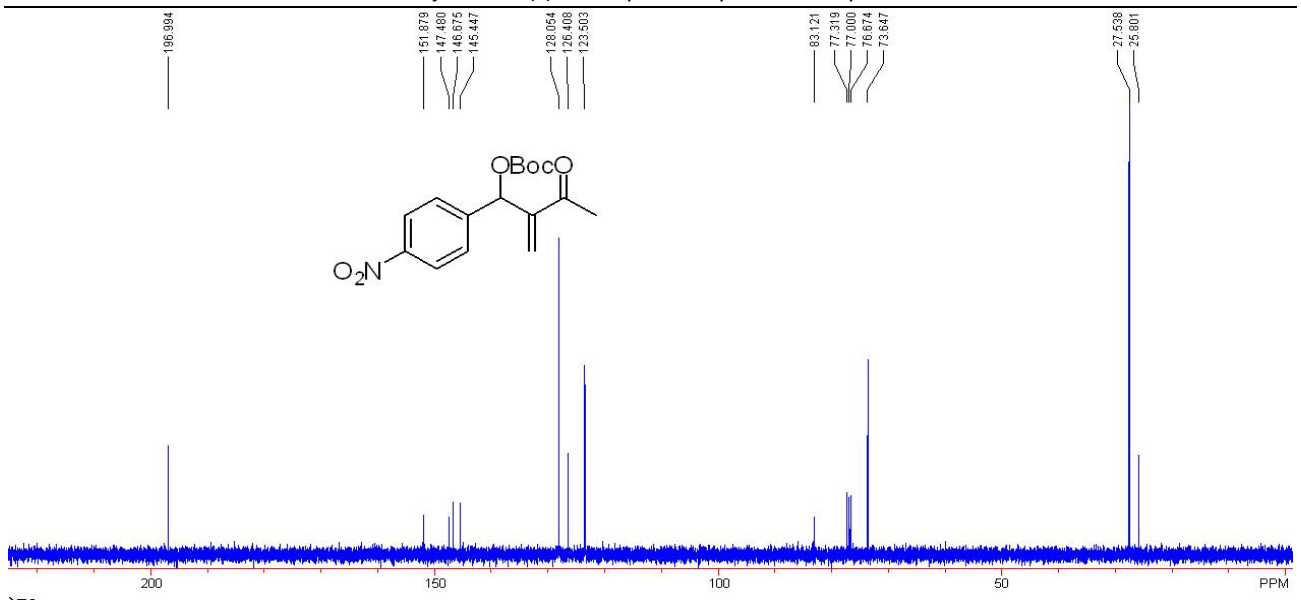


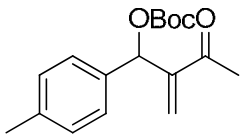


1c

tert-butyl 2-methylene-1-(4-nitrophenyl)-3-oxobutyl carbonate **1c**: a white solid; yield: 87%; m.p. 112-115 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.19-8.17 (m, 2H), 7.62-7.59 (m, 2H), 6.61 (s, 1H), 6.33 (s, 1H), 6.27 (s, 1H), 2.35 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.0, 151.9, 147.5, 146.7, 145.4, 128.1, 126.4, 123.5, 83.1, 73.6, 27.5, 25.8. IR (neat) ν 3478, 3341, 3112, 2982, 2936, 1747, 1681, 1608, 1526, 1370, 1252, 1156, 1086, 975, 853 cm^{-1}; MS (ESI) m/e 344 (M+Na); HRMS (ESI) for $C_{16}H_{19}NNaO_6$ (M+Na): 344.1105; Found: 344.1105.

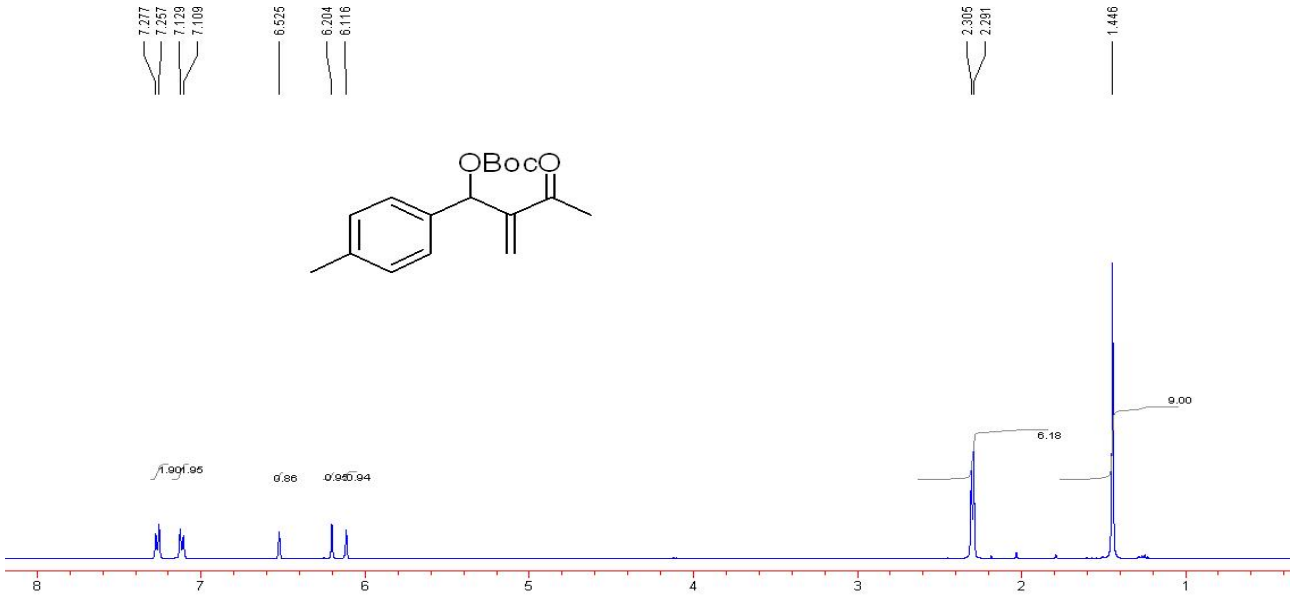


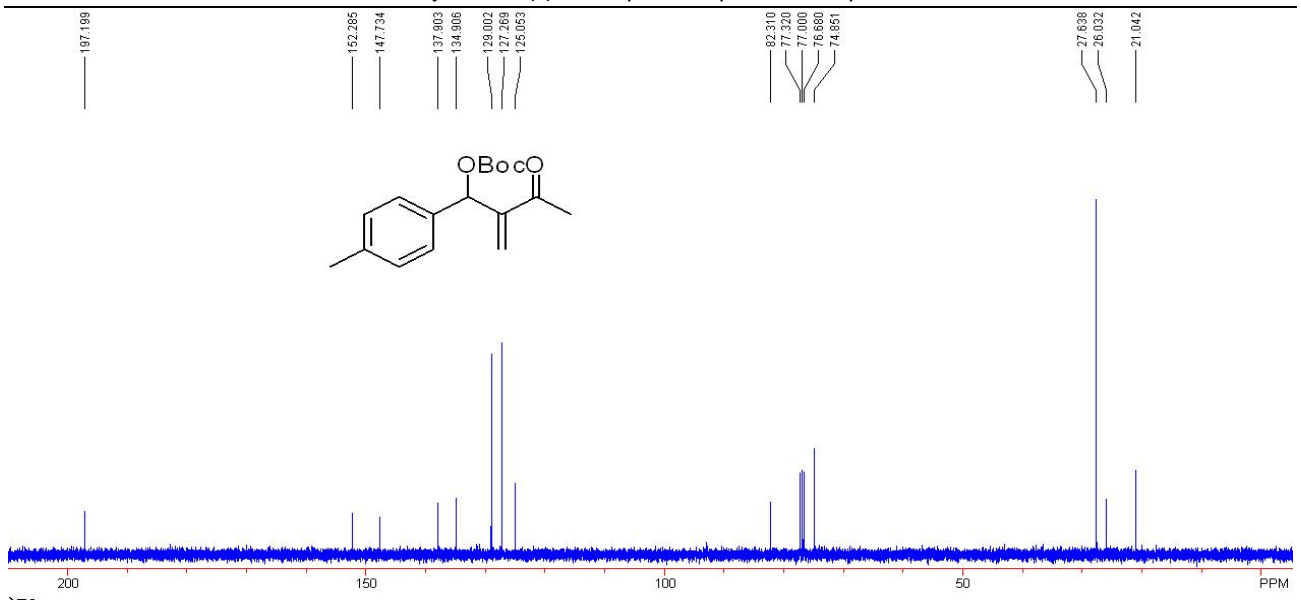


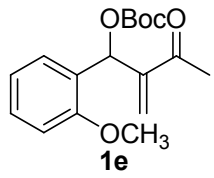


1d

tert-butyl 2-methylene-3-oxo-1-p-tolylbutyl carbonate **1d**: a white solid; yield: 57%; m.p. 79-82 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.27 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.53 (s, 1H), 6.20 (s, 1H), 6.12 (s, 1H), 2.31 (s, 3H), 2.30 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 152.3, 147.7, 137.9, 134.9, 129.0, 127.3, 125.5, 82.3, 74.9, 27.6, 26.0, 21.0; IR (neat) ν 3476, 3348, 2981, 2932, 1745, 1682, 1515, 1370, 1276, 1160, 1083, 973, 884 cm^{-1}; MS (ESI) m/e 313 (M+Na); HRMS (ESI) for $C_{17}H_{22}NaO_4$ (M+Na): 313.1410; Found: 313.1414.

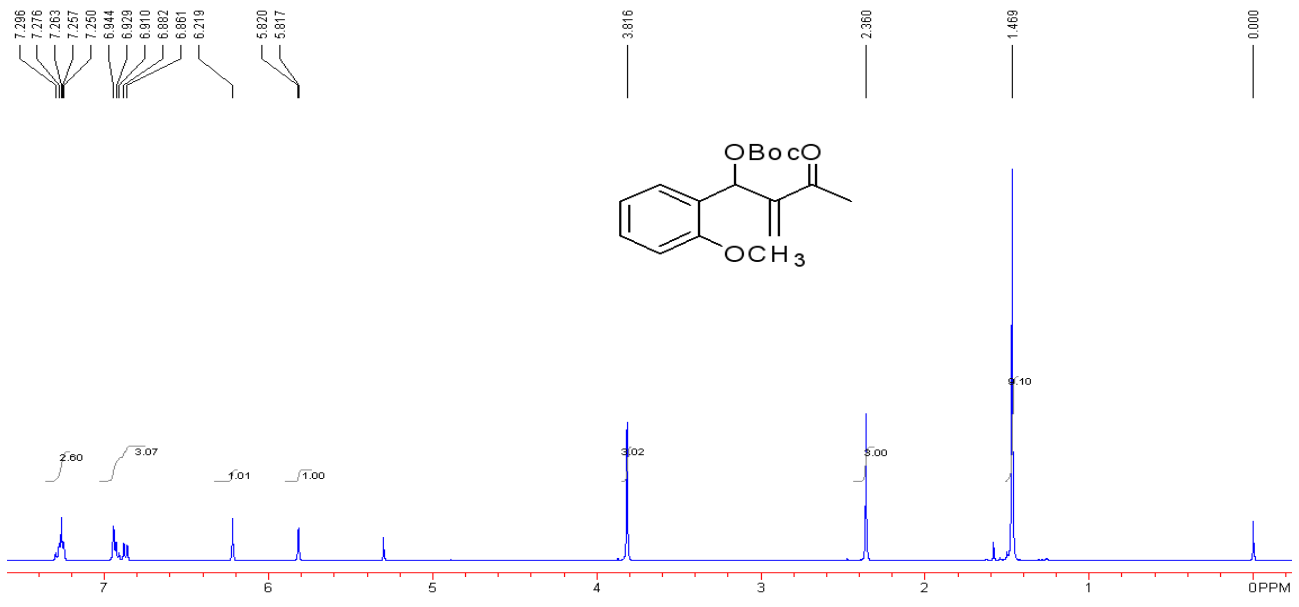


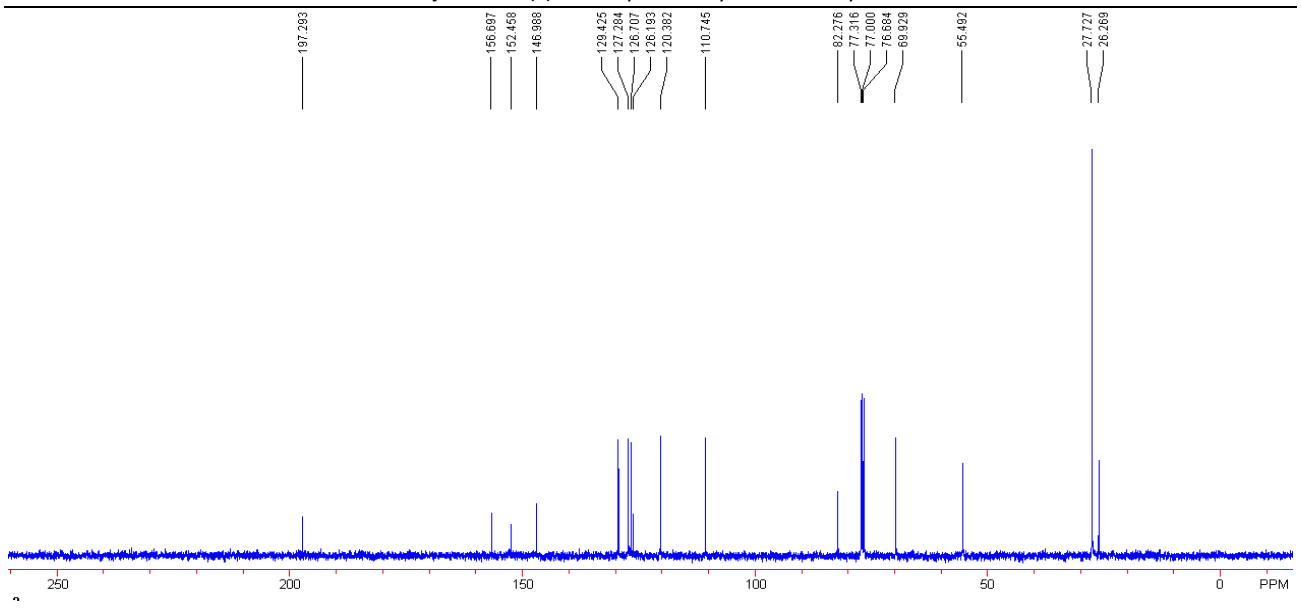


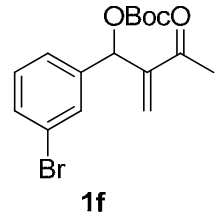


1e

tert-butyl 1-(2-methoxyphenyl)-2-methylene-3-oxobutyl carbonate **1e**: a white solid. yield: 52%; m.p 119-121 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.30-7.25 (m, 2H), 6.94-6.88 (m, 2H), 6.87 (d, 1H, *J* = 8.4 Hz), 6.22 (s, 1H), 5.82 (d, *J* = 1.2 Hz, 1H), 3.82 (s, 3H), 2.36 (s, 3H), 2.30 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197, 156.7, 152.5, 147.0, 129.4, 127.3, 126.7, 126.2, 120.4, 110.8, 82.3, 69.9, 55.5, 27.7, 26.3; IR (CH_2Cl_2) ν 2982, 1738, 1674, 1634, 1602, 1495, 1467, 1392, 1368, 1272, 1243, 1080, 985, 961, 942, 872 cm^{-1}; MS (EI) *m/z* (%) 306.(2.61) (M^+), 250 (6.02), 206 (41.08), 205 (94.30), 189 (23.01), 175 (35.34), 145 (23.06), 131 (36.81), 121 (13.11), 97 (28.71), 77 (19.60), 57 (87.43), 43 (100); HRMS (EI) Calcd for $C_{17}H_{22}O_5$ (M^+) requires 306.1467, Found 306.1460.

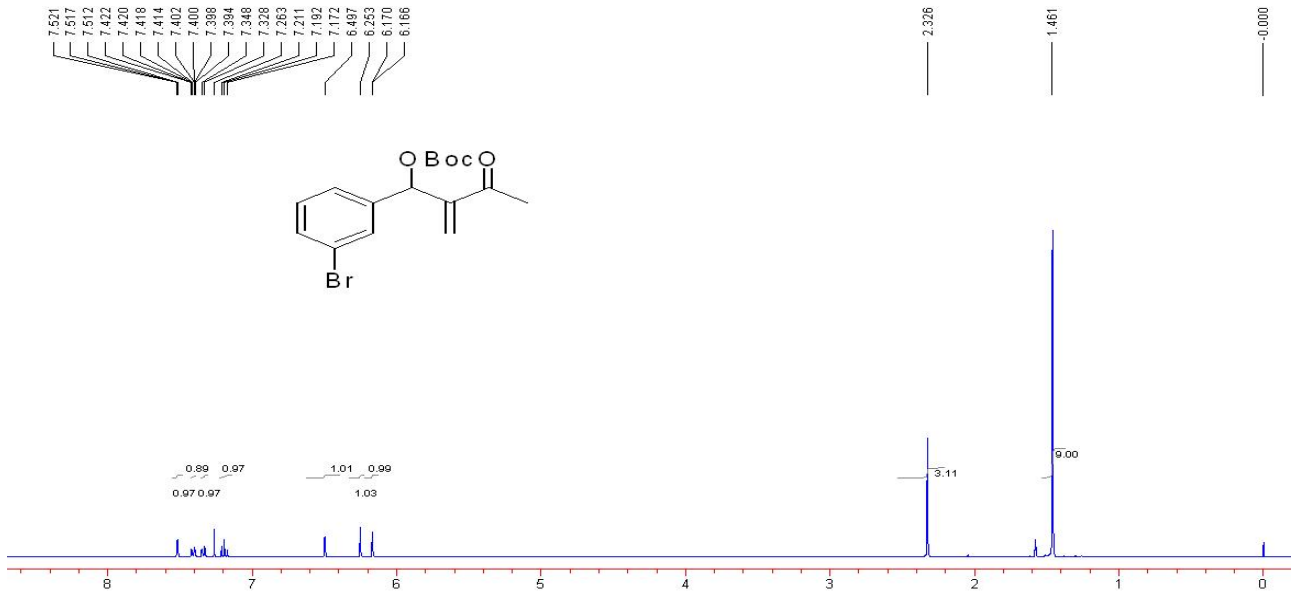


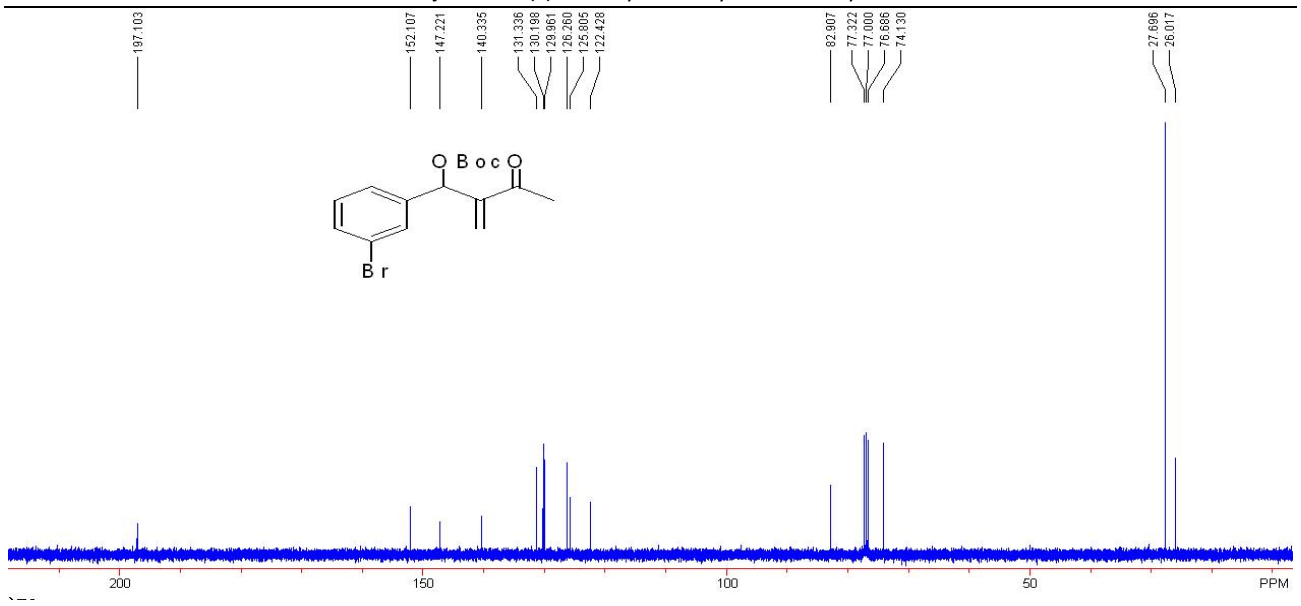


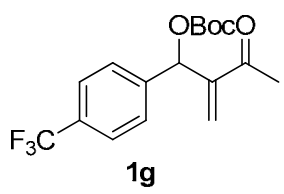


1f

1-(3-bromophenyl)-2-methylene-3-oxobutyl tert-butyl carbonate **1f**: a white solid; yield: 52%; m.p. 100-103 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.52-7.51 (m, 1H), 7.42-7.39 (m, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 8.0 Hz, 1H), 6.50 (s, 1H), 6.25 (s, 1H), 6.17 (d, *J* = 1.2 Hz, 1H), 2.33 (s, 3H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 152.1, 147.2, 140.3, 131.3, 130.2, 130.0, 126.3, 125.8, 122.4, 82.9, 74.1, 27.7, 26.0; IR (neat) ν 2981, 2927, 1746, 1681, 1573, 1475, 1370, 1280, 1159, 1085, 971, 789 cm^{-1}; MS (ESI) m/e 377 (M+Na); HRMS (ESI) for $C_{16}H_{19}BrNaO_4$ (M+Na): 377.0359; Found: 377.0354.

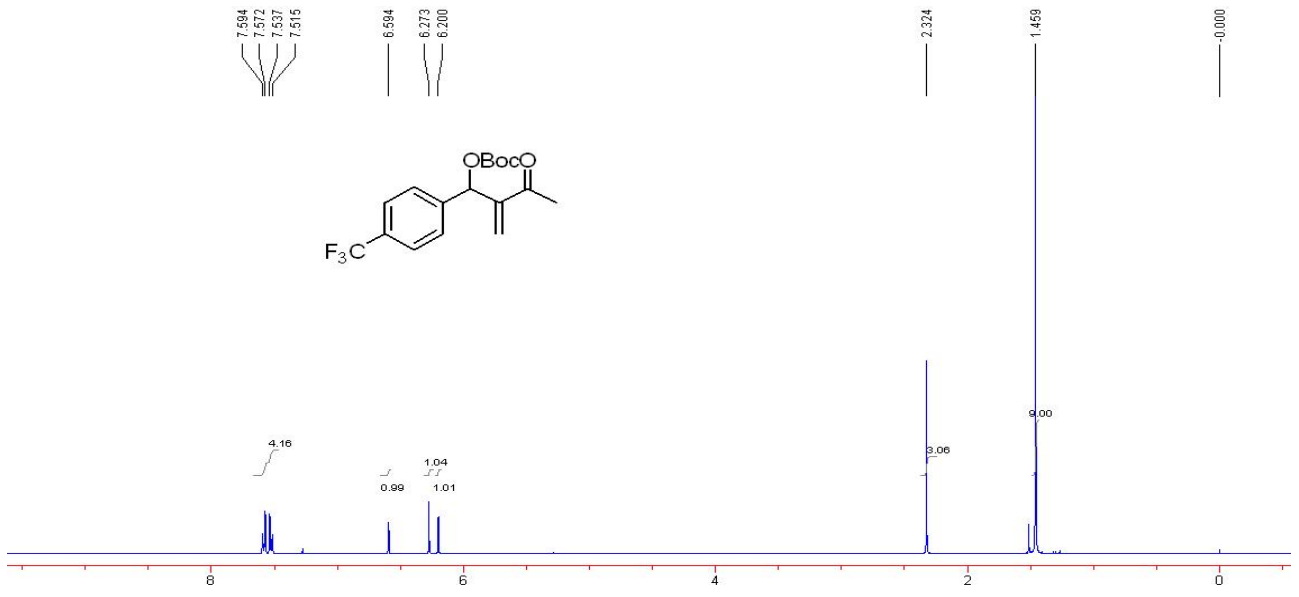


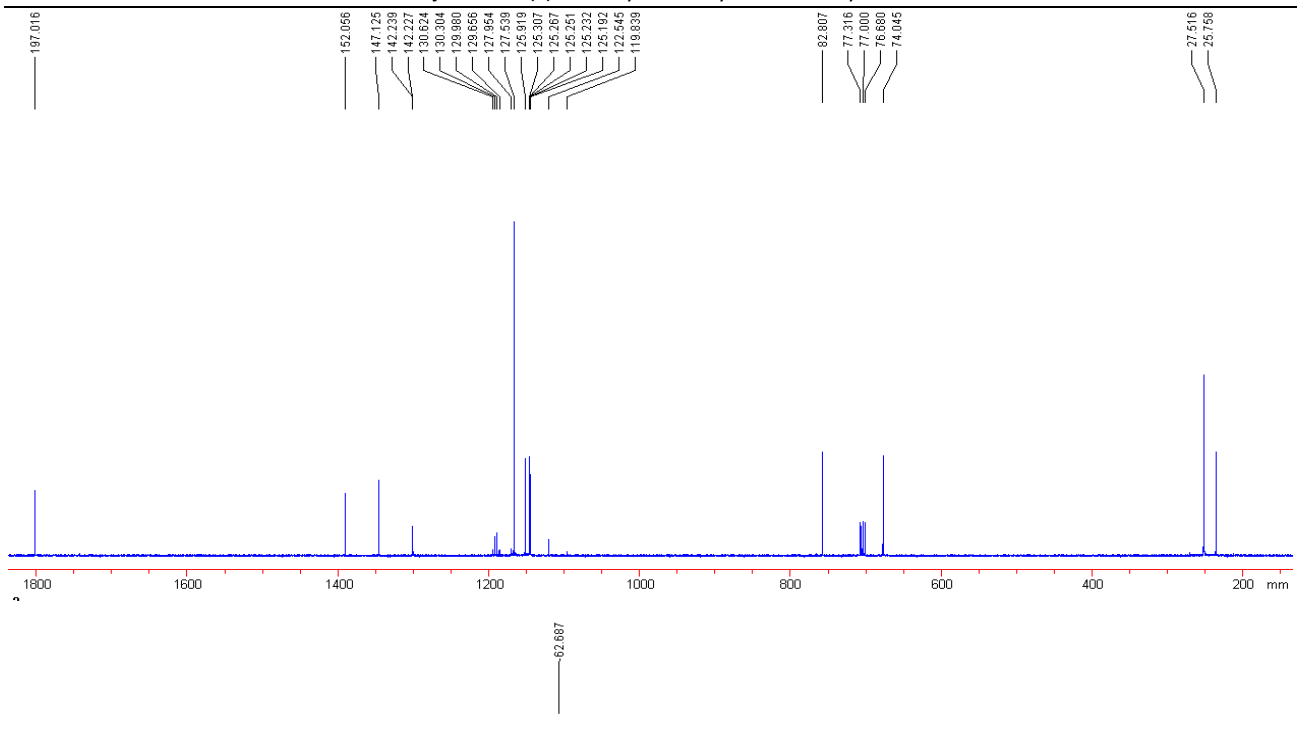


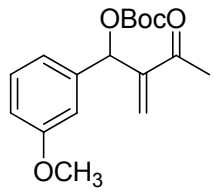


1g

tert-butyl 2-methylene-3-oxo-1-(4-(trifluoromethyl)phenyl)butyl carbonate **1g**: a white solid; yield: 45%; m.p. 89-93 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.58 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H), 6.59 (s, 1H), 6.27 (s, 1H), 6.20 (s, 1H), 2.32 (s, 3H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197, 152.1, 147.1, 142.2 (d, $J_{C\text{-}F}$ = 1.2 Hz), 130.2 (q, $J_{C\text{-}F}$ = 32.4 Hz), 127.5, 125.9, 125.3 (q, $J_{C\text{-}F}$ = 4.0 Hz), 123.9(q, $J_{C\text{-}F}$ = 271.0 Hz), 82.8, 74.1, 27.5; ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$): δ -62.7. IR (neat) ν 2983, 2936, 1748, 1682, 1608, 1421, 1371, 1277, 1165, 1068, 974, 853 cm^{-1}; MS (ESI) m/e 367 (M+Na); HRMS (ESI) for $C_{17}H_{19}F_3NaO_4$ (M+Na): 367.1128; Found: 367.1126.

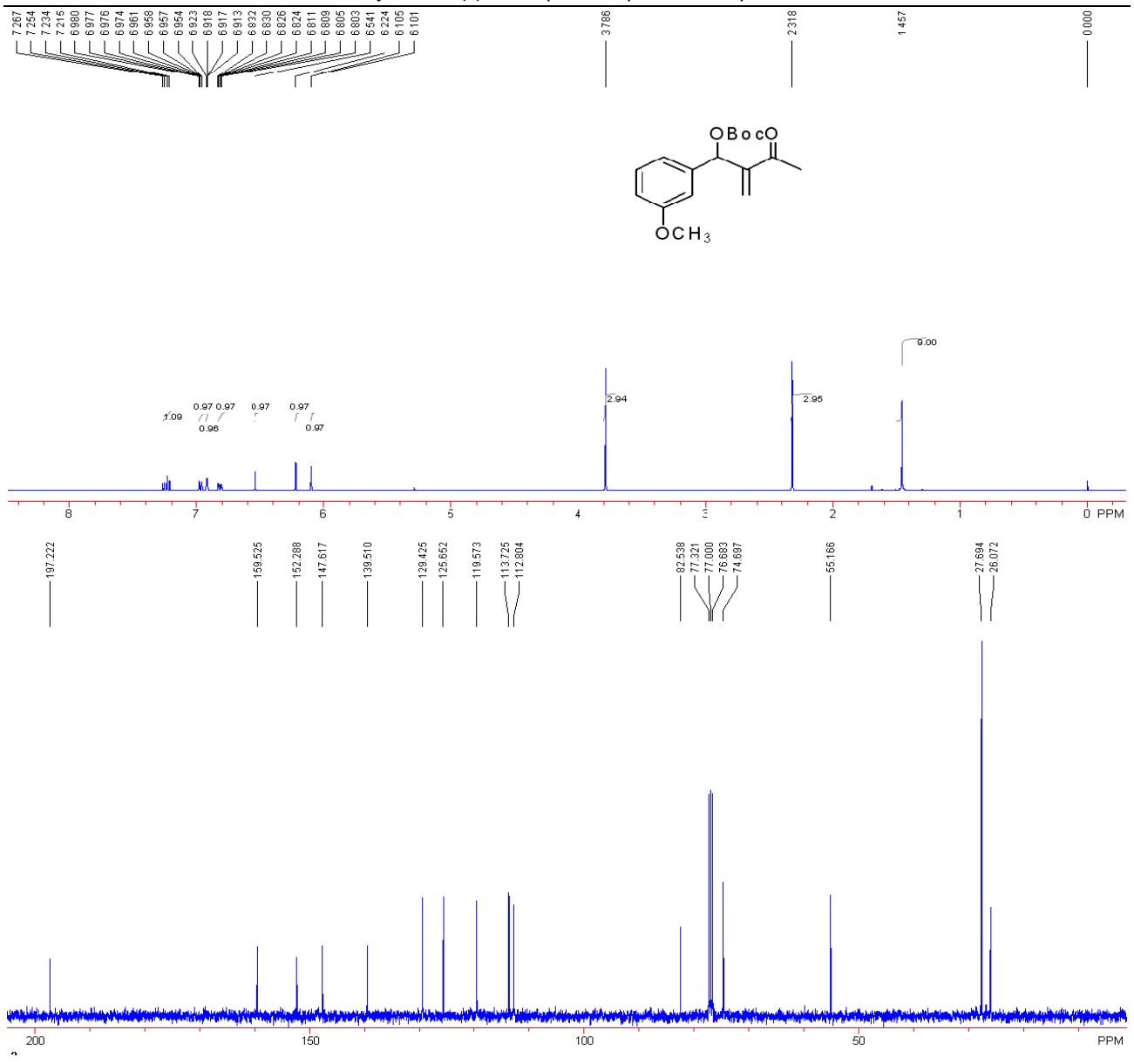






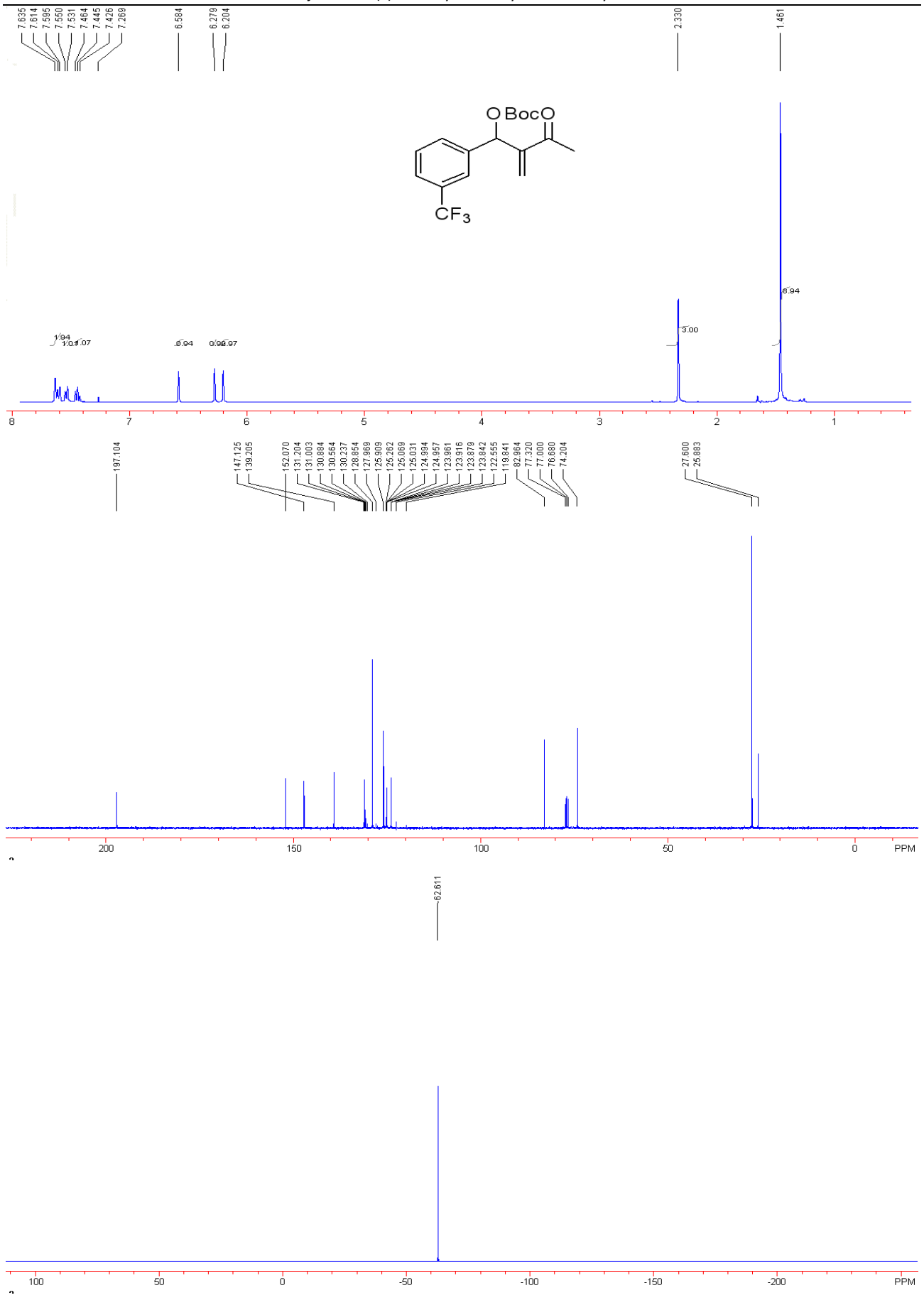
1h

tert-butyl 1-(3-methoxyphenyl)-2-methylene-3-oxobutyl carbonate **1h**: a colorless oil. yield: 75%; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.23 (t, *J* = 7.6 Hz, 1H), 6.98-6.95 (m, 1H), 6.92-6.91 (m, 1H), 6.83-6.81 (m, 1H), 6.54 (s, 1H), 6.22 (s, 1H), 6.10 (d, *J* = 1.2 Hz, 1H), 3.78 (s, 3H), 2.32 (s, 3H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 159.5, 152.3, 147.6, 139.5, 129.4, 125.7, 119.6, 113.7, 112.8, 82.5, 74.7, 55.2, 27.7, 26.1; IR (CH_2Cl_2) ν 2977, 2937, 1741, 1679, 1460, 1394, 1369, 1305, 1274, 1251, 1161, 1089, 1045, 942, 898 cm^{-1}; MS (EI) *m/z* (%) 306.(6.86) [M^+], 250 (4.51), 206 (42.71), 205 (55.37), 189 (16.61), 175 (59.06), 163 (6.09), 145 (10.07), 135 (11.34), 121 (20.08), 103 (15.47), 84 (11.10), 77 (13.19), 57 (100), 43 (87.19); HRMS (EI) Calcd for $C_{17}H_{22}O_5$ [M^+] requires 306.1467, Found 306.1462.



1i

tert-butyl 2-methylene-3-oxo-1-(3-(trifluoromethyl)phenyl)butyl carbonate **1i**: a white solid; yield: 61%; m.p. 48-49 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.61 (t, J = 8.4 Hz, 2H), 7.54 (d, J = 7.6 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 6.59 (s, 1H), 6.28 (s, 1H), 6.20 (s, 1H), 2.33 (s, 3H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197, 152.1, 147.1, 139.2, 131.0, 130.7 (q, $J_{C\text{-}F}$ = 32.0 Hz), 128.9, 128.0,125.9, 125.0 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.91 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.90 (q, $J_{C\text{-}F}$ = 270.7 Hz), 83.0, 74.2, 27.6; ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$): δ -62.6; IR (neat) ν 2983, 2972, 1749, 1675, 1327, 1285, 1272, 1251, 1160, 1119, 1072, 971, 956, 847 cm^{-1}; MS (ESI) m/e 367 (M+Na); HRMS (ESI) for $C_{17}H_{19}F_3NaO_4$ (M+Na): 367.1128; Found: 367.1130.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7.531
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7.445
7.426
7.269
6.584
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6.204
2.330
1.461
O BocO
CF3
1.94
1.01
1.07
0.94
0.96
0.97
3.00
8.94
8
7
6
5
4
3
2
1
197.104
147.125
139.205
152.070
131.204
131.003
130.884
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128.854
127.969
125.909
125.262
125.069
125.031
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123.842
122.555
119.841
82.964
77.320
77.000
76.680
74.204
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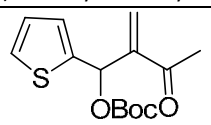
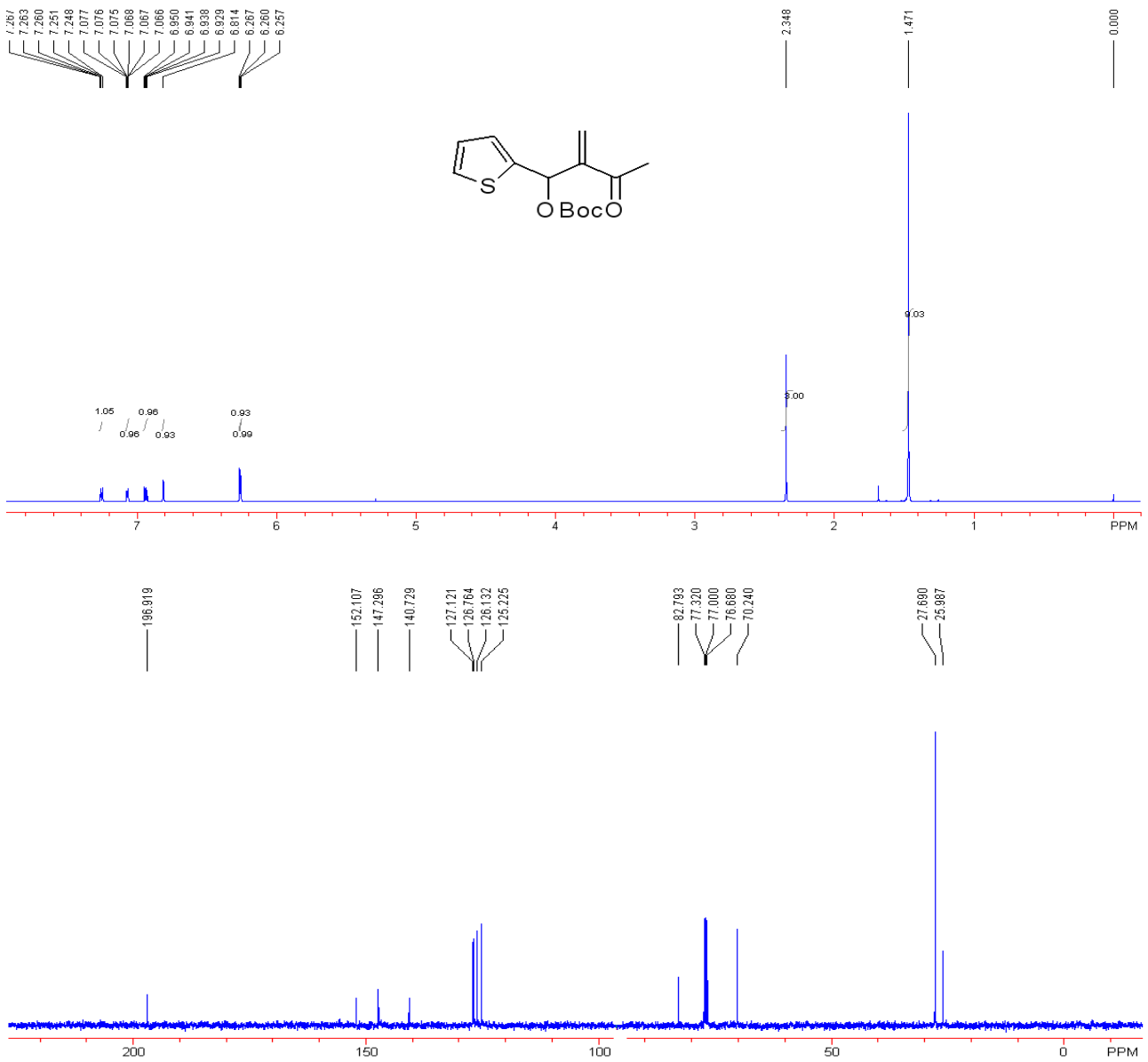
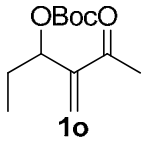
PPM



1n

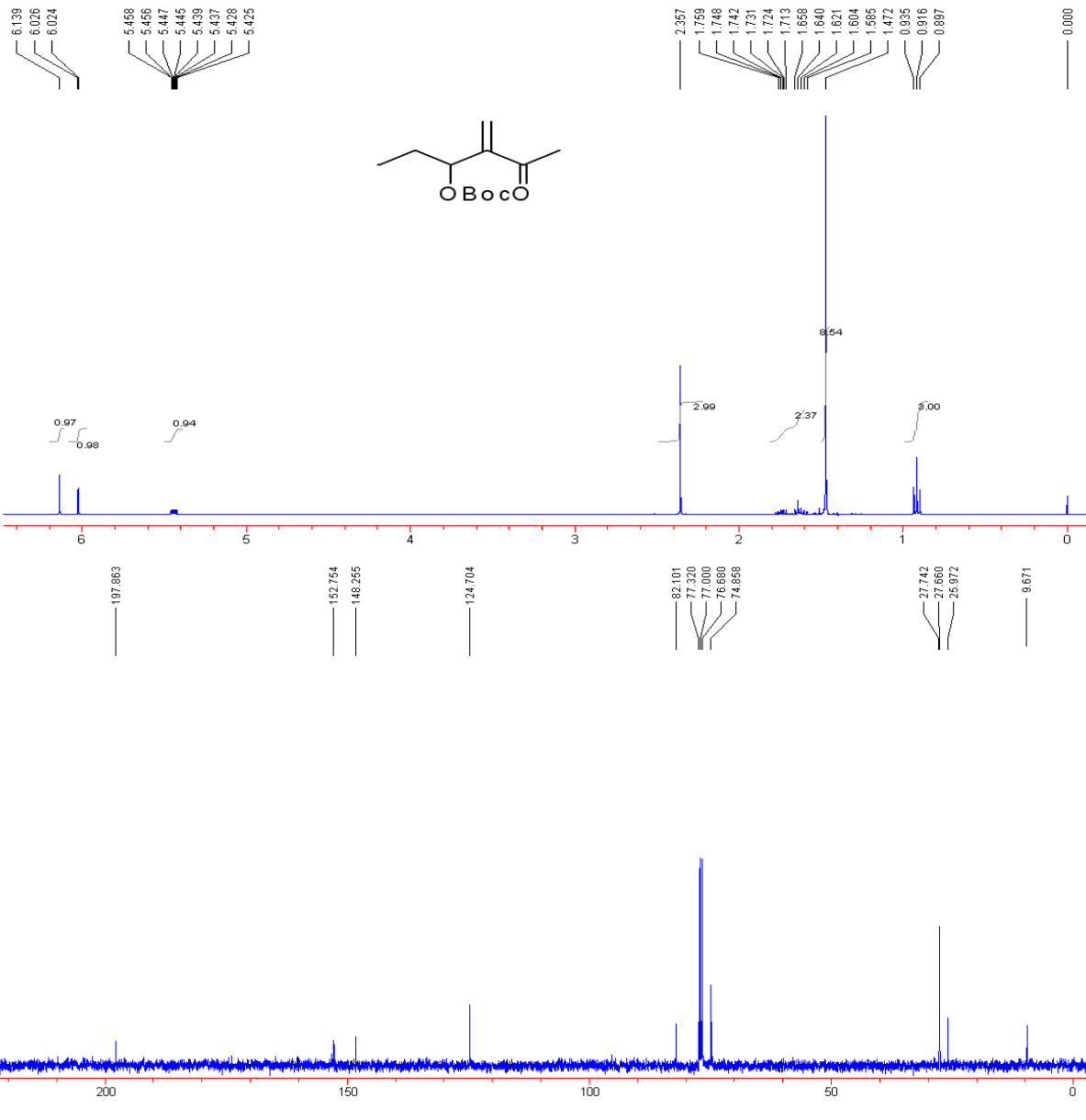
tert-butyl 2-methylene-3-oxo-1-(thiophen-2-yl)butyl carbonate **1n**: a white solid. yield: 32%; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.27-7.25 (m, 1H), 7.08-7.07 (m, 1H), 6.94 (dd, J_1 = 5.2, J_2 = 3.6, 1H), 6.81 (s, 1H), 6.27 (s, 1H), 6.26 (d, J = 1.2 Hz, 1H), 2.35 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 152.1, 147.3, 140.7, 127.1, 126.8, 126.1, 125.2, 82.8, 70.2, 27.7, 26.0; IR (CH_2Cl_2) ν 2978, 2926, 1736, 1631, 1431, 1393, 1370, 1316, 1344, 1299, 1252, 1155, 1076, 1043, 962, 923, 868, 847 cm^{-1}; MS (EI) *m/z* (%) 306.(6.86) [M^{+}], 250 (4.51), 206 (42.71), 205 (55.37), 189 (16.61), 175 (59.06), 163 (6.09), 145 (10.07), 135 (11.34), 121 (20.08), 103 (15.47), 84 (11.10), 77 (13.19), 57 (100), 43 (87.19); MS (ESI) m/e 305 (M+Na); HRMS (ESI) for $C_{14}H_{18}NaO_4S$ (M+Na): 305.0818; Found : 305.0821.



