

Supplementary Information

Concise synthesis of chiral tfb ligands and their application to rhodium-catalyzed asymmetric arylation of aldehydes

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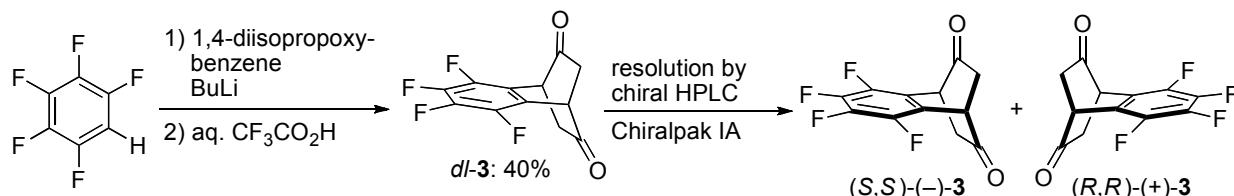
General

All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or glovebox techniques under argon. NMR spectra were recorded on a JEOL JNM LA-500 spectrometer (500 MHz for ¹H, 125 MHz for ¹³C). Chemical shifts are reported in δ (ppm) referenced to an internal SiMe₄ standard or the residual peak of dichloromethane-*d*₂ (CDHCl₂, δ 5.32) for ¹H NMR, and chloroform-*d* (δ 77.00) for ¹³C NMR. The following abbreviations are used; s, singlet, d, doublet, t, triplet, q, quartet, m, multiplet, br, broad. Optical rotations were measured on a JASCO P-2200 polarimeter. High-resolution mass spectra were obtained with a Bruker micrOTOF spectrometer. Preparative recycling gel permeation chromatography was performed with JAI LC-908 equipped with JAIGEL-1H and -2H using chloroform as eluent.

Materials

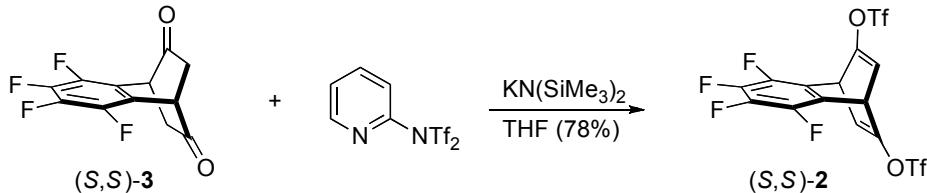
All solvents were deoxygenized by bubbling N₂. 1,4-Dioxane was distilled over benzophenone ketyl under N₂. Methanol was distilled over Mg turnings under N₂. CH₂Cl₂ were distilled over CaH₂ under N₂. 2-Propanol and *tert*-butyl alcohol were purchased and used as received. 1,4-Diisopropoxybenzene was purchased and distilled over CaH₂ under vacuum. Rhodium complex [RhCl(C₂H₄)₂]₂¹ and ligands, **1b**,² **1c**,³ and (*R,R*)-Ph-bod*(**4**),⁴ were prepared according to the reported procedures. The starting aldehydes were purchased and solid aldehydes were used as received. Liquid aldehydes were distilled under reduced pressure before use. Arylboronic acids **6s** [127972-00-3],⁵ **6t** [23112-96-1],⁶ and **6u** [5980-97-2]⁷ were prepared according to the reported procedures. Other arylboronic acids were purchased and used as received. Diarylmethanols except for **7an**, **7ap**, **7as**, **7at**, **7bu**, **7eu**, and **9** are reported compounds.

Preparation of chiral diene ligands



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- (1) R. Cramer, *Inorg. Synth.*, 1974, **15**, 14.
(2) T. Nishimura, M. Nagaosa and T. Hayashi, *Chem. Lett.* 2008, **37**, 860.
(3) T. Nishimura, Y. Yasuhara, M. Nagaosa and T. Hayashi, *Tetrahedron: Asymmetry*, 2008, **19**, 1778.
(4) (a) N. Tokunaga, Y. Otomaru, K. Okamoto, K. Ueyama, R. Shintani and T. Hayashi, *J. Am. Chem. Soc.*, 2004, **126**, 13584. (b) Y. Otomaru, K. Okamoto, R. Shintani and T. Hayashi, *J. Org. Chem.*, 2005, **70**, 2503.
(5) C. J. Davies, A. Gregory, P. Griffith, T. Perkins, K. Singh and G. A. Solan, *Tetrahedron*, 2008, **64**, 9857.
(6) T. Fukuda, E. Sudo, K. Shimokawa and M. Iwao, *Tetrahedron*, 2008, **64**, 328.
(7) P. Wipf and J.-K. Jung, *J. Org. Chem.*, 2000, **65**, 6319.

Compound 3 [27282-42-4]:⁸ To a solution of pentafluorobenzene (1.68 g, 10.0 mmol) and 1,4-diisopropoxybenzene (30 mL) in hexane (20 mL) was slowly added BuLi (1.65 M in hexane, 6.1 mL, 10 mmol) at -20 °C with vigorous stirring over 15 min, and the mixture was stirred at this temperature for 1 h. Stirring was further continued at 0 °C for 6 h. After the mixture was warmed up to room temperature, it was filtered through a pad of Celite® eluted with hexane, and the filtrate was concentrated on a rotary evaporator. The residue was further concentrated under vacuum (120 °C, ca. 20 Pa) for removal of unreacted 1,4-isopropoxybenzene. The residue was dissolved in THF (20 mL) and 50% (v/v) aqueous trifluoroacetic acid (10 mL), and the mixture was stirred at room temperature for 6 h. Aqueous Na₂CO₃ was added for neutralization, and the mixture was extracted with Et₂O. The organic layer was washed with brine, dried over Na₂SO₄, filtered, and concentrated on a rotary evaporator. The crude product was chromatographed on silica gel with hexane/ethyl acetate (4/1) and further purified by GPC with chloroform to give diketone *dl*-3 (1.04 g, 4.0 mmol, 40%) as a white solid. Optical resolution was carried out by use of a chiral stationary phase column [Chiraldak IA (2.0 cm I.D. × 25 cm), hexane/ethyl acetate = 3/2, flow 8 mL/min, *t*₁ = 10 min for (-)-3, *t*₂ = 14 min for (+)-3] to give both enantiomers (-)-3 and (+)-3. An injection of 120 mg of *dl*-3 in hexane/ethyl acetate (3/2) (4.5 mL) gave (-)-3 and (+)-3, quantitatively. ¹H NMR (CDCl₃) δ 2.52 (dd, *J* = 19.1, 3.2 Hz, 2H), 2.75 (dd, *J* = 19.1, 2.4 Hz, 2H), 4.27 (dd, *J* = 3.2, 2.4 Hz, 2H); ¹³C NMR (CDCl₃) δ 36.1 (2C), 46.1 (2C), 118.8–119.1 (m, 2C), 139.2–144.9 (m, 4C), 202.7 (2C). [α]²⁰_D -529 (*c* 1.00, CHCl₃) for (S,S)-3.

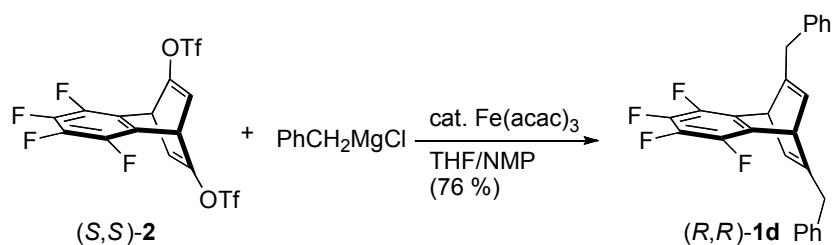


Compound 2: To a solution of diketone 3 (516 mg, 2.00 mmol) and *N*-(2-pyridyl)triflimide (1.72 g, 4.80 mmol) in THF (30 mL) was slowly added KN(SiMe₃)₂ (0.5 M in toluene, 9.2 mL, 4.6 mmol) at -78 °C over 1 h, and the mixture was stirred for further 30 min.⁹ The mixture was quenched with aqueous NH₄Cl at -78 °C. The aqueous layer was extracted with Et₂O, and the combined organic layer was washed with brine, dried over MgSO₄, filtered, and concentrated on a rotary evaporator. The crude product was chromatographed on silica gel with hexane/ethyl acetate (97/3) to give 2 (816 mg, 1.56 mmol, 78%) as colorless oil. ¹H NMR (CDCl₃) δ 5.09 (dd, *J* = 6.7, 2.7 Hz, 2H), 6.80 (dd, *J* = 6.7, 2.7 Hz, 2H); ¹³C NMR (CDCl₃) δ 43.5 (2C), 118.4 (q, *J*_{F-C} = 321 Hz, 2C), 124.1 (2C), 126.6–126.9 (m, 2C), 137.3–143.7 (m, 4C), 163.9 (2C). HRMS (ESI-TOF) calcd for C₁₄H₄F₄NaO₆S₂ (M+Na⁺) 544.9182, found 544.9164. [α]²⁰_D

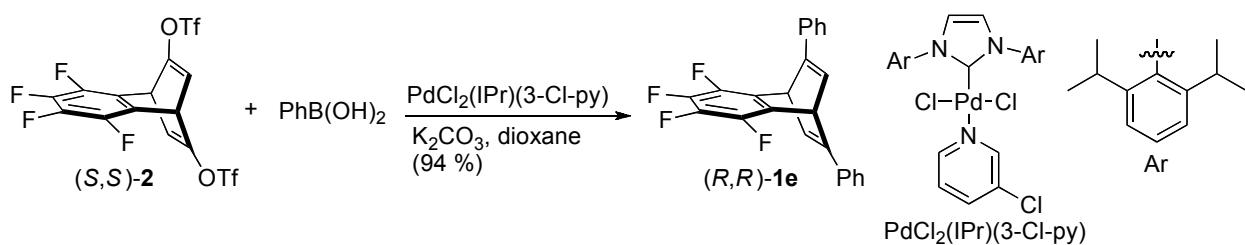
(8) (a) Hankinson, B and Heaney, H. *Tetrahedron Lett.*, 1970, **16**, 1335. (b) P. C. Buxton, N. J. Hales, B. Hankinson, H. Heaney, S. V. Lay and R. P. Sharma, *J. Chem. Soc. Perkin Trans. 1*, 1974, 2681.

(9) K. Vandyck, B. Matthys, M. Willen, K. Robeyns, L. Van Meervelt and J. Van der Eycken, *Org. Lett.*, 2006, **8**, 363.

+4 (*c* 0.82, CHCl₃) for (*S,S*)-**2**.



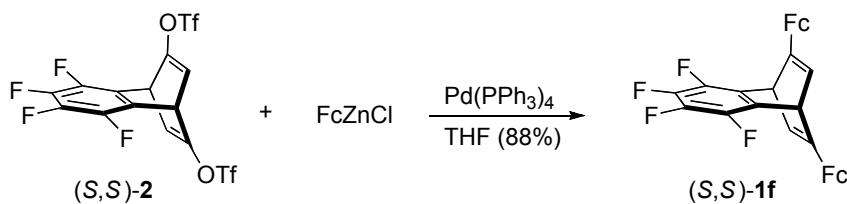
Compound 1d [1067879-52-0]:³ To a solution of **2** (261 mg, 0.50 mmol), Fe(acac)₃ (8.8 mg, 0.025 mmol), and NMP (0.25 mL) in THF (5 mL) was added PhCH₂MgCl (0.8 M in Et₂O, 2.5 mL, 2.0 mmol) at 0 °C over 10 min, and the mixture was stirred for 0.5 h.¹⁰ Aqueous NH₄Cl was added, and the mixture was extracted with Et₂O. The organic layer was dried over MgSO₄, filtered, and concentrated on a rotary evaporator. The residue was subjected to column chromatography on silica gel with hexane to give Bn-tfb* (**1d**) (154 mg, 0.38 mmol, 76%).



Compound 1e: A mixture of **2** (261 mg, 0.50 mmol), PhB(OH)₂ (244 mg, 2.00 mmol), PdCl₂(IPr)(3-chloropyridine)¹¹ (13.6 mg, 0.020 mmol), and K₂CO₃ (346 mg, 2.50 mmol) in dioxane (2 mL) was heated at 60 °C for 8 h. The mixture was passed through a short silica gel column with Et₂O/hexane (1/1), and it was concentrated on a rotary evaporator. The residue was subjected to column chromatography on silica gel with hexane to give Ph-tfb* (**1e**) (177 mg, 0.47 mmol, 94%). ¹H NMR (CDCl₃) δ 5.76 (d, *J* = 6.1 Hz, 2H), 7.03 (dd, *J* = 6.1, 2.0 Hz, 2H), 7.25–7.30 (m, 2H), 7.33–7.38 (m, 4H), 7.41–7.46 (m, 4H); ¹³C NMR (CDCl₃) δ 44.2 (2C), 124.7 (4C), 128.1 (2C), 128.8 (4C), 129.3–129.8 (m, 2C), 132.8 (2C), 136.0 (2C), 136.3–142.9 (m, 4C), 153.3 (2C). HRMS (APCI-TOF) calcd for C₂₄H₁₄F₄ (M⁺) 378.1026, found 378.1016. [α]²⁰_D +12 (*c* 1.18, CHCl₃) for (*R,R*)-**1e**.

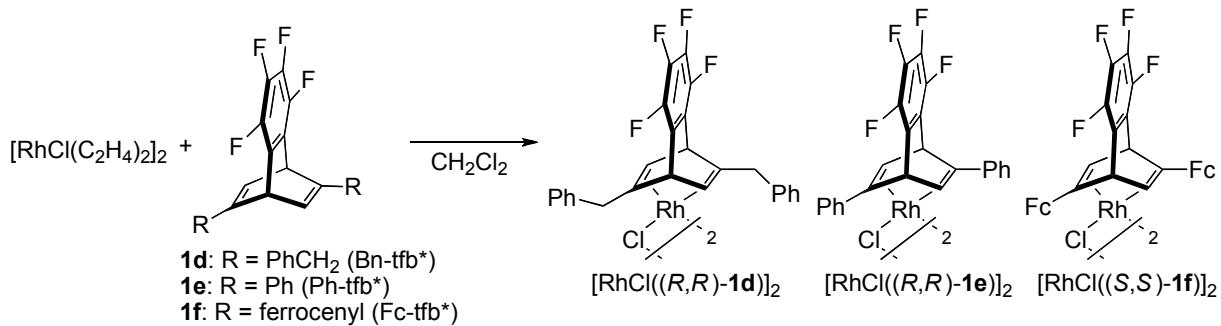
(10) (a) B. Scheiper, M. Bonnekessel, H. Krause and A. Fürstner, *J. Org. Chem.*, 2004, **69**, 3943. (b) G. Berthon-Gelloz and T. Hayashi, *J. Org. Chem.*, 2006, **71**, 8957.

(11) C. J. O'Brien, E. A. B. Kantchev, C. Valente, N. Hadei, G. A. Chass, A. Lough, A. C. Hopkinson and M. G. Organ, *Chem. –Eur. J.*, 2006, **12**, 4743.



Compound 1f: To a solution of ferrocene (3.57 g, 19.2 mmol) in THF (20 mL) was slowly added *t*-BuLi (1.77 M in pentane, 9.5 mL, 16.8 mmol) at -50 °C, and the mixture was allowed to warm to room temperature, and it was stirred for 2 h.¹² To the mixture was added ZnCl₂ (2.29 g, 16.8 mmol) in THF (10 mL), and the mixture was stirred at room temperature for 0.5 h. After the mixture was concentrated to ca. 30 mL under the flow of dry N₂, Pd(PPh₃)₄ (231 mg, 0.21 mmol) and ditriflate **2** (1.05 g, 2.01 mmol) in THF (5 mL) were added, and the mixture was stirred at 50 °C for 15 h. The mixture was poured into aqueous NH₄Cl, and it was extracted with Et₂O. The organic layer was dried over MgSO₄, filtered, and concentrated on a rotary evaporator. The crude product was subjected to column chromatography on silica gel with hexane/ethyl acetate (19/1) and further purified by GPC with chloroform to give Fc-tfb* (**1f**) (1.04 g, 1.76 mmol, 88%) as a red solid. ¹H NMR (CDCl₃) δ 4.10 (s, 10H), 4.30 (s, 4H), 4.42 (s, 4H), 5.33 (d, *J* = 5.6 Hz, 2H), 6.64 (d, *J* = 5.6 Hz, 2H); ¹³C NMR (CDCl₃) δ 44.1 (2C), 65.3 (2C), 65.5 (2C), 68.7 (10C), 69.4 (2C), 69.5 (2C), 81.2 (2C), 126.7 (2C), 129.3–129.6 (m, 2C), 136.3–142.5 (m, 4C), 151.4 (2C). HRMS (ESI-TOF) calcd for C₃₂H₂₂F₄Fe (M⁺) 594.0352, found 594.0351. [α]²⁰_D +173 (c 0.50, CHCl₃) for (S,S)-**1f**.

Preparation of rhodium/chiral diene complexes



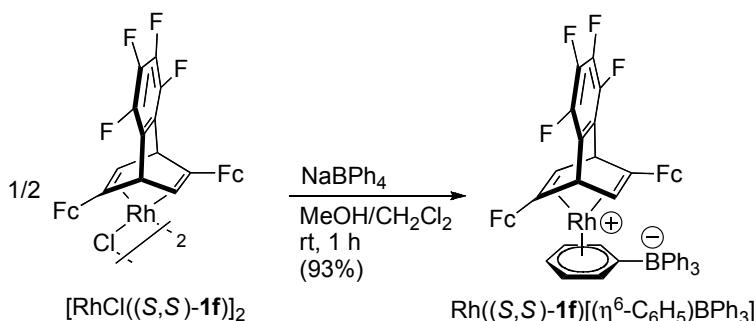
[RhCl((R,R)-1d)]₂: A mixture of (*R,R*)-Bn-tfb* (**1d**) (103 mg, 0.25 mmol) and [RhCl(C₂H₄)₂]₂ (54 mg, 0.14 mmol, 0.28 mmol of Rh) in CH₂Cl₂ (5 mL) was stirred at room temperature for 12 h. After concentration of the mixture, the residue was subjected to column chromatography on silica gel with hexane/ethyl acetate (9/1) to give the pure complex as a yellow solid (134 mg, 0.12 mmol, 98% yield). ¹H NMR (CDCl₃) δ 2.84 (d, *J* = 14.3 Hz, 4H), 3.58 (d, *J* = 14.3 Hz, 4H), 3.62 (d, *J* = 5.8 Hz, 4H), 5.32 (d, *J* = 5.8 Hz, 4H), 7.08–7.22 (m, 20H); ¹³C NMR

(12) M. Enders, G. Kohl and H. Pritzkow, *J. Organomet. Chem.*, 2001, **622**, 66.

(CDCl₃) δ 41.7 (4C), 44.8 (d, *J*_{F-C} = 3.1 Hz, 4C), 49.4 (d, *J*_{Rh-C} = 11.4 Hz, 4C), 69.7 (d, *J*_{Rh-C} = 12.4 Hz, 4C), 125.2–125.6 (m, 4C), 126.8 (4C), 128.5 (8C), 128.9 (8C), 136.1 (4C), 136.9–140.2 (m, 8C). HRMS (ESI-TOF) calcd for C₅₂H₃₆Cl₃F₈Rh₂ (M+Cl⁻) 1122.9870, found 1122.9841. [α]²⁰_D +78 (*c* 0.26, CHCl₃) for [RhCl((*R,R*)-**1d**)₂].

[RhCl((*R,R*)-1e**)₂]:** This compound was prepared by the reaction of (*R,R*)-Ph-tfb* (**1e**) (93 mg, 0.25 mmol) with [RhCl(C₂H₄)₂]₂ (53 mg, 0.14 mmol, 0.28 mmol of Rh) in CH₂Cl₂ (5 mL) at room temperature for 12 h. The crude product was purified by column chromatography on silica gel with CHCl₃/ethyl acetate (19/1) to give the pure complex (121 mg, 0.12 mmol, 95% yield) as a orange solid. ¹H NMR (CDCl₃) δ 3.59 (d, *J* = 6.1 Hz, 4H), 6.10 (d, *J* = 6.1 Hz, 4H), 7.35–7.42 (m, 12H), 7.54–7.60 (m, 8H); ¹³C NMR (CDCl₃) δ 42.7 (d, *J*_{F-C} = 3.6 Hz, 4C), 43.4 (d, *J*_{Rh-C} = 11.4 Hz, 4C), 65.7 (d, *J*_{Rh-C} = 10.9 Hz, 4C), 125.6–126.9 (m, 4C), 127.2 (8C), 128.5 (4C), 128.7 (8C), 136.9 (4C), 137.8–141.2 (m, 8C). HRMS (ESI-TOF) calcd for C₄₈H₂₈Cl₂F₈NaRh₂ (M+Na⁺) 1054.9443, found 1054.9399. [α]²⁰_D –1118 (*c* 0.13, CHCl₃) for [RhCl((*R,R*)-**1e**)₂].

[RhCl((*S,S*)-1f**)₂]:** This compound was prepared by the reaction of (*S,S*)-Fc-tfb* (**1f**) (297 mg, 0.50 mmol) with [RhCl(C₂H₄)₂]₂ (107 mg, 0.28 mmol, 0.55 mmol of Rh) in CH₂Cl₂ (10 mL) at room temperature for 12 h. The crude product was purified by column chromatography on silica gel with CHCl₃/ethyl acetate (19/1) to give the pure complex (352 mg, 0.24 mmol, 96%) as a red solid. ¹H NMR (CDCl₃) δ 3.13 (d, *J* = 5.7 Hz, 4H), 3.89 (s, 20H), 4.08 (br s, 4H), 4.27 (br s, 4H), 4.45 (br s, 4H), 4.79 (br s, 4H), 5.61 (d, *J* = 5.7 Hz, 4H); ¹³C NMR (CDCl₃) δ 39.9 (d, *J*_{Rh-C} = 11.4 Hz, 4C), 43.5 (4C), 65.5 (d, *J*_{Rh-C} = 10.3 Hz, 4C), 67.8 (4C), 68.3 (4C), 69.4 (20C), 69.9 (4C), 70.2 (4C), 83.0 (br, 4C), 125.5–126.0 (m, 4C), 137.6–141.0 (m, 8C). HRMS (ESI-TOF) calcd for C₆₄H₄₄Cl₃F₈Fe₄Rh₂ (M+Cl⁻) 1498.7903, found 1498.7956. [α]²⁰_D –831 (*c* 0.048, CHCl₃) for [RhCl((*S,S*)-**1f**)₂].



Rh((*S,S*)-1f**)[(η⁶-C₆H₅)BPh₃]:** To a solution of [RhCl((*S,S*)-**1f**)₂] (29.3 mg, 0.020 mmol) in CH₂Cl₂ (1.0 mL) was added a solution of NaBPh₄ (16.4 mg, 0.048 mmol) in MeOH (1 mL). The mixture was stirred at room temperature for 1 h, and the solvent was removed under

vacuum. The residue was triturated with MeOH, and the mixture was filtered. The resulting solid was washed with MeOH and dried under vacuum to give the complex Rh((S,S)-**1f**) $[(\eta^6\text{-C}_6\text{H}_5)\text{BPh}_3]$ (38.0 mg, 0.037 mmol, 93%). ^1H NMR (CD_2Cl_2) δ 3.23 (br s, 2H), 3.62 (s, 10 H), 3.72 (br s, 2H), 4.20 (br s, 2H), 4.34 (br s, 2H), 4.68 (br s, 2H), 5.02 (t, J = 6.3 Hz, 1H), 5.25 (d, J = 6.1 Hz, 2H), 5.62 (br s, 2H), 6.33 (d, J = 6.3 Hz, 1H), 6.88 (br s, 1H), 7.07 (t, J = 7.3 Hz, 3H), 7.21 (t, J = 7.3 Hz, 6H), 7.37 (d, J = 7.3 Hz, 6H). HRMS (ESI-TOF) calcd for $\text{C}_{56}\text{H}_{42}\text{BF}_4\text{Fe}_2\text{NaRh}$ ($\text{M}+\text{Na}^+$) 1039.0973, found 1039.0963. $[\alpha]^{20}_D$ -92 (c 0.12, CHCl_3). Orange crystals of Rh((S,S)-**1f**) $[(\eta^6\text{-C}_6\text{H}_5)\text{BPh}_3]$ suitable for X-ray crystallographic analysis were obtained by recrystallization from CH_2Cl_2 /MeOH. The ORTEP drawing of Rh((S,S)-**1f**) $[(\eta^6\text{-C}_6\text{H}_5)\text{BPh}_3]$ is shown in Figure S1. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC734763). The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif. The crystal data are summarized in Tables S1–S3.

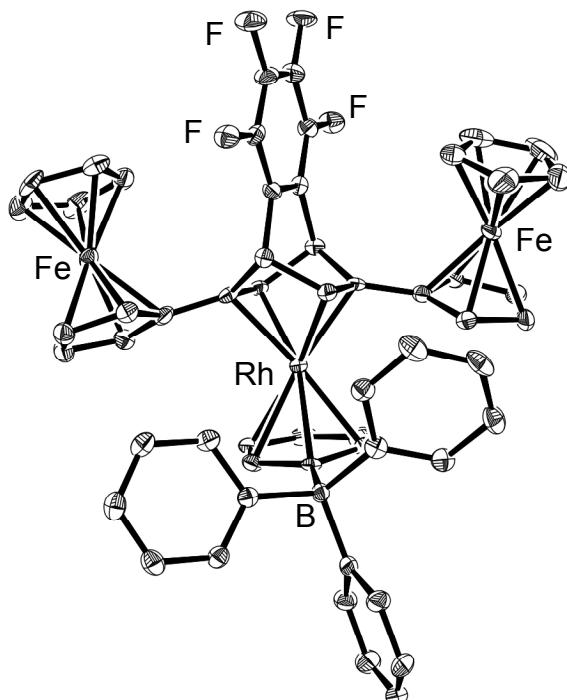


Figure S1. ORTEP illustration of Rh((S,S)-**1f**) $[(\eta^6\text{-C}_6\text{H}_5)\text{BPh}_3]$ with thermal ellipsoids drawn at 50% probability level. The solvent molecule (CH_2Cl_2) and hydrogens are omitted for clarity. Crystal data for Rh((S,S)-**1f**) $[(\eta^6\text{-C}_6\text{H}_5)\text{BPh}_3]\cdot(\text{CH}_2\text{Cl}_2)$: $\text{C}_{57}\text{H}_{44}\text{BCl}_2\text{F}_4\text{Fe}_2\text{Rh}$, M_w = 1101.28, space group $\text{P}2_1$ (#4), a = 11.067(4) Å, b = 9.614(2) Å, c = 22.413(6) Å, β = 104.655(12) $^\circ$, V = 2307.2(11) Å³, Z = 2, D_{calcd} = 1.585 g/cm³, T = 123 K, R = 0.0429 ($I > 2.00\sigma(I)$), wR_2 = 0.1089, GOF = 1.056, Flack Parameter = -0.009(16), 22685 reflections measured, 10496 unique ($R_{\text{int}} = 0.048$).

The structure was solved by direct methods¹³ and expanded using Fourier techniques.¹⁴ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F² was based on 10496 observed reflections and 605 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of: R₁ = 0.0429, wR₂ = 0.1089.

The standard deviation of an observation of unit weight was 1.06. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 2.34 and -1.14 e⁻/Å³, respectively. The absolute structure was deduced based on Flack parameter, -0.009(16), using 4903 Friedel pairs.¹⁵

Neutral atom scattering factors were taken from Cromer and Waber.¹⁶ Anomalous dispersion effects were included in F_{calc};¹⁷ the values for Δf' and Δf'' were those of Creagh and McAuley.¹⁸ The values for the mass attenuation coefficients are those of Creagh and Hubbell.¹⁹ All calculations were performed using the CrystalStructure²⁰ crystallographic software package except for refinement, which was performed using SHELXL-97.²¹

Table S1. Crystal data of Rh((S,S)-**1f**)[(η⁶-C₆H₅)BPh₃]

Empirical Formula	C ₅₇ H ₄₄ BF ₄ Fe ₂ RhCl ₂
Formula Weight	1101.28
Crystal Color, Habit	orange, prism
Crystal Dimensions	0.30 × 0.15 × 0.05 mm
Crystal System	monoclinic
Lattice Type	Primitive
Indexing Images	3 oscillations at 60.0 seconds
Detector Position	127.40 mm
Pixel Size	0.100 mm
Lattice Parameters	a = 11.067(4) Å b = 9.614(2) Å c = 22.413(6) Å b = 104.655(12) ° V = 2307.2(11) Å ³
Space Group	P2 ₁ (#4)

13 SIR2004: M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori and R. Spagna (2005).

14 DIRDIF99: P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel and J. M. M. Smits, (1999). The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

15 H. D. Flack, *Acta Cryst.*, 1983, **A39**, 876.

16 D. T. Cromer and J. T. Waber, "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

17 J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 1964, **17**, 781.

18 D. C. Creagh and W. J. McAuley, "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219 (1992).

19 D. C. Creagh and J. H. Hubbell, "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200 (1992).

20 CrystalStructure 3.8: Crystal Structure Analysis Package, Rigaku and Rigaku Americas (2000-2007).

21 SHELX97: G. M. Sheldrick (1997).

Z value	2
D _{calc}	1.585 g/cm ³
F ₀₀₀	1116.00
μ(MoKa)	11.445 cm ⁻¹

Table S2. Intensity measurements

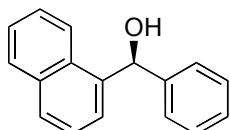
Diffractometer	Rigaku RAXIS-RAPID
Radiation	MoKα ($\lambda = 0.71075 \text{ \AA}$)
Detector Aperture	graphite monochromated
Data Images	280 mm × 256 mm
ω oscillation Range ($\chi=45.0, \phi=0.0$)	44 exposures
Exposure Rate	130.0–190.0°
ω oscillation Range ($\chi=45.0, \phi=180.0$)	360.0 sec./°
Exposure Rate	0.0–160.0°
Detector Position	360.0 sec./°
Pixel Size	127.40 mm
2θ _{max}	0.100 mm
No. of Reflections Measured	55.0°
Corrections	Total: 22685
	Unique: 10496 ($R_{\text{int}} = 0.041$)
	Friedel pairs: 4903
	Lorentz-polarization
	Absorption
	(trans. factors: 0.482–0.944)

Table S3. Structure solution and refinement

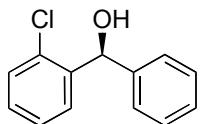
Structure Solution	Direct Methods
Refinement	Full-matrix least-squares on F ²
Function Minimized	$\Sigma w (Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1 / [\sigma^2(Fo^2) + (0.0532 \cdot P)^2 + 2.7630 \cdot P]$ where P = (Max(Fo ² , 0) + 2Fc ²)/3
2θ _{max} cutoff	55.0°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	10496
No. Variables	605
Reflection/Parameter Ratio	17.35
Residuals: R (All reflections)	0.0471
Residuals: R ₁ ($I > 2.00\sigma(I)$)	0.0429
Residuals: wR ₂ (All reflections)	0.1089
Goodness of Fit Indicator	1.056
Flack Parameter (Friedel pairs = 4903)	-0.009(16)
Max Shift/Error in Final Cycle	0.002
Maximum peak in Final Diff. Map	2.34 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-1.14 e ⁻ /Å ³

A typical procedure for rhodium-catalyzed asymmetric phenylation of aldehyde 1a

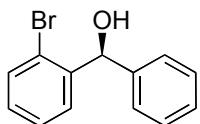
(Table 2, entry 1). To a mixture of $[\text{RhCl}((S,S)\text{-Fc-tfb}^*(\mathbf{1f})]_2$ (1.8 mg, 1.75 μmol , 2.5 μmol of Rh), phenylboronic acid (**6m**) (61.0 mg, 0.50 mmol), powdered KOH (25 mg, 0.38 mmol, assay; 85%, pellets) was added *tert*-butyl alcohol (1 mL), and the mixture was stirred at room temperature for 2 min. 1-Naphthaldehyde (**5a**) (39.0 mg, 0.25 mmol) was added to the mixture, and it was stirred at 30 °C for 3 h. The mixture was diluted with hexane, and it was passed through a short column of silica gel with Et₂O as eluent. After evaporation of the solvent, the residue was subjected to column chromatography on silica gel (hexane/ethyl acetate, 9/1) to give compound **7am** (55.6 mg, 0.24 mmol, 95%). The absolute configurations of known diarylmethanols **7** produced by use of $(S,S)\text{-Fc-tfb}^*(\mathbf{1f})$ were determined by comparison of its specific rotation and the retention time of the chiral HPLC analysis with those reported previously. For others, they were assigned by consideration of the stereochemical pathway.



