Electronic and steric tuning of chiral diene ligands for rhodium-catalyzed asymmetric arylation of imines

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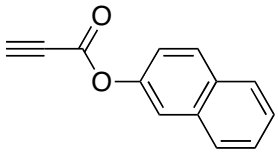
1. General.

NMR spectra were recorded on a JEOL JNM LA-500 spectrometer (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR). Chemical shifts are reported in δ ppm referenced to $CDCl_3$ (δ 7.26 for ^{1}H NMR and δ 77.00 for ^{13}C NMR). Toluene and THF were purified by passing through a neutral alumina column under nitrogen atmosphere. 1,4-Dioxane and benzene were distilled over benzophenone ketyl under nitrogen. Dichloromethane was distilled over CaH_2 under nitrogen. EtOH was distilled over magnesium turnings under nitrogen. $[RhCl(C_2H_4)_2]_2$[1] was prepared following the literature procedures. *N*-Sulfonylimines[2] were prepared following the literature procedures and assigned by comparison of their NMR spectra with the reported data.[3,4] Arylboroxines were prepared following the literature procedures. [5] (*R*)-α-Phellandrene was purchased from Kanto Chemical Co., Inc. (Catalog No. 32641-32). All other materials were purchased and used without further purification.

2. Improved synthesis of the chiral diene ligands from (*R*)-α-phellandrene.

2-Naphthyl propiolate [CAS: 91805-17-3]



To a solution of 2-naphthol (10.0 g, 69.4 mmol) and 4-dimethylaminopyridine (DMAP, 84.7 mg, 0.69 mmol) in dichloromethane (150 mL) was added propiolic acid (5.35 g, 76.3 mmol) and subsequently dicyclohexylcarbodiimide (DCC, 15.7 g, 76.3 mmol) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 4 h. The precipitates were filtered off and the filtrate was concentrated under vacuum. The residue was chromatographed on silica gel (hexane/EtOAc = 20/1) to give 11.9 g (60.6 mmol, 88% yield) of the desired ester as a white solid.

Mp 71–73 °C. IR (neat) cm^{-1}: 3246, 2120, 1711, 1248, 814, 756, 737. ^{1}H NMR ($CDCl_3$): δ 3.11 (s, 1H), 7.28 (dd, *J* = 11.2, 2.3 Hz, 1H), 7.50 (td, *J* = 6.9, 1.6 Hz, 1H), 7.53 (td, *J* = 6.8, 1.6 Hz, 1H), 7.64 (d, *J* = 2.3 Hz, 1H), 7.80–7.90 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 74.2, 76.9, 118.4, 120.3, 126.1, 126.8, 127.7, 127.8, 129.7, 131.7, 133.5, 147.4, 151.0.

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[1] R. Cramer, *Inorg. Synth.*, 1974, **15**, 16.

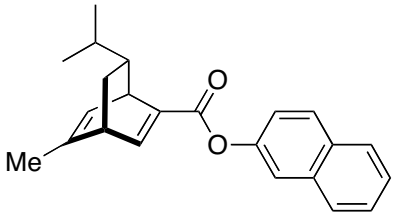
[2] B. E. Love, P. S. Raje and T. C. Williams II, *Synlett* 1994, 493.

[3] N. Tokunaga, Y. Otomaru, K. Okamoto, K. Ueyama, R. Shintani and T. Hayashi, *J. Am. Chem. Soc.*, 2004, **126**, 13584.

[4] Y. Otomaru, N. Tokunaga, R. Shintani and T. Hayashi, *Org. Lett.*, 2005, **7**, 307.

[5] F.-X. Chen, A. Kina and T. Hayashi, *Org. Lett.*, 2006, **8**, 341.

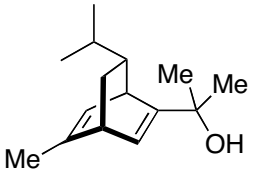
(1*R*,4*R*,7*R*)-2-Naphthyl 7-isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxylate ((*R*)-1a)



To a solution of (*R*)-α-phellandrene (~70% chemical purity, 7.6 g, 39.3 mmol) and 2-naphthyl propiolate (7.00 g, 35.7 mmol) in CH_2Cl_2 (120 mL) was added Me_2AlCl (1.0 M in hexane, 36.7 mL, 39.3 mmol) slowly at –78 °C. The resulting orange solution was allowed to sit in the cold bath and slowly warm to room temperature. After stirring for 18 h, the solution was carefully poured into a vigorously stirred, ice-cooled aqueous solution of 1N HCl (150 mL). The mixture was filtered and washed with 50 mL of dichloromethane. The filtrate was then extracted with dichloromethane (3 × 50 mL). The combined organic extracts were washed with brine (150 mL), dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel (hexane/EtOAc = 20/1) to give 11.3 g of a mixture of **1a** and (*E*)-2-naphthyl 3-(5-isopropyl-2-methylenecyclohex-3-enyl)propenoate in a ratio of 20 to 1. The enantiomeric purity of **1a** was 99.0 ± 0.2% ee. The mixture was diluted with 2.5 mL of dichloromethane and 36 mL of hexane. The flask was placed at room temperature overnight. The crystals precipitated were collected by filtration and washed with 5 mL of ice-cooled hexane, and then dried under vacuum to give 5.2 g of **1a** (15.6 mmol, 44% yield, 99.6% ee) as a white needle. The mother liquor was subject to the same procedure using 1.0 mL of dichloromethane and 15 mL of hexane to give 2.7 g of **1a** (8.1 mmol, 23% yield, 99.6% ee).

The enantiomeric purity of **1a** was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 97/3, flow = 0.5 mL/min. Retention times: 18.2 min [(1*R*,4*R*,7*R*)-enantiomer], 22.2 min [(1*S*,4*S*,7*S*)-enantiomer]. $[\alpha]^{20}_{D}$ +4.4 (*c* 1.12, $CHCl_3$). Mp 92–94 °C. IR (neat) cm^{-1}: 2957, 1724, 1354, 1238, 1209, 1157, 1126, 1059, 1007, 806. ^1H NMR ($CDCl_3$): δ 0.86 (d, *J* = 6.4 Hz, 3H), 1.02 (d, *J* = 6.6 Hz, 3H), 1.05 (ddd, *J* = 11.7, 4.9, 2.4 Hz, 1H), 1.10–1.20 (m, 1H), 1.25–1.35 (m, 1H), 1.67 (ddd, *J* = 11.7, 8.9, 2.9 Hz, 1H), 1.88 (d, *J* = 1.7 Hz, 3H), 3.49 (dq, *J* = 6.2, 2.5 Hz, 1H), 4.22 (dt, *J* = 6.1, 1.9 Hz, 1H), 5.90 (br d, *J* = 6.0 Hz, 1H), 7.26 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.45 (t, *J* = 6.9 Hz, 1H), 7.48 (t, *J* = 6.8 Hz, 1H), 7.58–7.61 (m, 2H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.82–7.86 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 19.0, 21.3, 21.8, 31.5, 33.8, 39.8, 44.3, 47.8, 118.6, 121.4, 124.3, 125.5, 126.4, 127.6, 127.7, 129.2, 131.3, 133.8, 140.5, 143.3, 148.2, 148.7, 163.6. HRMS (ESI) calcd for $C_{23}H_{24}O_2Na$ $(M+Na)^+$ 355.1669, found 355.1659.

(1*R*,4*R*,7*R*)-7-Isopropyl-2-(1-hydroxy-1-methylethyl)-5-methylbicyclo[2.2.2]octa-2,5-diene ((*R*)-2) [CAS: 1063949-39-2]

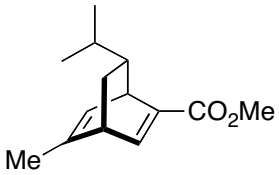


To a solution of **1a** (7.80 g, 23.5 mmol) in THF (50 mL) was added MeLi (1.09 M in Et_2O, 47.0 mL, 51.2 mmol) slowly at 0 °C. After stirring at room temperature for 3 h, the reaction mixture was poured carefully

into a vigorously stirred, ice-cooled sat. NH_4Cl aq (100 mL). The aqueous layer was separated and extracted with EtOAc (3×50 mL). The combined organic extracts were washed with brine (100 mL), dried over $MgSO_4$, filtered and concentrated under vacuum. The residue was chromatographed on silica gel (hexane/EtOAc = 6/1) to give 4.52 g of **2** (20.5 mmol, 87% yield) as a pale yellow oil. Compound **2** was assigned by comparison of its NMR spectra with the reported data.[6]

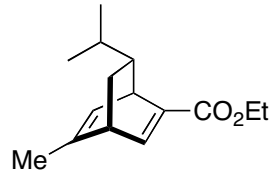
(1*R*,4*R*,7*R*)-Methyl 7-isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxylate ((*R*)-1b)

[CAS: 1063949-34-7]



A solution of **1a** (332 mg, 1.0 mmol) and NaOMe (108 mg, 2.0 mmol) in MeOH (5 mL) was stirred at room temperature for 24 h. The reaction mixture was concentrated under vacuum. The residue was chromatographed on silica gel (hexane/EtOAc = 20/1) to give 217 mg of **1b** (0.98 mmol, 98% yield) as a colorless oil. Compound **1b** was assigned by comparison of its NMR spectra with the reported data.[3]

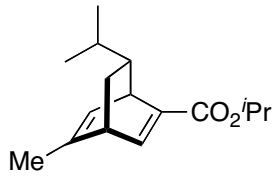
(1*R*,4*R*,7*R*)-Ethyl 7-isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxylate ((*R*)-1c)



A solution of **1a** (332 mg, 1.0 mmol) and NaOEt (102 mg, 1.5 mmol) in dry EtOH (4 mL) was stirred at room temperature for 12 h. The reaction mixture was concentrated under vacuum. The residue was chromatographed on silica gel (hexane/EtOAc = 10/1) to give 219 mg of **1c** (0.93 mmol, 93% yield) as a colorless oil.

$[\alpha]^{20}_{D}$ +9.7 (*c* 0.61, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.82 (d, *J* = 6.5 Hz, 3H), 0.96 (ddd, *J* = 11.7, 4.7, 2.3 Hz, 1H), 0.99 (d, *J* = 6.5 Hz, 3H), 1.05–1.20 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.56 (ddd, *J* = 11.5, 8.7, 2.8 Hz, 1H), 1.81 (d, *J* = 1.3 Hz, 3H), 3.37 (dq, *J* = 6.0, 2.1 Hz, 1H), 4.08 (br d, *J* = 6.0 Hz, 1H), 4.17 (dq, *J* = 14.0, 7.1 Hz, 1H), 4.18 (dq, *J* = 14.0, 7.1 Hz, 1H), 5.80 (br d, *J* = 5.9 Hz, 1H), 7.27 (dd, *J* = 6.6, 1.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 14.3, 18.9, 21.3, 21.8, 31.5, 33.8, 39.6, 43.9, 47.7, 60.1, 124.2, 141.3, 143.4, 145.6, 165.2. HRMS (ESI) calcd for $C_{15}H_{22}O_2Na$ $(M+Na)^+$ 257.1512, found 257.1511.

(1*R*,4*R*,7*R*)-Isopropyl 7-isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxylate ((*R*)-1d)



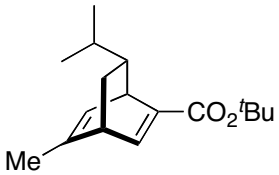
BuLi (1.54 M in hexane, 0.65 mL, 1.0 mmol) was added to a solution of dry *i*PrOH (1.1 mmol) in THF (5

[6] K. Okamoto, T. Hayashi, V. H. Rawal, *Org. Lett.* **2008**, *10*, 4387.

mL) at 0 °C and the mixture was stirred for 10 min. 2-Naphthyl ester **1a** (332 mg, 1.0 mmol) was added and the solution was stirred at room temperature for 12 h. The reaction mixture was concentrated under vacuum. The residue was chromatographed on silica gel (hexane/EtOAc = 10/1) to give 223 mg of **1d** (0.90 mmol, 90% yield) as a colorless oil.

$[\alpha]^{20}_{D}$ –0.6 (*c* 0.98, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.82 (d, *J* = 6.3 Hz, 3H), 0.95 (ddd, *J* = 11.7, 4.9, 2.4 Hz, 1H), 0.99 (d, *J* = 6.3 Hz, 3H), 1.05–1.20 (m, 2H), 1.25 (d, *J* = 6.3 Hz, 3H), 1.26 (d, *J* = 6.3 Hz, 3H), 1.56 (ddd, *J* = 11.9, 8.8, 3.1 Hz, 1H), 1.81 (d, *J* = 1.1 Hz, 3H), 3.36 (dq, *J* = 6.2, 2.3 Hz, 1H), 4.07 (dt, *J* = 5.5, 1.7 Hz, 1H), 5.04 (sept, *J* = 6.2 Hz, 1H), 5.80 (br d, *J* = 6.1 Hz, 1H), 7.24 (dd, *J* = 6.2, 1.5 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 18.9, 21.3, 21.8, 21.91, 21.93, 31.6, 33.8, 39.5, 43.9, 47.7, 67.3, 124.3, 141.6, 143.4, 145.2, 164.7. HRMS (ESI) calcd for $C_{16}H_{24}O_2Na$ $(M+Na)^+$ 271.1669, found 271.1666.

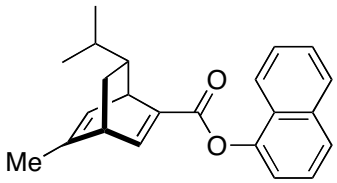
(1*R*,4*R*,7*R*)-*tert*-Butyl 7-isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxylate ((*R*)-1e)



A solution of **1a** (332 mg, 1.0 mmol) and Li*O*t*Bu (400 mg, 5.0 mmol) in THF (10 mL) was stirred at room temperature for 12 h. The reaction mixture was concentrated under vacuum. The residue was chromatographed on silica gel (hexane/EtOAc = 10/1) to give 259 mg of **1e** (0.99 mmol, 99% yield) as a white solid.

Mp 61–63 °C (recrystallization from hexane). $[\alpha]^{20}_{D}$ +5.8 (*c* 2.39, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.81 (d, *J* = 6.3 Hz, 3H), 0.94 (ddd, *J* = 11.6, 4.7, 2.4 Hz, 1H), 0.98 (d, *J* = 6.3 Hz, 3H), 1.04–1.19 (m, 2H), 1.48 (s, 9H), 1.56 (ddd, *J* = 11.7, 8.6, 2.9 Hz, 1H), 1.80 (d, *J* = 1.6 Hz, 3H), 3.34 (dq, *J* = 8.7, 2.3 Hz, 1H), 4.03 (dt, *J* = 6.0, 1.8 Hz, 1H), 5.79 (br d, *J* = 5.9 Hz, 1H), 7.15 (dd, *J* = 6.3, 1.8 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 19.0, 21.3, 21.8, 28.2, 31.7, 33.8, 39.5, 43.9, 47.7, 79.8, 124.3, 142.6, 143.4, 144.5, 164.6. HRMS (ESI) calcd for $C_{17}H_{26}O_2Na$ $(M+Na)^+$ 285.1825, found 285.1826.

(1*R*,4*R*,7*R*)-1-Naphthyl 7-isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxylate ((*R*)-1f)



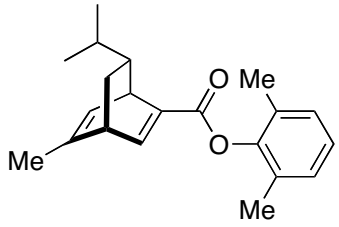
A solution of methyl ester **1b** (80.0 mg, 0.363 mmol) and $LiOH{\cdot}H_2O$ (58.7 mg, 1.40 mmol) in MeOH (2 mL) and H_2O (1 mL) was stirred at 50 °C for 12 h. It was cooled to room temperature and 2N HCl (5 mL) was added. The mixture was extracted with $CHCl_3$ (3 × 10 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under vacuum to give the crude carboxylic acid. It was used for the next step without furthur purification.

To a solution of 1-naphthol (50.5 mg, 0.350 mmol) and DMAP (2.1 mg, 17 μmol) in dichloromethane (5 mL) were added successively the crude carboxylic acid and DCC (86.6 mg, 0.420 mmol) at 0 °C. The mixture was stirred at room temperature for 3 h. The precipitates were filtered off and the filtrate was concentrated under vacuum. The residue was chromatographed on silica gel (hexane/EtOAc = 20/1) to give

113 mg (0.34 mmol, 94% yield) of **1f** as a colorless oil.

$[\alpha]^{20}_{D}$ +8.6 (*c* 1.33, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.88 (d, *J* = 6.6 Hz, 3H), 1.03 (d, *J* = 6.5 Hz, 3H), 1.08 (ddd, *J* = 11.7, 4.9, 2.4 Hz, 1H), 1.12–1.22 (m, 1H), 1.31–1.39 (m, 1H), 1.71 (ddd, *J* = 11.6, 8.8, 3.0 Hz, 1H), 1.90 (d, *J* = 1.7 Hz, 3H), 3.53 (dq, *J* = 6.2, 2.5 Hz, 1H), 4.27 (dt, *J* = 6.0, 1.9 Hz, 1H), 5.92 (br d, *J* = 6.1 Hz, 1H), 7.26 (dd, *J* = 7.4, 0.9 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.47–7.52 (m, 2H), 7.71 (dd, *J* = 6.2, 1.8 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.85–7.90 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 19.0, 21.3, 21.9, 31.6, 33.8, 39.8, 44.3, 47.9, 118.2, 121.4, 124.3, 125.4, 125.6, 126.25, 126.29, 127.2, 127.9, 134.6, 140.4, 143.3, 146.9, 148.4, 163.4. HRMS (ESI) calcd for $C_{23}H_{24}O_2Na$ $(M+Na)^+$ 355.1669, found 355.1655.

