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Organocatalytic domino formation of (3*R*,3a*S*,9b*R*)-configured 3-aryl-3a-benzamido-1,3a,4,9b-tetrahydrochromeno[4,3-*b*]pyrroles in carbon dioxide medium

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General information

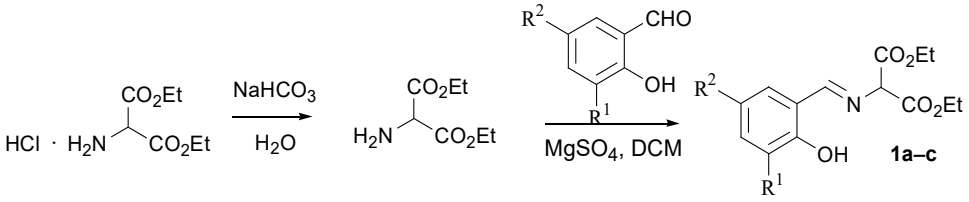
Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Analytical thin-layer chromatography (TLC) was performed on silica gel plates with F-254 indicator and the compounds were visualized by irradiation with UV light. Flash chromatography was carried out utilizing silica gel 200-300 mesh. ^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer (300 MHz ^{1}H, 75 MHz ^{13}C) and Bruker CLONED (300 MHz ^{1}H, 125 MHz ^{13}C). The spectra were recorded in $CDCl_3$ or DMSO-d_6 as solvent at room temperature, ^{1}H and ^{13}C NMR chemical shifts are reported in ppm. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported as chemical shift. IR spectra were recorded using Simex FT-801 FT-IR instrument and are reported in wavenumbers (cm^{-1}). The high-resolution mass spectra (HRMS) were measured on a Bruker microTOF II spectrometer by using electrospray ionization (ESI). Enantiomeric excess values (*ee*) of products were determined by HPLC (Stayer-A, 250 mm × 4.6 mm Chiralpak AD-H column, *n*-hexane : Pr^{i}OH = 70 : 30, 1 mL/min, 230 nm, 30 °C). Solvents of 'For chromatography' grade were purchased and used for HPLC analysis as they are. Optical rotations were measured with a Jasco P-2000 instrument at 589 nm with $[\alpha]_D^{20}$ values reported in degrees; concentration (c) is reported in g/100 mL.

X-ray diffraction data were collected at 100K on a Bruker Quest D8 diffractometer equipped with a Photon-III area-detector (graphite monochromator, shutterless φ- and ω-scan technique), using Mo K_α-radiation. The intensity data were integrated by the SAINT program[S1] and were corrected for absorption and decay using SADABS.[S2] The structure was solved by direct methods using SHELXT[S3] and refined on F^2 using SHELXL-2018.[S4] All non-hydrogen atoms were refined with individual anisotropic displacement parameters. The location of atom H1 was found from the electron density-difference map; it was refined with an individual isotropic displacement parameter. All other hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. The SHELXTL program suite[S1] was used for molecular graphics.

General procedure for the synthesis of *o*-hydroxy aromatic aldimines 3a–c (*cf.* Refs. S5,S6)

To a stirred solution of diethyl aminomalonate hydrochloride (3.0 g, 14.2 mmol) and H_2O (30 mL) in a 50 mL round-bottomed flask was added $NaHCO_3$ (1.31 g, 15.6 mmol). After stirring for 15 min, the solution was extracted with AcOEt three times. The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum to afford diethyl aminomalonate (2.3 g, 13.1 mmol), which was used without further purification.

Substituted salicylaldehyde (13.1 mmol) was added to a mixture of diethyl aminomalonate (2.3 g, 13.1 mmol) and $MgSO_4$ (7.86 g, 65.5 mmol) in CH_2Cl_2 (30 mL). After stirring for 48 h, $MgSO_4$ was removed by filtration. The filtrate was concentrated under reduced pressure. The crude product can be purified by flash chromatography on Al_2O_3 or recrystallization with petroleum ether/ethyl acetate (PE/EA) to afford products **1**.

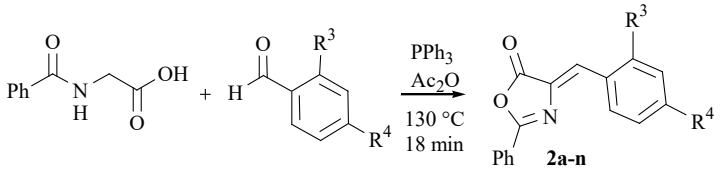


Scheme S1 Synthesis of *o*-hydroxy aromatic aldimines **1a–c.**

Diethyl (E)-2-[(2-hydroxybenzylidene)amino]malonate **1a** ($R^1 = R^2 = H$).[S5] Yellow solid; Purified by recrystallization, yield: 74%; mp 50–52 °C [lit.[S5]: 44–46 °C]. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.30 (t, 6H, $2OCH_2CH_3$, *J* 7.1 Hz), 4.28 (q, 4H, $2OCH_2CH_3$, *J* 7.1 Hz), 4.84 (s, 1H, CH–N), 6.90 (t, 1H, CH_{Ar}, *J* 7.4 Hz), 6.98 (d, 1H, CH_{Ar}, *J* 8.3 Hz), 7.29–7.35 (m, 2H, CH_{Ar}), 8.47 (s, 1H, CH=N), 12.67 (s, 1H, OH).
Diethyl (E)-2-[(5-bromo-2-hydroxybenzylidene)amino]malonate **1b** ($R^1 = H$, $R^2 = Br$).[S5] Yellow solid; Purified by recrystallization, yield: 73%; mp 90–92 °C [lit.[S5]: 78–80 °C]. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.30 (t, 6H, $2OCH_2CH_3$, *J* 7.1 Hz), 4.28 (q, 4H, $2OCH_2CH_3$, *J* 7.1 Hz), 4.86 (s, 1H, CH–N), 6.86–6.89 (m, 1H, CH_{Ar}), 7.41–7.42 (m, 2H, CH_{Ar}), 8.40 (s, 1H, CH=N),12.69 (s, 1H, OH).
Diethyl (E)-2-[(3,5-dichloro-2-hydroxybenzylidene)amino]malonate **1c** ($R^1 = R^2 = Cl$).[S7] Yellow solid; Purified by recrystallization, yield: 73%; mp 100.5–101.5 °C [lit.[S7]: 105 °C]. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.30 (t, 6H, $2OCH_2CH_3$, *J* 7.1 Hz), 4.28 (q, 4H, $2OCH_2CH_3$, *J* 7.1 Hz), 4.90 (s, 1H, CH–N), 7.44 (d, 1H, CH_{Ar}, *J* 2.2 Hz), 7.22 (d, 1H, CH_{Ar}, *J* 2.1 Hz), 8.42 (s, 1H, CH=N), 13.50 (s, 1H, OH).

General procedure for the synthesis of alkylidene azlactones 2a-n (*cf.* Ref. S8)

To the aromatic aldehyde (1.63 g, 11.6 mmol), hippuric acid (2.5 g, 14 mmol), anhydrous acetic anhydride (3.14 g, 31 mmol) and 10 mol% triphenylphosphine. The reaction mixture was stirred at 130 °C for 18 min under solvent-free condition. After completion of the reaction (TLC monitoring), reaction mixture was cooled to room temperature, 5 mL of 95% ethyl alcohol was added, a yellow solid was obtained. The yellow solid was filtered off and washed with water and recrystallized from acetone to afford 4-arylidene-2-phenyl-5(4*H*)-oxazolones (**4a-n**).



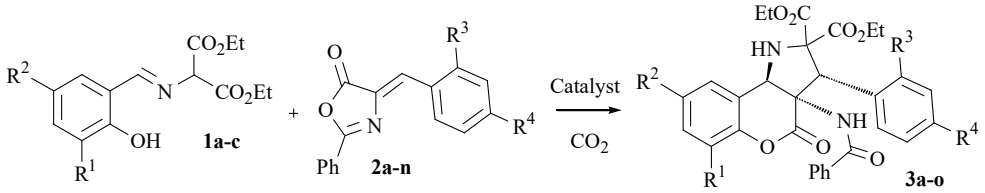
Scheme S2 Synthesis of alkylidene azlactones **2a-n.**

(Z)-4-Benzylidene-2-phenyloxazol-5(4H)-one **2a** ($R^3 = R^4 = H$).[S8-S10] Pale yellow solid; yield: 64%; mp 165.0–165.5 °C [lit.: 168–170 °C,[S8] 166 °C,[S9] 165–167 °C[S10]]. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.36 (s, 1H, CH), 7.53–7.76 (m, 6H, CH_{Ar}, Ph), 8.13–8.15 (m, 2H, $2CH_{Ar}$), 8.30–8.33 (m, 2H, $2CH_{Ar}$).
(Z)-4-(4-Chlorobenzylidene)-2-phenyloxazol-5(4H)-one **2b** ($R^3 = H$, $R^4 = Cl$).[S8-S10] Pale yellow solid; yield: 61%; mp 196–197 °C [lit.: 205–207 °C,[S8] 196 °C,[S9] 204–205 °C[S10]]. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.21 (s, 1H, CH), 7.46 (d, 2H, CH_{Ar}, *J* 8.4 Hz), 7.52–7.60 (m, 2H, CH_{Ar}), 7.62–7.69 (m, 1H, CH_{Ar}), 8.14–8.23 (m, 4H, CH_{Ar}).
(Z)-4-(4-Methoxybenzylidene)-2-phenyloxazol-5(4H)-one **2c** ($R^3 = H$, $R^4 = OMe$).[S8-S10] Yellow solid; yield: 64%; mp 157.5–158.0 °C [lit.: 160–163 °C,[S8] 159 °C,[S9] 163–164 °C[S10]]. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.91 (s, 3H, OMe), 7.02 (d, 2H, CH_{Ar}, *J* 8.7 Hz), 7.24 (s, 1H, CH), 7.42–7.69 (m, 3H, CH_{Ar}), 8.26–8.15 (m, 4H, CH_{Ar}).
(Z)-4-(4-Nitrobenzylidene)-2-phenyloxazol-5(4H)-one **2d** ($R^3 = H$, $R^4 = NO_2$).[S8-S10] Orange solid; yield: 58%; mp 241–242 °C [lit.: 238–240 °C,[S8] 238 °C,[S9] 241–242 °C[S10]]; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.47 (s, 1H, CH), 7.63–7.71 (m, 2H, CH_{Ar}), 7.81–7.73 (m, 1H, CH_{Ar}), 8.18 (d, 2H, CH_{Ar}, *J* 7.5 Hz), 8.34 (d, 2H, CH_{Ar}, *J* 8.7 Hz), 8.55 (d, 2H, CH_{Ar}, *J* 8.7 Hz).
(Z)-4-(4-Bromobenzylidene)-2-phenyloxazol-5(4H)-one **2e** ($R^3 = H$, $R^4 = Br$).[S9,S10] Pale yellow solid; yield: 54%; mp 203–204 °C [lit.: 204 °C,[S9] 197–198 °C[S10]]. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.36 (s, 1H, CH), 7.61–7.69 (m, 2H, CH_{Ar}), 7.70–7.79 (m, 3H, CH_{Ar}), 8.14 (d, 2H, CH_{Ar}, *J* 7.3 Hz), 8.25 (d, 2H, CH_{Ar}, *J* 8.1 Hz).
(Z)-4-(4-Fluorobenzylidene)-2-phenyloxazol-5(4H)-one **2f** ($R^3 = H$, $R^4 = F$).[S10] Yellow solid; yield: 54%; mp 185–187°C [lit.[S10]: 183–184 °C]. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.33–7.43 (m, 3H, CH, $2CH_{Ar}$), 7.60–7.68 (m, 2H, CH_{Ar}), 7.69–7.77 (m, 1H, CH_{Ar}), 8.12 (d, 2H, CH_{Ar}, *J* 7.4 Hz), 8.25 (dd, 2H, CH_{Ar}, *J* 8.6 Hz, *J* 5.9 Hz).
(Z)-4-(2-Chlorobenzylidene)-2-phenyloxazol-5(4H)-one **2g** ($R^3 = Cl$, $R^4 = H$).[S9,S10] Pale yellow solid; yield: 58%; mp 159.5–160.5 °C [lit.: 162 °C,[S9] 155–156 °C[S10]]. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.40–7.89 (m, 7H, CH, $6CH_{Ar}$), 8.14 (d, 2H, CH_{Ar}, *J* 7.5 Hz), 8.89 (d, 1H, CH_{Ar}, *J* 7.5 Hz).
(Z)-4-(2-Nitrobenzylidene)-2-phenyloxazol-5(4H)-one **2h** ($R^3 = NO_2$, $R^4 = H$).[S10] Orange solid; yield: 61%; mp 164–165 °C [lit.[S10]: 163–164 °C]. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.57 (s, 1H, CH), 7.59–7.69 (m, 2H, CH_{Ar}), 7.71–7.78 (m, 2H, CH_{Ar}), 7.81–7.98 (m, 1H, CH_{Ar}), 8.05–8.20 (m, 3H, CH_{Ar}), 8.57 (d, 1H, CH_{Ar}, *J* 7.8 Hz).

(Z)-4-(2-Methylbenzylidene)-2-phenyloxazol-5(4H)-one **2i** (R^3 = Me, R^4 = H).[S12,S13] Pale yellow solid; yield: 44%; mp 134.5–135.0 °C [lit.: 140–142 °C,[S12] 142 °C[S13]]. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 2.53 (s, 3H, Me), 7.15–7.30 (m, 1H, CH_{Ar}), 7.30–7.45 (m, 2H, CH_{Ar}), 7.45–7.71 (m, 4H, CH, 3CH_{Ar}), 8.18 (d, 1H, CH_{Ar}, *J* 7.6 Hz), 8.60–8.98 (m, 1H, CH_{Ar}).
(Z)-4-(2-Methoxybenzylidene)-2-phenyloxazol-5(4H)-one **2j** (R^3 = OMe, R^4 = H).[S11] Yellow solid; yield: 49%; mp 161.5–162.0 °C [lit.[S11]: 156–157 °C]. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 3.91 (s, 3H, OMe), 7.05–7.17 (m, 2H, CH_{Ar}), 7.40–7.80 (m, 5H, CH, 4CH_{Ar}), 8.10 (d, 2H, CH_{Ar}, *J* 7.5 Hz), 8.76 (d, 1H, CH_{Ar}, *J* 7.7 Hz).
(Z)-2-Phenyl-4-(2-trifluoromethylbenzylidene)oxazol-5(4H)-one **2k** (R^3 = CF_3, R^4 = H). Pale yellow solid; yield: 42%; mp 128.5–131 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.29 (s, 1H, CH_{Ar}), 7.60–7.81 (m, 4H, CH, 3CH_{Ar}), 7.89 (d, 2H, CH_{Ar}, *J* 6.9 Hz), 8.14 (d, 2H, CH_{Ar}, *J* 7.6 Hz), 8.54 (d, 1H, CH_{Ar}, *J* 8.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 123.9 (q, CF_3, $^1J_{CF}$ 274 Hz), 125.2 (C), 125.4 (q, CH, J_{CF} 2.7 Hz), 126.1 (q, CH, $^3J_{CF}$ 5.5 Hz), 128.6 (2CH), 129.0 (2CH), 130.0 (q, C, $^2J_{CF}$ 30.0 Hz), 130.2 (CH), 131.1 (q, C, J_{CF} 1.6 Hz), 131.9 (q, CH, J_{CF} 1.1 Hz), 133.4 (CH), 133.8 (CH), 135.3 (q, C, J_{CF} 1.1 Hz), 165.2 (C=N), 166.8 (C=O). IR (neat, ν/cm^{-1}): 3064, 1795, 1646, 1602, 1551, 1487, 1489, 1389, 1285, 1149, 1100, 1065, 1033, 978, 885, 853, 766, 698, 683, 661. HRMS (ESI), *m/z*: 318.0728 [M+H]$^+$, (calc. for $C_{17}H_{10}F_3NO_2$, *m/z*: 318.0742).
(Z)-4-(2-Bromobenzylidene)-2-phenyloxazol-5(4H)-one **2l** (R^3 = Br, R^4 = H).[S14] Yellow solid; yield: 49%; mp 154–155 °C [lit.[S14]: 130–132 °C]. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.32–7.48 (m, 2H, CH, CH_{Ar}), 7.52–7.69 (m, 3H, CH_{Ar}), 7.70–7.8 (m, 2H, CH_{Ar}), 8.13 (d, 2H, CH_{Ar}, *J* 7.6 Hz), 8.85 (d, 1H, CH_{Ar}, *J* 7.8 Hz).
(Z)-4-(2-Fluorobenzylidene)-2-phenyloxazol-5(4H)-one **2m** (R^3 = F, R^4 = H).[S15] Pale yellow solid; yield: 56%; mp 167–168 °C [lit.[S15]: 172–174 °C]. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.29 (s, 1H, CH), 7.32–7.48 (m, 2H, CH_{Ar}), 7.52–7.69 (m, 3H, CH_{Ar}), 7.70–7.82 (m, 1H, CH_{Ar}), 8.15 (d, 2H, CH_{Ar}, *J* 7.6 Hz), 8.87–8.75 (m, 1H, CH_{Ar}).
(Z)-4-(2-Hydroxybenzylidene)-2-phenyloxazol-5(4H)-one **2n** (R^3 = OH, R^4 = H).[S12] Pale yellow solid; yield: 32%; mp 174–175 °C [lit.[S12]: 106 °C]. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.28–7.39 (m, 2H, OH, CH_{Ar}), 7.42–7.49 (m, 1H, CH_{Ar}), 7.50–7.65 (m, 4H, CH, 3CH_{Ar}), 7.89–7.98 (m, 2H, CH_{Ar}), 8.82–8.89 (m, 2H, CH_{Ar}).

General procedure for the synthesis of chromeno[4,3-*b*]pyrrolidines 3a–o

Alkylidene azlactone (0.150 mmol), *o*-hydroxy aromatic aldimine (0.100 mmol) and a catalyst (0.001 mmol) were placed in a stainless steel autoclave (*V* = 2 mL) equipped with a magnetic stirring bar. The autoclave was filled with CO_2 by means of a syringe-press to a total pressure of 45 bar and heated to specified temperature. Then was added CO_2 to a final pressure, and the reaction mixture was stirred at that conditions for a required time (unless otherwise specified). The autoclave was slowly depressurized, the residue was taken into EtOAc and purified by column chromatography on silica gel (hexane/EtOAc = 4:1 as the eluent). Racemic products were prepared similarly with a racemic (**4g**+*ent*-**4g**) or non-chiral (Et_3N) catalyst.



Scheme S3 Synthesis of chromeno[4,3-*b*]pyrrolidines **3a–o.**

Diethyl (3R,3aS,9bR)-3a-benzamido-4-oxo-3-phenyl-1,3a,4,9b-tetrahydrochromeno[4,3-b]pyrrole-2,2(3H)-dicarboxylate **3a** (R^1 = R^2 = R^3 = R^4 = H).[S16] White solid; $[\alpha]_D^{25}$ = –107.38 (*c* 1, $CHCl_3$); mp 104–105 °C [lit.[S16]: 70–72 °C]. The enantiomeric excess was determined by HPLC with an AD–H column (*n*-hexane/Pr^{i}OH = 70 : 30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 9.5 min, $t_{R(major)}$ = 21.0 min, *ee* >98.6%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.85 (t, 3H, OCH_2CH_3, *J* 7.2 Hz), 1.14 (t, 3H, OCH_2CH_3, *J* 7.2 Hz), 3.73–4.10 (m, 5H, $2OCH_2CH_3$, CHN*H*), 4.98 (s, 1H, C*H*Ar), 5.24 (s, 1H, C*H*NH), 6.76 (s, 1H, NHC=O), 7.11–7.21 (m, 2H, CH_{Ar}), 7.31–7.54 (m, 10H, CH_{Ar}), 7.57 (d, 2H, CH_{Ar}, *J* 7.4 Hz).
Diethyl (3R,3aS,9bR)-3a-benzamido-3-(4-chlorophenyl)-4-oxo-1,3a,4,9b-tetrahydrochromeno[4,3-b]pyrrole-2,2(3H)-dicarboxylate **3b** (R^1 = R^2 = R^3 = H, R^4 = Cl).[S16] White solid; $[\alpha]_D^{25}$ = –58.92 (*c* 1, $CHCl_3$); mp 83–85 °C [lit.[S16]: 80–82 °C]. The enantiomeric excess was determined by HPLC with an AD–H column (*n*-hexane/Pr^{i}OH = 70 : 30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 10.0 min, $t_{R(major)}$ = 29.6 min, *ee* = 93.8%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.90 (t, 3H, OCH_2CH_3, *J* 7.1 Hz), 1.15 (t, 3H, OCH_2CH_3, *J* 7.0 Hz), 3.30–4.15 (m, 5H, $2OCH_2CH_3$, CHN*H*), 4.94 (s, 1H, C*H*Ar), 5.34 (s, 1H, C*H*NH), 6.78 (s, 1H, NHC=O), 7.06–7.25 (m, 2H, CH_{Ar}), 7.28–7.89 (m, 11H, CH_{Ar}).

Diethyl (3R,3aS,9bR)-3a-benzamido-3-(4-methoxyphenyl)-4-oxo-1,3a,4,9b-tetrahydrochromeno[4,3-b]pyrrole-2,2(3H)-dicarboxylate **3c** ($R^1 = R^2 = R^3 = H$, $R^4 = OMe$).[S16] White solid; $[\alpha]_D^{25} = -78.08$ (*c* 1, $CHCl_3$); mp 92–94 °C [lit.: 72–74 °C**Error! Bookmark not defined.**]. The enantiomeric excess was determined by HPLC with an AD–H column (*n*-hexane/Pr^{i}OH = 70 : 30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 9.3 min, $t_{R(major)}$ = 22.0 min, *ee* = 94.6%; ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 0.81 (t, 3H, OCH_2CH_3, *J* 7.1 Hz), 1.05 (t, 3H, OCH_2CH_3, *J* 7.1 Hz), 3.65–4.10 (m, 7H, OMe, $2OCH_2CH_3$), 4.84 (s, 1H, CHAr), 5.14–5.25 (m, 1H, C*H*NH), 6.70 (s, 1H, NHC=O), 6.86 (d, 2H, CH_{Ar}, *J* 8.7 Hz), 6.98–7.11 (m, 2H, CH_{Ar}), 7.21–7.36 (m, 5H, CH_{Ar}), 7.37–7.50 (m, 2H, CH_{Ar}), 7.52 (d, 2H, CH_{Ar}, *J* 7.6 Hz).

Diethyl (3R,3aS,9bR)-3a-benzamido-3-(4-nitrophenyl)-4-oxo-1,3a,4,9b-tetrahydrochromeno[4,3-b]pyrrole-2,2(3H)-dicarboxylate **3d** ($R^1 = R^2 = R^3 = H$, $R^4 = NO_2$).[S16] Pale yellow solid; $[\alpha]_D^{25} = -13.90$ (*c* 1, $CHCl_3$); mp 110–111 °C [lit.[S16]: 96–98 °C]. The enantiomeric excess was determined by HPLC with an AD–H column (*n*-hexane/Pr^{i}OH = 70 : 30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 9.4 min, $t_{R(major)}$ = 25.3 min, *ee* = 91.6%. ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 0.94 (t, 3H, OCH_2CH_3, *J* 7.1 Hz), 1.21 (t, 3H, OCH_2CH_3, *J* 7.1 Hz), 3.70–3.85 (m, 1H from OCH_2CH_3), 3.95–4.15 (m, 3H from $2OCH_2CH_3$), 5.03 (s, 1H, C*H*Ar), 5.28 (s, 1H, C*H*NH), 7.02 (s, 1H, NHC=O), 7.10–7.23 (m, 2H, CH_{Ar}), 7.35–7.60 (m, 6H, CH_{Ar}), 7.68 (d, 2H, CH_{Ar}, *J* 7.5 Hz), 7.79 (d, 2H, CH_{Ar}, *J* 8.6 Hz), 8.25 (d, 2H, CH_{Ar}, *J* 8.5Hz).

Diethyl (3R,3aS,9bR)-3a-benzamido-3-(4-bromophenyl)-4-oxo-1,3a,4,9b-tetrahydrochromeno[4,3-b]pyrrole-2,2(3H)-dicarboxylate **3e** ($R^1 = R^2 = R^3 = H$, $R^4 = Br$).[S16] White solid; $[\alpha]_D^{25} = -50.60$ (*c* 1, $CHCl_3$); mp 150–152 °C [lit.[S16]: 150–152 °C]. The enantiomeric excess was determined by HPLC with an AD–H column (*n*-hexane/Pr^{i}OH = 70 : 30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 10.5 min, $t_{R(major)}$ = 27.7 min, *ee* = 89.7%. ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 0.93 (t, 3H, OCH_2CH_3, *J* 7.1 Hz), 1.15 (t, 3H, OCH_2CH_3, *J* 7.0 Hz), 3.74–4.16 (m, 5H, $2OCH_2CH_3$, CHN*H*), 4.90 (s, 1H, CHAr), 5.26 (s, 1H, C*H*NH), 6.78 (s, 1H, NHC=O), 7.22–7.08 (m, 2H, CH_{Ar}), 7.66–7.30 (m, 11H, CH_{Ar}).

Diethyl (3R,3aS,9bR)-3a-benzamido-3-(4-fluorophenyl)-4-oxo-1,3a,4,9b-tetrahydrochromeno[4,3-b]pyrrole-2,2(3H)-dicarboxylate **3f** ($R^1 = R^2 = R^3 = H$, $R^4 = F$).[S16] White solid; $[\alpha]_D^{25} = -84.00$ (*c* 1, $CHCl_3$); mp 79–81 °C [lit.[S16]: 78–80 °C]. The enantiomeric excess was determined by HPLC with an AD–H column (*n*-hexane/Pr^{i}OH = 70 : 30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 9.6 min, $t_{R(major)}$ = 37.3 min, *ee* = 91.9%. ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 0.91 (t, 3H, OCH_2CH_3, *J* 7.2 Hz), 1.15 (t, 3H, OCH_2CH_3, *J* 7.1 Hz), 3.73–4.13 (m, 5H, $2OCH_2CH_3$, CHN*H*), 4.96 (s, 1H, CHAr), 5.29 (s, 1H, C*H*NH), 6.75 (s, 1H, NHC=O), 7.05–7.22 (m, 4H, CH_{Ar}), 7.30–7.46 (m, 3H, CH_{Ar}), 7.47–7.65 (m, 6H, CH_{Ar}).

Diethyl (3R,3aS,9bR)-3a-benzamido-3-(2-chlorophenyl)-4-oxo-1,3a,4,9b-tetrahydrochromeno[4,3-b]pyrrole-2,2(3H)-dicarboxylate **3g** ($R^1 = R^2 = R^4 = H$, $R^3 = Cl$).[S16] White solid; $[\alpha]_D^{25} = -165.86$ (*c* 1, $CHCl_3$); mp 139–141 °C [lit.[S16]: 150–152 °C]. The enantiomeric excess was determined by HPLC with an AD–H column (*n*-hexane/Pr^{i}OH = 70 : 30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 7.1 min, $t_{R(major)}$ = 18.4 min, *ee* >96.8%. ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 0.90 (t, 3H, OCH_2CH_3, *J* 7.1 Hz), 1.13 (t, 3H, OCH_2CH_3, *J* 7.1 Hz), 3.72–4.18 (m, 5H, $2OCH_2CH_3$, CHN*H*), 5.36 (s, 1H, C*H*Ar), 5.92 (s, 1H, C*H*NH), 6.60 (s, 1H, NHC=O), 7.14–7.20 (m, 2H, CH_{Ar}), 7.29–7.65 (m, 11H, CH_{Ar}).

Diethyl (3R,3aS,9bR)-3a-benzamido-3-(2-nitrophenyl)-4-oxo-1,3a,4,9b-tetrahydrochromeno[4,3-b]pyrrole-2,2(3H)-dicarboxylate **3h** ($R^1 = R^2 = R^4 = H$, $R^3 = NO_2$). Pale yellow solid; $[\alpha]_D^{25} = +36.50$ (*c* 1, $CHCl_3$); mp 159–161 °C. The enantiomeric excess was determined by HPLC with an AD–H column (*n*-hexane/Pr^{i}OH = 70 : 30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 12.8 min, $t_{R(major)}$ = 42.3 min, *ee* = 97.6%. ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 0.90 (t, 3H, OCH_2CH_3, *J* 7.1 Hz), 1.13 (t, 3H, OCH_2CH_3, *J* 7.1 Hz), 2.87 (br.s, 1H, CHN*H*), 3.70–3.85 (m, 1H from OCH_2CH_3), 3.91–4.15 (m, 3H from $2OCH_2CH_3$), 5.48 (s, 1H, C*H*Ar), 5.67 (s, 1H, C*H*NH), 7.08 (s, 1H, NHC=O), 7.17–7.25 (m, 2H, CH_{Ar}), 7.30–7.70 (m, 9H, CH_{Ar}), 7.77 (d, 1H, CH_{Ar}, *J* 7.9 Hz), 7.88 (d, 1H, CH_{Ar}, *J* 7.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) *δ*: 13.4, 13.6, 49.2, 62.6, 62.9, 63.1, 66.5, 67.2, 76.6, 117.3, 121.7, 124.9, 125.7, 127.0, 127.2, 128.1, 128.8, 129.7, 130.0, 130.2, 132.1, 132.4, 133.2, 147.6, 149.3, 152.3, 165.9, 168.1, 169.4, 169.5. IR (neat, ν/cm^{-1}): 3322, 2985, 1723, 1671, 1529, 1460, 1350, 1286, 1233, 767, 717. HRMS (ESI), *m/z*: 574.1814 $[M+H]^+$, (calc. for $C_{30}H_{27}N_3O_9$, *m/z*: 574.1821).

Diethyl (3R,3aS,9bR)-3a-benzamido-4-oxo-3-(o-tolyl)-1,3a,4,9b-tetrahydrochromeno[4,3-b]pyrrole-2,2(3H)-dicarboxylate **3i** ($R^1 = R^2 = R^4 = H$, $R^3 = Me$).[S16] White solid; $[\alpha]_D^{25} = -162.68$ (*c* 1, $CHCl_3$); mp 105–108 °C [lit.[S16]: 76–78 °C]. The enantiomeric excess was determined by HPLC with an AD–H column (*n*-hexane/Pr^{i}OH = 70 : 30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 8.3 min, $t_{R(major)}$ = 15.2 min, *ee* = 96.6%. ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 0.78 (t, 3H, OCH_2CH_3, *J* 7.1 Hz), 1.10 (t, 3H, OCH_2CH_3, *J* 7.1 Hz), 2.51 (s, 3H, Me), 3.38 (br.s, 1H, CHN*H*), 3.66–4.00 (m, 4H, OCH_2CH_3), 5.28 (s, 1H, C*H*Ar), 5.52 (s, 1H, C*H*NH), 6.66 (s, 1H, NHC=O), 7.00–7.65 (m, 13H, CH_{Ar}).

Diethyl (3R,3aS,9bR)-3a-benzamido-3-(2-methoxyphenyl)-4-oxo-1,3a,4,9b-tetrahydrochromeno[4,3-b]pyrrole-2,2(3H)-dicarboxylate **3j** ($R^1 = R^2 = R^4 = H$, $R^3 = OMe$). White solid; $[\alpha]_D^{25} = -147.30$ (*c* 1, $CHCl_3$); mp 81–

83 °C. The enantiomeric excess was determined by HPLC with an AD–H column (*n*-hexane/Pr^{i}OH = 70 : 30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 13.4 min, $t_{R(major)}$ = 27.2 min, *ee* = 98.9%. ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 0.99 (t, 3H, OCH_2CH_3, *J* 7.1 Hz), 1.16 (t, 3H, OCH_2CH_3, *J* 7.1 Hz), 3.75–3.90 (m, 4H, 1H from OCH_2CH_3, OMe), 4.00 (q, 2H, OCH_2CH_3, *J* 7.1 Hz), 4.24–4.41 (m, 1H from OCH_2CH_3), 5.27 (s, 1H, CHAr), 5.31 (s, 1H, CHNH), 6.93 (d, 1H, CH_{Ar}, *J* 8.3 Hz), 7.00 (t, 1H, CH_{Ar}, *J* 7.5 Hz), 7.14 (t, 2H, CH_{Ar}, *J* 7.4 Hz), 7.21–7.61 (m, 7H, CH_{Ar}), 7.68–7.77 (m, 2H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$) *δ*: 13.5, 13.8, 55.6, 62.5, 62.8, 62.9, 76.6, 111.3, 116.9, 119.8, 121.4, 121.9, 124.6, 127.3, 128.6, 128.8, 130.1, 130.7, 132.0, 133.9, 149.4, 157.4, 165.3, 168.1, 168.8, 169.5. IR (neat, ν/cm^{-1}): 3336, 2928, 1727, 1664, 1529, 1457, 1366, 1195, 1125, 758, 714. HRMS (ESI), *m/z*: 559.2071 $[M+H]^+$, (calc. for $C_{31}H_{30}N_2O_8$, *m/z*: 559.2080).

