Supplementary Information

Diene-transmissive hetero-Diels–Alder reaction of β,γ-unsaturated α-keto esters: facile access to optically active polyheterocycles

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1 Experimental Details

1.1 General Information

All melting points were determined on a Yanaco melting point apparatus and are uncorrected. Infrared spectra were recorded on a Horiba FT-710 model spectrophotometer. ^{1}H and ^{13}C NMR spectral data were obtained with a Bruker Avance-600, a JEOL JNM-EX 500, or a JEOL JNM-EX 300 instrument and chemical shifts are reported in ppm down field from tetramethylsilane (TMS) using an internal standard of TMS or $CDCl_3$. HRMS analysis were performed on a Bruker Daltonics microTOF.

1.2. Initial Diels–Alder reaction

a) Under thermal conditions (Table 1, entry 1). A mixture of **1** (238 mg, 1.2 mmol), ethyl vinyl ether (2.76 mL, 24 mmol) in 1,2-dichloroethane (10 mL) was heated at reflux for 39 h. The reaction mixture was evaporated, and the resulting residue was chromatographed on a column of silica gel with CH_2Cl_2/hexane (1/2) as an eluent to give ethyl 2-ethoxy-4-phenyl-3,4-dihydro-2*H*-pyran-6-carboxylate (**3**) (305 mg, *endo*:*exo* = 88:12, 95%) as a colorless oil.[1]

b) With 20 mol % amount of $Yb(OTf)_3$ at –40 °C (Table 1, entry 2). To a cooled solution of **1** (98 mg, 0.48 mmol) and $Yb(OTf)_3$ (59.6 mg, 0.096 mmol) in CH_2Cl_2 (10 mL) at –40 °C was added ethyl vinyl ether (180 μL, 1.9 mmol). The mixture was stirred at the same temperature for 1 h and then quenched by addition of aqueous $NaHCO_3$. The organic layer was separated, washed with H_2O, dried over $MgSO_4$ and evaporated. The residue was chromatographed on a column of silica gel with CH_2Cl_2/hexane (1/2) as an eluent to give **3** (123 mg, *endo*:*exo* = 90:10, 93%) as a colorless oil.

c) With 20 mol % amount of $Yb(OTf)_3$ (Table 1, entry 4). To a heated solution of **1** (102 mg, 0.5 mmol) and $Yb(OTf)_3$ (62 mg, 0.1 mmol) in CH_2Cl_2 (10 mL) at 40 °C was added slowly ethyl vinyl ether (0.72 mL, 10 mmol, 0.25 mL/h, 3 h) using a syringe pump. The mixture was cooled to room temperature and then quenched by addition of aqueous $NaHCO_3$. The organic layer was separated, dried over $MgSO_4$ and evaporated. The resulting residue was chromatographed on a column of silica gel with CH_2Cl_2/hexane (1/2) as the eluent to give the adduct **3** (127 mg, *endo*:*exo* = 5:95, 92%) as a colorless oil.

d) Enantioselective reaction (Scheme 4).[1a] To a solution of **1** (803 mg, 3.93 mmol), molecular sieves 3Å (267 mg) and **20** (53 mg, 0.079 mmol, 2.0 mol%) in THF (5 mL) cooled at 0 °C was added ethyl vinyl ether (180 μL, 1.9 mmol). After stirring at the same temperature for 14 h, the mixture was evaporated. The residue was chromatographed on a column of silica gel with AcOEt/hexane (1/30) as an eluent to give (2*R*,4*R*)-**3**[1a] (975 mg, *endo*:*exo* = 96:4, 89%, 98% ee) as a colorless oil. Ee was determined by HPLC analysis using a chiral column (Chiralpak IB: 4.6×150 mm, 254 nm, UV

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[1] (*a*) D. A. Evans, J. S. Johnson and E. J. Olhava, *J. Am. Chem. Soc.*, 2000, **122**, 1635. (*b*) A. Barba, S. Barroso, G. Blay, L. Cardona, M. Melegari and J. R. Pedro, *Synlett*, 2011, 1592.

detector, rt, eluent: *i*PrOH/hexane (1/50), flow rate: 1 mL/min, retention time 6.9 min for major isomer and 7.5 min for minor isomer).

1.3. Tebbe methylenation

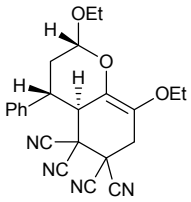
Typical procedure for Tebbe methylenation: Synthesis of 2-ethoxy-6-(1-ethoxyvinyl)-4-phenyl-3,4-dihydro- 2*H*-pyran (5): To a solution of *endo*-**3** (300 mg, 1.08 mmol) in THF (0.8 mL) was added 0.5 M toluene solution of Tebbe reagent (2.60 mL, 1.30 mmol) at 0 °C. After stirring for 1 h, the reaction mixture was diluted with 5 mL of diethyl ether, quenched with 0.1 M aqueous NaOH (1 mL), and filtered through a pad of alumina with AcOEt/hexane (1/50). The filtrate was dried over $MgSO_4$ and evaporated. The resulting residue was purified by passing a short column of alumina with AcOEt/hexane (1/50) as the eluent to give (2*R**,4*R**)-2-ethoxy-6-(1-ethoxyvinyl)-4-phenyl- 3,4-dihydro-2*H*-pyran (*endo*-**5**) as a colorless oil (242 mg, 81%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.26 (t, J = 7.0 Hz, 3H), 1.30 (t, J = 7.0 Hz, 3H), 1.90 (ddd, J = 8.9, 10.9, 13.1 Hz, 1H), 2.27 (dddd, J = 1.2, 1.8, 6.7, 13.1 Hz, 1H), 3.63 (dq, J = 7.0, 9.8 Hz, 1H), 3.70 (ddd, J = 2.8, 6.7, 10.4 Hz, 1H), 3.78–3.84 (m, 2H), 4.02 (dq, J = 7.0, 9.8 Hz, 1H), 4.15 (d, J = 1.8 Hz, 1H), 4.68 (d, J = 1.8 Hz, 1H), 5.09 (dd, J = 1.8, 8.9 Hz, 1H), 5.45 (dd, J = 1.2, 2.8 Hz, 1H), 7.20–7.32 (m, 5H). ^{13}C-NMR (76 MHz, $CDCl_3$) δ 14.4 (CH_3), 15.2 (CH_3), 37.1 (CH_2), 38.2 (CH), 63.1 (CH_2), 64.4 (CH_2), 82.4 (CH_2), 100.0 (CH), 102.0 (CH), 126.4 (CH), 127.4 (2×CH), 128.4 (2×CH), 144.5 (C), 146.1 (C), 154.7 (C).

(2*S,4*R**)-2-(ethylthio)-6-(1-ethoxyvinyl)-4-phenyl-3,4-dihydro-2*H*-pyran (*endo*-6):** yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.30 (t, J = 6.8 Hz, 3H), 1.35 (t, J = 7.5 Hz, 3H), 1.95 (ddd, J = 11.0, 11.0, 13.4 Hz, 1H), 2.37 (dddd, J = 1.7, 1.8, 6.6, 13.4 Hz, 1H), 2.75 (dq, J = 7.5, 12.9 Hz, 1H) 2.84 (dq, J = 7.5, 12.9 Hz, 1H), 3.71 (ddd, J = 2.4, 6.6, 11.0 Hz, 1H), 3.76–3.85 (m, 2H), 4.15 (d, J = 1.8 Hz, 1H), 4.69 (d, J = 1.8 Hz, 1H), 5.22 (dd, J = 1.8, 11.0 Hz, 1H), 5.50 (dd, J = 1.7, 2.4 Hz, 1H), 7.19–7.33 (m, 5H). ^{13}C-NMR (76 MHz, $CDCl_3$) δ 14.4 (CH_3), 15.2 (CH_3), 24.7 (CH_2), 37.8 (CH_2), 39.2 (CH), 63.1 (CH_2), 80.7 (CH), 82.6 (CH_2), 101.9 (CH), 126.6 (CH), 127.3 (2×CH), 128.5 (2×CH), 144.3 (C), 148.0 (C), 154.5 (C).

(2*S,4*R**)-2-ethoxy-6-(1-ethoxyvinyl)-4-phenyl-3,4-dihydro-2*H*-pyran (*exo*-5):** colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.24 (t, J = 7.0 Hz, 3H), 1.31 (t, J = 7.0 Hz, 3H), 1.85 (ddd, J = 2.8, 11.0, 13.4 Hz, 1H), 2.15 (dddd, J = 1.2, 3.1, 6.1, 13.4 Hz, 1H), 3.65 (dq, J = 7.0, 9.8 Hz, 1H), 3.73 (ddd, J = 2.8, 6.1, 11.0 Hz, 1H), 3.78–3.84 (m, 2H), 3.90 (dq, J = 7.0, 9.8 Hz, 1H), 4.13 (d, J = 1.8 Hz, 1H), 4.67 (d, J = 1.8 Hz, 1H), 5.19 (dd, J = 2.8, 3.1 Hz, 1H), 5.54 (dd, J = 1.2, 2.8 Hz, 1H), 7.20–7.32 (m, 5H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 14.4 (CH_3), 15.2 (CH_3), 34.0 (CH), 35.7 (CH_2), 63.1 (CH_2), 63.8 (CH_2), 81.9 (CH_2), 96.6 (CH), 102.3 (CH), 126.4 (CH), 127.7 (2×CH), 128.5 (2×CH), 144.4 (C), 145.2 (C), 155.0 (C).

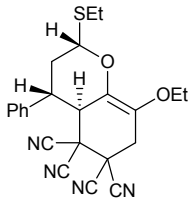
1.4. Second DA Reaction

a) Typical experimental procedure for the DA reaction with tetracyanoethylene (TCNE): Synthesis of 7 (Scheme 2). A mixture of *endo*-**5** (97 mg, 0.35 mmol) and TCNE (54 mg, 0.43 mmol) in CH_2Cl_2 (10 mL) was stirred at room



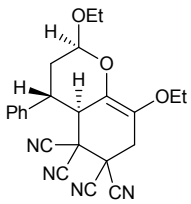
temperature for 4 h. The reaction mixture was evaporated, and the resulting residue was chromatographed on a column of silica gel with AcOEt/hexane (1/2) as an eluent to give (2*R**,4*R**,4a*R**)-2,8-diethoxy-4-phenyl- 3,4,4a,7-tetrahydro-2*H*-chromene-5,5,6,6-tetracarbonitrile (**7**) (125 mg, 88%) as colorless crystals. Mp: 101.3–102.0 °C. IR (KBr): *v* 1149.4 (s), 1380.8 (m), 1442.5 (m), 1689.3 (m), 2985.3 (s) cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 1.30 (3H, t, *J* = 7.1 Hz), 1.32 (3H, t, *J* = 7.1 Hz), 2.22 (1H, ddd, *J* = 7.4, 11.5, 14.2 Hz), 2.37 (1H, ddd, *J* = 3.1, 5.2, 14.0 Hz), 3.08 (1H, d, *J* = 17.4 Hz), 3.14 (1H, ddd, *J* = 5.2, 11.5, 11.5 Hz), 3.24 (1H, dd, *J* = 3.1, 17.5 Hz), 3.40 (1H, dd, *J* = 2.1, 11.5 Hz), 3.65 (1H, dq, *J* = 7.1, 9.3 Hz), 3.96 (1H, dq, *J* = 7.1, 9.4 Hz), 3.99 (1H, dq, *J* = 7.1, 9.4 Hz), 4.17 (1H, dq, *J* = 7.1, 9.4 Hz), 4.85 (1H, dd, *J* = 3.1, 7.4 Hz), 7.41–7.47 (5H, m). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 15.1 (CH_3), 15.6 (CH_3), 33.8 (CH_2), 38.0 (CH_2), 39.7 (C), 43.1 (CH), 43.3 (C), 44.6 (CH), 65.3 (CH_2), 67.8 (CH_2), 100.7 (CH), 108.7 (C), 108.9 (C), 109.9 (C), 110.4 (C), 128.4 (2×CH), 129.7 (CH), 129.8 (2×CH), 131.0 (C), 131.0 (C), 137.3 (C). HRMS (ESI) Calcd for $C_{23}H_{22}N_4NaO_3$ $[M+Na]^+$: 425.1590, Found: 425.1584. Anal. Calcd for $C_{23}H_{22}N_4O_3$: C, 68.64; H, 5.51; N, 13.92. Found: C, 68.60; H, 5.57; N, 13.61.

(2*S,4*R**,4a*R**)-8-ethoxy-2-(ethylthio)-4-phenyl-3,4,4a,7-tetrahydro-2*H*-chromene-5,5,6,6-tetracarbonitrile (8):** Colorless



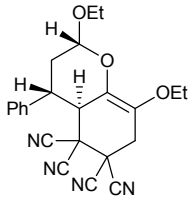
crystals. Mp: 134.7–136.4 °C. IR (KBr): ν 1079.9 (s), 1203.4 (s), 1450.2 (m), 1689.3 (m), 2977.6 (s) 3448.1 (br) cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.32 (t, *J* = 7.0 Hz, 3H), 1.36 (t, *J* = 7.3 Hz, 3H), 2.30–2.34 (m, 2H), 2.77 (dq, *J* = 7.3, 12.8 Hz, 1H), 2.83 (dq, *J* = 7.3, 12.8 Hz, 1H), 3.09 (dd, *J* = 0.9, 17.7 Hz, 1H), 3.14–3.19 (m, 1H), 3.24 (dd, *J* = 2.7, 17.7 Hz, 1H), 3.29 (ddd, *J* = 0.9, 2.7, 11.3 Hz, 1H), 3.93 (dq, *J* = 7.0, 9.5 Hz, 1H), 4.15 (dq, *J* = 7.0, 9.5 Hz, 1H), 4.81–4.87 (m, 1H), 7.38–7.40 (m, 2H), 7.43–7.45 (m, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 14.9 (CH_3), 15.4 (CH_3), 25.0 (CH_2), 33.5 (CH_2), 38.6 (CH_2), 39.6 (C), 43.4 (C), 44.8 (CH), 46.1 (CH), 67.7 (CH_2), 83.6 (CH), 108.6 (C), 108.9 (C), 109.8 (C), 110.3 (C), 129.72 (CH), 129.73 (4×CH), 132.1 (C), 132.3 (C), 136.9 (C). HRMS (ESI) Calcd for $C_{23}H_{22}N_4NaO_2S$ $[M+Na]^+$: 441.1356, Found: 441.1373. Anal. Calcd for $C_{23}H_{22}N_4O_2S$: C, 66.01; H, 5.50; N, 13.39. Found: C, 65.61; H, 5.38; N, 13.17.

(2*S,4*R**,4a*R**)-2,8-diethoxy-4-phenyl-3,4,4a,7-tetrahydro-2*H*-chromene-5,5,6,6-tetracarbonitrile (16):** Colorless crystals. Mp 101.3–102.0 °C. IR (KBr): ν 1149.4 (s), 1380.8 (m), 1442.5 (m), 1689.3 (m), 2985.3 (s) cm^{-1}. ^{1}H-



NMR (600 MHz, $CDCl_3$) δ 1.30 (3H, t, *J* = 7.1 Hz), 1.32 (3H, t, *J* = 7.1 Hz), 2.22 (1H, ddd, *J* = 7.4, 11.5, 14.2 Hz), 2.37 (1H, ddd, *J* = 3.1, 5.2, 14.0 Hz), 3.08 (1H, d, *J* = 17.4 Hz), 3.14 (1H, ddd, *J* = 5.2, 11.5, 11.5 Hz), 3.24 (1H, dd, *J* = 3.1, 17.5 Hz), 3.40 (1H, dd, *J* = 2.1, 11.5 Hz), 3.65 (1H, dq, *J* = 7.1, 9.3 Hz), 3.96 (1H, dq, *J* = 7.1, 9.4 Hz), 3.99 (1H, dq, *J* = 7.1, 9.4 Hz), 4.17 (1H, dq, *J* = 7.1, 9.4 Hz), 4.85 (1H, dd, *J* = 3.1, 7.4 Hz), 7.41–7.47 (5H, m). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 15.1 (CH_3), 15.6 (CH_3), 33.8 (CH_2), 38.0 (CH_2), 39.7 (C), 43.1 (CH), 43.3 (C), 44.6 (CH), 65.3 (CH_2), 67.8 (CH_2), 100.7 (CH), 108.7 (C), 108.9 (C), 109.9 (C), 110.4 (C), 128.4 (2×CH), 129.7 (CH), 129.8 (2×CH), 130.96 (C), 130.99 (C), 137.3 (C). HRMS (ESI) Calcd for $C_{23}H_{22}N_4NaO_3$ $[M+Na]^+$: 425.1593, Found: 425.1584.

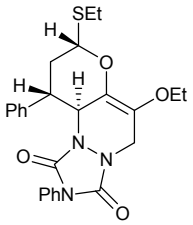
(2*R*,4*R*,4a*R*)-2,8-diethoxy-4-phenyl-3,4,4a,7-tetrahydro-2*H*-chromene-5,5,6,6-tetracarbonitrile ((–)-7): Colorless



solid. Mp: 48.6–50.0 °C. $[\alpha]_D^{20} = -78.7$ (*c* 1.06, methanol). HPLC conditions: Chiralpak IC-3: 4.6×250 mm, 254 nm, UV detector, rt, eluent: *i*PrOH/hexane (1/20), flow rate: 1 mL/min, retention time 22.0 min for minor isomer and 22.8 min for major isomer.

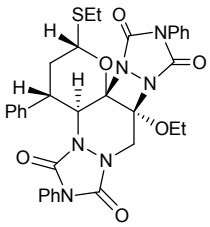
b) Typical experimental procedure for the DA reaction with *N*-phenyl-1,3,5-triazoline-2,4-dione (PTAD): Synthesis of 10 and 11 (Scheme 2). To a stirred solution of *endo*-**5** (66 mg, 0.22 mmol) in CH_2Cl_2 (5 mL) was added PTAD (48 mg, 0.27 mmol) at room temperature. After being stirred for 3 h, the reaction mixture was evaporated. The residue was chromatographed on a column of silica gel with AcOEt/hexane (1/2) as an eluent to give monoadduct **10** (56 mg, 53%) as colorless crystals and bisadduct **11** (23 mg, 15%) as colorless crystals.

