Organocatalytic Asymmetric Desymmetrization of Cyclopentene-1,3-diones via Formal Diaza-ene Reaction with Donor-Acceptor Hydrazones

Subhankar Biswas,[a] Subhas Chandra Pan*[a]

Email: span@iitg.ac.in

[a]Department of Chemistry, Indian Institute of Technology Guwahati, North Guwahati, Assam, India, 781039

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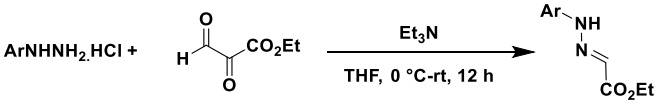
1. General Information:

Chemicals and solvents were purchased from commercial suppliers and used as received. ^{1}H NMR spectra were recorded on 400 MHz, 500 MHz and 600 MHz spectrometer. ^{13}C NMR spectra were recorded on 100 MHz, 125 MHz and 150 MHz. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton ($CDCl_3$: δ 7.260), carbon ($CDCl_3$: δ 77.16). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), brs (broad singlet). Coupling constants were reported in Hertz (Hz). Using ESI mode HRMS spectra were recorded. Enantiomeric ratios were determined by HPLC analysis performed on Chiral Columns using a Daicel Chiralpak ID Column, Daicel Chiralpak IE Column, Daicel Chiralpak IF Column, and Daicel Chiralpak ADH Column. For visualizing the products UV light and I_2 were used. DCM was distilled over CaH_2 under argon and stored over 4Å molecular sieves. Silica gel (230-400 mesh size) was used for the flash column chromatography. Reactions were monitored by TLC on silica gel 60 F254 (0.25 mm).

2. General procedure for the synthesis of hydrazone (1):

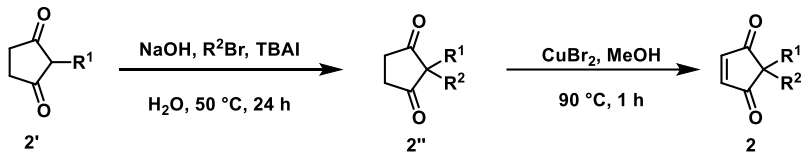
Hydrazones were prepared according to previously reported procedures. [1]



Hydrazone derivatives were prepared according to literature procedure as followed. A suspension of the corresponding hydrazine hydrochloride (10 mmol, 1.0 eq.) in anhydrous tetrahydrofuran (10 mL) was treated with triethylamine (10 mmol, 1.0 eq.) before the corresponding aldehyde (10 mmol, 1.0 eq.) was added dropwise to the reaction mixture at 0 °C. The mixture was stirred at this temperature for 30 minutes and then for 12 h at room temperature. The crude was filtered under vacuum and the filtrates were concentrated in vacuo. The resulting solids were dissolved in dichloromethane (15 mL) and washed with HCl 1M (2 × 10 mL) and water (2 × 10 mL). The resulting organic layer was dried over Na_2SO_4 and concentrated in vacuo. The resulting solids were triturated with diethyl ether or purified by flash column chromatography to obtain the desired hydrazone.

3. General procedure for the synthesis of 2,2-disubstituted cyclopentene-1,3-dione (2):

2,2-Disubstituted cyclopentene-1,3-diones (2) were prepared according to previously reported procedures. [2]



To a solution of **2'** (20 mmol, 1.0 equiv.) in H_2O (80 mL) was added NaOH (20 mmol, 1.0 equiv.) and TBAI (0.2 mmol, 0.01 equiv.). The mixture was stirred at room temperature for 20 min. Then R^2Br (30 mmol, 1.5 equiv.) was added. The reaction mixture was stirred at 50 °C for 24 h and then cooled to room temperature. The reaction mixture was extracted with EtOAc (3 x 40 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel to afford target compounds.

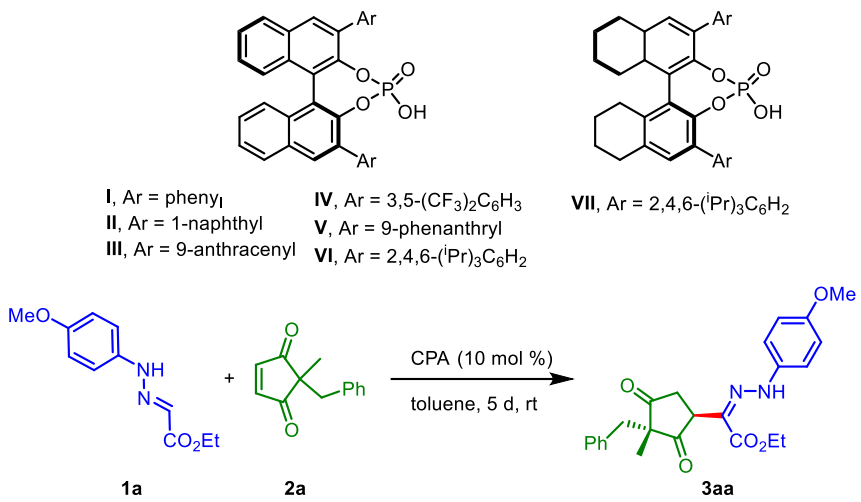
To a solution of **2''** (2.41 g, 11.92 mmol, 1.0 equiv.) in 86 mL of MeOH was added copper(II) bromide (5.86 g, 26.22 mmol, 2.2 equiv.) and the resulting brown solution was stirred at 90 °C under argon atmosphere. After 1 h the reaction mixture was cooled to r.t., quenched with 20 mL of distilled water followed by 20 mL of 1 M aq. HCl solution, 50 mL of Et2O was added and the organic phase was separated from aqueous phase. Aqueous phase was back-extracted with Et2O (2 × 20 mL). The combined organic phase was dried over anh. MgSO4 and concentrated under reduced pressure. The crude reaction mixture was purified by silica-gel column chromatography (10% EtOAc in petroleum ether) to obtain a yellow crystalline solid.

4. General procedure for the synthesis of catalyst:

The catalyst (**I - VII**) was prepared according to reported procedures. [3]

5. Reaction condition optimization:

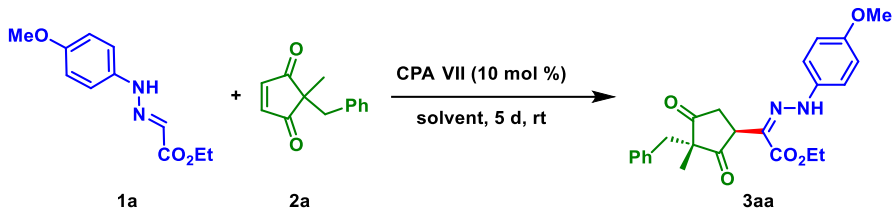
Table S1: Optimization of catalyst[a]



entry[a]	cat.	yield[b]	dr[c]	er[d]
1.	I	48	7:1	69:31
2.	II	32	9:1	55:45
3.	III	36	7:1	73:27
4.	IV	52	6:1	60:40
5.	V	28	5:1	61:39
6.	VI	50	16:1	85:15
7.	**VII**	**72**	**>20:1**	**89:11**

[a] Reaction conditions: 0.075 mmol of **1a** and 0.05 mmol of **2a**, 10 mol% of catalyst, 0.1 (M) toluene, rt, under Ar atmosphere. [b] Isolated yield after flash chromatography. [c] Determined by ^{1}HNMR. [d] Determined by HPLC analysis.

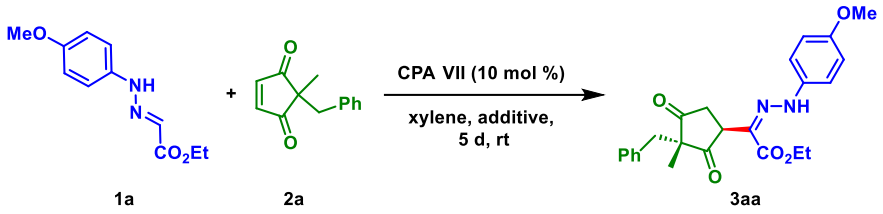
Table S2: Optimization of solvent[a]



entry[a]	cat.	solvent	yield[b]	dr[c]	er[d]
1.	VII	toluene	72	>20:1	89:11
2.	VII	CH_2Cl_2	36	>20:1	79:21
3.	VII	$CHCl_3$	44	>20:1	80:20
4.	**VII**	**xylene**	**73**	**>20:1**	**90:10**
5.	VII	mesitylene	50	>20:1	87:13
6.	VII	Benzene	38	>20:1	86:14
7.	VII	$PhCF_3$	34	>20:1	84:16
8.	VII	n-hexane	18	>20:1	85:15

[a] Reaction conditions: 0.075 mmol of **1a** and 0.05 mmol of **2a**, 10 mol% of catalyst, 0.1 (M) solvent, rt, under Ar atmosphere. [b] Isolated yield after flash chromatography. [c] Determined by ^{1}HNMR. [d] Determined by HPLC analysis.

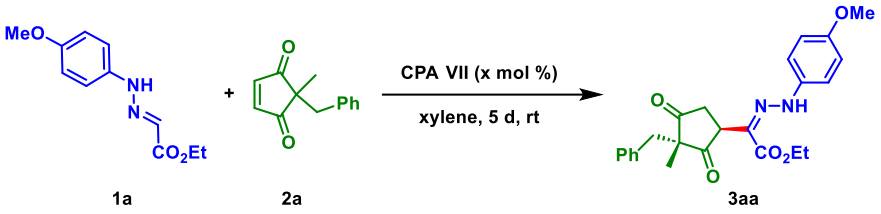
Table S3: Optimization of additives[a]



entry[a]	additive	yield[b]	dr[c]	er[d]
1.	**no additive**	**73**	**>20:1**	**90:10**
2.	4 A^0 MS	<5	-	-
3.	Amberlite IR 120	60	>20:1	85:15
4.	Amberlyst 15	50	>20:1	86:14

[a] Reaction conditions: 0.075 mmol of **1a** and 0.05 mmol of **2a**, 10 mol% of catalyst, 0.1 (M) xylene, rt, under Ar atmosphere. [b] Isolated yield after flash chromatography. [c] Determined by ^{1}HNMR. [d] Determined by HPLC analysis.

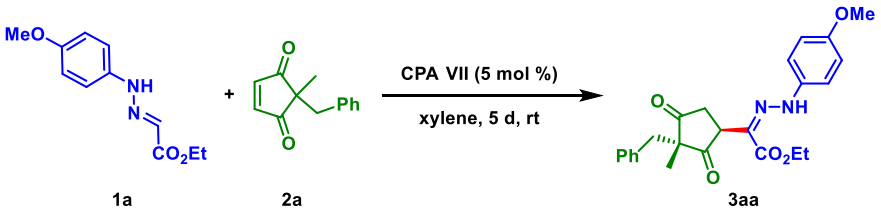
Table S4: Optimization of catalyst loading[a]



entry[a]	mol %	yield[b]	dr[c]	er[d]
1.	20	75	>20:1	88.5:11.5
2.	15	75	>20:1	89:11
3.	10	73	>20:1	90:10
4.	**5**	**70**	**>20:1**	**94.5:5.5**

[a] Reaction conditions: 0.075 mmol of **1a** and 0.05 mmol of **2a**, 0.1 (M) xylene, rt, under Ar atmosphere. [b] Isolated yield after flash chromatography. [c] Determined by ^{1}HNMR. [d] Determined by HPLC analysis.

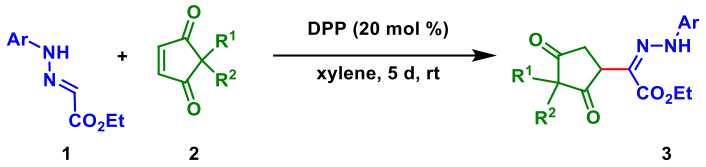
Table S5: Optimization of solvent concentration[a]



entry[a]	Concentration (M)	solvent	yield[b]	dr[c]	er[d]
1.	0.1	xylene	70	>20:1	94.5:5.5
2.	**0.05**	**xylene**	**68**	**>20:1**	**95.5:4.5**
3.	0.033	xylene	54	>20:1	96:4

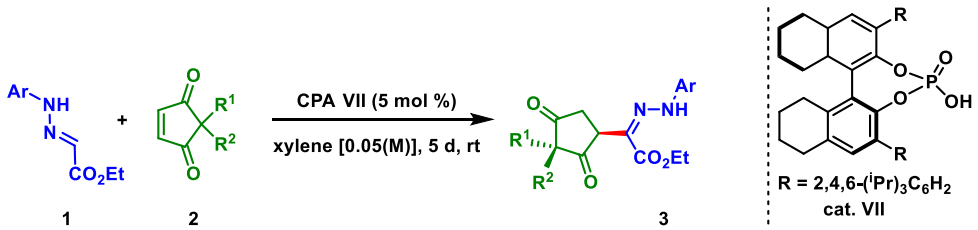
[a] Reaction conditions: 0.075 mmol of **1a** and 0.05 mmol of **2a**, 5 mol% of catalyst, xylene, rt, under Ar atmosphere. [b] Isolated yield after flash chromatography. [c] Determined by ^{1}HNMR. [d] Determined by HPLC analysis.

6. General procedure for the synthesis of racemic products (*rac*-3):



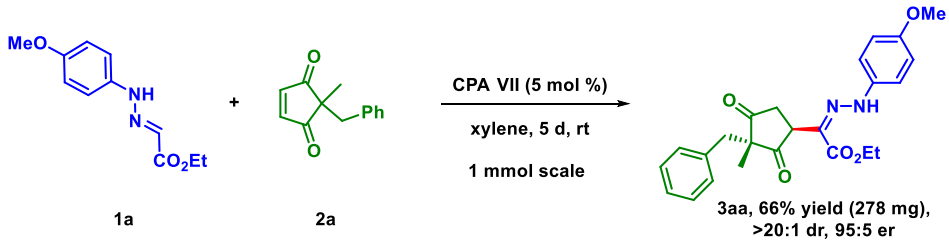
In an oven dried 5 mL rb, hydrazone **1** (0.15 mmol), 2,2-disubstituted cyclopentene-1,3-dione **2** (0.1 mmol) and 20 mol% of diphenyl phosphate were taken under Ar. Then 1 mL of dry xylene was added to the reaction mixture and stirred at rt for 5 days. Progress of the reaction was monitored by TLC. After the completion of reaction, the racemic (*rac*-**3**) samples for HPLC analysis were obtained by preparative TLC (Merck silica-gel 60 F254 pre-coated plates of 0.25 mm thickness) using 5-10% EtOAc in petroleum ether.

7. General procedure for the catalytic enantioselective synthesis of 3:



In an oven dried 5 mL rb, hydrazone **1** (0.15 mmol), 2,2-disubstituted cyclopentene-1,3-dione **2** (0.1 mmol) and 5 mol% of catalyst **VII** were taken under Ar. Then 2 mL of dry xylene was added to the reaction mixture and stirred at rt for 5 days. Progress of the reaction was monitored by TLC. After the completion of reaction, the reaction mixture was subjected to directly in flash chromatography to obtain the product **3** (5-10% EtOAc in petroleum ether).

8. Procedure for the scale-up experiment:

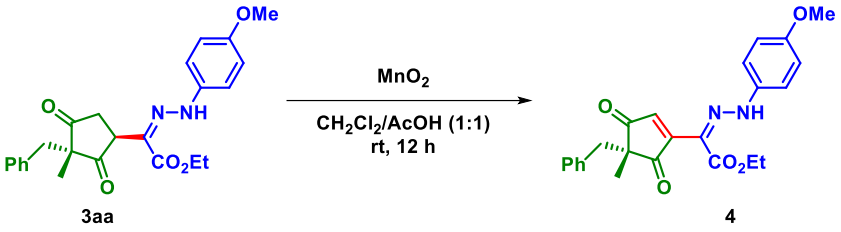


In an oven dried 50 mL rb, hydrazone **1a** (333 mg, 1.5 mmol), 2,2-disubstituted cyclopentene-1,3-dione **2a** (200 mg, 1.0 mmol) and catalyst **VII** (38 mg, 5 mol%) were taken under Ar. Then 20 mL of dry xylene was added to the reaction mixture and stirred at rt for 5 days. Progress of the reaction was monitored by TLC. After the completion of reaction, the reaction mixture was

subjected to directly in flash chromatography (5-10% EtOAc in petroleum ether) to obtain the product **3aa** (278 mg, 66% yield, >20:1 dr, 95:5 er).

9. Procedure for synthetic transformations:

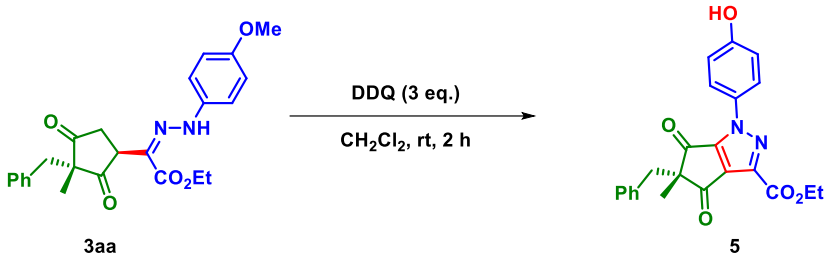
a. Procedure for the preparation of 4:



3aa 4

In a screw cap vial, equipped with a magnetic stirring bar, to a solution of **3aa** (0.05 mmol) in AcOH:DCM (1:1) 1 mL was added MnO_2 (0.5 mmol, 10 equiv). The mixture was stirred at room temperature for overnight. After full conversion of **3aa**, the crude reaction mixture was directly purified by silica-gel flash column chromatography (5-10% EtOAc in petroleum ether) to obtain **4** as a yellow solid (10.9 mg, 52% yield).

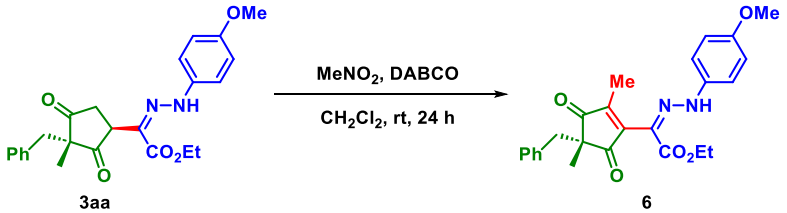
b. Procedure for the preparation of 5:



3aa 5

In a screw cap vial, equipped with a magnetic stirring bar, to a solution of **3aa** (0.05 mmol) in 0.5 mL DCM was added DDQ (0.15 mmol, 3 eq.) and the mixture was stirred for 2 h at room temperature. After full conversion of **3aa**, the crude reaction mixture was directly purified by silica-gel flash column chromatography (5-10% EtOAc in petroleum ether) to obtain **5** as a yellow semi-solid (9.2 mg, 46% yield).

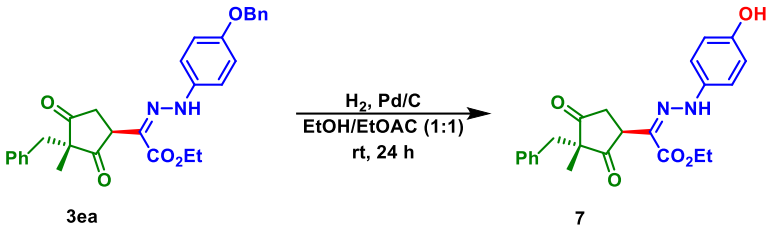
c. Procedure for the preparation of 6:



3aa 6

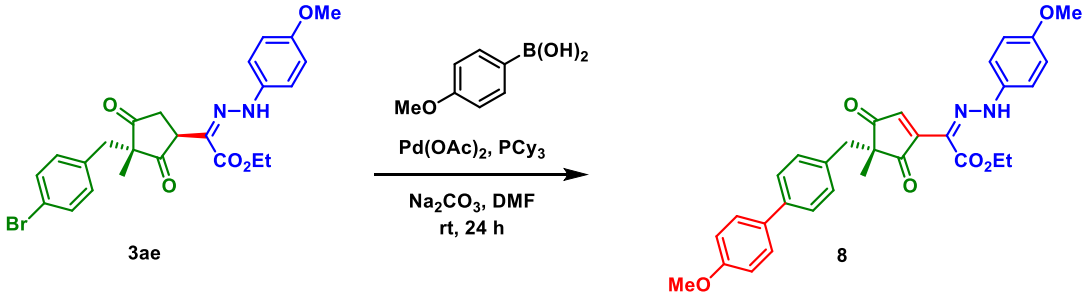
In a screw cap vial, equipped with a magnetic stirring bar, to a solution of **3aa** (0.05 mmol) in DCM (1 mL) was added CH_3NO_2 (10 equiv) and DABCO (1.5 equiv). The mixture was stirred at room temperature for 24 h. The reaction was monitored by TLC. After full conversion of **3aa**, the crude reaction mixture was directly purified by silica-gel flash column chromatography (5-10% EtOAc in petroleum ether) to obtain **6** as a yellow solid (12.5 mg, 58% yield).

d. Procedure for the preparation of 7:



In an oven dried 5 mL rb, **3ea** (0.0.05 mmol) was dissolved in 1 ml methanol/ethyl acetate (1:1), and Pd/C (10 mol %) was added. The resulting mixture was stirred at room temperature under H_2 atmosphere. The reaction was monitored by TLC. After full conversion of **3ea**, the crude reaction mixture was directly purified by silica-gel flash column chromatography (10-20% EtOAc in petroleum ether) to obtain **7** as a yellow semi-solid (13.8 mg, 68% yield).

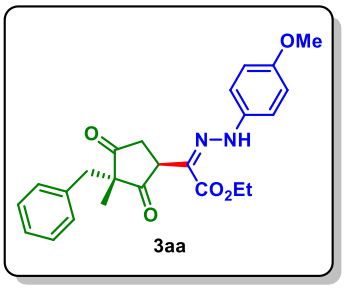
e. Procedure for the preparation of 8:



To a round 5 ml round bottom flask, **3ae** (0.05 mmol), $Pd(OAc)_2$ (5 mol%), PCy_3 (5 mol%), 4-methoxy phenyl boronic acid (1.5 eq.) and Na_2CO_3 (2 eq.) were added under nitrogen atomosphere. Then 0.5 ml DMF was added to the reaction mixture and the reaction mixture was stirred at room temperature for 24 h. Next H_2O was added to the mixture and the mixture was extracted with ethyl acetate. Then the combined organic layers were again washed with H_2O twice and the organic layer was dried over Na_2SO_4 and concentrated in vacuo and the crude product was purified by flash chromatography (10-20% EtOAc in petroleum ether) to obtain **8** as a yellow solid (18.6 mg, 71% yield).

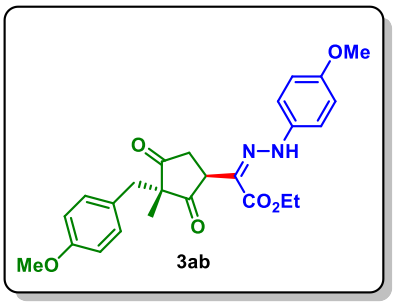
10. Characterisation of the products:

Ethyl (Z)-2-((1S,3R)-3-benzyl-3-methyl-2,4-dioxocyclopentyl)-2-(2-(4-methoxyphenyl)hydrazineylidene)acetate (3aa)



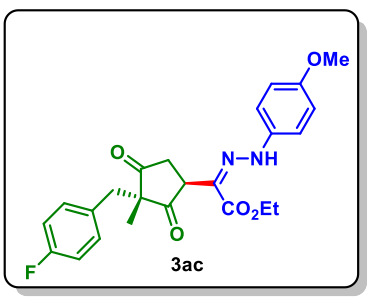
Yellow solid (28.7 mg, yield: 68%); R_f = 0.5 in 2:8 ethyl acetate/hexane; dr >20:1; **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 12.14 (s, 1H), 7.31 – 7.26 (m, 3H), 7.11 – 7.06 (m, 2H), 7.06 – 7.01 (m, 2H), 6.89 – 6.82 (m, 2H), 4.32 – 4.13 (m, 2H), 3.78 (s, 3H), 3.22 (dd, *J* = 11.4, 7.9 Hz, 1H), 2.97 (q, *J* = 12.8 Hz, 2H), 2.76 (dd, *J* = 19.0, 7.9 Hz, 1H), 2.41 (dd, *J* = 19.0, 11.4 Hz, 1H), 1.28 (m, 6H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 216.62, 216.07, 162.43, 155.81, 136.64, 135.60, 129.79, 128.85, 127.60, 123.62, 115.34, 114.83, 61.24, 58.80, 55.73, 52.17, 44.50, 42.02, 19.88, 14.38. **ESI HRMS**: calcd. for $C_{24}H_{27}N_2O_5$ $[M+H]^+$ 423.1914, found 423.1914. **HPLC Analysis**: er = 95.5:4.5, Chiralpak ADH Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 17.5 min, t_{minor} = 11.1 min).

ethyl (Z)-2-((1S,3R)-3-(4-methoxybenzyl)-3-methyl-2,4-dioxocyclopentyl)-2-(2-(4-methoxyphenyl)hydrazineylidene)acetate (3ab)



Yellow solid (28.0 mg, yield: 62%); R_f = 0.3 in 2:8 ethyl acetate/hexane; dr 16:1; **^{1}H NMR (500 MHz, CDCl$_3$)** δ 12.14 (s, 1H), 7.08 – 6.96 (m, 4H), 6.89 – 6.77 (m, 4H), 4.27 (dq, *J* = 10.1, 7.2 Hz, 1H), 4.19 (qd, *J* = 7.1, 3.9 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.27 (dd, *J* = 11.4, 7.7 Hz, 1H), 2.92 (q, *J* = 13.1 Hz, 2H), 2.75 (dd, *J* = 18.9, 7.8 Hz, 1H), 2.44 (dd, *J* = 18.9, 11.4 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.25 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 216.83, 216.30, 162.41, 158.99, 155.81, 136.66, 130.83, 127.55, 123.74, 115.35, 114.83, 114.17, 61.22, 58.91, 55.70, 55.34, 52.16, 43.79, 42.06, 19.67, 14.36. **ESI HRMS**: calcd. for $C_{25}H_{29}N_2O_6$ $[M+H]^+$ 453.2020, found 453.2024. **HPLC Analysis**: er = 90:10, Chiralpak ADH Column, n-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 31.6 min, t_{minor} = 14.1 min).

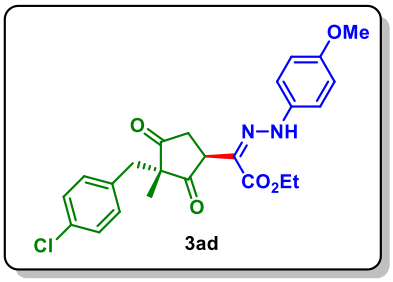
ethyl (Z)-2-((1S,3R)-3-(4-fluorobenzyl)-3-methyl-2,4-dioxocyclopentyl)-2-(2-(4-methoxyphenyl)hydrazineylidene)acetate (3ac)



Yellow solid (24.2 mg, yield: 55%); R_f = 0.55 in 2:8 ethyl acetate/hexane; dr 7:1; **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 12.15 (s, 1H), 7.08 – 7.02 (m, 4H), 7.01 – 6.95 (m, 2H), 6.87 – 6.83 (m, 2H), 4.28 (dq, *J* = 10.5, 7.2 Hz, 1H), 4.19 (dq, *J* = 10.9, 7.1 Hz, 1H), 3.83 (s, 1H), 3.78 (s, 3H), 3.26 (dd, *J* = 11.2, 8.1 Hz, 1H), 3.01 – 2.89 (m, 2H), 2.81 (dd, *J* = 18.9, 8.1 Hz, 1H), 2.46 (dd, *J* = 18.9, 11.2 Hz, 1H), 1.30 – 1.26 (m, 6H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 216.35, 215.81, 162.41, 155.87, 136.59, 131.45, 131.40, 123.41, 115.79, 115.64, 115.37, 114.85, 61.26, 58.64, 55.71, 52.18, 43.13, 41.96, 20.00, 14.38. **^{19}F NMR (471 MHz, CDCl$_3$)** δ -114.75. **ESI HRMS**: calcd. for $C_{24}H_{26}FN_2O_5$ $[M+H]^+$ 441.1820, found 441.18221. **HPLC Analysis**: er =

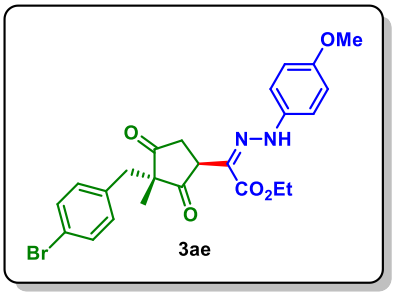
95:5, Chiralpak ADH Column, n-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 24.4 min, t_{minor} = 13.5 min).

ethyl (Z)-2-((1S,3R)-3-(4-chlorobenzyl)-3-methyl-2,4-dioxocyclopentyl)-2-(2-(4-methoxyphenyl)hydrazineylidene)acetate (3ad)



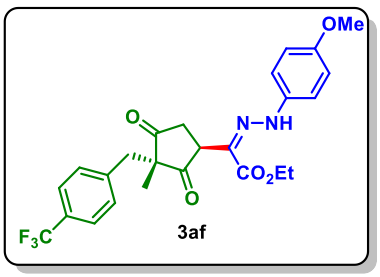
Yellow solid (29.2 mg, yield: 64%); R_f = 0.55 in 2:8 ethyl acetate/hexane; dr >20:1; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 12.17 (s, 1H), 7.30 – 7.25 (m, 2H), 7.07 (d, *J* = 9.0 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 4.30 (dt, *J* = 10.9, 7.1 Hz, 1H), 4.25 – 4.18 (m, 1H), 3.80 (s, 3H), 3.31 (dd, *J* = 11.2, 8.1 Hz, 1H), 2.99 (d, *J* = 13.0 Hz, 1H), 2.92 (d, *J* = 13.1 Hz, 1H), 2.85 (dd, *J* = 18.9, 8.1 Hz, 1H), 2.50 (dd, *J* = 18.9, 11.2 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.28 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 216.11, 215.59, 162.42, 155.87, 136.58, 134.19, 133.55, 131.21, 128.97, 123.34, 115.37, 114.85, 61.27, 58.52, 55.71, 52.14, 43.08, 41.93, 20.12, 14.38. **ESI HRMS**: calcd. for $C_{24}H_{26}ClN_2O_5$ $[M+H]^+$ 457.1525, found 457.1528. **HPLC Analysis**: er = 93.5:6.5, Chiralpak ADH Column, n-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 28.1 min, t_{minor} = 15.8 min).

ethyl (Z)-2-((1S,3R)-3-(4-bromobenzyl)-3-methyl-2,4-dioxocyclopentyl)-2-(2-(4-methoxyphenyl)hydrazineylidene)acetate (3ae)



Yellow solid (31.5 mg, yield: 63%); R_f = 0.6 in 2:8 ethyl acetate/hexane; dr 12:1; **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 12.16 (s, 1H), 7.44 – 7.39 (m, 2H), 7.07 – 7.03 (m, 2H), 6.98 – 6.93 (m, 2H), 6.87 – 6.83 (m, 2H), 4.31 – 4.25 (m, 1H), 4.20 (dq, *J* = 10.9, 7.1 Hz, 1H), 3.78 (s, 3H), 3.30 (dd, *J* = 11.2, 8.1 Hz, 1H), 2.97 – 2.87 (m, 2H), 2.84 (dd, *J* = 18.9, 8.1 Hz, 1H), 2.48 (dd, *J* = 18.9, 11.2 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.26 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 216.10, 215.58, 162.43, 155.87, 136.57, 134.69, 131.94, 131.57, 123.31, 121.68, 115.38, 114.85, 61.28, 58.46, 55.72, 52.14, 43.10, 41.93, 20.15, 14.40. **ESI HRMS**: calcd. for $C_{24}H_{26}BrN_2O_5$ $[M+H]^+$ 501.1020, found 501.1025. **HPLC Analysis**: er = 94.5:5.5, Chiralpak ADH Column, n-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 26.7 min, t_{minor} = 13.9 min).

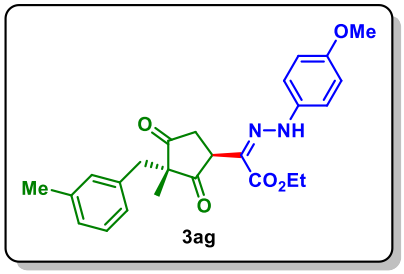
ethyl (Z)-2-(2-(4-methoxyphenyl)hydrazineylidene)-2-((1S,3R)-3-methyl-2,4-dioxo-3-(4-(trifluoromethyl)benzyl)cyclopentyl)acetate (3af)



Yellow solid (25.4 mg, yield: 52%); R_f = 0.6 in 2:8 ethyl acetate/hexane; dr 10:1; **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 12.18 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.08 – 7.03 (m, 2H), 6.90 – 6.84 (m, 2H), 4.29 (dd, *J* = 11.0, 7.1 Hz, 1H), 4.22 (dq, *J* = 10.9, 7.1 Hz, 1H), 3.80 (s, 3H), 3.31 (dd, *J* = 11.0, 8.4 Hz, 1H), 3.08 (d, *J* = 12.7 Hz, 1H), 3.00 (d, *J* = 13.0 Hz, 1H), 2.91 (dd, *J* = 18.9, 8.4 Hz, 1H), 2.53 (dd, *J* = 18.8, 11.1 Hz, 1H), 1.32 – 1.27 (m, 7H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 215.67, 215.12, 162.46, 155.93, 139.89, 136.56, 130.32, 125.70 (q, J_{C-F} = 3.02 Hz), 123.09, 117.20, 115.37, 115.09, 114.88, 61.29, 58.34, 55.72, 52.12, 42.97, 41.80, 20.34, 14.35. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -62.56. **ESI HRMS**: calcd. for $C_{25}H_{25}F_3N_2NaO_5$

[M+Na]$^+$ 513.1608, found 513.1610. **HPLC Analysis**: er = 95:5, Chiralpak ADH Column, n-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 20.4 min, t_{minor} = 10.1 min).

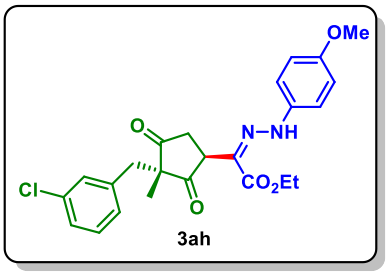
ethyl (Z)-2-(2-(4-methoxyphenyl)hydrazineylidene)-2-((1S,3R)-3-methyl-3-(3-methylbenzyl)-2,4-dioxocyclopentyl)acetate (3af)



3ag

Yellow solid (30.5 mg, yield: 70%); R_f = 0.65 in 2:8 ethyl acetate/hexane; dr >20:1; **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 12.14 (s, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.10 – 7.01 (m, 3H), 6.90 – 6.82 (m, 4H), 4.32 – 4.13 (m, 2H), 3.78 (s, 3H), 3.24 (dd, *J* = 11.4, 7.7 Hz, 1H), 2.98 – 2.88 (m, 2H), 2.74 (dd, *J* = 19.0, 7.7 Hz, 1H), 2.42 (dd, *J* = 19.0, 11.4 Hz, 1H), 2.32 (s, 3H), 1.29 – 1.26 (m, 6H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 216.67, 216.14, 162.41, 155.80, 138.46, 136.65, 135.47, 130.45, 128.72, 128.34, 126.80, 123.71, 115.32, 114.83, 61.23, 58.83, 55.71, 52.21, 44.57, 42.07, 21.49, 19.78, 14.37. **ESI HRMS**: calcd. for $C_{25}H_{29}N_2O_5$ [M+H]$^+$ 437.2071, found 437.2071. **HPLC Analysis**: er = 95:5, Chiralpak ADH Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 16.8 min, t_{minor} = 10.7 min).

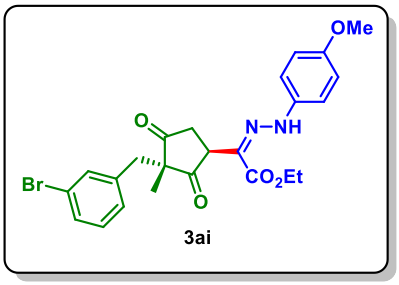
ethyl (Z)-2-((1S,3R)-3-(3-chlorobenzyl)-3-methyl-2,4-dioxocyclopentyl)-2-(2-(4-methoxyphenyl)hydrazineylidene)acetate (3ah)



3ah

Yellow solid (26.9 mg, yield: 59%); R_f = 0.55 in 2:8 ethyl acetate/hexane; dr 7:1; **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 12.16 (s, 1H), 7.26 – 7.21 (m, 2H), 7.08 (q, *J* = 2.0 Hz, 1H), 7.05 (dd, *J* = 8.8, 2.0 Hz, 2H), 6.99 – 6.94 (m, 1H), 6.87 – 6.83 (m, 2H), 4.29 (tt, *J* = 8.4, 5.3 Hz, 1H), 4.21 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.83 (s, 1H), 3.78 (s, 3H), 3.34 (dd, *J* = 11.2, 8.3 Hz, 1H), 3.00 – 2.89 (m, 2H), 2.87 (dd, *J* = 18.9, 8.2 Hz, 1H), 2.51 (dd, *J* = 18.9, 11.2 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.27 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 215.89, 215.35, 162.50, 155.88, 137.71, 136.62, 134.62, 130.07, 129.88, 128.11, 127.84, 123.27, 115.38, 114.87, 61.30, 58.42, 55.73, 52.09, 43.22, 41.79, 20.12, 14.41. **ESI HRMS**: calcd. for $C_{24}H_{26}ClN_2O_5$ [M+H]$^+$ 457.1525, found 457.1526. **HPLC Analysis**: er = 94:6, Chiralpak ADH Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 32.3 min, t_{minor} = 21.7 min).

ethyl (Z)-2-((1S,3R)-3-(3-bromobenzyl)-3-methyl-2,4-dioxocyclopentyl)-2-(2-(4-methoxyphenyl)hydrazineylidene)acetate (3ai)

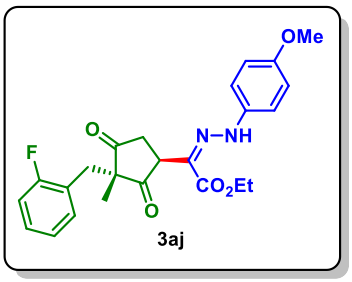


3ai

Yellow solid (30.5 mg, yield: 61%); R_f = 0.6 in 2:8 ethyl acetate/hexane; dr >20:1; **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 12.16 (s, 1H), 7.41 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.24 (d, *J* = 1.9 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 7.07 – 7.03 (m, 2H), 7.02 (dt, *J* = 7.8, 1.4 Hz, 1H), 6.88 – 6.83 (m, 2H), 4.25 (ddq, *J* = 50.3, 10.9, 7.1 Hz, 2H), 3.78 (s, 3H), 3.34 (dd, *J* = 11.2, 8.3 Hz, 1H), 2.98 – 2.88 (m, 2H), 2.88 – 2.83 (m, 1H), 2.52 (dd, *J* = 18.9, 11.2 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.27 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 215.90, 215.36, 162.49, 155.88, 138.00, 136.62, 132.77, 130.79, 130.35, 128.59, 123.28, 122.82, 115.39, 114.86, 61.32, 58.44, 55.74, 52.12, 43.15, 41.81, 20.12, 14.43. **ESI HRMS**: $C_{24}H_{26}BrN_2O_5$ [M+H]$^+$ 501.1020, found 501.1022.

HPLC Analysis: er = 95:5, Chiralpak ADH Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 22.9 min, t_{minor} = 16.2 min).

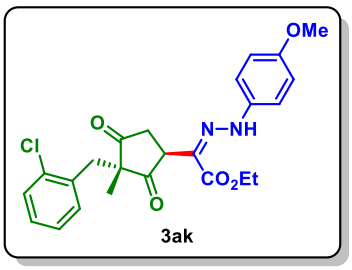
ethyl (Z)-2-((1S,3R)-3-(2-fluorobenzyl)-3-methyl-2,4-dioxocyclopentyl)-2-(2-(4-methoxyphenyl)hydrazineylidene)acetate (3aj)



3aj

Yellow solid (25.5 mg, yield: 58%); R_f = 0.55 in 2:8 ethyl acetate/hexane; dr >20:1; **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.16 (s, 1H), 7.30 – 7.24 (m, 1H), 7.16 – 6.98 (m, 5H), 6.88 – 6.82 (m, 2H), 4.26 (dq, *J* = 10.9, 7.2 Hz, 1H), 4.17 (dq, *J* = 10.9, 7.1 Hz, 1H), 3.84 – 3.75 (m, 4H), 2.98 (s, 2H), 2.92 (dd, *J* = 19.0, 11.5 Hz, 1H), 2.82 (dd, *J* = 19.0, 7.5 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.23 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 214.76, 214.41, 162.35, 161.96 (d, J_{C-F} = 247.64 Hz), 155.83, 136.65, 132.42 (d, J_{C-F} = 3.02 Hz), 129.67 (d, J_{C-F} = 9.06 Hz), 124.33 (d, J_{C-F} = 4.53 Hz), 123.84, 122.23 (d, J_{C-F} = 16.61 Hz), 115.80 (d, J_{C-F} = 22.65 Hz), 115.40, 114.83, 61.30, 57.69, 55.72, 51.39, 41.50, 36.26 (d, J_{C-F} = 3.02 Hz), 17.84, 14.30. **^{19}F NMR (471 MHz, CDCl$_3$)** δ -114.75. **ESI HRMS**: calcd. for $C_{24}H_{26}FN_2O_5$ $[M+H]^+$ 441.1820, found 441.18223. **HPLC Analysis**: er = 95:5, Chiralpak ADH Column, n-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 21.0 min, t_{minor} = 16.8 min).

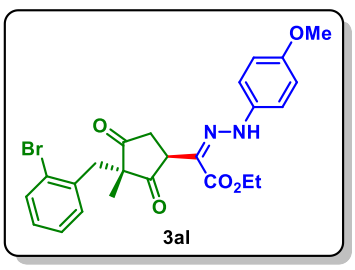
ethyl (Z)-2-((1S,3R)-3-(2-chlorobenzyl)-3-methyl-2,4-dioxocyclopentyl)-2-(2-(4-methoxyphenyl)hydrazineylidene)acetate (3ak)



3ak

Yellow solid (31.0 mg, yield: 68%); R_f = 0.55 in 2:8 ethyl acetate/hexane; dr >20:1; **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 12.16 (s, 1H), 7.41 – 7.35 (m, 1H), 7.25 – 7.19 (m, 2H), 7.19 – 7.13 (m, 1H), 7.10 – 7.04 (m, 2H), 6.88 – 6.82 (m, 2H), 4.26 (dq, *J* = 10.8, 7.2 Hz, 1H), 4.17 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.83 – 3.79 (m, 1H), 3.78 (s, 3H), 3.18 – 3.10 (m, 2H), 2.91 (dd, *J* = 19.0, 11.7 Hz, 1H), 2.82 (dd, *J* = 19.0, 7.4 Hz, 1H), 1.27 – 1.24 (m, 6H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 214.89, 214.50, 162.37, 155.84, 136.67, 134.88, 133.14, 132.34, 130.08, 129.11, 126.98, 123.84, 115.41, 114.84, 61.29, 57.67, 55.73, 51.59, 41.81, 39.95, 18.18, 14.32. **ESI HRMS**: $C_{24}H_{26}ClN_2O_5$ $[M+H]^+$ 457.1525, found 457.1529. **HPLC Analysis**: er = 95:5, Chiralpak ADH Column, n-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 22.5 min, t_{minor} = 18.3 min).

ethyl (Z)-2-((1S,3R)-3-(2-bromobenzyl)-3-methyl-2,4-dioxocyclopentyl)-2-(2-(4-methoxyphenyl)hydrazineylidene)acetate (3al)

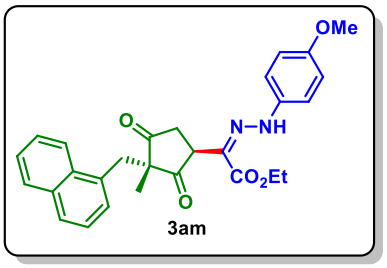


3al

Yellow solid (30.0 mg, yield: 60%); R_f = 0.6 in 2:8 ethyl acetate/hexane; dr >20:1; **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 12.16 (s, 1H), 7.57 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.20 – 7.10 (m, 2H), 7.09 – 7.05 (m, 2H), 6.87 – 6.83 (m, 2H), 4.26 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.18 (dq, *J* = 10.9, 7.1 Hz, 1H), 3.83 – 3.79 (m, 1H), 3.78 (s, 3H), 3.20 – 3.14 (m, 2H), 2.92 (dd, *J* = 19.0, 11.7 Hz, 1H), 2.82 (dd, *J* = 19.0, 7.4 Hz, 1H), 1.27 – 1.24 (m, 6H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 214.89, 214.49, 162.37, 155.85, 136.67, 134.98, 133.51, 132.16, 129.26, 127.60, 125.58, 123.83, 115.41, 114.85, 61.29, 57.67, 55.73, 51.70, 42.20, 41.93, 18.29, 14.34. **ESI HRMS**: $C_{24}H_{26}BrN_2O_5$

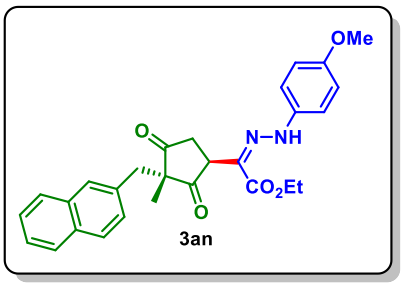
$[M+H]^+$ 501.1020, found 501.1025. **HPLC Analysis**: er = 90:10, Chiralpak ADH Column, n-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 25.3 min, t_{minor} = 20.0 min).

ethyl (Z)-2-(2-(4-methoxyphenyl)hydrazineylidene)-2-((1S,3R)-3-methyl-3-(naphthalen-1-ylmethyl)-2,4-dioxocyclopentyl)acetate (3am)



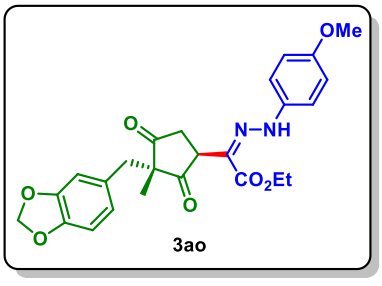
Yellow solid (32.0 mg, yield: 68%); R_f = 0.55 in 2:8 ethyl acetate/hexane; dr >20:1; **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 12.05 (s, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.85 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.51 (dddd, *J* = 23.1, 8.0, 6.8, 1.3 Hz, 2H), 7.41 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.27 (dd, *J* = 7.0, 5.8 Hz, 1H), 6.99 – 6.94 (m, 2H), 6.84 – 6.79 (m, 2H), 4.18 (dq, *J* = 10.7, 7.1 Hz, 1H), 4.09 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.77 (s, 3H), 3.55 – 3.43 (m, 2H), 2.96 (dd, *J* = 11.7, 7.3 Hz, 1H), 2.58 (dd, *J* = 19.1, 7.4 Hz, 1H), 2.10 (dd, *J* = 19.1, 11.8 Hz, 1H), 1.38 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 216.78, 216.30, 162.28, 155.78, 136.62, 133.97, 132.00, 131.90, 128.82, 128.65, 128.53, 126.56, 126.13, 125.42, 124.20, 123.71, 115.30, 114.79, 61.15, 58.86, 55.71, 52.26, 42.27, 40.77, 19.96, 14.29. **ESI HRMS**: calcd. for $C_{28}H_{28}N_2NaO_5$ $[M+Na]^+$ 495.1890, found 495.1892. **HPLC Analysis**: er = 96.5:3.5, Chiralpak ADH Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 39.2 min, t_{minor} = 21.9 min).

ethyl (Z)-2-(2-(4-methoxyphenyl)hydrazineylidene)-2-((1S,3R)-3-methyl-3-(naphthalen-2-ylmethyl)-2,4-dioxocyclopentyl)acetate (3an)



Yellow solid (30.2 mg, yield: 64%); R_f = 0.55 in 2:8 ethyl acetate/hexane; dr >20:1; **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.11 (s, 1H), 7.88 – 7.73 (m, 3H), 7.55 (d, *J* = 1.8 Hz, 1H), 7.48 (td, *J* = 5.8, 5.3, 3.2 Hz, 2H), 7.20 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.02 – 6.95 (m, 2H), 6.86 – 6.78 (m, 2H), 4.23 (dq, *J* = 10.9, 7.1 Hz, 1H), 4.14 (dq, *J* = 10.9, 7.1 Hz, 1H), 3.76 (s, 3H), 3.23 – 3.08 (m, 3H), 2.76 (dd, *J* = 18.9, 7.9 Hz, 1H), 2.37 (dd, *J* = 19.0, 11.3 Hz, 1H), 1.33 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 216.56, 216.03, 162.42, 155.79, 136.61, 133.46, 133.21, 132.64, 128.64, 128.52, 127.99, 127.80, 127.78, 126.44, 126.17, 123.53, 115.32, 114.80, 61.19, 58.89, 55.70, 52.12, 44.50, 42.06, 20.15, 14.33. **ESI HRMS**: calcd. for $C_{28}H_{28}N_2NaO_5$ $[M+Na]^+$ 495.1890, found 495.1897. **HPLC Analysis**: er = 95:5, Chiralpak ADH Column, n-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 25.8 min, t_{minor} = 18.2 min).

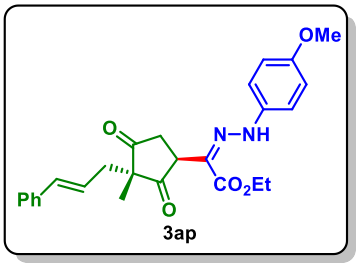
ethyl (Z)-2-((1S,3R)-3-(benzo[d][1,3]dioxol-5-ylmethyl)-3-methyl-2,4-dioxocyclopentyl)-2-(2-(4-methoxyphenyl)hydrazineylidene)acetate (3ao)



Yellow semi-solid (25.1 mg, yield: 54%); R_f = 0.25 in 2:8 ethyl acetate/hexane; dr >20:1; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 12.16 (s, 1H), 7.08 – 7.03 (m, 2H), 6.87 – 6.83 (m, 2H), 6.73 (d, *J* = 7.9 Hz, 1H), 6.58 – 6.51 (m, 2H), 5.95 (s, 2H), 4.31 – 4.25 (m, 1H), 4.19 (dq, *J* = 10.9, 7.1 Hz, 1H), 3.78 (s, 3H), 3.36 (dd, *J* = 11.3, 8.0 Hz, 1H), 2.94 – 2.84 (m, 2H), 2.81 (dd, *J* = 18.9, 8.0 Hz, 1H), 2.52 (dd, *J* = 18.9, 11.3 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.24 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ

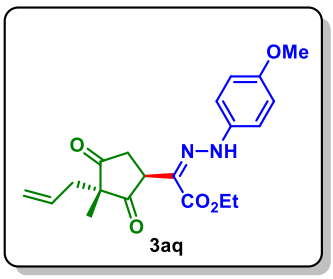
216.58, 216.01, 162.47, 155.81, 147.82, 146.98, 136.63, 129.19, 123.54, 123.01, 115.36, 114.82, 110.15, 108.56, 101.22, 61.26, 58.81, 55.71, 52.16, 44.09, 41.98, 19.81, 14.37. **ESI HRMS**: calcd. for $C_{25}H_{27}N_2O_7$ $[M+H]^+$ 467.1813, found 467.1818. **HPLC Analysis**: er = 92:8, Chiralpak ADH Column, n-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 31.3 min, t_{minor} = 19.4 min).

ethyl (Z)-2-((1S,3R)-3-cinnamyl-3-methyl-2,4-dioxocyclopentyl)-2-(2-(4-methoxyphenyl)hydrazineylidene)acetate (3ap)



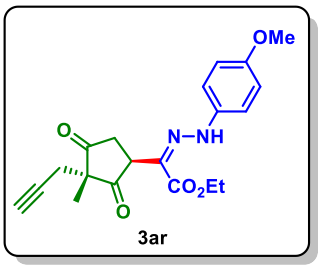
Yellow semi-solid (19.2 mg, yield: 43%); R_f = 0.55 in 2:8 ethyl acetate/hexane; dr 5:1; **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.20 (s, 1H), 7.36 – 7.28 (m, 5H), 7.24 (td, *J* = 7.0, 6.4, 3.5 Hz, 2H), 7.10 – 7.05 (m, 2H), 6.93 (d, *J* = 9.0 Hz, 1H), 6.88 – 6.82 (m, 2H), 6.45 (d, *J* = 15.7 Hz, 1H), 6.03 (dt, *J* = 16.1, 7.9 Hz, 1H), 4.33 – 4.24 (m, 2H), 4.24 – 4.17 (m, 1H), 3.99 (dd, *J* = 11.3, 7.6 Hz, 1H), 3.82 (s, 1H), 3.78 (s, 3H), 3.06 (dd, *J* = 18.9, 11.3 Hz, 1H), 2.91 (dd, *J* = 18.9, 7.6 Hz, 1H), 2.63 – 2.58 (m, 1H), 2.52 (ddd, *J* = 7.9, 5.3, 1.3 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 1H), 1.26 (t, *J* = 2.6 Hz, 3H), 1.24 (s, 1H), 1.23 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 215.39, 215.03, 162.40, 155.87, 136.69, 136.64, 135.15, 128.75, 127.93, 126.52, 123.83, 122.42, 115.42, 114.86, 61.34, 57.50, 55.73, 51.68, 41.74, 40.71, 18.11, 14.34. **ESI HRMS**: calcd. for $C_{26}H_{29}N_2O_5$ $[M+H]^+$ 449.2071, found 449.2075. **HPLC Analysis**: er = 82:18, Chiralpak Phenomenex Lux C4 Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 19.2 min, t_{minor} = 15.8 min).

ethyl (Z)-2-((1S,3R)-3-allyl-3-methyl-2,4-dioxocyclopentyl)-2-(2-(4-methoxyphenyl)hydrazineylidene)acetate (3aq)



Yellow semi-solid (21.2 mg, yield: 57%); R_f = 0.75 in 2:8 ethyl acetate/hexane; dr 5:1; **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 12.20 (s, 1H), 7.10 (d, *J* = 9.0 Hz, 2H), 6.86 (d, *J* = 8.9 Hz, 2H), 5.66 (ddt, *J* = 17.4, 10.1, 7.5 Hz, 1H), 5.20 – 5.10 (m, 2H), 4.24 (ddq, *J* = 41.7, 10.8, 7.1 Hz, 2H), 3.99 (dd, *J* = 11.4, 7.5 Hz, 1H), 3.79 (s, 3H), 3.06 (dd, *J* = 19.0, 11.4 Hz, 1H), 2.90 (dd, *J* = 18.9, 7.5 Hz, 1H), 2.42 – 2.31 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.19 (s, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 215.22, 214.80, 162.37, 155.89, 136.67, 131.24, 123.92, 120.36, 115.44, 114.87, 61.33, 57.23, 55.73, 51.75, 41.67, 41.50, 17.83, 14.35. **ESI HRMS**: calcd. for $C_{20}H_{24}N_2NaO_5$ $[M+Na]^+$ 395.1577, found 395.1580. **HPLC Analysis**: er = 89:11, Chiralpak Phenomenex Lux C4 Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 15.6 min, t_{minor} = 11.8 min).

