Organocatalytic Enamine-Activation of Cyclopropanes for Highly Stereoselective Formation of Cyclobutanes

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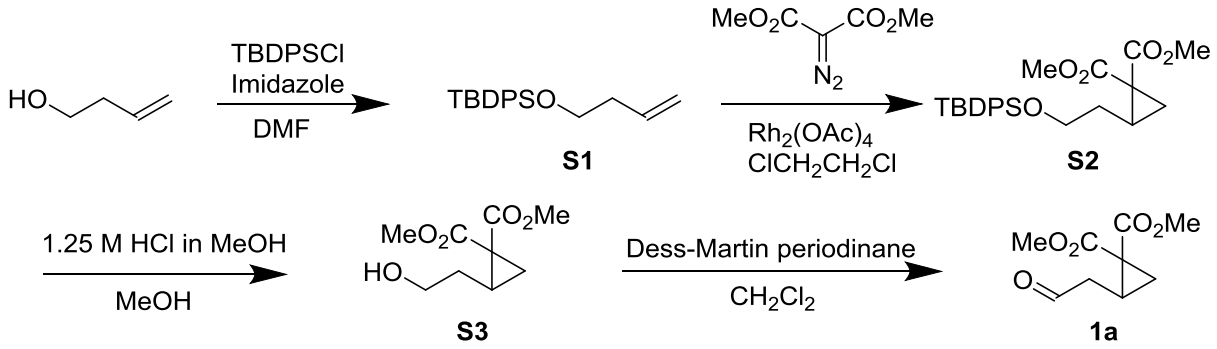
1. General methods

NMR spectra were acquired on a Bruker AVANCE III HD spectrometer running at 400 MHz for ^{1}H, 100 MHz for ^{13}C and 162 MHz for ^{31}P. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CHCl_3$, 7.26 ppm for ^{1}H NMR, $CDCl_3$, 77.0 ppm for ^{13}C NMR). For ^{31}P NMR an internal standard of 85% H_3PO_4 was used. The following abbreviations are used to indicate the multiplicity in NMR spectra: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; bs, broad signal. ^{13}C spectra were acquired in broad band decoupled mode. Mass spectra were recorded on a micromass LCT spectrometer using electrospray (ES^+) ionization (referenced to the mass of the neutral species) or on a Bruker Maxis Impact mass spectrometer using electronspray (ES^+) ionization (referenced to the mass of the charged species). Dry solvents were obtained from a MBraun MB SPS-800 solvent purification system. Analytical thin layer chromatography (TLC) was performed using pre-coated aluminium-backed plates (Merck Kieselgel 60 F254) and visualized by UV radiation, $KMnO_4$ or *p*-anisaldehyde stains. For flash chromatography (FC) silica gel (Silica gel 60, 230-400 mesh, Sigma-Aldrich) or Iatrobeads 6RS-8060 were used. Optical rotations were measured on a Perkin-Elmer 241 polarimeter, α values are given in $deg \cdot cm^3 \cdot g^{-1} \cdot dm^{-1}$; concentration c in g $(100\ mL)^{-1}$. The diastereomeric ratio (dr) of products was evaluated by ^{1}H NMR analysis of the crude mixture. The enantiomeric excess (ee) of products was determined by chiral stationary phase HPLC (Daicel Chiralpak) or chiral stationary phase Waters ACQUITY UPC^2 (Daicel Chiralpak). Reference samples for UPC^2 analysis were prepared using a mixture of products obtained from reactions with cat **2a** and *ent*-cat **2a**. Unless otherwise noted, analytical grade solvents and commercially available reagents were used without further purification.

2. Synthesis of starting materials

2.1 Synthesis of cyclopropylacetaldehydes **1**



Scheme S1: Synthesis of 1a

Aldehyde **1a** was prepared from 3-buten-1-ol by a synthetic procedure similar to a previous report from Kerr *et al.* [1] (Scheme S1).

To a stirred solution of imidazole (1.2 eq.) in DMF (0.3 M of 3-buten-1-ol) 3-buten-1-ol was added (1.0 eq.). *tert*-Butyl(chloro)diphenylsilane was then added slowly. The reaction was stirred at ambient temperature and monitored by TLC. Upon completed reaction (approximately 3.5 h) the solution was diluted with Et_2O and water. The layers were separated and the aqueous layer was extracted three additional times with Et_2O. The combined organic layers were washed twice with water and once with brine. The organic solution was then dried using $MgSO_4$, filtered and concentrated to give compound **S1**. The compound was used without further purification.

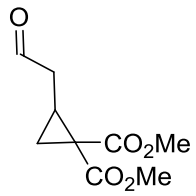
Compound **S1** was dissolved in 1,2-dichloroethane (0.25 M of **S1**) along with $Rh_2(OAc)_4$ (0.015 eq.). The mixture was heated to 60 °C. A solution of 2-diazo-malonic acid dimethyl ester in 1,2-dichloroethane (1.6 M), was then added via syringe pump over an extended period (approximately 2 h). The mixture was sturred overnight at 60 °C. After cooling to room temperature, the mixture was concentrated under reduced pressure. The crude material was then purified by flash chromatography (EtOAC/pentane 1:20 -> 1:10) to yield **S2**.

Compound **S2** was dissolved in MeOH (0.5 M). A 1.25 M solution of HCl in MeOH was added (2.5 eq.) and the mixture was stirred at ambient temperature until completion as monitored by TLC (approximately 3 h). The mixture was then neutralized with 6M NaOH, and then concentrated under reduced pressure. Water was then added and an extraction was performed 4 times using EtOAc. The combined organic layers were washed once with water and once with brine, dried over $MgSO_4$, and then filtered and concentrated. The crude material was then purified by flash chromatography (EtOAc/pentane 1:1) to yield **S3**.

Compound **S3** was dissolved in dry CH_2Cl_2 (0.2 M) and cooled to 0 °C. Dess-Martin periodinane (1.2 eq.) was then added in one portion. The reaction mixture was stirred at 0 °C for 15 min and at ambient temperature for 2h. Et_2O was then added and the milky suspension was washed with a 20% $Na_2S_2O_3$ solution. The

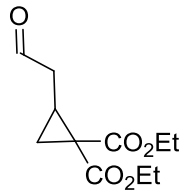
[1] Dias, D. A.; Kerr, M. A. *Org. Lett.* **2009**, *11*, 3694.

aqueous phase was reextracted with Et_2O (for compound **1d** CH_2Cl_2 was used), the combined organic phases were washed with water and brine and dried over $MgSO_4$. The crude material was then purified by flash chromatography on Iatrobeads using EtOAc/pentane 2:3 as eluent to afford **1a**.



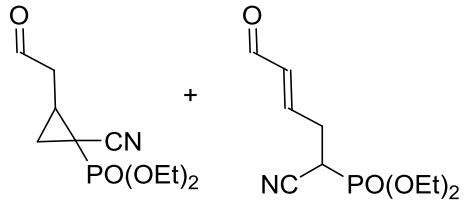
1a

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.77 (t, *J* = 1.3 Hz, 1H), 3.75 (s, 3H), 3.75 (s, 3H), 2.55 (dddd, *J* = 29.6, 18.0, 7.3, 1.3 Hz, 2H), 2.21 (dq, *J* = 9.1, 7.4 Hz, 1H), 1.59 (dd, *J* = 9.1, 4.9 Hz, 1H), 1.42 (dd, J = 7.6, 4.9 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 199.6, 170.1, 168.6, 53.0, 52.9, 42.9, 33.0, 21.5, 20.7. **HRMS** (ESI+) *m/z* calcd. for $C_9H_{12}O_5$ $[M+H]^+$: 201.0757; found: 201.0759.



1c

Aldehyde **1c** was prepared in an analogous fashion to compound **1a**. For the deprotection step a solution of HCl in EtOH was used in order to avoid undesired transesterification. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.79 (t, *J* = 1.4 Hz, 1H), 4.30-4.11 (m, 4H), 2.58 (ddd, *J* = 17.9; 6.9; 1.3 Hz, 1H), 2.58 (ddd, *J* = 18.4; 7.3; 1.0 Hz, 1H), 2.25-2.14 (m, 1H), 1.55 (dd, *J* = 9.1; 4.9 Hz, 1H), 1.39 (dd, *J* = 7.3; 4.9 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 199.6, 169.5, 168.0, 61.6 (2C), 42.7, 33.1, 20.9, 20.1, 14.1 (2C). **HRMS** (ESI+) *m/z* calcd. for $C_{11}H_{16}O_5$ $[M+Na]^+$: 251.0890; found: 251.0895.



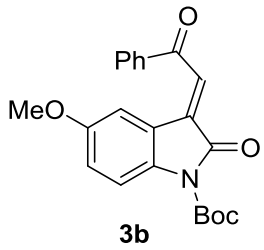
1d

Aldehyde **1d** was prepared in an analogous fashion to compound **1a**. The cyclopropanation step was performed with $Rh_2(esp)_2$ as the catalyst using similar conditions as those reported by Charette and co-workers.[2] The deprotection step was performed with a TBAF solution. The oxidation step required 20 h reaction time to reach full conversion. During purification of **1d** a minor amount of the cyclopropane spontaneously ring-opened and was thus employed in the reaction as a mixture of the closed and ring-opened compounds. For NMR characterization * denotes the ring-opened isomer, + denotes overlap of signals of both isomers, whereas no sign denotes cyclopropane isomer. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.85 (s, 1H), 9.58* (d, *J* = 7.6 Hz, 1H), 6.84* (dt, *J* = 15.6, 7.0 Hz, 1H), 6.28* (dd, *J* = 15.6, 7.6 Hz, 1H), 4.43-4.16$^+$ (m, 8H), 3.09* (ddd, *J* = 23.0, 9.3, 5.0 Hz, 1H), 2.98-2.83$^+$ (m, 3H), 2.73 (dd, *J* = 19.1, 8.3 Hz, 1H), 2.26-2.09 (m, 1H), 1.88-1.75 (m, 1H), 1.47-1.31$^+$ (m, 12H), 1.28 (ddd, *J* = 9.0, 7.2, 5.2 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 198.1, 192.9*, 149.6* (d, *J* = 11.7 Hz), 135.9*, 117.5 (d, *J* = 4.0 Hz), 115.4* (d, *J* = 9.4 Hz), 64.8* (d, *J* = 7.1 Hz), 64.5$^+$ (d, *J* = 6.3 Hz, 2C), 64.1 (d, *J* = 6.6 Hz), 44.4 (d, *J* = 1.2 Hz), 30.3 (d, *J* = 4.0 Hz)*, 29.3* (d, *J* = 143.7 Hz), 19.5 (d, *J* = 3.1 Hz), 19.3 (d, *J* = 1.6 Hz), 16.7-16.5 (m, 4C)$^+$, 10.7 (d, *J* = 198.6 Hz). **^{31}P NMR (162 MHz, $CDCl_3$)**: δ 17.9-17.3 (m), 16.5-15.8 (m)*. **HRMS** (ESI+) *m/z* calcd. for $C_{10}H_{16}NO_4P$ $[M+H]^+$: 246.0890; found: 246.0894.

[2] Lindsay, V. N. G.; Fiset, D.; Gritsch, P. J.; Azzi, S.; Charette, A. B. *J. Am. Chem. Soc.* **2013**, *135*, 1463.

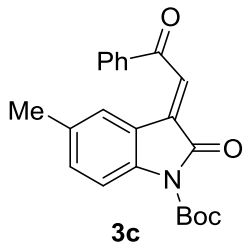
2.2 Synthesis of oxindoles **3**

Synthesis and characterization of compounds **3a**,**l** are described in the literature.[3] Compounds **3b**-**h** were synthesized in an analogous fashion to **3a** from their respective isatins. Compound **3i** was synthesized by performing the Wittig reaction directly on isatin. Synthesis of compound **3j** is described below. Compound **3k** was synthesized analogously to compounds **3a**-**h** with the employment of the appropriate Wittig reagent. Compound **3m** was synthesized as described in previous reports.[4]



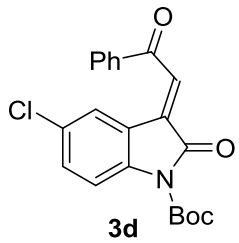
3b

Compound **3b** was isolated as a dark red solid by FC on silica gel using pentane/EtOAc as eluent (20:1 → 10:1) in 61% yield over two steps. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.10-8.06 (m, 2H), 8.00 (d, *J* = 2.8 Hz, 1H), 7.88 (s, 1H), 7.84 (d, *J* = 9.0 Hz, 1H), 7.67-7.61 (m, 1H), 7.53 (dd, *J* = 8.4; 7.0 Hz, 2H), 6.99 (dd, *J* = 9.0; 2.8 Hz, 1H), 3.82 (s, 3H), 1.66 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 191.2, 166.5, 156.6, 149.1, 137.7, 135.9, 135.5, 134.1, 129.1, 129.0, 127.4, 121.3, 119.6, 116.2, 111.6, 87.4, 55.9, 28.3 (3C). **HRMS** (ESI+) *m/z* calcd. for $C_{22}H_{21}NO_5$ $[M+H]^+$: 380.1492; found: 380.1499; $[M+Na]^+$: 402.1312; found: 402.1322.



3c

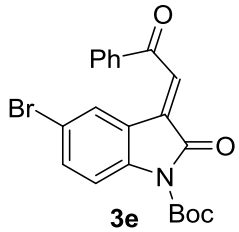
Compound **3c** was isolated as an orange solid by FC on silica gel using pentane/EtOAc as eluent (20:1 → 10:1) in 63% yield over two steps. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.16 (s, 1H), 8.10-8.05 (m, 2H), 7.85 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.66-7.60 (m, 1H), 7.52 (dd, *J* = 8.4; 7.0 Hz, 2H), 7.25-7.20 (m, 1H), 2.33 (s, 3H), 1.66 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 191.2, 166.5, 149.0, 139.8, 137.6, 135.3, 134.3, 134.0, 133.6, 129.0 (2C), 128.9 (2C), 127.5, 127.0, 120.4, 114.9, 84.6, 28.2 (3C), 21.2. **HRMS** (ESI+) *m/z* calcd. for $C_{22}H_{21}NO_4$ $[M+H]^+$: 364.1543; found: 364.1549; $[M+Na]^+$: 386.1363; found: 386.1368.



3d

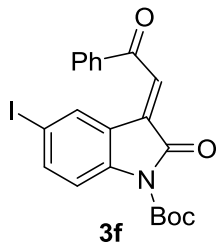
Compound **3d** was isolated as a yellow solid by FC on silica using pentane/EtOAc as eluent (20:1 → 10:1) in 47% yield over two steps. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.42 (d, *J* = 2.3Hz, 1H), 8.11-8.06 (m, 2H), 7.94 (s, 1H), 7.90 (d, *J* = 8.8 Hz, 1H), 7.69-7.62 (m, 1H), 7.57-7.51 (m, 2H), 7.41 (dd, *J* = 8.8; 2.3 Hz, 1H), 1.66 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 190.7, 165.7, 148.8, 140.4, 137.4, 134.4, 132.7, 130.3, 129.2 (2C), 129.0 (2C), 128.7, 127.1, 121.7, 116.4 (2C), 85.3, 28.2 (3C). **HRMS** (ESI+) *m/z* calcd. for $C_{21}H_{18}ClNO_4$ $[M+H]^+$: 384.0997; found: 384.1000; $[M+Na]^+$: 406.0817; found: 406.0820.

[3] Halskov, K. S.; Johansen, T. K.; Davis, R. L.; Steurer, M.; Jensen, F.; Jørgensen, K. A. *J. Am. Chem. Soc.* **2012**, *134*, 12943.
[4] Zhou, Q.-Q.; Xin, Y.; Xiao, Y.-C.; Dong, L.; Chen, Y.-C. *Tetrahedron* **2013**, *69*, 10369.



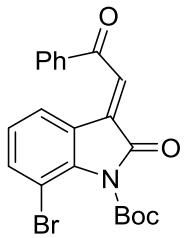
3e

Compound **3e** was isolated as a yellow solid by FC on silica gel using pentane/EtOAc as eluent (20:1 → 10:1) in 50% yield over two steps.**^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.57 (d, *J* = 2.1 Hz, 1H), 8.08 (dd, *J* = 8.4; 1.3 Hz, 2H), 7.93 (s, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.69-7.62 (m, 1H), 7.59-7.50 (m, 3H), 1.66 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 190.7, 165.6, 148.8, 140.9, 137.4, 135.6, 134.3, 134.2, 130.0, 129.2 (2C), 129.0 (2C), 128.7, 122.1, 117.8, 116.8, 85.3, 28.2 (3C). **HRMS** (ESI+) *m*/*z* calcd. for $C_{21}H_{18}BrNO_4$ $[M+H]^+$: 428.0492; found: 428.0495; $[M+Na]^+$: 450.0311; found: 450.0316.



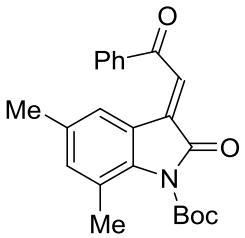
3f

Compound **3f** was isolated as a yellow solid by FC on silica gel using pentane/EtOAc as eluent (20:1 → 10:1) in 52% yield over two steps. The compound was isolated as a E/Z mixture. For NMR characterization * denotes the minor isomer, + denotes overlap of signals of both isomers, whereas no sign denotes major isomer. For ^{13}C NMR only signals for major isomer is given. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.12 – 8.08* (m, 2H), 8.02 – 7.96 (m, 2H), 7.94* (s, 1H), 7.89 (d, *J* = 1.3 Hz, 1H), 7.77 – 7.68^{+} (m, 4H), 7.67-7.66* (m, 1H), 7.68 – 7.59 (m, 1H), 7.56* (t, *J* = 7.7 Hz, 2H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.27^{+} (d, *J* = 7.3 Hz, 2H), 1.68* (s, 9H), 1.57 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 193.7, 162.3, 148.9, 141.6, 140.0, 135.7, 134.3, 133.3, 129.6, 129.1 (2), 129.0 (2), 128.6, 123.4, 117.8, 87.7, 85.1, 28.2 (3). **HRMS** (ESI+) *m*/*z* calcd. for $C_{21}H_{18}INO_4$ $[M+H]^+$: 476.0353; found: 476.0354; $[M+Na]^+$: 498.0173; found: 498.0177.



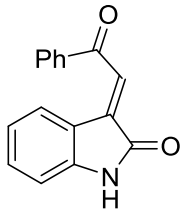
3g

Compound **3g** was isolated as a yellow solid by FC on silica gel using pentane/EtOAc as eluent (20:1 → 10:1) in 50% yield over two steps. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.27 (dd, *J* = 7.8; 1.1 Hz, 1H), 8.09-8.05 (m, 2H), 7.89 (s, 1H), 7.68-7.62 (m, 1H), 7.59-7.51 (m, 3H), 7.02 (t, *J* = 8.0 Hz, 1H), 1.67 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 190.9, 166.9, 147.8, 140.9, 137.3, 137.2, 134.8, 134.4, 129.2 (2C), 129.1, 129.0 (2C), 126.2, 125.7, 123.7, 107.0, 86.0, 27.9 (3C). **HRMS** (ESI+) *m*/*z* calcd. for $C_{21}H_{18}BrNO_4$ $[M+H]^+$: 428.0492; found: 428.0494; $[M+Na]^+$: 450.0311; found: 450.0313.



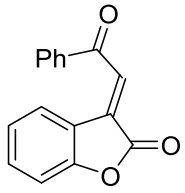
3h

Compound **3h** was isolated as an orange solid by FC on silica gel using pentane/EtOAc as eluent (20:1 → 10:1) in 56% yield over two steps. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.10-8.06 (m, 2H), 7.98 (s, 1H), 7.81 (s, 1H), 7.66-7.60 (m, 1H), 7.55-7.50 (m, 2H), 7.06 (s, 1H), 2.30 (s, 3H), 2.21 (s, 3H), 1.65 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 191.4, 167.7, 149.1, 138.6, 137.6, 136.8, 135.9, 134.3, 134.0, 129.1 (2C), 128.9 (2C), 127.0, 125.2, 123.7, 121.7, 85.0, 28.0 (3C), 21.1, 19.6. **HRMS** (ESI+) *m*/*z* calcd. for $C_{23}H_{23}NO_4$ $[M+H]^+$: 378.1700; found: 378.1706; $[M+Na]^+$: 400.1519; found: 400.1529.



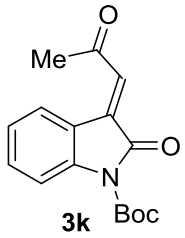
3i

Compound **3i** was isolated as an orange solid by FC on silica gel using pentane/EtOAc as eluent (10:1 → 3:2) in 79% yield. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.32 (d, *J* = 7.7 Hz, 1H), 8.16-8.08 (m, 2H), 7.87 (s, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.33 (td, *J* = 7.7, 1.0 Hz, 1H), 7.02 (td, *J* = 7.7, 0.9 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 191.1, 169.1, 143.1, 137.6, 136.6, 133.8, 132.7, 128.9 (2C), 128.8 (2C), 128.1, 126.5, 122.9, 120.8, 110.0. **HRMS** (ESI+) *m/z* calcd. for $C_{16}H_{11}NO_2$ $[M+H]^+$: 250.0863; found: 250.0860.



3j

To a solution of benzofuran-2(3*H*)one (1.0 g, 7.46 mmol, 1.0 equiv.) in dry toluene (20 mL) was added sodium sulfate, phenylglyoxal monohydrate (1.19 g, 7.83 mmol, 1.05 equiv.) and triethylamine (155.9 µL, 1.12 mmol, 0.15 equiv.). The mixture was stirred under reflux conditions for 6 h. The reaction mixture was then poured into cold water (40 mL) and extracted with Et_2O (3 x 20 mL), the layers were separated and the organic phase was washed with water (2 x 12 mL) and dried with Na_2SO_4. Flash chromatography on silica gel using pentane/EtOAc as eluent (20:1 → 10:1) afforded the product **3j** in 43% yield as a red solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.49 (dd, *J* = 7.8; 1.3 Hz, 1H), 8.13-8.08 (m, 2H), 7.94 (s, 1H), 7.69-7.62 (m, 1H), 7.59-7.53 (m, 2H), 7.49 (td, *J* = 7.8; 1.4 Hz, 1H), 7.24-7.13 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 190.0, 168 .5, 156.5, 137.4, 134.3, 134.3, 132.6, 129.2 (2C), 128.9 (2C), 128.6, 128.3, 124.8, 121.1, 111.2. **HRMS** (ESI+) *m/z* calcd. for $C_{16}H_{10}O_3$ $[M+H]^+$: 251.0703; found: 251.0705; $[M+Na]^+$: 273.0522; found: 273.0525.



3k

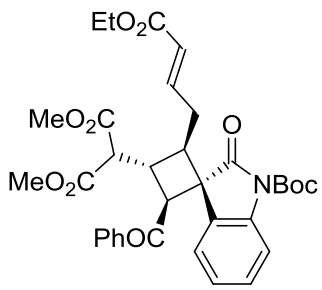
Compound **3k** was isolated as a yellow oil by FC on silica gel using pentane/EtOAc as eluent (20:1 → 10:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.60 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.46-7.39 (m, 1H), 7.20-7.13 (m, 2H), 2.47 (s, 3H), 1.64 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 198.4, 166.6, 148.9, 142.1, 134.0, 133.3, 128.4, 127.8, 124.7, 120.5, 115.0, 84.9, 32.5, 28.2 (3). **HRMS** (ESI+) *m/z* calcd. for $C_{16}H_{17}NO_4$ $[M+H]^+$: 288.1230; found: 288.1232; $[M+Na]^+$: 310.1050; found: 310.1055.

3. General procedures and characterization data for organocatalytic reactions

3.1 Organocatalytic cyclopropane ring-opening and asymmetric cycloaddition of cyclopropylacetaldehydes **1** with 3-olefinic oxindoles and benzofuranone **3**.

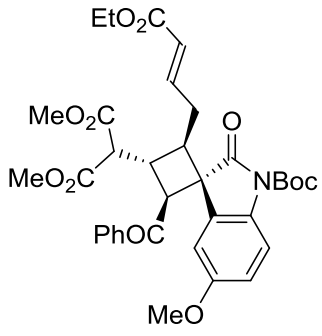
A glass vial equipped with a magnetic stirring bar was charged with 3-olefinic oxindole **3** (0.10 mmol, 1.0 eq.), catalyst **2a** (0.01 mmol, 0.10 eq. or 0.02 mmol, 0.20 eq.) and $PhCO_2H$ (0.01 mmol, 0.10 eq. or 0.02 mmol, 0.20 eq.). In a second glas vial aldehyde **1** was dissolved in $CHCl_3$ (0.3 mL). Both mixtures were cooled to -20 ^{o}C. Subsequently, the aldehyde solution was added to the mixture of oxindole, catalyst and acid. The reaction mixture was stirred at -20 ^{o}C for 48 h. After this time Wittig reagent **4** (0.2 mmol, 2.0 eq.) was added and the mixture was stirred at room temperature for 2.5 h. The crude mixture was purified by FC on Iatrobeads yielding products **5**.

In some cases other catalyst loadings, temperatures or reaction times were applied. For this reason these parameters will be specified for each entry below. Note that compounds **5m** and **5o** were isolated as aldehydes.



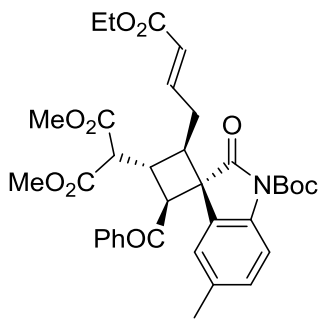
5a

Catalyst **2a** (0.10 eq.), $PhCO_2H$ (0.10 eq.), -20 °C, 48 h. Isolated as a yellow oil by FC on Iatrobeads using pentane/EtOAc 5:1 as eluent. $[\alpha]_D^{22}$ = +92.9 (*c* 0.5, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.49-7.40 (m, 3H), 7.39-7.31 (m, 2H), 7.25-7.21 (m, 3H), 7.13 (td, *J* = 7.9; 1.3 Hz, 1H), 7.09-7.02 (m, 1H), 6.32-6.21 (m, 1H), 4.98 (d, *J* = 15.7 Hz, 1H), 4.59-4.49 (m, 1H), 4.07-3.94 (m, 2H), 3.82 (s, 3H), 3.71-3.66 (m, 1H), 3.65 (s, 3H), 3.02-2.90 (m, 1H), 2.54 (dt, *J* = 10.3; 4.3 Hz, 1H), 2.31-2.18 (m, 1H), 1.61 (s, 9H), 1.17 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 195.7, 176.5, 168.6, 168.3, 166.0, 148.8, 143.6, 140.3, 135.8, 133.5, 129.2, 128.8 (2C), 127.8 (2C), 125.2, 124.3, 123.7, 123.4, 115.1, 84.8, 60.3, 55.9, 54.1, 53.1, 53.0, 50.8, 45.5, 37.2, 32.6, 28.4 (3C), 14.2. **HRMS** (ESI+) *m*/*z* calcd. for $C_{29}H_{29}NO_8$ [M-Boc+H^++H]$^+$: 520.1966; found: 520.1972. **UPC^2**: IC, CO_2/*i*PrOH gradient, 3.0 mL·min^{-1}; t_{major} = 4.01 min; t_{minor} = 4.38 min.



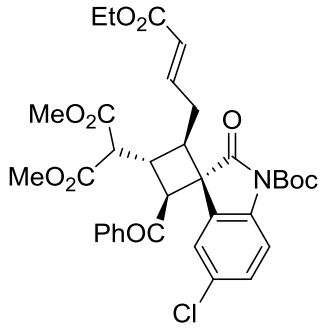
5b

Catalyst **2a** (0.10 eq.), $PhCO_2H$ (0.10 eq.), -20 °C, 48 h. Isolated as an orange oil by FC on Iatrobeads using pentane/EtOAc 5:1 as eluent. $[\alpha]_D^{22}$ = +55.2 (*c* 1.8, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.45 – 7.36 (m, 2H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 7.7 Hz, 2H), 6.73 (d, *J* = 2.6 Hz, 1H), 6.59 (dd, *J* = 9.0; 2.6 Hz, 1H), 6.28-6.16 (m, 1H), 4.99 (d, *J* = 15.7 Hz, 1H), 4.48 (dd, *J* = 9.8; 5.3 Hz, 1H), 4.05-3.89 (m, 2H), 3.87 (s, 1H), 3.75 (s, 3H), 3.72 (s, 3H), 3.62 (m, 1H), 3.57 (s, 3H), 2.95-2.81 (m, 1H), 2.53-2.43 (m, 1H), 2.29-2.14 (m, 1H), 1.54 (s, 9H), 1.11 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 195.6, 176.6, 168.6, 168.3, 165.9, 156.7, 148.9, 143.7, 135.8, 133.7, 133.5, 128.8 (2C), 127.8 (2C), 124.6, 123.7, 116.0, 114.5, 111.4, 84.6, 60.3, 56.2, 55.9, 54.5, 53.1, 53.0, 50.6, 45.6, 37.1, 32.6, 28.4 (3C), 14.4. **HRMS** (ESI+) *m*/*z* calcd. for $C_{35}H_{39}NO_{11}$ [M-Boc+H^++H]$^+$: 550.2072; found: 550.2078. **UPC^2**: IC, CO_2/*i*PrOH gradient, 3.0 mL·min^{-1}; t_{major} = 3.92 min; t_{minor} = 4.30 min.



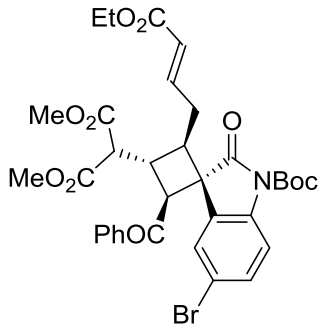
5c

Catalyst **2a** (0.10 eq.), $PhCO_2H$ (0.10 eq.), -20 °C, 48h. Isolated as a light yellow solid by FC on Iatrobeads using pentane/EtOAc 5:1 as eluent. $[\alpha]_D^{22}$ = +85.9 (*c* 0.3, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48-7.15 (m, 6H), 7.04 (s, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 6.27 (ddd, *J* = 15.4; 8.3; 6.5 Hz, 1H), 5.00 (d, *J* = 15.4 Hz, 1H), 4.56-4.47 (m, 1H), 4.08-3.92 (m, 2H), 3.82-3.75 (m, 1H), 3.81 (s, 3H), 3.70-3.64 (m, 1H), 3.64 (s, 3H), 2.98-2.87 (m, 1H), 2.58-2.46 (m, 1H), 2.29 (s, 3H), 2.31-2.17 (m, 1H), 1.59 (s, 9H), 1.17 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 195.5, 176.3, 168.2, 167.9, 165.6, 148.5, 143.4, 137.6, 135.5, 133.6, 133.0, 129.3, 128.4 (2C), 127.4 (2C), 125.3, 123.2, 122.9, 114.4, 84.2, 59.9, 55.6, 53.9, 52.7, 52.6, 50.5, 45.2, 36.9, 32.2, 28.0 (3C), 21.0, 14.1. **HRMS** (ESI+) *m*/*z* calcd. for $C_{35}H_{39}NO_{10}$ $[M\text{-}Boc+H+H]^+$: 534.2122; found: 534.2135. Enatiomeric excess was determined by performing a Ramirez olefination on the aldehyde intermediate.[5] **UPC^2**: IC, CO_2/*i*PrOH gradient, 3.0 mL·min^{-1}; t_{major} = 3.16 min; t_{minor} = 3.50 min.



5d

Catalyst **2a** (0.10 eq.), $PhCO_2H$ (0.10 eq.), -20 °C, 48 h. Isolated as a light yellow solid by FC on Iatrobeads using pentane/EtOAc 5:1 as eluent. $[\alpha]_D^{22}$ = +62.2 (*c* 0.2, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.51-7.33 (m, 4H), 7.23 (dt, *J* = 10.6, 5.2 Hz, 3H), 7.18-7.07 (m, 1H), 6.29 (ddd, *J* = 21.4, 9.6, 5.3 Hz, 1H), 5.05 (d, *J* = 15.8 Hz, 1H), 4.55 (d, *J* = 9.3 Hz, 1H), 4.11-3.93 (m, 2H), 3.82 (s, 3H), 3.70-3.66 (m, 1H), 3.65 (s, 3H), 2.97 (td, *J* = 11.0, 4.6 Hz, 1H), 2.63-2.51 (m, 1H), 2.31-2.17 (m, 2H), 1.60 (s, 9H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 195.4, 175.8, 168.5, 168.2, 165.8, 148.6, 143.3 (2), 138.9, 135.8, 133.7, 129.9, 129.3, 128.9 (2C), 127.8 (2C), 125.3, 125.2, 123.8, 116.2, 85.2, 60.4, 55.8, 54.1, 53.1, 53.1, 50.5, 45.6, 37.2, 28.3 (3C), 14.5. **HRMS** (ESI+) *m*/*z* calcd. for $C_{34}H_{36}ClNO_{10}$ $[M\text{-}Boc+H^++H]^+$: 554.1576; found: 554.1578. **UPC^2**: IC, CO_2/*i*PrOH gradient, 3.0 mL·min^{-1}; t_{major} = 3.60 min; t_{minor} = 3.85 min.

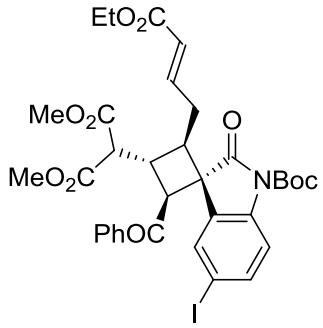


5e

Catalyst **2a** (0.10 eq.), $PhCO_2H$ (0.10 eq.), -20 °C, 48 h. Isolated as a light orange solid by FC on Iatrobeads using pentane/EtOAc 5:1 as eluent. $[\alpha]_D^{22}$ = +55.6 (*c* 1.0, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.47-7.41 (m, 2H), 7.40-7.32 (m, 3H), 7.25-7.19 (m, 3H), 6.28 (ddd, *J* = 15.6; 8.6; 5.6 Hz, 1H), 5.04 (dt, *J* = 15.9; 1.3 Hz, 1H), 4.54 (d, *J* = 9.3 Hz, 1H), 4.10-3.94 (m, 2H), 3.81 (s, 3H), 3.65 (s, 3H), 3.68-3.59 (m, 2H), 2.96 (ddd, *J* = 10.9; 9.3; 4.5 Hz, 1H), 2.57 (dddd, *J* = 15.3; 6.1; 4.6; 1.8 Hz, 1H), 2.30-2.16 (m, 1H), 1.60 (s, 9H), 1.17 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 195.2, 175.5, 168.2, 167.9, 165.6, 148.4, 143.1, 139.1, 135.5, 133.4, 132.0, 128.7 (2C), 127.8, 127.6 (2C), 125.5, 123.6, 117.1, 116.4, 85.0, 60.2, 55.6, 53.8, 52.9, 52.8, 50.4, 45.4, 37.0, 32.3, 28.1 (3C),

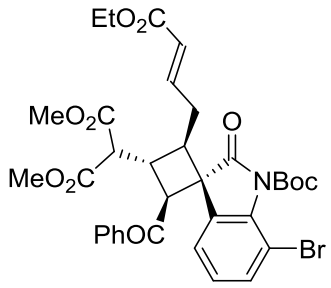
[5] See *e.g.*: Albrecht, Ł.; Dickmeiss, G.; Weise, C. F.; Rodríguez-Escrich, C.; Jørgensen, K. A., *Angew. Chem. Int. Ed.* **2012**, *51*, 13109.

14.3. **HRMS** (ESI+) *m*/*z* calcd. for $C_{34}H_{36}BrNO_{10}$ $[M+Na]^+$: 720.1415; found: 720.1423. **UPC²**: IC, CO_2/*i*PrOH 90:10, 3.0 mL·min^{-1}; t_{major} = 3.29 min; t_{minor} = 3.37 min.



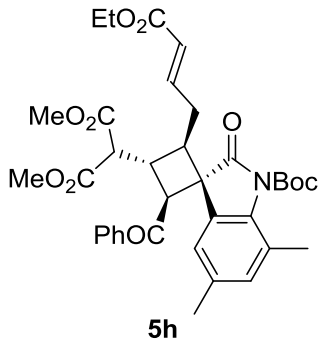
5f

Catalyst **2a** (0.10 eq.), $PhCO_2H$ (0.10 eq.). Isolated as a green oil by FC on Iatrobeads using pentane/EtOAc 5:1 as eluent. $[\alpha]_D^{22}$ = +48.4 (*c* 0.5, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.53 (d, *J* = 1.8 Hz, 1H), 7.49-7.41 (m, 3H), 7.41-7.35 (m, 1H), 7.23 (t, *J* = 8.1 Hz, 3H), 6.28 (ddd, *J* = 15.7; 8.6; 5.7 Hz, 1H), 5.05 (d, *J* = 15.9 Hz, 1H), 4.53 (d, *J* = 9.3 Hz, 1H), 4.08-3.98 (m, 2H), 3.82 (s, 3H), 3.66 (s, 3H), 3.71-3.59 (m, 2H), 2.95 (ddd, *J* = 11.1; 9.6; 4.5 Hz, 1H), 2.62-2.53 (m, 1H), 2.30-2.17 (m, 1H), 1.60 (s, 9H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 195.2, 175.3, 168.3, 167.9, 165.6, 148.3, 143.1, 139.8, 138.0, 135.6, 133.5, 133.4, 128.7 (2C), 127.6 (2C), 125.7, 123.6, 116.7, 87.2, 85.0, 60.2, 55.6, 53.6, 52.9, 52.9, 50.4, 45.4, 37.0, 32.3, 28.1 (3C), 14.3. **HRMS** (ESI+) *m*/*z* calcd. for $C_{34}H_{36}INO_{10}$ $[M+Na]^+$: 768.1276; found: 768.1287. **UPC²**: IC, CO_2/*i*PrOH gradient, 3.0 mL·min^{-1}; t_{major} = 3.29 min; t_{minor} = 3.41 min.