Diethyl (3R,3aS,9bR)-3a-benzamido-4-oxo-3-(2-trifluoromethylphenyl)-1,3a,4,9b-tetrahydrochromeno[4,3-b]-pyrrole-2,2(3H)-dicarboxylate **3k** ($R^1 = R^2 = R^4$ = H, $R^3 = CF_3$). White solid; $[\alpha]_D^{25}$ = –117.56 (*c* 1, $CHCl_3$); mp 148–150 °C. The enantiomeric excess was determined by HPLC with an AD–H column (hexane-Pr^{i}OH = 70 : 30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 6.4 min, $t_{R(major)}$ = 13.7 min, *ee* = 99.7%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.75 (t, 3H, OCH_2CH_3, *J* 7.1 Hz), 1.14 (t, 3H, OCH_2CH_3, *J* 7.0 Hz), 3.60–3.75 (m, 1H, 1H from OCH_2CH_3), 3.77–4.10 (m, 3H, 3H from OCH_2CH_3), 5.28 (s, 1H, CHAr), 5.68 (s, 1H, CHNH), 6.33 (s, 1H, NHC=O), 7.11–7.24 (m, 2H, CH_{Ar}), 7.25–7.50 (m, 7H, CH_{Ar}), 7.57 (t, 1H, CH_{Ar}, *J* 7.6 Hz), 7.70 (t, 1H, CH_{Ar}, *J* 7.6 Hz), 7.87 (d, 1H, CH_{Ar}, *J* 7.8 Hz), 7.98 (d, 1H, CH_{Ar}, *J* 7.7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 13.1, 13.5, 52.6 q ($^4J_{CF}$ 2.2 Hz), 62.1, 62.9, 63.3, 65.9, 77.2, 116.9, 121.7, 123.5 q ($^1J_{CF}$ 274.8 Hz), 123.7 q ($^3J_{CF}$ 6.0 Hz), 124.7, 126.8, 128.2, 128.6, 129.2, 129.9, 130.8, 131.5 q ($^2J_{CF}$ 29.9 Hz), 131.8, 132.3, 132.5 q ($^3J_{CF}$ 1.1 Hz), 132.7, 149.8, 166.8, 167.6, 168.0, 169.2. IR (neat, ν/cm^{-1}): 3448, 2984, 1731, 1676, 1459, 1306, 1285, 1231, 1151, 1124, 765, 703. HRMS (ESI), *m/z*: 597.1841 $[M+H]^+$, (calc. for $C_{31}H_{27}F_3N_2O_7$, *m/z*: 597.1848).

Diethyl (3R,3aS,9bR)-3a-benzamido-3-(2-bromophenyl)-4-oxo-1,3a,4,9b-tetrahydrochromeno[4,3-b]pyrrole-2,2(3H)-dicarboxylate **3l** ($R^1 = R^2 = R^4$ = H, R^3 = Br).[S16] White solid; $[\alpha]_D^{25}$ = –167.18 (c 1, $CHCl_3$); mp 173–176 °C [lit.[S16]: 164–166 °C]. The enantiomeric excess was determined by HPLC with an AD–H column (*n*-hexane/Pr^{i}OH = 70 : 30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 8.2 min, $t_{R(major)}$ = 21.9 min, *ee* = 99.1%. ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 0.90 (t, 3H, OCH_2CH_3, *J* 7.1 Hz), 1.13 (t, 3H, OCH_2CH_3, *J* 7.1 Hz), 3.74–4.16 (m, 5H, $2OCH_2CH_3$, CHN*H*), 5.34 (s, 1H, CHAr), 5.90 (s, 1H, CHNH), 6.58 (s, 1H, NHC=O), 7.12–7.64 (m, 12H, CH_{Ar}), 7.76 (d, 1H, CH_{Ar}, *J* 7.9 Hz).

Diethyl (3R,3aS,9bR)-3a-benzamido-3-(2-fluorophenyl)-4-oxo-1,3a,4,9b-tetrahydrochromeno[4,3-b]pyrrole-2,2(3H)-dicarboxylate **3m** ($R^1 = R^2 = R^4$ = H, R^3 = F).[S16] White solid; $[\alpha]_D^{25}$ = –128.46 (*c* 1, $CHCl_3$); mp 76–78 °C [lit.[S16]: 78–80 °C]. The enantiomeric excess was determined by HPLC with an AD–H column (*n*-hexane/Pr^{i}OH = 70 : 30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 11.8 min, $t_{R(major)}$ = 33.2 min, *ee* = 99.5%. ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 0.99 (t, 3H, OCH_2CH_3, *J* 7.1 Hz), 1.16 (t, 3H, OCH_2CH_3, *J* 7.1 Hz), 3.88–4.10 (m, 3H, $1.5OCH_2CH_3$), 4.17–4.32 (m, 1H, $0.5OCH_2CH_3$), 4.33 (s, 1H, CHN*H*), 5.18 (s, 1H, CHAr), 5.30 (s, 1H, CHNH), 7.10–7.27 (m, 4H, NHC=O, $3CH_{Ar}$), 7.30–7.60 (m, 8H, CH_{Ar}), 7.68–7.77 (m, 2H, CH_{Ar}).

Diethyl (3R,3aS,9bR)-3a-benzamido-8-bromo-4-oxo-3-phenyl-1,3a,4,9b-tetrahydrochromeno[4,3-b]pyrrole-2,2(3H)-dicarboxylate **3n** ($R^1 = R^3 = R^4$ = H, R^2 = Br).[S16] White solid; $[\alpha]_D^{25}$ = –65.96 (*c* 1, $CHCl_3$); mp 80–83 °C [lit.[S16]: 78–80 °C]. The enantiomeric excess was determined by HPLC with an AD–H column (*n*-hexane/Pr^{i}OH = 70 : 30), 1.0 mL/min, λ = 254 nm, $t_{R(minor)}$ = 7.9 min, $t_{R(major)}$ = 23.7 min, *ee* = 99.8%. ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 0.87 (t, 3H, OCH_2CH_3, *J* 7.1 Hz), 1.23 (t, 3H, OCH_2CH_3, *J* 7.1 Hz), 3.73–3.89 (m, 1H, $0.5OCH_2CH_3$), 4.00–4.17 (m, 3H, $1.5OCH_2CH_3$, CHN*H*), 4.95 (s, 1H, CHAr), 5.23 (d, 1H, CHNH, *J* 4.7 Hz), 6.78 (s, 1H, NHC=O), 7.35–7.69 (m, 13H, CH_{Ar}).

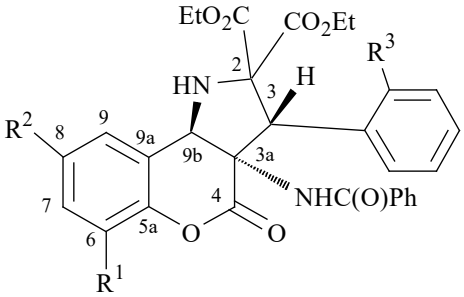
Diethyl (3R,3aS,9bR)-3a-benzamido-6,8-dichloro-4-oxo-3-phenyl-1,3a,4,9b-tetrahydrochromeno[4,3-b]pyrrole-2,2(3H)-dicarboxylate **3o** ($R^1 = R^2$ = Cl, $R^3 = R^4$ = H). White solid; $[\alpha]_D^{25}$ = –76.44 (c 1, $CHCl_3$); mp 85–87 °C. The enantiomeric excess was determined by HPLC with an AD–H column (*n*-hexane/Pr^{i}OH = 70 : 30), 1.0 mL/min, λ = 254 nm, $t_{R(minor)}$ = 9.2 min, $t_{R(major)}$ = 20.2 min, *ee* = 98.1%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (t, 3H, OCH_2CH_3, *J* 7.1 Hz), 1.23 (t, 3H, OCH_2CH_3, *J* 7.1 Hz), 3.70–3.89 (m, 1H, $0.5OCH_2CH_3$), 3.95–4.25 (m, 4H, $1.5OCH_2CH_3$, CHNH), 4.95 (s, 1H, CHAr), 5.23 (d, 1H, CHNH, *J* 4.8 Hz), 6.78 (s, 1H, NHC=O), 7.35–7.63 (m, 12H, CH_{Ar}). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 13.3, 13.7, 57.4, 62.7, 62.9, 63.2, 66.1, 76.4, 122.7, 125.0, 126.7, 127.0, 128.7, 129.3, 129.4, 129.5, 129.9, 130.3, 132.0, 132.4, 132.5, 144.3, 164.9, 167.9, 169.1, 169.8. HRMS (ESI), *m/z*: 597.1200 $[M+H]^+$, (calc. for $C_{30}H_{26}Cl_2N_2O_7$, *m/z*: 596.1117).

Table S1 Yields, *ee* values and rotations of products **3a–o**

Compound	Yield, %		*ee*, %		$[\alpha]_D^{25}$ *
	with **4d**	with **4e**	with **4d**	with **4e**	
3a	75	95	95	99	-107.4 (-99.4)
3b	77	94	95	94	-58.9 (-61.7)
3c	57	67	87	95	-78.1 (-81.0)
3d	73	92	76	92	-13.9 (-19.9)
3e	43	80	96	90	-50.6 (-51.5)
3f	65	83	79	92	-84.0 (-80.0)
3g	51	81	83	97	-165.9 (-162.5)
3h	75	72	95	98	+36.5
3i	34	88	50	97	-162.7 (-140.1)
3j	64	72	94	99	-147.3
3k	89	97	99	>99	-117.6
3l	70	91	96	99	-167.2 (-163.8)
3m	81	99	99	>99	-128.5 (-118.4)
3n	-	75	-	>99	-66.0 (-63.6)
3o	-	86	-	98	-76.4

* In $CHCl_3$, $c \sim 1$. The values in parentheses from Ref. S16.

Table S2 Selected principal ^{13}C NMR data for new compounds **3h,j,k,o**

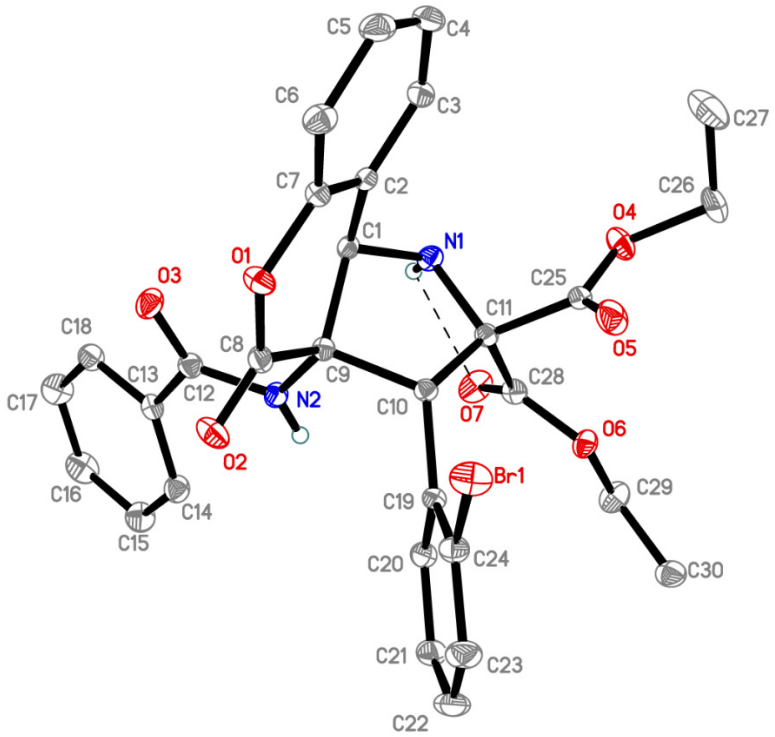


3a $R^1 = R^2 = R^3 = H$
3h $R^1 = R^2 =$ H, $R^3 = NO_2$
3j $R^1 = R^2 =$ H, $R^3 =$ OMe
3k $R^1 = R^2 =$ H, $R^3 = CF_3$
3o $R^1 = R^2 =$ Cl, $R^3 =$ H

Atom	Compound				
	3a*	**3h**	**3j**	**3k**	**3o**
2	76.4	76.6	76.6	77.2	76.4
3	57.5	49.2	55.6	52.6 q ($^4J_{CF}$ = 2.2 Hz)	57.4
3a	66.1	67.2	62.9	65.9	66.1
4	169.8	169.5	169.5	169.2	169.8
5a	149.4	149.3	149.4	149.8	144.3
6	116.8	117.3	116.9	116.9	122.7
9a	121.8	121.7	121.4	121.7	125.0
9b	63.2	63.1	62.9	62.1	63.2

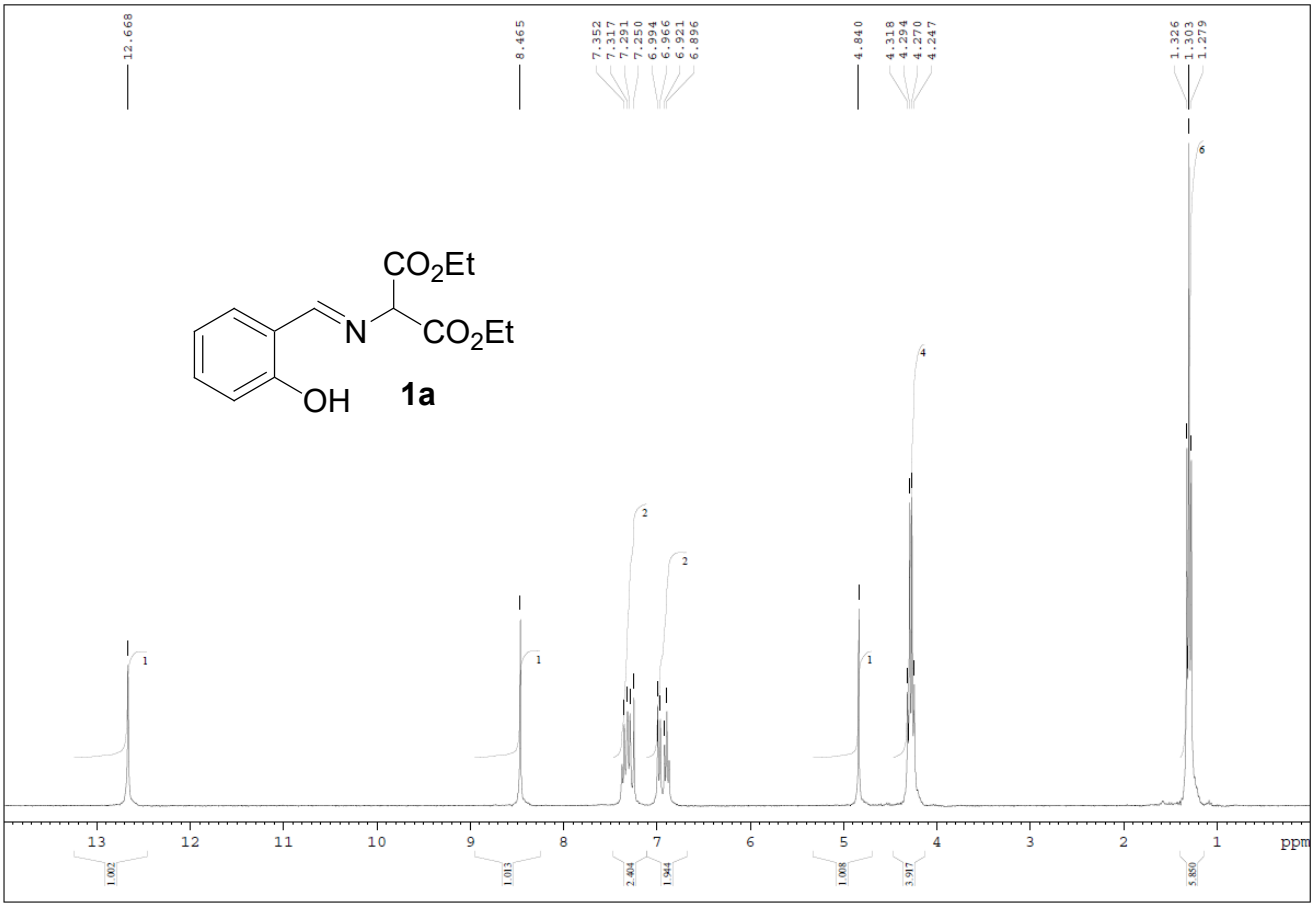
* Data from Ref. S16.

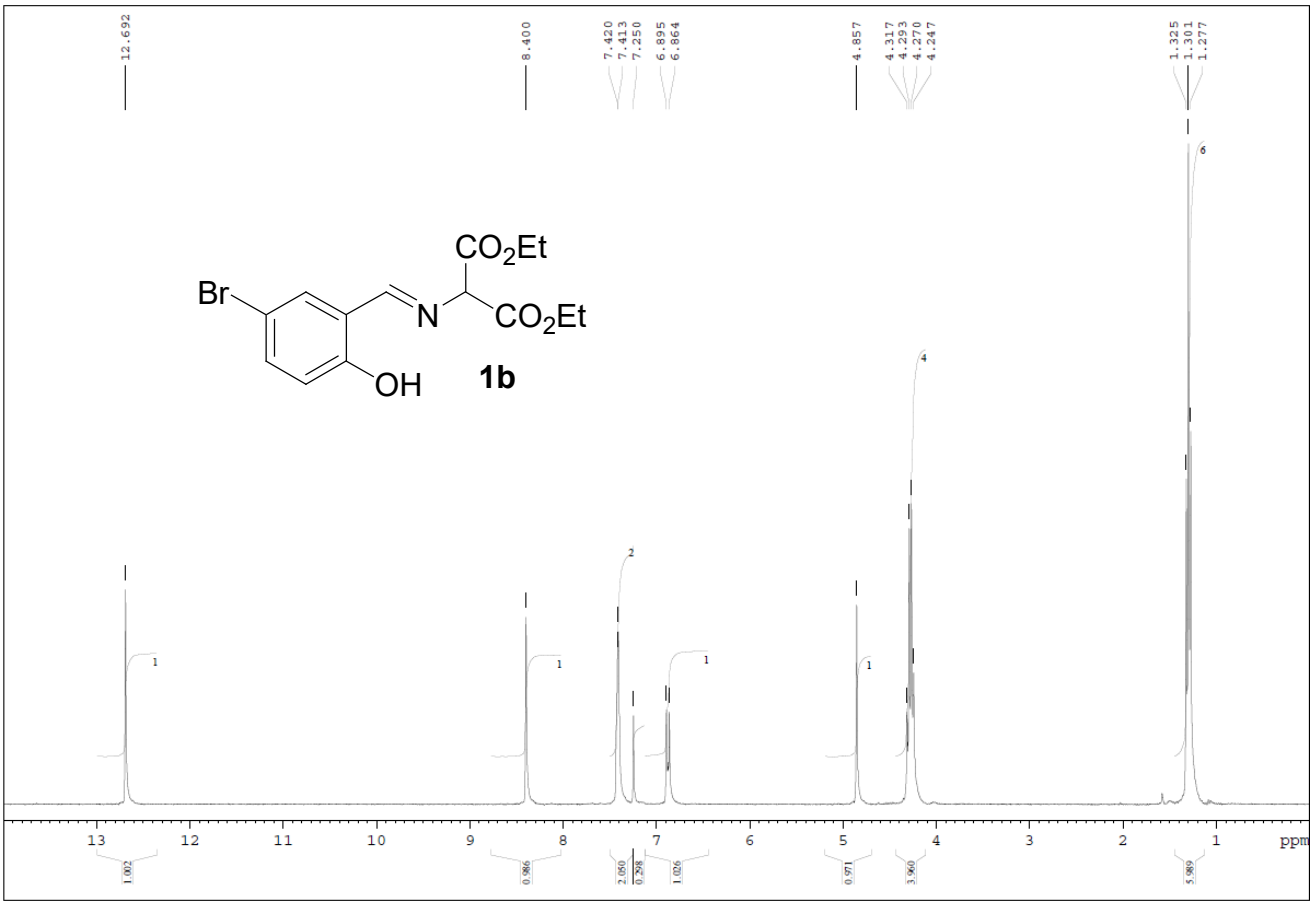
X-ray Crystallographic data of 3l

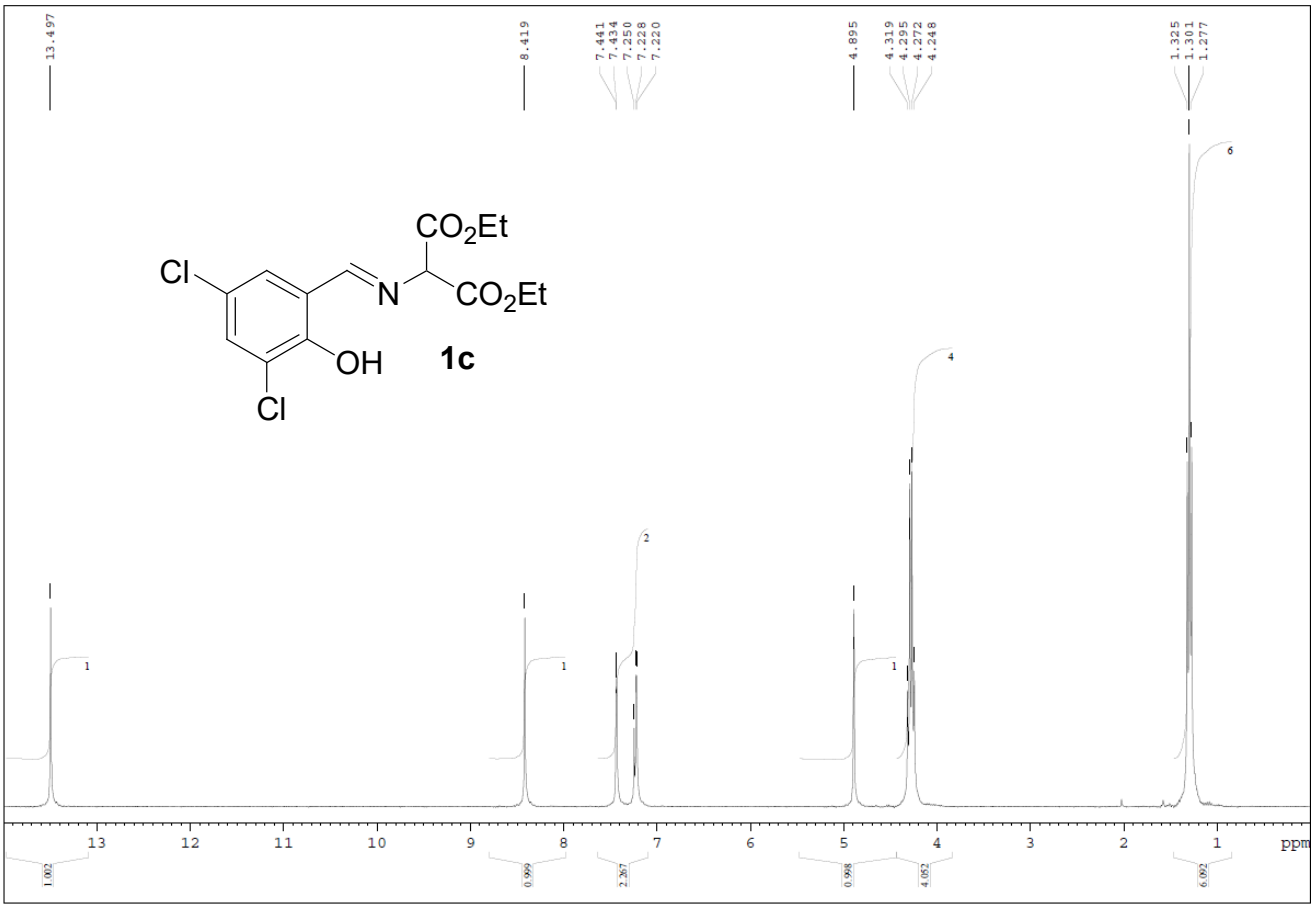


Empirical formula	$C_{30}H_{27}BrN_2O_7$
Formula weight	607.44
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 9.3103(2) Å α= 90°. b = 15.2513(3) Å β= 90°. c = 19.5267(4) Å γ = 90°.
Volume	2772.68(10) $Å^3$
Z	4
Density (calculated)	1.455 g/cm^3
Absorption coefficient	1.533 mm^{-1}
F(000)	1248
Crystal size	0.589 x 0.570 x 0.523 mm^3
Theta range for data collection	2.424 to 36.341°.
Index ranges	-15<=h<=15, -23<=k<=25, -29<=l<=32
Reflections collected	64944
Independent reflections	13357 [R(int) = 0.0460]
Observed reflections	10828
Completeness to theta = 25.242°	99.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7471 and 0.6117
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13357 / 0 / 372
Goodness-of-fit on F^2	1.006
Final R indices [I>2sigma(I)]	R^1 = 0.0346, wR2 = 0.0628
R indices (all data)	R^1 = 0.0542, wR2 = 0.0680
Absolute structure parameter	0.006(4)
Extinction coefficient	n/a
Largest diff. peak and hole	0.339 and -0.582 e.$Å^{-3}$

