Supporting Information

Lewis acid catalyzed diastereoselective [3+4]-annulation of donor–acceptor cyclopropanes with anthranils: synthesis of tetrahydro-1-benzazepine derivatives†

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1. General information

Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Analytical thin-layer chromatography (TLC) was performed on silica gel plates with F-254 indicator and compounds were visualized by irradiation with UV light. Flash chromatography was carried out utilizing silica gel 200-300 mesh. The ^{1}H NMR spectra was recorded on 400 MHz or 600 MHz spectrometers, and the ^{13}C NMR was recorded on 100 MHz spectrometer. The spectra were recorded in $CDCl_3$, DMSO-d_6 and CD_3OD at room temperature. ^{1}H and ^{13}CNMR chemical shifts are reported in ppm relative to either the residual solvent peak (^{13}C) (δ = 77.00 ppm) or TMS (^{1}H) (δ = 0 ppm, DMSO-d_6 δ = 2.50 ppm, CD_3OD δ = 3.31 ppm) as an internal standard. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), integration, coupling constant (Hz) and assignment. HRMS were performed on FT–ICRMS mass instrument (ESI). Enantiomeric excess values were determined by HPLC with a CHIRALPAK IC-3 column with *i*-PrOH and *n*-hexane.

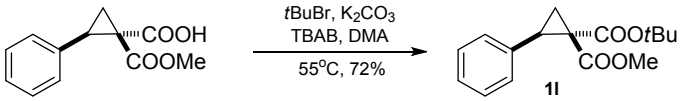
2. Experimental procedures

Cyclopropanes used in this work were prepared according to the methods reported in literature.[1] Anthranils were synthesized according to the report of S. Fletcher's group.[2]

1. M. Skvorcova, L. Grigorjeva and A. Jirgensons, *Org. Lett*., 2015, **17**, 2902–2904.

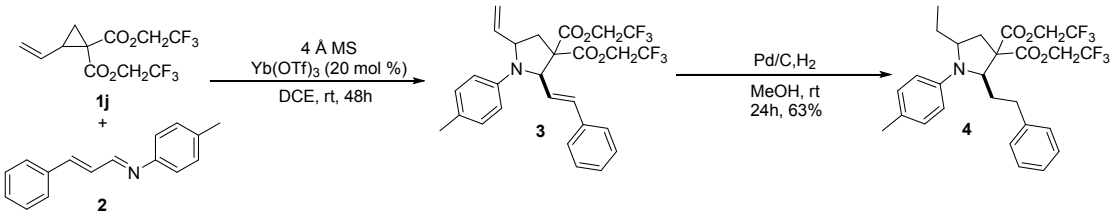
2. J. Chauhan and S. Fletcher, *Tetrahedron Lett.,* 2012*,* **53***,* 4951–4954.

2.1 Procedure for the synthesis of compound 1l[3]



1l was synthesis according to the method of literature 3 with a little modification, To a solution of 1-(methoxycarbonyl)-2-phenylcyclopropanecarboxylic acid[4] (1 mmol, 220mg) in *N*,*N*-dimethylacetamide (5 mL) in the presence of anhydrous potassium carbonate (25 mmol, 3.5g) and tetrabutylammonium bromide (1 mmol, 322mg), *tert*-butyl bromide (48 mmol, 5.4ml) was added dropwise at 0 °C, then the mixture was stirred at 55 °C for overnight. After cooling to room temperature, cold water was added into the reaction, then the mixture extracted with EtOAc. The organic layer was washed with H_2O, brine, dried over $MgSO_4$, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel petroleum ether/ethyl acetate (v/v = 25:1) to give the desired product **1l** in 72% yield.

2.2 Procedure for the synthesis of compound 4



The 4 Å MS (200 mg), $Yb(OTf)_3$ (0.08 mmol, 0.2 equiv), bis(2,2,2-trifluoroethyl) 2-vinylcyclopropane **1j** (0.40 mmol, 1.0 equiv) and 4-methyl-N-3-phenylallylidene) -aniline **2**[5] (0.80 mmol, 2.0 equiv) were sequentially added into a dry flask equipped with a stirring bar. Then 1,2-dichloroethane (2 mL) was added into the flask, and the reaction mixture was stirred under argon atmosphere at room temperature. After 48h,

3. L. Wang, Y. Murai, T. Yoshida, A. Ishida, K. Masuda, Y. Sakihama, Y. Hashidoko, Y. Hatanaka and M. Hashimoto, *Org. Lett.*, 2015, **17**, 616–619.

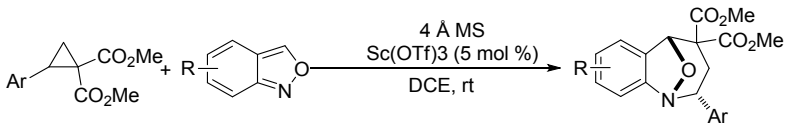
4. M. R. Emmett and M. A. Kerr, *Org. Lett.,* 2011, **13**, 4180–4183.

5. C. Wang, K. Huang, J. Wang, H. Wang, L. Liu, W. Chang and J. li , *Adv. Synth. Catal*., 2015, **357**, 2795– 2802.

the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to give a mixture of cyclopropane and the result product.

A solution of the mixture (185 mg) in MeOH (5 mL) was carefully triple evacuated/N_2 filled before the addition of 10% palladium on carbon (80 mg, 0.08 mmol). The flask was then triple evacuated/H_2 filled before being stirred under an atmosphere of H_2 at room temperature for 24 hours. The reaction was filtered through a plug of Celite, eluting with EtOAc, and the filtrate concentrated in vacuo to give the crude product. Purification by flash using petroleum ether and ethyl acetate (v/v = 50:1) gave the title compound **4** (118 mg, 63%) as a colorless oil.

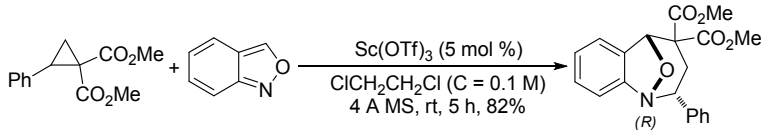
2.3 General procedure for the [3+4]-annulation reaction of D-A cyclopropanes with anthranils



1 **6a** **7a**

The 4 Å MS (100 mg), $Sc(OTf)_3$ (0.01 mmol, 0.05 equiv), D-A cyclopropanes **1** (0.20 mmol, 1.0 equiv) and anthranils **6a** (0.24 mmol, 1.2 equiv) were sequentially added into a dry flask equipped with a stirring bar. Then 1,2-dichloroethane (1 mL) was added into the flask, and the reaction mixture was stirred under argon atmosphere at room temperature. Upon completion of the reaction (monitored by TLC), the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to give the corresponding product.

2.4. Detailed procedure for the preparation of 7a in gram-scale



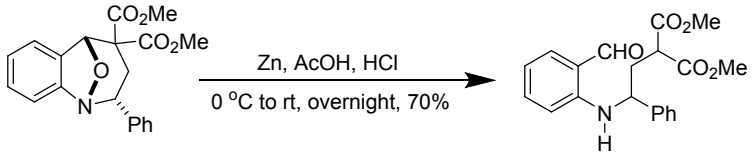
1a (1.00 g, 4.27 mmol) **6a** (0.61 g, 5.13 mmol) **7a** (1.23 g, 3.48 mmol)

The 4 Å MS (2.00 g), $Sc(OTf)_3$ (0.21 mmol, 0.05 equiv, 0.10 g), D-A cyclopropane **1a** (4.27 mmol, 1.0 equiv, 1.00g) and anthranil **6a** (5.13 mmol, 1.2 equiv, 0.61 g) were sequentially added into a dry flask equipped with a stirring bar, then added 1,2-dichloroethane (20 mL). The reaction mixture was stirred under an atmosphere of argon at room temperature. After 5 hours, cyclopropane **1a** had been exhausted. Then the solvent was removed by rotary evaporator, and the residue was purified by means of silica gel column chromatography with elution consisting of petroleum ether and ethyl acetate (v/v = 8:1). Product **7a** was obtained in 82 % yield (1.23 g, 3.48 mmol).

2.5. Procedure for the reductive cleavage of N-O bond in annulation product 7a

In this work, in order to cleave N-O bond in annulation product **7a**, two different methods were tried.

Method 1

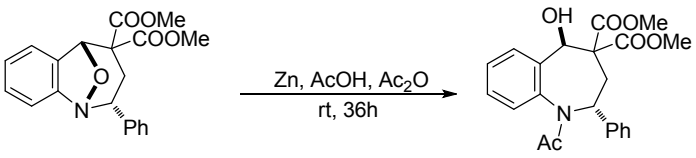


7a **8**

Annulation product **7a** (106 mg, 0.30 mmol) and methanol (2 mL) were added into a flask with stirring bar. Then, the flask was immersed into the mixture of ice and water. Under stirring, zinc dust (196mg, 3.00 mmol), acetic acid (80μL, 0.14 mmol), concentrated hydrochloric acid (75 μL, 2.40 mmol) were sequentially added in to the flask. Then the reaction was allowed to warm up to room temperature naturally. When

the annulation product **7a** disappeared (monitored by TLC), the reaction mixture was filtered. The filtrate was neutralized with aqueous ammonia (25%) to pH=8 and extracted with EtOAc for several times. The combined organic layers were dried by anhydrous Na_2SO_4 and concentrated. Then, the crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate, v/v = 4:1) to give the desired product in 70 % yield.

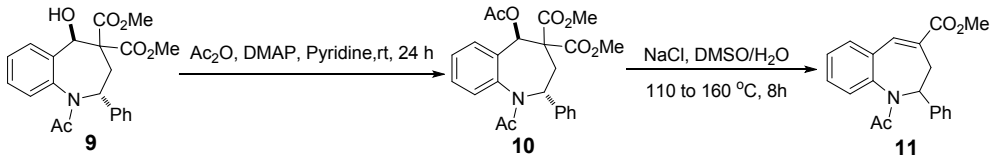
Method 2



7a **9**

Annulatuon product **7a** (212 mg, 0.6 mmol, 1.0equiv) was dissolved in 3 ml each acetic acid and acetic anhydride and then stirred vigorously for 36 hours with activated zinc dust (784 mg, 12 mmol, 20 equiv). The mixture was then filtered (using ethyl acetate to aid in transfers), concentrated under high vacuum, the crude product was purified by silica gel column chromatography using petroleum ether/AcOEt (v/v = 2:1), then using pure AcOEt to give 2,3,4,5-tetrahydro-1H-1-benzaze-pine **9** as a white solid in 80 % yield.

2.6. Procedure for the synthesis of 2,3-dihydro-1H-1-benzazepine 11



9 **10** **11**

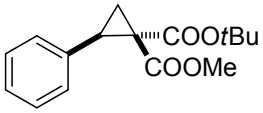
To a solution of 2,3,4,5-tetrahydro-1H-1-benzazepine **9** (120 mg, 0.30 mmol) in pyridine (1 mL), 4-dimethylaminopyridine (18 mg, 0.15 mmol) and acetic anhydride (0.24 ml, 4.20 mmol) were added. The reaction mixture was stirred under argon atmosphere at room temperature. Upon completion of the reaction (monitored by TLC), the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel using petroleum ether and ethyl acetate (v/v

= 2:1) to give 2,3-dihydro-1H-1-benzazepine **10** in 90 % yield.

A solution of 2,3-dihydro-1-benzazepine **10** (65.9mg, 0.15 mmol) in a mixture of DMSO (1 mL) and H_2O (0.1 mL) in the presence of NaCl (35.1mg, 0.60 mmol) was heated from 110 to 160°C for a period of 3h and kept at 160°C for 8h with stirring. After being cooled to room temperature, the solution was diluted with saturated aqueous $NaHCO_3$ (2 mL) and extracted with EtOAc. Then the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel using petroleum ether and ethyl acetate (v/v = 3:1) to give 2,3-dihydro-1-benzazepine **11** in 88 % yield.

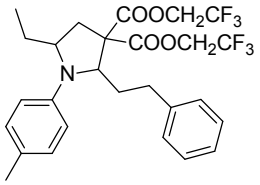
3. Characterization data of Products

1-tert-butyl 1-methyl 2-phenylcyclopropane-1,1-dicarboxylate (1l)



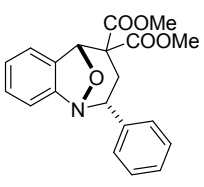
Purification by flash chromatography on silica gel petroleum ether/EtOAc (V/V = 25:1) gave the title compound as white solid (198.5 mg, 0.72 mmol, 72 % yield); mp: 46–48 °C; R_f = 0.25 (EtOAc/ petroleum ether, v/v = 1/25); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.17 (m, 5H), 3.37 (s, 3H), 3.12 (t, *J* = 8.8 Hz, 1H), 2.09 (dd, *J* = 8.0 Hz, 5.2 Hz, 1H), 1.65 (dd, *J* = 8.0 Hz, 5.2 Hz, 1H), 1.48 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 167.5, 135.0, 128.3, 128.1, 127.1, 82.0, 52.0, 38.5, 31.5, 28.0, 18.5; HRMS calcd for $C_{16}H_{20}O_4$ $[M+Na]^+$: 299.1254, found for: 299.1253.

Bis(2,2,2-trifluoroethyl) 5-ethyl-2-phenethyl-1-(p-tolyl)pyrrolidine-3,3-dicarboxylate (4)



Purification by flash chromatography on silica gel petroleum ether/EtOAc (V/V = 50:1) gave the title compound as colorless oil (118.0 mg, 0.22 mmol, 63 % yield); R_f = 0.27 (EtOAc/ petroleum ether, v/v = 1/50); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.2 Hz, 2H), 7.21–7.17 (m, 1H), 7.13–7.10 (m, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.53 (d, *J* = 8.8 Hz, 2H), 4.64–4.60 (m, 1H), 4.58–4.49 (m, 2H), 4.47–4.41 (m, 1H), 4.40–4.31 (m, 1H), 3.47 (ddd, *J* = 16.4 Hz, 9.6 Hz, 2.8 Hz, 1H), 2.78 (dd, *J* = 13.6 Hz, 7.2 Hz, 1H), 2.73–2.69 (m, 2H), 2.64 (dd, *J* = 13.6 Hz, 9.6 Hz, 1H), 2.24 (s, 3H), 2.12–2.03 (m, 1H), 1.91–1.82 (m, 1H), 1.76–1.66 (m, 1H), 1.47–1.39 (m, 1H), 0.98 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 166.3, 145.5, 141.4, 129.7, 128.5, 128.4, 128.3, 128.2, 126.3, 126.0, 112.1, 63.6, 62.5, 61.3, 61.2, 61.1, 61.0, 58.5, 36.9, 35.7, 32.7, 28.3, 20.2, 9.9; HRMS calcd for $C_{27}H_{30}F_6NO_4$ $[M+H]^+$: 546.2074, found for: 546.2075.

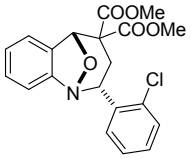
Dimethyl 2-phenyl-2,3-dihydro-1,5-epoxybenzo[*b*]azepine-4,4(5*H*)-dicarboxylate (7a)



Purification by flash chromatography on silica gel petroleum ether/EtOAc (V/V = 8:1) gave **7a** as white solid (63.5 mg, 0.18 mmol, 90 % yield); mp:

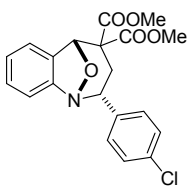
138–140 °C; R_f = 0.45 (EtOAc/ petroleum ether, v/v = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.2 Hz, 1H), 7.34–7.30 (m, 5H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.13 (d, *J* = 7.6 Hz, 1H), 5.77 (s, 1H), 5.06 (dd, *J* = 12.0 Hz, 3.6 Hz, 1H), 3.90 (s, 3H), 3.77 (s, 3H), 2.66 (dd, *J* = 14.4 Hz, 3.2 Hz, 1H), 1.84 (dd, *J* = 13.6 Hz, 12.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 168.4, 148.0, 136.8, 136.6, 128.5, 128.2, 128.1, 128.0, 126.0, 122.7, 116.9, 79.7, 61.2, 55.7, 53.4, 52.8, 24.9; HRMS calcd for $C_{20}H_{20}NO_5$ $[M+H]^+$: 354.1336, found for: 354.1337. The enantiomeric excess of (1*R*, 2*R*, 5*R*)-**7a** was determined to be 99.4 % *ee* by HPLC with an IC-H column. (*n*-hexane:*i*-PrOH = 80:20), 1 mL/min; major enantiomer t_R = 13.93 min, minor enantiomer t_R = 33.90 min; $[\alpha]^D_{20}$ = –165.0 (c = 1.00, CH_2Cl_2).

Dimethyl 2-(2-chlorophenyl)-2,3-dihydro-1,5-epoxybenzo[*b*]azepine-4,4(5*H*)-dicarboxylate (7b)



Purification by flash chromatography on silica gel petroleum ether/EtOAc (V/V = 8:1) gave **7b** as white solid (15.5 mg, 0.04 mmol, 20 % yield); mp: 100–102 °C; R_f = 0.39 (EtOAc/ petroleum ether, v/v = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.2 Hz, 1H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.32–7.29 (m, 1H), 7.15 (dd, *J* = 15.2 Hz, 7.6 Hz, 2H), 7.10–7.06 (m, 1H), 6.71 (d, *J* = 7.6 Hz, 1H), 6.14 (d, *J* = 7.6 Hz, 1H) 5.79 (s, 1H), 5.48 (dd, *J* = 12.4 Hz, 3.2 Hz, 1H), 3.92 (s, 3H), 3.78 (s, 3H), 2.46 (dd, *J* = 14.0 Hz, 2.4 Hz, 1H), 1.98–1.92 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 168.3, 147.6, 136.9, 133.6, 130.2, 129.7, 128.5, 127.9, 126.2, 126.1, 122.8, 117.3, 79.7, 58.6, 55.7, 53.5, 52.9, 24.5; HRMS calcd for $C_{20}H_{19}ClNO_5$ $[M+H]^+$: 388.0946, found for: 388.0944.

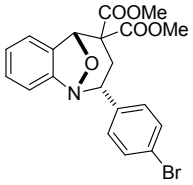
Dimethyl 2-(4-chlorophenyl)-2,3-dihydro-1,5-epoxybenzo[*b*]azepine-4,4(5*H*)-dicarboxylate (7c)



Purification by flash chromatography on silica gel petroleum ether/EtOAc (V/V = 8:1) gave **7c** as white solid (58.2 mg, 0.15 mmol, 75 % yield); mp: 100–102 °C; R_f = 0.43 (EtOAc/ petroleum ether, v/v = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 9.2 Hz, 2H), 7.13 (td, *J* = 7.2 Hz, 0.8 Hz, 1H), 7.03 (td, *J* = 7.6 Hz, 1.2 Hz, 1H),

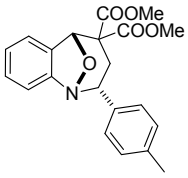
6.16 (d, *J* = 7.6 Hz, 1H), 5.76 (s, 1H), 5.02 (dd, *J* = 12.0 Hz, 3.2 Hz, 1H), 3.90 (s, 3H), 3.77 (s, 3H), 2.64 (ddd, *J* = 14.0 Hz, 3.6 Hz, 1.6 Hz, 1H), 1.77 (dd, *J* = 14.0 Hz, 12.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 168.3, 147.8, 136.5, 135.4, 134.1, 129.8, 128.6, 128.4, 128.1, 128.0, 126.2, 122.9, 116.8, 79.7, 60.6, 55.6, 53.5, 52.9, 24.9; HRMS calcd for $C_{20}H_{19}ClNO_5$ $[M+H]^+$: 388.0946, found for: 388.0945.

Dimethyl 2-(4-bromophenyl)-2,3-dihydro-1,5-epoxybenzo[*b*]azepine-4,4(5*H*)-dicarbo -xylate (7d)



Purification by flash chromatography on silica gel petroleum ether/EtOAc (V/V = 8:1) gave **7d** as white solid (71.8 mg, 0.17 mmol, 83 % yield); mp: 146–148 °C; R_f = 0.48 (EtOAc/ petroleum ether, v/v = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.05–7.01 (m, 1H), 6.16 (d, *J* = 7.6 Hz, 1H), 5.76 (s, 1H), 4.99 (dd, *J* = 12.0 Hz, 3.6 Hz, 1H), 3.90 (s, 3H), 3.77 (s, 3H), 2.63 (ddd, *J* = 14.0 Hz, 3.6 Hz, 1.2 Hz, 1H), 1.77 (dd, *J* = 14.0 Hz, 12.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 168.3, 147.8, 136.6, 135.9, 131.4, 130.1, 128.1, 126.2, 122.8, 122.3, 116.8, 79.7, 60.6, 55.6, 53.4, 52.9, 24.8; HRMS calcd for $C_{20}H_{19}BrNO_5$ $[M+H]^+$: 432.0441, found for: 432.0439.

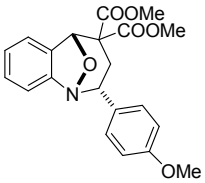
Dimethyl 2-(p-tolyl)-2,3-dihydro-1,5-epoxybenzo[*b*]azepine-4,4(5*H*)-dicarboxylate (7e)



Purification by flash chromatography on silica gel petroleum ether/EtOAc (V/V = 8:1) gave **7e** as white solid (58.7 mg, 0.16 mmol, 80 % yield); mp: 142–144 °C; R_f = 0.47 (EtOAc/ petroleum ether, v/v = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.2 Hz, 1H), 7.19–7.09 (m, 5H), 7.01 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 6.16 (d, *J* = 7.6 Hz, 1H), 5.76 (s, 1H), 5.02 (dd, *J* = 12.0 Hz, 3.6 Hz, 1H), 3.89 (s, 3H), 3.77 (s, 3H), 2.62 (ddd, *J* = 14.0 Hz, 3.6 Hz, 1.2 Hz, 1H), 2.36 (s, 3H), 1.82 (dd, *J* = 14.0 Hz, 12.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 148.1, 137.9, 136.6, 133.8, 128.9, 128.4, 127.9, 126.0, 122.7, 117.0, 79.7, 61.0, 55.7, 53.4, 52.8, 24.9, 21.2; HRMS calcd for $C_{21}H_{22}NO_5$ $[M+H]^+$: 368.1492, found for: 368.1493.

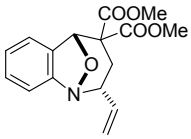
Dimethyl 2-(4-methoxyphenyl)-2,3-dihydro-1,5-epoxybenzo[*b*]azepine-4,4(5*H*)-dicarbo-

xylate (7f)



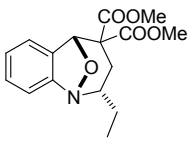
Purification by flash chromatography on silica gel petroleum ether/EtOAc (V/V = 6:1) gave **7f** as white solid (28.4 mg, 0.07 mmol, 37 % yield); mp: 122–124 °C; R_f = 0.32 (EtOAc/ petroleum ether, v/v = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.2 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.13–7.09 (m, 1H), 7.02 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.16 (d, *J* = 7.6 Hz, 1H), 5.75 (s, 1H), 5.00 (dd, *J* = 12.0 Hz, 3.6 Hz, 1H), 3.89 (s, 3H), 3.81 (s, 3H), 3.76 (s, 3H), 2.61 (ddd, *J* = 14.0 Hz, 3.6 Hz, 1.2 Hz, 1H), 1.80 (dd, *J* = 14.0 Hz, 12.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 168.5, 159.4, 148.0, 136.7, 129.7, 129.0, 127.9, 126.0, 122.7, 117.0, 113.5, 79.7, 60.8, 55.7, 55.2, 53.4, 52.8, 25.1; HRMS calcd for $C_{21}H_{22}NO_6$ $[M+H]^+$: 384.1442, found for: 384.1447.

Dimethyl 2-vinyl-2,3-dihydro-1,5-epoxybenzo[*b*]azepine-4,4(5*H*)-dicarboxylate (7g)



Purification by flash chromatography on silica gel petroleum ether/EtOAc (V/V = 8:1) gave **7g** as white solid (35.2 mg, 0.12 mmol, 58 % yield); mp: 62–64 °C; R_f = 0.32 (EtOAc/ petroleum ether, v/v = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 6.8 Hz, 1H), 7.24–7.13 (m, 2H), 6.95 (d, *J* = 7.6 Hz, 1H), 5.80–5.70 (m, 1H), 5.69 (s, 1H), 5.25 (dt, *J* = 10.4 Hz, 1.2 Hz, 1H), 5.18 (dt, *J* = 17.6 Hz, 1.2 Hz, 1H), 4.45–4.38 (m, 1H), 3.87 (s, 3H), 3.73 (s, 3H), 2.42 (ddd, *J* = 14.0 Hz, 3.6 Hz, 1.2 Hz, 1H), 1.38 (dd, *J* = 14.0 Hz, 11.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 168.3, 148.1, 136.5, 134.7, 128.1, 126.1, 122.9, 118.9, 116.6, 79.6, 60.2, 55.3, 53.3, 52.7, 25.8; HRMS calcd for $C_{16}H_{18}NO_5$ $[M+H]^+$: 304.1179, found for: 304.1178.

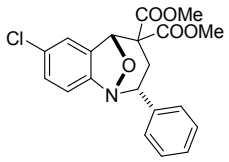
dimethyl 2-ethyl-2,3-dihydro-1,5-epoxybenzo[*b*]azepine-4,4(5*H*)-dicarboxylate (7h)



Purification by flash chromatography on silica gel petroleum ether/EtOAc (V/V = 9:1) gave **7h** as yellow oil (47.6 mg, 0.16 mmol, 78 % yield); R_f = 0.40 (EtOAc/ petroleum ether, v/v = 1/6); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.2 Hz, 1H), 7.23 (dd, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.18–7.12 (m, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 5.66 (s, 1H), 3.86 (s, 3H), 3.71 (s, 3H), 2.34 (ddd, *J* = 14.0 Hz, 3.6 Hz, 1.2 Hz, 1H), 1.50–1.39 (m, 1H), 1.23–1.14 (m, 1H), 1.12–1.10 (m, 2H), 1.09–1.07 (m, 3H) ppm; ^{13}C

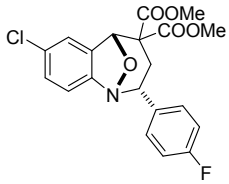
NMR (100 MHz, $CDCl_3$) δ 168.6, 168.5, 148.1, 136.9, 128.2, 125.9, 123.0, 116.4, 79.6, 60.1, 55.8, 53.2, 52.6, 27.6, 26.0, 10.6; HRMS calcd for $C_{16}H_{20}NO_5$ $[M+H]^+$: 306.1336, found for: 306.1337.

Dimethyl 7-chloro-2-phenyl-2,3-dihydro-1,5-epoxybenzo[*b*]azepine-4,4(5*H*)-dicarboxylate (7i)



Purification by flash chromatography on silica gel petroleum ether/EtOAc (V/V = 9:1) gave **7i** as colorless oil (58.1 mg, 0.15 mmol, 75 % yield); R_f = 0.50 (EtOAc/ petroleum ether, v/v = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 2.0 Hz, 1H), 7.34–7.28 (m, 5H), 6.98 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 6.03 (d, *J* = 8.4 Hz, 1H), 5.73 (s, 1H), 5.06 (dd, *J* = 12.0 Hz, 3.6 Hz, 1H), 3.89 (s, 3H), 3.78 (s, 3H), 2.68 (dd, *J* = 14.0 Hz, 2.4 Hz, 1H), 1.85 (dd, *J* = 14.0 Hz, 12.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 168.2, 146.8, 138.7, 136.4, 131.4, 128.4, 128.3, 128.0, 123.5, 117.8, 79.7, 61.1, 55.4, 53.5, 53.0, 24.8; HRMS calcd for $C_{20}H_{19}ClNO_5$ $[M+H]^+$: 388.0946, found for: 388.0945.