(8*S,10*S**,10a*S**)-6-ethoxy-8-(ethylthio)-2,10-diphenyl-8,9,10,10a-tetrahydro-1*H*,5*H*-pyrano[3,2-*c*][1,2,4]triazolo- [1,2-*a*]pyridazine-1,3(2*H*)-dione (10):** Colorless crystals. Mp: 181.2–183.6 °C. ^{1}H-NMR (500



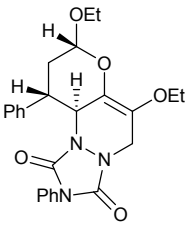
MHz, $CDCl_3$) δ 1.30 (t, *J* = 7.0 Hz, 3H), 1.40 (t, *J* = 7.3 Hz, 3H), 2.30 (ddd, *J* = 2.4, 4.0, 14.0 Hz, 1H), 2.43 (ddd, *J* = 11.6, 12.2, 14.0 Hz, 1H), 2.82 (dq, *J* = 7.3, 12.8 Hz, 1H), 2.90 (dq, *J* = 7.3, 12.8 Hz, 1H), 3.29 (ddd, *J* = 4.0, 10.4, 12.2 Hz, 1H), 3.91 (dd, *J* = 1.5, 14.7 Hz, 1H), 4.08 (dq, *J* = 7.0, 9.5 Hz, 1H), 4.24 (dq, *J* = 7.0, 9.5 Hz, 1H), 4.28 (d, *J* = 14.7 Hz, 1H), 4.55 (d, *J* = 10.4 Hz, 1H), 4.96 (dd, *J* = 2.4, 11.6 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 2H), 7.21–7.24 (m, 2H), 7.27–7.32 (m, 4H), 7.36 (dd, *J* = 7.6, 7.6 Hz, 2H). ^{13}C-NMR (76 MHz, $CDCl_3$) δ 14.9 (CH_3), 15.5 (CH_3), 25.4 (CH_2), 37.4 (CH_2), 47.1 (CH_2), 49.2 (CH), 56.6 (CH), 68.4 (CH_2), 86.2 (CH), 125.2 (2×CH), 127.9 (2×CH), 128.0 (CH), 128.1 (CH), 128.7 (2×CH), 128.9 (2×CH), 131.0 (C), 133.6 (C), 134.3 (C), 138.9 (C), 149.1 (C), 154.8 (C). HRMS (ESI) Calcd for $C_{25}H_{27}N_3O_4S$ $[M]^+$: 465.1722, Found: 465.1714. Anal. Calcd for $C_{25}H_{27}N_3O_4S$: C, 64.50; H, 5.85; N, 9.03. Found: C, 64.44; H, 5.92; N, 9.00.

(2*S,4*S**,4a*S**,10a*R**,15a*S**)-10a-ethoxy-2-(ethylthio)-4,7,13-triphenylhexahydro-6*H*,12*H*-[1,2,4]triazolo[1',2':1,2][1,2]diazeto[3,4-*d*]pyrano[3,2-*c*][1,2,4]triazolo[1,2-*a*]pyridazine-6,8,12,14(7*H*,13*H*)-**



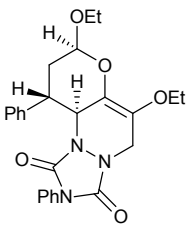
tetraone (11): Colorless crystals. Mp: 194.1–195.0 °C. IR (KBr): ν 1396.2 (m), 1419.4 (m), 1727.9 (s) cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 1.40 (t, *J* = 7.2 Hz, 3H), 1.42 (t, *J* = 7.2 Hz, 3H), 2.28 (ddd, *J* = 2.3, 3.8, 14.0 Hz, 1H), 2.37 (ddd, *J* = 11.3, 12.1, 14.0 Hz, 1H), 2.86 (dq, *J* = 7.2, 12.5 Hz, 1H), 2.94 (dq, *J* = 7.2, 12.5 Hz, 1H), 3.19 (ddd, *J* = 3.8, 12.1, 12.1 Hz, 1H), 3.94 (d, *J* = 14.0 Hz, 1H), 4.18 (dq, *J* = 7.2, 9.1 Hz, 1H), 4.29 (dq, *J* = 7.2, 9.1 Hz, 1H), 5.04 (d, *J* = 12.1 Hz, 1H), 5.19 (d, *J* = 14.0 Hz, 1H), 5.27 (dd, *J* = 2.3, 11.3 Hz, 1H), 6.78–6.80 (m, 2H), 7.22–7.36 (m, 13H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 15.1 (CH_3), 15.3 (CH_3), 24.8 (CH_2), 35.7 (CH_2), 43.9 (CH_2), 44.8 (CH), 54.7 (CH), 62.6 (CH_2), 81.0 (CH), 93.7 (C), 94.3 (C), 124.9 (2×CH), 125.6 (2×CH), 127.6 (2×CH), 128.3 (CH), 128.5 (CH), 128.8 (CH), 128.9 (2×CH), 129.1 (2×CH), 129.2 (2×CH), 130.3 (C), 130.7 (C), 136.6 (C), 148.5 (C), 149.1 (C), 155.9 (C), 156.6 (C). HRMS (ESI) Calcd for $C_{33}H_{32}N_6O_6S$ $[M]^+$: 640.2104, Found: 640.2111.

(8*R,10*S**,10a*S**)-6,8-diethoxy-2,10-diphenyl-8,9,10,10a-tetrahydro-1*H*,5*H*-pyrano[3,2-*c*][1,2,4]triazolo[1,2-*a*]pyrida- zine-1,3(2*H*)-dione (9):** Mp: 213.7–215.0 °C. IR (KBr): ν 1419.6 (s), 1720.2 (s), 1781.9 (m) cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 1.31 (t, *J* = 7.2 Hz, 3H), 1.33 (t, *J* = 7.2 Hz, 3H), 2.26 (ddd, *J* = 2.6, 4.5, 14.0 Hz, 1H), 2.33 (ddd, *J* = 8.7, 12.1, 14.0 Hz, 1H), 3.23 (ddd, *J* = 4.5, 10.6, 12.1 Hz, 1H), 3.71 (dq, *J* = 7.2, 9.4 Hz, 1H), 3.90 (dd, *J* = 1.5,



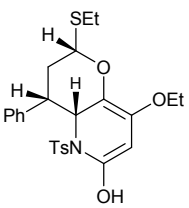
14.7 Hz, 1H), 4.10 (dq, *J* = 7.2, 9.4 Hz, 1H), 4.12 (dq, *J* = 7.2, 9.8 Hz, 1H), 4.26 (d, *J* = 14.8 Hz, 1H), 4.28 (dq, *J* = 7.2, 9.8 Hz, 1H), 4.56 (d, *J* = 10.6 Hz, 1H), 4.84 (dd, *J* = 2.6, 8.7 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.27–7.31 (m, 4H), 7.36 (dd, *J* = 7.6, 7.6 Hz, 2H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 15.1 (CH_3), 15.6 (CH_3), 37.0 (CH_2), 46.2 (CH), 47.2 (CH_2), 56.6 (CH), 65.4 (CH_2), 68.3 (CH_2), 103.9 (CH), 125.2 (2×CH), 127.97 (2×CH), 128.00 (2×CH), 128.7 (2×CH), 128.9 (2×CH), 130.7 (C), 131.1 (C), 133.9 (C), 139.2 (C), 149.1 (C), 154.9 (C). HRMS (ESI) Calcd for $C_{25}H_{28}N_3O_5$ $[M+H]^+$: 450.2023, Found: 450.2028.

(8*S,10*S**,10a*S**)-6,8-diethoxy-2,10-diphenyl-8,9,10,10a-tetrahydro-1*H*,5*H*-pyrano[3,2-*c*][1,2,4]triazolo[1,2-*a*]-pyridazine-1,3(2*H*)-dione (17):** Colorless crystals. Mp 147.9–148.8 °C. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.2 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 2.15 (dd, *J* = 3.4, 13.6 Hz, 1H), 2.45 (ddd, *J* = 3.4, 13.6, 13.6 Hz, 1H), 3.60 (dq, *J* = 7.2, 9.4 Hz, 1H), 3.62 (ddd, *J* = 3.4, 10.6, 13.6 Hz, 1H), 3.92 (d, *J* = 14.4 Hz, 1H), 3.94 (dq, *J* = 7.2, 9.4 Hz, 1H), 4.05 (dq, *J* = 7.2, 9.4 Hz, 1H), 4.18 (dq, *J* = 7.2, 9.4 Hz, 1H), 4.33 (d, *J* = 14.4 Hz, 1H), 4.52 (d, *J* = 10.6 Hz, 1H), 5.16 (d, *J* = 3.4 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.27–7.31 (m, 4H), 7.36 (dd, *J* = 7.6, 7.6 Hz, 2H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 15.0 (CH_3), 15.5 (CH_3), 36.2 (CH_2), 43.4 (CH_2), 47.3 (CH_2), 57.3 (CH), 64.1 (CH), 67.9 (CH_2), 99.5 (CH), 125.3 (2×CH), 127.9 (CH), 128.0 (CH), 128.1 (2×CH), 128.6 (2×CH), 129.0 (2×CH), 129.9 (C), 131.2 (C), 135.0 (C), 139.5 (C), 149.1 (C), 155.0 (C). HRMS (ESI) Calcd for $C_{25}H_{27}N_3NaO_5$ $[M+Na]^+$: 472.1843, Found: 472.1833.



c) Typical experimental procedure for the DA reaction with *p*-toluenesulfonyl isocyanate: Synthesis of 12 (Scheme 2). To a solution of *endo*-**5** (86 mg, 0.31 mmol) in CH_2Cl_2 (10 mL) was added *p*-toluenesulfonyl isocyanate (70 μL, 0.47 mmol). After being stirred at room temperature for 4 h, the reaction was quenched with aqueous $NaHCO_3$. The organic phase was separated, dried over $MgSO_4$ and evaporated. The residue was chromatographed on a column of silica gel with AcOEt/hexane (1:2) as an eluent to give (2*R**,4*S**,4a*R**)-2,8-diethoxy-4-phenyl-5-tosyl-3,4,4a,5- tetrahydro-2*H*-pyrano[3,2-*b*]pyridin-6-ol (**12**) (132 mg, 90%) as colorless crystals. Mp: 127.3–128.0 °C. IR (KBr): ν 1164.8 (s), 1434.8 (s), 1604.5 (s), 1689.3 (s), 3286.1 (br) cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.22 (t, *J* = 7.0 Hz, 3H), 1.47 (t, *J* = 7.0 Hz, 3H), 1.88 (ddd, *J* = 8.9, 10.4, 13.4 Hz, 1H), 2.30 (dddd, *J* = 0.9, 1.8, 6.7, 13.4 Hz, 1H), 2.42 (s, 3H), 3.59 (dq, *J* = 7.0, 9.5 Hz, 1H), 3.71 (ddd, *J* = 2.7, 6.7, 10.4 Hz, 1H), 3.95 (dq, *J* = 7.0, 9.5 Hz, 1H), 4.14 (dq, *J* = 7.0, 9.8 Hz, 1H), 4.21 (dq, *J* = 7.0, 9.8 Hz, 1H), 5.09 (dd, *J* = 1.8, 8.9 Hz, 1H), 5.43 (dd, *J* = 0.9, 2.8 Hz, 1H), 5.59 (s, 1H), 7.15–7.18 (m, 2H), 7.24 (tt, *J* = 1.2, 7.3 Hz, 1H), 7.29–7.33 (m, 4H), 7.97–8.00 (m, 2H), 9.82 (s, 1H). ^{13}C-NMR (151 MHz, $CDCl_3$) δ 15.0 (CH_3), 15.3 (CH_3), 21.5 (CH_3), 36.6 (CH_2), 38.2 (CH), 64.8 (CH_2), 70.4 (CH_2), 100.3 (CH), 105.5 (CH), 109.9 (CH), 126.9 (CH), 127.1 (2×CH), 128.4 (2×CH), 128.7 (2×CH), 129.3 (2×CH), 136.1 (C), 142.9 (C), 144.6 (C), 144.8 (C), 160.0 (C), 162.1 (C). HRMS (ESI) Calcd for $C_{25}H_{29}NNaO_6S$ $[M+Na]^+$: 494.1608, Found: 494.1599.

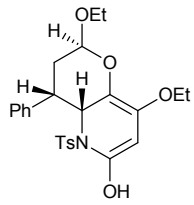
(2*S,4*S**,4a*R**)-8-ethoxy-2-(ethylthio)-4-phenyl-5-tosyl-3,4,4a,5-tetrahydro-2*H*-pyrano[3,2-*b*]pyridin-6-ol (13):**



Colorless crystals. Mp 112.1–115.8 °C. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.30 (t, *J* = 7.3 Hz, 3H, $SCH_2\underline{CH_3}$), 1.48 (t, *J* = 7.0 Hz, 3H), 1.94 (ddd, *J* = 11.0, 11.0 13.7 Hz, 1H), 2.40 (dddd, *J* = 1.2, 1.8, 6.7, 13.7 Hz, 1H), 2.42 (s, 3H), 2.71 (dq, *J* = 7.3, 12.8 Hz, 1H), 2.77 (dq, *J* = 7.3, 12.8 Hz, 1H), 3.72

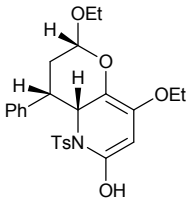
(ddd, J = 2.4, 6.7, 11.0 Hz, 1H), 4.14 (dq, J = 7.0, 9.8 Hz, 1H), 4.21 (dq, J = 7.0, 9.8 Hz, 1H), 5.21 (dd, J = 1.8, 11.0 Hz, 1H), 5.47 (dd, J = 1.2, 2.4 Hz, 1H), 5.57 (s, 1H), 7.14–7.17 (m, 2H), 7.25 (tt, J = 1.5, 7.3 Hz, 1H), 7.30–7.34 (m, 4H), 7.98 (d, J = 8.2 Hz, 2H), 9.83 (s, 1H). ^{13}C-NMR (76 MHz, $CDCl_3$) δ 14.9 (CH_3), 15.3 (CH_3), 21.6 (CH_3), 24.7 (CH_2), 37.1 (CH_2), 39.3 (CH), 70.4 (CH_2), 81.3 (CH), 105.6 (CH), 109.9 (CH), 127.05 (2×CH), 127.12 (CH), 128.4 (2×CH), 128.8 (2×CH), 129.4 (2×CH), 135.9 (C), 142.7 (C), 144.7 (C), 146.6 (C), 159.9 (C), 162.1 (C). HRMS (ESI) Calcd for $C_{25}H_{29}NNaO_5S_2$ $[M+Na]^+$, 488.1560, Found: 488.1567.

(2*S,4*S**,4a*R**)-2,8-diethoxy-4-phenyl-5-tosyl-3,4,4a,5-tetrahydro-2*H*-pyrano[3,2-*b*]pyridin-6-ol (18)**: Colorless



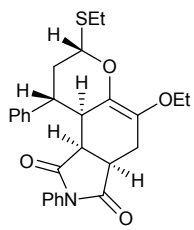
crystals. Mp: 126.9–127.8 °C. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.21 (t, J = 7.0 Hz, 3H), 1.47 (t, J = 7.0 Hz, 3H), 1.80 (ddd, J = 2.4, 11.3, 13.4 Hz, 1H), 2.16 (dddd, J = 1.2, 2.4, 6.1, 13.4 Hz, 1H), 2.42 (s, 3H), 3.61 (dq, J = 7.0, 9.8 Hz, 1H), 3.74 (ddd, J = 2.4, 6.1, 11.3 Hz, 1H), 3.82 (dq, J = 7.0, 9.8Hz, 1H), 4.16 (dq, J = 7.0, 9.8 Hz, 1H), 4.19 (dq, J = 7.0, 9.8 Hz, 1H), 5.18 (dd, J = 2.4, 2.4 Hz, 1H), 5.53 (dd, J = 1.2, 2.4 Hz, 1H), 5.62 (s, 1H), 7.18–7.21 (m, 2H), 7.23–7.27 (m, 1H), 7.30–7.35 (m, 4H), 7.99 (d, J = 8.24 Hz, 2H), 9.88 (br s, 1H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 15.1 (CH_3), 15.3 (CH_3), 21.6 (CH_3), 34.1 (CH), 35.2 (CH_2), 64.3 (CH_2), 70.6 (CH_2), 97.1 (CH), 105.4 (CH), 110.4 (CH), 126.8 (CH), 127.4 (2×CH), 128.4 (2×CH), 128.8 (2×CH), 129.4 (2×CH), 136.1 (C), 143.1 (C), 143.6 (C), 144.6 (C), 160.4 (C), 162.2 (C). HRMS (ESI) Calcd for $C_{25}H_{29}NO_6SNa$ $[M+Na]^+$: 494.1606, Found: 494.1610.

(2*R*,4*S*,4a*R*)-2,8-diethoxy-4-phenyl-5-tosyl-3,4,4a,5-tetrahydro-2*H*-pyrano[3,2-*b*]pyridin-6-ol ((–)-12): Colorless solid.



