Electronic Supplementary Information

Phosphine-Catalyzed Asymmetric [3 + 2] Annulation of Chalcones with Allenoates for Enantioselective Synthesis of Functionalized Cyclopentenes

Zhenzhen Gao, Chang Wang, Chunhao Yuan, Leijie Zhou, Zhanhu Sun, Yumei Xiao*, and Hongchao Guo*

Department of Applied Chemistry, China Agricultural University, Beijing 100193, China

Email: xiaoyumei23@126.com, hchguo@cau.edu.cn

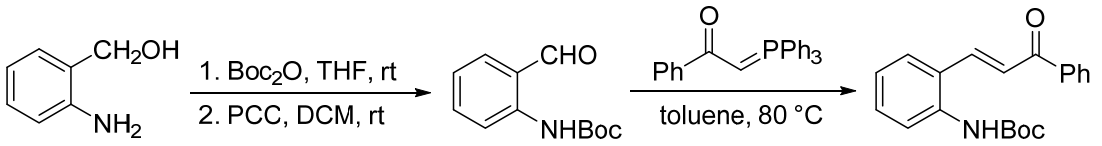
Contents

General Information

All reactions were performed under N_2 atmospheres in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents were purified and dried according to standard methods prior to use. Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. Reactions were monitored through thin layer chromatography (TLC) on silica gel–precoated glass plates. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). Infrared spectra were recorded using a Bruker Optics TENSOR 27 instrument. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 using a 300 MHz NMR instrument (referenced internally to Me_4Si). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet; d = doublet; q = quartet; m = multiplet; br = broad), coupling constant (Hz), and integral. Data for ^{13}C NMR spectra are reported in terms of chemical shift. Optical rotation was obtained on a Perkin-Elmer 343 polarimeter. Accurate mass measurements were performed using an Agilent instrument with the ESI-MS technique. Melting points were determined on a Stuard SMP3 melting point apparatus. X-ray crystallographic data were collected using a MM007HF Saturn724+. HPLC analysis was performed on Agilent 1100 series, UV detection monitored at 254 nm, using a Chiralpak AD-H column or a Chiralpak IC column with hexane and *i*-PrOH as the eluent.

Typical Procedure for Preparation of Boc-Amino-Substituted Chalcones (1)

The Boc-amino-substituted chalcones were prepared according to the literature procedure.[1] A typical procedure is as follows.



A dry and nitrogen-flushed 100-mL of Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of 2-aminobenzyl alcohol (2.46 g, 20 mmol) in dry THF (66 mL). $(Boc)_2O$ (4.79 g, 1.1 equiv) was added. The reaction mixture was stirred for 12 h at rt, then the solvent was removed by evaporation in vacuo. The resulting crude product was dissolved in dichloromethane (50 mL) and then PCC (5.173 g, 1.2 equiv) was added. The reaction mixture was stirred for 4 h at rt and then filtered through celite followed by washing with CH_2Cl_2. The resulting solution was concentrated by evaporation in vacuo. The crude product was purified by flash chromatography (ethyl acetate/hexanes: 1/10) to afford Boc-amino-substituted aldehyde (3.54 g, 80%yield).

A dry and nitrogen-flushed 100-mL of Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of the above aldehyde (3.23 g, 10 mmol) in toluene (50 mL). The reagent 1-phenyl-2-(triphenylphosphoranylidene)ethanone (4.18 g, 1.1 equiv) was added, and the reaction mixture was stirred for 12 h at 80 °C. Then, the solvent was removed by evaporation in vacuo. The crude product was purified by flash chromatography (ethyl acetate/hexanes: 1/6) to give Boc-smino-substituted chalcone **1a** (2.58 g, 80%yield).

General Procedure for Chiral Phosphine-Catalyzed Asymmetric [3 + 2] Annulation of Boc-Amino-Substituted with Allenoates:

Under a nitrogen atmosphere, to a stirred solution of 2-tert-butoxycarbonyl aminochalcones **1** (0.05 mmol, 1.0 equiv) in CH_2Cl_2 (1 mL) was sequentially added 2,3-butadienoate **2** (0.075 mmol, 1.5 equiv) and the catalyst **P5** (0.01 mmol, 20 mol %) via syringes. Then the reaction solution was vigorously stirred at 0 °C, and monitored by TLC. After the reaction was complete, the mixture was directly purified by column chromatography on silica gel (11% EtOAc / petroleum ether as the eluent) to furnish the corresponding product **3**.

A Typical Procedure for Epoxidation of the Product:

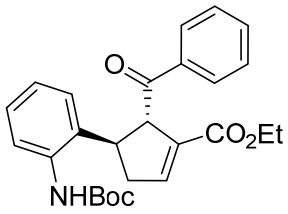
Under a nitrogen atmosphere, a mixture of **7** (65.3 mg, 0.15 mmol) and MCPBA (129.5 mg, 0.75 mmol, 5 equiv) in 2 mL of DCE was stirred for 12 h at room temperature, then the solution was concentrated. The residue was purified by flash column (petroleum ether/EtOAc) to afford the product **8** as yellow liquid (60.2 mg, 89% yield).

---

[1] (a) Y. T. Lee, Y. J. Jang, S. Syu, S. C. Chou, C. J. Lee and W. W. Lin, *Chem. Commun.*, 2012, **48**, 8135; (b) S. Thielges, E. Meddah, P. Bisseret and J. Eustache, *Tetrahedron Lett.*, 2004, **45**, 907.

Characterization Data of the Products 3

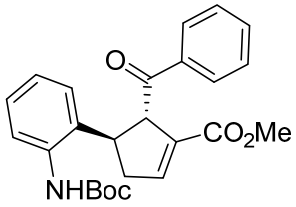
Ethyl (4S,5S)-5-benzoyl-4-(2-((tert-butoxycarbonyl)amino)phenyl)cyclopent-1-ene-1-carboxylate (3aa)



3aa

White semi-solid, 92%yield; $[\alpha]^{20}_{D} = -35.8$ (*c* 0.61, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 – 7.73 (m, 2H), 7.60 – 7.46 (m, 2H), 7.41 – 7.26 (m, 3H), 7.25 – 7.07 (m, 3H), 6.02 (s, 1H), 4.98 – 4.79 (m, 1H), 4.11 (dd, *J* = 7.1, 1.8 Hz, 2H), 3.85 – 3.71 (m, 1H), 3.40 – 3.15 (m, 1H), 2.75 – 2.62 (m, 1H), 1.38 (s, 9H), 1.14 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.6, 163.5, 153.2, 145.0, 138.0, 135.7, 135.3, 134.7, 131.5, 129.8, 127.5, 127.0, 126.7, 125.7, 124.5, 122.6, 80.2, 60.4, 59.6, 42.9, 41.3, 27.9, 13.8; IR (film) ν_{max} 3345, 2979, 2934, 1715, 1639, 1587, 1515, 1449, 1392, 1368, 1332, 1270, 1244, 1160, 1100, 1048, 1024, 848, 751, 698 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{29}NNaO_5^+$ $[M + Na]^+$ 458.1938, found 458.1934; HPLC analysis: 94% ee (CHIRALPAK OD-H, 90:10 isopropanol:hexane, 1.0 mL/min, UV: 254 nm), t_R = 6.68 min (minor), 12.16 min (major).

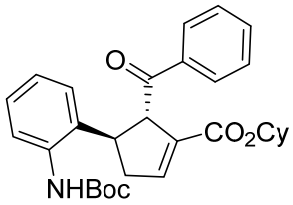
Methyl (4S,5S)-5-benzoyl-4-(2-((tert-butoxycarbonyl)amino)phenyl)cyclopent-1-ene-1-carboxylate (3ab)



3ab

White semi-solid, 75%yield; $[\alpha]^{20}_{D} = -68.6$ (*c* 0.8, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (m, 2H), 7.61 – 7.47 (m, 2H), 7.42 – 7.31 (m, 2H), 7.31 – 7.21 (m, 2H), 7.15 (m, 1H), 7.10 (m, 1H), 5.95 (s, 1H), 4.98 – 4.77 (m, 1H), 3.88 – 3.69 (m, 1H), 3.68 (s, 3H), 3.24 (ddt, *J* = 19.2, 9.3, 2.6 Hz, 1H), 2.75 – 2.56 (m, 1H), 1.38 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.5, 164.1, 153.2, 145.0, 136.7, 136.1, 135.2, 134.7, 133.1, 128.5, 128.4, 127.4, 126.7, 125.5, 124.3, 80.2, 59.5, 51.4, 42.6, 41.4, 28.0; IR (film) ν_{max} 3346, 2977, 2928, 1717, 1641, 1587, 1515, 1449, 1392, 1367, 1343, 1245, 1160, 1102, 1049, 1021, 913, 847, 803, 749, 696, 671 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{29}NNaO_5^+$ $[M + Na]^+$ 458.1938, found 458.1934; HPLC analysis: 92% ee (CHIRALPAK OD-H, 95:5 isopropanol:hexane, 1.0 mL/min, UV: 254 nm), t_R = 15.2 min (minor), 35.4 min (major).

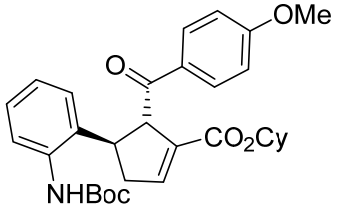
Cyclohexyl (4S,5S)-5-benzoyl-4-(2-((tert-butoxycarbonyl)amino)phenyl)cyclopent-1-ene-1-carboxylate (3ac)



3ac

White semi-solid, 95%yield; $[\alpha]^{20}_{D} = -57.8$ (*c* 0.315, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 – 7.73 (m, 2H), 7.60 – 7.45 (m, 2H), 7.39 – 7.27 (m, 3H), 7.27 – 7.05 (m, 3H), 6.01 (s, 1H), 5.04 – 4.81 (m, 1H), 4.74 (dt, *J* = 8.4, 4.4 Hz, 1H), 3.75 (m, *J* = 10.1, 1H), 3.22 (m, 9.2, 1H), 2.81 – 2.38 (m, 1H), 1.77 (s, 1H), 1.75 – 1.41 (m, 5H), 1.37 (s, 9H), 1.34 – 1.17 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.0, 163.2, 153.3, 144.7, 136.6, 136.5, 136.2, 134.9, 133.1, 128.6, 128.5, 127.5, 126.9, 125.5, 124.3, 80.3, 72.8, 59.4, 43.0, 41.3, 31.4, 31.2, 28.1, 25.2, 23.42, 23.37; IR (film) ν_{max} 3343, 3062, 2937, 2860, 1712, 1642, 1587, 1515, 1449, 1392, 1367, 1239, 1160, 1104, 1048, 1015, 948, 909, 850, 751, 699, 671 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{35}NNaO_5^+$ $[M + Na]^+$ 512.2407, found 512.2403; HPLC analysis: 98%ee (CHIRALPAK AD-H, 90:10 isopropanol:hexane, 1.0 mL/min, UV: 254 nm), t_R = 12.3 min (major), 22.2 min (minor).

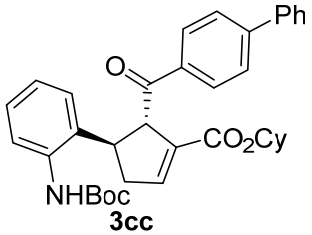
Cyclohexyl (4S,5S)-4-(2-((tert-butoxycarbonyl)amino)phenyl)-5-(4-methoxybenzoyl) cyclopent-1-ene-1-carboxylate (3bc)



3bc

White semi-solid, 97%yield; $[\alpha]^{20}_{D} = -69.7$ (*c* 0.81, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 – 7.74 (m, 2H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.31 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.24 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.20 – 7.12 (m, 1H), 7.10 (dd, *J* = 4.0, 2.4 Hz, 1H), 6.88 – 6.80 (m, 2H), 6.05 (s, 1H), 4.88 – 4.70 (m, 2H), 3.83 (s, 3H), 3.79 – 3.69 (m, 1H), 3.24 (ddt, *J* = 19.0, 9.3, 2.6 Hz, 1H), 2.75 – 2.61 (m, 1H), 1.85 – 1.68 (m, 2H), 1.66 – 1.46 (m, 3H), 1.40 (s, 9H), 1.35 – 1.21 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.2, 163.4, 163.1, 153.1, 144.3, 136.3, 136.2, 134.7, 130.8, 129.2, 127.3, 126.7, 125.2, 123.8, 113.5, 80.1, 72.6, 58.9, 55.2, 42.9, 41.1, 31.2, 31.1, 28.0, 25.1, 23.23, 23.18; IR (film) ν_{max} 3344, 2937, 2859, 1711, 1641, 1586, 1514, 1488, 1451, 1392, 1367, 1257, 1161, 1104, 1021, 948, 906, 795, 753, 681 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{37}NNaO_6^+$ $[M + Na]^+$ 542.2513, found 542.2508; HPLC analysis: 98% ee (CHIRALPAK OD-H, 90:10 isopropanol:hexane, 1.0 mL/min, UV: 254 nm), t_R = 8.7 min (minor), 16.3 min (major).

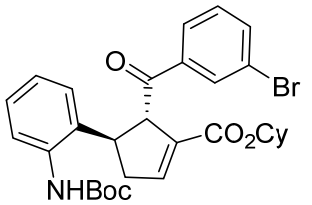
Cyclohexyl (4S,5S)-5-([1,1'-biphenyl]-4-carbonyl)-4-(2-((tert-butoxycarbonyl)amino)phenyl)-cyclopent-1-ene-1-carboxylate (3cc)



3cc

White semi-solid, 98%yield; $[\alpha]^{20}_{D} = -67.1$ (*c* 1.175, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 – 7.84 (m, 2H), 7.66 – 7.57 (m, 5H), 7.51 – 7.43 (m, 2H), 7.43 – 7.32 (m, 2H), 7.32 – 7.22 (m, 1H), 7.23 – 7.16 (m, 1H), 7.16 – 7.10 (m, 1H), 6.08 (s, 1H), 4.99 – 4.89 (m, 1H), 4.86 – 4.72 (m, 1H), 3.89 – 3.77 (m, 1H), 3.28 (ddt, *J* = 19.0, 9.3, 2.6 Hz, 1H), 2.80 – 2.63 (m, 1H), 1.83 – 1.69 (m, 2H), 1.66 – 1.54 (m, 2H), 1.52 – 1.43 (m, 2H), 1.38 (s, 9H), 1.36 – 1.25 (m, 4H), 1.20 (m , *J* = 13.7, 5.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.5, 163.0, 153.2, 145.6, 144.5, 139.6, 136.5, 136.2, 135.0, 134.8, 129.1, 128.7, 128.0, 127.4, 127.0, 126.9, 126.8, 125.4, 124.1, 80.1, 72.7, 59.3, 43.0, 41.2, 31.2, 31.1, 27.9, 25.1, 23.3, 23.2; IR (film) ν_{max} 3342, 2964, 2937, 2860, 1711, 1680, 1603, 1560, 1515, 1450, 1406, 1367, 1261, 1159, 1097, 1022, 800, 755, 698 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{39}ClNNaO_5^+$ $[M + Na]^+$ 588.2720, found 588.2718; HPLC analysis: 97% ee (CHIRALPAK OD-H, 90:10 isopropanol:hexane, 1.0 mL/min, UV: 254 nm), t_R = 6.8 min (minor), 13.8 min (major).

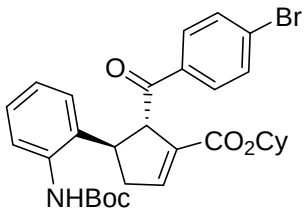
Cyclohexyl (4S,5S)-5-(3-bromobenzoyl)-4-(2-((tert-butoxycarbonyl)amino)phenyl)cyclopent -1-ene-1-carboxylate (3dc)



3dc

Pale yellow semi-solid, 93%yield; $[\alpha]^{20}_{D} = -114.3$ (*c* 0.965, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 – 7.85 (m, 1H), 7.85 – 7.76 (m, 2H), 7.60 – 7.48 (m, 1H), 7.44 – 7.35 (m, 2H), 7.30 – 7.22 (m, 1H), 7.19 – 7.13 (m, 1H), 7.12 – 7.03 (m, 1H), 6.12 (s, 1H), 4.93 – 4.79 (m, 1H), 4.80 – 4.68 (m, 1H), 3.70 (dt, *J* = 9.9, 5.1 Hz, 1H), 3.24 (ddt, *J* = 19.0, 9.2, 2.6 Hz, 1H), 2.78 – 2.47 (m, 1H), 1.80 – 1.68 (m, 2H), 1.64 – 1.45 (m, 3H), 1.40 (s, 9H), 1.35 – 1.18 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.6, 162.8, 152.8, 144. 2, 138.1, 136.2, 136.0, 133.9, 133.2, 130.4, 129.6, 128.5, 128.4, 125.3, 118.1, 80.5, 72.9, 59.0, 42.6, 40.9, 31.2, 31.0, 27.9, 25.0, 23.29, 23.24; IR (film) ν_{max} 3345, 3065, 2936, 2859, 1708, 1639, 1588, 1566, 1514, 1451, 1421, 1367, 1245, 1212, 1160, 1104, 1047, 1019, 947, 907, 752, 701, 671 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{34}BrNNaO_5^+$ $[M + Na]^+$ 590.1513, found 590.1510. HPLC analysis: 96%ee (CHIRALPAK AD-H, 90:10 isopropanol:hexane, 1.0 mL/min, UV: 254 nm), t_R = 11.8 min (major), 25.2 min (minor).

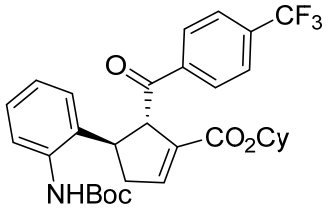
Cyclohexyl (4S,5S)-5-(4-bromobenzoyl)-4-(2-((tert-butoxycarbonyl)amino)phenyl)cyclopent-1-ene-1-carboxylate (3ec)



3ec

Pale yellow semi-solid, 96%yield; $[\alpha]^{20}_{D} = -61.6$ (*c* 1.025, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 – 7.60 (m, 2H), 7.60 – 7.45 (m, 3H), 7.35 – 7.22 (m, 2H), 7.21 – 7.13 (m, 1H), 7.13 – 7.05 (m, 1H), 6.06 (s, 1H), 4.88 – 4.69 (m, 1H), 3.83 – 3.72 (m, 1H), 3.24 (ddd, *J* = 11.7, 9.2, 4.6 Hz, 1H), 2.77 – 2.61 (m, 1H), 1.86 – 1.70 (m, 2H), 1.67 – 1.44 (m, 4H), 1.39 (s, 9H), 1.36 – 1.16 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.0, 162.9, 153.2, 144.6, 136.6, 135.9, 135.0, 134.6, 131.6, 130.0, 128.2, 127.5, 126.7, 125.6, 124.3, 80.2, 72.8, 59.3, 42.9, 41.2, 31.2, 31.1, 28.0, 25.0, 23.29, 23.25; IR (film) ν_{max} 3344, 2937, 2859, 1711, 1641, 1586, 1514, 1488, 1451, 1392, 1367, 1257, 1161, 1104, 1021, 948, 906, 795, 753, 681 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{34}BrNNaO_5^+$ $[M + Na]^+$ 590.1513, found 590.1509; HPLC analysis: 95% ee (CHIRALPAK OD-H, 90:10 isopropanol:hexane, 1.0 mL/min, UV: 254 nm), t_R = 6.86 min (minor), 12.7 min (major).

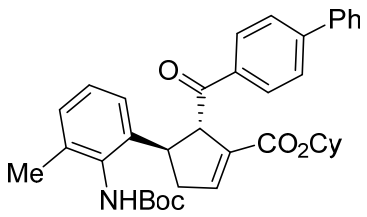
Cyclohexyl (4S,5S)-4-(2-((tert-butoxycarbonyl)amino)phenyl)-5-(4-(trifluoromethyl)benzoyl) cyclopent-1-ene-1-carboxylate (3fc)



3fc

White semi-solid, 92%yield; $[\alpha]^{20}_{D} = -73.5$ (*c* 0.96, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.64 (m, 2H), 7.54 (m, 1H), 7.37 – 7.29 (m, 1H), 7.29 – 7.24 (m, 1H), 7.20 (m, 1H), 7.15 – 7.09 (m, 1H), 6.04 (s, 1H), 4.94 – 4.83 (m, 1H), 4.82 – 4.67 (m, 1H), 3.92 – 3.75 (m, 1H), 3.28 (ddt, *J* = 19.1, 9.2, 2.6 Hz, 1H), 2.81 – 2.65 (m, 1H), 1.82 – 1.70 (m, 1H), 1.68 – 1.55 (m, 3H), 1.55 – 1.41 (m, 2H), 1.37 (s, 9H), 1.34 – 1.19 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.4, 162.9, 153.2, 144.8, 139.2, 136.8, 135.9, 134.6, 128.8, 127.6, 126.7, 125.8, 125.33, 125.28, 124.6, 80.3, 72.9, 59.6, 42.9, 41.3, 31.2, 31.1, 27.9, 25.0, 23.31, 23.27; IR (film) ν_{max} 3345, 2938, 2861, 1703, 1639, 1586, 1512, 1451, 1410, 1367, 1323, 1261, 1166, 1131, 1112, 1067, 1014, 853, 801, 750, 702, 596 cm^{-1} HRMS (ESI) calcd for $C_{31}H_{34}F_3NNaO_5^+$ $[M + Na]^+$ 580.2281, found 580.2282; HPLC analysis: 97% ee (CHIRALPAK OD-H, 90:10 isopropanol:hexane, 1.0 mL/min, UV: 254 nm), t_R = 5.7 min (minor), 10.2 min (major).

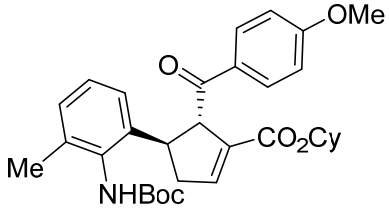
Cyclohexyl (4S,5S)-5-([1,1'-biphenyl]-4-carbonyl)-4-(2-((tert-butoxycarbonyl)amino)-3-methylphenyl)cyclopent-1-ene-1-carboxylate (3gc)



3gc

White semi-solid, 96%yield; $[\alpha]^{20}_{D} = -87.7$ (*c* 0.97, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 – 7.84 (m, 2H), 7.67 – 7.55 (m, 4H), 7.52 – 7.34 (m, 4H), 7.19 – 7.11 (m, 2H), 7.11 – 7.03 (m, 1H), 5.92 (s, 1H), 4.91 (d, *J* = 2.5 Hz, 1H), 4.86 – 4.73 (m, 1H), 3.87 – 3.68 (m, 1H), 3.26 (ddt, *J* = 19.1, 9.3, 2.7 Hz, 1H), 2.81 – 2.64 (m, 1H), 2.35 (s, 3H), 1.86 – 1.67 (m, 2H), 1.68 – 1.41 (m, 4H), 1.36 (s, 9H), 1.34 – 0.95 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.5, 163.2, 153.5, 145.5, 144.6, 139.6, 136.1, 135.4, 135.1, 132.0, 129.1, 128.7, 128.1, 127.9, 127.1, 127.0, 126.9, 124.7, 79.9, 72.7, 59.5, 42.8, 41.4, 31.2, 31.1, 27.9, 25.1, 23.3, 23.2, 20.9; IR (film) ν_{max} 2938, 2861, 1709, 1603, 1515, 1486, 1450, 1406, 1366, 1262, 1161, 1101, 1007, 810, 758, 698 cm^{-1}; HRMS (ESI) calcd for $C_{37}H_{41}NNaO_5^+$ $[M + Na]^+$ 602.2877, found 602.2873; HPLC analysis: 97% ee (CHIRALPAK RC-OD-H, 90:10 isopropanol:hexane, 1.0 mL/min, UV: 254 nm), t_R = 6.5 min (minor), 11.9 min (major).

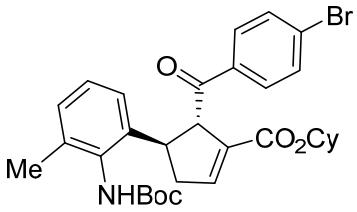
Cyclohexyl (4S,5S)-4-(2-((tert-butoxycarbonyl)amino)-3-methylphenyl)-5-(4-methoxybenzoyl) cyclopent-1-ene-1-carboxylate (3hc)



3hc

White semi-solid, 94%yield; $[\alpha]^{20}_{D} = -86.3$ (*c* 1.05, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.5 Hz, 2H), 7.26 – 7.17 (m, 2H), 7.17 – 7.09 (m, 1H), 7.08 – 7.00 (m, 1H), 6.88 – 6.75 (m, 2H), 5.60 (s, 1H), 4.85 (s, 1H), 4.81 – 4.69 (m, 1H), 3.97 – 3.83 (m, 1H), 3.81 (s, 3H), 3.20 (ddt, *J* = 19.1, 9.3, 2.5 Hz, 1H), 2.61 (d, *J* = 19.1 Hz, 1H), 2.22 (s, 3H), 1.87 – 1.67 (m, 1H), 1.65 – 1.50 (m, 2H), 1.37 (s, 9H), 1.32 – 1.06 (m, 6H), 0.95 – 0.74 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.5, 163.5, 163.4, 153.9, 144.7, 143.3, 136.8, 136.2, 132.9, 131.0, 129.6, 129.0, 128.0, 124.3, 113.5, 79.9, 72.6, 59.4, 55.3, 43.5, 42.1, 31.4, 31.2, 28.1, 25.3, 23.41, 23.37, 18.4; IR (film) ν_{max} 3331, 2937, 2860, 1710, 1674, 1600, 1576, 1510, 1454, 1421, 1366, 1262, 1170, 1103, 1017, 911, 862, 842, 783, 738, 615, 514 cm^{-1}; HRMS (ESI) calcd for $C_{32}H_{39}NNaO_6^+$ $[M + Na]^+$ 556.2670, found 556.2669; HPLC analysis: 97% ee (CHIRALPAK AD-H, 90:10 isopropano- l:hexane, 1.0 mL/min, UV: 254 nm), t_R = 13.4 min (major), 20.3 min (minor).

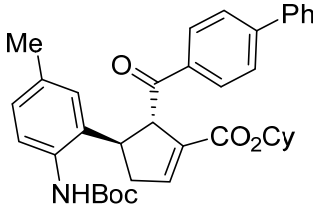
Cyclohexyl (4S,5S)-5-(4-bromobenzoyl)-4-(2-((tert-butoxycarbonyl)amino)-3-methylphenyl) cyclopent-1-ene-1-carboxylate (3ic)



3ic

White semi-solid, 94%yield; $[\alpha]^{20}_{D} = -73.6$ (*c* 0.83, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 – 7.59 (m, 2H), 7.55 – 7.43 (m, 2H), 7.23 – 7.18 (m, 2H), 7.18 – 7.09 (m, 1H), 5.62 (s, 1H), 4.84 (s, 1H), 4.79 – 4.66 (m, 1H), 3.98 – 3.80 (m, 1H), 3.21 (ddt, *J* = 19.1, 9.2, 2.5 Hz, 1H), 2.61 (d, *J* = 19.2 Hz, 1H), 2.22 (s, 3H), 1.83 – 1.67 (m, 3H), 1.66 – 1.52 (m, 2H), 1.51 – 1.40 (m, 2H), 1.35 (s, 9H), 1.29 – 1.07 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.4, 163.3, 153.9, 145.1, 143.0, 136.7, 136.0, 135.4, 132.9, 131.6, 130.3, 129.2, 128.1, 128.0, 124.3, 80.0, 59.6, 43.5, 42.2, 31.4, 31.3, 28.0, 25.2, 23.5, 23.4, 18.4; IR (film) ν_{max} 3336, 2979, 2931, 1716, 1641, 1596, 1580, 1495, 1448, 1392, 1368, 1333, 1245, 1219, 1165, 1102, 1052, 1024, 912, 843, 780, 749, 694 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{36}BrNNaO_5^+$ $[M + Na]^+$ 604.1669, found 604.1666; HPLC analysis: 97% ee (CHIRALPAK AD-H, 95:5 isopropanol:hexane, 1.0 mL/min, UV: 254 nm), t_R = 9.7 min (minor), 11.7 min (major).

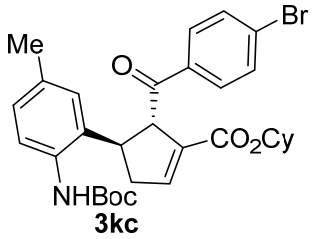
Cyclohexyl (4S,5S)-5-([1,1'-biphenyl]-4-carbonyl)-4-(2-((tert-butoxycarbonyl)amino)-5-methylphenyl)cyclopent-1-ene-1-carboxylate (3jc)



3jc

White semi-solid, 85%yield; $[\alpha]^{20}_{D} = -93.7$ (*c* 0.97, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 – 7.84 (m, 2H), 7.67 – 7.55 (m, 4H), 7.52 – 7.34 (m, 4H), 7.19 – 7.11 (m, 2H), 7.11 – 7.03 (m, 1H), 5.92 (s, 1H), 4.91 (d, *J* = 2.5 Hz, 1H), 4.86 – 4.73 (m, 1H), 3.87 – 3.68 (m, 1H), 3.26 (ddt, *J* = 19.1, 9.3, 2.7 Hz, 1H), 2.81 – 2.64 (m, 1H), 2.35 (s, 3H), 1.86 – 1.67 (m, 2H), 1.68 – 1.41 (m, 4H), 1.36 (s, 9H), 1.34 – 0.95 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.5, 163.2, 153.5, 145.5, 144.6, 139.6, 136.1, 135.4, 135.1, 132.0, 129.1, 128.7, 128.1, 127.9, 127.1, 127.0, 126.9, 124.7, 79.9, 72.7, 59.5, 42.8, 41.4, 31.2, 31.1, 27.9, 25.1, 23.3, 23.2, 20.9; IR (film) ν_{max} 2938, 2861, 1709, 1603, 1515, 1486, 1450, 1406, 1366, 1262, 1161, 1101, 1007, 810, 758, 698 cm^{-1}; HRMS (ESI) calcd for $C_{37}H_{41}NNaO_5^+$ $[M + Na]^+$ 602.2877, found 602.2873; HPLC analysis: 96%ee (CHIRALPAK RC-OD-H, 90:10 isopropanol:hexane, 1.0 mL/min, UV: 254 nm), t_R = 6.5 min (minor), 11.9 min (major).

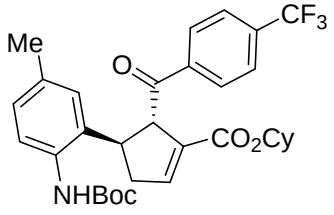
Cyclohexyl (4S,5S)-5-(4-bromobenzoyl)-4-(2-((tert-butoxycarbonyl)amino)-5-methylphenyl) cyclopent-1-ene-1-carboxylate (3kc)



3kc

White semi-solid, 92%yield; $[\alpha]^{20}_{D} = -73.6$ (*c* 0.83, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 – 7.59 (m, 2H), 7.56 – 7.45 (m, 2H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.09 (dd, *J* = 11.7, 4.9 Hz, 3H), 5.89 (s, 1H), 4.85 – 4.65 (m, 2H), 3.84 – 3.67 (m, 1H), 3.23 (ddt, *J* = 19.2, 9.3, 2.6 Hz, 1H), 2.81 – 2.61 (m, 1H), 2.34 (s, 1H), 1.85 – 1.70 (m, 2H), 1.67 – 1.55 (m, 2H), 1.54 – 1.42 (m, 1H), 1.38 (s, 9H), 1.34 – 1.10 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.0, 163.0, 153.5, 144.7, 137.3, 135.8, 135.6, 135.1, 131.9, 131.6, 130.0, 128.2, 127.1, 124.9, 80.0, 72.8, 59.5, 42.7, 41.4, 31.2, 31.1, 28.0, 25.1, 23.29, 23.26, 20.8; IR (film) ν_{max} 3336, 2979, 2931, 1716, 1641, 1596, 1580, 1495, 1448, 1392, 1368, 1333, 1245, 1219, 1165, 1102, 1052, 1024, 912, 843, 780, 749, 694 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{36}BrNNaO_5^+$ $[M + Na]^+$ 604.1669, found 604.1666; HPLC analysis: 98%ee (CHIRALPAK RC-OD-H, 90:10 isopropanol:hexane, 1.0 mL/min, UV: 254 nm), t_R = 5.4 min (minor), 9.3 min (major).

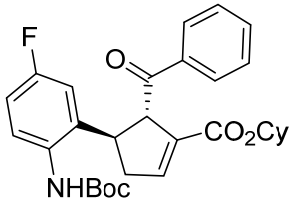
Cyclohexyl (4S,5S)-4-(2-((tert-butoxycarbonyl)amino)-5-methylphenyl)-5-(4-(trifluoromethyl) benzoyl)cyclopent-1-ene-1-carboxylate (3lc)



3lc

White semi-solid, 80%yield; $[\alpha]^{20}_{D} = -95.8$ (*c* 0.48, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 – 7.83 (m, 2H), 7.74 – 7.54 (m, 2H), 7.40 – 7.29 (m, 1H), 7.16 – 6.98 (m, 3H), 5.90 (s, 1H), 4.95 – 4.82 (m, 1H), 4.82 – 4.66 (m, 1H), 3.89 – 3.67 (m, 1H), 3.42 – 3.12 (m, 1H), 2.84 – 2.59 (m, 1H), 2.34 (s, 3H), 1.83 – 1.39 (m, 8H), 1.35 (s, 9H), 1.32 – 1.12 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.4, 163.0, 153.5, 144.9, 139.2, 137.6, 135.9, 135.8, 131.9, 128.8, 128.2, 127.1, 125.3, 125.2, 80.1, 72.9, 59.8, 42.8, 41.4, 31.2, 31.1, 27.9, 25.0, 23.30, 23.27, 20.8; IR (film) νmax 2940, 2863, 1705, 1514, 1485, 1453, 1410, 1367, 1323, 1246, 1166, 1132, 1067, 1012, 851, 766 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{33}ClF_3NNaO_5^+$ $[M + Na]^+$ 594.2438, found 594.2434; HPLC analysis: 96%ee (CHIRALPAK RC-OD-H, 90:10 isopropanol:hexane, 1.0 mL/min, UV: 254 nm), t_R = 5.0 min (minor), 8.3 min (major).

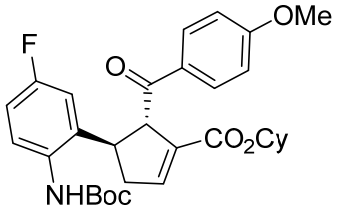
Cyclohexyl (4S,5S)-5-benzoyl-4-(2-((tert-butoxycarbonyl)amino)-5-fluorophenyl)cyclopent-1-ene-1-carboxylate (3mc)



3mc

White semi-solid, 93%yield; $[\alpha]^{20}_{D} = -78.1$ (*c* 0.91, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.4 Hz, 2H), 7.59 – 7.48 (m, 1H), 7.48 – 7.32 (m, 3H), 7.14 – 7.00 (m, 2H), 6.99 – 6.86 (m, 1H), 5.89 (s, 1H), 4.91 – 4.80 (m, 1H), 4.79 – 4.63 (m, 1H), 3.90 – 3.67 (m, 1H), 3.34 – 3.15 (m, 1H), 2.75 – 2.58 (m, 1H), 1.86 – 1.66 (m, 2H), 1.65 – 1.46 (m, 4H), 1.36 (s, 9H), 1.33 – 1.05 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.6, 162.9, 153.4, 144.3, 136.3, 136.0, 133.0, 130.50, 130.46, 128.42, 128.35, 127.0, 114.3, 114.0, 113.2, 112.9, 80.3, 72. 8, 59.2, 42.7, 41.1, 31.2, 31.0, 27.9, 25.0, 23.3, 23.2; IR (film) ν_{max} 3338, 3061, 2937, 2860, 1708, 1640, 1614, 1596, 1581, 1510, 1449, 1420, 1392, 1367, 1262, 1218, 1161, 1100, 1051, 10151, 9071, 8601, 844, 810, 734, 697 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{34}FNNaO_5^+$ $[M + Na]^+$ 530.2313, found 530.2315. HPLC analysis: 96% ee (CHIRALPAK OD-H, 90:10 isopropanol:hexane, 1.0 mL/min, UV: 254 nm), t_R = 6.0 min (minor), 10.8 min (major).

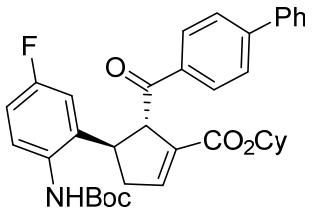
Cyclohexyl (4S,5S)-4-(2-((tert-butoxycarbonyl)amino)-5-fluorophenyl)-5-(4-methoxybenzoyl) cyclopent-1-ene-1-carboxylate (3nc)



3nc

White semi-solid, 98%yield; $[\alpha]^{20}_{D} = -78.2$(*c* 0.715, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 – 7.75 (m, 2H), 7.53 – 7.41 (m, 1H), 7.11 – 6.99 (m, 2H), 6.99 – 6.90 (m, 1H), 6.89 – 6.82 (m, 2H), 5.92 (s, 1H), 4.87 – 4.65 (m, 2H), 3.84 (s, 3H), 3.81 – 3.63 (m, 1H), 3.34 – 3.09 (m, 1H), 2.64 (d, *J* = 19.3 Hz, 1H), 1.84 – 1.67 (m, 3H), 1.65 – 1.52 (m, 2H), 1.51 – 1.42 (m, 1H), 1.38 (s, 9H), 1.34 – 1.14 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.9, 163.5, 162.9, 153.4, 144.1, 136.1, 130.8, 130.54, 130.50, 129.2, 126.7, 114.2, 113.9, 113.6, 113.2, 112.9, 80.2, 72.7, 58.8, 55.2, 42.8, 41.1, 31.2, 31.0, 27.9, 25.1, 23.24, 23.20; IR (film) ν_{max} 3337, 3062, 2938, 2860, 1712, 1674, 1601, 1576, 1511, 1454, 1420, 1392, 1367, 1320, 1264, 1171, 1104, 1051, 1028, 968, 908, 863, 841, 814, 770, 735, 704, 639, 616, 514 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{36}FNNaO_6^+$ $[M + Na]^+$ 560.2419, found 560.2414; HPLC analysis: 97.4%ee (CHIRALPAK OD-H, 90:10 isopropanol:hexane, 1.0 mL/min, UV: 254 nm), t_R = 7.6 min (minor), 15.3 min (major).

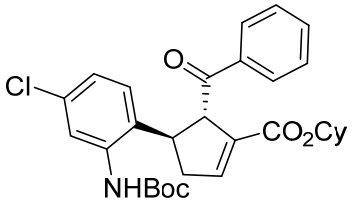
Cyclohexyl (4S,5S)-5-([1,1'-biphenyl]-4-carbonyl)-4-(2-((tert-butoxycarbonyl)amino)-5-fluorophenyl)cyclopent-1-ene-1-carboxylate (3oc)



3oc

White semi-solid, 69%yield; $[\alpha]^{20}_{D}$ = –52.2 (*c* 0.68, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.5 Hz, 2H), 7.68 – 7.56 (m, 4H), 7.52 – 7.36 (m, 4H), 7.15 – 7.04 (m, 2H), 7.00 – 6.91 (m, 1H), 5.92 (s, 1H), 4.89 (d, *J* = 2.6 Hz, 1H), 4.83 – 4.70 (m, 1H), 3.91 – 3.70 (m, 1H), 3.35 – 3.17 (m, 1H), 2.70 (dd, *J* = 11.8, 9.4 Hz, 1H), 1.85 – 1.67 (m, 3H), 1.66 – 1.53 (m, 2H), 1.52 – 1.41 (m, 1H), 1.36 (s, 9H), 1.35 – 1.16 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.2, 162.9, 153.5, 145.7, 144.3, 139.5, 136.1, 135.0, 130.54, 130.50, 129.1, 128.7, 128.0, 127.0, 114.3, 114.0, 113.3, 113.0, 80.3, 72.8, 59.2, 42.8, 41.2, 31.2, 31.1, 27.9, 25.1, 23.29, 23.25; IR (film) ν_{max} 3338, 2963, 2938, 2860, 1708, 1603, 1560, 1509, 1486, 1450, 1406, 1367, 1261, 1160, 1097, 1015, 862, 800, 760, 739, 698 cm^{-1}; HRMS (ESI) calcd for $C_{36}H_{38}FNNaO_5^+$ $[M + Na]^+$ 606.2626, found 606.2630; HPLC analysis: 97.5%ee (CHIRALPAK RC-OD-H, 90:10 isopropanol:hexane, 1.0 mL/min, UV: 254 nm), t_R = 6.2 min (minor), 12.2 min (major).

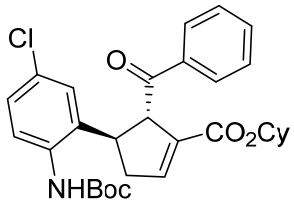
Cyclohexyl (4S,5S)-5-benzoyl-4-(2-((tert-butoxycarbonyl)amino)-4-chlorophenyl)cyclopent-1-ene-1-carboxylate (3pc)



3pc

White semi-solid, 81%yield; $[\alpha]^{20}_{D}$ = –124.5(*c* 0.615, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 – 7.75 (m, 3H), 7.60 – 7.49 (m, 1H), 7.45 – 7.36 (m, 2H), 7.25 – 7.18 (m, 1H), 7.14 – 7.06 (m, 2H), 6.14 (s, 1H), 4.91 – 4.80 (m, 1H), 4.80 – 4.65 (m, 1H), 3.79 – 3.60 (m, 1H), 3.23 (ddt, *J* = 19.1, 9.2, 2.6 Hz, 1H), 2.78 – 2.59 (m, 1H), 1.82 – 1.67 (m, 2H), 1.64 – 1.52 (m, 2H), 1.51 – 1.43 (m, 1H), 1.40 (s, 9H), 1.34 – 1.20 (m, 5H), 1.19 – 1.09 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.6, 162.8, 152.9, 144.2, 136.2, 136.0, 133.4, 133.1, 130.4, 128.5, 128.4, 127.4, 126.6, 80.5, 72.8, 59.1, 42.6, 40.9, 31.2, 31.0, 27.9, 25.0, 23.3, 23.2; IR (film) ν_{max} 3336, 2937, 2860, 1709, 1597, 1579, 1512, 1449, 1414, 1367, 1274, 1235, 1158, 1103, 1013, 930, 859, 812, 749, 700 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{34}ClNNaO_5^+$ $[M + Na]^+$ 546.2018, found 546.2016; HPLC analysis: 97%ee (chiralpak OD-H, 95:5 isopropanol:hexane, 1.0 mL/min, UV: 254 nm), t_R = 8.2 min (major), 18.7 min (minor).

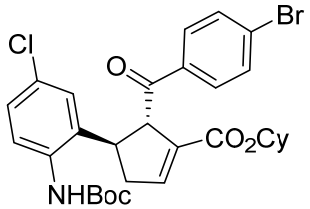
Cyclohexyl (4S,5S)-5-benzoyl-4-(2-((tert-butoxycarbonyl)amino)-5-chlorophenyl)cyclopent-1-ene-1-carboxylate (3qc)



3qc

White semi-solid, 92%yield; $[\alpha]^{20}_{D} = -135.8$ (*c* 0.83, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 – 7.75 (m, 3H), 7.60 – 7.49 (m, 1H), 7.45 – 7.36 (m, 3H), 7.25 – 7.18 (m, 1H), 7.14 – 7.06 (m, 2H), 6.14 (s, 1H), 4.91 – 4.80 (m, 1H), 4.80 – 4.65 (m, 1H), 3.79 – 3.60 (m, 1H), 3.23 (ddt, *J* = 19.1, 9.2, 2.6 Hz, 1H), 2.78 – 2.59 (m, 1H), 1.82 – 1.67 (m, 2H), 1.64 – 1.52 (m, 2H), 1.51 – 1.43 (m, 1H), 1.40 (s, 9H), 1.34 – 1.20 (m, 5H), 1.19 – 1.09 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.6, 162.8, 152.9, 144.2, 136.2, 136.0, 133.4, 133.1, 130.4, 128.5, 128.4, 127.4, 126.6, 80.5, 72.8, 59.1, 42.6, 40.9, 31.2, 31.0, 27.9, 25.0, 23.3, 23.2; IR (film) ν_{max} 3337, 2937, 2860, 1708, 1595, 1577, 1510, 1449, 1410, 1367, 1275, 1235, 1157, 1104, 1013, 927, 854, 809, 748 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{34}ClNNaO_5^+$ $[M + Na]^+$ 546.2018, found 546.2016; HPLC analysis: 97%ee (chiralpak OD-H, 95:5 isopropanol:hexane, 1.0 mL/min, UV: 254 nm), t_R = 8.2 min (major), 18.7 min (minor).