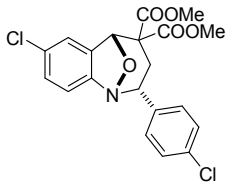
Dimethyl 7-chloro-2-(4-fluorophenyl)-2,3-dihydro-1,5-epoxybenzo[*b*]azepine-4,4(5*H*)-dicarboxylate (7j)



Purification by flash chromatography on silica gel petroleum ether/EtOAc (V/V = 9:1) gave **7j** as white solid (72.2 mg, 0.18 mmol, 89 % yield); mp: 100–102 °C; R_f = 0.53 (EtOAc/ petroleum ether, v/v = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 2.0 Hz, 1H), 7.28 (dd, *J* = 8.8 Hz, 5.2 Hz, 2H), 7.06–6.98 (m, 3H), 6.04 (d, *J* = 8.0 Hz, 1H), 5.73 (s, 1H), 5.02 (dd, *J* = 12.0 Hz, 3.6 Hz, 1H), 3.90 (s, 3H), 3.79 (s, 3H), 2.67 (ddd, *J* = 14.0 Hz, 3.6 Hz, 1.2 Hz, 1H), 1.79 (dd, *J* = 14.0 Hz, 12.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 168.1, 163.8, 146.5, 138.7, 132.3 (d, *J* = 3.0 Hz), 131.6, 130.1 (d, *J* = 8.0 Hz), 128.1, 123.6, 117.7, 115.2 (d, *J* = 22.0 Hz), 79.6, 60.5, 55.3, 53.6, 53.0, 24.9; HRMS calcd for $C_{20}H_{18}ClFNO_5$ $[M+H]^+$: 406.0852, found for: 406.0849.

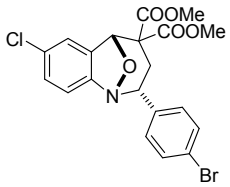
Dimethyl 7-chloro-2-(4-chlorophenyl)-2,3-dihydro-1,5-epoxybenzo[*b*]azepine-4,4(5*H*)-

Dicarboxylate (7k)



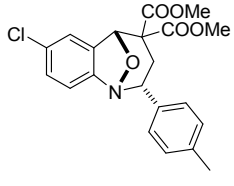
Purification by flash chromatography on silica gel petroleum ether/EtOAc (V/V = 8:1) gave **7k** as white solid (74.3 mg, 0.18 mmol, 88 % yield); mp: 146–148 °C; R_f = 0.51 (EtOAc/ petroleum ether, v/v = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 2.0 Hz, 1H), 7.32 (dd, *J* = 6.8 Hz, 2.0 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.00 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 6.06 (d, *J* = 8.0 Hz, 1H), 5.72 (s, 1H), 5.02 (dd, *J* = 12.0 Hz, 3.6 Hz, 1H), 3.90 (s, 3H), 3.79 (s, 3H), 2.67 (ddd, *J* = 14.0 Hz, 3.6 Hz, 1.2 Hz, 1H), 1.78 (dd, *J* = 14.0 Hz, 12.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 168.1, 146.5, 138.7, 135.0, 134.3, 131.7, 129.7, 128.5, 128.1, 123.6, 117.7, 79.6, 60.5, 55.3, 53.6, 53.0, 24.8; HRMS calcd for $C_{20}H_{18}Cl_2NO_5$ $[M+H]^+$: 422.0557, found for: 422.0558.

Dimethyl 2-(4-bromophenyl)-7-chloro-2,3-dihydro-1,5-epoxybenzo[*b*]azepine-4,4(5*H*)-dicarboxylate (7l)



Purification by flash chromatography on silica gel petroleum ether/EtOAc (V/V = 9:1) gave **7l** as white solid (75.6 mg, 0.16 mmol, 81 % yield); mp: 108–110 °C; R_f = 0.55 (EtOAc/ petroleum ether, v/v = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 2.0 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.01 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 6.07 (d, *J* = 8.4 Hz, 1H), 5.72 (s, 1H), 5.00 (dd, *J* = 12.0 Hz, 3.6 Hz, 1H), 3.90 (s, 3H), 3.78 (s, 3H), 2.65 (dd, *J* = 14.0 Hz, 2.4 Hz, 1H), 1.78 (dd, *J* = 14.0 Hz, 12.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 168.1, 146.5, 138.6, 135.5, 131.7, 131.5, 130.1, 128.2, 123.6, 122.5, 117.7, 79.6, 60.5, 55.3, 53.6, 53.0, 24.7; HRMS calcd for $C_{20}H_{18}BrClNO_5$ $[M+H]^+$: 466.0051, found for: 466.0054.

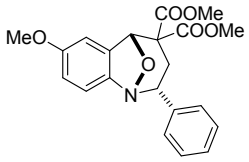
Dimethyl 7-chloro-2-(p-tolyl)-2,3-dihydro-1,5-epoxybenzo[*b*]azepine-4,4(5*H*)-dicarboxylate (7m)



Purification by flash chromatography on silica gel petroleum ether/EtOAc (V/V = 9:1) gave **7m** as white solid (55.5 mg, 0.14 mmol, 69 % yield); mp: 126–128 °C; R_f = 0.55 (EtOAc/ petroleum ether, v/v =

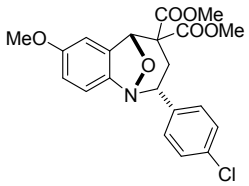
1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 2.0 Hz, 1H), 7.18–7.13 (m, 4H), 6.99 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 6.06 (d, *J* = 8.4 Hz, 1H), 5.72 (s, 1H), 5.02 (dd, *J* = 12.0 Hz, 3.6 Hz, 1H), 3.89 (s, 3H), 3.78 (s, 3H), 2.65 (ddd, *J* = 14.0 Hz, 3.6 Hz, 1.2 Hz, 1H), 2.36 (s, 3H), 1.83 (dd, *J* = 14.0 Hz, 12.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 168.2, 146.8, 138.7, 138.1, 133.4, 131.4, 129.0, 128.3, 128.0, 123.5, 117.9, 79.6, 60.9, 55.4, 53.5, 53.0, 24.8, 21.2; HRMS calcd for $C_{21}H_{21}ClNO_5$ $[M+H]^+$: 402.1103, found for: 402.1102.

Dimethyl 7-methoxy-2-phenyl-2,3-dihydro-1,5-epoxybenzo[*b*]azepine-4,4(5*H*)-dicarboxylate (7n)



Purification by flash chromatography on silica gel petroleum ether/EtOAc (V/V = 8:1) gave **7n** as white solid (57.5 mg, 0.15 mmol, 75 % yield); mp: 118–120 °C; R_f = 0.34 (EtOAc/ petroleum ether, v/v = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.28 (m, 5H), 6.95 (d, *J* = 2.4 Hz, 1H), 6.51 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.05 (d, *J* = 8.4 Hz, 1H), 5.72 (s, 1H), 5.02 (dd, *J* = 12.0 Hz, 3.6 Hz, 1H), 3.89 (s, 3H), 3.78 (s, 3H), 3.77 (s, 3H), 2.65 (ddd, *J* = 14.0 Hz, 3.6 Hz, 1.6 Hz, 1H), 1.85 (dd, *J* = 14.0 Hz, 12.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 158.1, 140.9, 138.2, 137.0, 128.5, 128.2, 128.1, 117.3, 112.3, 109.5, 79.9, 61.4, 55.7, 55.6, 53.4, 52.8, 24.8; HRMS calcd for $C_{21}H_{22}NO_6$ $[M+H]^+$: 384.1442, found for: 384.1444.

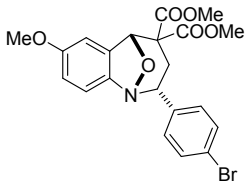
Dimethyl 2-(4-chlorophenyl)-7-methoxy-2,3-dihydro-1,5-epoxybenzo[*b*]azepine-4,4(5*H*)-dicarboxylate (7o)



Purification by flash chromatography on silica gel petroleum ether/EtOAc (V/V = 8:1) gave **7o** as colorless oil (61.0 mg, 0.15 mmol, 73 % yield); R_f = 0.36 (EtOAc/ petroleum ether, v/v = 1/5); ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 2.4 Hz, 1H), 6.52 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.07 (d, *J* = 8.4 Hz, 1H), 5.71 (s, 1H), 4.98 (dd, *J* = 12.0 Hz, 3.6 Hz, 1H), 3.89 (s, 3H), 3.78 (s, 3H), 3.77 (s, 3H), 2.63 (ddd, *J* = 14.0 Hz, 8.4 Hz, 2.4 Hz 1H), 1.78 (dd, *J* = 14.0 Hz, 12.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 168.3, 158.2, 140.6, 138.1, 135.6, 134.0, 129.8, 128.4, 117.2, 112.3, 109.6, 79.9, 60.8, 55.7, 55.5, 53.5, 52.9, 24.8; HRMS calcd for $C_{21}H_{21}ClNO_6$ $[M+H]^+$: 418.1052,

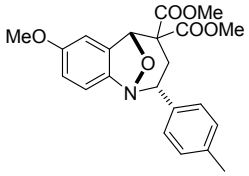
found for: 418.1054.

Dimethyl 2-(4-bromophenyl)-7-methoxy-2,3-dihydro-1,5-epoxybenzo[*b*]azepine-4,4(5*H*)-dicarboxylate (7p)



Purification by flash chromatography on silica gel petroleum ether/EtOAc (V/V = 8:1) gave **7p** as colorless oil (68.4 mg, 0.15 mmol, 74 % yield); R_f = 0.48 (EtOAc/ petroleum ether, v/v = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* =2.4 Hz, 1H), 6.53 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.08 (d, *J* = 8.4 Hz, 1H), 5.71 (s, 1H), 4.96 (dd, *J* = 12.0 Hz, 3.6 Hz, 1H), 3.89 (s, 3H), 3.77 (s, 3H), 3.76 (s, 3H), 2.63 (ddd, *J* =14.0 Hz, 3.6 Hz, 1.2 Hz, 1H), 1.78 (dd, *J* = 14.0 Hz, 12.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 168.3, 158.2, 140.6, 138.1, 136.1, 131.3, 130.2, 122.2, 117.2, 112.3, 109.6, 79.9, 60.8, 55.7, 55.5, 53.5, 52.9, 24.8; HRMS calcd for $C_{21}H_{21}BrNO_6$ $[M+H]^+$: 462.0547, found for: 462.0544.

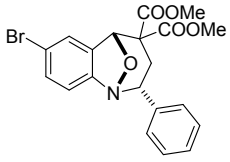
Dimethyl 7-methoxy-2-(p-tolyl)-2,3-dihydro-1,5-epoxybenzo[*b*]azepine-4,4(5*H*)-dicarboxylate (7q)



Purification by flash chromatography on silica gel petroleum ether/EtOAc (V/V = 8:1) gave **7q** as white solid (57.2 mg, 0.14 mmol, 72 % yield); mp: 138–140 °C; R_f = 0.38 (EtOAc/ petroleum ether, v/v = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18–7.12 (m, 4H), 6.94 (d, *J* = 2.0 Hz, 1H), 6.52 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.08 (d, *J* = 8.4 Hz, 1H), 5.71 (s, 1H), 4.98 (dd, *J* = 12.0 Hz, 3.2 Hz, 1H), 3.88 (s, 3H), 3.77 (s, 6H), 2.62 (dd, *J* = 14.0 Hz, 2.8 Hz, 1H), 2.35 (s, 3H), 1.86–1.80 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 158.0, 141.0, 138.2, 137.8, 134.0, 128.9, 128.4, 117.4, 112.3, 109.4, 79.9, 61.2, 55.7, 55.6, 53.4, 52.8, 24.9, 21.2; HRMS calcd for $C_{22}H_{24}NO_6$ $[M+H]^+$: 398.1598, found for: 398.1600.

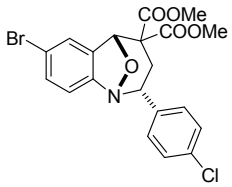
Dimethyl 7-bromo-2-phenyl-2,3-dihydro-1,5-epoxybenzo[*b*]azepine-4,4(5*H*)-dicarboxylate (7r)

Purification by flash chromatography on silica gel petroleum ether/EtOAc (V/V = 8:1) gave



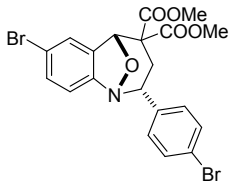
7r as colorless oil (73.5 mg, 0.17 mmol, 85 % yield); R_f = 0.46 (EtOAc/ petroleum ether, v/v = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 1.6 Hz, 1H), 7.35–7.28 (m, 5H), 7.13 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 5.98 (d, *J* = 8.0 Hz, 1H), 5.73 (s, 1H), 5.06 (dd, *J* = 12.0 Hz, 3.6 Hz, 1H), 3.89 (s, 3H), 3.78 (s, 3H), 2.68 (ddd, *J* = 14.0 Hz, 3.6 Hz, 1.2 Hz, 1H), 1.85 (dd, *J* = 14.0 Hz, 12.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 168.1, 147.3, 139.0, 136.3, 130.9, 128.4, 128.3, 128.2, 126.3, 119.1, 118.2, 79.5, 61.0, 55.3, 53.4, 52.9, 24.7; HRMS calcd for $C_{20}H_{19}BrNO_5$ $[M+H]^+$: 432.0441, found for: 432.0440. the enantiomeric excess of (1*R*, 2*R*, 5*R*)-**7r** was determined to be 93.7 % ee by HPLC with an IC-H column. (*n*-hexane:*i*-PrOH = 80:20), 1 mL/min; minor enantiomer t_R = 7.78 min, major enantiomer t_R = 16.36 min. $[\alpha]^D_{20}$ = –241.0 (c = 1.00, CH_2Cl_2).

Dimethyl 7-bromo-2-(4-chlorophenyl)-2,3-dihydro-1,5-epoxybenzo[*b*]azepine-4,4(5*H*)-dicarboxylate (7s)



Purification by flash chromatography on silica gel petroleum ether/EtOAc (V/V = 9:1) gave **7s** as white solid (80.3 mg, 0.17 mmol, 86 % yield); mp: 130–132 °C; R_f = 0.52 (EtOAc/ petroleum ether, v/v = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 1.6 Hz, 1H), 7.33–7.30 (m, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.15 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 6.01 (d, *J* =8.0 Hz, 1H), 5.72 (s, 1H), 5.02 (dd, *J* = 12.0 Hz, 3.6 Hz, 1H), 3.89 (s, 3H), 3.78 (s, 3H), 2.67 (ddd, *J* = 14.0 Hz, 3.6 Hz, 1.2 Hz, 1H), 1.79 (dd, *J* = 14.0 Hz, 12.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 168.0, 147.0, 138.9, 134.9, 134.2, 131.0, 129.7, 128.5, 126.4, 119.3, 118.1, 79.4, 60.3, 55.2, 53.5, 53.0, 24.7; HRMS calcd for $C_{20}H_{18}BrClNO_5$ $[M+H]^+$: 466.0051, found for: 466.0056.

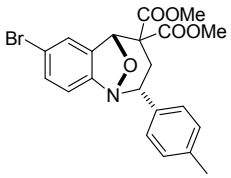
Dimethyl 7-bromo-2-(4-bromophenyl)-2,3-dihydro-1,5-epoxybenzo[*b*]azepine-4,4(5*H*)-dicarboxylate (7t)



Purification by flash chromatography on silica gel petroleum ether/EtOAc (V/V = 9:1) gave **7t** as white solid (76.3 mg, 0.15 mmol, 75 % yield); mp: 140–142 °C; R_f = 0.58 (EtOAc/ petroleum ether, v/v =

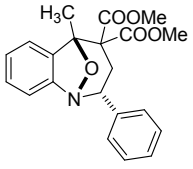
1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 1.6 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.19–7.14 (m, 3H), 6.02 (d, *J* = 8.0 Hz, 1H), 5.72 (s, 1H), 5.00 (dd, *J* = 12.0 Hz, 3.6 Hz, 1H), 3.90 (s, 3H), 3.78 (s, 3H), 2.67 (ddd, *J* = 14.0 Hz, 3.6 Hz, 1.2 Hz, 1H), 1.78 (dd, *J* = 14.0 Hz, 12.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 168.1, 147.0, 139.0, 135.5, 131.5, 131.3, 131.1, 130.2, 130.1, 126.5, 122.5, 119.4, 118.1, 79.5, 60.5, 55.3, 53.6, 53.1, 24.7; HRMS calcd for $C_{20}H_{18}Br_2NO_5$ $[M+H]^+$: 511.1296, found for: 511.1284.

Dimethyl 7-bromo-2-(p-tolyl)-2,3-dihydro-1,5-epoxybenzo[*b*]azepine-4,4(5*H*)-dicarboxylate (7u)



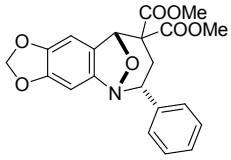
Purification by flash chromatography on silica gel petroleum ether/EtOAc (V/V = 9:1) gave **7u** as white solid (75.0 mg, 0.17 mmol, 84 % yield); mp: 138–140 °C; R_f = 0.58 (EtOAc/ petroleum ether, v/v = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 2.0 Hz, 1H), 7.18–7.12 (m, 5H), 6.00 (d, *J* = 8.0 Hz, 1H), 5.72 (s, 1H), 5.01 (dd, *J* = 12.0 Hz, 3.6 Hz, 1H), 3.89 (s, 3H), 3.78 (s, 3H), 2.65 (ddd, *J* = 14.0 Hz, 3.6 Hz, 1.2 Hz, 1H), 2.35 (s, 3H), 1.83 (dd, *J* = 14.0 Hz, 12.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 168.2, 147.4, 139.1, 138.1, 133.4, 130.9, 129.0, 128.3, 126.3, 119.0, 118.4, 79.5, 60.9, 55.4, 53.5, 53.0, 24.9, 21.2; HRMS calcd for $C_{21}H_{21}BrNO_5$ $[M+H]^+$: 446.0598, found for: 446.0596.

Dimethyl 5-methyl-2-phenyl-2,3-dihydro-1,5-epoxybenzo[*b*]azepine-4,4(5*H*)-dicarboxylate (7v)



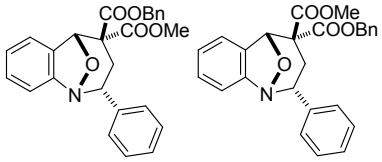
Purification by flash chromatography on silica gel petroleum ether/EtOAc (V/V = 9:1) gave **7v** as white solid (44.1 mg, 0.12 mmol, 60 % yield); mp: 118–120 °C; R_f = 0.58 (EtOAc/ petroleum ether, v/v = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.2 Hz, 1H), 7.36–7.29 (m, 5H), 7.13 (t, *J* =7.2 Hz, 1H), 6.99 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 6.11 (d, *J* = 7.6 Hz, 1H), 5.41 (dd, *J* = 12.0 Hz, 3.6 Hz, 1H), 3.86 (s, 3H), 3.71 (s, 3H), 2.52 (dd, *J* = 14.0 Hz, 3.6 Hz, 1H), 1.90 (s, 3H), 1.81 (dd, *J* = 14.0 Hz, 12.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 169.3, 148.4, 140.3, 137.2, 128.4, 128.2, 128.1, 127.5, 126.0, 123.2, 116.7, 84.2, 60.8, 57.9, 52.8, 52.5, 27.9, 19.4; HRMS calcd for $C_{21}H_{22}NO_5$ $[M+H]^+$: 368.1492, found for: 368.1490.

Dimethyl 6-phenyl-6,7-dihydro-5,9-epoxy[1,3]dioxolo[4',5':4,5]benzo[1,2-*b*]azepine-8,8(9*H*)-dicarboxylate (7w)



Purification by flash chromatography on silica gel petroleum ether/EtOAc (V/V = 8:1) gave **7w** as white solid (35.7 mg, 0.09 mmol, 45 % yield); mp: 134–136 °C; R_f = 0.33 (EtOAc/ petroleum ether, v/v = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.29 (m, 5H), 6.86 (s, 1H), 5.91 (d, *J* = 1.6 Hz, 2H), 5.66 (s, 1H), 5.65 (s, 1H), 5.00 (dd, *J* = 12.0 Hz, 3.6 Hz, 1H), 3.88 (s, 3H), 3.78 (s, 3H), 2.68 (ddd, *J* = 14.0 Hz, 3.6 Hz, 1.2 Hz, 1H), 1.90 (dd, *J* = 14.0 Hz, 12.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 168.5, 147.1, 145.6, 142.3, 136.8, 129.0, 128.4, 128.3, 128.2, 103.8, 101.7, 99.6, 80.1, 61.0, 55.5, 53.4, 52.9, 24.8; HRMS calcd for $C_{21}H_{20}NO_7$ $[M+H]^+$: 398.1234, found for: 398.1236.

4-benzyl4-methyl 2-phenyl-2,3-dihydro-1,5-epoxybenzo[*b*]azepine-4,4(5*H*)-dicarboxylate (7x, 7x')

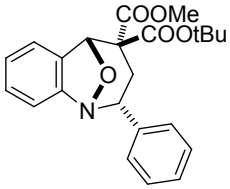


7x **7x'**

Purification by flash chromatography on silica gel petroleum ether/EtOAc (V/V = 8:1) gave **7x** and **7x'** as colorless oil (68.6 mg, 0.16 mmol, 80 % yield); R_f = 0.40 (EtOAc/ petroleum ether, v/v = 1/5); the minor product ^{1}H NMR (600 MHz, CD_3OD) δ 7.31–7.29 (m, 8H), 7.20–7.19 (m, 2H), 7.03 (t, *J* = 7.8 Hz, 1H), 7.00–6.98 (m, 1H), 6.03 (d, *J* = 7.8 Hz, 1H), 5.69 (s, 1H), 5.33 (d, *J* = 12.6 Hz, 1H), 5.25 (d, *J* = 4.2 Hz, 1H), 5.11 (d, *J* = 12.0 Hz, 1H), 4.95 (dd, *J* = 12.6 Hz, 3.6 Hz, 1H), 3.75 (d, *J* = 0.6 Hz, 3H), 2.55 (d, *J* = 13.8 Hz, 1H), 1.83 (dd, *J* = 13.8 Hz, 12.6 Hz, 1H) ppm; the major product ^{1}H NMR (600 MHz, CD_3OD) δ 7.41–7.33 (m, 7H), 7.20–7.19 (m, 3H), 7.12 (t, *J* = 7.8 Hz, 1H), 6.98–6.94 (m, 1H), 6.05 (d, *J* = 7.8 Hz, 1H), 5.72 (s, 1H), 5.33 (d, *J* = 12.6 Hz, 1H), 5.27 (d, *J* = 4.8 Hz, 1H), 5.11 (d, *J* = 12.0 Hz, 1H), 4.97 (dd, *J* = 12.0 Hz, 3.6 Hz, 1H), 3.64 (d, *J* = 0.6 Hz, 3H), 2.55 (d, *J* = 13.8 Hz, 1H), 1.83 (dd, *J* = 13.8 Hz, 12.6 Hz, 1H) ppm; HRMS calcd for $C_{26}H_{24}NO_5$ $[M+H]^+$: 430.1649, found for: 430.1650.

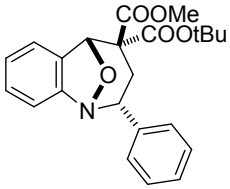
4-tert-butyl 4-methyl 2-phenyl-2,3-dihydro-1,5-epoxybenzo[*b*]azepine-4,4(5*H*)-dicarbo-

Xylate (7y)



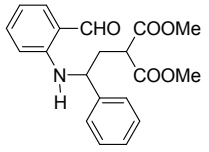
Compound **7y** was prepared according to the procedure for the [3+4]-annulation reaction of D-A cyclopropanes with anthranils in 0.5 mmol scale, Purification by flash chromatography on silica gel petroleum ether/EtOAc (V/V = 20:1) gave **7y** as white solid (20.8 mg, 0.05 mmol, 10 % yield); mp: 110–112 °C; R_f = 0.34 (EtOAc/ petroleum ether, v/v = 1/20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.2 Hz, 1H), 7.33–7.30 (m, 5H), 7.10 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 6.99 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 6.13 (d, *J* = 7.6 Hz, 1H), 5.70 (s, 1H), 5.08 (dd, *J* = 12.0 Hz, 3.6 Hz, 1H), 3.76 (s, 3H), 2.59 (ddd, *J* = 14.0 Hz, 3.6 Hz, 1.2 Hz, 1H), 1.77 (dd, *J* = 13.6 Hz, 12.0 Hz, 1H), 1.55 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 166.8, 148.1, 137.1, 137.0, 128.5, 128.1, 128.0, 127.8, 125.9, 122.7, 116.8, 83.0, 79.9, 61.2, 56.2, 52.5, 27.9, 24.8; HRMS calcd for $C_{23}H_{26}NO_5$ $[M+H]^+$: 396.1805, found for: 396.1808.

4-tert-butyl 4-methyl 2-phenyl-2,3-dihydro-1,5-epoxybenzo[*b*]azepine-4,4(5*H*)-dicarbo-Xylate (7y')



Compound **7y'** was prepared according to the procedure for the [3+4]-annulation reaction of D-A cyclopropanes with anthranils in 0.5 mmol sacle, Purification by flash chromatography on silica gel petroleum ether/EtOAc (V/V = 20:1) gave **7y'** as colorless oil (3.4 mg, 0.01 mmol, 2 % yield); R_f = 0.27 (EtOAc/ petroleum ether, v/v = 1/20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.6 Hz, 1H), 7.34–7.32 (m, 5H), 7.11 (td, *J* = 7.2 Hz, 1.2 Hz, 1H), 7.00 (td, *J* = 7.6 Hz, 0.8 Hz, 1H), 6.14 (d, *J* = 7.6 Hz, 1H), 5.72 (s, 1H), 5.03 (dd, *J* = 12.4 Hz, 3.6 Hz, 1H), 3.89 (s, 3H), 2.58 (ddd, *J* = 14.0 Hz, 3.6 Hz, 1.6 Hz, 1H), 1.81 (dd, *J* = 14.0 Hz, 12.0 Hz, 1H), 1.47 (s, 9H) ppm; HRMS calcd for $C_{23}H_{26}NO_5$ $[M+H]^+$: 396.1805, found for: 396.1803.

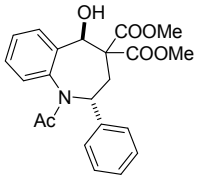
Dimethyl 2-(2-((2-formylphenyl)amino)-2-phenylethyl)malonate (8)



White solid (74.6 mg, 0.21 mmol, 70 % yield); mp: 78-80 °C; R_f = 0.75 (EtOAc/ petroleum ether, v/v = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H), 8.79 (d, *J* = 7.2 Hz, 1H), 7.47 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.34–7.33 (m, 4H), 7.27–7.26 (m, 1H), 7.25–7.23 (m, 1H), 6.68 (t, *J* = 7.6 Hz, 1H), 6.55 (d, *J* = 8.4

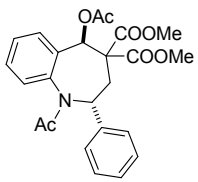
Hz, 1H), 4.60 (dd, *J* = 14.4 Hz, 7.2 Hz, 1H), 3.76 (s, 3H), 3.69 (s, 3H), 3.53 (t, *J* = 7.6 Hz, 1H), 2.55–2.42 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 169.4, 169.2, 149.6, 141.6, 136.6, 135.8, 128.9, 127.6, 126.3, 118.8, 115.6, 112.0, 55.0, 52.7, 52.6, 48.9, 37.0; HRMS calcd for $C_{20}H_{22}NO_5$ $[M+H]^+$: 356.1492, found for: 356.1491.

Dimethyl 1-acetyl-5-hydroxy-2-phenyl-2,3-dihydro-1H-benzo[*b*]azepine-4,4(5*H*)-dicarboxylate (9)



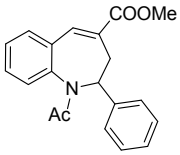
White solid (191.0 mg, 0.48 mmol, 80 % yield); mp: 182-184 °C; R_f = 0.19 (EtOAc/ petroleum ether, v/v = 1/1); ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.52(d, *J* = 7.8 Hz, 1H), 7.49–7.45 (m, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.33–7.31 (m, 4H), 7.23–7.20 (m, 1H), 6.04 (d, *J* = 5.4 Hz, 1H), 5.65 (dd, *J* = 12.6 Hz, 1.8 Hz, 1H), 5.36 (d, *J* = 5.4 Hz, 1H), 3.74 (s, 3H), 3.52 (s, 3H), 2.31 (d, *J* = 14.4 Hz 1H), 1.64 (s, 3H), 1.36 (dd, *J* = 15.0 Hz, 12.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 170.0, 169.4, 144.3, 139.0, 135.5, 130.6, 130.5, 129.4, 128.4, 127.7, 127.0, 126.4, 74.5, 60.1, 54.7, 53.0, 52.8, 36.5, 23.3; HRMS calcd for $C_{22}H_{24}NO_6$ $[M+H]^+$: 398.1598, found for: 398.1600.

