Electronic Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

Atroposelective [2+2+2] Cycloadditions Catalyzed by a Rhodium/Chiral Phosphate System

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Table of content

General experimental methods: ^{1}H NMR spectra were recorded at 400 MHz or 300 MHz and data are reported as follows: chemical shift in ppm from tetramethylsilane with the solvent as an internal indicator ($CDCl_3$ δ 7.26 ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, or overlap of non-equivalent resonances), integration, coupling constant if relevant. ^{13}C NMR spectra were recorded at 100 MHz or 75 MHz and data are reported as follows: chemical shift in ppm from tetramethylsilane with the solvent as an internal indicator ($CDCl_3$ δ 77.00 ppm), multiplicity. Glassware was oven-dried prior to use. All reactions were carried out under an argon atmosphere. [2+2+2] reactions were run using standard schlenk techniques if hydrogenation is required; or in a microwave-type vessel, equipped with a stirring bar and sealed in a glove box with a septum-cap (Biotage, n°354905) if not. $[Rh(cod)Cl]_2$ was purchased from Strem Chemicals® and stocked in a glove boxe. CH_2Cl_2 and 1,2-dichloroethane were distilled from CaH_2. Other reagents were obtained from commercial suppliers and used as received. TLC were performed on Merck 60 F254 silica gel plates visualized either with a UV lamp (254 nm), or using a solution of $KMnO_4$–K_2CO_3 in water followed by heating. Flash chromatography was performed on Merck Geduran SI 60 Å silica gel (40-63 µm). Infra-red spectra were measured using Tensor 27 (ATR diamond) Bruker spectrometer. IR data are reported as characteristic bands (cm^{-1}). The melting points were recorded with a SMP3 Stuart Scientific melting point apparatus. High Resolution Mass Spectra were performed by the Institut de Chimie Moléculaire (FR2769), Université Pierre et Marie Curie (Paris 6) (electrospray source). Enantioselective excess were determined using an HPLC *Waters 1525* analysis with a chiral stationary phase column (Daicel CHIRALPAK AD-H or AS-H) coupled to a UV-detector, with a mixture of *n*-hexanes and isopropanol as the mobile phase. Optical rotations were measured using a Perkin–Elmer 341 polarimeter or a Jasco P-2000 polarimeter.

1. Preparation of the starting material

Diynes **1a**,[1] **1b**,[2] **1c**,[3] **1d**[4] and **1e**[5] have already been described in the literature. Isocyanates **2** are commercially available.

2. [2+2+2] cycloaddition reaction

Pyridones **3aa**, **3ba**, **3bc**, **3be**, **3bg** and **3da** have already been described in the literature.[6]

General procedure 1: preparation of racemic pyridones 3: Using classical schlenk techniques, $[Rh(cod)Cl]_2$ (2.5 mg, 5.0 µmol, 0.025 eq), *rac*-2,2'-bis(diphenylphosphino)-1,1′-binaphthyl (6.2 mg,

[1] K. Tanaka, K. Takeishi, K. Noguchi, *J. Am. Chem. Soc.*, 2006, **128**, 4586.
[2] R. S. Atkinson, M. J. Grimshire, *J. Chem. Soc., Perkin Trans 1*, 1986, 1215.
[3] J. Louie, J. E. Gibby, M. V. Farnworth, T. N. Tekavec, *J. Am. Chem. Soc.*, 2002, **124,** 15188.
[4] M. Nishida, H. Shiga, M. Mori, *J. Org. Chem.*, 1998, **63**, 8606.
[5] Y. Han, C. J. Harlan, P. Stoessel, B. J. Frost, J. R. Norton, S. Miller, B. Bridgewater, Q. Xu, *Inorg. Chem.*, 2001, **40**, 2942.
[6] K. Tanaka, Y. Takahashi, T. Suda, M. Hirano, *Synlett*, 2008, 1724.

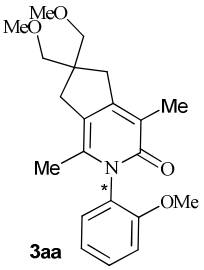
10.0 µmol, 0.05 eq) and $AgBF_4$ (1.9 mg, 10.0 µmol, 0.05 eq) were dissolved in CH_2Cl_2 (1 mL) and stirred for 5 min at rt. The resulting solution was then stirred under H_2 atmosphere (1 atm, rt) for 1 h, then concentrated to dryness at the vacuum-line. The residue was dissolved in CH_2Cl_2 (1 mL) under Ar and a solution of diyne **1** (0.20 mmol, 1 eq) and isocyanate **2** (0.22 mmol, 1.1 eq) in CH_2Cl_2 (1 mL) was added. After stirring at rt for 18 h, the resulting reaction mixture was concentrated under vacuum, then purified by flash chromatography on silica gel, using a pentane/EtOAc eluant system, to yield pyridone **3**.

General procedure 2: preparation of enantioenriched pyridones 3 *via* the chiral counter-ion strategy, using a hydrogenation procedure. Using classical schlenk techniques, $[Rh(cod)Cl]_2$ (2.5 mg, 5.0 µmol, 0.025 eq), ligand (10.0 µmol, 0.05 eq) and chiral silver salt **4** (10.0 µmol, 0.05 eq) were dissolved in CH_2Cl_2 (1 mL) and stirred for 5 min at rt. The resulting solution was then stirred under H_2 atmosphere (1 atm, rt) for 1 h, then concentrated to dryness at the vacuum-line. The residue was dissolved in CH_2Cl_2 (1 mL) under Ar and a solution of diyne **1** (0.20 mmol, 1eq) and isocyanate **2** (0.22 mmol, 1.1 eq) in CH_2Cl_2 (1 mL) was added. After stirring at rt for 18 h, the resulting reaction mixture was concentrated under vacuum, then purified by flash chromatography on silica gel, using a pentane/EtOAc eluant system, to yield pyridone **3**.

General procedure 3: preparation of enantioenriched pyridones 3 *via* the chiral counter-ion strategy, without hydrogenation procedure. In a glove box, $[Rh(cod)Cl]_2$ (2.5 mg, 5.0 µmol, 0.025 eq), dppb (4.3 mg, 10.0 µmol, 0.05 eq) and chiral silver salt **4** (15.0 µmol, 0.075 eq) were introduced into a vial equipped with a magnetic stirring bar that was sealed with a septum-cap. The vial was taken out of the glove box and dichloroethane (1 mL) was added through the cap. The vial was immersed in a pre-heated oil bath at 80-85 °C. After stirring for 15 min, a solution of diyne **1** (0.2 mmol, 1eq) and isocyanate **2** (0.22 mmol, 1.1 eq) in dichloroethane (1 mL) was added directly through the cap, in the vial at 80 °C. After 15h at 80 °C, the vessel was cooled to rt, opened and the reaction mixture was concentrated *in vacuo*. Purification by flash-chromatography on silica gel (pentane/EtOAc) afforded the desired pyridone **3**.

General procedure 4: preparation of enantioenriched pyridones 3 *via* the chiral ligand strategy. Using classical schlenk techniques, $[Rh(cod)Cl]_2$ (2.5 mg, 5.0 µmol, 0.025 eq), (*R*)-2,2'-bis(diphenylphosphino)-1,1′-binaphthyl (6.2 mg, 10.0 µmol, 0.05 eq) and $AgBF_4$ (1.9 mg, 10.0 µmol, 0.05 eq) were dissolved in CH_2Cl_2 (1 mL) and stirred for 5 min at rt. The resulting solution was then stirred under H_2 atmosphere (1 atm, rt) for 1 h, then concentrated to dryness at the vacuum-line. The residue was dissolved in CH_2Cl_2 (1 mL) under Ar and a solution of diyne **1** (0.20 mmol, 1eq) and isocyanate **2** (0.22 mmol, 1.1 eq) in CH_2Cl_2 (1 mL) was added. After stirring at rt for 18 h, the

resulting reaction mixture was concentrated under vacuum, then purified by flash chromatography on silica gel, using a pentane/EtOAc eluant system, to yield pyridone **3**.

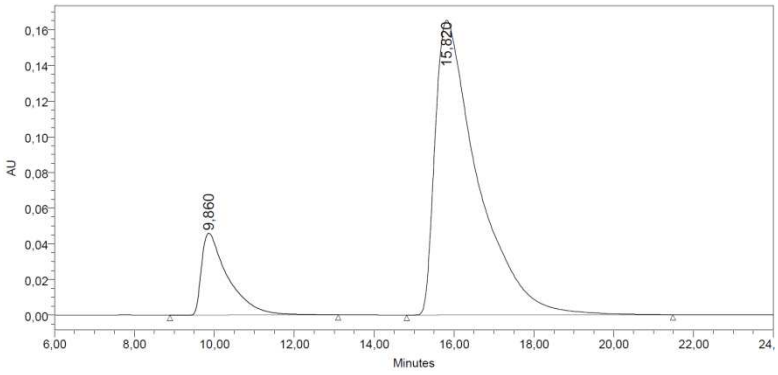


3aa

Chemical Formula: $C_{21}H_{27}NO_4$
Molecular Weight: 357,44

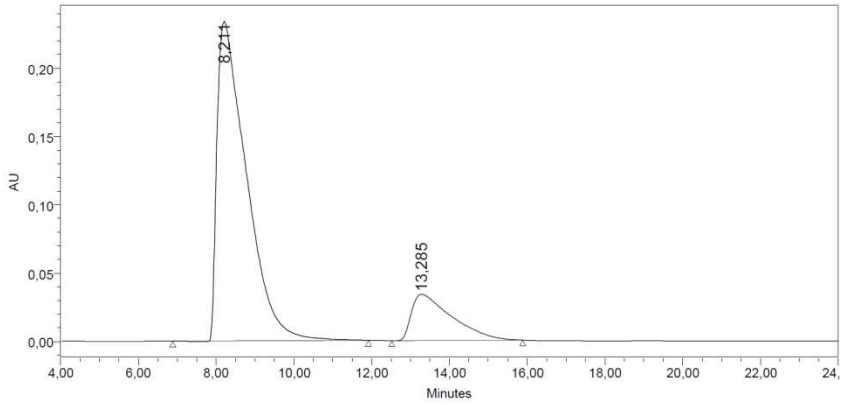
3aa, white solid; mp = 126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.34 (m, 1H), 7.09-7.00 (m, 3H), 3.76 (s, 3H), 3.38-3.34 (m, 10H), 2.73 (d, AB syst, 1H, *J* = 18.4 Hz), 2.69 (d, AB syst, 1H, *J* = 18.4 Hz), 2.66 (d, AB syst, 1H, *J* = 16.6 Hz), 2.62 (d, AB syst, 1H, *J* = 16.6 Hz), 2.03 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 154.7, 153.0, 136.7, 129.7, 129.5, 128.3, 121.1, 120.4, 118.4, 112.0, 75.9, 75.8, 59.2 (2C), 55.7, 47.3, 37.7, 35.7, 17.3, 13.1. Characterization data are in agreement with the one reported in the literature.[6]

*Chiral counterion approach (General procedure **3**):* **3aa**, 55 mg, 77% yield; [α_D] –16.6 (*c* 1.0 $CHCl_3$, ee = 71%). Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 312 nm. Retention time for major enantiomer = 15.8 min; for minor enantiomer = 9.9 min (ee = 71%).



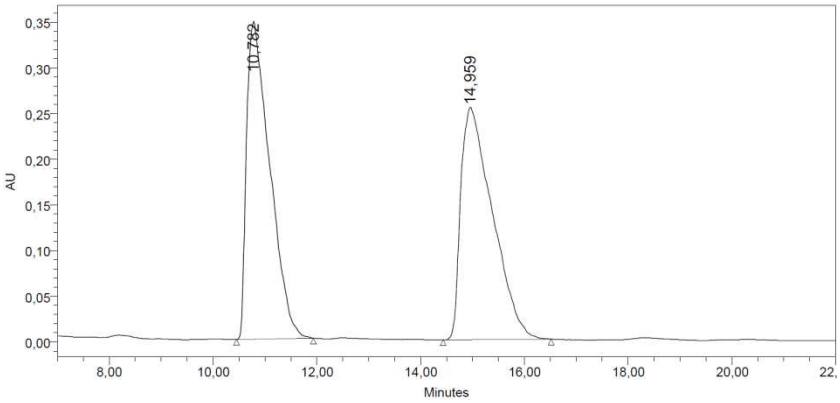
	RT	Area	% Area	Height
1	9,860	2103092	14,68	45971
2	15,820	12219476	85,32	165224

*Chiral ligand approach (General procedure **4**):* **3aa**, 60 mg, 84 % yield; [α_D] +16.3 (*c* 1.0 $CHCl_3$, ee = 67%). Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 312 nm. Retention time for major enantiomer = 8.2 min; for minor enantiomer = 13.3 min (ee = 67%).

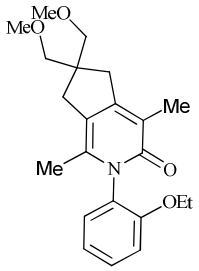


	RT	Area	% Area	Height
1	8,211	12290540	83,51	233992
2	13,285	2426236	16,49	33873

*Racemate (general procedure **1**):* Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 312 nm. Retention time for both enantiomers: 10.8 min and 15.0 min.



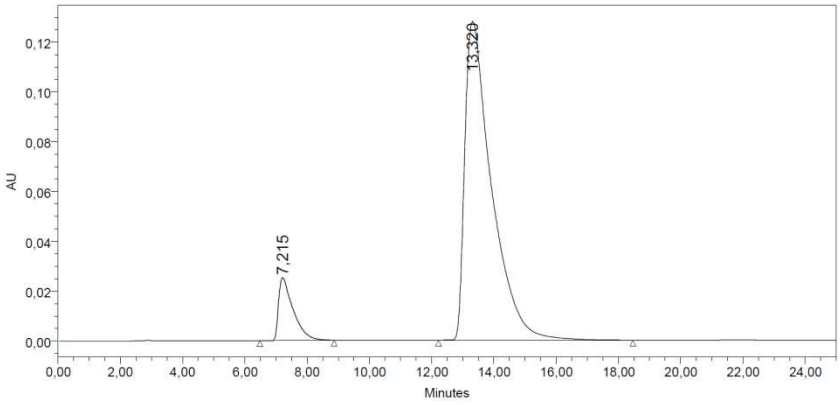
	RT	Area	% Area	Height
1	10,782	10797576	50,03	348056
2	14,959	10783542	49,97	254856



Chemical Formula: $C_{22}H_{29}NO_4$
Molecular Weight: 371,46996

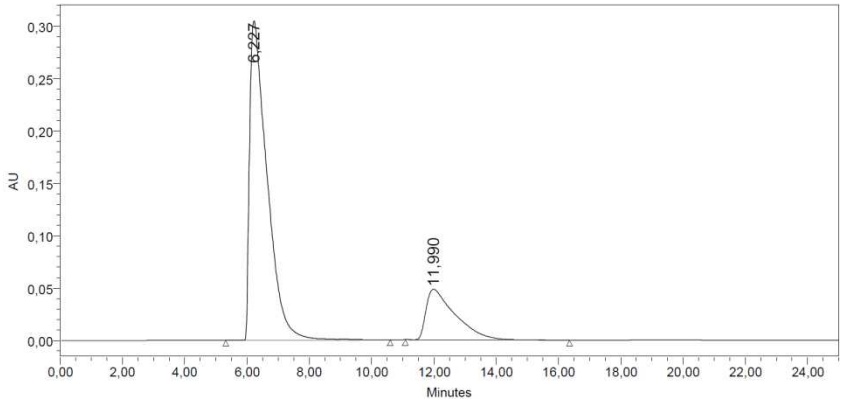
3ab, white solid; mp = 89-91°C; IR (neat): ν_{max} = 2990, 2937, 2860, 1665, 1611, 1571, 1197, 729 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.36-7.30 (m, 1H), 7.08 (dd, 1H, *J* = 1.7, 7.6 Hz), 7.03-6.98 (m, 2H), 4.02 (qd, 2H, *J* = 1.3, 7.0 Hz), 3.37-3.36 (m, 8H), 3.34 (s, 2H), 2.71 (s, 2H), 2.63 (s, 2H), 2.02 (s, 3H), 1.79 (s, 3H), 1.24 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.7, 154.0, 152.7, 136.7, 129.6, 129.5, 128.7, 121.0, 120.4, 118.1, 113.3, 75.8, 75.7, 64.1, 59.3 (2C), 47.4, 37.7, 35.6, 17.2, 14.6, 13.1; HRMS (ES+) Calcd for $C_{22}H_{29}NNaO_4$ $[M+Na]^+$: 394.1994. Found: 394.1996.

*Chiral counterion approach (General procedure **3**):* **3ab**, 54 mg, 73% yield; $[\alpha_D]$ –20.8 (*c* 0.45, $CHCl_3$, ee = 81%). Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 312 nm. Retention time for major enantiomer = 13.3 min; for minor enantiomer = 7.2 min (ee = 81%).



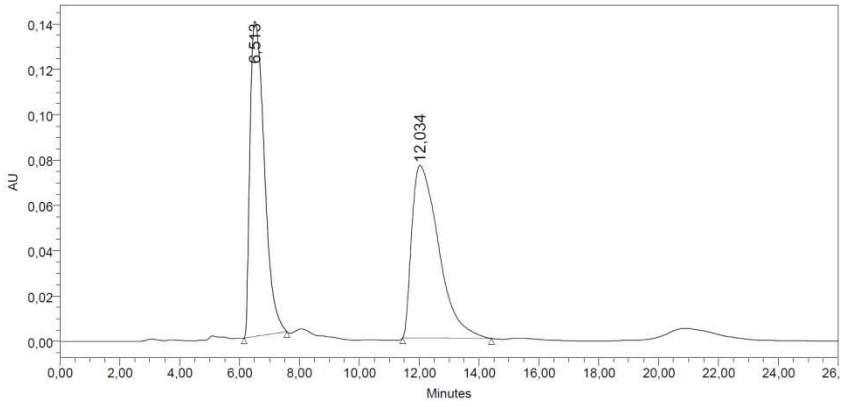
	RT	Area	% Area	Height
1	7,215	815170	9,63	25278
2	13,320	7653565	90,37	128041

*Chiral ligand approach (General procedure **4**):* **3ab**, 69 mg, 93 % yield; [α_D] +11.6 (*c* 1.0 $CHCl_3$, ee = 59%). Characterization data are in agreement with the one reported in the literature.[6] Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 312 nm. Retention time for major enantiomer = 6.2 min; for minor enantiomer = 12.0 min (ee = 59%).

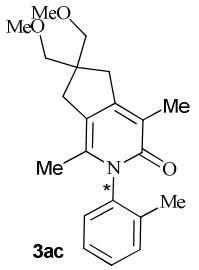


	RT	Area	% Area	Height
1	6,227	11915096	79,25	304768
2	11,990	3119704	20,75	48226

*Racemate (general procedure **1**):* Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 235 nm. Retention time for both enantiomers: 6.5 min and 12.0 min.



	RT	Area	% Area	Height
1	6,513	4616686	49,26	139043
2	12,034	4755152	50,74	76169

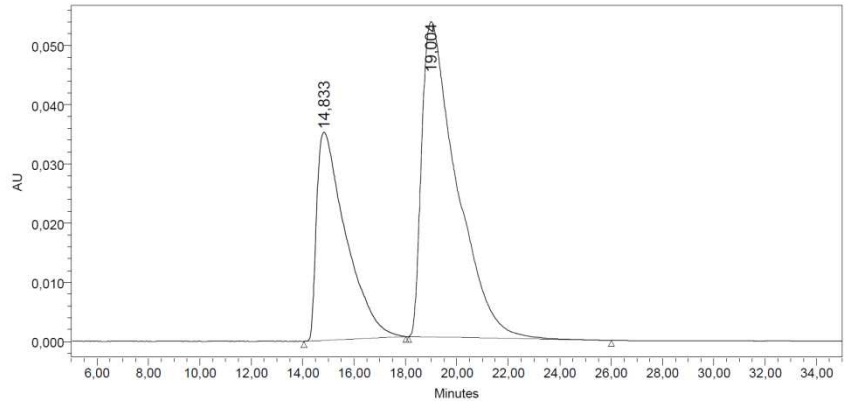


3ac

Chemical Formula: $C_{21}H_{27}NO_3$
Molecular Weight: 341,44

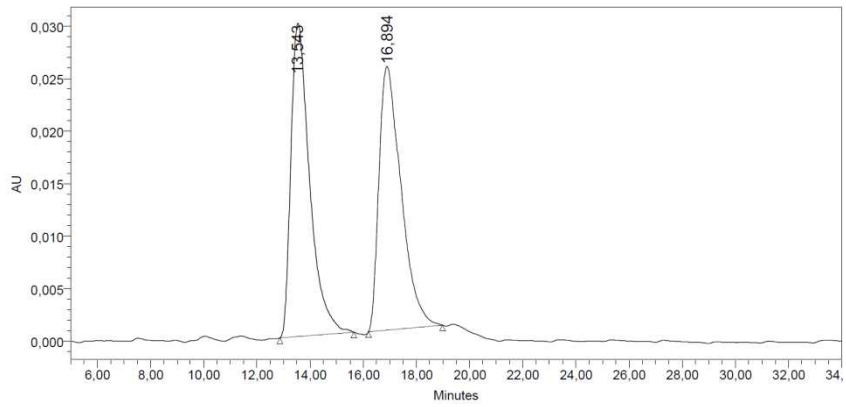
3ac, pale yellow oil; IR (neat): ν_{max} = 2979, 2921, 2878, 1662, 1569, 1106, 727 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.32-7.26 (m, 3H), 7.04-7.01 (m, 1H), 3.40-3.37 (m, 8H), 3.35 (s, 2H), 2.73 (s, 2H), 2.65 (s, 2H), 2.03 (s, 6H), 1.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 153.0, 138.9, 135.8, 135.3, 131.0, 128.5, 127.9, 127.1, 120.8, 118.8, 75.84, 75.79, 59.3 (2C), 47.4, 37.7, 35.7, 17.5, 17.3, 13.1; HRMS (ES+): Calcd for $C_{21}H_{27}NNaO_3$ $[M+Na]^+$: 364.1889. Found: 364.1871.

*Chiral counterion approach (general procedure **3**):* **3ac**, 47 mg, 69% yield, $[\alpha_D]$ = –30.0 (*c* 1.0, $CHCl_3$, ee = 29%); Chiral HPLC analysis: AD-H column, 95/5 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 312 nm. Retention time for major enantiomer = 19.0 min; for minor enantiomer = 14.8 min (ee = 29%).

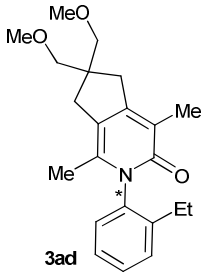


	RT	Area	% Area	Height
1	14,833	2768792	35,61	35181
2	19,004	5006404	64,39	53261

*Racemate (general procedure **1**):* Chiral HPLC analysis: AD-H column, 95/5 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 235 nm. Retention time for both enantiomers: 13.5 min and 16.9 min.



	RT	Area	% Area	Height
1	13,543	1464297	50,20	29809
2	16,894	1452612	49,80	25108

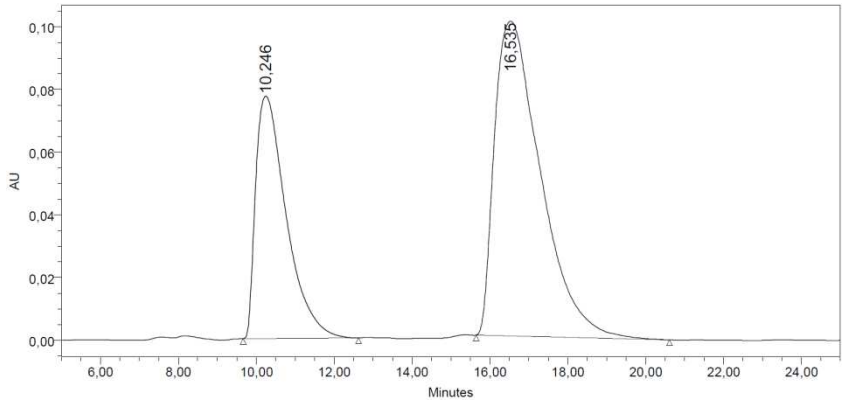


3ad

Chemical Formula: $C_{22}H_{29}NO_3$
Molecular Weight: 355,47

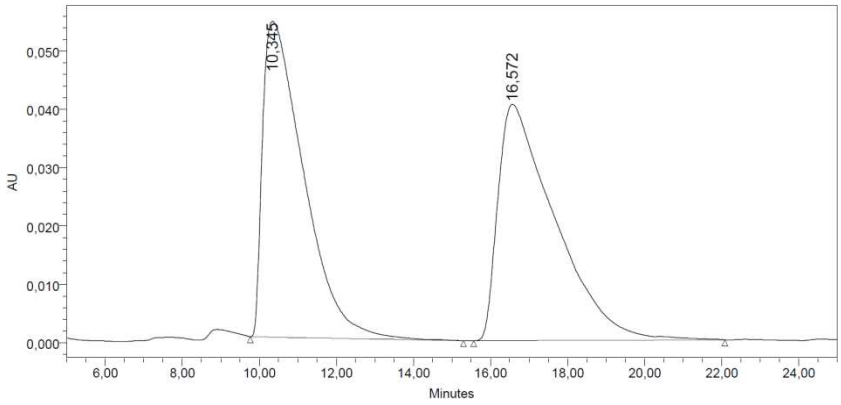
3ad, pale yellow solid; mp = 74-76°C; IR (neat): ν_{max} = 2969, 2923, 2877, 1664, 1614, 1570, 1109 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39-7.27 (m, 3H), 7.02 (d, 1H, J = 7.5 Hz), 3.39-3.38 (m, 8H), 3.35 (s, 2H), 2.74 (s, 2H), 2.65 (s, 2H), 2.39 (dq, 1H, J = 7.6, 15.3 Hz), 2.29 (dq, 1H, J = 7.6, 15.3 Hz), 2.04 (s, 3H), 1.75 (s, 3H), 1.14 (t, 3H, J = 7.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.6, 153.0, 140.7, 138.4, 136.0, 128.8, 128.6, 128.0, 127.0, 120.8, 118.8, 75.9, 75.8, 59.3 (2C), 47.4, 37.7, 35.7, 23.4, 17.7, 13.3, 13.1; HRMS (ES+): Calcd for $C_{22}H_{30}NO_3$ $[M+H]^+$: 356.2226. Found: 356.2224.