(1*R*,4*R*,7*R*)-2,6-Dimethylphenyl 7-isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxylate ((*R*)-1g)



A solution of methyl ester **1b** (440 mg, 2.00 mmol) and $LiOH{\cdot}H_2O$ (309 mg, 7.36 mmol) in MeOH (10 mL) and H_2O (3 mL) was stirred at 50 °C for 5 h. It was cooled to room temperature and 2N HCl (10 mL) was added. The mixture was extracted with $CHCl_3$ (3 × 20 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under vacuum to give the crude carboxylic acid. It was used for the next step without furthur purification.

To a solution of 2,6-dimethylphenol (244 mg, 2.00 mmol) and DMAP (11.2 mg, 92 μmol) in dichloromethane (10 mL) were added successively the crude carboxylic acid and DCC (455 mg, 2.21 mmol) at 0 °C. The mixture was stirred at room temperature for 3 h. The precipitates were filtered off and the filtrate was concentrated under vacuum. The residue was chromatographed on silica gel (hexane/EtOAc = 20/1) to give 589 mg (1.90 mmol, 95% yield) of **1g** as a white solid.

Mp 74–76 °C (recrystallization from hexane). $[\alpha]^{20}_{D}$ +12.3 (*c* 1.19, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.85 (d, *J* = 6.5 Hz, 3H), 1.00 (d, *J* = 6.5 Hz, 3H), 1.03 (ddd, *J* = 11.5, 4.8, 2.4 Hz, 1H), 1.08–1.30 (m, 2H), 1.64 (ddd, *J* = 11.7, 8.8, 2.9 Hz, 1H), 1.87 (d, *J* = 1.7 Hz, 3H), 2.13 (s, 6H), 3.47 (dq, *J* = 8.6, 2.6 Hz, 1H), 4.20 (dt, *J* = 6.0, 1.9 Hz, 1H), 5.87 (br d, *J* = 5.8 Hz, 1H), 7.00–7.08 (m, 3H), 7.56 (dd, *J* = 6.2, 1.8 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 16.4, 19.0, 21.3, 21.9, 31.5, 33.8, 39.8, 44.2, 48.0, 124.1, 125.5, 128.4, 130.4, 140.3, 143.3, 147.9, 148.4, 162.7. HRMS (ESI) calcd for $C_{21}H_{26}O_2Na$ $(M+Na)^+$ 333.1825, found 333.1824.

3. Rhodium-catalyzed asymmetric addition reactions.

General procedure for Table 1. A solution of $[RhCl(C_2H_4)_2]_2$ (0.58 mg, 3.0 μmol Rh) and diene (3.3 μmol) in 1,4-dioxane (0.20 mL) was stirred at room temperature for 10 min. KOH (6.5 μL, 20 μmol; 3.1 M aqueous), $(PhBO)_3$ (**8m**) (37.4 mg, 0.12 mmol), and imine **7a** (32.5 mg, 0.10 mmol) were added with additional 1,4-dioxane (0.60 mL), and the mixture was stirred at 60 °C for 3 h. The reaction mixture was directly passed through a pad of silica gel with Et_2O, and the solvent was removed under vacuum. The residue was chromatographed on silica gel (hexane/EtOAc) to give **9am** as a white solid.

General procedure for kinetic experiments (Figure 1). A solution of $[RhCl(C_2H_4)_2]_2$ (0.88 mg, 4.5

μmol Rh) and ligand (5.0 μmol) in 1,4-dioxane (1.0 mL) was stirred at room temperature for 10 min. KOH (27 μL, 90 μmol; 3.3 M aqueous), hexamethylbenzene (40.6 mg, 0.250 mmol), $(PhBO)_3$ (**8m**) (312 mg, 1.0 mmol), and imine **7a** (487 mg, 1.50 mmol) were added with additional 1,4-dioxane (3.0 mL), and the mixture was stirred at 60 °C. The reaction was monitored by sampling the reaction mixture using a gas-tight syringe. The sample was passed through a pad of silica gel with Et_2O, and it was concentrated under vacuum. The yield of **9am** in each sample was calculated from ratio of **9am** to hexamethylbenzene in ^1H NMR analysis.

	Yield of **9am** (%)			
Ligand Time (min)	**1a**	**3a**	**3b**	**5**
10	24	5	7	9
20	43	12	11	12
30	57	18	17	16
50	84	30	27	17
70	97	39	37	17
90	100	44	42	19
180	—	66	66	21
360	—	81	69	21

General procedure for Table 2. A solution of $[RhCl(C_2H_4)_2]_2$ (0.88 mg, 4.5 μmol Rh) and **1g** (1.6 mg, 5.1 μmol) in 1,4-dioxane (1.0 mL) was stirred at room temperature for 10 min. KOH (27 μL, 90 μmol; 3.3 M aqueous), $(ArBO)_3$ (1.0 mmol), and an imine (1.50 mmol) were added with additional 1,4-dioxane (3.0 mL), and the mixture was stirred at 60 °C for 12 h. The reaction mixture was directly passed through a pad of silica gel with Et_2O, and the solvent was removed under vacuum. The residue was chromatographed on silica gel (hexane/EtOAc) to give the desired products. The products except for **9bo** and **9cn** are known compounds and they were assigned by comparison of their NMR spectra with the reported data.[3,4]

(*S*)-*N*-[(4-Chlorophenyl)phenylmethyl]-4-nitrobenzenesulfonamide (9am) [CAS: 260997-46-4]

98% yield, 98% ee (Table 2, Entry 1). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 4/1, flow = 0.8 mL/min, wavelength = 230 nm. Retention times: 32.3 min [(*S*)-enantiomer], 58.8 min [(*R*)-enantiomer].

(*S*)-*N*-[(4-Methoxyphenyl)phenylmethyl]-4-nitrobenzenesulfonamide (9bm) [CAS: 840529-68-2]

97% yield, 98% ee. The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 4/1, flow = 0.8 mL/min, wavelength = 230 nm. Retention times: 21.9 min [(*R*)-enantiomer], 39.7 min [(*S*)-enantiomer].

(*S*)-*N*-[(2-Methylphenyl)phenylmethyl]-4-nitrobenzenesulfonamide (9cm) [CAS: 840529-69-3]

91% yield, 98% ee. The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol

= 4/1, flow = 0.5 mL/min, wavelength = 230 nm. Retention times: 19.9 min [(*R*)-enantiomer], 30.8 min [(*S*)-enantiomer].

(*R*)-*N*-[(4-Methoxyphenyl)phenylmethyl]-4-nitrobenzenesulfonamide (9dn) [CAS: 260997-47-5]

Enantiomer of **9bm**. 98% yield, >99.5% ee.

(*R*)-*N*-[(4-Chlorophenyl)phenylmethyl]-4-nitrobenzenesulfonamide (9do) [CAS: 840529-66-0]

Enantiomer of **9am**. 95% yield, 98.5% ee.

(*R*)-*N*-[(3-Methoxyphenyl)phenylmethyl]-4-nitrobenzenesulfonamide (9dp) [CAS: 840529-73-9]

90% yield, 97% ee. The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 4/1, flow = 0.8 mL/min, wavelength = 230 nm. Retention times: 20.0 min [(*R*)-enantiomer], 22.2 min [(*S*)-enantiomer].

(*R*)-*N*-[(2-Methylphenyl)phenylmethyl]-4-nitrobenzenesulfonamide (9dq) [CAS: 840529-70-6]

Enantiomer of **9dm**. 95% yield, >99.5% ee.

(*R*)-*N*-[(4-Chlorophenyl)(4-methoxyphenyl)methyl]-4-nitrobenzenesulfonamide (9bo)

90% yield, 99.1% ee. The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 2/1, flow = 0.8 mL/min, wavelength = 230 nm. Retention times: 13.7 min [(*S*)-enantiomer], 14.5 min [(*R*)-enantiomer]. $[\alpha]^{20}_{D}$ –12.2 (*c* 1.13, THF). ^{1}H NMR ($CDCl_3$): δ 3.74 (s, 3H), 5.26 (br s, 1H), 5.63 (d, *J* = 7.2 Hz, 1H), 6.72 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 7.08 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.8 Hz, 2H), 8.15 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 55.3, 60.6, 114.2, 123.9, 128.3, 128.6, 128.7, 128.8, 131.1, 134.0, 138.4, 146.2, 149.8, 159.5. HRMS (ESI) calcd for $C_{20}H_{17}O_5N_2SClNa$ $(M+Na)^+$ 455.0439, found 455.0445.

(*S*)-*N*-[(4-Methoxyphenyl)(2-methylphenyl)methyl]-4-nitrobenzenesulfonamide (9cn)

98% yield, 98% ee. The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 2/1, flow = 0.5 mL/min, wavelength = 230 nm. Retention times: 17.4 min [(*R*)-enantiomer], 45.4 min [(*S*)-enantiomer]. $[\alpha]^{20}_{D}$ +16.3 (*c* 1.52, THF). ^{1}H NMR ($CDCl_3$): δ 2.24 (s, 3H), 3.74 (s, 3H), 5.34 (br s, 1H), 5.91 (d, *J* = 7.2 Hz, 1H), 6.72 (d, *J* = 8.5 Hz, 2H), 6.89–6.97 (m, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 7.05–7.15 (m, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 8.08 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 19.3, 55.3, 57.9, 114.0, 123.7, 126.1, 126.8, 127.8, 128.1, 128.9, 130.8, 130.9, 135.7, 137.2, 146.3, 149.6, 159.3. HRMS (ESI) calcd for $C_{21}H_{20}O_5N_2SNa$ $(M+Na)^+$ 435.0985, found 435.0993.

(*S*)-*N*-[(4-Chlorophenyl)phenylmethyl]-4-methylbenzenesulfonamide (11am) [CAS: 258277-18-8]

96% yield, 99.3% ee. The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 85/15, flow = 0.8 mL/min, wavelength = 230 nm. Retention times: 17.1 min [(*S*)-enantiomer], 22.3 min [(*R*)-enantiomer].

General procedure for Eq. 1. A solution of $[RhCl(C_2H_4)_2]_2$ (0.88 mg, 4.5 μmol Rh) and **1g** (1.6 mg, 5.1 μmol) in 1,4-dioxane (1.0 mL) was stirred at room temperature for 10 min. KOH (50 μL, 75 μmol; 1.5 M aqueous), $PhB(OH)_2$ (**13**, 364 mg, 3.00 mmol), and enone **12** (1.50 mmol) were added with additional 1,4-dioxane (4.0 mL), and the mixture was stirred at 50 °C for 12 h. The reaction mixture was directly passed through a pad of silica gel with Et_2O, and the solvent was removed under vacuum. The residue was purified by silica gel chromatography with EtOAc/hexane to give the desired products. All the products are

known compounds and they were assigned by comparison of their NMR spectra with the reported data.[7]

(*R*)-3-Phenylcyclohexanone (**14a**) [CAS: 34993-51-6]

Pale yellow oil. 96% yield, 99.0% ee. The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 100/1, flow = 0.5 mL/min, wavelength = 224 nm. Retention times: 27.9 min [(*S*)-enantiomer], 33.4 min [(*R*)-enantiomer].

(*S*)-4-Phenyl-2-nonanone (**14b**) [CAS: 501919-45-5]

Pale yellow oil. 97% yield, 98% ee. The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 98/2, flow = 0.5 mL/min, wavelength = 210 nm. Retention times: 44.5 min [(*S*)-enantiomer], 48.0 min [(*R*)-enantiomer].

[7] Y. Takaya, M. Ogasawara, T. Hayashi, M. Sakaki and N. Miyaura, *J. Am. Chem. Soc.*, 1998, **120**, 5579.

3. X-ray crystallographic analysis of Rh(acac)((*R*)-1a).

Yellow crystals of [Rh(acac)((*R*)-**1a**)] suitable for X-ray crystallographic analysis were obtained by recrystallization from CH_2Cl_2/hexane. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 718052). The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request /cif.

Crystal data: $C_{28}H_{31}O_4Rh$, yellow prism, orthorhombic, FW = 534.44, space group $P2_12_12_1$, a = 6.7928(7) Å, b = 8.4033(8) Å, c = 41.694(4) Å, V = 2380.0(4) Å^3, Z = 4, T = 90 K, ρ = 1.491 g/cm^3, R_{int} = 0.024, R = 0.0447, wR = 0.0939, GOF = 1.319, Flack parameter = 0.02(4).[8]

Occupancy of disordered two naphthyl rings: A; 0.613(7), B; 0.387(7).

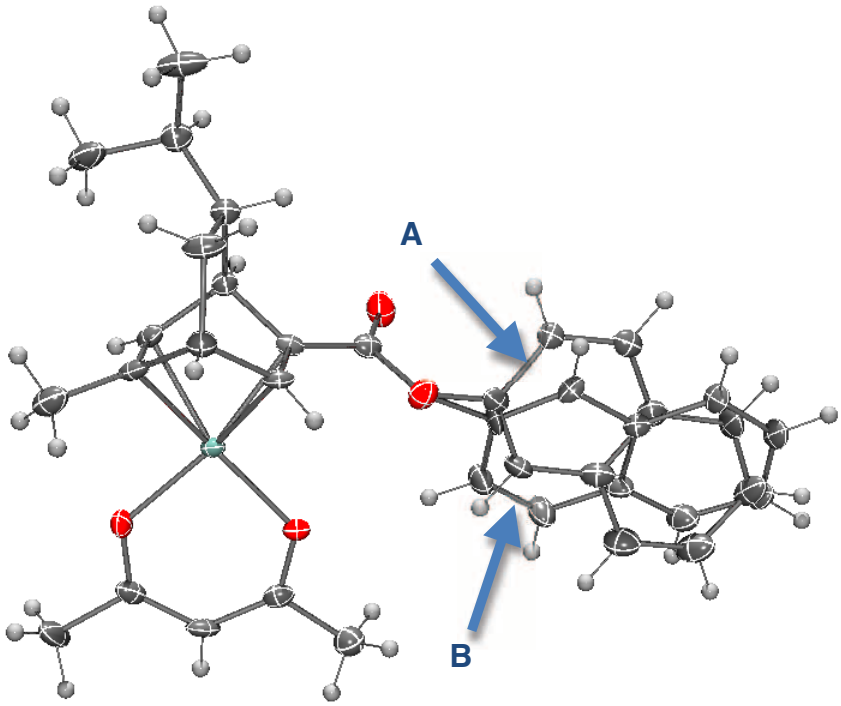


Table S1. Crystal Data

Empirical Formula	$C_{28}H_{31}O_4Rh$
Formula Weight	534.46
Crystal Color, Habit	yellow, prism
Crystal Dimensions	0.30 X 0.20 X 0.10 mm
Crystal System	orthorhombic
Lattice Type	Primitive
Detector Position	0.00 mm
Pixel Size	0.120 mm
Lattice Parameters	a = 6.7928(7) Å
	b = 8.4033(8) Å
	c = 41.694(4) Å
	V = 2380.0(4) Å^3

[8] H. D. Flack, *Acta Cryst.*, 1983, **A39**, 876.

Space Group	$P2_12_12_1$ (#19)
Z value	4
D_{calc}	1.491 g/cm^3
F_{000}	1104.00
m(MoKa)	7.482 cm^{-1}