Dimethyl 5-acetoxy-1-acetyl-2-phenyl-2,3-dihydro-1H-benzo[*b*]azepine-4,4(5*H*)-dicarboxylate (10)



White solid (118.5 mg, 0.27 mmol, 90 % yield); mp: 190-192 °C; R_f = 0.37 (EtOAc/ petroleum ether, v/v = 1/1); ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.63–7.59 (m, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.45 (dd, *J* = 15.0 Hz, 7.2 Hz, 1H), 7.37–7.32 (m, 4H), 7.25 (t, *J* = 7.2 Hz, 1H), 6.45 (s, 1H), 5.67 (dd, *J* = 12.6 Hz, 1.8 Hz, 1H), 3.77 (s, 3H), 3.58 (s, 3H), 2.43 (d, *J* = 14.4 Hz, 1H), 1.91 (s, 3H), 1.60 (s, 3H), 1.53 (d, *J* = 12.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 169.0, 168.8, 167.7, 144.3, 139.1, 132.2, 131.9, 130.2, 130.1, 129.0, 128.5, 128.0, 127.1, 126.3, 125.8, 74.6, 58.3, 54.7, 53.0, 52.8, 36.6, 23.4, 20.4; HRMS calcd for $C_{24}H_{26}NO_7$ $[M+H]^+$: 440.1704, found for: 440.1707.

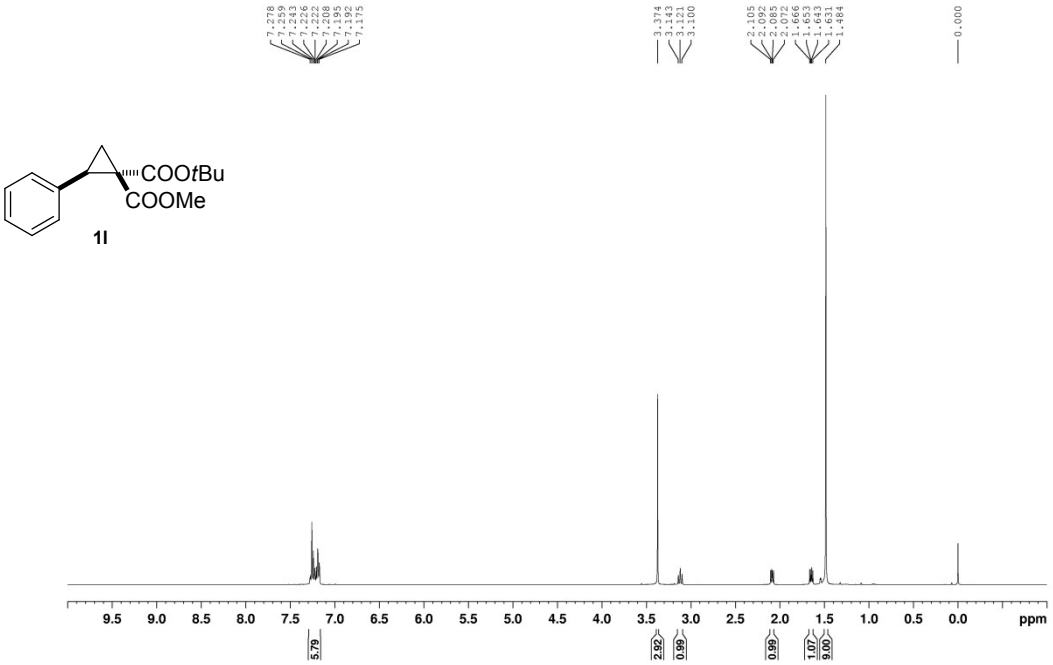
Methyl 1-acetyl-2-phenyl-2,3-dihydro-1H-benzo[*b*]azepine-4-carboxylate(11)



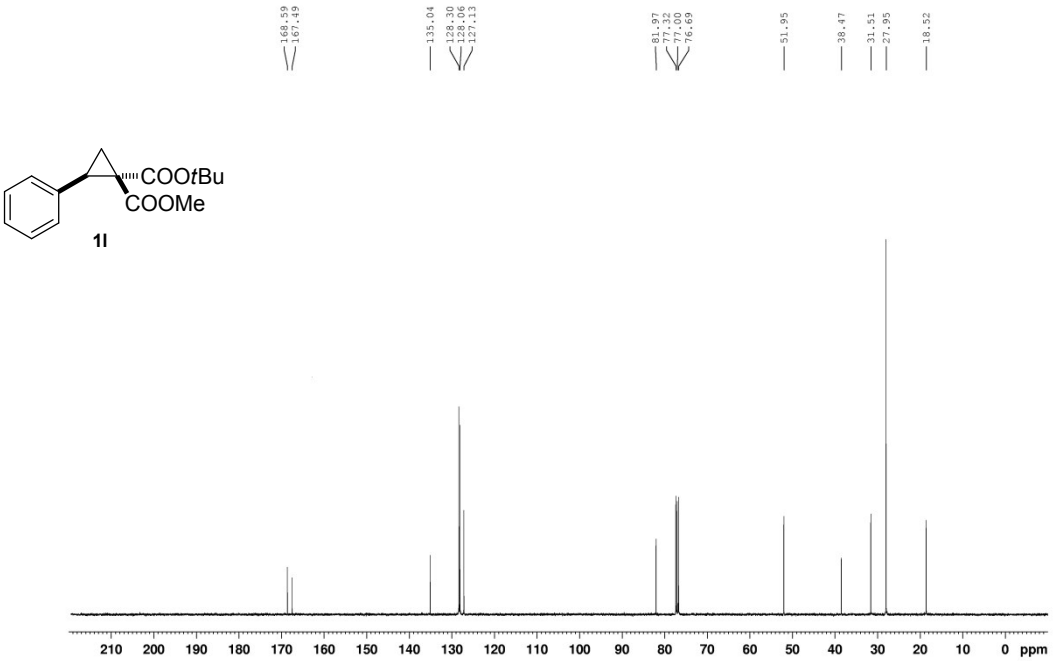
Colorless oil (42.5 mg, 0.13mmol, 88 % yield); R_f = 0.53 (EtOAc/ petroleum ether, v/v = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.37–7.30 (m, 5H), 7.27–7.18 (m, 3H), 7.09 (d, J = 6.4 Hz, 1H), 6.24 (dd, J = 10.8 Hz, 5.2 Hz, 1H), 3.86 (s, 3H), 3.20 (dd, J = 15.6 Hz, 5.2 Hz, 1H), 2.71 (ddd, J = 15.6 Hz, 10.8 Hz, 1.2 Hz, 1H), 1.73 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 167.2, 140.2, 139.9, 138.4, 134.8, 133.0, 130.9, 130.7, 129.4, 128.3, 127.9, 127.4, 127.1, 64.6, 52.3, 31.1, 23.2; HRMS calcd for $C_{20}H_{20}NO_3$ $[M+H]^+$: 322.1438, found for: 322.1437.

4. ^{1}H-NMR and ^{13}C-NMR spectra of the compounds

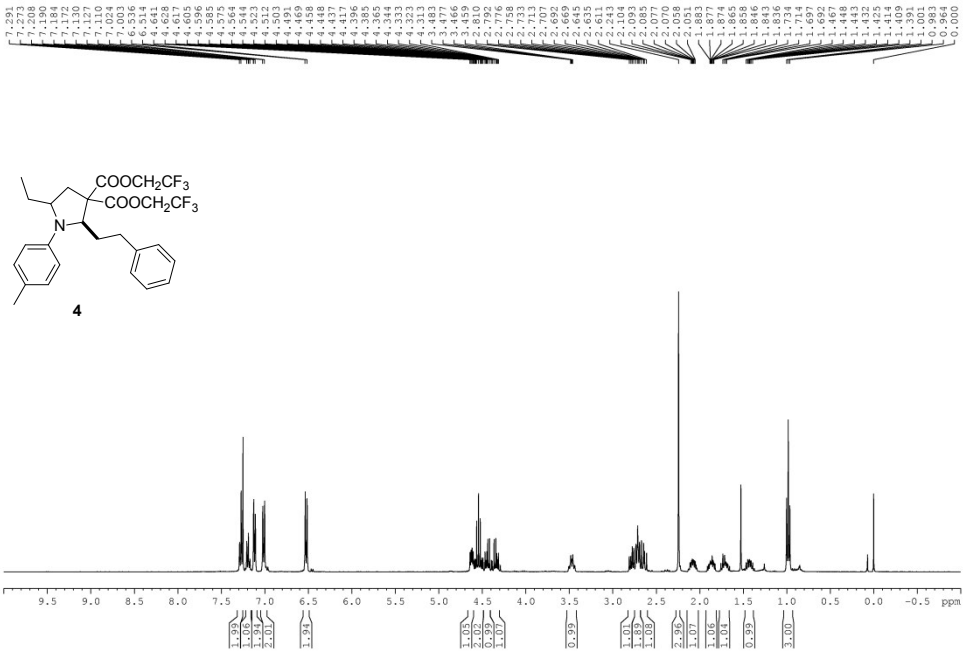
^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **1l**



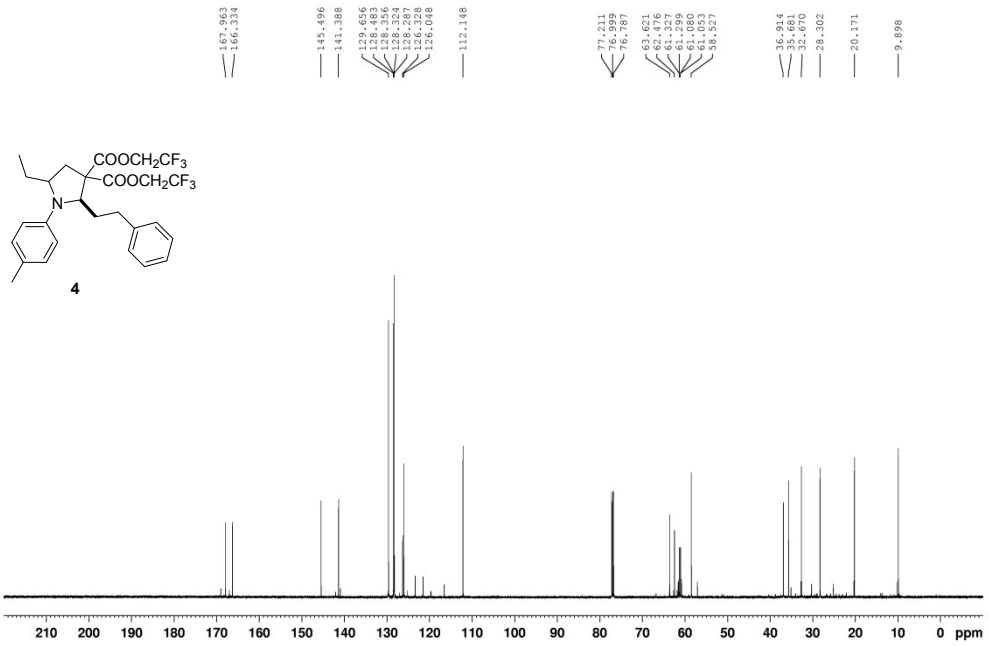
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **1l**



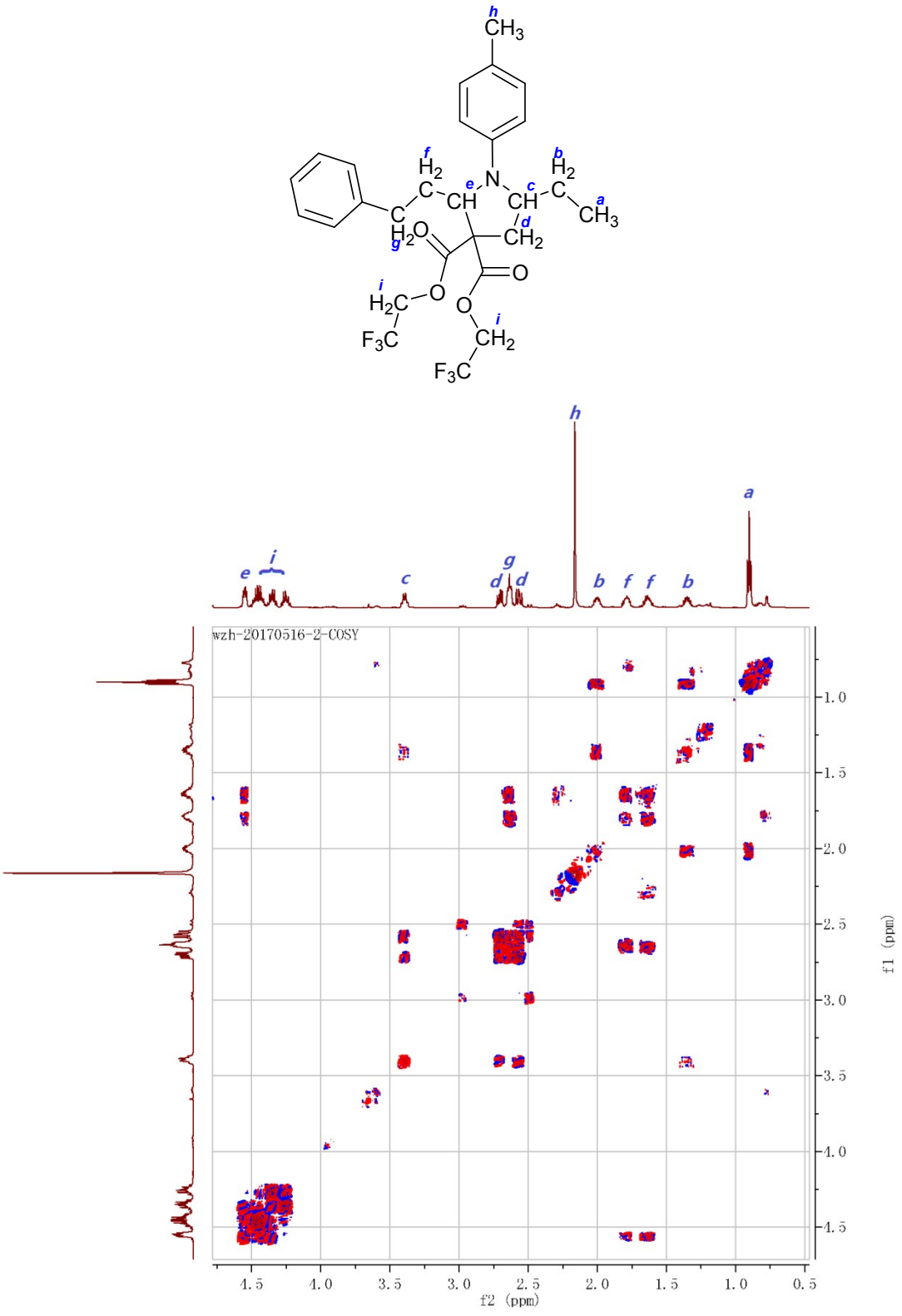
^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **4**



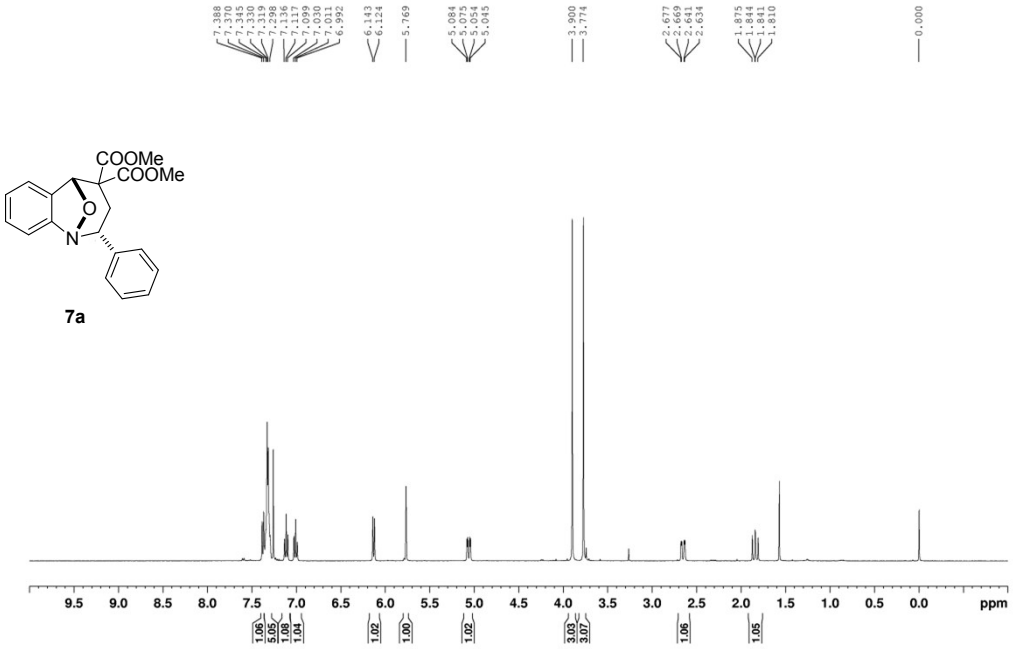
^{13}C-NMR (150 MHz, $CDCl_3$) spectra of compound **4**



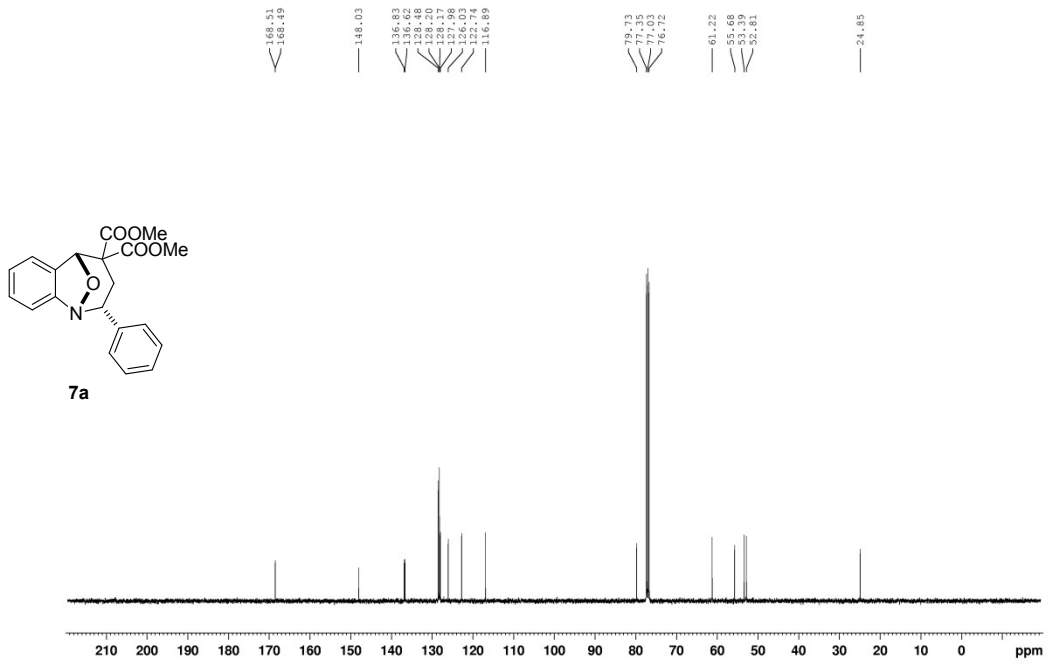
H-H COSY (600 MHz, $CDCl_3$) spectra of compound **4**



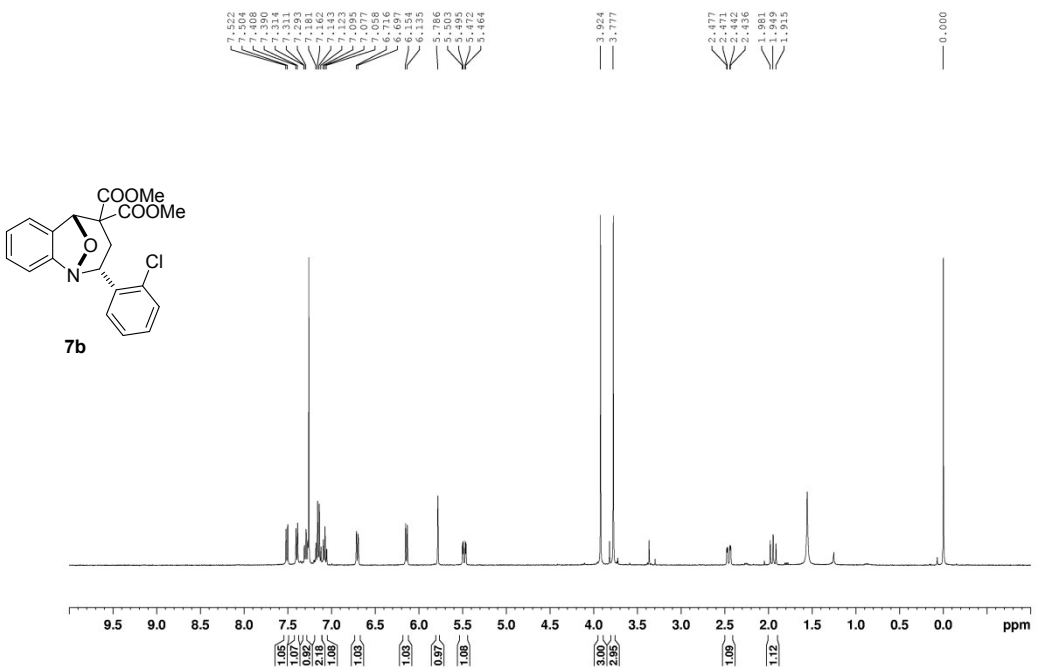
^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **7a**



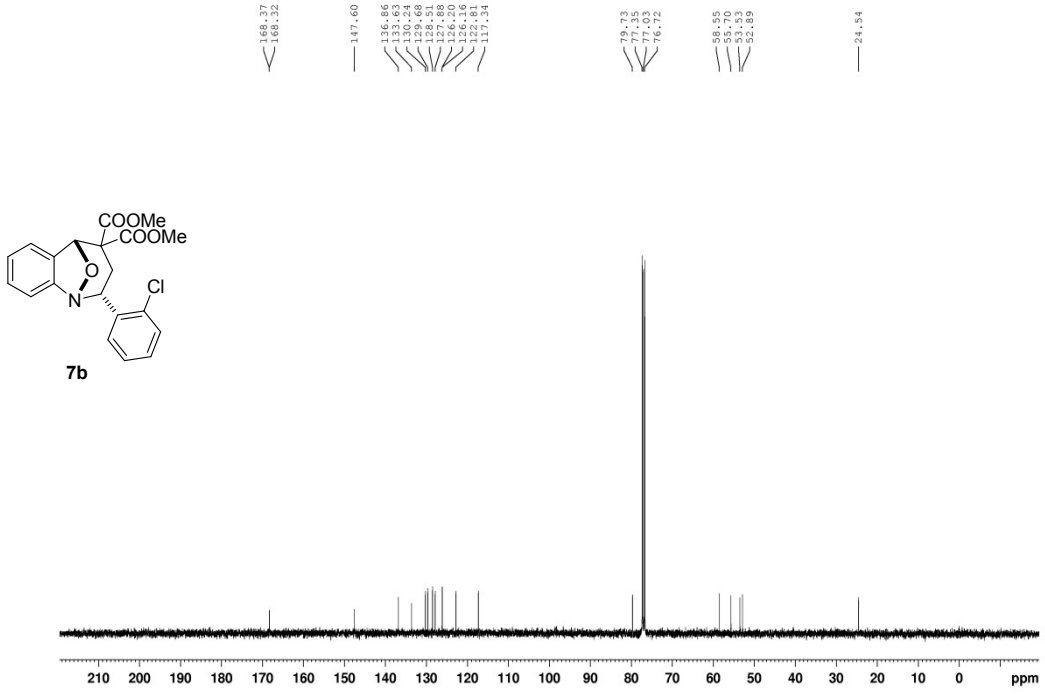
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **7a**



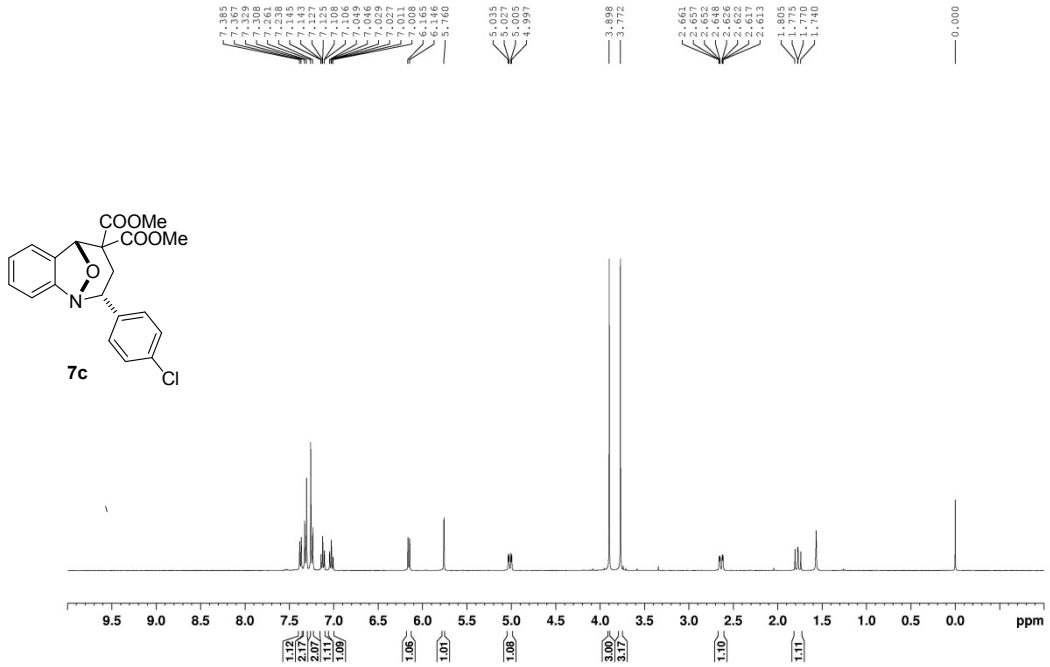
^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **7b**



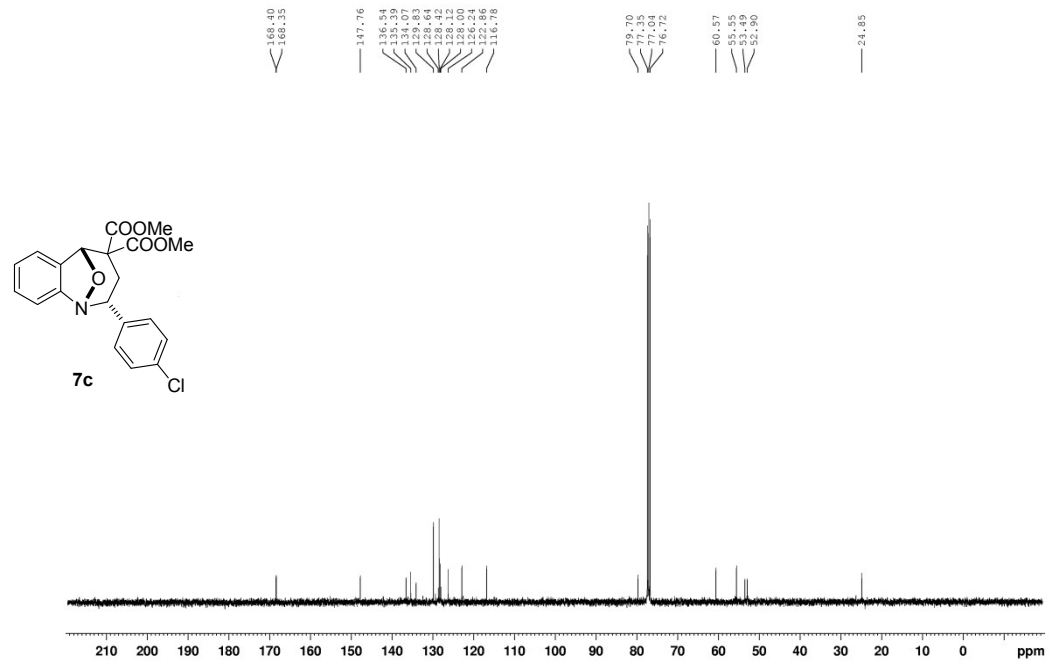
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **7b**



