Supplementary Information for:

Diastereodivergent organocatalysis for the asymmetric synthesis of chiral annulated furans

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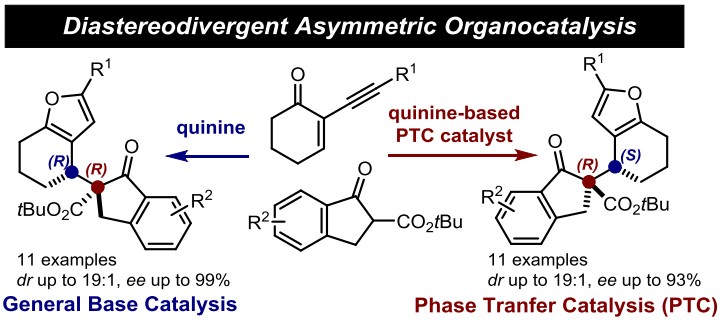

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A. General Information

The ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz and 500 MHz for ^{1}H and 100 or 125 MHz for ^{13}C. The chemical shift (δ) for 1H and 13C are given in ppm relative to residual signals of the solvents ($CHCl_3$ @ 7.26 ppm ^{1}H NMR and 77.16 ppm ^{13}C NMR). Coupling constants are given in Hertz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; q, quartet; m, multiplet; bs, broad signal.
High resolution mass spectra (HRMS) were obtained from the ICIQ HRMS unit on Waters GCT gas chromatograph coupled time-of-flight mass spectrometer (GC/MS-TOF) with electrospray ionization (ESI). X-ray data were obtained from the ICIQ X-Ray unit using a Brucker-Nonius diffractometer equipped with an APPEX 2 4K CCD area detector. Optical rotations are reported as follws: $[\alpha]^{rt}_{D}$ (c in g per 100 mL, solvent).
Unless specified, all the reactions were set up under air using puriss. grade solvents, without any precaution to exclude oxygen or moisture. Chromatographic purification of the products was accomplished using force-flow chromatography (FC) on silica gel (60-200 mesh). Thin layer chromatography (TLC) analysis were carried out on Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm), using UV light as the visualizing agent and acidic ceric ammonium molybdate or aqueous basic potassium permanganate as stain developing solutions. Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator.

The authors are indebted to the team of the Research Support Area at ICIQ and to Grace Fox for proof-reading the manuscript.

Determination of Diastereoisomeric ratios. The diastereoisomeric ratios were determined by ^{1}H NMR of the crude reaction mixtures after silver-mediated cyclization, and further confirmed by ^{1}H NMR of the purified compounds.

Determination of Enantiomeric Purity: HPLC analyses on chiral stationary phases were performed on an Agilent 1200-series instrumentation. Daicel Chiralpack AD-H and IA-3, hexane, *i*Pr-OH and/or DCM as the eluent were used. HPLC traces were compared to racemic samples prepared using benzyltriethylammonium chloride as the achiral catalyst.

Determination of yield and conversion in the optimization studies. The conversion of the starting material and the yield of products during the optimization studies were determined by ^{1}H NMR analysis adding to the crude reaction mixture 1,4-dinitrobenzene as the internal standard (δ 8.40 ppm (s, 4H).

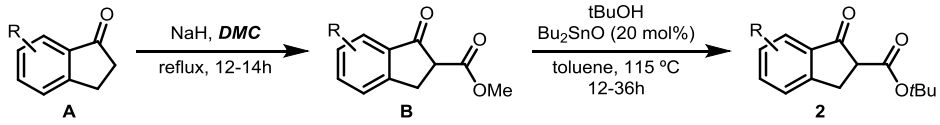
Materials. Commercial grade reagents and solvents were purchased from sigma-Aldrich, Fluka, Alfa Aesar and used as received, without further purifications. The 2-alkynyl-enones **1**[1] were synthesized according to literature procedures.

B. Representative Procedure for the Synthesis of the Cyclic *tert*-Butyl-Ketoesters 2

NaH (5.2 mmol, 210 mg, 2.2 eq., 60% dispersion in mineral oil) and anhydrous dimethyl carbonate (***DMC***, 10 mL) were added sequentially to a dry three-necked flask equipped with a septum, condenser, argon inlet, and a large stirring egg. The indan-1-one derivative **A** (2.37 mmol, 1 eq), partially solubilized in anhydrous dimethyl carbonate (10 mL), was added *via* a syringe pump over the course of 30 minutes (Scheme S1). The heterogeneous mixture was brought to reflux (80 ºC),

[1] T. Yao, X. Zhang and R. C. Larock *J. Am. Chem. Soc.* **2004**, *126*, 11164-11165.

and heated overnight at this temperature. The reaction was allowed to cool and cautiously quenched at 0ºC under an argon atmosphere with H_2O (10 mL). The mixture was transferred to a separative funnel with EtOAc while adding additional 50 mL of 1M HCl. The reaction was extracted with EtOAc (50 mL x 3) and the combined organic layers washed with a saturated brine solution before being dried over solid anhydrous magnesium sulfate and concentrated. The crude material was then dissolved in toluene (20 mL), and *t*BuOH (30 eq, 71.1 mmol, 6.5 mL), and dibutyl-tin oxide (0.2 eq, 118 mg) was added. The flask was fitted with a condenser and the heterogeneous mixture was heated at 115ºC until the starting methyl ester **B** was fully consumed (12-36 h), as judged by TLC. The mixture was allowed to cool to room temperature and concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (eluent Et_2O/Hexane1:9 to 2:8) to yield the pure keto-ester **2**.



Scheme S1: Synthesis of cyclic *tert*-butyl-ketoesters **2**.

C. Catalyst Screening and Optimization Studies for the Base Catalyzed Addition

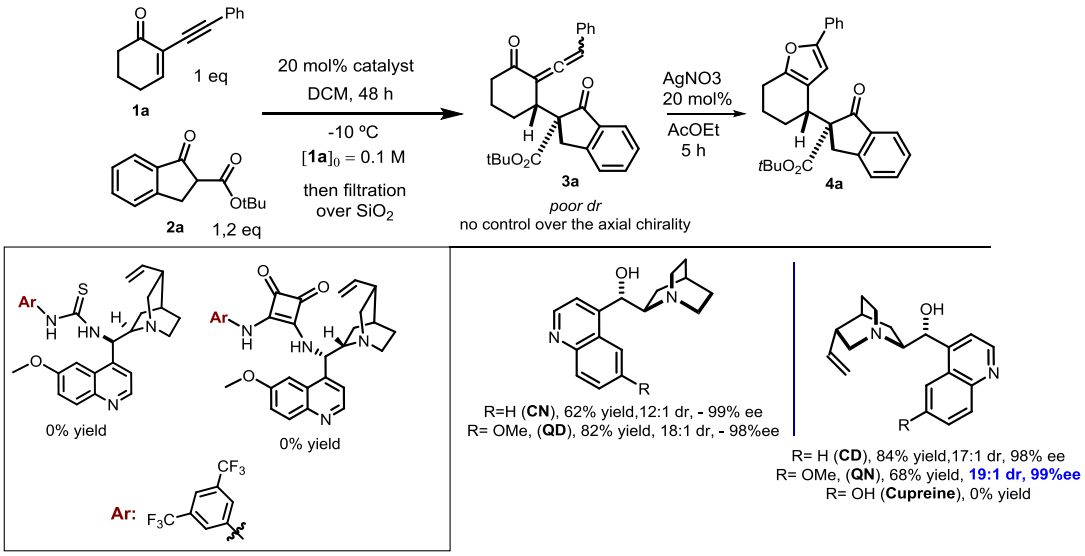
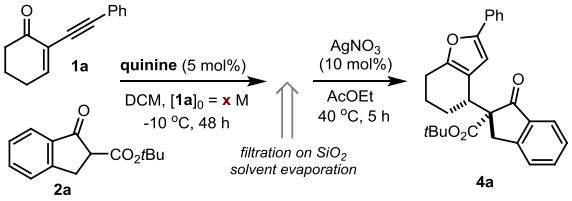


Figure S1: General Base Catalysts Screening; the minor diastereoisomer **5a** is not shown

Table S1. Effect of the concentration on the quinine-catalyzed reaction[a]



entry	x (M)	% yield[b]	dr[c]	% ee
1	0.1	66	19:1	99
2	0.2	76	19:1	99
3	**0.5**	89	19:1	99

[a] Reactions performed on a 0.05 mmol scale using 1.2 equiv of **2a**. After 48 hours, the 4,5'-addition was quenched by filtration through a pad of silica. Upon evaporation of the solvent, the cycloisomerization of the intermediate **3a** was conducted by dissolving the crude residue in 0.5 mL of AcOEt and adding 10 mol% of $AgNO_3$. [b] Yield of the isolated products **4a**. [c] Diastereomeric ratio determined by ^1H NMR analysis of the crude mixture upon cycloisomerization.

D. Catalyst Screening and Optimization Studies for the PTC-mediated Addition

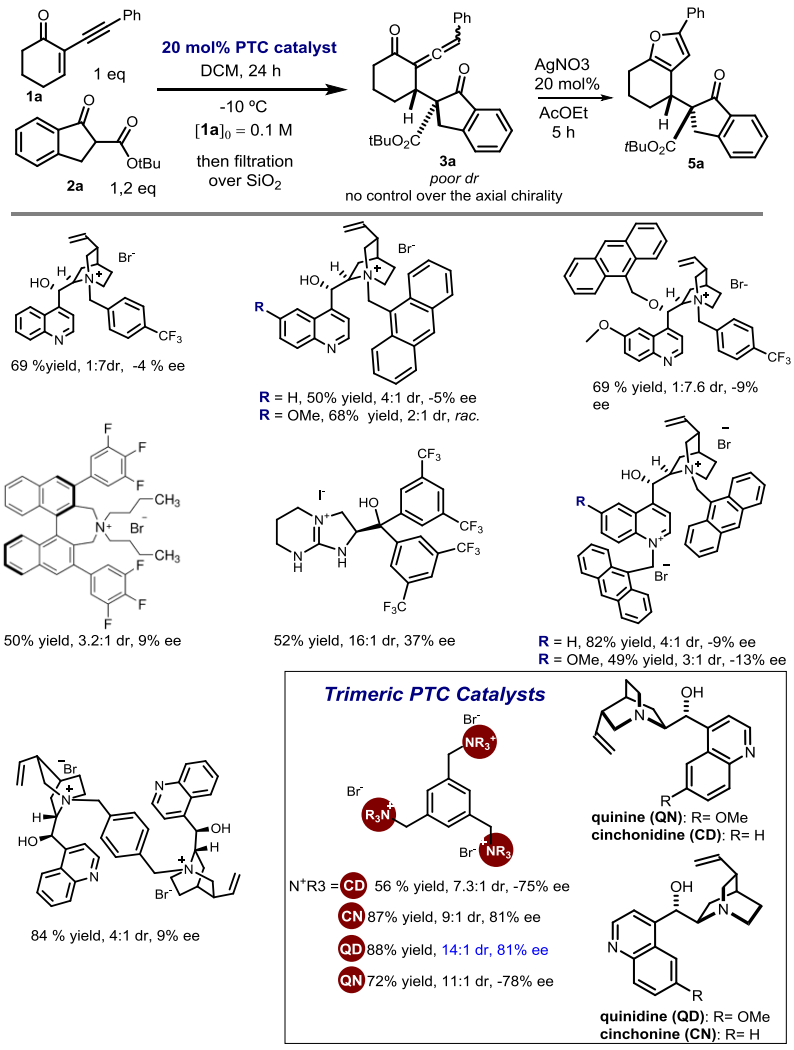
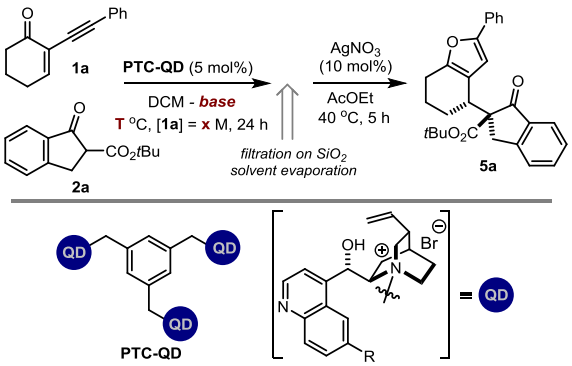


Figure S2: PTC Catalysts Screening; the minor diastereoisomer **4a** is not shown

Table S2. Refinements of the Conditions for the PTC-mediated Addition[a]



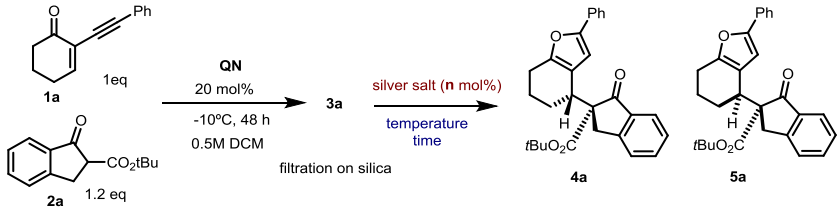
entry	base	T (°C)	**x** (M)	% yield[b]	dr[c]	% ee
1	33% aq K_2CO_3	-10	0.1	72	19:1	79
2	10% aq K_2CO_3	-10	0.1	63	17:1	79
3	66% aq Cs_2CO_3	-10	0.1	80	18:1	68
4	10% aq Cs_2CO_3	-10	0.1	50	9:1	75
5	33% aq K_2CO_3	-10	**0.25**	89	19:1	83
6	**33% aq K_2CO_3**	**-20**	**0.25**	**87**	**19:1**	**87**

[a] Reactions performed on a 0.05 mmol scale using 1.2 equiv of **2a**. After 24 hours, the 4,5'-addition was quenched by filtration through a pad of silica. Upon evaporation of the solvent, the cycloisomerization of the intermediate **3a** was conducted by dissolving the crude residue in 0.5 mL of AcOEt and adding 10 mol% of $AgNO_3$. [b] Yield of the isolated products **5a**. [c] Diastereomeric ratio determined by ^{1}H NMR analysis of the crude mixture upon cycloisomerization.

Additional comment: Other solvents (hexane, Et_2O, THF, toluene, MTBE), tested under the reaction conditions detailed in entry 5, provided ee values inferior than 10%.

E. Optimization of the Marshall conditions for the Silver-Catalyzed Cyclisation

Table S3. Optimizing the Silver-Catalyzed Cyclization.

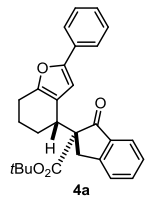


entry	Silver salt	**n** mol%	solvent	time (h)	T (°C)	Degradation **3a**	% conv **3a** to furan[a]
1	$AgNO_3$	5	acetone	14	25	no	20
2	$AgSbF_6$	5	acetone	14	25	no	5
3	Ag_2O	5	acetone	14	25	yes	45
4	Ag-imidazolate/PPh_3	5	acetone	14	25	no	0
5	$AgNO_3$	10	acetone	3	40	no	75
6	$AgNO_3$	10	toluene	3	40	no	85
7	$AgNO_3$	10	AcOEt	3	40	no	>95
8	$AgNO_3$	5	AcOEt	2	70	yes	>95

[a] Determined by ^{1}H NMR analysis of the crude mixture upon cycloisomerization.

F. General Procedures for the Base-Catalyzed Process (*Table 2 of the main manuscript*)

All the reactions were carried out in DCM (synthesis grade, >99%), without any precaution to exclude air and moisture (open air chemistry on the benchtop). An ordinary vial equipped with a Teflon-coated stir bar and a plastic screw cap was charged with the 2-alkynyl enone **1** (0.2 mmol), the ketoester **2** (1.2 eq) and quinine (3.2 mg, 5 mol%, 0.05 eq), and cooled down to -10ºC. Dichloromethane was then added (0.4 mL, $[\mathbf{1}]_0$ =0.5 M), the vial was sealed and stirring continued over 48 hours. The reaction was diluted with a 1:1 mixture of hexane and ethyl acetate and filtered through a short pad of silica, then rinsed with the same mixture. Solvents were removed under reduced pressure, and replaced by ethyl acetate (2.0 mL, 0.1 M). A solution of silver nitrate (50 mg/mL in MeCN) was then added (68µL, 3.4 mg, 10 mol%, 0.1 eq), the flask covered with an aluminum foil, and the solution was heated at 40ºC for 5 h. Solvent was then removed under reduced pressure, and the crude mixture was analyzed by ^{1}H NMR spectroscopy to determine the distereomeric ratio (dr) of the reaction. The crude material was purified by column chromatography on silica gel to afford the pure annulated furan products **4**.



4a

***tert*-butyl (*R*)-1-oxo-2-((*R*)-2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-2,3-dihydro-1H-indene-2-carboxylate 4a.** Following the general procedure, 2-alkynyl enone **1a** (39 mg, 0.2 mmol, 1 eq) and ketoester **2a** (55 mg, 1,2 eq) were reacted to afford, after column chromatography (eluent toluene/hexane 8:2), the product **4a** (71 mg, 0.166 mmol, 83% yield) as a white solid (19:1 mixture of inseparable diastereoisomers, ee_{major} = 99%).

When using quinidine as the catalyst of the 4,5'-addition reaction, the opposite enantiomer of the annulated furan **4a** was obtained in 82% yield, 18:1 dr, and 98% ee.

Major diastereoisomer **4a**:

IR (neat): 2933, 2861, 1738, 1704 cm^{-1}.

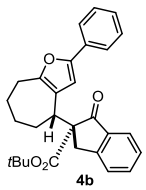
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (ddd, *J* = 7.8, 1.3, 0.7 Hz, 1H), 7.65 – 7.58 (m, 3H), 7.45 (dt, *J* = 7.7, 0.9 Hz, 1H), 7.43 – 7.34 (m, 3H), 7.28 – 7.22 (m, 1H), 6.45 (s, 1H), 3.92 – 4.09 (m, 1H), 3.70 (d, *J* = 17.9 Hz, 1H), 2.86 (d, *J* = 17.9 Hz, 1H), 2.75 – 2.65 (m, 1H), 2.62 – 2.50 (m, 1H), 2.01 – 1.90 (m, 1H), 1.84 – 1.70 (m, 2H), 1.55 (s, 9H), 0.89 – 0.78 (m, 1H).

^{13}C NMR: (125 MHz, $CDCl_3$) δ 22.4, 23.5, 25.4, 28.2, 33.6, 38.4, 66.0, 82.6, 105.0, 120.6, 123.6, 124.8, 126.5, 127.2, 127.8, 129.0, 131.4, 135.6, 136.0, 152.2, 152.7, 155.0, 170.1, 202.3.

HRMS: Calcd for $(C_{28}H_{28}O_4Na)^+$: 451.1880; found: 451.1875.

HPLC: Analysis on a Daicel Chiralpak IA-3, Hex/IPA 96:4, 0.7 mL/min, 20ºC, λ = 310 nm. τ_{major} = 8.4 min, τ_{minor} = 11.7 min, 99% ee, $[\alpha]^{26}_D$ = -219.2 (*c* = 1.0, $CHCl_3$, 19:1 dr, 99% ee)

***ent*-4a**: $[\alpha]^{26}_D$ = +206.8 (*c* = 1.0, $CHCl_3$, 18:1 dr, 98% ee)



4b

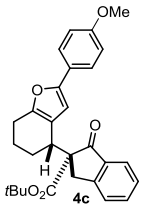
***tert*-butyl (*R*)-1-oxo-2-((*R*)-2-phenyl-5,6,7,8-tetrahydro-4H-cyclohepta[b]furan-4-yl)-2,3-dihydro-1H-indene-2-carboxylate 4b.** Following the general procedure, 2-alkynyl enone **1b** (42 mg, 0.2 mmol, 1 eq) and ketoester **2a** (55 mg, 1,2 eq) were reacted to afford, after column chromatography (eluent toluene/hexane 8:2), the product **4b** (66 mg, 0.15 mmol, 75% yield) as a white solid (12:1 mixture of inseparable diastereoisomers, ee_{major} = 97%).

Major diastereoisomer **4b**:

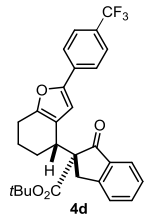
IR (neat): 2926, 2851, 1740, 1704 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.62 (td, *J* = 7.4, 1.2 Hz, 1H), 7.60 – 7.56 (m, 2H), 7.51 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.39 (ddd, *J* = 7.8, 7.1, 1.0 Hz, 1H), 7.37 – 7.32 (m, 2H), 7.20 (ddt, *J* = 7.8, 7.0, 1.2 Hz, 1H), 6.40 (s, 1H), 4.00 (d, *J* = 17.4 Hz, 1H), 3.92 (dt, *J* = 10.9, 1.5 Hz, 1H), 3.18 (d, *J* = 17.4 Hz, 1H), 2.96 – 2.65 (m, 1H), 2.86 – 2.77 (m, 1H), 1.97 – 1.82 (m, 2H), 1.71 – 1.59 (m, 1H), 1.50 – 1.42 (m, 2H), 1.41 (s, 9H), 1.17 (dtd, *J* = 13.7, 11.4, 2.4 Hz, 1H).

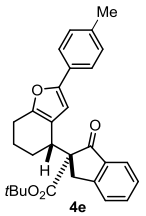
^{13}C NMR: (125 MHz, $CDCl_3$) δ 202.6, 169.6, 155.1, 154.1, 149.8, 135.9, 135.7, 131.4, 128.9, 127.9, 127.0, 126.6, 124.9, 124.3, 123.4, 106.8, 82.6, 67.0, 41.6, 34.1, 30.2, 30.1, 28.8, 28.0, 26.0.
HRMS: Calcd for $(C_{29}H_{31}O_4)^+$: 443.2217; found: 443.2216.
HPLC: Analysis on a Daicel Chiralpak IA-3 column, eluent hex/DCM 85:15, flow rate 1.0 mL/min, 20ºC, λ = 290 nm. τ_{major} = 5.4 min, τ_{minor} = 5.9 min, 97% ee. $[\alpha]^{26}_D$ = -211.5 (*c* = 1.0, $CHCl_3$, 12:1 dr, 97% ee)



***tert*-butyl (*R*)-2-((*R*)-2-(4-methoxyphenyl)-4,5,6,7-tetrahydrobenzofuran-4-yl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 4c.** Following the general procedure, 2-alkynyl enone **1c** (45 mg, 0.2 mmol, 1 eq) and ketoester **2a** (55 mg, 1.2 eq) were reacted to afford, after column chromatography (eluent MTBE/hexane 1:9), the product **4c** (76 mg, 0.166 mmol, 83% yield) as a white solid (19:1 mixture of inseparable diastereoisomers, ee_{major} = 99%).
Major diastereoisomer **4c**:
IR (neat): 2934, 2847, 1739, 1704 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.60 (td, *J* = 7.5, 1.2 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.47 – 7.42 (m, 1H), 7.39 (ddd, *J* = 7.7, 7.2, 1.0 Hz, 1H), 6.96 – 6.88 (m, 2H), 6.31 (s, 1H), 4.06 – 3.95 (m, 1H), 3.85 (s, 3H), 3.69 (d, *J* = 17.9 Hz, 1H), 2.86 (d, *J* = 17.9 Hz, 1H), 2.72 – 2.62 (m, 1H), 2.62 – 2.40 (m, 1H), 1.98 – 1.85 (m, 1H), 1.81 – 1.68 (m, 2H), 1.55 (s, 9H), 0.89 – 0.76 (m, 1H).
^{13}C NMR: (75 MHz, $CDCl_3$) δ 202.3, 170.1, 159.1, 155.1, 152.3, 151.9, 136.0, 135.6, 127.8, 126.5, 125.0, 124.8, 124.5, 120.4, 114.4, 103.4, 82.6, 66.0, 55.6, 38.5, 33.6, 28.2, 25.4, 23.4, 22.4.
HRMS: Calcd for $(C_{29}H_{31}O_5)^+$: 459.2166, found: 443.2161.
HPLC: Analysis on a Daicel Chiralpak IA-3 column, eluent Hex/IPA 96:4, flow rate 1.5 mL/min, 20ºC, λ = 290 nm. τ_{major} = 4.7 min, τ_{minor} = 6.9 min, 99% ee. $[\alpha]^{26}_D$ = -293.3 (*c* = 1.0, $CHCl_3$, 19:1 dr, 99% ee).

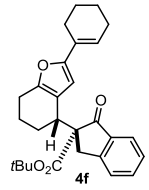


***tert*-butyl (*R*)-1-oxo-2-((R)-2-(4-(trifluoromethyl)phenyl)-4,5,6,7-tetrahydrobenzofuran-4-yl)-2,3-dihydro-1H-indene-2-carboxylate 4d.** Following the general procedure, 2-alkynyl enone **1d** (53 mg, 0.2 mmol, 1 eq) and ketoester **2a** (55 mg, 1,2 eq) were reacted to afford, after column chromatography (eluent toluene/hexane 8:2), the product **4d** (89 mg, 0.18 mmol, 90% yield) as a white solid (19:1 mixture of inseparable diastereoisomers, ee_{major} >99% ee).
Major diastereoisomer **4d**:
IR (neat): 2934, 2861, 1738, 1705, 1323 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (dt, *J* = 7.7, 0.9 Hz, 1H), 7.69 – 7.64 (m, 2H), 7.62 – 7.56 (m, 3H), 7.43 (dt, *J* = 7.7, 0.9 Hz, 1H), 7.40 – 7.34 (m, 1H), 6.54 (s, 1H), 4.05 – 3.92 (m, 1H), 3.67 (d, *J* = 17.8 Hz, 1H), 2.83 (d, *J* = 17.8 Hz, 1H), 2.74 – 2.63 (m, 1H), 2.56 (m, 1H), 1.99 – 1.88 (m, 1H), 1.79 – 1.68 (m, 2H), 1.52 (s, 9H), 0.82 (tdd, *J* = 13.3, 11.0, 3.1 Hz, 1H).
^{13}C NMR: (126 MHz, $CDCl_3$) δ 202.1, 170.1, 154.9, 154.1, 150.8, 136.0, 135.7, 134.5, 128.7 (q, J_{C-F} = 32 Hz) 127.9, 127.8, 126.0 (q, *J* = 4 Hz), 125.6, 125.0 (d, J_{C-F} = 205 Hz), 123.5, 121.0, 107.1, 82.7, 65.9, 38.3, 33.6, 28.1, 25.3, 23.5, 22.3.
HRMS: Calcd for $(C_{29}H_{27}F_3NaO_4)^+$: 519.1754, found 519.1776.
HPLC: Analysis on a Daicel Chiralpak IA-3 column, eluent Hex/IPA 96:4, flow rate 1.0 mL/min, 20ºC, λ = 290 nm. τ_{major} = 5.8 min, τ_{minor} = 7.2 min, >99% ee. $[\alpha]^{26}_D$ = -310.5 (*c* = 1.0, $CHCl_3$, 19:1 dr, >99% ee).



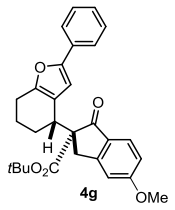
***tert*-butyl (*R*)-1-oxo-2-((*R*)-2-(p-tolyl)-4,5,6,7-tetrahydrobenzofuran-4-yl)-2,3-dihydro-1H-indene-2-carboxylate 4e.** Following the general procedure, 2-alkynyl enone **1e** (53 mg, 0.2 mmol, 1 eq) and ketoester **2a** (55 mg, 1,2 eq) were reacted to afford, after column chromatography (eluent toluene/hexane 8:2), the product **4e** (74 mg, 0.166 mmol, 83% yield) as a white solid (19:1 mixture of inseparable diastereoisomers, ee_{major} = 99%).

Major diastereoisomer **4e**:
IR (neat): 2926, 2860, 1739, 1705 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (dt, *J* = 7.7, 0.9 Hz, 1H), 7.58 (td, *J* = 7.5, 1.2 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.42 (dt, *J* = 7.7, 0.9 Hz, 1H), 7.37 (ddd, *J* = 7.8, 7.1, 1.0 Hz, 1H), 7.20 – 7.12 (m, 2H), 6.36 (s, 1H), 3.98 (m, 1H), 3.67 (d, *J* = 17.9 Hz, 1H), 2.84 (d, *J* = 17.9 Hz, 1H), 2.71 – 2.61 (m, 1H), 2.61 – 2.48 (m, 1H), 2.35 (s, 3H), 1.97 – 1.86 (m, 1H), 1.80 – 1.66 (m, 2H), 1.52 (s, 9H), 0.86 – 0.73 (m, 1H).
^{13}C NMR: (126 MHz, $CDCl_3$) δ 202.3, 170.1, 155.1, 152.5, 152.3, 137.0, 136.0, 135.6, 129.7, 128.7, 127.8, 126.5, 124.8, 123.6, 120.5, 104.3, 82.6, 66.0, 38.5, 33.6, 28.2, 25.4, 23.5, 22.4, 21.6.
HRMS: Calcd for $(C_{29}H_{31}O_4)^+$: 443.2217; found 443.2215.
HPLC: Analysis on a Daicel Chiralpak IA-3 column, eluent Hex/IPA 98:2, flow rate 1.0 mL/min, 30ºC, λ = 290 nm. τ_{major} = 6.6 min, τ_{minor} = 10.2 min, 99% ee. $[\alpha]^{26}_D$ = -280.13 (*c* = 1.0, $CHCl_3$, 19:1 dr, 99% ee).



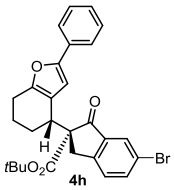
***tert*-butyl (*R*)-2-((*R*)-2-(cyclohex-1-en-1-yl)-4,5,6,7-tetrahydrobenzofuran-4-yl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 4f.** Following the general procedure, 2-alkynyl enone **1f** (41 mg, 0.2 mmol, 1 eq) and ketoester **2a** (55 mg, 1,2 eq) were reacted to afford, after column chromatography (eluent toluene/hexane 8:2), the product **4f** (25 mg, 0.05 mmol, 25% yield) as a white solid (19:1 mixture of inseparable diastereoisomers, ee_{major} = 95%).

Major diastereoisomer **4f**:
IR (neat): 2926, 2855, 1739, 1705 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.41 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.38 – 7.32 (m, 1H), 6.23 (dt, *J* = 4.2, 2.4 Hz, 1H), 5.91 (s, 1H), 3.99 – 3.84 (m,1H), 3.63 (d, *J* = 17.8 Hz, 1H), 2.78 (d, *J* = 17.9 Hz, 1H), 2.57 (dd, *J* = 16.8, 5.9 Hz, 1H), 2.57 – 2.41 (m, 1H), 2.26 – 2.14 (m, 4H), 1.95 – 1.81 (m, 1H), 1.77 – 1.60 (m, 6 H), 1.49 (s, 9H), 0.81 – 0.66 (m, 1H).
^{13}C NMR: (126 MHz, $CDCl_3$) δ 201.3, 169.0, 154.1, 152.9, 150.5, 135.0, 134.5, 126.8, 126.5, 125.5, 123.8, 120.7, 118.6, 102.6, 81.5, 65.1, 37.5, 32.6, 27.2, 24.5, 24.4, 24.2, 22.4, 21.8, 21.7, 21.4.
HRMS: Calcd for $(C_{28}H_{32}NaO_4)^+$: 455.2193; found: 455.2198.
HPLC: Analysis on a Daicel Chiralpak IA-3 column, eluent hex/DCM/IPA 89.5:15:0.5, flow rate 0.7 mL/min, 20ºC, λ = 254 nm. τ_{major} = 6.9 min, τ_{minor} = 7.8 min, 95% ee. $[\alpha]^{26}_D$ = -139.6 (*c* = 1.0, $CHCl_3$, 19:1 dr, 95% ee).

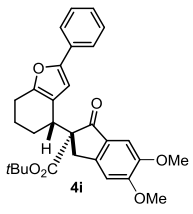


***tert*-butyl (*R*)-5-methoxy-1-oxo-2-((*R*)-2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-2,3-dihydro-1H-indene-2-carboxylate 4g:** Following the general procedure, 2-alkynyl enone **1a** (39 mg, 0.2 mmol, 1 eq) and ketoester **2g** (63 mg, 1,2 eq) were reacted to afford, after column chromatography (eluent AcOEt/hexane 1:9), the product **4g** (57 mg, 0.124 mmol, 62% yield) as a colorless oil (19:1 mixture of inseparable diastereoisomers, ee_{major} = 99%).
Major diastereoisomer **4g**:
IR (neat): 2932, 2851, 1733, 1699, 1597 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.6 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.37 (dd, *J* = 8.4, 7.1 Hz, 2H), 7.27 – 7.21 (m, 1H), 6.92 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.86 (d, *J* = 2.2 Hz, 1H), 6.44 (s, 1H), 4.03 – 3.94 (m, 1H), 3.88 (s, 3H), 3.63 (d, *J* = 17.9 Hz, 1H), 2.79 (d, *J* = 17.9 Hz, 1H), 2.74 – 2.64 (m, 1H), 2.64 – 2.50 (m, 1H), 2.00 – 1.89 (m, 1H), 1.83 – 1.70 (m, 2H), 1.55 (s, 9 H), 0.83 (tdd, *J* = 13.3, 10.0, 2.6 Hz, 1H).
^{13}C NMR: (126 MHz, $CDCl_3$) δ 200.1, 170.4, 166.1, 158.0, 152.7, 152.2, 131.4, 129.2, 129.0, 127.2, 126.5, 123.6, 120.7, 116.0, 109.5, 105.0, 82.5, 66.2, 56.0, 38.2, 33.6, 28.2, 25.3, 23.5, 22.4.
HRMS: Calcd for $(C_{29}H_{30}NaO_5)^+$: 481.1985; found: 481.1988.
HPLC: Analysis on a Daicel Chiralpak AD-H column, eluent Hex/IPA 97.3, flow rate 1.5 mL/min, 30ºC, λ = 310 nm. τ_{major} = 6.9 min, τ_{minor} = 20.1 min, 99% ee. $[\alpha]^{26}_D$ = -282.53 (*c* = 1.0, $CHCl_3$, 19:1 dr, 99% ee).

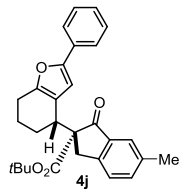


***tert*-butyl (*R*)-6-bromo-1-oxo-2-((*R*)-2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-2,3-dihydro-1H-indene-2-carboxylate 4h.** Following the general procedure, 2-alkynyl enone **1a** (39 mg, 0.2 mmol, 1 eq) and ketoester **2h** (63 mg, 1,2 eq) were reacted to afford, after column chromatography (eluent toluene/hexane 8:2), the product **4h** (83 mg, 0.164 mmol, 82% yield) as a white solid (19:1 mixture of inseparable diastereoisomers, ee_{major} = 98%).
Major diastereoisomer **4h**:
IR (neat): 2928, 2854, 1740, 1706 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 1.9 Hz, 1H), 7.68 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.37 – 7.33 (m, 2H), 7.31 (dd, *J* = 8.1, 0.8 Hz, 1H), 7.24 – 7.20 (m, 1H), 6.39 (s, 1H), 3.90 – 3.99 (m, 1H), 3.60 (d, *J* = 18.0 Hz, 1H), 2.77 (d, *J* = 18.0 Hz, 1H), 2.67 (dd, *J* = 16.6, 5.7 Hz, 1H), 2.62 – 2.50 (m, 1H), 1.96 – 1.84 (m, 1H), 1.80 – 1.66 (m, 2H), 1.52 (s, 9H), 0.79 (m,1H).
^{13}C NMR: (126 MHz, $CDCl_3$) δ 200.9, 169.6, 153.6, 152.8, 152.3, 138.3, 137.8, 131.3, 129.0, 128.1, 127.7, 127.3, 123.6, 122.0, 120.3, 104.8, 83.0, 66.6, 38.5, 33.3, 28.2, 25.4, 23.4, 22.4.
HRMS: Calcd for $(C_{28}H_{27}BrNaO_4)^+$: 529.0985; found: 529.0986.
HPLC: Analysis on a Daicel Chiralpak IA-3 column, eluent hex/IPA 97.3, flow rate 0.7 mL/min, 30ºC, λ = 310 nm. τ_{major} = 5.4 min, τ_{minor} = 7.3 min, 98% ee. $[\alpha]^{26}_D$ = -157.1 (*c* = 1.0, $CHCl_3$, 19:1 dr, 98% ee).
The relative and absolute configuration for **4h** was unambiguously inferred by anomalous dispersion X-ray crystallographic analysis, see X-ray Crystallographic Data section.



***tert*-butyl (*R*)-5,6-dimethoxy-1-oxo-2-((*R*)-2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-2,3-dihydro-1H-indene-2-carboxylate 4i:** Following the general procedure, 2-alkynyl enone **1a** (39 mg, 0.2 mmol, 1 eq) and ketoester **2i** (70 mg, 1,2 eq) were reacted to afford, after column chromatography (eluent AcOEt/hexane 2:8), the product **4i** (65 mg, 0.134 mmol, 67% yield) as a white solid (19:1 mixture of inseparable diastereoisomers, ee_{major} = 99%).
Major diastereoisomer **4i**:
IR (neat): 2936, 2860, 1733, 1697, 1499 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.56 (m, 2H), 7.38 – 7.31 (m, 2H), 7.24 – 7.19 (m, 1H), 7.16 (s, 1H), 6.82 (s, 1H), 3.98 – 3.94 (m, 2H), 3.92 (d, *J* = 13.2 Hz, 6H), 3.55 (dd, *J* = 17.6, 0.8 Hz, 1H), 2.72 (dd, *J* = 17.5, 0.8 Hz, 1H), 2.67 (dd, *J* = 17.0, 5.2 Hz, 1H), 2.62 – 2.49 (m, 1H), 1.96 – 1.89 (m, 1H), 1.80 – 1.68 (m, 2H), 1.53 (s, 9H), 0.85 – 0.74 (m, 1H).
^{13}C NMR: (126 MHz, $CDCl_3$) δ 200.6, 170.4, 156.3, 152.3, 152.1, 150.6, 149.9, 131.4, 128.9, 128.6, 127.2, 123.6, 120.8, 107.3, 105.04, 105.03, 82.5, 66.3, 56.5, 56.4, 38.1, 33.3, 28.2, 25.3, 23.5, 22.4.
HRMS: Calcd for $(C_{30}H_{32}NaO_6)^+$: 511.2091, found 511.2095.

HPLC: Analysis on a Daicel Chiralpak IA-3 column, eluent Hex/IPA 97.3, flow rate 1.2 mL/min, 30ºC, λ = 310 nm. τ_{major} = 7.90 min, τ_{minor} = 17.38 min, 99% ee. $[\alpha]^{26}_{D}$ = -291.55 (*c* = 1.0, $CHCl_3$, 19:1 dr, 99% ee).



***tert*-butyl (*R*)-5,6-dimethoxy-1-oxo-2-((*R*)-2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-2,3-dihydro-1H-indene-2-carboxylate 4j:** Following the general procedure, 2-alkynyl enone **1a** (39 mg, 0.2 mmol, 1 eq) and ketoester **2j** (59 mg, 1,2 eq) were reacted to afford, after column chromatography (eluent toluene/hexane 8:2), the product **4j** (77 mg, 0.174 mmol, 87% yield) as a white solid (20:1 mixture of inseparable diastereoisomers, ee_{major} = 97%). Major diastereoisomer **4j**:

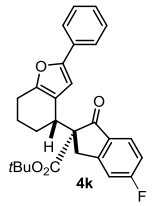
IR (neat): 2926, 2859, 1738, 1704 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 3H), 7.40 (ddd, *J* = 7.8, 1.8, 0.8 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.31 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.24 – 7.19 (m, 1H), 6.43 (s, 1H), 3.97 (dddd, *J* = 11.3, 4.5, 2.9, 1.5 Hz, 1H), 3.62 (d, *J* = 17.8 Hz, 1H), 2.78 (d, *J* = 17.7 Hz, 1H), 2.71 – 2.62 (m, 1H), 2.50 – 2.60 (m, 1H), 2.40 (s, 3H), 1.97 – 1.86 (m, 1H), 1.79 – 1.64 (m, 2H), 1.53 (s, 9H), 0.87 – 0.74 (m, 1H).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 202.3, 170.2, 152.7, 152.4, 152.2, 137.8, 136.9, 136.2, 131.4, 129.0, 127.2, 126.2, 124.7, 123.6, 120.6, 105.0, 82.5, 66.3, 38.4, 33.2, 28.2, 25.3, 23.5, 22.4, 21.4.