5g

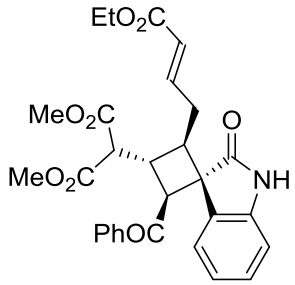
Catalyst **2a** (0.10 eq.), $PhCO_2H$ (0.10 eq.), -20 °C, 48 h. Isolated as an orange oil by FC on Iatrobeads using pentane/EtOAc 5:1 as eluent. $[\alpha]_D^{22}$ = +97.2 (*c* 0.5, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.47-7.42 (m, 2H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.31-7.20 (m, 3H), 7.17 (dd, *J* = 7.6; 1.1 Hz, 1H), 6.90 (t, *J* = 7.8 Hz, 1H), 6.31 (ddd *J* = 15.6; 8.7; 5.5 Hz, 1H), 5.00 (d, *J* = 15.7 Hz, 1H), 4.54 (m, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 3.77-3.69 (m, 1H), 3.65 (s, 3H), 3.05-2.95 (m, 1H), 2.58-2.51 (m, 1H), 2.28-2.15 (m, 1H), 1.61 (s, 9H), 1.39 (s, 1H), 1.21 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 195.3, 176.3, 168.3, 168.0, 165.5, 147.3, 142.9, 139.0, 135.2, 133.8, 133.6, 128.8 (2C), 127.6 (2C), 126.9, 124.8, 124.1, 123.7, 106.4, 85.5, 60.2, 55.5, 54.3, 52.9, 52.8, 50.2, 45.0, 37.0, 32.5, 27.8 (3C), 14.3. **HRMS** (ESI+) *m*/*z* calcd. for $C_{34}H_{36}BrNO_{10}$ $[M+Na]^+$: 720.1415; found: 720.1427. **UPC²**: IC, CO_2/*i*PrOH gradient, 3.0 mL·min^{-1}; t_{major} = 4.46 min; t_{minor} = 4.63 min.



5h

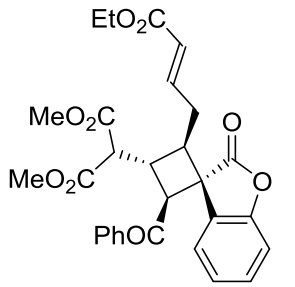
Catalyst **2a** (0.10 eq.), $PhCO_2H$ (0.10 eq.), -20 °C, 48 h. Isolated as an orange oil by FC on Iatrobeads using pentane/EtOAc 5:1 as eluent. $[\alpha]_D^{22}$ = +65.6 (*c* 0.5, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48-7.28 (m, 3H), 7.20 (t, *J* = 7.8 Hz, 2H), 6.86 (s, 1H), 6.72 (s, 1H), 6.30 (ddd, *J* = 15.7; 8.6; 5.8 Hz, 1H), 4.93 (d, *J* = 15.8 Hz, 1H), 4.51-4.47 (m, 1H), 4.04 (dq, *J* = 7.1; 2.2 Hz, 2H), 3.81 (s, 3H), 3.64 (s, 3H), 3.69-3.62 (m, 2H), 2.92 (ddd, *J* = 14.6; 7.5; 4.3 Hz, 1H), 2.53-2.46 (m, 1H), 2.29-2.18 (m, 1H), 2.25 (s, 3H), 1.89 (s, 3H), 1.60 (s, 9H), 1.19 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 195.7, 177.0, 168.4, 168.1, 165.7, 148.6, 143.5, 136.3, 135.4, 133.4, 133.1 132.4, 128.5 (2C), 127.5 (2C), 124.2, 123.3, 123.2, 123.1, 84.5, 60.1, 55.7, 54.2, 52.9, 52.8, 50.4, 45.1, 37.0, 32.3, 27.8 (3C), 21.0, 19.1, 14.3. **HRMS** (ESI+) *m*/*z*

calcd. for $C_{36}H_{41}NO_{10}$ $[M+Na]^+$: 670.2623; found: 670.2633. **UPC²**: IC, CO_2/*i*PrOH gradient, 3.0 mL·min^{-1}; t_{major} = 3.72 min; t_{minor} = 3.85 min.



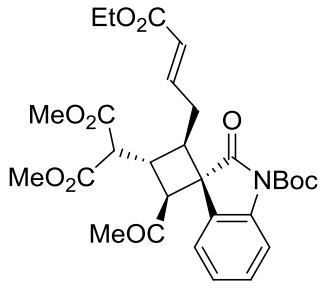
5i

Catalyst **2a** (0.10 eq.), $PhCO_2H$ (0.10 eq.), -20 °C, 144 h. Isolated as a yellow oil by FC on Iatrobeads using pentane/EtOAc as eluent (1:0 → 7:3). $[\alpha]_D^{22}$ = +54.6 (*c* 0.5 CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.55 (bs, 1H), 7.52 (d, *J* = 7.3 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.22 (t, *J* = 7.8 Hz, 3H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 7.7 Hz, 1H), 6.34-6.22 (m, 1H), 5.06 (d, *J* = 15.7 Hz, 1H), 4.52 (d, *J* = 9.0 Hz, 1H), 4.10-3.96 (m, 2H), 3.81 (s, 3H), 3.72-3.68 (m, 1H), 3.63 (s, 3H), 2.97-2.87 (m, 1H), 2.55 (dt, *J* = 15.1, 4.4 Hz, 1H), 2.36-2.22 (m, 1H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 195.7, 178.8, 168.7, 168.3, 166.3, 144.1, 141.3, 135.9, 133.4, 129.0, 128.8 (2C), 128.0 (2C), 126.0, 124.8, 123.4, 122.5, 109.9, 60.4, 56.0, 54.2, 53.0, 52.9, 49.6, 44.9, 37.2, 33.0, 14.0. **HRMS** (ESI+) *m*/*z* calcd. for $C_{29}H_{29}NO_8$ $[M+H]^+$: 520.1971; found: 520.1968. **UPC²**: IC, CO_2/*i*PrOH gradient, 3.0 mL·min^{-1}; t_{major} = 3.85 min; t_{minor} = 4.20 min.



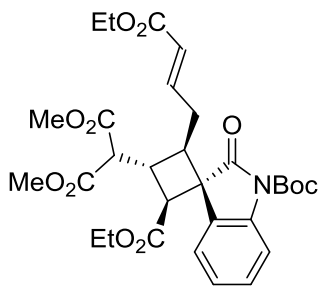
5j

Catalyst **2a** (0.20 eq.), $PhCO_2H$ (0.20 eq.), -20 °C, 72 h. Isolated as an orange oil by FC on Iatrobeads using pentane/EtOAc 5:1 as eluent. $[\alpha]_D^{22}$ = +74.0 (*c* 0.5, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.51-7.47 (m, 2H), 7.44-7.37 (m, 1H), 7.29-7.25 (m, 3H), 7.15 (td, *J* = 7.9, 1.4 Hz, 1H), 7.05 (td, *J* = 7.6; 1.1 Hz, 1H), 6.78 (dd, *J* = 7.8; 1.0 Hz, 1H), 6.30 (ddd, *J* = 15.6; 8.6; 5.8 Hz, 1H), 5.02 (dt, *J* = 15.6; 1.3 Hz, 1H), 4.64-4.47 (m, 1H), 4.06 (qt, *J* = 7.1; 3.6 Hz, 2H), 3.82 (s, 3H), 3.75-3.68 (m, 2H), 3.65 (s, 3H), 3.06-2.97 (m, 1H), 2.59 (dddd, *J* = 15.1; 6.0; 4.4; 1.8 Hz, 1H), 2.34-2.21 (m, 1H), 1.19 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 194.7, 177.9, 168.3, 167.9, 165.6, 153.5, 142.8, 135.2, 133.6, 129.9, 128.9 (2C), 127.5 (2C), 125.5, 124.1, 123.8, 122.6, 110.7, 60.3, 55.3, 53.0, 52.9, 51.6, 50.0, 45.4, 31.9, 32.5, 14.3. **HRMS** (ESI+) *m*/*z* calcd. for $C_{29}H_{28}O_9$ $[M+H]^+$: 521.1806; found: 521.1816. IC, CO_2/*i*PrOH gradient, 3.0 mL·min^{-1}; t_{major} = 3.80 min; t_{minor} = 4.00 min.



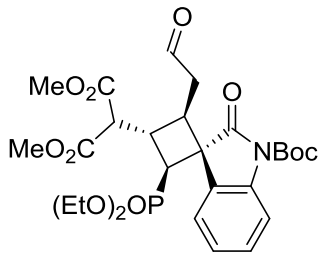
5k

Catalyst **2a** (0.20 eq.), $PhCO_2H$ (0.20 eq.), -20 °C, 72 h. Isolated as a green oil by FC on Iatrobeads using pentane/EtOAc 5:1 as eluent. $[\alpha]_D^{22}$ = +86.1 (*c* 0.4, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.84 (d, *J* = 8.2 Hz, 1H), 7.41-7.30 (m, 1H), 7.22-7.14 (m, 2H), 6.34-6.21 (m, 1H), 4.95 (d, *J* = 15.8 Hz, 1H), 4.12-3.95 (m, 2H), 3.79 (s, 3H), 3.70 (s, 3H), 3.58 (d, *J* = 8.9 Hz, 1H), 3.41 (dd, *J* = 19.0; 9.8 Hz, 1H), 2.84-2.72 (m, 1H), 2.49 (dt, *J* = 15.1, 4.1 Hz, 1H), 2.25-2.10 (m, 1H), 2.02 (s, 1H), 1.64 (s, *J* = 5.6 Hz, 9H), 1.53 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 203.0, 176.3, 168.5, 168.2, 165.9, 149.1, 143.5 (2C), 140.7, 129.7, 125.1, 124.7, 123.6, 115.7, 85.1, 60.4, 55.7, 54.1, 53.3, 53.1, 53.0, 45.8, 36.9, 32.6, 28.5, 28.4 (3C), 14.5. **HRMS** (ESI+) *m*/*z* calcd. for $C_{29}H_{35}NO_{10}$ $[M\text{-}Boc+H^+ +H]^+$: 458.1809; found: 458.1814. **UPC²**: IC, CO_2/*i*PrOH gradient, 3.0 mL·min^{-1}; t_{major} = 3.28 min; t_{minor} = 3.79 min.



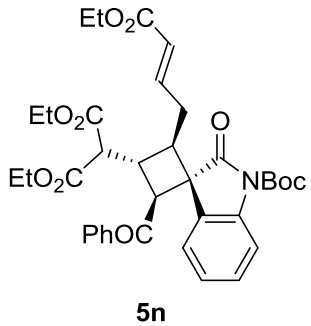
5l

Catalyst **2a** (0.20 eq.), $PhCO_2H$ (0.20 eq.), -20 °C, 48 h. Isolated as an yellow oil by FC on Iatrobeads using pentane/EtOAc 5:1 as eluent. $[\alpha]_D^{22}$ = +57.7 (*c* 0.2, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.83 (dd, *J* = 8.6; 1.2 Hz, 1H), 7.37-7.30 (m, 2H), 7.16 (dt, *J* = 7.6; 0.9 Hz, 1H), 6.29 (ddd, *J* = 15.7; 8.5; 5.9 Hz, 1H), 5.02 (d, *J* = 15.7 Hz, 1H), 4.09-3.96 (m, 4H), 3.80 (s, 3H), 3.76-3.61 (m, 2H), 3.72 (s, 3H), 3.46-3.31 (m, 1H), 2.79 (dt, *J* = 10.5; 4.5 Hz, 1H), 2.59-2.46 (m, 1H), 2.32-2.20 (m, 1H), 1.63 (s, 9H), 1.19 (t, *J* = 7.2 Hz, 3H), 0.71 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 175.6, 168.6, 168.1, 167.8, 165.6, 148.9, 143.2, 140.7, 129.2, 124.2, 124.1, 123.9, 123.3, 115.2, 84.5, 60.6, 60.0, 55.5, 52.8, 52.71, 52.67, 47.0, 45.1, 38.3, 32.3, 28.0 (3C), 14.2, 13.7. **HRMS** (ESI+) *m*/*z* calcd. for $C_{30}H_{37}NO_{11}$ $[M+Na]^+$: 610.2259; found: 610.2268. **UPC^2**: IA, CO_2/MeCN gradient, 3.0 mL·min^{-1}; t_{major} = 3.25 min; t_{minor} = 2.85 min.



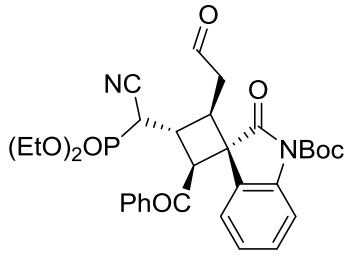
5m

Catalyst **2a** (0.20 eq.), $PhCO_2H$ (0.20 eq.), 5 °C, 48 h. Isolated as an yellow oil by FC on Iatrobeads using pentane/EtOAc 1:3 as eluent. $[\alpha]_D^{22}$ = +13.0 (*c* 0.2, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.29 (s, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 7.6, 1H), 7.28 (t, *J* = 8.2 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 3.92-3.69 (m, 3H), 3.82 (s, 3H), 3.77 (s, 3H), 3.66-3.56 (m, 1H), 3.50-3.36 (m, 2H), 3.34-3.22 (m, 1H), 3.21-3.11 (m, 1H), 2.92 (dd, *J* = 19.5; 4.7 Hz, 1H), 2.70 (dd, *J* = 19.5; 10.1 Hz, 1H), 1.65 (s, 9H), 1.17 (t, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 199.1, 175.6 (d, *J* = 2.5 Hz), 173.3, 167.9 (d, *J* = 16.7 Hz), 149.1, 140.6, 128.9, 126.5, 124.0 (d, *J* = 5.1 Hz), 123.2, 115.0, 84.3, 61.9 (d, *J* = 6.8 Hz), 61.7 (d, *J* = 6.9 Hz), 55.4 (d, *J* = 1.3 Hz), 52.8 (d, *J* = 12.9 Hz), 51.3 (d, *J* = 3.7 Hz), 43.8 (d, *J* = 4.9 Hz), 41.6 (d, *J* = 22.5 Hz), 40.6 (d, *J* = 151.7 Hz), 37.5 (d, *J* = 3.1 Hz), 28.1 (3C), 16.1 (d, *J* = 6.3 Hz), 15.9 (d, *J* = 6.3 Hz). **^{31}P NMR (162 MHz, $CDCl_3$):** δ 21.7-21.1 (m). **HRMS** (ESI+) *m*/*z* calcd. for $C_{26}H_{36}NO_{11}P$ $[M+Na]^+$: 604.1918; found: 604.1919. Enantiomeric excess was measured after the Wittig reaction was performed. Residual triphenylphosphine oxide was present in the analytical samples; however, this separated from the product in the UPC^2 traces. **UPC^2**: IA, CO_2/MeOH gradient, 3.0 mL·min^{-1}; t_{major} = 3.01 min; t_{minor} = 3.21 min.



5n

Catalyst **2a** (0.10 eq.), $PhCO_2H$ (0.10 eq.), -20 °C, 48 h. Isolated as an yellow oil by FC on Iatrobeads using pentane/EtOAc 5:1 as eluent. $[\alpha]_D^{22}$ = +115.0 (*c* 0.3, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48-7.40 (m, 3H), 7.39-7.30 (m, 1H), 7.28-7.16 (m, 3H), 7.12 (dt, *J* = 7.9; 1.4 Hz, 1H), 7.05 (dt, *J* = 7.4; 1.0 Hz, 1H), 6.26 (ddd, *J* = 15.5; 8.6; 5.7 Hz, 1H), 4.96 (d, *J* = 15.5 Hz, 1H), 4.57 (d, *J* = 9.2 Hz, 1H), 4.31-4.22 (m, 2H), 4.15-3.94 (m, 4H), 3.75-3.61 (m, 2H), 2.96 (dd, *J* = 14.0; 9.5; 4.5 Hz, 1H), 2.61-2.51 (m, 1H), 2.32-2.19 (m, 1H), 1.61 (s, 9H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H), 1.13 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 195.3, 176.3, 167.9, 167.6, 165.6, 148.5, 143.4, 139.9, 135.5, 133.1, 128.8, 128.4 (2C), 127.5 (2C), 125.0, 123.9, 123.2, 123.1, 114.7, 84.4, 61.8, 61.7, 60.0, 56.0, 53.8, 50.4, 45.3, 36.6, 32.3, 28.0 (3C), 14.13, 14.10, 13.8. **HRMS** (ESI+) *m*/*z* calcd. for $C_{36}H_{41}NO_{10}$ $[M+Na]^+$: 670.2623; found: 670.2631. **UPC^2**: IC, CO_2/*i*-PrOH gradient, 3.0 mL·min^{-1}; t_{major} = 3.70 min; t_{minor} = 4.16 min.



5o

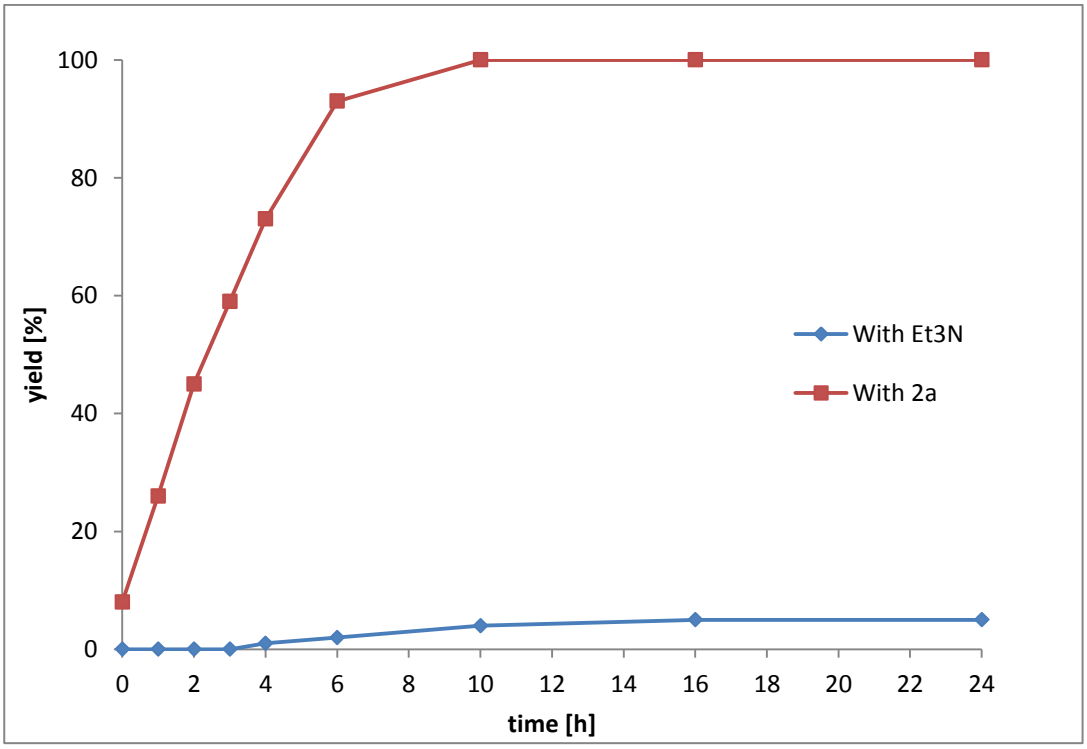
Catalyst **2b** (0.20 eq.), $PhCO_2H$ (0.20 eq.), -20 °C, 48 h. Isolated as an orange oil by FC on Iatrobeads using pentane/EtOAc as eluent (1:1 → 1:2). $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{22}}$ = +60.0 (*c* 0.2, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$):** 9.25 (s, 1H), 7.56-6.94 (m, 9H), 4.62 (d, *J* = 9.2 Hz, 1H), 4.41-4.14 (m, 4H), 3.65-3.01 (m, 4H), 2.74 (dd, *J* = 19.7; 11.6 Hz, 1H), 1.66 (s, 9H), 1.44-1.32 (m, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 198.4, 194.3, 175.7, 148.8, 140.2, 135.0, 133.4, 128.9, 128.5 (2C), 128.2, 127.8, 127.5 (2C), 124.5, 123.5, 115.5, 84.3, 64.7 (*J* = 7.7 Hz), 63.9 (*J* = 7.0 Hz), 52.5 (*J* = 6.1 Hz), 43.1, 40.5 (*J* = 12.4 Hz), 34.2 (*J* = 141.1 Hz), 33.8 (*J* = 4.5 Hz), 28.1 (3C), 27.8, 16.4 (*J* = 2.3 Hz), 16.3 (*J* = 2.3 Hz).). **^{31}P NMR (162 MHz, $CDCl_3$):** δ 15.0-14.6 (m). **HRMS** (ESI+) *m/z* calcd. for $C_{31}H_{35}N_2O_8P$ $[M+Na]^+$: 617.2023; found: 617.2031. Enantiomeric excess was measured after Wittig reaction followed by *N*-Boc deprotection. **UPC^2**: ID, CO_2/*i*-PrOH gradient, 3.0 mL·min^{-1}; t_{major} = 4.18 min; t_{minor} = 5.55 min.

4. Kinetic studies of ring-opening with Et_3N and catalyst 2a

A glass vial equipped with a magnetic stirring bar was charged with catalyst **2a** or Et_3N (0.01 mmol, 0.05 eq.) and $PhCO_2H$ (0.01 mmol, 0.05 eq.) in $CDCl_3$ (0.3 mL). The mixture was cooled to -20 °C. Cyclopropylacetaldehyde **1a** (0.20 mmol, 1.0 eq.), was then added. The mixture was stirred at this temperature and the conversion was measured over 24 h by ^1H NMR.

With 2a	
Time (h)	Conversion (%)
0	8
1	26
2	45
3	59
4	73
6	93
10	100
16	100
24	100

With Et_3N	
Time (h)	Conversion (%)
0	0
1	0
2	0
3	0
4	1
6	2
10	4
16	5
24	5

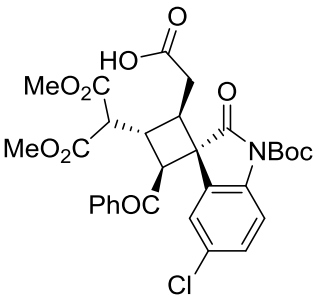


In order to test if the low activity of Et_3N was due to the presence of $PhCO_2H$, an experiment was conducted in the absence of $PhCO_2H$.

With Et_3N, no $PhCO_2H$	
Time (h)	Conversion (%)
0	0
1	0
2	0
3	0
4	0
6	0
10	0
24	0

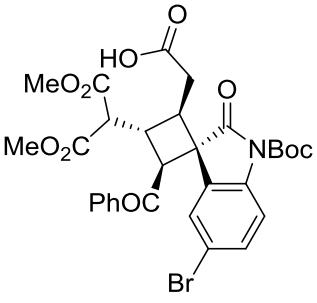
5. Formation of products 6a and 6b and X-ray crystal structure of 6b

Compounds **6a** and **6b** were synthesized from the crude aldehyde mixture, which was concentrated *in vacou.*The mixture was redissolved and the carboxylic acid was formed following a general procedure described in the literature.[6]



6a

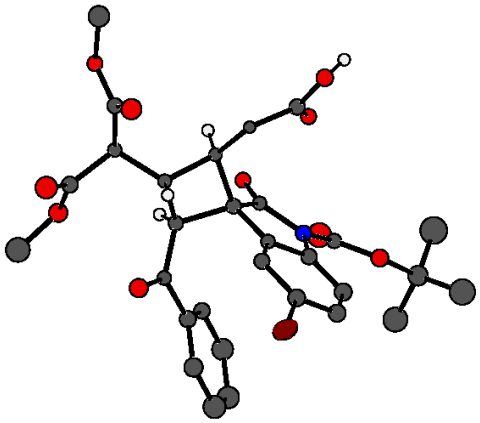
Compound **6a** was isolated as an orange solid by FC on silica gel using CH_2Cl_2/MeOH as eluent (100:0 → 100:2 → 100:3 → 100:4) in 57% yield over two steps. $[\alpha]_D^{22}$ = +38.5 (*c* 0.5, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.45-7.28 (m, 4H), 7.24-7.00 (m, 4H), 4.52 (d, *J* = 9.5 Hz, 1H), 3.79 (s, 3H), 3.69-3.45 (m, 2H), 3.63 (s, 3H), 3.18-3.05 (m, 1H), 2.90-2.71 (m, 1H), 2.40 (dd, *J* = 18.1, 11.0 Hz, 1H), 1.58 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 195.4, 176.6, 175.5, 168.4, 168.0, 148.6, 138.7, 135.4, 133.5, 129.4, 129.0, 128.7 (2C), 127.5 (2C), 125.0, 124.6, 115.9, 84.9, 55.8, 53.8, 53.0, 52.9, 51.2, 41.8, 36.2, 33.2, 28.1 (3C). **HRMS** (ESI+) *m*/*z* calcd. for $C_{30}H_{30}ClNO_{10}$ [M-Boc+H^++H]$^+$: 500.1107; found: 500.1113.



6b

Compound **6b** was isolated as an orange solid by FC on silica gel using CH_2Cl_2/MeOH as eluent (100:0 → 100:2 → 100:3 → 100:4) in 44% yield over two steps. $[\alpha]_D^{22}$ = +68.2 (*c* 0.5, CH_2Cl_2). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48-7.33 (m, 4H), 7.32-7.16 (m, 4H), 4.53 (d, *J* = 9.8 Hz, 1H), 3.80 (s, 3H), 3.69-3.49 (m, 2H), 3.63 (s, 3H), 3.12 (td, *J* = 10.7, 4.6 Hz, 1H), 2.91-2.74 (m, 1H), 2.41 (dd, *J* = 18.3, 11.2 Hz, 1H), 1.59 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 195.5, 176.3, 175.7, 168.7, 168.2, 148.7, 139.5, 135.6, 133.6, 132.2, 128.8 (2C), 127.8 (2C), 127.6, 125.6, 117.0, 116.5, 85.1, 55.9, 53.9, 53.2, 53.1, 51.5, 42.0, 36.4, 33.4, 28.4 (3C). **HRMS** (ESI+) *m*/*z* calcd. for $C_{30}H_{30}BrNO_{10}$ [M-Boc+H^++H]$^+$: 544.0602; found: 544.0606.

[6] Travis, B. R.; Sivakumar, M.; Hollist, G. O.; Borhan, B. *Org. Lett.* **2003**, *5*, 1031.



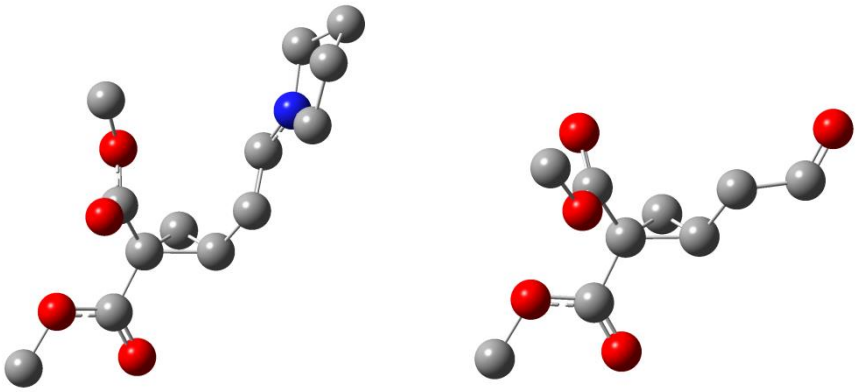
Crystal data for [**6b**]: $C_{30}H_{30}BrNO_{10}$, M = 644.46, monoclinic, space group P 2_1 (no. 6), a = 14.737(16) Å, b = 27.527(3) Å, c = 15.2903(17) Å, β = 95.821(4)°, Flack parameter = -0.009, V = 6170.6(12) Å^3, T = 100 K, Z = 8, d_c = 1.387 g cm^{-3}, μ(Mo Kα, λ = 0.56086 Å) = 0.75 mm^{-1}, 26438 reflections collected, 12646 unique [R_{int} = 0.0818], which were used in all calculations. Refinement on F^2, final R(F) = 0.0809, R_w(F2) = 0.1394. CCDC number 1039270.

6. Computational data

6.1 Methods

All DFT-calculations were run using GAUSSIAN09.[7] All structures were optimized with wB97xD/pcseg-1. Solvent effects were estimated with IEFPCM, using chloroform and water as solvents.

Optimized structures of cyclopropyl-enamine and cyclopropylacetaldehyde



[7] Gaussian 09, Revision **D.01**, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, M. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

6.2 Coordinates

Cyclopropyl aldehyde_CHCl3

Energy = -270.3945525650 hartrees

Atom	x	y	z
C	-1.670338	0.904826	-0.133433
C	-0.775567	-0.145929	0.469422
C	-2.140479	-0.519032	-0.033311
H	-2.112534	1.645023	0.530667
H	-1.413587	1.287214	-1.121321
H	-0.663669	-0.108658	1.553815
H	-2.198122	-1.102022	-0.952049
H	-2.907658	-0.760237	0.699765
C	0.461359	-0.610315	-0.264359
H	0.248575	-0.663791	-1.344223
H	0.777577	-1.610672	0.055854
C	1.612730	0.341446	-0.099817
O	2.748107	0.008621	0.146713
H	1.358337	1.418205	-0.227224

Cyclopropyl iminium-ion_CHCl3

Energy = -406.9349627890 hartrees

Atom	x	y	z
C	3.334679	0.795548	0.602123
C	2.654665	0.020422	-0.494659
C	3.843755	-0.562003	0.210000
H	3.919055	1.669433	0.321889
H	2.819464	0.888377	1.558137
H	2.821504	0.372718	-1.512823
H	3.671924	-1.388197	0.898814
H	4.779950	-0.625496	-0.339891
C	1.282438	-0.561221	-0.261860
H	1.216897	-1.037205	0.729936
C	0.210464	0.462751	-0.343347
H	0.471257	1.508239	-0.521673
C	-1.594177	-1.135024	0.080878
C	-2.111505	1.230922	-0.251103
C	-3.102725	-0.917241	0.061593
H	-1.226791	-1.447569	1.065515
H	-1.232096	-1.844286	-0.668549
C	-3.263146	0.547517	0.467121
H	-2.337855	1.413322	-1.307603
H	-1.758671	2.154950	0.211193
H	-3.494552	-1.079892	-0.949305
H	-3.615521	-1.608941	0.734188
H	-4.227388	0.971470	0.176582
H	-3.153775	0.666245	1.552040
N	-1.034836	0.208699	-0.198623
H	1.063757	-1.364079	-0.982556

Cyclopropyl enamine _CHCl3

Energy = -406.4849483180 hartrees

Atom	x	y	z
C	3.359201	0.913273	0.037837
C	2.729429	-0.360838	-0.455277
C	3.646979	-0.383630	0.743455
H	4.149277	1.361867	-0.562080
H	2.726552	1.635248	0.552163

H	3.180292	-0.768139	-1.364266
H	3.184639	-0.536745	1.718267
H	4.635707	-0.827222	0.633196
C	1.273445	-0.628840	-0.305629
H	0.982824	-1.674242	-0.185325
C	0.329297	0.332470	-0.334959
H	0.626974	1.374631	-0.468126
C	-1.628637	-1.136470	0.004081
C	-1.971750	1.257953	-0.149863
C	-3.126673	-0.831888	0.004283
H	-1.293794	-1.569397	0.963108
H	-1.343246	-1.844648	-0.787462
C	-3.194751	0.614484	0.498064
H	-2.208944	1.638172	-1.157314
H	-1.574128	2.094584	0.438165
H	-3.523192	-0.900155	-1.017306
H	-3.696861	-1.528030	0.627649
H	-4.129231	1.119520	0.232763
H	-3.093992	0.644685	1.591115
N	-1.017446	0.160113	-0.209501

Cyclopropyl aldehyde - monoester_CHCl3

Energy = -498.1659724130 hartrees

Atom	x	y	z
C	-0.366191	-0.145957	0.583454
C	0.870959	0.215844	-0.207010
C	0.521556	1.006186	1.005811
H	0.666509	0.705429	-1.160162
H	1.107140	0.857441	1.911764
H	0.121371	2.007921	0.864244
C	2.047812	-0.730877	-0.203700
H	1.906425	-1.496687	-0.982577
H	2.151882	-1.254507	0.754145
C	3.341250	-0.026176	-0.509339
O	4.386592	-0.255136	0.050256
H	3.290622	0.740358	-1.315181
C	-1.683684	0.175714	-0.014620
O	-1.915880	1.142315	-0.707033
O	-2.602149	-0.741495	0.302557
C	-3.917938	-0.528557	-0.220146
H	-4.502148	-1.390763	0.102975
H	-4.343005	0.394308	0.185182
H	-3.890188	-0.470248	-1.311853
H	-0.339691	-1.055794	1.178516

Cyclopropyl iminium-ion - monoester_CHCl3

Energy = -634.7047318890 hartrees

Atom	x	y	z
C	2.150729	0.073144	0.632035
C	0.921470	-0.500472	-0.026226
C	1.481789	-1.165556	1.185494
H	2.047752	0.999548	1.192401
H	1.109191	-1.004923	-0.974438
H	0.962837	-1.051130	2.136131
H	2.001811	-2.110638	1.046287
C	-0.373163	0.268581	0.043730
H	-0.424086	1.030745	-0.749196
C	-1.557217	-0.618748	-0.083578

H	-1.419506	-1.693805	-0.216850
C	-3.166611	1.216999	0.100557
C	-3.957624	-1.078536	-0.190961
C	-4.685908	1.158489	0.209528
H	-2.828720	1.753905	-0.793618
H	-2.669975	1.644254	0.976032
C	-5.057913	-0.101920	-0.570388
H	-4.137050	-1.540372	0.786458
H	-3.752469	-1.856756	-0.929043
H	-4.984123	1.061454	1.259906
H	-5.149791	2.064095	-0.188549
H	-6.046225	-0.490763	-0.313605
H	-5.038848	0.087585	-1.650321
N	-2.765531	-0.201850	-0.052864
C	3.445573	-0.096485	-0.077253
O	3.721405	-1.037774	-0.786766
O	4.271695	0.919572	0.166947
C	5.559848	0.857373	-0.460321
H	6.079278	1.762380	-0.145182
H	6.100316	-0.032729	-0.126913
H	5.449991	0.835633	-1.548006
H	-0.452292	0.822870	0.991396

Cyclopropyl enamine - monoester_CHCl3

Energy = -634.2587124580 hartrees

Atom	x	y	z
C	-1.992714	-0.260232	-0.425305
C	-0.966277	-0.666409	0.634632
C	-1.414985	-1.657301	-0.379833
H	-1.646839	0.406414	-1.211330
H	-1.422043	-0.796371	1.619031
H	-0.745693	-1.924856	-1.194912
H	-2.086460	-2.448096	-0.051798
C	0.385467	-0.054130	0.622307
H	0.474956	0.930381	1.082757
C	1.471799	-0.665425	0.107052
H	1.373363	-1.663391	-0.324804
C	3.083911	1.166363	0.497234
C	3.836317	-0.848321	-0.619194
C	4.501655	1.372776	-0.041215
H	3.038176	1.241092	1.595765
H	2.374388	1.904054	0.092412
C	5.054341	-0.048416	-0.170626
H	3.715545	-0.802789	-1.714930
H	3.889060	-1.904750	-0.328998
H	4.458191	1.847569	-1.029970
H	5.107822	2.014253	0.606271
H	5.889287	-0.123471	-0.874667
H	5.400946	-0.413403	0.805195
N	2.740536	-0.175564	0.063636
C	-3.392423	-0.065588	0.002177
O	-3.973102	-0.733928	0.831330
O	-3.963019	0.966079	-0.635233
C	-5.323267	1.246967	-0.296321
H	-5.600040	2.114759	-0.896509
H	-5.962765	0.394037	-0.542859
H	-5.415622	1.474608	0.769664

Cyclopropyl aldehyde - diester_CHCl3

Energy = -725.9281730980 hartrees

Atom	x	y	z
C	0.214086	-0.369990	0.334949
C	-1.114781	-0.936711	-0.130332
C	-0.700416	-1.114029	1.288087
H	-0.993469	-1.809636	-0.772623
H	-1.175748	-0.494943	2.047430
H	-0.371677	-2.097136	1.616939
C	-2.245888	-0.010459	-0.511305
H	-2.084412	0.361112	-1.535300
H	-2.318547	0.860533	0.150400
C	-3.572315	-0.721913	-0.506397
O	-4.594740	-0.240746	-0.082944
H	-3.568713	-1.745648	-0.942894
C	0.315649	1.122151	0.475097
O	-0.010969	1.755600	1.449814
O	0.755589	1.668180	-0.656423
C	1.442495	-1.104974	-0.100309
O	1.438986	-2.218625	-0.570503
O	2.545101	-0.405320	0.152497
C	3.791161	-1.020422	-0.197287
H	4.557653	-0.301856	0.092730
H	3.917407	-1.959641	0.347979
H	3.829503	-1.209546	-1.273576
C	0.913812	3.091716	-0.660010
H	1.616709	3.395915	0.120397
H	1.308129	3.335779	-1.646549
H	-0.051393	3.580124	-0.499410

Cyclopropyl iminium-ion - diester_CHCl3

Energy = -862.4653081860 hartrees

Atom	x	y	z
C	1.711427	-0.374530	0.238302
C	0.907343	-1.652677	0.046558
C	1.353427	-1.273422	1.412611
H	1.501397	-2.427948	-0.433625
H	0.652487	-0.860336	2.132590
H	2.169808	-1.843969	1.849290
C	-0.525198	-1.636650	-0.454491
H	-0.830912	-2.686204	-0.603788
C	-1.553509	-1.098952	0.464263
H	-1.442755	-1.256129	1.537334
C	-3.015017	-0.246151	-1.320696
C	-3.713221	-0.107538	1.019123
C	-4.317514	0.535602	-1.197443
H	-3.150726	-1.205186	-1.832257
H	-2.206689	0.304321	-1.810575
C	-4.923054	0.028589	0.110492
H	-3.414284	0.855837	1.447016
H	-3.815888	-0.843936	1.818734
H	-4.110833	1.610293	-1.132409
H	-4.963281	0.371989	-2.063485
H	-5.668102	0.708891	0.530220
H	-5.398950	-0.948850	-0.033219
N	-2.638243	-0.534813	0.086441
C	3.150031	-0.432865	-0.198257
O	3.681123	-1.430302	-0.625988

O	3.770879	0.714984	0.022253
C	5.159740	0.775703	-0.332907
H	5.466327	1.798221	-0.113556
H	5.733323	0.063266	0.266004
H	5.286571	0.556173	-1.396082
C	1.000056	0.923274	0.021881
O	1.251532	1.701888	-0.860513
O	-0.017438	1.088138	0.883357
C	-0.786882	2.289276	0.727218
H	-1.479620	2.303047	1.568975
H	-0.130691	3.162549	0.761276
H	-1.323822	2.276854	-0.226182
H	-0.580189	-1.170816	-1.444138