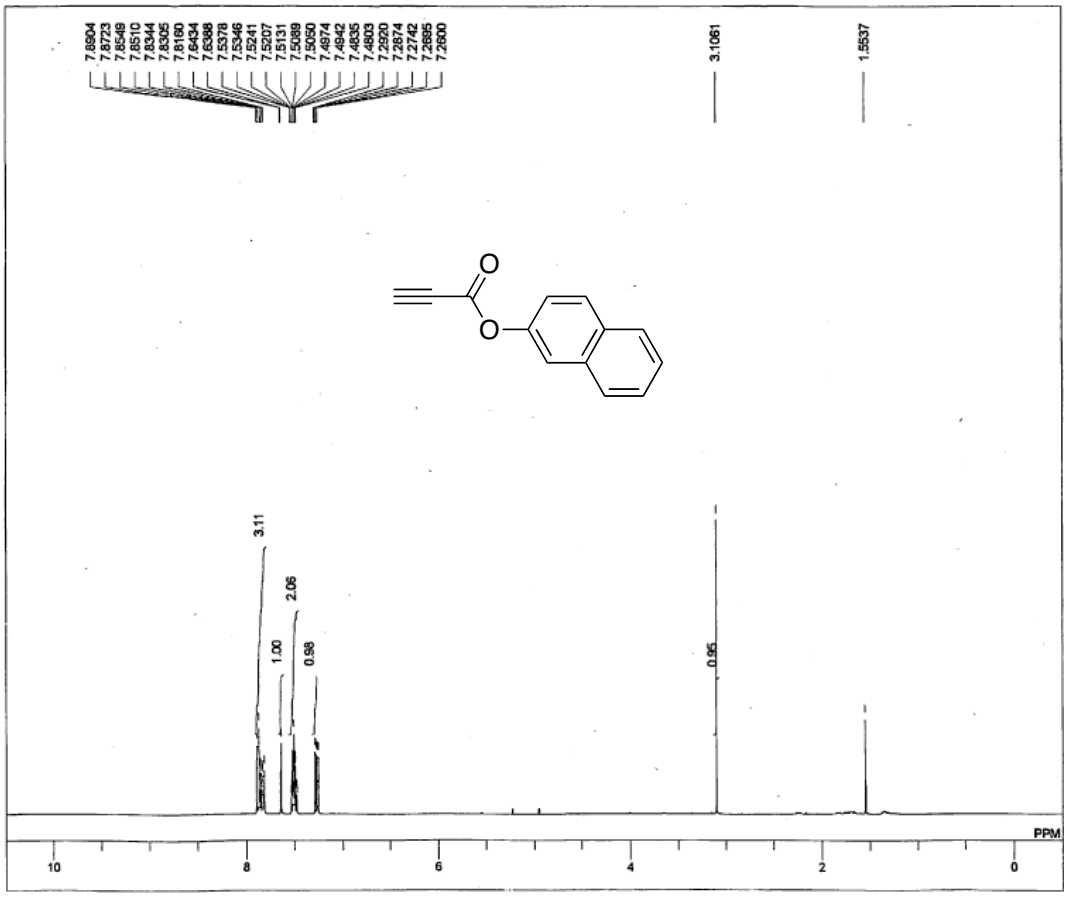
Table S2. Intensity Measurements

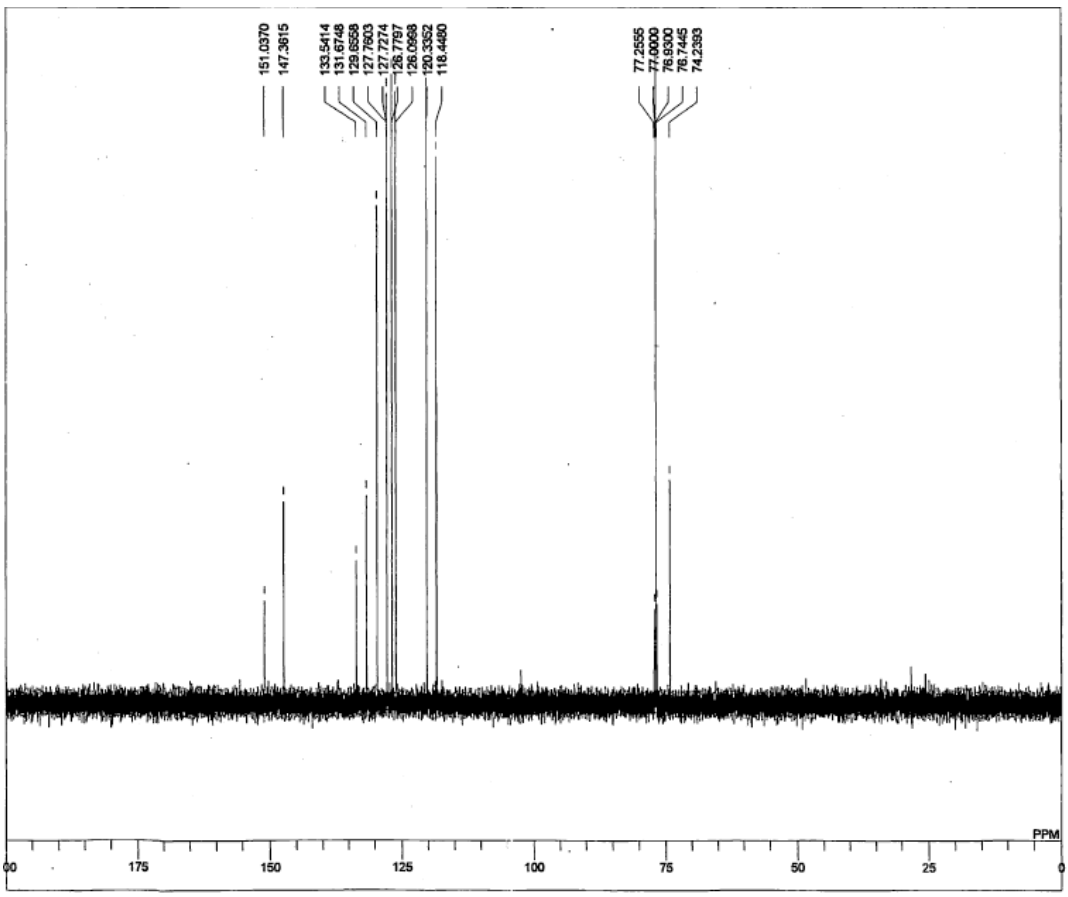
Detector	Rigaku CCD
Goniometer	Rigaku Unknown
Radiation	MoKa (l = 0.71073 Å)
	graphite monochromated
Detector Aperture	70 mm x 70 mm
Data Images	0 exposures
Detector Position	0.00 mm
Pixel Size	0.120 mm
$2q_{max}$	56.6^o
No. of Reflections Measured	Total: 0
	Unique: 0 (R_{int} = 0.024)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.806 - 0.928)

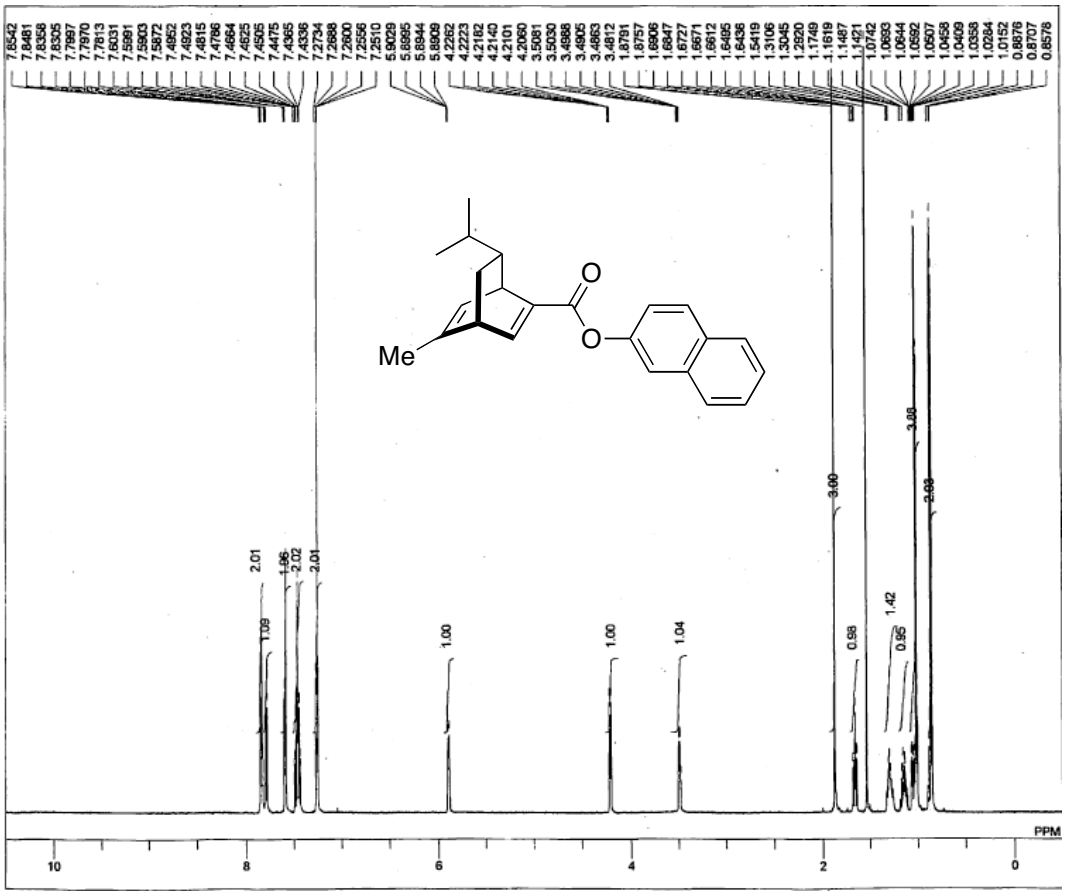
Table S3. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F^2
Function Minimized	S w (Fo^2 - Fc^2)^2
Least Squares Weights	w = 1/ [$s^2(Fo^2)$ + (0.0000 · P)^2
	+ 0.0000 · P]
	where P = (Max(Fo^2,0) + 2Fc^2)/3
$2q_{max}$ cutoff	56.6^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	5431
No. Variables	407
Reflection/Parameter Ratio	13.34
Residuals: R1 (I>2.00s(I))	0.0447
Residuals: R (All reflections)	0.0000
Residuals: wR2 (All reflections)	0.0944
Goodness of Fit Indicator	1.319
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	1.45 e/Å^3
Minimum peak in Final Diff. Map	-1.38 e/Å^3