*Chiral counterion approach (general procedure **3**):* **3ad**, 62 mg, 87% yield, $[\alpha_D]$ = –27.1 (*c* 1.06, $CHCl_3$, ee = 32%); Chiral HPLC analysis: AD-H column, 95/5 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 235 nm. Retention time for major enantiomer = 16.5 min; for minor enantiomer = 10.2 min (ee = 32%).

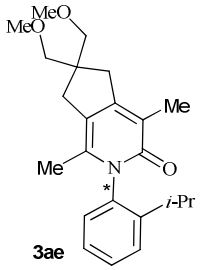


	RT	Area	% Area	Height
1	10,246	4217604	33,82	77307
2	16,535	8252366	66,18	100410

*Racemate (general procedure **1**):* Chiral HPLC analysis: AD-H column, 95/5 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 235 nm. Retention time for both enantiomers: 10.3 min and 16.6 min.



	RT	Area	% Area	Height
1	10,345	4015951	49,07	54159
2	16,572	4167637	50,93	40522

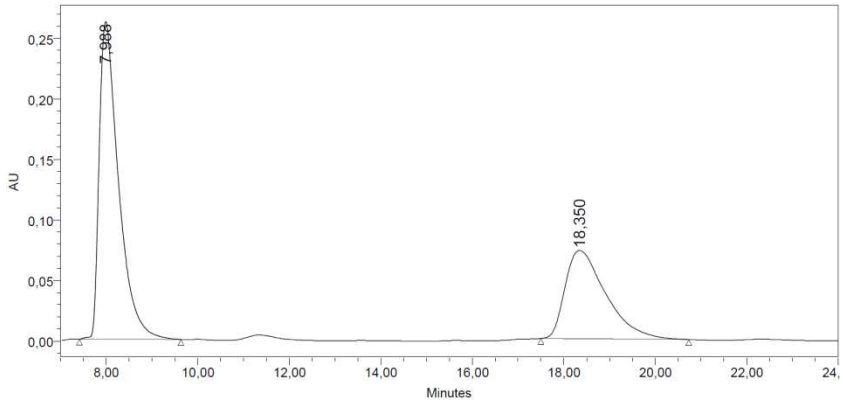


3ae

Chemical Formula: $C_{23}H_{31}NO_3$
Molecular Weight: 369,50

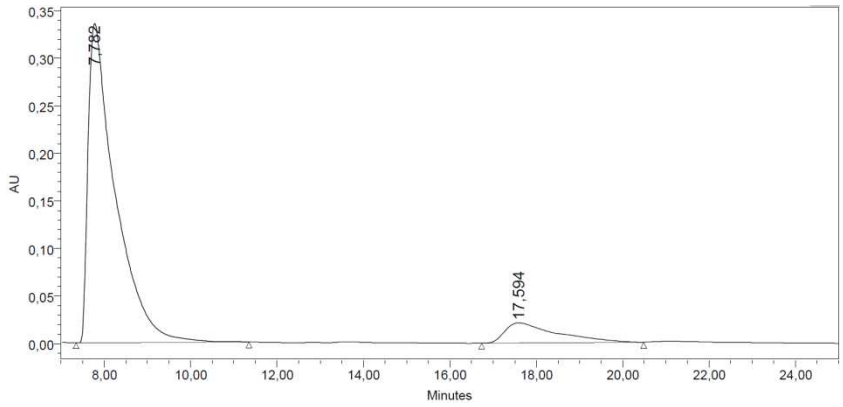
3ae, yellow oil; IR (neat): ν_{max} = 3050, 3029, 2960, 1665, 1613, 1571, 1109 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44-7.36 (m, 2H), 7.28-7.24 (m, 1H), 6.99 (dd, 1H, J = 1.3, 7.7 Hz), 3.40 (s, 5H), 3.38 (s, 3H), 3.34 (s, 2H), 2.71 (d, AB syst, 1H, J = 17.3 Hz), 2.69 (d, AB syst, 1H, J = 17.3 Hz), 2.67(d, AB syst, 1H, J = 17.3 Hz), 2.62 (d, AB syst, 1H, J = 17.3 Hz), 2.58 (heptuplet, 1H, J = 6.9 Hz), 2.03 (s, 3H), 1.75 (s, 3H), 1.17 (d, 3H, J = 6.9 Hz), 1.14 (d, 3H, J = 6.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 152.8, 145.7, 137.5, 136.2, 128.9, 128.1, 126.8, 126.7, 120.8, 118.6, 75.9, 75.8, 59.33, 59.30, 47.4, 37.7, 35.7, 28.0, 24.0, 23.1, 17.9, 13.2; HRMS (ES+) Calcd for $C_{23}H_{31}NNaO_3$ $[M+Na]^+$: 392.2202. Found: 392.2181.

*Chiral counterion approach (general procedure **3**):* **3ae**, 65 mg, 88% yield, $[\alpha_D]$ = +12.0 (*c* 0.90, $CHCl_3$, ee = 26%); Chiral HPLC analysis: AD-H column, 95/5 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 235 nm. Retention time for major enantiomer = 8.0 min; for minor enantiomer = 18.4 min (ee = 26%).



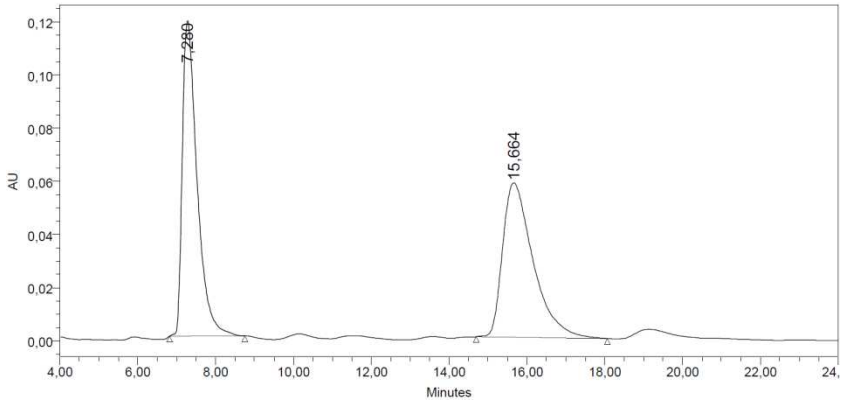
	RT	Area	% Area	Height
1	7,988	7723198	63,13	262386
2	18,350	4509886	36,87	72892

*Chiral ligand approach (General procedure **4**):* **3ae**, 41 mg, 55% yield, $[\alpha_D]$ = +58.1 (*c* 1.25, $CHCl_3$, ee = 79%); Chiral HPLC analysis: AD-H column, 95/5 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 235 nm. Retention time for major enantiomer = 7.8 min; for minor enantiomer = 17.6 min (79% ee).

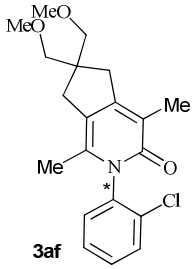


	RT	Area	% Area	Height
1	7,782	14673722	89,26	335740
2	17,594	1765658	10,74	21221

*Racemate (general procedure **1**):* Chiral HPLC analysis: AD-H column, 95/5 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 235 nm. Retention time for both enantiomers: 7.3 min and 15.7 min.



	RT	Area	% Area	Height
1	7,280	3124338	49,72	118648
2	15,664	3160122	50,28	58089

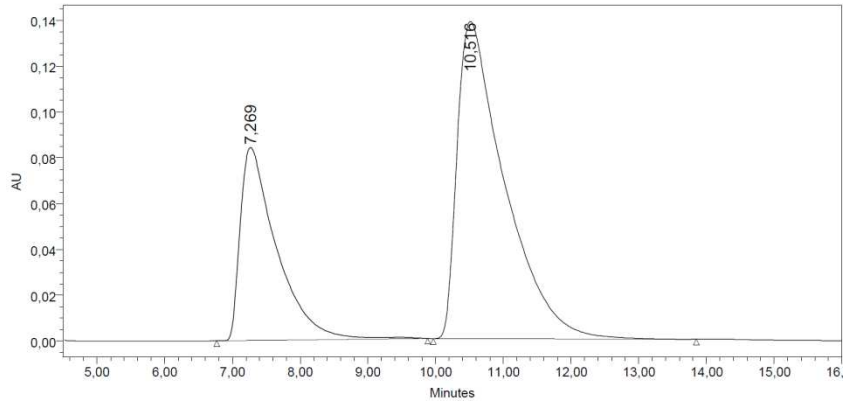


3af

Chemical Formula: $C_{20}H_{24}ClNO_3$
Molecular Weight: 361,86

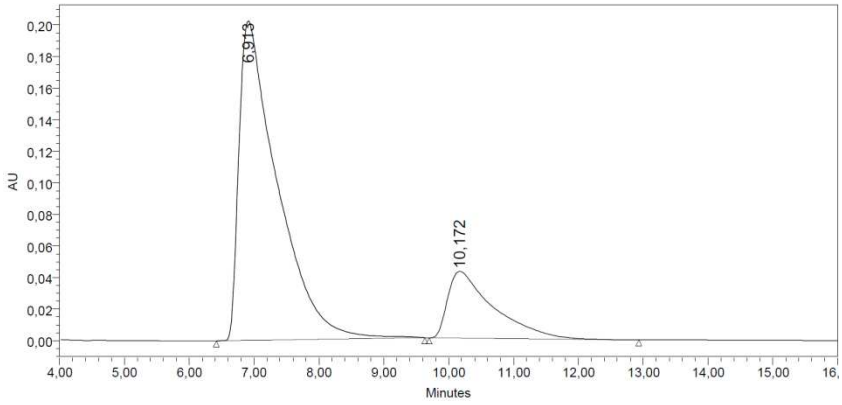
3af, colorless oil; IR (neat): ν_{max} = 2980, 2921, 2883, 1667, 1617, 1572, 1477, 1108 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55-7.51 (m, 1H), 7.40-7.33 (m, 2H), 7.24-7.20 (m, 1H), 3.38-3.37 (m, 8H), 3.35 (m, 2H), 2.73 (s, 2H), 2.65 (m, 2H), 2.04 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3, 153.5, 137.5, 135.5, 132.5, 130.3, 130.0, 129.7, 127.9, 120.8, 118.9, 75.8, 75.7, 59.2 (2C), 47.4, 37.7, 35.5, 17.2, 13.0; HRMS (ES+) Calcd for $C_{20}H_{24}ClNNaO_3$ [M+Na^+]: 384.1342. Found: 384.1347.

*Chiral counterion approach (general procedure **3**):* **3af**, 13 mg, 18% yield, [α_D] = –16.5 (*c* 0.25, $CHCl_3$, ee = 36%); Chiral HPLC analysis: 90/10 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 312 nm. Retention time for major enantiomer = 10.5 min; for minor enantiomer = 7.3 min (36% ee).



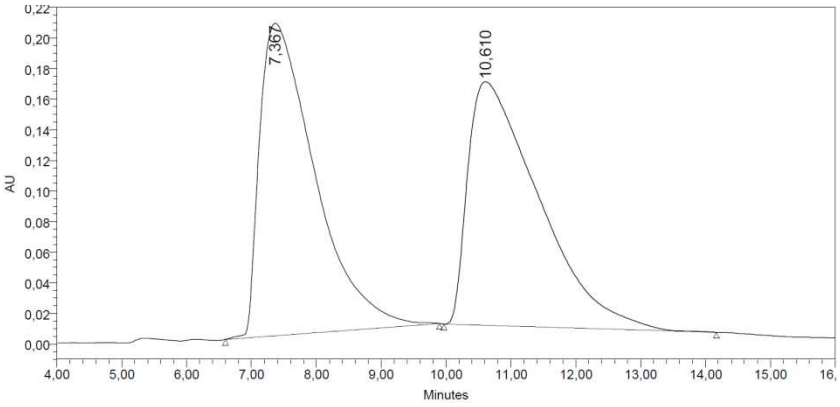
	RT	Area	% Area	Height
1	7,269	3146844	31,80	84336
2	10,516	6748066	68,20	138494

*Chiral ligand approach (General procedure **4**):* **3af**, 48 mg, 66% yield, colorless oil, $[\alpha_D]$ = +22.5 (*c* 0.90, $CHCl_3$, ee = 60%); Chiral HPLC analysis: 90/10 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 312 nm. Retention time for major enantiomer = 6.9 min; for minor enantiomer = 10.2 min (60 % ee).

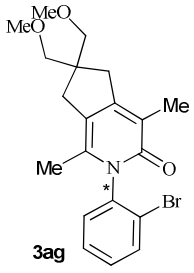


	RT	Area	% Area	Height
1	6,913	8315640	80,13	202320
2	10,172	2061692	19,87	42357

*Racemate (general procedure **1**):* Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 312 nm. Retention time for both enantiomers: 7.4 min and 10.6 min.



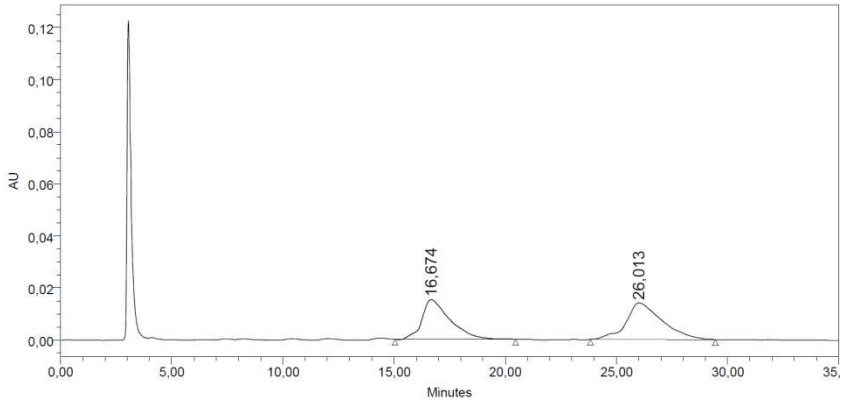
	RT	Area	% Area	Height
1	7,367	12128288	50,02	204231
2	10,610	12120525	49,98	159254



Chemical Formula: $C_{20}H_{24}BrNO_3$
Molecular Weight: 406,31

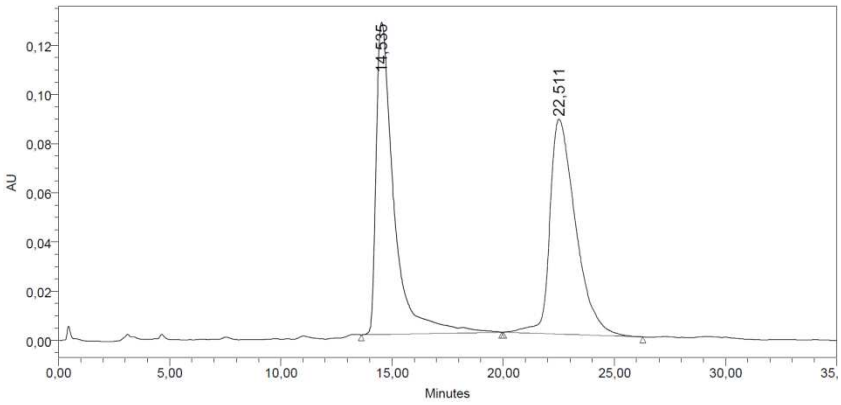
3ag, yellow oil; IR (neat): ν_{max} = 2921, 2885, 1667, 1617, 1591, 1109 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.70 (dd, 1H, *J* = 1.4, 7.9 Hz), 7.42 (td, 1H, *J* = 1.4, 7.6 Hz), 7.34-7.19 (m, 2H), 3.46-3.35 (m, 10H), 2.74 (s, 2H), 2.65 (s, 2H), 2.04 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 153.5, 139.2, 135.4, 133.5, 130.0, 129.8, 128.6, 122.9, 121.0, 118.9, 75.8, 75.7, 59.3 (2C), 47.4, 37.7, 35.6, 17.4, 13.0; HRMS (ES+) Calcd for $C_{20}H_{24}BrNNaO_3$ $[M+Na]^+$: 384.1342. Found: 384.1347.

*Chiral counterion approach (General procedure **3**):* **3ag**, 15 mg, 18% yield, [α_D] = –5.6 (*c* 0.81, $CHCl_3$, ee = 8%); Chiral HPLC analysis: AD-H column, 95/5 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 235 nm. Retention time for major enantiomer = 26.0 min; for minor enantiomer = 16.7 min (ee = 8%).

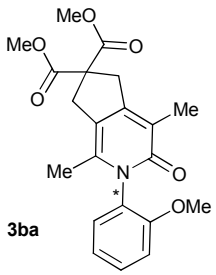


	RT	Area	% Area	Height
1	16,674	1339520	45,80	15238
2	26,013	1585466	54,20	14080

*Racemate (general procedure **1**):* Chiral HPLC analysis: AD-H column, 95/5 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 235 nm. Retention time for both enantiomers: 14.5 min and 22.5 min.



	RT	Area	% Area	Height
1	14,535	7061066	50,06	126857
2	22,511	7042973	49,94	87339

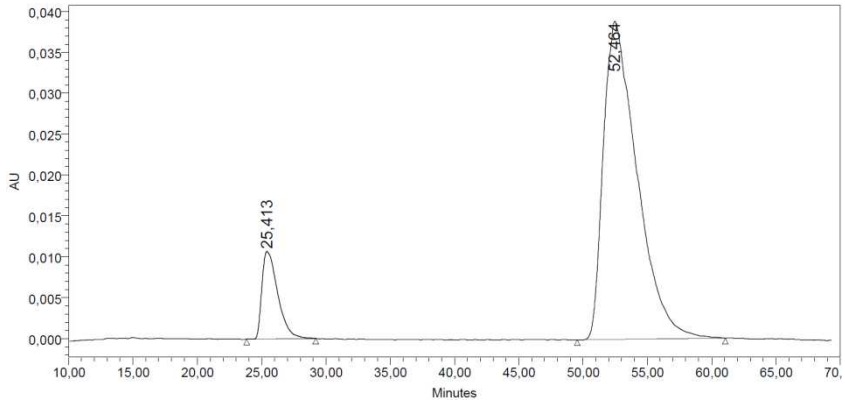


3ba

Chemical Formula: $C_{21}H_{23}NO_6$
Molecular Weight: 385,41

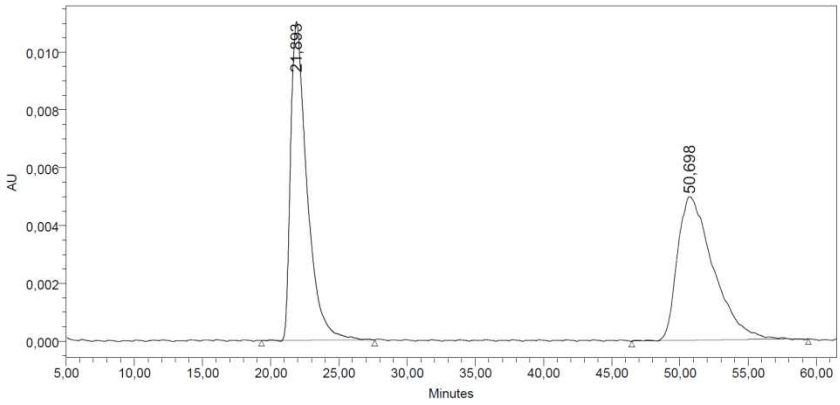
3ba; white solid; mp = 136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.33 (m, 1H), 7.07-6.99 (m, 3H), 3.76 (s, 3H), 3.75 (s, 3H), 3.74 (s, 3H), 3.48 (d, AB syst, 1H, *J* = 17.6 Hz), 3.43 (d, AB syst, 1H, *J* = 17.6 Hz), 3.38 (s, 2H), 2.04 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 171.4, 163.4, 154.5, 150.0 , 136.6, 129.8, 129.3, 127.9, 121.0, 120.2, 116.0, 111.9, 59.1, 55.6, 53.04, 53.00, 39.3, 37.5, 17.3, 13.1. Characterization data are in agreement with the one reported in the literature.[6]

*Chiral counterion approach (General procedure **3**):* **3ba**, 65 mg, 84% yield; [α_D] = –15.1 (*c* 0.77, $CHCl_3$, ee = 77%). Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 254 nm. Retention time for major enantiomer = 52.5 min; for minor enantiomer = 25.4 min (ee = 77%).

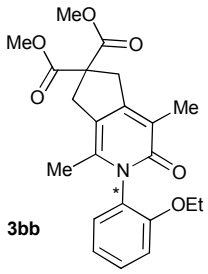


	RT	Area	% Area	Height
1	25,413	915112	11,45	10689
2	52,464	7080176	88,55	38865

*Racemate (general procedure **1**):* Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 235 nm. Retention time for both enantiomers: 21.9 min and 50.7 min.



	RT	Area	% Area	Height
1	21,893	923378	50,43	11018
2	50,698	907626	49,57	4965

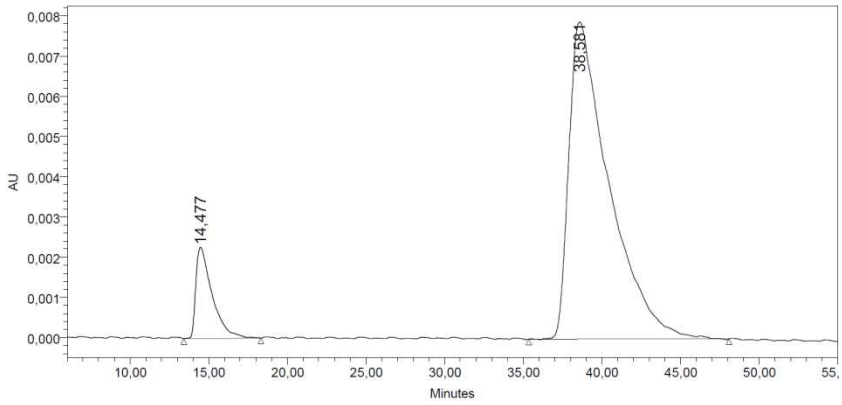


Chemical Formula: $C_{22}H_{25}NO_6$
Molecular Weight: 399,44

3bb

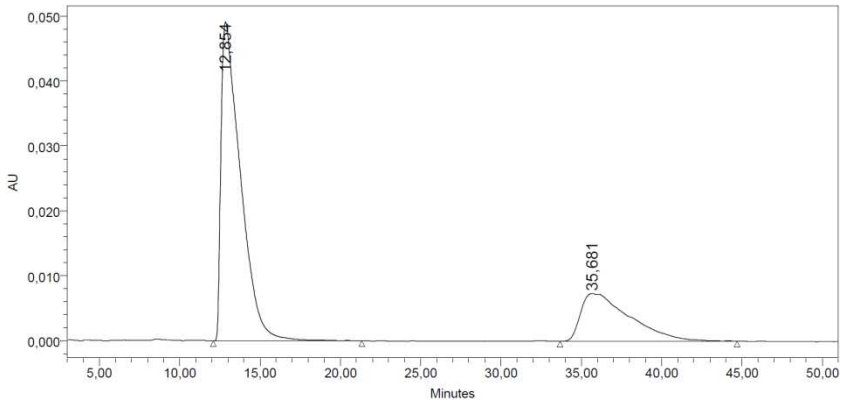
3bb, white solid; mp = 149-151°C; IR (neat): ν_{max} = 2954, 1733, 1667, 1617, 1574, 1261, 729 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.37-7.31 (m, 1H), 7.08 (dd, 1H, *J* = 1.8, 7.6 Hz), 7.04-6.98 (m, 2H), 4.02 (dq, 2H, *J* = 7,0 Hz, 7.8 Hz), 3.78 (s, 6H), 3.47 (br s, 2H), 3.39 (br s, 2H), 2.06 (s, 3H), 1.83 (s, 3H), 1.24 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 171.5, 163.6, 153.9, 149.9, 136.7, 129.7, 129.4, 128.3, 121.0, 120.2, 115.8, 113.2, 64.0, 59.3, 53.1, 53.0, 39.3, 37.6, 17.3, 14.6, 13.1; HRMS (ES+) Calcd for $C_{22}H_{25}NNaO_6$ $[M+Na]^+$: 422.1580. Found: 422.1567.

