Supplementary information for

Catalytic Asymmetric Synthesis of 5-Membered Alicyclic α-Quaternary β-Amino Acids via [3+2]-Photocycloaddition of α-Substituted Acrylates

Yuto Kimura,[1] Daisuke Uraguchi,[2] Takashi Ooi*,[1]

[1] *Institute of Transformative Bio-Molecules (WPI-ITbM) and Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, Nagoya University, Nagoya 464-8601, Japan*

[2] *Institute for Catalysis, Hokkaido University, Sapporo 001-0021, Japan*

tooi@chembio.nagoya-u.ac.jp

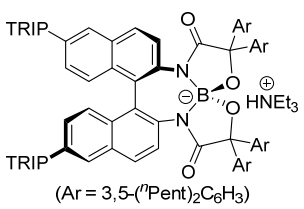
1. General Information

Infrared spectra were recorded on a Shimadzu IRAffinity-1 spectrometer. ^{1}H NMR spectra were recorded on a JEOL JNM-ECS400 (400 MHz) and JEOL JNM-ECA500II (500 MHz) spectrometers. Chemical shifts are reported in ppm from tetramethylsilane (0.0 ppm) resonance as the internal standard ($(CD_3)_2CO$ and $CDCl_3$). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sex = sextet, sept = septet, m = multiplet, br = broad) and coupling constants (Hz). ^{13}C NMR spectra were recorded on a JEOL JNM-ECS400 (101 MHz), JEOL JNM-ECA500II (126 MHz), and JEOL JNM-ECS600 (151 MHz) spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($(CD_3)_2CO$; 29.84 ppm, $CDCl_3$; 77.16 ppm). ^{19}F NMR spectra were recorded on a JEOL JNM-ECA500II (471 MHz) spectrometer. Chemical shifts are reported in ppm from benzotrifluoride (–64.0 ppm) resonance as the external standard. ^{11}B NMR spectra were recorded on a JEOL JNM-ECA500II (161 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from $BF_3 \cdot OEt_2$ resonance (0.0 ppm) as the external standard. Optical rotations were measured on a HORIBA SEPA-500 polarimeter. The high resolution mass spectra were measured on Thermo Fisher Scientific Exactive (ESI). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm). Manual flash column chromatography was conducted on silica gel 60N (spherical, 40–50 μm; Kanto Chemical Co., Inc.), PSQ60AB (spherical, av. 55 μm; Fuji Silysia Chemical ltd.), Silica gel 60 (Merck 1.09385.9929, 230–400 mesh), and CHROMATOREX NH-DM-2035 (spherical, av. 60 μm; Fuji Silysia Chemical ltd.). Enantiomeric excesses were determined by HPLC analysis using chiral columns [ϕ 4.6 mm x 250 mm, DAICEL CHIRALPAK IB-3 (IB3), CHIRALPAK IB N-3 (IBN3), CHIRALPAK IC-3 (IC3), and CHIRALCEL OZ-3 (OZ3)] with hexane (H), 2-propanol (^{i}PrOH), and ethanol (EtOH) as eluent.

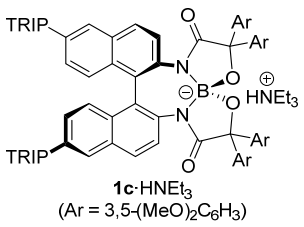
Tetrahydrofurane (THF), dichloromethane (CH_2Cl_2), toluene, and acetonitrile (MeCN) were supplied from Kanto Chemical Co., Inc. as "Dehydrated" and further purified by passing through neutral alumina under nitrogen atmosphere. α-Substituted methyl acrylates were synthesized by following the literature procedures.[1] Other simple chemicals were purchased and used as such.

2. Experimental Section

2.1 Characterization of a Chiral Iridium Borate [*rac*-Ir]·1 (TRIP = 2,4,6-^{i}Pr$_3$C$_6$H$_2$)

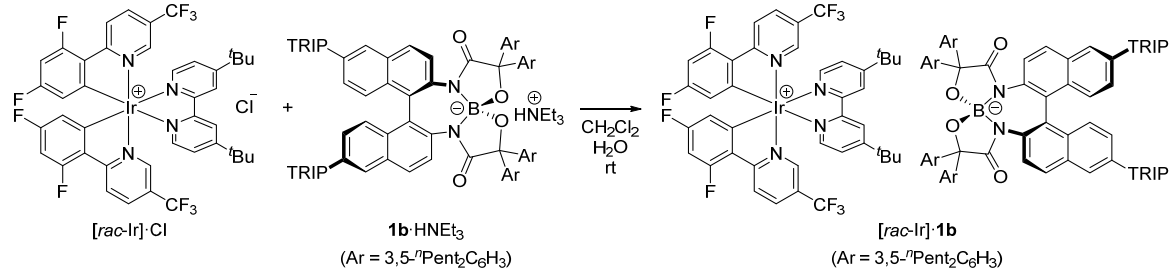


The synthesis was implemented by following the literature procedure[2] on 0.14 mmol scale and purification was performed by column chromatography on silica gel (ethyl acetate (EA)/H = 3:100 to 1:1 as eluent) to afford **1b·HNEt$_3$** (0.22 g, 0.12 mmol, 87%) as an off-white solid. **1b·HNEt$_3$ (Ar = 3,5-^{n}Pent$_2$C$_6$H$_3$):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.64 (1H, br), 7.87 (2H, d, J = 9.0 Hz), 7.77 (2H, d, J = 9.0 Hz), 7.66 (2H, s), 7.45 (4H, s), 7.05_3 (2H, s), 7.04_8 (2H, d, J = 9.0 Hz), 7.04 (2H, s), 6.90 (2H, s), 6.86 (2H, d, J = 9.0 Hz), 6.49 (2H, s), 6.33 (4H, s), 2.94 (2H, sept, J = 6.9 Hz), 2.64 (2H, sept, J = 6.9 Hz), 2.63-2.55 (2H, m), 2.58 (8H, t, J = 7.3 Hz), 2.28-2.12 (6H, m), 2.10-2.01 (4H, m), 2.00-1.90 (4H, m), 1.59 (8H, quin, J = 7.3 Hz), 1.39-1.31 (8H, m), 1.31-1.26 (16H, m), 1.30 (12H, d, J = 6.9 Hz), 1.24 (8H, sex, J = 7.3 Hz), 1.20-1.14 (8H, m), 1.13 (6H, d, J = 6.9 Hz), 1.09 (6H, d, J = 6.9 Hz), 0.93_3 (6H, d, J = 6.9 Hz), 0.92_6 (6H, d, J = 6.9 Hz), 0.85 (12H, t, J = 7.3 Hz), 0.83 (12H, t, J = 7.3 Hz), 0.61 (9H, t, J = 7.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.7, 148.0, 146.9, 146.5, 144.9, 144.2, 142.3, 141.3, 137.9, 137.2, 137.1, 132.4, 132.0, 130.2, 128.9, 128.0, 127.7_9, 127.7_5, 127.2, 126.9, 125.3, 125.2, 120.6_3, 120.5_9, 85.8, 45.7, 36.3, 35.7, 34.4, 31.8, 31.7, 31.5, 31.3, 30.4, 30.3, 24.6, 24.5, 24.4, 24.2_2, 24.1_9, 23.9, 22.7, 14.2, 8.2, two carbon atoms were not found probably due to overlapping.; ^{11}B NMR (160 MHz, $CDCl_3$) δ 11.0; IR (film): 2927, 2855, 1635, 1590, 1487, 1409, 1396, 1122, 1063, 909 cm^{-1}; HRMS (ESI) Calcd for $C_{118}H_{156}N_2O_4B^-$ ([M−HNEt$_3$]$^-$) 1676.2153. Found 1676.2155; $[\alpha]_D^{22}$ −91.0 (c = 5.4, $CHCl_3$).

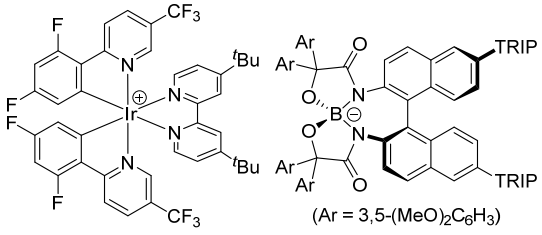


The synthesis was implemented by following the literature procedure[2] on 0.11 mmol scale and purification by column chromatography on silica gel (EA/H = 1:10 to 100:0 as eluent) afforded **1c**·HNEt$_3$ (0.15 g, 0.10 mmol, 93%) as an off-white solid. **1c·HNEt$_3$ (Ar = 3,5-(MeO)$_2$C$_6$H$_3$):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.08 (1H, br), 7.78 (2H, d, J = 8.4 Hz), 7.68 (2H, d, J = 8.4 Hz), 7.57 (2H, s), 7.03 (2H, s), 7.01 (2H, s), 6.97 (2H, d, J = 8.4 Hz), 6.85 (2H, d, J = 8.4 Hz), 6.78 (4H, s), 6.17 (2H, s), 6.13 (4H, s), 5.95 (2H, s), 3.47 (12H, s), 3.26 (12H, s), 2.92 (2H, sept, J = 6.8 Hz), 2.55 (2H, sept, J = 6.8 Hz), 2.49 (2H, sept, J = 6.8 Hz), 2.43-2.33 (6H, m), 1.28 (12H, d, J = 6.8 Hz), 1.11 (6H, d, J = 6.8 Hz), 1.03 (6H, d, J = 6.8 Hz), 0.90 (6H, d, J = 6.8 Hz), 0.89 (6H, d, J = 6.8 Hz), 0.61 (9H, t, J = 7.3 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.9, 160.6, 159.7, 148.1, 146.9, 146.4, 146.0, 137.6, 137.0, 136.8, 132.2, 129.7, 129.2, 128.1, 128.0, 127.4, 127.0, 120.7, 120.6, 105.9, 105.6, 99.0, 98.9, 85.6, 55.3, 55.1, 46.2, 34.4, 30.4, 24.5, 24.3_1, 24.2_6, 24.2_4, 24.1_8, 23.9, 8.1, two carbon atoms were not found probably due to overlapping.; ^{11}B NMR (160 MHz, $CDCl_3$) δ 10.6; IR (film): 2959, 2906, 1651, 1591, 1452, 1414, 1343, 1288, 1142, 1038, 910 cm^{-1}; HRMS (ESI) Calcd for $C_{86}H_{92}N_2O_{12}B^-$ ([M−HNEt$_3$]$^-$) 1355.6738. Found 1355.6745; $[\alpha]_D^{22}$ −69.4 (c = 6.0, $CHCl_3$).

Representative Procedure for the Preparation of Chiral Iridium Borate [*rac*-Ir]·1



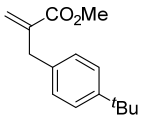
A solution of iridium chloride [*rac*-Ir]·Cl (47.6 mg, 0.047 mmol)[3] and **1b**·$HNEt_3$ (117.0 mg, 0.066 mmol) in CH_2Cl_2 (10.0 mL) was vigorously washed with distilled water (15.0 mL) four times. The organic phase was dried over Na_2SO_4 and concentrated under vacuum to afford [*rac*-Ir]·**1b** (0.17 g, 0.064 mmol) as a yellow solid, which was used as a catalyst for the asymmetric [3+2] radical cycloaddition reaction without further purification. **[*rac*-Ir]·1b (Ar = 3,5-^{n}Pent$_2$C$_6$H$_3$):** ^{1}H NMR (500 MHz, $CDCl_3$) *mixture of diastereomers* δ 8.48 (1H, dd, $J_{H\text{-}H}$ = 8.6 Hz, $J_{H\text{-}F}$ = 2.0 Hz), 8.44 (1H, dd, $J_{H\text{-}H}$ = 8.6 Hz, $J_{H\text{-}F}$ = 2.0 Hz), 8.34 (2H, s), 8.01 (1H, d, J = 8.6 Hz), 7.96 (1H, d, J = 8.6 Hz), 7.92 (2H, d, J = 5.7 Hz), 7.78 (4H, s), 7.77 (2H, d, J = 8.8 Hz), 7.71 (2H, d, J = 8.8 Hz), 7.63 (1H, dd, J = 5.7, 1.5 Hz), 7.62 (2H, s), 7.59 (1H, dd, J = 5.7, 1.5 Hz), 7.29 (2H, s), 7.20 (2H, d, J = 8.8 Hz), 7.06 (2H, s), 7.04 (2H, s), 6.85 (2H, d, J = 8.8 Hz), 6.82 (2H, s), 6.64 (1H, ddd, $J_{H\text{-}F}$ = 12.1, 9.3 Hz, $J_{H\text{-}H}$ = 2.3 Hz), 6.60 (1H, ddd, $J_{H\text{-}F}$ = 12.1, 9.3 Hz, $J_{H\text{-}H}$ = 2.3 Hz), 6.40 (2H, s), 6.20 (4H, s), 5.61 (1H, dd, $J_{H\text{-}F}$ = 7.9 Hz, $J_{H\text{-}H}$ = 2.3 Hz), 5.60 (1H, dd, $J_{H\text{-}F}$ = 7.9 Hz, $J_{H\text{-}H}$ = 2.3 Hz), 2.94 (2H, sept, J = 6.8 Hz), 2.77 (2H, sept, J = 6.8 Hz), 2.68 (2H, sept, J = 6.8 Hz), 2.61 (8H, t, J = 7.1 Hz), 2.00 (4H, dt, J = 13.8, 7.1 Hz), 1.82 (4H, dt, J = 13.8, 7.1 Hz), 1.61 (8H, quin, J = 7.1 Hz), 1.41 (9H, s), 1.39 (9H, s), 1.35-1.30 (8H, m), 1.31 (12H, d, J = 6.8 Hz), 1.30-1.24 (16H, m), 1.19 (8H, sex, J = 7.1 Hz), 1.15-1.08 (8H, m), 1.13 (6H, d, J = 6.8 Hz), 1.09 (6H, d, J = 6.8 Hz), 0.96 (6H, d, J = 6.8 Hz), 0.93 (6H, d, J = 6.8 Hz), 0.83 (12H, t, J = 7.1 Hz), 0.78 (12H, t, J = 7.1 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) *mixture of diastereomers* δ 178.2, 168.1 (d, $J_{C\text{-}F}$ = 6.0 Hz), 166.7, 165.1 (ddd, $J_{C\text{-}F}$ = 263.0, 12.7, 3.7 Hz), 155.3, 153.8 (d, $J_{C\text{-}F}$ = 6.0 Hz), 150.7, 150.6, 147.5, 147.2, 146.9$_2$, 146.9$_0$, 144.5, 144.2 (d, $J_{C\text{-}F}$ = 4.9 Hz), 143.0, 140.8, 140.6, 139.4, 137.8, 137.2, 137.1, 136.2, 132.7, 131.9, 130.9, 128.6, 128.4, 128.3, 127.7, 127.6, 127.1, 126.9$_0$, 126.8$_6$, 126.4, 126.3, 126.0$_3$ (q, $J_{C\text{-}F}$ = 35.1 Hz), 125.9$_8$ (d, $J_{C\text{-}F}$ = 35.1 Hz), 125.9$_4$, 125.8$_9$, 125.8, 124.4$_2$ (d, $J_{C\text{-}F}$ = 20.5 Hz), 124.3$_5$ (d, $J_{C\text{-}F}$ = 20.7 Hz), 121.7 (q, $J_{C\text{-}F}$ = 273.3 Hz), 121.6, 120.5, 120.4, 114.1 (d, $J_{C\text{-}F}$ = 18.1 Hz), 100.4$_2$ (t, $J_{C\text{-}F}$ = 26.6 Hz), 100.3$_7$ (t, $J_{C\text{-}F}$ = 26.6 Hz), 85.4, 36.4, 36.2, 35.6, 34.4, 31.8, 31.6, 31.5, 31.3, 30.3, 24.8, 24.5, 24.4, 24.2$_3$, 24.1$_8$, 23.9, 27.8, 14.3, 14.2, 57 carbon atoms were not found probably due to overlapping.; ^{19}F NMR (470 MHz, $CDCl_3$) *mixture of diastereomers* δ −62.8, −100.3, −100.5, −104.6, two fluorine atoms were not found probably due to overlapping.; ^{11}B NMR (160 MHz, $CDCl_3$) *mixture of diastereomers* δ 11.0 (overlapped); IR (film): 2931, 1653, 1602, 1569, 1465, 1397, 1330, 1298, 1143, 1112, 1027, 903 cm^{-1}.



[*rac*-Ir]·1c (Ar = 3,5-(MeO)$_2$C$_6$H$_3$): ^{1}H NMR (500 MHz, $CDCl_3$) *mixture of diastereomers* δ 8.46-8.41 (2H, m), 8.36 (2H, s), 8.00 (2H, d, J = 9.0 Hz), 7.94$_2$ (1H, d, J = 6.2 Hz), 7.93$_8$ (1H, d, J = 6.2 Hz), 7.70 (2H, d, J = 8.6 Hz), 7.65 (2H, d, J = 8.6 Hz), 7.63 (1H, dd, J = 6.2, 1.6 Hz), 7.61 (1H, dd, J = 6.2, 1.6 Hz), 7.54 (2H, s),

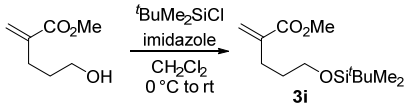
7.33_3 (2H, s), 7.33_0 (4H, d, J = 2.2 Hz), 7.13 (2H, d, J = 8.6 Hz), 7.06 (2H, s), 7.03 (2H, s), 6.85 (2H, d, J = 8.6 Hz), 6.65 (2H, t, $J_{H\text{-}F}$ = 10.3 Hz), 6.20 (4H, d, J = 2.2 Hz), 6.19 (2H, t, J = 2.2 Hz), 5.91 (2H, t, J = 2.2 Hz), 5.62 (2H, dd, $J_{H\text{-}F}$ = 8.0 Hz, $J_{H\text{-}H}$ = 2.0 Hz), 3.71 (12H, s), 3.19 (12H, s), 2.94 (2H, sept, J = 6.8 Hz), 2.73 (2H, sept, J = 6.8 Hz), 2.59 (2H, sept, J = 6.8 Hz), 1.39_1 (9H, s), 1.38_7 (9H, s), 1.31 (12H, d, J = 6.8 Hz), 1.17 (6H, d, J = 6.8 Hz), 1.06 (6H, d, J = 6.8 Hz), 1.03 (6H, d, J = 6.8 Hz), 0.92 (6H, d, J = 6.8 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) *mixture of diastereomers* δ 176.9, 168.2 (d, $J_{C\text{-}F}$ = 6.0 Hz), 168.1 (d, $J_{C\text{-}F}$ = 6.0 Hz), 166.7, 165.1 (dd, $J_{C\text{-}F}$ = 263.1, 12.7 Hz), 162.8 (dd, $J_{C\text{-}F}$ = 265.5, 12.7 Hz), 159.8, 159.5, 155.2_8, 155.2_6, 153.9 (d, $J_{C\text{-}F}$ = 6.0 Hz), 150.7, 150.6, 148.6, 147.9, 147.7, 147.2, 146.7, 144.3 (d, $J_{C\text{-}F}$ = 4.9 Hz), 138.7, 137.5, 137.0, 136.9, 136.4, 132.5, 132.0, 130.3, 128.4, 128.1, 127.7, 127.1, 126.9, 126.3, 126.0 (q, $J_{C\text{-}F}$ = 35.1 Hz), 124.3 (d, $J_{C\text{-}F}$ = 20.5 Hz), 124.2 (d, $J_{C\text{-}F}$ = 20.5 Hz), 121.7 (q, $J_{C\text{-}F}$ = 273.3 Hz), 121.6_3, 121.6_1, 120.6, 120.5, 114.1 (d, $J_{C\text{-}F}$ = 18.1 Hz), 106.1, 105.8, 100.4 (t, $J_{C\text{-}F}$ = 26.6 Hz), 99.6, 99.5, 85.4, 55.4, 54.9, 36.2, 34.3, 30.3_4, 30.2_8, 24.6, 24.5, 24.3, 24.2_4, 24.1_8, 23.9, 50 carbon atoms were not found probably due to overlapping.; ^{19}F NMR (470 MHz, $CDCl_3$) *mixture of diastereomers* δ −62.8, −100.5, −104.7, three fluorine atoms were not found probably due to overlapping.; ^{11}B NMR (160 MHz, $CDCl_3$) *mixture of diastereomers* δ 11.0 (overlapped); IR (film): 2965, 1660, 1600, 1560, 1455, 1389, 1329, 1295, 1146, 1109, 1057, 903, 841 cm^{-1}.

2.2 Synthesis and Characterization of α-Substituted Methyl Acrylates



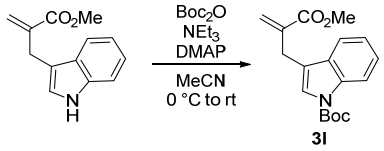
Methyl 2-(4-(*tert*-butyl)benzyl)acrylate 3e: The title compound was prepared from diethyl malonate and 4-*tert*-butylbenzyl bromide by following the literature procedure.[1a] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (2H, d, J = 8.5 Hz), 7.13 (2H, d, J = 8.5 Hz), 6.22 (1H, d, J = 1.4 Hz), 5.47 (1H, q, J = 1.4 Hz), 3.74 (3H, s), 3.60 (2H, brs), 1.30 (9H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 149.3, 140.3, 135.7, 128.8, 126.3, 125.5, 52.0, 37.6, 34.5, 31.5; IR (film): 2960, 2867, 1719, 1631, 1517, 1440, 1193, 1137, 1110, 947, 813 cm^{-1}; HRMS (ESI) Calcd for $C_{15}H_{20}O_2Na^+$ ([M+Na]$^+$) 255.1356. Found 255.1355.

Preparation of methyl 5-(*tert*-butyldimethylsilyloxy)-2-methylenepentanoate 3i



To a solution of methyl 5-hydroxy-2-methylenepentanoate (0.14 g, 1.0 mmol)[1d] in CH_2Cl_2 (5.0 mL) were added imidazole (0.17 g, 2.5 mmol) and ^{t}BuMe$_2$SiCl (0.30 g, 2.0 mmol) at 0 °C. After being stirred for 20 min, the mixture was warmed to ambient temperature and stirred for 21 h. The reaction was quenched by adding water and the aqueous phase was extracted with CH_2Cl_2 three times. The combined organic phases were dried over Na_2SO_4, filtered, and concentrated. Purification of the residue was performed by column chromatography on silica gel (H/Et$_2$O = 100:1 to 10:1 as eluent) to afford methyl 5-(*tert*-butyldimethylsilyloxy)-2-methylenepentanoate **3i** (0.23 g, 0.89 mmol, 89%) as a colorless oil. **Methyl 5-(*tert*-butyldimethylsilyloxy)-2-methylenepentanoate 3i:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.15 (1H, dt, J = 1.3, 0.5 Hz), 5.55 (1H, q, J = 1.3 Hz), 3.75 (3H, s), 3.63 (2H, t, J = 6.4 Hz), 2.37 (2H, td, J = 7.8, 1.3 Hz), 1.69 (2H, tt, J = 7.8, 6.4 Hz), 0.90 (9H, s), 0.05 (6H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9, 140.4, 125.0, 62.5, 51.9, 31.6, 28.4, 26.1, 18.5, −5.2; IR (film): 2950, 2849, 1724, 1477, 1250, 1149, 1096, 1066, 946, 836 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{26}O_3SiNa^+$ ([M+Na]$^+$) 281.1543. Found 281.1541.