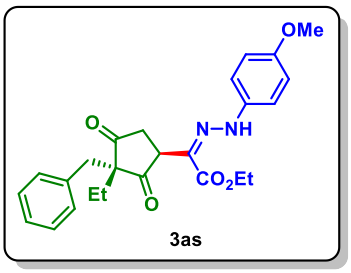
ethyl (Z)-2-(2-(4-methoxyphenyl)hydrazineylidene)-2-((1S,3R)-3-methyl-2,4-dioxo-3-(prop-2-yn-1-yl)cyclopentyl)acetate (3ar)



Yellow semi-solid (18.8 mg, yield: 51%); R_f = 0.75 in 2:8 ethyl acetate/hexane; dr >20:1; **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 12.22 (s, 1H), 7.10 (d, *J* = 8.9 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 4.37 – 4.20 (m, 2H), 4.14 (dd, *J* = 11.2, 7.9 Hz, 1H), 3.79 (s, 3H), 3.16 (dd, *J* = 18.9, 11.2 Hz, 1H), 2.99 (dd, *J* = 18.9, 7.9 Hz, 1H), 2.48 (t, *J* = 3.0 Hz, 2H), 2.11 (t, *J* = 2.7 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.22 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 214.55, 214.09,

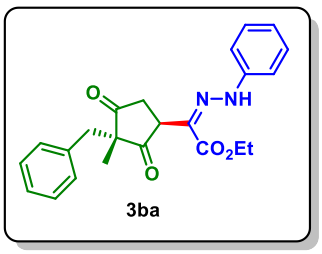
162.43, 155.93, 136.64, 123.77, 115.46, 114.89, 78.65, 71.72, 61.37, 55.75, 55.52, 52.63, 42.36, 26.12, 19.10, 14.41. **ESI HRMS**: calcd. for $C_{20}H_{23}N_2O_5$ $[M+H]^+$ 371.1601, found 371.1606. **HPLC Analysis**: er = 89:11, Chiralpak ADH Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 36.4 min, t_{minor} = 27.0 min).

ethyl (Z)-2-((1S,3R)-3-benzyl-3-ethyl-2,4-dioxocyclopentyl)-2-(2-(4-methoxyphenyl)hydrazineylidene)acetate (3as)



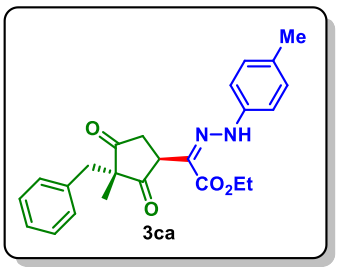
Yellow semi-solid (20.4 mg, yield: 47%); R_f = 0.55 in 2:8 ethyl acetate/hexane; dr 10:1 **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 12.18 (s, 1H), 7.30 – 7.24 (m, 3H), 7.11 – 7.06 (m, 2H), 7.02 – 6.98 (m, 2H), 6.84 – 6.81 (m, 2H), 4.30 (dq, *J* = 10.8, 7.2 Hz, 1H), 4.21 – 4.14 (m, 1H), 3.77 (s, 3H), 3.15 – 3.04 (m, 2H), 2.97 – 2.85 (m, 2H), 2.49 (dd, *J* = 18.8, 10.7 Hz, 1H), 1.84 (h, *J* = 7.3 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.85 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 216.79, 215.90, 163.16, 155.68, 136.83, 135.89, 129.87, 128.77, 127.38, 122.36, 115.14, 114.84, 63.88, 61.02, 55.72, 51.37, 42.96, 42.51, 28.74, 14.35, 9.46. **ESI HRMS**: calcd. for $C_{25}H_{28}N_2NaO_5$ $[M+Na]^+$ 459.1890, found 459.1892. **HPLC Analysis**: er = 90:10, Chiralpak ADH Column, n-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 10.8 min, t_{minor} = 7.2 min).

ethyl (Z)-2-((1S,3R)-3-benzyl-3-methyl-2,4-dioxocyclopentyl)-2-(2-phenylhydrazineylidene)acetate (3ba)



Yellow solid (20.3 mg, yield: 52%); R_f = 0.6 in 2:8 ethyl acetate/hexane; dr >20:1; **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.13 (s, 1H), 7.32 – 7.25 (m, 5H), 7.13 – 7.05 (m, 4H), 6.98 (t, *J* = 7.3 Hz, 1H), 4.24 (ddq, *J* = 46.7, 11.0, 7.2 Hz, 2H), 3.24 (dd, *J* = 11.3, 8.0 Hz, 1H), 3.04 – 2.92 (m, 2H), 2.78 (dd, *J* = 19.0, 8.0 Hz, 1H), 2.43 (dd, *J* = 19.0, 11.3 Hz, 1H), 1.30 – 1.26 (m, 6H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 216.38, 215.77, 162.29, 142.76, 135.58, 129.78, 129.46, 128.84, 127.61, 124.83, 122.91, 114.14, 61.41, 58.80, 52.19, 44.47, 41.84, 19.87, 14.34. **ESI HRMS**: calcd. for $C_{23}H_{25}N_2O_4$ $[M+H]^+$ 393.1809, found 393.1809. **HPLC Analysis**: *er* = 95:5, Chiralpak Phenomenex Lux C4 Column, n-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 15.0 min, t_{minor} = 17.2 min).

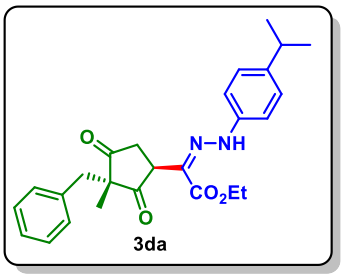
ethyl (Z)-2-((1S,3R)-3-benzyl-3-methyl-2,4-dioxocyclopentyl)-2-(2-(p-tolyl)hydrazineylidene)acetate (3ca)



Yellow solid (21.9 mg, yield: 54%); R_f = 0.65 in 2:8 ethyl acetate/hexane; dr >20:1; **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 12.11 (s, 1H), 7.32 – 7.26 (m, 3H), 7.08 (dd, *J* = 7.8, 1.5 Hz, 4H), 7.02 – 6.96 (m, 2H), 4.23 (ddq, *J* = 55.3, 10.9, 7.1 Hz, 2H), 3.24 (dd, *J* = 11.3, 7.9 Hz, 1H), 3.03 – 2.93 (m, 2H), 2.77 (dd, *J* = 19.0, 7.9 Hz, 1H), 2.42 (dd, *J* = 19.0, 11.3 Hz, 1H), 2.29 (s, 3H), 1.29 – 1.26 (m, 6H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 216.51,

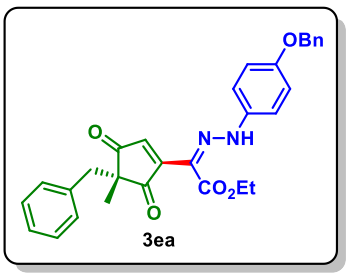
215.93, 162.36, 140.50, 135.61, 132.46, 129.99, 129.79, 128.84, 127.60, 124.11, 114.13, 61.30, 58.80, 52.16, 44.47, 41.95, 20.87, 19.89, 14.37. **ESI HRMS**: calcd. for $C_{24}H_{27}N_2O_4$ $[M+H]^+$ 407.1965, found 407.1966. **HPLC Analysis**: er = 89:11, Chiralpak ADH Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 21.8 min, t_{minor} = 13.8 min).

ethyl (Z)-2-((1S,3R)-3-benzyl-3-methyl-2,4-dioxocyclopentyl)-2-(2-(4-isopropylphenyl)hydrazineylidene)acetate (3da)



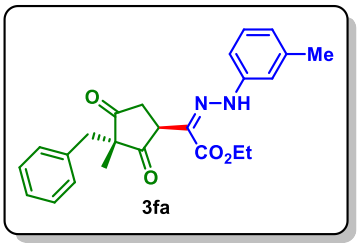
Yellow solid (17.3 mg, yield: 40%); R_f = 0.68 in 2:8 ethyl acetate/hexane; dr >20:1; **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 12.12 (s, 1H), 7.30 – 7.26 (m, 3H), 7.16 – 7.13 (m, 2H), 7.08 (dd, *J* = 7.5, 2.1 Hz, 2H), 7.04 – 7.00 (m, 2H), 4.32 – 4.24 (m, 1H), 4.22 – 4.15 (m, 1H), 3.25 (dd, *J* = 11.3, 7.9 Hz, 1H), 2.97 (q, *J* = 12.9 Hz, 2H), 2.89 – 2.83 (m, 1H), 2.78 (dd, *J* = 18.9, 7.9 Hz, 1H), 2.41 (dd, *J* = 19.0, 11.3 Hz, 1H), 1.28 (d, *J* = 3.0 Hz, 6H), 1.22 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 216.61, 215.96, 162.38, 143.70, 140.72, 135.61, 129.79, 128.85, 127.60, 127.38, 124.10, 114.18, 61.31, 58.80, 52.12, 44.44, 41.96, 33.61, 24.21, 19.94, 14.37. **ESI HRMS**: calcd. for $C_{26}H_{30}N_2NaO_4$ $[M+Na]^+$ 457.2098, found 457.2099. **HPLC Analysis**: er = 87.5:12.5, Chiralpak ADH Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 21.8 min, t_{minor} = 14.0 min).

ethyl (R,Z)-2-(4-benzyl-4-methyl-3,5-dioxocyclopent-1-en-1-yl)-2-(2-(4-(benzyloxy)phenyl)hydrazineylidene)acetate (3ea)



Yellow semi-solid (21.8 mg, yield: 44%); R_f = 0.52 in 2:8 ethyl acetate/hexane; dr >20:1; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 12.16 (s, 1H), 7.47 – 7.43 (m, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.37 – 7.29 (m, 4H), 7.13 – 7.08 (m, 2H), 7.08 – 7.03 (m, 2H), 6.96 – 6.92 (m, 2H), 5.06 (s, 2H), 4.29 (dq, *J* = 10.9, 7.2 Hz, 1H), 4.20 (dq, *J* = 10.9, 7.2 Hz, 1H), 3.25 (dd, *J* = 11.3, 7.9 Hz, 1H), 3.05 – 2.94 (m, 2H), 2.78 (dd, *J* = 18.9, 7.9 Hz, 1H), 2.44 (dd, *J* = 18.9, 11.3 Hz, 1H), 1.31 – 1.28 (m, 6H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 216.56, 216.00, 162.41, 154.98, 137.20, 136.87, 135.60, 129.78, 128.84, 128.70, 128.08, 127.61, 127.59, 123.72, 115.98, 115.31, 70.63, 61.25, 58.80, 52.16, 44.49, 41.98, 19.87, 14.37. **ESI HRMS**: calcd. for $C_{30}H_{29}N_2O_5$ $[M+H]^+$ 497.2071, found 497.2071. **HPLC Analysis**: er = 94:6, Chiralpak ADH Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 43.0 min, t_{minor} = 26.8 min).

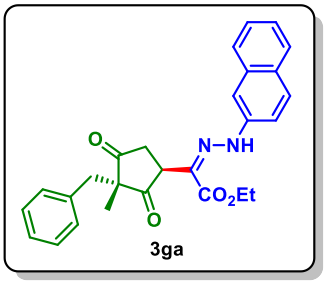
ethyl (Z)-2-((1S,3R)-3-benzyl-3-methyl-2,4-dioxocyclopentyl)-2-(2-(m-tolyl)hydrazineylidene)acetate (3fa)



Yellow semi-solid (19.0 mg, yield: 47%); R_f = 0.55 in 2:8 ethyl acetate/hexane; dr >20:1; **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.10 (s, 1H), 7.32 – 7.24 (m, 3H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.12 – 7.05 (m, 2H), 6.95 – 6.85 (m, 2H), 6.80 (d, *J* = 7.6 Hz, 1H), 4.28 (dq, *J* = 9.3, 7.0 Hz, 1H), 4.19 (dq, *J* = 10.9, 7.1 Hz, 1H), 3.25 (dd, *J* = 11.3, 7.9 Hz, 1H), 3.03 – 2.93 (m, 2H), 2.78 (dd, *J* = 19.0, 7.9 Hz, 1H), 2.42 (dd, *J* = 18.8, 11.6 Hz, 1H), 2.33 (s, 3H), 1.29 (d, *J* = 7.4 Hz, 6H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 216.53, 215.89, 162.27,

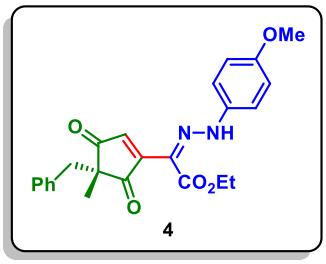
142.71, 139.43, 135.57, 129.78, 129.31, 128.86, 127.61, 124.57, 123.82, 114.76, 111.36, 61.39, 58.81, 52.21, 44.49, 41.90, 21.67, 19.85, 14.36. **ESI HRMS**: calcd. for $C_{24}H_{26}N_2NaO_4$ $[M+Na]^+$ 429.1785, found 429.1789. **HPLC Analysis**: er = 92.5:7.5, Chiralpak ADH Column, n-Hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 22.1 min, t_{minor} = 20.1 min).

ethyl (Z)-2-((1S,3R)-3-benzyl-3-methyl-2,4-dioxocyclopentyl)-2-(2-(naphthalen-2-yl)hydrazineylidene)acetate (3ga)



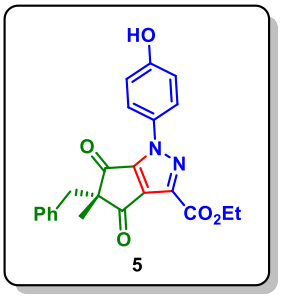
Yellow semi-solid (18.5 mg, yield: 42%); R_f = 0.55 in 2:8 ethyl acetate/hexane; dr >20:1; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 12.33 (s, 1H), 7.79 – 7.70 (m, 3H), 7.46 – 7.40 (m, 2H), 7.38 – 7.27 (m, 5H), 7.10 (dd, *J* = 7.5, 2.0 Hz, 2H), 4.31 (dq, *J* = 10.9, 7.2 Hz, 1H), 4.22 (dq, *J* = 10.9, 7.1 Hz, 1H), 3.30 (dd, *J* = 11.4, 8.0 Hz, 1H), 3.05 – 2.94 (m, 2H), 2.82 (dd, *J* = 19.0, 8.0 Hz, 1H), 2.47 (dd, *J* = 19.0, 11.4 Hz, 1H), 1.32 – 1.27 (m, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 216.37, 215.77, 162.33, 140.45, 135.60, 134.32, 130.39, 129.82, 129.60, 128.89, 127.96, 127.65, 127.21, 126.86, 125.29, 124.34, 115.41, 109.66, 61.52, 58.85, 52.32, 44.54, 41.89, 19.87, 14.37. **ESI HRMS**: calcd. for $C_{27}H_{27}N_2O_4$ $[M+H]^+$ 443.1965, found 443.1965. **HPLC Analysis**: er = 85:15, Chiralpak ADH Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 17.5 min, t_{minor} = 14.8 min).

ethyl (R,Z)-2-(4-benzyl-4-methyl-3,5-dioxocyclopent-1-en-1-yl)-2-(2-(4-methoxyphenyl)hydrazineylidene)acetate (4)



Yellow solid (10.9 mg, yield: 52%); R_f = 0.4 in 2:8 ethyl acetate/hexane; **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 13.03 (s, 1H), 7.38 – 7.30 (m, 2H), 7.15 – 7.07 (m, 3H), 7.06 – 6.98 (m, 3H), 6.98 – 6.90 (m, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 3.09 – 2.97 (m, 2H), 1.33 – 1.28 (m, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 206.35, 204.41, 163.55, 157.44, 152.71, 139.86, 136.10, 135.97, 130.00, 128.29, 126.93, 117.65, 117.10, 115.07, 61.43, 55.75, 53.37, 41.80, 19.73, 14.21. **ESI HRMS**: calcd. for $C_{24}H_{25}N_2O_5$ $[M+H]^+$ 421.1758, found 421.1760. **HPLC Analysis**: er = 89:11, Chiralpak ADH Column, n-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 30.3 min, t_{minor} = 12.5 min).

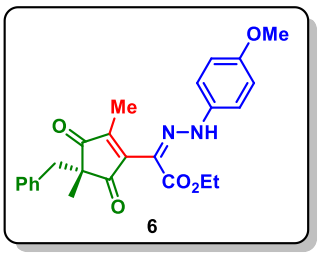
ethyl (S)-5-benzyl-1-(4-hydroxyphenyl)-5-methyl-4,6-dioxo-1,4,5,6-tetrahydrocyclopenta[c]pyrazole-3-carboxylate (5)



Yellow semi-solid (9.2 mg, yield: 46%); R_f = 0.38 in 2:8 ethyl acetate/hexane; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 9.0 Hz, 2H), 7.08 (dq, *J* = 14.4, 7.1 Hz, 3H), 7.03 – 7.00 (m, 2H), 6.98 (d, *J* = 9.0 Hz, 2H), 6.19 (s, 1H), 4.49 (q, *J* = 7.2 Hz, 2H), 3.22 (d, *J* = 13.5 Hz, 1H), 3.11 (d, *J* = 13.4 Hz, 1H), 1.49 – 1.44 (m, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 190.76, 189.25, 160.10, 157.12, 150.23, 137.59, 136.30, 135.59, 130.91, 129.78, 128.51, 127.36, 123.39, 116.26, 65.61, 62.48, 42.15, 20.66, 14.32. **ESI HRMS**: calcd. for $C_{23}H_{21}N_2O_5$ $[M+H]^+$ 405.1445, found 405.1446. **HPLC Analysis**: er = 95:5,

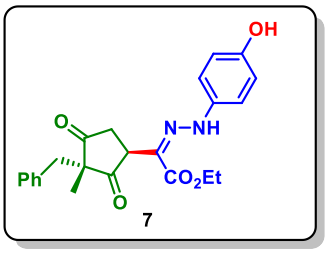
Chiralpak IC Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 12.1 min, t_{minor} = 18.2 min).

ethyl (R,Z)-2-(4-benzyl-2,4-dimethyl-3,5-dioxocyclopent-1-en-1-yl)-2-(2-(4-methoxyphenyl)hydrazineylidene)acetate (6)



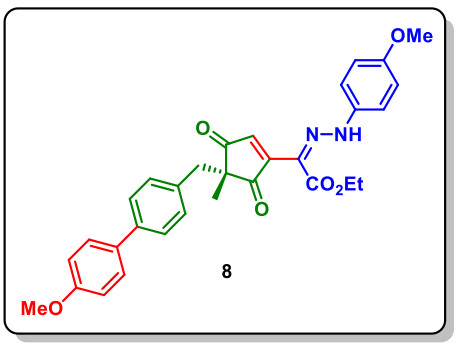
Yellow solid (12.5 mg, yield: 58%); R_f = 0.55 in 2:8 ethyl acetate/hexane; **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 12.56 (s, 1H), 7.20 – 7.07 (m, 5H), 6.99 (dd, *J* = 7.4, 2.1 Hz, 2H), 6.92 – 6.83 (m, 2H), 4.21 (qt, *J* = 7.3, 3.7 Hz, 2H), 3.80 (s, 3H), 3.02 (s, 2H), 1.94 (s, 3H), 1.29 – 1.22 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 206.77, 204.19, 162.90, 156.65, 154.23, 150.69, 136.19, 129.99, 128.21, 126.89, 118.04, 116.10, 114.93, 61.11, 55.74, 52.11, 41.34, 19.84, 14.13, 10.46. **ESI HRMS**: calcd. for $C_{25}H_{27}N_2O_5$ $[M+H]^+$ 435.1914, found 435.1918. **HPLC Analysis**: er = 94.5:5.5, Chiralpak ADH Column, n-Hexane/*i*-PrOH = 93/7, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 21.3 min, t_{minor} = 24.0 min).

ethyl (Z)-2-((1S,3R)-3-benzyl-3-methyl-2,4-dioxocyclopentyl)-2-(2-(4-hydroxyphenyl)hydrazineylidene)acetate (7)



Yellow semi-solid (13.8 mg, yield: 68%); R_f = 0.3 in 2:8 ethyl acetate/hexane; dr >20:1; **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 12.11 (s, 1H), 7.29 (dt, *J* = 7.2, 2.6 Hz, 3H), 7.13 – 7.05 (m, 2H), 7.03 – 6.94 (m, 2H), 6.85 – 6.72 (m, 2H), 4.34 – 4.14 (m, 2H), 3.22 (dd, *J* = 11.4, 7.9 Hz, 1H), 2.98 (q, *J* = 12.9 Hz, 2H), 2.75 (dd, *J* = 19.0, 7.9 Hz, 1H), 2.41 (dd, *J* = 19.0, 11.4 Hz, 1H), 1.30 – 1.26 (m, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 216.69, 216.22, 162.43, 151.70, 136.71, 135.59, 129.80, 128.87, 127.62, 123.59, 116.28, 115.52, 61.28, 58.85, 52.18, 44.52, 42.02, 19.88, 14.38. **ESI HRMS**: calcd. for $C_{23}H_{25}N_2O_5$ $[M+H]^+$ 409.1758, found 409.1760. **HPLC Analysis**: er = 91.5:8.5, Chiralpak ADH Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 19.9 min, t_{minor} = 23.4 min).

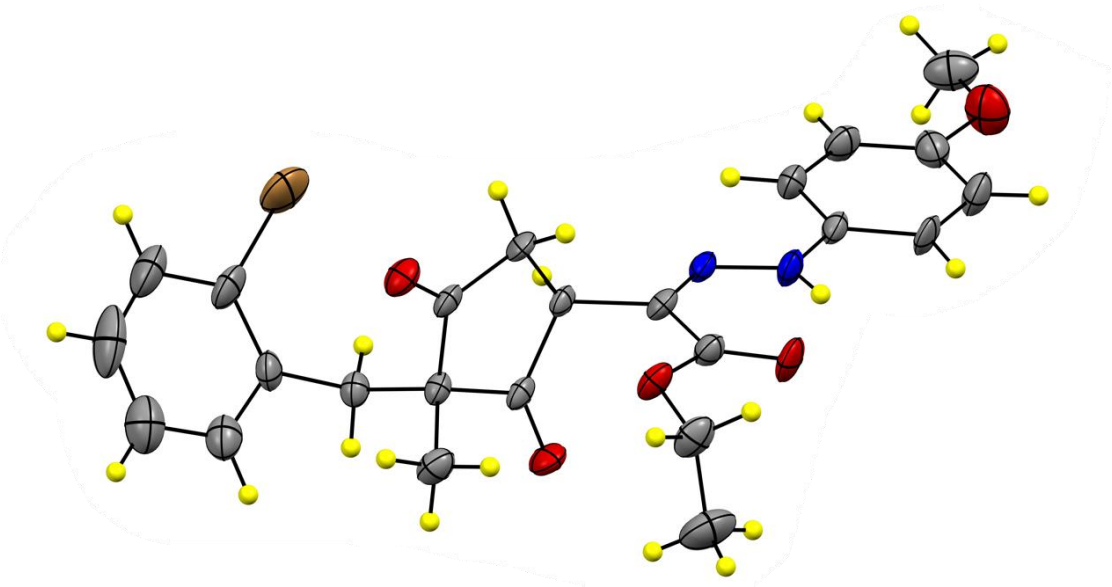
ethyl (R,Z)-2-(4-((4'-methoxy-[1,1'-biphenyl]-4-yl)methyl)-4-methyl-3,5-dioxocyclopent-1-en-1-yl)-2-(2-(4-methoxyphenyl)hydrazineylidene)acetate (8)



Yellow solid (18.6 mg, yield: 71%); R_f = 0.3 in 2:8 ethyl acetate/hexane; **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.92 – 7.83 (m, 2H), 7.26 – 7.21 (m, 2H), 7.05 – 6.97 (m, 2H), 6.95 – 6.87 (m, 2H), 6.83 – 6.70 (m, 5H), 4.86 (s, 1H), 4.49 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 3.76 (s, 3H), 3.16 (d, *J* = 13.5 Hz, 1H), 3.05 (d, *J* = 13.5 Hz, 1H), 1.49 – 1.40 (m, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 190.33, 188.84, 160.52, 159.81, 153.83, 150.00, 149.77, 137.95, 136.27, 134.68, 131.64, 130.99, 123.15, 121.40, 116.17, 114.95, 114.64, 65.39, 62.40, 55.92, 55.78, 40.76, 21.25, 14.33. **ESI HRMS**: calcd. for $C_{31}H_{31}N_2O_6$ $[M+H]^+$ 527.2177, found 527.2180. **HPLC Analysis**: er = 94:6, Chiralpak ADH Column, n-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 43.3 min, t_{minor} = 26.8 min).

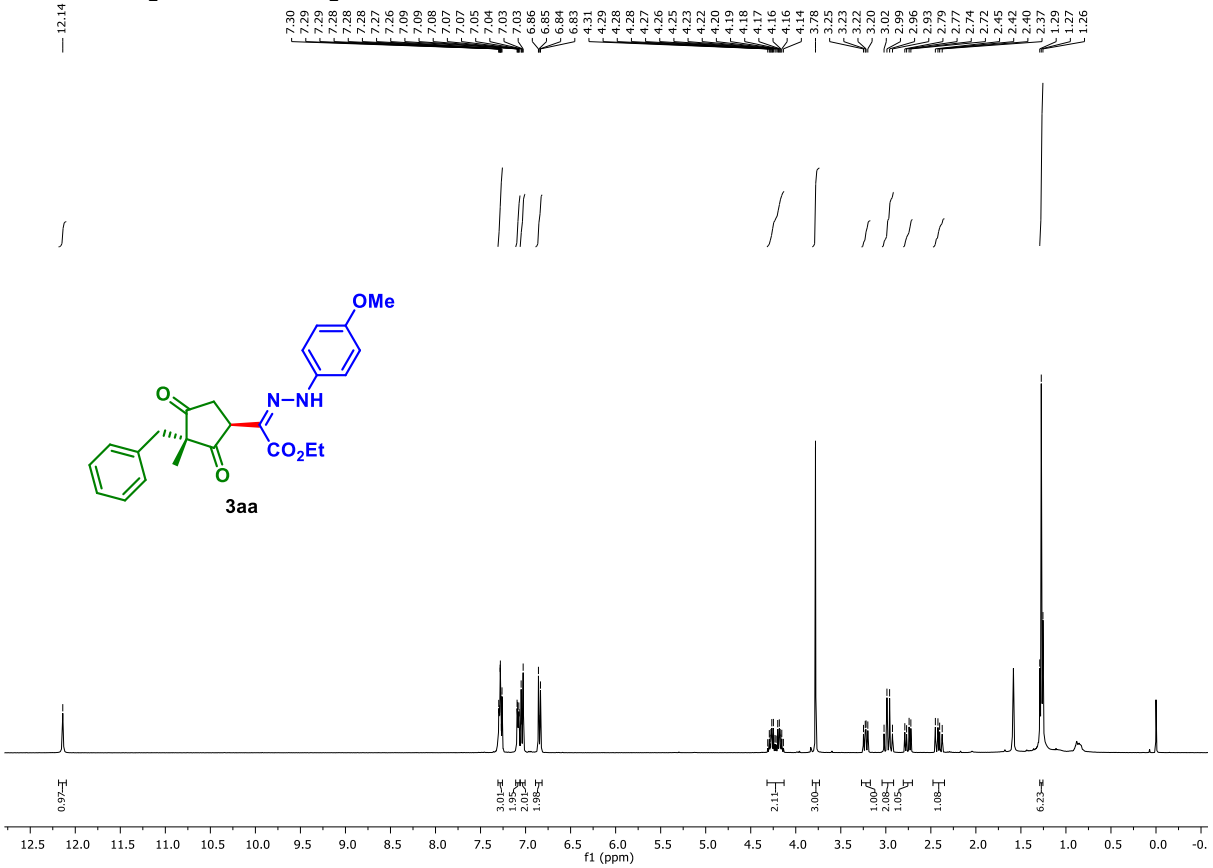
11. Single crystal X-ray diffraction analysis of 3al:

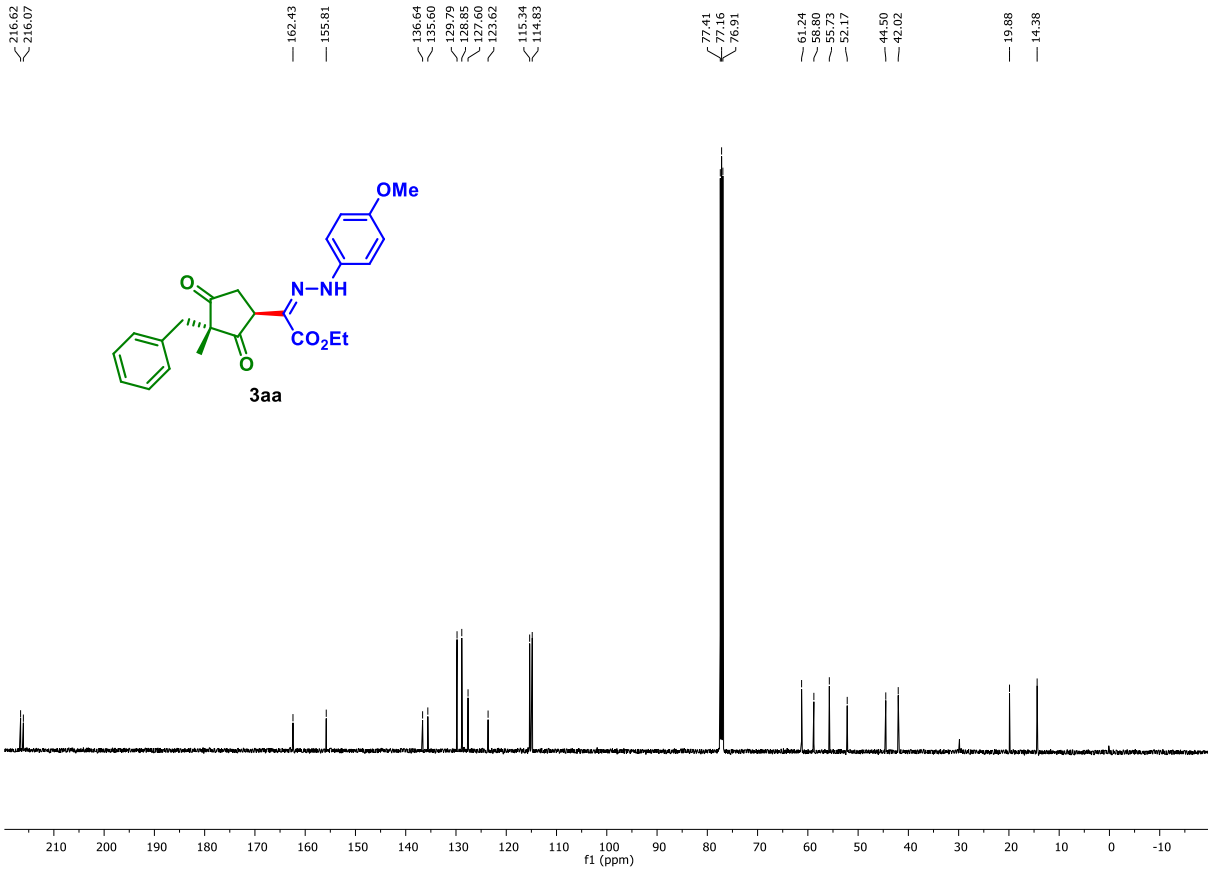
CCDC No.	2405612
Empirical formula	$C_{24}H_{25}BrN_2O_5$
Formula weight	501.36
Crystal habit, colour	needle / yellow
Temperature, T	295 K
Wavelength, λ (Å)	0.71073
Crystal system	monoclinic
Space group	'P 21'
Unit cell dimensions	a = 5.5791(8) Å
	b = 31.801(4) Å
	c = 12.9476(18) Å
	α = 90°, β = 90°, γ = 90°
Volume, V ($Å^3$)	2297.2(5)
Z	2
Calculated density, $g \cdot cm^{-3}$	1.450
F (000)	1032.0
Refinement method	'SHELXL–2018/3'
Goodness–of–fit on F^2	0.999
Theta(max)	25.245
Data completeness	1.96/1.00
R(reflections)	0.0747 (4457)
wR2(reflections)	0.2014 (8329)

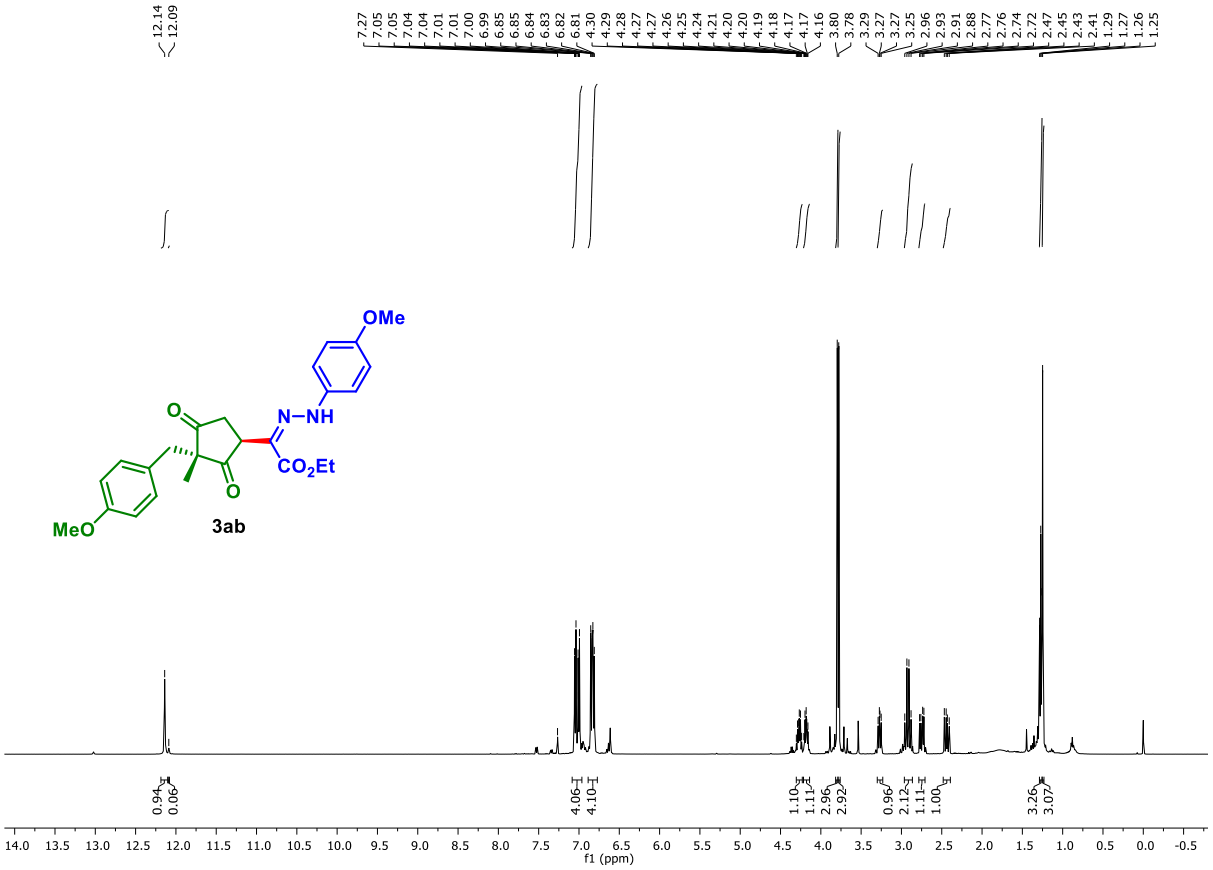


ORTEP representation of the X-ray structure of **3al** (thermal ellipsoids at 30% probability)