*Chiral counterion approach (general procedure **3**):* **3bb**, 64 mg, 80% yield, $[\alpha_D]$ = –15.9 (*c* 1.0, $CHCl_3$, ee = 79%); Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 254 nm. Retention time for major enantiomer = 38.6 min; for minor enantiomer = 14.5 min (ee = 79%).



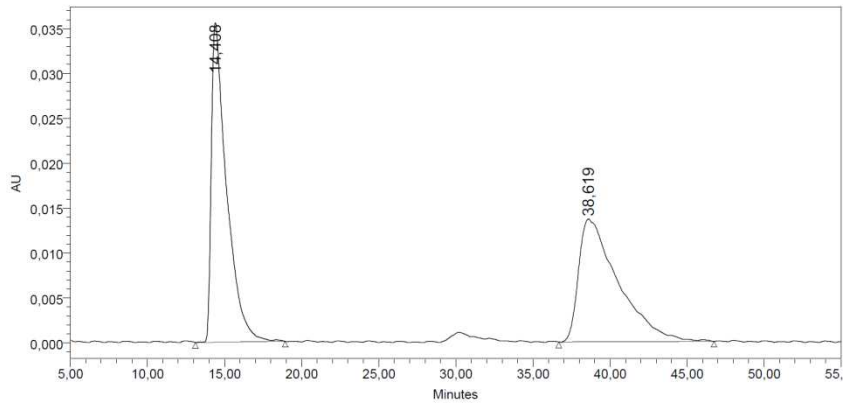
	RT	Area	% Area	Height
1	14,477	163637	10,50	2267
2	38,581	1395412	89,50	7884

*Chiral ligand approach (General procedure **4**):* **3ba**, 65 mg, 81% yield; $[\alpha_D]$ = +8.2 (*c* 1.0, $CHCl_3$, ee = 46%). Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 254 nm. Retention time for major enantiomer = 12.9 min; for minor enantiomer = 35.7 min (ee = 46%).

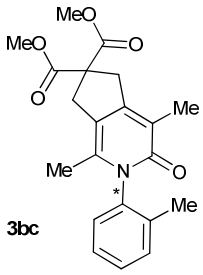


	RT	Area	% Area	Height
1	12,854	4144081	72,80	49146
2	35,681	1548213	27,20	7359

*Racemate (general procedure **1**):* Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 254 nm. Retention time for both enantiomers: 14.4 min and 38.6 min.



	RT	Area	% Area	Height
1	14,408	2449634	50,13	35588
2	38,619	2437001	49,87	13674

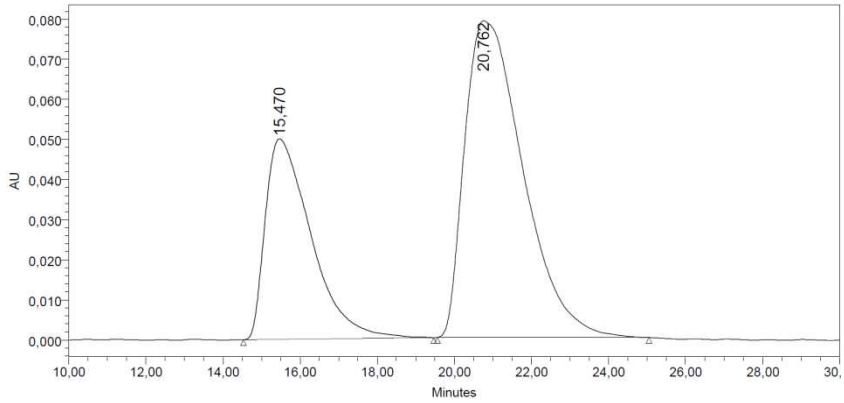


3bc

Chemical Formula: $C_{21}H_{23}NO_5$
Molecular Weight: 369,41

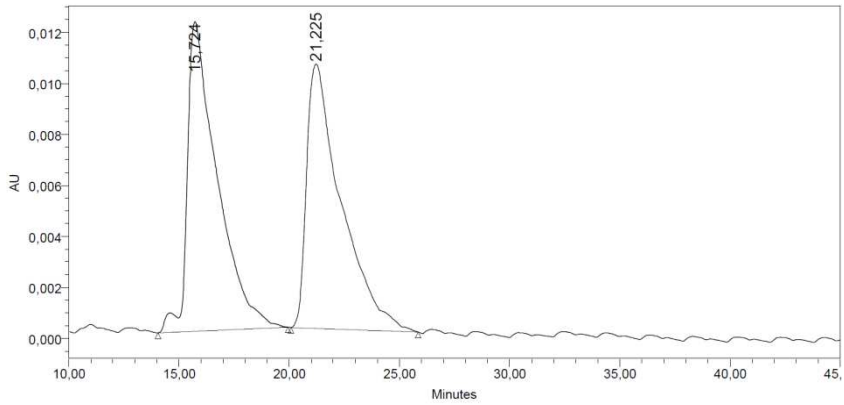
3bc, white solid; mp = 169 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.26 (m, 3H), 7.04-7.02 (m, 1H), 3.79 (s, 6H), 3.52 (d, AB syst, 1H, J = 17.9 Hz), 3.46 (d, AB syst, 1H, J = 17.9 Hz), 3.40 (s, 2H), 2.08 (s, 3H), 2.02 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.53, 171.46, 163.2, 150.4, 138.5, 136.0, 135.2, 131.1, 128.7, 127.8, 127.2, 120.7, 116.9, 59.2, 53.2, 53.1, 39.4, 37.6, 17.6, 17.3, 13.2. Characterization data are in agreement with the one reported in the literature.[6]

*Chiral counterion approach (General procedure **3**):* **3bc**, 62 mg, 84% yield; [α_D] = –26.0 (*c* 0.93, $CHCl_3$, ee = 34%). Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1 mL/min, λ 235 nm. Retention time for major enantiomer = 20.8 min; for minor enantiomer = 15.5 min (ee = 34%).

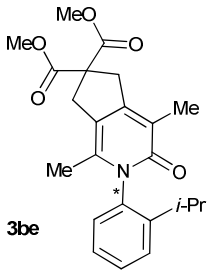


	RT	Area	% Area	Height
1	15,470	4119173	33,16	50026
2	20,762	8304719	66,84	78989

*Racemate (general procedure **1**):* Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 235 nm. Retention time for both enantiomers: 15.7 min and 21.2 min.



	RT	Area	% Area	Height
1	15,724	1144256	50,31	12135
2	21,225	1129987	49,69	10369

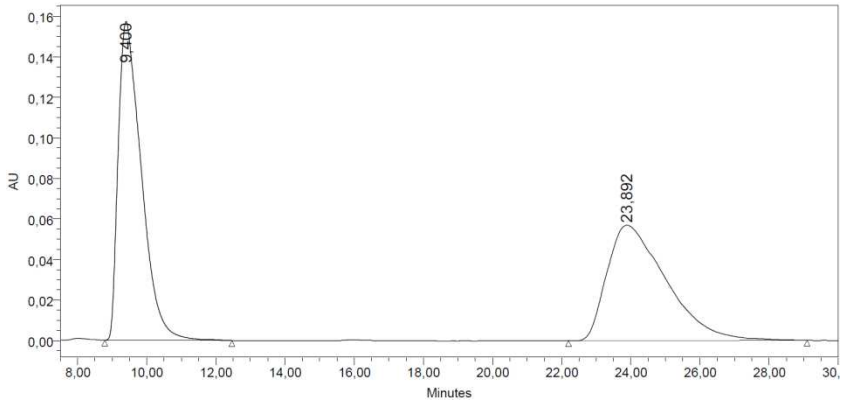


3be

Chemical Formula: $C_{23}H_{27}NO_5$
Molecular Weight: 397,46

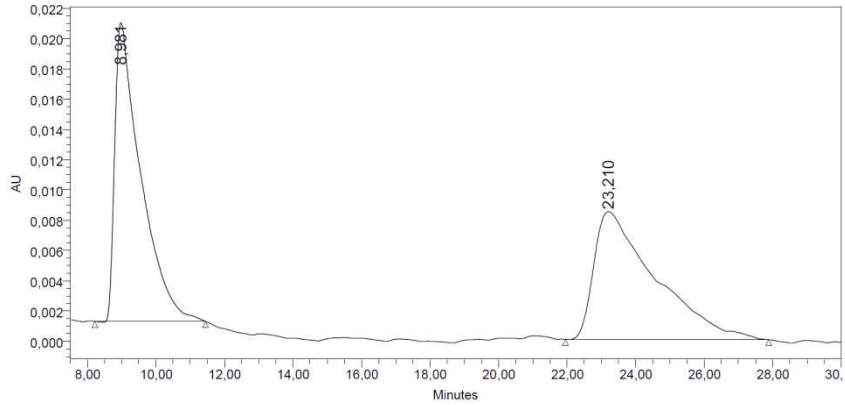
3be, white solid; mp = 38 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.36 (m, 2H), 7.28-7.24 (m, 1H), 6.98-6.96 (m, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.51 (d, AB syst, 1H, J = 17.0 Hz), 3.45 (d, AB syst, 1H, J = 17.0 Hz), 3.40 (s, 2H), 2.55 (septuplet, 1H, J = 6.9 Hz), 2.06 (s, 3H), 1.79 (s, 3H), 1.15 (d, 3H, J = 6.9 Hz), 1.13 (d, 3H, J = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.6, 171.5, 163.6, 150.2, 145.5, 137.0, 136.3, 129.0, 127.9, 126.9, 126.8, 120.6, 116.6, 59.2, 53.2, 53.1, 39.4, 37.7, 27.9, 24.0, 23.1, 17.9, 13.2. Characterization data are in agreement with the one reported in the literature.[6]

*Chiral counterion approach (General procedure **3**):* **3be**, 60 mg, 75% yield; [α_D] = +3.1 (*c* 1.06, $CHCl_3$, ee = 4%). Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1 mL/min, λ 235 nm. Retention time for major enantiomer = 9.4 min; for minor enantiomer = 23.9 min (ee = 4%).

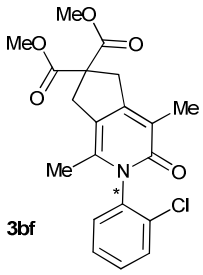


	RT	Area	% Area	Height
1	9,400	7303927	52,04	157342
2	23,892	6730744	47,96	56927

*Racemate (general procedure **1**):* Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 312 nm. Retention time for both enantiomers: 9.0 min and 23.2 min.



	RT	Area	% Area	Height
1	8,981	1041937	49,99	19729
2	23,210	1042237	50,01	8430

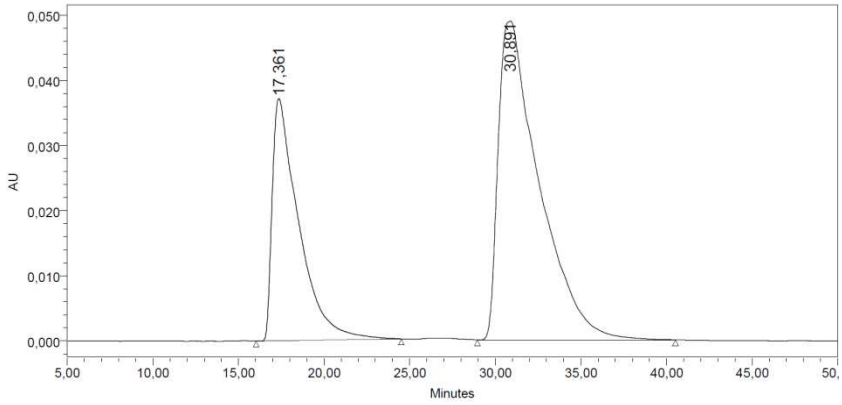


3bf

Chemical Formula: $C_{20}H_{20}ClNO_5$
Molecular Weight: 389,83

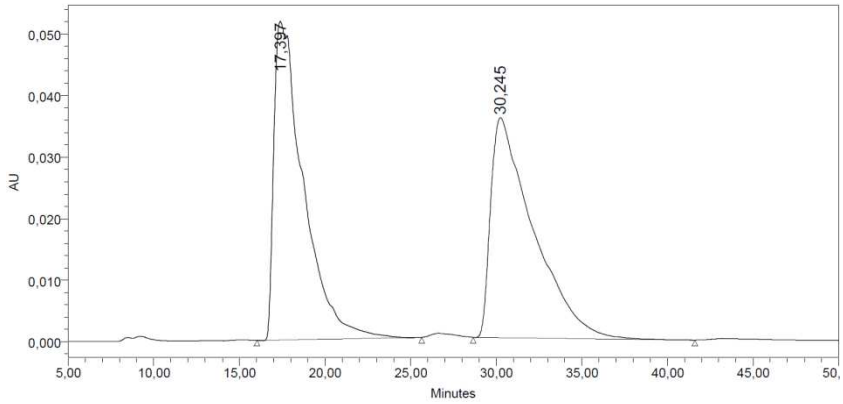
3bf, white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.52 (m, 1H), 7.40-7.35 (m, 2H), 7.22-7.20 (m, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.48 (s, 2H), 3.41 (s, 2H), 2.07 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 171.3, 163.1, 150.8, 137.1, 135.8, 132.4, 130.4, 129.9, 129.9, 128.0, 120.7, 116.8, 59.2, 53.2, 53.1, 39.4, 37.5, 17.4, 13.1. Characterization data are in agreement with the one reported in the literature.[6]

*Chiral counterion approach (General procedure **3**):* **3bf**, 40 mg, 51% yield; [α_D] = –16.9 (*c* 0.40, $CHCl_3$, ee = 34%). Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1 mL/min, λ 312 nm. Retention time for major enantiomer = 30.9 min; for minor enantiomer = 17.4 min (ee = 34%).

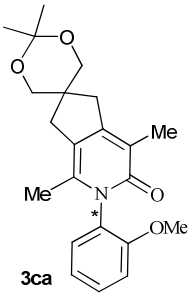


	RT	Area	% Area	Height
1	17,361	4001815	33,02	37215
2	30,891	8118587	66,98	48965

*Racemate (general procedure **1**):* Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 312 nm. Retention time for both enantiomers: 17.4 min and 30.2 min.



	RT	Area	% Area	Height
1	17,397	6198807	50,11	51762
2	30,245	6172233	49,89	35749

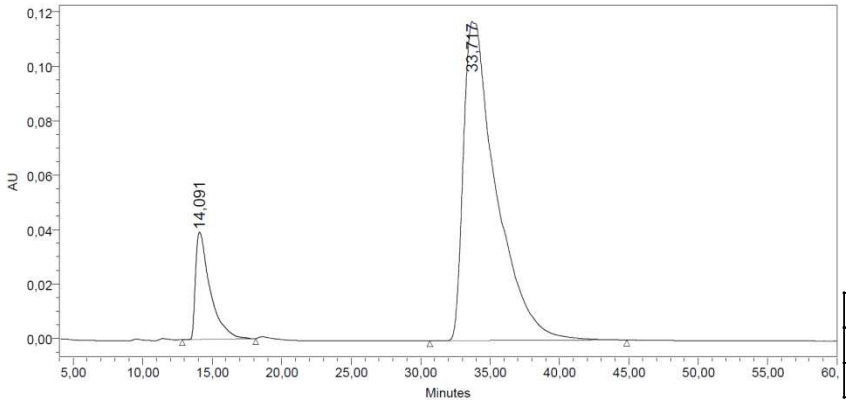


3ca

Chemical Formula: $C_{22}H_{27}NO_4$
Molecular Weight: 369,45

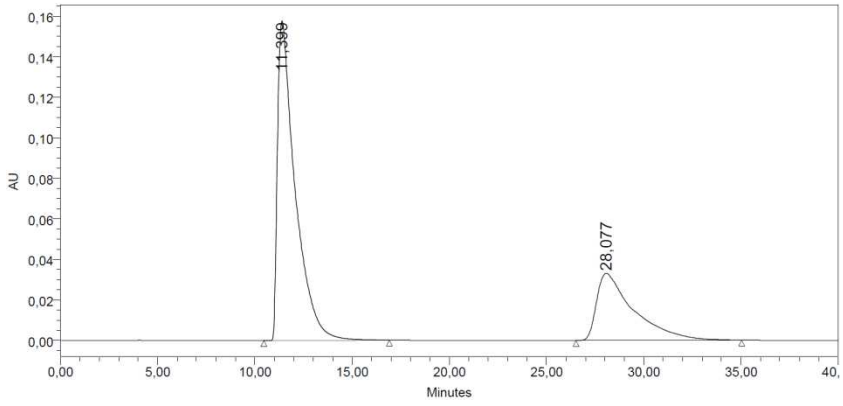
3ca, white solid; mp = 205-207°C; IR (neat): ν_{max} = 2992, 2940, 2858, 1664, 1570, 1499, 727 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.41-7.35 (m, 1H), 7.10-7.01 (m, 3H), 3.82-3.69 (m, 7H), 2.80-2.65 (m, 4H), 2.05 (s, 3H), 1.82 (s, 3H), 1.49 (s, 3H), 1.47 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.6, 154.7, 151.8, 137.1, 129.8, 129.5, 128.2, 121.2, 120.8, 117.5, 112.0, 98.1, 68.6 (2C), 55.7, 41.4, 38.7, 37.2, 24.7, 22.9, 17.4, 13.2; HRMS (ES+) Calcd for $C_{22}H_{28}NO_4$ $[M+H]^+$: 370.2018. Found: 370.2020.

*Chiral counterion approach (general procedure **3**):* **3ca**, 50 mg, 68% yield, $[\alpha_D]$ = –19.4 (*c* 0.79, $CHCl_3$, ee = 74%); Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 312 nm. Retention time for major enantiomer = 33.7 min; for minor enantiomer = 14.1 min (ee = 74%).



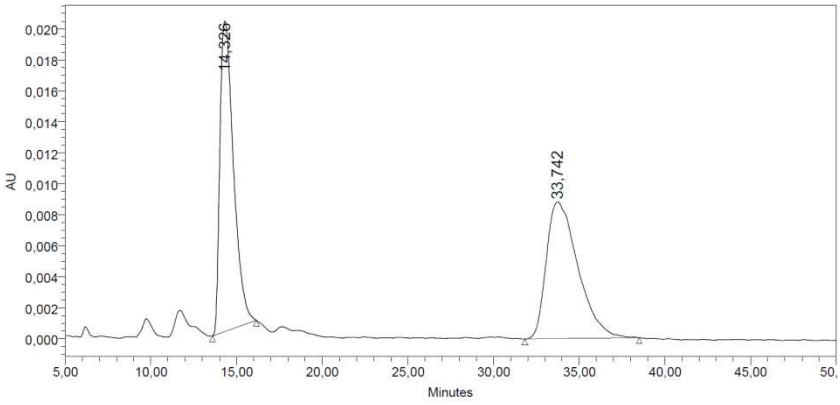
	RT	Area	% Area	Height
1	14,091	2884235	13,06	39387
2	33,717	19206814	86,94	117269

*Chiral ligand approach (General procedure **4**):* **3ca**, 65 mg, 88% yield; $[\alpha_D]$ = +10.9 (*c* 1.0, $CHCl_3$, ee = 39%). Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 312 nm. Retention time for major enantiomer = 11.4 min; for minor enantiomer = 28.1 min (ee = 39%).

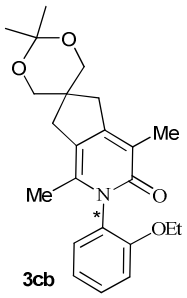


	RT	Area	% Area	Height
1	11,399	9977214	69,63	157605
2	28,077	4351500	30,37	33094

*Racemate (general procedure **1**):* Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 312 nm. Retention time for both enantiomers: 14.3 min and 33.7 min.



	RT	Area	% Area	Height
1	14,326	1111141	49,65	20016
2	33,742	1126922	50,35	8801

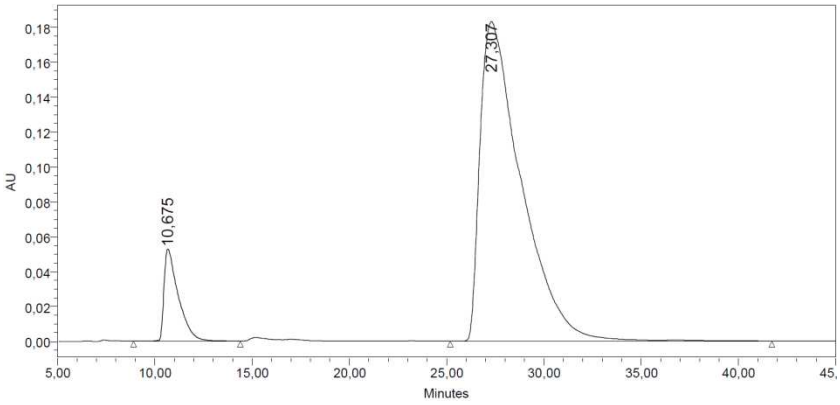


3cb

Chemical Formula: $C_{23}H_{29}NO_4$
Molecular Weight: 383,48

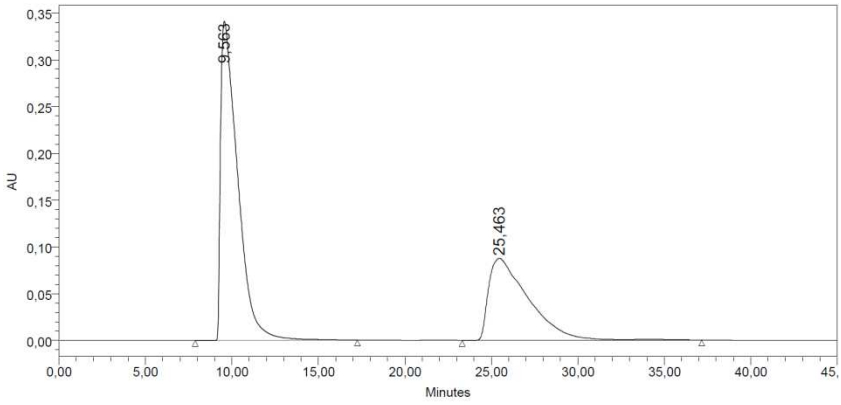
3cb, white solid; IR (neat): ν_{max} = 2979, 2922, 2880, 1665, 1614, 1572, 1044, 749 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.37-7.31 (m, 1H), 7.08 (dd, 1H, *J* = 1.9, 7.5 Hz), 7.04-6.98 (m, 2H), 4.02 (q, 2H, *J* = 7,0 Hz), 3.81-3.69 (m, 4H), 2.80-2.67 (m, 4H), 2.04 (s, 3H), 1.82 (s, 3H), 1.48 (s, 3H), 1.46 (s, 3H) 1.23 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.7, 154.0, 151.6, 137.2, 129.7, 129.6, 128.7, 121.1, 120.8, 117.3, 113.3, 98.1, 68.6 (2C), 64.1, 41.4, 38.7, 37.2, 24.6, 23.0, 17.3, 14.7, 13.2; HRMS (ES+) Calcd for $C_{23}H_{29}NNaO_4$ [*M*+Na^+]: 406.1994. Found: 406.1985.

*Chiral counterion approach (general procedure **3**):* **3cb**, 49 mg, 64% yield, [α_D] = –22.1 (*c* 1.0, $CHCl_3$, ee = 82%). Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1 mL/min, λ 312 nm. Retention time for major enantiomer = 27.3 min; for minor enantiomer = 10.7 min (ee = 82%).



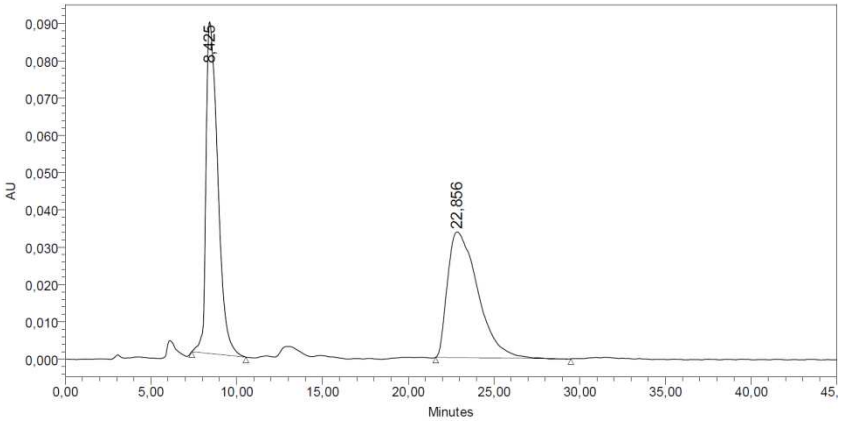
	RT	Area	% Area	Height
1	10,675	2713116	9,12	52867
2	27,307	27031540	90,88	183230

*Chiral ligand approach (General procedure **4**):* **3cb**, 37 mg, 48% yield; [α_D] = +8.4 (*c* 0.50, $CHCl_3$, ee = 25%). Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 312 nm. Retention time for major enantiomer = 25.5 min; for minor enantiomer = 9.6 min (ee = 25%).