4. NMR and HPLC analyses.



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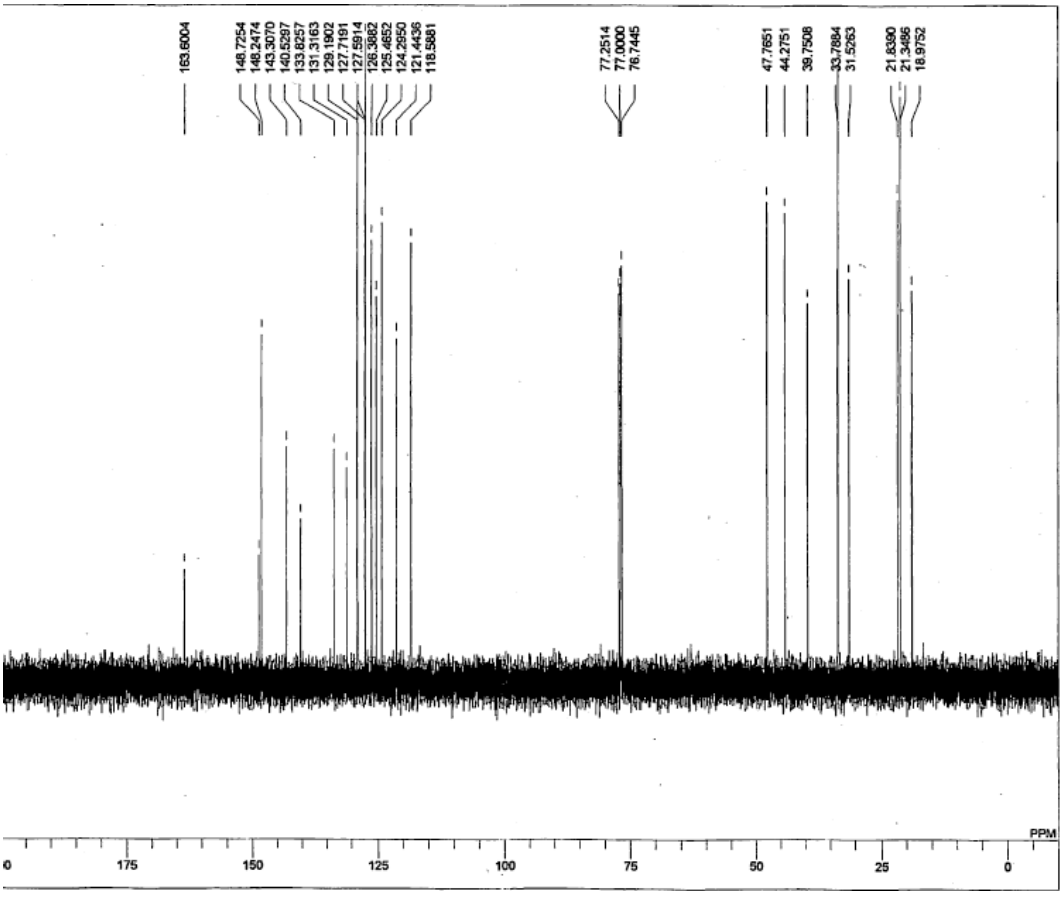
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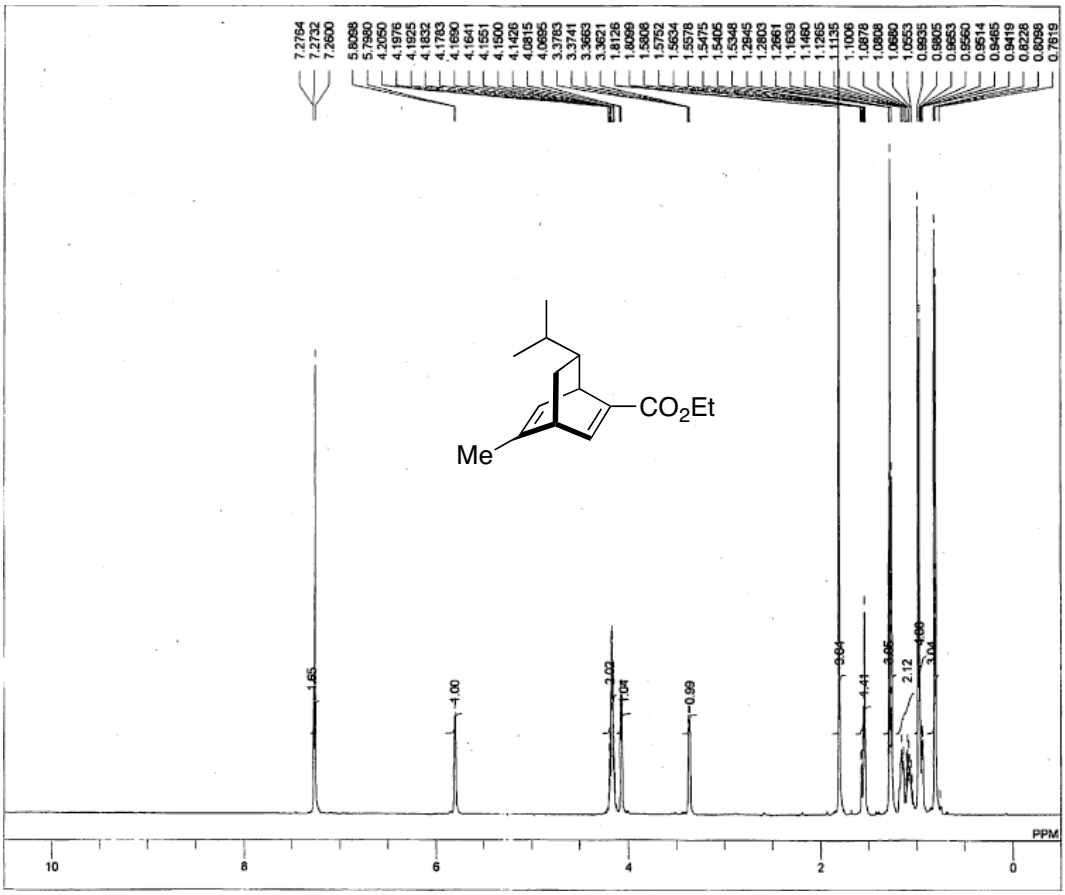
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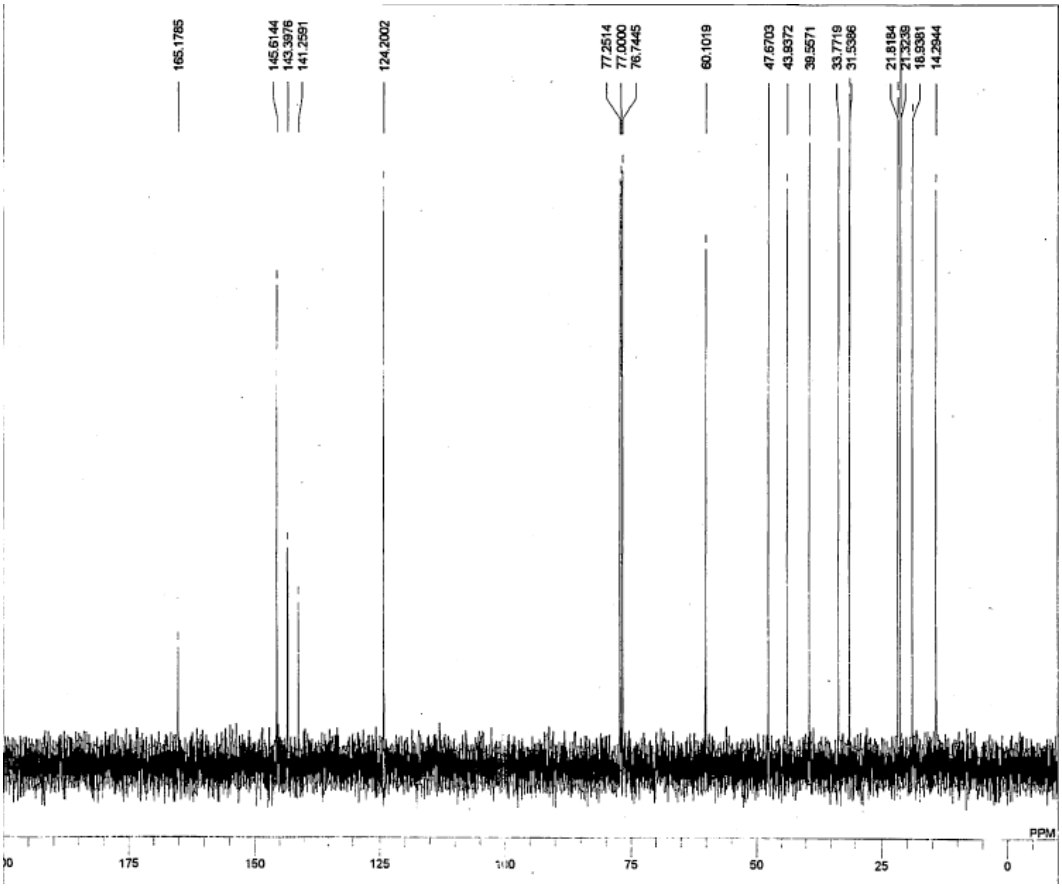
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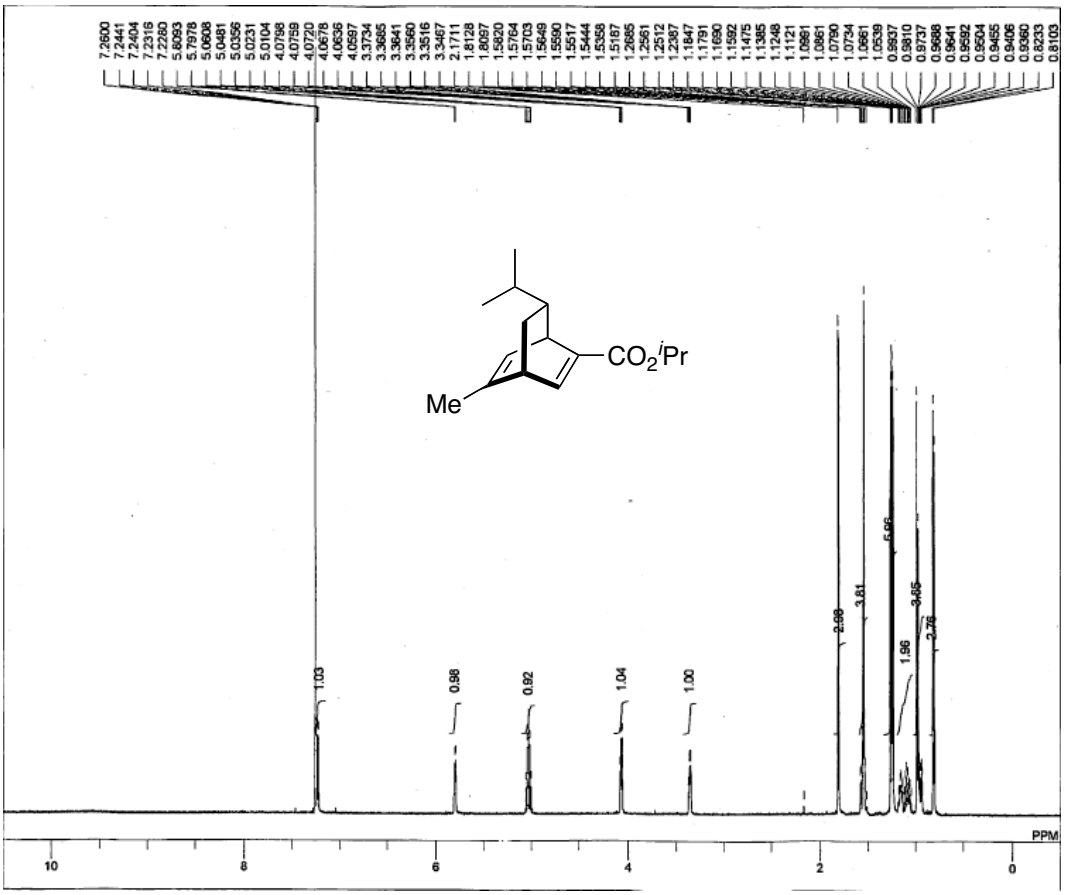
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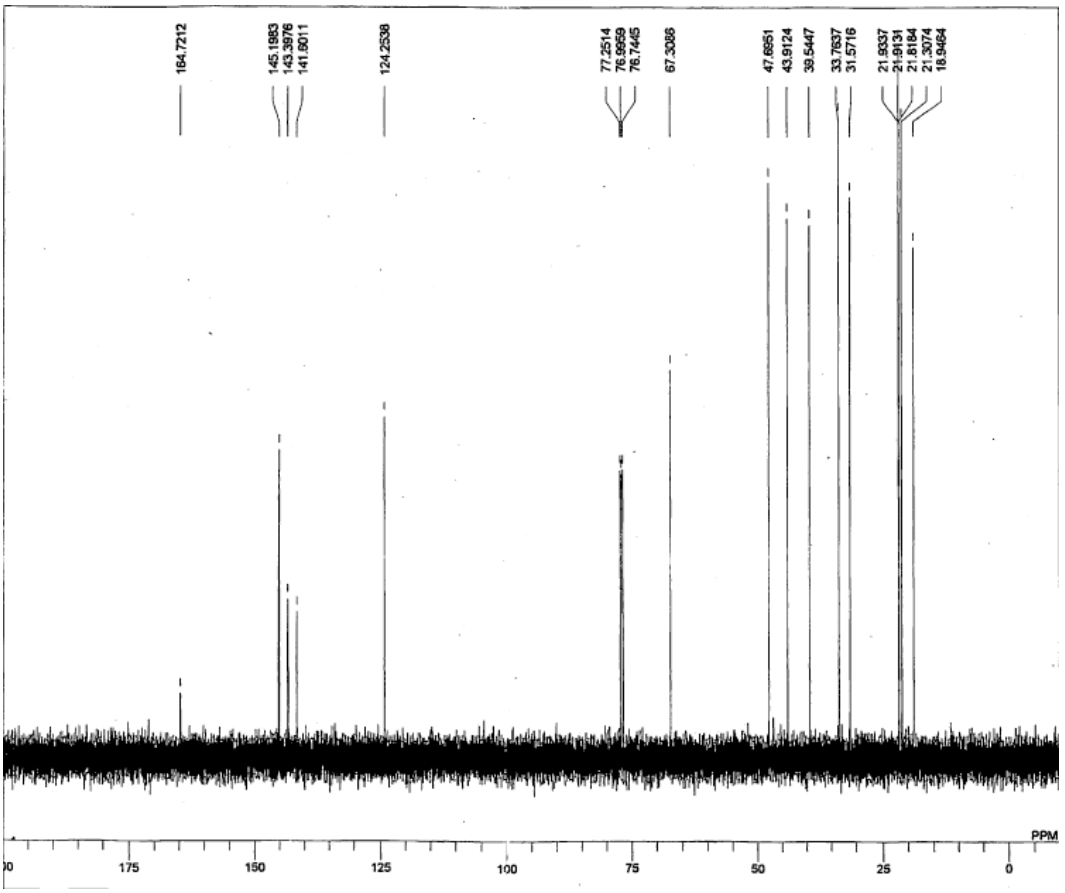
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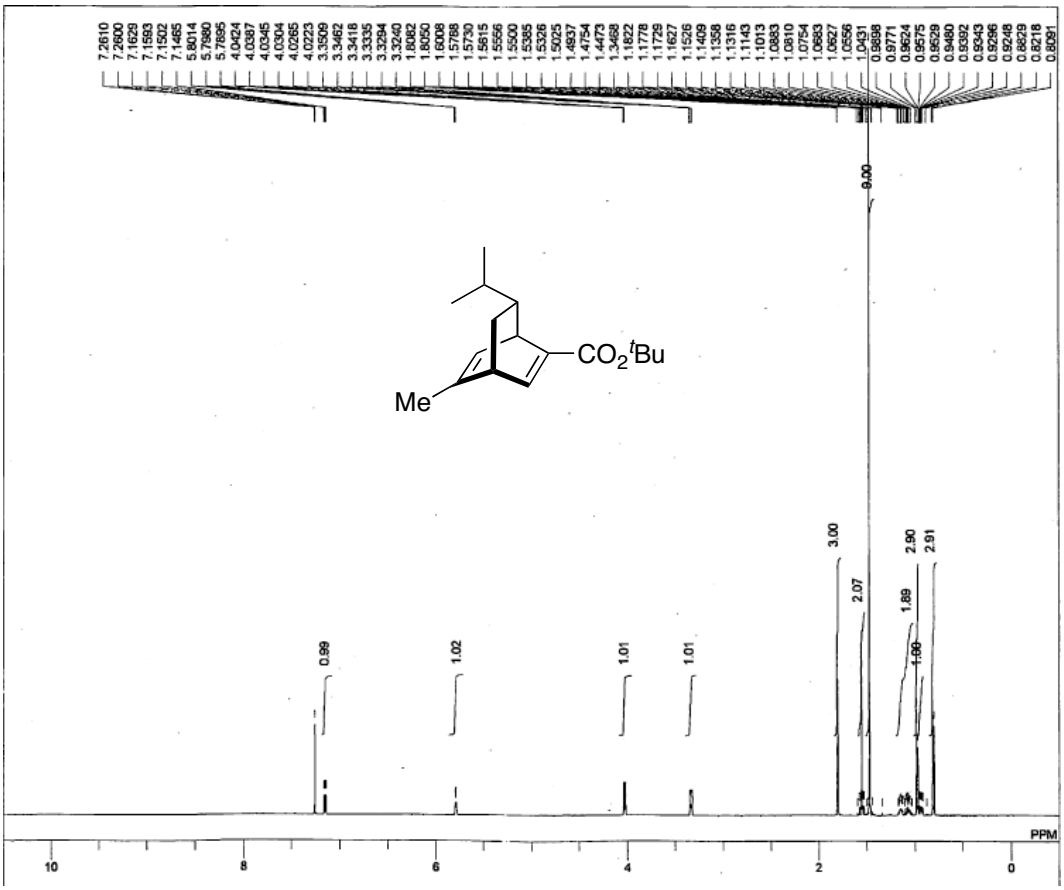
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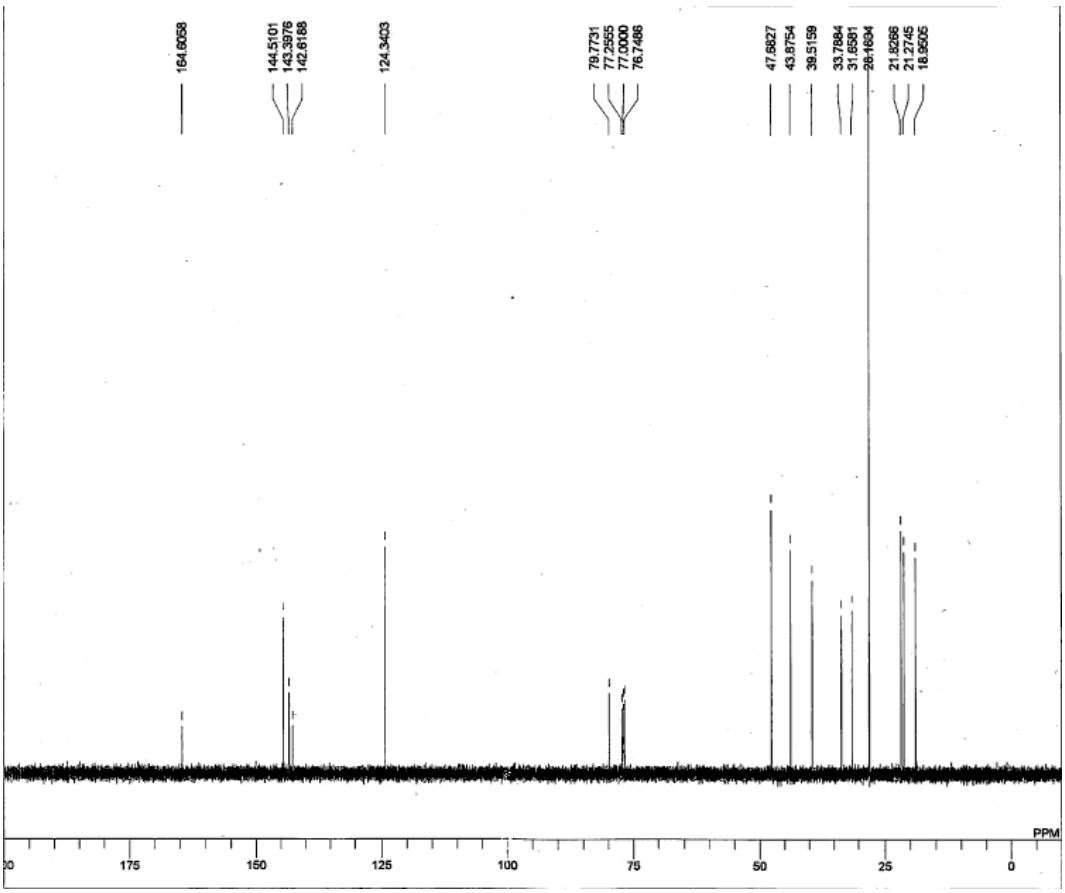
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Me