HRMS: Calcd for $(C_{29}H_{30}NaO_4)^+$: 465.2036, found 465.2045.

HPLC: Analysis on a Daicel Chiralpak IA-3 column, eluent hex/DCM 85.15, flow rate 0.7 mL/min, 30ºC, λ = 310 nm. τ_{major} = 7.8 min, τ_{minor} = 9.4 min, 97% ee. $[\alpha]^{26}_{D}$ = -282.53 (*c* = 1.0, $CHCl_3$, 19:1 dr, 97% ee).



***tert*-butyl (*R*)-5,6-dimethoxy-1-oxo-2-((*R*)-2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-2,3-dihydro-1H-indene-2-carboxylate 4k.** Following the general procedure, 2-alkynyl enone **1a** (39 mg, 0.2 mmol, 1 eq) and ketoester **2k** (60 mg, 1,2 eq) were reacted to afford, after column chromatography (eluent toluene/hexane 8:2), the product **4k** (78 mg, 0.175 mmol, 88% yield) as a white solid (19:1 mixture of inseparable diastereoisomers, ee_{major} = 98%).
Major diastereoisomer **4k**:

IR (neat): 2929, 2854, 1739, 1706, 1593 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.73 (m, 1H), 7.62 – 7.54 (m, 2H), 7.40 – 7.31 (m, 2H), 7.25 – 7.18 (m, 1H), 7.11 – 7.04 (m, 2H), 6.40 (s, 1H), 3.98 (dtd, *J* = 11.3, 2.9, 1.5 Hz, 1H), 3.71 – 3.61 (m, 1H), 2.82 (d, *J* = 18.1 Hz, 1H), 2.72 – 2.63 (m, 1H), 2.62 – 2.48 (m, 1H), 1.98 – 1.88 (m, 1H), 1.80 – 1.67 (m, 2H), 1.53 (s, 9H), 0.86 – 0.73 (m, 1H).

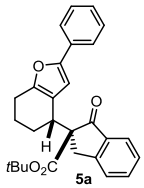
^{13}C NMR: (126 MHz, $CDCl_3$) δ 200.3, 169.8, 167.8 (d, J_{C-F} = 257 Hz), 158.0 (d, J_{C-F} = 11.3 Hz) 152.7, 152.3, 132.4 (d, J_{C-F} = 1.3 Hz) 131.3, 129.0, 127.3, 127.3 (d, J_{C-F} = 10.1 Hz) 123.6, 120.3, 116.3 (d, J_{C-F} = 21.4 Hz),113.2 (d, J_{C-F} = 21.4 Hz), 104.8, 82.8, 66.4, 38.3, 33.5, 28.1, 25.4, 23.4, 22.4.

HRMS: Calcd for $(C_{28}H_{27}FNaO_4)^+$: 469.1786; found: 469.1785.

HPLC: Analysis on a Daicel Chiralpak IA-3 column, eluent hex/DCM 85.15, flow rate 0.7 mL/min, 30ºC, λ = 310 nm. τ_{major} = 8.3 min, τ_{minor} = 10.0 min, 98% ee. $[\alpha]^{26}_{D}$ = -265.58 (*c* = 1.0, $CHCl_3$, 19:1 dr, 98% ee).

G. General Procedures for the PTC-mediated Process (*Table 3 in the main manuscript*)

All the reactions were carried out without any precaution to exclude air and moisture (open air chemistry on the benchtop). An ordinary vial equipped with a Teflon-coated stir bar and a plastic screw cap was charged with the 2-alkynyl enone **1** (0.2 mmol), the ketoester **2** (1.2 eq) and the quinidine-derived phase-transfer catalyst **PTC-QD** (13.4 mg, 0.01 mmol, 5 mol%, 0.05 eq), and cooled down to -20ºC. Dichloromethane (0.8 mL, 0.25M) was added followed by 33% aqueous potassium carbonate (160 μL), the vial was sealed and stirring continued over 24 hours. The reaction was diluted with a 1:1 mixture of hexane and ethyl acetate and filtered on a short pad of silica, then rinsed with the same mixture. Solvents were removed under reduced pressure, and replaced by ethyl acetate (2.0 mL, 0.1 M). A solution of silver nitrate (50 mg/mL in MeCN) was then added (68μL, 3.4 mg, 10 mol%, 0.1 eq), the flask covered with an aluminum foil, and the solution was heated at 40ºC for 5 h. Solvent was then removed under reduced pressure, and the crude mixture was analyzed by ^{1}H NMR spectroscopy to determine the diastereomeric ratio (dr) of the reaction. The crude material was purified by column chromatography on silica gel to afford the pure annulated furan products **5**.



***tert*-butyl (*S*)-1-oxo-2-((*R*)-2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-2,3-dihydro-1H-indene-2-carboxylate 5a.** Following the general procedure, 2-alkynyl enone **1a** (39 mg, 0.2 mmol, 1 eq) and ketoester **2a** (55 mg, 1,2 eq) were reacted to afford, after column chromatography (eluent toluene/hexane 8:2), the product **4a** (76.5 mg, 0.178 mmol, 89% yield) as a white solid (19:1 mixture of inseparable diastereoisomers, 87% ee).

When using the quinine derivative **PTC-QN** (10 mol%, 48h of reaction at -20ºC) as the catalyst of the 4,5'-addition reaction, the opposite enantiomer of the annulated furan **5a** (***ent*-5a**) was obtained in 73% yield, 13:1 dr, and 86% ee.

Major diastereoisomer **5a**:

IR (neat): 2931, 2859, 1738, 1709 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 1H), 7.54 (td, *J* = 7.4, 1.2 Hz, 1H), 7.40 – 7.33 (m, 4H), 7.23 (ddd, *J* = 8.0, 7.1, 1.4 Hz, 2H), 7.12 (td, *J* = 7.3, 1.3 Hz, 1H), 5.91 (s, 1H), 4.03 –3.91 (m, 1H), 3.68 (d, *J* = 16.7 Hz, 1H), 2.85 (d, *J* = 16.7 Hz, 1H), 2.74 – 2.57 (m, 2H), 2.12 – 1.96 (m, 2H), 1.85 – 1.75 (m, 1H), 1.51 – 1.39 (m, 1H), 1.43 (s, 9H).

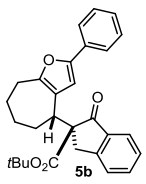
^{13}C NMR: (125 MHz, $CDCl_3$) δ 202.6, 168.3, 154.7, 152.7, 151.8, 136.0, 135.5, 131.2, 128.8, 127.8, 127.0, 126.8, 124.6, 123.6, 118.8, 105.2, 82.6, 67.9, 38.5, 32.8, 28.1, 26.9, 23.6, 22.4.

HRMS: Calcd for $(C_{28}H_{28}O_4Na)^+$: 451.1880; found: 451.1878.

HPLC: Analysis on a Daicel Chiralpak IA-3 column, eluent hex/DCM 80/20, flow rate 1.0 mL/min, 30ºC, λ = 310 nm. τ_{minor} = 6.3 min, τ_{major} = 6.7 min, 87% ee. $[\alpha]^{26}_D$ = -21.6 (*c* = 1.0, $CHCl_3$, 19:1 dr, 87% ee).

***ent*-5a**: $[\alpha]^{26}_D$ = +26.3 (*c* = 1.0, $CHCl_3$, 13:1 dr, 86% ee)

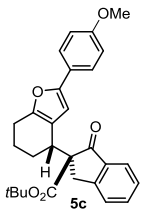
The relative and absolute configuration for **5a** was unambiguously inferred by anomalous dispersion X-ray crystallographic analysis, see X-ray Crystallographic Data section.



***tert*-butyl (*S*)-1-oxo-2-((*R*)-2-phenyl-5,6,7,8-tetrahydro-4H-cyclohepta[b]furan-4-yl)-2,3-dihydro-1H-indene-2-carboxylate 5b.** Following the general procedure, 2-alkynyl enone **1b** (42 mg, 0.2 mmol, 1 eq) and ketoester **2a** (55 mg, 1,2 eq) were reacted to afford, after column chromatography (eluent toluene/hexane 8:2), the product **5b** (72mg, 0.163 mmol, 81%) as a colorless oil (9.5:1 mixture of unseparable diastereoisomers, 93% ee).

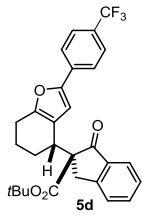
Major diastereoisomer:

IR (neat): 2926, 2854, 1738, 1712 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (dt, *J* = 7.6, 0.9 Hz, 1H), 7.55 (td, *J* = 7.5, 1.2 Hz, 1H), 7.44 (dt, *J* = 7.7, 0.9 Hz, 1H), 7.37 – 7.31 (m, 3H), 7.25 – 7.21 (m, 2H), 7.13 – 7.09 (m, 1H), 6.09 (s, 1H), 4.06 – 3.91 (m, 1H), 3.84 (d, *J* = 16.7 Hz, 1H), 3.10 (d, *J* = 16.6 Hz, 1H), 2.90 (t, *J* = 5.9 Hz, 2H), 1.99 – 1.70 (m, 6H), 1.43 (s, 10H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ 201.9, 168.6, 154.3, 153.8, 150.2, 135.6, 135.5, 131.2, 128.8, 127.8, 126.9, 126.6, 124.8, 123.5, 122.2, 108.1, 82.6, 69.0, 40.6, 33.9, 31.1, 28.3, 28.1, 27.6, 26.1.
HRMS: Calcd for $(C_{29}H_{30}NaO_4)^+$: 465.2036; found: 465.2057.
HPLC: Analysis on a Daicel Chiralpak IA-3 column, eluent hex/DCM 85:15, flow rate 1.0 mL/min, 20ºC, λ = 290 nm. τ_{minor} = 6.9 min , τ_{major} = 7.3 min, 93% ee. $[\alpha]^{26}_D$ = -5.1 (*c* = 1.0, $CHCl_3$, 9.5:1 dr, 93% ee).



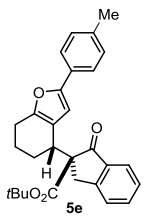
***tert*-butyl (*S*)-2-((*R*)-2-(4-methoxyphenyl)-4,5,6,7-tetrahydrobenzofuran-4-yl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 5c.** Following the general procedure, 2-alkynyl enone **1c** (45 mg, 0.2 mmol, 1 eq) and ketoester **2a** (55 mg, 1,2 eq were reacted to afford, after column chromatography (eluent MTBE/hexane 1:9), the product **5c** (80 mg, 0.174 mmol, 87 %) after column chromatography (Eluent MTBE/hexane 1:9) as a white solid (19:1 mixture of unseparable diastereoisomers, ee_{major} = 89%).

Major diastereoisomer:
IR (neat): 2934, 2854, 1737, 1709, 1499 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.6 Hz, 1H), 7.53 (td, *J* = 7.6, 1.2 Hz, 1H), 7.41 – 7.33 (m, 2H), 7.28 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 5.77 (s, 1H), 4.05 – 3.90 (m, 1H), 3.75 (s, 3H), 3.67 (d, *J* = 16.8 Hz, 1H), 2.85 (d, *J* = 16.8 Hz, 1H), 2.72 – 2.55 (m, 2H), 2.12 – 1.98 (m, 2H), 1.86 – 1.72 (m, 1H), 1.50 – 1.37 (m, 1H), 1.43 (s, 9H).
^{13}C NMR: (100 MHz, $CDCl_3$) δ 202.6, 168.3, 158.9, 154.7, 151.9, 151.8, 136.0, 135.5, 127.7, 126.7, 125.0, 124.5, 124.4, 118.7, 114.2, 103.6, 82.5, 67.9, 55.5, 38.5, 32.8, 28.1, 26.9, 23.6, 22.4.
HRMS: Calcd for $(C_{29}H_{31}O_5)^+$: 459.2166; found: 459.2171.
HPLC: Analysis on a Daicel Chiralpak IA-3 column, eluent Hex/IPA 96:4, flow rate 1.5 mL/min, 20ºC, λ = 290 nm. τ_{minor} = 9.3 min, τ_{major} = 11.4 min, 89% ee. $[\alpha]^{26}_D$ = -53.3 (*c* = 1.0, $CHCl_3$, 19:1 dr, 89% ee).



***tert*-butyl (*S*)-1-oxo-2-((*R*)-2-(4-(trifluoromethyl)phenyl)-4,5,6,7-tetrahydrobenzofuran-4-yl)-2,3-dihydro-1H-indene-2-carboxylate 5d:** Following the general procedure, 2-alkynyl enone **1d** (53 mg, 0.2 mmol, 1 eq) and ketoester **2a** (55 mg, 1,2 eq) were reacted to afford, after column chromatography (eluent toluene/hexane 8:2) product **5d** (84 mg, 0.169 mmol, 84 %) after column chromatography (eluent toluene/hexane 8:2) as a white solid (8:1 mixture of unseparable diastereoisomers, ee_{major} = 81%).

Major diastereoisomer:
IR (neat): 2932, 2860, 1739, 1712 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dt, *J* = 7.6, 1.1 Hz, 1H), 7.57 (ddd, *J* = 7.6, 7.1, 1.1 Hz, 1H), 7.51 – 7.38 (m, 7H), 6.04 (s, 1H), 4.01 (ddt, *J* = 9.2, 5.2, 2.1 Hz, 1H), 2.85 (d, *J* = 17.0 Hz, 1H), 2.77 – 2.60 (m, 2H), 2.16 – 2.04 (m, 2H), 1.88 – 1.78 (m, 1H), 1.55 – 1.44 (m, 1H), 1.45 (s, 9H).
^{13}C NMR: (100 MHz, $CDCl_3$) δ 202.6, 168.2, 154.6, 154.0, 150.5, 135.9, 135.6, 134.3 (d, J_{C-F} = 1 Hz) 127.93, 127.89, 126.5, 125.8 (q, J_{C-F} = 4 Hz), 125.7 (d, J_{C-F} = 217 Hz) 124.9, 123.5, 119.3, 107.2, 82.7, 67.8, 38.4, 32.9, 28.1, 26.8, 23.7, 22.3.
HRMS: Calcd for $(C_{29}H_{27}F_3NaO_4)^+$: 519.1754; found: 519.1754.
HPLC: Analysis on a Daicel Chiralpak IA-3 column, eluent hex/IPA 96:4, flow rate 1.0 mL/min, 20ºC, λ = 290 nm. τ_{minor} = 7.8 min, τ_{major} = 8.4 min, 81% ee. $[\alpha]^{26}_D$ = -11.7 (*c* = 1.0, $CHCl_3$, 8:1 dr, 81% ee).



***tert*-butyl (*S*)-1-oxo-2-((*R*)-2-(p-tolyl)-4,5,6,7-tetrahydrobenzofuran-4-yl)-2,3-dihydro-1H-indene-2-carboxylate 5e.** Following the general procedure, 2-alkynyl enone **1e** (43 mg, 0.2 mmol, 1 eq) and ketoester **2a** (55 mg, 1,2 eq) were reacted to afford, after column chromatography (eluent toluene/hexane 8:2),product **5e** (73 mg, 0.165 mmol, 82 %) after column chromatography as a white solid (19:1 mixture of unseparable diastereoisomers, ee_{major} = 91%).

Major diastereoisomer:

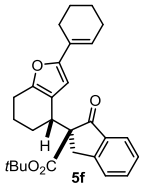
IR (neat): 2929, 2860, 1738, 1712 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.39 – 7.33 (m, 2H), 7.26 – 7.23 (m, 2H), 7.05 – 7.01 (m, 2H), 5.85 (s, 1H), 3.97 (ddt, *J* = 9.3, 4.9, 2.0 Hz, 1H), 3.69 – 3.65 (d, *J* = 17.0 Hz, 1H), 2.85 (d, *J* = 17.0 Hz, 1H), 2.71 – 2.55 (m, 2H), 2.26 (s, 3H), 2.10 – 1.99 (m, 2H), 1.85 – 1.73 (m, 1H), 1.50 – 1.39 (m, 1H), 1.43 (s, 9H).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 202.6, 168.3, 154.7, 152.2, 152.0, 136.8, 136.0, 135.5, 129.4, 128.6, 127.7, 126.7, 124.6, 123.6, 118.7, 104.4, 82.5, 67.9, 38.5, 32.8, 28.1, 26.9, 23.6, 22.4, 21.5.

HRMS: Calcd for $(C_{29}H_{30}NaO_4)^+$: 465.2036; found: 465.2045.

HPLC: Analysis on a Daicel Chiralpak IA-3 column, eluent hex/IPA 98:2, flow rate 1.0 mL/min, 30ºC, λ = 290 nm. τ_{minor} = 9.5 min, τ_{major} = 12.1 min, 91% ee. $[\alpha]^{26}_D$ = -24.9 (*c* = 1.0, $CHCl_3$, 19:1 dr, 91% ee).



***tert*-butyl (*S*)-2-((*R*)-2-(cyclohex-1-en-1-yl)-4,5,6,7-tetrahydrobenzofuran-4-yl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 5f:** Following a modified general procedure (reaction at -10 ºC using 1.6 mol% of **PTC-QD**), 2-alkynyl enone **1f** (41 mg, 0.2 mmol, 1 eq) and ketoester **2a** (55 mg, 1,2 eq) were reacted to afford, after column chromatography (eluent toluene/hexane 8:2), product **5f** (46 mg, 0.106 mmol, 53 %) as a colorless oil (only one diastereoisomer detected, ee = 93%).

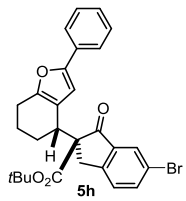
IR (neat): 2926, 2854, 1739, 1714 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.76 (m, 1H), 7.54 (td, *J* = 7.5, 1.2 Hz, 1H), 7.42 – 7.30 (m, 2H), 6.12–5.98 (m, 1H), 5.38 (s, 1H), 3.99 –3.86 (m, 1H), 3.64 (d, *J* = 16.8 Hz, 1H), 2.79 (d, *J* = 16.8 Hz, 1H), 2.63 – 2.49 (m, 2H), 2.12 – 1.91 (m, 5H), 1.80 – 1.68 (m, 2H), 1.61 – 1.48 (m, 4H), 1.42 (s, 10H), 0.91 – 0.85 (m, 1H).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 202.6, 168.4, 154.7, 153.4, 151.5, 136.1, 135.3, 127.7, 127.5, 126.8, 124.5, 121.33, 117.9, 103.9, 82.5, 67.8, 38.6, 32.8, 28.2, 26.9, 25.4, 24.9, 23.5, 22.6, 22.5, 22.4.

HRMS: Calcd for $(C_{28}H_{32}NaO_4)^+$: 455.2193; found: 455.2206.

HPLC: Analysis on a Daicel Chiralpak IA-3 column, eluent hex/DCM/IPA 89.5:15:0.5, flow rate 0.7 mL/min, 20ºC, λ = 254 nm. τ_{minor} = 8.9 min, τ_{major} = 9.4 min, ee = 93%. $[\alpha]^{26}_D$ = -35.3 (*c* = 1.0, $CHCl_3$, 93% ee).



***tert*-butyl (S)-6-bromo-1-oxo-2-((R)-2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-2,3-dihydro-1H-indene-2-carboxylate 5h.**

Following a modified general procedure (reaction at -10 ºC using 1.6 mol% of **PTC-QD**), 2-alkynyl enone **1a** (39 mg, 0.2 mmol, 1 eq) and ketoester **2g** (75 mg, 1,2 eq) were reacted to afford, after column chromatography (eluent toluene/hexane 8:2), product **5h** (79 mg, 0.156 mmol, 78 %) as a colorless oil (11:1 mixture of unseparable diastereoisomers, ee_{major} = 77 %).

Major diastereoisomer:

IR (neat): 2930, 2858, 1736, 1710 cm^{-1}.

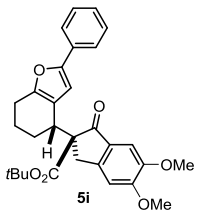
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 2.0, 0.6 Hz, 1H), 7.64 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.41 – 7.37 (m, 2H), 7.29 – 7.25 (m, 3H), 7.17 – 7.12 (m, 1H), 5.88 (s, 1H), 4.04 – 3.90 (m, 1H), 3.62 (d, *J*

= 16.9 Hz, 1H), 2.82– 2.74 (m, 1H), 2.72 – 2.57 (m, 2H), 2.09 – 1.99 (m, 2H), 1.85 – 1.72 (m, 1H), 1.50 – 1.40 (m, 1H), 1.43 (s, 9H).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 201.2, 167.9, 153.3, 152.8, 152.1, 138.3, 137.7, 131.1, 128.4, 128.4, 127.4, 127.2, 123.7, 121.9, 118.6, 104.9, 82.9, 68.6, 38.4, 32.5, 28.1, 26.9, 23.6, 22.3.

HRMS: Calcd for $(C_{28}H_{27}BrNaO_4)^+$: 529.0985; found: 529.0982.

HPLC: Analysis on a Daicel Chiralpak IA-3 column, eluent hex/IPA 97:3, flow rate 0.7 mL/min, 30ºC, λ = 310 nm. τ_{minor} = 6.8 min, τ_{major} = 8.3 min, 77% ee. $[\alpha]^{26}_D$ = +43.5 (*c* = 1.0, $CHCl_3$, 11:1 dr, 77% ee).



***tert*-butyl (*S*)-5,6-dimethoxy-1-oxo-2-((*R*)-2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-2,3-dihydro-1H-indene-2-carboxylate 5i.** Following the general procedure, 2-alkynyl enone **1a** (39 mg, 0.2 mmol, 1 eq) and ketoester **2i** (70 mg, 1,2 eq) were reacted to afford, after column chromatography (eluent AcOEt/hexane 2:8), product **5i** (61 mg, 0.124 mmol, 62%) as a colorless oil (1:16 mixture of unseparable diastereoisomers, ee_{major} = 73%).

Major diastereoisomer:

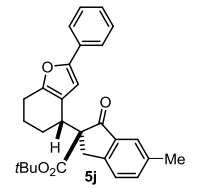
IR (neat): 2936, 2860, 1733, 1697 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ7.42 – 7.38 (m, 2H), 7.28 – 7.24 (m, 3H), 7.15 (ddt, *J* = 7.9, 6.9, 1.3 Hz, 1H), 6.82 (s, 1H), 5.97 (s, 1H), 4.0 – 3.95 (m, 1H), 3.97 (s, 3H), 3.92 (s, 3H), 3.60 (d, *J* = 16.5 Hz, 1H), 2.78 – 2.73 (m, 1H), 2.73 – 2.62 (m, 2H), 2.15 – 1.98 (m, 2H), 1.87 – 1.76 (m, 1H), 1.52 – 1.40 (m, 1H) 1.47 (s, 9H).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 200.8, 168.7, 156.1, 152.6, 151.8, 150.3, 149.8, 131.3, 128.8, 128.5, 127.0, 123.56, 118.9, 107.7, 105.2, 105.0, 82.4, 77.6, 68.0, 56.5, 38.2, 32.5, 28.2, 27.0, 23.6, 22.4.

HRMS: Calcd for $(C_{30}H_{32}NaO_6)^+$: 511.2091; found: 511.2094.

HPLC: Analysis on a Daicel Chiralpak IA-3 column, eluent hex/IPA 97:3, flow rate 1.2 mL/min, 30ºC, λ = 310 nm. τ_{minor} = 18.1 min, τ_{major} = 20.5 min, 73% ee. $[\alpha]^{26}_D$ = -32.8 (C= 1.0, $CHCl_3$, 16:1 dr, 73% ee).



***tert*-butyl (*S*)-5,6-dimethoxy-1-oxo-2-((*R*)-2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-2,3-dihydro-1H-indene-2-carboxylate 5j.** Following the general procedure, 2-alkynyl enone **1a** (39 mg, 0.2 mmol, 1 eq) and ketoester **2j** (60 mg, 1,2 eq) were reacted to afford, after column chromatography (eluent toluene/hexane 8:2), product **5j** (77 mg, 0.174 mmol, 87 %) as a colorless oil (19:1 mixture of unseparable diastereoisomers, ee_{major} = 87%).

Major diastereoisomer:

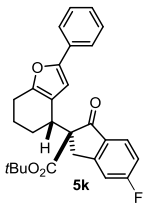
IR (neat): 2934, 2860, 1737, 1708 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (dt, *J* = 1.7, 0.9 Hz, 1H), 7.43 – 7.36 (m, 3H), 7.31 – 7.24 (m, 3H), 7.17 – 7.12 (m, 1H), 5.96 (s, 1H), 4.04 – 3.96 (m, 1H), 3.65 (d, *J* = 16.7 Hz, 1H), 2.81 (d, *J* = 16.7 Hz, 1H), 2.75 – 2.60 (m, 2H), 2.43 (s, 3H), 2.15 – 2.03 (m, 2H), 1.88 – 1.75 (m, 1H), 1.54 – 1.42 (m, 1H), 1.46 (s, 9H).

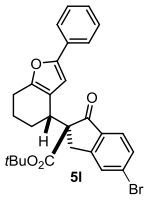
^{13}C NMR: (126 MHz, $CDCl_3$) δ 202.6, 168.4, 152.7, 152.1, 151.8, 137.6, 136.8, 136.1, 131.3, 128.7, 127.0, 126.4, 124.5, 123.6, 118.9, 105.2, 82.4, 68.2, 38.3, 32.4, 28.1, 26.9, 23.6, 22.4, 21.41.

HRMS: Calcd for $(C_{29}H_{30}NaO_4)^+$: 465.2036; found: 465.2028.

HPLC: Analysis on a Daicel Chiralpak IA-3 column, eluent hex/DCM 85:15, flow rate 0.7 mL/min, 30ºC, λ = 310 nm. τ_{minor} = 10.2 min, τ_{major} = 12.6 min, 87% ee. $[\alpha]^{26}_D$ = +10.52 (*c* = 1.0, $CHCl_3$, 19:1 dr, 87% ee).



***tert*-butyl (*S*)-5,6-dimethoxy-1-oxo-2-((*R*)-2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-2,3-dihydro-1H-indene-2-carboxylate 5k.**
Following the general procedure, 2-alkynyl enone **1a** (39 mg, 0.2 mmol, 1 eq) and ketoester **2k** (60 mg, 1,2 eq) were reacted to afford, after column chromatography (eluent toluene/hexane 8:2), product **5k** (77 mg, 0.174 mmol, 87 %) as a colorless oil (1:15 mixture of unseparable diastereoisomers, ee_{major} = 85%).
Major diastereoisomer:
IR (neat): 2935, 2860, 1738, 1712 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.3, 5.2 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.26 – 7.22 (m, 2H), 7.16 – 7.11 (m, 1H), 7.10 – 7.03 (m, 2H), 5.91 (s, 1H), 4.03 – 3.94 (m, 0H), 3.67 (d, *J* = 17.0 Hz, 1H), 2.88 – 2.80 (m, 1H), 2.74 – 2.51 (m, 2H), 2.11 – 1.99 (m, 2H), 1.85 – 1.75 (m, 1H), 1.49 – 1.38 (m, 1H), 1.44 (s, 9H).
^{13}C NMR: (126 MHz, $CDCl_3$) δ 200.7, 168.1, 167.7 (d, J_{C-F} = 255 Hz), 157.8 (d, J_{C-F} = 10 Hz) 152.8, 152.0, 132.3 (d, J_{C-F} = 1.2 Hz) 131.2, 128.8, 127.2, 126.9 (d, J_{C-F} = 12 Hz) 123.6, 118.7, 116.2 (d, J_{C-F} = 24 Hz), 113.5 (d, J_{C-F} = 22.5 Hz) 105.0, 82.8, 68.2, 38.3, 32.8, 28.1, 26.9, 23.6, 22.3.
HRMS: Calcd for $(C_{28}H_{27}FNaO_4)^+$: 469.1786; found: 469.1777.
HPLC: Analysis on a Daicel Chiralpak IA-3 column, eluent hex/DCM 85:15, flow rate 0.7 mL/min, 30ºC, λ = 310 nm. τ_{major} = 12.2 min, τ_{minor} = 13.0 min, 85% ee. $[\alpha]^{26}_D$ = -18.1 (*c* = 1.0, $CHCl_3$, 15:1 dr, 85% ee).

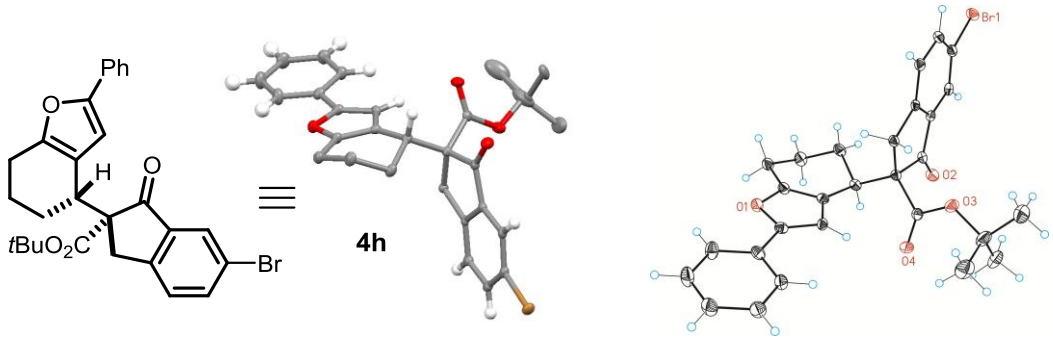


tert-butyl (*S*)-5-bromo-1-oxo-2-((*R*)-2-phenyl-4,5,6,7-tetrahydrobenzofuran-4-yl)-2,3-dihydro-1H-indene-2-carboxylate 5l.
Following the general procedure, 2-alkynyl enone **1a** (39 mg, 0.2 mmol, 1 eq) and ketoester **2l** (75 mg, 1,2 eq) were reacted to afford, after column chromatography (eluent toluene/hexane 8:2), product **5l** (71 mg, 0.14 mmol, 70%) as a colorless oil (19:1 mixture of unseparable diastereoisomers, ee_{major} = 83 %).
Major diastereoisomer:
IR (neat): 2930, 2866, 1731, 1698 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.2, 0.6 Hz, 1H), 7.57 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.53 – 7.50 (m, 1H), 7.40 – 7.35 (m, 2H), 7.28 – 7.22 (m, 2H), 7.16 – 7.11 (m, 1H), 5.89 (s, 1H), 4.00 – 3.95 (m, 1H), 3.66 (d, *J* = 17.1 Hz, 1H), 2.84 (d, *J* = 16.9, 1H), 2.73 – 2.58 (m, 2H), 2.12 –2.01 (m, 2H), 1.86 – 1.74 (m, 1H), 1.44 (s, 9H), 0.91 – 0.84 (m, 1H).
^{13}C NMR: (125 MHz, $CDCl_3$) δ 201.4, 167.9, 156.2, 152.8, 152.1, 134.8, 131.5, 131.1, 130.1, 128.8, 127.2, 125.7, 123.6, 118.6, 104.9, 82.9, 68.1, 38.4, 32.6, 30.0, 28.1, 26.8, 23.6, 22.3.
HRMS: Calcd for $(C_{28}H_{27}BrNaO_4)^+$: 529.0985; found: 529.0988.
HPLC: Analysis on a Daicel Chiralpak IA-3 column, eluent Hex/DCM 75:25, flow rate 0.5 mL/min, 30ºC, λ = 310 nm. τ_{major} = 10.0 min, τ_{minor} = 10.6 min, 83% ee. $[\alpha]^{26}_D$ = -77.6 (*c* = 1.0, $CHCl_3$, 19:1 dr, 83% ee).

H. X-ray Crystallographic Data

Single Crystal X-ray Diffraction Data for compound 4h (synthesized using quinine)

X-ray structure determinations: Crystals of compound **4h** were obtained from a mixture of DCM and hexane at 0 degree. *Data Collection*. Measurements were made on a Bruker-Nonius diffractometer equipped with an APPEX 2 4K CCD area detector, a FR591 rotating anode with $Mo_{K\alpha}$ radiation, Montel mirrors and a Cryostream Plus low temperature device (*T* = 100K). Full-sphere data collection was used with ω and φ scans.

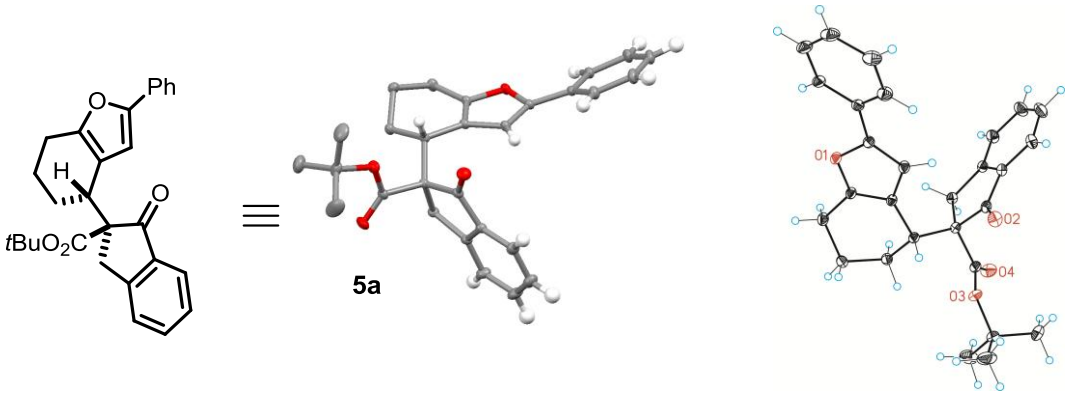


Crystal data for **4h** at 100 K: **CCDC 1046068**

Identification code	mo_CV438_0m	
Empirical formula	C28 H27 Br O4	
Formula weight	507.40	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 8.7857(6)Å	α= 90°.
	b = 16.2342(7)Å	β = 90°.
	c = 17.0357(10)Å	γ = 90°.
Volume	2429.8(2) $Å^3$	
Z	4	
Density (calculated)	1.387 Mg/m^3	
Absorption coefficient	1.723 mm^{-1}	
F(000)	1048	
Crystal size	0.15 x 0.12 x 0.10 mm^3	
Theta range for data collection	1.733 to 32.555°.	
Index ranges	-8<=h<=12,-22<=k<=14,-10<=l<=25	
Reflections collected	14745	
Independent reflections	7325[R(int) = 0.0289]	
Completeness to theta =32.555°	86.5%	
Absorption correction	Empirical	
Max. and min. transmission	0.847 and 0.788	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7325/ 56/ 316	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0345, wR2 = 0.0694	
R indices (all data)	R1 = 0.0456, wR2 = 0.0727	
Flack parameter	x =-0.007(4)	
Largest diff. peak and hole	0.480 and -0.321 $e.Å^{-3}$	

Single Crystal X-ray Diffraction Data for compound 5a (synthesized using quinidine-derived PTC catalyst)

X-ray structure determinations: Crystals of compound **5a** were obtained from a mixture of DCM and hexane at 0 degree. The measured crystal was then analyzed by chiral HPLC to confirm the enantiopurity of the sample (see HPLC traces, 98% ee). *Data Collection*. Measurements were made on a Rigaku XtaLab P200 diffractometer equipped with a Pilatus 200K area detector, a Microfocus-HF007 rotating anode with $Mo_{K\alpha}$ radiation, Confocal Max Flux optic and a Cryostream Plus low temperature device (T = 100K). Full-sphere data collection was used with ω and φ scans.