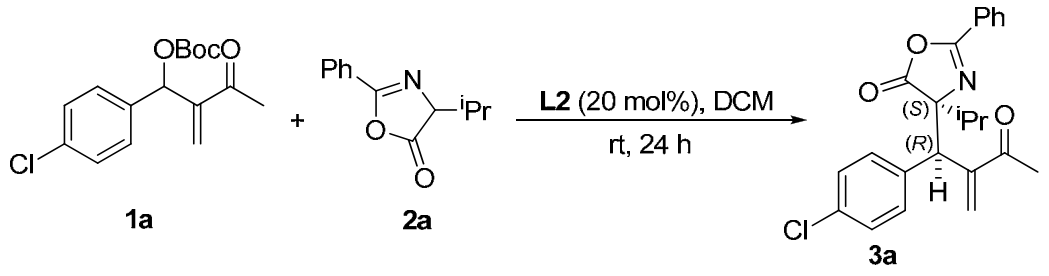


1o

tert-butyl 1-(3-methoxyphenyl)-2-methylene-3-oxobutyl carbonate **1o**: a colorless oil. yield: 16%; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 6.14 (s, 1H), 6.03 (d, *J* = 0.8 Hz, 1H), 5.46-5.43 (m, 1H), 2.36 (s, 3H), 1.78-1.59 (m, 2H), 1.47 (s, 9H), 0.91 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 152.8, 148.3, 124.7, 82.1, 74.9, 27.7, 27.6, 26.0, 9.7; IR (CH_2Cl_2) ν 2976, 1741, 1679, 1459, 1394, 1369, 1305, 1275, 1251, 1161, 1089, 1044, 942, 898 cm^{-1}; MS (ESI) m/e 251 (M+Na); HRMS (ESI) for $C_{12}H_{20}NaO_4$ (M+Na): 251.1254; Found: 251.1260.



General Procedure for the Preparation of 3 from the Reaction of 1a with 2a Using 3a as an Example in the Presence of L2



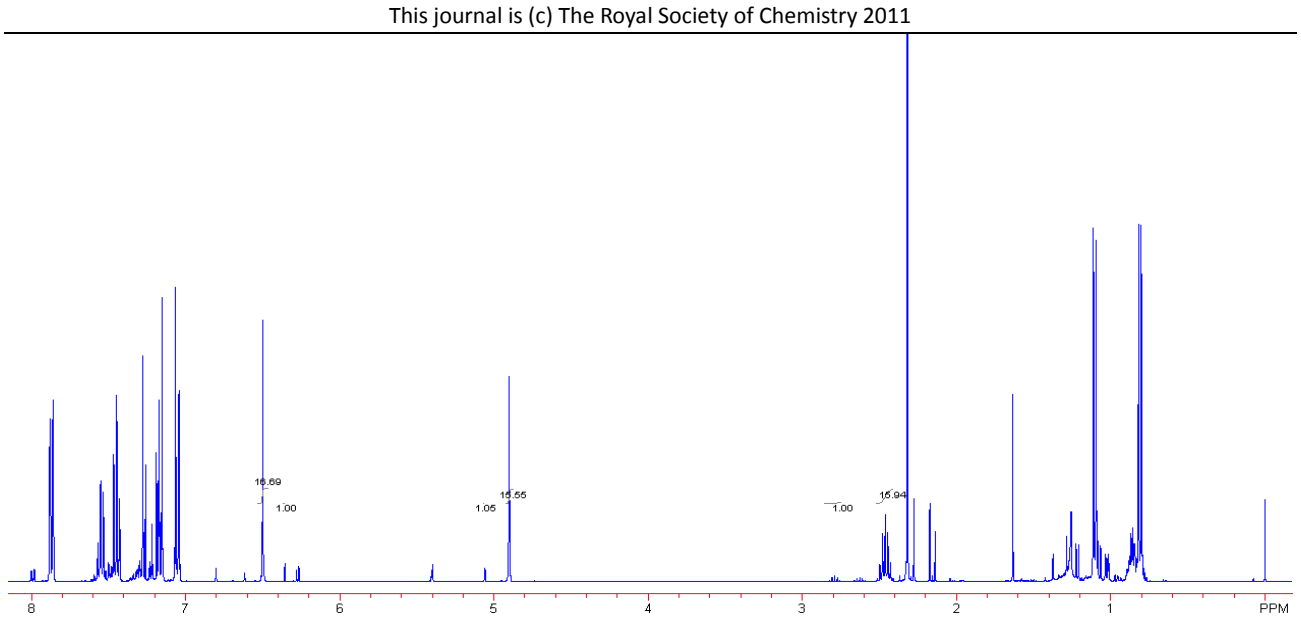
To a mixture of **1a** (0.11 mmol, 34 mg**)**, **2a** (0.10 mmol, 21 mg) and catalyst **L2** (13 mg, 0.020 mmol) was added 1.0 mL of dichloromethane at room temperature (20 ^{o}C) under argon. The reaction solution was monitored by TLC .After the reaction complete, the solution was concentrated under reduced pressure and the residue was further purified by silica gel column chromatography (EtOAc/PE = 1/16) to give the target product **3a**.

Preparative thin layer chromatography was performed to obtain the pure *syn*-adduct for spectroscopic analyses (eluent: DCM/PE = 2/1).

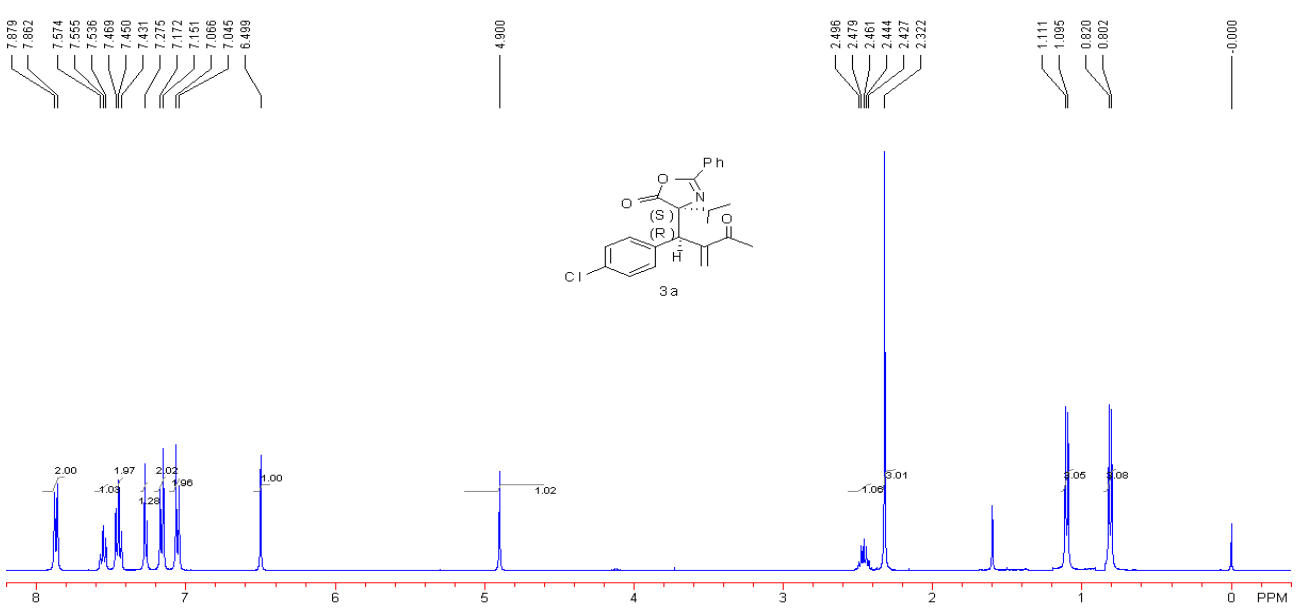
(*S*)-4-((*R*)-1-(4-chlorophenyl)-2-methylene-3-oxobutyl)-4-isopropy-2-phenyloxazol-5(4H)-one

3a: Following the general procedure, the *syn/anti* ratio (16:1) was determined by ^{1}H NMR spectroscopic analysis of the crude product (δ major 2.46 ppm, δ minor: 2.79 ppm). The mixture was purified by column chromatography using silica gel to give a mixture of diastereoisomer along with trace amount of impurity (34 mg, 86% overall yield in a diastereomeric ratio = 16:1). m.p. for *syn*-**3a** = 107-109 ^{o}C; $[\alpha]^{20}_{D}$ (*syn*-**3a**) = -52.0 (c 0.5, $CHCl_3$). IR (CH_2Cl_2): ν 2972, 1811, 1672, 1651, 1488, 1453, 1295, 1200, 1157, 1110, 1046, 1016, 961, 914, 887, 811, 783 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) for *syn*-**3a**: δ 7.87 (2H, d, *J* = 6.8 Hz, Ph-H), 7.56 (1H, t, *J* = 7.6 Hz, Ph-H), 7.45 (2H, t, *J* = 7.6 Hz, Ph-H), 7.27 (1H, s, =CH_2), 7.16 (2H, d, *J* = 8.4 Hz, Ar-H), 7.05 (2H, d, *J* = 8.4 Hz, Ar-H), 6.50 (1H, s, =CH_2), 4.90 (1H, s, Ar-CH), 2.46 (1H, qu, *J* = 6.8 Hz, -$CH(CH_3)_2$), 2.32 (3H, s, $COCH_3$), 1.10 (3H, d, *J* = 6.8 Hz, -$CH(CH_3)_2$), 0.81 (3H, d, *J* = 6.8 Hz, -$CH(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) for *syn*-***3a***: δ 198.0, 177.9, 160.3, 145.9, 135.0, 133.3, 132.7, 131.5, 128.8, 128.7, 128.0, 127.8, 125.4, 79.8, 46.2, 32.3, 25.6, 17.5, 15.3; MS (EI(*syn*-***3a***)) *m/z* (%) 395 (1.86) [M^+], 193 (35.40), 105 (84.48), 86 (51.69), 84 (82.05), 77 (32.57), 71 (8.47), 57 (11.35), 43 (100); HRMS (EI) Calcd for $C_{23}H_{22}ClNO_3$ [M^+] requires 395.1292, Found 395.1288; The ee of the *syn*-diastereomer was determined to be 97% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 90:10, 0.7 mL/min, λ = 230 nm, t (major) = 6.98 min, t (minor) = 8.57 min].

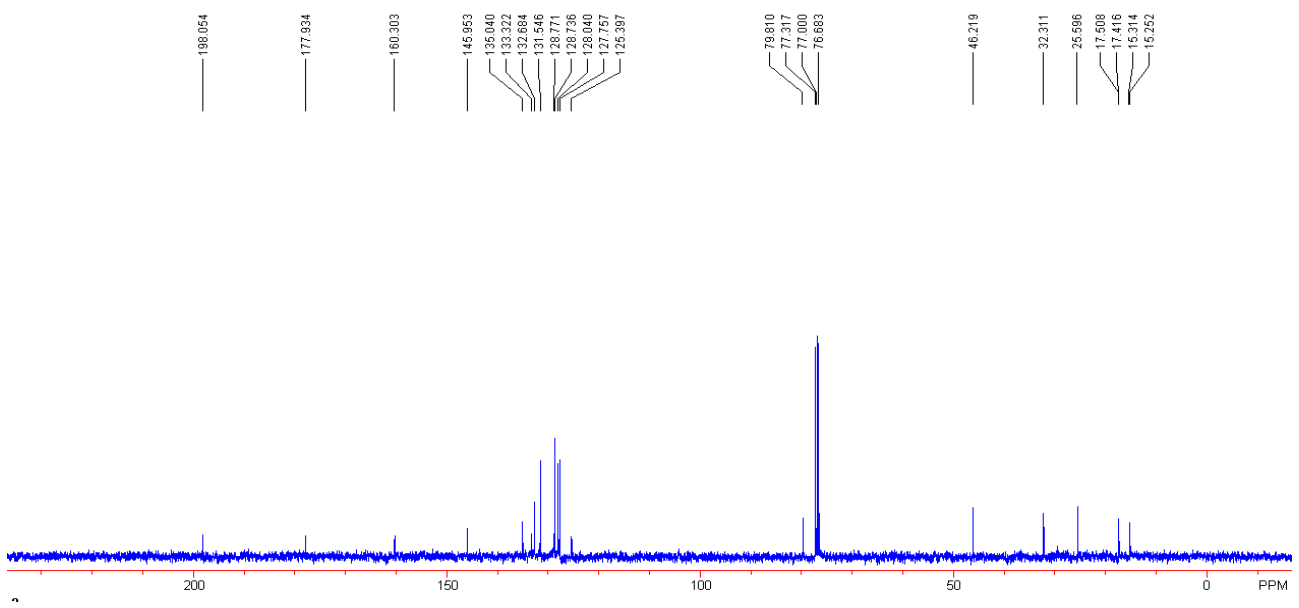
^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the crude product:

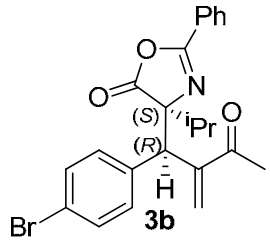


^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer



^{13}C NMR ($CDCl_3$, 100 MHz) for the *syn*-diastereomer



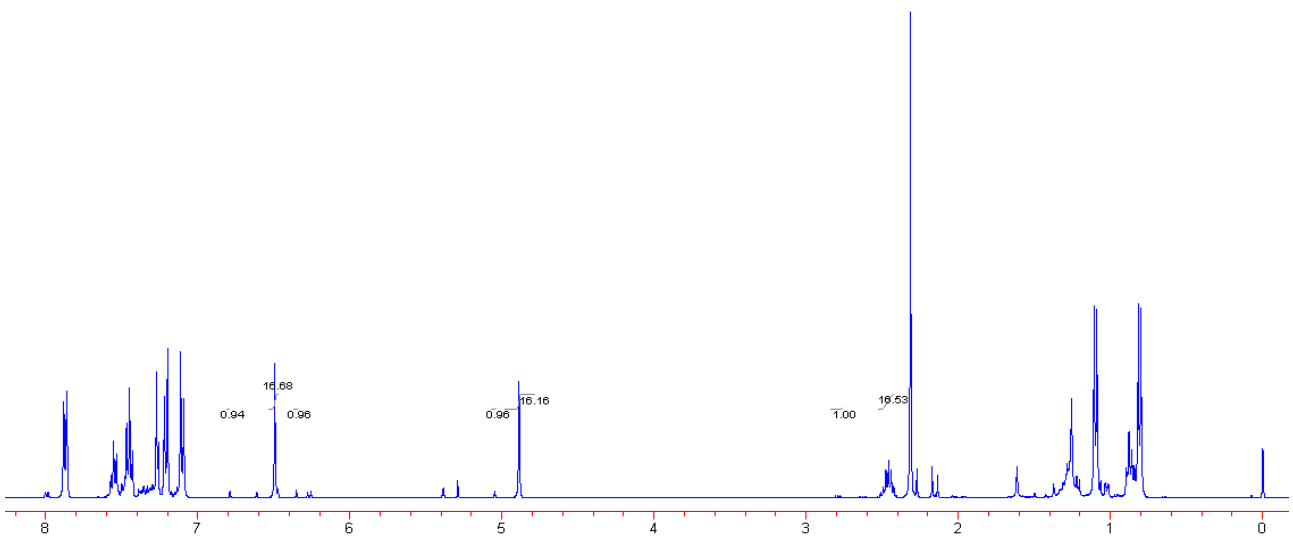


3b

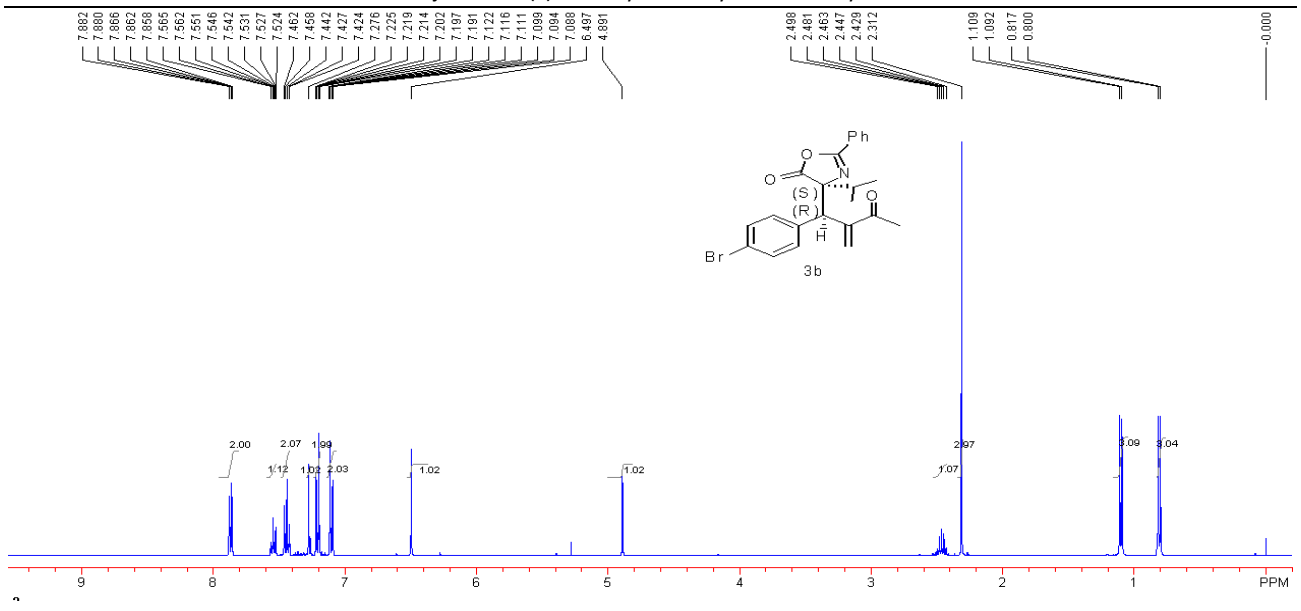
(*S*)-4-((*R*)-1-(4-bromophenyl)-2-methylene-3-oxobutyl)-4-isopropy-2-phenyloxazol-5(4H)-one

3b: Following the general procedure, the *syn/anti* ratio (16:1) was determined by ^{1}H NMR spectroscopic analysis of the crude product (δ major: 2.46 ppm, δ minor: 2.79 ppm). The mixture was purified by column chromatography using silica gel to give a mixture of diastereoisomer along with trace amount of impurity (36 mg, 82% overall yield in a diastereomeric ratio = 16:1); a white solid. m.p. for *syn*-**3b** = 103-105 ^{o}C; $[\alpha]^{20}_D$ (*syn*-**3b**) = -42.5 (c 1.0, $CHCl_3$). IR (CH_2Cl_2): ν 2922, 1811, 1678, 1651, 1485, 1454, 1342, 1296, 1157, 1113, 1072, 1047, 1022, 1010, 964, 911, 884, 811, 784 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$, TMS) for *syn*-**3b**: δ 7.88-7.86 (2H, m, Ph-H), 7.57-7.52 (1H, m, Ph-H), 7.46-7.42 (2H, m, Ph-H), 7.28 (1H, s, =CH_2), 7.21 (2H, d, *J* = 8.8 Hz, Ar-H), 7.10 (2H, d, *J* = 8.8 Hz, Ar-H), 6.50 (1H, s, =CH_2), 4.89 (1H, s, Ar-CH), 2.46 (1H, qu, *J* = 6.8 Hz, -$CH(CH_3)_2$), 2.31 (3H, s, $COCH_3$), 1.10 (3H, d, *J* = 6.8 Hz, -$CH(CH_3)_2$), 0.81 (3H, d, *J* = 6.8 Hz, -$CH(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 100 MHz) for *syn*-**3b**: δ 198.0, 177.9, 160.3, 145.9, 135.6, 132.9, 131.9, 130.9, 128.8, 128.7, 127.7, 125.3, 121.6, 79.7, 46.2, 32.3, 25.5, 17.5, 15.3; MS (EI(*syn*-**3b**)) *m/z* (%) 439 (2.07) [M^+], 239 (32.76), 237 (33.60), 202 (6.34), 158 (31.42), 115 (12.37), 105 (100.00), 77 (36.26), 43 (88.45); HRMS (EI) Calcd for $C_{23}H_{22}BrNO_3$ [M^+] requires 439.0783, Found 439.0785; The ee of the *syn*-diastereomer was determined to be 97% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 90:10, 0.7 mL/min, λ = 230 nm, t (major) = 7.28 min, t (minor) = 8.61 min].

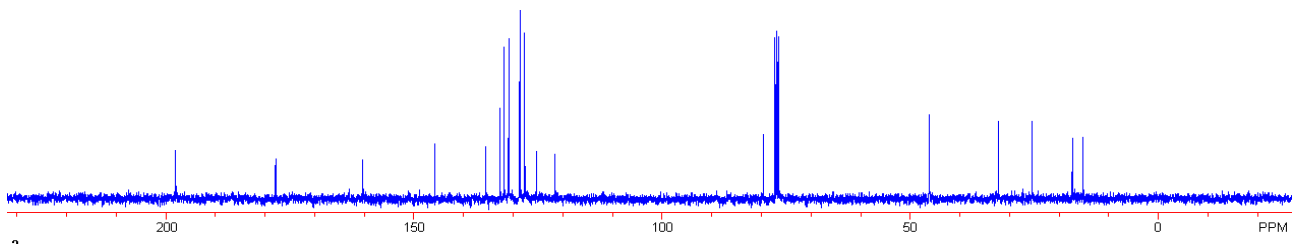
^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the crude product:

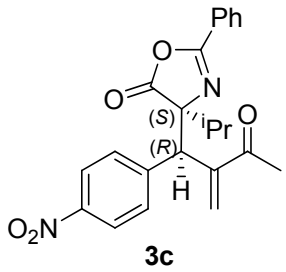


^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer



^{13}C NMR ($CDCl_3$, 100 MHz) for the *syn*-diastereomer



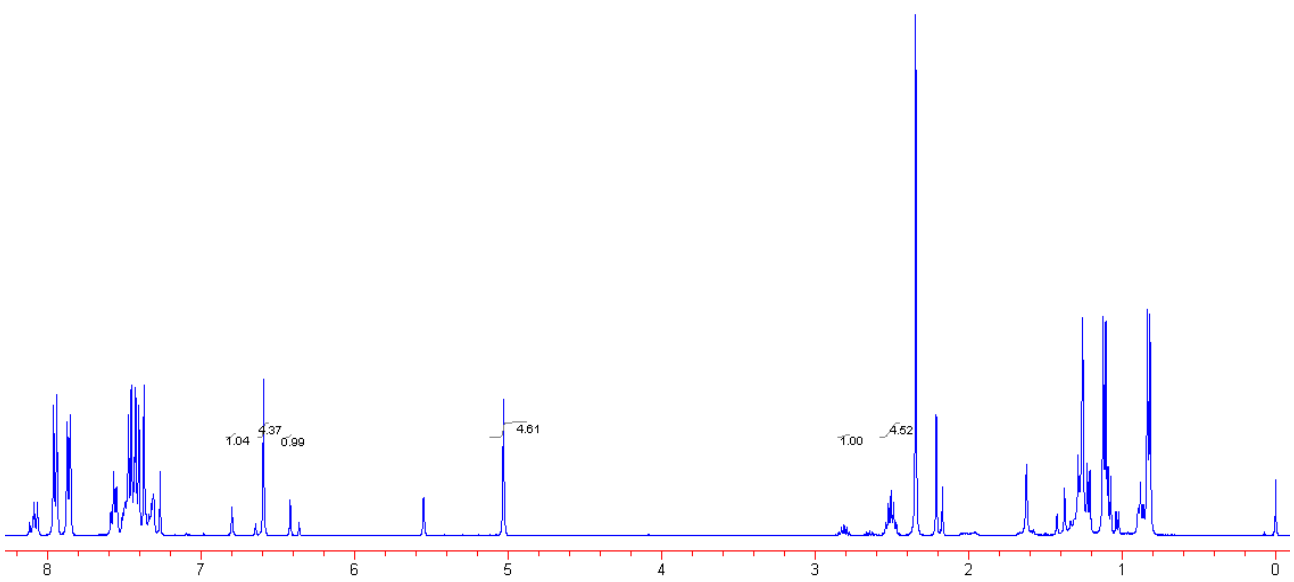


3c

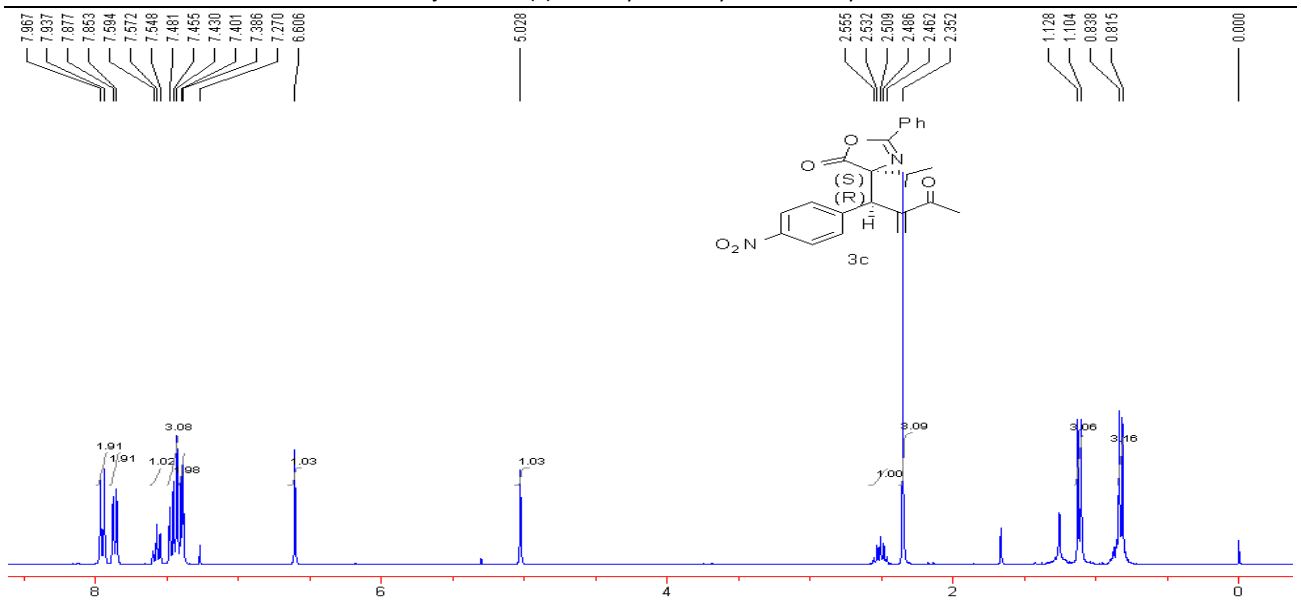
(*S*)-4-((*R*)-1-(4-nitrophenyl)-2-methylene-3-oxobutyl)-4-isopropy-2-phenyloxazol-5(4H)-one 3c: Following the general procedure, the *syn/anti* ratio (4:1) was determined by ^{1}H NMR spectroscopic analysis of the crude product (δ major: 2.51 ppm, δ minor: 2.79 ppm). The mixture was purified by column chromatography using silica gel to give a mixture of diastereoisomer along with trace amount of impurity (39 mg, 95% overall yield in a diastereomeric ratio = 4:1); a white solid. m.p. for *syn*-**3c** = 114-117 ^{o}C; $[\alpha]^{20}_{D}$ (*syn*-**3c**) = -79.7 (c 1.0, $CHCl_3$); $[\alpha]^{20}_{D}$ (*anti*-**3c**) = -139.5 (c 0.5,

$CHCl_3$). IR (CH_2Cl_2): ν(*syn*-**3c**) 2922, 1813, 1676, 1645, 1604, 1522, 1453, 1367, 1342, 1320, 1289, 1163, 1106, 1044, 1025, 973, 910, 877, 855, 833, 783 cm^{-1}; R (CH_2Cl_2): ν(*anti*-**3c**) 2961, 2925, 1782, 1680, 1646, 1605, 1522, 1493, 1450, 1347, 1258, 1174, 1070, 1015, 964, 859. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) for *syn*-**3c**: δ 7.95 (2H, d, *J* = 9.0 Hz, Ar-H), 7.87 (2H, d, *J* = 7.2 Hz, Ar-H), 7.57 (1H, t, *J* = 7.2 Hz, Ph-H), 7.48-7.39 (5H, m, Ph-H and $=CH_2$), 6.60 (1H, s, $=CH_2$), 5.03 (1H, s, Ar-CH), 2.51 (1H, qu, *J* = 7.2 Hz, $-CH(CH_3)_2$), 2.35 (3H, s, $COCH_3$), 1.11 (3H, d, *J* = 7.2 Hz, $-CH(CH_3)_2$), 0.81 (3H, d, *J* = 7.2 Hz, $-CH(CH_3)_2$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) for *anti*-**3c**: δ 8.10-8.05 (2H, m), 7.56-7.41 (4H, m), 7.36-7.31 (3H, m), 6.79 (1H, s), 6.41 (1H, s), 5.55 (1H, s), 2.79 (1H, qu, *J* = 6.8 Hz), 2.21 (3H, s), 1.22 (3H, d, *J* = 6.8 Hz), 1.10 (3H, d, *J* = 6.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) for *syn*-**3c**: δ 198.0, 177.6, 160.5, 147.0, 145.1, 144.2, 133.0, 131.1, 129.8, 128.8, 127.7, 124.9, 123.0, 79.4, 46.5, 32.4, 25.5, 17.4, 15.2; ^{13}C NMR (100 MHz, $CDCl_3$) for *anti*-**3c**: δ 197.2, 169.4, 163.3, 147.2, 144.5, 142.8, 137.1, 131.5, 130.8, 129.2, 128.5, 126.6, 123.1, 106.7, 51.2, 28.1, 25.1, 18.9; MS (EI(*syn*-**3c**)) *m/z* (%) 406 (0.12) [M^+], 202 (19.95), 174 (5.82), 115 (1.70), 105 (100.00), 77 (15.77), 51 (2.09), 43 (11.30); HRMS (EI) Calcd for $C_{23}H_{22}N_2O_5$ [M^+] requires 406.1529, Found 406.1531; MS (ESI(*anti*-**3c**)) m/e 407 (M^++H); HRMS (ESI) for $C_{23}H_{23}N_2O_5$ (M+H): 407.1610, Found: 407.1602; The ee of the *syn*-diastereomer was determined to be 98% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 90:10, 0.7 mL/min, λ = 230 nm, t (major) = 9.77 min, t (minor) = 12.36 min]; The ee of the *anti*-diastereomer was determined to be 94% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 90:10, 0.5 mL/min, λ = 230 nm, t (major) = 21.78 min, t (minor) = 20.54 min].

^{1}H NMR (300 MHz, $CDCl_3$, TMS) for the crude product:

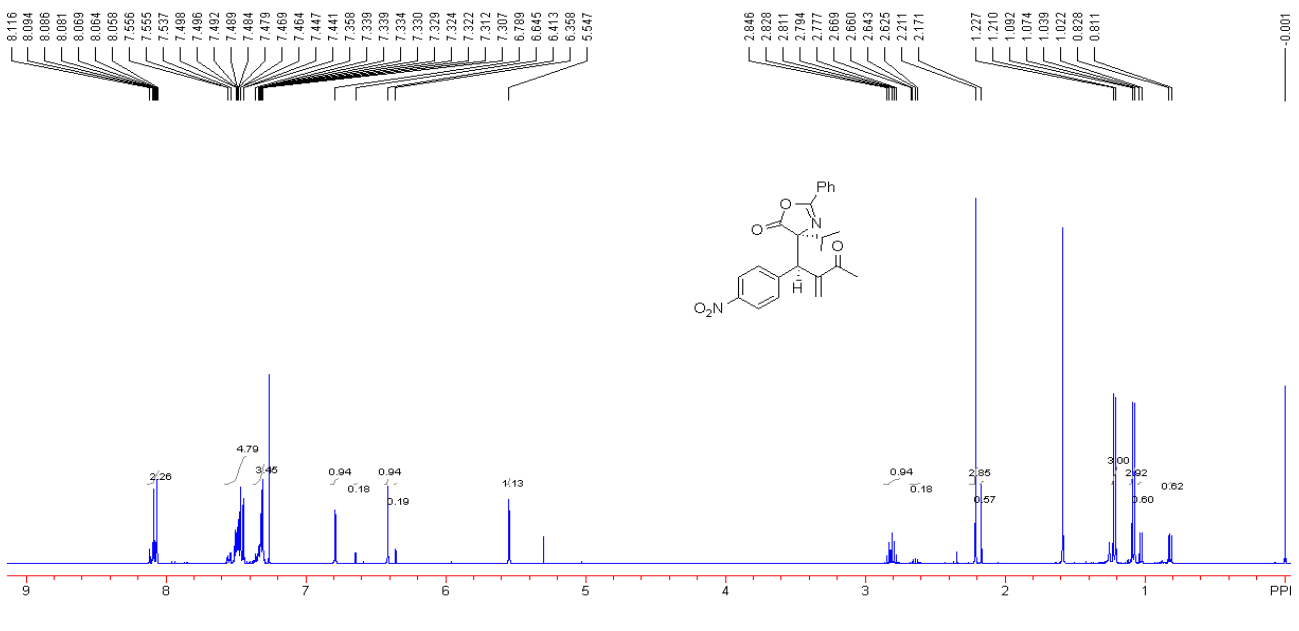


^{1}H NMR (300 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer

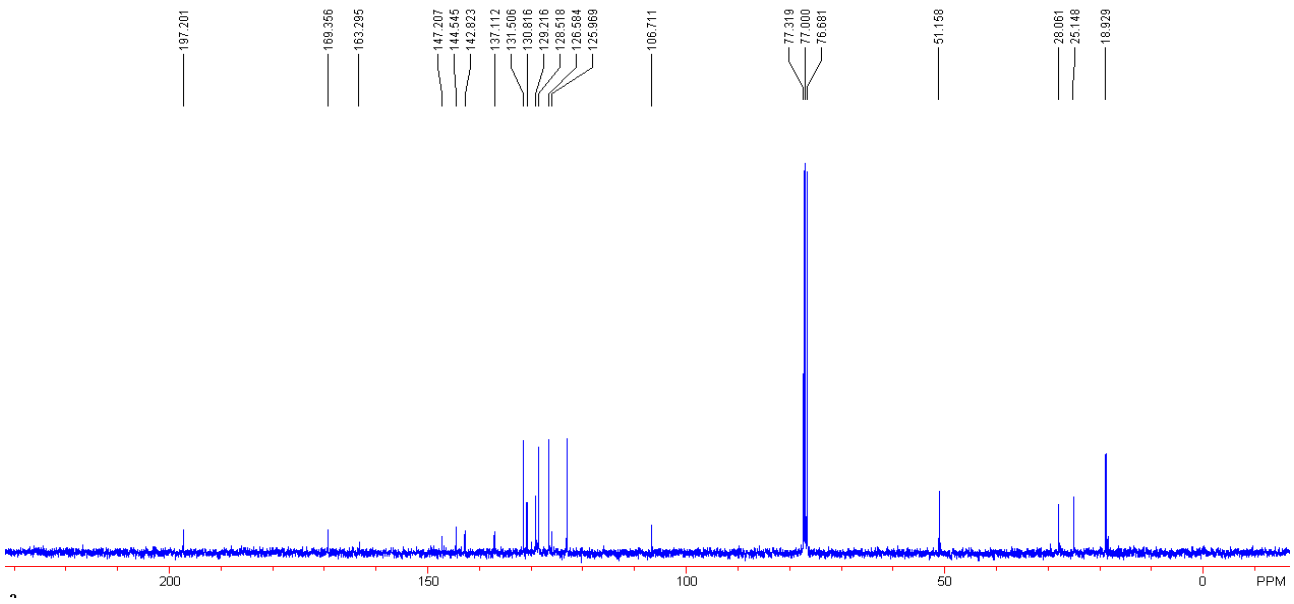


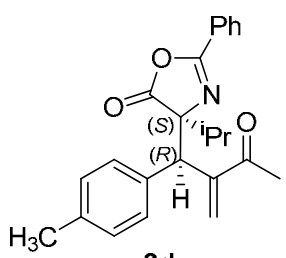
^{13}C NMR (75 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer

^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the *anti*-diastereomer



^{13}C NMR (100 MHz, $CDCl_3$, TMS) for the *anti*-diastereomer

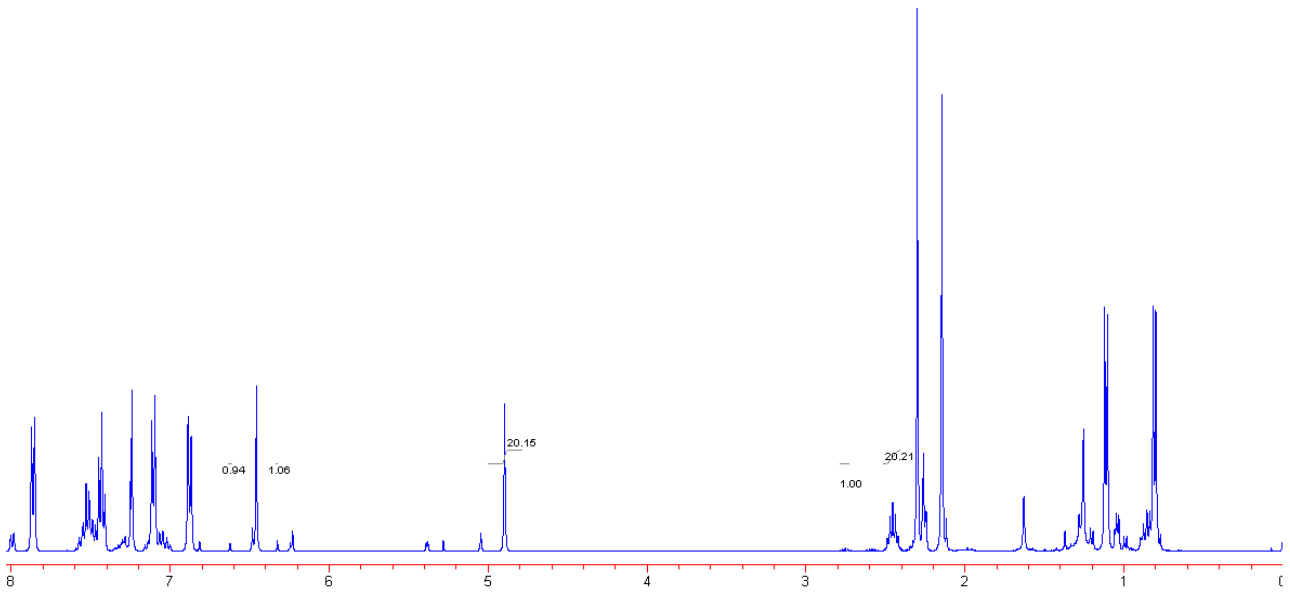




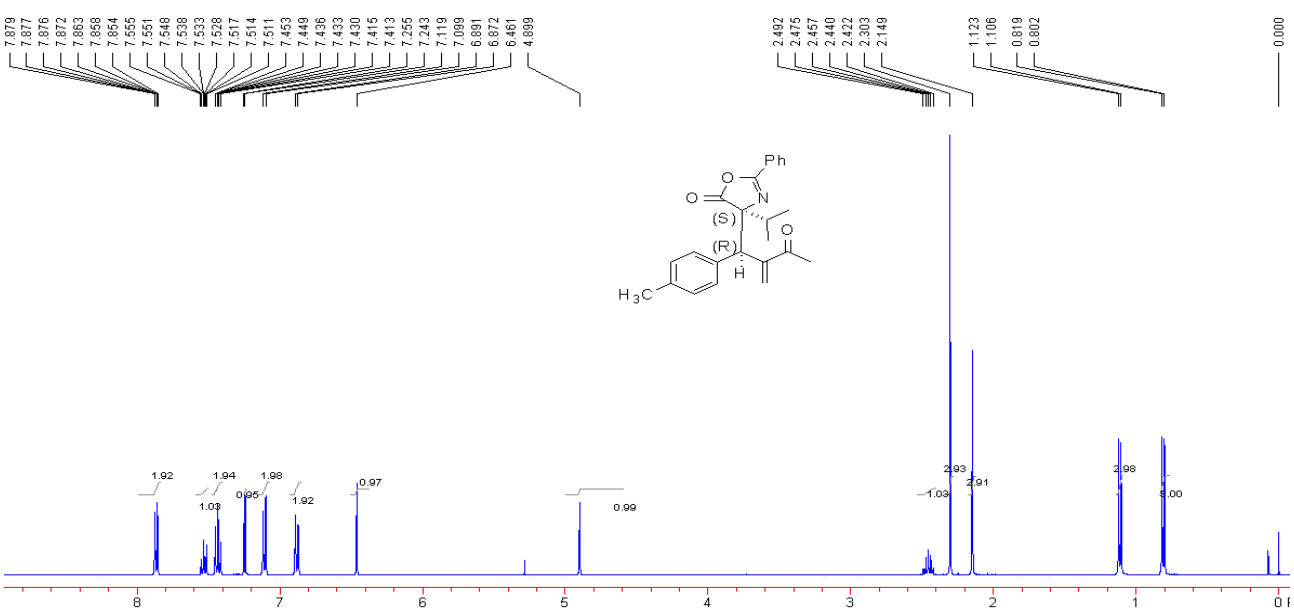
3d

(*S*)-4-isorpopyl-4-((*R*)-2-methylene-3-oxo-1-*p*-tolylbutyl)-2-phenyloxazol-5(4H)-one **3d**: Following the general procedure, the *syn/anti* ratio (20:1) was determined by ^{1}H NMR spectroscopic analysis of the crude product (δ major: 2.46 ppm, δ minor: 2.75 ppm). The mixture was purified by column chromatography using silica gel to give a mixture of diastereoisomers along with trace amount of impurity (34 mg, 91% overall yield in a diastereomeric ratio = 20:1); a white solid. m.p. for *syn*-**3d** = 90-93 ^oC; $[\alpha]^{20}_D$ (*syn*-**3d**) = -53.3 (c 0.7, $CHCl_3$). IR (CH_2Cl_2): ν 2921, 1812, 1679, 1652, 1322, 1294, 1046, 1022, 963, 909, 882, 810, 785 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) for *syn*-**3d**: δ 7.88-7.85 (2H, m, Ph-H), 7.55-7.51 (1H, m, Ph-H), 7.46-7.41 (2H, m, Ph-H), 7.24 (1H, s, $=CH_2$), 7.10 (2H, d, *J* = 8.0 Hz, Ar-H), 6.88 (2H, d, *J* = 7.6 Hz, Ar-H), 6.46 (1H, s, $=CH_2$), 4.90 (1H, s, Ar-CH), 2.46 (1H, qu, *J* = 6.8 Hz, $-CH(CH_3)_2$), 2.30 (3H, s, $COCH_3$), 2.15 (3H, s, $PhCH_3$), 1.11 (3H, d, *J* = 6.8 Hz, $-CH(CH_3)_2$), 0.81 (3H, d, *J* = 6.8 Hz, $-CH(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) for *syn*-**3d**: δ 198.2, 178.1, 160.0, 146.4, 136.9, 133.3, 132.4, 130.0, 128.6, 128.5, 128.3, 127.7, 125.7, 80.1, 46.5, 32.3, 25.7, 20.9, 17.6, 15.4; MS (EI(*syn*-**3d**)) *m/z* (%) 375 (1.26) [M^+], 173 (41.78), 131 (8.05), 115 (4.62), 105 (33.00), 86 (14.60), 84 (22.95), 77 (22.56), 43 (100); HRMS (EI) Calcd for $C_{24}H_{25}NO_3$ [M^+] requires 375.1834, Found 375.1834; The ee of the *syn*-diastereomer was determined to be 96% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 90:10, 0.7 mL/min, λ = 230 nm, t (major) = 6.78 min, t (minor) = 7.78 min].