12. NMR spectra of the products:



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7.05
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7.04
7.04
7.01
7.01
7.00
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6.83
6.82
6.81
4.30
4.29
4.28
4.27
4.27
4.26
4.25
4.24
4.21
4.20
4.20
4.19
4.18
4.17
4.17
4.16
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3.27
3.25
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1.26
1.25
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N–NH
CO2Et
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O
MeO
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0.06
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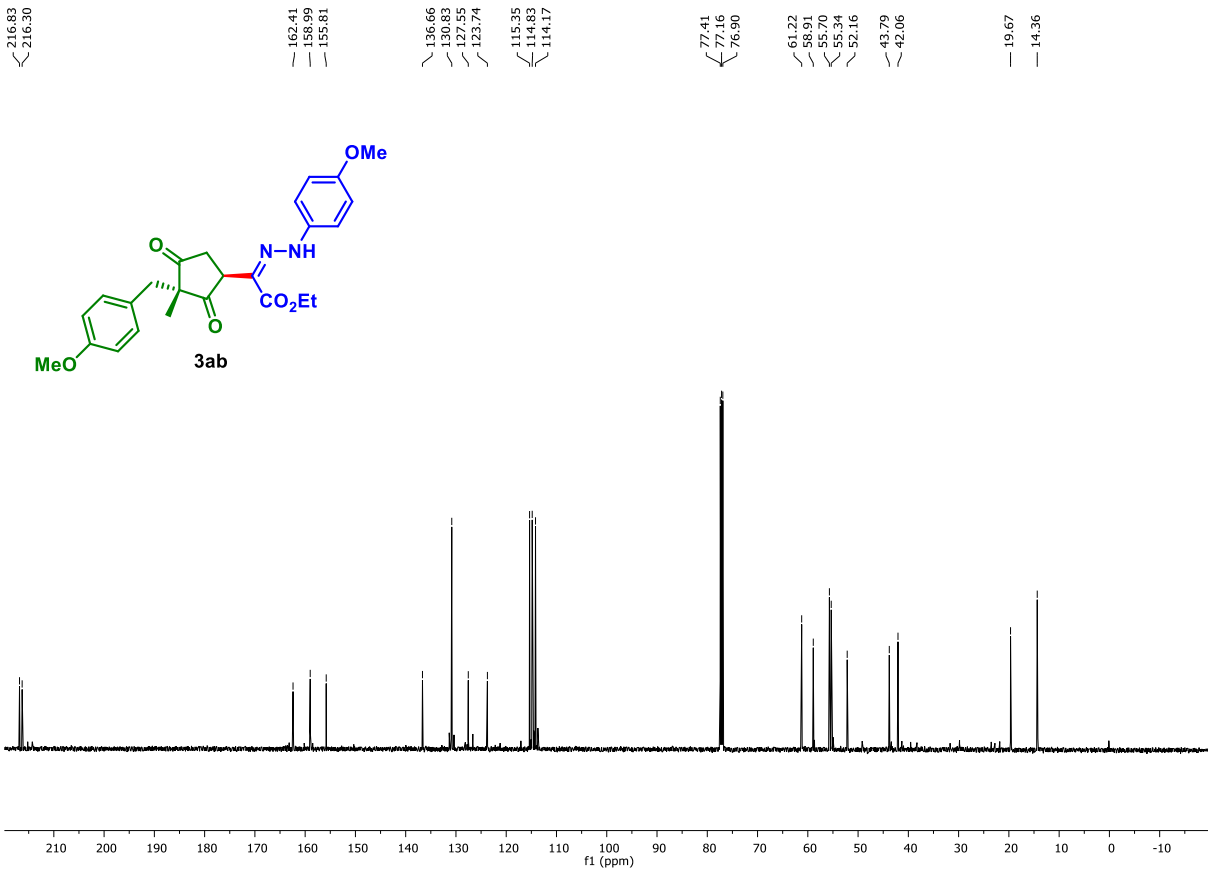
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114.83
114.17
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61.22
58.91
55.70
55.34
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CO2Et
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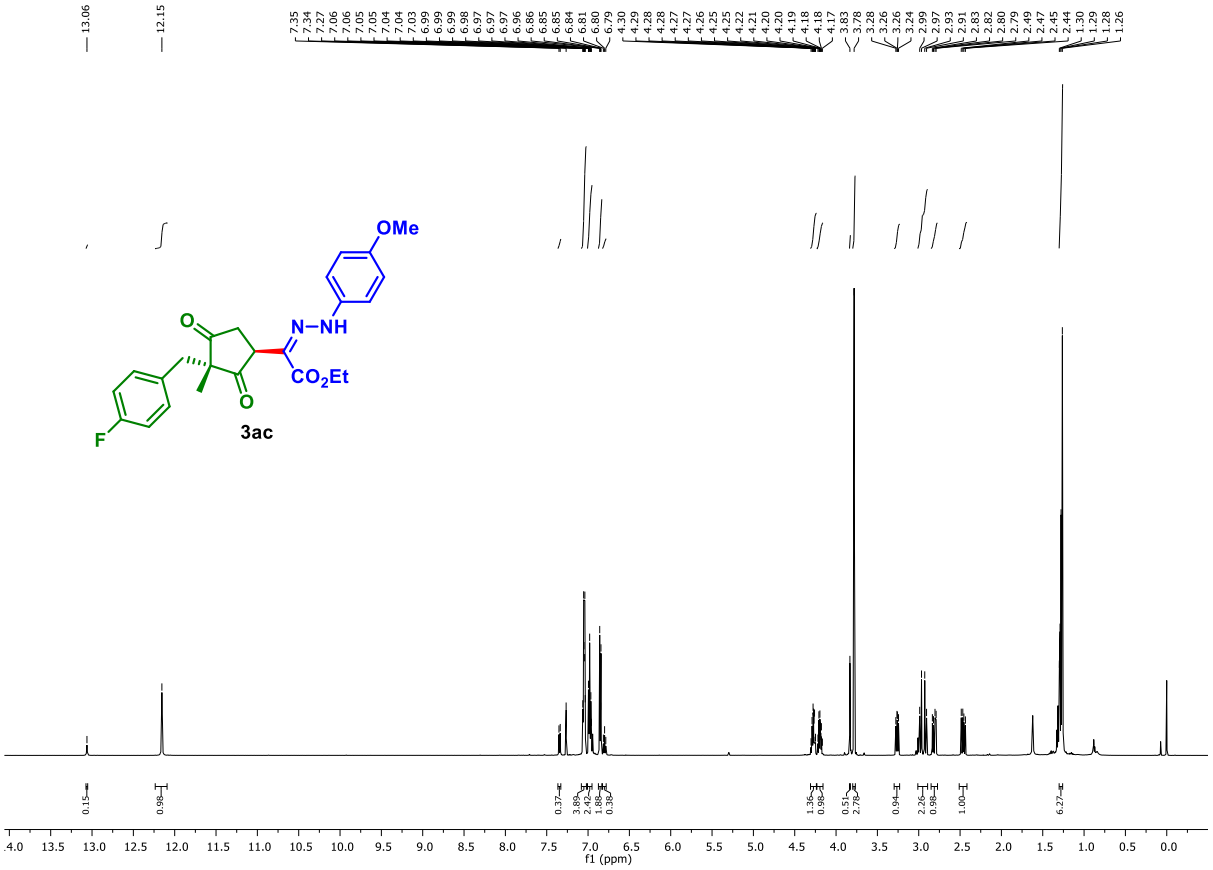
MeO
3ab
f1 (ppm)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12.15
7.35 7.34 7.27 7.06 7.06 7.05 7.05 7.05 7.04 7.04 7.03 6.99 6.99 6.99 6.98 6.97 6.97 6.97 6.96 6.86 6.85 6.85 6.84 6.81 6.80 6.79 4.30 4.29 4.28 4.28 4.27 4.27 4.26 4.25 4.25 4.22 4.21 4.20 4.20 4.19 4.18 4.18 4.17 3.83 3.78 3.28 3.26 3.26 3.24 2.99 2.97 2.93 2.91 2.83 2.82 2.80 2.79 2.49 2.47 2.45 2.44 1.30 1.29 1.28 1.26
OMe
N–NH
CO2Et
O
O
F
3ac
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0.37
3.89
2.42
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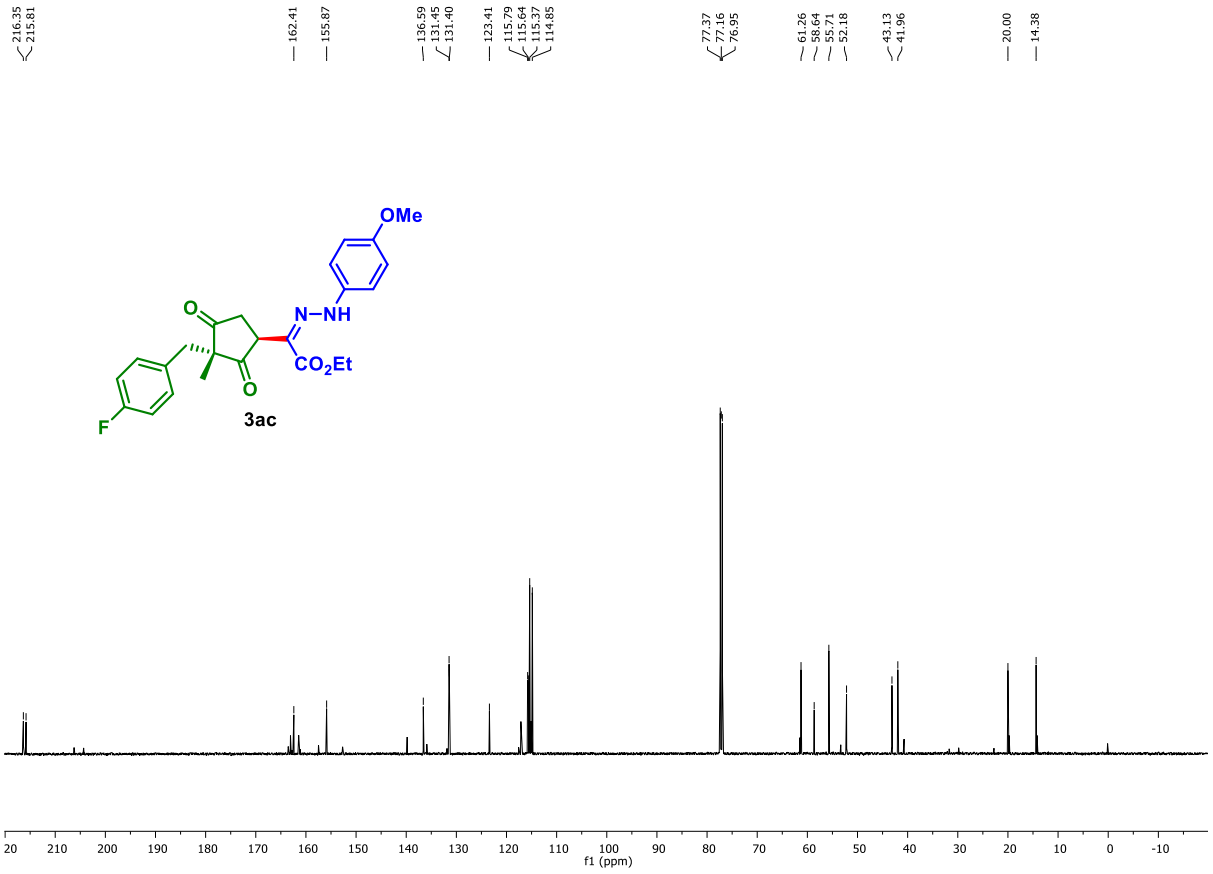
f1 (ppm)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CO2Et
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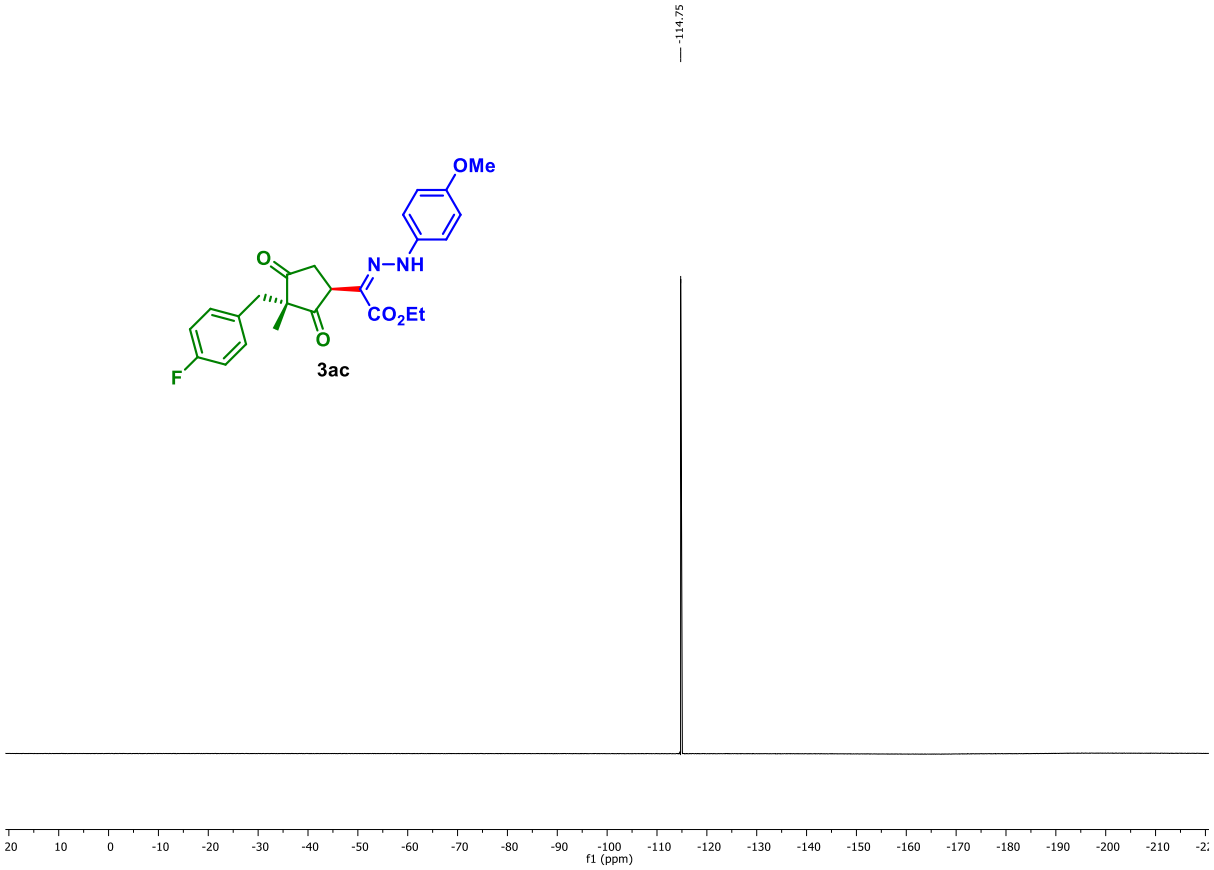
3ac
f1 (ppm)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-70
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-130
-140
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-160
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-180
-190
-200
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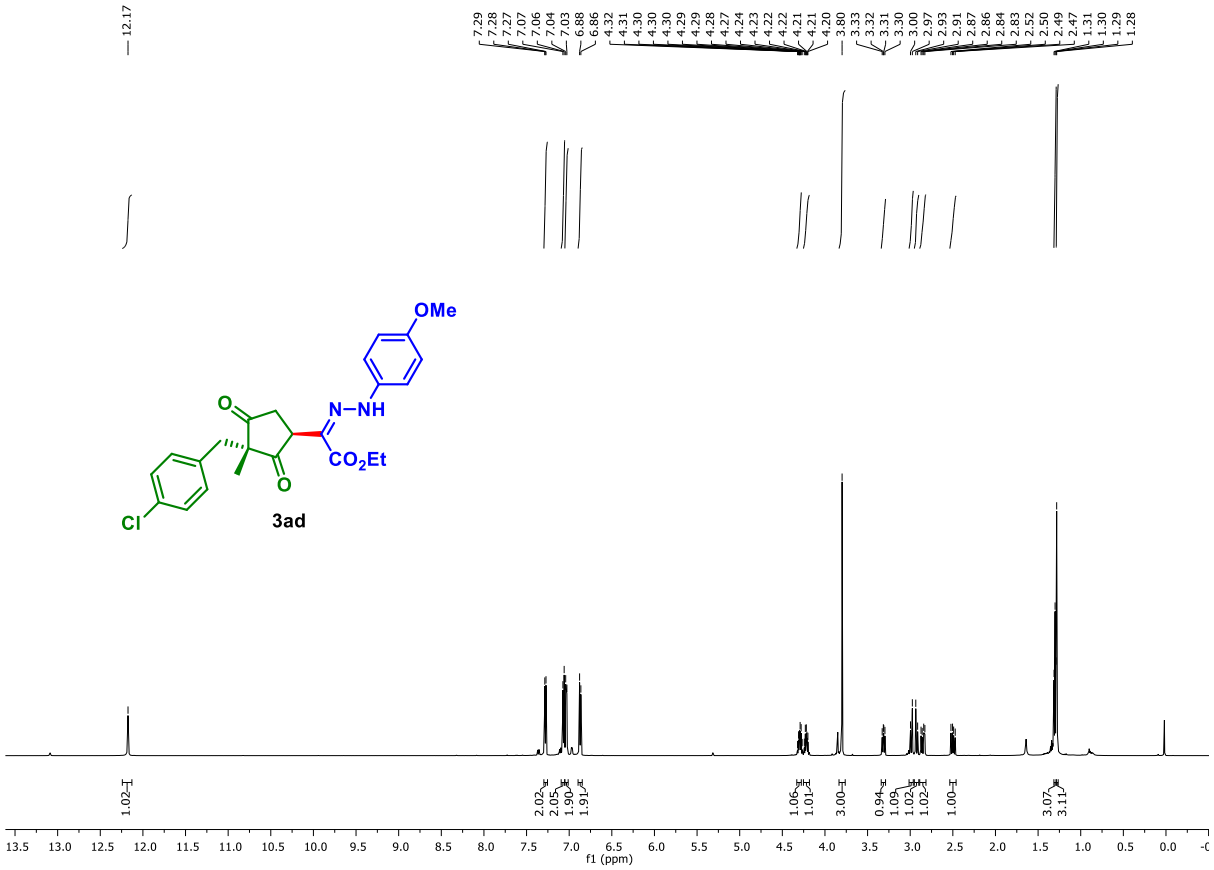
f1 (ppm)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CO2Et
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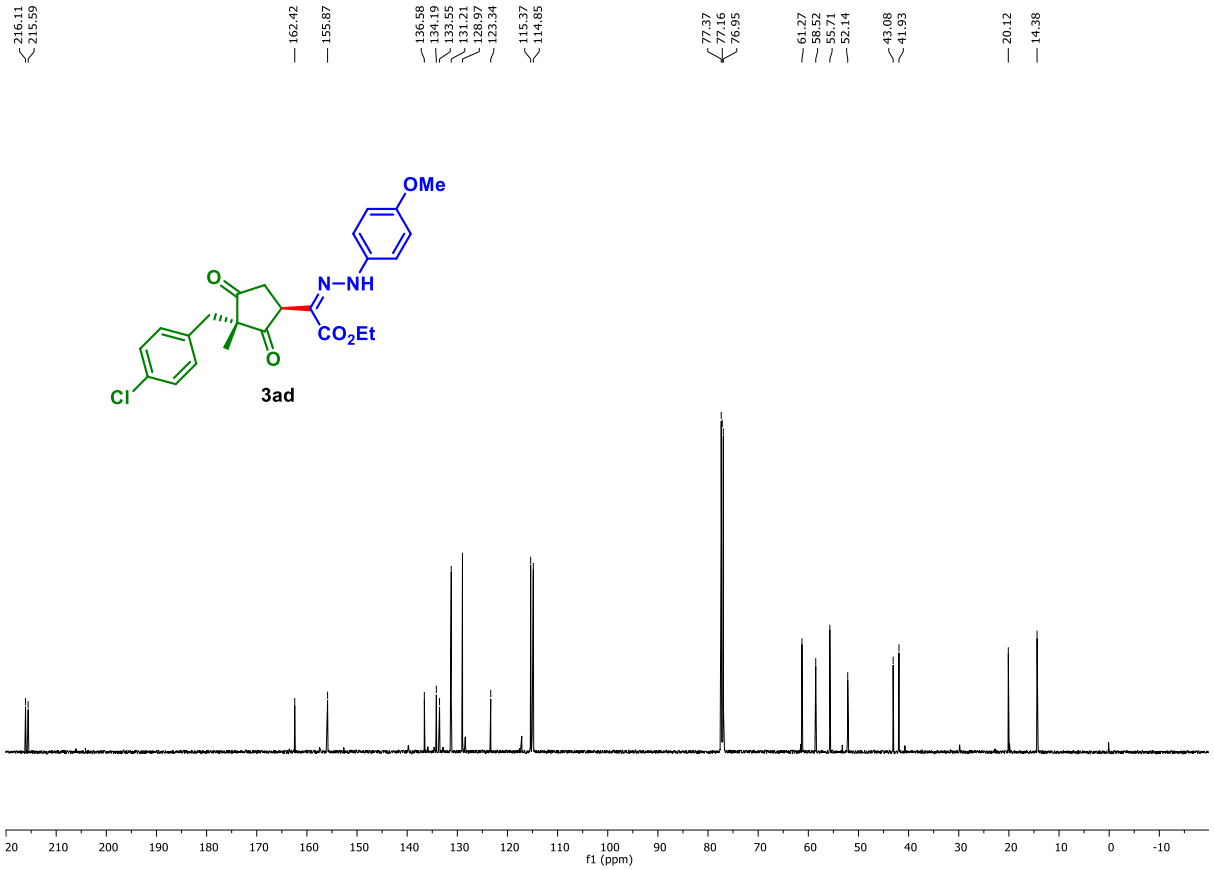
f1 (ppm)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76.95
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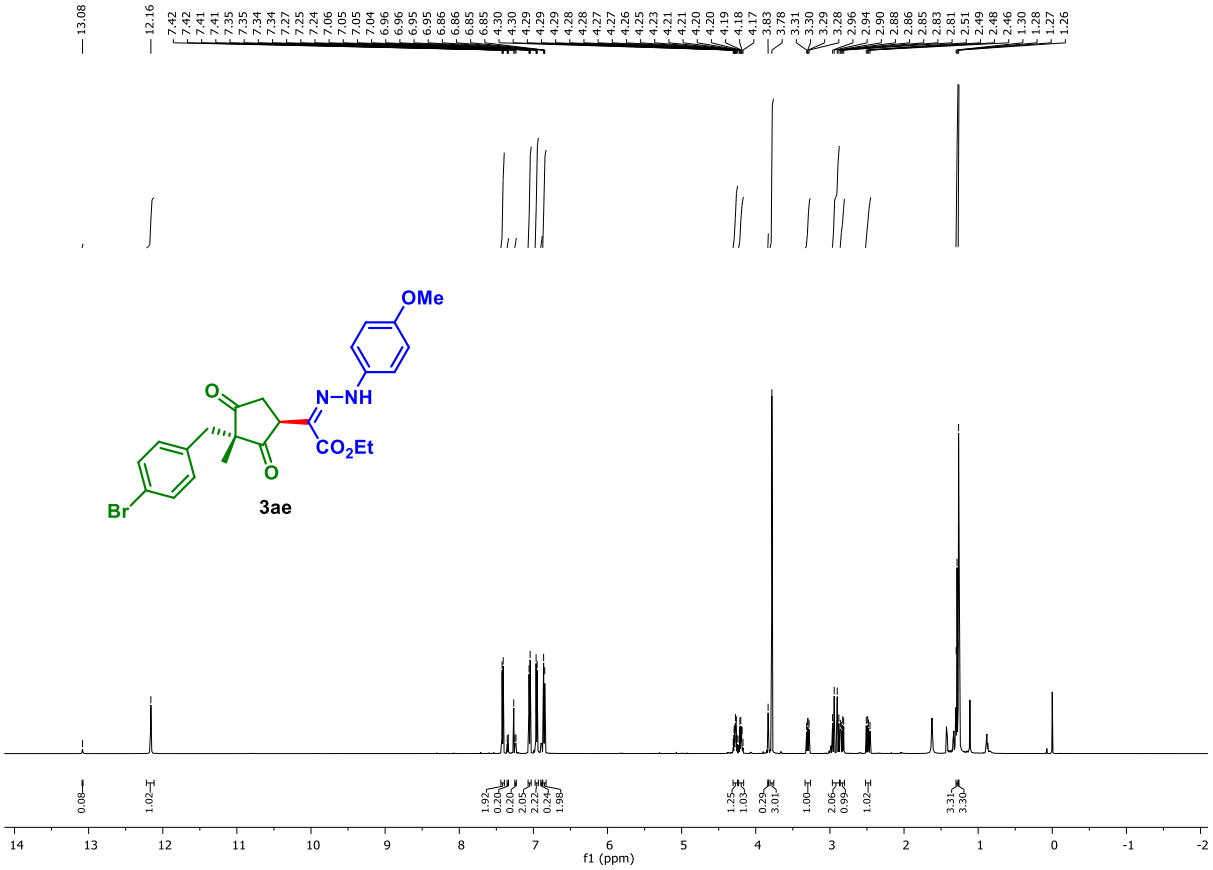
O
CO2Et
Cl
3ad
f1 (ppm)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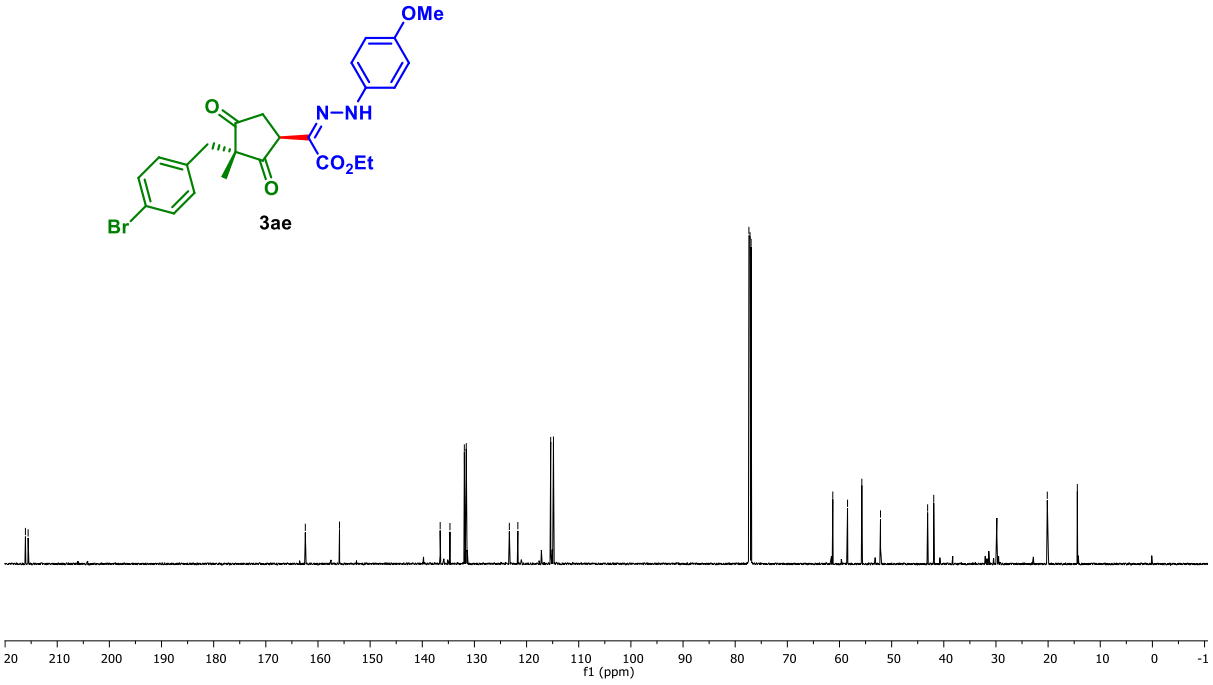
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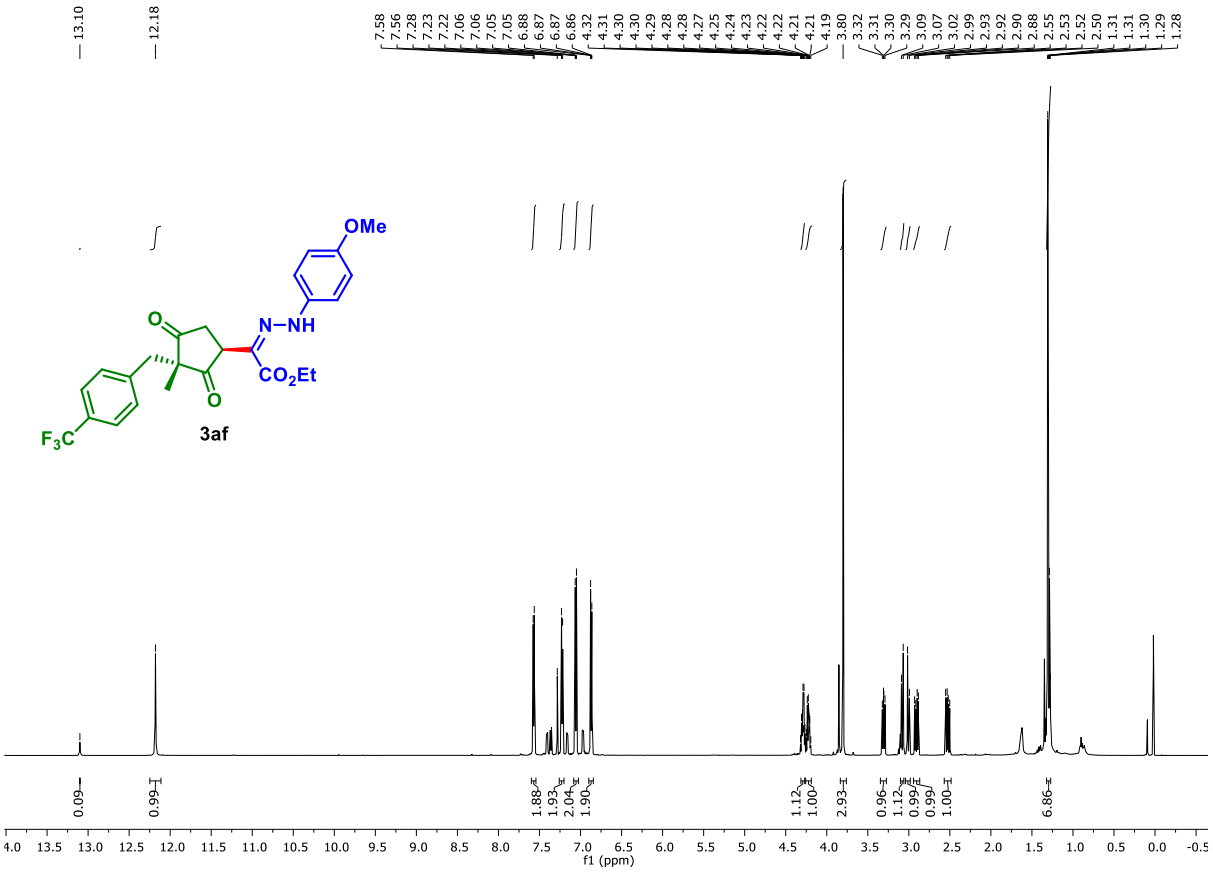
CO2Et
Br
3ae
f1 (ppm)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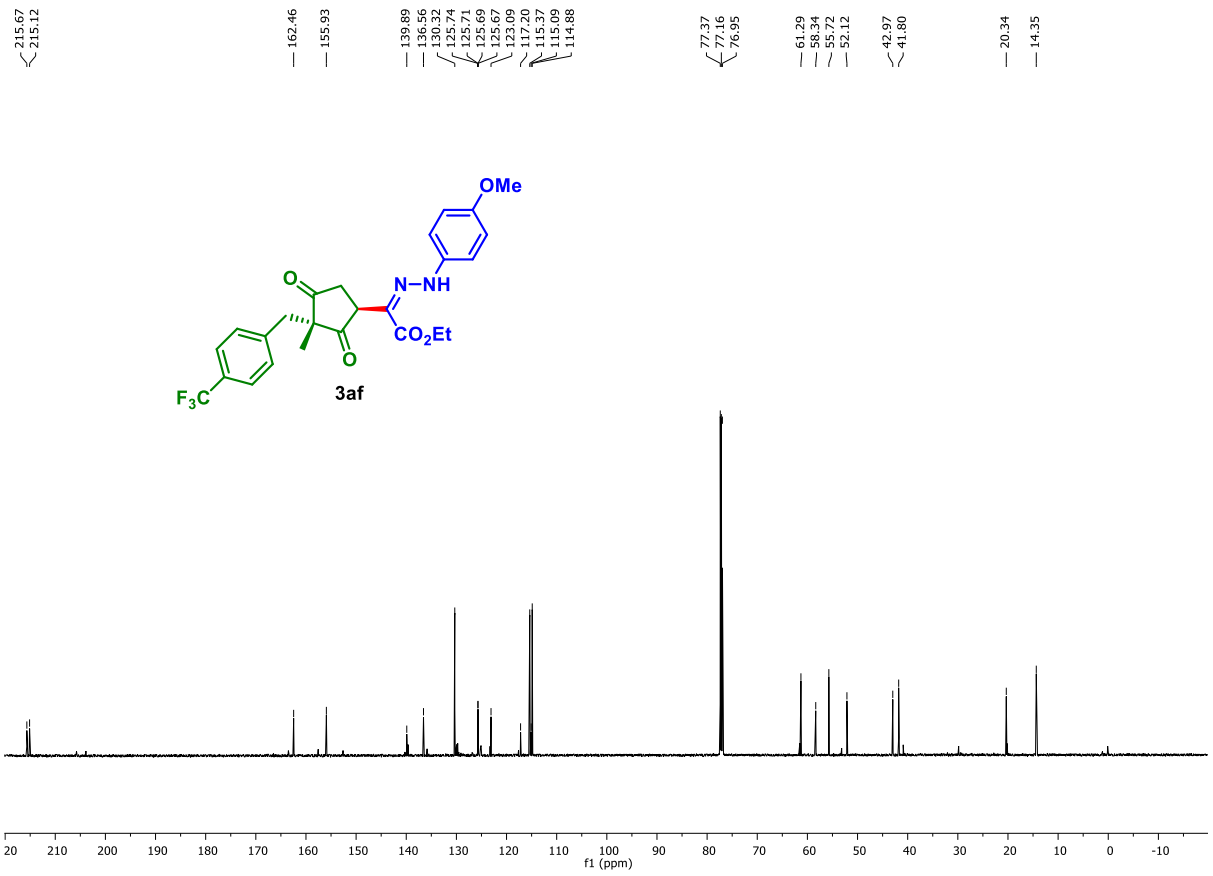
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115.09
114.88
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76.95
61.29
58.34
55.72
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42.97
41.80
20.34
14.35
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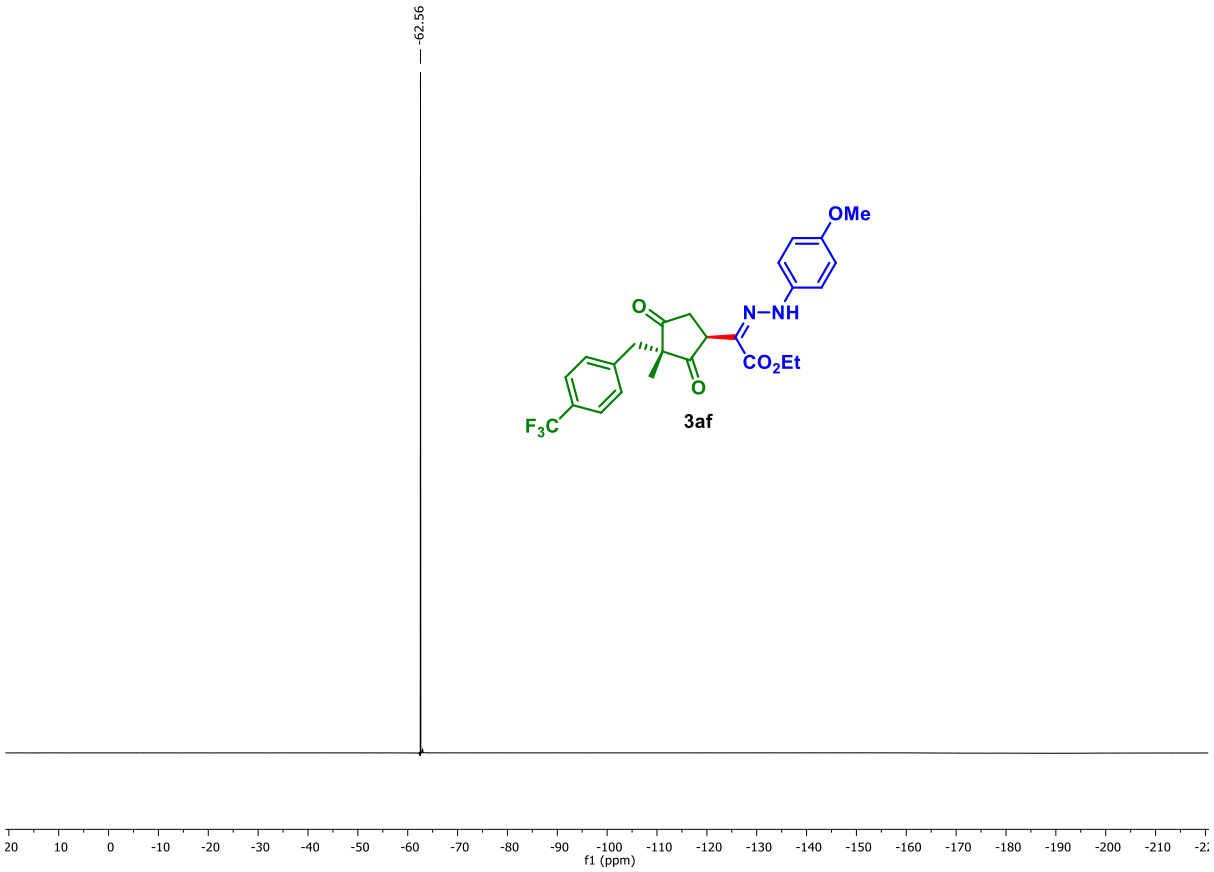
CO2Et
O
O
F3C
3af
f1 (ppm)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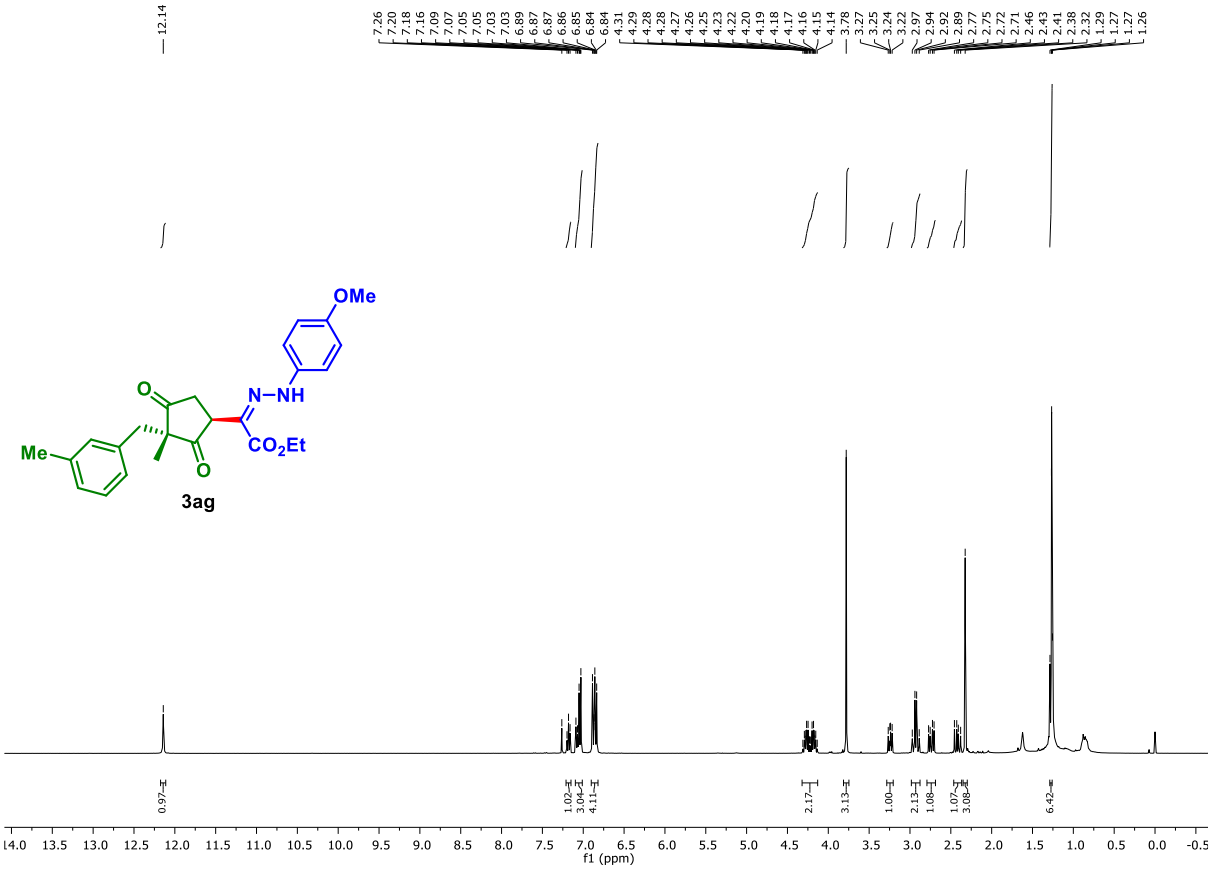
f1 (ppm)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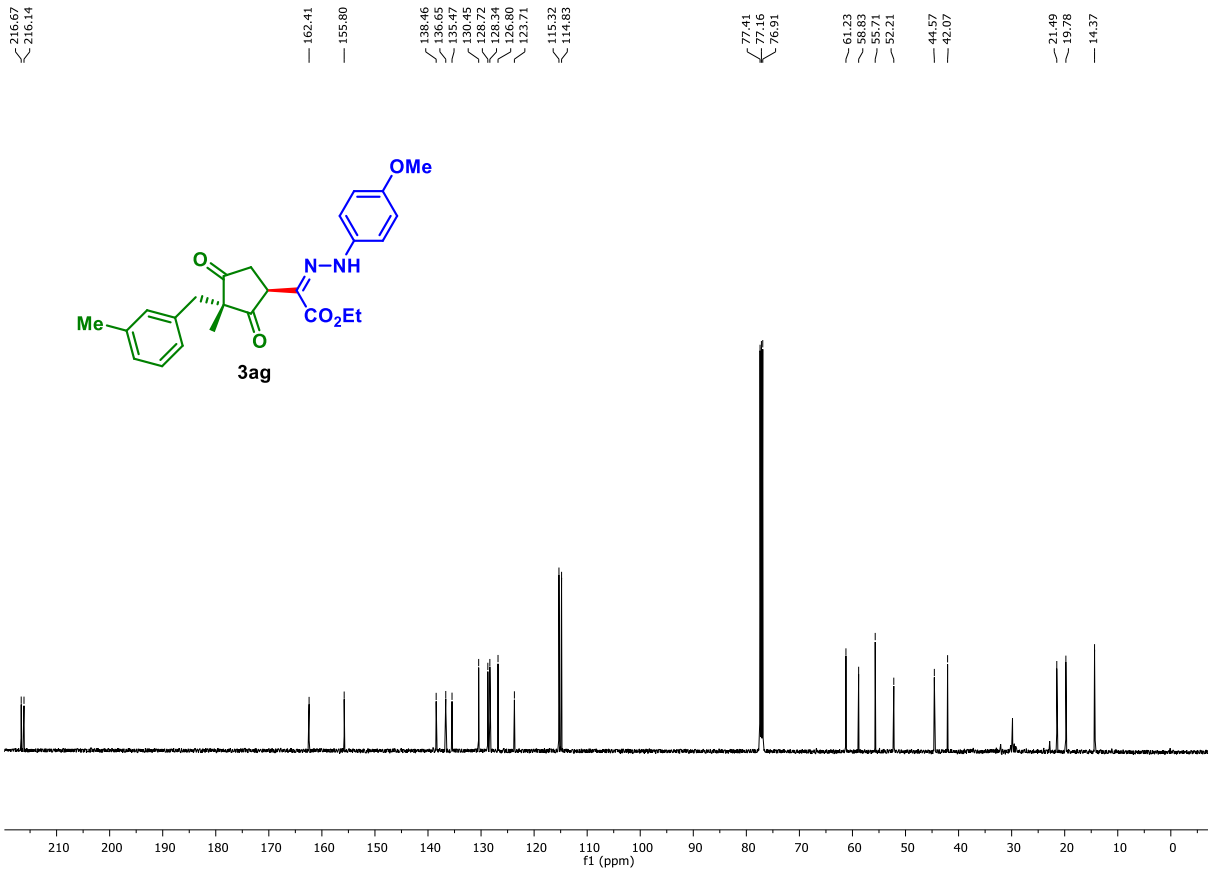
1.07
3.08
6.42
f1 (ppm)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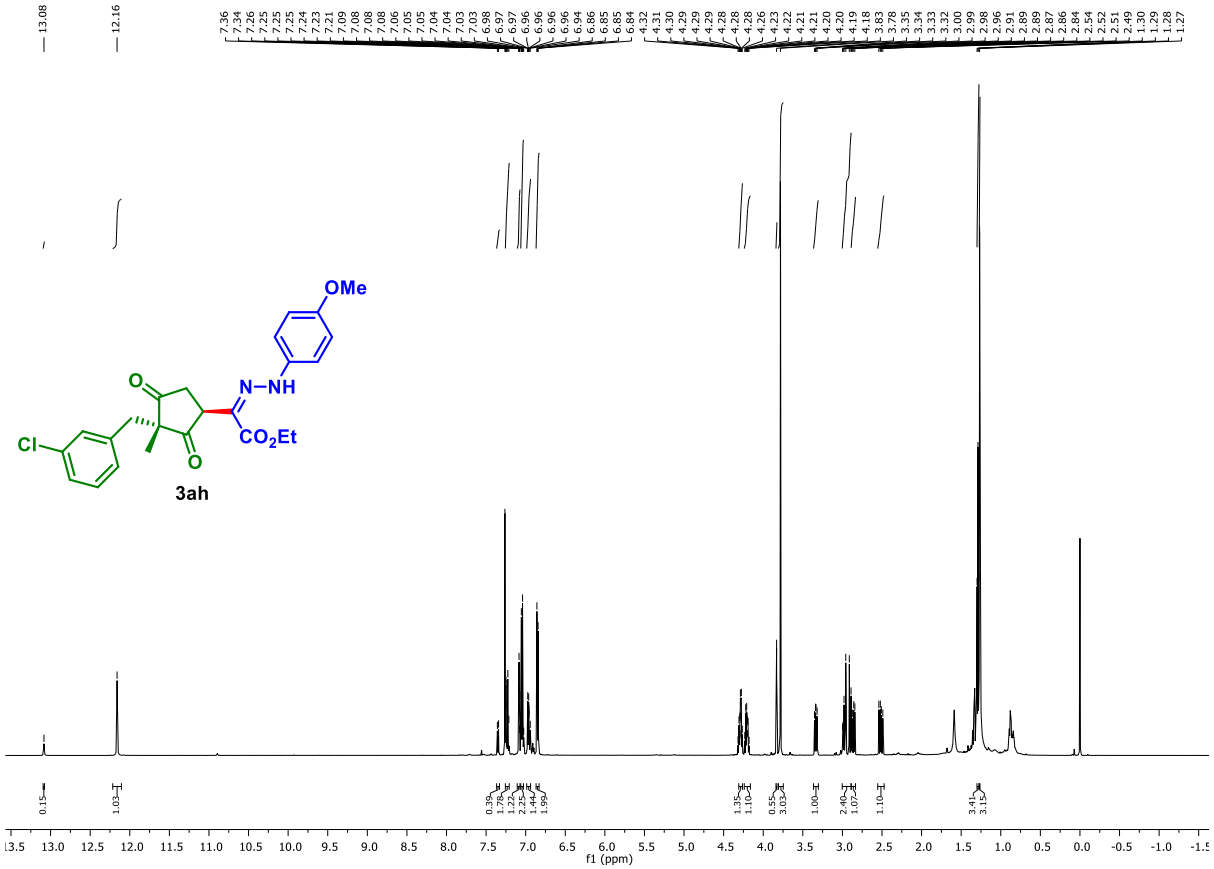
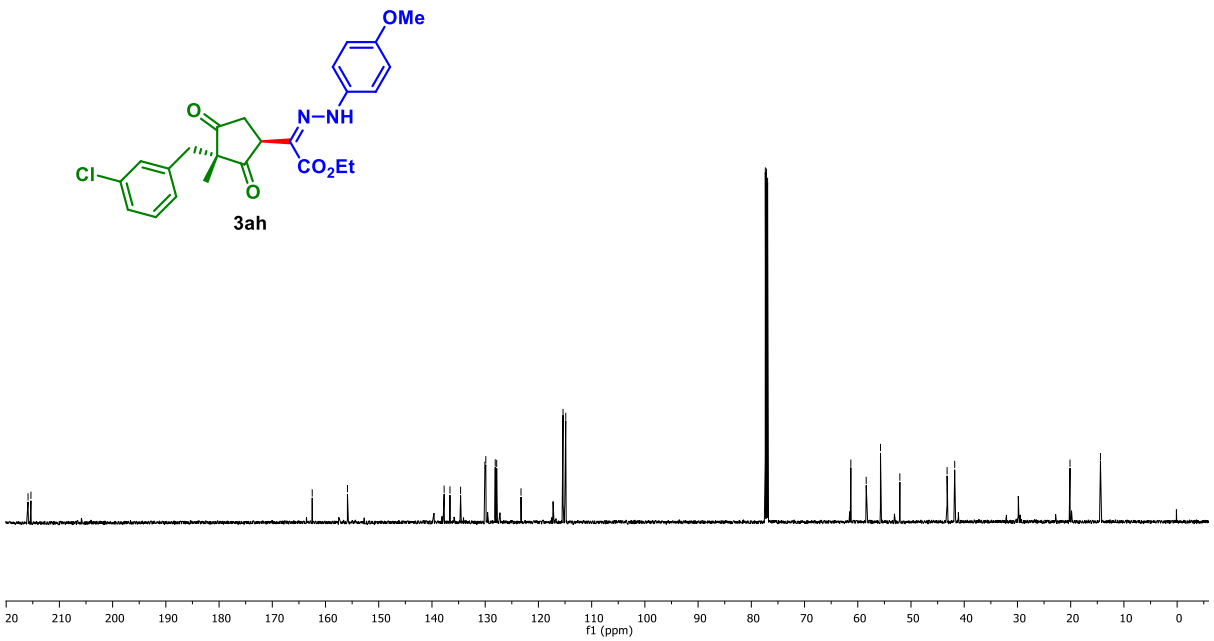
114.83
77.41
77.16
76.91
61.23
58.83
55.71
52.21
44.57
42.07
21.49
19.78
14.37
OMe
N–NH
O
CO2Et
Me
O
3ag
f1 (ppm)


OMe
N–NH
O
Cl
CO2Et
O
3ah
f1 (ppm)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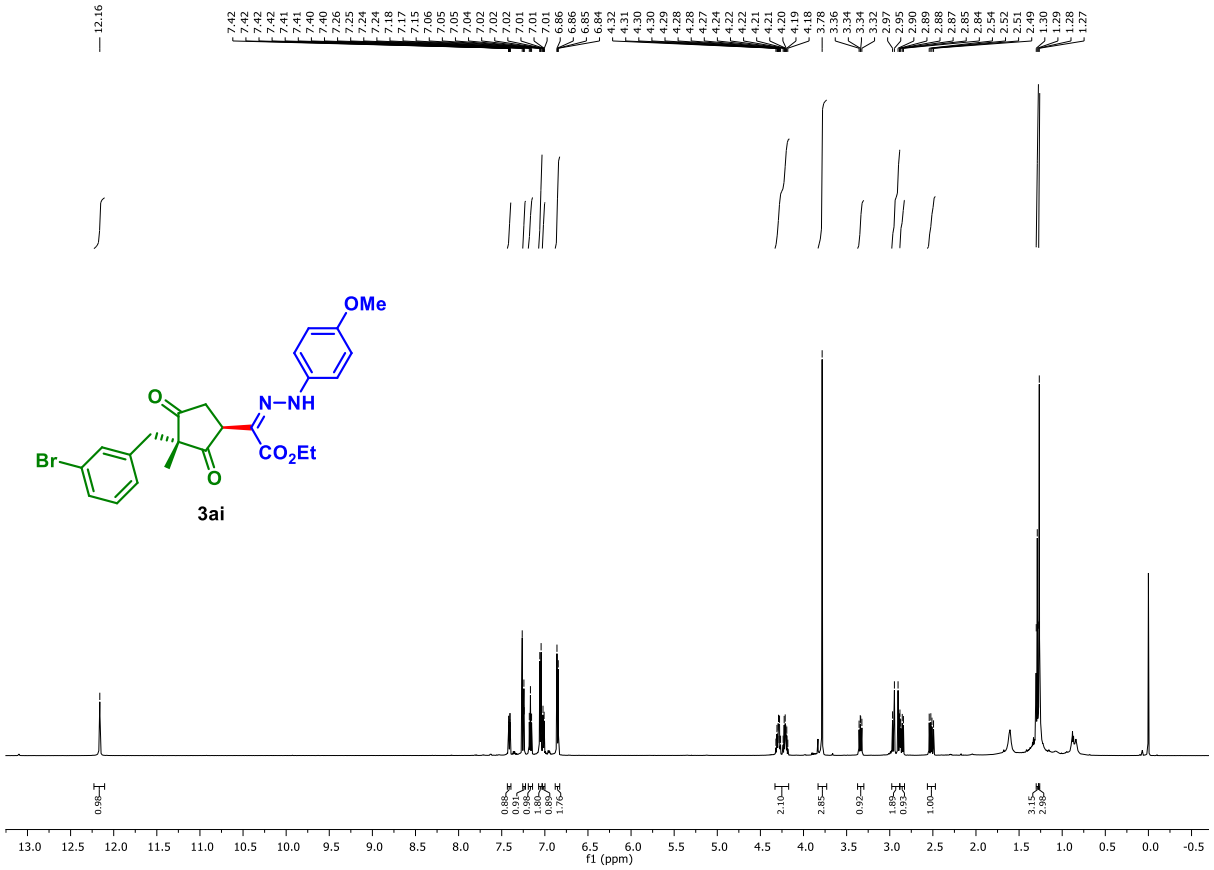
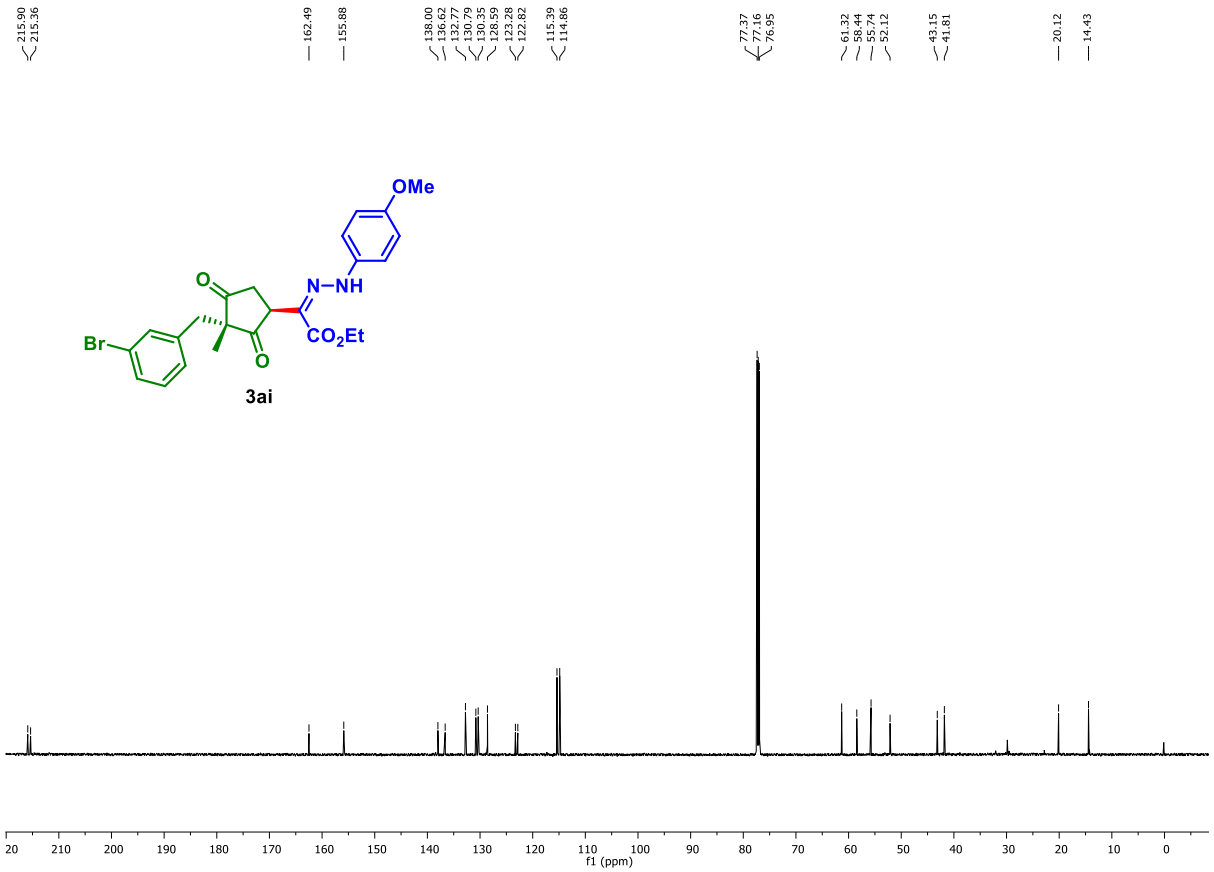
N–NH
O
Cl
CO2Et
O
3ah
f1 (ppm)


12.16
7.42 7.42 7.42 7.42 7.41 7.41 7.40 7.40 7.26 7.25 7.24 7.24 7.18 7.17 7.15 7.06 7.05 7.05 7.04 7.02 7.02 7.02 7.01 7.01 7.01 6.86 6.86 6.85 6.84 4.32 4.31 4.30 4.30 4.29 4.28 4.28 4.27 4.24 4.22 4.22 4.21 4.21 4.20 4.19 4.18 3.78 3.36 3.34 3.34 3.32 2.97 2.95 2.90 2.89 2.88 2.87 2.85 2.84 2.54 2.52 2.51 2.49 1.30 1.29 1.28 1.27
OMe
N–NH
CO2Et
Br
O
O
3ai
0.98
0.88
0.91
0.98
1.80
0.89
1.76
2.10
2.85
0.92
1.08
0.93
1.00
3.15
2.88
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 -0.5
f1 (ppm)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130.79
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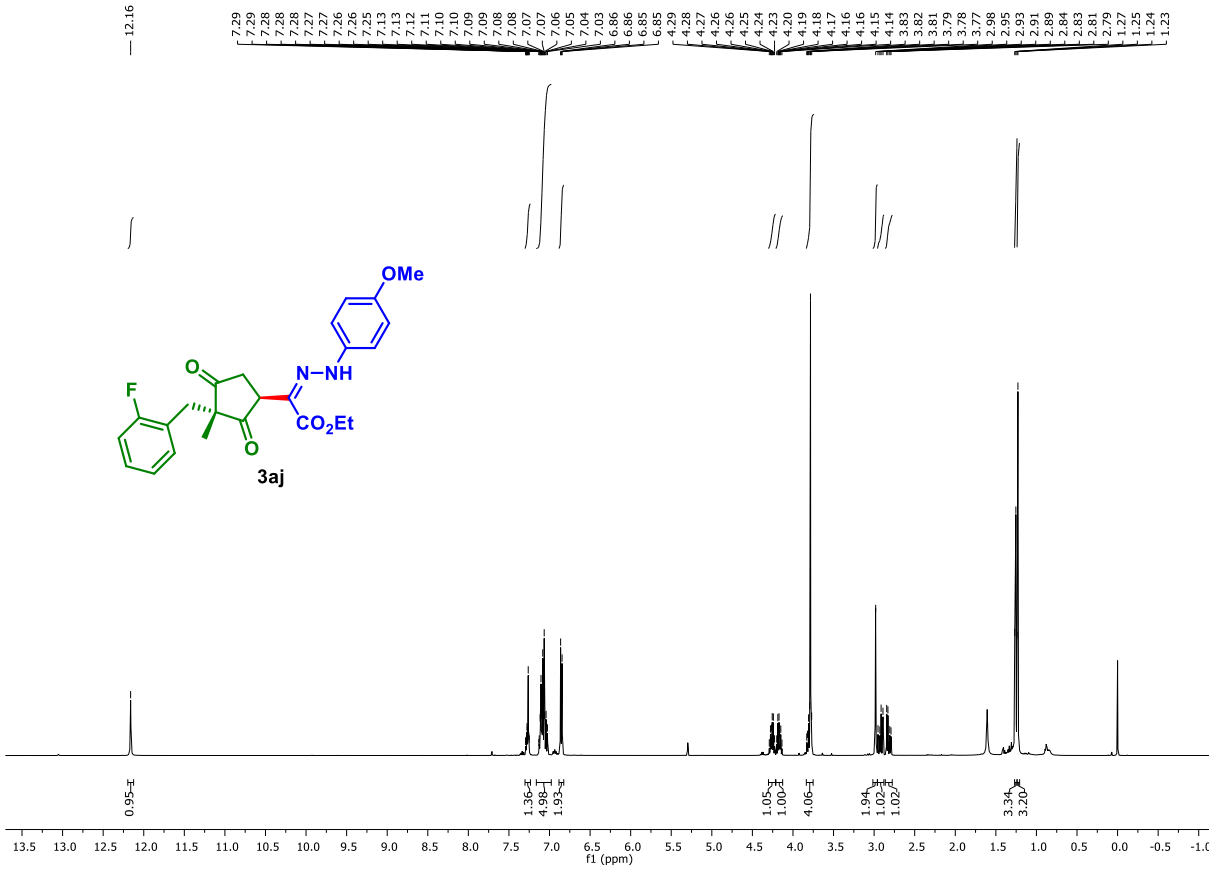
128.59
123.28
122.82
115.39
114.86
77.37
77.16
76.95
61.32
58.44
55.74
52.12
43.15
41.81
20.12
14.43
OMe
N–NH
CO2Et
Br
O
O
3ai
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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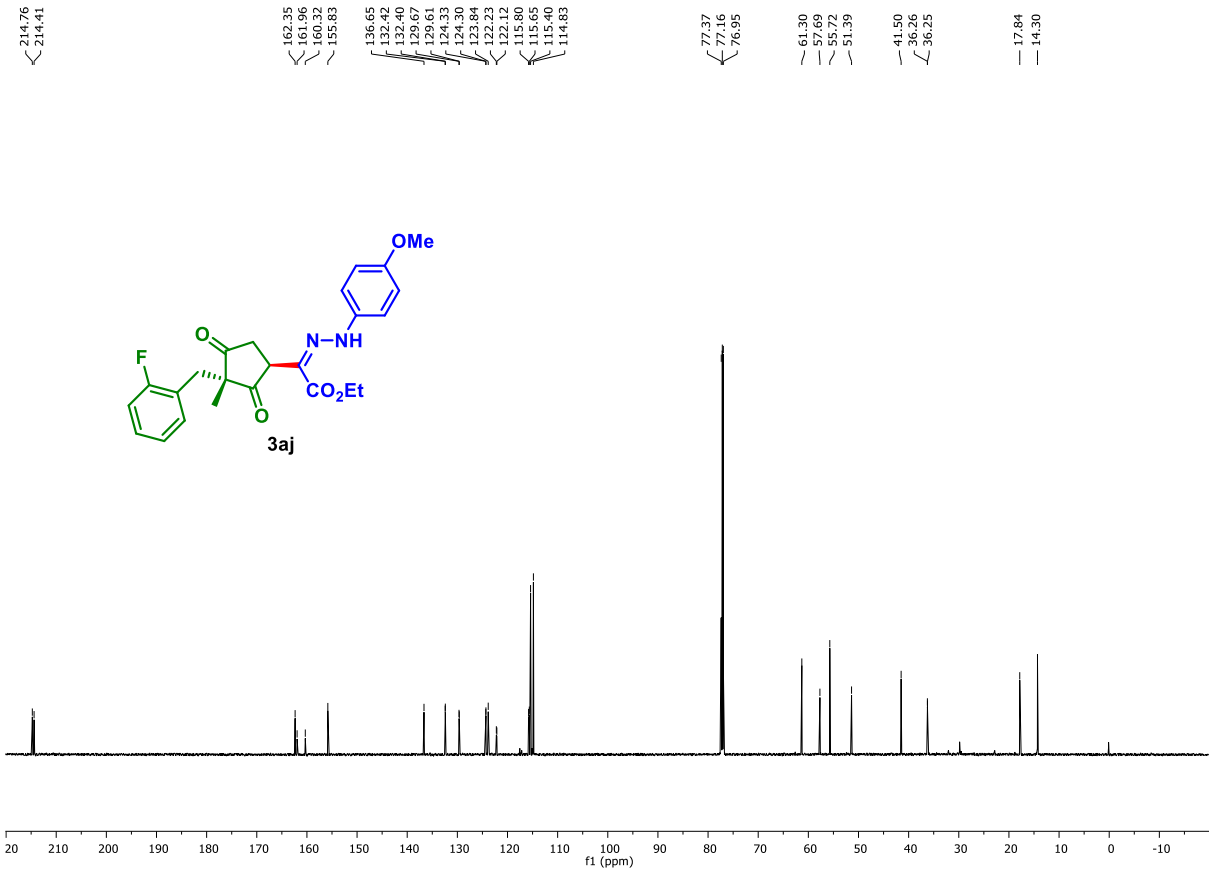
7.29 7.29 7.28 7.28 7.28 7.27 7.27 7.26 7.26 7.25 7.13 7.13 7.12 7.11 7.10 7.10 7.09 7.09 7.08 7.08 7.07 7.07 7.06 7.05 7.04 7.03 6.86 6.86 6.85 6.85
4.29 4.28 4.27 4.26 4.26 4.25 4.24 4.23 4.20 4.19 4.18 4.17 4.16 4.16 4.15 4.14 3.83 3.82 3.81 3.79 3.78 3.77 2.98 2.95 2.93 2.91 2.89 2.84 2.83 2.81 2.79 1.27 1.25 1.24 1.23
OMe
N–NH
CO2Et
F
O
O
3aj
0.95
1.36
4.98
1.93
1.05
1.00
4.06
1.94
1.02
1.02
3.34
3.20
f1 (ppm)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124.30
123.84
122.23
122.12
115.80
115.65
115.40
114.83
77.37
77.16
76.95
61.30
57.69
55.72
51.39
41.50
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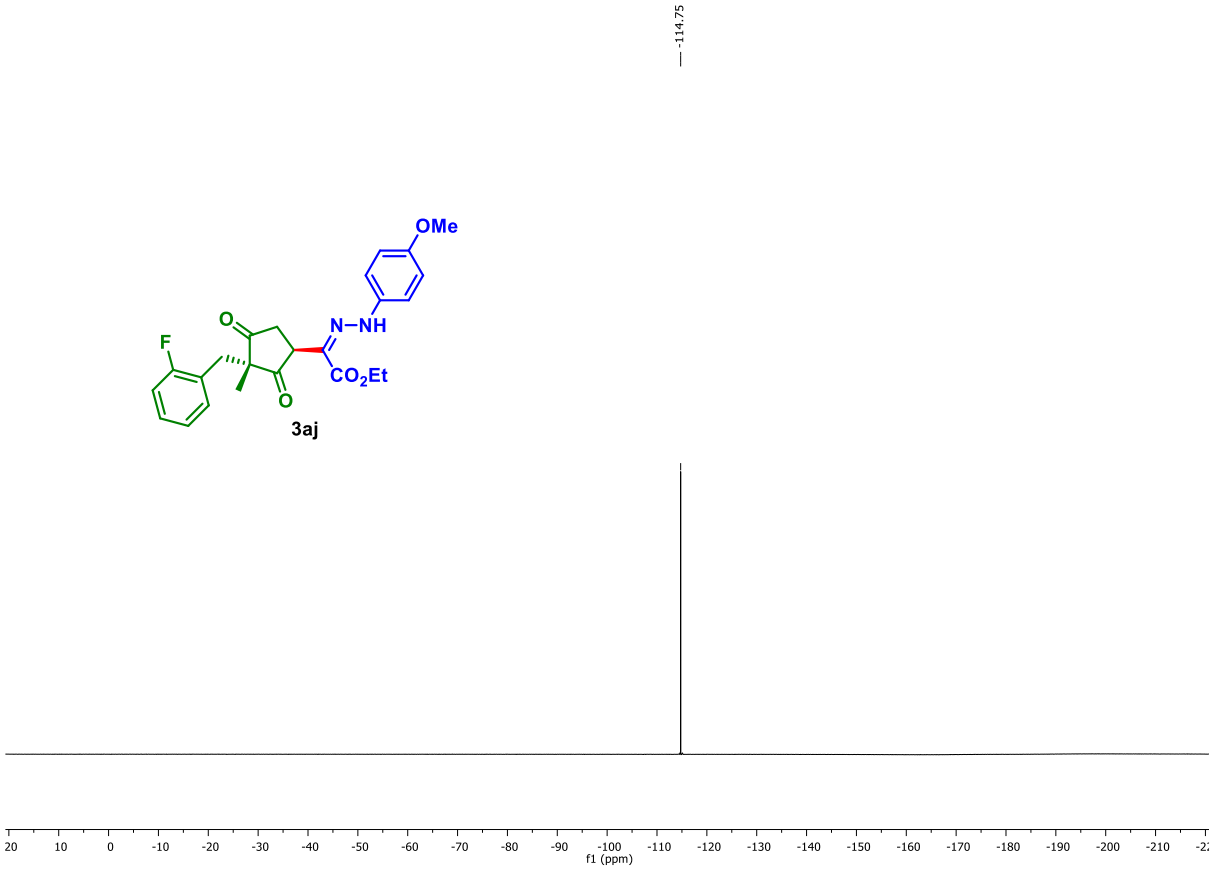
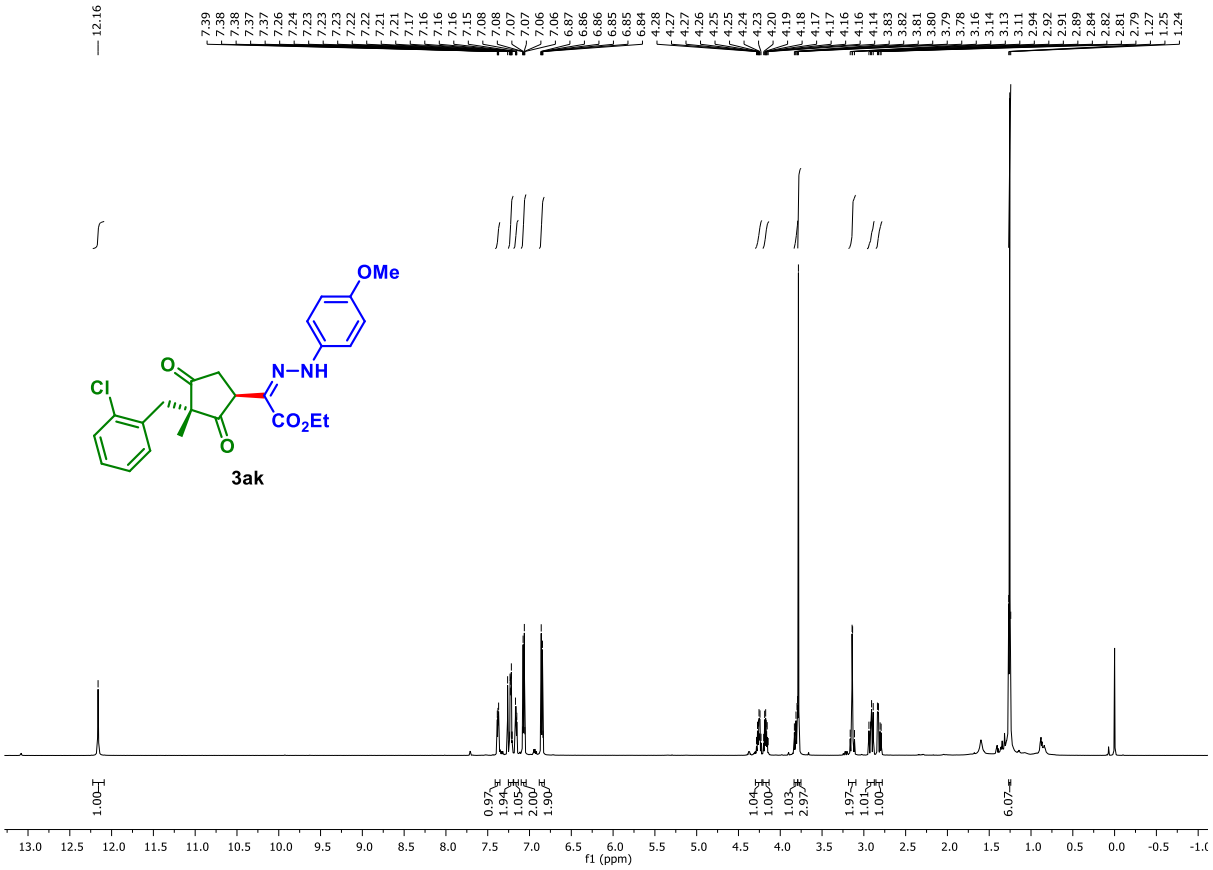
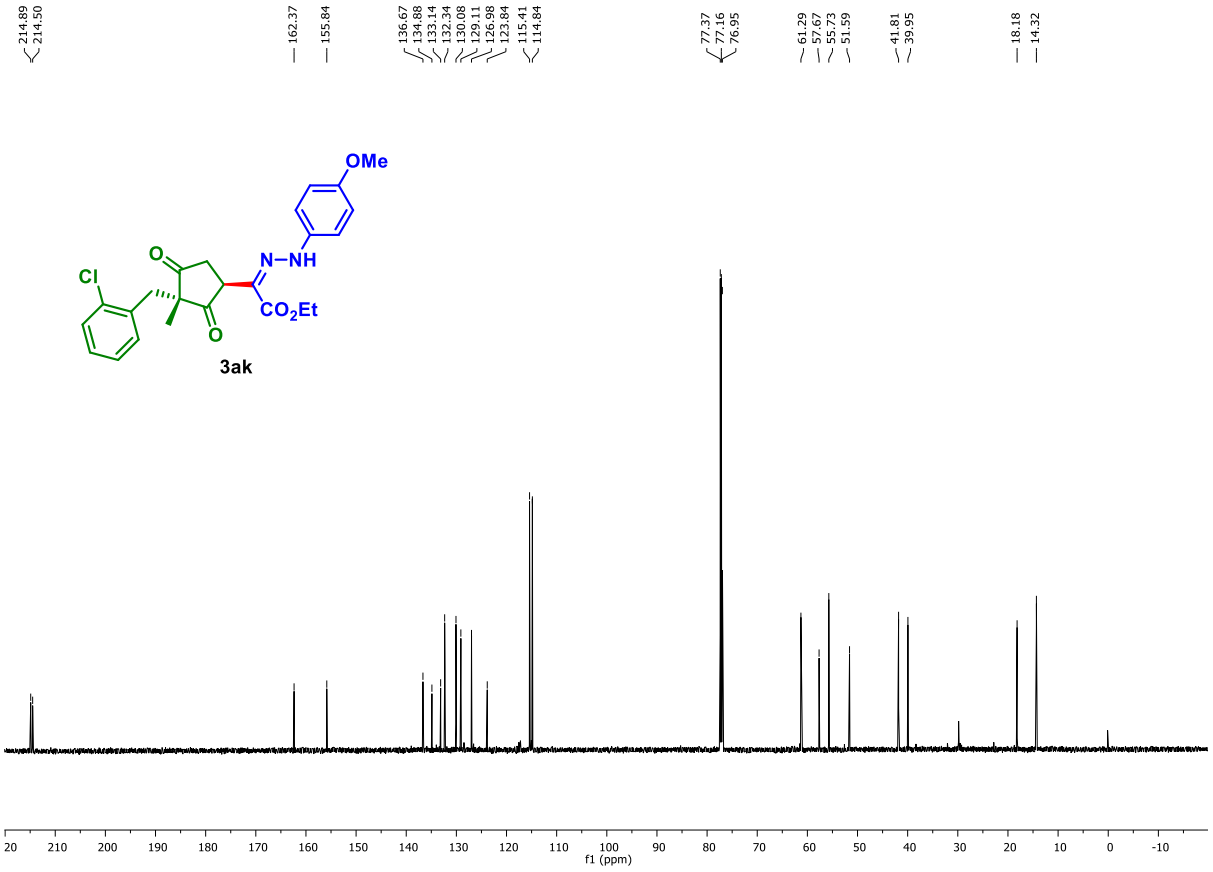
36.25
17.84
14.30
OMe
N–NH
CO2Et
F
O
O
3aj
f1 (ppm)