^{1}H NMR and ^{13}C NMR spectra



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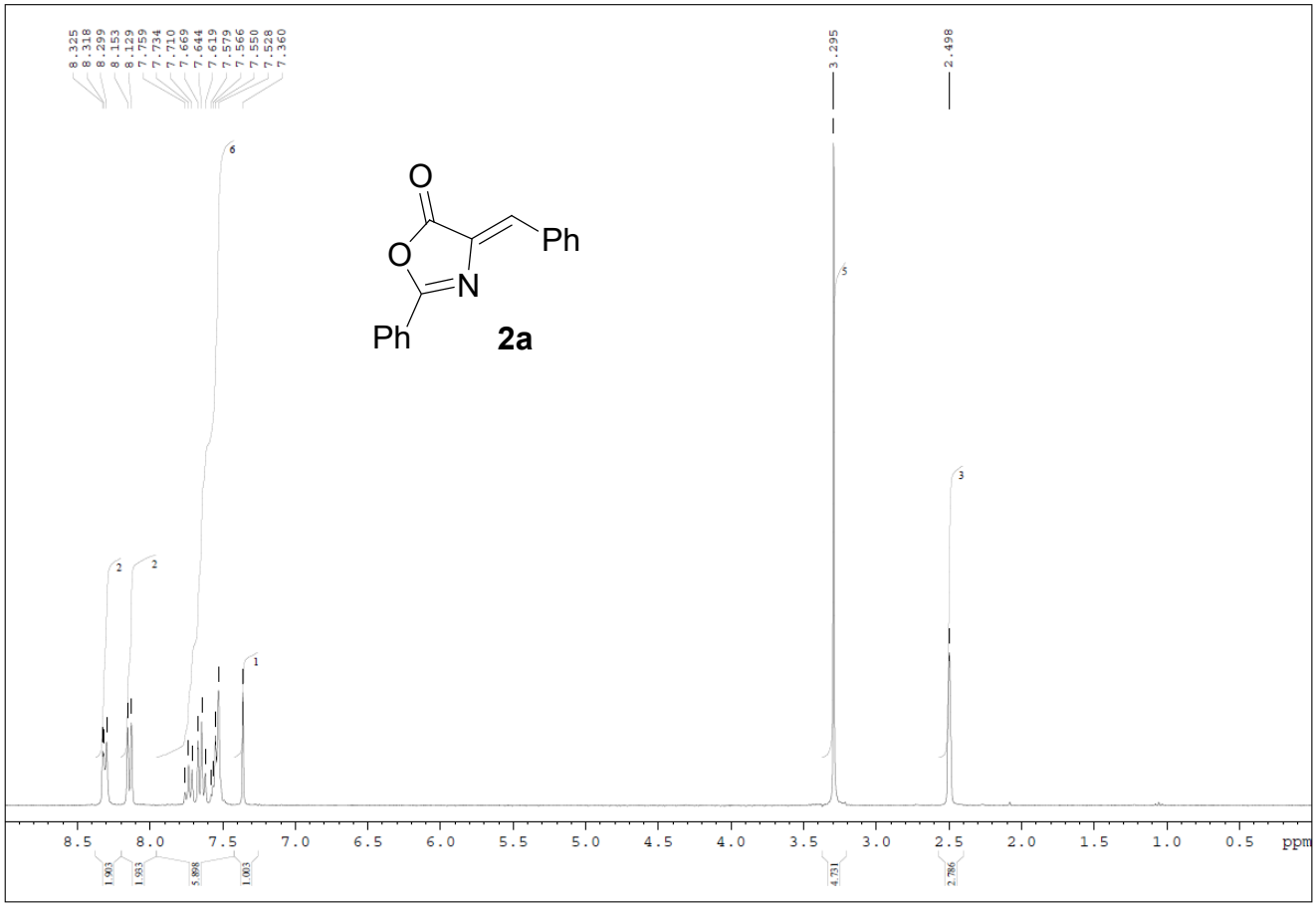
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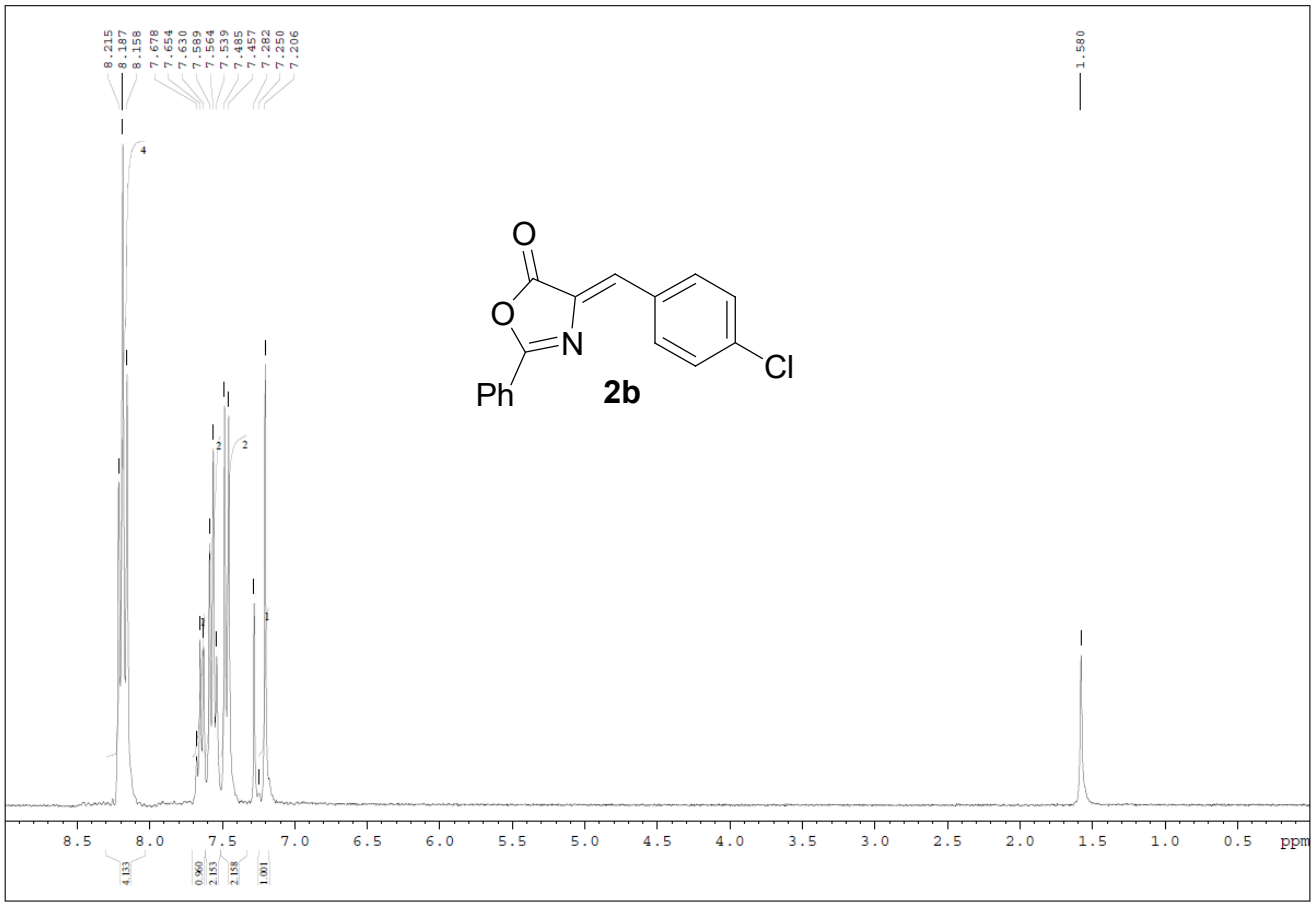
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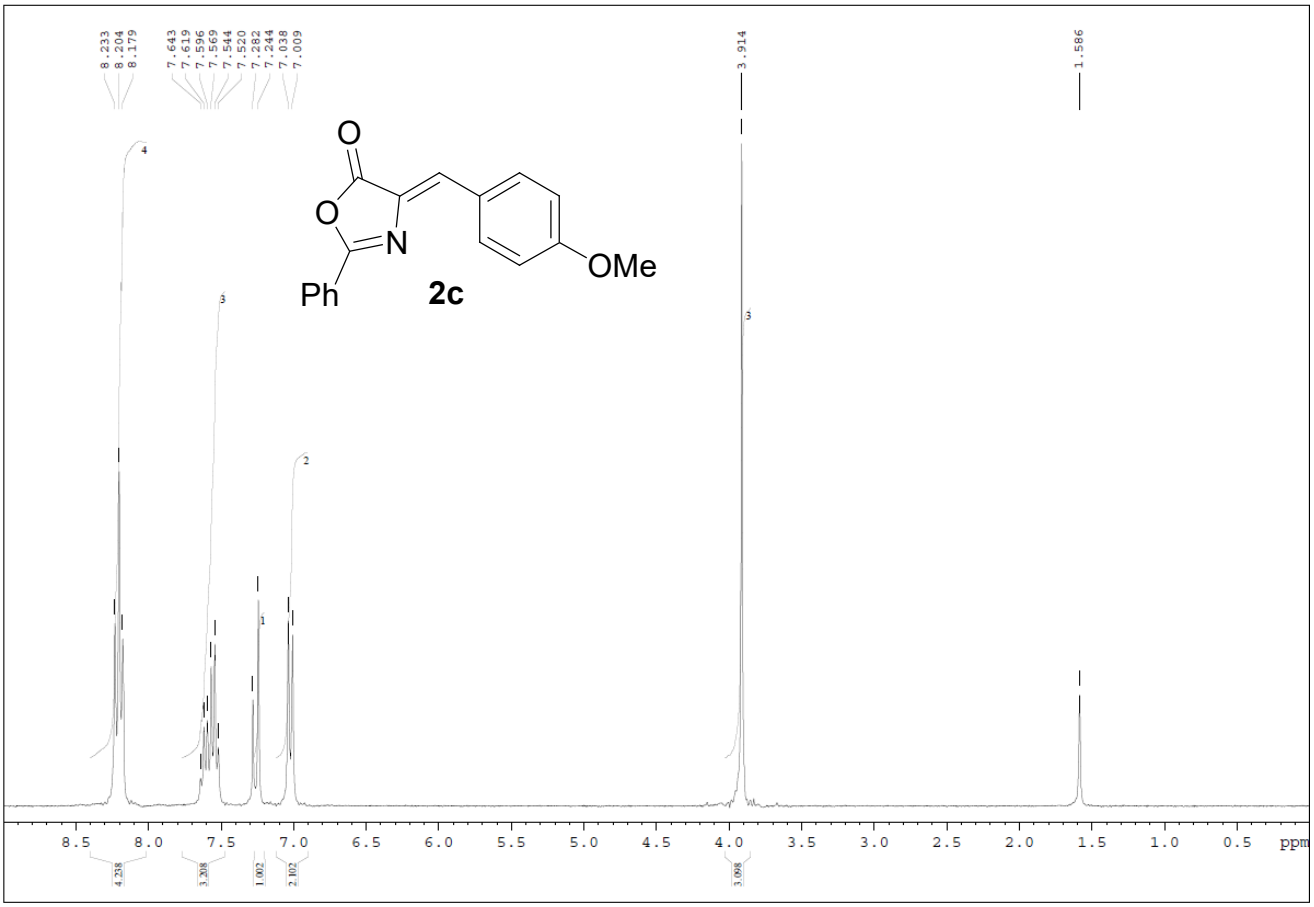
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7.009
3.914
1.586
O
O
N
Ph
OMe
2c
8.5
8.0
7.5
7.0
6.5
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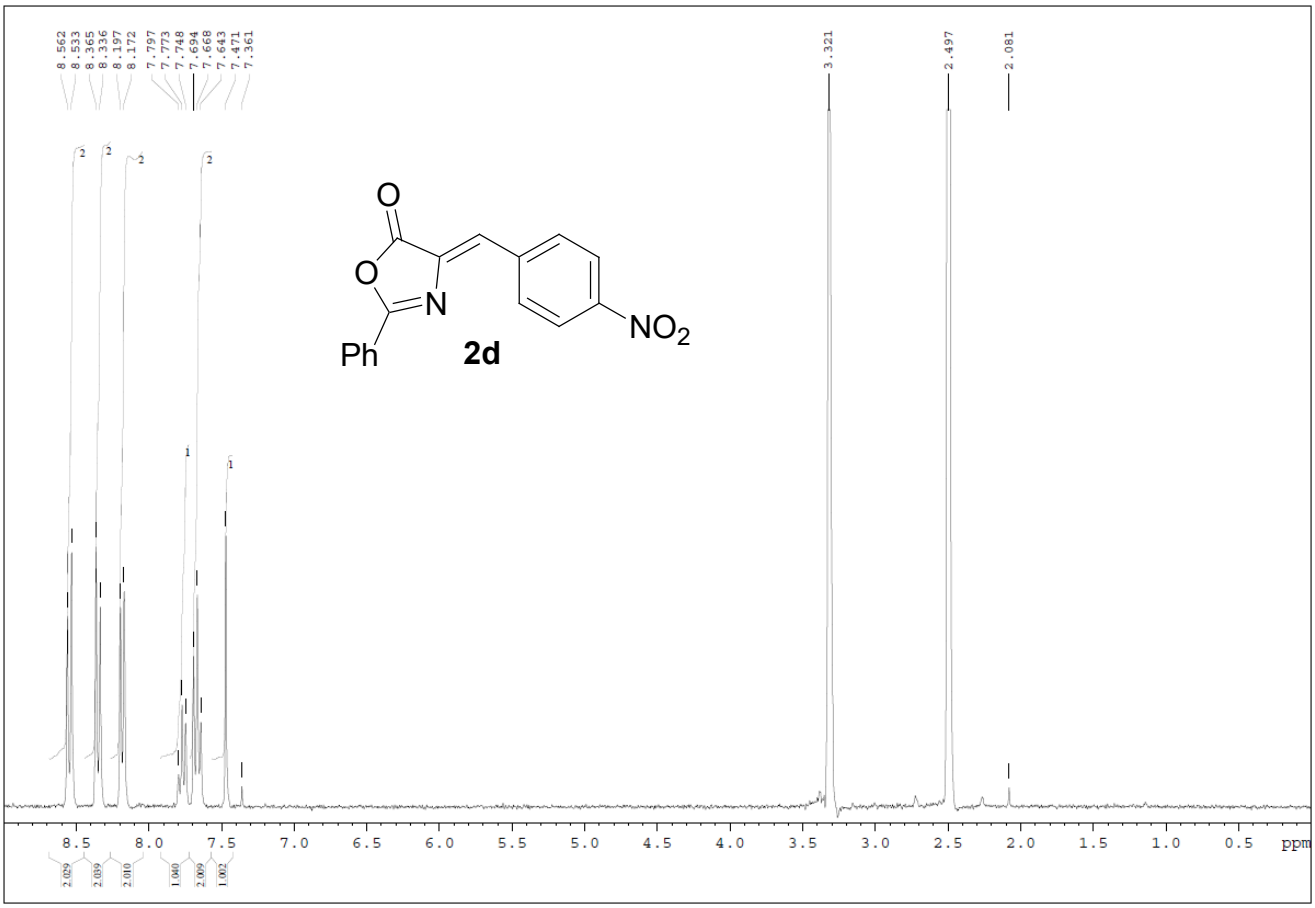
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7.773
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7.668
7.643
7.471
7.361
3.321
2.497
2.081
O
O
N
Ph
NO2
2d
8.5
8.0
7.5
7.0
6.5
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1.0
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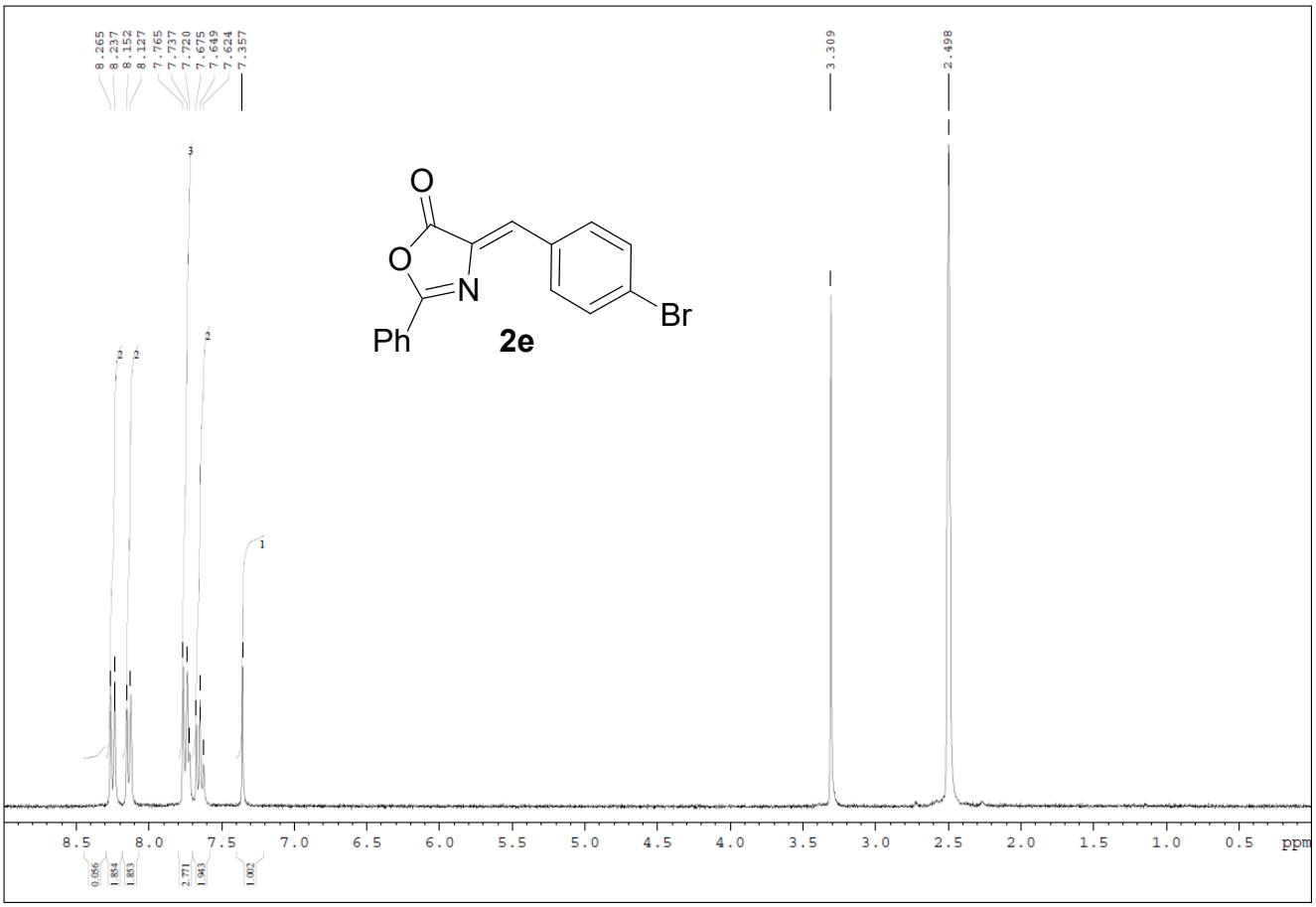
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8.152
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7.675
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7.624
7.357
3.309
2.498
O
O
N
Ph
Br
2e
8.5
8.0
7.5
7.0
6.5
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4.5
4.0
3.5
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1.0
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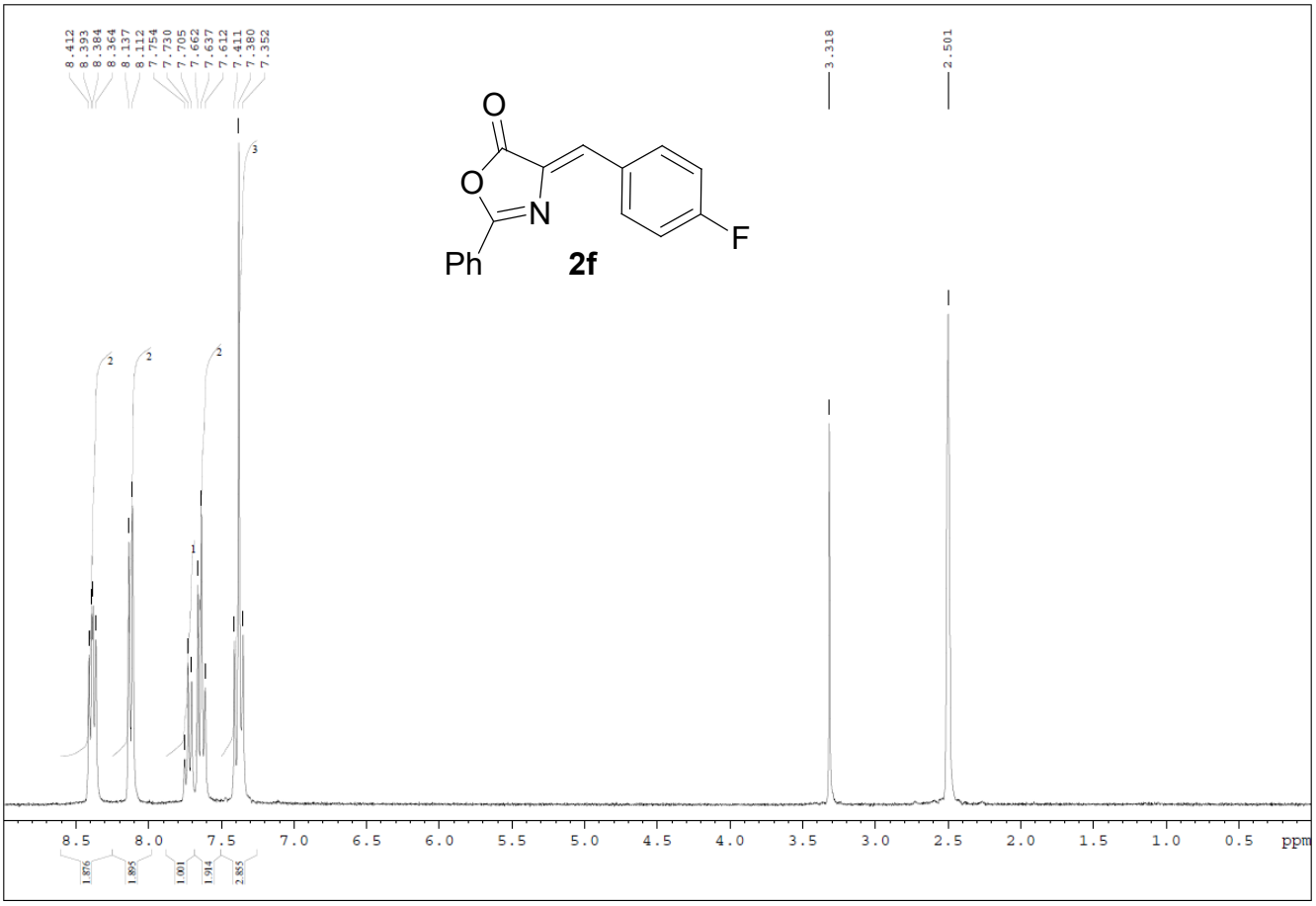
ppm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7.637
7.612
7.411
7.380
7.352
3.318
2.501
O
O
N
Ph
F
2f
8.5
8.0
7.5
7.0
6.5
6.0
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4.5
4.0
3.5
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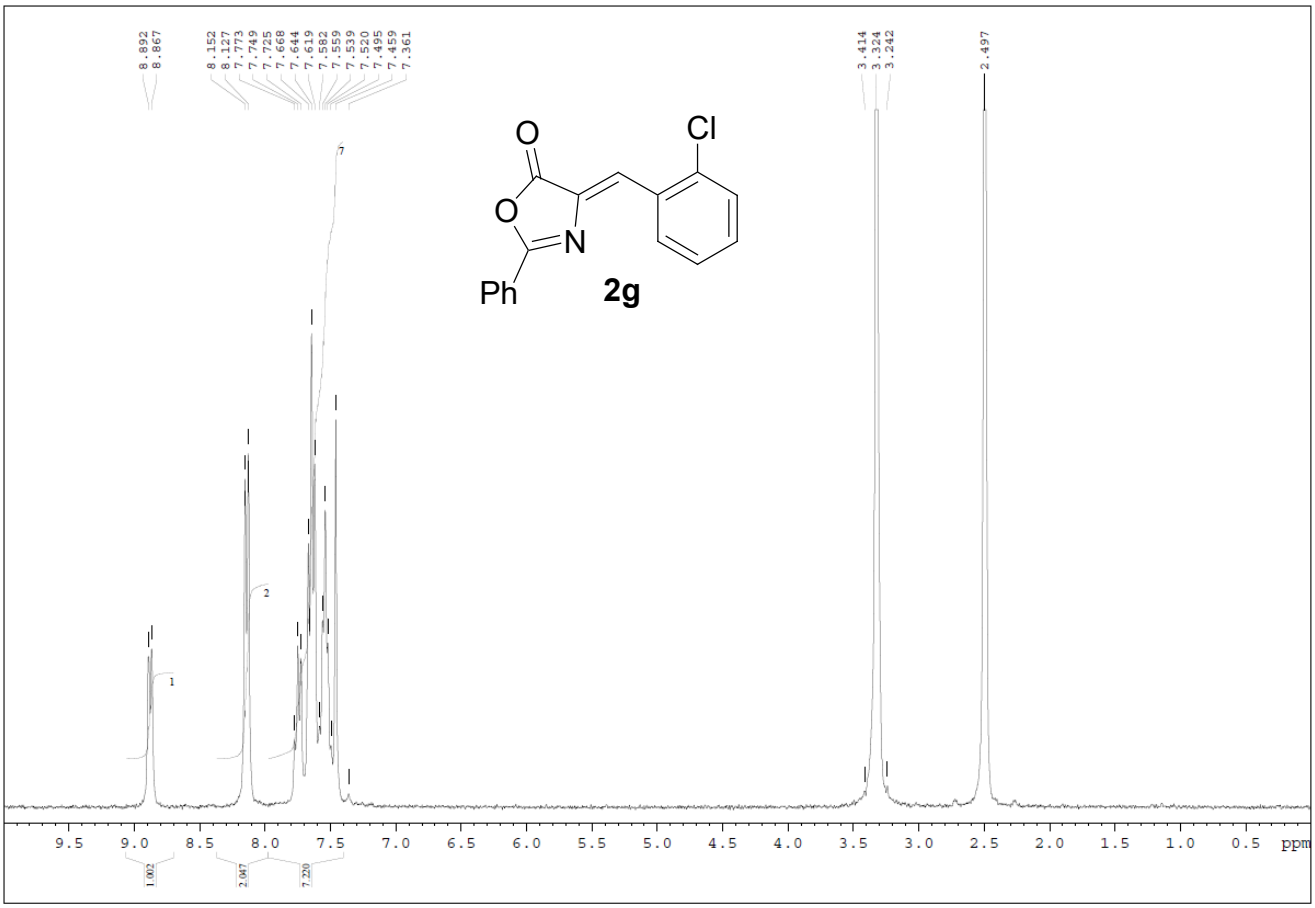
2.5
2.0
1.5
1.0
0.5
ppm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7.539
7.520
7.495
7.459
7.361
3.414
3.324
3.242
2.497
O
O
N
Ph
Cl
2g
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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1.0
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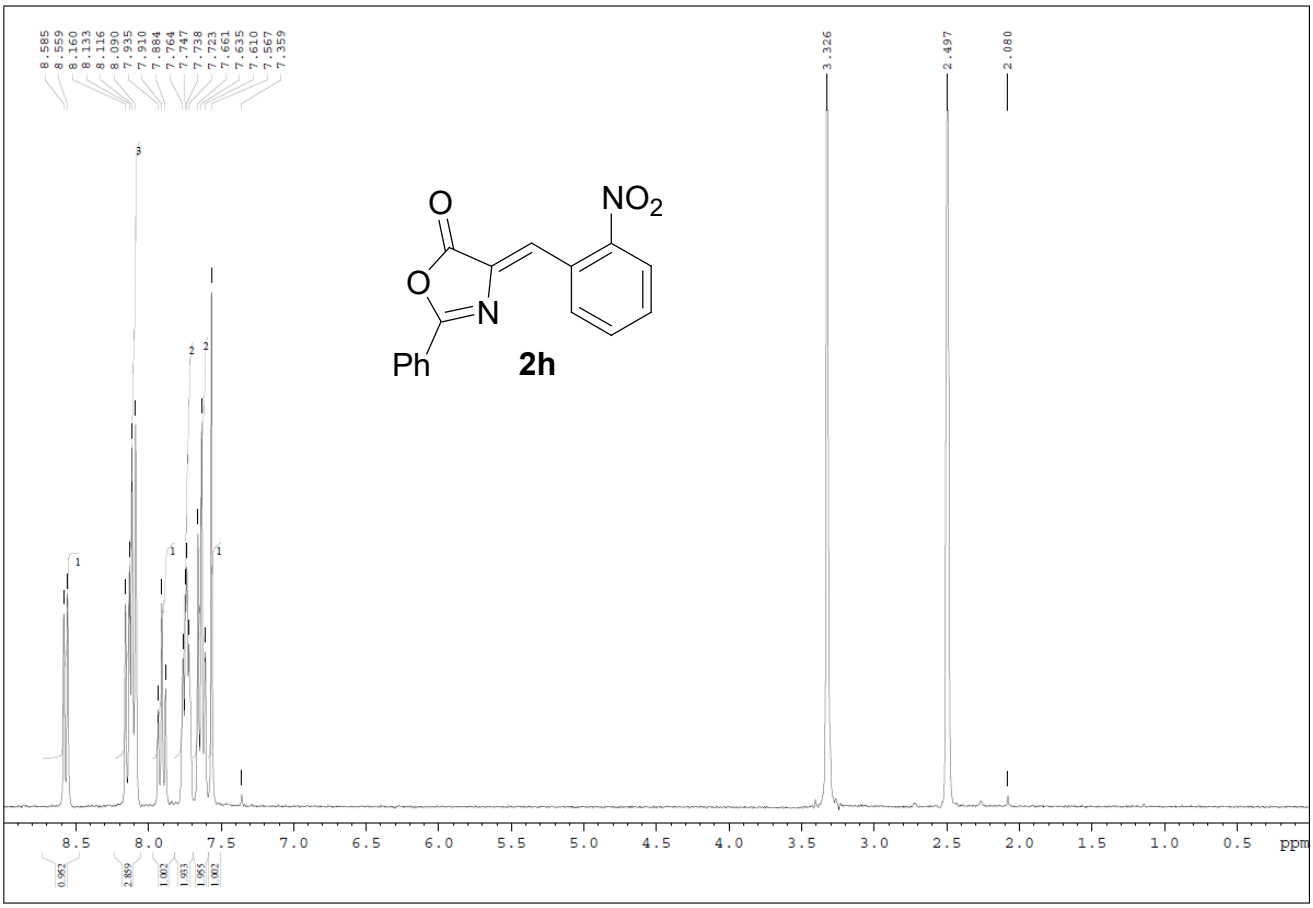
ppm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7.910
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7.747
7.738
7.723
7.661
7.635
7.610
7.567
7.359
3.326
2.497
2.080
O
NO2
O
N
Ph
2h
8.5
8.0
7.5
7.0
6.5
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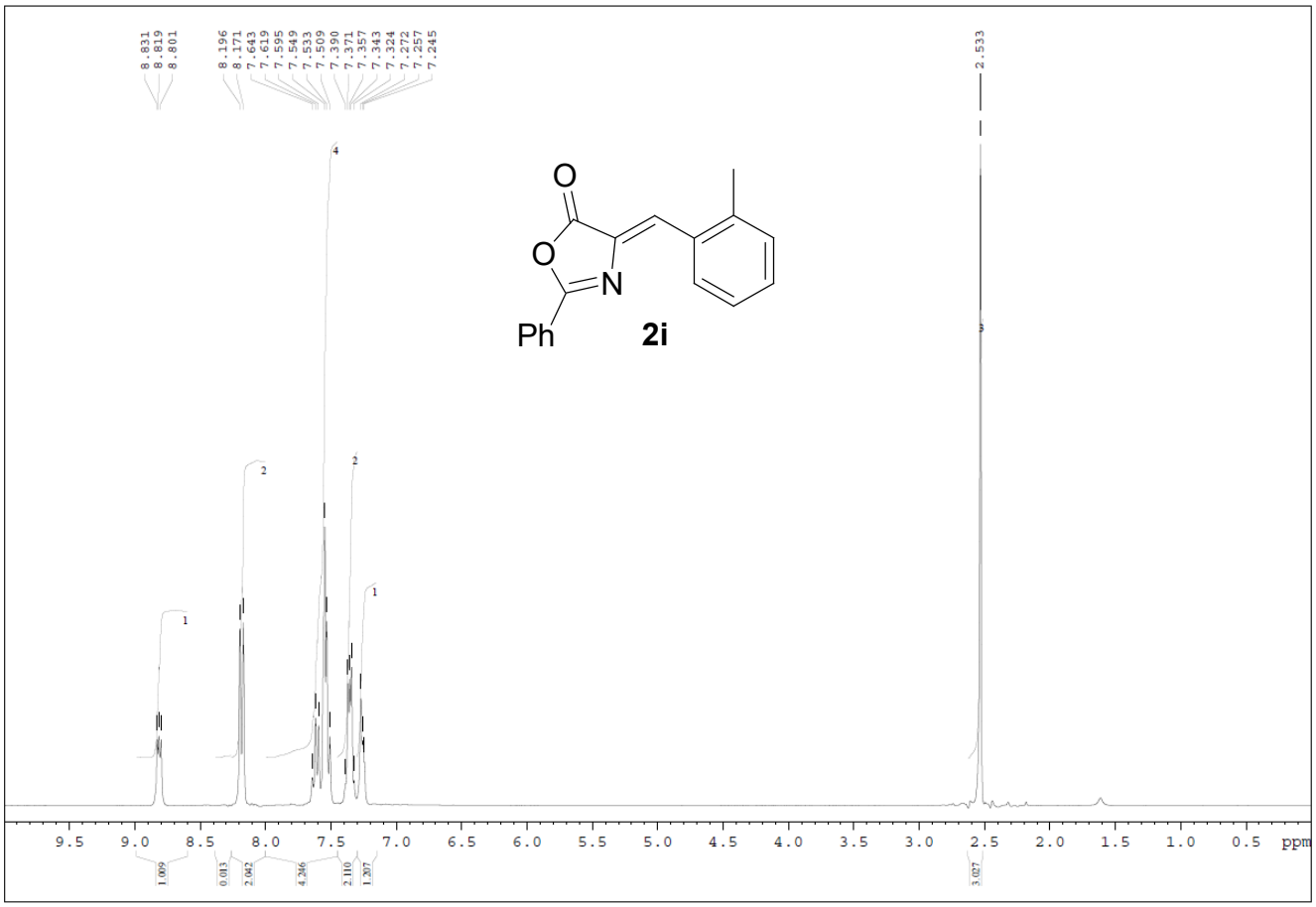
ppm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7.595
7.549
7.533
7.509
7.390
7.371
7.357
7.343
7.324
7.272
7.257
7.245
2.533
O
O
N
Ph
2i