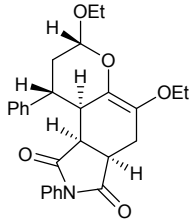
Mp: 45.6–46.1 °C. $[\alpha]_D^{20}$ = –9.45 (c 0.82, methanol).

d) Typical experimental procedure for the DA reaction with *N*-phenylmaleimide: Synthesis of 15 (Scheme 3). A mixture of *endo*-**6** (57.9 mg, 0.20 mmol) and *N*-phenylmaleimide (51.0 mg, 0.30 mmol) in toluene (1.5 mL) was heated at 80 °C for 48 h. The mixture was evaporated, and the resulting residue was chromatographed by preparative TLC with hexane/AcOEt (5:1) to give (3a*R**,7*S**,9*R**,9a*R**,9b*S**)-5-ethoxy-7-(ethylthio)-2,9-diphenyl-3a,7,8,9,9a,9b-hexahydrothiopyrano[3,2-*e*]isoindole-1,3(2*H*,4*H*)-dione (**15**) (79.5 mg, 86%) as pale yellow crystals. Mp: 140.8–141.3 °C. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 1.22 (t, J = 7.1 Hz, 3H), 1.31 (t, J = 7.6 Hz, 3H), 1.76 (dt, J = 10.1, 13.4 Hz, 1H),



2.39 (ddd, J = 3.1, 6.7, 13.7 Hz, 1H), 2.48 (ddd, J = 1.5, 7.5, 15.5 Hz, 1H), 2.52 (ddd, J = 1.4, 5.3, 11.9 Hz, 1H), 2.69 (dq, J = 12.8, 7.6 Hz, 1H), 2.83 (d, J = 13.7 Hz, 1H), 2.84 (dq, J = 13.0, 7.5 Hz, 1H), 2.94 (dd, J = 5.1, 8.8 Hz, 1H), 3.10 (ddd, J = 1.5, 7.5, 8.7 Hz, 1H), 3.82–3.94 (m, 3H), 5.63 (dd, J = 6.7, 10.1 Hz, 1H), 7.20–7.46 (m, 10H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 14.8 (CH_3), 15.6 (CH_3), 25.0 (CH_2), 28.3 (CH_2), 37.1 (CH), 37.6 (CH_2), 40.6 (CH), 41.5 (CH), 44.3 (CH), 66.4 (CH_2), 81.9 (CH), 126.5 (2×CH), 127.2 (CH), 127.9 (2×CH), 128.69 (CH), 128.72 (2×CH), 129.1 (2×CH), 130.7 (C), 131.8 (C), 133.9 (C), 141.8 (C), 176.5 (C), 178.4 (C). HRMS (EI) calcd for $C_{27}H_{29}NO_4S$ $[M]^+$: 463.1817, found: 463.1811.

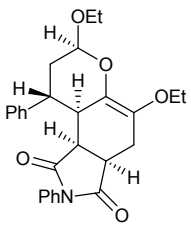
(3a*R,7*R**,9*R**,9a*R**,9b*S**)-5,7-Diethoxy-2,9-diphenyl-3a,7,8,9,9a,9b-hexahydropyrano[3,2-*e*]isoindole-1,3(2*H*,4*H*)-dione**



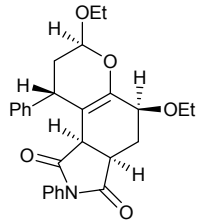
(14): Colorless crystals. Mp: 161.3–161.8 °C. IR (ATR): ν 1377.9 (s), 1455.0 (s), 1597.7 (s), 1703.8 (s),

2928.4 (s), 2974.7 (s), 3031.6 (s), 3063.4 (s) cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.25 (dd, J = 7.0, 7.0 Hz, 3H), 1.26 (dd, J = 7.0, 7.0 Hz, 3H), 1.84 (ddd, J = 7.7, 13.9, 13.9 Hz, 1H), 2.34 (ddd, J = 3.0, 6.2, 13.9 Hz, 1H), 2.45 (ddd, J = 1.1, 7.4, 15.5 Hz, 1H), 2.55 (ddd, J = 1.1, 5.2, 11.7 Hz, 1H), 2.84 (dd, J = 1.2, 15.5 Hz, 1H), 2.96 (dd, J = 5.2, 8.7 Hz, 1H), 3.12 (ddd, J = 1.2, 7.4, 8.7 Hz, 1H), 3.61 (dq, J = 9.5, 7.0 Hz, 1H), 3.80 (ddd, J = 3.1, 11.7, 13.9 Hz, 1H), 3.88 (dq, J = 7.0, 9.4 Hz, 1H), 3.91 (dq, J = 7.0, 9.4 Hz, 1H), 4.00 (dq, J = 9.5, 7.0 Hz, 1H), 5.19 (dd, J = 6.2, 7.7 Hz, 1H), 7.29–7.61 (m, 10H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 15.0 (CH_3), 15.6 (CH_3), 28.3 (CH_2), 35.3 (CH), 37.4 (CH_2), 40.9 (CH), 41.4 (CH), 44.6 (CH), 63.9 (CH_2), 66.3 (CH_2), 100.1 (CH), 126.5 (2×CH), 127.1 (CH), 128.0 (2×CH), 128.65 (C), 128.67 (2×CH), 129.1 (2×CH), 131.4 (C), 131.8 (C), 132.7 (C), 142.1 (C), 176.5 (C), 178.4 (C). HRMS (ESI) calcd for $C_{27}H_{29}NO_5Na$ [M+Na]$^+$: 470.1938, found: 470.1937.

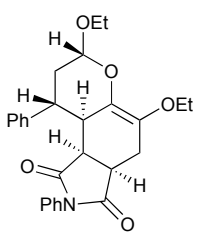
(3a*R,5*S**,7*S**,9*S**,9b*R**)-5,7-diethoxy-2,9-diphenyl-3a,5,7,8,9,9b-hexahydropyrano[3,2-*e*]isoindole-1,3(2*H*,4*H*)-dione (19):** Colorless solid. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 1.12 (t, J = 7.0 Hz, 3H), 1.23 (t, J = 7.0 Hz, 3H), 2.03 (ddd, J = 2.4, 6.1, 16.0 Hz, 1H), 2.05 (ddd, J = 2.4, 11.1, 16.0 Hz, 1H), 2.35 (ddd, J = 2.4, 7.0, 15.6 Hz, 1H), 2.70 (ddd, J = 2.4, 6.0, 11.1 Hz, 1H), 2.86 (dd, J = 1.9, 15.6 Hz, 1H), 2.98 (dd, J = 6.0, 9.0 Hz, 1H), 3.08 (ddd, J = 1.9, 7.0, 9.0 Hz, 1H), 3.57 (dq, J = 9.6, 7.0 Hz, 1H), 3.71 (dq, J = 9.7, 6.9 Hz, 1H), 3.77 (dq, J = 9.7, 7.1 Hz, 1H), 3.85 (dq, J = 9.7, 7.0 Hz, 1H), 4.47 (ddd, J = 6.1, 11.1, 11.1 Hz, 1H), 5.18 (dd, J = 2.4, 2.4 Hz, 1H), 7.22–7.52 (m, 10H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 15.1 (CH_3), 15.5 (CH_3), 26.0 (CH_2), 31.1 (CH), 35.6 (CH_2), 40.0 (CH), 40.6 (CH), 41.1 (CH), 63.6 (CH_2), 64.5 (CH_2), 96.5 (CH), 126.3 (2×CH), 127.0 (CH), 128.2 (2×CH), 128.6 (CH), 128.7 (2×CH), 129.1 (2×CH), 130.1 (C), 132.0 (C), 133.3 (C), 143.7 (C), 176.0 (C), 178.5 (C). HRMS (ESI) calcd for $C_{27}H_{29}NO_5Na$ [M+Na]$^+$: 470.1939, found: 470.1938.



(3a*R,5*S**,7*S**,9*S**,9b*R**)-5,7-diethoxy-2,9-diphenyl-3a,5,7,8,9,9b-hexahydropyrano[3,2-*e*]isoindole-1,3(2*H*,4*H*)-dione (19'):** Colorless solids. Mp: 42.4–42.8 °C. IR (NaCl): ν 2924, 1712 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.06 (t, J = 7.0 Hz, 3H), 1.22 (t, J = 7.0 Hz, 3H), 1.87 (ddd, J = 2.6, 7.7, 14.4 Hz, 1H), 2.02 (ddd, J = 2.5, 9.8, 13.4 Hz, 1H), 2.25 (ddd, J = 4.0, 6.5, 13.4 Hz, 1H), 2.83 (ddd, J = 1.4, 2.8, 14.4 Hz, 1H), 3.06 (ddd, J = 1.4, 7.7, 9.4 Hz, 1H), 3.27 (d, J = 9.4 Hz, 1H), 3.43 (dq, J = 8.9, 7.1 Hz, 1H), 3.57. (dq, J = 8.9, 7.1 Hz, 1H), 3.59 (dq, J = 9.4, 7.1 Hz, 1H), 3.90 (dd, J = 2.8, 2.6 Hz, 1H), 3.92 (dq, J = 7.1, 9.4 Hz, 1H), 4.20 (dd, J = 6.5, 9.8 Hz, 1H), 5.08 (dd, J = 2.5, 4.0 Hz, 1H), 7.29–7.61 (m, 10H, Ph). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 15.1 (CH_3), 15.4 (CH_3), 27.9 (CH), 35.3 (CH), 36.5 (CH), 36.8 (CH), 39.8 (CH), 63.6 (CH_2), 64.7 (CH_2), 72.7 (CH), 96.3 (CH) 105.9 (C) 126.5 (2×CH) 126.8 (CH) 128.3 (CH) 128.7 (2×CH) 128.85 (2×CH) 128.93 (2×CH) 132.4 (C) 143.1 (C) 148.7 (C) 176.4 (C) 178.8 (C). HRMS (EI) calcd for $C_{27}H_{29}NO_5$ [M]$^+$: 447.2046, found: 447.2046.

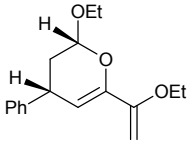


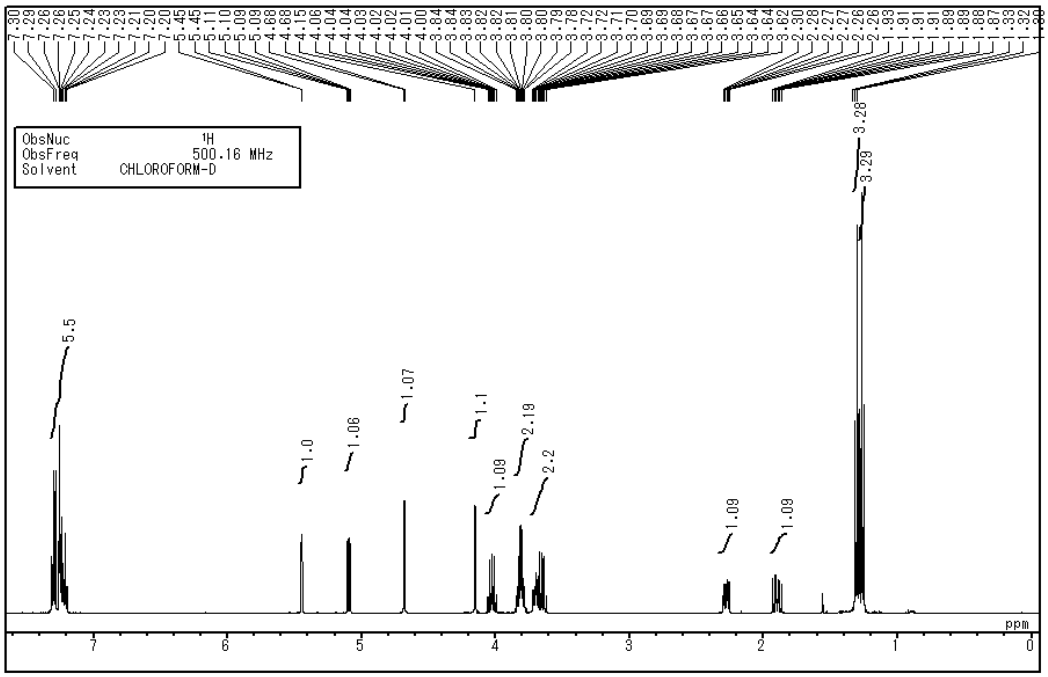
(3a*R*,7*R*,9*R*,9a*R*,9b*S*)-5,7-diethoxy-2,9-diphenyl-3a,7,8,9,9a,9b-hexahydropyrano[3,2-*e*]isoindole-1,3(2*H*,4*H*)-dione ((–)-14): Colorless solids. Mp: 79.3–80.0 °C. $[\alpha]_D^{20}$ = –105.5 (c 1.00, methanol). HPLC conditions: Chiralpak IC-3: 4.6×250 mm, 254 nm, UV detector, rt, eluent: *i*PrOH/hexane (1/10), flow rate: 1 mL/min, retention time 14.9 min for minor isomer and 31.9 min for major isomer.



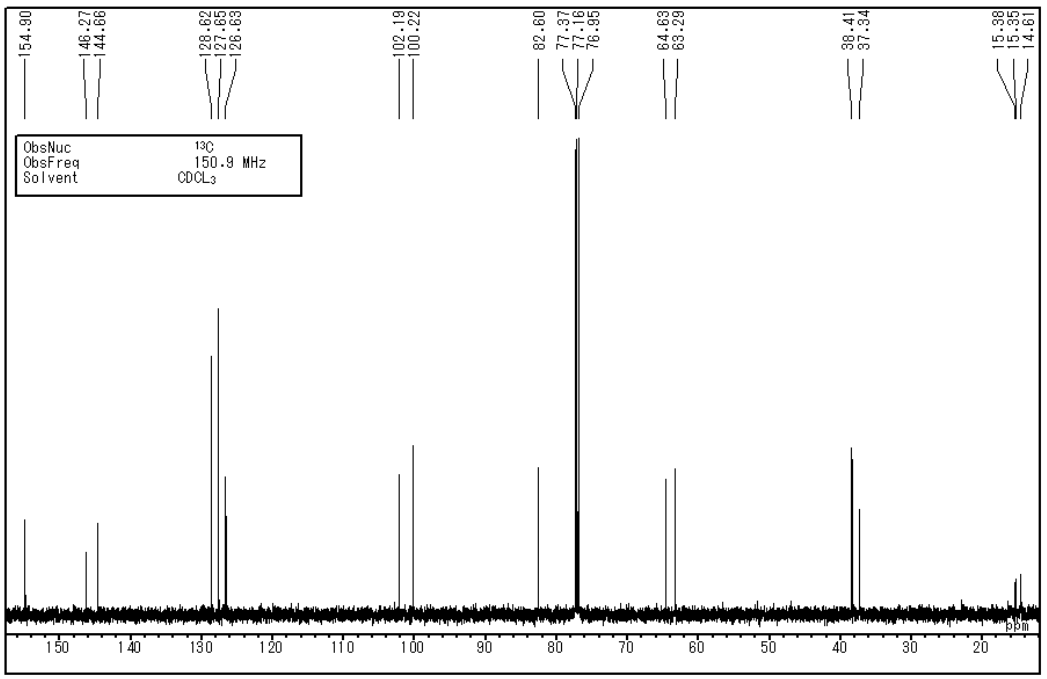
2 ^{1}H and ^{13}C NMR spectra of new compounds