-114.75
OMe
N–NH
F
O
O
CO2Et
O
3aj
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


12.16
7.39 7.38 7.38 7.37 7.37 7.26 7.24 7.23 7.23 7.23 7.22 7.22 7.21 7.21 7.17 7.16 7.16 7.16 7.15 7.08 7.08 7.07 7.07 7.06 7.06 6.87 6.86 6.86 6.85 6.85 6.84 4.28 4.27 4.27 4.26 4.25 4.25 4.24 4.23 4.20 4.19 4.18 4.17 4.17 4.16 4.16 4.14 3.83 3.82 3.81 3.80 3.79 3.78 3.16 3.14 3.13 3.11 2.94 2.92 2.91 2.89 2.84 2.82 2.81 2.79 1.27 1.25 1.24
OMe
N–NH
CO2Et
Cl
O
O
3ak
1.00 0.97 1.94 1.05 2.00 1.90 1.04 1.00 1.03 2.97 1.97 1.01 1.00 6.07
f1 (ppm)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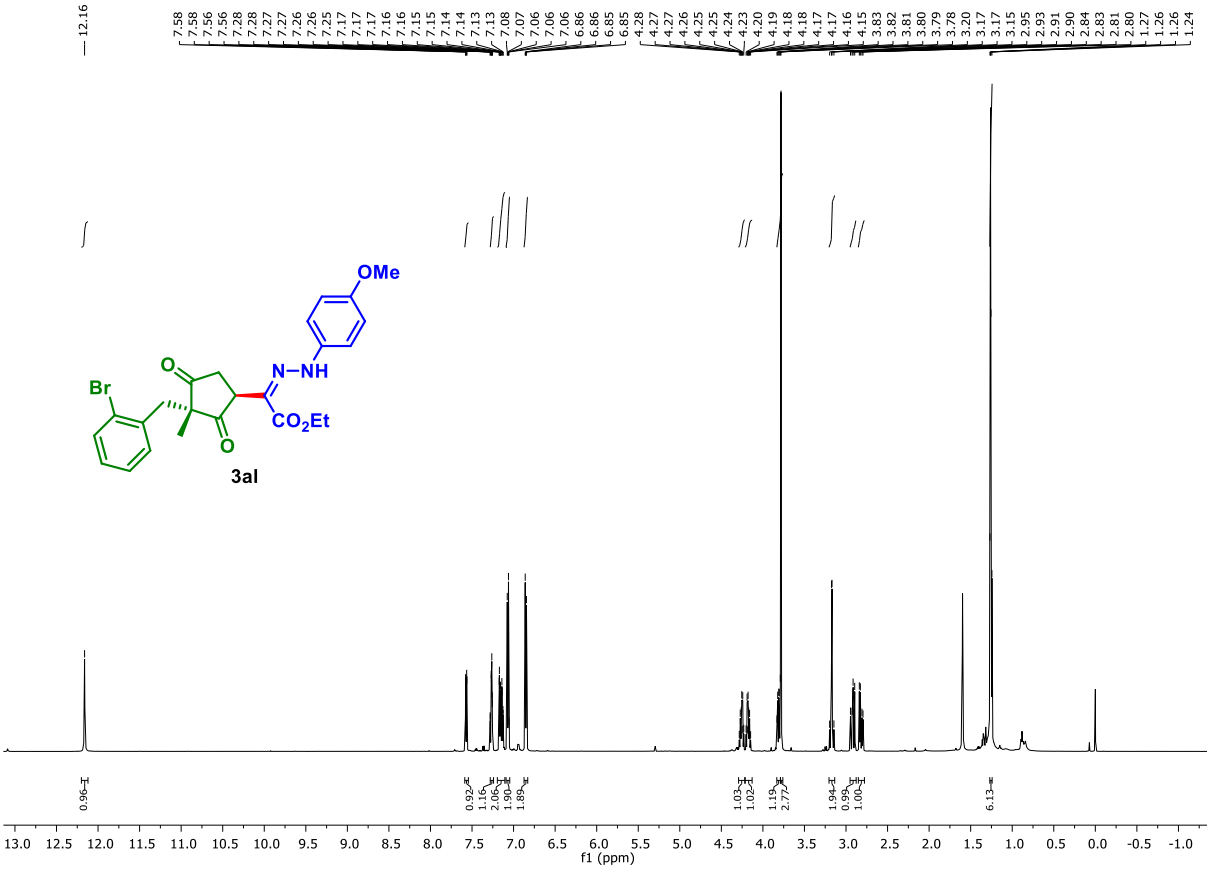
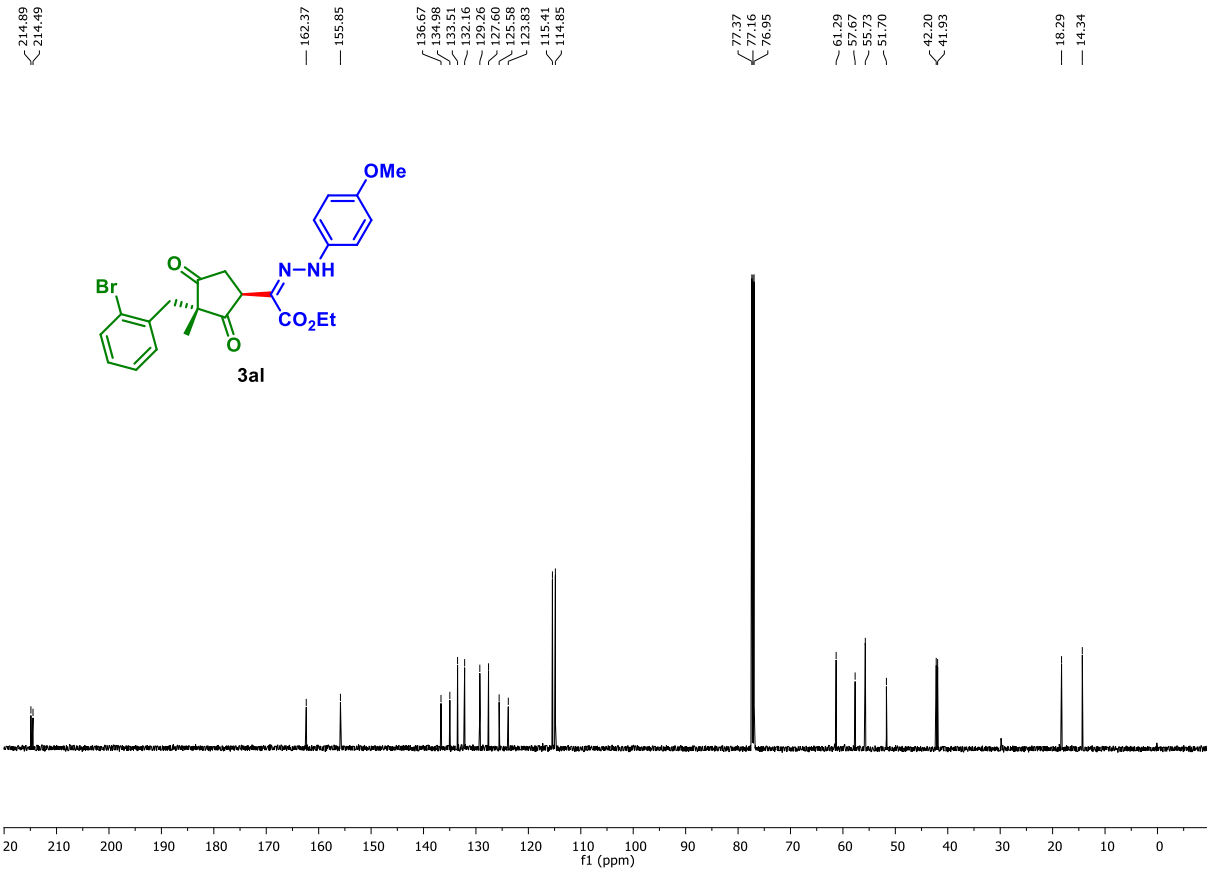
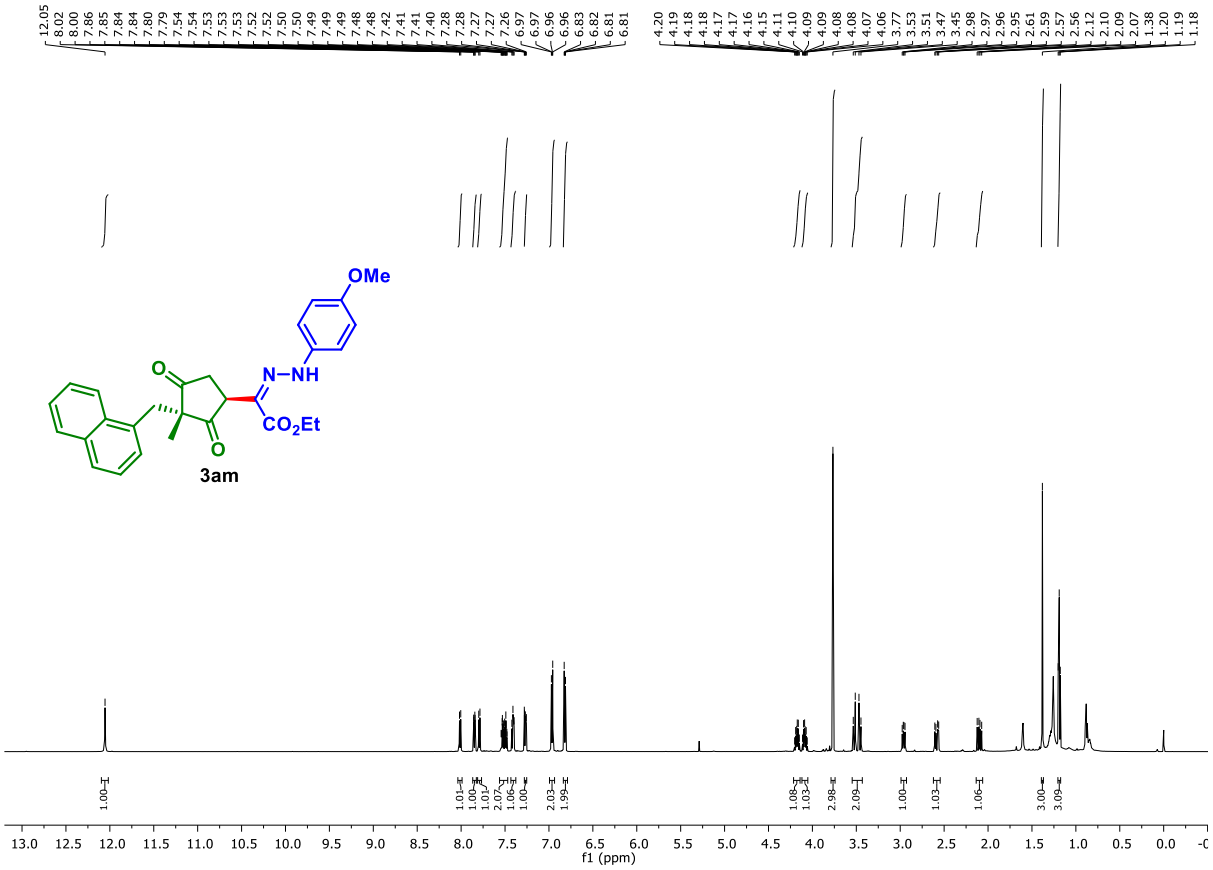
132.34
130.08
129.11
126.98
123.84
115.41
114.84
77.37
77.16
76.95
61.29
57.67
55.73
51.59
41.81
39.95
18.18
14.32
OMe
N–NH
CO2Et
Cl
O
O
3ak
f1 (ppm)


OMe
N–NH
Br
O
O
CO2Et
3al
f1 (ppm)


OMe
N–NH
Br
O
O
CO2Et
3al
f1 (ppm)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7.52
7.52
7.50
7.50
7.49
7.49
7.49
7.48
7.48
7.42
7.41
7.41
7.40
7.28
7.28
7.27
7.27
7.26
6.97
6.97
6.96
6.96
6.83
6.82
6.81
6.81
4.20
4.19
4.18
4.18
4.17
4.17
4.16
4.15
4.11
4.10
4.09
4.09
4.08
4.08
4.07
4.06
3.77
3.53
3.51
3.47
3.45
2.98
2.97
2.96
2.95
2.61
2.59
2.57
2.56
2.12
2.10
2.09
2.07
1.38
1.20
1.19
1.18
OMe
N–NH
CO2Et
O
O
O
3am
1.00
1.01
1.06
1.01
2.07
1.06
1.00
2.03
1.99
1.08
1.03
2.98
2.09
1.00
1.03
1.06
3.00
3.09
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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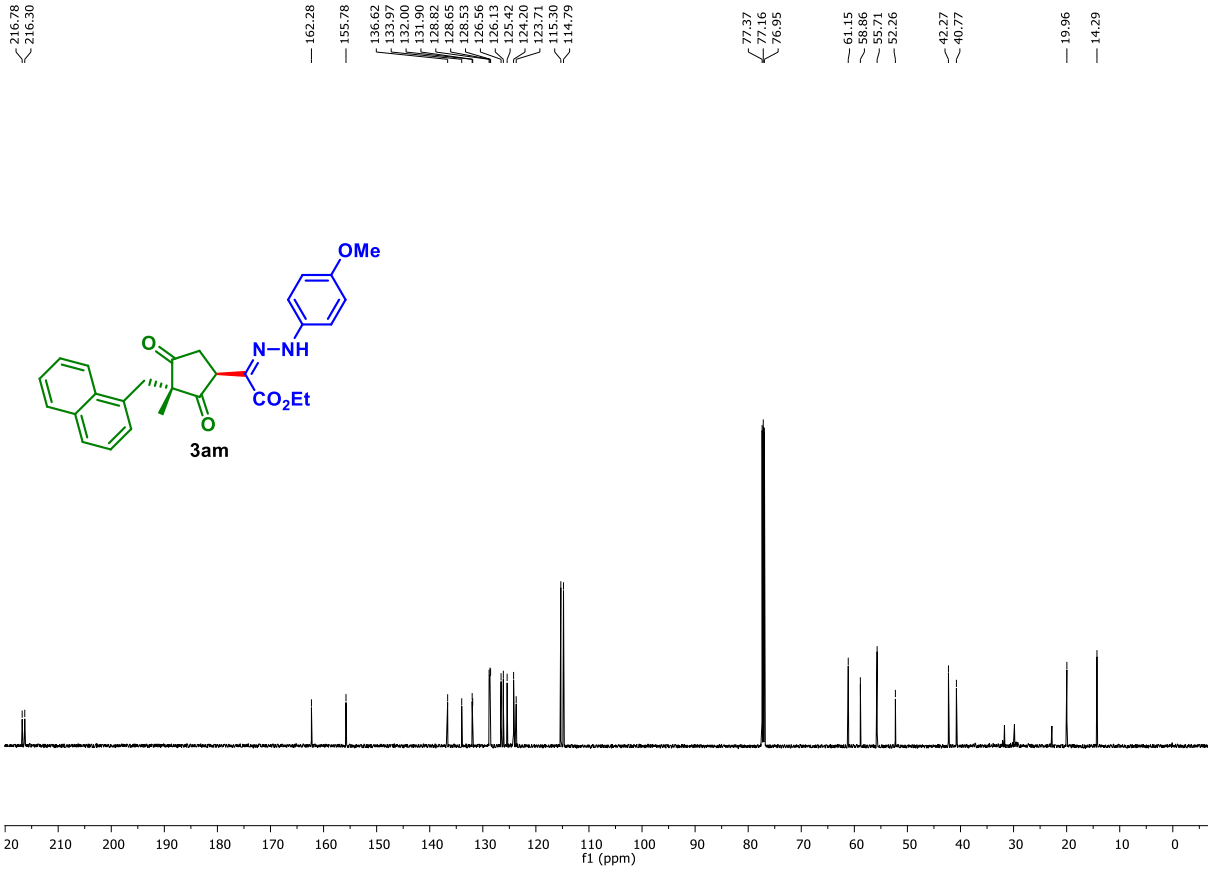
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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133.97
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131.90
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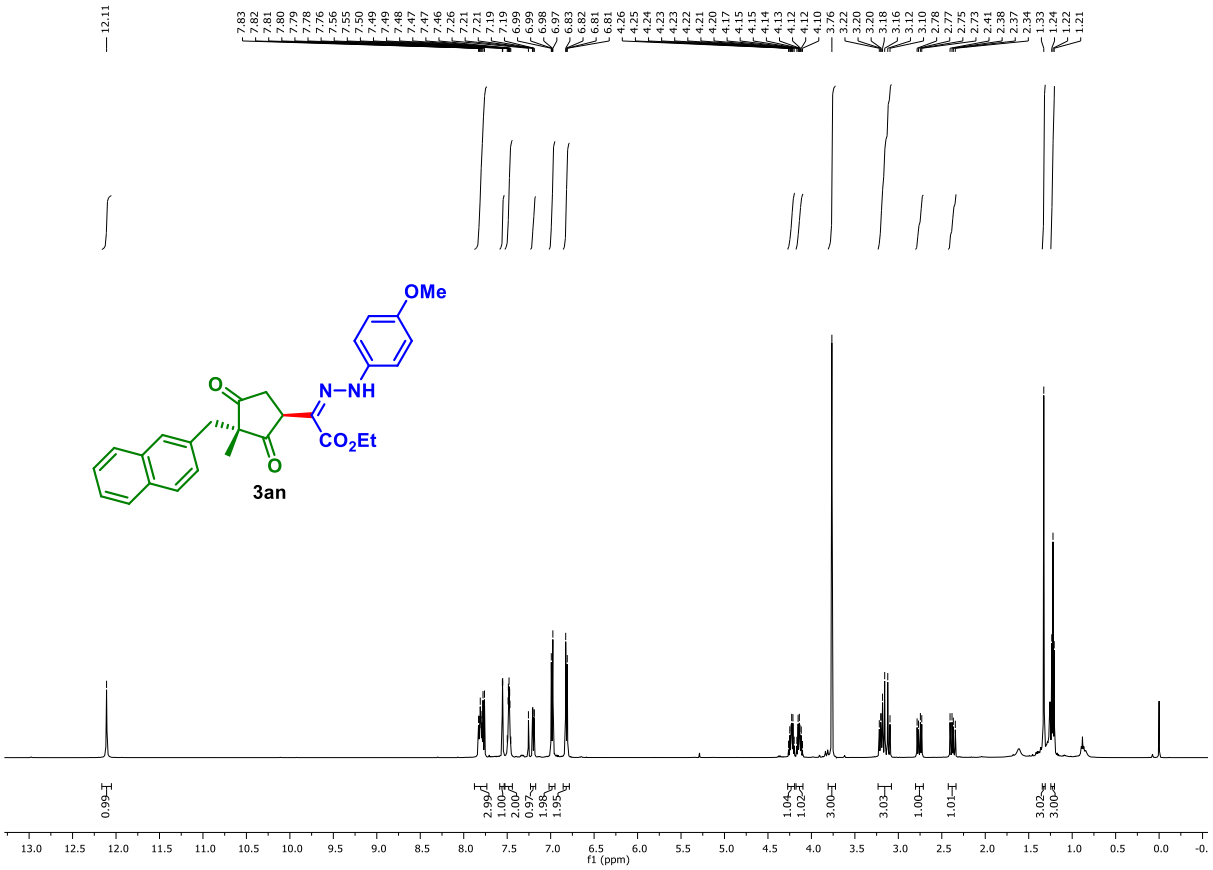
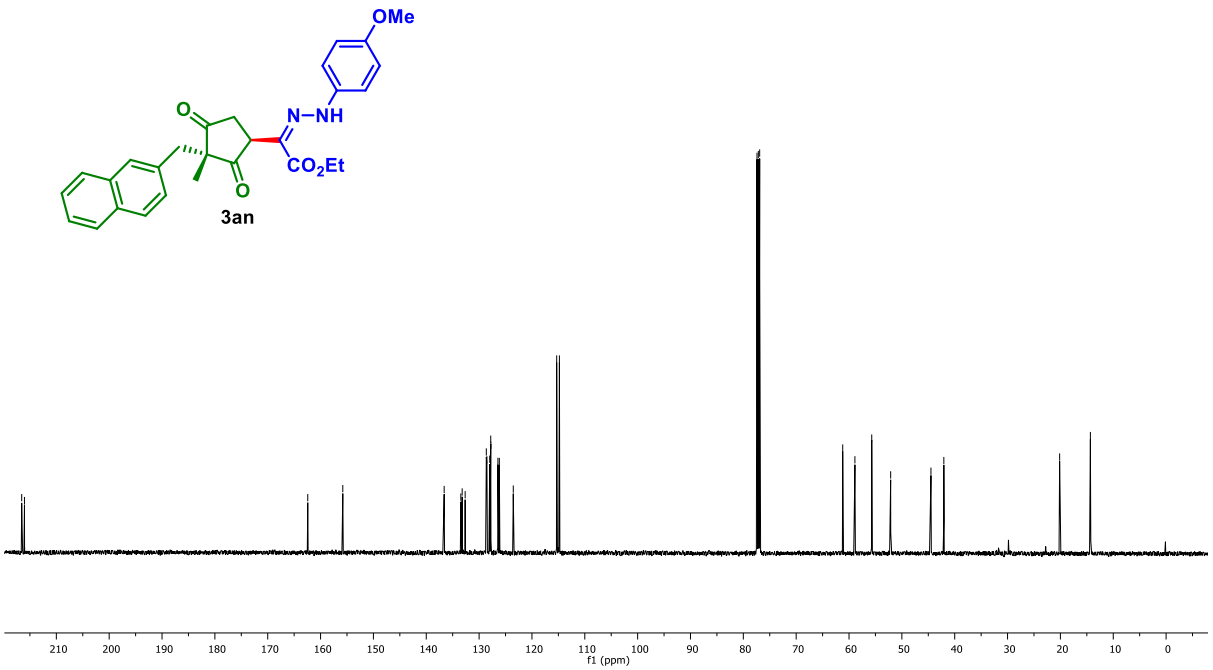
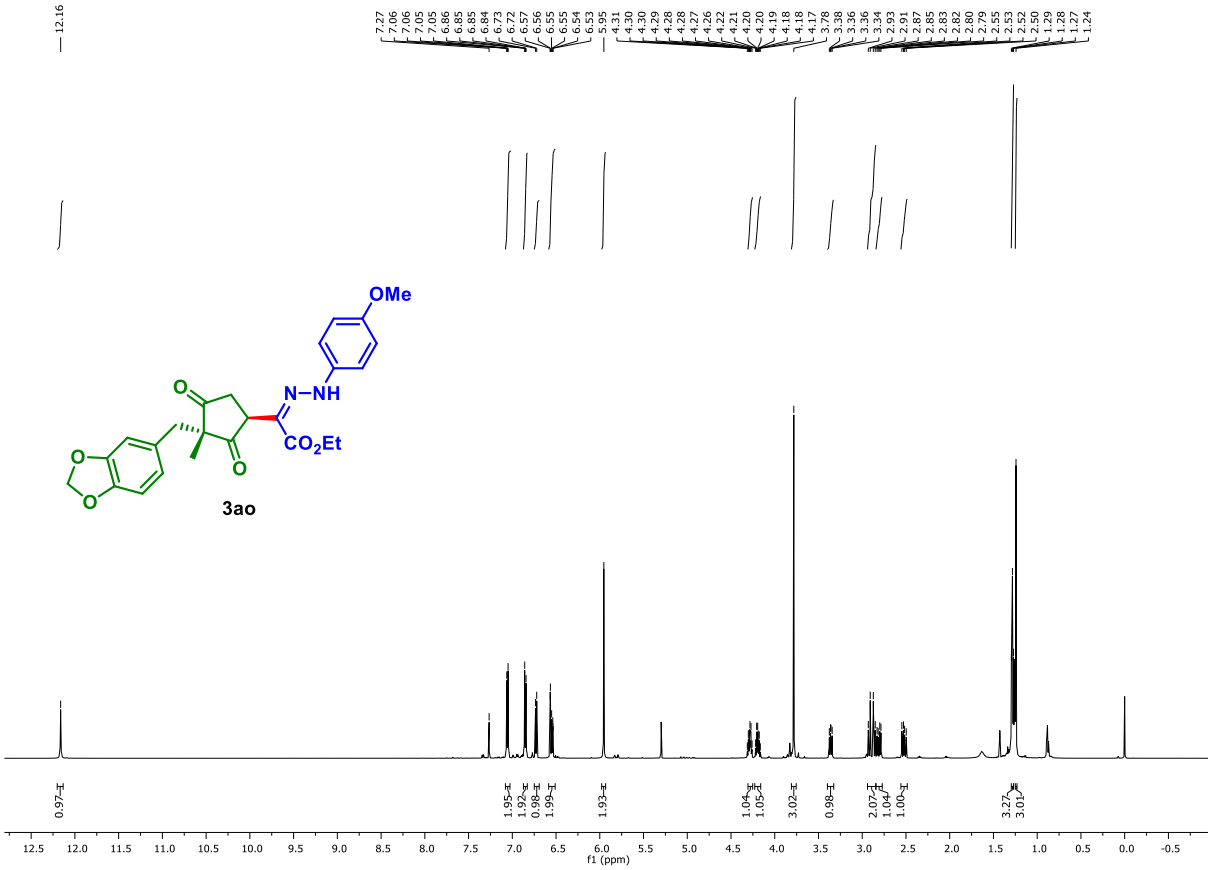
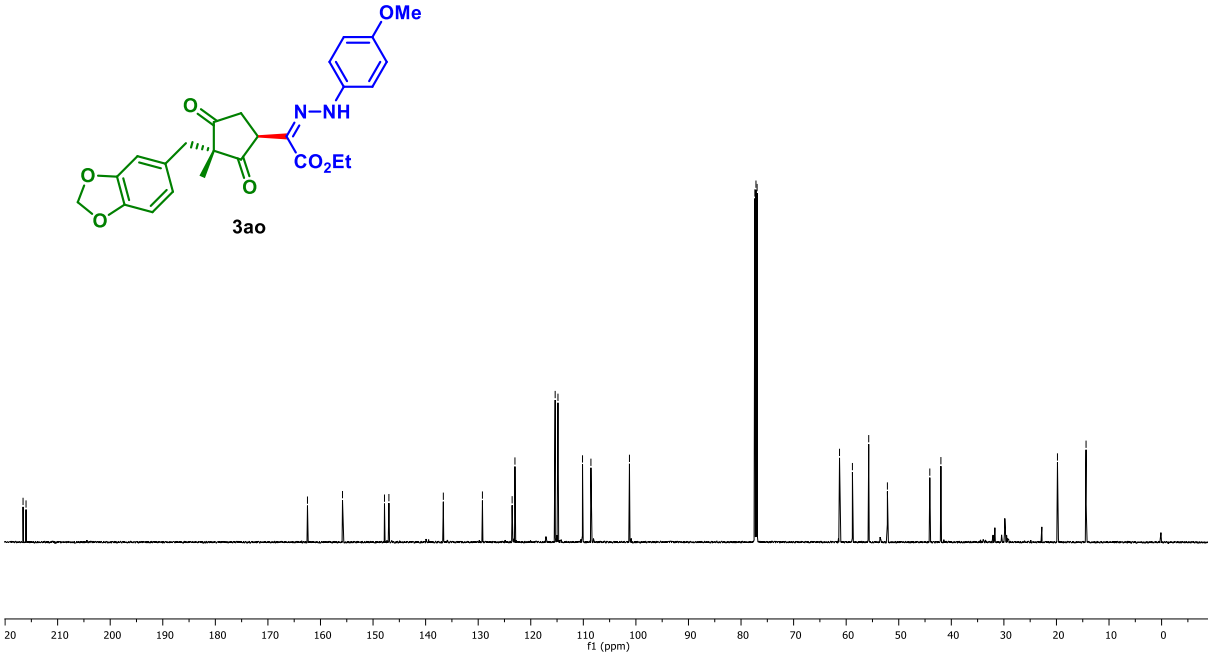
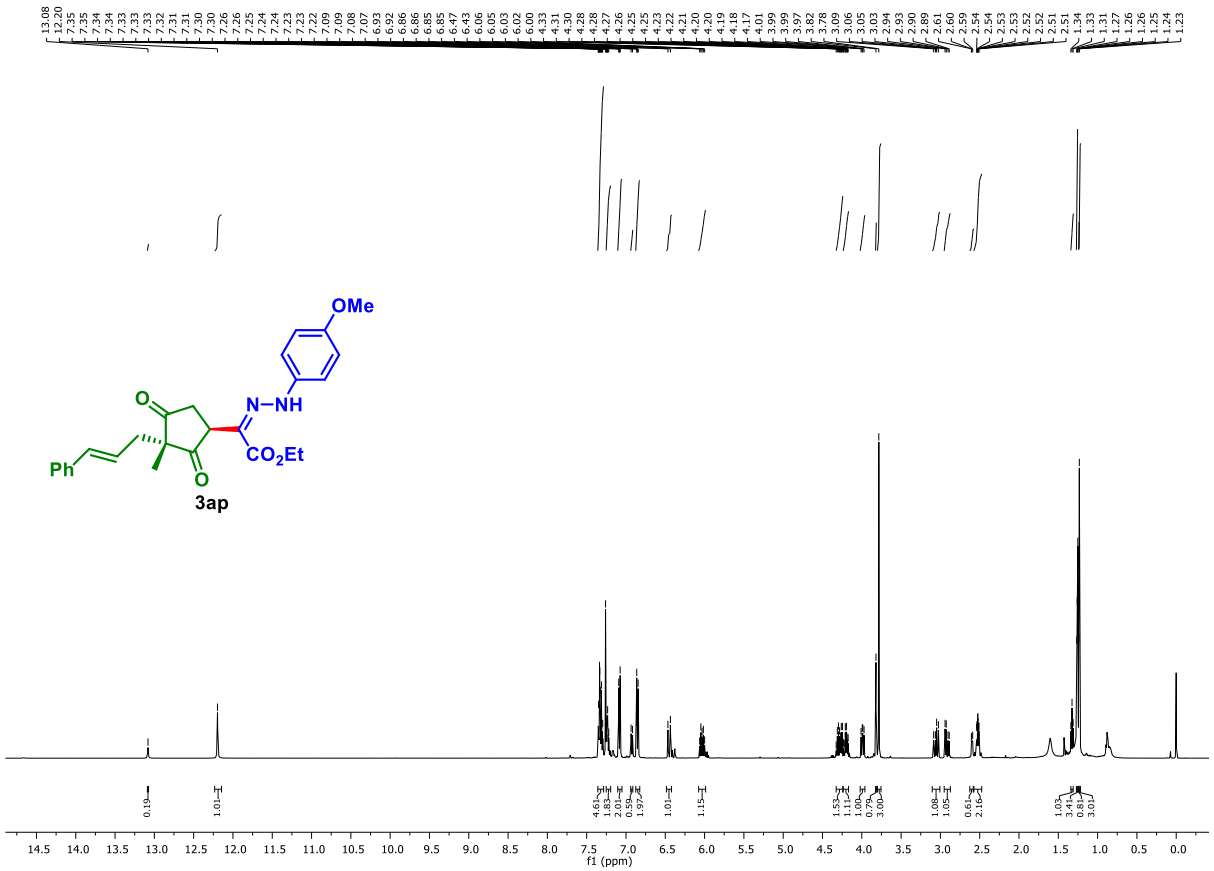
128.65
128.53
126.56
126.13
125.42
124.20
123.71
115.30
114.79
77.37
77.16
76.95
61.15
58.86
55.71
52.26
42.27
40.77
19.96
14.29
OMe
N–NH
CO2Et
O
O
O
3am
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

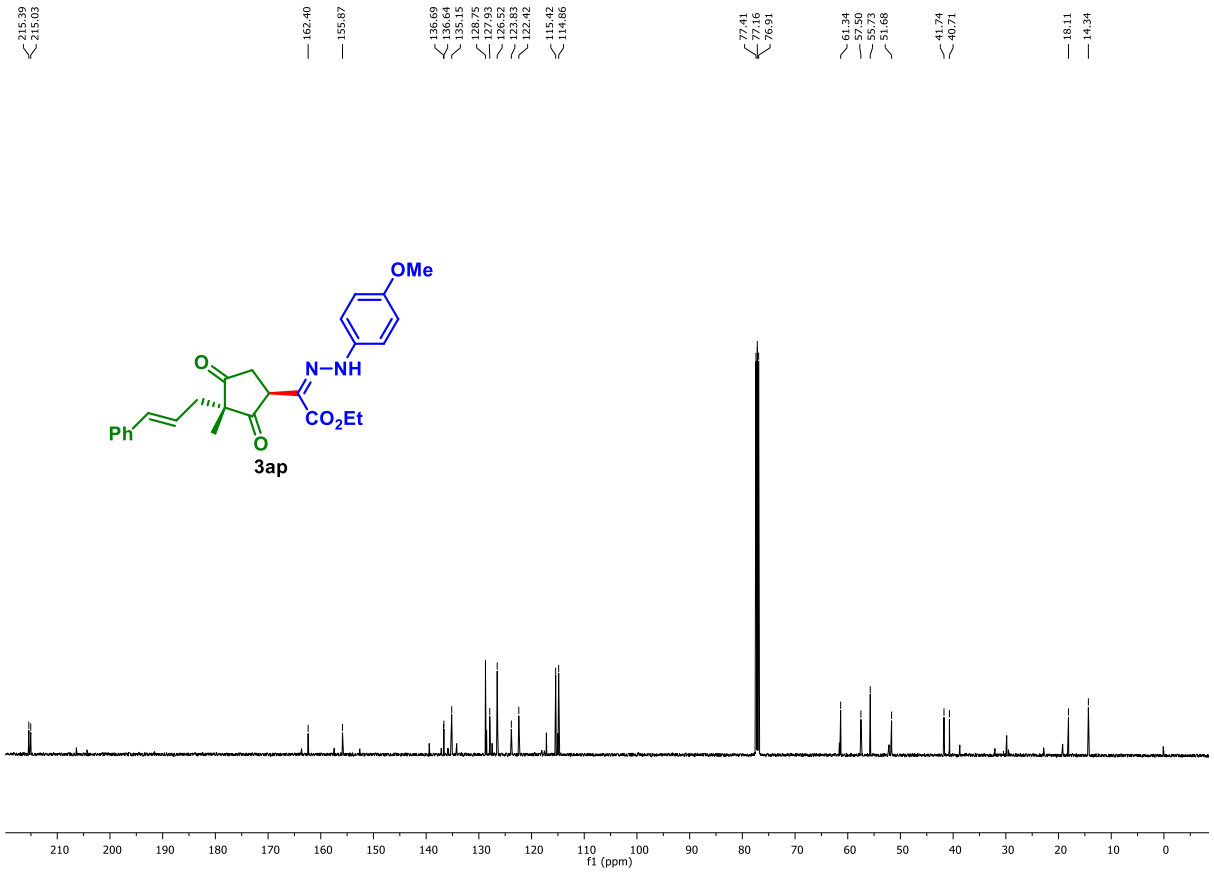

OMe
N–NH
CO2Et
O
O
3an
f1 (ppm)

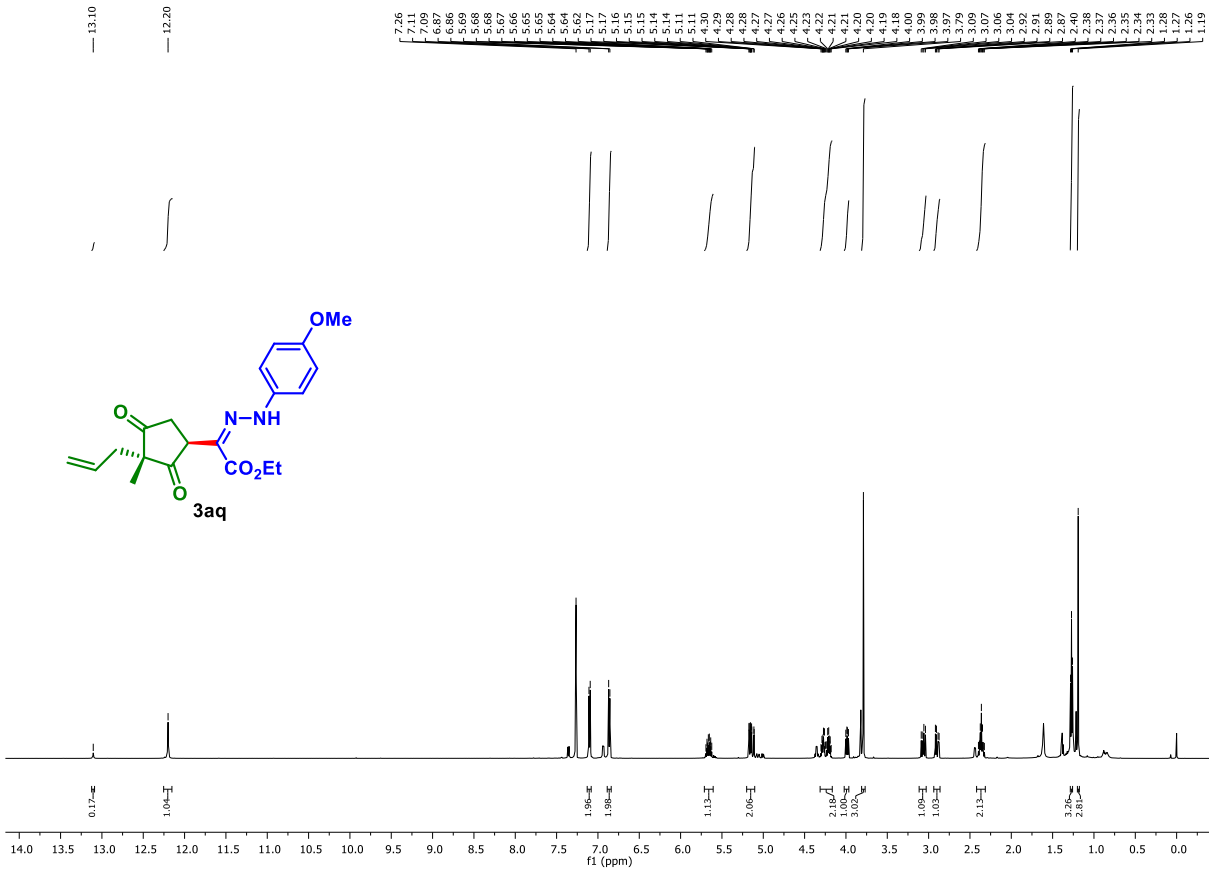

OMe
N–NH
CO2Et
O
O
3an
f1 (ppm)


OMe
N–NH
CO2Et
O
O
O
O
3ao
f1 (ppm)


OMe
N–NH
CO2Et
O
O
O
O
3ao
f1 (ppm)


OMe
N–NH
O
CO2Et
Ph
O
3ap
f1 (ppm)


OMe
N–NH
O
CO2Et
Ph
O
3ap
f1 (ppm)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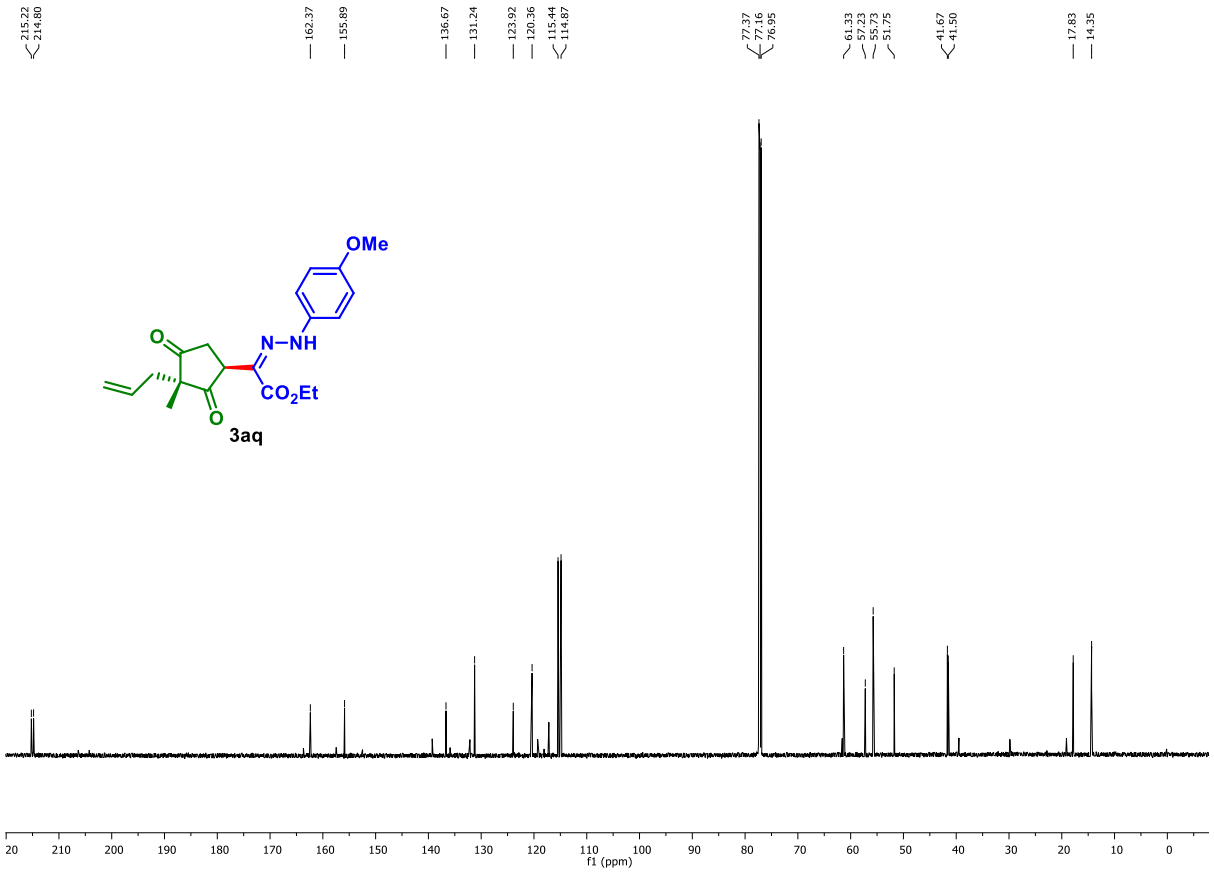
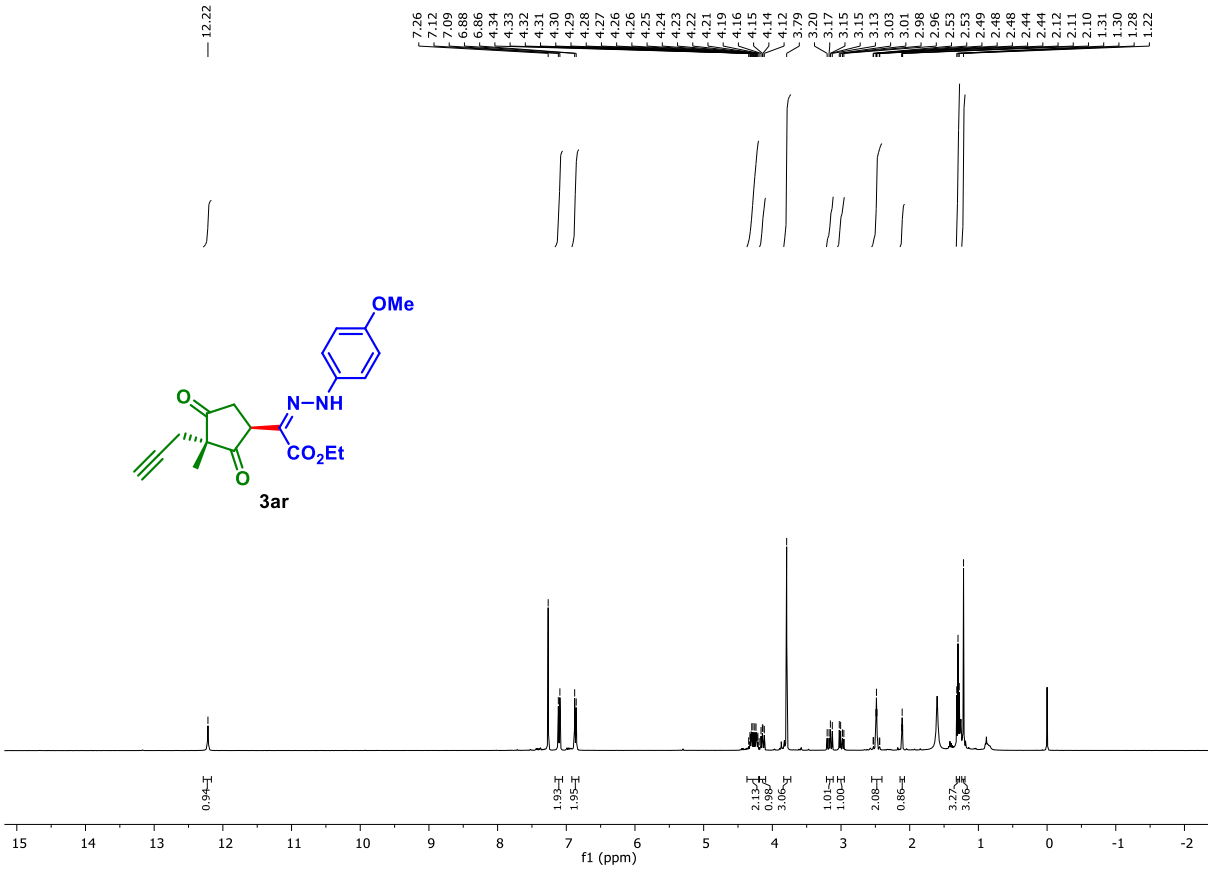
N–NH
CO2Et
O
O
3aq
f1 (ppm)