Compound 7am (86% ee, *(S)*; [1517-61-9] for *(S)*-**7am**):²² The ee was measured by HPLC (Chiralcel OD-H column, flow 0.8 mL/min, hexane/2-propanol = 4/1, 224 nm, $t_1 = 11.1$ min (*S*), $t_2 = 21.6$ min (*R*)).



Compound 7bm (84% ee (*S*); [16071-25-3] for *(S)*-**7bm**):²³ The ee was measured by HPLC (Chiralcel OD-H column, flow 0.8 mL/min, hexane/2-propanol = 19/1, 224 nm, $t_1 = 16.5$ min (*R*), $t_2 = 20.2$ min (*S*)).

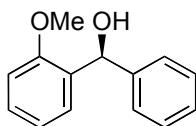


Compound 7cm (84% ee (*S*); [143880-86-8] for *(S)*-**7cm**):²⁴ The ee was measured by HPLC (Chiralcel OD-H column, flow 1.0 mL/min, hexane/2-propanol = 9/1, 224 nm, $t_1 = 9.2$ min (*R*), $t_2 = 12.1$ min (*S*)).

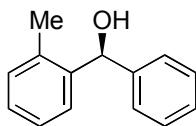
(22) H.-F. Duan, J.-H. Xie, W.-J. Shi, Q. Zhang and Q.-L. Zhou, *Org. Lett.* 2006, **8**, 1479.

(23) X. Wu, X. Liu and G. Zhao, *Tetrahedron: Asymmetry*, 2005, **70**, 1093.

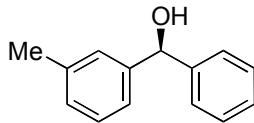
(24) J.-X. Ji, J. Wu, T. T.-L. Au-Yeung, C.-W. Yip, R. K. Haynes and A. S. C. Chan, *J. Org. Chem.*, 2005, **70**, 1093.



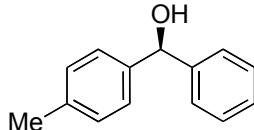
Compound 7dm (85% ee (*S*); [123436-08-8] for (*S*)-**7dm**):²⁵ The ee was measured by HPLC (Chiralcel OD-H column, flow 1.0 mL/min, hexane/2-propanol = 9/1, 224 nm, t_1 = 20.5 min (*S*), t_2 = 23.6 min (*R*)).



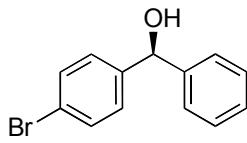
Compound 7em (86% ee (*S*); [1517-59-5] for (*S*)-**7em**):²⁶ The ee was measured by HPLC (Chiralcel OB-H column, flow 1.0 mL/min, hexane/2-propanol = 19/1, 224 nm, t_1 = 20.3 min (*R*), t_2 = 24.1 min (*S*)).



Compound 7fm (80% ee (*S*); [137474-27-2] for (*S*)-**7fm**):¹⁷ The ee was measured by HPLC (Chiralcel OB-H column, flow 1.0 mL/min, hexane/2-propanol = 9/1, 224 nm, t_1 = 16.8 min (*R*), t_2 = 30.6 min (*S*)).



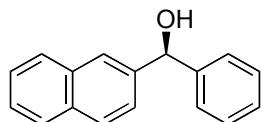
Compound 7gm (78% ee (*S*); [24218-12-0] for (*S*)-**7gm**):¹⁵ The ee was measured by HPLC (Chiralcel OB-H column, flow 1.0 mL/min, hexane/2-propanol = 9/1, 224 nm, t_1 = 12.2 min (*R*), t_2 = 14.3 min (*S*)).



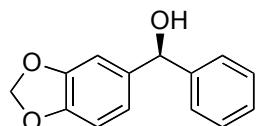
Compound 7hm (78% ee (*S*); [73773-07-6] for (*S*)-**7hm**):¹⁷ The ee was measured by HPLC (Chiralcel OB-H column, flow 1.0 mL/min, hexane/2-propanol = 9/1, 224 nm, t_1 = 16.5 min (*R*), t_2 = 23.1 min (*S*)).

(25) M.-C. Wang, X.-D. Wang, X. Ding, Z.-K. Liu, *Tetrahedron*, 2008, **64**, 2559.

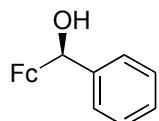
(26) J. Shannon, D. Bernier, D. Rawson and S. Woodward, *Chem. Commun.*, 2007, 3945.



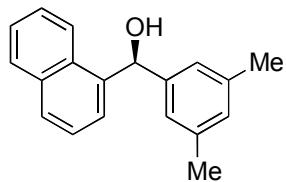
Compound 7im (82% ee (*S*); [99412-45-0] for (*S*)-**7im**):¹⁴ The ee was measured by HPLC (Chiralcel OD-H column, flow 1.0 mL/min, hexane/2-propanol = 9/1, 224 nm, t_1 = 15.4 min (*S*), t_2 = 18.3 min (*R*)).



Compound 7jm (79% ee (*S*); [929214-02-8] for (*S*)-**7jm**):¹⁶ The ee was measured by HPLC (Chiralcel OB-H column, flow 0.8 mL/min, hexane/2-propanol = 4/1, 224 nm, t_1 = 31.7 min (*R*), t_2 = 45.7 min (*S*)).

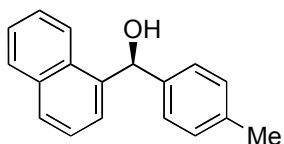


Compound 7km (85% ee (*S*); [57884-64-7] for (*R*)-**7km**):²⁷ The ee was measured by HPLC (Chiralcel OD-H column, flow 1.0 mL/min, hexane/2-propanol = 9/1, 224 nm, t_1 = 11.2 min (*R*), t_2 = 17.0 min (*S*)).

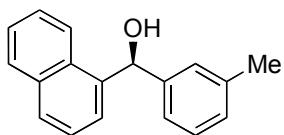


Compound 7an: The ee was measured by HPLC (Chiralcel OD-H column, flow 0.8 mL/min, hexane/2-propanol = 9/1, 224 nm, t_1 = 14.1 min (*S*), t_2 = 28.3 min (*R*)). $[\alpha]^{20}_D +34$ (*c* 1.81, CHCl_3) for (*S*)-**7an** (87% ee). ^1H NMR (CDCl_3) δ 2.24 (s, 6H), 2.39 (br d, J = 2.6 Hz, 1H), 6.39 (d, J = 2.6 Hz, 1H), 6.88 (s, 1H), 6.98 (s, 2H), 7.36–7.47 (m, 3H), 7.61 (d, J = 7.1 Hz, 1H), 7.77 (d, J = 8.3 Hz, 1H), 7.80–7.86 (m, 1H), 7.97–8.02 (m, 1H); ^{13}C NMR (CDCl_3) δ 21.3, 73.5, 123.9, 124.4, 124.8, 125.3, 125.5, 1260, 128.2, 128.7, 129.3, 130.7, 133.8, 138.0, 138.9, 143.1. HRMS (ESI-TOF) calcd for $\text{C}_{19}\text{H}_{18}\text{NaO} (\text{M}+\text{Na}^+)$ 285.1250, found 281.1256.

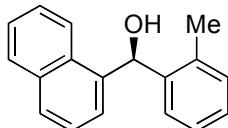
(27) R. J. Kloetzing, M. Lotz and P. Knochel, *Tetrahedron: Asymmetry*, 2003, **14**, 255.



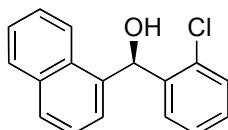
Compound 7ao (85% ee (*S*); [1002328-13-3] for (*S*)-7ao):²⁸ The ee was measured by HPLC (Chiralcel OD-H column, flow 1.0 mL/min, hexane/2-propanol = 4/1, 224 nm, t_1 = 8.1 min (*S*), t_2 = 16.6 min (*R*)).



Compound 7ap: The ee was measured by HPLC (Chiralcel OD-H column, flow 1.0 mL/min, hexane/2-propanol = 9/1, 224 nm, t_1 = 13.5 min (*S*), t_2 = 28.7 min (*R*)). $[\alpha]^{20}_D -34$ (*c* 1.81, CHCl₃) for (*S*)-7ap (87% ee). ¹H NMR (CDCl₃) δ 2.27 (s, 3H), 2.47 (br s, 1H), 6.40 (s, 1H), 7.04 (d, *J* = 7.2 Hz, 1H), 7.10–7.20 (m, 3H), 7.35–7.46 (m, 3H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (CDCl₃) δ 21.4, 73.5, 123.9, 124.1, 124.5, 125.3, 125.5, 126.0, 127.7, 128.31, 128.34, 128.4, 128.7, 130.7, 133.8, 138.1, 138.8, 143.0. HRMS (ESI-TOF) calcd for C₁₈H₁₆NaO (M+Na⁺) 271.1093, found 271.1090.

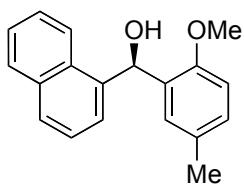


Compound 7aq (91% ee (*S*); [186407-92-1] for (*S*)-7aq):²⁹ The ee was measured by HPLC (Chiralcel OD-H column, flow 1.0 mL/min, hexane/2-propanol = 9/1, 224 nm, t_1 = 14.0 min (*S*), t_2 = 24.0 min (*R*)).

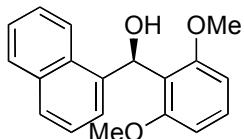


Compound 7ar (86% ee (*R*); [42074-40-8] for *rac*-7ar): The ee was measured by HPLC (Chiralcel OF column, flow 0.8 mL/min, hexane/2-propanol = 9/1, 224 nm, t_1 = 14.1 min (*S*), t_2 = 16.1 min (*R*)). $[\alpha]^{20}_D +30$ (*c* 1.40, CHCl₃) for (*R*)-7ar (86% ee).

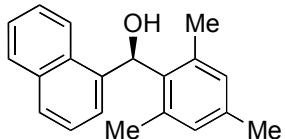
(28) F. Schmidt, J. Rudolph and C. Bolm, *Adv. Synth. Catal.*, 2007, **349**, 703.
(29) N. M. Maier and G. Uray, *Chirality*, 1996, **8**, 496.



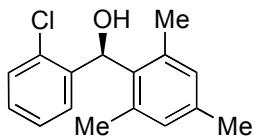
Compound 7as: The ee was measured by HPLC (Chiralcel OD-H column, flow 0.8 mL/min, hexane/2-propanol = 9/1, 224 nm, t_1 = 13.8 min (*R*), t_2 = 20.5 min (*S*)). $[\alpha]^{20}_D -15$ (*c* 0.42, CHCl₃) for (*R*)-7as (85% ee). ¹H NMR (CDCl₃) δ 2.12 (s, 3H), 3.01 (br s, 1H), 3.87 (s, 3H), 6.79 (d, *J* = 2.2 Hz, 1H), 6.83 (s, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 7.04 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.39–7.47 (m, 2H), 7.48 (d, *J* = 7.3 Hz, 1H), 7.64 (d, *J* = 7.1 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.82–7.88 (m, 1H), 7.98–8.04 (m, 1H); ¹³C NMR (CDCl₃) δ 20.5, 55.6, 68.3, 110.5, 124.15, 124.18, 125.3, 125.4, 125.9, 128.0, 128.6, 128.9, 129.2, 130.0, 130.96, 131.00, 133.7, 138.2, 154.8. HRMS (ESI-TOF) calcd for C₁₉H₁₈NaO₂ (M+Na⁺) 301.1199, found 301.1189.



Compound 7at: The ee was measured by HPLC (Chiraldak IA column, flow 0.8 mL/min, hexane/2-propanol = 4/1, 224 nm, t_1 = 10.0 min (*S*), t_2 = 13.1 min (*R*)). $[\alpha]^{20}_D -102$ (*c* 0.93, CHCl₃) for (*R*)-7at (84% ee). ¹H NMR (CDCl₃) δ 3.79 (s, 6H), 4.55 (d, *J* = 11.6 Hz, 1H), 6.69 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 11.6 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 1H), 7.28–7.35 (m, 2H), 7.52 (t, *J* = 7.0 Hz, 1H), 7.61 (dd, *J* = 7.0, 1.2 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 8.63 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (CDCl₃) δ 55.7, 67.0, 104.5, 117.8, 124.0, 124.9, 125.3, 125.4, 125.9, 128.1, 128.4, 129.0, 132.1, 134.0, 138.4, 158.2. HRMS (ESI-TOF) calcd for C₁₉H₁₈NaO₃ (M+Na⁺) 317.1148, found 317.1149.

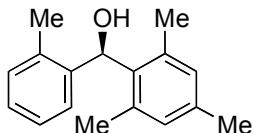


Compound 7au (94% ee (*R*); [186407-89-6] for (*R*)-7au):²⁰ The ee was measured by HPLC (Chiraldak AD-H column \times 2, flow 0.5 mL/min, hexane/2-propanol = 19/1, 224 nm, t_1 = 50.2 min (*S*), t_2 = 53.6 min (*R*)).

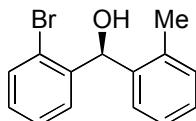


Compound 7bu: The ee was measured by HPLC (Chiralcel OD-H column, flow 0.8 mL/min,

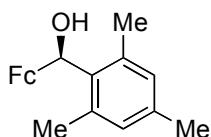
hexane/2-propanol = 9/1, 224 nm, t_1 = 7.5 min (*S*), t_2 = 9.1 min (*R*). $[\alpha]^{20}_D$ +42 (*c* 0.96, CHCl₃) for (*S*)-**7bu** (94% ee). ¹H NMR (CDCl₃) δ 2.23 (s, 6H), 2.26 (s, 3H), 2.43 (br s, 1H), 6.34 (s, 1H), 6.83 (s, 2H), 7.16–7.24 (m, 2H), 7.30–7.36 (m, 1H), 7.42–7.47 (m, 1H); ¹³C NMR (CDCl₃) δ 20.8, 21.0, 70.4, 126.4, 128.5, 129.0, 129.7, 130.1, 133.0, 134.0, 137.1, 137.3, 139.9. HRMS (ESI-TOF) calcd for C₁₆H₁₇ClNaO (M+Na⁺) 283.0860, found 283.0860.



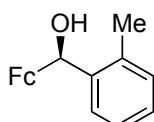
Compound 7eu: The ee was measured by HPLC (Chiralcel OD-H column, flow 0.8 mL/min, hexane/2-propanol = 4/1, 224 nm, t_1 = 7.4 min (*R*), t_2 = 9.8 min (*S*)). $[\alpha]^{20}_D$ +28 (*c* 0.99, CHCl₃) for (*R*)-**7eu** (93% ee). ¹H NMR (CDCl₃) δ 1.97 (br s, 1H), 2.19 (s, 3H), 2.20 (s, 6H), 2.26 (s, 3H), 6.23 (s, 1H), 6.83 (s, 2H), 7.09–7.18 (m, 3H), 7.33–7.36 (m, 1H); ¹³C NMR (CDCl₃) δ 19.5, 20.8, 21.0, 70.9, 125.5, 126.8, 127.2, 130.2, 130.6, 135.2, 136.1, 136.9, 137.1, 140.2. HRMS (ESI-TOF) calcd for C₁₇H₂₀NaO (M+Na⁺) 263.1406, found 263.1407.



Compound 7cq (86% ee (*S*); [1029874-77-8] for *rac*-**7cq**): The ee was measured by HPLC (Chiralcel OD-H column, flow 0.8 mL/min, hexane/2-propanol = 9/1, 224 nm, t_1 = 13.9 min (*R*), t_2 = 34.3 min (*S*)). $[\alpha]^{20}_D$ -11 (*c* 2.10, CHCl₃) for (*S*)-**7cq** (86% ee).



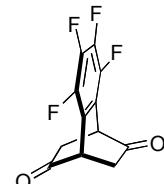
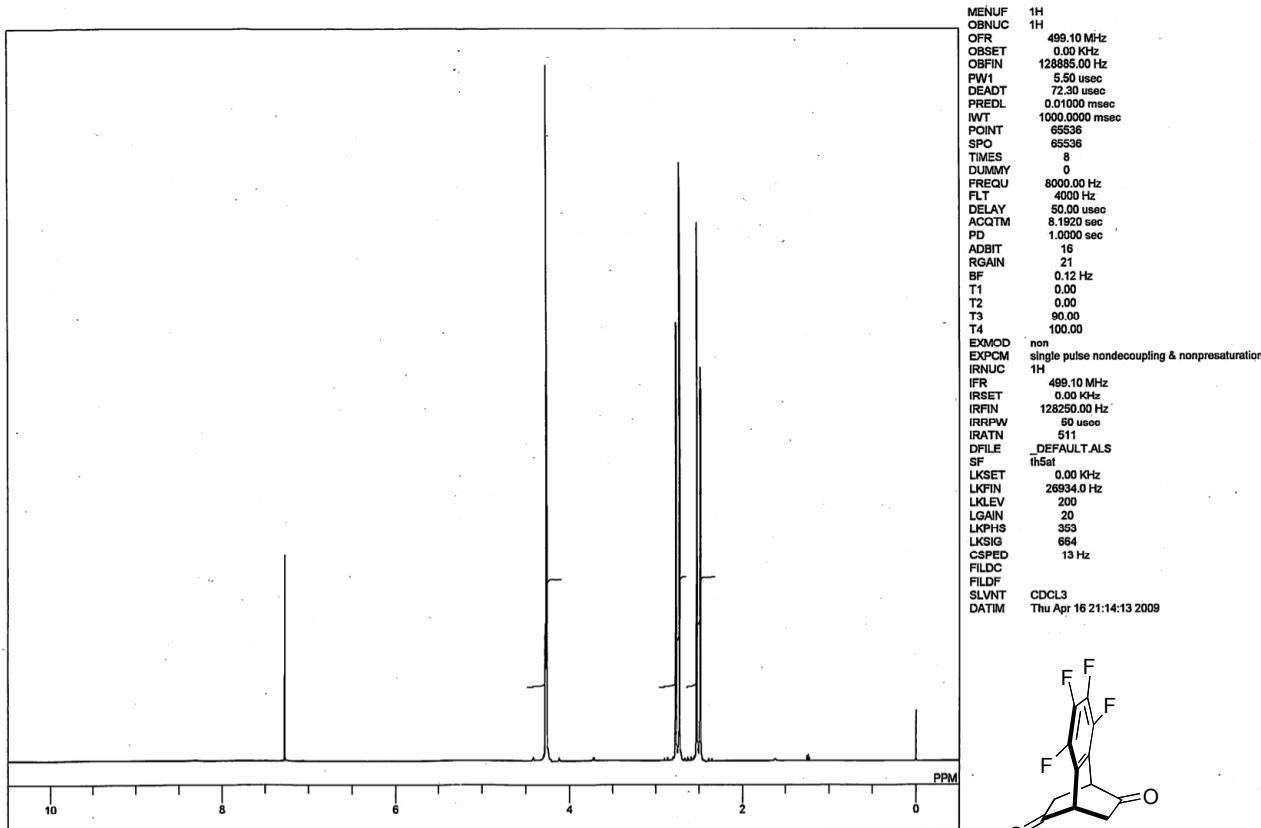
Compound 7ku (84% ee (*S*); [118034-73-4] for *rac*-**7ku**): The ee was measured by HPLC (Chiralcel OD-H column, flow 0.8 mL/min, hexane/2-propanol = 9/1, 224 nm, t_1 = 14.8 min (*S*), t_2 = 20.3 min (*R*)). $[\alpha]^{20}_D$ -172 (*c* 2.26, CHCl₃) for (*S*)-**7ku** (84% ee).



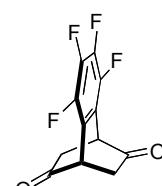
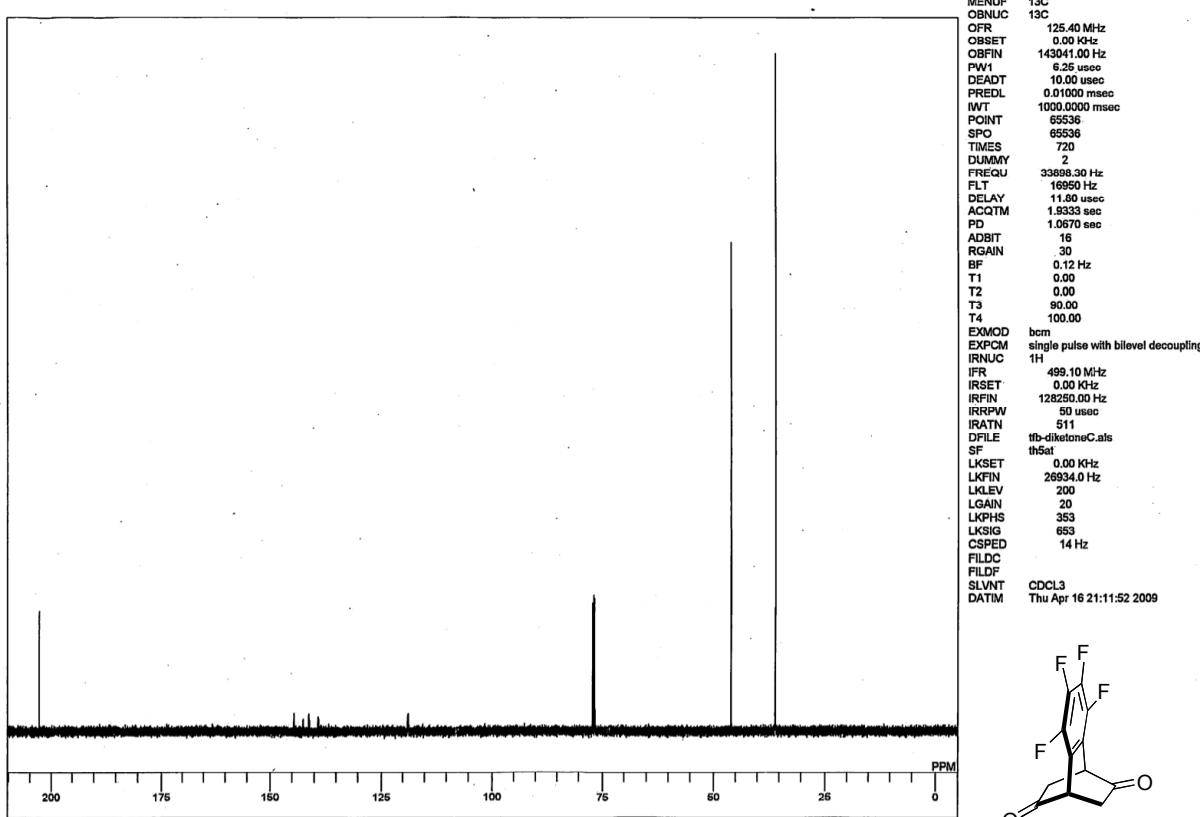
Compound 7kq (86% ee (*S*); [221527-96-4] for (*R*)-**7kq**):¹⁸ The ee was measured by HPLC (Chiralcel OD-H column, flow 0.5 mL/min, hexane/2-propanol = 19/1, 224 nm, t_1 = 25.0 min (*R*), t_2 = 26.9 min (*S*)).

A procedure for rhodium-catalyzed asymmetric double arylation of isophthalaldehyde (8) (Scheme 4).

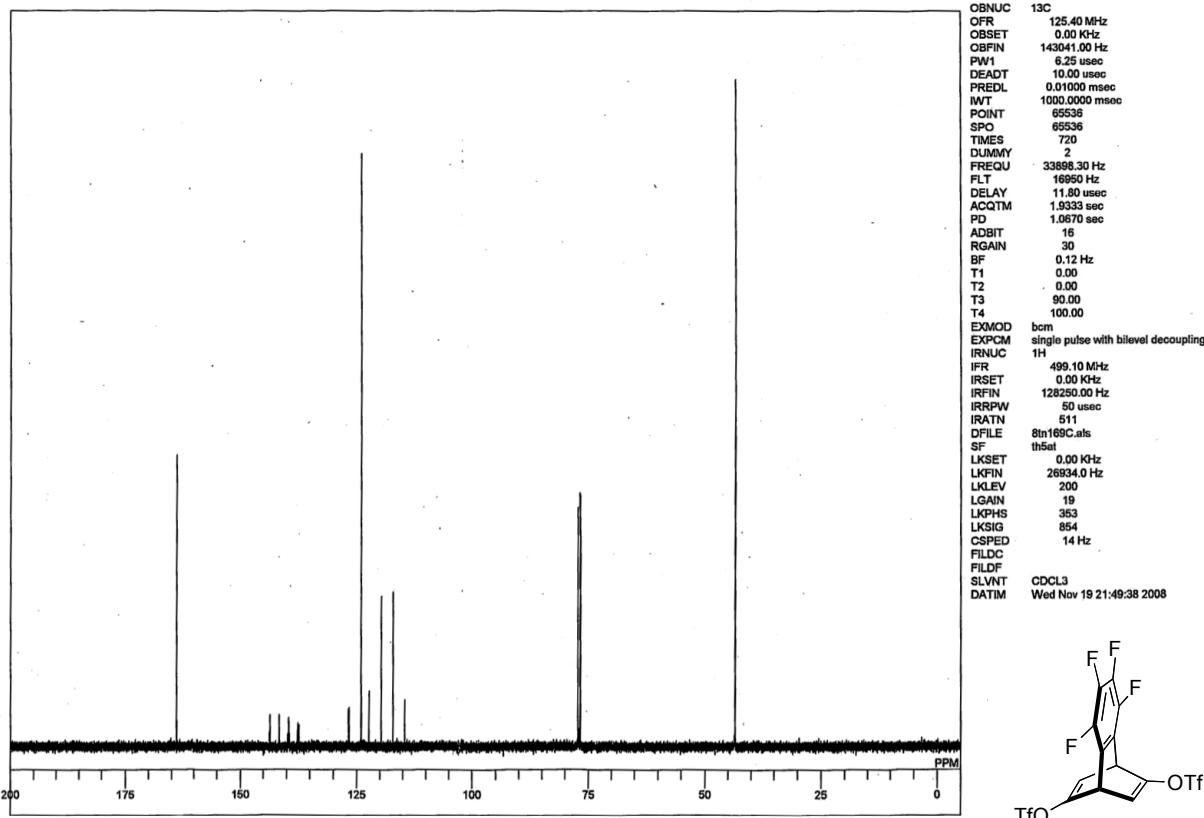
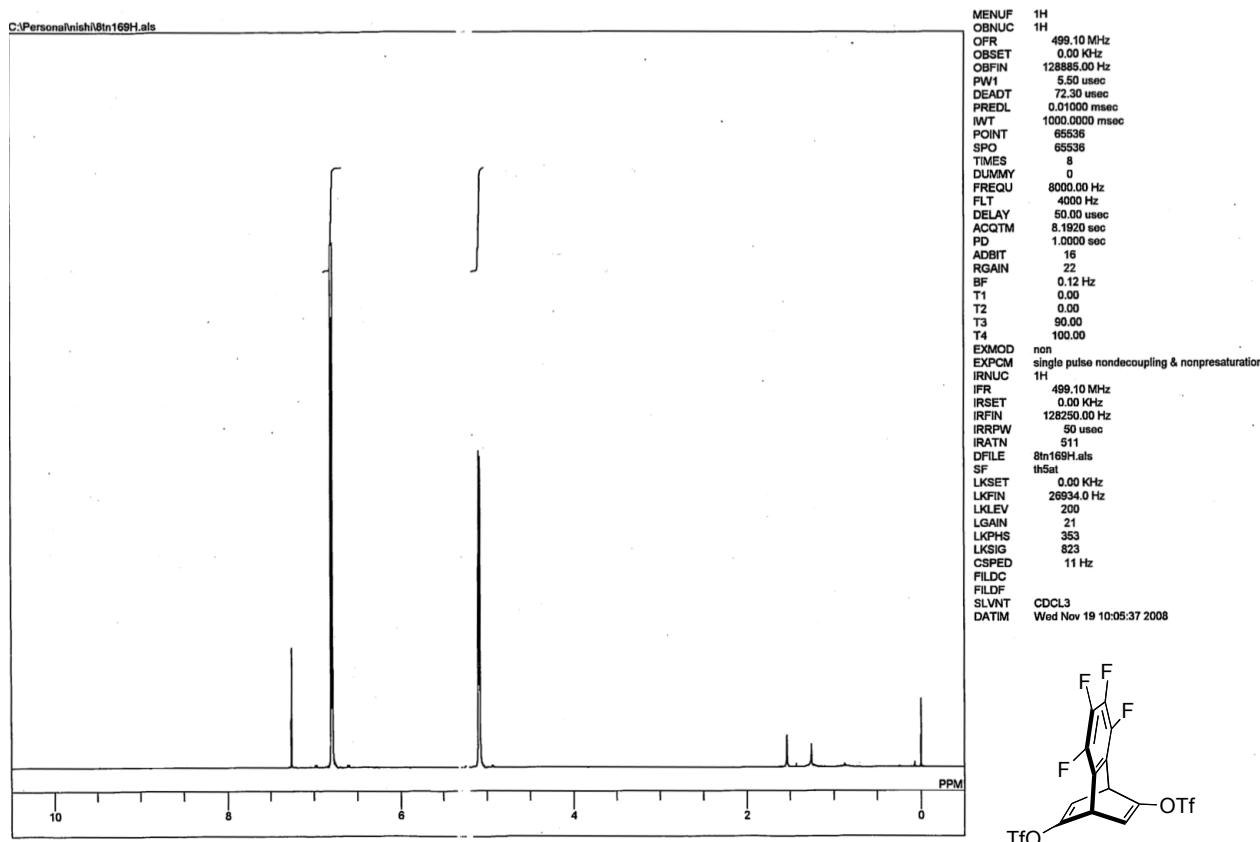
A mixture of $[\text{RhCl}((S,S)\text{-Fc-tfb}^*(\mathbf{1f})]_2$ (5.5 mg, 3.75 μmol , 7.5 μmol of Rh), mesitylboronic acid (**6u**) (123 mg, 0.75 mmol), isophthalaldehyde (**8**) (33.5 mg, 0.25 mmol), and aqueous KOH (1.5 M, 0.50 mL, 0.75 mmol) in *tert*-butyl alcohol (2.0 mL) was stirred at 30 °C for 6 h. The mixture was diluted with hexane, and it was passed through a short column of silica gel with Et_2O as eluent. After evaporation of the solvent, the residue was subjected to PTLC on silica gel (hexane/ethyl acetate, 2/1) to give compound **9** (70.5 mg, 0.19 mmol, 75%, *dl/meso* = 85/15). The ee was measured by HPLC (Chiralpak AS-H column, flow 0.8 mL/min, hexane/2-propanol = 9/1, 224 nm, t_1 = 8.3 min (*S,S*), t_2 = 17.1 min (*R,R*), (t = 10.4 min for *meso-9*)). *dl-9* (98% ee (*R,R*)): ^1H NMR (CDCl_3) δ 2.07 (br s, 2H), 2.20 (s, 12H), 2.27 (s, 6H), 6.30 (s, 2H), 6.83 (s, 4H), 7.00 (d, J = 7.0 Hz, 2H), 7.16 (t, J = 7.0 Hz, 1H), 7.46 (s, 1H); ^{13}C NMR (CDCl_3) δ 20.5, 20.8, 71.0, 123.0, 123.8, 127.9, 129.9, 136.4, 136.9, 137.1, 143.2. HRMS (ESI-TOF) calcd for $\text{C}_{26}\text{H}_{30}\text{NaO}_2$ ($\text{M}+\text{Na}^+$) 397.2138, found 397.2131. *meso-9*: ^1H NMR (CDCl_3) δ 2.07 (br s, 2H), 2.20 (s, 12H), 2.27 (s, 6H), 6.30 (s, 2H), 6.82 (s, 4H), 7.00 (d, J = 7.0 Hz, 2H), 7.16 (t, J = 7.0 Hz, 1H), 7.40 (s, 1H).