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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2.0
1.5
1.0
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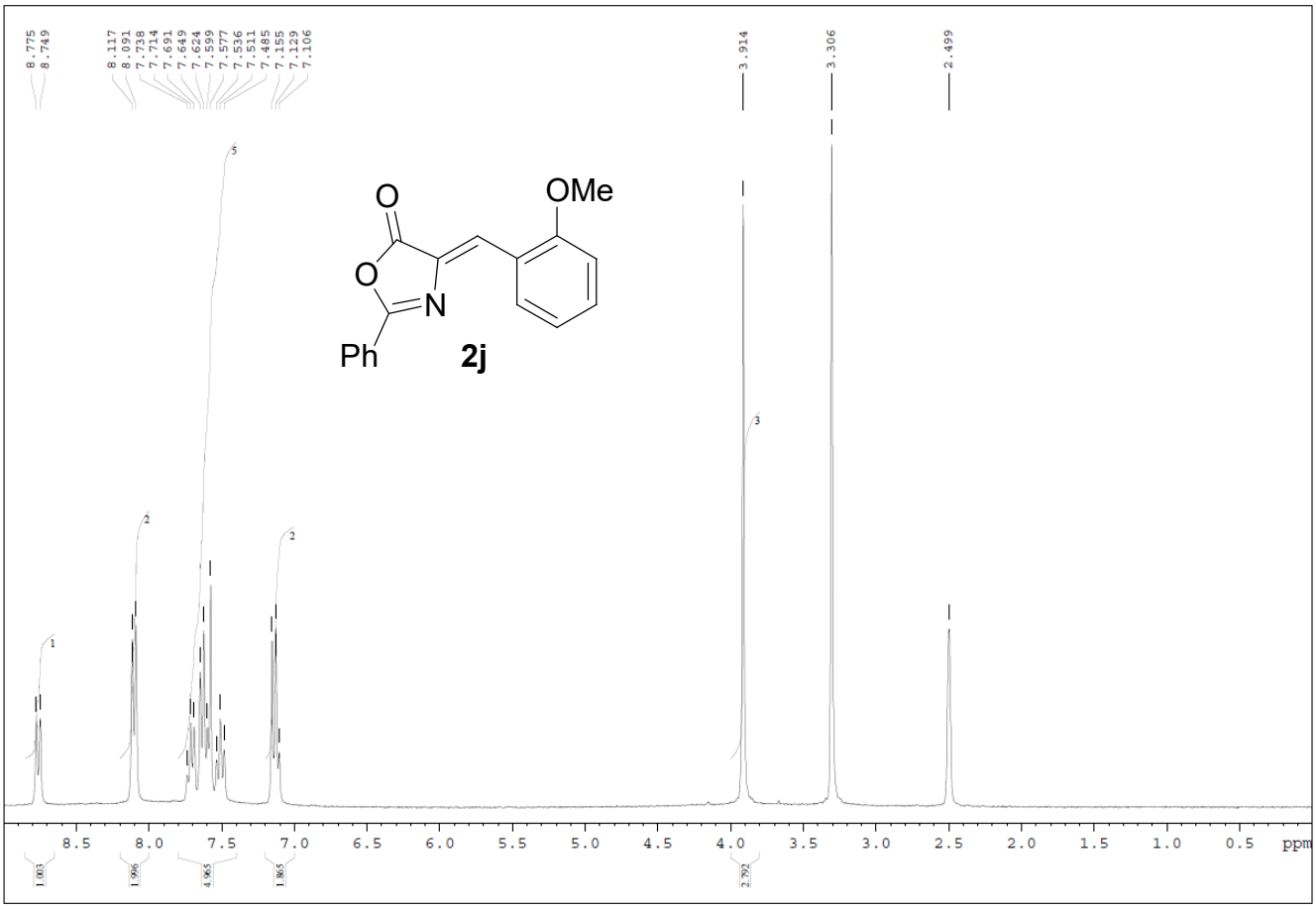
ppm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8.117
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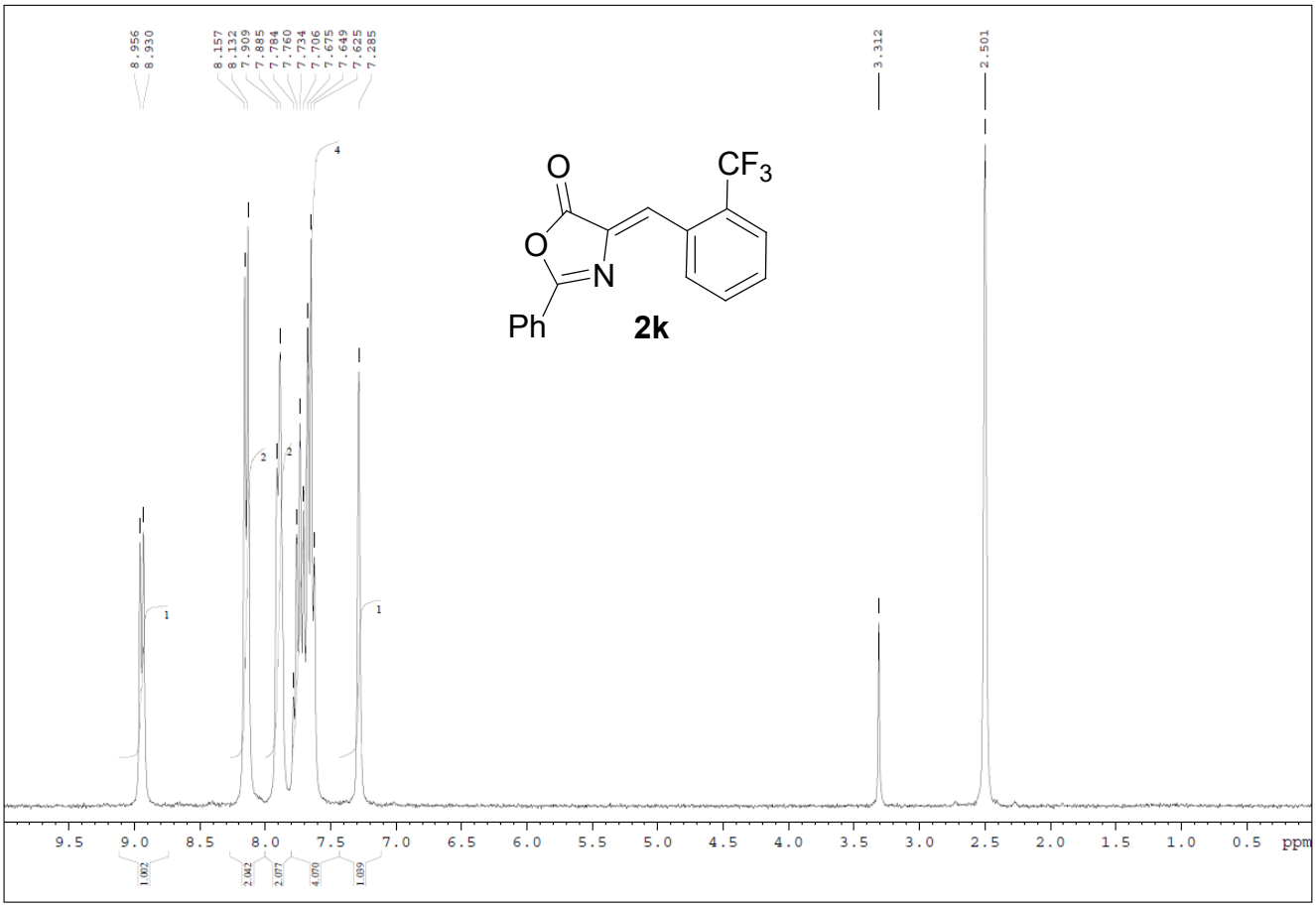
7.714
7.691
7.649
7.624
7.599
7.577
7.536
7.511
7.485
7.155
7.129
7.106
3.914
3.306
2.499
O
OMe
O
N
Ph
2j
ppm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8.930
8.157
8.132
8.109
7.885
7.784
7.760
7.734
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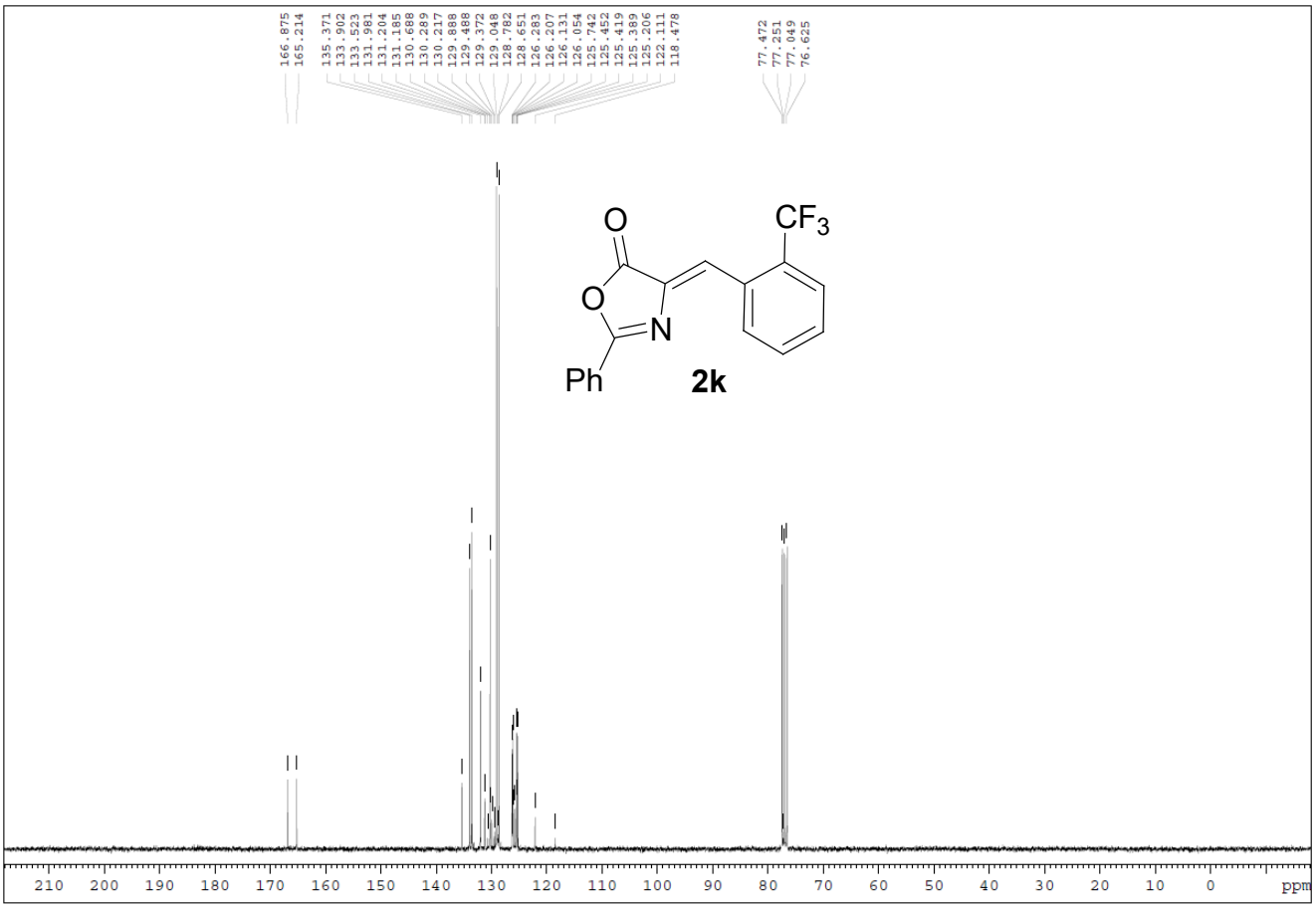
7.649
7.625
7.285
3.312
2.501
O
CF3
O
N
Ph
2k
ppm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131.185
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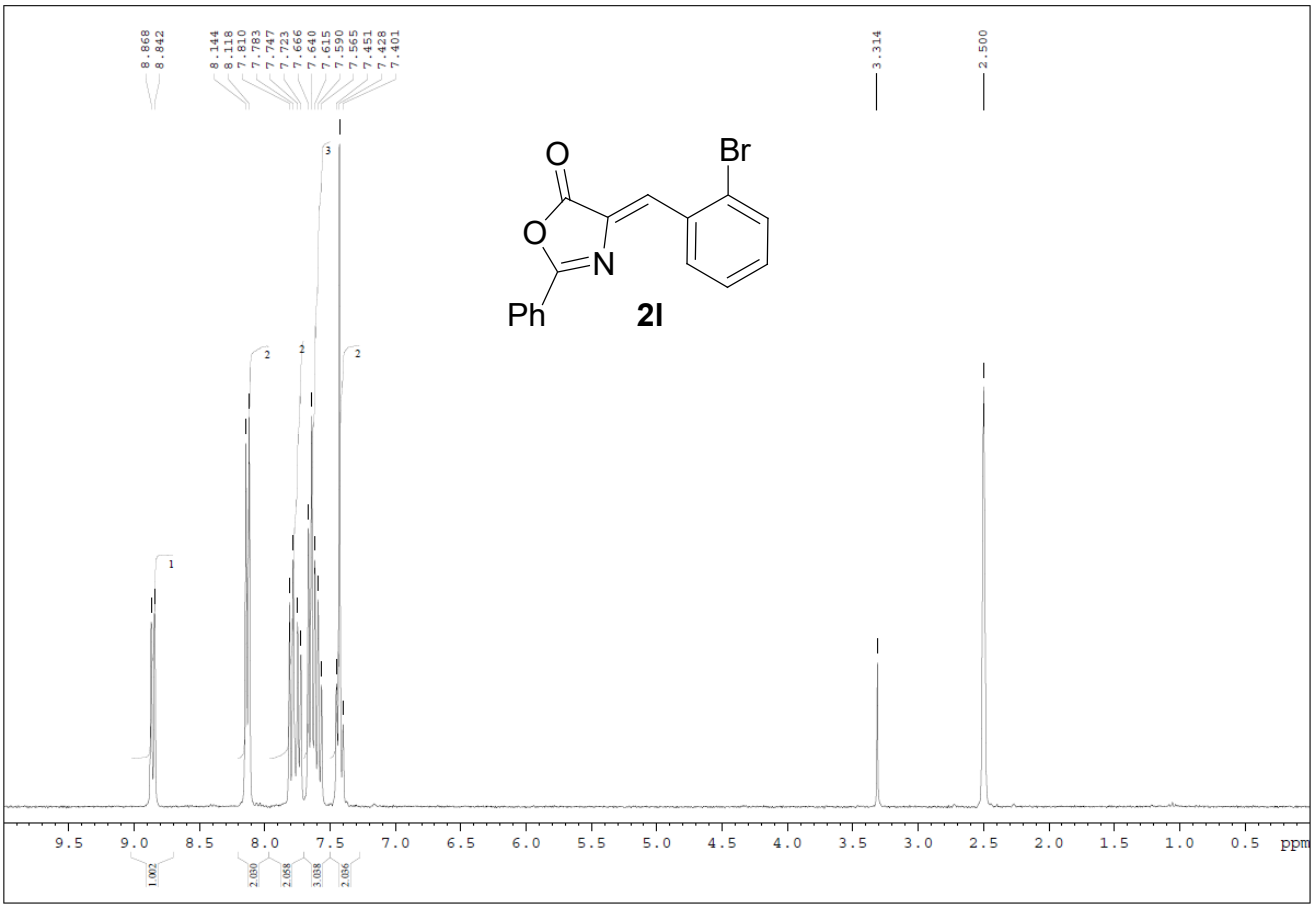
130.217
129.888
129.488
129.372
129.048
128.782
128.651
126.283
126.207
126.131
126.054
125.742
125.452
125.419
125.389
125.206
122.111
118.478
77.472
77.251
77.049
76.625
O
CF3
O
N
Ph
2k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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8.144
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7.783
7.747
7.723
7.666
7.640
7.615
7.590
7.565
7.451
7.428
7.401
3.314
2.500
O
Br
O
N
Ph
2l
1
2
3
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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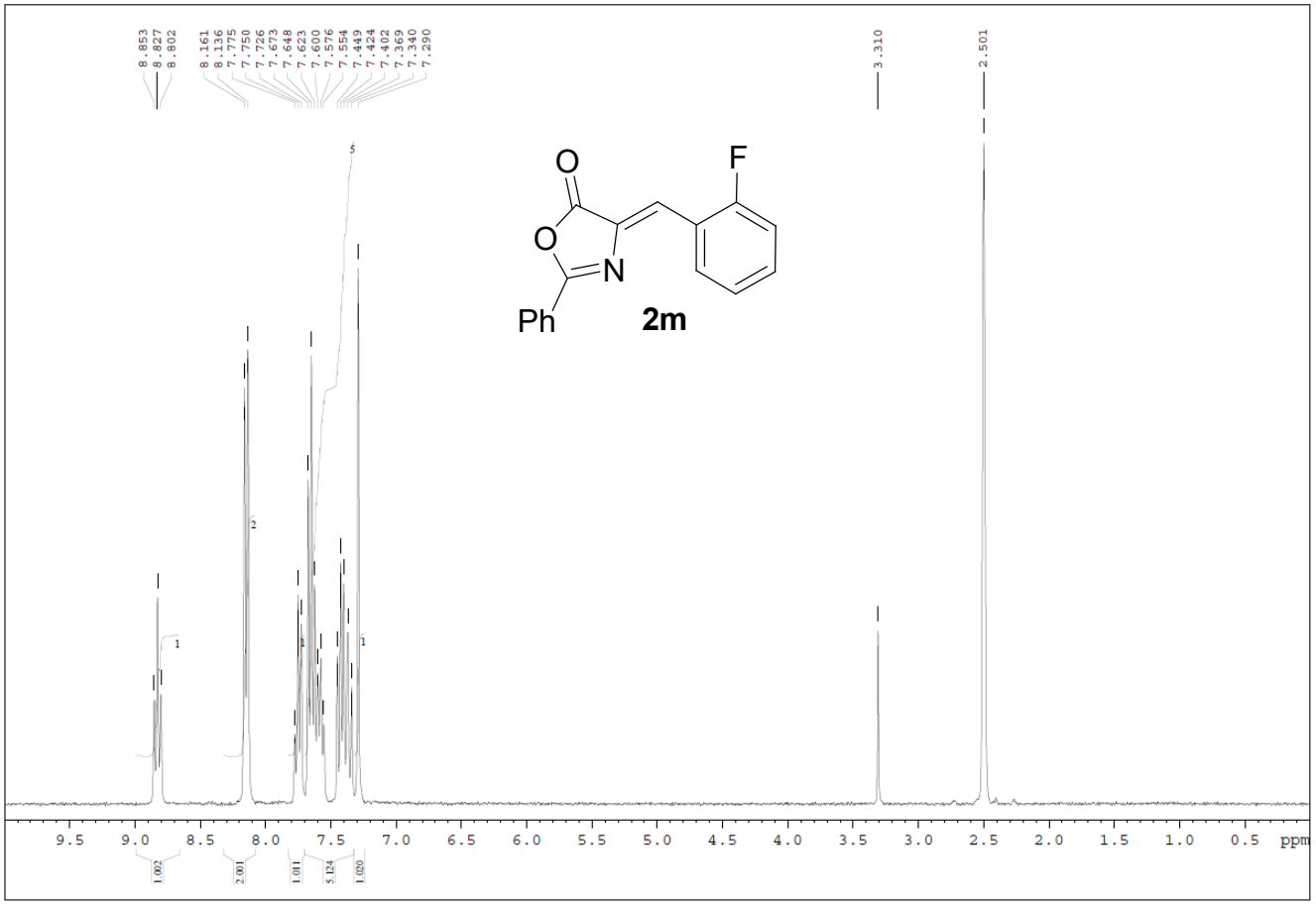
2.000
2.068
3.038
2.036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8.161
8.136
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7.750
7.726
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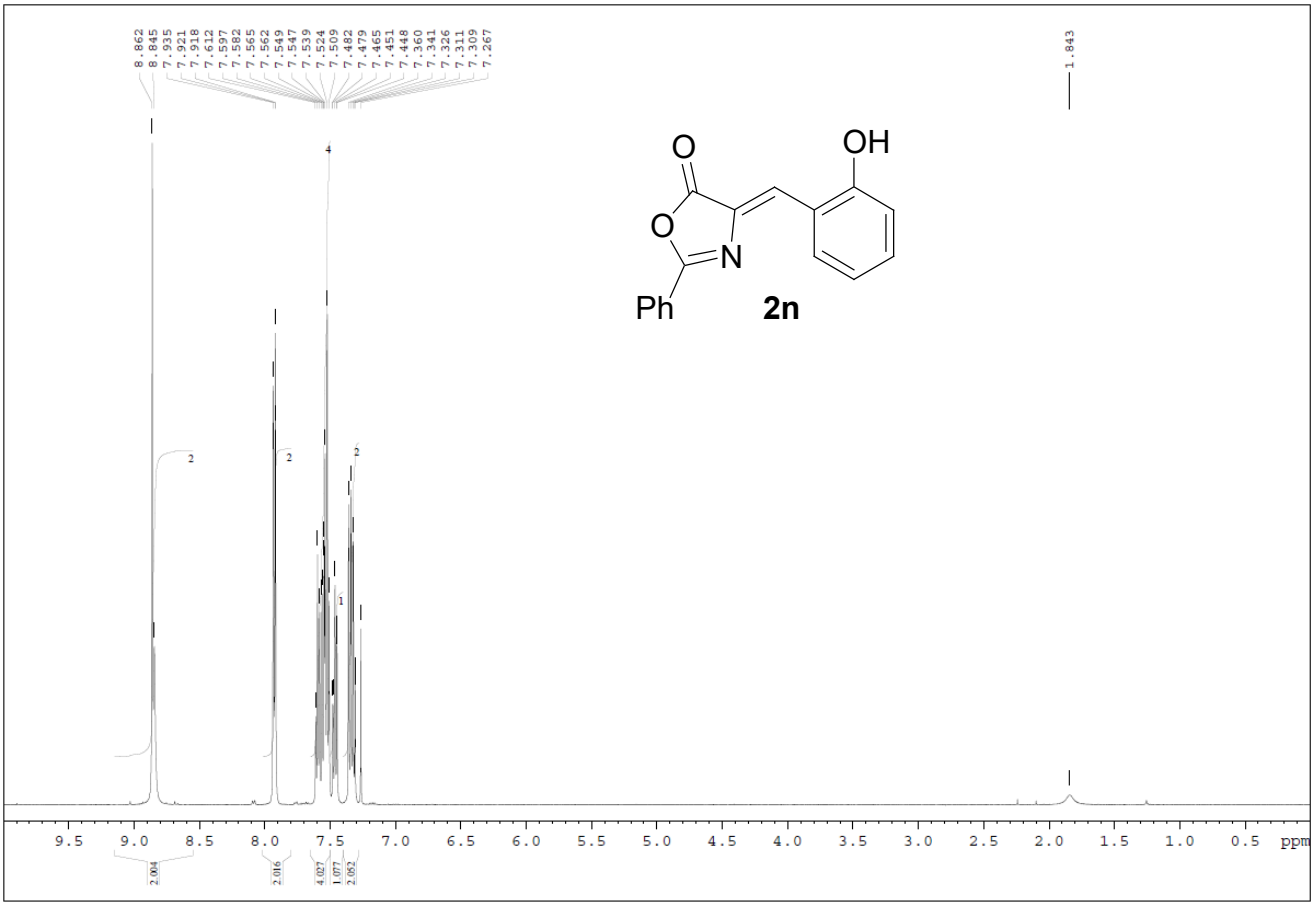
7.648
7.623
7.600
7.576
7.554
7.449
7.424
7.402
7.369
7.340
7.290
3.310
2.501
O
F
O
N
Ph
2m
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.002
2.001
1.011
5.124
1.020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7.597
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7.565
7.562
7.549
7.547
7.539
7.524
7.509
7.492
7.479
7.465
7.451
7.448
7.360
7.341
7.326
7.311
7.309
7.267
1.843
O
OH
O
N
Ph
2n
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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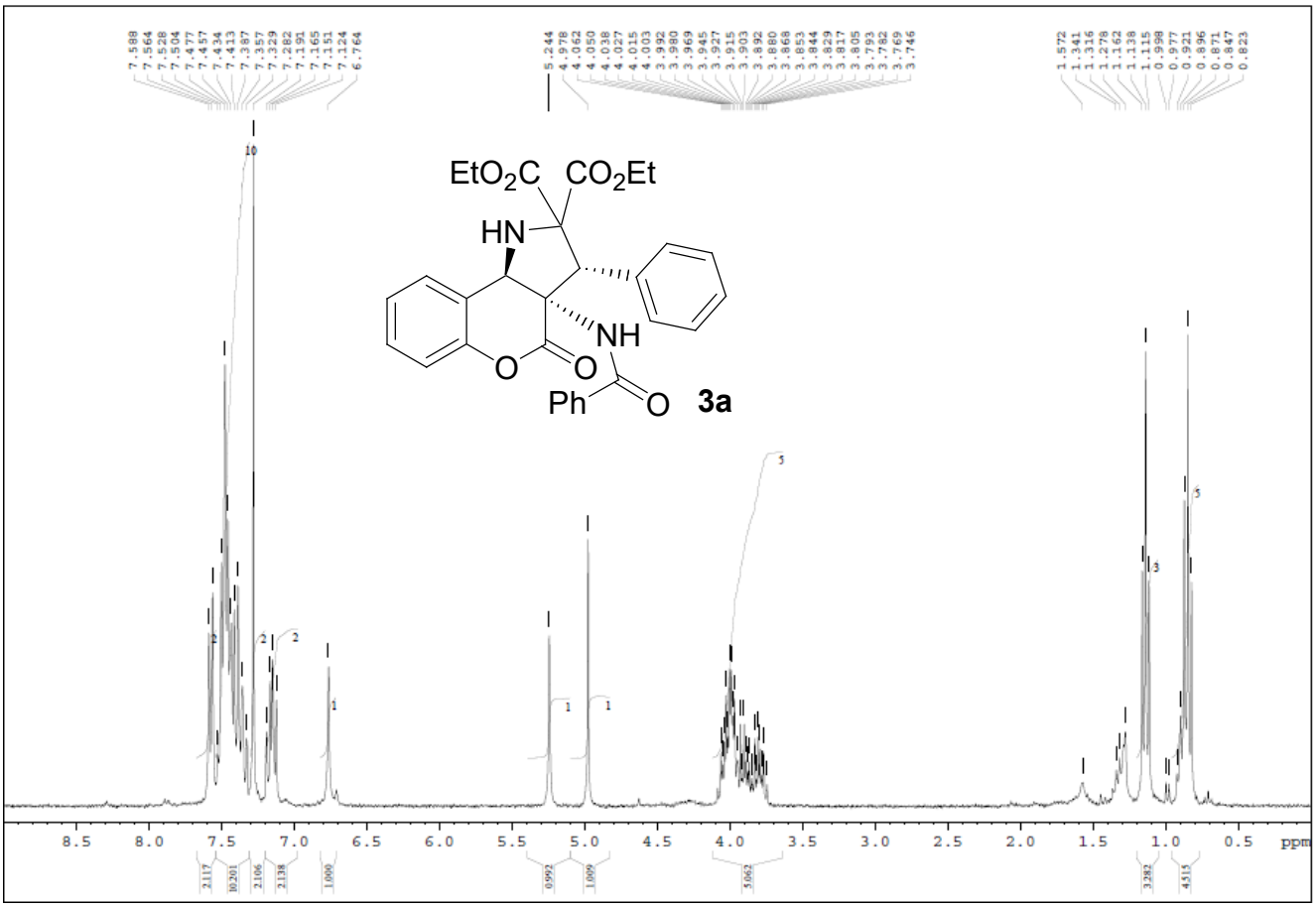
2.016
4.027
1.077
2.052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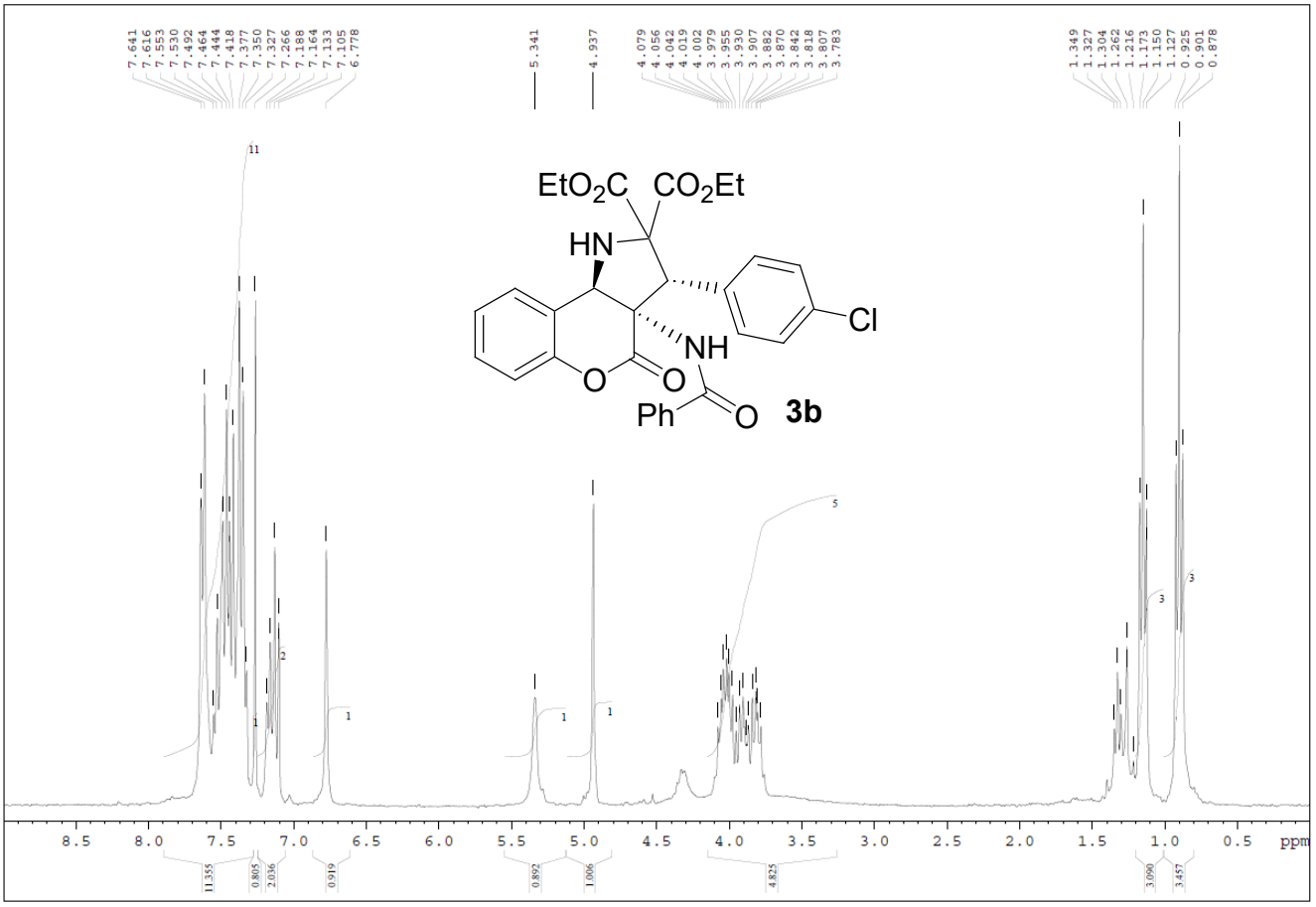
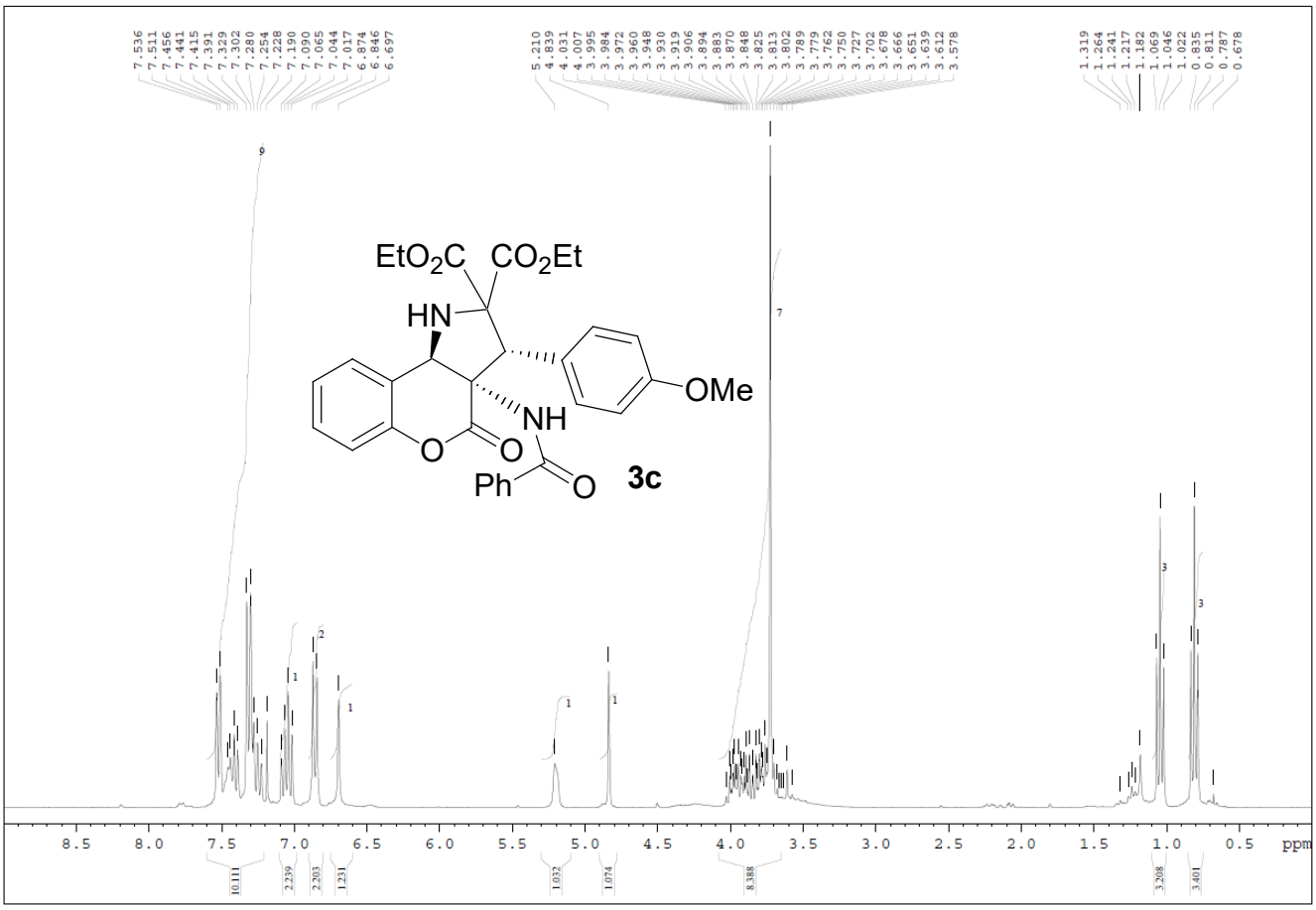
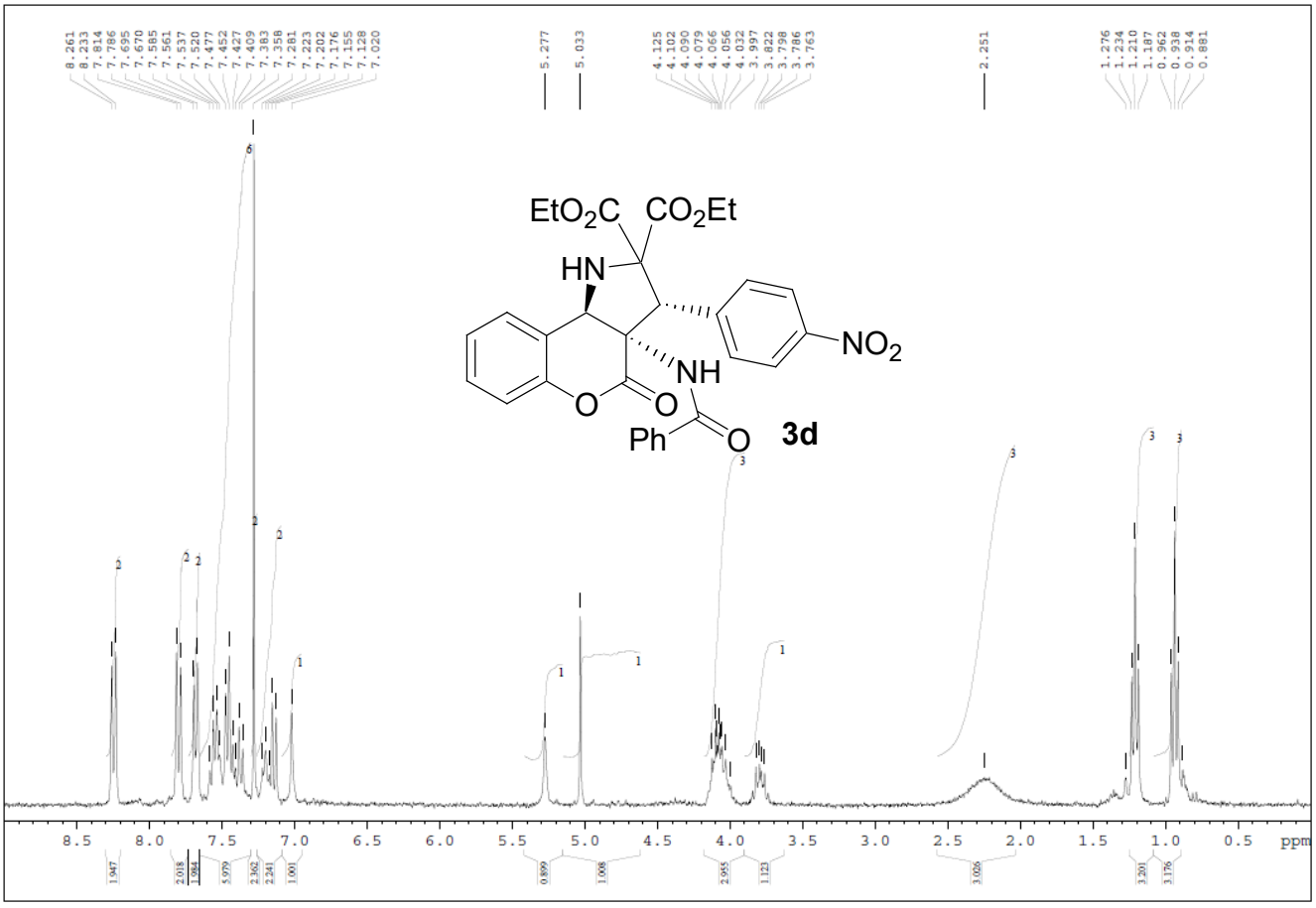
CO2Et
HN
NH
O
O
Ph
O
3a