OMe
N–NH
CO2Et
O
O
3aq
f1 (ppm)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6.86
6.34
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4.32
4.31
4.30
4.29
4.28
4.27
4.26
4.26
4.25
4.24
4.23
4.22
4.21
4.19
4.16
4.15
4.14
4.12
3.79
3.20
3.17
3.15
3.15
3.13
3.03
3.01
2.98
2.96
2.53
2.53
2.49
2.48
2.48
2.44
2.44
2.12
2.11
2.10
1.31
1.30
1.28
1.22
OMe
N–NH
CO2Et
O
O
O
3ar
0.94
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1.95
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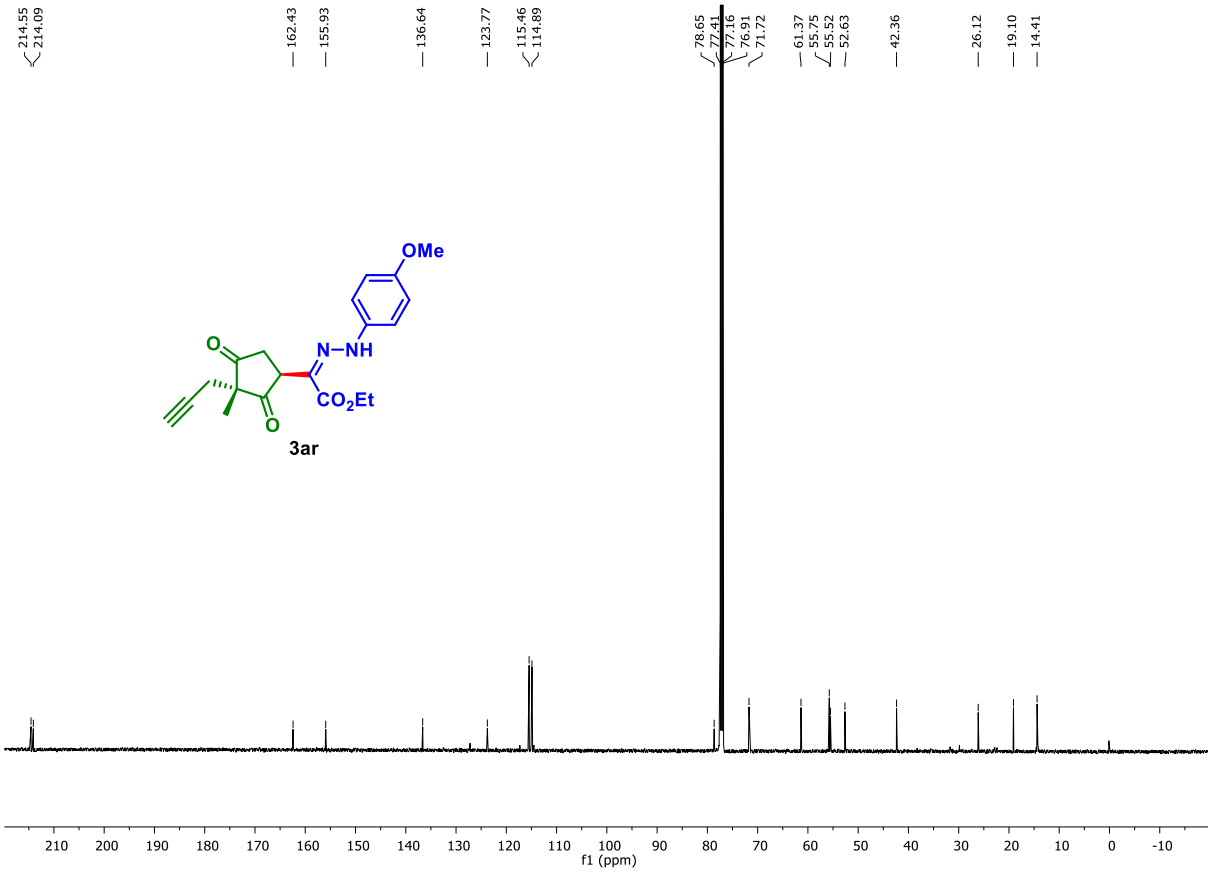
0.98
3.06
1.01
1.00
2.08
0.86
3.27
3.06
f1 (ppm)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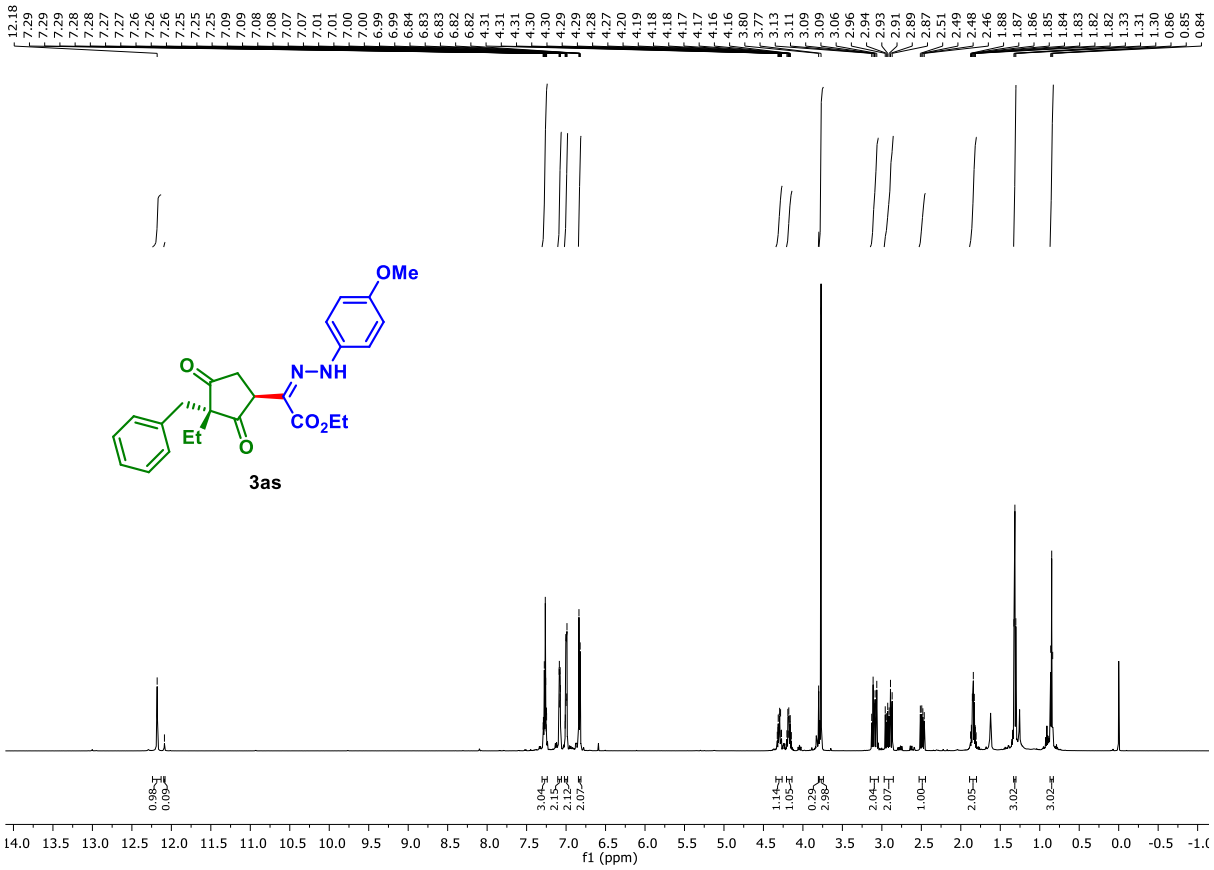
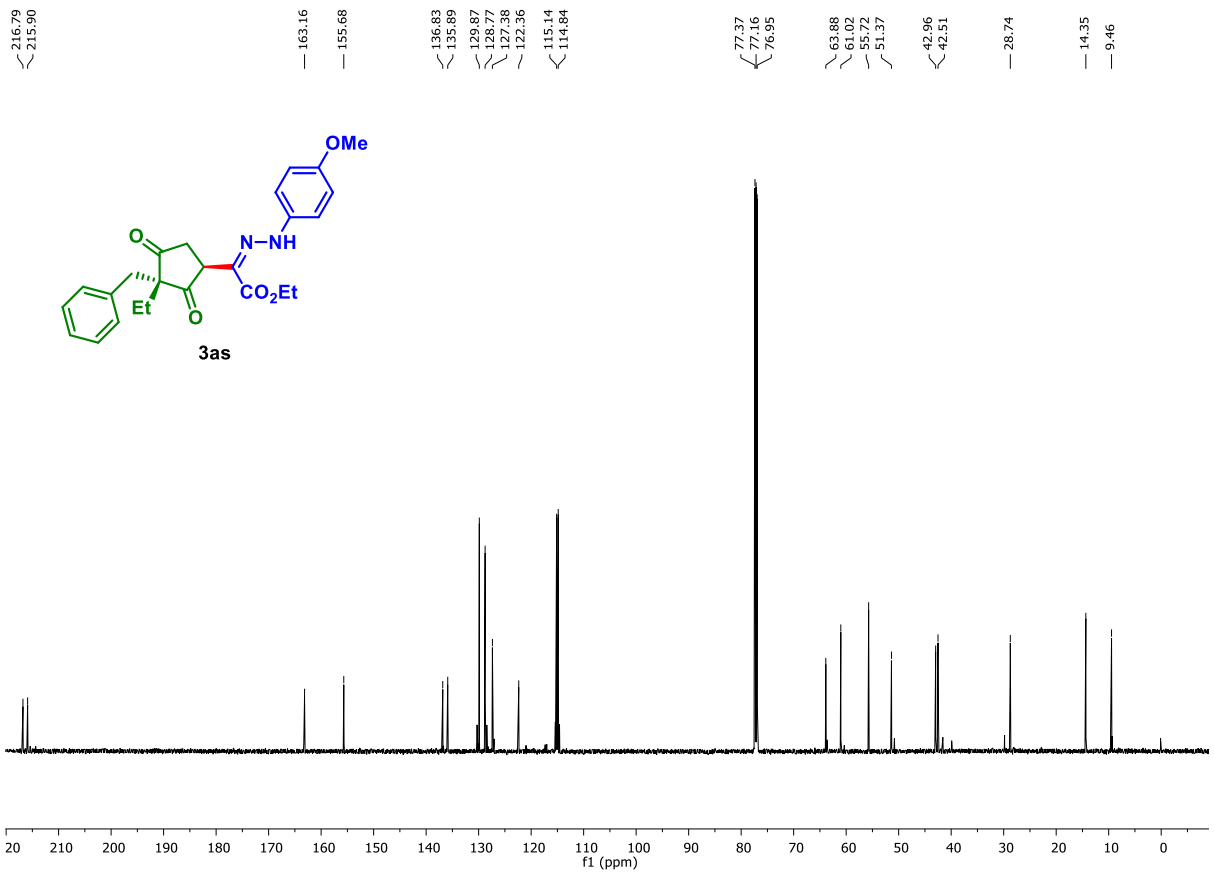
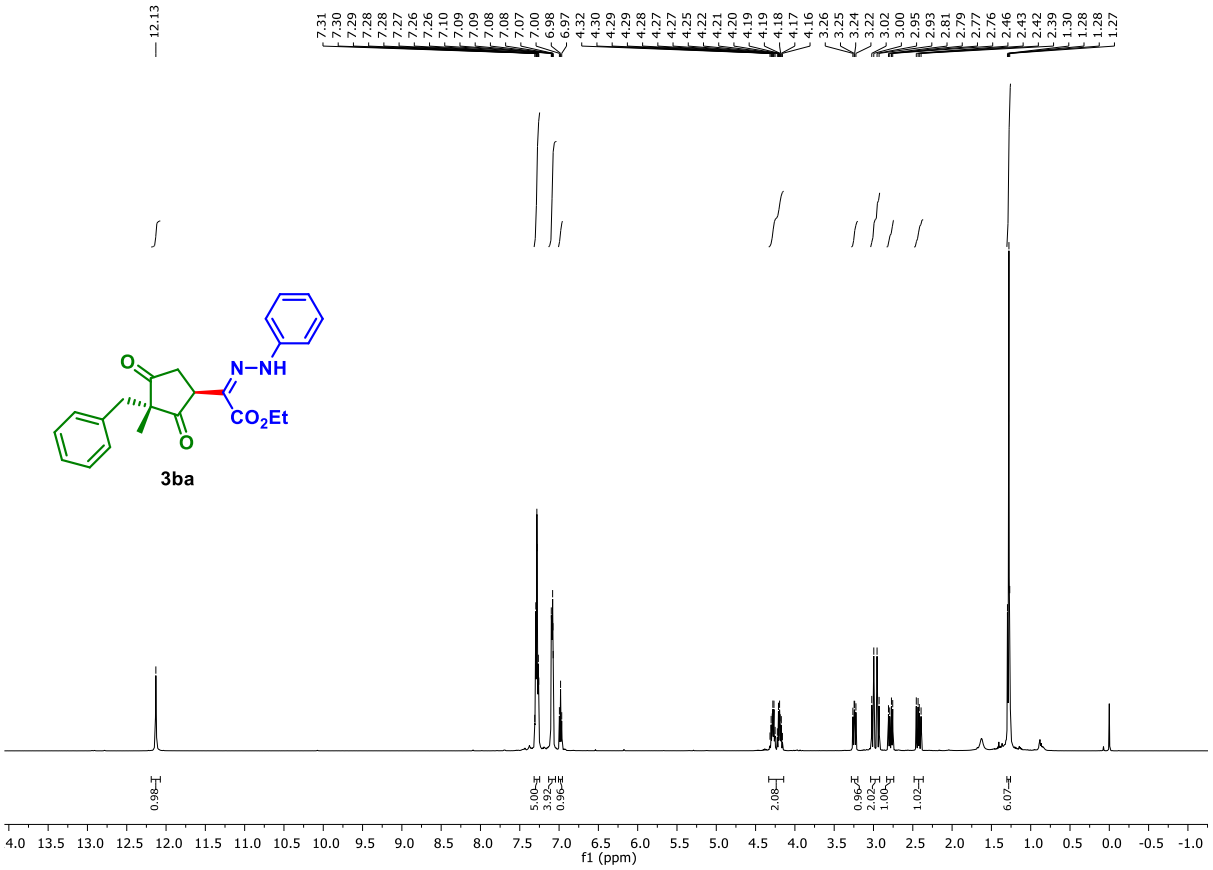
114.89
78.65
77.41
77.16
76.91
71.72
61.37
55.75
55.52
52.63
42.36
26.12
19.10
14.41
OMe
N–NH
CO2Et
O
O
O
3ar
f1 (ppm)


OMe
N–NH
O
CO2Et
Et
O
3as
f1 (ppm)


OMe
N–NH
O
CO2Et
Et
O
3as
f1 (ppm)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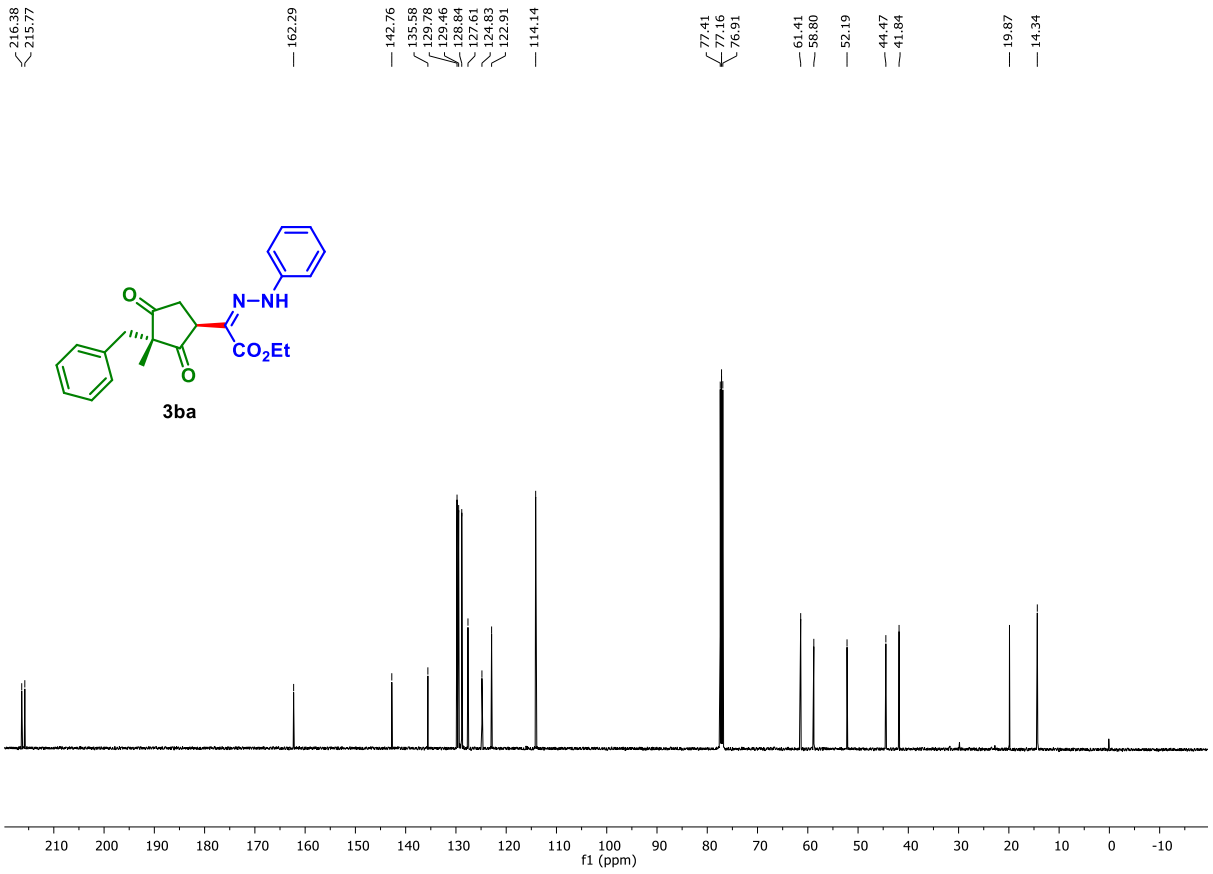
7.28
7.27
7.26
7.26
7.10
7.09
7.09
7.08
7.08
7.07
7.00
6.98
6.97
4.32
4.30
4.29
4.29
4.28
4.27
4.27
4.25
4.22
4.21
4.20
4.19
4.19
4.18
4.17
4.16
3.26
3.25
3.24
3.22
3.02
3.00
2.95
2.93
2.81
2.79
2.77
2.76
2.46
2.43
2.42
2.39
1.30
1.28
1.28
1.27
N–NH
CO2Et
O
O
3ba
0.98
5.00
3.92
0.96
2.08
0.96
2.02
1.00
1.02
6.07
f1 (ppm)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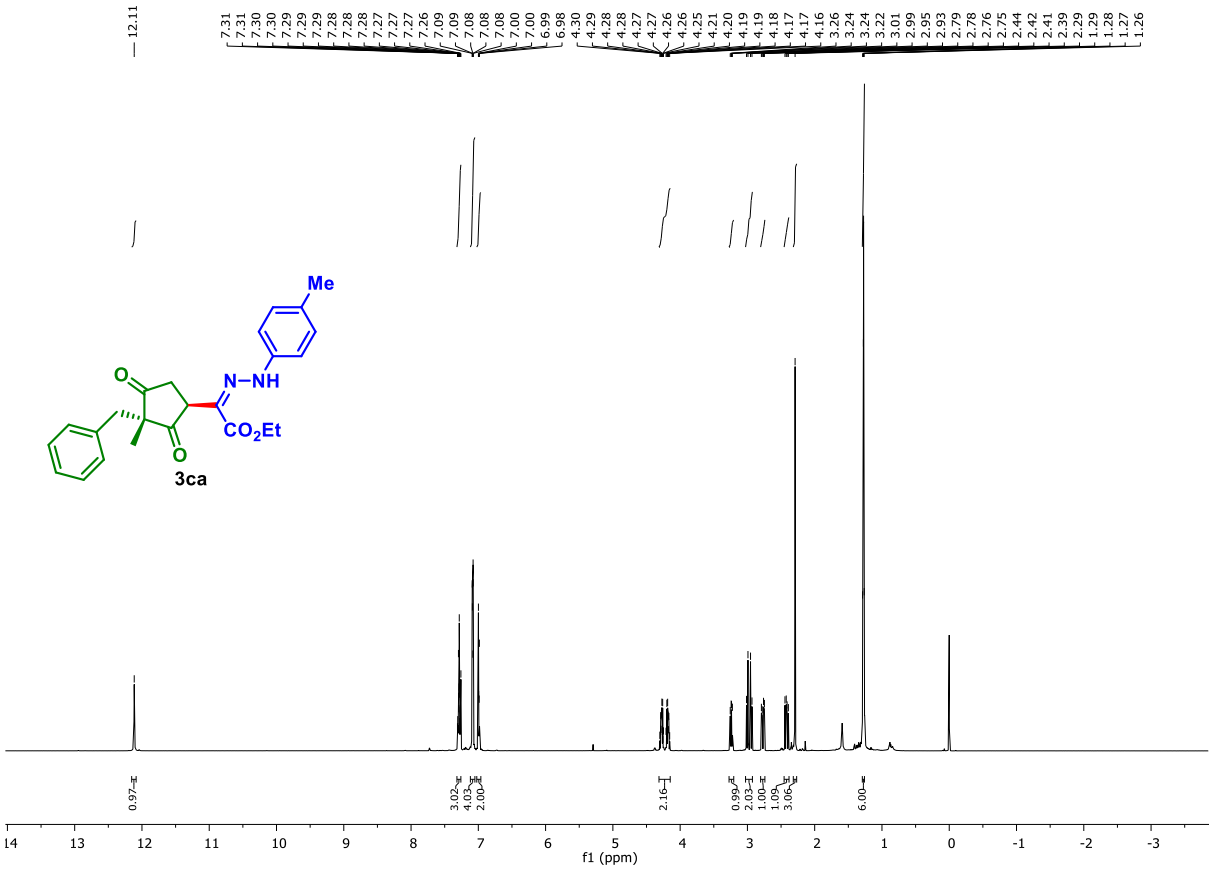
124.83
122.91
114.14
77.41
77.16
76.91
61.41
58.80
52.19
44.47
41.84
19.87
14.34
N–NH
CO2Et
O
O
3ba
f1 (ppm)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7.28
7.28
7.28
7.27
7.27
7.27
7.27
7.26
7.09
7.09
7.08
7.08
7.08
7.00
7.00
6.99
6.98
4.30
4.29
4.28
4.28
4.27
4.27
4.26
4.26
4.25
4.21
4.20
4.19
4.19
4.18
4.17
4.17
4.16
3.26
3.24
3.24
3.22
3.01
2.99
2.95
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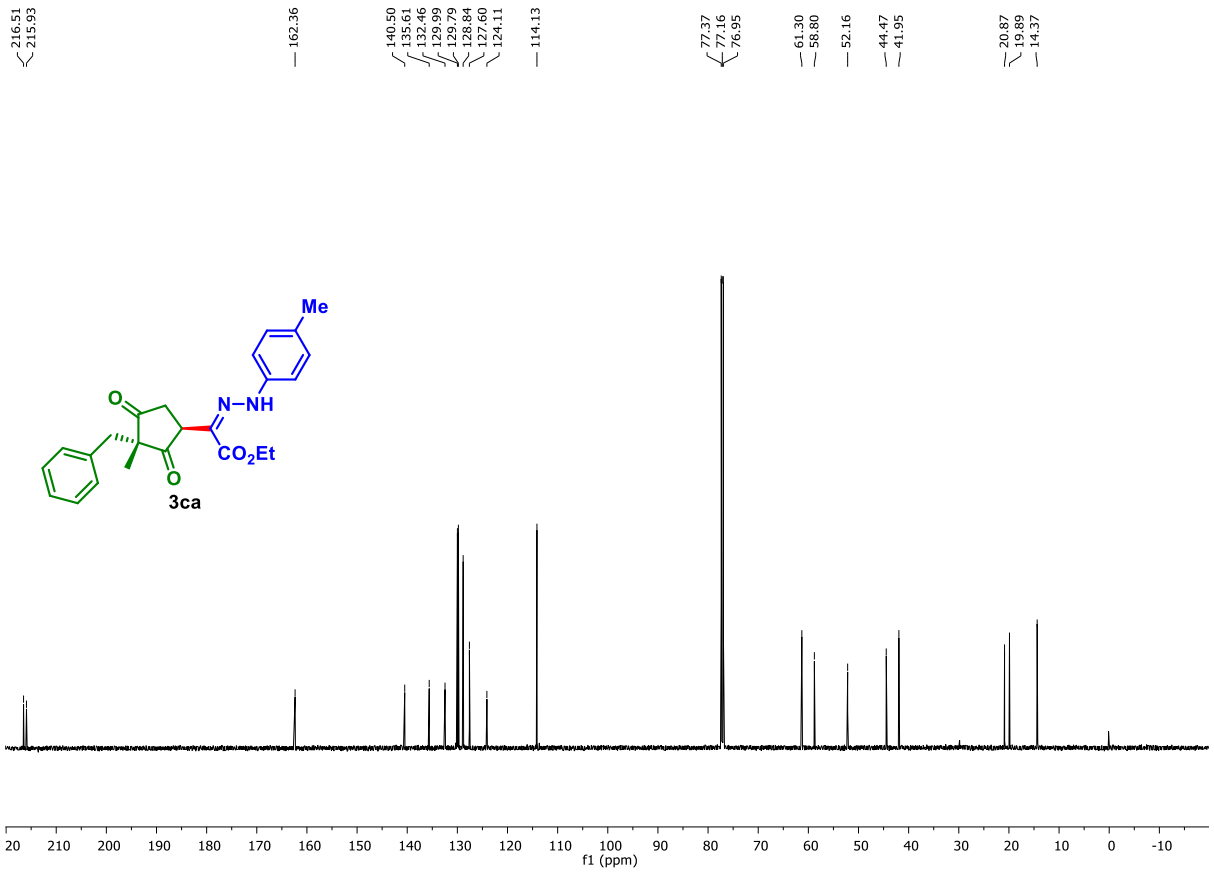
2.79
2.78
2.76
2.75
2.44
2.42
2.41
2.39
2.29
1.29
1.28
1.27
1.26
Me
N–NH
CO2Et
O
O
3ca
0.97
3.02
4.03
2.00
2.16
0.99
2.03
1.00
1.09
3.06
6.00
f1 (ppm)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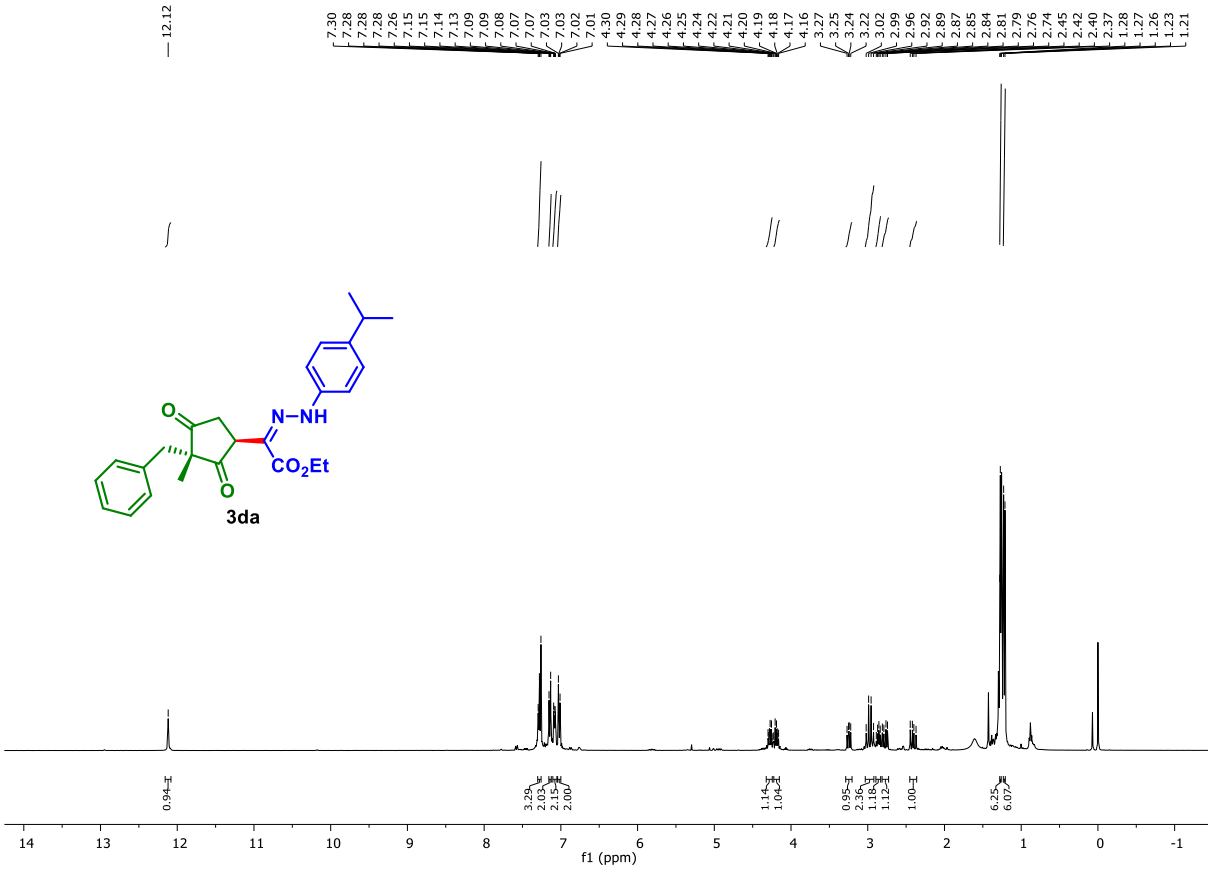
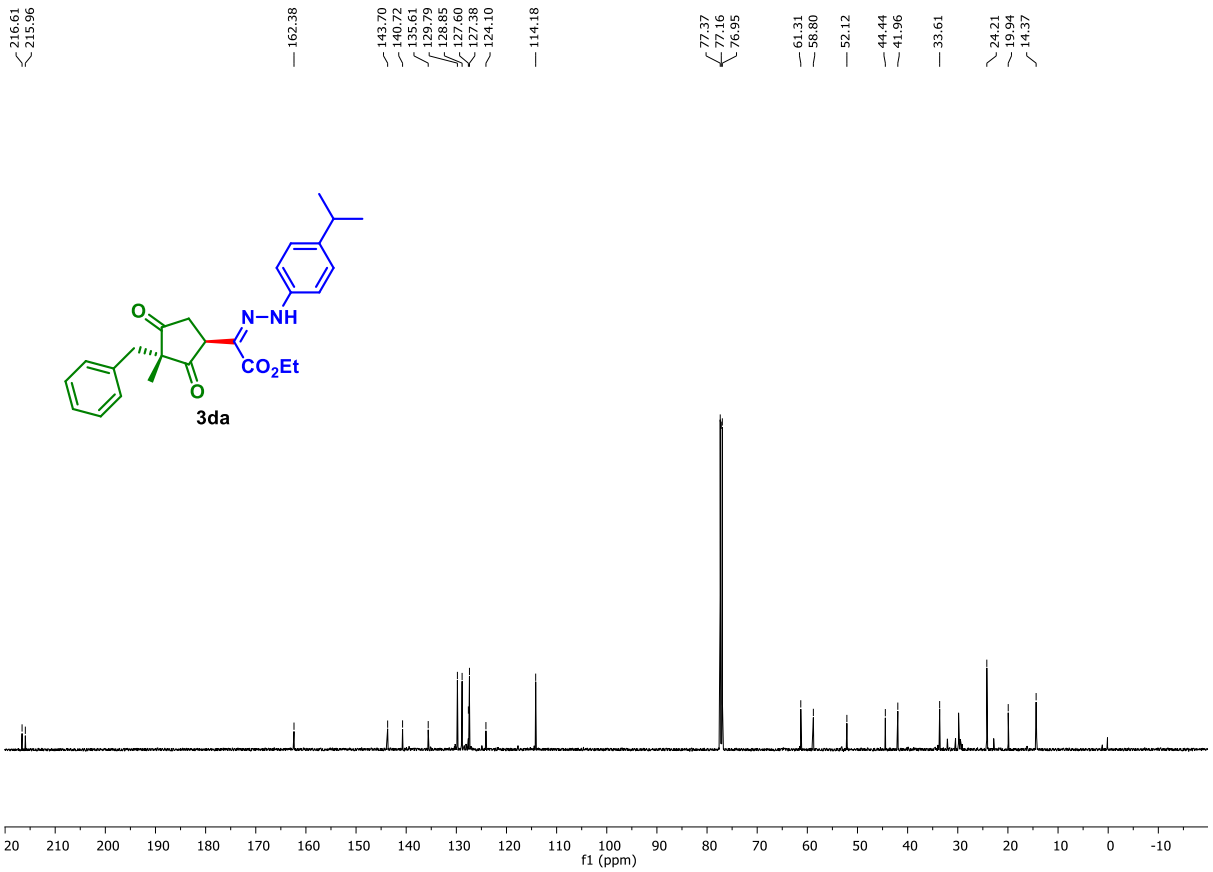
215.93
162.36
140.50
135.61
132.46
129.99
129.79
128.84
127.60
124.11
114.13
77.37
77.16
76.95
61.30
58.80
52.16
44.47
41.95
20.87
19.89
14.37
Me
N–NH
CO2Et
O
O
3ca
f1 (ppm)


12.12
7.30 7.28 7.28 7.28 7.26 7.15 7.15 7.14 7.13 7.09 7.09 7.08 7.07 7.07 7.03 7.03 7.02 7.01
4.30 4.29 4.28 4.27 4.26 4.25 4.24 4.22 4.21 4.20 4.19 4.18 4.17 4.16
3.27 3.25 3.24 3.22 3.02 2.99 2.96 2.92 2.89 2.87 2.85 2.84 2.81 2.79 2.76 2.74 2.45 2.42 2.40 2.37 1.28 1.27 1.26 1.23 1.21
N–NH
CO2Et
O
O
3da
0.94
3.29
2.03
2.15
2.00
1.14
1.04
0.95
2.36
1.18
1.12
1.00
6.25
6.07
f1 (ppm)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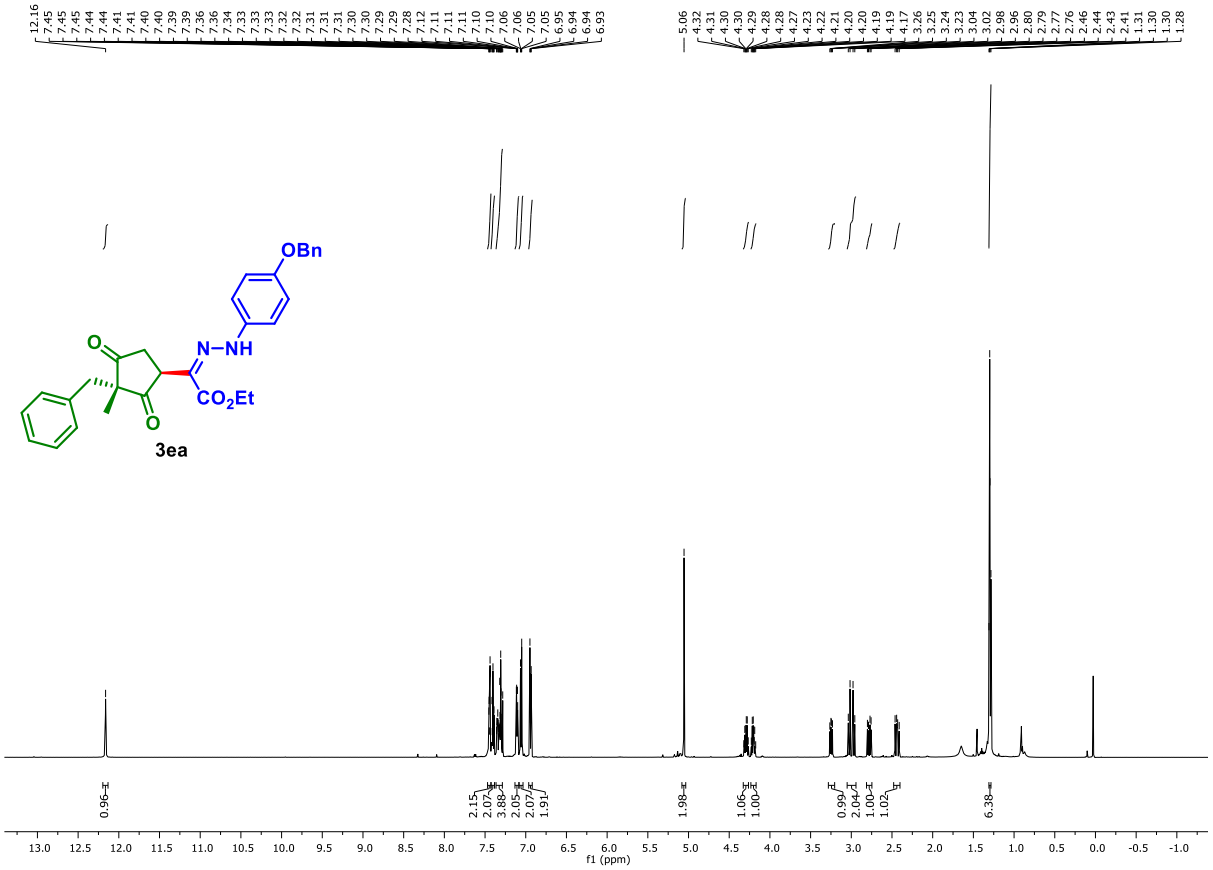
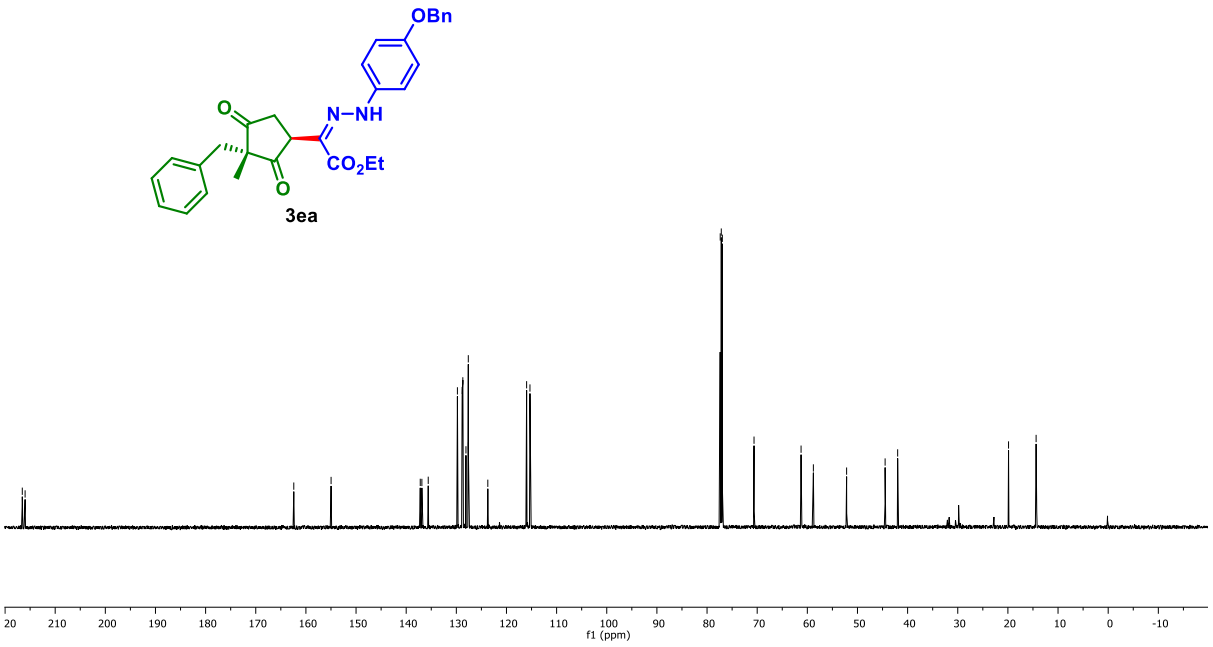
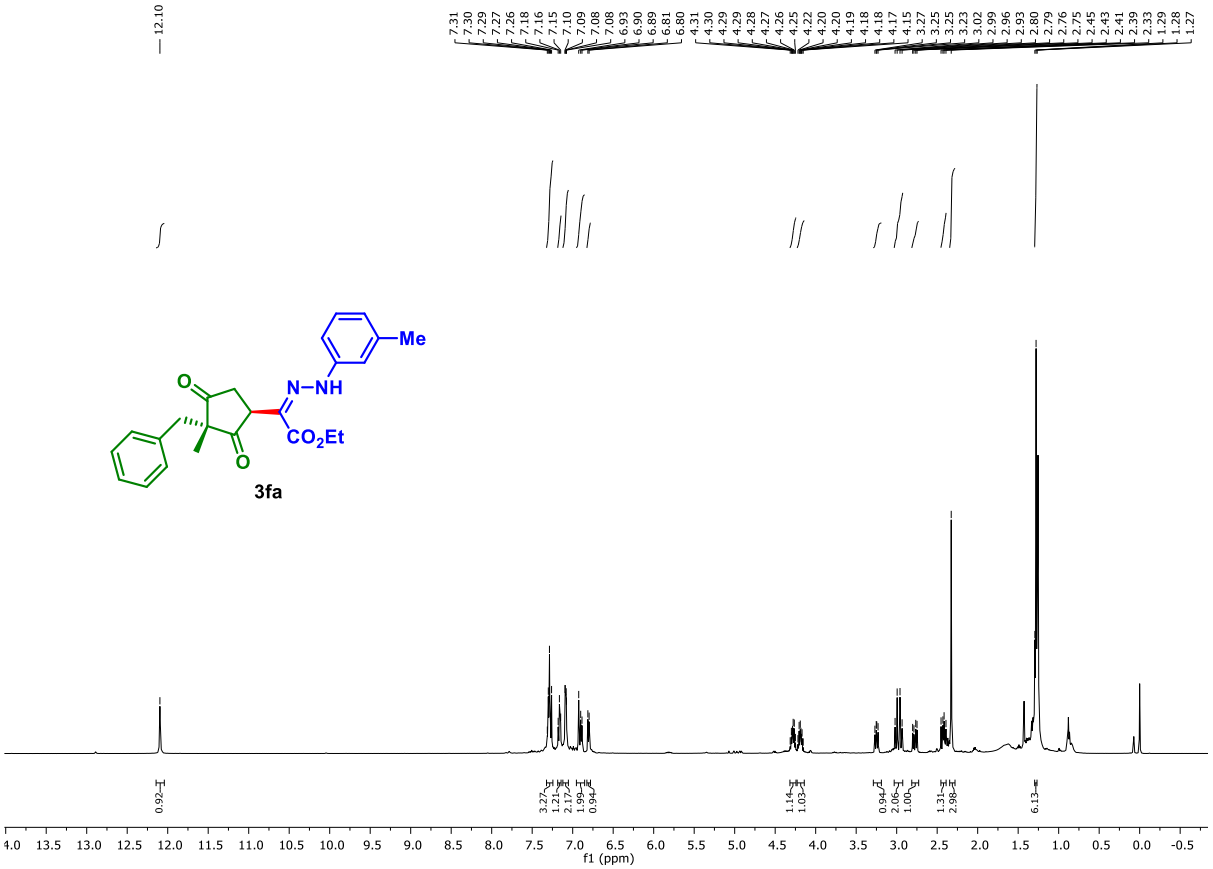
127.38
124.10
114.18
77.37
77.16
76.95
61.31
58.80
52.12
44.44
41.96
33.61
24.21
19.94
14.37
N–NH
CO2Et
O
O
3da
f1 (ppm)


OBn
N–NH
CO2Et
O
O
3ea
f1 (ppm)