Preparation of *tert*-butyl 3-(2-(methoxycarbonyl)allyl)-1*H*-indole-1-carboxylate 3l

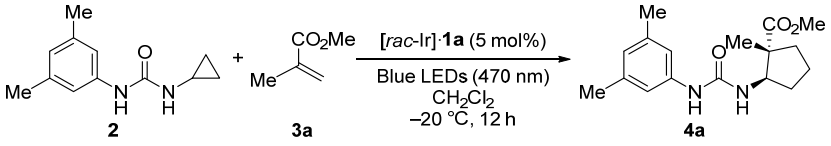


3l

To a solution of methyl 2-((1*H*-indol-3-yl)methyl)acrylate (0.68 g, 3.1 mmol)[1e] in MeCN (31.0 mL) were added DMAP (47.6 mg, 0.39 mmol), NEt_3 (0.52 mL, 3.8 mmol), and Boc_2O (1.73 mL, 7.5 mmol) at 0 °C. After being stirred for 1.5 h at 0 °C, the reaction mixture was allowed to warm to ambient temperature and stirred for 4 h. The reaction was quenched by adding a saturated aqueous solution of NH_4Cl at 0 °C and the aqueous phase was extracted with CH_2Cl_2 three times. The combined organic phases were dried over Na_2SO_4, filtered, and concentrated. Purification of the residue was performed by column chromatography on silica gel (H/EA = 50:1 to 5:1 as eluent) to afford *tert*-butyl 3-(2-(methoxycarbonyl)allyl)-1*H*-indole-1-carboxylate **3l** (0.96 g, 3.0 mmol, 97%) as a colorless sticky oil. ***tert*-Butyl 3-(2-(methoxycarbonyl)allyl)-1*H*-indole-1-carboxylate 3l:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (1H, brs), 7.46 (1H, d, J = 7.6 Hz), 7.41 (1H, brs), 7.31 (1H, t, J = 7.6 Hz), 7.22 (1H, t, J = 7.6 Hz), 6.24 (1H, d, J = 1.5 Hz), 5.52 (1H, d, J = 1.5 Hz), 3.78 (3H, s), 3.71 (2H, s), 1.67 (9H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 149.9, 138.4, 135.7, 130.4, 126.4, 124.5, 124.2, 122.6, 119.4, 117.7, 115.4, 83.7, 52.1, 28.4, 27.4 cm^{-1}; IR (film): 1720, 1452, 1368, 1256, 1156, 1083, 1017, 938, 840 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{21}O_4NNa^+$ ($[M+Na]^+$) 338.1363. Found 338.1363.

2.3 Asymmetric [3+2] Photocycloaddition Reaction

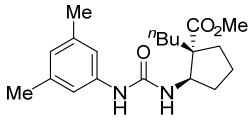
Representative Procedure for the Asymmetric [3+2] Photocycloaddition Reaction



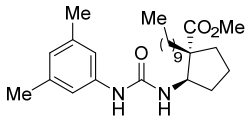
2 **3a** **4a**

To a mixture of 1-cyclopropyl-3-(3,5-dimethylphenyl)urea (**2**) (20.4 mg, 0.10 mmol) and [*rac*-Ir]·**1a** (13.4 mg, 0.0050 mmol) in CH_2Cl_2 (0.5 mL) was added methyl methacrylate (**3a**) (50.1 mg, 0.50 mmol) under argon (Ar) atmosphere. The suspension was then subjected to freeze-pump-thaw process (1 cycle) and backfilled with Ar. The reaction mixture was illuminated with blue LEDs (470 nm) at −20 °C for 12 h. After exposing to air, the reaction mixture was concentrated to give the crude residue, which was analyzed by ^{1}H NMR (500 MHz) to determine the diastereomeric ratio of the product (dr = 15:1). Purification of the residue by column chromatography on silica gel (H/Et_2O = 3:1 to 1:1 as eluent) afforded **4a** (25.3 mg, 0.083 mmol, 83%) as a mixture of diastereomers. Enantiomeric excess of the major diastereomer of **4a** was determined by HPLC analysis on chiral stationary phase. **4a**: HPLC OZ3, H/^{i}PrOH = 10:1, flow rate = 1.0 mL/min, rt, λ = 254 nm, 8.3 min (minor diastereomer), 9.7 min (minor diastereomer), 13.7 min (minor enantiomer of major diastereomer), 24.3 min (major enantiomer of major diastereomer); ^{1}H NMR (500 MHz, $(CD_3)_2CO$) *major diastereomer* δ 7.67 (1H, br), 7.07 (2H, s), 6.55 (1H, s), 5.71 (1H, brd, J = 8.6 Hz), 4.53 (1H, q, J = 8.6 Hz), 3.63 (3H, s), 2.21 (1H, ddd, J = 13.0, 8.8, 6.8 Hz), 2.20 (6H, s), 2.07 (1H, ddt, J = 16.0, 8.6, 4.4 Hz), 1.74-1.64 (2H, m), 1.59-1.47 (2H, m), 1.13 (3H, s); ^{13}C NMR (126 MHz, $(CD_3)_2CO$)

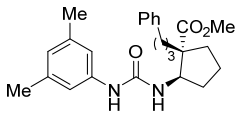
major diastereomer δ 177.8, 155.5, 141.4, 138.7, 123.9, 116.7, 58.0, 52.1, 51.7, 37.3, 31.8, 21.5, 21.4, 18.1; IR (film): 3324, 2917, 2823, 1727, 1653, 1559, 1437, 1203, 1127, 941, 854 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{24}O_3N_2Na^+$ ($[M+Na]^+$) 327.1679. Found 327.1672.



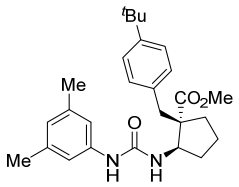
4b: HPLC IC3, H/^{i}PrOH = 10:1, flow rate = 1.0 mL/min, 30 °C, λ = 254 nm, 16.9 min (minor diastereomer), 19.3 min (minor diastereomer), 30.1 min (major enantiomer of major diastereomer), 35.7 min (minor enantiomer of major diastereomer); ^{1}H NMR (500 MHz, $(CD_3)_2CO$) major diastereomer δ 7.73 (1H, br), 7.07 (2H, s), 6.56 (1H, s), 5.82 (1H, brd, J = 9.6 Hz), 4.55 (1H, dt, J = 9.6, 7.0 Hz), 3.63 (3H, s), 2.26 (1H, ddd, J = 12.9, 7.9, 5.1 Hz), 2.20 (6H, s), 1.97 (1H, dddd, J = 12.9, 8.9, 7.0, 5.8 Hz), 1.83 (1H, ddd, J = 12.9, 11.1, 5.1 Hz), 1.72-1.60 (2H, m), 1.60-1.48 (2H, m), 1.44-1.36 (1H, m), 1.32-1.23 (2H, m), 1.23-1.14 (2H, m), 0.86 (3H, t, J = 7.3 Hz); ^{13}C NMR (126 MHz, $(CD_3)_2CO$) major diastereomer δ 177.0, 155.6, 141.3, 138.7, 124.0, 116.8, 57.4$_2$, 57.3$_7$, 52.1, 32.8, 32.6, 32.4, 28.3, 24.0, 21.5, 21.4, 14.3; IR (film): 3325, 2942, 2870, 1726, 1637, 1560, 1430, 1270, 1203, 1145, 1128, 838 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{30}O_3N_2Na^+$ ($[M+Na]^+$) 369.2149. Found 369.2155.



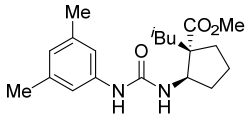
4c: HPLC IC3, H/^{i}PrOH = 10:1, flow rate = 1.0 mL/min, 30 °C, λ = 254 nm, 12.7 min (minor diastereomer), 14.5 min (minor diastereomer), 21.8 min (major enantiomer of major diastereomer), 24.5 min (minor enantiomer of major diastereomer); ^{1}H NMR (500 MHz, $(CD_3)_2CO$) major diastereomer δ 7.67 (1H, br), 7.08 (2H, s), 6.56 (1H, s), 5.76 (1H, brd, J = 9.4 Hz), 4.55 (1H, dt, J = 9.4, 6.7 Hz), 3.64 (3H, s), 2.26 (1H, ddd, J = 12.7, 7.8, 4.8 Hz), 2.20 (6H, s), 1.97 (1H, ddt, J = 13.2, 9.1, 6.7 Hz), 1.86-1.78 (1H, m), 1.72-1.60 (2H, m), 1.60-1.48 (2H, m), 1.45-1.35 (1H, m), 1.31-1.19 (16H, m), 0.86 (3H, t, J = 6.8 Hz); ^{13}C NMR (126 MHz, $(CD_3)_2CO$) major diastereomer δ 177.0, 155.4, 141.4, 138.7, 123.9, 116.7, 57.5, 57.3, 52.1, 33.0, 32.9, 32.6, 32.4, 31.0, 30.3, 30.2, 30.1, 26.1, 23.3, 21.5, 21.4, 14.4, one carbon atom was not found probably due to overlapping.; IR (film): 3329, 2925, 2858, 1727, 1636, 1558, 1450, 1237, 1167, 1043, 833 cm^{-1}; HRMS (ESI) Calcd for $C_{26}H_{42}O_3N_2Na^+$ ($[M+Na]^+$) 453.3088. Found 453.3109.



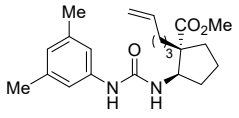
4d: HPLC IC3, H/^{i}PrOH = 10:1, flow rate = 1.0 mL/min, 30 °C, λ = 254 nm, 21.5 min (minor diastereomer), 25.7 min (minor diastereomer), 35.5 min (major enantiomer of major diastereomer), 44.1 min (minor enantiomer of major diastereomer); ^{1}H NMR (500 MHz, $(CD_3)_2CO$) major diastereomer δ 7.72 (1H, br), 7.21 (2H, t, J = 7.1 Hz), 7.15 (2H, d, J = 7.1 Hz), 7.12 (1H, t, J = 7.1 Hz), 7.10 (2H, s), 6.57 (1H, s), 5.84 (1H, br), 4.60 (1H, dt, J = 9.0, 6.6 Hz), 3.63 (3H, s), 2.58 (1H, ddd, 13.8, 8.3, 5.7 Hz), 2.54 (1H, ddd, 13.8, 8.3, 5.7 Hz), 2.25 (1H, ddd, J = 12.7, 7.8, 5.3 Hz), 2.21 (6H, s), 1.98 (1H, ddt, J = 13.0, 8.6, 6.6 Hz), 1.92-1.83 (1H, m), 1.69-1.45 (7H, m); ^{13}C NMR (126 MHz, $(CD_3)_2CO$) major diastereomer δ 176.9, 155.6, 143.1, 141.3, 138.8, 129.1, 129.0, 126.4, 124.0, 116.8, 57.6, 57.1, 52.1, 37.1, 33.1, 32.7, 32.4, 28.2, 21.5, 21.4; IR (film): 3301, 2957, 2862, 1725, 1640, 1559, 1448, 1230, 1153, 840 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{32}O_3N_2Na^+$ ($[M+Na]^+$) 431.2305. Found 431.2322.



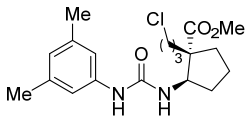
4e: The title compound was purified by column chromatography on silica gel topped with 4 cm of CHROMATOREX NH-DM-2035 (H/EA = 6:1 to 2:1 as eluent). HPLC IBN3, H/EtOH = 92:8, flow rate = 1.0 mL/min, rt, λ = 254 nm, 6.8 min (minor diastereomer), 9.2 min (major enantiomer of major diastereomer), 15.0 min (minor diastereomer), 16.8 min (minor enantiomer of major diastereomer); ^{1}H NMR (500 MHz, $(CD_3)_2CO$) major diastereomer δ 7.75 (1H, br), 7.27 (2H, d, J = 8.3 Hz), 7.12 (2H, s), 7.08 (2H, d, J = 8.3 Hz), 6.57 (1H, s), 5.95 (1H, brd, J = 9.1 Hz), 4.58 (1H, dt, J = 9.1, 7.1 Hz), 3.62 (3H, s), 3.33 (1H, d, J = 13.5 Hz), 2.59 (1H, d, J = 13.5 Hz), 2.21 (6H, s), 2.16-2.07 (1H, m), 2.05-1.98 (1H, m), 1.82-1.72 (1H, m), 1.72-1.58 (3H, m), 1.27 (9H, s); ^{13}C NMR (151 MHz, $(CD_3)_2CO$) major diastereomer δ 176.2, 155.5, 149.6, 141.4, 138.8, 136.4, 130.3, 125.8, 124.0, 116.8, 58.7, 58.5, 52.0, 37.1, 34.8, 31.7, 31.6, 31.3, 21.5, 20.7; IR (film): 3272, 2965, 1729, 1702, 1634, 1560, 1319, 1244, 1040, 814 cm^{-1}; HRMS (ESI) Calcd for $C_{27}H_{36}O_3N_2Na^+$ ([M+Na]$^+$) 459.2618. Found 459.2611.



4f: HPLC IC3, H/^{i}PrOH = 10:1, flow rate = 1.0 mL/min, 30 °C, λ = 254 nm, 18.1 min (minor diastereomer), 20.9 min (minor diastereomer), 28.3 min (major enantiomer of major diastereomer), 32.5 min (minor enantiomer of major diastereomer); ^{1}H NMR (500 MHz, $(CD_3)_2CO$) major diastereomer δ 7.73 (1H, br), 7.07 (2H, s), 6.56 (1H, s), 5.82 (1H, brd. J = 9.5 Hz), 4.52 (1H, dt, J = 9.5, 6.5 Hz), 3.63 (3H, s), 2.34 (1H, ddd, J = 12.9, 7.6, 5.6 Hz), 2.20 (6H, s), 1.92 (1H, ddt, J = 13.1, 8.9, 6.5 Hz), 1.85 (1H, dd, J = 13.6, 6.6 Hz), 1.71-1.47 (5H, m), 1.40 (1H, dd, J = 13.6, 6.6 Hz), 0.88 (3H, d, J = 6.5 Hz), 0.80 (3H, d, J = 6.5 Hz); ^{13}C NMR (126 MHz, $(CD_3)_2CO$) major diastereomer δ 177.3, 155.6, 141.3, 138.8, 124.0, 116.8, 58.2, 57.1, 52.0, 41.3, 32.4, 32.0, 26.3, 24.6, 23.5, 21.5, 21.3; IR (film): 3324, 2958, 1734, 1701, 1644, 1559, 1457, 1244, 1038, 842 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{30}O_3N_2Na^+$ ([M+Na]$^+$) 369.2149. Found 369.2144.

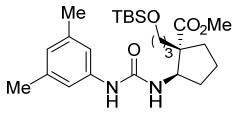


4g: HPLC IC3, H/^{i}PrOH = 10:1, flow rate = 1.0 mL/min, 30 °C, λ = 254 nm, 16.7 min (minor diastereomer), 19.4 min (minor diastereomer), 29.5 min (major enantiomer of major diastereomer), 34.0 min (minor enantiomer of major diastereomer); ^{1}H NMR (500 MHz, $(CD_3)_2CO$) major diastereomer δ 7.72 (1H, br), 7.07 (2H, s), 6.56 (1H, s), 5.83 (1H, brd, J = 9.3 Hz), 5.77 (1H, ddt, J = 17.2, 10.3, 6.8 Hz), 4.96 (1H, ddt, J = 17.2, 2.3, 1.3 Hz), 4.88 (1H, ddt, J = 10.3, 2.3, 1.3 Hz), 4.56 (1H, dt, J = 9.3, 7.0 Hz), 3.64 (3H, s), 2.26 (1H, ddd, J = 13.0, 8.3, 5.3 Hz), 2.20 (6H, s), 2.01-1.93 (3H, m), 1.84 (1H, td, J = 12.4, 4.2 Hz), 1.72-1.48 (4H, m), 1.46-1.37 (1H, m), 1.37-1.23 (2H, m); ^{13}C NMR (126 MHz, $(CD_3)_2CO$) major diastereomer δ 176.9, 155.6, 141.3, 139.4, 138.7, 124.0, 116.8, 114.9, 57.4, 52.1, 35.0, 32.9, 32.3, 25.5, 21.5, 21.3, two carbon atoms were not found probably due to overlapping.; IR (film): 3345, 2916, 2847, 1728, 1638, 1560, 1456, 1272, 1236, 1193, 1170, 839 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{30}O_3N_2Na^+$ ([M+Na]$^+$) 381.2149. Found 381.2142.

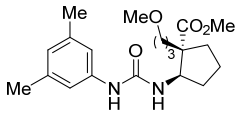


4h: HPLC IC3, H/^{i}PrOH = 10:1, flow rate = 1.0 mL/min, 30 °C, λ = 254 nm, 18.5 min (minor diastereomer), 22.2 min (minor diastereomer), 30.4 min (minor enantiomer of major diastereomer), 33.8 min (major enantiomer of major diastereomer); ^{1}H NMR (500 MHz, $(CD_3)_2CO$) major diastereomer δ 7.73 (1H, br), 7.07 (2H, s), 6.56 (1H, s), 5.88 (1H, brd, J = 8.8 Hz), 4.58 (1H, dt, J = 8.8, 6.7 Hz), 3.65 (3H, s), 3.58 (1H, dt, J = 10.7, 6.4 Hz), 3.53 (1H, dt, J = 10.7, 6.4 Hz), 2.26 (1H, ddd, J = 13.1,

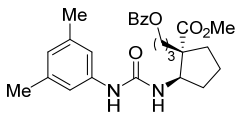
8.1, 5.1 Hz), 2.20 (6H, s), 2.00 (1H, ddt, *J* = 12.9, 8.5, 6.7 Hz), 1.92 (1H, td, *J* = 12.5, 4.3 Hz), 1.83-1.72 (1H, m), 1.72-1.49 (6H, m); ^{13}C NMR (126 MHz, $(CD_3)_2CO$) major diastereomer δ 176.7, 155.6, 141.2, 138.8, 124.0, 116.8, 57.5, 56.9, 52.2, 46.2, 33.0, 32.2, 21.5, 21.4, two carbon atoms were not found probably due to overlapping.; IR (film): 3317, 2952, 2868, 1724, 1641, 1561, 1428, 1276, 1235, 1162, 835 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{27}O_3N_2{}^{35}ClNa^+$ ([M+Na]$^+$) 389.1602. Found 389.1595.



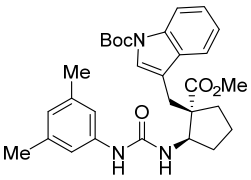
4i: HPLC IBN3, H/*i*PrOH = 10:1, flow rate = 1.0 mL/min, rt, λ = 254 nm, 6.9 min (minor diastereomer), 8.9 min (major enantiomer of major diastereomer), 23.3 min (minor diastereomer), 24.7 min (minor enantiomer of major diastereomer); ^{1}H NMR (500 MHz, $(CD_3)_2CO$) major diastereomer δ 7.71 (1H, br), 7.07 (2H, s), 6.55 (1H, s), 5.83 (1H, br), 4.56 (1H, dt, *J* = 9.3, 6.6 Hz), 3.64 (3H, s), 3.63-3.52 (2H, m), 2.27 (1H, ddd, *J* = 13.1, 8.1, 5.4 Hz), 2.20 (6H, s), 1.98 (1H, ddt, *J* = 13.1, 8.3, 6.6 Hz), 1.84 (1H, td, *J* = 10.4, 2.7 Hz), 1.73-1.60 (2H, m), 1.60-1.35 (5H, m), 0.86 (9H, s), 0.02_2 (3H, s), 0.01_5 (3H, s); ^{13}C NMR (126 MHz, $(CD_3)_2CO$) major diastereomer δ 176.9, 155.5, 141.3, 138.7, 123.9, 116.8, 64.0, 57.4_0, 57.3_5, 52.1, 32.8, 32.3, 29.7, 29.1, 26.3, 21.5, 21.3, 18.8, -5.1_0, -5.1_3; IR (film): 3314, 2952, 2857, 1730, 1654, 1560, 1460, 1243, 1194, 1097, 832 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{43}O_4N_2Si^+$ ([M+H]$^+$) 463.2987. Found 463.3006.



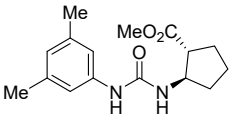
4j: The title compound was purified by column chromatography on silica gel topped with 4 cm of CHROMATOREX NH-DM-2035 (H/EA = 6:1 to 2:1 as eluent). HPLC IC3, H/*i*PrOH = 85:15, flow rate = 1.0 mL/min, 30 °C, λ = 254 nm, 18.1 min (minor diastereomer), 21.1 min (minor diastereomer), 37.3 min (minor enantiomer of major diastereomer), 42.1 min (major enantiomer of major diastereomer); ^{1}H NMR (500 MHz, $(CD_3)_2CO$) major diastereomer δ 7.75 (1H, br), 7.07 (2H, s), 6.56 (1H, s), 5.84 (1H, brd, *J* = 9.0 Hz), 4.55 (1H, dt, *J* = 9.0, 6.6 Hz), 3.64 (3H, s), 3.30 (1H, dt, *J* = 9.4, 6.3 Hz), 3.27 (1H, dt, *J* = 9.4, 6.3 Hz), 3.21 (3H, s), 2.26 (1H, ddd, *J* = 12.9, 7.9, 5.4 Hz), 2.20 (6H, s), 1.98 (1H, ddt, *J* = 13.0, 8.3, 6.6 Hz), 1.88-1.80 (1H, m), 1.72-1.60 (2H, m), 1.60-1.40 (5H, m); ^{13}C NMR (126 MHz, $(CD_3)_2CO$) major diastereomer δ 176.9, 155.6, 141.3, 138.7, 124.0, 116.8, 73.4, 58.3, 57.5, 57.0, 52.1, 32.9, 32.3, 26.3, 21.5, 21.3, one carbon atom was not found probably due to overlapping.; IR (film): 3327, 2944, 2869, 1724, 1641, 1569, 1450, 1278, 1237, 1209, 1117, 839 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{30}O_4N_2Na^+$ ([M+Na]$^+$) 385.2098. Found 385.2094.



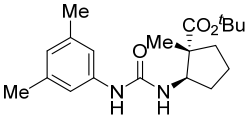
4k: HPLC IBN3, H/EtOH = 94:6, flow rate = 1.0 mL/min, rt, λ = 254 nm, 15.4 min (minor diastereomer), 21.6 min (major enantiomer of major diastereomer), 30.6 min (minor enantiomer of major diastereomer), 33.5 min (minor diastereomer); ^{1}H NMR (500 MHz, $(CD_3)_2CO$) major diastereomer δ 7.99 (2H, d, *J* = 7.5 Hz), 7.71 (1H, br), 7.59 (1H, t, *J* = 7.5 Hz), 7.44 (2H, t, *J* = 7.5 Hz), 7.07 (2H, s), 6.55 (1H, s), 5.88 (1H, br), 4.61 (1H, q, *J* = 7.5 Hz), 4.26 (2H, t, *J* = 6.3 Hz), 3.65 (3H, s), 2.32-2.25 (1H, m), 2.19 (6H, s), 2.04-1.97 (2H, m), 1.83-1.73 (1H, m), 1.73-1.50 (6H, m); ^{13}C NMR (126 MHz, $(CD_3)_2CO$) major diastereomer δ 176.8, 166.7, 155.6, 141.2, 138.7, 133.7, 131.4, 130.1, 129.3, 124.0, 116.8, 65.8, 57.4, 57.1, 52.2, 33.0, 32.3, 29.1, 25.6, 21.5, 21.4; IR (film): 3292, 2937, 1719, 1653, 1555, 1452, 1264, 1119, 1070, 1026, 835 cm^{-1}; HRMS (ESI) Calcd for $C_{26}H_{31}O_5N_2^-$ ([M−H]$^-$) 451.2227. Found 451.2235.