EtO2C
CO2Et
HN
Cl
NH
O
O
Ph
O
3b


EtO2C
CO2Et
HN
OMe
NH
O
O
Ph
O
3c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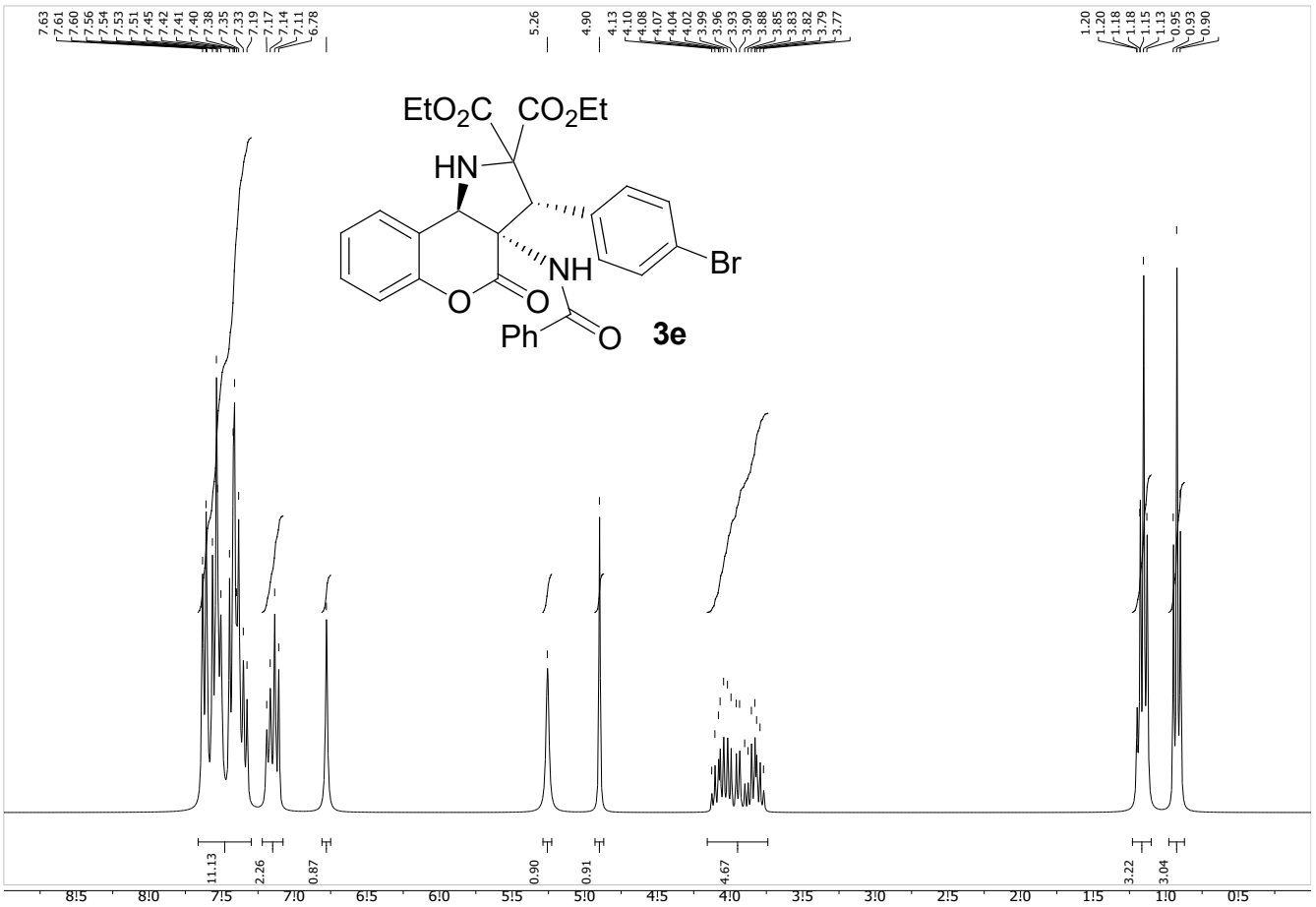
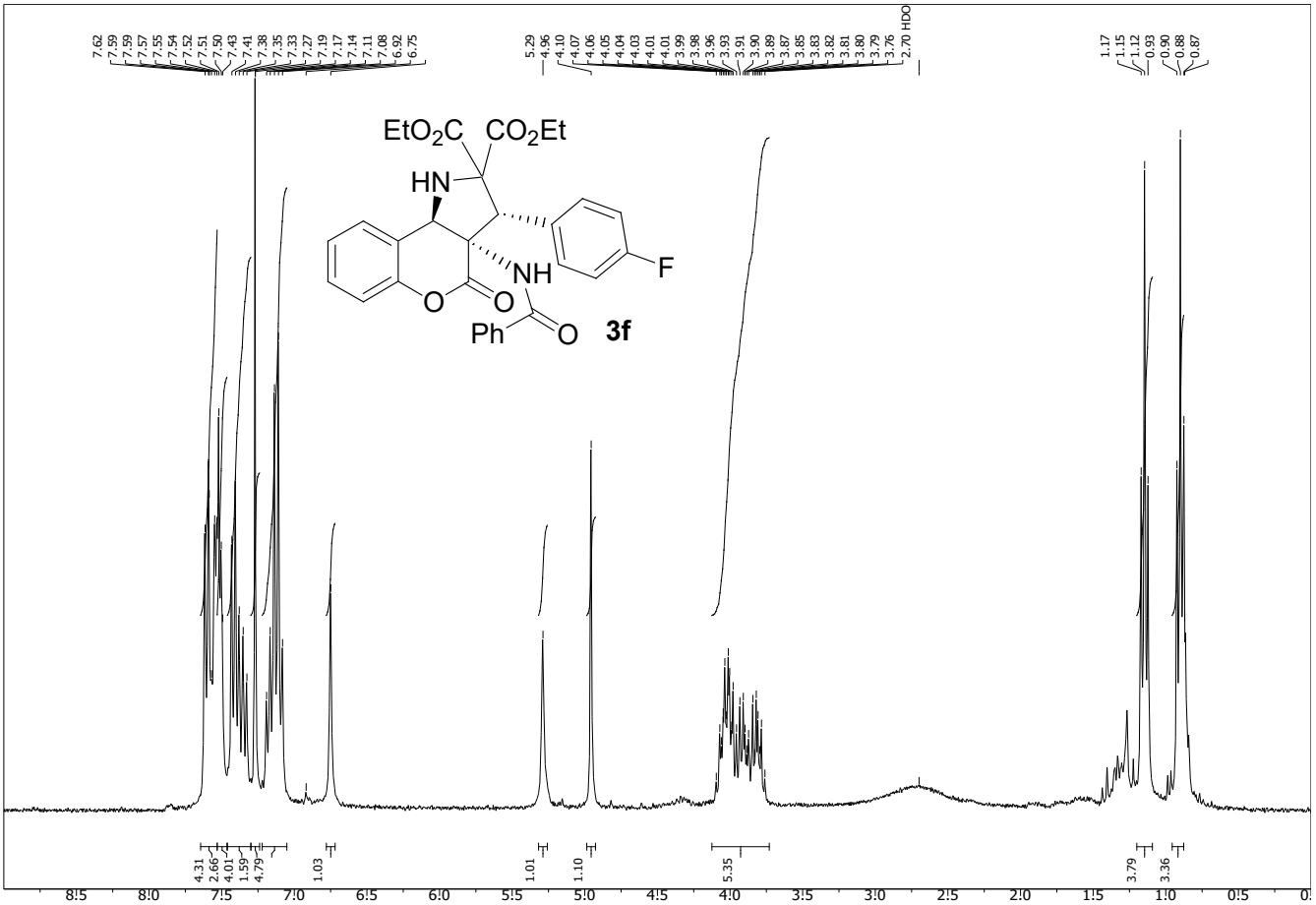
CO2Et
HN
NO2
NH
O
O
Ph
O
3d