OBn
N–NH
CO2Et
O
O
3ea
f1 (ppm)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7.16
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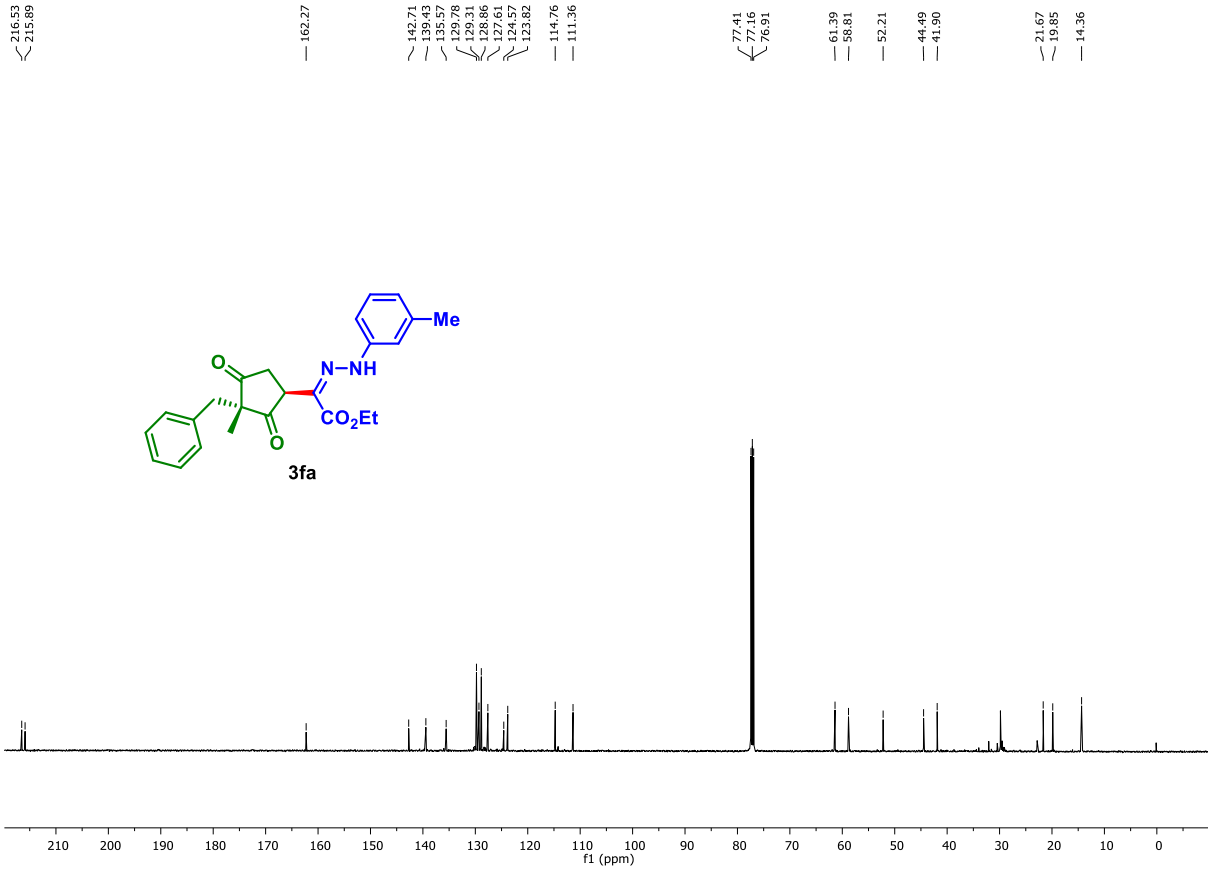
7.10
7.09
7.08
7.08
6.93
6.90
6.89
6.81
6.80
4.31
4.30
4.29
4.29
4.28
4.27
4.26
4.25
4.22
4.20
4.20
4.19
4.18
4.18
4.17
4.15
3.27
3.25
3.25
3.23
3.02
2.99
2.96
2.93
2.80
2.79
2.76
2.75
2.45
2.43
2.41
2.39
2.33
1.29
1.28
1.27
Me
N–NH
CO2Et
O
O
3fa
0.92
3.27
1.21
2.12
1.99
0.94
1.14
1.03
0.94
2.06
1.00
1.31
2.98
6.13
f1 (ppm)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111.36
77.41
77.16
76.91
61.39
58.81
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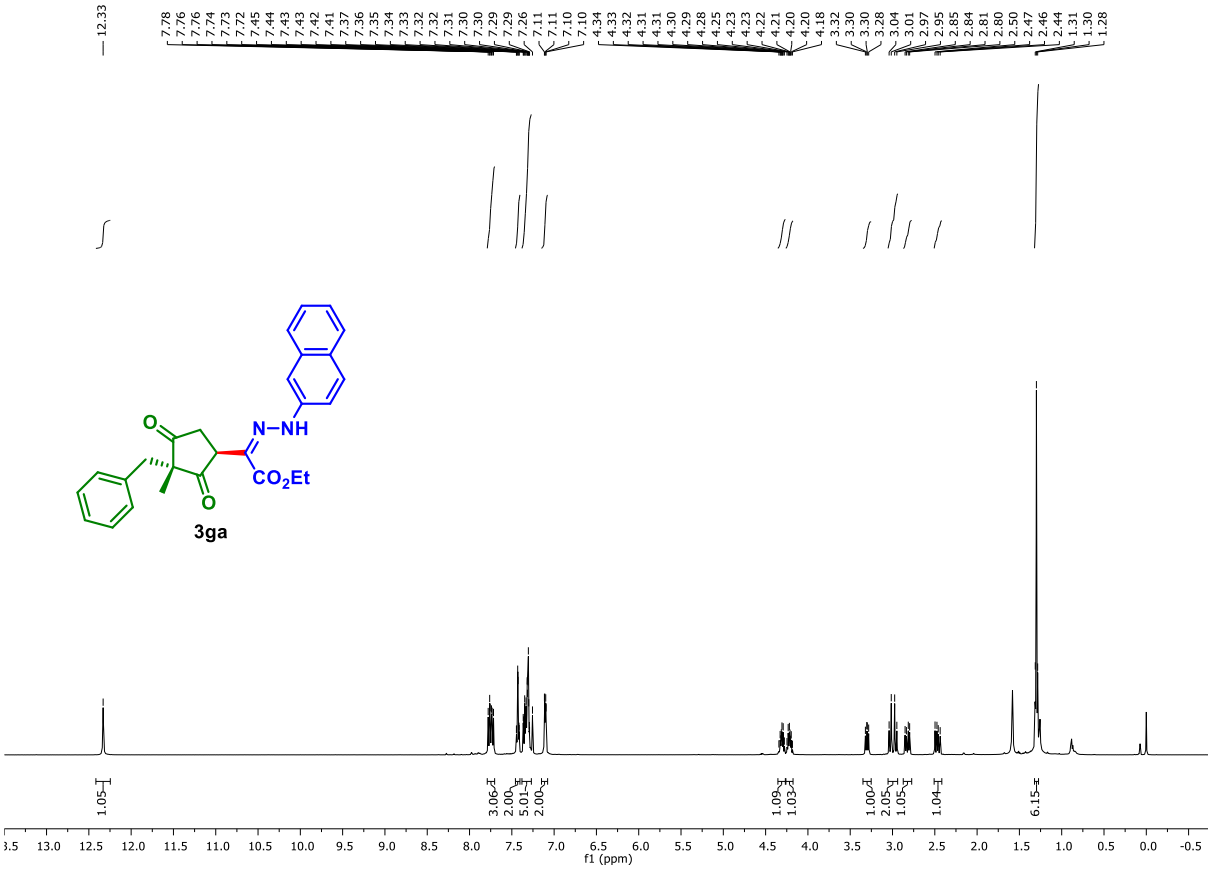
21.67
19.85
14.36
Me
N–NH
CO2Et
O
O
3fa
f1 (ppm)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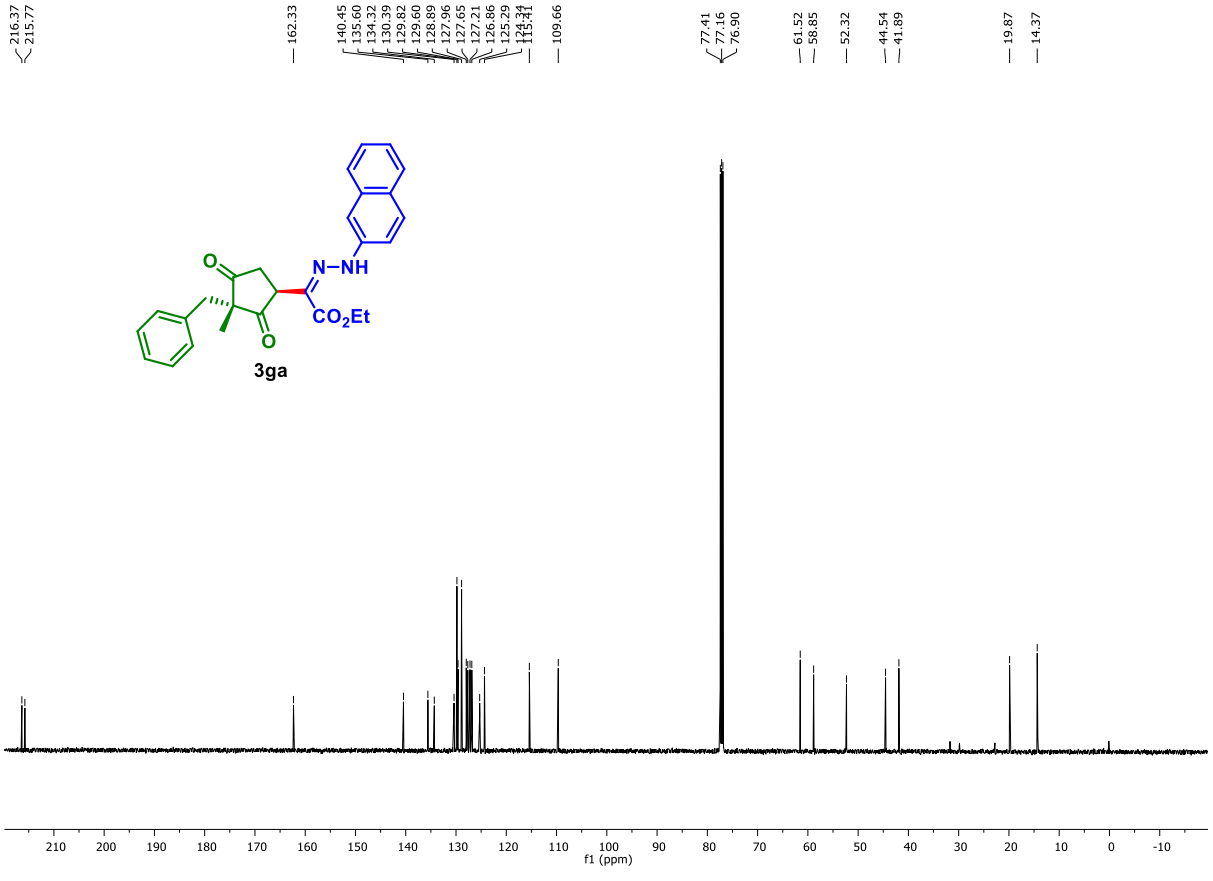
7.78 7.76 7.76 7.74 7.73 7.72 7.45 7.44 7.43 7.43 7.42 7.41 7.41 7.37 7.36 7.35 7.34 7.33 7.32 7.32 7.31 7.30 7.30 7.29 7.29 7.26 7.11 7.11 7.10 7.10 4.34 4.33 4.32 4.31 4.31 4.30 4.29 4.28 4.25 4.23 4.23 4.22 4.21 4.20 4.20 4.18 3.32 3.30 3.30 3.28 3.04 3.01 2.97 2.95 2.85 2.84 2.81 2.80 2.50 2.47 2.46 2.44 1.31 1.30 1.28
N–NH
CO2Et
O
O
3ga
1.05 3.06 2.00 5.01 2.00 1.09 1.03 1.00 2.05 1.05 1.04 6.15
f1 (ppm)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134.32
130.39
129.82
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128.89
127.96
127.65
127.21
126.86
125.29
124.34
115.41
109.66
77.41
77.16
76.90
61.52
58.85
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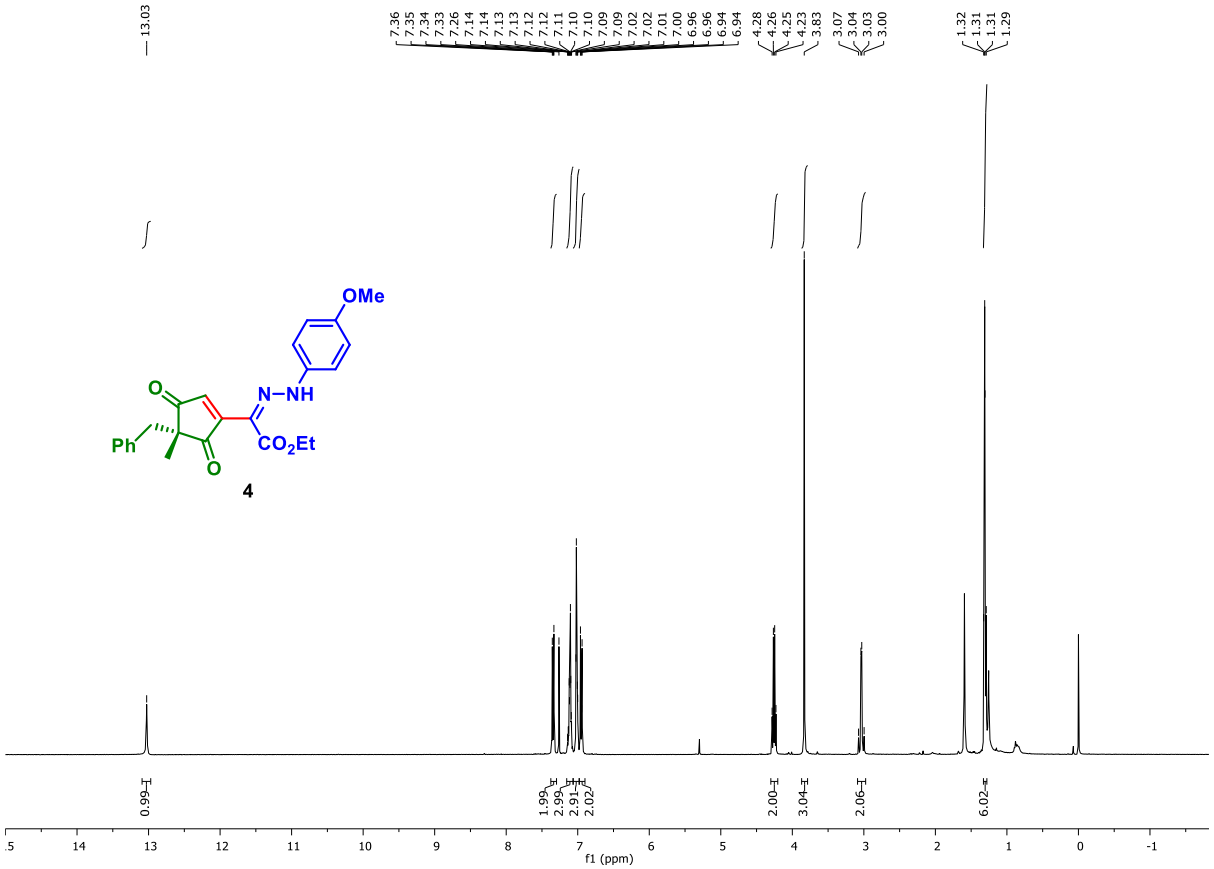
44.54
41.89
19.87
14.37
N–NH
CO2Et
O
O
3ga
f1 (ppm)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7.34
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7.26
7.14
7.14
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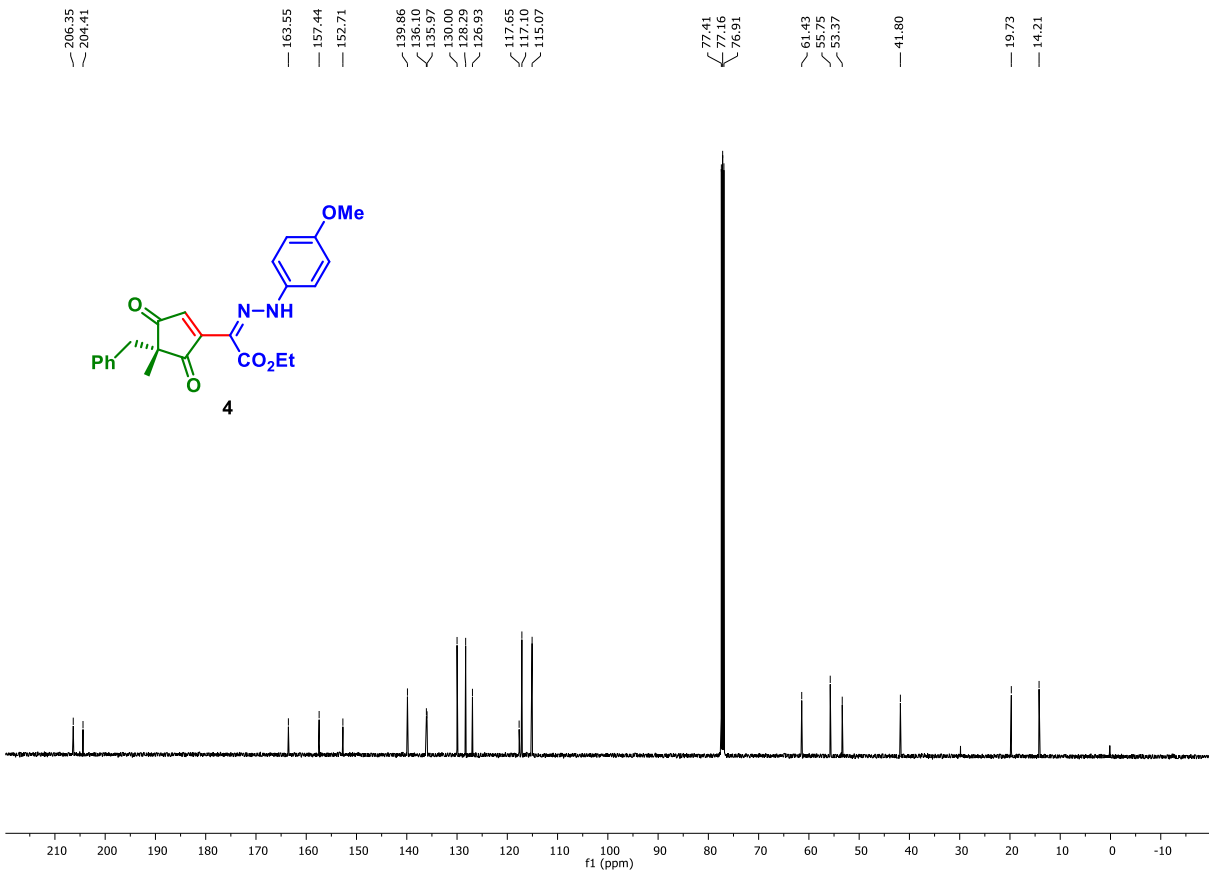
7.13
7.12
7.12
7.11
7.10
7.10
7.09
7.09
7.02
7.02
7.01
7.00
6.96
6.96
6.94
6.94
4.28
4.26
4.25
4.23
3.83
3.07
3.04
3.03
3.00
1.32
1.31
1.31
1.29
OMe
N–NH
O
Ph
CO2Et
O
4
0.99
1.99
2.99
2.91
2.02
2.00
3.04
2.06
6.02
f1 (ppm)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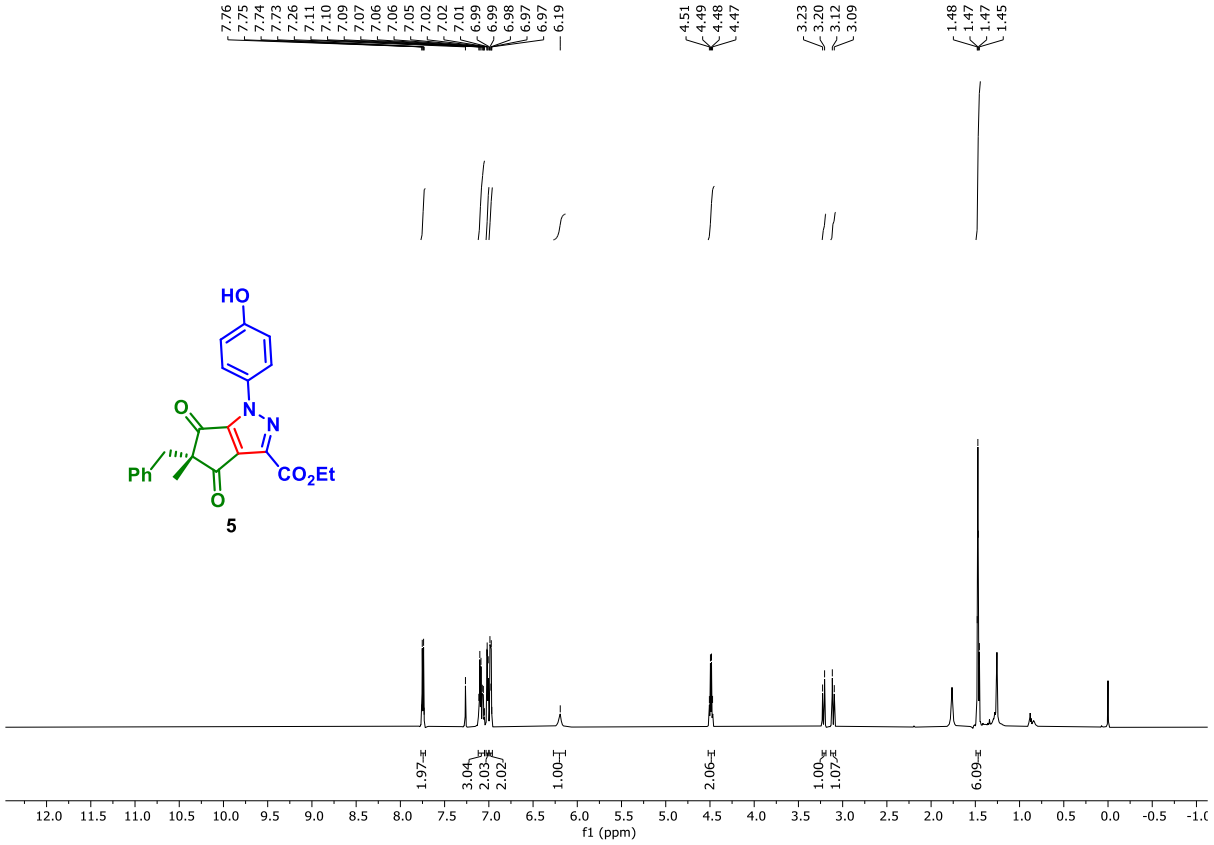
152.71
139.86
136.10
135.97
130.00
128.29
126.93
117.65
117.10
115.07
77.41
77.16
76.91
61.43
55.75
53.37
41.80
19.73
14.21
OMe
N–NH
O
Ph
CO2Et
O
4
f1 (ppm)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7.75
7.74
7.73
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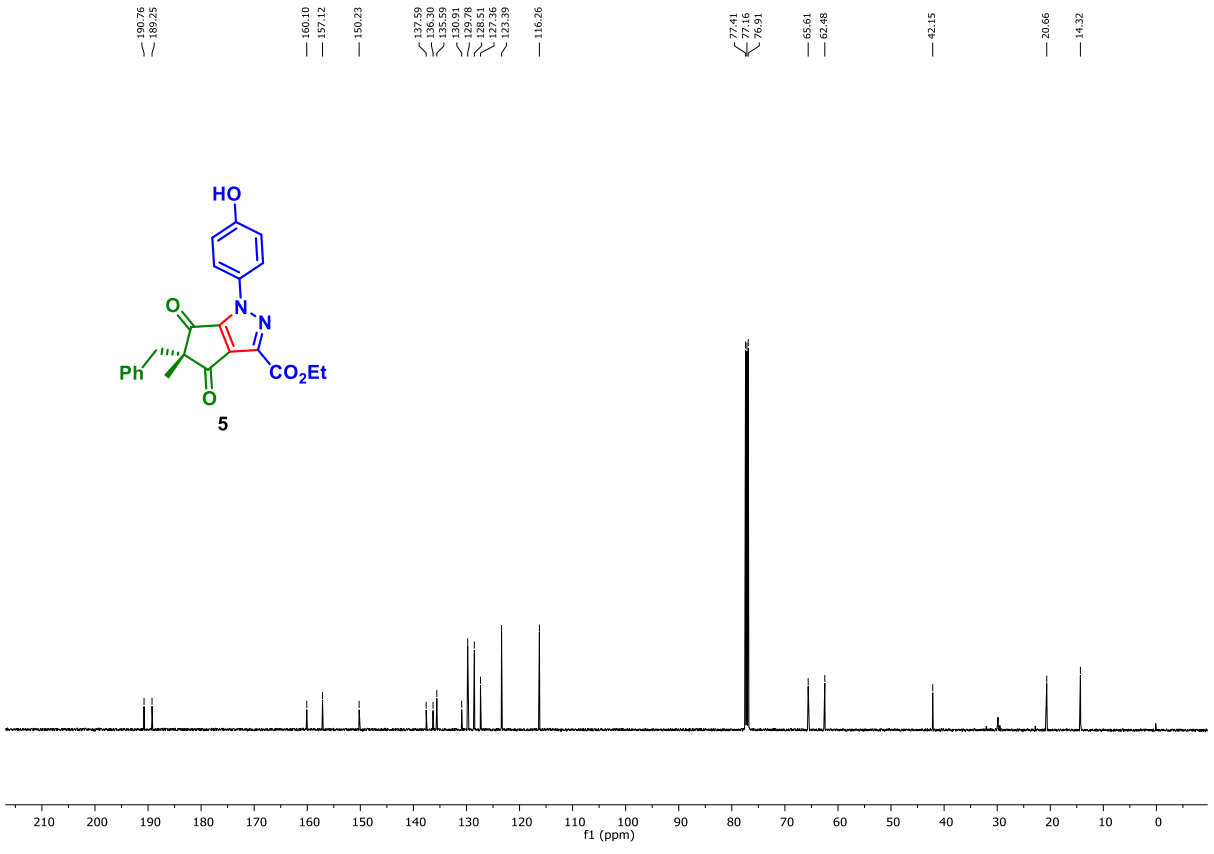
7.10
7.09
7.07
7.06
7.06
7.05
7.02
7.02
7.01
6.99
6.99
6.98
6.97
6.97
6.19
4.51
4.49
4.48
4.47
3.23
3.20
3.12
3.09
1.48
1.47
1.47
1.45
HO
O
N
N
Ph
CO2Et
O
5
1.97
3.04
2.03
2.02
1.00
2.06
1.00
1.07
6.09
f1 (ppm)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189.25
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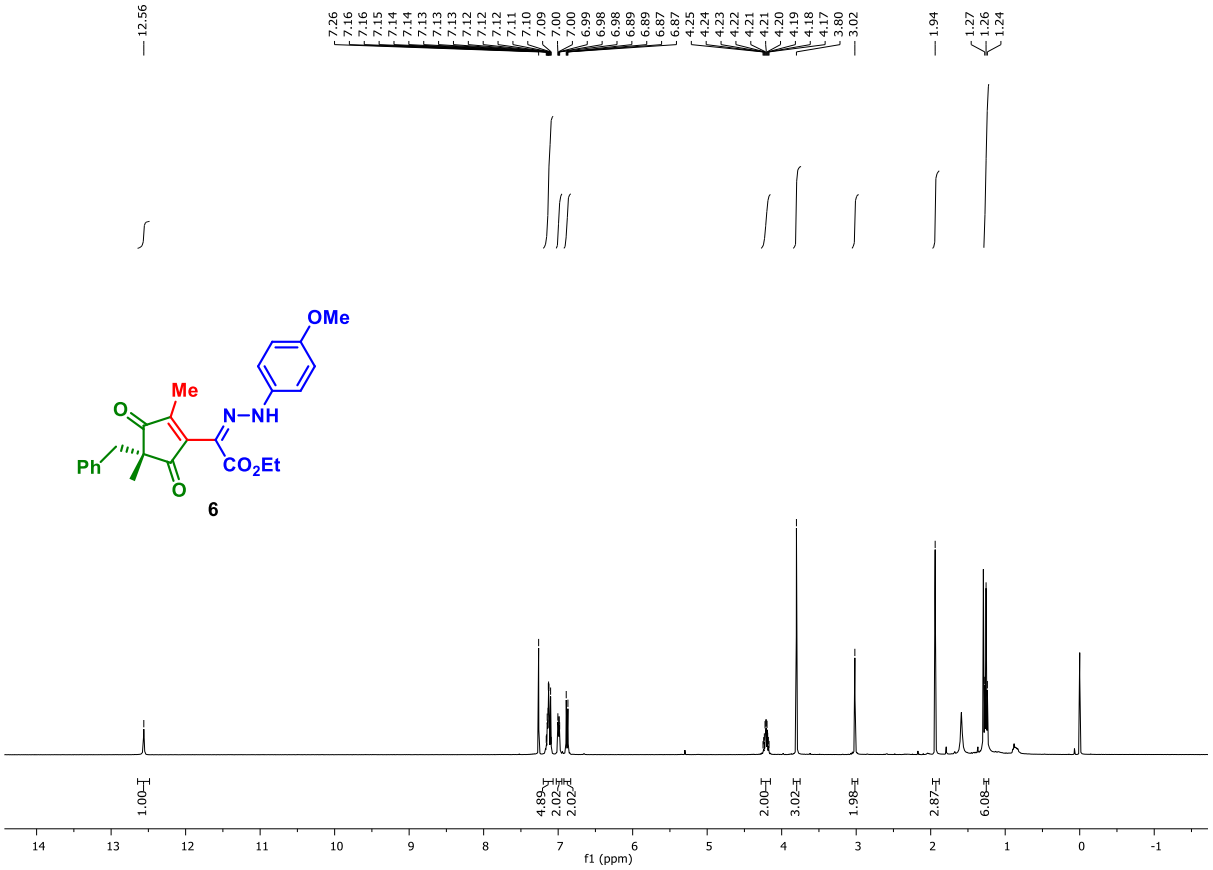
157.12
150.23
137.59
136.30
135.59
130.91
129.78
128.51
127.36
123.39
116.26
77.41
77.16
76.91
65.61
62.48
42.15
20.66
14.32
HO
O
N
N
Ph
CO2Et
O
5
f1 (ppm)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7.13
7.13
7.13
7.12
7.12
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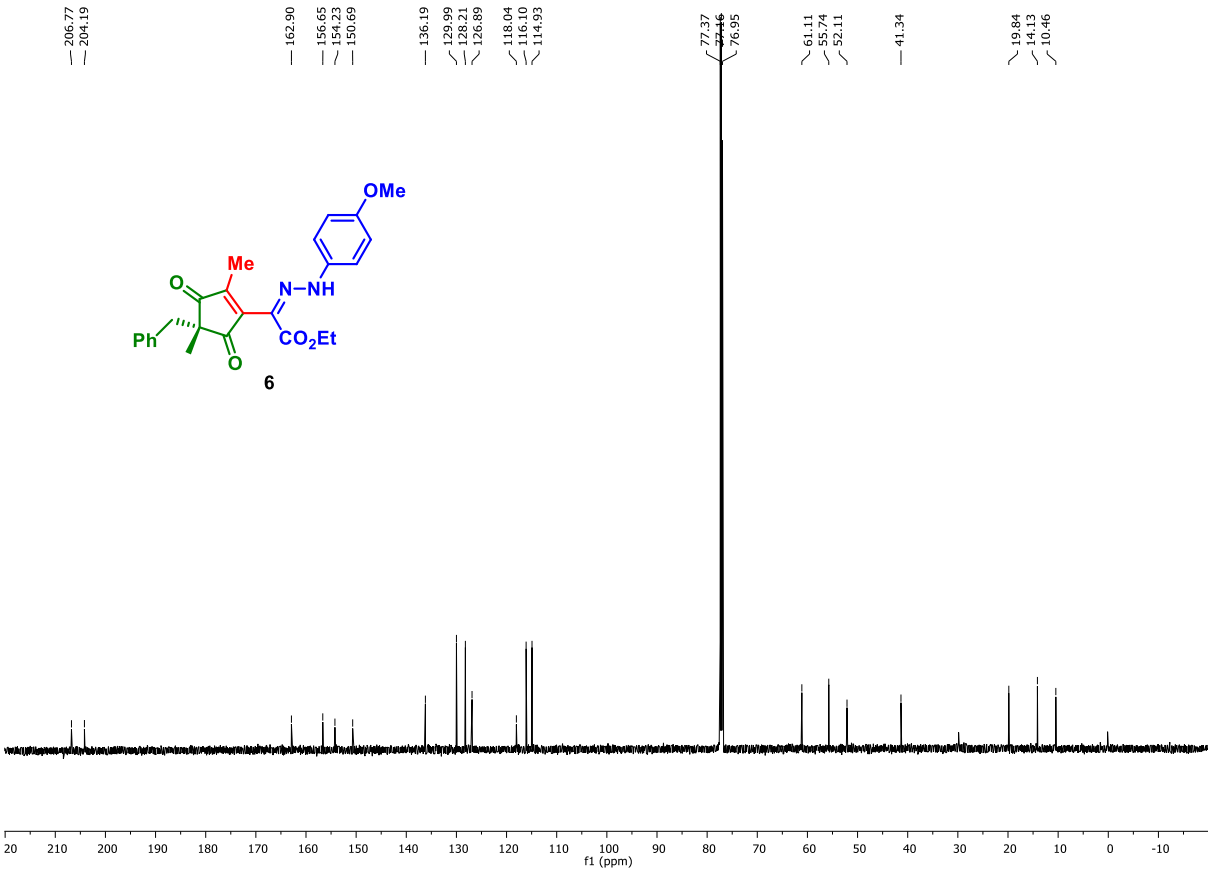
7.11
7.11
7.10
7.09
7.00
7.00
6.99
6.98
6.98
6.89
6.89
6.87
6.87
4.25
4.24
4.23
4.22
4.21
4.21
4.20
4.19
4.18
4.17
3.80
3.02
1.94
1.27
1.26
1.24
OMe
Me
N–NH
O
Ph
CO2Et
O
6
1.00
4.89
2.02
2.02
2.00
3.02
1.98
2.87
6.08
f1 (ppm)


206.77
204.19
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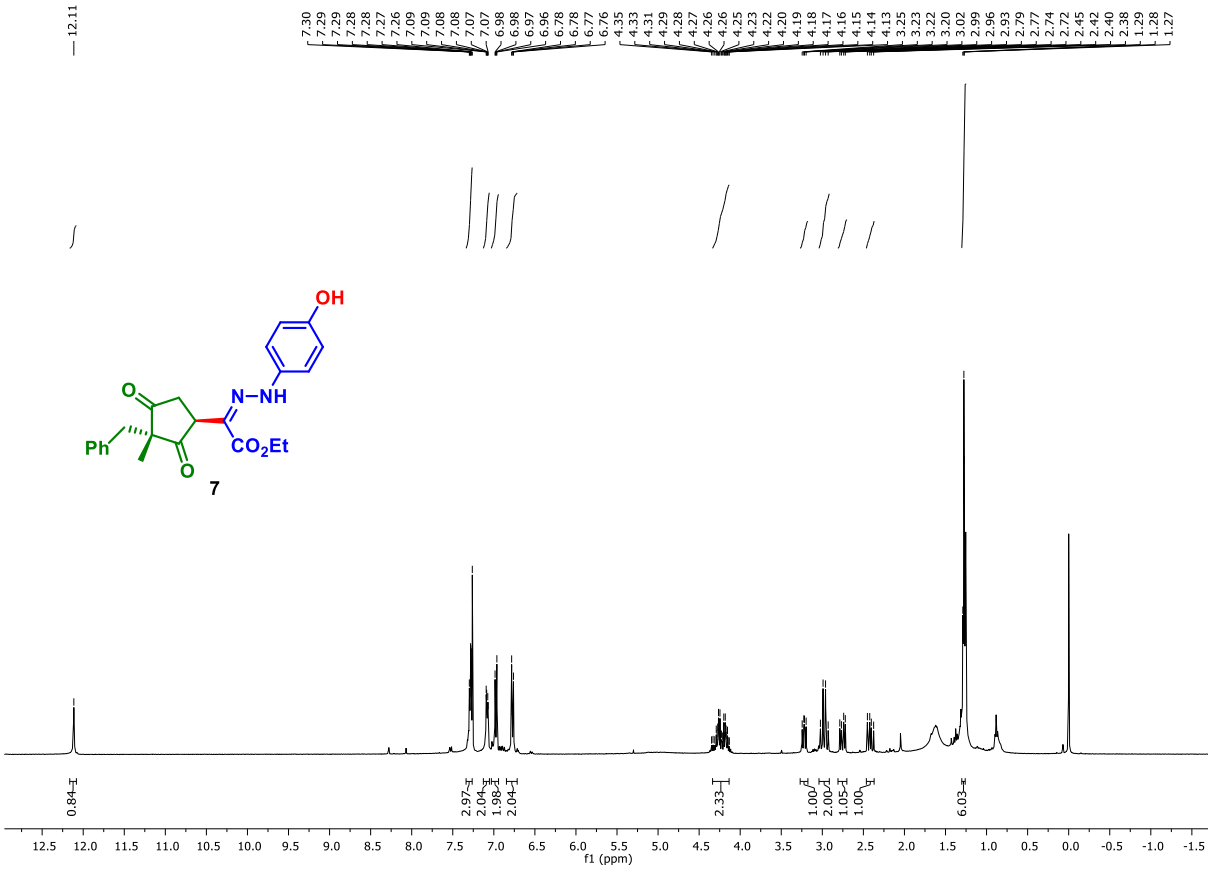
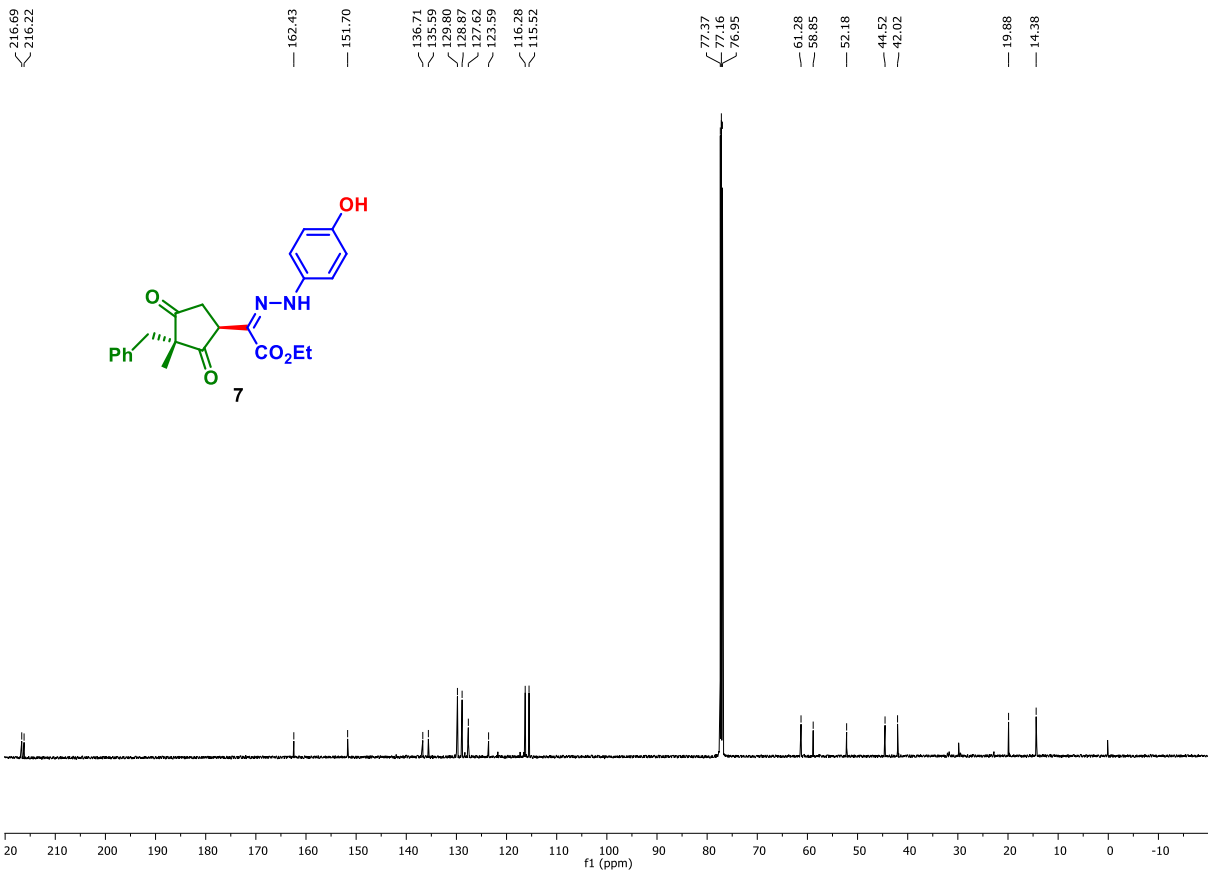
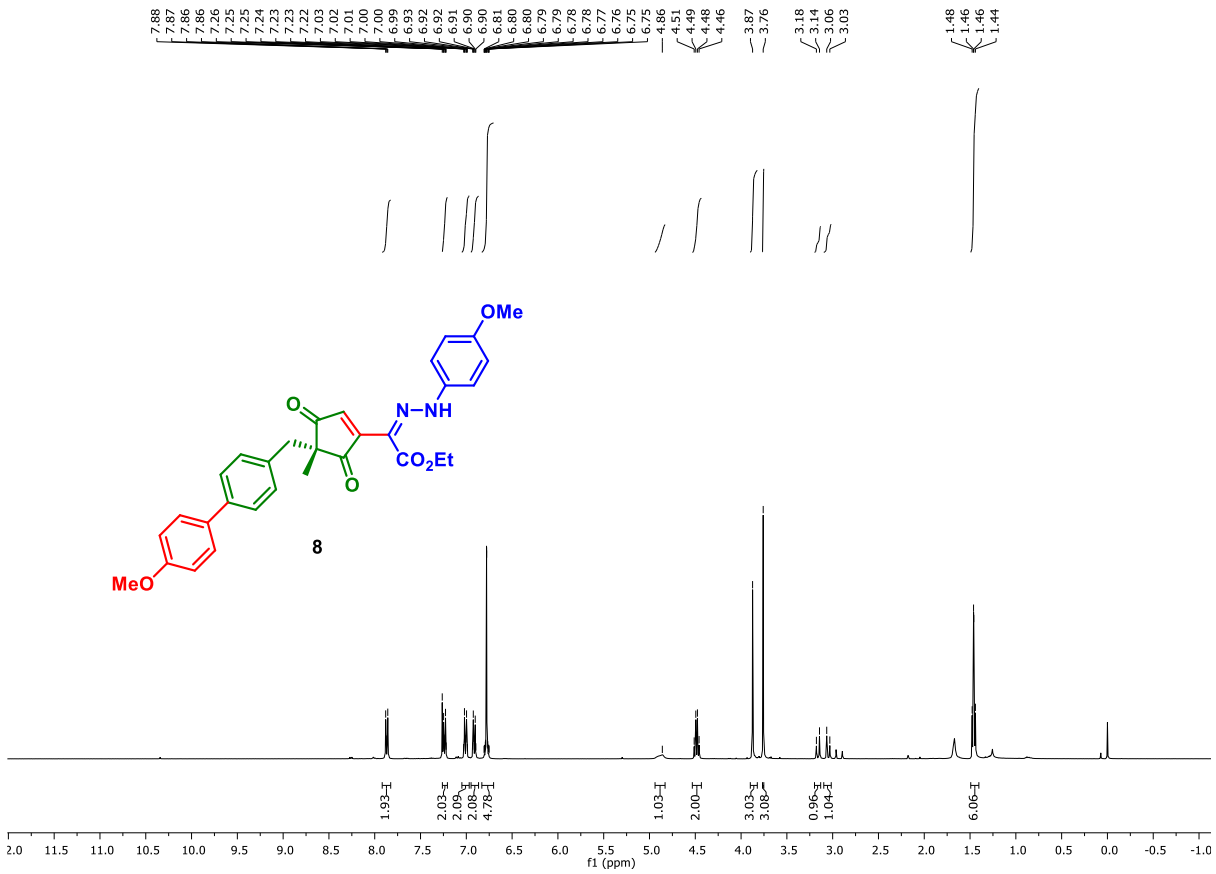
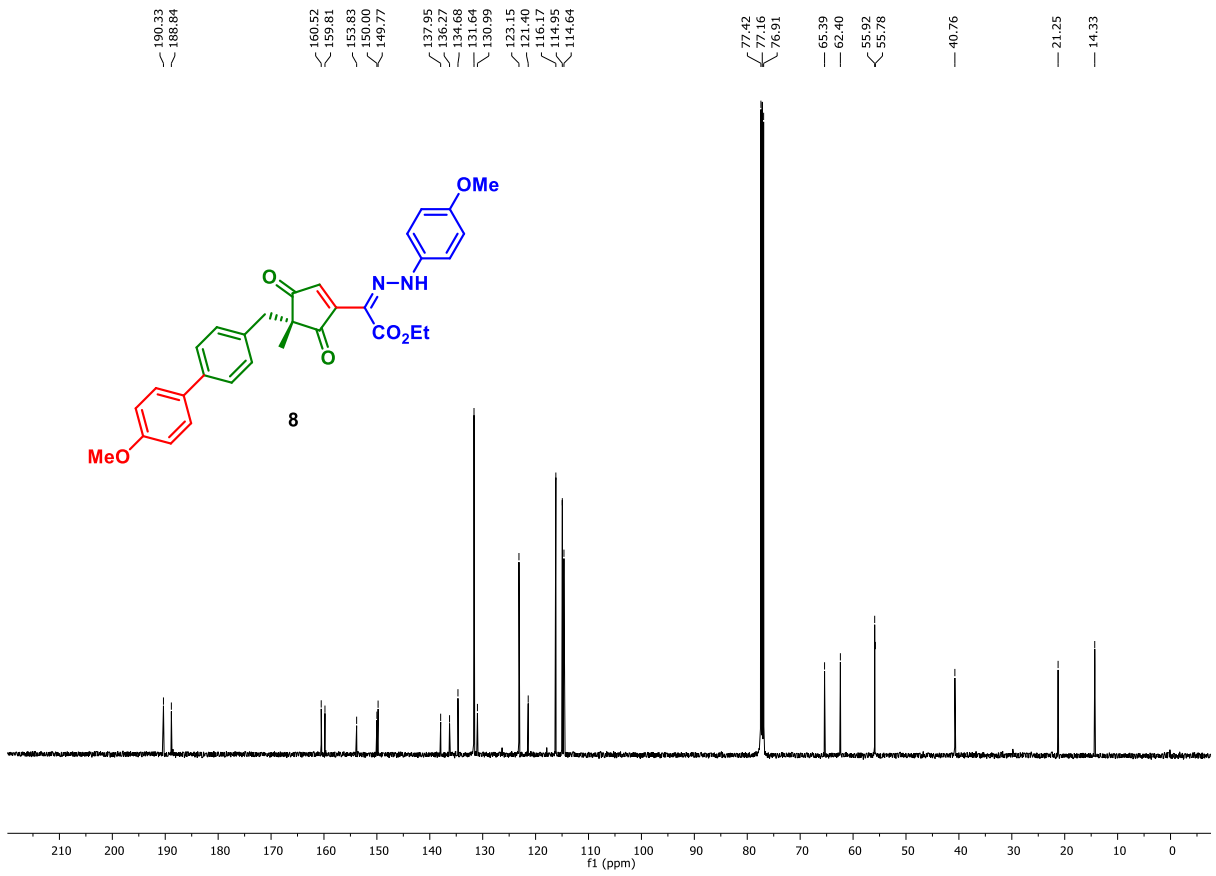
150.69
136.19
129.99
128.21
126.89
118.04
116.10
114.93
77.37
77.16
76.95
61.11
55.74
52.11
41.34
19.84
14.13
10.46
OMe
Me
N–NH
O
Ph
CO2Et
O
6
f1 (ppm)

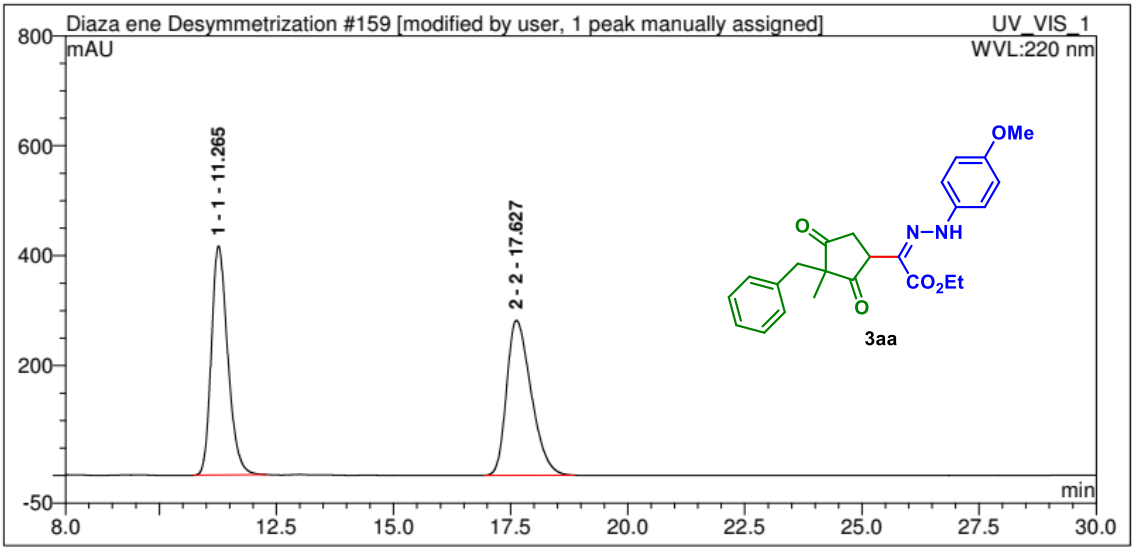

12.11
7.30 7.29 7.29 7.28 7.28 7.27 7.26 7.09 7.09 7.08 7.08 7.07 7.07 6.98 6.98 6.97 6.96 6.78 6.78 6.77 6.76
4.35 4.33 4.31 4.29 4.28 4.27 4.26 4.26 4.25 4.23 4.22 4.20 4.19 4.18 4.17 4.16 4.15 4.14 4.13 3.25 3.23 3.22 3.20 3.02 2.99 2.96 2.93 2.79 2.77 2.74 2.72 2.45 2.42 2.40 2.38 1.29 1.28 1.27
OH
N–NH
O
Ph
CO2Et
O
7
0.84 2.97 2.04 1.98 2.04 2.33 1.00 2.00 1.05 1.00 6.03
f1 (ppm)


216.69 216.22
162.43
151.70
136.71 135.59 129.80 128.87 127.62 123.59
116.28 115.52
77.37 77.16 76.95
61.28 58.85
52.18
44.52 42.02
19.88
14.38
OH
N–NH
O
Ph
CO2Et
O
7
f1 (ppm)

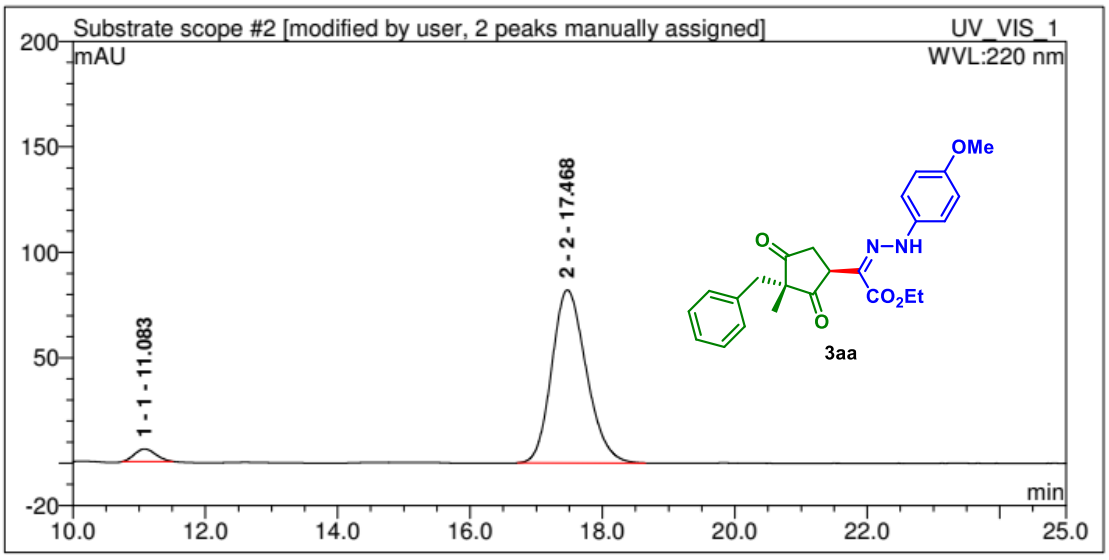

7.88 7.87 7.86 7.86 7.26 7.25 7.25 7.24 7.23 7.23 7.22 7.03 7.02 7.01 7.00 7.00 6.99 6.93 6.92 6.92 6.91 6.90 6.90 6.90 6.81 6.80 6.80 6.79 6.79 6.78 6.78 6.77 6.76 6.75 6.75 4.86 4.51 4.49 4.48 4.46 3.87 3.76 3.18 3.14 3.06 3.03 1.48 1.46 1.46 1.44
OMe
N–NH
CO2Et
O
O
MeO
8
1.93 2.03 2.09 2.08 4.78 1.03 2.00 3.03 3.08 0.96 1.04 6.06
f1 (ppm)


190.33 188.84 160.52 159.81 153.83 150.00 149.77 137.95 136.27 134.68 131.64 130.99 123.15 121.40 116.17 114.95 114.64 77.42 77.16 76.91 65.39 62.40 55.92 55.78 40.76 21.25 14.33
OMe
N–NH
CO2Et
O
O
MeO
8
f1 (ppm)

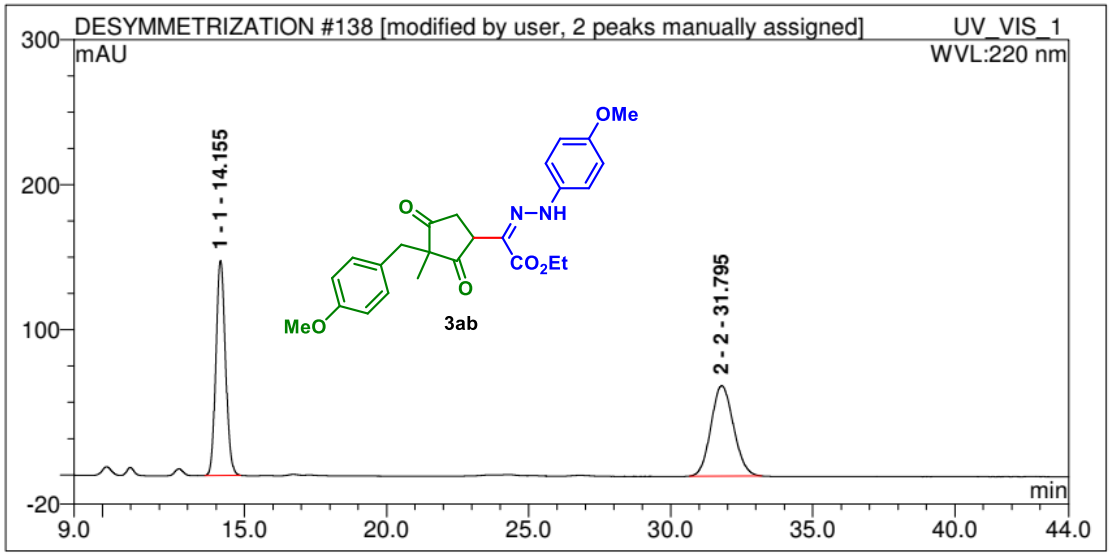
13. HPLC chromatogram of the products:



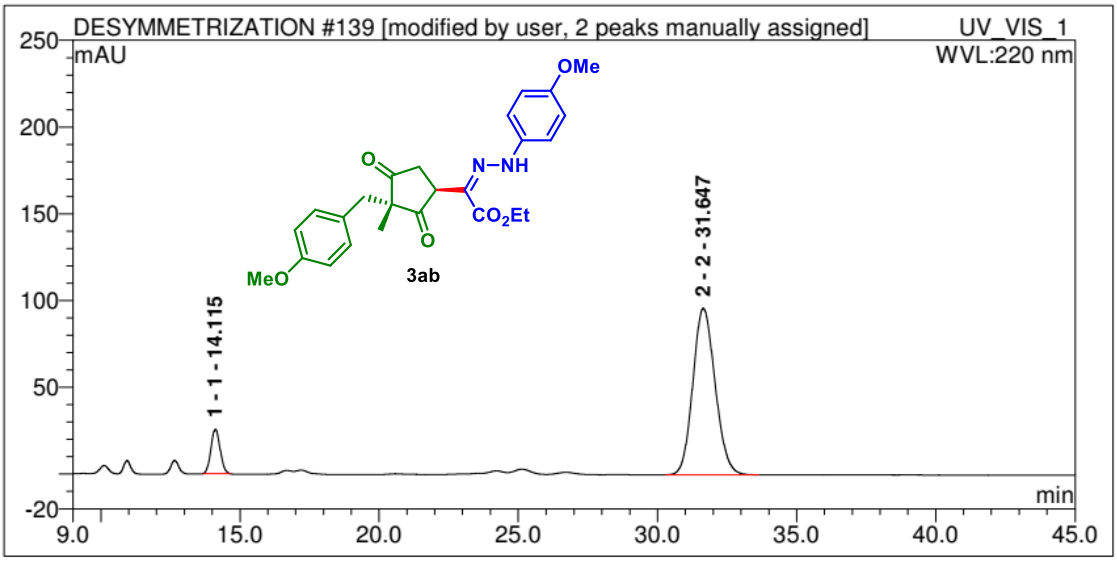
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	11.265	169.5394	49.7435331	417.0445	n.a.
2	2	17.62666667	171.2876	50.2564669	281.9515	n.a.



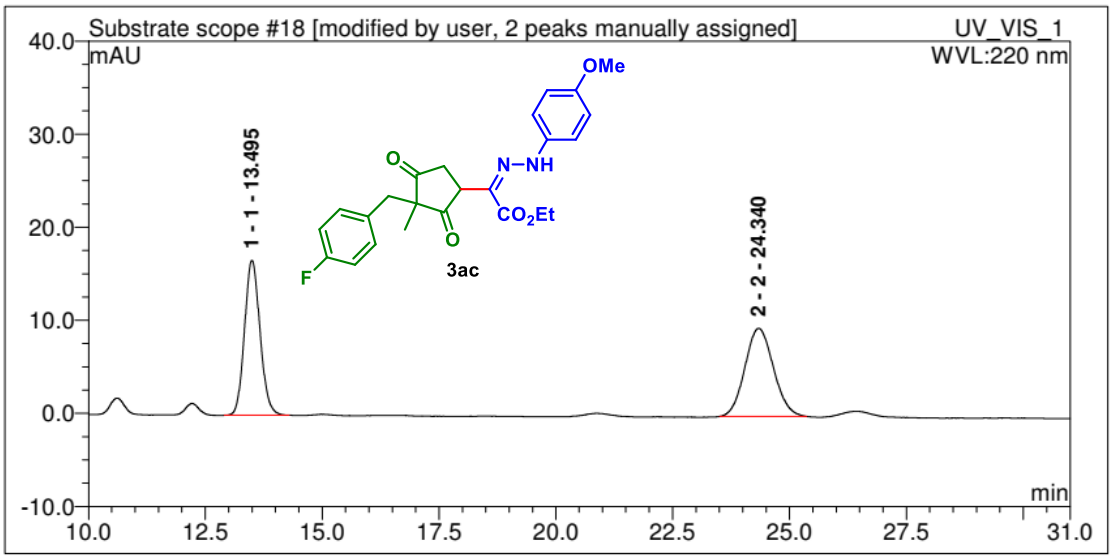
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	11.08	2.205346	4.255002122	5.96611	n.a.
2	2	17.47	49.624	95.74499788	81.998	n.a.



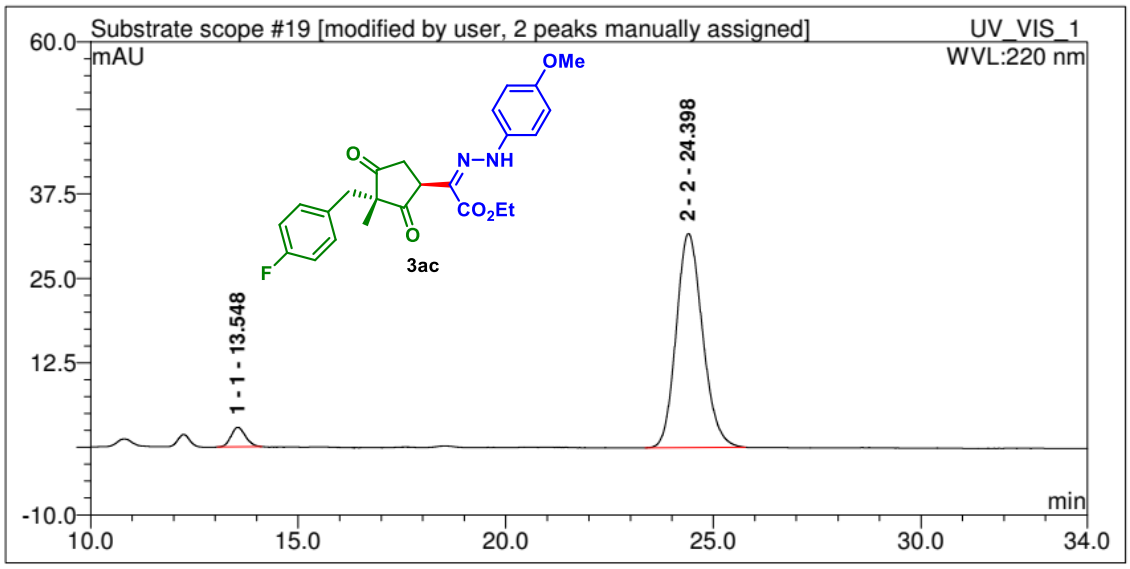
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	14.16	57.77494	50.20144409	147.7121	n.a.
2	2	31.80	57.311	49.79855591	62.286	n.a.



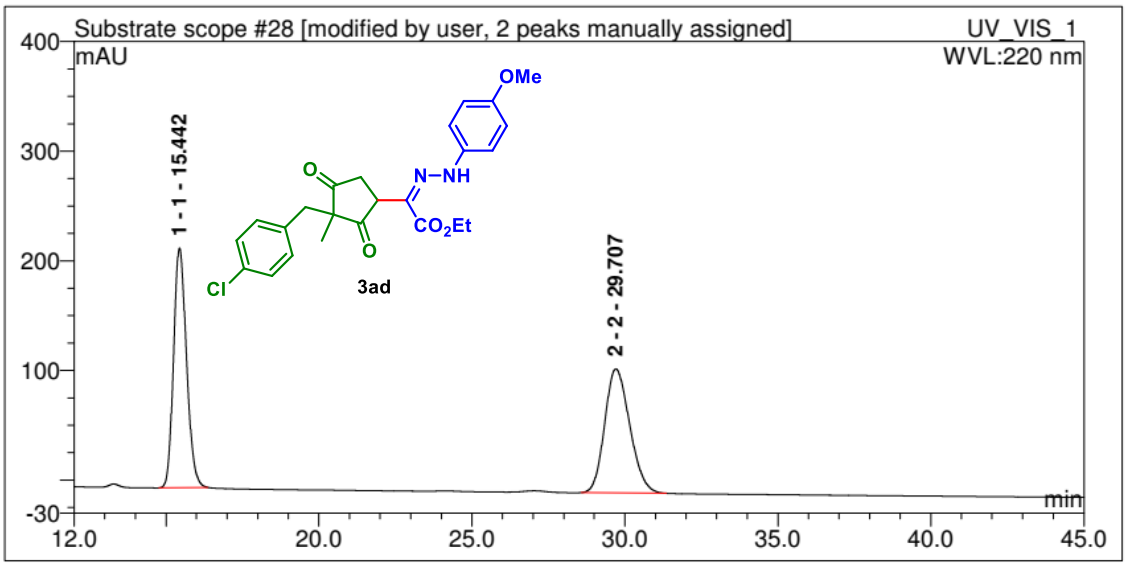
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	14.12	9.809155	9.911373824	25.6382	n.a.
2	2	31.65	89.160	90.08862618	95.974	n.a.



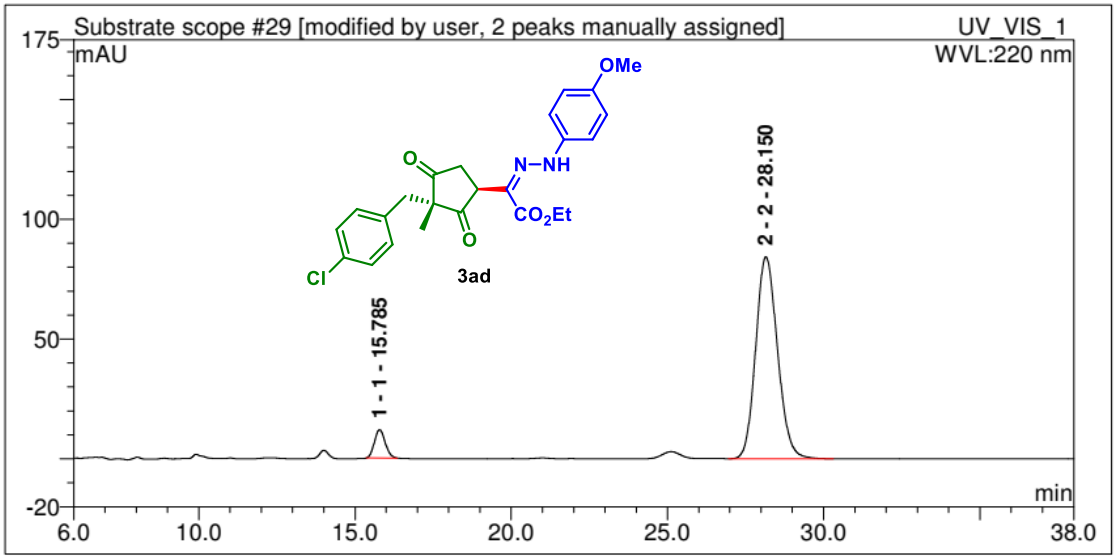
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	13.50	6.416684	48.90934974	16.63816	n.a.
2	2	24.34	6.703	51.09065026	9.471	n.a.