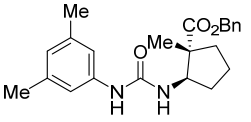
4l: HPLC IC3, H/^{i}PrOH = 10:1, flow rate = 1.0 mL/min, 30 °C, λ = 254 nm, 23.0 min (minor diastereomer), 48.1 min (minor enantiomer of major diastereomer), 52.5 min (major enantiomer of major diastereomer), 63.8 min (minor diastereomer); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) major diastereomer δ 8.11 (1H, brd, J = 7.6 Hz), 7.72 (1H, br), 7.57 (1H, d, J = 7.6 Hz), 7.42 (1H, s), 7.29 (1H, t, J = 7.6 Hz), 7.22 (1H, t, J = 7.6 Hz), 7.13 (2H, s), 6.58 (1H, s), 6.00 (1H, brd, J = 9.1 Hz), 4.66 (1H, dt, J = 9.1, 6.8 Hz), 3.60 (3H, s), 3.36 (1H, d, J = 14.6 Hz), 2.87 (1H, d, J = 14.6 Hz), 2.30-2.20 (1H, m), 2.22 (6H, s), 2.10-2.02 (1H, m), 1.88-1.67 (4H, m), 1.66 (9H, s); ^{13}C NMR (126 MHz, $(CD_3)_2CO$) major diastereomer δ 176.5, 155.6, 150.2, 141.3, 138.8, 135.9, 132.3, 125.0, 124.9, 124.1, 123.1, 119.8, 118.0, 116.9, 115.8, 84.1, 58.5, 58.3, 52.1, 32.4, 31.8, 28.2, 26.9, 21.5, 21.1; IR (film): 3320, 2982, 1724, 1642, 1614, 1555, 1452, 1364, 1244, 1223, 1150, 1073, 1017, 837 cm^{-1}; HRMS (ESI) Calcd for $C_{30}H_{37}O_5N_3Na^+$ ([M+Na]$^+$) 542.2625. Found 542.2620.



4m: HPLC OZ3, H/^{i}PrOH = 10:1, flow rate = 1.0 mL/min, 30 °C, λ = 254 nm, 11.1 min (minor diastereomer), 12.4 min (minor diastereomer), 19.0 min (minor enantiomer of major diastereomer), 25.7 min (major enantiomer of major diastereomer); ^{1}H NMR (500 MHz, $(CD_3)_2CO$) *major diastereomer* δ 7.68 (1H, br), 7.07 (2H, s), 6.56 (1H, s), 5.88 (1H, brd, J = 7.6 Hz), 4.29 (1H, quin, J = 7.6 Hz), 3.62 (3H, s), 2.66 (1H, q, J = 7.6 Hz), 2.20 (6H, s), 2.06 (1H, dq, J = 12.8, 7.6 Hz), 1.98 (1H, dq, J = 13.7, 7.6 Hz), 1.82 (1H, dtd, J = 13.7, 7.6, 6.7 Hz), 1.76-1.65 (2H, m), 1.54 (1H, dq, J = 12.8, 7.6 Hz); ^{13}C NMR (126 MHz, $(CD_3)_2CO$) *major diastereomer* δ 175.8, 155.7, 141.3, 138.7, 124.0, 116.8, 56.2, 51.9, 51.3, 33.8, 29.2, 23.7, 21.5; IR (film): 3333, 2943, 2866, 1734, 1647, 1612, 1558, 1423, 1284, 1156, 1035, 835 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{22}O_3N_2Na^+$ ([M+Na]$^+$) 313.1523. Found 313.1519.



4n: HPLC IB3, H/EtOH = 97:3, flow rate = 1.0 mL/min, 30 °C, λ = 254 nm, 10.3 min (minor diastereomer), 11.1 min (major enantiomer of major diastereomer), 16.7 min (minor enantiomer of major diastereomer), 22.2 min (minor diastereomer); ^{1}H NMR (500 MHz, $(CD_3)_2CO$) *major diastereomer* δ 7.74 (1H, br), 7.08 (2H, s), 6.55 (1H, s), 5.69 (1H, brd, J = 8.3 Hz), 4.56 (1H, q, J = 8.3 Hz), 2.19 (6H, s), 2.18 (1H, ddd, J = 13.0, 9.0, 6.0 Hz), 2.04 (1H, ddt, J = 16.0, 8.3, 4.3 Hz), 1.72-1.58 (2H, m), 1.54-1.45 (2H, m), 1.44 (9H, s), 1.11 (3H, s); ^{13}C NMR (126 MHz, $(CD_3)_2CO$) *major diastereomer* δ 176.6, 155.5, 141.4, 138.7, 123.9, 116.8, 80.2, 57.4, 52.6, 37.1, 32.2, 28.1, 21.4$_9$, 21.4$_5$, 18.6; IR (film): 3288, 2969, 2859, 1718, 1696, 1654, 1613, 1539, 1456, 1367, 1247, 1153, 834 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{30}O_3N_2Na^+$ ([M+Na]$^+$) 369.2149. Found 369.2151.

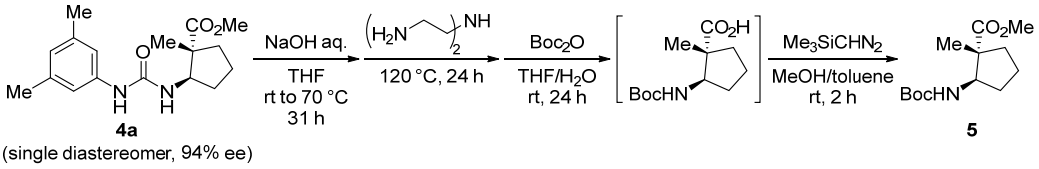


4o: HPLC IC3, H/^{i}PrOH = 10:1, flow rate = 1.0 mL/min, 30 °C, λ = 254 nm, 20.6 min (minor diastereomer), 24.7 min (minor diastereomer), 32.1 min (minor enantiomer of major diastereomer), 40.7 min (major enantiomer of major diastereomer); ^{1}H NMR (500 MHz, $(CD_3)_2CO$) *major diastereomer* δ 7.74 (1H, br), 7.41 (2H, d, J = 7.8 Hz), 7.35 (1H, t, J = 7.8 Hz), 7.28 (2H, t, J = 7.8 Hz), 7.08 (2H, s), 6.56 (1H, s), 5.81 (1H, brd, J = 8.5 Hz), 5.11 (1H, d, J = 12.5 Hz), 5.09 (1H, d, J = 12.5 Hz), 4.62 (1H, q, J = 8.5 Hz), 2.25 (1H, ddd, J = 12.8, 8.8, 6.5 Hz), 2.20 (6H, s), 2.07 (1H, ddt, J = 15.5, 8.5, 4.3 Hz), 1.75-

1.62 (2H, m), 1.61-1.48 (2H, m), 1.16 (3H, s); ^{13}C NMR (126 MHz, $(CD_3)_2CO$) *major diastereomer* δ 177.2, 155.7, 141.3, 138.7, 137.8, 129.2, 128.7, 128.6, 124.0, 116.9, 66.9, 58.1, 51.8, 37.3, 31.8, 21.5, 21.4, 18.0; IR (film): 3336, 2952, 2858, 1719, 1638, 1616, 1558, 1454, 1231, 1149, 857 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{28}O_3N_2Na^+$ ($[M+Na]^+$) 403.1992. Found 403.1989.

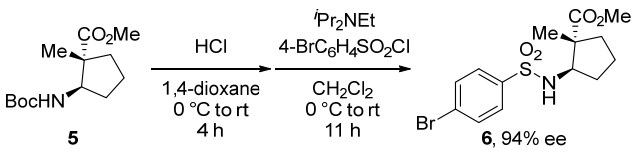
2.4 Deprotection and Sulfonylation of 4a

Removal of Urea to Give *N*- Boc-protected β-amino ester 5



To a solution of diastereomerically-pure cycloadduct **4a** (22.8 mg, 0.075 mmol) in THF (0.70 mL) was added a 2 N aqueous solution of NaOH (0.38 mL, 0.75 mmol) at ambient temperature. After being stirred for 12 h in a test tube sealed with a screw cap, the mixture was heated at 70 °C and stirred for another 19 h. The resulting mixture was concentrated in vacuo at 20 °C and then treated with diethylenetriamine (49.0 μL, 0.45 mmol)[4] at 120 °C for 24 h in a test tube sealed with a screw cap. The reaction mixture was cooled to ambient temperature and diluted with THF (0.55 mL) and H_2O (0.35 mL). Boc_2O (0.37 mL, 1.58 mmol) was added to the solution and the resulting mixture was stirred there for 24 h. The reaction was quenched by addition of a 2 N aqueous solution of NaOH (0.75 mL). The aqueous phase was washed with Et_2O (one time) and then acidified to pH = 1 with a 2 N aqueous solution of $KHSO_4$. The resulting aqueous phase was extracted with EA (three times). The combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure after filtration. The crude mixture was passed through a silica gel column (CH_2Cl_2/MeOH = 100:1 to 20:1 as eluent) and fractions containing the *N*-Boc-protected amino acid were concentrated. The obtained material was dissolved in toluene (0.38 mL) and MeOH (0.18 mL). After adding trimethylsilyldiazomethane (*ca*. 0.6 M in hexane, 0.82 mL, 0.49 mmol), the mixture was stirred for 2 h at ambient temperature and concentrated in vacuo. The crude residue was purified by column chromatography on silica gel (H/EA = 10:1 to 3:1 as eluent) to furnish **5** (10.9 mg, 0.042 mmol, 56% from **4a**). Preservation of the enantiomeric excess was confirmed after exchanging the *N*-protecting group from Boc to 4-bromophenylsulfonyl (see below). **5:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.46 (1H, br), 4.32 (1H, q, J = 7.8 Hz), 3.69 (3H, s), 2.31-2.18 (1H, m), 2.12 (1H, dtd, J = 12.9, 7.8, 5.4 Hz), 1.75-1.64 (2H, m), 1.55 (1H, dt, J = 12.8, 7.4 Hz), 1.47-1.38 (1H, m), 1.43 (9H, s), 1.12 (3H, s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.5, 155.4, 79.4, 58.1, 52.2, 51.0, 36.3, 31.0, 28.5, 20.6, 17.5; IR (film): 2983, 1723, 1698, 1517, 1458, 1364, 1243, 1164, 1055 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{23}O_4NNa^+$ ($[M+Na]^+$) 280.1519. Found 280.1517; $[\alpha]_D^{24}$ +14.9 (c = 10.9, acetone).

Removal of the *N*-protecting group of 5 and Subsequent Sulfonylation to Give Sulfonamide 6



N-Boc β-amino ester **5** (9.9 mg, 0.038 mmol) was dissolved into a solution of hydrochloric acid in 1,4-dioxane (4 M, 0.39 mL) at 0 °C. The solution was allowed to warm to ambient temperature and stirred there for 4 h. After concentration of the reaction mixture, anhydrous CH_2Cl_2 (0.40 mL), 4-$BrC_6H_4SO_2Cl$ (15.6 mg, 0.061 mmol), and diisopropylethylamine (0.13 mL, 0.77 mmol) were added to the residue at 0 °C. The reaction mixture was allowed to warm to ambient temperature and stirred there for 11 h. The reaction was quenched by adding 1 N hydrochloric acid at 0 °C and the aqueous phase was extracted with CH_2Cl_2 three times. The combined organic phases were dried over Na_2SO_4 and filtered. All volatiles were removed under reduced pressure to give the crude residue. Purification of the residue was performed by column chromatography on silica gel (H/EA = 10:1 to 1.5:1 as eluent) to afford **6** (13.2 mg, 0.035 mmol, 91%). Enantiomeric excess of **6** was determined by HPLC analysis on chiral stationary phase. Absolute stereochemistry of **6** was unambiguously determined by X-ray diffraction analysis of its single crystal (see below). **6**: HPLC IBN3, H/^{i}PrOH = 10:1, flow rate = 1.0 mL/min, rt, λ = 254 nm, 15.0 min (major enantiomer), 17.2 min (minor enantiomer); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (2H, d, J = 8.5 Hz), 7.65 (2H, d, J = 8.5 Hz), 4.90 (1H, brd, J = 8.1 Hz), 3.86 (1H, dt, J = 9.9, 8.1 Hz), 3.57 (3H, s), 2.03 (1H, ddd, J = 13.8, 10.2, 6.7 Hz), 1.98 (1H, dtd, J = 13.0, 8.1, 4.2 Hz), 1.73-1.63 (1H, m), 1.63-1.54 (2H, m), 1.47 (1H, dtd, J = 13.0, 9.9, 7.9 Hz), 1.16 (3H, s); ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.9, 139.5, 132.4, 129.0, 127.7, 60.1, 52.3, 51.2, 36.2, 31.1, 20.2, 17.7; IR (film): 3244, 2951, 1734, 1576, 1436, 1332, 1263, 1158, 1068, 1009, 825 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{18}O_4N^{79}BrSNa^+$ ([M+Na]$^+$) 398.0032. Found 398.0051; $[\alpha]_D^{23}$ +25.3 (c = 13.0, acetone).

2.5 Crystallographic Analysis

Recrystallization of 4e: Recrystallization was performed by using a H_2O/DMF solvent system at ambient temperature to afford single crystals of **4e**. The crystallographic data are summarized in Table S1 and the ORTEP diagram is shown in Figure S1.

Crystallographic Structure Determination of 4e: The single crystal, which was obtained by the above procedure, was mounted on MicroMesh. Data of X-ray diffraction were collected at 123 K on a RAPID 100x100 IP-Cu diffractometer with fine-focus sealed tube Cu/Kα radiation (λ = 1.54187 Å). An absorption correction was made using Primary Mu Option. The structure was solved by direct methods and Fourier syntheses, and refined by full-matrix least squares on F^2 by using SHELXL-2014.[5] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom bonded to the nitrogen atom was located from a difference synthesis, and its coordinates and isotropic thermal parameters were refined. The other hydrogen atoms were placed in calculated positions and their isotropic thermal parameters were refined.

Table S1. Crystal data and structure refinement for **4e** (CCDC 2051437).

Empirical formula	$C_{27}H_{36}N_2O_3$	
Formula weight	436.58	
Temperature	123(2) K	
Wavelength	1.54187 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 8.29650(10) Å	α = 90°.
	b = 8.9484(2) Å	β = 90°.
	c = 34.1519(6) Å	γ = 90°.
Volume	2535.45(8) $Å^3$	
Z	4	
Density (calculated)	1.144 Mg/m^3	
Absorption coefficient	0.585 mm^{-1}	
F(000)	944	
Crystal size	1.000000 x 0.300000 x 0.010000 mm^3	
Theta range for data collection	5.110 to 68.196°.	
Index ranges	−9<=h<=9, −10<=k<=10, −41<=l<=40	
Reflections collected	29661	
Independent reflections	4629 [R(int) = 0.0210]	
Completeness to theta = 67.687°	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	1.0000 and 0.8270	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4629 / 0 / 308	
Goodness-of-fit on F^2	1.058	
Final R indices [I>2sigma(I)]	R_1 = 0.0301, wR_2 = 0.0797	
R indices (all data)	R_1 = 0.0305, wR_2 = 0.0800	
Absolute structure parameter	0.04(3)	
Extinction coefficient	0	
Largest diff. peak and hole	0.162 and −0.178 $e.Å^{-3}$	

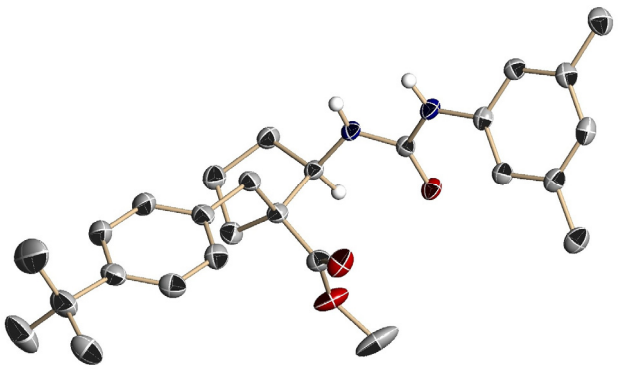


Figure S1. Molecular structure of **4e**. The thermal ellipsoids of non-hydrogen atoms are shown at the 50% probability level. Calculated hydrogen atoms except for those attached to the stereogenic carbon are omitted for clarity. Blue = nitrogen, red = oxygen, gray = carbon.

3. References

1) (a) A. J. M. Farley, C. Sandford, D. J. Dixon, *J. Am. Chem. Soc.*, 2015, **137**, 15992. (b) M.-C. Fu, R. Shang, W.-M. Cheng, Y. Fu, *ACS Catal.*, 2016, **6**, 2501. (c) C. Shu, R. S. Mega, B. J. Andreassen, A. Noble, V. K. Aggarwal, *Angew. Chem. Int. Ed.*, 2018, **57**, 15430. (d) C. Shu, A. Noble, V. K. Aggarwal, *Angew. Chem. Int. Ed.*, 2019, **58**, 3870. (e) X. Ji, Y. Li, L. Xie, H. Lu, W. Ding, Q. Zhang, *Angew. Chem. Int. Ed.*, 2016, **55**, 11845.

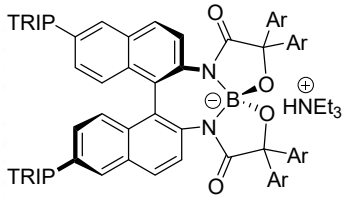
2) (a) D. Uraguchi, F. Ueoka, N. Tanaka, T. Kizu, W. Takahashi, T. Ooi, *Angew. Chem. Int. Ed.*, 2020, **59**, 11456. (b) D. Uraguchi, Y. Kimura, F. Ueoka, T. Ooi, *J. Am. Chem. Soc.*, 2020, **142**, 19462.

3) S. Rohe, A. O. Morris, T. McCallum, L. Barriault, *Angew. Chem. Int. Ed.*, 2018, **57**, 15664.

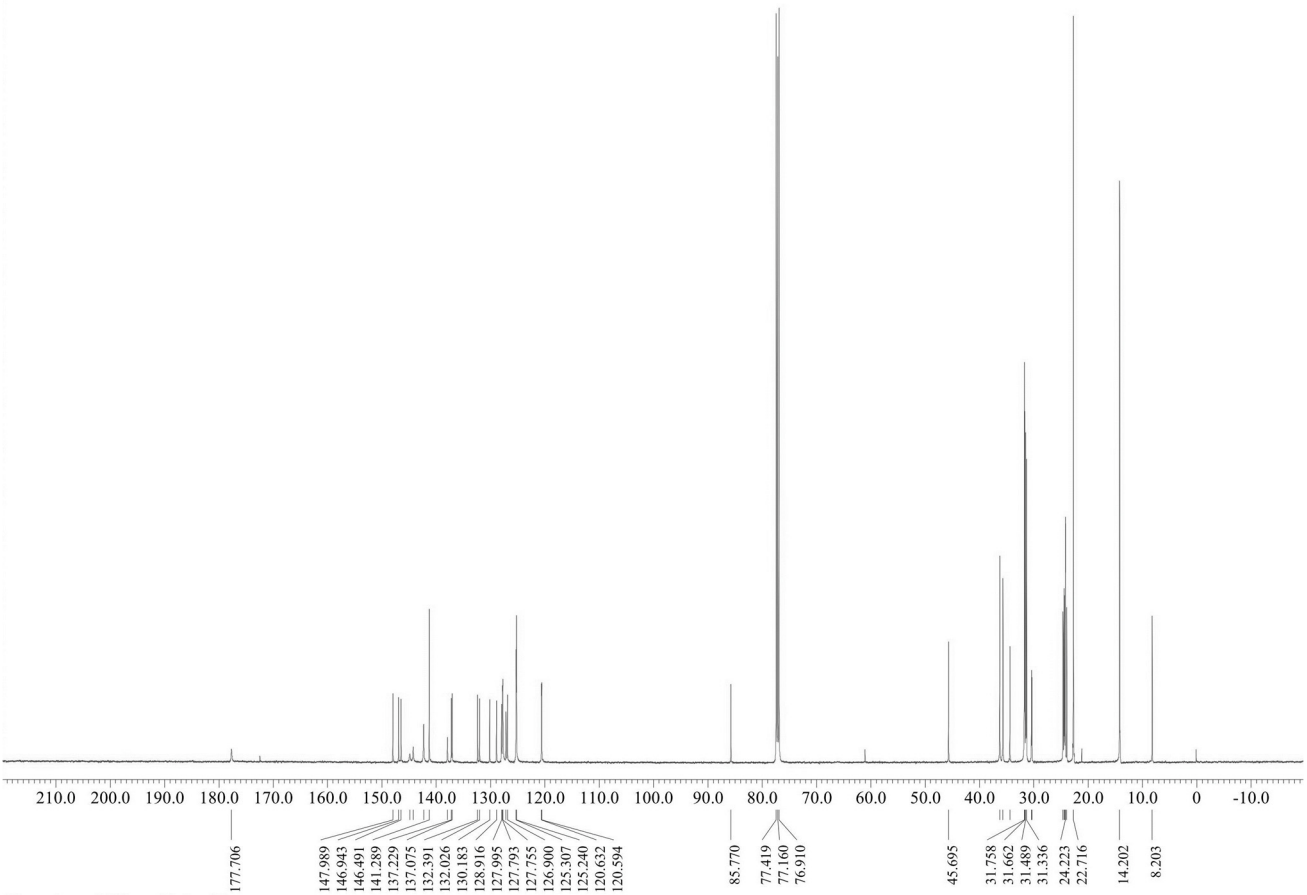
4) M. Noshita, Y. Shimizu, H. Morimoto, T. Ohshima, *Org. Lett.*, 2016, **18**, 6062.

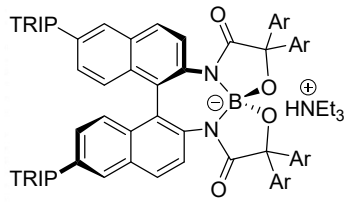
5) G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3.