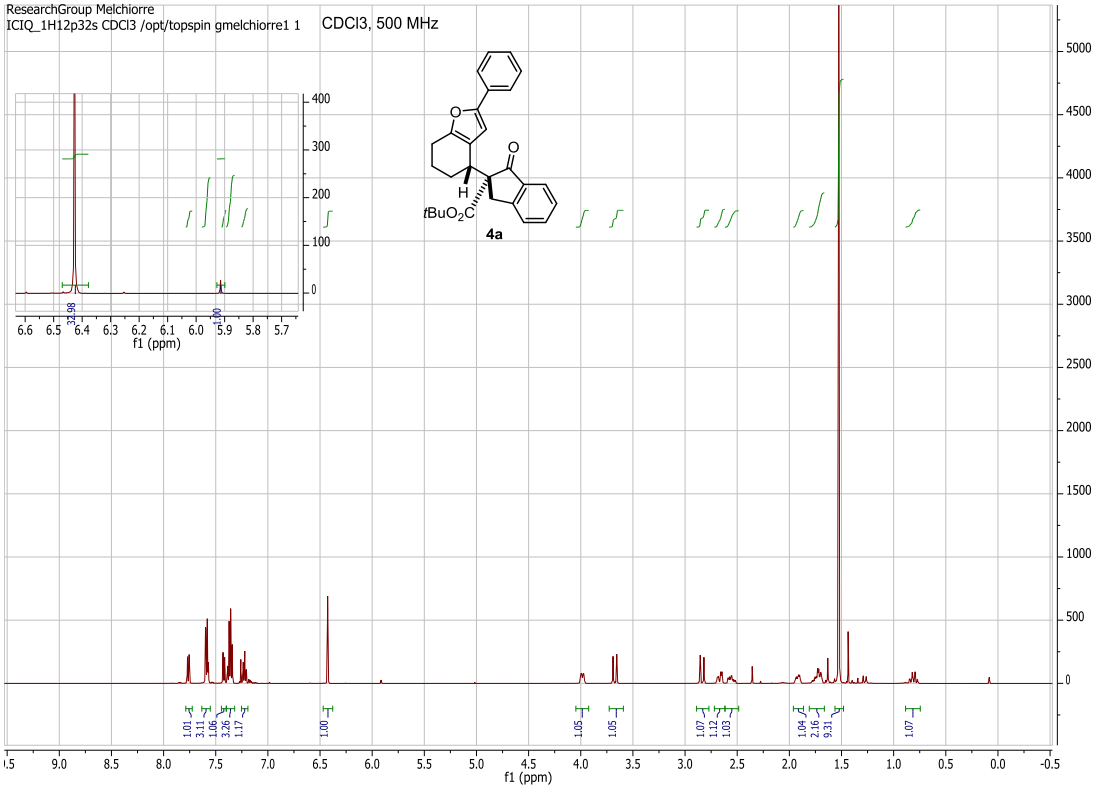
For the absolute configuration determination of the light-atom molecule **5a** the methodology described in the following work has been followed:

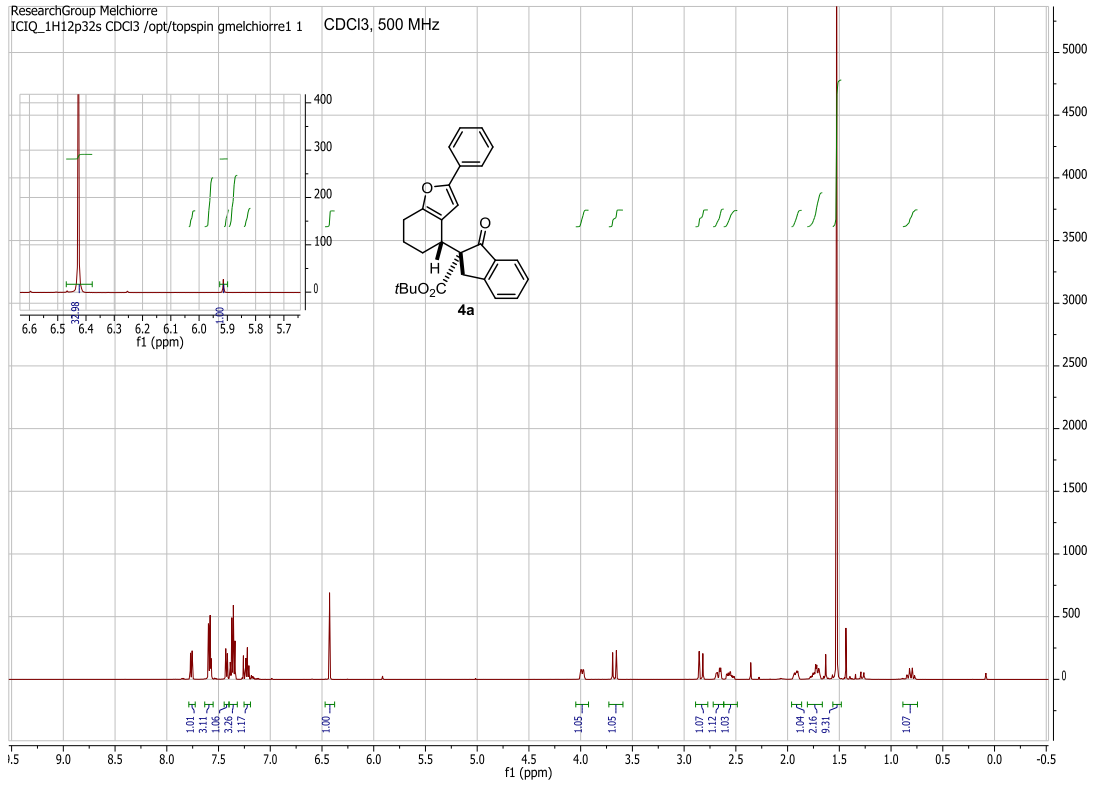
The use of Mo Kα radiation in the assignment of the absolute configuration of light-atom molecules; the importance of high-resolution data
E. C. Escudero-Adán, J. Benet-Buchholz, P. Ballester
Acta Cryst. B, **2014**, *70*, 660-668

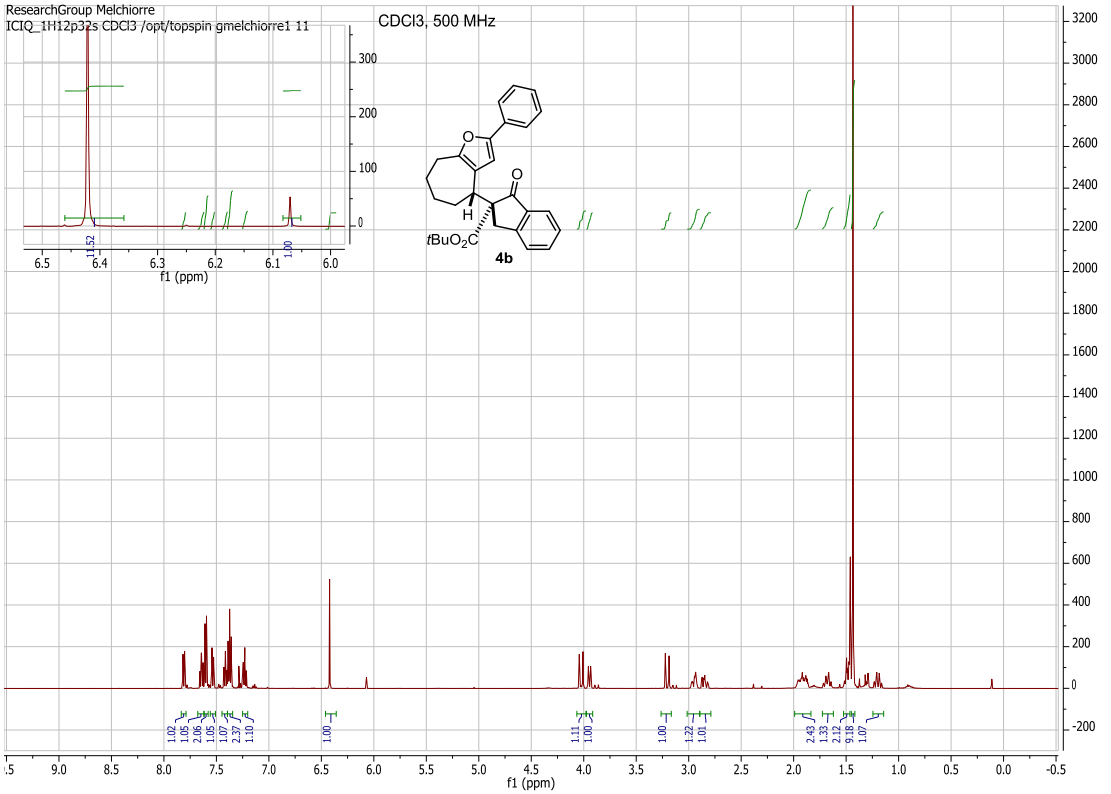
Crystal data for **5a** at 100 K: **CCDC 1046069**

Identification code	CV469-1	
Empirical formula	C14 H14 O2	
Formula weight	214.25	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	a = 22.183(11)Å	α= 90°.
	b = 7.950(3)Å	β = 122.929(5)°.
	c = 15.744(8)Å	γ = 90°.
Volume	2330.6(19) $Å^3$	
Z	8	
Density (calculated)	1.221 Mg/m^3	
Absorption coefficient	0.081 mm^{-1}	
F(000)	912	
Crystal size	0.20 x 0.20 x 0.20 mm^3	
Theta range for data collection	3.291 to 52.126°.	
Index ranges	-48<=h<=48,-17<=k<=17,-34<=l<=34	
Reflections collected	70335	
Independent reflections	25244[R(int) = 0.0226]	
Completeness to theta =52.126°	98.1%	
Absorption correction	Empirical	
Max. and min. transmission	0.984 and 0.757	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	25244/ 1/ 292	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0373, wR2 = 0.0947	
R indices (all data)	R1 = 0.0497, wR2 = 0.1022	
Flack parameter	x =0.09(10)	
Largest diff. peak and hole	0.486 and -0.247 e.$Å^{-3}$	