Cyclopropyl enamine - diester_CHCl3

Energy = -862.0230856910 hartrees

Atom	x	y	z
C	1.782612	-0.329112	0.332832
C	0.788687	-1.522427	0.201405
C	1.283714	-1.111874	1.535636
H	1.294350	-2.389747	-0.223597
H	0.629603	-0.565914	2.209511
H	2.018370	-1.752072	2.018765
C	-0.586663	-1.284209	-0.293900
H	-0.732460	-1.418206	-1.365118
C	-1.604193	-0.860938	0.485393
H	-1.450505	-0.739260	1.558627
C	-3.261015	-0.524596	-1.316064
C	-3.890800	-0.040938	0.976765
C	-4.614326	0.187465	-1.291748
H	-3.338528	-1.550279	-1.711551
H	-2.517038	0.006622	-1.927869
C	-5.147234	-0.096924	0.114079
H	-3.673789	0.992978	1.293742
H	-3.964178	-0.662209	1.877472
H	-4.469275	1.267219	-1.427059
H	-5.284808	-0.157753	-2.084933
H	-5.911672	0.616149	0.438603
H	-5.584562	-1.102934	0.157934
N	-2.859204	-0.543245	0.079114
C	3.188432	-0.593594	-0.079958
O	3.680025	-1.700274	-0.124878
O	3.865697	0.522298	-0.342284
C	5.232365	0.359268	-0.733900
H	5.608892	1.369284	-0.898051
H	5.799175	-0.137977	0.058484
H	5.296174	-0.226749	-1.655080
C	1.180367	0.997415	-0.002317
O	1.274400	1.532473	-1.081198
O	0.445738	1.490644	0.999608
C	-0.369233	2.621267	0.682236
H	-0.891028	2.872828	1.606391
H	0.247905	3.460311	0.348893
H	-1.085350	2.354487	-0.101700

Cyclopropyl aldehyde_gas

Energy = -270.3898620110 hartrees

Atom	x	y	z
C	1.673754	0.903730	0.132186
C	0.773667	-0.145263	-0.466348
C	2.140886	-0.520206	0.027802
H	2.114957	1.645169	-0.531083
H	1.425382	1.286316	1.122152
H	0.656487	-0.106675	-1.550332
H	2.204590	-1.104746	0.945080
H	2.905232	-0.762062	-0.707853
C	-0.461239	-0.607731	0.271222
H	-0.244245	-0.661506	1.350390
H	-0.779027	-1.607995	-0.047517
C	-1.618471	0.342545	0.102818
O	-2.746250	0.006489	-0.152882
H	-1.364958	1.421136	0.236136

Cyclopropyl iminium-ion_gas

Energy = -406.8765454330 hartrees

Atom	x	y	z
C	3.333815	0.728909	0.702428
C	2.659439	0.086406	-0.483627
C	3.847038	-0.569406	0.157306
H	3.917240	1.631290	0.533361
H	2.818573	0.706050	1.662985
H	2.829973	0.548495	-1.456791
H	3.679461	-1.473155	0.741945
H	4.784904	-0.567087	-0.392934
C	1.290504	-0.528176	-0.326218
H	1.209160	-1.076905	0.626143
C	0.202841	0.482340	-0.376721
H	0.449338	1.528756	-0.577583
C	-1.577224	-1.129218	0.111734
C	-2.130771	1.228321	-0.240330
C	-3.088839	-0.938490	0.062010
H	-1.222433	-1.407658	1.112191
H	-1.187602	-1.852814	-0.610690
C	-3.280856	0.524100	0.462424
H	-2.352435	1.422790	-1.296449
H	-1.793837	2.152990	0.234841
H	-3.459325	-1.112256	-0.955443
H	-3.605175	-1.638208	0.724033
H	-4.249007	0.930319	0.158475
H	-3.194058	0.647297	1.549021
N	-1.037276	0.218997	-0.193963
H	1.100468	-1.281605	-1.109410

Cyclopropyl enamine_gas

Energy = -406.4823673600 hartrees

Atom	x	y	z
C	3.361859	0.912646	0.040044
C	2.727124	-0.356370	-0.459277
C	3.651233	-0.390037	0.732837
H	4.148112	1.366114	-0.560999
H	2.734894	1.630911	0.566163
H	3.167335	-0.756715	-1.376249
H	3.193917	-0.549824	1.708586

H	4.638305	-0.834853	0.614725
C	1.273196	-0.624349	-0.299400
H	0.985271	-1.669010	-0.170044
C	0.330706	0.334785	-0.329433
H	0.627220	1.375701	-0.472408
C	-1.626907	-1.135134	0.009153
C	-1.971108	1.256872	-0.143843
C	-3.125928	-0.834094	-0.006231
H	-1.301004	-1.571368	0.970007
H	-1.331537	-1.839676	-0.782270
C	-3.202165	0.611798	0.488250
H	-2.197696	1.643646	-1.152204
H	-1.582694	2.092289	0.453242
H	-3.511537	-0.901882	-1.032157
H	-3.703071	-1.531604	0.609583
H	-4.134727	1.115986	0.213624
H	-3.114546	0.640542	1.582528
N	-1.018044	0.161862	-0.194960

Cyclopropyl aldehyde - monoester_gas

Energy = -498.1578555640 hartrees

Atom	x	y	z
C	-0.365513	-0.169567	0.578356
C	0.869017	0.206563	-0.208503
C	0.522289	0.974362	1.020245
H	0.657071	0.715849	-1.150049
H	1.113814	0.811881	1.920120
H	0.118334	1.976958	0.896096
C	2.050186	-0.734346	-0.224576
H	1.911240	-1.488988	-1.014992
H	2.159619	-1.273355	0.724363
C	3.343740	-0.014552	-0.511352
O	4.380288	-0.232895	0.059876
H	3.290622	0.756864	-1.315670
C	-1.682896	0.172568	-0.012416
O	-1.906553	1.149041	-0.687818
O	-2.609335	-0.744594	0.294043
C	-3.918148	-0.503991	-0.225390
H	-4.516069	-1.363091	0.082280
H	-4.330594	0.419873	0.191774
H	-3.888918	-0.423332	-1.316115
H	-0.342376	-1.091301	1.155201

Cyclopropyl iminium-ion - monoester_gas

Energy = -634.6433414200 hartrees

Atom	x	y	z
C	2.161122	0.754105	-0.407180
C	0.725571	0.540690	-0.000723
C	1.463658	1.746689	0.488820
H	2.376446	1.053053	-1.430984
H	0.587525	-0.255009	0.733006
H	1.239075	2.719474	0.052482
H	1.757609	1.762031	1.536360
C	-0.370745	0.652843	-1.047440
H	-0.482686	-0.284850	-1.599848
C	-1.620213	1.053394	-0.359406
H	-1.661258	2.045647	0.097057
C	-2.810890	-1.082675	-0.676593

C	-3.851997	0.737081	0.588008
C	-4.251994	-1.430770	-0.322223
H	-2.086138	-1.705374	-0.139208
H	-2.594453	-1.124162	-1.747087
C	-4.540019	-0.579065	0.912863
H	-4.462732	1.365115	-0.071618
H	-3.538805	1.321983	1.456466
H	-4.921794	-1.154129	-1.145382
H	-4.373811	-2.502510	-0.145652
H	-5.607752	-0.440142	1.100610
H	-4.098477	-1.028302	1.810957
N	-2.650747	0.314031	-0.184649
C	3.163432	-0.155606	0.225282
O	3.008235	-0.670991	1.305902
O	4.229425	-0.312753	-0.548618
C	5.273094	-1.151669	-0.028461
H	6.041295	-1.166948	-0.801207
H	5.665735	-0.729495	0.900504
H	4.887874	-2.157592	0.158709
H	-0.119820	1.442834	-1.768582

Cyclopropyl enamine - monoester_gas

Energy = -634.2524003370 hartrees

Atom	x	y	z
C	-1.990164	-0.248638	-0.426077
C	-0.966116	-0.663061	0.628912
C	-1.417344	-1.647730	-0.391181
H	-1.645934	0.423126	-1.208396
H	-1.419023	-0.800837	1.613328
H	-0.749210	-1.912696	-1.208219
H	-2.092363	-2.436131	-0.064502
C	0.386506	-0.053322	0.616072
H	0.475587	0.934352	1.069327
C	1.472629	-0.669868	0.114546
H	1.375101	-1.672292	-0.306563
C	3.082458	1.165676	0.492691
C	3.836522	-0.850633	-0.612526
C	4.500750	1.372849	-0.045874
H	3.033148	1.253701	1.590204
H	2.370763	1.895962	0.077185
C	5.055912	-0.047886	-0.171795
H	3.712420	-0.809462	-1.709225
H	3.895255	-1.906894	-0.320786
H	4.457920	1.845537	-1.035832
H	5.107153	2.017198	0.598920
H	5.890002	-0.124184	-0.877154
H	5.405432	-0.408873	0.804461
N	2.746083	-0.181249	0.075263
C	-3.391372	-0.061110	0.005493
O	-3.965216	-0.728806	0.834680
O	-3.970071	0.967941	-0.636574
C	-5.328879	1.228440	-0.291687
H	-5.619536	2.097204	-0.884946
H	-5.959466	0.368139	-0.538214
H	-5.422957	1.443513	0.777270

Cyclopropyl aldehyde - diester_gas

Energy = -725.9175766190 hartrees

Atom	x	y	z
C	0.215048	-0.361554	0.337491
C	-1.116083	-0.931156	-0.116423
C	-0.694970	-1.094953	1.302400
H	-0.991712	-1.811434	-0.749061
H	-1.161855	-0.464773	2.058159
H	-0.365319	-2.075992	1.636842
C	-2.250360	-0.011416	-0.501130
H	-2.086214	0.362817	-1.524174
H	-2.328585	0.859966	0.159691
C	-3.578005	-0.727732	-0.497371
O	-4.607814	-0.237744	-0.115163
H	-3.558337	-1.769478	-0.896643
C	0.312373	1.130973	0.467404
O	-0.054982	1.774581	1.417257
O	0.795821	1.667657	-0.656074
C	1.437176	-1.106007	-0.099889
O	1.425779	-2.214984	-0.574630
O	2.549376	-0.417996	0.162370
C	3.779973	-1.050896	-0.193621
H	4.560766	-0.348841	0.100994
H	3.890997	-1.999283	0.340117
H	3.814114	-1.235539	-1.271374
C	0.955033	3.087133	-0.653624
H	1.632178	3.391802	0.149802
H	1.379943	3.332514	-1.627701
H	-0.012528	3.579769	-0.518156

Cyclopropyl iminium-ion - diester_gas

Energy = -862.4136282210 hartrees

Atom	x	y	z
C	-1.586801	-0.447870	-0.484440
C	-0.747316	-1.708797	-0.307145
C	-1.210804	-1.328145	-1.666031
H	-1.319516	-2.517747	0.145697
H	-0.513896	-0.897514	-2.382683
H	-2.030365	-1.896645	-2.100572
C	0.681948	-1.712279	0.201894
H	1.040942	-2.754780	0.158319
C	1.676923	-0.929041	-0.566054
H	1.564566	-0.835896	-1.645192
C	3.147492	-0.482563	1.354524
C	3.777189	0.262208	-0.884838
C	4.393215	0.397674	1.414105
H	3.352531	-1.520355	1.642690
H	2.315062	-0.103445	1.954685
C	5.000421	0.270957	0.017147
H	3.384585	1.271335	-1.060290
H	3.918998	-0.242991	-1.843715
H	4.109315	1.437770	1.613956
H	5.073301	0.082612	2.209761
H	5.684716	1.086568	-0.230531
H	5.553176	-0.671276	-0.084840
N	2.769157	-0.466856	-0.077747
C	-2.998489	-0.580224	0.030463
O	-3.806137	-1.331628	-0.450112
O	-3.189802	0.154928	1.117546
C	-4.502660	0.093175	1.698972

H	-4.479080	0.790861	2.535849
H	-5.252111	0.394791	0.962818
H	-4.713101	-0.922863	2.043568
C	-0.912601	0.881596	-0.454212
O	0.301826	1.017472	-0.478805
O	-1.754770	1.885534	-0.476887
C	-1.204618	3.213138	-0.493805
H	-2.067980	3.877574	-0.500558
H	-0.597690	3.376240	0.400200
H	-0.599147	3.355094	-1.392629
H	0.699268	-1.430764	1.260290

Cyclopropyl enamine - diester_gas

Energy = -862.0131407430 hartrees

Atom	x	y	z
C	1.777368	-0.338788	0.325080
C	0.771482	-1.508202	0.168821
C	1.264606	-1.129352	1.515133
H	1.262198	-2.379453	-0.266170
H	0.617000	-0.580672	2.193298
H	1.985919	-1.791857	1.988274
C	-0.597138	-1.229966	-0.325023
H	-0.727667	-1.278017	-1.405488
C	-1.625457	-0.878544	0.469514
H	-1.488822	-0.848943	1.551501
C	-3.254183	-0.396953	-1.326185
C	-3.950727	-0.182243	0.986439
C	-4.620941	0.284795	-1.263622
H	-3.307693	-1.386584	-1.810171
H	-2.509641	0.196198	-1.877392
C	-5.182832	-0.169832	0.085153
H	-3.785191	0.806915	1.447105
H	-4.029601	-0.919749	1.795369
H	-4.494430	1.375600	-1.270721
H	-5.263153	0.021248	-2.110179
H	-5.977259	0.481094	0.464800
H	-5.593213	-1.184595	-0.000475
N	-2.877321	-0.524799	0.067742
C	3.180632	-0.621496	-0.090428
O	3.649258	-1.733110	-0.168372
O	3.880728	0.491878	-0.313128
C	5.234532	0.306215	-0.722431
H	5.637783	1.310926	-0.856569
H	5.796317	-0.237415	0.043451
H	5.275465	-0.251436	-1.662934
C	1.204265	1.007040	0.010084
O	1.300307	1.553092	-1.058561
O	0.490025	1.507977	1.031123
C	-0.271641	2.674087	0.729637
H	-0.772658	2.945516	1.660527
H	0.380048	3.485139	0.391311
H	-1.006499	2.450429	-0.051255

Cyclopropyl aldehyde_water

Energy = -270.3964798830 hartrees

Atom	x	y	z
C	-1.667491	0.905951	-0.131617
C	-0.775828	-0.147528	0.470555
C	-2.140436	-0.517612	-0.036002
H	-2.108892	1.644731	0.534643
H	-1.406419	1.289737	-1.117748
H	-0.665696	-0.112789	1.555134
H	-2.196459	-1.097940	-0.956556
H	-2.908727	-0.759068	0.695940
C	0.461360	-0.612098	-0.263128
H	0.248646	-0.666355	-1.342831
H	0.778322	-1.611785	0.058594
C	1.610062	0.341020	-0.102156
O	2.747085	0.009860	0.147803
H	1.356541	1.416200	-0.235512

Cyclopropyl iminium-ion_water

Energy = -406.9507791220 hartrees

Atom	x	y	z
C	-3.322801	-0.705131	0.731536
C	-2.654367	-0.105696	-0.475588
C	-3.834784	0.580878	0.145456
H	-3.910438	-1.610130	0.592103
H	-2.792078	-0.653426	1.681986
H	-2.831096	-0.604444	-1.428679
H	-3.652755	1.502106	0.697744
H	-4.776391	0.562374	-0.399199
C	-1.282922	0.507559	-0.343819
H	-1.192017	1.073585	0.595639
C	-0.197435	-0.503559	-0.387816
H	-0.432428	-1.551287	-0.585205
C	1.558342	1.126948	0.099610
C	2.135135	-1.224349	-0.237438
C	3.071259	0.950192	0.070400
H	1.189179	1.409209	1.092589
H	1.173356	1.838805	-0.635213
C	3.271893	-0.509868	0.474617
H	2.366567	-1.415643	-1.290855
H	1.800926	-2.149272	0.236314
H	3.450852	1.122102	-0.943527
H	3.568339	1.655411	0.740859
H	4.244971	-0.908884	0.177764
H	3.170291	-0.629573	1.559931
N	1.036682	-0.226186	-0.201193
H	-1.099967	1.240521	-1.145638

Cyclopropyl enamine_water

Energy = -406.4861794880 hartrees

Atom	x	y	z
C	3.356995	0.913354	0.035555
C	2.730535	-0.364653	-0.451973
C	3.642773	-0.378523	0.751608
H	4.150117	1.357483	-0.563726
H	2.720890	1.638953	0.540543
H	3.188006	-0.778151	-1.354936
H	3.176653	-0.525647	1.725739

H	4.632454	-0.821715	0.648040
C	1.273226	-0.631968	-0.309176
H	0.980703	-1.677549	-0.192784
C	0.328775	0.330807	-0.340546
H	0.627427	1.373325	-0.469573
C	-1.629319	-1.136882	0.000723
C	-1.971275	1.258767	-0.152531
C	-3.126640	-0.830355	0.011017
H	-1.288440	-1.566294	0.959206
H	-1.350265	-1.848814	-0.789537
C	-3.189168	0.616004	0.505230
H	-2.216188	1.638393	-1.157893
H	-1.566848	2.094456	0.431599
H	-3.530218	-0.898241	-1.007782
H	-3.692549	-1.525966	0.638656
H	-4.124893	1.122023	0.246836
H	-3.079845	0.646115	1.597445
N	-1.017488	0.158903	-0.221611

Cyclopropyl aldehyde - monoester_water

Energy = -498.1692898520 hartrees

Atom	x	y	z
C	-0.366724	-0.130881	0.589094
C	0.870882	0.218721	-0.206697
C	0.521326	1.027821	0.993234
H	0.668549	0.692302	-1.168171
H	1.105322	0.892326	1.902161
H	0.122244	2.027800	0.836893
C	2.045993	-0.730037	-0.189249
H	1.902528	-1.505789	-0.957692
H	2.148651	-1.240256	0.775911
C	3.339284	-0.034417	-0.509052
O	4.389058	-0.266616	0.044549
H	3.288617	0.726232	-1.319079
C	-1.683971	0.177569	-0.014414
O	-1.920386	1.136924	-0.718023
O	-2.598290	-0.739501	0.309523
C	-3.915566	-0.542782	-0.218798
H	-4.495096	-1.402652	0.117967
H	-4.346545	0.383565	0.171706
H	-3.886192	-0.504904	-1.311248
H	-0.338486	-1.031047	1.198464

Cyclopropyl iminium-ion - monoester_water

Energy = -634.7226845850 hartrees

Atom	x	y	z
C	2.188192	0.169030	-0.678850
C	0.893089	0.499469	0.021844
C	1.550441	1.534681	-0.824304
H	2.150216	-0.502176	-1.533536
H	0.984510	0.638650	1.098992
H	1.119754	1.765206	-1.797317
H	2.038975	2.365055	-0.319324
C	-0.376471	-0.181504	-0.426944
H	-0.479130	-1.170030	0.037125
C	-1.573004	0.648642	-0.141896
H	-1.459403	1.727848	-0.022481
C	-3.132528	-1.243432	-0.157301

C	-3.955143	1.025498	0.236295
C	-4.655635	-1.226280	-0.122009
H	-2.702746	-1.767830	0.703620
H	-2.708697	-1.656061	-1.075950
C	-4.984927	0.013281	0.708430
H	-4.246297	1.495466	-0.709256
H	-3.697198	1.797516	0.963276
H	-5.055070	-1.122750	-1.137616
H	-5.054707	-2.149594	0.304812
H	-6.003777	0.376529	0.553256
H	-4.852959	-0.188374	1.778075
N	-2.759712	0.187258	-0.036872
C	3.409489	0.057615	0.155856
O	3.613776	0.685654	1.172551
O	4.270340	-0.823226	-0.354169
C	5.497527	-1.009045	0.362713
H	6.081340	-1.707316	-0.237164
H	6.025801	-0.057335	0.464946
H	5.298265	-1.430054	1.352225
H	-0.359995	-0.352719	-1.515621

Cyclopropyl enamine - monoester_water

Energy = -634.2614137020 hartrees

Atom	x	y	z
C	-1.991530	-0.265234	-0.421471
C	-0.966468	-0.669706	0.641909
C	-1.415500	-1.663085	-0.369733
H	-1.642788	0.396369	-1.210539
H	-1.425585	-0.794099	1.625565
H	-0.746050	-1.934452	-1.183335
H	-2.087482	-2.453181	-0.040800
C	0.386411	-0.059701	0.632759
H	0.478394	0.919714	1.103807
C	1.470783	-0.665264	0.103243
H	1.369972	-1.656955	-0.342343
C	3.085774	1.160220	0.511666
C	3.831671	-0.839987	-0.637157
C	4.500152	1.372977	-0.032489
H	3.047428	1.219081	1.611406
H	2.374294	1.904095	0.122334
C	5.051634	-0.046492	-0.183141
H	3.704510	-0.777433	-1.730815
H	3.884264	-1.900421	-0.362981
H	4.450550	1.859688	-1.015061
H	5.109590	2.006274	0.619805
H	5.882560	-0.112399	-0.892626
H	5.403173	-0.424562	0.785959
N	2.738227	-0.175853	0.060814
C	-3.390434	-0.063368	0.002890
O	-3.972774	-0.723538	0.839698
O	-3.958960	0.961763	-0.642999
C	-5.320568	1.251271	-0.310279
H	-5.590744	2.117230	-0.915598
H	-5.962607	0.400531	-0.557045
H	-5.414747	1.485911	0.753793

Cyclopropyl aldehyde - diester_water

Energy = -725.9325407350 hartrees

Atom	x	y	z
C	0.220402	-0.378028	0.340395
C	-1.105532	-0.946897	-0.130189
C	-0.691750	-1.133215	1.287051
H	-0.985198	-1.814234	-0.779822
H	-1.173076	-0.524124	2.050659
H	-0.358991	-2.117049	1.609432
C	-2.236594	-0.017706	-0.504961
H	-2.071092	0.365950	-1.523583
H	-2.313273	0.845249	0.166819
C	-3.561115	-0.729738	-0.516703
O	-4.584291	-0.257710	-0.080278
H	-3.558891	-1.741420	-0.977447
C	0.318894	1.114130	0.488778
O	0.046432	1.735857	1.488854
O	0.691235	1.672783	-0.658522
C	1.454323	-1.100740	-0.097549
O	1.462264	-2.223432	-0.548035
O	2.547569	-0.378312	0.124380
C	3.801986	-0.976895	-0.230833
H	4.558895	-0.243085	0.044884
H	3.947952	-1.907473	0.323769
H	3.833282	-1.174270	-1.305699
C	0.832798	3.099505	-0.664982
H	1.580934	3.408134	0.070097
H	1.160139	3.352143	-1.673372
H	-0.126814	3.574196	-0.442972

Cyclopropyl iminium-ion - diester_water

Energy = -862.4843681930 hartrees

Atom	x	y	z
C	1.722878	-0.347522	0.212436
C	0.877966	-1.603816	0.046542
C	1.330935	-1.210743	1.405547
H	1.453751	-2.403762	-0.414166
H	0.638595	-0.755105	2.108548
H	2.125336	-1.795680	1.863515
C	-0.553156	-1.572341	-0.457010
H	-0.856880	-2.616823	-0.638209
C	-1.582571	-1.063620	0.475836
H	-1.452167	-1.211095	1.547764
C	-3.097484	-0.272306	-1.290470
C	-3.768258	-0.151160	1.058700
C	-4.393775	0.513204	-1.146755
H	-3.248700	-1.239256	-1.782582
H	-2.302117	0.269211	-1.809017
C	-4.986079	-0.008158	0.161150
H	-3.482688	0.802822	1.514141
H	-3.857402	-0.911762	1.836506
H	-4.177966	1.585376	-1.068839
H	-5.048861	0.361933	-2.008056
H	-5.727715	0.666575	0.595773
H	-5.460210	-0.985199	0.009519
N	-2.690767	-0.539422	0.110905
C	3.159095	-0.460996	-0.218223
O	3.633952	-1.439774	-0.746796
O	3.857157	0.611224	0.126580
C	5.252436	0.605214	-0.206832

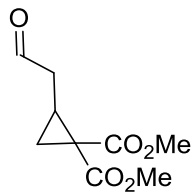
H	5.638640	1.560039	0.149349
H	5.756207	-0.224692	0.296087
H	5.381207	0.517830	-1.288912
C	1.070613	0.978847	-0.009406
O	1.440870	1.797088	-0.814547
O	-0.021791	1.129437	0.747794
C	-0.761299	2.348169	0.571063
H	-1.551938	2.318343	1.320348
H	-0.109675	3.208261	0.743818
H	-1.179652	2.396656	-0.438375
H	-0.611704	-1.080146	-1.433260

Cyclopropyl enamine - diester_water

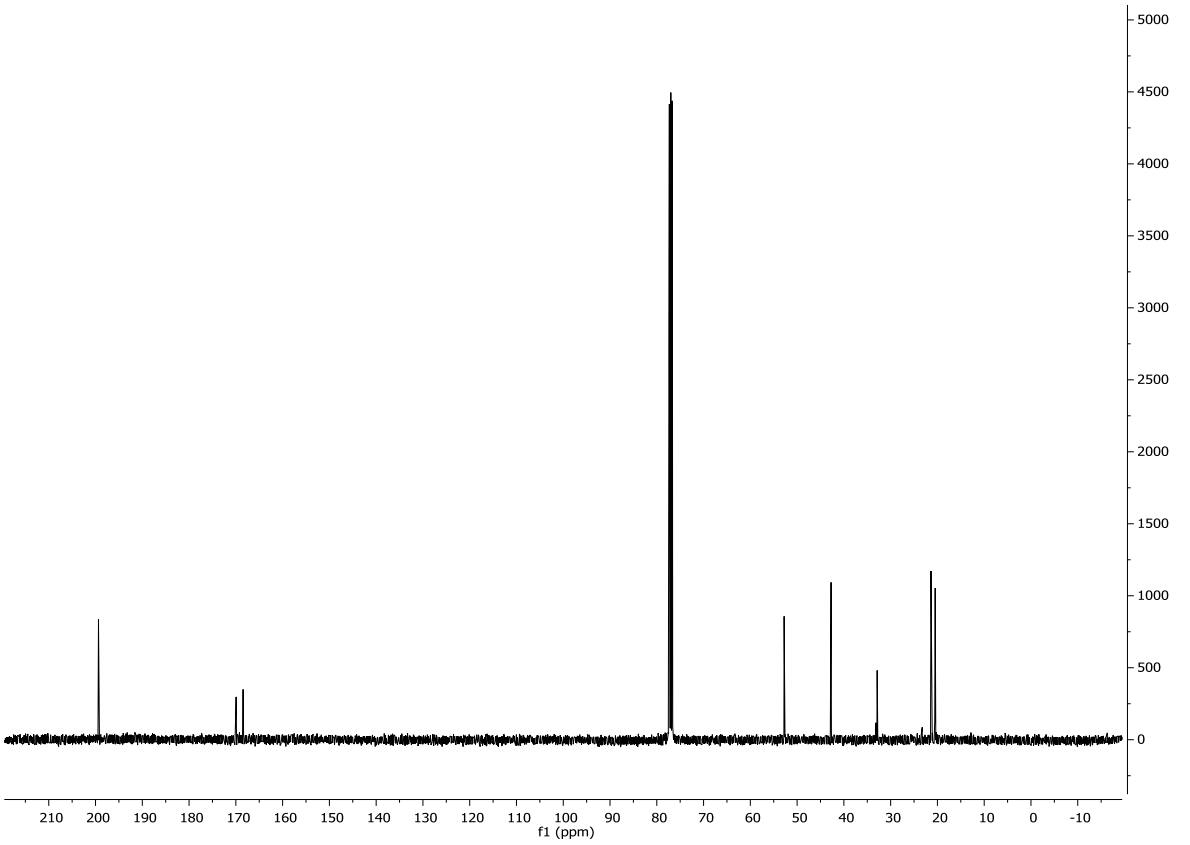
Energy = -862.0274934090 hartrees

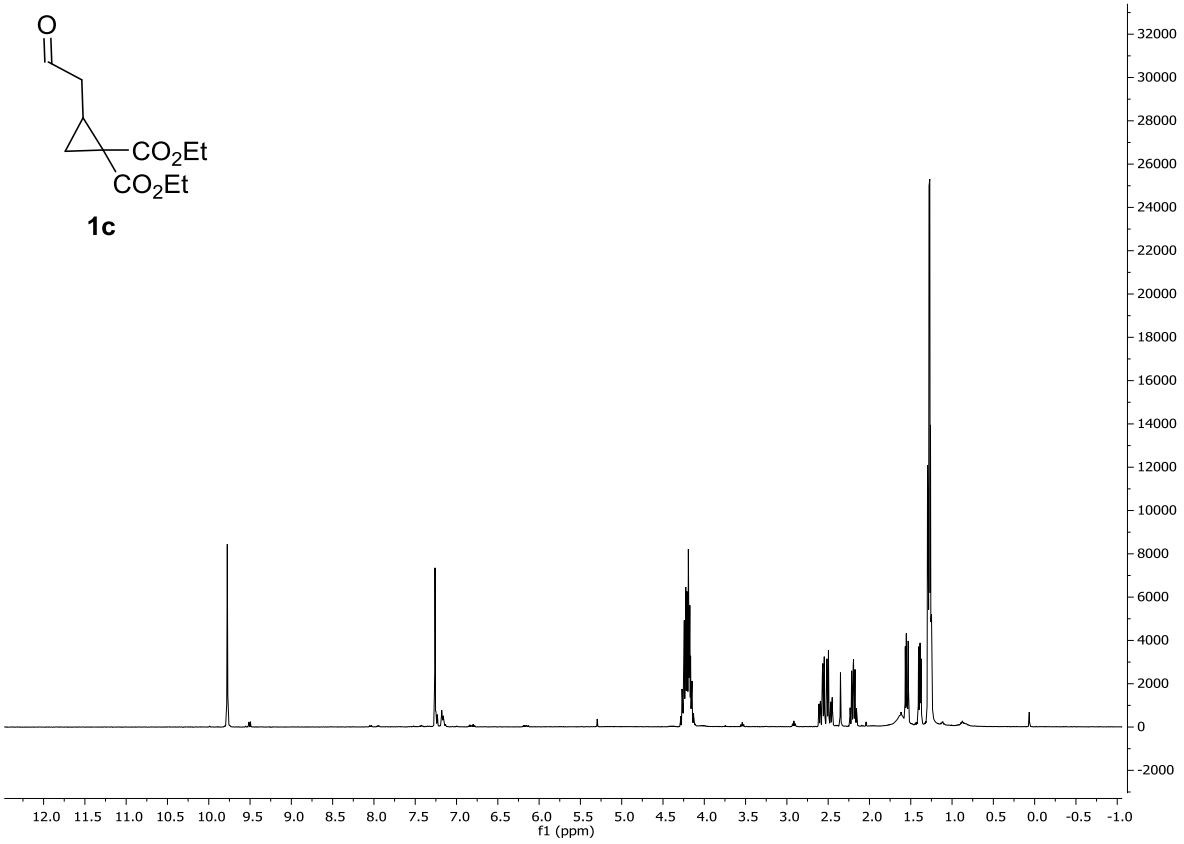
Atom	x	y	z
C	1.784676	-0.328347	0.337706
C	0.803899	-1.537002	0.193770
C	1.295792	-1.133253	1.530403
H	1.321610	-2.391453	-0.242736
H	0.634399	-0.605598	2.211738
H	2.040611	-1.767136	2.006043
C	-0.573510	-1.310088	-0.300204
H	-0.720098	-1.446365	-1.371227
C	-1.591883	-0.883217	0.479327
H	-1.438292	-0.759514	1.552345
C	-3.239227	-0.526258	-1.325132
C	-3.868167	-0.036421	0.967144
C	-4.581975	0.205850	-1.302014
H	-3.329237	-1.546382	-1.731346
H	-2.483604	0.000184	-1.926890
C	-5.122765	-0.072903	0.101845
H	-3.629810	0.994538	1.275947
H	-3.953232	-0.650770	1.871059
H	-4.420294	1.283449	-1.434198
H	-5.255039	-0.128557	-2.097542
H	-5.876251	0.651855	0.425576
H	-5.575489	-1.072202	0.143328
N	-2.844352	-0.565034	0.072677
C	3.192197	-0.569380	-0.079337
O	3.705212	-1.668205	-0.108909
O	3.846109	0.552753	-0.368878
C	5.217743	0.412035	-0.758807
H	5.569461	1.426294	-0.948510
H	5.796231	-0.049030	0.046477
H	5.294457	-0.194755	-1.665268
C	1.156652	0.989393	0.016679
O	1.233965	1.533101	-1.061457
O	0.419541	1.459556	1.023336
C	-0.432958	2.569662	0.723505
H	-0.961120	2.788585	1.651840
H	0.156873	3.433533	0.404738
H	-1.142187	2.290484	-0.062163

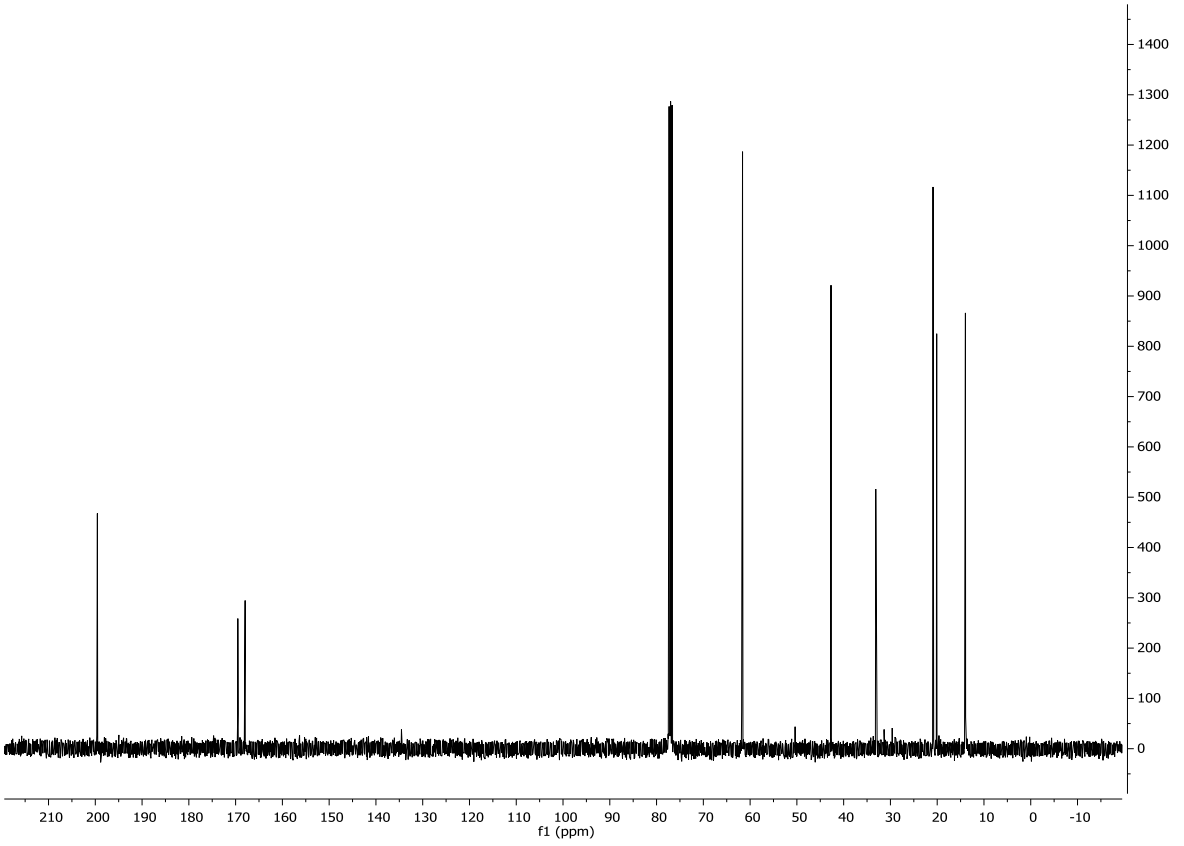
7. NMR spectra of novel compounds

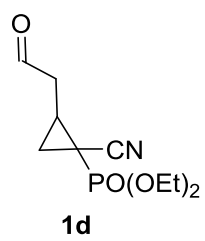


1a




O
CO2Et
CO2Et
1c
f1 (ppm)


f1 (ppm)