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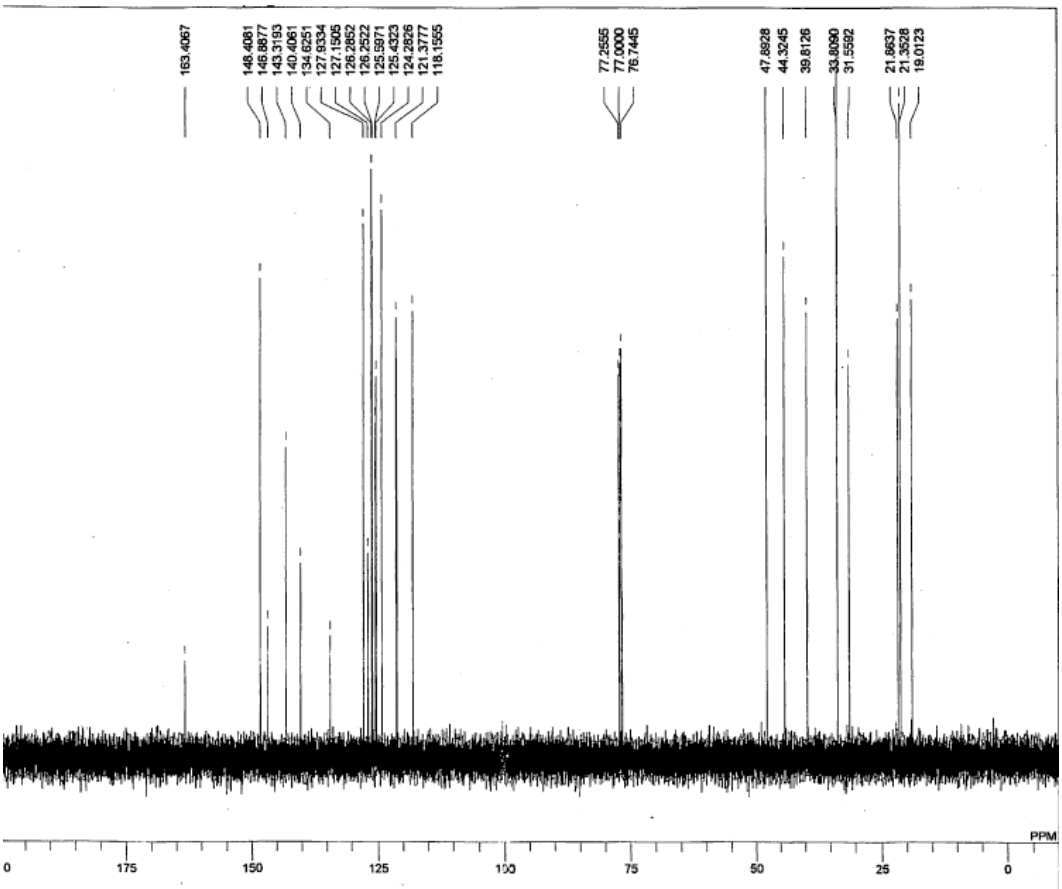
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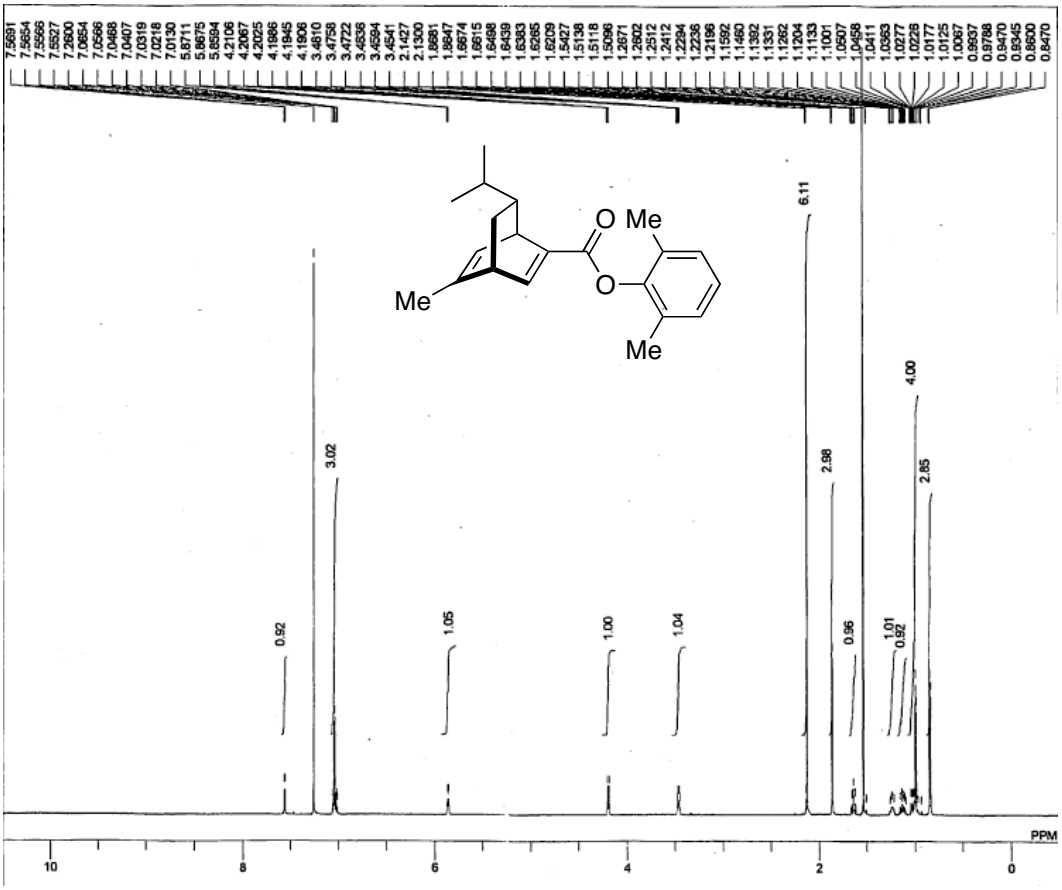
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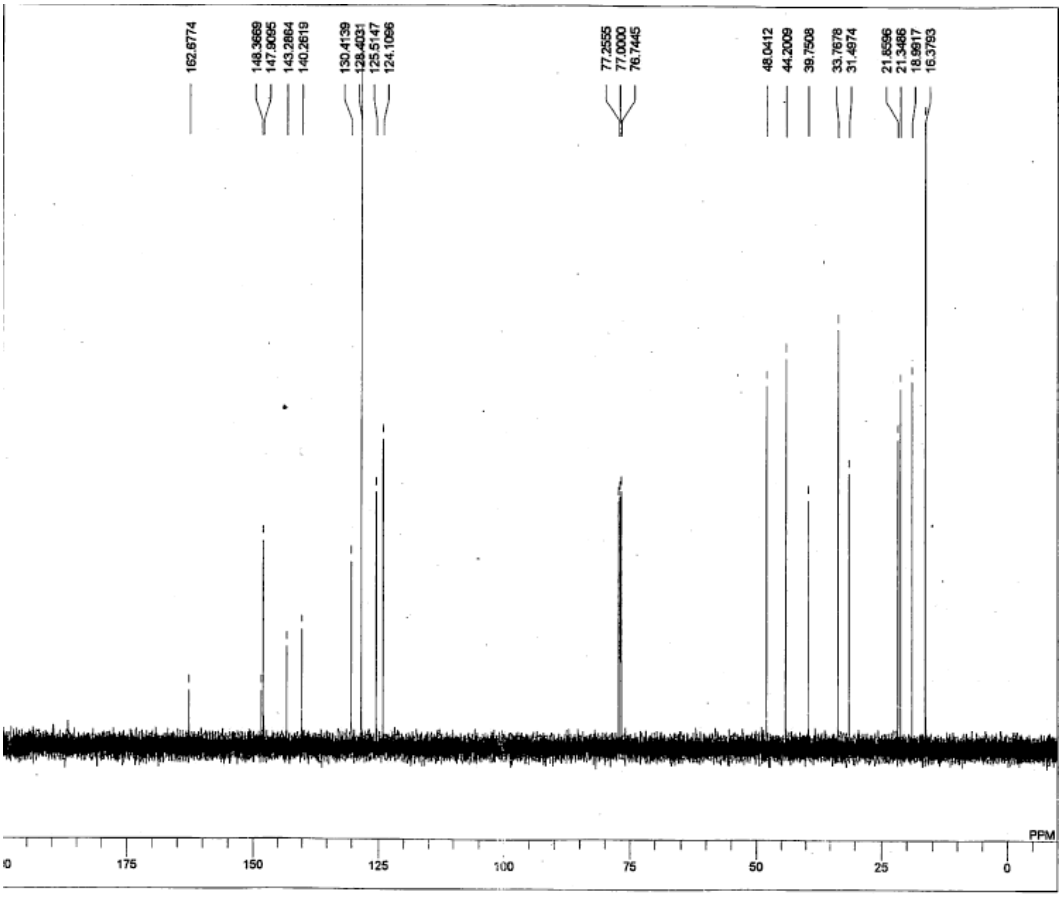
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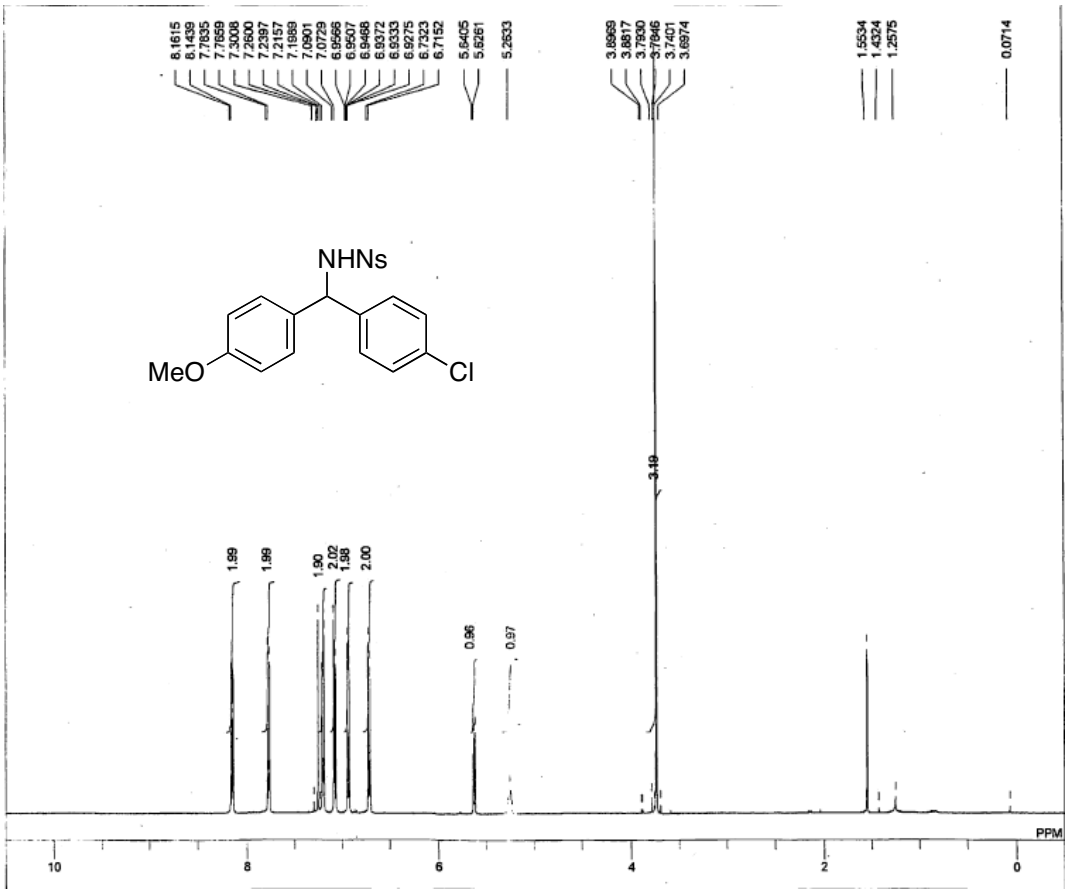
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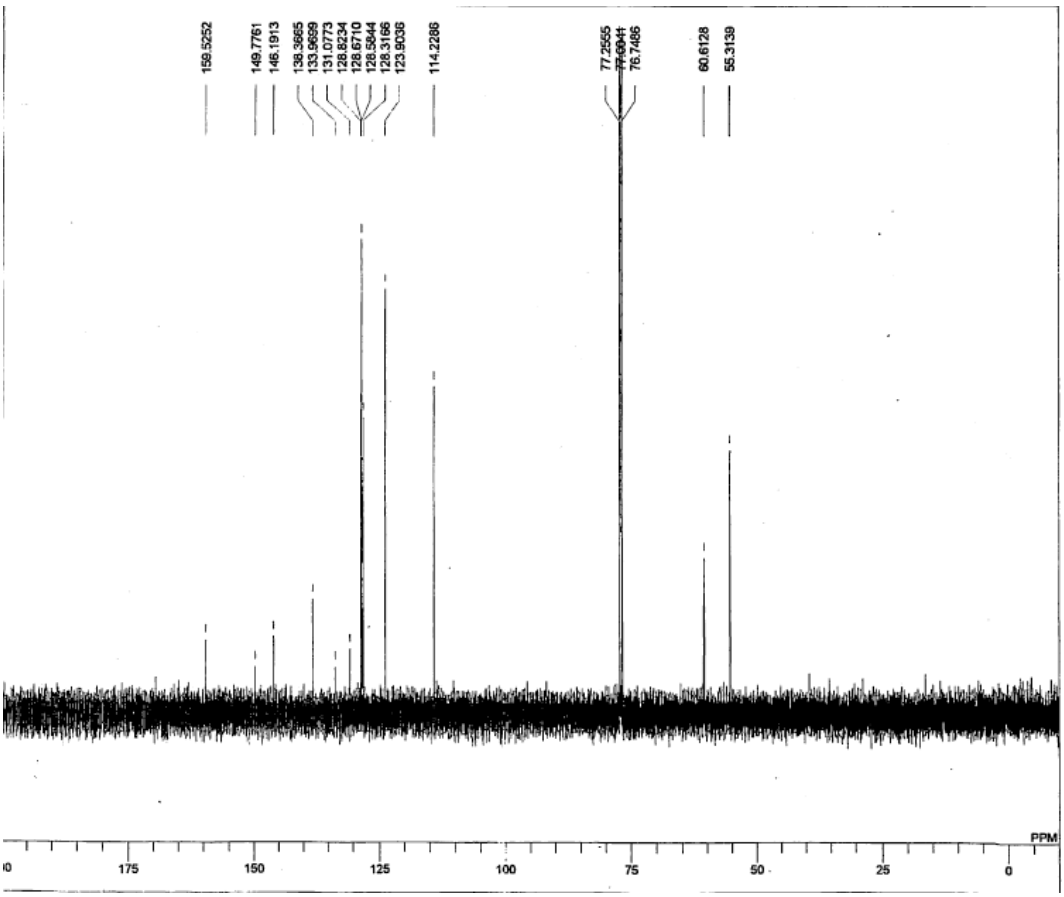
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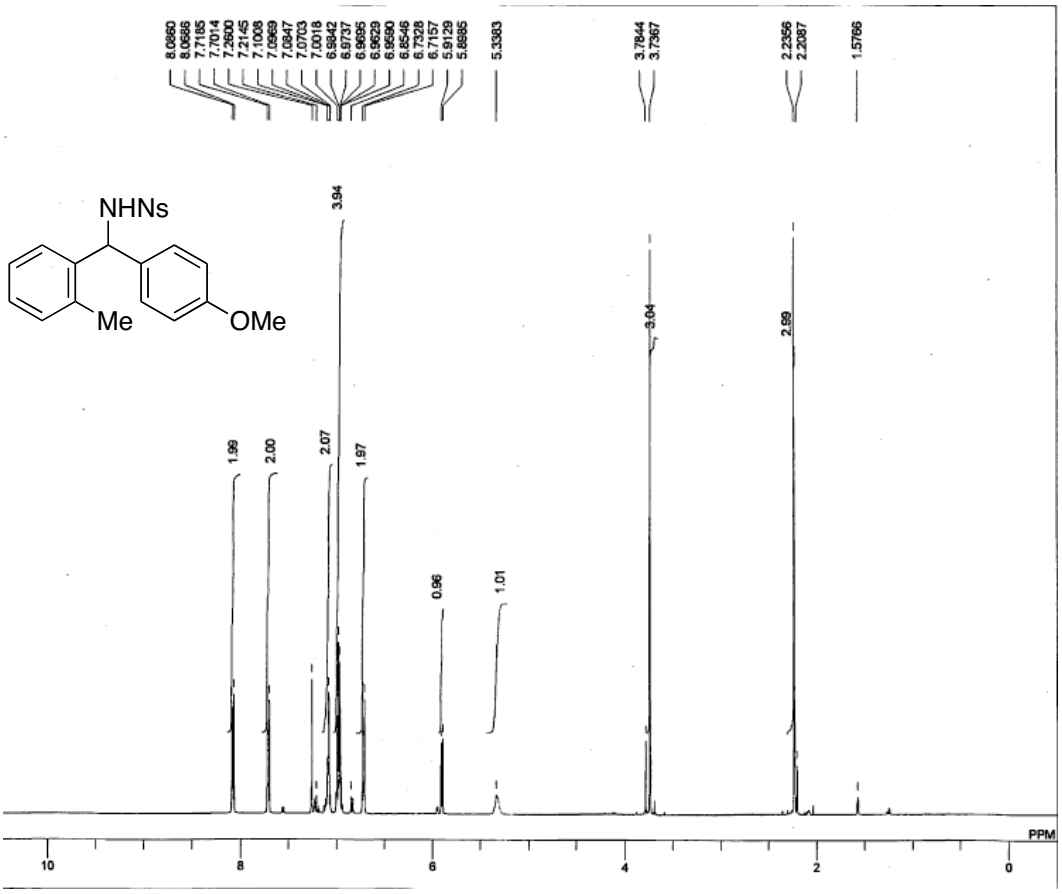
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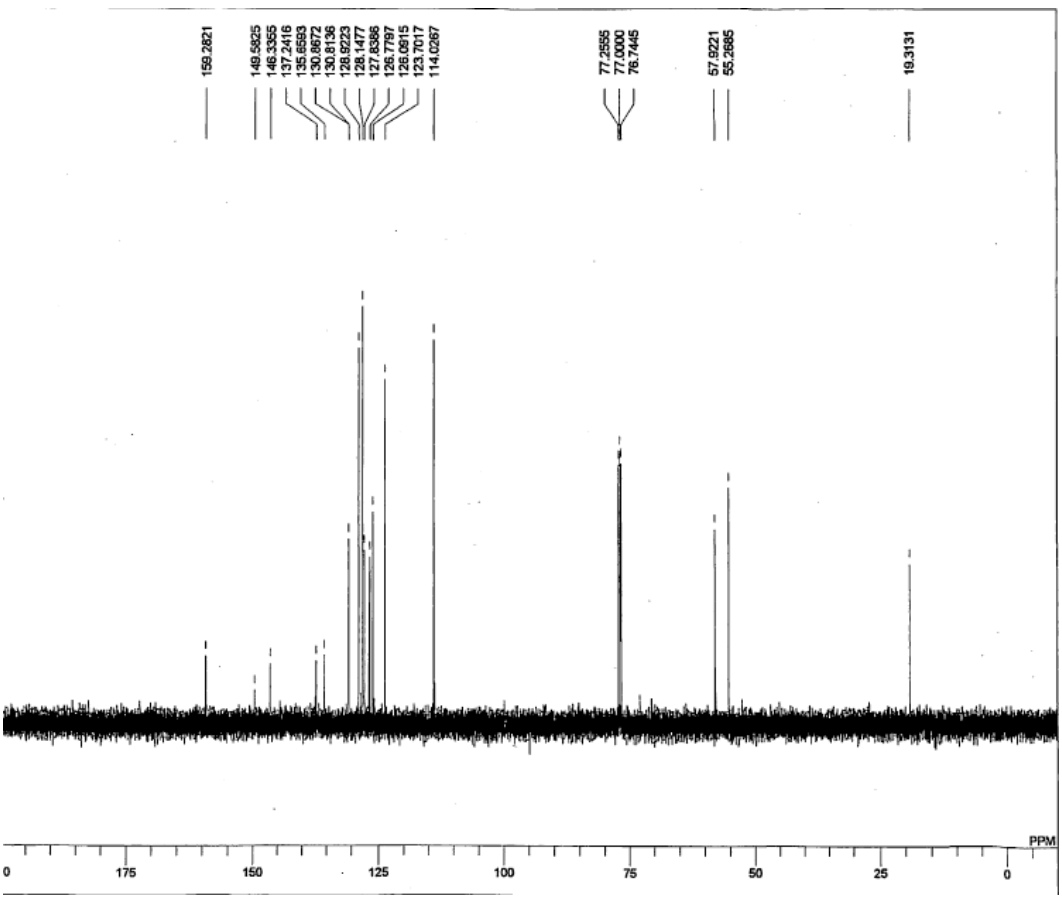
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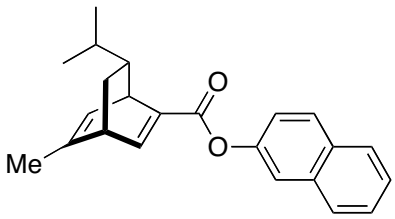
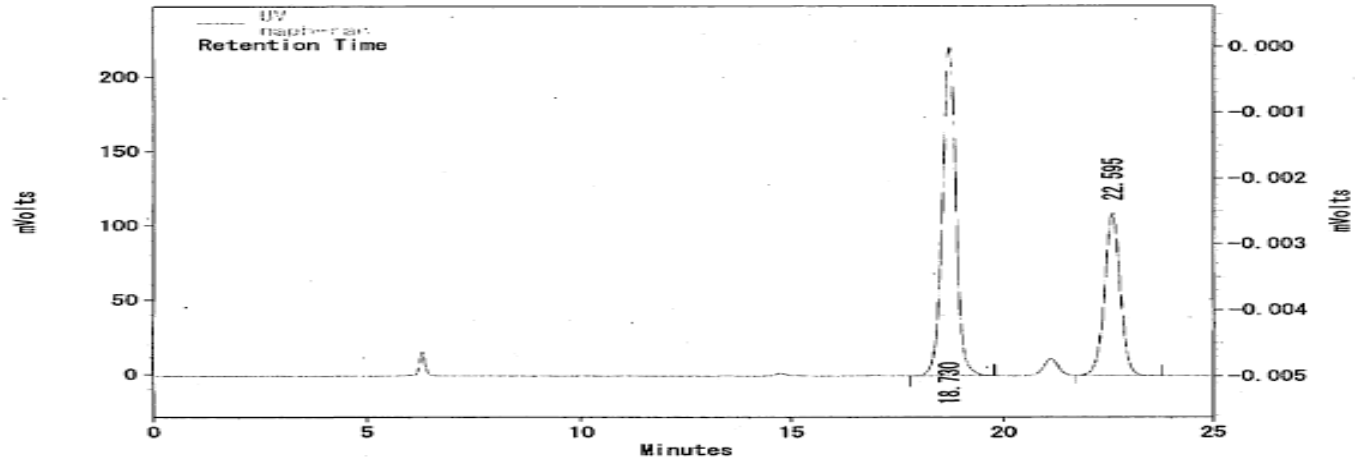
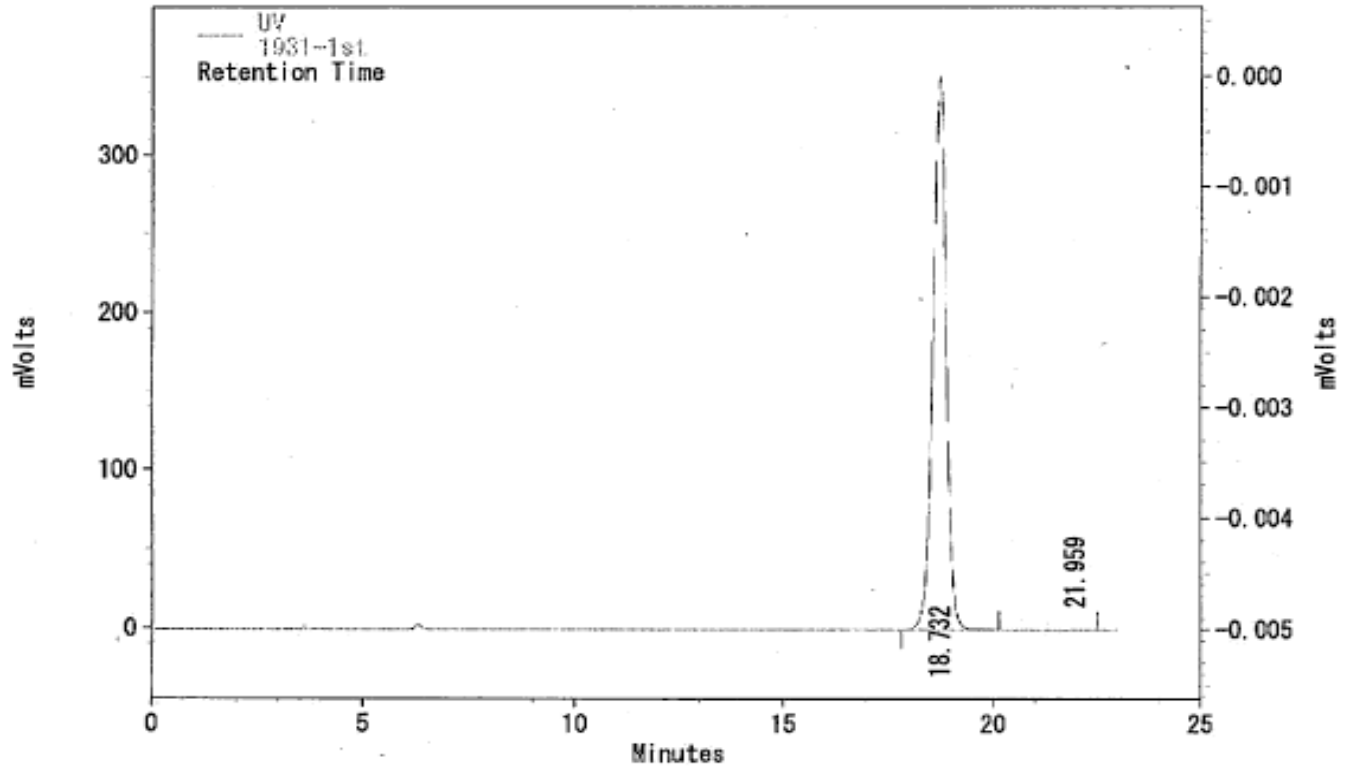