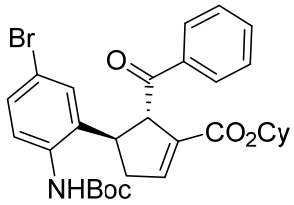
Cyclohexyl (4S,5S)-5-(4-bromobenzoyl)-4-(2-((tert-butoxycarbonyl)amino)-5-chlorophenyl) cyclopent-1-ene-1-carboxylate (3rc)



3rc

White semi-solid, 87%yield; $[\alpha]^{20}_{D} = -126.0$ (*c* 0.635, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 2H), 7.57 – 7.50 (m, 2H), 7.46 – 7.36 (m, 1H), 7.12 – 7.07 (m, 1H), 7.06 – 7.00 (m, 1H), 6.99 – 6.90 (m, 1H), 5.93 (s, 1H), 4.85 – 4.64 (m, 2H), 3.90 – 3.72 (m, 1H), 3.24 (ddt, *J* = 19.0, 9.1, 2.5 Hz, 1H), 2.78 – 2.56 (m, 1H), 1.84 – 1.61 (m, 2H), 1.61 – 1.40 (m, 4H), 1.37 (s, 9H), 1.33 – 1.24 (m, 4H), 1.23 – 1.15 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.7, 162.8, 162.1, 158.9, 153.5, 144.5, 140.4, 135.9, 135.0, 131.7, 130.4, 130.0, 128.4, 127.1, 114.4, 114.1, 113.2, 112.9, 80.4, 72.9, 59.2, 42.7, 41.2, 31.2, 31.1, 27.9, 25.0, 23.30, 23.27; IR (film) ν_{max} 3339, 2937, 2860, 1706, 1638, 1614, 1585, 1512, 1485, 1453, 1420, 1395, 1367, 1276, 1244, 1160, 1103, 1070, 1051, 1007, 907, 860, 837, 813, 771, 736 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{33}BrClNNaO_5^+$ $[M + Na]^+$ 624.1123, found 624.1129; HPLC analysis: 97.5%ee (chiralpak IA-H, 95:5 isopropanol:hexane, 1.0 mL/min, UV: 254 nm), t_R = 15.6 min (major), 20.5 min (minor).

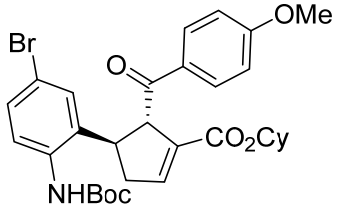
Cyclohexyl (4S,5S)-5-benzoyl-4-(5-bromo-2-((tert-butoxycarbonyl)amino)phenyl)cyclopent-1-ene-1-carboxylate (3sc)



3sc

White semi-solid, 90%yield; $[\alpha]^{20}_{D}$ = –130.2(*c* 1.045, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 2H), 7.61 – 7.47 (m, 2H), 7.46 – 7.31 (m, 4H), 7.14 – 7.00 (m, 1H), 5.98 (s, 1H), 4.98 – 4.80 (m, 1H), 4.81 – 4.65 (m, 1H), 3.78 – 3.64 (m, 1H), 3.24 (ddt, *J* = 19.1, 9.3, 2.6 Hz, 1H), 2.84 – 2.58 (m, 1H), 1.83 – 1.65 (m, 2H), 1.64 – 1.54 (m, 2H), 1.52 – 1.43 (m, 1H), 1.39 (s, 9H), 1.35 – 1.12 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.6, 162.8, 152.8, 144.2, 138.1, 136.2, 136.0, 133.9, 133.2, 130.4, 129.6, 128.5, 128.4, 125.3, 118.1, 80.5, 72.9, 59.0, 42.6, 40.9, 31.2, 31.0, 27.9, 25.0, 23.29, 23.24; IR (film) ν_{max} 3337, 3061, 2936, 2860, 1712, 1597, 1580, 1505, 1449, 1392, 1367, 1261, 1158, 1098, 1016, 802, 747, 702 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{34}BrNNaO_5^+$ $[M + Na]^+$ 590.1513, found 590.1509; HPLC analysis: 96%ee (CHIRALPAK OD-H, 90:10 isopropanol:hexane, 1.0 mL/min, UV: 254 nm), t_R = 6.1 min (minor), 12.2 min (major).

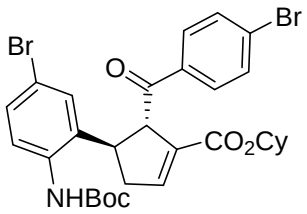
Cyclohexyl (4S,5S)-4-(5-bromo-2-((tert-butoxycarbonyl)amino)phenyl)-5-(4-methoxybenzoyl) cyclopent-1-ene-1-carboxylate (3tc)



3tc

White semi-solid, 89%yield; $[\alpha]^{20}_{D}$ = –143.5 (*c* 0.71, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 – 7.73 (m, 2H), 7.59 – 7.50 (m, 1H), 7.44 – 7.39 (m, 1H), 7.38 – 7.32 (m, 1H), 7.08 (d, *J* = 1.6 Hz, 1H), 6.95 – 6.81 (m, 2H), 6.05 (s, 1H), 4.77 (t, *J* = 6.2 Hz, 1H), 3.84 (s, 2H), 3.76 – 3.63 (m, 1H), 3.23 (ddt, *J* = 19.1, 9.2, 2.6 Hz, 1H), 2.83 – 2.55 (m, 1H), 1.75 (d, *J* = 11.1 Hz, 1H), 1.65 – 1.54 (m, 2H), 1.47 (m, 4H), 1.39 (s, 9H), 1.33 – 1.14 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.9, 163.6, 162.9, 152.8, 144.0, 136.1, 134.0, 130.9, 130.3, 129.5, 129.1, 125.1, 117.9, 113.6, 80.5, 72.7, 58.7, 55.2, 42.6, 40.8, 31.2, 31.1, 27.9, 25.1, 23.25, 23.21; IR (film) ν_{max} 3337, 2936, 2859, 1711, 1674, 1600, 1576, 1510, 1455, 1421, 1392, 1367, 1319, 1263, 1228, 1170, 1103, 1050, 1026, 908, 839, 770, 738, 640, 615 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{36}BrNNaO_6^+$ $[M + Na]^+$ 620.1618, found 620.1612; HPLC analysis: 97.4%ee (CHIRALPAK OD-H, 90:10 isopropanol:hexane, 1.0 mL/min, UV: 254 nm), t_R = 7.6 min (minor), 15.3 min (major).

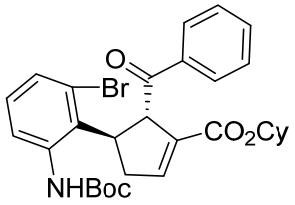
Cyclohexyl (4S,5S)-4-(5-bromo-2-((tert-butoxycarbonyl)amino)phenyl)-5-(4-bromobenzoyl) cyclopent-1-ene-1-carboxylate (3uc)



3uc

White semi-solid, 80%yield; $[\alpha]^{20}_{D} = -125.9$ (*c* 0.635, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 – 7.65 (m, 2H), 7.54 (m, 3H), 7.44 – 7.34 (m, 2H), 7.15 – 7.05 (m, 1H), 6.01 (s, 1H), 4.76 (d, *J* = 2.7 Hz, 1H), 3.73 (m, 1H), 3.25 (ddt, *J* = 19.1, 9.2, 2.6 Hz, 1H), 2.84 – 2.60 (m, 1H), 1.84 – 1.68 (m, 2H), 1.62 (m, 3H), 1.48 (m, 1H), 1.39 (s, 9H), 1.36 – 1.13 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.8, 162.7, 152.8, 144.4, 138.3, 135.9, 135.0, 133.9, 131.7, 130.5, 130.0, 129.5, 128.5, 125.6, 118.3, 80.7, 73.0, 59.1, 42.5, 41.0, 31.2, 31.1, 27.9, 25.0, 23.32, 23.29; IR (film) ν_{max} 3341, 2936, 2860, 1706, 1641, 1585, 1505, 1453, 1397, 1367, 1262, 1159, 1102, 1070, 1050, 1007, 908, 853, 806, 770, 735 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{33}Br_2NNaO_5^+$ $[M + Na]^+$ 670.0600, found 670.0599; HPLC analysis: 96%ee (CHIRALPAK RC-OD-H, 90:10 isopropanol:hexane, 1.0 mL/min, UV: 254 nm), t_R = 8.2 min (minor), 19.0 min (major).

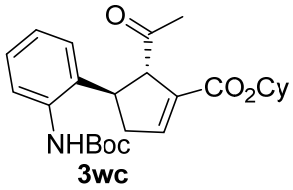
Cyclohexyl (4S,5S)-5-benzoyl-4-(2-bromo-6-((tert-butoxycarbonyl)amino)pheny-l)cyclopent -1-ene-1-carboxylate (3vc)



3vc

White semi-solid, 97%yield; $[\alpha]^{20}_{D} = -106.1$ (*c* 0.89, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 1.9 Hz, 1H), 7.83 – 7.77 (m, 2H), 7.58 – 7.50 (m, 1H), 7.44 – 7.36 (m, 2H), 7.29 – 7.22 (m, 1H), 7.19 – 7.13 (m, 1H), 7.12 – 7.05 (m, 1H), 6.12 (s, 1H), 4.83 (d, *J* = 2.6 Hz, 1H), 4.80 – 4.68 (m, 1H), 3.79 – 3.62 (m, 1H), 3.23 (ddt, *J* = 19.0, 9.2, 2.6 Hz, 1H), 2.78 – 2.53 (m, 1H), 1.82 – 1.67 (m, 2H), 1.64 – 1.50 (m, 2H), 1.40 (s, 9H), 1.34 – 1.18 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.6, 162.8, 152.6, 144.3, 136.2, 136.1, 134.1, 133.2, 128.44, 128.41, 128.1, 127.8, 120.7, 80.7, 72.8, 58.8, 42.6, 40.8, 31.2, 31.0, 27.9, 25.0, 23.3, 23.2; IR (film) ν_{max} 3337, 3062, 2937, 2860, 1712, 1641, 1595, 1577, 1511, 1449, 1410, 1392, 1367, 1263, 1158, 1103, 1051, 1014, 919, 855, 806, 747, 700, 572 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{34}BrNNaO_5^+$ $[M + Na]^+$ 590.1513, found 590.1518; HPLC analysis: 97%ee (CHIRALPAK AD-H, 90:10 isopropanol:hexane, 1.0 mL/min, UV: 254 nm), t_R = 16.5 min (major), 40.7 min (minor).

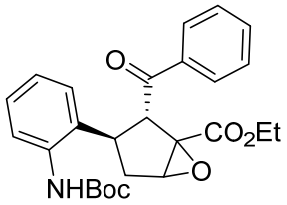
Cyclohexyl (4S,5S)-5-acetyl-4-(2-((tert-butoxycarbonyl)amino)phenyl)cyclopent-1-ene-1-carboxylate (3wc)



3wc

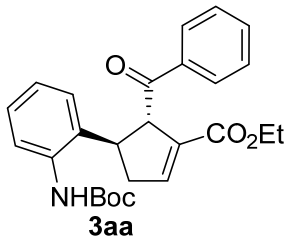
Colorless liquid, 96%yield; $[\alpha]^{20}_{D}$ = –49.1 (*c* 0.56, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.9 Hz, 1H), 7.27 – 7.18 (m, 2H), 7.17 – 7.09 (m, 1H), 7.04 (dd, *J* = 4.2, 2.5 Hz, 1H), 6.65 (s, 1H), 4.82 (td, *J* = 8.8, 3.9 Hz, 1H), 3.93 (d, *J* = 2.4 Hz, 1H), 3.80 (dt, *J* = 10.0, 5.0 Hz, 1H), 3.11 (ddt, *J* = 19.1, 8.9, 2.6 Hz, 1H), 2.73 – 2.57 (m, 1H), 2.24 (s, 3H), 1.94 – 1.64 (m, 4H), 1.57 (d, *J* = 3.2 Hz, 1H), 1.52 (s, 9H), 1.48 – 1.38 (m, 3H), 1.31 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.0, 163.2, 153.6, 144.8, 136.5, 135.3, 134.7, 127.2, 126.1, 125.2, 124.3, 80.2, 73.0, 64.6, 42.0, 40.1, 31.4, 31.3, 30.0, 28.1, 25.1, 23.5; IR (film) ν_{max} 3336, 2979, 2932, 1714, 1634, 1587, 1514, 1451, 1392, 1368, 1246, 1164, 1100, 1048, 1023, 910, 860, 752, 617 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{27}NNaO_5^+$ $[M + Na]^+$ 450.2251, found 450.2247; HPLC analysis: 97%ee (chiralpak AD-H, 95:5 isopropanol:hexane, 1.0 mL/min, UV: 254 nm), t_R = 13.6 min (major), 19.4 min (minor).

Ethyl (2S,3S)-2-benzoyl-3-(2-((tert-butoxycarbonyl)amino)phenyl)-6-oxabicyclo[3.1.0]-hexane-1-carboxylate (8)

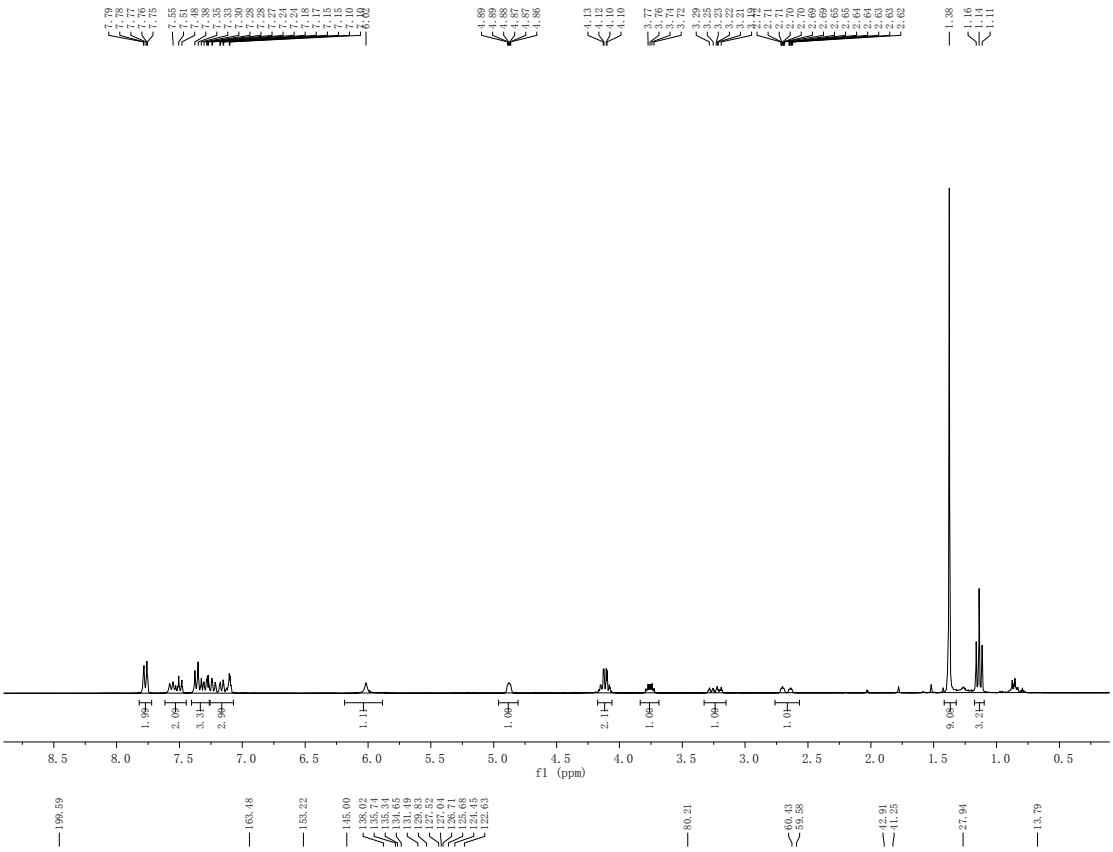


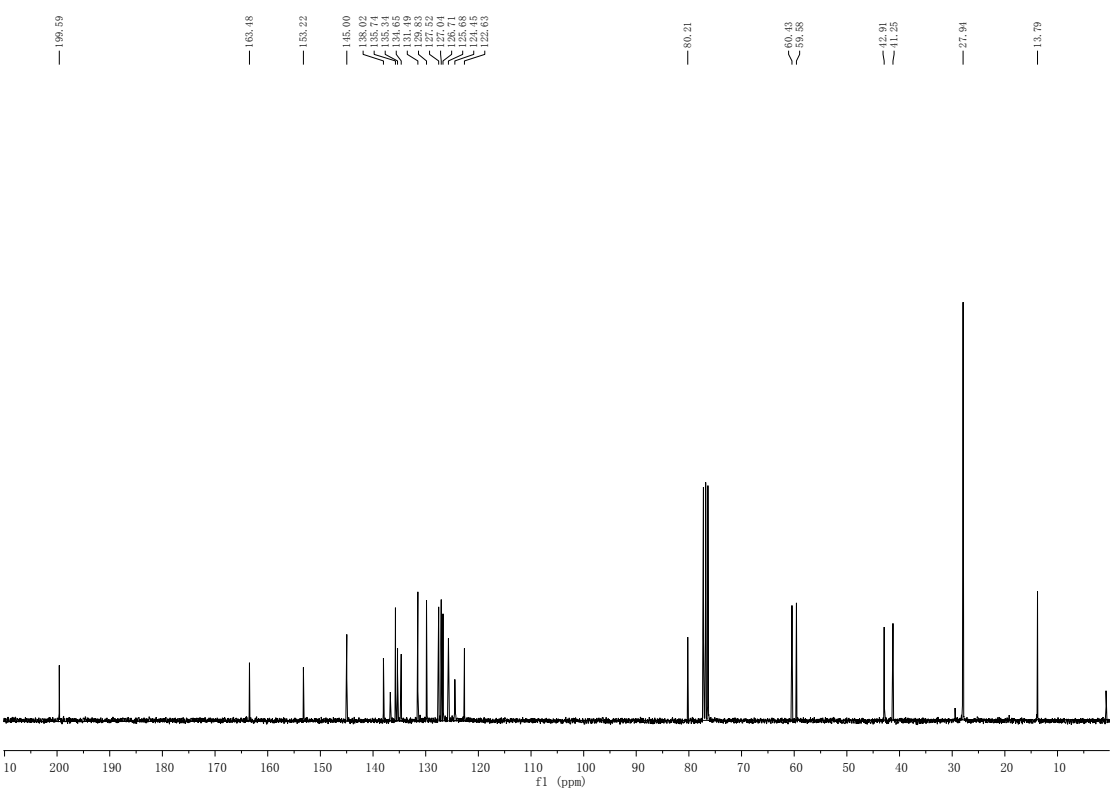
8

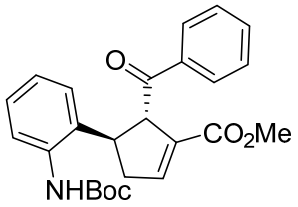
Prepared according to the general procedure as described above in 89 % yield. It was purified by flash chromatography (10% EtOAc/PE) to afford yellow liquid. $[\alpha]^{20}_{D}$ = –105.9 (*c* 0.62, CH_2Cl_2) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 – 7.63 (m, 2H), 7.55 – 7.42 (m, 2H), 7.41 – 7.34 (m, 1H), 7.33 – 7.26 (m, 2H), 7.20 – 7.09 (m, 2H), 4.42 (d, *J* = 9.9 Hz, 1H), 4.06 (q, *J* = 7.1 Hz, 1H), 3.85 (s, 1H), 3.71 (dt, *J* = 17.8, 8.9 Hz, 1H), 2.65 (dd, *J* = 14.6, 7.6 Hz, 1H), 2.16 (dd, *J* = 13.5, 10.3 Hz, 1H), 1.49 (s, 6H), 1.08 (t, *J* = 7.1 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 199.5, 167.5, 153.4, 136.8, 135.9, 133.1, 131.2, 128.4, 128.0, 127.4, 127.1, 124.7, 123.8, 80.2, 64.1, 61.8, 61.2, 55.0, 35.8, 35.4, 28.2, 13.6; IR (film) ν_{max} 3358, 2979, 2932, 1727, 1677, 1589, 1517, 1478, 1450, 1391, 1367, 1299, 1226, 1159, 1122, 1072, 1053, 1023, 946, 885, 752, 690 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{29}NNaO_6^+$ $[M + Na]^+$ 474.1894, found 474.1898 ; HPLC analysis: 96%ee (CHIRALPAK RC-OD-H, 90:10 isopropanol:hexane, 1.0 mL/min, UV: 254 nm), t_R = 13.0 min (major), 18.6 min (minor).



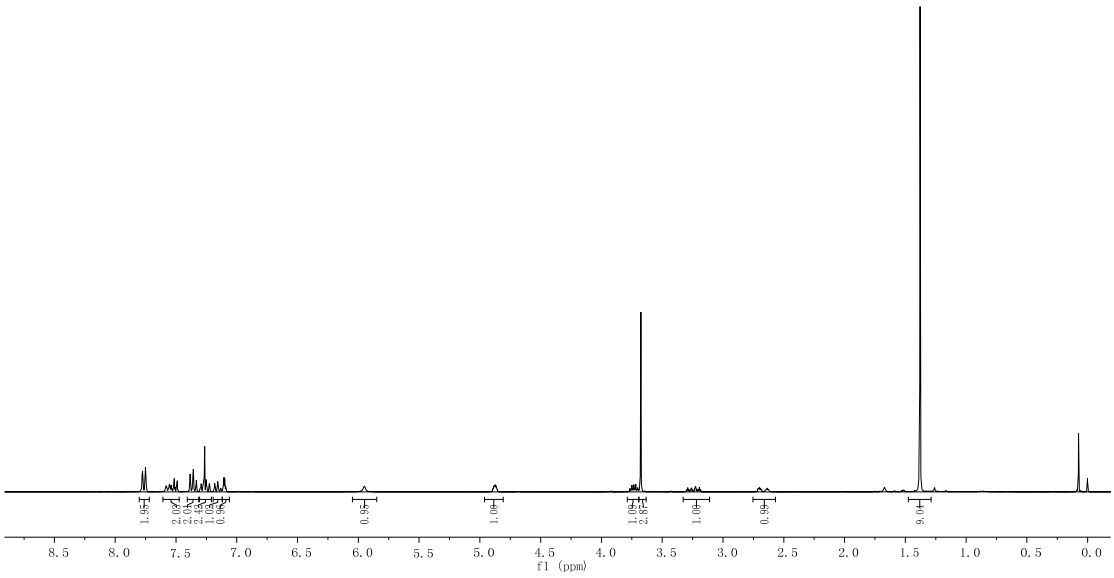
3aa

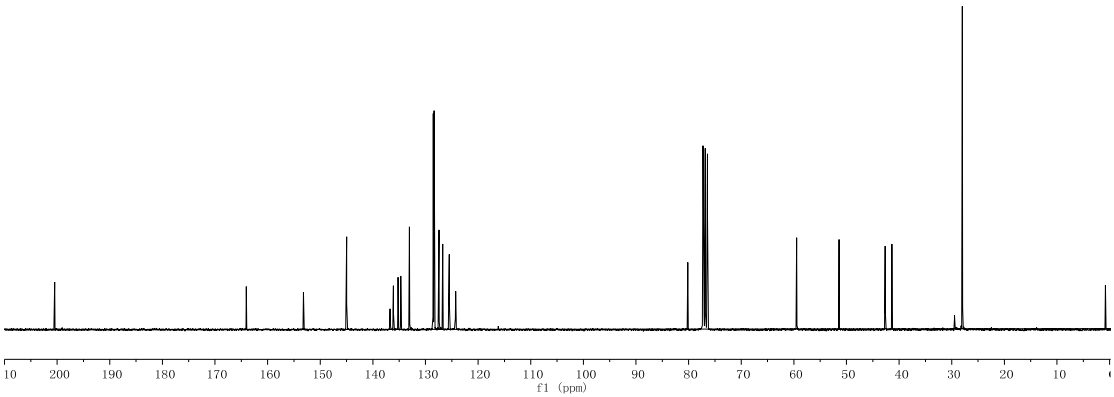


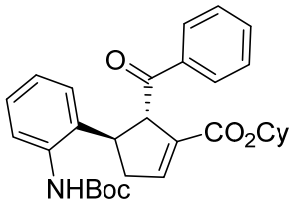



O
CO2Me
NHBoc

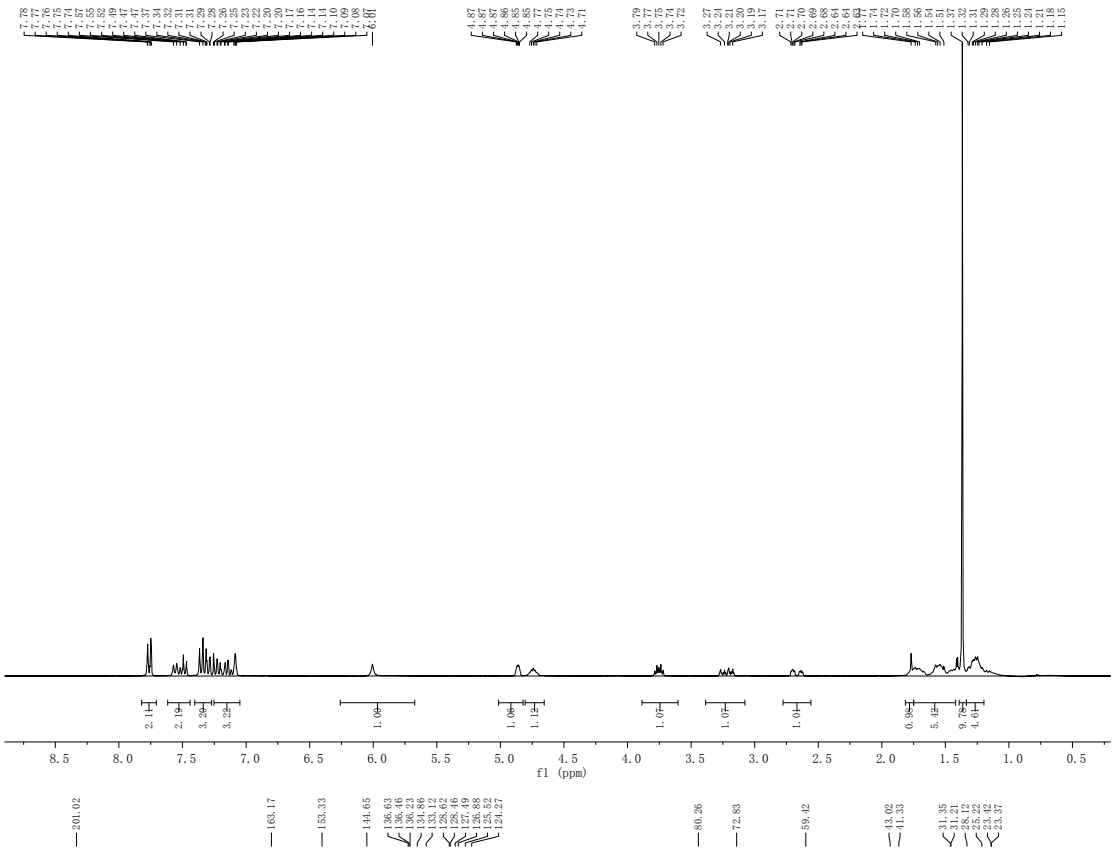
3ab

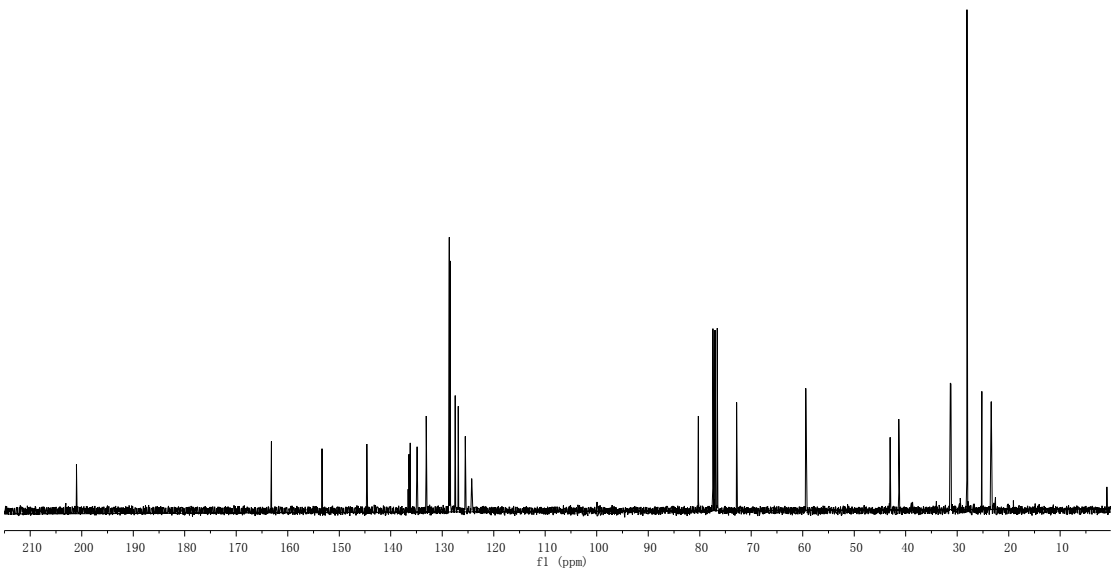

1.95
2.08
2.05
2.00
0.98
0.95
1.08
1.09
2.83
1.00
0.99
9.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