I. NMR spectra



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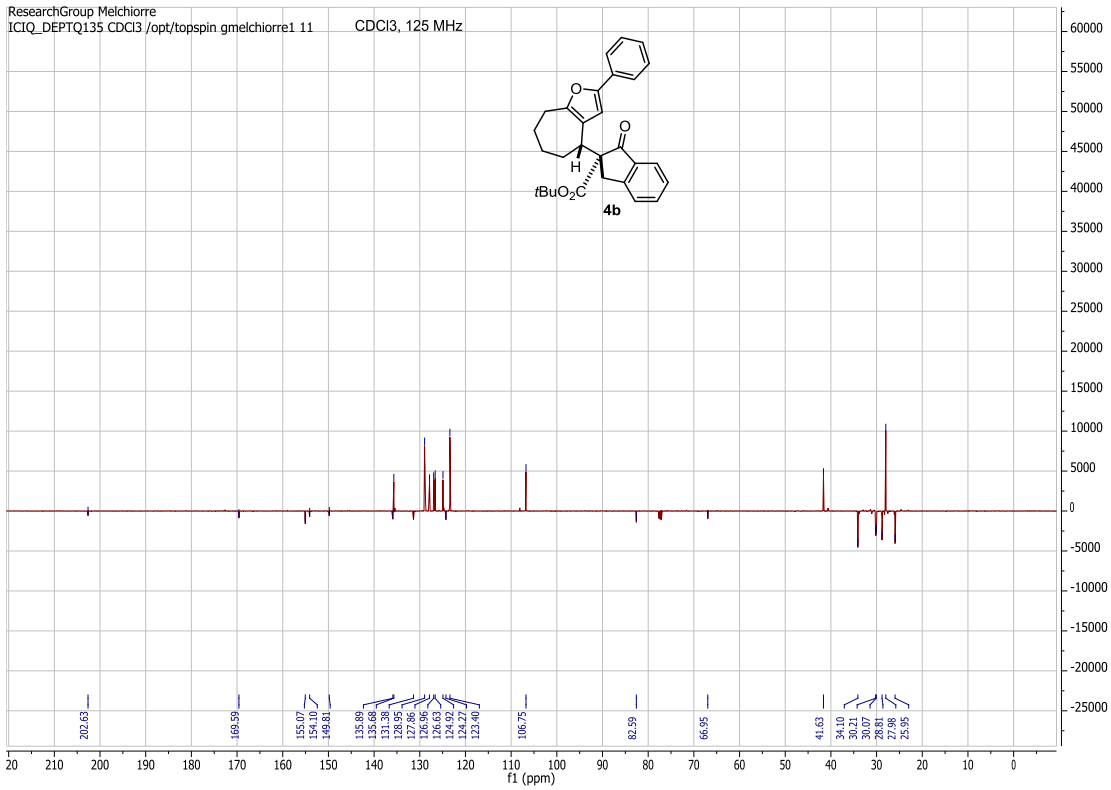
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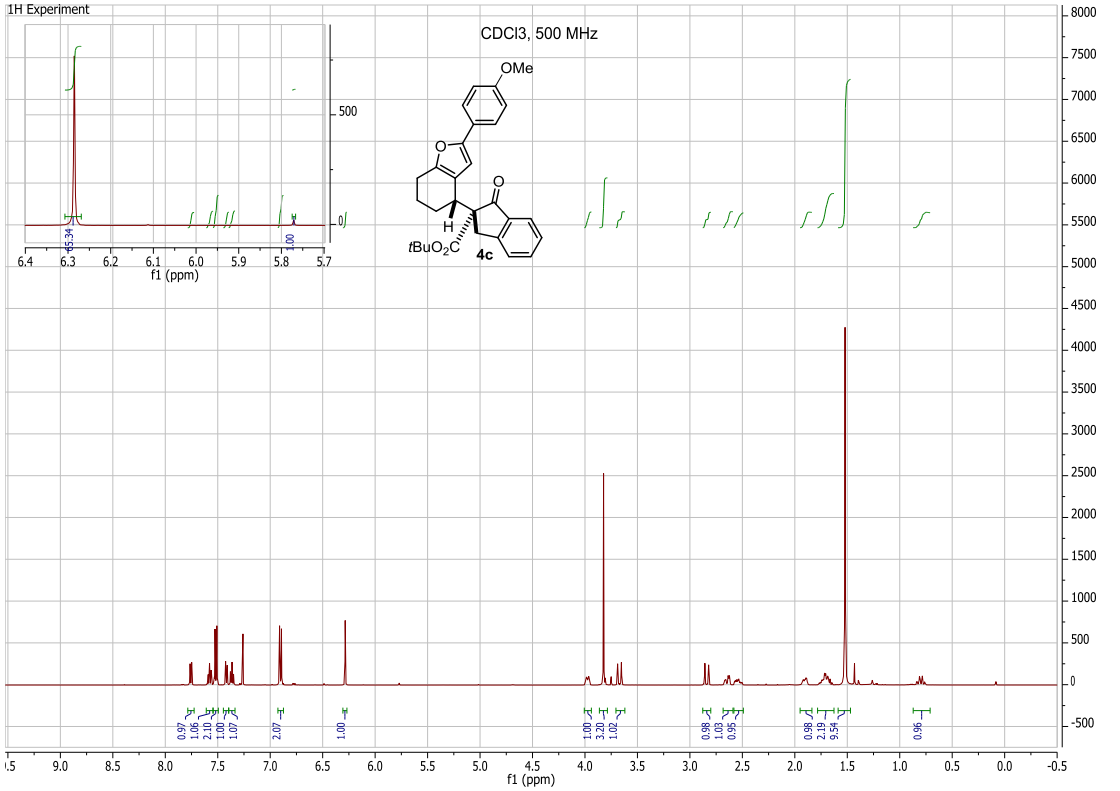
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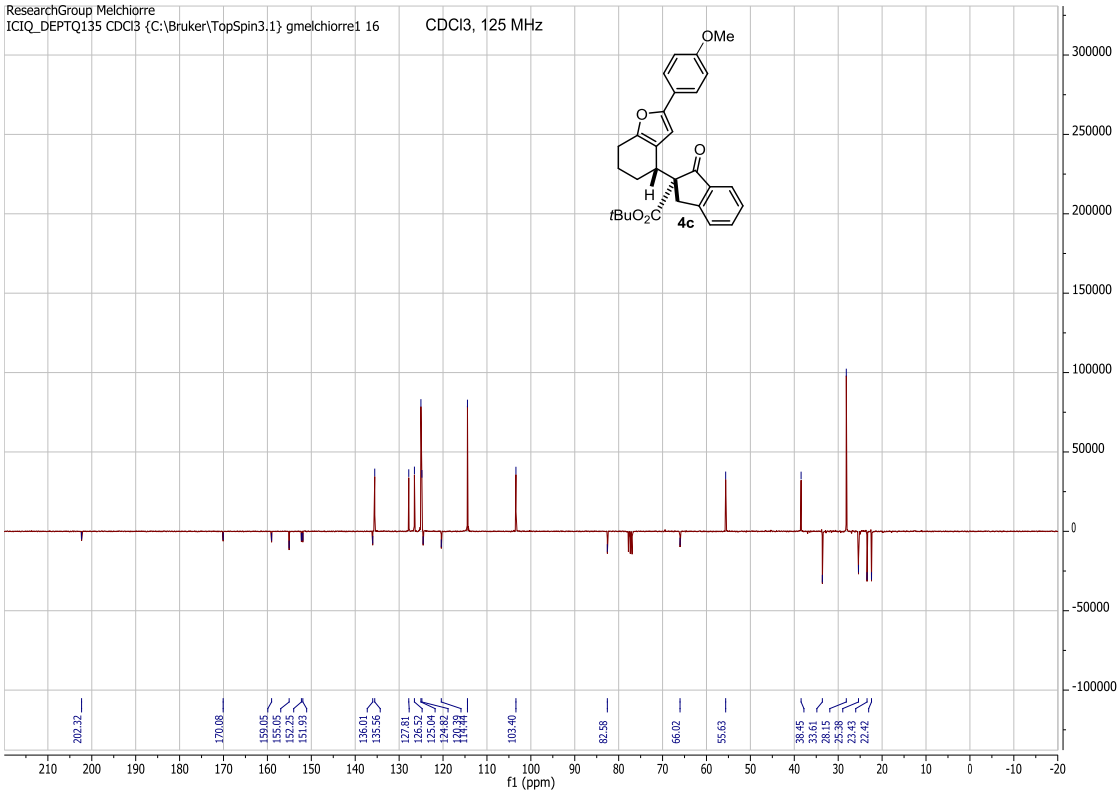
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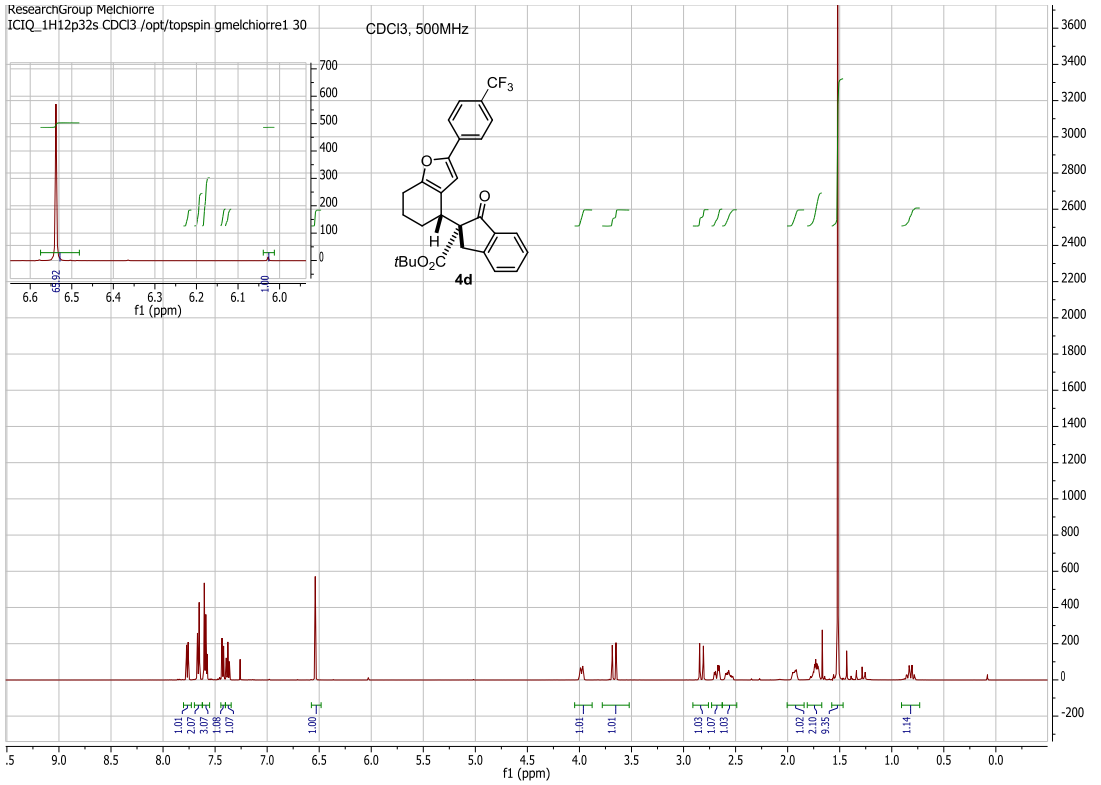
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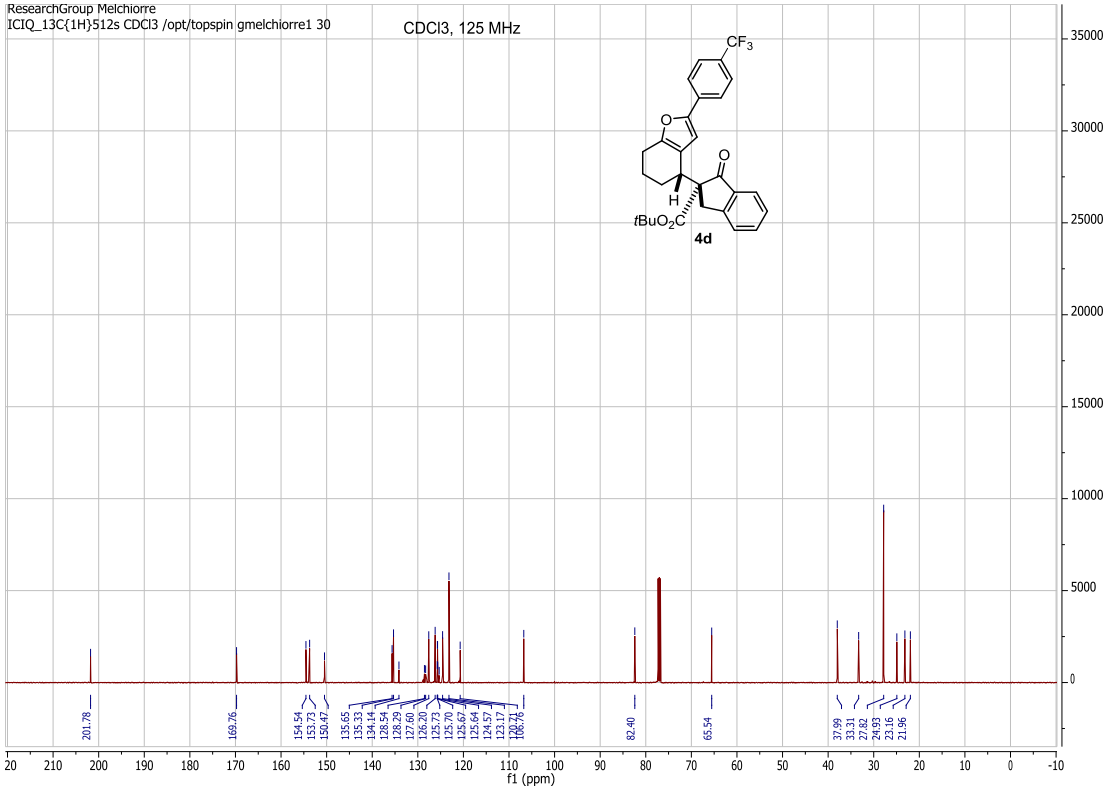
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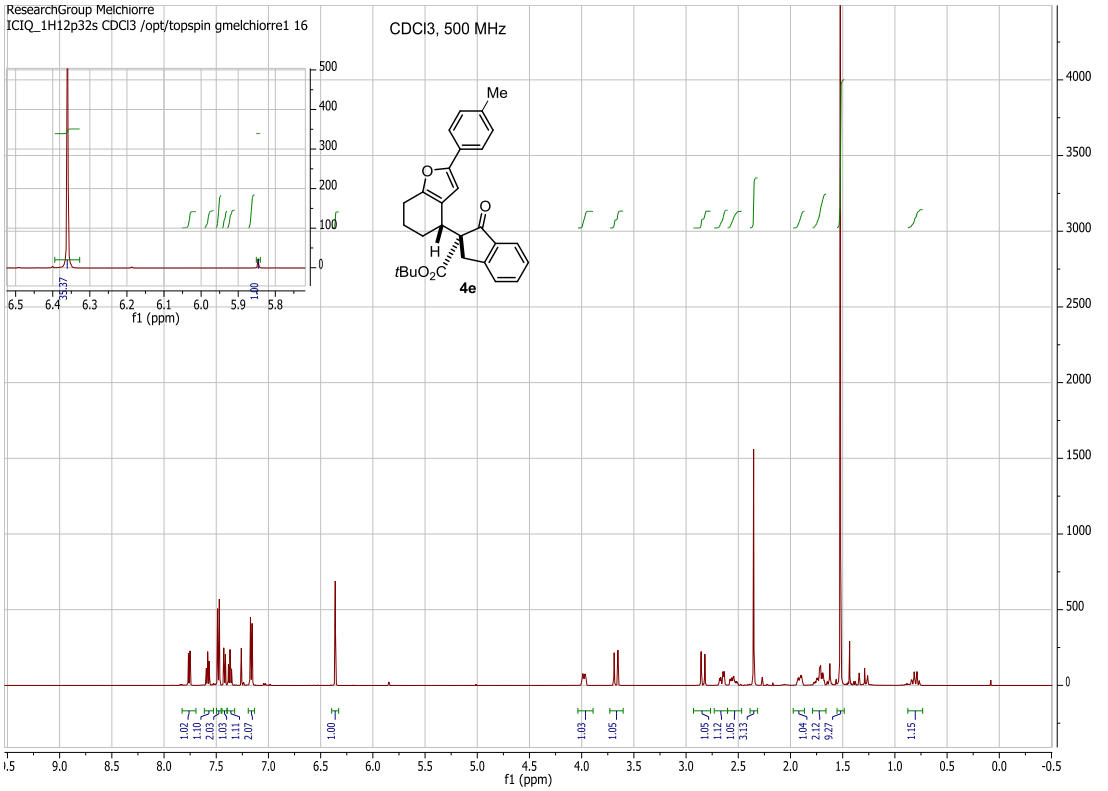
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4e
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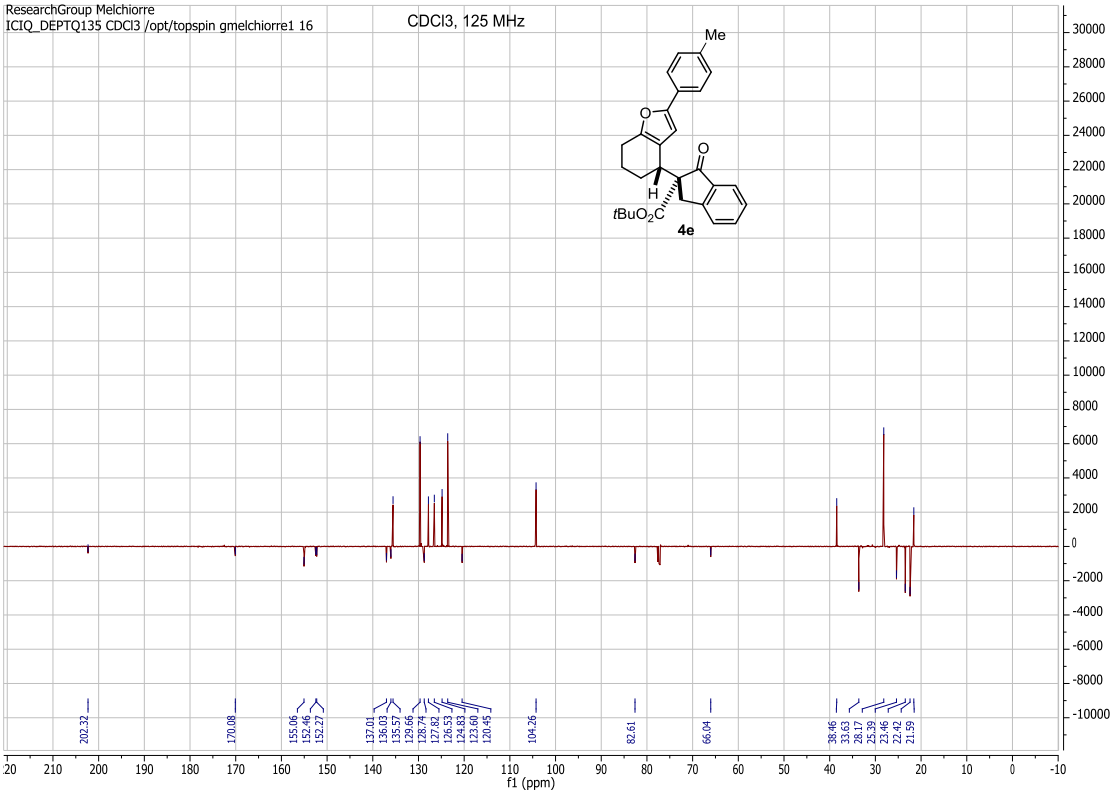
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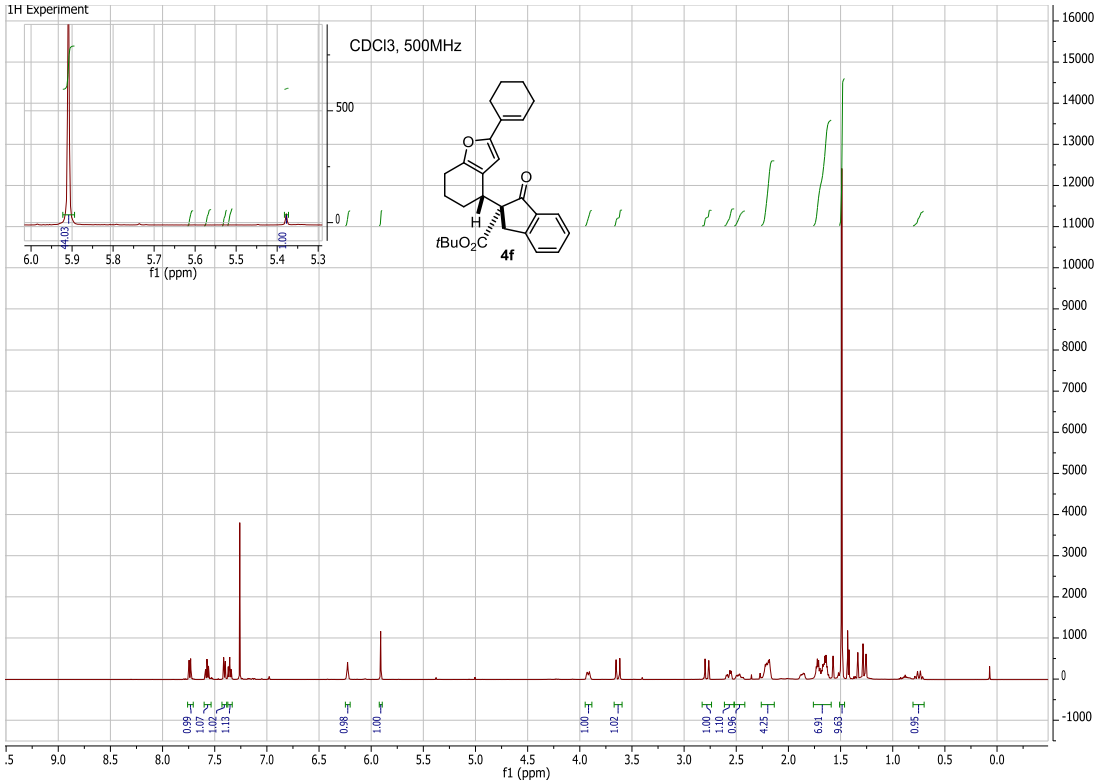
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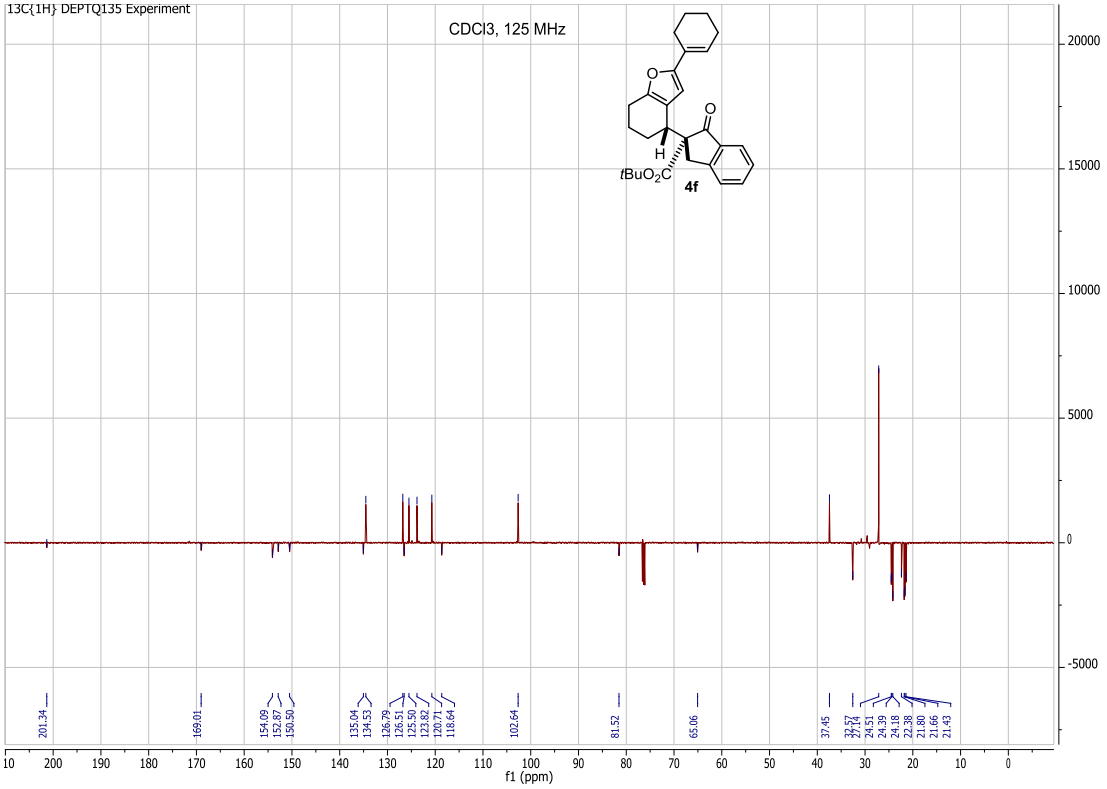
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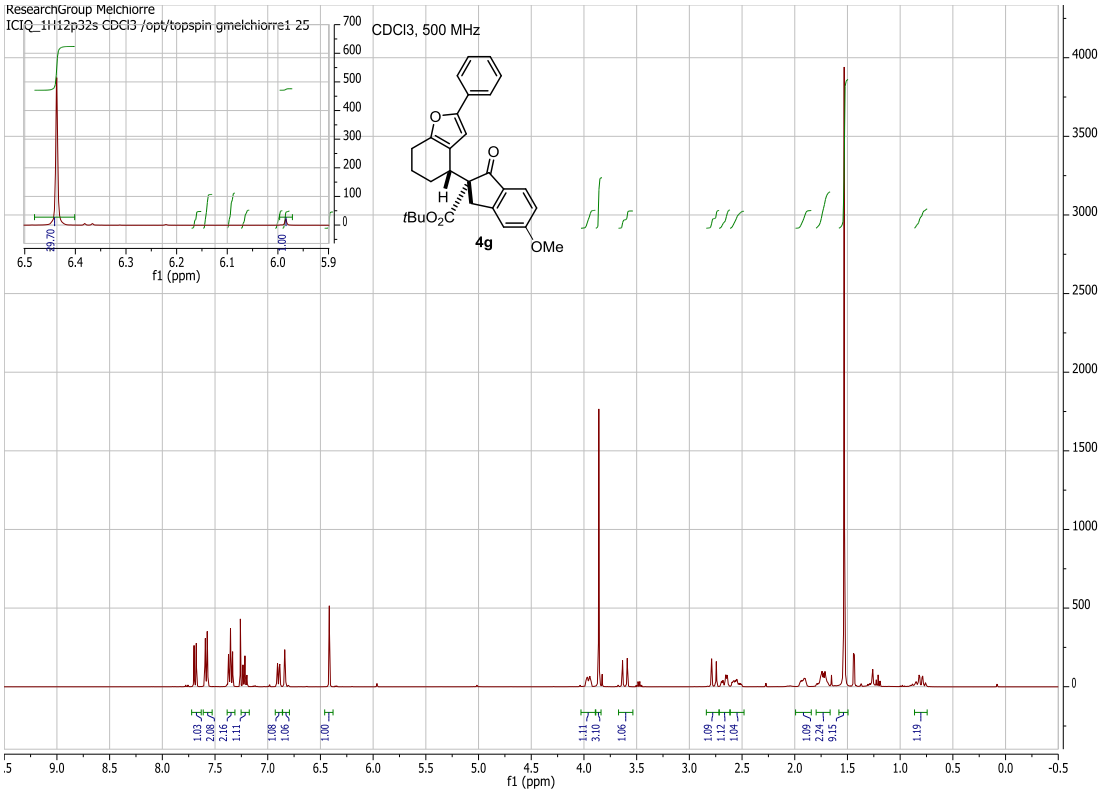
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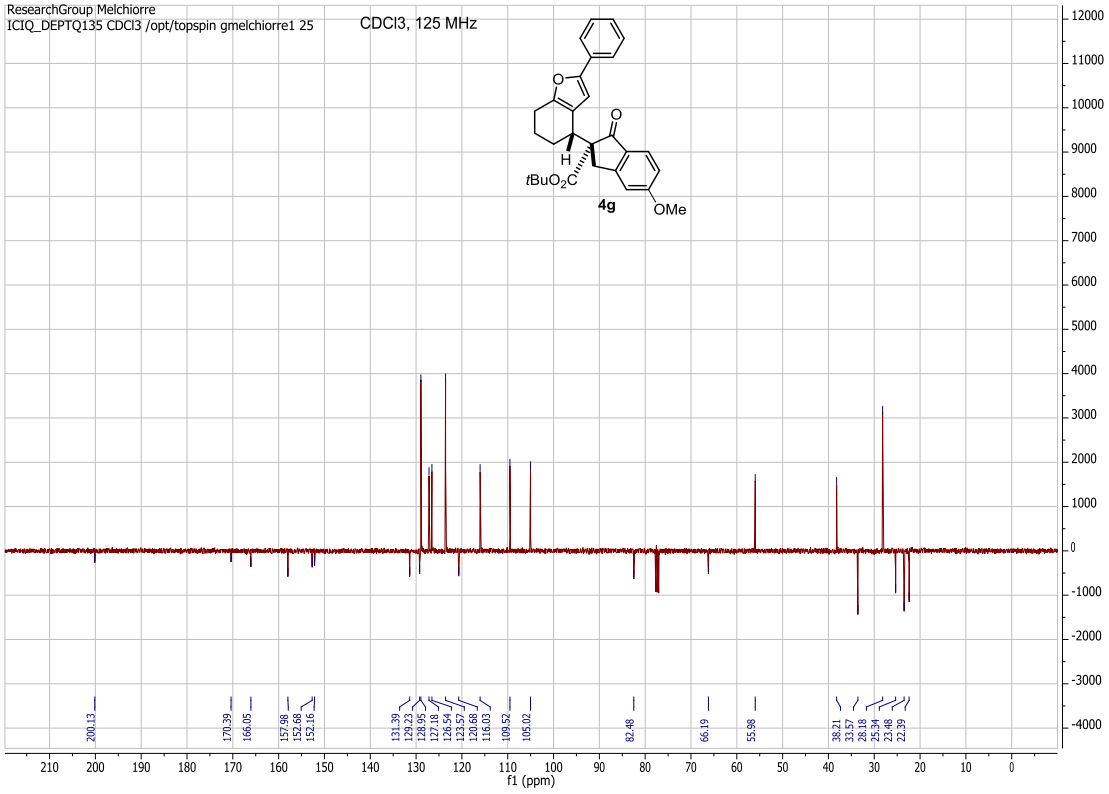
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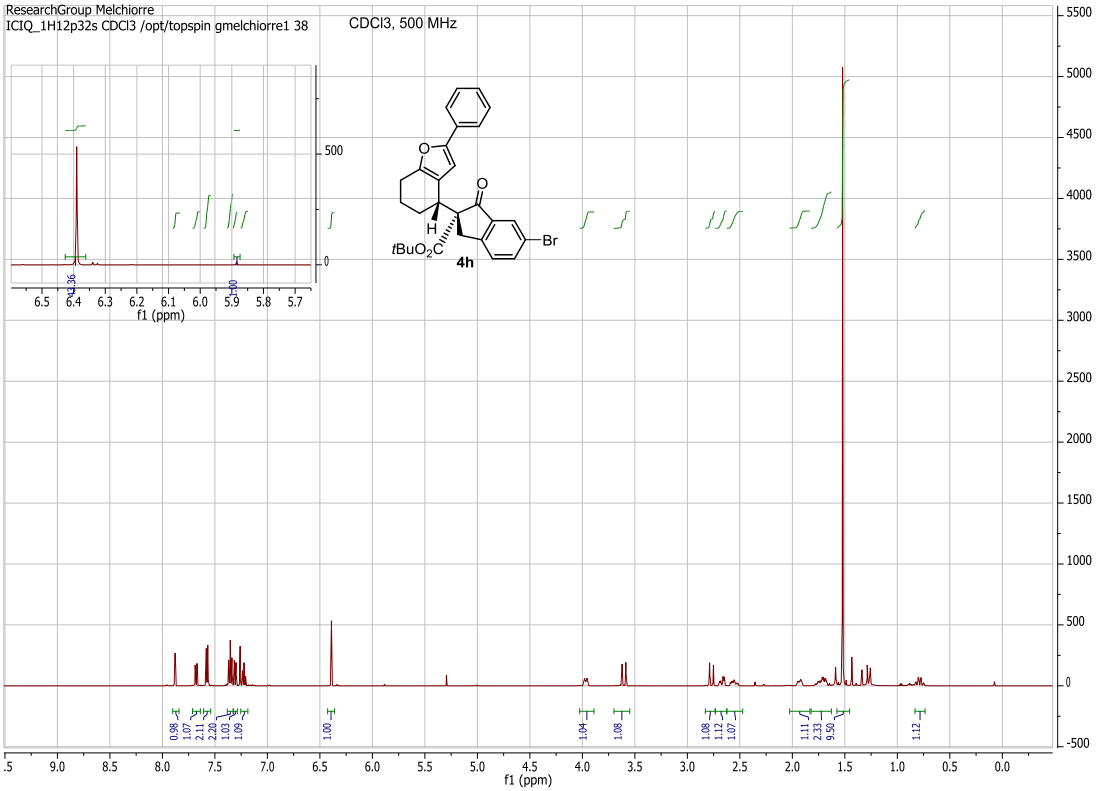
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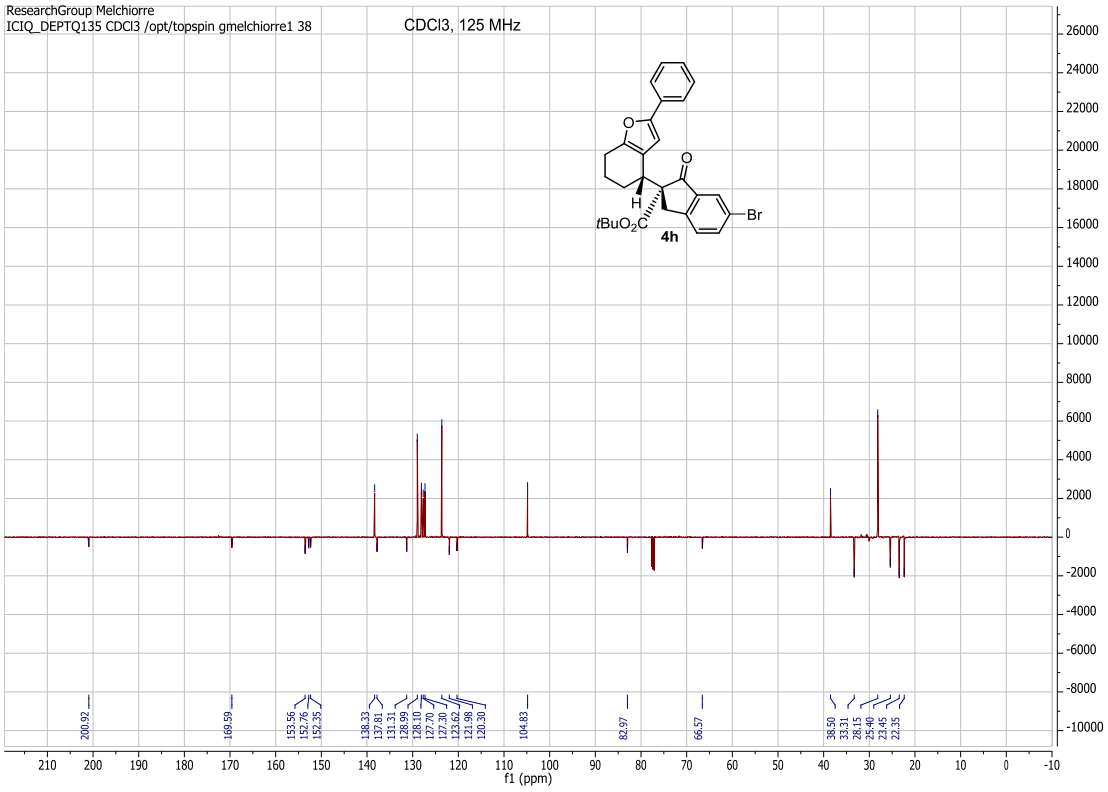
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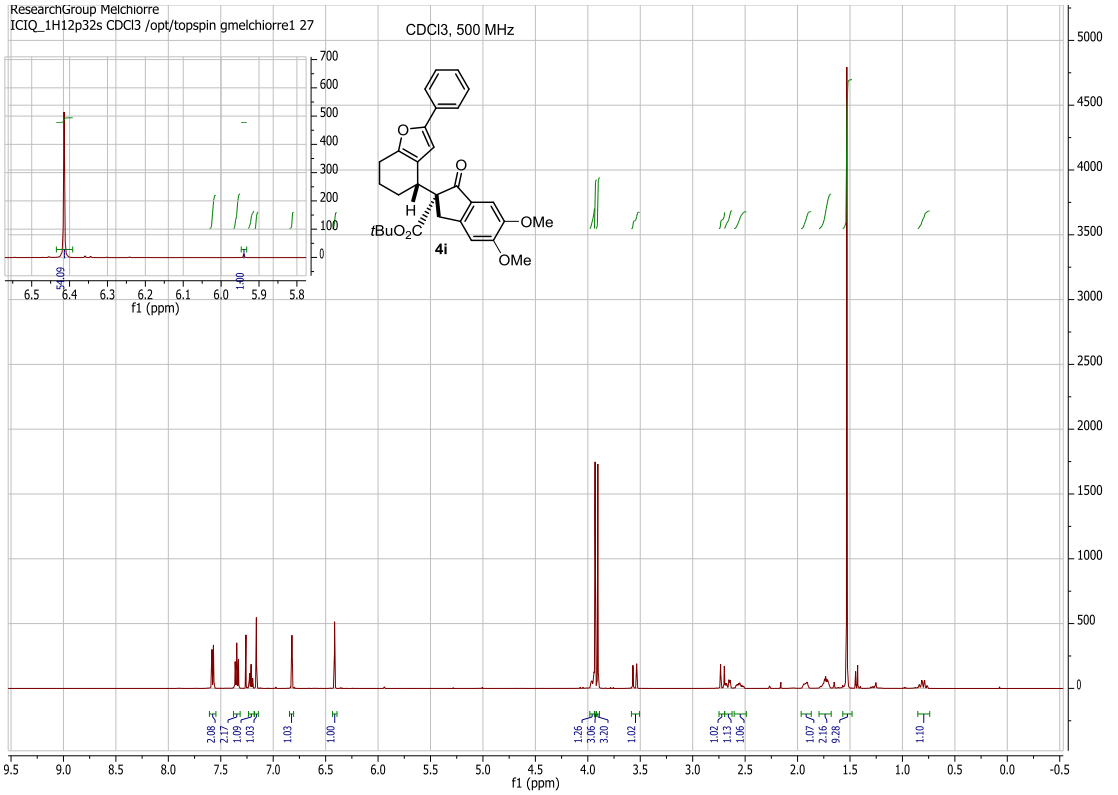
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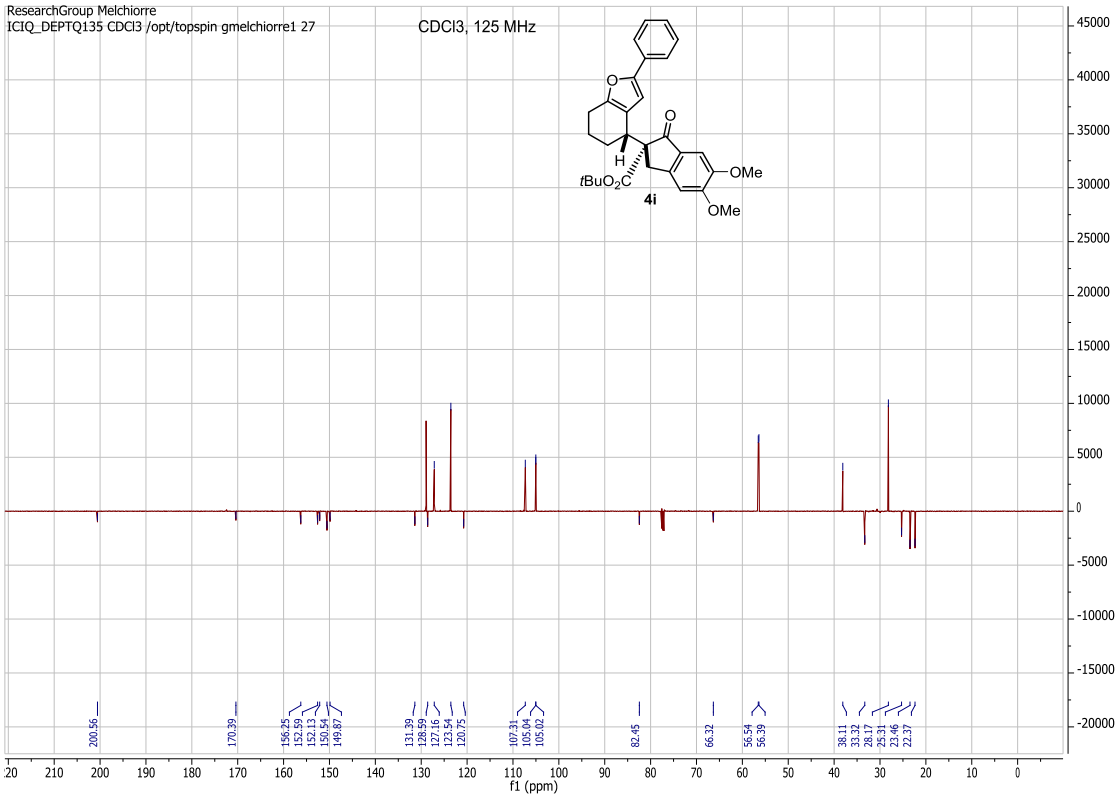
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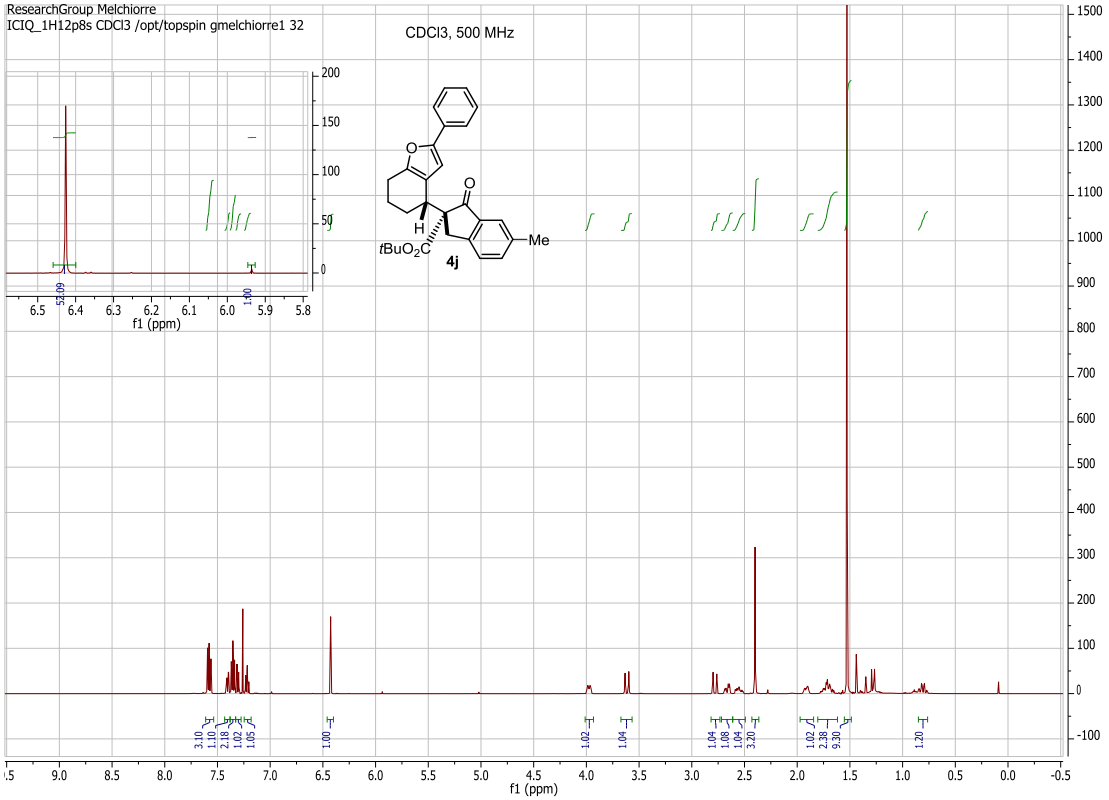
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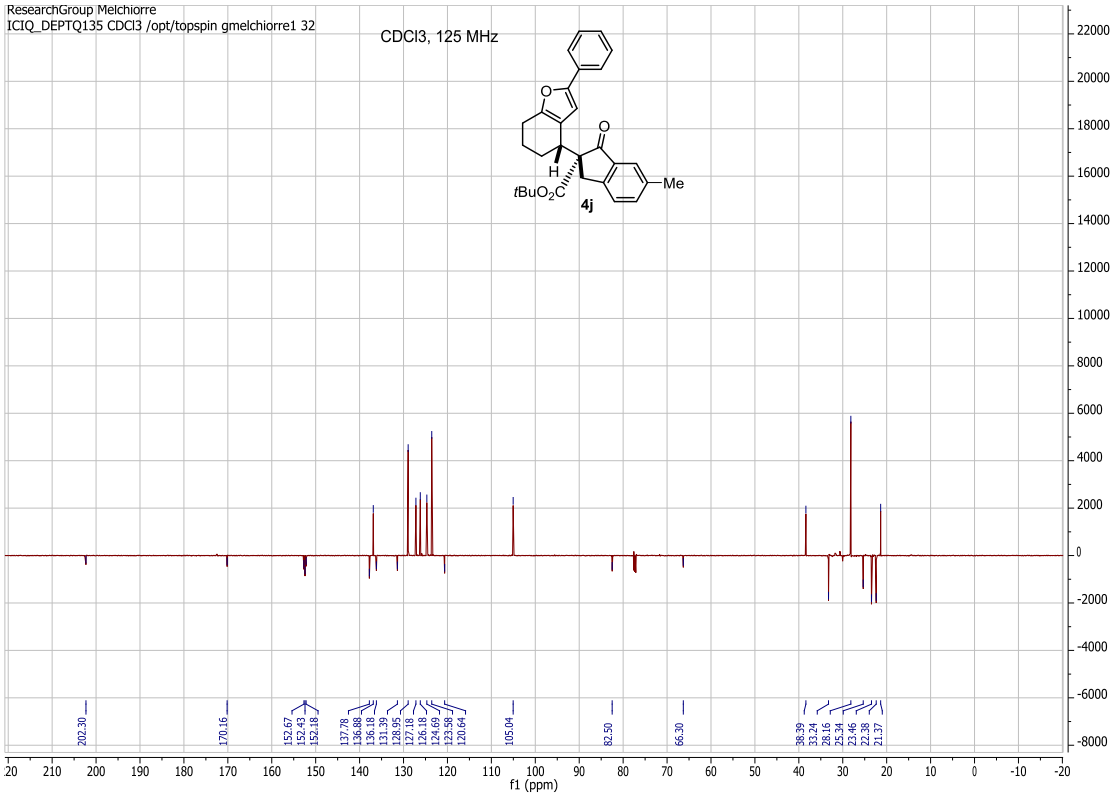
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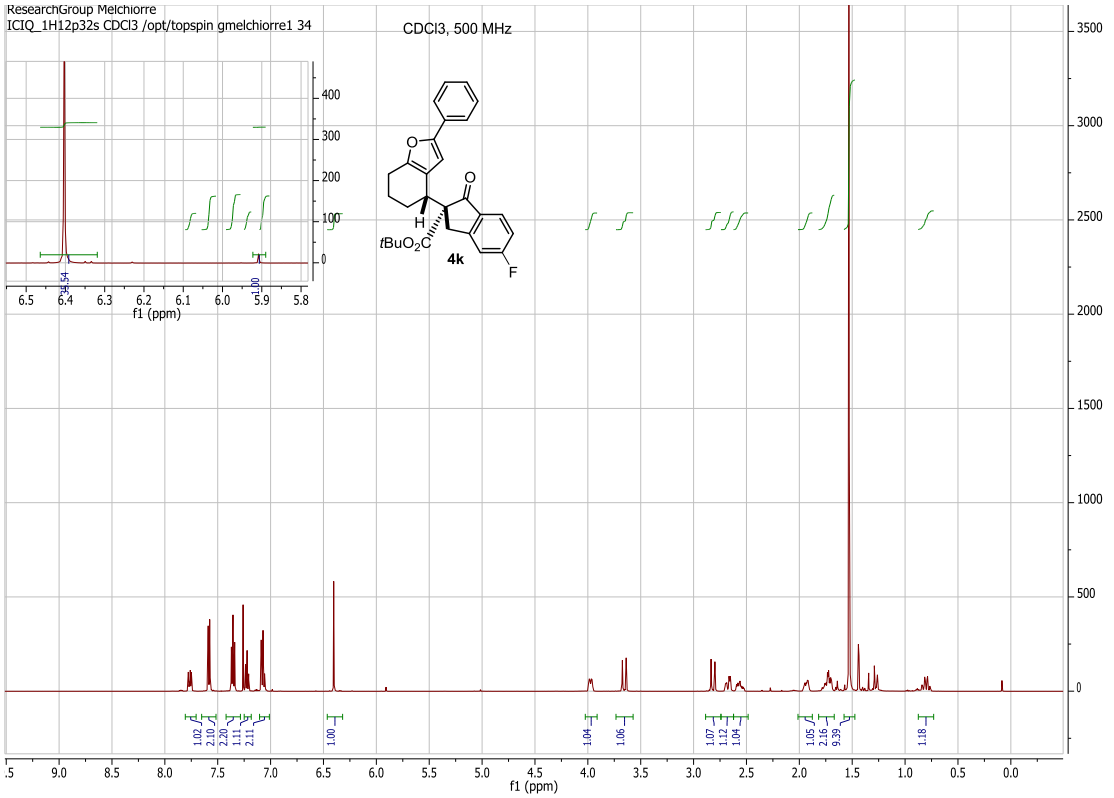
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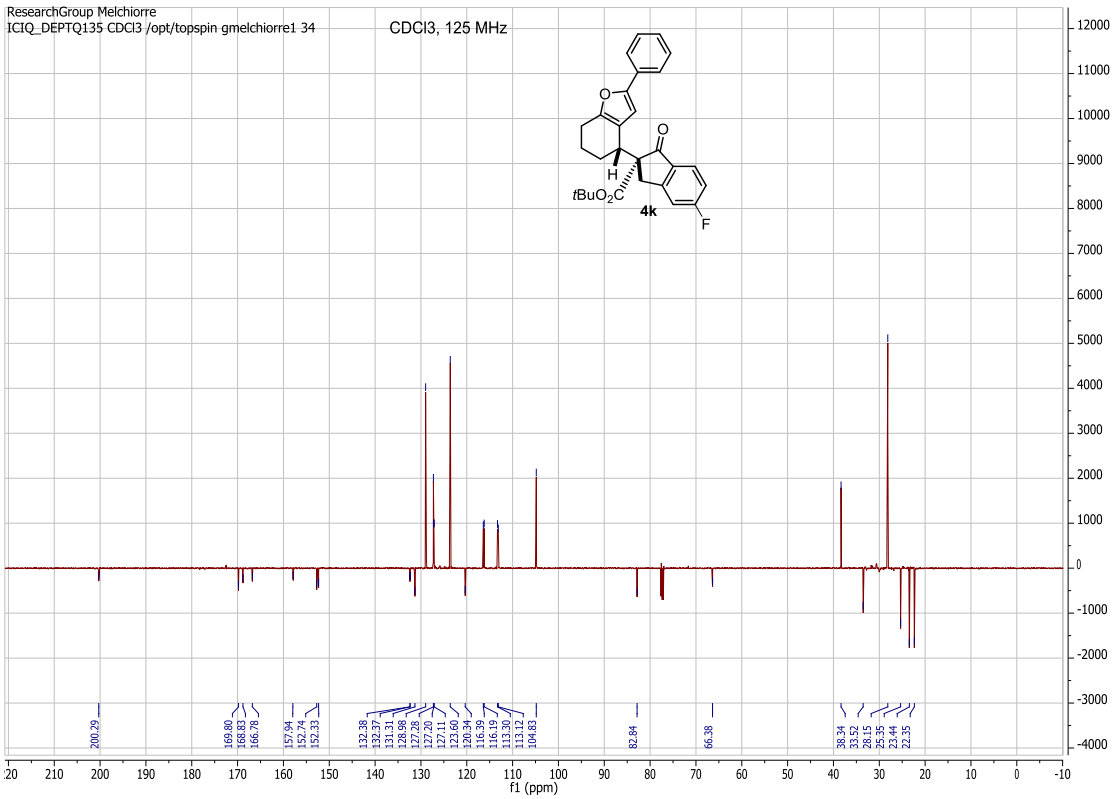
