Electronic Supplementary Information for

Chiral Ionic Brønsted Acid-Achiral Brønsted Base Synergistic Catalysis for Asymmetric Sulfa-Michael Addition to Nitroolefins

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General Information:

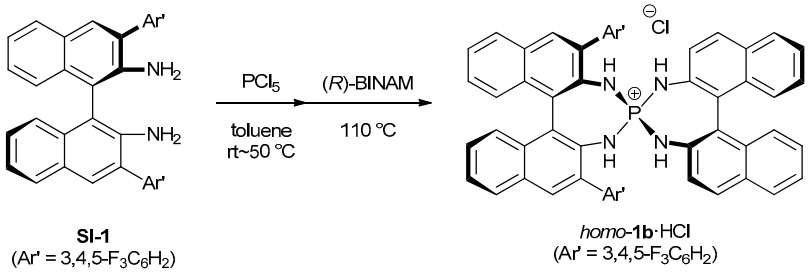
Infrared spectra were recorded on a JASCO FT/IR-300E and a Shimadzu IRAffinity-1 spectrometers. ^{1}H NMR spectra were recorded on a JEOL JNM-ECS400 (400 MHz). Chemical shifts are reported in ppm from the solvent resonance (CD_3OD; 3.31 ppm, and D_2O; 4.79 ppm) and the tetramethylsilane (0.0 ppm) resonance ($CDCl_3$ and acetone-d_6) as the internal standard. Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sept = septet, m = multiplet, br = broad), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a JEOL JNM-ECS400 (101 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$; 77.16 ppm, CD_3OD; 49.00 ppm, and acetone-d_6; 29.84 ppm). ^{31}P NMR spectra were recorded on a JEOL JNM-ECS400 (162 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from H_3PO_4 (0.0 ppm) resonance as the external standard. ^{19}F NMR spectra were recorded on a JEOL JNM-ECS400 (376 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from $CF_3C_6H_5$ (–64.0 ppm) resonance as the external standard. Optical rotations were measured on a HORIBA SEPA-500 polarimeter. The high resolution mass spectra were conducted on Thermo Fisher Scientific Exactive (ESI). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm). Flash column chromatography was performed on silica gel 60 (spherical, 40-50 μm; Kanto Chemical Co., Inc.). Enantiomeric excesses were determined by HPLC analysis using chiral columns (ϕ 4.6 mm x 250 mm, DAICEL CHIRALPAK AD-H (ADH), CHIRALCEL OJ-H (OJH), CHIRALCEL OD-3 (OD3), or CHIRALPAK AS-H (ASH) with hexane (H), 2-propanol (IPA), and ethanol (EtOH) as eluent.

Toluene, tetrahydrofuran (THF), and dichloromethane were supplied from Kanto Chemical Co., Inc. as "Dehydrated" and further purified by passing through neutral alumina under nitrogen atmosphere. Chiral arylaminophosphonium barfate *hetero*-**1**·HBArF and *homo*-**1a**·HBArF,[1] and nitroolefins **2**[2] were prepared by following the literature procedure. 3,4-Dimethoxythiophenol was supplied by Aldrich and distilled prior to use. Other simple chemicals were purchased and used as such.

[1] D. Uraguchi, D. Nakashima and T. Ooi, *J. Am. Chem. Soc.*, 2009, **131**, 7242.
[2] (*a*) R. G. Andrew and R. A. Raphael, *Tetrahedron*, 1987, **43**, 4803; (*b*) L. Palais and A. Alexakis, *Chem. Eur. J.*, 2009, **15**, 10473.

Experimental Section:

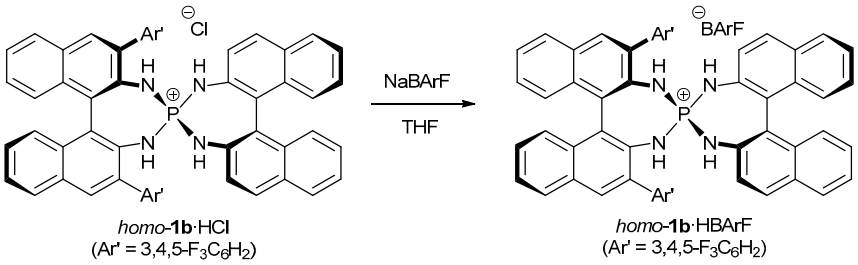
Preparation of *homo*-1b·HBArF:



SI-1
(Ar' = 3,4,5-$F_3C_6H_2$)

homo-**1b**·HCl
(Ar' = 3,4,5-$F_3C_6H_2$)

Procedure for Preparation of Chiral Arylaminophosphonium Chloride *homo*-1b·HCl: To a solution of PCl_5 (20.8 mg, 0.10 mmol) in toluene (1.0 mL) was added (*R*)-3,3'-bis(3,4,5-trifluorophenyl)-2,2'-diamino-1,1'-binaphthalene **SI-1** (54.4 mg, 0.10 mmol) at room temperature. The reaction mixture was stirred for 1 h at 50 °C. Then, (*R*)-2,2'-diamino-1,1'-binaphthalene (BINAM) (42.6 mg, 0.15 mmol) was added and the resulting mixture was stirred overnight at 110 °C. After removal of all volatiles under reduced pressure, purification of the residue by column chromatography on silica gel ($CHCl_3$/MeOH = 20:1 as eluent) gave homochiral arylaminophosphonium chloride *homo*-**1b**·HCl in 72% yield (64.2 mg, 0.072 mmol) as white solid. ***homo*-1b·HCl:** ^{1}H NMR (400 MHz, $CD_3OD/CDCl_3$ = 9:1) δ 8.21 (2H, s), 8.09 (2H, d, J = 8.2 Hz), 7.90 (2H, d, J = 8.2 Hz), 7.84 (2H, d, J = 8.2 Hz), 7.59-7.49 (6H, m), 7.39 (2H, t, J = 8.2 Hz), 7.27 (2H, t, J = 8.2 Hz), 7.14 (2H, d, J = 8.2 Hz), 7.10 (2H, t, J = 8.2 Hz), 7.01 (2H, d, J = 8.2 Hz), 6.79 (2H, d, J = 8.2 Hz), NH protons were not found probably due to deuteration; ^{13}C NMR (101 MHz, $CD_3OD/CDCl_3$ = 9:1) δ 152.0 (ddd, $J_{F\text{-}C}$ = 253.2, 10.0, 3.9 Hz), 140.9 (dt, $J_{F\text{-}C}$ = 254.7, 15.1 Hz), 136.0, 135.5 (td, $J_{F\text{-}C}$ = 9.0, 5.1 Hz), 134.5 (d, $J_{P\text{-}C}$ = 4.8 Hz), 134.2, 133.8, 133.0, 132.8, 132.6, 131.7, 131.4 (d, $J_{F\text{-}C}$ =1.9 Hz), 130.0, 129.4, 129.0, 128.3$_2$, 128.2$_6$, 127.9, 127.7, 127.5, 126.8, 126.6, 124.4 (d, $J_{P\text{-}C}$ = 3.4 Hz), 116.0 (dd, $J_{F\text{-}C}$ = 16.3, 6.2 Hz); ^{19}F NMR (376 MHz, $CD_3OD/CDCl_3$ = 9:1) δ –137.4, –166.0; ^{31}P NMR (162 MHz, $CD_3OD/CDCl_3$ = 9:1) δ 42.9; IR (film) 3057, 2361, 1616, 1528, 1420, 1225, 1043, 1007, 988, 818, 750 cm^{-1}; HRMS (ESI) Calcd for $C_{52}H_{30}N_4F_6P^+$ ([M–Cl]$^+$) 855.2107. Found 855.2102; $[\alpha]_D^{20}$ –314.2 (c = 0.34, MeOH).



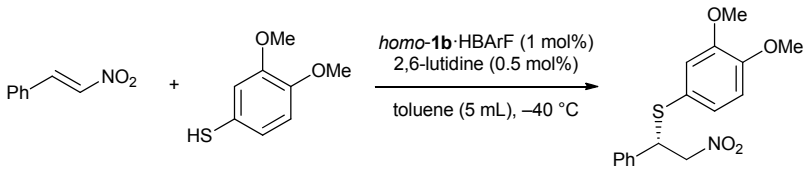
homo-**1b**·HCl
(Ar' = 3,4,5-$F_3C_6H_2$)

homo-**1b**·HBArF
(Ar' = 3,4,5-$F_3C_6H_2$)

Procedure for the Anion Exchange to Arylaminophosphonium Barfate *homo*-1b·HBArF: Arylaminophosphonium chloride *homo*-**1b**·HCl (64.2 mg, 0.072 mmol) and Na[B(3,5-$(CF_3)_2C_6H_3)_4$] (NaBArF) (67.0 mg, 0.076 mmol) were dissolved into THF (0.72 mL). The mixture was stirred for 10 min at room temperature and diluted with water. The aqueous phase was extracted with diethyl ether three times and the combined organic extracts were dried over Na_2SO_4. After concentration, purification of the residue was performed by column chromatography on silica gel ($CHCl_3$/MeOH = 20/1 as eluent) to afford homochiral arylaminophosphonium barfate *homo*-**1b**·HBArF in 99% yield (123.9 mg, 0.072 mmol) as white solid. ***homo*-1b·HBArF:** ^{1}H NMR (400 MHz, acetone-d_6) δ 8.34 (2H, s), 8.22 (2H, d, J = 8.2 Hz), 8.03 (2H, d, J = 8.2 Hz), 7.98 (2H, d, J = 8.2 Hz), 7.88 (8H, brs), 7.73 (4H, brs), 7.70-7.55 (6H, m), 7.48 (2H, t, J = 8.2 Hz), 7.47 (2H, d, J = 8.2 Hz), 7.39 (2H, t, J = 8.2 Hz), 7.22 (2H, t, J = 8.2 Hz), 7.13 (2H, d, J = 8.2 Hz), 6.91 (2H, d, J = 8.2 Hz), NH protons were not found probably due to broadening; ^{13}C NMR (101 MHz, acetone-d_6) δ 162.6 (q, $J_{B\text{-}C}$ = 50.3 Hz), 151.6 (ddd, $J_{F\text{-}C}$ = 252.6, 9.7, 3.9 Hz), 140.4 (dt, $J_{F\text{-}C}$ = 254.5, 15.5 Hz), 135.6, 135.2 (q, $J_{F\text{-}C}$ = 4.8 Hz), 134.2 (d, $J_{P\text{-}C}$ = 4.8 Hz), 133.9, 133.5, 132.7, 132.5, 131.3, 130.8 (d, $J_{P\text{-}C}$ = 1.9 Hz), 130.1 (qq, $J_{F\text{-}C}$ = 31.9, 2.9 Hz), 129.9, 129.4, 129.1, 128.3, 128.2, 127.8 (d, $J_{P\text{-}C}$ = 4.8 Hz), 127.5, 126.6, 126.3 (d, $J_{P\text{-}C}$ = 1.9 Hz), 125.4 (q, $J_{F\text{-}C}$ = 275.8 Hz), 124.6 (d, $J_{P\text{-}C}$ = 2.9 Hz), 118.5 (t, $J_{F\text{-}C}$ = 3.9 Hz), 116.0 (dd, $J_{F\text{-}C}$ = 16.5, 6.8 Hz), two carbons were not found probably due

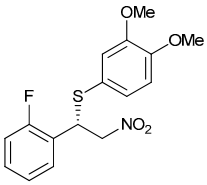
to overlapping; ^{19}F NMR (376 MHz, acetone-d_6) δ –63.0, –135.4, –164.0; ^{31}P NMR (162 MHz, acetone-d_6) δ 44.0; IR (film) 3379, 1701, 1616, 1531, 1354, 1277, 1125, 1049, 887, 754; HRMS (ESI) Calcd for $C_{52}H_{30}N_4F_6P^+$ ([M–BArF]$^+$) 855.2107. Found 855.2099; $[\alpha]_D^{20}$ –162.0 (c = 0.12, MeOH).

Representative Procedures for Chiral Arylaminophosphonium Barfate-Catalyzed Asymmetric Sulfa-Michael Addition to Nitroolefin:

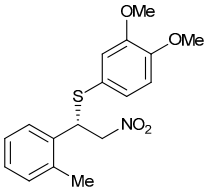


2a **3c** **6a**

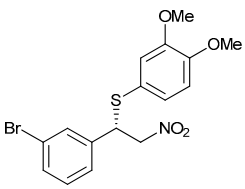
Method for β-Aryl Substituted Nitroolefins: To a dried test tube were weighted nitroolefin **2a** (14.9 mg, 0.10 mmol) and *homo*-**1b**·HBArF (1.72 mg, 0.0010 mmol) under Ar atmosphere. These solid materials were dissolved into toluene (5.0 mL) at room temperature, to which a 0.01 M toluene solution of 2,6-lutidine (50.0 μL, 0.00050 mmol) was added. Then, 3,4-dimethoxythiolphenol (**3c**) (15.9 μL, 0.11 mmol) was introduced dropwise slowly at –40 °C and the stirring was continued for 5 h. After the completion of the reaction was confirmed by TLC analysis, the reaction mixture was directly subjected to the purification by column chromatography on silica gel (H/ethyl acetate (EA) = 20:1-3:1 as eluent) to afford β-thio nitroalkane **6a** in 99% yield (31.6 mg, 0.099 mmol) as white solid. The enantiomeric ratio of the product was determined to be 97.8:2.2 by HPLC analysis. **6a:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.28 (3H, m), 7.20-7.16 (2H, m), 7.00 (1H, dd, J = 8.4, 2.1 Hz), 6.80 (1H, d, J = 8.4 Hz), 6.71 (1H, d, J = 2.1 Hz), 4.87-4.72 (3H, m), 3.88 (3H, s), 3.75 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3, 149.0, 136.7, 129.0, 128.6, 128.5, 127.8, 121.7, 118.1, 111.5, 78.3, 56.0$_1$, 55.9$_5$, 50.4; IR (film) 2958, 2838, 1583, 1554, 1504, 1454, 1439, 1375, 1254, 1231, 1137, 1023 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{17}NNaO_4S^+$ ([M+Na]$^+$) 342.0770. Found 342.0771; $[\alpha]_D^{20}$ +73.7 (c = 0.31, $CHCl_3$) for 95.6% ee; HPLC ADH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 13.0 min (*S*), 14.7 min (*R*).



6b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.26 (1H, m), 7.12-6.98 (4H, m), 6.80 (1H, d, J = 8.2 Hz), 6.74 (1H, d, J = 2.3 Hz), 5.04 (1H, dd, J = 8.7, 7.3 Hz), 4.88 (1H, dd, J = 13.3, 8.7 Hz), 4.81 (1H, dd, J = 13.3, 7.3 Hz), 3.89 (3H, s), 3.76 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4 (d, $J_{F\text{-}C}$ = 252.6 Hz), 150.4, 149.1, 130.2 (d, $J_{F\text{-}C}$ = 8.7 Hz), 128.9, 128.5 (d, $J_{F\text{-}C}$ = 2.9 Hz), 124.4 (d, $J_{F\text{-}C}$ = 2.9 Hz), 124.2 (d, $J_{F\text{-}C}$ = 13.5 Hz), 121.6, 118.2, 116.2 (d, $J_{F\text{-}C}$ = 21.2 Hz), 111.5, 77.2, 56.0$_4$, 55.9$_8$, 44.2; IR (film) 2960, 2840, 1584, 1555, 1504, 1462, 1440, 1375, 1254, 1232, 1178, 1137, 1024, 761 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{16}FNNaO_4S^+$ ([M+Na]$^+$) 360.0676. Found 360.0674; $[\alpha]_D^{20}$ +59.1 (c = 0.39, $CHCl_3$) for 96.7% ee; HPLC ADH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 12.9 min (major), 14.3 min (minor).

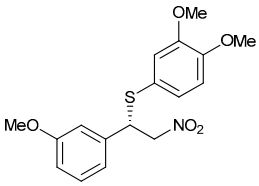


6c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (1H, dd, J = 7.8, 2.3 Hz), 7.18 (1H, t, J = 7.8 Hz), 7.09 (1H, td, J = 7.8, 2.3 Hz), 7.00 (1H, dd, J = 8.7, 2.3 Hz), 6.84 (1H, d, J = 7.8 Hz), 6.80 (1H, d, J = 8.7 Hz), 6.61 (1H, d, J = 2.3 Hz), 4.98 (1H, dd, J = 8.7, 7.6 Hz), 4.86 (1H, dd, J = 13.2, 8.7 Hz), 4.78 (1H, dd, J = 13.2, 7.6 Hz), 3.88 (3H, s), 3.71 (3H, s), 2.45 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 148.9, 136.7, 134.5, 131.2, 129.0, 128.3, 126.3, 126.0, 121.4, 118.5, 111.4, 77.7, 56.0, 55.9, 46.0, 19.5; IR (film) 2953, 1551, 1503, 1462, 1439, 1375, 1252, 1231, 1179, 1136, 1022, 856, 806, 762 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{19}NNaO_4S$ ([M+Na]$^+$) 356.0927. Found 356.0922; $[\alpha]_D^{21}$ –4.3 (c = 0.33, $CHCl_3$) for 91.1% ee; HPLC ADH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 9.8 min (major), 10.8 min (minor).

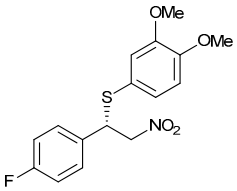


6d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (1H, ddd, J = 8.2, 1.8, 1.4 Hz), 7.33 (1H, dd, J = 1.8, 1.4 Hz), 7.19 (1H, t, J = 8.2 Hz), 7.09 (1H, dt, J = 8.2, 1.4 Hz), 6.98 (1H, dd, J = 8.2, 1.8 Hz), 6.82 (1H, d, J = 8.2 Hz), 6.75 (1H, d, J = 1.8 Hz), 4.83-4.68 (3H, m), 3.89 (3H, s), 3.79 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 149.2, 139.0, 131.7, 131.0, 130.5, 128.9, 126.4, 122.9, 121.1, 118.2, 111.6, 77.9, 56.0$_9$, 56.0$_6$, 49.9; IR (film) 2957, 2837, 1583, 1555, 1504, 1462, 1438, 1374, 1254, 1231, 1178, 1137, 1023 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{16}BrNNaO_4S$ ([M+Na]$^+$)

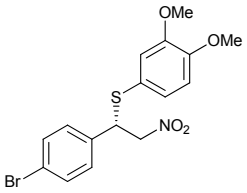
419.9876. Found 419.9874; $[\alpha]_D^{20}$ +48.1 (*c* = 0.50, $CHCl_3$) for 89.6% ee; HPLC ADH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 14.0 min (major), 16.3 min (minor).