racemic sample



after recrystallization



UV Results

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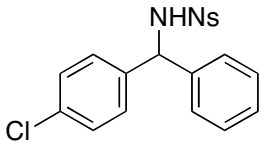
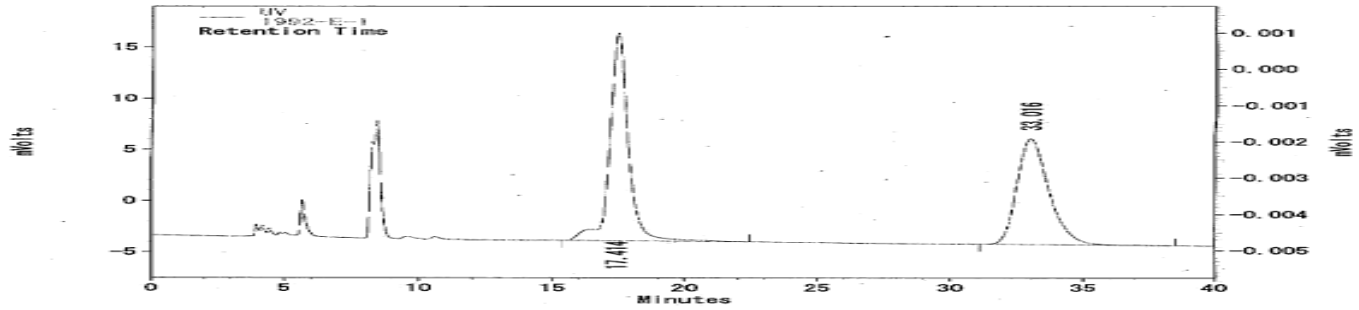
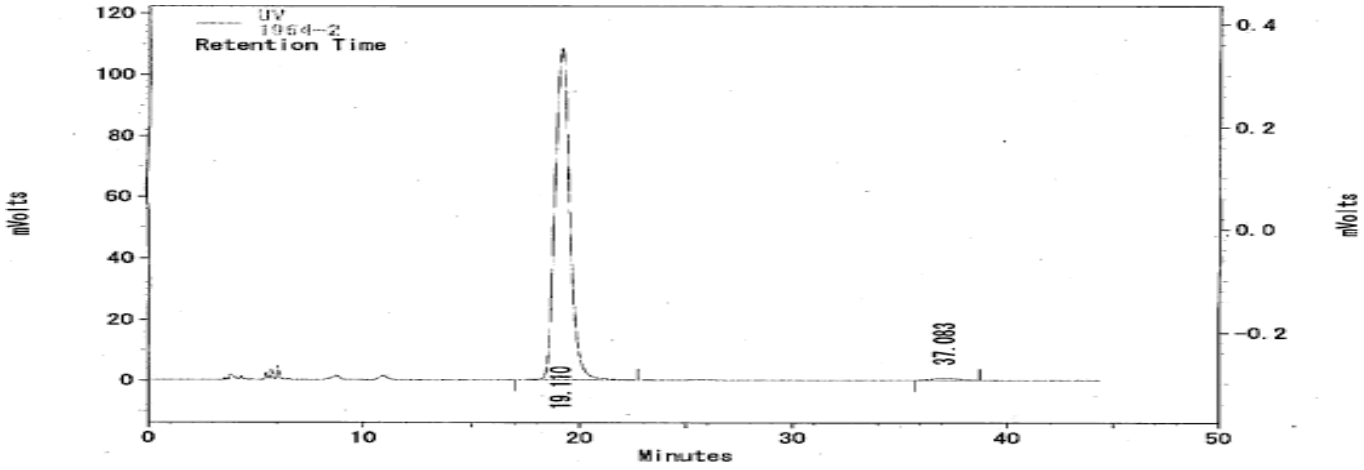
2		21.959	894	0.012	38
Totals			7575043	100.000	351174





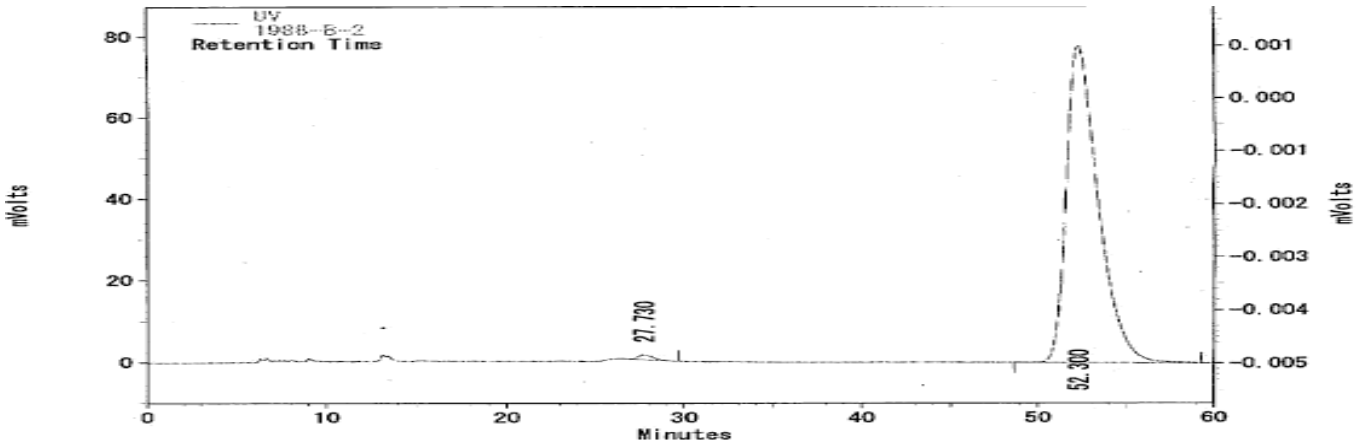
9am *(S)*



UV Results

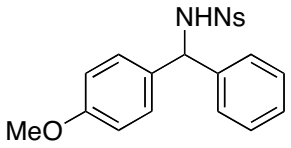
Pk #	Name	Retention Time	Area	Area Percent	Height
1		19.110	5176046	98.839	108450
2		37.083	60795	1.161	742
Totals			5236841	100.000	109192

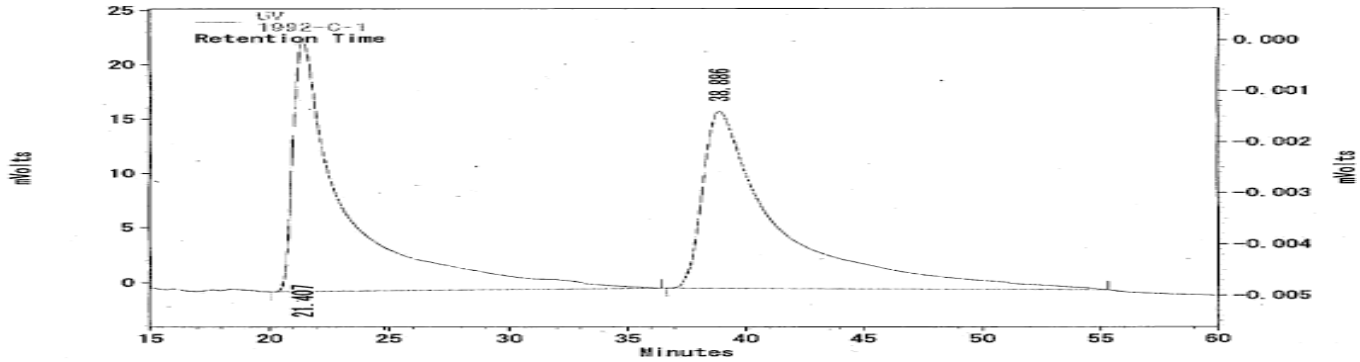
9do *(R)*



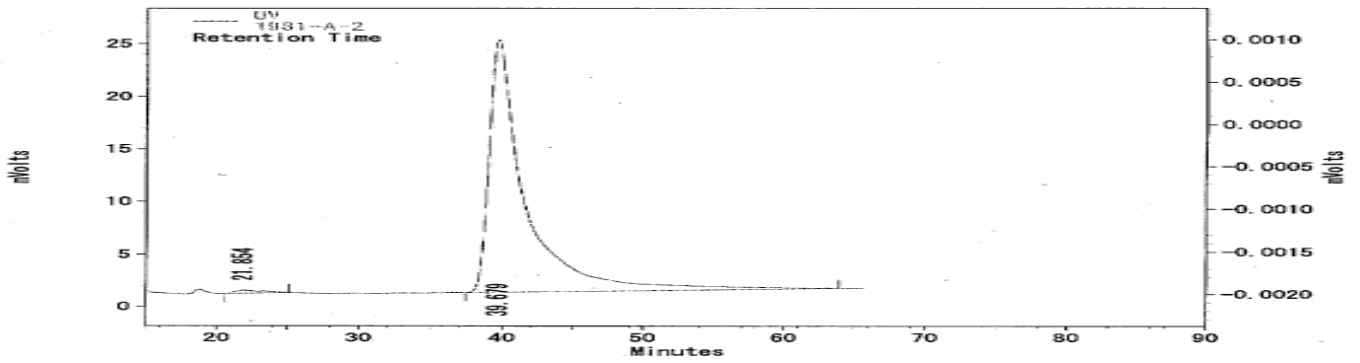
UV Results

Pk #	Name	Retention Time	Area	Area Percent	Height
1		27.730	72277	0.736	1216
2		52.300	9749079	99.264	77669
Totals			9821356	100.000	78885





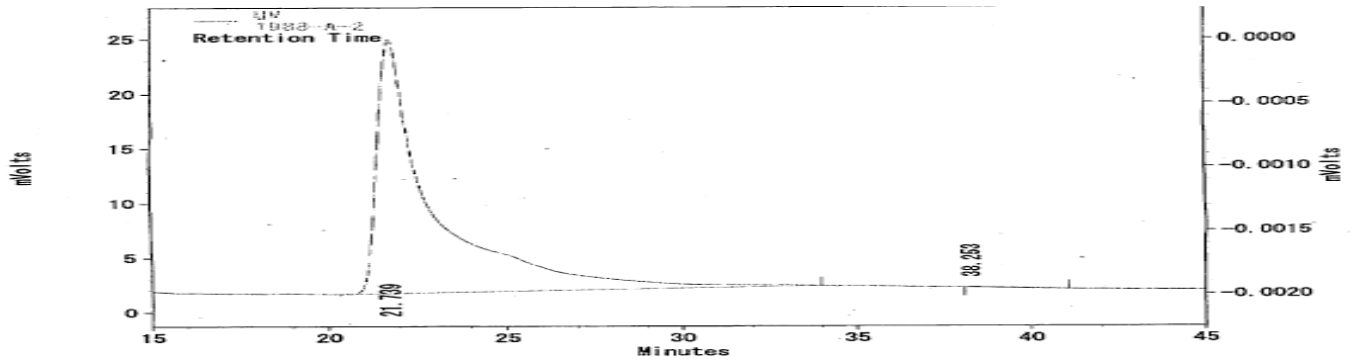
9bm *(S)*



UV Results

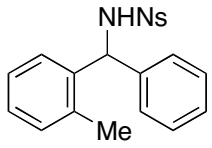
Pk #	Name	Retention Time	Area	Area Percent	Height
1		21.854	42557	0.983	308
2		39.679	4288748	99.017	23984
Totals			4331305	100.000	24292

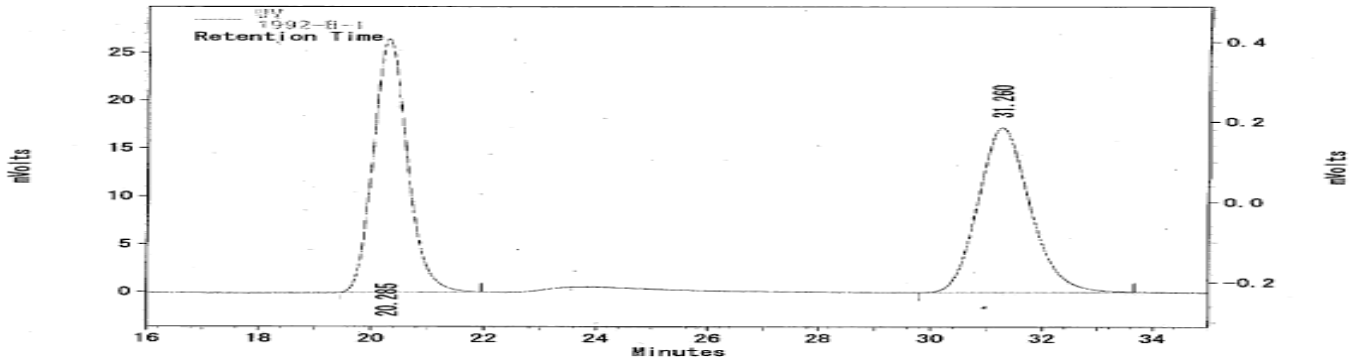
9dn *(R)*



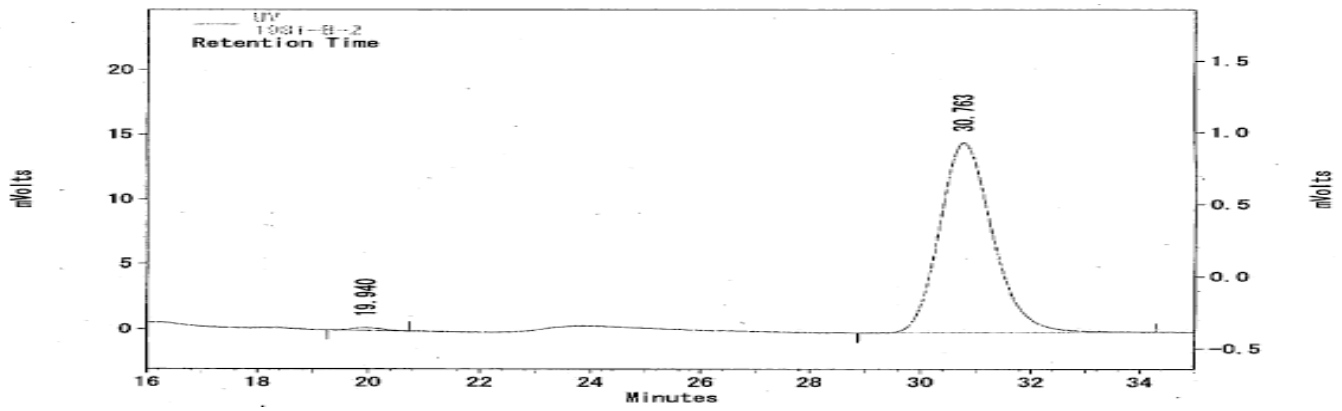
UV Results

Pk #	Name	Retention Time	Area	Area Percent	Height
1		21.739	2564889	99.853	23212
2		38.253	3775	0.147	23
Totals			2568664	100.000	23235





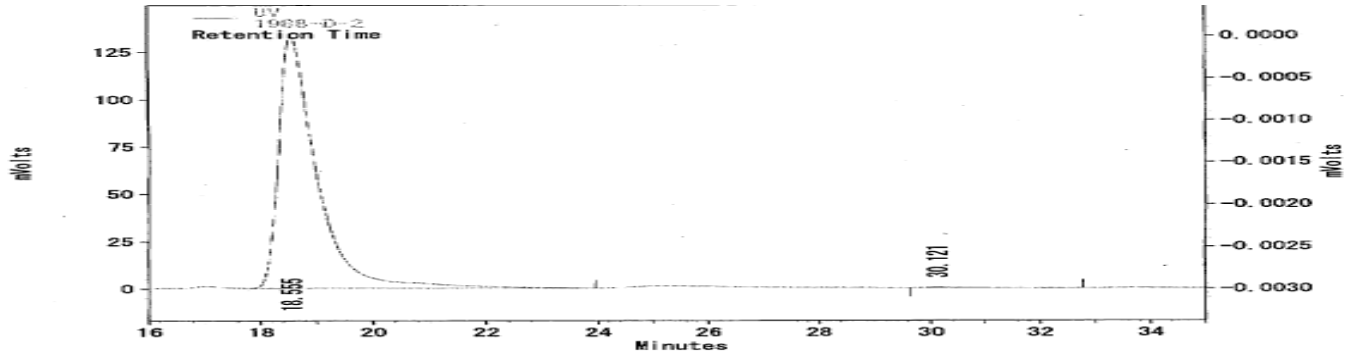
9cm *(S)*



UV Results

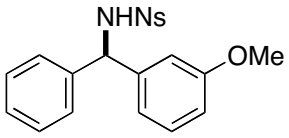
Pk #	Name	Retention Time	Area	Area Percent	Height
1		19.940	9027	0.921	249
2		30.763	970772	99.079	14612
Totals			979799	100.000	14861