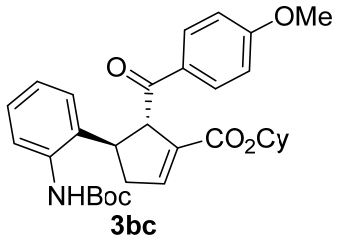

10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



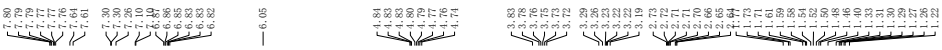
3ac

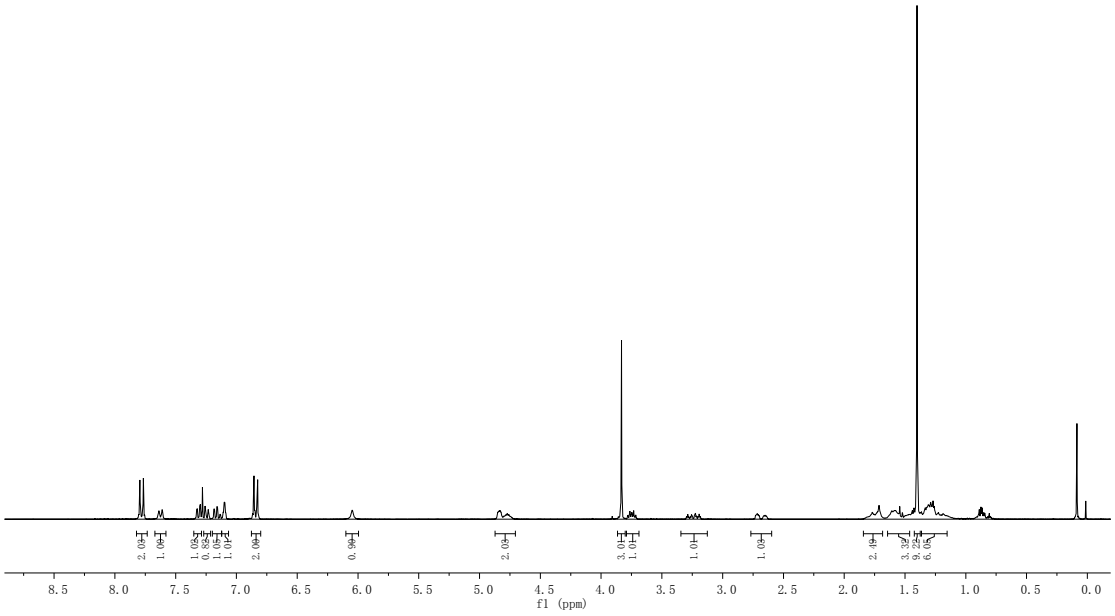


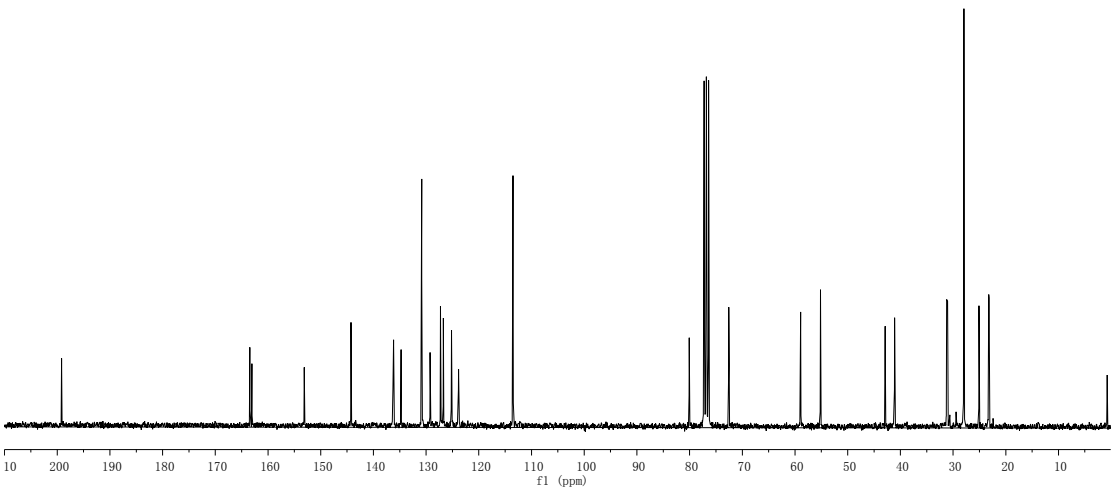


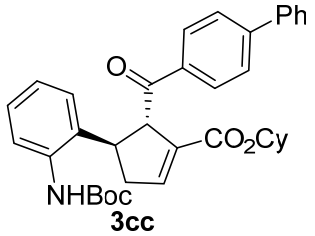


3bc

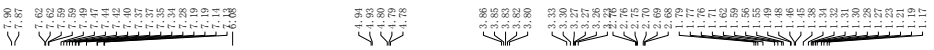


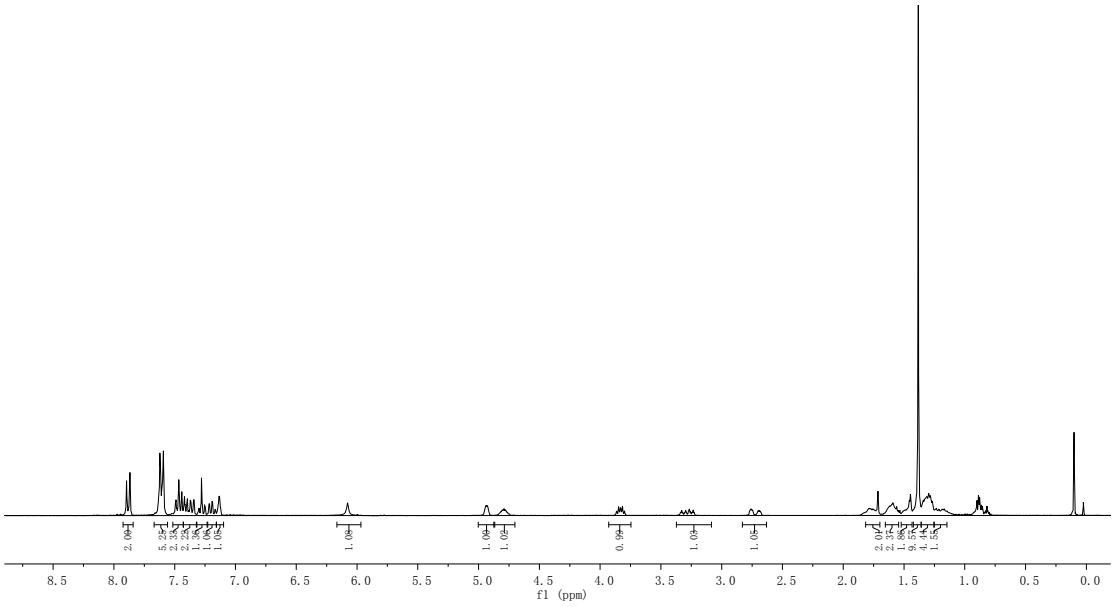


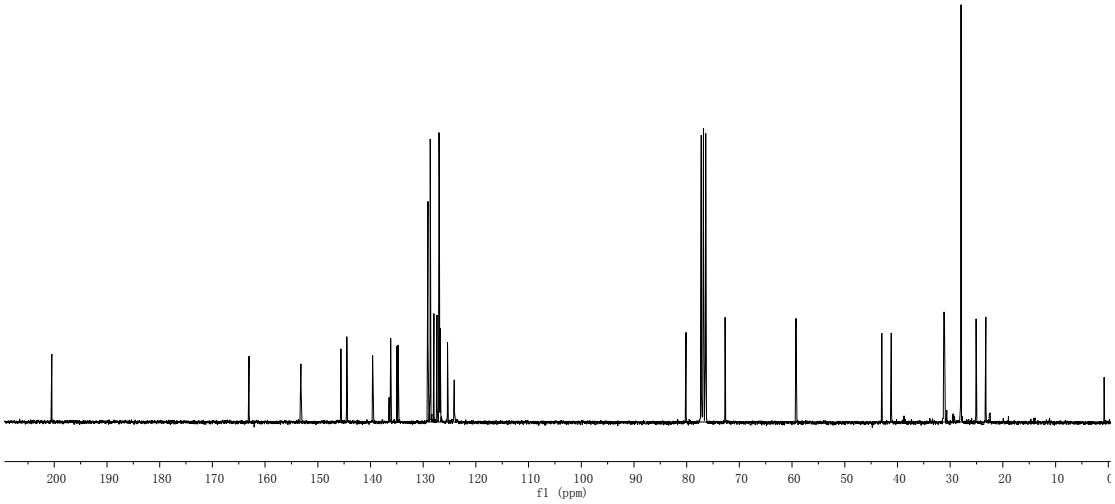


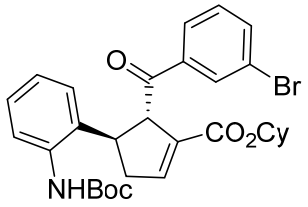


3cc

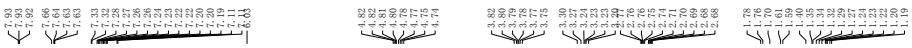


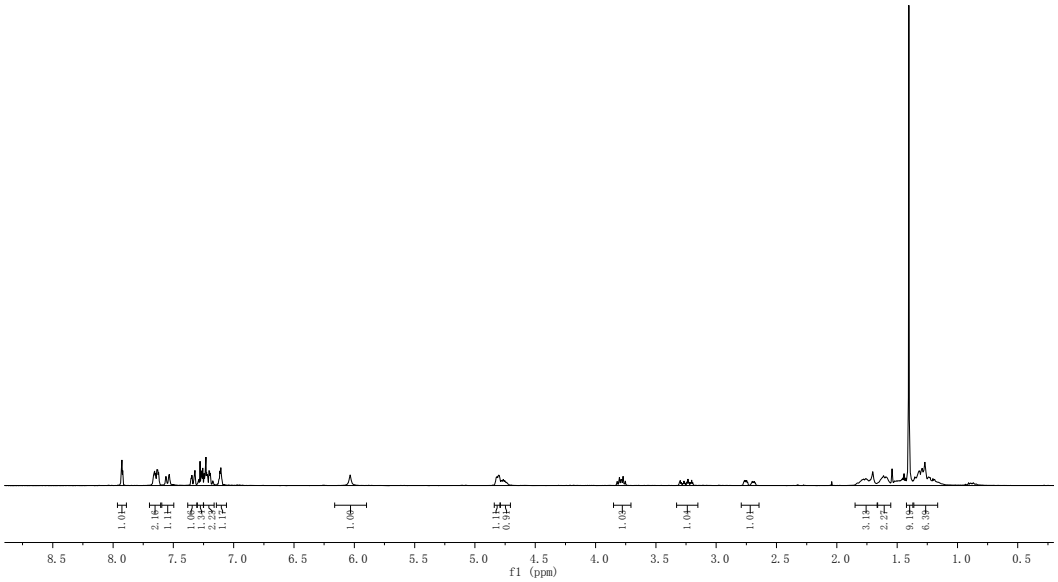


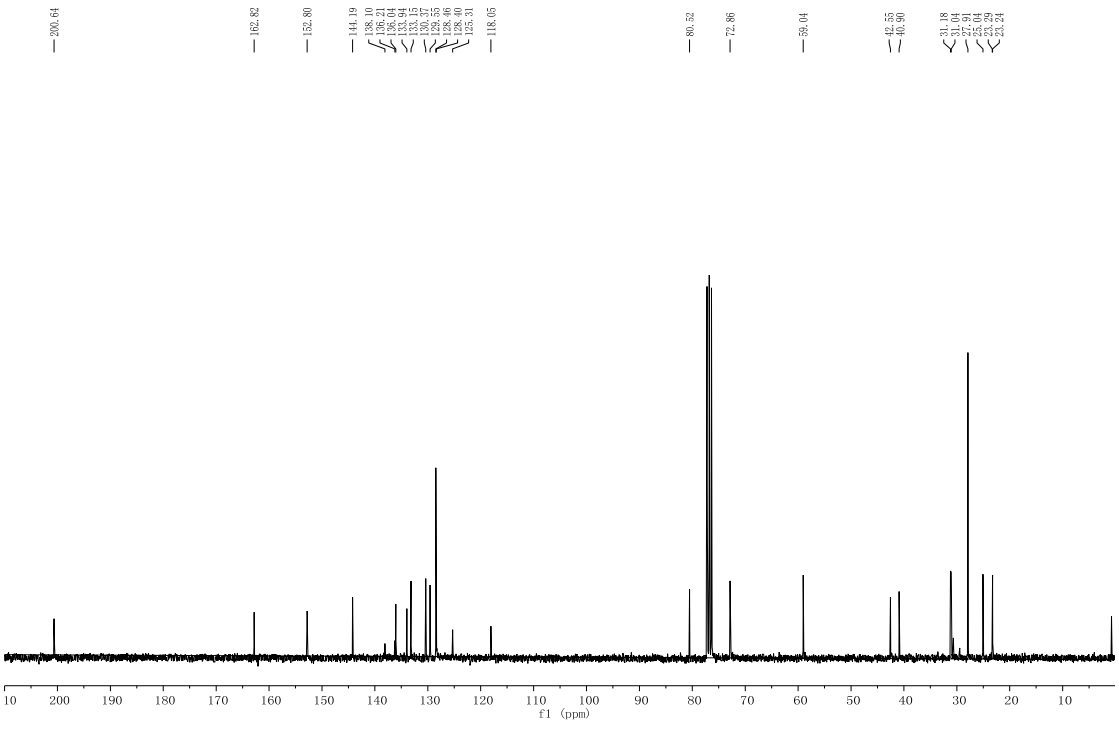


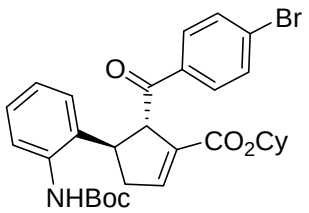


3dc

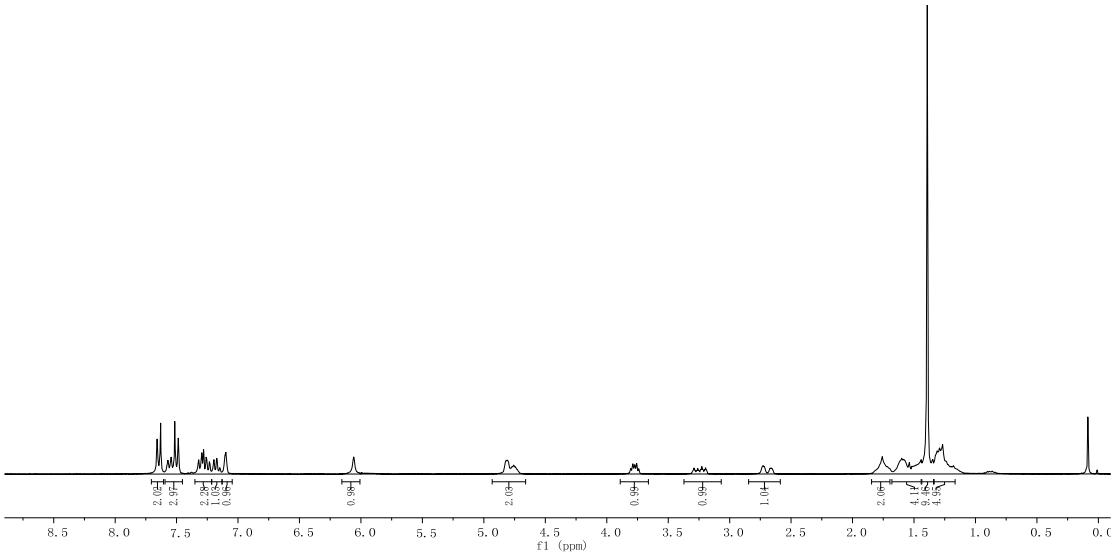


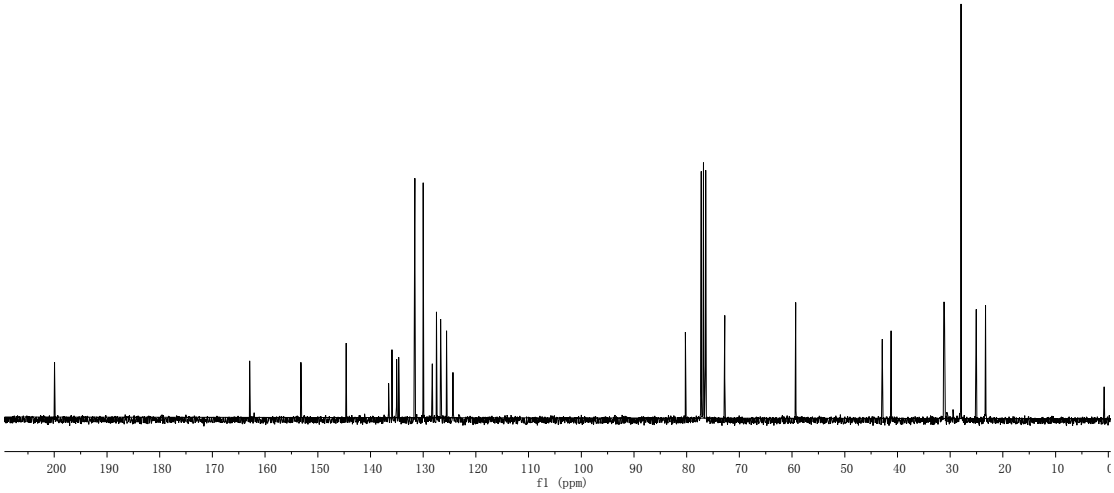


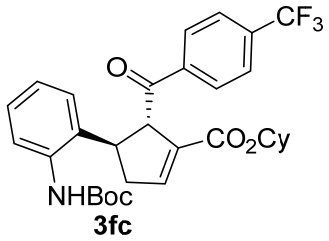




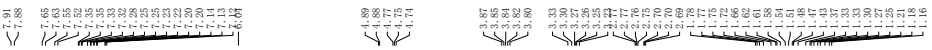
3ec

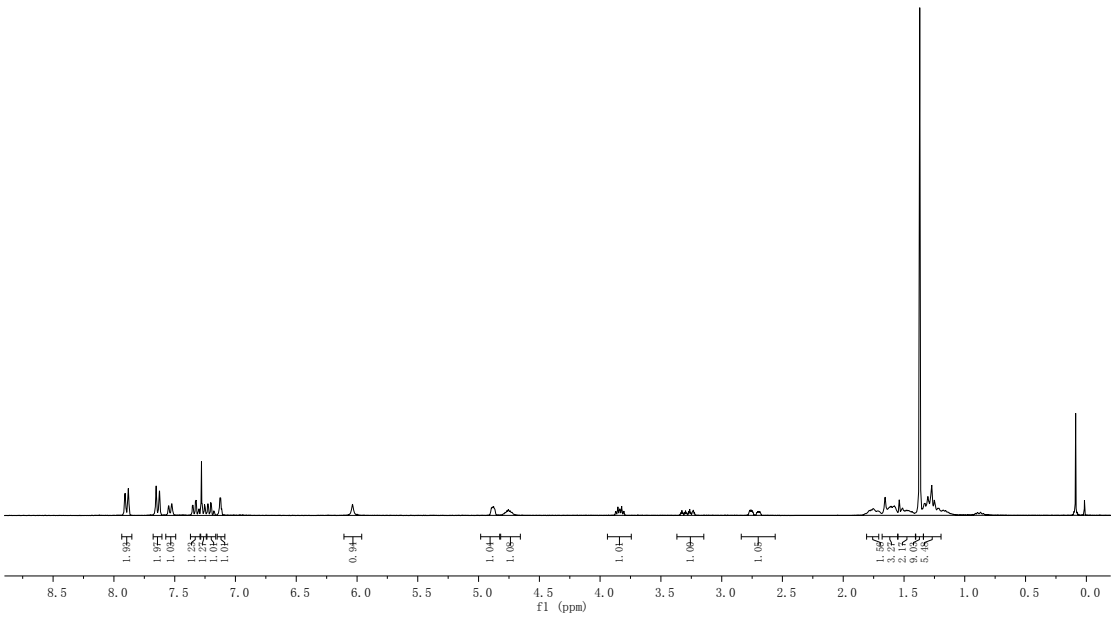


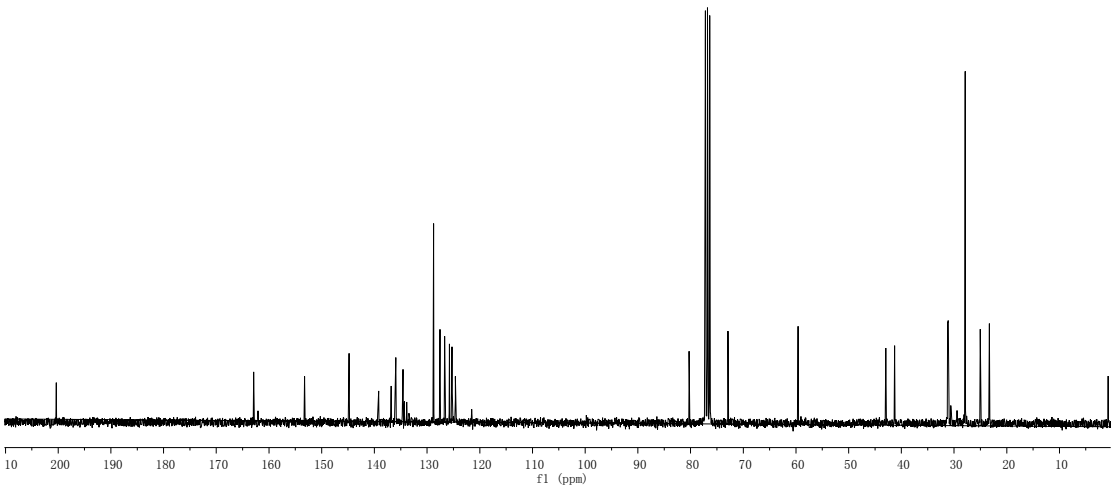


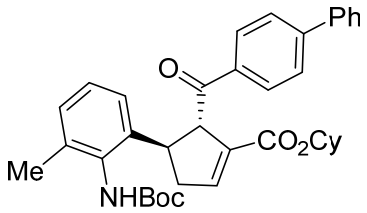


3fc

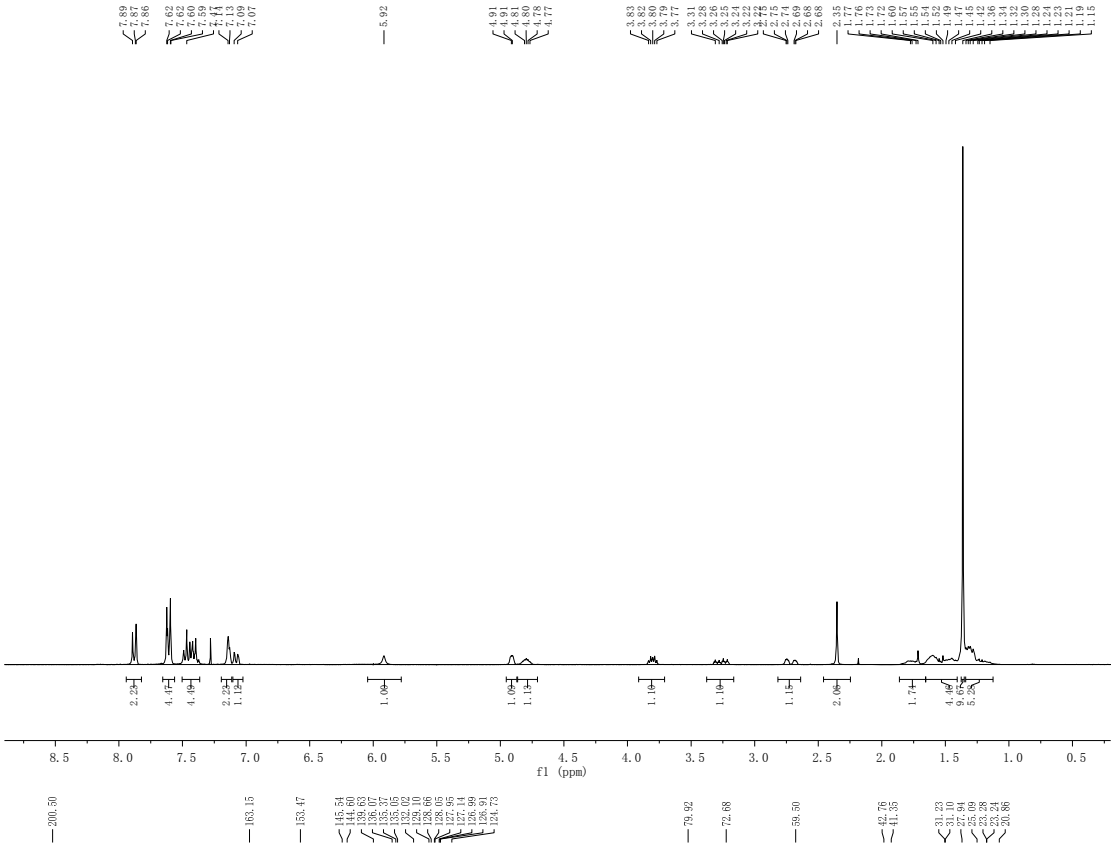


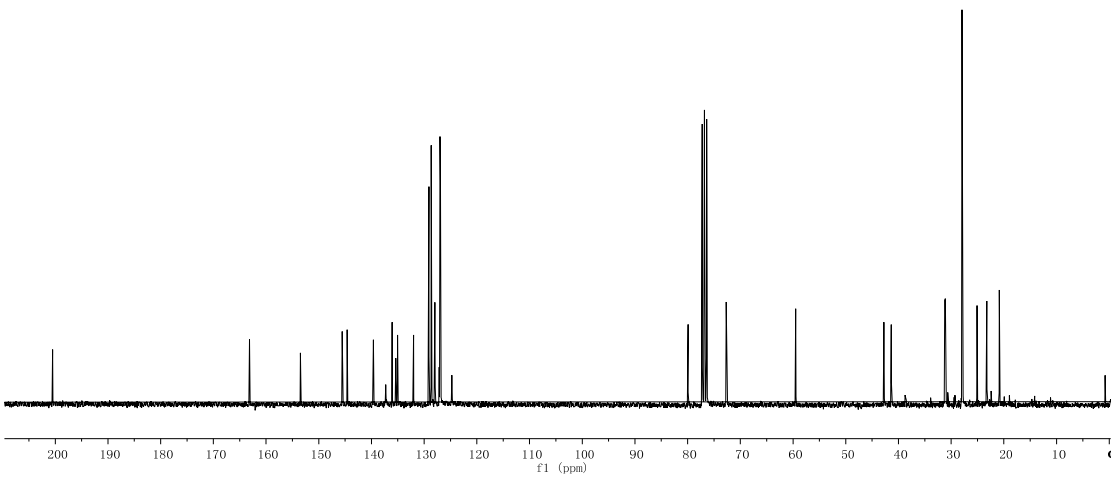


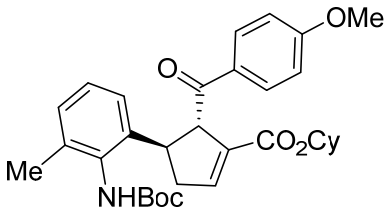




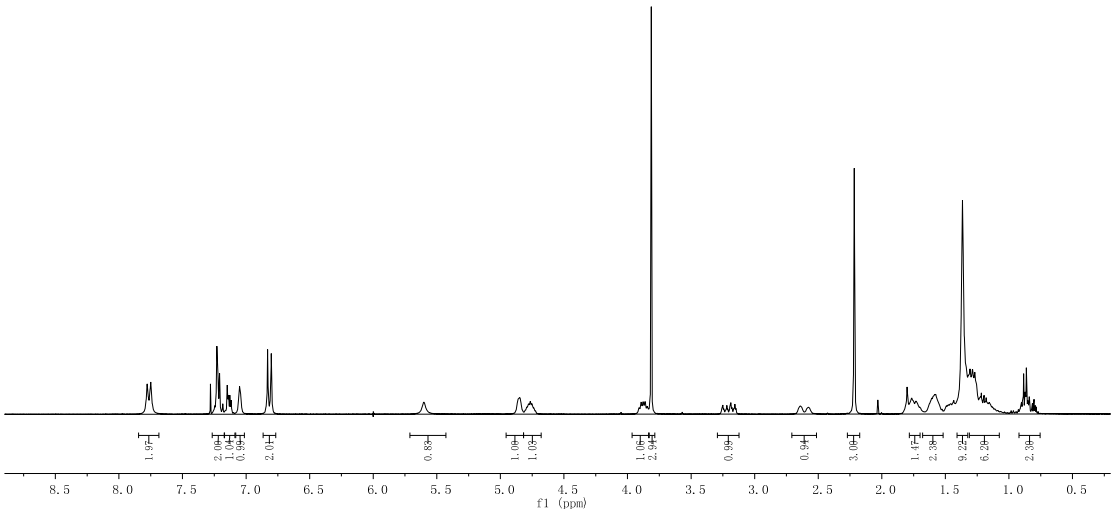
3gc

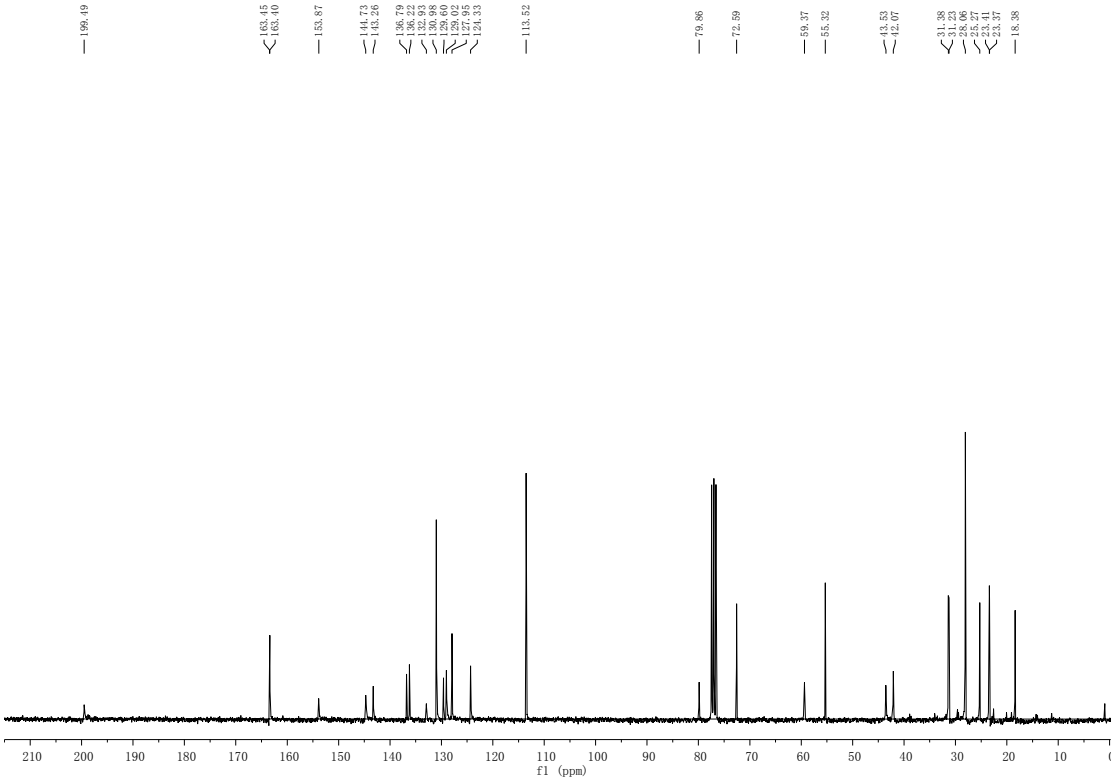


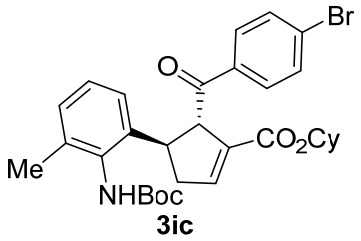




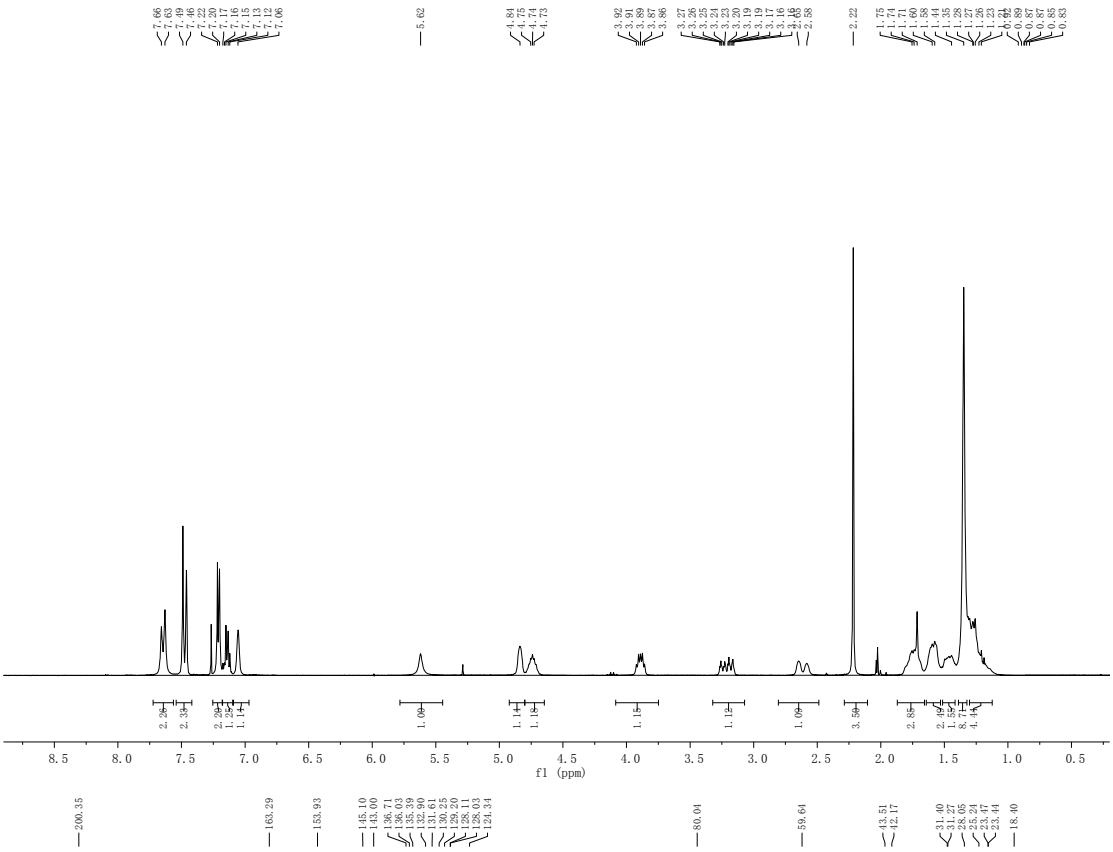
3hc

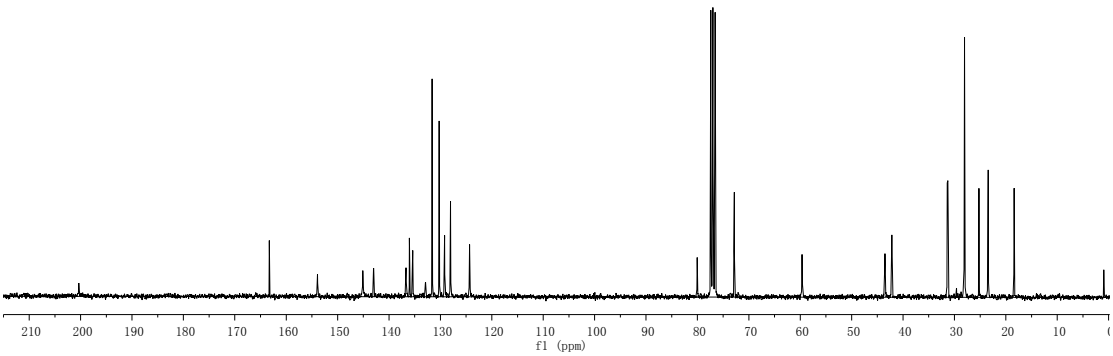


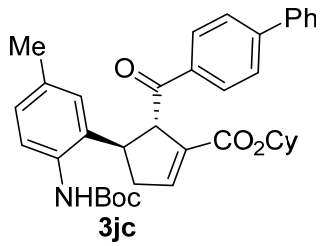




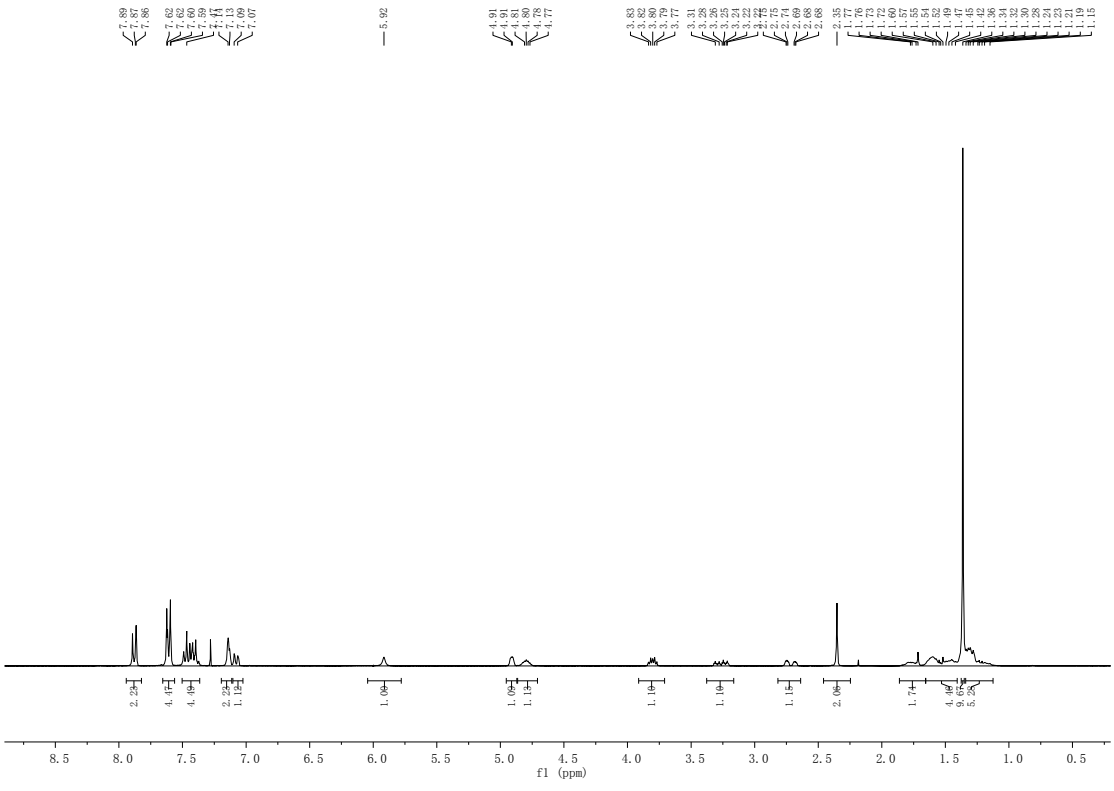
3ic

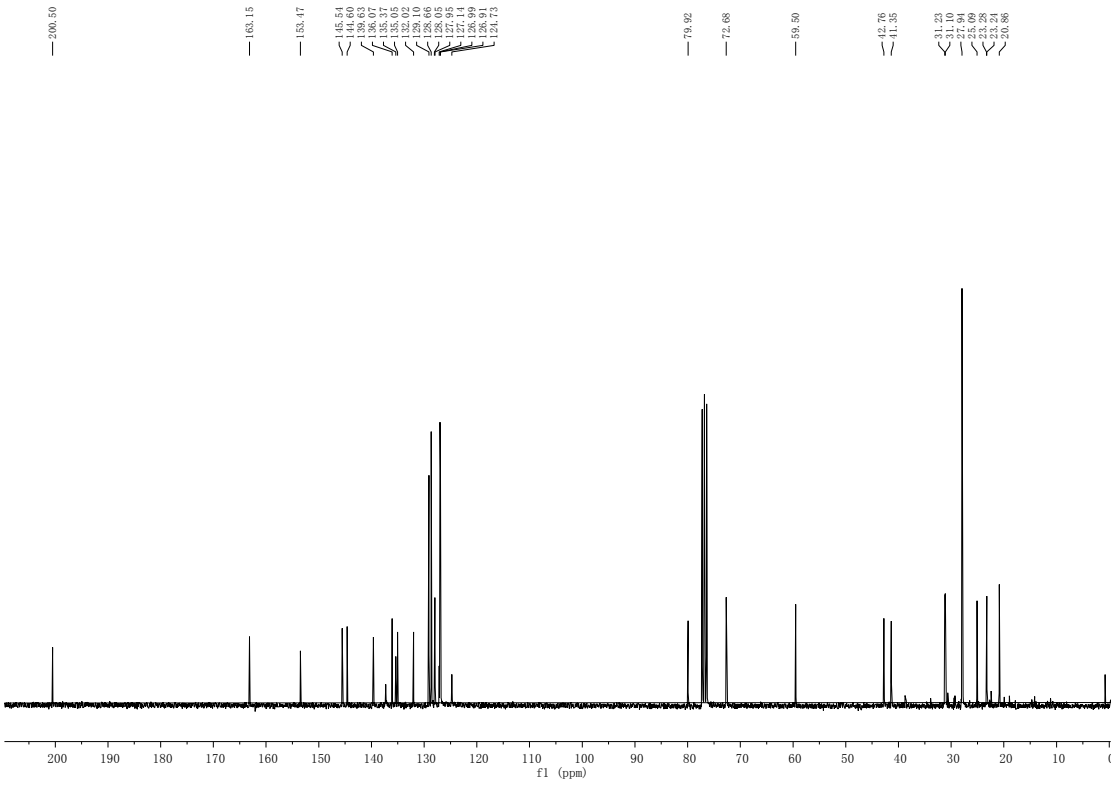


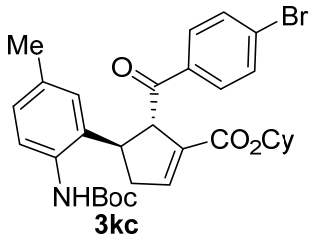




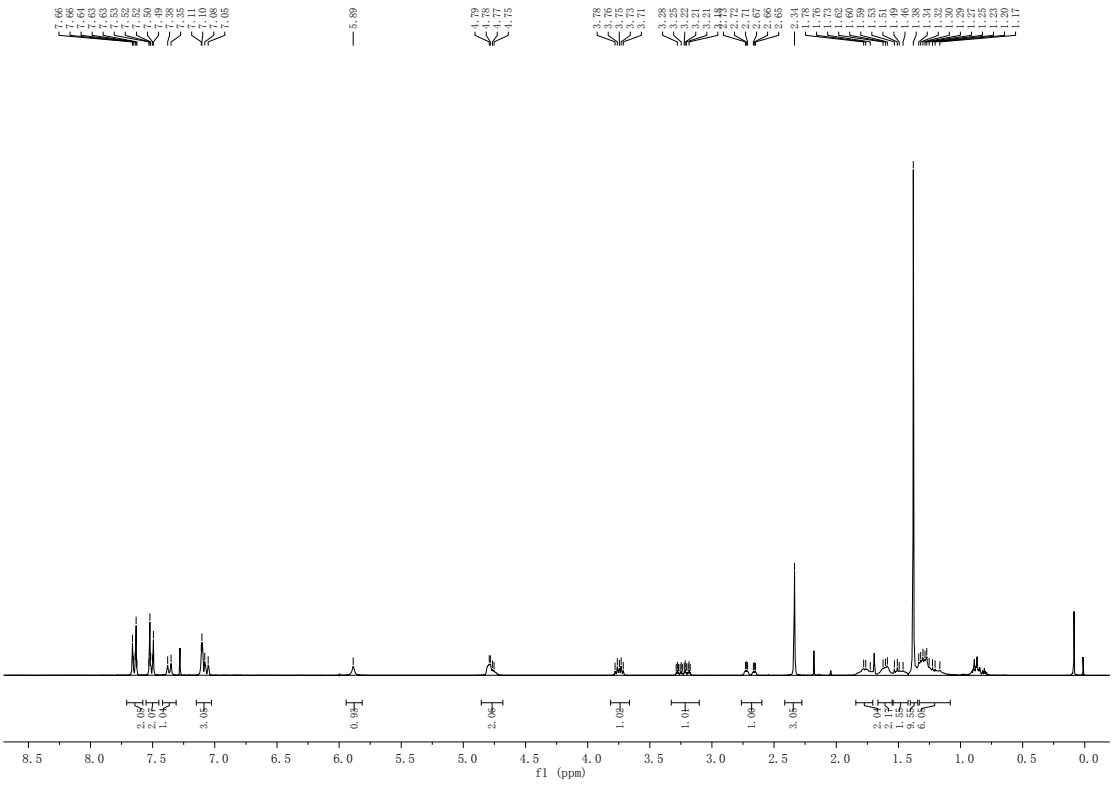
3jc

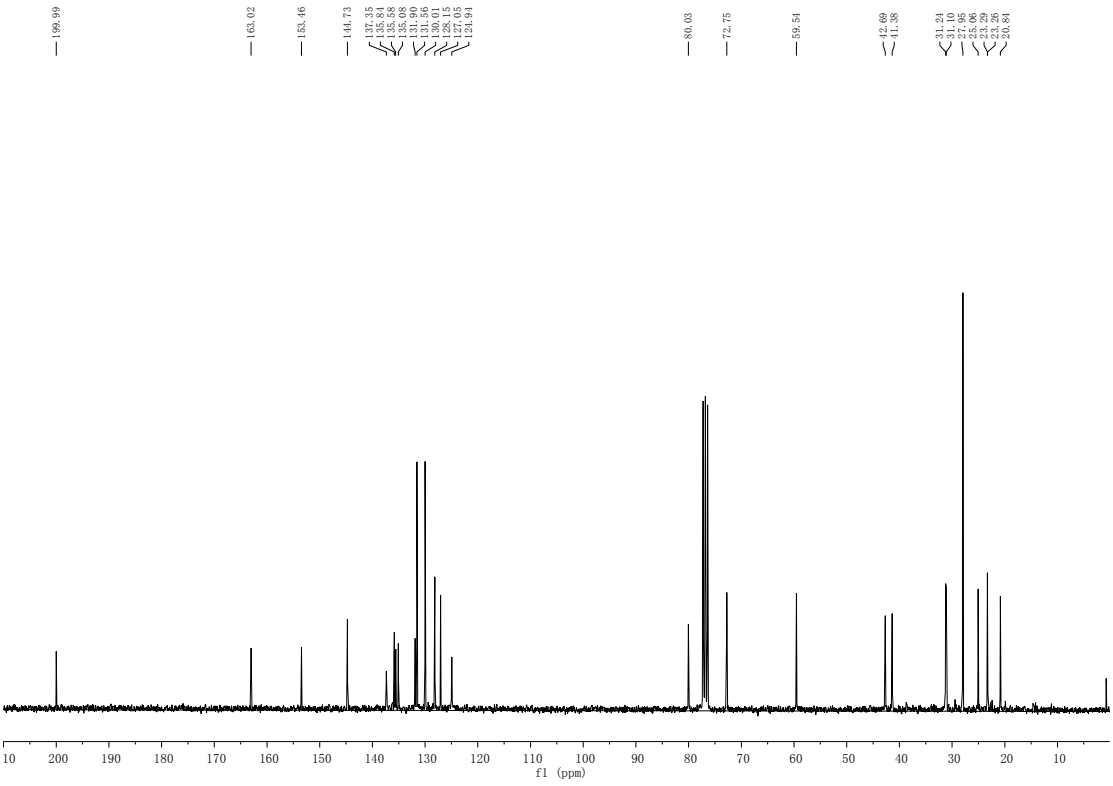


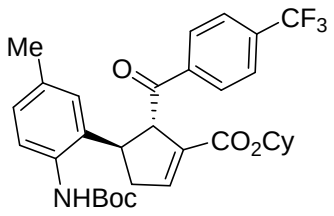




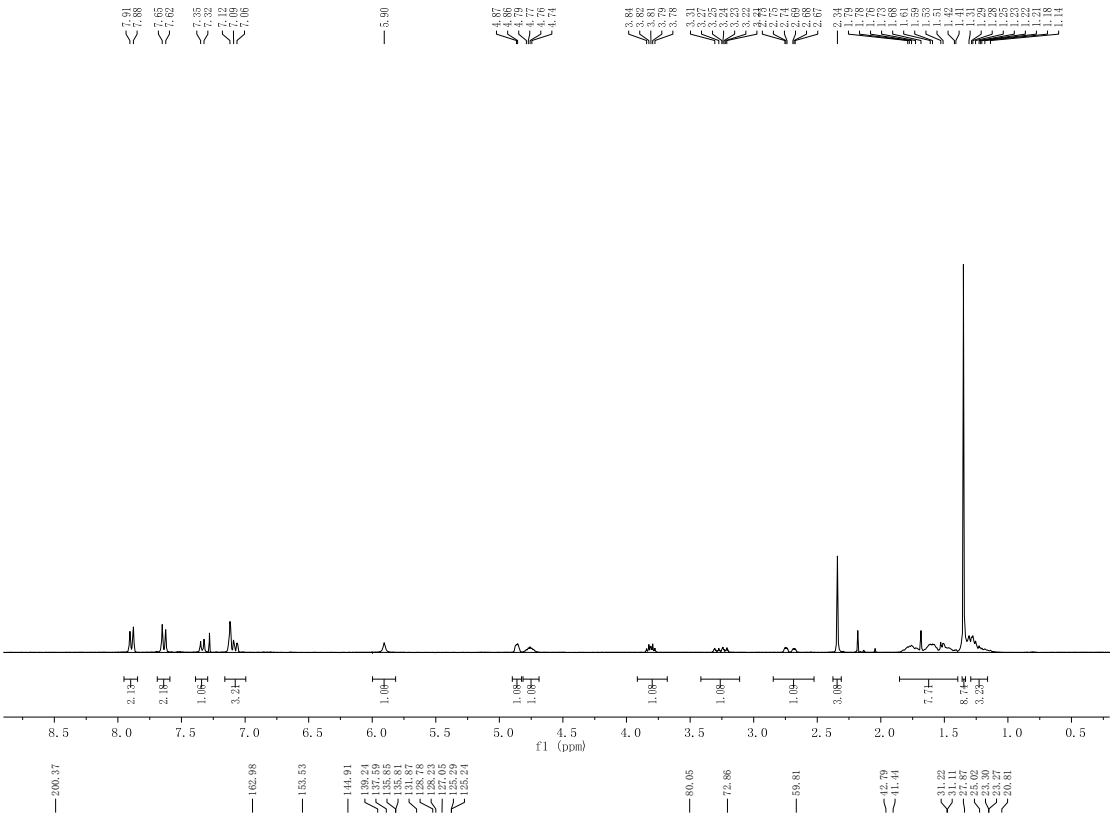
3kc

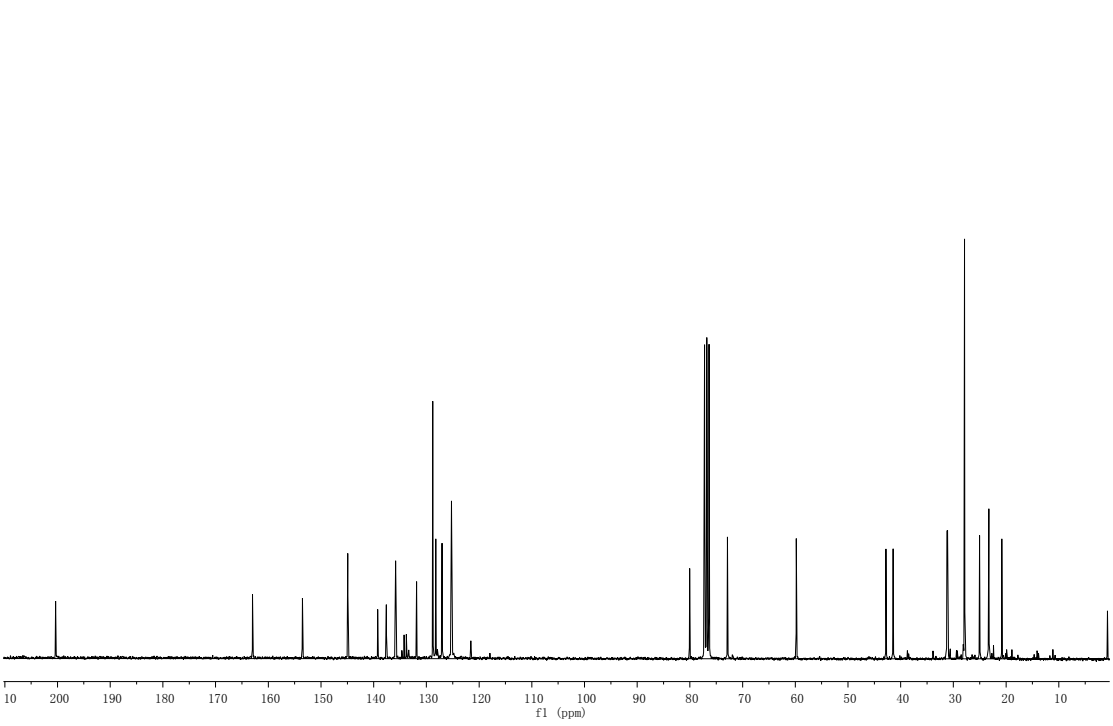


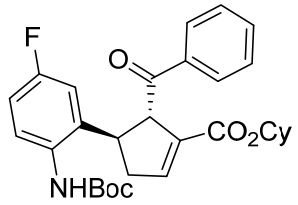