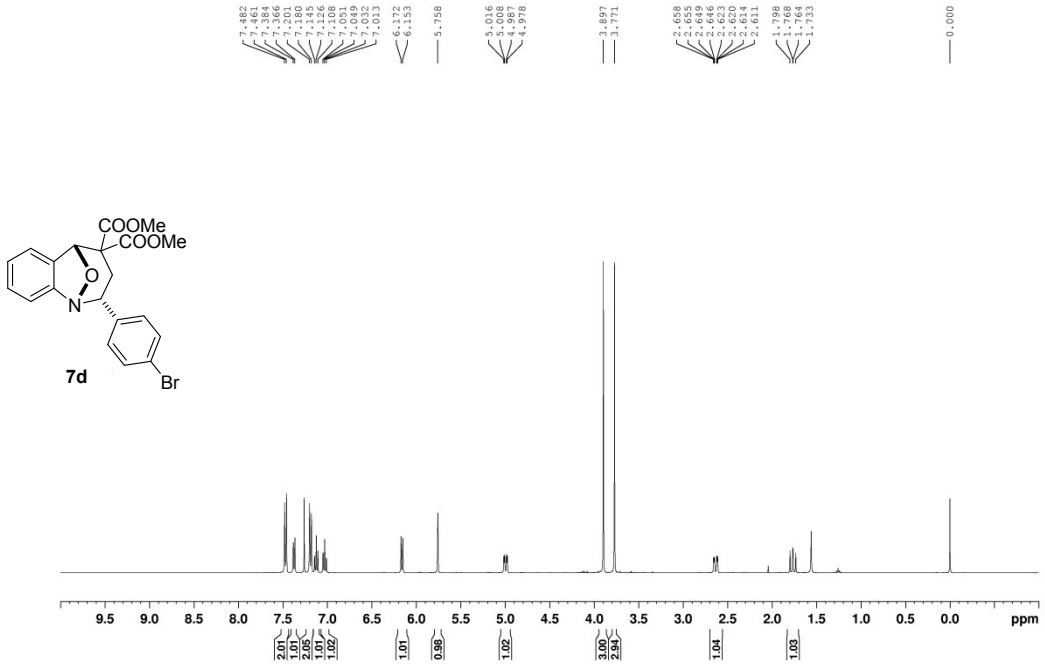
^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **7c**



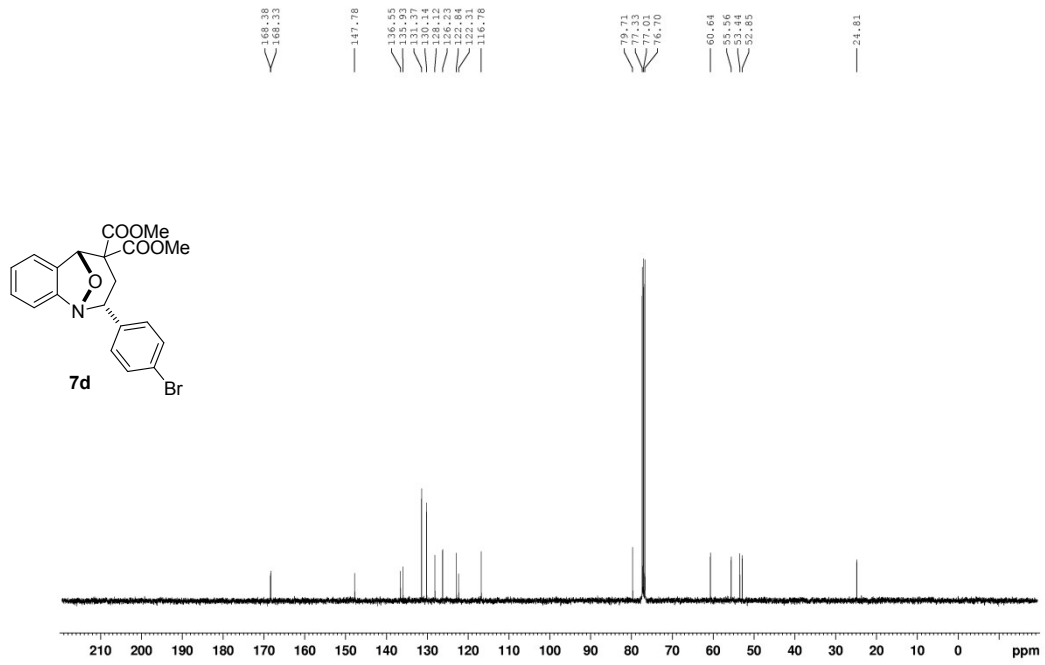
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **7c**



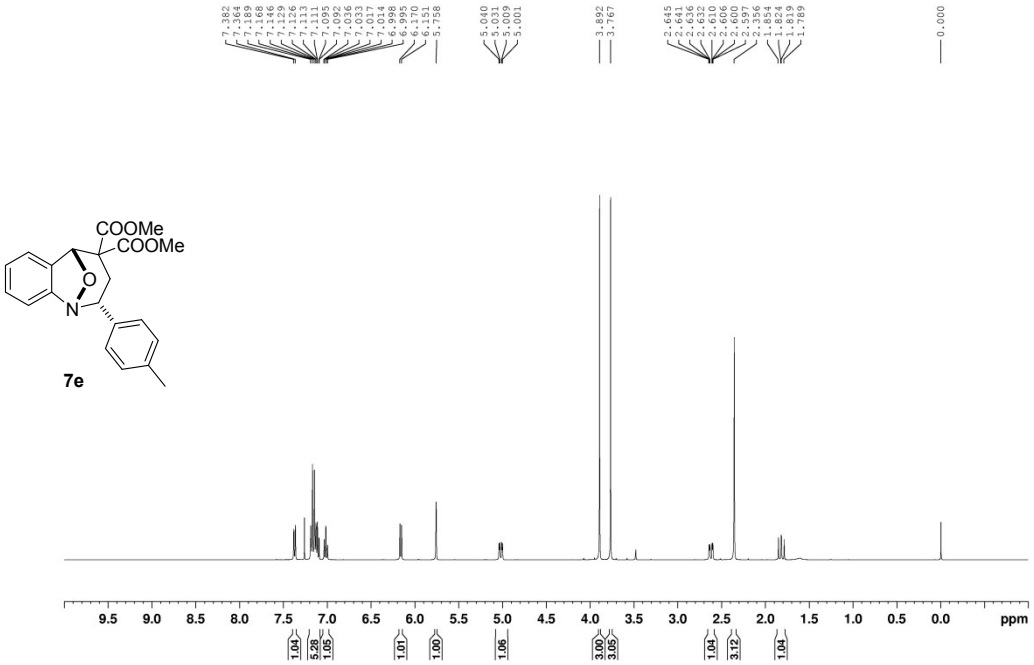
^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **7d**



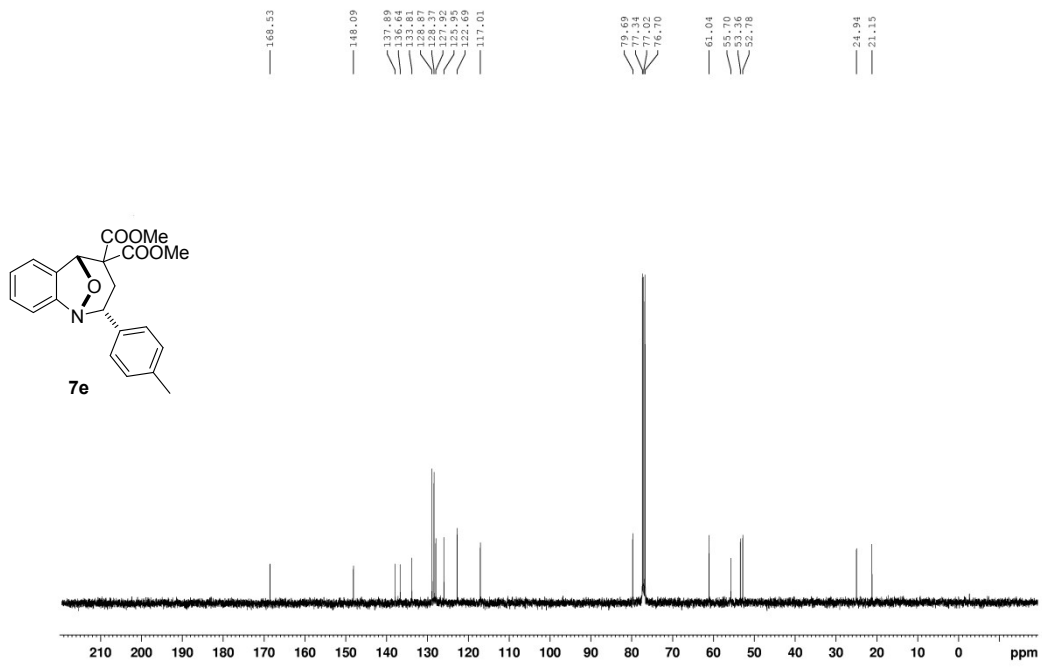
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **7d**



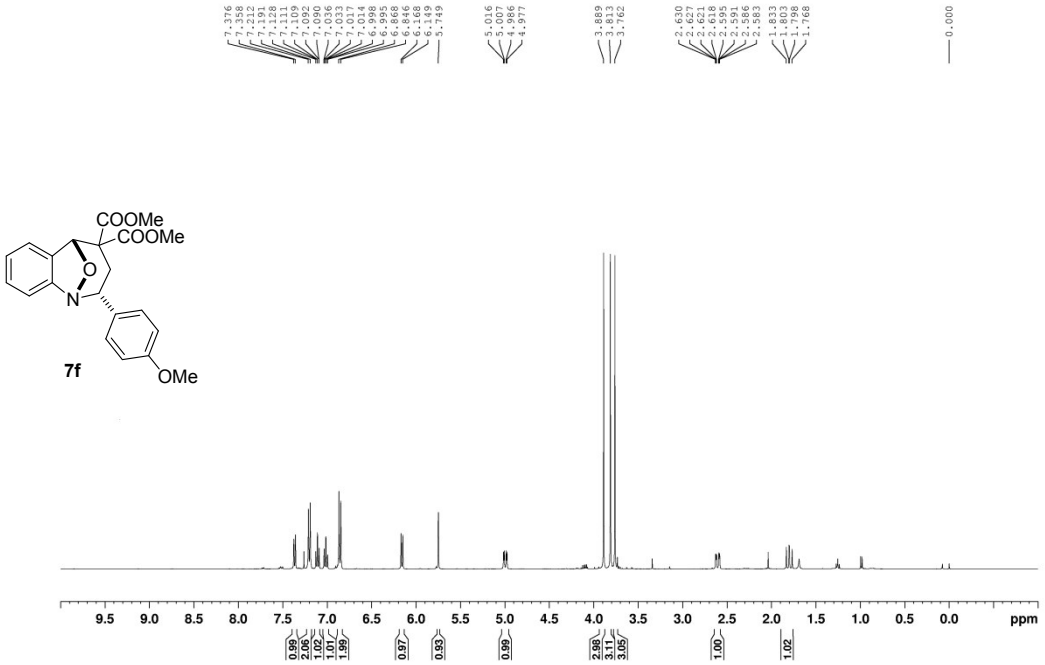
^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **7e**



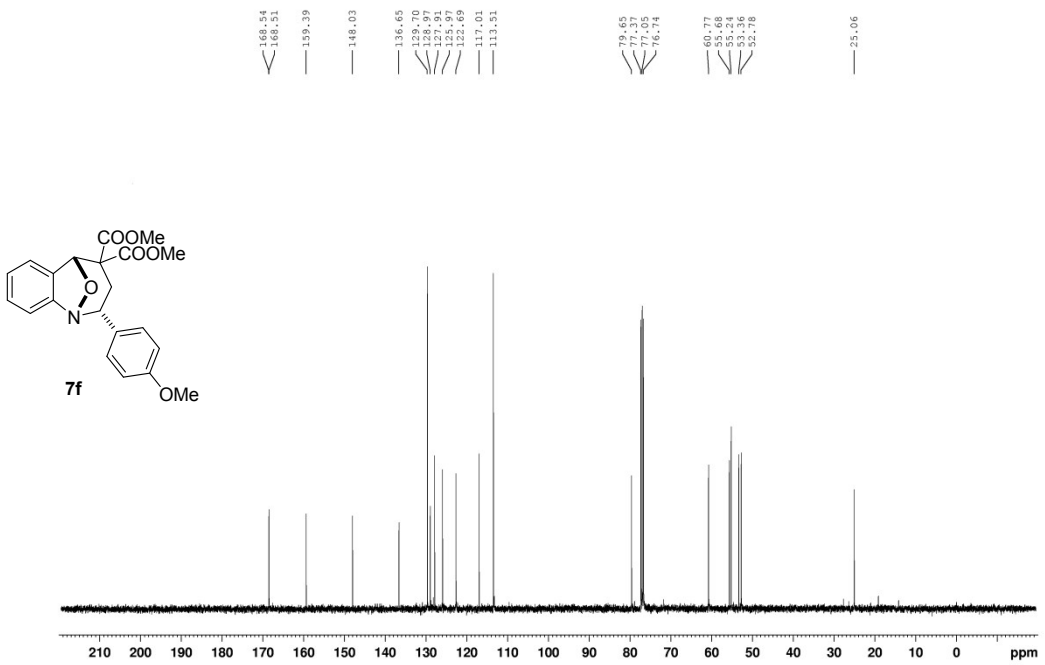
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **7e**



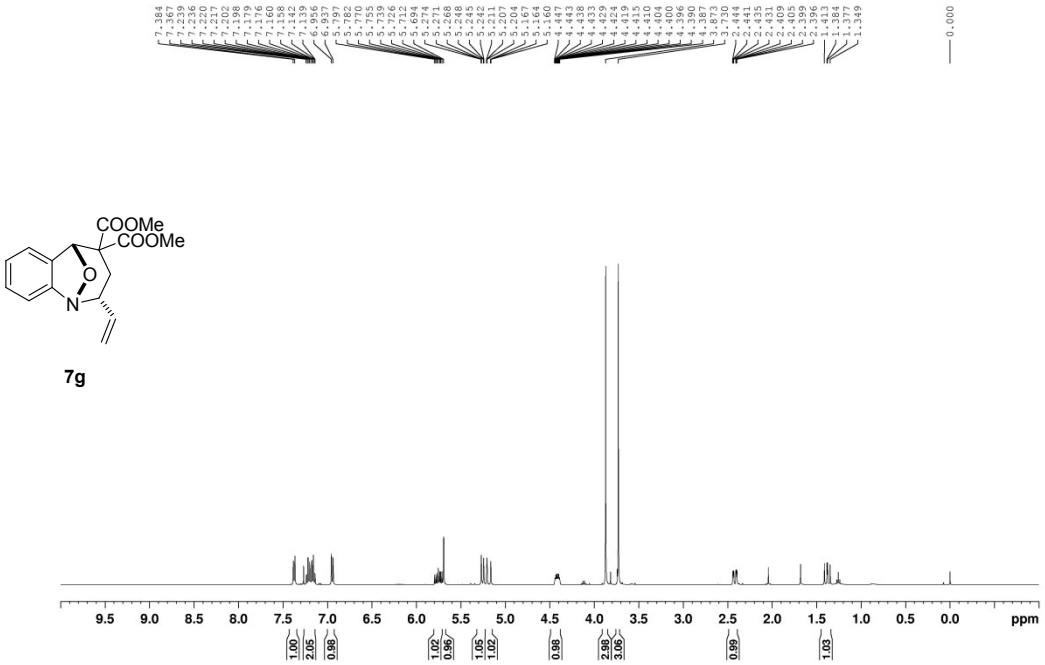
^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **7f**



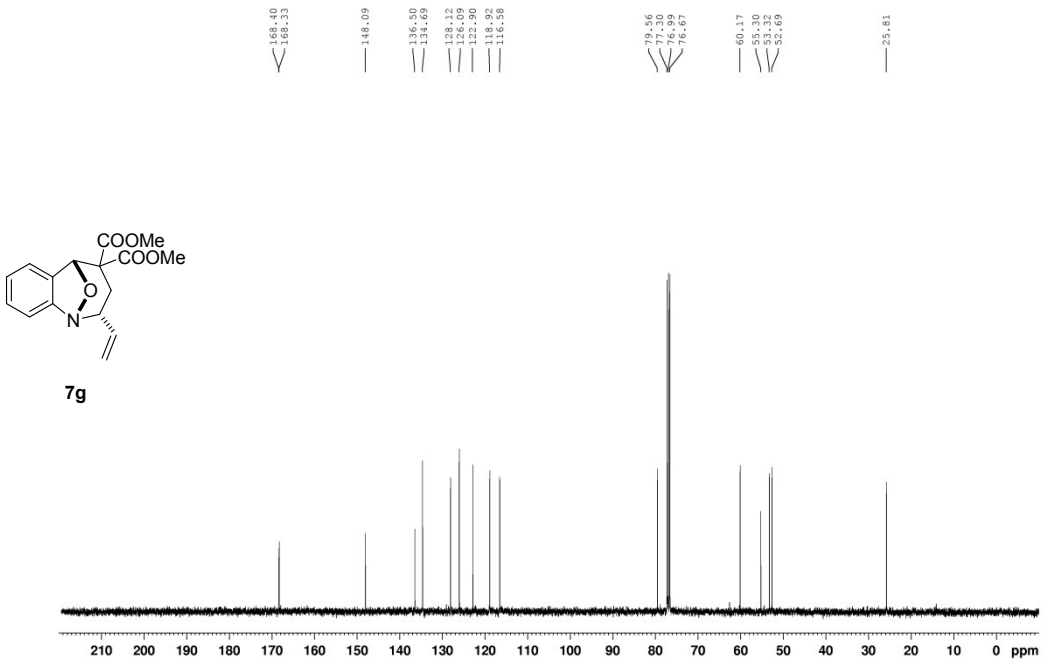
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **7f**



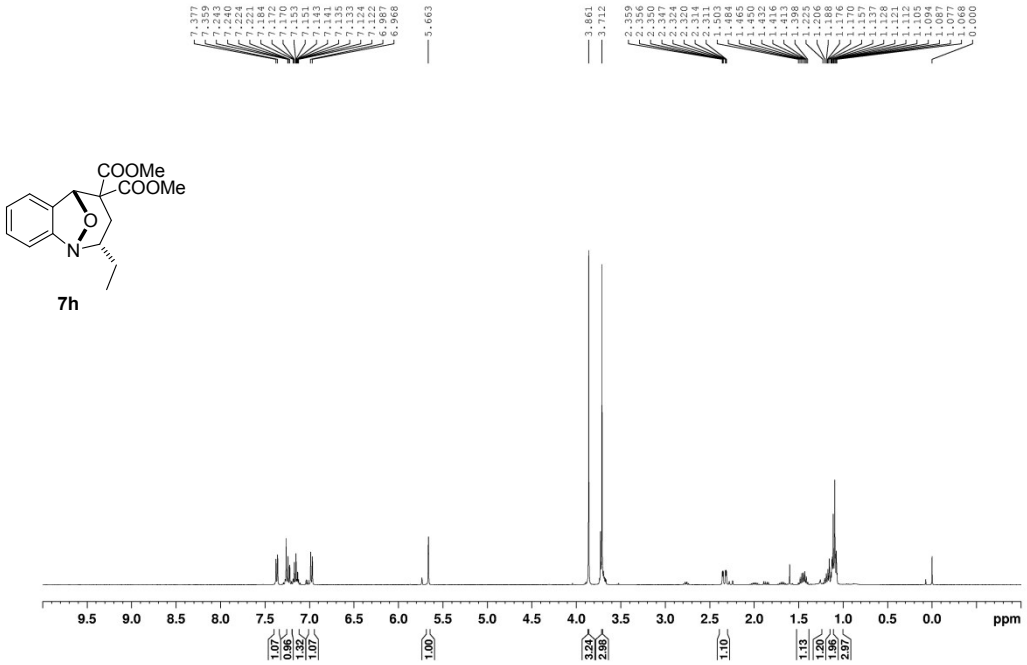
^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **7g**



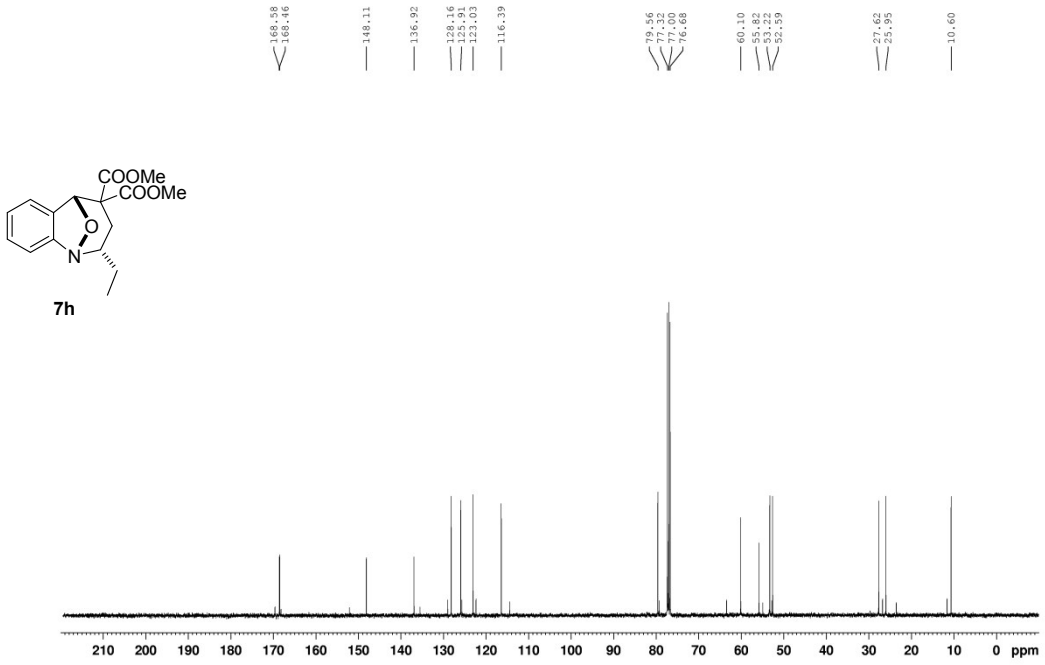
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **7g**



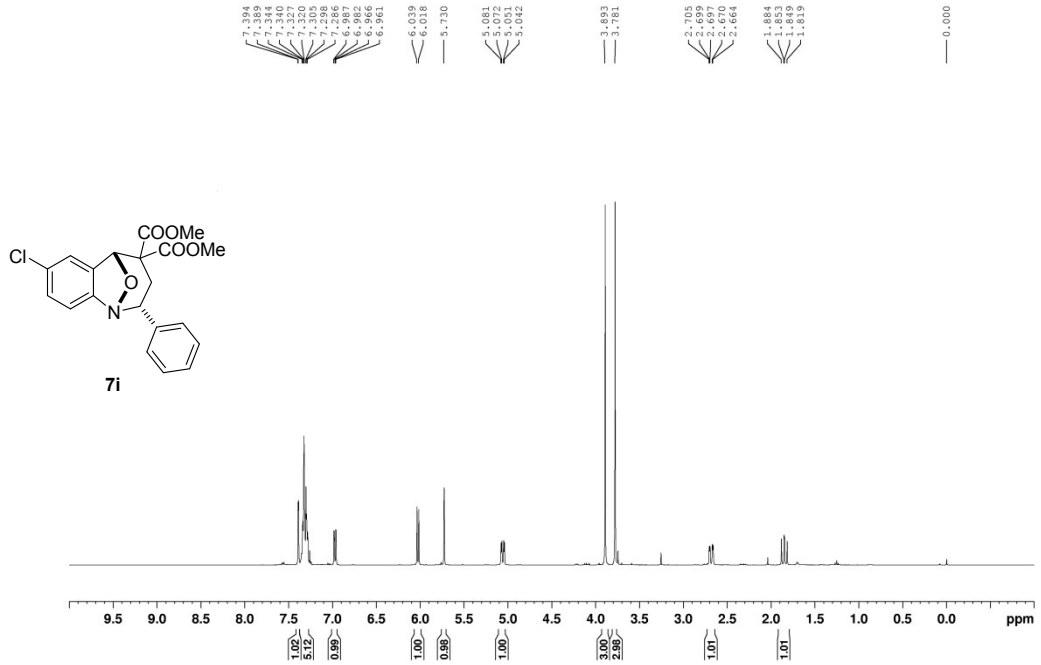
^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **7h**



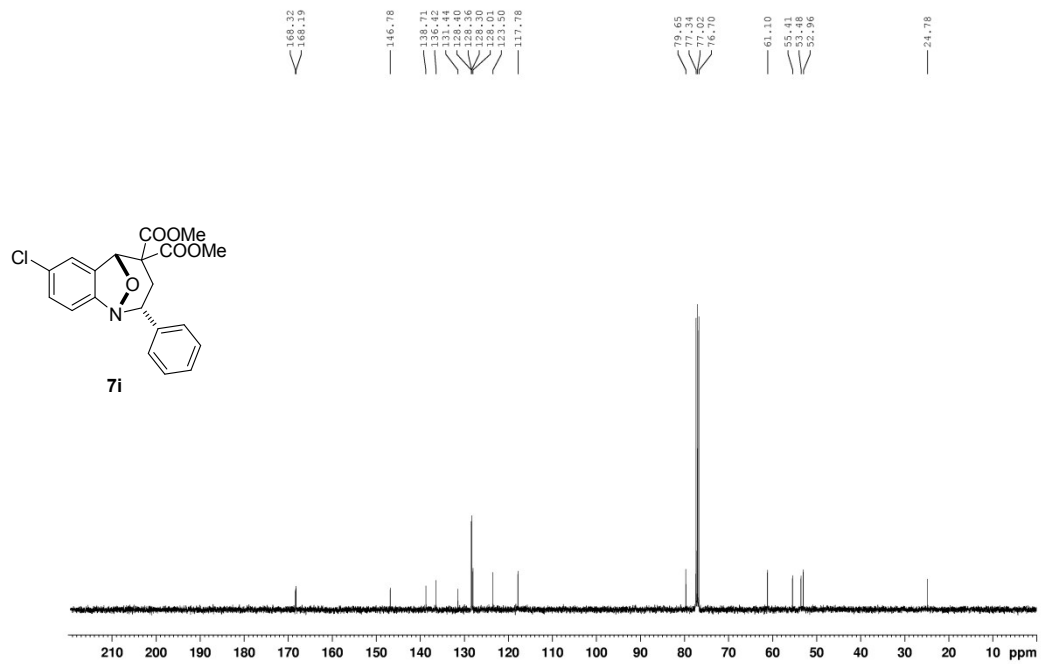
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **7h**



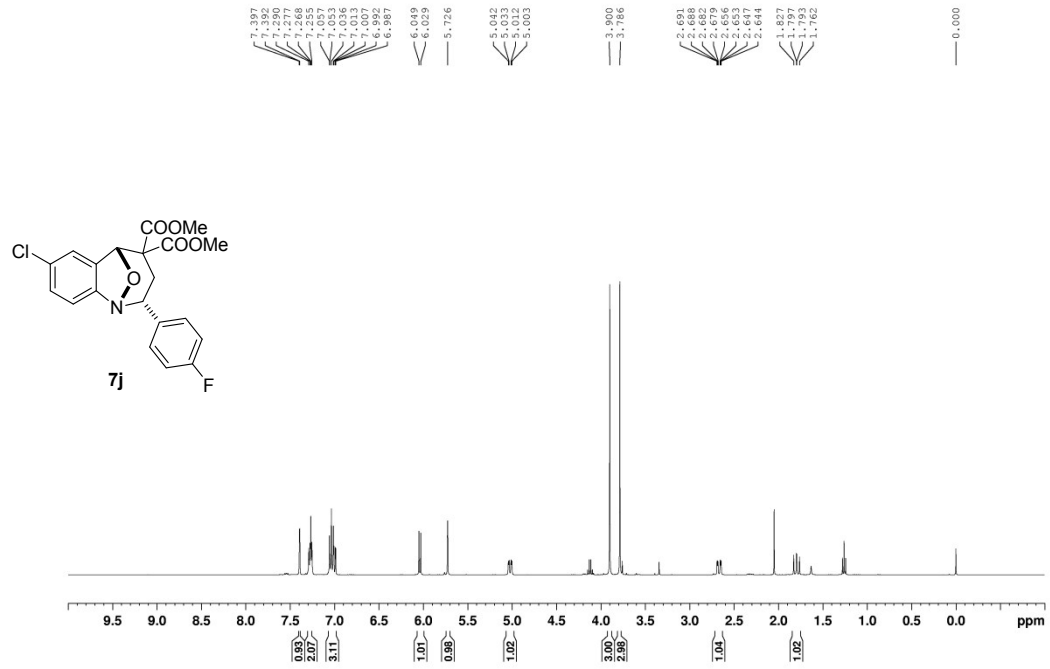
^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **7i**