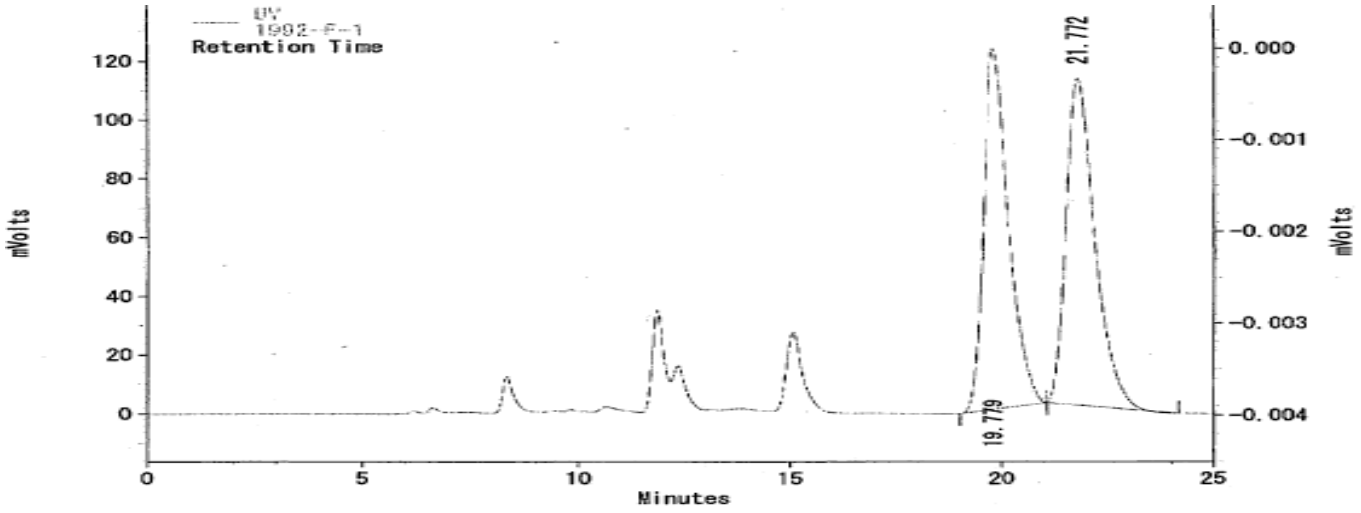
9dq *(R)*



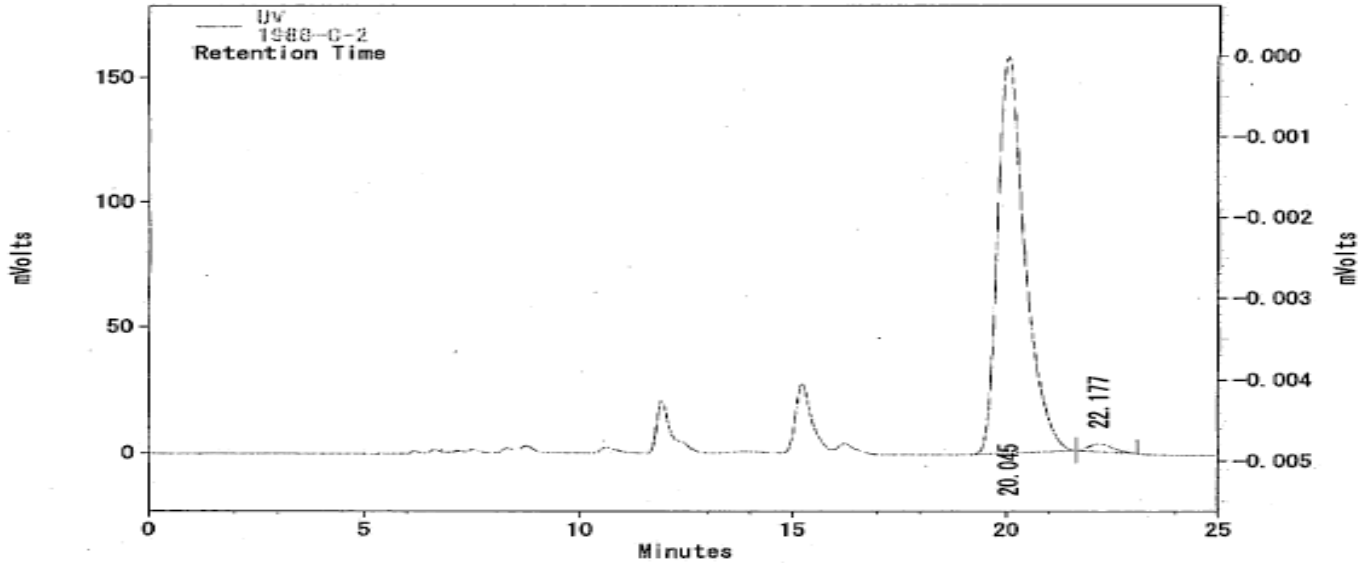
UV Results

Pk #	Name	Retention Time	Area	Area Percent	Height
1		18.555	6294496	99.873	132914
2		30.121	7987	0.127	184
Totals			6302483	100.000	133098



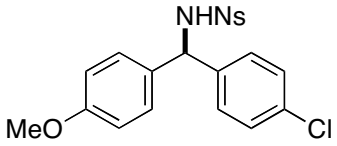


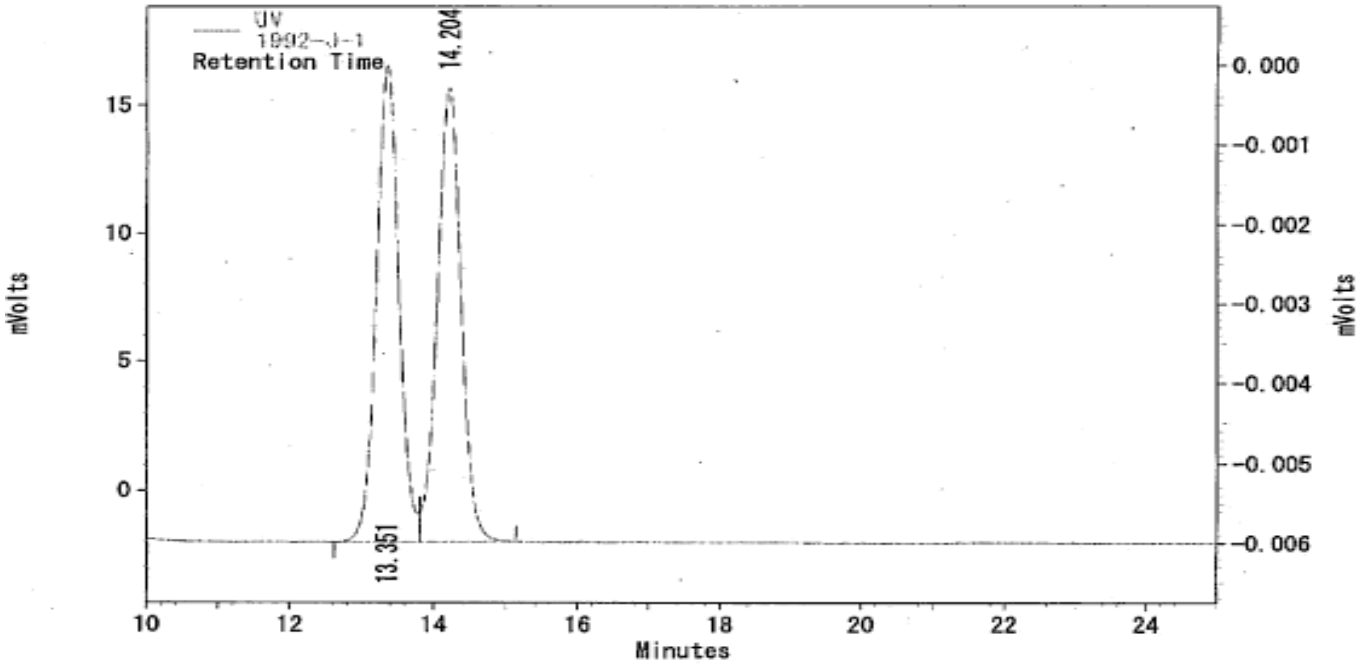
9dp *(R)*



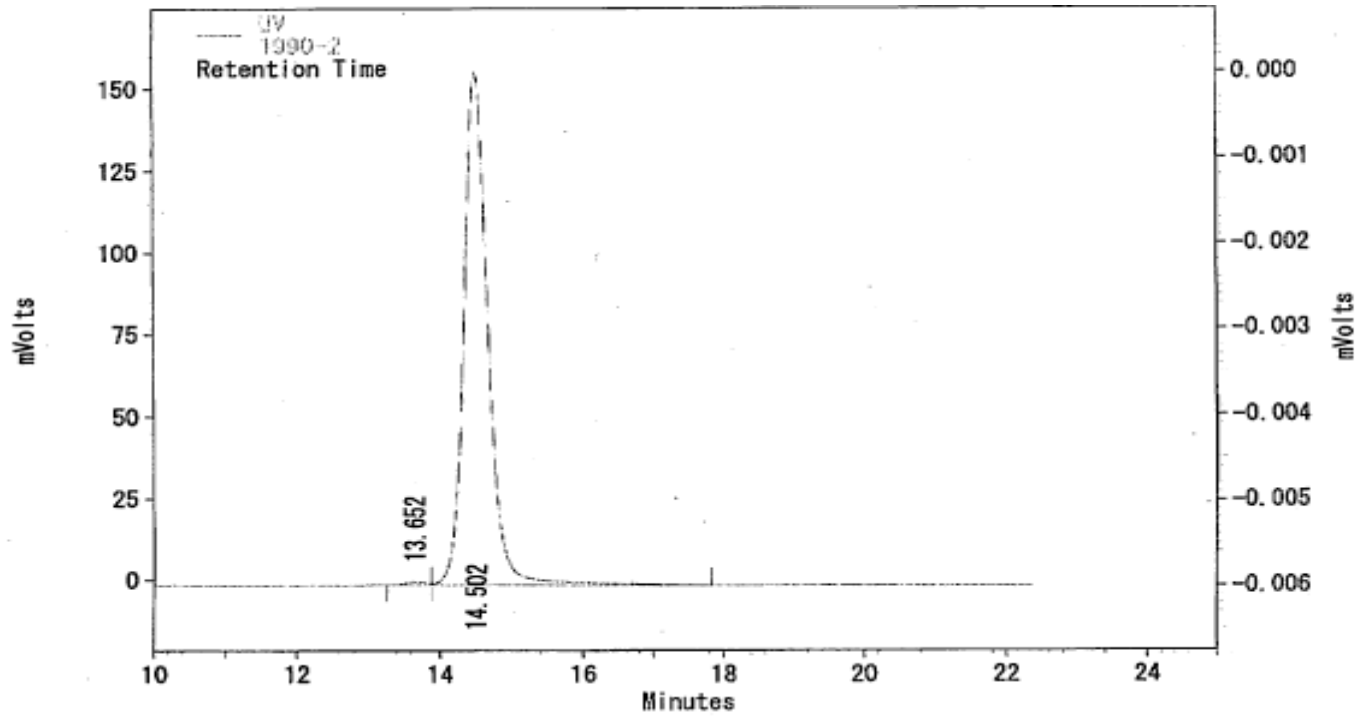
UV Results

Pk #	Name	Retention Time	Area	Area Percent	Height
1		20.045	7112858	98.294	158383
2		22.177	123432	1.706	3068
Totals			7236290	100.000	161451



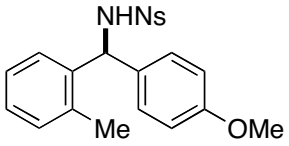


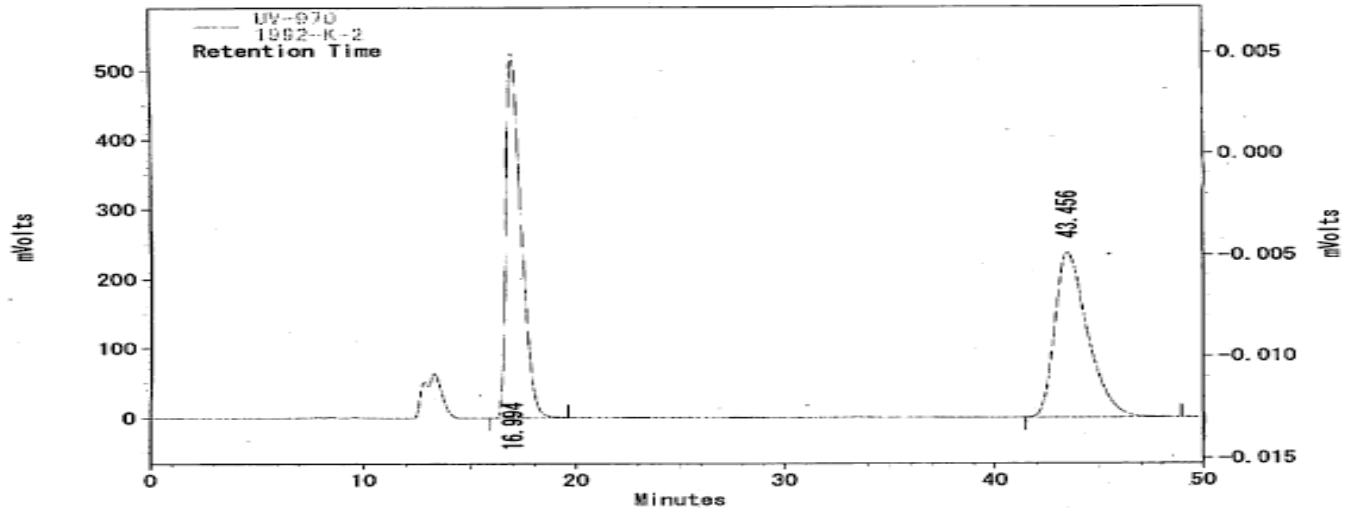
9bo *(R)*



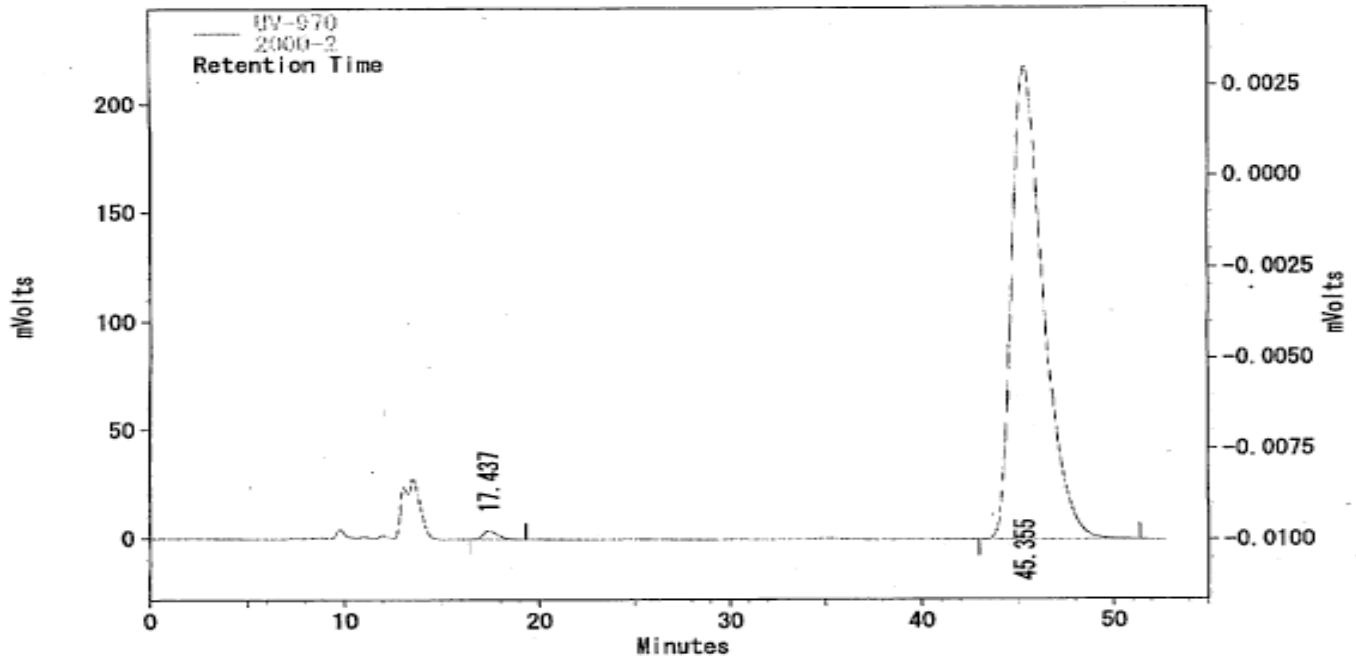
UV Results

Pk #	Name	Retention Time	Area	Area Percent	Height
1		13.652	17449	0.472	966
2		14.502	3678320	99.528	156519
Totals			3695769	100.000	157485