4. Copies of ^{1}H, ^{13}C, and ^{19}F NMR

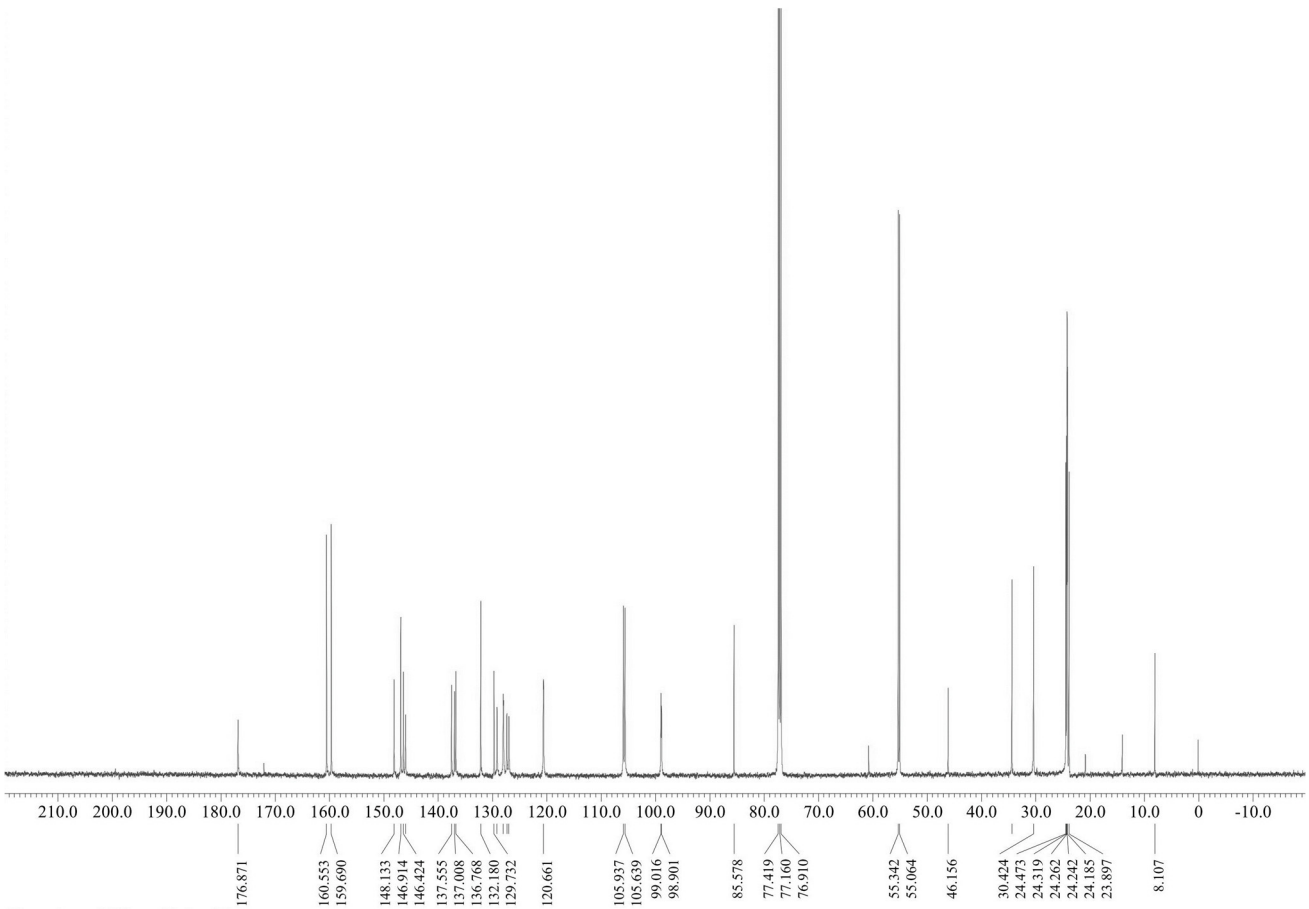


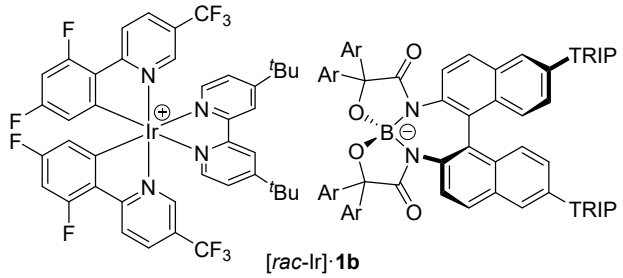
1b·$HNEt_3$
(Ar = 3,5-(^{n}Pent)$_2$C$_6$H$_3$)



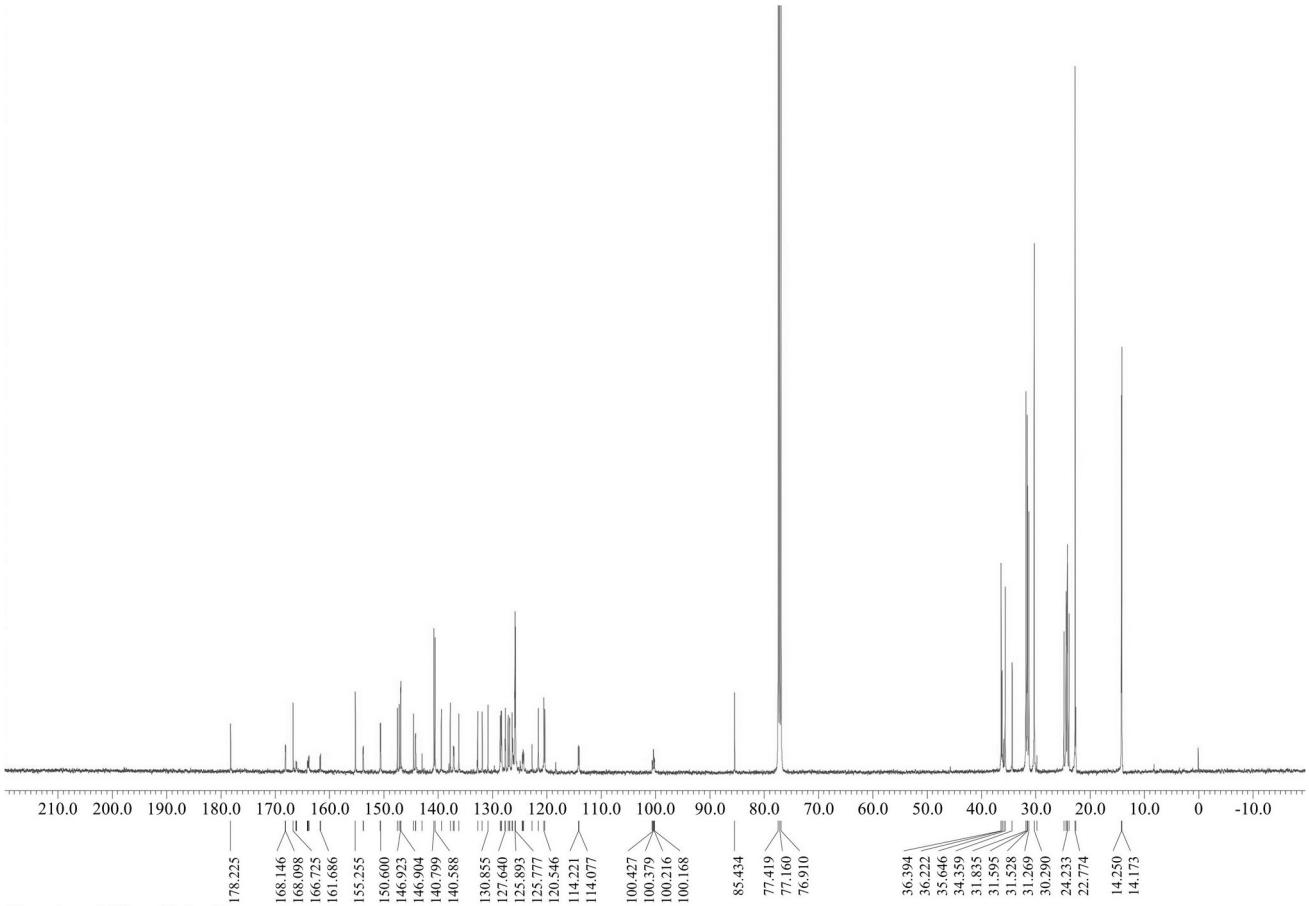


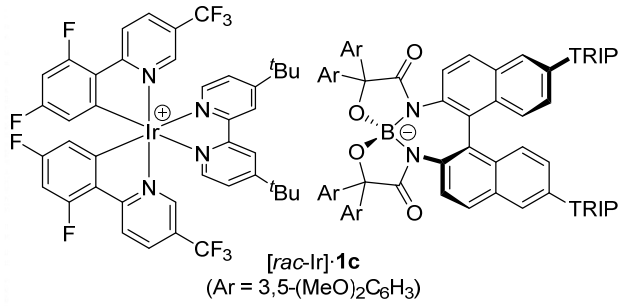
1c·$HNEt_3$
(Ar = 3,5-$(MeO)_2C_6H_3$)



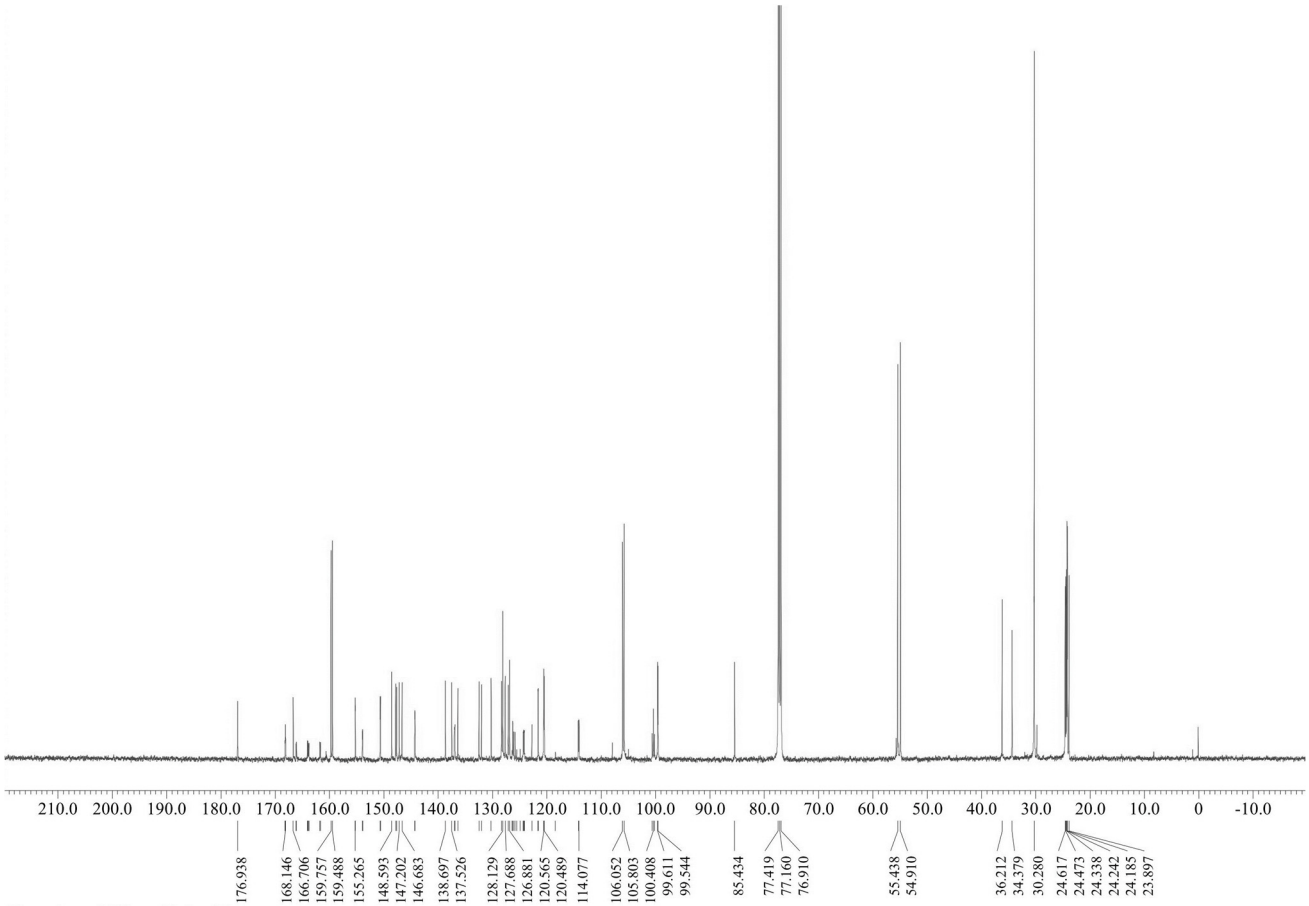


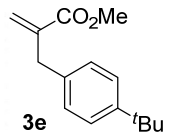
[*rac*-Ir]·**1b**
(Ar = 3,5-(^{n}Pent)$_2$C$_6$H$_3$)





[*rac*-Ir]·**1c**
(Ar = 3,5-$(MeO)_2C_6H_3$)

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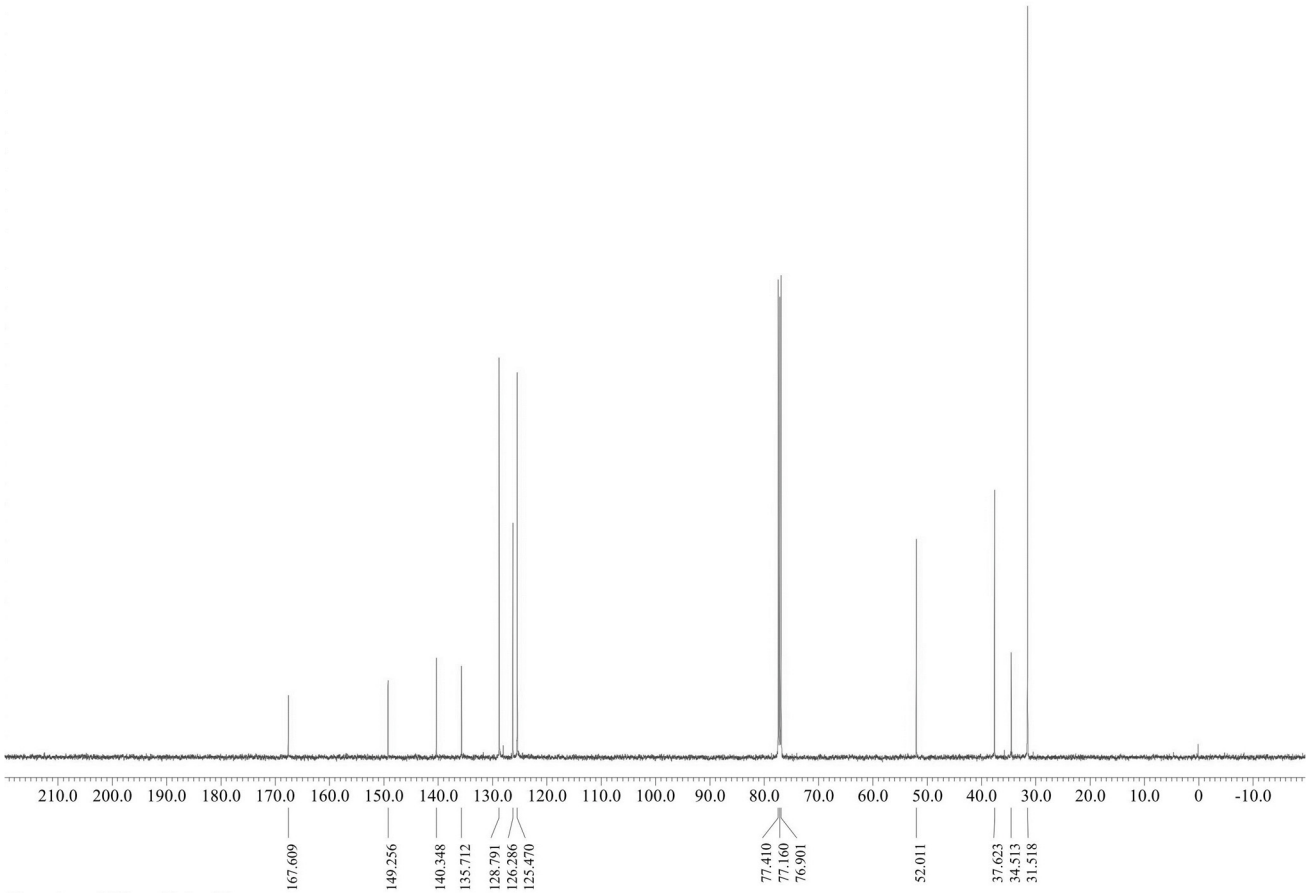
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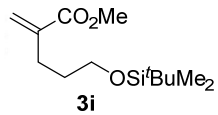
CO2Me
OSitBuMe2

3i

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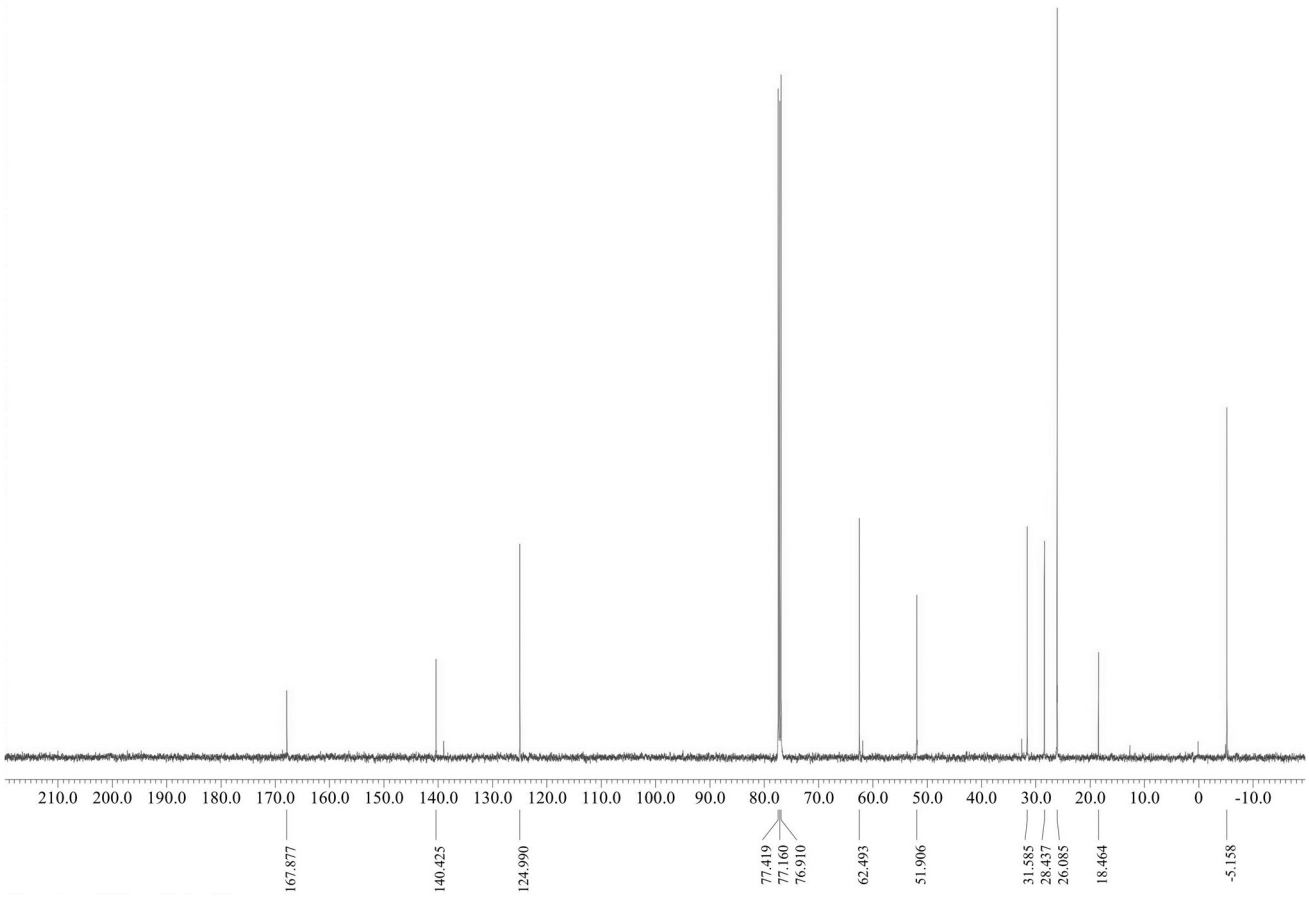
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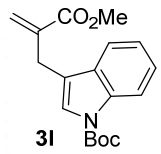
CO2Me
N
Boc

3l

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1.02
1.00
1.01
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7.0
6.0
5.0
4.0
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2.0
1.0
0
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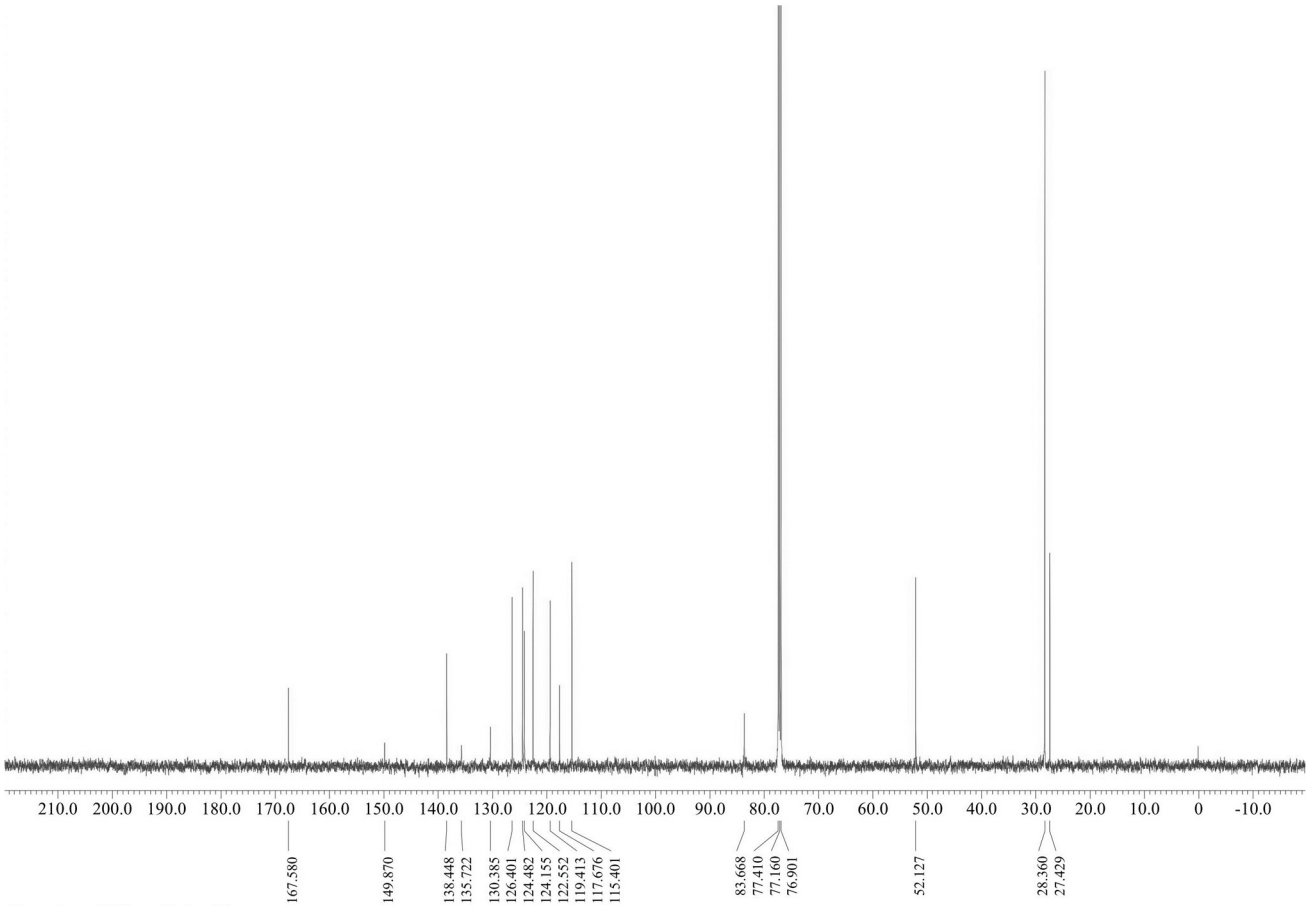
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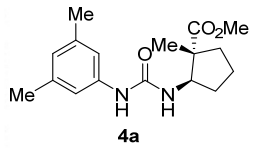
Me
CO2Me
O
Me
Me
N
H
N
H