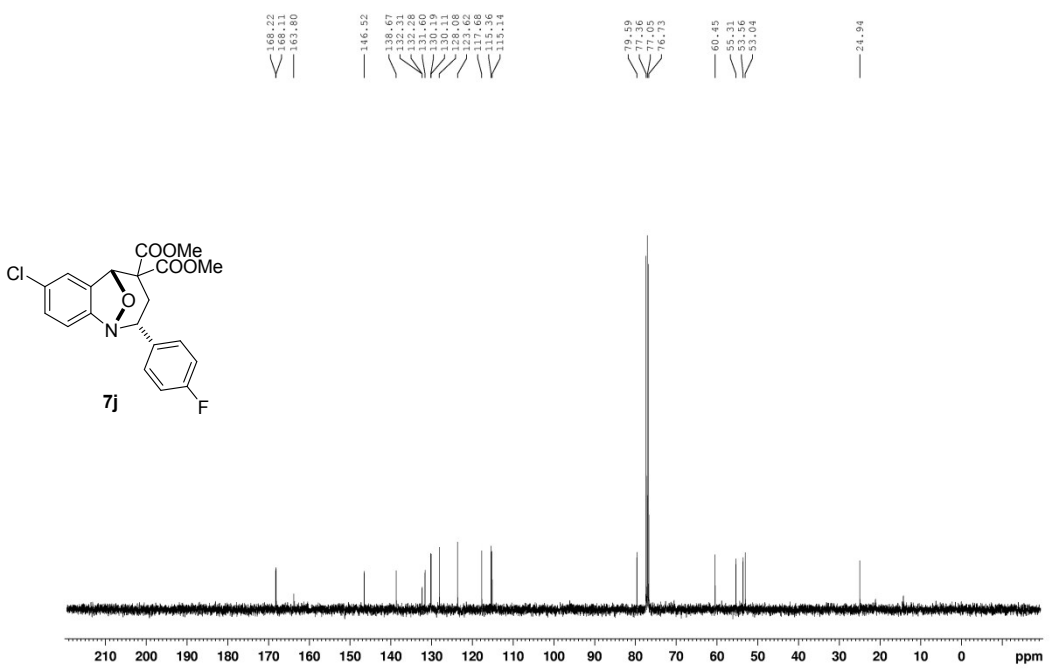
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **7i**



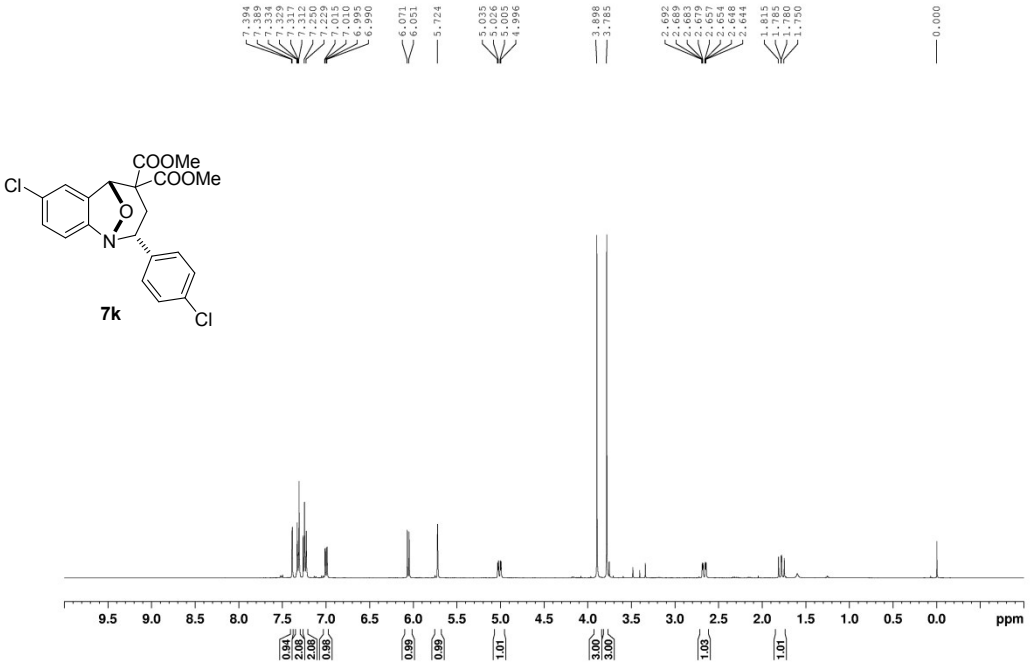
^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **7j**



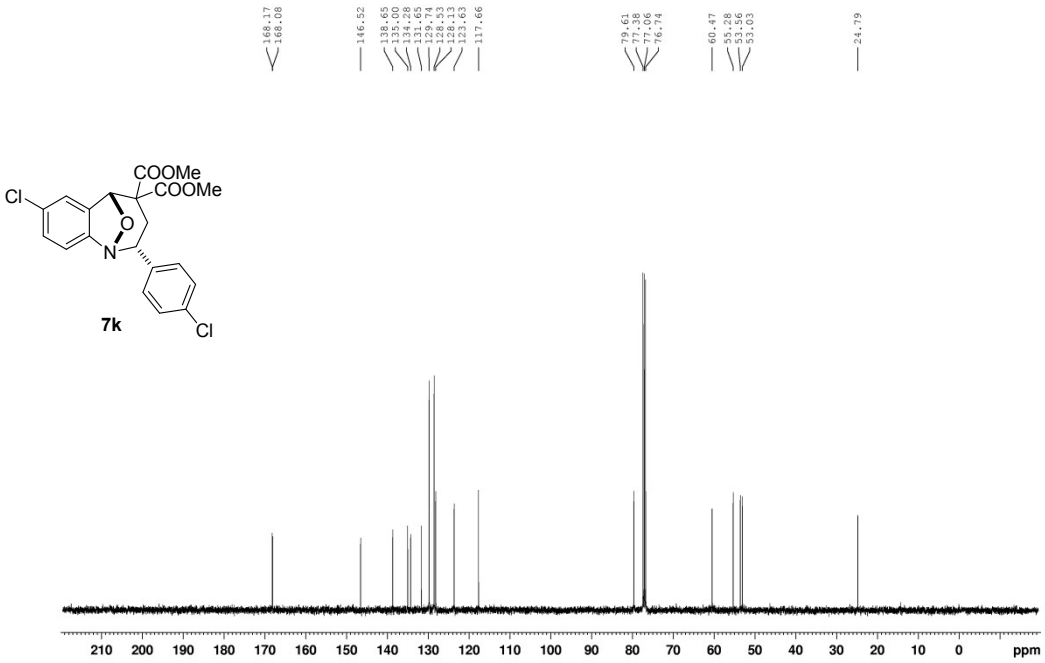
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **7j**



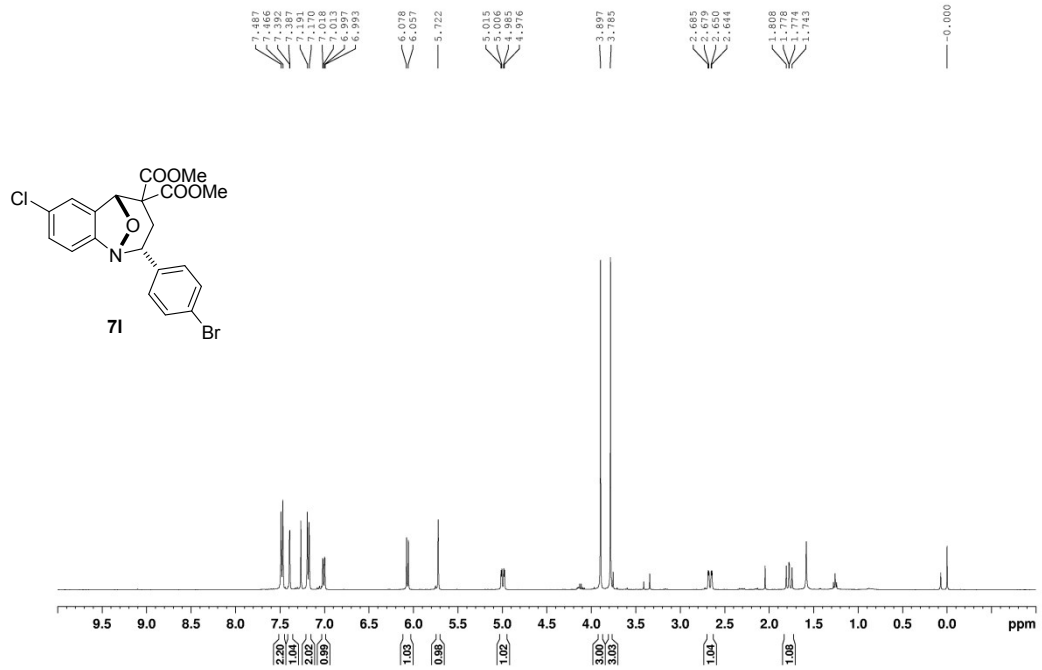
^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **7k**



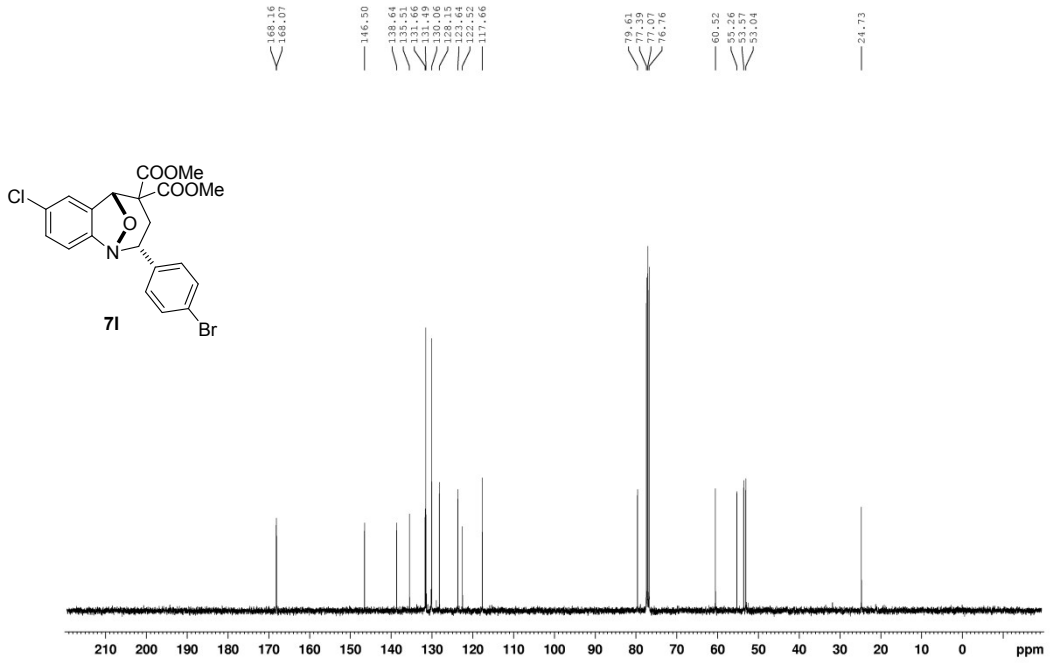
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **7k**



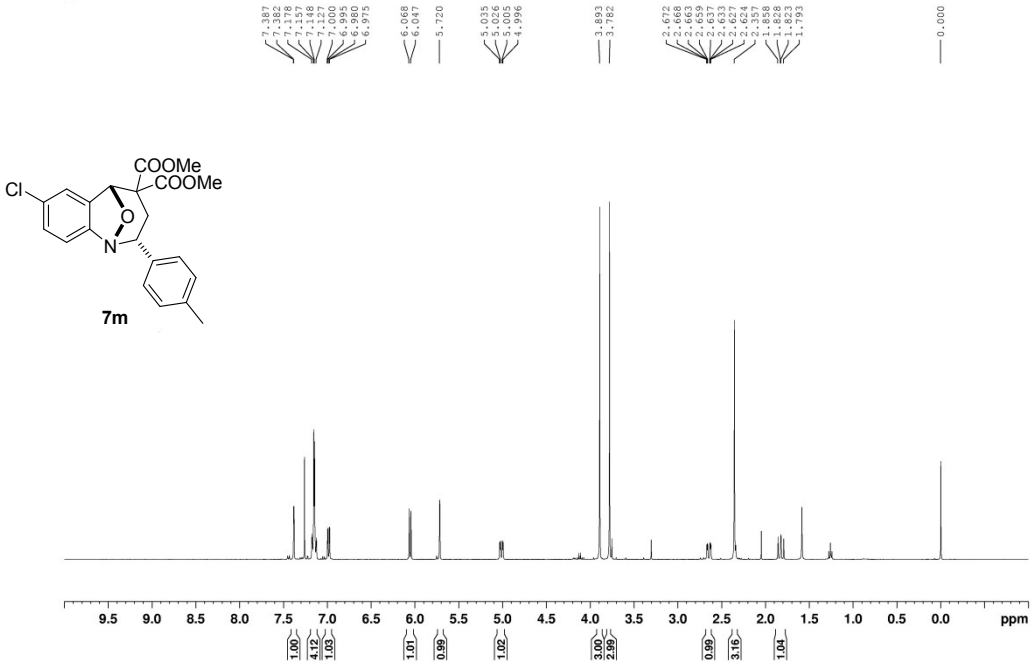
^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **7l**



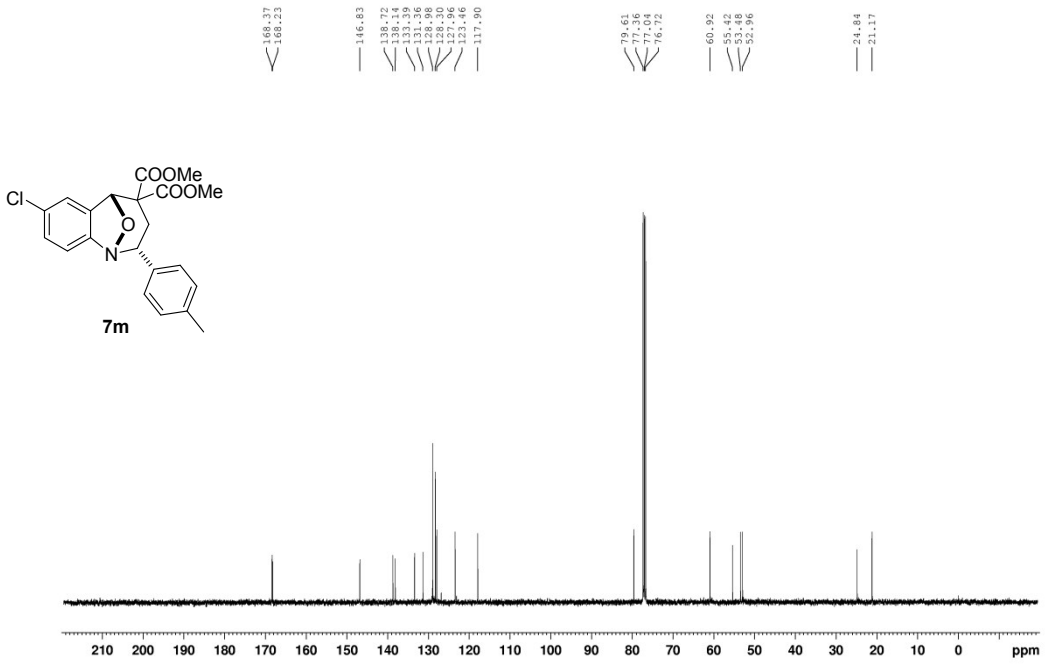
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **7l**



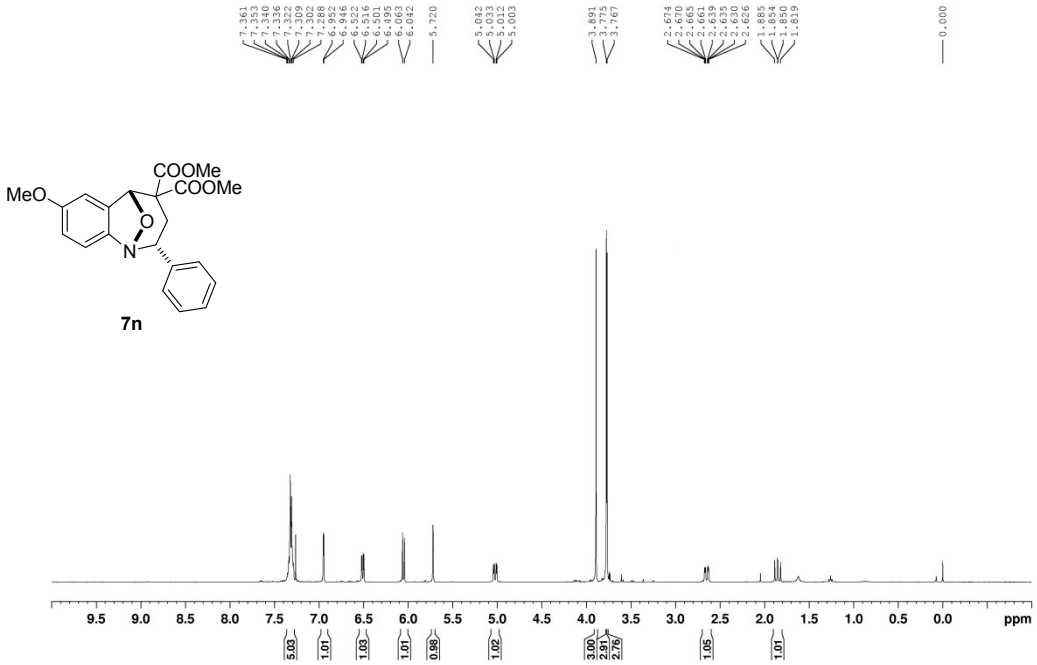
^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **7m**



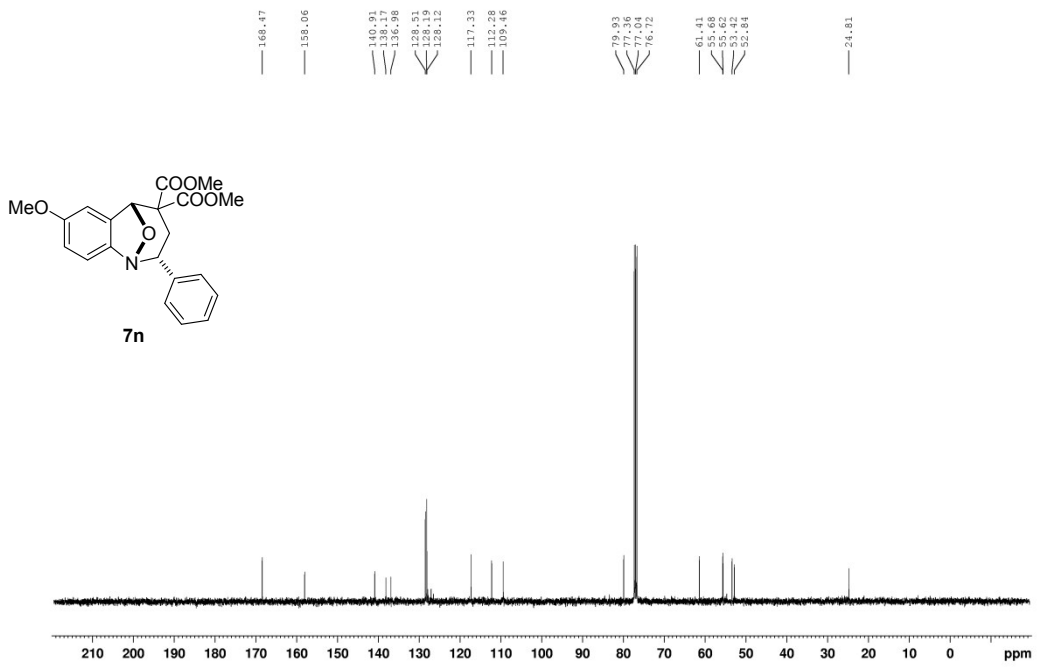
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **7m**



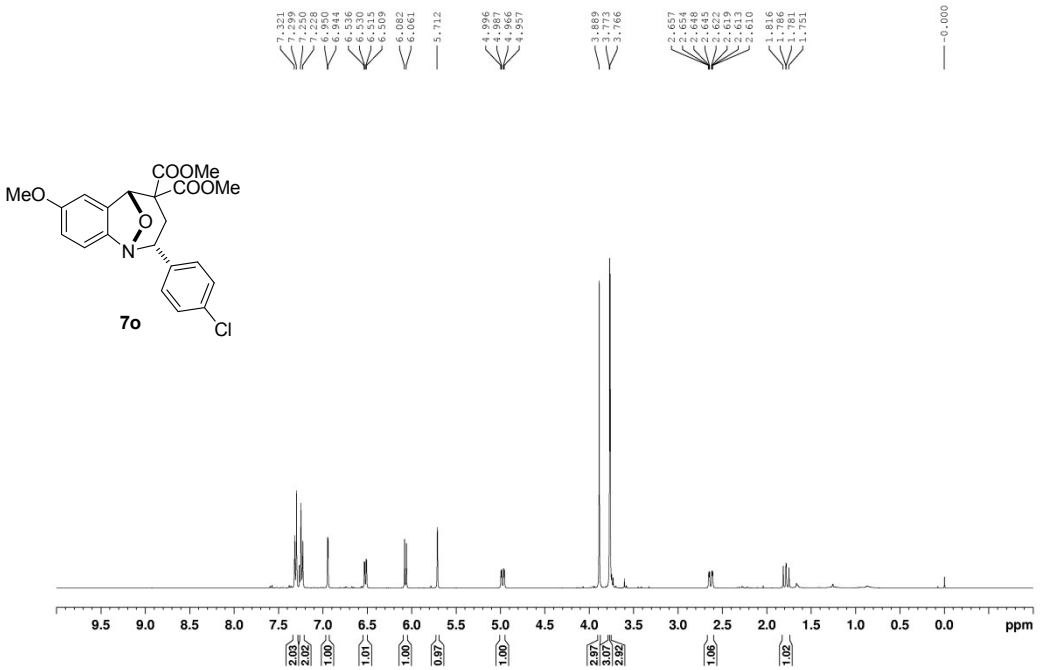
^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **7n**



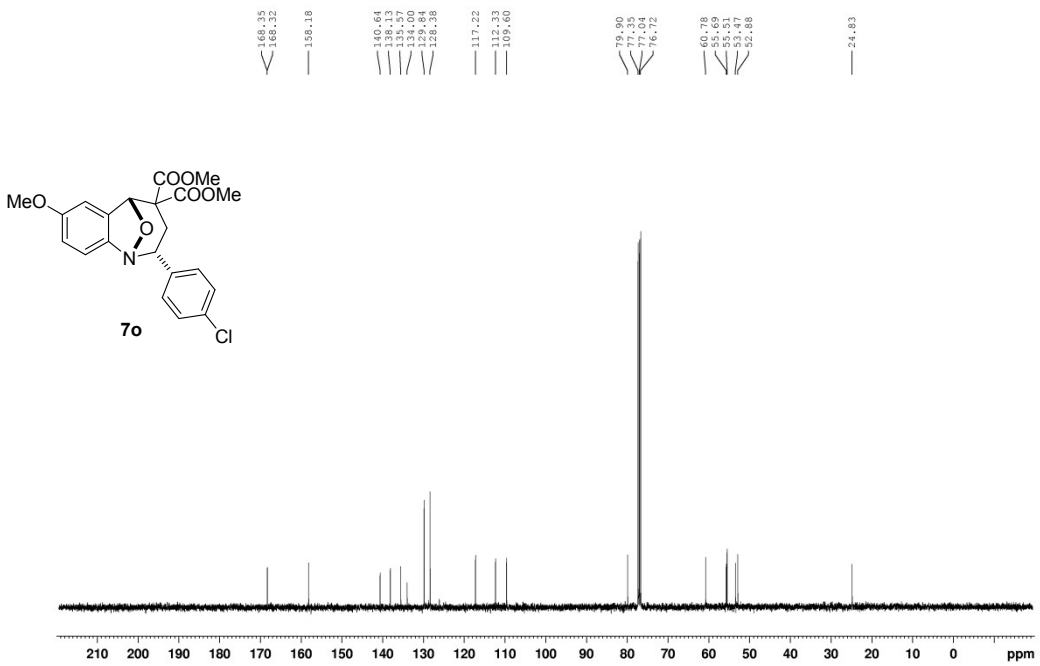
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **7n**



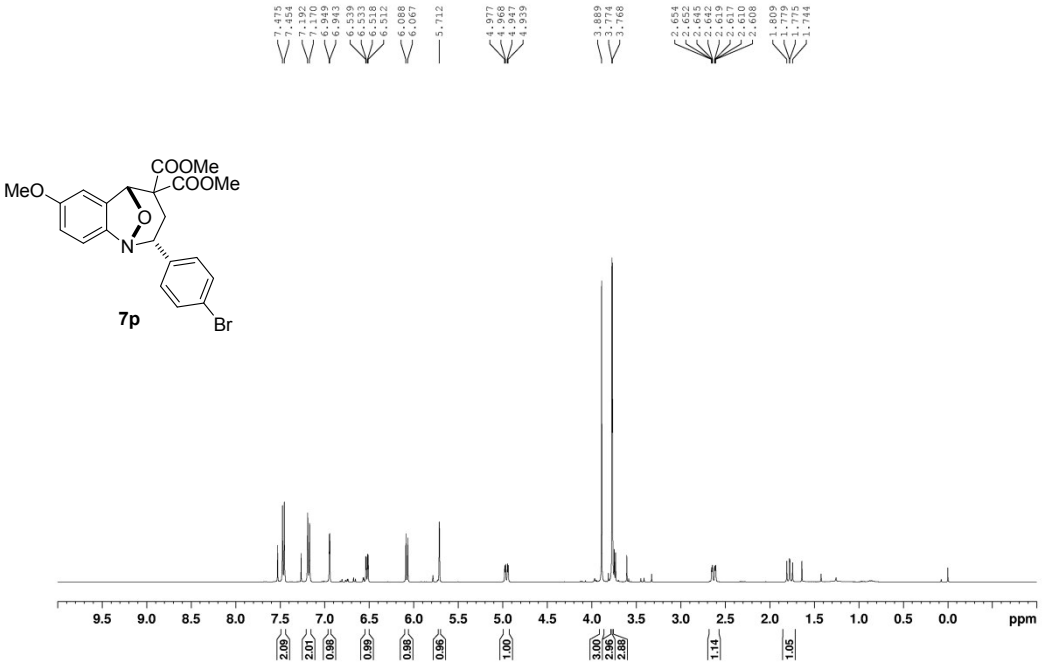
^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **7o**