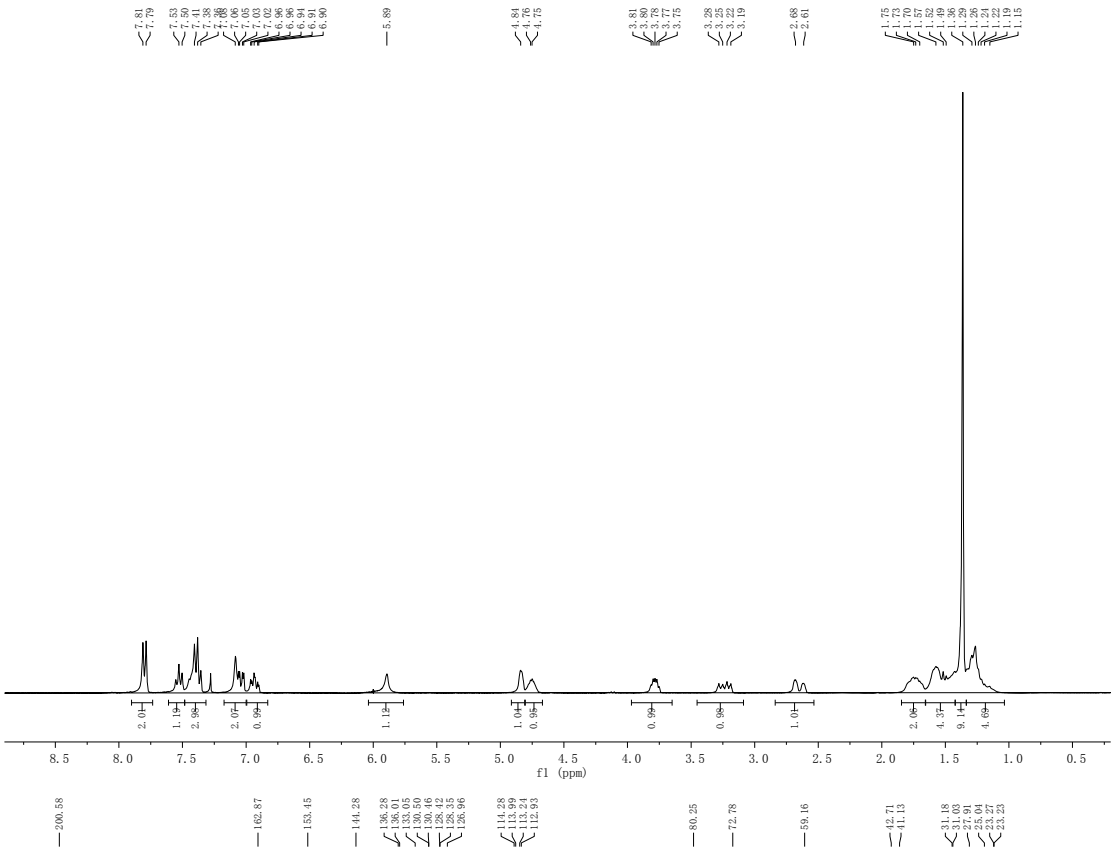
3lc

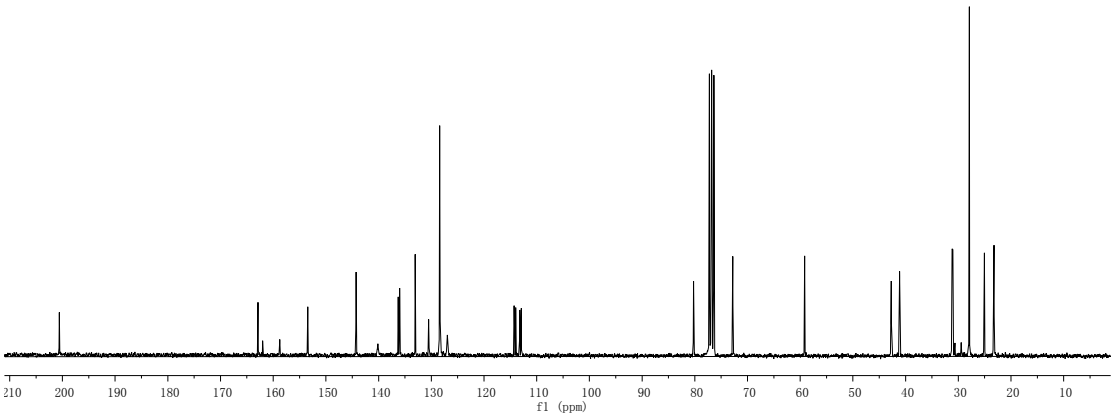


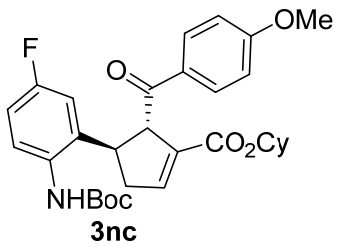




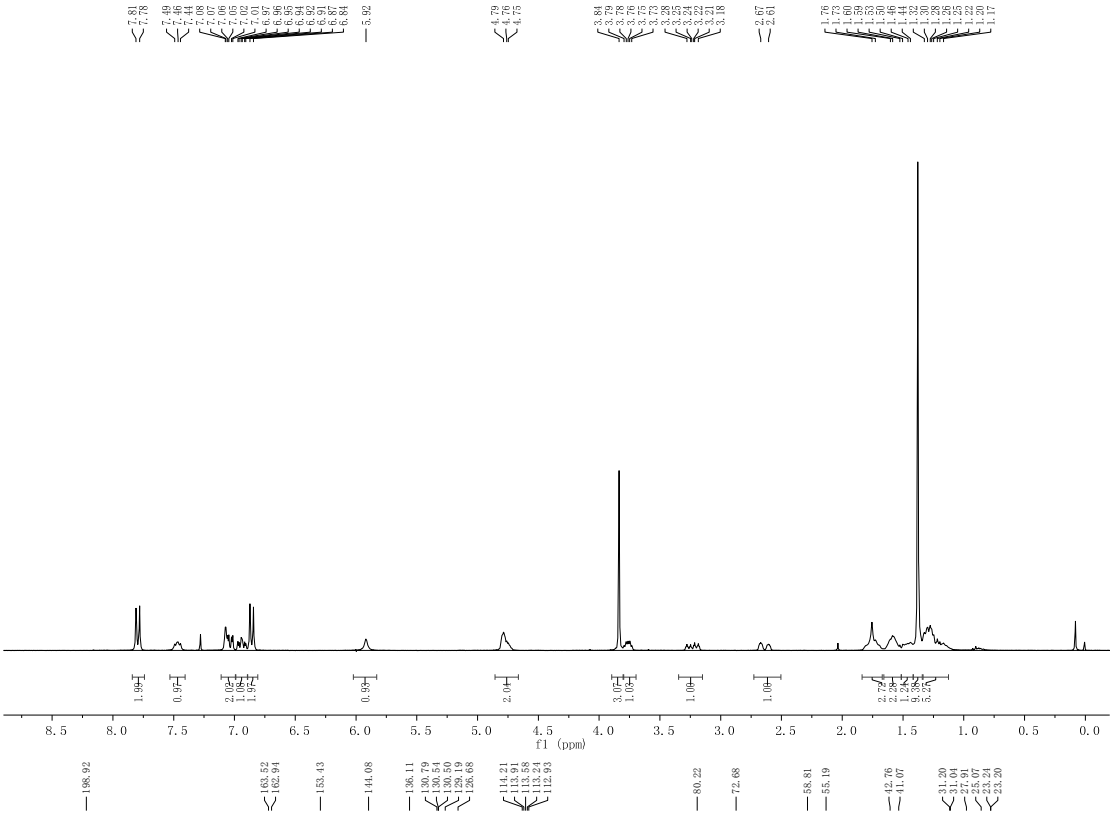
3mc

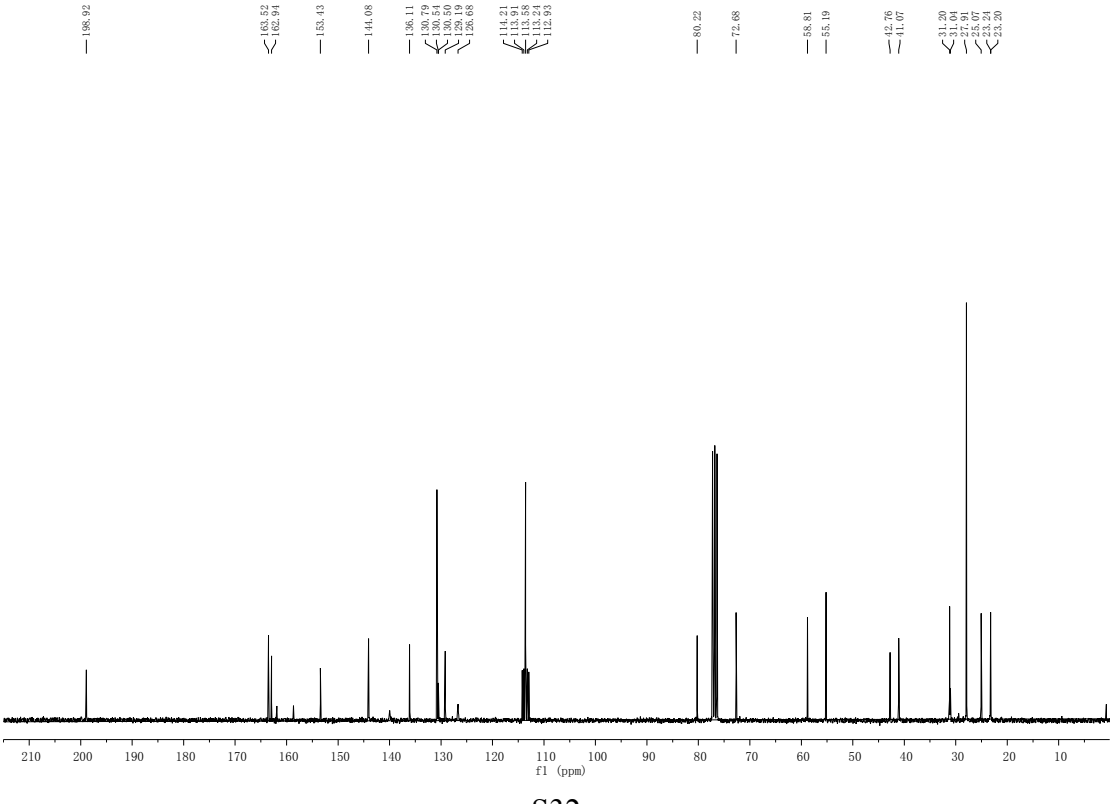


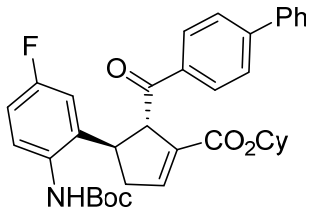




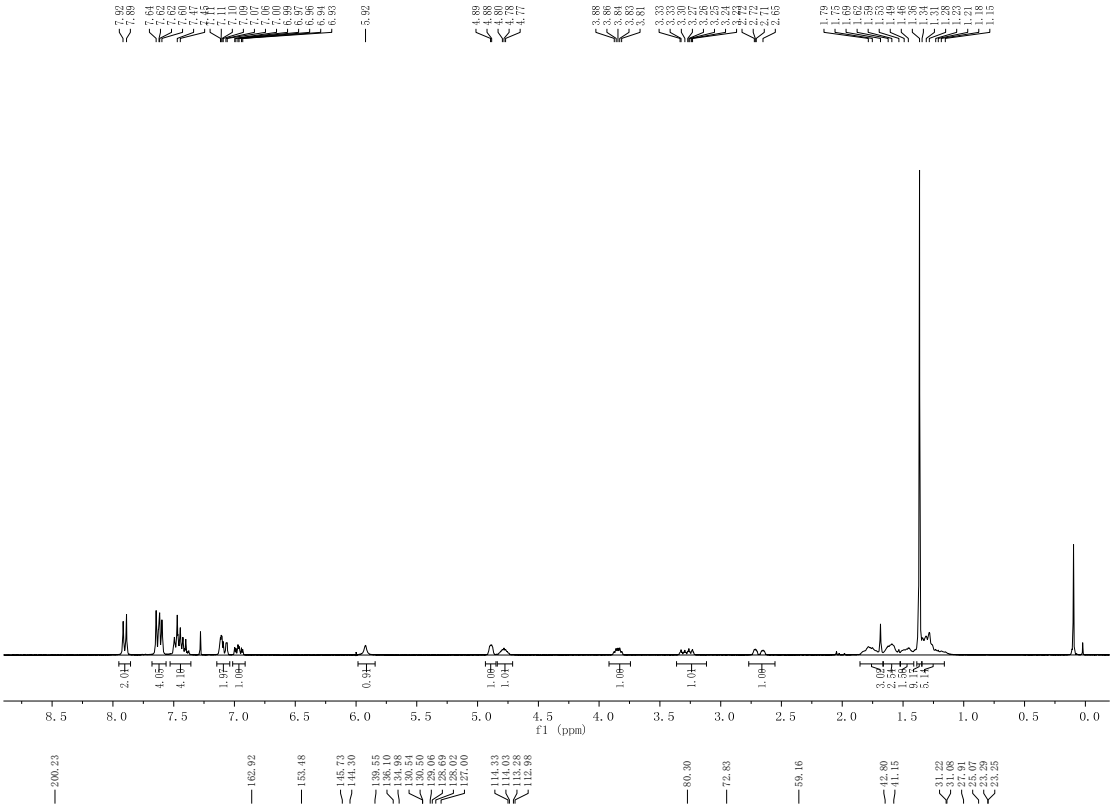
3nc

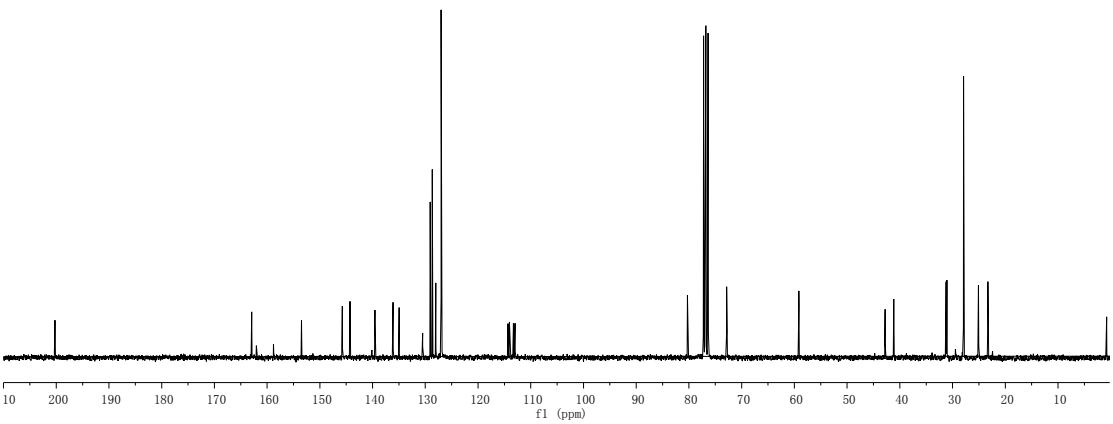


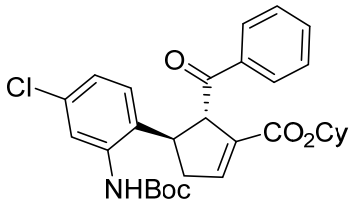




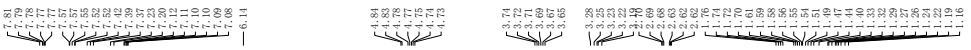
3oc

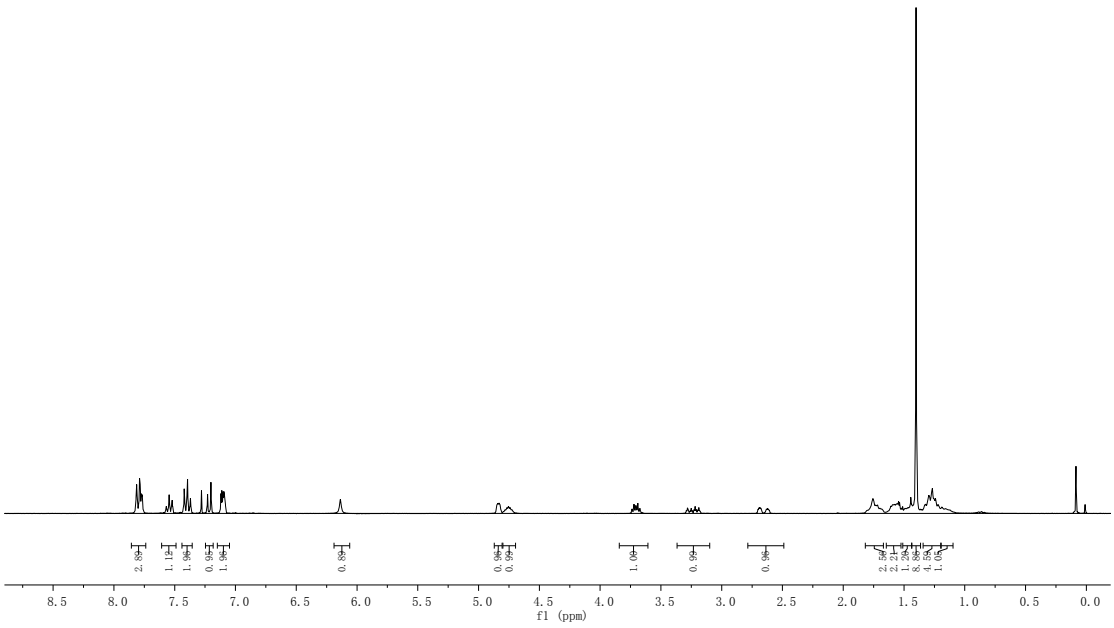


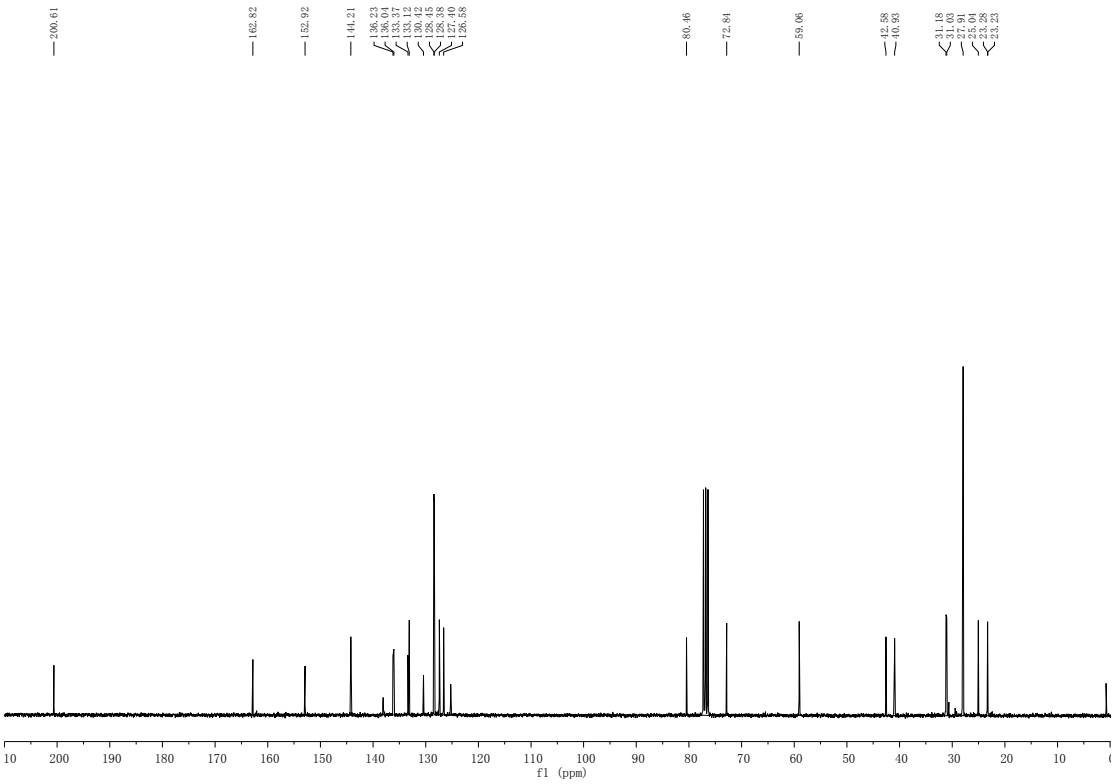


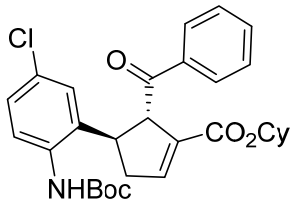


3pc

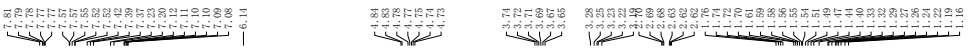


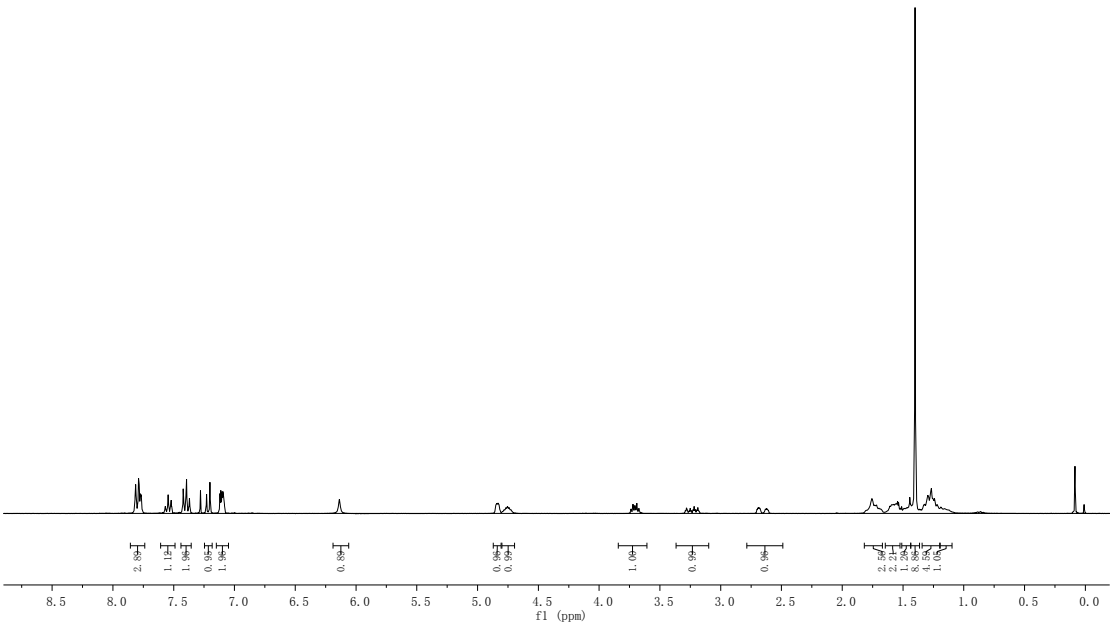


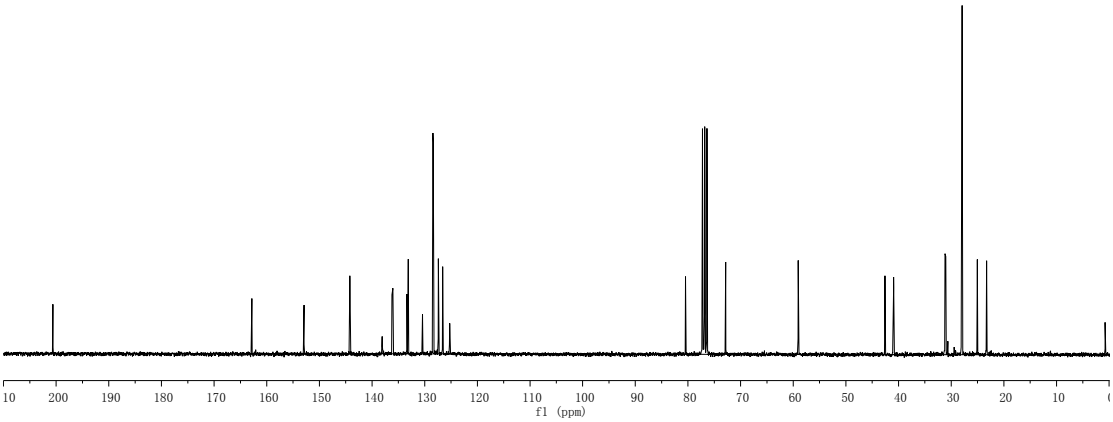


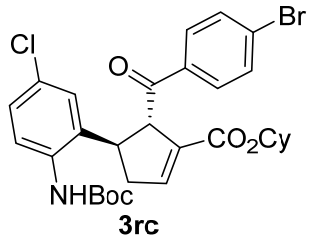


3qc

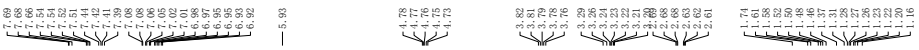


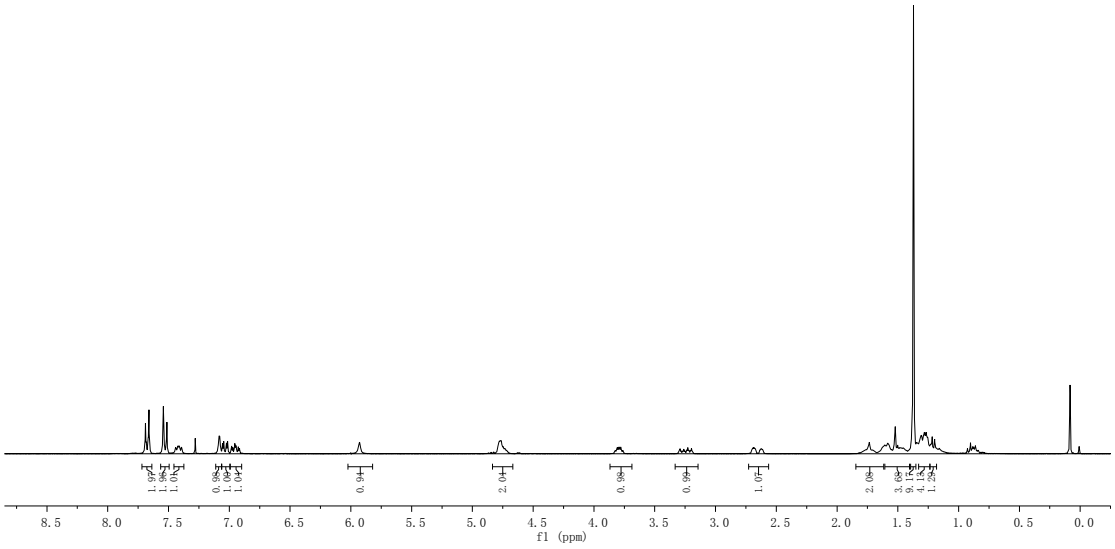


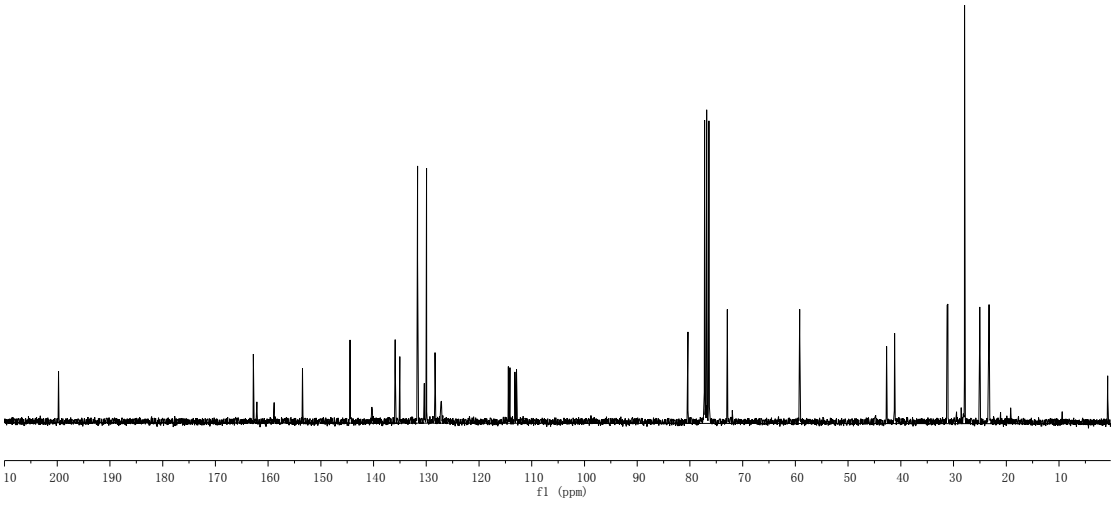


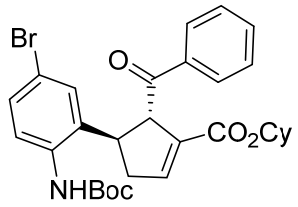


3rc

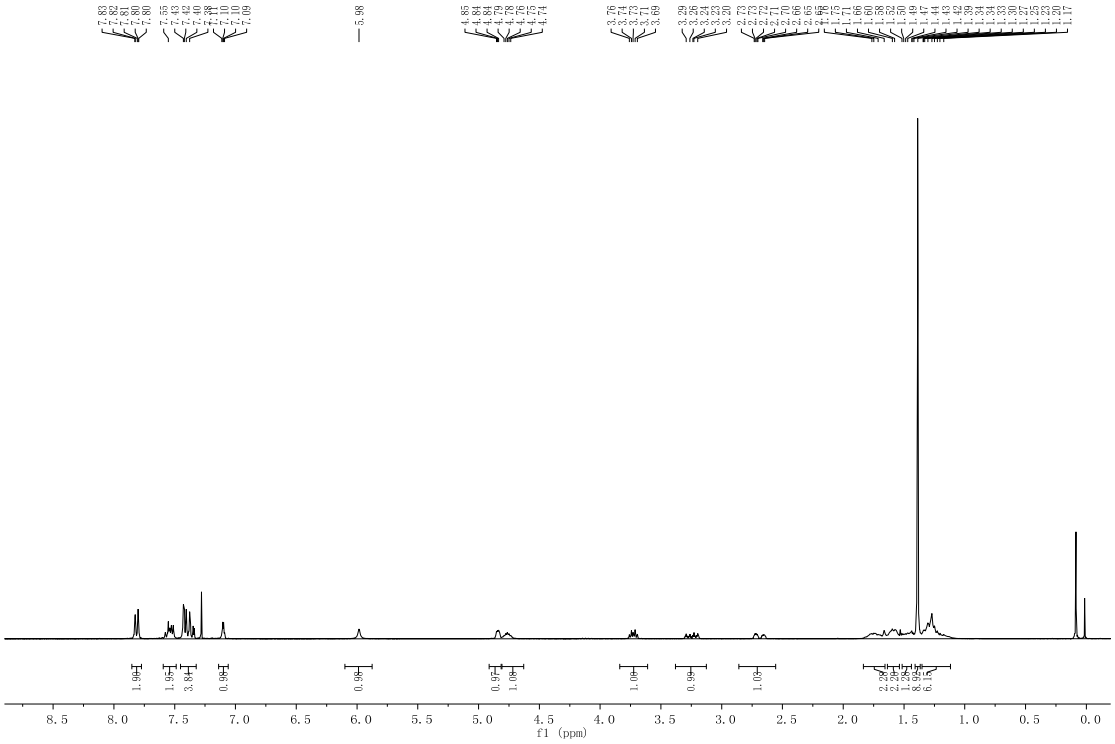


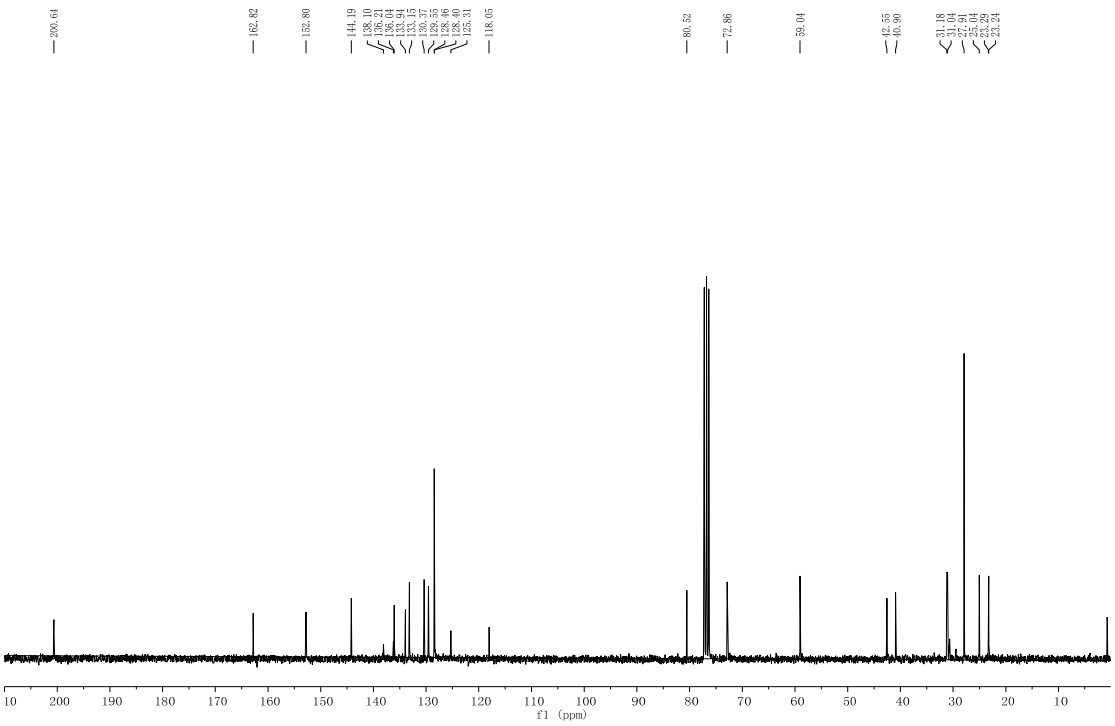


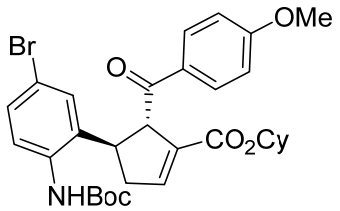




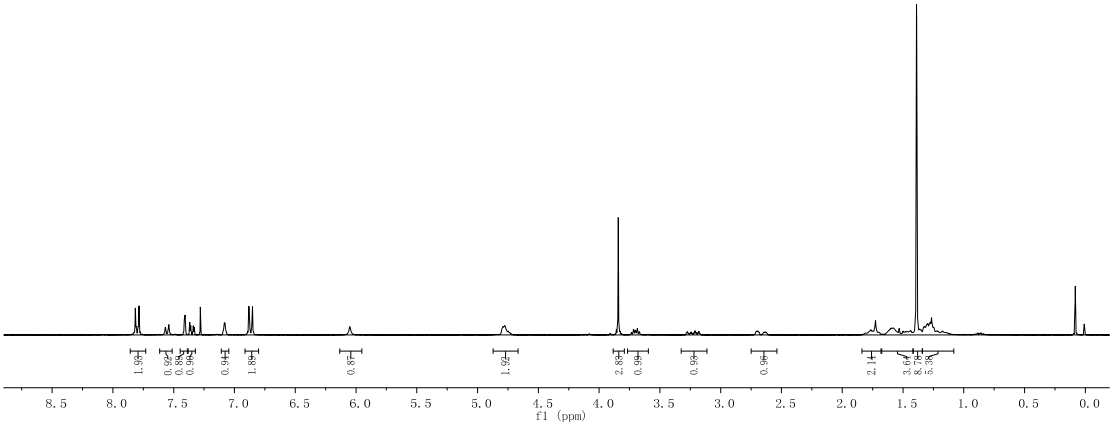
3sc

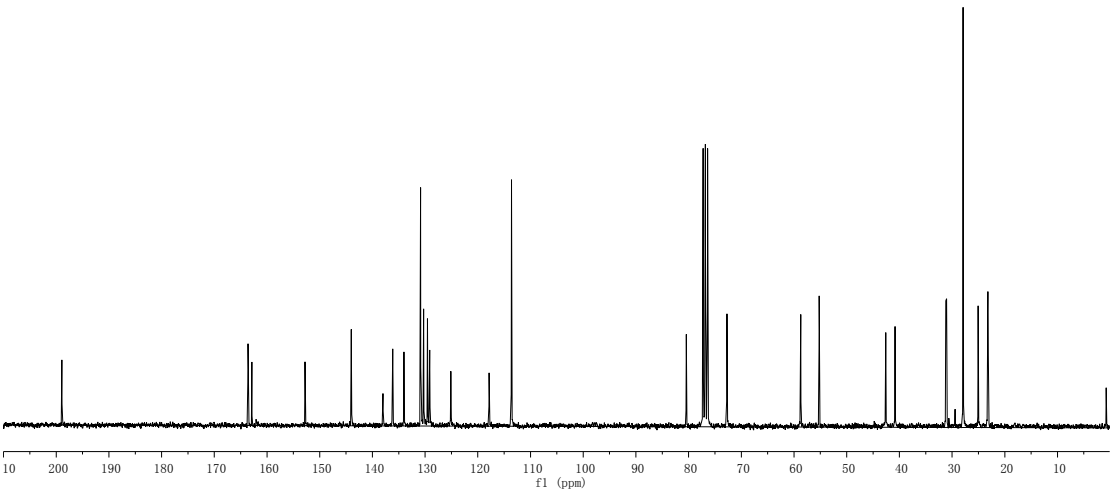


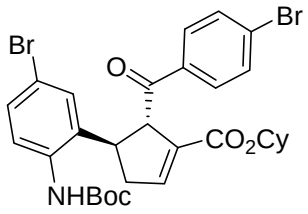




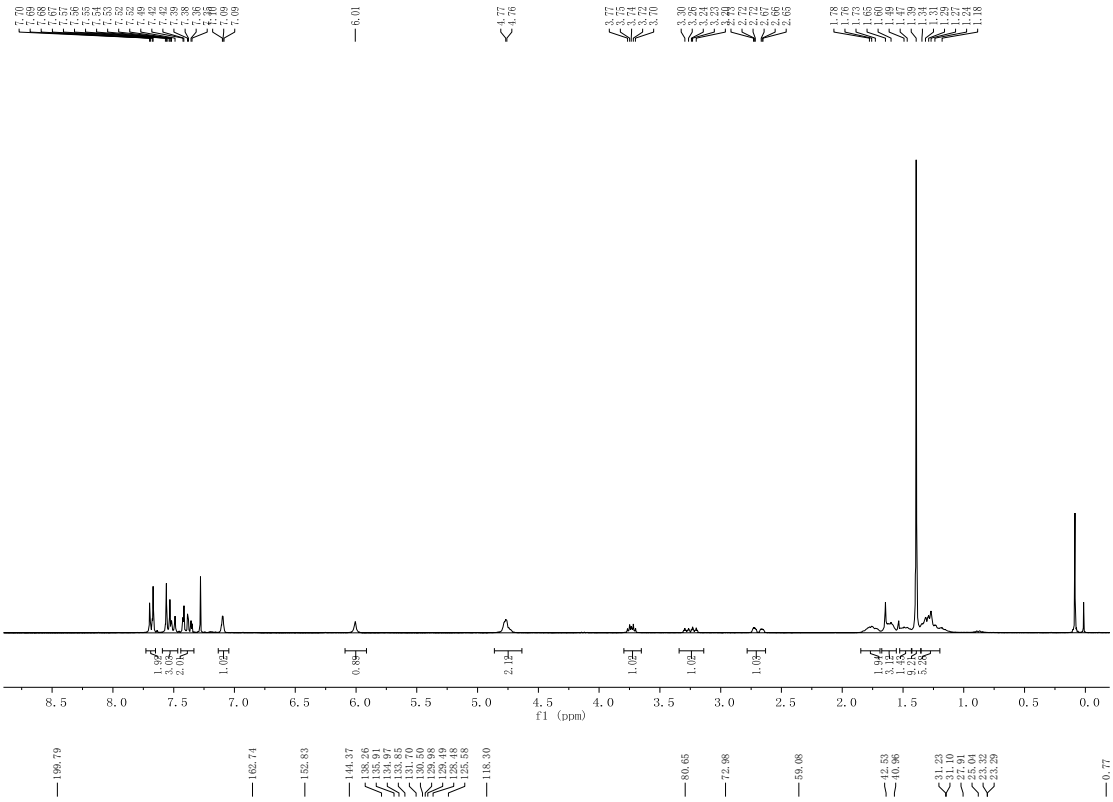
3tc

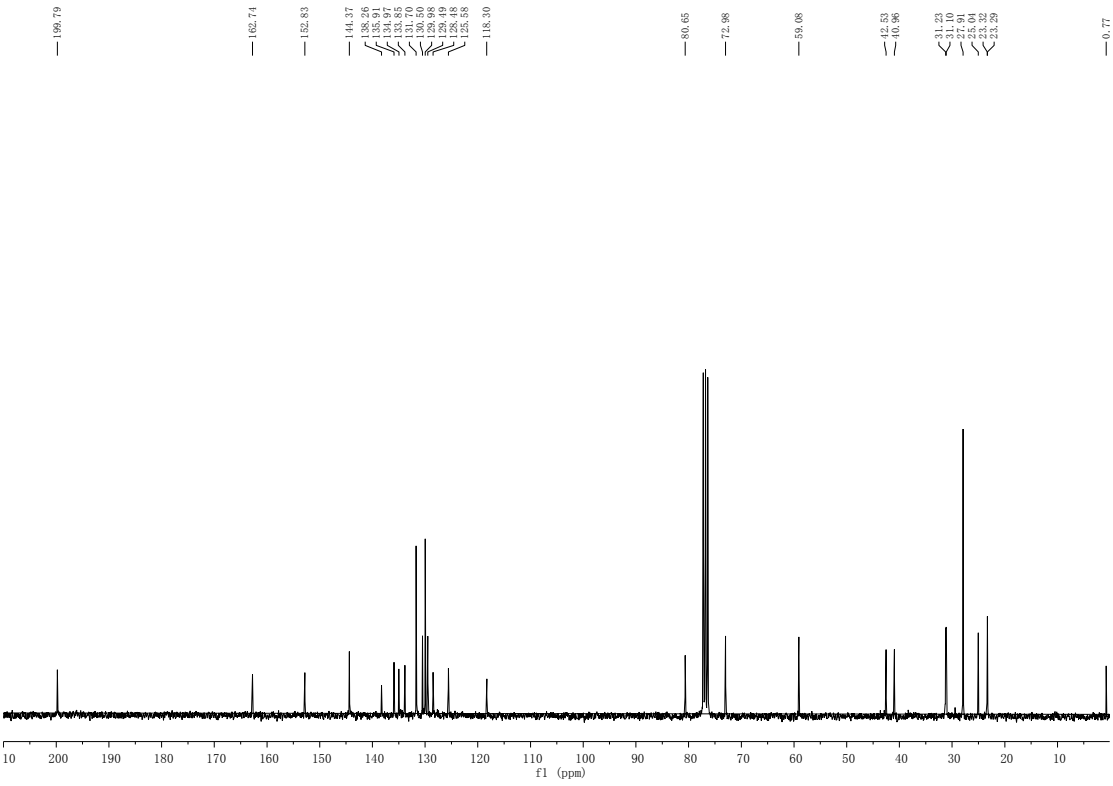


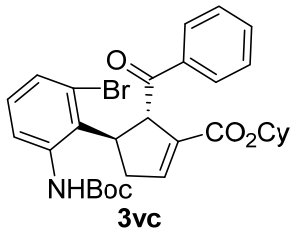




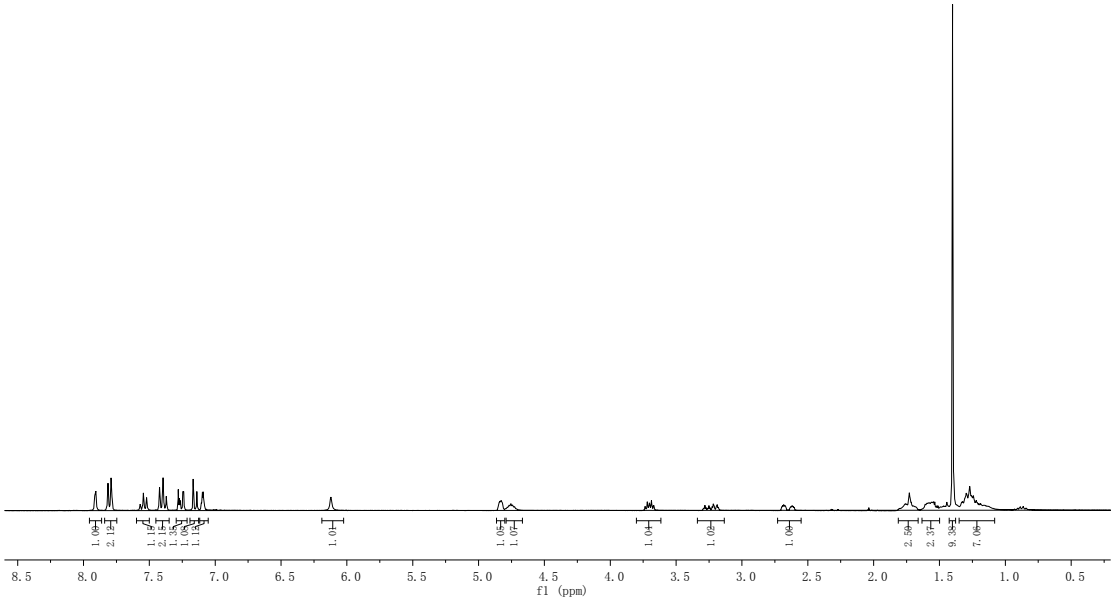
3uc

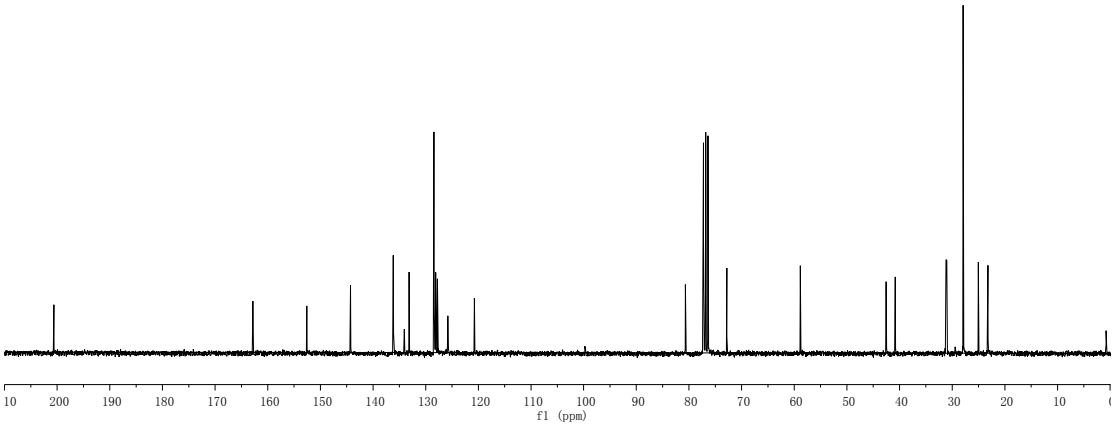


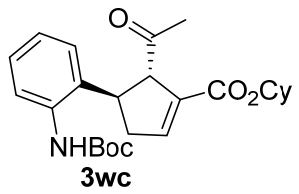




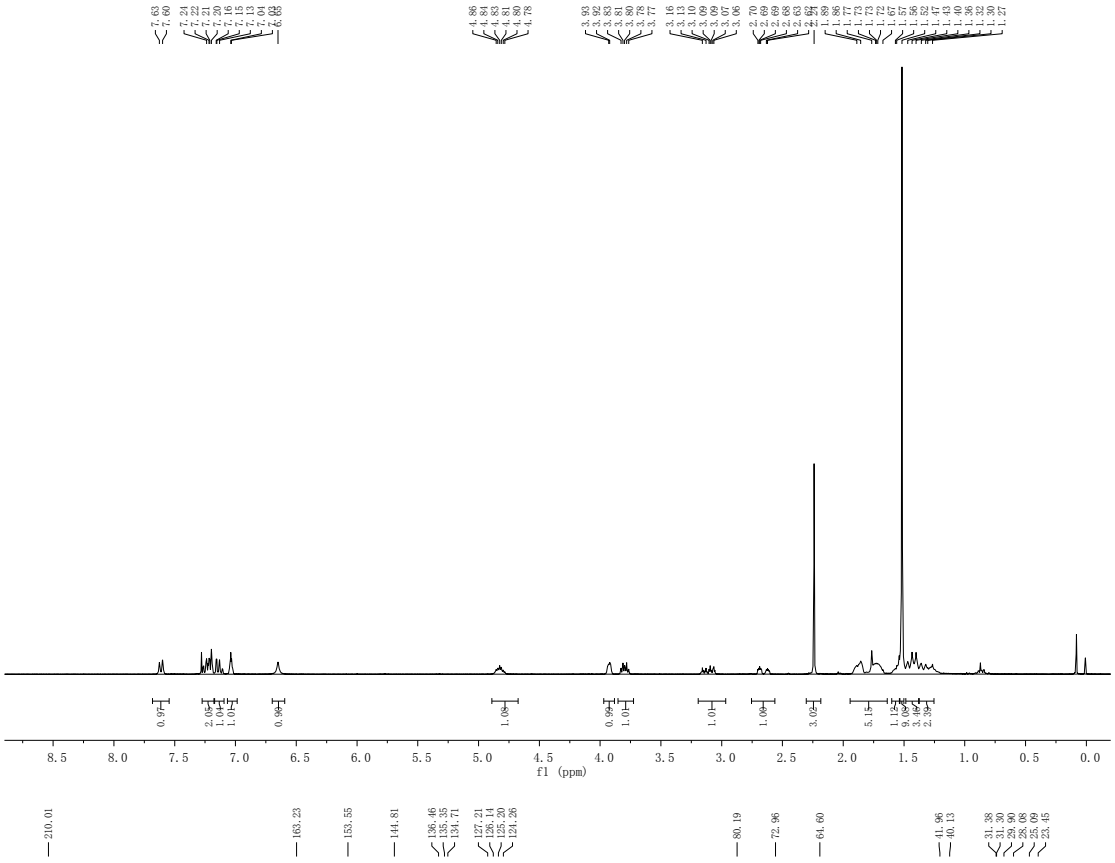
3vc

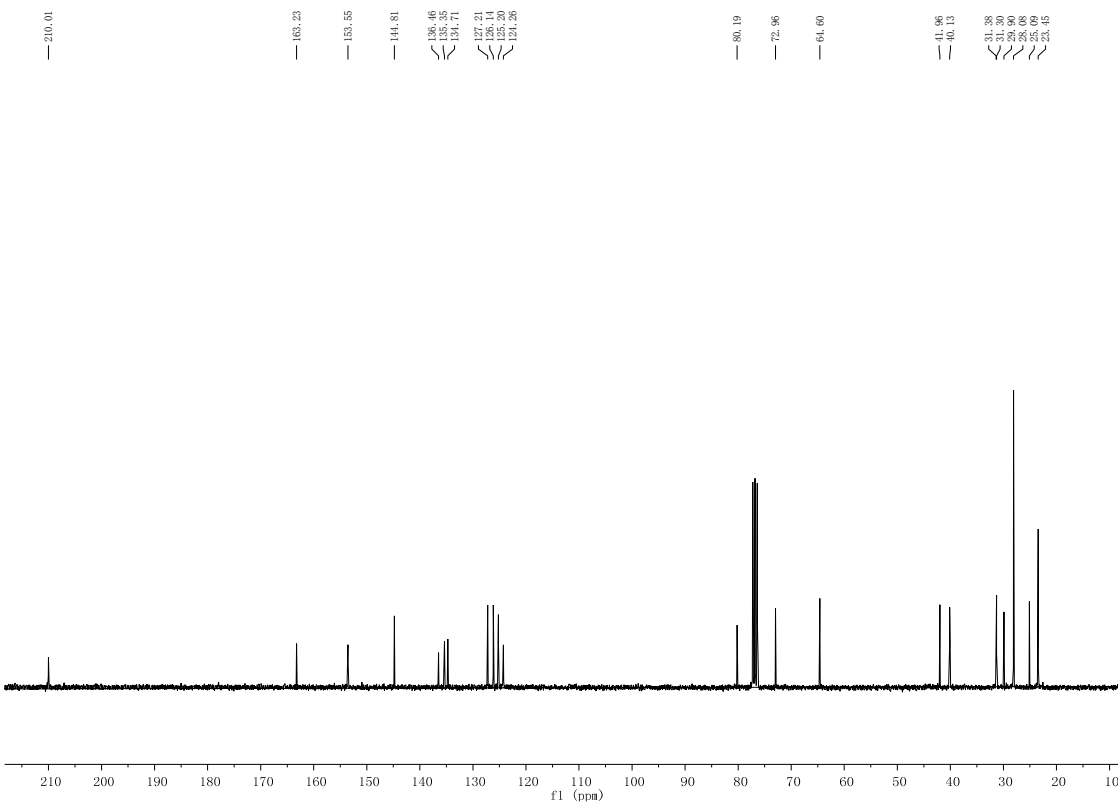


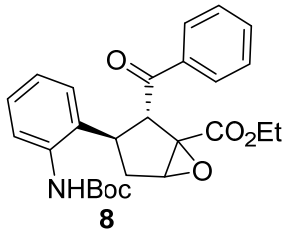




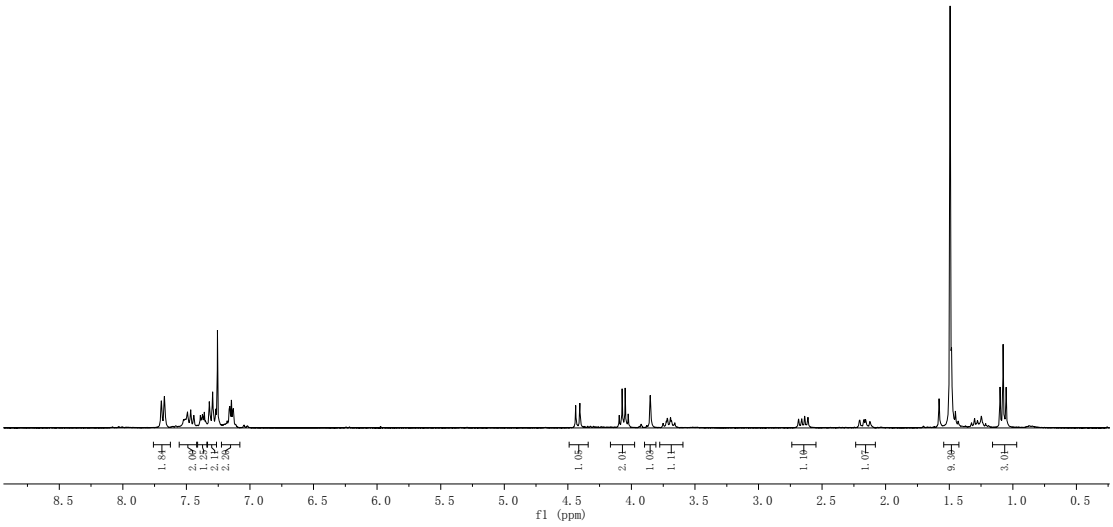
3wc

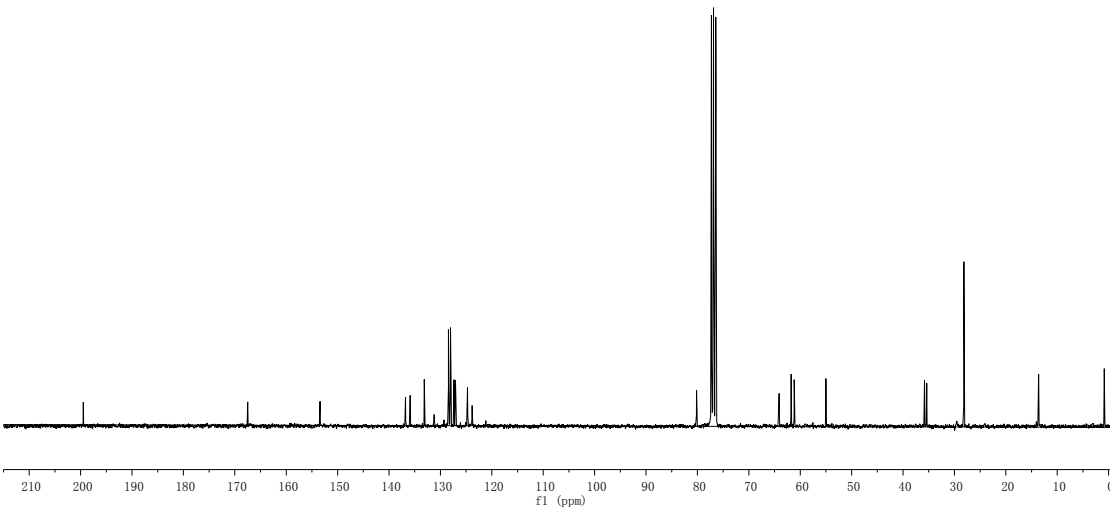