• ^{1}H-NMR spectrum of *endo*-**5**

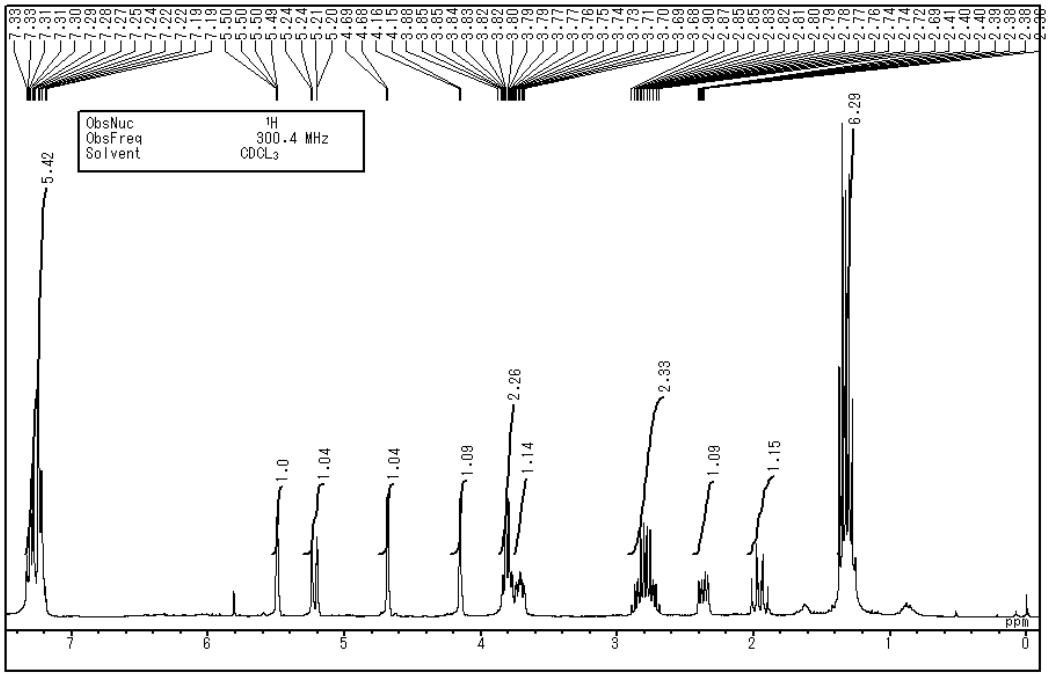


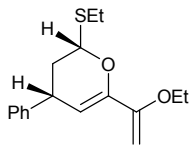


• ^{13}C-NMR spectrum of *endo*-**5**

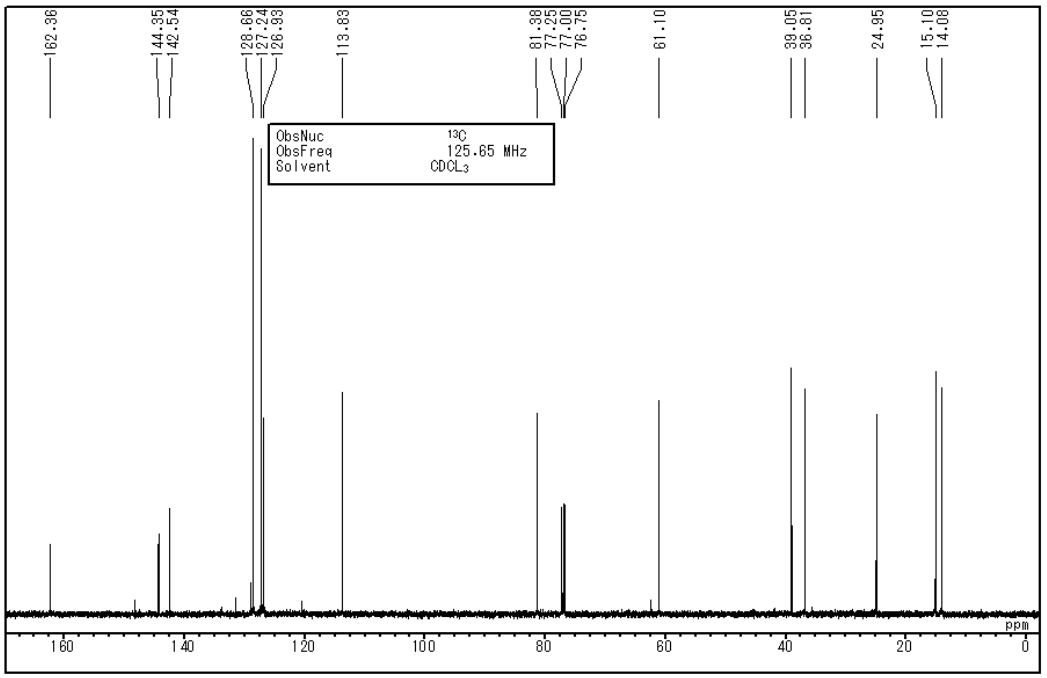


• ^{1}H-NMR spectrum of *endo*-**6**

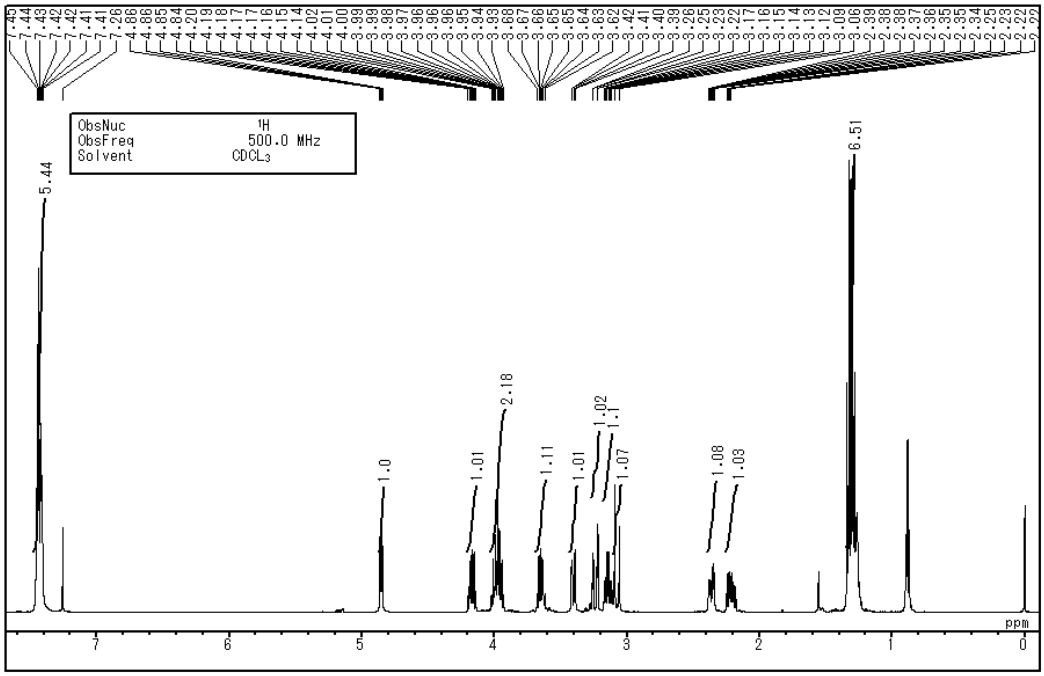


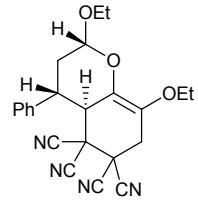


• ^{13}C-NMR spectrum of *endo*-**6**

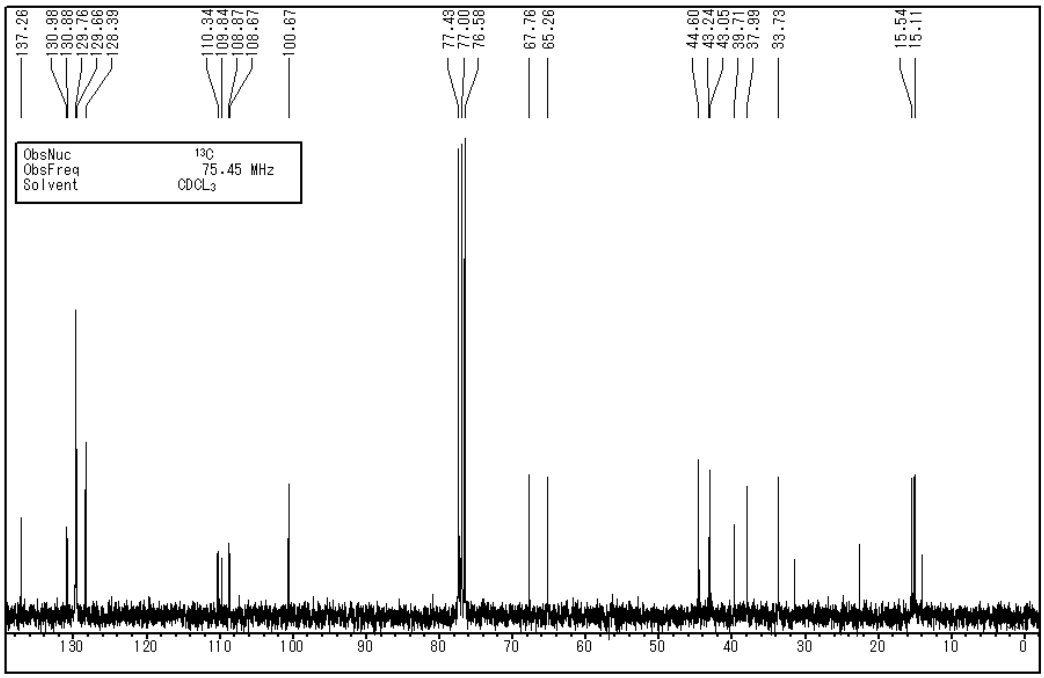


• ^{1}H-NMR spectrum of **7**

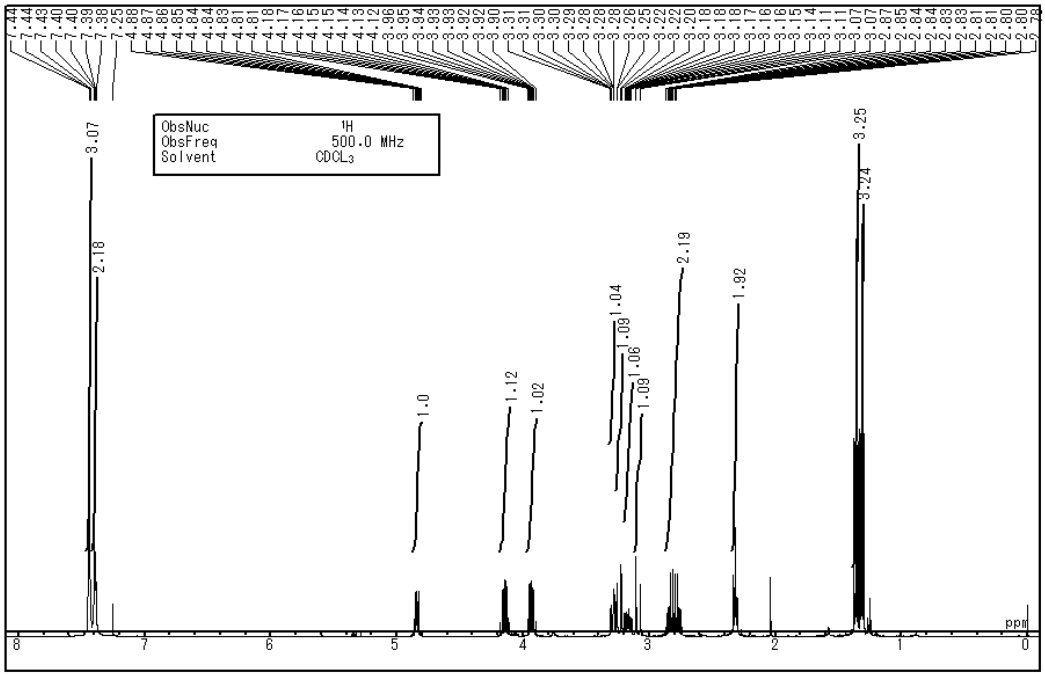


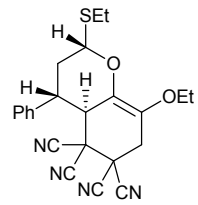


• ^{13}C-NMR spectrum of **7**

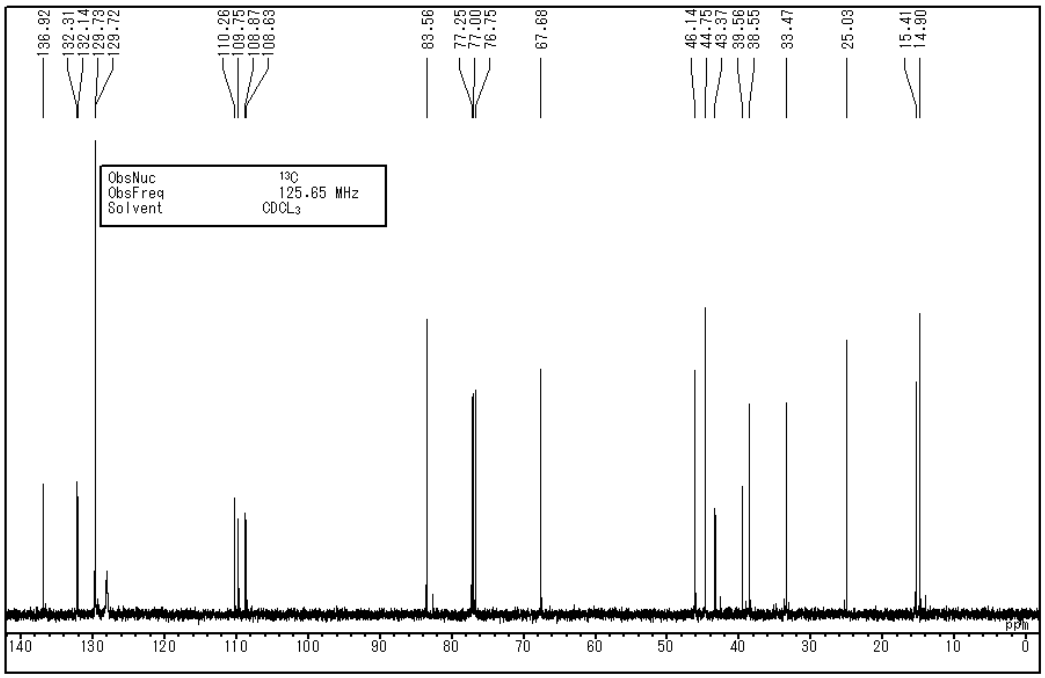


• ^{1}H-NMR spectrum of **8**

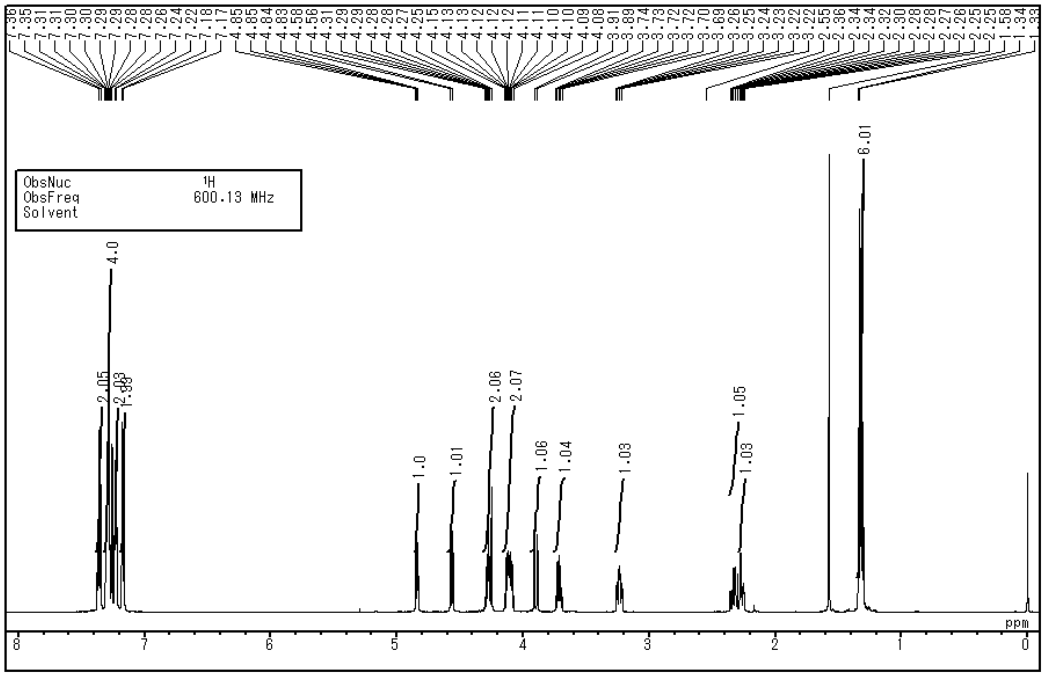


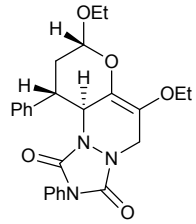


• ^{13}C-NMR spectrum of **8**

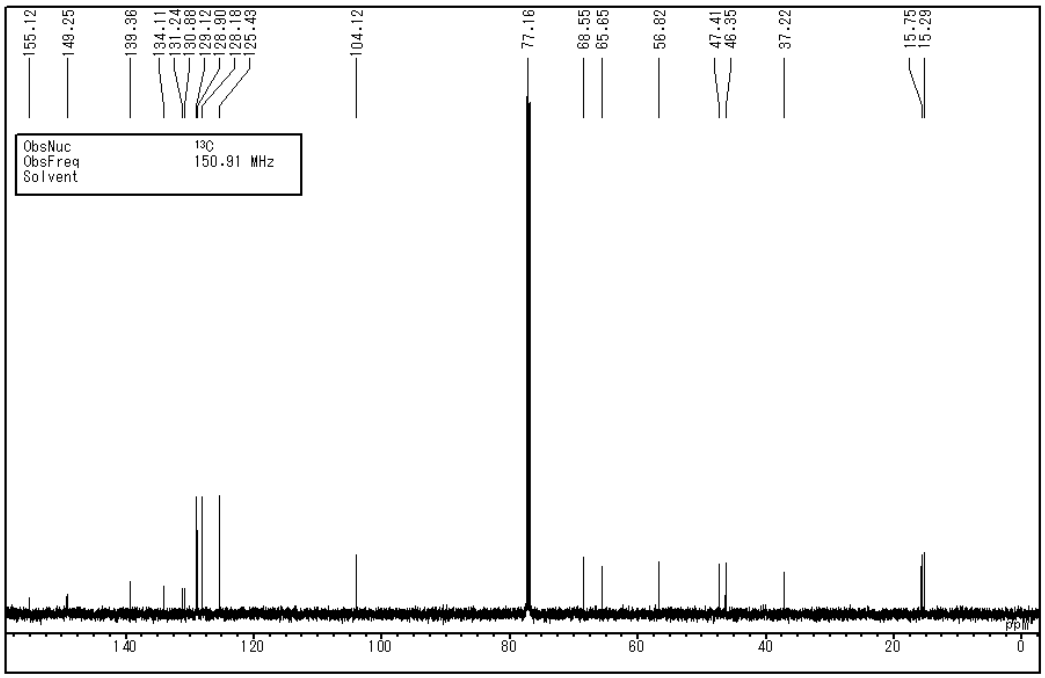


• ^{1}H-NMR spectrum of **9**

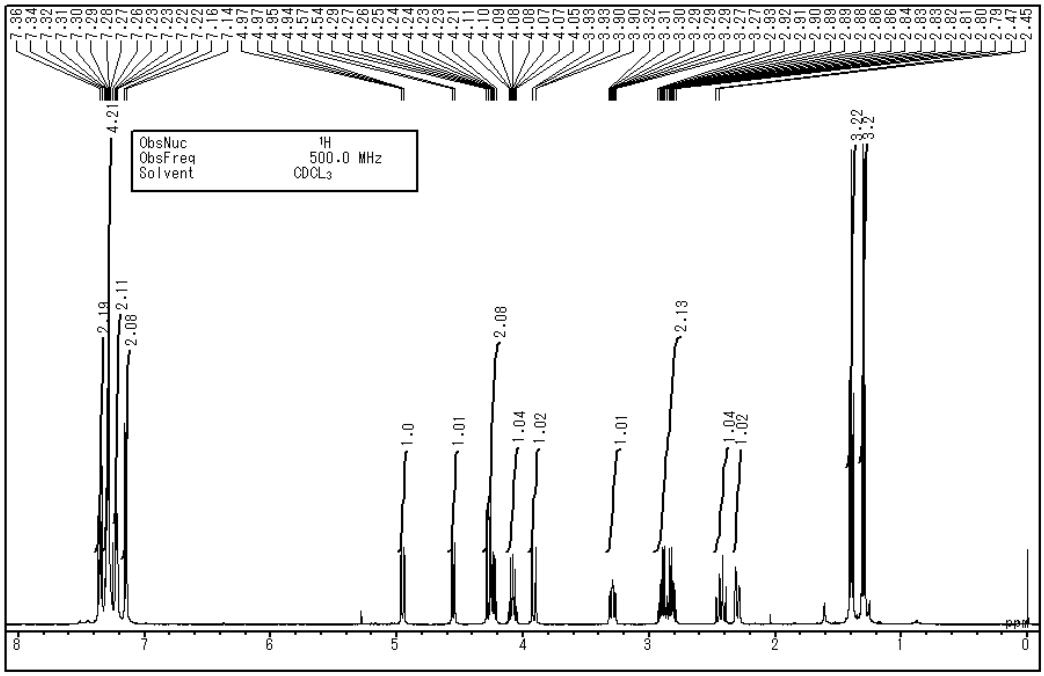