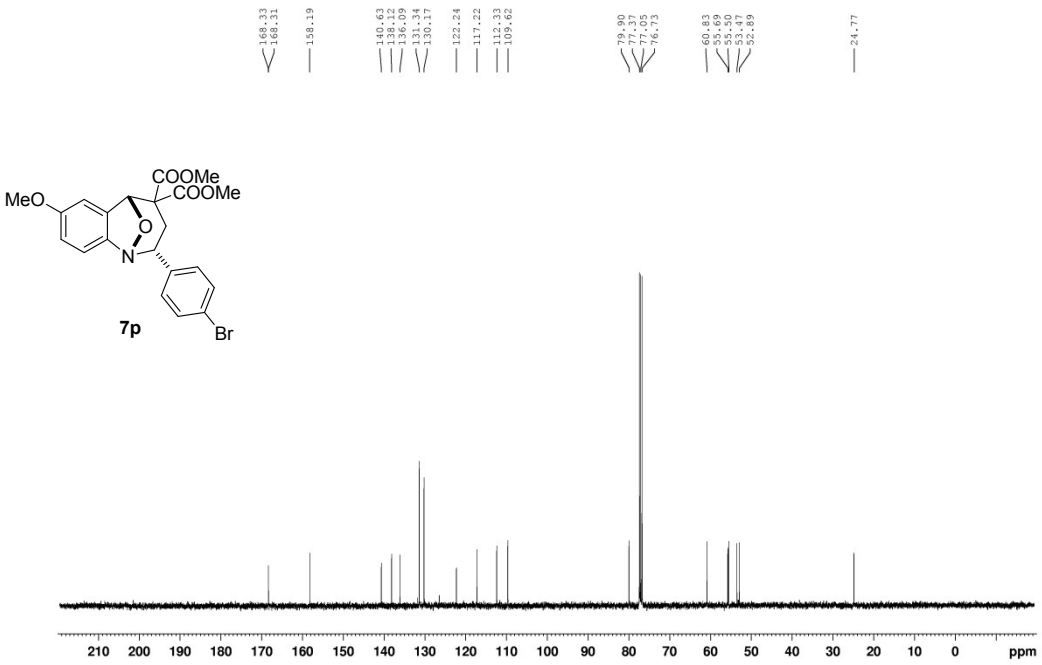
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **7o**



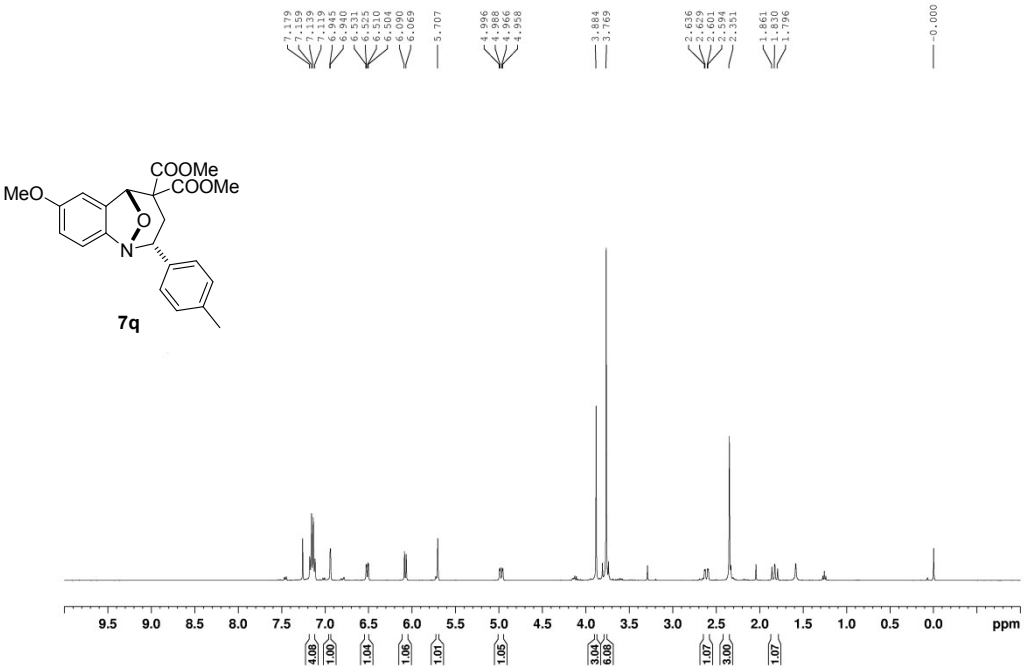
^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **7p**



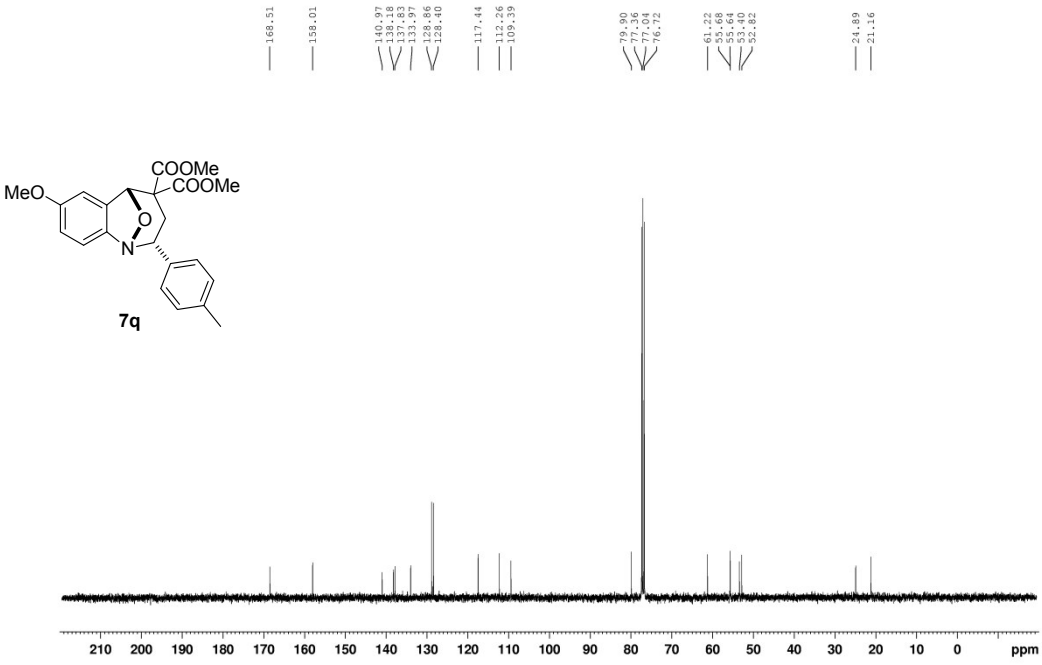
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **7p**



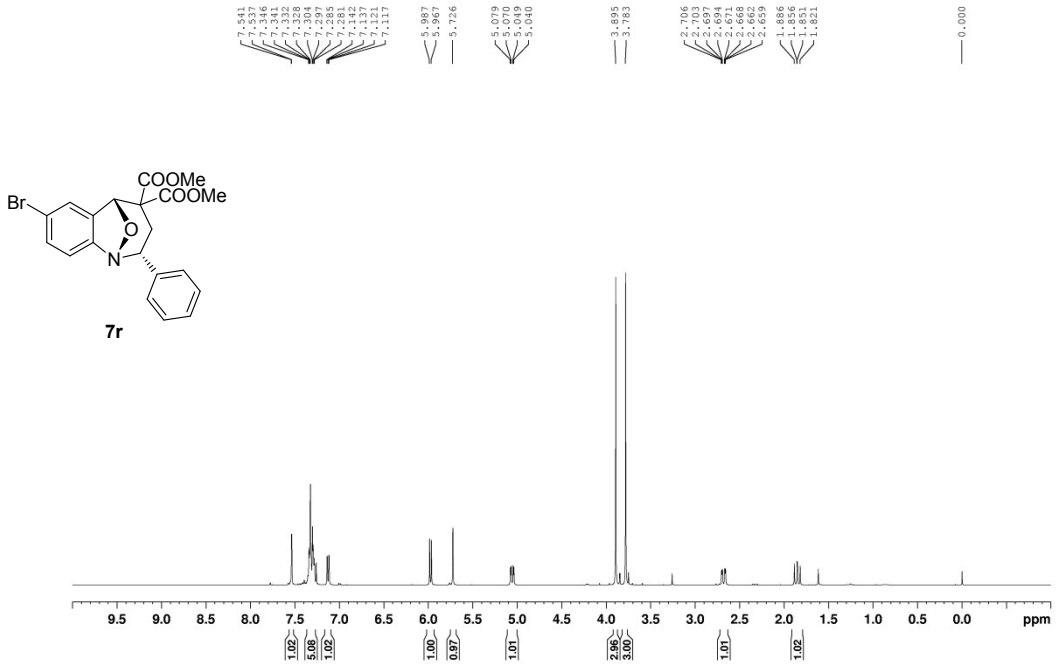
^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **7q**



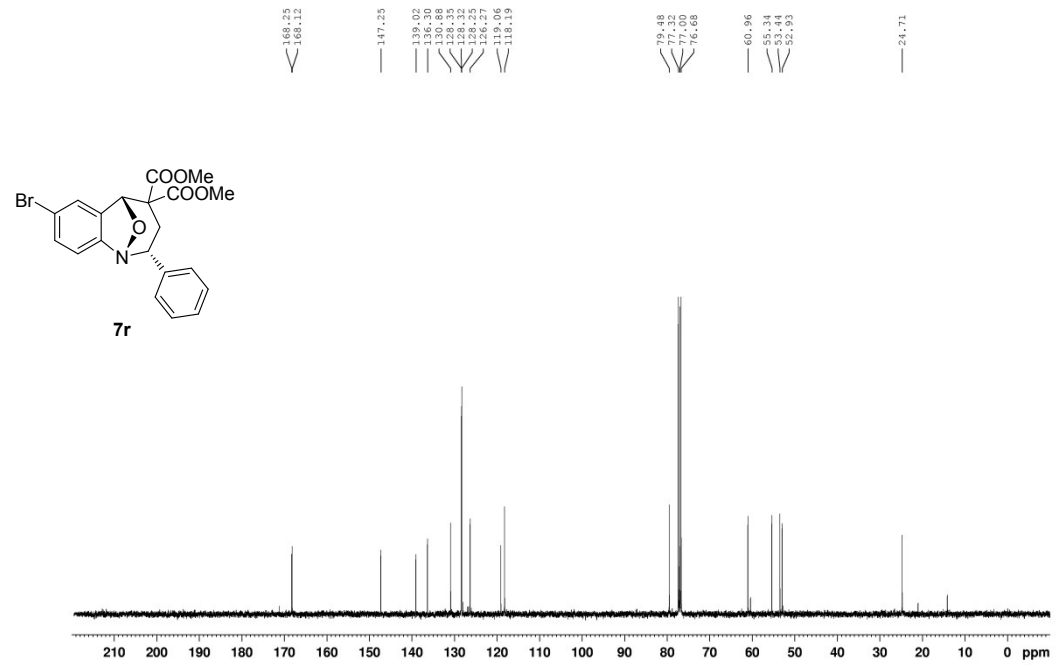
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **7q**



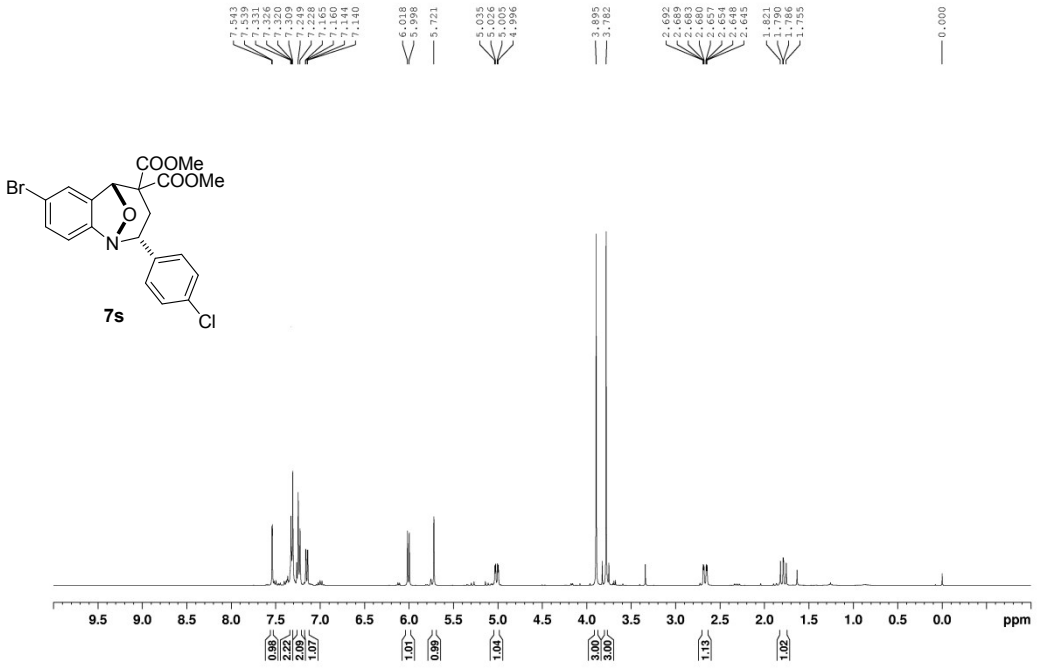
^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **7r**



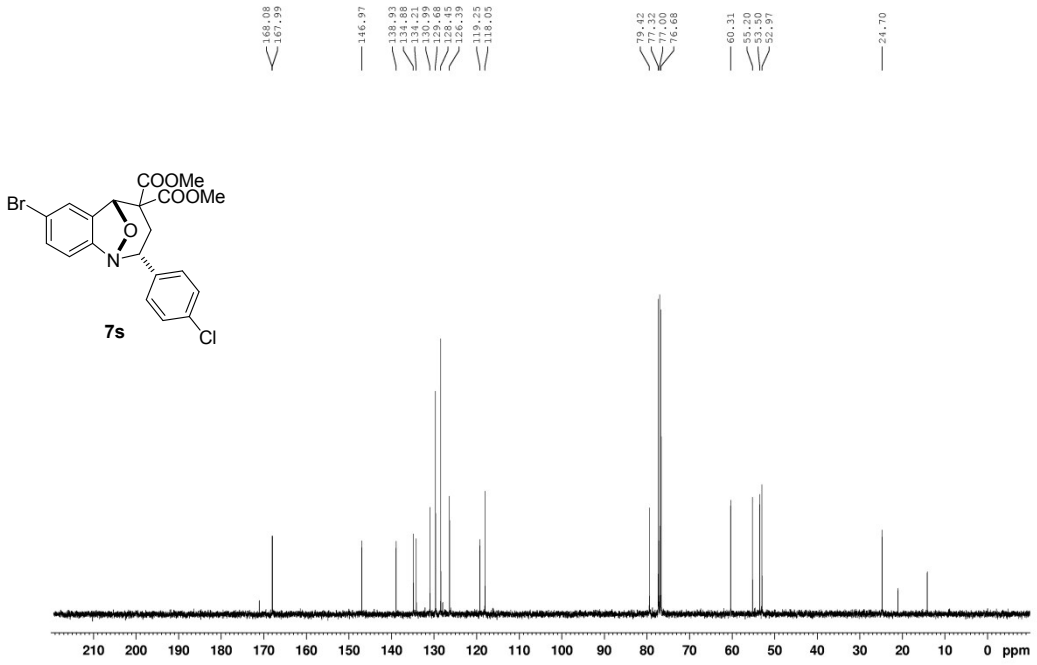
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **7r**



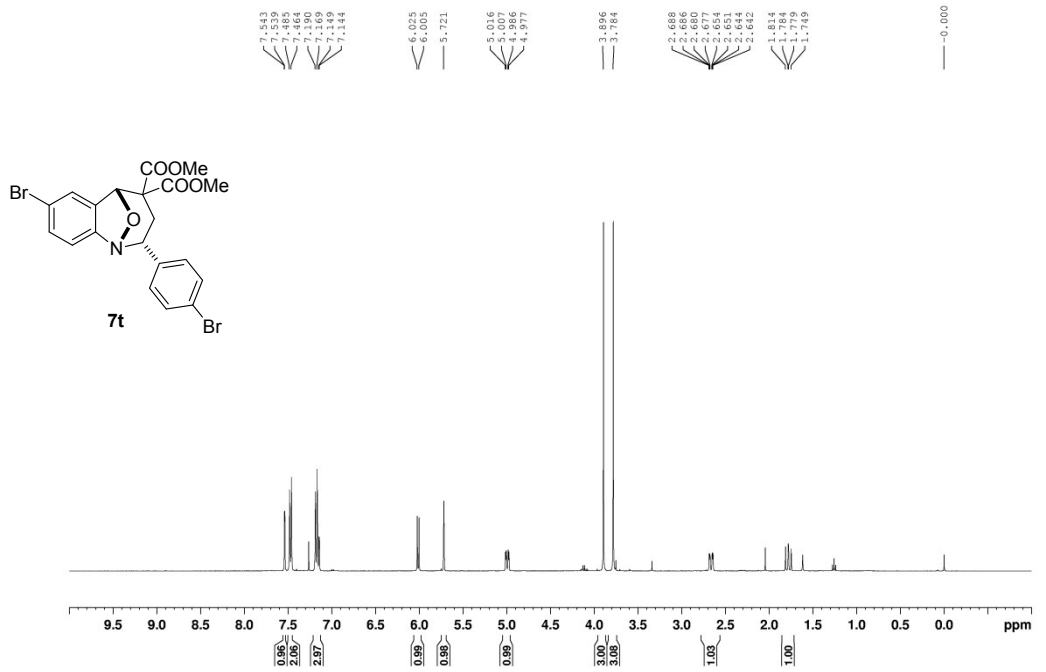
^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **7s**



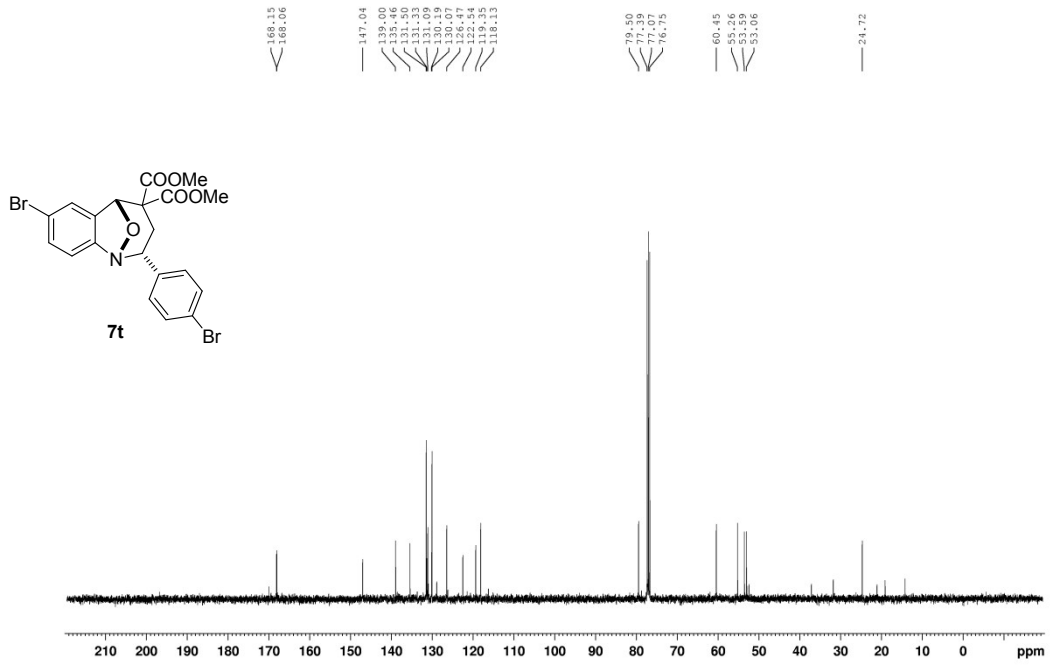
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **7s**



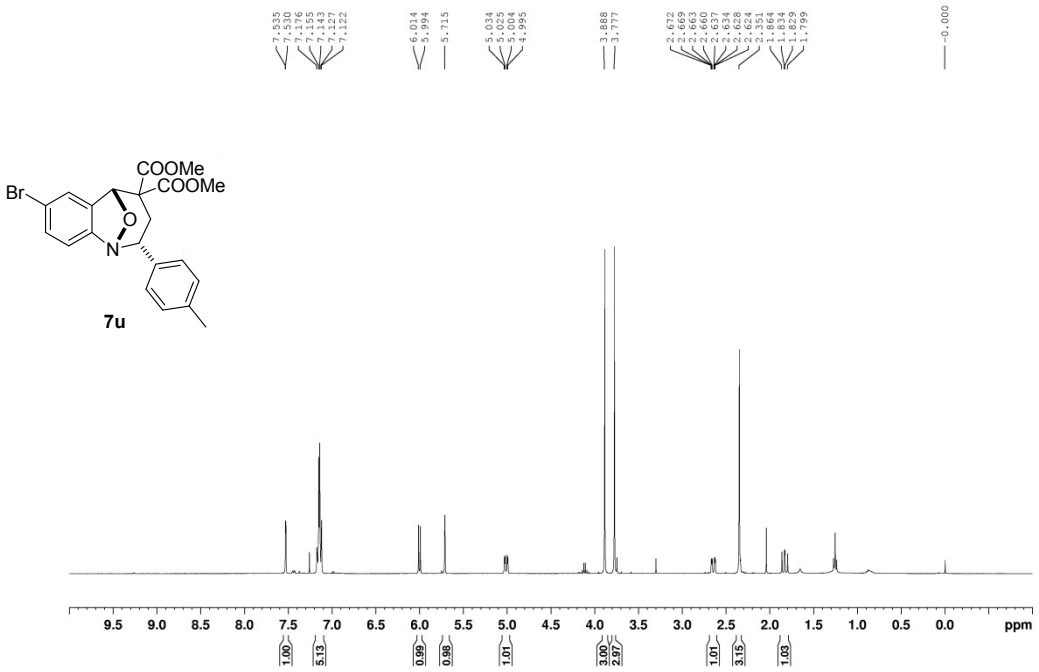
^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **7t**



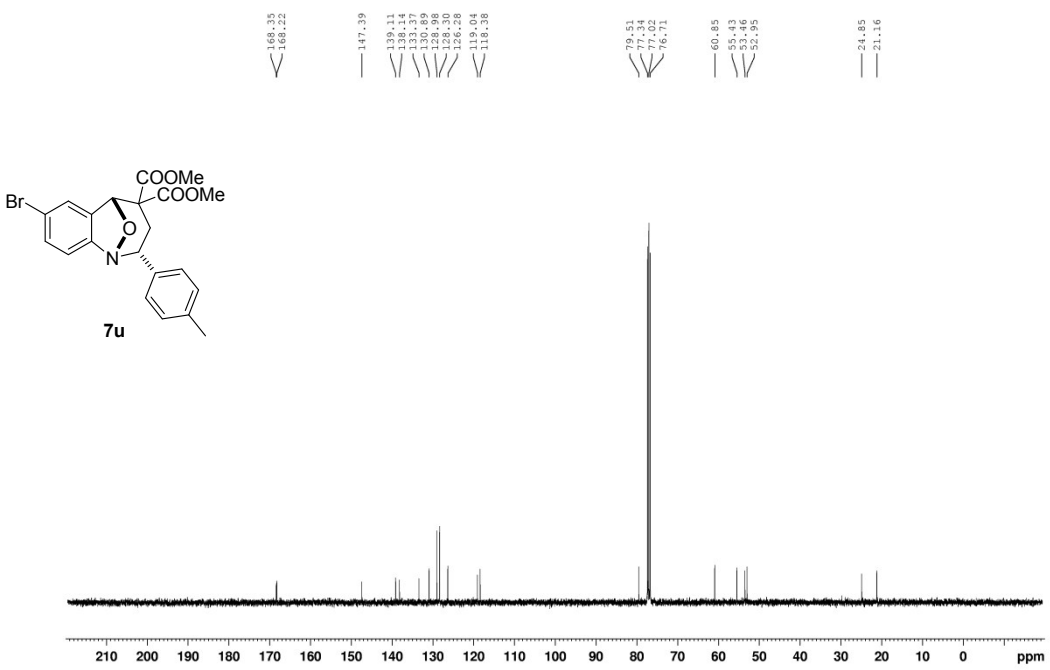
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **7t**



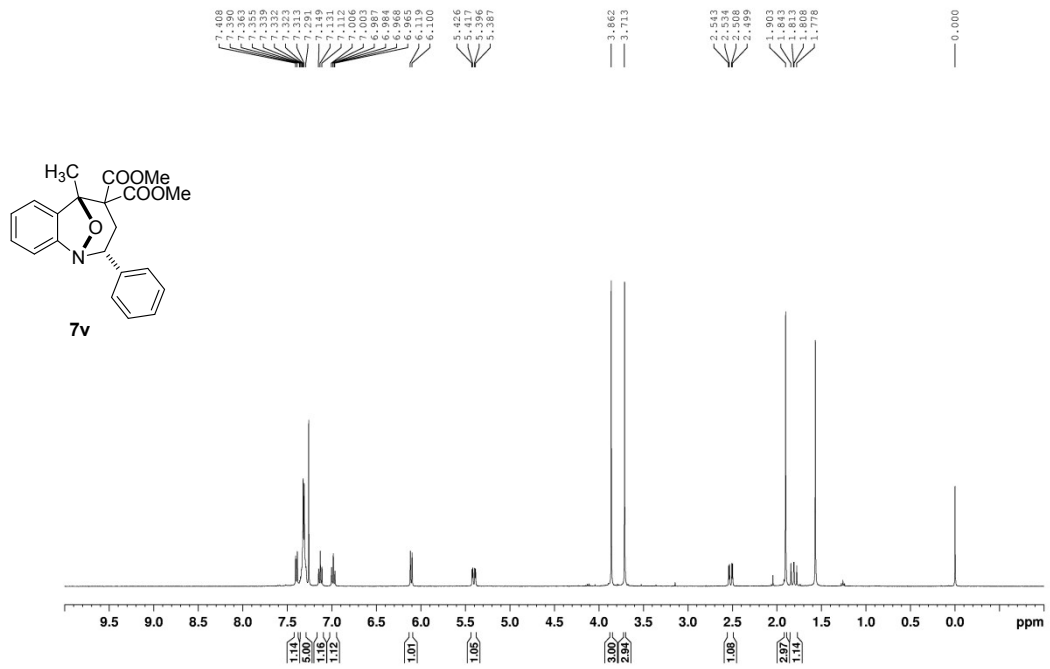
^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **7u**



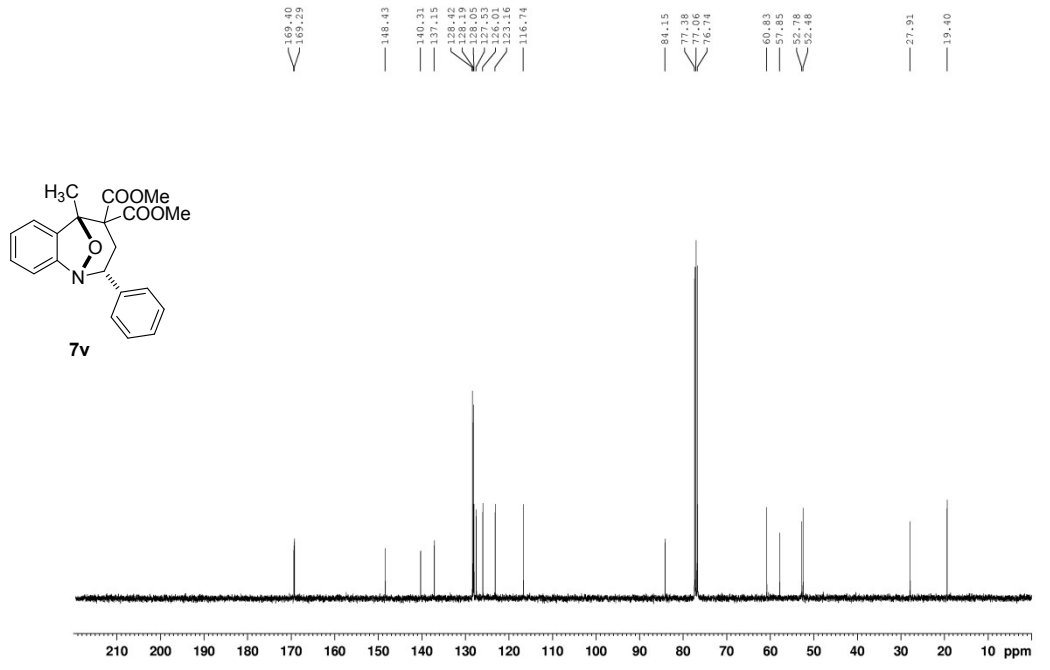
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **7u**