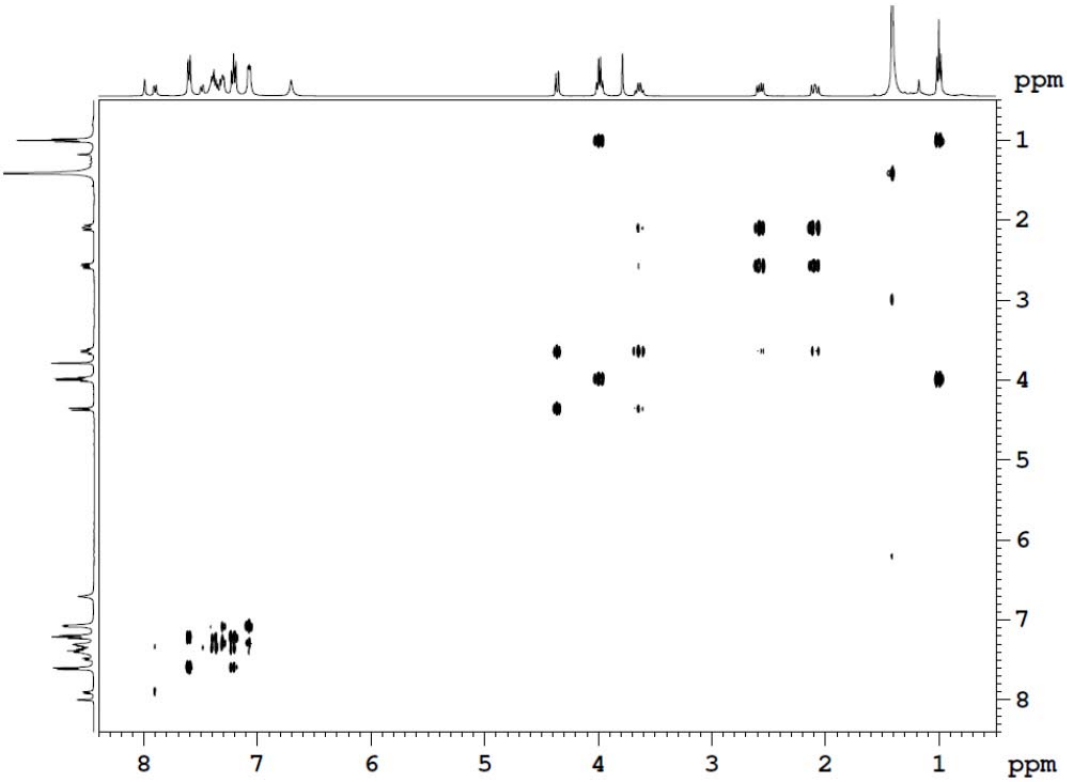


8

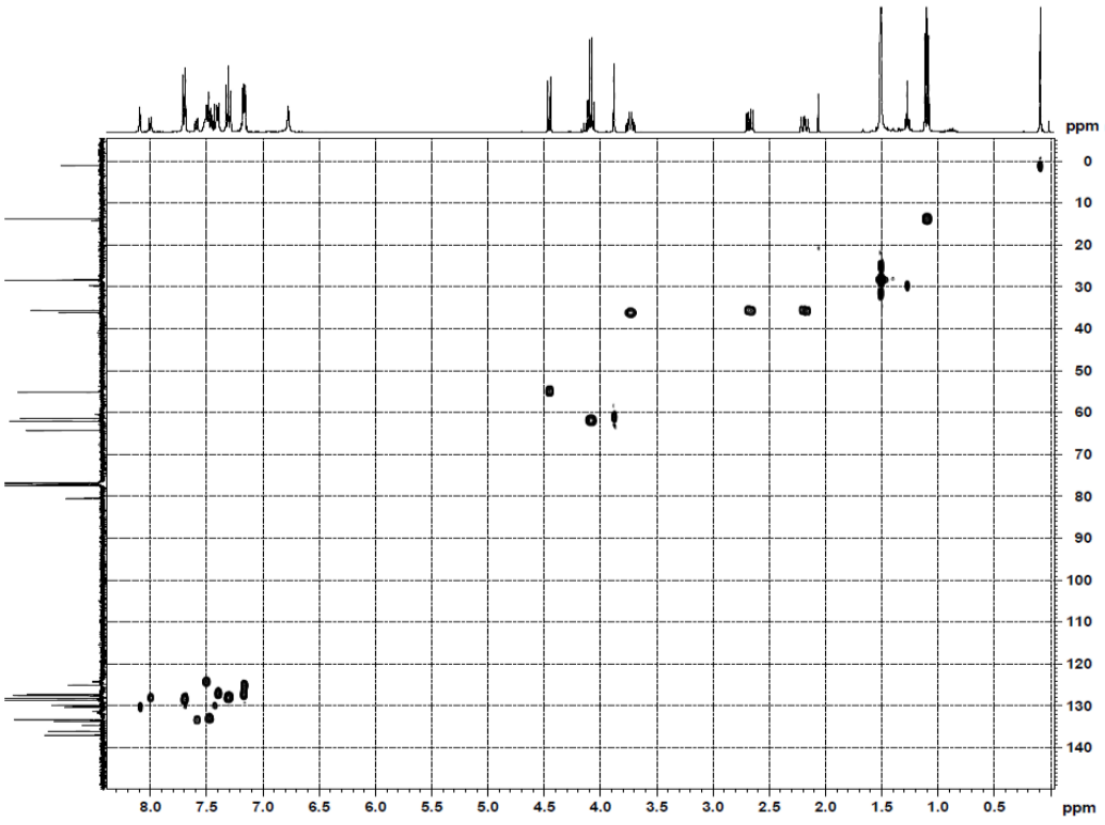




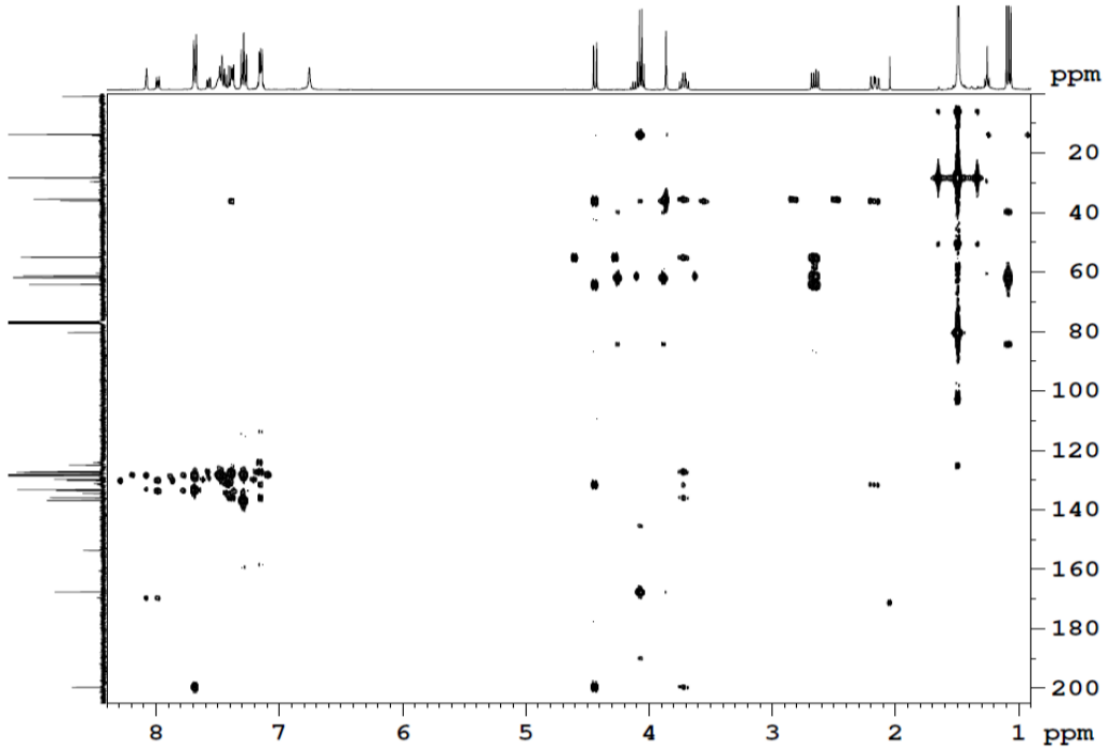
COSY, 2D NMR of **8**



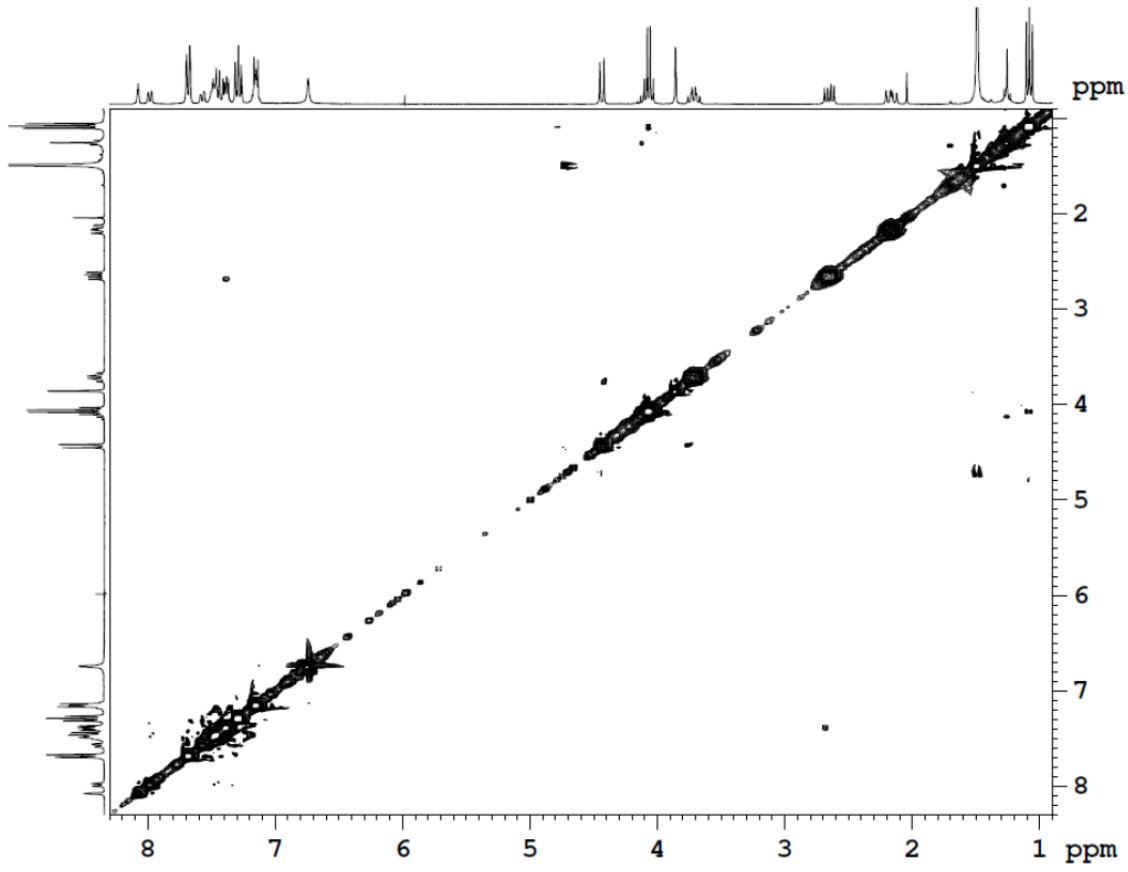
HSQC, 2D NMR of **8**



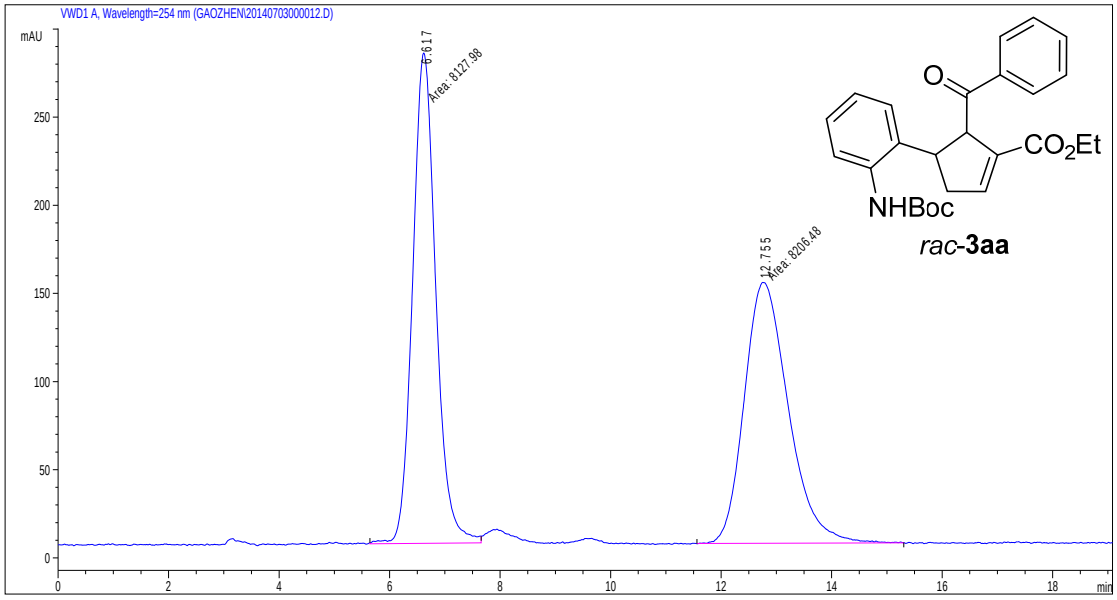
HMBC, 2D NMR of **8**



NOSEY, 2D NMR of **8**

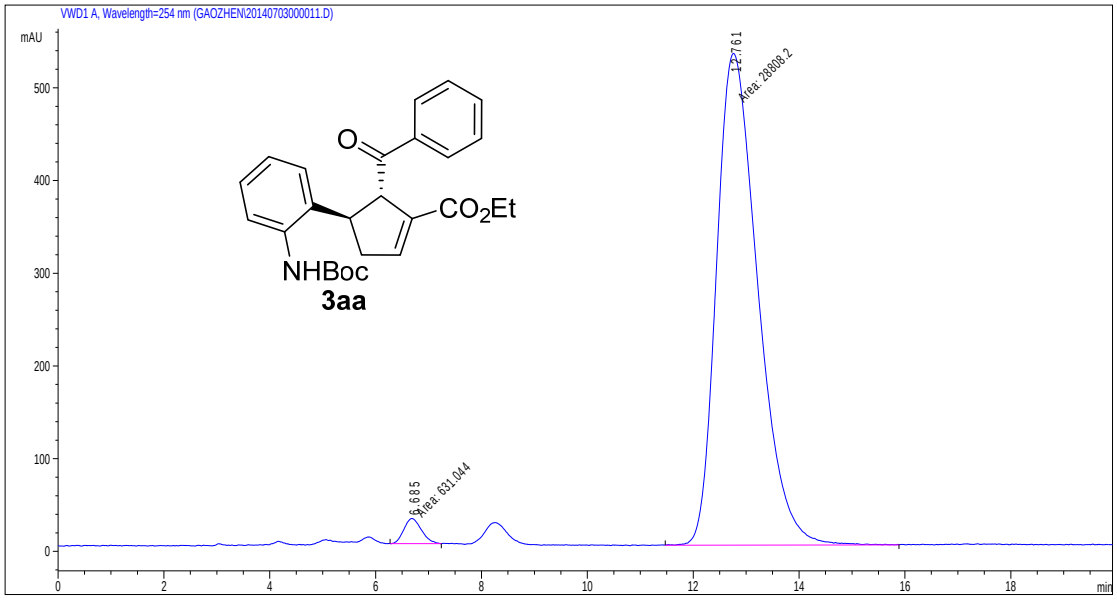


HPLC chromatogram of racemic 3aa



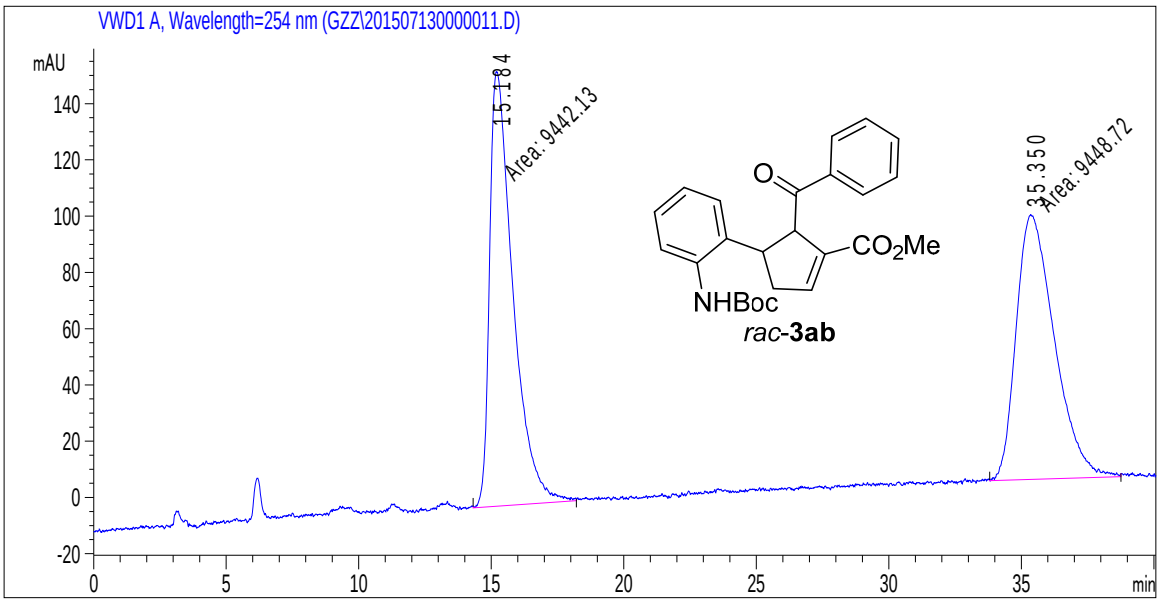
#	Time	Area	Height	Width	Area%	Symmetry
1	6.617	8128	278.1	0.4871	49.760	0.88
2	12.755	8206.5	148	0.9242	50.240	0.708

HPLC chromatogram of chiral 3aa



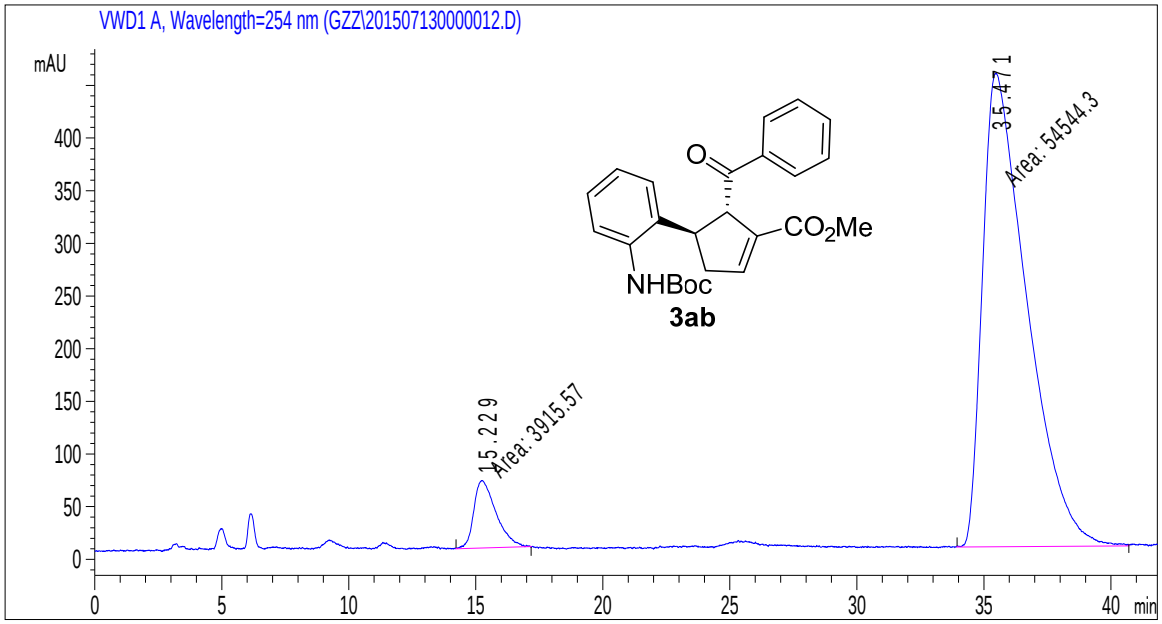
#	Time	Area	Height	Width	Area%	Symmetry
1	6.685	631	27.3	0.3856	2.144	0.819
2	12.761	28808.2	530.4	0.9052	96.156	0.67

HPLC chromatogram of racemic 3ab



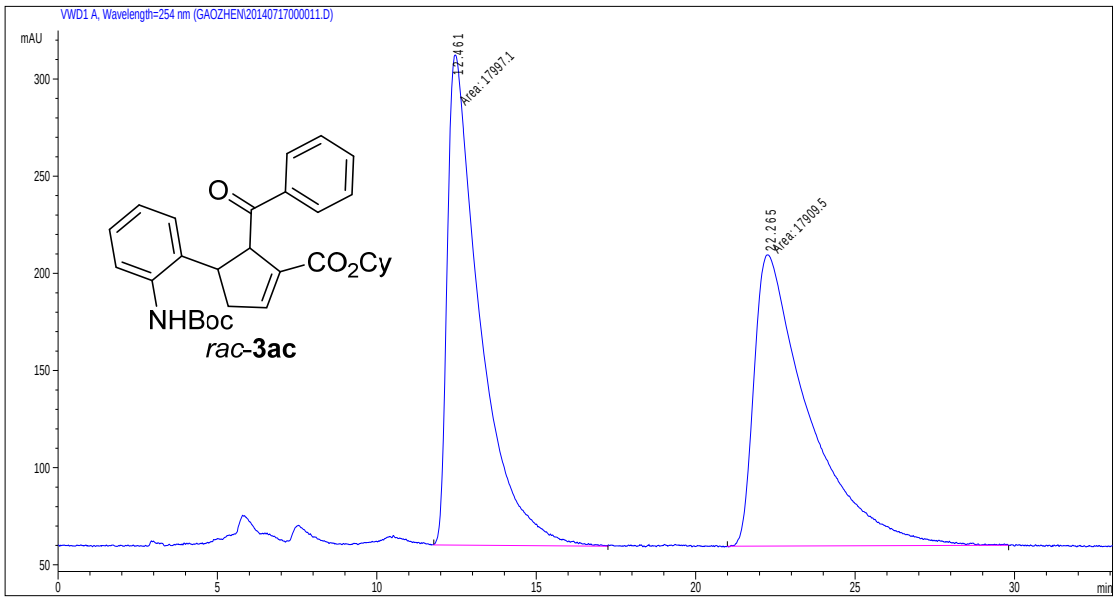
#	Time	Area	Height	Width	Area%	Symmetry
1	15.18	9442.1	154.5	1.0185	49.983	0.39
2	35.35	9448.7	94.2	1.6714	50.017	0.6

HPLC chromatogram of chiral 3ab



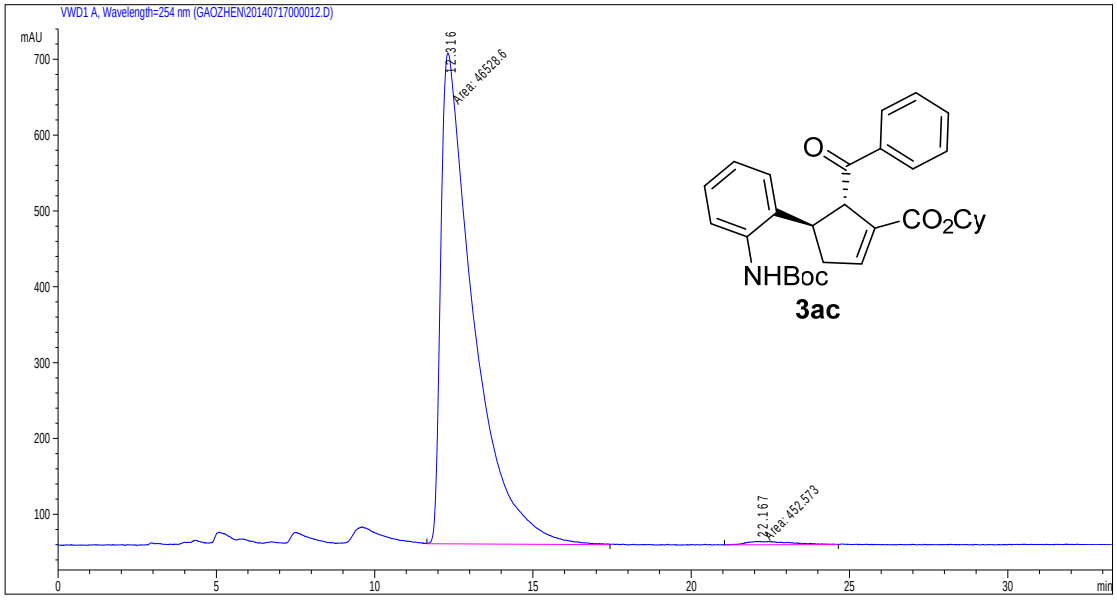
#	Time	Area	Height	Width	Area%	Symmetry
1	15.229	3915.6	64.2	1.016	4.098	0.547
2	35.471	54544.3	449.9	2.0206	95.902	0.421

HPLC chromatogram of racemic 3ac



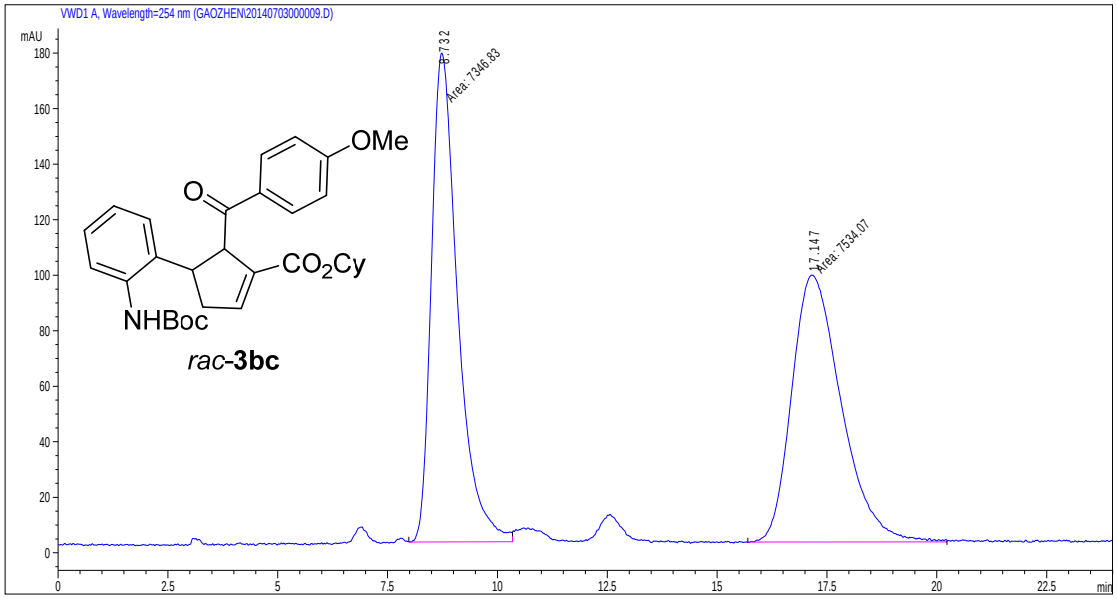
#	Time	Area	Height	Width	Area%	Symmetry
1	12.461	17997.1	252.2	1.1893	50.122	0.316
2	22.265	17909.5	149.9	1.9915	49.878	0.327

HPLC chromatogram of chiral 3ac



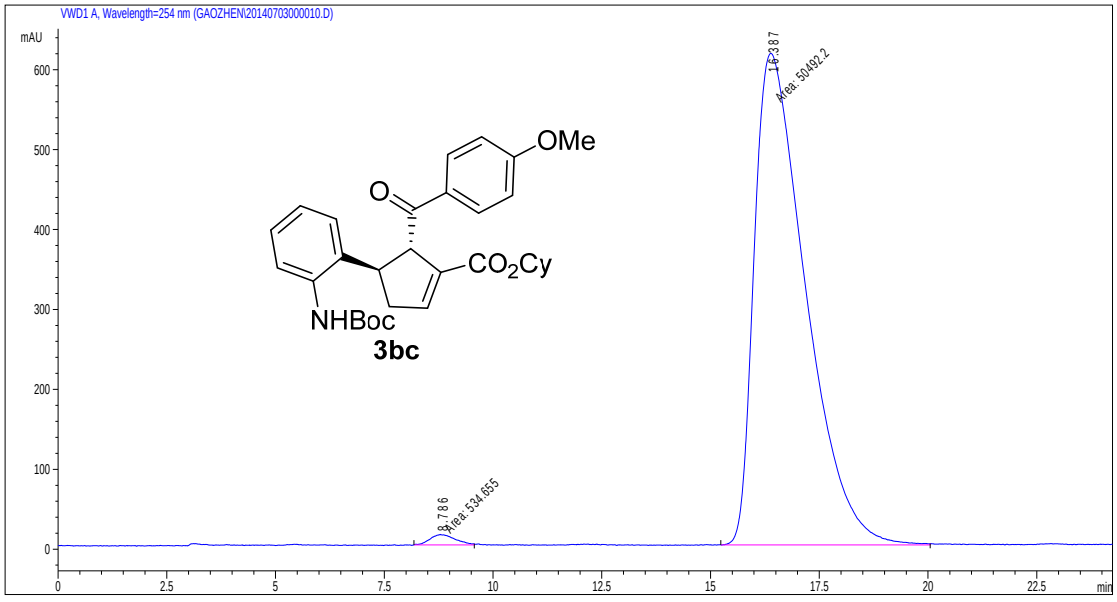
#	Time	Area	Height	Width	Area%	Symmetry
1	12.316	46528.6	646.8	1.1989	99.037	0.273
2	22.167	452.6	4.4	1.7141	0.963	0.451

HPLC chromatogram of racemic 3bc



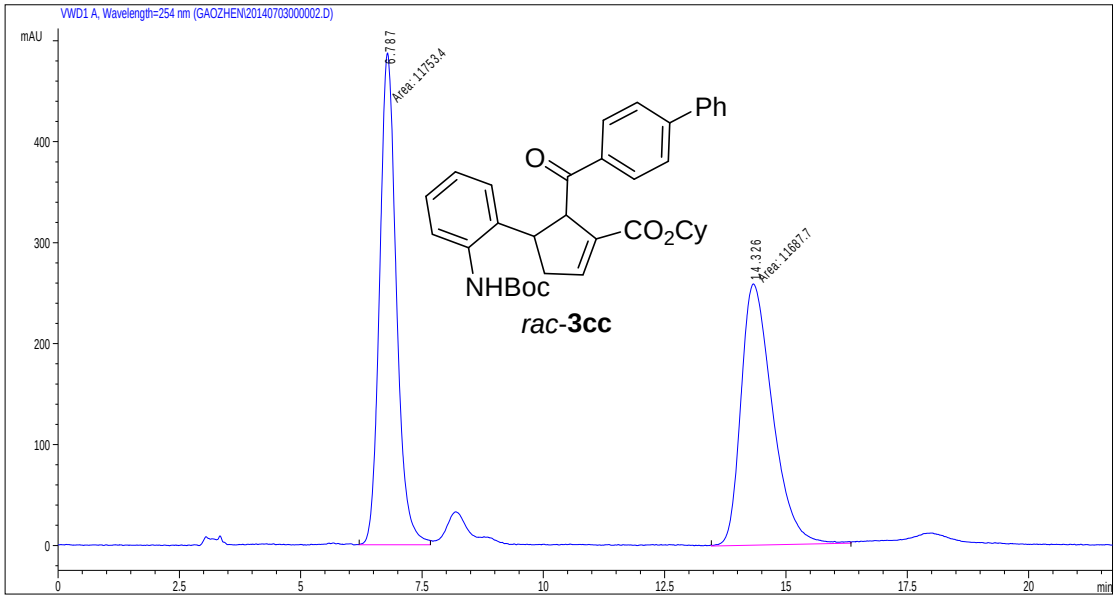
#	Time	Area	Height	Width	Area%	Symmetry
1	8.732	7346.8	176.1	0.6953	49.371	0.619
2	17.147	7534.1	96.2	1.3056	50.629	0.648