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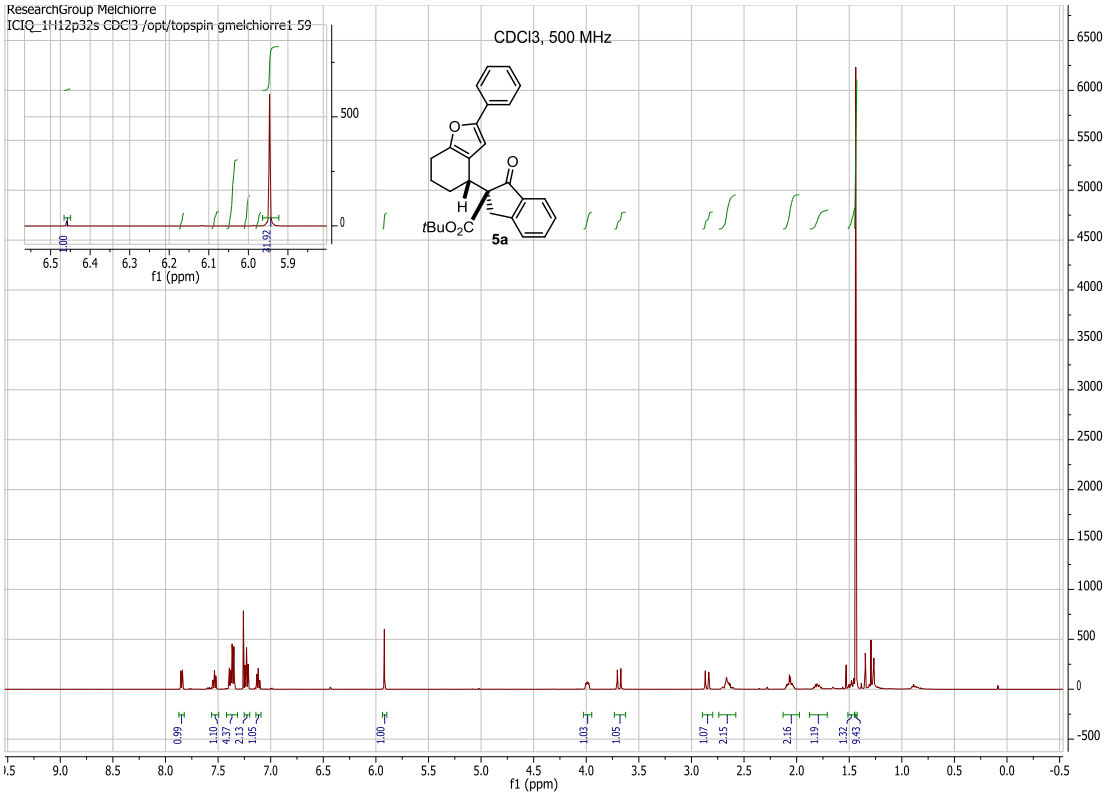
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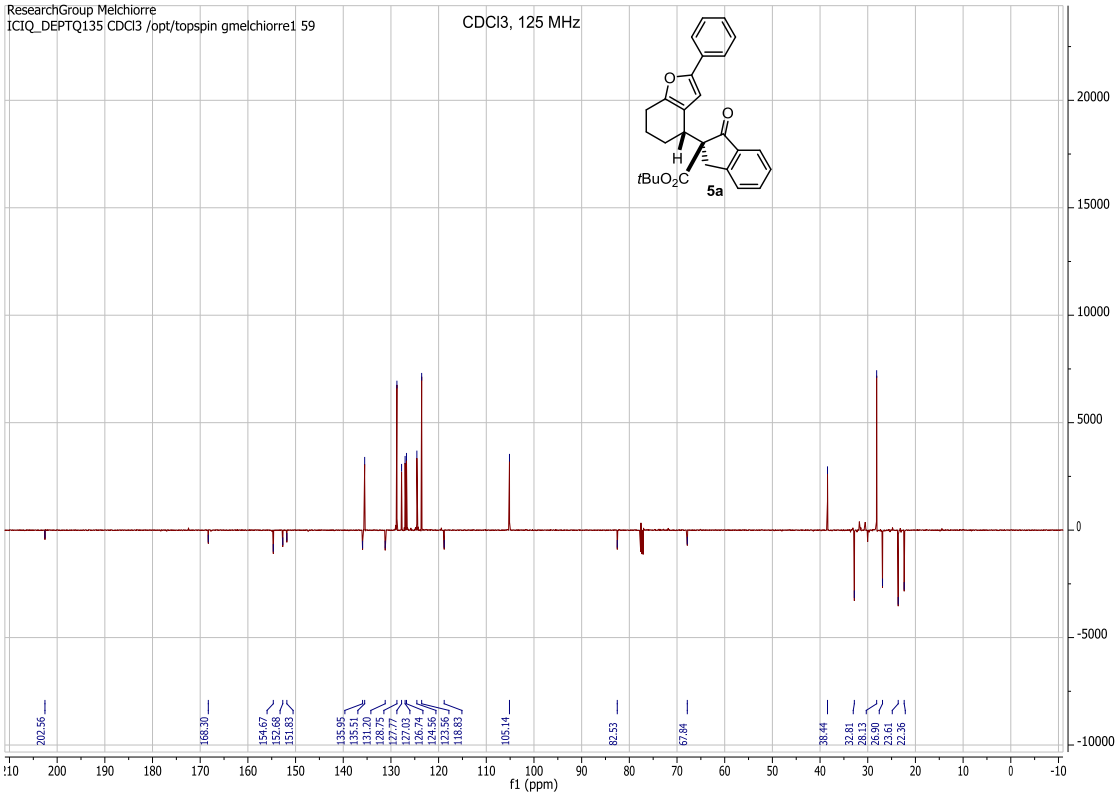
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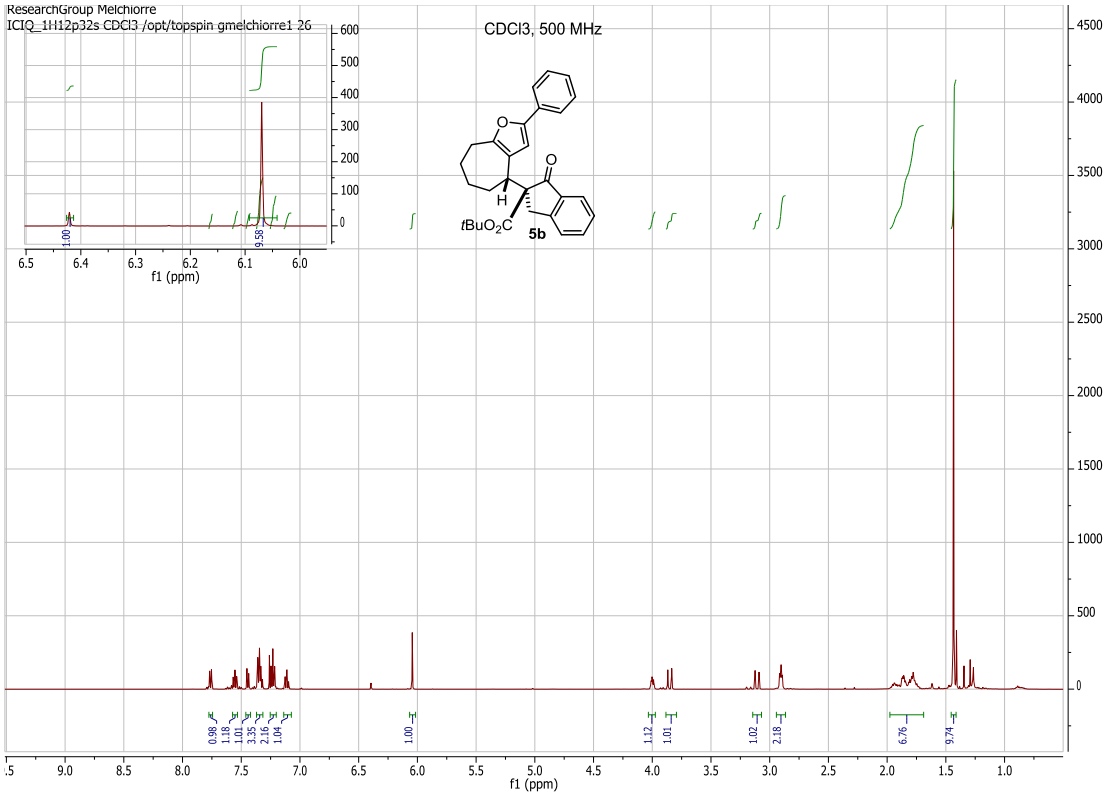
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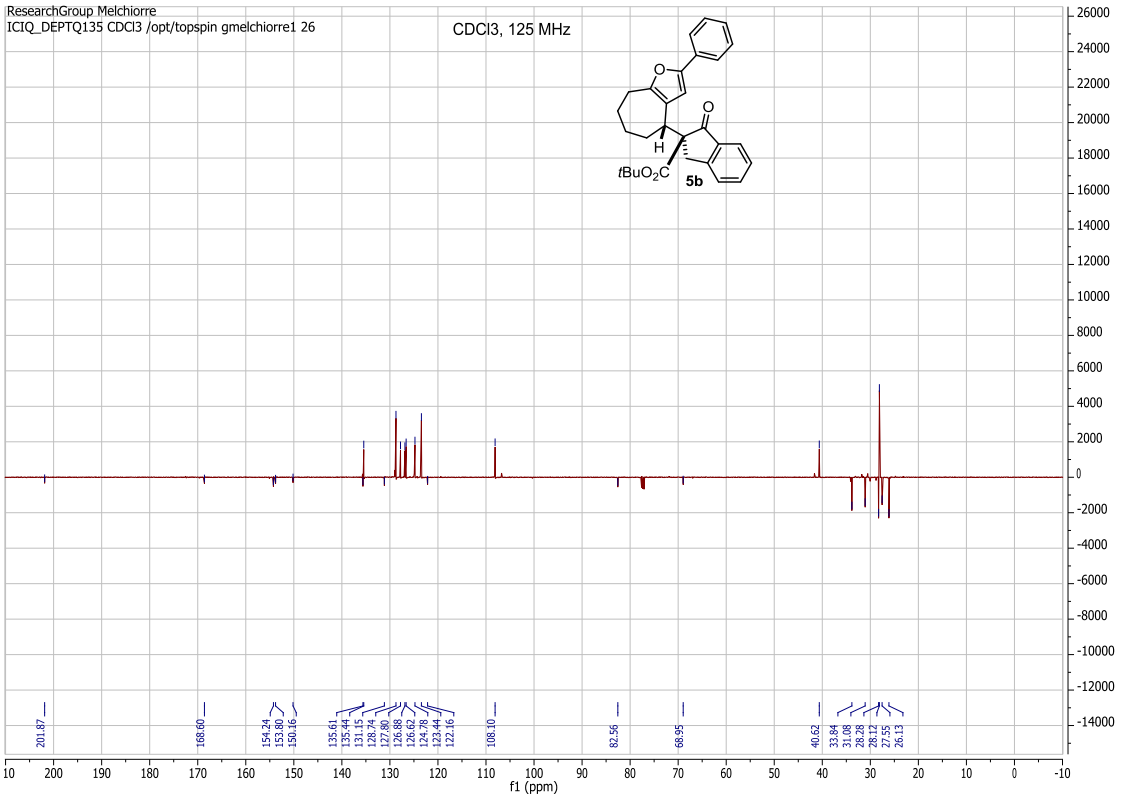
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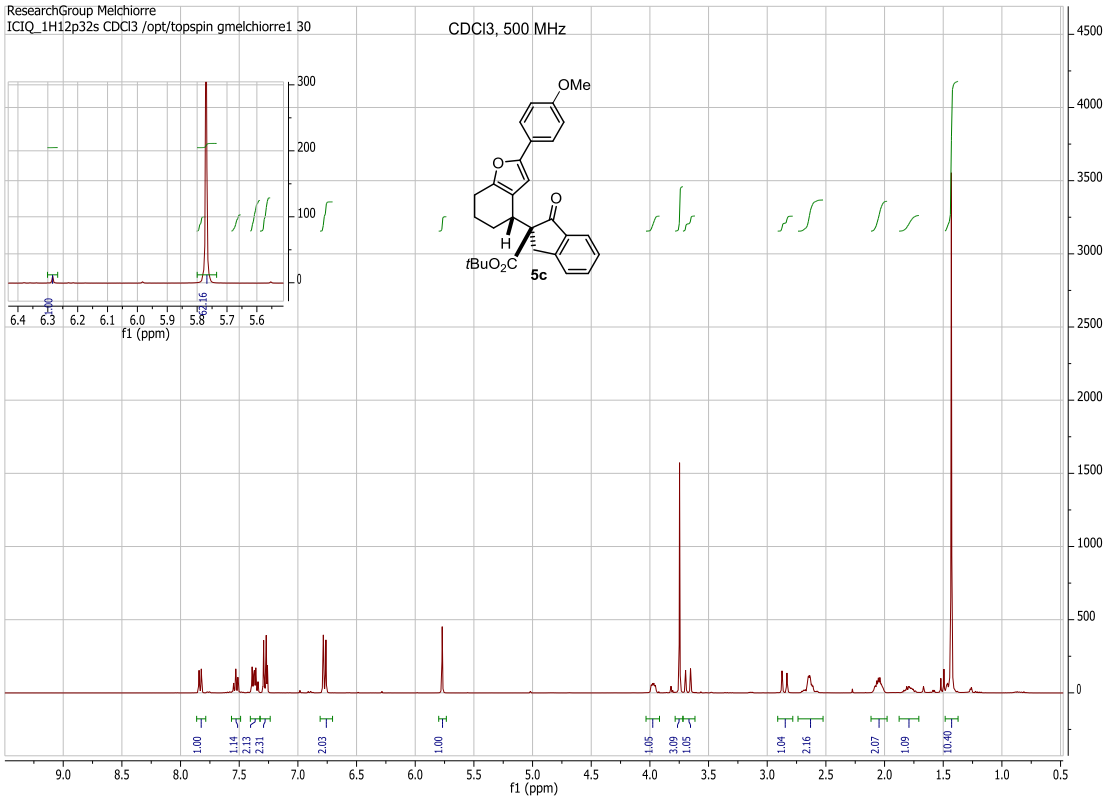
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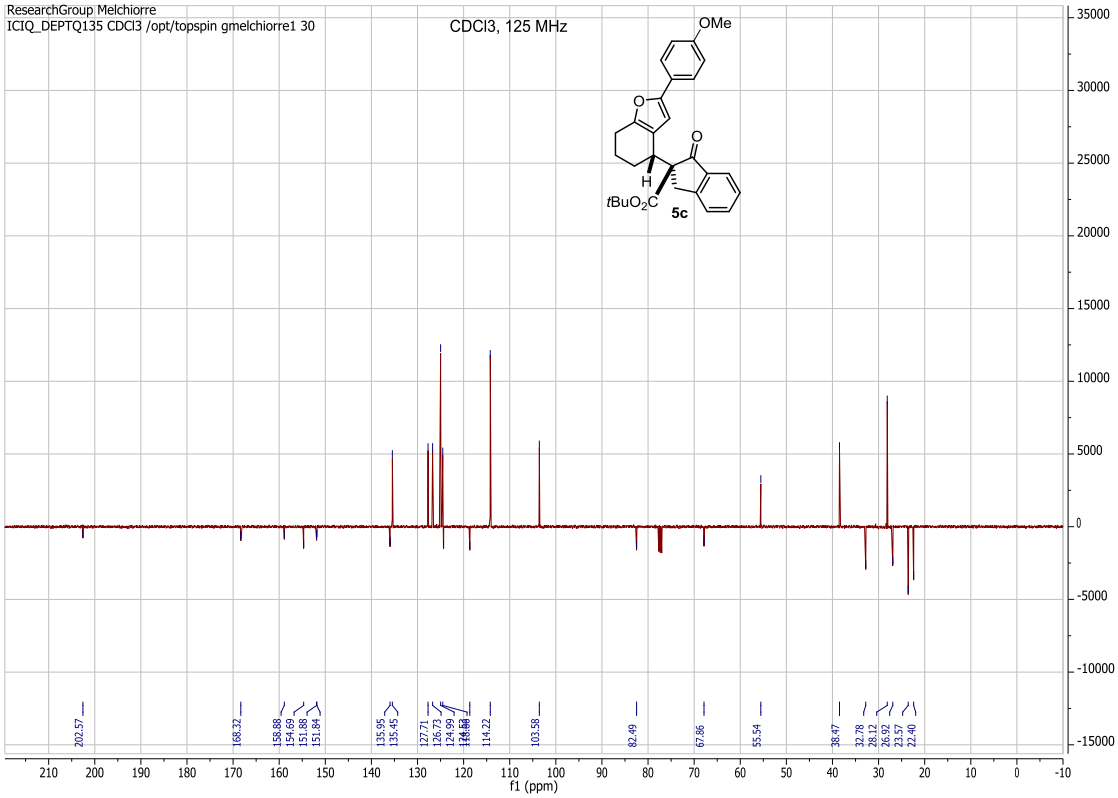
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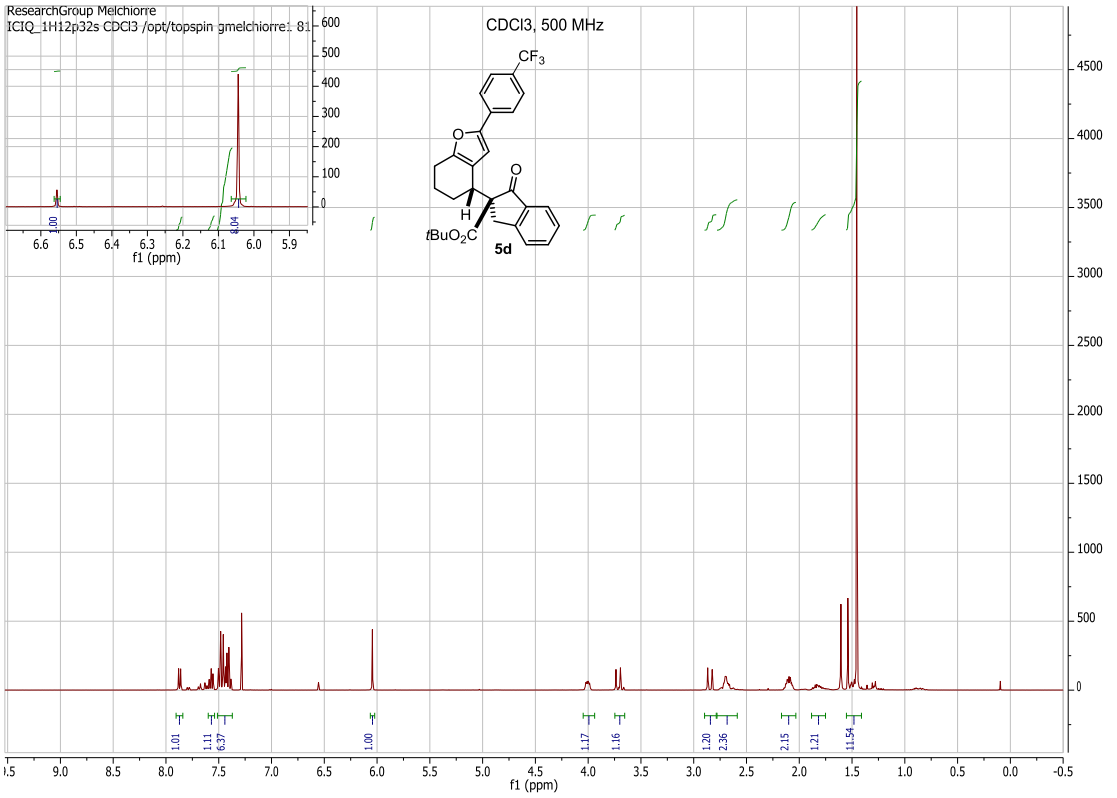
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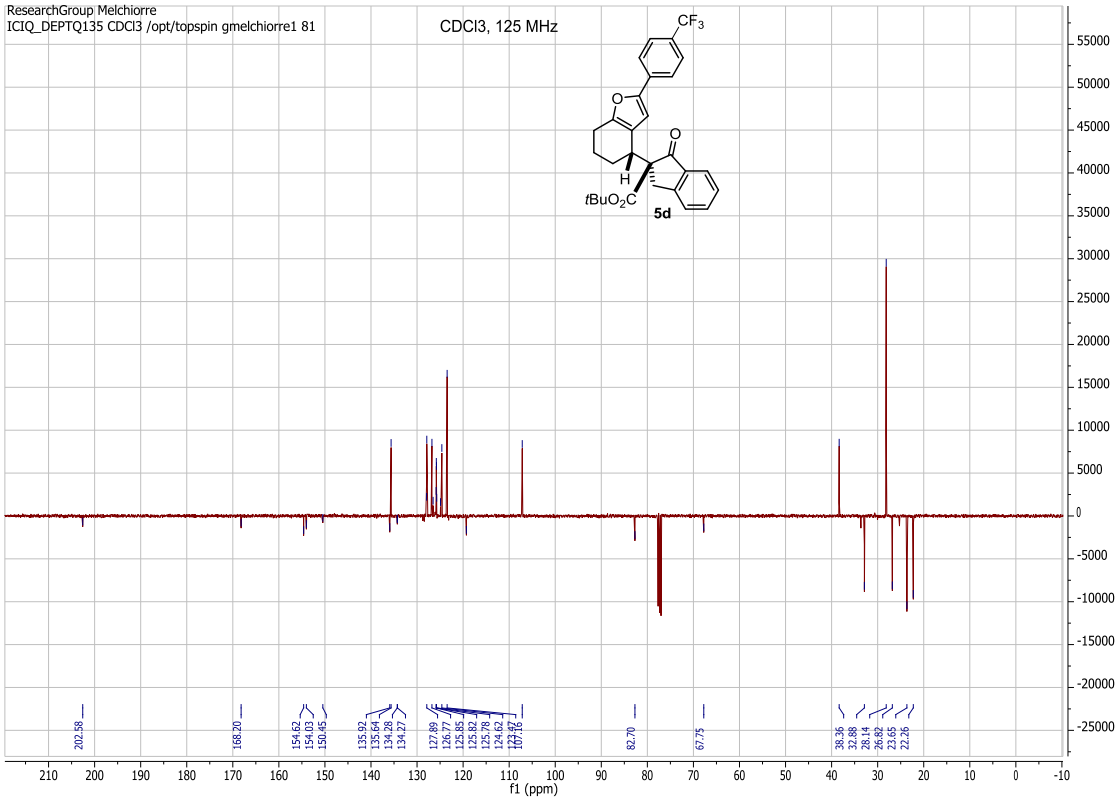
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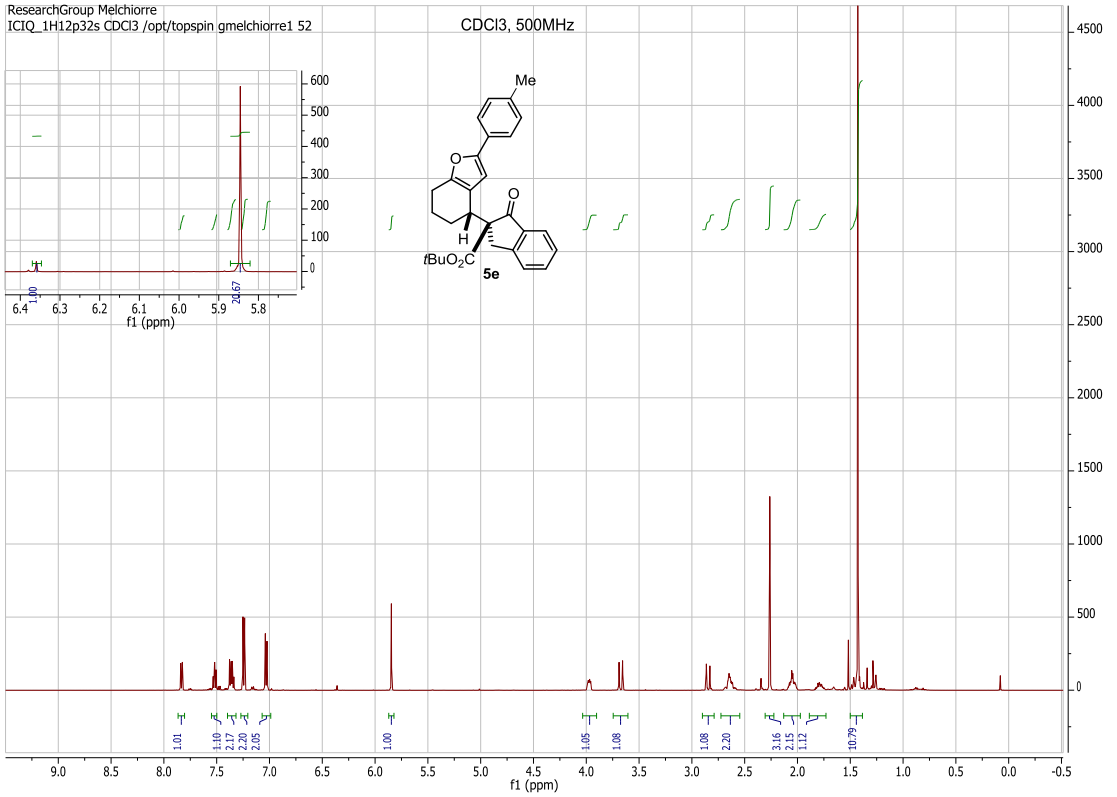
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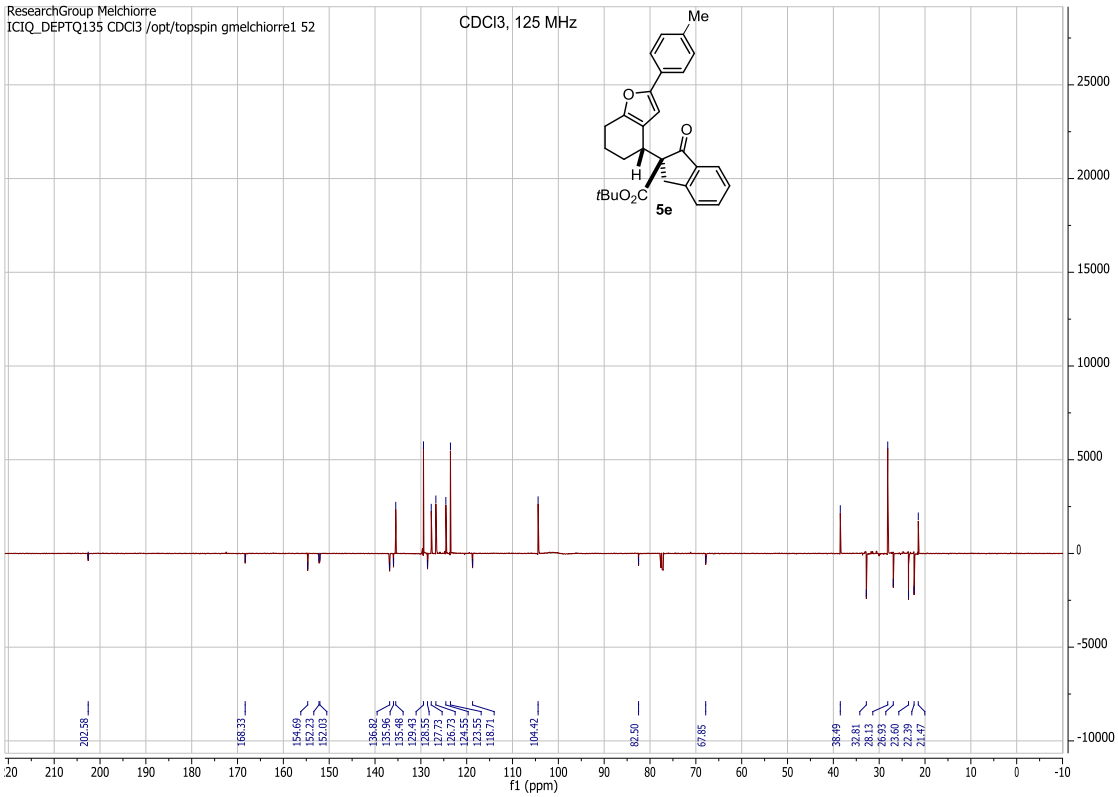
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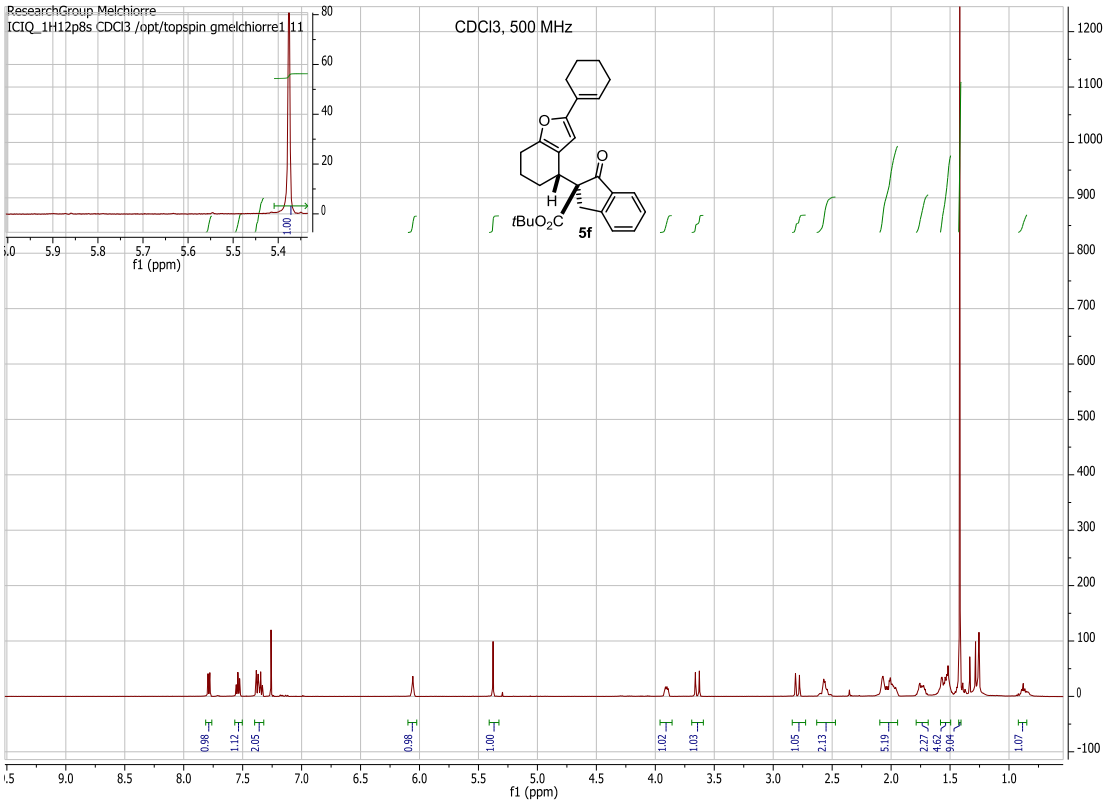
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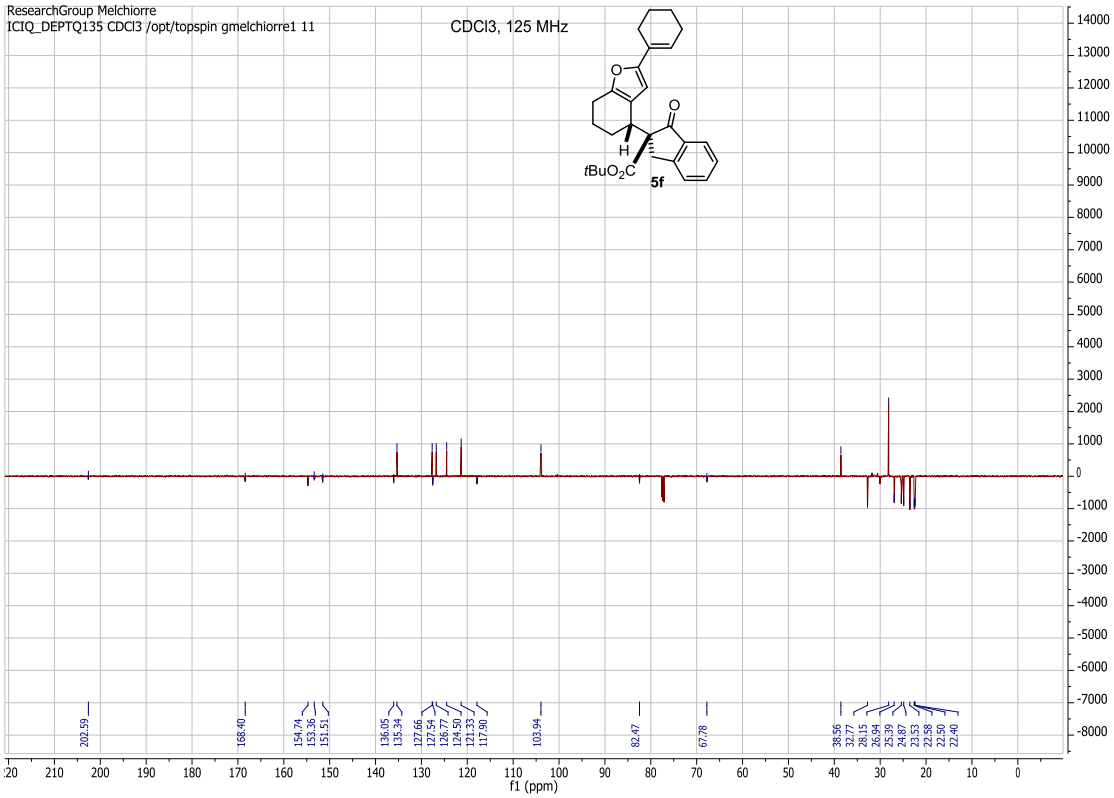
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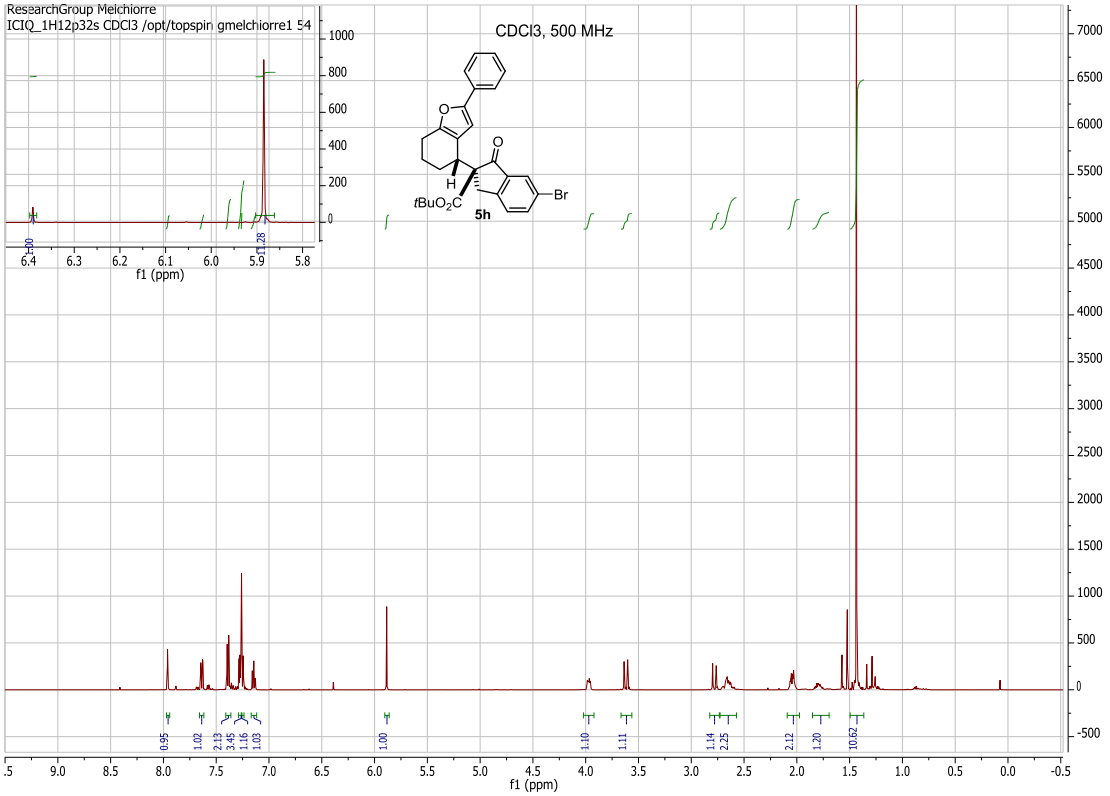
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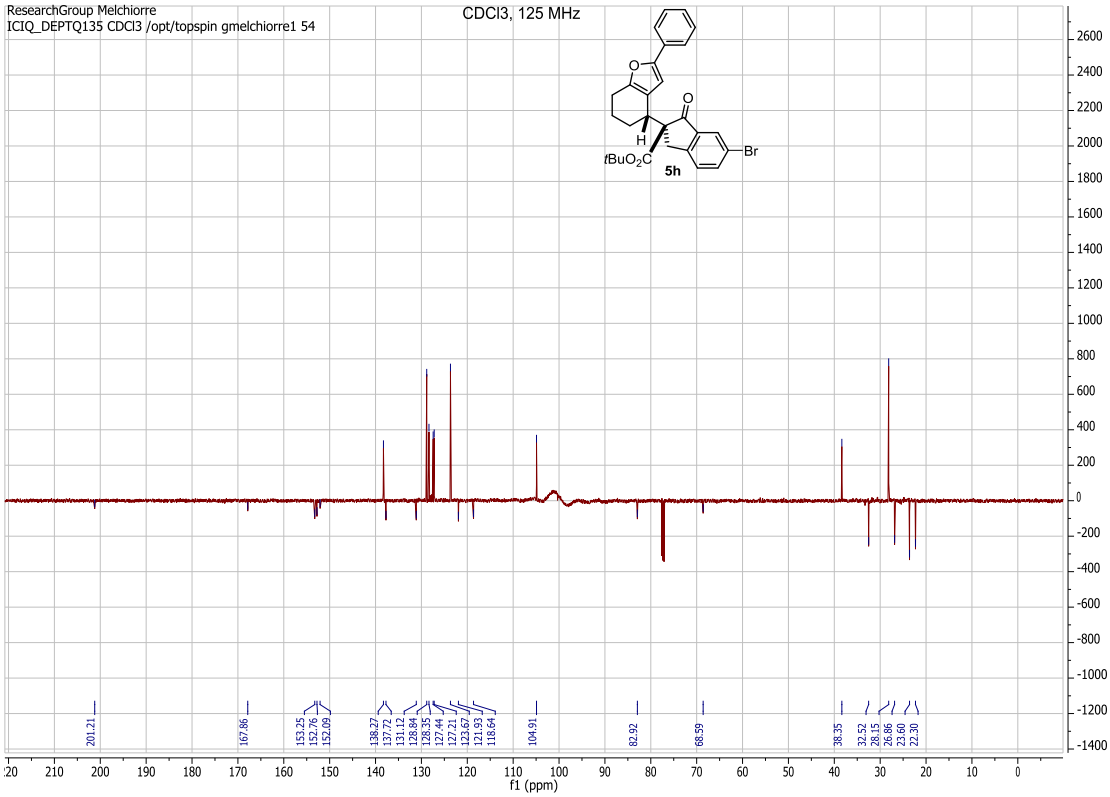
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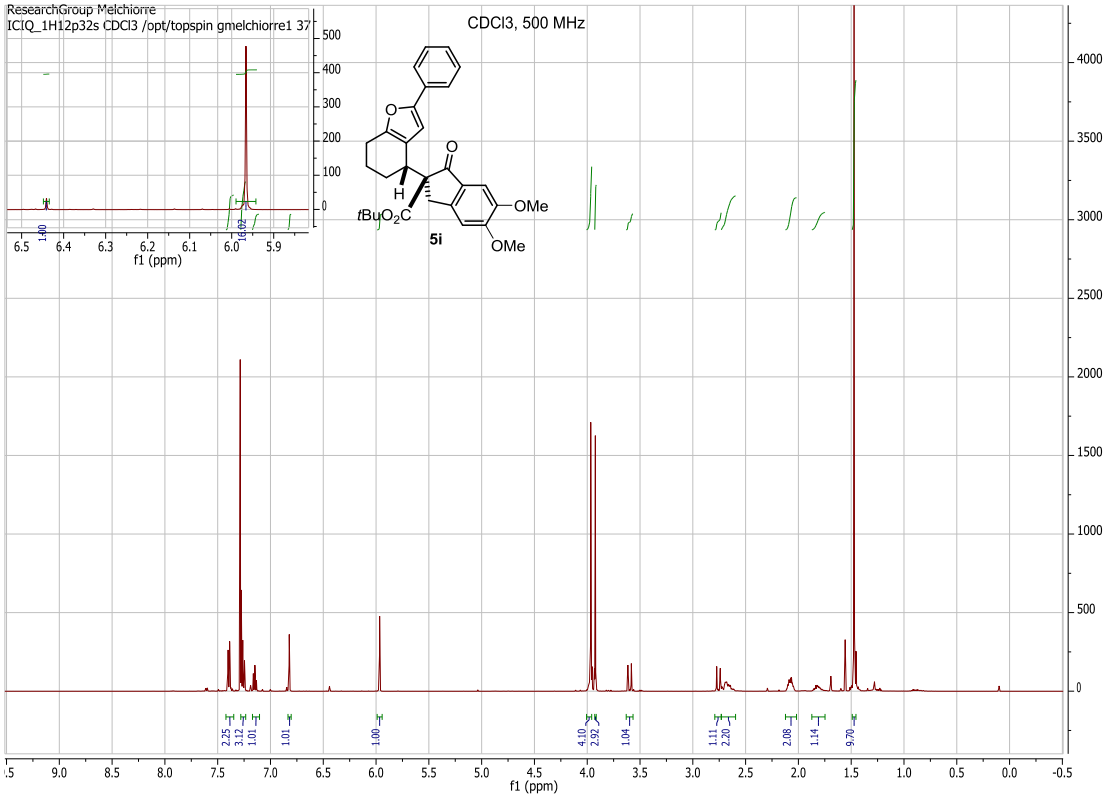
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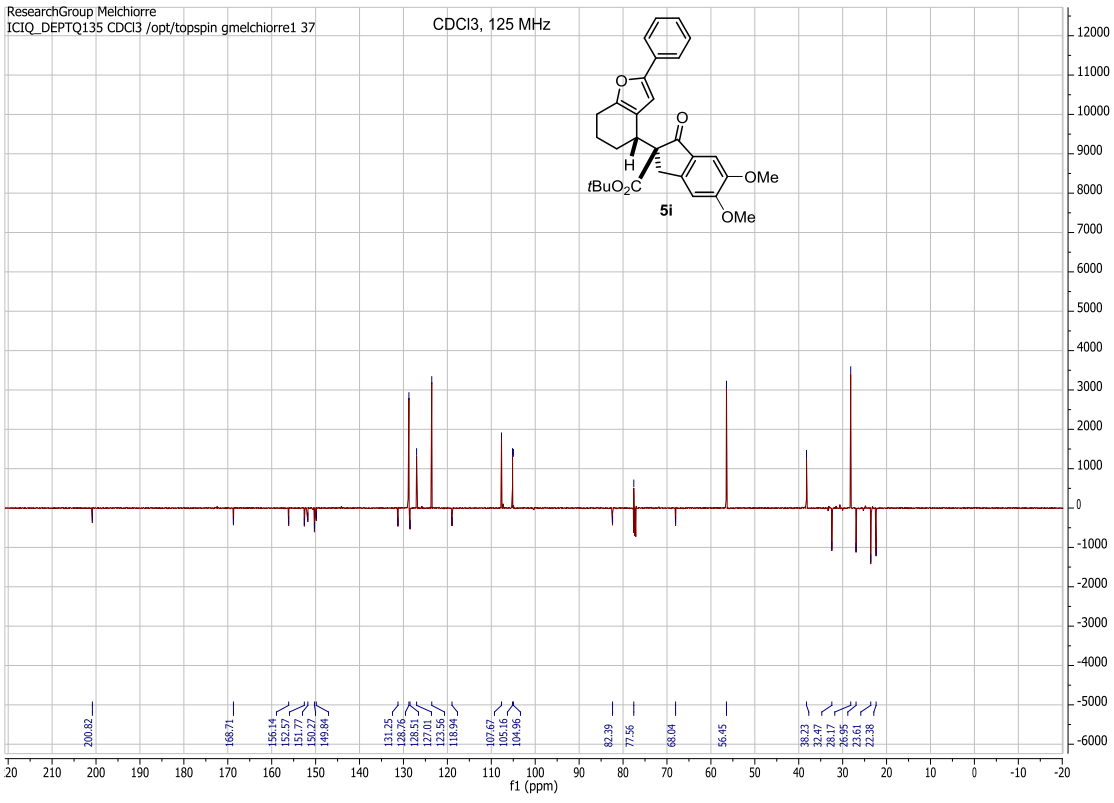
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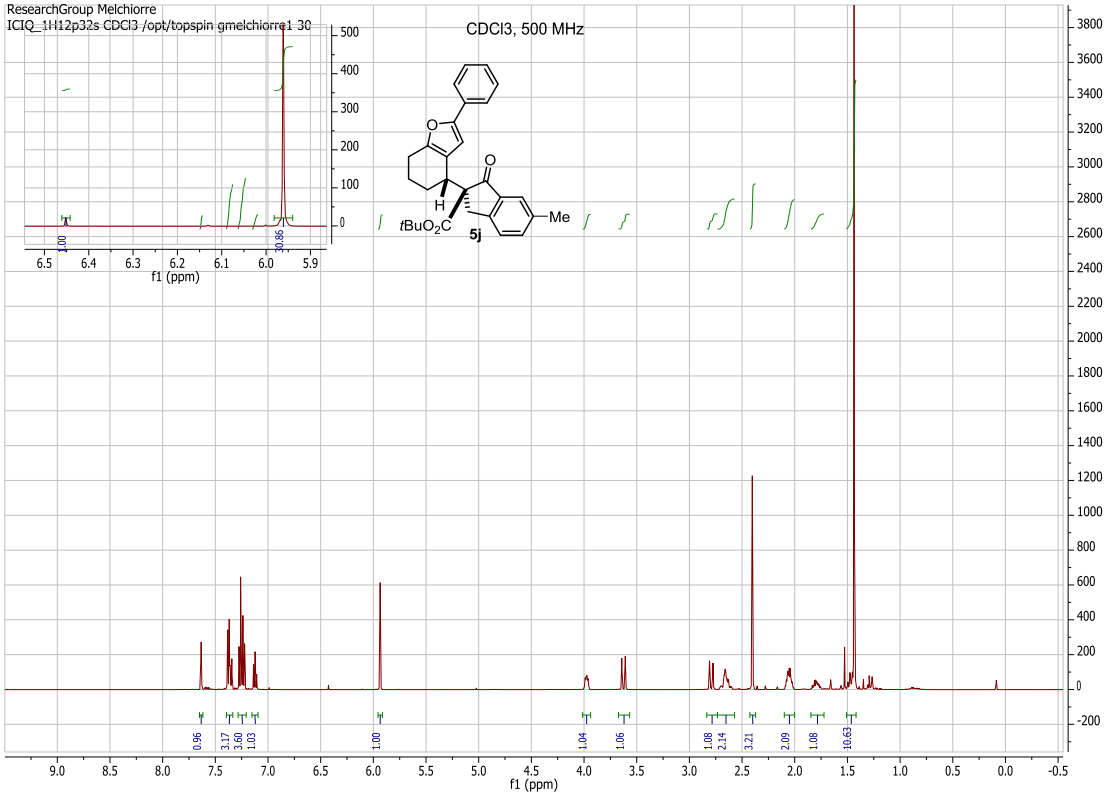
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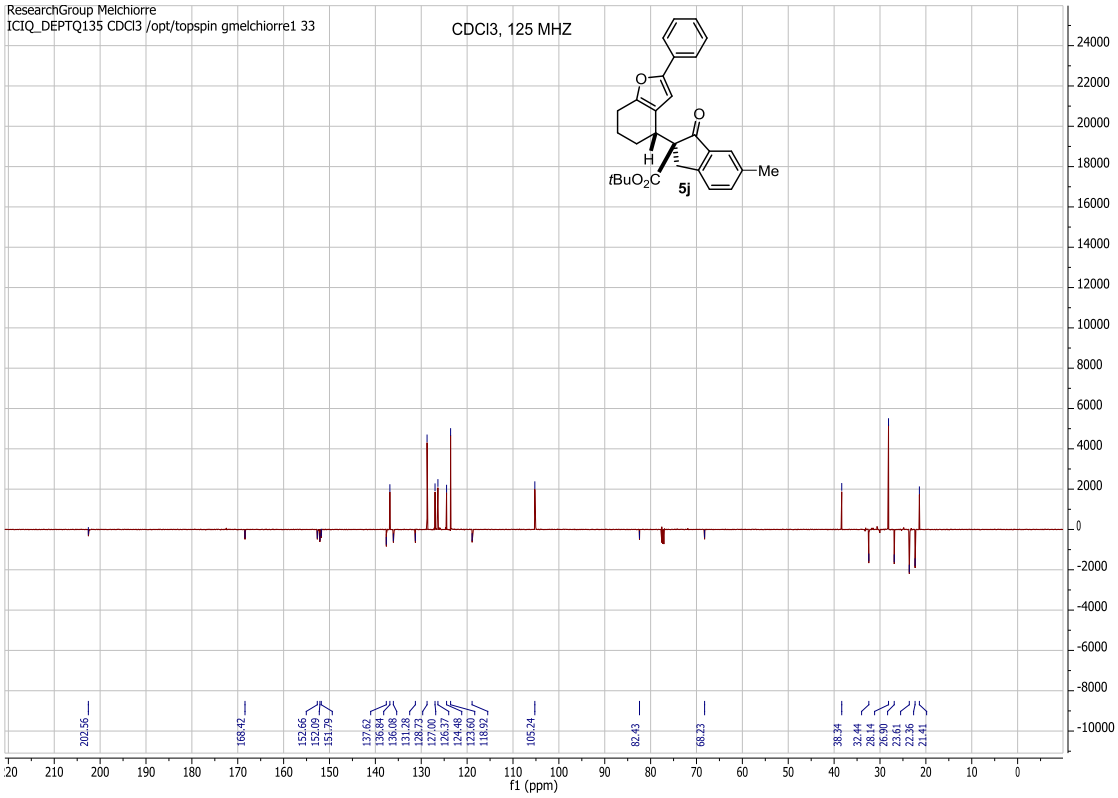
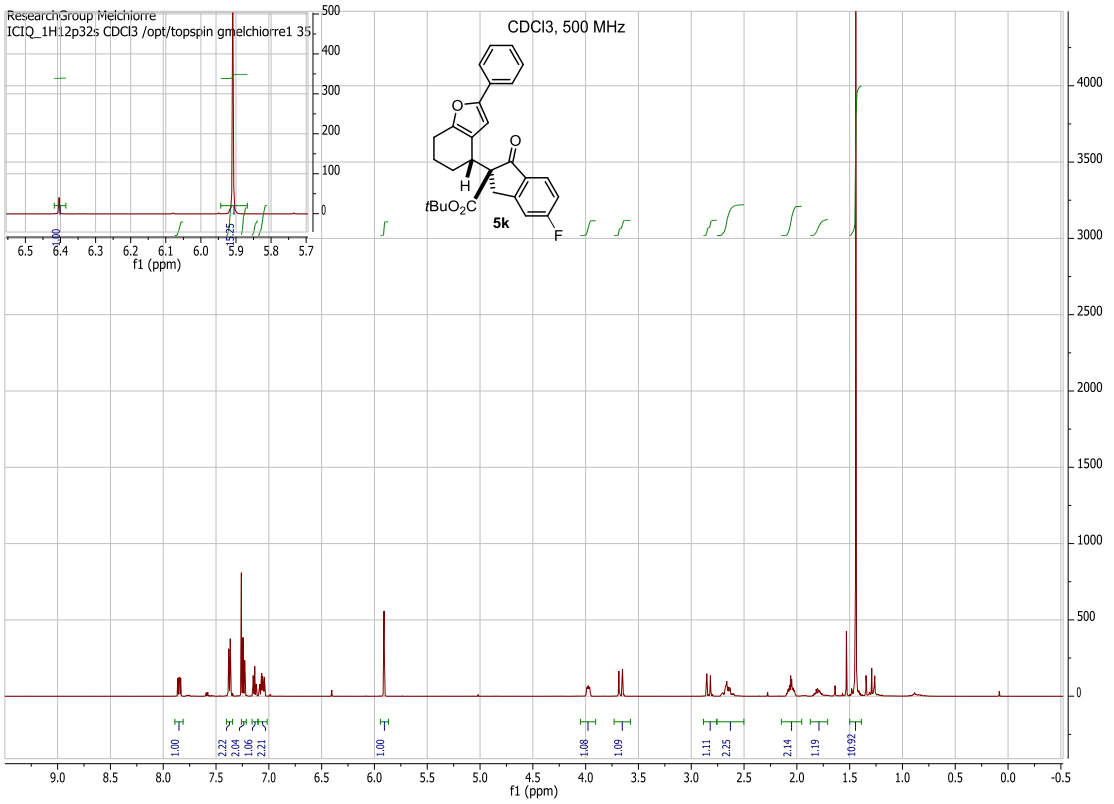
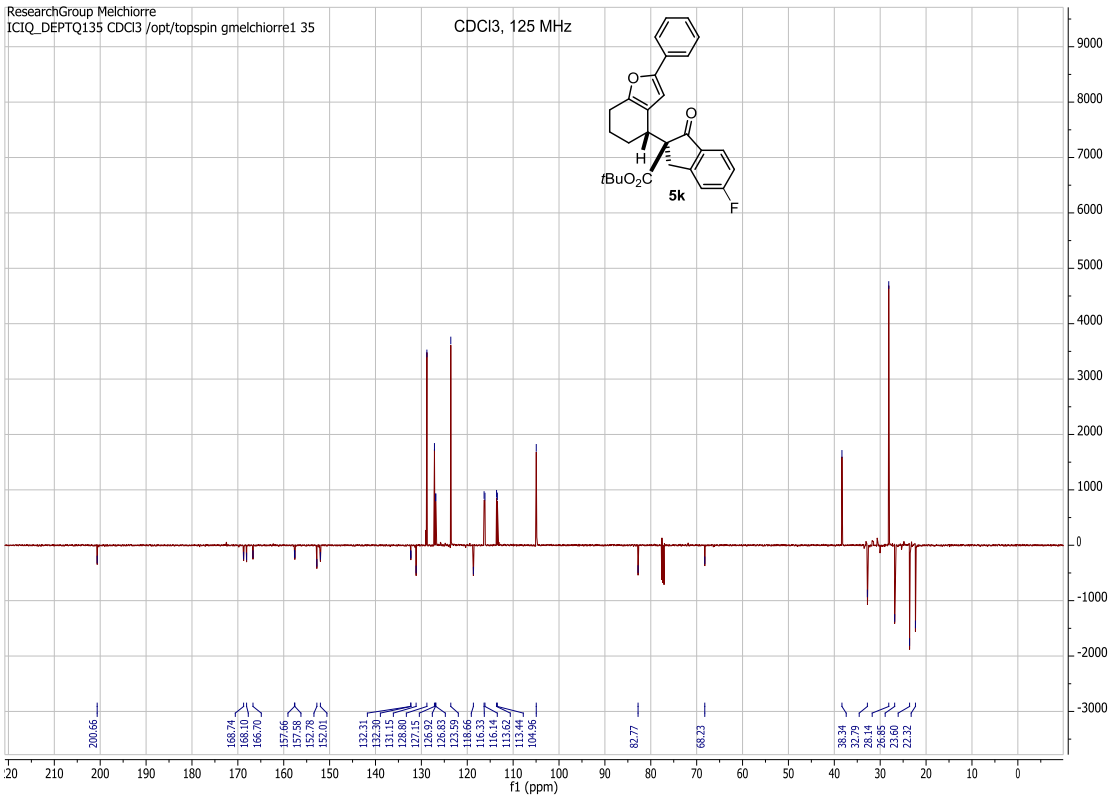
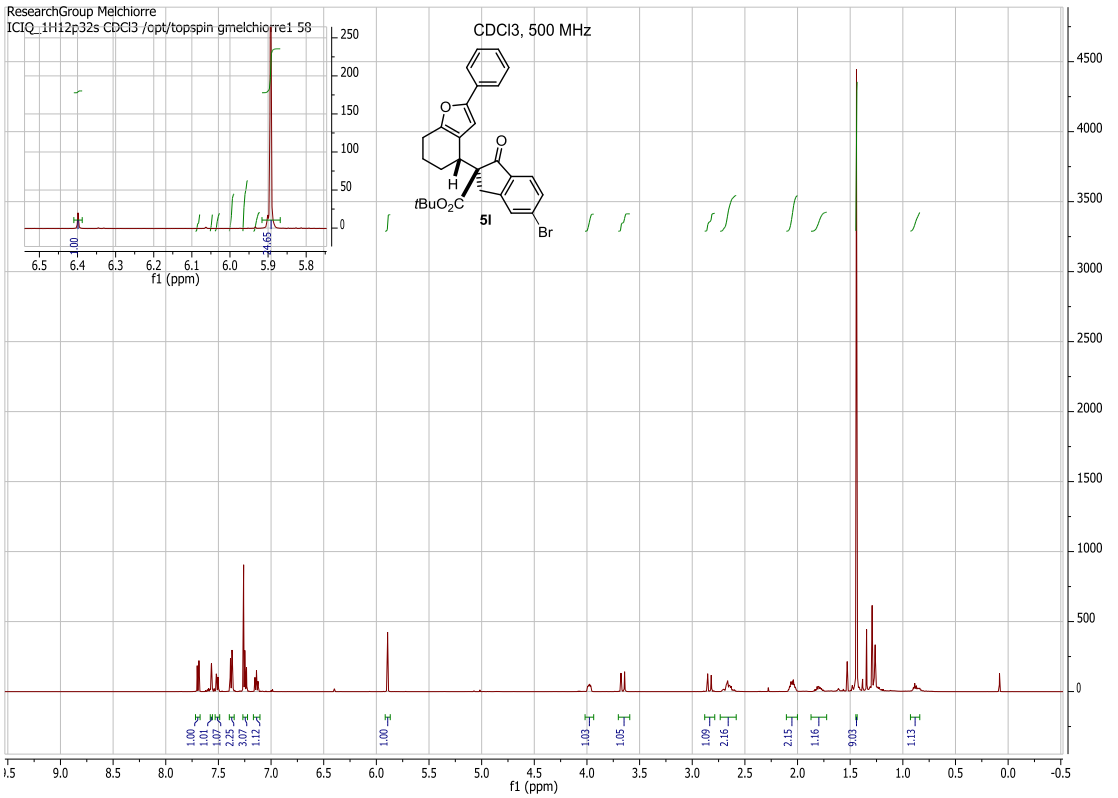
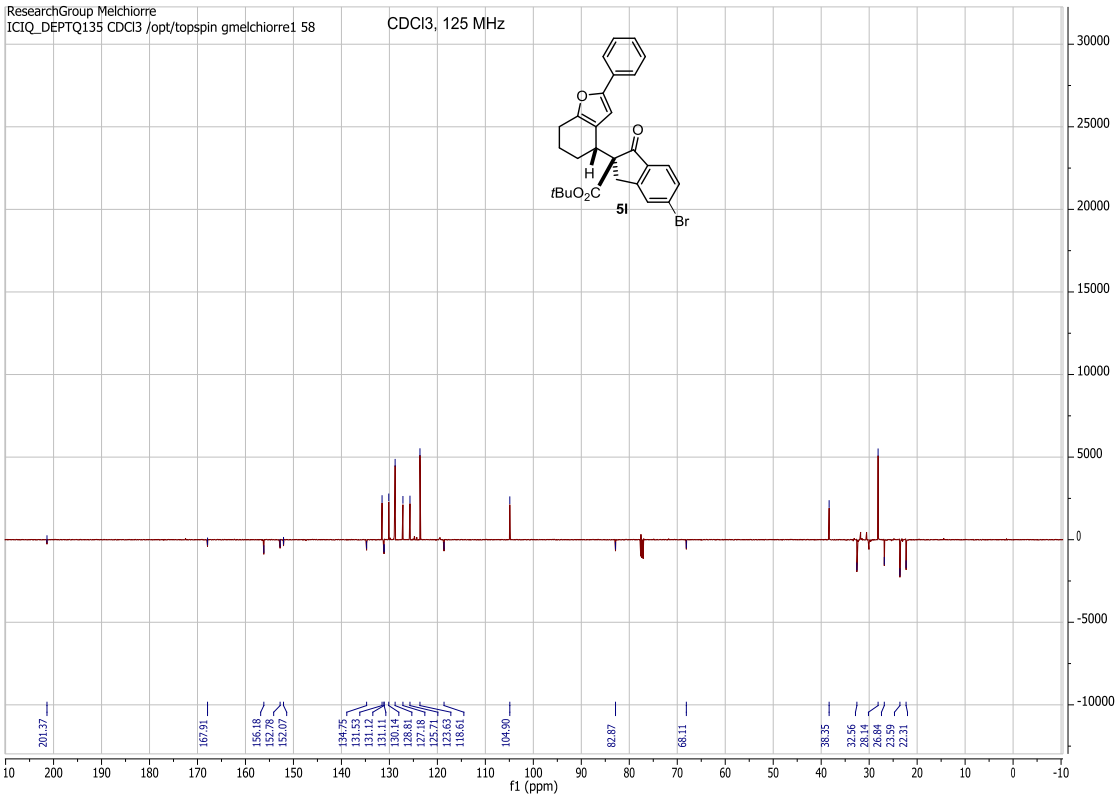
CDCl3, 500 MHz
5j
f1 (ppm)