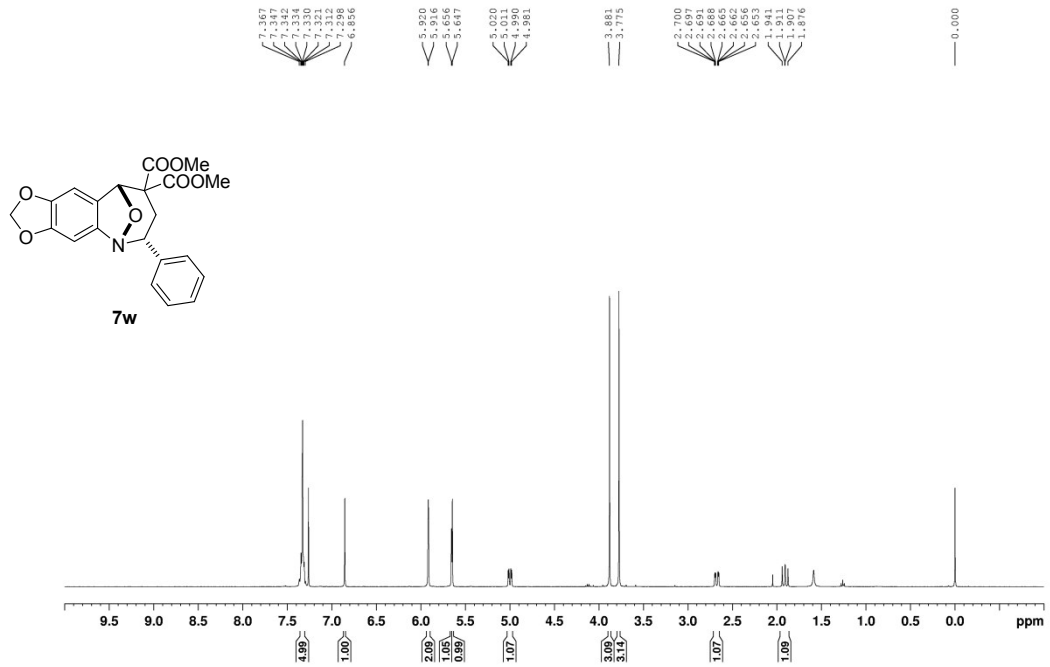
^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **7v**



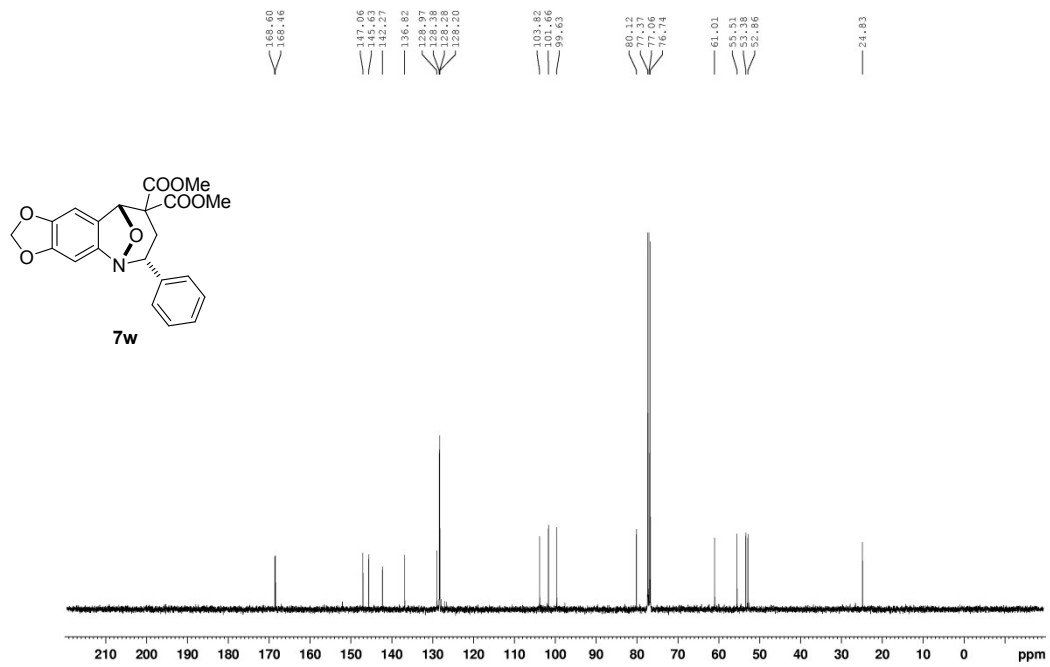
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **7v**



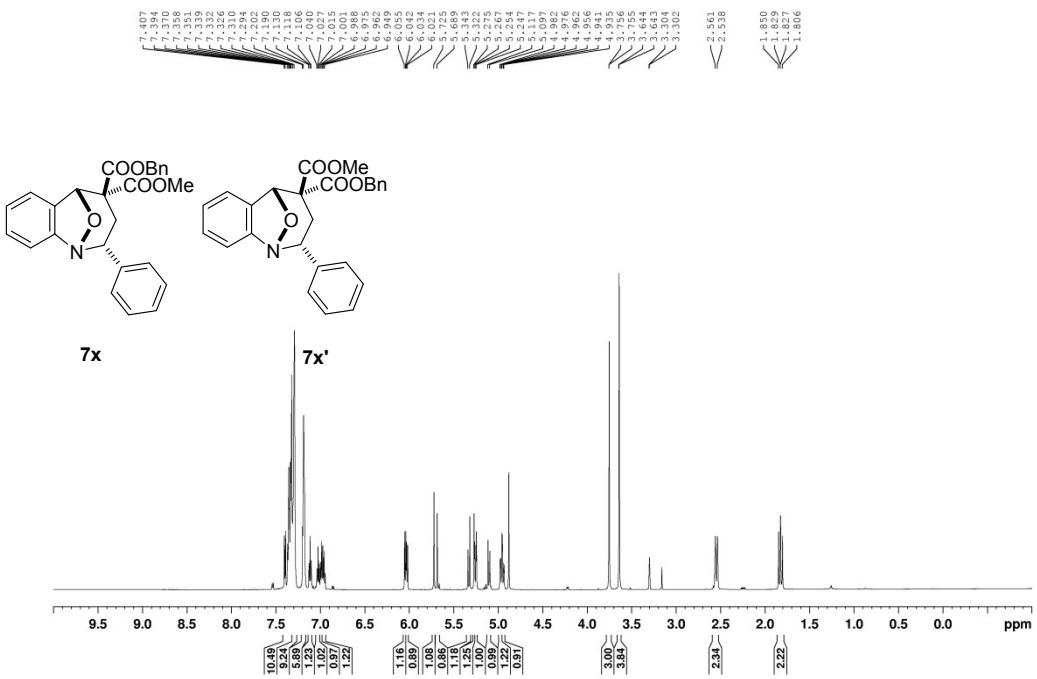
^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **7w**



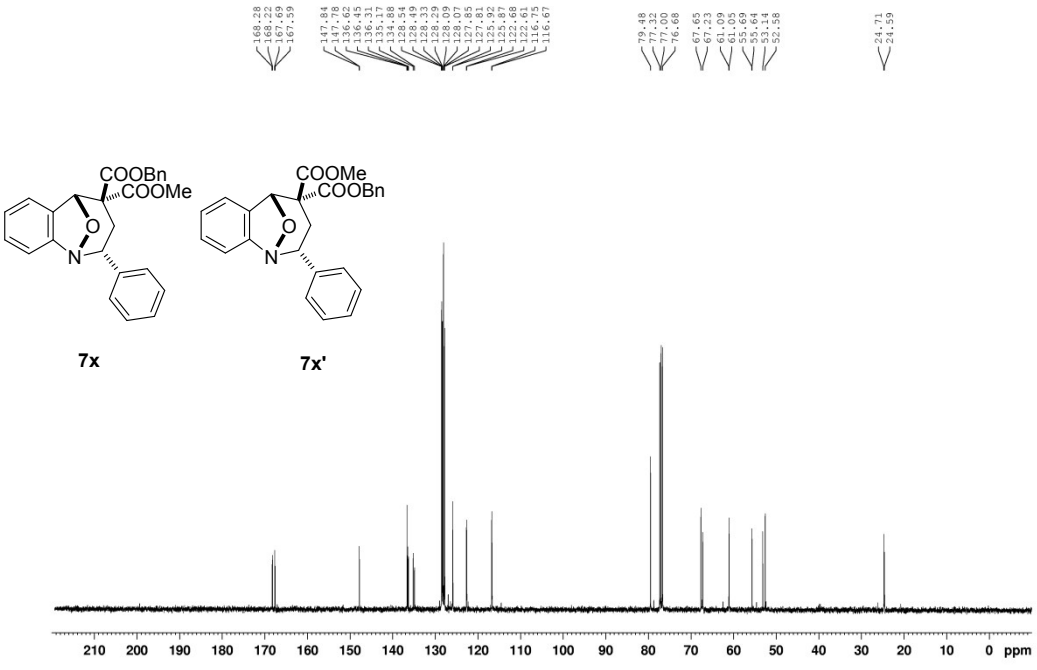
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **7w**



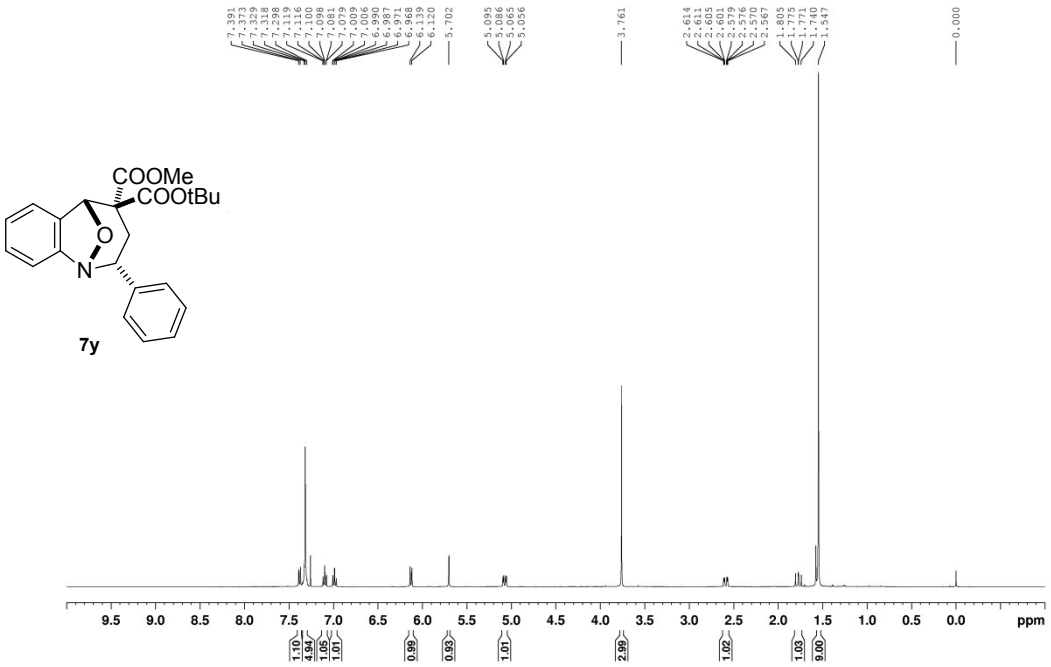
^{1}H-NMR **(**600 MHz, CD_3OD) spectra of the mixture of **7x** and **7x'**



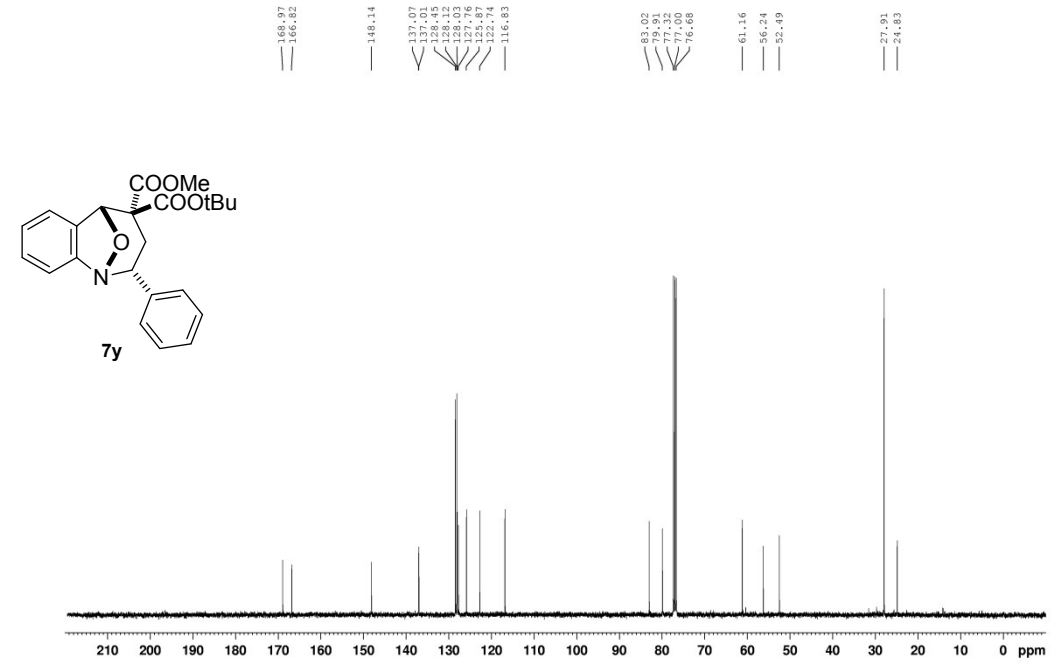
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of the mixture of **7x** and **7x'**



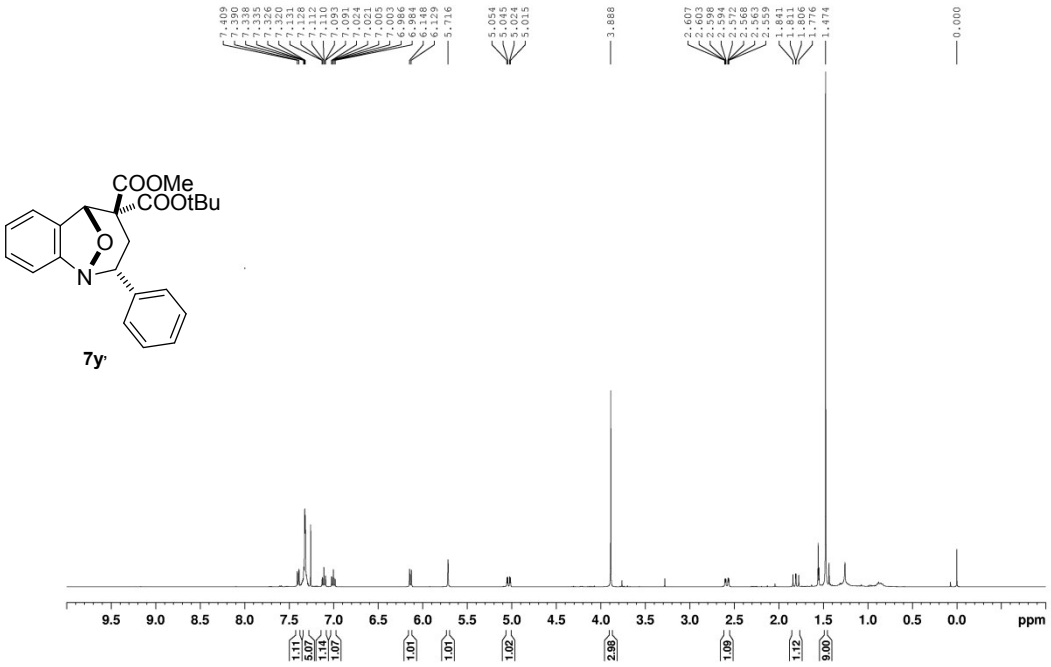
^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **7y**



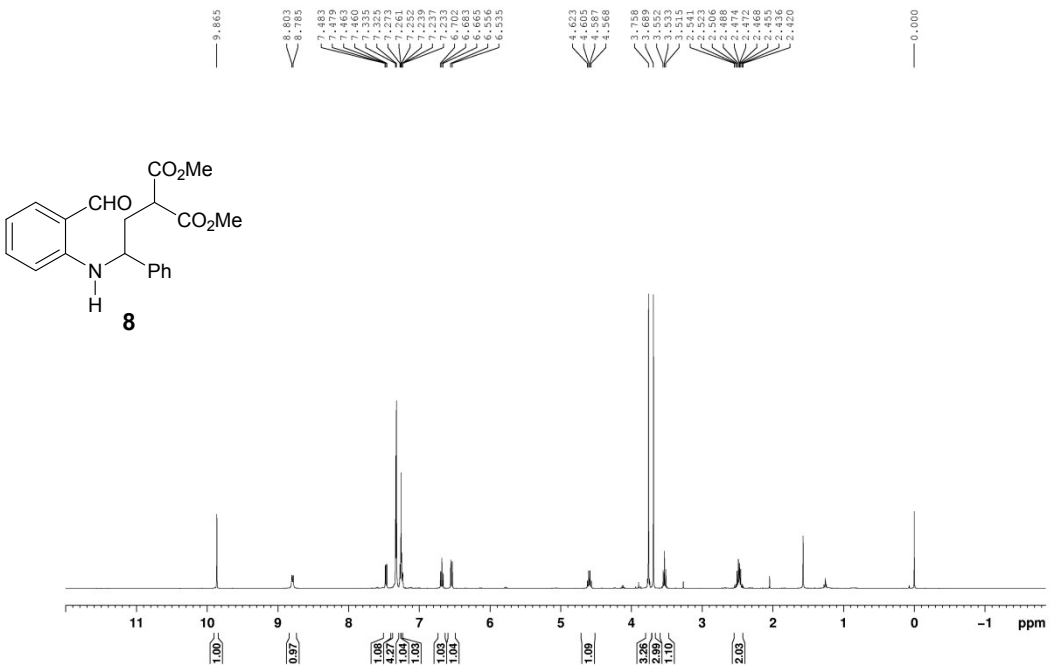
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **7y**



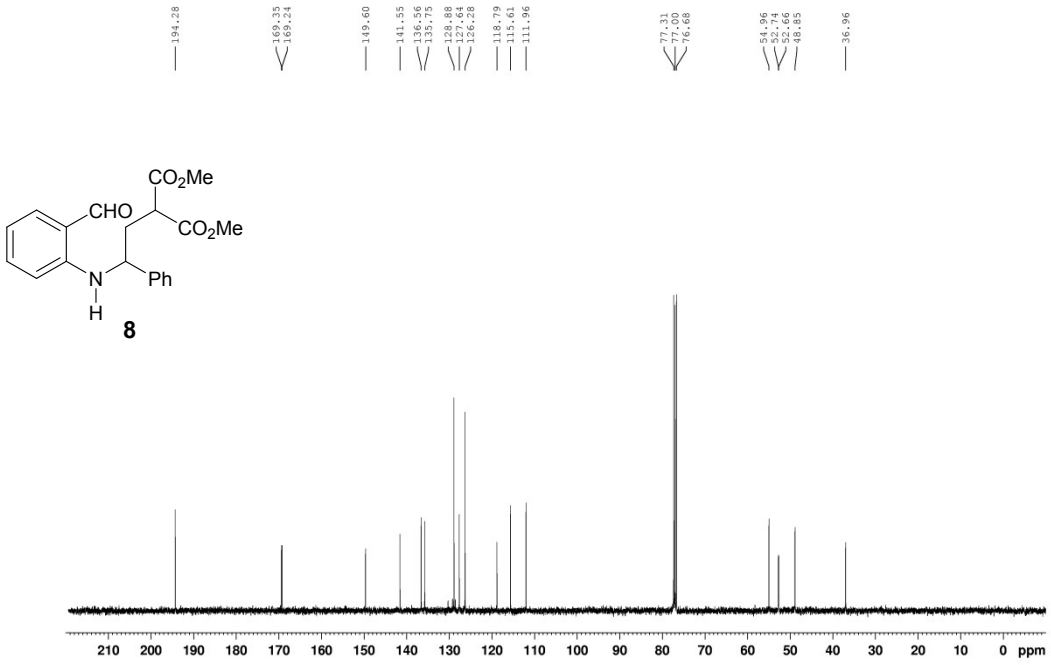
^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **7y**,



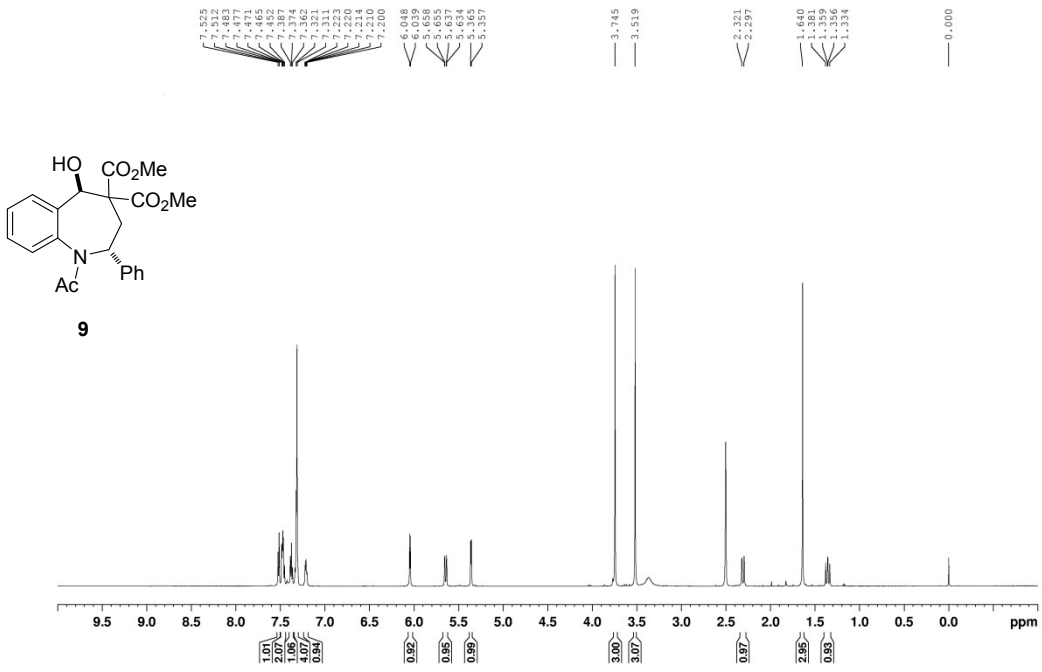
^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **8**



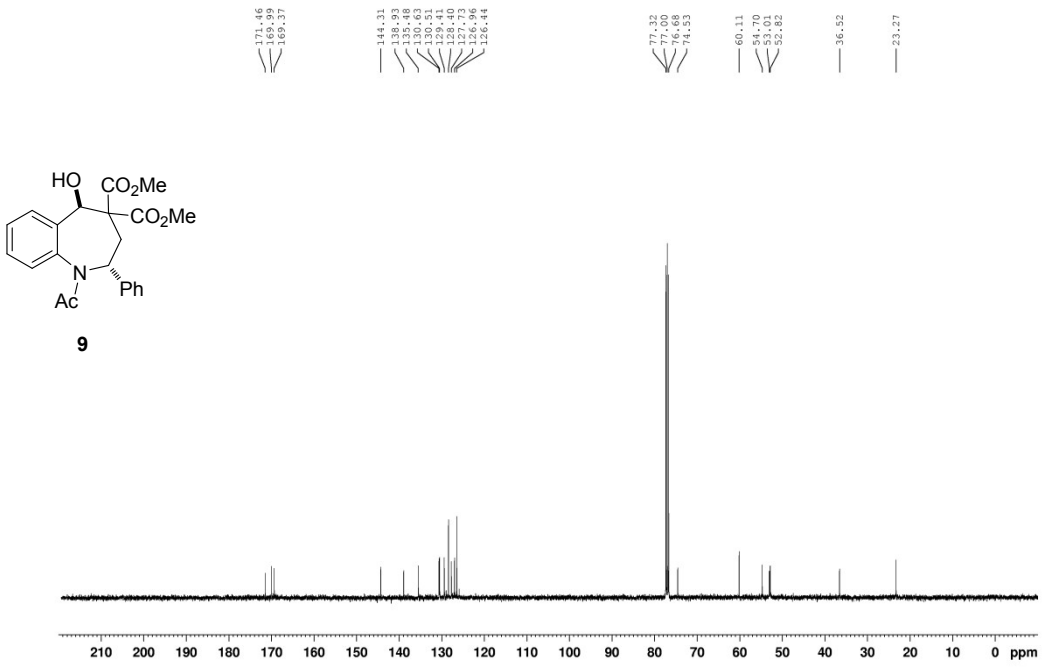
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **8**



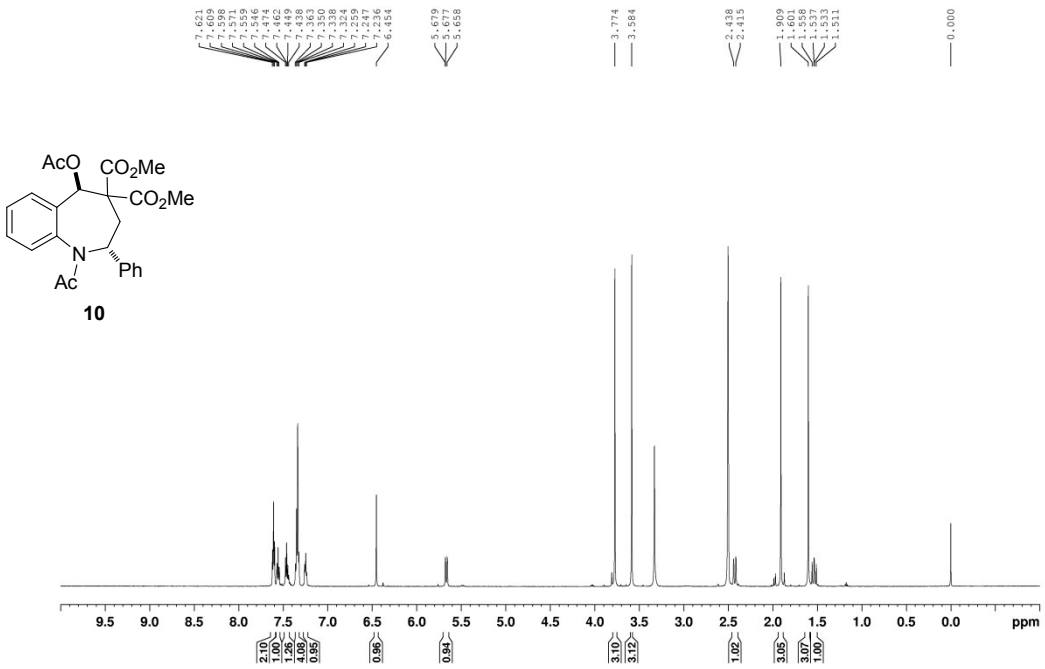
^{1}H-NMR **(**600 MHz, DMSO-d_6) spectra of compound **9**



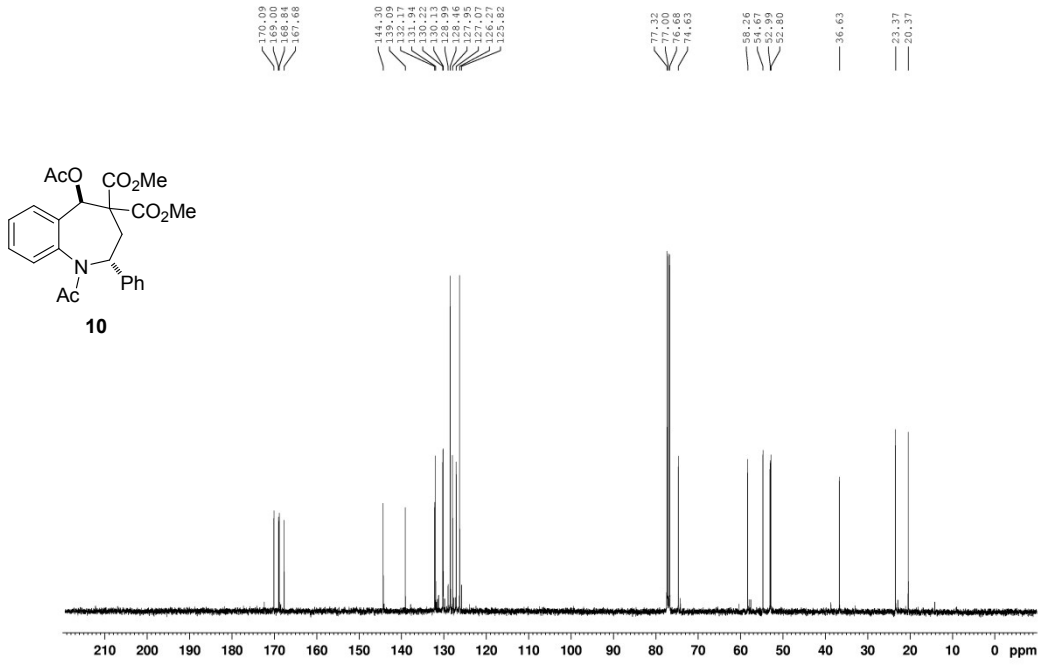
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **9**