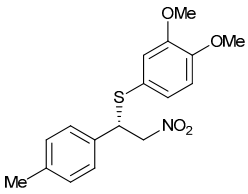
6e: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (1H, t, *J* = 8.2 Hz), 7.02 (1H, dd, *J* = 8.2, 2.3 Hz), 6.83 (1H, dd, *J* = 8.2, 2.3 Hz), 6.81 (1H, d, *J* = 8.2 Hz), 6.77 (1H, d, *J* = 2.3 Hz), 6.76 (1H, dd, *J* = 8.2, 2.3 Hz), 6.73 (1H, t, *J* = 2.3 Hz), 4.85-4.69 (3H, m), 3.89 (3H, s), 3.78 (6H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 150.3, 149.1, 138.2, 130.0, 128.6, 121.9, 120.0, 118.0, 114.0, 113.6, 111.5, 78.3, 56.1, 56.0, 55.4, 50.5; IR (film) 2957, 2836, 1584, 1552, 1504, 1457, 1438, 1375, 1254, 1231, 1178, 1137, 1023 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{19}NNaO_5S$ ($[M+Na]^+$) 372.0876. Found 372.0860; $[\alpha]_D^{20}$ +62.4 (*c* = 0.37, $CHCl_3$) for 93.1% ee; HPLC ADH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 16.2 min (major), 18.2 min (minor).



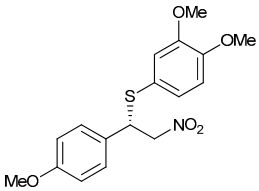
6f: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (2H, dd, *J* = 8.7, 5.2 Hz), 7.01 (2H, t, *J* = 8.7 Hz), 6.98 (1H, dd, *J* = 8.7, 2.3 Hz), 6.80 (1H, d, *J* = 8.7 Hz), 6.75 (1H, d, *J* = 2.3 Hz), 4.83-4.68 (3H, m), 3.88 (3H, s), 3.79 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 (d, J_{F-C} = 251.6 Hz), 150.4, 149.1, 132.4 (d, J_{F-C} = 2.9 Hz), 129.5 (d, J_{F-C} = 8.7 Hz), 128.6, 121.5, 118.0, 115.9 (d, J_{F-C} = 22.3 Hz), 111.5, 78.3, 56.0$_1$, 55.9$_9$, 49.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ –114.4; IR (film) 2936, 2839, 1584, 1551, 1503, 1439, 1375, 1254, 1229, 1136, 1022 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{16}FNNaO_4S$ ($[M+Na]^+$) 360.0676. Found 360.0674; $[\alpha]_D^{20}$ +72.7 (*c* = 0.26, $CHCl_3$) for 93.8% ee; HPLC ADH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 13.7 min (major), 15.1 min (minor).



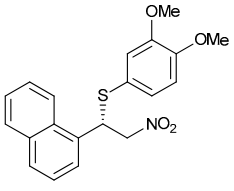
6g: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (2H, d, *J* = 8.5 Hz), 7.05 (2H, d, *J* = 8.5 Hz), 6.98 (1H, dd, *J* = 8.2, 2.3 Hz), 6.81 (1H, d, *J* = 8.2 Hz), 6.71 (1H, d, *J* = 2.3 Hz), 4.82-4.68 (3H, m), 3.89 (3H, s), 3.78 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 149.2, 135.8, 132.1, 129.5, 128.8, 122.6, 121.2, 118.1, 111.6, 78.0, 56.1, 56.0, 49.9; IR (film) 2932, 2839, 1583, 1552, 1503, 1462, 1439, 1374, 1254, 1231, 1178, 1137, 1023, 731 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{16}BrKNO_4S$ ($[M+K]^+$) 435.9615. Found 435.9612; $[\alpha]_D^{20}$ +53.5 (*c* = 0.41, $CHCl_3$) for 90.9% ee; HPLC ADH, H/EtOH = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 24.3 min (minor), 26.0 min (major).



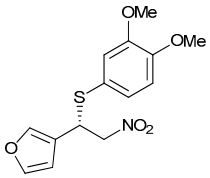
6h: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (2H, d, *J* = 8.2 Hz), 7.08 (2H, d, *J* = 8.2 Hz), 7.02 (1H, dd, *J* = 8.2, 2.3 Hz), 6.81 (1H, d, *J* = 8.2 Hz), 6.74 (1H, d, *J* = 2.3 Hz), 4.85-4.68 (3H, m), 3.89 (3H, s), 3.76 (3H, s), 2.33 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 149.1, 138.5, 133.5, 129.7, 128.5, 127.7, 122.1, 118.0, 111.5, 78.4, 56.0, 55.9, 50.3, 21.3; IR (film) 2932, 2835, 1583, 1553, 1504, 1463, 1439, 1375, 1254, 1231, 1178, 1137, 1024 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{19}KNO_6S$ ($[M+K]^+$) 372.0666. Found 372.0665; $[\alpha]_D^{20}$ +65.2 (*c* = 0.35, $CHCl_3$) for 92.0% ee; HPLC ADH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 11.7 min (major), 13.0 min (minor).



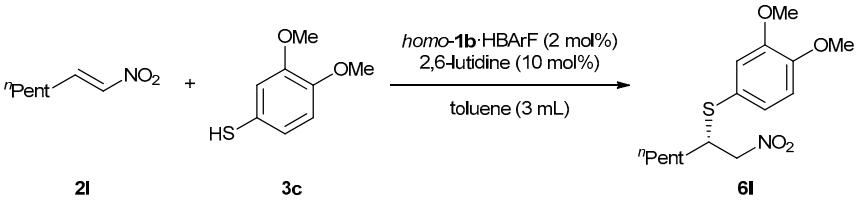
6i: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (2H, d, *J* = 8.7 Hz), 7.00 (1H, dd, *J* = 8.4, 1.4 Hz), 6.84 (2H, d, *J* = 8.7 Hz), 6.80 (1H, d, *J* = 8.4 Hz), 6.76 (1H, d, *J* = 1.4 Hz), 4.81-4.67 (3H, m), 3.88 (3H, s), 3.78$_0$ (3H, s), 3.77$_6$ (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 150.2, 149.1, 129.0, 128.5, 128.4, 122.1, 118.0, 114.3, 111.5, 78.5, 56.0$_2$, 55.9$_8$, 55.4, 50.0; IR (film) 2957, 2911, 1584, 1549, 1503, 1439, 1250, 1231, 1177, 1136, 1024, 808 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{19}NNaO_5S$ ($[M+Na]^+$) 372.0876. Found 372.0859; $[\alpha]_D^{21}$ +60.5 (*c* = 0.36, $CHCl_3$) for 89.6% ee; HPLC ADH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 19.6 min (major), 21.1 min (minor).



6j: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (1H, d, *J* = 8.2 Hz), 7.89 (1H, d, *J* = 8.2 Hz), 7.80 (1H, d, *J* = 8.2 Hz), 7.64 (1H, td, *J* = 8.2, 1.4 Hz), 7.55 (1H, t, *J* = 8.2 Hz), 7.30 (1H, t, *J* = 8.2 Hz), 6.97-6.90 (2H, m), 6.76 (1H, d, *J* = 8.2 Hz), 6.45 (1H, s), 5.58 (1H, t, *J* = 7.9 Hz), 4.97 (2H, d, *J* = 7.9 Hz), 3.86 (3H, s), 3.59 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 148.8, 134.2, 132.0, 130.7, 129.3, 129.2, 127.0, 126.3, 124.9, 124.3, 123.0, 121.3, 118.7, 111.3, 77.8, 56.0, 55.8, 45.3, one carbon was not found probably due to overlapping; IR (film) 2959, 2839, 1551, 1503, 1439, 1373, 1252, 1231, 1179, 1136, 1022, 775, 762 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{19}NNaO_4S$ ($[M+Na]^+$) 392.0927. Found 392.0924; $[\alpha]_D^{20}$ –137.8 (*c* = 0.48, $CHCl_3$) for 89.6% ee; HPLC ADH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 14.0 min (major), 17.9 min (minor).

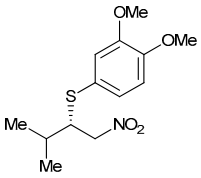


6k: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (1H, t, J = 1.8 Hz), 7.18 (1H, d, J = 0.9 Hz), 7.01 (1H, dd, J = 8.2, 2.3 Hz), 6.81$_8$ (1H, d, J = 8.2 Hz), 6.81$_6$ (1H, d, J = 2.3 Hz), 6.41 (1H, dd, J = 1.8, 0.9 Hz), 4.73 (1H, dd, J = 8.2, 7.3 Hz), 4.66 (1H, dd, J = 12.8, 7.3 Hz), 4.62 (1H, dd, J = 12.8, 8.2 Hz), 3.89 (3H, s), 3.82 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 149.1, 143.8, 140.3, 128.8, 121.4, 121.3, 118.2, 111.5, 109.6, 78.1, 56.1, 42.1, one carbon was not found probably due to overlapping; IR (film) 2959, 2839, 1583, 1555, 1504, 1463, 1439, 1374, 1254, 1231, 1178, 1137, 1023 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{15}NNaO_5S$ ([M+Na]$^+$) 332.0563. Found 332.0563; $[\alpha]_D^{20}$ +38.7 (c = 0.34, $CHCl_3$) for 91.8% ee; HPLC ADH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 15.5 min (major), 18.8 min (minor).

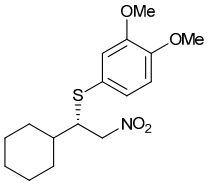


2l **3c** **6l**

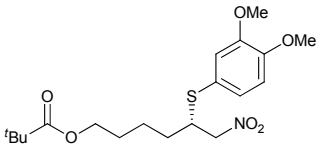
Method for β-Alkyl Substituted Nitroolefins: To a solution of *homo*-**1b**·HBArF (3.44 mg, 0.0020 mmol) in toluene (3.0 mL) were introduced nitroolefin **2l** (14.3 mg, 0.10 mmol) and a 1 M toluene solution of 2,6-lutidine (10.0 μL, 0.010 mmol) at room temperature under Ar atmosphere. 3,4-Dimethoxythiolphenol (**3c**) (15.9 μL, 0.11 mmol) was then added dropwise slowly at –40 ºC and the stirring was continued for 24 h. After the completion of the reaction, the reaction mixture was directly subjected to the purification by column chromatography on silica gel (H/EA = 20:1-4:1 as eluent) to afford β-thio nitroalkanes **6l** in 99% yield (31.0 mg, 0.099 mmol) as colorless oil. The enantiomeric ratio of the product was determined to be 97.0:3.0 by HPLC analysis. **6l**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (1H, dd, J = 8.4, 2.3 Hz), 7.00 (1H, d, J = 2.3 Hz), 6.84 (1H, d, J = 8.4 Hz), 4.43 (1H, dd, J = 12.8, 7.8 Hz), 4.38 (1H, dd, J = 12.8, 7.8 Hz), 3.89 (3H, s), 3.88 (s, 3H), 3.52 (1H, qd, J = 7.8, 4.6 Hz), 1.73-1.43 (4H, m), 1.39-1.23 (4H, m), 0.91 (3H, t, J = 7.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 149.1, 128.2, 121.6, 117.9, 111.5, 78.9, 55.9$_5$, 55.8$_8$, 46.9, 31.5, 31.3, 26.2, 22.4, 14.0; IR (film) 2932, 2857, 1551, 1504, 1464, 1439, 1252, 1231, 1179, 1138, 1024, 764 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{23}NNaO_4S$ ([M+Na]$^+$) 336.1240. Found 336.1238; $[\alpha]_D^{20}$ +12.1 (c = 0.33, $CHCl_3$) for 93.9% ee; HPLC ADH, H/IPA = 10:1, flow rate = 0.5 mL/min, λ = 210 nm, 13.6 min (major), 15.7 min (minor).



6m: The reaction was performed at 0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (1H, dd, J = 8.2, 2.3 Hz), 6.99 (1H, d, J = 2.3 Hz), 6.82 (1H, d, J = 8.2 Hz), 4.59 (1H, dd, J = 13.1, 8.2 Hz), 4.43 (1H, dd, J = 13.1, 7.3 Hz), 3.90 (3H, s), 3.88 (3H, s), 3.55 (1H, ddd, J = 8.2, 7.3, 4.6 Hz), 2.01 (1H, sept-d, J = 6.9, 4.6 Hz), 1.14 (3H, d, J = 6.9 Hz), 1.06 (3H, d, J = 6.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 149.3, 127.2, 123.7, 117.0, 111.7, 77.6, 56.1$_3$, 56.0$_5$, 55.0, 30.1, 20.3, 18.4; IR (film) 2963, 2939, 1551, 1504, 1464, 1439, 1377, 1252, 1231, 1179, 1136, 1024, 764 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{19}NNaO_4S$ ([M+Na]$^+$) 308.0927. Found 308.0924; $[\alpha]_D^{20}$ +34.7 (c = 0.25, $CHCl_3$) for 90.1% ee; HPLC ADH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 7.4 min (major), 9.2 min (minor).

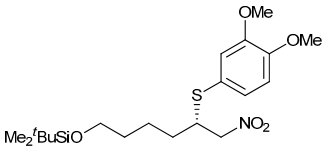


6n: The reaction was performed at 0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (1H, dd, J = 8.2, 2.3 Hz), 6.98 (1H, d, J = 2.3 Hz), 6.82 (1H, d, J = 8.2 Hz), 4.63 (1H, dd, J = 12.8, 7.4 Hz), 4.41 (1H, dd, J = 12.8, 7.4 Hz), 3.90 (3H, s), 3.88 (3H, s), 3.52 (1H, td, J = 7.4, 4.9 Hz), 1.94 (1H, d, J = 12.4 Hz), 1.85-1.56 (5H, m), 1.42 (1H, qd, J = 12.1, 3.1 Hz), 1.33-1.07 (4H, m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 149.3, 127.2, 123.8, 117.0, 111.7, 77.3, 56.1, 56.0, 54.1, 39.8, 30.6, 29.1, 26.3, 26.2$_1$, 26.1$_6$; IR (film) 2928, 2852, 1551, 1504, 1439, 1377, 1252, 1231, 1179, 1136, 1024, 764 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{23}NNaO_4S$ ([M+Na]$^+$) 348.1240. Found 348.1240; $[\alpha]_D^{20}$ +41.0 (c = 0.32, $CHCl_3$) for 95.5% ee; HPLC ADH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 7.8 min (major), 10.2 min (minor).



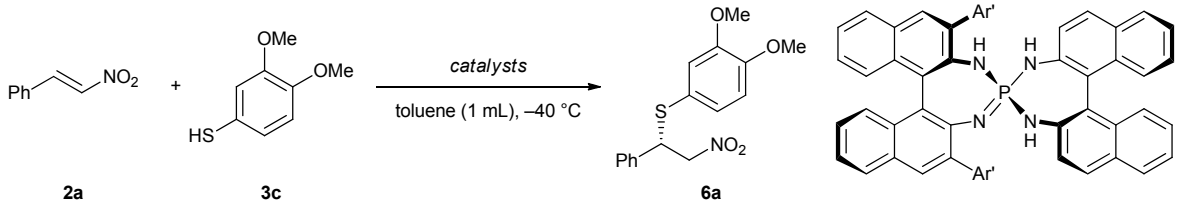
6o: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (1H, dd, J = 8.4, 2.1 Hz), 6.99 (1H, d, J = 2.1 Hz), 6.84 (1H, d, J = 8.4 Hz), 4.44 (1H, dd, J = 12.7, 6.6 Hz), 4.38 (1H, dd, J = 12.7, 8.2 Hz), 4.08 (2H, t, J = 6.0 Hz), 3.90$_2$ (3H, s), 3.89$_6$ (3H, s), 3.57-3.49 (1H, m), 1.84-1.49 (6H, m), 1.21 (9H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.7, 150.1, 149.3,

128.3, 121.5, 117.9, 111.7, 78.9, 63.9, 56.2, 56.1, 46.8, 38.9, 31.3, 28.4, 27.3, 23.2; IR (film) 2957, 2870, 1722, 1553, 1504, 1462, 1377, 1285, 1254, 1233, 1155, 1138, 1024, 764 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{29}NNaO_6S$ ($[M+Na]^+$) 422.1608. Found 422.1600; $[\alpha]_D^{20}$ +5.3 (*c* = 0.33, $CHCl_3$) for 91.8% ee; HPLC OJH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 32.9 min (minor), 38.7 min (major).



6p: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (1H, dd, *J* = 8.5, 2.0 Hz), 7.00 (1H, d, *J* = 2.0 Hz), 6.83 (1H, d, *J* = 8.5 Hz), 4.44 (1H, dd, *J* = 12.8, 7.3 Hz), 4.40 (1H, dd, *J* = 12.8, 7.3 Hz), 3.90 (3H, s), 3.89 (3H, s), 3.65 (2H, t, *J* = 5.9 Hz), 3.57 (1H, dtd, *J* = 9.0, 7.3, 4.9 Hz), 1.96-1.83 (1H, m), 1.77-1.65 (2H, m), 1.64-1.52 (1H, m), 0.89 (9H, s), 0.05 (6H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 149.2, 128.4, 121.6, 118.0, 111.6, 79.0, 62.4, 56.1, 56.0, 46.8, 29.8, 28.4, 26.0, 18.4, –5.2; IR (film) 2930, 2855, 1553, 1505, 1377, 1252, 1231, 1138, 1099, 1024, 835, 775 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{33}NNaO_5SSi$ ($[M+Na]^+$) 438.1741. Found 438.1734; $[\alpha]_D^{20}$ +7.8 (*c* = 0.43, $CHCl_3$) for 95.2% ee; HPLC OD3, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 6.9 min (major), 7.8 min (minor).

Use of Chiral Iminophosphorane as a Base for the Sulfa-Michael Addition:

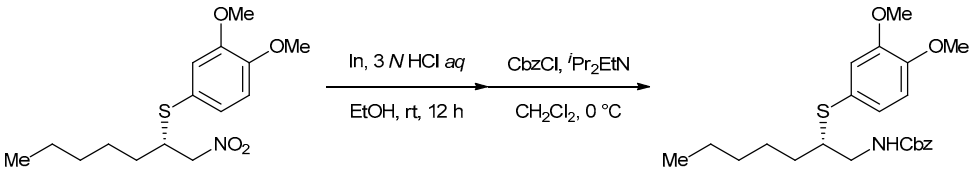


2a **3c** **6a** *homo*-**1b** (Ar' = 3,4,5-$F_3C_6H_2$)

catalysts	
homo-**1b** (2 mol%)	9 h, 99%, er = 55.4:44.6
homo-**1b**·HBArF (2 mol%)/*homo*-**1b** (1 mol%)	12 h, 88%, er = 94.6:5.4

Although the sulfa-Michael reaction of **2a** and **3c** was effectively catalyzed by chiral iminophosphorane *homo*-**1b**, enantioselectivity of the product **6a** was negligible. However, synergistic catalysis of *homo*-**1b** and *homo*-**1b**·HBArF significantly improved the enantioselectivity of **6a** to a comparable level with that of entry 11 (Table 1 of the manuscript), which suggested the possible intervention of *homo*-**1b** in the reaction catalyzed by DBU.