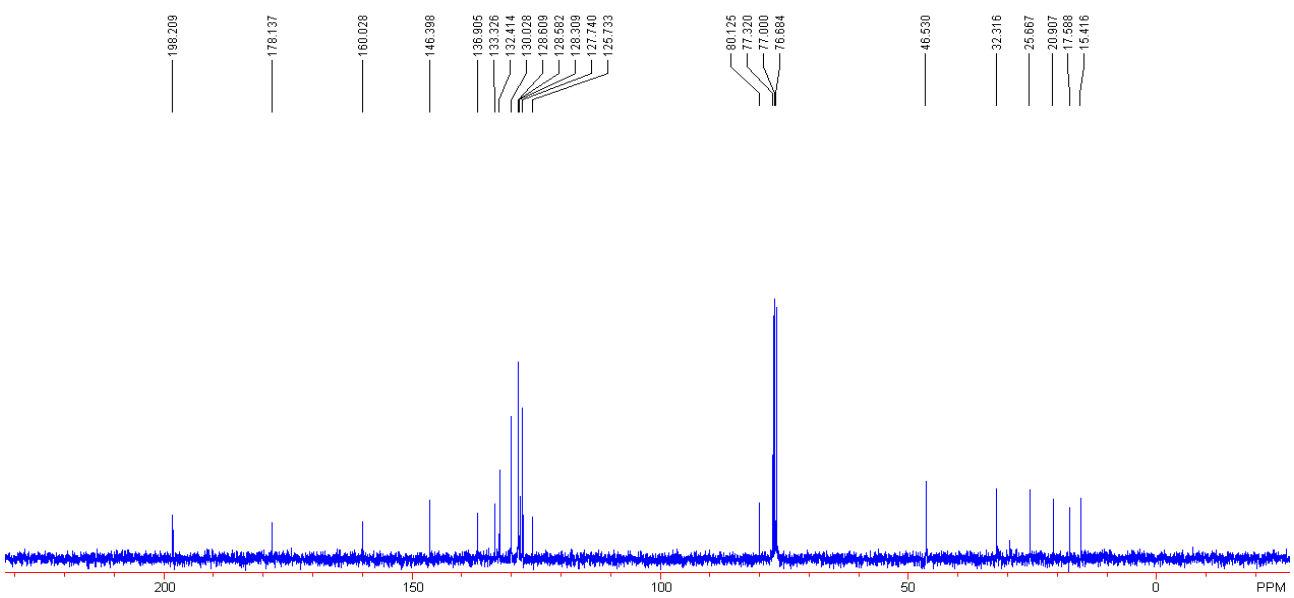
^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the crude product

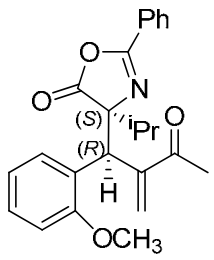


^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer



^{13}C NMR (100 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer

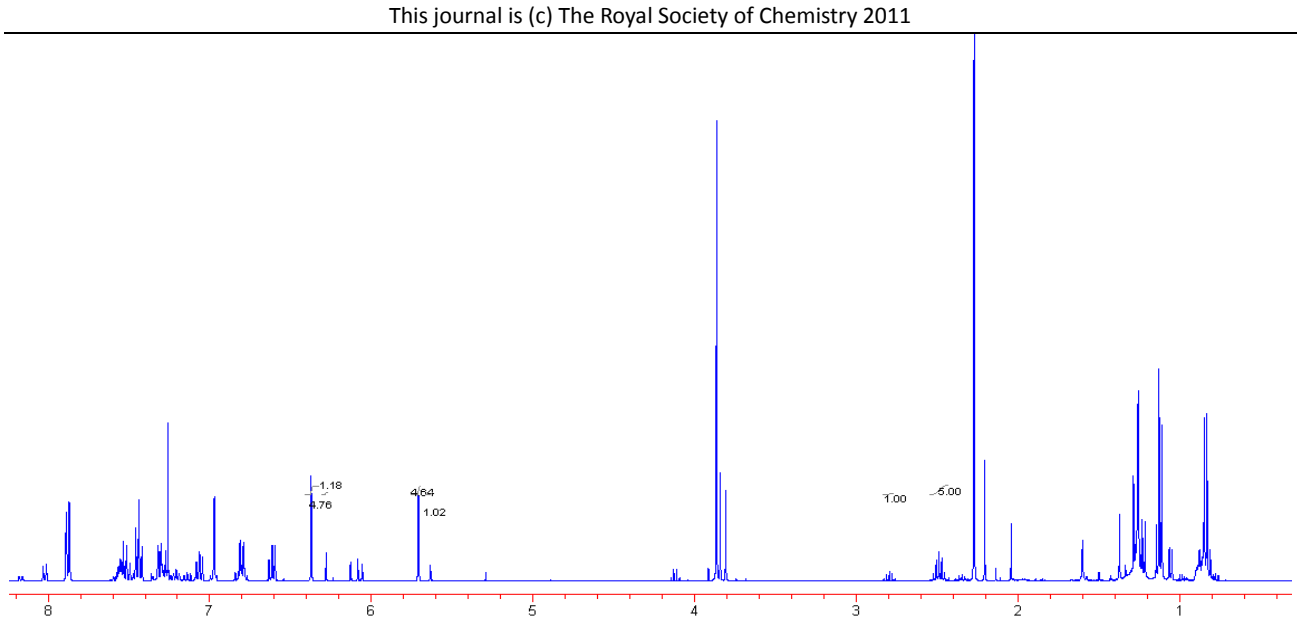




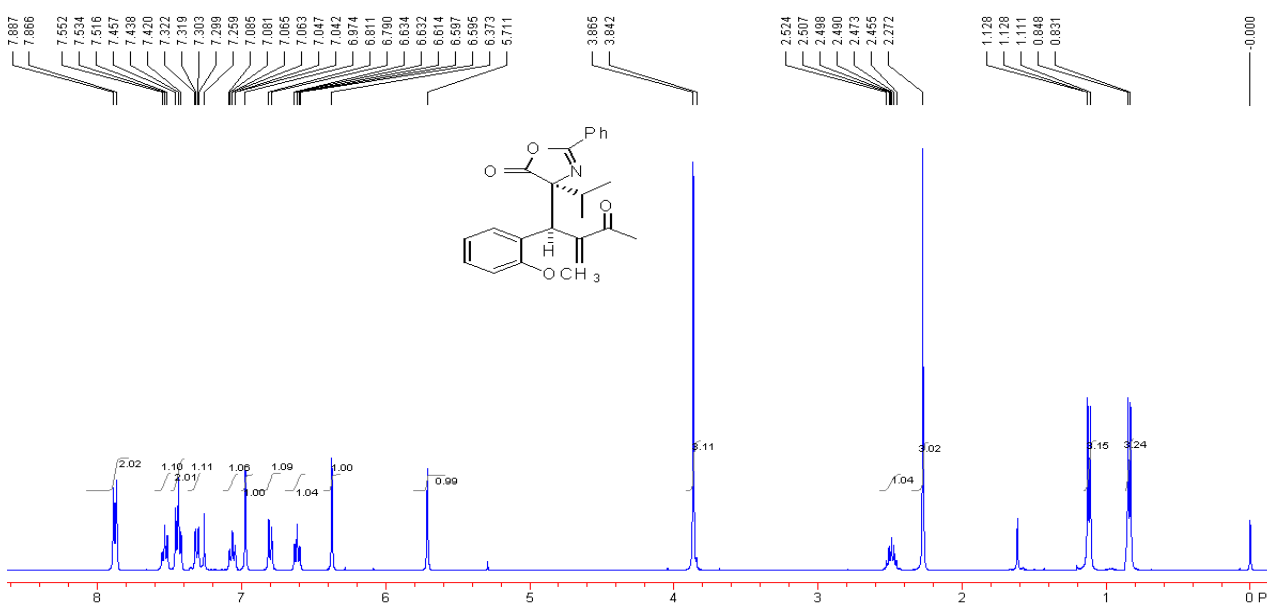
3e

(*S*)-4-isorpopyl-4-((*R*)-1-(2-methoxyphenyl)-2-methylene-3-oxobutyl)-2-phenyloxazol-5(4H)-one 3e: Following the general procedure, the *syn/anti* ratio (5:1) was determined by ^{1}H NMR spectroscopic analysis of the crude product (δ major: 2.45 ppm, δ minor: 2.79 ppm). The mixture was purified by column chromatography using silica gel to give a mixture of diastereoisomers along with trace amount of impurity (37 mg, 94% overall yield in a diastereomeric ratio = 5:1). m.p. for *syn*-**3e** = 119-121 ^{o}C; $[\alpha]^{20}_{D}$ (*syn*-**3e**) = +55.5 (c 0.7, $CHCl_3$); $[\alpha]^{20}_{D}$ (*anti*-**3e**) = -7.7 (c 0.5, $CHCl_3$). IR (CH_2Cl_2): ν(*syn*-**3e**) 2921, 1817, 1676, 1647, 1489, 1461, 1449, 1344, 1290, 1240, 1198, 1154, 1109, 1043, 1023, 955, 910, 882, 787, 728 cm^{-1}; IR (CH_2Cl_2): ν(*anti*-**3e**) 2961, 2926, 2854, 1826, 1780, 1685, 1655, 1599, 1492, 1258, 1216, 1169, 1105, 1072, 1022, 951, 881, 800.^{1}H NMR (400 MHz, $CDCl_3$, TMS) for *syn*-**3e**: δ 7.88 (2H, d, J = 8.4 Hz, Ph-H), 7.53 (1H, t, J = 7.2 Hz, Ph-H), 7.44 (2H, t, J = 7.2 Hz, Ph-H), 7.31 (1H, dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, Ar-H), 7.09-7.04 (1H, m, Ar-H), 6.97 (1H, s, $=CH_2$), 6.83-6.81 (1H, m, Ar-H), 6.63-6.60 (1H, m, Ar-H), 6.37 (1H, s, $=CH_2$), 5.71 (1H, s, Ar-CH), 3.87 (3H, s, Ar-OCH_3), 2.45 (1H, qu, J = 6.8 Hz, -$CH(CH_3)_2$), 2.27 (3H, s, $COCH_3$), 1.12 (3H, d, J = 6.8 Hz, -$CH(CH_3)_2$), 0.84 (3H, d, J = 6.8 Hz, -$CH(CH_3)_2$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) for *anti*-**3e**: δ 7.57-7.55 (2H, m), 7.34-7.24 (5H, m), 6.88-6.73 (2H, m), 6.60 (1H, s), 6.29 (1H, s), 6.01 (1H, s), 3.84 (3H, s), 2.79 (1H, qu, J = 6.8 Hz), 2.21 (3H, s), 1.22 (3H, d, J = 6.8 Hz), 1.13 (3H, d, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) for *syn*-**3e**: δ 198.5, 177.7, 159.9, 157.1, 147.4, 132.4, 130.9, 128.6, 128.4, 128.3, 127.7, 125.8, 125.3, 119.4, 111.4, 80.0, 56.0, 38.1, 32.5, 26.0, 17.4, 15.8; ^{13}C NMR (100 MHz, $CDCl_3$) for *anti*-**3e**: δ 197.7, 168.5, 158.1, 146.1, 137.8, 130.5, 129.9, 128.7, 128.3, 128.1, 127.3, 126.7, 126.1, 119.6, 111.3, 69.9, 56.1, 43.3, 28.0, 27.7, 25.7, 19.0, 18.8; MS (EI(syn-**3e**)) *m/z* (%) 391 (0.51) [M^+], 190 (6.62), 189 (47.94), 147 (20.16), 131 (6.13), 115 (4.41), 105 (31.61), 86 (61.28), 84 (100.00), 77 (23.16), 43 (89.95); HRMS (EI) Calcd for $C_{24}H_{25}NO_4$ [M^+] requires 391.1784, Found 391.1785; MS (ESI(*anti*-**3e**)) m/e 392 (M^++H); HRMS (ESI) for $C_{24}H_{26}NO_4$ (M^++H): 392.1861, Found: 392.1856. The ee of the *syn*-diastereomer was determined to be 95% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 90:10, 0.7 mL/min, λ = 230 nm, t (major) = 7.02 min, t (minor) = 8.57 min]; The ee of the *anti*-diastereomer was determined to be 94% [determined by HPLC, Chiralpak IC-H, n-hexane/isopropanol = 95:5, 0.3 mL/min, λ = 230 nm, t (major) = 31.09 min, t (minor) = 31.33 min].

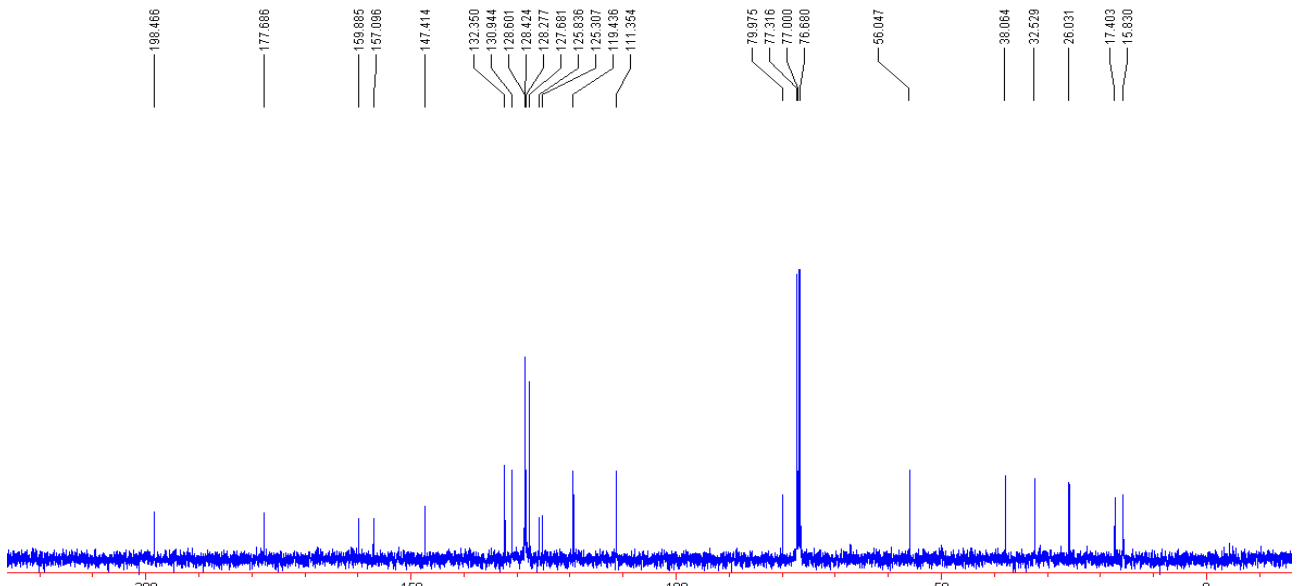
^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the crude product



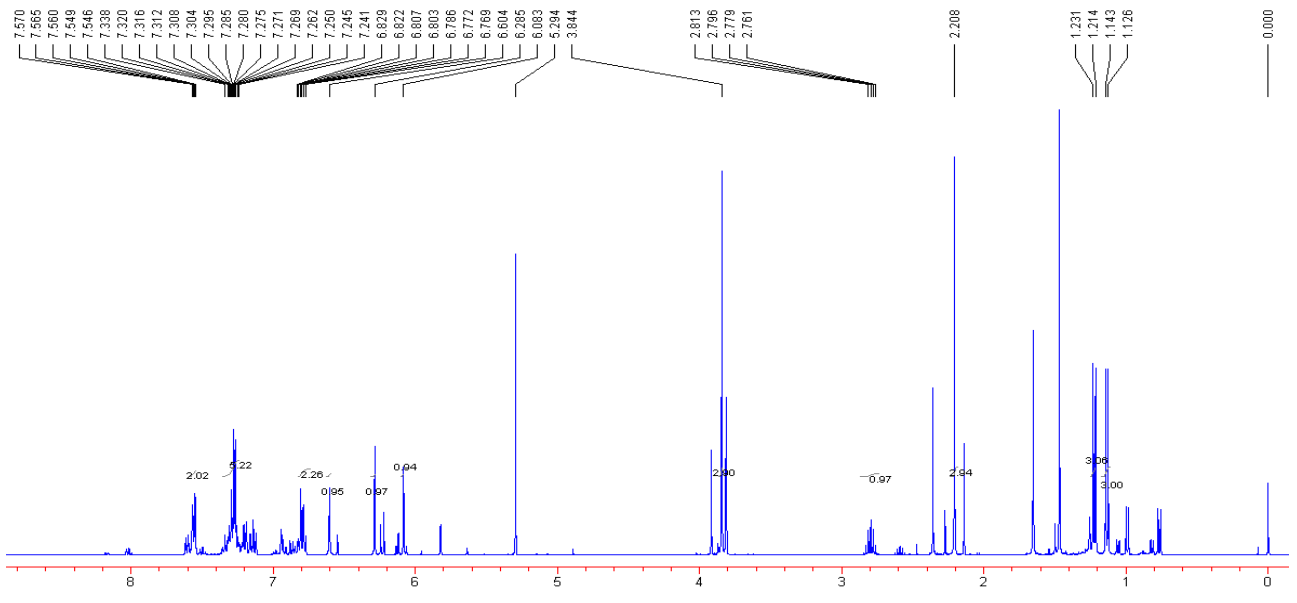
^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer



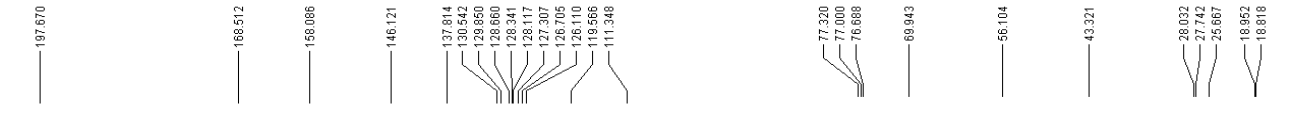
^{13}C NMR (100 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer

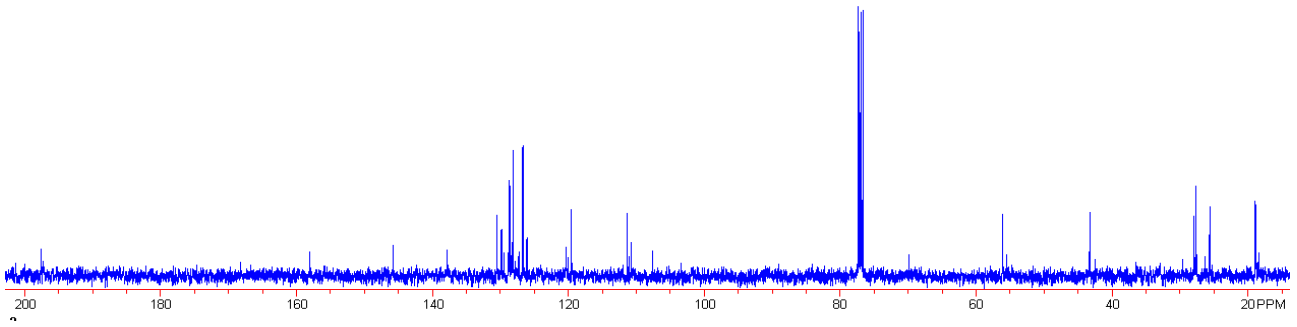


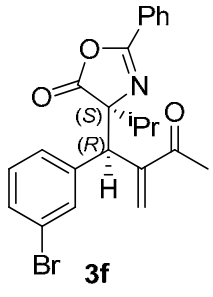
^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the *anti*-diastereomer (containing some impurities)



^{13}C NMR (100 MHz, $CDCl_3$, TMS) for the *anti*-diastereomer (containing some impurities)







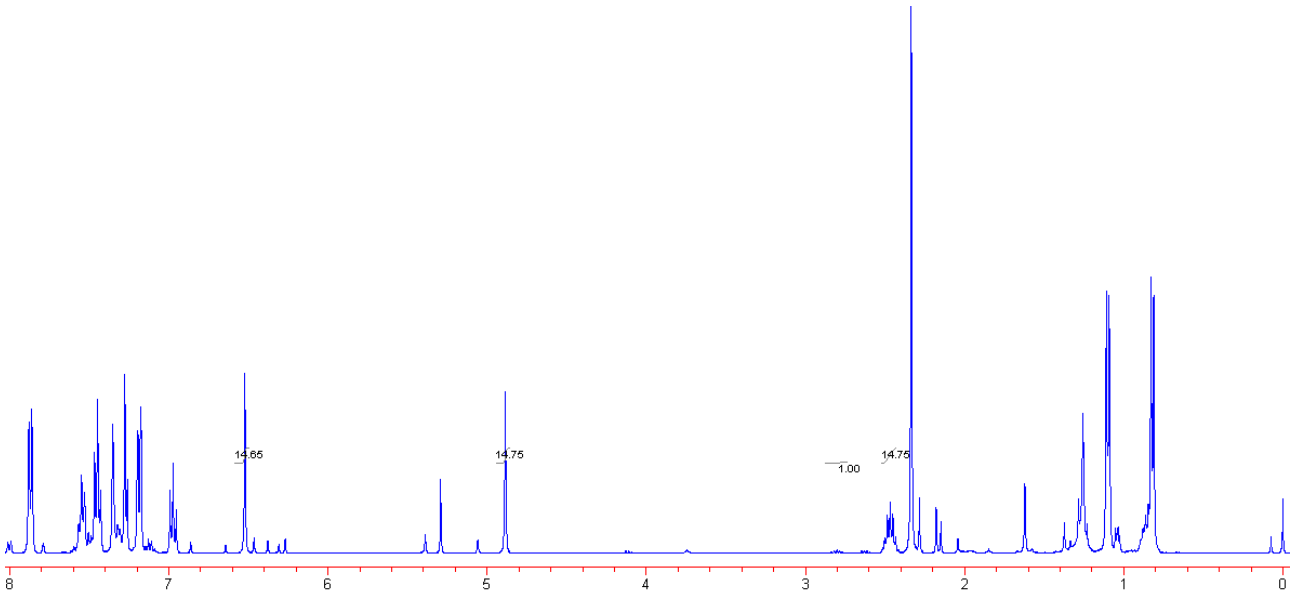
3f

(*S*)-4-((*R*)-1-(3-bromophenyl)-2-methylene-3-oxobutyl)-4-isopropy-2-phenyloxazol-5(4H)-one

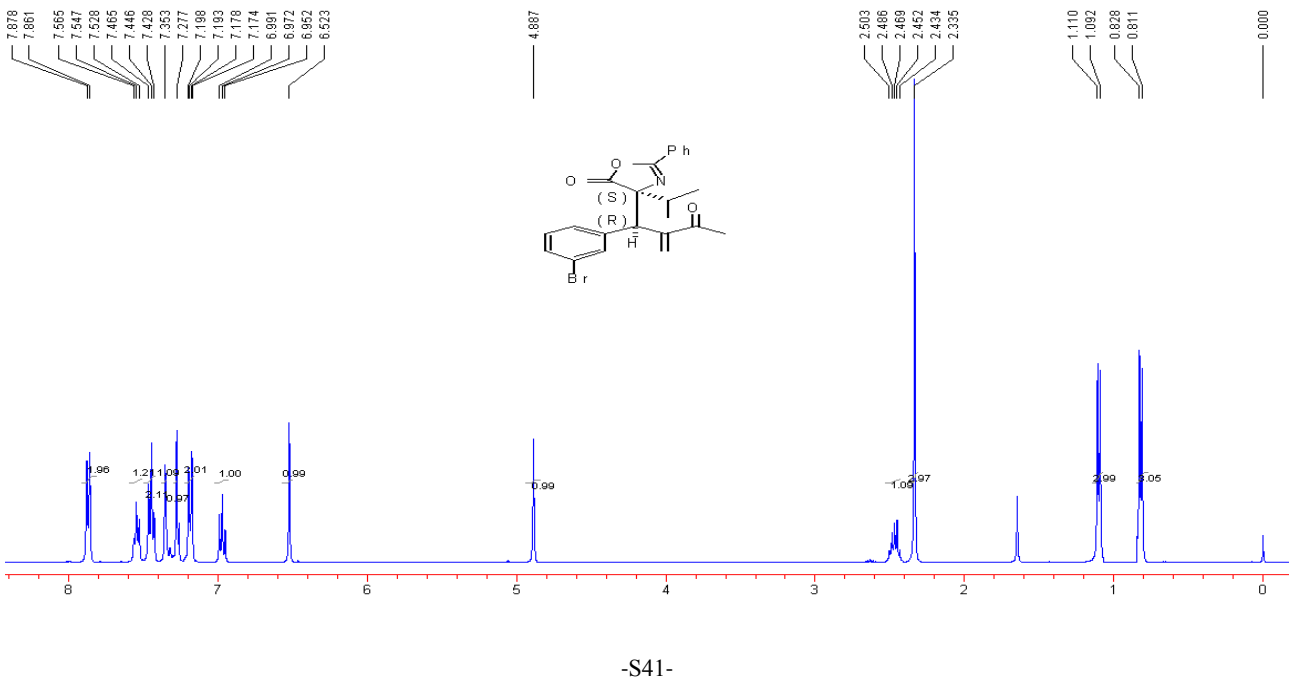
3f: Following the general procedure, the *syn/anti* ratio (15:1) was determined by ^{1}H NMR spectroscopic analysis of the crude product (δ major: 2.47 ppm, δ minor: 2.80 ppm). The mixture was purified by column chromatography using silica gel to give a mixture of diastereoisomer along with trace amount of impurity (40 mg, 91% overall yield in a diastereomeric ratio = 15:1); a white solid. m.p. for *syn*-**3f** = 154-156 ^{o}C; $[\alpha]^{20}_{D}$ (*syn*-**3f**) = -71.8 (c 0.8, $CHCl_3$). IR (CH_2Cl_2): ν 2974, 2954, 1811, 1673, 1655, 1470, 1288, 1196, 1159, 1111, 1041, 1019, 978, 916, 888, 876, 800, 731

cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) for *syn*-**3f**: δ 7.87 (2H, d, *J* = 6.8 Hz, Ph-H), 7.55 (1H, t, *J* = 7.6 Hz, Ph-H), 7.45 (2H, t, *J* = 7.2 Hz, Ph-H) , 7.35 (1H, s, Ar-H), 7.28 (1H, s, =CH_2), 7.19 (2H, dd, J_1 = 8.0 Hz, J_1 = 2.0 Hz, Ar-H), 6.97 (1H, t, *J* = 8.0 Hz, Ar-H), 6.52 (1H, s, =CH_2), 4.89 (1H, s, Ar-CH), 2.47 (1H, qu, *J* = 6.8 Hz, -$CH(CH_3)_2$), 2.34 (3H, s, $COCH_3$), 1.10 (3H, d, *J* = 6.8 Hz, -$CH(CH_3)_2$), 0.82 (3H, d, *J* = 6.8 Hz, -$CH(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 100 MHz) for *syn*-**3f**: δ 198.0, 177.8, 160.4, 145.6, 138.8, 133.0, 132.7, 130.5, 129.5, 129.1, 129.0, 128.7, 127.8, 125.3, 121.6, 79.7, 46.6, 32.2, 25.6, 17.5, 15.3; MS (EI(*syn*-**3f**)) *m/z* (%) 439 (2.18) [M^+], 237 (5.17), 202 (20.39), 174 (5.64), 158 (8.15), 115 (6.41), 105 (100.00), 84 (11.45), 77 (25.88), 43 (39.26); HRMS (EI) Calcd for $C_{23}H_{22}BrNO_3$ [M^+] requires 439.0783, Found 439.0790; The ee of the *syn*-diastereomer was determined to be 97% [determined by HPLC, Chiralpak IC-H, n-hexane/isopropanol = 99:1, 0.7 mL/min, λ = 230 nm, t (major) = 15.63 min, t (minor) = 8.57 min].

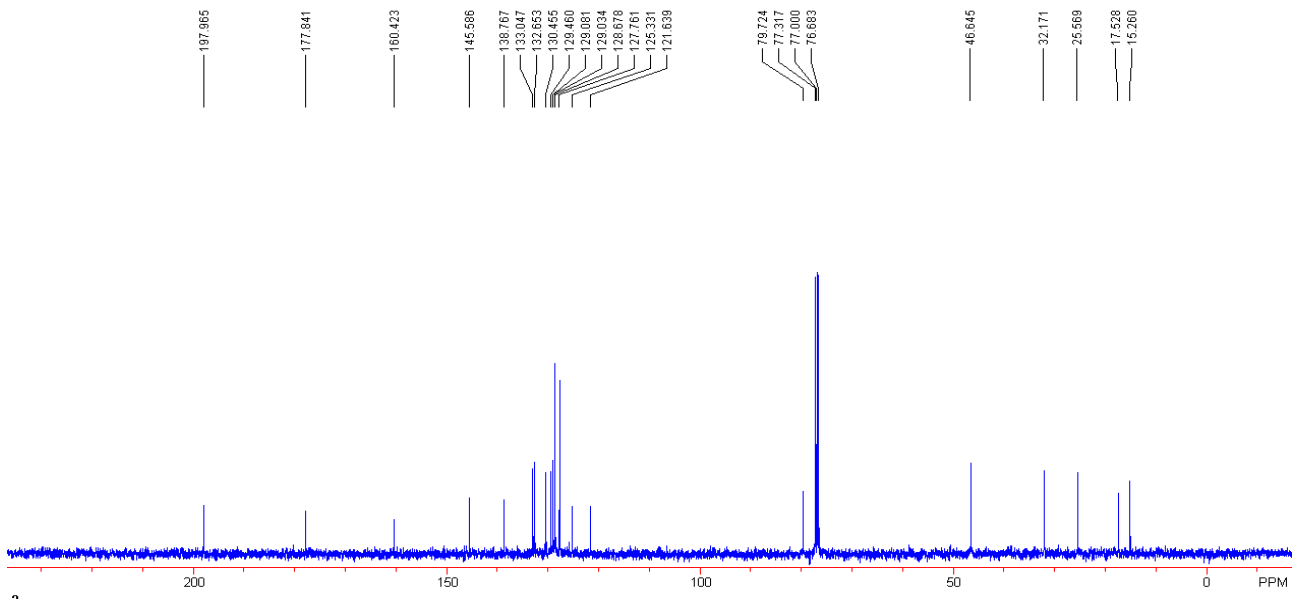
^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the crude product

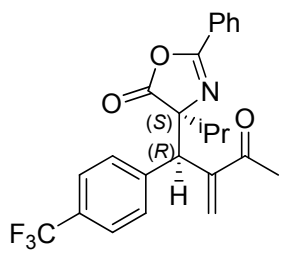


^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer



^{13}C NMR (100 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer



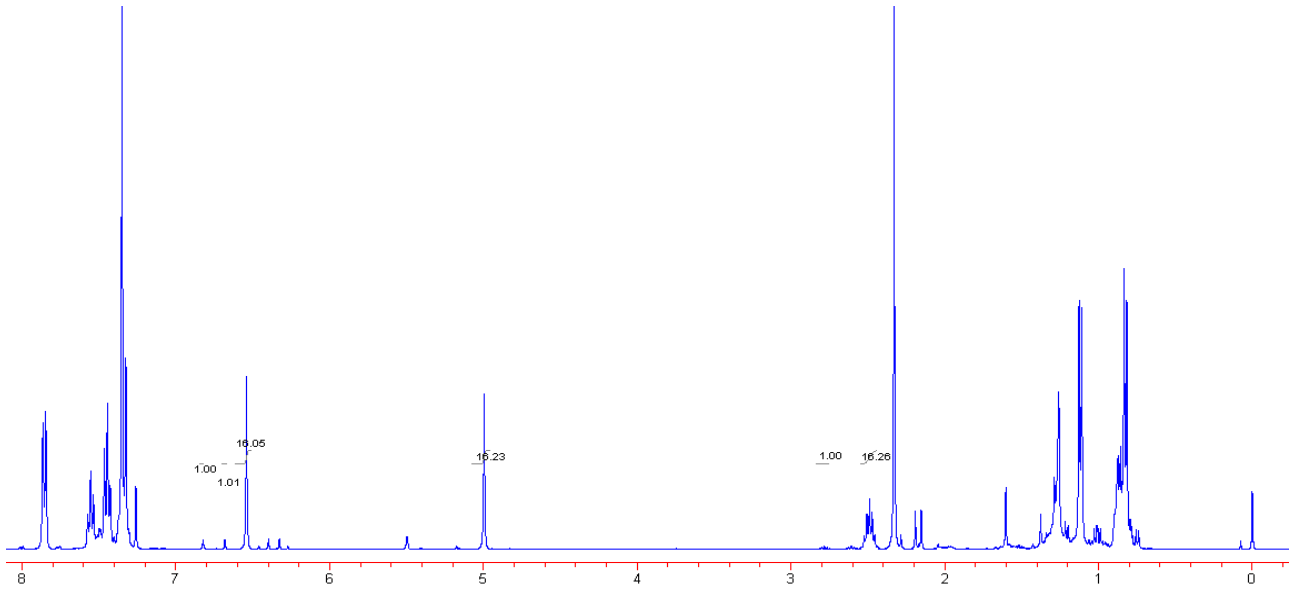


3g

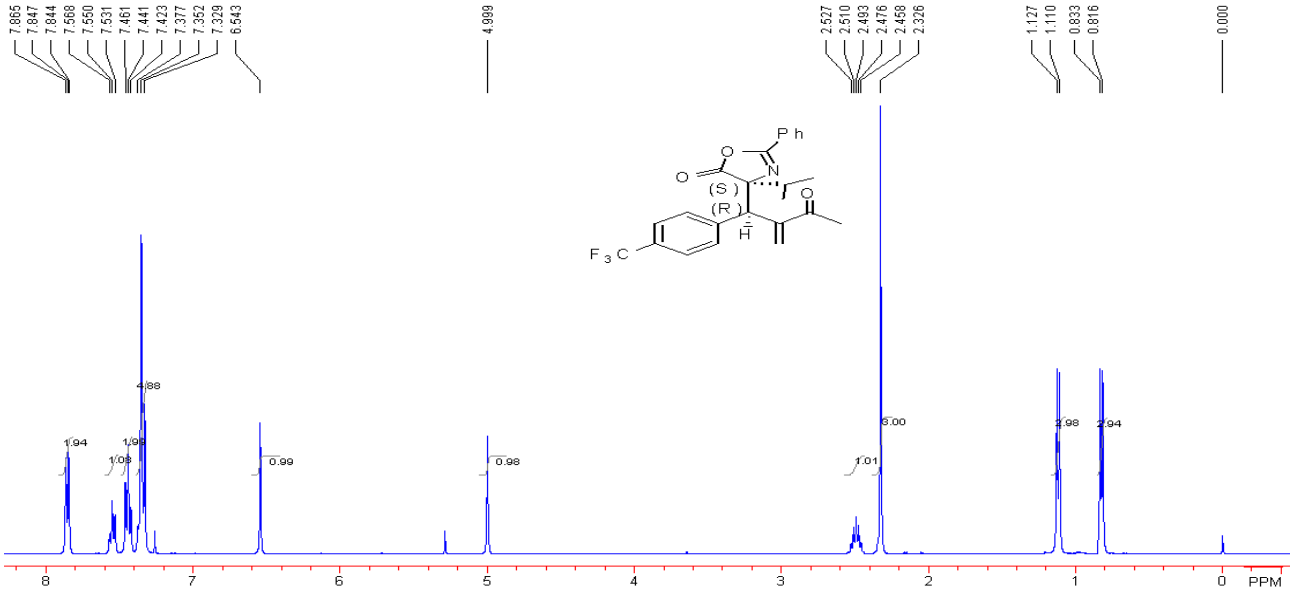
(*S*)-4-isorpopyl-4-((*R*)-2-methylene-3-oxo-1-(4-(trifluorophenyl))butyl)-2-phenyloxazol-5(4H)-one 3g: Following the general procedure, the *syn/anti* ratio (16:1) was determined by ^{1}H NMR spectroscopic analysis of the crude product (δ major: 2.50 ppm, δ minor: 2.78 ppm). The mixture was purified by column chromatography using silica gel to give a mixture of diastereoisomer along with trace amount of impurity (37 mg, 86% overall yield in a diastereomeric ratio = 16:1); a white solid. m.p. for *syn*-**3g** = 122-123 ^oC; $[\alpha]^{20}_D$ (*syn*-**3g**) = -57.3 (c 0.8, $CHCl_3$). IR (CH_2Cl_2): ν 2978, 2881, 1813, 1673, 1650, 1617, 1493, 1451, 1323 1292, 1251, 1198, 1128, 1110, 1043, 1018, 986, 969, 911, 881, 821, 781 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) for *syn*-**3g**: δ 7.86 (2H, d, *J* = 7.2 Hz, Ph-H), 7.55 (1H, t, *J* = 7.8 Hz, Ph-H), 7.44 (2H, t, *J* = 7.2 Hz, Ph-H), 7.33-7.38 (5H, m, Ar-H and $=CH_2$), 6.54 (1H, s, $=CH_2$), 5.00 (1H, s, Ar-CH), 2.50 (1H, qu, *J* = 6.8 Hz, $-CH(CH_3)_2$), 2.33 (3H, s, $COCH_3$), 1.11 (3H, d, *J* = 6.8 Hz, $-CH(CH_3)_2$), 0.82 (3H, d, *J* = 6.8 Hz, $-CH(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) for *syn*-**3g**: δ 198.0, 177.8, 160.4, 145.6, 140.7, 132.8, 130.6, 129.5 (q, $J_{C\text{-}F}$ = 32.0 Hz), 129.2, 128.7, 127.7, 125.3, 124.8 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.9 (q, $J_{C\text{-}F}$ = 207.7 Hz), 79.7, 46.6, 32.3, 25.5, 17.4, 15.3; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ (*syn*-**3g**) -62.7; MS (EI(*syn*-**3g**)) *m/z* (%) 429 (1.67) [M^+], 202 (24.30), 174 (5.44), 165 (0.60), 106 (8.18), 105 (100.00), 84 (9.37), 77 (23.72), 43 (26.76); HRMS (EI) Calcd for $C_{24}H_{22}F_3NO_3$ [M^+] requires 429.1552, Found 429.1557; The ee of the *syn*-diastereomer was determined to be 96% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 95:5, 0.7 mL/min, λ = 230 nm, t (major) = 7.02 min, t

(minor) = 8.57 min].

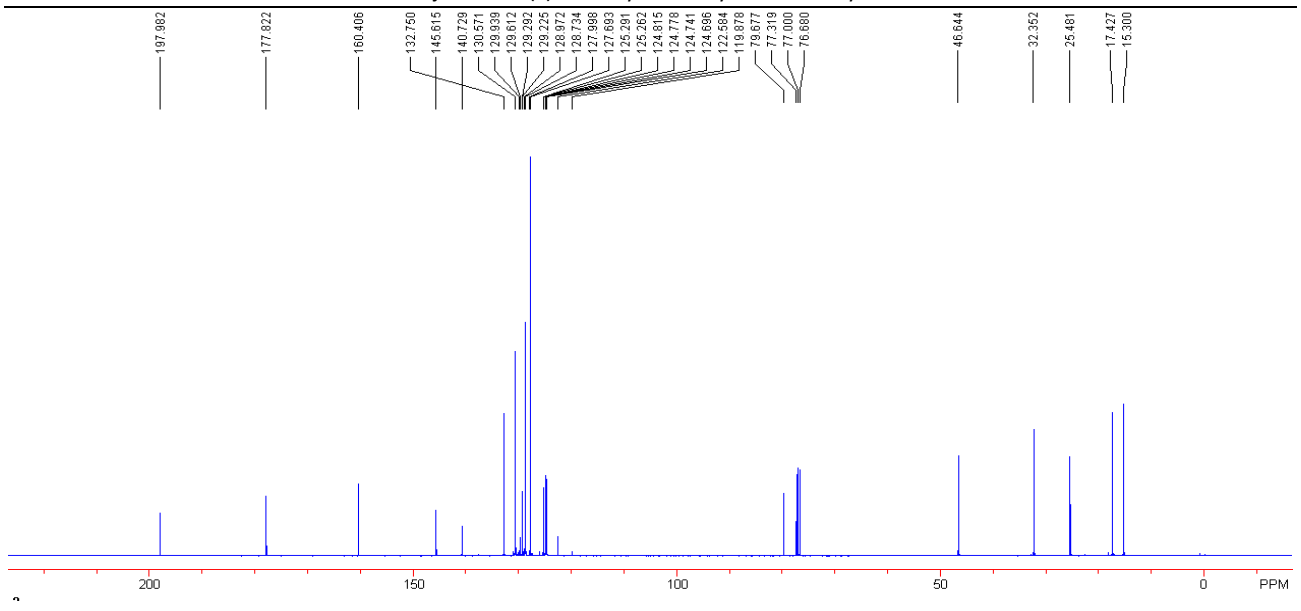
^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the crude product



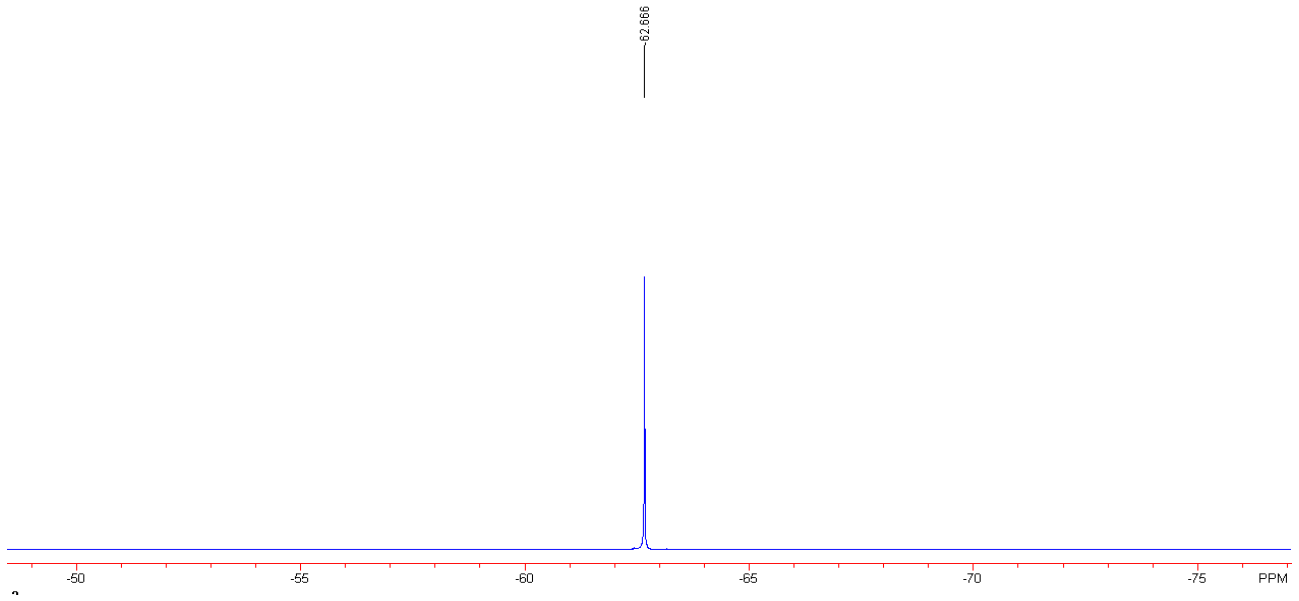
^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer

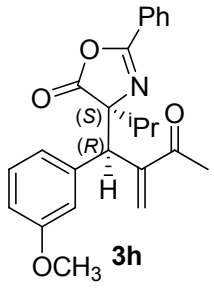


^{13}C NMR (100 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer



^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) for the *syn*-diastereomer



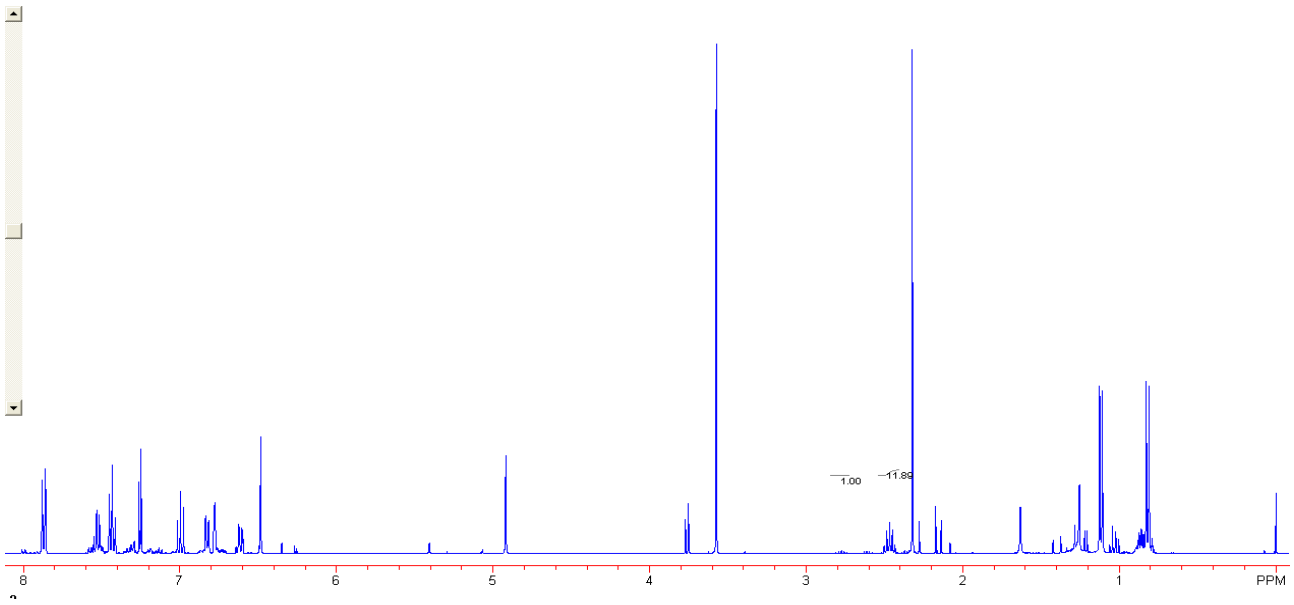


3h

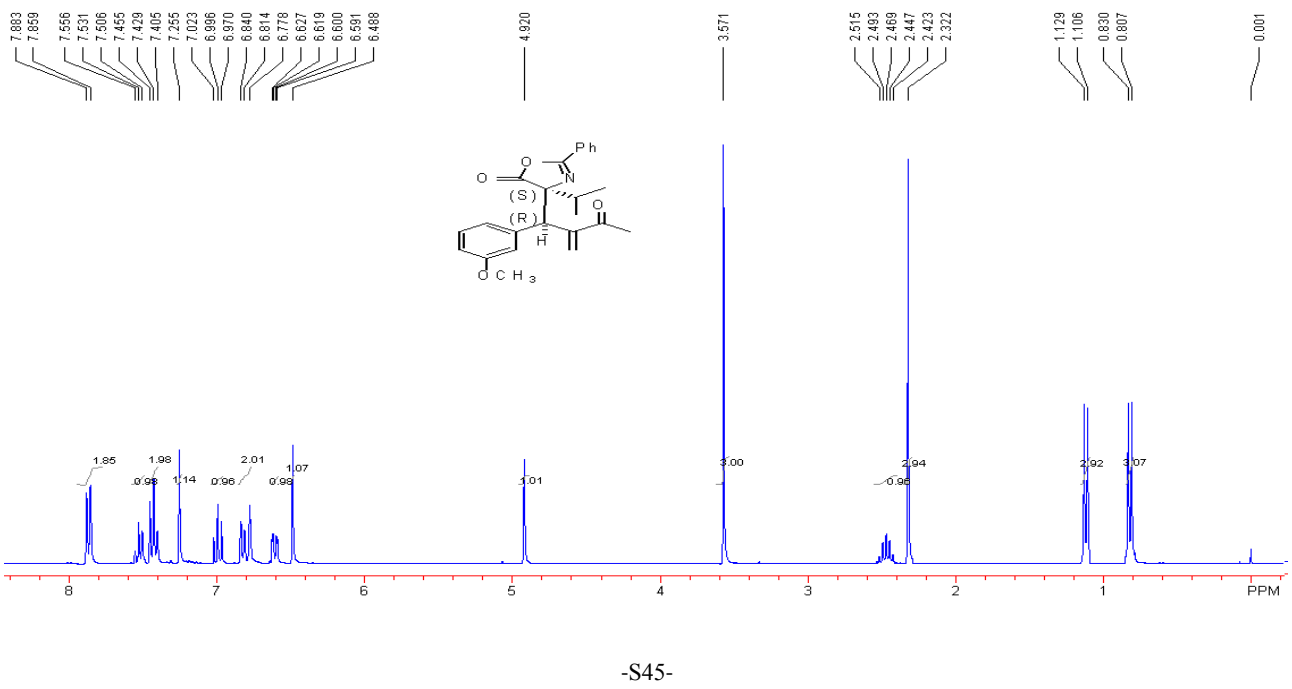
(*S*)-4-isorpopyl-4-((*R*)-1-(3-methoxyphenyl)-2-methylene-3-oxobutyl)-2-phenyloxazol-5(4H)-one 3h: Following the general procedure, the *syn/anti* ratio (12:1) was determined by ^{1}H NMR spectroscopic analysis of the crude product (δ major: 2.47 ppm, δ minor: 2.77 ppm). The mixture was purified by column chromatography using silica gel to give a mixture of diastereoisomer along with trace amount of impurity (36 mg, 92% overall yield in a diastereomeric ratio = 12:1); a white solid. m.p. for *syn*-**3h** = 117-119 ^oC; $[\alpha]^{20}_D$ (*syn*-**3h**) = -49.8 (c 0.7, $CHCl_3$). IR (CH_2Cl_2): ν 2974, 1818, 1680, 1651, 1597, 1491, 1467, 1451, 1294, 1259, 1244, 1199, 1154, 1111, 1045, 1021, 969,

902, 864, 794, 779, 729 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS) for *syn*-**3h**: δ 7.87 (2H, d, *J* = 7.2 Hz, Ph-H), 7.53 (1H, t, *J* = 7.5 Hz, Ph-H), 7.43 (2H, t, *J* = 7.2 Hz, Ph-H), 7.26 (1H, s, $=CH_2$), 7.00 (1H, t, *J* = 7.8 Hz, Ar-H), 6.82 (1H, d, *J* = 6.8 Hz, Ar-H), 6.78-6.76 (1H, m), 6.61 (1H, dd, J_1 = 10.8 Hz, J_2 = 3.2 Hz, Ar-H), 6.49 (1H, s, $=CH_2$), 4.92 (1H, s, Ar-CH), 3.57 (3H, s, Ar-OCH_3), 2.47 (1H, qu, *J* = 7.2 Hz, -$CH(CH_3)_2$), 2.32 (3H, s, $COCH_3$), 1.12 (3H, d, *J* = 7.2 Hz, -$CH(CH_3)_2$), 0.84 (3H, d, *J* = 7.2 Hz, -$CH(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) for *syn*-**3h**: δ 198.2, 178.0, 160.1, 158.9, 146.1, 137.9, 132.5, 128.7, 128.6, 127.7, 125.6, 122.7, 115.3, 113.5, 80.0, 55.0, 46.9, 32.3, 25.7, 17.6, 15.4; MS (EI(*syn*-**3h**)) *m/z* (%) 391 (4.95) [M^+], 203 (4.09), 189 (77.39), 147 (45.34), 132 (6.29), 115 (8.73), 105 (100.00), 77 (52.88), 51 (5.77), 43 (84.84); HRMS (EI) Calcd for $C_{24}H_{25}NO_4$ [M^+] requires 391.1784, Found 391.1788; The ee of the *syn*-diastereomer was determined to be >99% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 90:10, 0.7 mL/min, λ = 230 nm, t (major) = 7.21 min, t (minor) = 17.78 min].