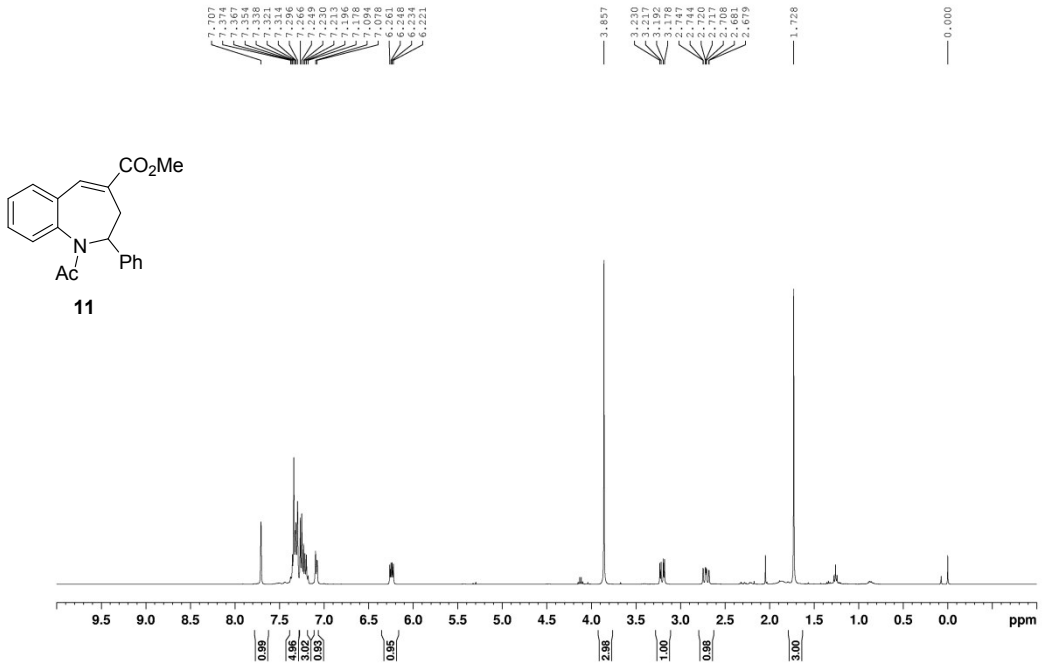
^{1}H-NMR **(**600 MHz, DMSO-d_6) spectra of compound **10**



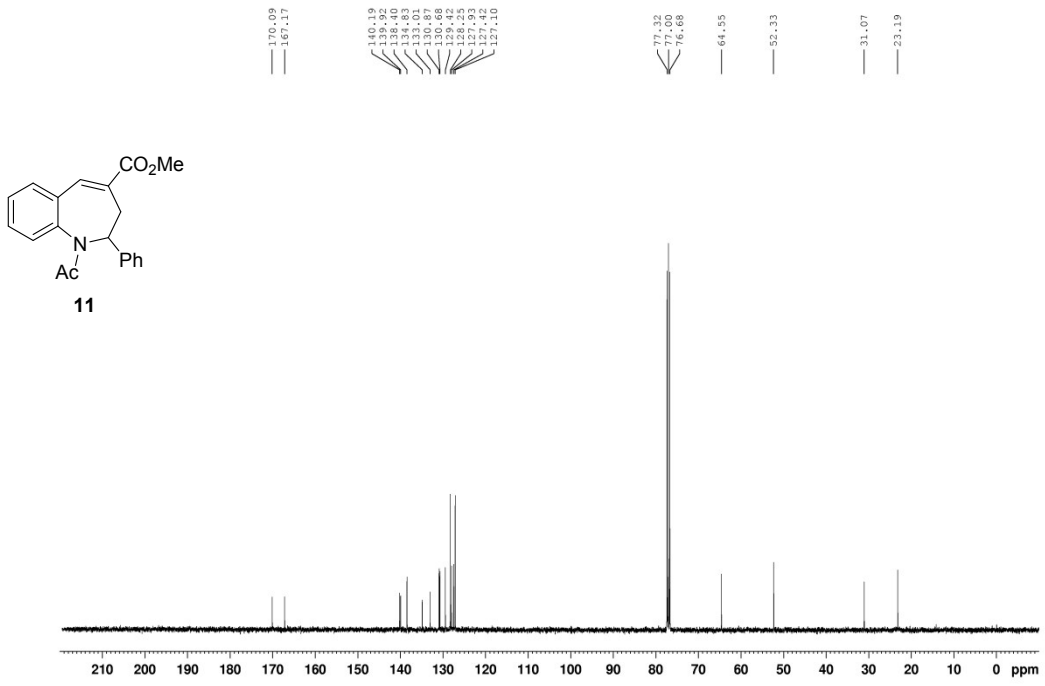
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **10**



^{1}H-NMR (400 MHz, $CDCl_3$) spectra of compound **11**

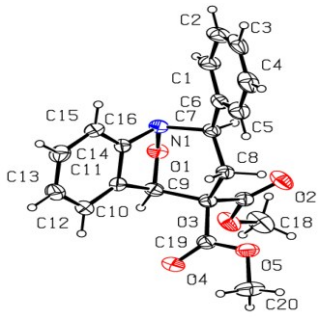


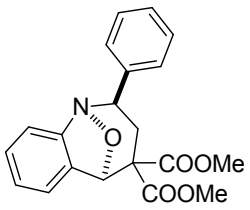
^{13}C-NMR (100 MHz, $CDCl_3$) spectra of compound **11**



5. X-ray crystallographic data

X-ray Crystallographic Data of Compound 7a





CCDC 1540957

Bond precision:	C-C = 0.0047 A	Wavelength=0.71073	
Cell:	a=16.8611(8)	b=7.7647(3)	c=27.0984(13)
	alpha=90	beta=98.764(5)	gamma=90
Temperature:	293 K		
	Calculated	Reported	
Volume	3506.3(3)	3506.3(3)	
Space group	P 2/n	P 1 2/n 1	
Hall group	-P 2yac	-P 2yac	
Moiety formula	$C_{20}H_{19}NO_5$	$C_{20}H_{19}NO_5$	
Sum formula	$C_{20}H_{19}NO_5$	$C_{20}H_{19}NO_5$	
Mr	353.36	353.36	
Dx,g cm^{-3}	1.339	1.339	
Z	8	8	
Mu (mm^{-1})	0.097	0.097	
F000	1488.0	1488.0	
F000’	1488.80		
h, k, lmax	20, 9, 33	20, 9, 33	
Nref	6924	6901	
Tmin,Tmax	0.980, 0.986	0.914, 1.000	
Tmin’	0.980		

Correction method= # Reported T Limits: Tmin= 0.914 Tmax= 1.000

AbsCorr = MULTI-SCAN

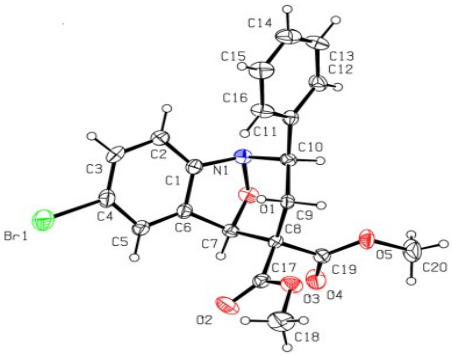
Data completeness= 0.997 Theta(max)= 26.020

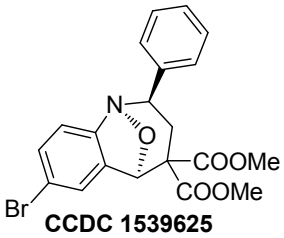
R(reflections)= 0.0660(3855) wR2(reflections)= 0.1784(6901)

S = 1.009 Npar= 473

Displacement ellipsoids are drawn at 30% probability level

X-ray Crystallographic Data of Compound 7r





CCDC 1539625

Bond precision:	C-C = 0.0082 A		Wavelength=0.71073
Cell:	a=6.8280(3)	b=11.7422(5)	c=23.4879(10)
	alpha=90	beta=90	gamma=90
Temperature:	293 K		
	Calculated		Reported
Volume	1883.16(14)		1883.16(13)
Space group	P 21 21 21		P 21 21 21
Hall group	P 2ac 2ab		P 2ac 2ab
Moiety formula	$C_{20}H_{18}BrNO_5$		$C_{20}H_{18}BrNO_5$
Sum formula	$C_{20}H_{18}BrNO_5$		$C_{20}H_{18}BrNO_5$
Mr	432.25		432.26
Dx,g cm^{-3}	1.525		1.525
Z	4		4
Mu (mm^{-1})	2.214		2.214
F000	880.0		880.0
F000’	879.27		
h, k, lmax	8, 14, 28		8, 14, 28
Nref	3715[2155]		3367
Tmin,Tmax	0.643, 0.733		0.736, 1.000
Tmin’	0.608		

Correction method= # Reported T Limits: Tmin= 0.736 Tmax= 1.000

AbsCorr = MULTI-SCAN

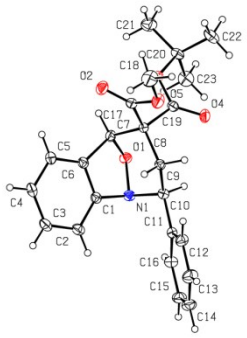
Data completeness= 1.56/0.91 Theta(max)= 26.022

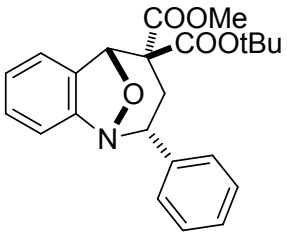
R(reflections)= 0.0513(2403) wR2(reflections)= 0.1013(3367)

S = 1.049 Npar= 246

Displacement ellipsoids are drawn at 30% probability level

X-ray Crystallographic Data of Compound 7y





CCDC 1559038

Bond precision:	C-C = 0.0036 A	Wavelength=0.71073	
Cell:	a=11.8383(9)	b=13.1551(10)	c=13.6364(10)
	alpha=78.762(7)	beta=85.450(6)	gamma=89.969(6)
Temperature:	173 K		
	Calculated	Reported	
Volume	2076.1(3)	2076.1(3)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	$C_{23}H_{25}NO_5$	$C_{23}H_{25}NO_5$	
Sum formula	$C_{23}H_{25}NO_5$	$C_{23}H_{25}NO_5$	
Mr	395.44	395.44	
Dx,g cm^{-3}	1.265	1.265	
Z	4	4	
Mu (mm^{-1})	0.089	0.089	
F000	840.0	840.0	
F000’	840.43		
h, k, lmax	14, 16, 16	14, 16, 16	
Nref	8194	8179	
Tmin,Tmax	0.984, 0.988	0.885, 1.000	
Tmin’	0.981		

Correction method= # Reported T Limits: Tmin= 0.885 Tmax= 1.000

AbsCorr = MULTI-SCAN

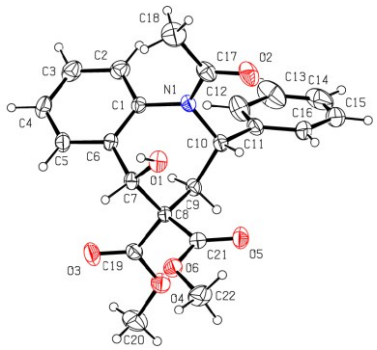
Data completeness= 0.998 Theta(max)= 26.020

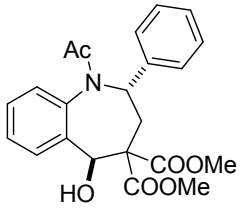
R(reflections)= 0.0599(5444) wR2(reflections)= 0.1546(8179)

S = 1.054 Npar= 531

Displacement ellipsoids are drawn at 30% probability level

X-ray Crystallographic Data of Compound 9





CCDC1540954

Bond precision:	C-C = 0.0037 A		Wavelength=0.71073
Cell:	a=10.9730(4)	b=15.1158(5)	c=25.0975(8)
	alpha=90	beta=90	gamma=90
Temperature:	293 K		
	Calculated		Reported
Volume	4162.8(2)		4162.8(2)
Space group	P b c a		P b c a
Hall group	-P 2ac 2ab		-P 2ac 2ab
Moiety formula	$C_{22}H_{23}NO_6$		$C_{22}H_{23}NO_6$
Sum formula	$C_{22}H_{23}NO_6$		$C_{22}H_{23}NO_6$
Mr	397.41		397.41
Dx,g cm^{-3}	1.268		1.268
Z	8		8
Mu (mm^{-1})	0.093		0.093
F000	1680.0		1680.0
F000’	1680.92		
h, k, lmax	13, 18, 30		13, 18, 30
Nref	4105		4097
Tmin,Tmax	0.976, 0.983		0.741, 1.000
Tmin’	0.976		

Correction method= # Reported T Limits: Tmin= 0.741 Tmax= 1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.998 Theta(max)= 26.020

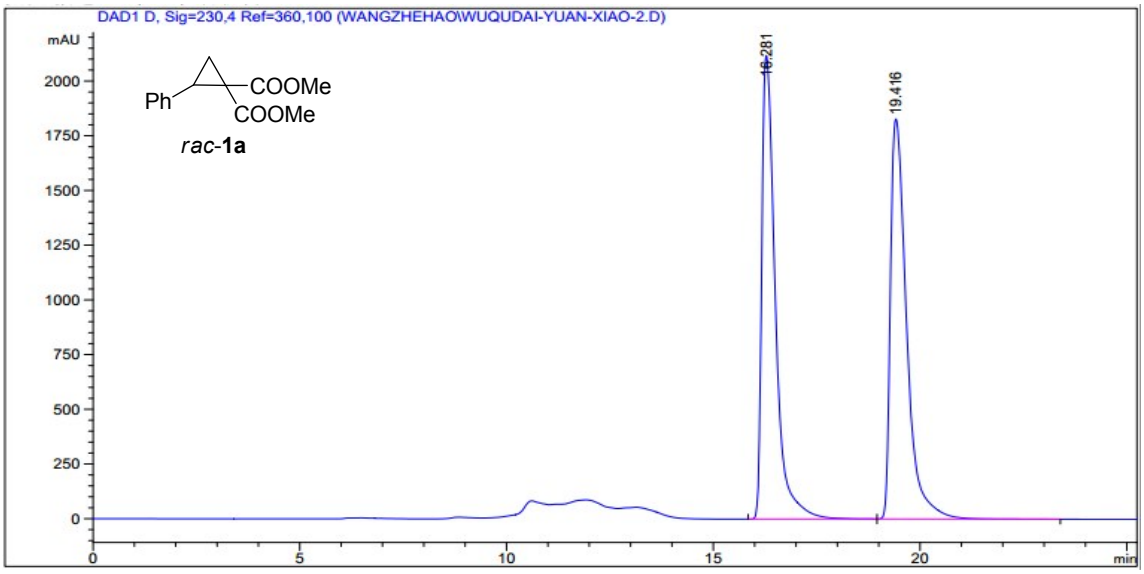
R(reflections)= 0.0562(2441) wR2(reflections)= 0.1458(4097)

S = 1.066 Npar= 266

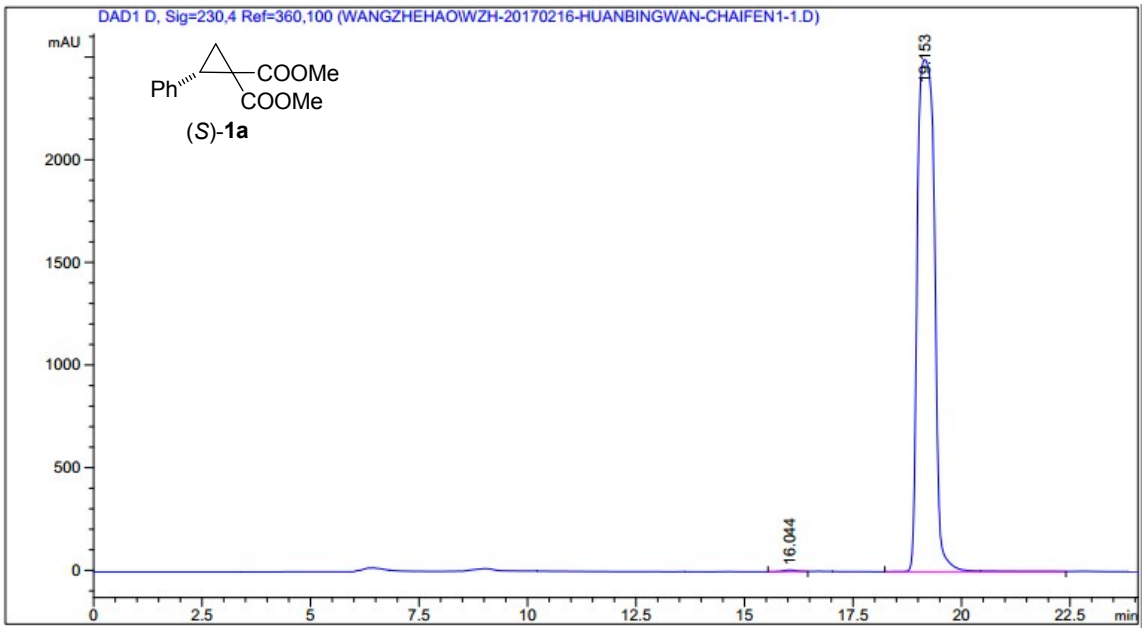
Displacement ellipsoids are drawn at 30% probability level

6. Chiral HPLC chromatograms

Chiral HPLC chromatogram of (*S*)-**1a**

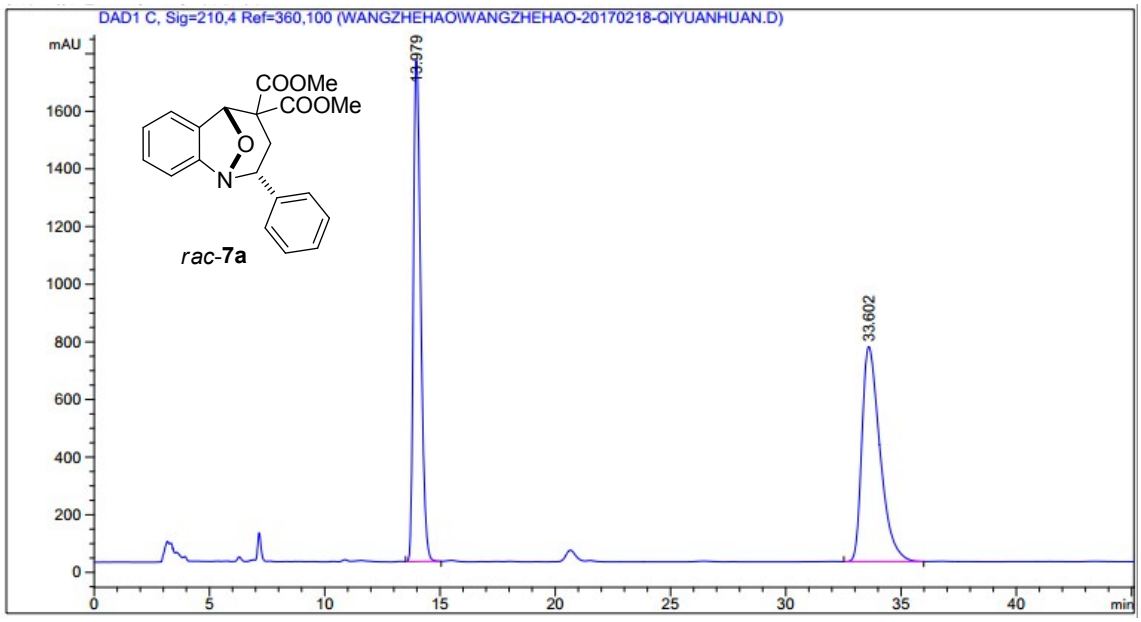


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Area (%)	Peak Height (mAU)
1	DAD 230.4 nm	16.281	4.80383e4	49.26	2118
2	DAD 230.4 nm	19.416	4.94755e4	50.74	1828

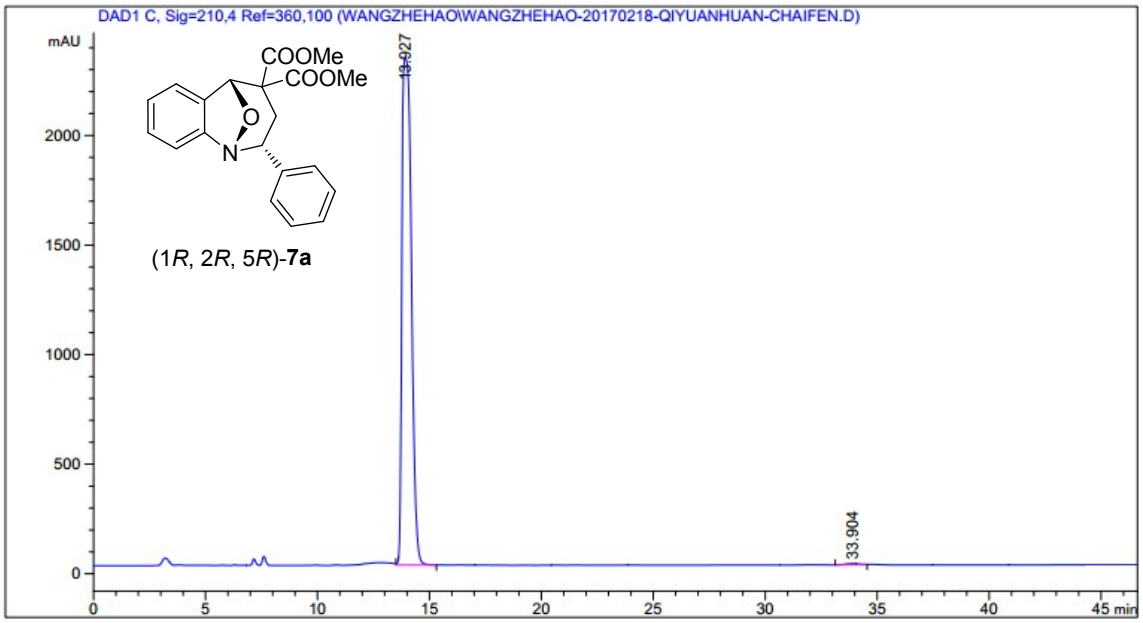


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Area (%)	Peak Height (mAU)
1	DAD 230.4 nm	16.044	148.80299	0.22	7
2	DAD 230.4 nm	19.153	6.79036e4	99.78	2495

Chiral HPLC chromatogram of (1*R*, 2*R*, 5*R*)-**7a**

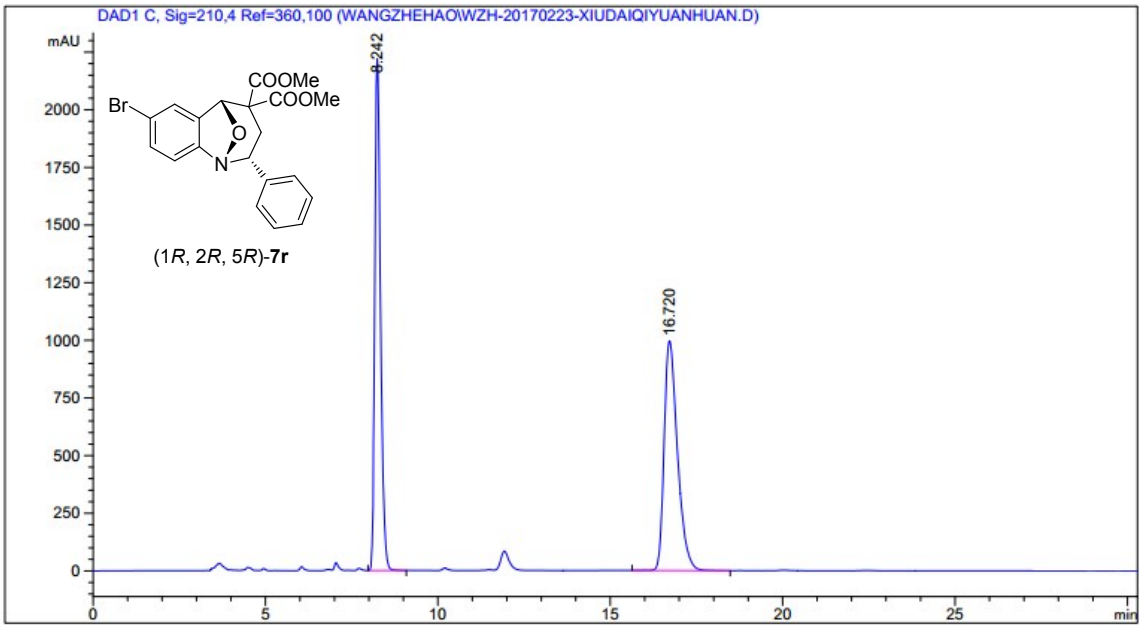


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Area (%)	Peak Height (mAU)
1	DAD 210.4 nm	13.979	3.81461e4	48.43	1739
2	DAD 210.4 nm	33.602	4.06175e4	51.57	746

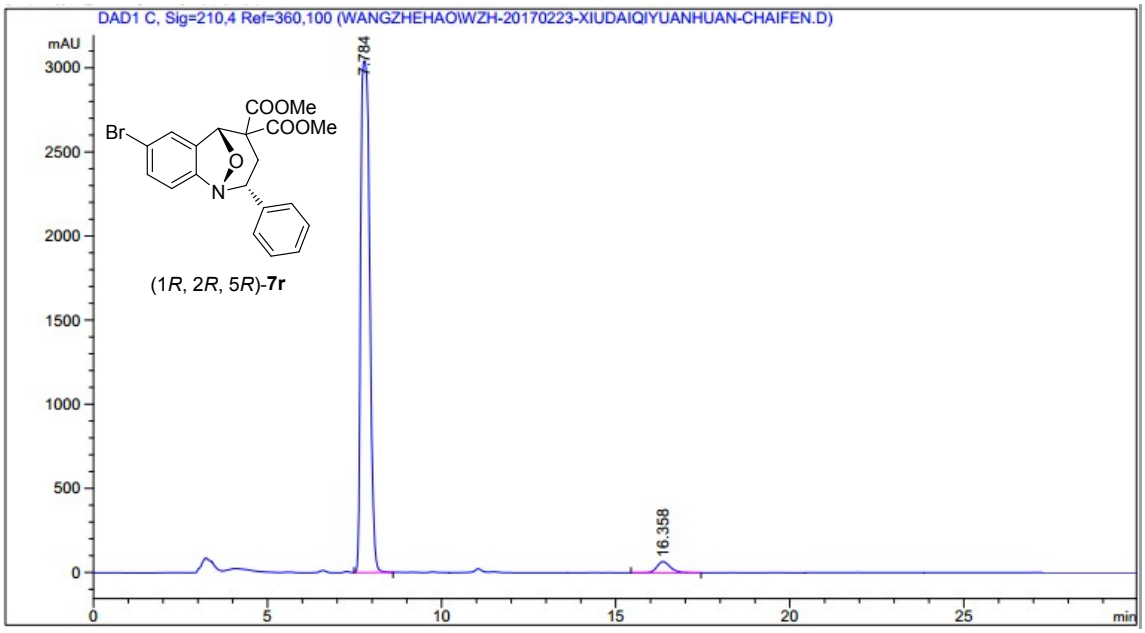


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Area (%)	Peak Height (mAU)
1	DAD 210.4 nm	13.927	6.74633e4	99.71	2313
2	DAD 210.4 nm	33.904	198.21735	0.29	5

Chiral HPLC chromatogram of (1*R*, 2*R*, 5*R*)-**7r**



Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Area (%)	Peak Height (mAU)
1	DAD 210.4 nm	8.242	2.57073e4	49.04	2222
2	DAD 210.4 nm	16.720	2.67155e4	50.96	997



Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Area (%)	Peak Height (mAU)
1	DAD 210.4 nm	7.784	5.41861e4	96.84	3042
2	DAD 210.4 nm	16.358	1767.09070	3.16	66