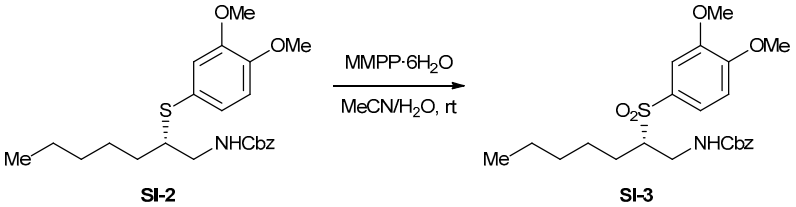
Procedures for Synthesis of Taurine Derivative 8 and β-Sultam 9 from 6l:



6l **SI-2**

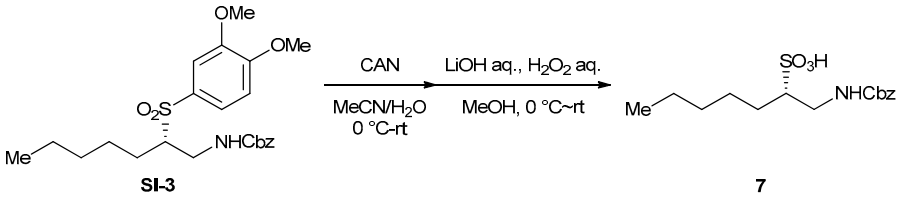
Conversion to SI-2 by Reduction of Nitro Group and Protection: Freshly cut indium metal (1.15 g, 10.0 mmol) and 3 *N* hydrochloric acid (3.3 mL, 10.0 mmol) were added to a solution of nitro sulfide **6l** (313.4 mg, 1.0 mmol) in EtOH (20.0 mL) at room temperature. The reaction mixture was stirred for 12 h and neutralized by saturated $NaHCO_3$ aqueous solution. The whole mixture was filtered through a pad of Celite with EA and the filtrate was evaporated for removing EtOH. The aqueous phase was extracted with EA three times and the combined organic phases were dried over Na_2SO_4. After filtration, all volatiles were removed under reduced pressure. The crude mixture was used for subsequent step without purification. To a solution of the crude amino sulfide in CH_2Cl_2 (10.0 mL) were added CbzCl (0.17 mL, 1.2 mmol) and ^{i}Pr_2EtN (0.20 mL, 1.2 mmol) at 0 ºC. After being stirred for 3 h, water was added to the resulting mixture and the aqueous phase was extracted with $CHCl_3$ three times. The combined organic phases were dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography on silica gel (H/EA = 10:1-4:1 as eluent) to give **SI-2** in quantitative yield (417.6 mg, 1.0 mmol) as colorless oil. **SI-2:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.27 (5H, m), 7.01 (1H, dd, *J* = 8.2, 1.5 Hz), 6.95

(1H, d, J = 1.5 Hz), 6.78 (1H, d, J = 8.2 Hz), 5.27 (1H, brt, J = 6.1 Hz), 5.11 (1H, d, J = 12.8 Hz), 5.08 (1H, d, J = 12.8 Hz), 3.86 (3H, s), 3.84 (3H, s), 3.35 (1H, dt, J = 13.7, 6.1 Hz), 3.21 (1H, dt, J = 13.7, 6.1 Hz), 3.05-2.96 (1H, m), 1.61-1.38 (4H, m), 1.36-1.18 (4H, m), 0.89 (3H, t, J = 6.7 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 149.3, 149.0, 136.6, 128.6, 128.2, 127.1, 123.7, 117.1, 111.5, 66.8, 56.0, 55.9, 50.5, 44.1, 32.1, 31.7, 26.7, 22.6, 14.1, one carbon was not found probably due to overlapping; IR (film) 3366, 2930, 2857, 1717, 1503, 1454, 1439, 1250, 1229, 1179, 1136, 1024 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{31}NNaO_4S$ ([M+Na]$^+$) 440.1866. Found 440.1868.



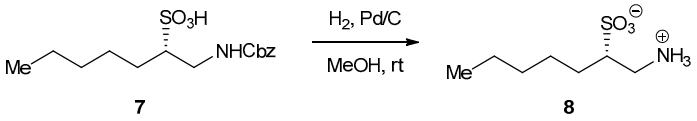
SI-2 **SI-3**

Oxidation of Sulfide to Sulfone SI-3: To a solution of **SI-2** (417.6 mg, 1.0 mmol) in MeCN (10.0 mL) and H_2O (1.0 mL) was added magnesium monoperoxyphthalate hexahydrate (MMPP·$6H_2O$) (1.48 g, 3.0 mmol) at ambient temperature. After 3 h of stirring, the resulting mixture was cooled to 0 ºC and quenched by the addition of saturated Na_2SO_3 aqueous solution. The aqueous phase was extracted with EA three times and the combined organic extracts were dried over Na_2SO_4. After concentration, the crude residue was purified by column chromatography on silica gel (H/EA = 5:1-2:1 as eluent) to afford **SI-3** in 96% yield (431.6 mg, 0.96 mmol) as colorless oil. **SI-3:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (1H, dd, J = 8.7, 2.0 Hz), 7.39-7.29 (5H, m), 7.28 (1H, d, J = 2.0 Hz), 6.97 (1H, d, J = 8.7 Hz), 5.70 (1H, t, J = 6.2 Hz), 5.12 (1H, d, J = 12.6 Hz), 5.07 (1H, d, J = 12.6 Hz), 3.94 (3H, s), 3.91 (3H, s), 3.64 (1H, ddd, J = 15.1, 6.2, 3.0 Hz), 3.57 (1H, dt, J = 15.1, 6.2 Hz), 3.12-3.02 (1H, m), 1.80-1.70 (1H, m), 1.58-1.40 (2H, m), 1.34-1.10 (5H, m), 0.84 (3H, t, J = 6.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 153.6, 149.3, 136.4, 128.7, 128.5, 128.1, 128.0, 122.9, 110.8, 110.6, 66.8, 64.5, 56.3$_0$, 56.2$_6$, 38.4, 31.4, 26.1, 25.6, 22.2, 13.9; IR (film) 3381, 2955, 2860, 1721, 1587, 1508, 1456, 1300, 1261, 1238, 1130, 1090, 1020 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{31}NNaO_6S$ ([M+Na]$^+$) 472.1764. Found 472.1766.



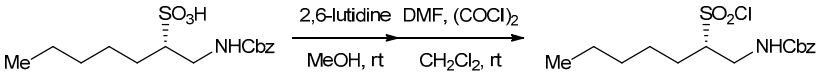
SI-3 **7**

Removal of Aromatic Substituent and Oxidation to Sulfonic Acid 7: To a solution of $(NH_4)_2[Ce(NO_3)_6]$ (CAN) (5.26 g, 9.6 mmol) in H_2O (9.6 mL) was slowly added a solution of **SI-3** (431.6 mg, 0.96 mmol) in MeCN (9.6 mL) at 0 ºC. The reaction mixture was allowed to warm up to room temperature and stirred there for 3 h. The resulting mixture was diluted with saturated $NaHCO_3$ aqueous solution and filtered through a pad of Celite with EA. The aqueous phase was extracted with EA three times. The combined organic extracts were dried over Na_2SO_4 and EA was removed by evaporation. The crude residue was dissolved in MeOH (9.6 mL) and the solution was cooled to 0 ºC, to which 1 N LiOH aqueous solution (0.96 mL) was added. After stirring for 5 min at 0 °C, 30% H_2O_2 aqueous solution (0.96 mL) was introduced and the reaction mixture was stirred for 2 days at room temperature. The resulting mixture was neutralized with 1 N hydrochloric acid and directly subjected to the purification by column chromatography on silica gel ($CHCl_3$/MeOH = 50:1-5:1 as eluent) to afford **7** in 63% yield (199.2 mg, 0.63 mmol) as yellow solid. **7:** ^{1}H NMR (400 MHz, CD_3OD) δ 7.41-7.24 (5H, m), 6.66 (1H, brt, J = 5.2 Hz), 5.10 (1H, d, J = 12.8 Hz), 5.05 (1H, d, J = 12.8 Hz), 3.53 (2H, t, J = 5.5 Hz), 2.82-2.71 (1H, m), 1.96-1.83 (1H, m), 1.60-1.18 (7H, m), 0.90 (3H, t, J = 7.3 Hz); ^{13}C NMR (101 MHz, CD_3OD) δ 158.5, 138.3, 129.4, 128.9, 128.8, 67.5, 60.9, 41.8, 33.0, 28.8, 27.9, 23.5, 14.4; IR (film) 3323, 2951, 2837, 2506, 1699, 1522, 1456, 1364, 1204, 1167, 1020, 719 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{22}NO_5S$ ([M–H]$^-$) 328.1213. Found 328.1229.



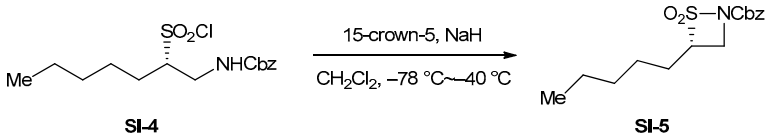
7 8

Removal of Cbz-Protective Group on Nitrogen to Taurine Derivative 8: 10% Pd/C (5.0 mg) was added to a solution of **7** (32.9 mg, 0.10 mmol) in MeOH (1.0 mL) at 0 °C under Ar atmosphere and then, the atmosphere was replaced with H_2 (balloon). After 24 h of stirring at room temperature, filtration through a pad of Celite with H_2O for removing Pd/C and concentration of the filtrate furnished analytically pure **8** in quantitative yield (19.5 mg, 0.10 mmol) as white solid. **8:** ^{1}H NMR (400 MHz, D_2O) δ 3.05 (1H, dd, J = 14.7, 5.3 Hz), 3.01 (1H, dd, J = 14.7, 6.2 Hz), 2.89-2.81 (1H, m), 1.86-1.76 (1H, m), 1.57-1.34 (3H, m), 1.34-1.22 (4H, m), 0.84 (3H, t, J = 7.1 Hz), NH protons were not found probably due to deuteration; ^{13}C NMR (101 MHz, D_2O) δ 60.3, 40.0, 30.9, 27.3, 25.8, 21.8, 13.3; IR (film) 3393, 2957, 2872, 1734, 1717, 1636, 1456, 1217, 1180, 1042 cm^{-1}; HRMS (ESI) Calcd for $C_7H_{17}NNaO_3S$ ([M+Na]$^+$) 218.0821. Found 218.0825; $[\alpha]_D^{20}$ –595.8 (c = 0.24, H_2O) for 92.7% ee.



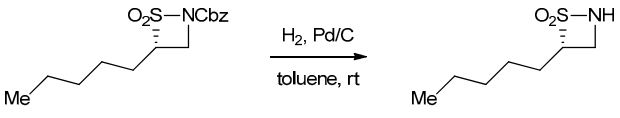
7 SI-4

Preparation of Sulfonyl Chloride SI-4: To a solution of **7** (65.9 mg, 0.20 mmol) in MeOH (2.0 mL) was added 2,6-lutidine (23.2 μL, 0.20 mmol). After removal of MeOH under reduced pressure, CH_2Cl_2 (2.0 mL), DMF (1 drop), and $(COCl)_2$ (50.8 μL, 0.60 mmol) were added sequentially and the reaction mixture was stirred for 3 h at room temperature. Then, CH_2Cl_2 was removed under vacuum and the residue was subjected to the purification by column chromatography on silica gel (H/EA = 5:1 as eluent) to give **SI-4** in 89% yield (61.9 mg, 0.18 mmol) as pale yellow oil. **SI-4:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.29 (5H, m), 5.44 (1H, brt, J = 5.5 Hz), 5.14 (1H, d, J = 12.4 Hz), 5.09 (1H, d, J = 12.4 Hz), 3.88 (1H, quin, J = 6.5 Hz), 3.72-3.62 (2H, m), 2.16-2.06 (1H, m), 1.80-1.69 (1H, m), 1.69-1.56 (1H, m), 1.56-1.45 (1H, m), 1.40-1.27 (4H, m), 0.90 (3H, t, J = 6.6 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.4, 136.1, 128.7, 128.4, 128.2, 76.5, 67.3, 40.1, 31.4, 27.8, 26.1, 22.3, 14.0; IR (film) 3420, 3337, 2957, 2932, 2872, 1715, 1520, 1456, 1364, 1244, 1159, 1111, 1003, 735 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{22}ClNNaO_4S$ ([M+Na]$^+$) 370.0850. Found 370.0853.



SI-4 SI-5

Cyclization of SI-4 to SI-5: A solution of **SI-4** (61.9 mg, 0.18 mmol) in CH_2Cl_2 (0.80 mL) and 15-crown-5 (35.6 μL, 0.18 mmol) was slowly added to a suspension of NaH (60% dispersion in mineral oil, 10.8 mg, 0.27 mmol) in CH_2Cl_2 (1.0 mL) at –78 ºC. After being stirred for 1 h, the reaction mixture was warmed up to –40 ºC and stirred there for additional 7 h. The reaction was then quenched by saturated NH_4Cl aqueous solution and extracted with CH_2Cl_2 three times. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography on silica gel (H/EA = 10:1-3:1 as eluent) to afford **SI-5** in 73% yield (40.5 mg, 0.13 mmol) as colorless oil. **SI-5:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.29 (5H, m), 5.27 (2H, s), 4.42-4.32 (1H, m), 3.80 (1H, dd, J = 8.2, 6.4 Hz), 3.23 (1H, t, J = 6.4 Hz), 2.11 (1H, dtd, J = 14.6, 8.9, 6.0 Hz), 1.91-1.80 (1H, m), 1.54-1.38 (2H, m), 1.38-1.28 (4H, m), 0.91 (3H, t, J = 7.1 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 134.9, 128.7, 128.6, 128.1, 71.9, 68.7, 39.4, 31.2, 28.9, 26.8, 22.3, 13.9; IR (film) 2930, 2860, 1732, 1456, 1387, 1339, 1310, 1179, 1138, 1126, 760 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{21}NNaO_4S$ ([M+Na]$^+$) 334.1084. Found 334.1082; HPLC ASH, H/IPA = 10:1, flow rate = 1.0 mL/min, λ = 210 nm, 20.7 min (minor), 24.2 min (major).



SI-5 **9**

Deprotection of SI-5 to β-Sultam 9: 10 % Pd/C (6.5 mg) was added to a solution of **SI-5** (40.5 mg, 0.13 mmol) in toluene (1.3 mL) at 0 °C under Ar atmosphere and then, the atmosphere was replaced with H_2 (balloon). After 36 h of stirring at room temperature, filtration through a pad of Celite was performed with the aid of toluene for removing Pd/C and the filtrate was concentrated to furnish analytically pure **9** in 81% yield (18.7 mg, 0.11 mmol) as colorless oil. **9:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.23 (brs, 1H), 4.51 (1H, tt, J = 8.5, 6.4 Hz), 3.48 (1H, ddd, J = 8.5, 6.4, 3.2 Hz), 2.97 (1H, td, J = 6.4, 3.2 Hz), 2.12 (1H, dtd, J = 14.7, 8.5, 6.4 Hz), 1.91-1.81 (1H, m), 1.53-1.38 (2H, m), 1.38-1.28 (4H, m), 0.90 (3H, t, J = 7.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 74.7, 35.9, 31.4, 29.0, 26.7, 22.4, 14.0; IR (film) 3292, 2957, 2930, 2860, 1468, 1304, 1250, 1155, 712 cm^{-1}; HRMS (ESI) Calcd for $C_7H_{15}NNaO_2S$ ($[M+Na]^+$) 200.0716. Found 200.0714; $[\alpha]_D^{20}$ –18.5 (c = 0.02, $CHCl_3$) for 92.7% ee.

Determination of Absolute Configuration:

Recrystallization of 4: Recrystallization of **4** was performed by using 2-propanol at room temperature. **4:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.26 (5H, m), 7.19 (2H, dd, J = 7.6, 1.6 Hz), 6.83 (2H, d, J = 8.7 Hz), 4.86-4.63 (3H, m), 3.80 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 137.0, 136.6, 129.0, 128.6, 127.7, 121.9, 114.9, 78.5, 55.5, 50.7.

Recrystallization of 6a: Recrystallization of **6a** was performed with a hexane/acetone solvent system at room temperature.

The single crystal thus obtained was mounted on CryoLoop. Data of X-ray diffraction were collected at 153 K on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An absorption correction was made using SADABS. The structures were solved by direct methods and Fourier syntheses, and refined by full-matrix least squares on F^2 by using SHELXTL.[3] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions and isotropic thermal parameters refined. The crystallographic data were summarized in the following table.

[3] G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112.

Table SI-1. Crystal data and structure refinement for **4**.

Empirical formula	$C_{15}H_{15}NO_3S$	
Formula weight	289.34	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 5.4774(13) Å	α = 90°.
	b = 10.390(2) Å	β = 90°.
	c = 25.084(6) Å	γ = 90°.
Volume	1427.5(6) $Å^3$	
Z	4	
Density (calculated)	1.346 Mg/m^3	
Absorption coefficient	0.233 mm^{-1}	
F(000)	608	
Crystal size	0.5 x 0.15 x 0.1 mm^3	
Theta range for data collection	2.12 to 28.40°.	
Index ranges	–7<=h<=5, –13<=k<=11, –27<=l<=33	
Reflections collected	10282	
Independent reflections	3559 [R_{int} = 0.0315]	
Completeness to theta = 28.40°	99.5 %	
Absorption correction	Empirical	
Max. and min. transmission	0.966 and 0.845	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3559 / 0 / 182	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2sigma(I)]	R_1 = 0.0392, wR_2 = 0.0961	
R indices (all data)	R_1 = 0.0408, wR_2 = 0.0972	
Absolute structure parameter	–0.03(7)	
Largest diff. peak and hole	0.402 and -0.170 e.$Å^{-3}$	

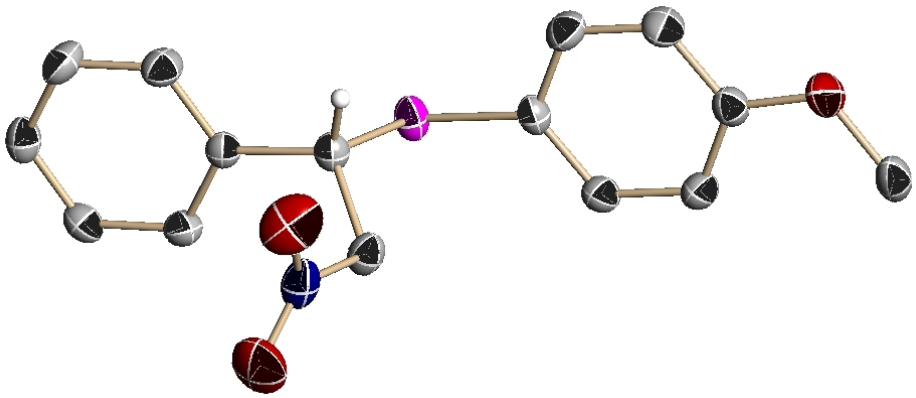


Figure SI-1. Molecular structure of **4**. Hydrogen atoms except for those attached to the stereogenic carbon are omitted for clarity. Blue = nitrogen, red = oxygen, pink = sulfur, gray = carbon. The thermal ellipsoids of non-hydrogen atoms are shown at the 50% probability level.