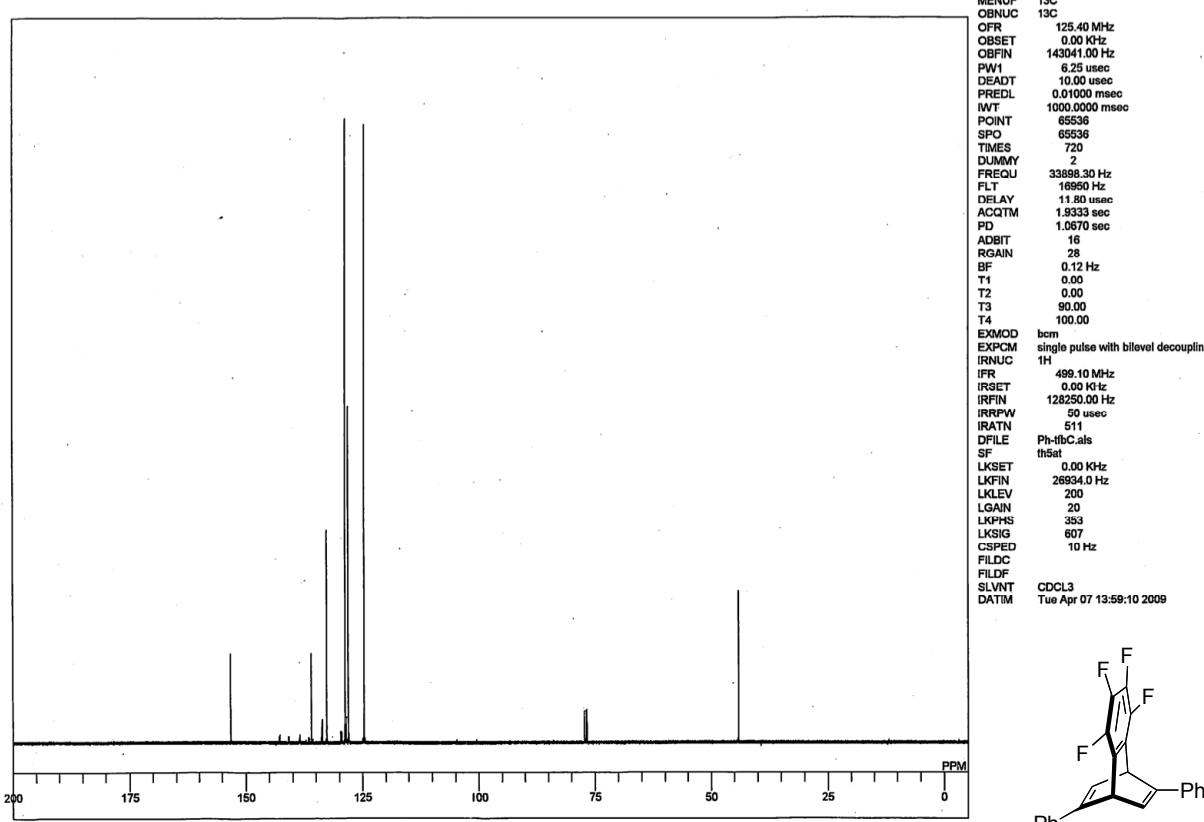
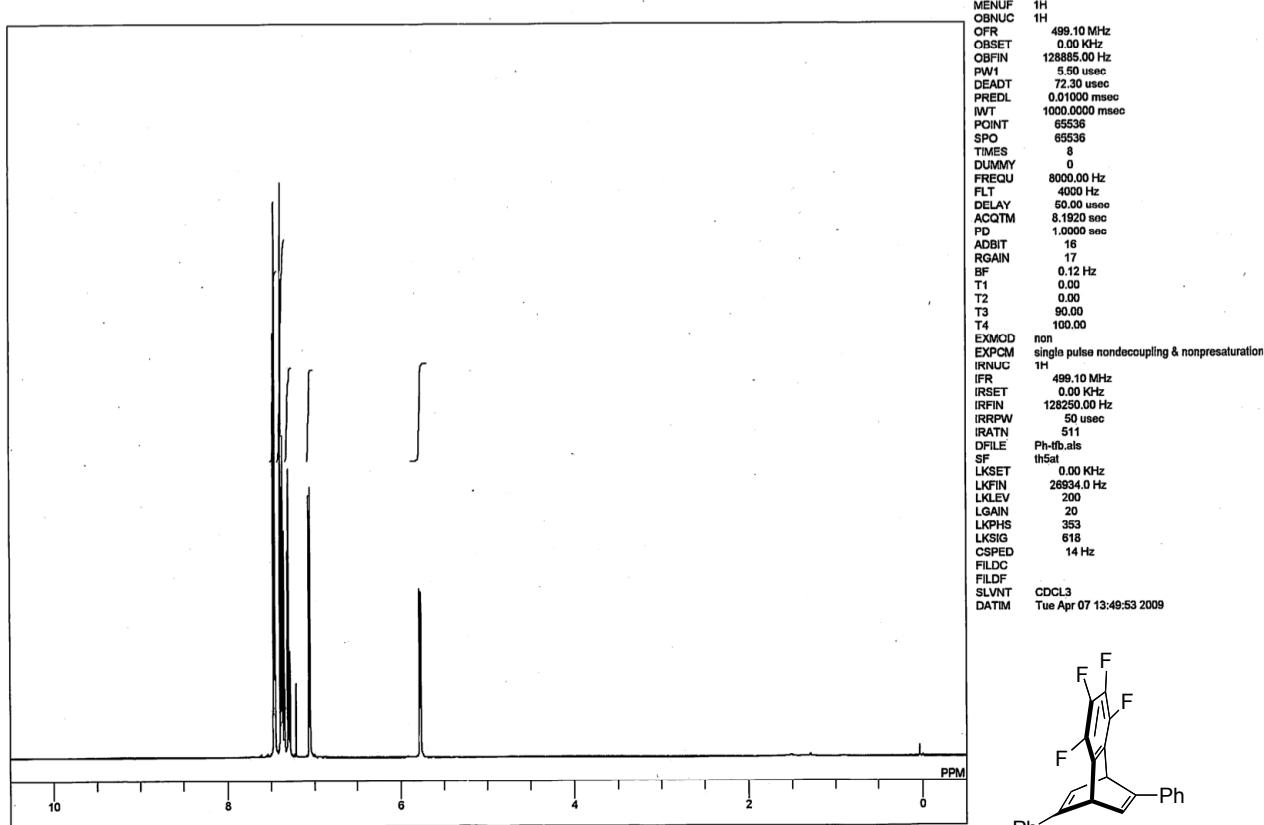


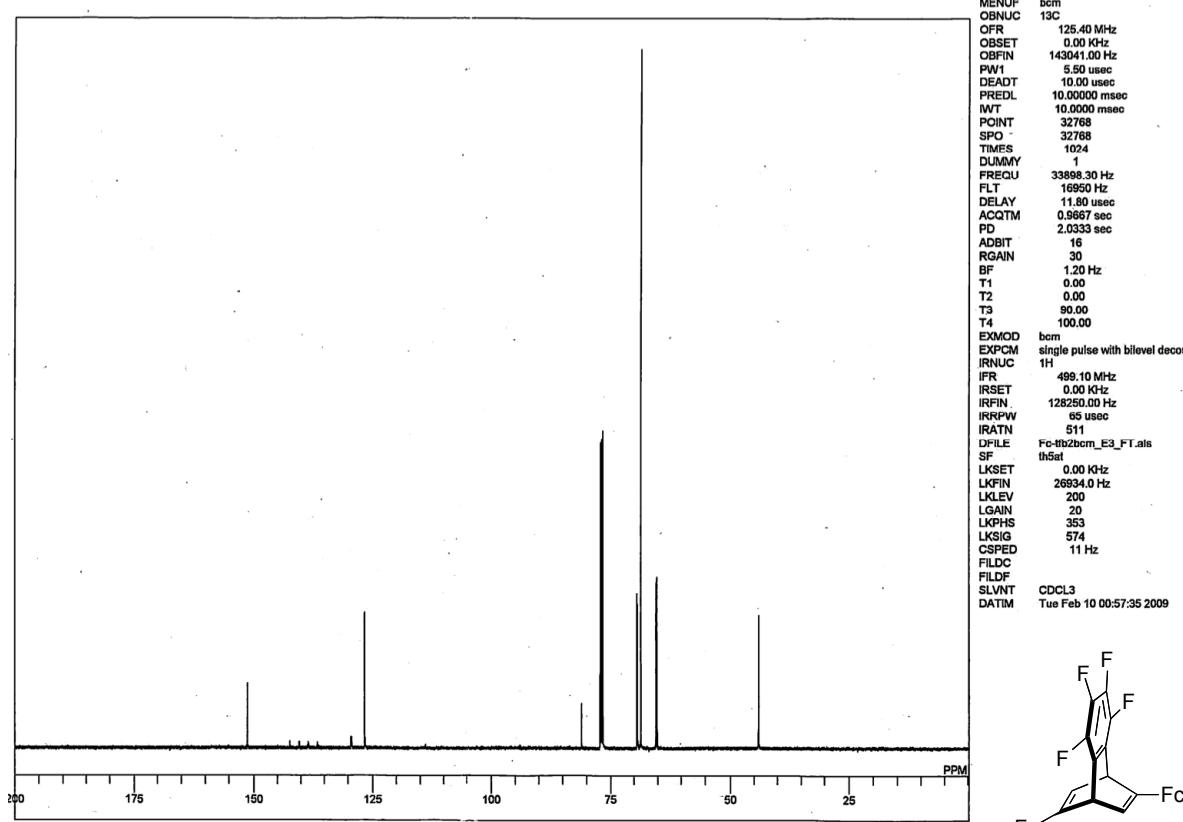
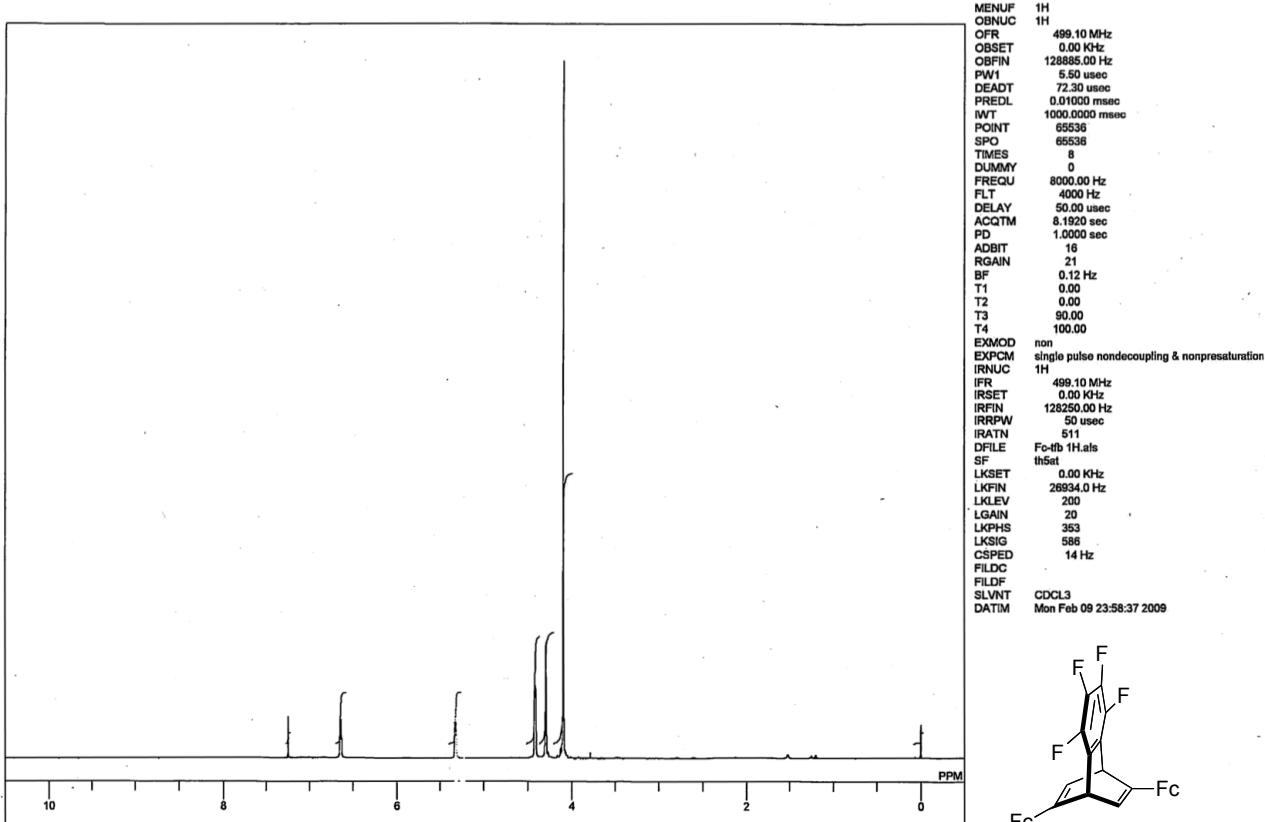
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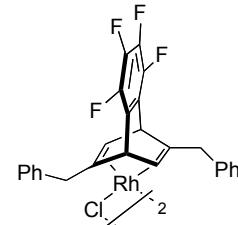
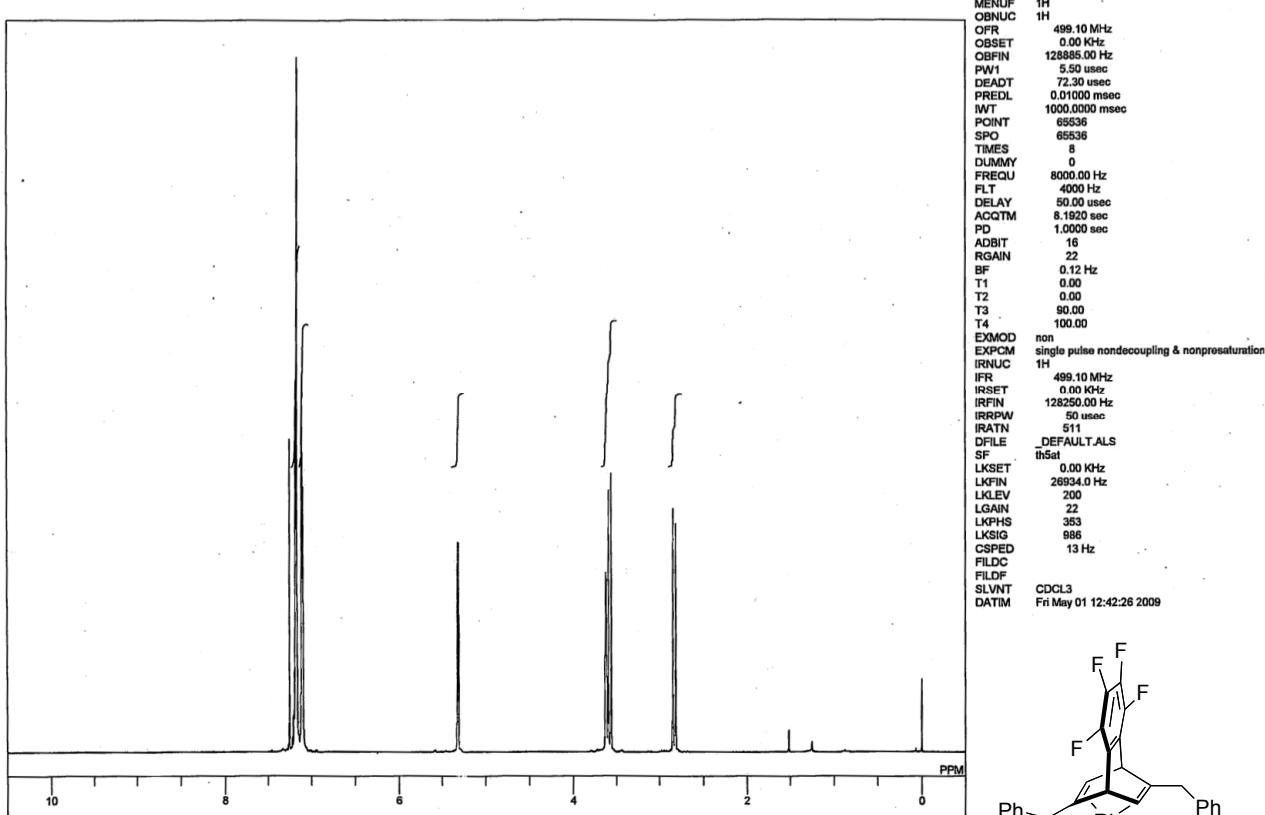


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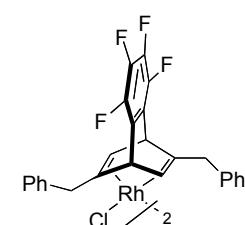
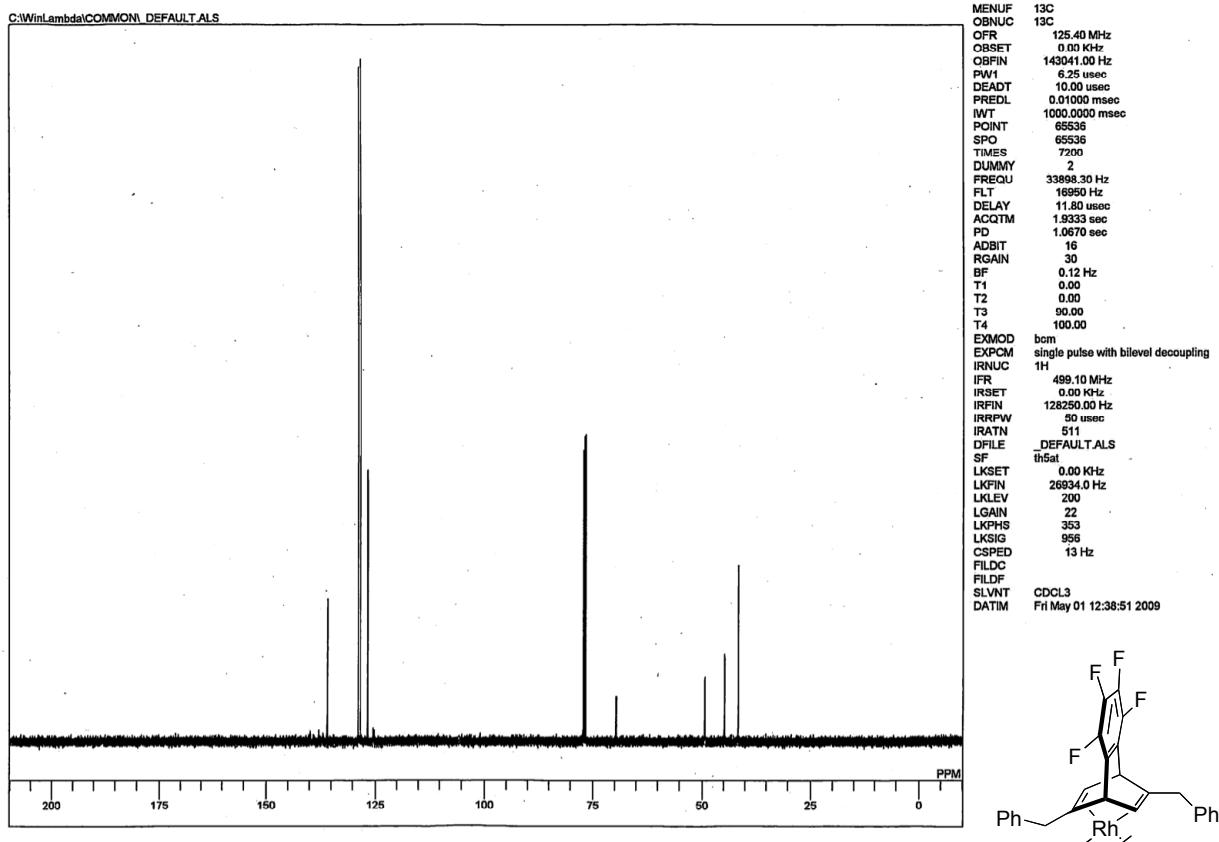




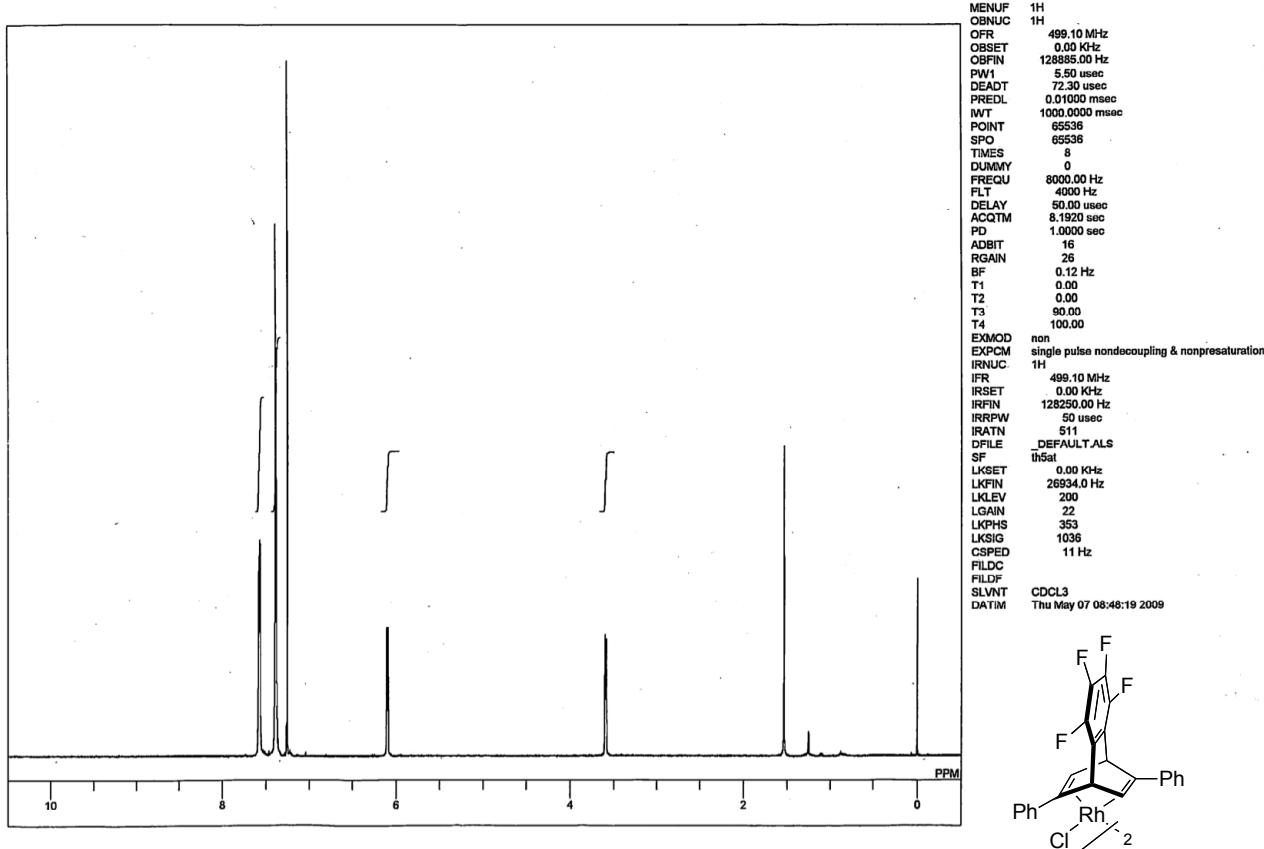




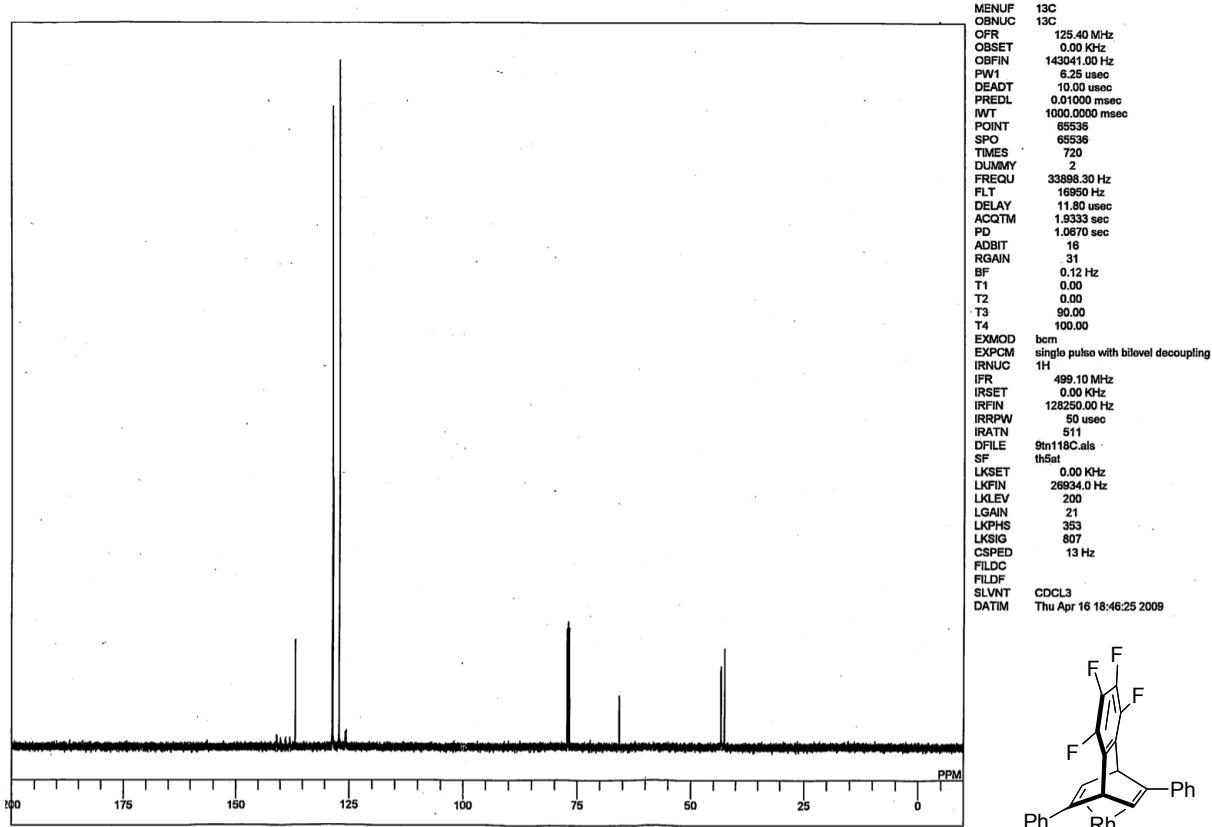
$[\text{RhCl}((\text{R},\text{R})-\mathbf{1d})]_2$



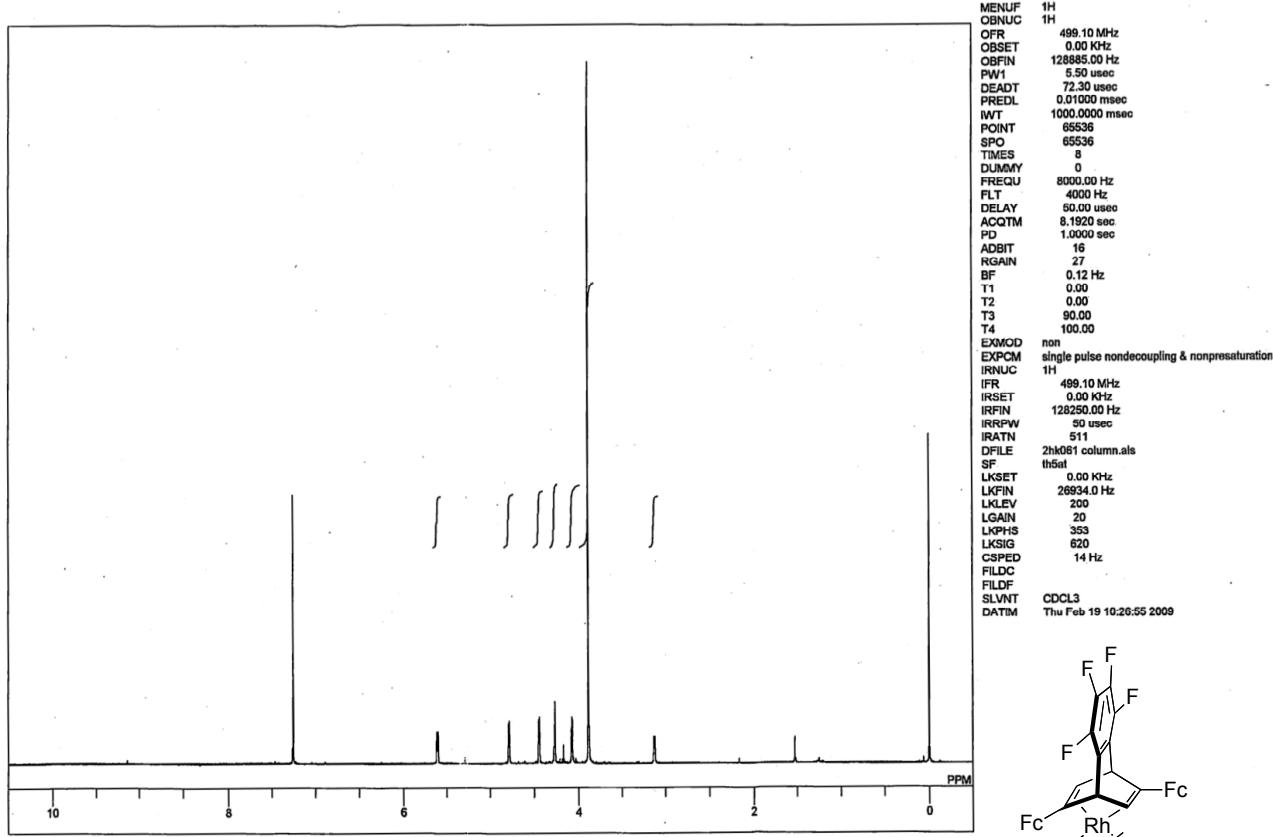
$[\text{RhCl}((\text{R},\text{R})-\mathbf{1d})]_2$