EtO2C CO2Et
HN
NH
Br
O
O
Ph
O
3e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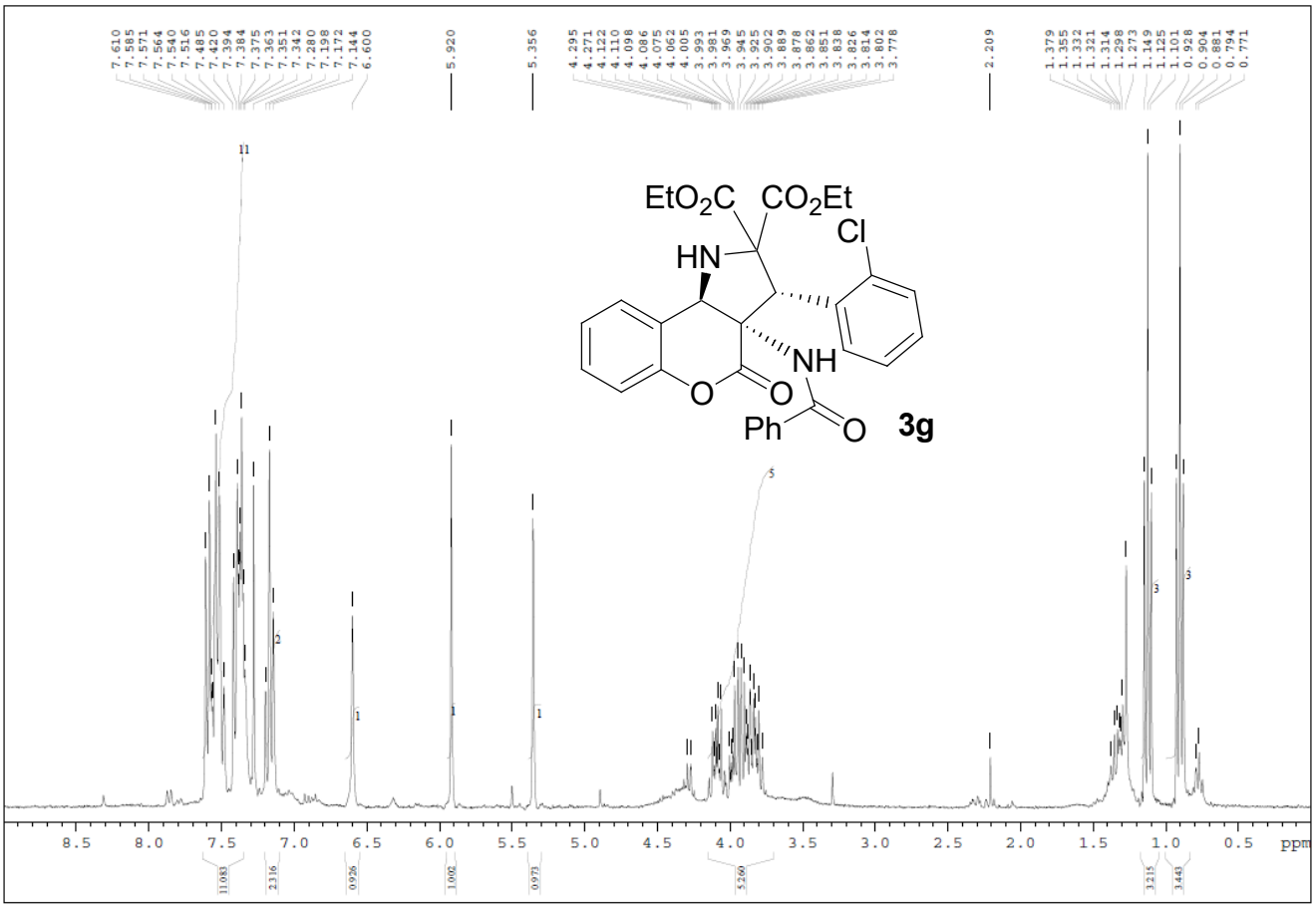
HN
NH
F
O
O
Ph
O
3f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CO2Et
Cl
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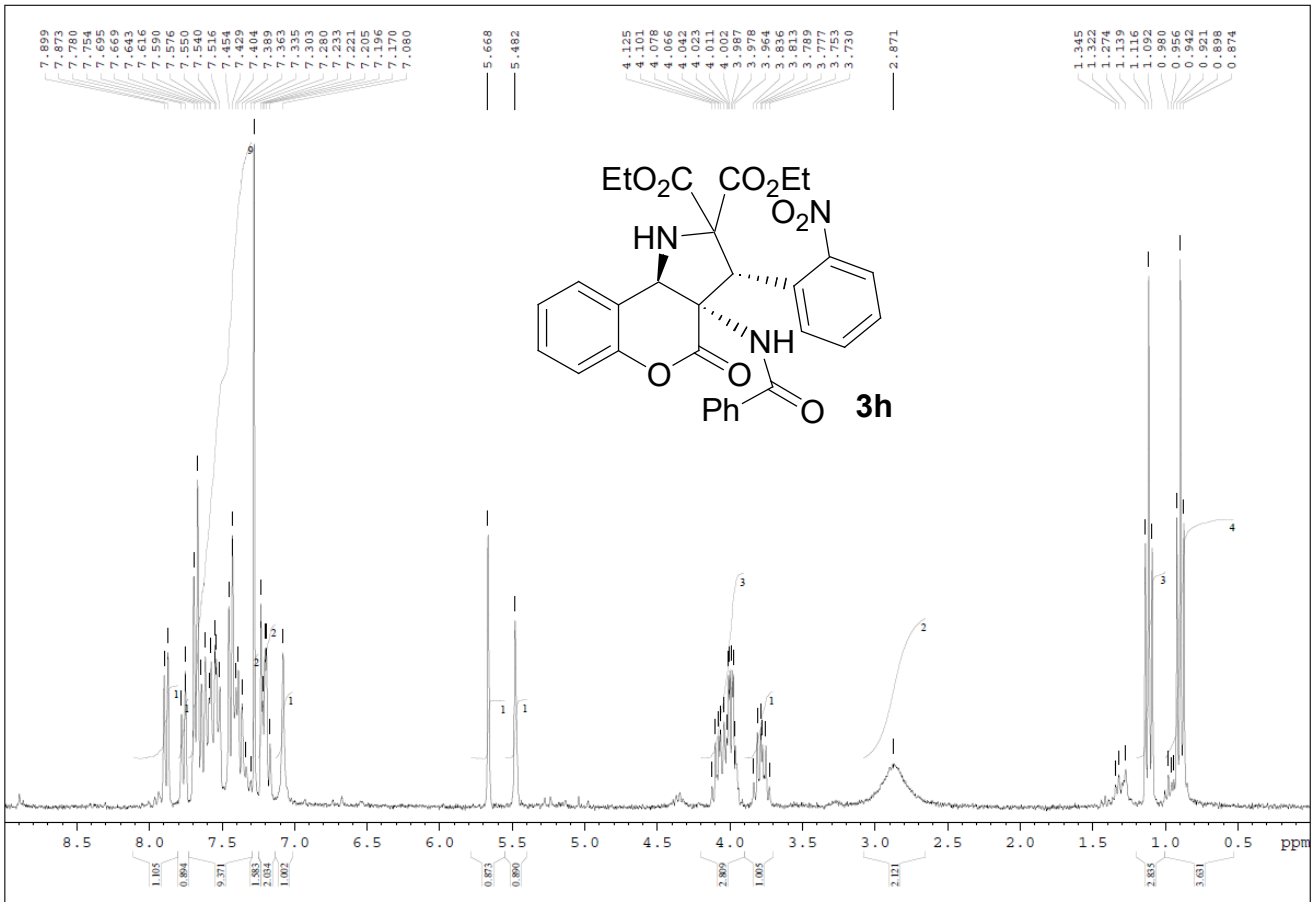
NH
O
O
Ph
O
3g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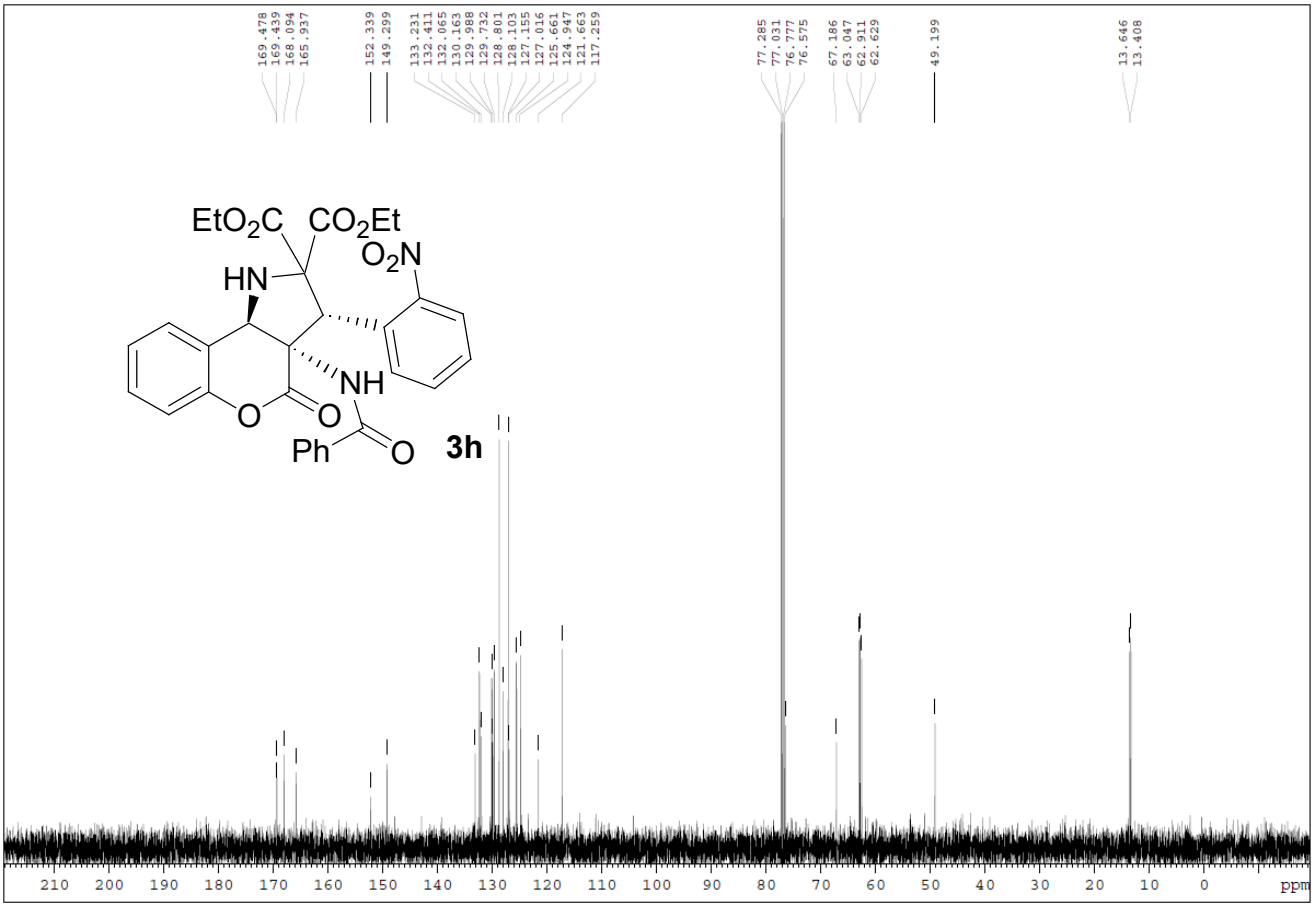
CO2Et
O2N
HN
NH
O
O
Ph
O
3h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165.937
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149.299
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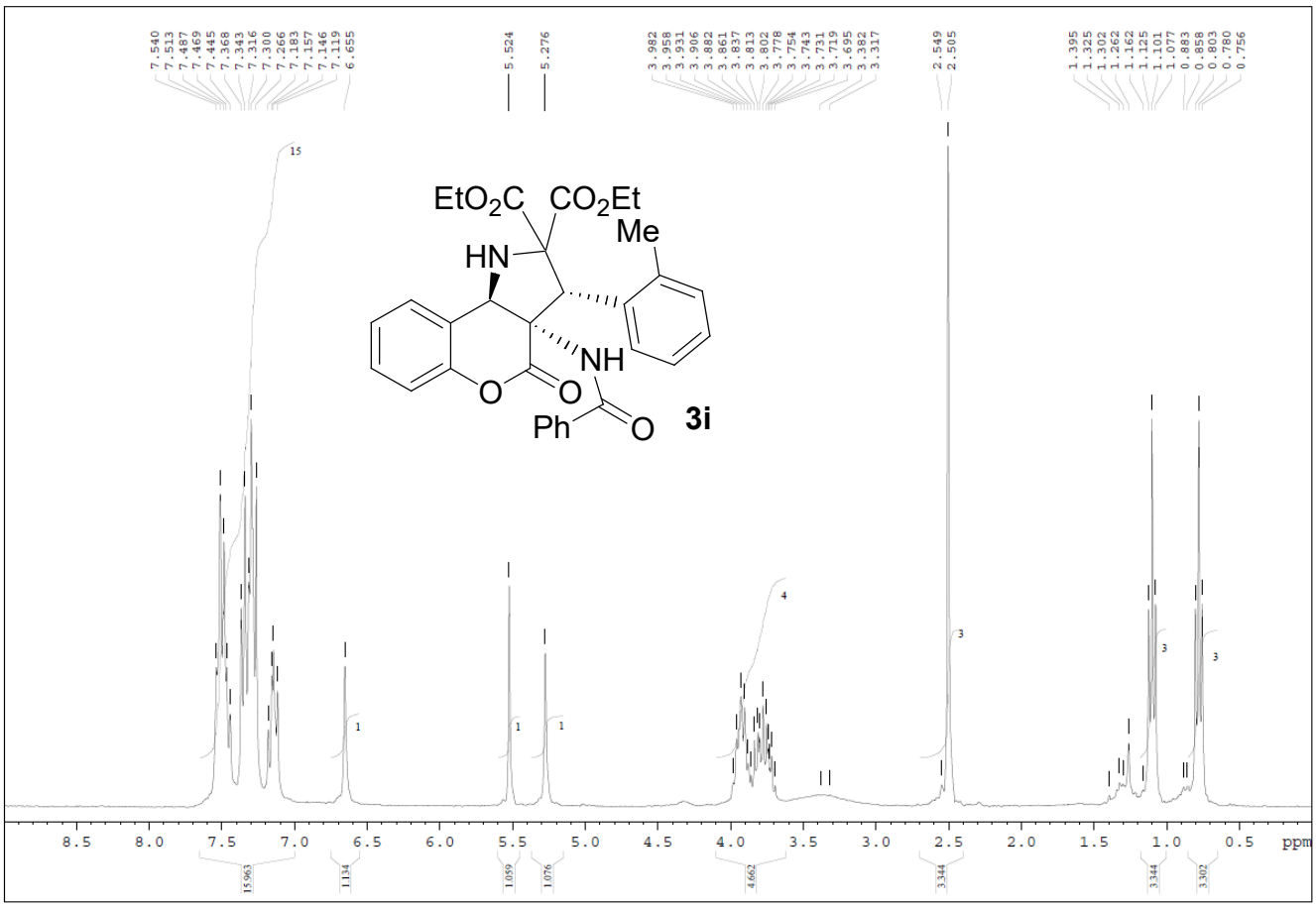
132.411
132.065
130.163
129.988
129.732
128.801
128.103
127.155
127.016
125.661
124.947
121.663
117.259
77.285
77.031
76.777
76.575
67.186
63.047
62.911
62.629
49.199
13.646
13.408
EtO2C
CO2Et
O2N
HN
NH
O
O
Ph
O
3h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.157
7.146
7.119
6.655
5.524
5.276
3.982
3.958
3.931
3.906
3.882
3.861
3.837
3.813
3.802
3.778
3.754
3.743
3.731
3.719
3.695
3.382
3.317
2.549
2.505
1.395
1.325
1.302
1.262
1.162
1.125
1.101
1.077
0.883
0.858
0.803
0.780
0.756
EtO2C
CO2Et
Me
HN
NH
O
O
Ph
O
3i
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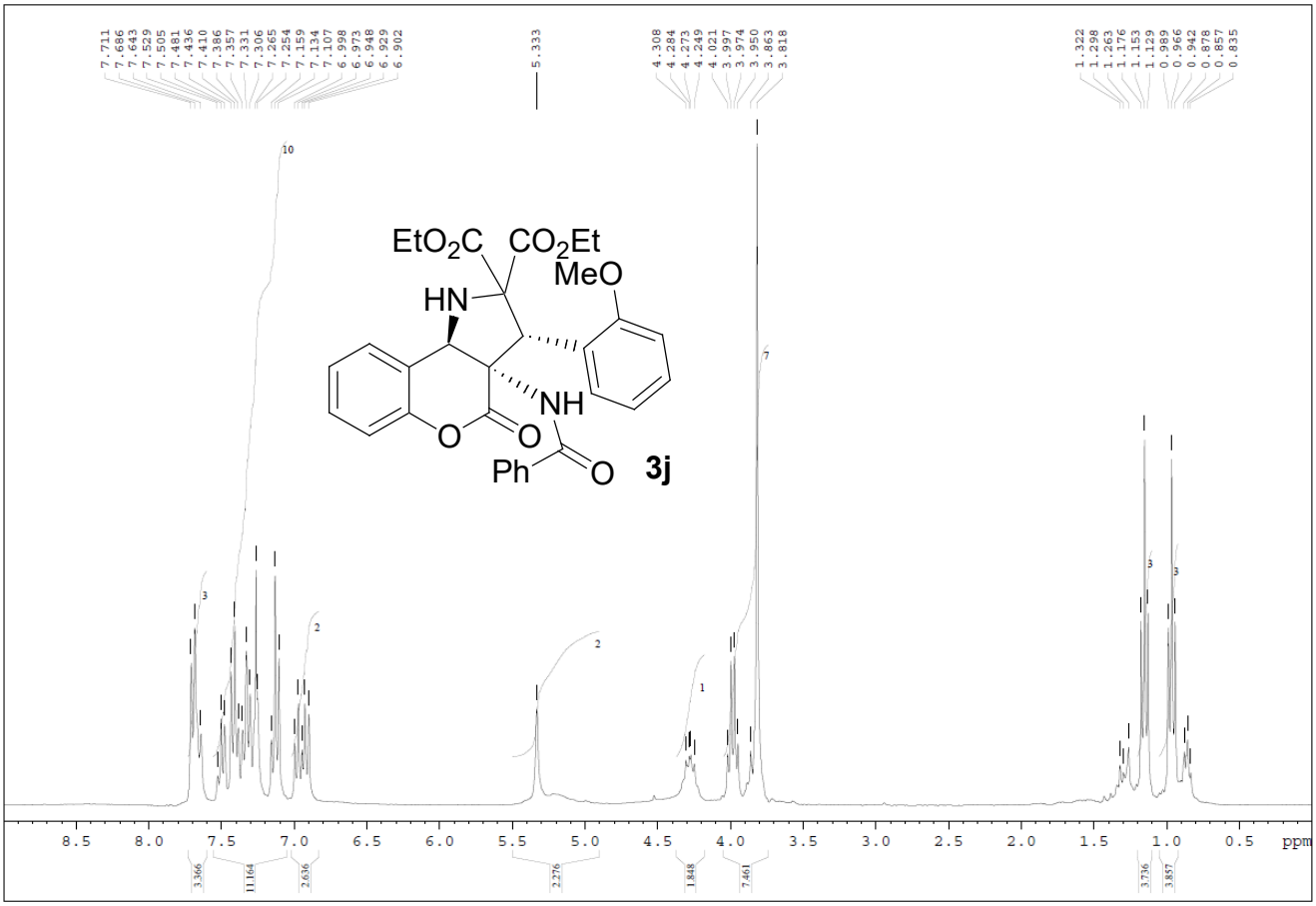
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7.331
7.306
7.265
7.254
7.159
7.134
7.107
6.998
6.973
6.948
6.929
6.902
5.333
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4.284
4.273
4.249
4.021
3.997
3.974
3.950
3.863
3.818
1.322
1.298
1.263
1.176
1.153
1.129
0.989
0.966
0.942
0.878
0.857
0.835
EtO2C
CO2Et
MeO
HN
NH
O
O
Ph
O
3j
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7.5
7.0
6.5
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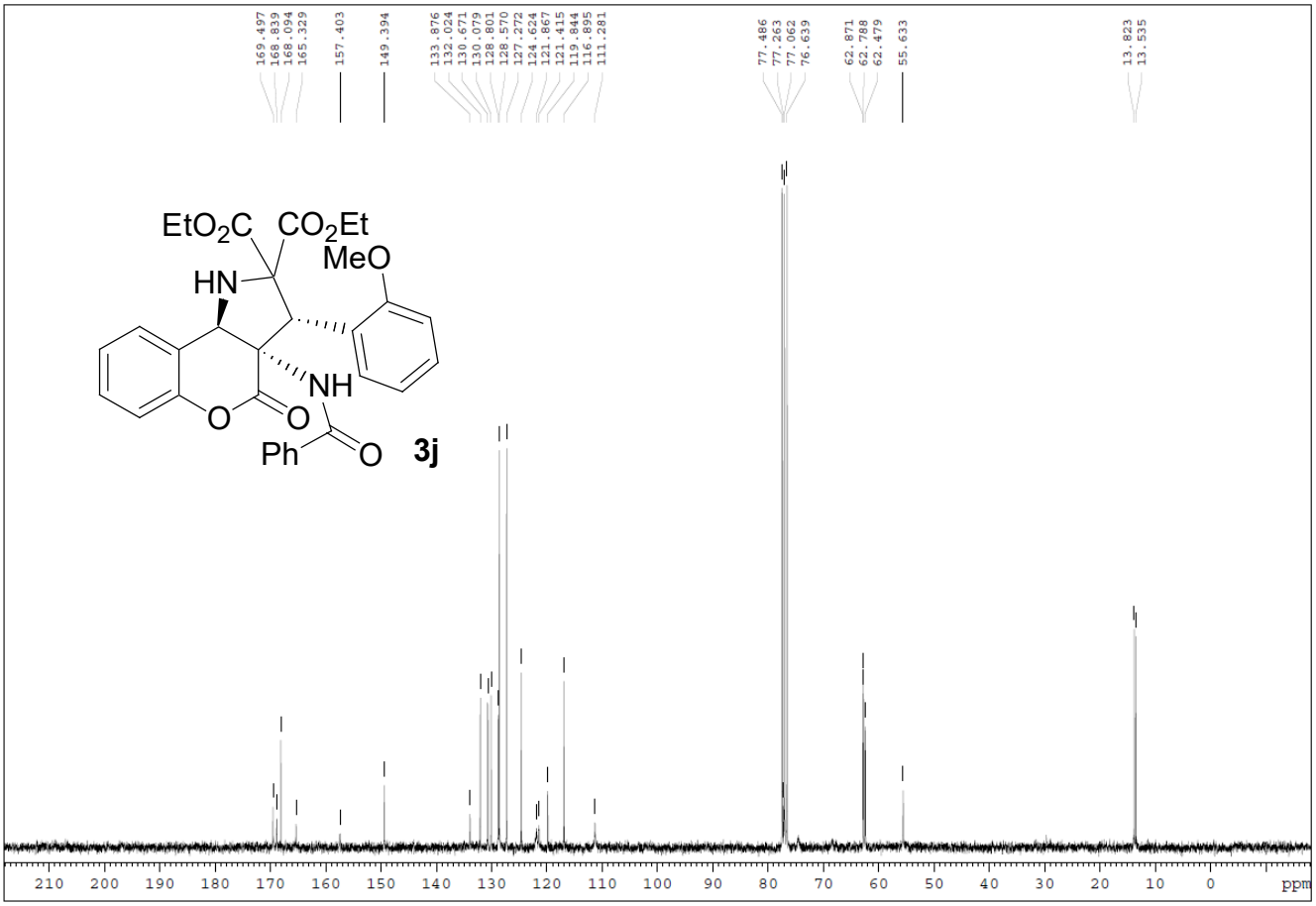
1.0
0.5
ppm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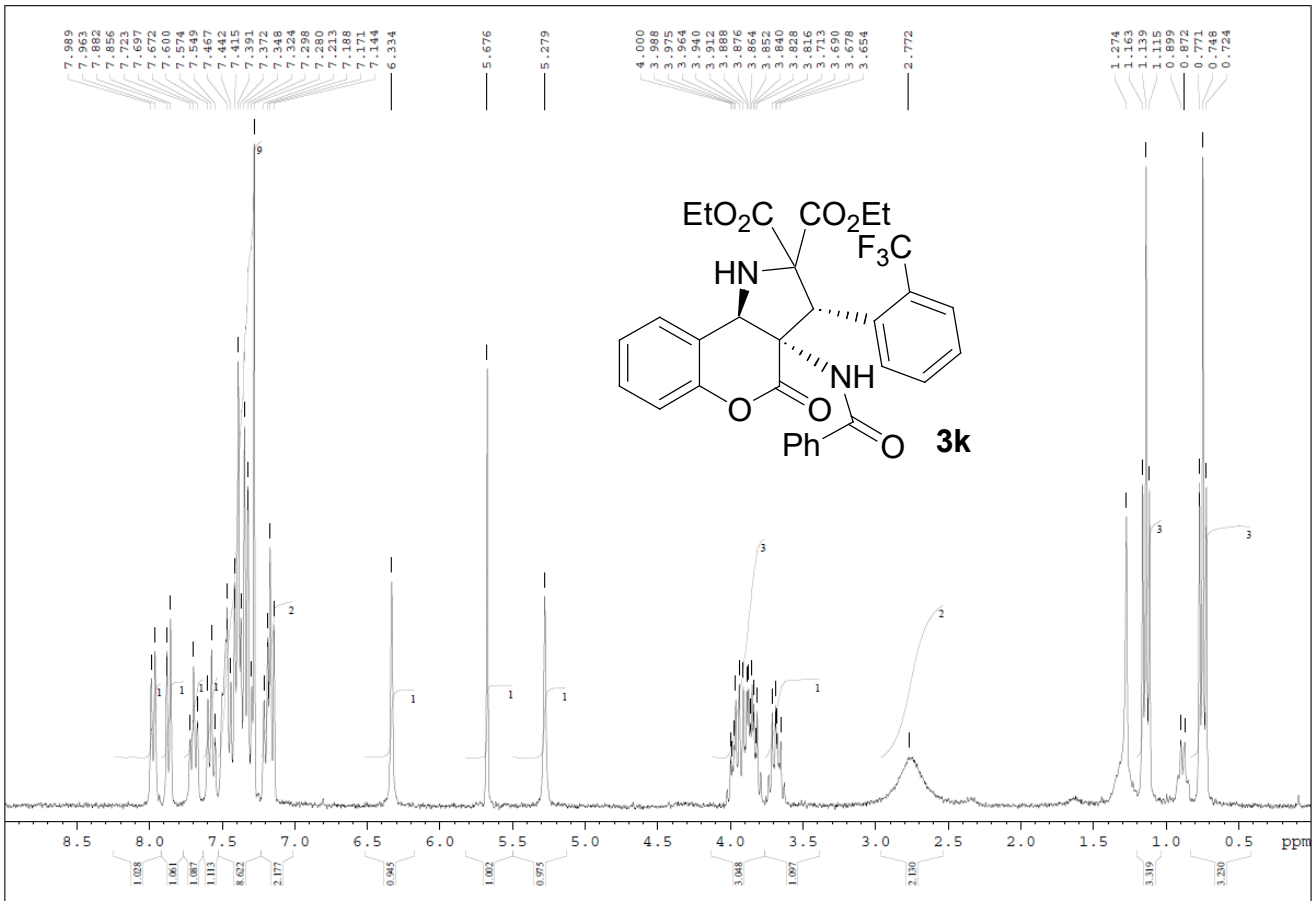
128.801
128.570
127.272
124.624
121.867
121.415
119.844
116.895
111.281
77.486
77.263
77.062
76.639
62.871
62.788
62.479
55.633
13.823
13.535
EtO2C
CO2Et
MeO
HN
NH
O
O
Ph
O
3j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.467
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7.415
7.391
7.372
7.348
7.324
7.298
7.280
7.213
7.188
7.171
7.144
6.334
5.676
5.279
4.000
3.988
3.975
3.964
3.940
3.912
3.888
3.876
3.864
3.852
3.840
3.828
3.816
3.713
3.690
3.678
3.654
2.772
1.274
1.163
1.139
1.115
0.899
0.872
0.771
0.748
0.724
EtO2C
CO2Et
F3C
HN
NH
O
O
Ph
O
3k
8.5
8.0
7.5
7.0
6.5
6.0
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4.5
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2.0
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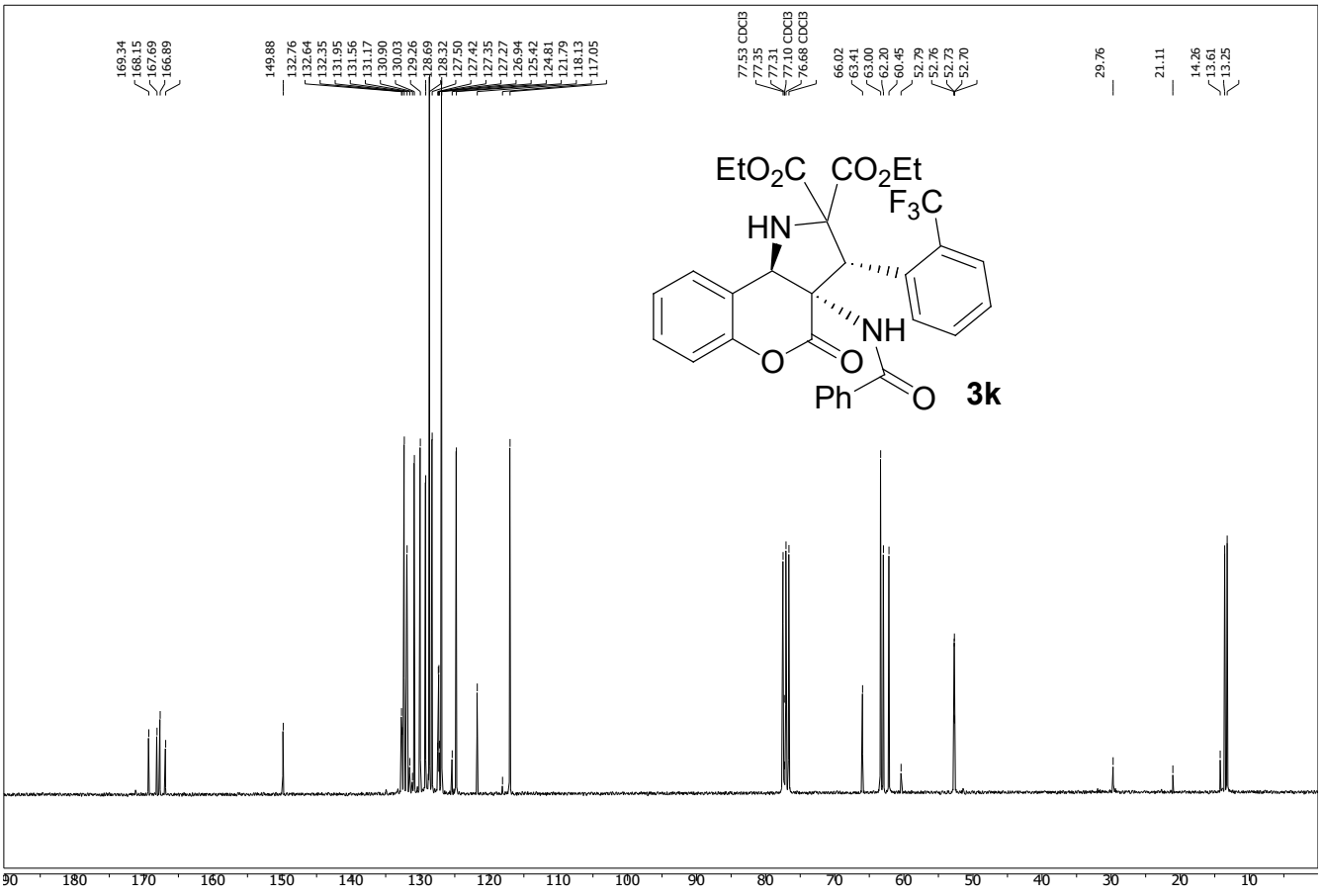
1.0
0.5
ppm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131.56
131.17
130.90
130.03
129.26
128.69
128.32
127.50
127.42
127.35
127.27
126.94
125.42
124.81
121.79
118.13
117.05
77.53 CDCl3
77.35
77.31
77.10 CDCl3
76.68 CDCl3
66.02
63.41
63.00
62.20
60.45
52.79
52.76
52.73
52.70
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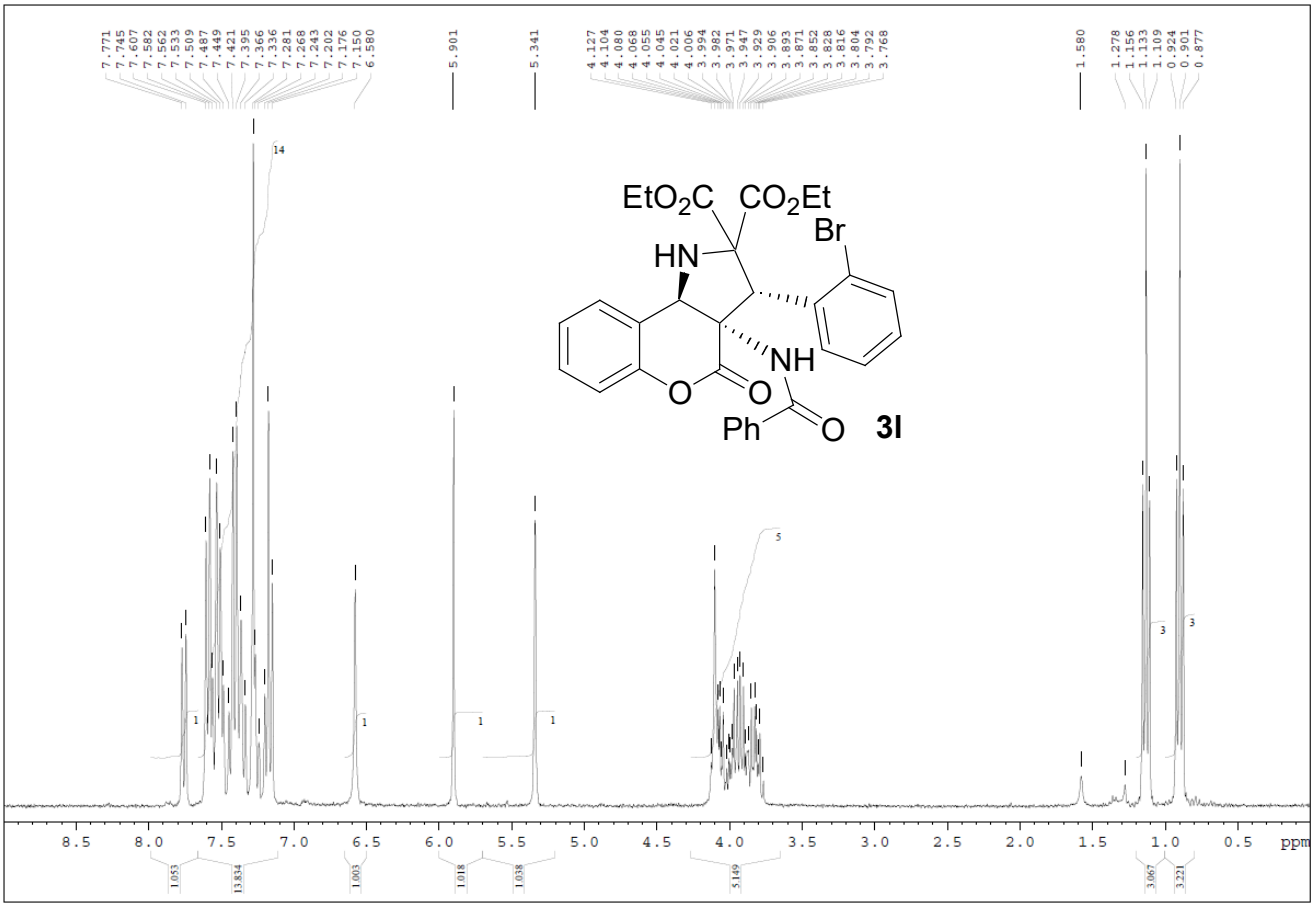
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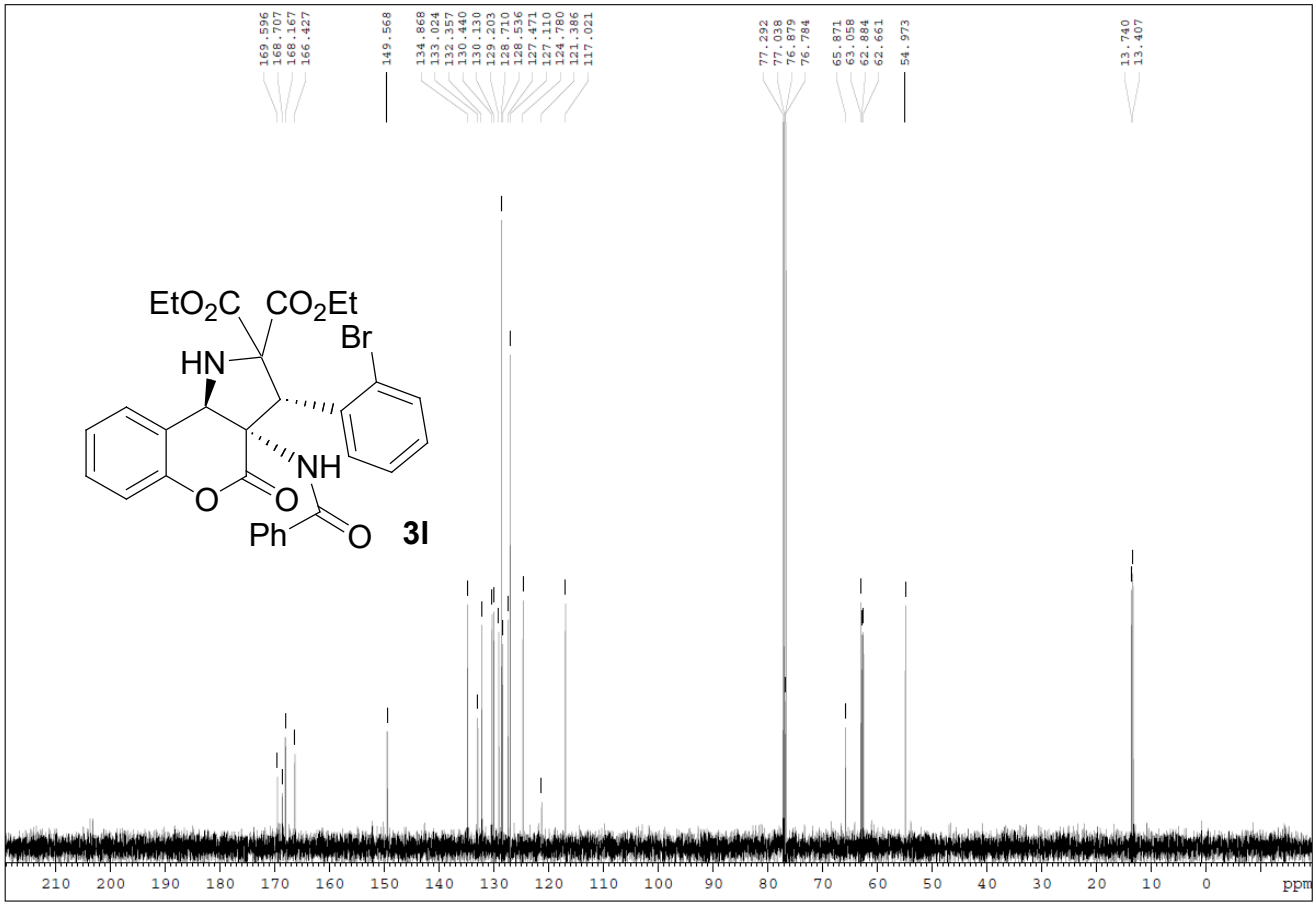
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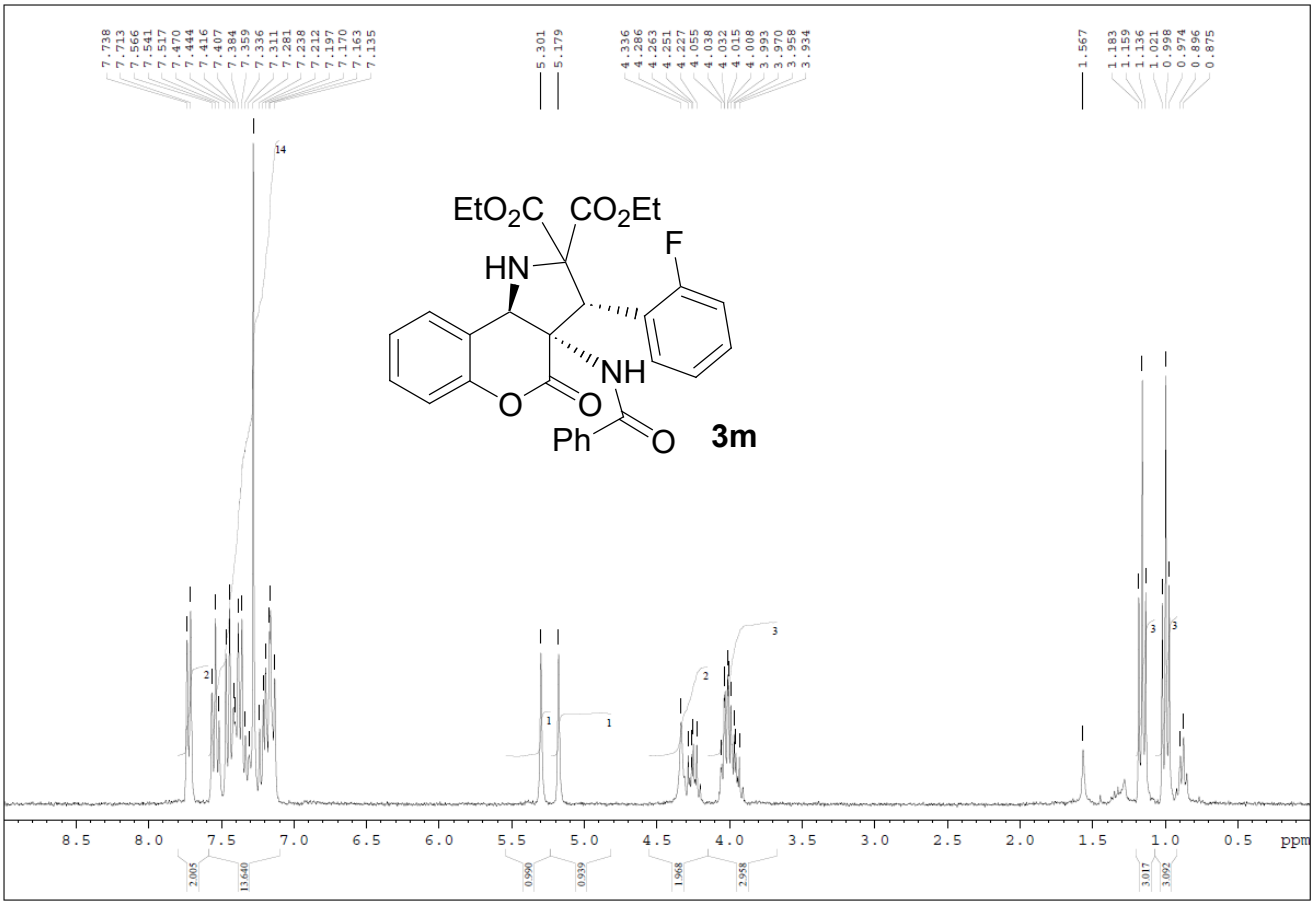
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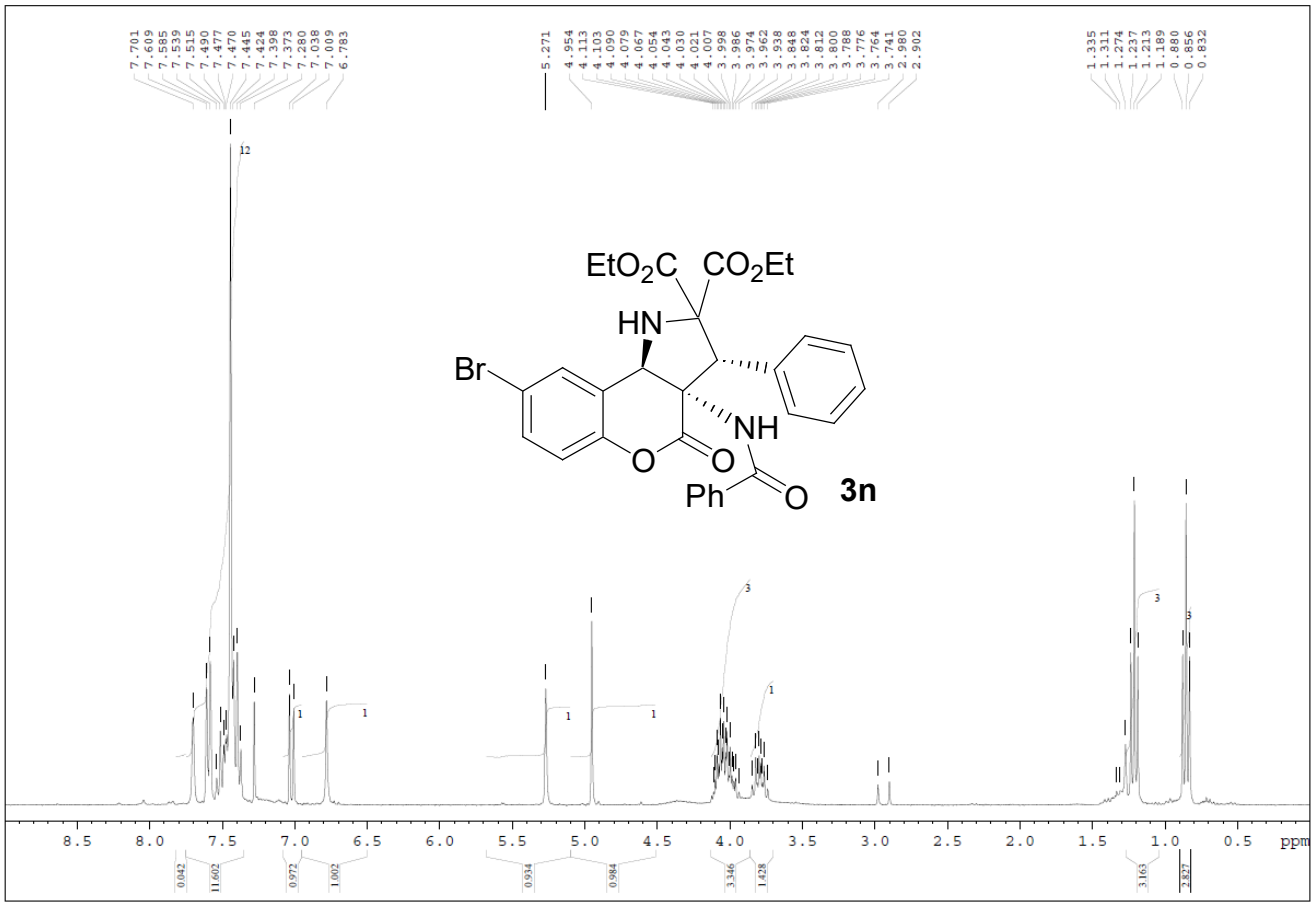
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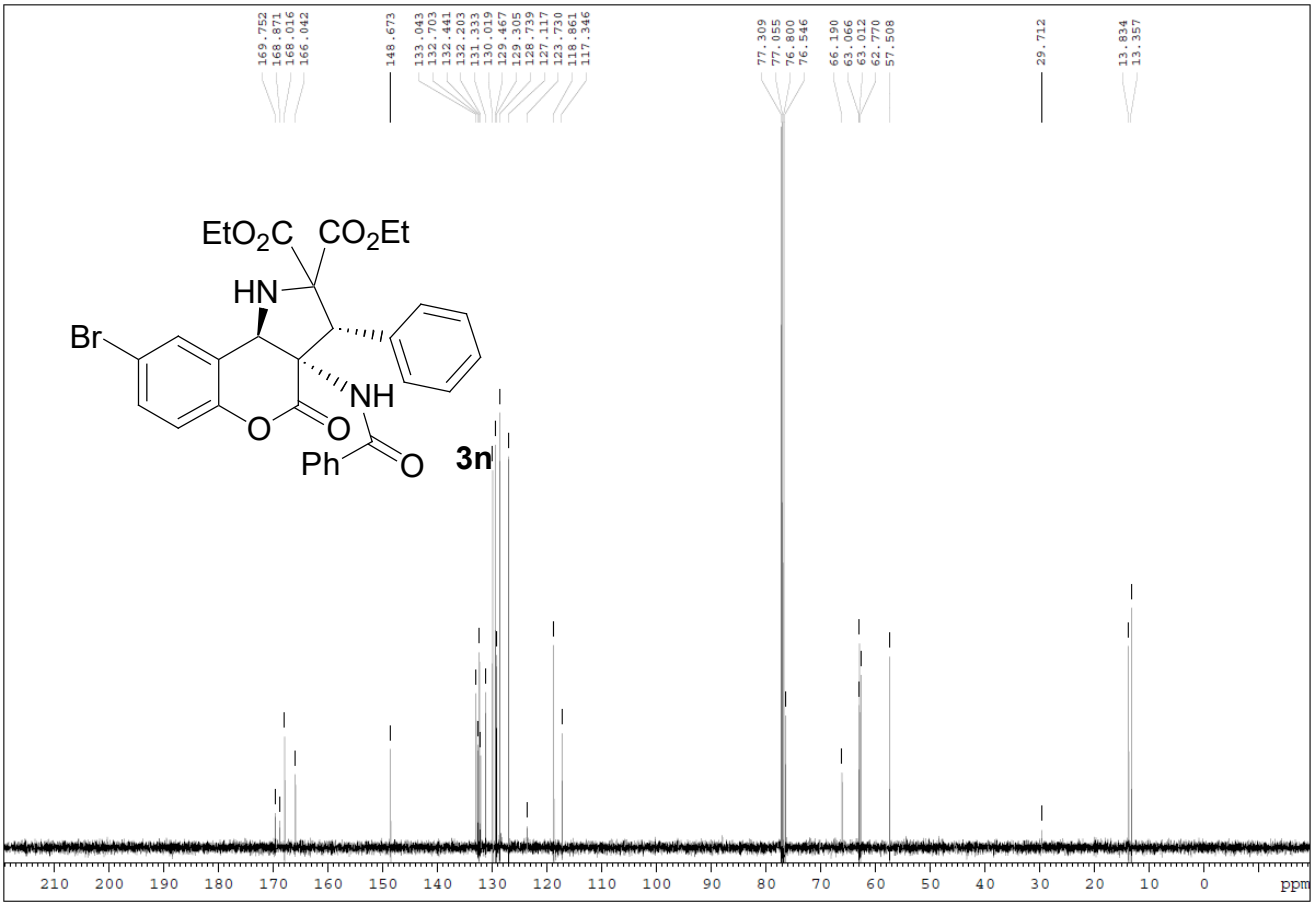
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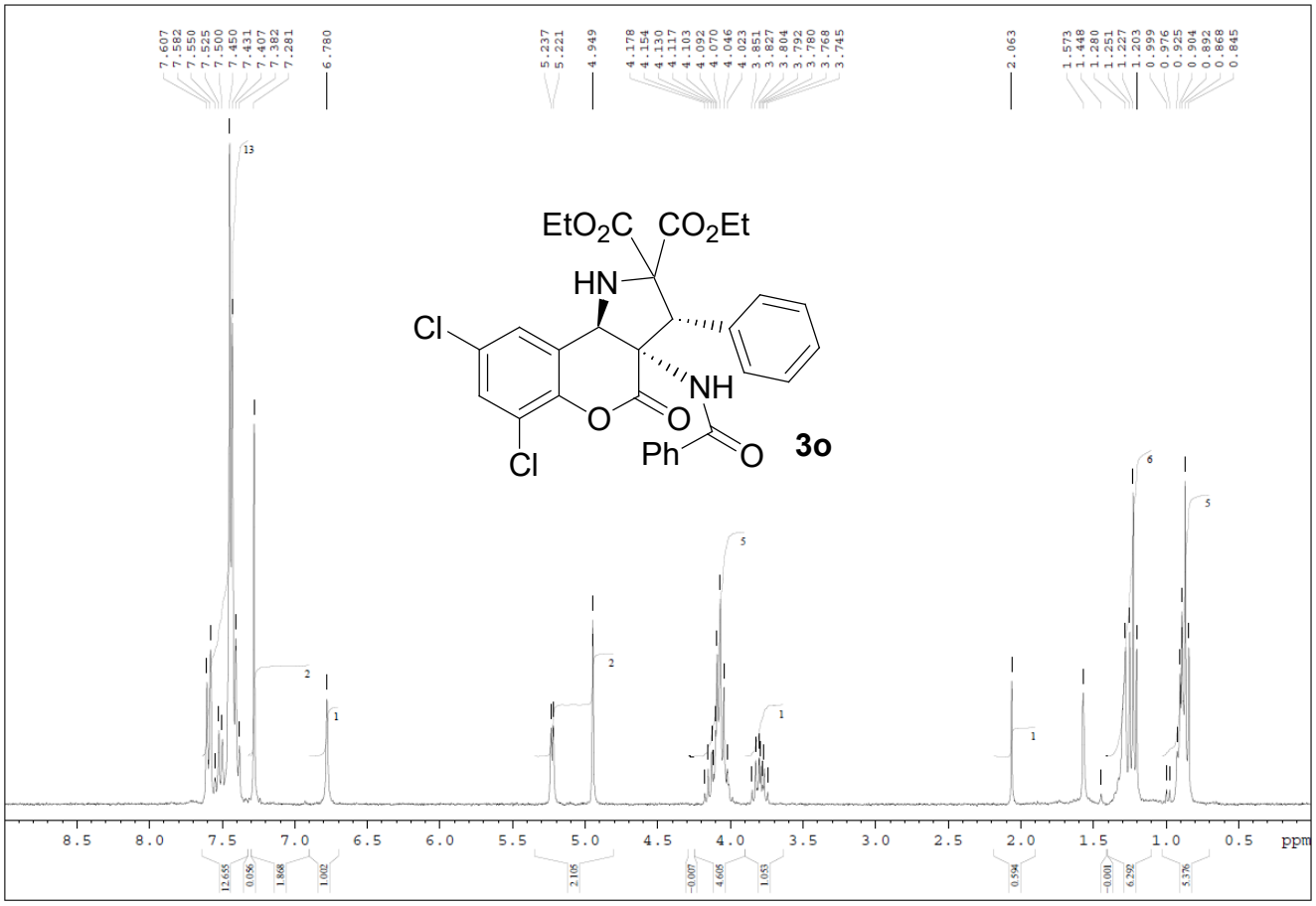
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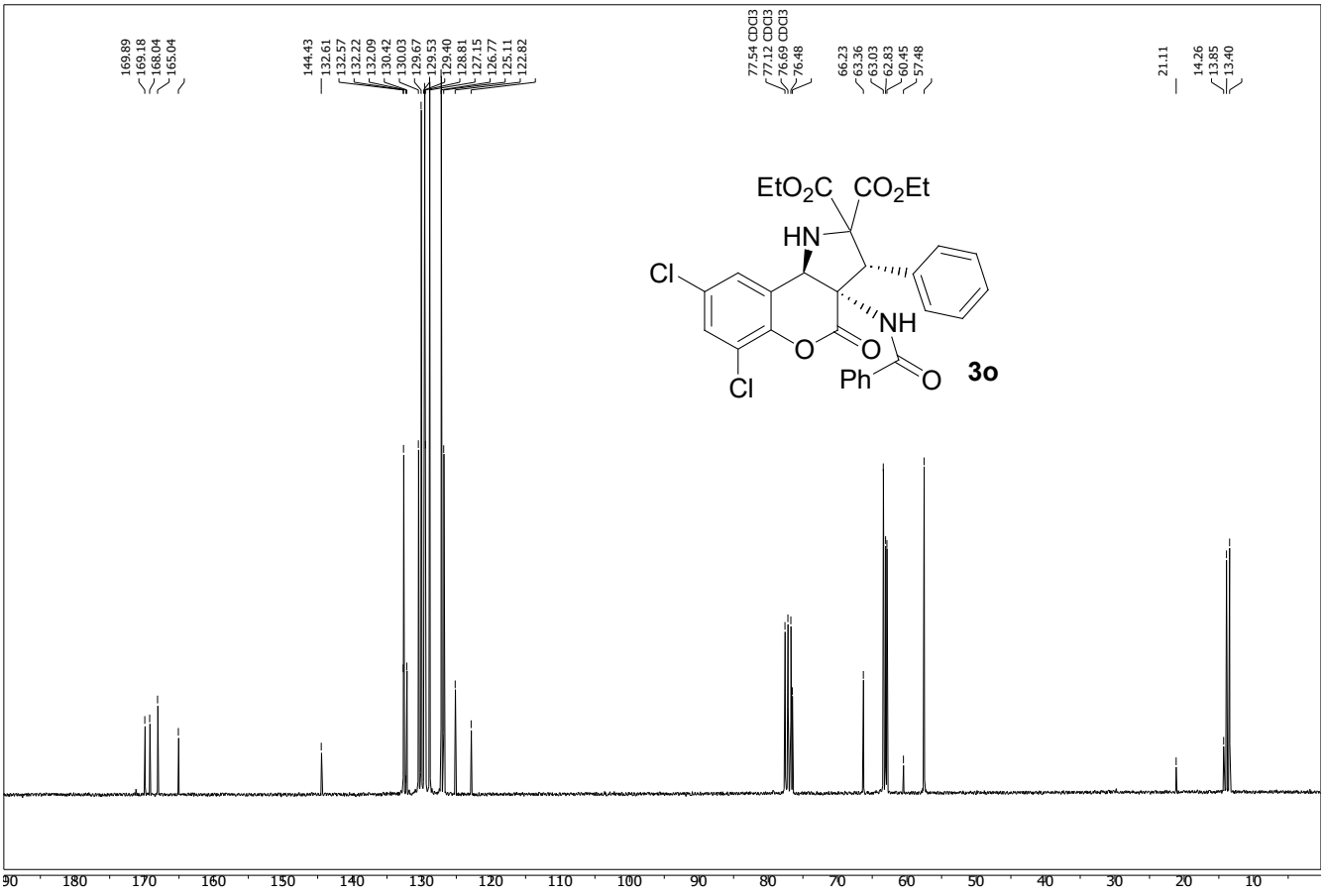
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21.11
14.26
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13.40
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CO2Et
HN
Cl
NH
O
O
Ph
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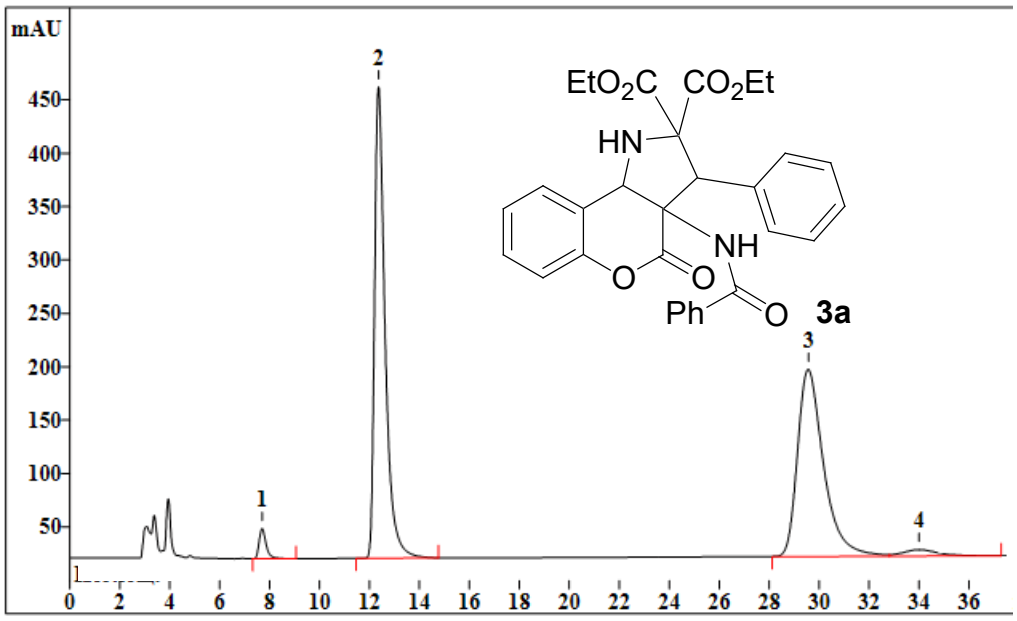
Cl
3o