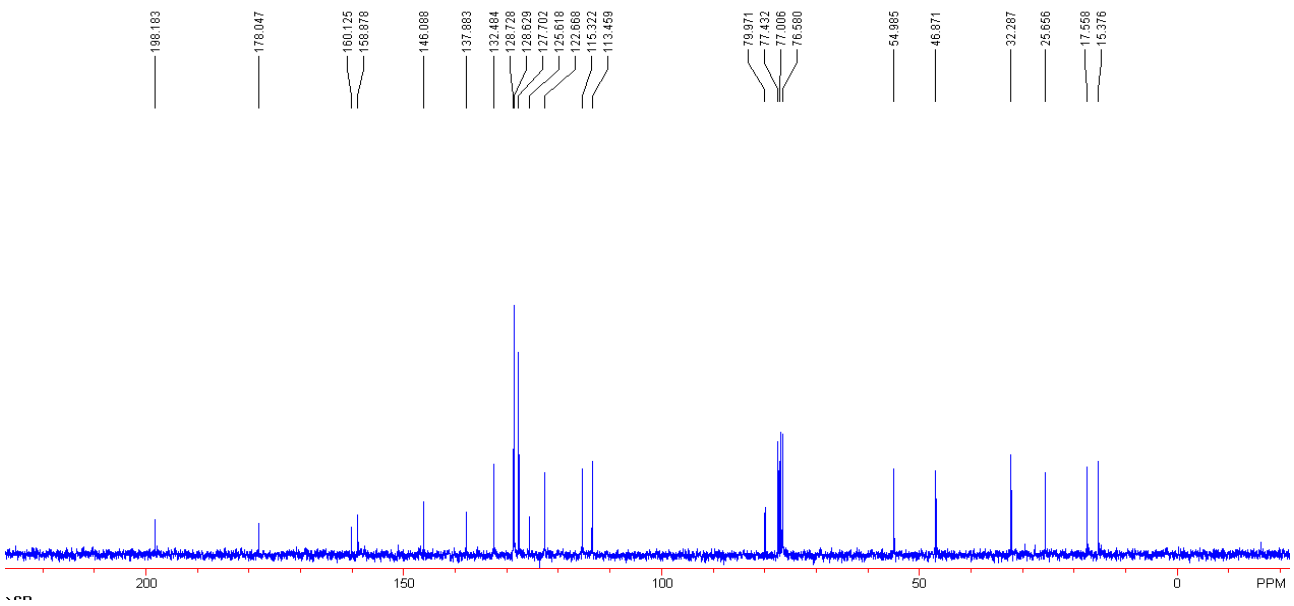
^1H NMR (400 MHz, $CDCl_3$, TMS) for the crude product

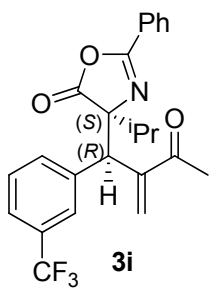


^1H NMR (300 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer



^{13}C NMR (75 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer



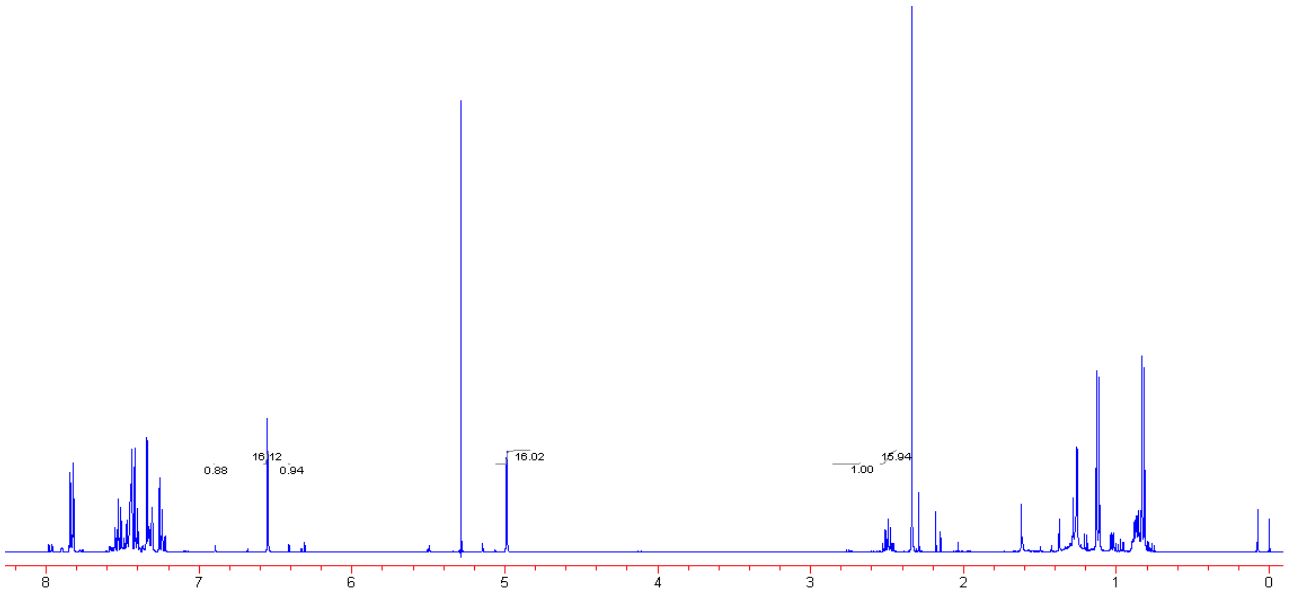


3i

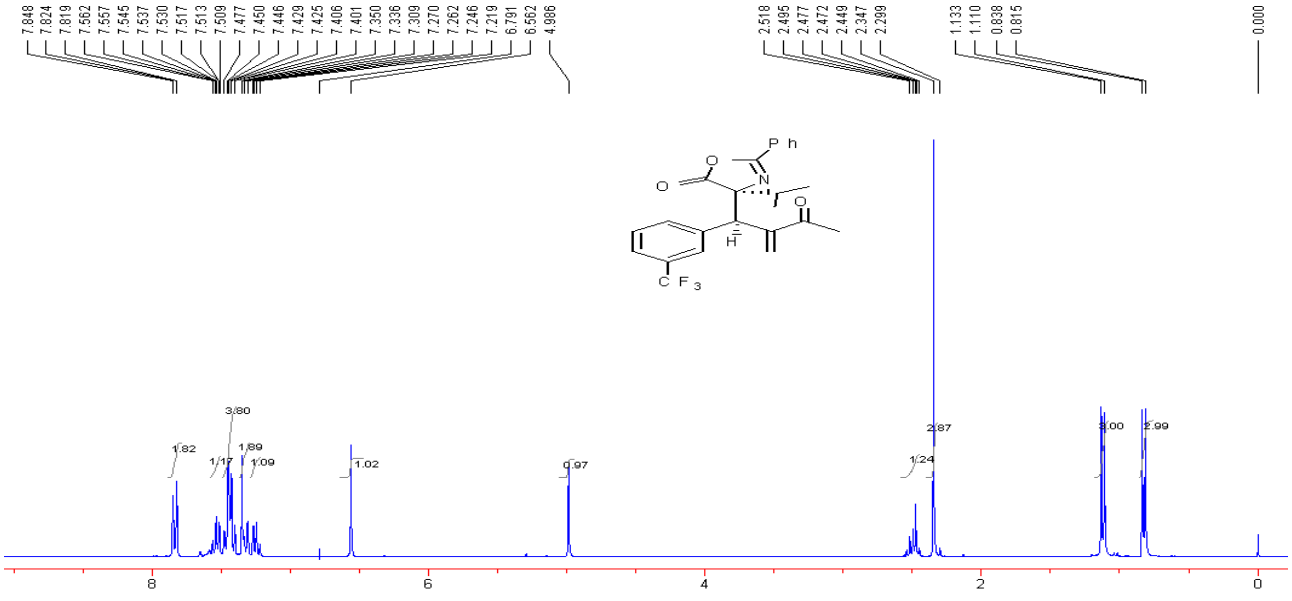
(*S*)-4-isorpopyl-4-((*R*)-2-methylene-3-oxo-1-(3-(trifluorophenyl))butyl)-2-phenyloxazol-5(4H)-one 3i: Following the general procedure, the *syn/anti* ratio (16:1) was determined by ^{1}H NMR spectroscopic analysis of the crude product (δ major: 2.50 ppm, δ minor: 2.75 ppm). The mixture was purified by column chromatography using silica gel to give a mixture of diastereoisomer along with trace amount of impurity (38 mg, 89% overall yield in a diastereomeric ratio = 16:1). a white solid. m.p. for *syn*-**3i** = 80-83 ^oC; $[\alpha]^{20}_D$ (*syn*-**3i**) = -45.2 (c 0.9, $CHCl_3$). IR (CH_2Cl_2): ν 2924, 1806, 1673, 1655, 1620, 1449, 1366 1288, 1161, 1177, 1131, 1096, 1042, 1021, 979, 968, 918, 891, 814, 729 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) for *syn*-**3i**: δ 7.82 (2H, d, *J* = 9.6 Hz, Ar-H), 7.56-7.51 (1H, m, Ar-H), 7.45-7.40 (4H, m, Ar-H), 7.35 (1H, s, $=CH_2$), 7.32 (1H, d, *J* = 10.8, Ar-H), 7.22-7.27 (1H, m, Ar-H), 6.56 (1H, s, $=CH_2$), 5.00 (1H, s, Ar-CH), 2.50 (1H, qu, *J* = 6.8 Hz, $-CH(CH_3)_2$), 2.35 (3H, s, $COCH_3$), 1.12 (3H, d, *J* = 6.8 Hz, $-CH(CH_3)_2$), 0.83 (3H, d, *J* = 6.8 Hz, $-CH(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 100 MHz) for *syn*-**3i**: δ 197.9, 177.8, 160.6, 145.8, 137.7, 134.1 (d, $J_{C\text{-}F}$ = 1.5 Hz), 132.7, 130.1 (q, $J_{C\text{-}F}$ = 30.0 Hz), 129.0, 128.6, 128.5, 126.7 (q, $J_{C\text{-}F}$ = 3.7 Hz), 125.3, 124.2 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.8 (q, $J_{C\text{-}F}$ = 270.6 Hz), 79.8, 46.9, 32.3, 25.4, 17.5, 15.3; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -62.8; MS (EI(*syn*-**3i**)) *m/z* (%) 429 (0.65) [M^+], 227 (0.91), 202 (23.69), 174 (5.14), 128 (0.71), 115 (3.23), 105 (100.00), 77 (23.72), 51 (2.72), 43 (26.76); HRMS (EI) Calcd for $C_{24}H_{22}F_3NO_3$ [M^+] requires 429.1552, Found 429.1554; The ee of the *syn*-diastereomer was determined to be 97% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 90:10, 0.7

mL/min, λ = 230 nm, t (major) = 5.38 min, t (minor) = 8.78 min].

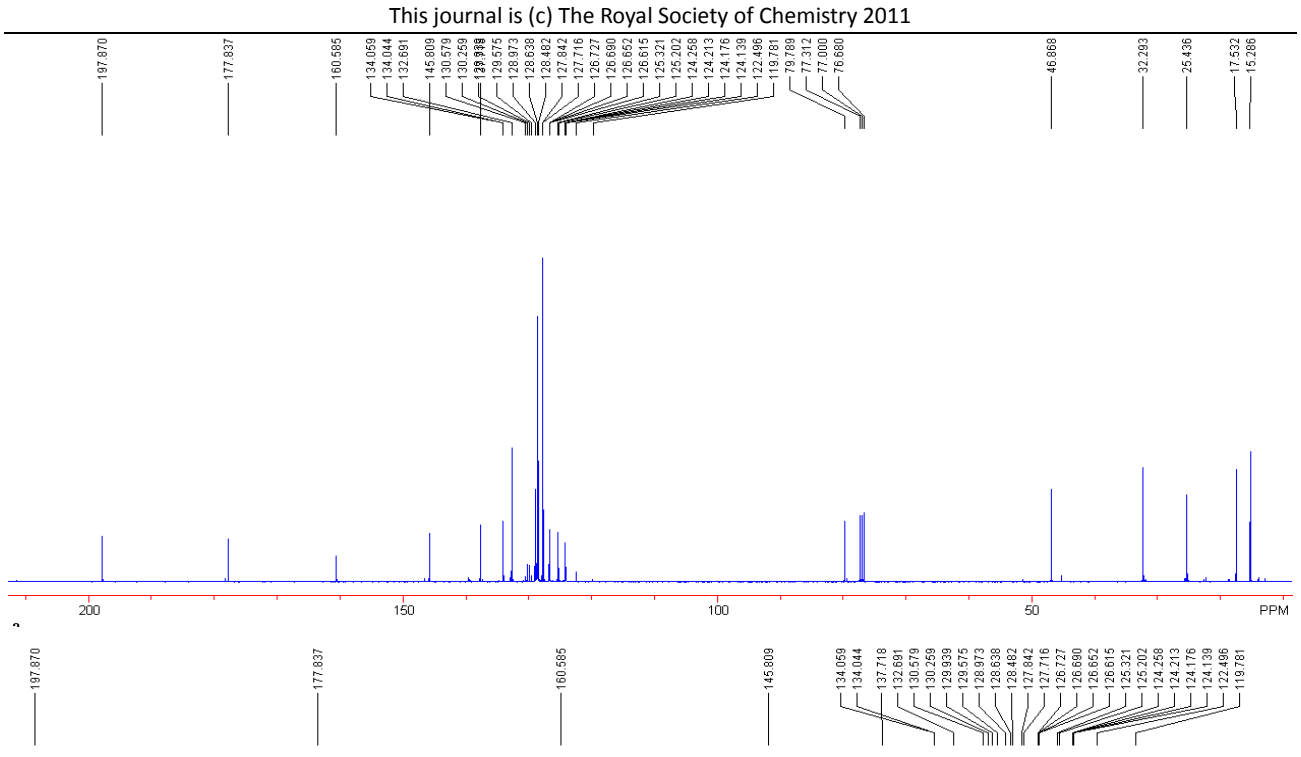
^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the crude product

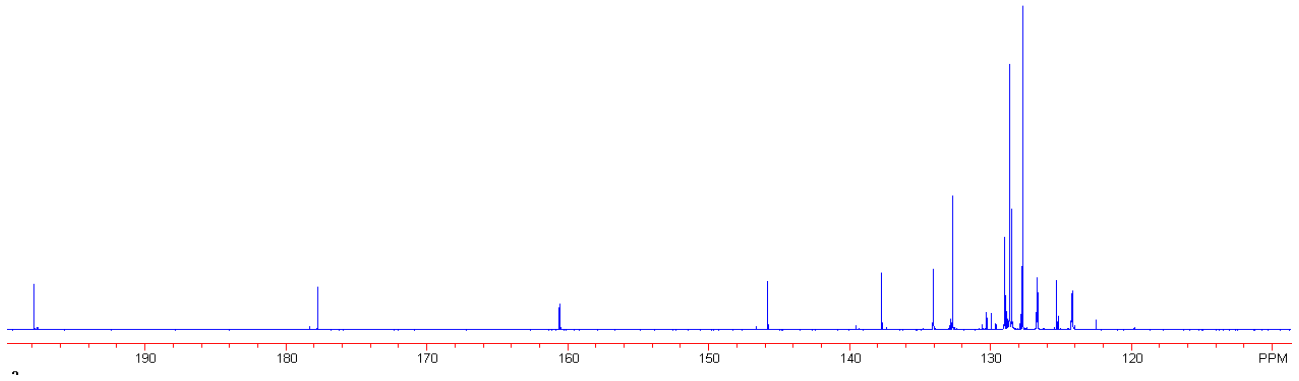


^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer

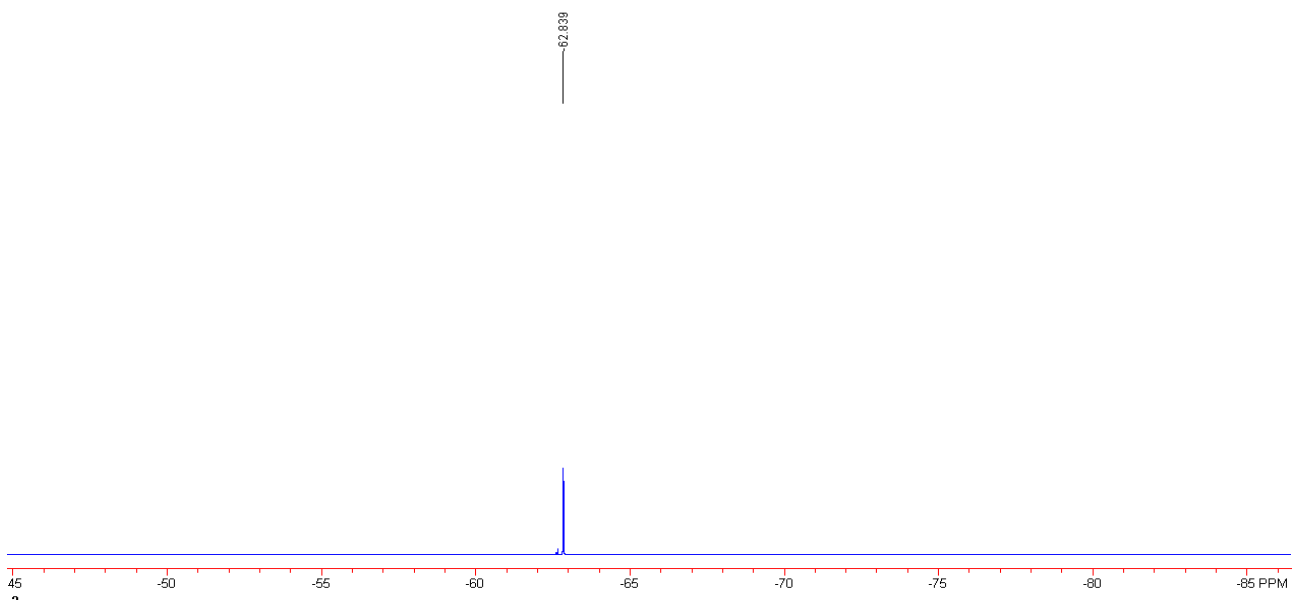


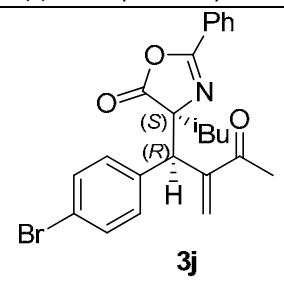
^{13}C NMR(100 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer





^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) for the *syn*-diastereomer



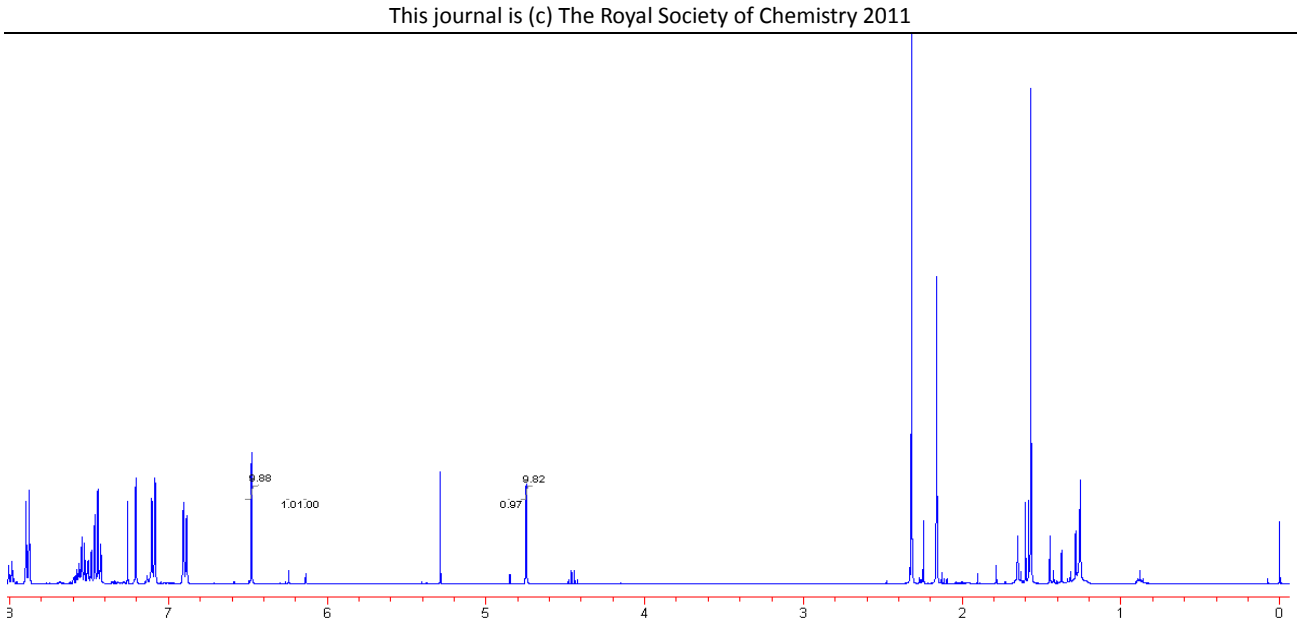


3j

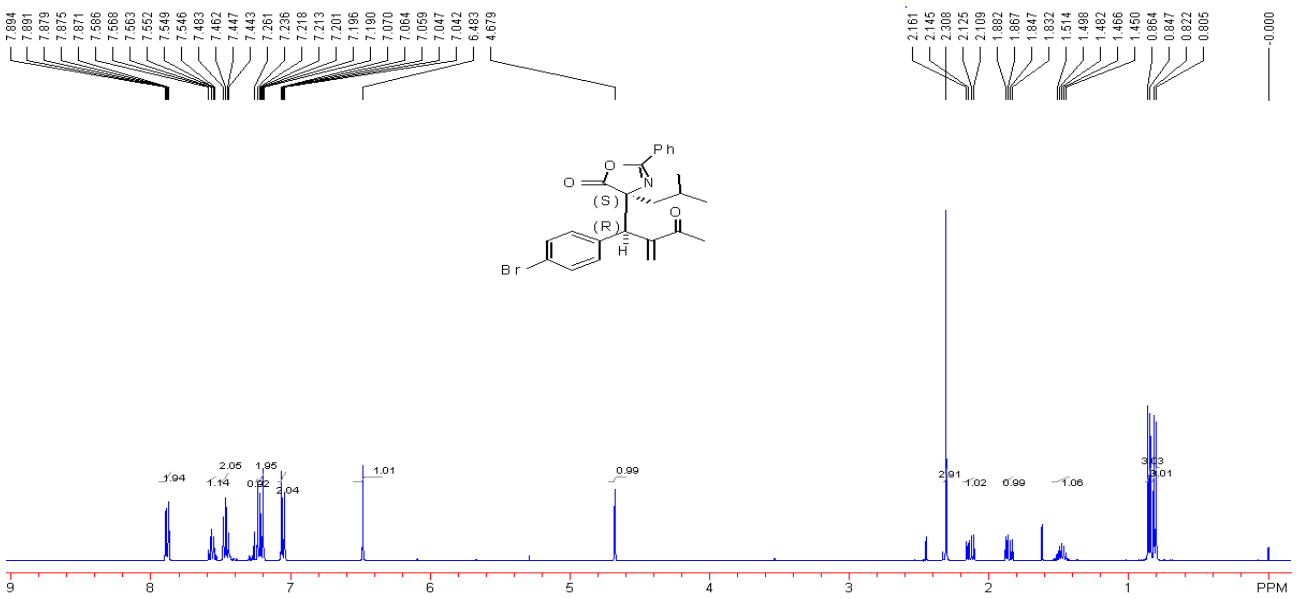
(*S*)-4-((*R*)-1-(4-bromophenyl)-2-methylene-3-oxobutyl)-4-isobutyl-2-phenyloxazol-5(4H)-one

3j: Following the general procedure, the *syn/anti* ratio (3:1) was determined by ^{1}H NMR spectroscopic analysis of the crude product (δ major: 4.68 ppm, δ minor: 4.86 ppm). The mixture was purified by column chromatography using silica gel to give a mixture of diastereoisomer along with trace amount of impurity (38 mg, 84% overall yield in a diastereomeric ratio = 3:1); a white solid. m.p. for *syn*-**3j** = 123-126 ^{o}C; $[\alpha]^{20}_D$ (*syn*-**3j**) = -28.1 (c 0.6, $CHCl_3$); $[\alpha]^{20}_D$ (*anti*-**3j**) = -2.1 (c 0.4, $CHCl_3$). IR (CH_2Cl_2): ν(*syn*-**3j**) 2920, 1808, 1671, 1652, 1486, 1452, 1357, 1318, 1293, 1157, 1242, 1148, 1114, 1073, 1045, 1023, 1014, 988, 975, 928, 891, 853, 818, 779 cm^{-1}; IR (CH_2Cl_2): ν(*anti*-**3j**) 2969, 1816, 1683, 1653, 1487, 1451, 1141, 1320, 1291, 1261, 1216, 1095, 1021, 869. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) for *syn*-**3j**: δ 7.89-7.87 (2H, m, Ph-H), 7.59-7.55 (1H, m, Ph-H), 7.48-7.44 (2H, m, Ph-H), 7.24 (1H, s, =CH_2), 7.22-7.19 (2H, m, Ar-H), 7.07-7.04 (2H, m, Ar-H), 6.48 (1H, s, =CH_2), 4.68 (1H, s, Ar-CH), 2.31 (3H, s, $COCH_3$), 2.13 (1H, dd, J_1 = 14.4 Hz; J_2 = 6.4 Hz, $CH_2CH(CH_3)_2$), 1.86 (1H, dd, J_1 = 14.4 Hz; J_2 = 6.0 Hz, $CH_2CH(CH_3)_2$), 1.49 (1H, qu, J = 6.8 Hz, $CH_2CH(CH_3)_2$), 0.86 (3H, d, J = 6.8 Hz, $CH_2CH(CH_3)_2$), 0.81 (3H, d, J = 6.8 Hz, $CH_2CH(CH_3)_2$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) for *anti*-**3j**: δ 8.05-8.03 (2H, m), 7.64-7.60 (1H, m), 7.55-7.49 (4H, m), 7.44-7.41 (2H, m), 6.21 (1H, s), 6.15 (1H, s), 4.86 (1H, s), 2.26 (3H, s), 1.84 (2H, d, J = 6.4 Hz), 1.45 (1H, qu, J = 6.8 Hz), 0.79 (6H, t, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) for *syn*-**3j**: δ 198.2, 179.8, 160.1, 146.7, 135.2, 132.7, 131.6, 131.1, 128.8, 128.5, 127.7, 125.5, 121.7, 49.9, 44.1, 25.6, 25.2, 23.8, 23.5; ^{13}C NMR (100 MHz, $CDCl_3$) for *anti*-**3j**: δ 197.6, 179.8, 160.3, 146.9, 138.1, 132.8, 131.6, 131.4, 129.0, 128.9, 127.9, 125.6, 121.3, 75.9, 47.8, 45.3, 25.3, 25.0, 23.9, 23.3; MS (EI(*syn*-**3j**)) *m/z* (%) 453 (0.34) [M^+], 366 (1.68), 239 (25.08), 237 (25.26), 216 (4.96), 202 (6.34), 158 (31.42), 115 (16.91), 105 (100.00), 77 (34.68), 43 (51.45); HRMS (EI) Calcd for $C_{24}H_{24}BrNO_3$ [M^+] requires 453.0940, Found 453.0941; MS (ESI(*anti*-**3j**)) m/e 454 (M^++H); HRMS (ESI) for $C_{24}H_{25}NO_3Br$ (M^++H): 454.1029, Found: 454.1012; The ee of the *syn*-diastereomer was determined to be 91% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 90:10, 0.7 mL/min, λ = 230 nm, t (major) = 7.55 min, t (minor) = 9.14 min]; The ee of the *anti*-diastereomer was determined to be 98% [determined by HPLC, Chiralpak IC-H, n-hexane/isopropanol = 98:2, 0.3 mL/min, λ = 230 nm, t (major) = 41.25 min, t (minor) = 51.36 min].

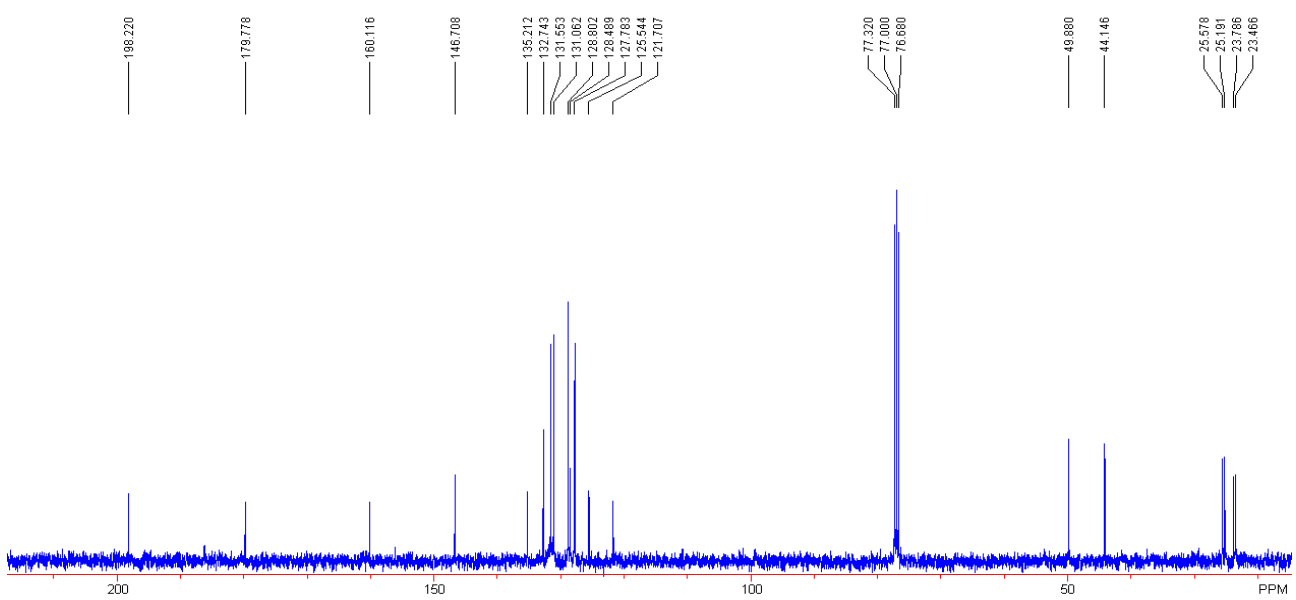
^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the crude product



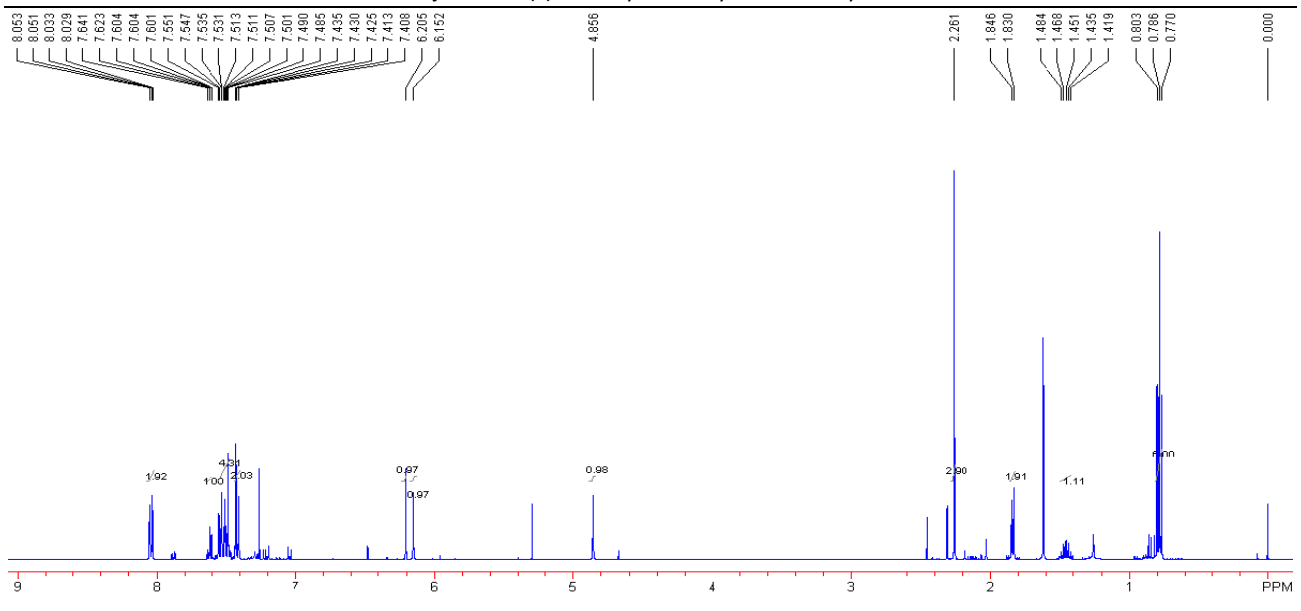
^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer



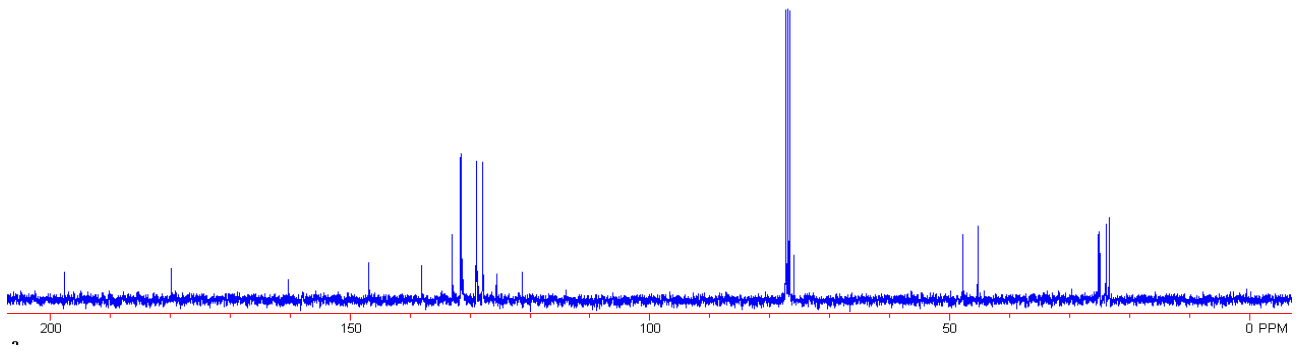
^{13}C NMR (100 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer

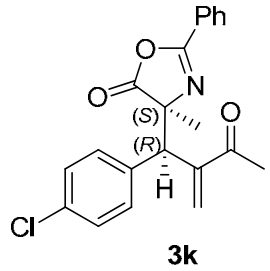


^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the *anti*-diastereomer (containing some impurities)



^{13}C NMR (100 MHz, $CDCl_3$, TMS) for the *anti*-diastereomer (containing some impurities)



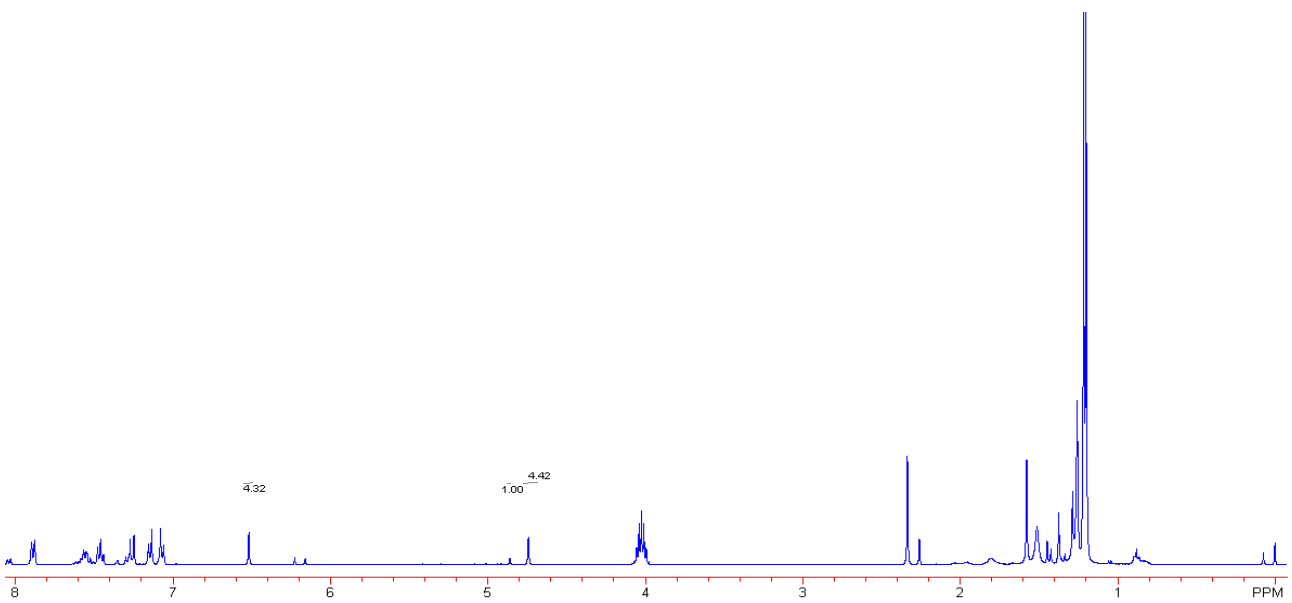


3k

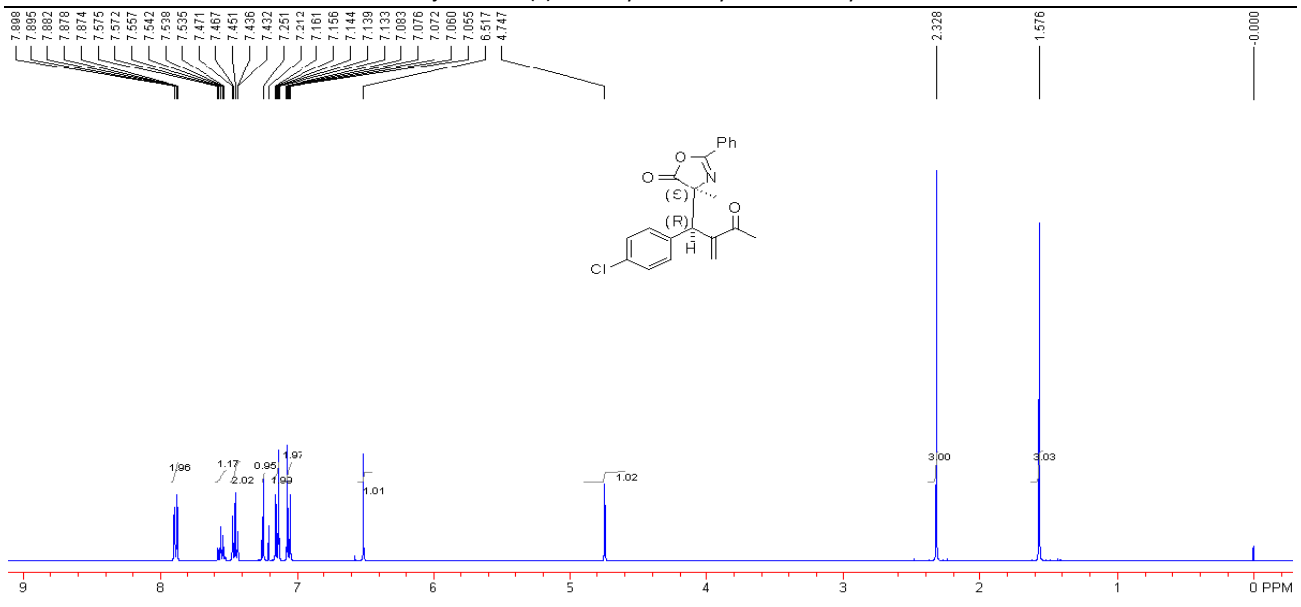
(*S*)-4-((*R*)-1-(4-chlorophenyl)-2-methylene-3-oxobutyl)-4-methyl-2-phenyloxazol-5(4H)-one 3k: Following the general procedure, the *syn/anti* ratio (4:1) was determined by ^{1}H NMR spectroscopic analysis of the crude product (δ major: 4.75 ppm, δ minor: 4.86 ppm). The mixture was purified by column chromatography using silica gel to give a mixture of diastereoisomers along with trace amount of impurity (33 mg, 90% overall yield in a diastereomeric ratio = 4:1); a white solid. m.p. for *syn*-**3k** = 123-125 ^{o}C; $[\alpha]^{20}_D$ (*syn*-**3k**) = -0.7 (c 0.7, $CHCl_3$); $[\alpha]^{20}_D$ (*anti*-**3k**) = -11.2 (c 0.4, $CHCl_3$). IR(CH_2Cl_2): ν(*syn*-**3k**) 1818, 1789, 1658, 1620, 1492, 1450, 1323, 1295, 1168, 1092, 1072,

1017, 982, 898, 818, 782 cm^{-1}; IR(CH_2Cl_2): ν(*anti*-**3k**) 2958, 2925, 2854, 1822, 1742, 1683, 1652, 1491, 1452, 1375, 1292, 1259, 1216, 1199, 1091, 917, 876. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) for *syn*-**3k**: δ 7.90-7.87 (2H, m, Ph-H), 7.58-7.54 (1H, m, Ph-H), 7.47-7.43 (2H, m, Ph-H), 7.25 (1H, s, $=CH_2$), 7.16-7.13 (2H, m, Ar-H), 7.08-7.06 (2H, m, Ar-H), 6.52 (1H, s, $=CH_2$), 4.75 (1H, s, Ar-CH), 2.33 (3H, s, $COCH_3$), 1.58 (3H, s, $PhCH_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) for *anti*-**3k**: δ 8.05-8.03 (2H, m), 7.64-7.51 (5H, m), 7.31-7.29 (2H, m), 6.23 (1H, s), 6.16 (1H, s), 4.86 (1H, s), 2.26 (3H, s), 1.45 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) for *syn*-**3k**: δ 198.3, 179.7, 160.2, 146.2, 135.1, 133.4, 132.8, 131.0, 128.7, 128.5, 128.1, 127.8, 125.5, 72.9, 48.9, 25.5, 22.5; ^{13}C NMR (100 MHz, $CDCl_3$) for *anti*-**3k**: δ 179.6, 179.7, 160.5, 147.4, 136.9, 133.2, 133.0, 131.1, 128.9, 128.6, 128.3, 127.9, 125.6, 72.0, 47.0, 25.3, 23.9; MS (EI) *m/z* (%) 367 (2.11) [M^+], 339 (1.06), 195 (19.54), 193 (58.52), 158 (3.08), 151 (3.21), 141 (2.81), 115 (21.09), 105 (69.94), 77 (44.95), 43 (100); HRMS (EI(*syn*-**3k**)) Calcd for $C_{21}H_{18}ClNO_3$ [M^+] requires 367.0975, Found 367.0973; MS (ESI(*anti*-**3k**)) m/e 368 (M^++H); HRMS (ESI) for $C_{21}H_{19}NO_3Cl$ (M^++H): 368.1057, Found: 368.1048; The ee of the *syn*-diastereomer was determined to be 97% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 90:10, 0.7 mL/min, λ = 230 nm, t (major) = 9.13 min, t (minor) = 12.97 min]; The ee of the *anti*-diastereomer was determined to be 90% [determined by HPLC, Chiralpak IC-H, n-hexane/isopropanol = 95:5, 0.7 mL/min, λ = 230 nm, t (major) = 15.92 min, t (minor) = 17.68 min].