Table SI-2. Crystal data and structure refinement for **6a**.

Empirical formula	$C_{16}H_{17}NO_4S$	
Formula weight	319.37	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 5.5219(8) Å	α = 90°.
	b = 12.1360(17) Å	β = 90°.
	c = 23.040(3) Å	γ = 90°.
Volume	1544.0(4) $Å^3$	
Z	4	
Density (calculated)	1.374 Mg/m^3	
Absorption coefficient	0.227 mm^{-1}	
F(000)	672	
Crystal size	0.70 x 0.20 x 0.20 mm^3	
Theta range for data collection	1.90 to 28.30°.	
Index ranges	–7<=h<=7, –15<=k<=16, –30<=l<=27	
Reflections collected	11444	
Independent reflections	3849 [R_{int} = 0.0239]	
Completeness to theta = 28.30°	100.0 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9560 and 0.8573	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3849 / 0 / 201	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R_1 = 0.0324, wR_2 = 0.0833	
R indices (all data)	R_1 = 0.0334, wR_2 = 0.0843	
Absolute structure parameter	0.00(6)	
Largest diff. peak and hole	0.273 and –0.252 e.$Å^{-3}$	

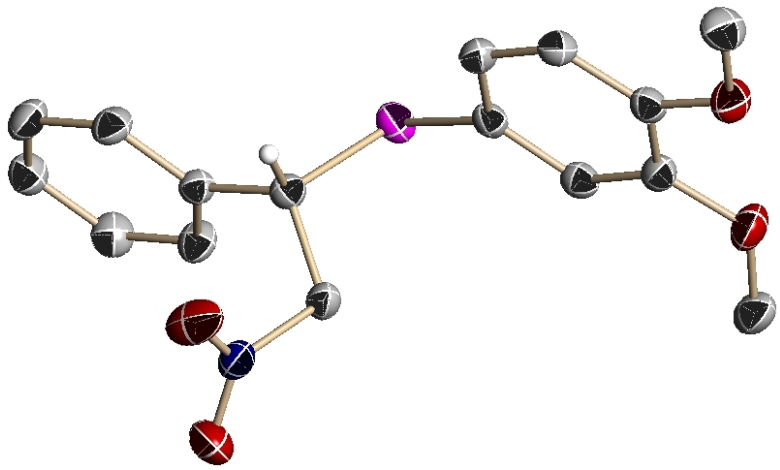
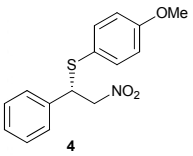


Figure SI-2. Molecular structure of **6a**. Hydrogen atoms except for those attached to the stereogenic carbon are omitted for clarity. Blue = nitrogen, red = oxygen, pink = sulfur, gray = carbon. The thermal ellipsoids of non-hydrogen atoms are shown at the 50% probability level.

Copies of ^{1}H and ^{13}C NMR Spectra:



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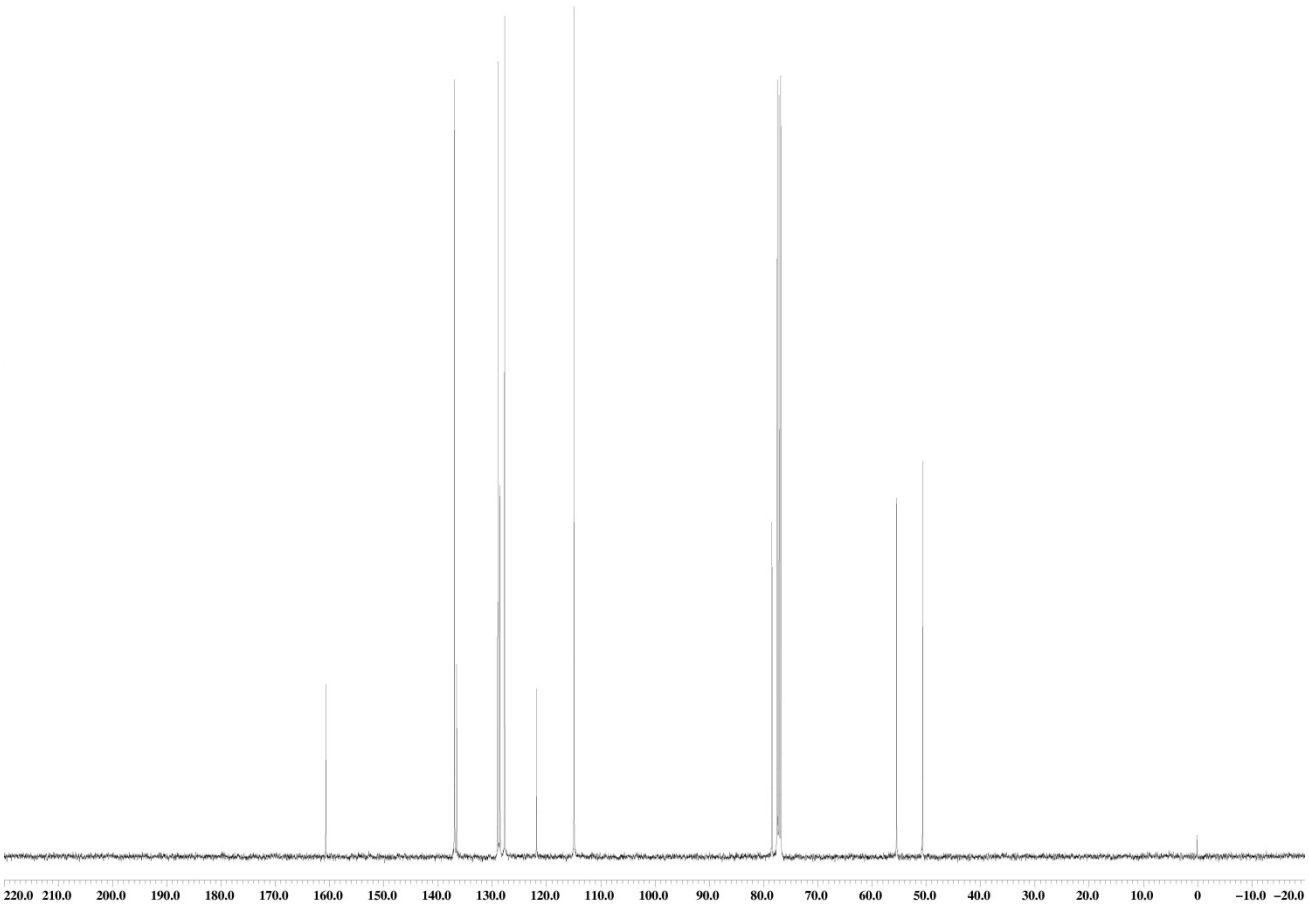
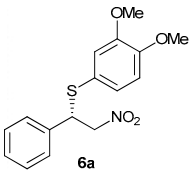
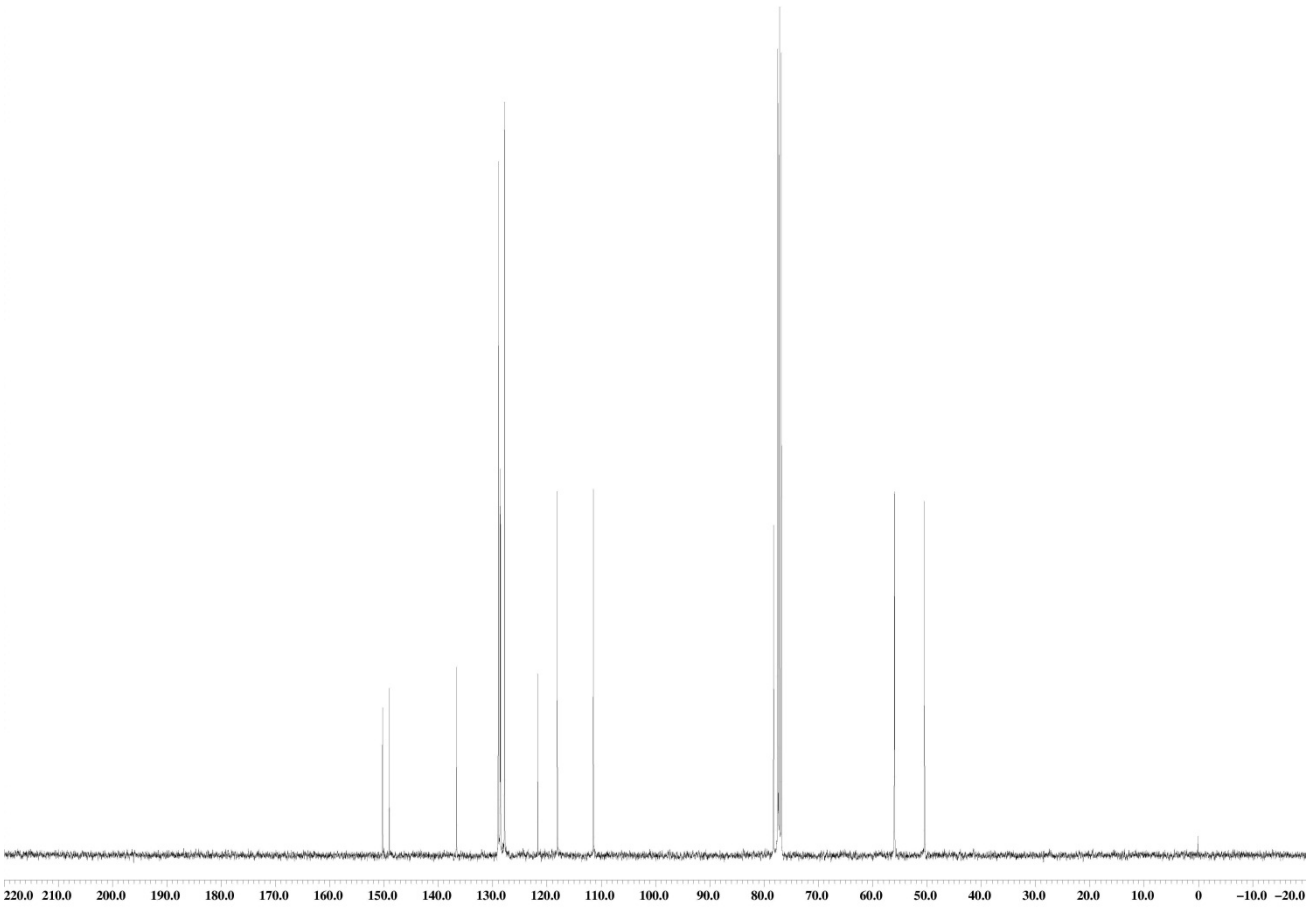
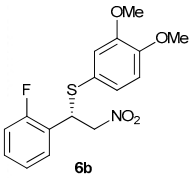




6a





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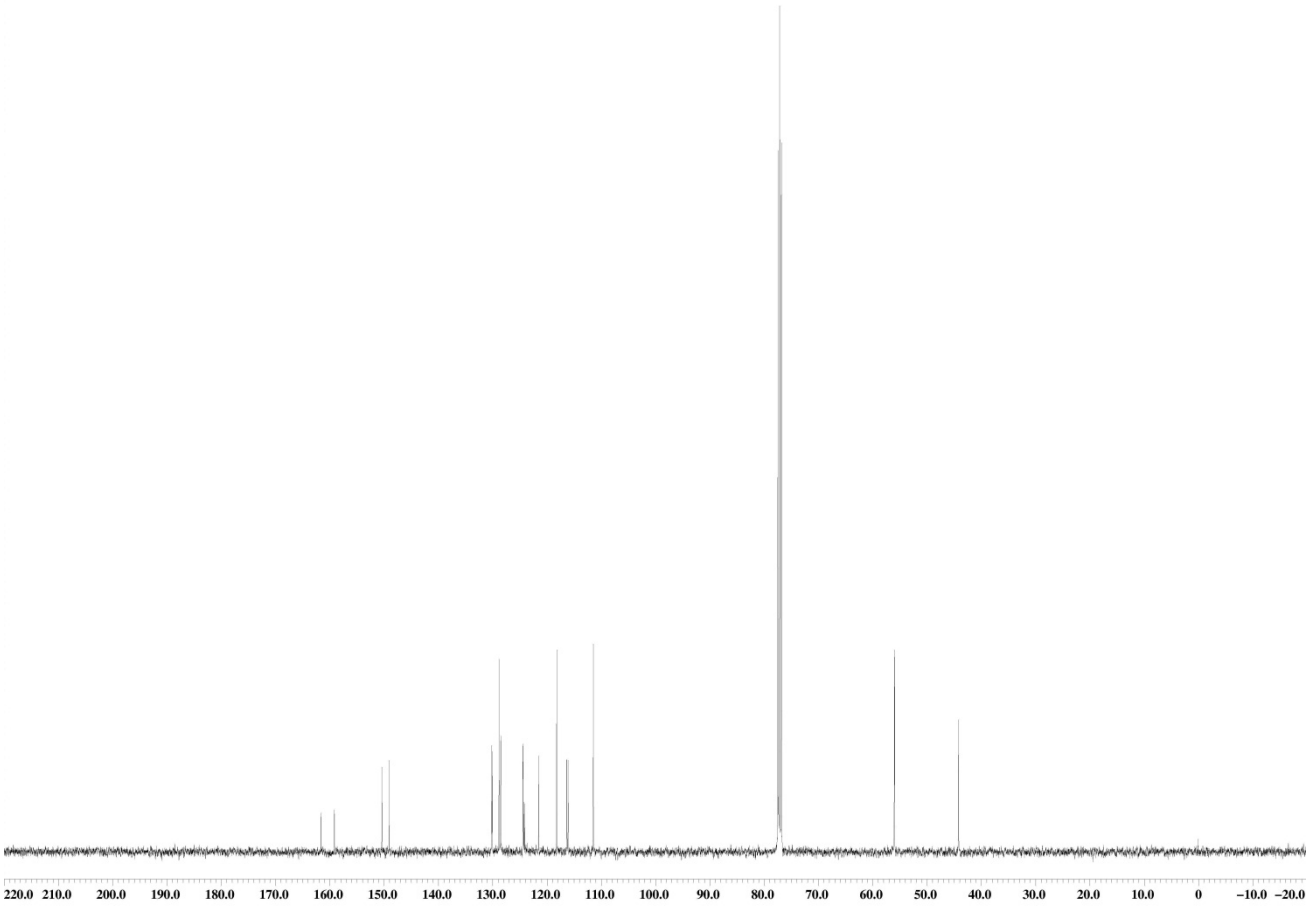

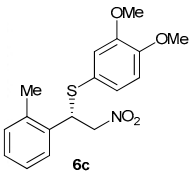

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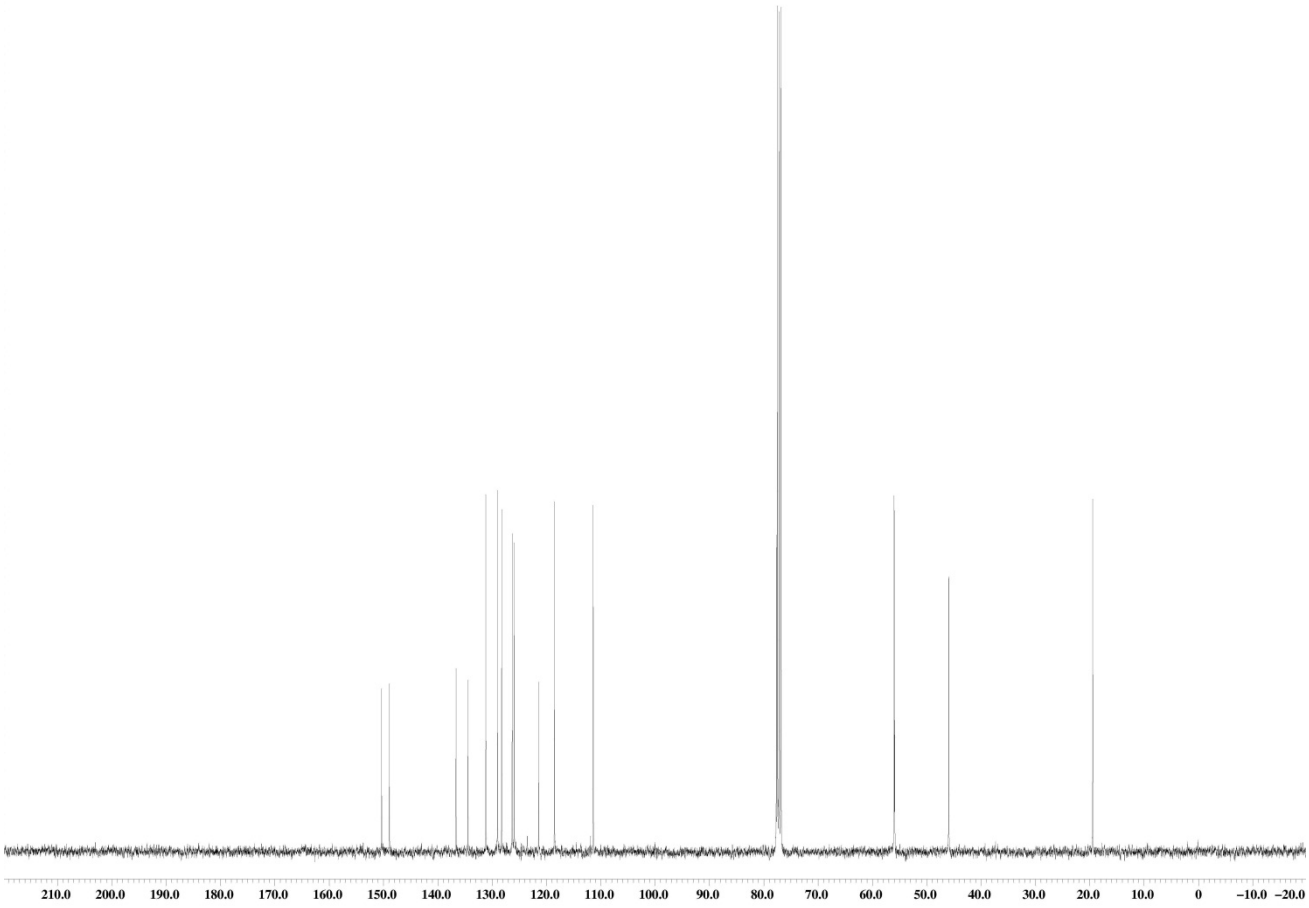