O
CN
PO(OEt)2

1d

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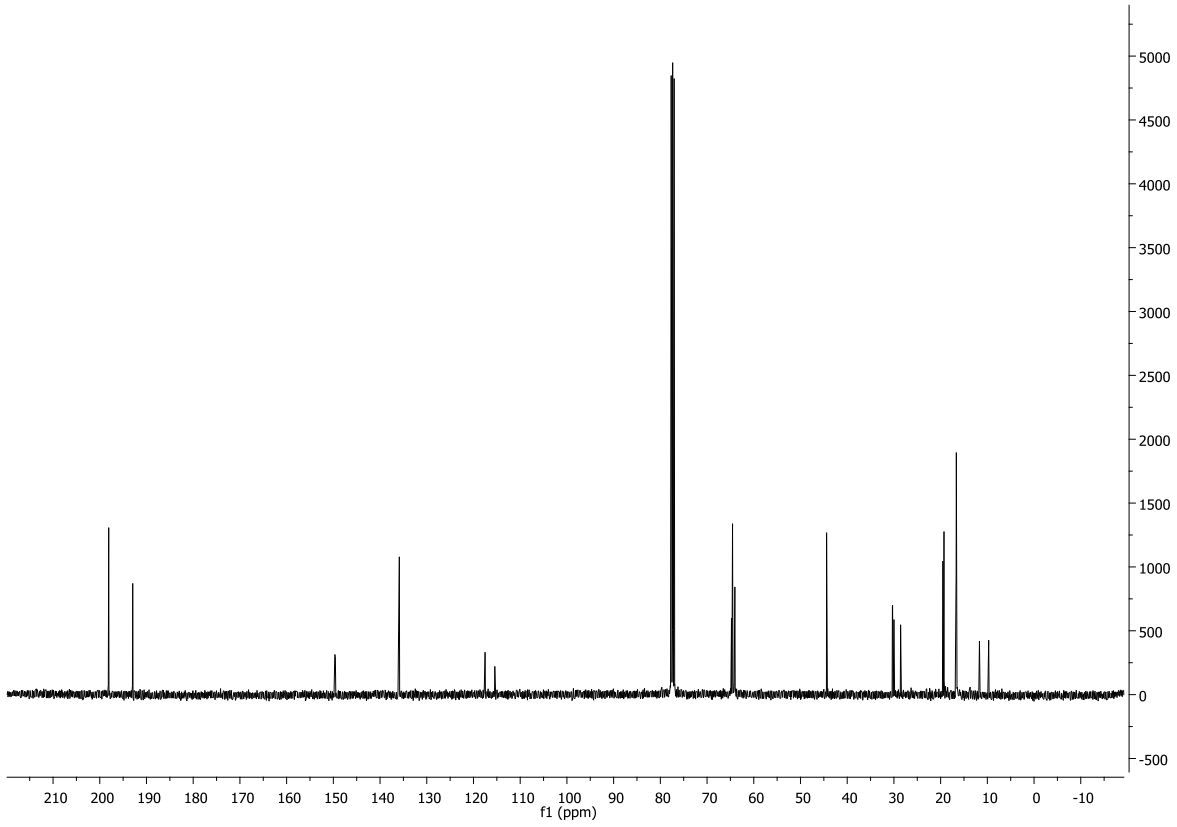
4000
3500
3000
2500
2000
1500
1000
500
0
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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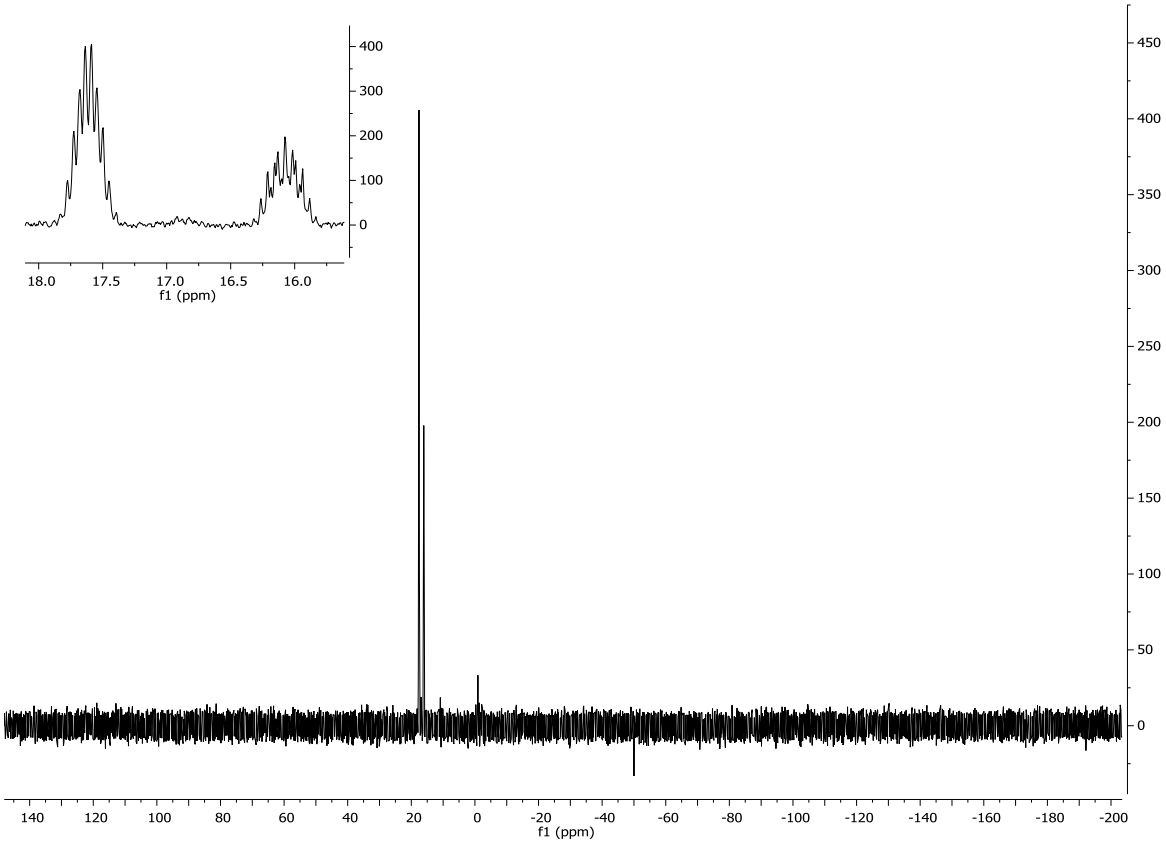
-500
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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17.5
17.0
16.5
16.0
f1 (ppm)
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300
200
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300
250
200
150
100
50
0
140
120
100
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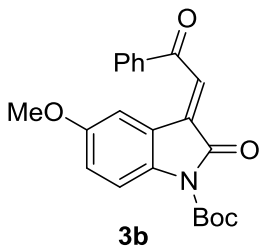
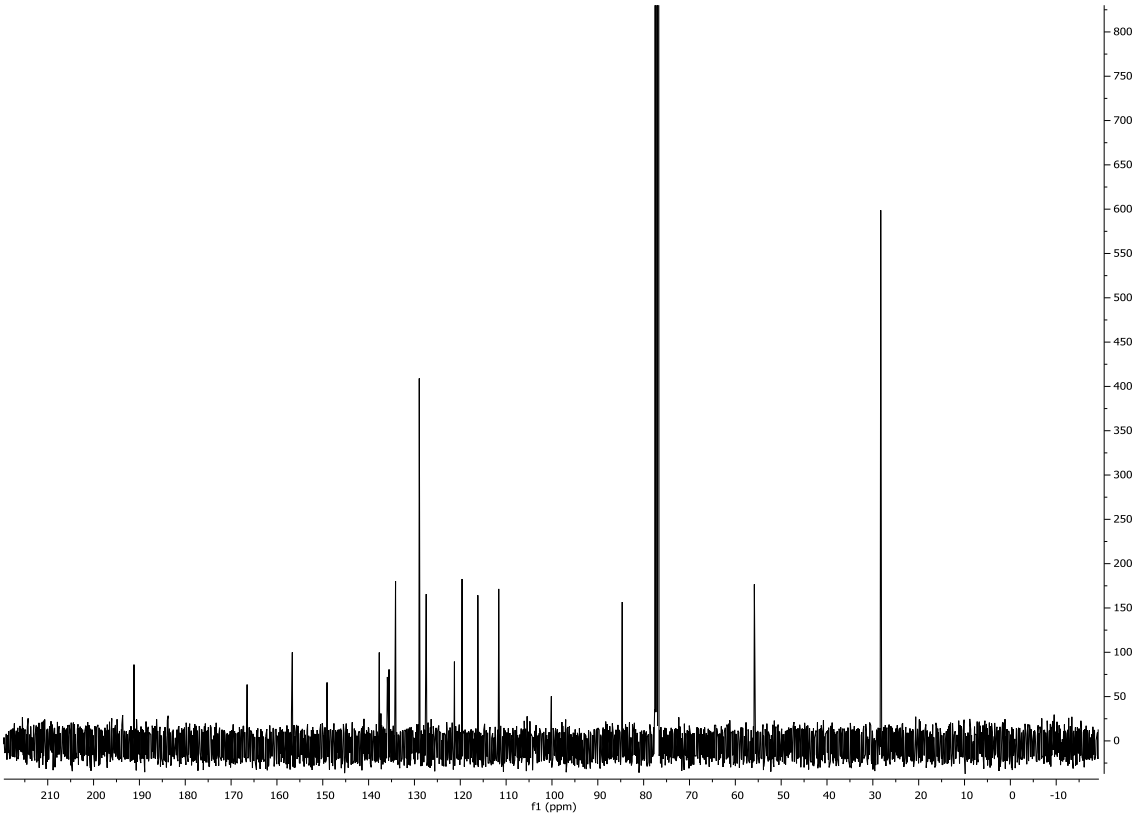
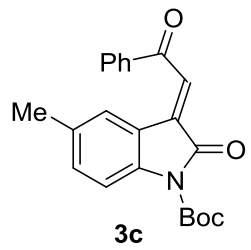
-180
-200
f1 (ppm)



3b





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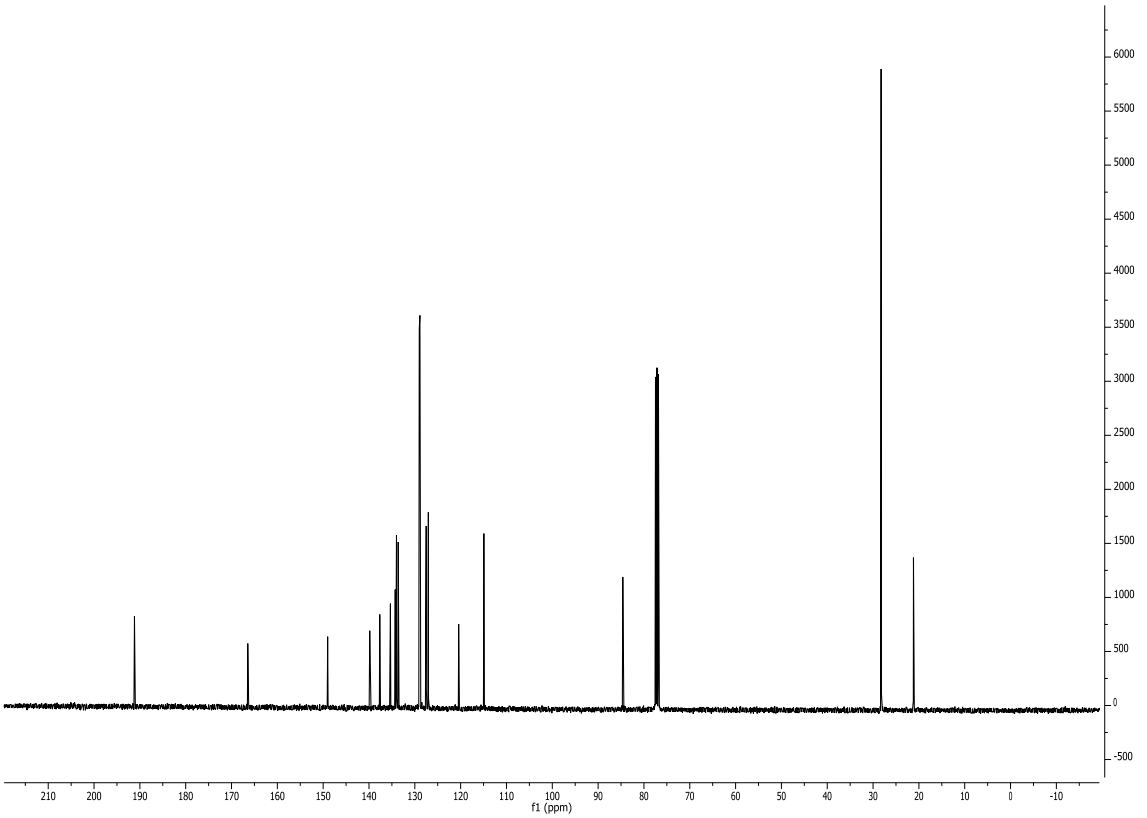
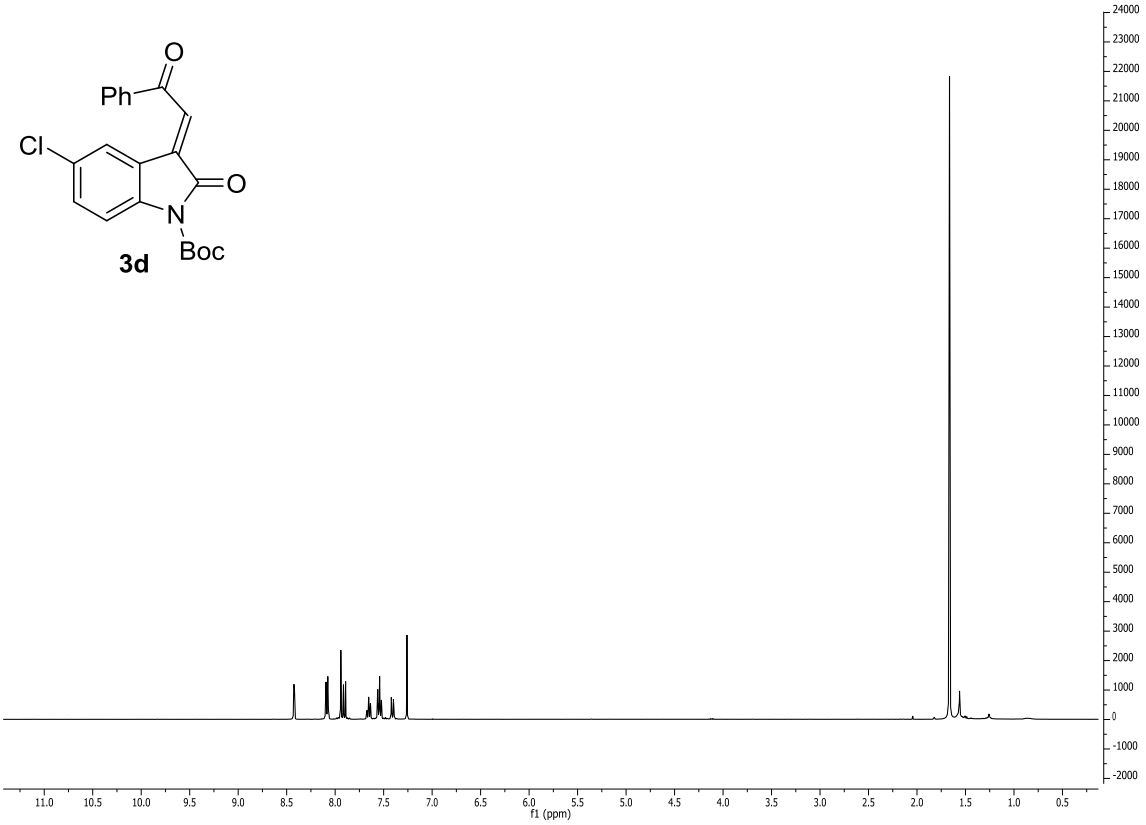
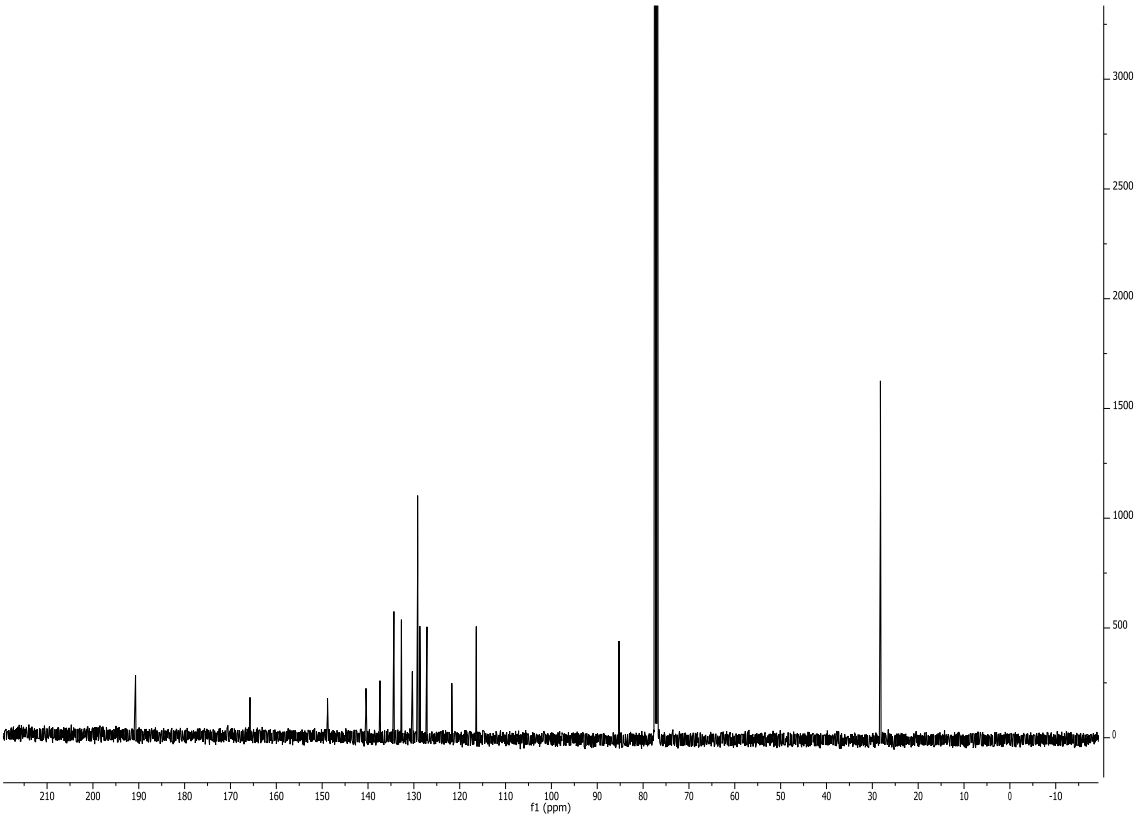
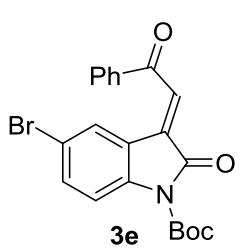



O
Ph
Cl
O
N
Boc
3d
f1 (ppm)


f1 (ppm)



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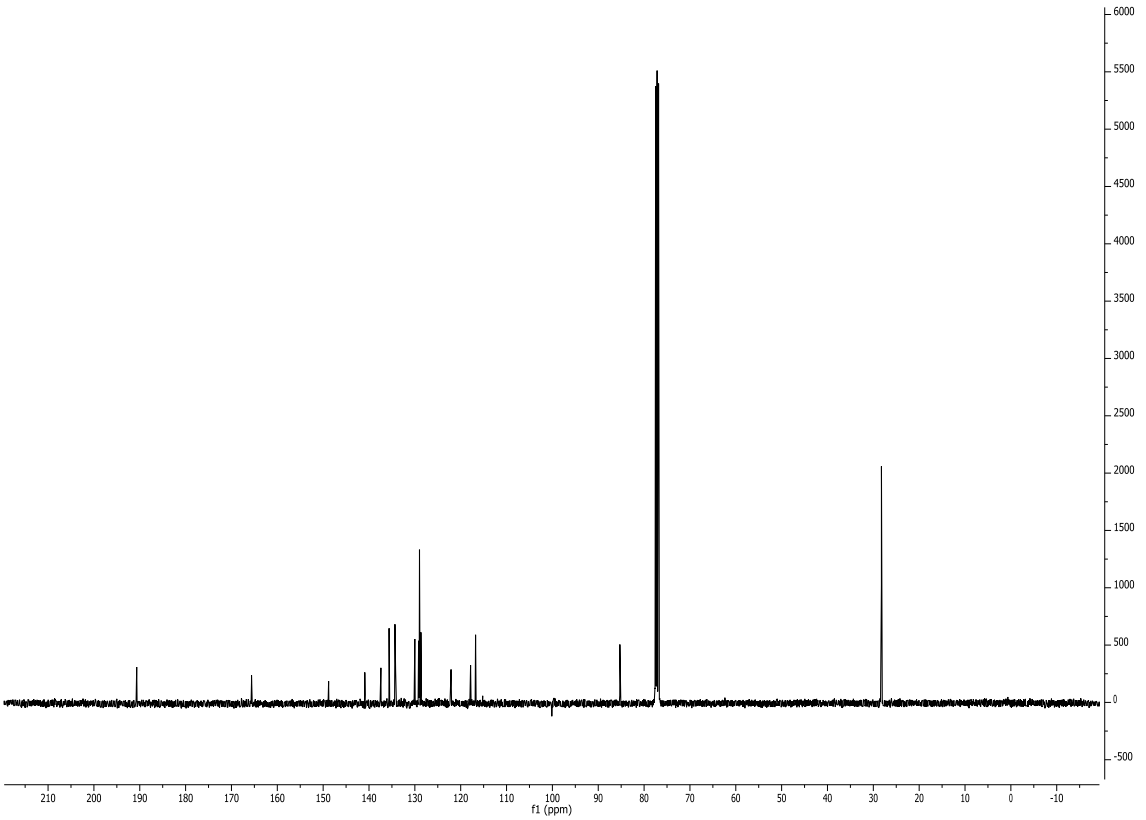

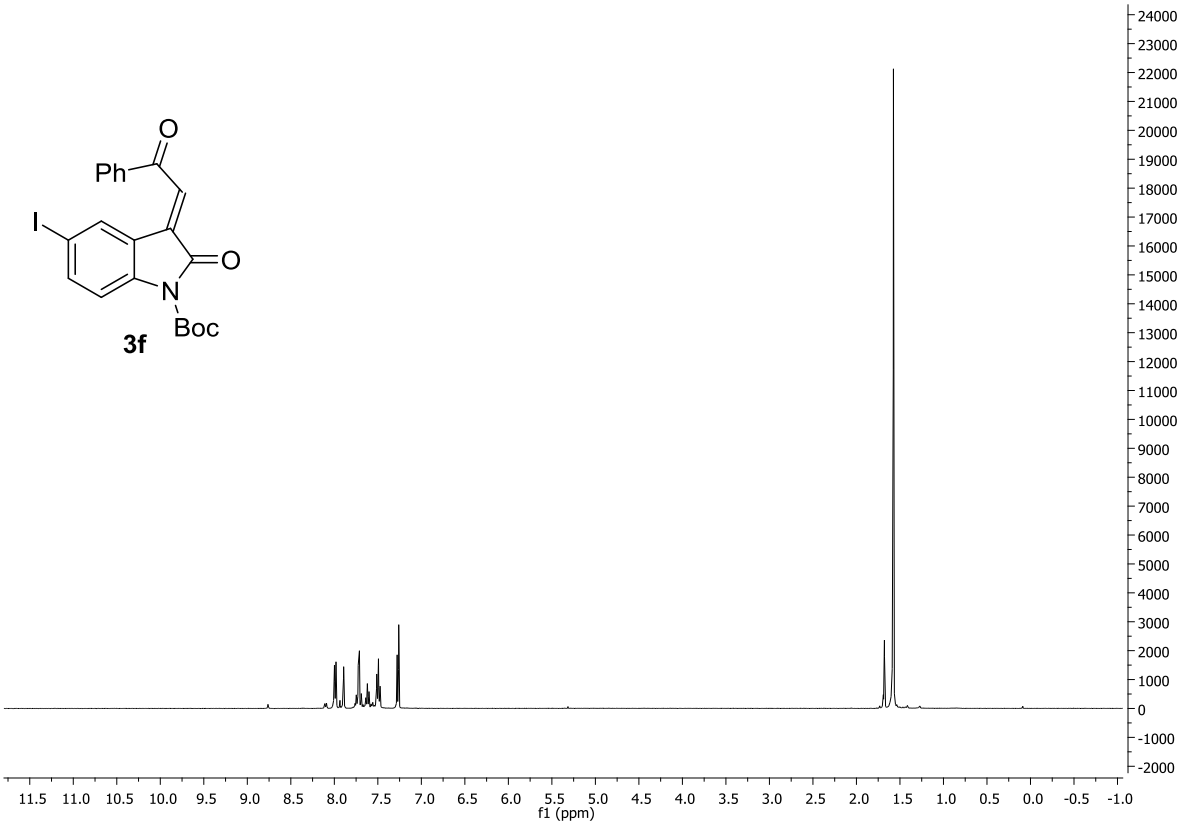
O
Ph
I
O
N
Boc
3f
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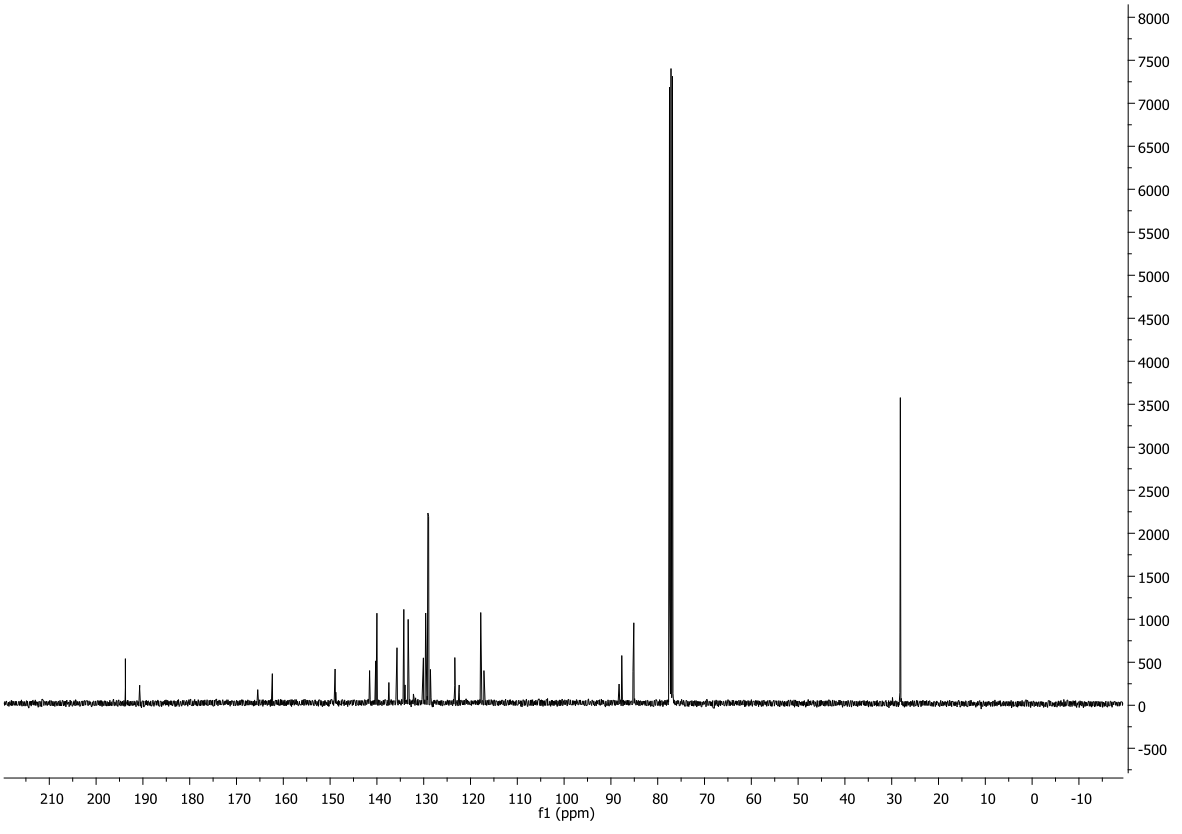
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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6000
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4000
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3000
2500
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1500
1000
500
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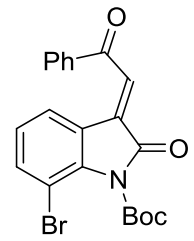
-500
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
Ph
O
N
Br
Boc

3g

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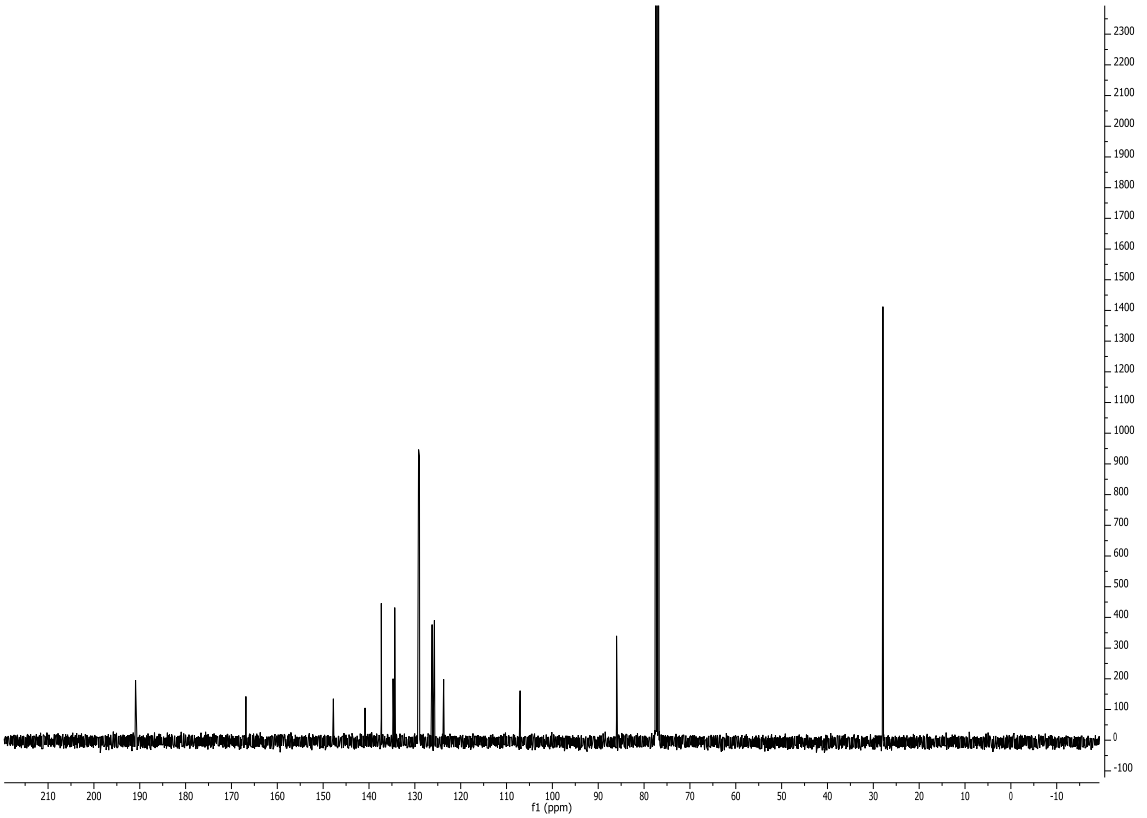
40000
35000
30000
25000
20000
15000
10000
5000
0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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1800
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1600
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1300
1200
1100
1000
900
800
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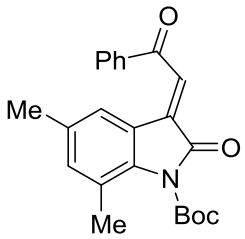
400
300
200
100
0
-100
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
Ph
Me
O
N
Boc
Me

3h

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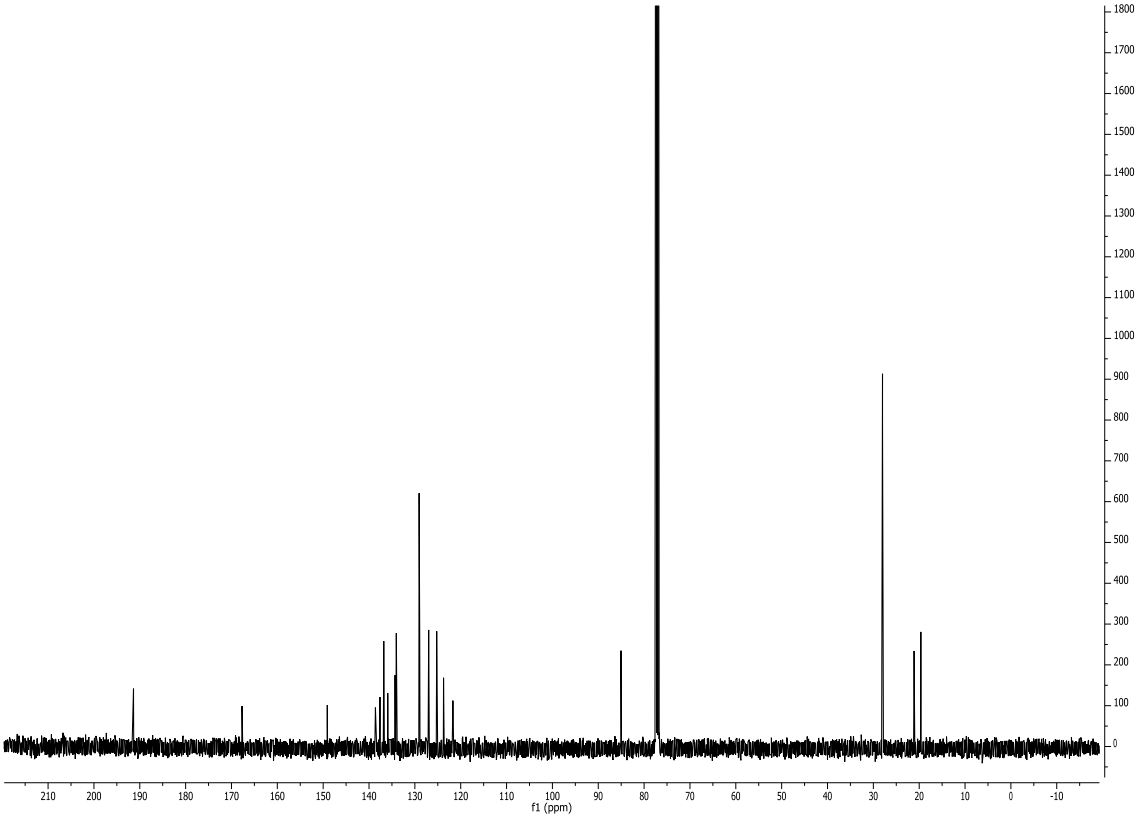
20000
15000
10000
5000
0
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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1500
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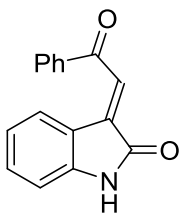
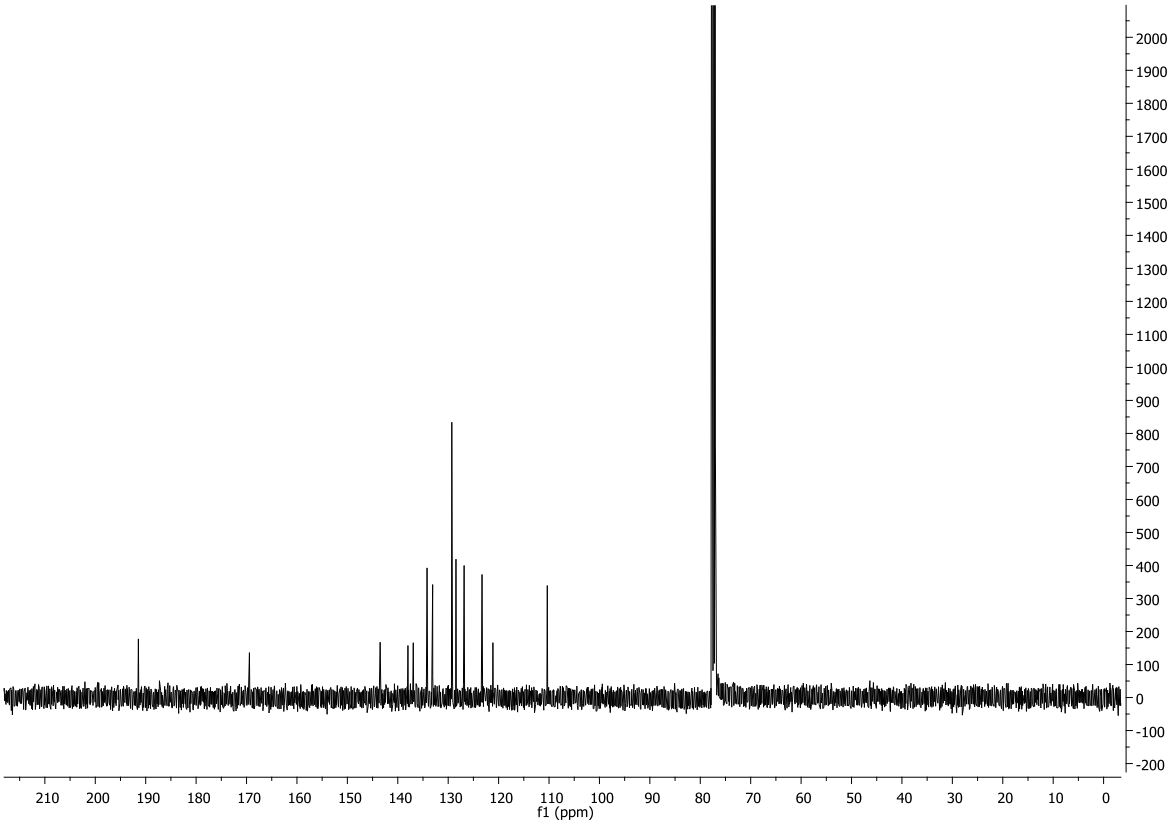
1100
1000
900
800
700
600
500
400
300
200
100
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
Ph
O
N
H

3i

9000
8000
7000
6000
5000
4000
3000
2000
1000
0
11.5 11.0 10.5 10.0 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 0.0
f1 (ppm)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500
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200
100
0
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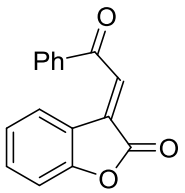
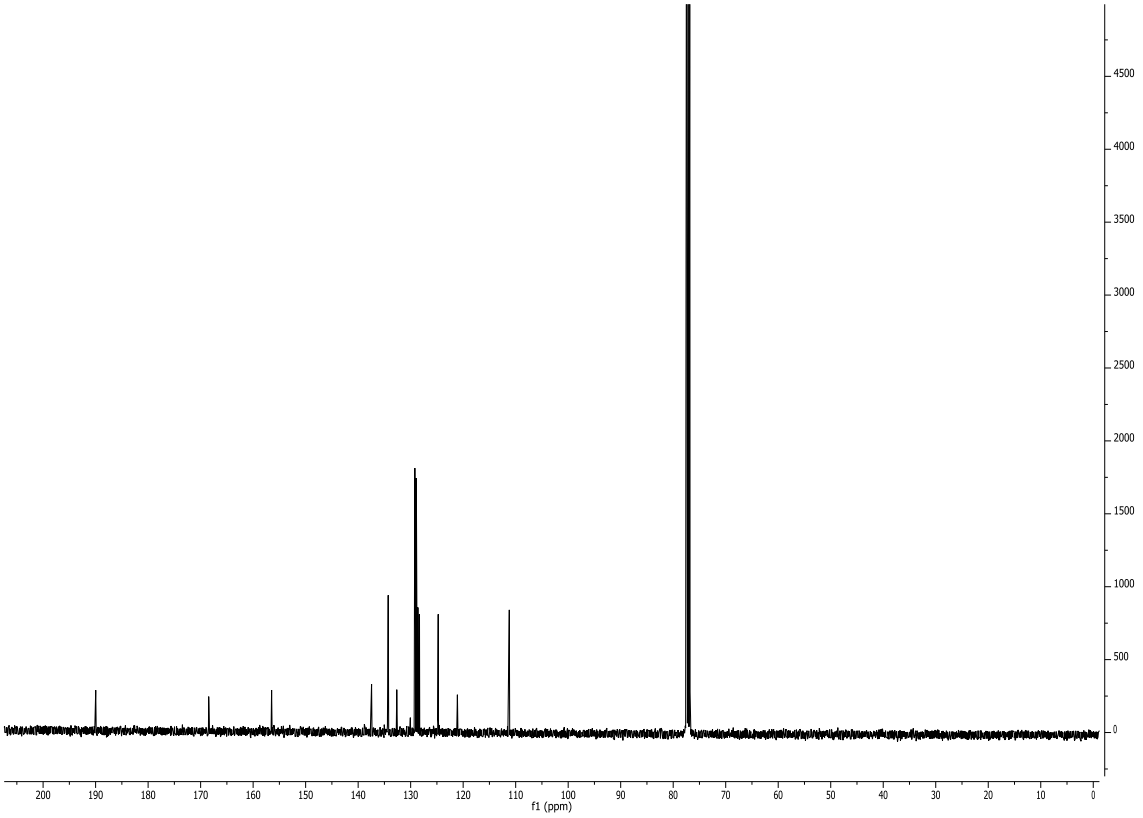
-200
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
Ph
O
O