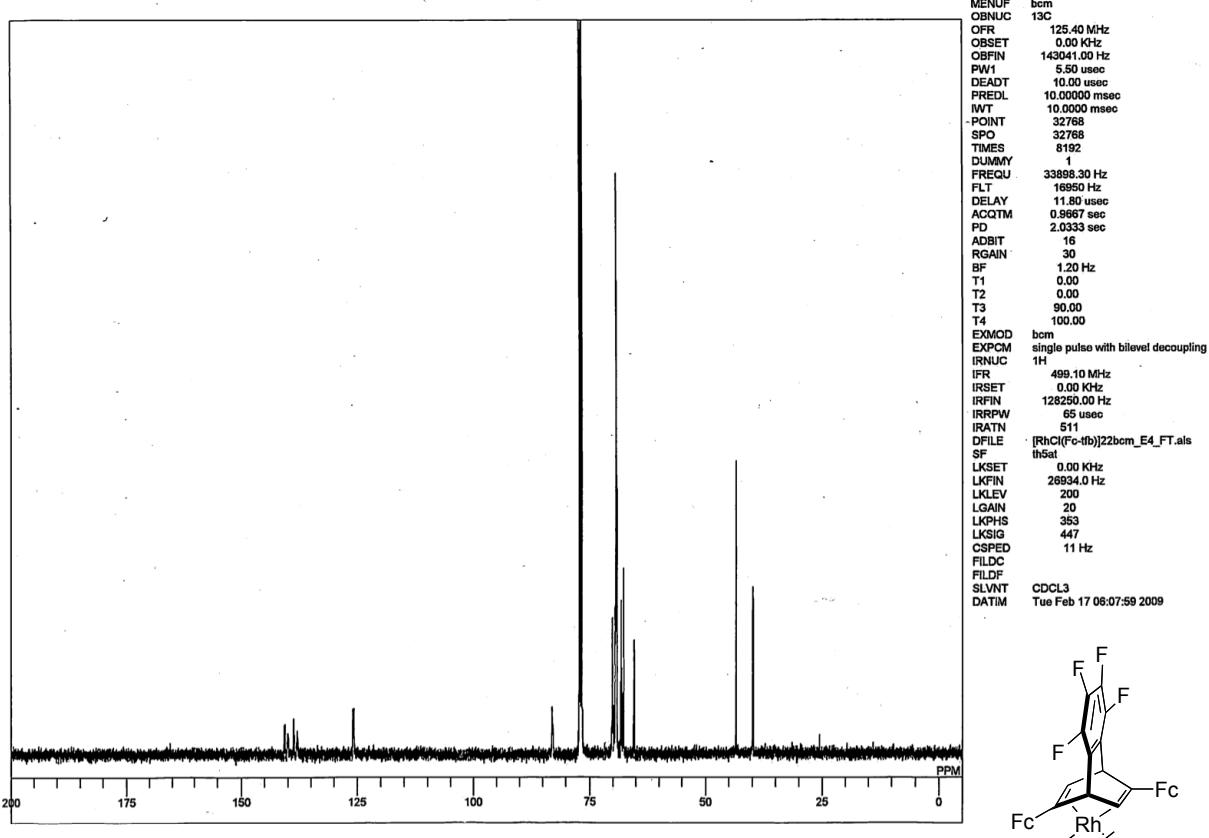
[RhCl((R,R)-1e)]



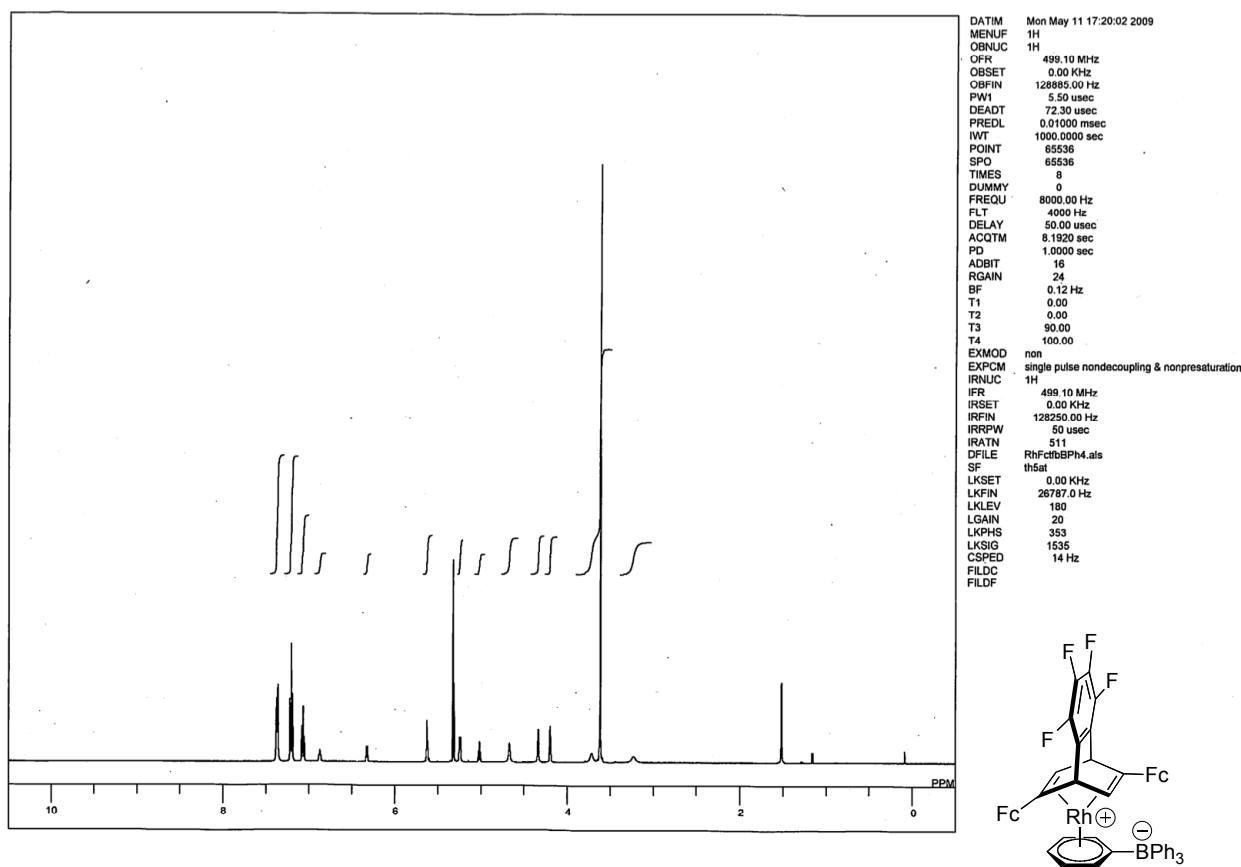
[RhCl((R,R)-1e)]₂



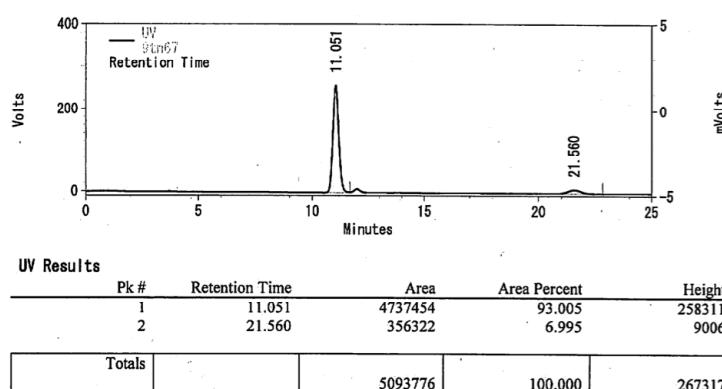
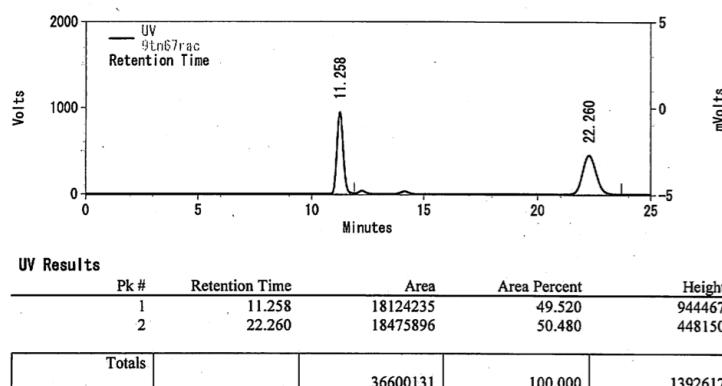
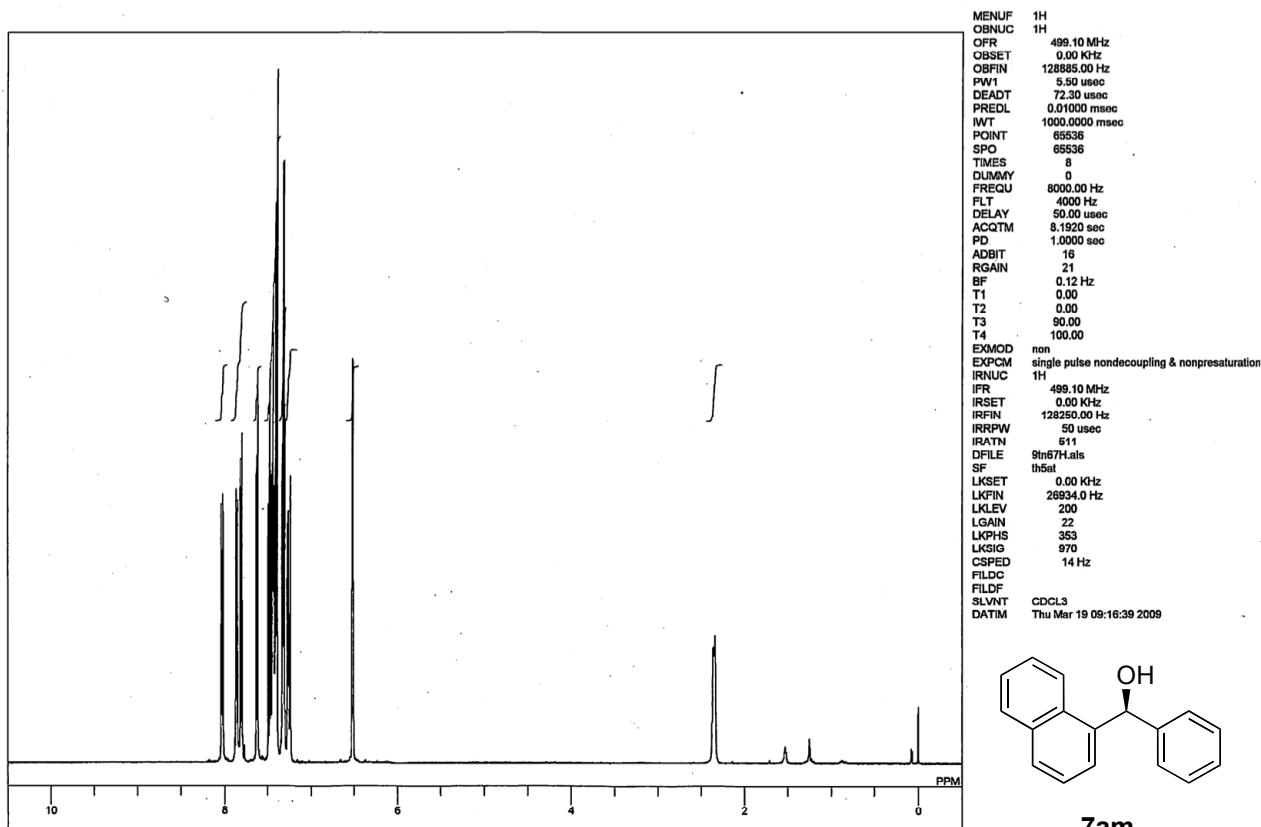
[RhCl((S,S)-1f)]₂

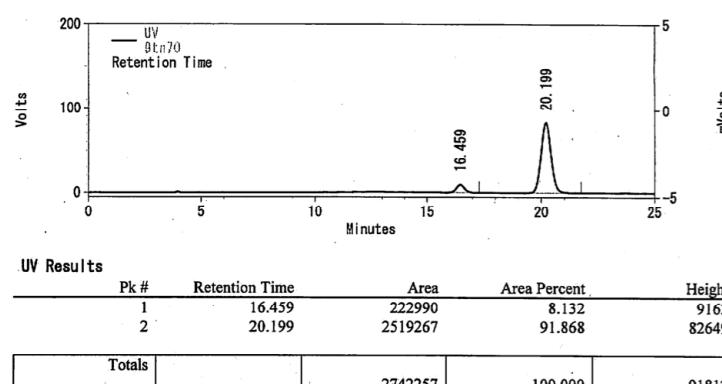
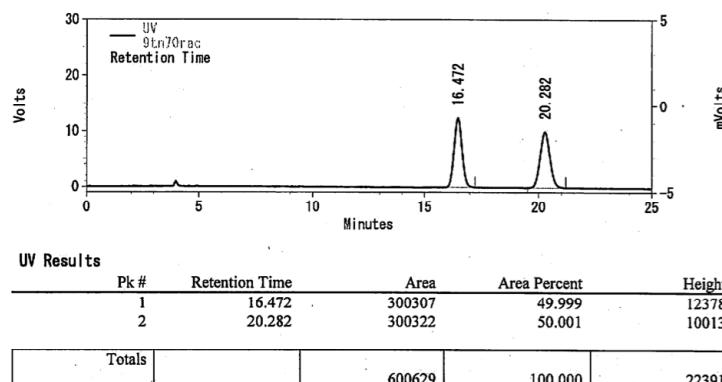
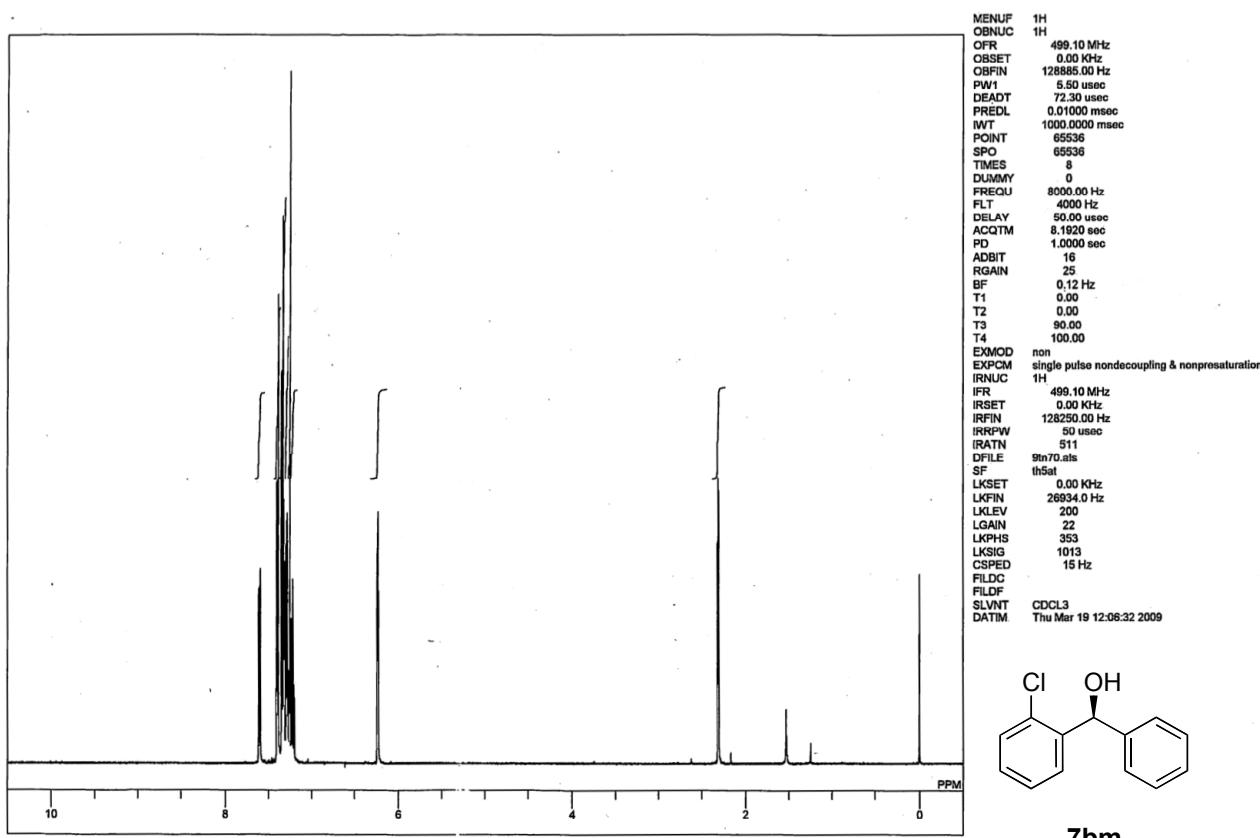


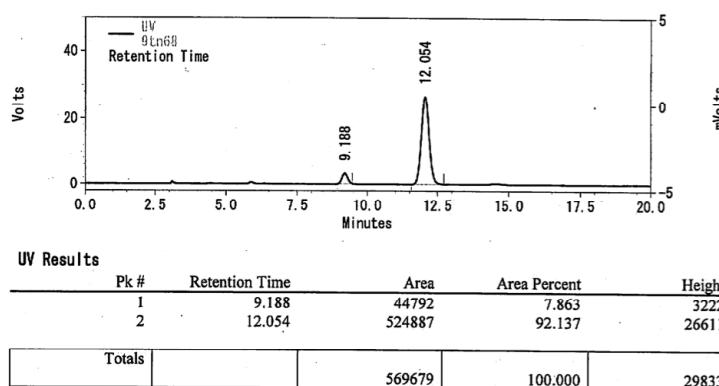
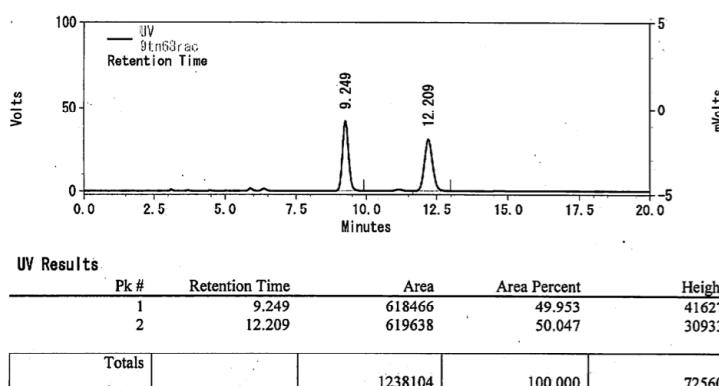
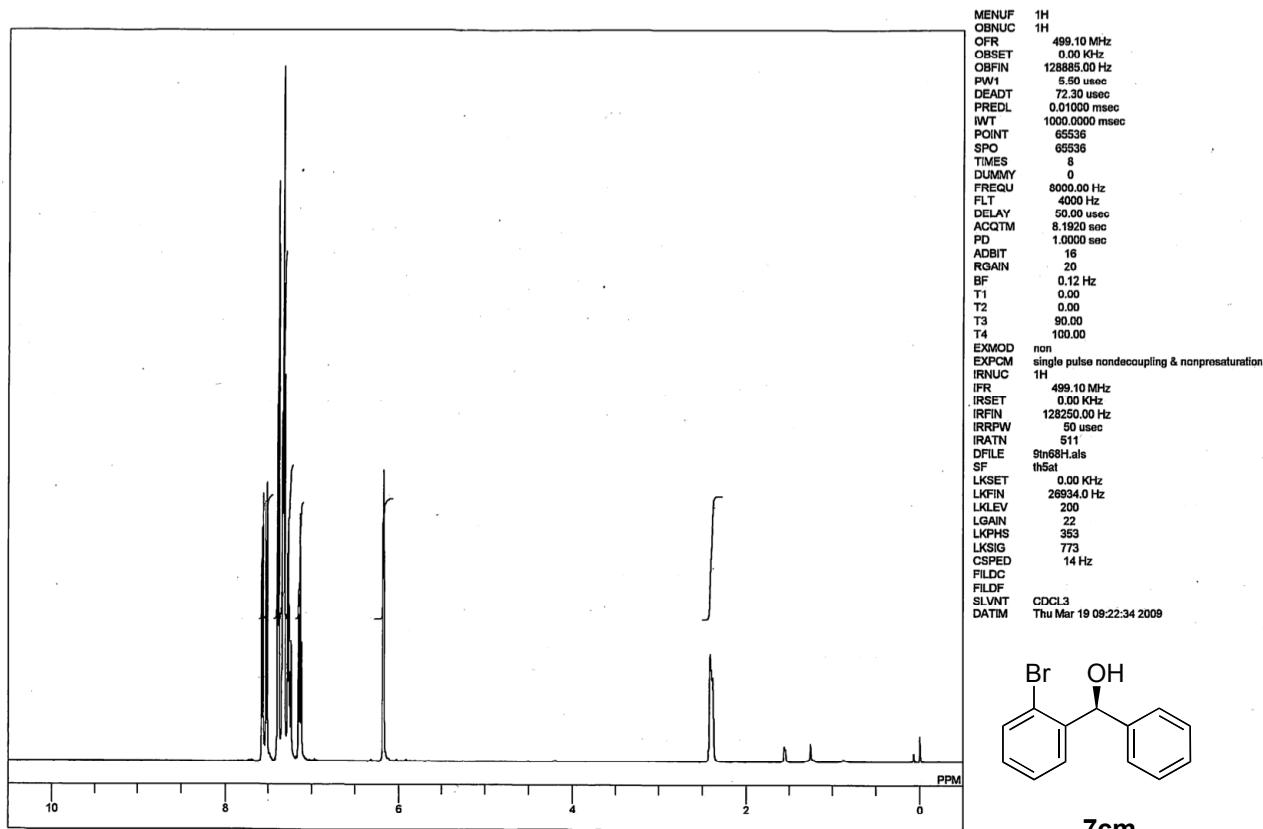
[RhCl((S,S)-1f)]₂

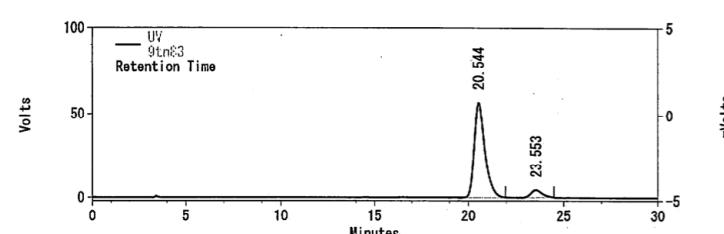
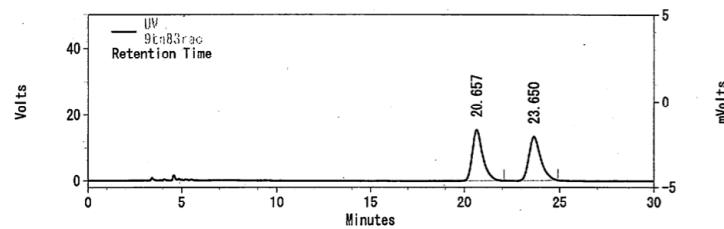
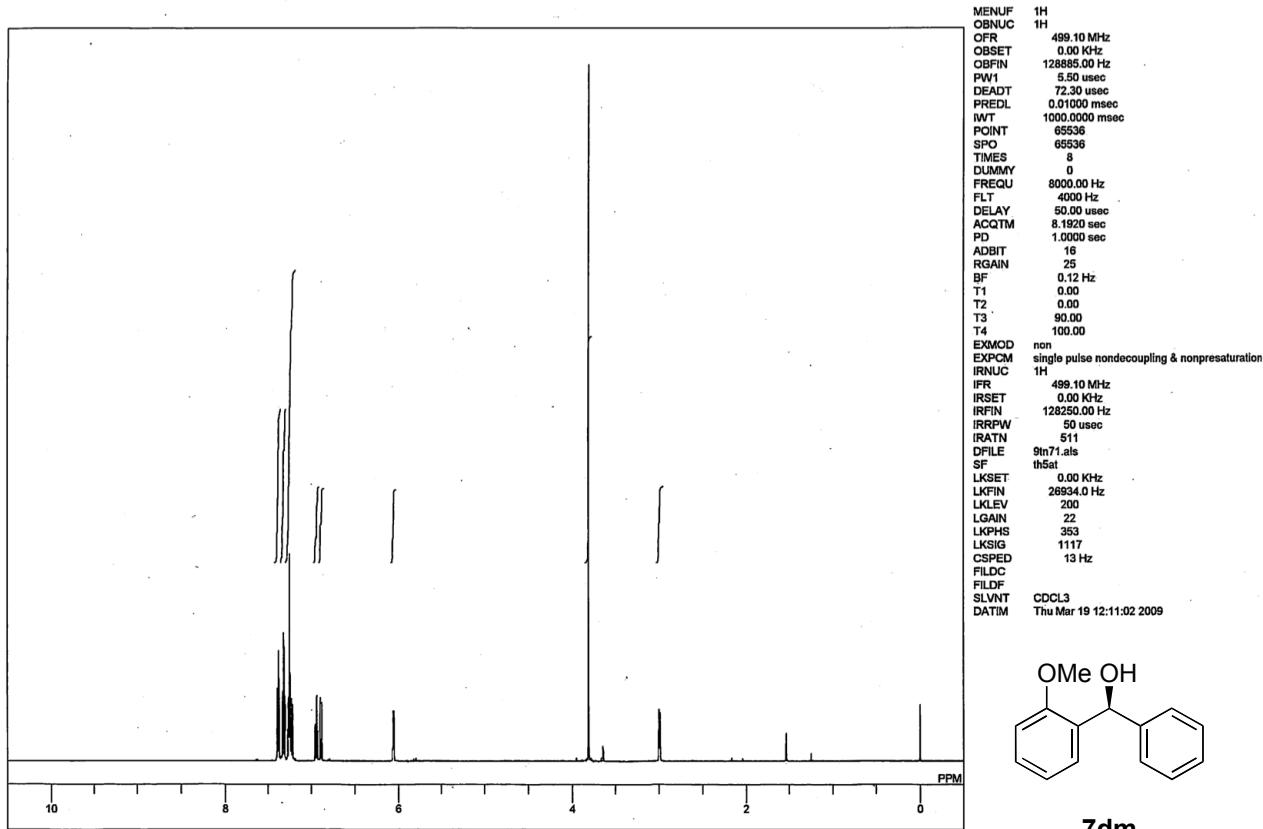


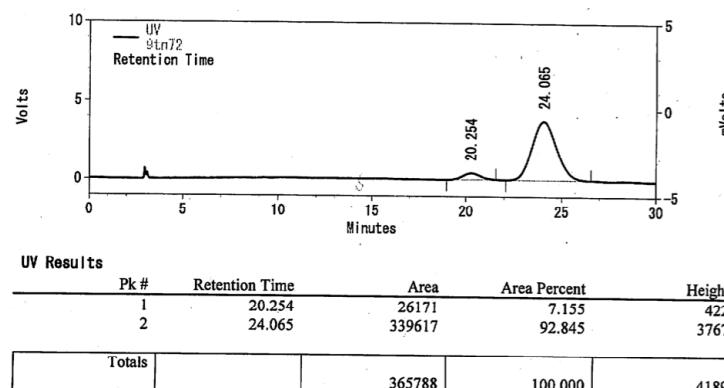
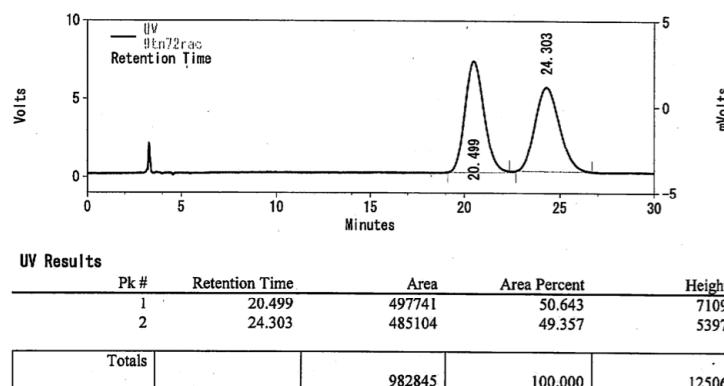
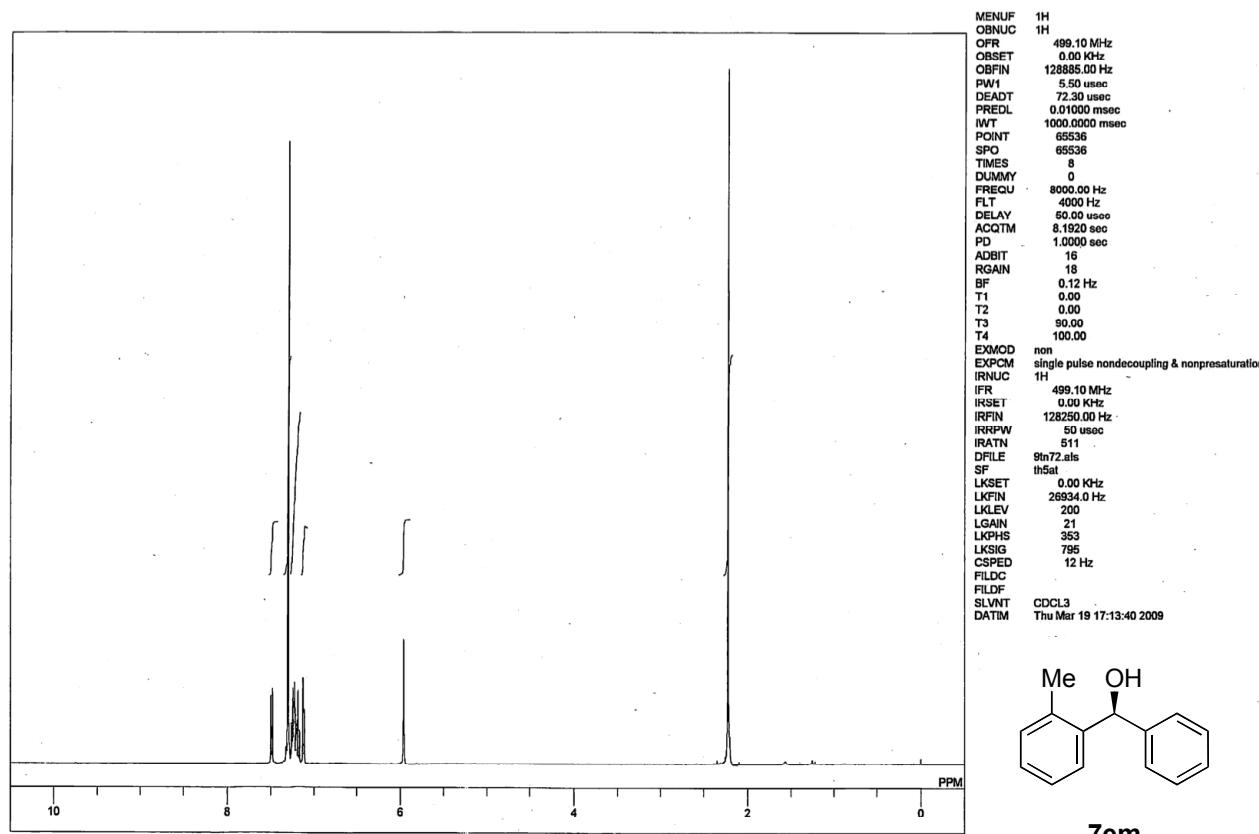
Rh((S,S)-1f)[(η⁶-C₆H₅)BPh₃]