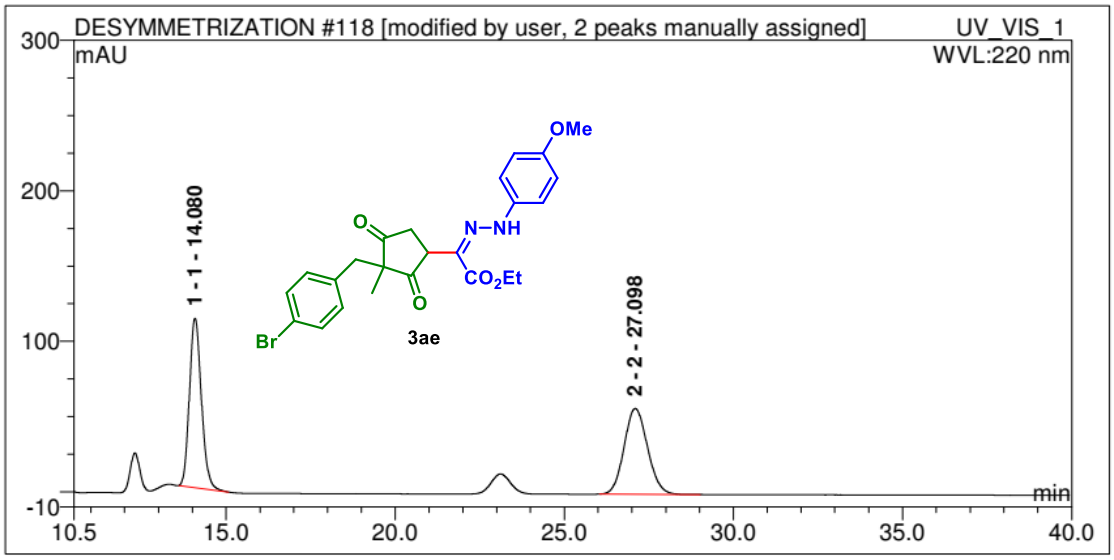
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	13.55	1.161889	4.742143532	2.87795	n.a.
2	2	24.40	23.339	95.25785647	31.655	n.a.



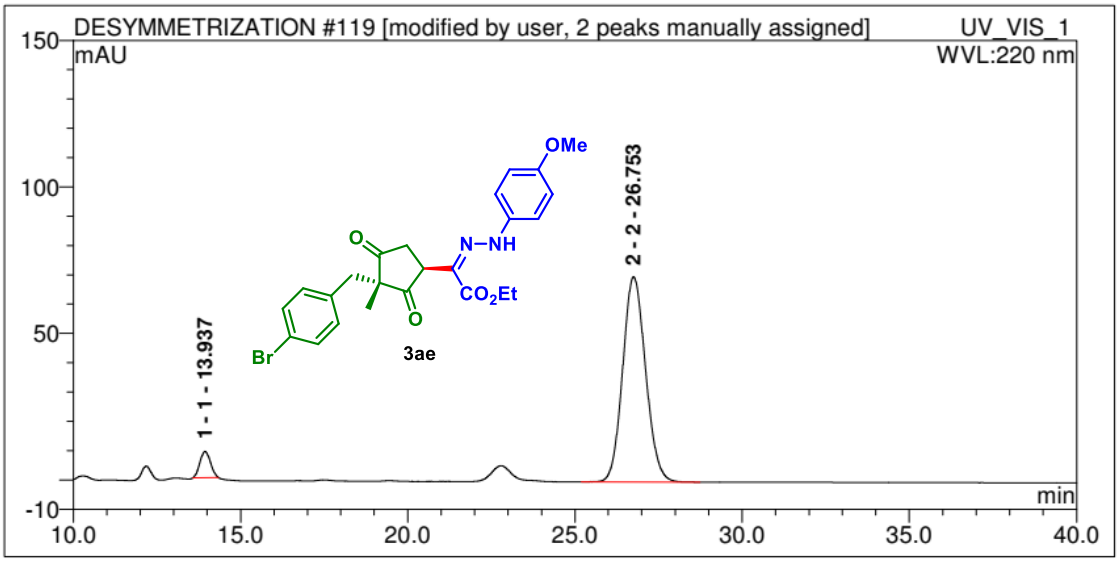
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	15.44	107.2853	49.98808051	218.6751	n.a.
2	2	29.71	107.336	50.01191949	113.006	n.a.



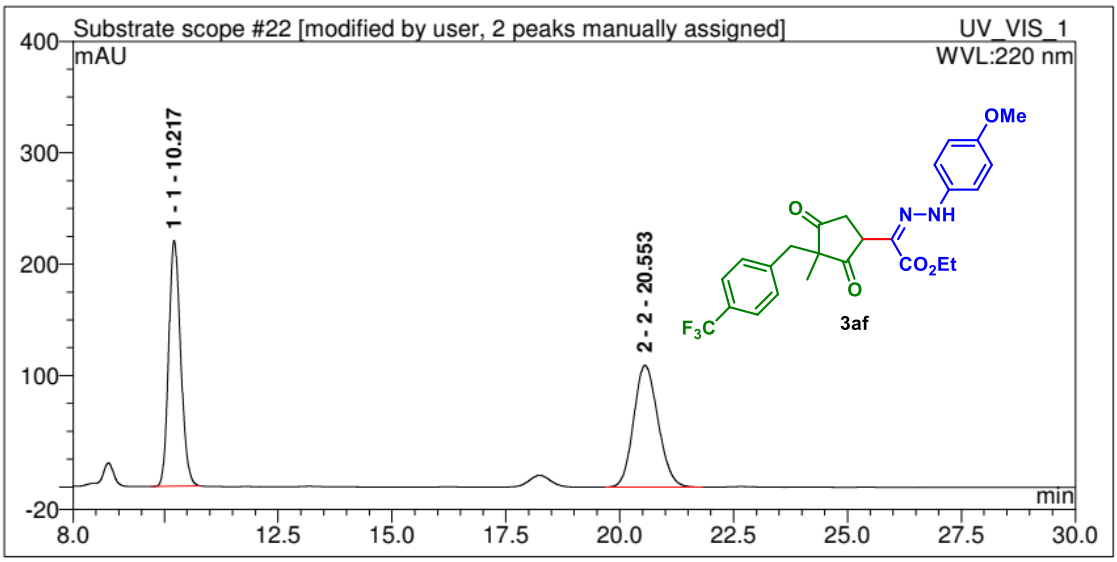
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	15.79	4.731273	6.48266107	11.81637	n.a.
2	2	28.15	68.252	93.51733893	84.344	n.a.



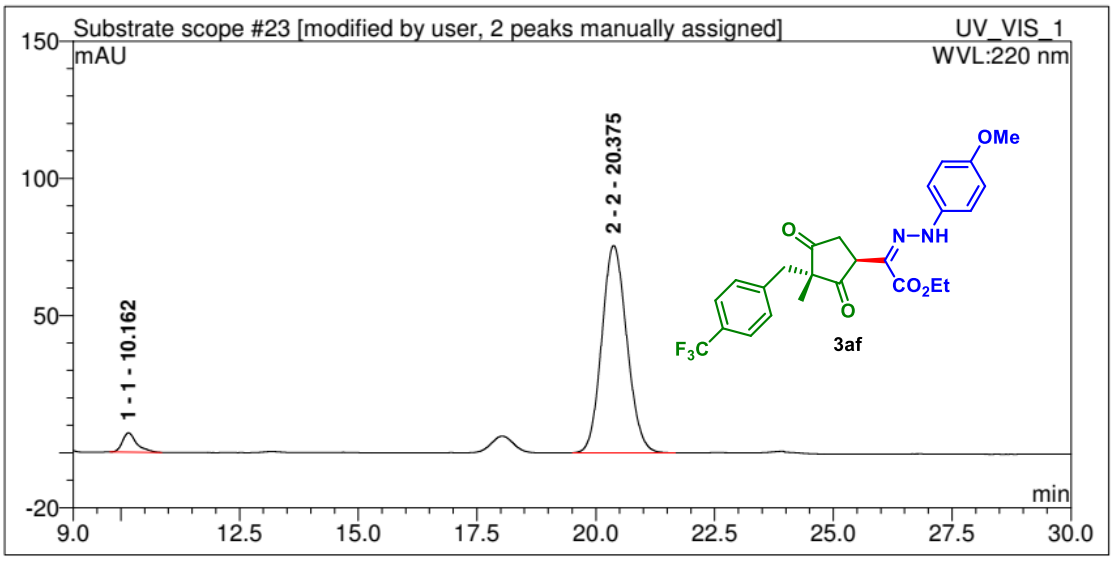
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	14.08	46.20699	50.24918728	112.5857	n.a.
2	2	27.10	45.749	49.75081272	57.027	n.a.



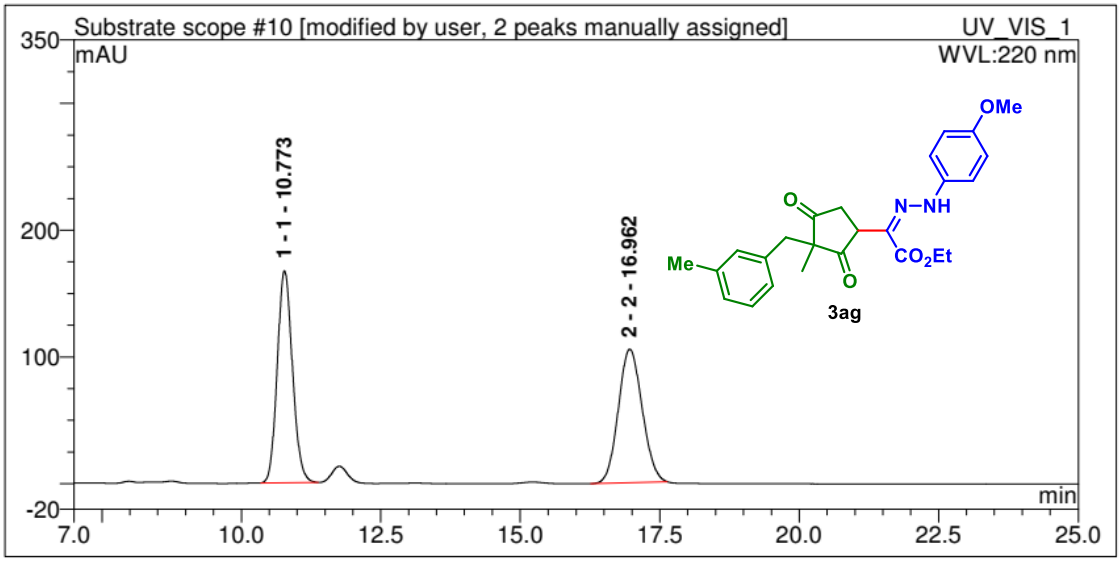
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	13.94	3.28822	5.576105392	8.97443	n.a.
2	2	26.75	55.682	94.42389461	70.055	n.a.



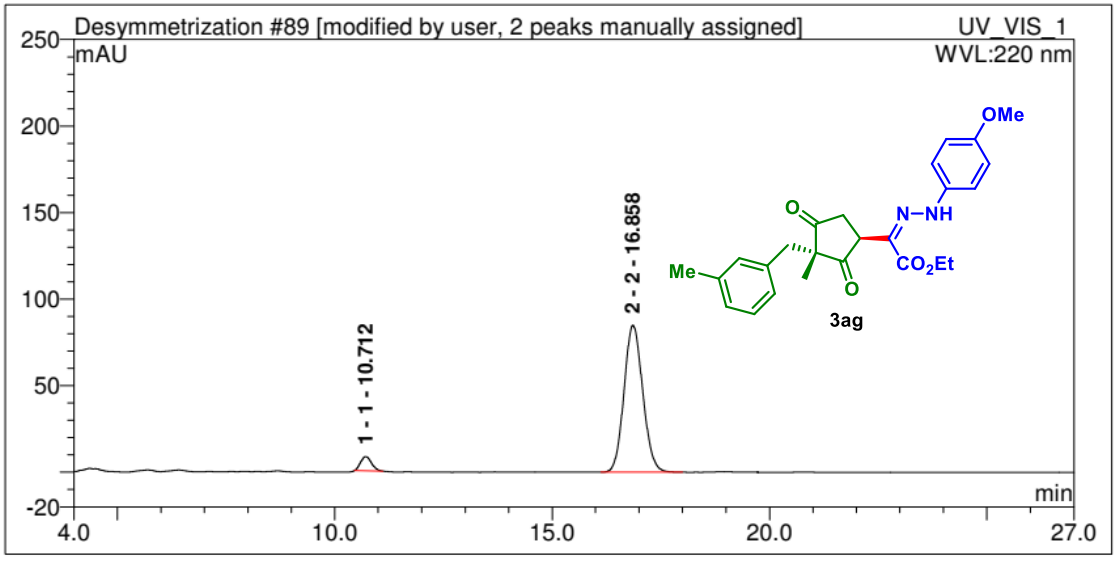
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	10.22	67.47583	49.79302964	220.6232	n.a.
2	2	20.55	68.037	50.20697036	109.446	n.a.



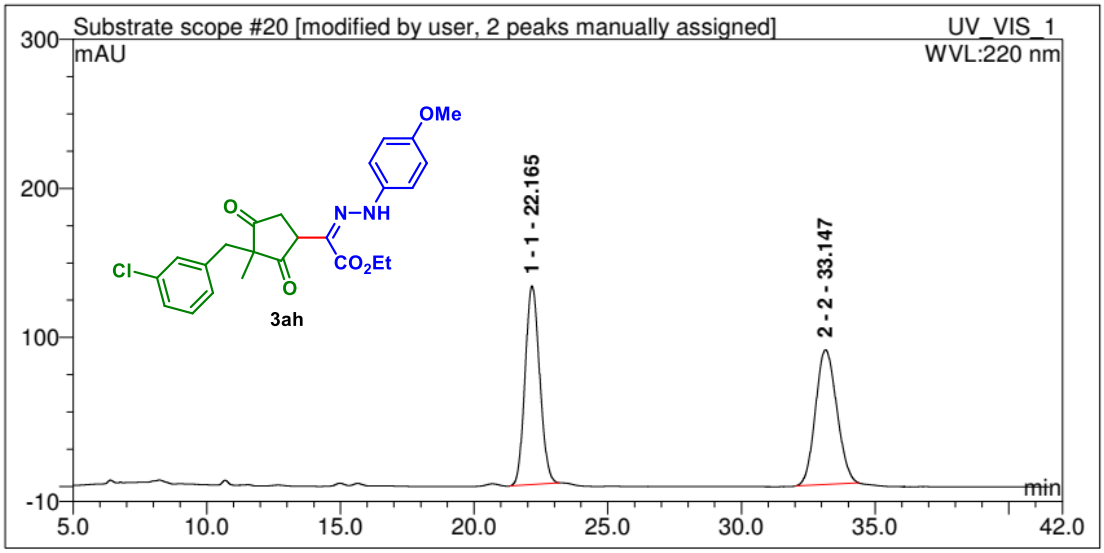
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	10.16	2.441155	5.003832498	7.03666	n.a.
2	2	20.38	46.345	94.9961675	75.521	n.a.



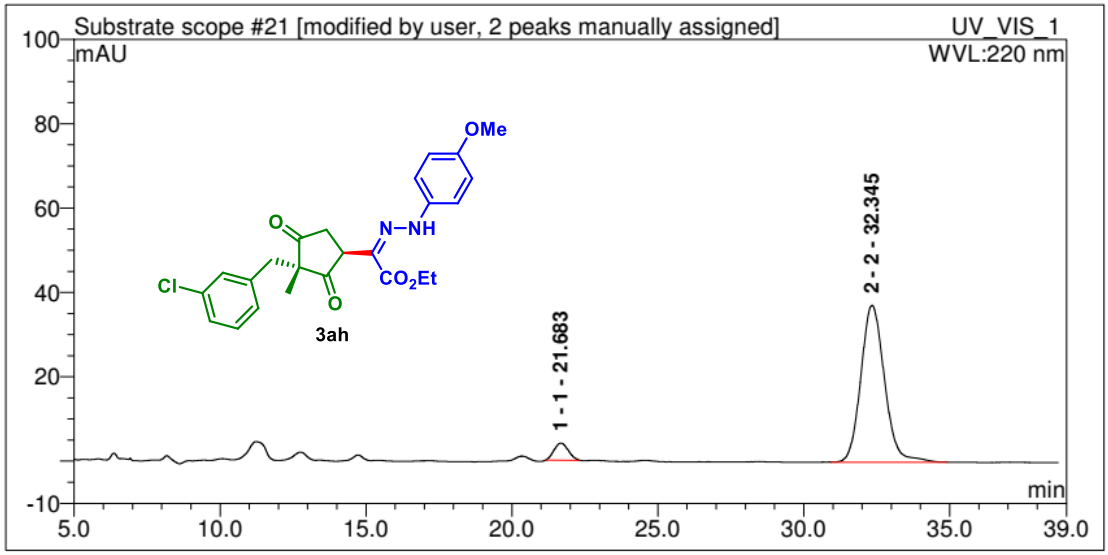
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	10.77	52.78691	50.27973145	167.2378	n.a.
2	2	16.96	52.200	49.72026855	105.295	n.a.



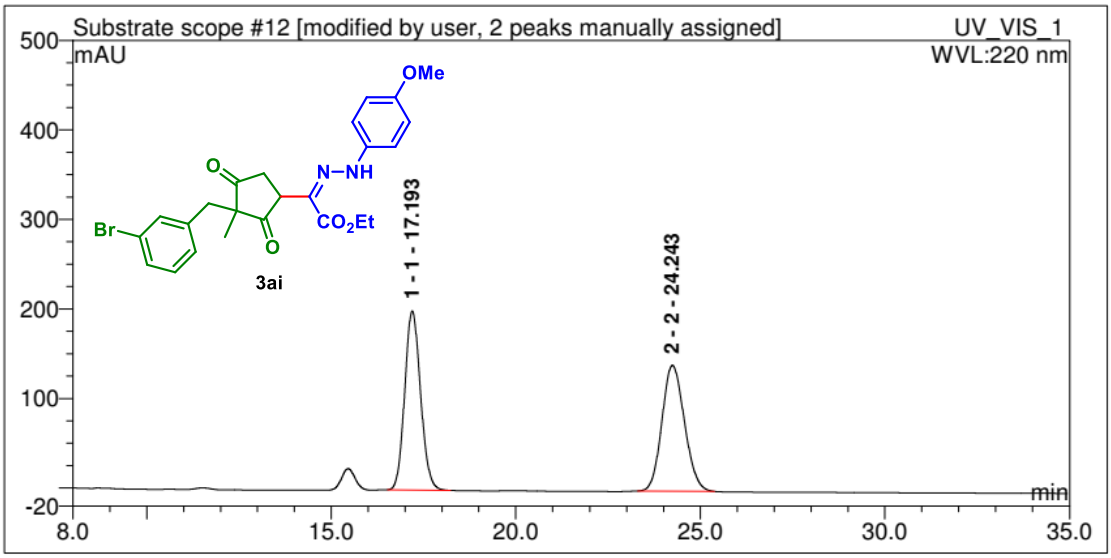
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	10.71	2.36954	5.275660793	8.1821	n.a.
2	2	16.86	42.545	94.72433921	84.890	n.a.



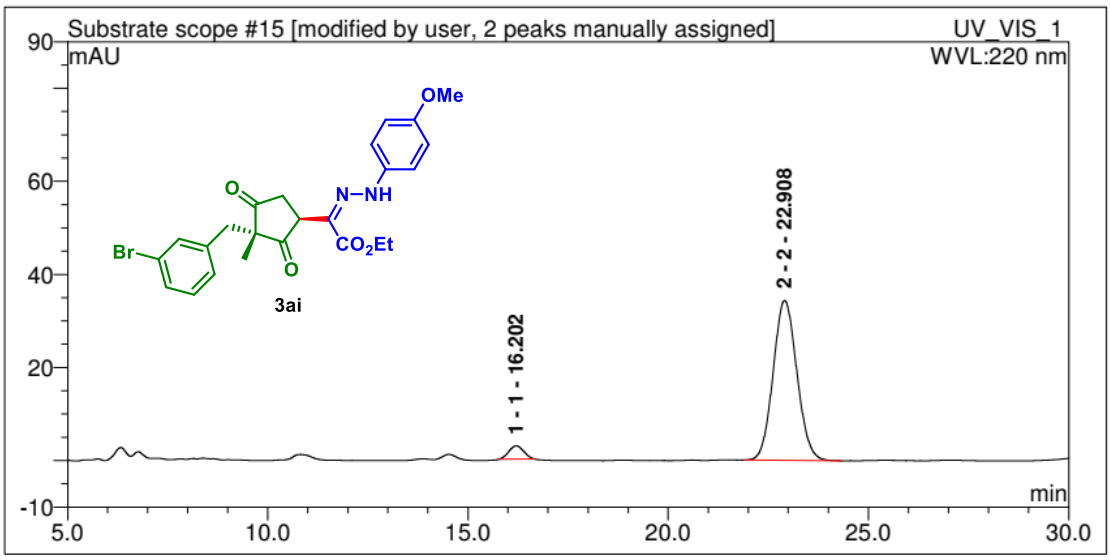
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	22.17	84.39849	50.20775754	133.3483	n.a.
2	2	33.15	83.700	49.79224246	90.500	n.a.



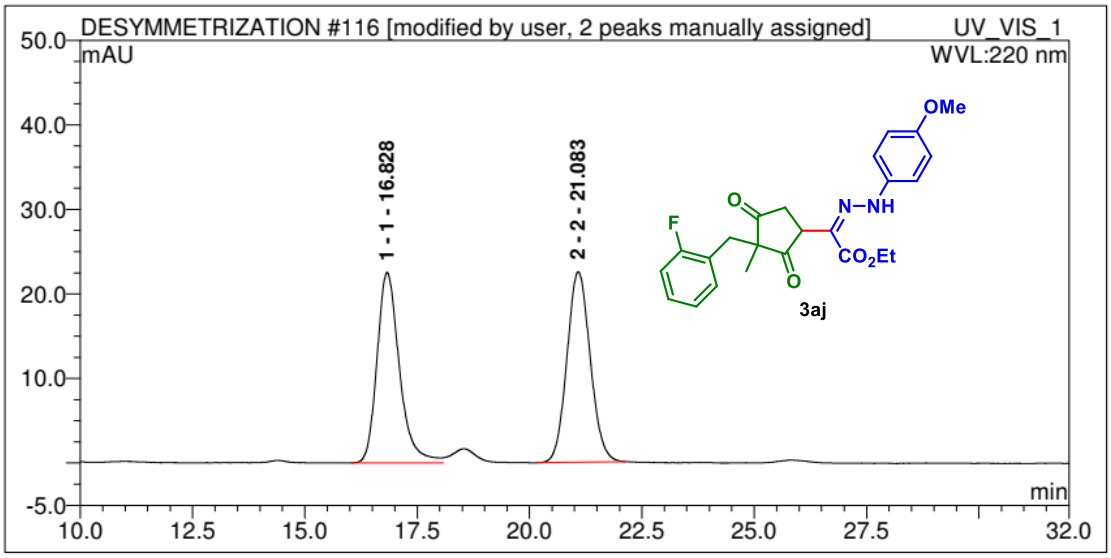
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	21.68	2.279328	6.118028065	4.03882	n.a.
2	2	32.35	34.977	93.88197193	37.192	n.a.



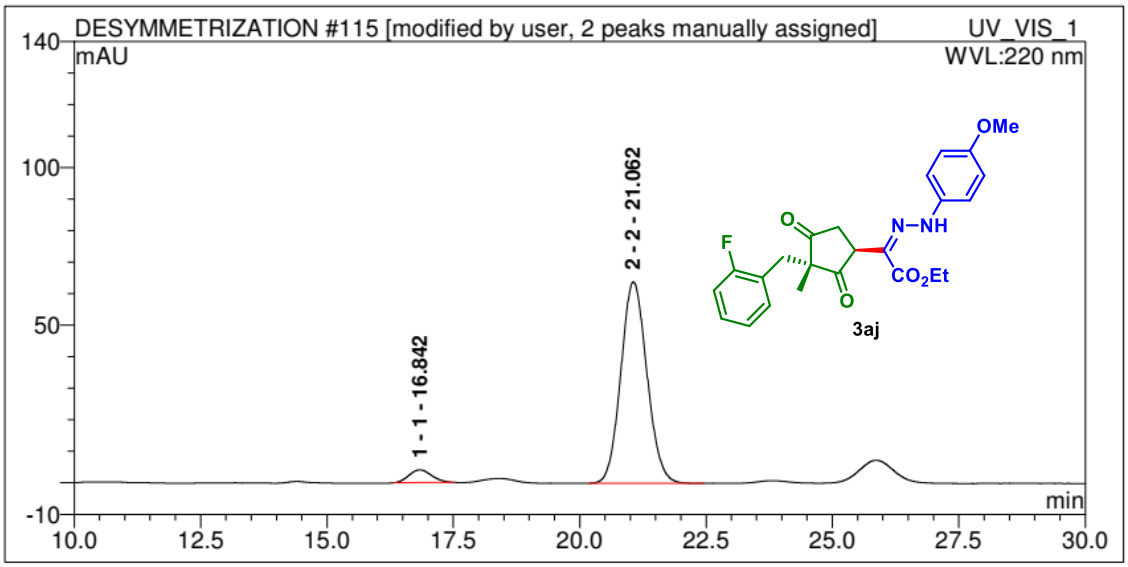
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	17.19	99.53906	50.01601078	199.9783	n.a.
2	2	24.24	99.475	49.98398922	140.663	n.a.



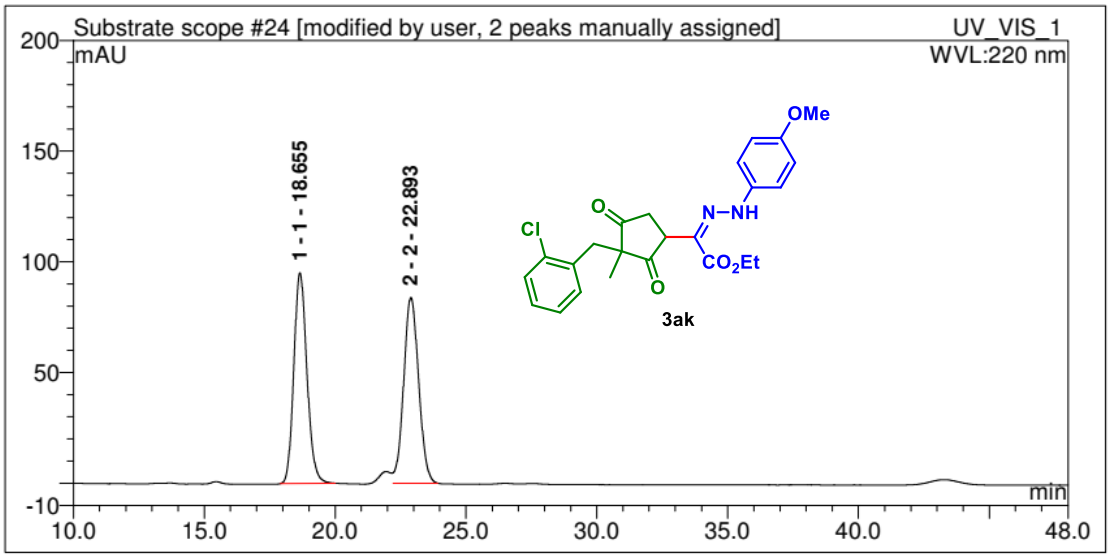
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	16.20	1.250233	5.024721158	2.86732	n.a.
2	2	22.91	23.631	94.97527884	34.342	n.a.



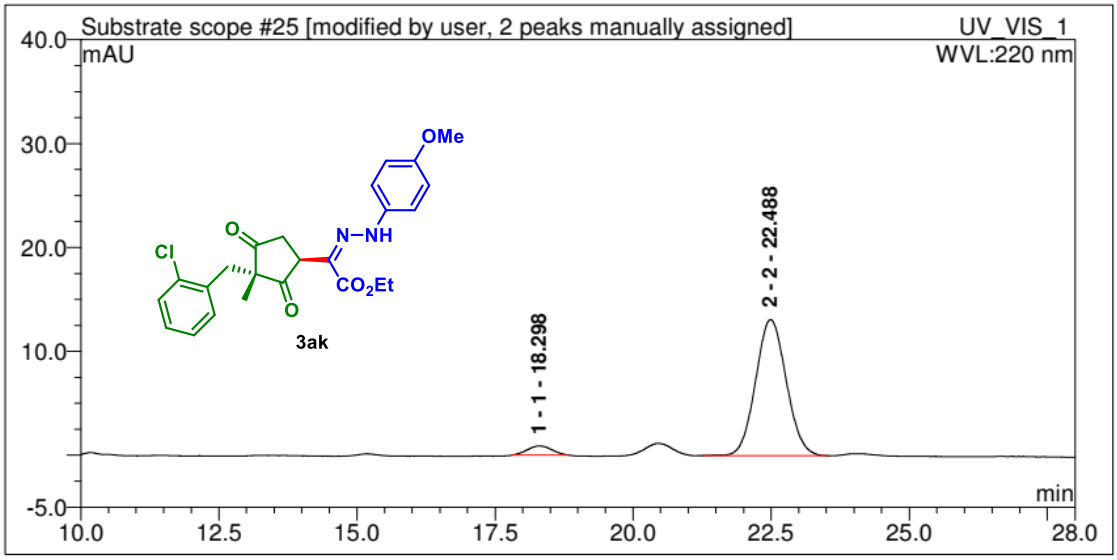
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	16.83	13.04391	49.08574121	22.51967	n.a.
2	2	21.08	13.530	50.91425879	22.541	n.a.



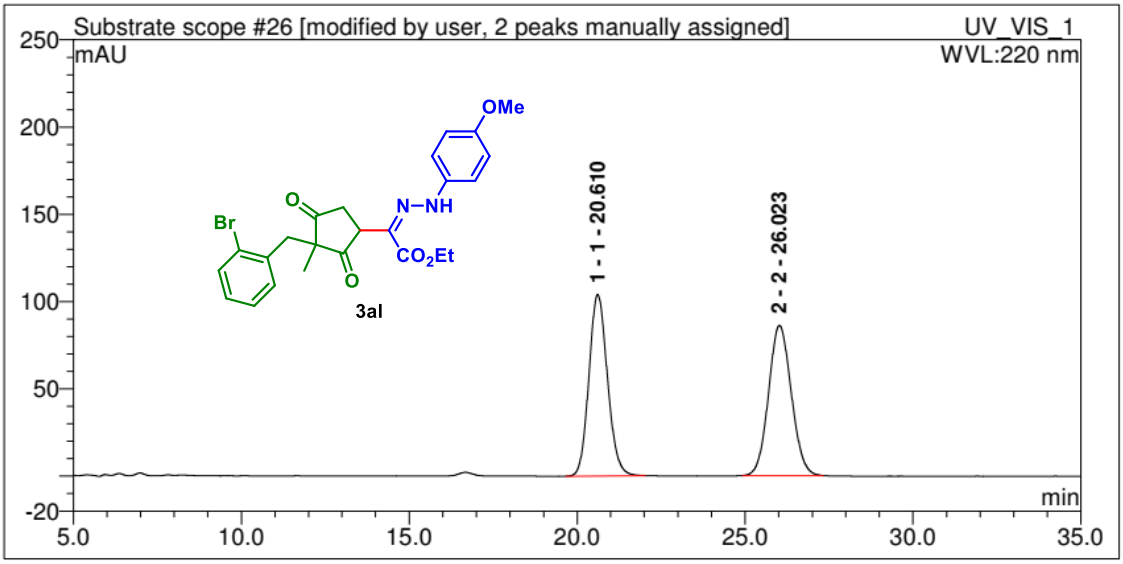
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	16.84	2.093752	5.188608216	4.05257	n.a.
2	2	21.06	38.259	94.81139178	63.892	n.a.



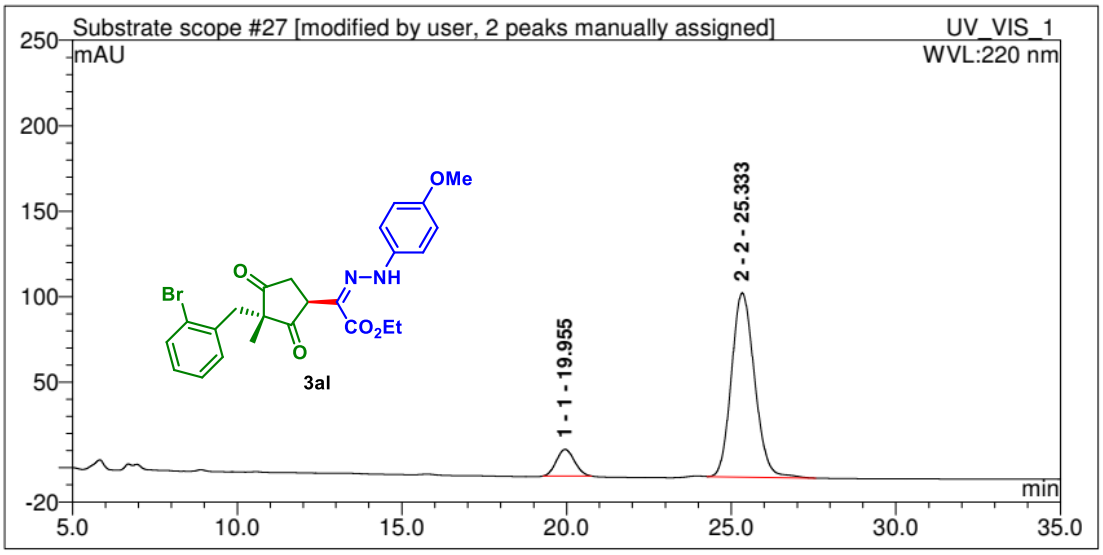
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	18.66	55.33137	49.82897257	95.2497	n.a.
2	2	22.89	55.711	50.17102743	83.930	n.a.



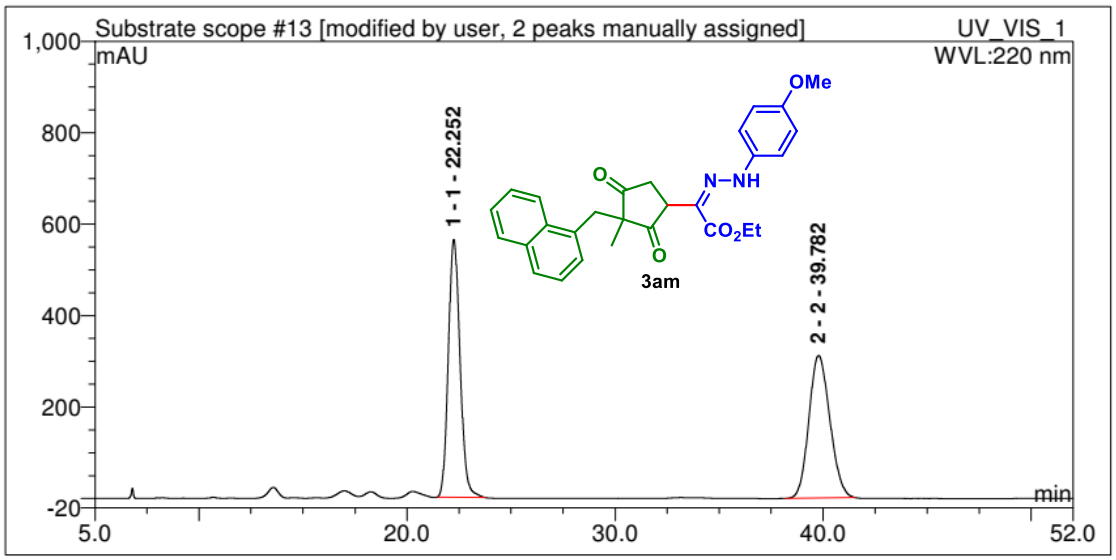
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	18.30	0.449241	5.051534668	0.8882	n.a.
2	2	22.49	8.444	94.94846533	13.110	n.a.



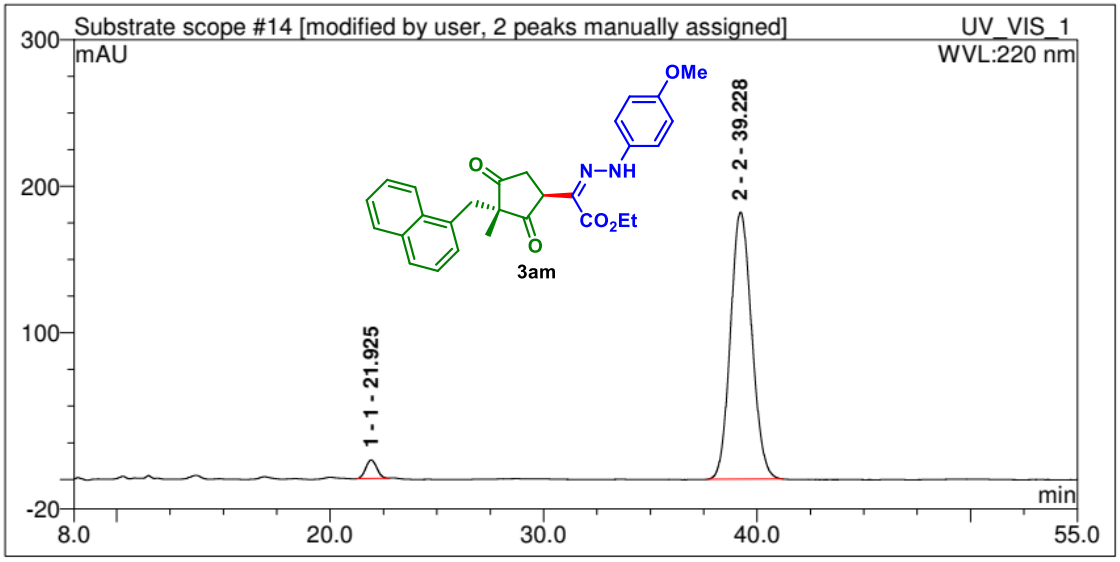
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	20.61	66.62214	49.62100584	104.0277	n.a.
2	2	26.02	67.640	50.37899416	85.978	n.a.



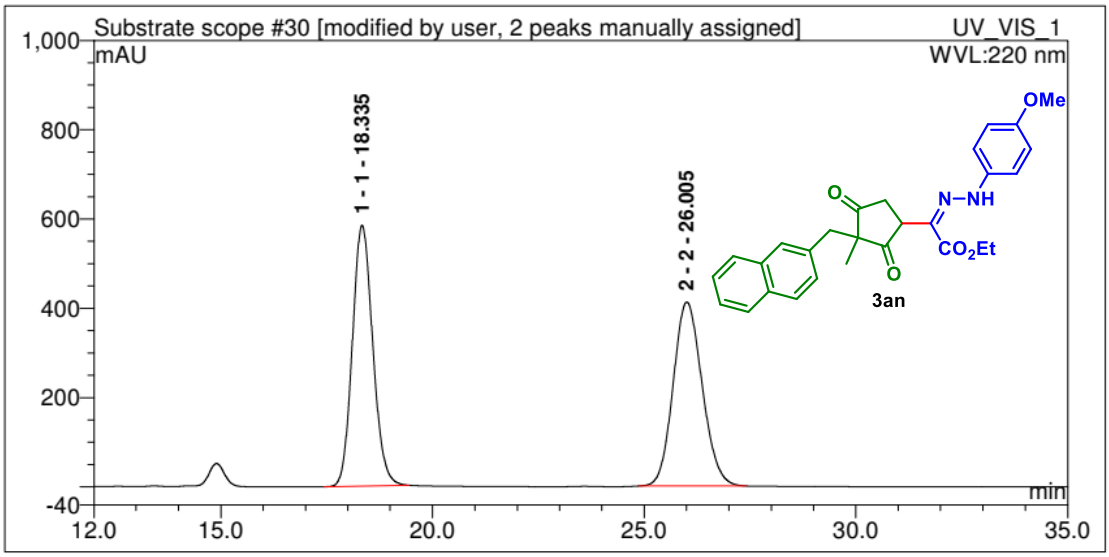
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	19.96	9.969988	10.19517222	15.60891	n.a.
2	2	25.33	87.821	89.80482778	107.720	n.a.



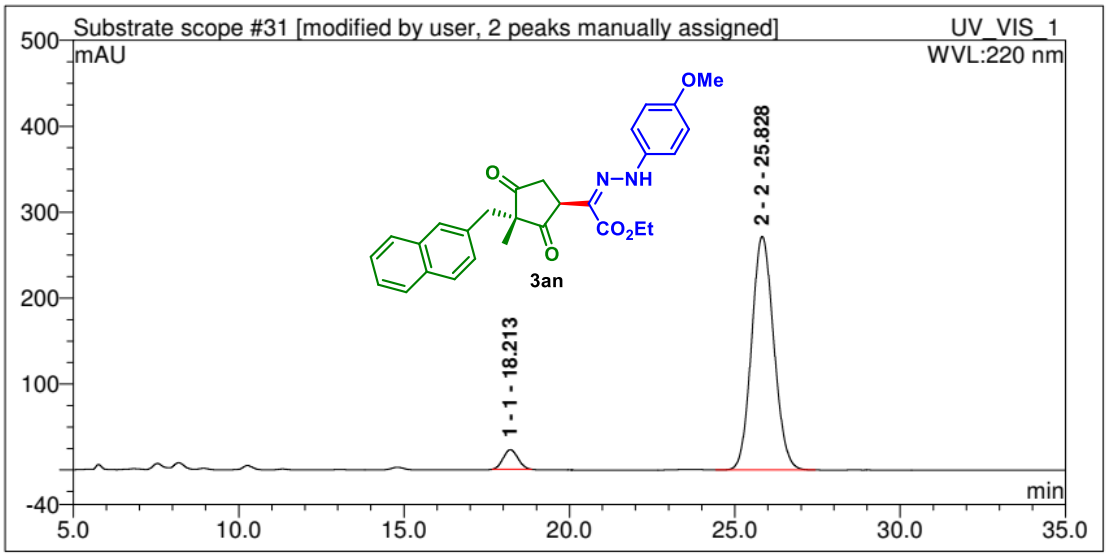
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	22.25	367.998	50.28589707	564.0957	n.a.
2	2	39.78	363.814	49.71410293	311.476	n.a.



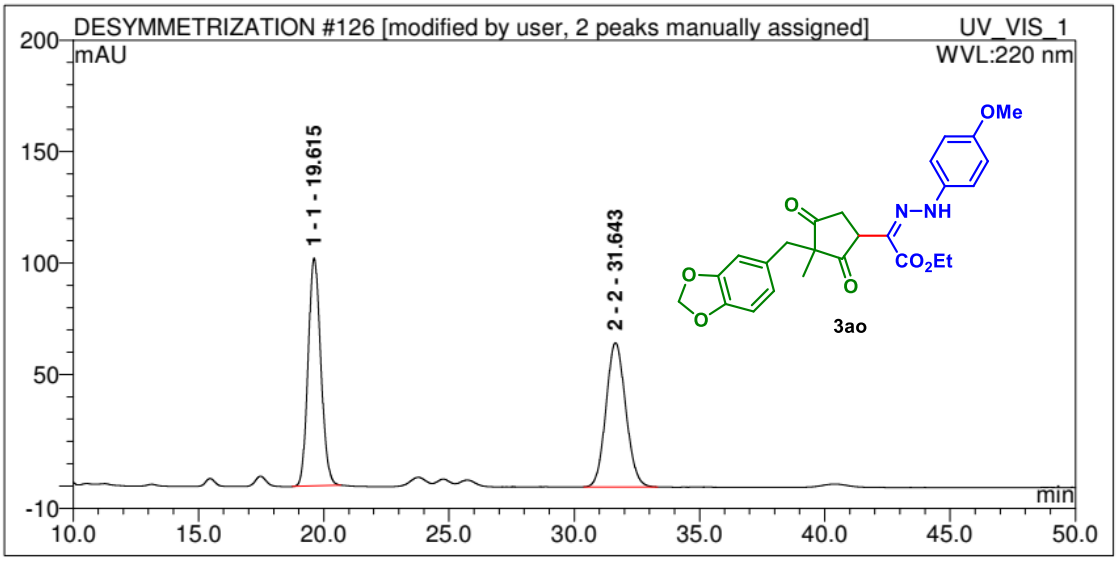
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	21.93	7.548438	3.463426656	12.64327	n.a.
2	2	39.23	210.399	96.53657334	182.228	n.a.



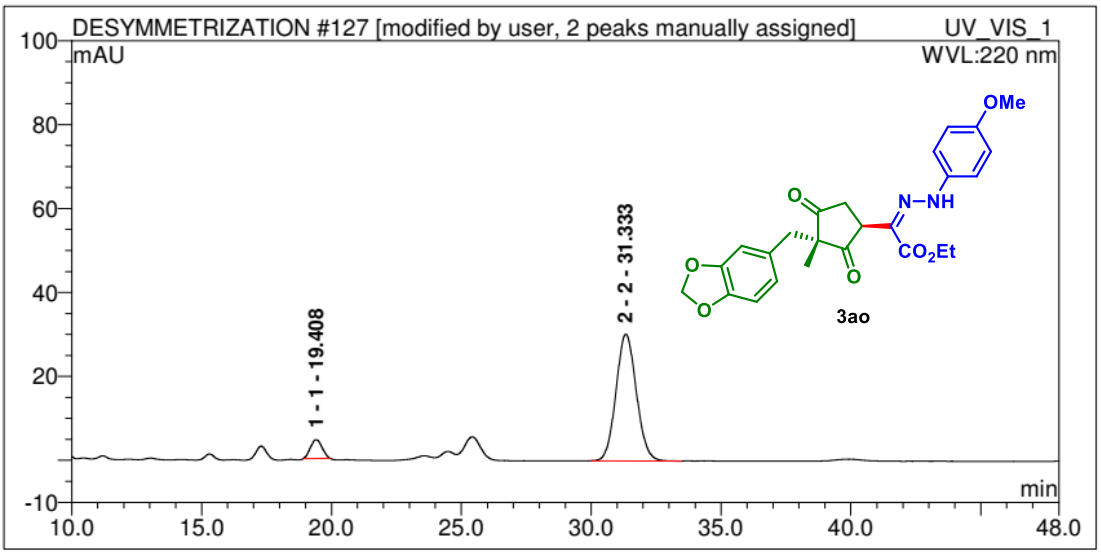
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	18.34	326.7501	49.95740671	584.4342	n.a.
2	2	26.01	327.307	50.04259329	411.995	n.a.



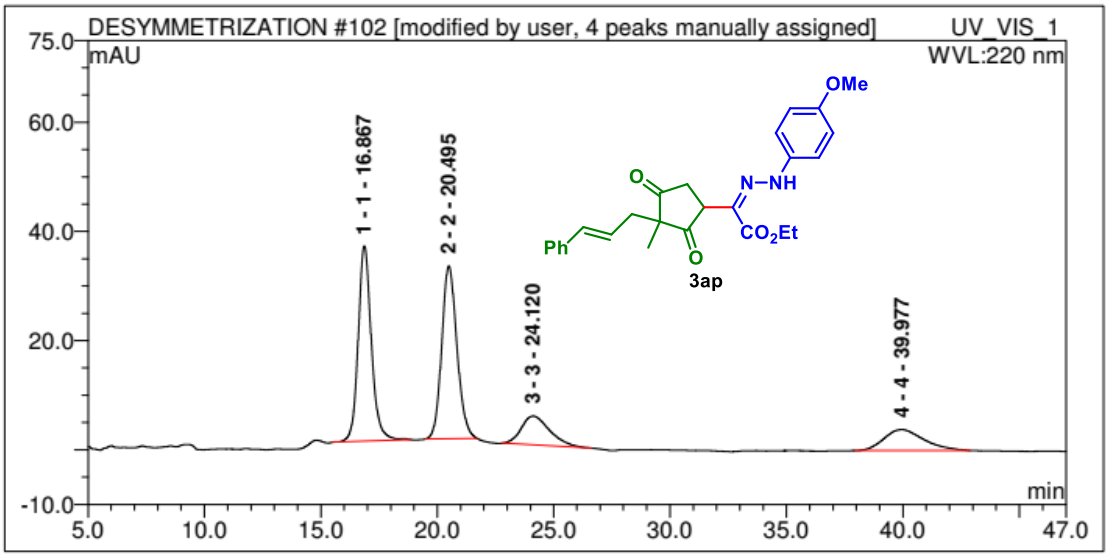
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	18.21	11.83788	5.298938427	22.82828	n.a.
2	2	25.83	211.563	94.70106157	271.642	n.a.



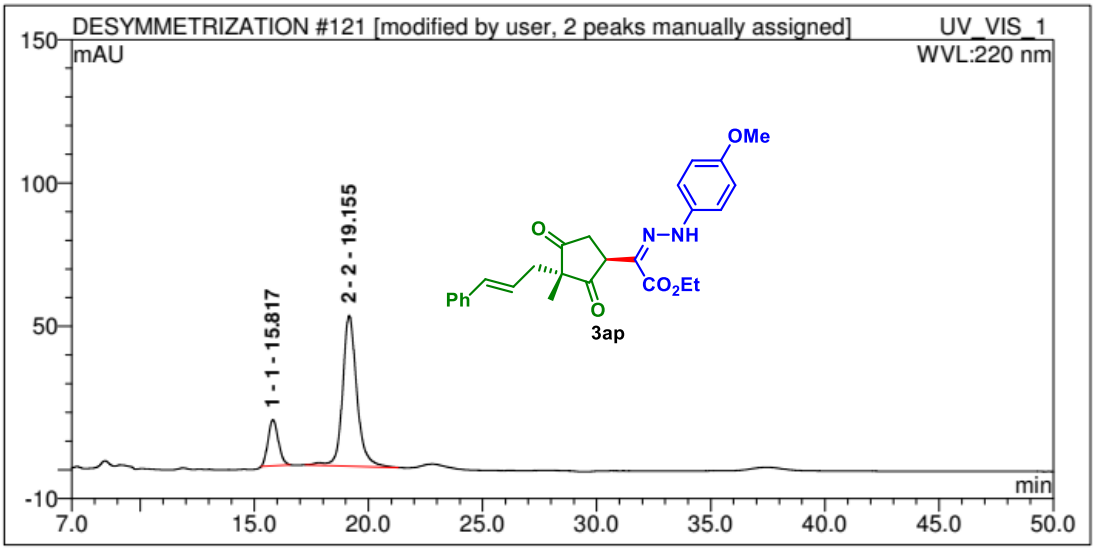
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	19.62	60.16649	50.43097135	102.2156	n.a.
2	2	31.64	59.138	49.56902865	64.622	n.a.



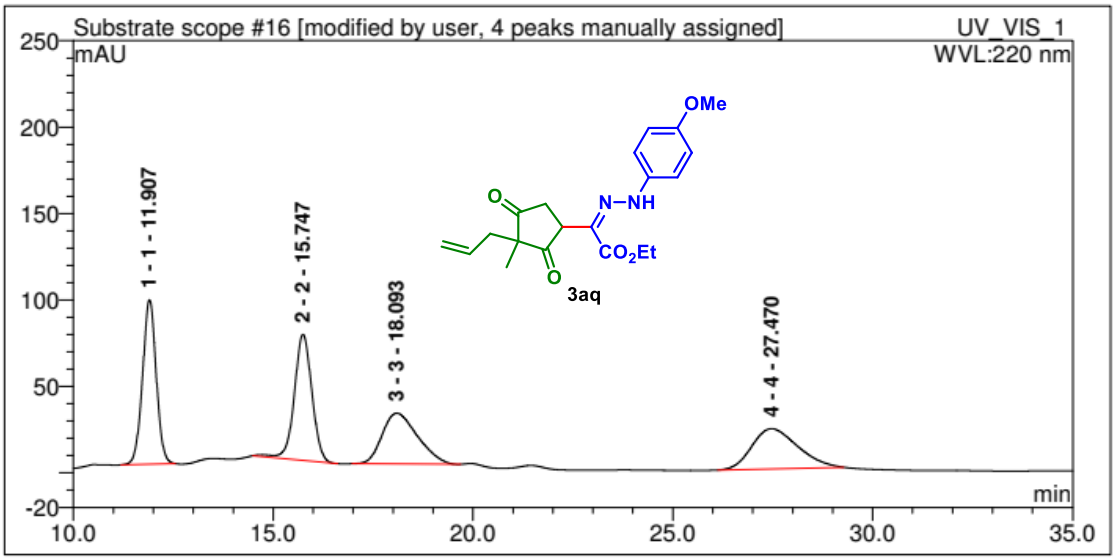
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	19.41	2.342643	7.879496117	4.50326	n.a.
2	2	31.33	27.388	92.12050388	30.173	n.a.



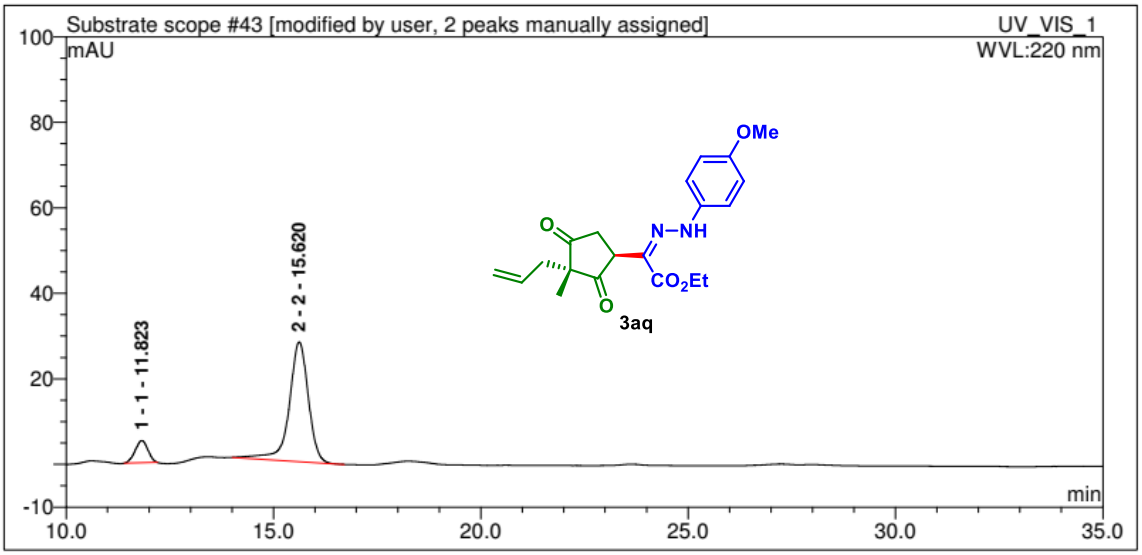
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	16.87	23.57825	37.58415971	35.75202	n.a.
2	2	20.50	23.99774	38.25282949	31.66729	n.a.
3	3	24.12	7.53258	12.00707099	5.29272	n.a.
4	4	39.98	7.626	12.15593981	3.835	n.a.