ResearchGroup Melchiorre
ICIQ_DEPTQ135 CDCl3 /opt/topspin gmelchiorre1 33
CDCl3, 125 MHZ
5j
f1 (ppm)

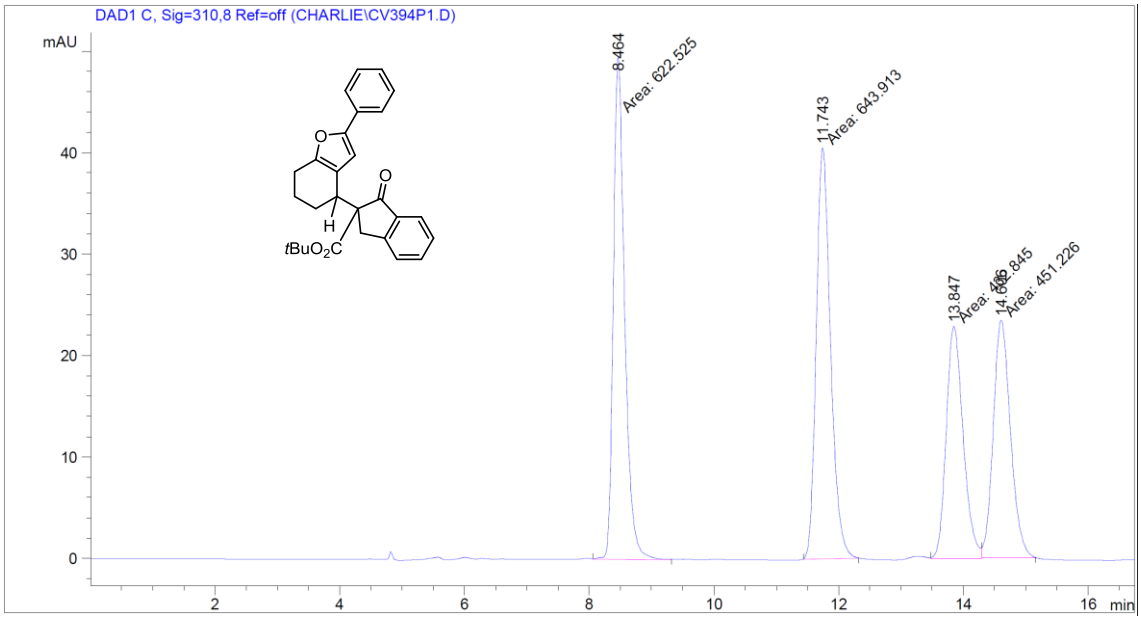

ResearchGroup Melchiorre
ICIQ_1H12p32s CDCl3 /opt/topspin gmelchiorre1 35
CDCl3, 500 MHz
5k
f1 (ppm)


ResearchGroup Melchiorre
ICIQ_DEPTQ135 CDCl3 /opt/topspin gmelchiorre1 35
CDCl3, 125 MHz
5k
f1 (ppm)

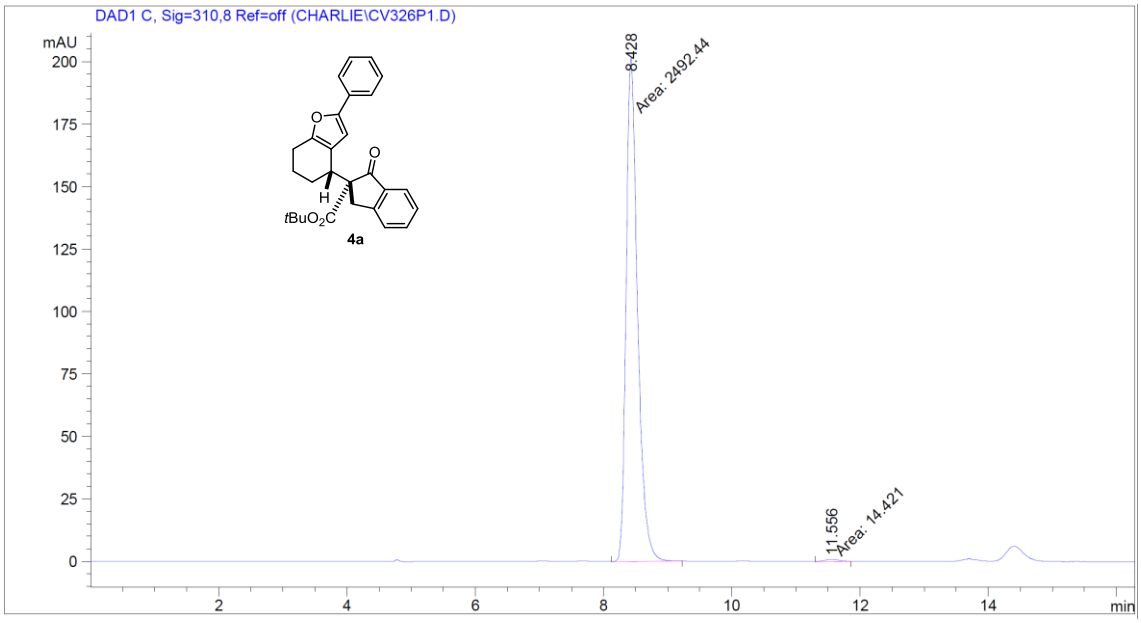

ResearchGroup Melchiorre
ICIQ_1H12p32s CDCl3 /opt/topspin gmelchiorre1 58
CDCl3, 500 MHz
5l
f1 (ppm)


ResearchGroup Melchiorre
ICIQ_DEPTQ135 CDCl3 /opt/topspin gmelchiorre1 58
CDCl3, 125 MHz
5l
f1 (ppm)

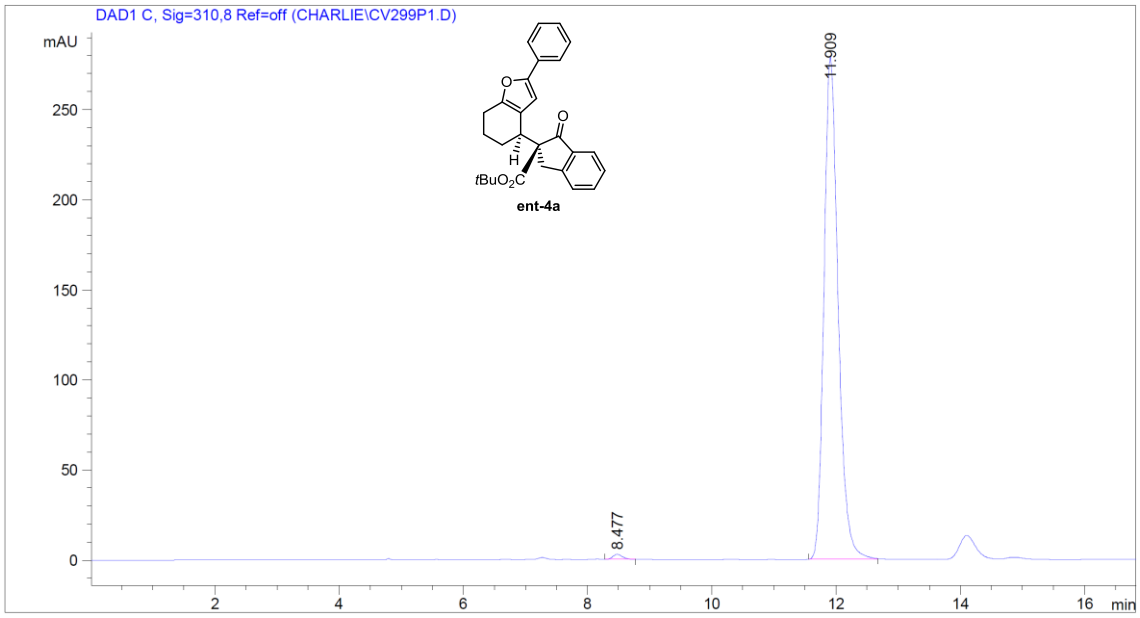
J. HPLC traces



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.464	MM	0.2097	622.52460	49.47841	28.9478
2	11.743	MM	0.2649	643.91327	40.51063	29.9424
3	13.847	MM	0.3149	432.84479	22.90557	20.1276
4	14.606	MM	0.3211	451.22604	23.42338	20.9823

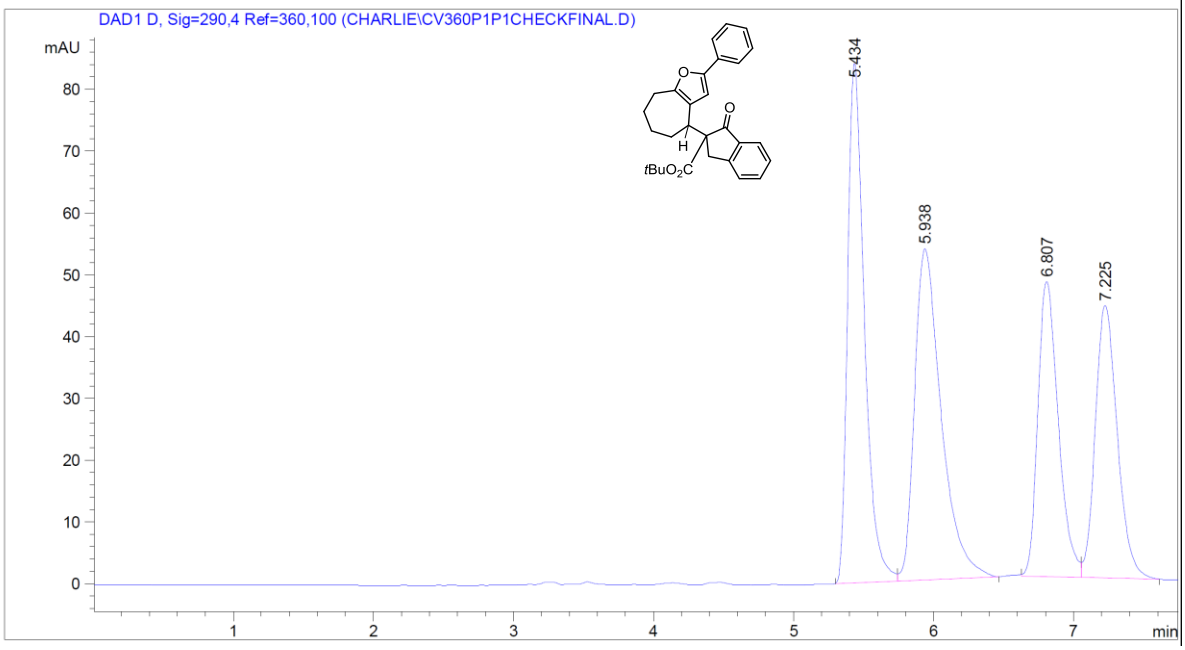


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.428	MM	0.2061	2492.43726	201.57222	99.4247
2	11.556	MM	0.2698	14.42099	8.90901e-1	0.5753



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.477	BB	0.1672	31.13586	2.85637	0.7013
2	11.909	BB	0.2426	4408.78174	278.62457	99.2987

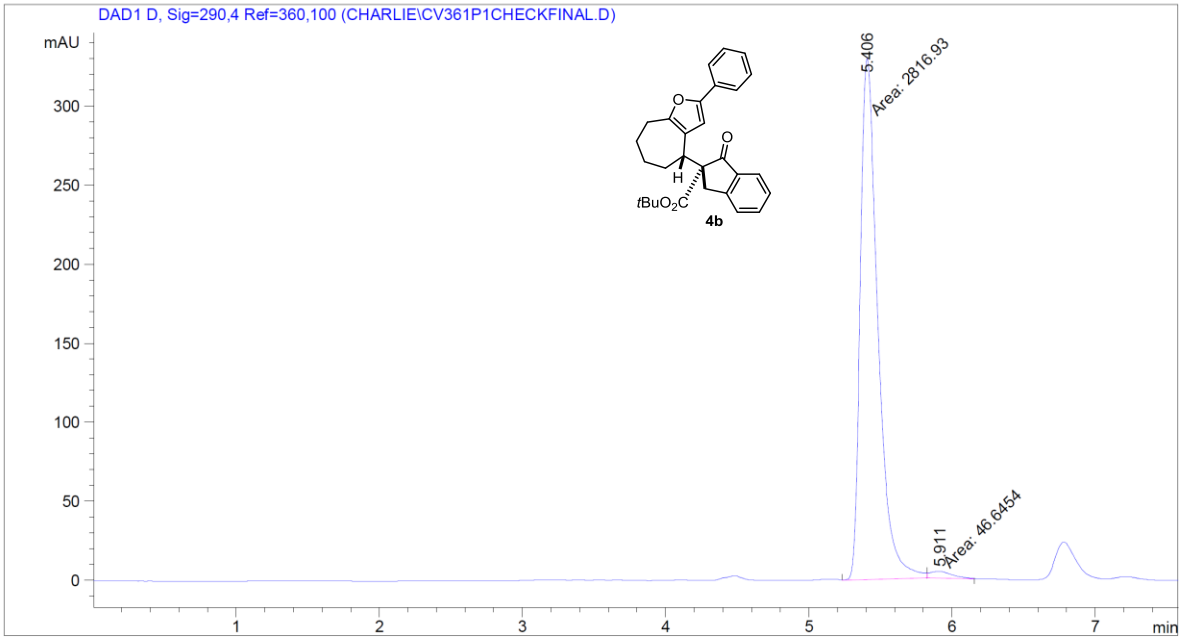
Sample Info : IA3, 20°C, 1.0 mL/min, H/DCM 85/15



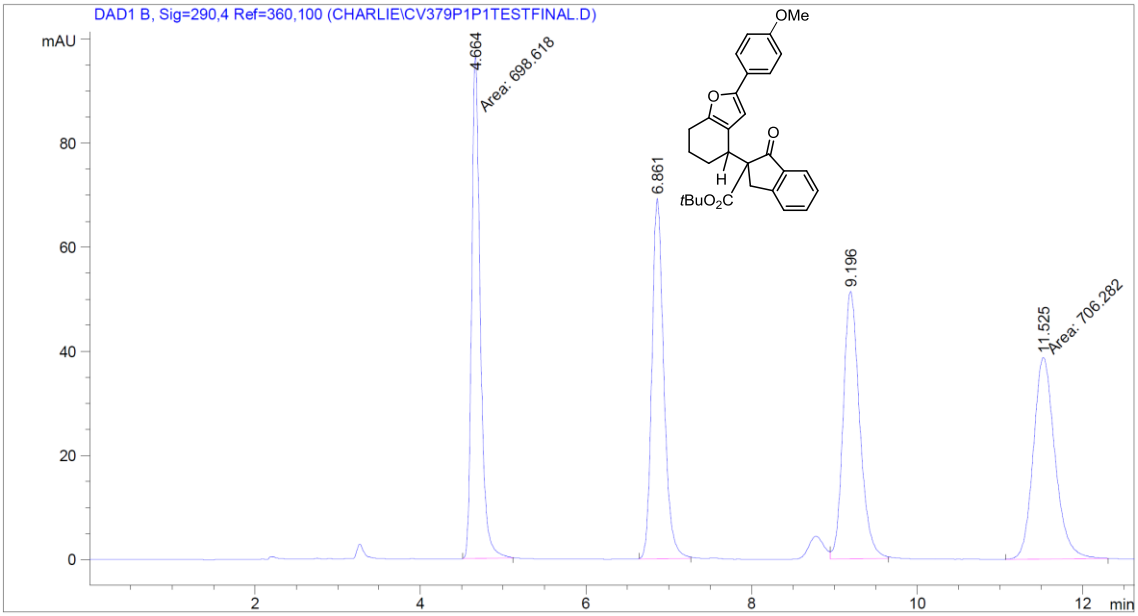
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.434	BV	0.1269	699.07312	84.15497	29.4541
2	5.938	VB	0.1999	706.72235	53.55787	29.7764
3	6.807	BV	0.1563	484.40717	47.76132	20.4096
4	7.225	VB	0.1698	483.22598	44.10889	20.3598

Sample Info : IA3, 20°C, 1.0 mL/min, H/DCM 85/15

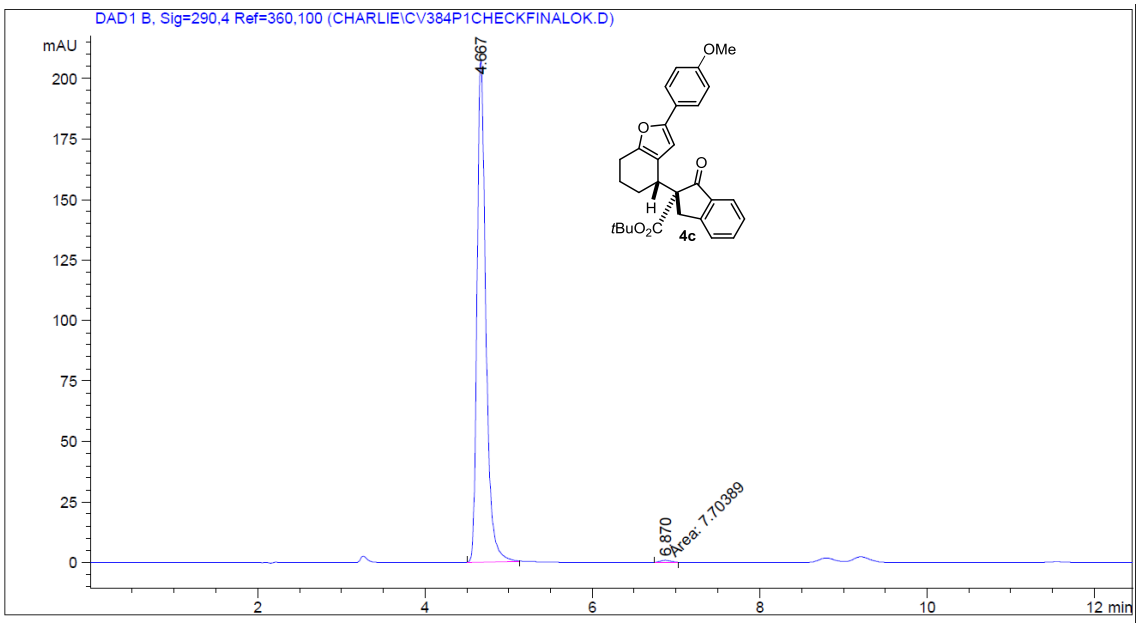
Additional Info : Peak(s) manually integrated



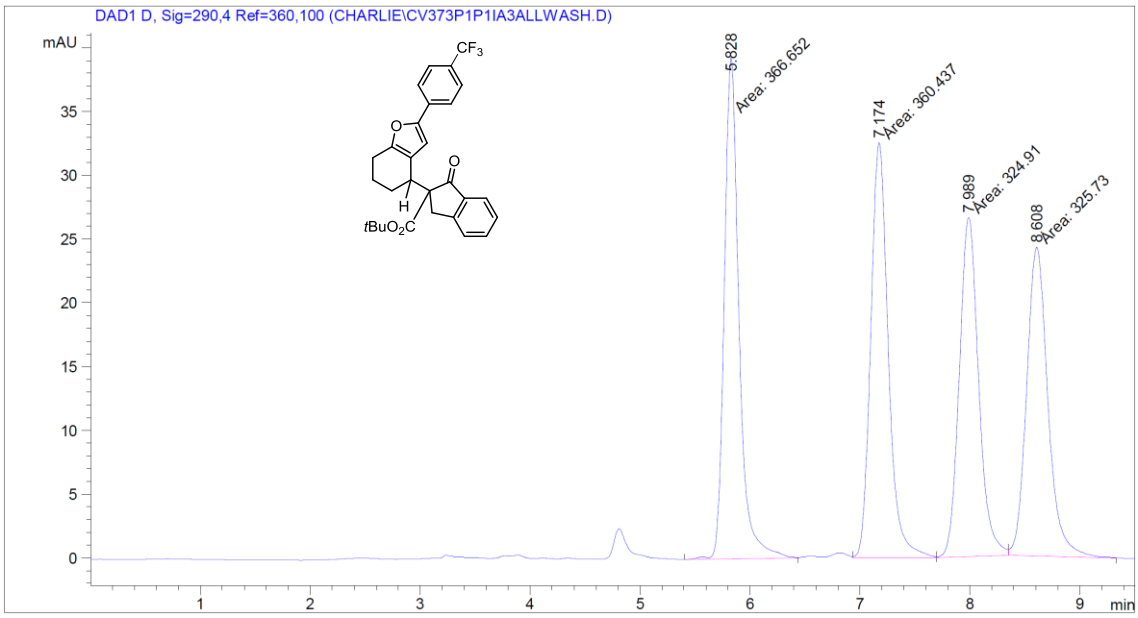
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.406	MM	0.1423	2816.93384	329.99423	98.3711
2	5.911	MM	0.1772	46.64541	4.38659	1.6289



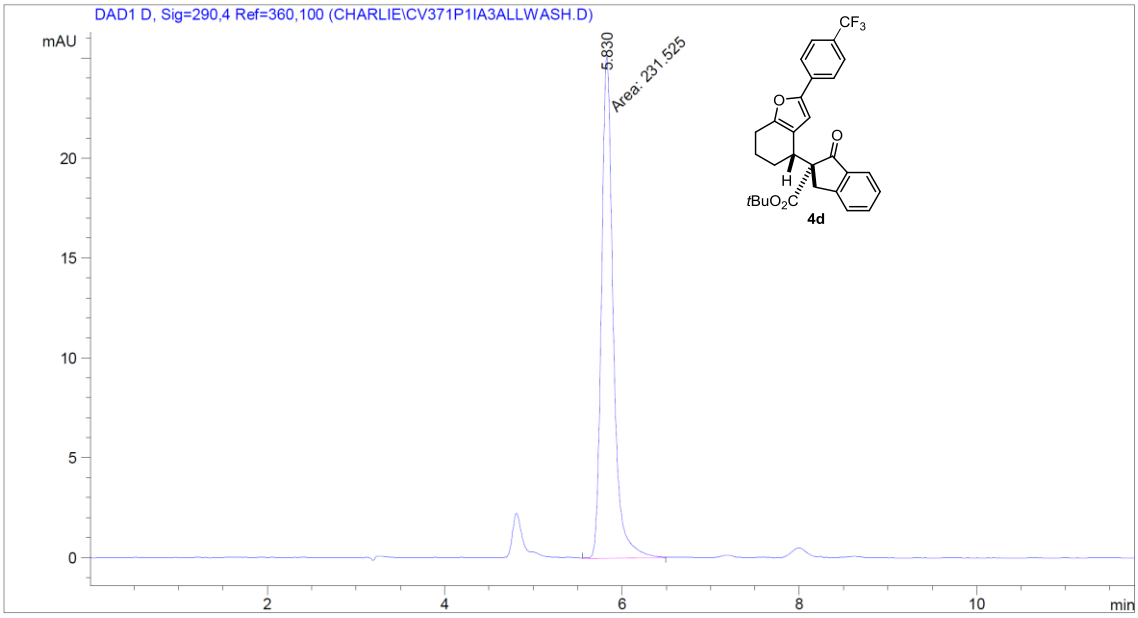
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.664	MM	0.1207	698.61780	96.46627	24.8707
2	6.861	BB	0.1529	693.47217	69.20596	24.6875
3	9.196	VB	0.2116	710.62610	51.31746	25.2982
4	11.525	MM	0.3038	706.28168	38.74936	25.1435



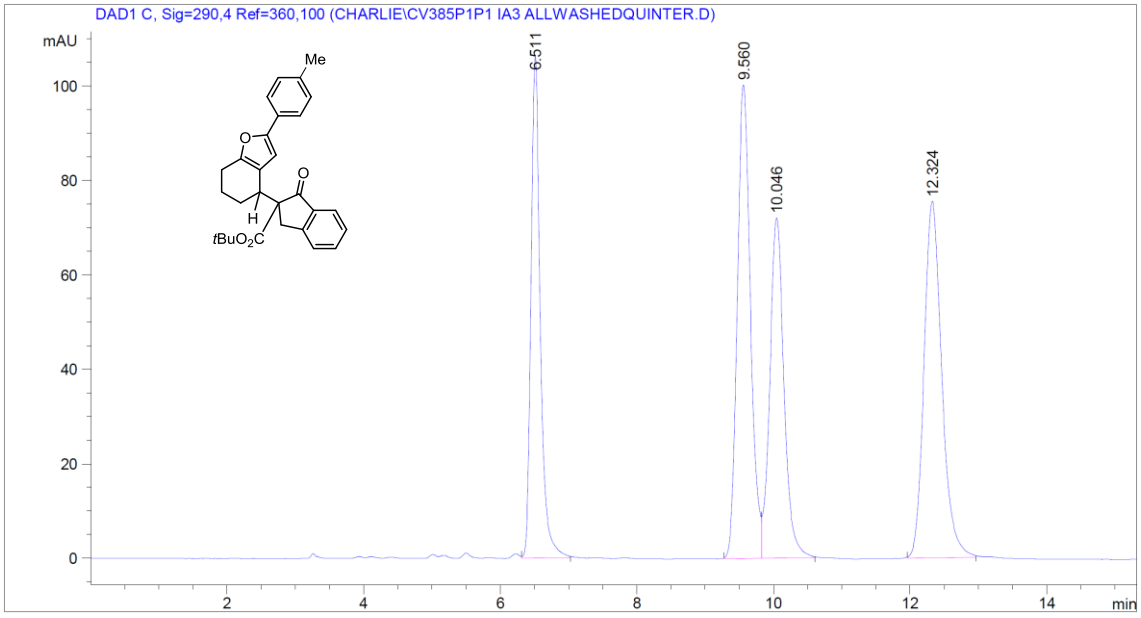
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.667	BB	0.1113	1514.55957	207.08298	99.4939
2	6.870	MM	0.1476	7.70389	8.69634e-1	0.5061



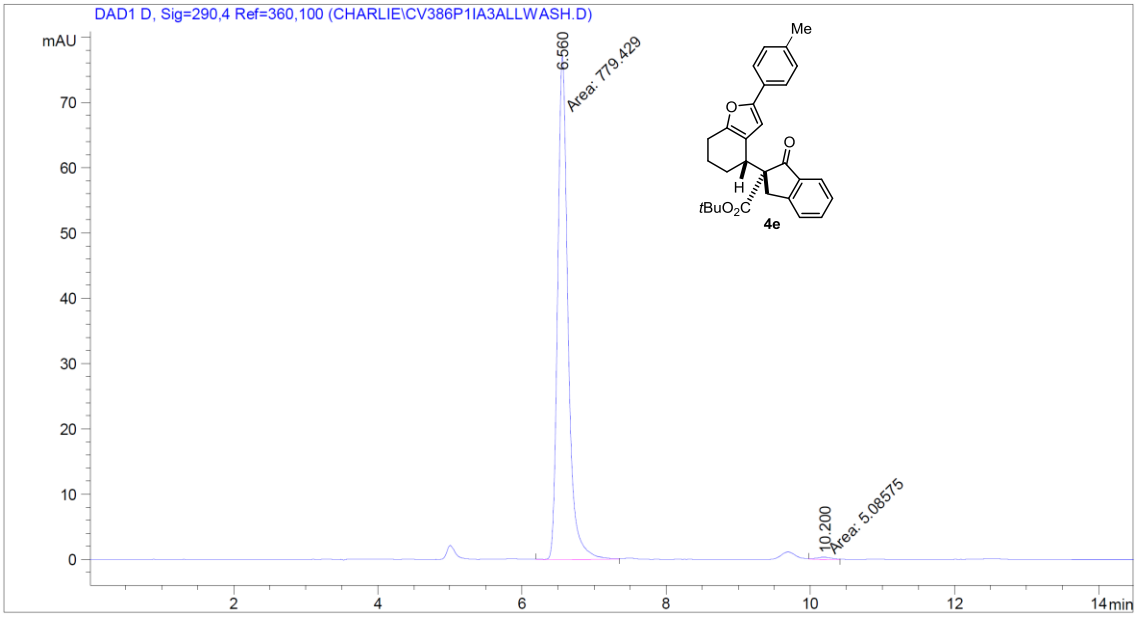
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.828	MM	0.1555	366.65216	39.29960	26.6128
2	7.174	MM	0.1845	360.43680	32.55625	26.1617
3	7.989	MM	0.2036	324.90997	26.59293	23.5830
4	8.608	MM	0.2242	325.72989	24.20884	23.6425



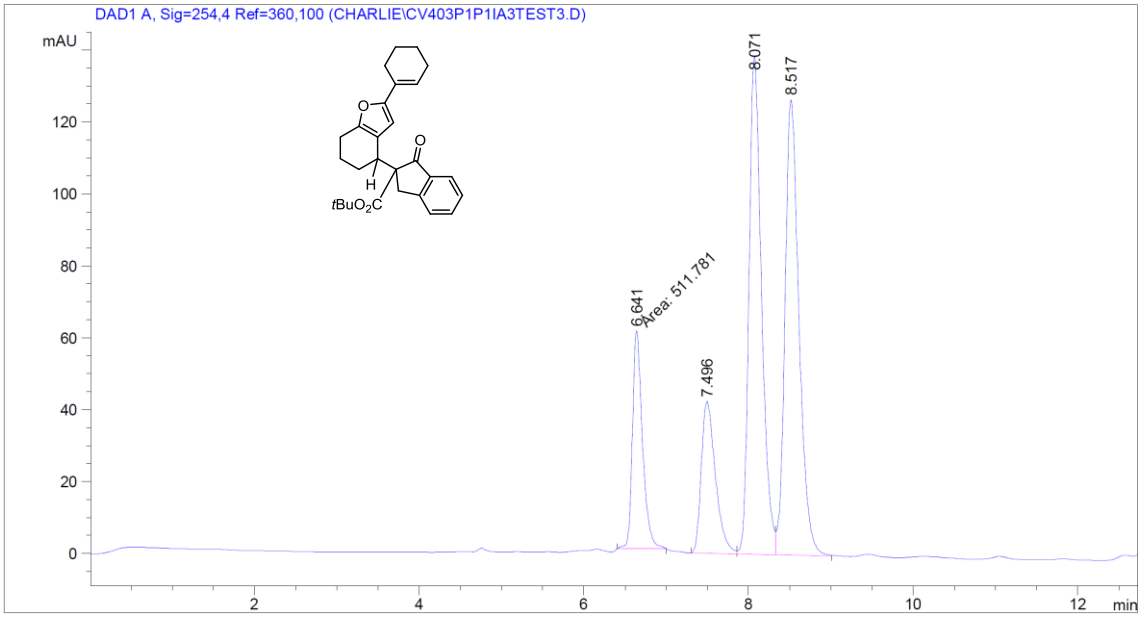
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.830	MM	0.1536	231.52487	25.12109	100.0000



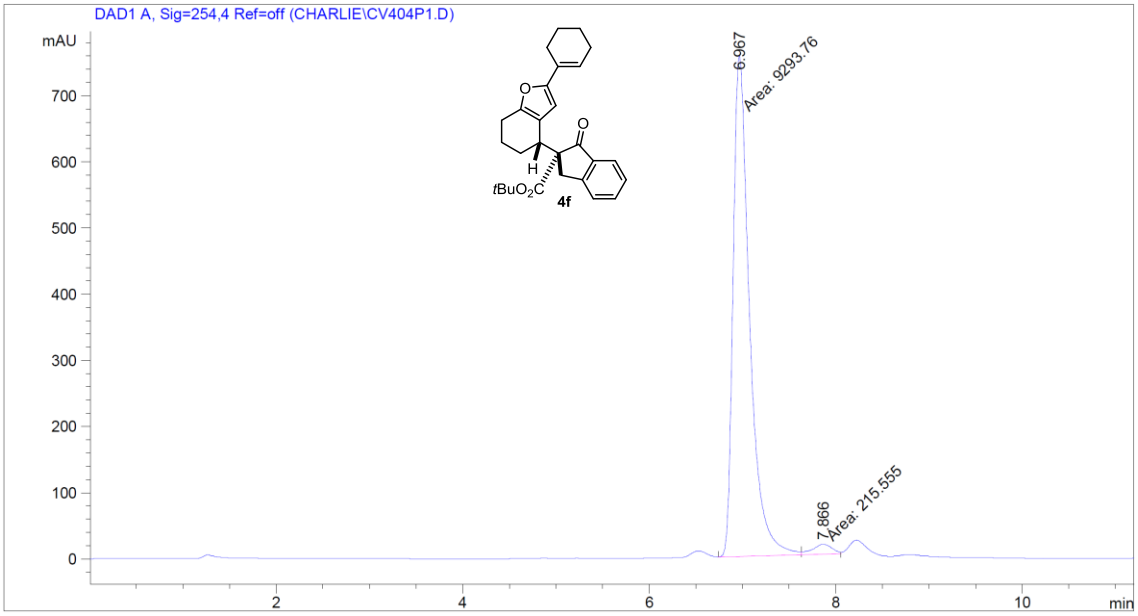
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.511	VB	0.1421	1001.88342	106.19474	21.1139
2	9.560	BV	0.2060	1341.53601	100.34072	28.2718
3	10.046	VB	0.2185	1040.27820	72.04583	21.9230
4	12.324	BB	0.2764	1361.44092	75.50639	28.6913



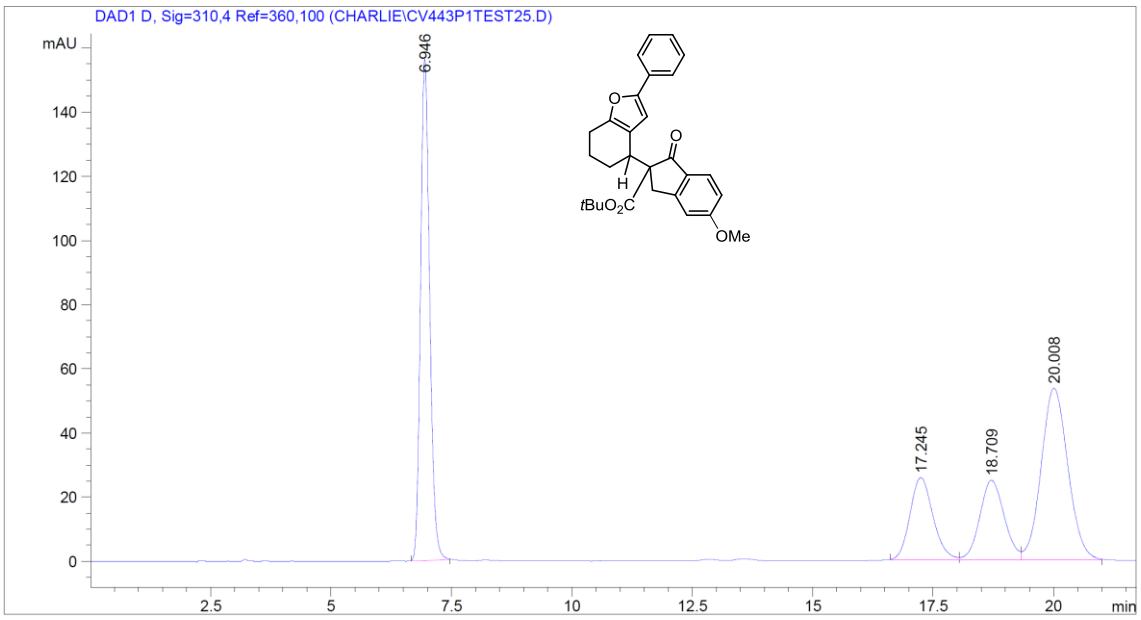
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.560	MM	0.1685	779.42896	77.08930	99.3517
2	10.200	MM	0.2623	5.08575	3.23146e-1	0.6483



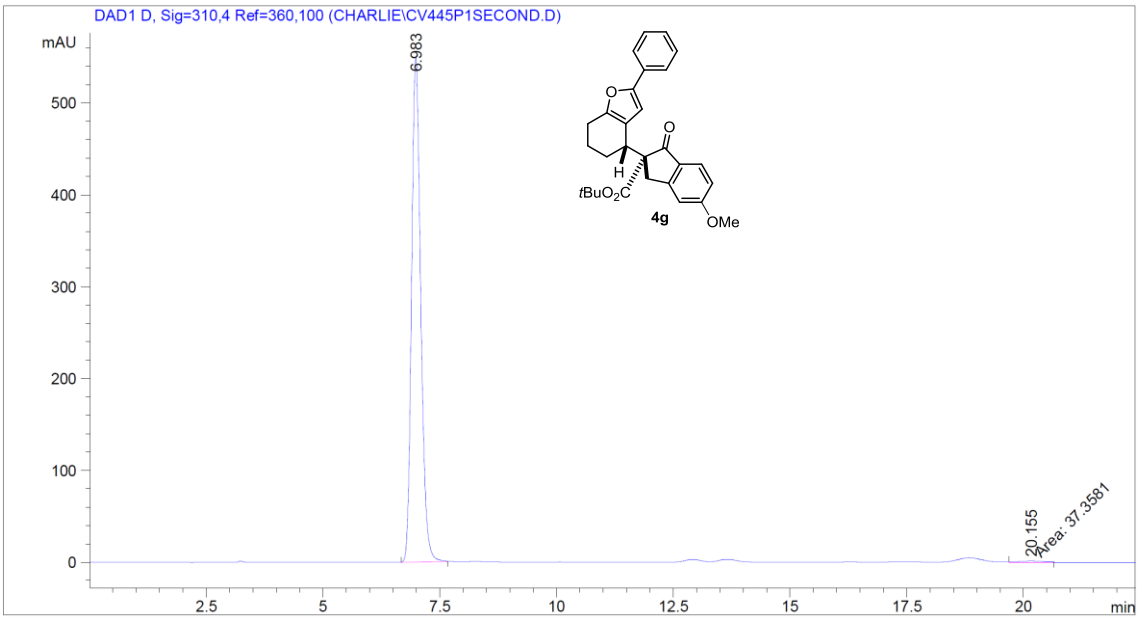
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.641	MM	0.1407	511.78128	60.61497	12.8551
2	7.496	BV	0.1808	502.16693	42.19896	12.6137
3	8.071	VV	0.1618	1468.41467	138.37799	36.8843
4	8.517	VB	0.1801	1498.77588	126.62607	37.6469