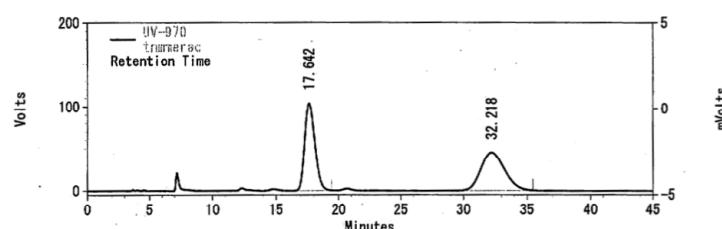
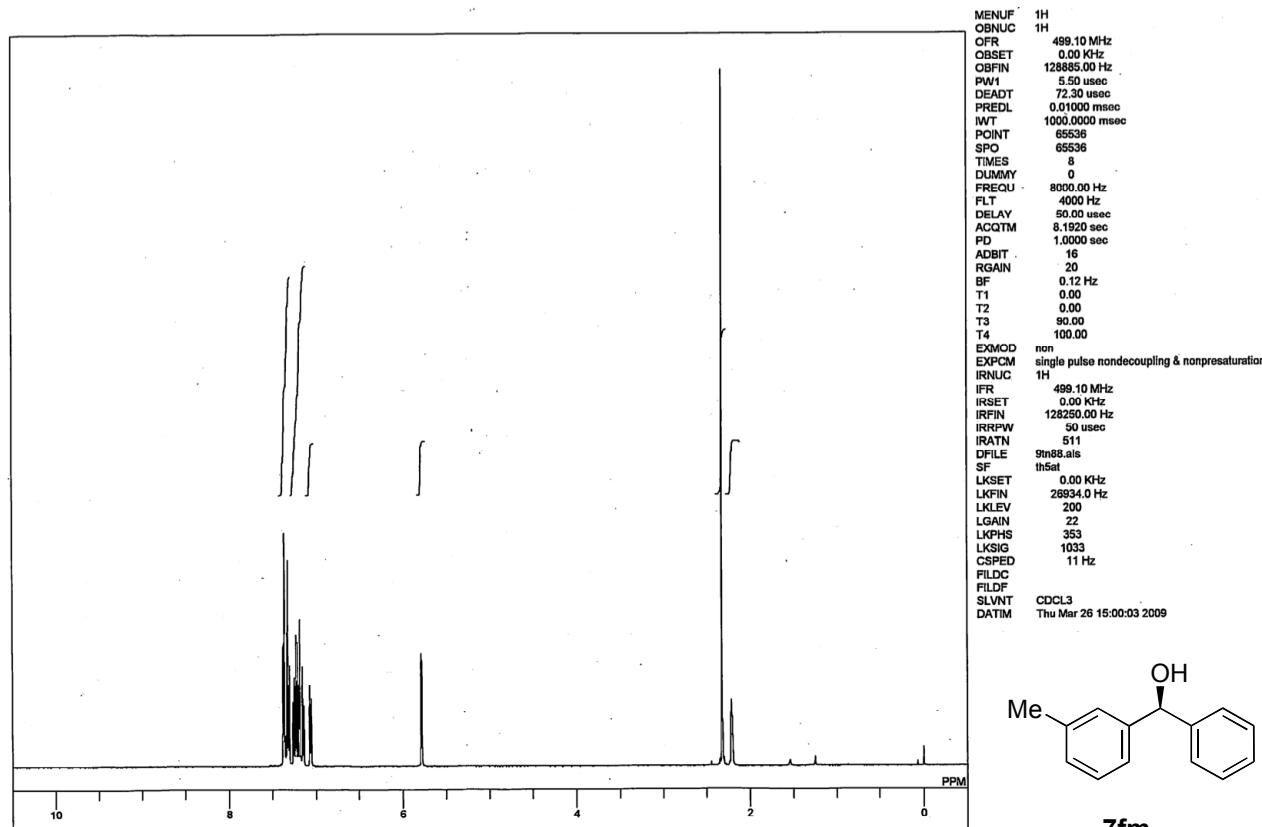




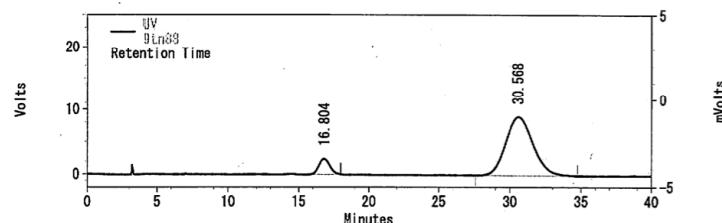




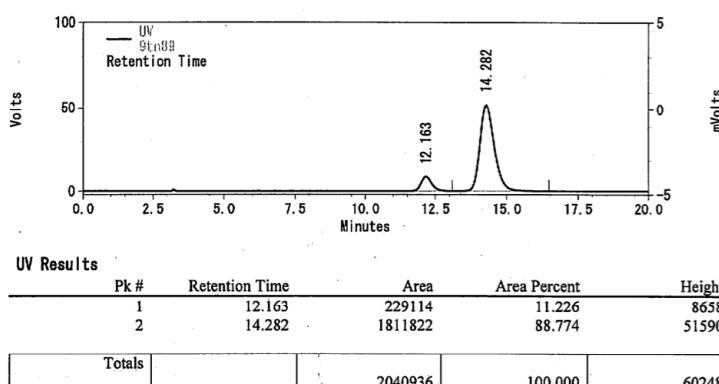
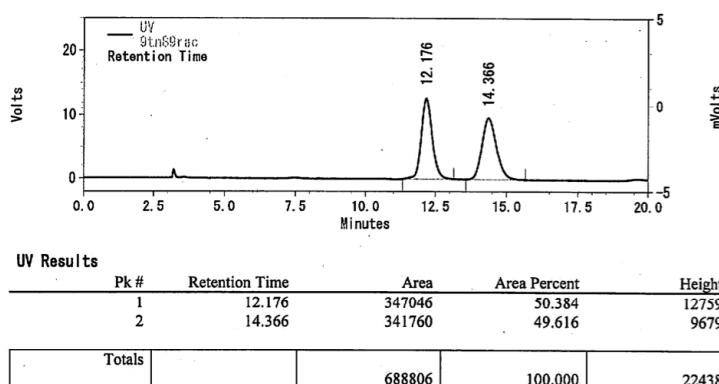
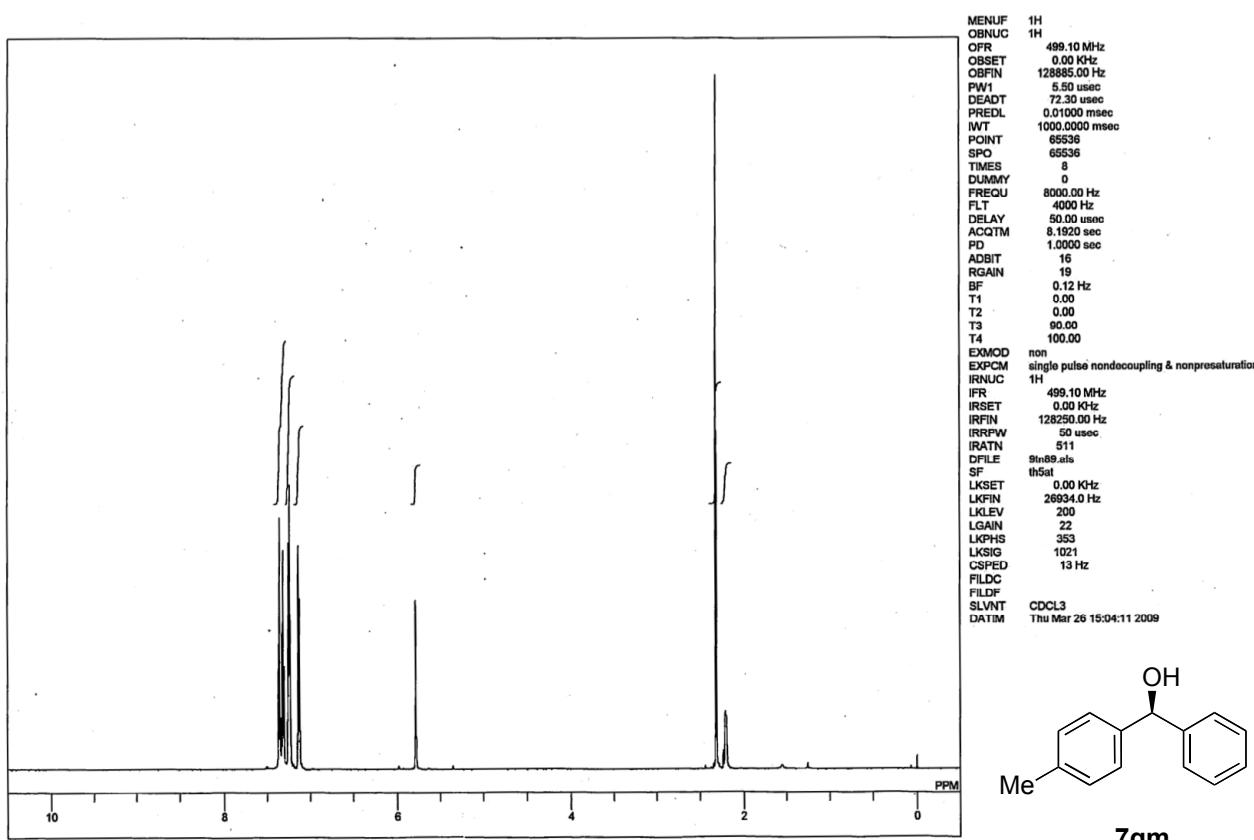


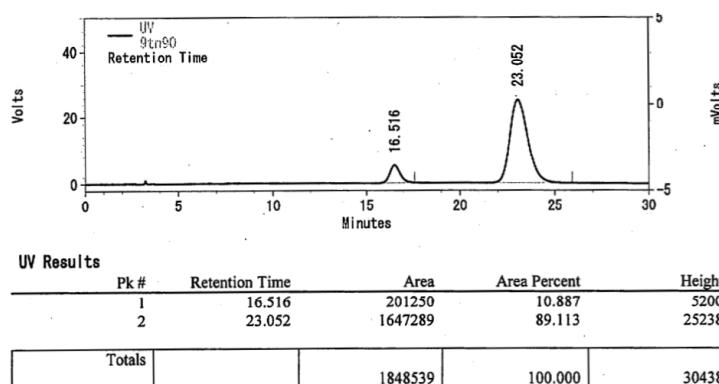
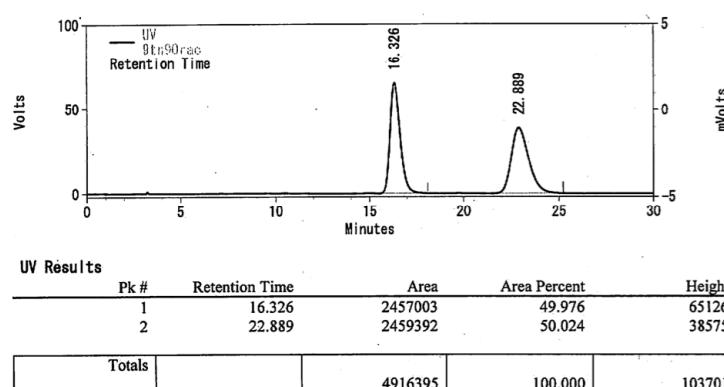
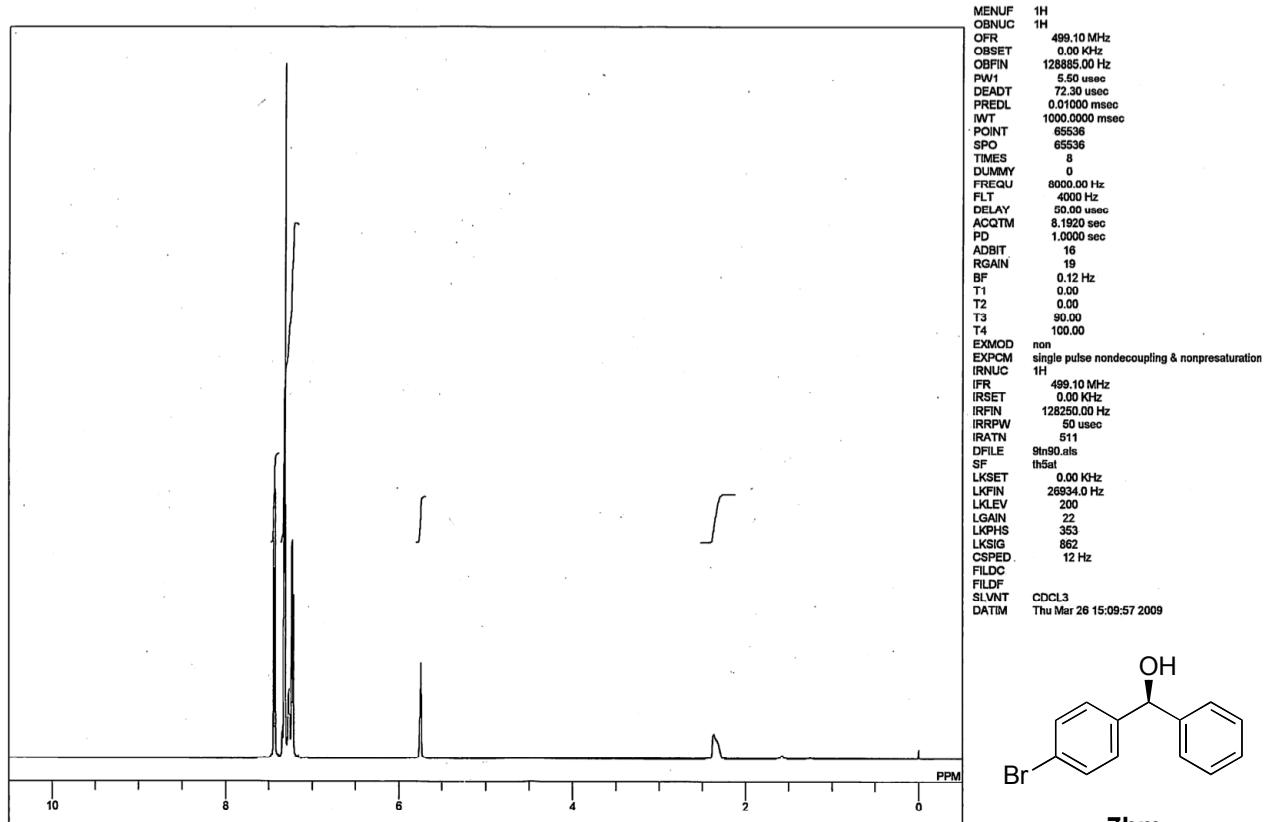


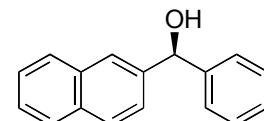
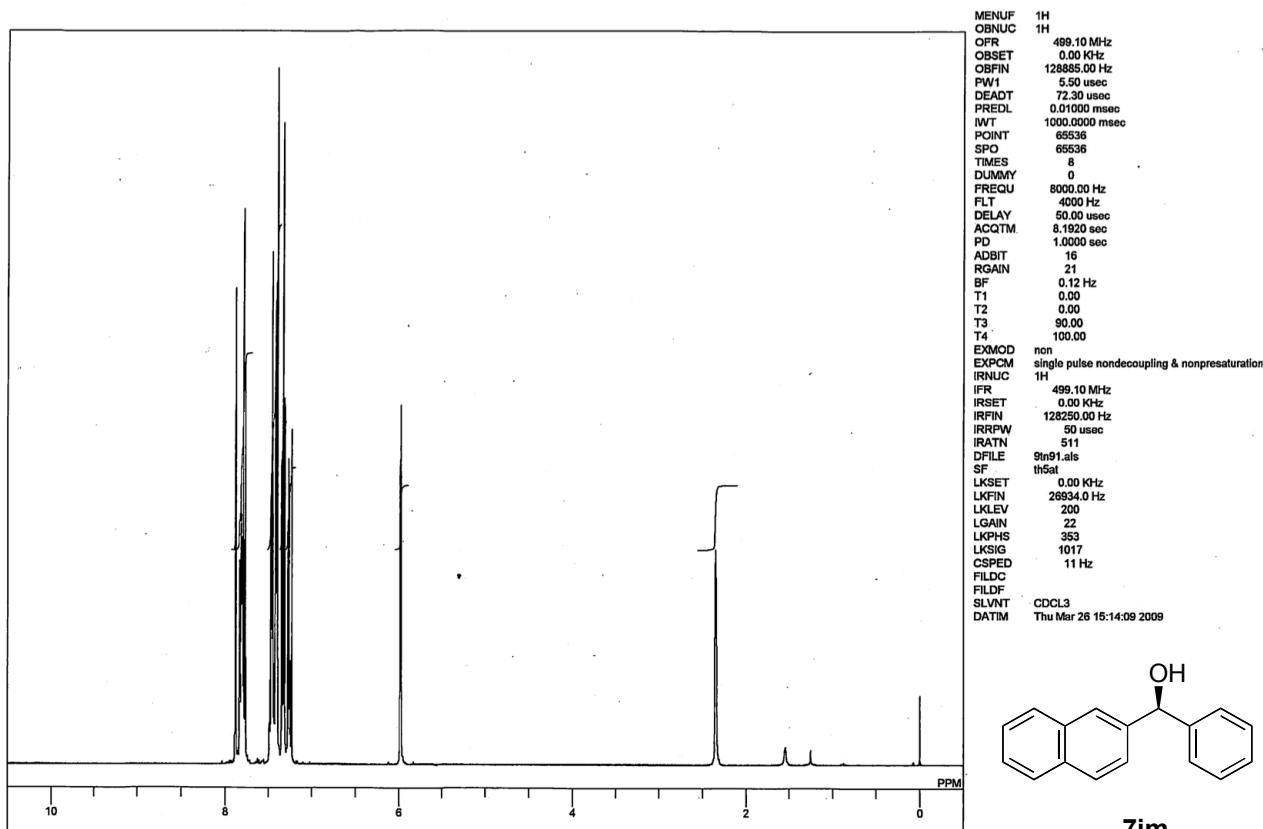
UV-970 Results				
Pk #	Retention Time	Area	Area Percent	Height
1	17.642	5833444	49.967	103789
2	32.218	5841156	50.033	45059
Totals		11674600	100.000	148848



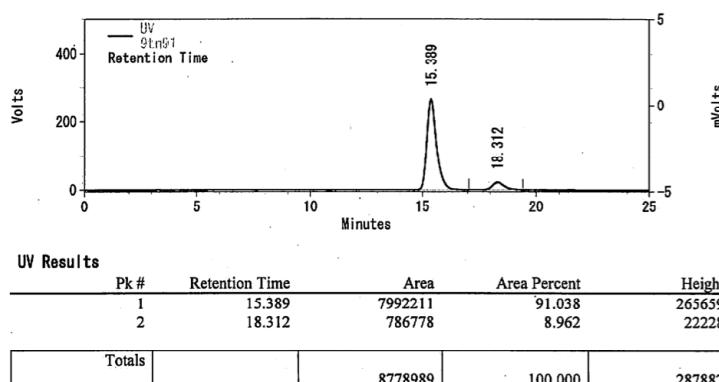
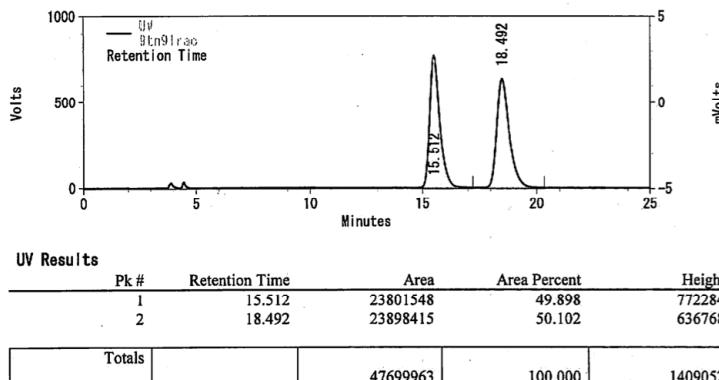
UV Results				
Pk #	Retention Time	Area	Area Percent	Height
1	16.804	130212	9.759	2396
2	30.568	1203997	90.241	9048
Totals		1334209	100.000	11444

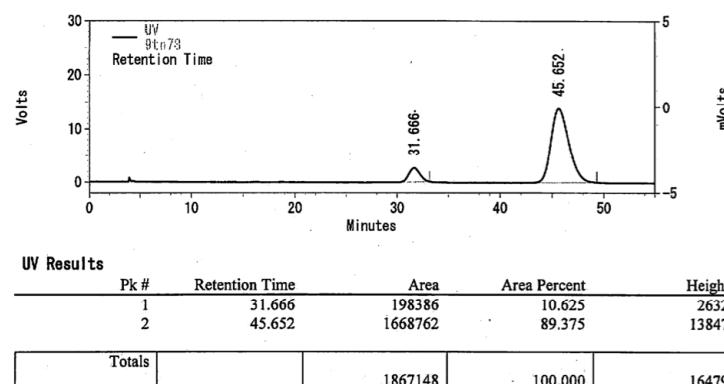
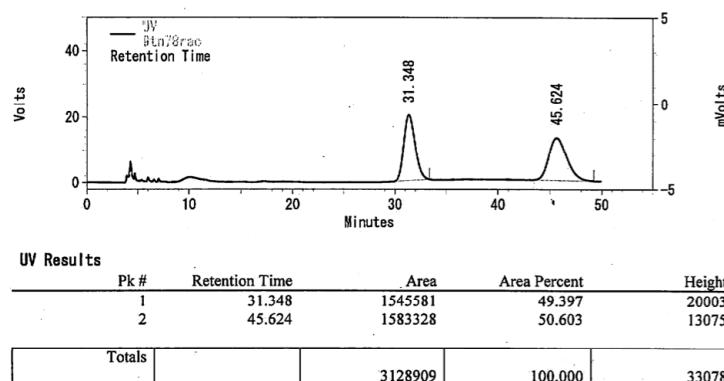
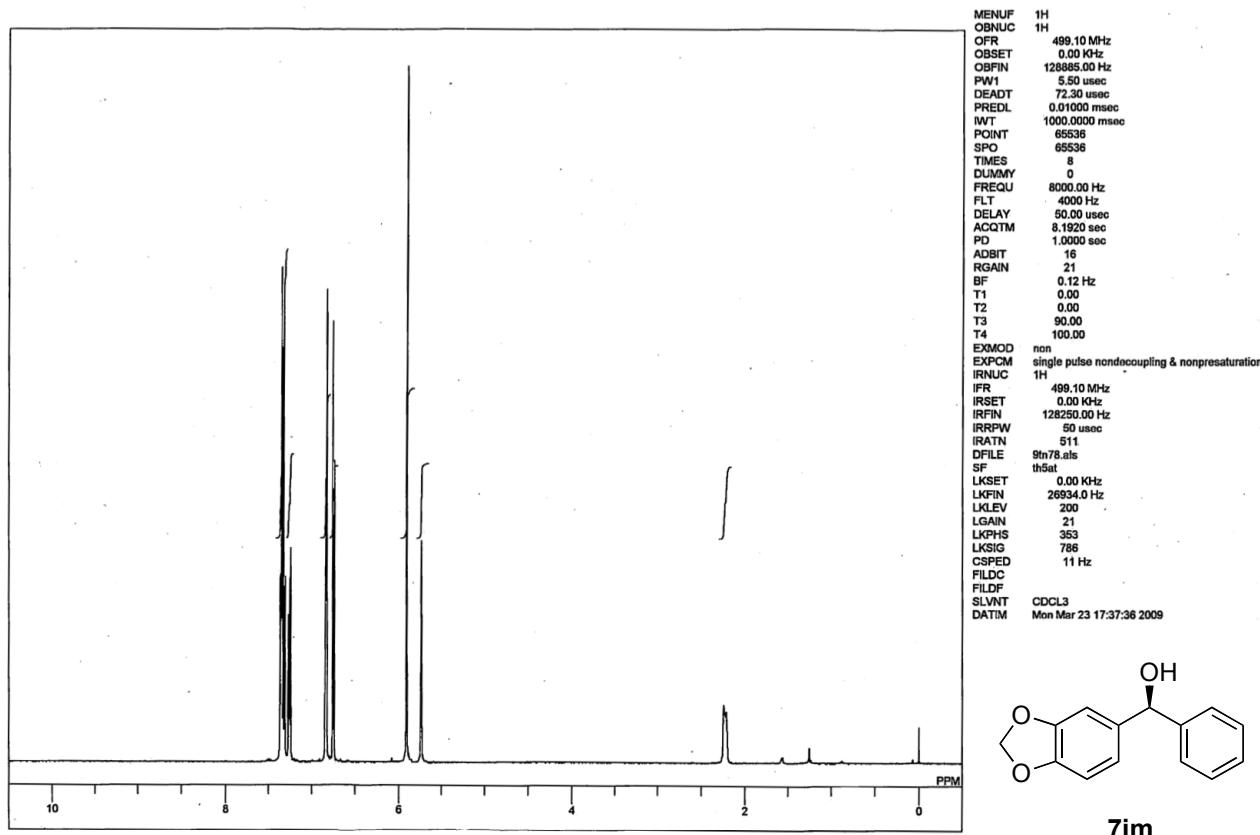


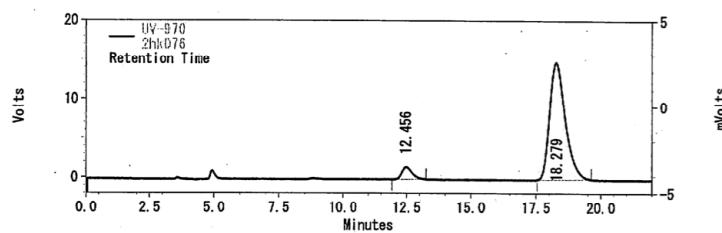
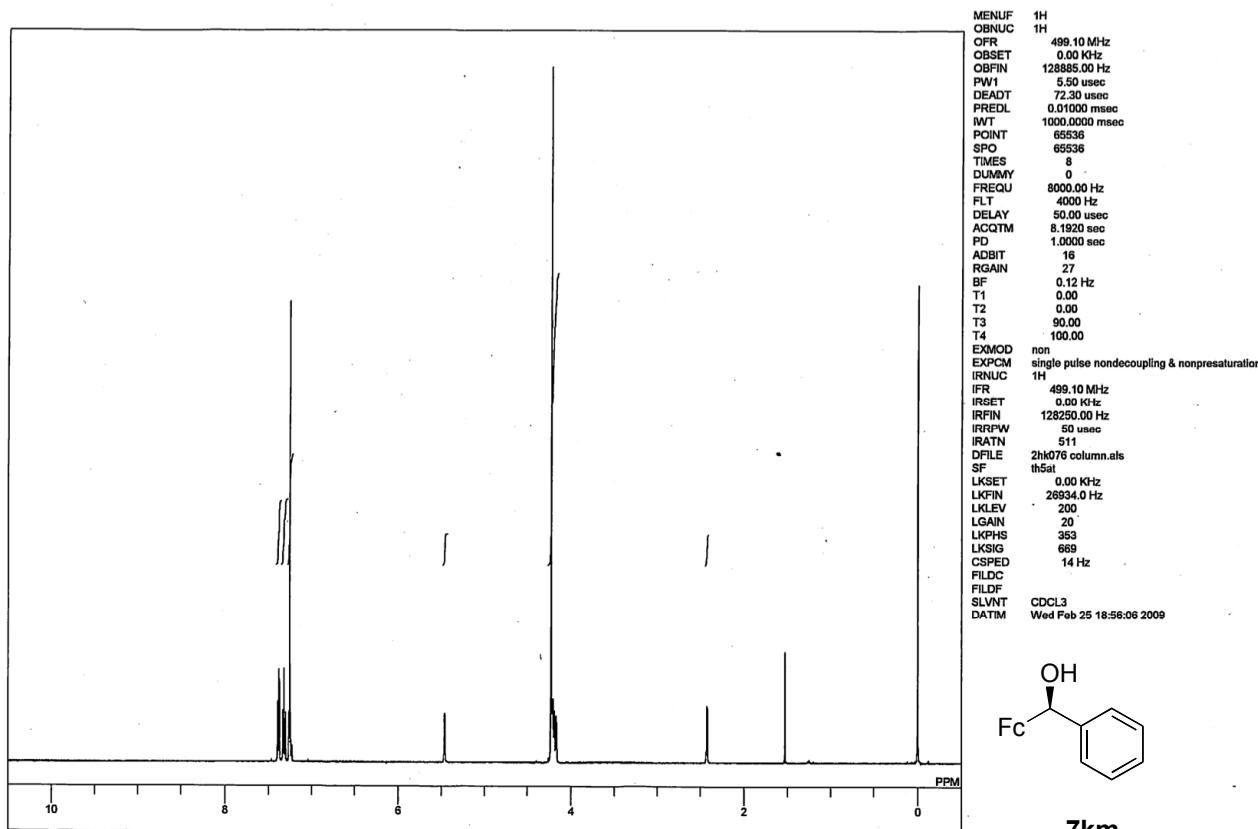