HPLC chromatogram of chiral 3bc



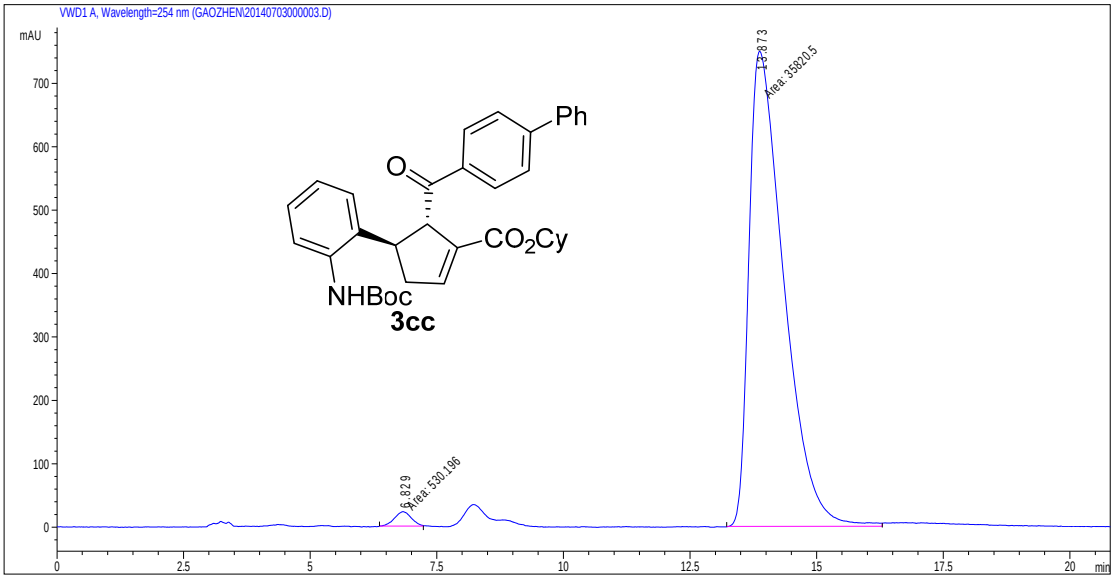
#	Time	Area	Height	Width	Area%	Symmetry
1	8.786	534.7	13.1	0.6811	1.048	0.674
2	16.387	50492.2 6	15.1	1.3681	98.952	0.464

HPLC chromatogram of racemic 3cc



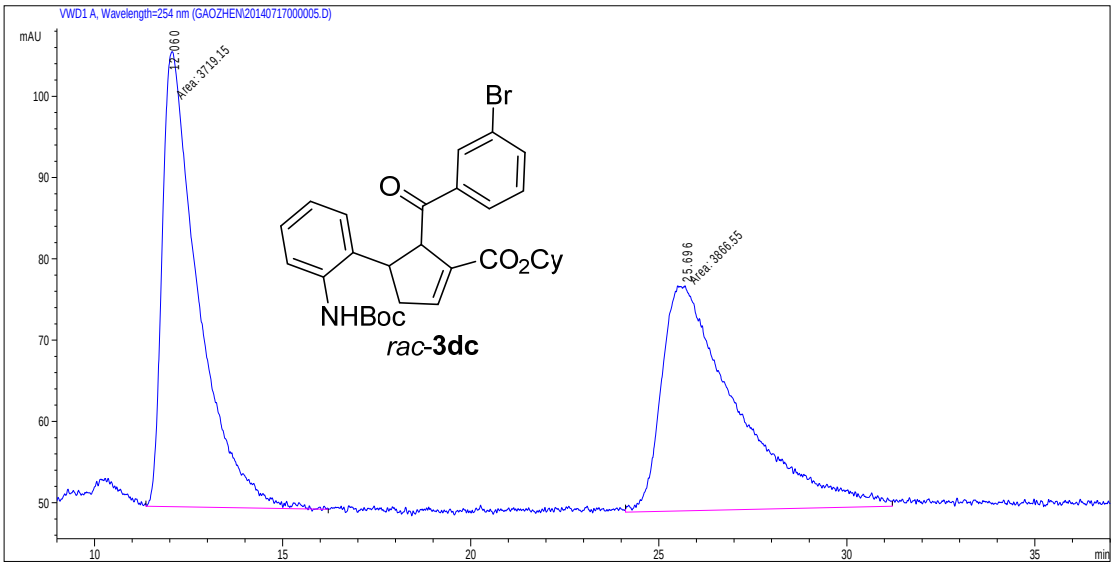
#	Time	Area	Height	Width	Area%	Symmetry
1	6.787	11842.6	488	0.3676	50.366	0.821
2	14.326	11670.6	259.2	0.6622	49.634	0.619

HPLC chromatogram of chiral 3cc



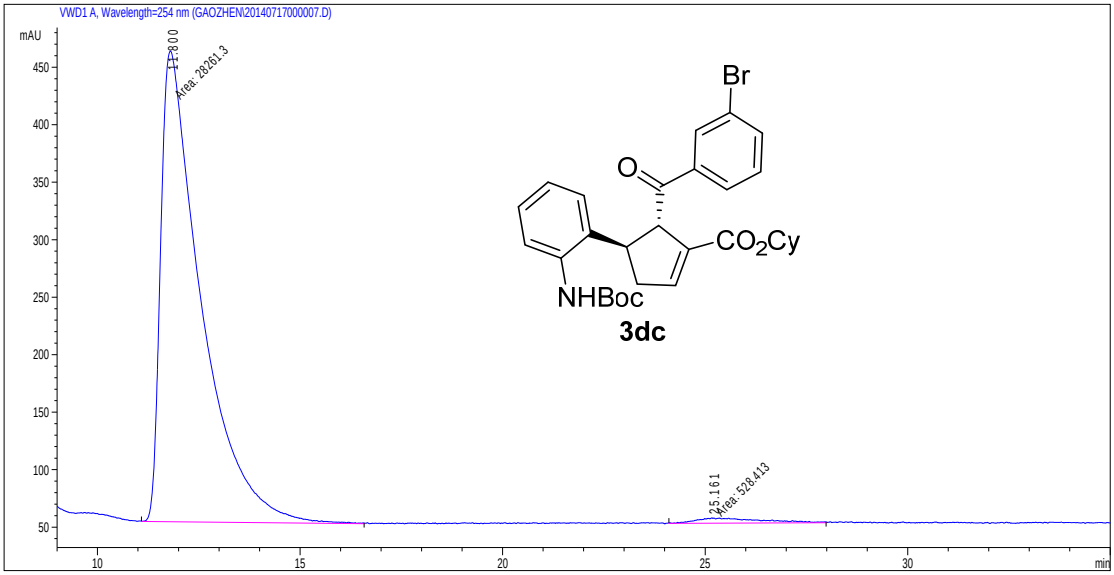
#	Time	Area	Height	Width	Area%	Symmetry
1	6.829	530.2	22.9	0.3851	1.459	0.982
2	13.873	35820.5	749.4	0.7967	98.541	0.428

HPLC chromatogram of racemic 3dc



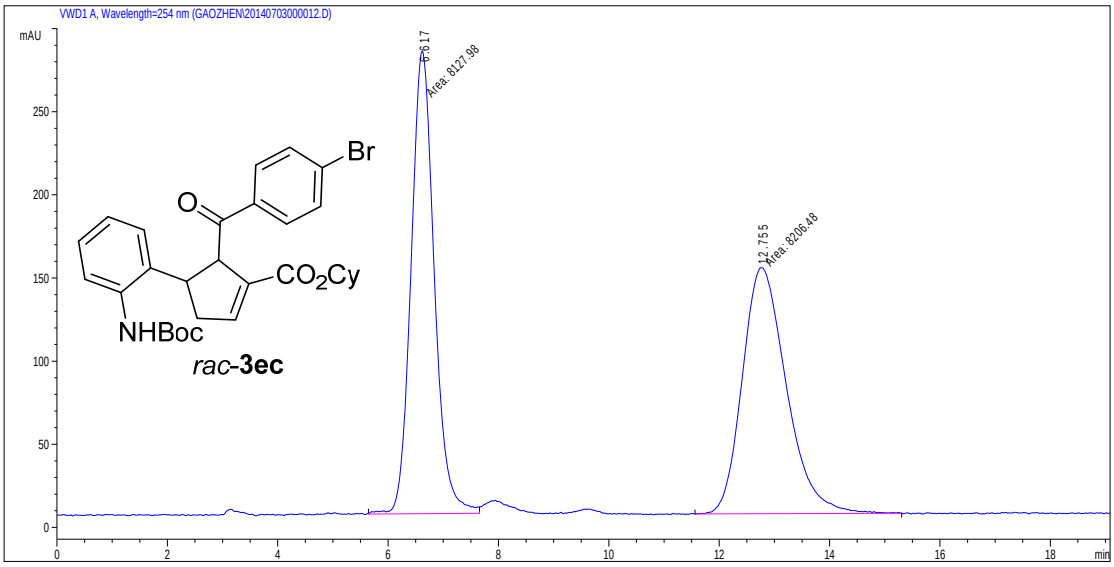
#	Time	Area	Height	Width	Area%	Symmetry
1	12.06	3719.1	56	1.1072	49.028	0.369
2	25.70	3866.5	27.7	2.3268	50.972	0.43

HPLC chromatogram of chiral 3dc



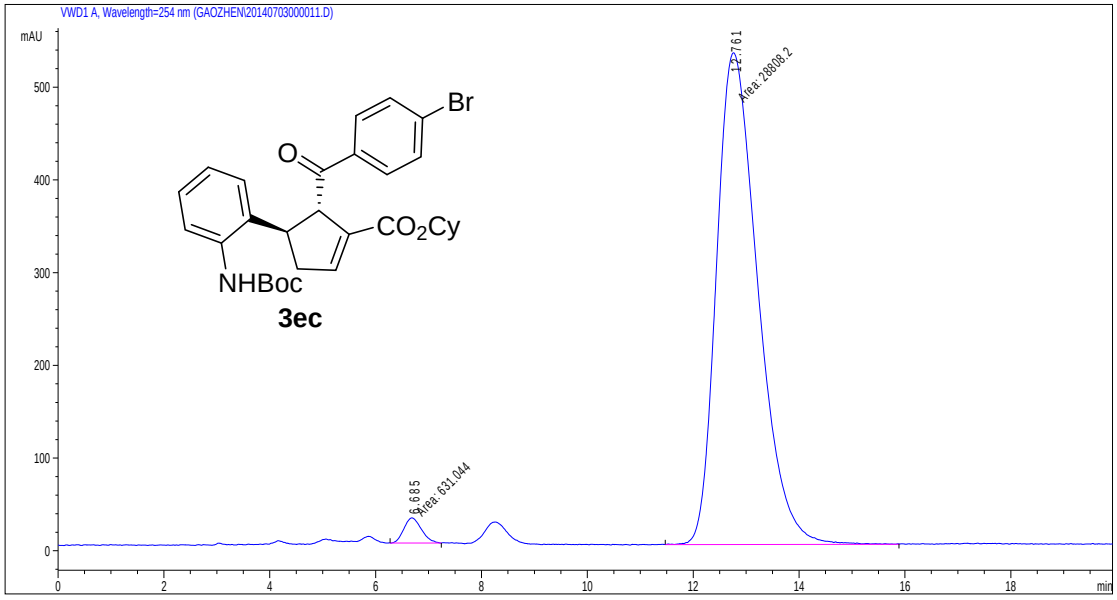
#	Time	Area	Height	Width	Area%	Symmetry
1	11.8	28261.3	409.3	1.1507	98.165	0.309
2	25.161	528.4	4.7	1.8696	1.835	0.333

HPLC chromatogram of racemic 3ec



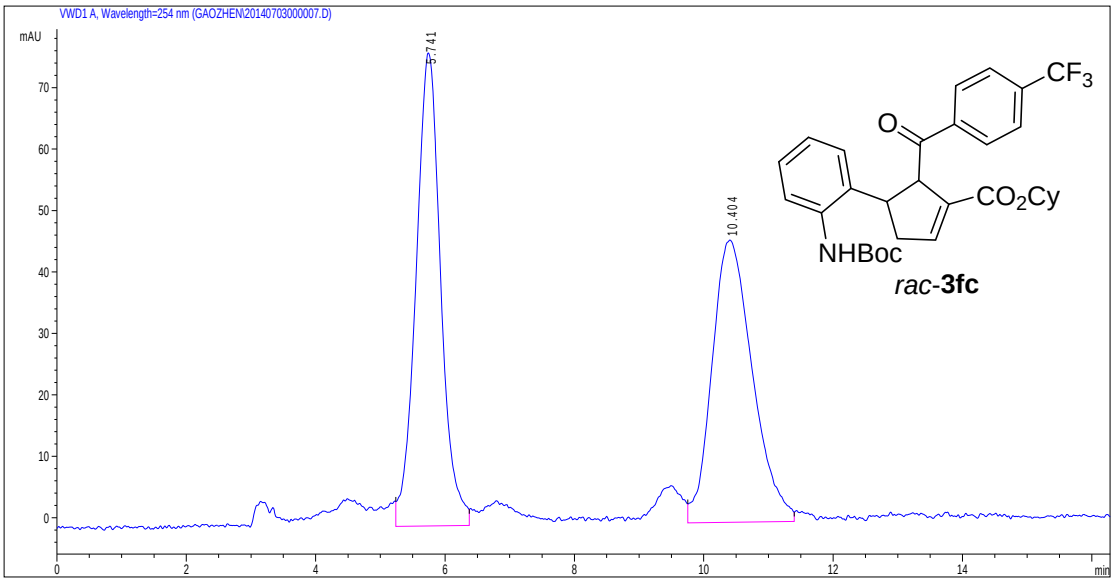
#	Time	Area	Height	Width	Area%	Symmetry
1	6.617	8128	278.1	0.4871	49.760	0.88
2	12.755	8206.5	148	0.9242	50.240	0.708

HPLC chromatogram of chiral 3ec



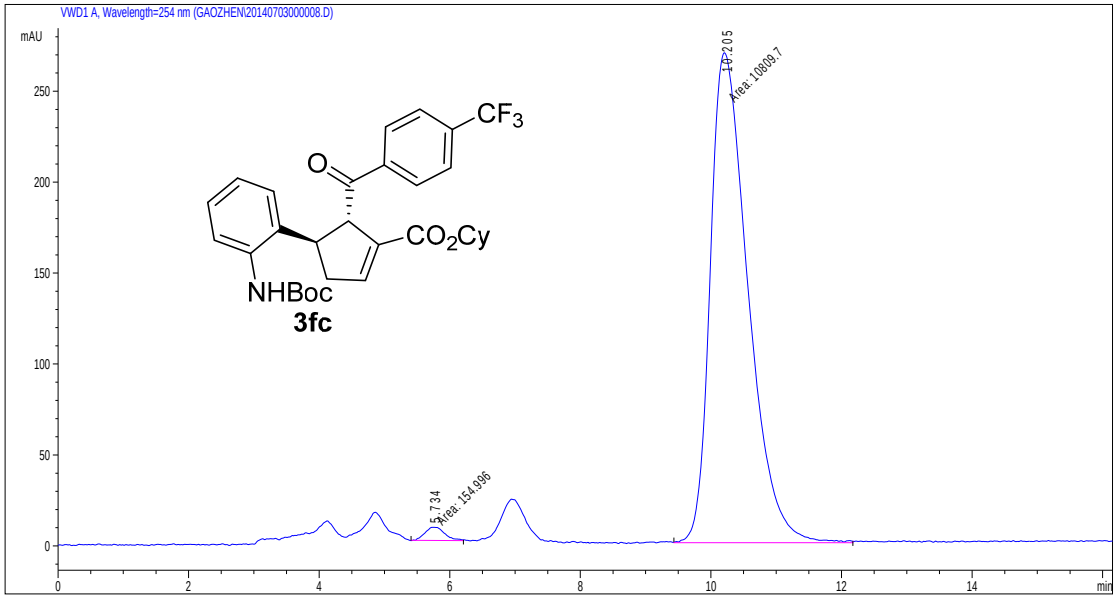
#	Time	Area	Height	Width	Area%	Symmetry
1	6.685	631	27.3	0.3856	2.144	0.819
2	12.761	28808.2	530.4	0.9052	97.856	0.67

HPLC chromatogram of racemic 3fc



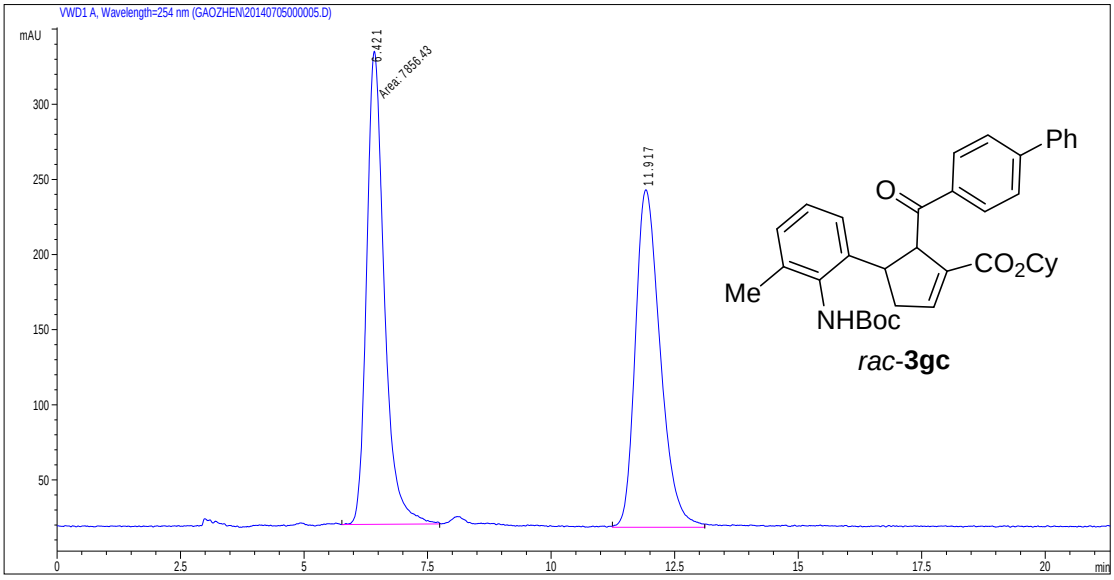
#	Time	Area	Height	Width	Area%	Symmetry
1	5.741	2048.4	77	0.4006	50.656	0.943
2	10.404	1995.4	45.9	0.5315	49.344	0.785

HPLC chromatogram of chiral 3fc



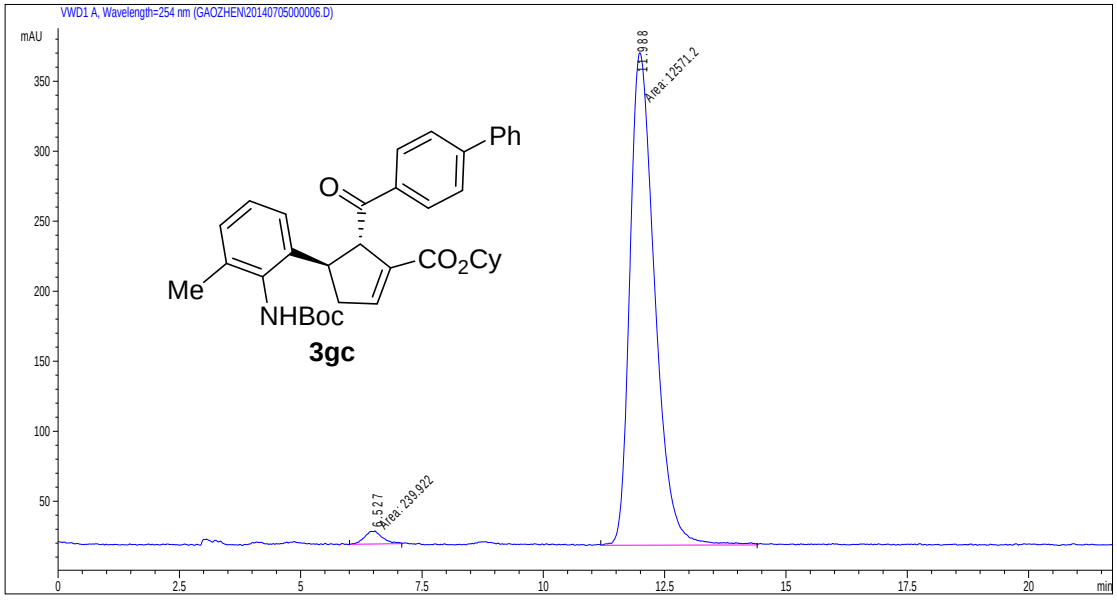
#	Time	Area	Height	Width	Area%	Symmetry
1	5.734	155	7.3	0.3545	1.414	0.623
2	10.205	10809.7	269.4	0.6688	98.586	0.575

HPLC chromatogram of racemic 3gc



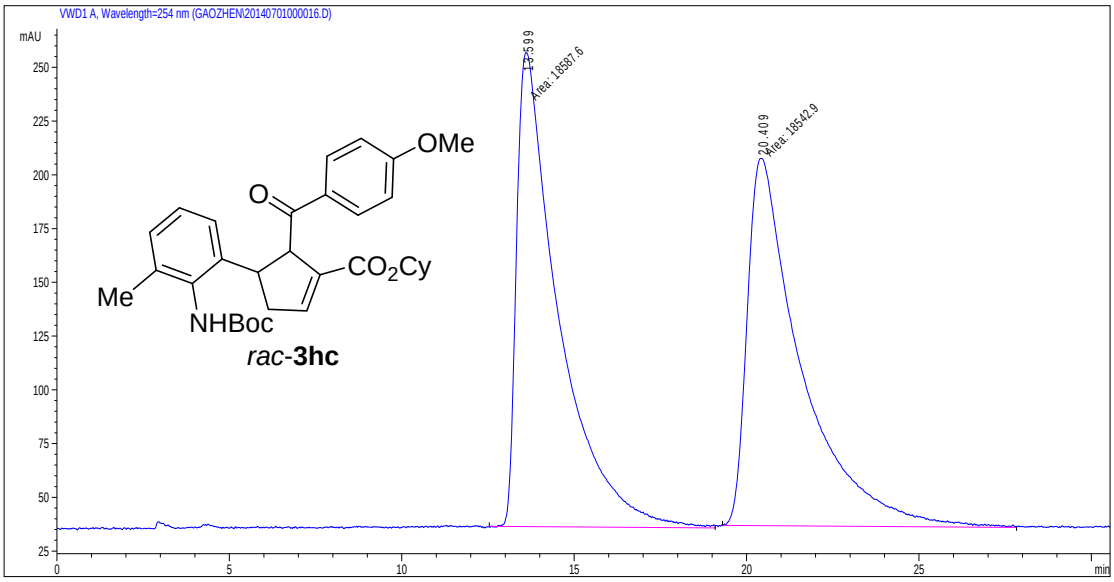
#	Time	Area	Height	Width	Area%	Symmetry
1	6.421	7856.4	314.9	0.4158	49.994	0.729
2	11.917	7858.4	224.7	0.526	50.006	0.693

HPLC chromatogram of chiral 3gc



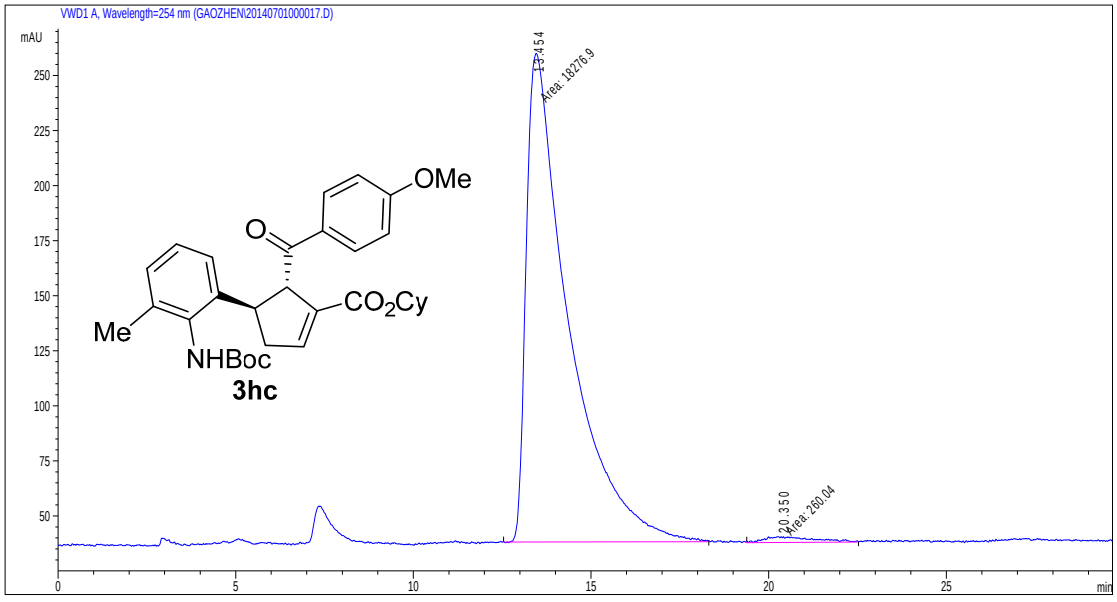
#	Time	Area	Height	Width	Area%	Symmetry
1	6.527	239.9	9.3	0.4318	1.473	1.227
2	11.988	12571.2	351.7	0.5957	98.527	0.638

HPLC chromatogram of racemic 3hc



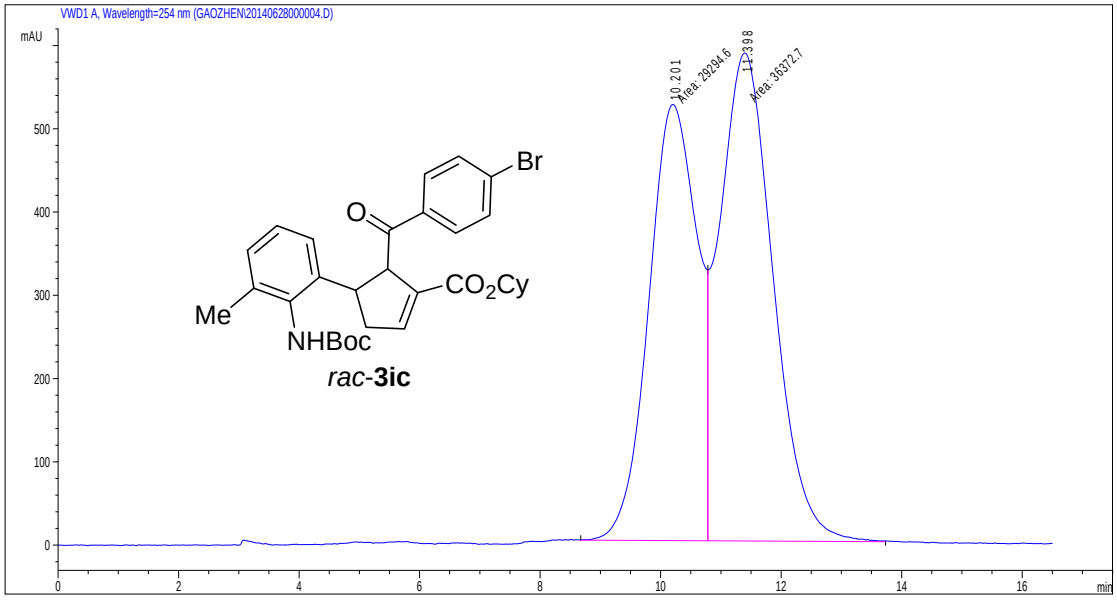
#	Time	Area	Height	Width	Area%	Symmetry
1	13.599	18587.6	220.5	1.4048	50.060	0.279
2	20.409	18542.9	170.9	1.8081	49.940	0.326

HPLC chromatogram of chiral 3hc



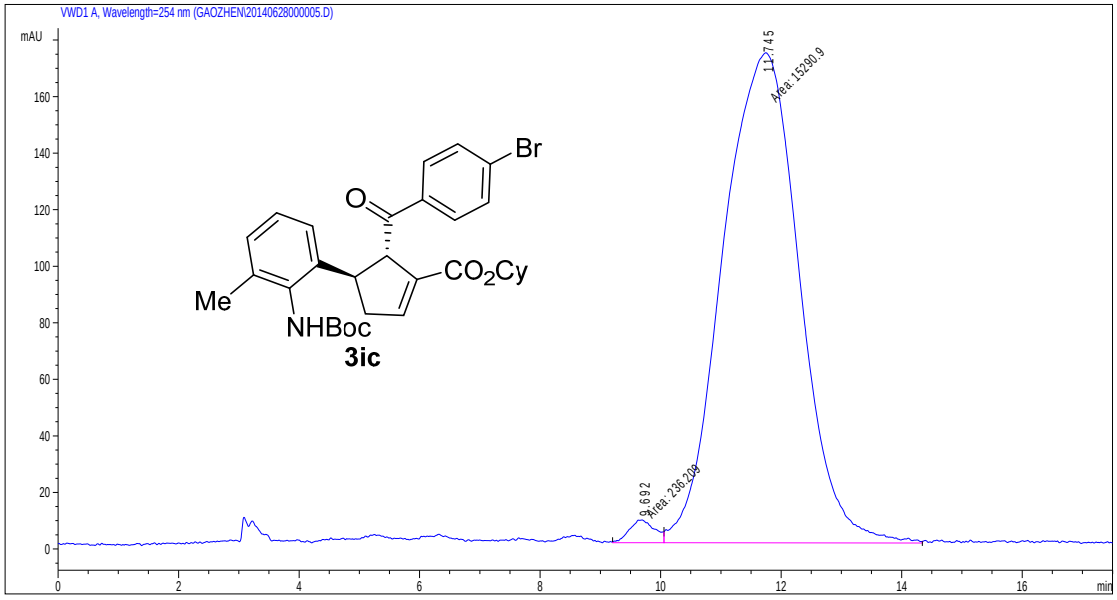
#	Time	Area	Height	Width	Area%	Symmetry
1	13.454	18276.9	221.9	1.3727	98.597	0.294
2	20.35	260 2.6	1.6507	1.403	0.488	

HPLC chromatogram of racemic 3ic



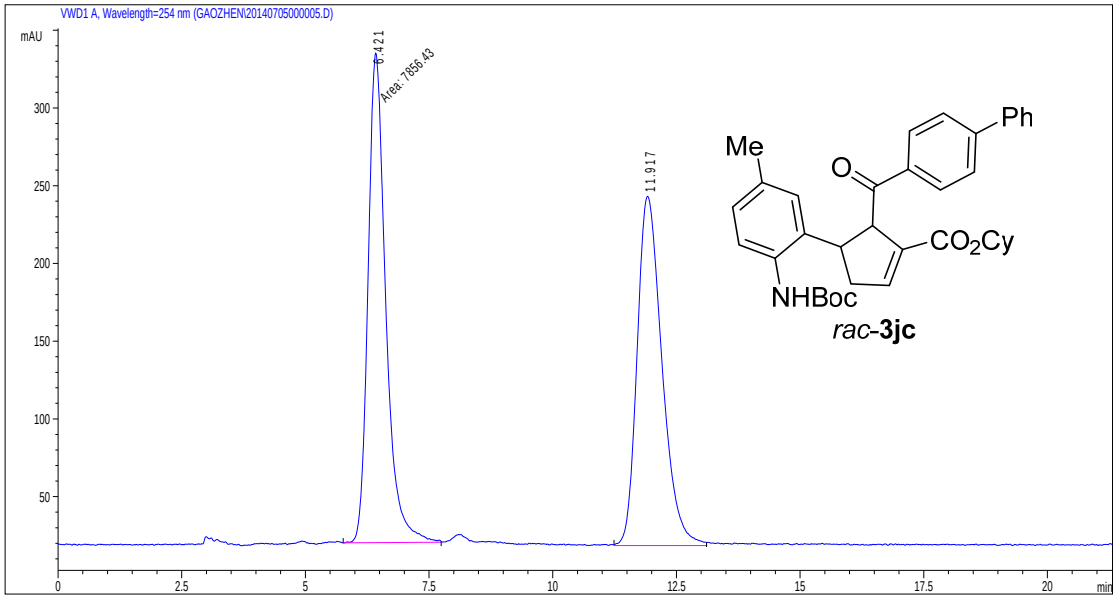
#	Time	Area	Height	Width	Area%	Symmetry
1	10.201	29294.6	537.3	0.4311	49.634	0.998
2	11.398	36372.7	581.4	0.5621	50.366	0.692

HPLC chromatogram of chiral 3ic



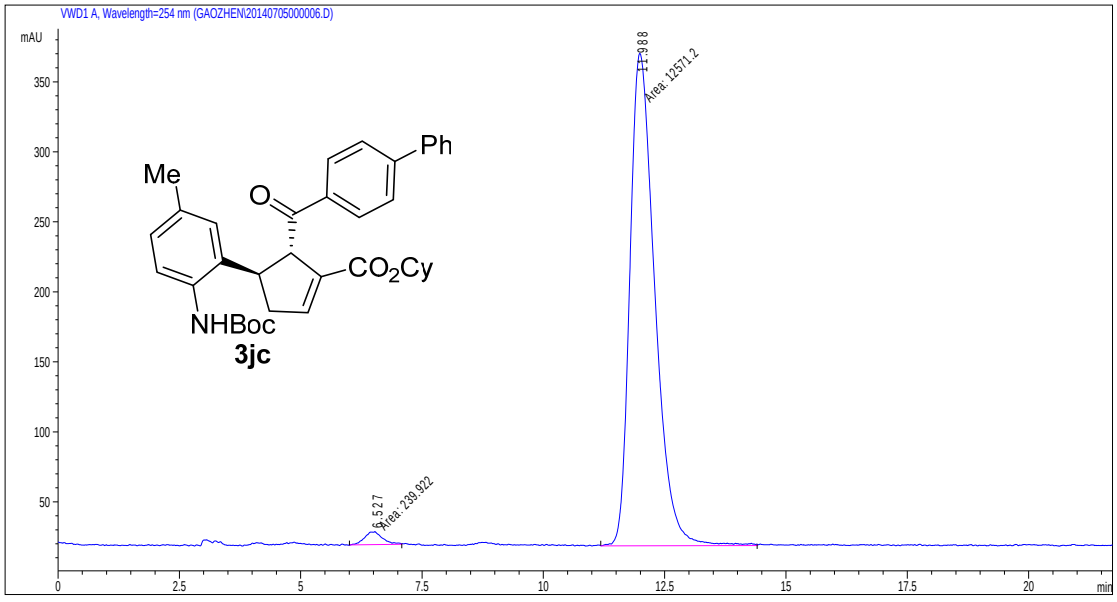
#	Time	Area	Height	Width	Area%	Symmetry
1	9.692	236.209	13.3	0.4622	1.521	0.971
2	11.745	15290.9	158.0	0.5784	98.479	0.473

HPLC chromatogram of racemic 3jc



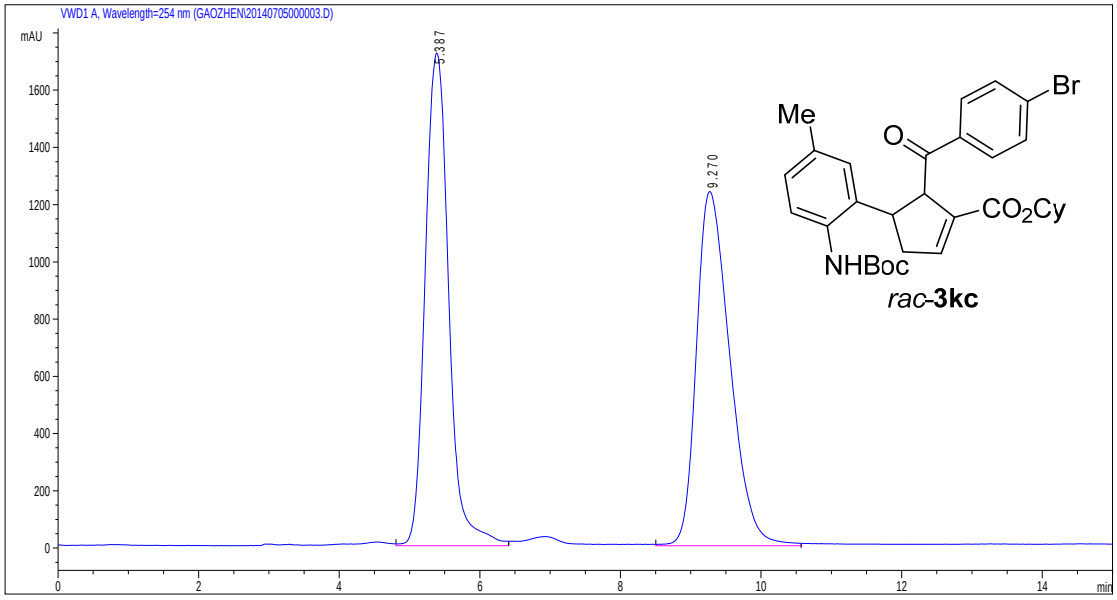
#	Time	Area	Height	Width	Area%	Symmetry
1	6.421	7856.4	314.9	0.4158	49.994	0.729
2	11.917	7858.4	224.7	0.526	50.006	0.693

HPLC chromatogram of chiral 3jc



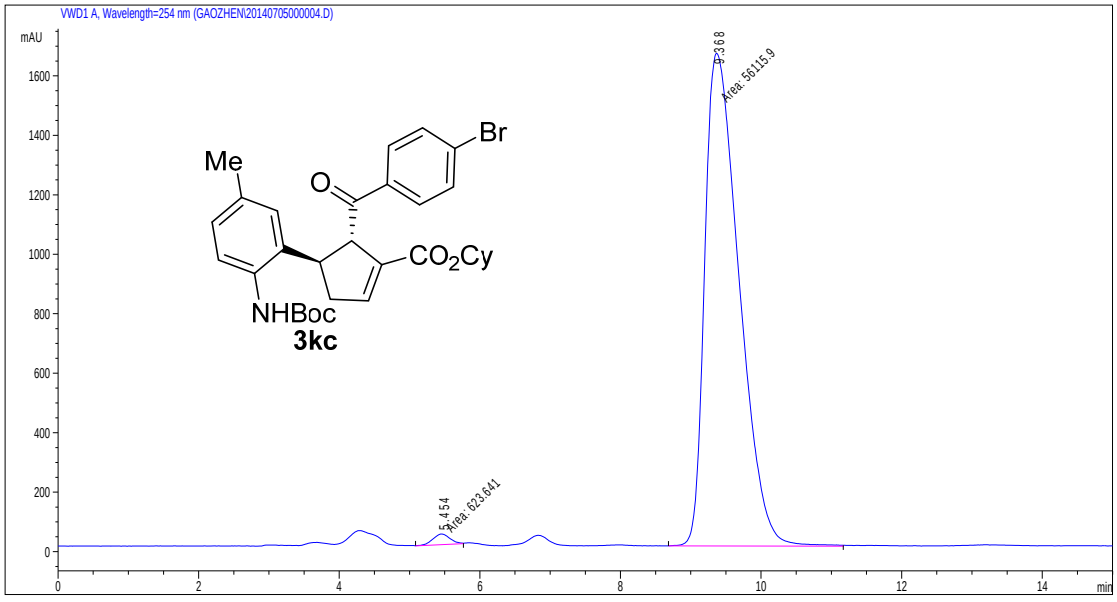
#	Time	Area	Height	Width	Area%	Symmetry
1	6.527	239.9	9.3	0.4318	1.873	1.227
2	11.988	12571.2	351.7	0.5957	98.127	0.638

HPLC chromatogram of racemic 3kc



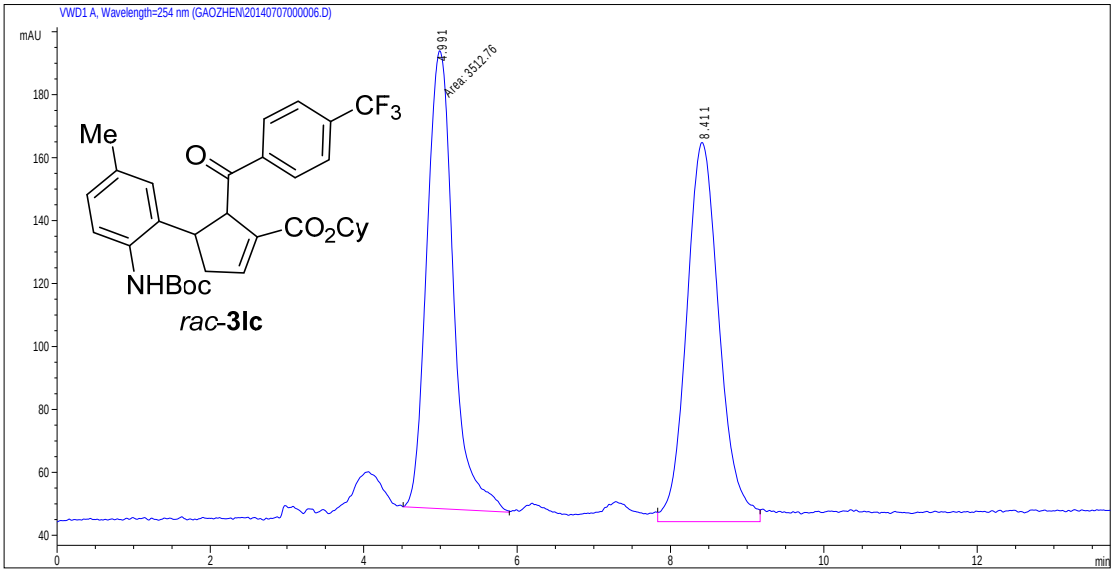
#	Time	Area	Height	Width	Area%	Symmetry
1	5.387	40091.6	1721.4	0.3649	49.547	0.886
2	9.27	40824.5	1237.6	0.5115	50.453	0.631

HPLC chromatogram of chiral 3kc



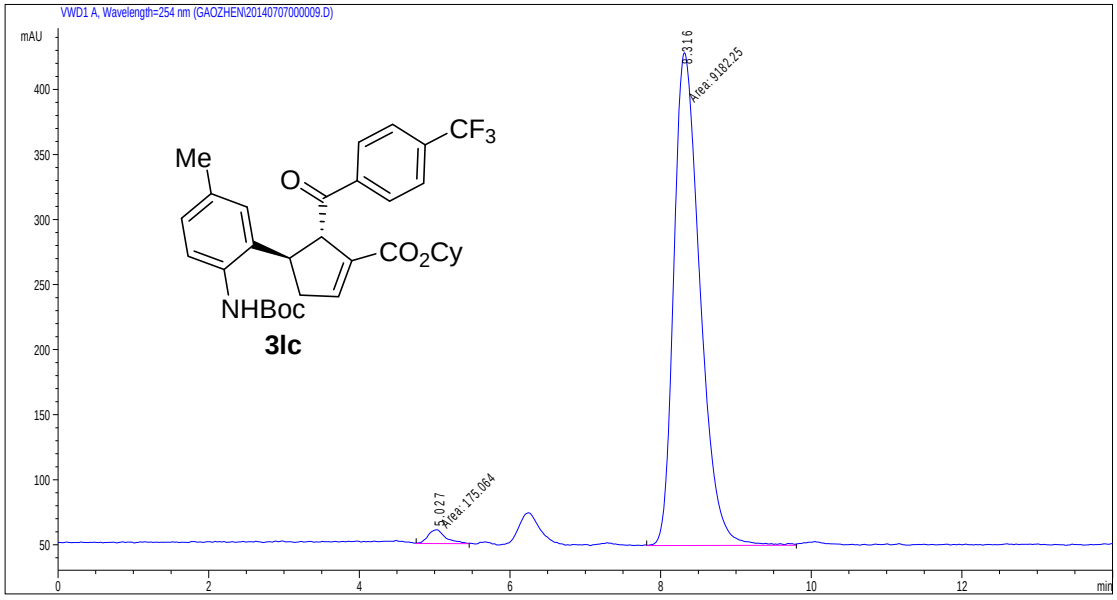
#	Time	Area	Height	Width	Area%	Symmetry
1	5.454	623.6	36.2	0.2873	1.099	1.026
2	9.368	56115.9	1656.3	0.5647	98.901	0.513