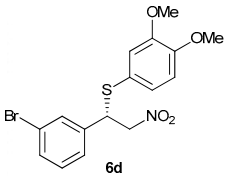
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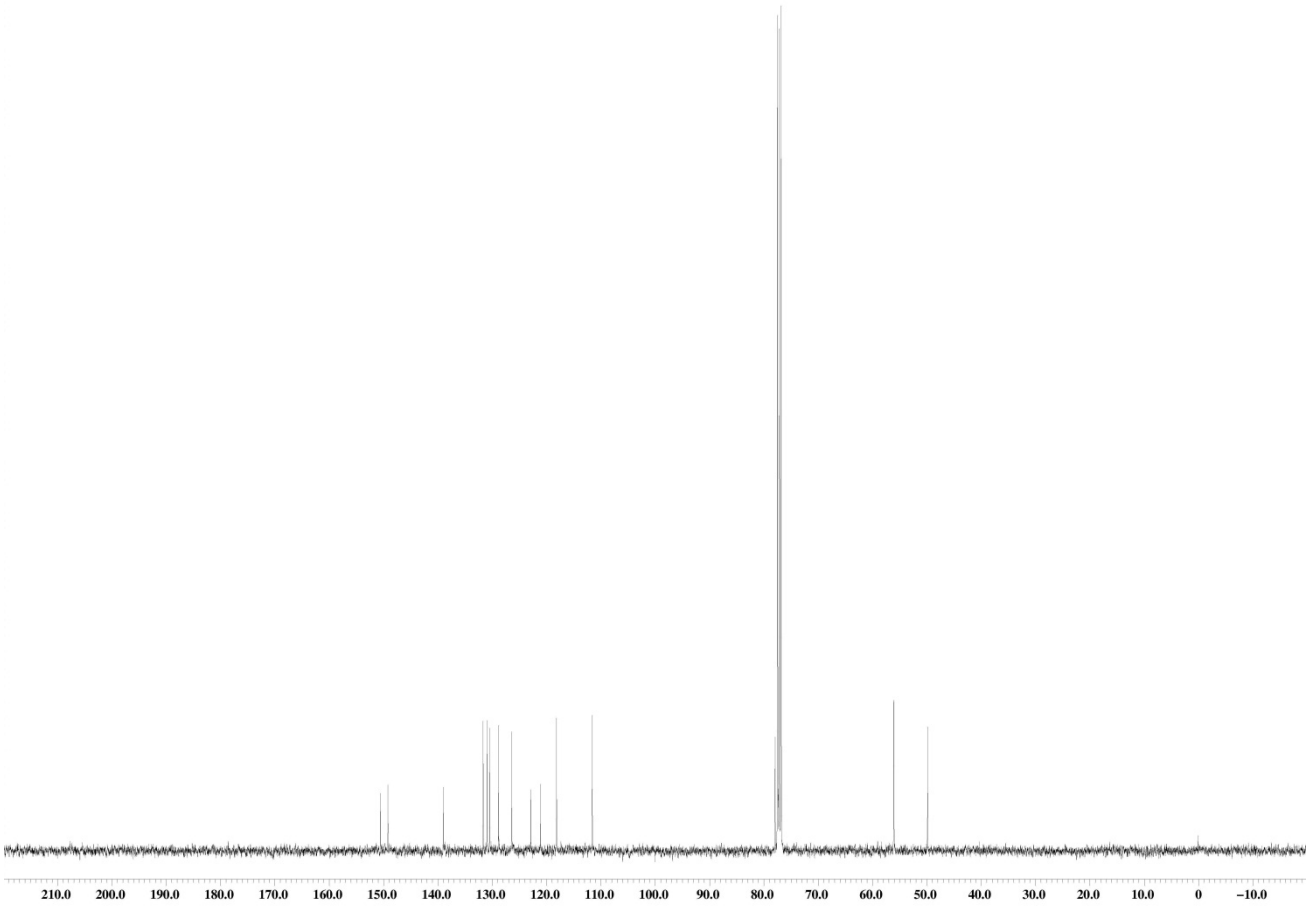
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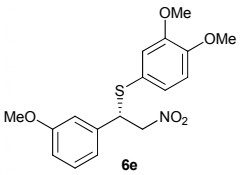

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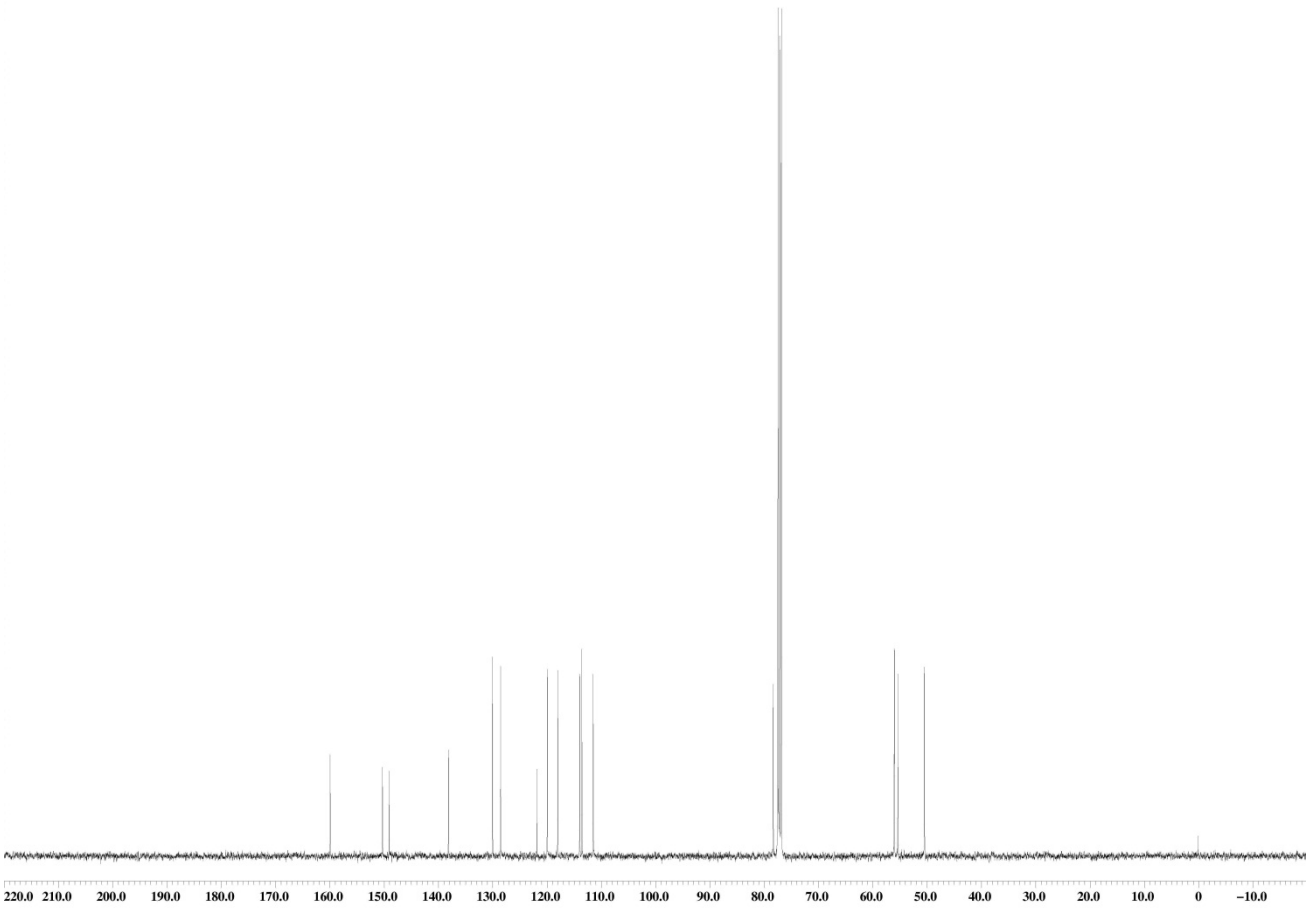

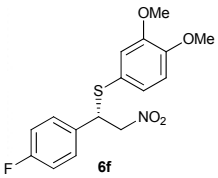

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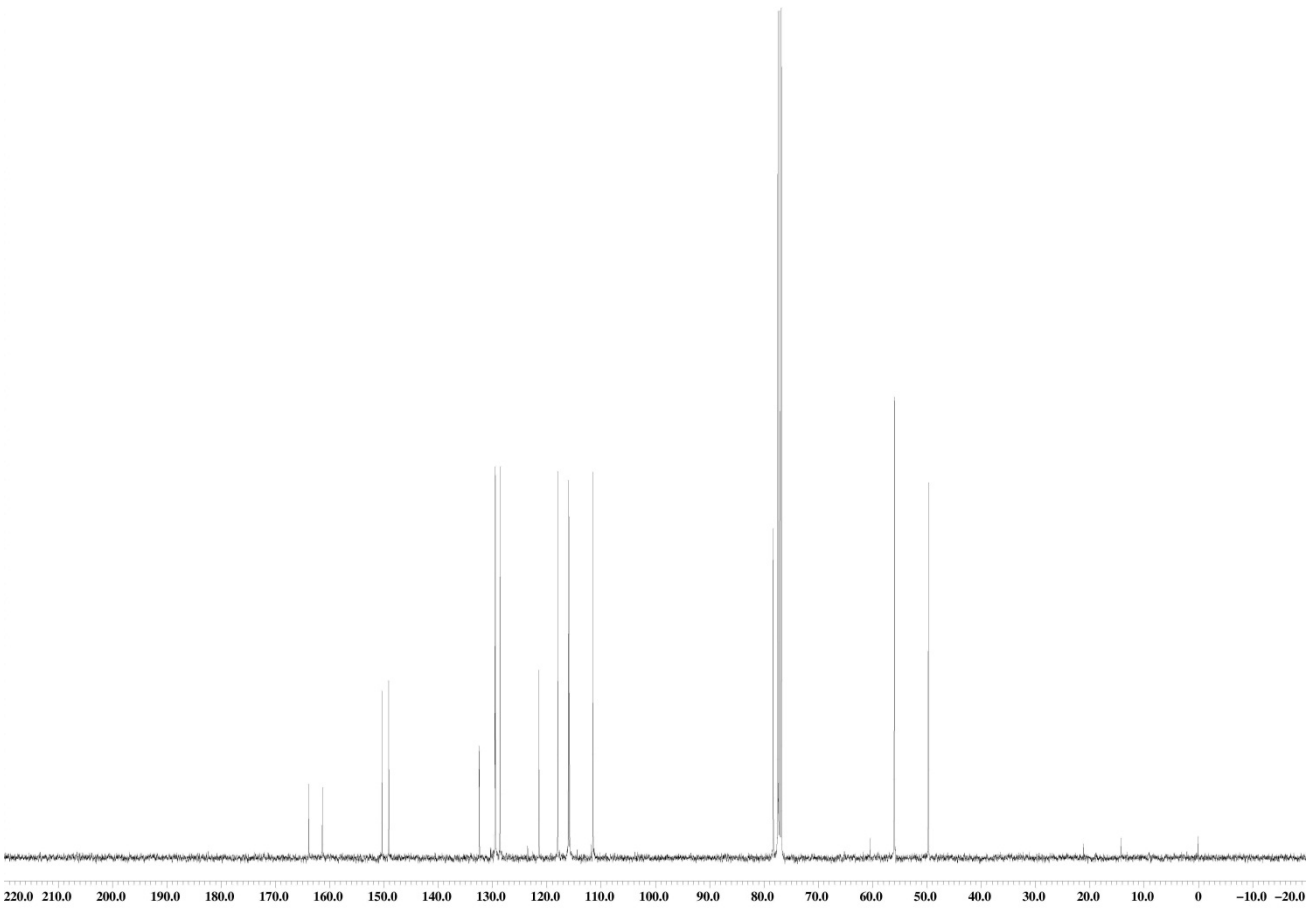

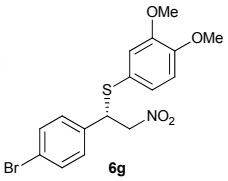

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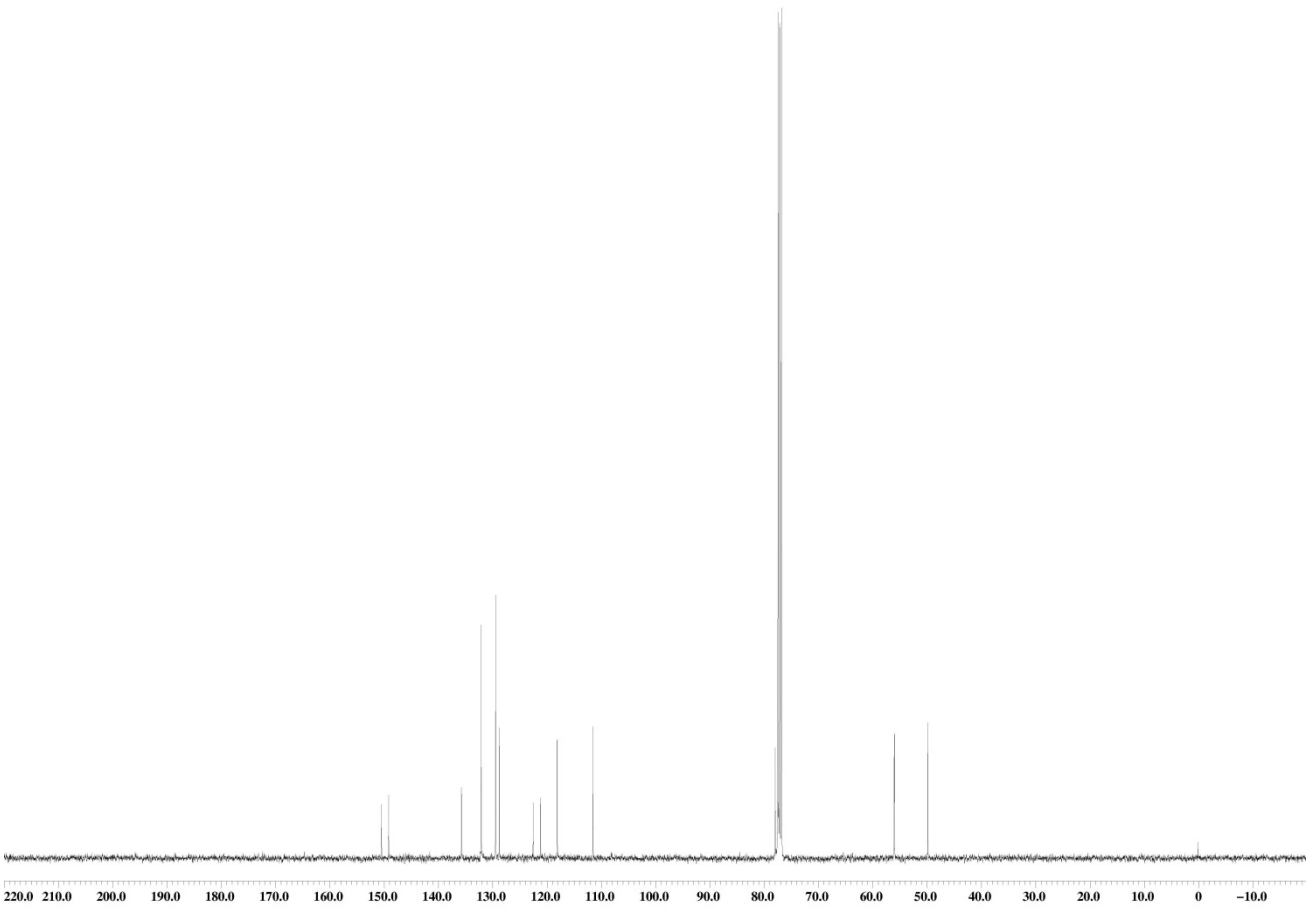

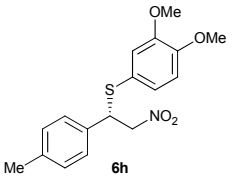

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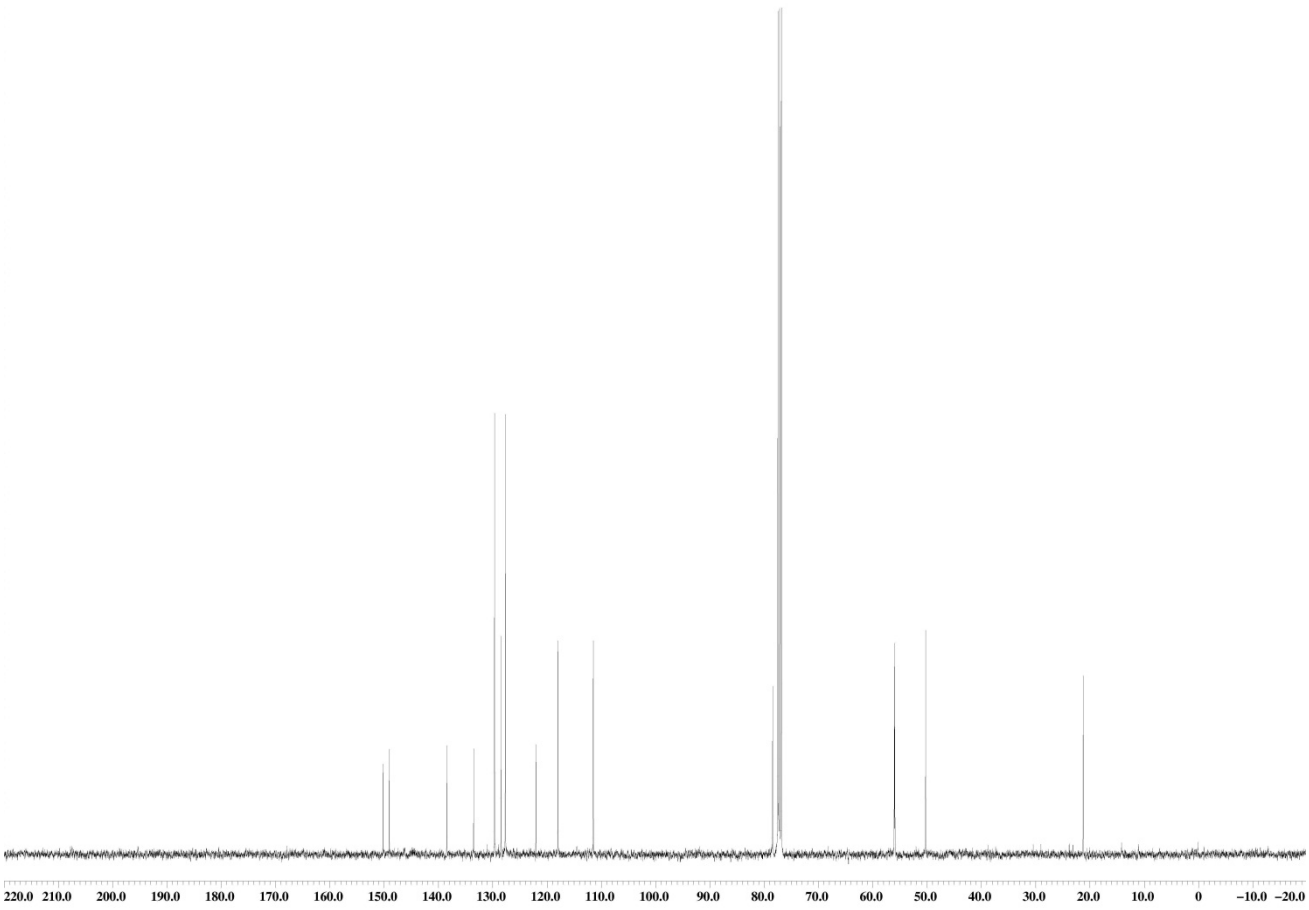