4a

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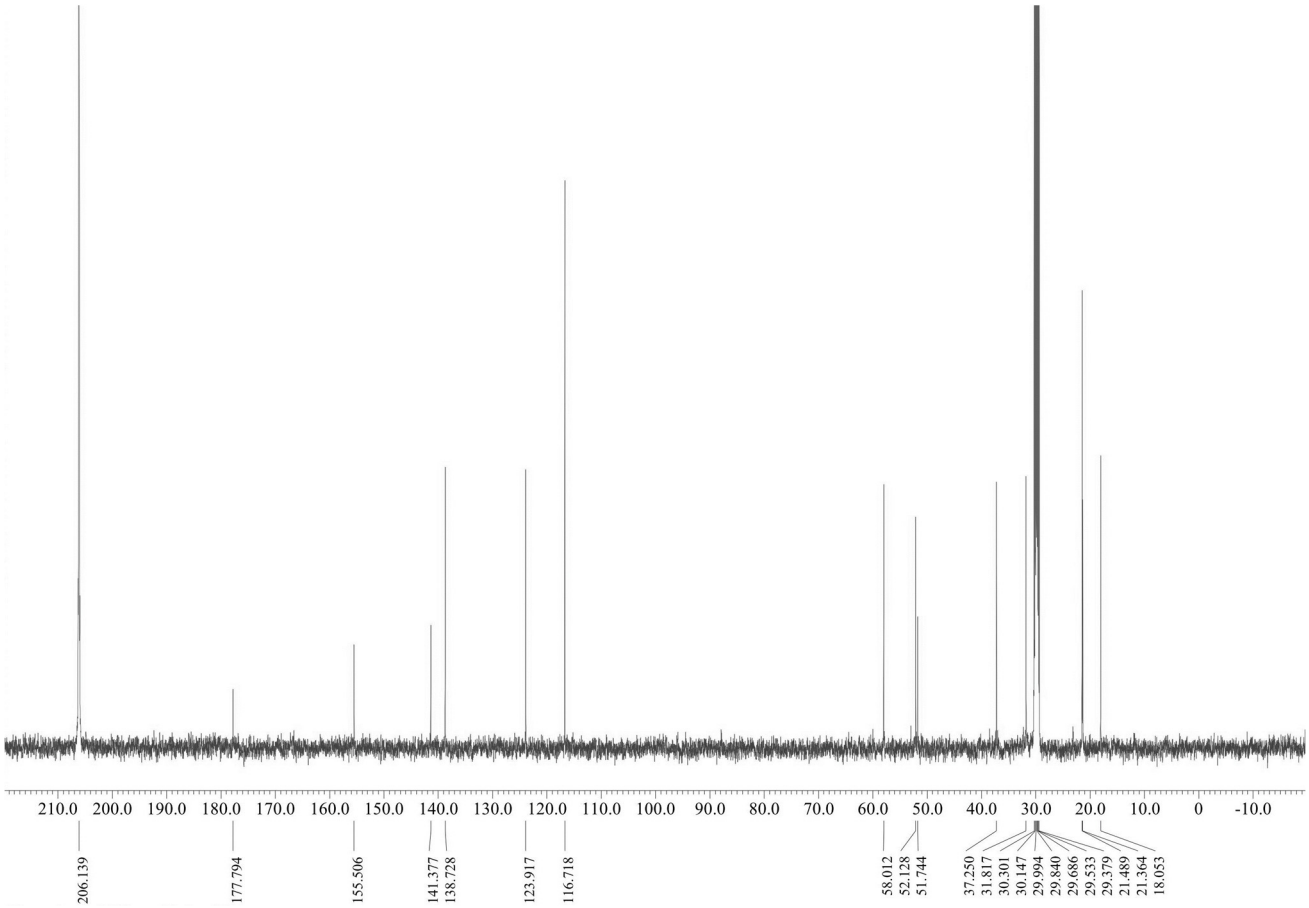
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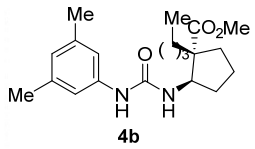
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Me
CO2Me
O
N
H
N
H
Me

4b

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2.18
2.07
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1.06
1.09
1.05
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0.90
1.00
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3.0
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1.0
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7.070
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5.834
5.814
4.569
4.556
4.550
4.542
4.537
4.523
3.633
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2.255
2.238
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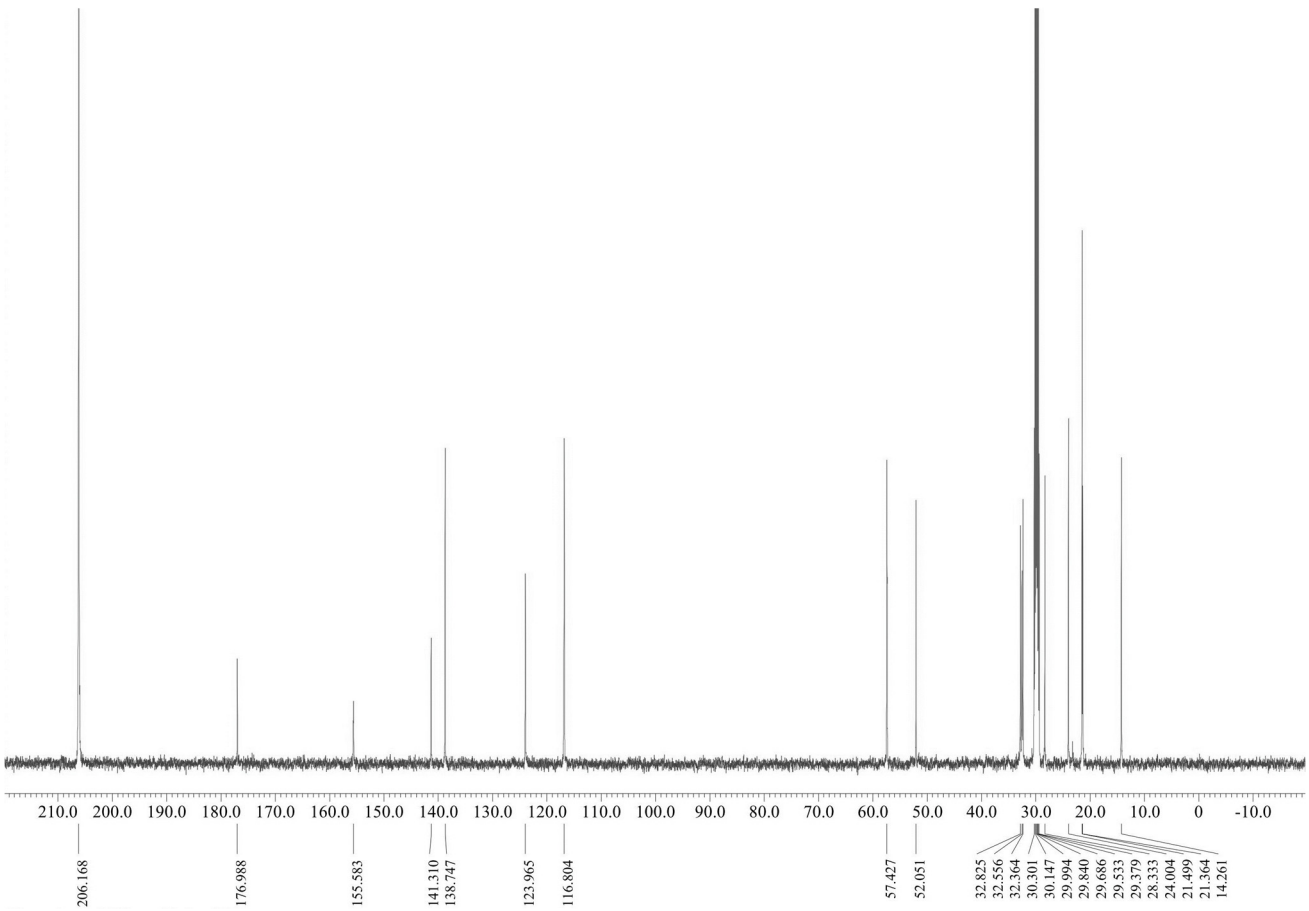
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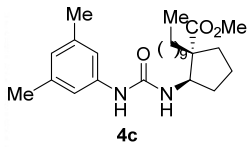
Me
Me
CO2Me
O
N
H
N
H
Me

4c

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2.57
2.16
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0.91
1.00
1.20
1.10
1.06
1.49
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9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
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4.562
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4.548
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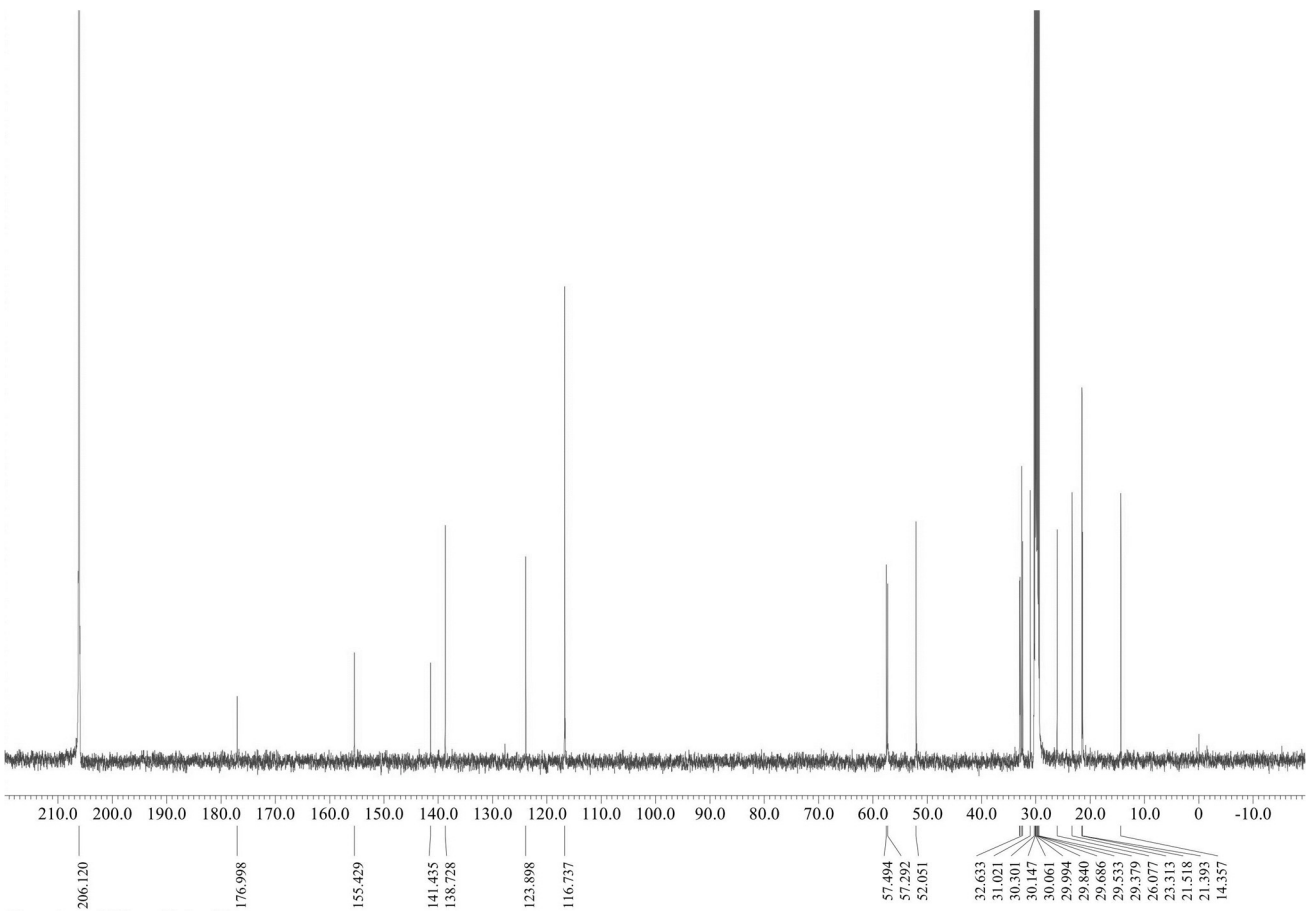
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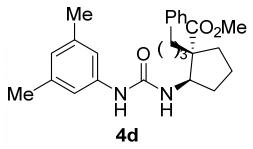
Me
Ph
CO2Me
O
3
Me
N
H
N
H

4d

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2.29
2.12
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1.16
1.05
1.04
1.04
0.98
0.91
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.727
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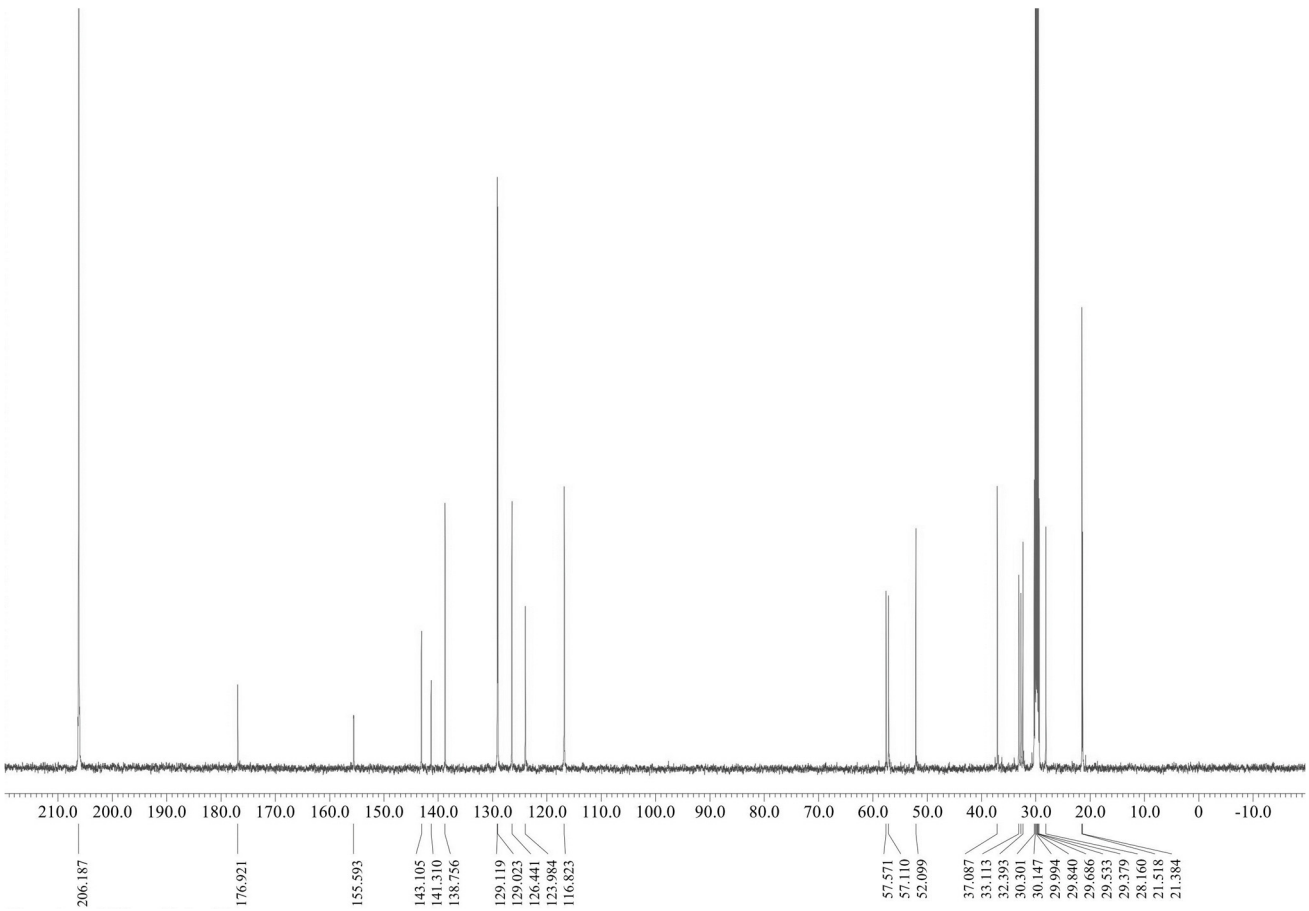
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-10.0
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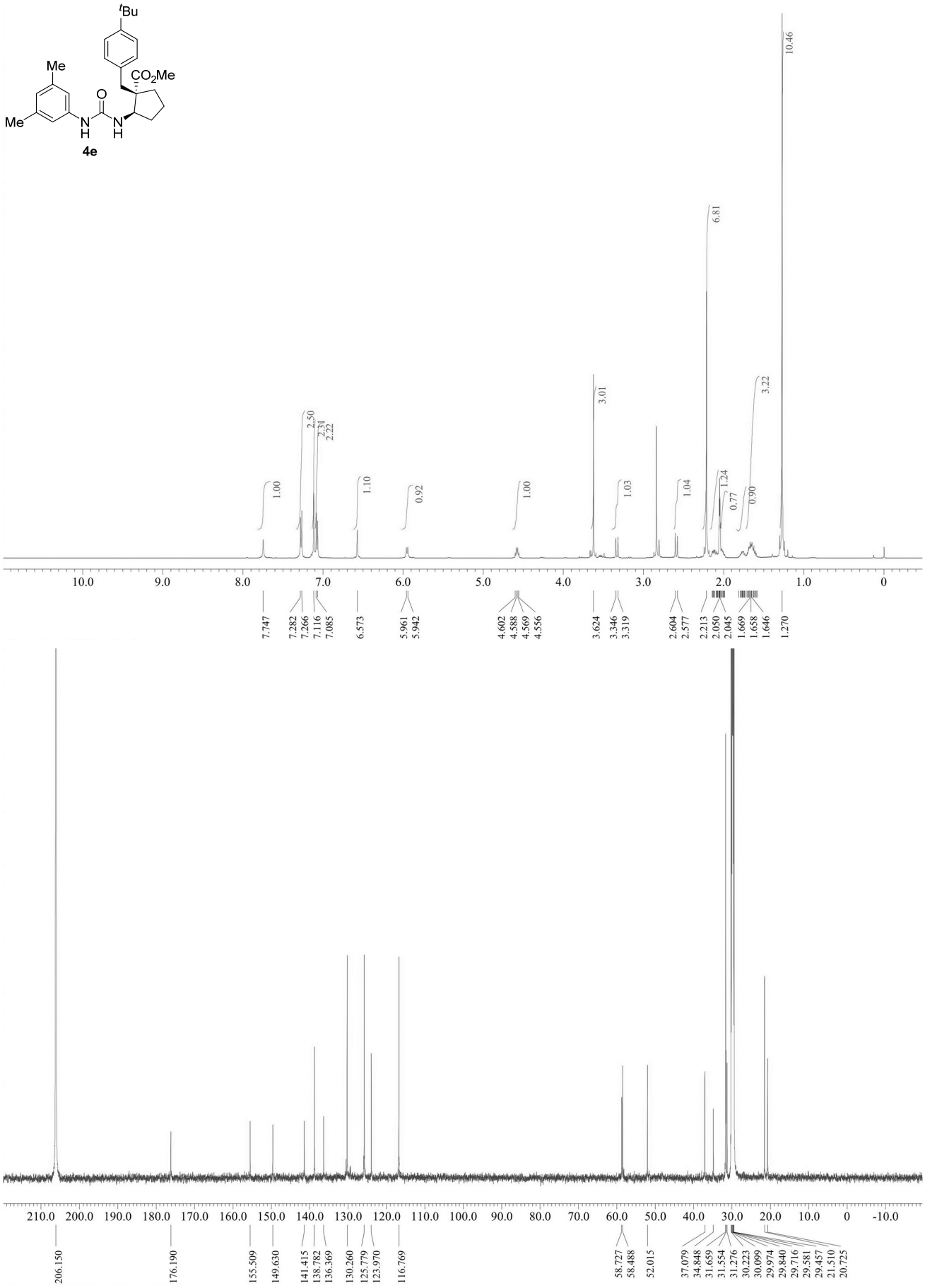
tBu
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CO2Me
O
N
H
N
H
Me
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2.31
2.22
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1.10
1.00
0.92
1.00
1.03
1.04
0.77
0.90
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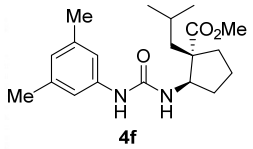
Me
CO2Me
O
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N
H
N
H

4f

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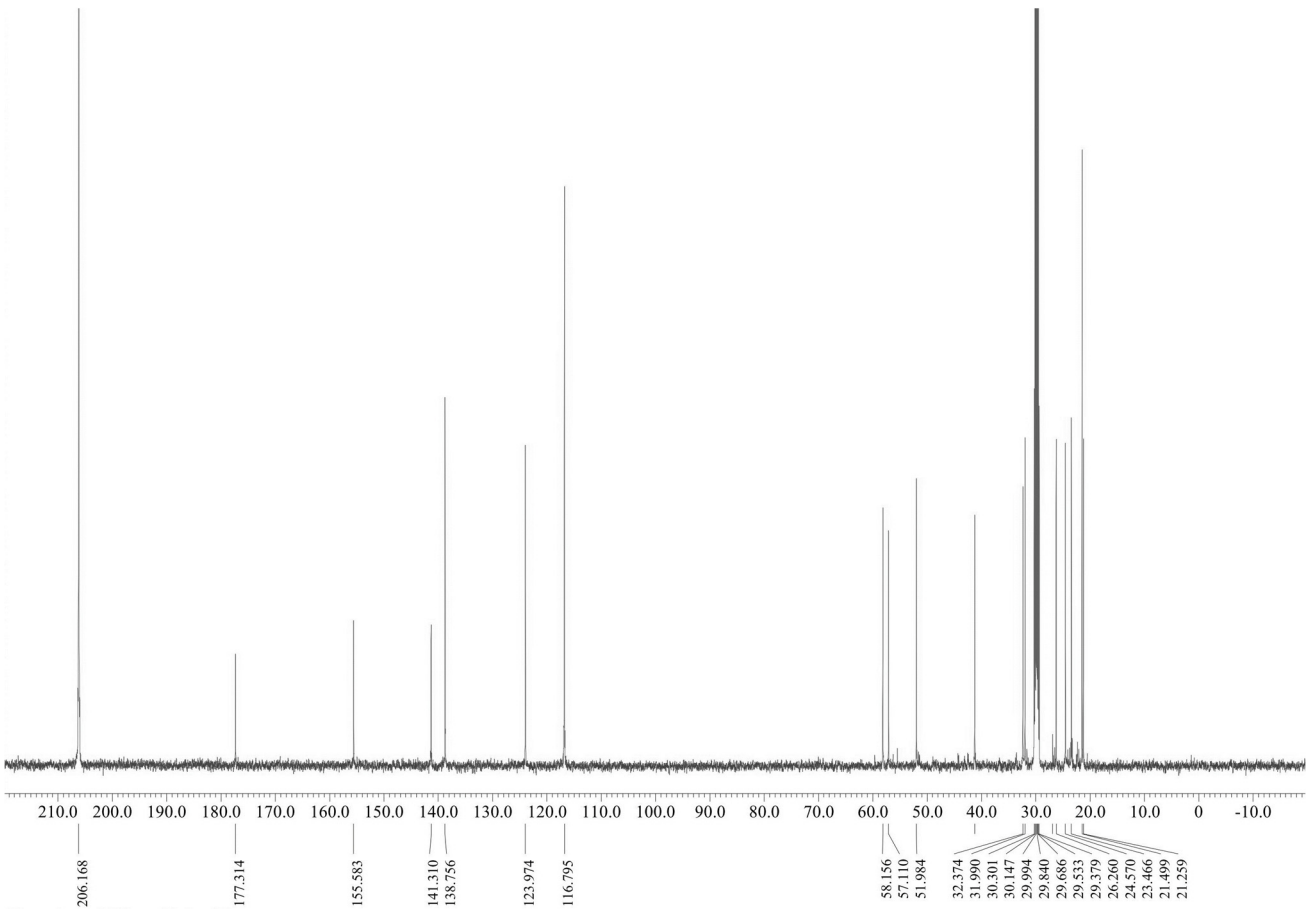
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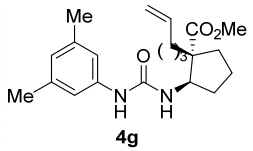
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N
H
N
H