HPLC chromatogram of racemic 3lc



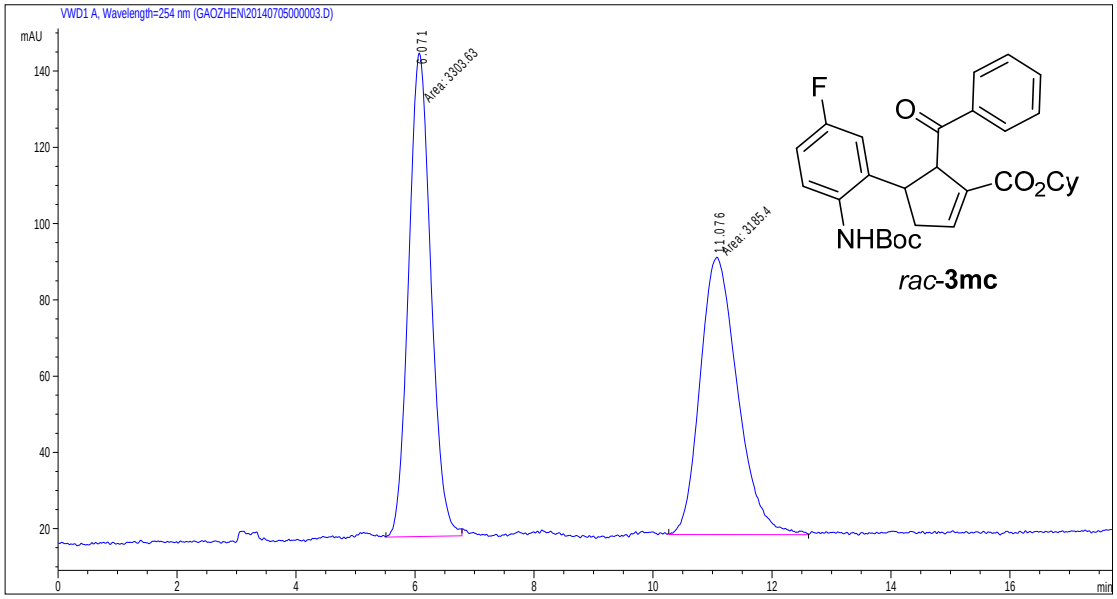
#	Time	Area	Height	Width	Area%	Symmetry
1	4.991	3512.8	145.5	0.4023	49.572	0.893
2	8.411	3573.4	120.5	0.4625	50.428	0.857

HPLC chromatogram of chiral 3lc



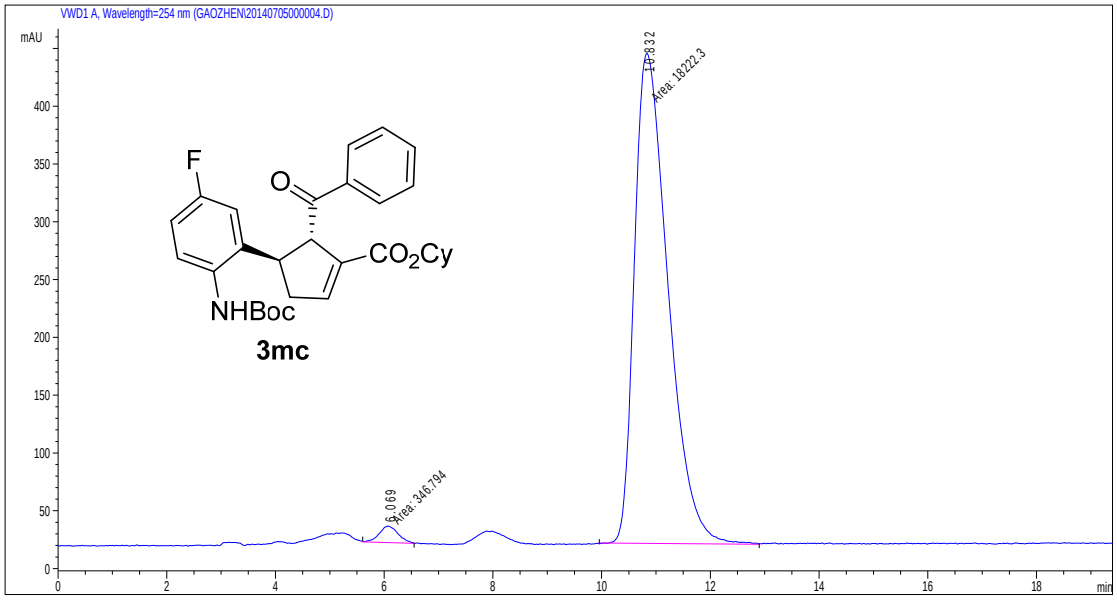
#	Time	Area	Height	Width	Area%	Symmetry
1	5.027	175.1	10.7	0.2737	1.871	0.901
2	8.316	9182.2	378.8	0.404	98.129	0.654

HPLC chromatogram of racemic 3mc



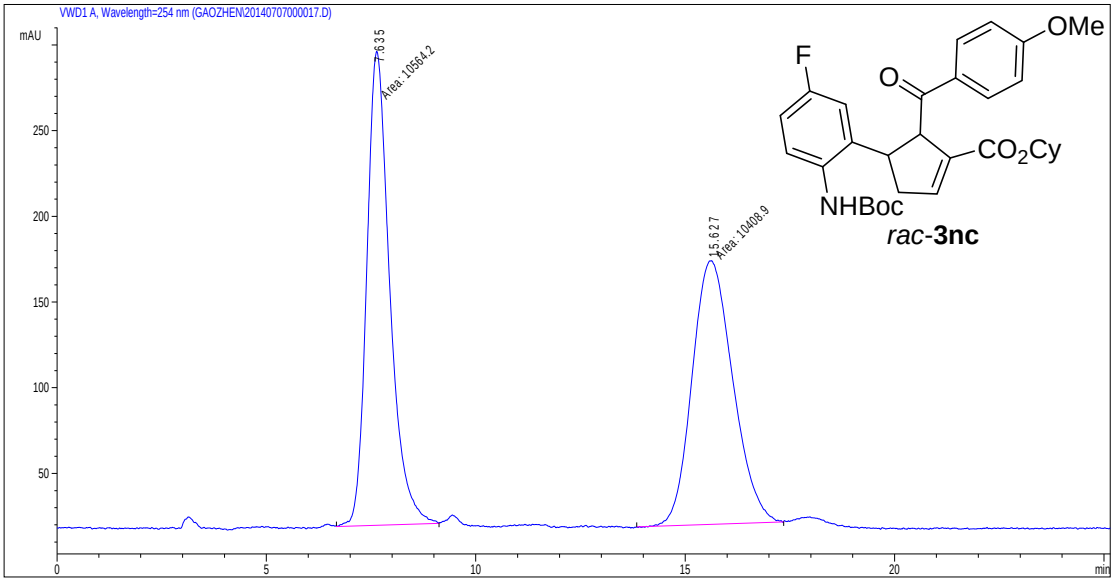
#	Time	Area	Height	Width	Area%	Symmetry
1	6.071	3303.6	126.8	0.4343	50.911	0.877
2	11.076	3185.4	72.7	0.7299	49.089	0.79

HPLC chromatogram of chiral 3mc



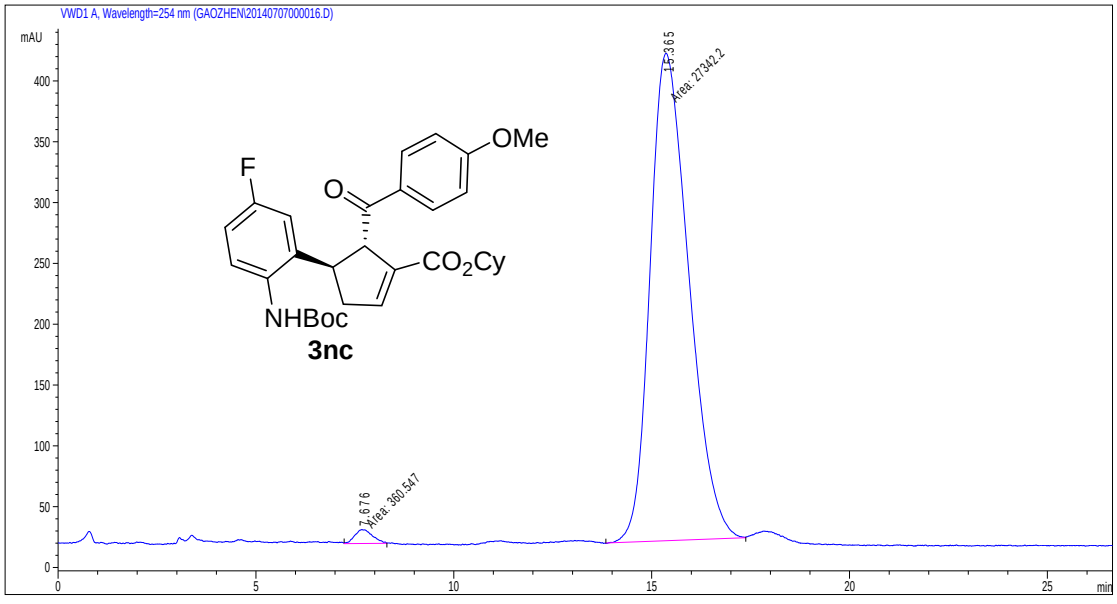
#	Time	Area	Height	Width	Area%	Symmetry
1	6.069	346.8	14.3	0.4034	1.868	0.855
2	10.832	18222.3	423.9	0.7165	98.132	0.568

HPLC chromatogram of racemic 3nc



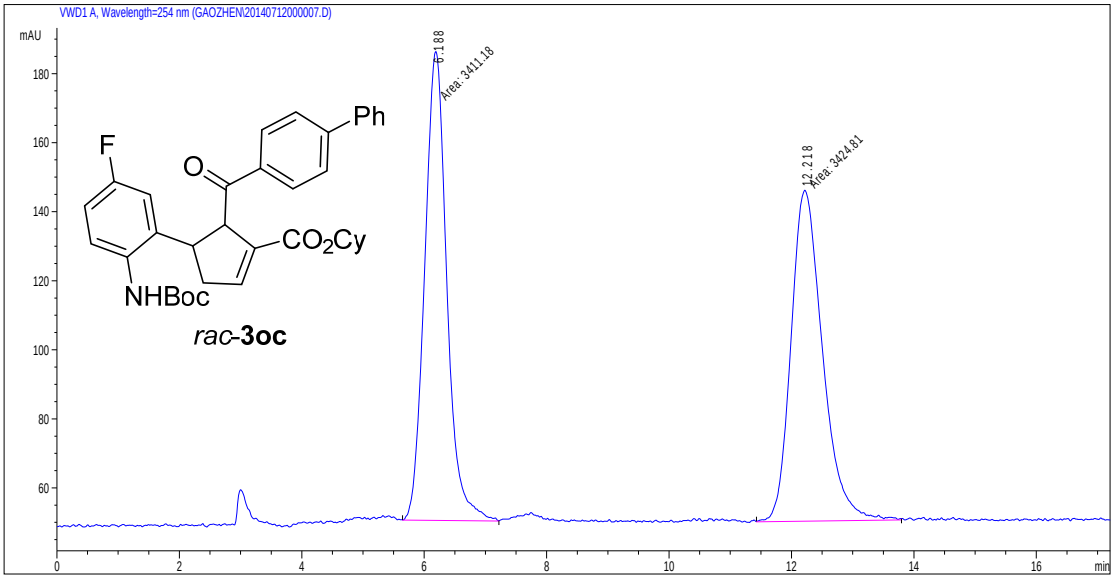
#	Time	Area	Height	Width	Area%	Symmetry
1	7.635	10564.2	276.5	0.6368	50.370	0.737
2	15.627	10408.9	153.8	1.1278	49.630	0.875

HPLC chromatogram of chiral 3nc



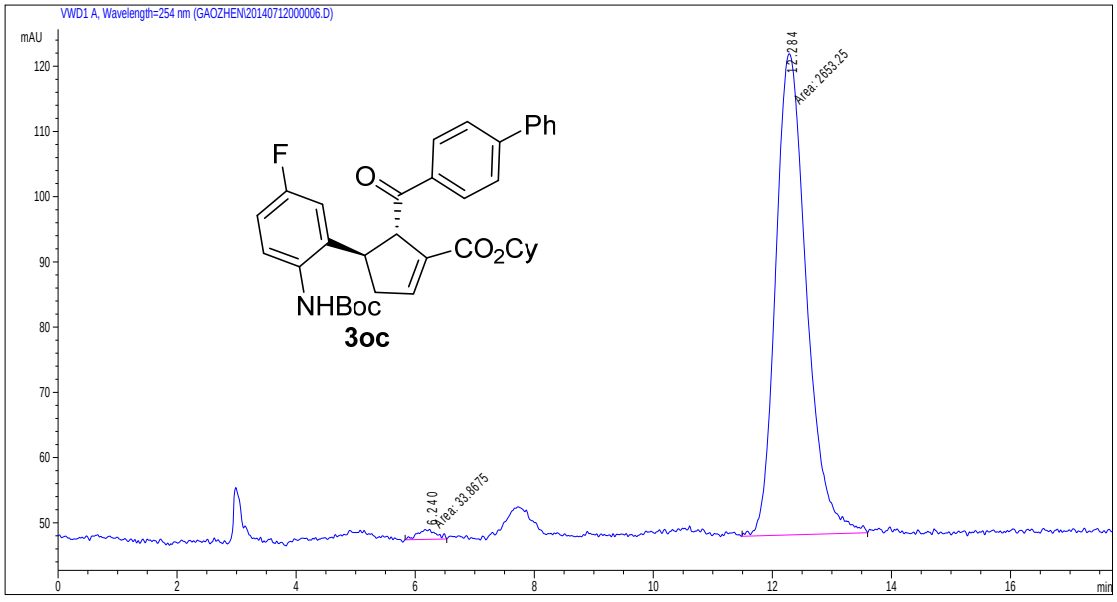
#	Time	Area	Height	Width	Area%	Symmetry
1	7.676	360.5	11.5	0.5236	1.301	0.669
2	15.365	27342.2	400.6	1.1375	98.699	0.689

HPLC chromatogram of racemic 3oc



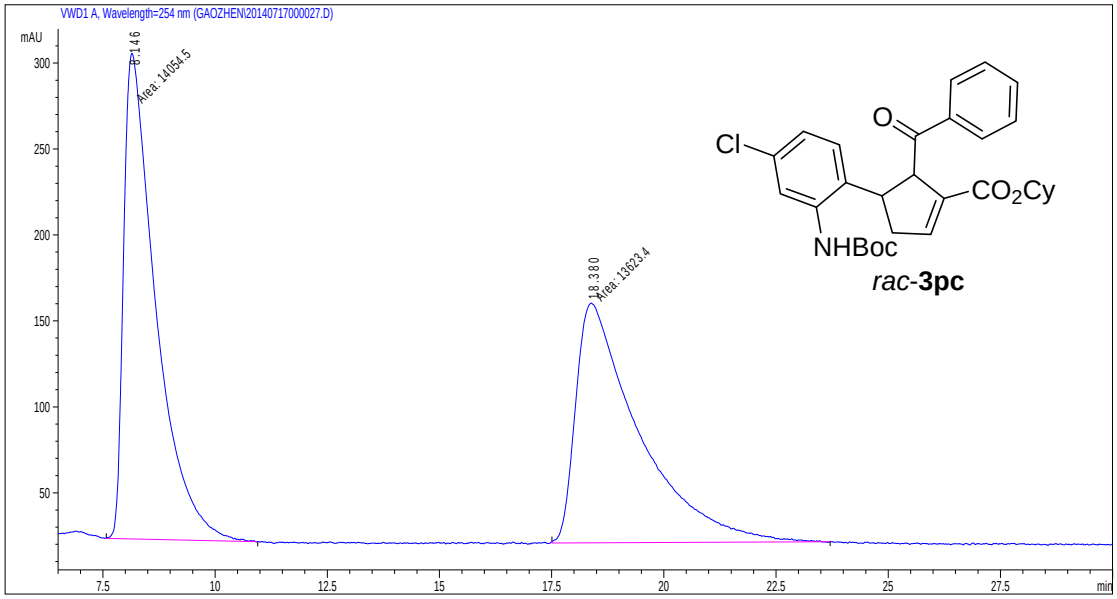
#	Time	Area	Height	Width	Area%	Symmetry
1	6.188	3411.2	135.8	0.4186	49.900	0.946
2	12.218	3424.8	95.9	0.5954	50.100	0.753

HPLC chromatogram of chiral 3oc



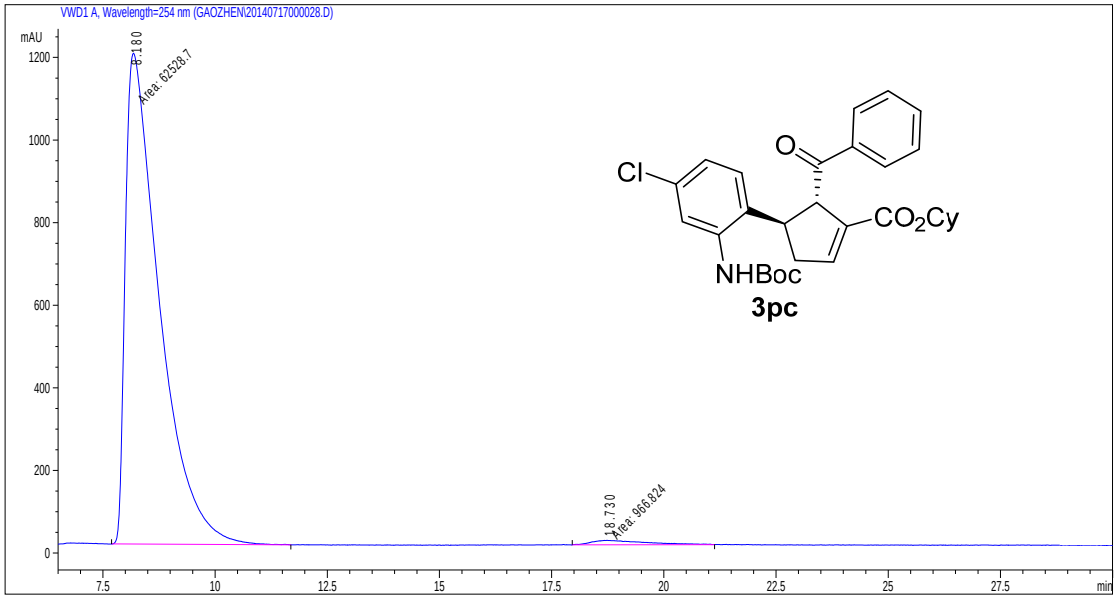
#	Time	Area	Height	Width	Area%	Symmetry
1	6.24	33.9	1.5	0.3669	1.260	1.57
2	12.284	2653.3	73.8	0.5994	98.740	0.762

HPLC chromatogram of racemic 3pc



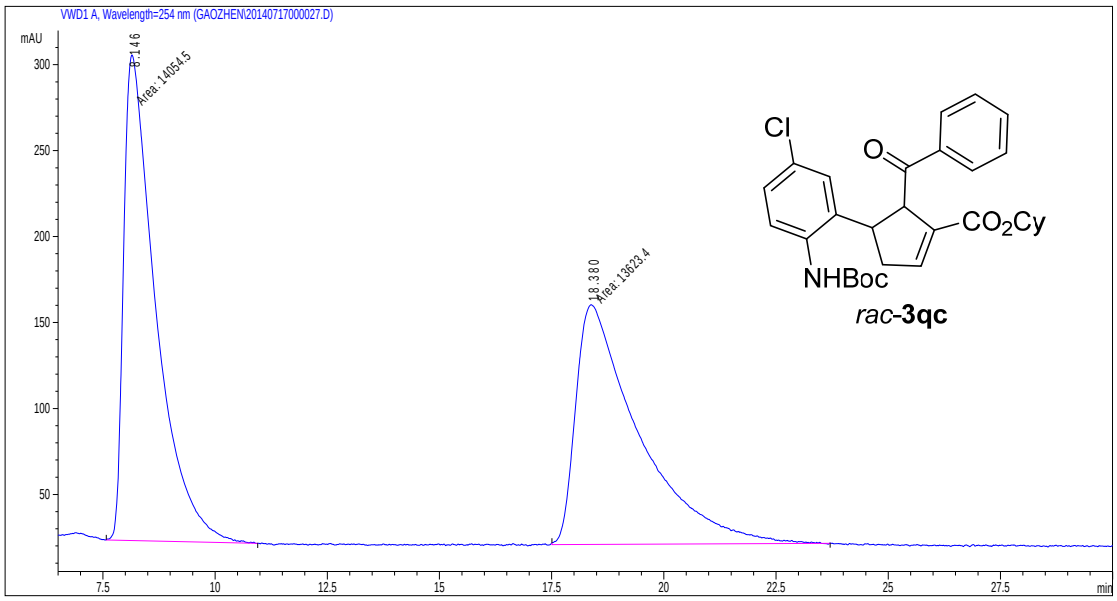
#	Time	Area	Height	Width	Area%	Symmetry
1	8.146	14054.5	282.5	0.8293	50.779	0.339
2	18.38	13623.4	139.5	1.6274	49.221	0.316

HPLC chromatogram of chiral 3pc



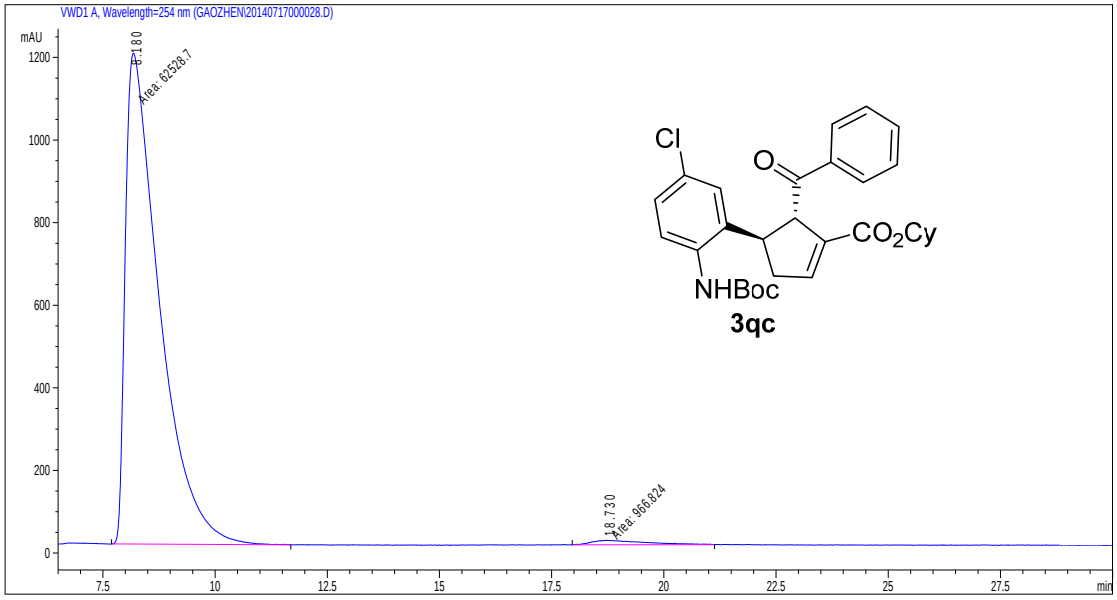
#	Time	Area	Height	Width	Area%	Symmetry
1	8.18	62528.7	1188.1	0.8771	98.477	0.302
2	18.73	966.8	11	1.4643	1.523	0.38

HPLC chromatogram of racemic 3qc



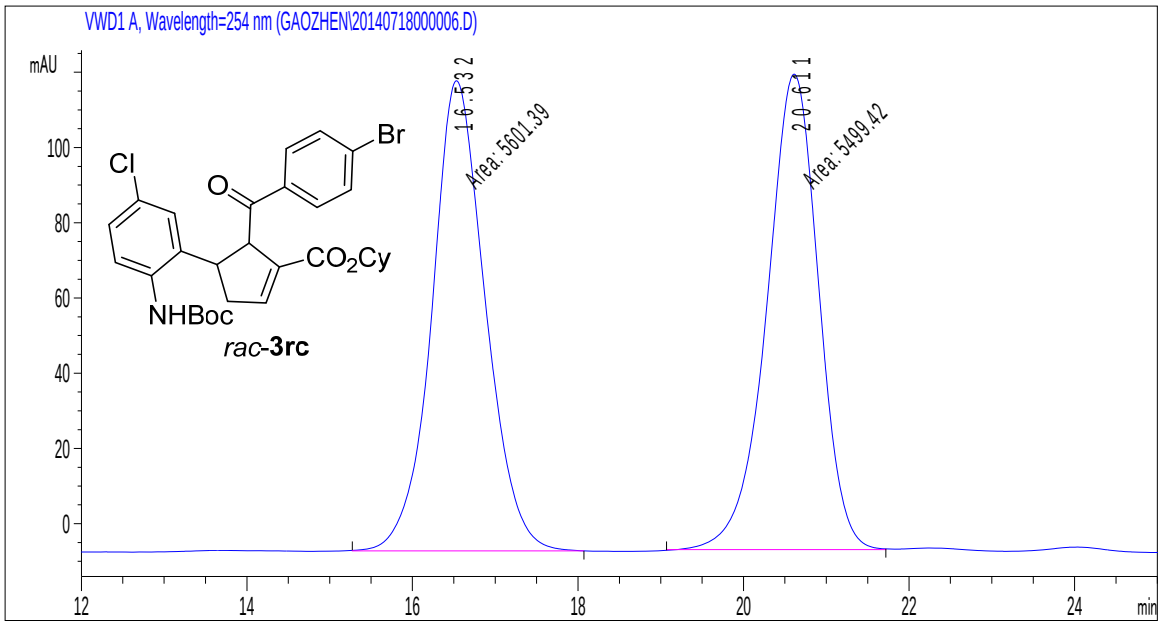
#	Time	Area	Height	Width	Area%	Symmetry
1	8.146	14054.5	282.5	0.8293	50.779	0.339
2	18.38	13623.4	139.5	1.6274	49.221	0.316

HPLC chromatogram of chiral 3qc



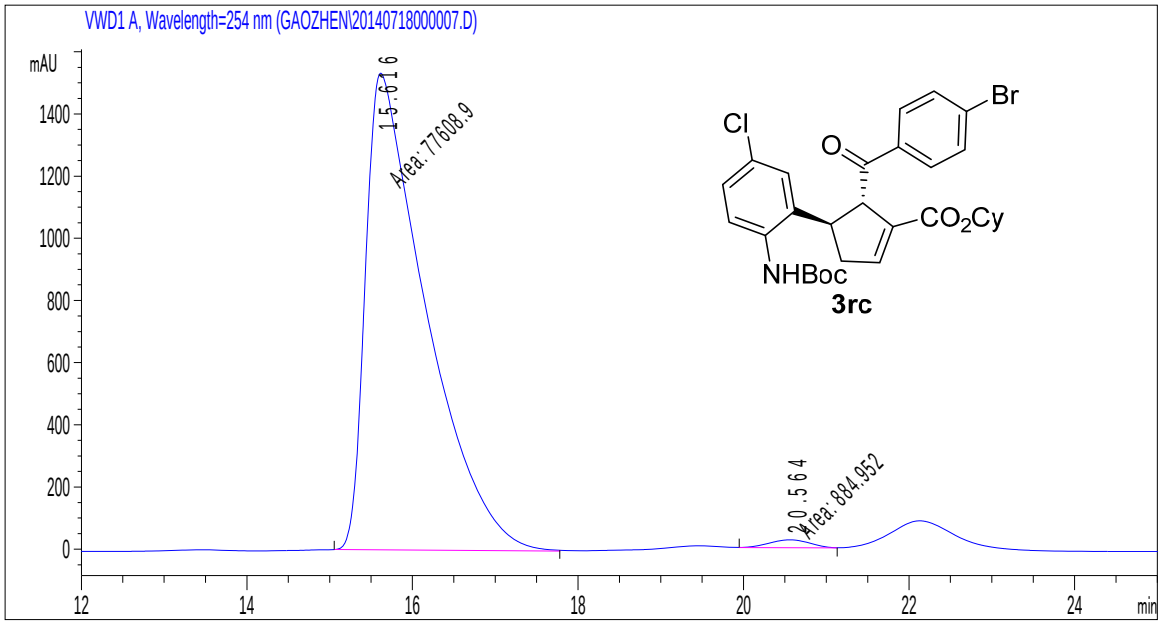
#	Time	Area	Height	Width	Area%	Symmetry
1	8.18	62528.7	1188.1	0.8771	98.477	0.302
2	18.73	966.8	11	1.4643	1.523	0.38

HPLC chromatogram of racemic 3rc



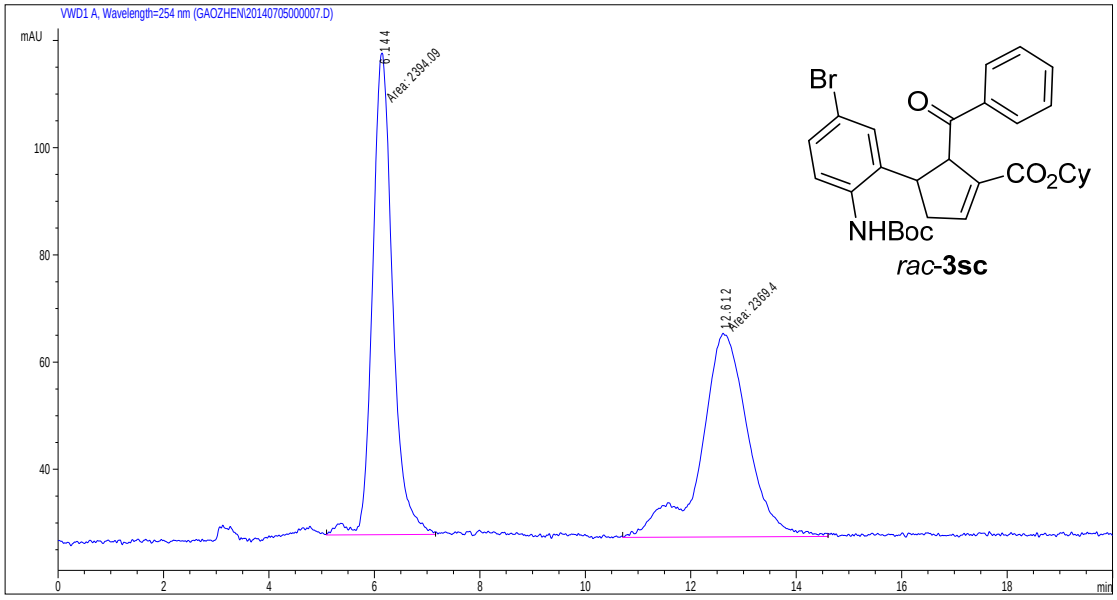
#	Time	Area	Height	Width	Area%	Symmetry
1	16.532	5601.4	125	0.7469	50.459	0.842
2	20.611	5499.4	126.4	0.7249	49.541	1.095

HPLC chromatogram of chiral 3rc



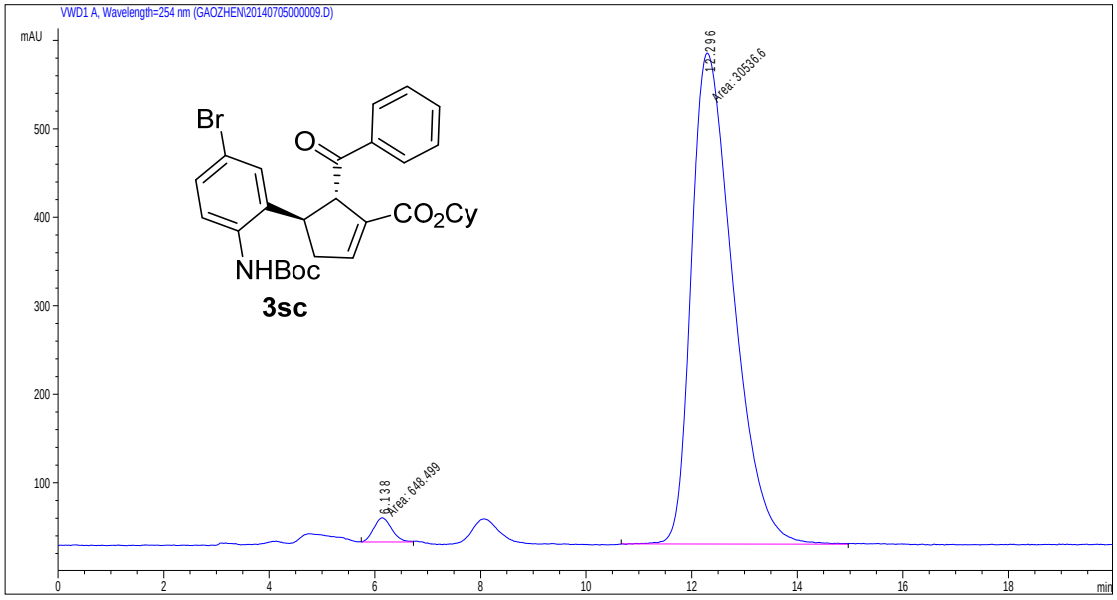
#	Time	Area	Height	Width	Area%	Symmetry
1	15.616	77608.9	1533.5	0.8435	98.873	0.329
2	20.564	885	25.7	0.5735	1.127	1.023

HPLC chromatogram of racemic 3sc



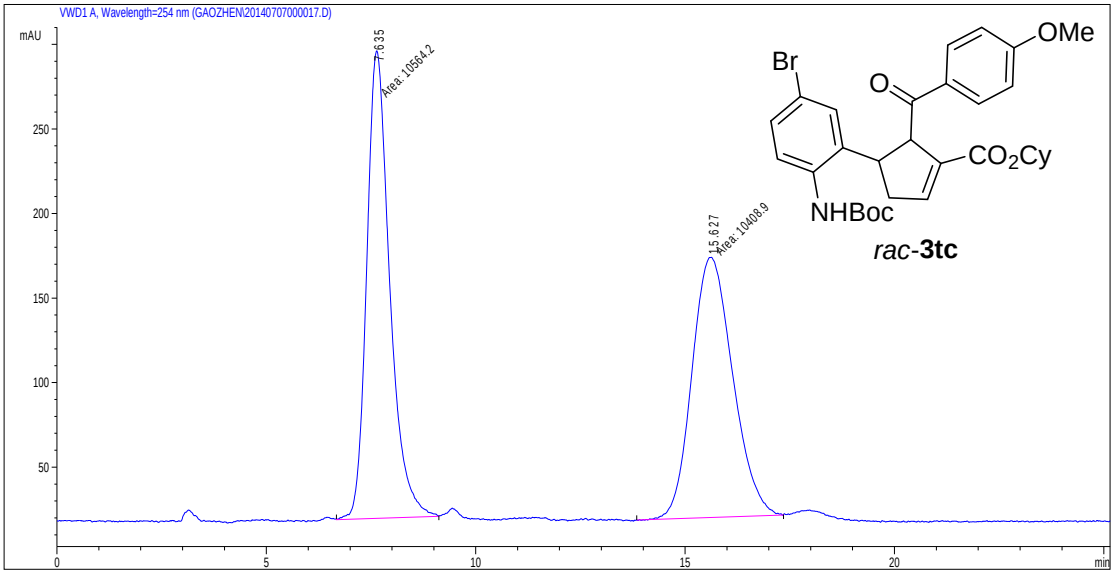
#	Time	Area	Height	Width	Area%	Symmetry
1	6.144	2394.1	89.8	0.4441	50.259	0.876
2	12.612	2369.4	38	1.0395	49.741	0.918

HPLC chromatogram of chiral 3sc



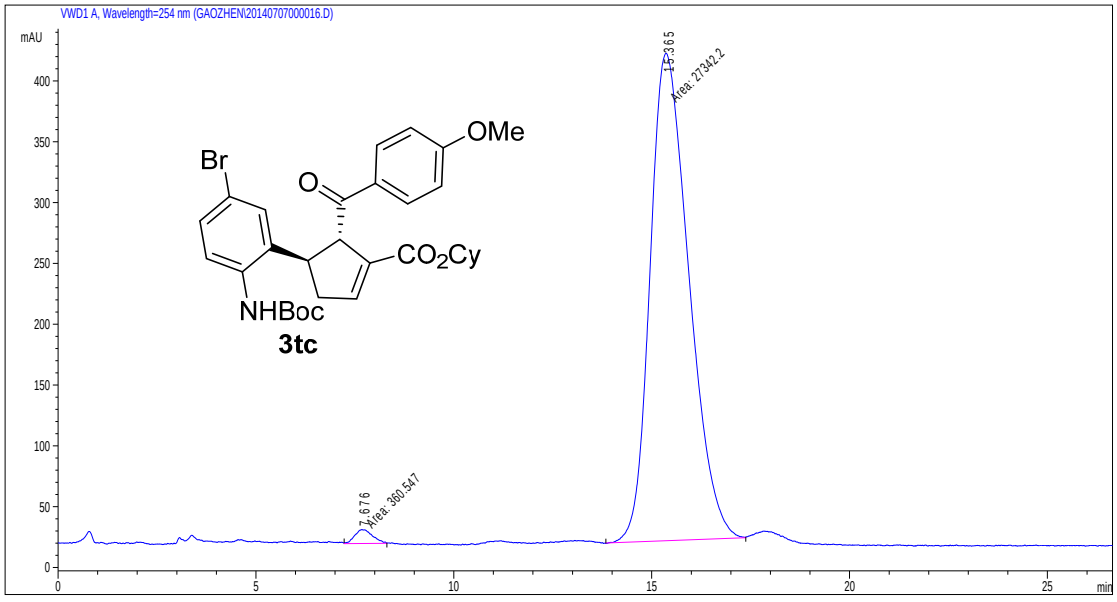
#	Time	Area	Height	Width	Area%	Symmetry
1	6.138	648.5	27.4	0.3941	2.080	0.848
2	12.296	30536.6	554.9	0.9172	97.920	0.595

HPLC chromatogram of racemic 3tc



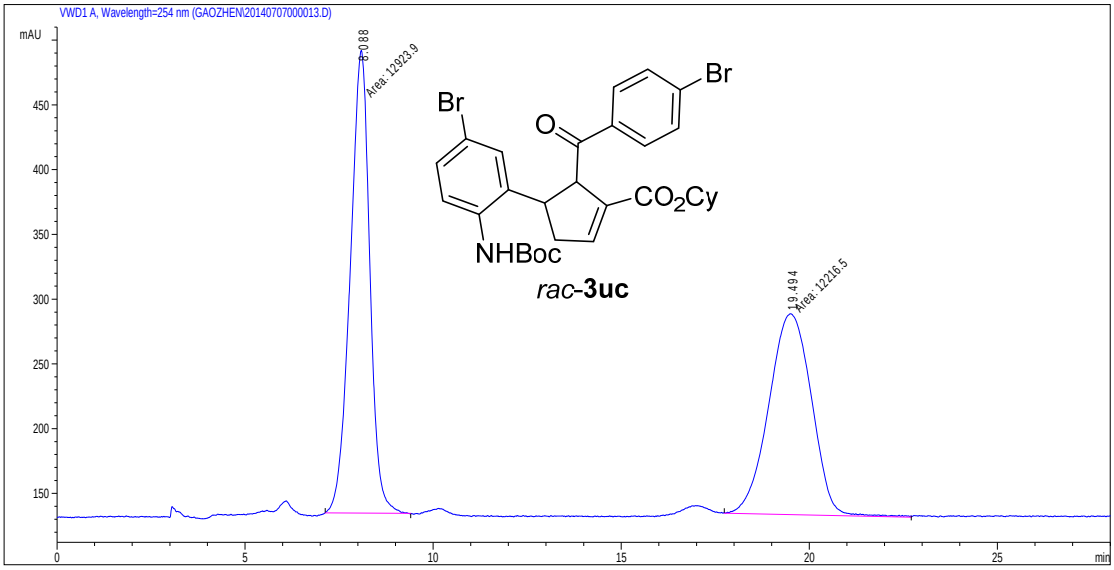
#	Time	Area	Height	Width	Area%	Symmetry
1	7.635	10564.2	276.5	0.6368	50.370	0.737
2	15.627	10408.9	153.8	1.1278	49.630	0.875

HPLC chromatogram of chiral 3tc



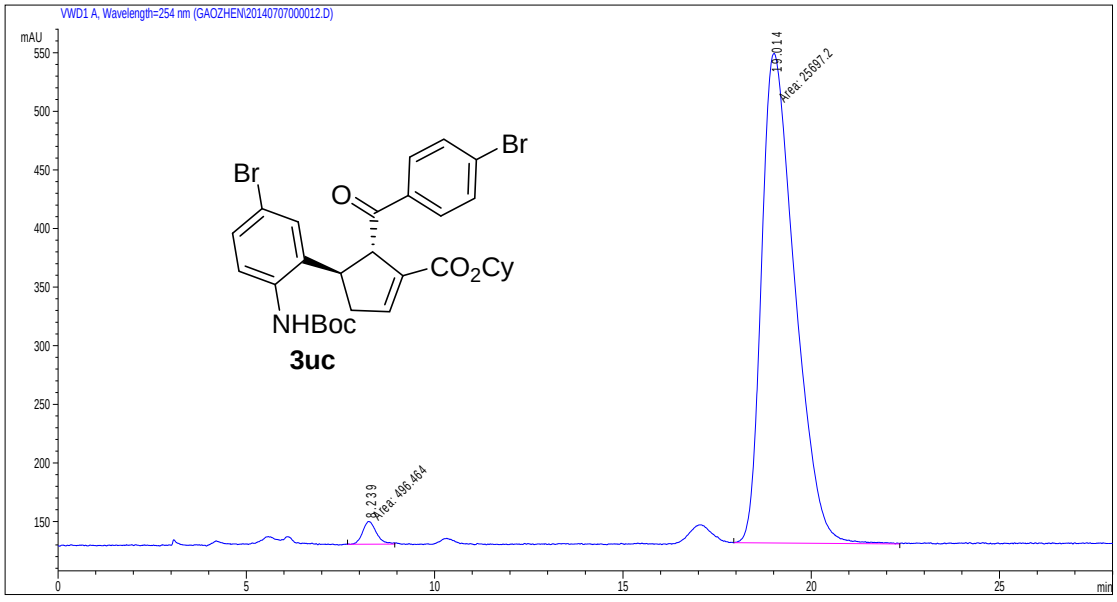
#	Time	Area	Height	Width	Area%	Symmetry
1	7.676	360.5	11.5	0.5236	1.301	0.669
2	15.365	27342.2	400.6	1.1375	98.699	0.689