3j

9000
8000
7000
6000
5000
4000
3000
2000
1000
0
11.0 10.5 10.0 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 0.0 -0.5
f1 (ppm)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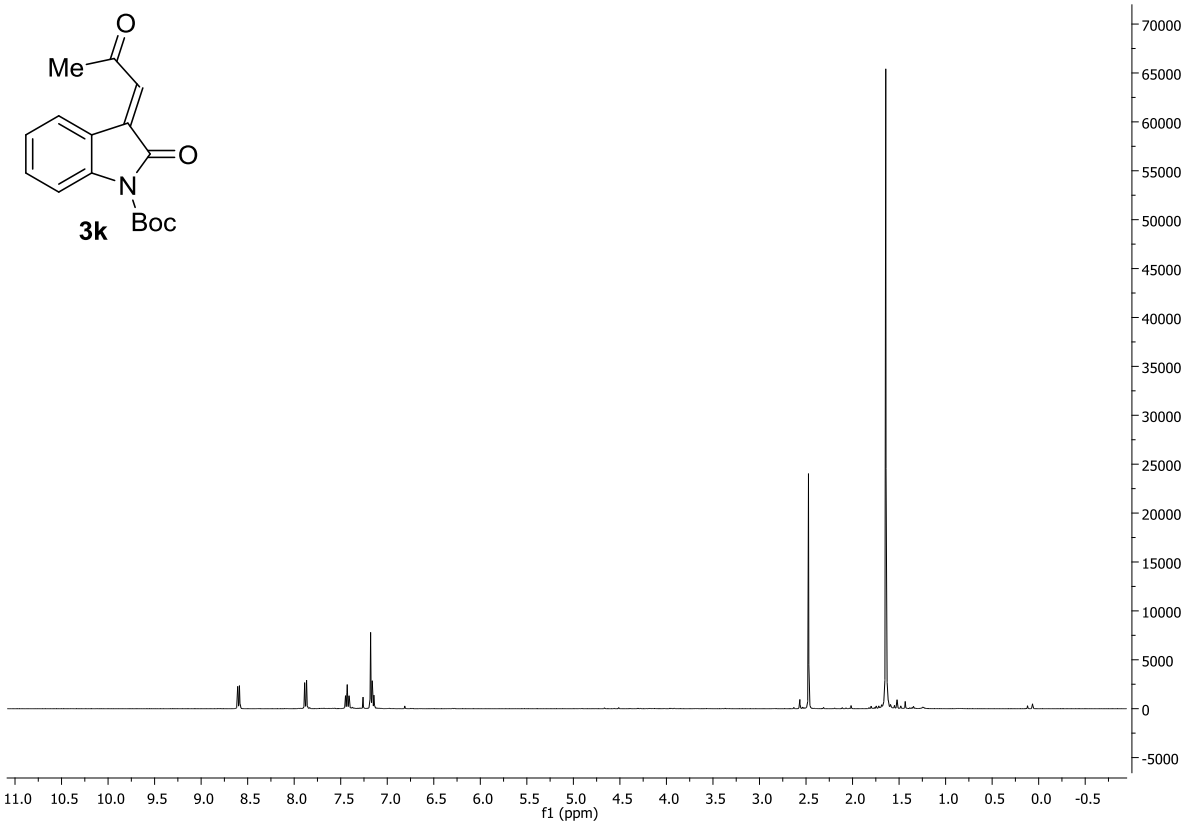
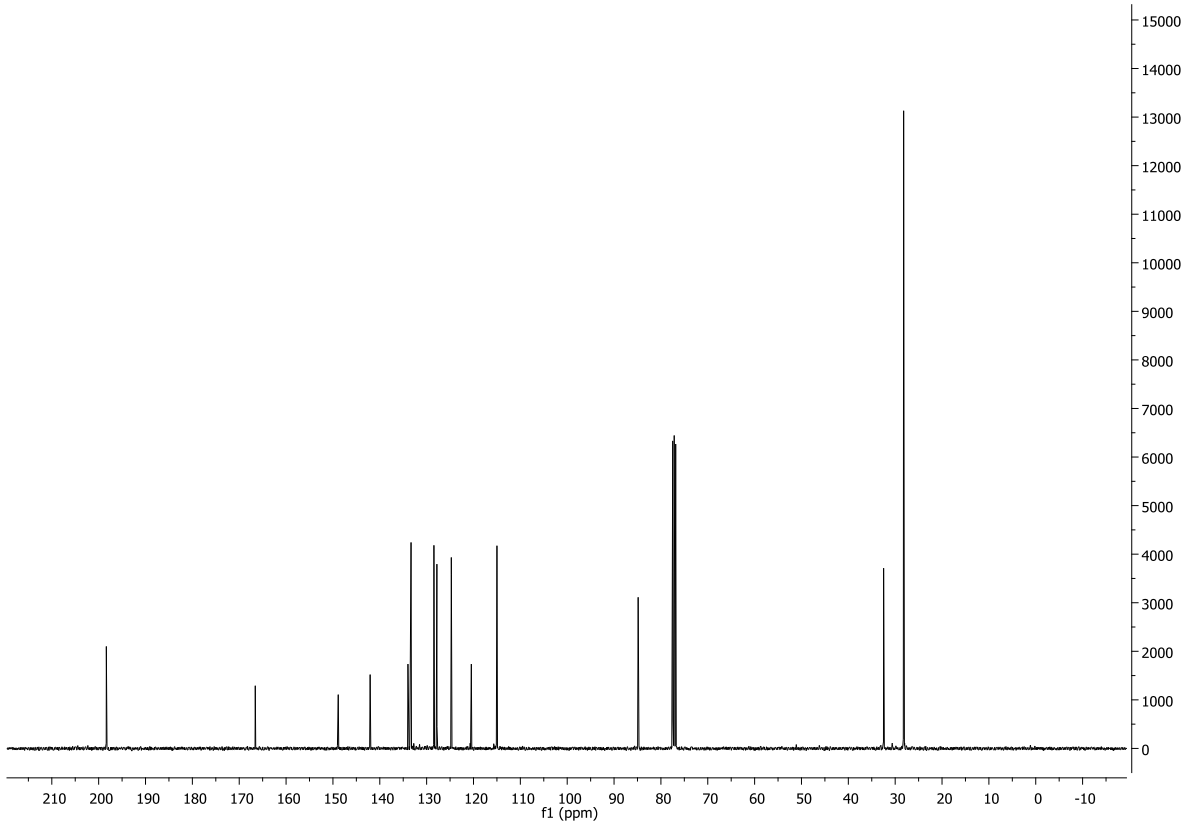
2500
2000
1500
1000
500
0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
Me
O
N
Boc
3k
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
11.0 10.5 10.0 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 0.0 -0.5
f1 (ppm)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13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
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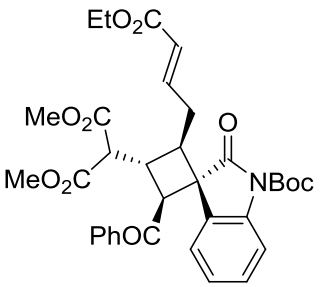
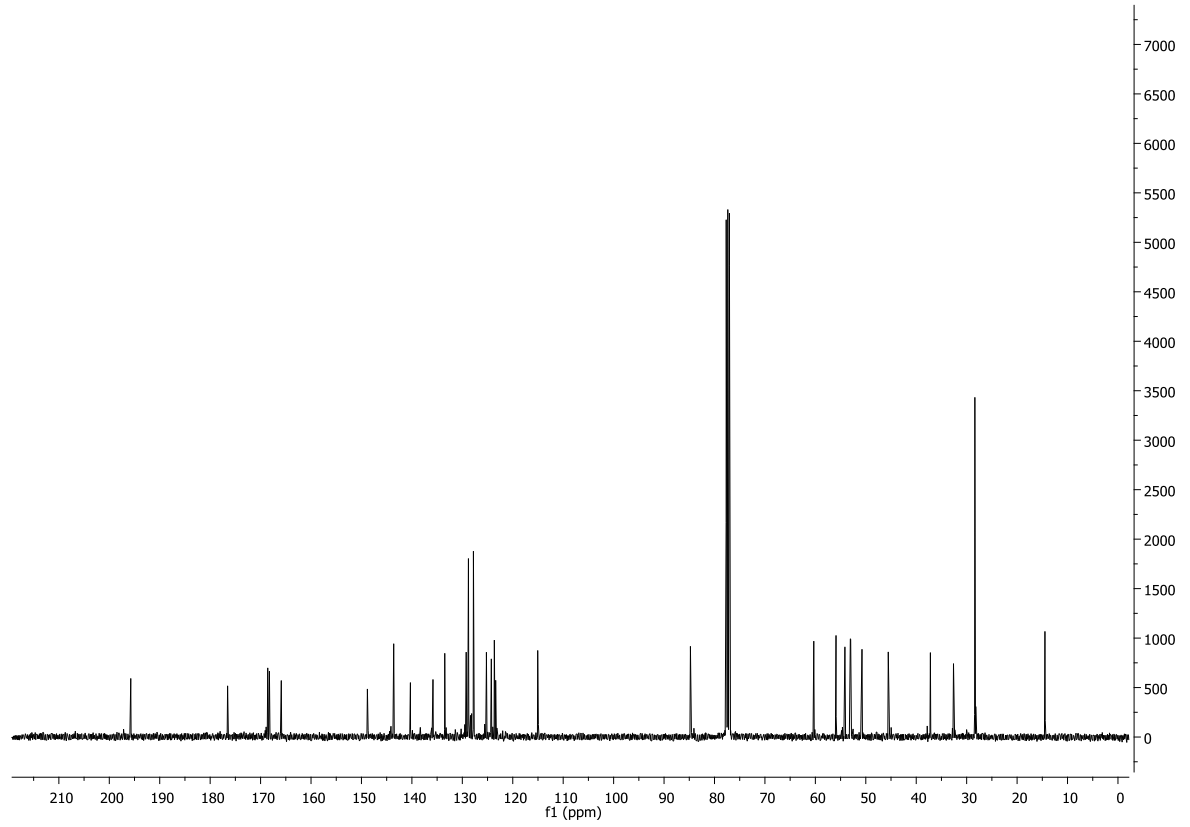
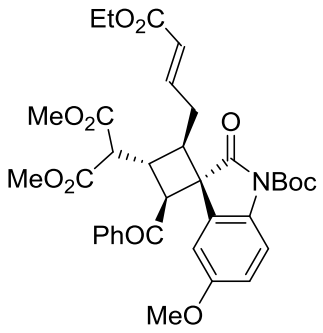
f1 (ppm)

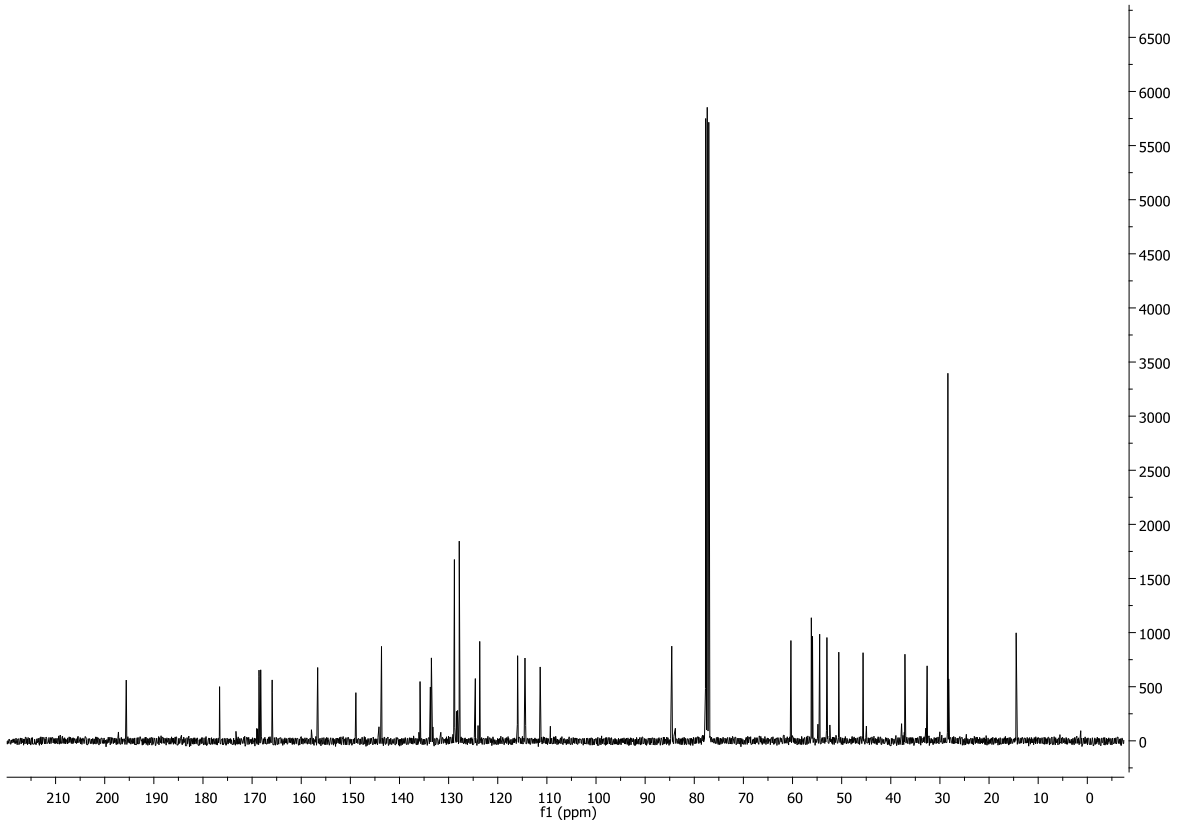


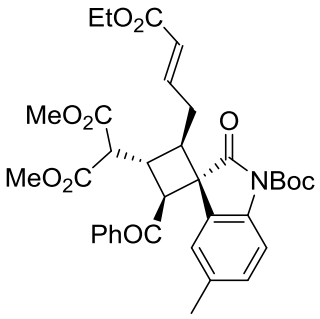
5a





5b




EtO2C
MeO2C
MeO2C
O
NBoc
PhOC

5c

28000
26000
24000
22000
20000
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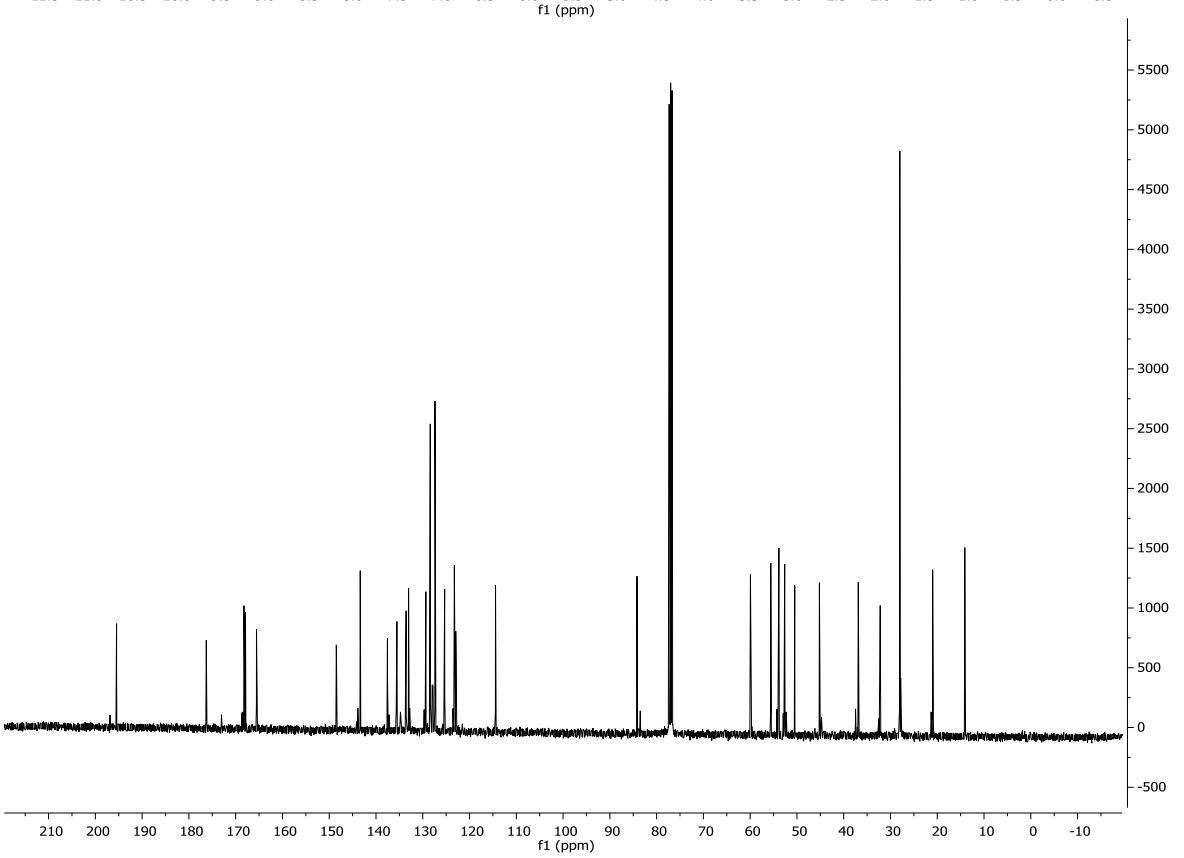
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


5500
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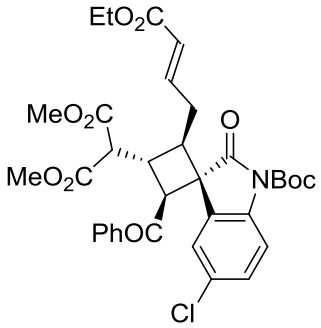
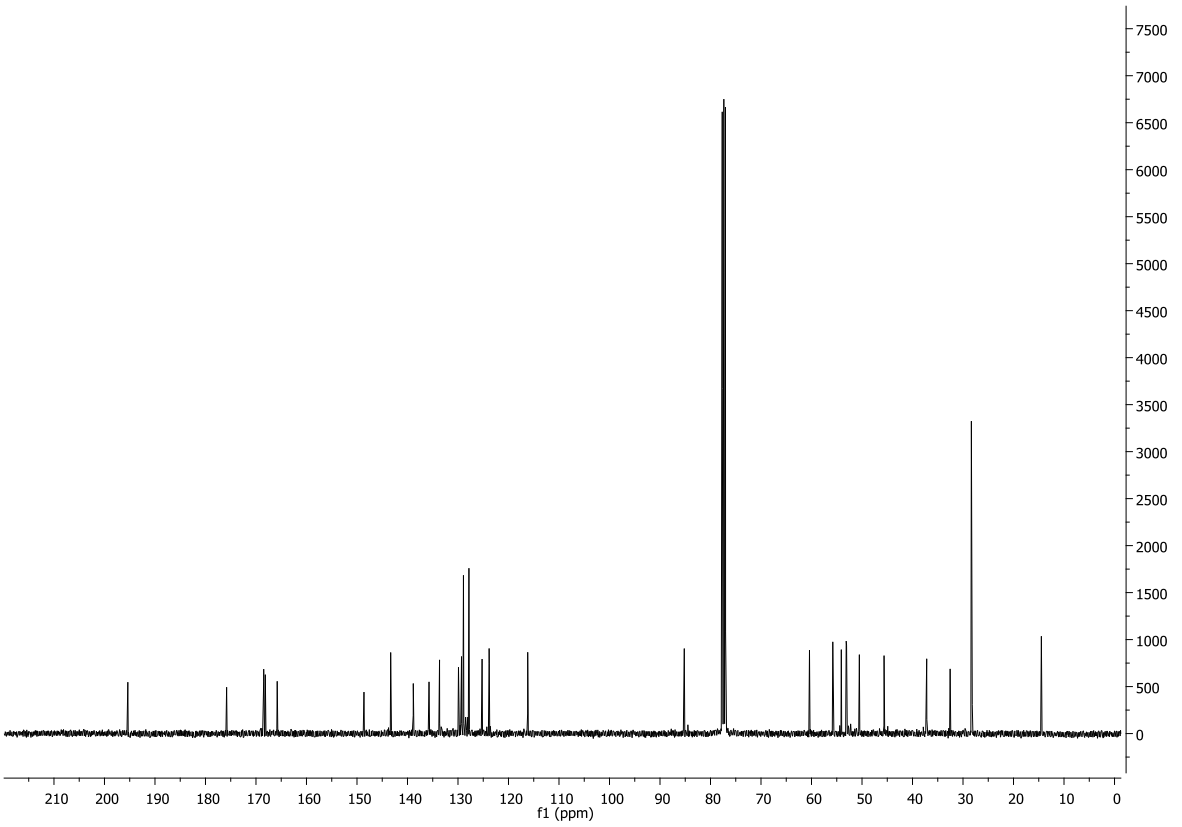
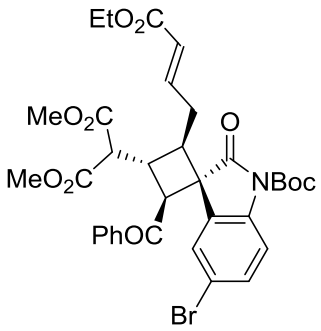
f1 (ppm)

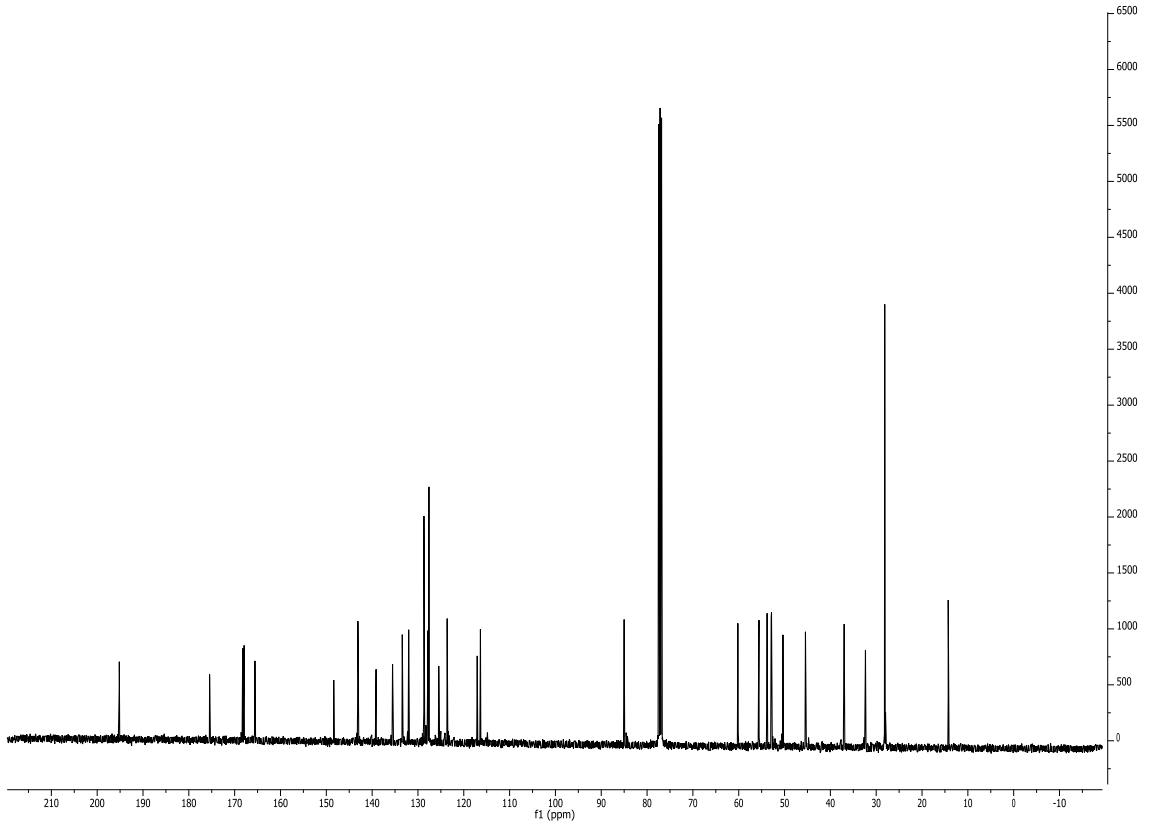


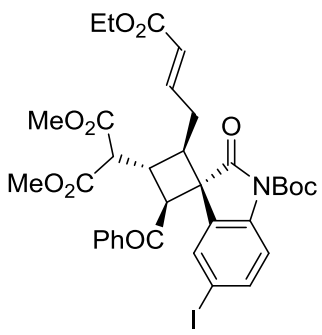
5d



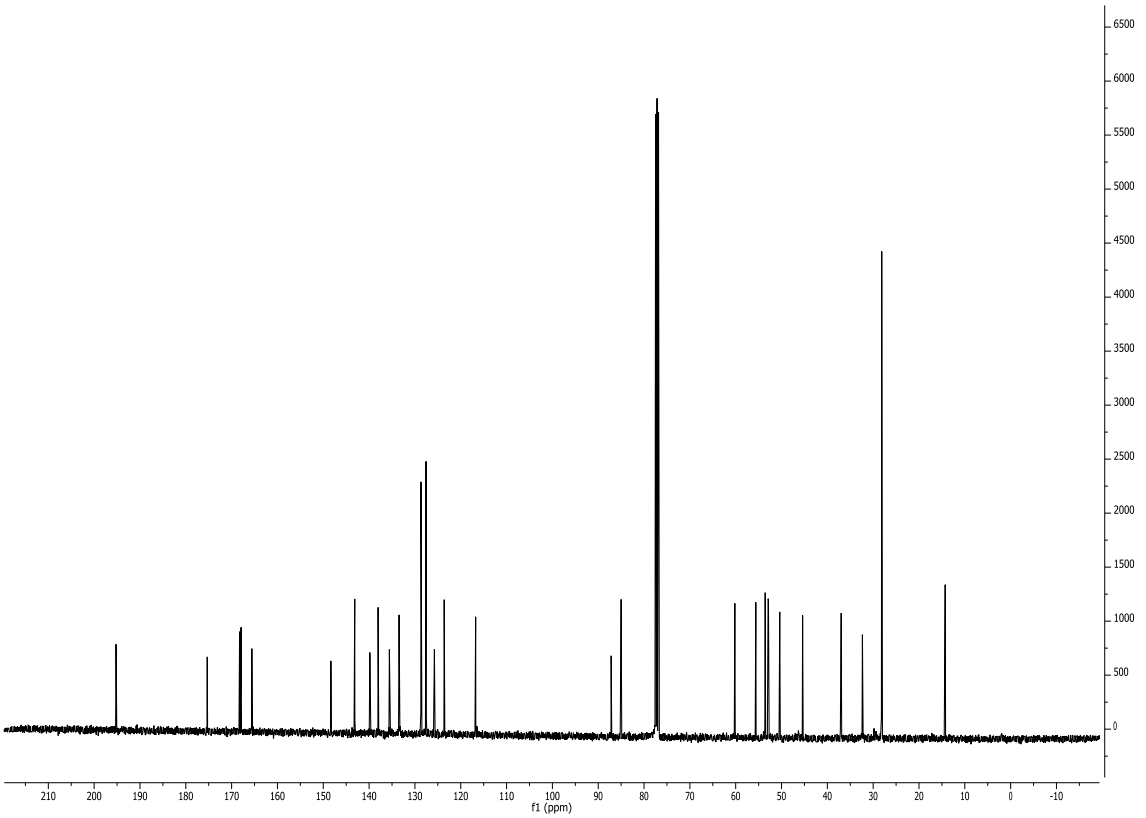


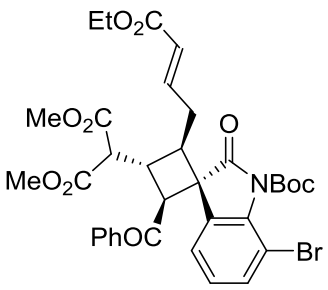
5e



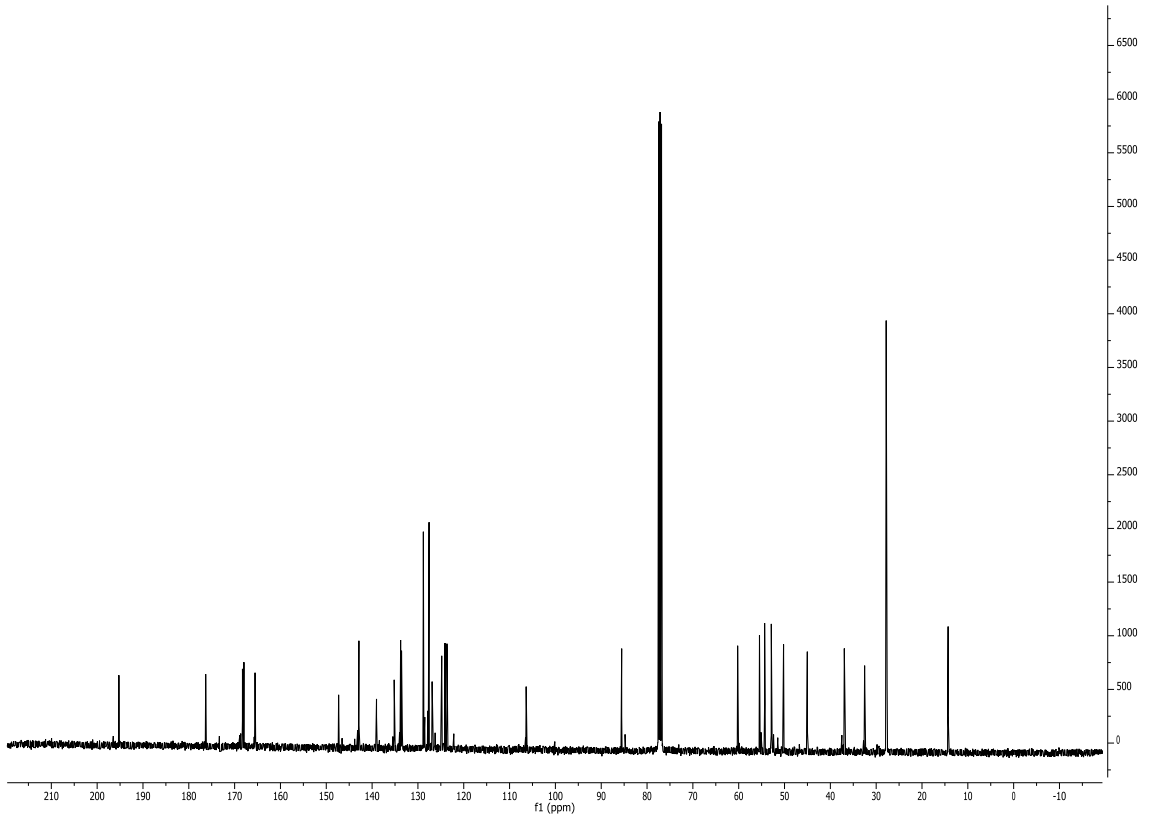


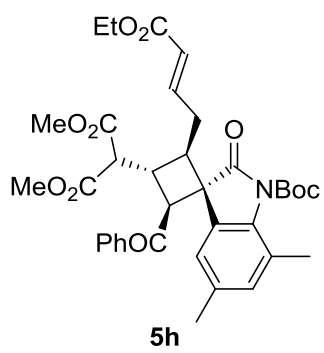
5f



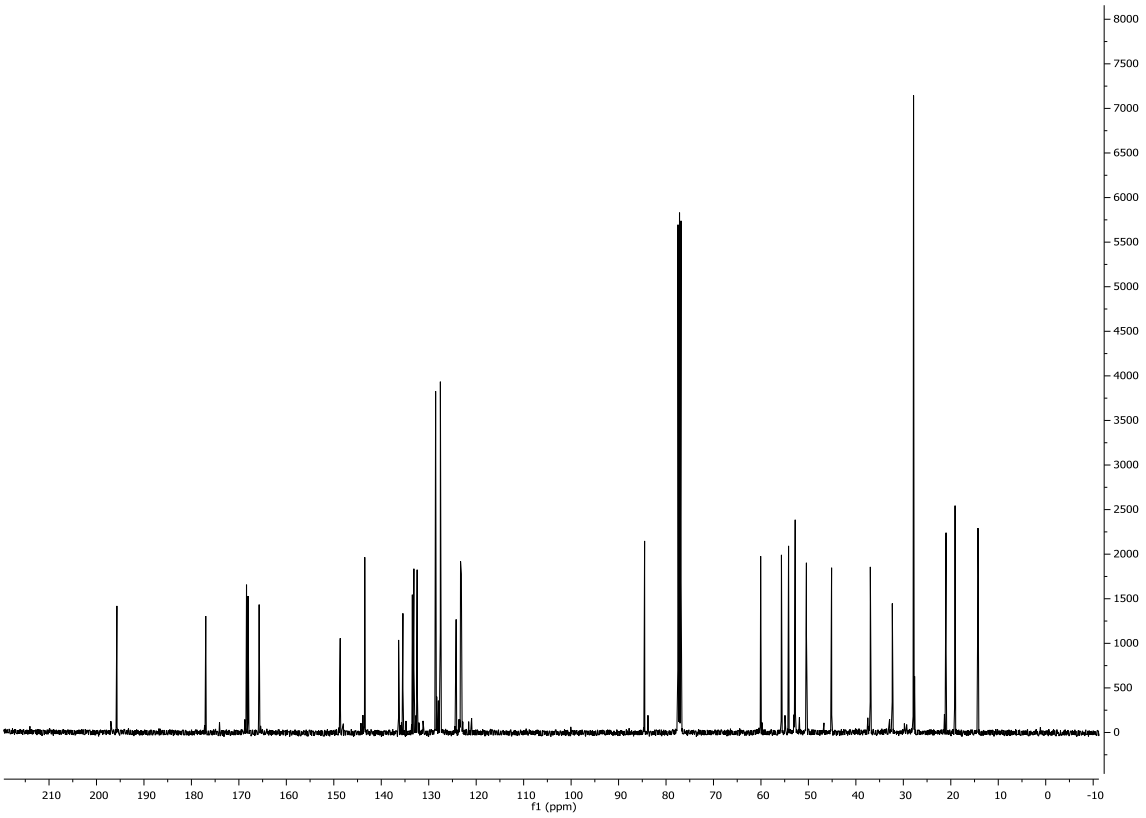


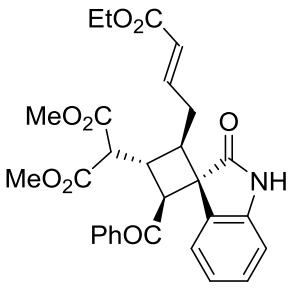
5g





5h




EtO2C
MeO2C
MeO2C
O
NH
PhOC

5i

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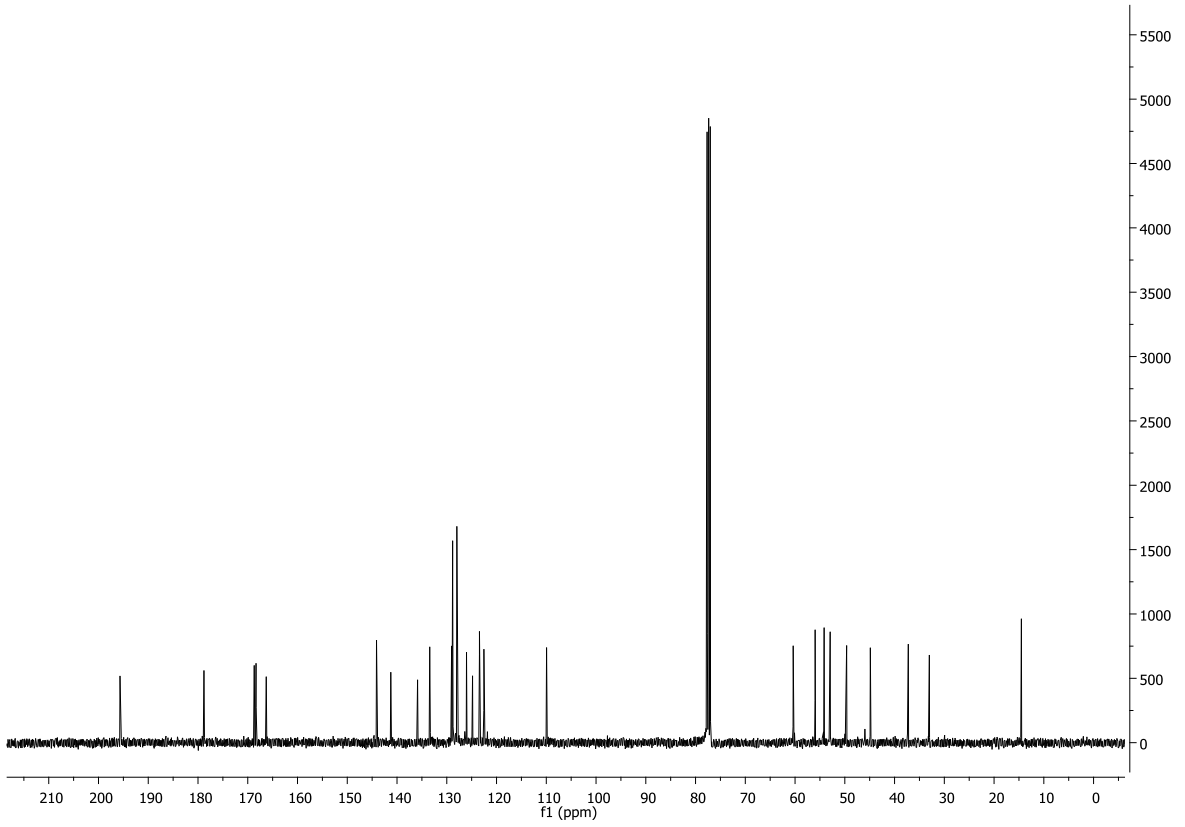
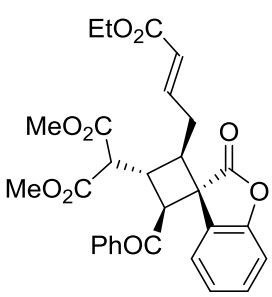
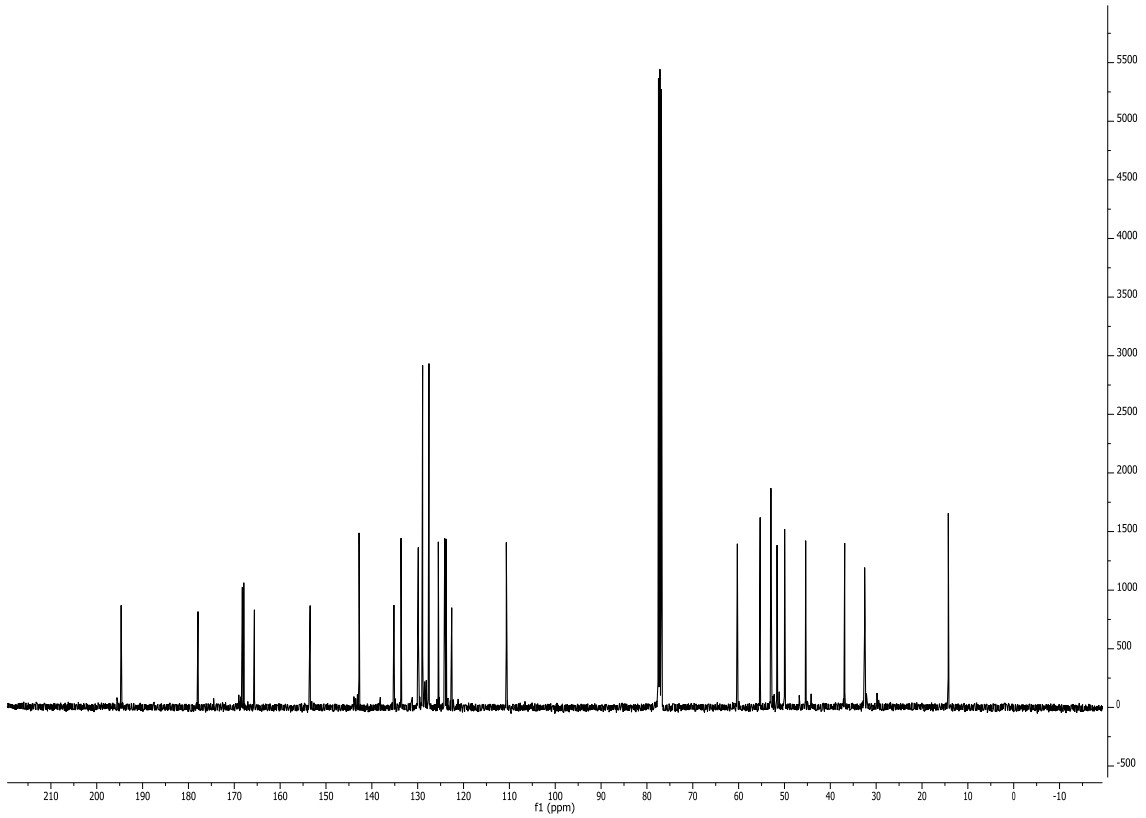
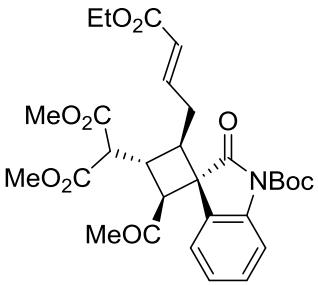
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