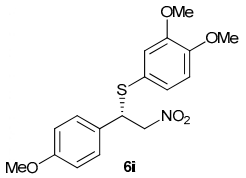
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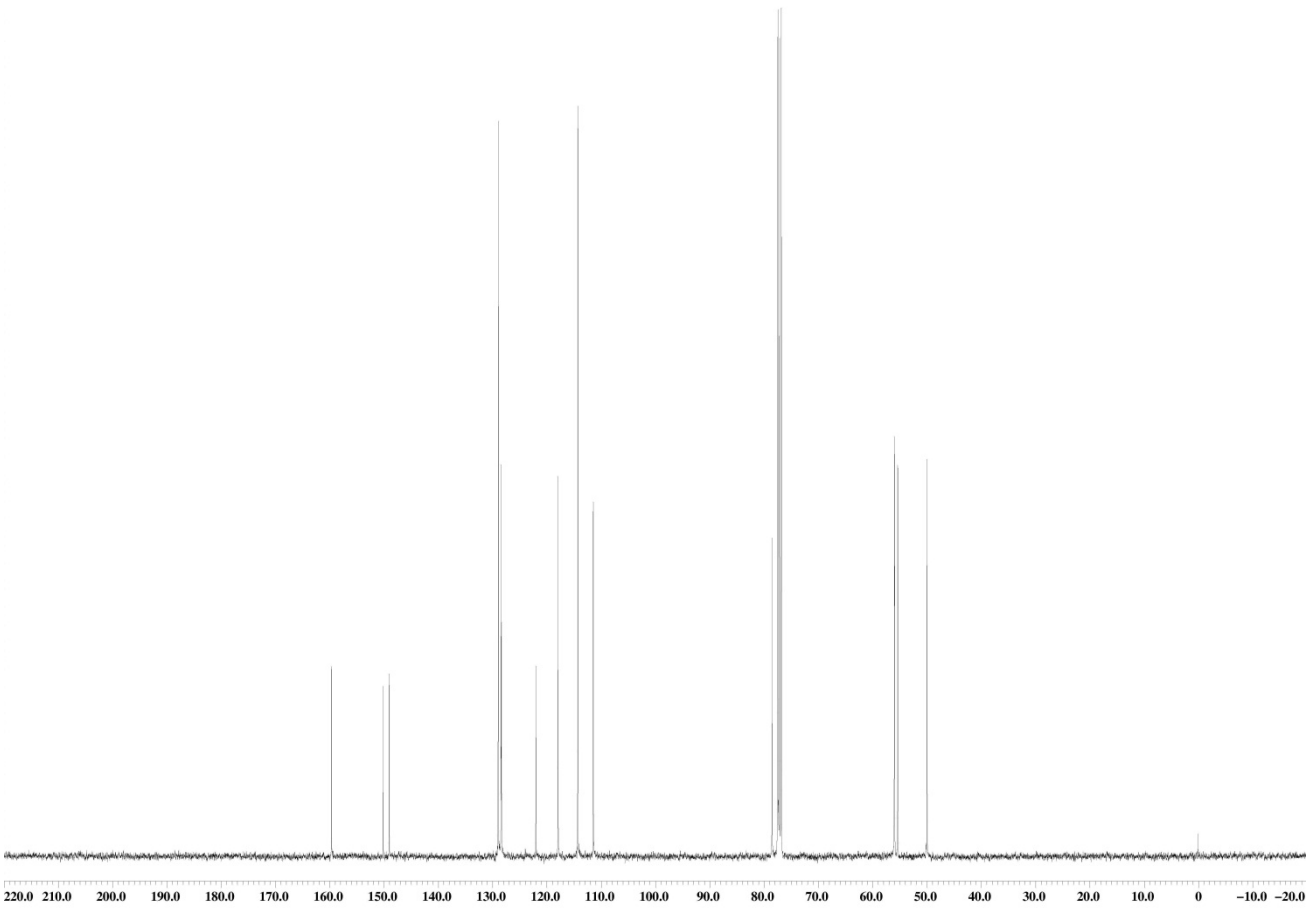
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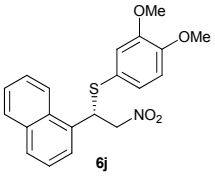

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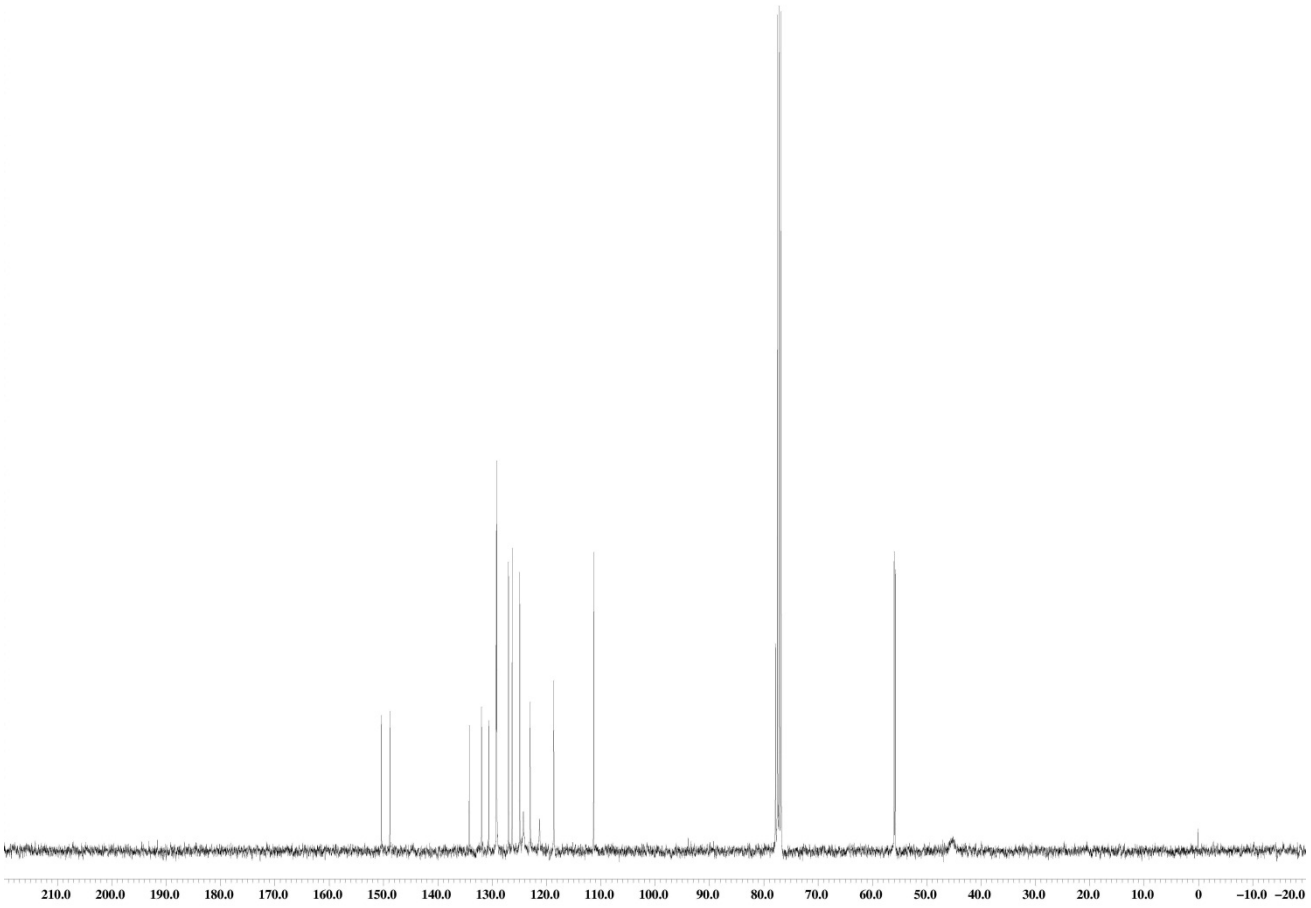

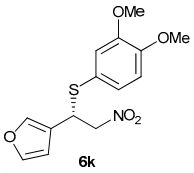
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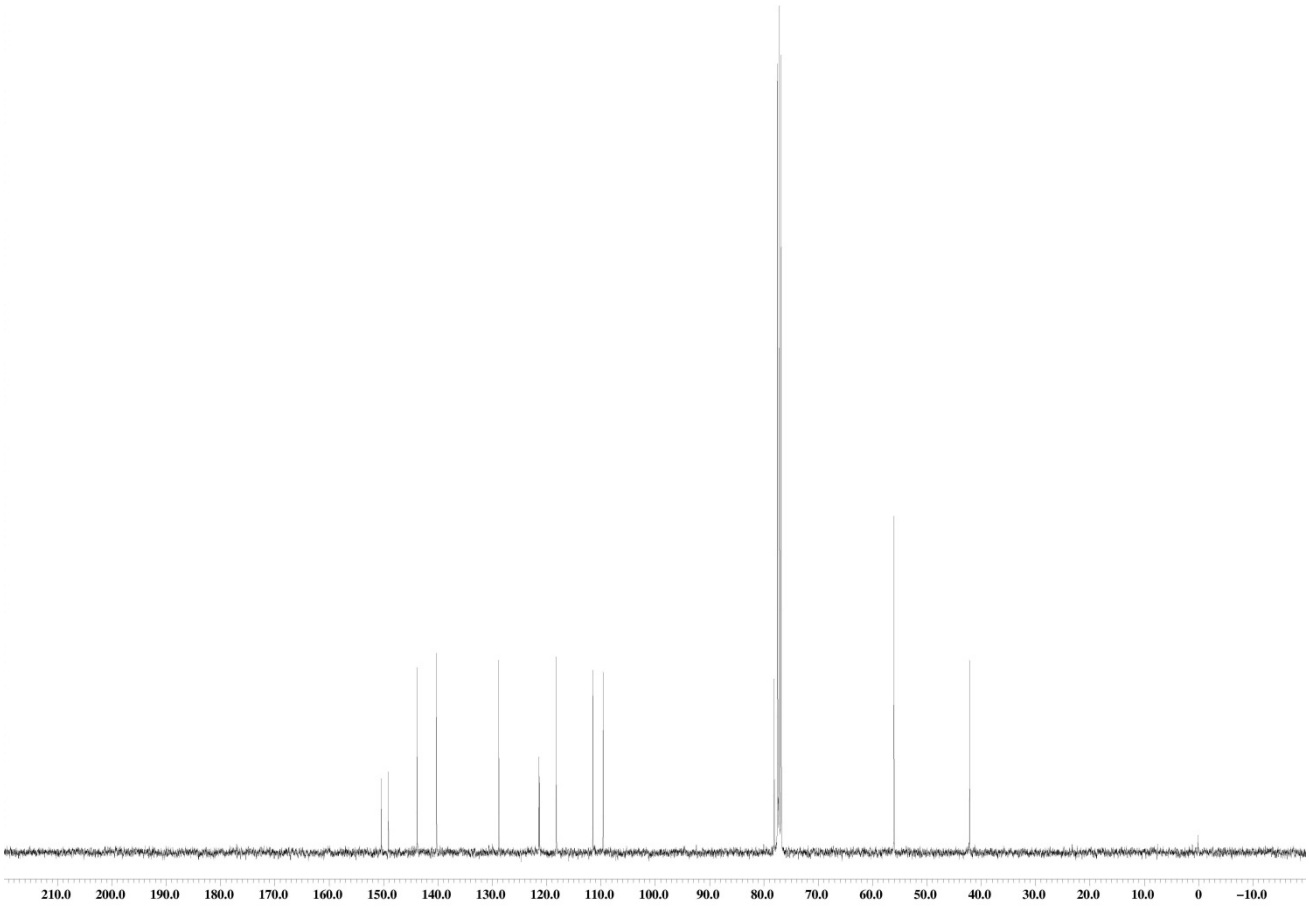
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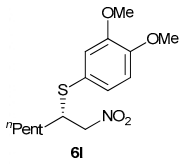
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6l

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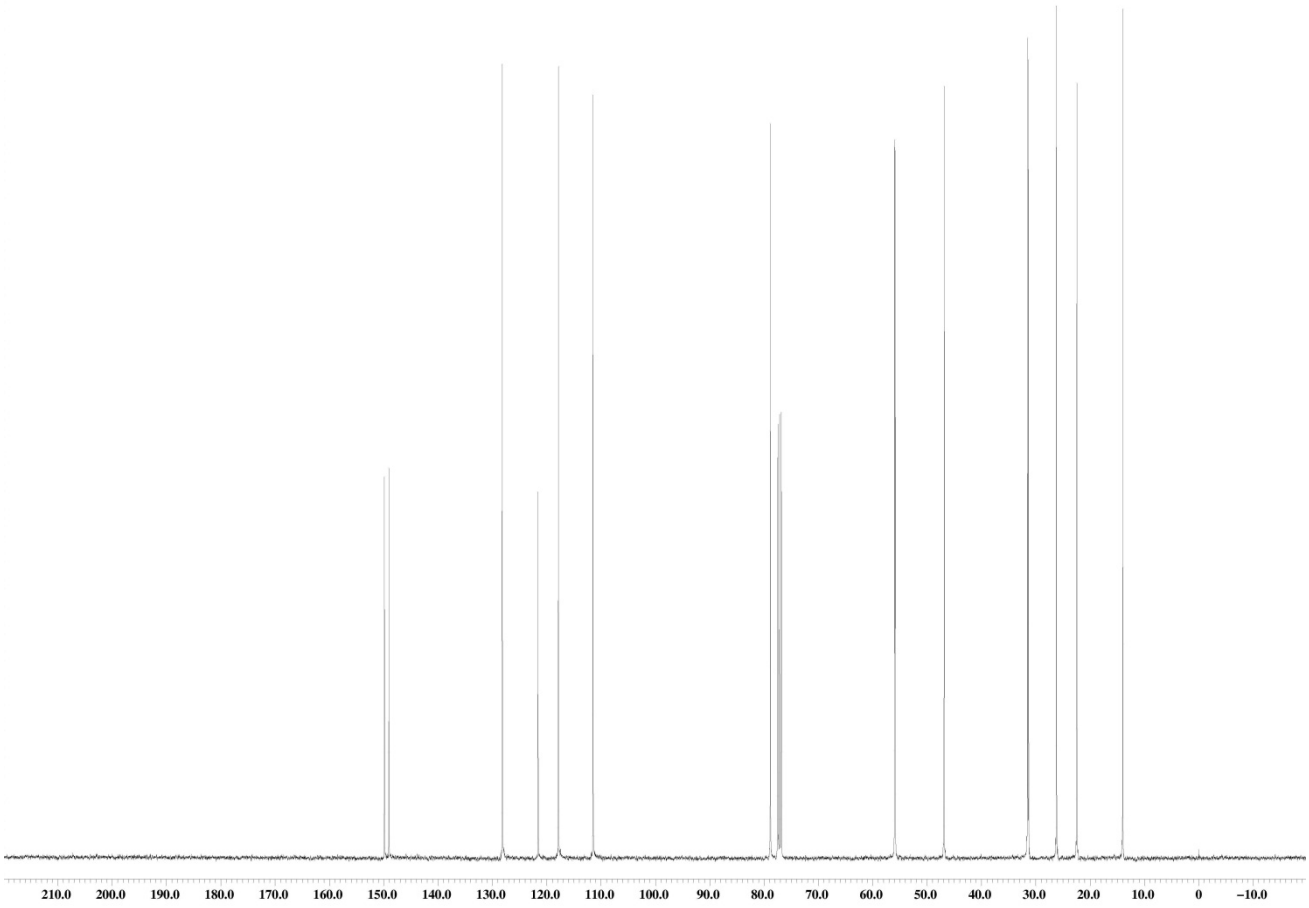
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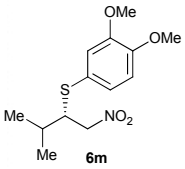
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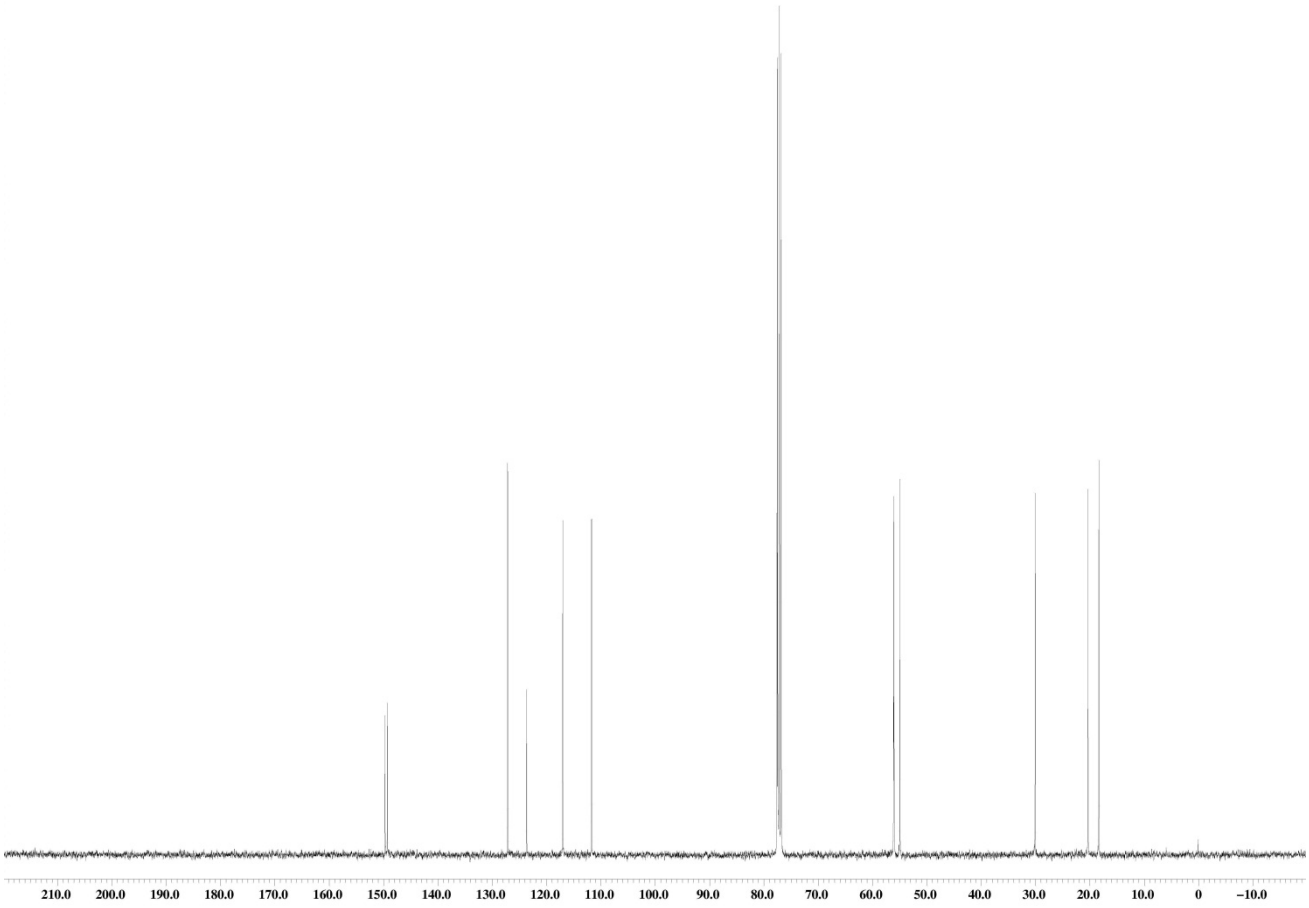
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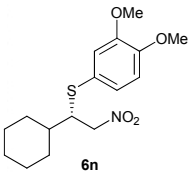