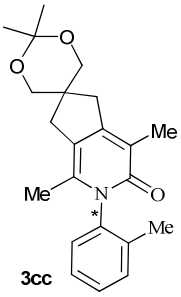


	RT	Area	% Area	Height
1	9,563	23392992	62,64	341002
2	25,463	13953572	37,36	87574

*Racemate (general procedure **1**):* Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 312 nm. Retention time for both enantiomers: 8.4 min and 22.9 min.



	RT	Area	% Area	Height
1	8,425	4257570	50,82	88944
2	22,856	4119575	49,18	33673

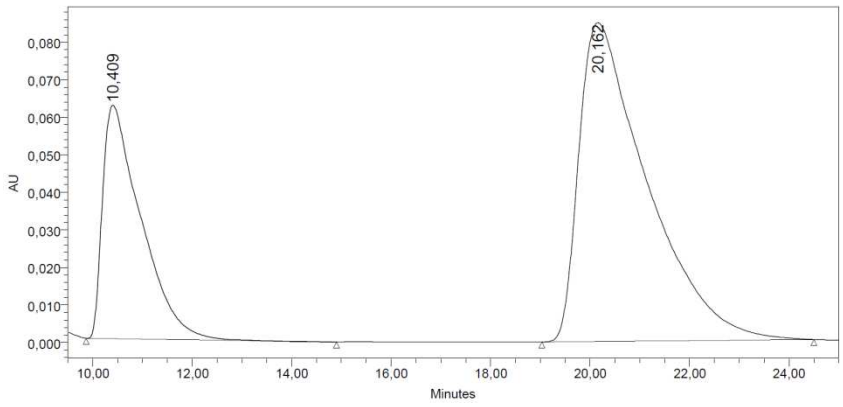


3cc

Chemical Formula: $C_{22}H_{27}NO_3$
Molecular Weight: 353,45

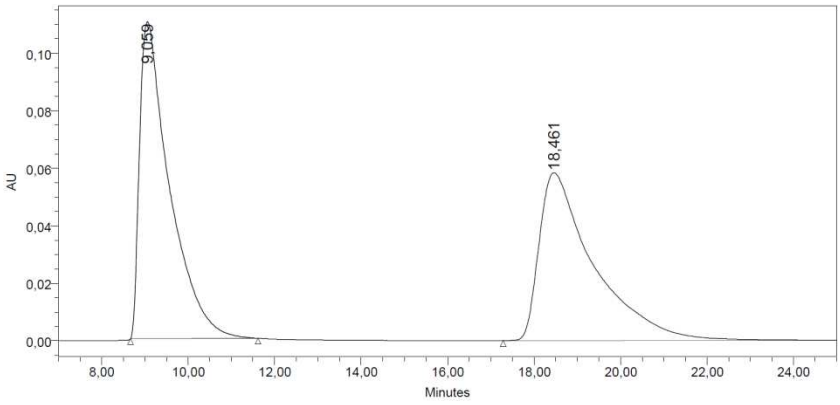
3cc, colorless oil; IR (neat): ν_{max} = 2991, 2922, 2857, 1703, 1661, 1610, 1568, 1591, 1196, 727 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.26 (m, 3H), 7.04-7.02 (m, 1H), 3.80-3.70 (m, 4H), 2.79-2.67 (m, 4H), 2.05 (s, 3H), 2.02 (s, 3H), 1.77 (s, 3H), 1.48 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 151.8, 138.8, 136.3, 135.2, 131.0, 128.5, 127.8, 127.1, 121.1, 117.9, 98.1, 68.6 (2C), 41.4, 38.6, 37.1, 24.6, 22.9, 17.6, 17.3, 13.1; HRMS (ES+) Calcd for $C_{22}H_{27}NNaO_3$ [M+Na^+]: 376.1889. Found: 376.1891.

*Chiral counterion approach (General procedure **3**):* **3cc**, 60 mg, 85% yield, [α_D] = –30.3 (*c* 1.0, $CHCl_3$, ee = 41%). Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1 mL/min, λ 312 nm. Retention time for major enantiomer = 20.2 min; for minor enantiomer = 10.4 min (ee = 41%).

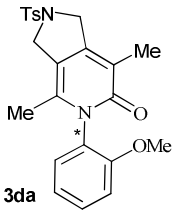


	RT	Area	% Area	Height
1	10,409	3350048	29,36	62230
2	20,162	8061658	70,64	84863

*Racemate (general procedure **1**):* Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 312 nm. Retention time for both enantiomers: 9.1 min and 18.5 min.



	RT	Area	% Area	Height
1	9,059	5297772	50,97	110274
2	18,461	5096109	49,03	58292

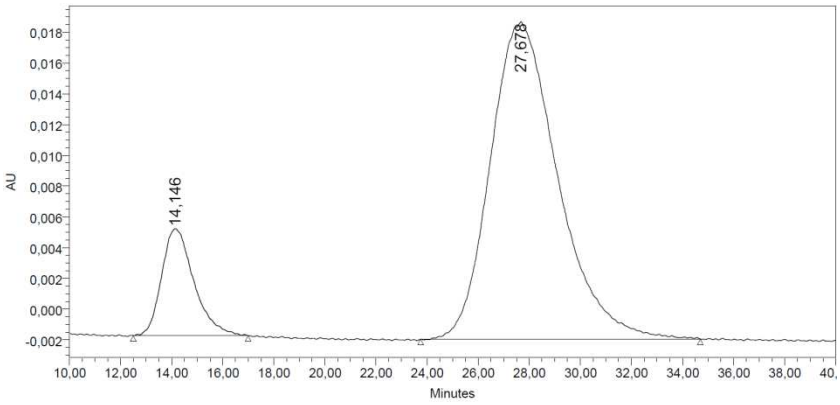


3da

Chemical Formula: $C_{23}H_{24}N_2O_4S$
Molecular Weight: 424,51

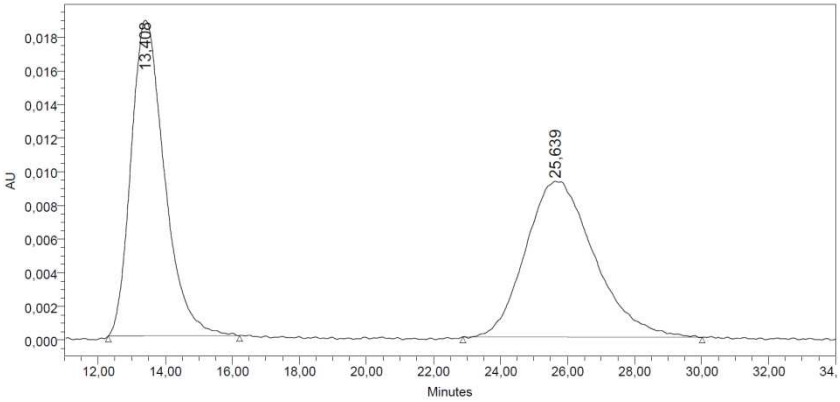
3da, white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, 2H, J = 8.2 Hz), 7.42-7.38 (m, 3H), 7.05-7.04 (m, 3H), 4.45 (s, 2H), 4.42 (s, 2H), 3.77 (s, 3H), 2.47 (s, 3H), 2.01 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2, 154.4, 146.0, 143.9, 136.7, 133.3, 130.2, 129.9 (2C), 129.2, 127.6 (2C), 127.2, 121.2, 119.5, 112.8, 112.1, 55.7, 52.2, 51.1, 21.5, 17.5, 13.1. Characterization data are in agreement with the one reported in the literature.[6]

*Chiral counterion approach (General procedure **3**):* **3da**, 32 mg, 38% yield; $[\alpha_D]$ = –14.3 (*c* 0.38, $CHCl_3$, ee = 72%). Chiral HPLC analysis: AS-H column, 60/40 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 254 nm. Retention time for major enantiomer = 27.7 min; for minor enantiomer = 14.1 min (ee = 72%).

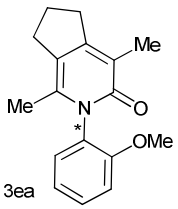


	RT	Area	% Area	Height
1	14,146	610845	13,91	6953
2	27,678	3780522	86,09	20619

*Racemate (general procedure **1**):* Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 312 nm. Retention time for both enantiomers: 13.4 min and 25.6 min.



	RT	Area	% Area	Height
1	13,408	1299972	49,69	18749
2	25,639	1315955	50,31	9248

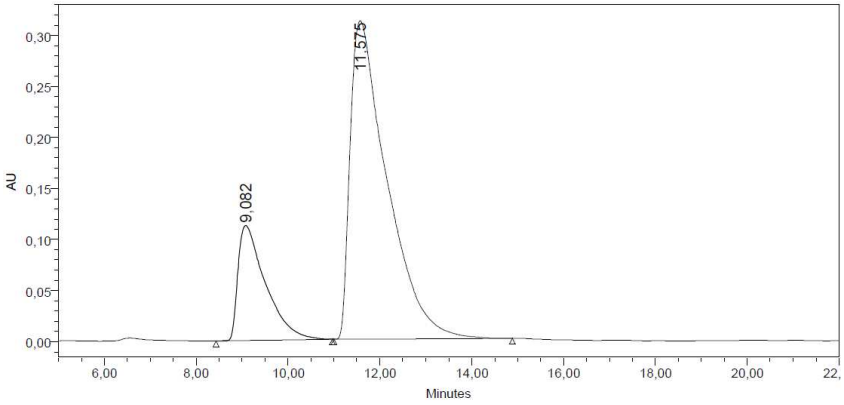


3ea

Chemical Formula: $C_{17}H_{19}NO_2$
Molecular Weight: 269,34

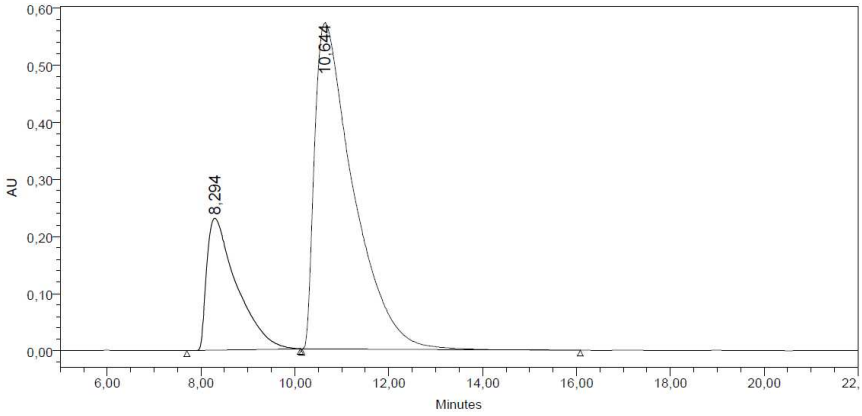
3ea, white solid; mp = 63 °C; IR (neat): ν_{max} = 2930, 1644, 1625, 1575, 1502, 1460, 1277, 1246, 1043, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.35 (m, 1H), 7.10-7.00 (m, 3H), 3.77 (s, 3H), 2.79 (t, 2H, J = 7.6 Hz), 2.72 (apparent t, 2H, J = 8.0 Hz), 2.07 (s, 3H), 2.07-2.00 (m, 2H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 154.7, 154.6, 135.8, 129.6, 129.5, 128.4, 121.1, 120.0, 119.7, 112.0, 55.7, 31.9, 29.8, 24.5, 17.4, 13.2. HRMS (ES+) Calcd for $C_{17}H_{19}NNaO_2$ $[M+Na]^+$: 292.1308. Found: 292.1317.

*Chiral counterion approach (General procedure **3**):* **3ea**, 35 mg, 65% yield; $[\alpha_D]$ –15.6 (*c* 0.67, $CHCl_3$, ee = 58%). Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 220 nm. Retention time for major enantiomer = 11.6 min; for minor enantiomer = 9.1 min (ee = 58%).



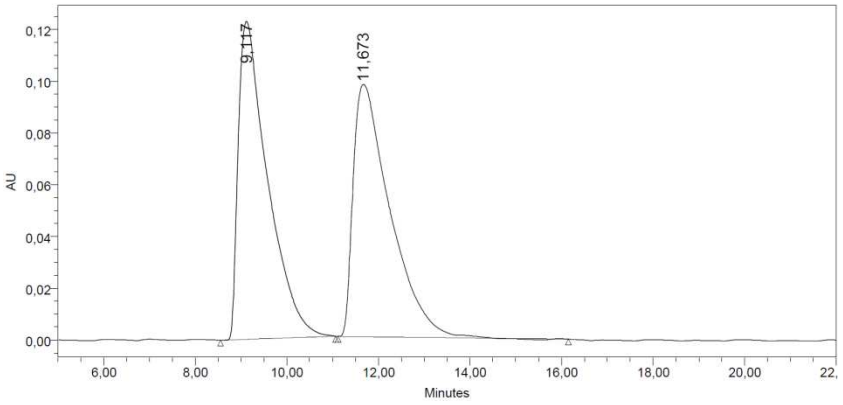
	RT	Area	% Area	Height
1	9,082	4678097	21,22	112595
2	11,575	17367702	78,78	312055

*Chiral ligand approach (General procedure **4**):* **3ea**, 32 mg, 59% yield; $[\alpha_D]$ = –14.9 (*c* 1.25, $CHCl_3$, ee = 52%). Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 220 nm. Retention time for major enantiomer = 10.6 min; for minor enantiomer = 8.3 min (ee = 52%).



	RT	Area	% Area	Height
1	8,294	10201399	23,79	230970
2	10,644	32687019	76,21	571136

*Racemate (General procedure **1**):* Chiral HPLC analysis: AD-H column, 90/10 *n*-hexanes/*i*-PrOH, 1.0 mL/min, λ 220 nm. Retention time for both enantiomers: 9.1 min and 11.7 min.