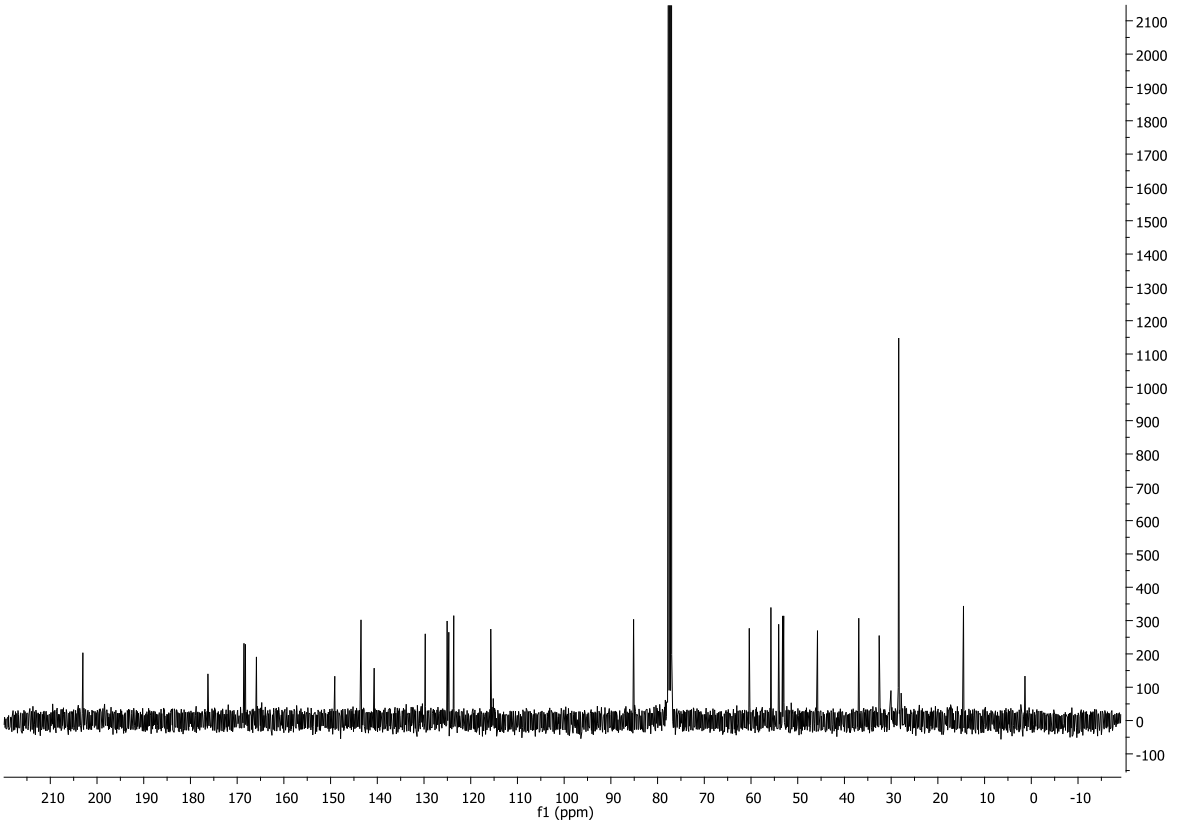
5j

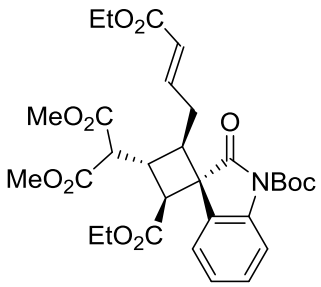



EtO2C
MeO2C
MeO2C
O
NBoc
MeOC

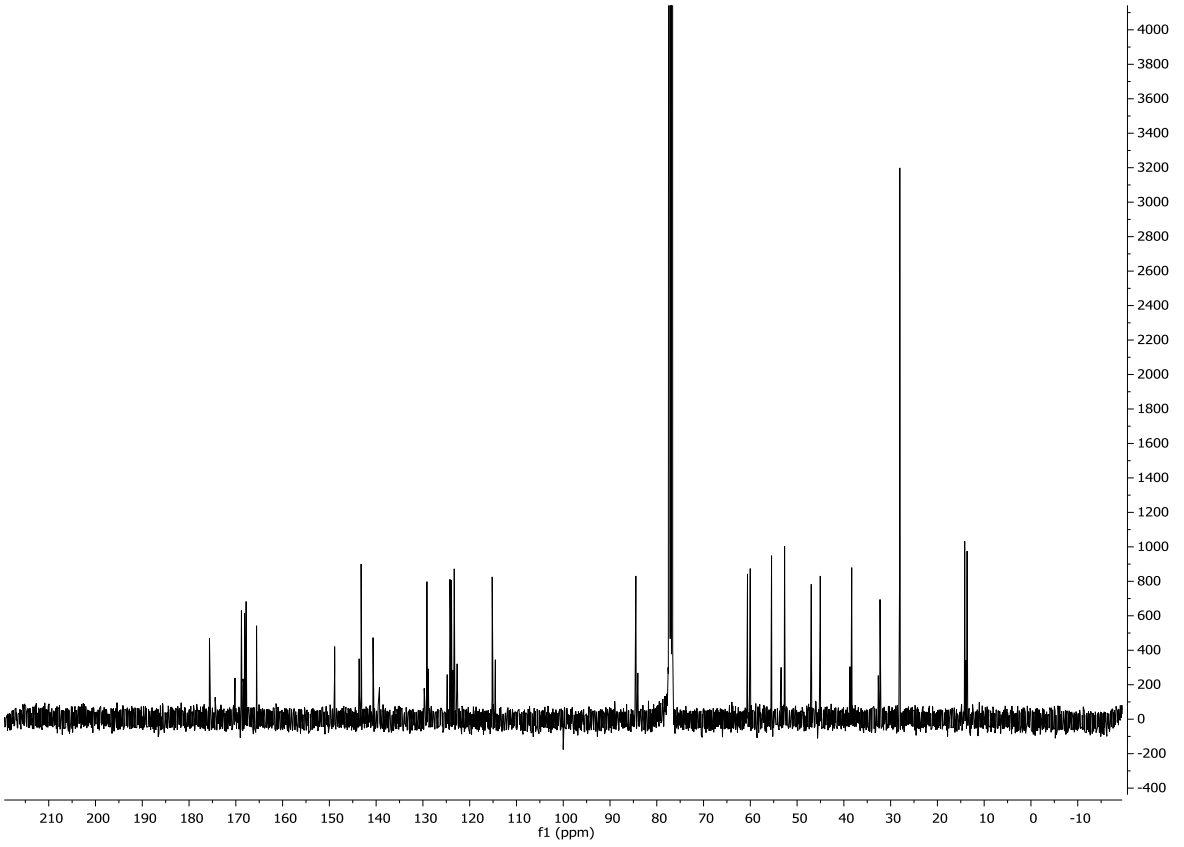
5k

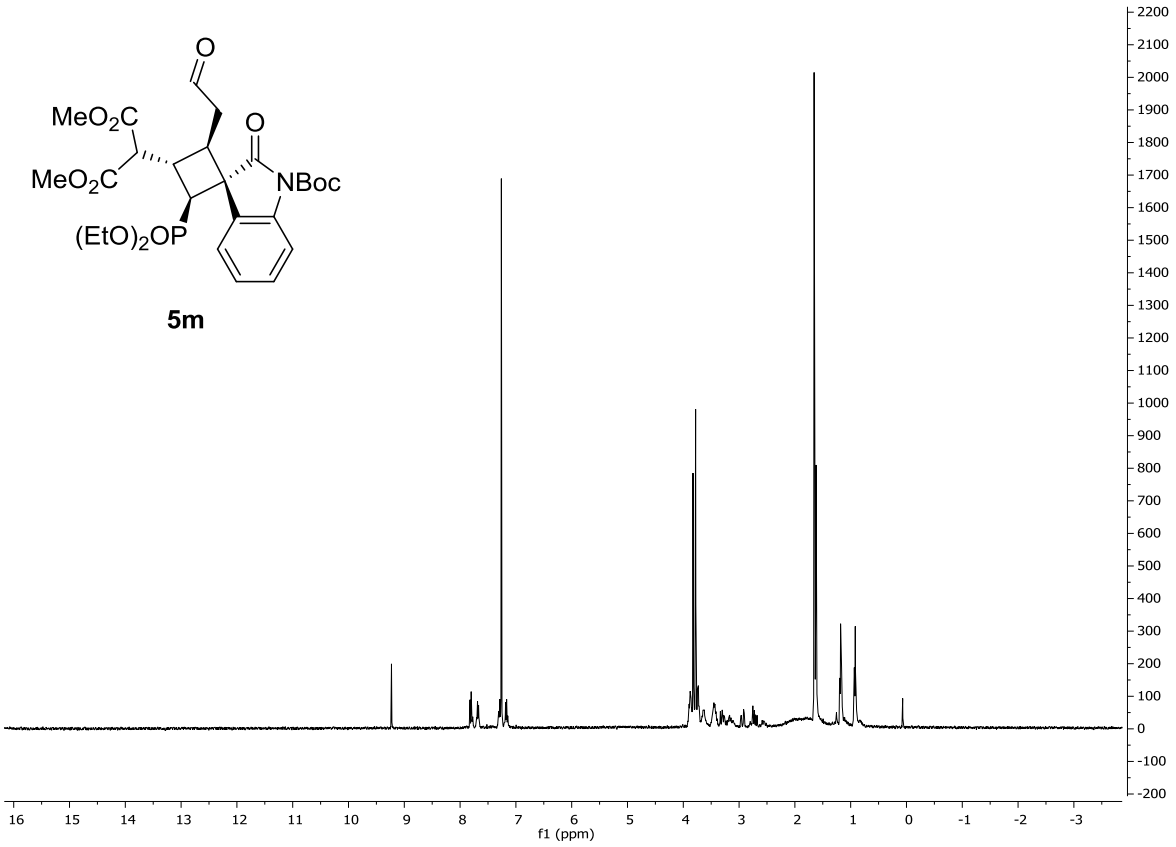
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

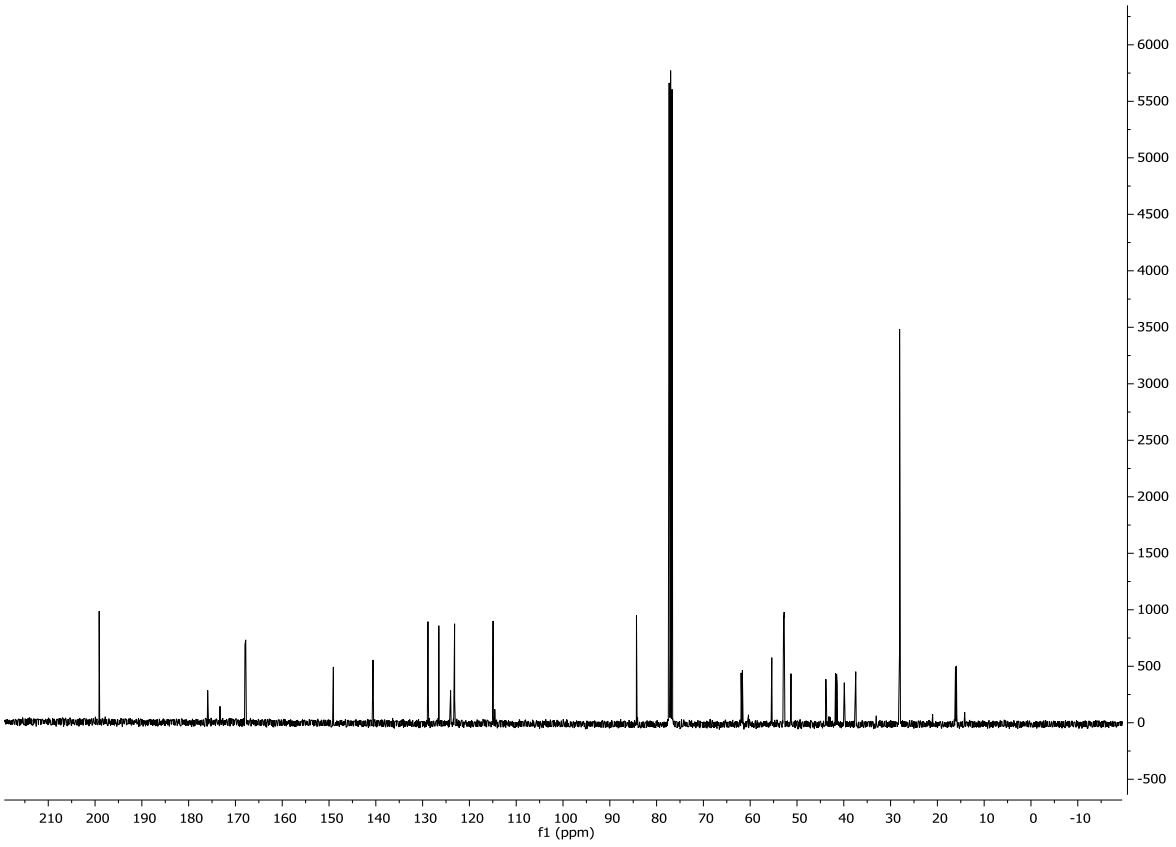


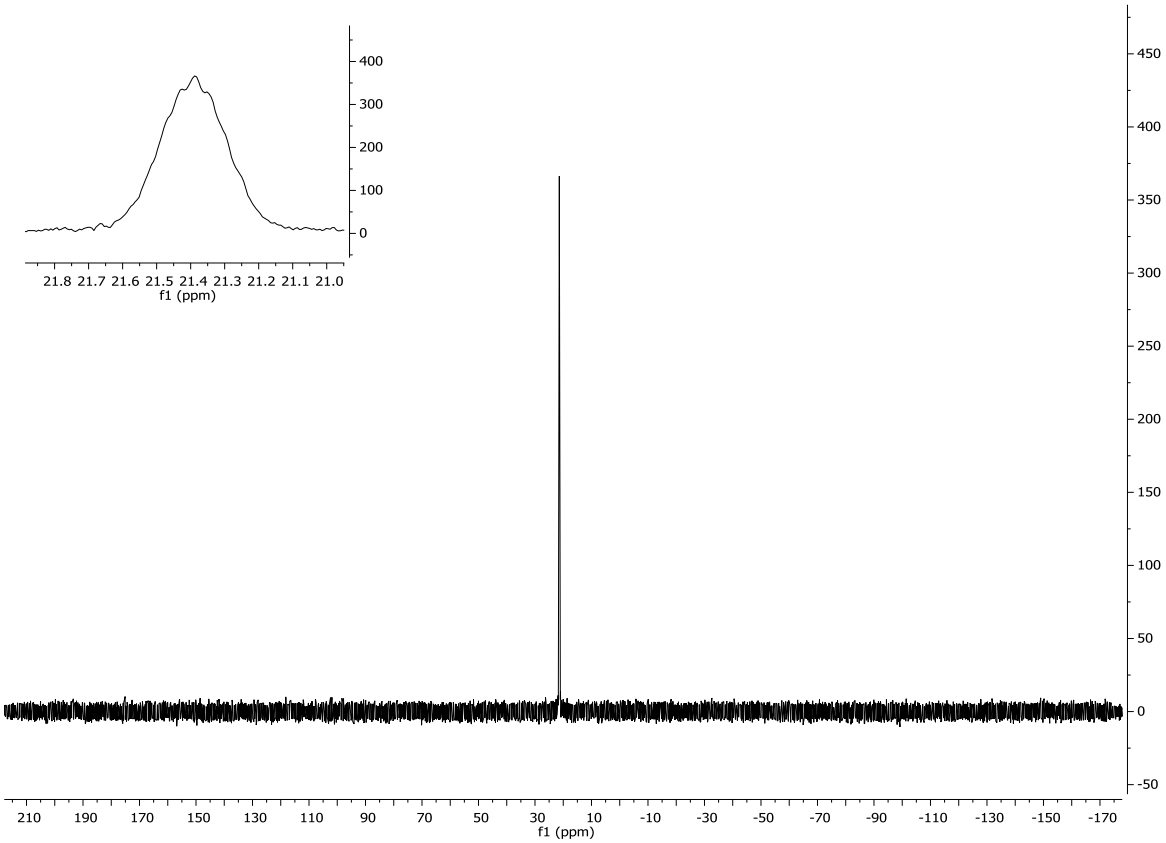
5l

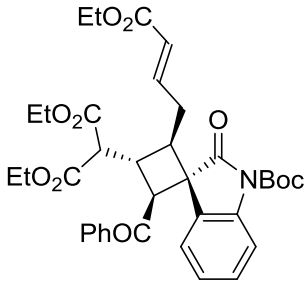




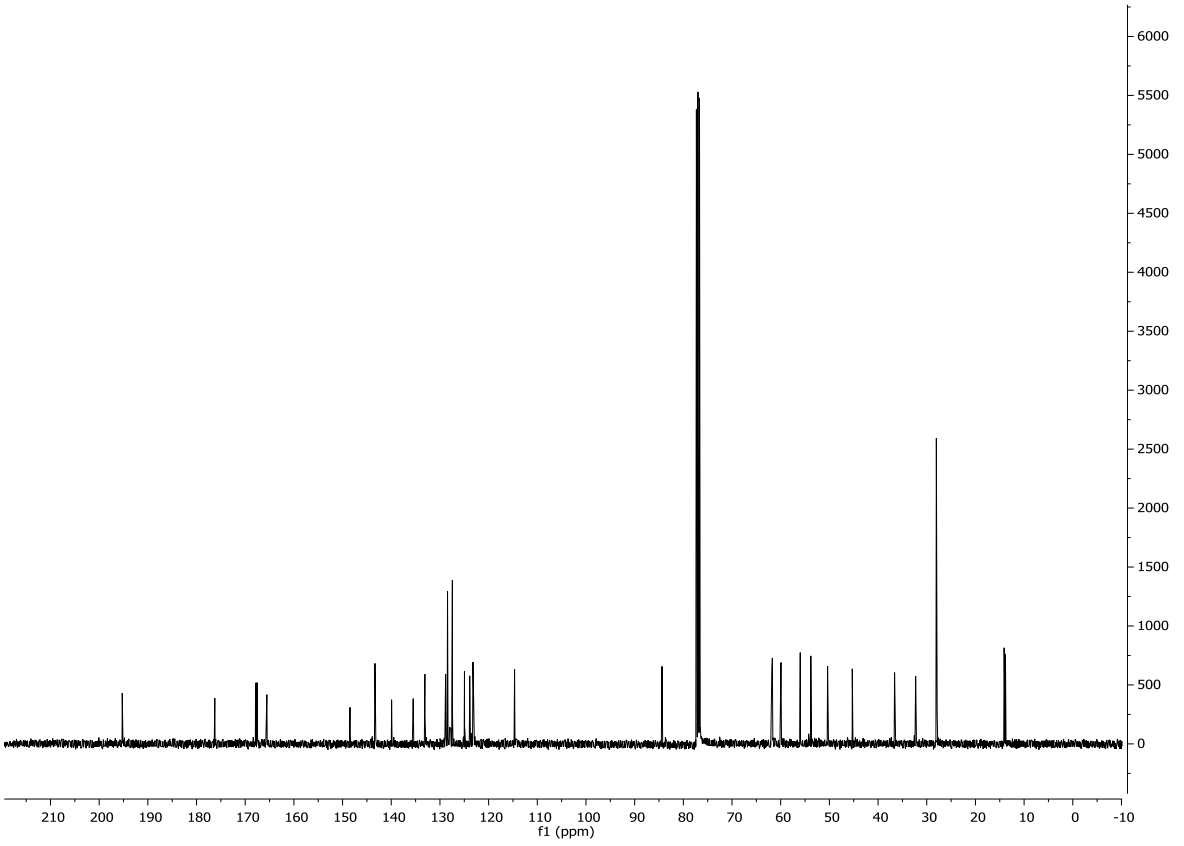
5m

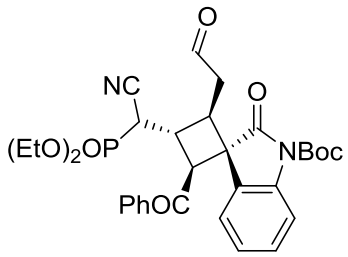



400
300
200
100
0
21.8 21.7 21.6 21.5 21.4 21.3 21.2 21.1 21.0
f1 (ppm)
450
400
350
300
250
200
150
100
50
0
-50
210 190 170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170
f1 (ppm)



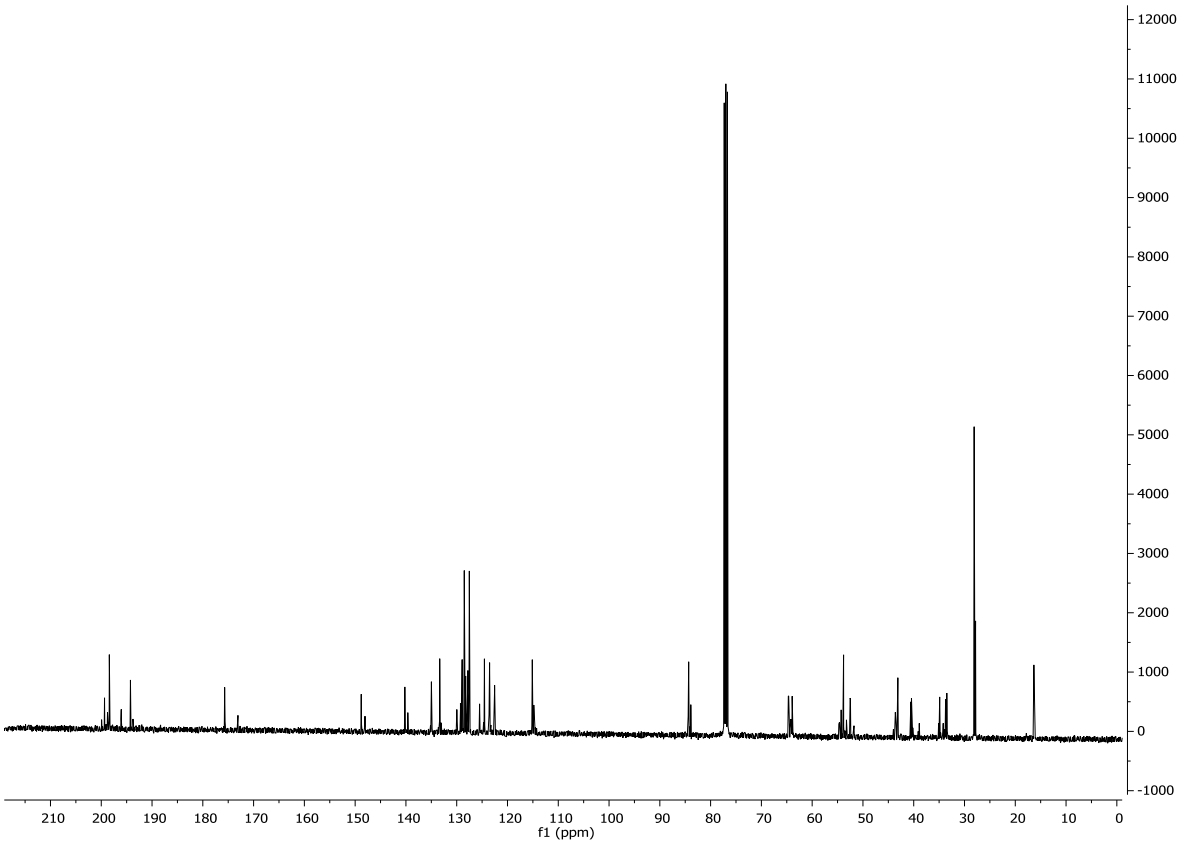
5n

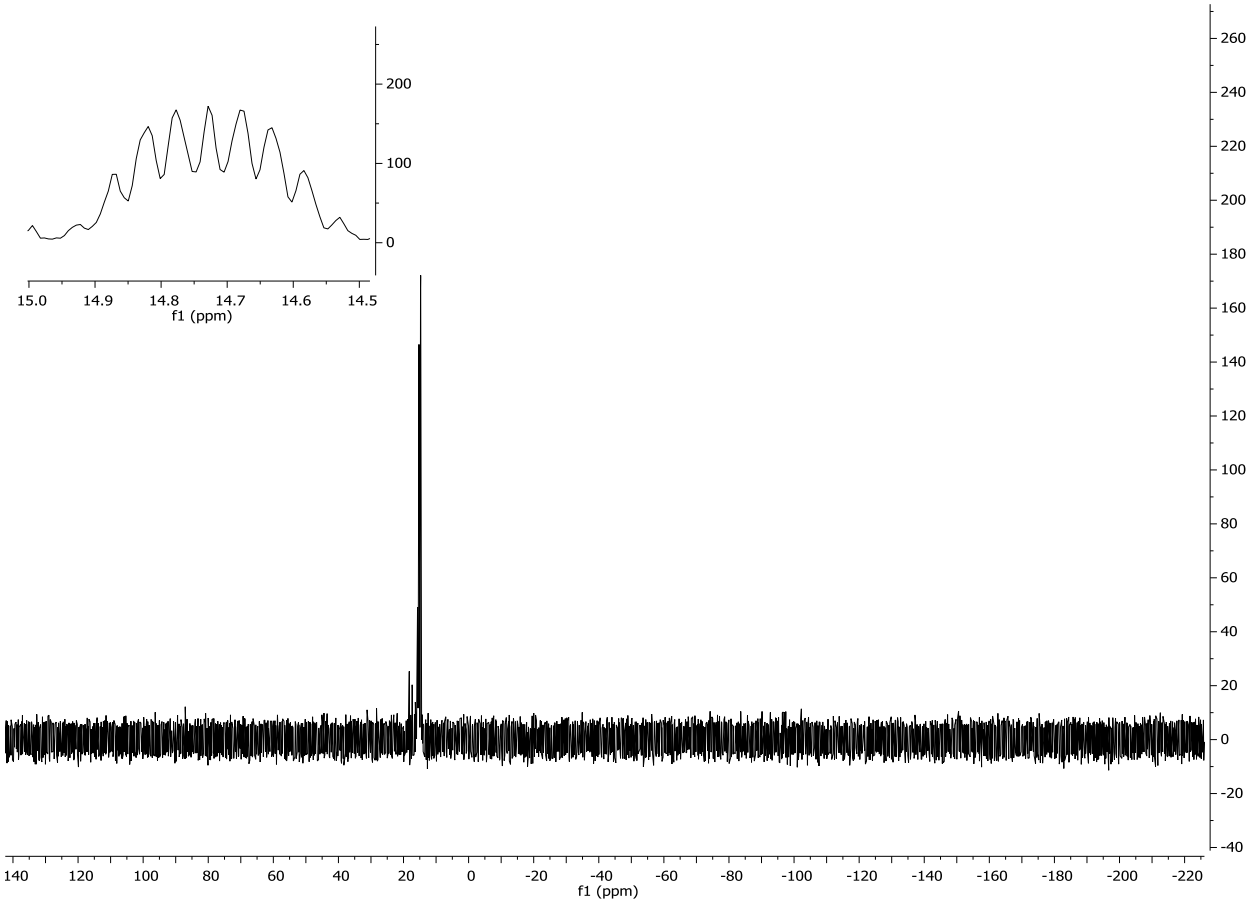


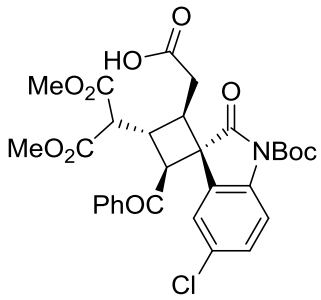

O
NC
O
(EtO)2OP
NBoc
PhOC

5o

16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
12.0 11.5 11.0 10.5 10.0 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 0.0 -0.5 -1.0 -1.5
f1 (ppm)

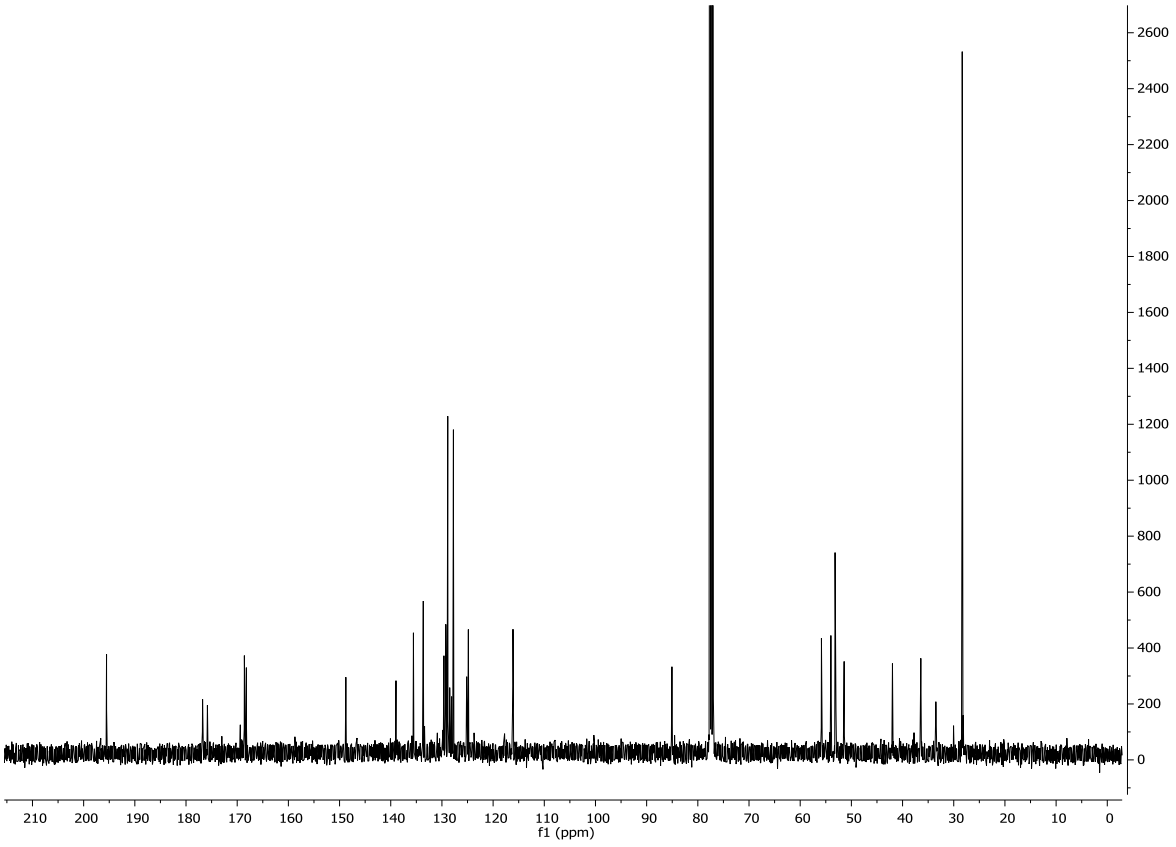

12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

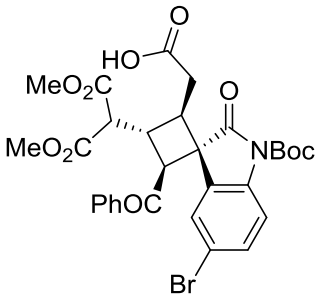

200
100
0
15.0
14.9
14.8
14.7
14.6
14.5
f1 (ppm)
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
f1 (ppm)


O
HO
MeO2C
O
MeO2C
NBoc
PhOC
Cl

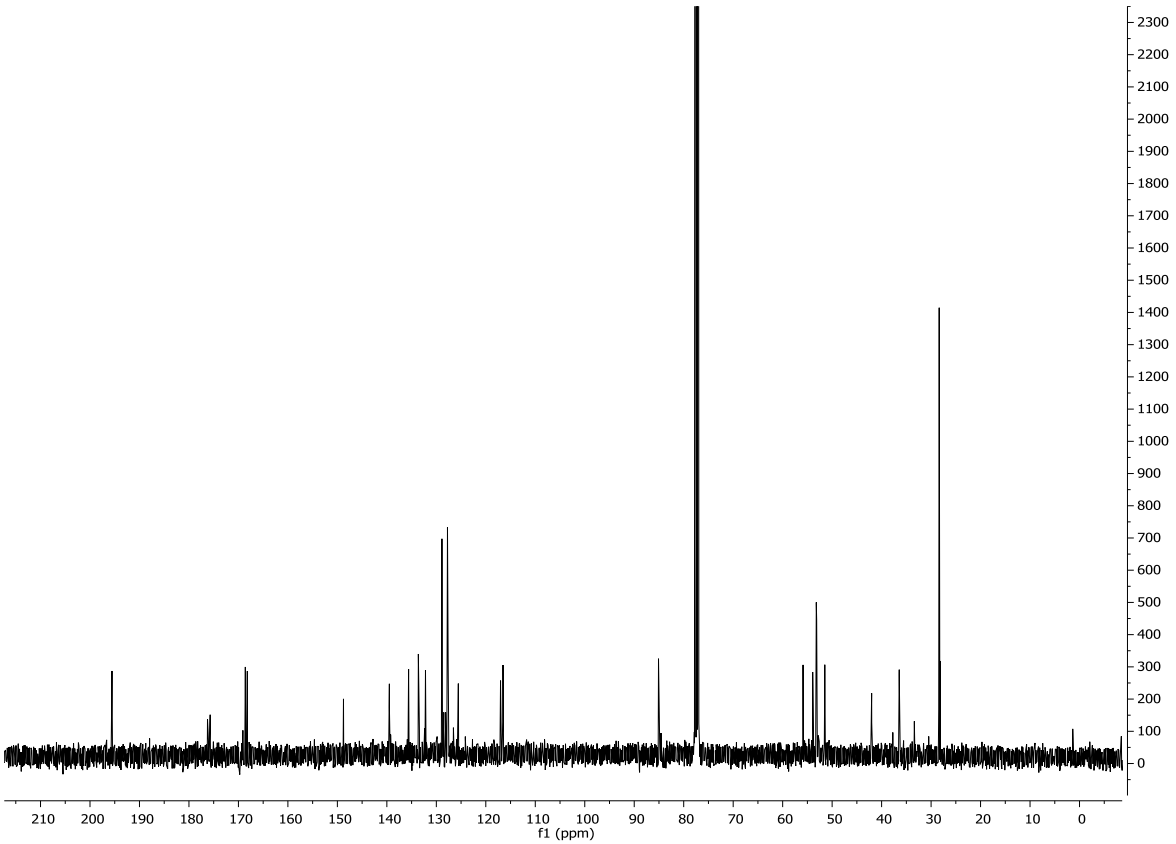
6a

5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
13.0 12.5 12.0 11.5 11.0 10.5 10.0 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 0.0
f1 (ppm)