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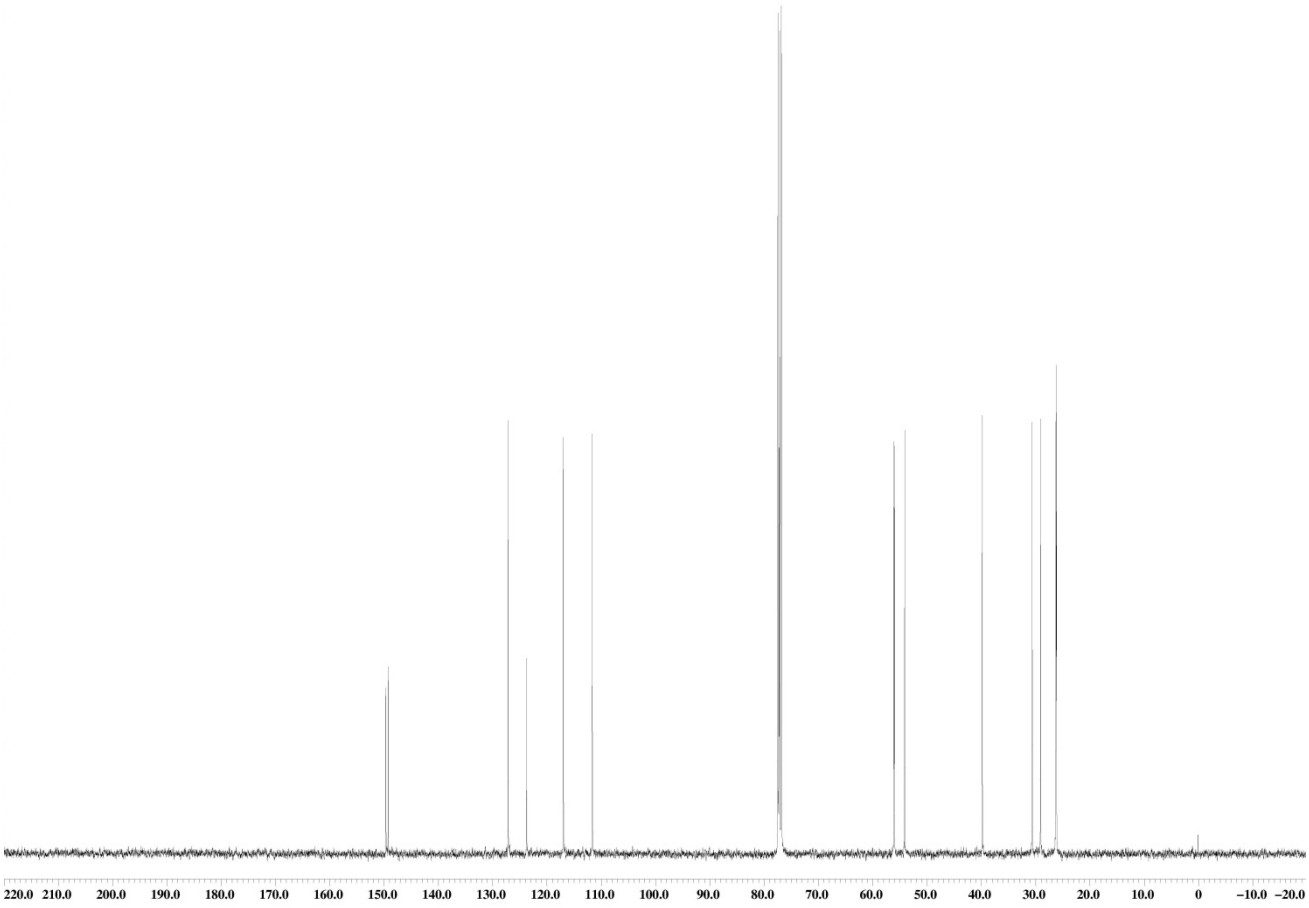
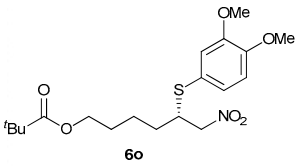
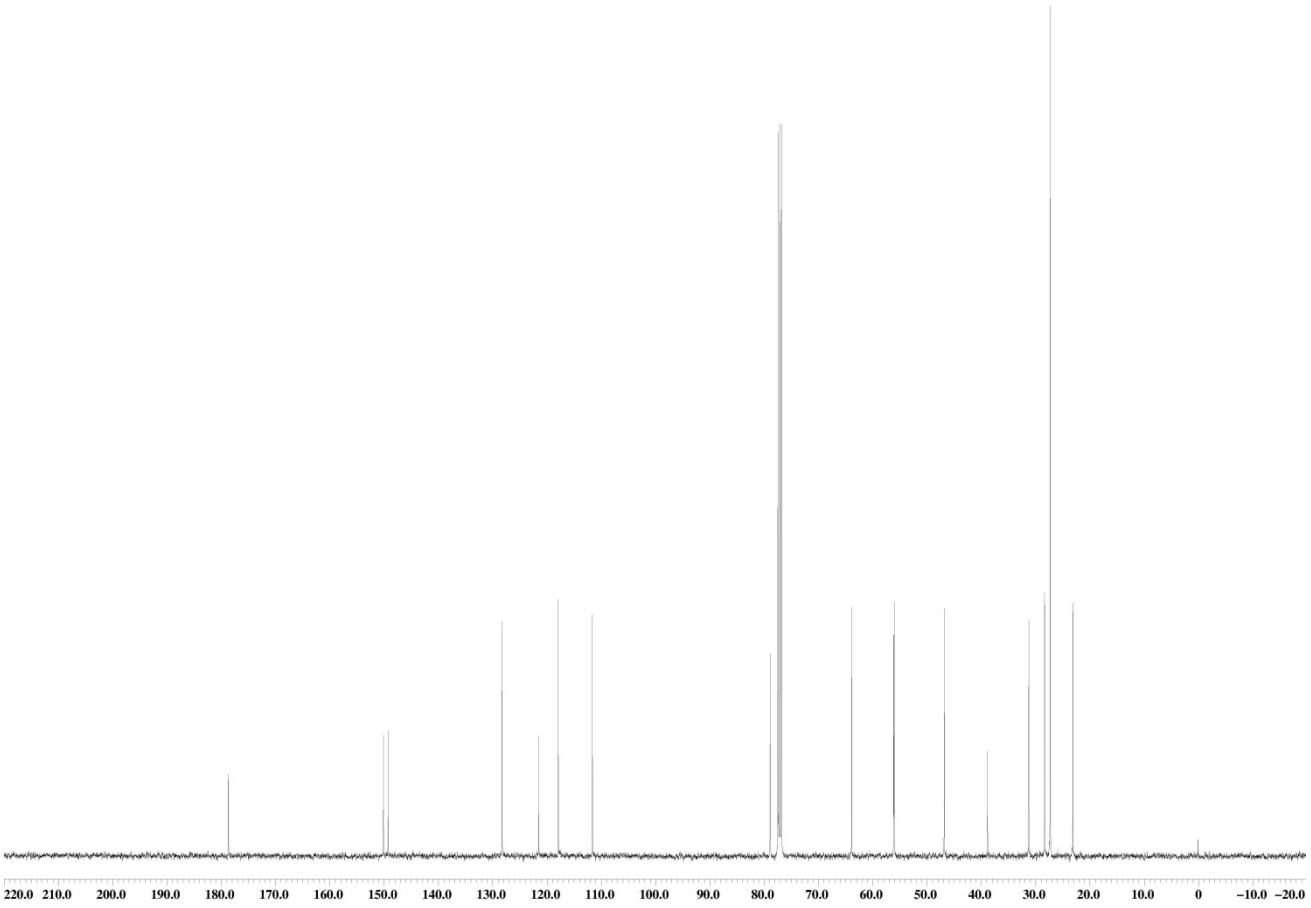
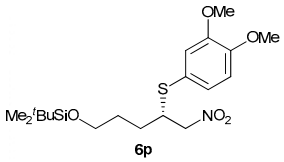




6o




OMe
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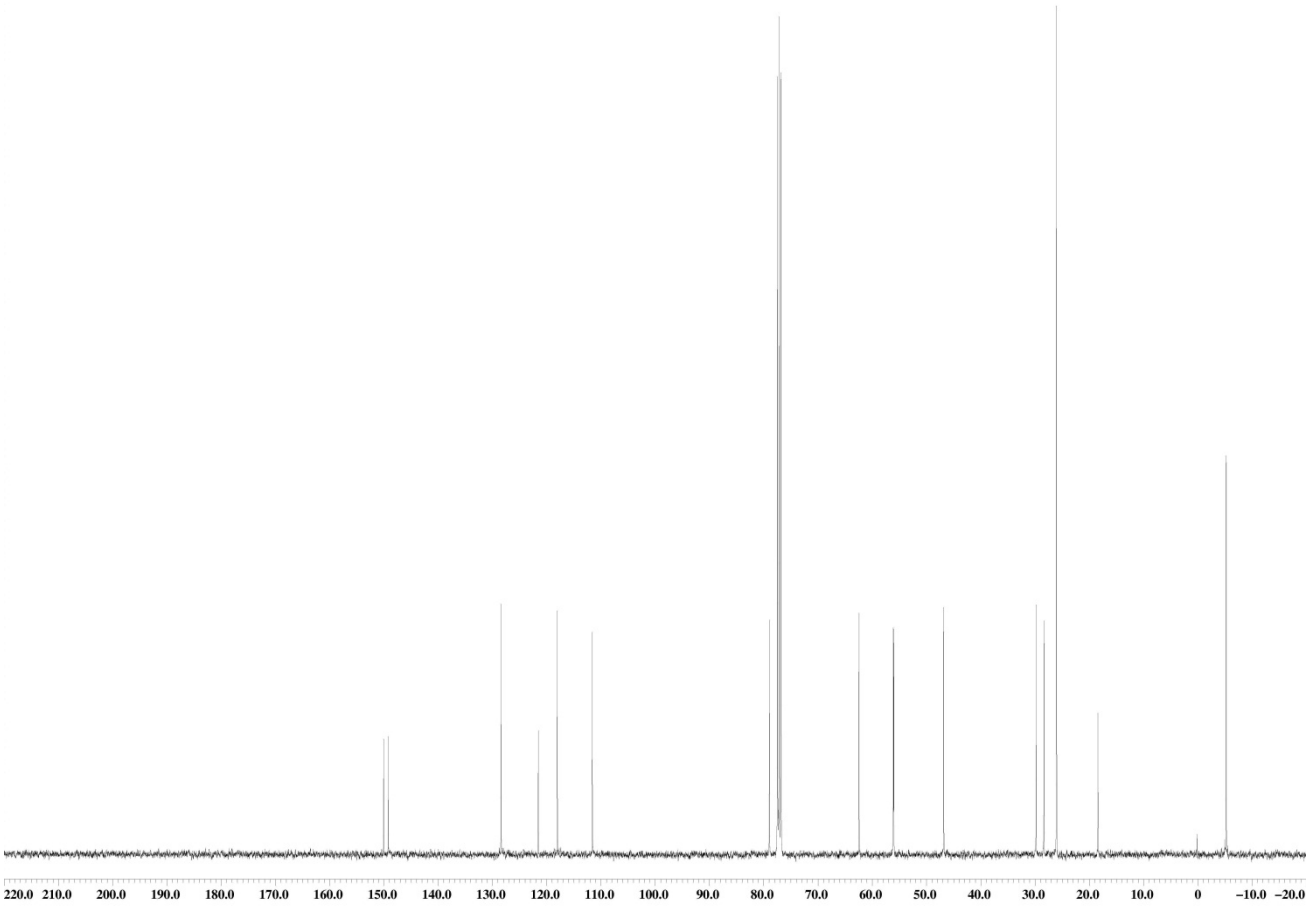
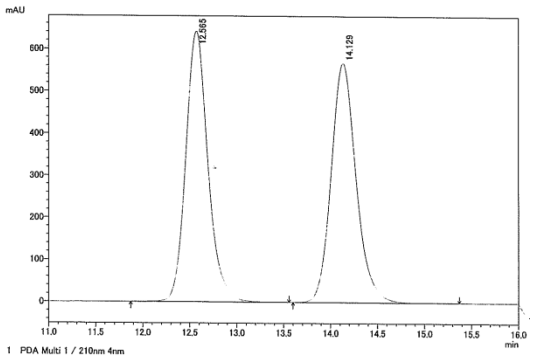
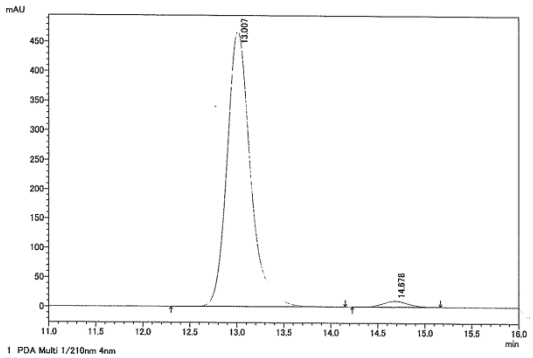

220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0

Copies of HPLC Chromatograms:

6a

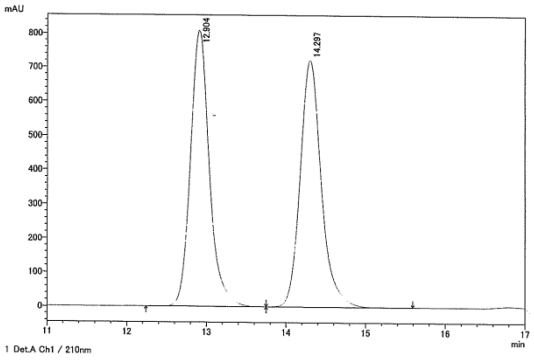


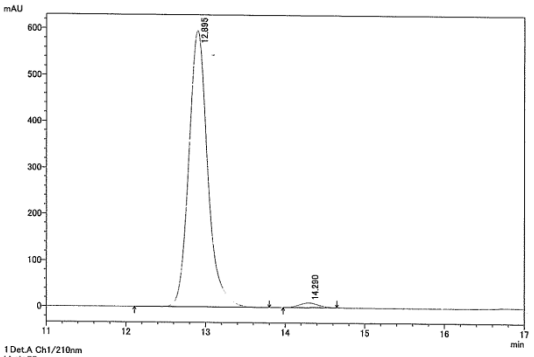


PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	13.007	97.818
2	14.678	2.182
合計		100.000