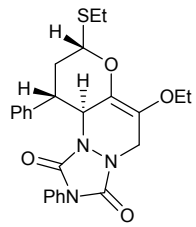


• ^{13}C-NMR spectrum of **9**

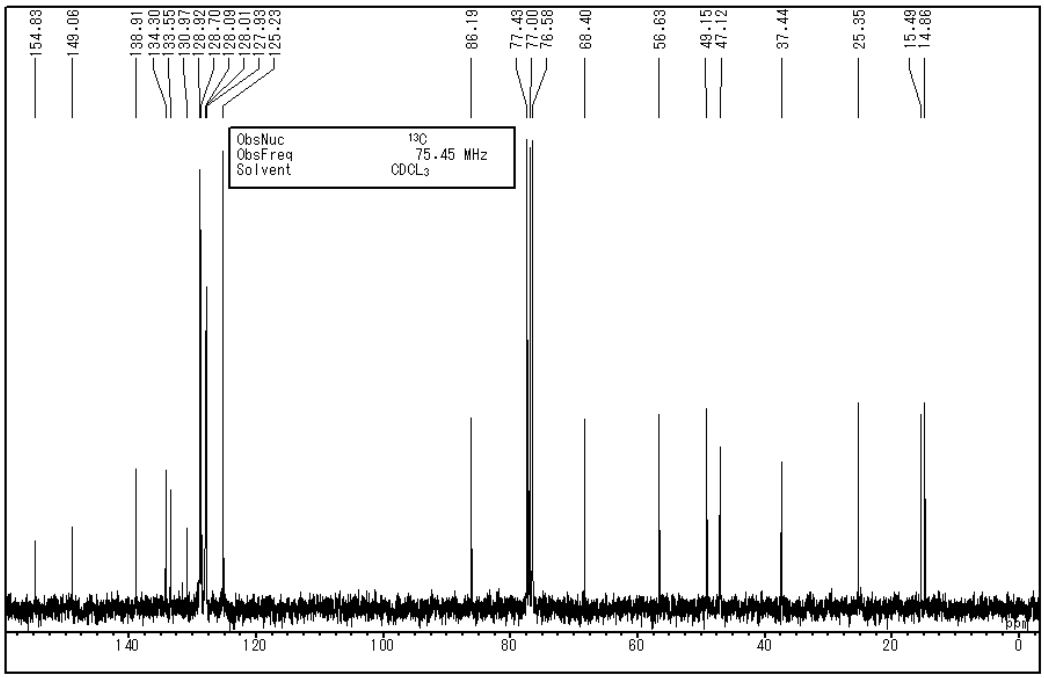


• ^{1}H-NMR spectrum of **10**

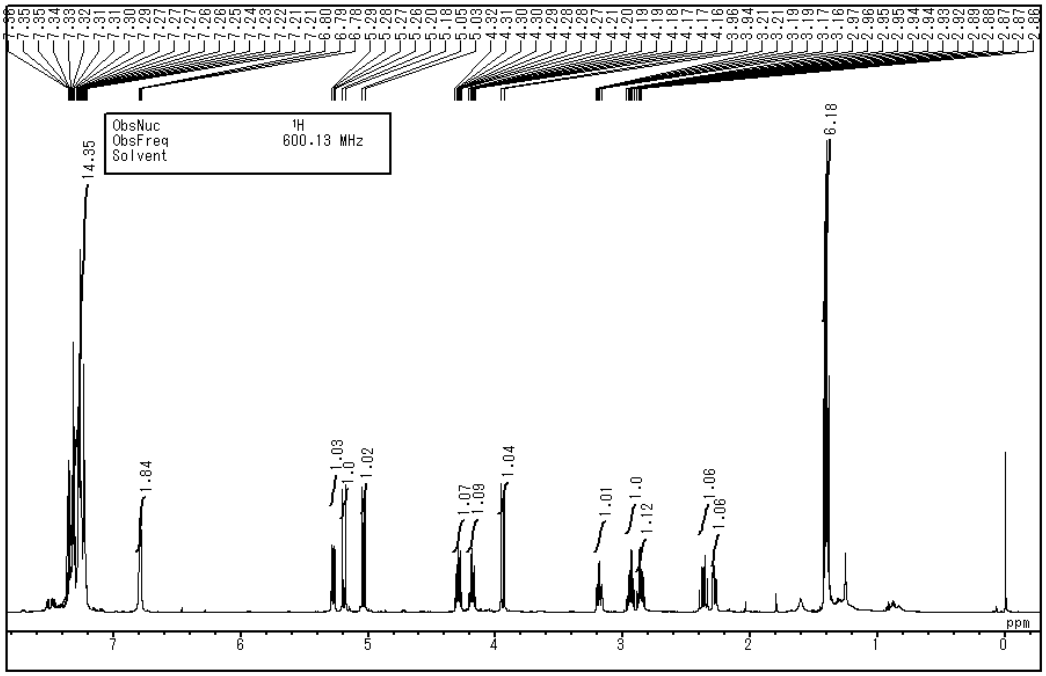


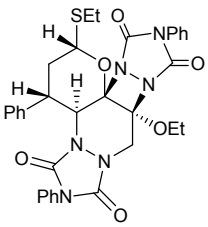


• ^{13}C-NMR spectrum of **10**

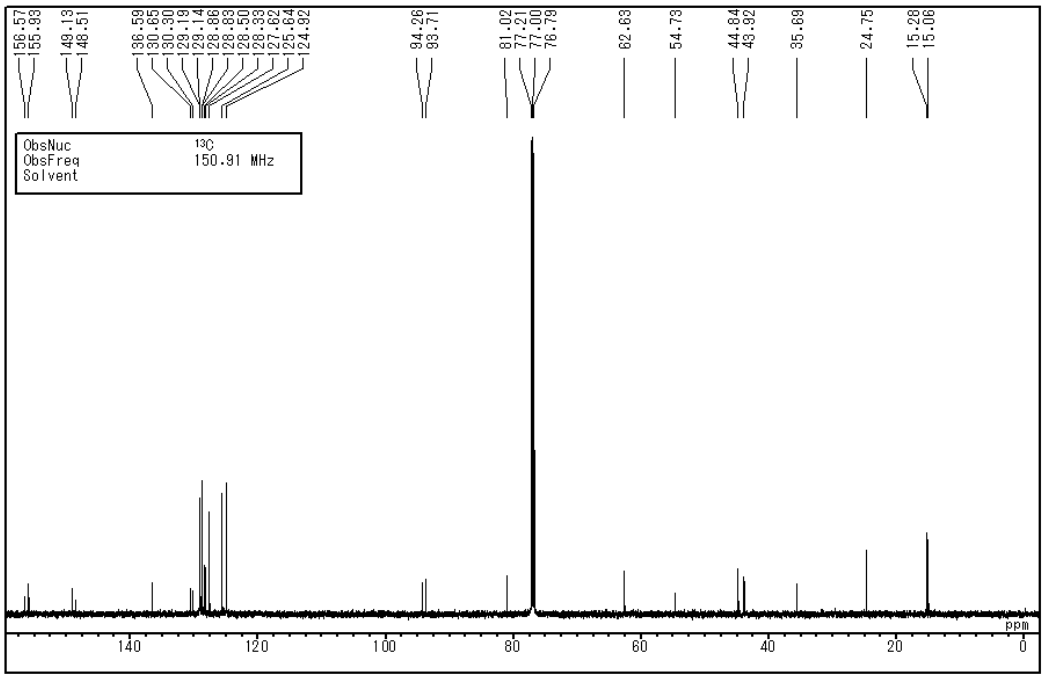


• ^{1}H-NMR spectrum of **11**

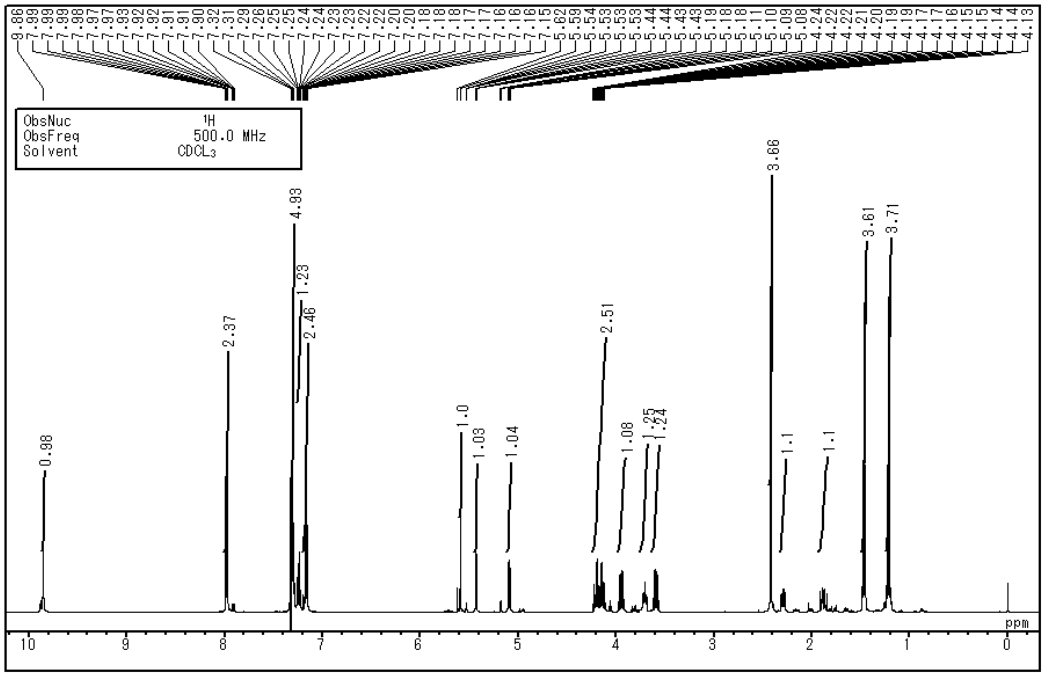


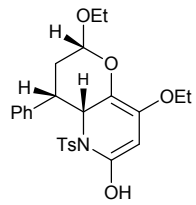


• ^{13}C-NMR spectrum of **11**

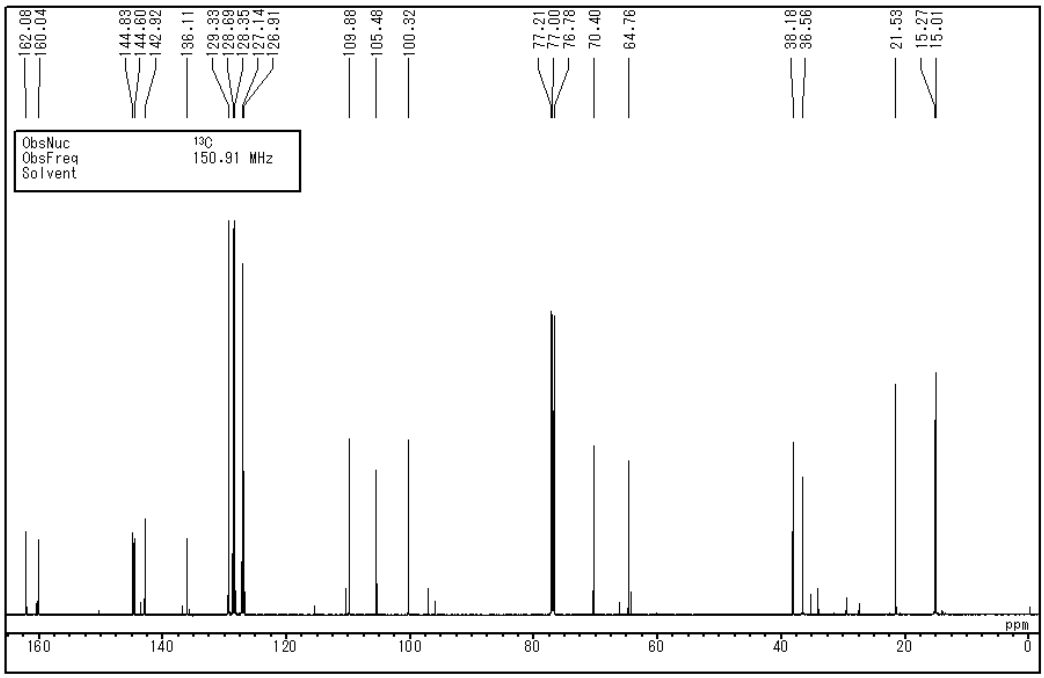


• ^{1}H-NMR spectrum of **12**

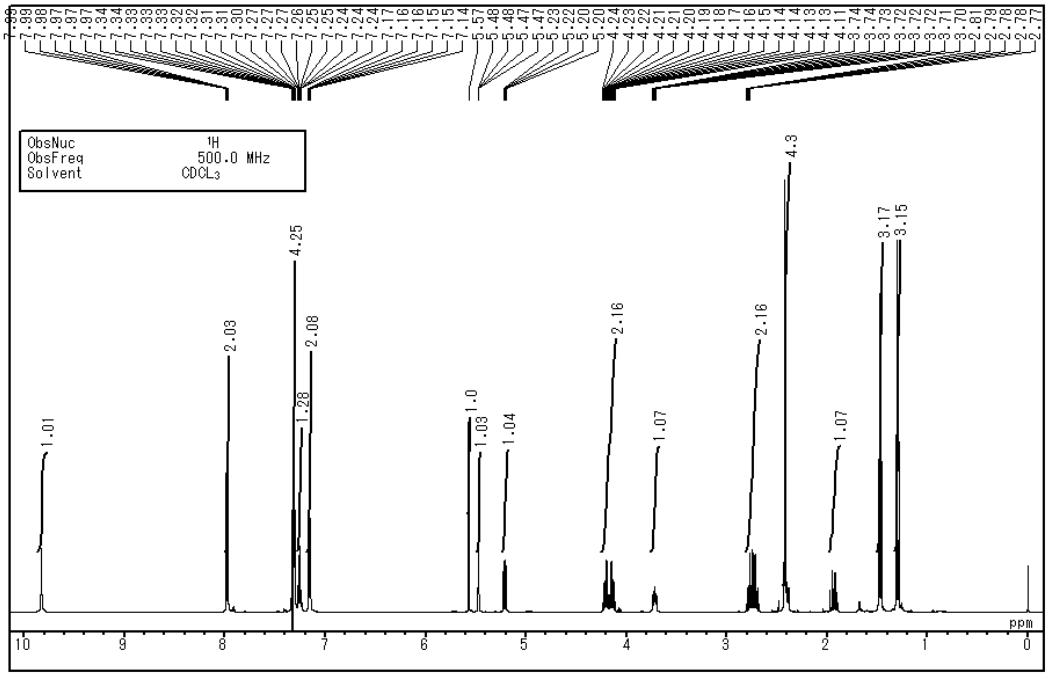


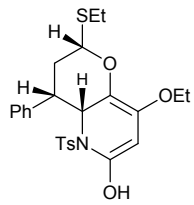


• ^{13}C-NMR spectrum of **12**

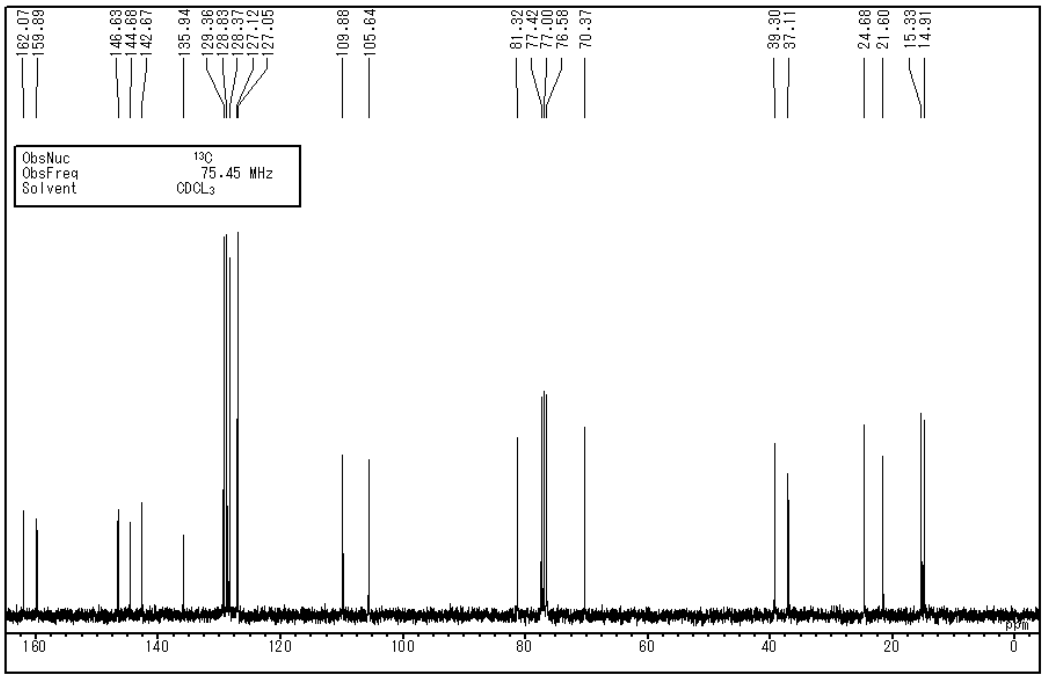


• ^{1}H-NMR spectrum of **13**

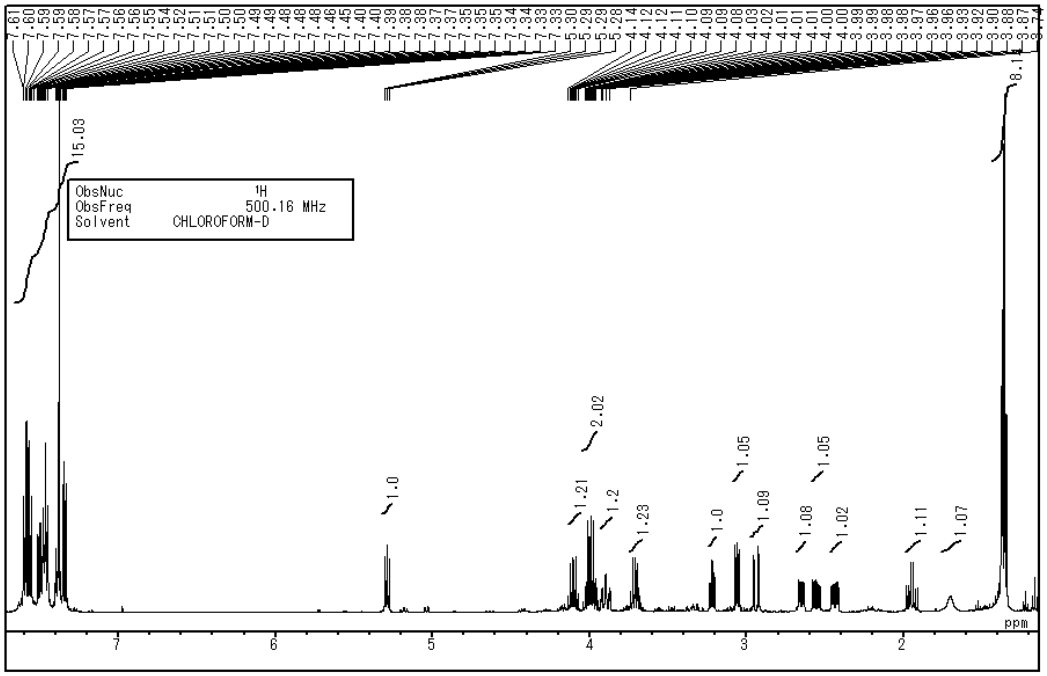


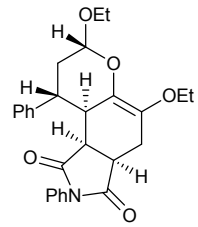


• ^{13}C-NMR spectrum of **13**

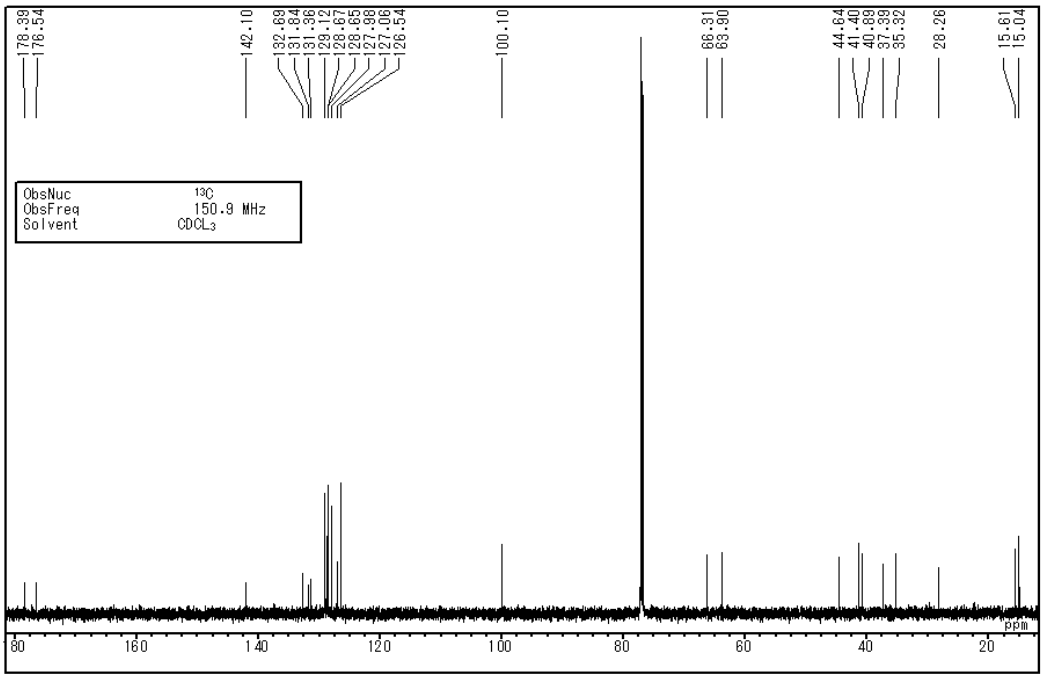