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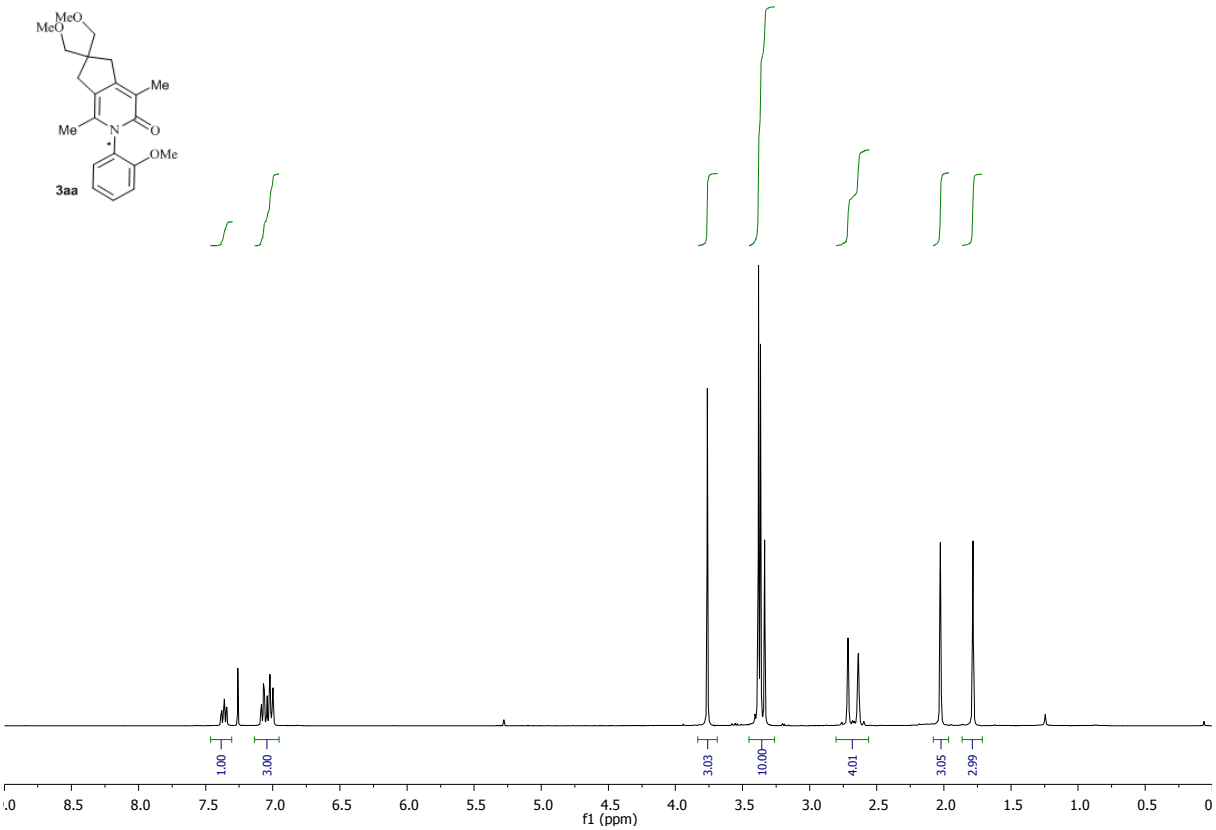
1	9,117	5459837	49,93	122850
2	11,673	5474391	50,07	97554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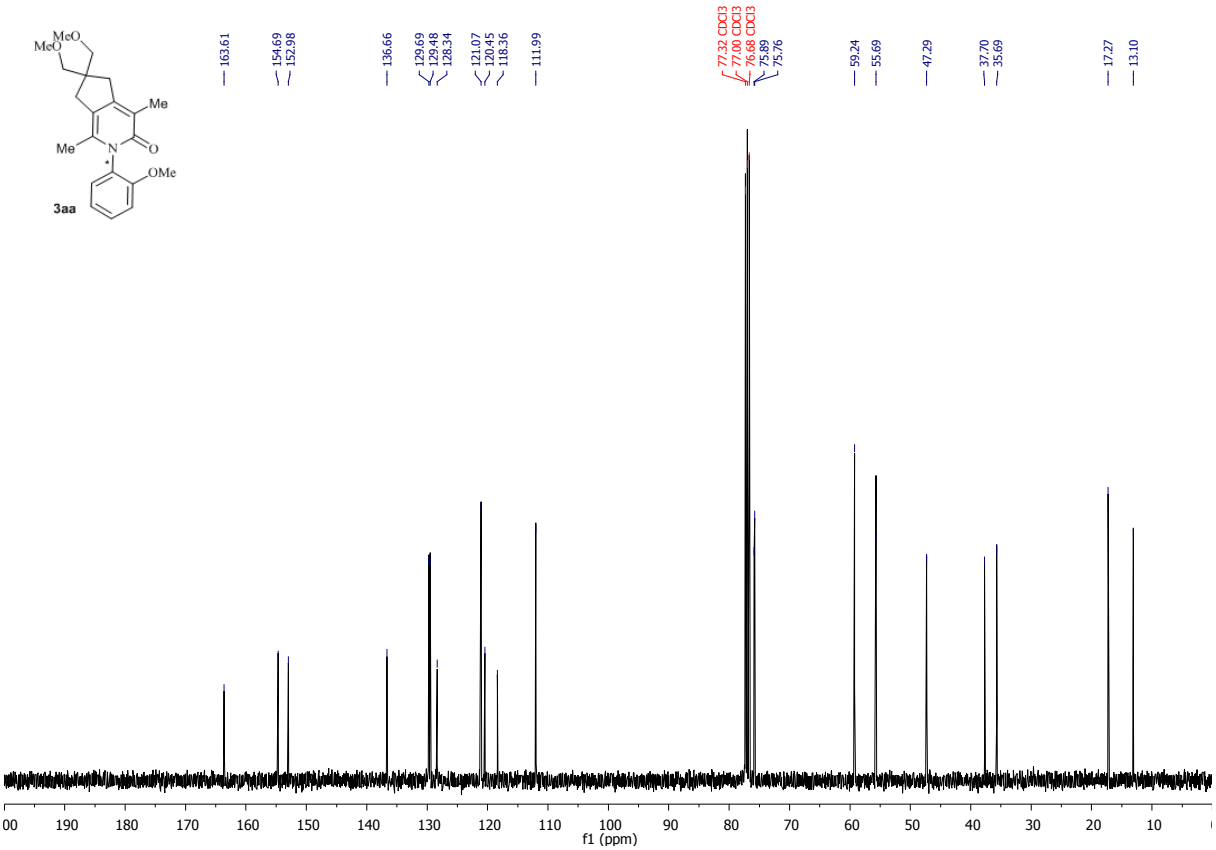
2.99
f1 (ppm)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OMe
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121.07
120.45
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111.99
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77.00 CDCl3
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35.69
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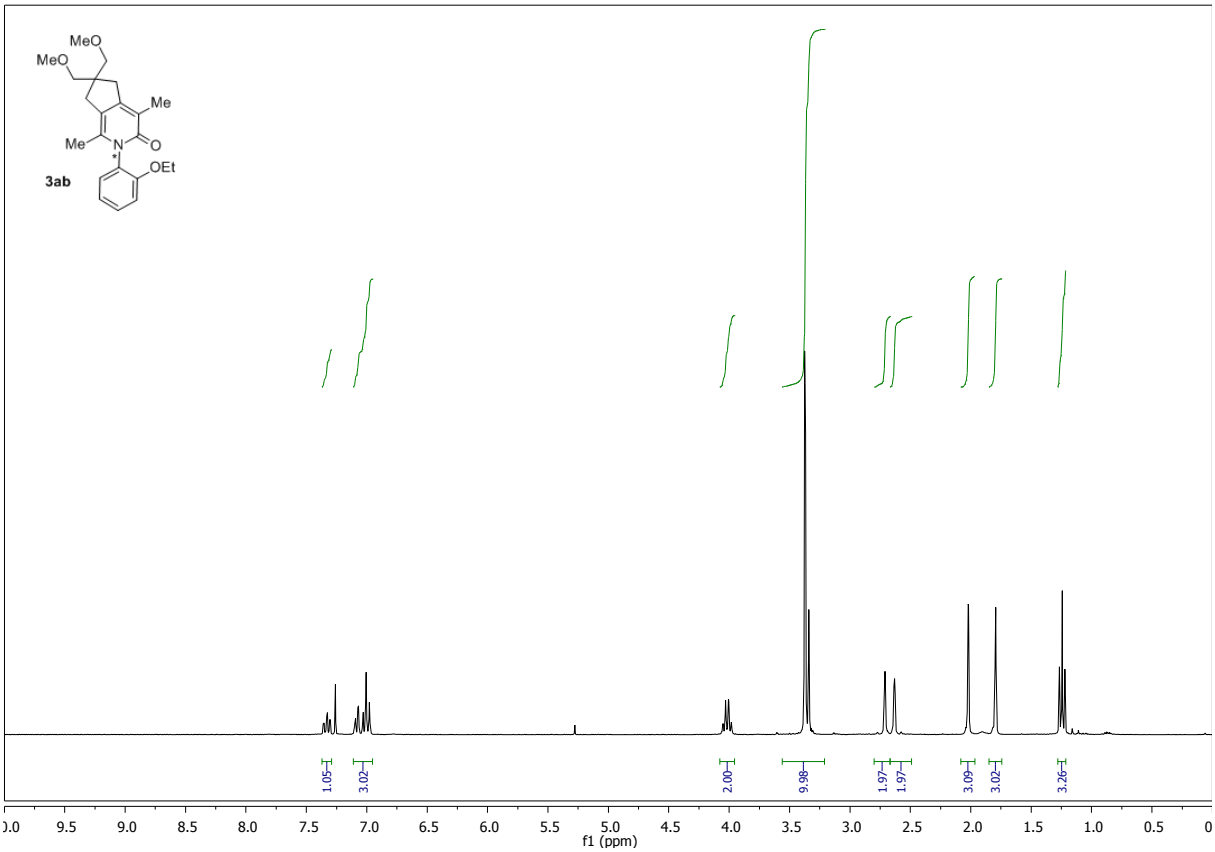
13.10
f1 (ppm)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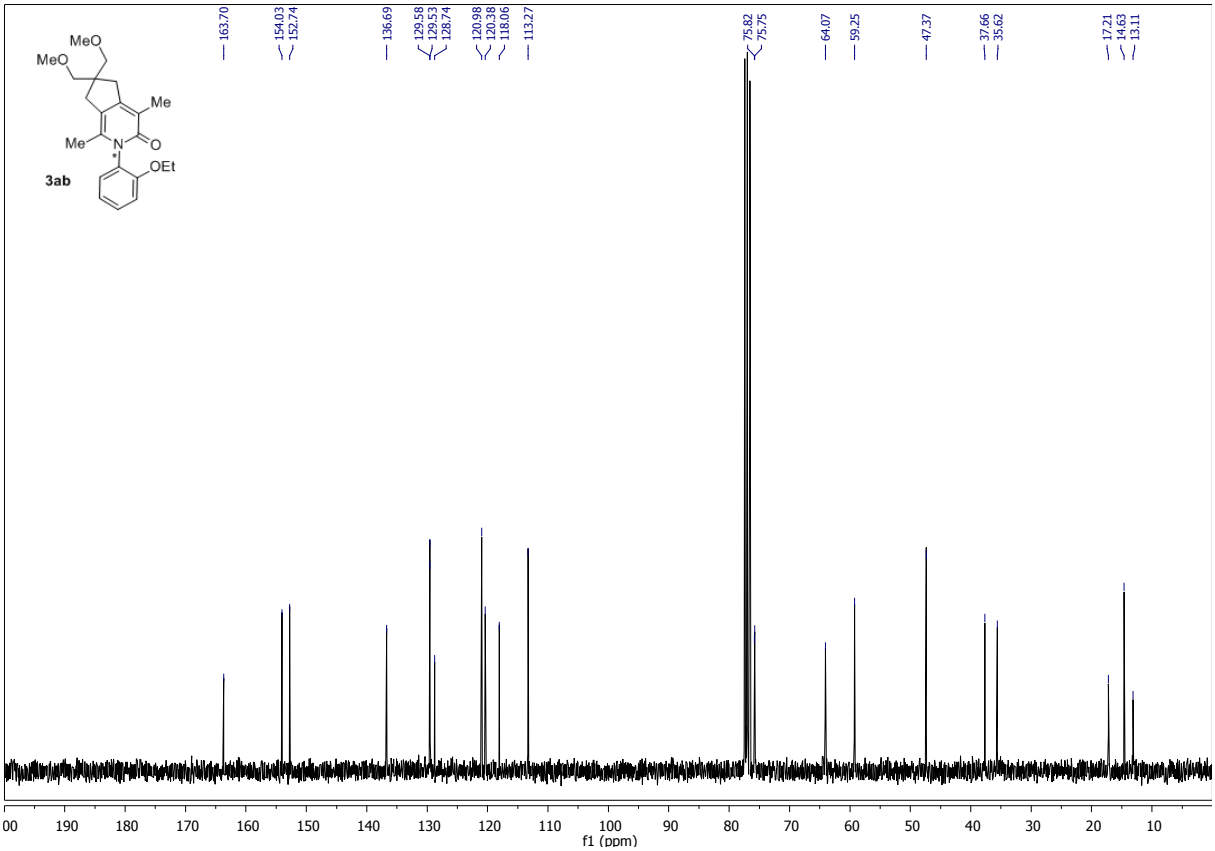
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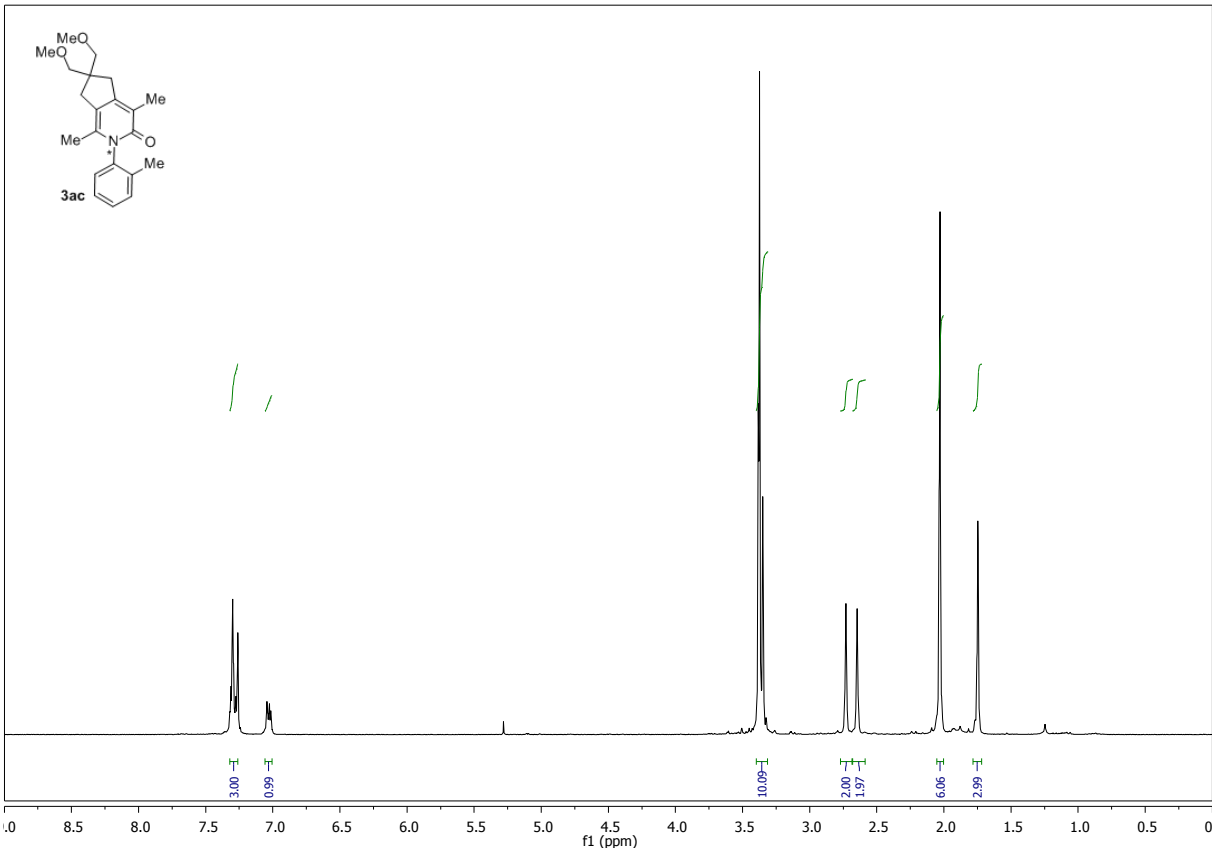
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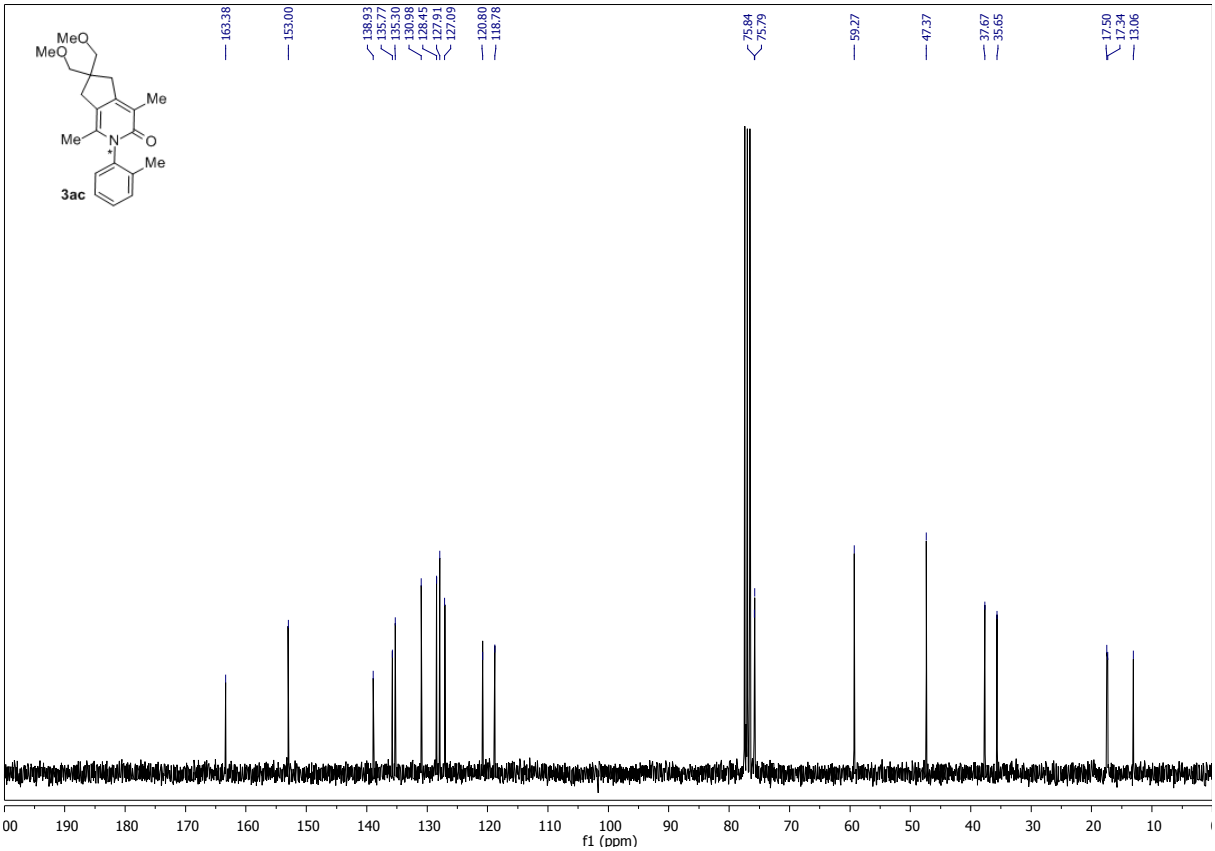
f1 (ppm)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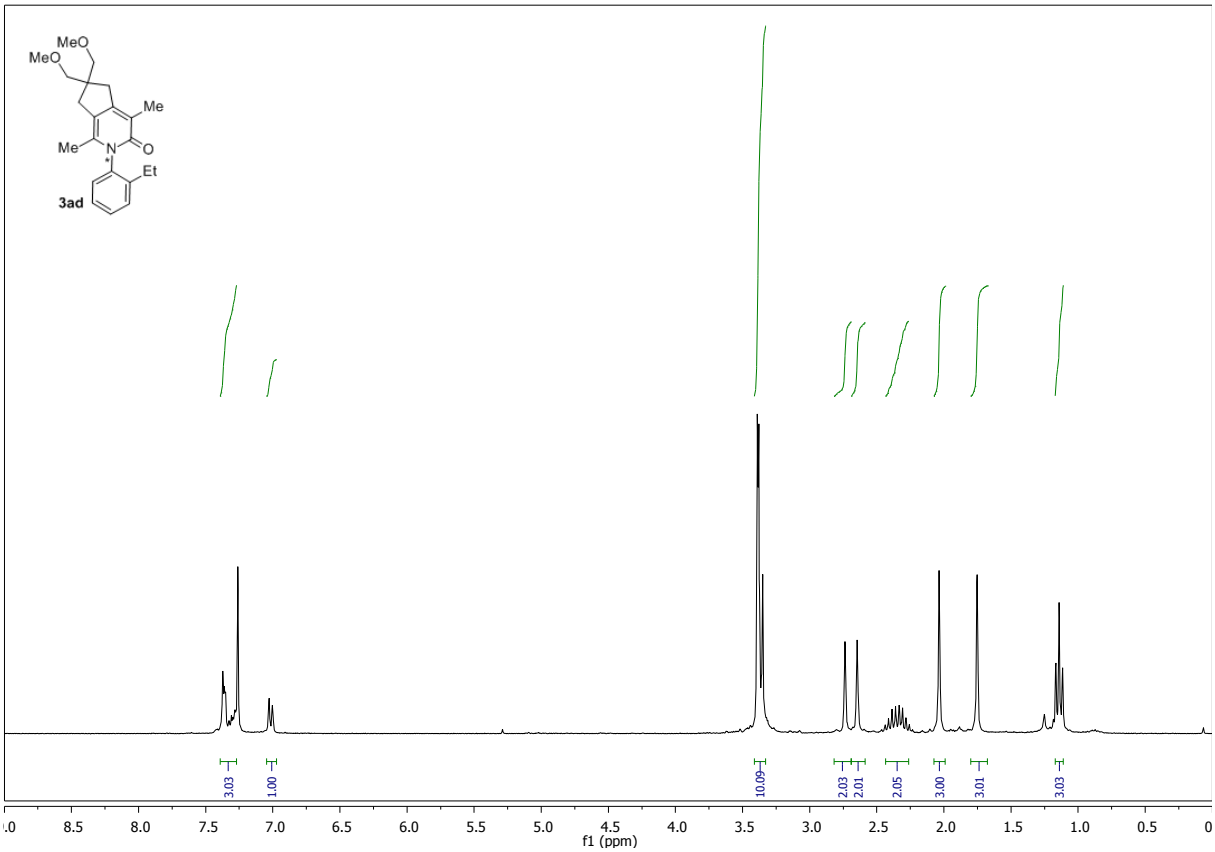
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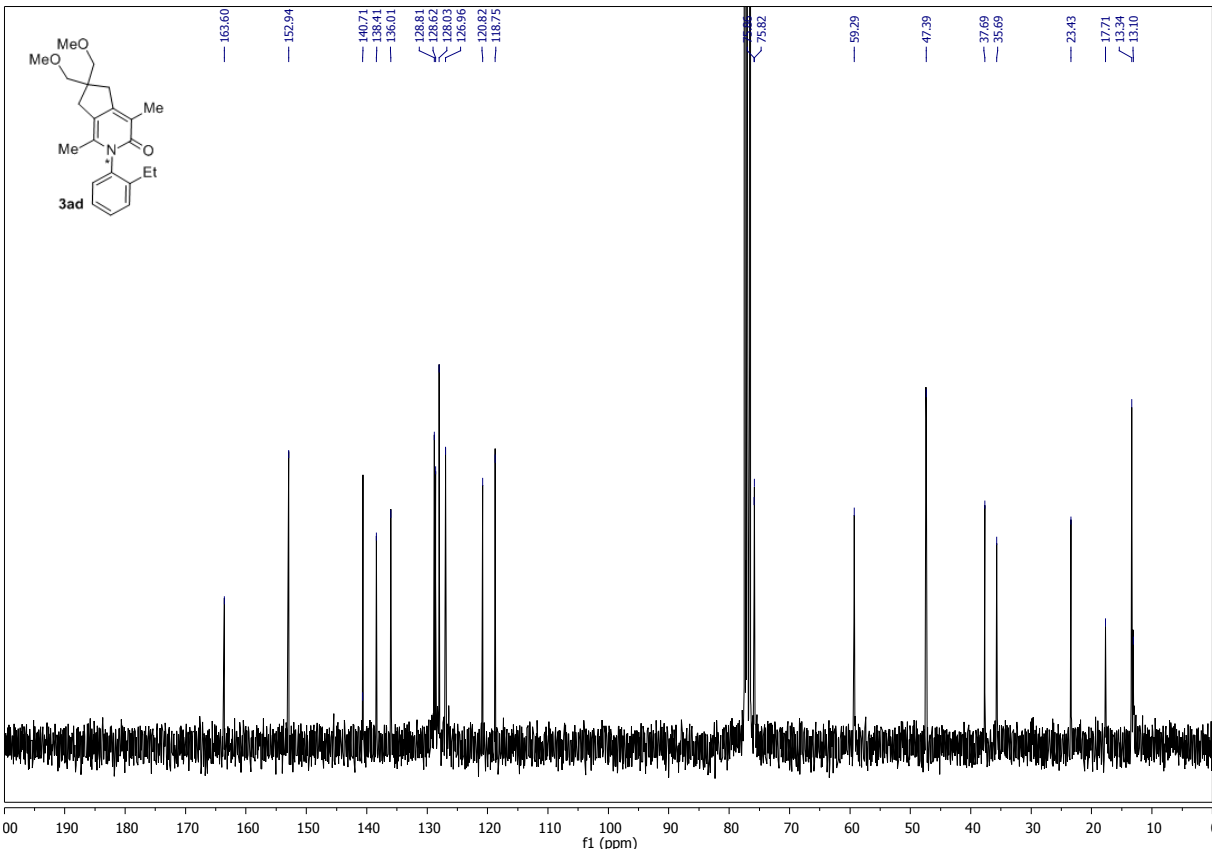
3.03
f1 (ppm)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17.71
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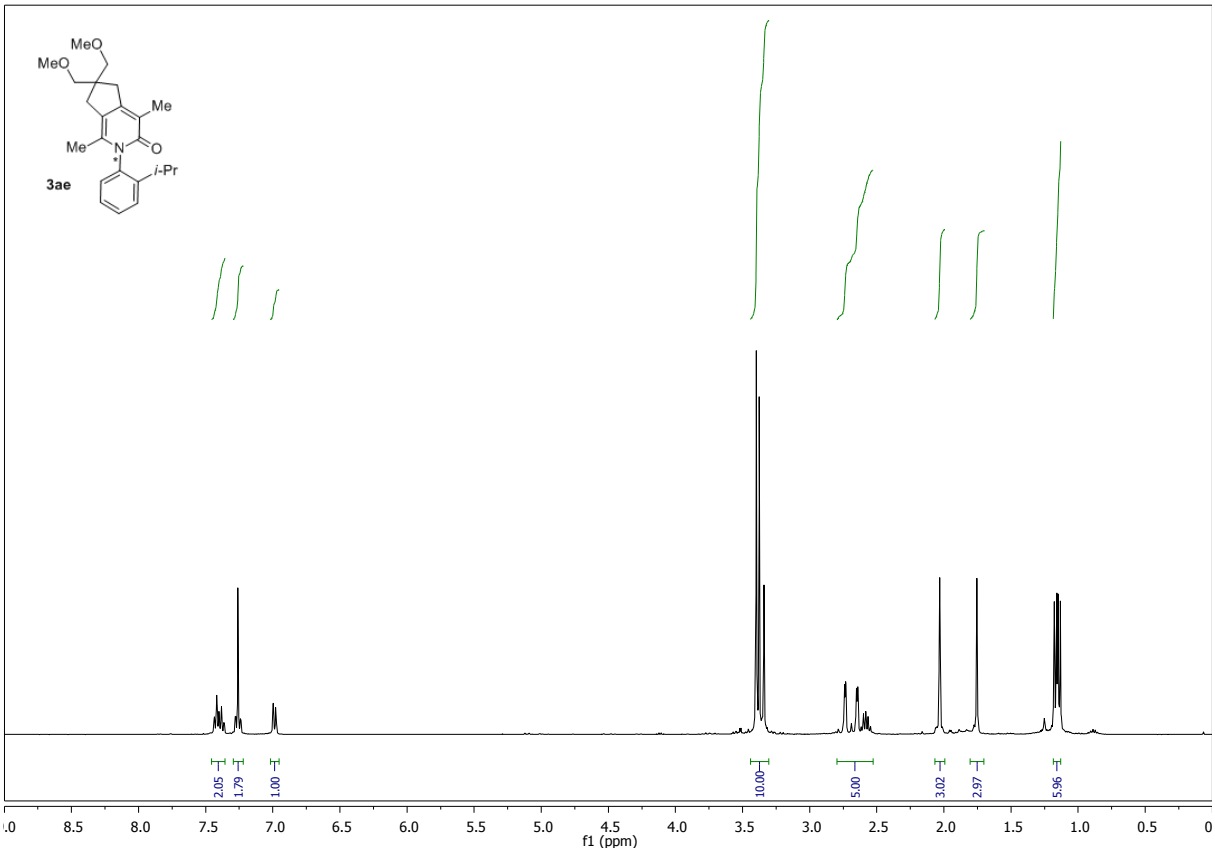
13.10
f1 (ppm)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Me
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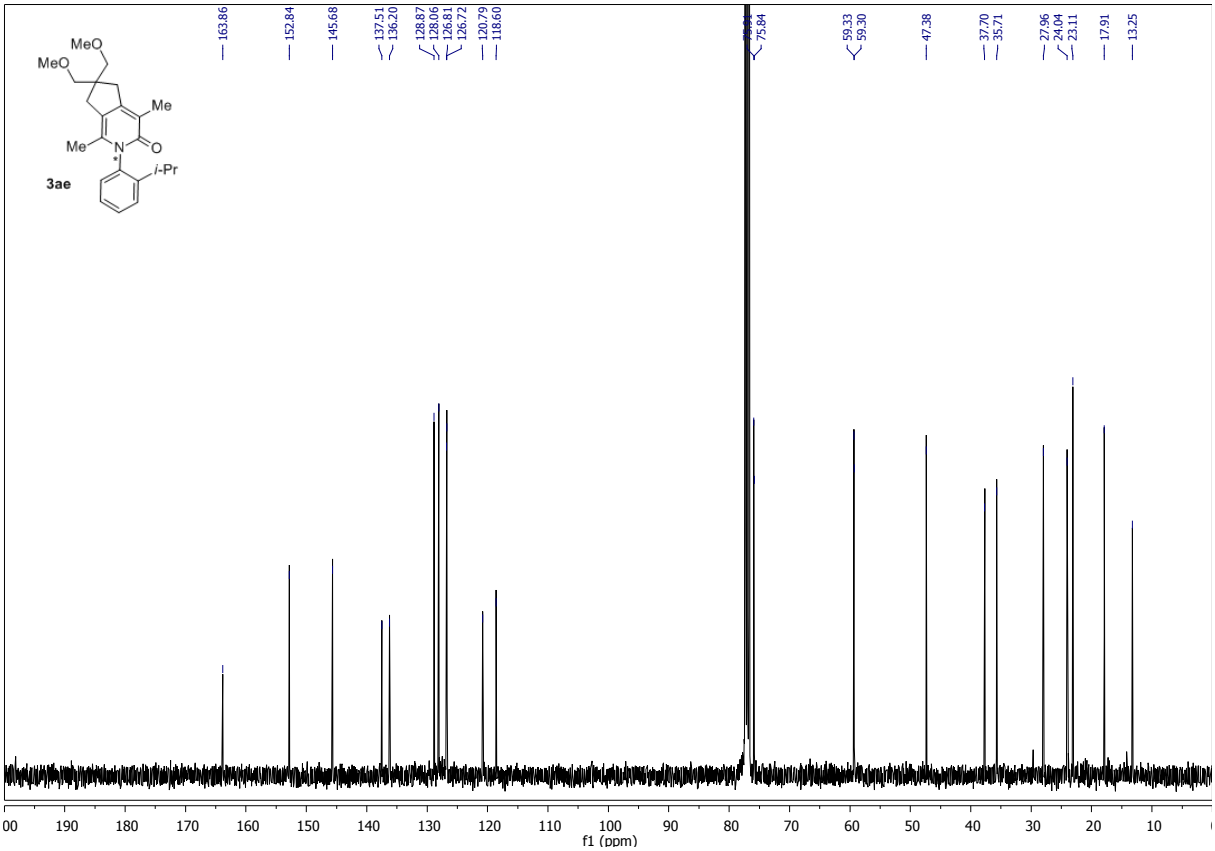
3.02
2.97
5.96
f1 (ppm)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Me
N
O
*
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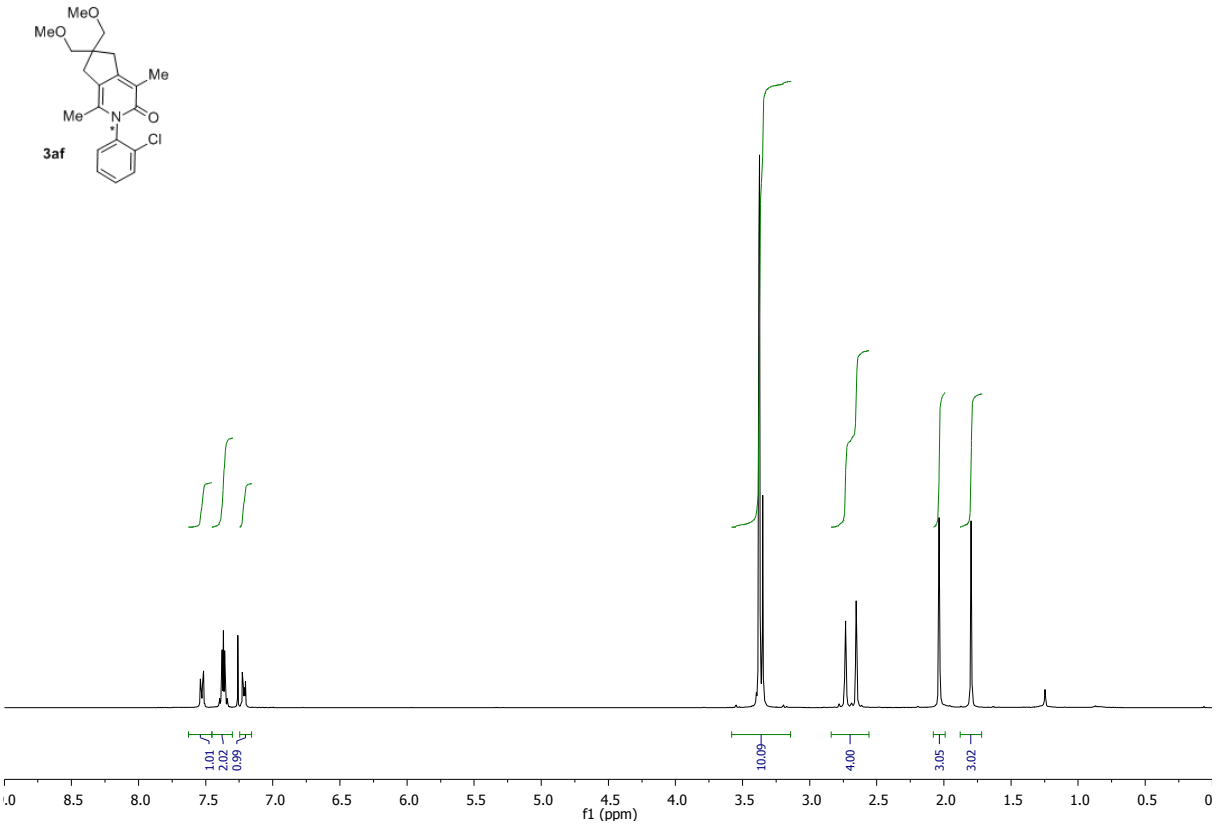
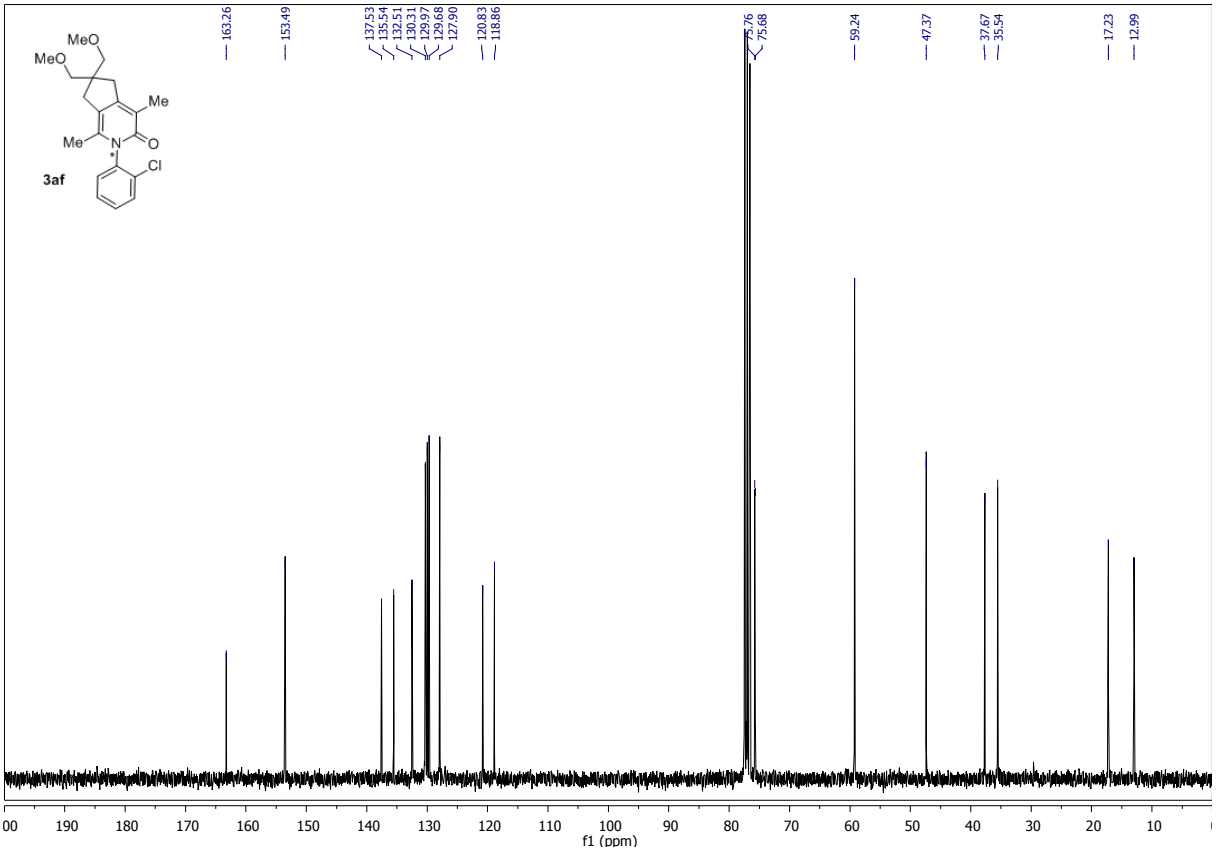
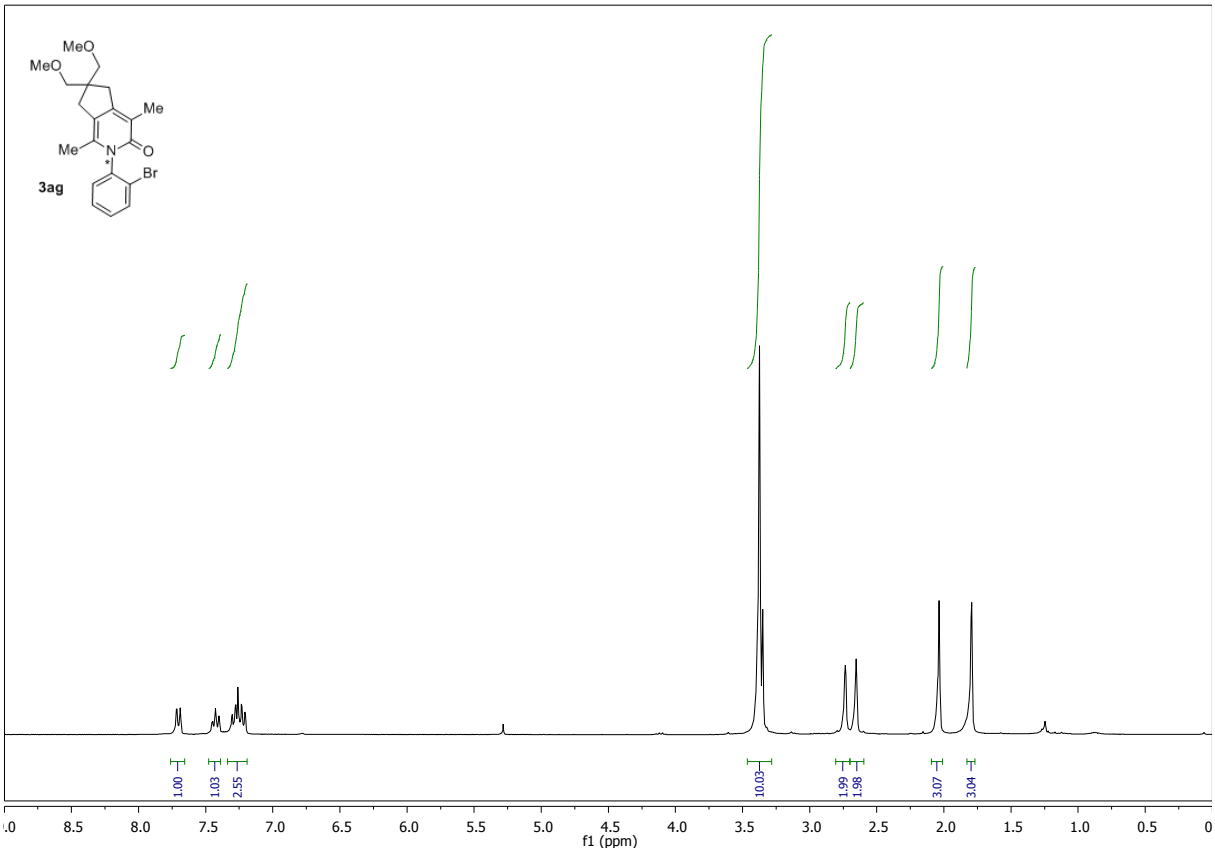
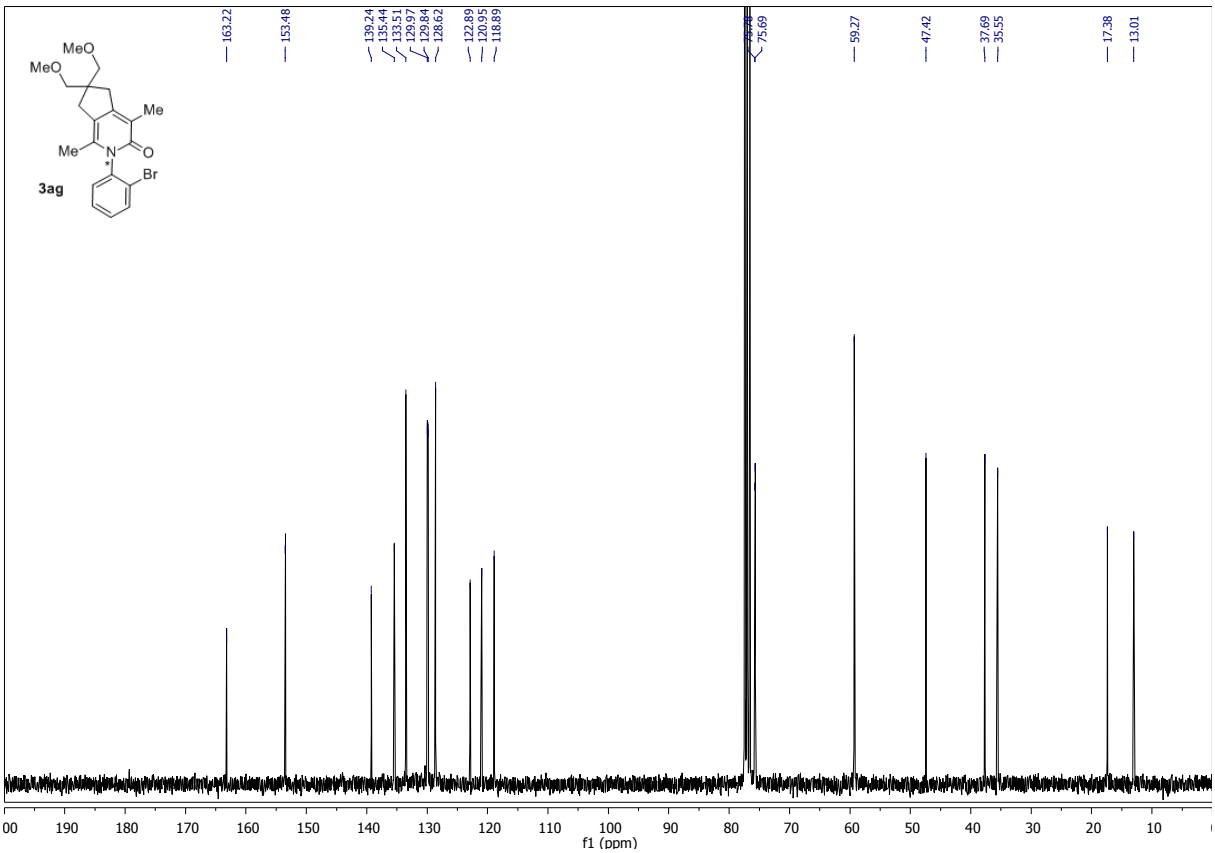
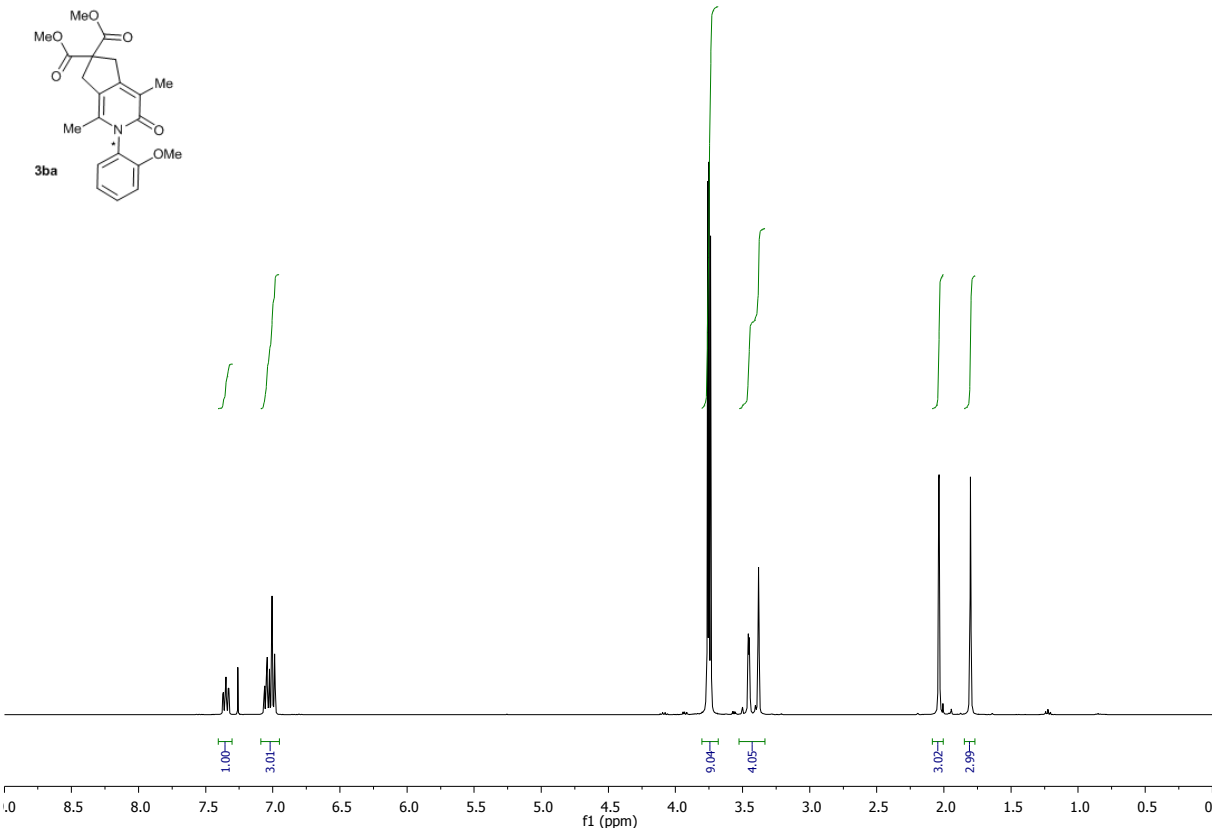
27.96
24.04
23.11
17.91
13.25
f1 (ppm)