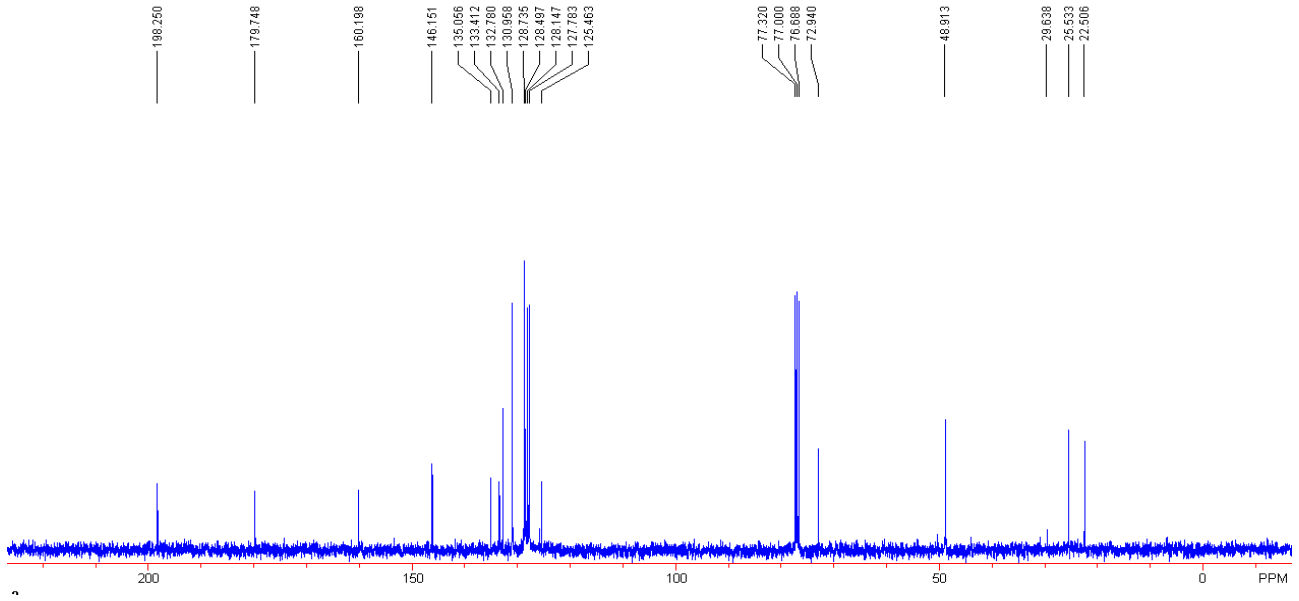
^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the crude product



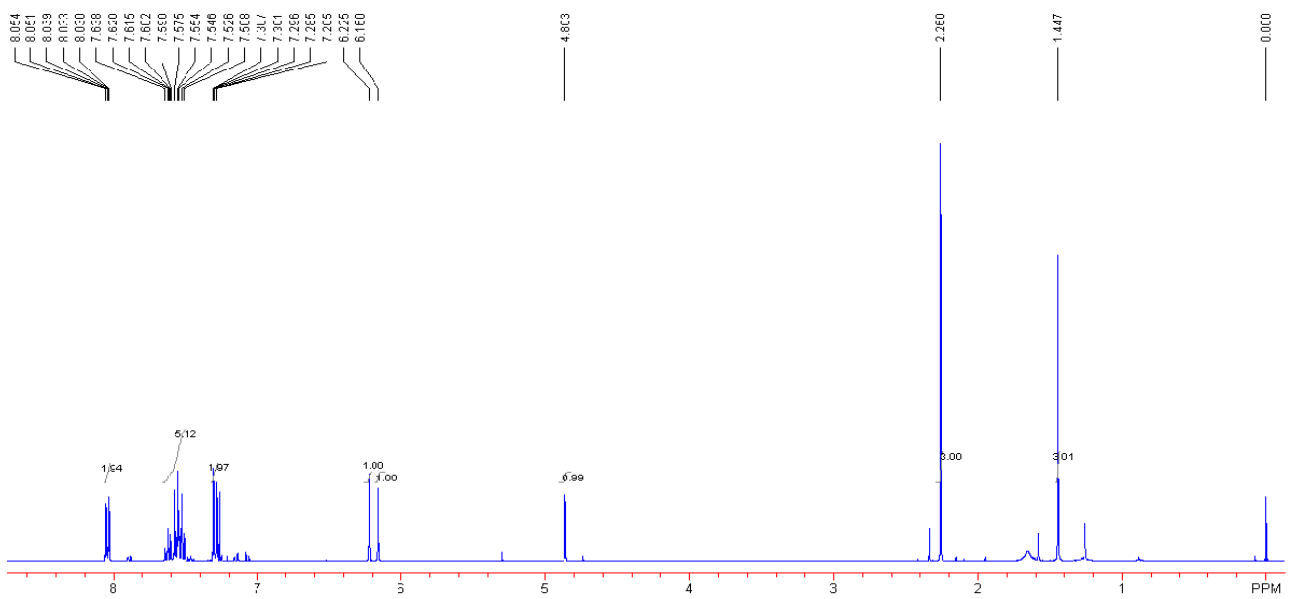
^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer



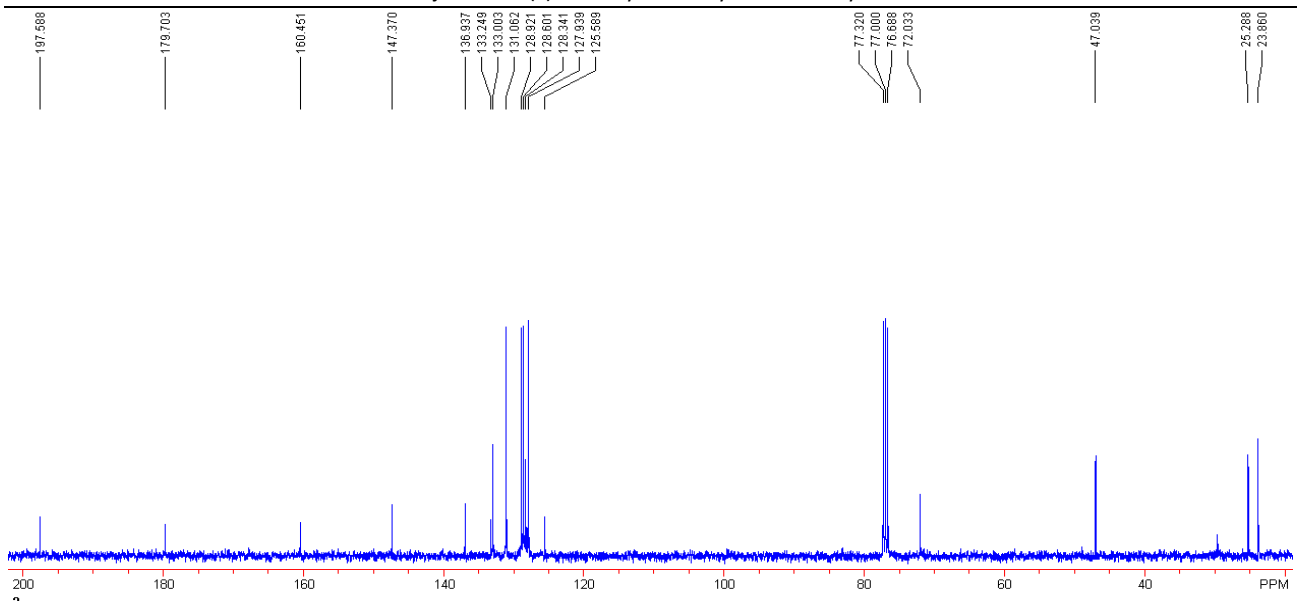
^{13}C NMR (100 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer

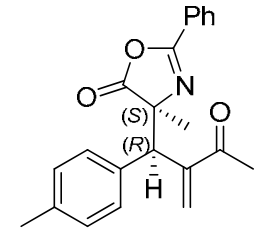


^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the *anti*-diastereomer



^{13}C NMR (100 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer

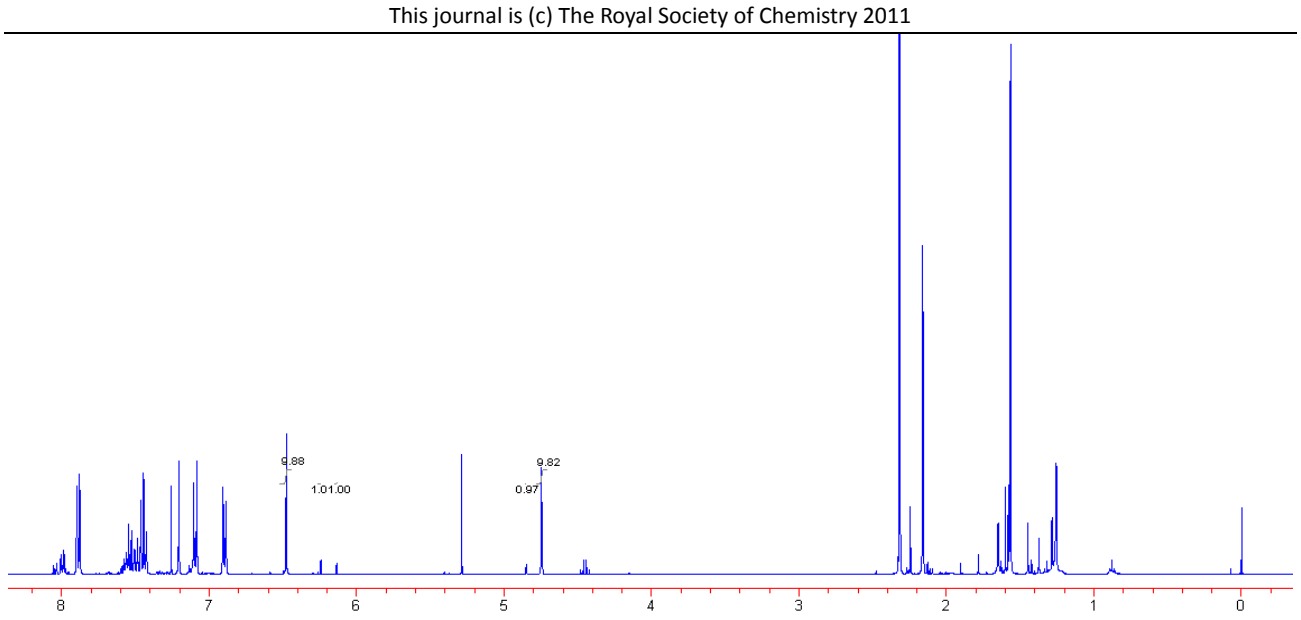




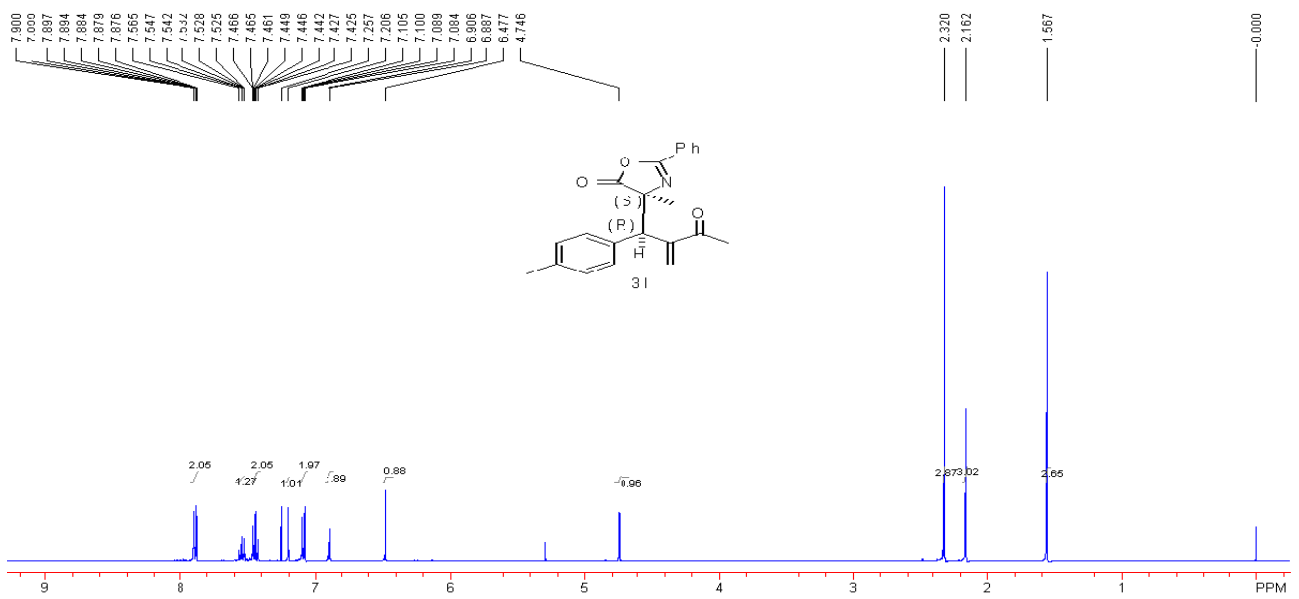
3l

(*S*)-4-methyl-4-((*R*)-2-methylene-3-oxo-1-*p*-tolylbutyl)-2-phenyloxazol-5(4H)-one 3l: Following the general procedure, the *syn/anti* ratio (10:1) was determined by ^{1}H NMR spectroscopic analysis of the crude product (δ major: 4.75 ppm, δ minor: 5.29 ppm). The mixture was purified by column chromatography using silica gel to give a mixture of diastereoisomer along with trace amount of impurity (31 mg, 90% overall yield in a diastereomeric ratio = 10:1); a white solid. m.p. for *syn*-**3l** = 113-114 ^{o}C; $[\alpha]^{20}_{D}$ (*syn*-**3l**) = +13.2 (c 0.9, $CHCl_3$). IR (CH_2Cl_2): ν 2924, 1820, 1672, 1651, 1450, 1289, 1170, 1008, 969, 900, 814, 721 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.90-7.8 (2H, m, Ph-H), 7.57-7.53 (1H, m, Ph-H), 7.47-7.43 (2H, m, Ph-H), 7.21 (1H, s, $=CH_2$), 7.09 (2H, dd, J_1 = 6.4 Hz; J_2 = 2.0 Hz, Ar-H), 6.90 (2H, d, J = 7.6 Hz, Ar-H), 6.45 (1H, s, $=CH_2$), 4.75 (1H, s, Ar-CH), 2.32 (3H, s, $COCH_3$), 2.17 (3H, s, $ArCH_3$), 1.58 (3H, s, $PhCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) for *syn*-**3l**: δ 198.5, 180.0, 160.0, 146.6, 137.0, 133.4, 132.5, 129.4, 128.7, 128.6, 128.1, 127.8, 125.8, 73.2, 49.2, 25.5, 22.5, 20.9; MS (EI(*syn*-**3l**)) *m/z* (%) 347(1.42) [M^+], 319 (1.82), 173 (74.97), 141 (3.11), 131 (14.80), 115 (12.13), 105 (37.01), 97 (3.87), 77 (34.49), 43 (100); HRMS (EI) Calcd for $C_{22}H_{21}NO_3$ [M^+] requires 347.1521, Found 347.1523; The ee of the *syn*-diastereomer was determined to be 96% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 90:10, 0.7 mL/min, λ = 230 nm, t (major) = 8.52 min, t (minor) = 11.32 min].

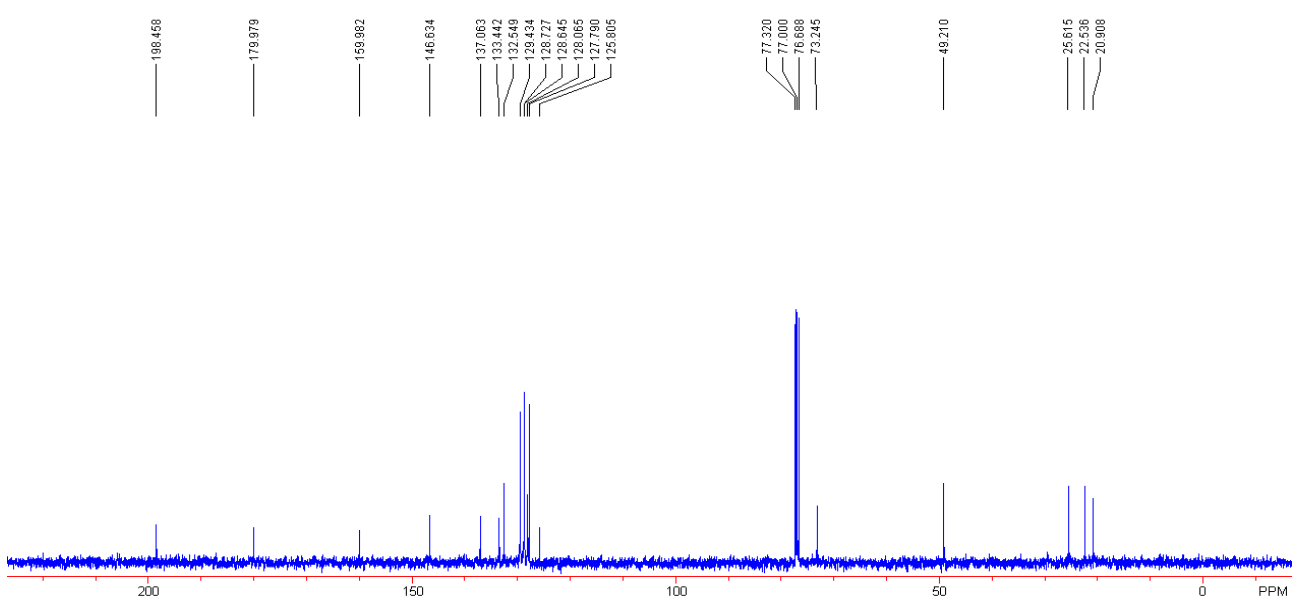
^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the crude product

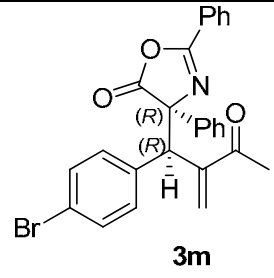


^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer



^{13}C NMR (100 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer

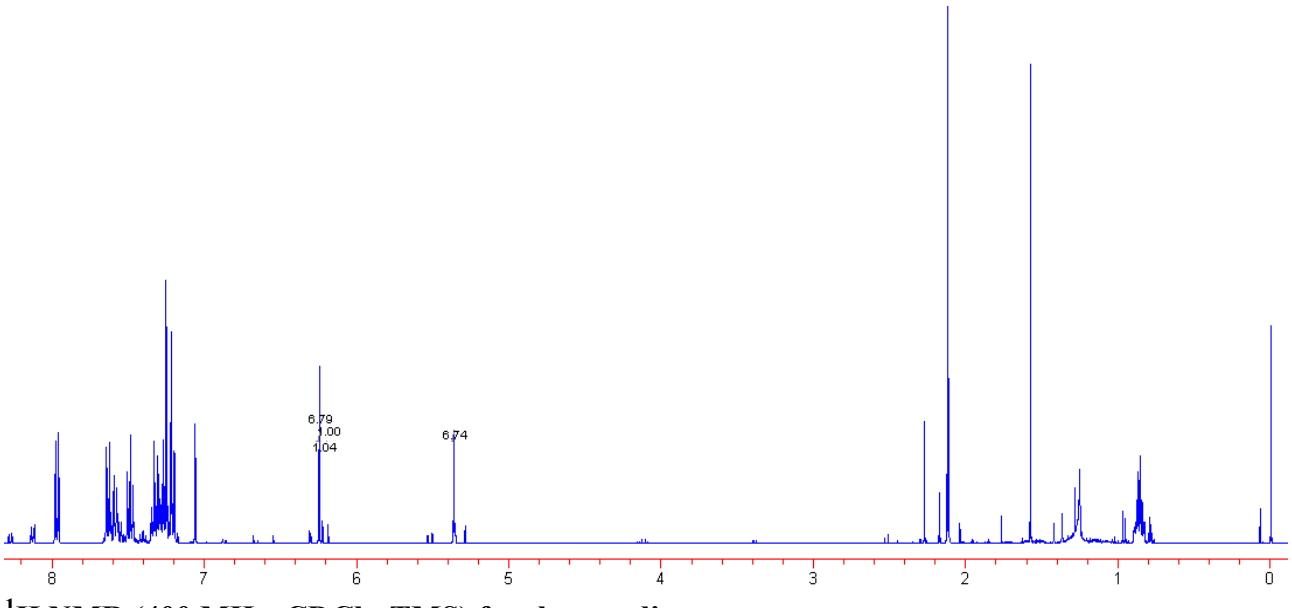




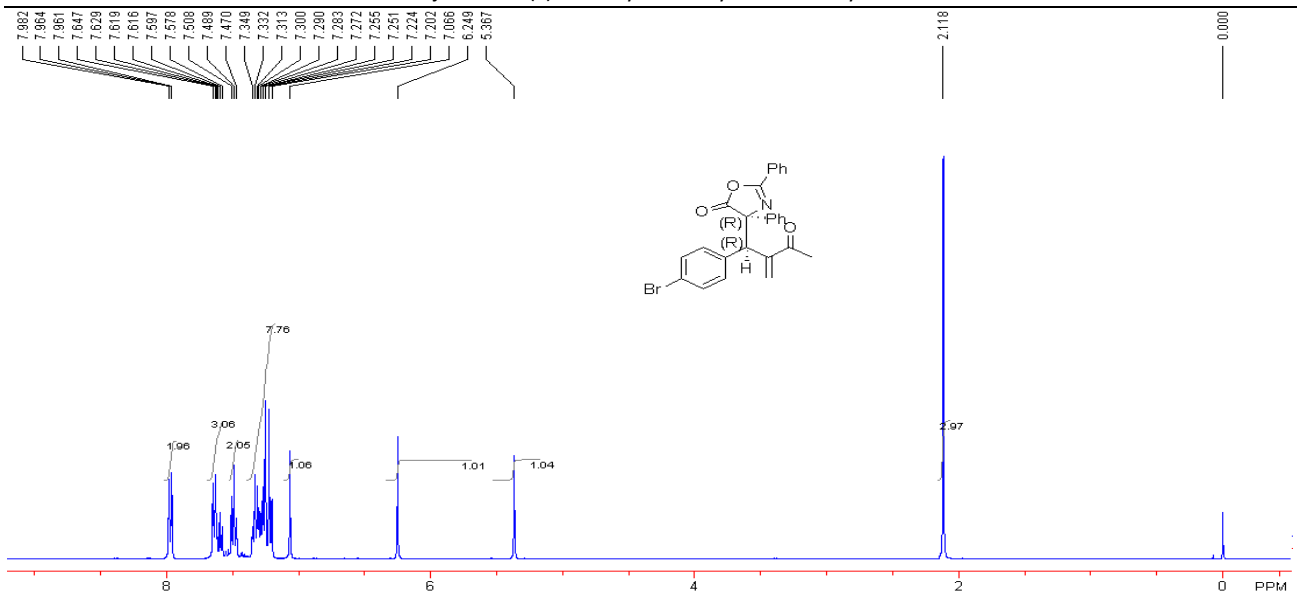
3m

(*R*)-4-((*R*)-1-(4-bromophenyl)-2-methylene-3-oxobutyl)-2,4-diphenyloxazol-5(4H)-one 3m: Following the general procedure, the *syn/anti* ratio (7:1) was determined by ^{1}H NMR spectroscopic analysis of the crude product (δ major: 6.25 ppm, δ minor: 6.22 ppm). The mixture was purified by column chromatography using silica gel to give a mixture of diastereoisomers along with trace amount of impurity (40 mg, 85% overall yield in a diastereomeric ratio = 7:1); a white solid. m.p. for *syn*-**3m** = 93-95 ^{o}C; $[\alpha]^{20}_{D}$ (*syn*-**3m**) = -192.6 (c 0.6, $CHCl_3$). IR (CH_2Cl_2): ν 2922, 1809, 1650, 1486, 1449, 1365, 1324, 1297, 1065, 1011, 988, 961, 925, 905, 883, 814, 786 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.97 (2H, d, *J* = 7.2 Hz, Ar-H), 7.65-7.58 (3H, m, Ar-H), 7.49 (2H, t, *J* = 6.8 Hz, Ar-H), 7.35-7.20 (7H, m, Ar-H), 7.07 (1H, s, =CH_2), 6.25 (1H, s, =CH_2), 5.37 (1H, s, Ar-CH), 2.12 (3H, s, $COCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) for *syn*-**3m**: δ 198.1, 177.7, 161.0, 145.5, 136.8, 134.8, 133.1, 131.9, 131.1, 129.3, 128.9, 128.7, 128.4, 128.0, 126.0, 125.3, 121.9, 77.4, 50.6, 25.4; MS (EI(*syn*-**3m**)) *m/z* (%) 428.(56.76) [M^{+}-$COCH_3$], 386 (100.00), 307 (16.38), 304 (37.96), 227 (16.95), 202 (88.69), 193 (10.03), 173 (21.15), 152 (16.34), 105 (67.55), 77 (37.81), 43 (56.29); HRMS (EI) Calcd for $C_{26}H_{20}BrNO_3$ [M^{+}] requires 473.0627, Found 473.0625; The ee of the *syn*-diastereomer was determined to be 92% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 90:10, 0.7 mL/min, λ = 230 nm, t (major) = 13.75 min, t (minor) = 14.80 min].

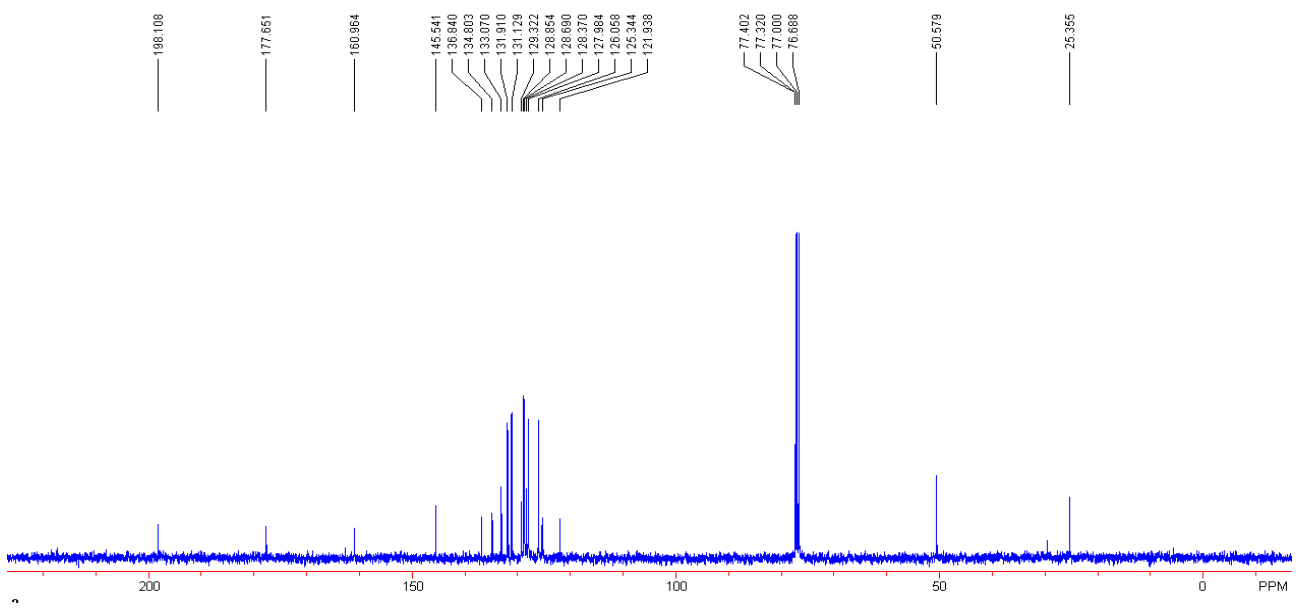
^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the crude product

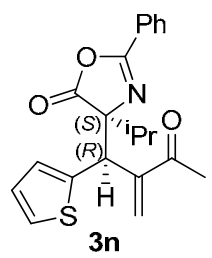


^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer



^{13}C NMR (100 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer





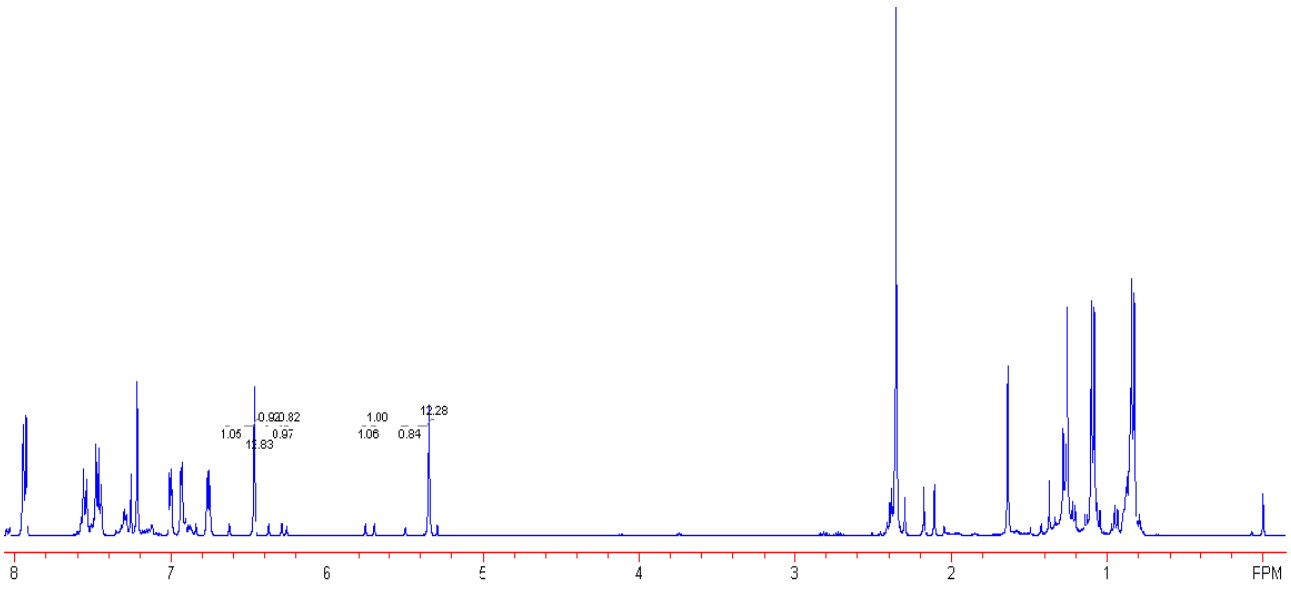
3n

(*S*)-4-isopropyl-4-((*R*)-2-methylene-3-oxo-1-(thiophen-2-yl)butyl)-2-phenyloxazol-5(4H)-one

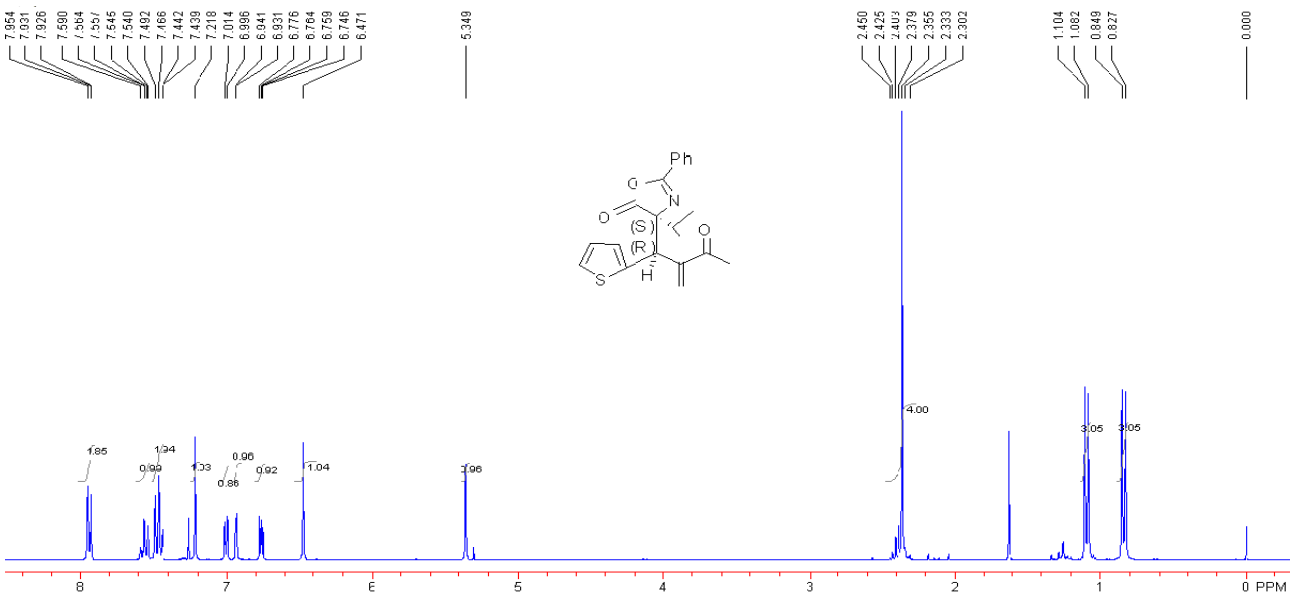
3n: Following the general procedure, the *syn/anti* ratio (12:1) was determined by ^{1}H NMR spectroscopic analysis of the crude product (δ major: 5.35 ppm, δ minor: 5.70 ppm). The mixture was purified by column chromatography using silica gel to give a mixture of diastereoisomers along with trace amount of impurity (35 mg, 95% overall yield in a diastereomeric ratio = 12:1); a white solid. m.p. for *syn*-**3n** = 78-80 ^oC; $[\alpha]^{20}_D$ (*syn*-**3n**) = -79.5 (c 0.4, $CHCl_3$). IR (CH_2Cl_2): ν 2922, 1817, 1653, 1622, 1451, 1427, 1390, 1361, 1336, 1322, 1293, 1254, 1234, 1198, 1156, 1111, 1069, 1042, 1020, 967, 904, 879, 856, 783 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) for *syn*-**3n**: δ 7.96-7.92 (2H,

m, Ph-H), 7.59-7.54 (1H, m, Ph-H), 7.49-7.44 (2H, m, Ph-H), 7.21 (1H, s, $=CH_2$), 7.01 (1H, d, J = 7.2 Hz, thiophen-H), 6.94 (1H, d, J = 3.0 Hz, thiophen-H), 6.76 (1H, dd, J_1 = 6.8 Hz; J_2 = 3.2 Hz, thiophen-H), 6.47 (1H, s, $=CH_2$), 5.35 (1H, s, Ar-CH), 2.32-2.45 (4H, m, $COCH_3$, $CH(CH_3)_2$), 1.09 (3H, d, J = 6.6 Hz, $CH(CH_3)_2$), 0.84 (3H, d, J = 6.6 Hz, $CH(CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) for *syn*-**3n**: δ 197.8, 178.0, 160.9, 146.7, 140.3, 132.6, 129.4, 128.7, 128.0, 127.9, 126.3, 125.7, 80.3, 41.6, 32.6, 25.5, 17.6, 15.4; MS (EI(*syn*-**3n**)) *m/z* (%) 367 (1.45) [M^+], 339 (1.65), 324 (2.02), 165 (89.62), 123 (23.90), 105 (57.74), 97 (3.87), 77 (43.30), 57 (6.77), 43 (100); HRMS (EI) Calcd for $C_{21}H_{20}NO_3S$ [M^+] requires 367.1242, Found 367.1248; The ee of the *syn*-diastereomer was determined to be 95% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 90:10, 0.7 mL/min, λ = 230 nm, t (major) = 6.91 min, t (minor) = 8.57 min].

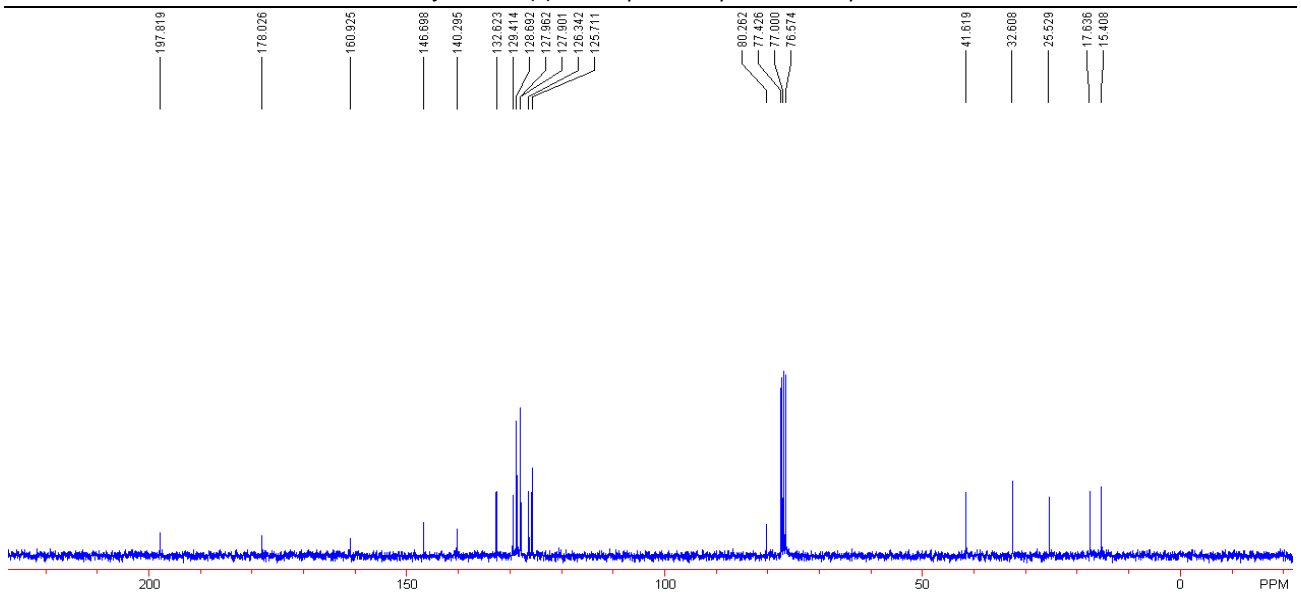
^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the crude product

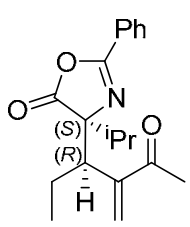


^{1}H NMR (300 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer



^{13}C NMR (75 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer





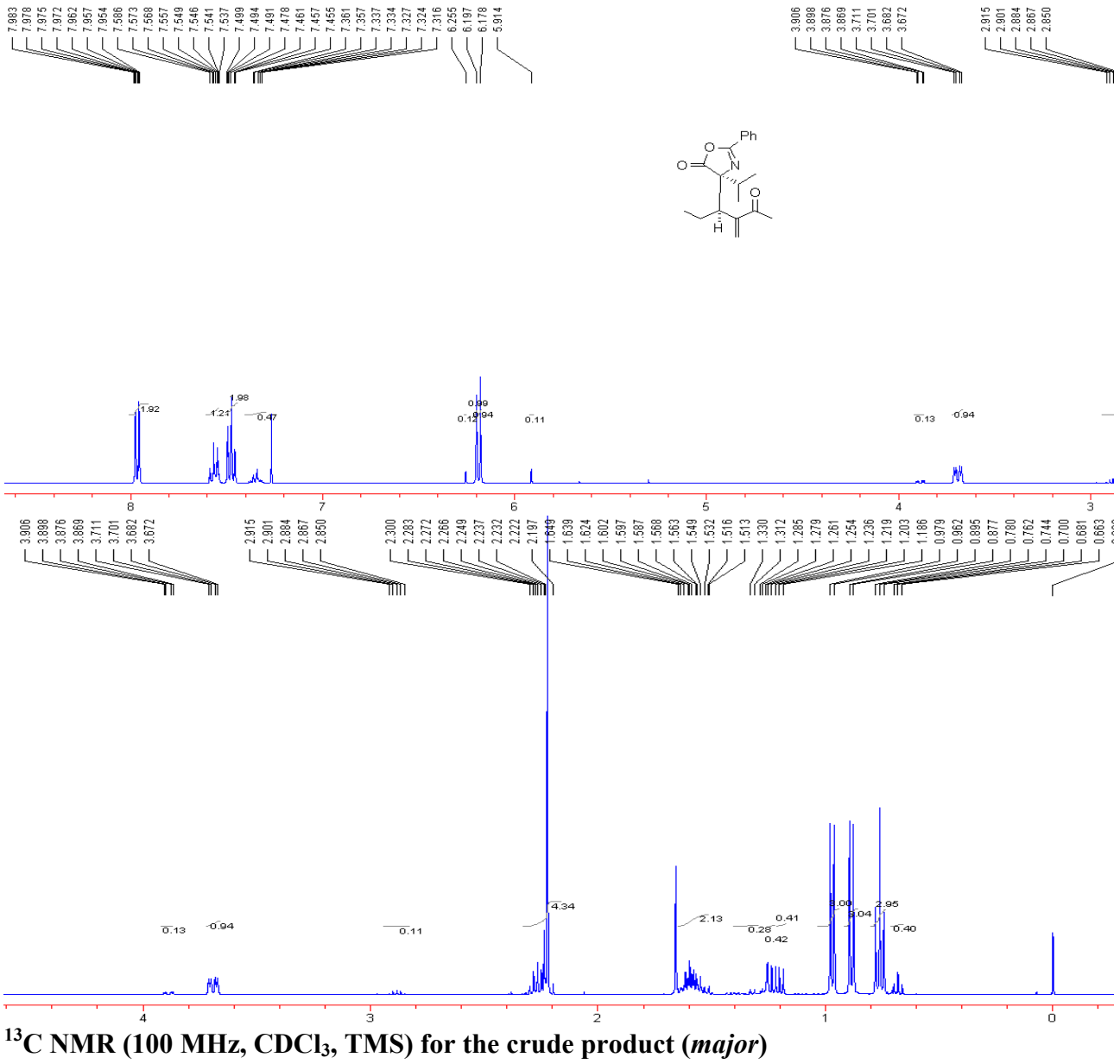
3o

(*S*)-4-isopropyl-4-((*R*)-3-methylene-4-oxopentan-2-yl)-2-phenyloxazol-5(4H)-one 3o:

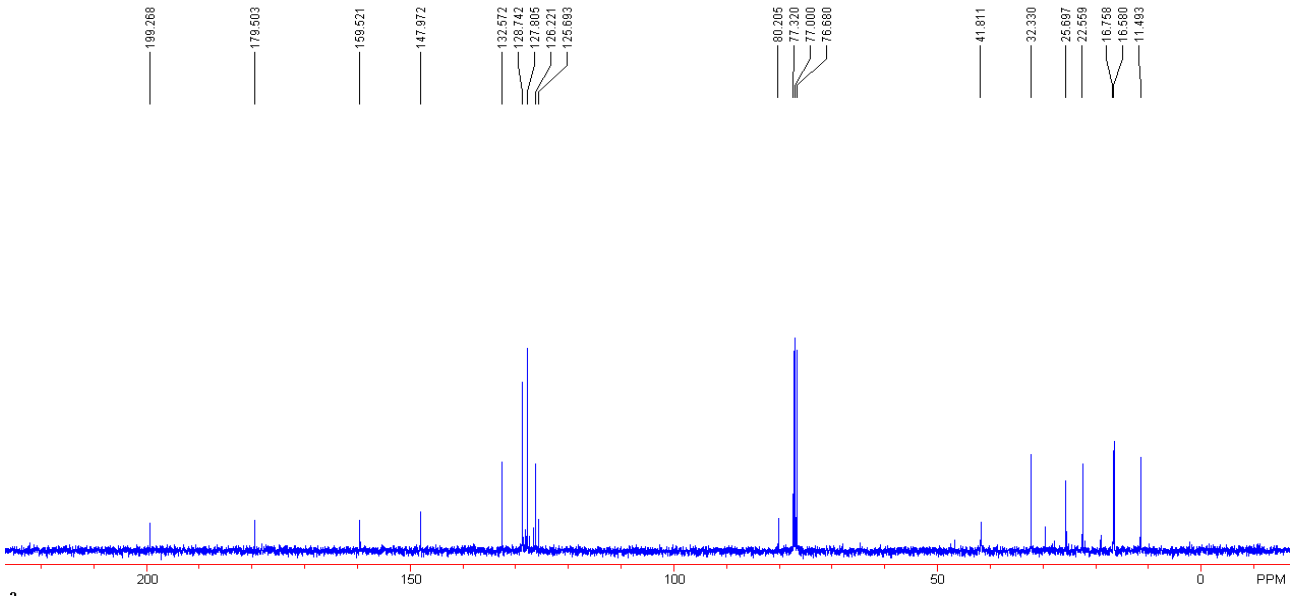
Following the general procedure, the *syn/anti* ratio (7:1) was determined by ^{1}H NMR spectroscopic analysis of the crude product (δ major: 0.76 ppm, δ minor: 0.68 ppm). The mixture was purified by column chromatography using silica gel to give a mixture of diastereoisomers along with trace amount of impurity (30 mg, 96% overall yield in a diastereomeric ratio = 7:1); a colorless liquid. $[\alpha]^{20}_{D}$ = +16.9 (c 1.0, $CHCl_3$). IR (CH_2Cl_2): ν 2965, 2916, 1817, 1774, 1681, 1655, 1580, 1451, 1371, 1336, 1321, 1293, 1261, 1163, 1094, 1022, 954, 920, 880, 799, 761 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.98-7.95 (2H, m, Ar-H), 7.59-7.54 (1H, m, Ar-H), 7.50-7.46 (2H, m, Ar-H), 7.36-7.32 (0.5H, (*anti*-**3o**), m, Ar-H), 6.23 (0.14H (*anti*-**3o**), s, $=CH_2$), 6.20 (1H, s, $=CH_2$), 6.18 (1H, s, $=CH_2$), 5.91 (0.14H (*anti*-**3o**), s, $=CH_2$), 3.89 (0.14H (*anti*-**3o**), dd, J_1 = 11.6 Hz; J_2 = 3.2 Hz, CH_2CH), 3.69 (1H, dd, J_1 = 11.6 Hz; J_2 = 4.0 Hz, CH_2CH), 2.92-2.85 (0.14H (*anti*-**3o**), m), 2.30-2.20 (4.4H, m, $CH(CH_3)_2$, $COCH_3$), 1.69-1.51 (2H, m, CH_3CH_2), 1.33-1.28 (0.28H (*anti*-**3o**), m, CH_3CH_2), 1.23 (0.42H (*anti*-**3o**), d, J = 6.8 Hz, $CH(CH_3)_2$), 1.19 (0.42H (*anti*-**3o**), d, J = 6.8 Hz, $CH(CH_3)_2$), 0.97 (3H, d, J = 6.8 Hz, $CH(CH_3)_2$), 0.89 (3H, d, J = 6.8 Hz, $CH(CH_3)_2$), 0.76 (3H, t, J = 7.2 Hz, CH_3CH_2), 0.68 (0.42H (*anti*-**3o**), t, J = 7.2 Hz, CH_3CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (major) 199.3, 179.5, 159.5, 148.0, 132.6, 128.7, 127.8, 126.2, 125.7, 80.2, 41.8, 32.3, 25.7, 22.6, 16.8, 16.6, 11.5; MS (EI) *m/z* (%) 313 (1.43) [M^+], 271 (4.10), 242 (8.07), 203 (11.73), 188 (2.29), 174 (3.13), 155 (1.12), 105 (100), 77 (24.27), 57 (11.42), 43 (25.48); HRMS (EI) Calcd for $C_{19}H_{23}NO_3$ [M^+] requires 313.1678, Found 313.1679; The ee of the *syn*-diastereomer was determined to be 85% [determined by HPLC, Chiralpak IC-H, n-hexane/isopropanol = 99:1, 0.5

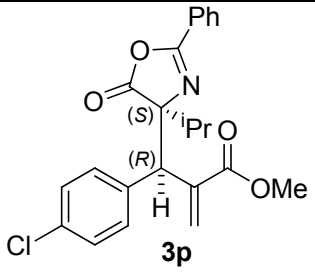
mL/min, λ = 214 nm, t (major) = 34.31 min, t (minor) = 22.87 min].