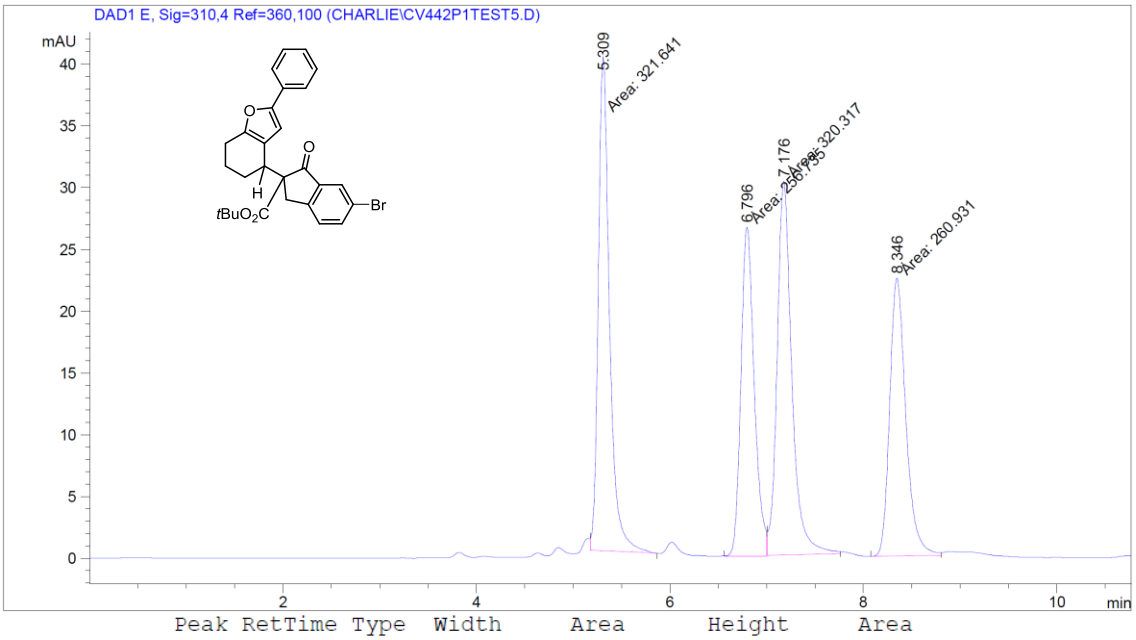
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.967	MM	0.2048	9293.75684	756.45245	97.7332
2	7.866	MM	0.2401	215.55508	14.96487	2.2668



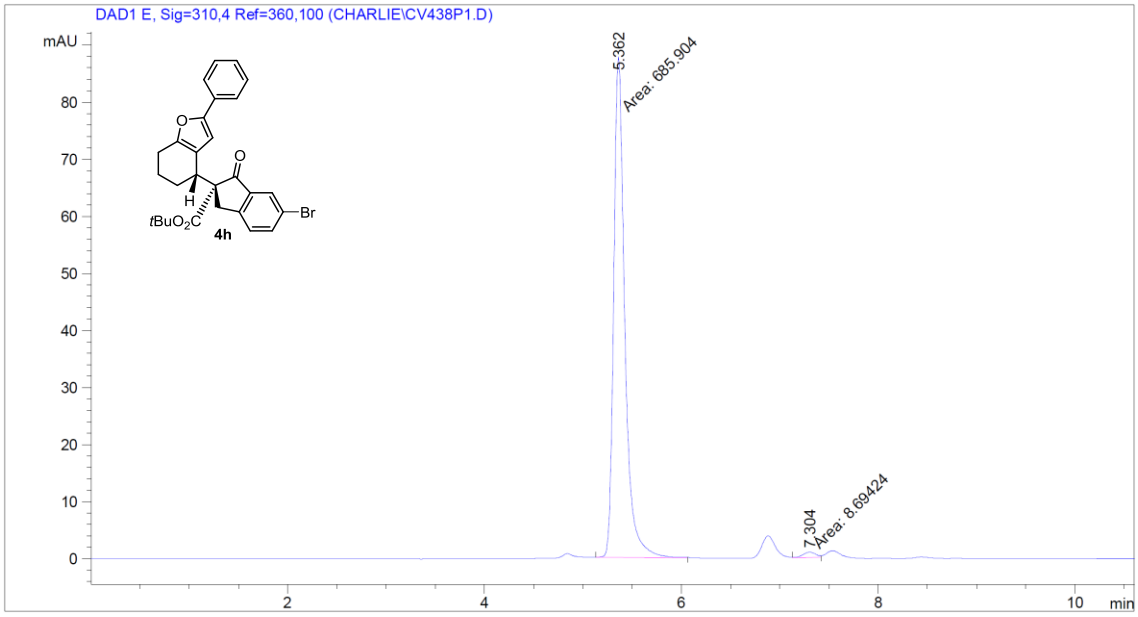
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.946	BB	0.2016	2059.94434	156.45685	35.2500
2	17.245	BV	0.5100	851.82043	25.61514	14.5764
3	18.709	VV	0.5395	870.92029	24.81473	14.9033
4	20.008	VB	0.5935	2061.13672	53.50070	35.2704



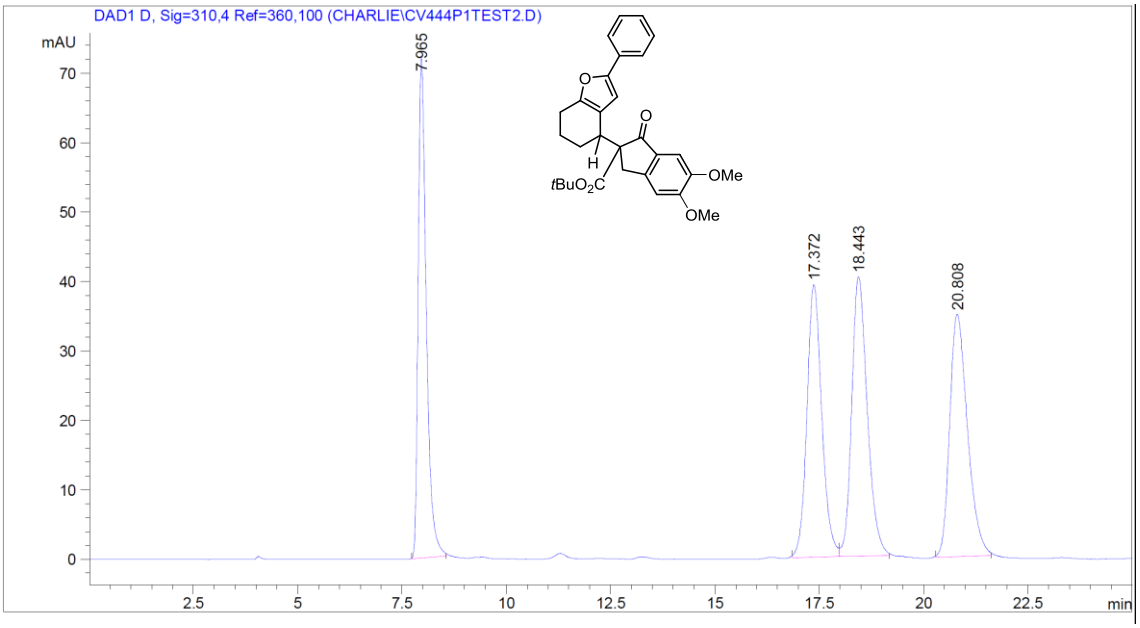
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.983	BB	0.2118	7515.97705	548.61072	99.5054
2	20.155	MM	0.5516	37.35805	1.12869	0.4946



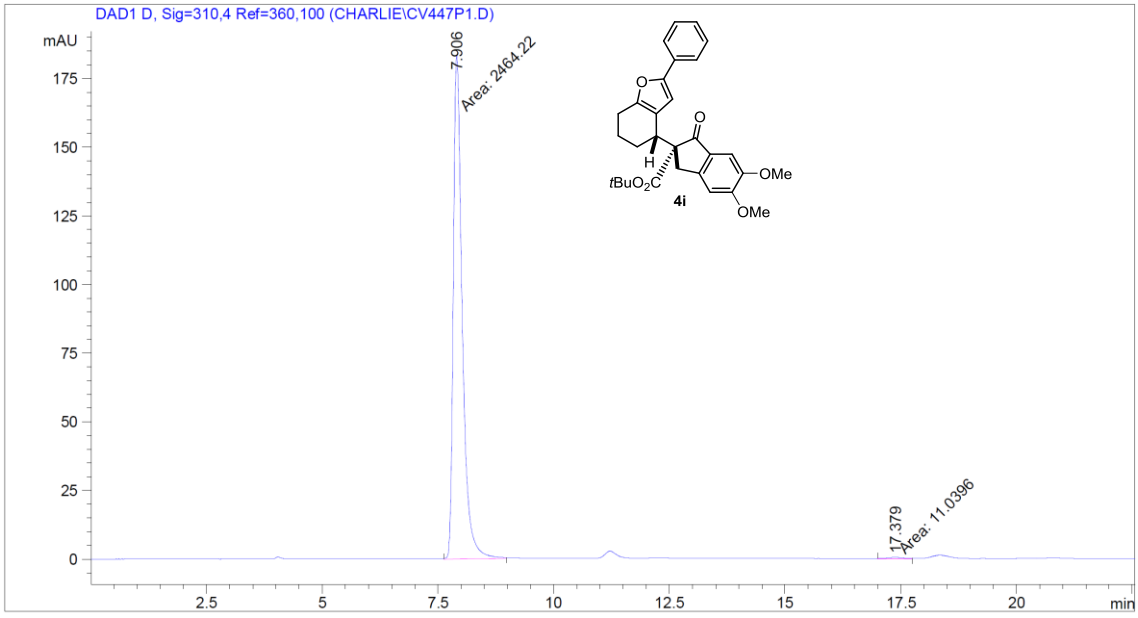
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.309	MM	0.1340	321.64099	40.01682	27.7367
2	6.796	MM	0.1603	256.73480	26.69082	22.1395
3	7.176	MM	0.1764	320.31735	30.26788	27.6225
4	8.346	MM	0.1931	260.93088	22.51860	22.5013



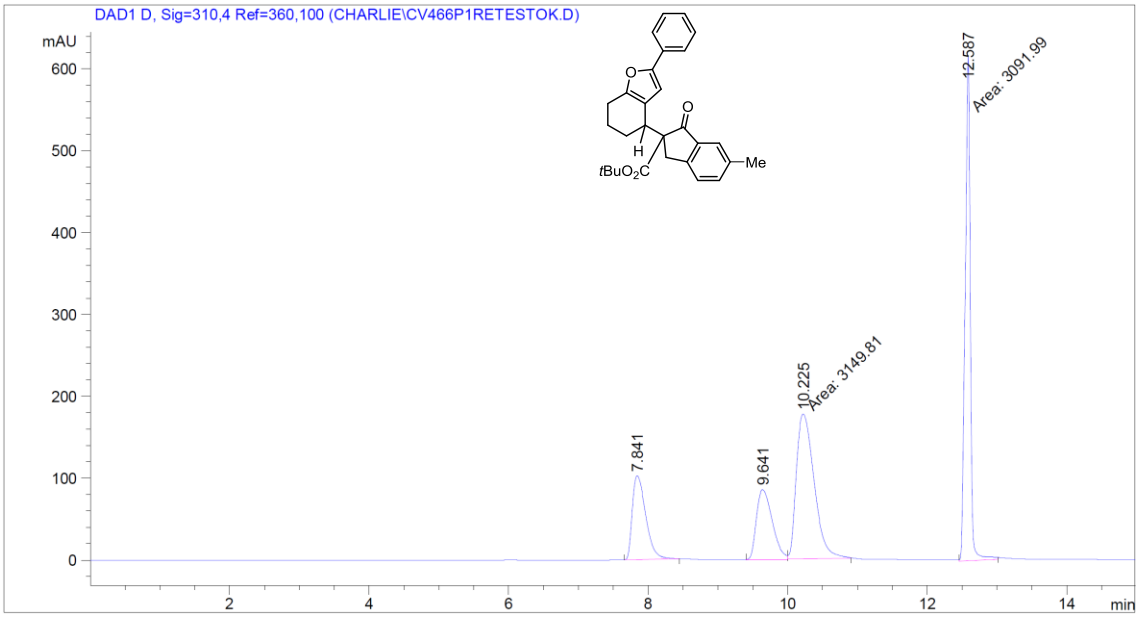
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.362	MM	0.1303	685.90411	87.76635	98.7483
2	7.304	MM	0.1536	8.69424	9.43345e-1	1.2517



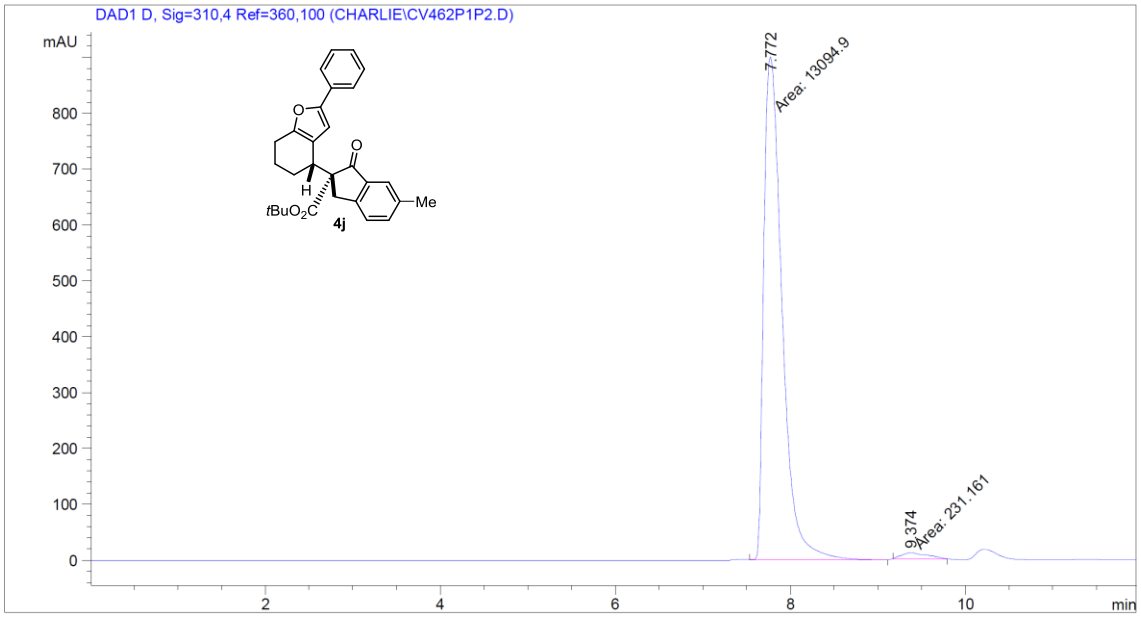
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.965	BB	0.2036	973.34015	72.04575	24.2036
2	17.372	BV	0.3749	972.00409	39.24632	24.1704
3	18.443	VB	0.3921	1043.04846	40.28711	25.9370
4	20.808	BB	0.4531	1033.06934	34.92126	25.6889



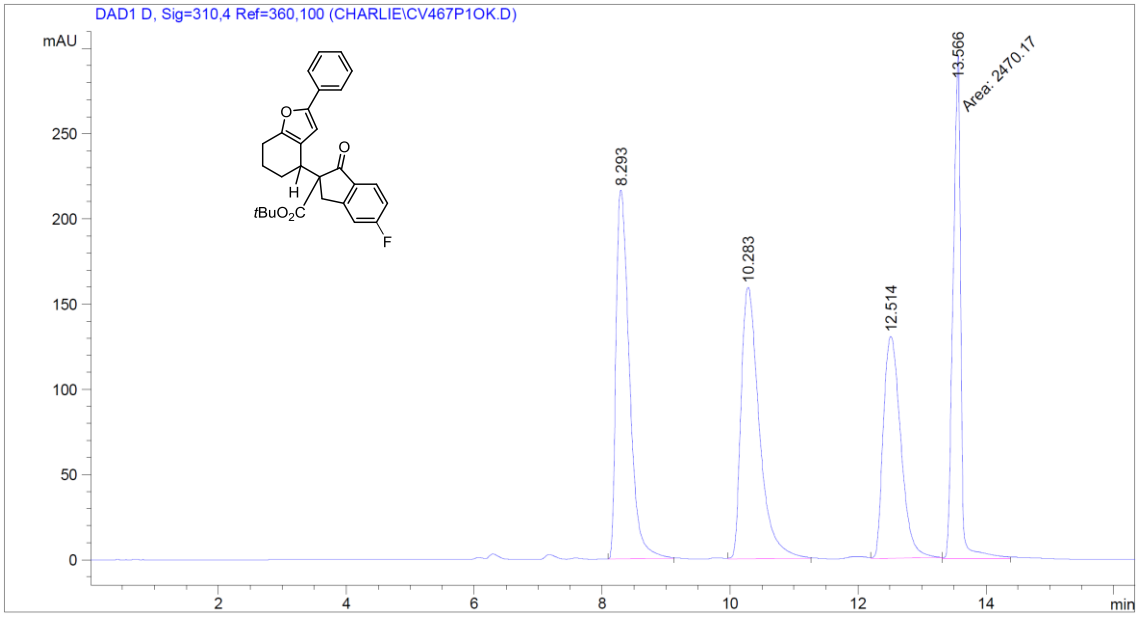
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.906	MM	0.2242	2464.21606	183.16763	99.5540
2	17.379	MM	0.4149	11.03957	4.43435e-1	0.4460



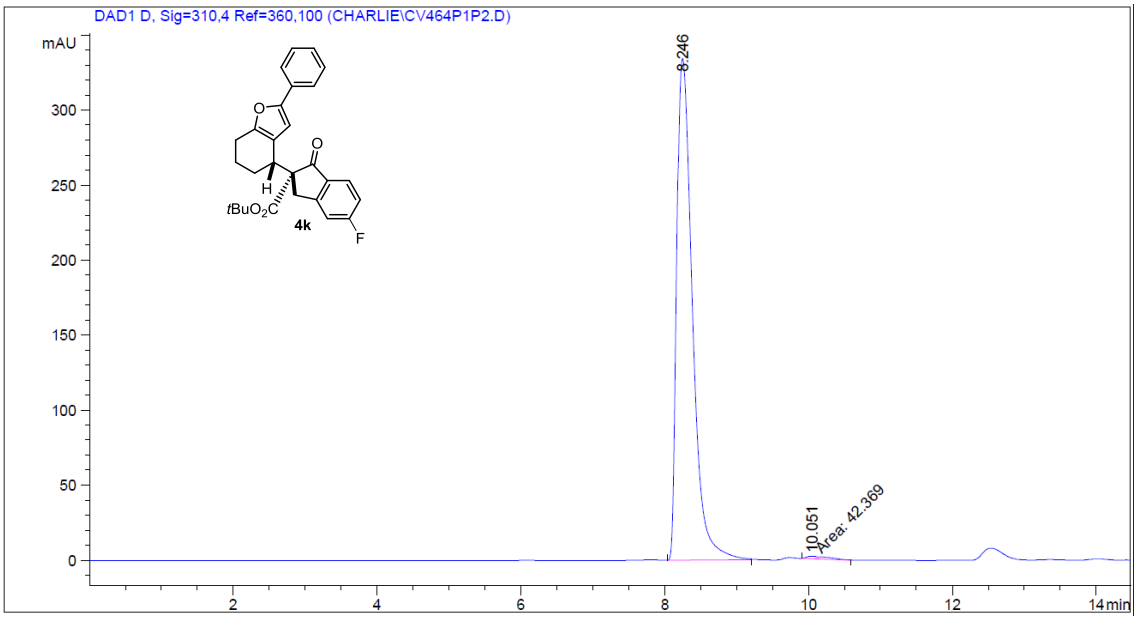
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.841	BB	0.2130	1377.96411	102.40431	15.3565
2	9.641	BV	0.2530	1353.40515	85.36687	15.0828
3	10.225	MM	0.2968	3149.81030	176.85168	35.1025
4	12.587	MM	0.0835	3091.99072	616.89056	34.4582



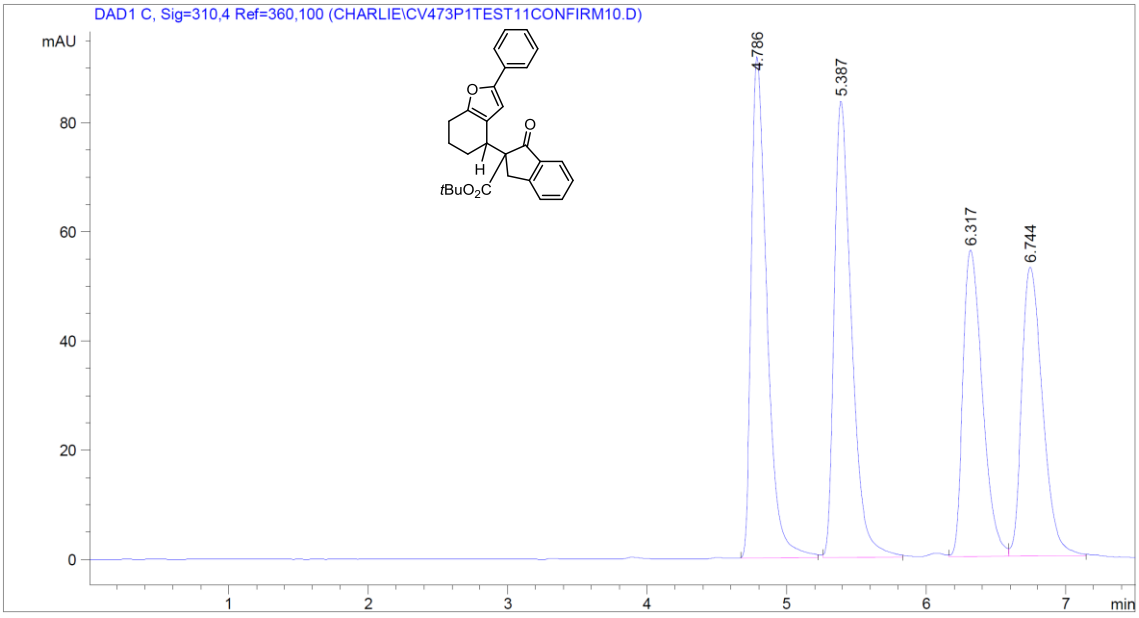
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.772	MM	0.2425	1.30949e4	900.06689	98.2653
2	9.374	MM	0.3430	231.16083	11.23239	1.7347



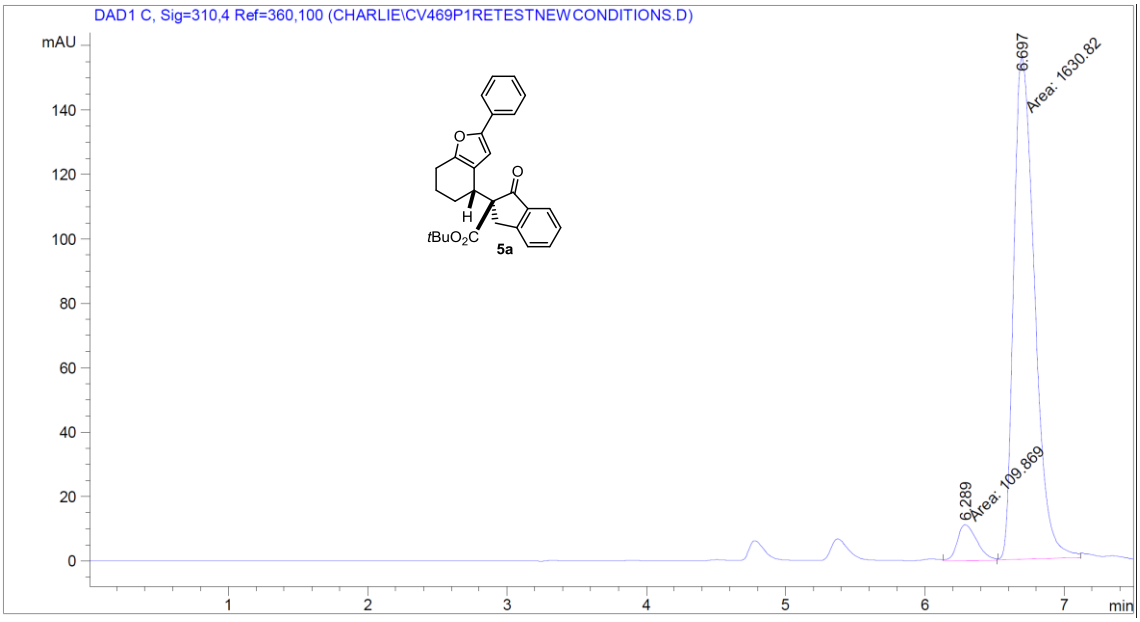
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.293	BB	0.2295	3144.58594	216.40015	27.9775
2	10.283	BB	0.3046	3148.91846	159.33759	28.0161
3	12.514	VB	0.3041	2476.00464	130.07881	22.0291
4	13.566	MM	0.1392	2470.17017	295.83997	21.9772



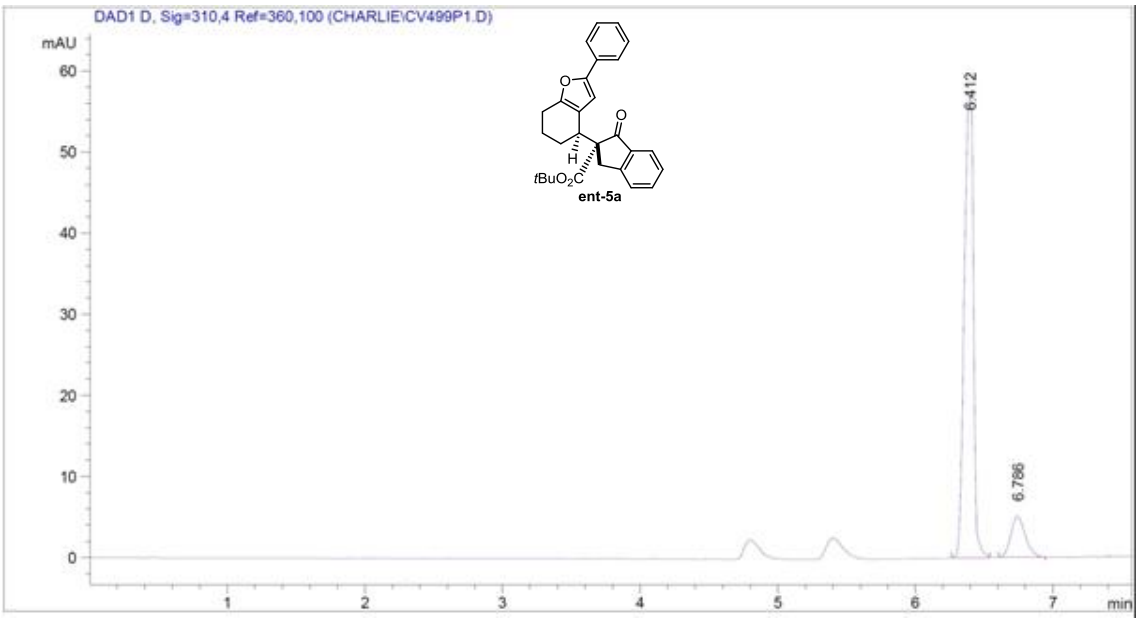
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.246	BB	0.2348	5010.56006	334.44986	99.1615
2	10.051	MM	0.4235	42.36898	1.66739	0.8385



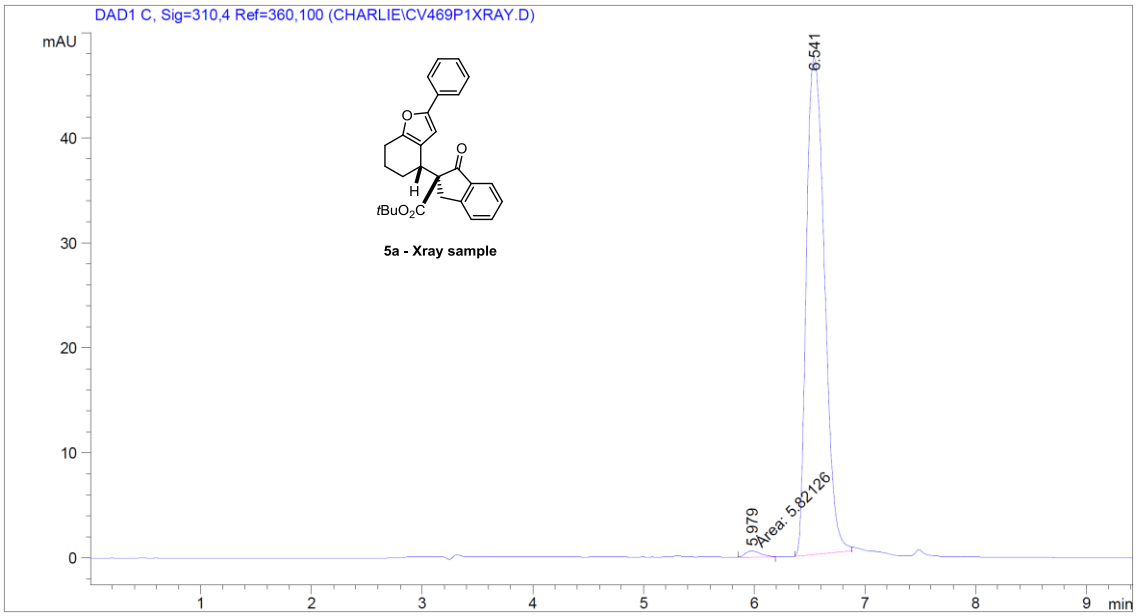
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.786	BB	0.1167	714.95465	91.91577	28.2071
2	5.387	BB	0.1327	722.21149	83.64573	28.4934
3	6.317	VV	0.1511	544.85712	56.18079	21.4963
4	6.744	VB	0.1637	552.63757	52.96164	21.8032



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.289	MM	0.1635	109.86890	11.20116	6.3118
2	6.697	MM	0.1745	1630.81848	155.76659	93.6882

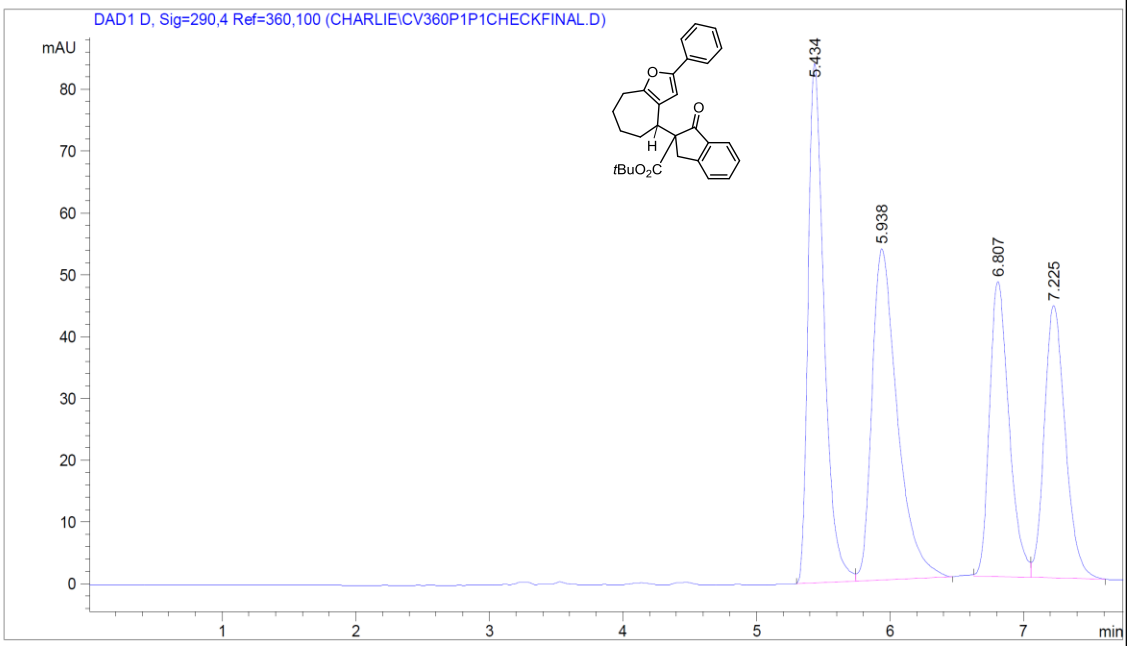


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.412	VV	0.1595	615.41608	61.08512	92.7110
2	6.786	VB	0.1678	41.81278	5.13327	6.2990

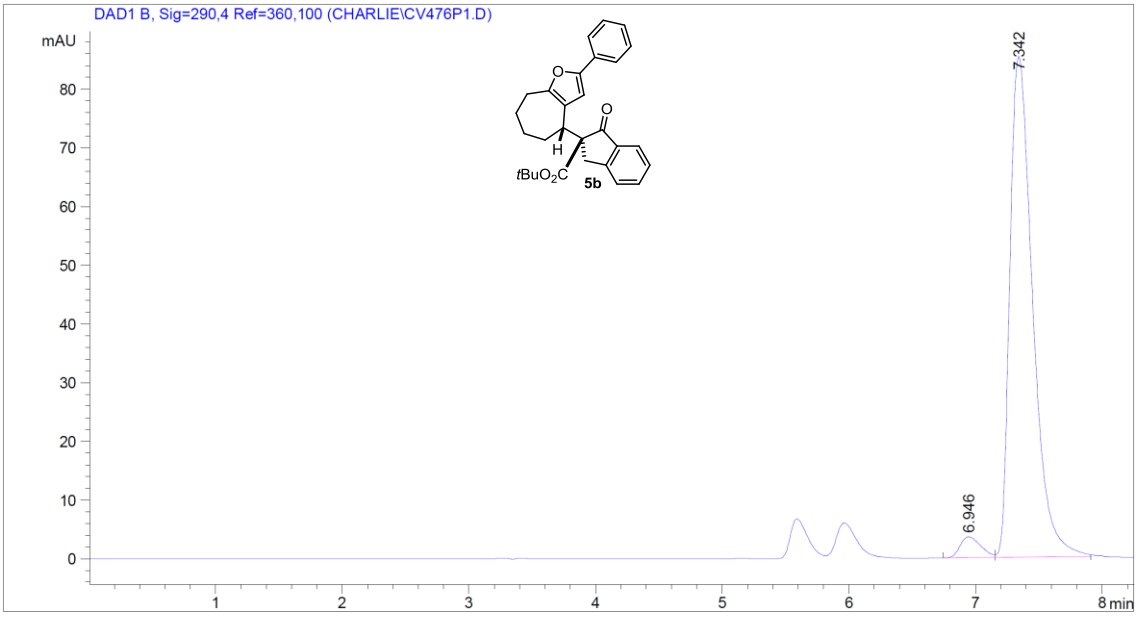


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.979	MM	0.1634	5.82126	5.93628e-1	1.0723
2	6.541	BB	0.1824	537.05682	47.34035	98.9277

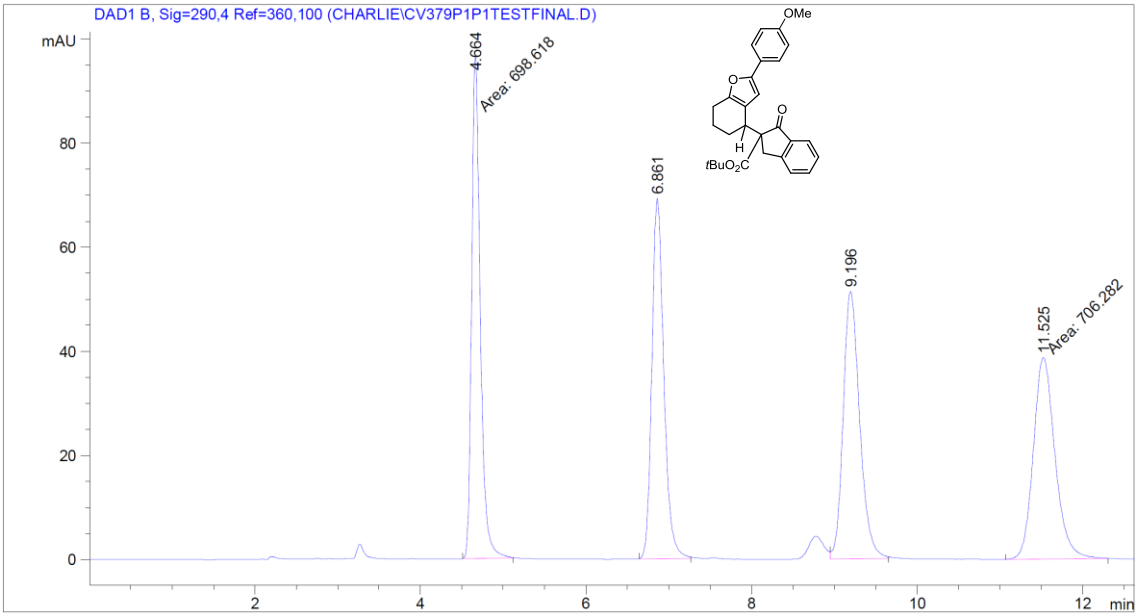
Sample Info : IA3, 20°C, 1.0 mL/min, H/DCM 85/15



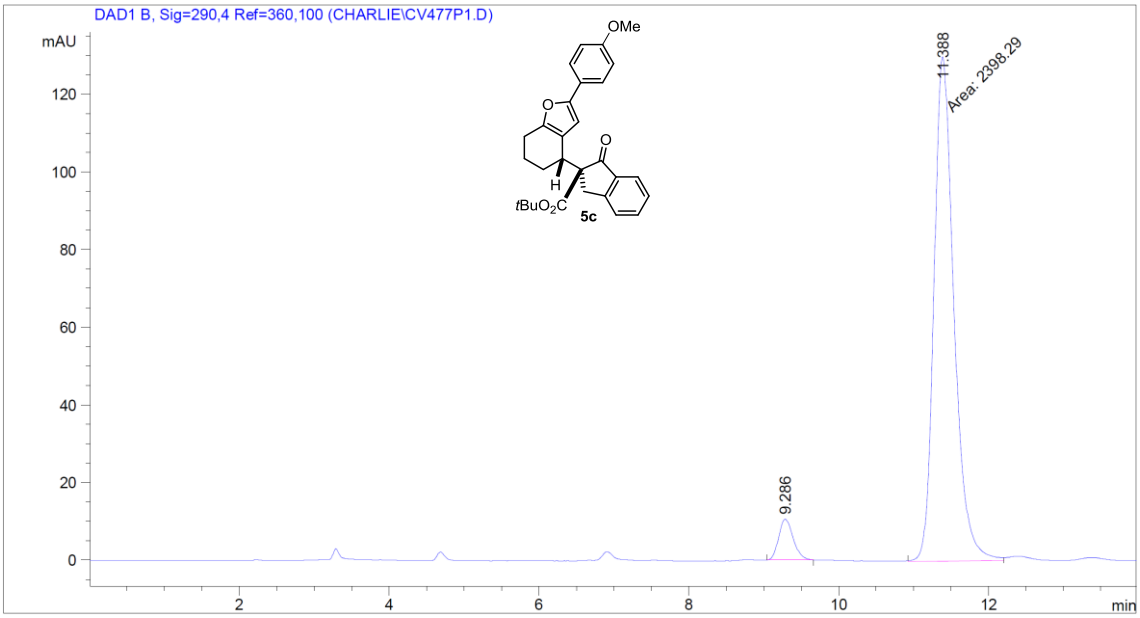
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.434	BV	0.1269	699.07312	84.15497	29.4541
2	5.938	VB	0.1999	706.72235	53.55787	29.7764
3	6.807	BV	0.1563	484.40717	47.76132	20.4096
4	7.225	VB	0.1698	483.22598	44.10889	20.3598