4g

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1.0
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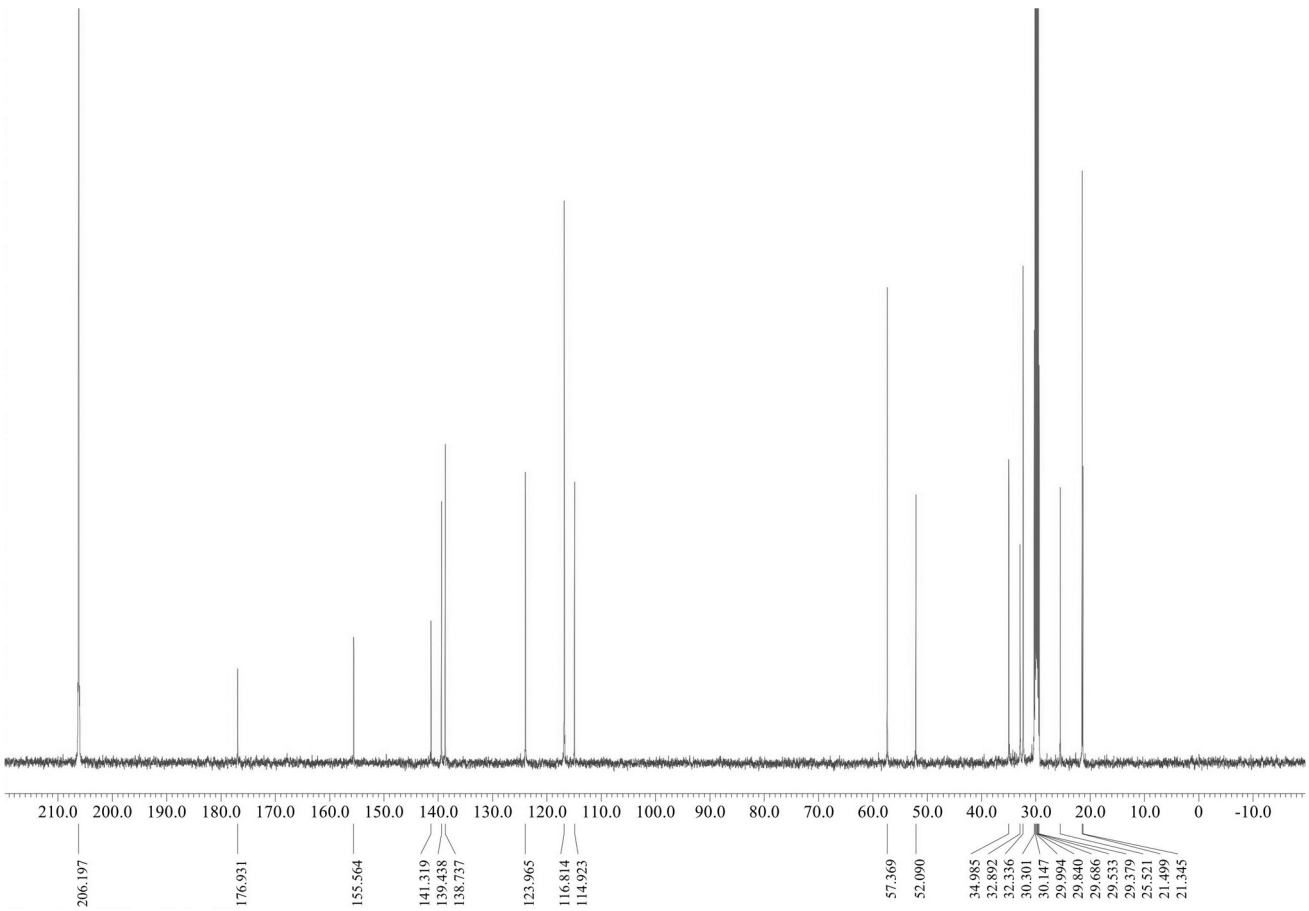
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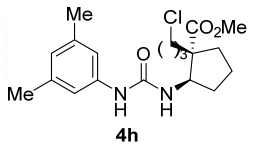
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H
N
H

4h

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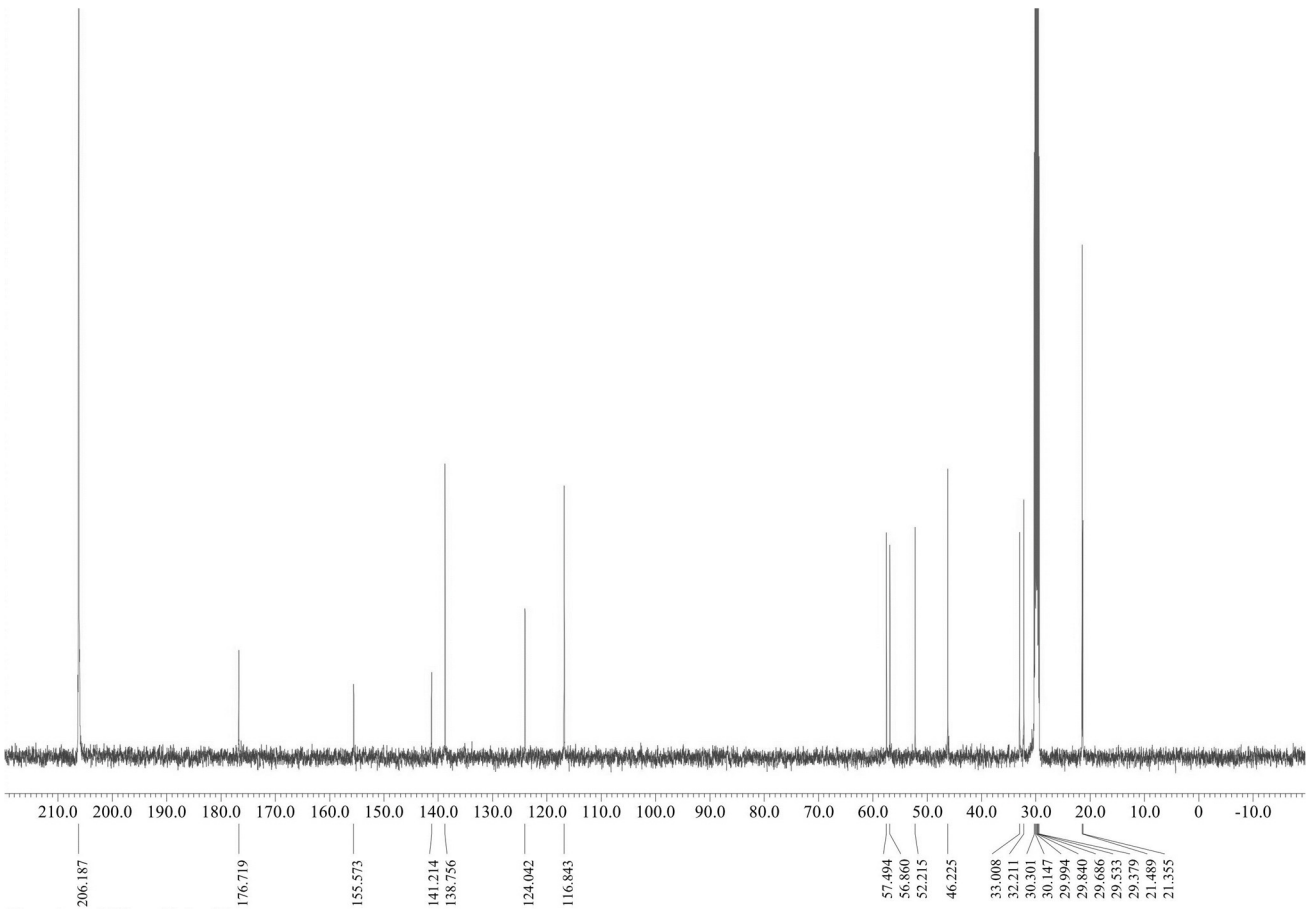
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176.719
155.573
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56.860
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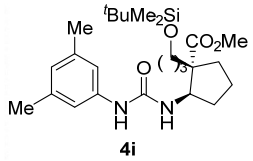
21.355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tBuMe2Si
O
CO2Me
O
Me
N
H
N
H

4i

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3.41
2.91
2.82
2.99
1.99
1.72
1.18
1.06
1.06
1.00
1.15
1.11
1.02
0.25
0.11
10.0
9.0
8.0
7.0
6.0
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4.0
3.0
2.0
1.0
0
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7.070
6.553
5.827
4.585
4.571
4.566
4.558
4.553
4.189
4.172
4.154
3.641
3.624
3.611
3.602
3.591
3.559
2.273
2.198
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1.499
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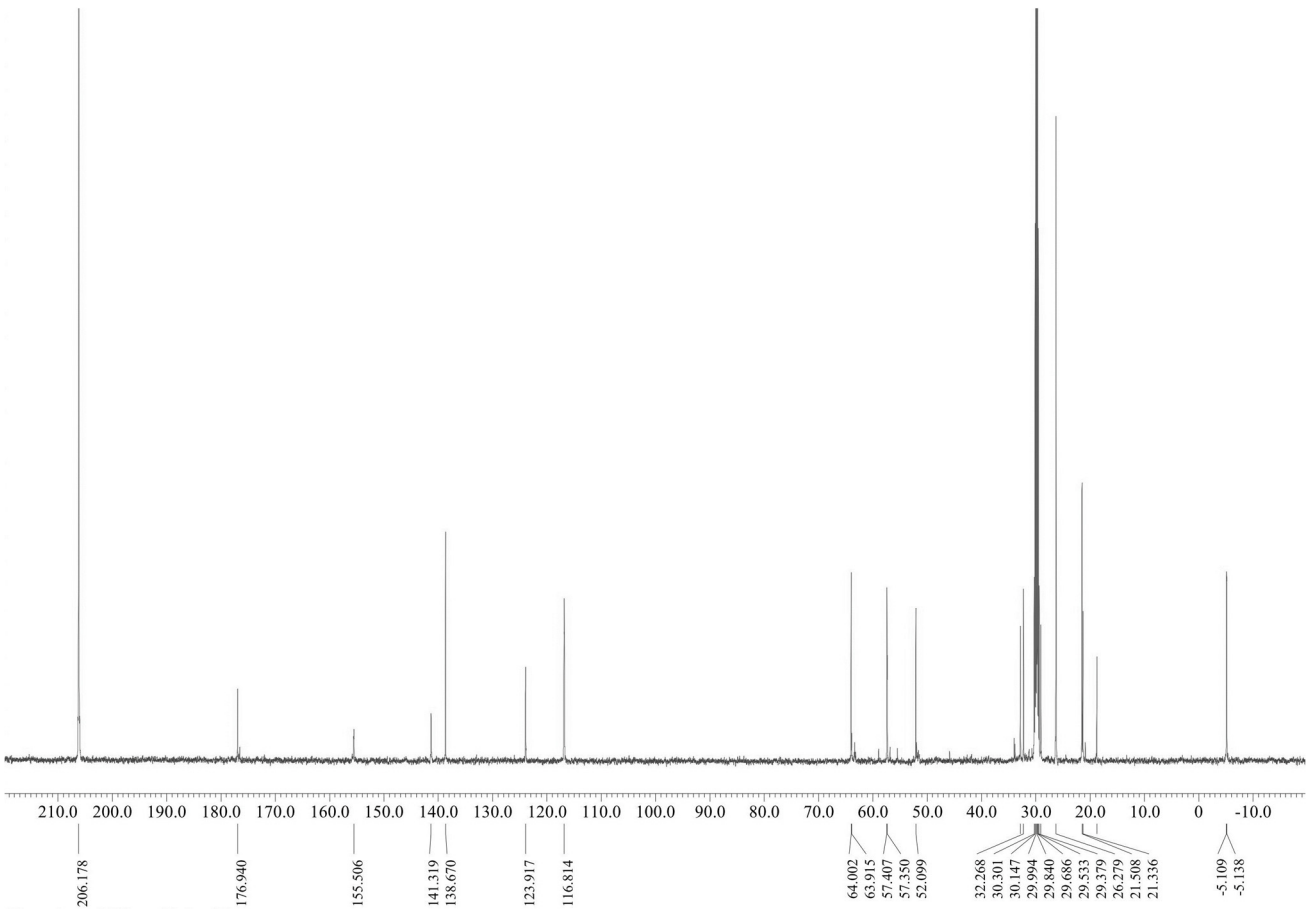
0.015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40.0
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20.0
10.0
0
-10.0
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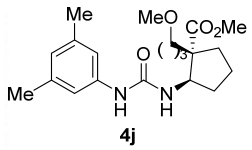
Me
MeO
CO2Me
O
Me
N
H
N
H

4j

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2.82
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2.18
2.16
2.07
1.35
1.06
1.03
1.00
0.97
0.96
0.94
0.36
74.48m
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.753
7.073
6.556
5.834
4.575
4.561
4.543
4.529
4.177
4.159
4.143
3.637
3.294
3.281
3.268
3.211
2.196
2.142
2.054
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2.045
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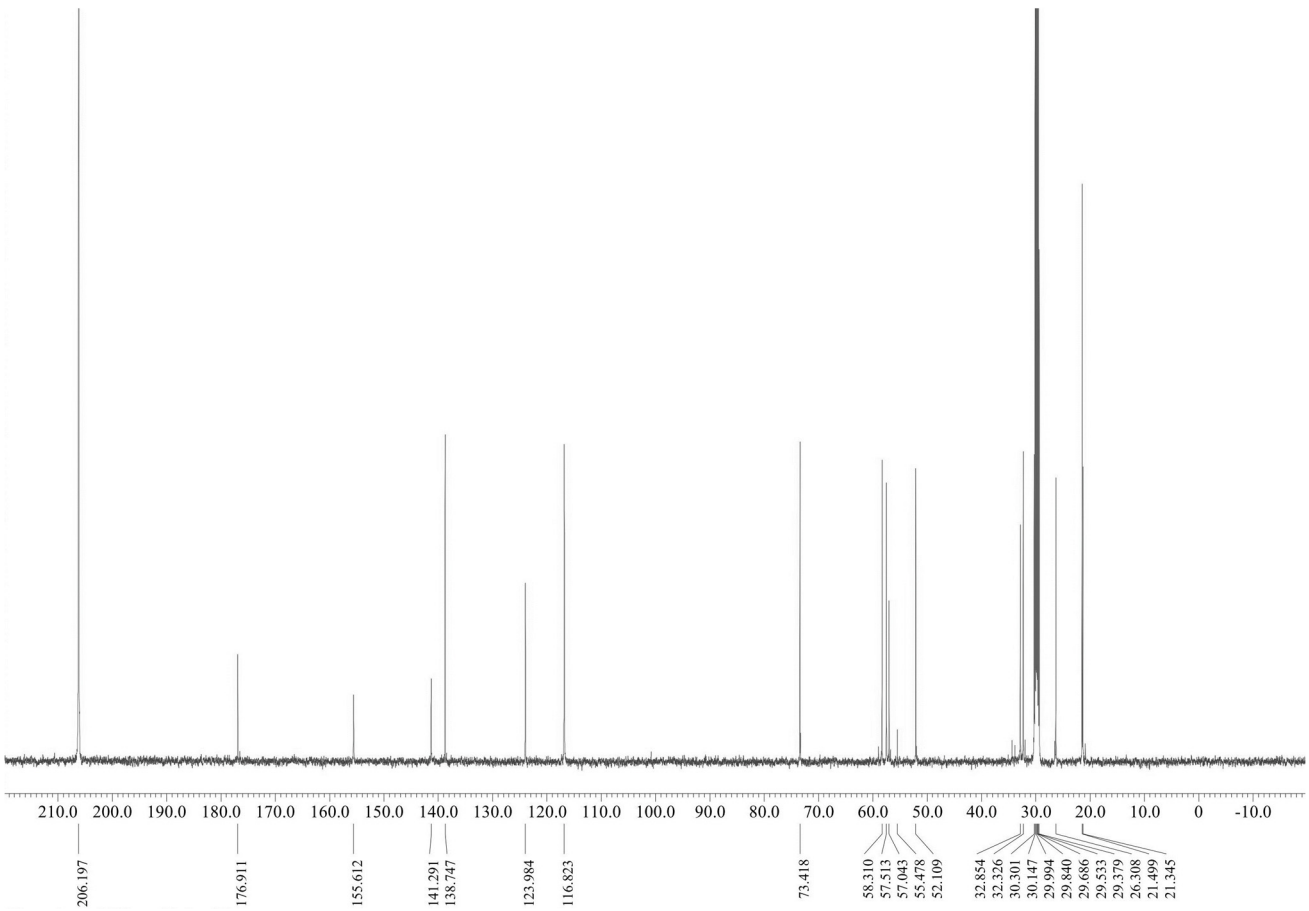
1.440
1.437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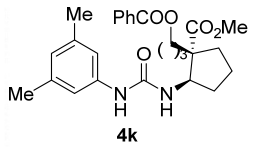
21.345


Me
PhCOO
CO2Me
O
Me
N
H
N
H

4k

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1.90
1.82
1.44
1.25
1.11
1.06
1.03
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1.00
0.24
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
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7.982
7.452
7.436
7.422
7.102
7.066
6.553
5.880
4.632
4.618
4.602
4.587
4.273
4.261
4.248
3.651
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2.055
2.050
2.046
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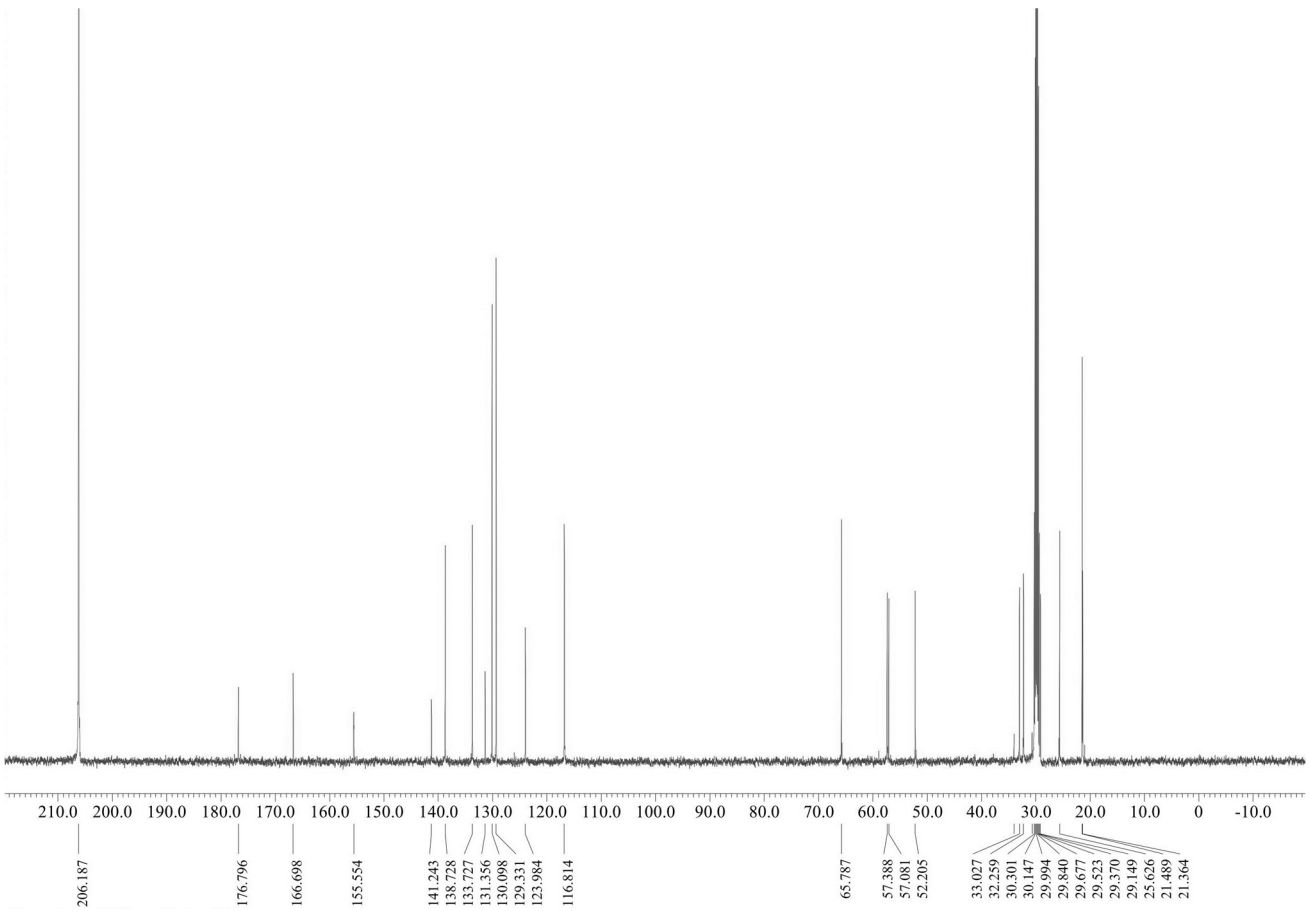
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20.0
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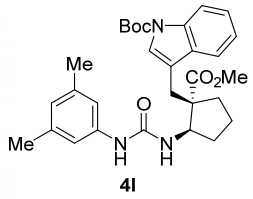
BocN
Me
CO2Me
O
N
H
N
H
Me

4l

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0.22
1.00
0.23
1.09
0.19
0.90
1.17
8.15
1.24
10.36
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
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8.117
8.096
7.558
7.556
7.423
7.238
7.222
7.128
6.581
6.579
6.011
5.988
5.921
5.897
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4.669
4.664
4.653
4.647
4.400
4.380
4.376
3.678
3.595
3.377
3.340
2.995
2.889
2.852
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2.050
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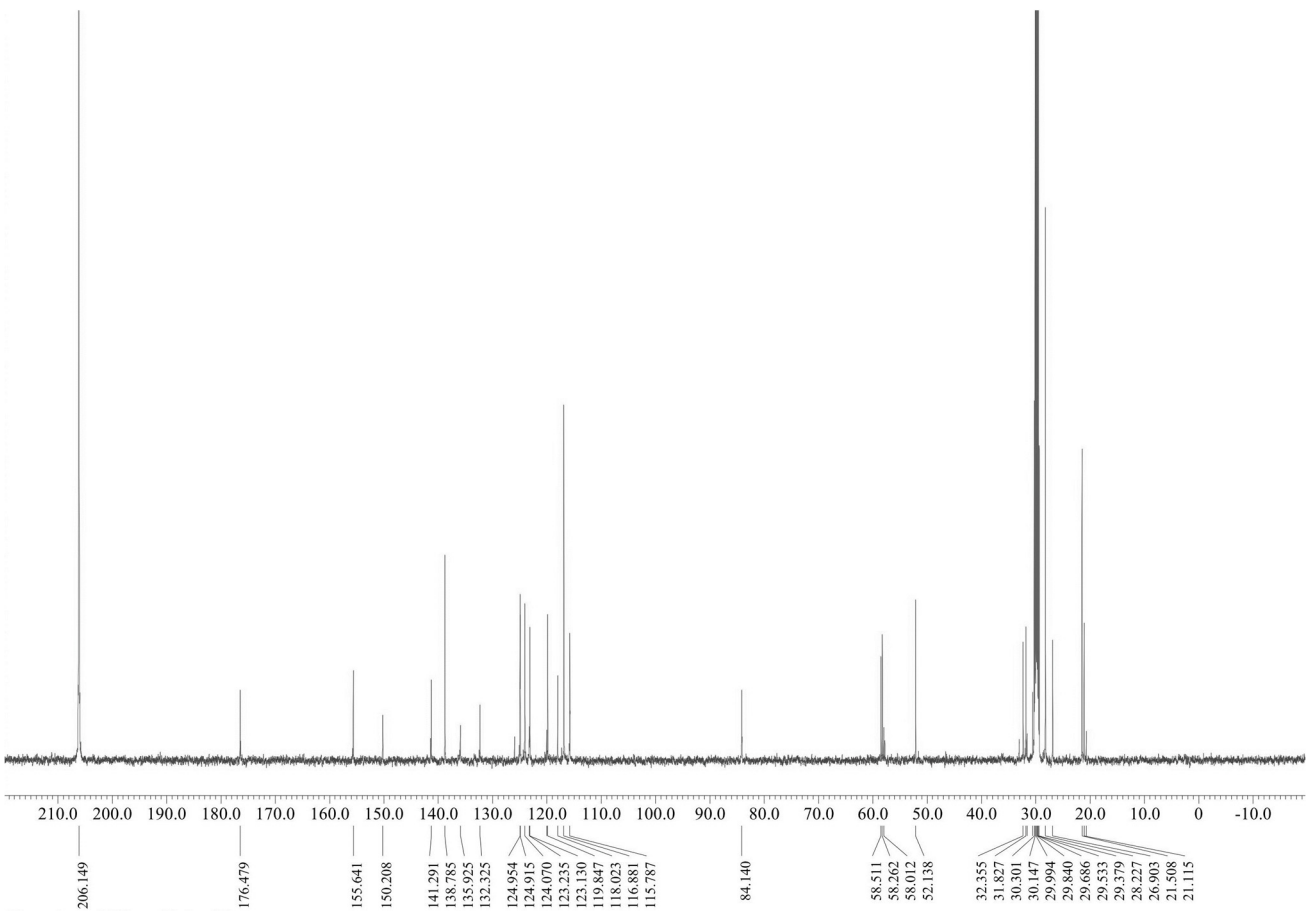
1.646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80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
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176.479
155.641
150.208
141.291
138.785
135.925
132.325
124.954
124.915
124.070
123.235
123.130
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118.023
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115.787
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58.262
58.012
52.138
32.355
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29.379
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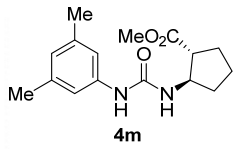
21.115