7im

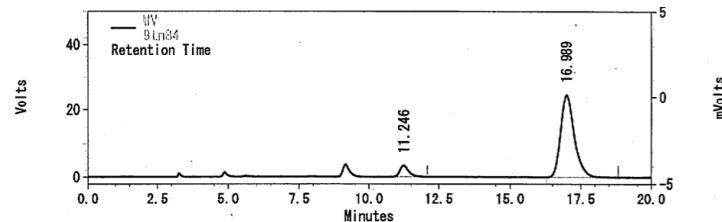






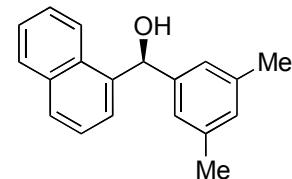
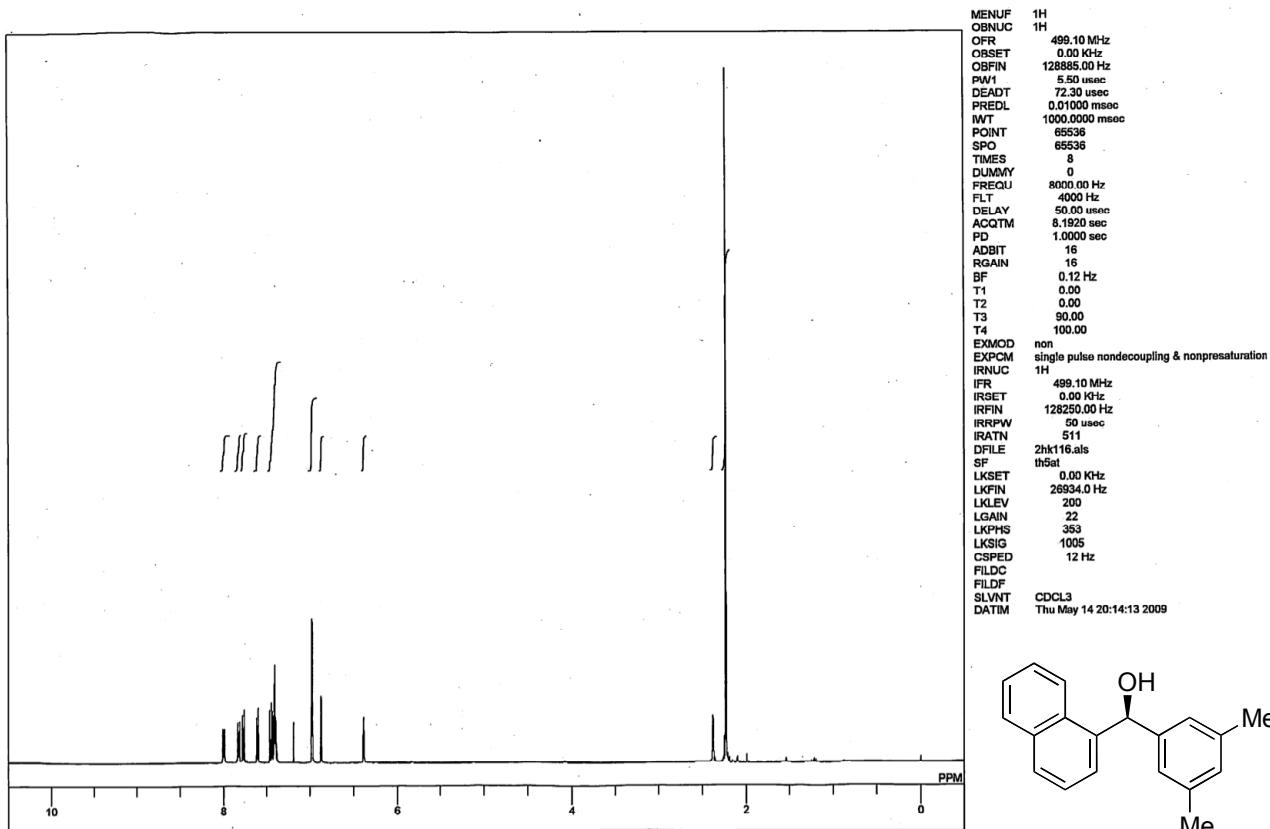
UV-970 Results

Pk #	Retention Time	Area	Area Percent	Height
1	12.456	44595	6.657	1583
2	18.279	625270	93.343	14904
Totals		669865	100.000	16487

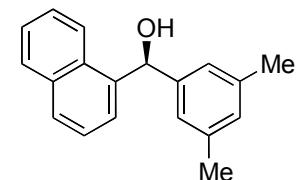
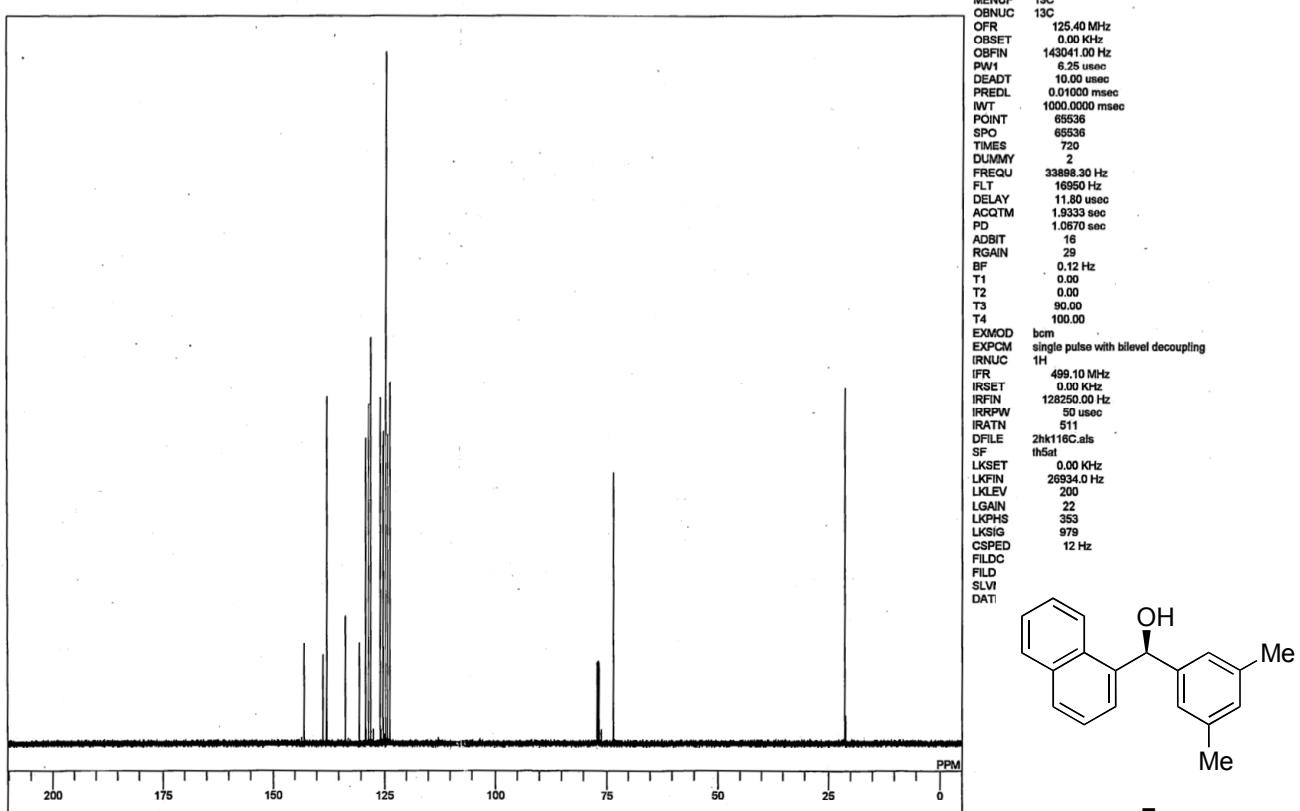


UV Results

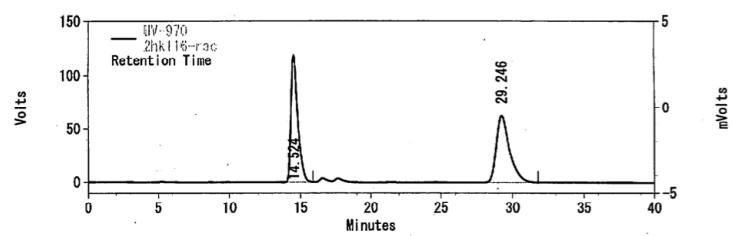
Pk #	Retention Time	Area	Area Percent	Height
1	11.246	69602	7.720	3259
2	16.989	832005	92.280	24639
Totals		901607	100.000	27898



7an

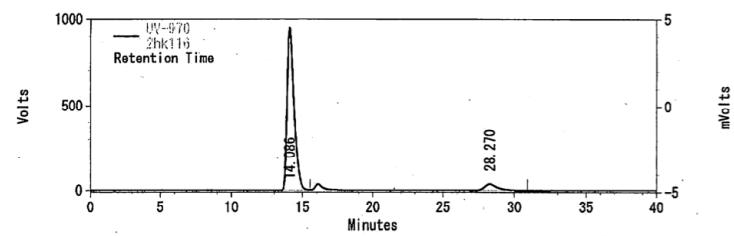


7an



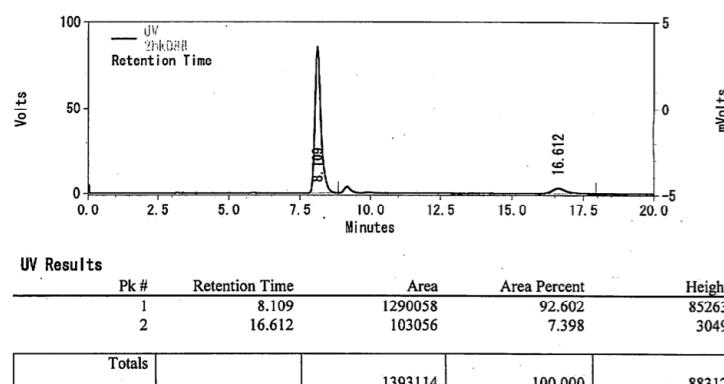
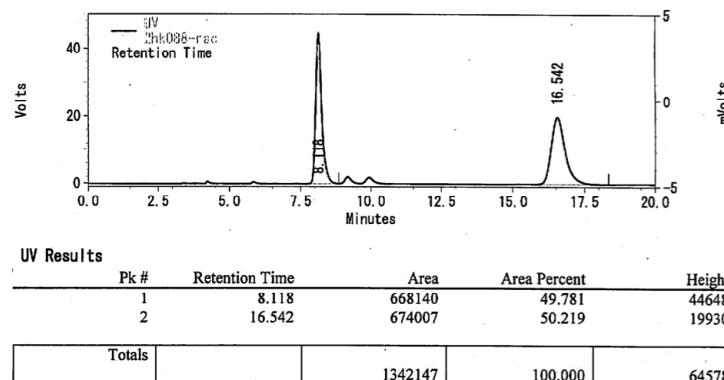
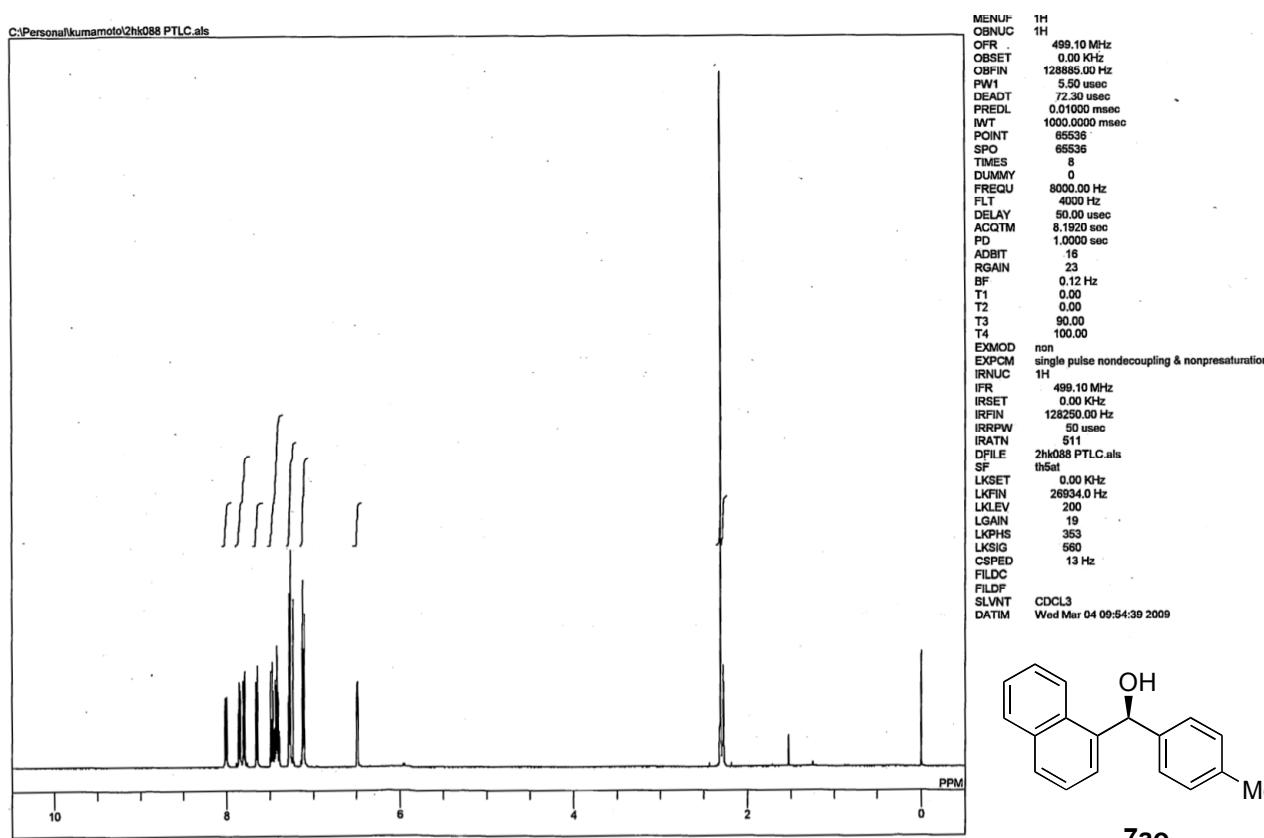
UV-970 Results

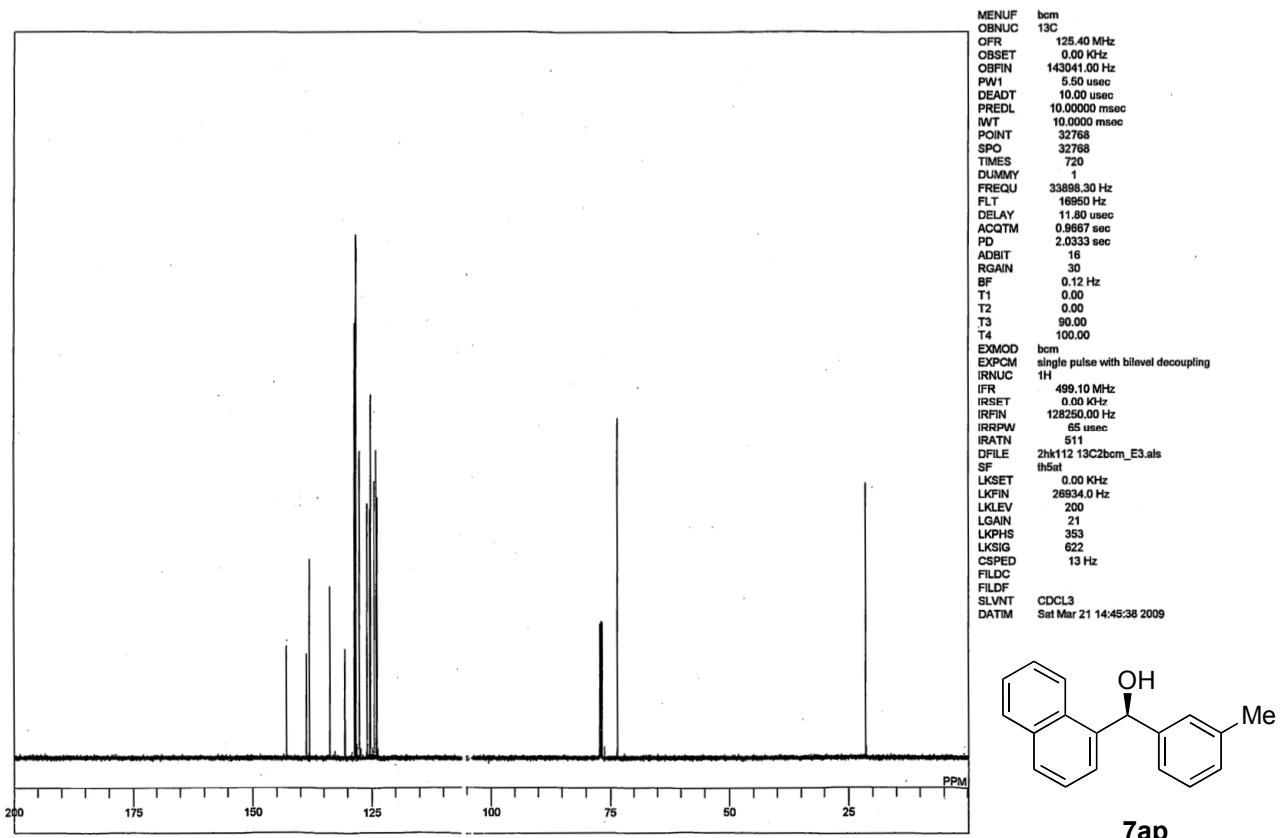
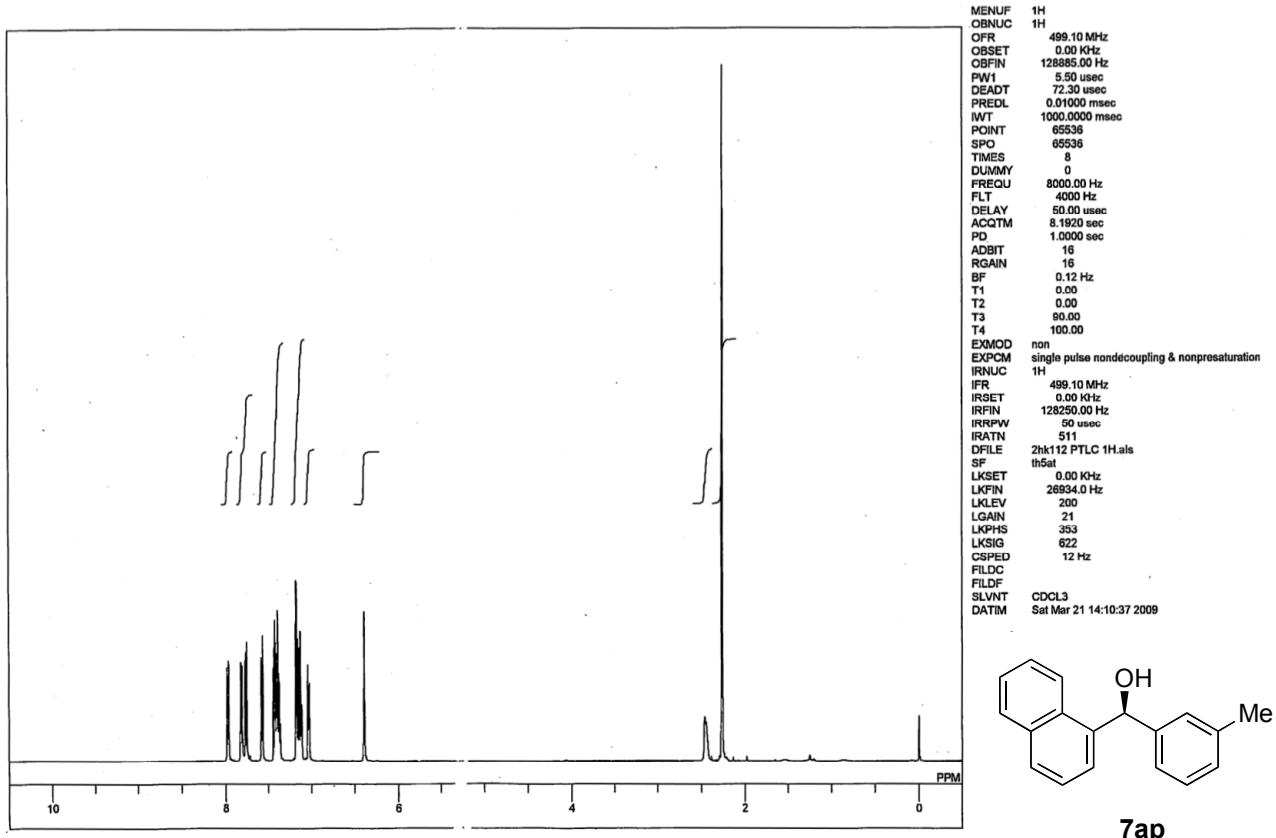
Pk #	Retention Time	Area	Area Percent	Height
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2	29.246	3987999	50.091	62539
Totals		7961560	100.000	181897

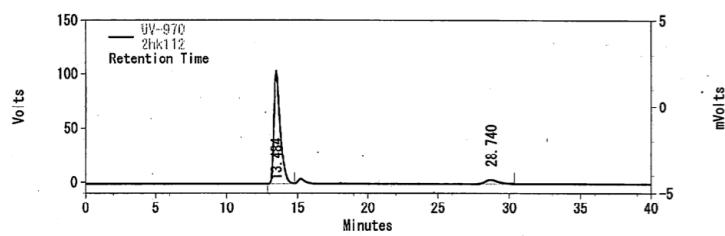
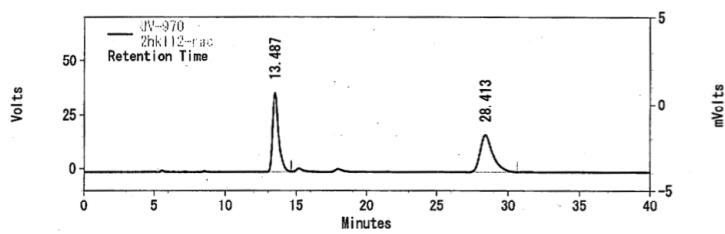


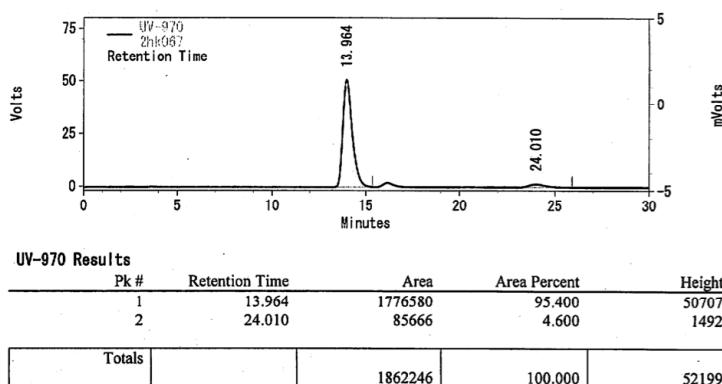
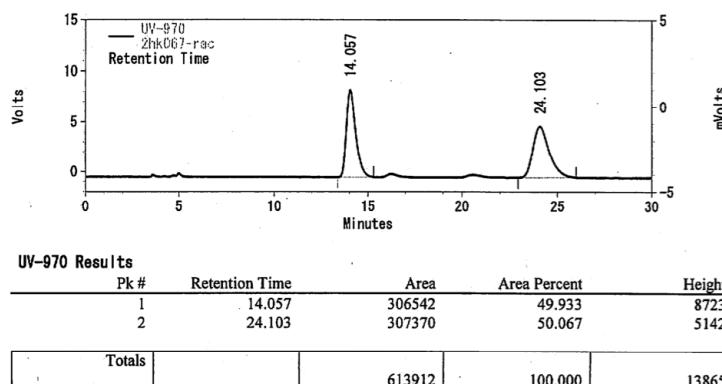
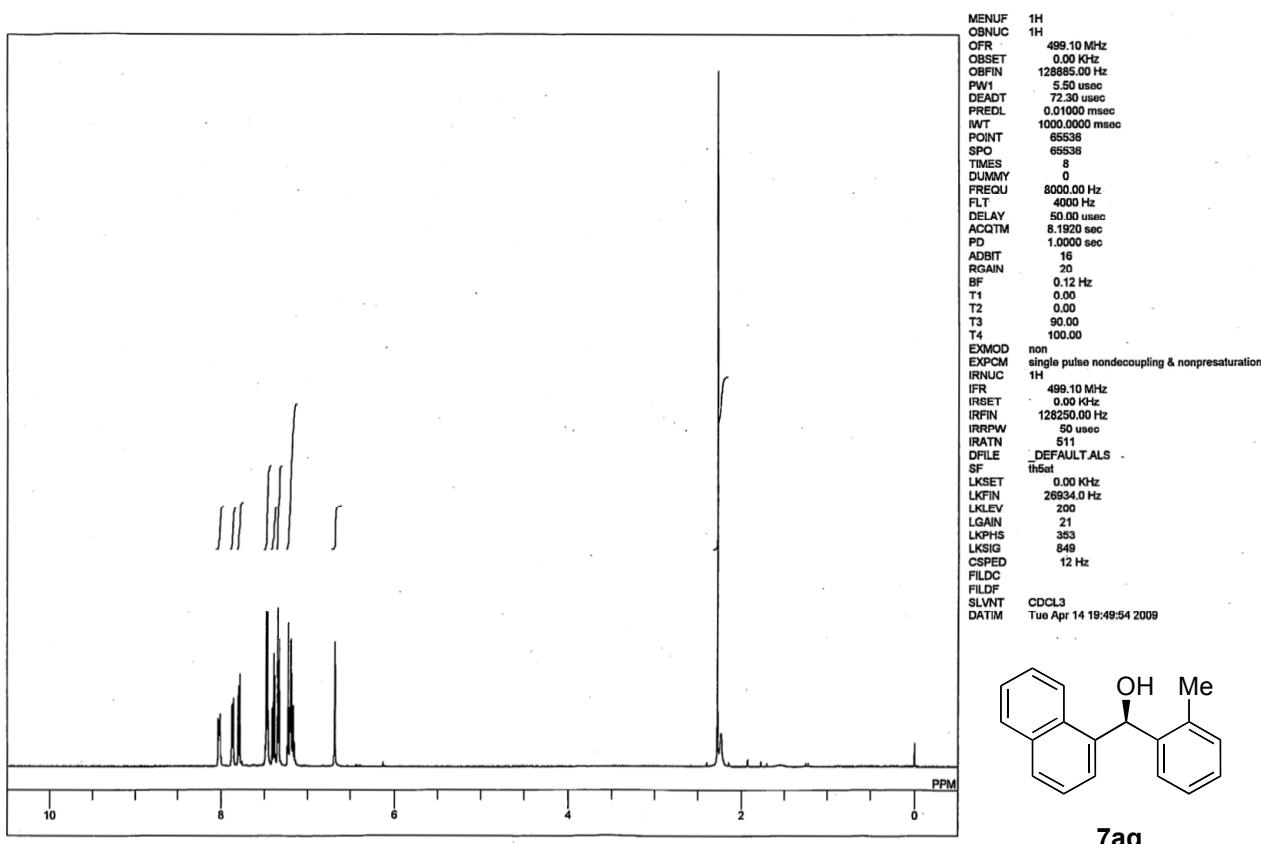
UV-970 Results

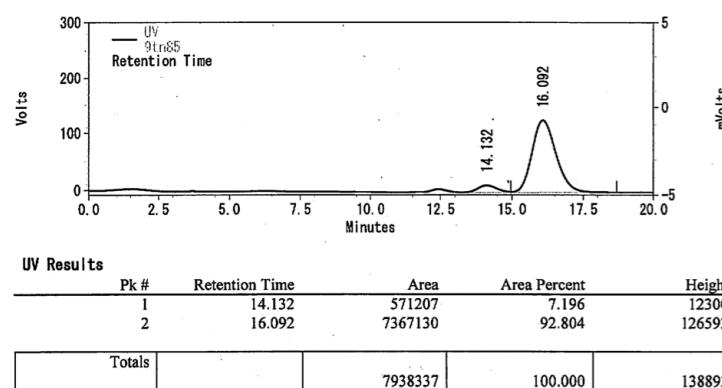
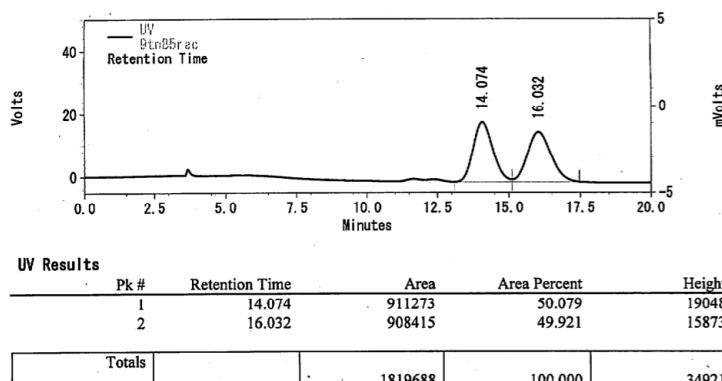
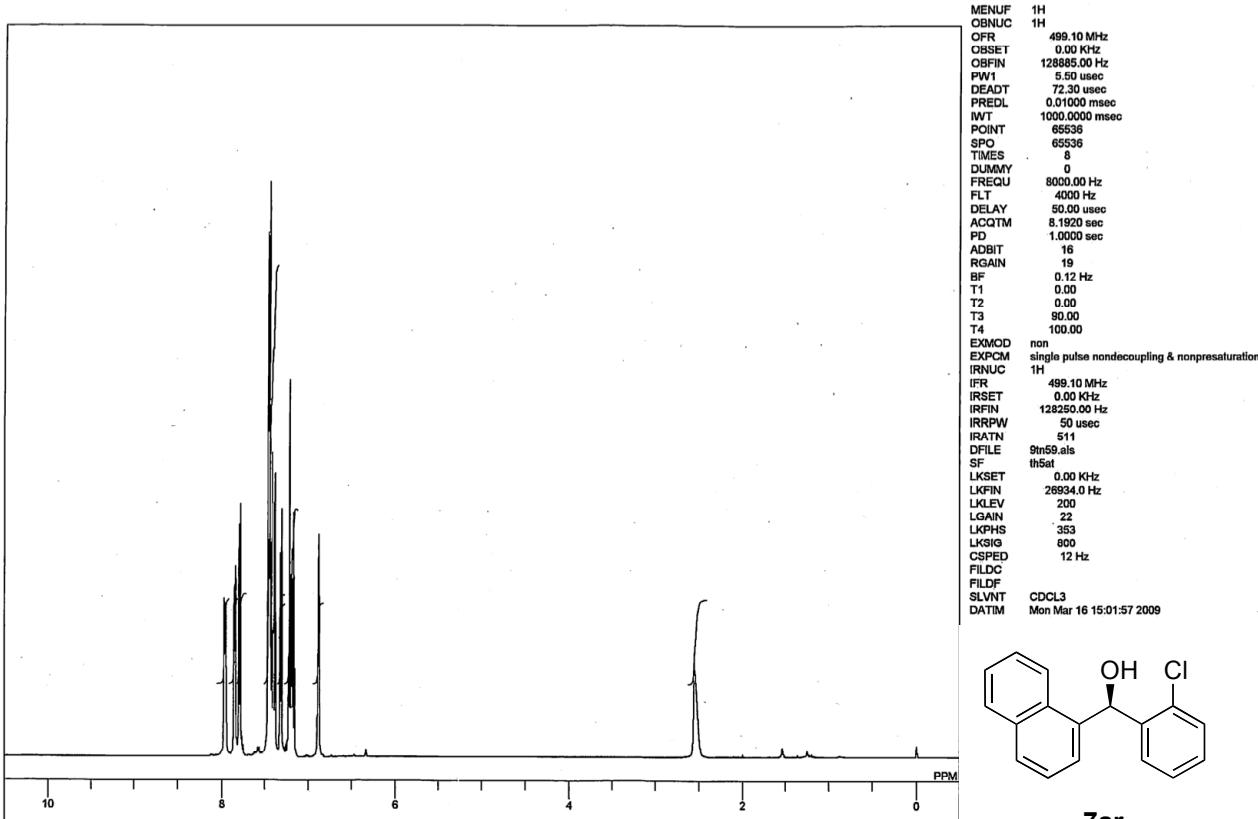
Pk #	Retention Time	Area	Area Percent	Height
1	14.086	32313623	93.334	949064
2	28.270	2307780	6.666	37757
Totals		34621403	100.000	986821