HPLC chromatogram of racemic 3uc



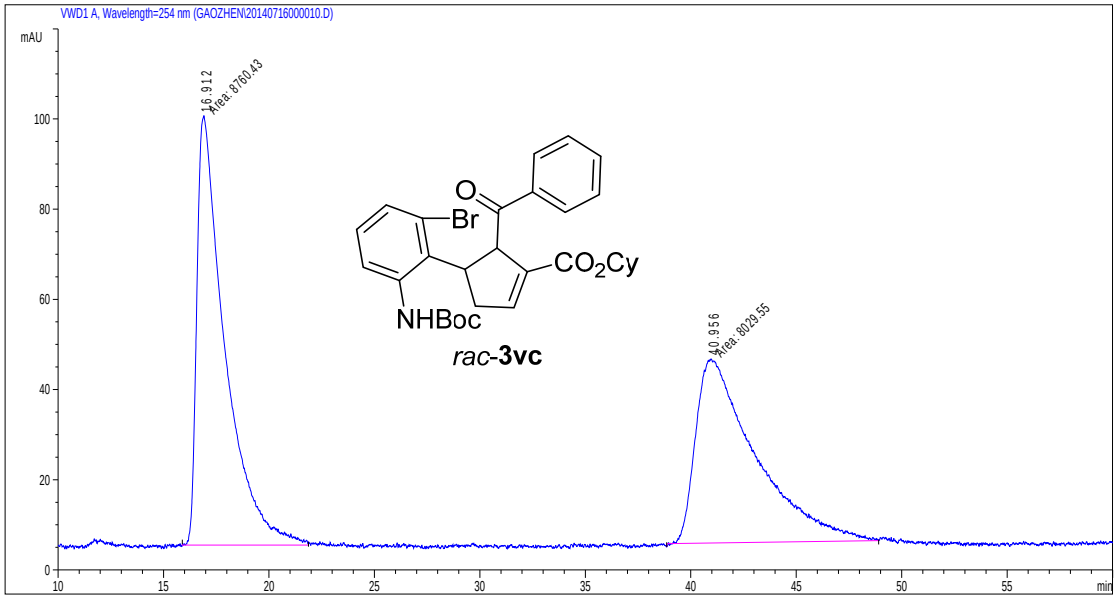
#	Time	Area	Height	Width	Area%	Symmetry
1	8.088	12923.9	357.2	0.6029	51.407	1.228
2	19.494	12216.5	155.1	1.3127	48.593	0.989

HPLC chromatogram of chiral 3uc



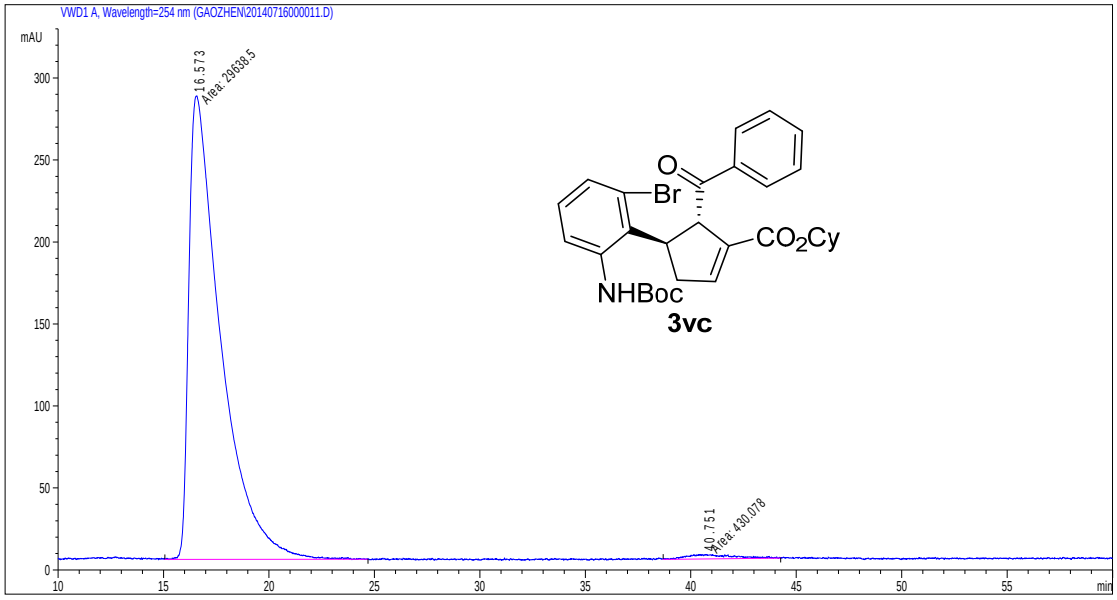
#	Time	Area	Height	Width	Area%	Symmetry
1	8.239	496.5	19.4	0.426	1.895	0.705
2	19.014	25697.2	417.8	1.0252	98.105	0.588

HPLC chromatogram of racemic 3vc



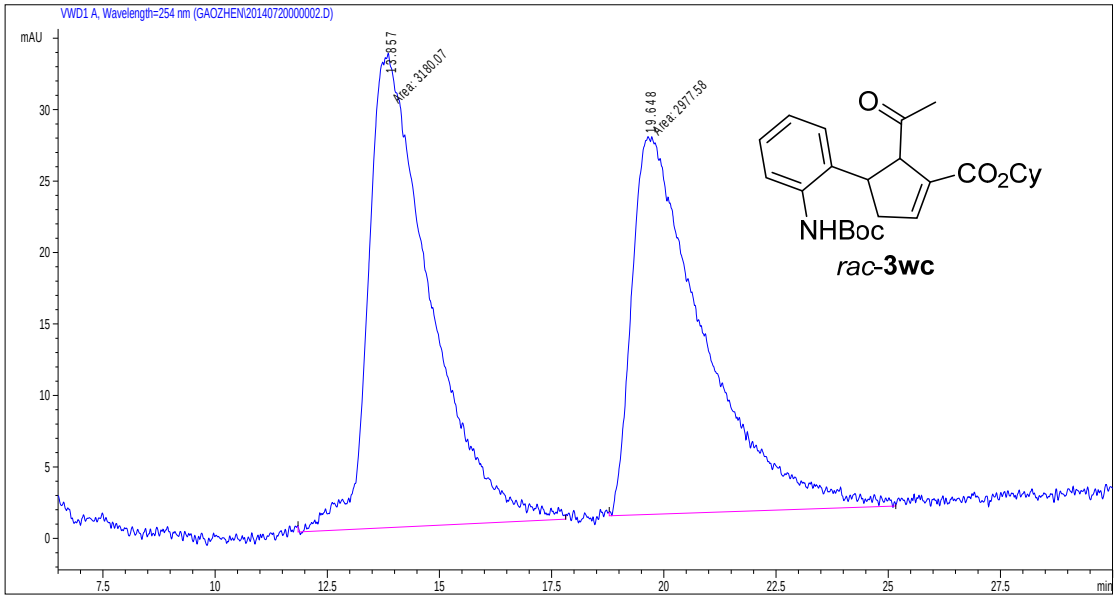
#	Time	Area	Height	Width	Area%	Symmetry
1	16.912	8760.4	95.4	1.5329	52.177	0.322
2	40.956	8029.5	40.8	3.2815	47.823	0.338

HPLC chromatogram of chiral 3vc



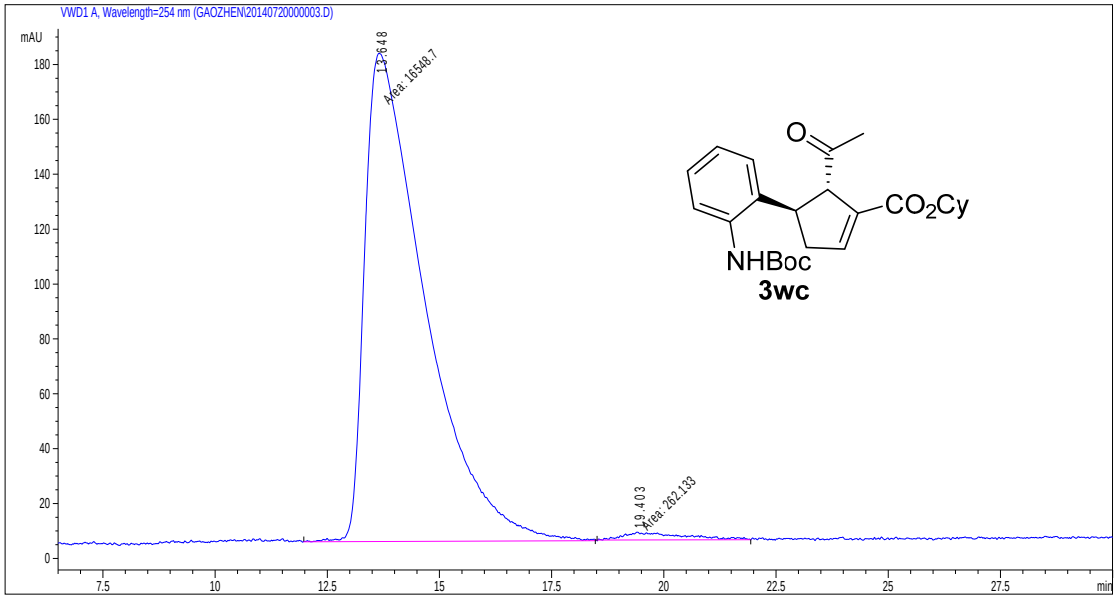
#	Time	Area	Height	Width	Area%	Symmetry
1	16.573	29638.5	282.7	1.7476	98.570	0.316
2	40.751	430.1	2.7	2.6236	1.430	0.759

HPLC chromatogram of racemic 3wc

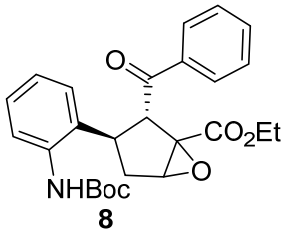


#	Time	Area	Height	Width	Area%	Symmetry
1	13.857	3180.1	33.2	1.5972	51.644	0.471
2	19.648	2977.6	26.4	1.877	48.356	0.284

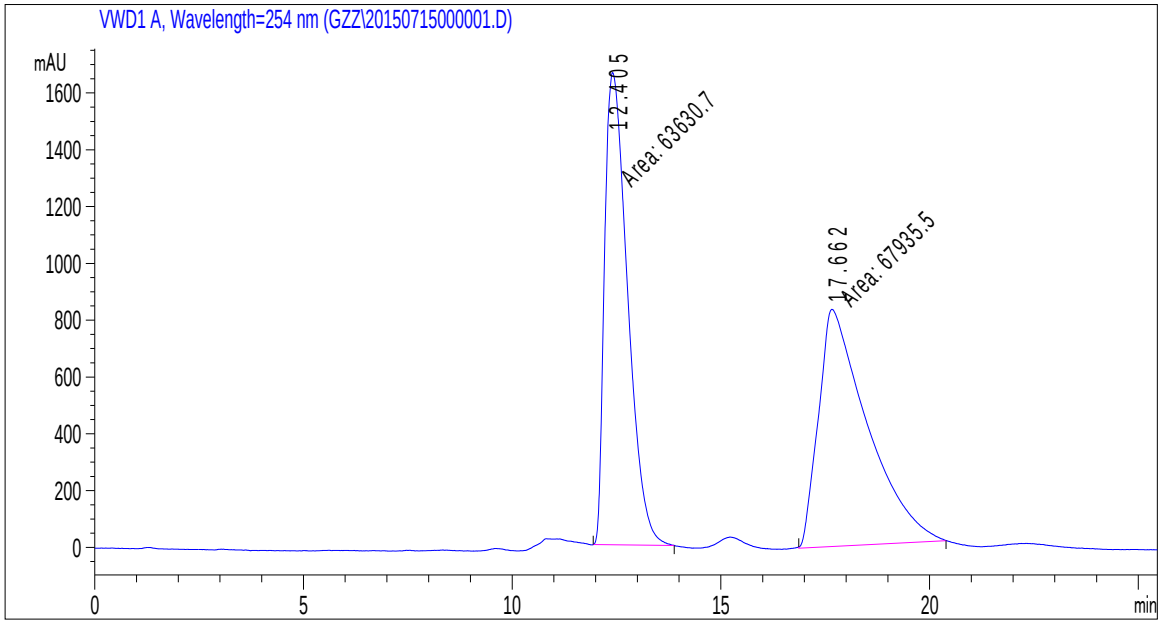
HPLC chromatogram of chiral 3wc



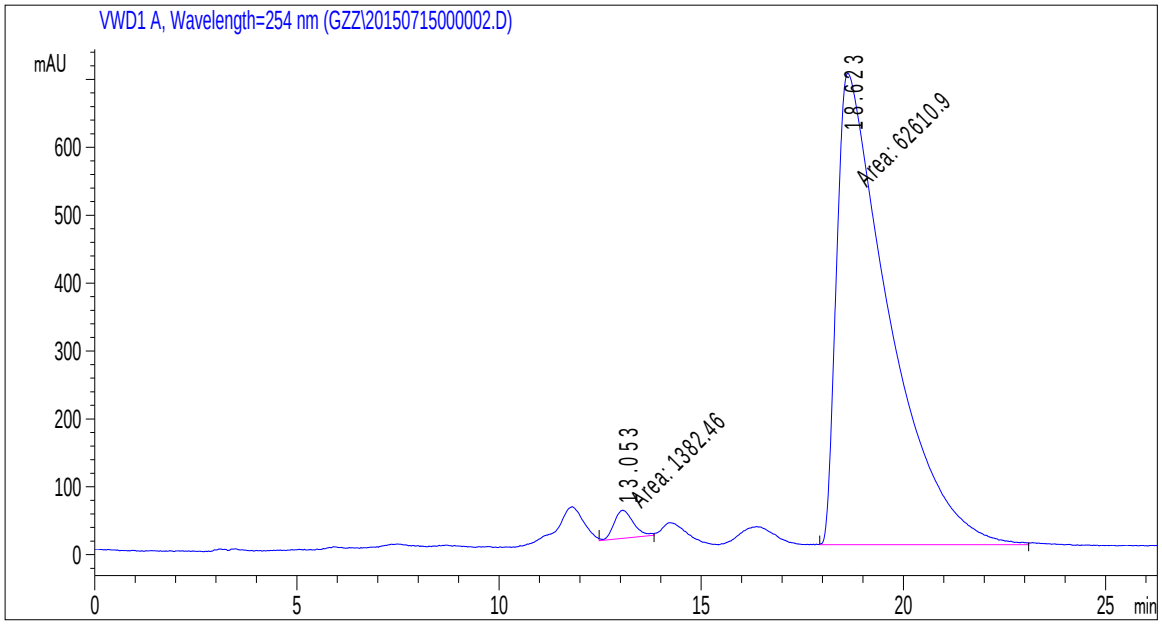
#	Time	Area	Height	Width	Area%	Symmetry
1	13.648	16548.7	177.9	1.5502	98.441	0.303
2	19.403	262.1	2.9	1.5257	1.559	0.311



8



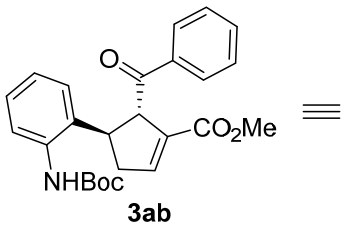
#	Time	Area	Height	Width	Area%	Symmetry
1	12.405	63630.7	1662.6	0.6379	48.364	0.515
2	17.662	67935.5	835.4	1.3553	51.636	0.379



#	Time	Area	Height	Width	Area%	Symmetry
1	13.053	1382.5	41.6	0.5537	2.160	0.785
2	18.623	62610.9	694.4	1.5027	97.840	0.265

X-Ray Crystallography Data

Crystallographic data for **3ab** has been deposited with the Cambridge Crystallographic Data Centre as deposition number CCDC 995194 and 995195. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.



3ab

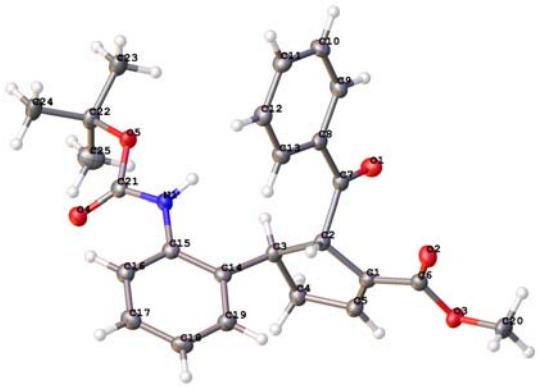


Table 1. Crystal data and structure refinement for **3ab**

Identification code	**3ab**	
Empirical formula	$C_{25}H_{27}NO_5$	
Formula weight	421.48	
Temperature	109.7 K	
Crystal system	monoclinic	
Space group	P21	
Unit cell dimensions	a = 10.7274(4) Å	= 90°.
	b = 10.1113(7) Å	= 99.118(4)°.
	c = 20.9352(11)Å	= 90°.
Volume	2242.1(2) Å3	
Z	4	
ρcalc	1.249 mg mm^{-3}	
μ	0.706 mm^{-1}	
F(000)	896	
Crystal size	0.45 × 0.35 × 0.08 mm3	
Theta range for data collection	8.34 to 141.92°	
Index ranges	-13 ≤ h ≤ 13, -10 ≤ k ≤ 12, -25 ≤ l ≤ 25	
Reflections collected	16436	
Independent reflections	7480[R(int) =0.0253 (inf-0.9Å)]	
Data/restraints/parameters	7480/1/567	
Goodness-of-fit on F2	1.040	
Final R indexes [I>2σ (I) i.e. Fo>4σ (Fo)]	R1 = 0.0391, wR2 = 0.1006	
Final R indexes [all data]	R1 = 0.0415, wR2 = 0.1032	
Largest diff. peak/hole	0.260/-0.194 e $Å^{-3}$	
Flack Parameters	-0.06(13)	
Completeness	0.983	

Table 2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å2$\times 10^3$) for **3ab**. U(eq) is defined as 1/3 of of the trace of the orthogonalised U^{ij} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
O1	-2396.8(13)	-3549.5(17)	-1981.2(7)	27.0(3)
O2	-3749.8(14)	-537.3(16)	-1801.3(6)	25.8(3)
O3	-5689.3(13)	-1356.2(17)	-1759.1(7)	25.9(3)
O4	-2488.4(13)	-5406.4(16)	-5384.1(6)	25.0(3)
O5	-1257.9(13)	-6227.2(16)	-4484.1(6)	23.4(3)
N1	-2300.5(15)	-4386.1(18)	-4388.9(7)	20.6(3)
C1	-4570.8(18)	-2236(2)	-2536.2(9)	20.7(4)
C2	-3417.2(17)	-2275(2)	-2869.4(9)	19.6(4)
C3	-3783.8(18)	-3323(2)	-3428.0(9)	19.7(4)
C4	-5124.3(19)	-3840(2)	-3340.3(9)	24.7(4)
C5	-5467.9(18)	-3059(2)	-2784.6(9)	22.3(4)
C6	-4596.6(17)	-1287(2)	-1997.3(9)	19.8(4)
C7	-2266.5(18)	-2742(2)	-2395.4(9)	20.5(4)
C8	-979.6(18)	-2221(2)	-2460.6(9)	20.2(4)
C9	41.1(19)	-2631(2)	-2008.9(9)	24.1(4)
C10	1255.1(19)	-2192(2)	-2045.2(10)	26.5(5)
C11	1453.2(18)	-1324(2)	-2539(1)	25.9(5)
C12	443.6(19)	-922(2)	-2992.8(9)	25.6(4)
C13	-771.3(19)	-1365(2)	-2959.2(9)	23.1(4)
C14	-3772.2(17)	-2729(2)	-4095.9(9)	19.7(4)
C15	-3071.3(17)	-3262(2)	-4548.9(9)	20.1(4)
C16	-3132.7(18)	-2670(2)	-5157.5(9)	24.3(4)
C17	-3881(2)	-1570(2)	-5322.1(10)	26.7(5)
C18	-4589.8(19)	-1034(2)	-4881.3(10)	25.8(4)
C19	-4525.8(18)	-1623(2)	-4276.6(10)	23.8(4)
C20	-5859(2)	-356(3)	-1285(1)	29.5(5)
C21	-2059.2(17)	-5355(2)	-4811.9(9)	20.4(4)

C22	-1008.6(19)	-7514(2)	-4776.4(9)	24.6(4)
C23	-125(2)	-8179(3)	-4229.7(10)	30.4(5)
C24	-348(2)	-7297(3)	-5364.5(10)	33.4(5)
C25	-2229(2)	-8286(3)	-4932.7(13)	37.7(5)
O6	-2424.7(14)	-8244(2)	-3190.6(7)	34.7(4)
O7	-1125.8(13)	-5113.4(16)	-3081.1(6)	23.9(3)
O8	846.3(13)	-5906.2(17)	-2847.0(7)	26.7(3)
O9	-2601.1(17)	-9587.4(19)	618.8(7)	35.4(4)
O10	-3217.6(14)	-11012.3(17)	-213.2(7)	28.4(3)
N2	-2467.7(17)	-9084.4(19)	-443.8(8)	24.2(4)
C26	-729.6(18)	-6889(2)	-2340.3(9)	20.8(4)
C27	-2079.5(18)	-6961(2)	-2212.9(9)	20.1(4)
C28	-1963.5(18)	-7874(2)	-1605.2(9)	21.1(4)
C29	-774(2)	-8728(2)	-1664.4(10)	27.0(5)
C30	-33.2(19)	-7856(2)	-2048.0(9)	24.7(4)
C31	-384.7(18)	-5876(2)	-2793.4(8)	19.4(4)
C32	-2897.2(19)	-7680(2)	-2775.8(9)	21.9(4)
C33	-4297.2(18)	-7750(2)	-2782.2(9)	22.1(4)
C34	-4982(2)	-8621(2)	-3219.6(9)	24.7(4)
C35	-6271(2)	-8770(2)	-3241.7(10)	27.1(5)
C36	-6899.6(19)	-8012(3)	-2836.2(10)	29.5(5)
C37	-6230(2)	-7132(3)	-2403.5(10)	29.3(5)
C38	-4925(2)	-7003(2)	-2367.8(9)	24.4(4)
C39	-1743.3(18)	-7139(2)	-962.1(9)	20.1(4)
C40	-1946.5(18)	-7799(2)	-391.7(9)	21.9(4)
C41	-1612(2)	-7183(3)	207.1(10)	31.4(5)
C42	-1077(2)	-5932(3)	243.9(10)	35.8(6)
C43	-878(2)	-5258(3)	-307.2(11)	31.4(5)
C44	-1224.2(19)	-5876(2)	-906.1(10)	24.5(4)
C45	1226(2)	-4959(3)	-3302(1)	30.9(5)
C46	-2745.4(19)	-9875(2)	49.8(9)	24.7(4)

C47	-3488(2)	-12128(3)	203.1(11)	31.2(5)
C48	-2289(2)	-12495(3)	654.2(12)	36.5(6)
C49	-3877(3)	-13223(3)	-285.8(13)	40.8(6)
C50	-4570(2)	-11749(3)	563.1(12)	39.6(6)

Table 3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **3ab**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11}+...+2hka \times b \times U^{12}]$

Atom	$\mathbf{U_{11}}$	$\mathbf{U_{22}}$	$\mathbf{U_{33}}$	$\mathbf{U_{23}}$	$\mathbf{U_{13}}$	$\mathbf{U_{12}}$
O1	24.4(7)	29.1(9)	27.8(7)	6.7(6)	4.6(6)	0.5(6)
O2	28.9(7)	27.1(9)	21.3(6)	-4.9(6)	3.8(5)	-5.0(6)
O3	22.6(6)	30.3(9)	25.7(7)	-9.7(6)	6.0(5)	0.3(6)
O4	28.1(7)	26.3(9)	20.0(6)	0.2(6)	2.2(5)	3.3(6)
O5	26.5(7)	23.6(9)	20.0(6)	-2.4(6)	3.2(5)	7.5(6)
N1	22.5(7)	23.8(10)	15.2(7)	1.6(6)	2.7(6)	4.7(7)
C1	19.7(8)	23.4(12)	19.2(8)	2.4(8)	3.5(7)	3.7(8)
C2	19.6(8)	20.9(11)	18.6(8)	-1.8(8)	3.5(7)	0.5(8)
C3	22.3(9)	18.0(11)	18.9(9)	-1.6(7)	3.3(7)	1.6(8)
C4	26.8(10)	26.8(13)	20.6(9)	-2.9(8)	4.3(7)	-2.6(9)
C5	21.3(9)	25.0(12)	21.6(9)	-2.0(8)	5.7(7)	0.2(8)
C6	21.3(9)	19.7(11)	18.3(8)	0.9(7)	2.8(7)	2.4(8)
C7	23.0(9)	21.4(11)	17.3(8)	-1.4(8)	3.7(7)	0.8(8)
C8	20.1(8)	21.9(11)	18.5(8)	-6.3(8)	3.3(7)	-0.4(8)
C9	26.5(10)	26.9(12)	18.8(9)	1.0(8)	2.8(7)	-2.7(9)
C10	22.4(9)	33.6(14)	21.5(9)	-0.4(9)	-2.2(7)	0.0(9)
C11	20.8(9)	29.6(13)	28(1)	-3.6(9)	5.7(7)	-3.2(9)
C12	27.2(10)	27.1(13)	23.6(9)	3.5(8)	7.4(7)	0.0(9)
C13	24.0(9)	25.0(12)	19.7(9)	1.7(8)	2.0(7)	3.2(8)
C14	17.5(8)	21.6(11)	19.4(9)	-1.1(8)	1.1(6)	-1.6(8)
C15	18.0(8)	21.4(11)	20.7(8)	-0.4(7)	2.4(7)	-2.3(8)
C16	24.6(9)	26.7(13)	22.0(9)	-0.1(8)	5.3(7)	-0.5(9)
C17	28.9(10)	26.4(13)	24.1(9)	6.1(8)	1.6(8)	0.7(9)

C18	25.1(9)	21.6(12)	28.8(10)	3.2(9)	-1.4(7)	4.2(9)
C19	23.1(9)	23.3(12)	25.0(9)	-0.6(8)	3.7(7)	2.8(8)
C20	29.3(10)	34.3(14)	25.4(10)	-11.3(9)	5.9(8)	4.4(9)
C21	19.2(8)	23.0(12)	19.7(9)	1.5(8)	5.7(7)	-2.5(8)
C22	31.2(10)	21.0(12)	22.6(9)	-3.1(8)	7.3(8)	4.2(9)
C23	37.4(11)	28.9(13)	26.6(10)	1.7(9)	10.6(8)	12(1)
C24	44.2(12)	34.9(15)	23.8(10)	0.4(9)	13.5(9)	15.4(11)
C25	39.2(12)	25.6(14)	46.2(13)	-0.1(11)	0.1(10)	-0.7(11)
O6	27.9(7)	51.2(12)	26.4(7)	-13.2(7)	8.2(6)	-2.7(7)
O7	25.9(7)	27.3(9)	18.8(6)	3.1(6)	4.5(5)	3.9(6)
O8	22.5(7)	29.8(9)	28.4(7)	7.0(6)	6.1(5)	-1.1(6)
O9	52.9(10)	34.3(10)	19.8(7)	3.2(6)	8.2(6)	-9.4(8)
O10	35.6(8)	26.4(9)	22.5(7)	5.9(6)	2.1(6)	-7.9(7)
N2	33.6(9)	23.9(10)	15.1(7)	-0.6(7)	4.2(6)	-5.5(7)
C26	20.9(9)	23.0(12)	18.2(8)	-3.9(8)	2.2(7)	1.1(8)
C27	23.5(9)	20.7(12)	16.8(8)	1.3(7)	4.8(7)	-0.4(8)
C28	26.6(9)	19.0(11)	17.7(8)	0.6(8)	3.4(7)	-4.2(8)
C29	37.4(11)	22.2(12)	22.1(9)	1.1(8)	7.0(8)	3.2(9)
C30	27.6(9)	28.0(13)	18.8(9)	-1.6(8)	4.5(7)	3.2(9)
C31	21.5(9)	20.2(11)	16.2(8)	-3.8(7)	2.0(7)	0.9(8)
C32	26.2(9)	23.0(12)	17.0(8)	3.5(8)	4.9(7)	0.6(8)
C33	24.8(9)	24.8(12)	16.7(8)	6.0(8)	3.1(7)	2.1(8)
C34	29.1(10)	25.2(12)	20.0(9)	2.2(8)	4.5(7)	4.2(9)
C35	29(1)	28.0(13)	22.7(9)	1.0(8)	-0.5(8)	-4.1(9)
C36	22.4(9)	39.0(15)	27.2(10)	5.8(9)	4.3(8)	0.7(9)
C37	28.3(10)	33.9(14)	26.7(10)	0.4(9)	7.6(8)	1.3(9)
C38	27.9(10)	24.9(12)	20.0(9)	0.2(8)	2.8(7)	-0.3(8)
C39	20.0(8)	21.3(11)	19.2(8)	-1.0(8)	3.3(7)	0.4(8)
C40	24.2(9)	20.4(11)	21.0(9)	-1.2(8)	3.3(7)	-1.2(8)
C41	43.7(12)	32.3(14)	17.8(9)	1.4(9)	3.8(8)	-7.6(11)
C42	49.9(13)	35.5(15)	20.9(9)	-9.4(10)	1.9(9)	-9.8(12)

C43	37.7(11)	23.7(13)	32.5(11)	-5.0(9)	4.0(9)	-7.9(10)
C44	29.3(10)	20.7(12)	24.1(9)	-0.9(8)	5.6(7)	-3.3(9)
C45	29.6(10)	33.3(14)	31.6(10)	6.6(10)	10.7(8)	-4.2(10)
C46	26.6(10)	26.5(12)	20.5(9)	5.2(8)	2.0(7)	-1.6(9)
C47	35.8(11)	26.9(13)	30.5(11)	13.7(10)	4.3(9)	-4.6(10)
C48	36.7(12)	33.7(15)	38.0(12)	13.5(10)	2.6(9)	-1.5(11)
C49	47.3(14)	27.5(14)	44.4(13)	9.3(11)	-2.5(11)	-11.5(12)
C50	33.9(11)	44.5(17)	40.8(13)	18.9(12)	6.7(10)	-3.0(11)

Table 4. Bond Lengths for **3ab**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
O1	C7	1.216(3)	O6	C32	1.215(3)
O2	C6	1.204(3)	O7	C31	1.199(3)
O3	C6	1.346(2)	O8	C31	1.343(2)
O3	C20	1.448(2)	O8	C45	1.454(3)
O4	C21	1.214(2)	O9	C46	1.212(3)
O5	C21	1.342(3)	O10	C46	1.339(3)
O5	C22	1.480(3)	O10	C47	1.482(3)
N1	C15	1.414(3)	N2	C40	1.412(3)
N1	C21	1.373(3)	N2	C46	1.376(3)
C1	C2	1.514(3)	C26	C27	1.515(3)
C1	C5	1.315(3)	C26	C30	1.321(3)
C1	C6	1.485(3)	C26	C31	1.482(3)
C2	C3	1.581(3)	C27	C28	1.561(3)
C2	C7	1.531(3)	C27	C32	1.536(3)
C3	C4	1.568(3)	C28	C29	1.562(3)
C3	C14	1.524(3)	C28	C39	1.523(3)
C4	C5	1.500(3)	C29	C30	1.502(3)
C7	C8	1.504(3)	C32	C33	1.501(3)
C8	C9	1.392(3)	C33	C34	1.394(3)
C8	C13	1.401(3)	C33	C38	1.400(3)

C9	C10	1.389(3)	C34	C35	1.384(3)
C10	C11	1.398(3)	C35	C36	1.395(3)
C11	C12	1.384(3)	C36	C37	1.386(3)
C12	C13	1.390(3)	C37	C38	1.396(3)
C14	C15	1.408(3)	C39	C40	1.415(3)
C14	C19	1.396(3)	C39	C44	1.391(3)
C15	C16	1.400(3)	C40	C41	1.395(3)
C16	C17	1.383(3)	C41	C42	1.386(4)
C17	C18	1.395(3)	C42	C43	1.385(3)
C18	C19	1.391(3)	C43	C44	1.397(3)
C22	C23	1.522(3)	C47	C48	1.516(3)
C22	C24	1.530(3)	C47	C49	1.521(4)
C22	C25	1.514(3)	C47	C50	1.529(3)

Table 5. Bond Angles for **3ab**.

Atom	**Atom**	**Atom**	**Angle/˚**	**Atom**	**Atom**	**Atom**	**Angle/˚**
C6	O3	C20	115.39(16)	C31	O8	C45	114.88(16)
C21	O5	C22	120.61(15)	C46	O10	C47	120.53(16)
C21	N1	C15	125.72(16)	C46	N2	C40	127.37(17)
C5	C1	C2	113.71(18)	C30	C26	C27	111.63(18)
C5	C1	C6	127.48(17)	C30	C26	C31	128.91(18)
C6	C1	C2	118.79(17)	C31	C26	C27	119.25(17)
C1	C2	C3	103.43(16)	C26	C27	C28	102.54(16)
C1	C2	C7	110.08(15)	C26	C27	C32	109.47(15)
C7	C2	C3	110.70(17)	C32	C27	C28	107.93(16)
C4	C3	C2	105.21(15)	C27	C28	C29	102.87(15)
C14	C3	C2	112.18(17)	C39	C28	C27	114.38(17)
C14	C3	C4	112.33(15)	C39	C28	C29	109.01(15)
C5	C4	C3	104.93(16)	C30	C29	C28	103.08(17)
C1	C5	C4	112.66(17)	C26	C30	C29	111.97(18)
O2	C6	O3	124.07(18)	O7	C31	O8	123.71(19)
O2	C6	C1	124.19(17)	O7	C31	C26	123.57(17)

O3	C6	C1	111.73(17)	O8	C31	C26	112.72(17)
O1	C7	C2	119.85(18)	O6	C32	C27	121.22(18)
O1	C7	C8	120.73(18)	O6	C32	C33	120.11(18)
C8	C7	C2	119.40(17)	C33	C32	C27	118.55(17)
C9	C8	C7	117.95(18)	C34	C33	C32	117.26(18)
C9	C8	C13	119.29(18)	C34	C33	C38	119.51(18)
C13	C8	C7	122.75(17)	C38	C33	C32	123.22(19)
C10	C9	C8	120.72(19)	C35	C34	C33	120.7(2)
C9	C10	C11	119.66(18)	C34	C35	C36	119.8(2)
C12	C11	C10	119.87(19)	C37	C36	C35	120.02(19)
C11	C12	C13	120.6(2)	C36	C37	C38	120.4(2)
C12	C13	C8	119.87(18)	C37	C38	C33	119.6(2)
C15	C14	C3	123.38(18)	C40	C39	C28	119.50(18)
C19	C14	C3	118.40(17)	C44	C39	C28	121.78(17)
C19	C14	C15	118.20(18)	C44	C39	C40	118.39(18)
C14	C15	N1	120.20(17)	N2	C40	C39	118.77(17)
C16	C15	N1	120.05(18)	C41	C40	N2	121.52(18)
C16	C15	C14	119.75(19)	C41	C40	C39	119.7(2)
C17	C16	C15	120.83(19)	C42	C41	C40	120.2(2)
C16	C17	C18	120.25(19)	C43	C42	C41	121.3(2)
C19	C18	C17	118.8(2)	C42	C43	C44	118.2(2)
C18	C19	C14	122.18(19)	C39	C44	C43	122.2(2)
O4	C21	O5	126.1(2)	O9	C46	O10	126.3(2)
O4	C21	N1	125.86(19)	O9	C46	N2	126.1(2)
O5	C21	N1	108.06(15)	O10	C46	N2	107.63(16)
O5	C22	C23	102.07(16)	O10	C47	C48	109.09(18)
O5	C22	C24	110.08(19)	O10	C47	C49	102.51(18)
O5	C22	C25	109.62(17)	O10	C47	C50	109.5(2)
C23	C22	C24	110.85(18)	C48	C47	C49	110.9(2)
C25	C22	C23	110.4(2)	C48	C47	C50	112.93(19)
C25	C22	C24	113.23(19)	C49	C47	C50	111.4(2)

Table 6. Torsion Angles for **3ab**.

A	**B**	**C**	**D**	**Angle/˚**
O1	C7	C8	C9	-3.8(3)
O1	C7	C8	C13	175.2(2)
N1	C15	C16	C17	-179.97(19)
C1	C2	C3	C4	-2.4(2)
C1	C2	C3	C14	120.05(17)
C1	C2	C7	O1	33.8(3)
C1	C2	C7	C8	-147.93(18)
C2	C1	C5	C4	0.1(3)
C2	C1	C6	O2	-0.3(3)
C2	C1	C6	O3	178.96(17)
C2	C3	C4	C5	2.4(2)
C2	C3	C14	C15	125.6(2)
C2	C3	C14	C19	-56.4(2)
C2	C7	C8	C9	177.92(19)
C2	C7	C8	C13	-3.1(3)
C3	C2	C7	O1	-79.9(2)
C3	C2	C7	C8	98.3(2)
C3	C4	C5	C1	-1.7(2)
C3	C14	C15	N1	-1.7(3)
C3	C14	C15	C16	178.74(18)
C3	C14	C19	C18	-178.79(19)
C4	C3	C14	C15	-116.1(2)
C4	C3	C14	C19	61.8(2)
C5	C1	C2	C3	1.5(2)
C5	C1	C2	C7	-116.8(2)
C5	C1	C6	O2	-178.3(2)
C5	C1	C6	O3	1.0(3)
C6	C1	C2	C3	-176.73(17)
C6	C1	C2	C7	65.0(2)
C6	C1	C5	C4	178.15(19)
C7	C2	C3	C4	115.51(18)

C7	C2	C3	C14	-122.08(17)
C7	C8	C9	C10	179.6(2)
C7	C8	C13	C12	-179.8(2)
C8	C9	C10	C11	0.3(3)
C9	C8	C13	C12	-0.8(3)
C9	C10	C11	C12	-0.9(3)
C10	C11	C12	C13	0.6(3)
C11	C12	C13	C8	0.3(3)
C13	C8	C9	C10	0.6(3)
C14	C3	C4	C5	-119.88(18)
C14	C15	C16	C17	-0.4(3)
C15	N1	C21	O4	-1.4(3)
C15	N1	C21	O5	177.99(17)
C15	C14	C19	C18	-0.8(3)
C15	C16	C17	C18	-0.1(3)
C16	C17	C18	C19	0.1(3)
C17	C18	C19	C14	0.3(3)
C19	C14	C15	N1	-179.64(18)
C19	C14	C15	C16	0.8(3)
C20	O3	C6	O2	6.4(3)
C20	O3	C6	C1	-172.85(17)
C21	O5	C22	C23	-177.11(17)
C21	O5	C22	C24	65.1(2)
C21	O5	C22	C25	-60.0(2)
C21	N1	C15	C14	147.22(19)
C21	N1	C15	C16	-33.2(3)
C22	O5	C21	O4	-12.3(3)
C22	O5	C21	N1	168.32(16)
O6	C32	C33	C34	8.7(3)
O6	C32	C33	C38	-172.3(2)
N2	C40	C41	C42	178.6(2)
C26	C27	C28	C29	-26.53(19)
C26	C27	C28	C39	91.53(19)

C26	C27	C32	O6	9.8(3)
C26	C27	C32	C33	-174.19(18)
C27	C26	C30	C29	-1.1(2)
C27	C26	C31	O7	-1.6(3)
C27	C26	C31	O8	178.44(17)
C27	C28	C29	C30	26.09(19)
C27	C28	C39	C40	163.67(17)
C27	C28	C39	C44	-23.0(3)
C27	C32	C33	C34	-167.42(18)
C27	C32	C33	C38	11.6(3)
C28	C27	C32	O6	-101.1(2)
C28	C27	C32	C33	74.9(2)
C28	C29	C30	C26	-16.4(2)
C28	C39	C40	N2	-6.2(3)
C28	C39	C40	C41	172.83(19)
C28	C39	C44	C43	-172.1(2)
C29	C28	C39	C40	-81.8(2)
C29	C28	C39	C44	91.5(2)
C30	C26	C27	C28	18.2(2)
C30	C26	C27	C32	-96.2(2)
C30	C26	C31	O7	172.7(2)
C30	C26	C31	O8	-7.3(3)
C31	C26	C27	C28	-166.60(17)
C31	C26	C27	C32	79.0(2)
C31	C26	C30	C29	-175.78(19)
C32	C27	C28	C29	88.99(18)
C32	C27	C28	C39	-152.94(16)
C32	C33	C34	C35	178.11(19)
C32	C33	C38	C37	-179.7(2)
C33	C34	C35	C36	2.0(3)
C34	C33	C38	C37	-0.7(3)
C34	C35	C36	C37	-1.3(3)
C35	C36	C37	C38	-0.3(3)

C36	C37	C38	C33	1.3(3)
C38	C33	C34	C35	-1.0(3)
C39	C28	C29	C30	-95.69(18)
C39	C40	C41	C42	-0.4(3)
C40	N2	C46	O9	1.1(4)
C40	N2	C46	O10	-179.70(18)
C40	C39	C44	C43	1.3(3)
C40	C41	C42	C43	1.0(4)
C41	C42	C43	C44	-0.4(4)
C42	C43	C44	C39	-0.8(3)
C44	C39	C40	N2	-179.71(18)
C44	C39	C40	C41	-0.7(3)
C45	O8	C31	O7	-1.8(3)
C45	O8	C31	C26	178.13(17)
C46	O10	C47	C48	-57.3(3)
C46	O10	C47	C49	-174.84(19)
C46	O10	C47	C50	66.8(2)
C46	N2	C40	C39	-179.3(2)
C46	N2	C40	C41	1.7(3)
C47	O10	C46	O9	-7.0(3)
C47	O10	C46	N2	173.72(17)

Table 7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **3ab**.

Atom	***x***	***y***	***z***	**U(eq)**
H1	-1944	-4472	-3982	25
H2	-3258	-1388	-3052	24
H3	-3171	-4074	-3362	24
H4A	-5743	-3687	-3737	30
H4B	-5097	-4798	-3241	30
H5	-6249	-3148	-2629	27
H9	-94	-3218	-1672	29
H10	1947	-2480	-1736	32

H11	2279	-1011	-2563	31
H12	582	-339	-3330	31
H13	-1459	-1087	-3274	28
H16	-2654	-3029	-5461	29
H17	-3912	-1179	-5737	32
H18	-5107	-279	-4992	31
H19	-5011	-1261	-3977	29
H20A	-5143	-380	-930	44
H20B	-6642	-529	-1114	44
H20C	-5905	518	-1490	44
H23A	634	-7636	-4114	46
H23B	114	-9054	-4371	46
H23C	-554	-8274	-3852	46
H24A	-946	-6911	-5718	50
H24B	-43	-8146	-5504	50
H24C	367	-6695	-5248	50
H25A	-2653	-8309	-4551	57
H25B	-2043	-9191	-5056	57
H25C	-2779	-7858	-5292	57
H2A	-2634	-9417	-837	29
H27	-2424	-6070	-2131	24
H28	-2726	-8453	-1631	25
H29A	-287	-8929	-1233	32
H29B	-1013	-9567	-1895	32
H30	833	-7985	-2077	30
H34	-4560	-9119	-3506	30
H35	-6726	-9387	-3532	32
H36	-7787	-8098	-2856	35
H37	-6662	-6613	-2130	35
H38	-4466	-6413	-2065	29
H41	-1752	-7622	591	38
H42	-842	-5529	655	43
H43	-515	-4399	-279	38

H44	-1101	-5418	-1287	29
H45A	733	-5108	-3732	46
H45B	2126	-5070	-3323	46
H45C	1074	-4059	-3158	46
H48A	-1599	-12608	403	55
H48B	-2421	-13324	877	55
H48C	-2073	-11791	974	55
H49A	-4653	-12964	-572	61
H49B	-4028	-14039	-57	61
H49C	-3203	-13370	-544	61
H50A	-4305	-11012	858	59
H50B	-4793	-12510	812	59
H50C	-5305	-11482	250	59

[RSC Journal Format]

Experimental

Single crystals of **3ab** ($C_{25}H_{27}NO_5$) was recrystallized from **[hexane/ethyl acetate]** mounted in inert oil and transferred to the cold gas stream of the diffractometer.

Crystal structure determination of 3ab

Crystal Data. $C_{25}H_{27}NO_5$, M =421.48, monoclinic, a = 10.7274(4) Å, b = 10.1113(7) Å, c = 20.9352(11) Å, β = 99.118(4)°, U = 2242.1(2) Å^3, T = 109.7, space group $P2_1$ (no. 4), Z = 4, μ(Cu Kα) = 0.706, 16436 reflections measured, 7480 unique (R_{int} = 0.0253) which were used in all calculations. The final $wR(F_2)$ was 0.1032 (all data).

This report has been created with Olex2, compiled on 2011.02.15 svn.r1672. Please let us know if there are any errors or if you would like to have additional features.