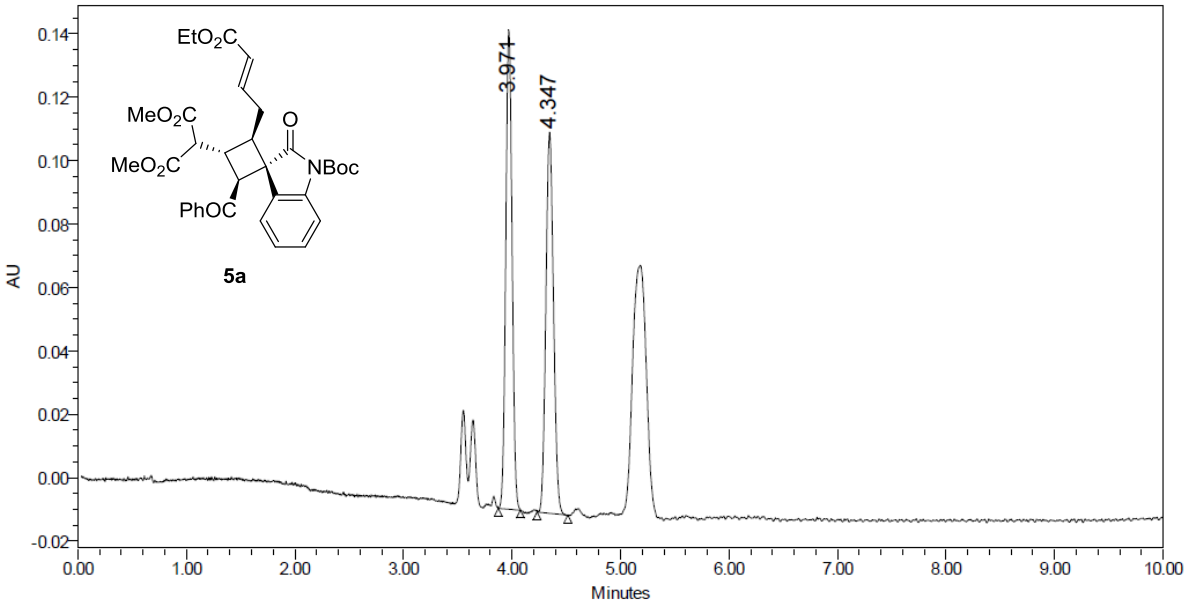

2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



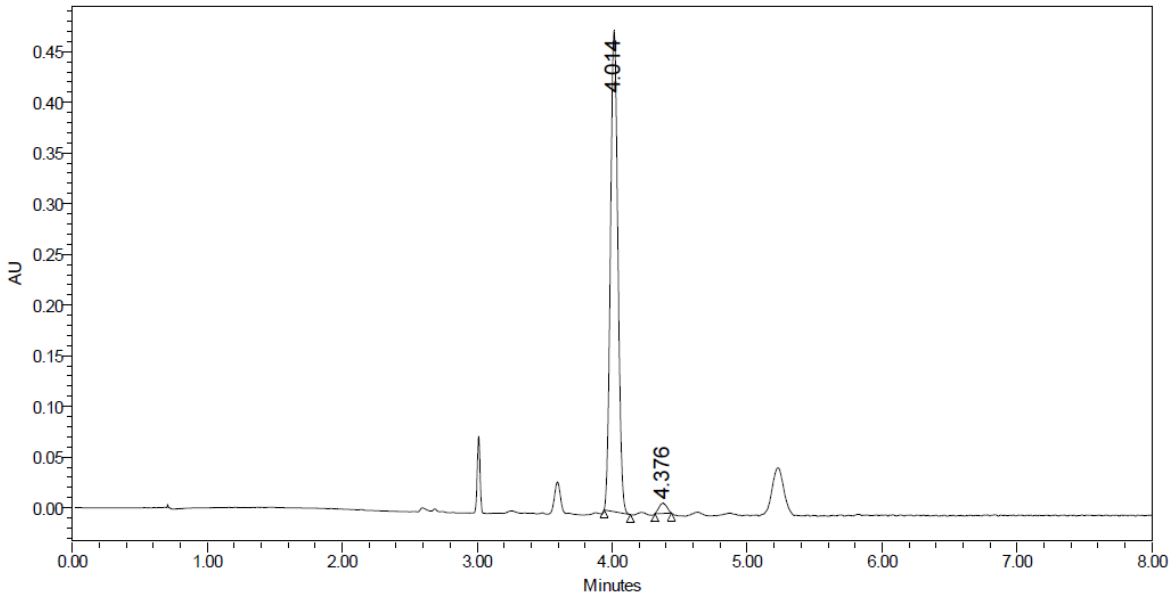
6b



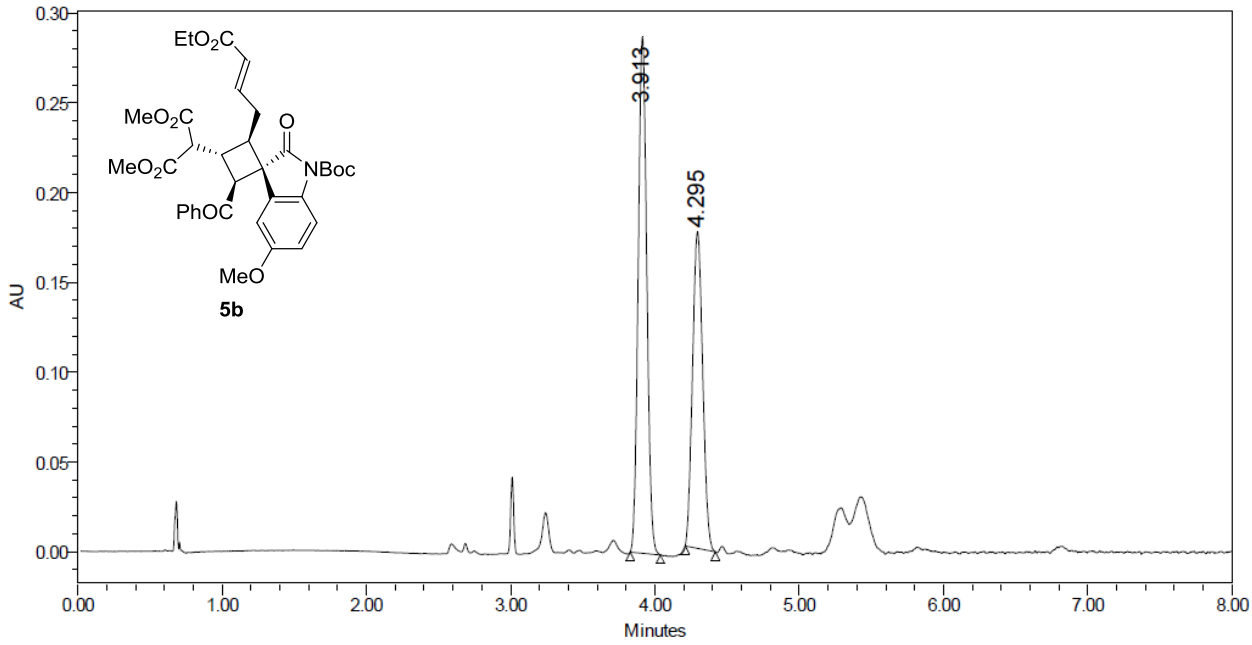
8. UPC^2 traces



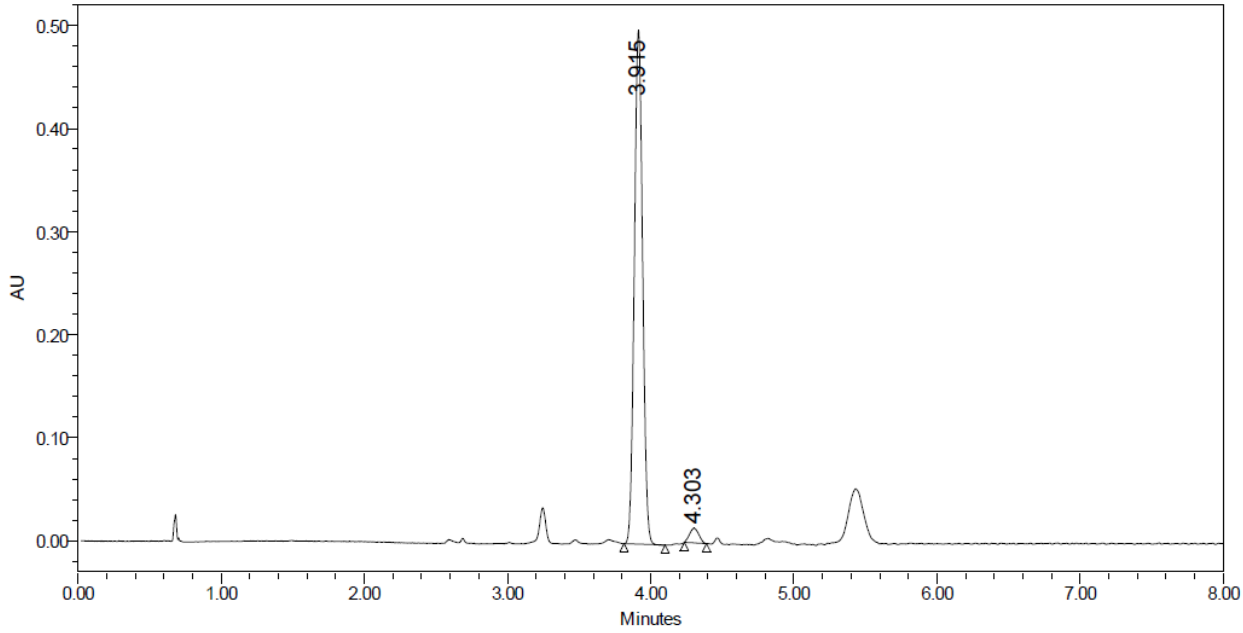
	Retention Time (min)	% Area
1	3.971	50.98
2	4.347	49.02



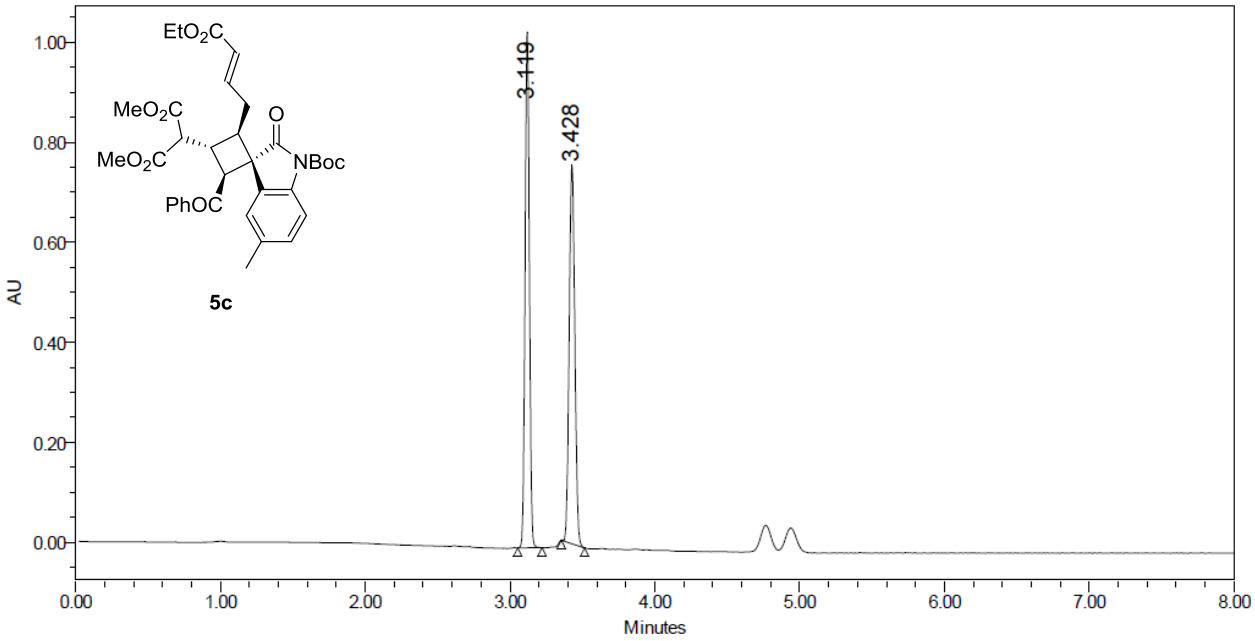
	Retention Time (min)	% Area
1	4.014	97.78
2	4.376	2.22



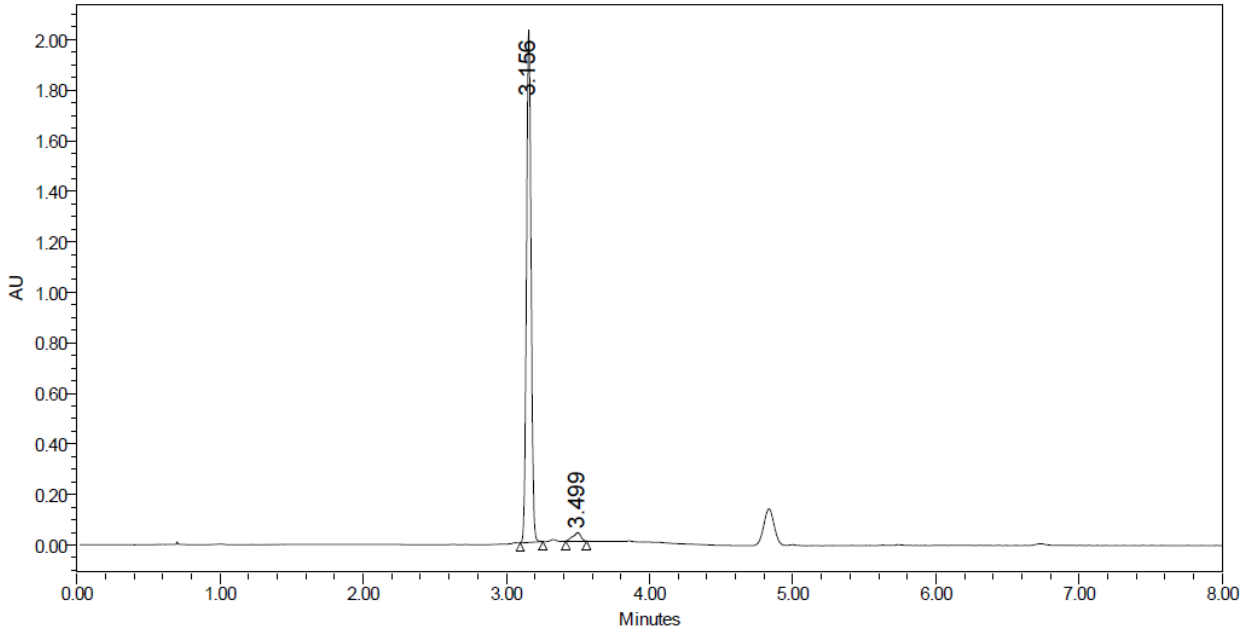
	Retention Time (min)	% Area
1	3.913	57.91
2	4.295	42.09



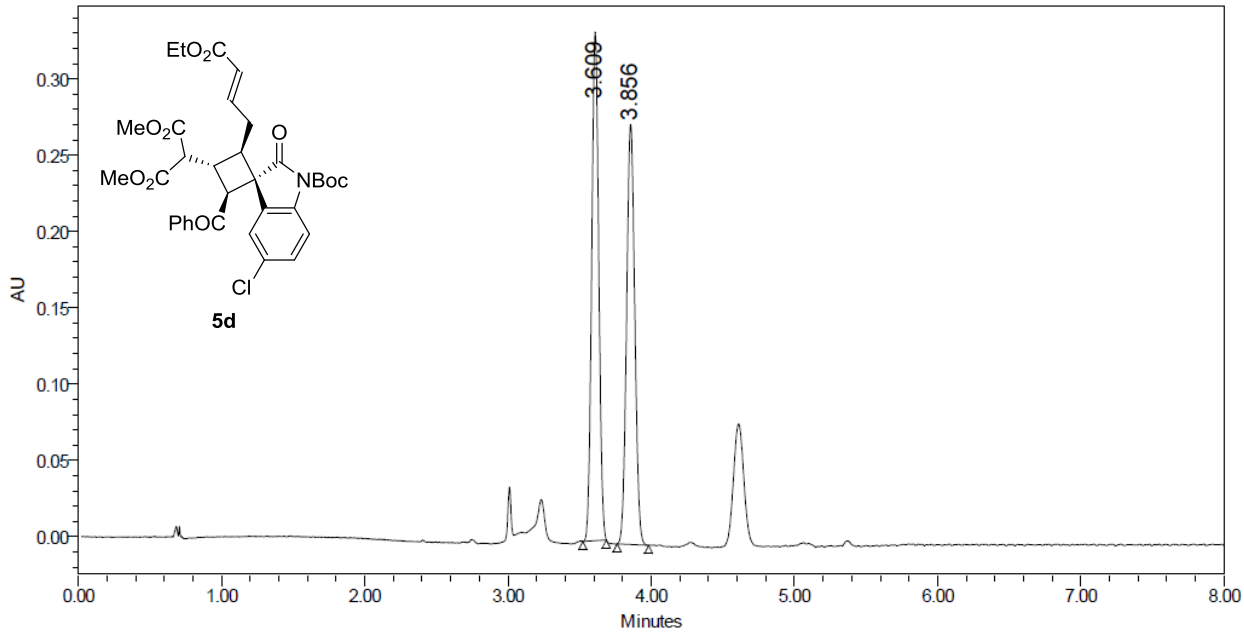
	Retention Time (min)	% Area
1	3.915	96.91
2	4.303	3.09



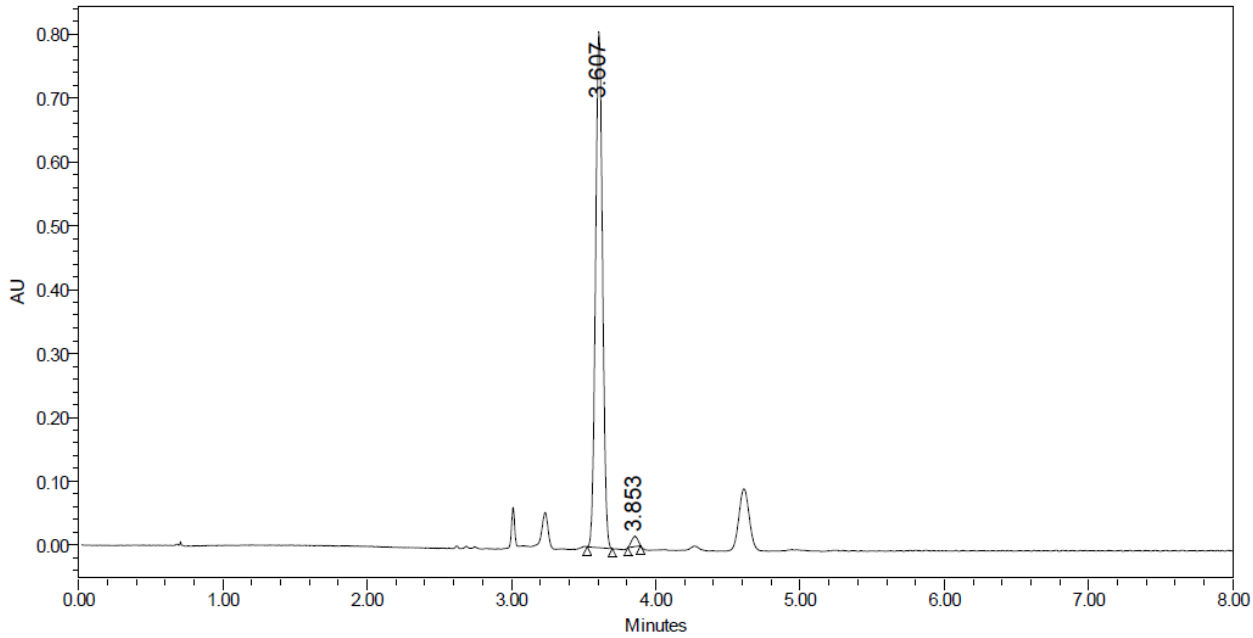
	Retention Time (min)	% Area
1	3.119	50.99
2	3.428	49.01



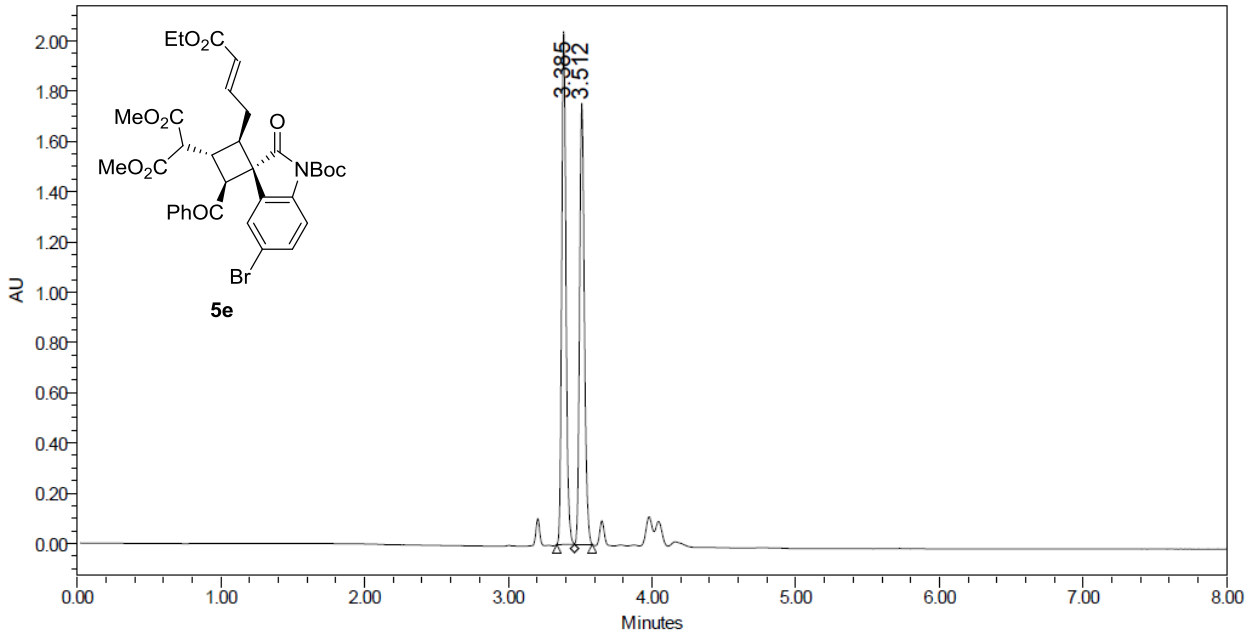
	Retention Time (min)	% Area
1	3.156	97.22
2	3.499	2.78



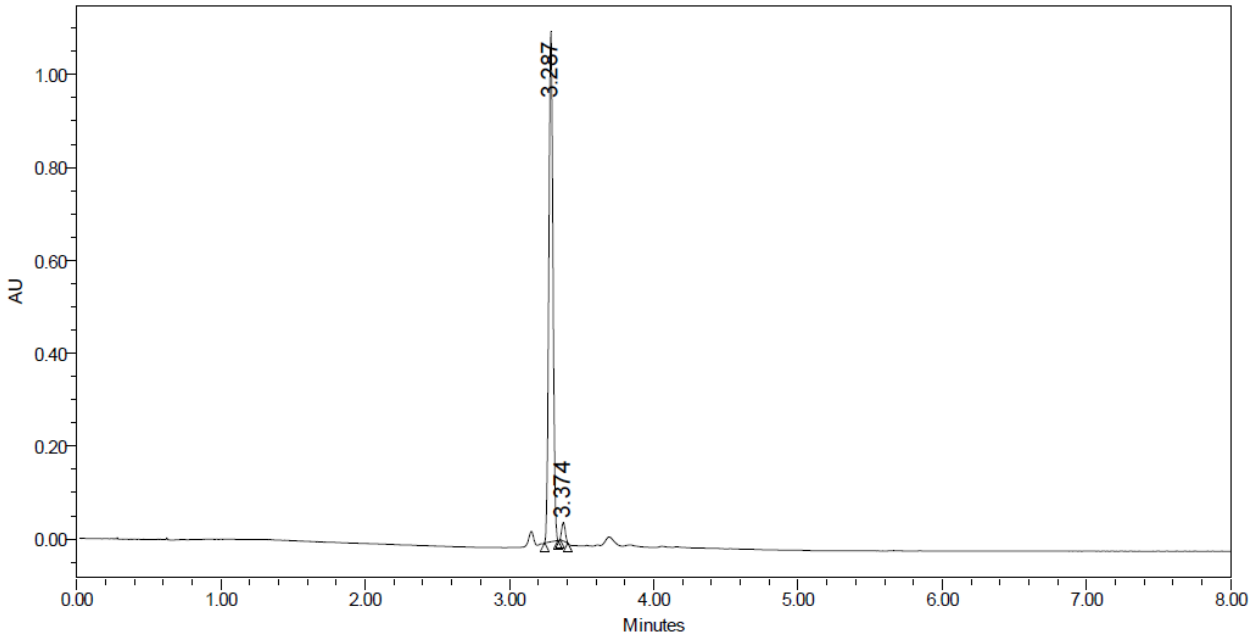
	Retention Time (min)	% Area
1	3.609	50.93
2	3.856	49.07



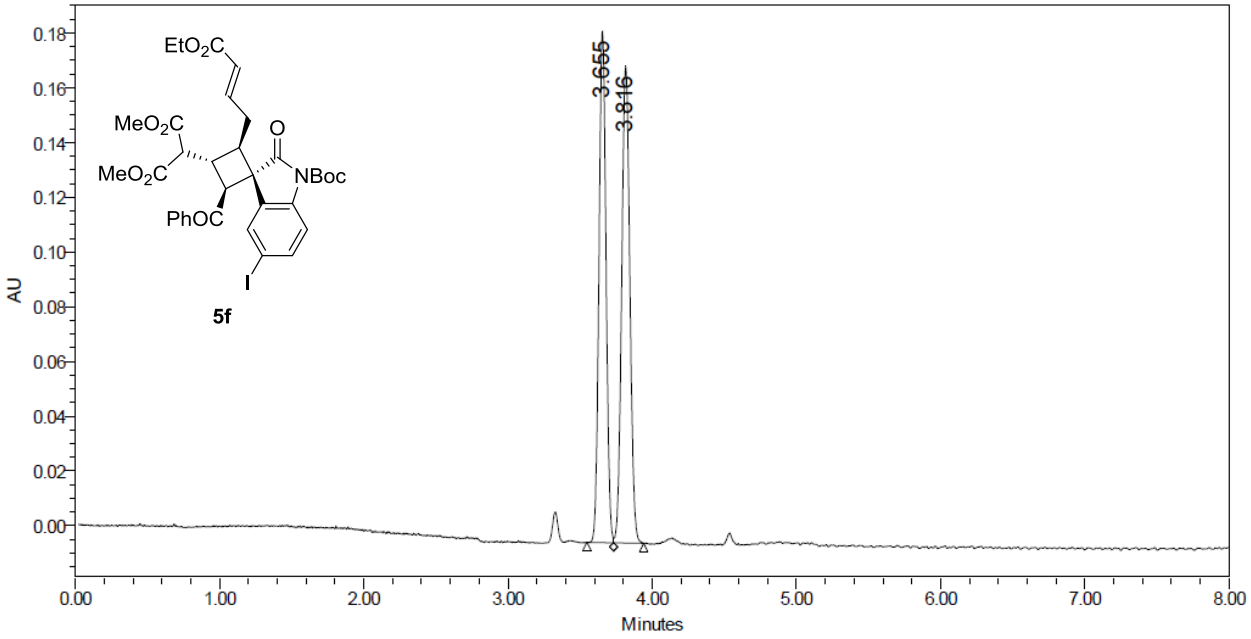
	Retention Time (min)	% Area
1	3.607	98.27
2	3.853	1.73



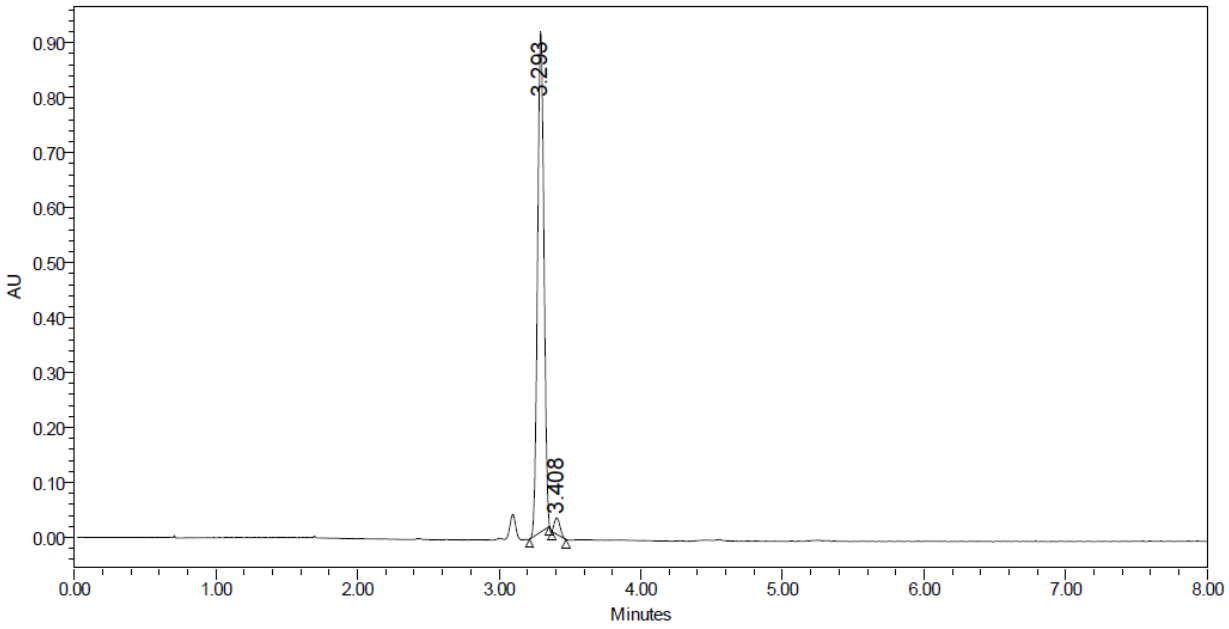
	Retention Time (min)	% Area
1	3.385	50.91
2	3.512	49.09



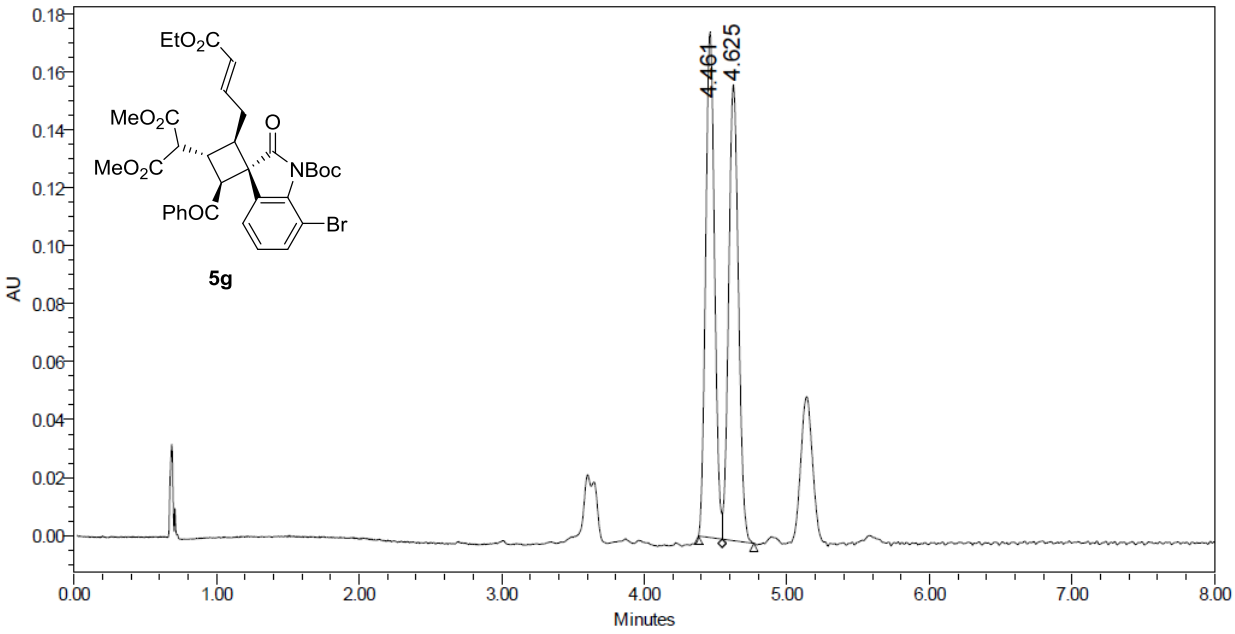
	Retention Time (min)	% Area
1	3.287	97.04
2	3.374	2.96



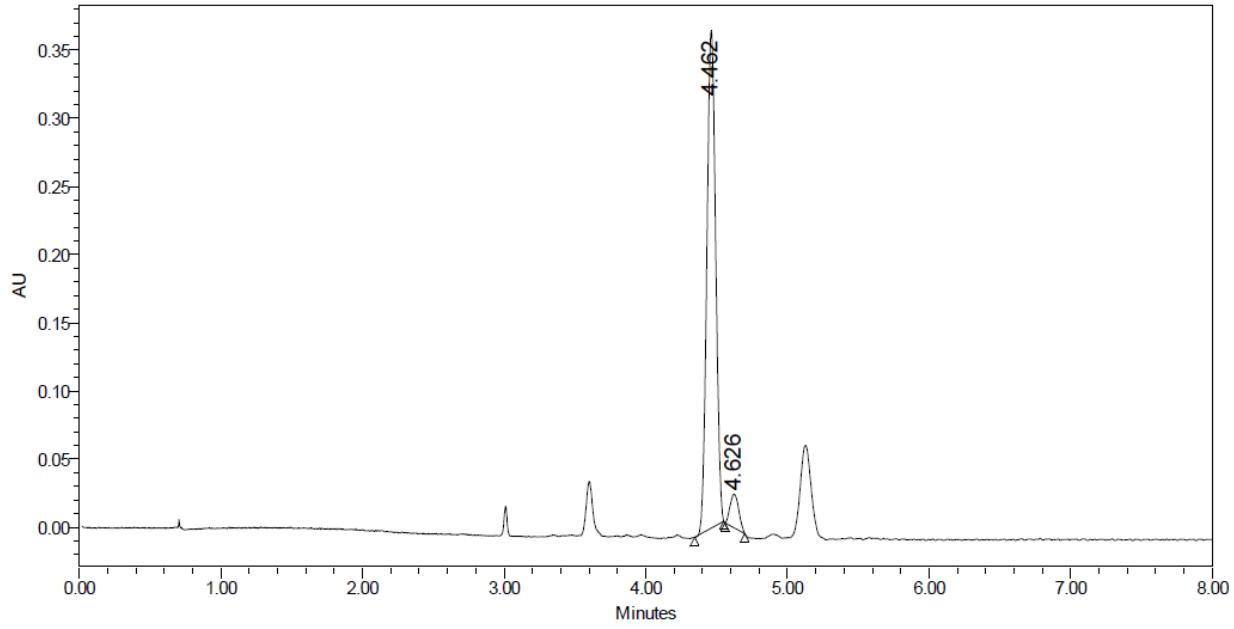
	Retention Time (min)	% Area
1	3.655	48.08
2	3.816	51.92



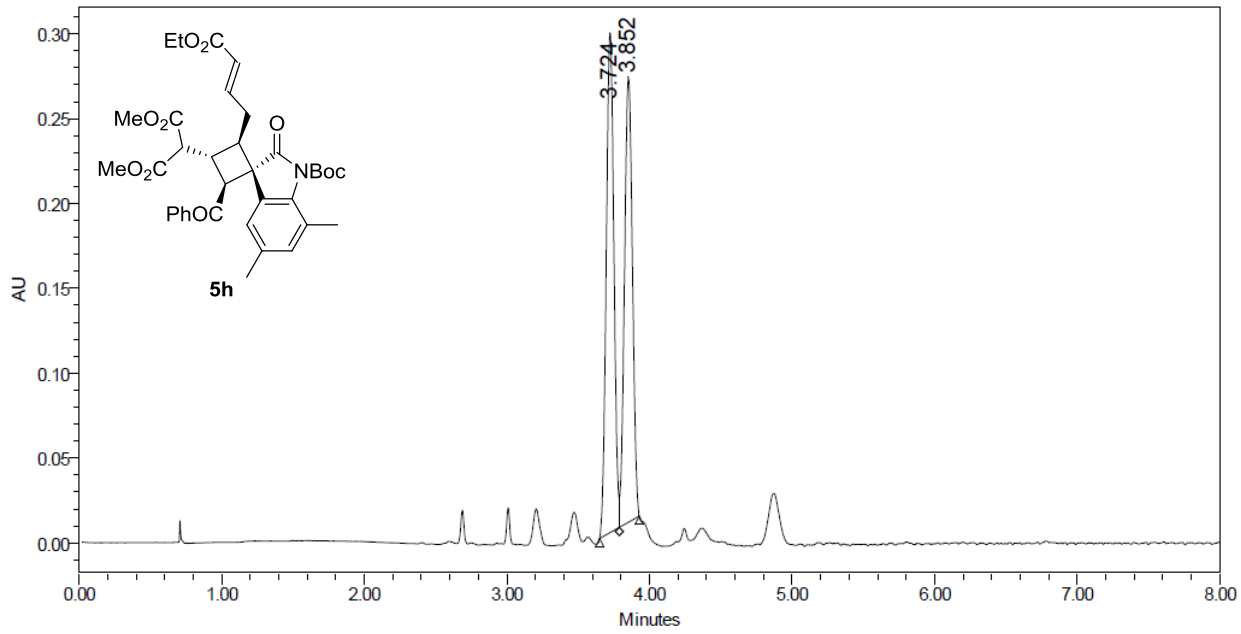
	Retention Time (min)	% Area
1	3.293	97.16
2	3.408	2.84