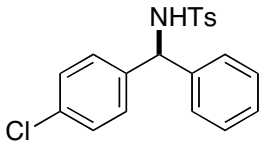


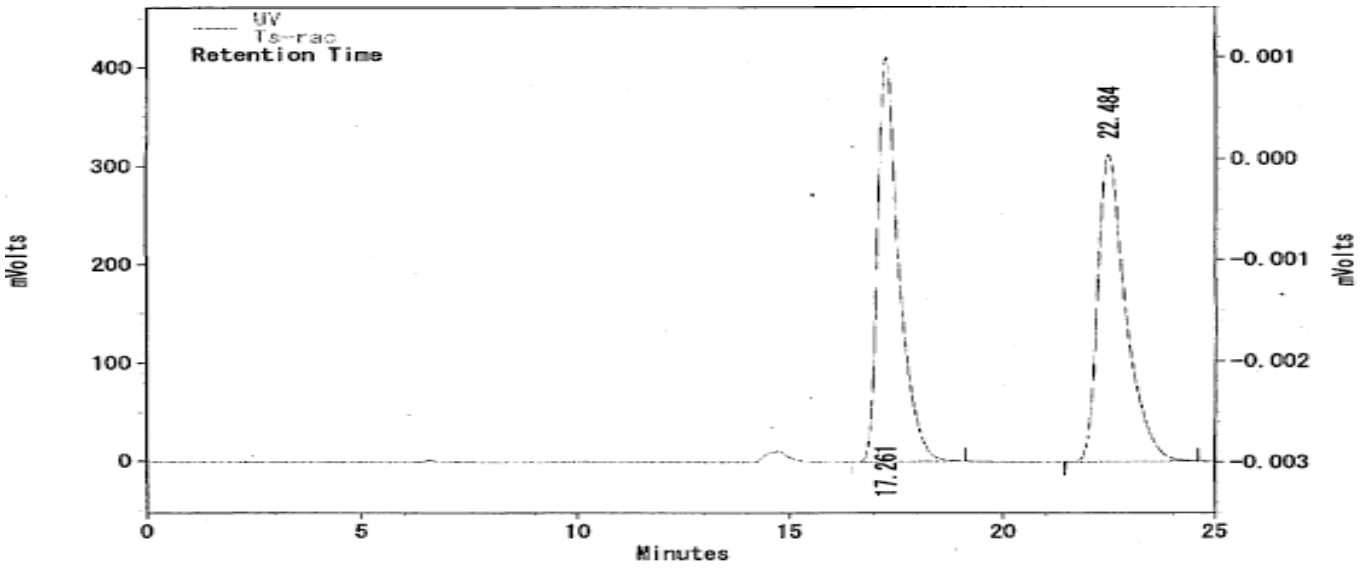
9cn *(S)*



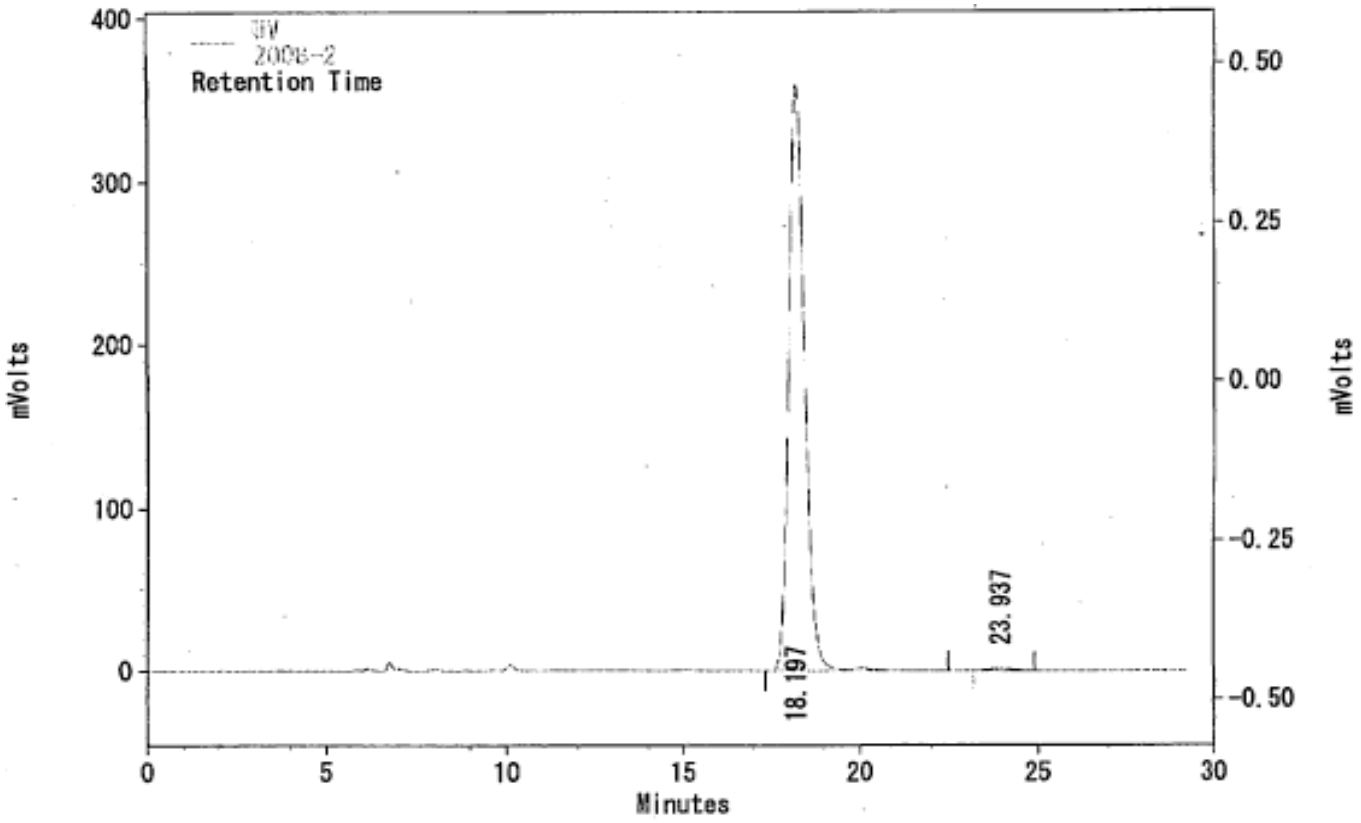
UV-970
Results

Pk #	Name	Retention Time	Area	Area Percent	Height
1		17.437	202471	0.805	3976
2		45.355	24946734	99.195	217723
Totals			25149205	100.000	221699



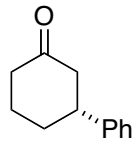


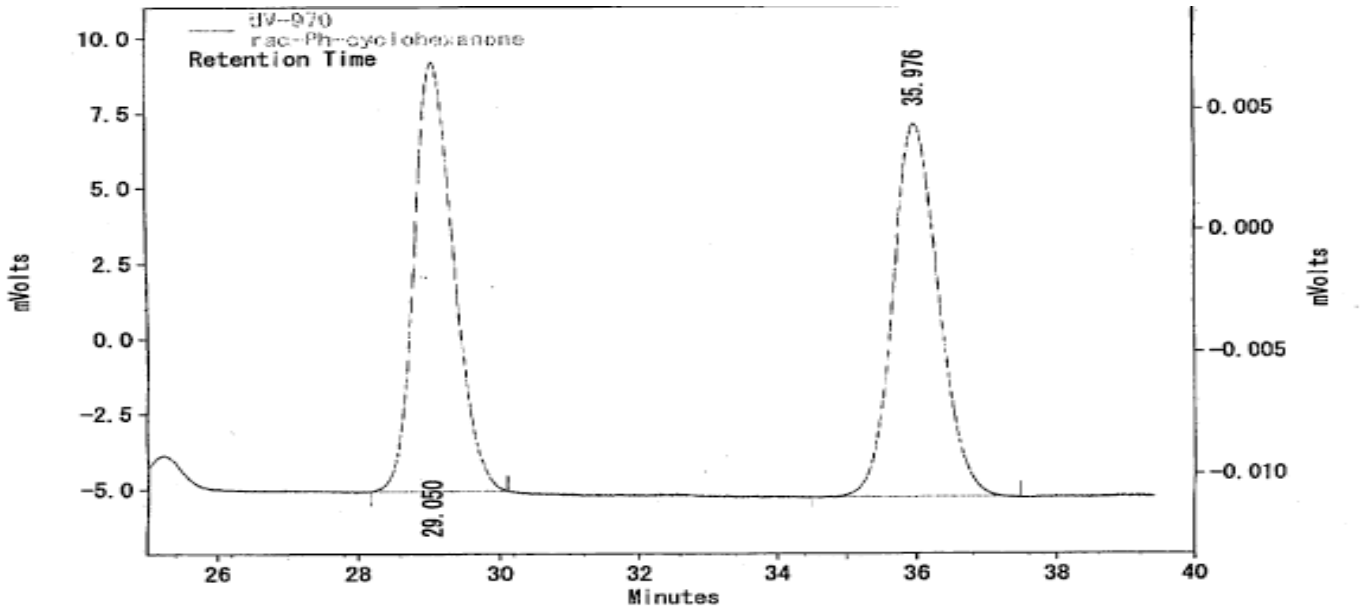
11am *(S)*



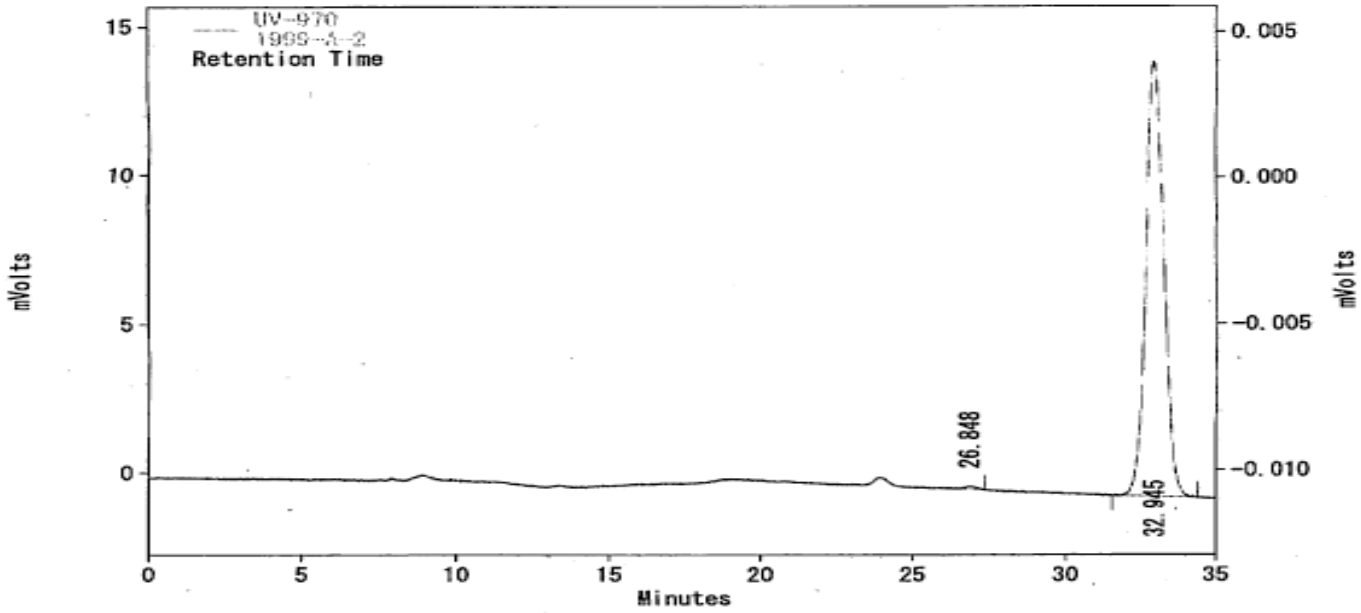
UV Results

Pk #	Name	Retention Time	Area	Area Percent	Height
1		18.197	11119988	99.481	358798
2		23.937	57987	0.519	1420
Totals			11177975	100.000	360218



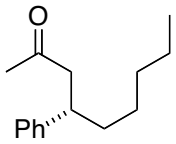


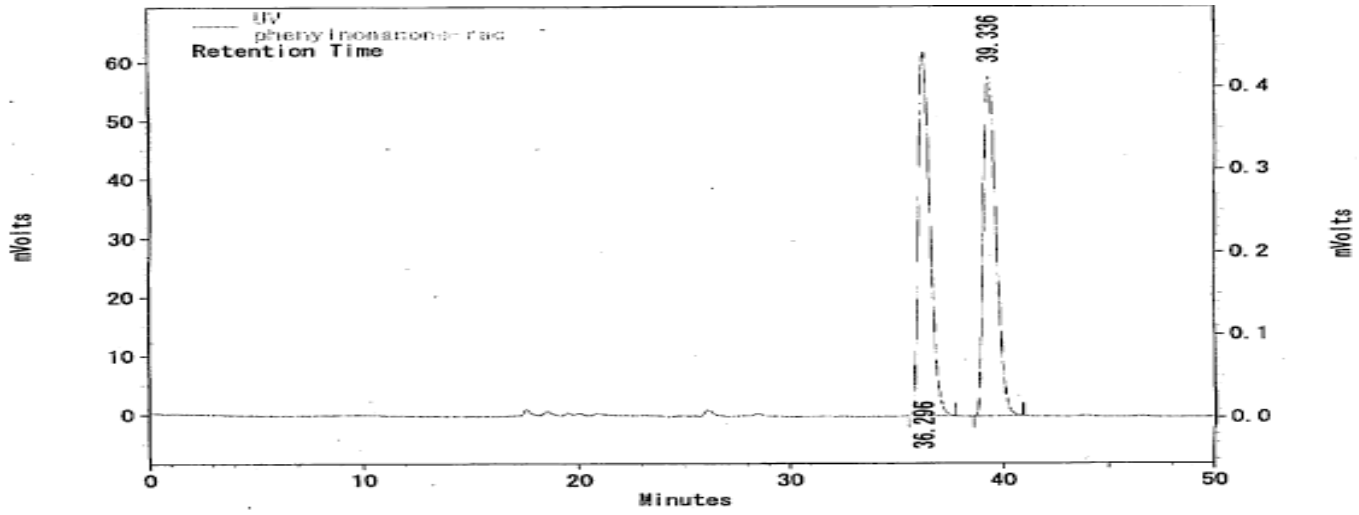
14a *(R)*



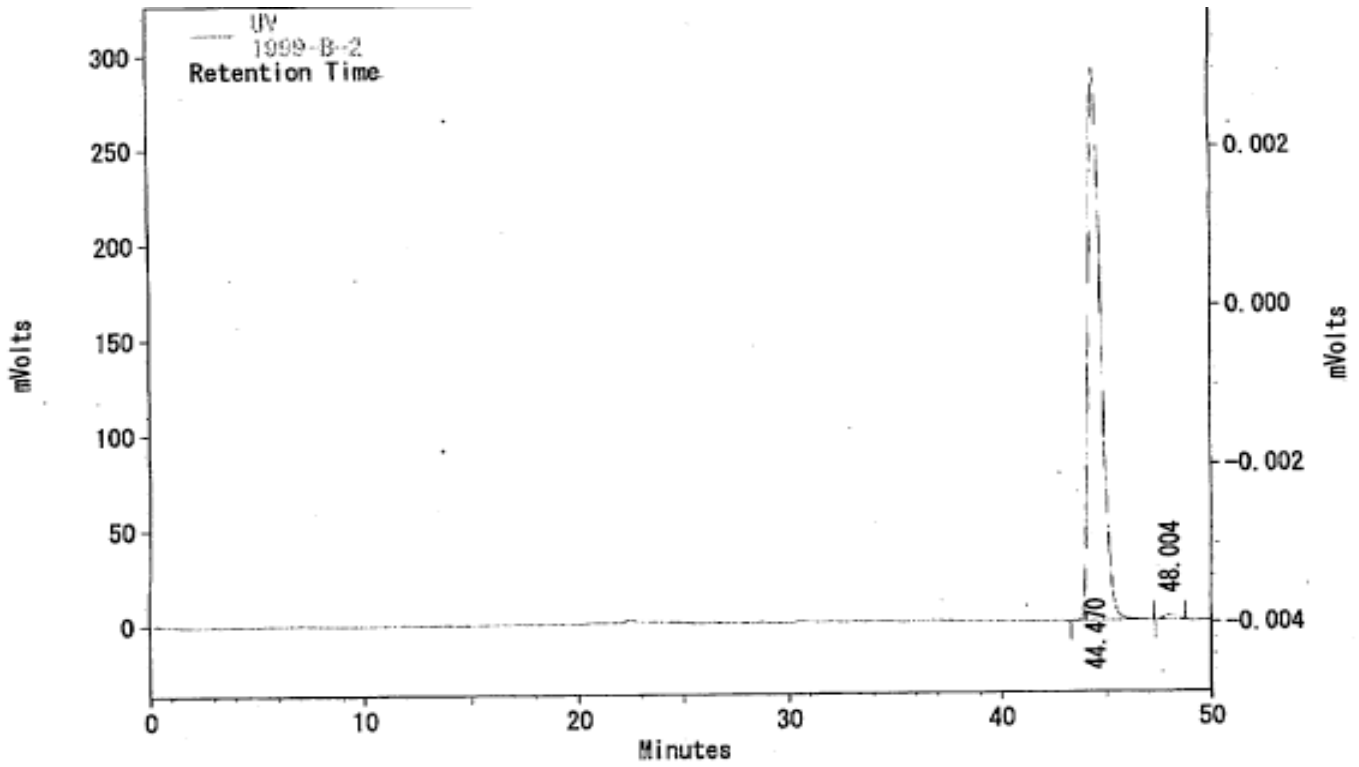
UV-970
Results

Pk #	Name	Retention Time	Area	Area Percent	Height
1		26.848	3149	0.524	131
2		32.945	598152	99.476	14613
Totals			601301	100.000	14744





14b *(S)*



UV Results

Pk #	Name	Retention Time	Area	Area Percent	Height
1		44.470	12168957	99.124	289492
2		48.004	107529	0.876	2662
Totals			12276486	100.000	292154