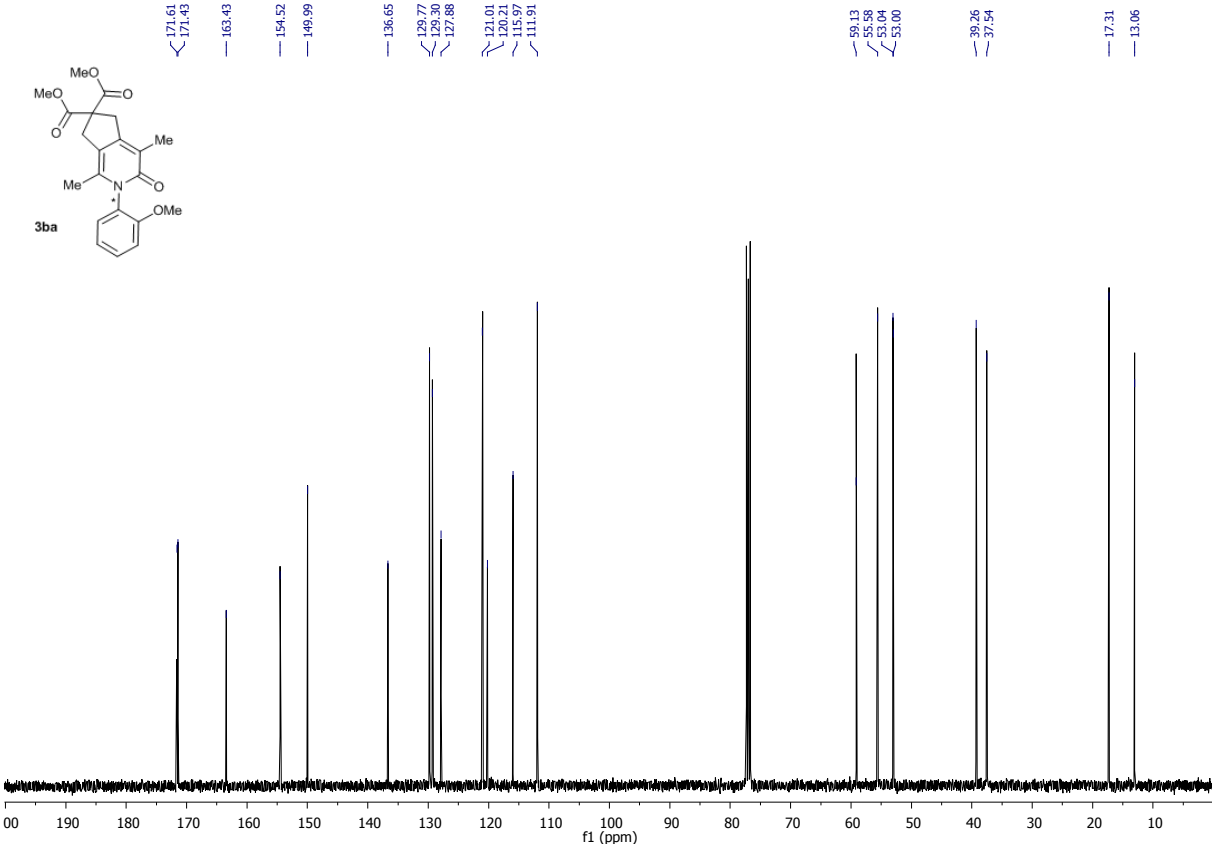

MeO
MeO
Me
Me
N
O
Cl
3af
1.01
2.02
0.99
10.09
4.00
3.05
3.02
f1 (ppm)

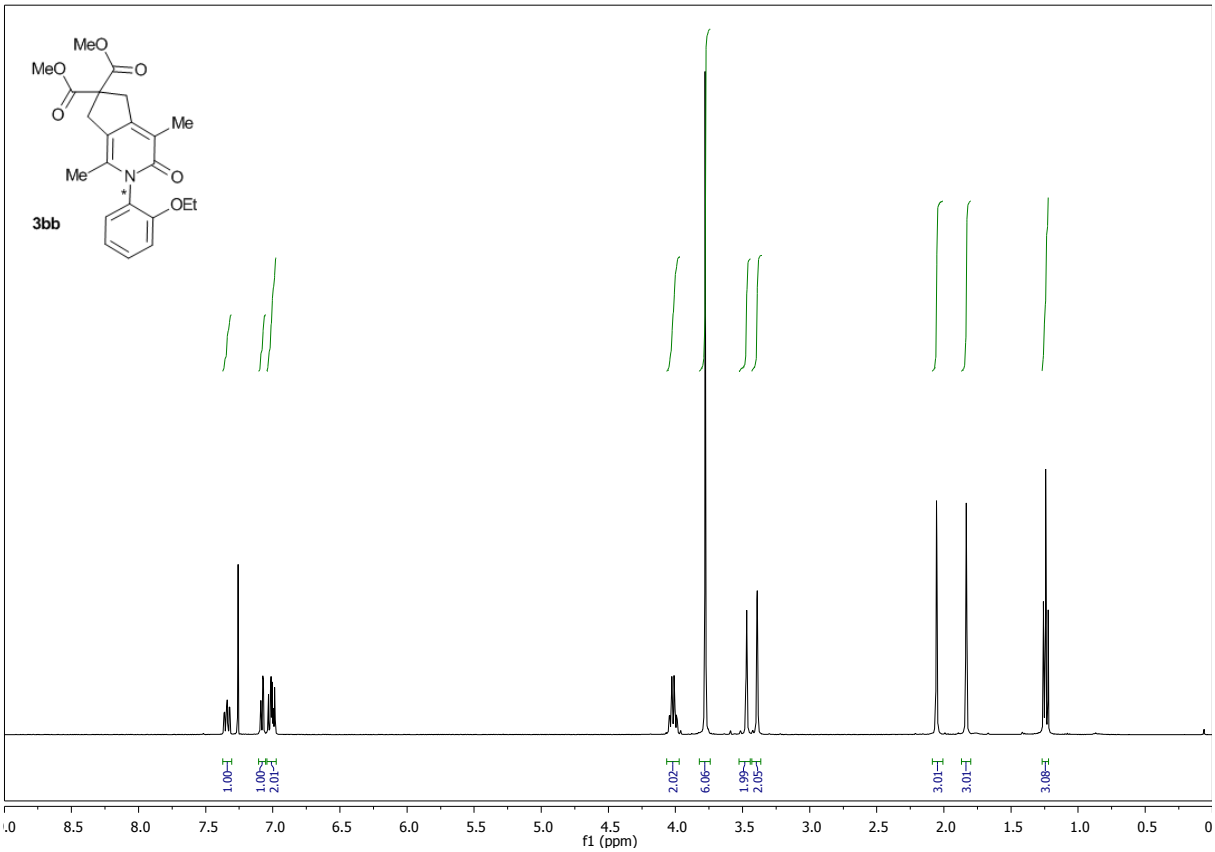

MeO
MeO
Me
Me
N
O
Cl
3af
163.26
153.49
137.53
135.54
132.51
130.31
129.97
129.68
127.90
120.83
118.86
75.76
75.68
59.24
47.37
37.67
35.54
17.23
12.99
f1 (ppm)

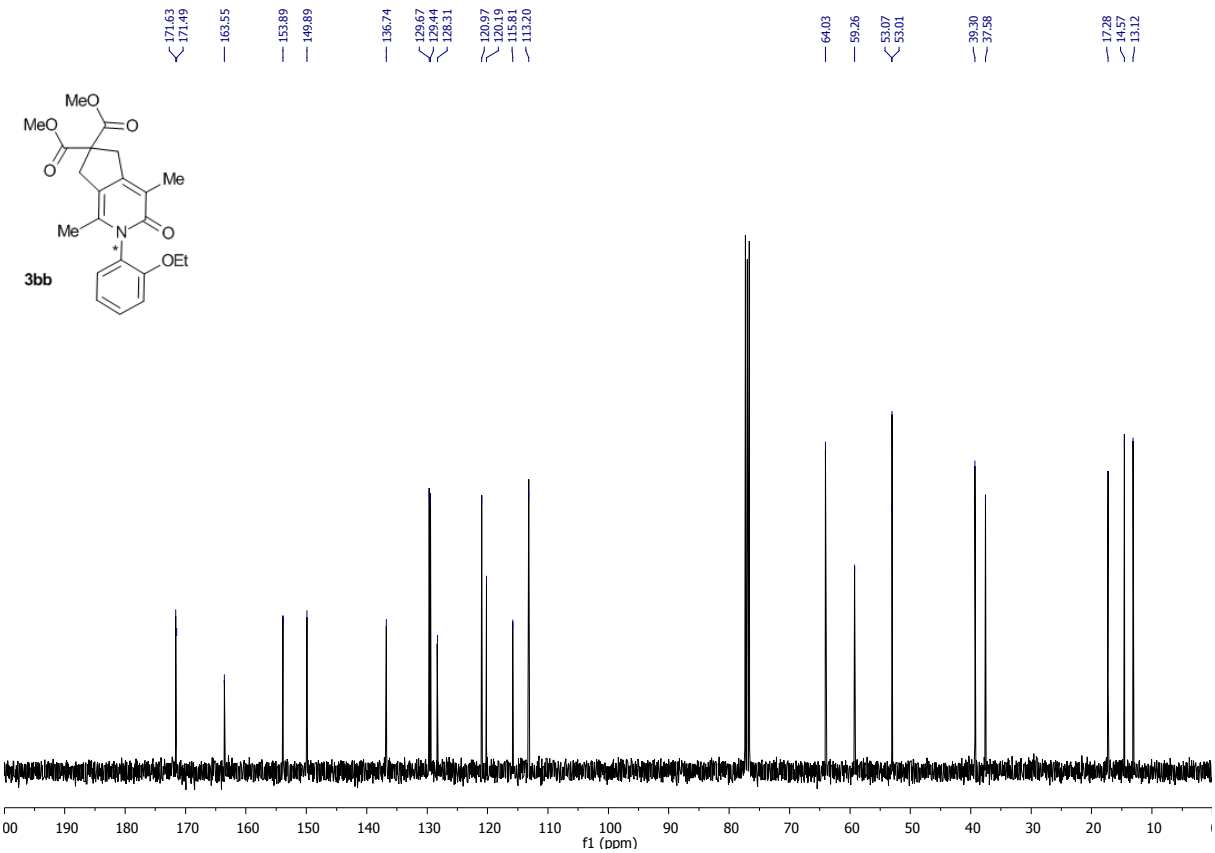

MeO
MeO
Me
Me
N
O
Br
3ag
1.00
1.03
2.55
10.03
1.99
1.98
3.07
3.04
f1 (ppm)