^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the crude product



^{13}C NMR (100 MHz, $CDCl_3$, TMS) for the crude product (*major*)

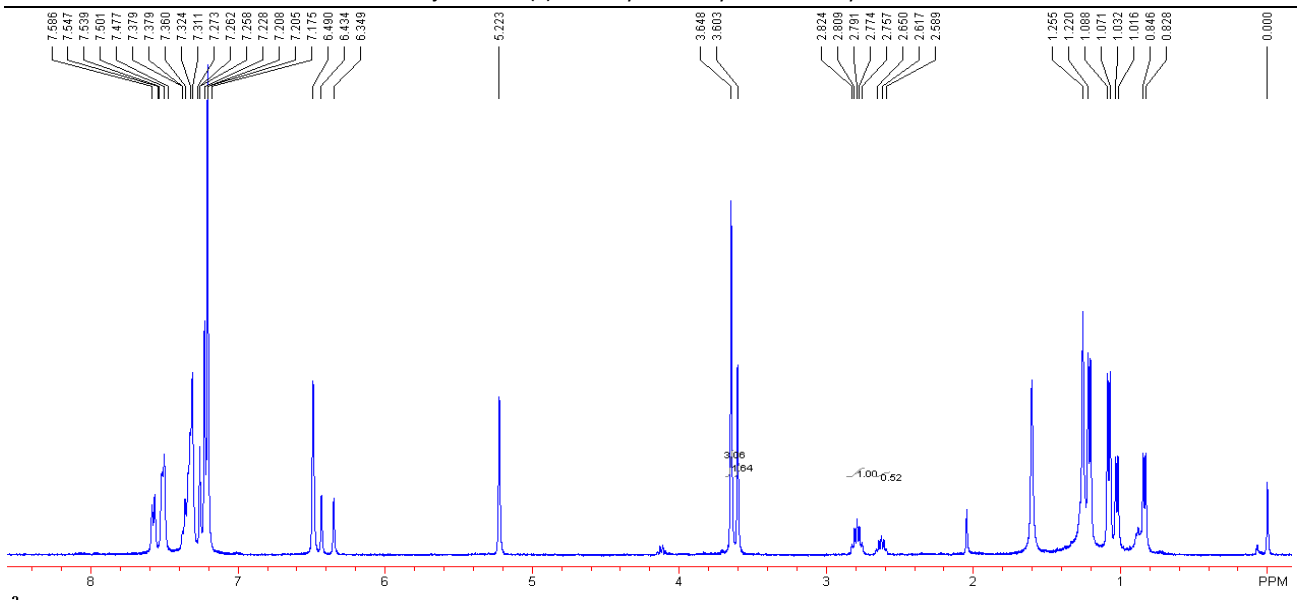




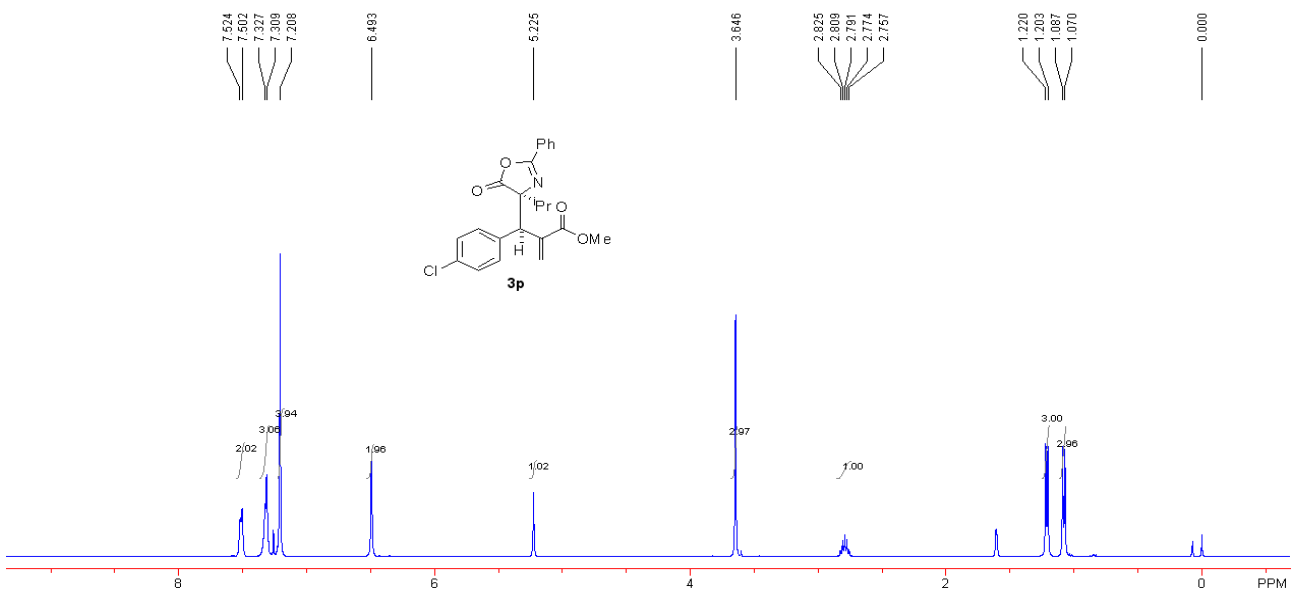
3p

Methyl 2-((R)-(4-chlorophenyl)((S)-4-isopropyl-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)methyl)acrylate **3p**: To a mixture of **1p** (0.11 mmol, 36 mg), **2a** (0.10 mmol, 21 mg) and catalyst **L2** (13 mg, 0.020 mmol) was added 1.0 mL of THF at room temperature under argon. The resulting mixture was heated to 40 ^{o}C and monitored by TLC. After the reaction complete, the solution was concentrated under reduced pressure and the residue was further purified by silica gel column chromatography (EtOAc/PE = 1/20) to give the target product **3p** (13 mg, 32% yield), a white solid, m.p. for *syn*-**3p** = 98-100 ^{o}C. The *syn/anti* ratio (2:1) was determined by ^{1}H NMR spectroscopic analysis of the crude product (δ major: 2.79 ppm, δ minor: 2.62 ppm). $[\alpha]^{20}_{D}$ (*syn*-**3p**) -100.3 (c 0.6, $CHCl_3$). IR (CH_2Cl_2): ν 2967, 1772, 1717, 1649, 1491, 1441, 1408, 1386, 1157, 1122, 1090, 1071, 1013, 1002, 969, 947, 921, 885, 782 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$, TMS) for *syn*-**3p**: δ 7.52-7.50 (2H, m), 7.33-7.31 (3H, m), 7.21 (4H, s), 6.49 (1H, s), 5.23 (1H, s), 3.65 (3H, S) 2.79 (1H, qu, *J* = 6.8 Hz, -CH(CH_3)$_2$), 1.21 (3H, d, *J* = 6.8 Hz, -CH(CH_3)$_2$), 1.08 (3H, d, *J* = 6.8 Hz, -CH(CH_3)$_2$); ^{13}C NMR ($CDCl_3$, 100 MHz) for *syn*-**3p**: δ 169.3, 166.5, 163.4, 137.4, 136.6, 133.7, 132.0, 130.3, 129.0, 128.4, 128.2, 126.7, 106.8, 53.4, 52.3, 28.0, 18.9, 18.7; MS (EI(*syn*-**3p**)) *m/z* (%) 411 (1.64) [M^{+}], 308 (14.13), 266 (5.64), 209 (69.26), 177 (4.46), 149 (38.93), 130 (13.74), 115 (22.47), 105 (100.00), 77 (33.65), 59 (11.86); HRMS (EI) Calcd for $C_{23}H_{22}ClNO_4$ [M^{+}] requires 411.1237, Found 411.1248; The ee of the *syn*-diastereomer was determined to be 86% [determined by HPLC, Chiralpak AD-H, n-hexane/isopropanol = 95:5, 0.7 mL/min, λ = 230 nm, t (major) = 11.42 min, t (minor) = 10.17 min].

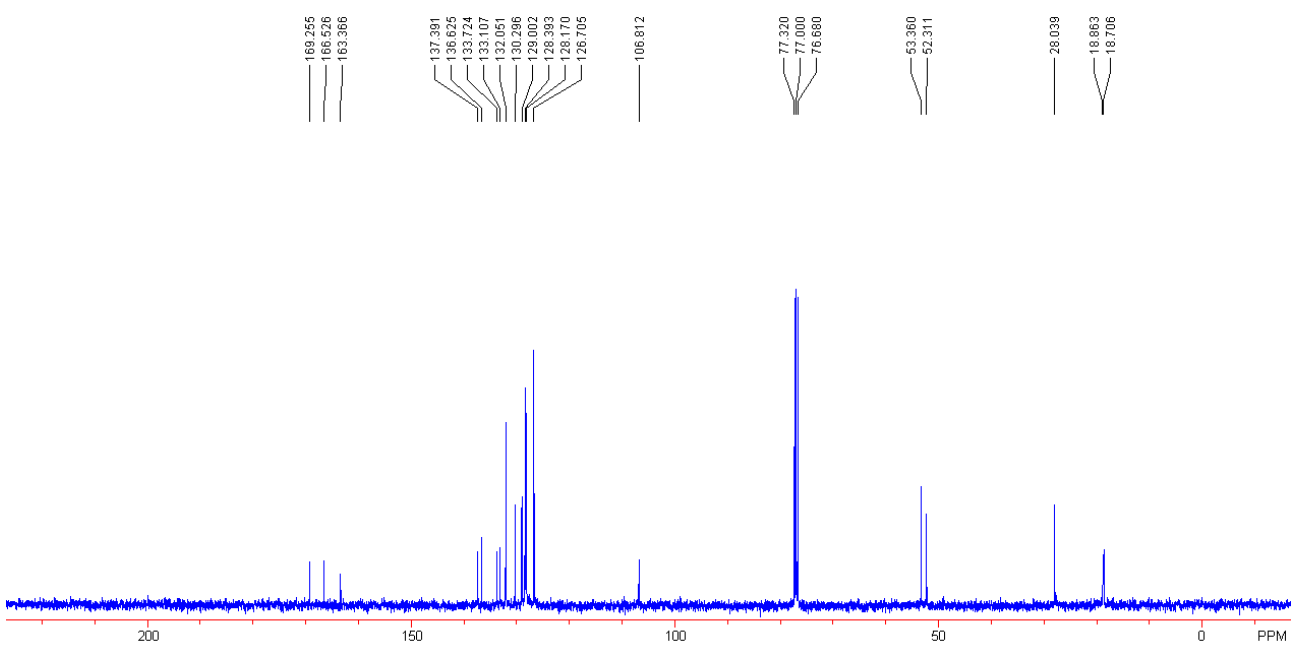
^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the crude product



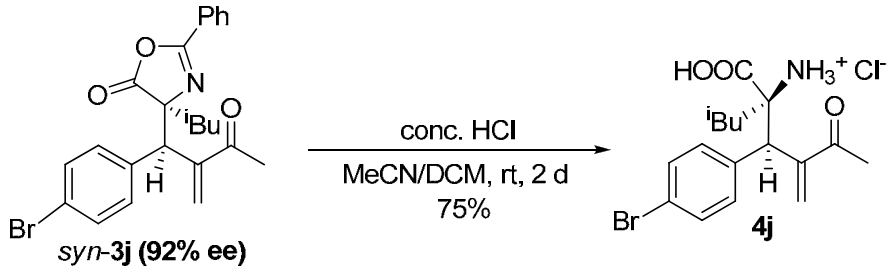
^{1}H NMR (400 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer



^{13}C NMR (100 MHz, $CDCl_3$, TMS) for the *syn*-diastereomer

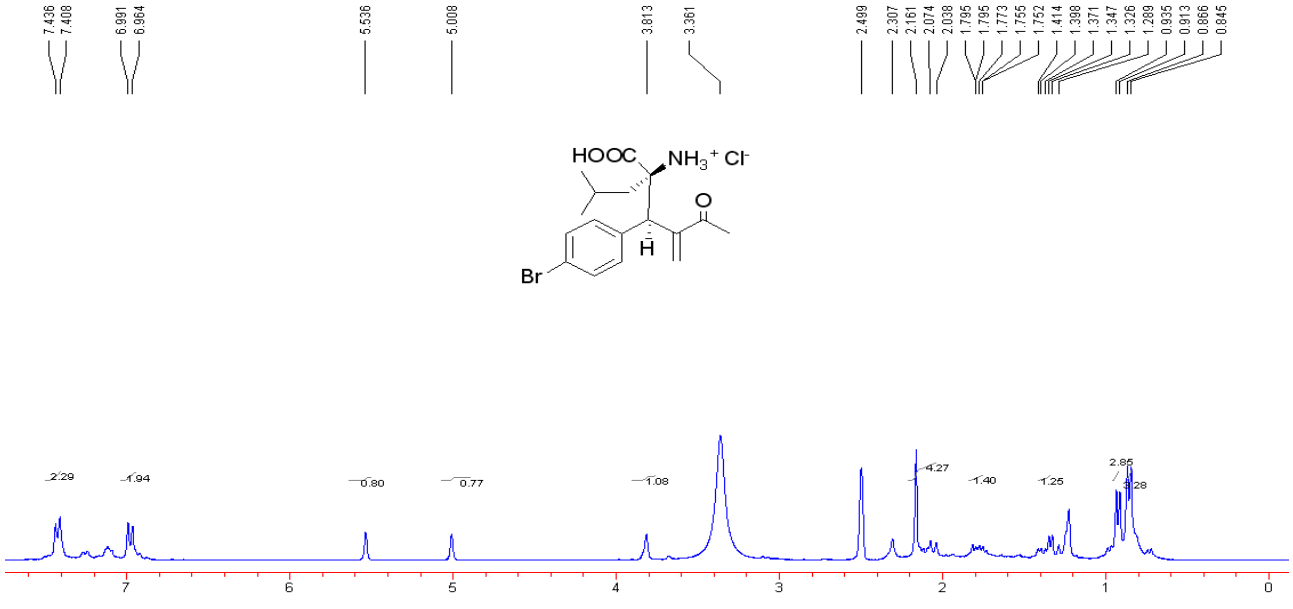


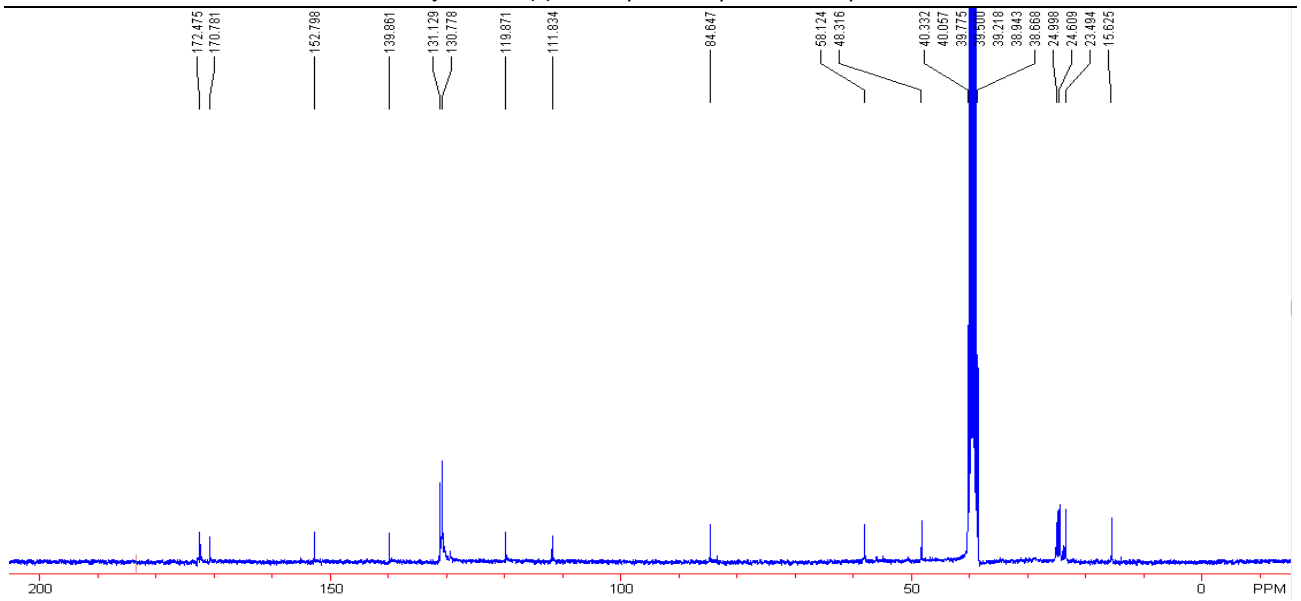
General procedure for the hydrolysis of addition products 3j and 3b to the corresponding amino acid.

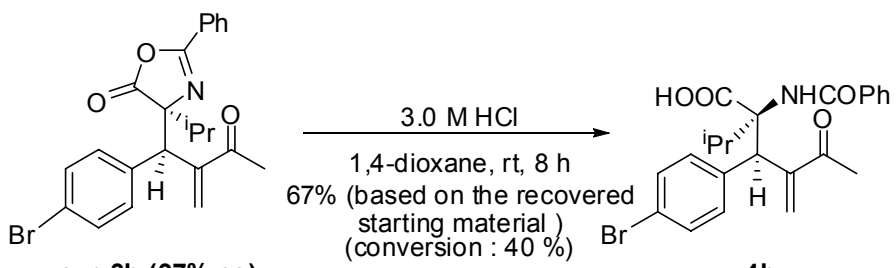


syn-**3j (92% ee)** **4j**

The addition product *syn*-**3j** (30 mg, 60 μmol) was dissolved in mixed solvent of MeCN/DCM (0.20 mL/0.10 mL), then 0.10 mL conc. HCl was added. The resulting mixture was stirred at room temperature for two days. The solvent was removed under reduced pressure and the residue was purified by column chromatography on SiO_2 gel (DCM/EtOH = 40/1 ~ 10/1 as eluent) to give the corresponding amido acid **4j** as white solid (18 mg, 45 μmol, 75% yield).m.p. 95-97 ^oC; $[\alpha]^{20}_D$ = +75.2 (c 0.7, $CHCl_3$). IR (neat): ν 2954, 2922, 2851, 1815, 1697, 1487, 1464, 1382, 1328, 1211, 1154, 1106, 1073, 1009, 909, 821 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 7.42 (2H, d, *J* = 8.4 Hz), 6.98 (2H, d, *J* = 8.4 Hz), 5.54 (1H, s), 5.01 (1H, s), 3.81 (1H, s), 2.31-2.04 (4H, m), 1.80-1.75 (1H, m), 1.42-1.29 (1H, m), 0.92 (3H, d, *J* = 6.6 Hz), 0.86 (3H, d, *J* = 6.6 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 172.5, 170.8, 152.8, 139.9, 131.1, 130.8, 119.9, 111.8, 84.6, 58.1, 48.3, 25.0, 24.6, 23.5, 15.6; MS (ESI) m/e 350 $(M\text{-}H_2O\text{-}HCl)^+$; HRMS (ESI) for $C_{17}H_{21}NO_2Br$ $(M\text{-}H_2O\text{-}HCl)^+$: 350.0750, Found: 350.0757.

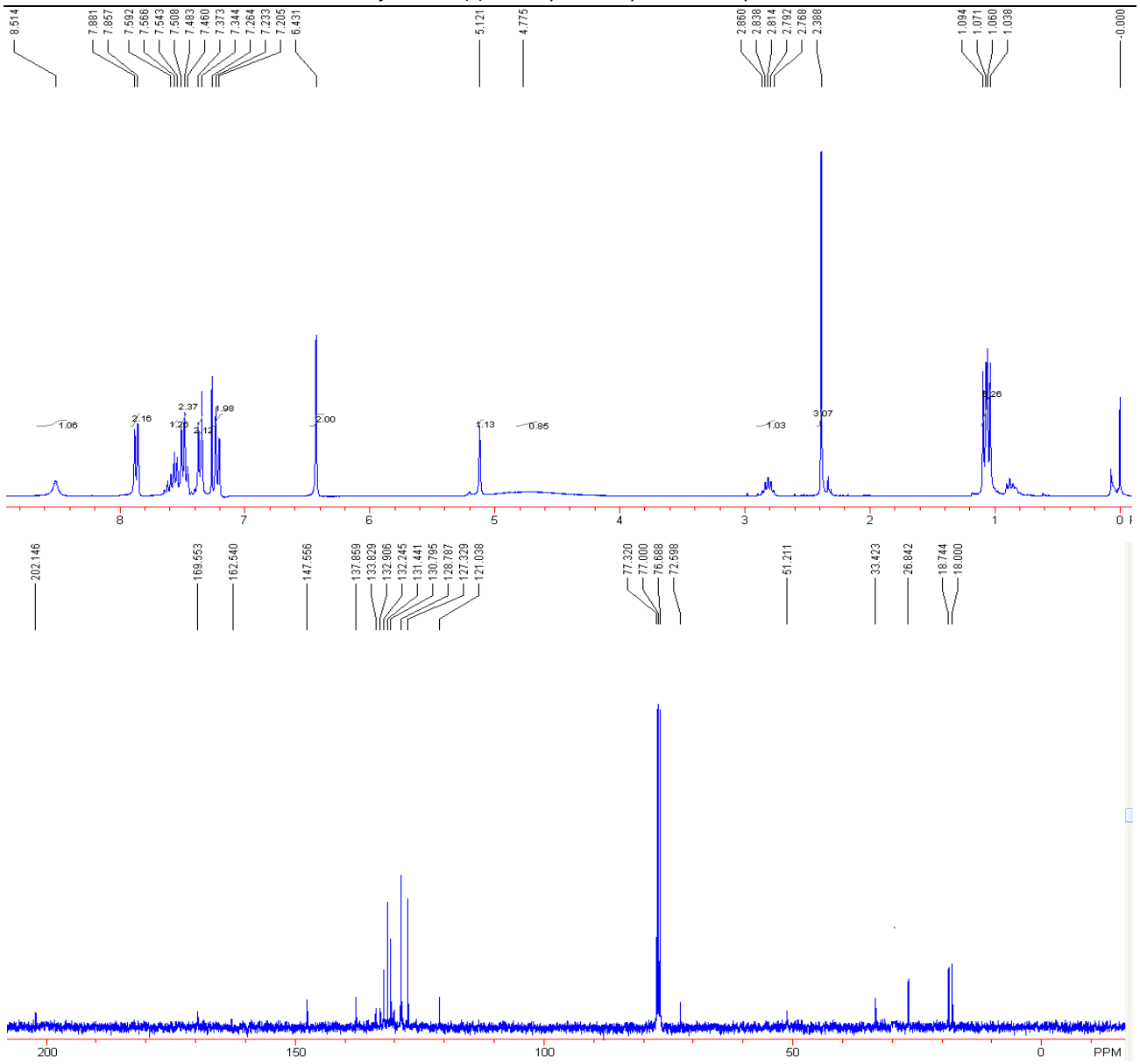






***syn*-3b (97% ee)** **4b**

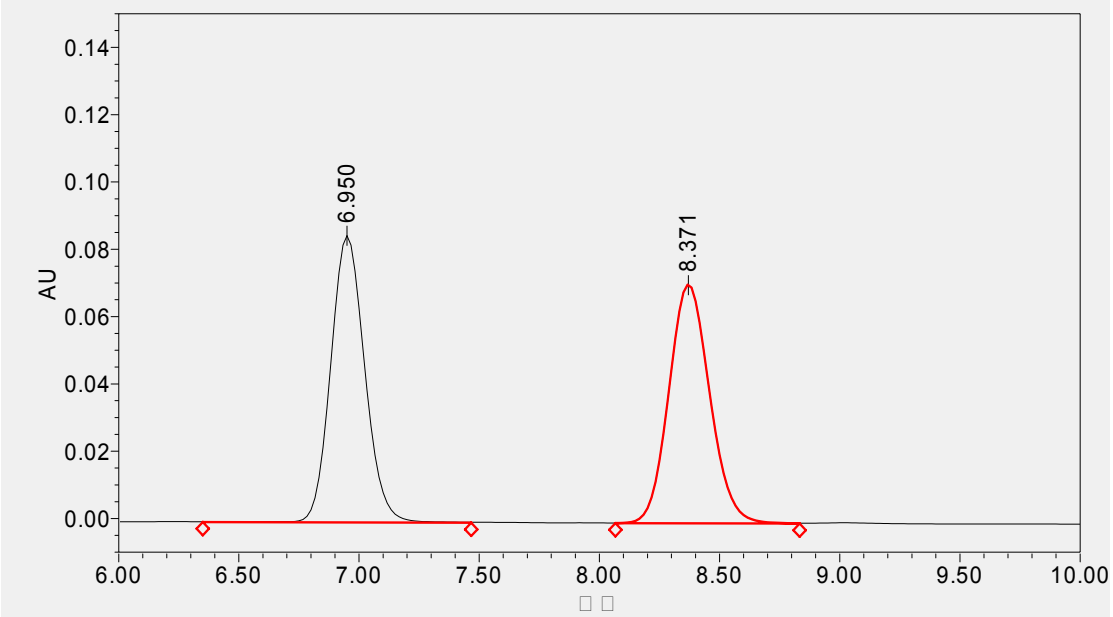
The addition product *syn*-**3b** (65.0 mg, 148 μmol) was dissolved in 500 μL 1,4-dioxane, then 80.0 μL, 3.0 M HCl aqueous solution was added. The resulting mixture was stirred at room temperature for 8 hours. The solvent was removed under reduced pressure and the residue was purified by column chromatography on SiO_2 gel (DCM/EtOH = 40/1 ~ 20/1 as eluent) to give the corresponding amino acid derivative **4b** as white solid (18.0 mg, 39 μmol, 67% yield based on the recovered **3b**, 39.0 mg starting material was recovered). m.p. 139-141 ^oC; $[\alpha]^{20}_D$ = +28.3 (c 0.9, $CHCl_3$). IR (CH_2Cl_2): ν 2927, 2855, 1780, 1714, 1674, 1520, 1487, 1394, 1365, 1264, 1218, 1074, 1011, 895, 801 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 8.51 (1H, bs), 7.87 (2H, d, *J* = 7.2 Hz), 7.57 (1H, d, *J* = 6.8 Hz), 7.48 (2H, d, *J* = 6.8 Hz), 7.36 (2H, d, *J* = 8.7 Hz), 7.22 (2H, d, *J* = 8.7 Hz), 6.43 (1H, s), 5.12 (1H, s), 4.78 (1H, bs), 2.81 (1H, qu, *J* = 7.2 Hz), 2.39 (3H, s), 1.08 (3H, d, *J* = 7.2 Hz), 1.05 (3H, d, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 202.1, 169.6, 162.5, 147.6, 137.9, 133.8, 132.9, 132.2, 131.4, 130.8, 128.8, 127.3, 121.0, 72.6, 51.2, 33.4, 26.8, 18.7, 18.0; MS (ESI) m/e 458 (M^++H); HRMS (ESI) for $C_{23}H_{25}NO_4Br$ (M^++H): 458.0952, Found: 458.0961.


8.514
7.881
7.857
7.592
7.566
7.543
7.508
7.483
7.460
7.373
7.344
7.264
7.233
7.205
6.431
5.121
4.775
2.860
2.838
2.814
2.792
2.768
2.388
1.094
1.071
1.060
1.038
-0.000
1.06
2.16
2.37
1.26
2.12
1.98
2.00
1.13
0.85
1.03
3.07
3.26
202.146
169.553
162.540
147.556
137.859
133.829
132.906
132.245
131.441
130.795
128.787
127.329
121.038
77.320
77.000
76.688
72.598
51.211
33.423
26.842
18.744
18.000
PPM

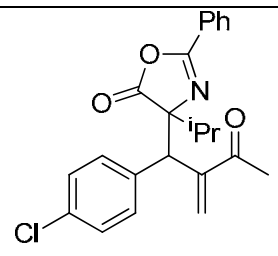
HPLC spectra:

HPLC REPORT

Sample Name: yyl-9-38 Date: ####
Column: AD-H Mobile Phase: hex/ipr = 90/10
Velocity (mL/min): 0.7 Detection Wavelength (nm): 230



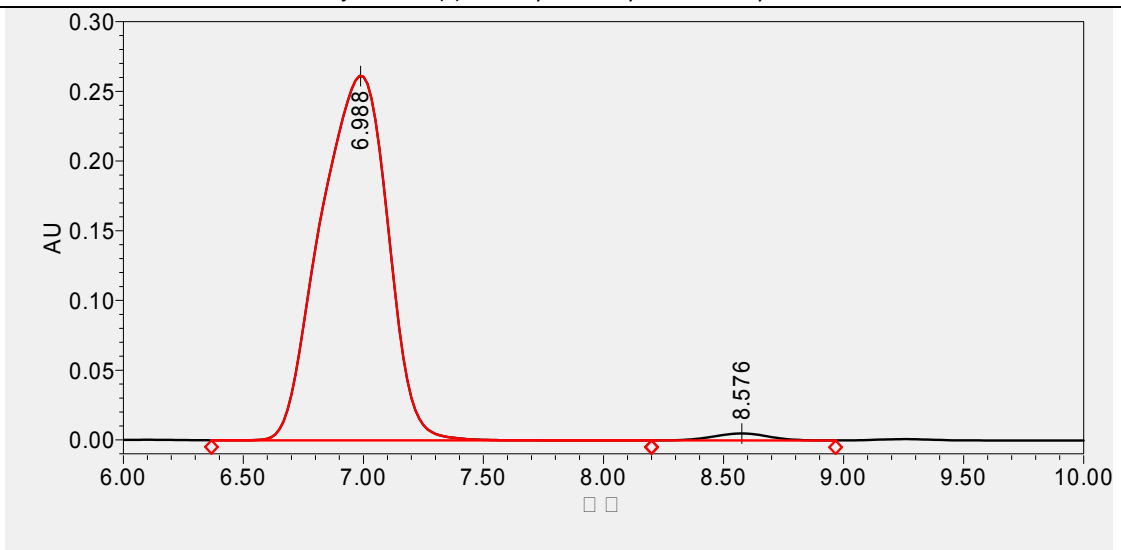
NO	R. Time	Peak Area	Percent	Peak Height
1	6.950	840267	50.11	85140
2	8.371	836746	49.89	70979



Chiral HPLC report: racemate (*syn*-**3a**)

HPLC REPORT

Sample Name: yyl-9-87 Date: ####
Column: AD-H Mobile Phase: hex/ipr = 90/10
Velocity (mL/min): 0.7 Detection Wavelength (nm): 230

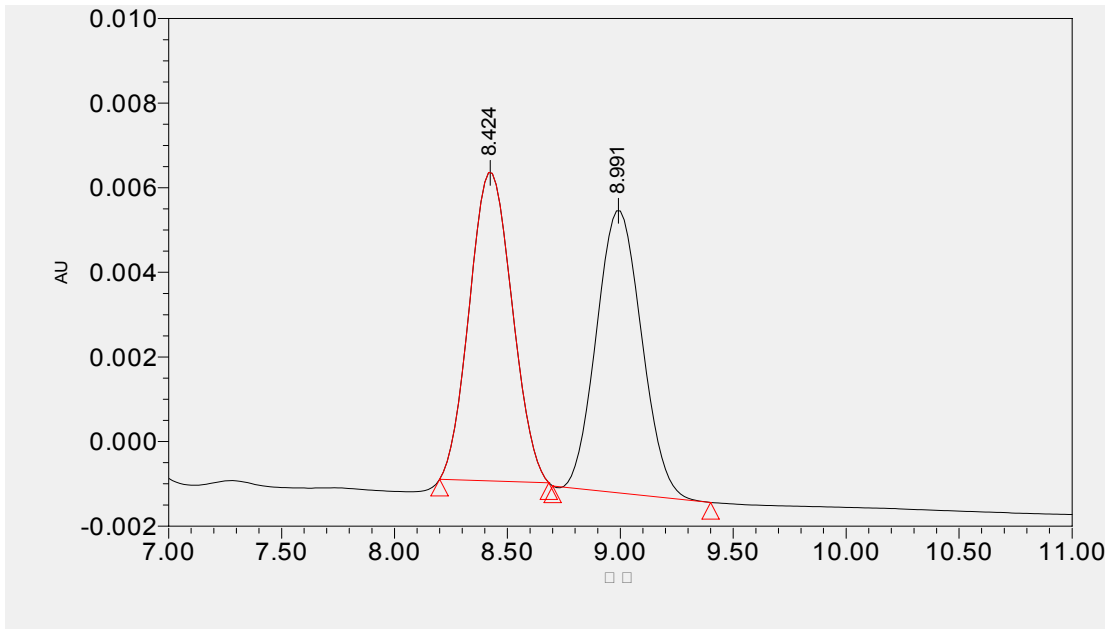


NO	R. Time	Peak Area	Percent	Peak Height
1	6.988	5098447	98.41	261670
2	8.576	82534	1.59	5082

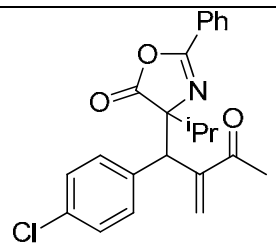
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.7 mL/min; t_{minor} = 8.57 min, t_{major} = 6.98 min; ee% = 97.

HPLC REPORT

Sample Name: yyl-9-64-2 Date: ####
Column: AD-H Mobile Phase: hex/ipr = 90/10
Velocity (mL/min): 0.7 Detection Wavelength (nm): 230



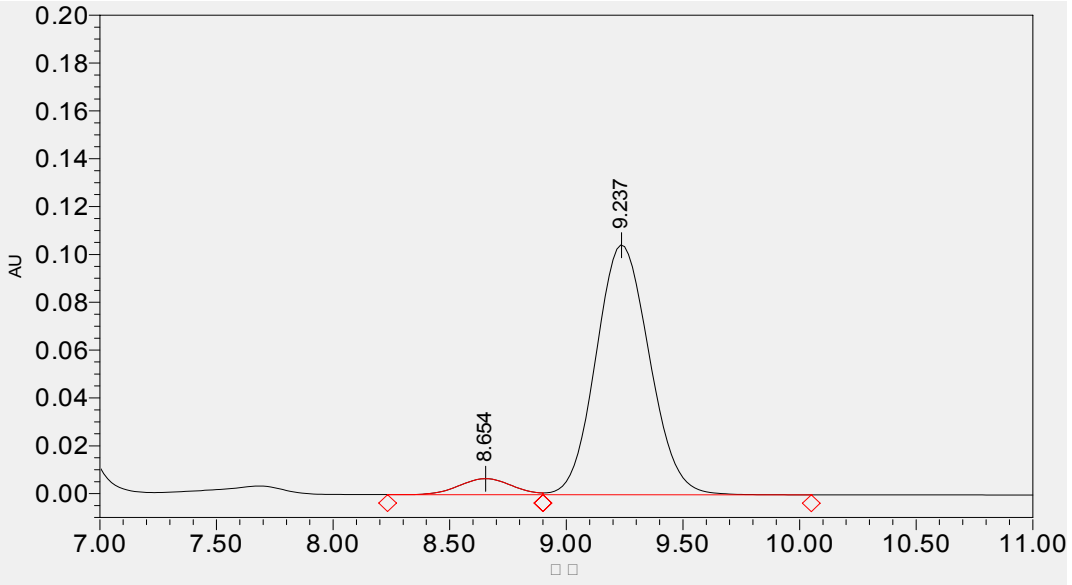
NO	R. Time	Peak Area	Percent	Peak Height
1	8.424	98792	51.47	7409
2	8.991	93152	48.53	6696



Chiral HPLC report: racemate (*anti*-**3a**)

HPLC REPORT

Sample Name: yyl-9-96-2 Date: ####
Column: AD-H Mobile Phase: hex/ipr = 90/10
Velocity (mL/min): 0.7 Detection Wavelength (nm): 230

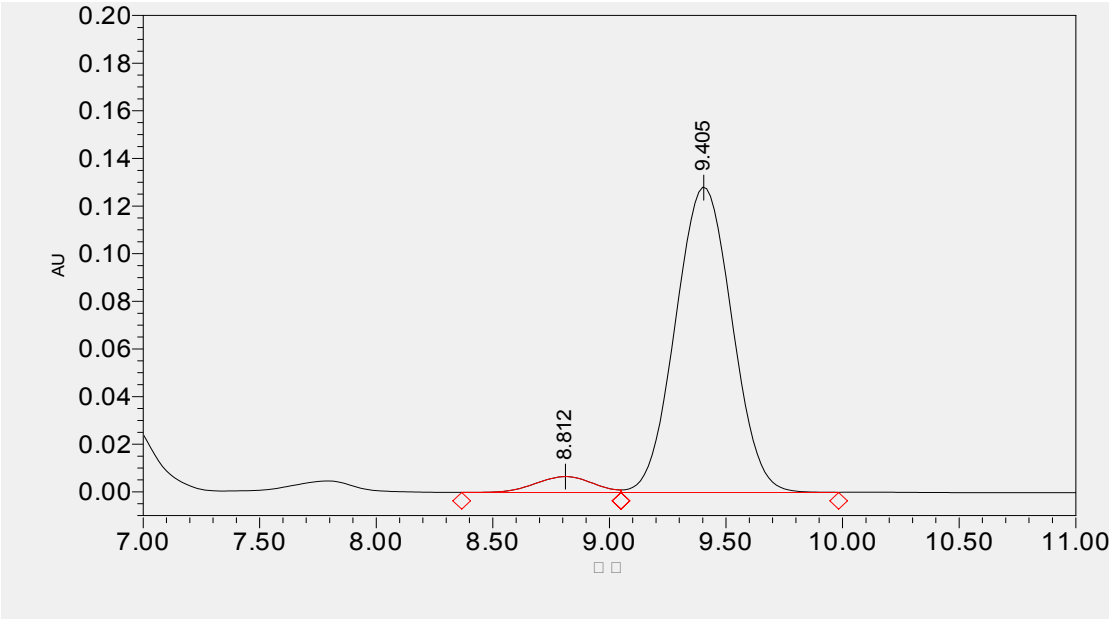


NO	R. Time	Peak Area	Percent	Peak Height
1	8.854	105468	5.95	6695
2	9.237	1668272	94.05	104513

Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.7 mL/min; t_{minor} = 8.85 min, t_{major} = 9.23 min; ee% = 88 (using **L4** as a chiral ligand).

HPLC REPORT

Sample Name: yyl-9-89-2 Date: ####
Column: AD-H Mobile Phase: hex/ipr = 90/10
Velocity (mL/min): 0.7 Detection Wavelength (nm): 230

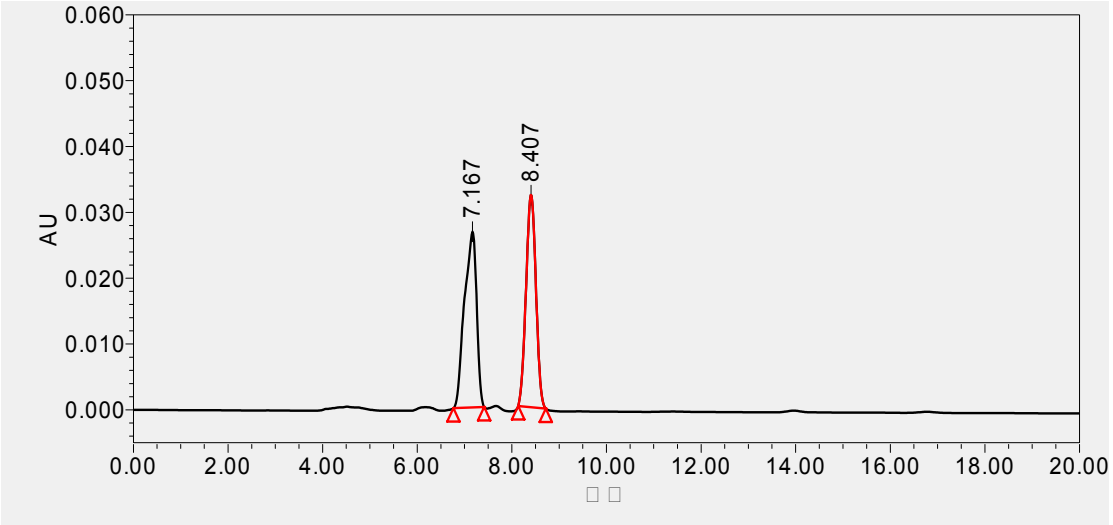


NO	R. Time	Peak Area	Percent	Peak Height
1	8.812	114653	5.04	6681
2	9.405	2161814	94.96	12.8299

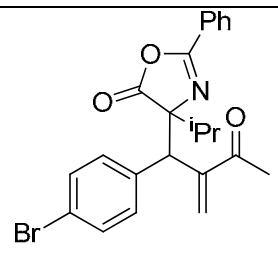
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.7 mL/min; t_{minor} = 8.81 min, t_{major} = 9.40 min; ee% = 90 (using **L2** as a chiral ligand in DMF).