HPLC profiles

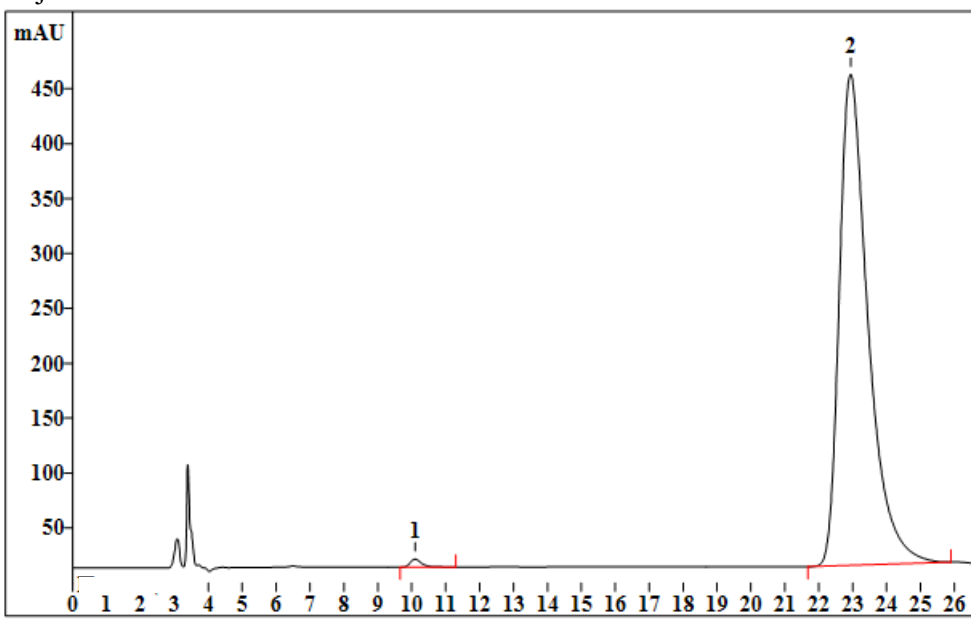
3a: HPLC analysis using chiral AD-H Column (*n*-hexane/Pr^{i}OH = 70:30, 1.0 mL/min)

Racemic **3a**



No	Time min	Height mAU	Area mAU*s	Area %
1	7.705	28.14	553.07	2.06
2	12.37	441.21	12952.26	48.26
3	29.56	175.15	12750.52	47.51
4	34.02	5.94	583.47	2.17
4	40	650.44	26839.32	100.00

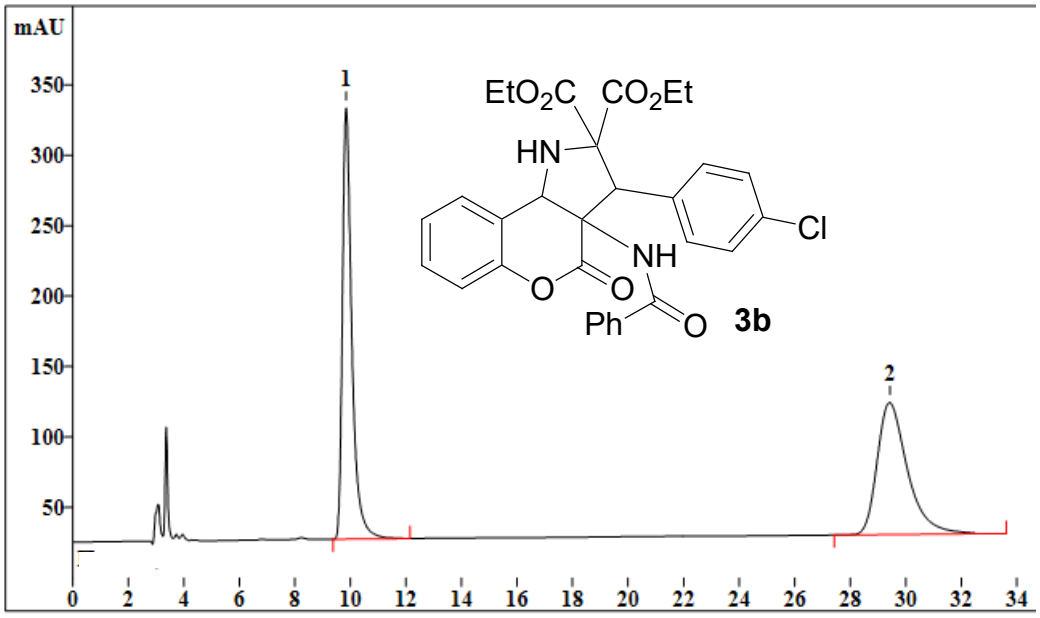
Major **3a**



No	Time min	Height mAU	Area mAU*s	Area %
1	10.11	7.35	177.96	0.67
2	22.94	447.11	26338.80	99.33
2	28.01	454.46	26516.76	100.00

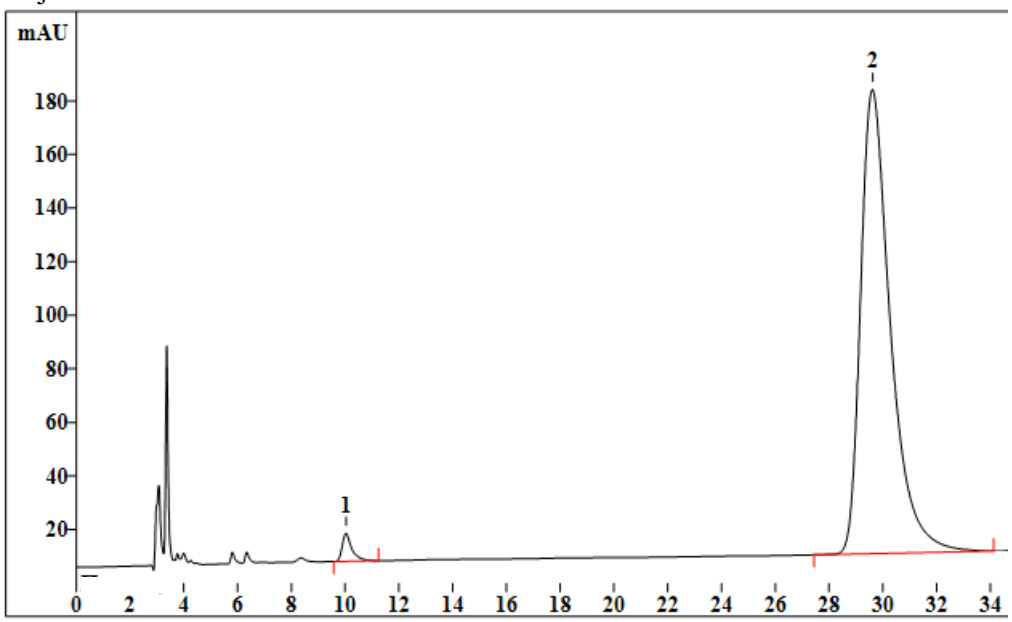
3b: HPLC analysis using chiral AD-H Column (*n*-hexane/Pr^{i}OH = 70:30, 1.0 mL/min)

Racemic **3b**



No	Time min	Height mAU	Area mAU*s	Area %
1	9.85	305.82	7213.98	50.31
2	29.42	93.69	7126.48	49.69
2	50	399.51	14340.45	100.00

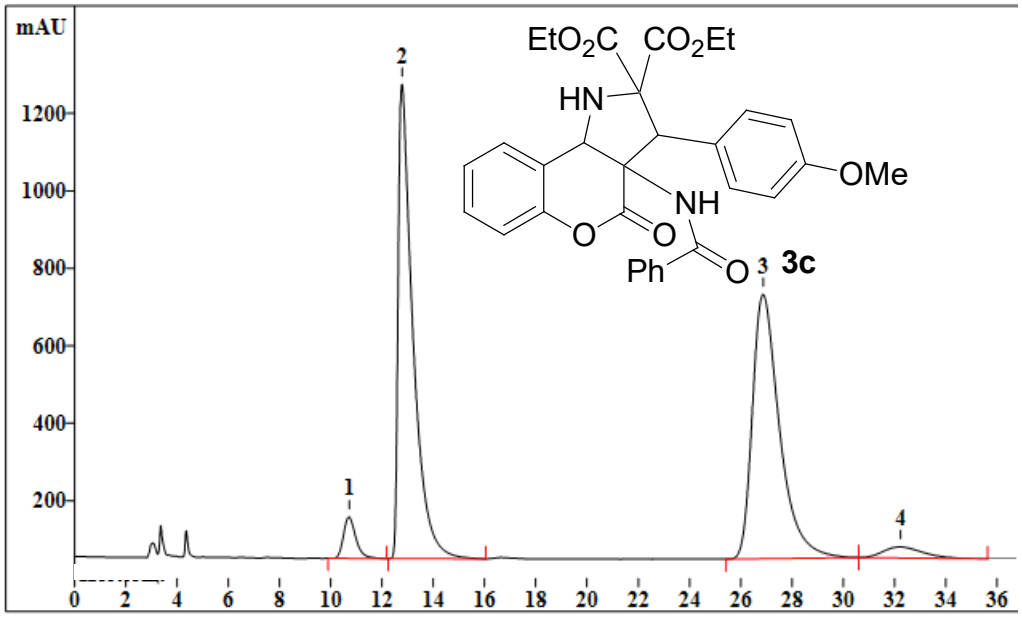
Major **3b**



No	Time min	Height mAU	Area mAU*s	Area %
1	10.04	10.31	259.89	1.91
2	29.62	173.15	13339.02	98.09
2	39.97	183.46	13598.91	100.00

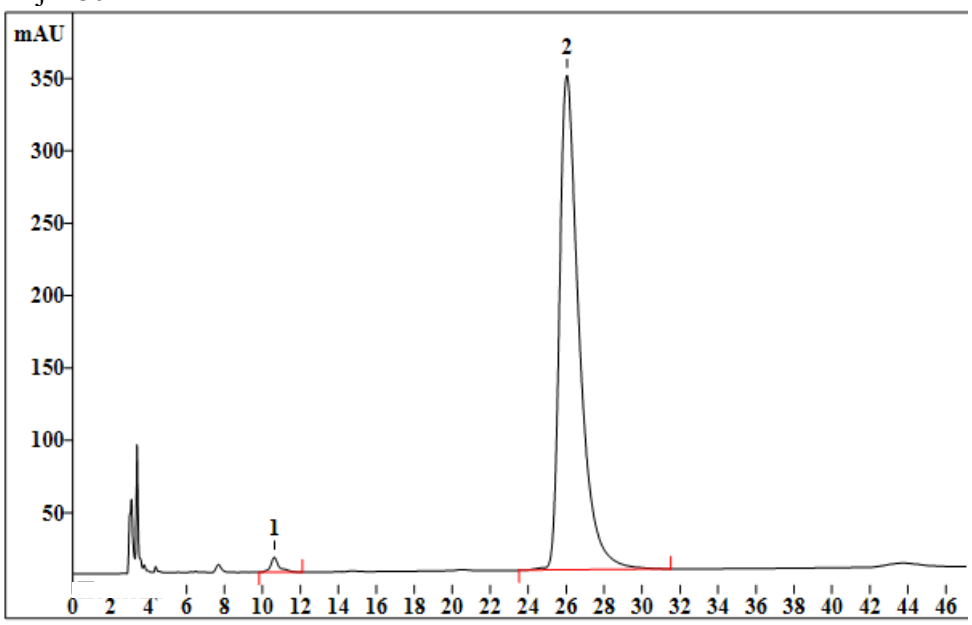
3c: HPLC analysis using chiral AD-H Column (*n*-hexane/Pr^{i}OH = 70:30, 1.0 mL/min)

Racemic **3c**



No	Time min	Height mAU	Area mAU*s	Area %
1	10.71	106.89	3580.94	3.38
2	12.78	1224.56	48957.23	46.27
3	26.87	682.34	50203.76	47.45
4	32.22	28.56	3071.87	2.90
4	41	2042.35	105813.80	100.00

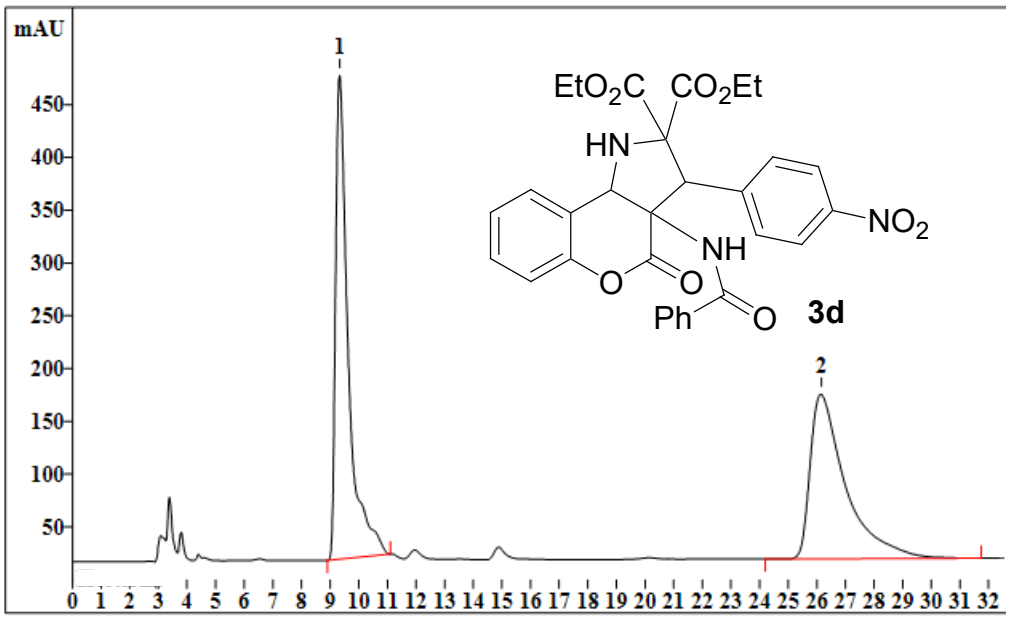
Major **3c**



No	Time min	Height mAU	Area mAU*s	Area %
1	10.63	10.11	328.19	1.32
2	26.04	341.56	24585.51	98.68
2	50.05	351.67	24913.70	100.00

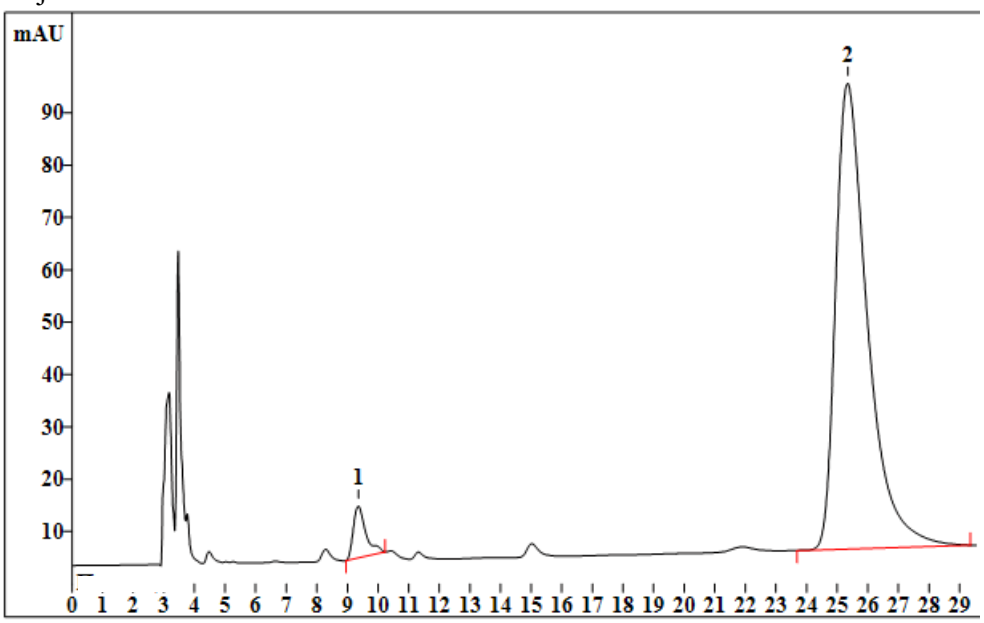
3d: HPLC analysis using chiral AD-H Column (*n*-hexane/Pr^{i}OH = 70:30, 1.0 mL/min)

Racemic **3d**



No	Time min	Height mAU	Area mAU*s	Area %
1	9.335	457.71	14173.85	51.42
2	26.14	155.76	13393.18	48.58
2	42.98	613.46	27567.03	100.00

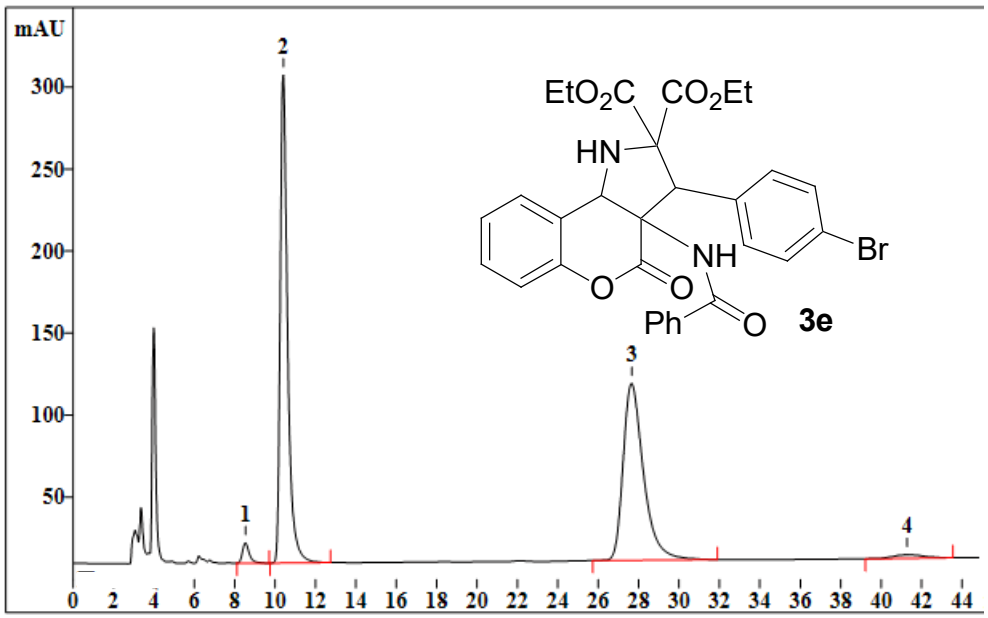
Major **3d**



No	Time min	Height mAU	Area mAU*s	Area %
1	9.354	9.83	281.25	4.19
2	25.34	88.96	6438.18	95.81
2	31.03	98.79	6719.43	100.00

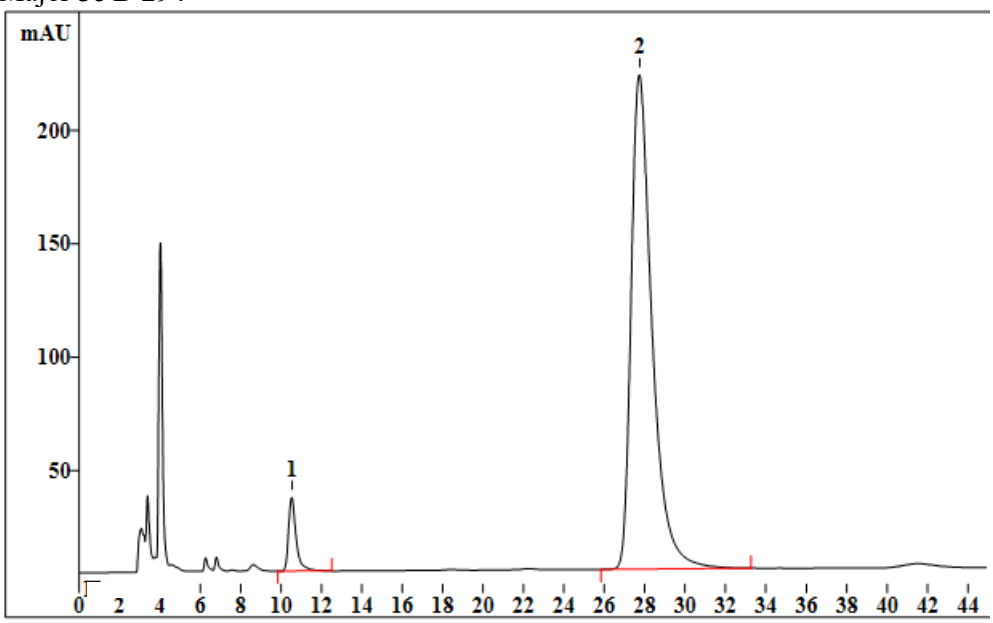
3e: HPLC analysis using chiral AD-H Column (*n*-hexane/Pr^{i}OH = 70:30, 1.0 mL/min)

Racemic **3e**



No	Time min	Height mAU	Area mAU*s	Area %
1	8.539	12.25	288.99	1.84
2	10.4	297.39	7570.93	48.26
3	27.65	107.66	7592.32	48.39
4	41.31	2.21	236.13	1.51
4	47.01	419.50	15688.37	100.00

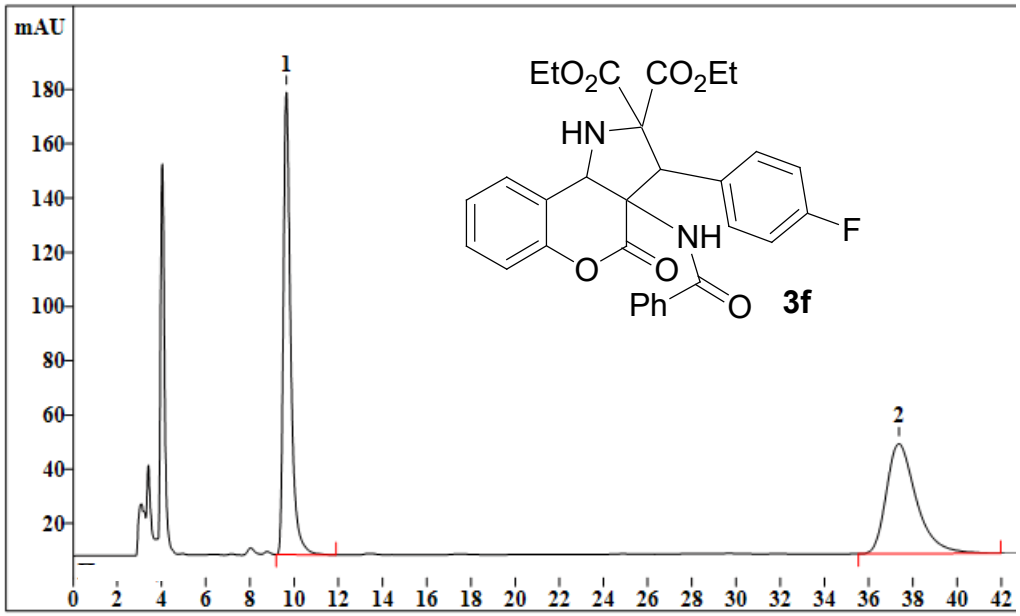
Major **3e** B-294



No	Time min	Height mAU	Area mAU*s	Area %
1	10.53	32.38	854.69	5.17
2	27.74	217.85	15677.61	94.83
2	47.01	250.23	16532.30	100.00

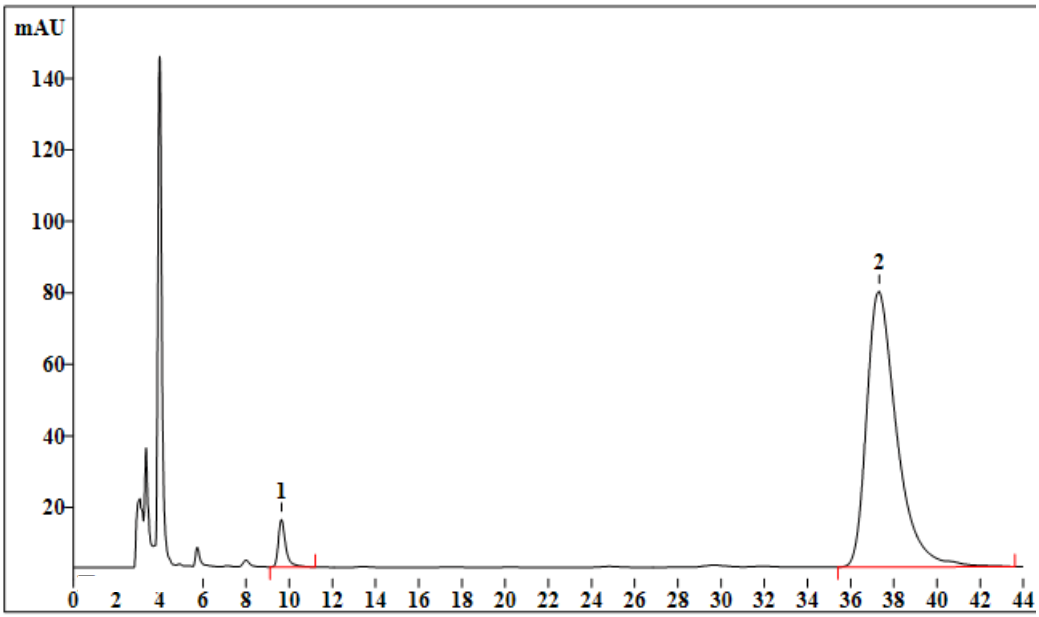
3f: HPLC analysis using chiral AD-H Column (*n*-hexane/Pr^{i}OH = 70:30, 1.0 mL/min)

Racemic **3f**



No	Time min	Height mAU	Area mAU*s	Area %
1	9.652	170.40	3922.50	50.54
2	37.38	40.53	3837.92	49.46
2	70	210.93	7760.42	100.00

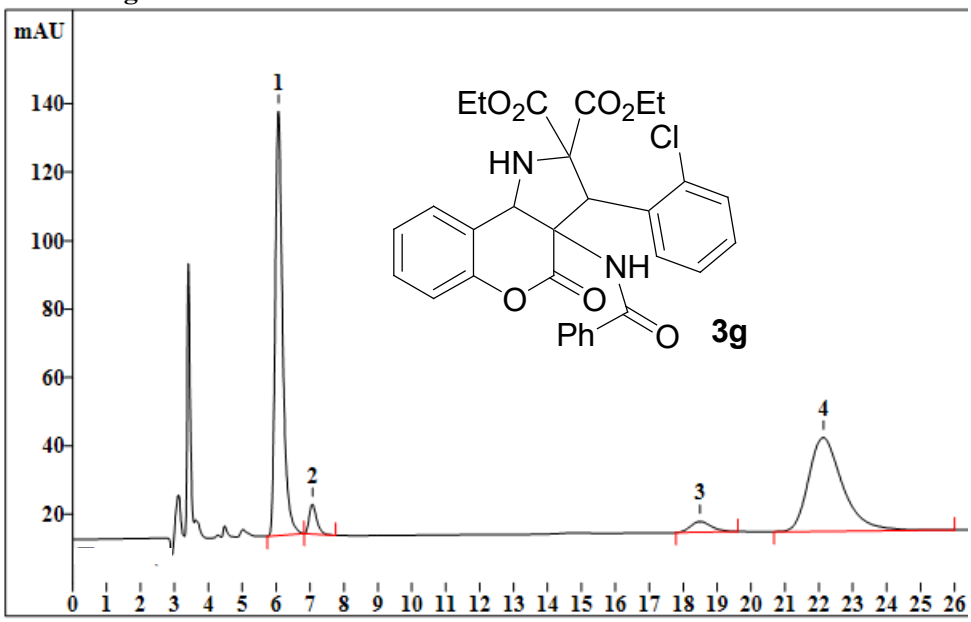
Major **3f**



No	Time min	Height mAU	Area mAU*s	Area %
1	9.646	13.22	313.79	4.03
2	37.31	77.03	7471.89	95.97
2	44	90.25	7785.68	100.00

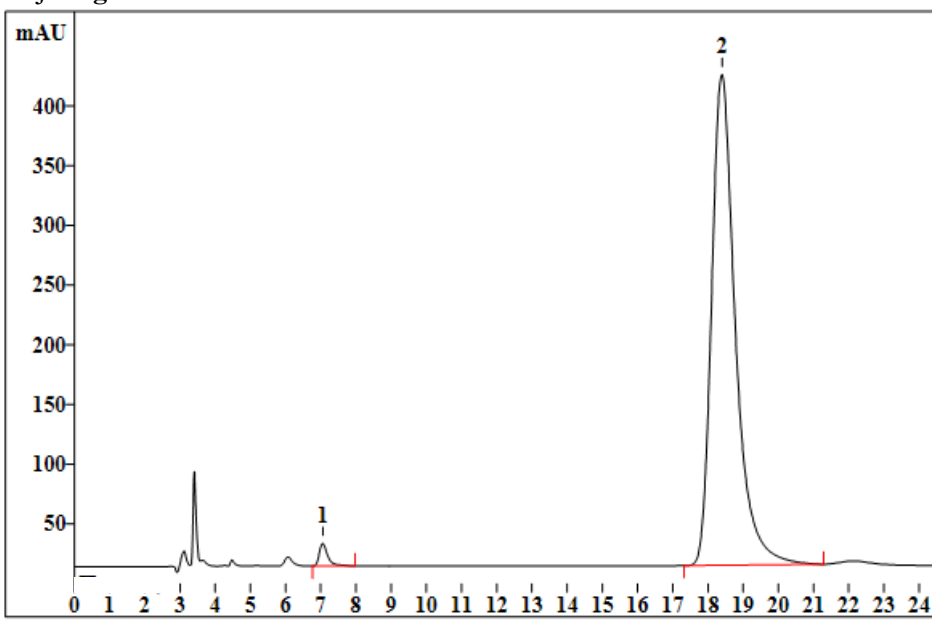
3g: HPLC analysis using chiral AD-H Column (*n*-hexane/Pr^{i}OH = 70:30, 1.0 mL/min)

Racemic **3g**



No	Time min	Height mAU	Area mAU*s	Area %
1	6.067	123.99	1900.25	46.49
2	7.075	8.65	134.90	3.30
3	18.5	3.11	134.77	3.30
4	22.13	27.38	1917.94	46.92
4	43.49	163.13	4087.87	100.00

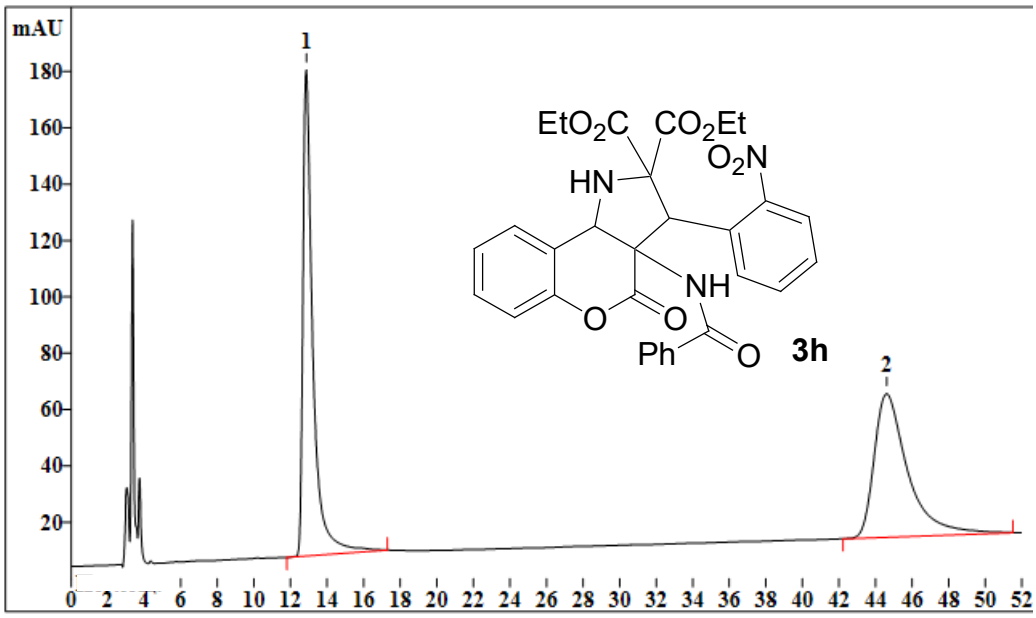
Major **3g**



No	Time min	Height mAU	Area mAU*s	Area %
1	7.056	18.78	317.03	1.62
2	18.4	410.88	19231.34	98.38
2	27.01	429.66	19548.38	100.00

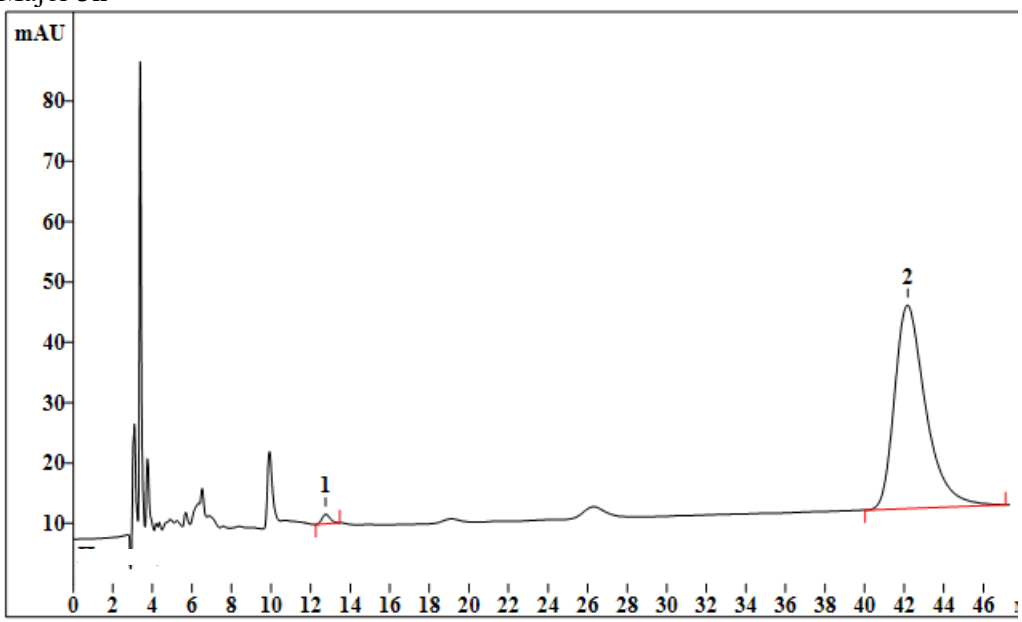
3h: HPLC analysis using chiral AD-H Column (*n*-hexane/Pr^{i}OH = 70:30, 1.0 mL/min)