Me
MeO2C
O
Me
N
H
N
H

4m

6.33
2.91
2.09
1.95
1.21
1.02
1.00
1.00
0.94
0.87
93.96m
0.92
0.59
0.95
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
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7.072
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4.324
4.308
4.294
4.278
4.263
3.621
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2.686
2.671
2.653
2.638
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2.045
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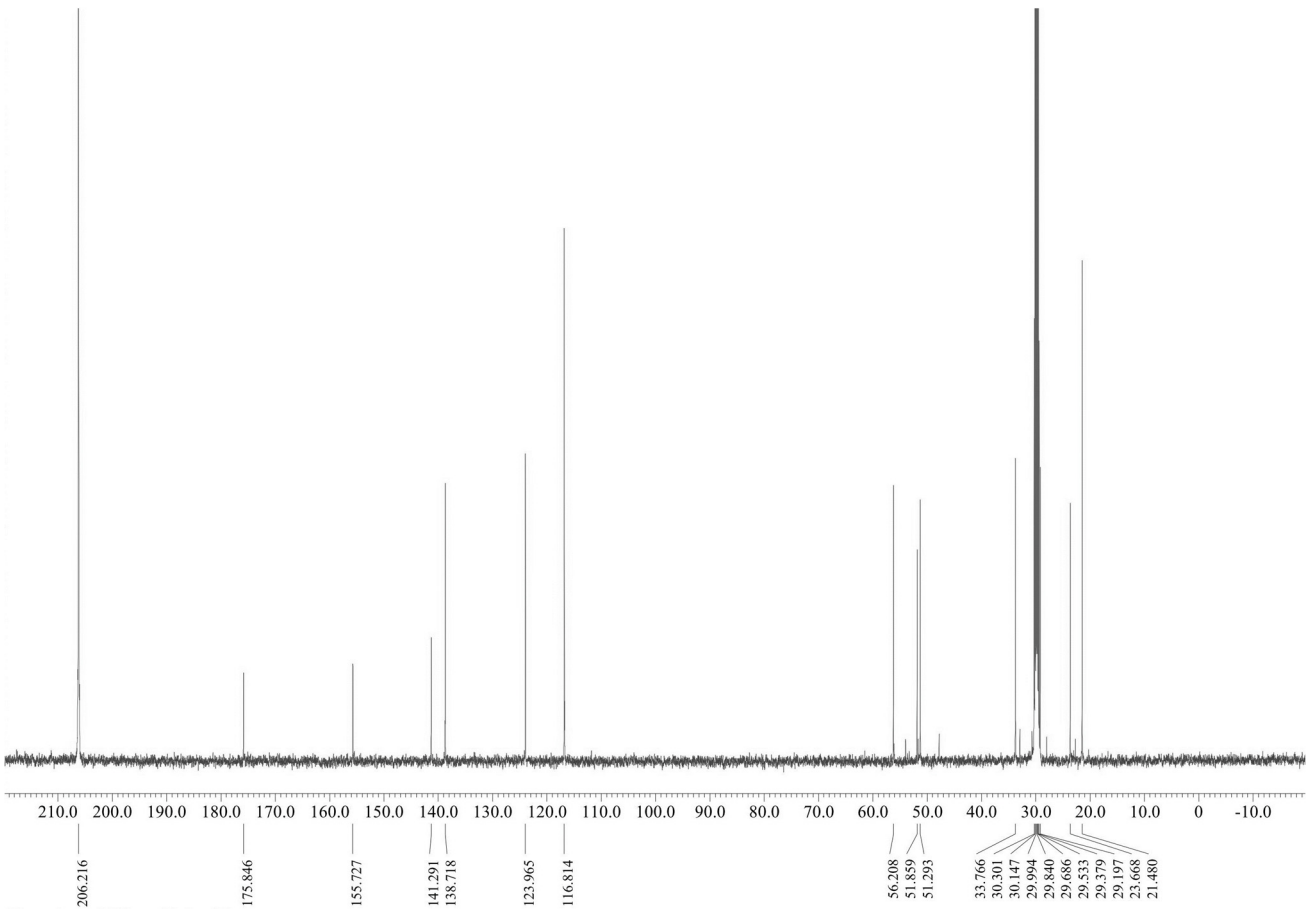
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140.0
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120.0
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90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
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175.846
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51.859
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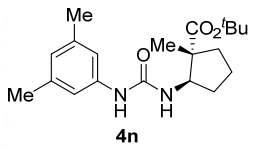
Me
CO2tBu
Me
O
Me
N
H
N
H
Me

4n

11.24
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3.34
3.37
2.25
2.21
1.08
1.00
0.88
0.83
66.41m
0.37
0.30
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
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5.681
4.583
4.566
4.550
4.533
4.097
4.078
4.062
4.044
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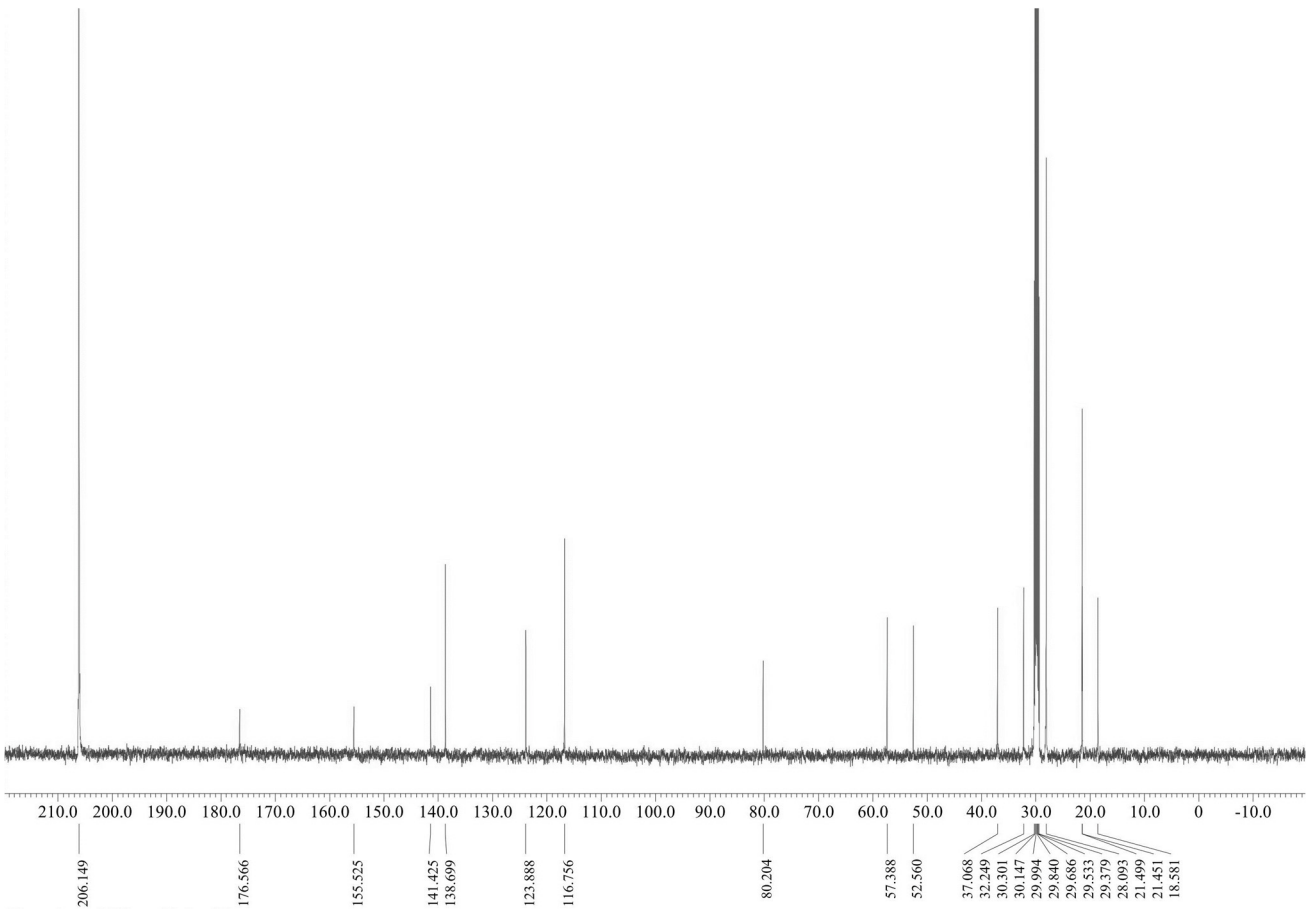
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40.0
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37.068
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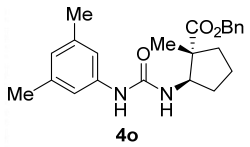
Me
CO2Bn
O
Me
Me
N
H
N
H

4o

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2.25
2.06
2.08
1.33
1.13
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0.93
1.00
1.42
0.81
83.95m
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
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5.105
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4.610
4.176
4.157
4.141
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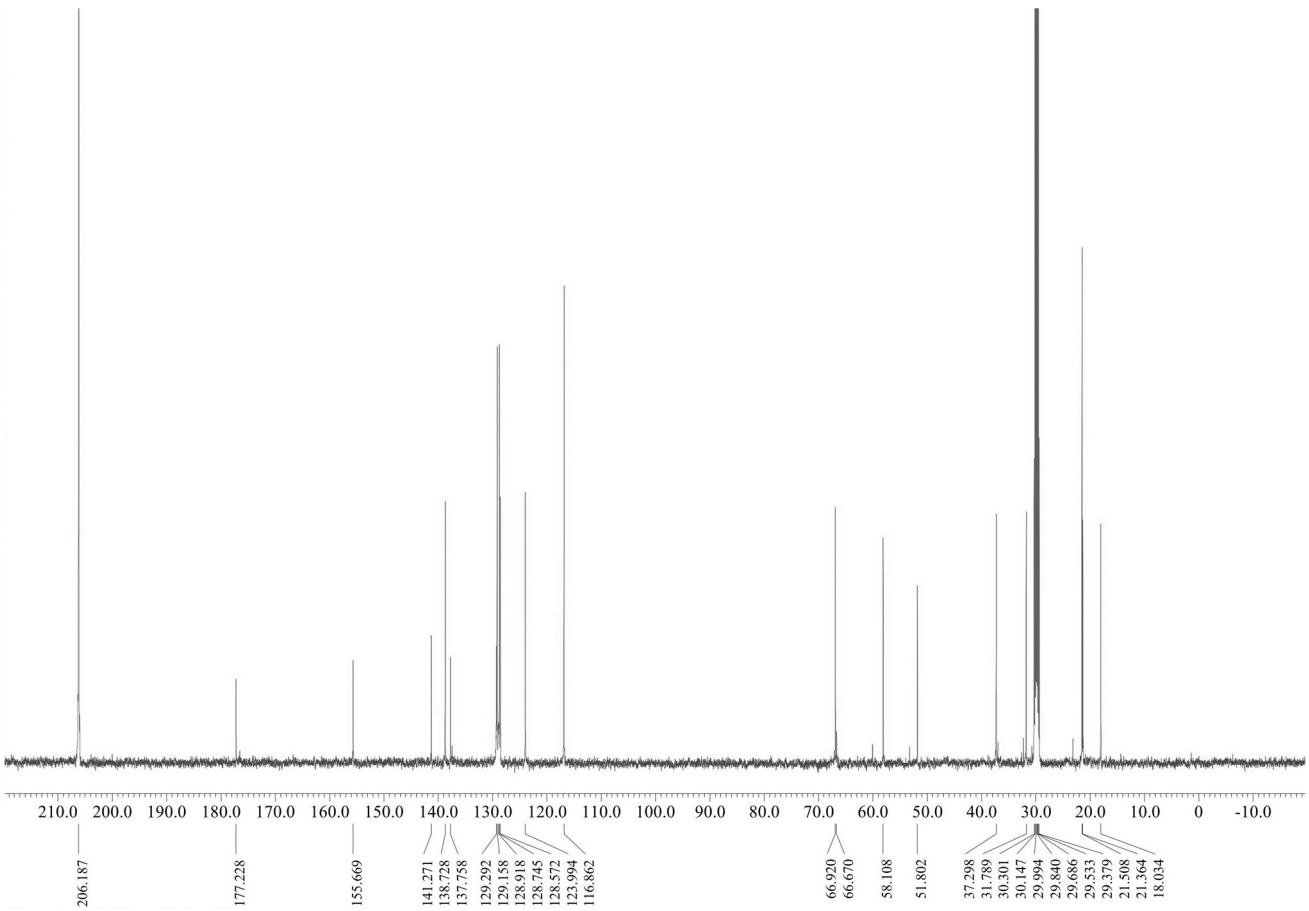
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66.670
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51.802
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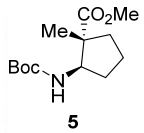
CO2Me
Me
Boc
N
H

5

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0.65
0.86
0.91
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
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4.326
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3.685
2.126
2.107
2.093
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1.699
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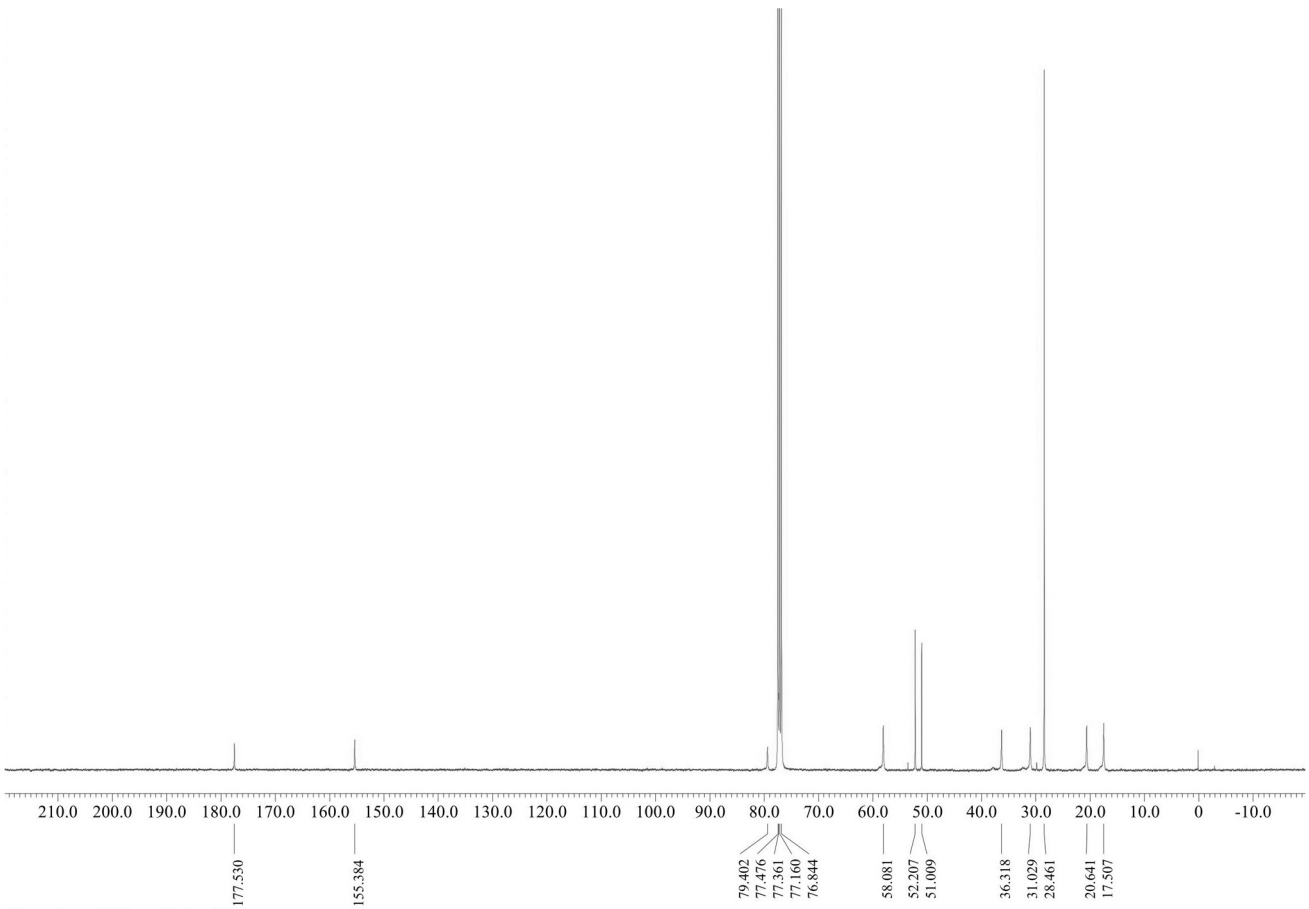
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79.402
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51.009
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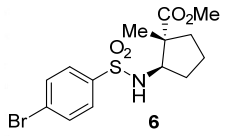
CO2Me
Me
O2
S
N
H
Br

6

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3.03
1.08
1.02
2.00
1.13
1.09
3.15
10.0
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6.0
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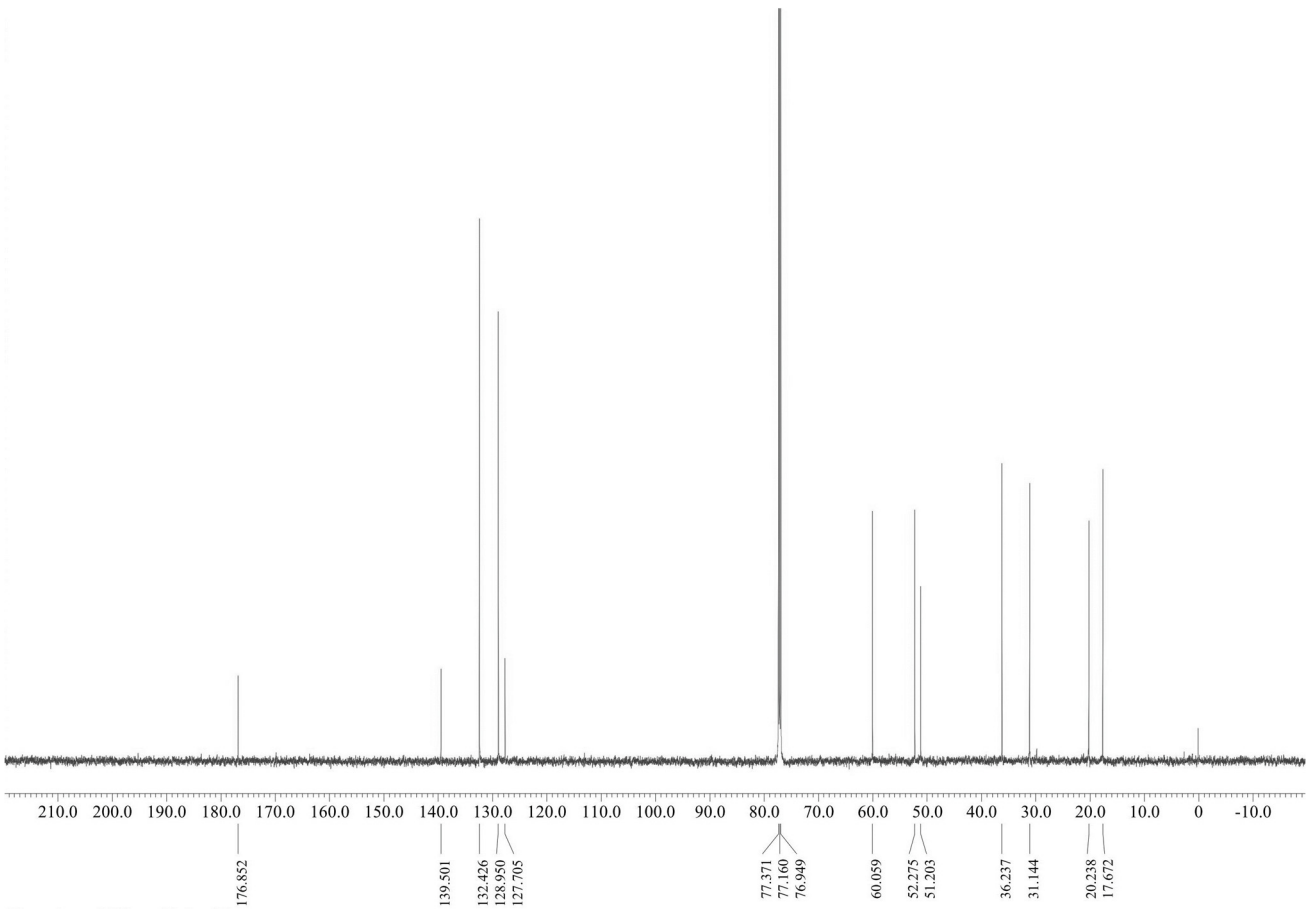
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128.950
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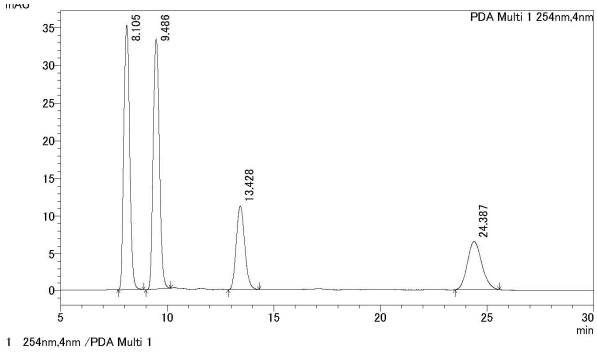
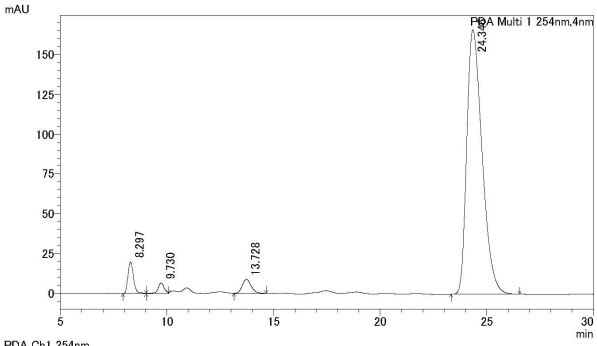
20.238
17.672

5. Copies of HPLC Traces

4a



1 254nm,4nm /PDA Multi 1



PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	λ max
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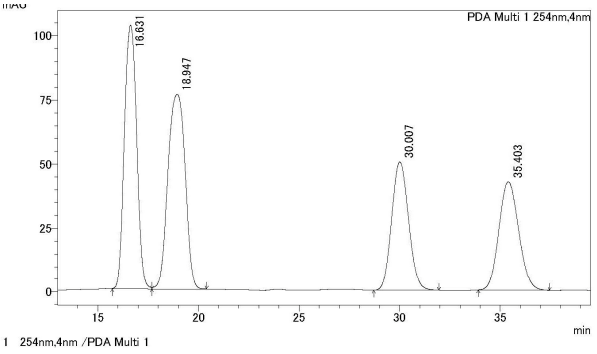
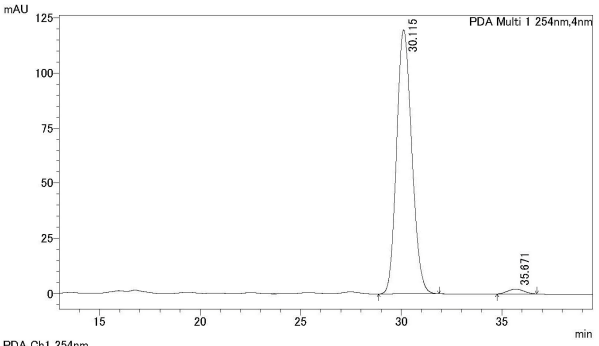
3	13.728	260839	8865	2.888	211/245
4	24.346	8282245	165818	91.709	211/245
合計		9031022	201036	100.000	