6b

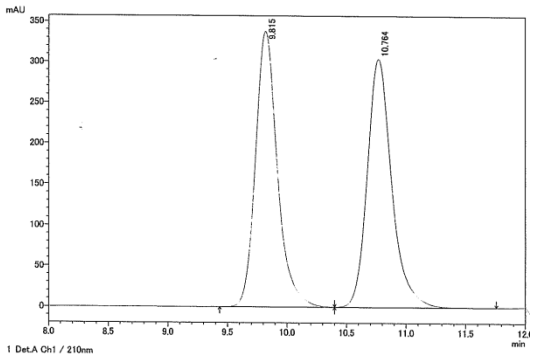


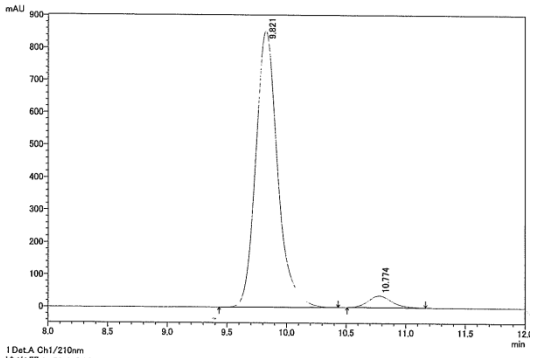


検出器A Ch1 210nm

ピーク#	保持時間	面積%
1	12.895	98.351
2	14.290	1.649
合計		100.000

6c

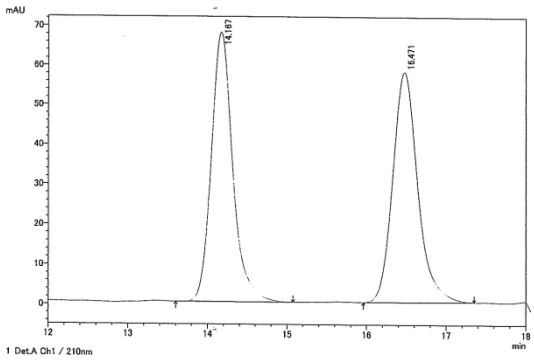


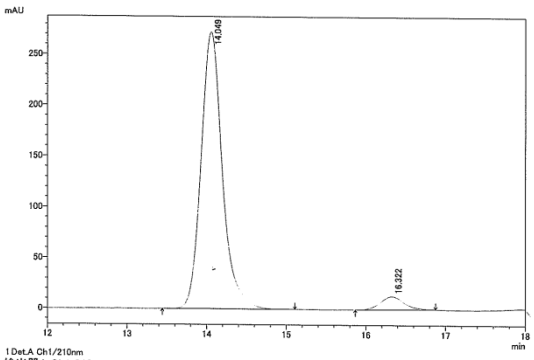


検出器A Ch1 210nm

ピーク#	保持時間	面積%
1	9.821	95.543
2	10.774	4.457
合計		100.000

6d

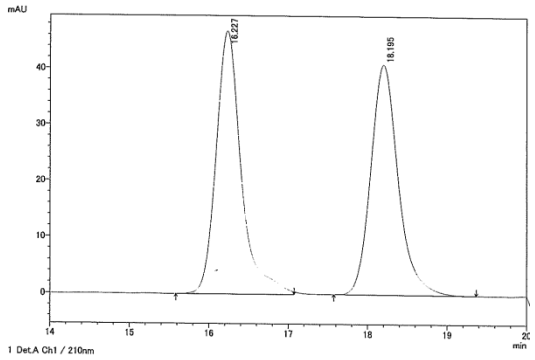


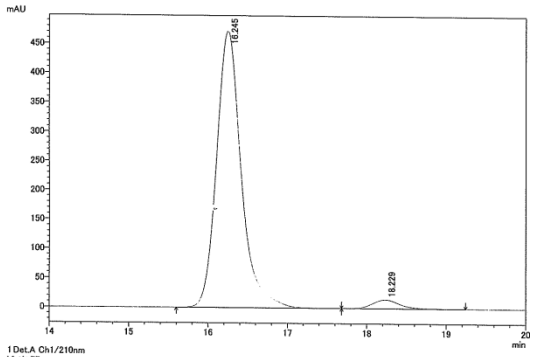


検出器A Ch1 210nm

ピーク#	保持時間	面積%
1	14.049	94.792
2	16.322	5.208
合計		100.000

6e

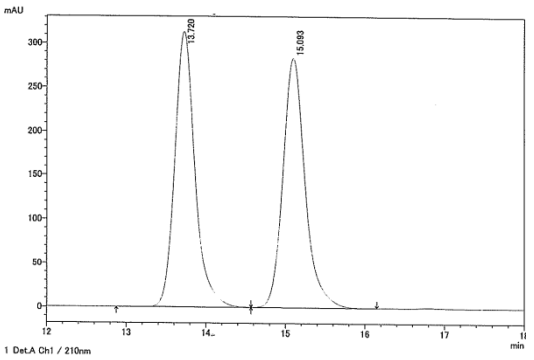


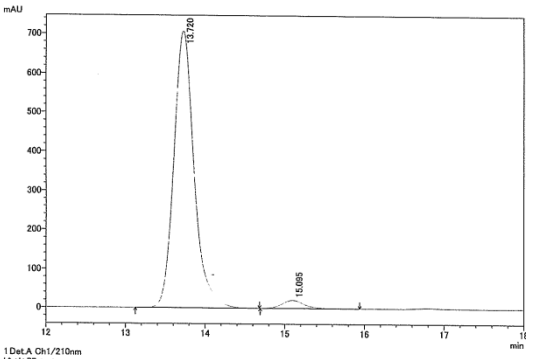


検出器A Ch1 210nm

ピーク#	保持時間	面積%
1	16.245	96.559
2	18.229	3.441
合計		100.000

6f

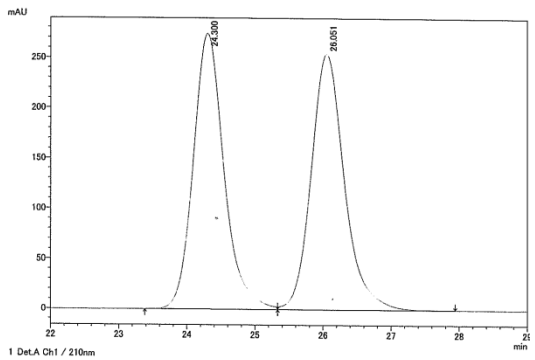


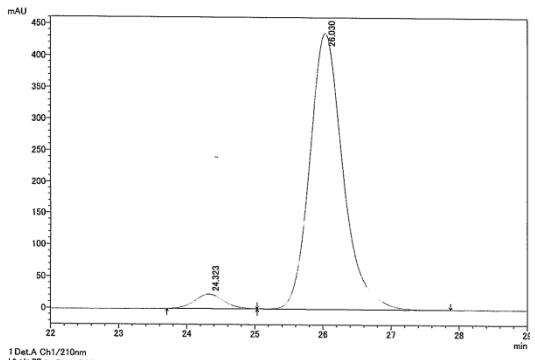


検出器A Ch1 210nm

ピーク#	保持時間	面積%
1	13.720	96.881
2	15.095	3.119
合計		100.000

6g

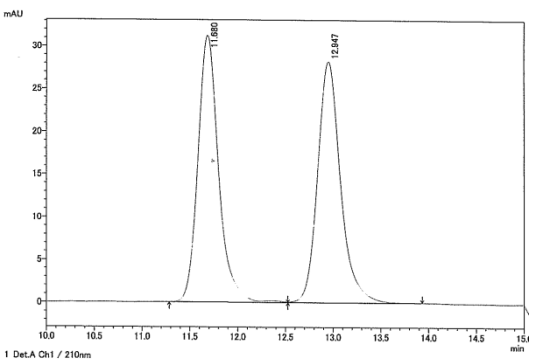


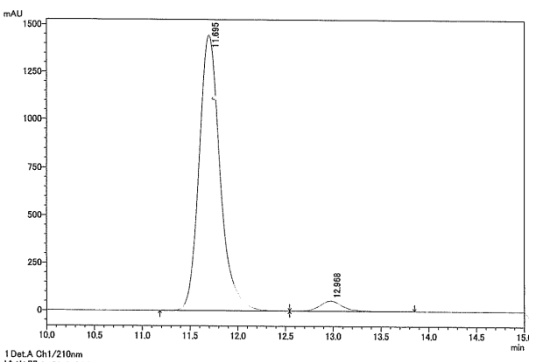


検出器A Ch1 210nm

ピーク#	保持時間	面積%
1	24.323	4.526
2	26.030	95.474
合計		100.000

6h

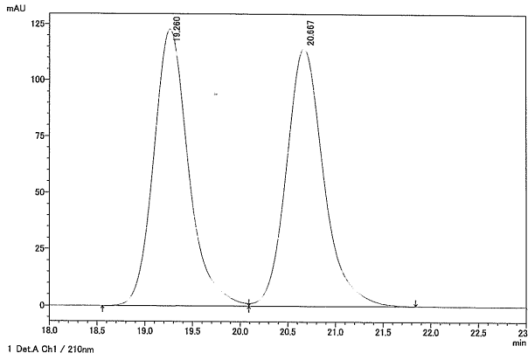


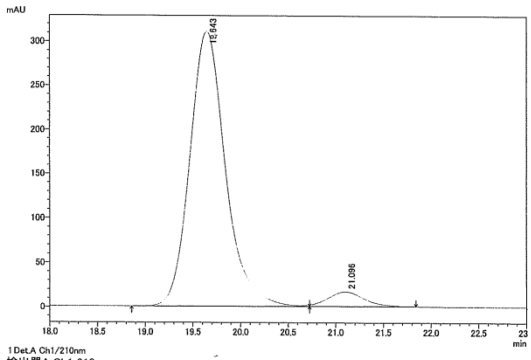


検出器A Ch1 210nm

ピーク#	保持時間	面積%
1	11.695	96.008
2	12.968	3.992
合計		100.000

6i

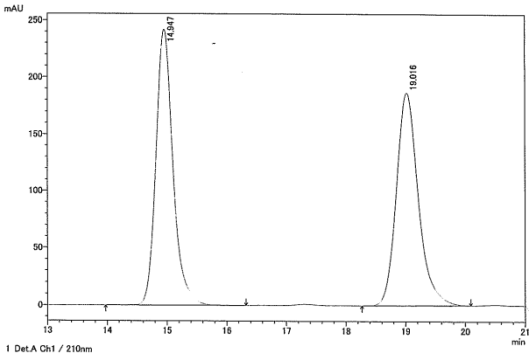


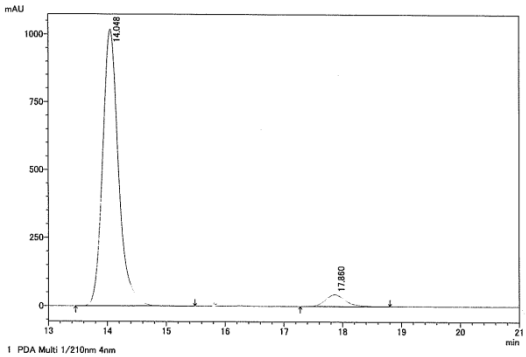


検出器A Ch1 210nm

ピーク#	保持時間	面積%
1	19.643	94.775
2	21.096	5.225
合計		100.000

6j

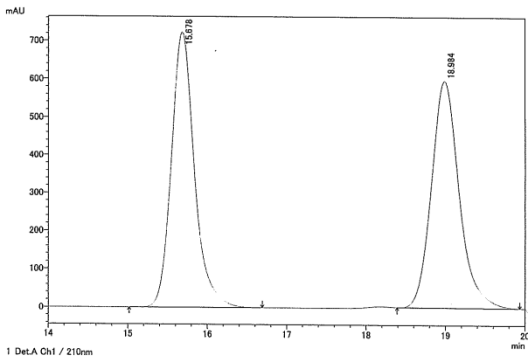


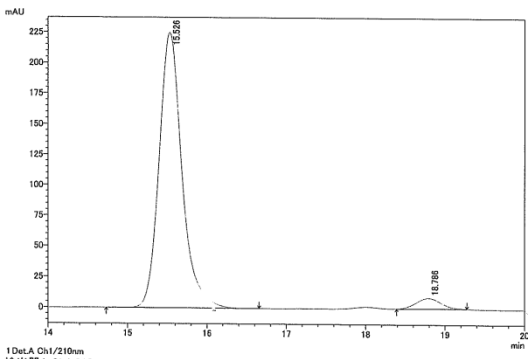


PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	14.048	94.778
2	17.860	5.222
合計		100.000

6k

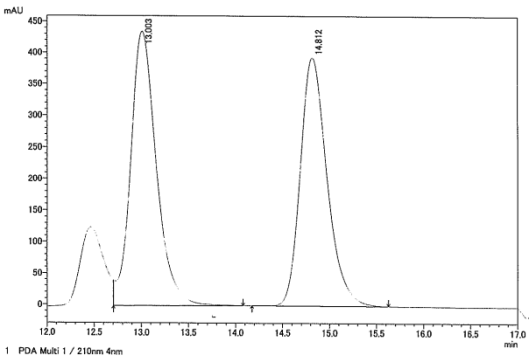


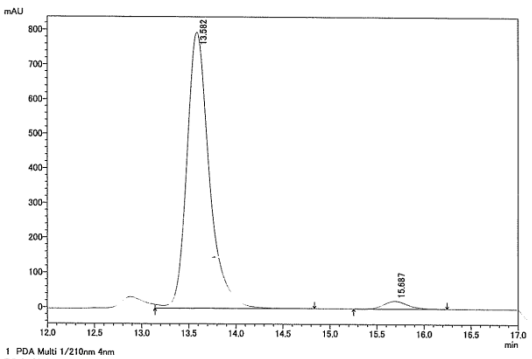


検出器A Ch1 210nm

ピーク#	保持時間	面積%
1	15.526	95.911
2	18.786	4.089
合計		100.000

6l

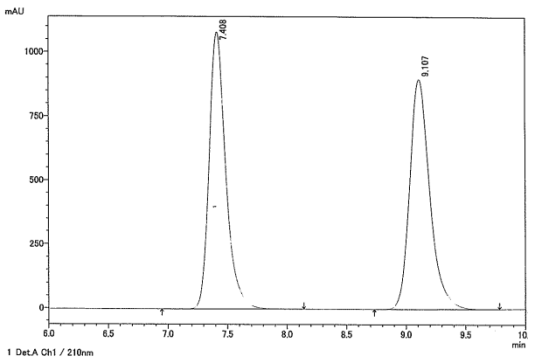


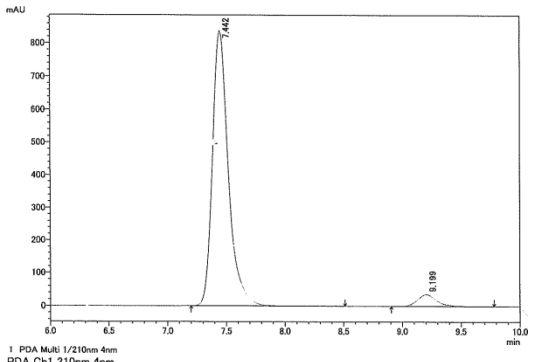


PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	13.582	96.956
2	15.687	3.044
合計		100.000

6m

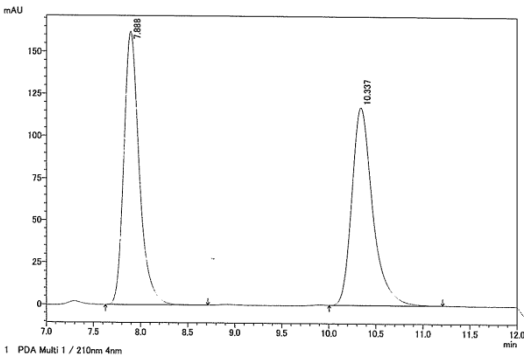


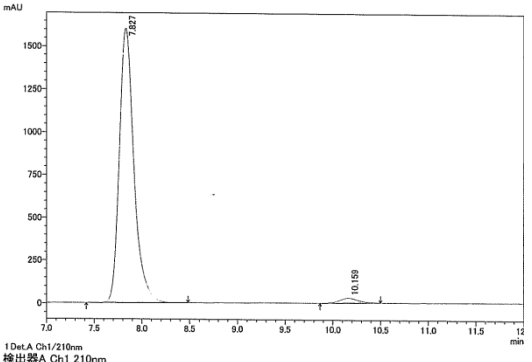


PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	7.442	95.072
2	9.199	4.928
合計		100.000

6n

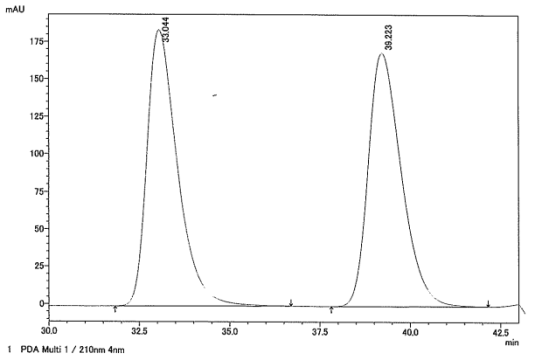


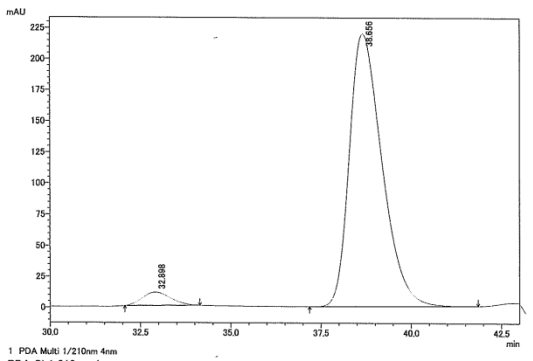


検出器A Ch1 210nm

ピーク#	保持時間	面積%
1	7.827	97.762
2	10.159	2.238
合計		100.000

6o

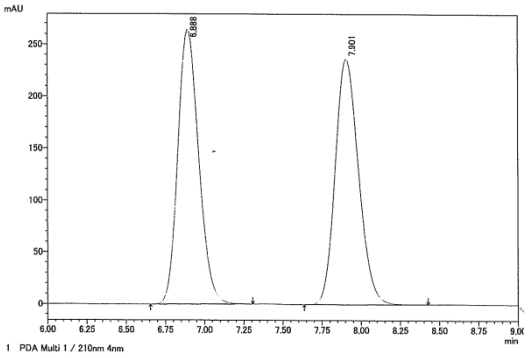


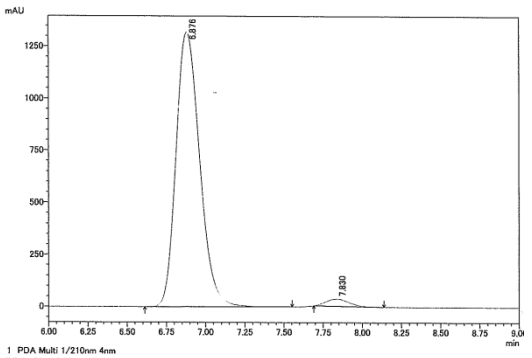


PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	32.898	4.078
2	38.656	95.922
合計		100.000

6p

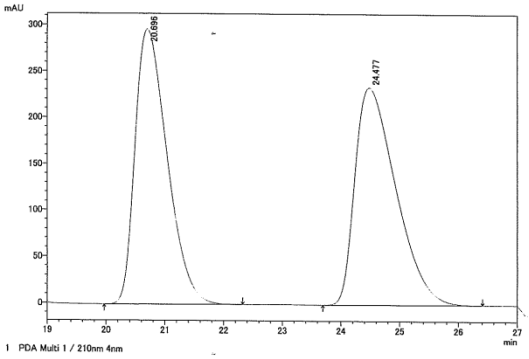


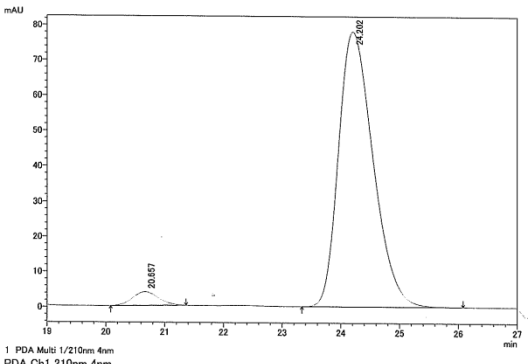


PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	6.876	97.556
2	7.830	2.444
合計		100.000

SI-5





PDA Ch1 210nm 4nm

ピーク#	保持時間	面積%
1	20.657	3.670
2	24.202	96.330
合計		100.000