Racemic **3h**



No	Time min	Height mAU	Area mAU*s	Area %
1	12.86	172.66	6545.86	50.11
2	44.61	50.90	6516.33	49.89
2	52.01	223.56	13062.19	100.00

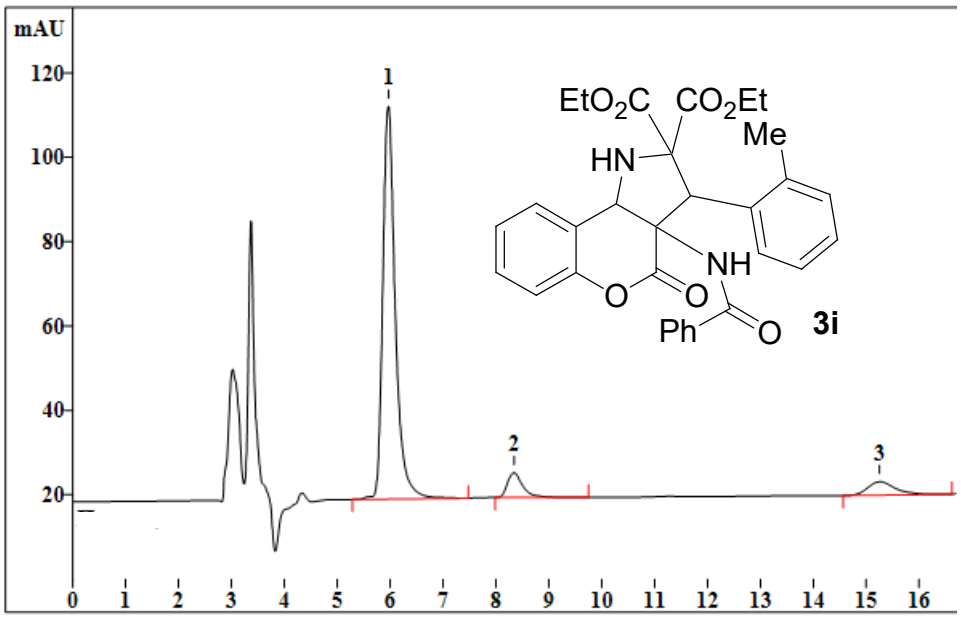
Major **3h**



No	Time min	Height mAU	Area mAU*s	Area %
1	12.77	1.55	45.41	1.21
2	42.17	33.68	3692.51	98.79
2	48.01	35.23	3737.92	100.00

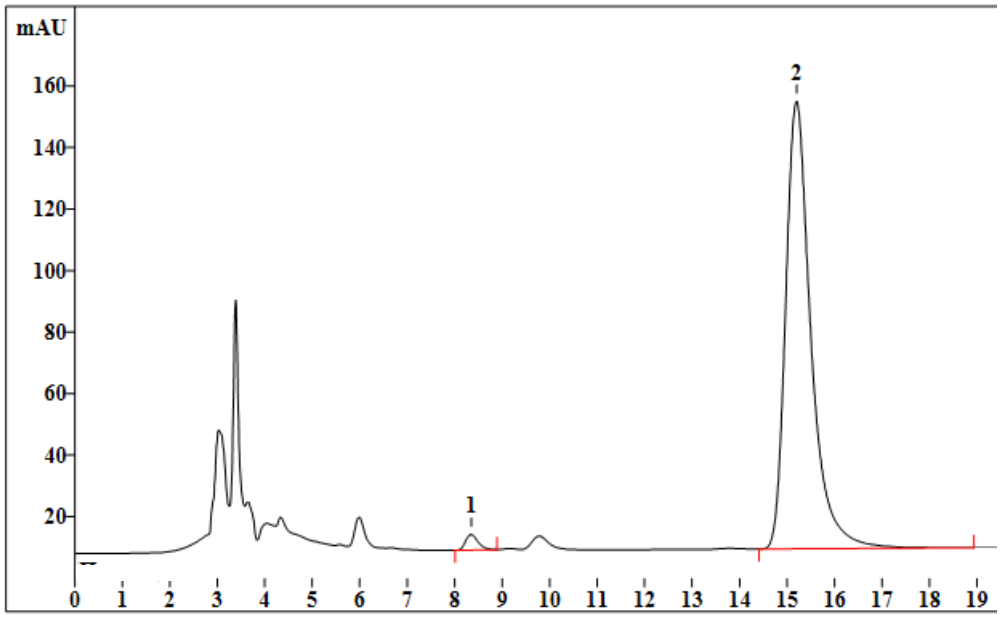
3i: HPLC analysis using chiral AD-H Column (*n*-hexane/Pr^{i}OH = 70:30, 1.0 mL/min)

Racemic **3i**



No	Time min	Height mAU	Area mAU*s	Area %
1	5.969	93.08	1534.15	86.72
2	8.345	5.85	119.38	6.75
3	15.27	3.14	115.56	6.53
3	32.31	102.07	1769.09	100.00

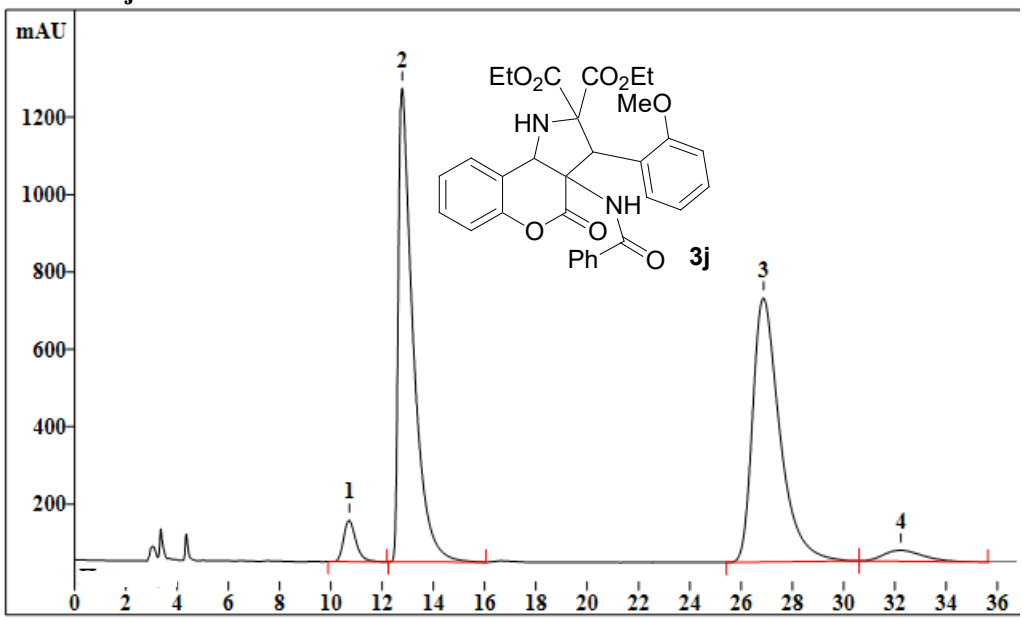
Major **3i**



No	Time min	Height mAU	Area mAU*s	Area %
1	8.346	5.08	92.93	1.70
2	15.2	145.57	5379.33	98.30
2	28.01	150.65	5472.26	100.00

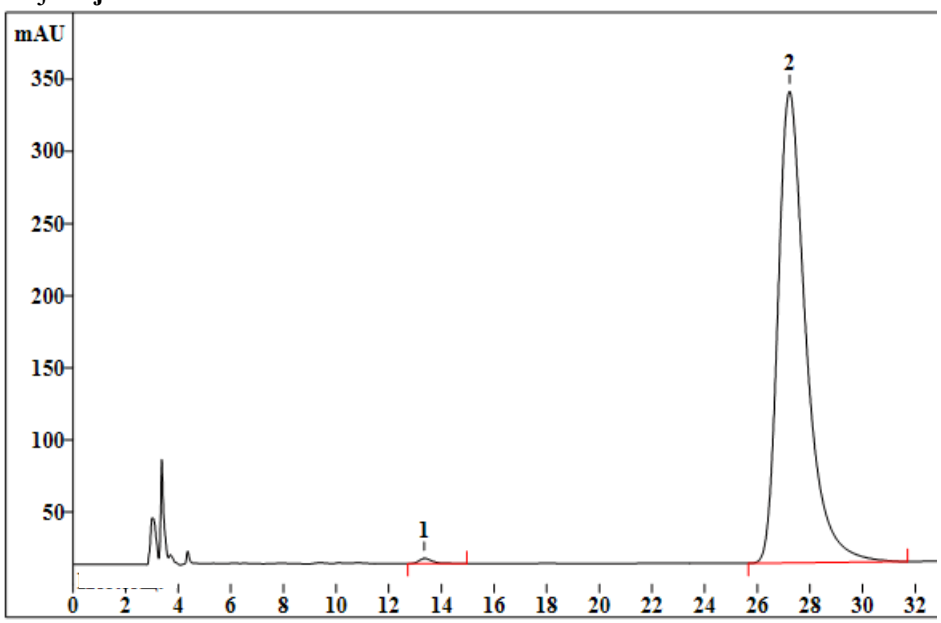
3j: HPLC analysis using chiral AD-H Column (*n*-hexane/Pr^{i}OH = 70:30, 1.0 mL/min)

Racemic **3j**



No	Time min	Height mAU	Area mAU*s	Area %
1	10.71	106.89	3580.94	3.38
2	12.78	1224.56	48957.23	46.27
3	26.87	682.34	50203.76	47.45
4	32.22	28.56	3071.87	2.90
4	41	2042.35	105813.80	100.00

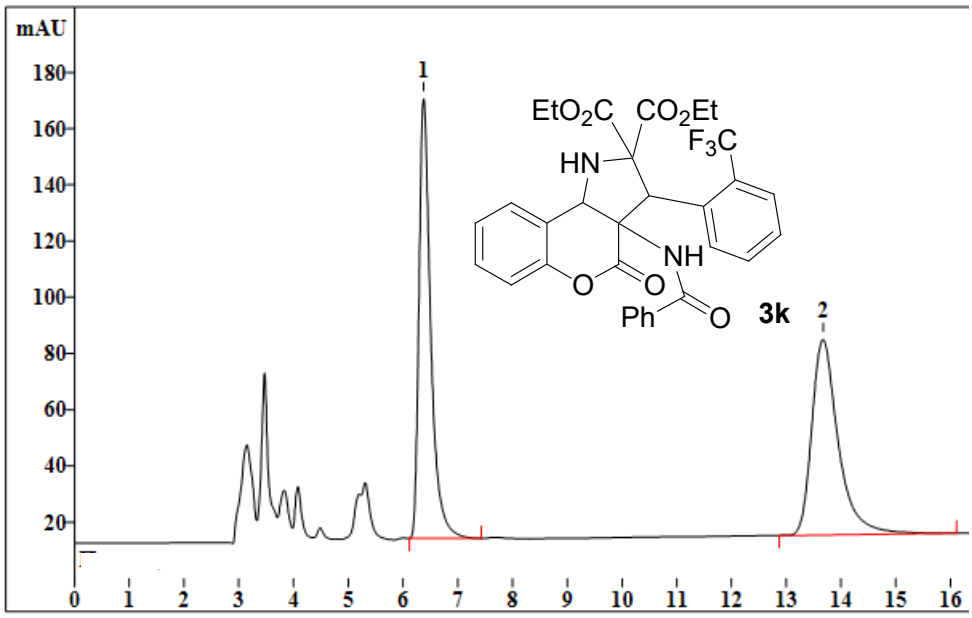
Major **3j**



No	Time min	Height mAU	Area mAU*s	Area %
1	13.37	3.69	135.58	0.56
2	27.23	326.65	24052.68	99.44
2	37.03	330.35	24188.26	100.00

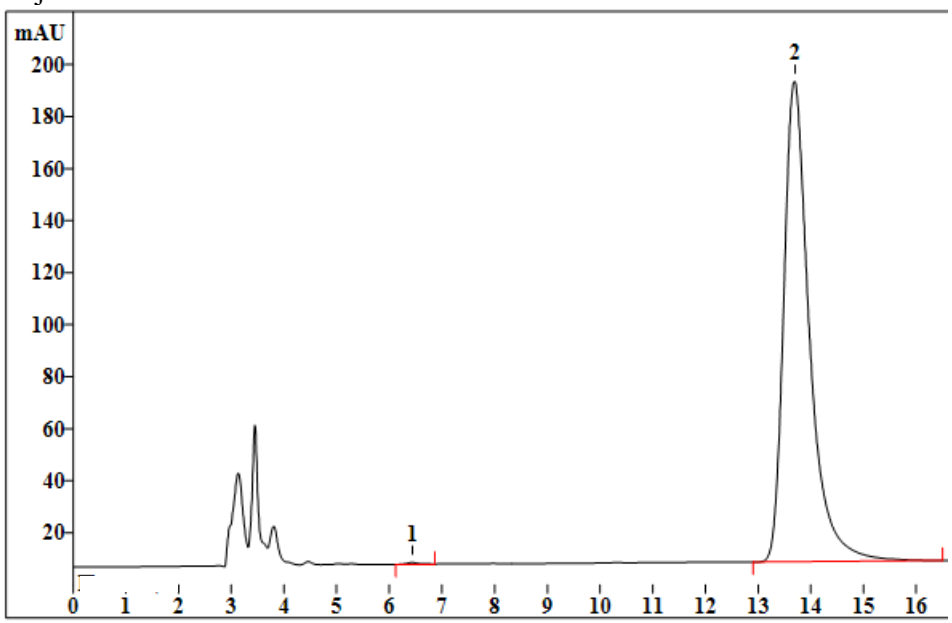
3k: HPLC analysis using chiral AD-H Column (*n*-hexane/Pr^{i}OH = 70:30, 1.0 mL/min)

Racemic **3k**



No	Time min	Height mAU	Area mAU*s	Area %
1	6.377	156.60	2338.28	49.96
2	13.67	69.52	2341.80	50.04
2	43.96	226.12	4680.08	100.00

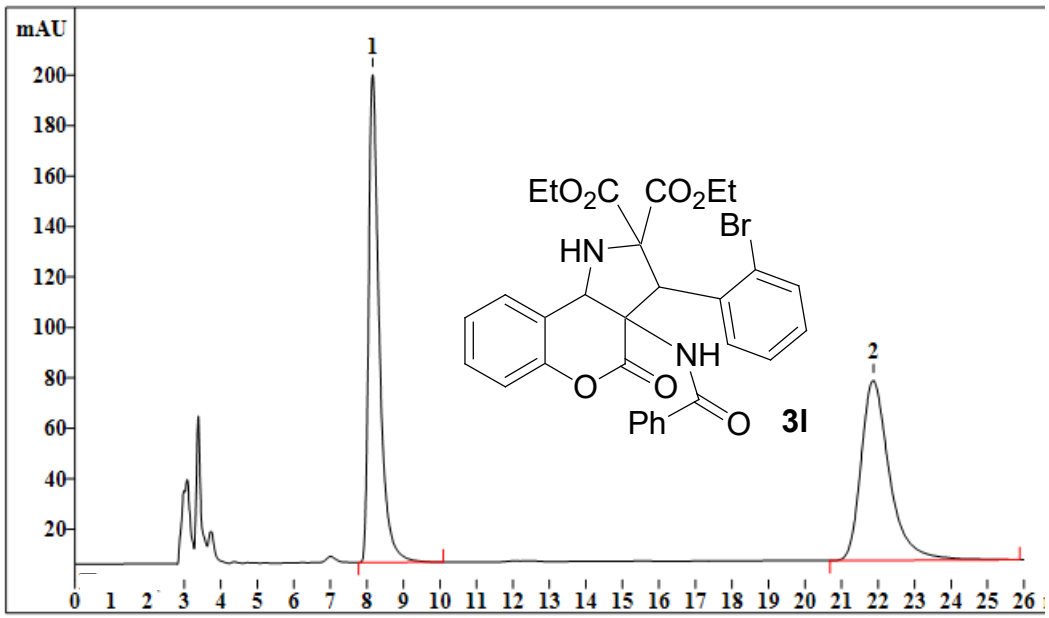
Major **3k**



No	Time min	Height mAU	Area mAU*s	Area %
1	6.436	0.63	9.96	0.16
2	13.7	184.75	6250.14	99.84
2	18.01	185.38	6260.09	100.00

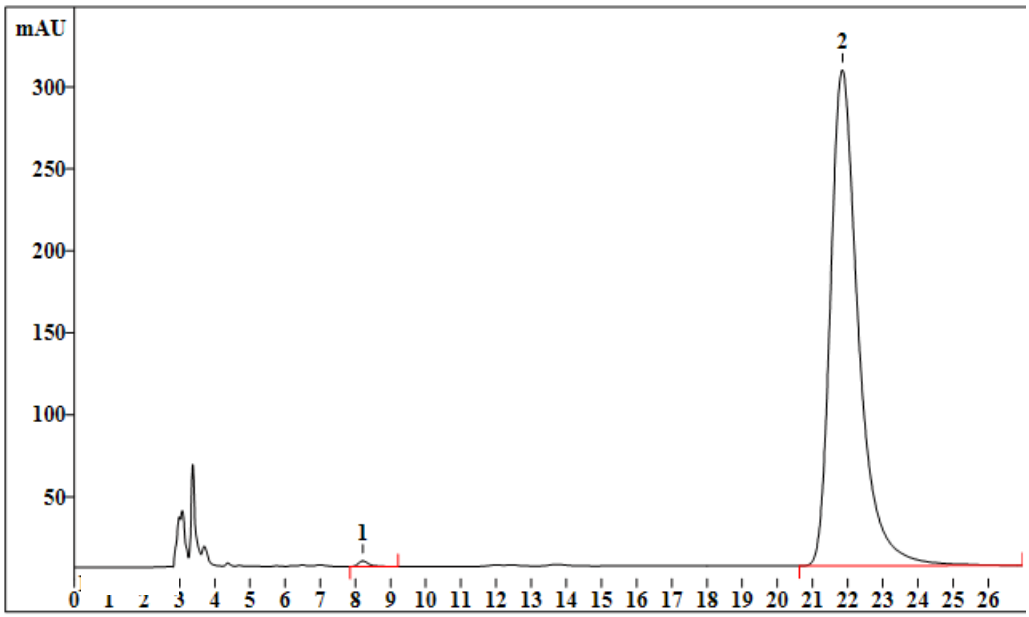
3l: HPLC analysis using chiral AD-H Column (*n*-hexane/Pr^{i}OH = 70:30, 1.0 mL/min)

Racemic **3l**



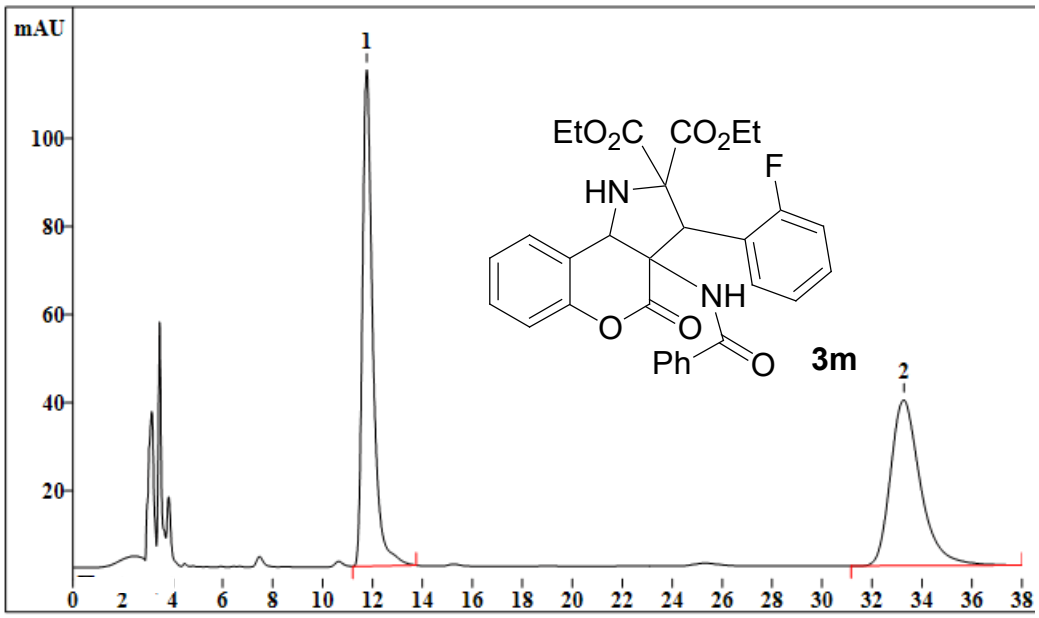
No	Time min	Height mAU	Area mAU*s	Area %
1	8.16	193.39	3925.89	50.42
2	21.87	71.25	3860.49	49.58
2	26.01	264.63	7786.38	100.00

Major **3l**



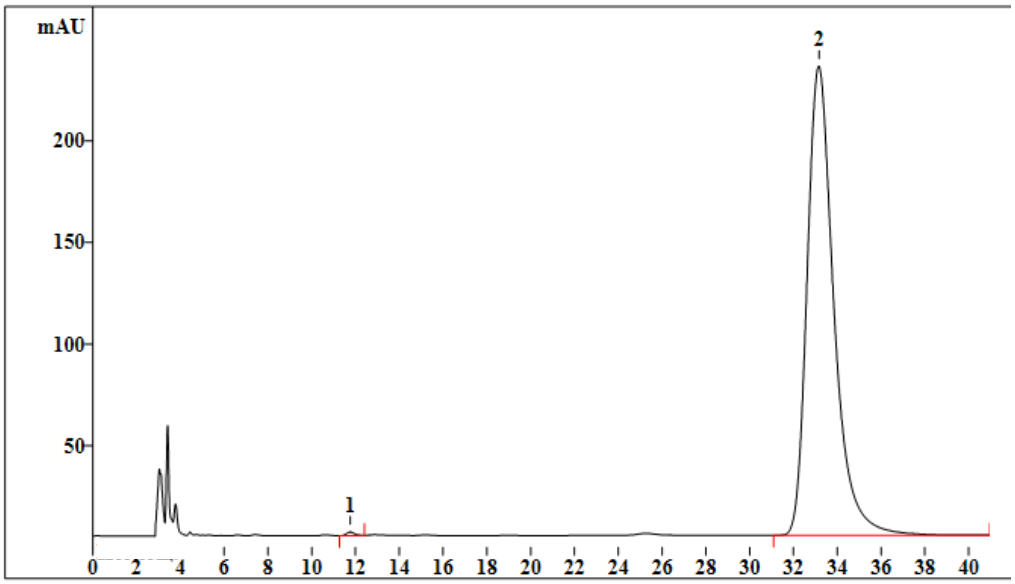
No	Time min	Height mAU	Area mAU*s	Area %
1	8.212	3.42	71.40	0.43
2	21.85	302.50	16680.83	99.57
2	26.99	305.92	16752.23	100.00

3m: HPLC analysis using chiral AD-H Column (*n*-hexane/Pr^{i}OH = 70:30, 1.0 mL/min)
Racemic **3m**



No	Time min	Height mAU	Area mAU*s	Area %
1	11.77	112.70	3262.67	50.87
2	33.27	37.63	3150.47	49.13
2	38.02	150.33	6413.14	100.00

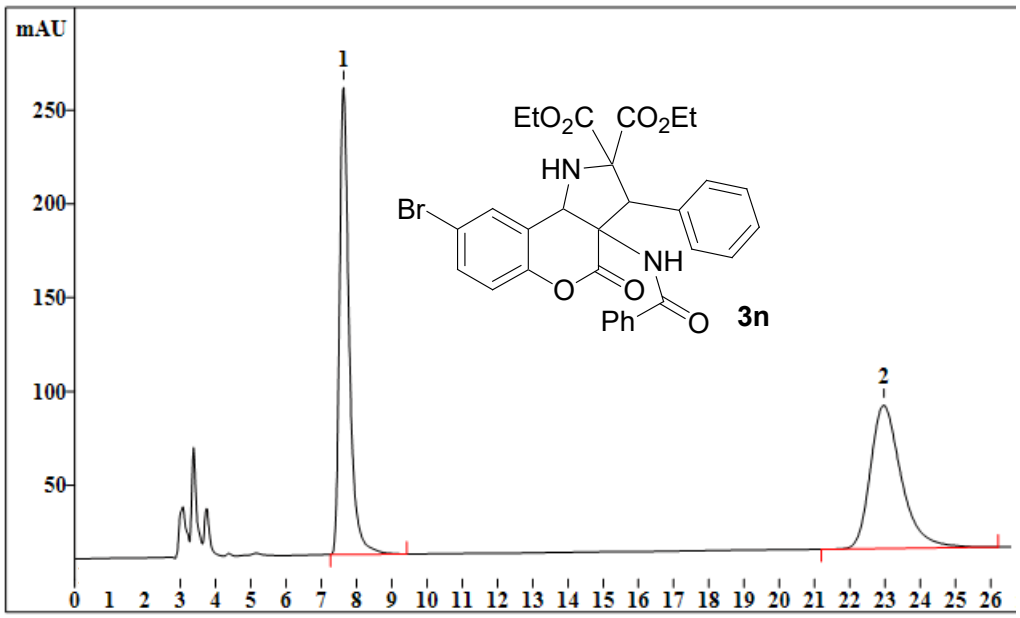
Major **3m**



No	Time min	Height mAU	Area mAU*s	Area %
1	11.77	1.70	44.35	0.23
2	33.16	231.00	19621.79	99.77
2	40.98	232.70	19666.15	100.00

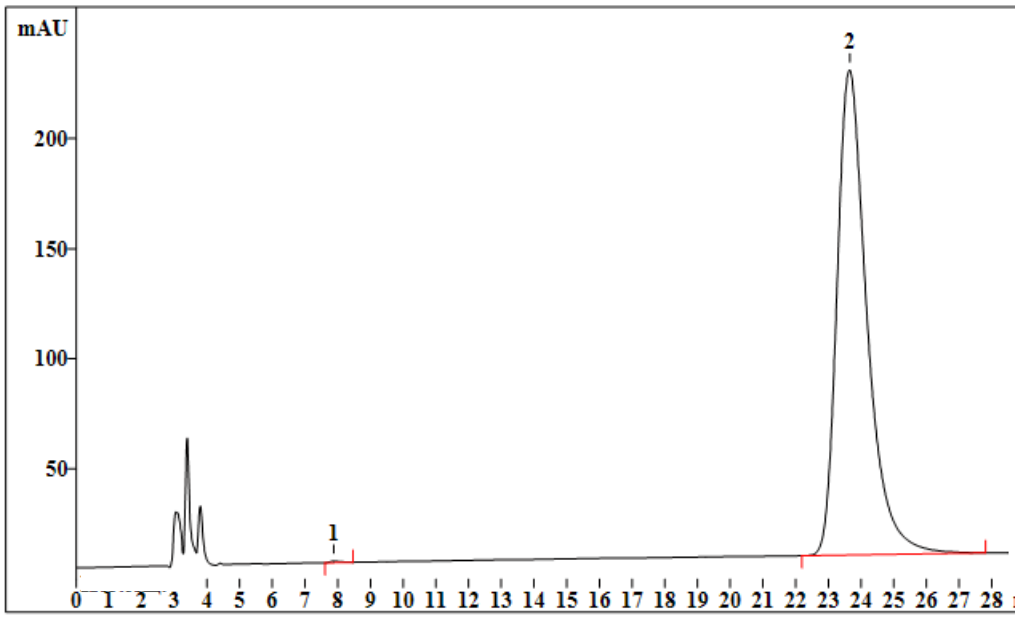
3n: HPLC analysis using chiral AD-H Column (*n*-hexane/Pr^{i}OH = 70:30, 1.0 mL/min)

Racemic **3n**



No	Time min	Height mAU	Area mAU*s	Area %
1	7.63	249.12	4780.85	50.52
2	22.96	76.36	4681.78	49.48
2	45.01	325.49	9462.63	100.00

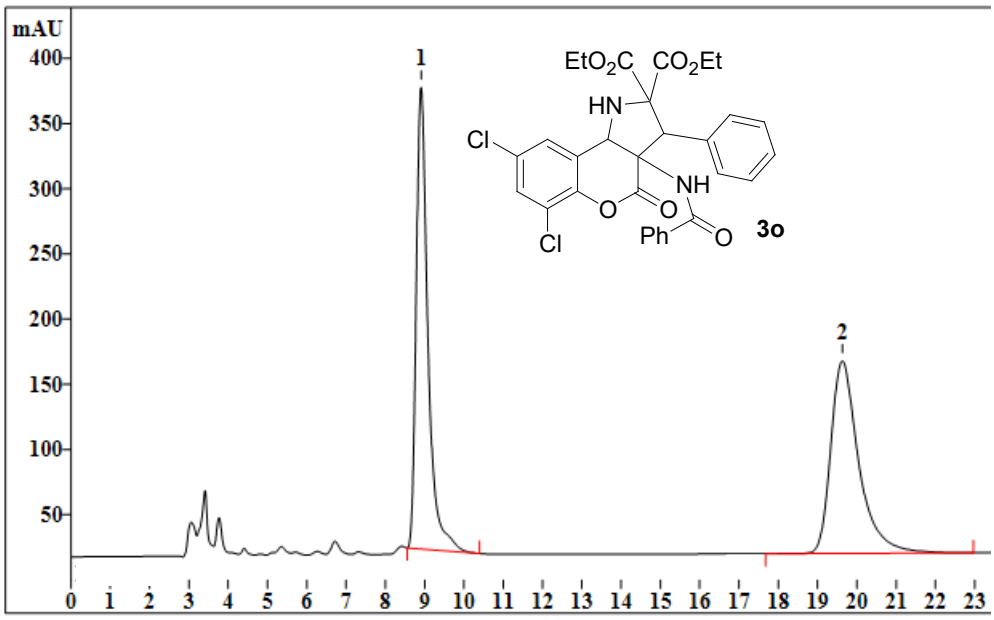
Major **3n**



No	Time min	Height mAU	Area mAU*s	Area %
1	7.872	0.51	12.90	0.09
2	23.65	220.25	14027.43	99.91
2	29.01	220.76	14040.33	100.00

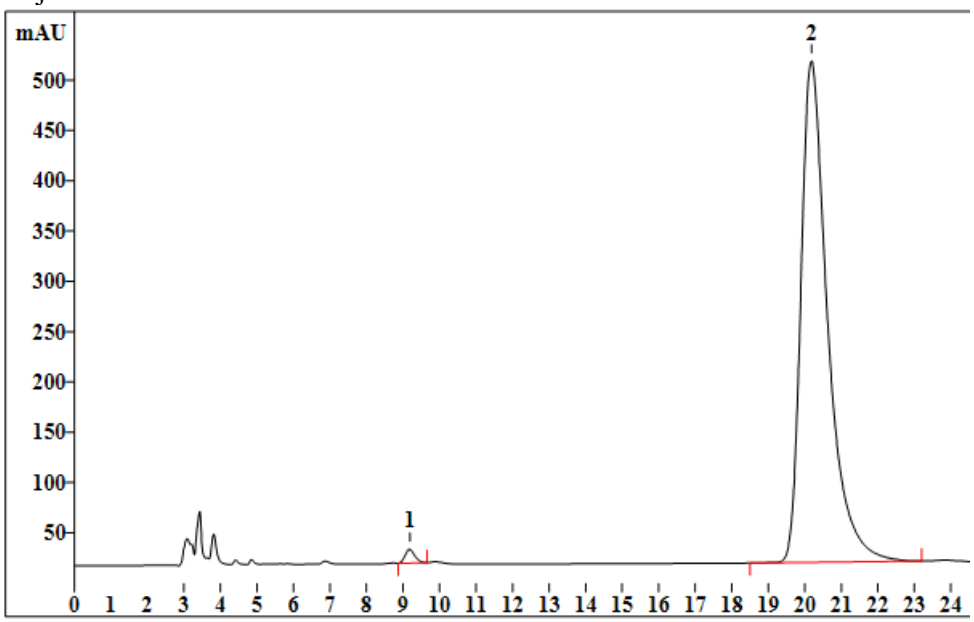
3o: HPLC analysis using chiral AD-H Column (*n*-hexane/Pr^{i}OH = 70:30, 1.0 mL/min)

Racemic **3o**



No	Time min	Height mAU	Area mAU*s	Area %
1	8.909	354.03	7331.56	50.06
2	19.63	147.54	7312.57	49.94
2	45	501.56	14644.14	100.00

Major **3o**



No	Time min	Height mAU	Area mAU*s	Area %
1	9.183	13.50	248.29	0.97
2	20.18	497.86	25262.39	99.03
2	26.02	511.37	25510.68	100.00

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