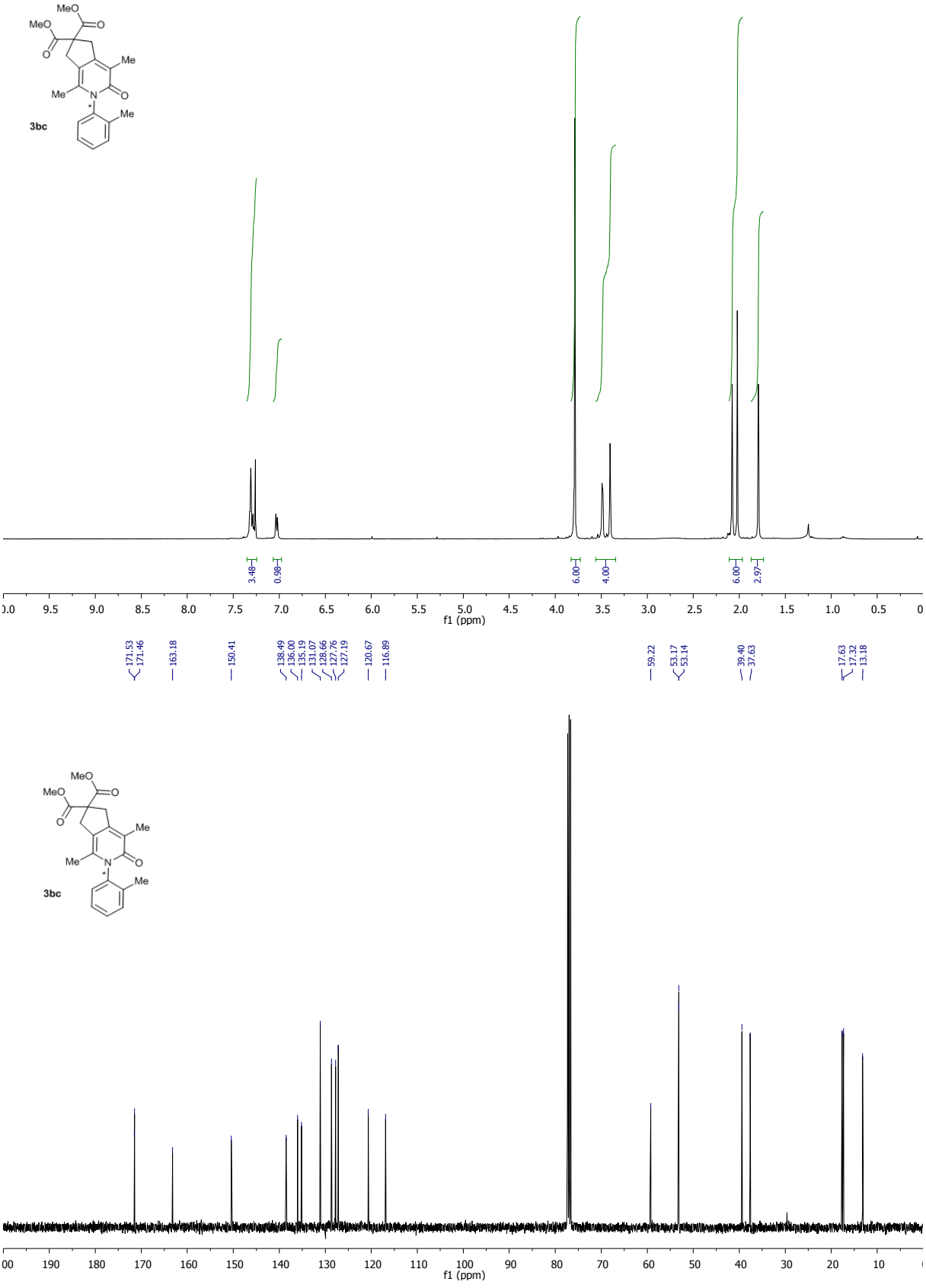

MeO
MeO
Me
Me
N
O
Br
3ag
163.22
153.48
139.24
135.44
133.51
129.97
129.84
128.62
122.89
120.95
118.89
75.69
59.27
47.42
37.69
35.55
17.38
13.01
f1 (ppm)

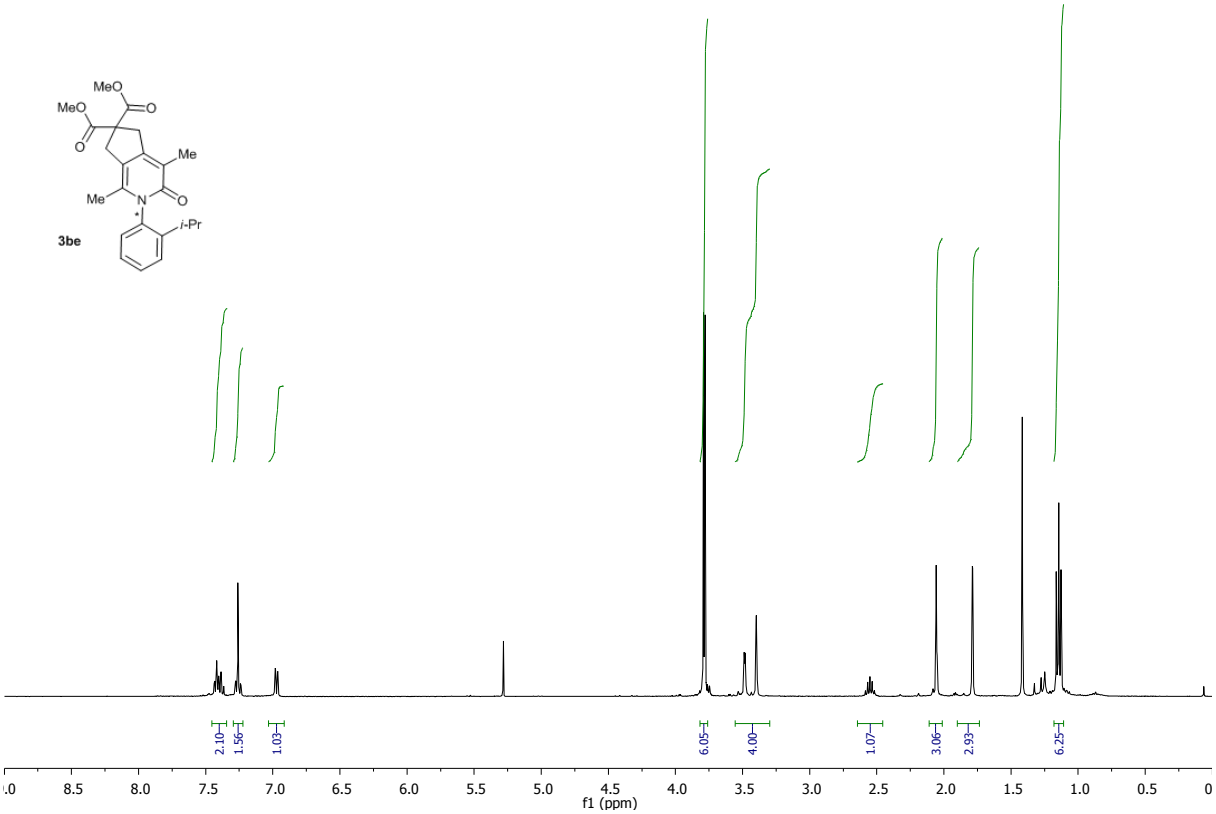

MeO
MeO
O
O
Me
Me
N
O
OMe
3ba
1.00
3.01
9.04
4.05
3.02
2.99
f1 (ppm)

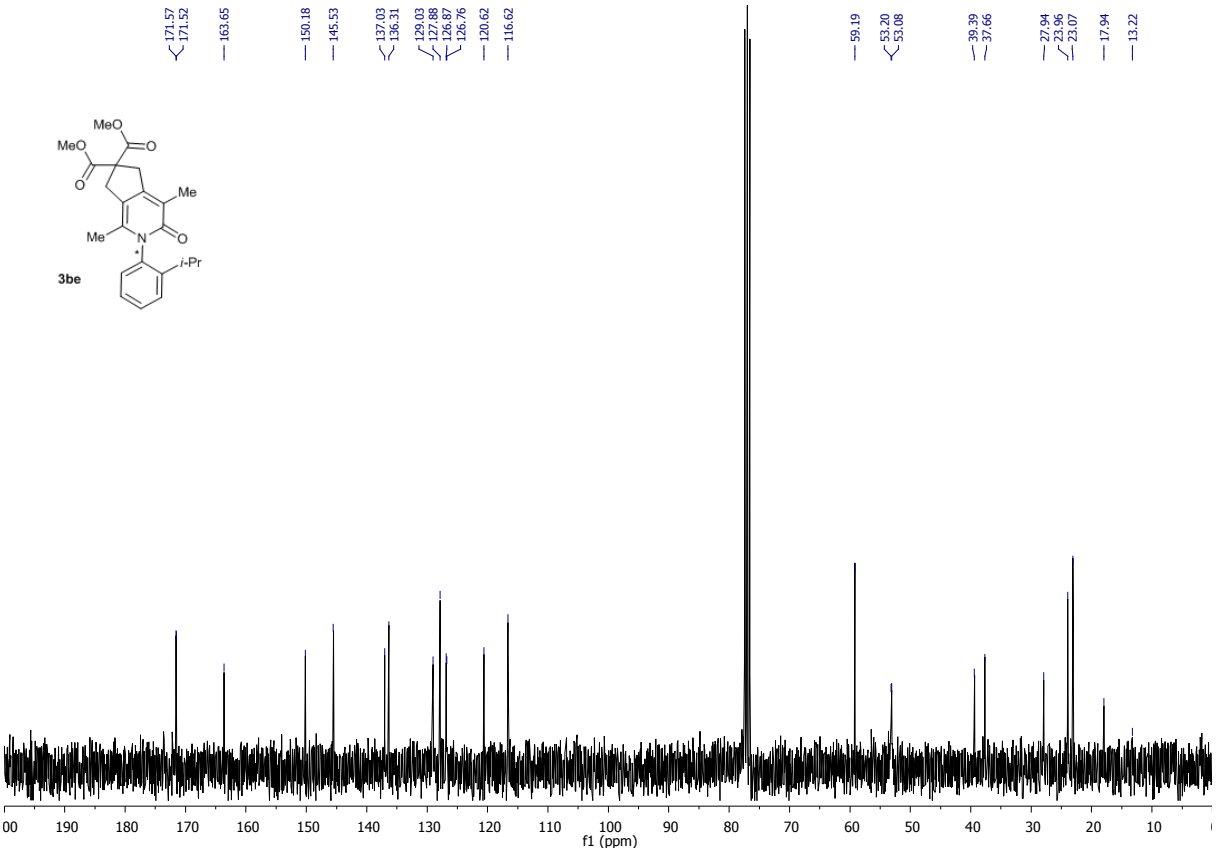

171.61
171.43
163.43
154.52
149.99
136.65
129.77
129.30
127.88
121.01
120.21
115.97
111.91
59.13
55.58
53.04
53.00
39.26
37.54
17.31
13.06
MeO
MeO
O
O
Me
Me
N
O
OMe
3ba
f1 (ppm)

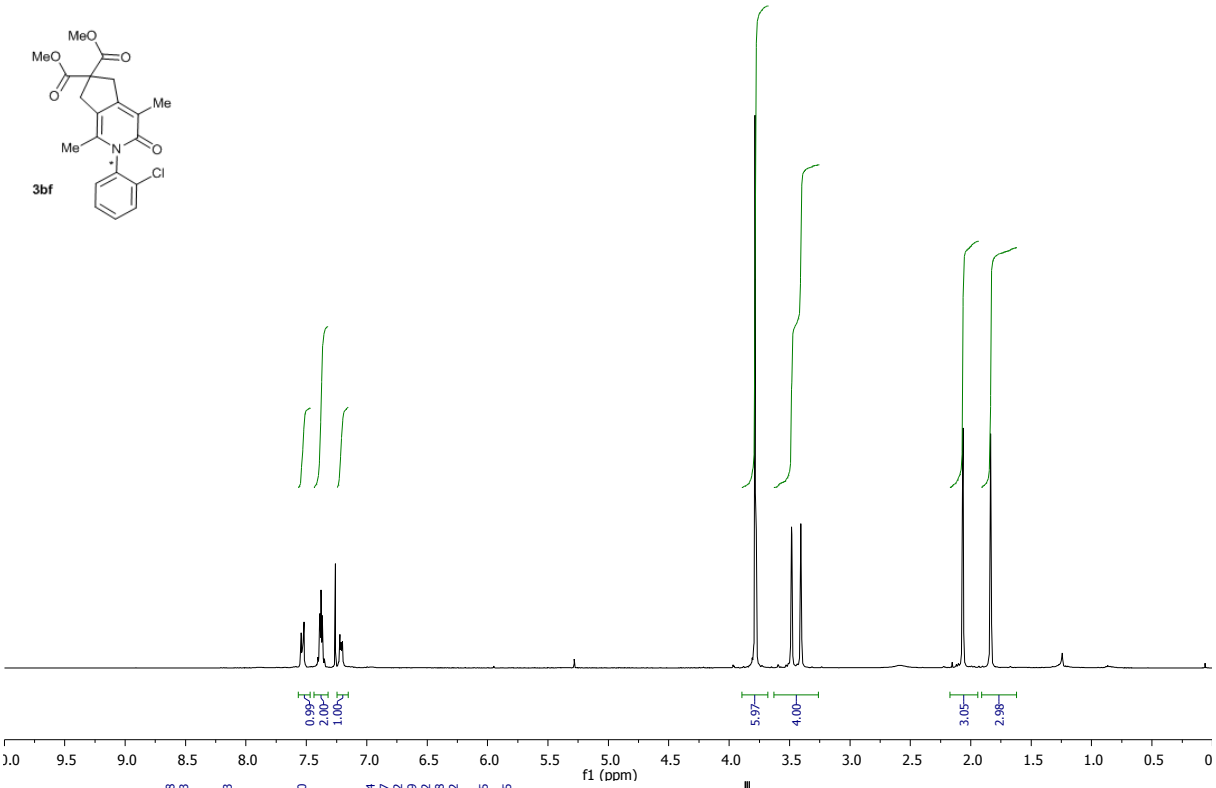

MeO
MeO
O
O
Me
Me
N
O
OEt
3bb
1.00
1.00
2.01
2.02
6.06
1.99
2.05
3.01
3.01
3.08
f1 (ppm)

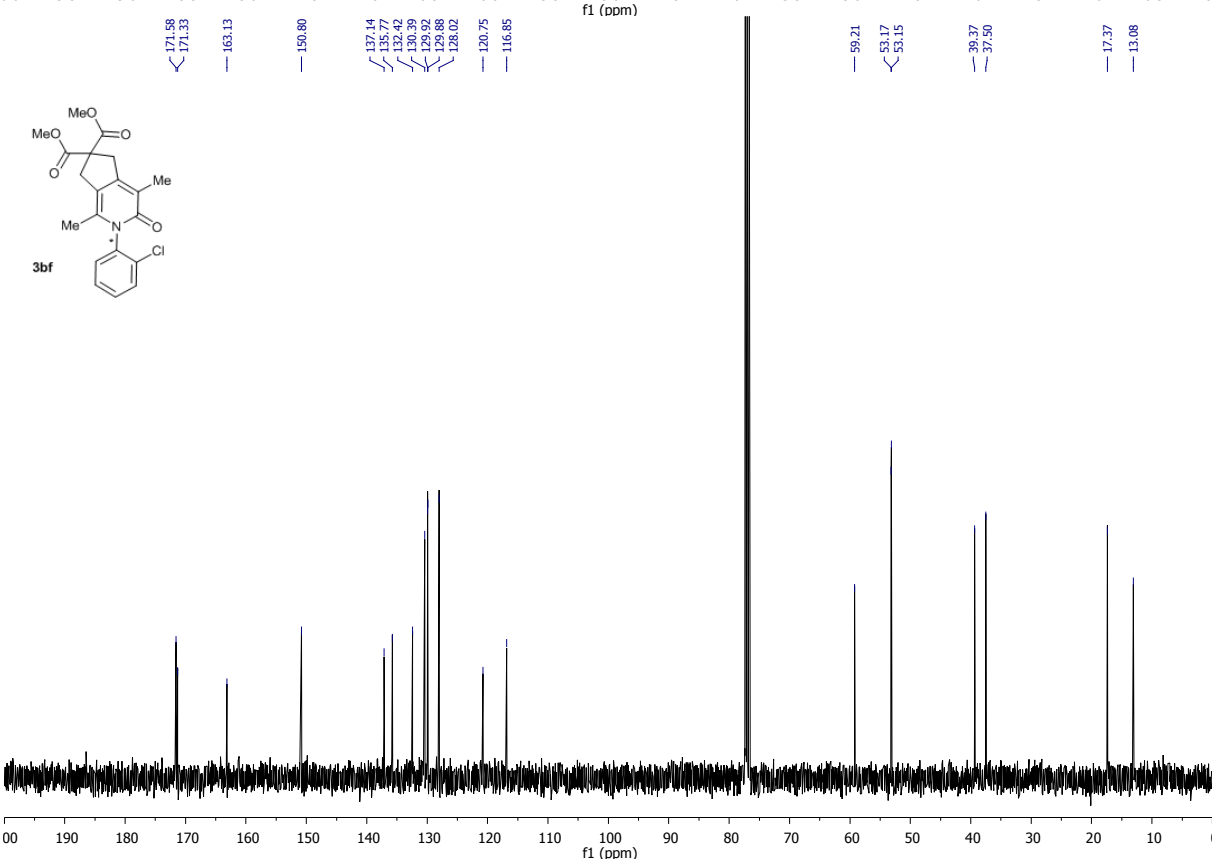

171.63
171.49
163.55
153.89
149.89
136.74
129.67
129.44
128.31
120.97
120.19
115.81
113.20
64.03
59.26
53.07
53.01
39.30
37.58
17.28
14.57
13.12
MeO
MeO
O
O
Me
Me
N
O
OEt
3bb
f1 (ppm)

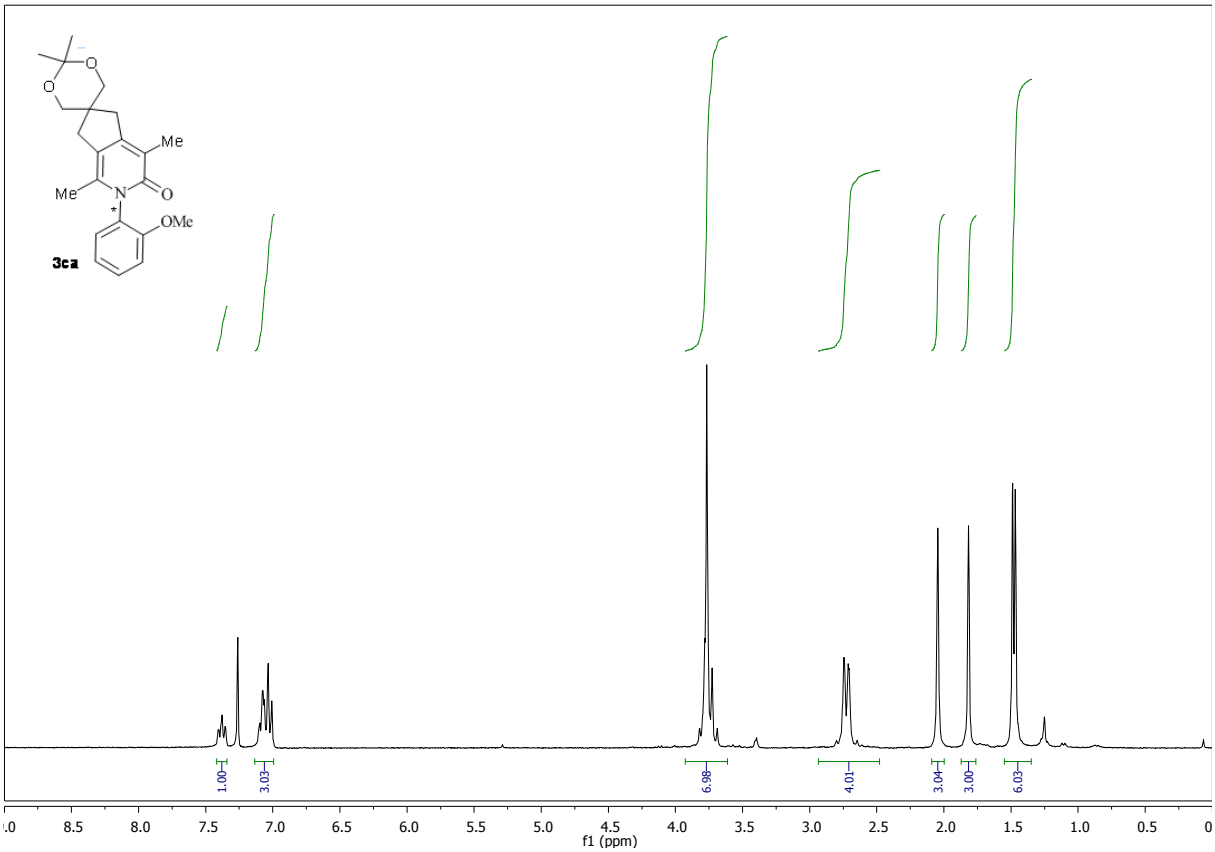

MeO
MeO
O
O
Me
Me
N
O
Me
3bc
3.48
0.98
6.00
4.00
6.00
2.97
f1 (ppm)
171.53
171.46
163.18
150.41
138.49
136.00
135.19
131.07
128.66
127.76
127.19
120.67
116.89
59.22
53.17
53.14
39.40
37.63
17.63
17.32
13.18
f1 (ppm)

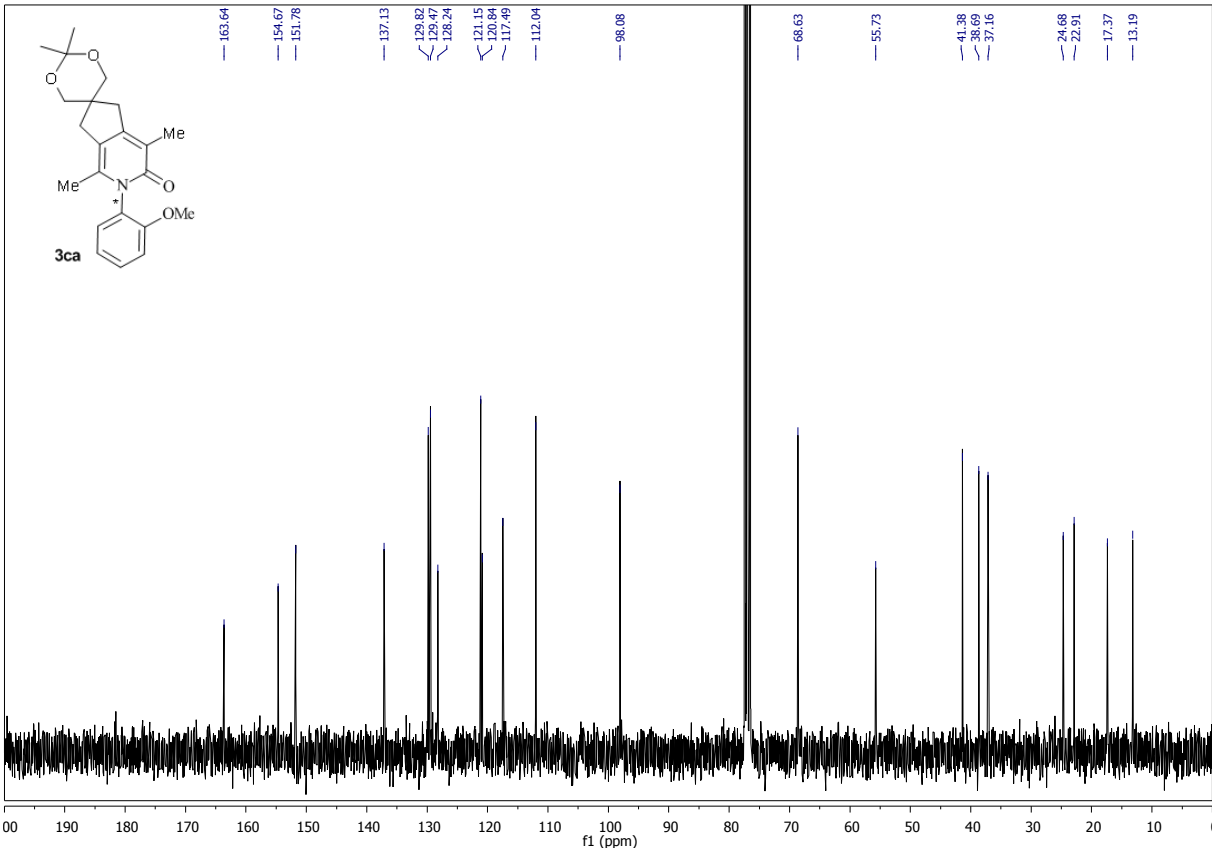

MeO
MeO
O
O
Me
Me
N
O
i-Pr
3be
2.10
1.56
1.03
6.05
4.00
1.07
3.06
2.93
6.25
f1 (ppm)