• ^{1}H-NMR spectrum of **14**

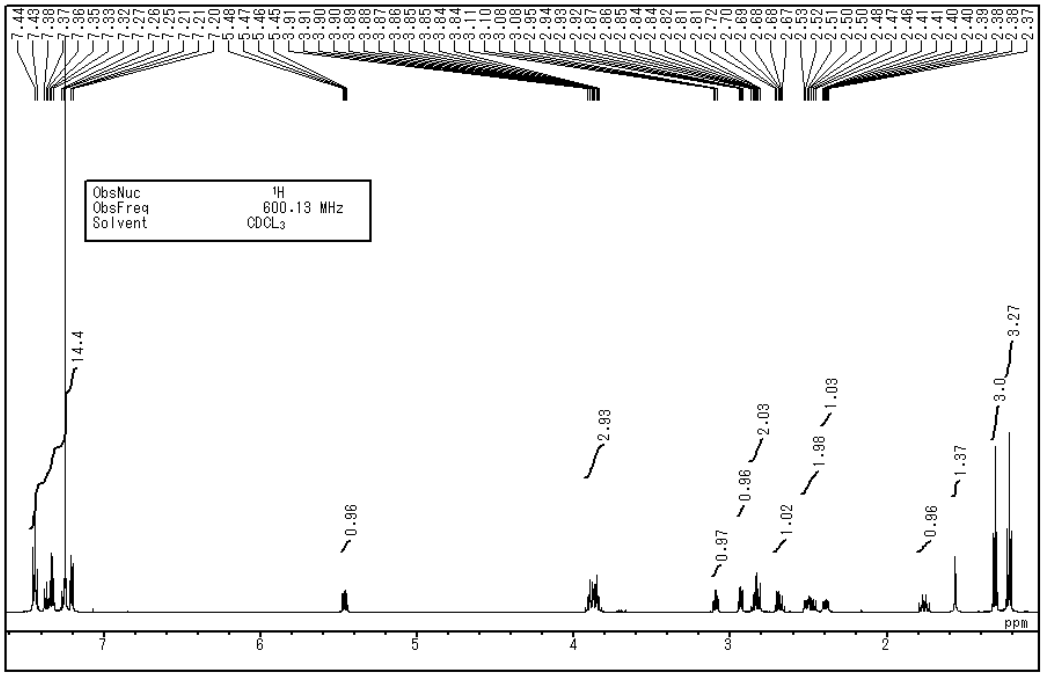


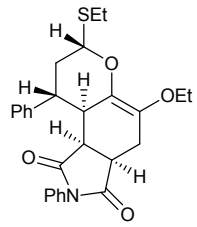


• ^{13}C-NMR spectrum of **14**

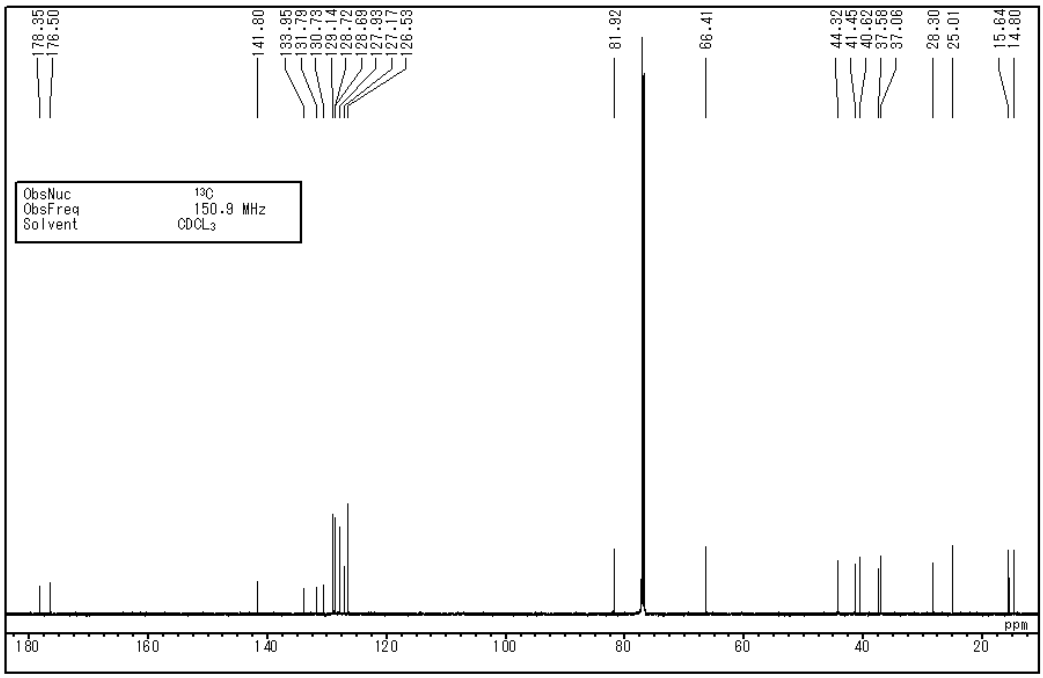


• ^{1}H-NMR spectrum of **15**

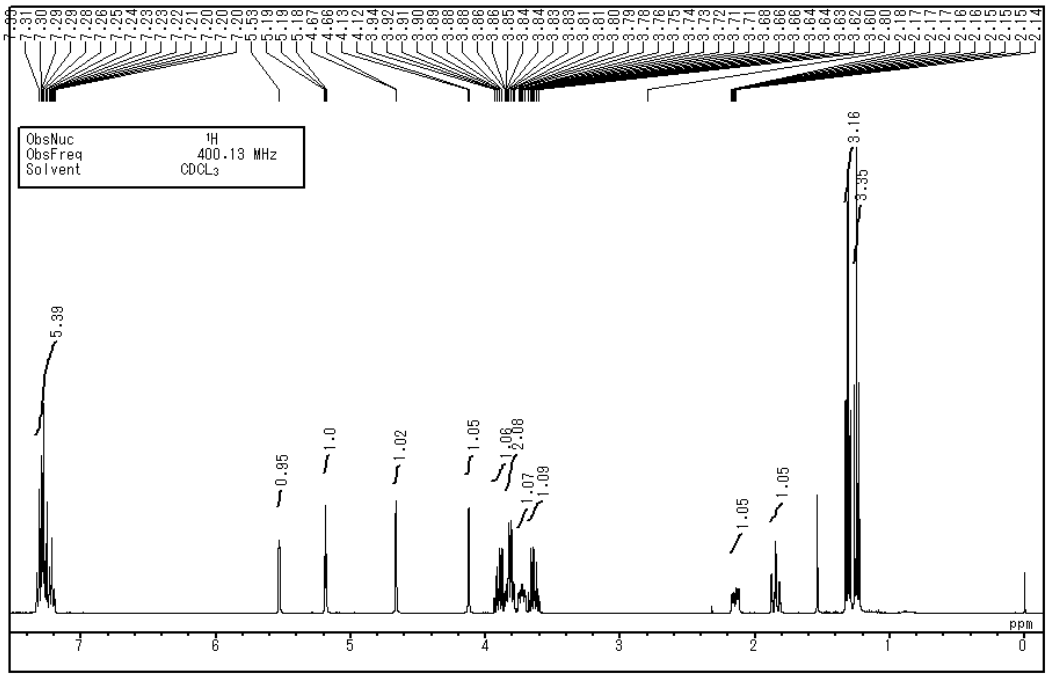


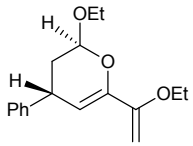


• ^{13}C-NMR spectrum of **15**

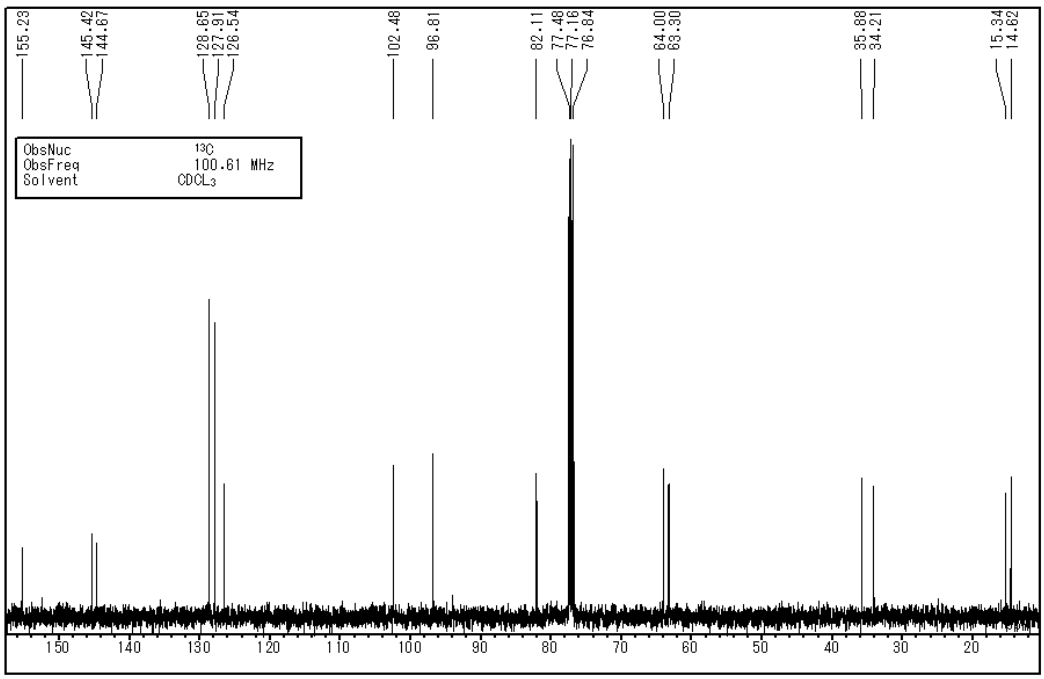


• ^{1}H-NMR spectrum of *exo*-**5**

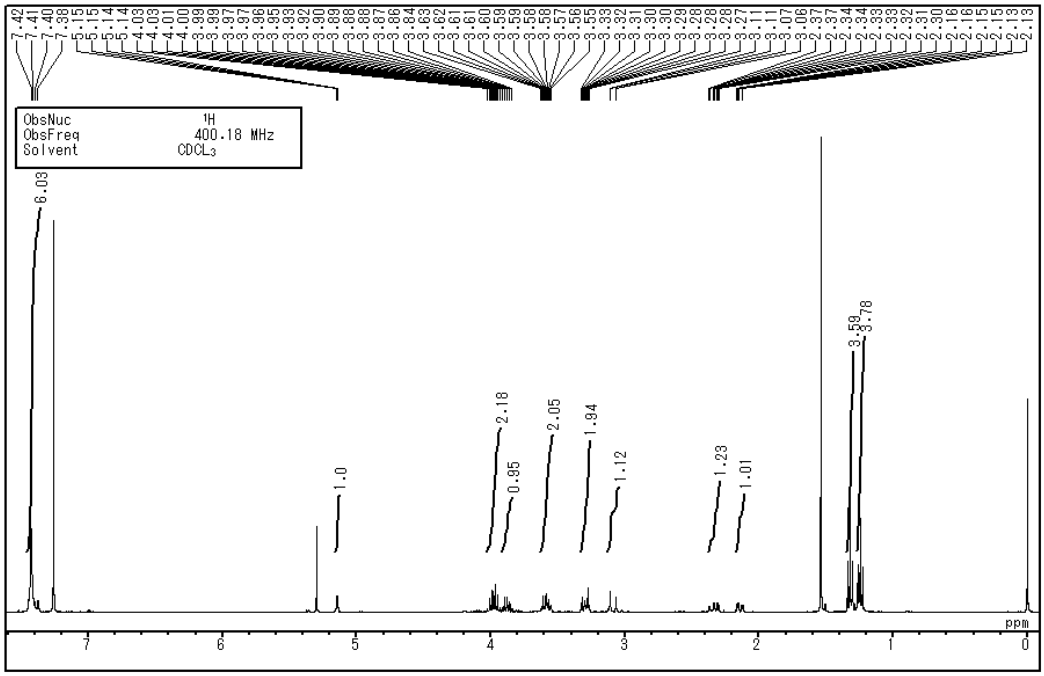


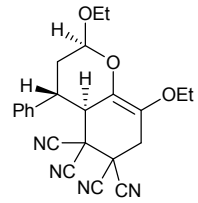


• ^{13}C-NMR spectrum of *exo*-**5**

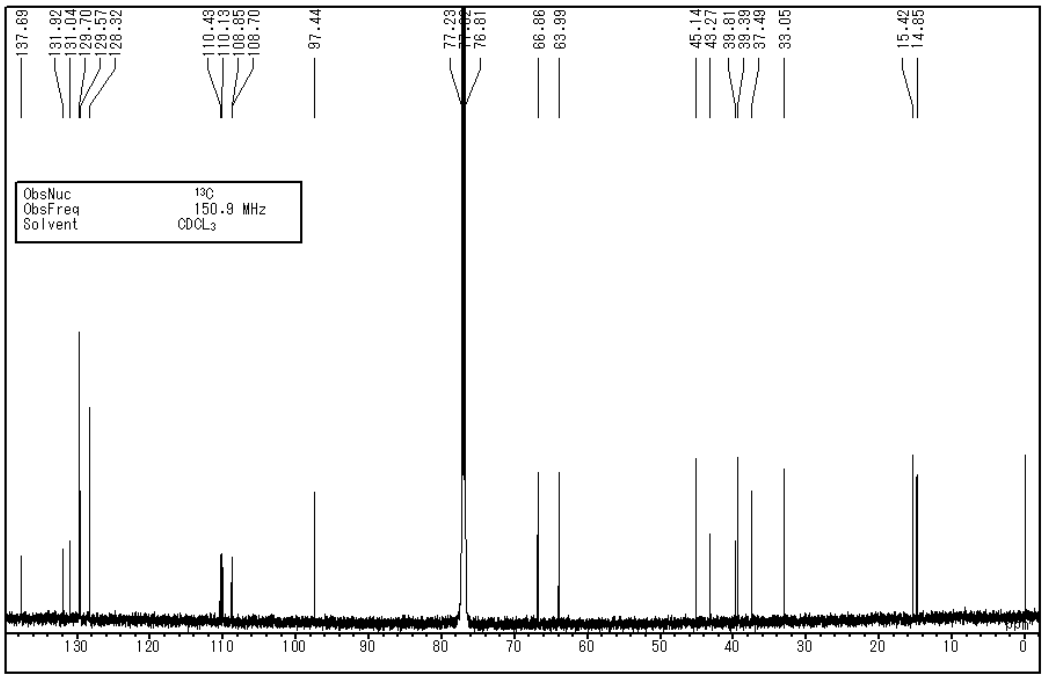


• ^{1}H-NMR spectrum of **16**

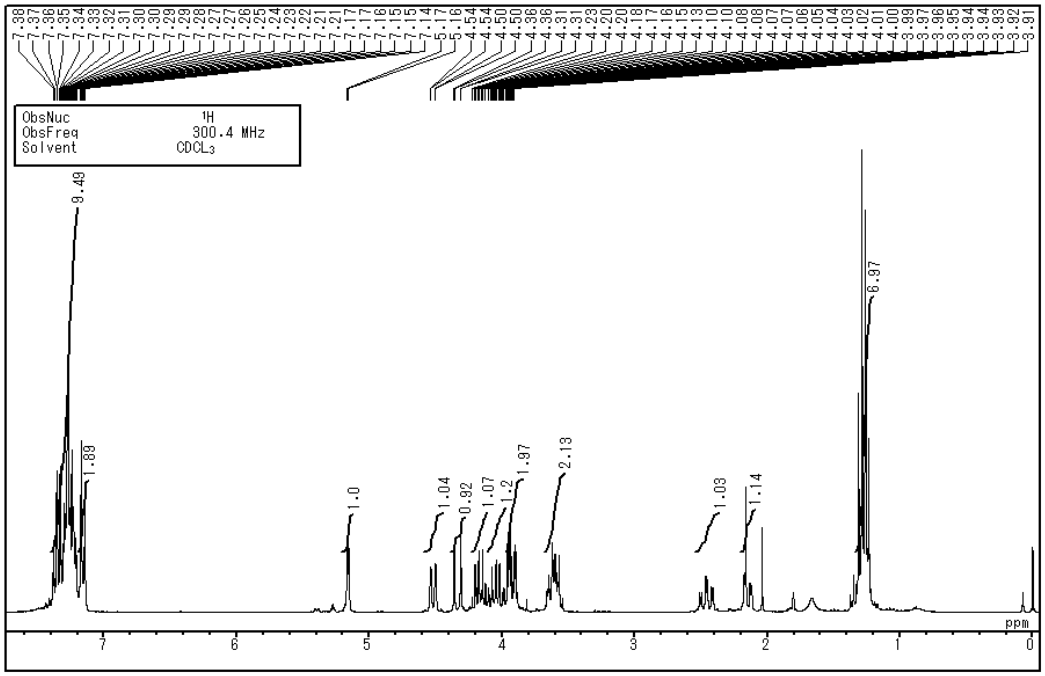


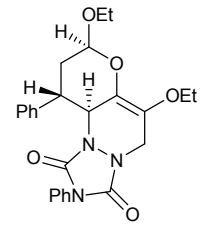


• ^{13}C-NMR spectrum of **16**

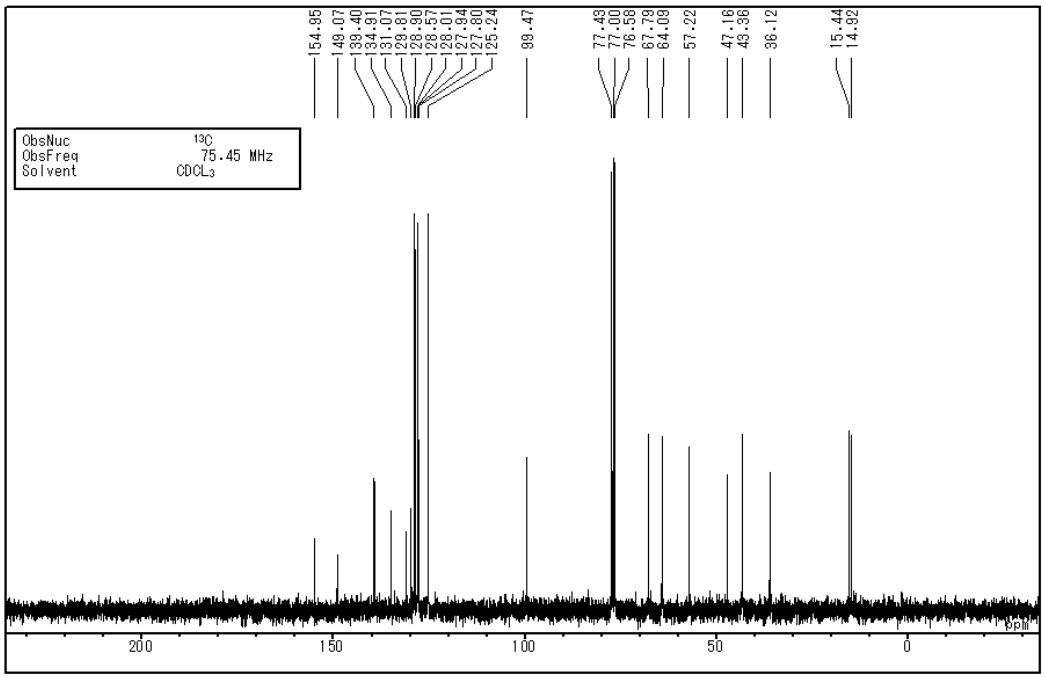


• ^{1}H-NMR spectrum of **17**

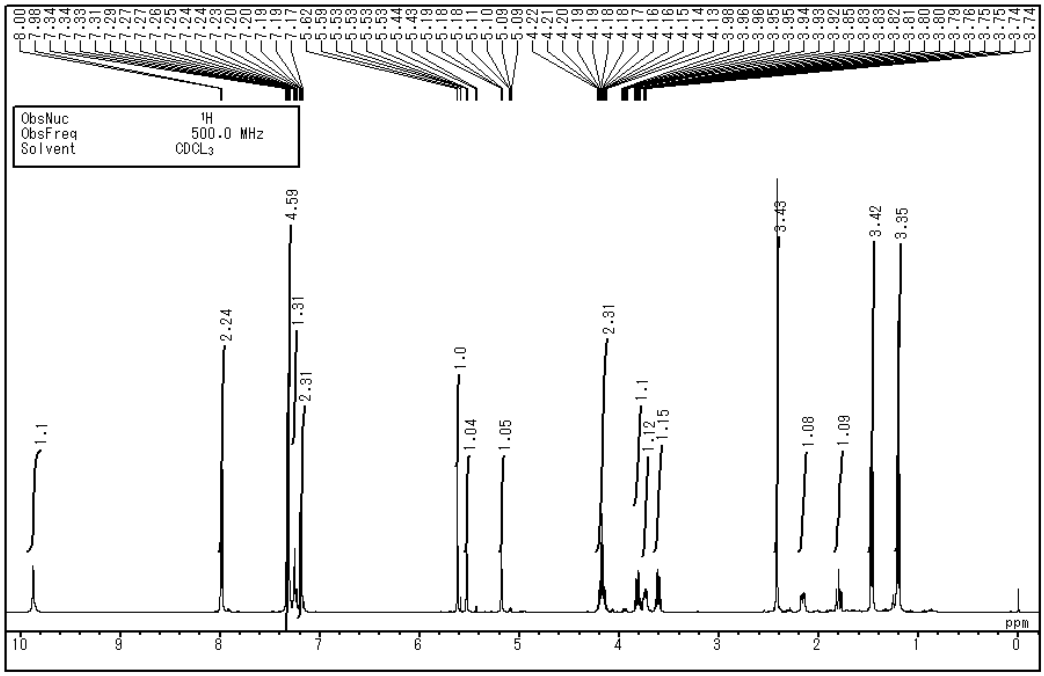