HPLC REPORT

Sample Name: yyl-10-14 Date: ####
Column: AD-H Mobile Phase: hex/ipr = 90/10
Velocity (mL/min): 0.7 Detection Wavelength (nm): 230



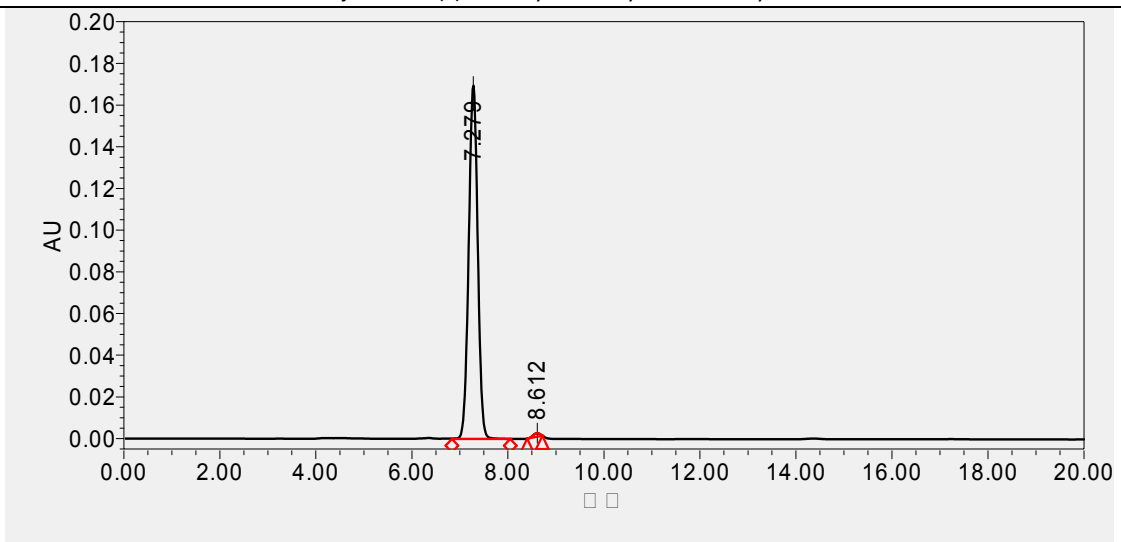
NO	R. Time	Peak Area	Percent	Peak Height
1	7.167	476710	50.38	26700
2	8.407	469426	49.62	32299



Chiral HPLC report: racemate (*syn*-**3b**)

HPLC REPORT

Sample Name: yyl-10-13 Date: ####
Column: AD-H Mobile Phase: hex/ipr = 90/10
Velocity (mL/min): 0.7 Detection Wavelength (nm): 230

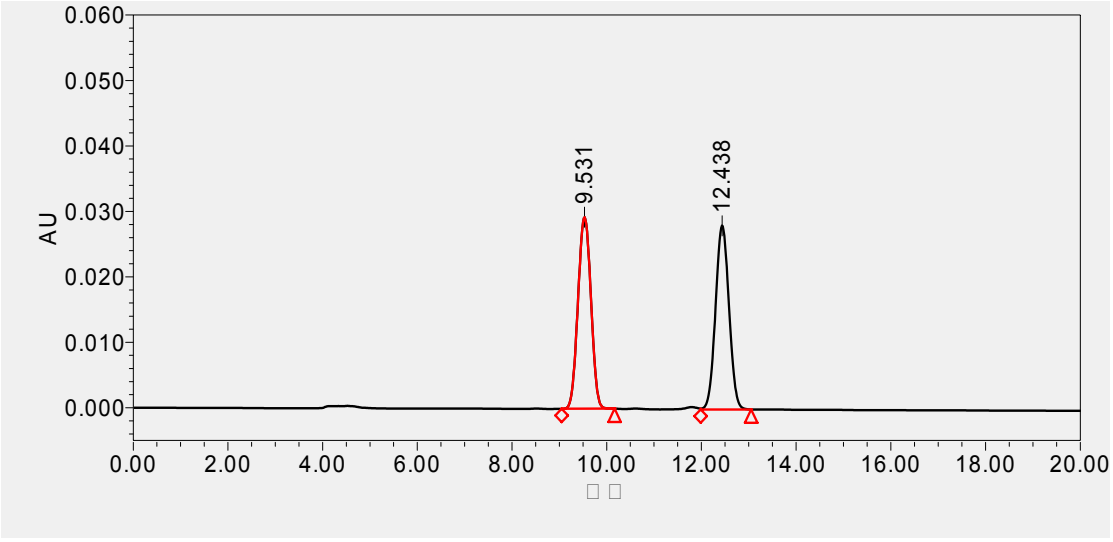


NO	R. Time	Peak Area	Percent	Peak Height
1	7.279	2212527	98.27	169606
2	8.612	38987	1.73	2767

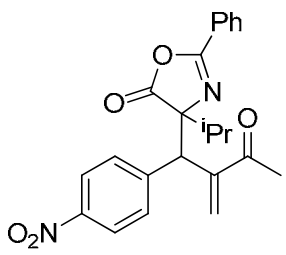
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.7 mL/min; t_{minor} = 8.61 min, t_{major} = 7.28 min; ee% = 97.

HPLC REPORT

Sample Name: yyl-10-16 Date: ####
Column: AD-H Mobile Phase: hex/ipr = 90/10
Velocity (mL/min): 0.7 Detection Wavelength (nm): 230



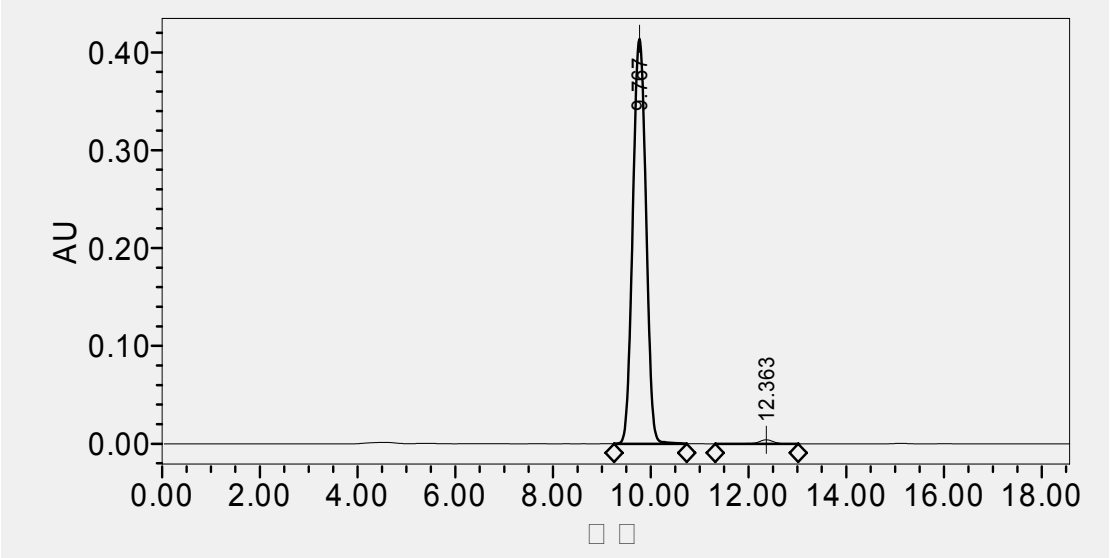
NO	R. Time	Peak Area	Percent	Peak Height
1	9.531	557139	50.06	29268
2	12.438	555823	49.94	28097



Chiral HPLC report: racemate (*syn*-**3c**)

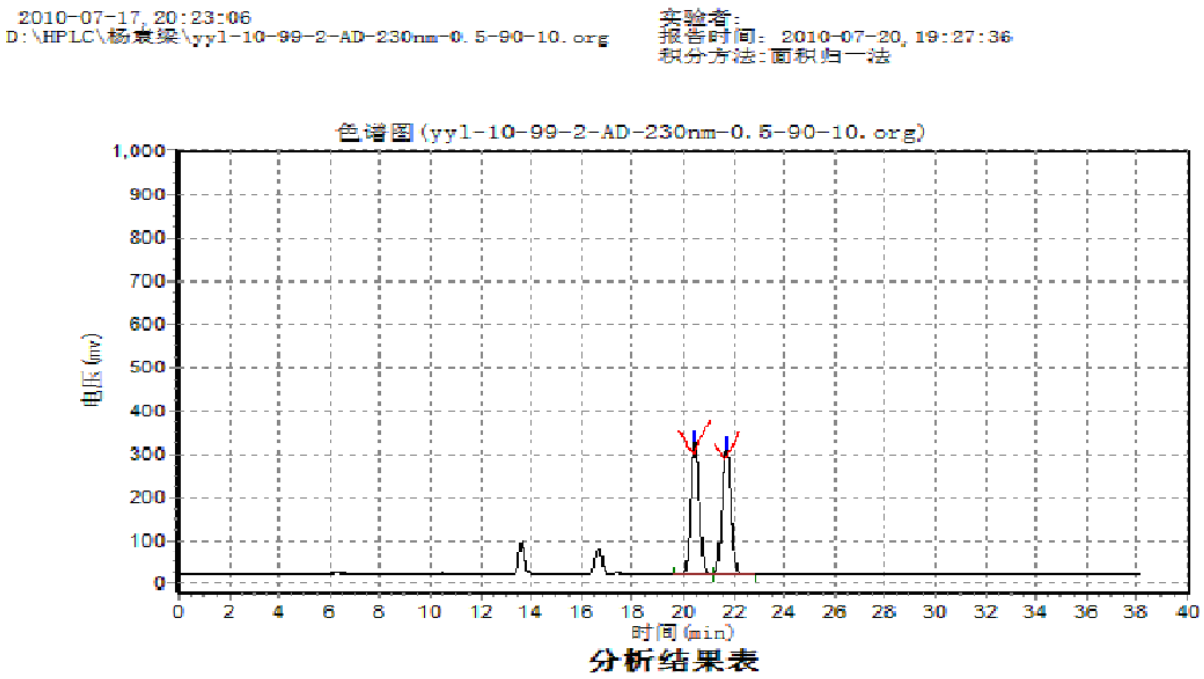
HPLC REPORT

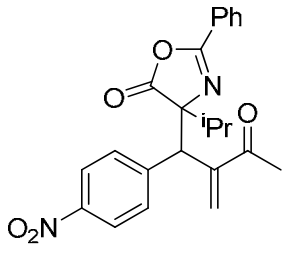
Sample Name: yyl-10-15 Date: ####
Column: AD-H Mobile Phase: hex/ipr = 90/10
Velocity (mL/min): 0.7 Detection Wavelength (nm): 230



NO	R. Time	Peak Area	Percent	Peak Height
1	9.767	7780443	98.91	413858
2	12.363	85683	1.09	4141

Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.7 mL/min; t_{minor} = 12.36 min, t_{major} = 9.77 min; ee% = 98.

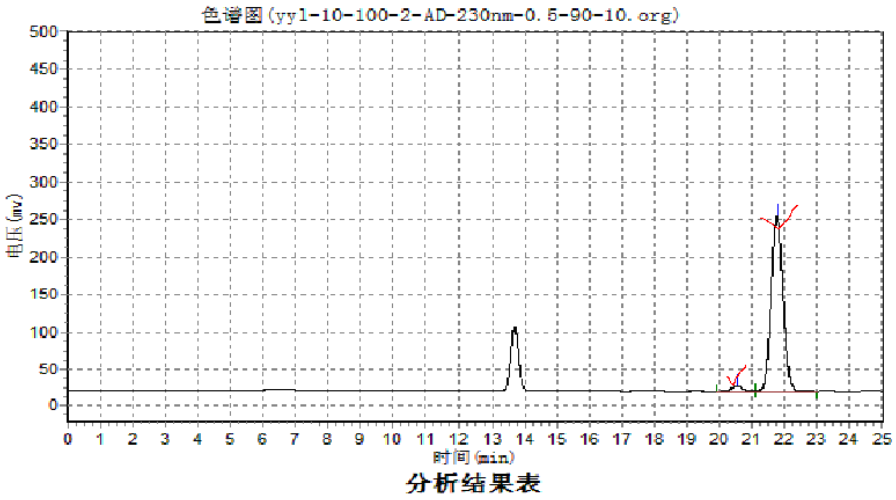




Chiral HPLC report: racemate (*anti*-**3c**)

N2000 数据工作站 1

实验时间：2010-07-17,20:54:46
谱图文件:D:\HPLC\杨袁梁\yyl-10-100-2-AD-230nm-0.5-90-10.org
实验者:
报告时间：2010-07-20,19:30:38
积分方法:面积归一法



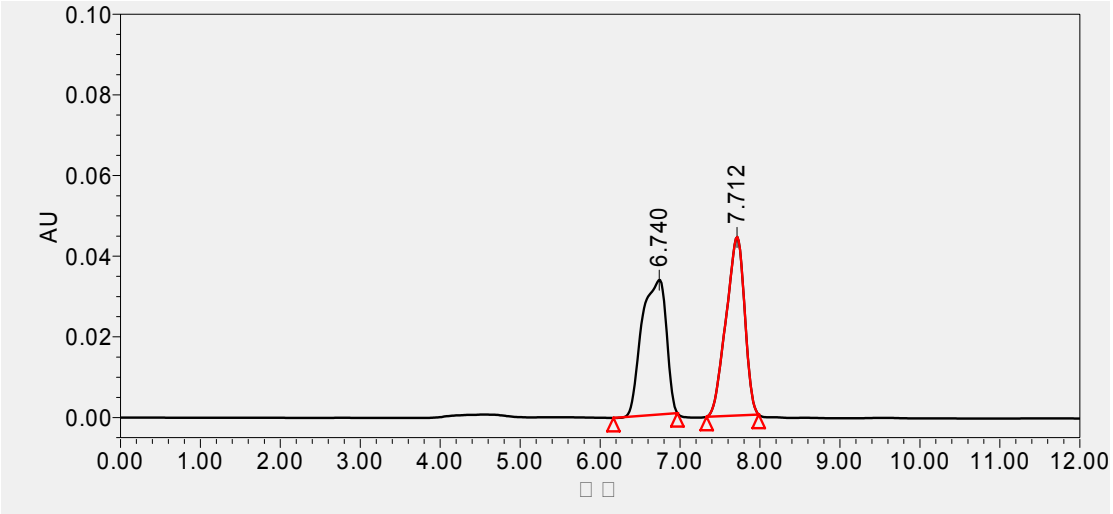
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		20.542	7050.819	170989.484	2.7903
2		21.785	233625.969	5957092.000	97.2097
总计			240676.788	6128081.484	100.0000

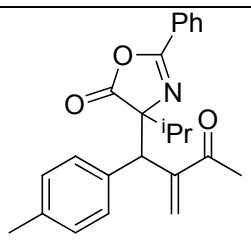
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.5 mL/min; t_{minor} = 20.54 min, t_{major} = 21.78 min; ee% = 94.

HPLC REPORT

Sample Name: yyl-10-17 Date: ####
Column: AD-H Mobile Phase: hex/ipr = 90/10
Velocity (mL/min): 0.7 Detection Wavelength (nm): 230



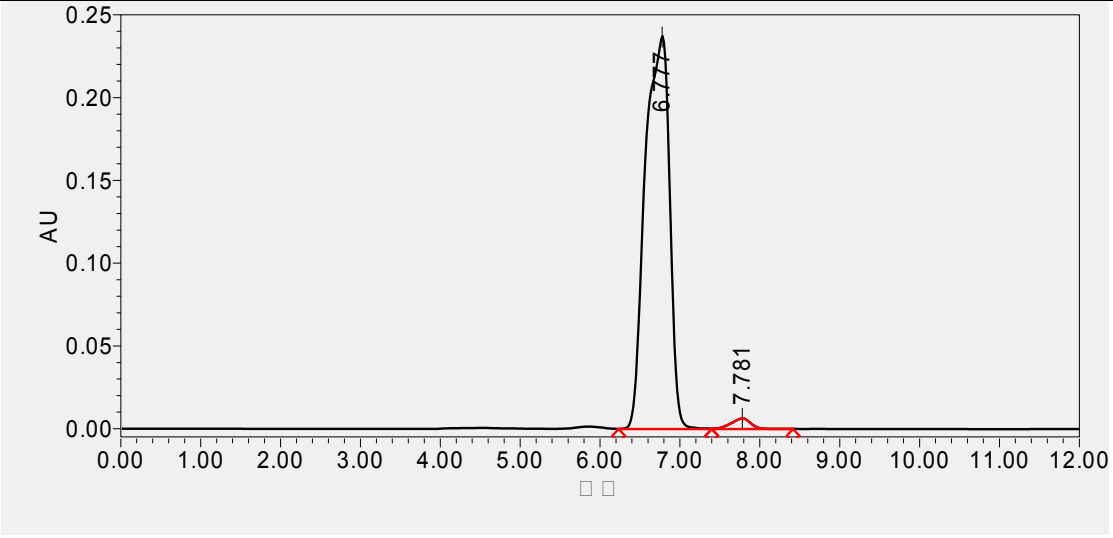
NO	R. Time	Peak Area	Percent	Peak Height
1	6.740	711099	49.78	33471
2	7.712	717438	50.22	44287



Chiral HPLC report: racemate (*syn*-**3d**)

HPLC REPORT

Sample Name: yyl-10-19 Date: ####
Column: AD-H Mobile Phase: hex/ipr = 90/10
Velocity (mL/min): 0.7 Detection Wavelength (nm): 230

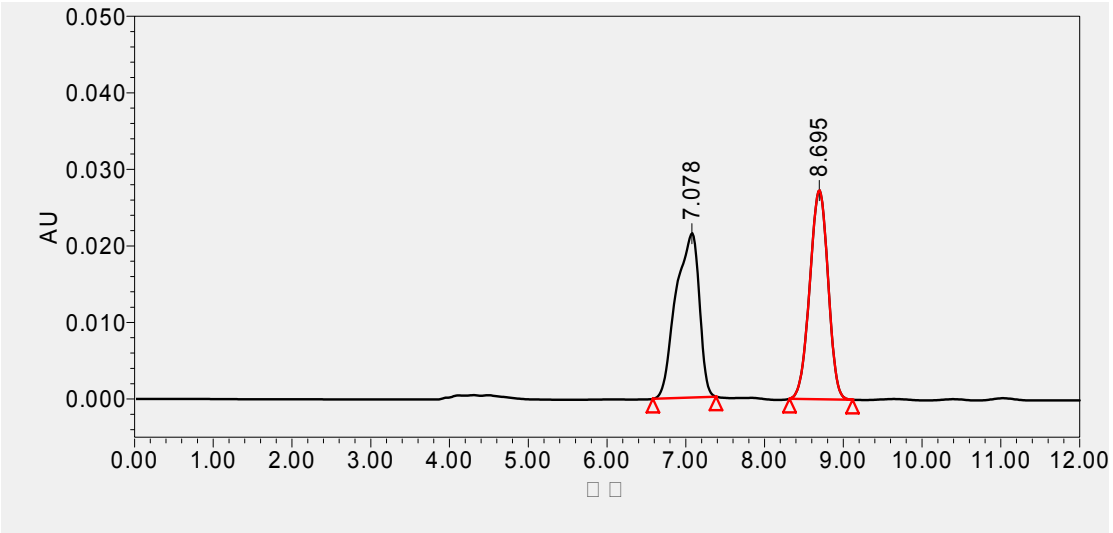


NO	R. Time	Peak Area	Percent	Peak Height
1	6.777	5040258	97.86	237452
2	7.781	110022	2.14	6420

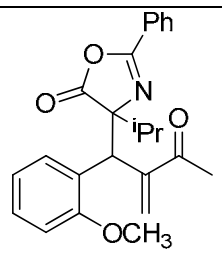
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.7 mL/min; t_{minor} = 7.78 min, t_{major} = 6.78 min; ee% = 96.

HPLC REPORT

Sample Name: yyl-10-20 Date: ####
Column: AD-H Mobile Phase: hex/ipr = 90/10
Velocity (mL/min): 0.7 Detection Wavelength (nm): 230



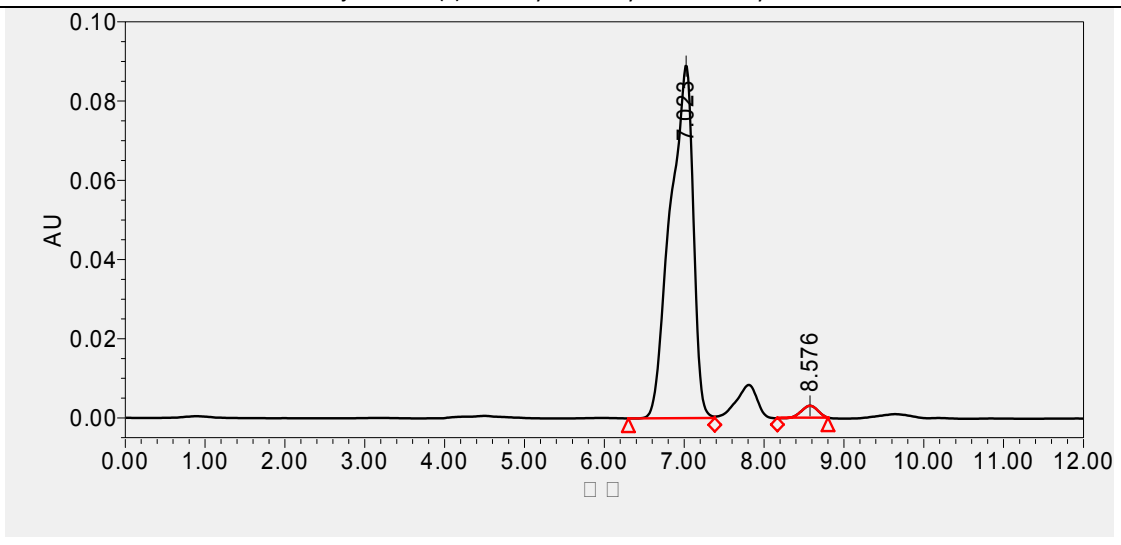
NO	R. Time	Peak Area	Percent	Peak Height
1	7.078	442027	49.99	21469
2	8.695	442129	50.01	27315



Chiral HPLC report: racemate (*syn*-**3e**)

HPLC REPORT

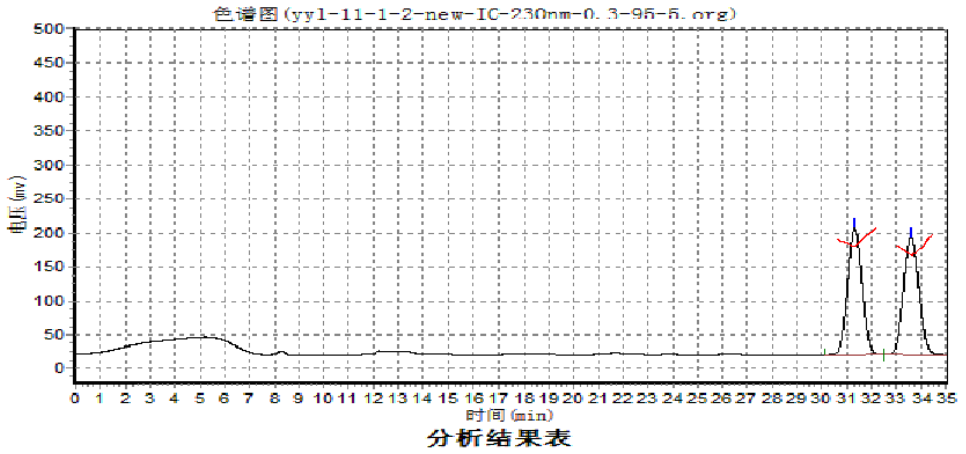
Sample Name: yyl-10-21 Date: ####
Column: AD-H Mobile Phase: hex/ipr = 90/10
Velocity (mL/min): 0.7 Detection Wavelength (nm): 230



NO	R. Time	Peak Area	Percent	Peak Height
1	7.023	1776713	97.63	89037
2	8.576	43154	2.37	2991

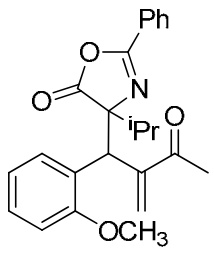
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.7 mL/min; t_{minor} = 8.57 min, t_{major} = 7.02 min; ee% = 95.

实验时间：2010-07-18, 17:32:44　　实验者：
谱图文件:D:\HPLC\杨袁梁\yyl-11-1-2-new-IC-230nm-0.3-95-5.org　　报告时间：2010-07-20, 19:35:12
积分方法:面积归一法



分析结果表

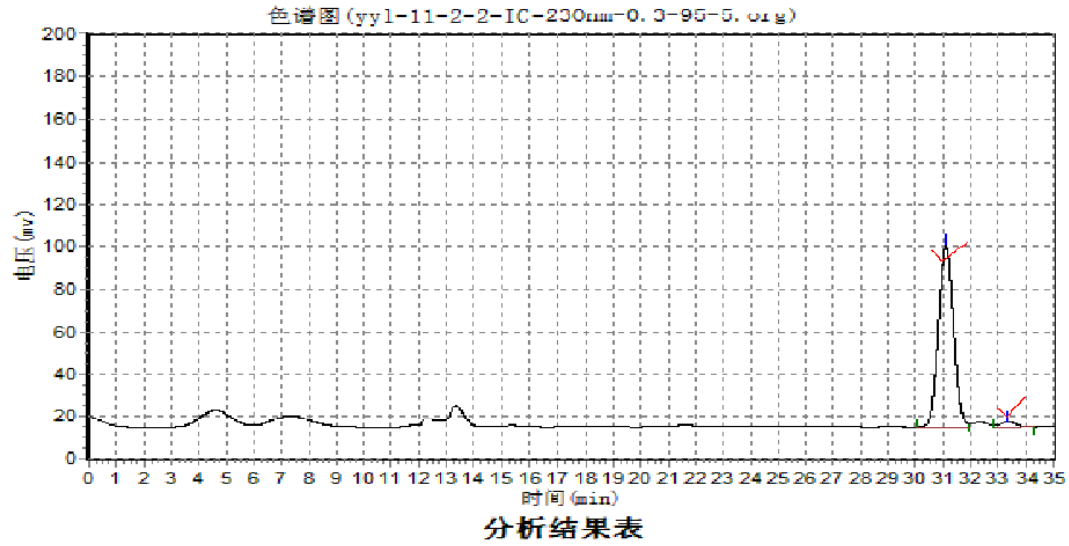
峰号	峰名	保留时间	峰高	峰面积	含量
1		31.317	185209.281	7503865.000	50.0961
2		33.603	171393.563	7475071.000	49.9039
总计			356602.844	14978936.000	100.0000



Chiral HPLC report: racemate (*anti*-**3e**)

时间：2010-07-18, 16:36:01
文件:D:\HPLC\杨袁骏\yyl-11-2-2-IC-230nm-0.3-95-5.org

实验者:
报告时间：2010-07-20, 19:40:09
积分方法:面积归一法

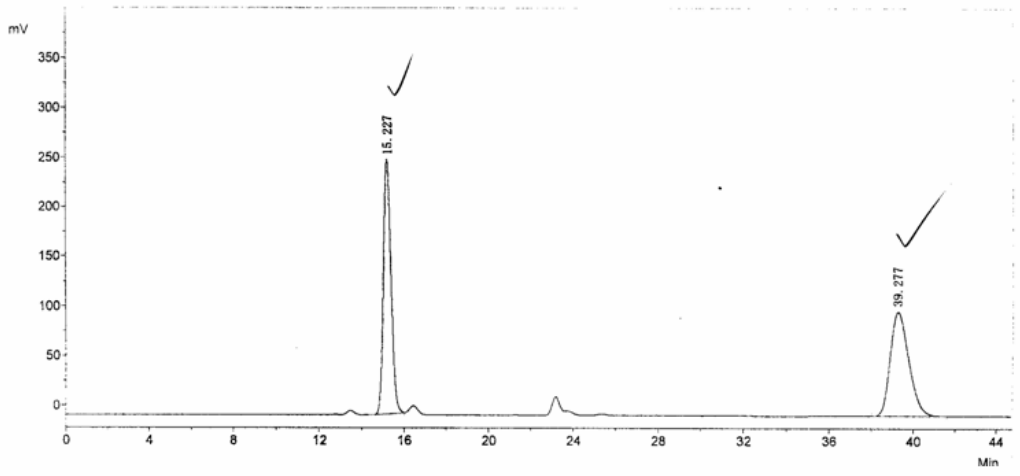


分析结果表

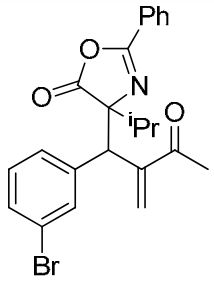
峰号	峰名	保留时间	峰高	峰面积	含量
1		31.097	85199.984	3256742.000	96.8823
2		33.337	2548.502	104802.445	3.1177
总计			87748.486	3361544.445	100.0000

Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak IC column; λ = 230 nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 0.3 mL/min; t_{minor} = 33.33 min, t_{major} = 31.09 min; ee% = 94.

Sample Name:yyl-10-38rac ic 99.che
Date:2010-05-18
Time:11:08
Method:
column: ZC
the mobile phase: 99/1
Velocity: 0.7
the detection wavelength: 230



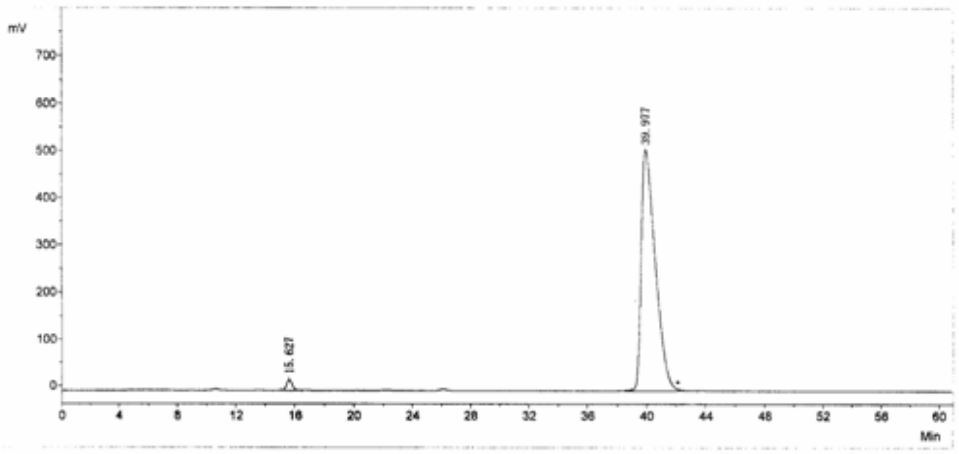
No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	15.227	254851.7	6365826.9	49.7065
2	2	39.277	104389.1	6441009.6	50.2935
Total			359240.8	12806836.5	100.0000



Chiral HPLC report: racemate (*syn*-**3f**)

HPLC REPORT

Sample Name:yyl-10-22.che
Date:2010-05-18
Time:10:06
Method:
column:
the mobile phase:
Velocity:
the detection wavelength:

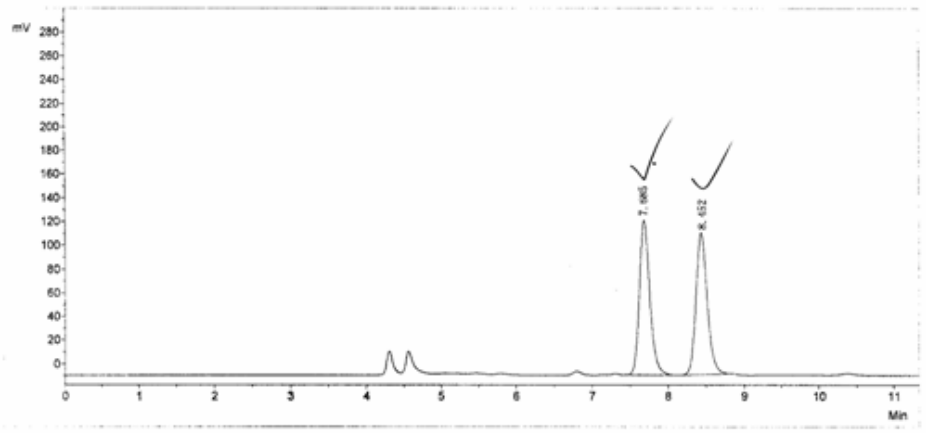


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	15.627	22523.8	589098.7	1.7000
2	2	39.977	511550.0	34063365.0	98.3000
Total			534073.8	34652463.7	100.0000

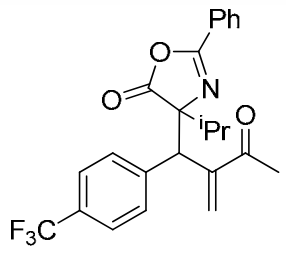
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak IC column; λ = 230 nm; eluent: Hexane/Isopropanol = 99/1; Flow rate: 0.7 mL/min; t_{minor} = 39.97 min, t_{major} = 15.63 min; ee% = 97.

HPLC REPORT

Sample Name:yyl-10-37rac ad250 95.che
Time:15:39
column: AD-H(250)
Velocity: 0.7
Date:2010-05-17
Method:
the mobile phase: 95/5
the detection wavelength: 230



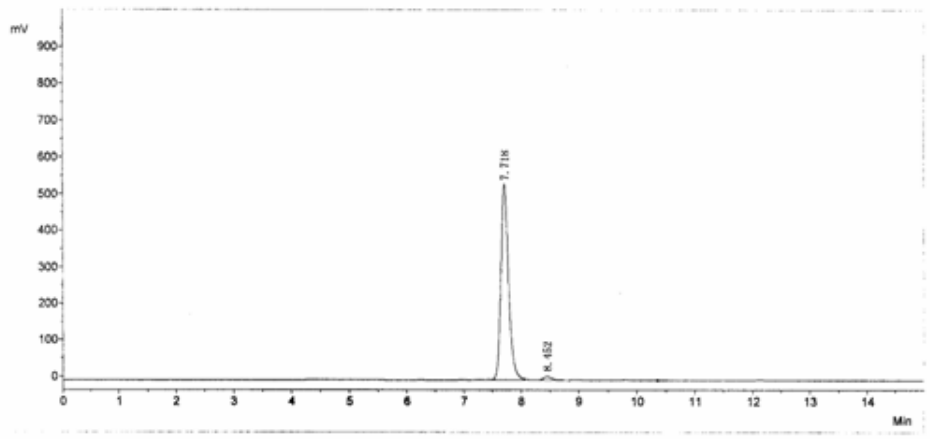
No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	7.685	129752.3	1256826.3	50.3942
2	2	8.452	117985.8	1237164.5	49.6058
Total			247738.1	2493990.8	100.0000



Chiral HPLC report: racemate (*syn*-**3g**)

HPLC REPORT

Sample Name:yyl-10-23.che
Date:2010-05-17
Time:16:40
Method:
column:
the mobile phase:
Velocity:
the detection wavelength:

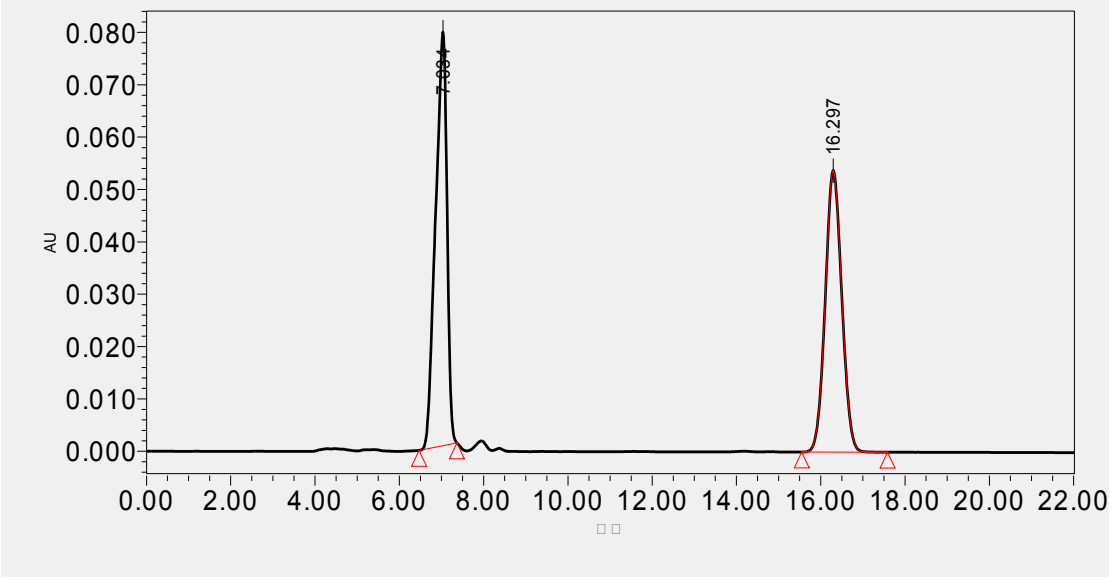


No.	PeakNo	R.Time	PeakHeight	PeakArea	PerCent
1	1	7.718	531329.9	5005319.2	98.1378
2	2	8.452	9374.6	94979.6	1.8622
Total			540704.6	5100298.8	100.0000

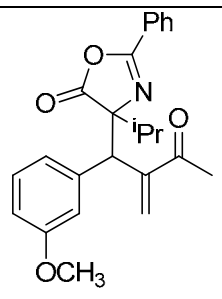
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 0.7 mL/min; t_{minor} = 8.45 min, t_{major} = 7.72 min; ee% = 96.

HPLC REPORT

Sample Name: yyl-10-41 Date: ####
Column: AD-H Mobile Phase: hex/ipr = 90/10
Velocity (mL/min): 0.7 Detection Wavelength (nm): 230



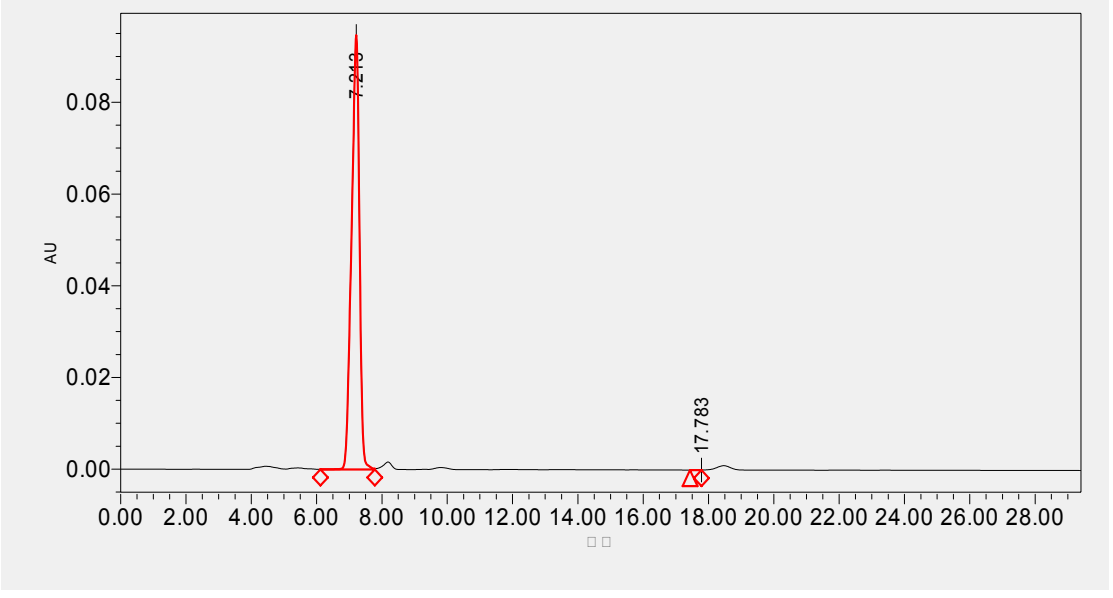
NO	R. Time	Peak Area	Percent	Peak Height
1	7.034	1484249	50.30	78970
2	16.297	1466305	49.70	53796



Chiral HPLC report: racemate (*syn*-**3h**)

HPLC REPORT

Sample Name: yyl-10-43 Date: ####
Column: AD-H Mobile Phase: hex/ipr = 90/10
Velocity (mL/min): 0.7 Detection Wavelength (nm): 230

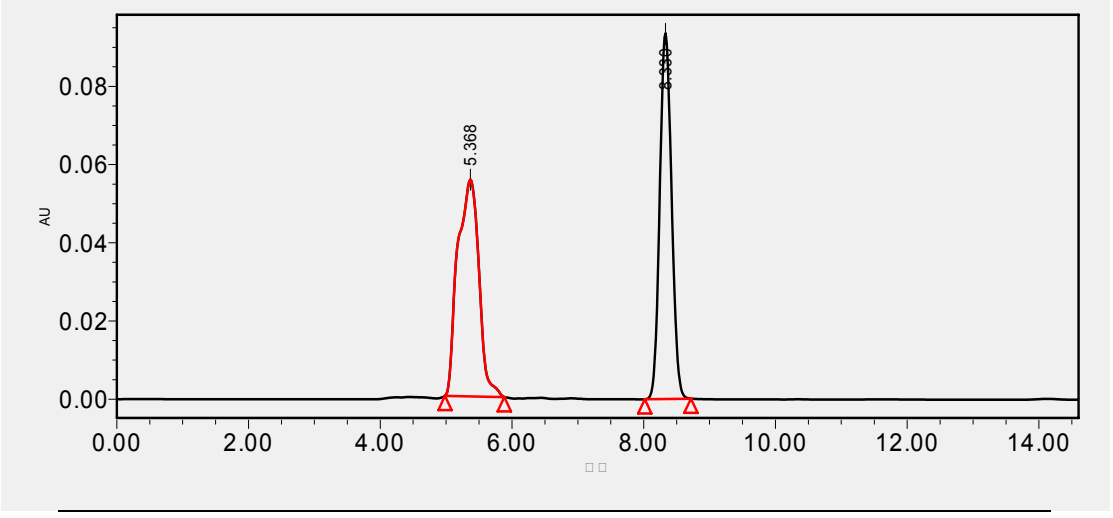


NO	R. Time	Peak Area	Percent	Peak Height
1	7.213	1591978	99.99	94766
2	17.783	220	0.01	20

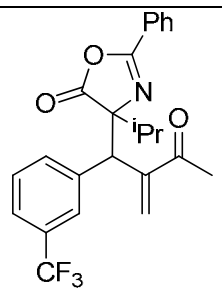
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.7 mL/min; t_{minor} = 17.78 min, t_{major} = 7.21 min; ee% = >99.

HPLC REPORT

Sample Name: yyl-10-40 Date: ####
Column: AD-H Mobile Phase: hex/ipr = 90/10
Velocity (mL/min): 0.7 Detection Wavelength (nm): 230



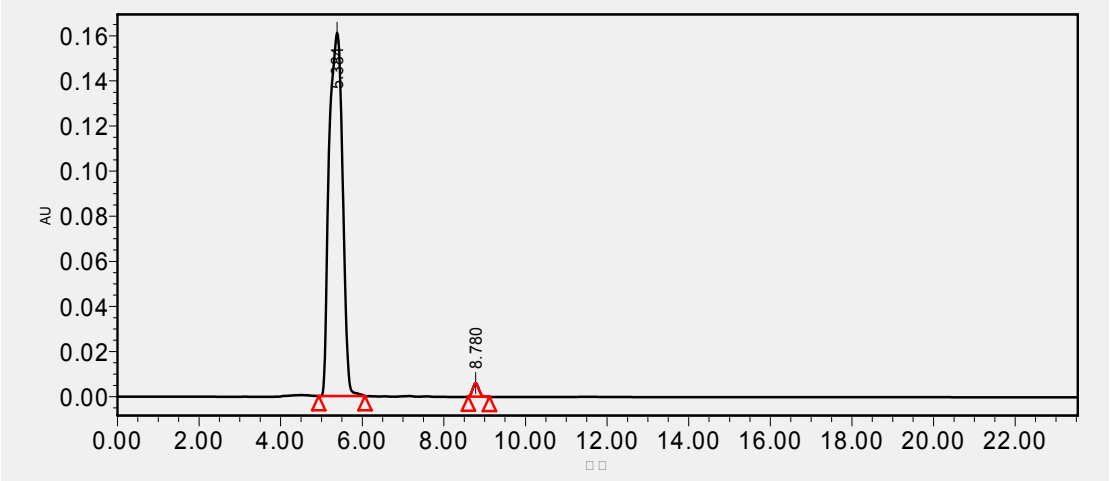
NO	R. Time	Peak Area	Percent	Peak Height
1	5.368	1244917	51.64	55442
2	8.330	1165709	48.36	93601



Chiral HPLC report: racemate (*syn*-**3i**)

HPLC REPORT

Sample Name: yyl-10-42 Date: ####
Column: AD-H Mobile Phase: hex/ipr = 90/10
Velocity (mL/min): 0.7 Detection Wavelength (nm): 230

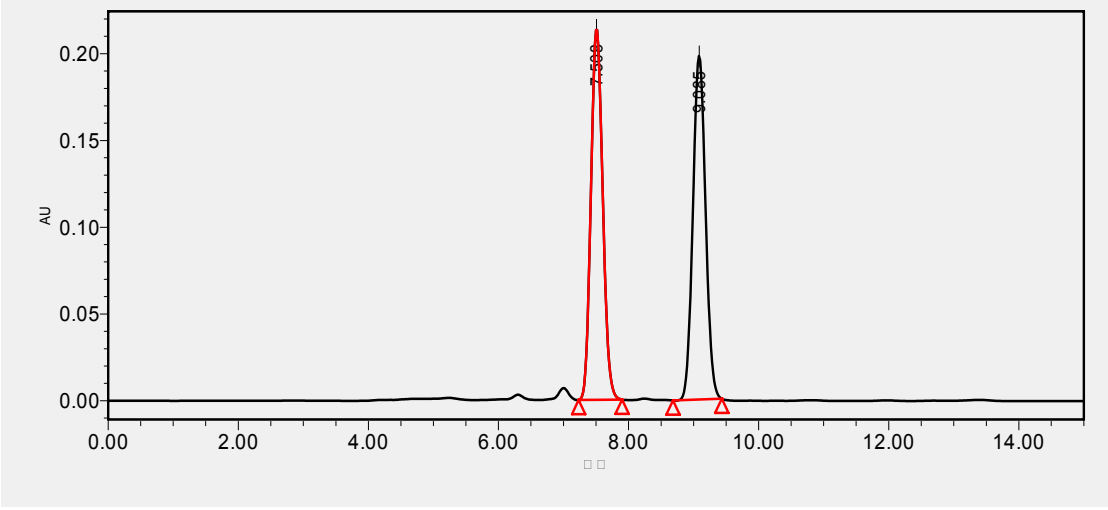


NO	R. Time	Peak Area	Percent	Peak Height
1	5.384	3673036	98.34	161115
2	8.780	62086	1.66	6066

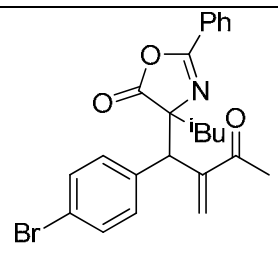
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.7 mL/min; t_{minor} = 8.78 min, t_{major} = 5.38 min; ee% = 97.