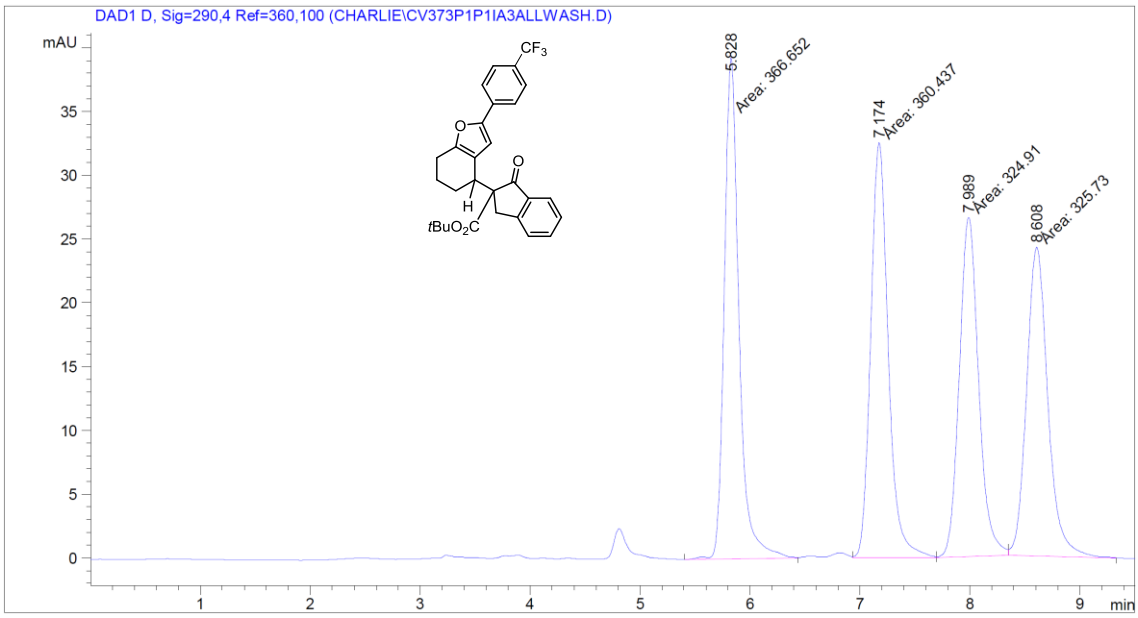
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.946	BV	0.1758	40.04792	3.54388	3.6220
2	7.342	VB	0.1937	1065.63025	85.32258	96.3780



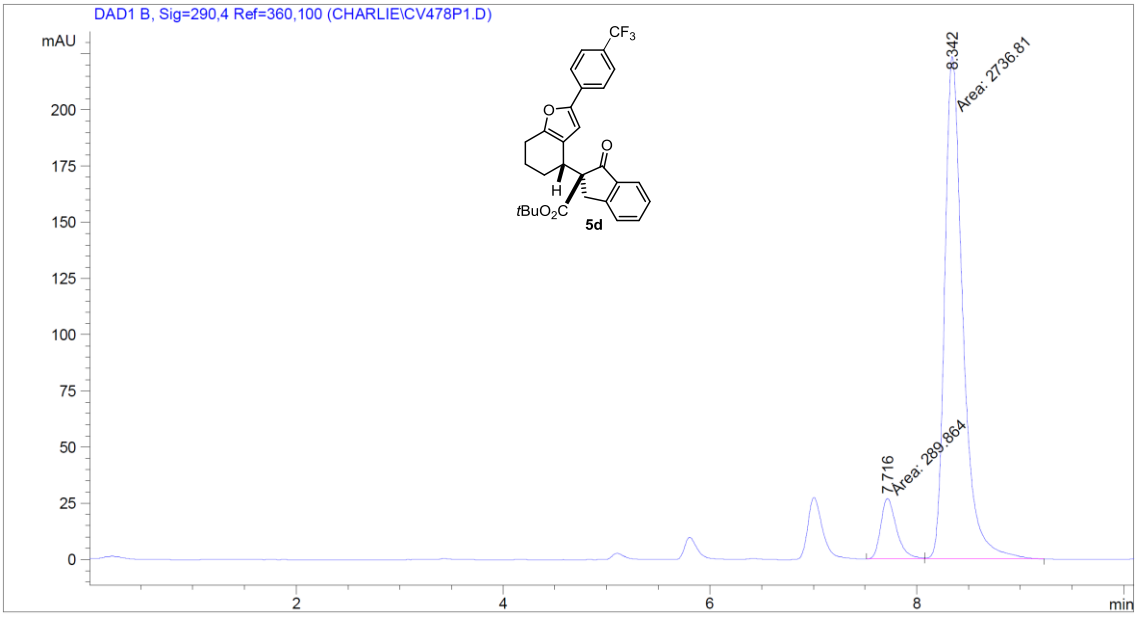
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.664	MM	0.1207	698.61780	96.46627	24.8707
2	6.861	BB	0.1529	693.47217	69.20596	24.6875
3	9.196	VB	0.2116	710.62610	51.31746	25.2982
4	11.525	MM	0.3038	706.28168	38.74936	25.1435



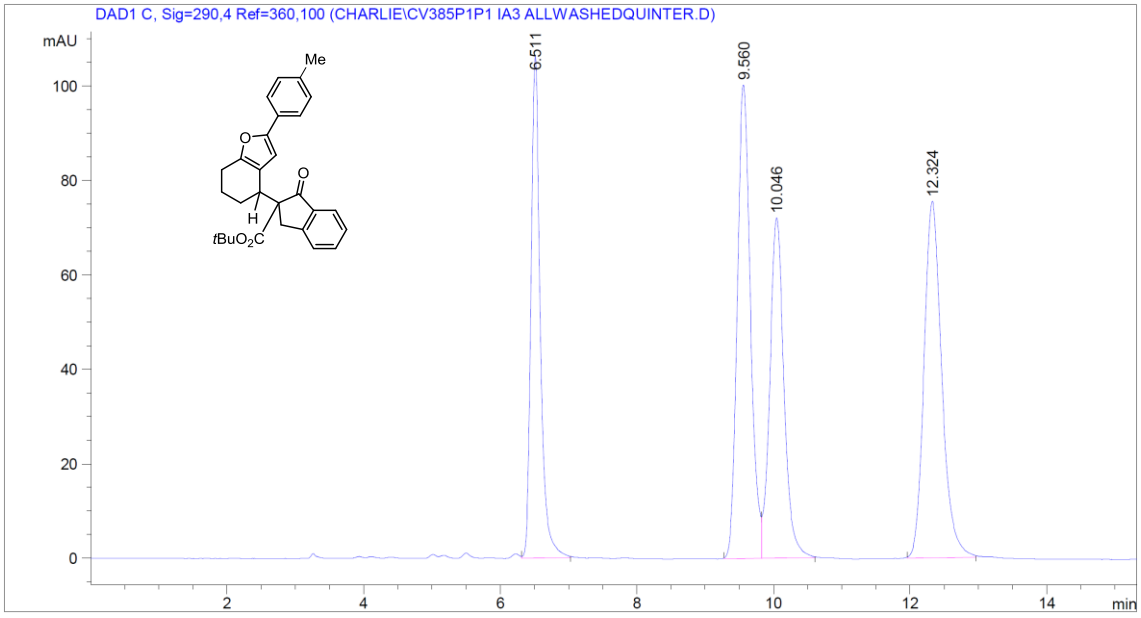
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.286	BB	0.2072	141.60855	10.51252	5.5754
2	11.388	MM	0.3079	2398.29224	129.83093	94.4246



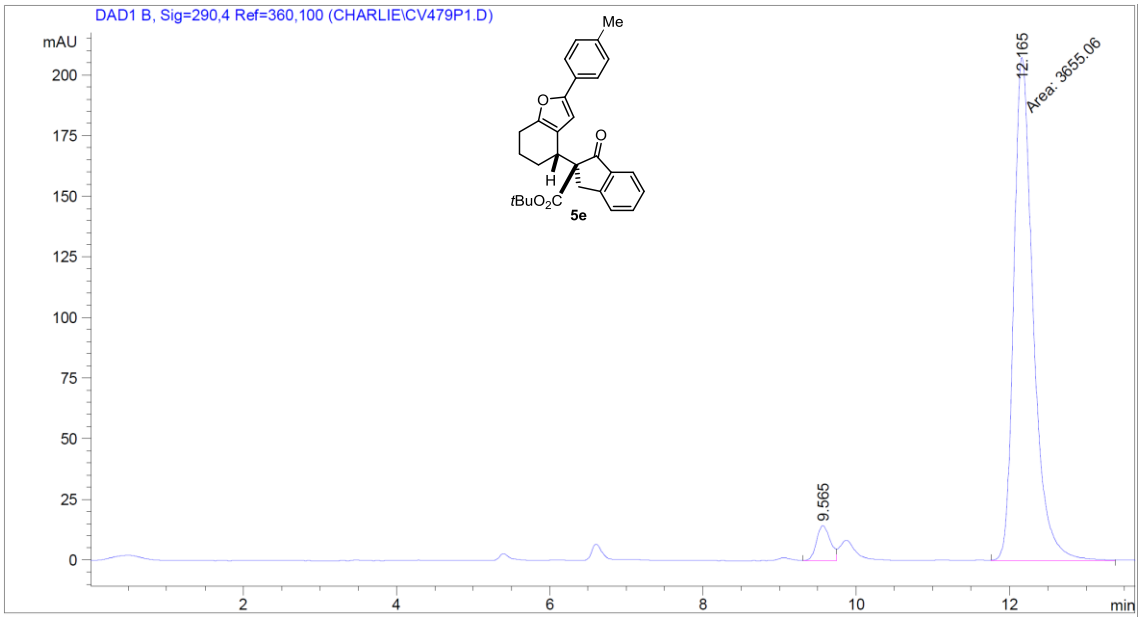
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.828	MM	0.1555	366.65216	39.29960	26.6128
2	7.174	MM	0.1845	360.43680	32.55625	26.1617
3	7.989	MM	0.2036	324.90997	26.59293	23.5830
4	8.608	MM	0.2242	325.72989	24.20884	23.6425



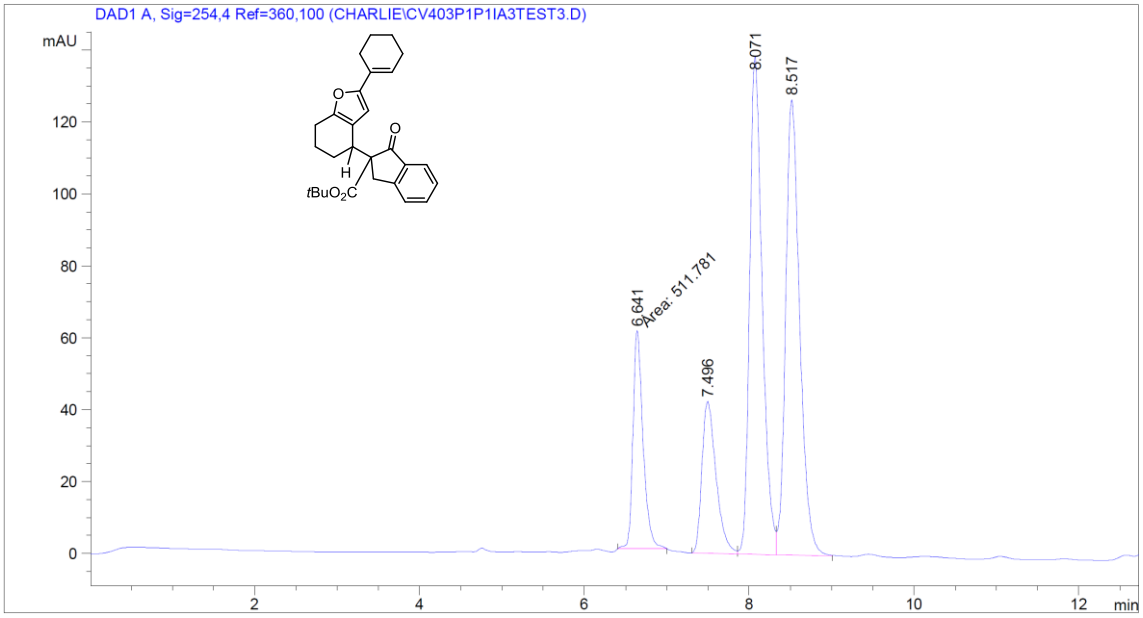
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.716	MM	0.1788	289.86420	27.02489	9.5770
2	8.342	MM	0.2039	2736.80957	223.66562	90.4230



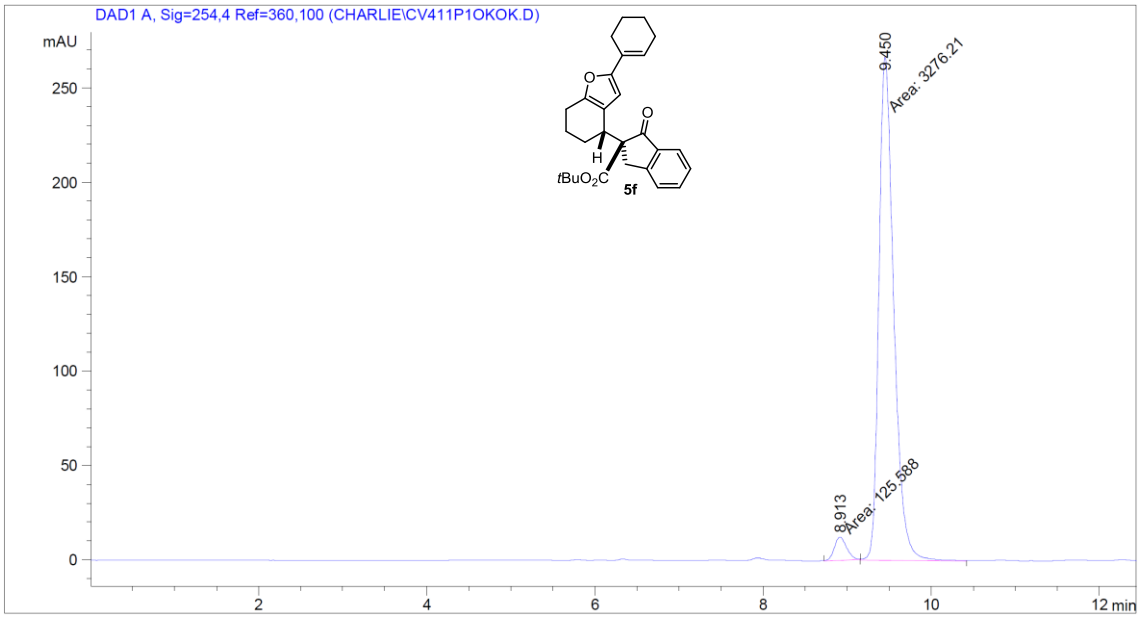
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.511	VB	0.1421	1001.88342	106.19474	21.1139
2	9.560	BV	0.2060	1341.53601	100.34072	28.2718
3	10.046	VB	0.2185	1040.27820	72.04583	21.9230
4	12.324	BB	0.2764	1361.44092	75.50639	28.6913



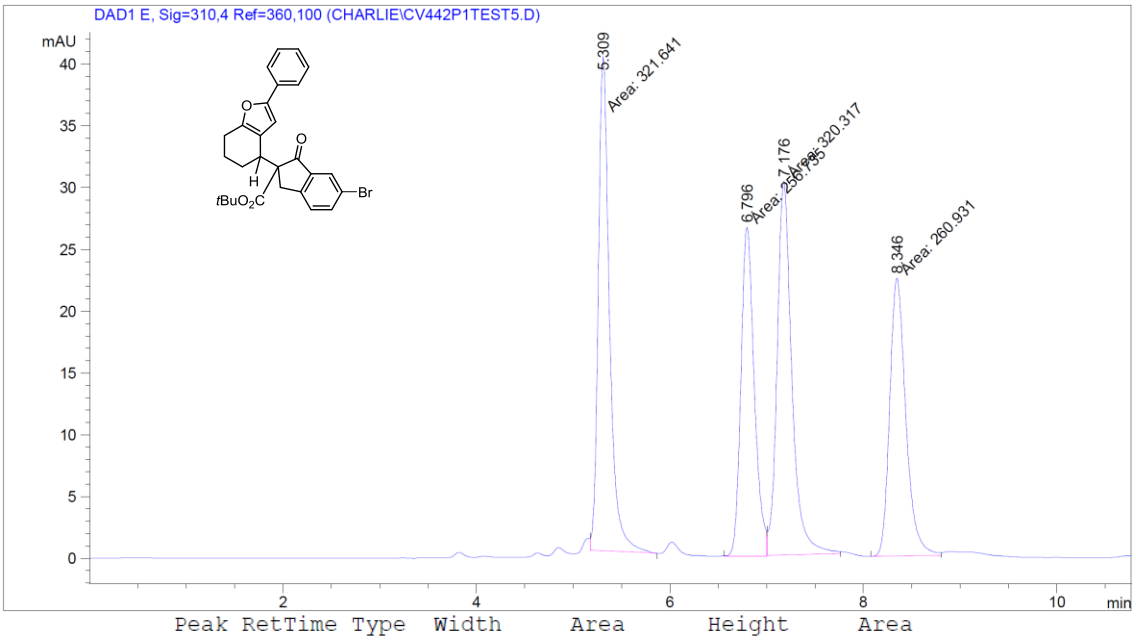
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.565	VV	0.1880	177.25731	14.36278	4.6253
2	12.165	MM	0.2937	3655.06128	207.44403	95.3747



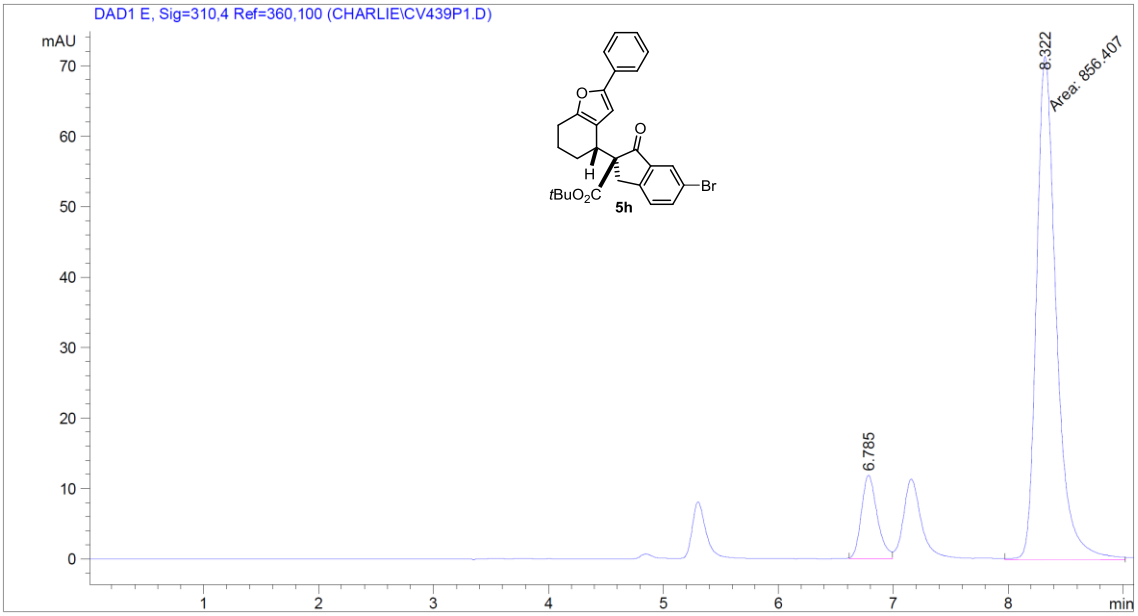
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.641	MM	0.1407	511.78128	60.61497	12.8551
2	7.496	BV	0.1808	502.16693	42.19896	12.6137
3	8.071	VV	0.1618	1468.41467	138.37799	36.8843
4	8.517	VB	0.1801	1498.77588	126.62607	37.6469



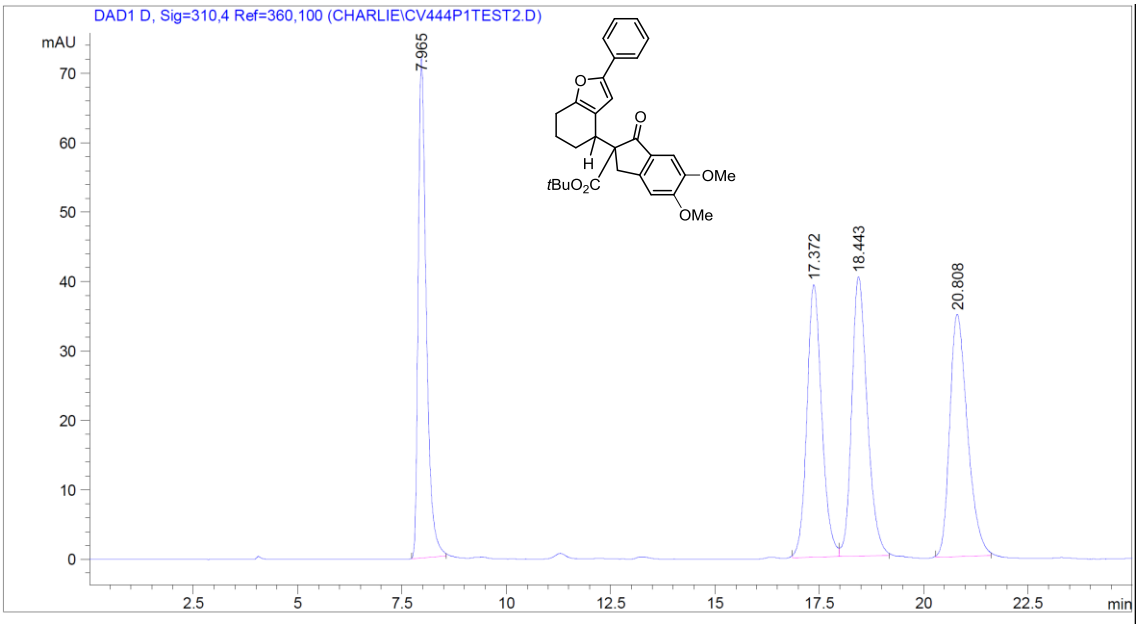
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.913	MM	0.1691	125.58755	12.38120	3.6918
2	9.450	MM	0.2049	3276.21045	266.54477	96.3082



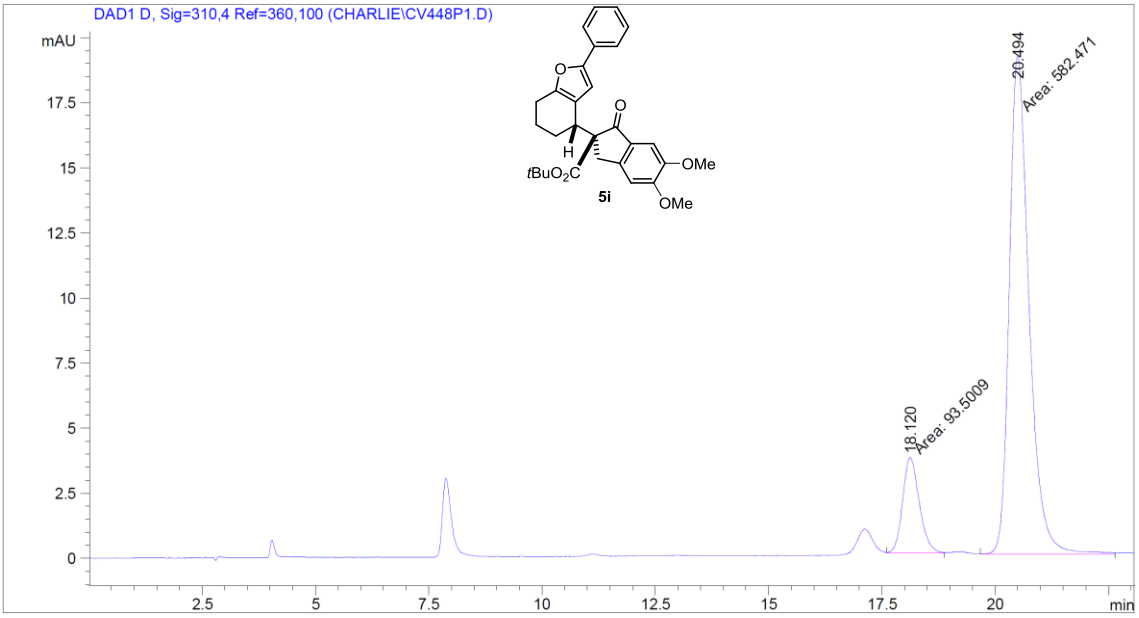
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.309	MM	0.1340	321.64099	40.01682	27.7367
2	6.796	MM	0.1603	256.73480	26.69082	22.1395
3	7.176	MM	0.1764	320.31735	30.26788	27.6225
4	8.346	MM	0.1931	260.93088	22.51860	22.5013



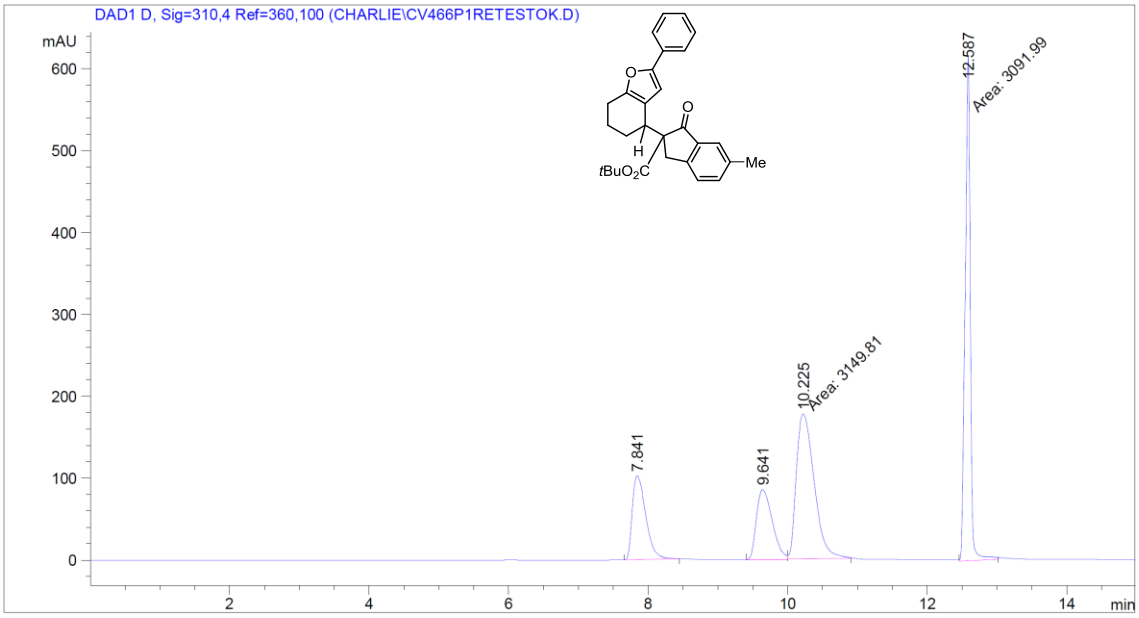
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.785	BV	0.1455	112.88604	11.81504	11.6462
2	8.322	MM	0.1997	856.40710	71.47701	88.3538



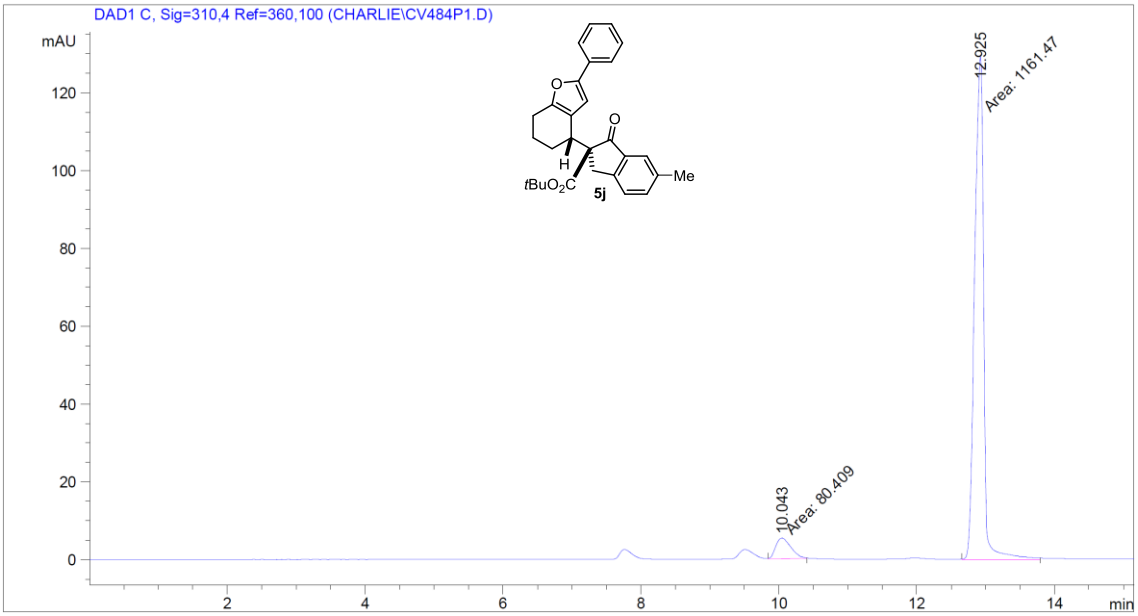
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.965	BB	0.2036	973.34015	72.04575	24.2036
2	17.372	BV	0.3749	972.00409	39.24632	24.1704
3	18.443	VB	0.3921	1043.04846	40.28711	25.9370
4	20.808	BB	0.4531	1033.06934	34.92126	25.6889



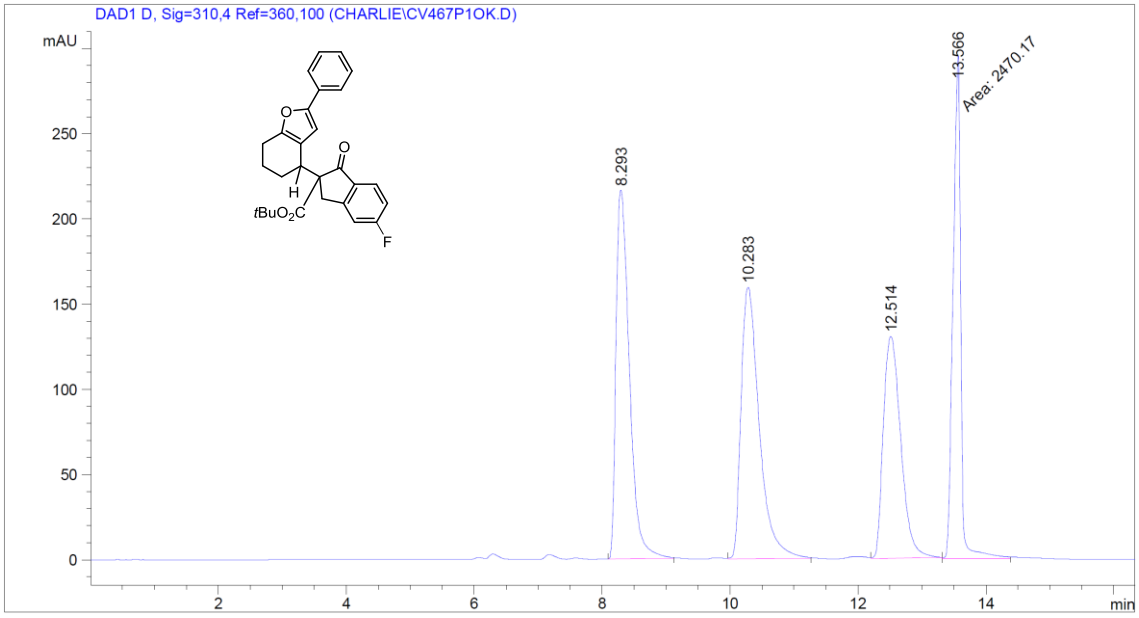
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.120	MM	0.4259	93.50088	3.65895	13.8321
2	20.494	MM	0.5076	582.47101	19.12447	86.1679



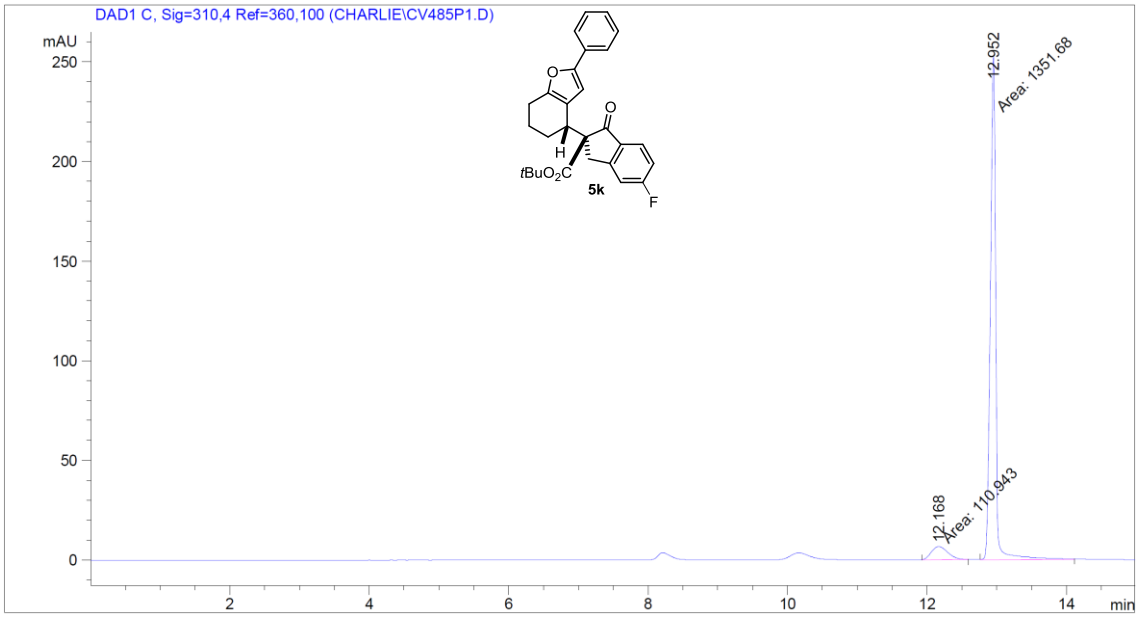
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.841	BB	0.2130	1377.96411	102.40431	15.3565
2	9.641	BV	0.2530	1353.40515	85.36687	15.0828
3	10.225	MM	0.2968	3149.81030	176.85168	35.1025
4	12.587	MM	0.0835	3091.99072	616.89056	34.4582



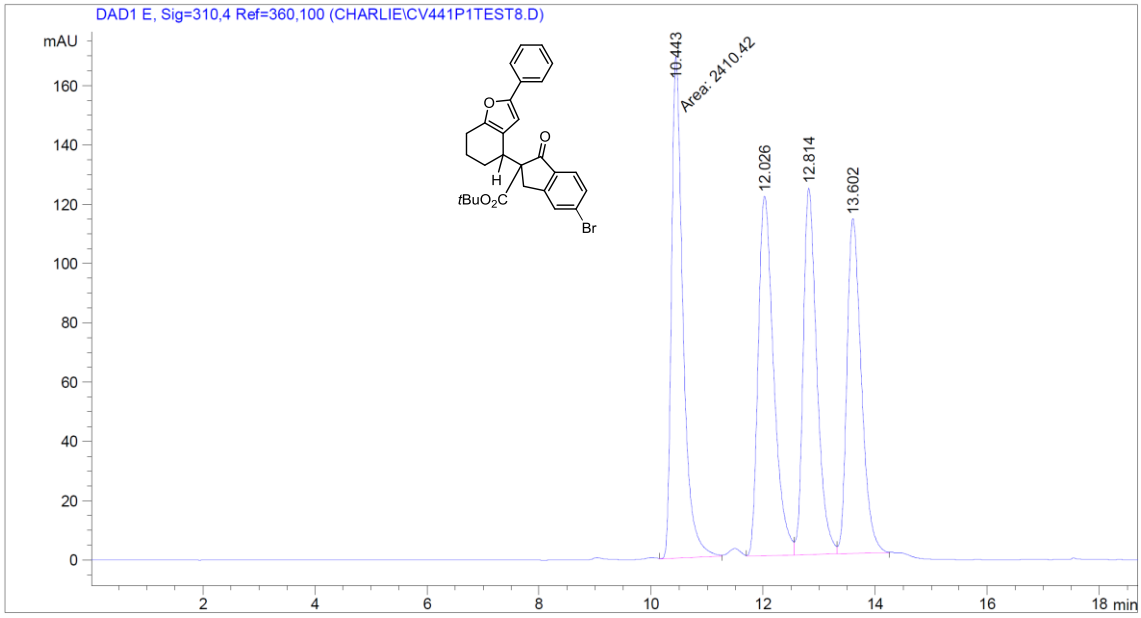
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.043	MM	0.2538	80.40902	5.28060	6.4748
2	12.925	MM	0.1496	1161.46509	129.37723	93.5252



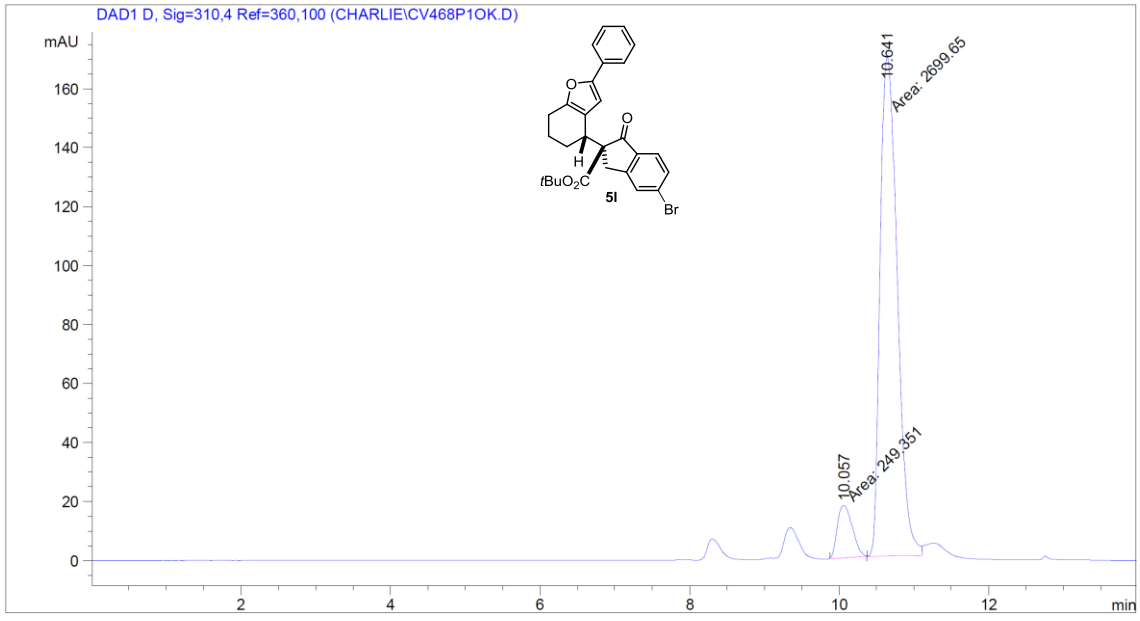
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.293	BB	0.2295	3144.58594	216.40015	27.9775
2	10.283	BB	0.3046	3148.91846	159.33759	28.0161
3	12.514	VB	0.3041	2476.00464	130.07881	22.0291
4	13.566	MM	0.1392	2470.17017	295.83997	21.9772



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.168	MM	0.2762	110.94254	6.69346	7.5852
2	12.952	MM	0.0888	1351.68372	253.67650	92.4148



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.443	MM	0.2375	2410.42065	169.12993	27.2026
2	12.026	VV	0.2946	2332.62476	121.19183	26.3247
3	12.814	VV	0.2581	2098.88696	123.61713	23.6868
4	13.602	VB	0.2746	2019.05151	112.93845	22.7859



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.057	MM	0.2322	249.35126	17.89855	8.4554
2	10.641	MM	0.2657	2699.65015	169.34174	91.5446