4b



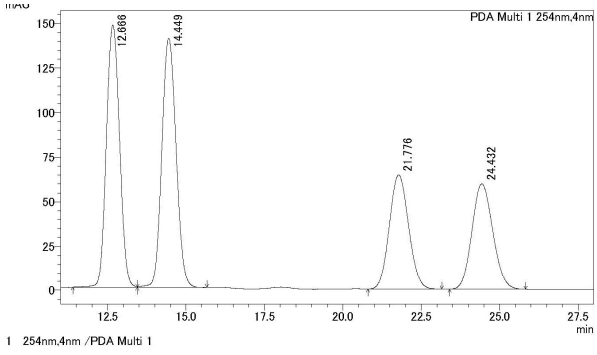
1 254nm,4nm /PDA Multi 1



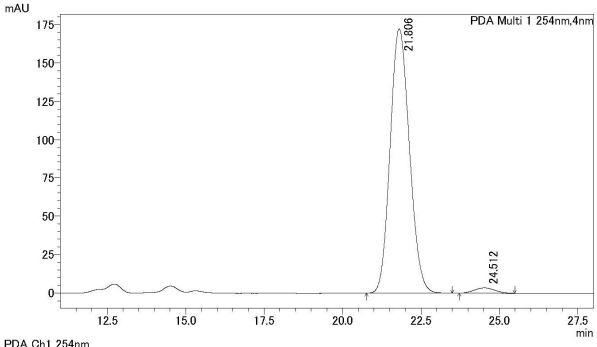
PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	λ max
1	30.115	6262147	119542	98.081	211/245
2	35.671	122550	2210	1.919	211/196/245
合計		6384697	121752	100.000	

4c



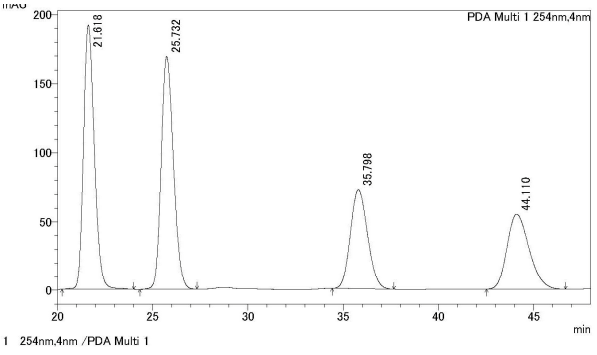
1 254nm,4nm /PDA Multi 1



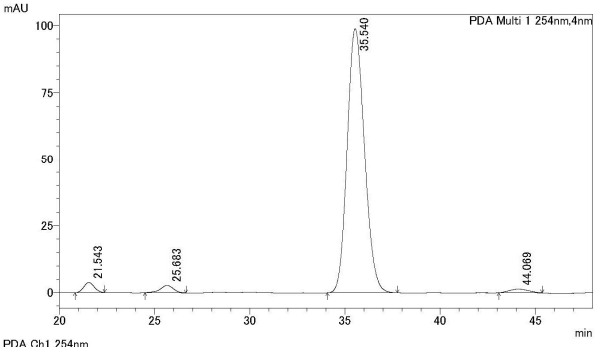
PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	λ max
1	21.806	7371671	172207	97.937	211/245/277
2	24.512	155254	3461	2.063	210/247/280
合計		7526925	175668	100.000	

4d



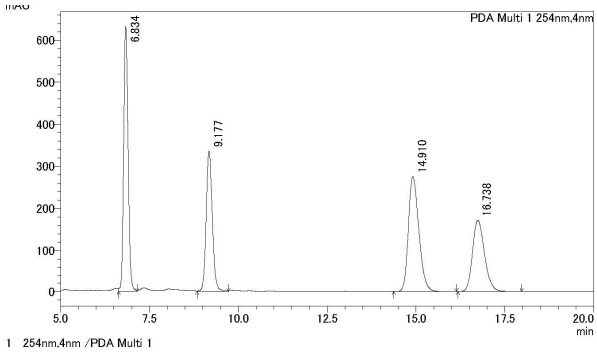
1 254nm,4nm /PDA Multi 1

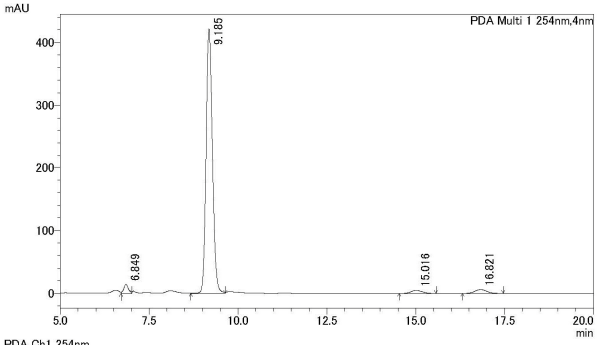


PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	λ max
1	21.543	142844	3741	2.161	209/248/227/281
2	25.683	128728	2737	1.948	208/248/227/281
3	35.540	6243473	98882	94.460	210/198/245/278
4	44.069	94594	1357	1.431	208/249/227/281
合計		6609640	106717	100.000	

4e

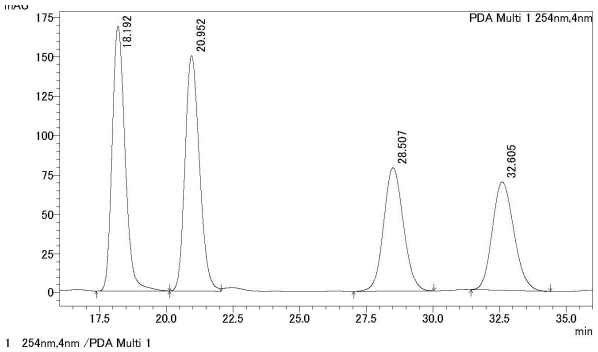


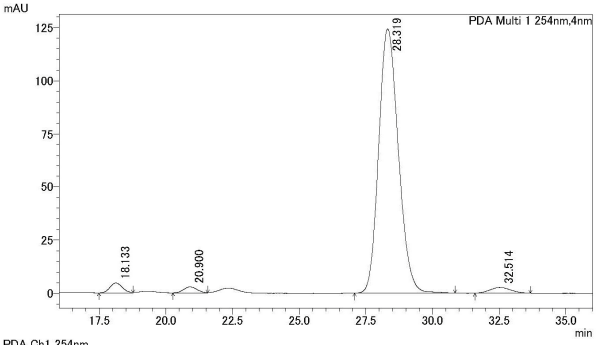


PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	λ max
1	6.849	131490	14411	2.358	212/244
2	9.185	5199122	421502	93.252	201/211/244
3	15.016	104887	4826	1.881	212/244
4	16.821	139843	6045	2.508	212/244
合計		5575342	446785	100.000	

4f

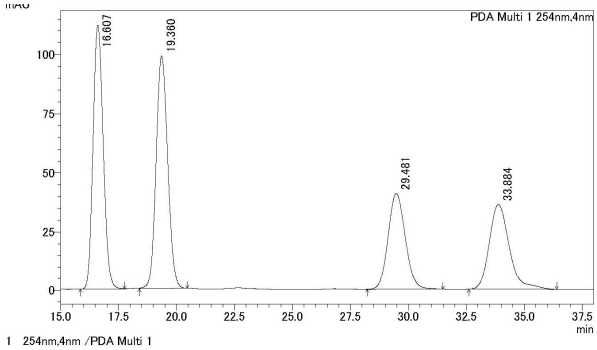


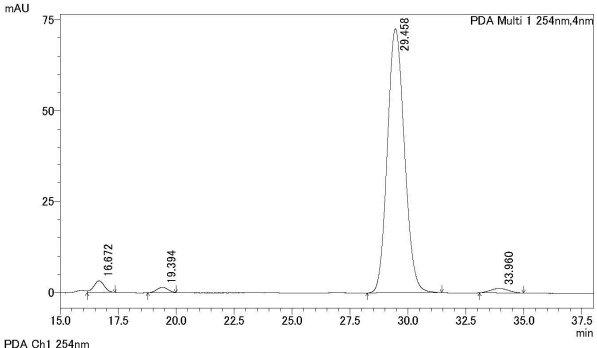


PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	λ max
1	18.133	148830	4636	2.206	209/248/227/281
2	20.900	99617	2837	1.476	208/248/227/280
3	28.319	6354767	124201	94.181	211/196/245/278
4	32.514	144216	2662	2.137	208/249/227/281
合計		6747429	134336	100.000	

4g

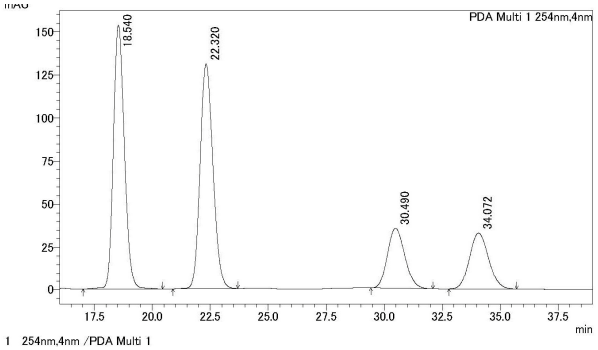


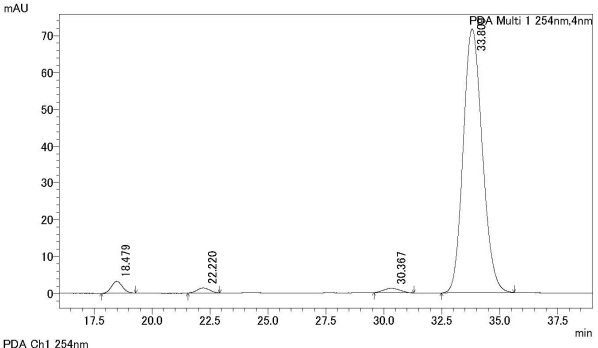


PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	λ max
1	16.672	100529	3191	2.566	209/247/281
2	19.394	46910	1444	1.197	209/248/227/281
3	29.458	3707070	72523	94.611	211/196/245/278
4	33.960	63704	1201	1.626	209/248/227/281
合計		3918212	78359	100.000	

4h

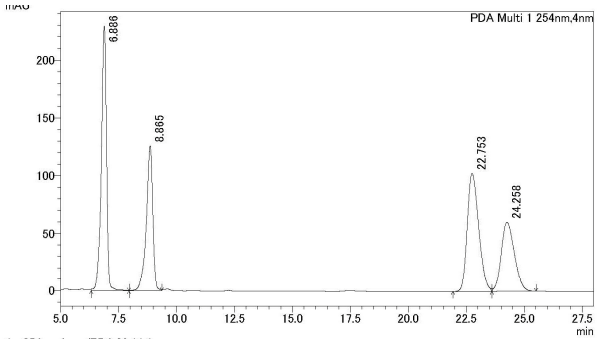


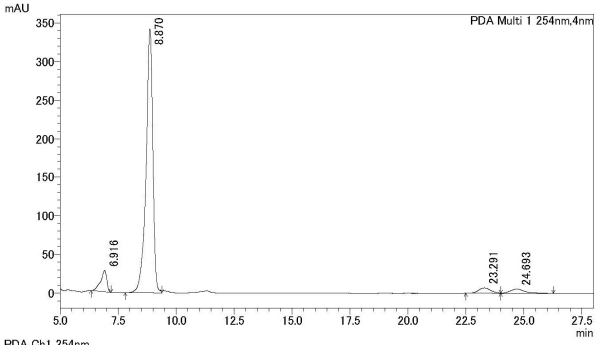


PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	λ max
1	18.479	106765	3229	2.466	211/245
2	22.220	50853	1370	1.174	210/244
3	30.367	57582	1197	1.330	211/245
4	33.809	4114989	71622	95.030	211/245
合計		4330189	77417	100.000	

4i

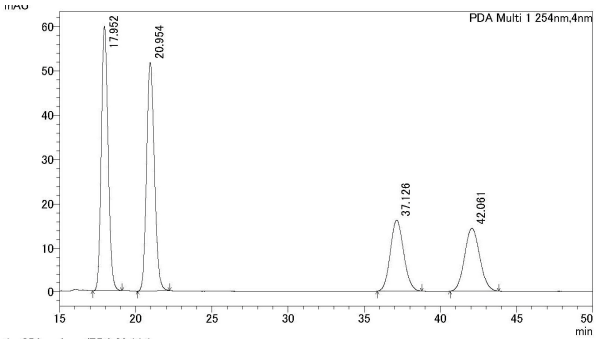


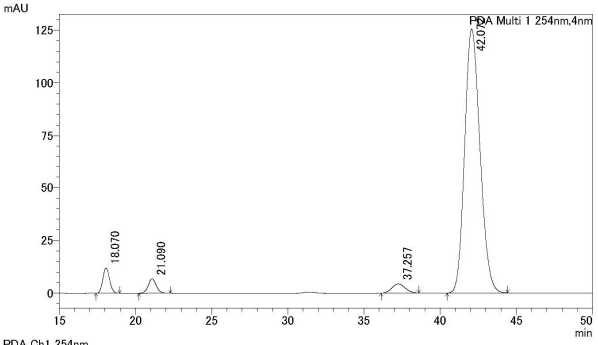


PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	λ max
1	6.916	504308	27409	6.376	212/244
2	8.870	6918682	341980	87.477	196/212/244/277
3	23.291	245736	6861	3.107	212/244
4	24.693	240391	5430	3.039	212/245
合計		7909116	381680	100.000	

4j

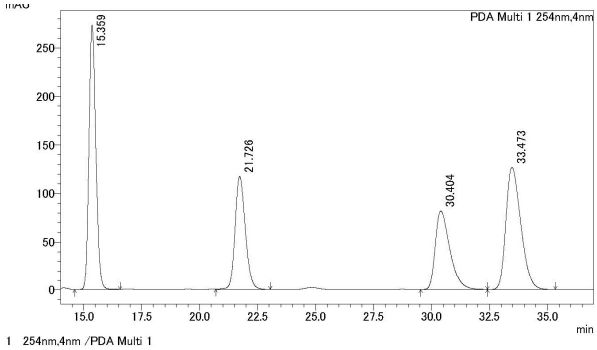


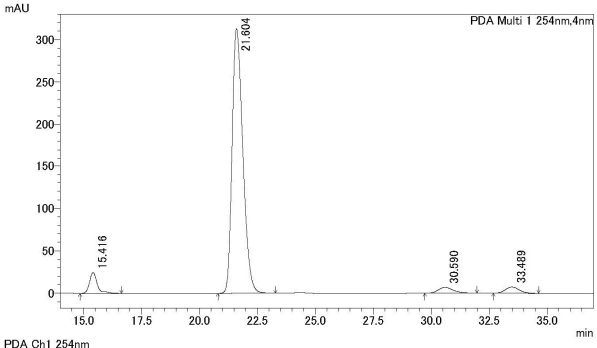


PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	λ max
1	18.070	368763	11947	3.803	211/198/246/280
2	21.090	252422	6850	2.603	210/247/200/280
3	37.257	261664	4364	2.699	209/248/280/200
4	42.072	8813335	125534	90.895	211/196/245/279
合計		9696183	148696	100.000	

4k

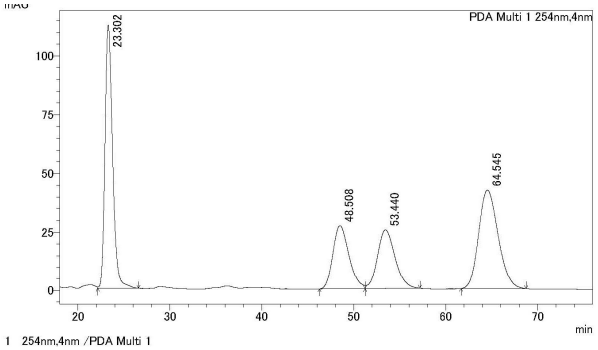


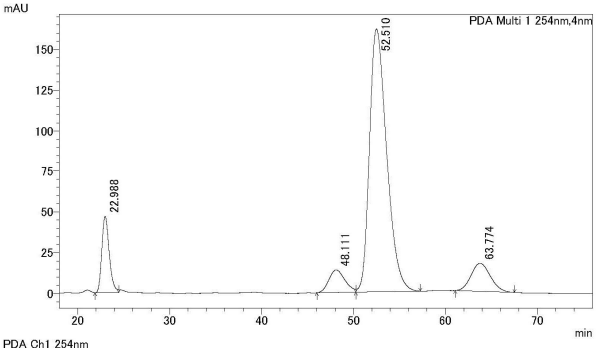


PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	λ max
1	15.416	560375	24501	4.993	212
2	21.604	10060311	312767	89.642	198/212/235
3	30.590	301176	6786	2.684	212/236
4	33.489	300963	7342	2.682	212/235
合計		11222824	351396	100.000	

4l

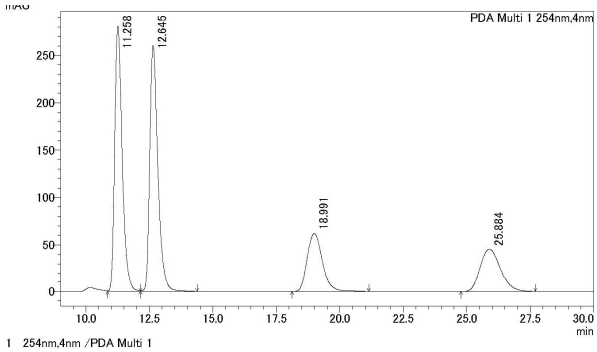




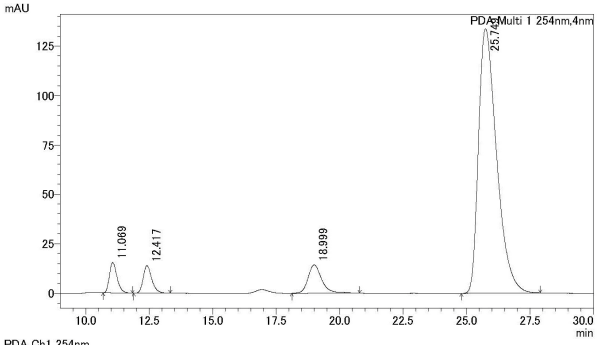
PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	λ max
1	22.988	2612355	46715	9.402	212/231/285
2	48.111	1664429	13768	5.991	212/232/286
3	52.510	21005848	161500	75.604	212/233/286/294
4	63.774	2501234	17162	9.002	212/231/285
合計		27783865	239145	100.000	

4m



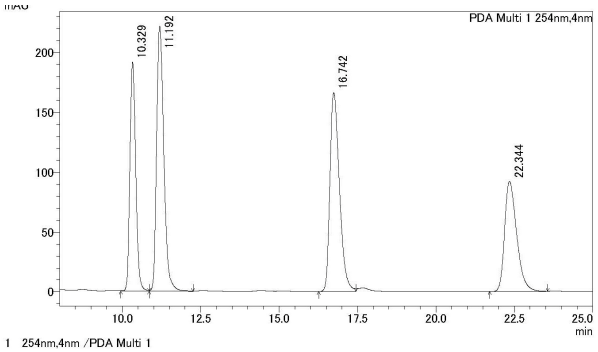
1 254nm,4nm /PDA Multi 1



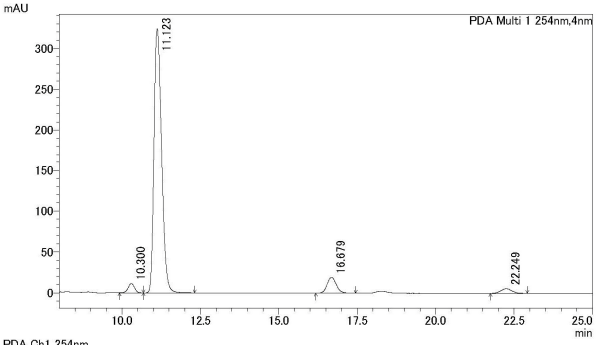
PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	λ max
1	11.069	317904	15240	4.072	211/245
2	12.417	323535	13827	4.144	211/245
3	18.999	537904	14295	6.890	211/245
4	25.749	6627199	133535	84.893	211/245
合計		7806541	176898	100.000	

4n



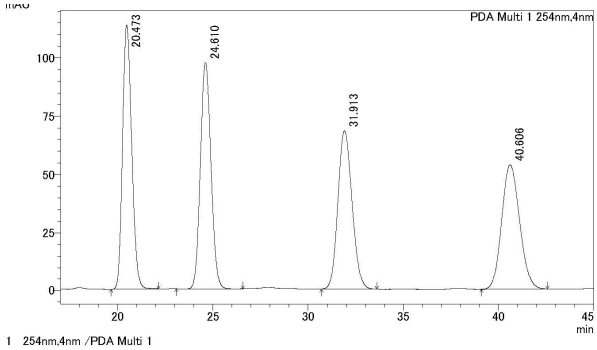
1 254nm,4nm /PDA Multi 1



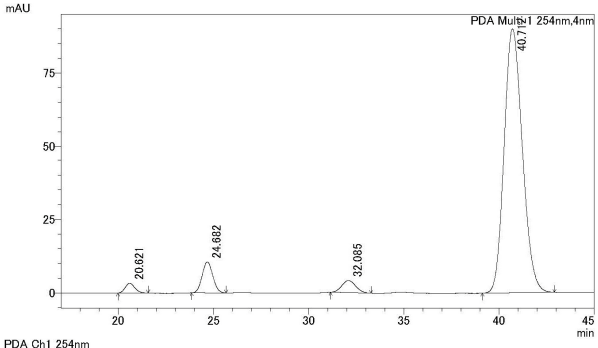
PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	λ max
1	10.300	161149	11443	2.628	211/244/276
2	11.123	5447818	323796	88.856	210/244
3	16.679	390263	19228	6.365	211/194/244/277
4	22.249	131832	5571	2.150	212/198/244
合計		6131062	360038	100.000	

4o



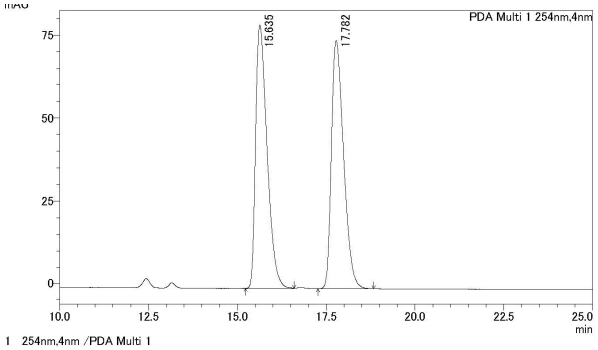
1 254nm,4nm /PDA Multi 1



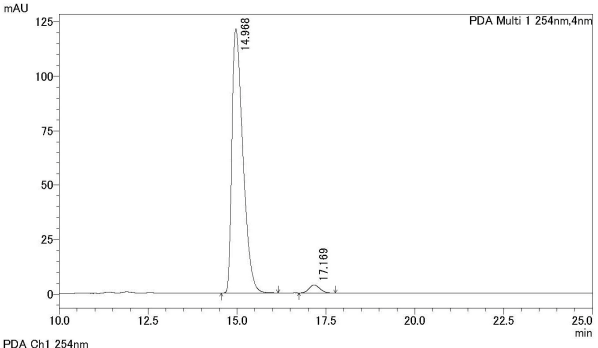
PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	λ max
1	20.621	115708	3281	1.724	210/245
2	24.682	405518	10488	6.041	210/245
3	32.085	208878	4113	3.111	210/245
4	40.712	5983193	89916	89.125	210/245
合計		6713297	107798	100.000	

6



1 254nm,4nm /PDA Multi 1



PDA Ch1 254nm

ピーク#	保持時間	面積	高さ	面積%	λ max
1	14.968	2601682	121184	97.127	237/206
2	17.169	76954	3635	2.873	237/205
合計		2678636	124819	100.000	