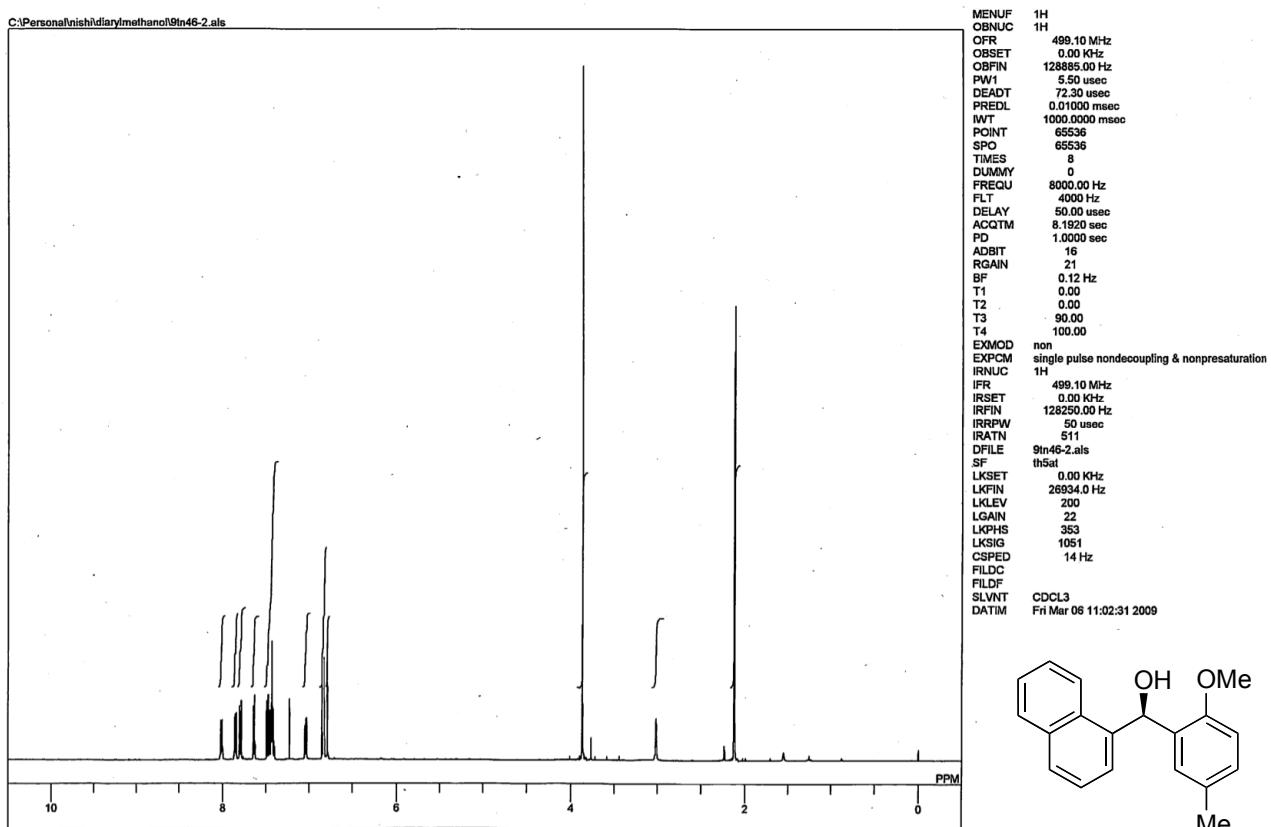




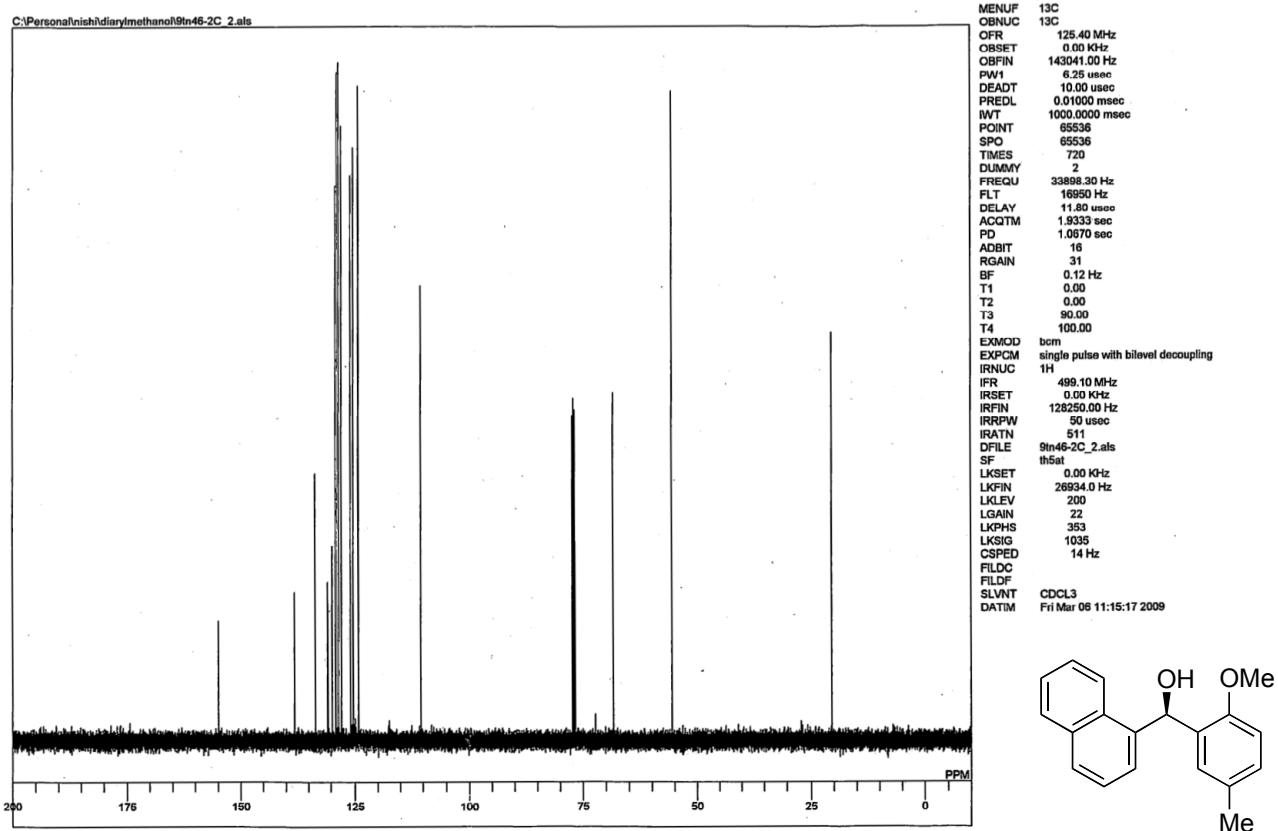




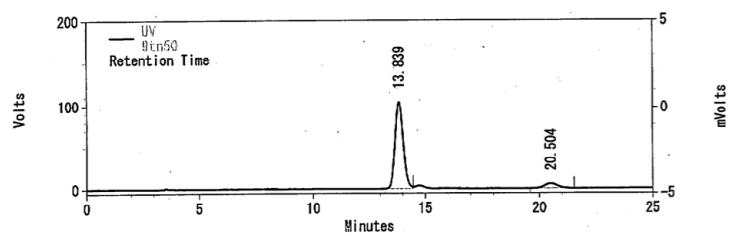
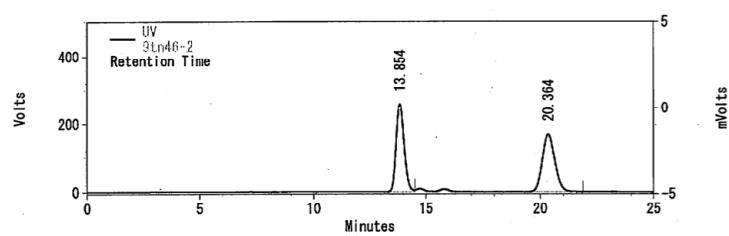


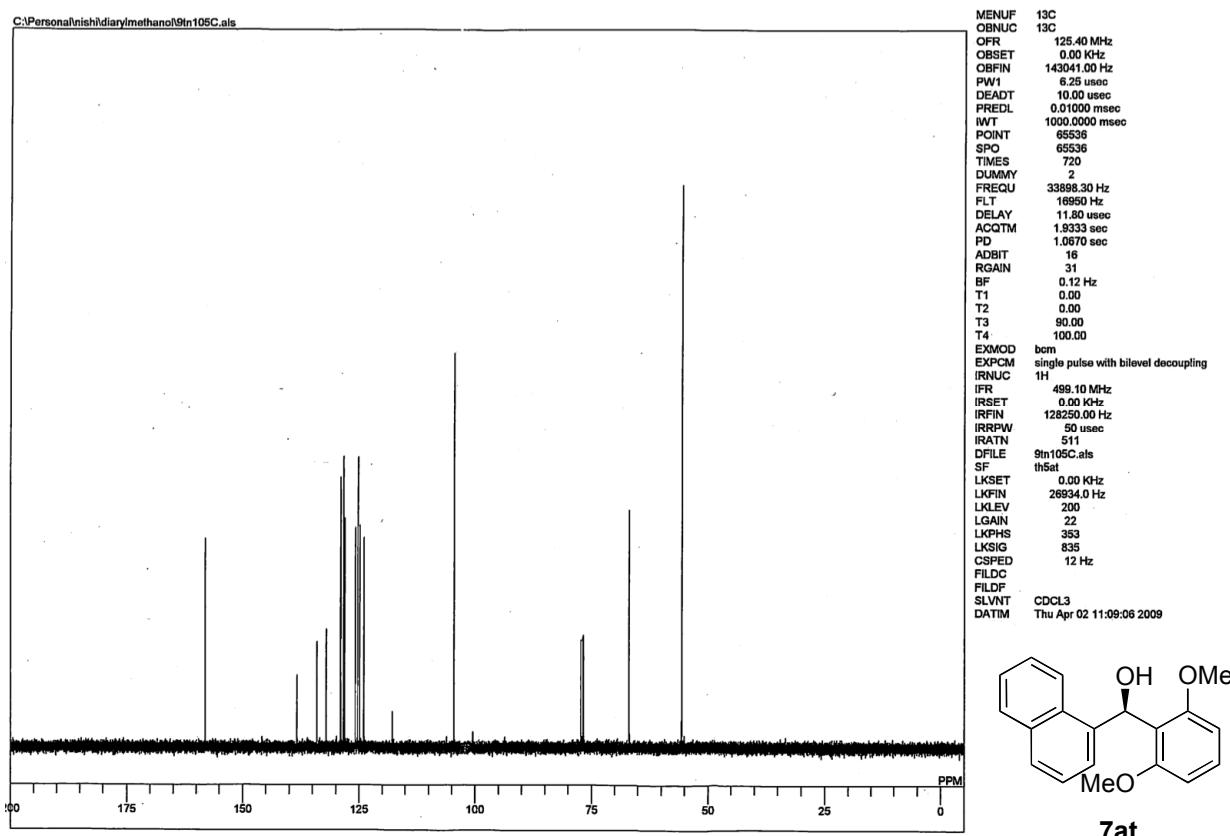
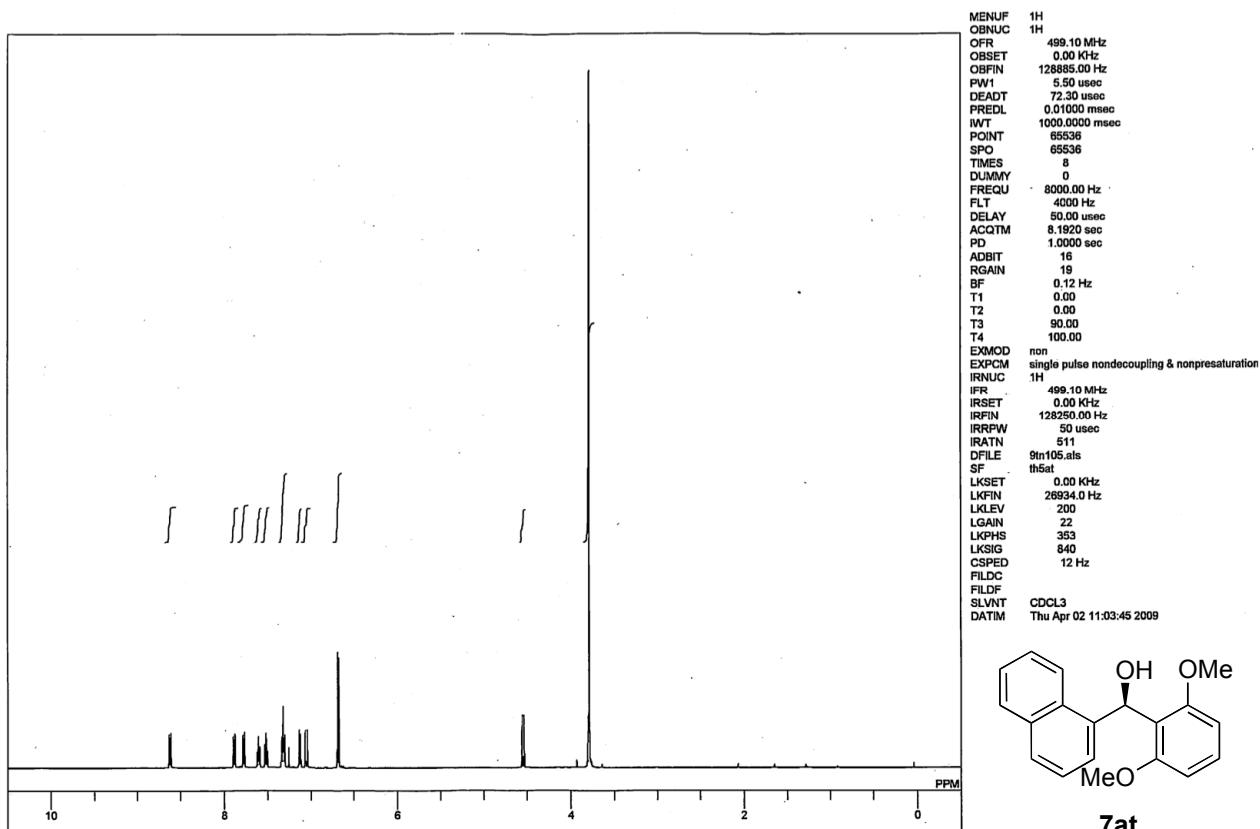


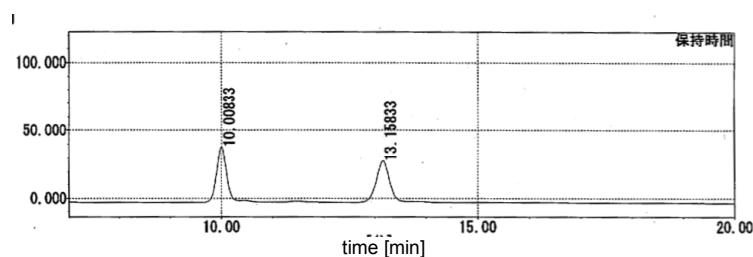
7as



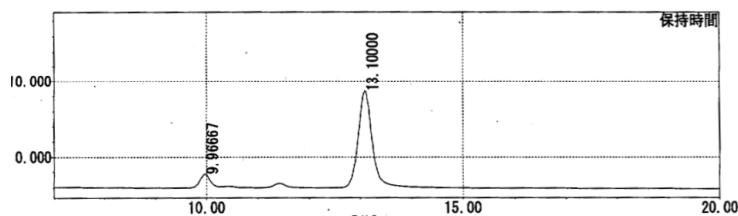
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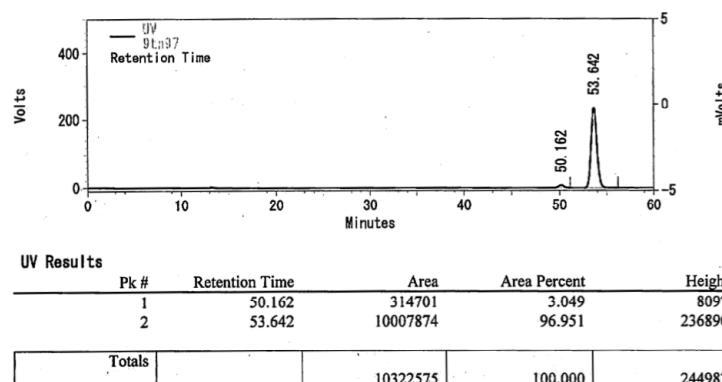
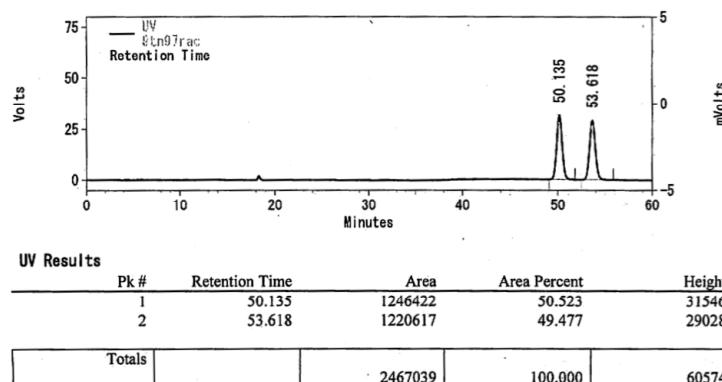
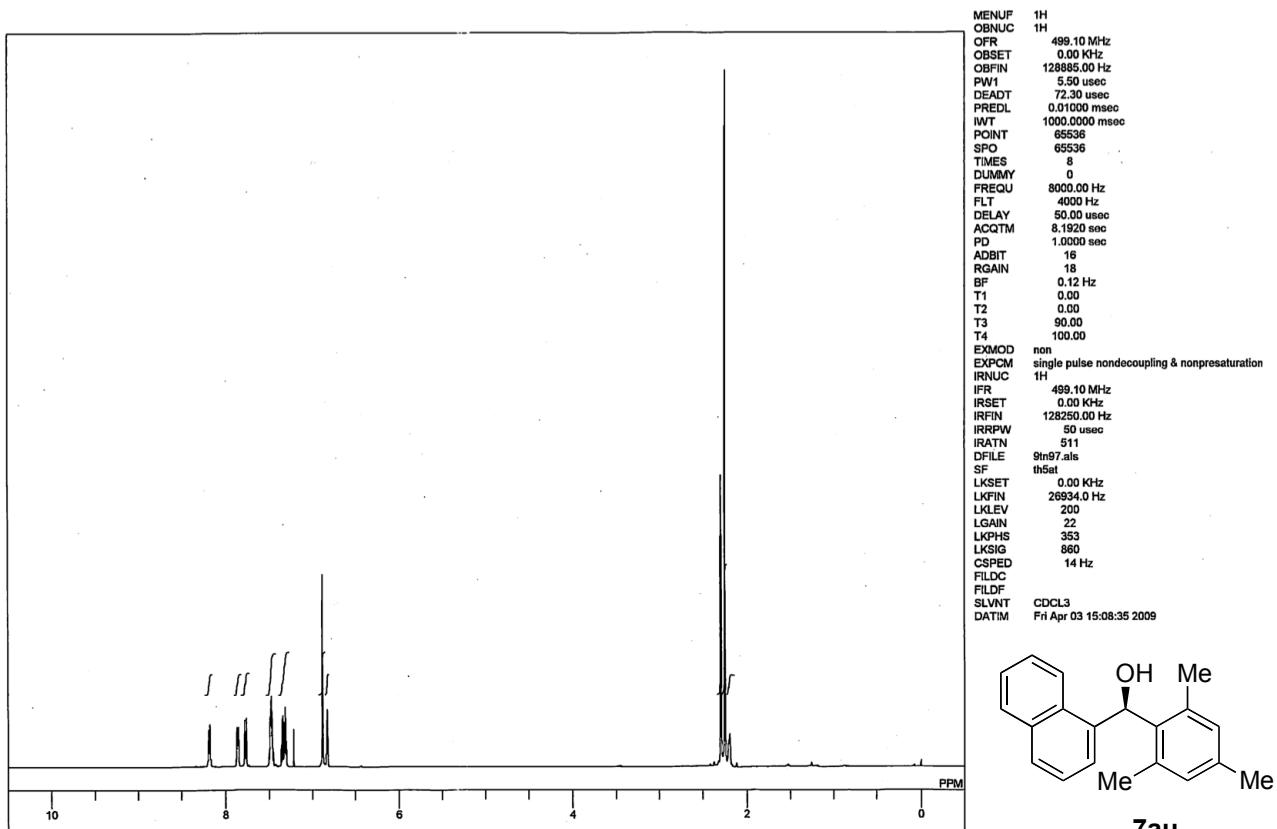


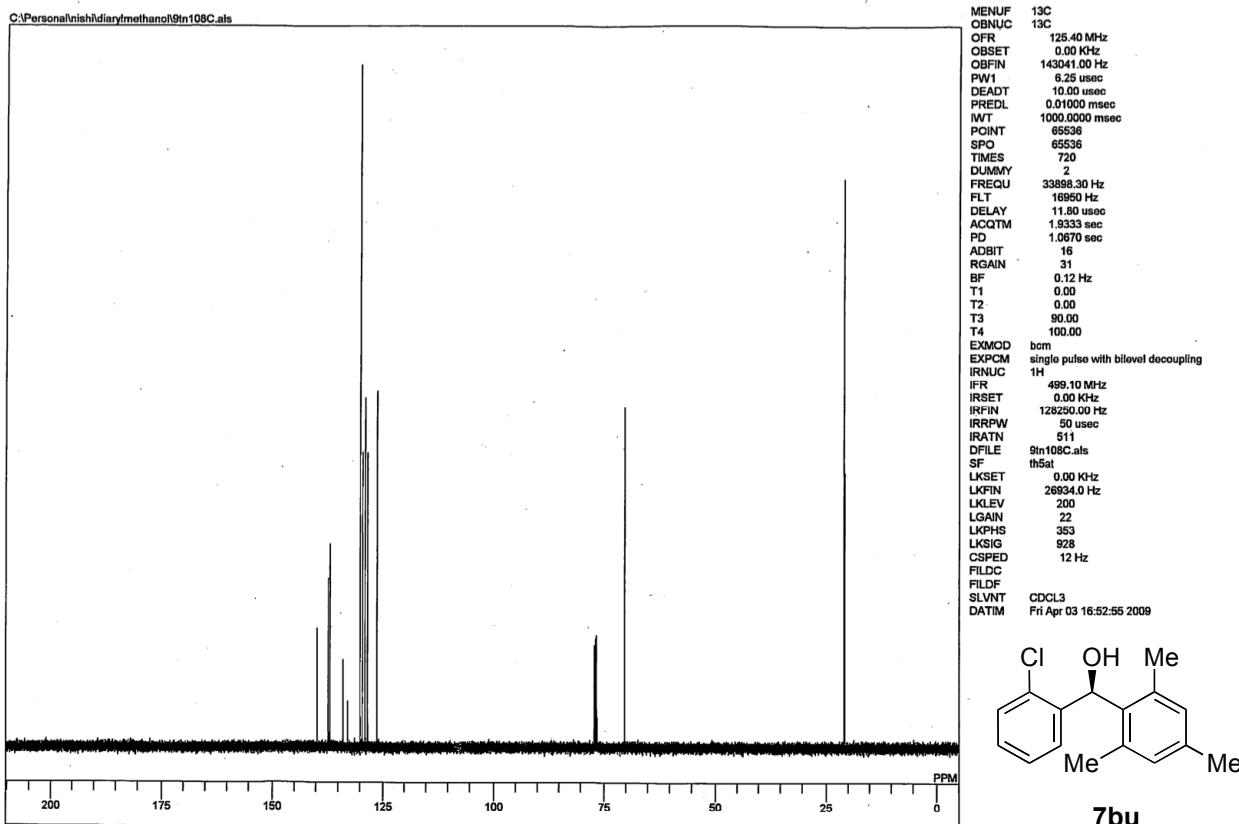
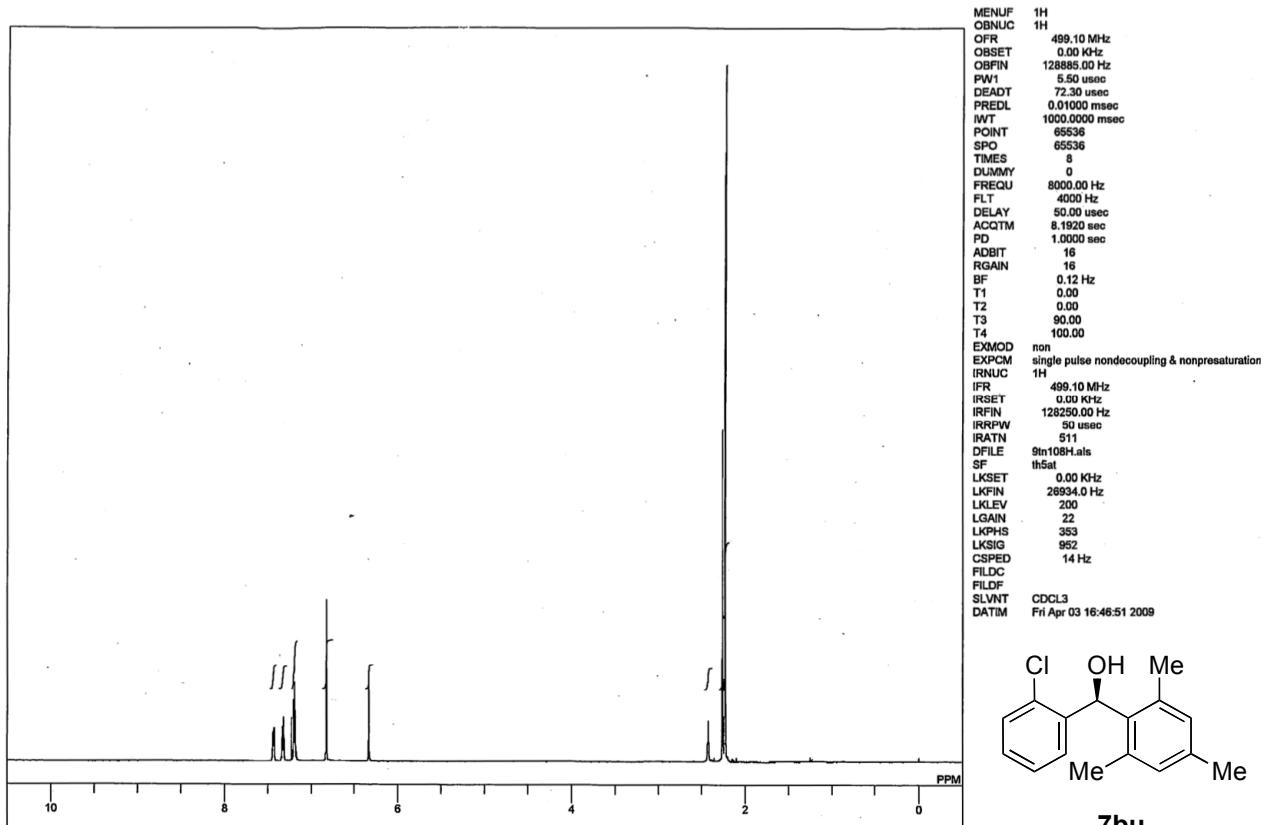


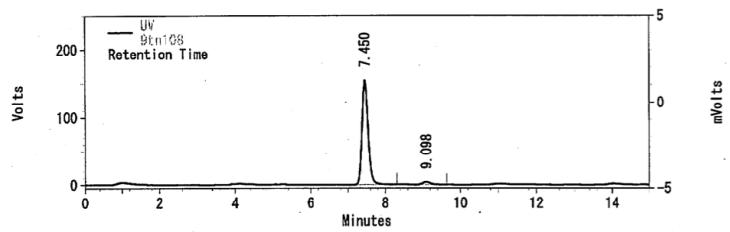
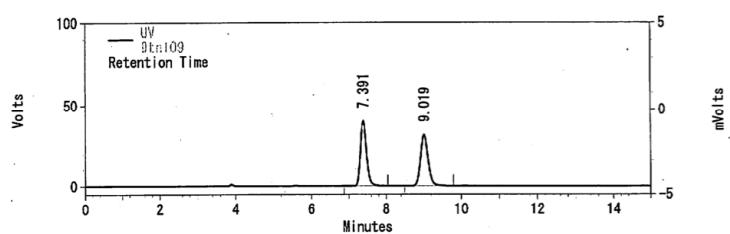
peak#	retention time	area	area (%)	height
1	10.008	528.23	49.408	40.344
2	13.158	540.990	50.592	30.629