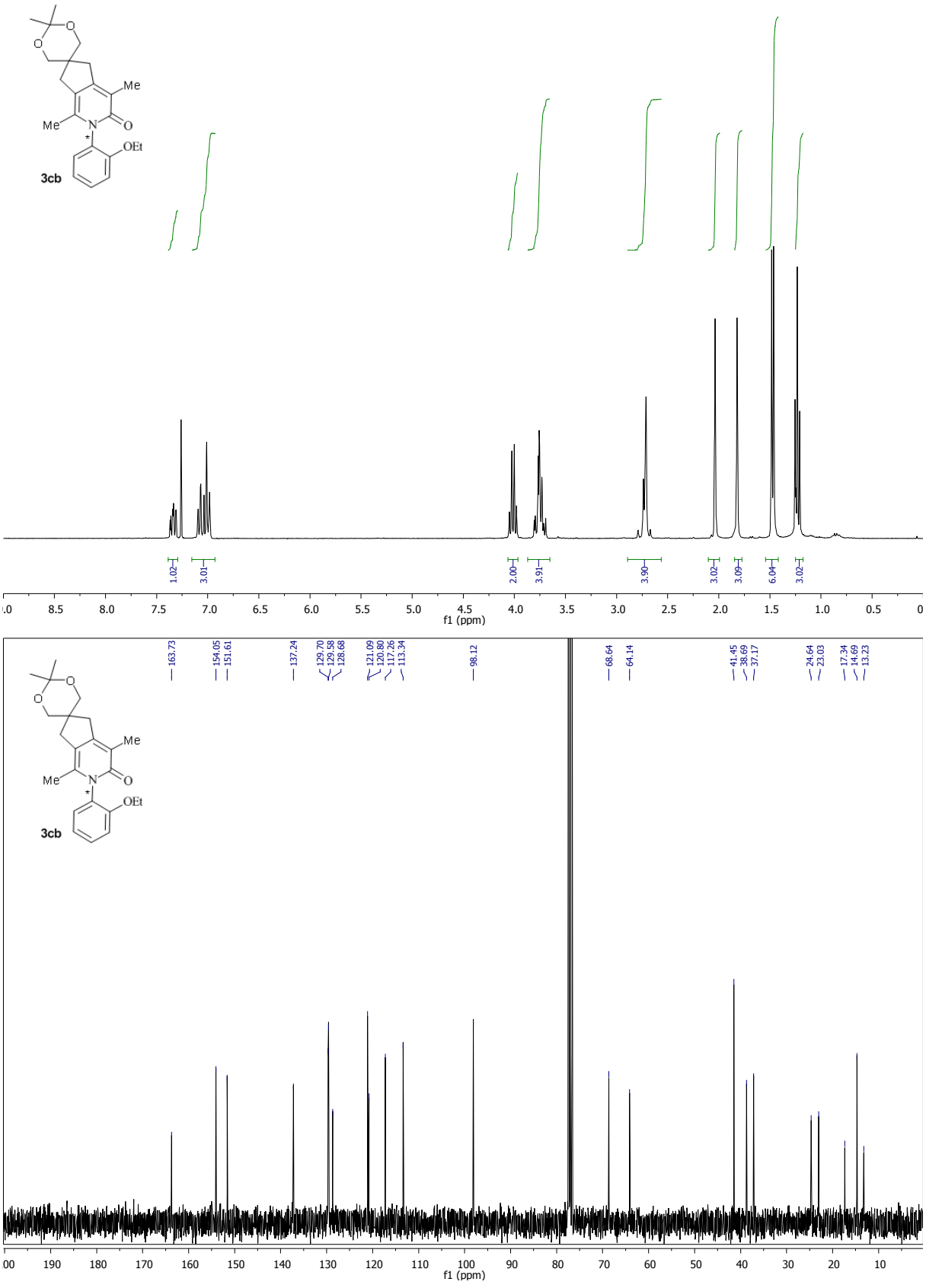

171.57
171.52
163.65
150.18
145.53
137.03
136.31
129.03
127.88
126.87
126.76
120.62
116.62
59.19
53.20
53.08
39.39
37.66
27.94
23.96
23.07
17.94
13.22
MeO
MeO
O
O
Me
Me
N
O
i-Pr
3be
f1 (ppm)

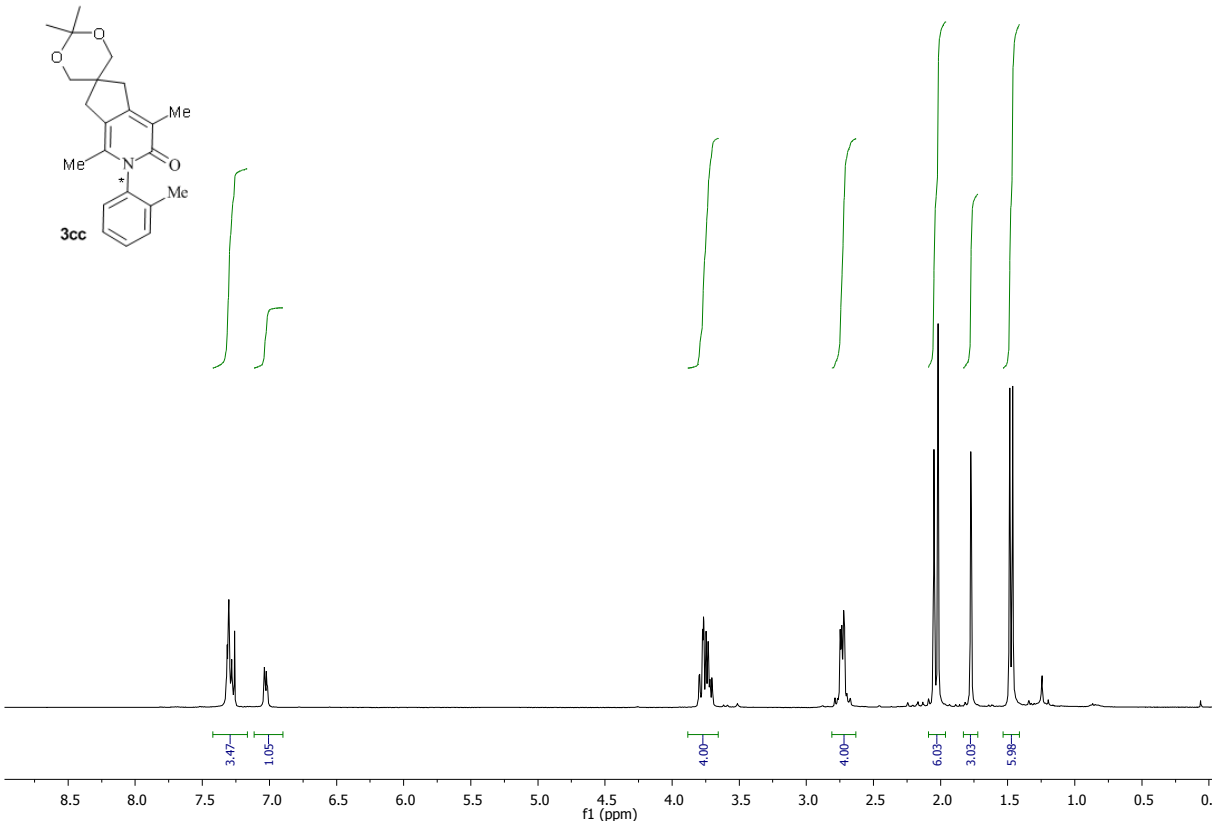

MeO
MeO
O
O
Me
Me
N
O
Cl
3bf
0.99
2.00
1.00
5.97
4.00
3.05
2.98
f1 (ppm)

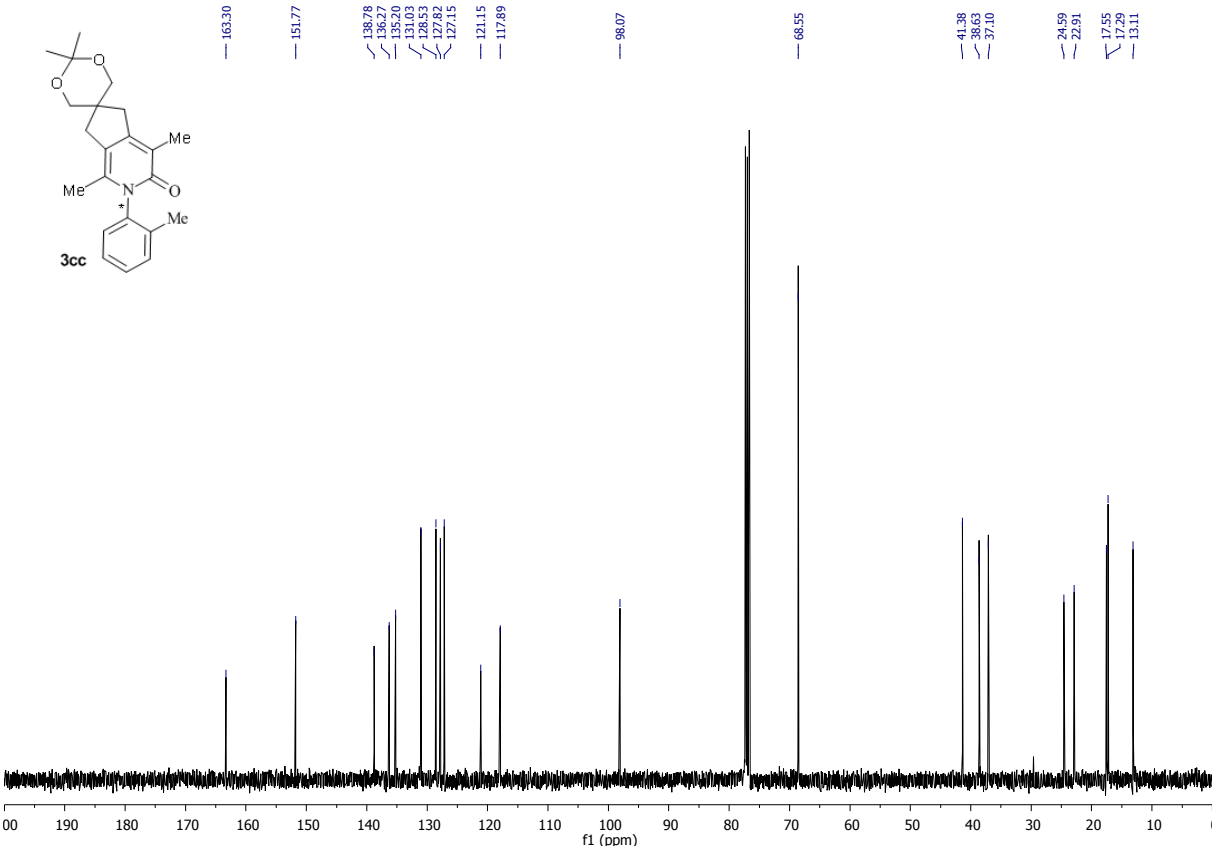

171.58
171.33
163.13
150.80
137.14
135.77
132.42
130.39
129.92
129.88
128.02
120.75
116.85
59.21
53.17
53.15
39.37
37.50
17.37
13.08
MeO
MeO
O
O
Me
Me
N
O
Cl
3bf
f1 (ppm)

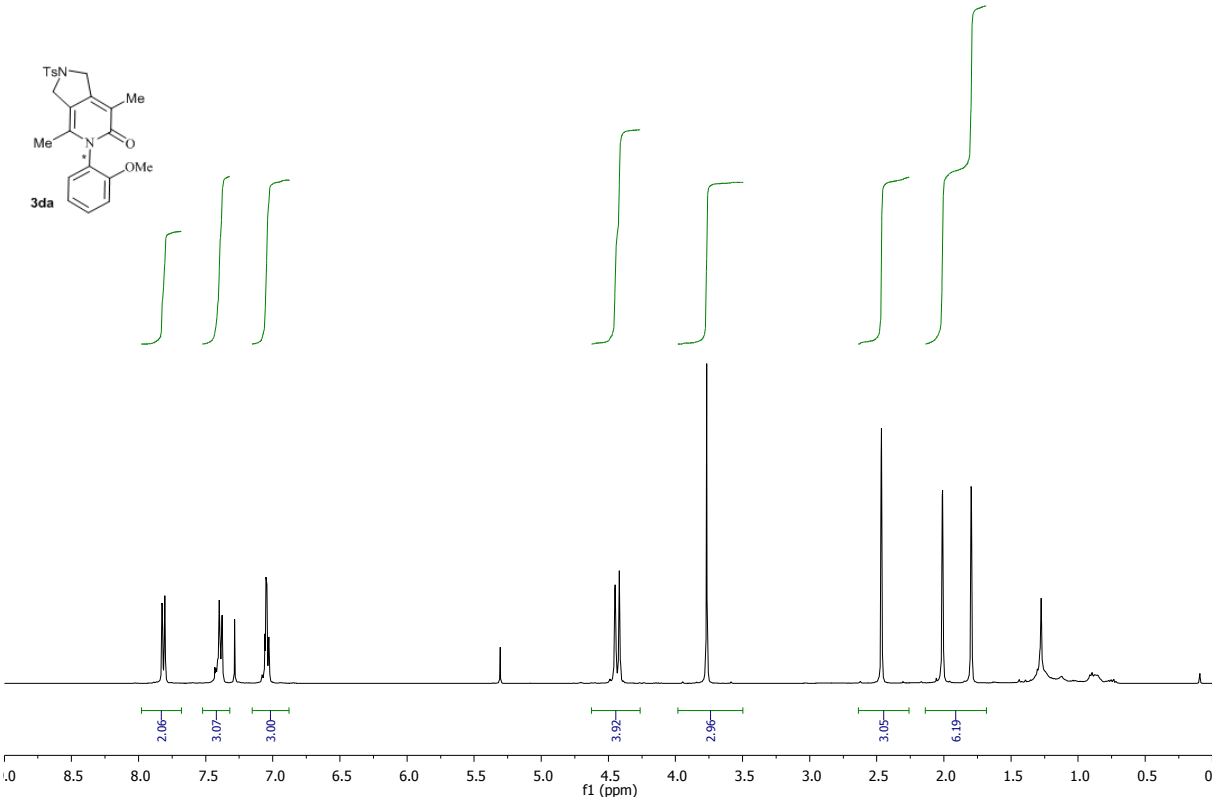

Me
Me
N
O
O
OMe
3ca
1.00
3.03
6.98
4.01
3.04
3.00
6.03
f1 (ppm)

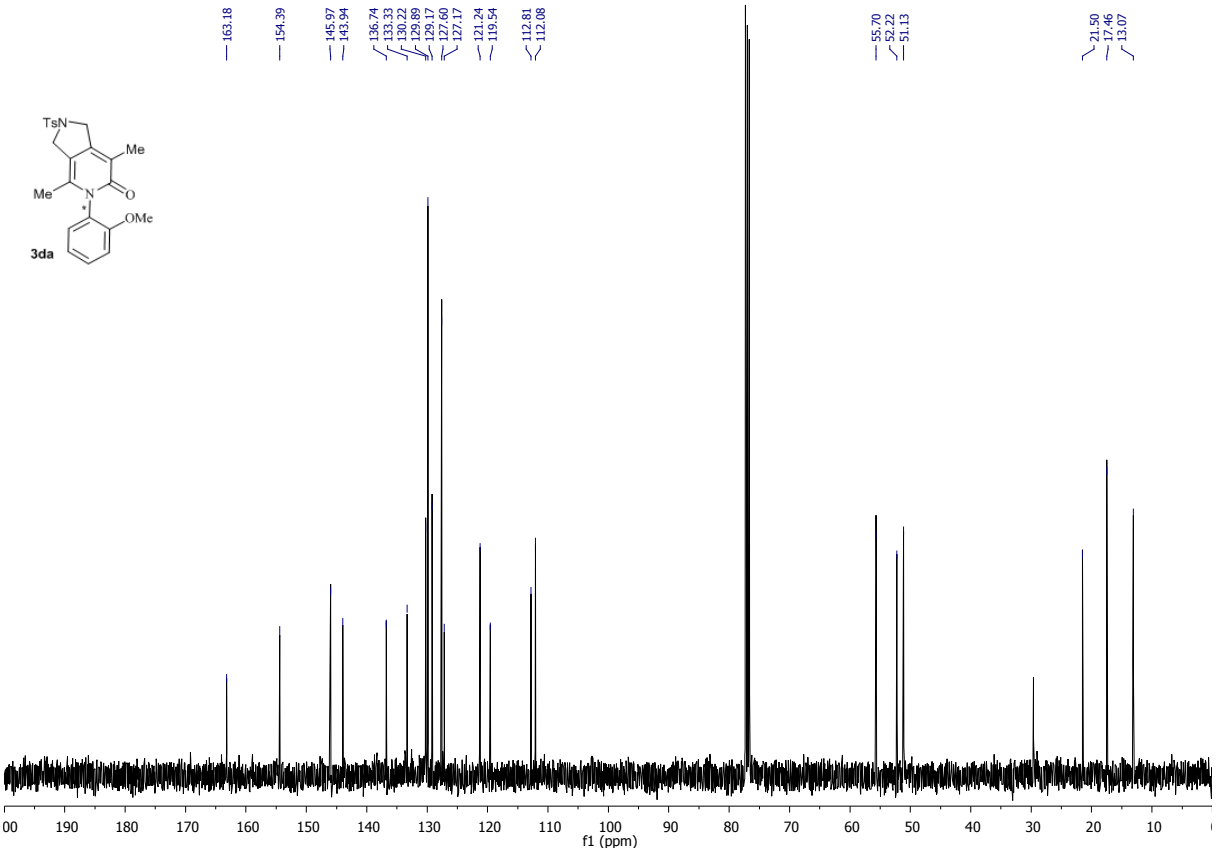

163.64
154.67
151.78
137.13
129.82
129.47
128.24
121.15
120.84
117.49
112.04
98.08
68.63
55.73
41.38
38.69
37.16
24.68
22.91
17.37
13.19
Me
Me
N
O
OMe
3ca
f1 (ppm)

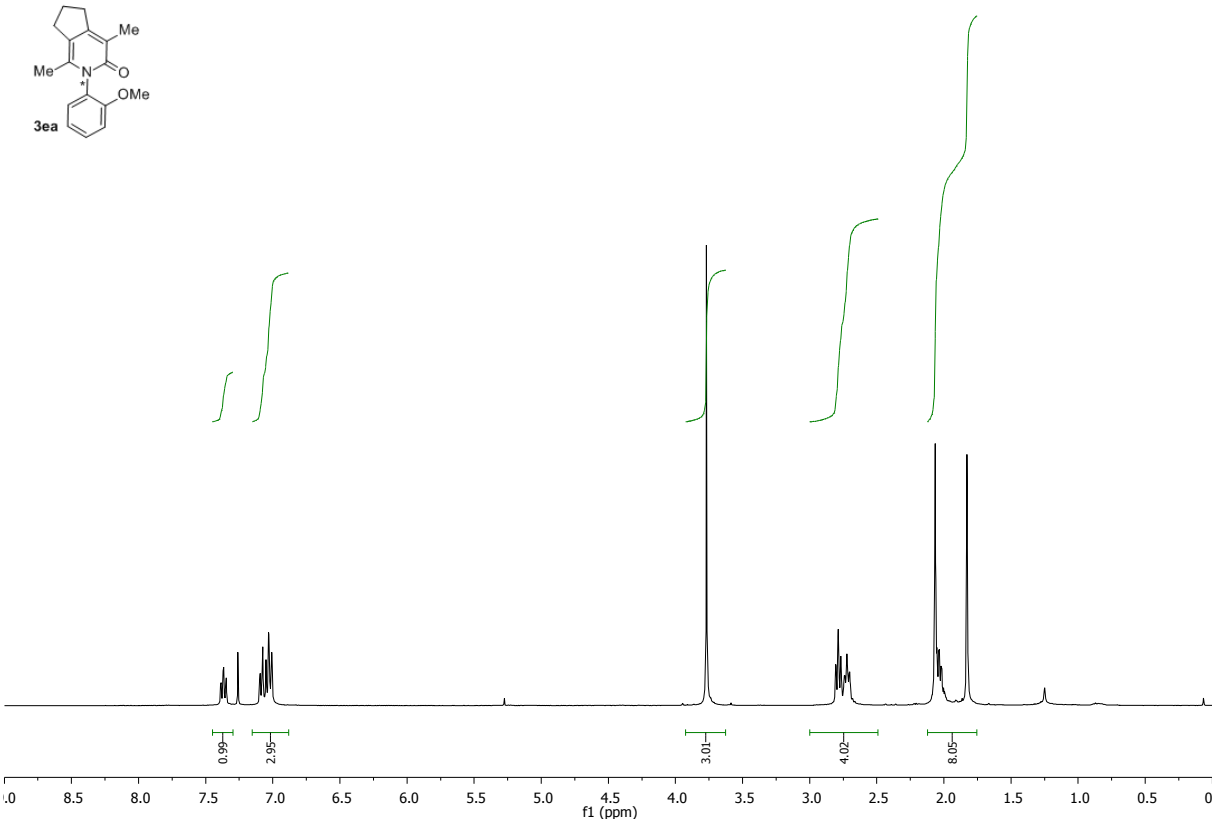

Me
Me
N
O
OEt
3cb
1.02
3.01
2.00
3.91
3.90
3.02
3.09
6.04
3.02
f1 (ppm)
163.73
154.05
151.61
137.24
129.70
129.58
128.68
121.09
120.80
117.26
113.34
98.12
68.64
64.14
41.45
38.69
37.17
24.64
23.03
17.34
14.69
13.23
f1 (ppm)

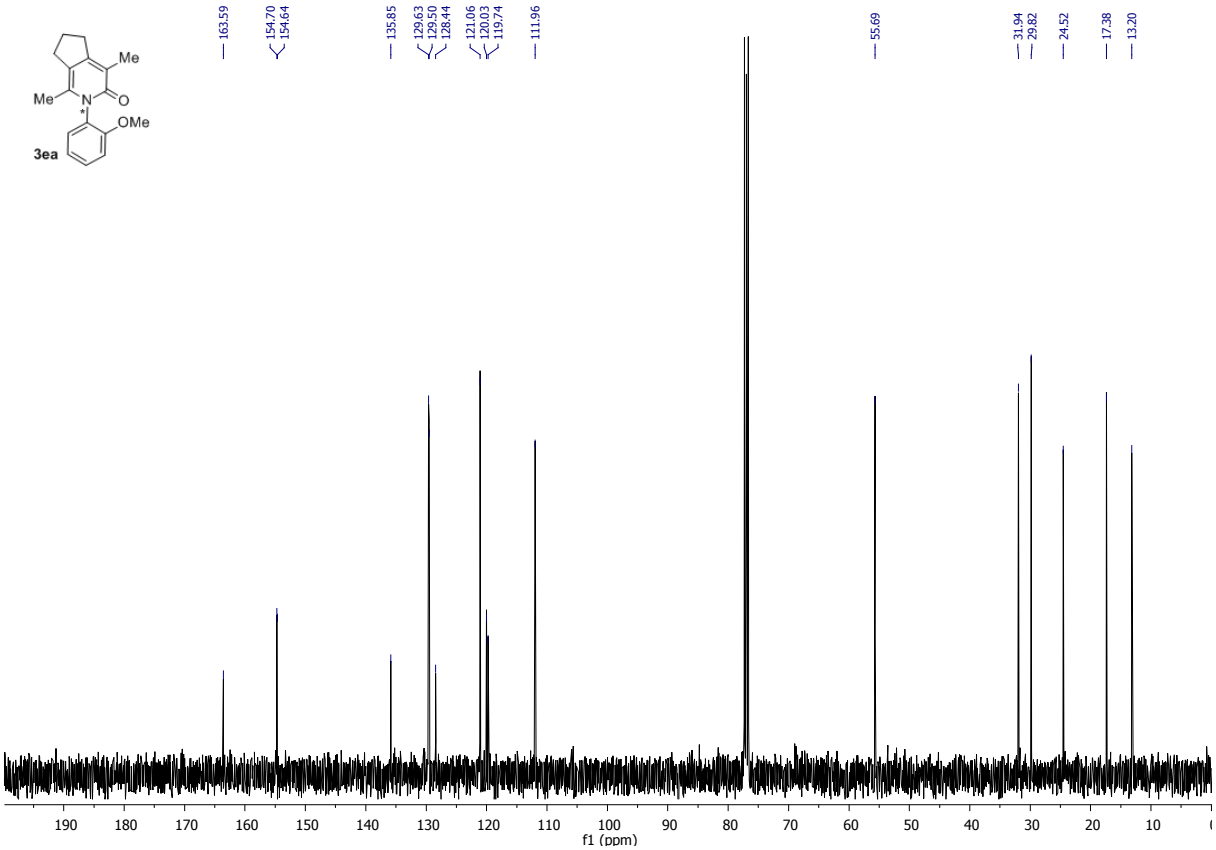

Me
Me
N
O
Me
3cc
3.47
1.05
4.00
4.00
6.03
3.03
5.98
f1 (ppm)


163.30
151.77
138.78
136.27
135.20
131.03
128.53
127.82
127.15
121.15
117.89
98.07
68.55
41.38
38.63
37.10
24.59
22.91
17.55
17.29
13.11
Me
Me
N
O
Me
3cc
f1 (ppm)


TsN
Me
Me
N
O
OMe
3da
2.06
3.07
3.00
3.92
2.96
3.05
6.19
f1 (ppm)


163.18
154.39
145.97
143.94
136.74
133.33
130.22
129.89
129.17
127.60
127.17
121.24
119.54
112.81
112.08
55.70
52.22
51.13
21.50
17.46
13.07
TsN
Me
Me
N
O
OMe
3da
f1 (ppm)


Me
Me
N
O
OMe
3ea
0.99
2.95
3.01
4.02
8.05
f1 (ppm)


Me
Me
N
O
OMe
3ea
163.59
154.70
154.64
135.85
129.63
129.50
128.44
121.06
120.03
119.74
111.96
55.69
31.94
29.82
24.52
17.38
13.20
f1 (ppm)