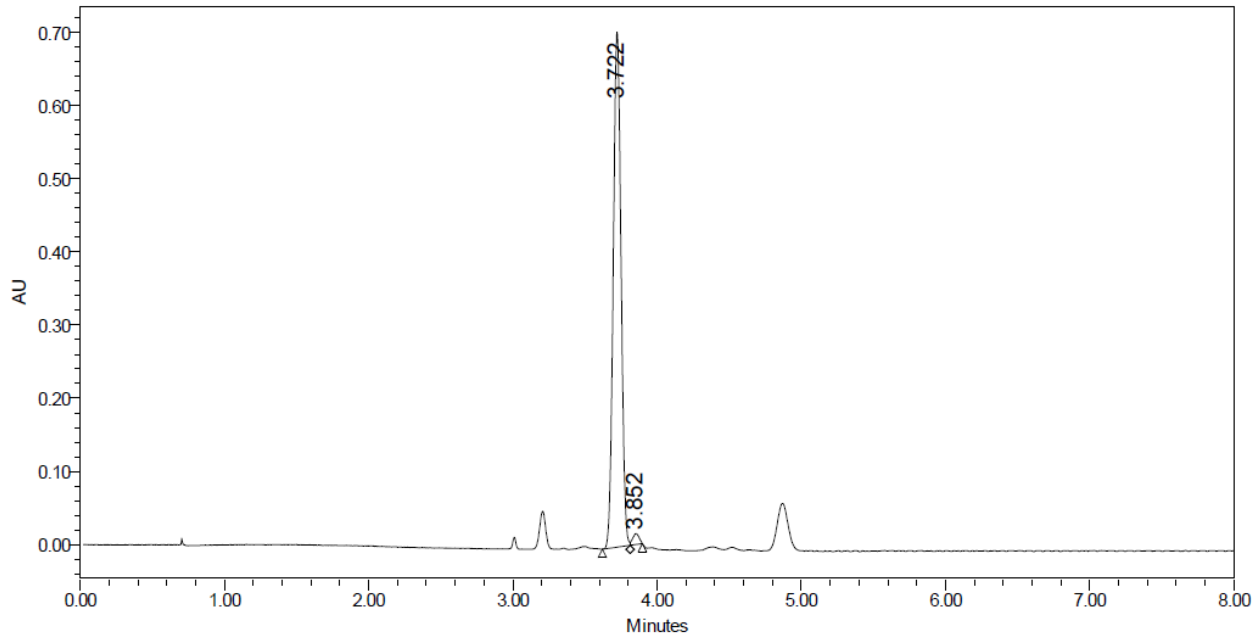
	Retention Time (min)	% Area
1	4.461	50.24
2	4.625	49.76



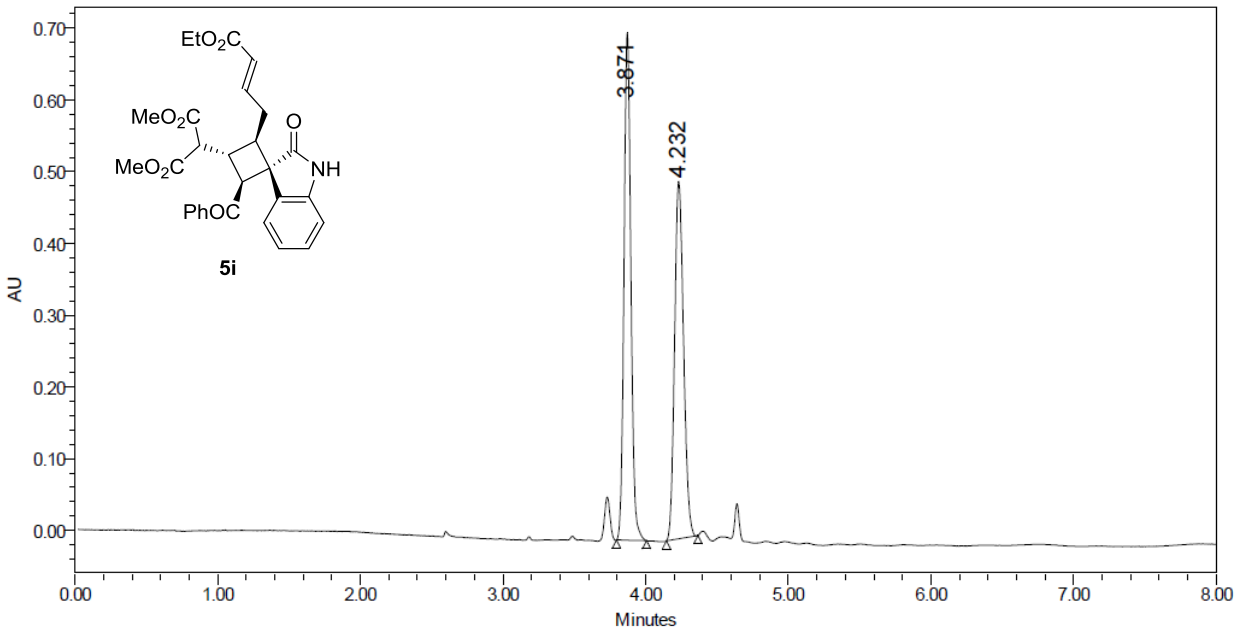
	Retention Time (min)	% Area
1	4.462	93.69
2	4.626	6.31



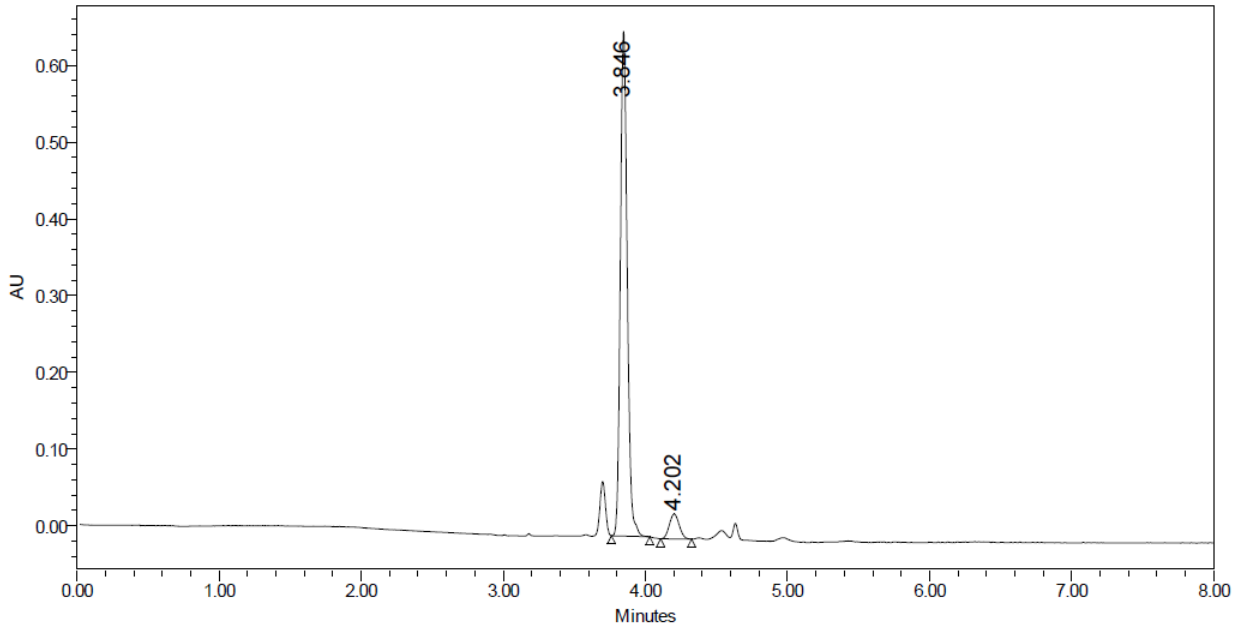
	Retention Time (min)	% Area
1	3.724	51.68
2	3.852	48.32



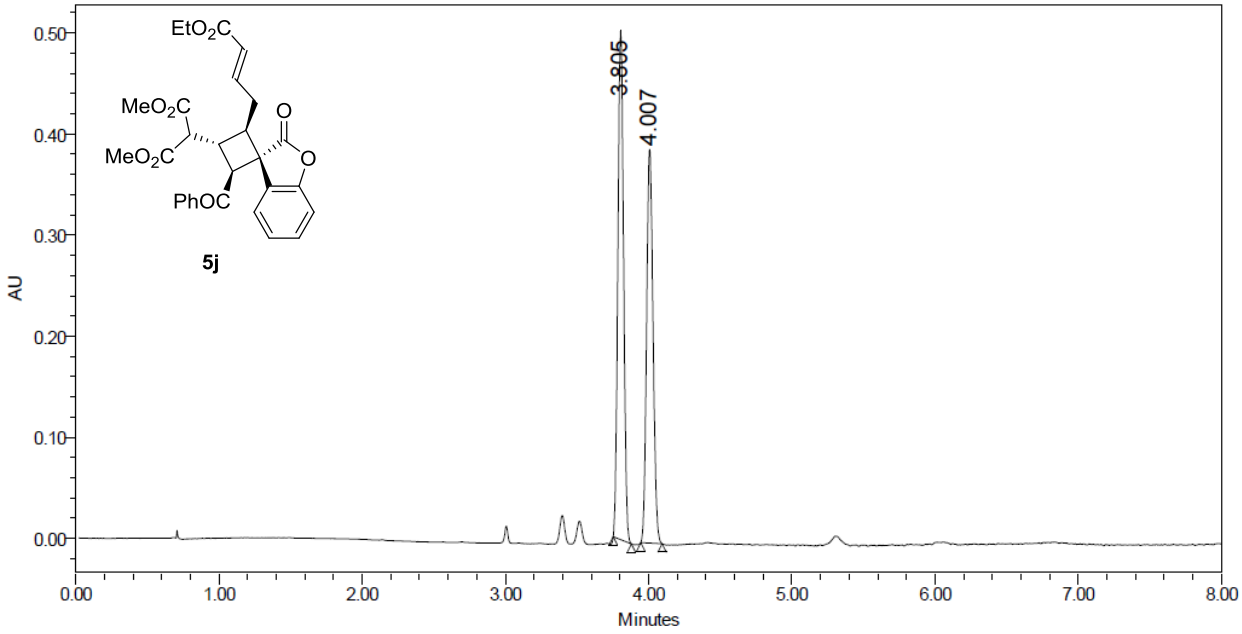
	Retention Time (min)	% Area
1	3.722	98.27
2	3.852	1.73



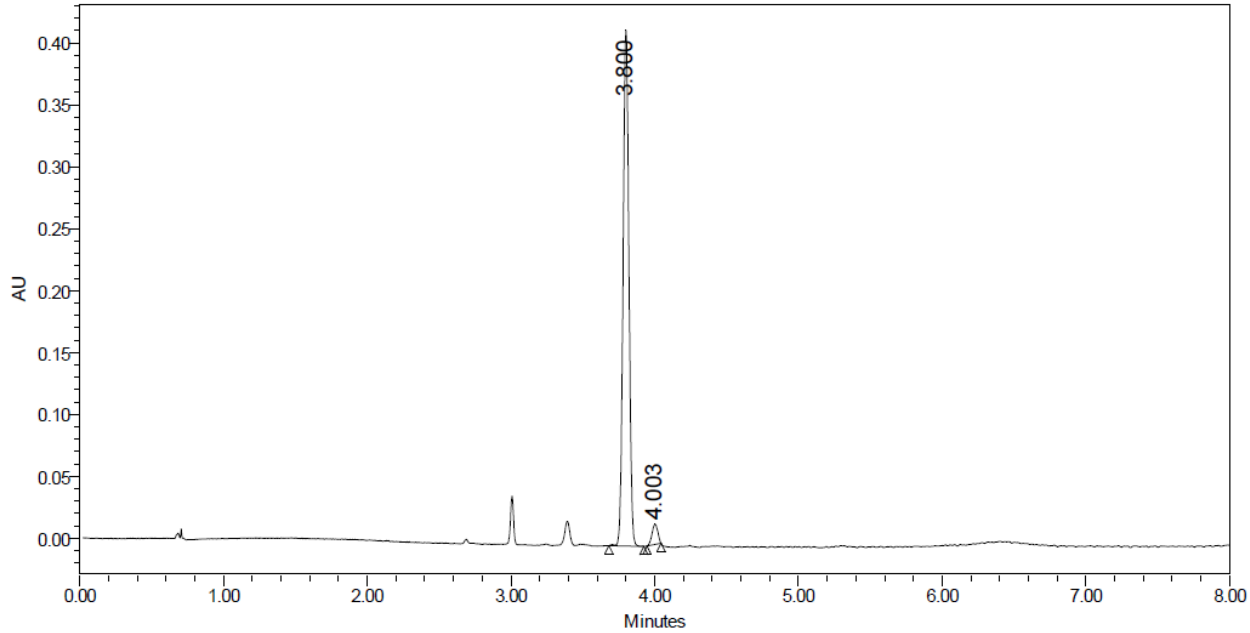
	Retention Time (min)	% Area
1	3.871	52.12
2	4.232	47.88



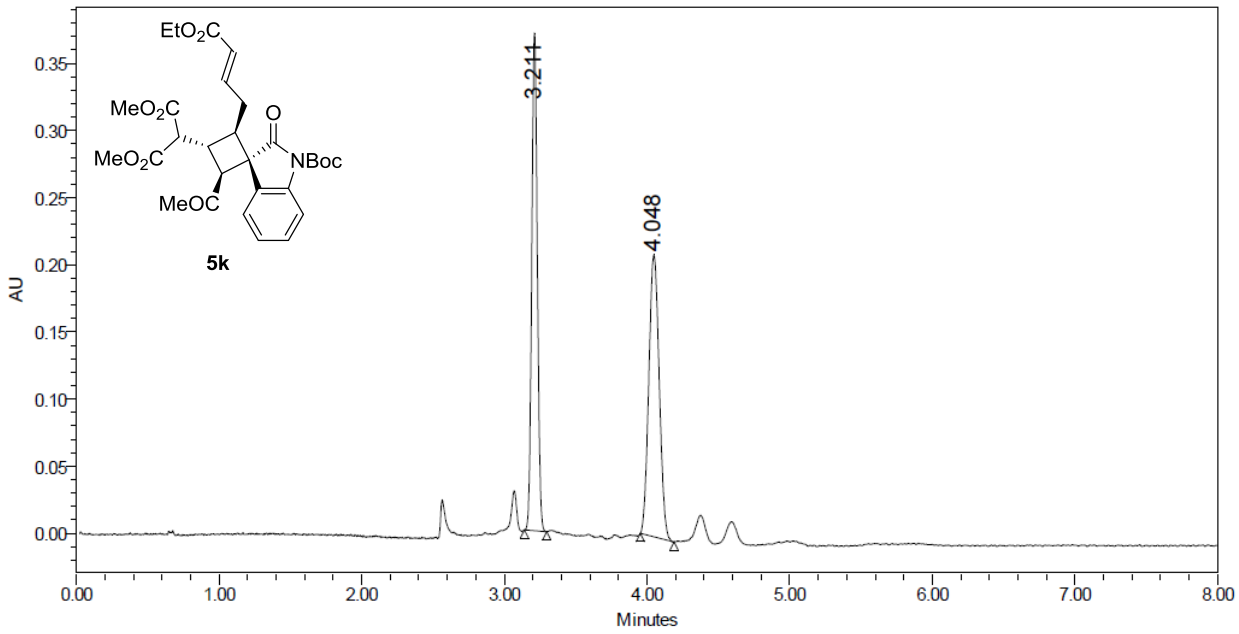
	Retention Time (min)	% Area
1	3.846	93.42
2	4.202	6.58



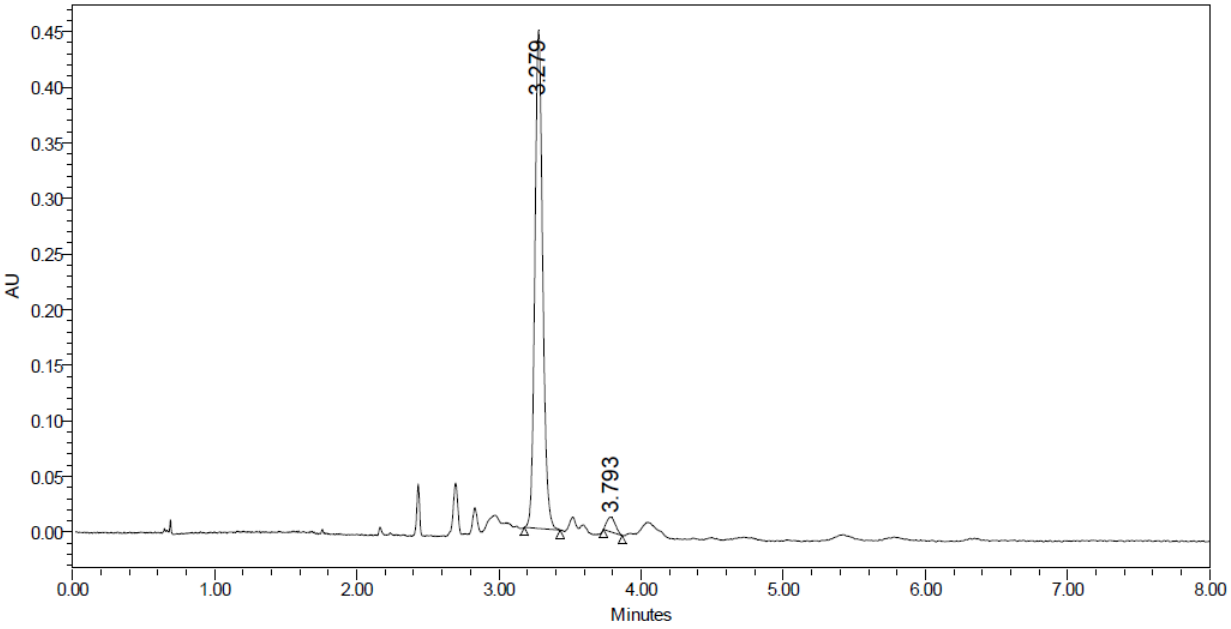
	Retention Time (min)	% Area
1	3.805	53.49
2	4.007	46.51



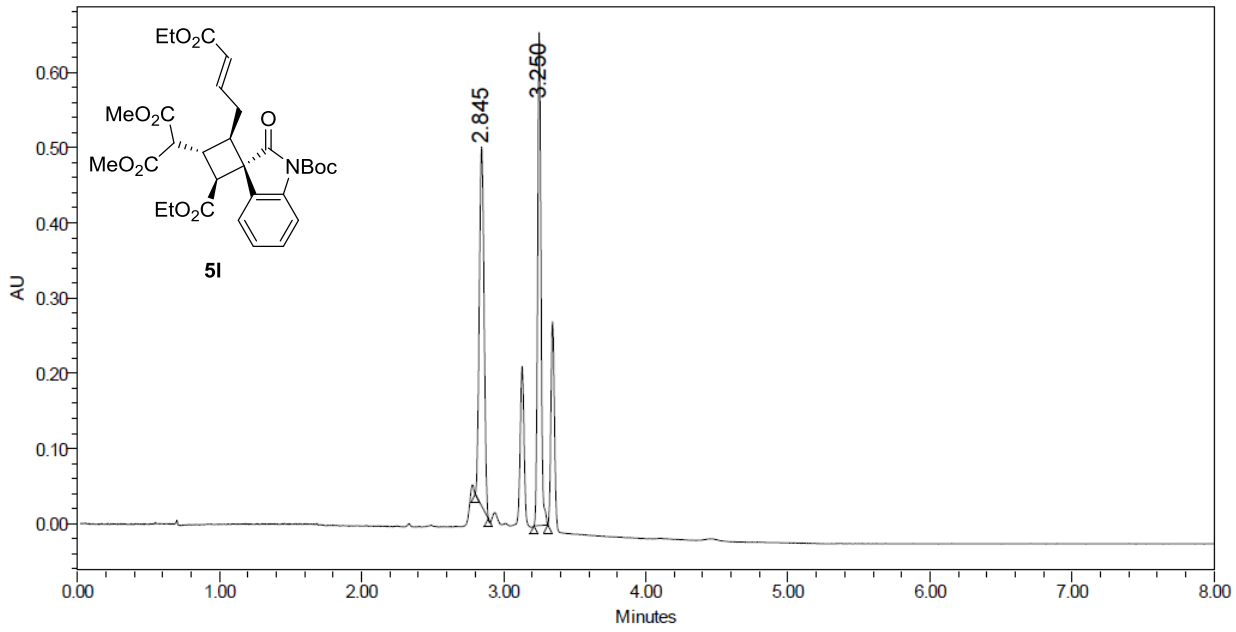
	Retention Time (min)	% Area
1	3.800	96.28
2	4.003	3.72



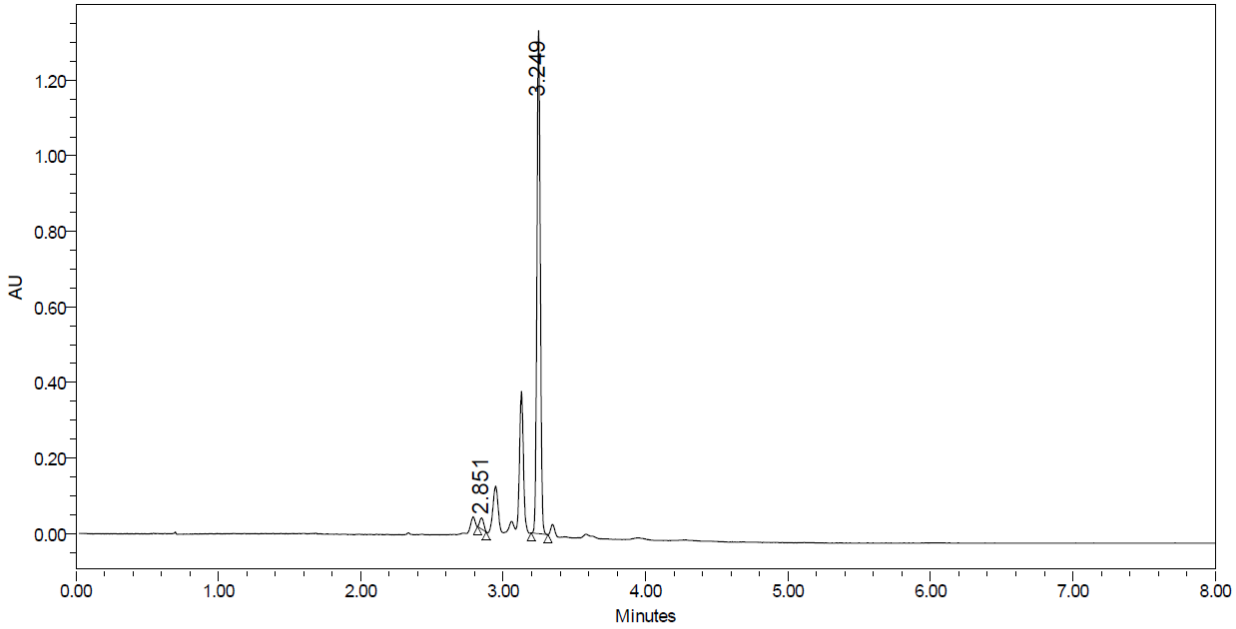
	Retention Time (min)	% Area
1	3.211	48.59
2	4.048	51.41



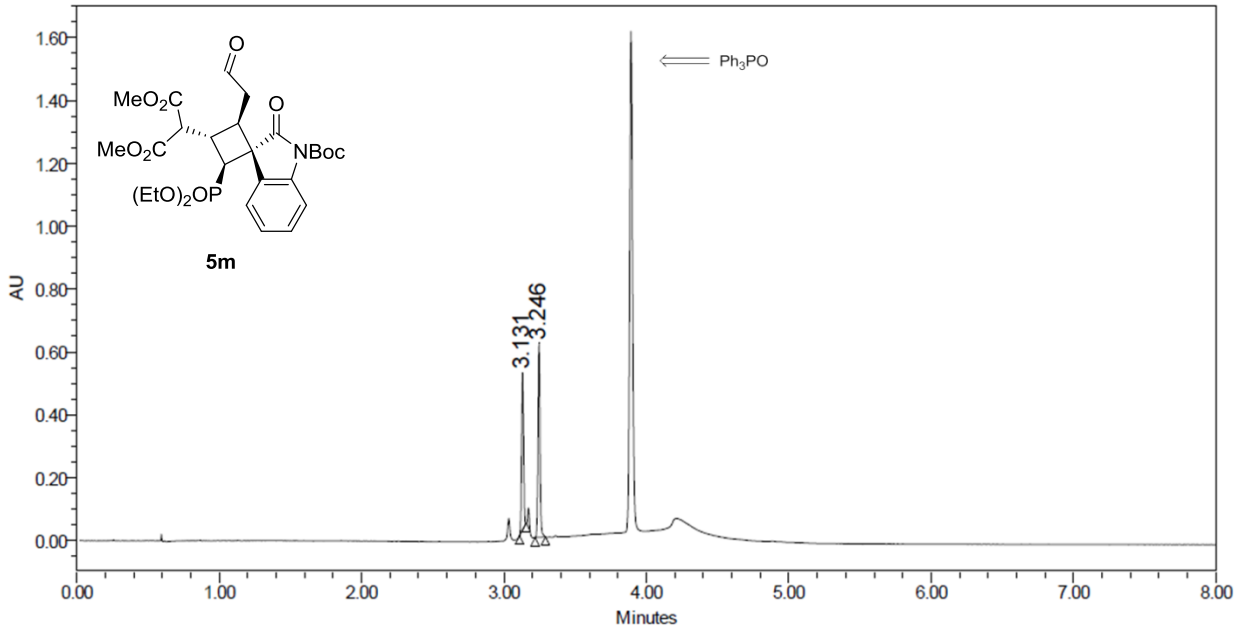
	Retention Time (min)	% Area
1	3.279	96.88
2	3.793	3.12



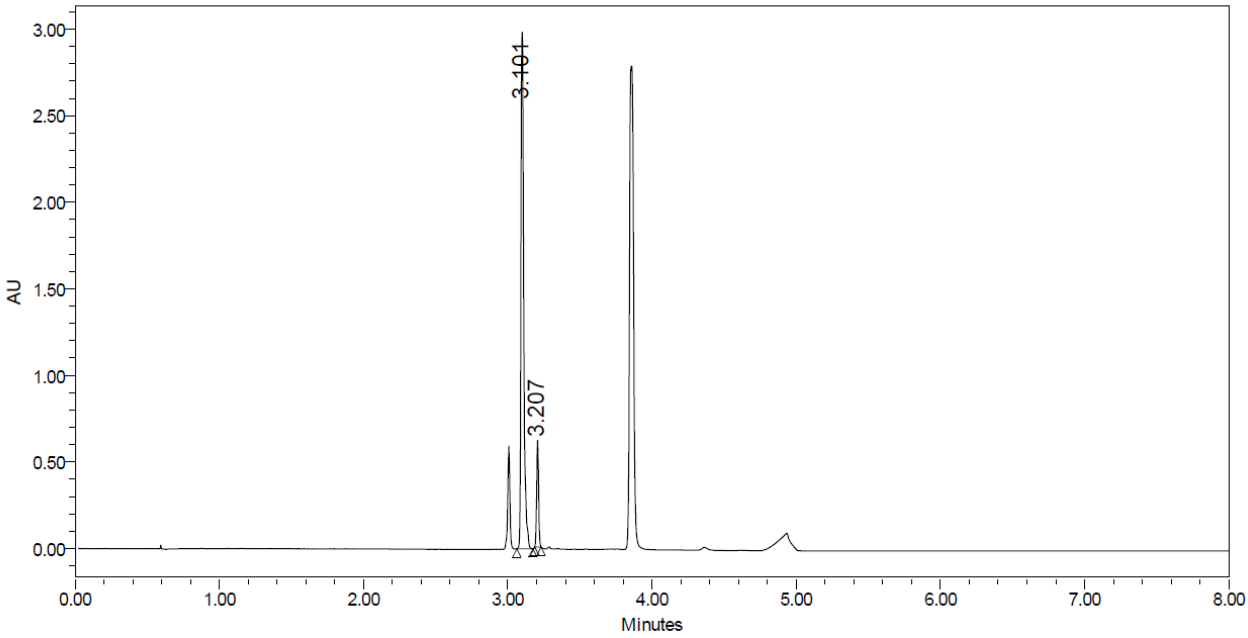
	Retention Time (min)	% Area
1	2.845	50.81
2	3.250	49.19



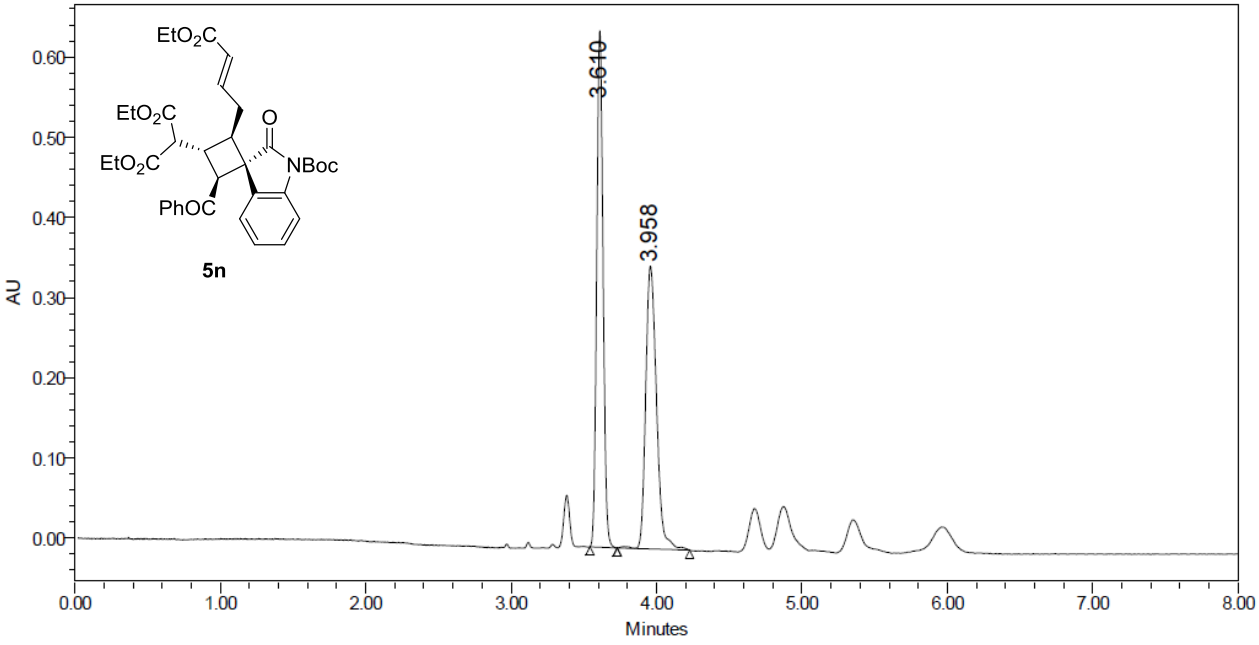
	Retention Time (min)	% Area
1	2.851	2.53
2	3.249	97.47



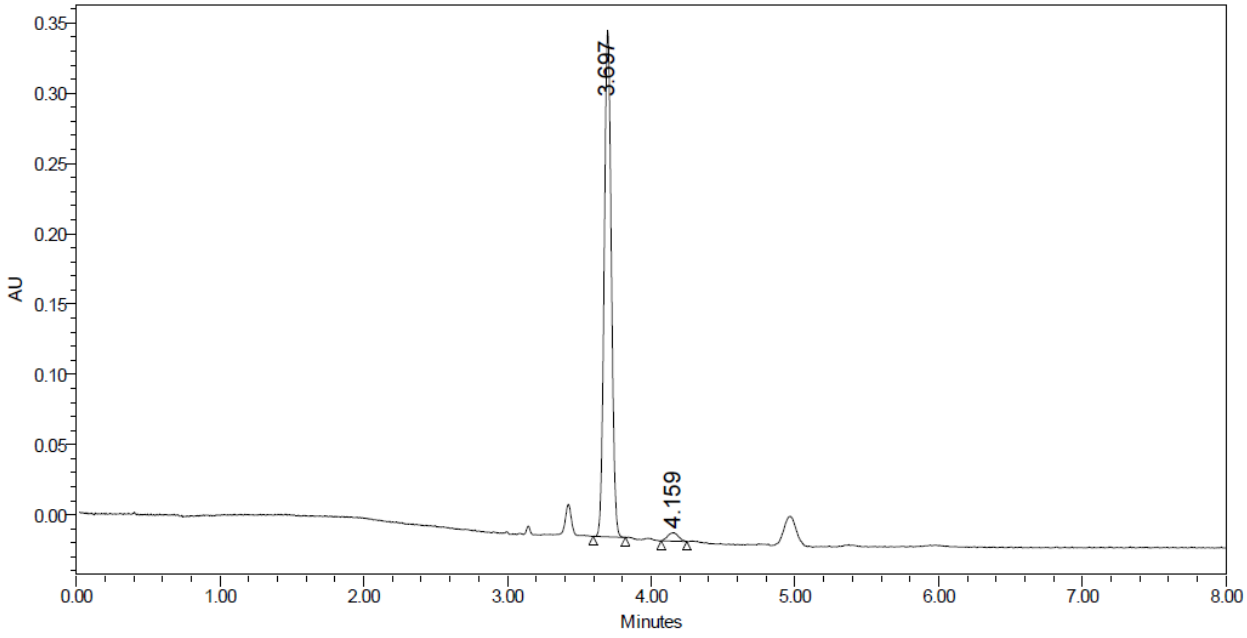
	Retention Time (min)	% Area
1	3.131	44.12
2	3.246	55.88



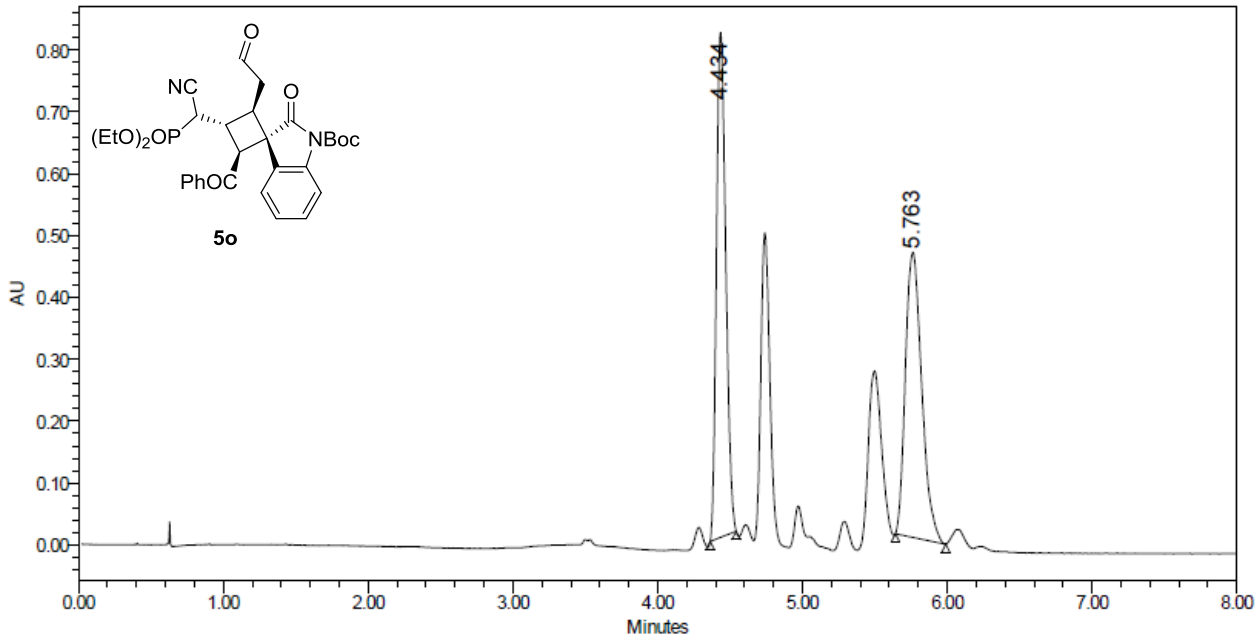
	Retention Time (min)	% Area
1	3.101	87.51
2	3.207	12.49



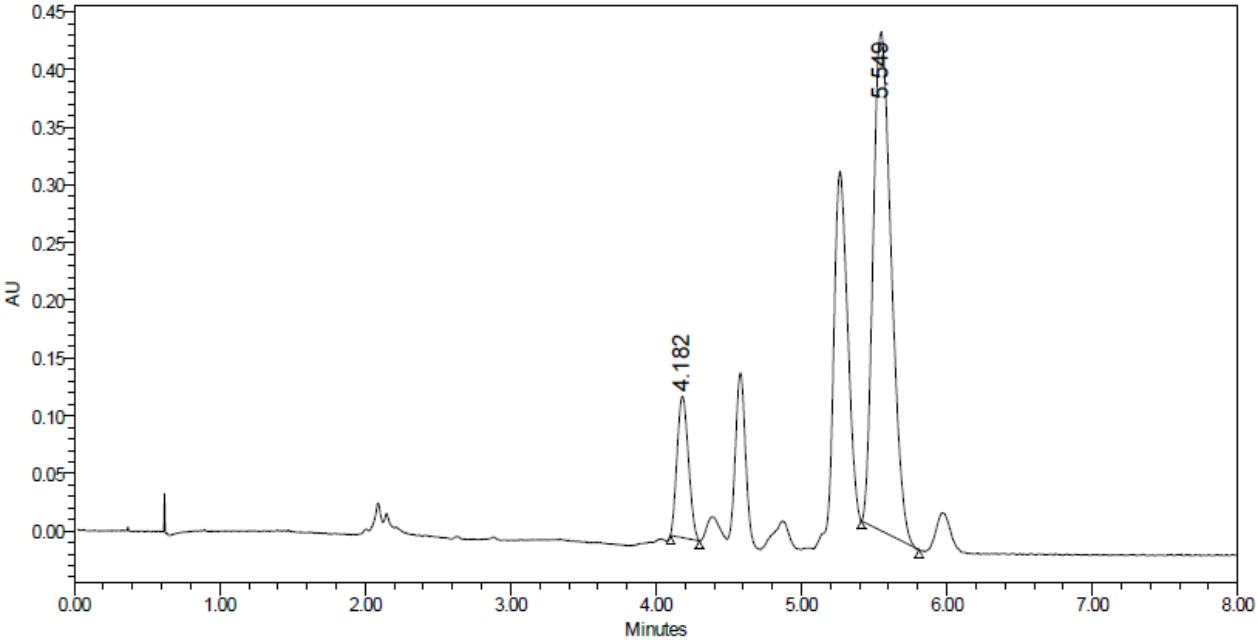
	Retention Time (min)	% Area
1	3.610	51.79
2	3.958	48.21



	Retention Time (min)	% Area
1	3.697	97.53
2	4.159	2.47



	Retention Time (min)	% Area
1	4.434	50.21
2	5.763	49.79



	Retention Time (min)	% Area
1	4.182	15.04
2	5.549	84.96