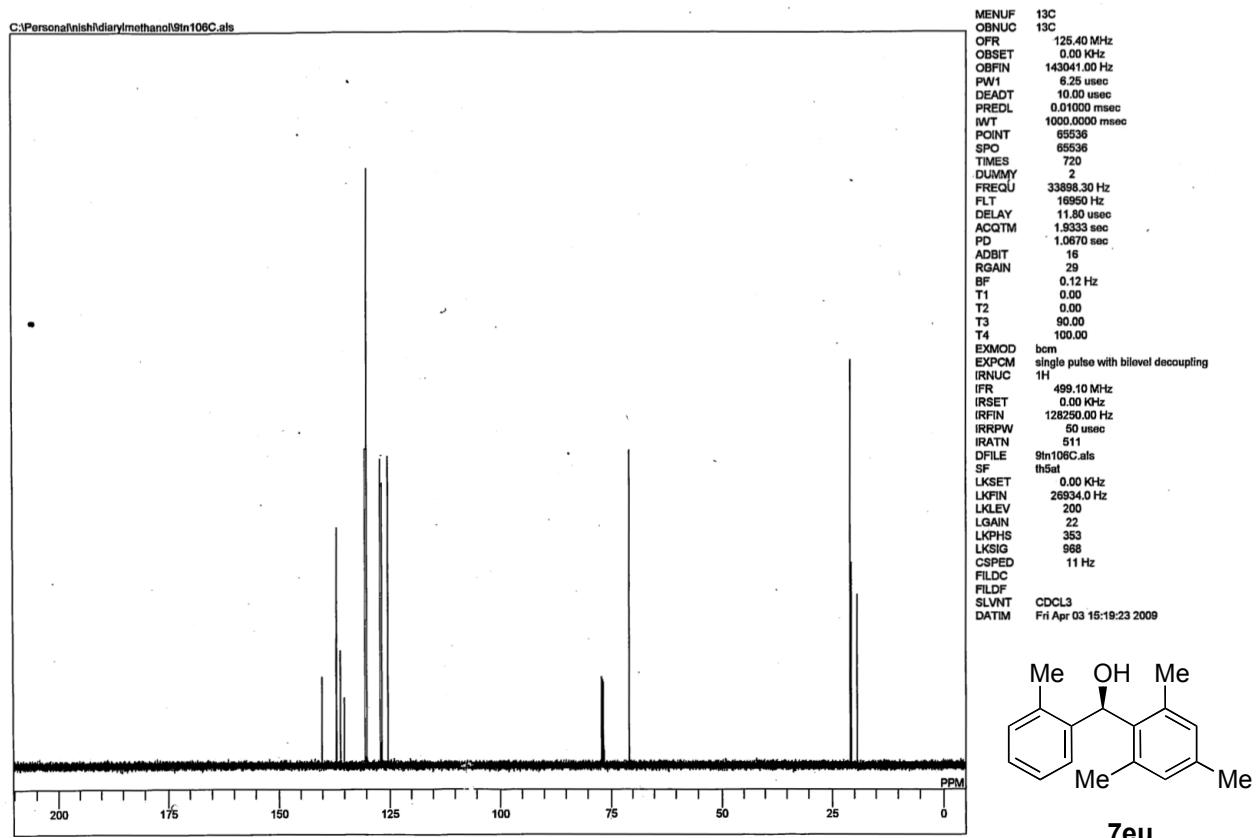
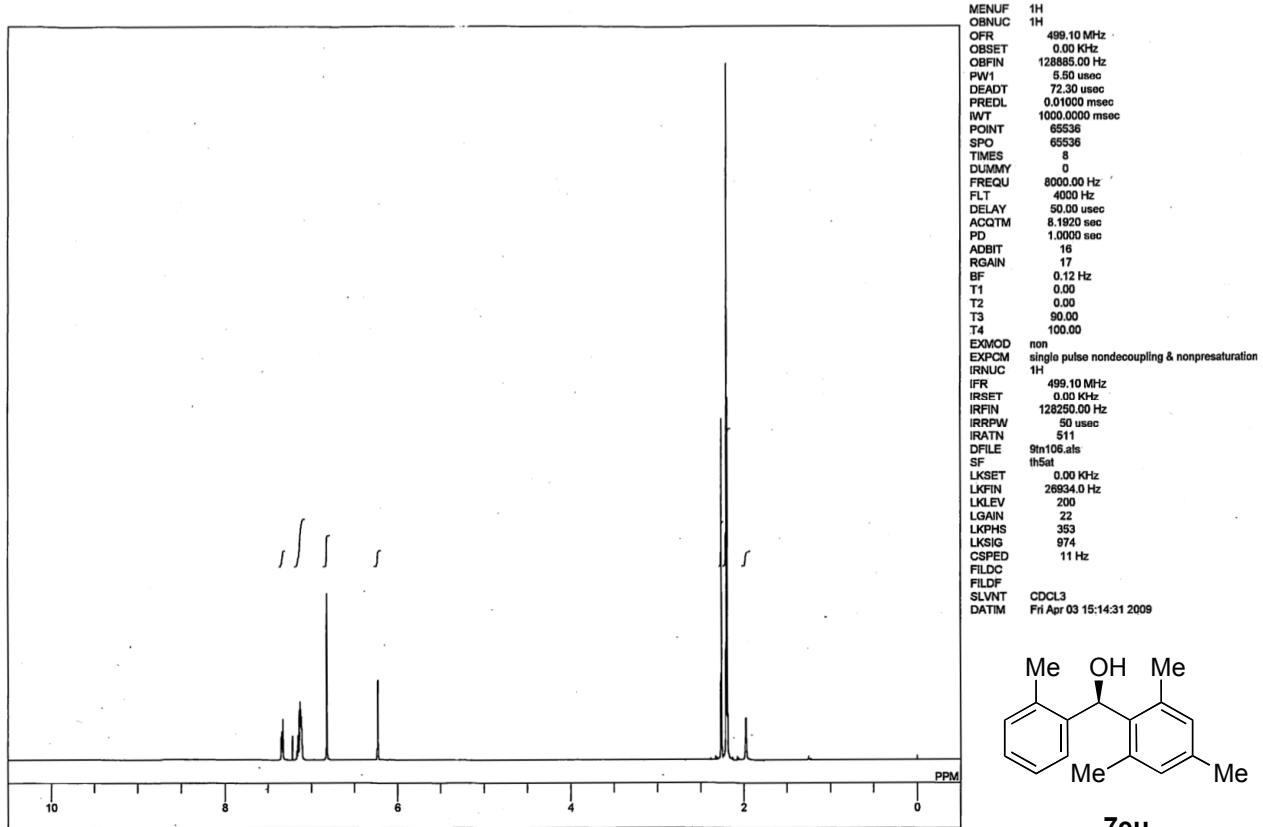


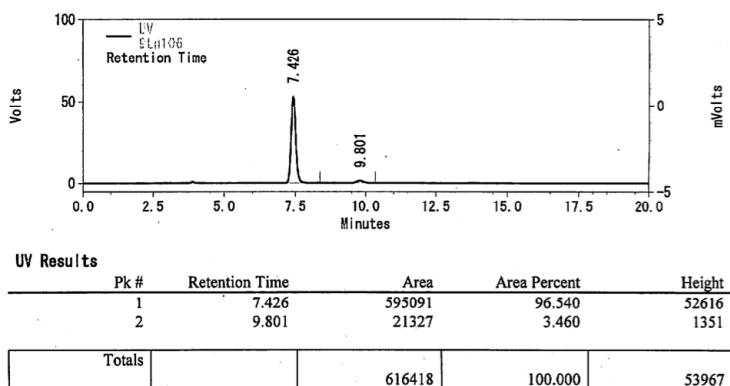
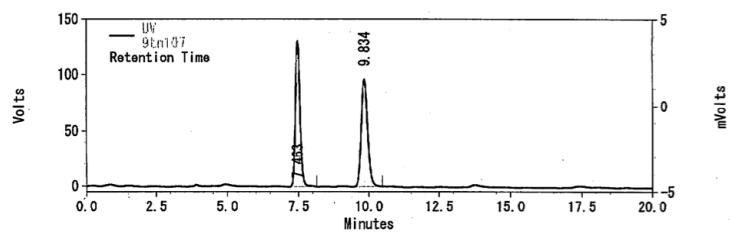
peak#	retention time	area	area (%)	height
1	9.967	21.673	8.153	1.653
2	13.100	244.153	91.847	12.654

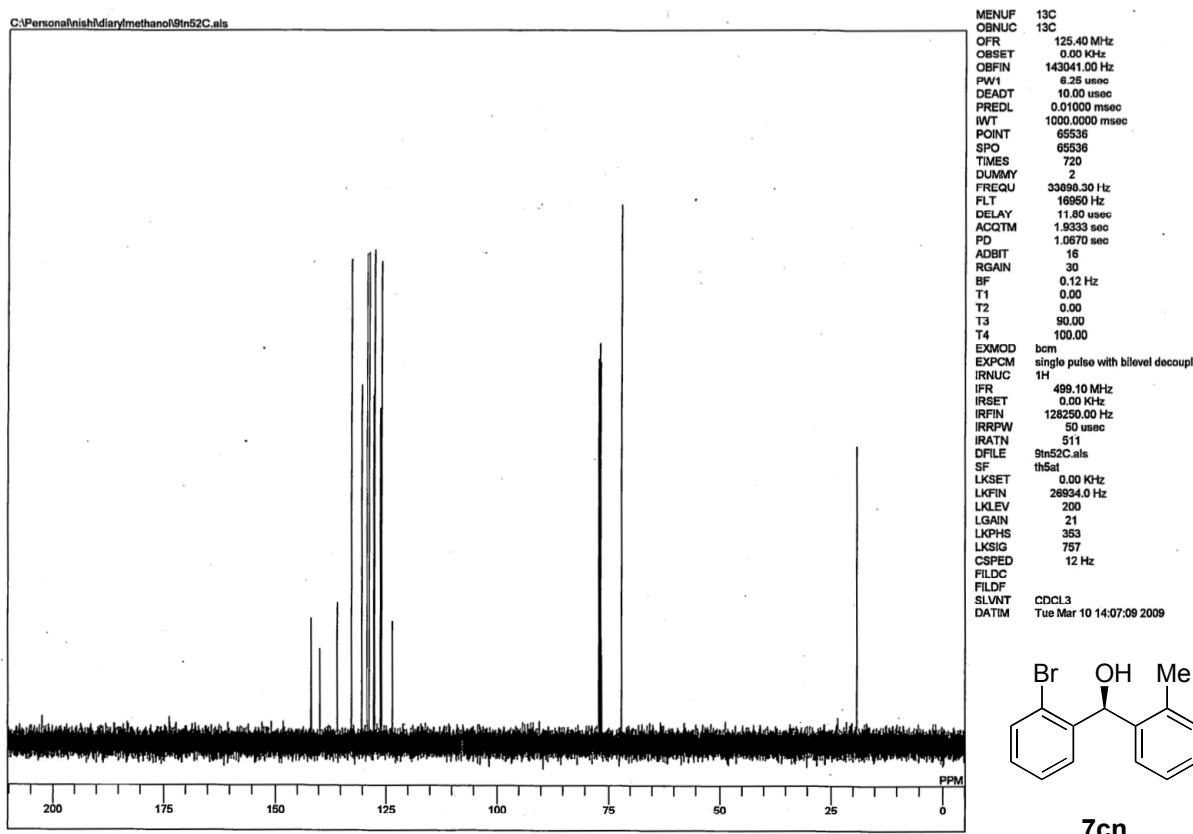
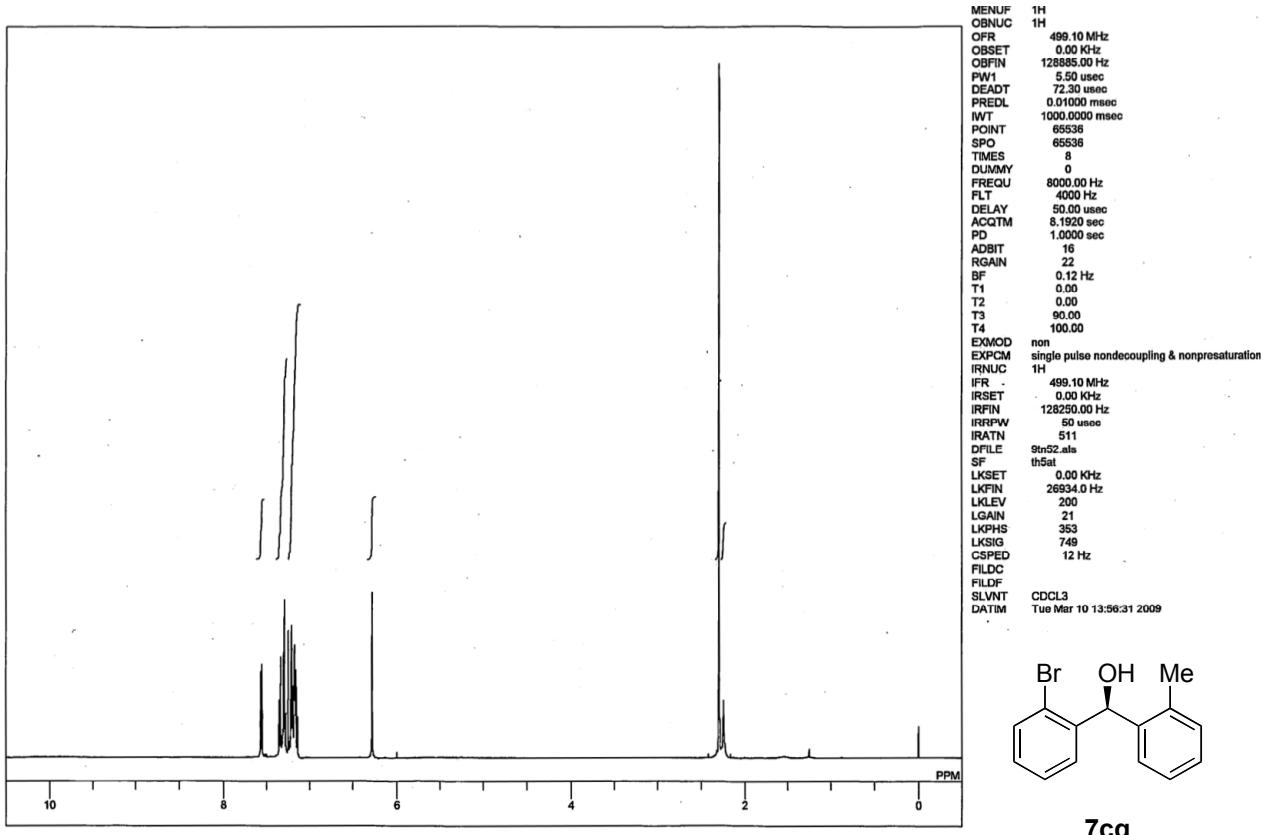


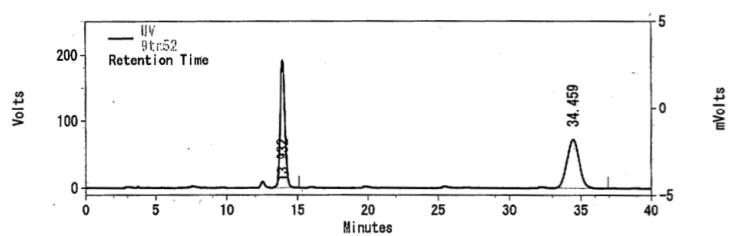






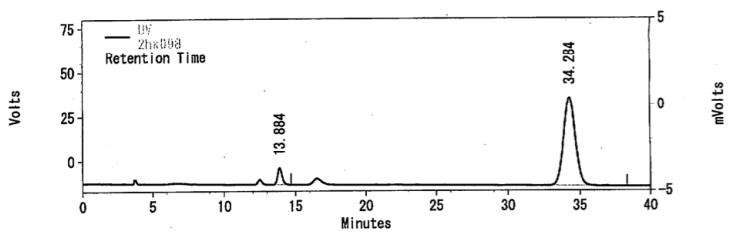






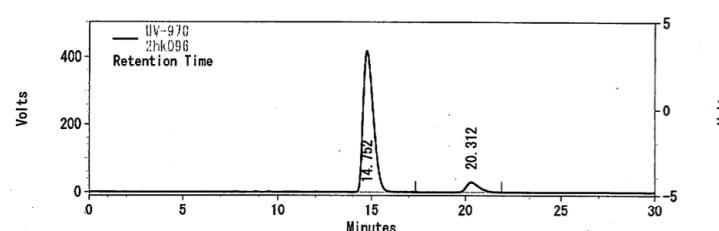
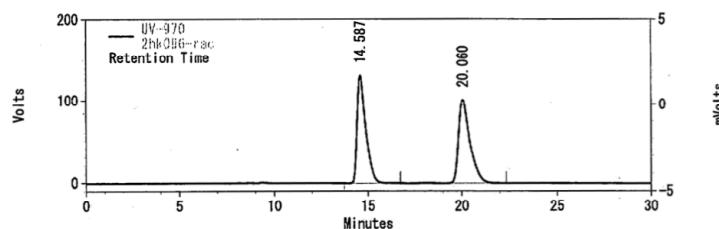
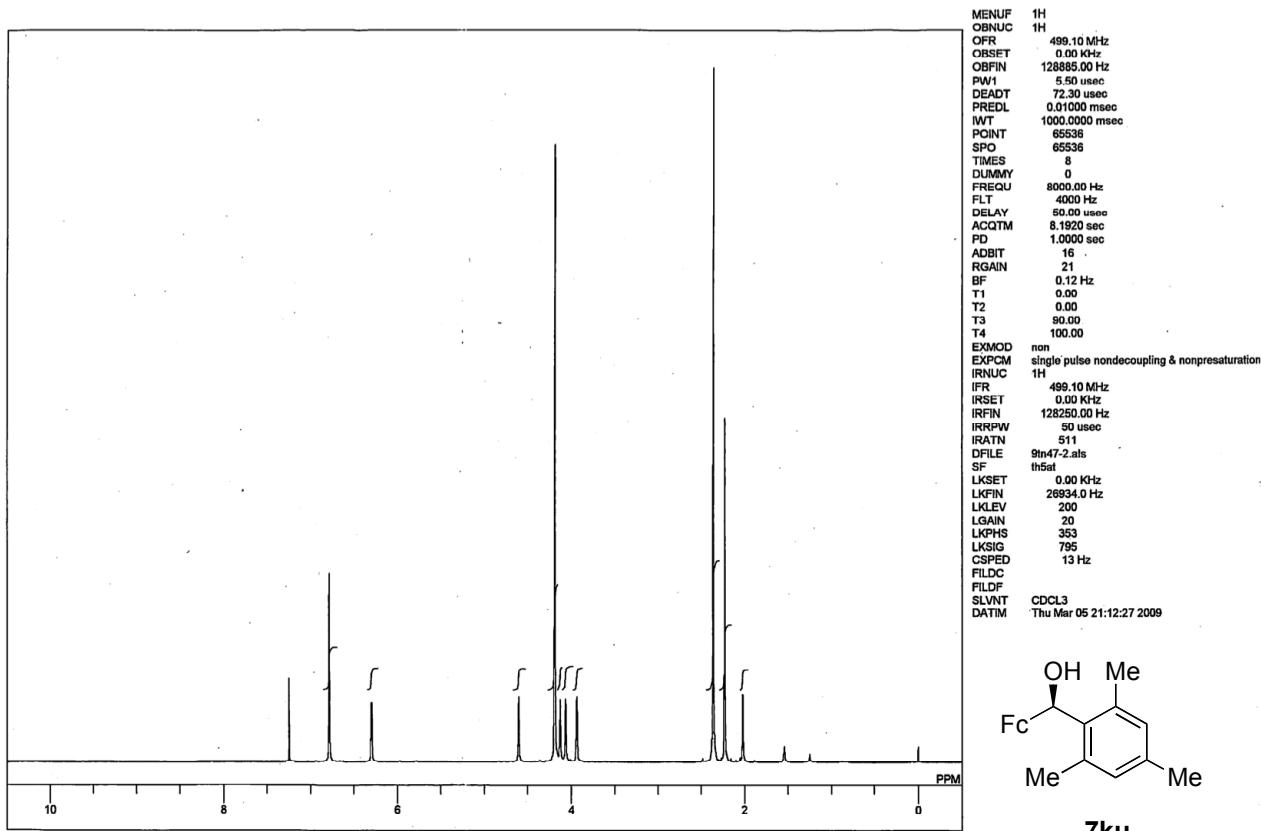
UV Results

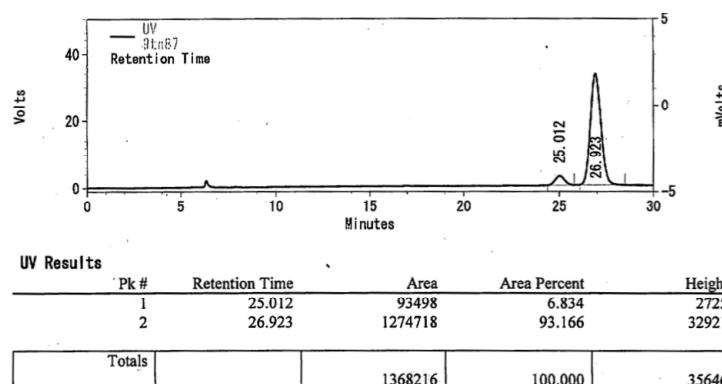
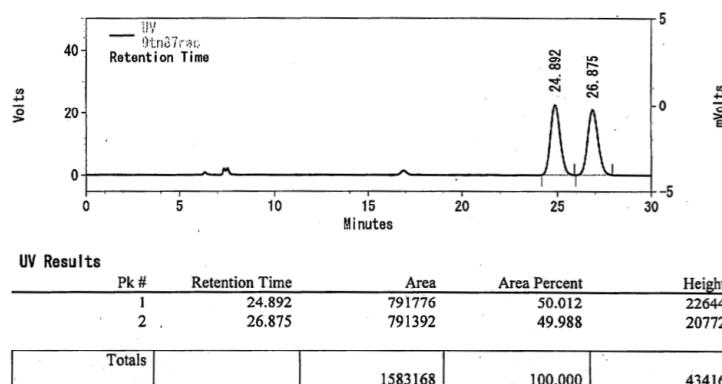
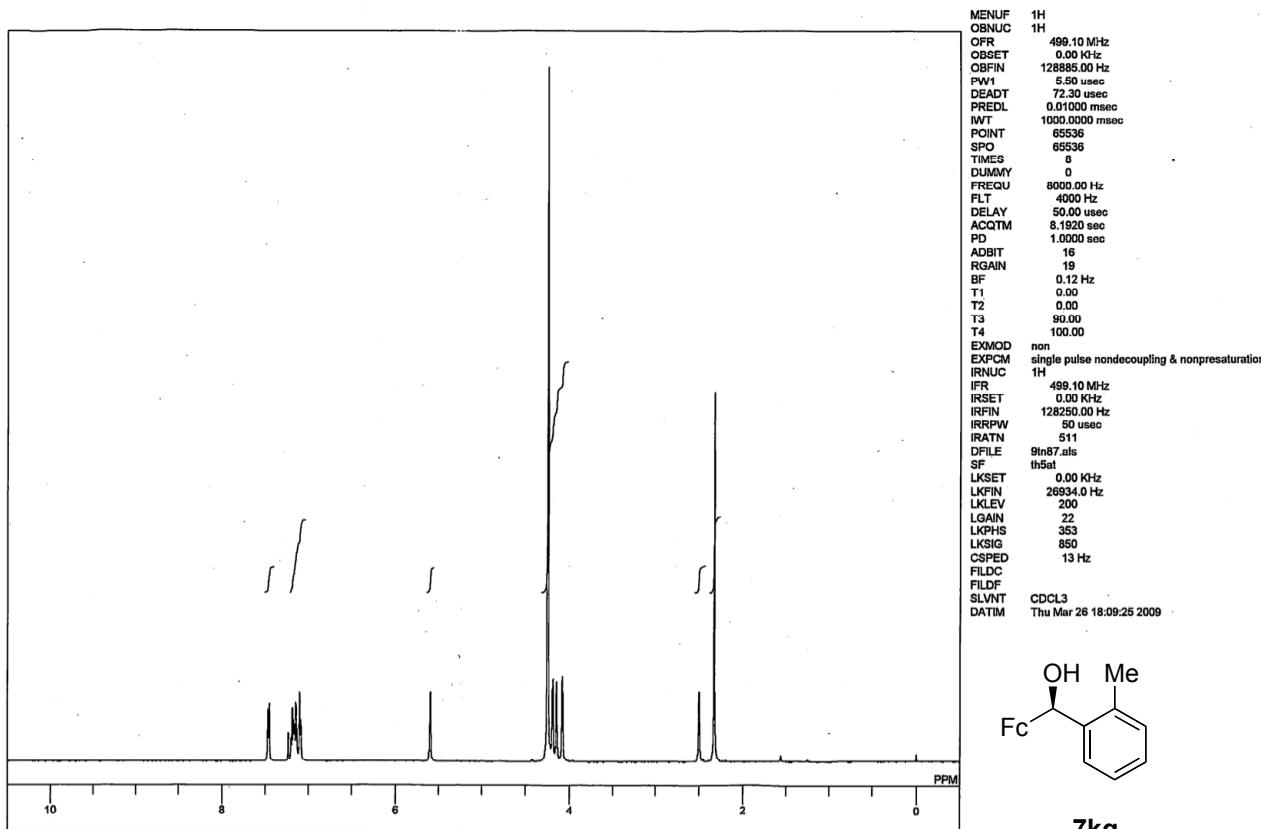
Pk #	Retention Time	Area	Area Percent	Height
1	13.932	4313807	50.275	191016
2	34.459	4266613	49.725	72367
Totals		8580420	100.000	263383

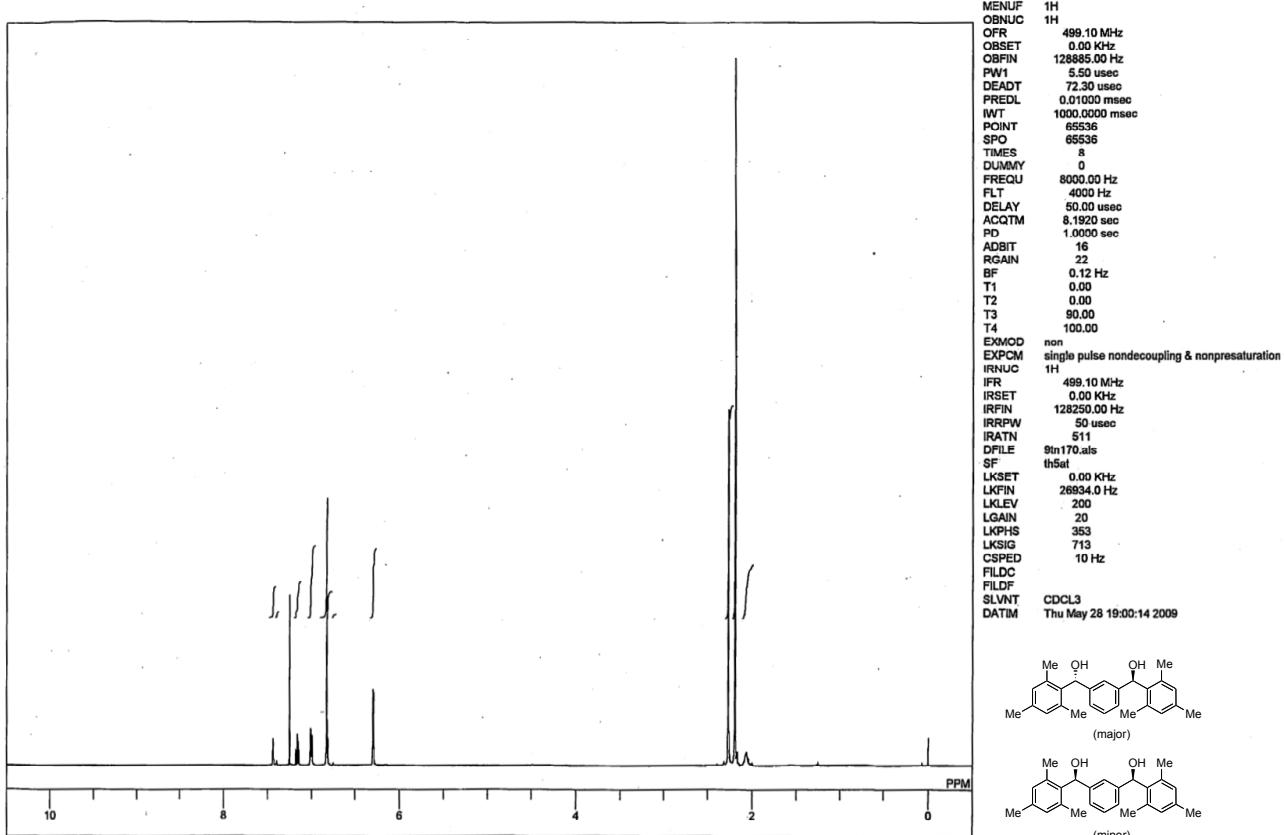


UV Results

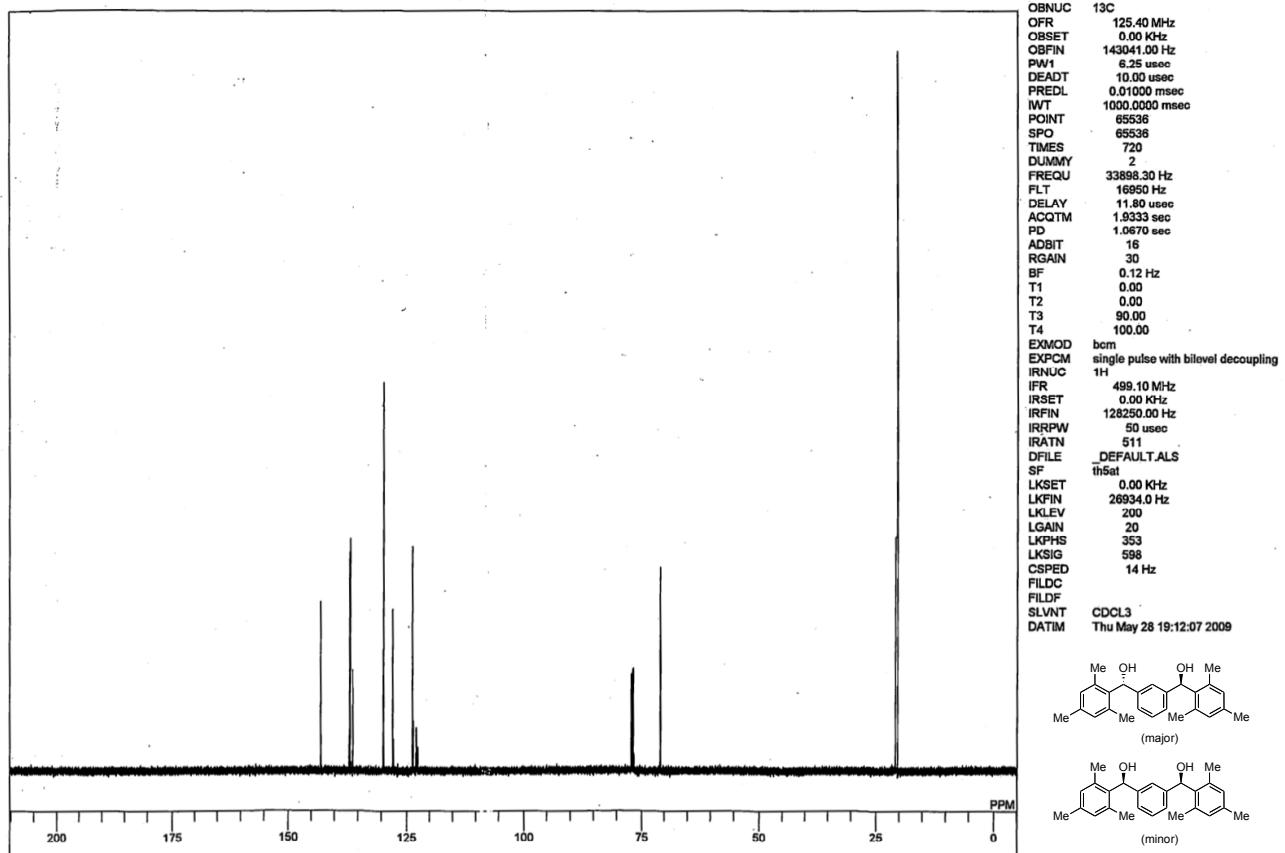
Pk #	Retention Time	Area	Area Percent	Height
1	13.884	208952	6.776	9288
2	34.284	2874861	93.224	49663
Totals		3083813	100.000	58951



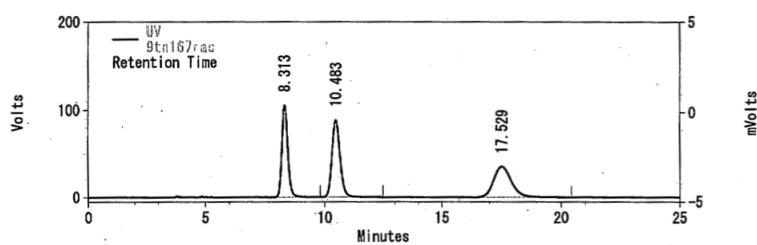




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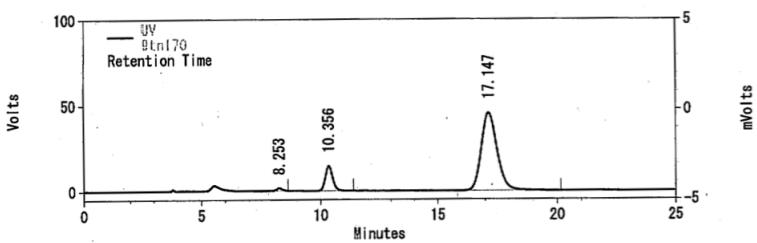


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UV Results

Pk #	Retention Time	Area	Area Percent	Height
1	8.313	1803917	31.557	105014
2	10.483	2117642	37.045	88164
3	17.529	1794899	31.399	34923
Totals		5716458	100.000	228101



UV Results

Pk #	Retention Time	Area	Area Percent	Height
1	8.253	24206	0.991	1570
2	10.356	315934	12.930	14499
3	17.147	2103357	86.080	45402
Totals		2443497	100.000	61471