HPLC REPORT

Sample Name: yyl-10-48 Date: ####
Column: AD-H Mobile Phase: hex/ipr= 90/10
Velocity (mL/min): 0.7 Detection Wavelength (nm): 230



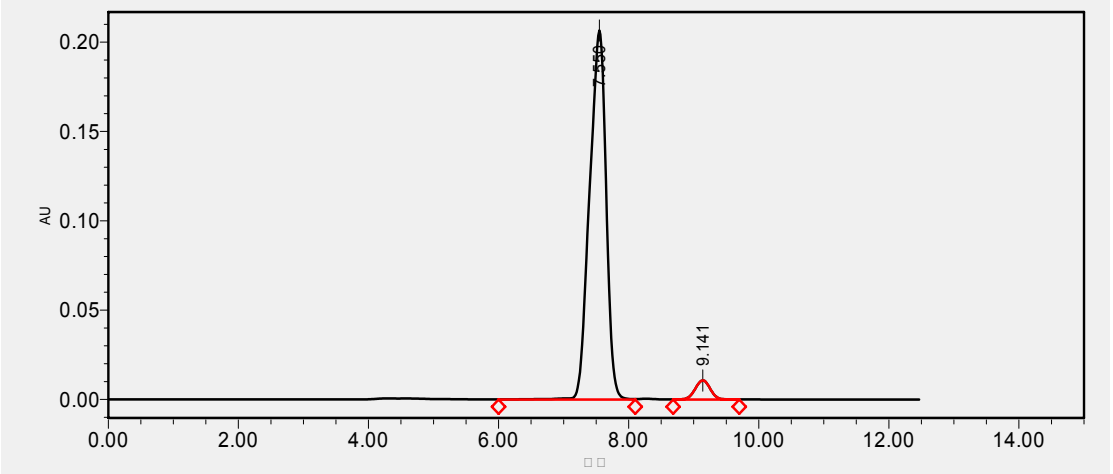
NO	R. Time	Peak Area	Percent	Peak Height
1	7.508	2694445	50.12	214074
2	9.085	2681332	49.88	197973



Chiral HPLC report: racemate (*syn*-**3j**)

HPLC REPORT

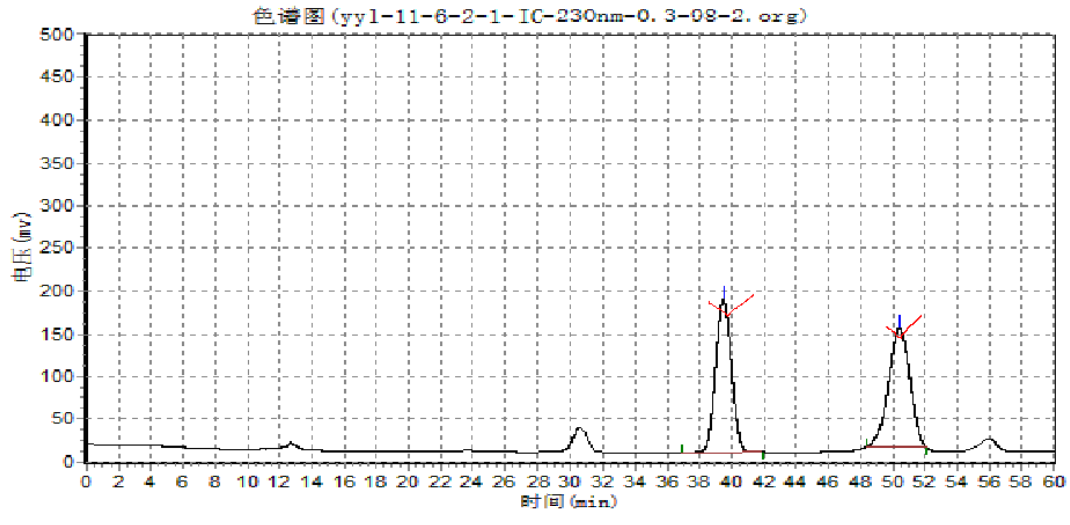
Sample Name: yyl-10-49 Date: ####
Column: AD-H Mobile Phase: hex/ipr = 90/10
Velocity (mL/min): 0.7 Detection Wavelength (nm): 230



NO	R. Time	Peak Area	Percent	Peak Height
1	7.550	3654600	95.46	206594
2	9.141	173792	4.54	10746

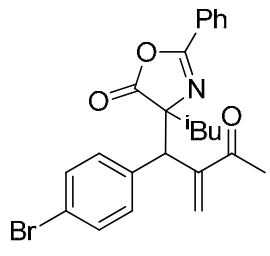
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.7 mL/min; t_{minor} = 9.14 min, t_{major} = 7.55 min; ee% = 91.

积分方法:面积归一法

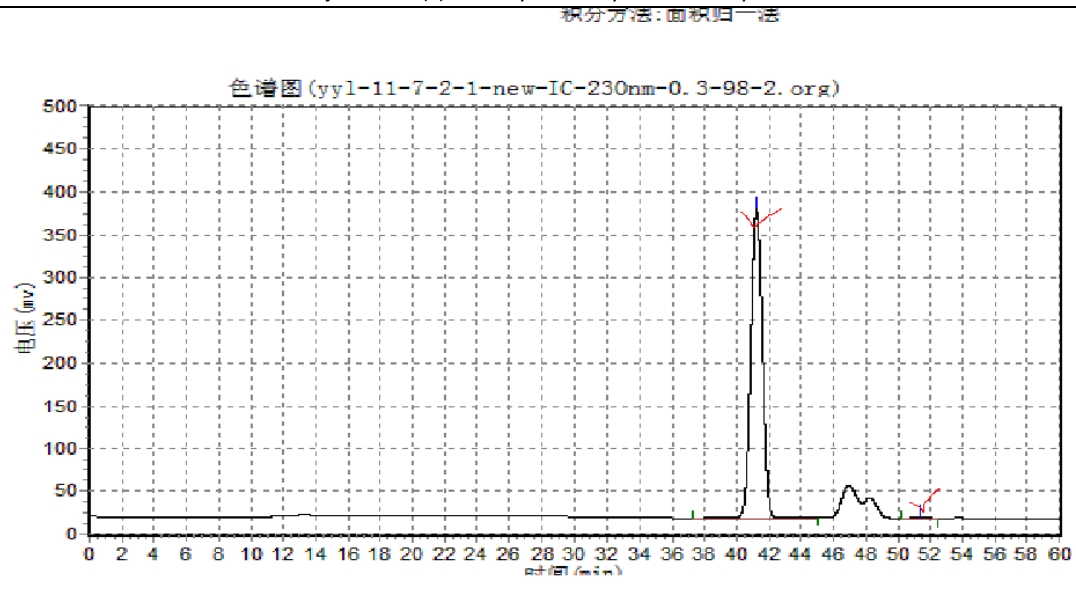


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		39.468	178487.797	12183999.000	48.8318
2		50.423	138391.859	12766958.000	51.1682
总计			316879.656	24950957.000	100.0000



Chiral HPLC report: racemate (*anti*-**3j**)



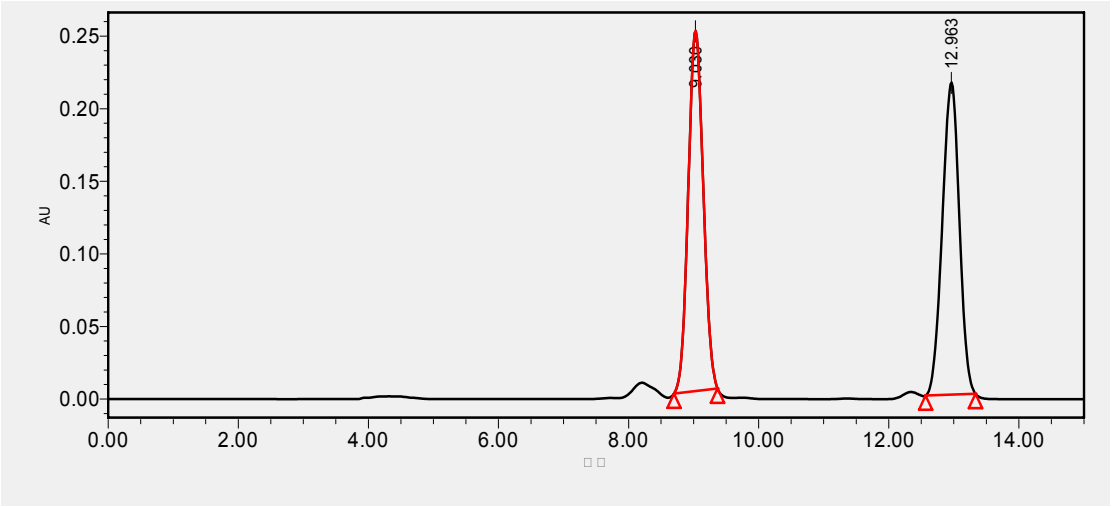
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		41.215	360279.219	18047374.000	99.1099
2		51.363	2385.264	162076.516	0.8901
总计			362664.482	18209450.516	100.0000

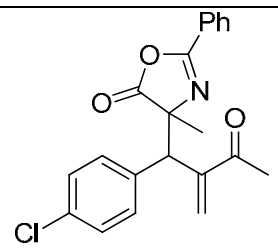
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak IC column; λ = 230 nm; eluent: Hexane/Isopropanol = 98/2; Flow rate: 0.3 mL/min; t_{minor} = 51.36 min, t_{major} = 41.25 min; ee% = 98.

HPLC REPORT

Sample Name: yyl-10-50 Date: ####
Column: AD-H Mobile Phase: hex/ipr = 90/10
Velocity (mL/min): 0.7 Detection Wavelength (nm): 230



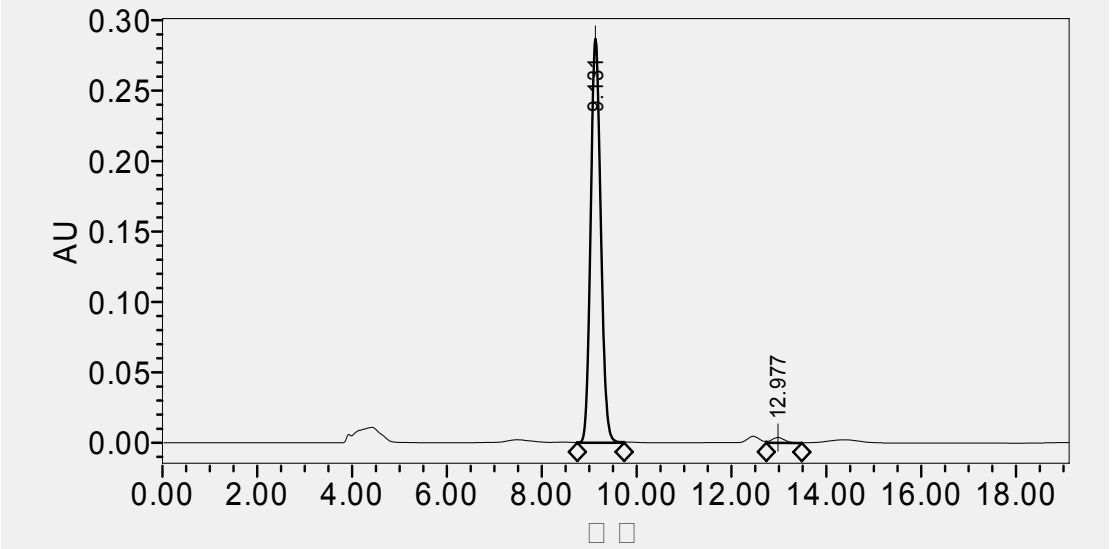
NO	R. Time	Peak Area	Percent	Peak Height
1	9.030	3982662	50.46	248157
2	12.963	3910095	49.54	215043



Chiral HPLC report: racemate (*syn*-**3k**)

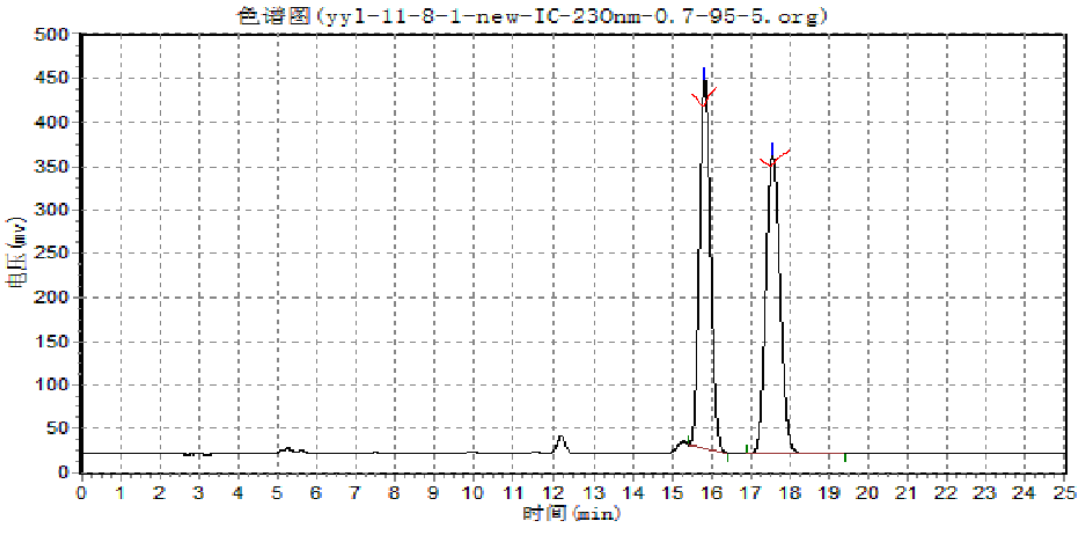
HPLC REPORT

Sample Name: yyl-10-51 Date: ####
Column: AD-H Mobile Phase: hex/ipr = 90/10
Velocity (mL/min): 0.7 Detection Wavelength (nm): 230



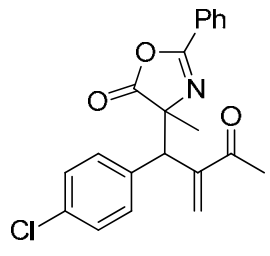
NO	R. Time	Peak Area	Percent	Peak Height
1	9.131	4267822	98.32	286796
2	12.977	72999	1.68	3811

Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.7 mL/min; t_{minor} = 12.97 min, t_{major} = 9.13 min; ee% = 97.



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		15.837	419188.063	8306206.000	49.2016
2		17.567	341142.906	8575762.000	50.7984
总计			760330.969	16881968.000	100.0000

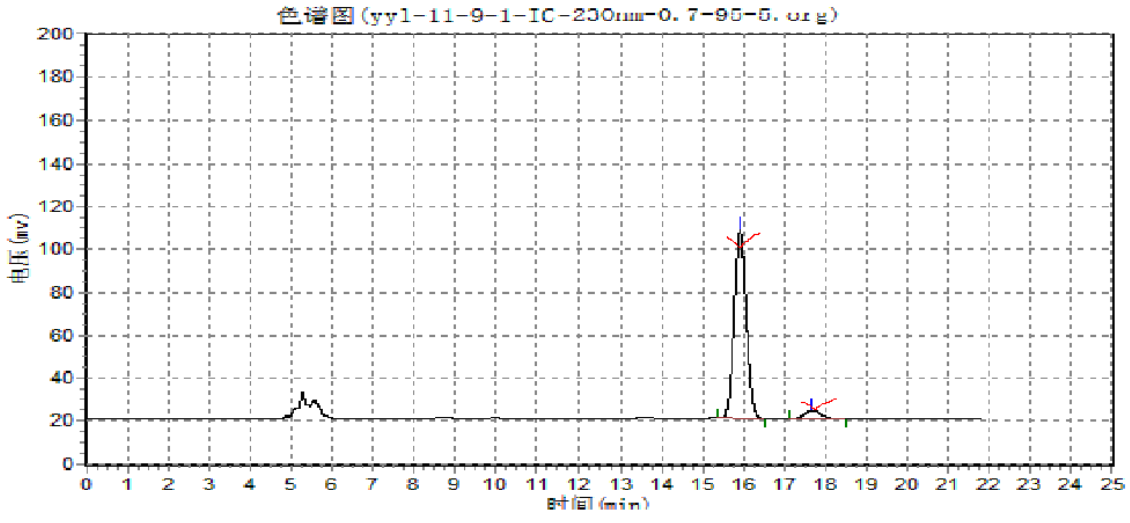


Chiral HPLC report: racemate (*anti*-**3k**)

数据工作站

010-07-18, 19:34:59
\HPLC\杨袁梁\yyl-11-9-1-IC-230nm-0.7-95-5.org

实验者:
报告时间: 2010-07-20, 19:53:06
积分方法:面积归一法



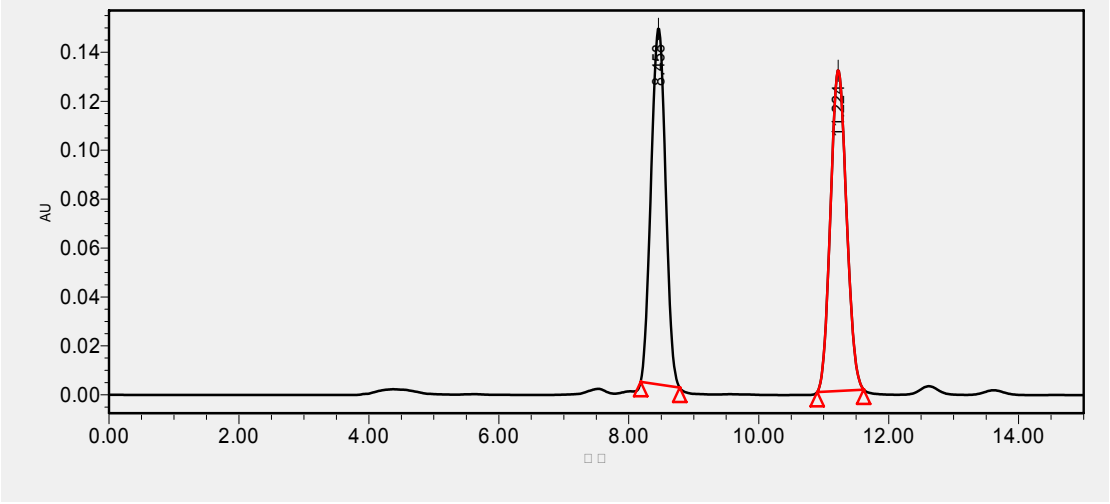
分析结果表

峰名	保留时间	峰高	峰面积	含量
	15.917	87196.570	1784704.875	94.4651
	17.680	3847.794	104568.766	5.5349
		91044.365	1889273.641	100.0000

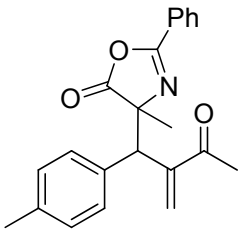
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak IC column; λ = 230 nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 0.7 mL/min; t_{minor} = 17.68 min, t_{major} = 15.92 min; ee% = 90.

HPLC REPORT

Sample Name: yyl-10-52 Date: ####
Column: AD-H Mobile Phase: hex/ipr = 90/10
Velocity (mL/min): 0.7 Detection Wavelength (nm): 230



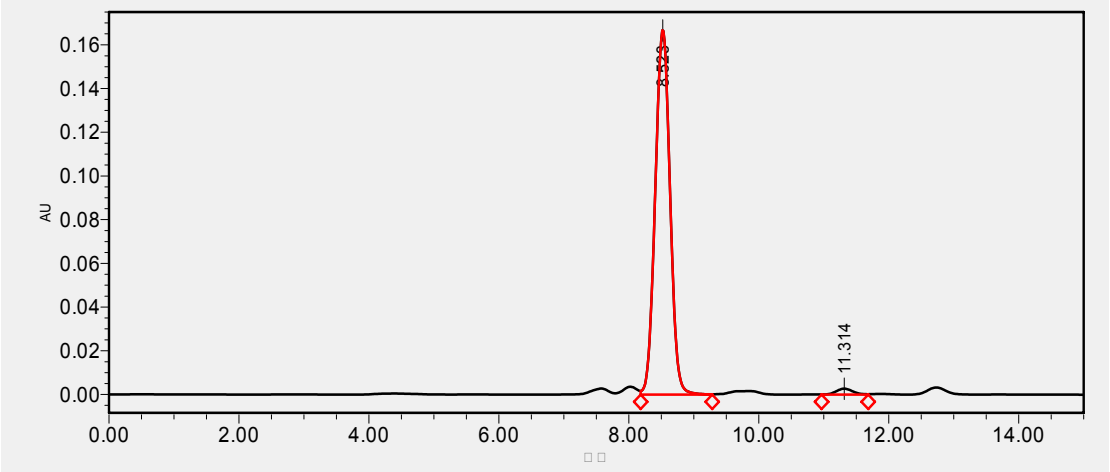
NO	R. Time	Peak Area	Percent	Peak Height
1	8.458	2257992	50.04	145742
2	11.224	2254124	49.96	131197



Chiral HPLC report: racemate (*syn*-**3l**)

HPLC REPORT

Sample Name: yyl-10-53 Date: ####
Column: AD-H Mobile Phase: hex/ipr = 90/10
Velocity (mL/min): 0.7 Detection Wavelength (nm): 230

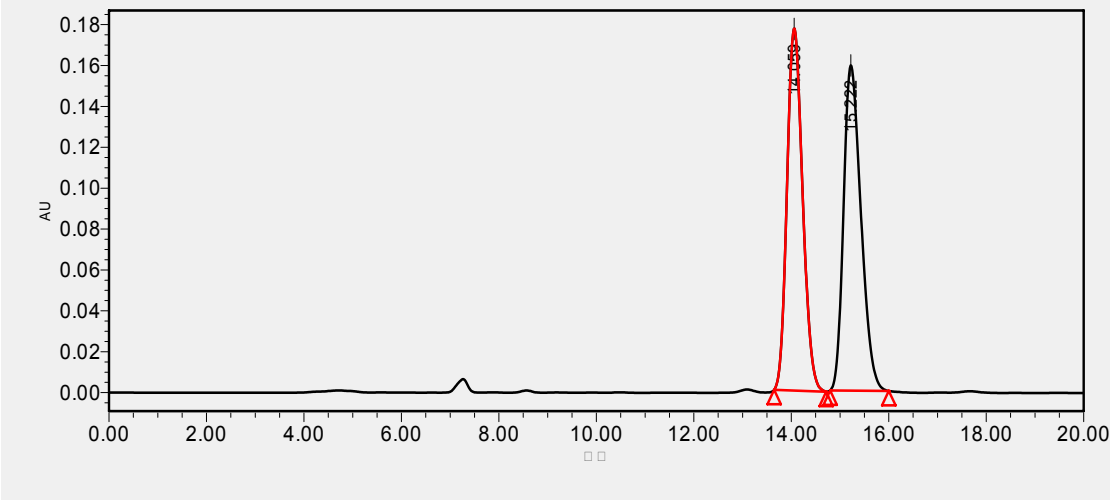


NO	R. Time	Peak Area	Percent	Peak Height
1	8.523	2650036	98.21	166994
2	11.314	48375	1.79	2730

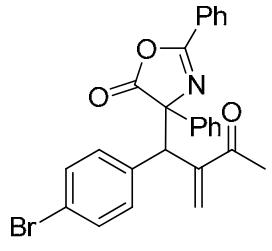
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.7 mL/min; t_{minor} = 11.31 min, t_{major} = 8.52 min; ee% = 96.

HPLC REPORT

Sample Name: yyl-10-56 Date: ####
Column: AD-H Mobile Phase: hex/ipr = 90/10
Velocity (mL/min): 0.7 Detection Wavelength (nm): 230



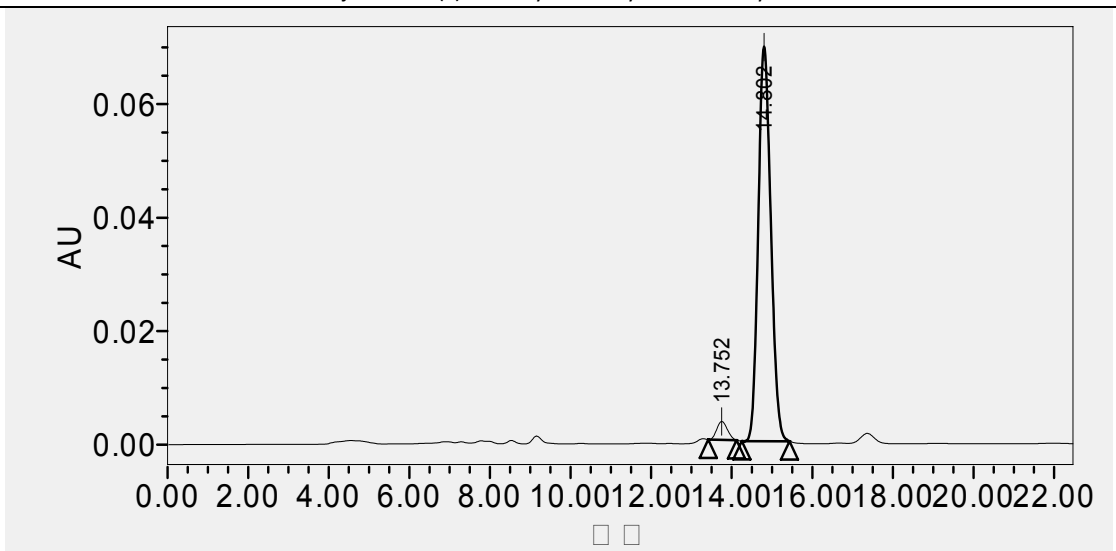
NO	R. Time	Peak Area	Percent	Peak Height
1	14.059	3922051	49.81	177148
2	15.222	3952340	50.19	159217



Chiral HPLC report: racemate (*syn*-**3m**)

HPLC REPORT

Sample Name: yyl-11-1-1 Date: ####
Column: AD-H Mobile Phase: hex/ipr = 90/10
Velocity (mL/min): 0.7 Detection Wavelength (nm): 230

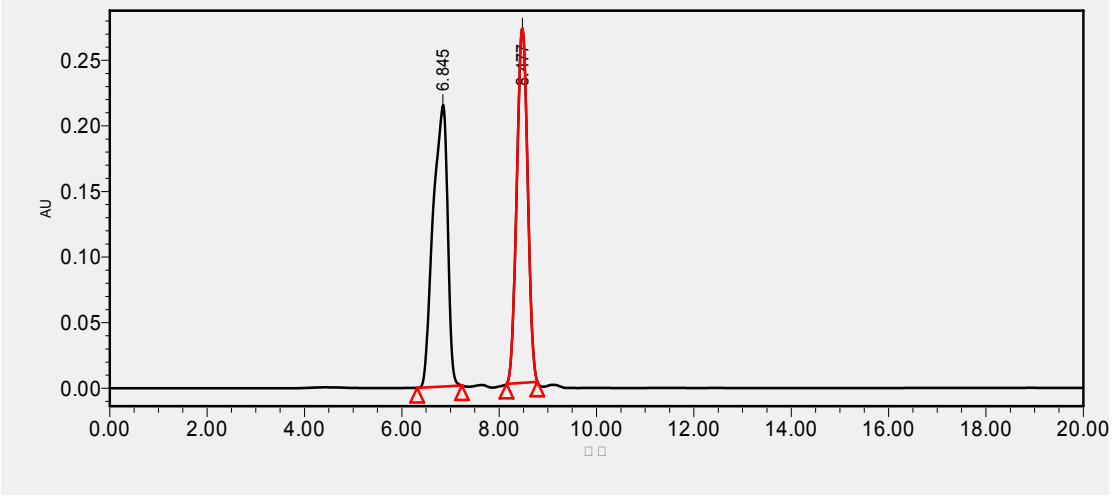


NO	R. Time	Peak Area	Percent	Peak Height
1	13.752	60016	3.83	3252
2	14.802	1505481	96.17	69496

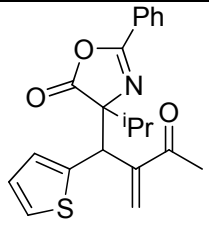
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.7 mL/min; t_{minor} = 13.75 min, t_{major} = 14.80 min; ee% = 92.

HPLC REPORT

Sample Name: yyl-10-91 Date:20100406
Column: AD-H Mobile Phase: hex/ipr = 90/10
Velocity (mL/min): 0.7 Detection Wavelength (nm): 230



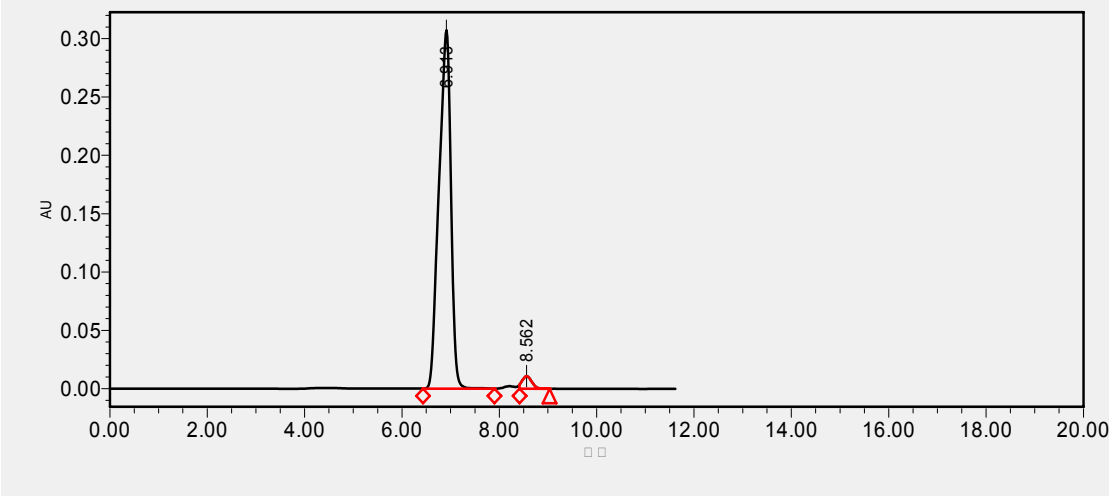
NO	R. Time	Peak Area	Percent	Peak Height
1	6.845	4411944	51.06	214922
2	8.477	4228739	48.94	270479



Chiral HPLC report: racemate (*syn*-**3n**)

HPLC REPORT

Sample Name: yyl-10-92 Date:20100406
Column: AD-H Mobile Phase: hex/ipr = 90/10
Velocity (mL/min): 0.7 Detection Wavelength (nm): 230



NO	R. Time	Peak Area	Percent	Peak Height
1	6.913	5259223	97.28	307423
2	8.562	147025	2.72	10728

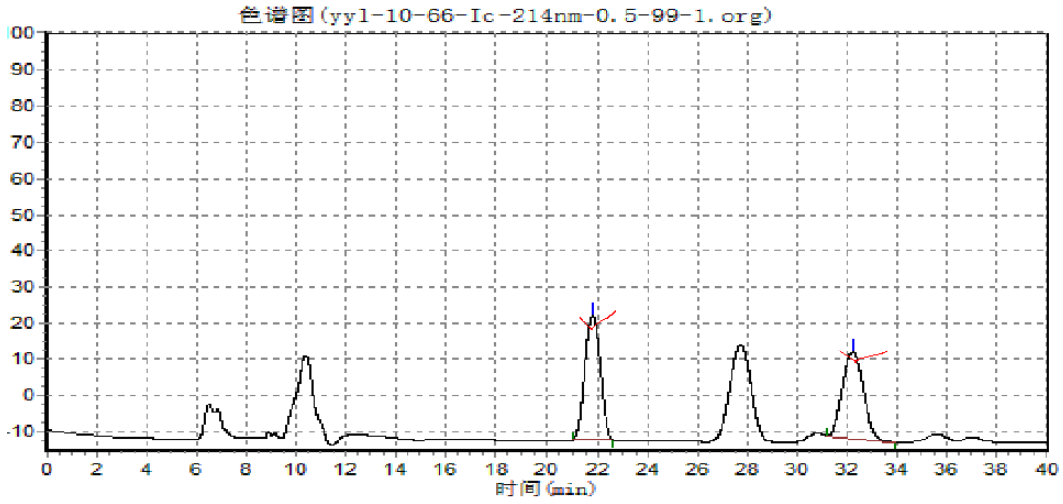
Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.7 mL/min; t_{minor} = 8.56 min, t_{major} = 6.91 min; ee% = 95.

工作站 1

30,15:20:01
5\袁梁\yyl-10-66-Ic-214nm-0.5-99-1.org

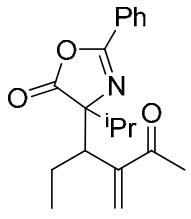
实验者:
报告时间: 2010-07-20,19:11:37
积分方法:面积归一法

色谱图(yyl-10-66-Ic-214nm-0.5-99-1.org)

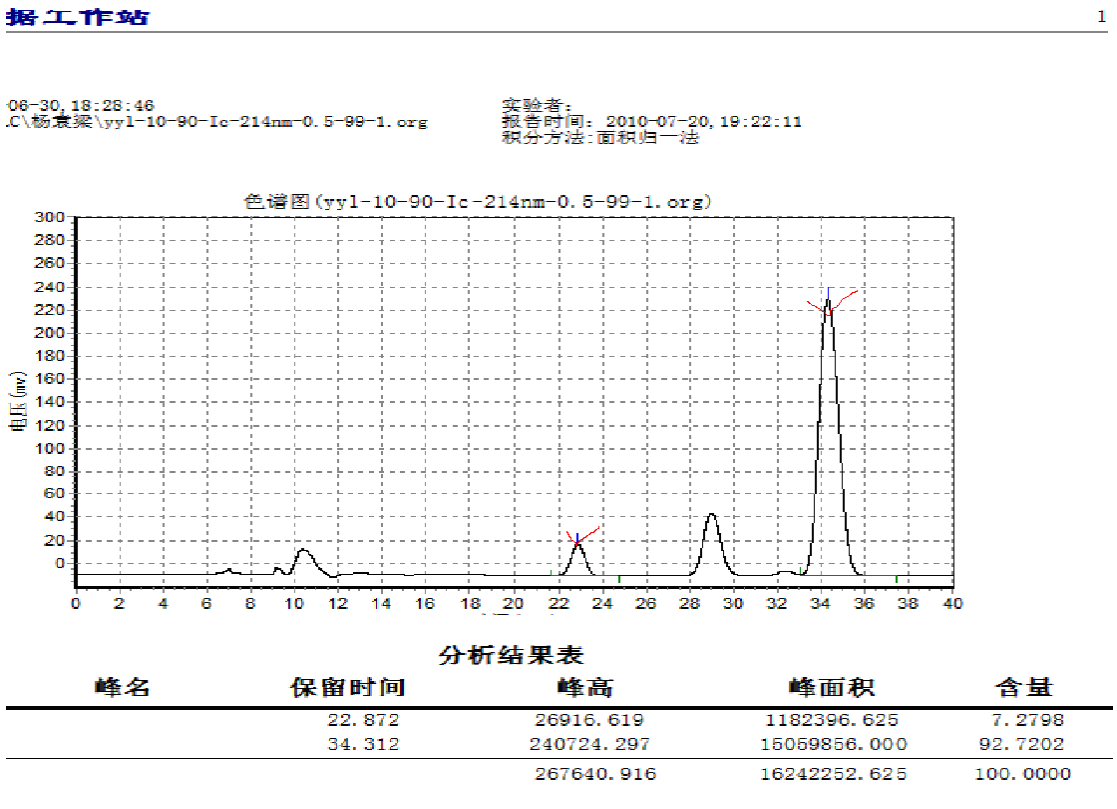


分析结果表

峰名	保留时间	峰高	峰面积	含量
	21.792	34139.031	1463015.500	51.5792
	32.230	23688.131	1373426.875	48.4208
		57827.162	2836442.375	100.0000



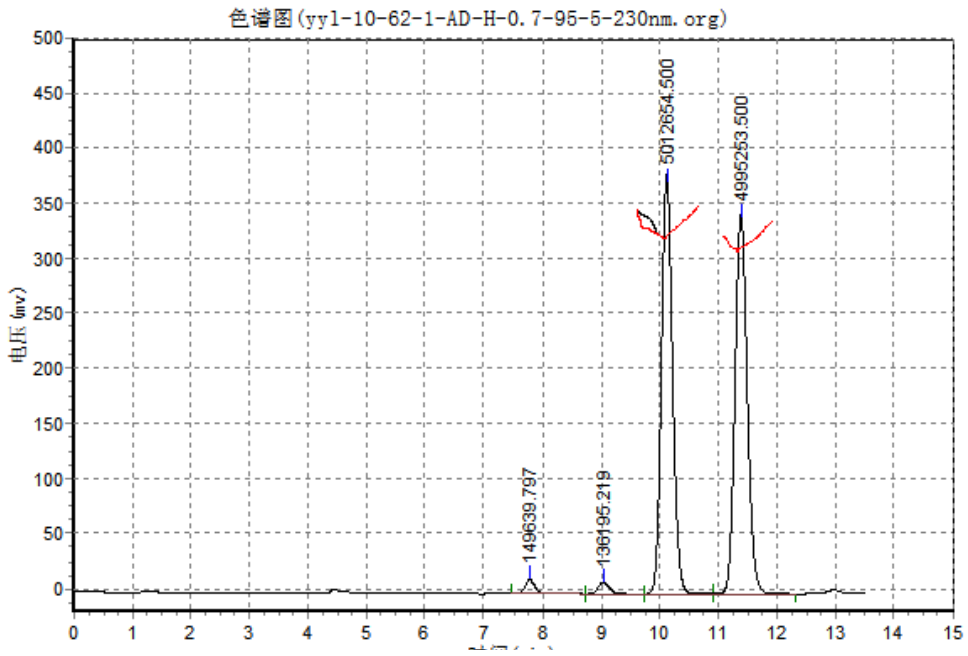
Chiral HPLC report: racemate (*syn*-**3o**)



Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak IC column; λ = 214 nm; eluent: Hexane/Isopropanol = 99/1; Flow rate: 0.5 mL/min; t_{minor} = 22.87 min, t_{major} = 34.31 min; ee% = 85%.

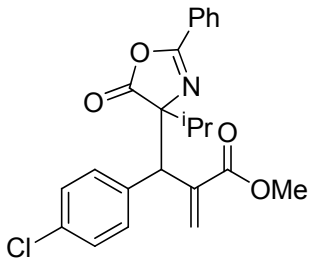
实验时间：2010-06-19,11:18:14
谱图文件:D:\HPLC\杨震梁\yyl-10-62-1-AD-H-0.7-95-5-230nm.org

实验者:
报告时间：2011-01-05,15:11:38
积分方法:面积归一法



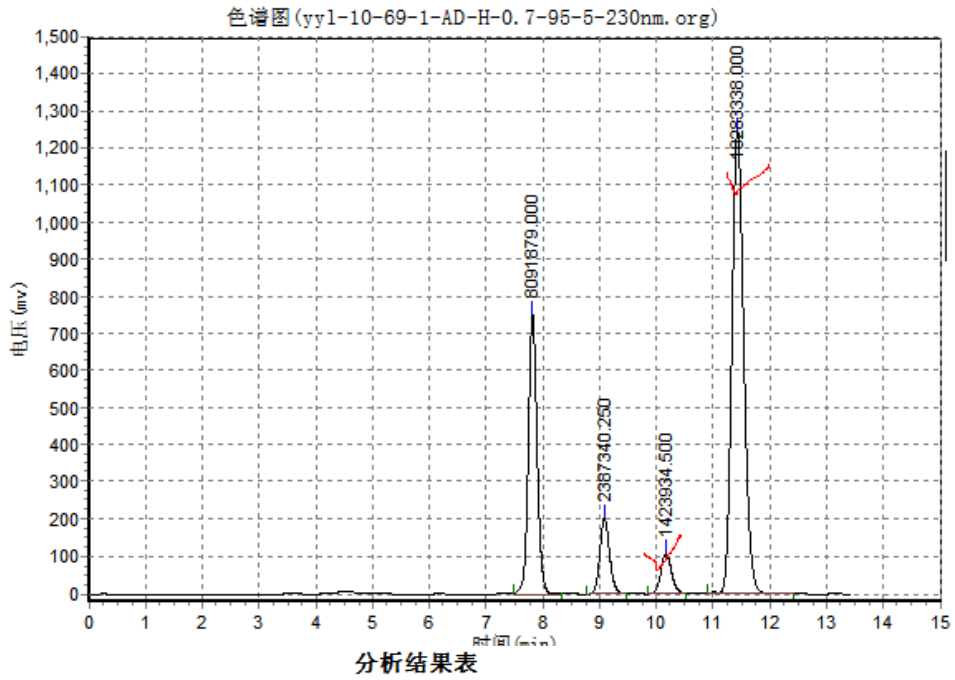
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		7.782	12622.818	149639.797	1.4537
2		9.048	10819.363	136195.219	1.3231
3		10.132	377768.219	5012654.500	48.6961
4		11.398	342439.125	4995253.500	48.5271
总计			743649.525	10293743.016	100.0000



Chiral HPLC report: racemate (*syn*-**3p**)

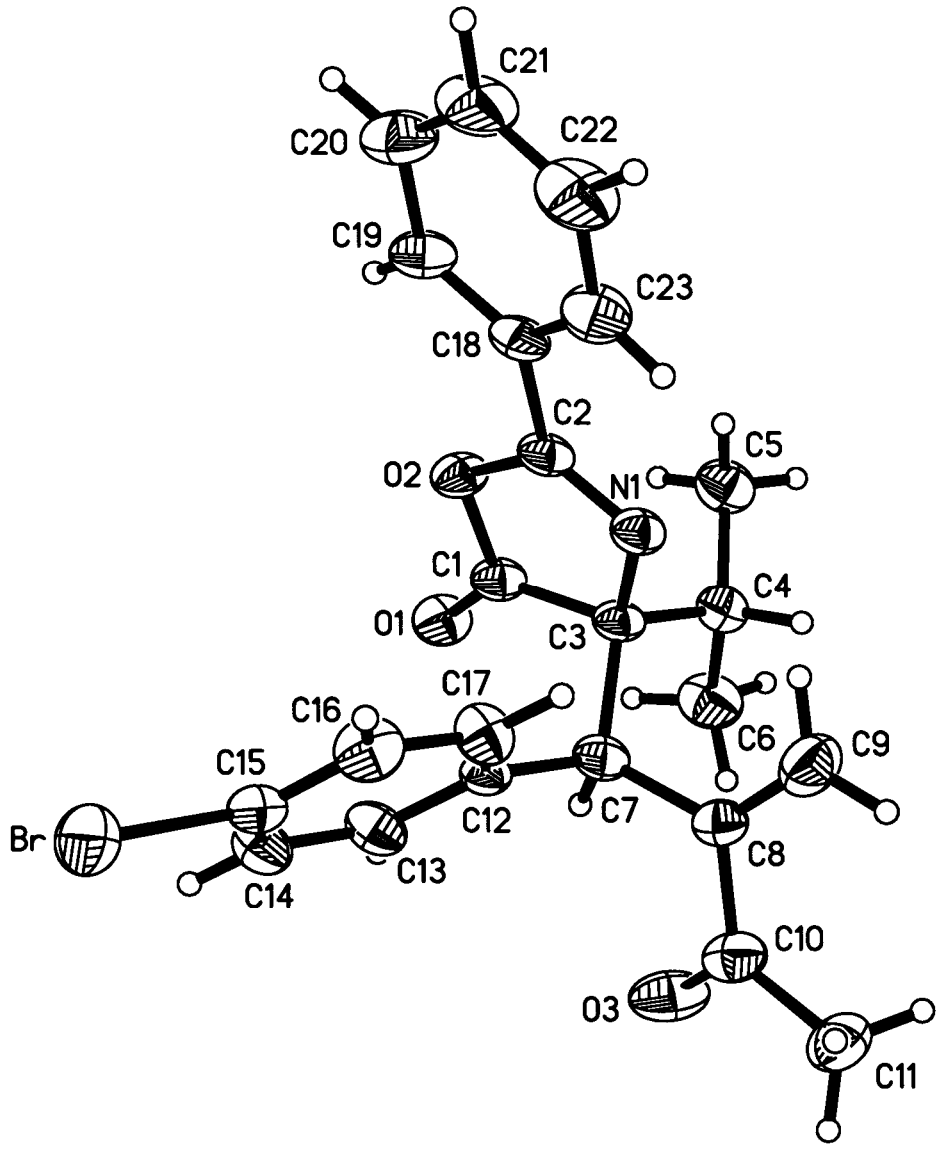
实验时间：2010-06-19,11:04:06
谱图文件:D:\HPLC\杨袁梁\yyl-10-69-1-AD-H-0.7-95-5-230nm.org
实验者:
报告时间：2011-01-05,15:20:27
积分方法:面积归一法



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		7.805	755848.375	8091879.000	26.8063
2		9.077	201733.328	2387340.250	7.9086
3		10.167	108164.961	1423934.500	4.7171
4		11.428	1249386.750	18283338.000	60.5679
总计			2315133.414	30186491.750	100.0000

Chiral HPLC report: Enantiomeric excess was determined by HPLC with a Chiralpak AD column; λ = 230 nm; eluent: Hexane/Isopropanol = 95/5; Flow rate: 0.7 mL/min; t_{minor} = 11.43 min, t_{major} = 10.17 min; ee% = 86%.



The crystal data of **3b** have been deposited in CCDC with number 779521. Empirical Formula: $C_{23}H_{22}BrNO_3$; Formula Weight: 440.33; Crystal Color, Habit: colorless, prismatic; Crystal Dimensions: 0.398 x 0.325 x 0.280 mm; Crystal System: Orthorhombic; Lattice Parameters: a = 10.5465(15)Å, b = 13.646(2)Å, c = 14.694(2)Å, $\alpha = 90^o$, $\beta = 90^o$, $\gamma = 90^o$, V = 2114.8(5)Å^3; Space group: P2(1)2(1)2(1); Z = 4; D_{calc} = 1.383 g/cm^3; F_{000} = 904; Diffractometer: Rigaku AFC7R; Residuals: R; R_w: 0.0406, 0.0835.