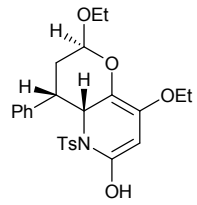


• ^{13}C-NMR spectrum of **17**

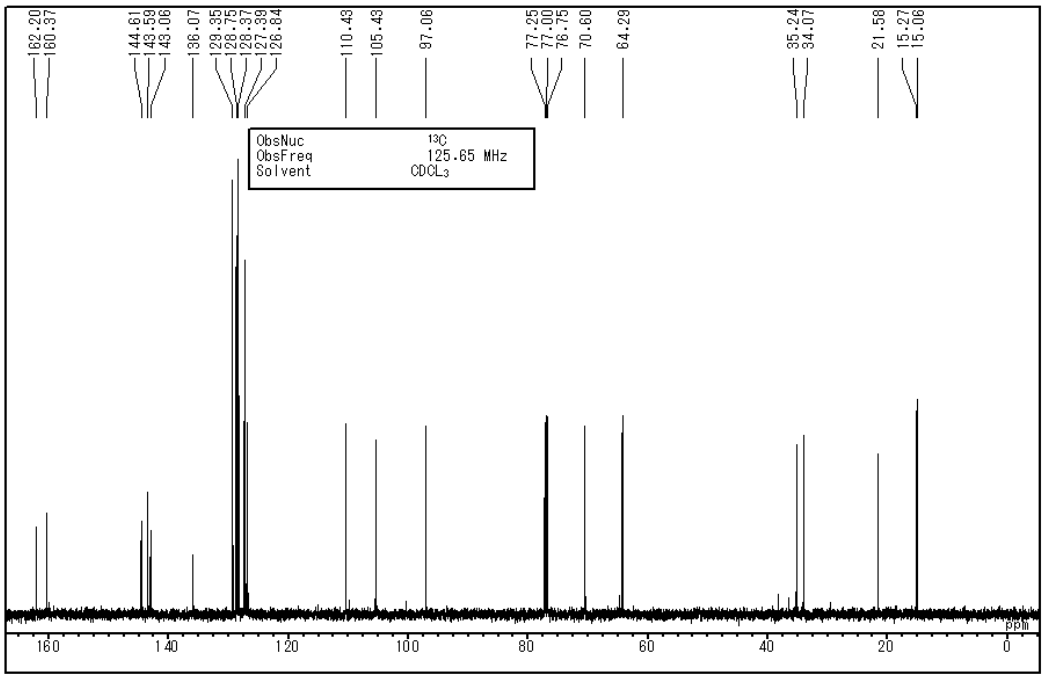


• ^{1}H-NMR spectrum of **18**

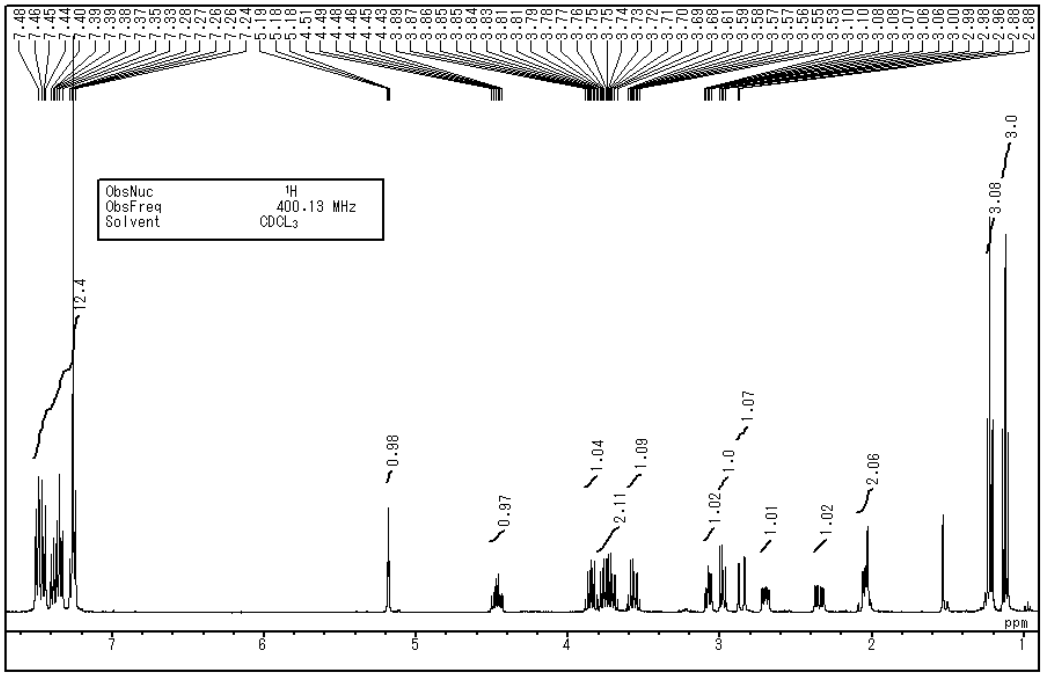


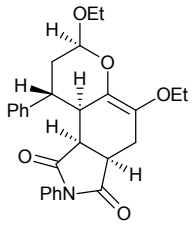


• ^{13}C-NMR spectrum of **18**

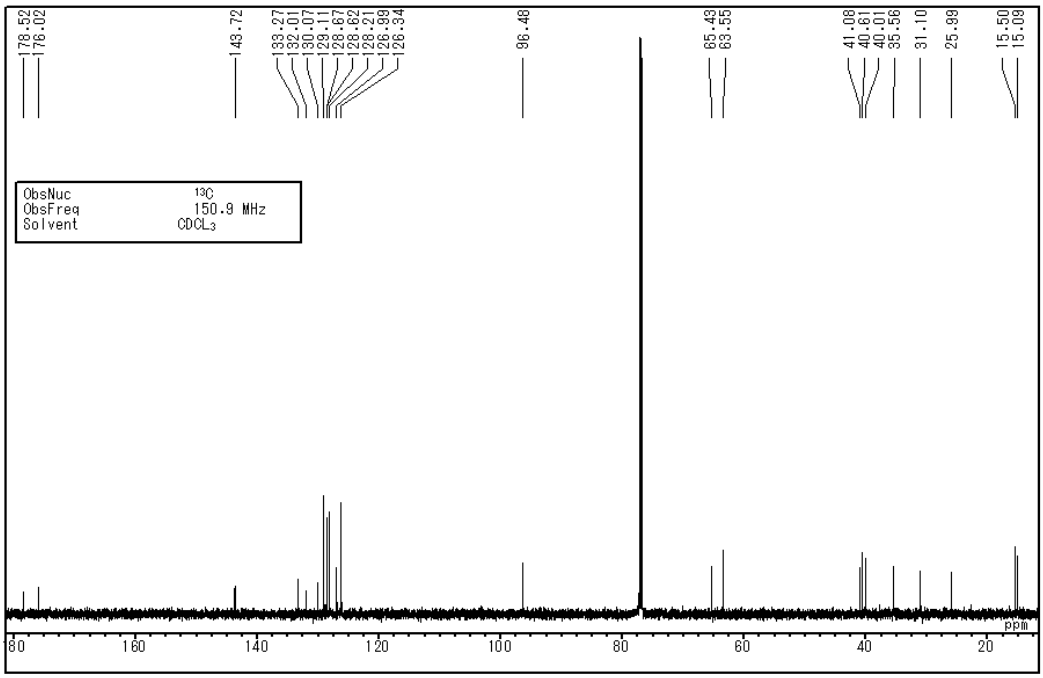


• ^{1}H-NMR spectrum of **19**

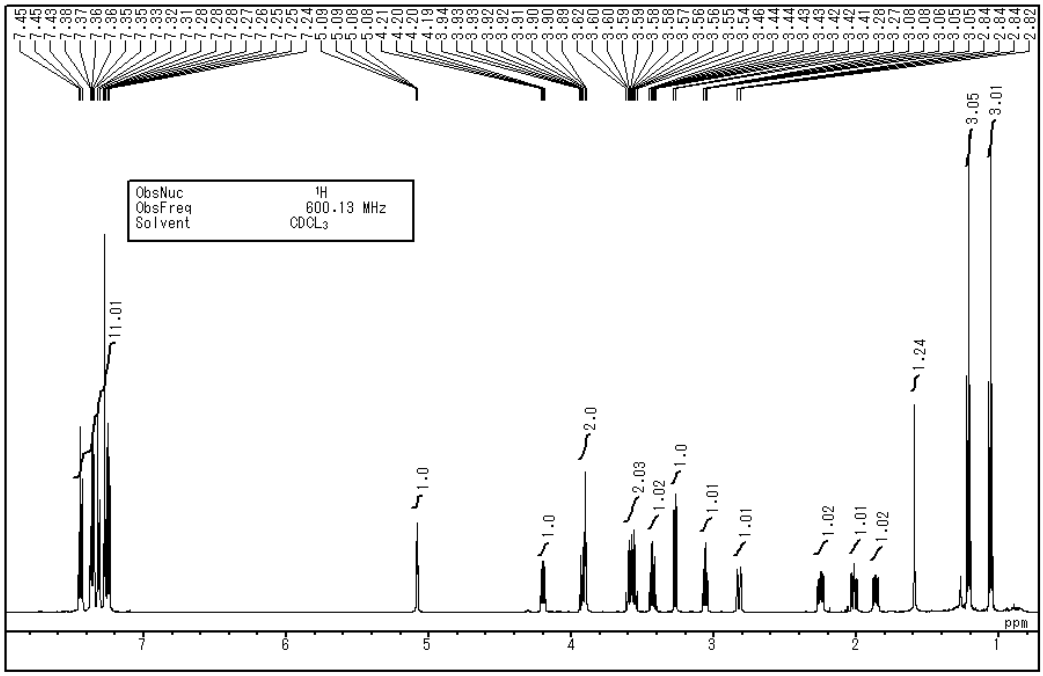


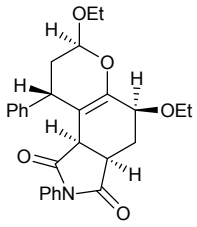


• ^{13}C-NMR spectrum of **19**

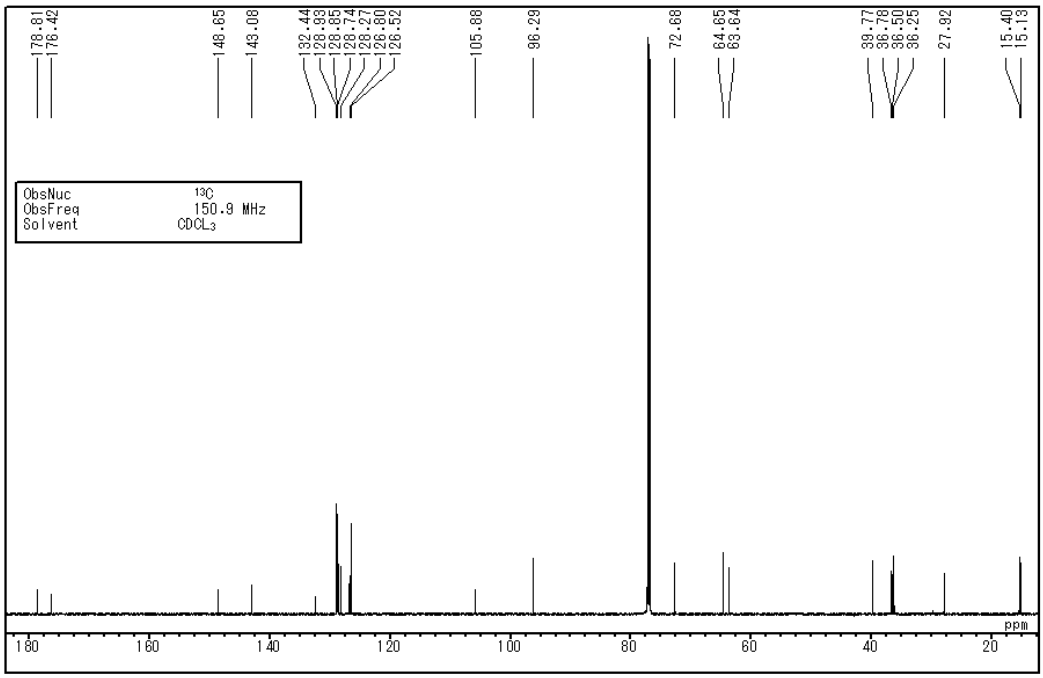


• ^{1}H-NMR spectrum of **19'**



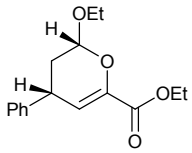


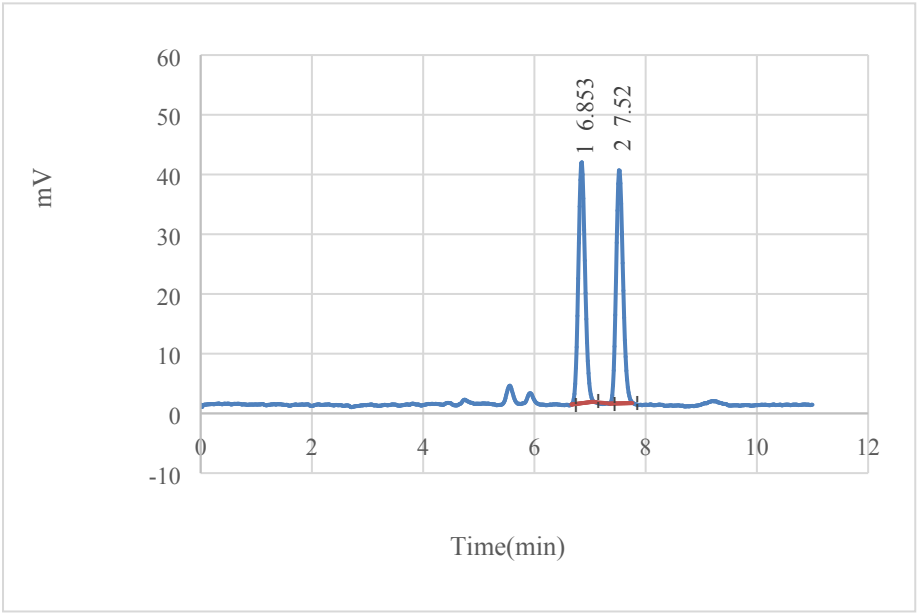
• ^{13}C-NMR spectrum of **19'**



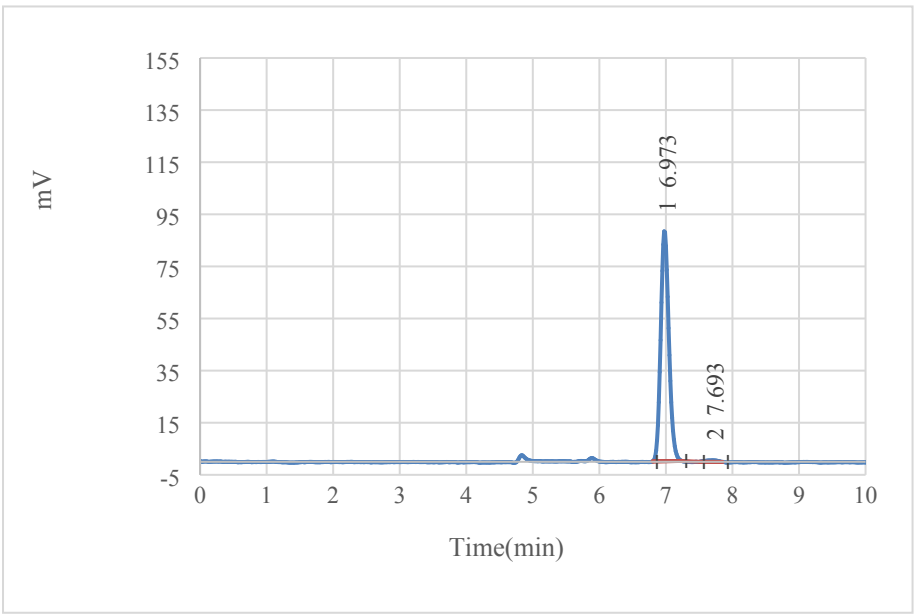
3 Copies of HPLC Chromatograms

• Copies of HPLC Chromatograms of racemic and chiral *endo*-**3**.



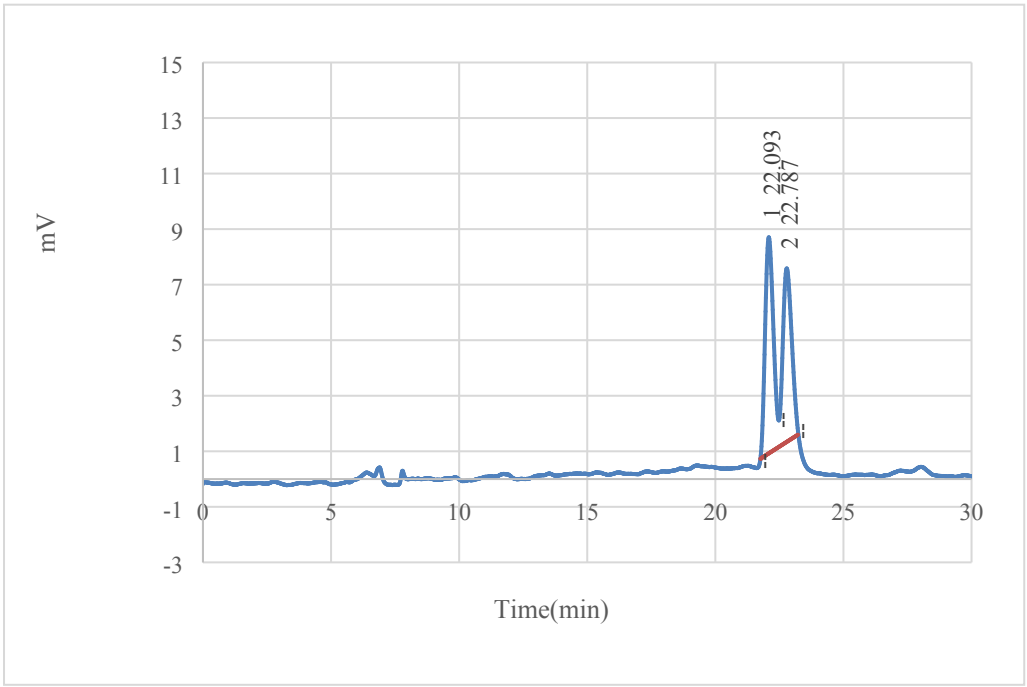


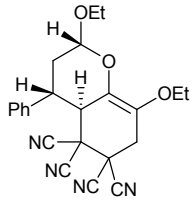
No.	Rt	Peak Name	Area	Area(%)
1	6.853	ent_1	338090.4	50.18
2	7.52	ent_2	335721.6	49.82
			673812	100



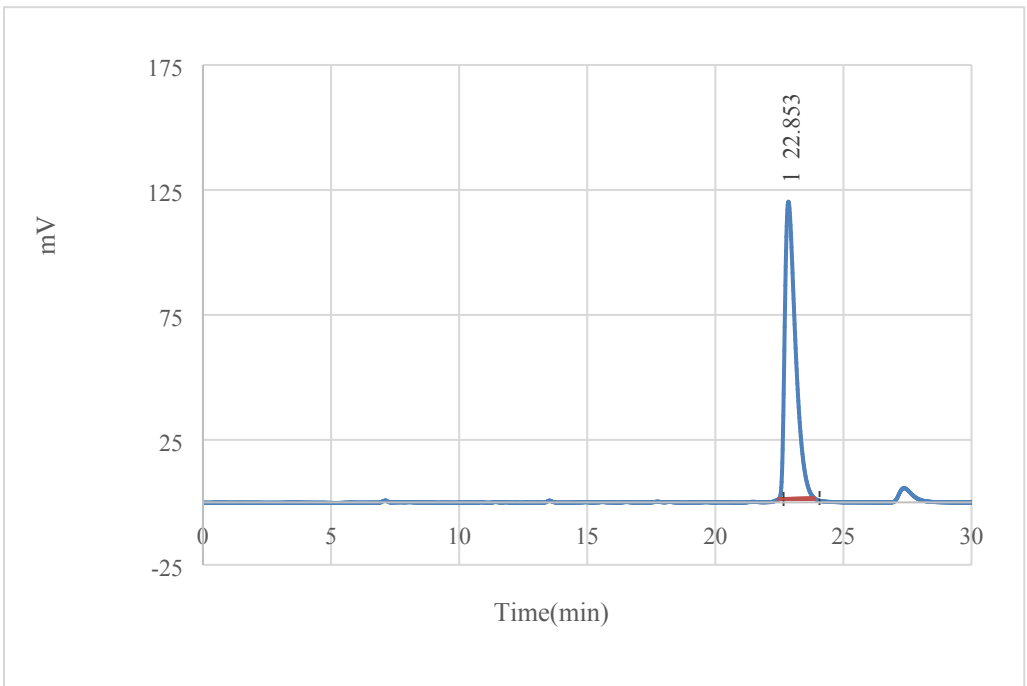
No.	Rt	Peak Name	Area	Area(%)
1	6.973	ent_1	753924	99.01
2	7.693	ent_2	7556	0.99
			761480	100

• Copies of HPLC Chromatograms of racemic and chiral **7**



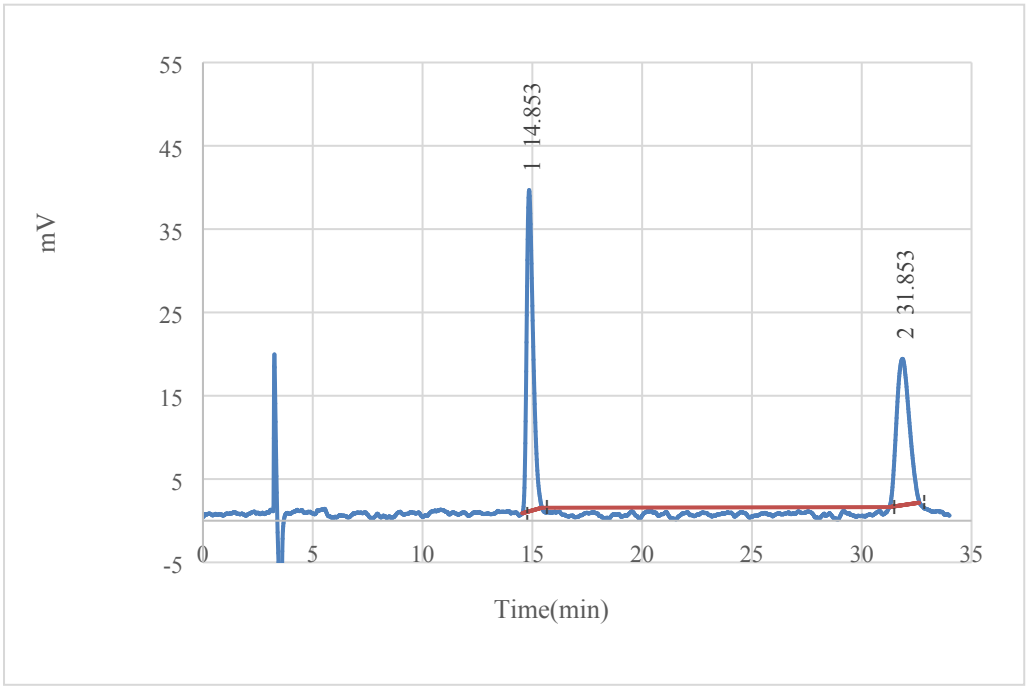


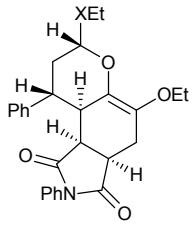
No.	Rt	Peak Name	Area	Area(%)
1	22.093	ent_1	174267.51	53.34
2	22.787	ent_2	152449.29	46.66
			326716.8	100



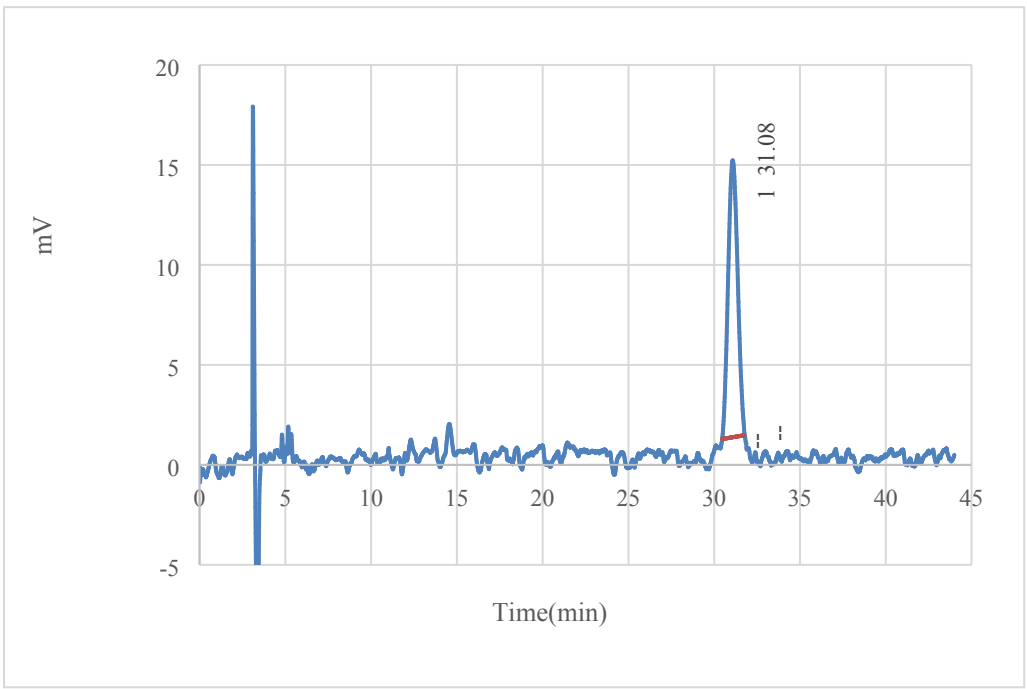
No.	Rt	Peak Name	Area	Area(%)
1	22.853	ent_2	3465476	100
			3465476	100

• Copies of HPLC Chromatograms of racemic and chiral **14.**





No.	Rt	Peak Name	Area	Area(%)
1	14.853	ent_1	783703.2	52.58
2	31.853	ent_2	706653.2	47.42
			1490356.4	100



No.	Rt	Peak Name	Area	Area(%)
1	31.08	ent_2	534082.4	100
			534082.4	100