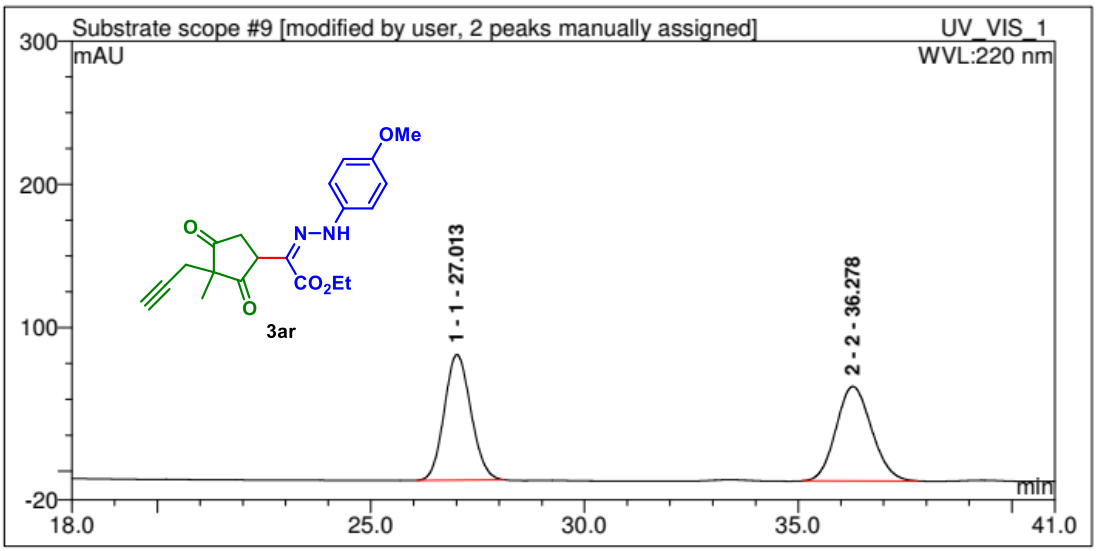
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	15.82	8.351399	18.00448944	16.0101	n.a.
2	2	19.16	38.034	81.99551056	52.555	n.a.



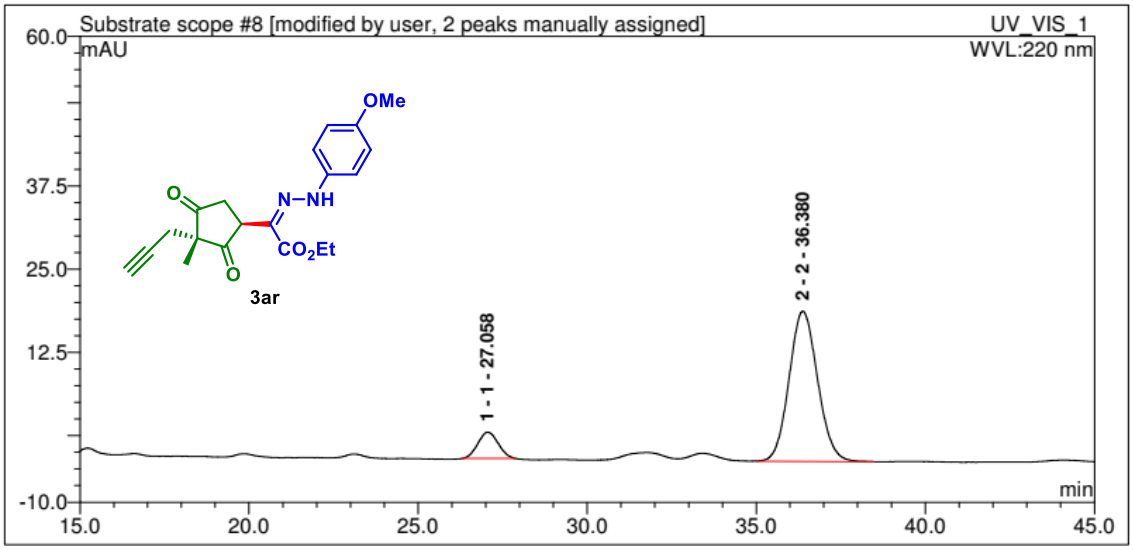
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	11.91	37.81715	27.75403716	95.15293	n.a.
2	2	15.75	37.37109	27.42667558	72.85905	n.a.
3	3	18.09	30.17387	22.14463023	29.38467	n.a.
4	4	27.47	30.896	22.67465703	23.239	n.a.



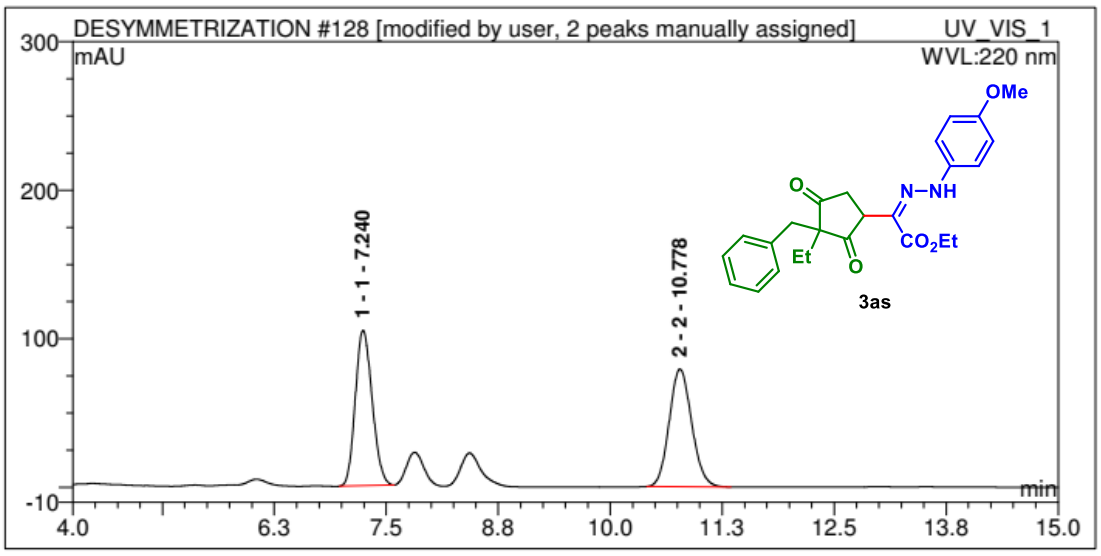
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	11.82333333	1.85259	10.9821226	5.17825	n.a.
2	2	15.62	15.01655	89.0178774	27.96807	n.a.



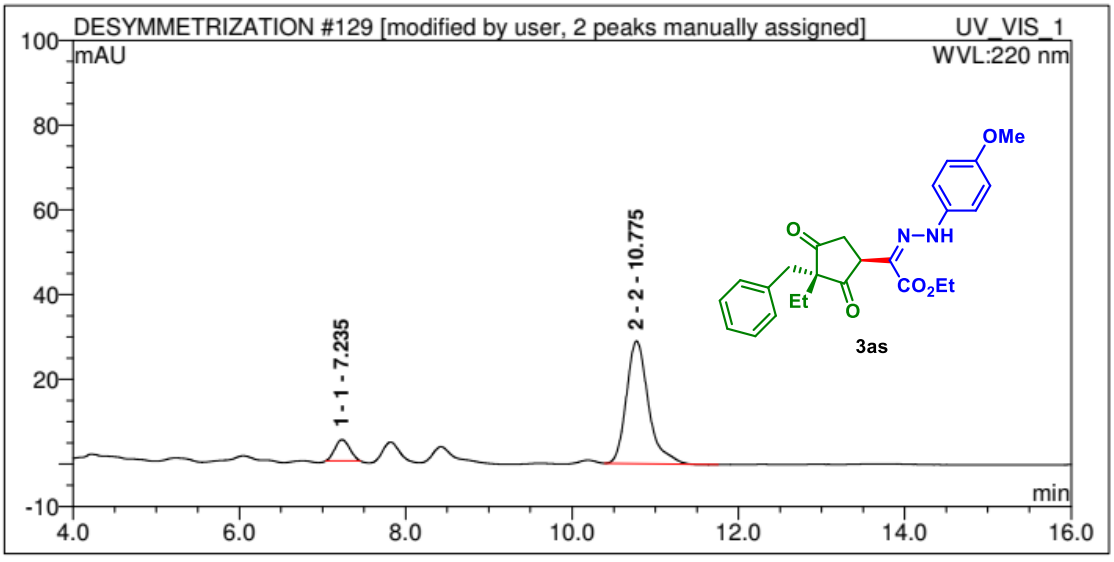
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	27.01	63.43288	49.94622601	87.54499	n.a.
2	2	36.28	63.569	50.05377399	65.920	n.a.



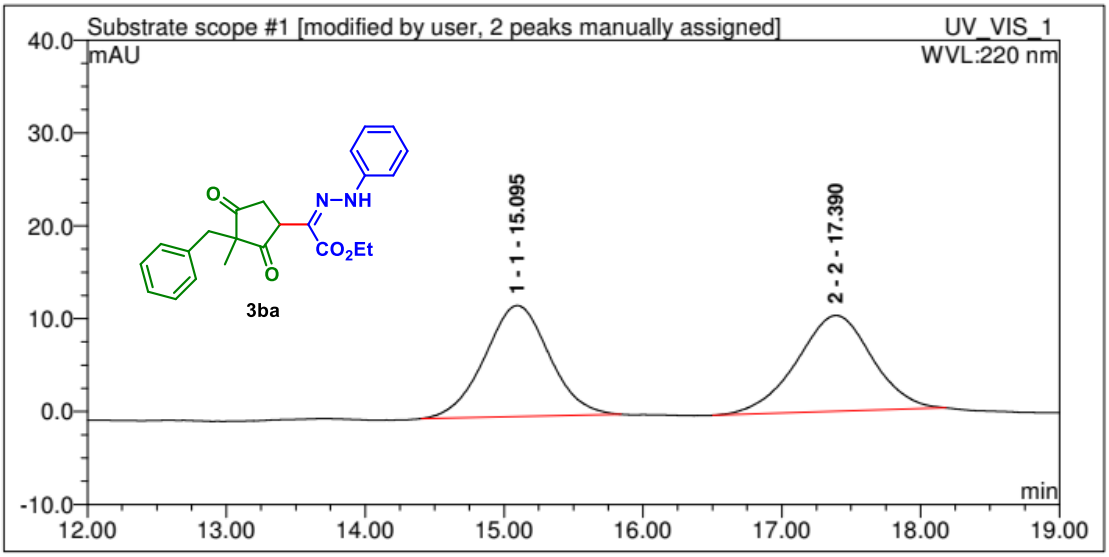
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	27.05833333	2.762719	11.12629649	3.94737	n.a.
2	2	36.38	22.06781	88.87370351	22.56129	n.a.



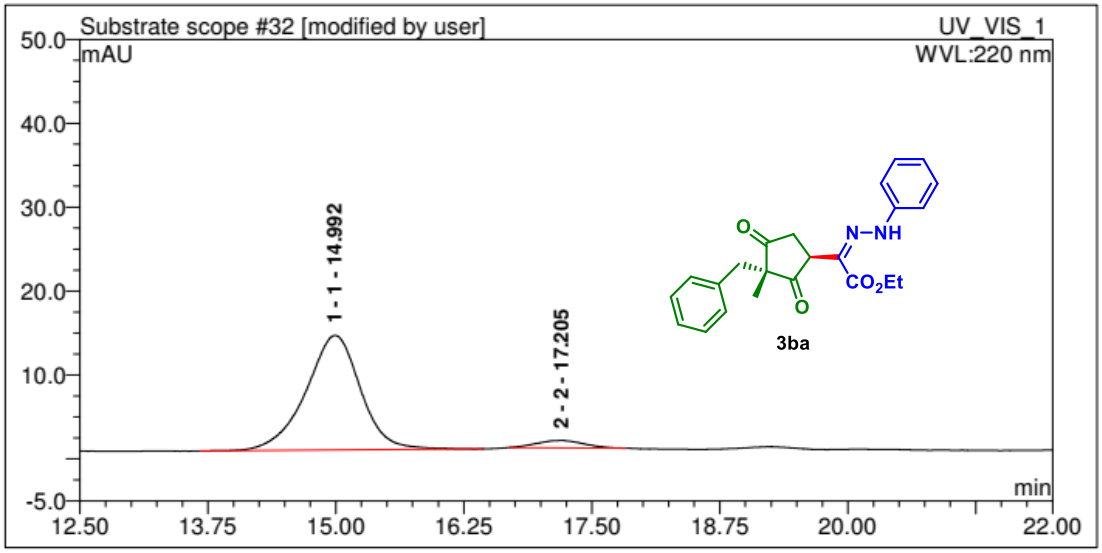
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	7.24	22.84206	49.71356456	104.6578	n.a.
2	2	10.78	23.105	50.28643544	79.316	n.a.



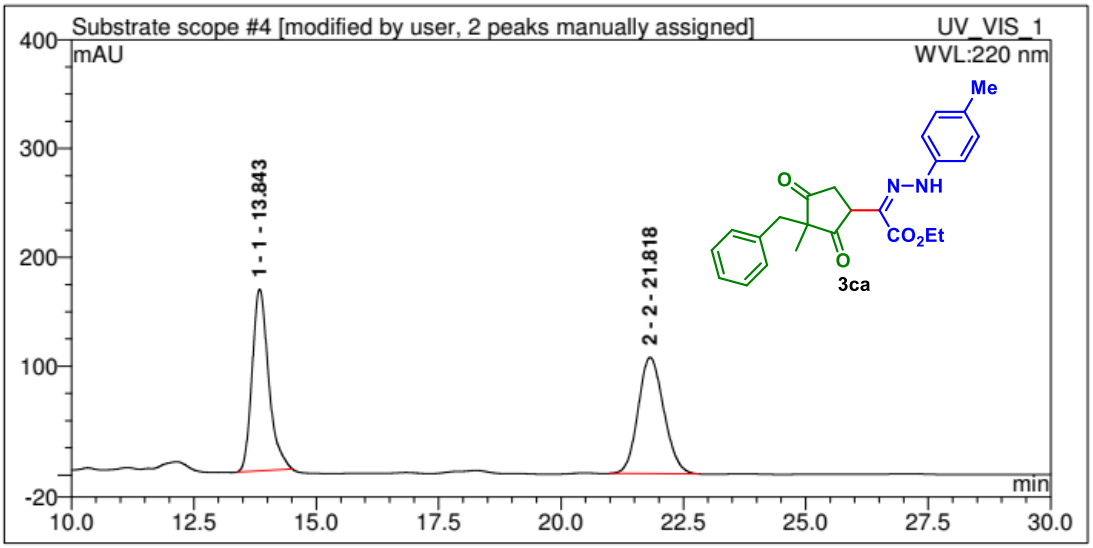
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	7.24	1.032543	10.38746807	5.01773	n.a.
2	2	10.78	8.908	89.61253193	28.949	n.a.



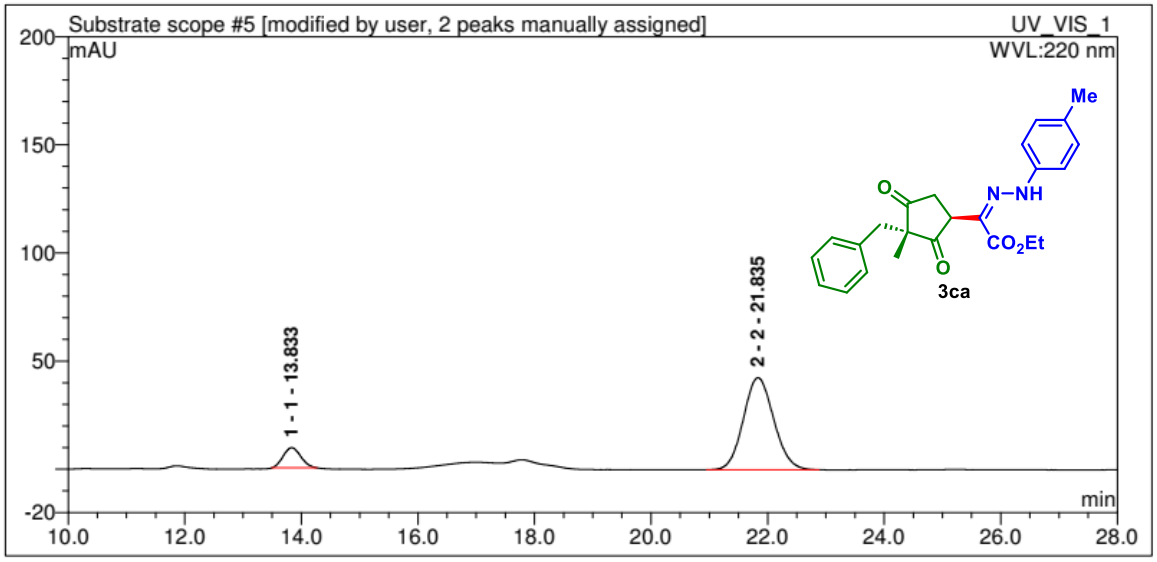
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	15.10	6.453198	49.7350124	11.9479	n.a.
2	2	17.39	6.522	50.2649876	10.326	n.a.



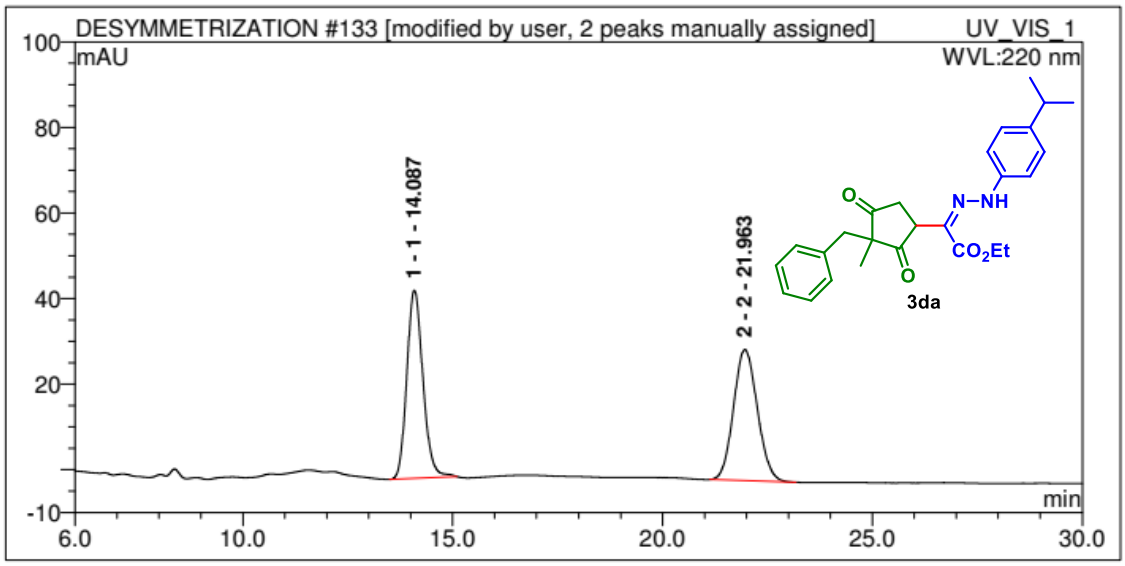
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	14.99	8.485401	94.78126492	13.65843	n.a.
2	2	17.21	0.467	5.218735078	0.876	n.a.



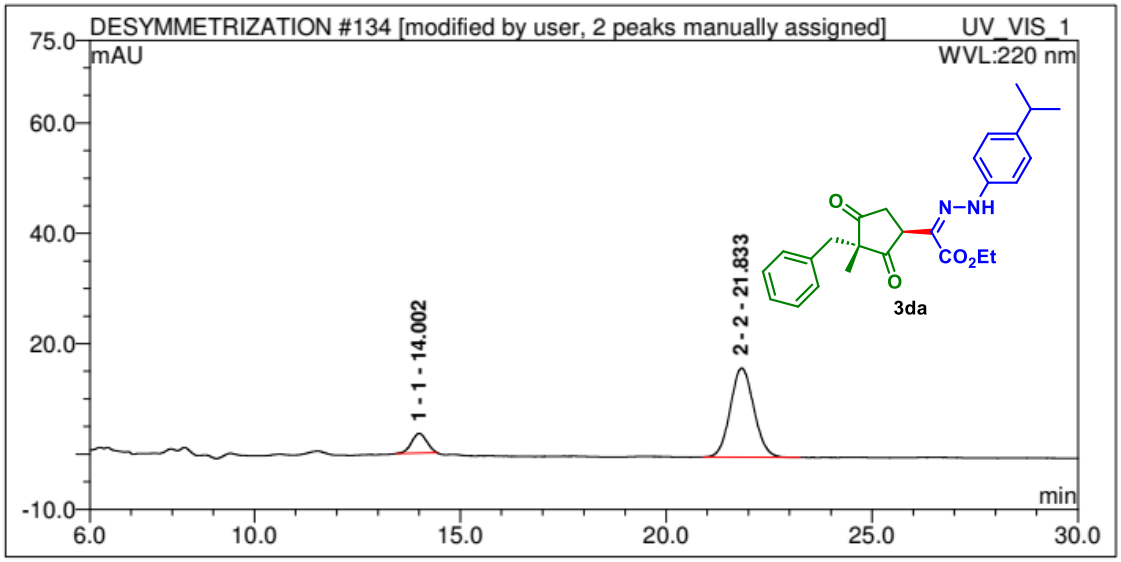
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	13.84	65.3778	50.14201349	166.6606	n.a.
2	2	21.82	65.007	49.85798651	106.907	n.a.



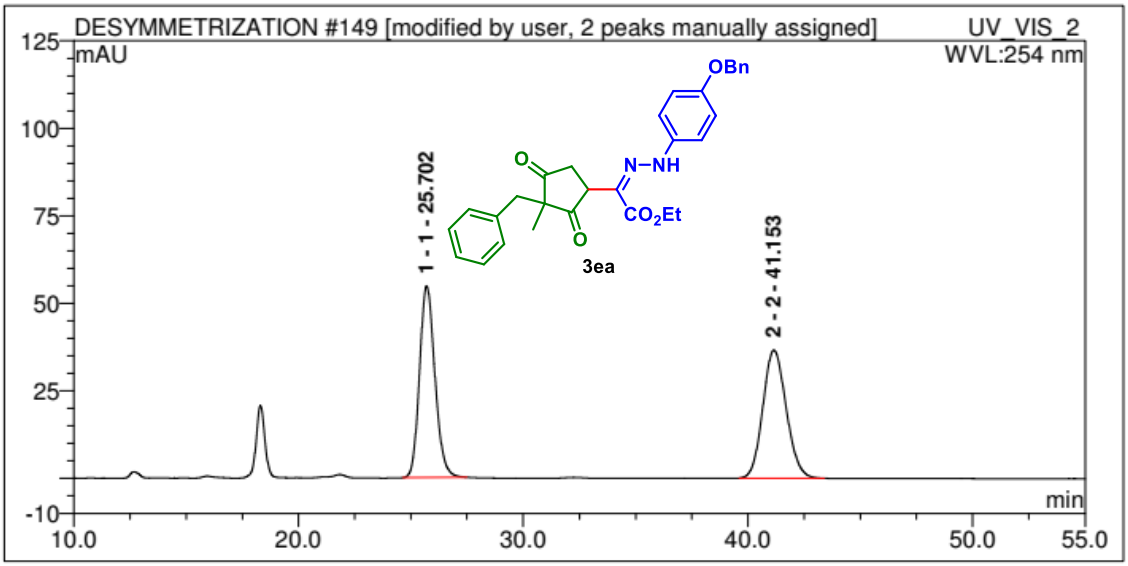
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	13.83333333	3.262675	11.2545512	9.31566	n.a.
2	2	21.835	25.72715	88.7454488	42.5821	n.a.



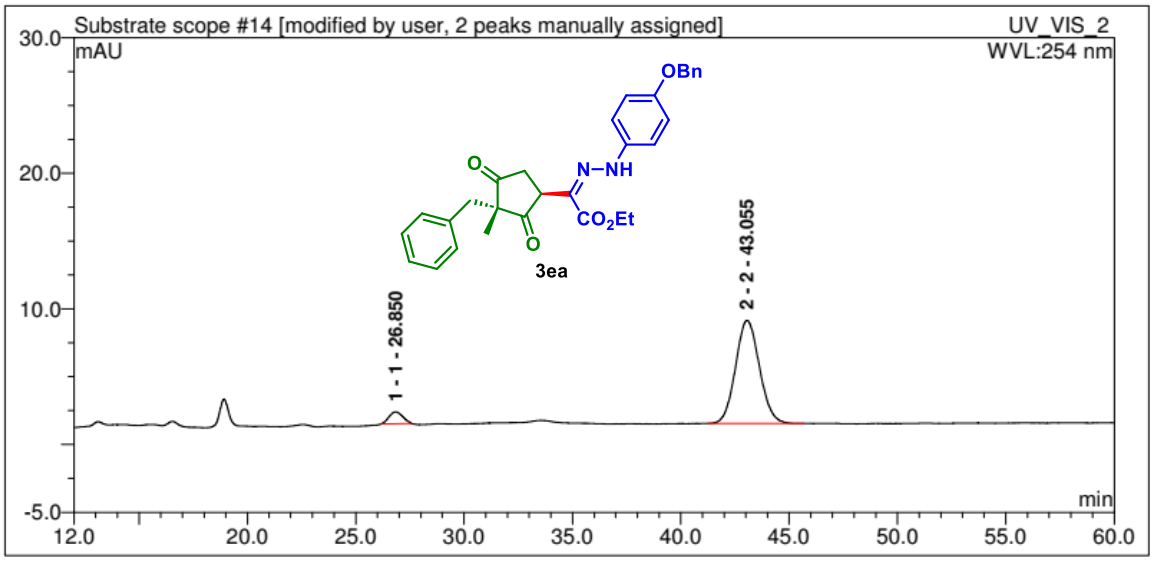
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	14.09	19.57938	49.22943495	43.99143	n.a.
2	2	21.96	20.192	50.77056505	30.655	n.a.



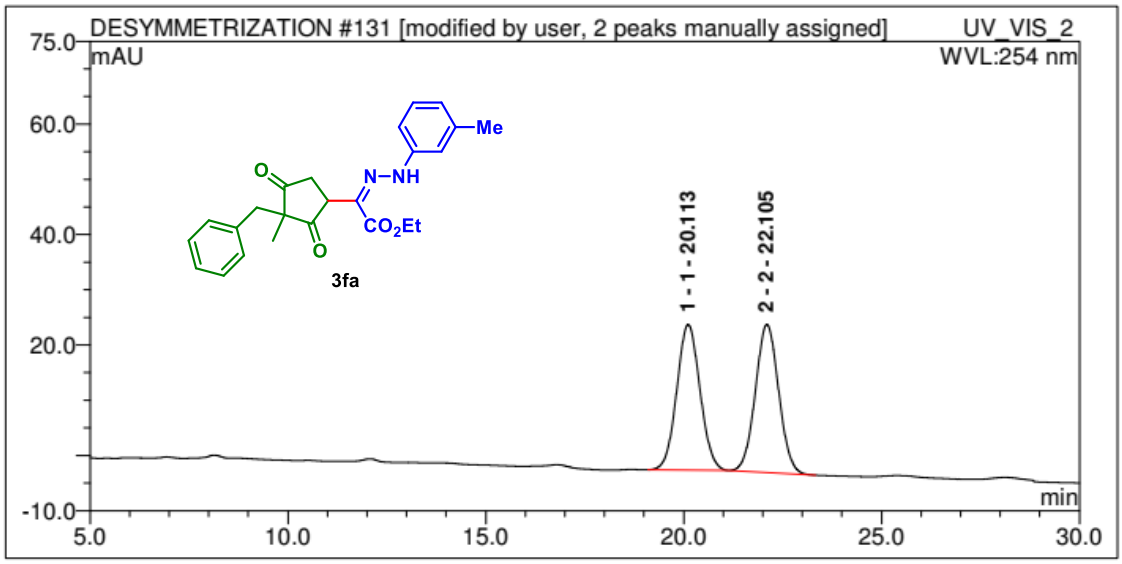
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	14.00	1.527933	12.48655274	3.55173	n.a.
2	2	21.83	10.709	87.51344726	16.178	n.a.



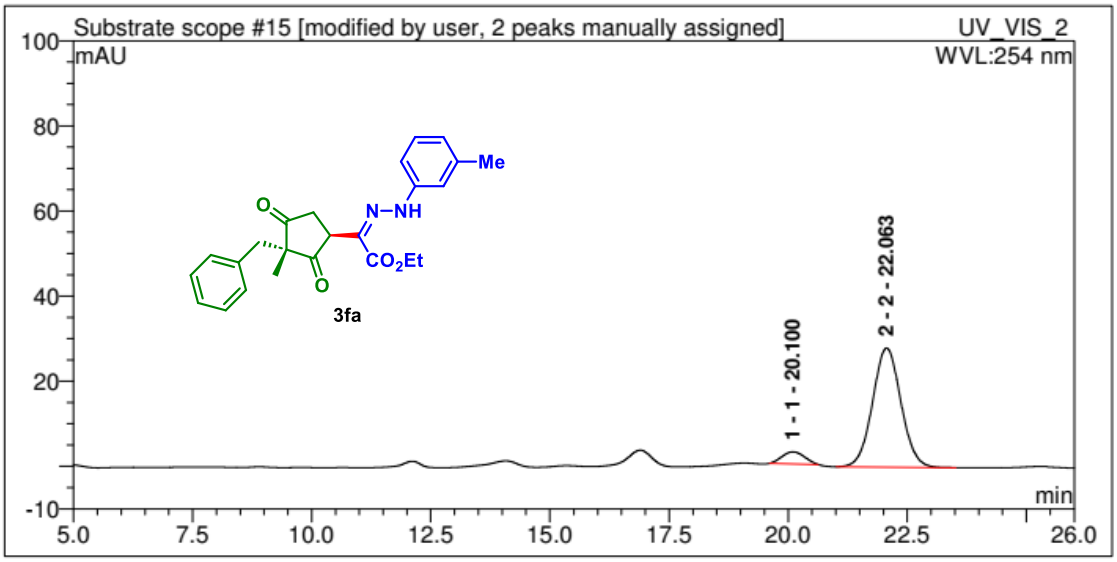
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	25.70	43.55493	49.66035555	54.79045	n.a.
2	2	41.15	44.151	50.33964445	36.605	n.a.



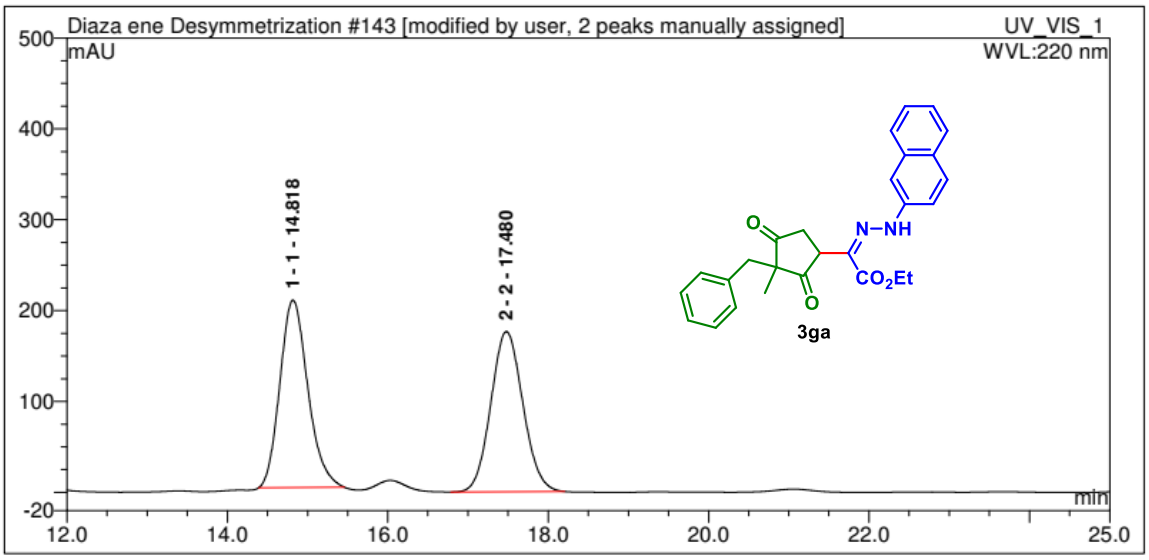
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	26.85	0.63896	6.172187589	0.87808	n.a.
2	2	43.055	9.713284	93.82781241	7.59159	n.a.



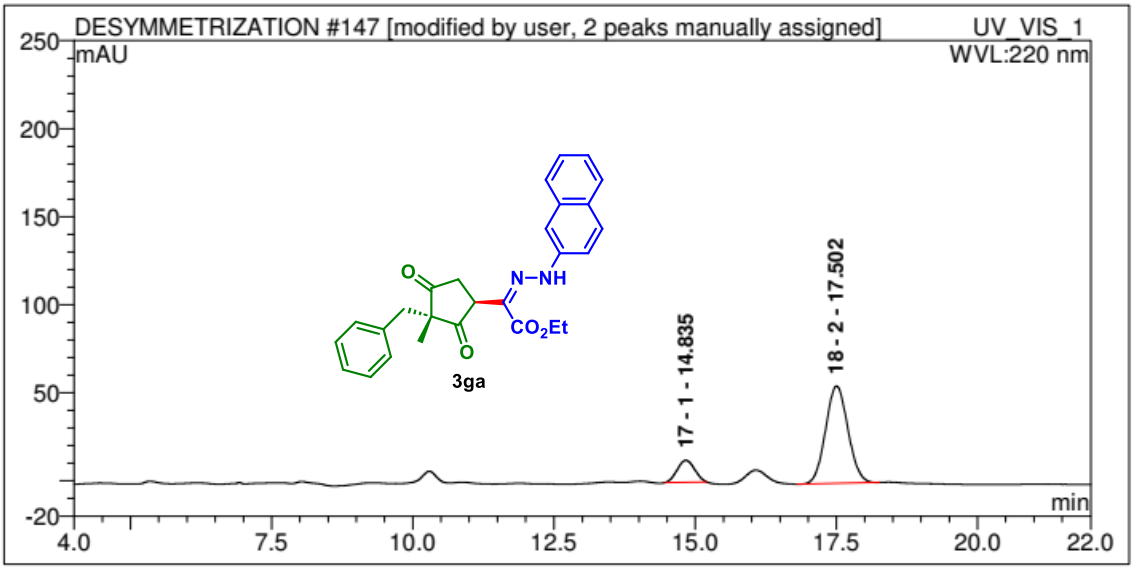
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	20.11	17.97218	49.50329131	26.35803	n.a.
2	2	22.11	18.333	50.49670869	26.805	n.a.



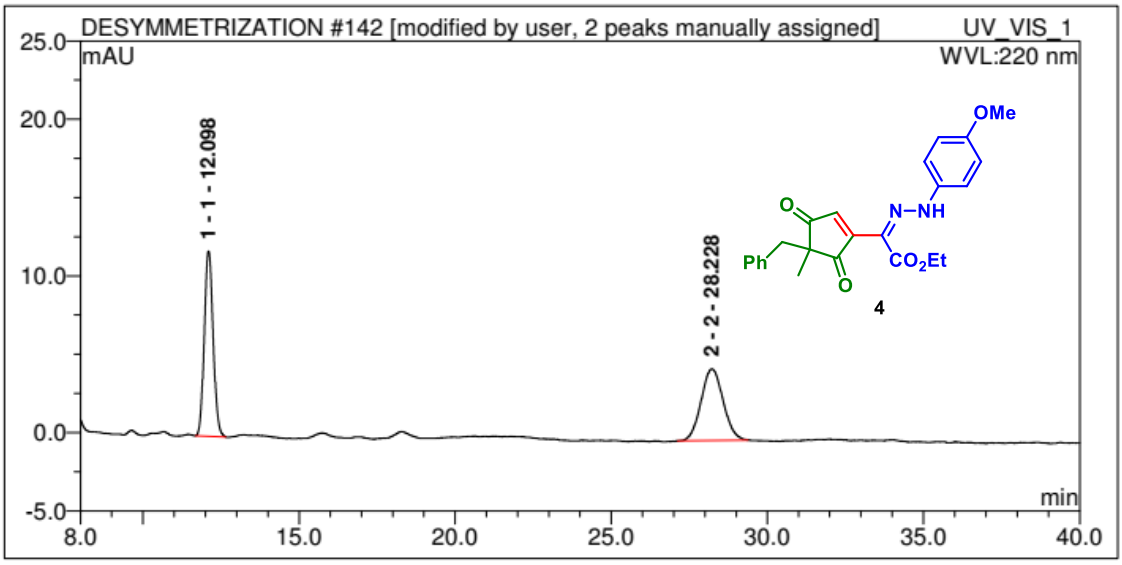
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	20.10	1.55533	7.439006748	2.84769	n.a.
2	2	22.06	19.352	92.56099325	27.985	n.a.



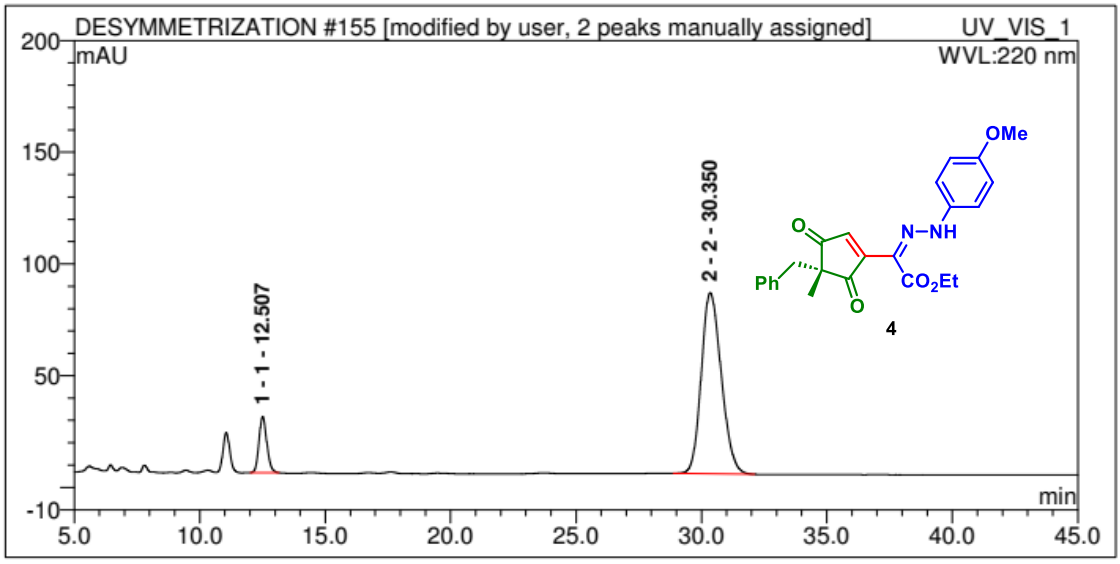
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	14.81833333	83.40159	50.53945785	206.4285	n.a.
2	2	17.48	81.62114	49.46054215	176.3503	n.a.



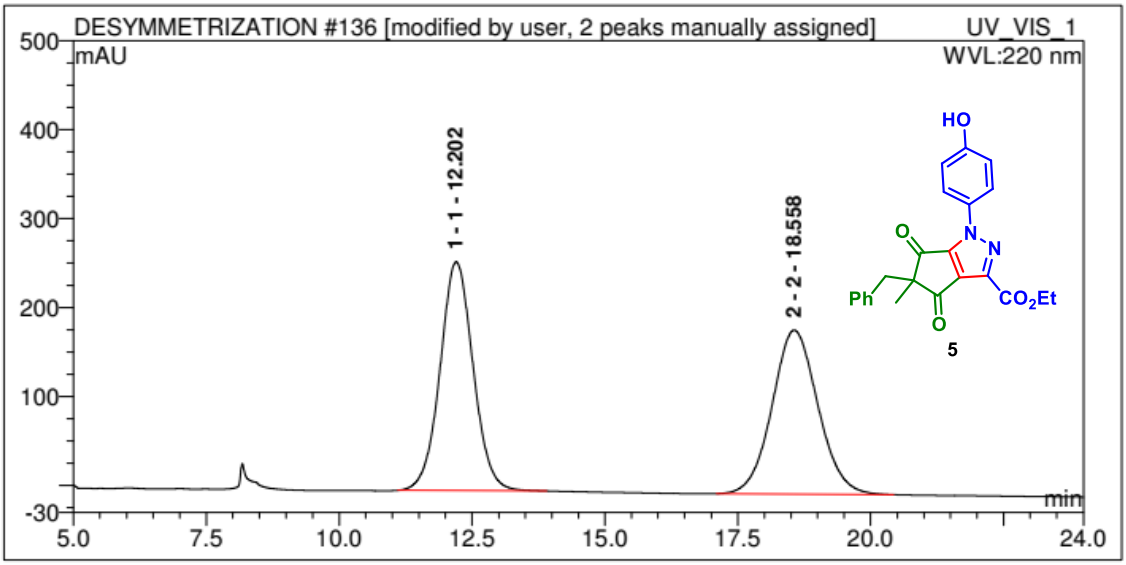
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
17	1	14.84	4.421706	14.83539914	12.42681	n.a.
18	2	17.50	25.383	85.16460086	55.305	n.a.



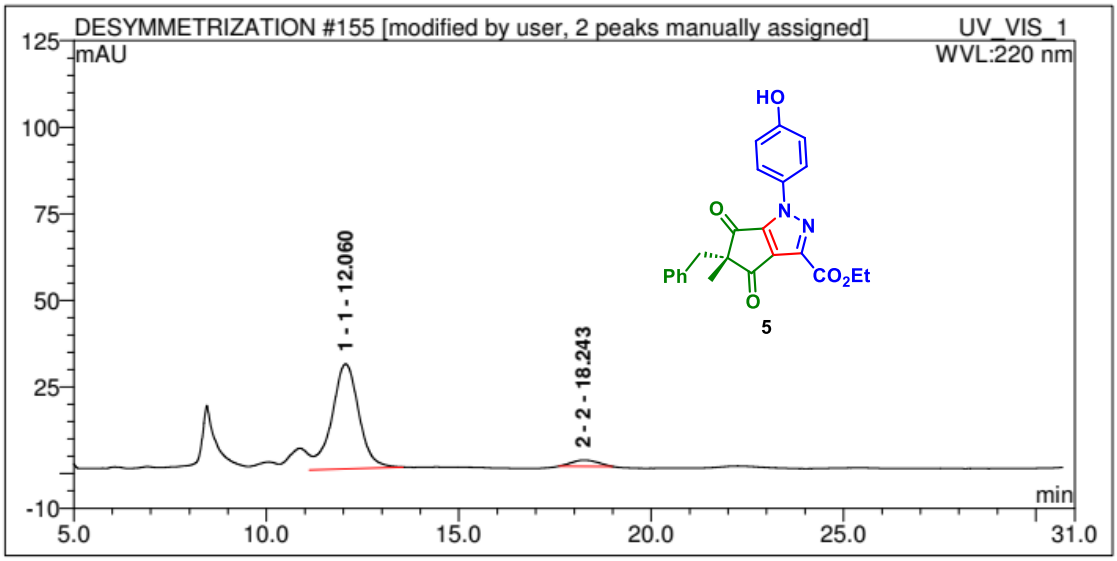
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	12.10	3.87357	50.86337505	11.82052	n.a.
2	2	28.23	3.742	49.13662495	4.573	n.a.



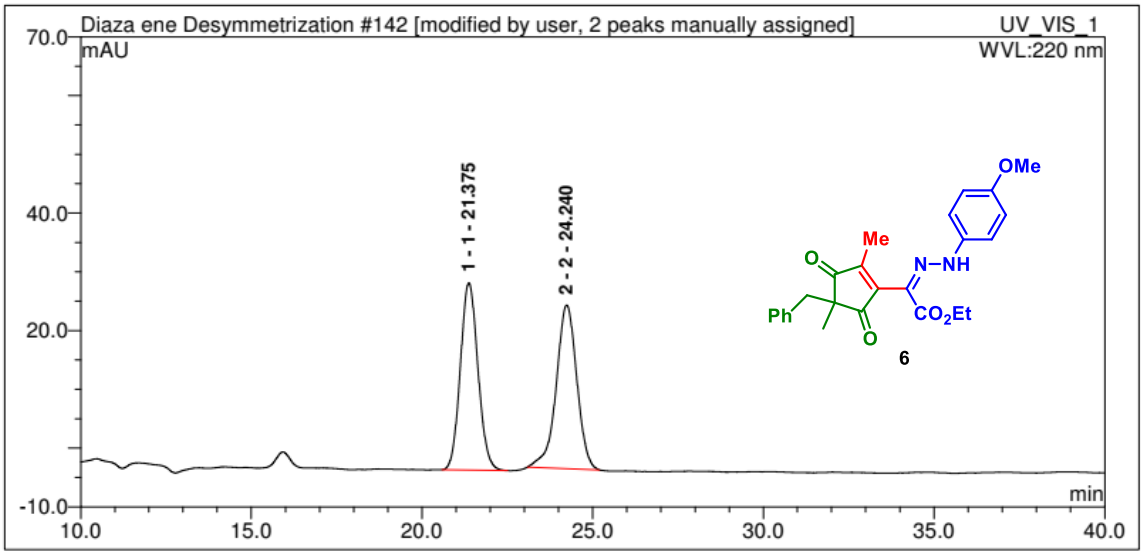
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	12.51	9.127844	10.8547259	25.11445	n.a.
2	2	30.35	74.963	89.1452741	80.985	n.a.



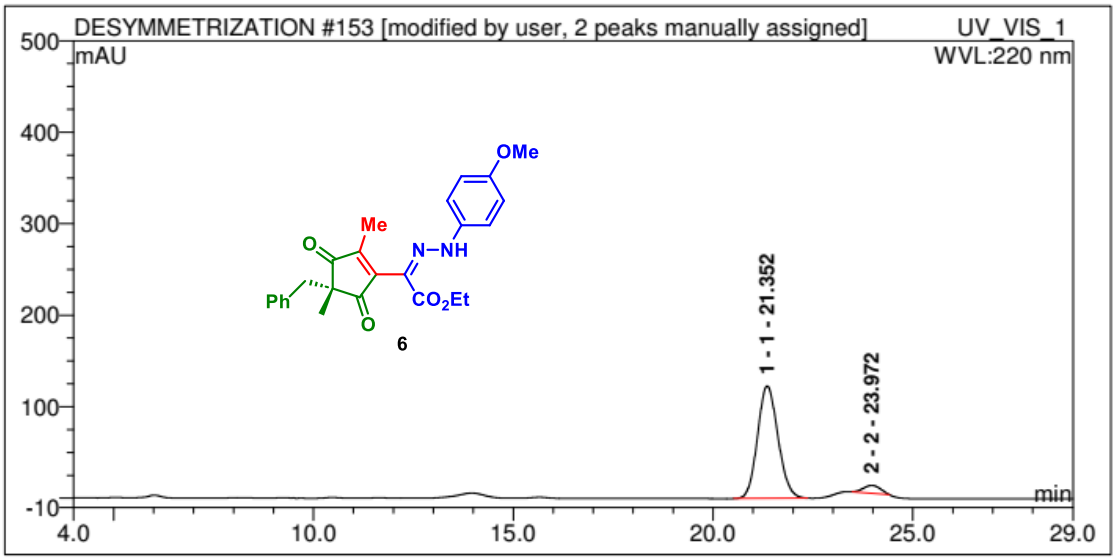
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	12.20	185.7593	50.17319986	257.0801	n.a.
2	2	18.56	184.477	49.82680014	184.153	n.a.



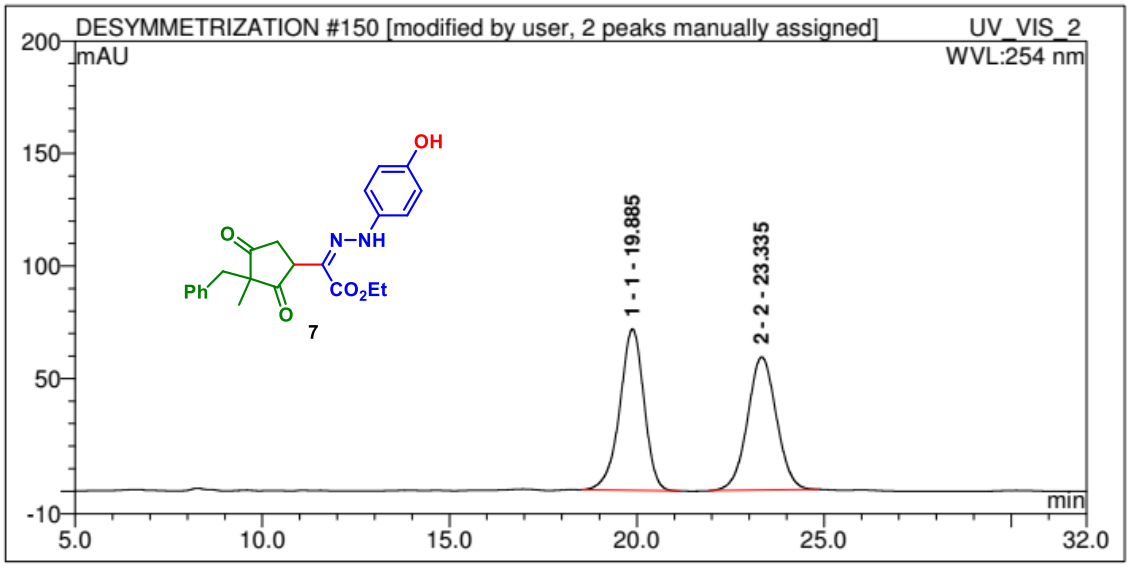
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	12.06	24.86157	94.60223001	30.30491	n.a.
2	2	18.24	1.419	5.39776999	1.801	n.a.



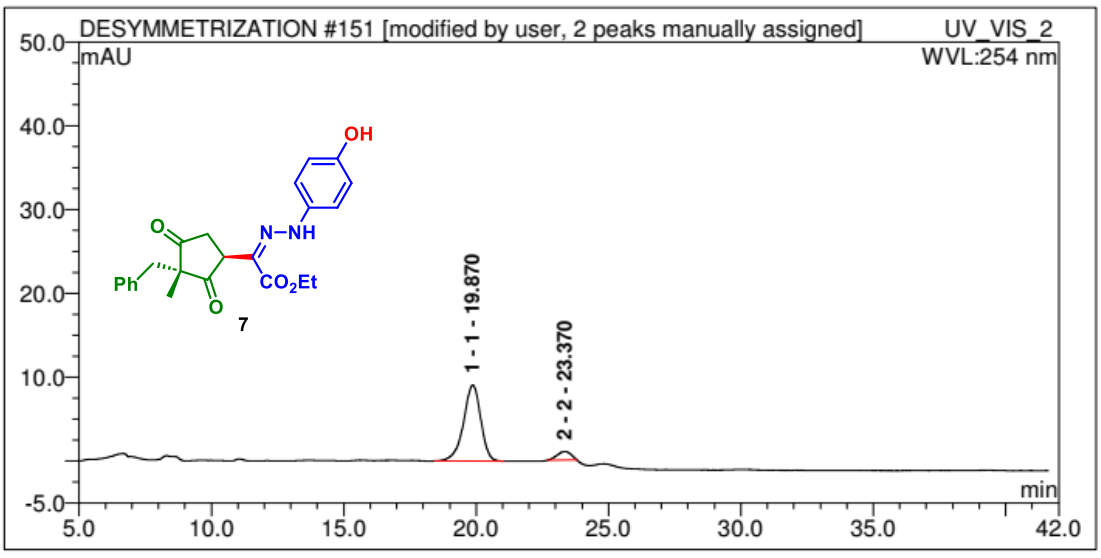
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	21.375	19.07126	49.45478025	31.8721	n.a.
2	2	24.24	19.49177	50.54521975	27.84066	n.a.



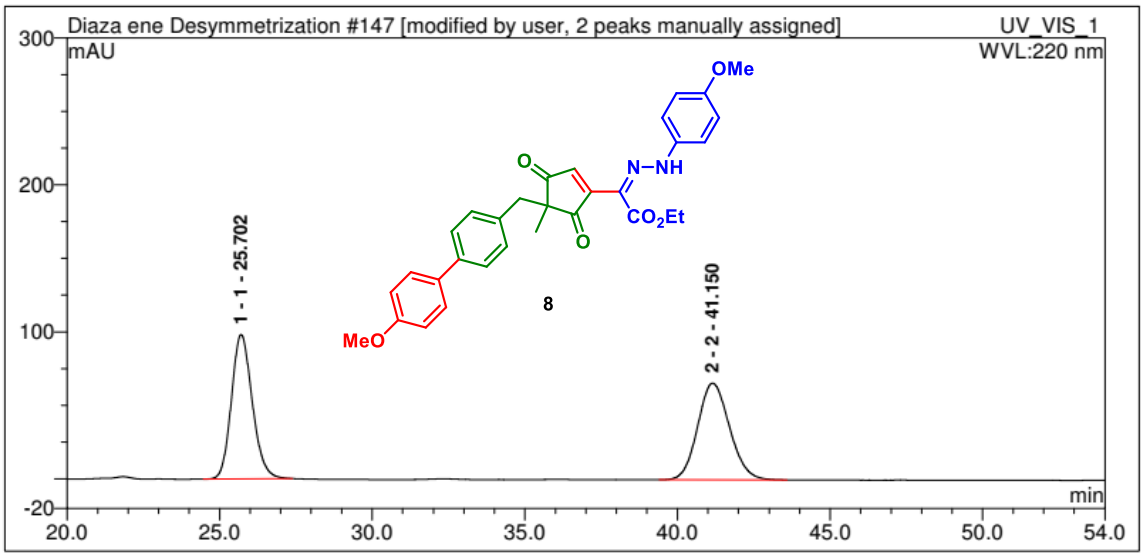
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	21.35	73.01147	94.54186935	122.7903	n.a.
2	2	23.97	4.215	5.458130647	8.564	n.a.



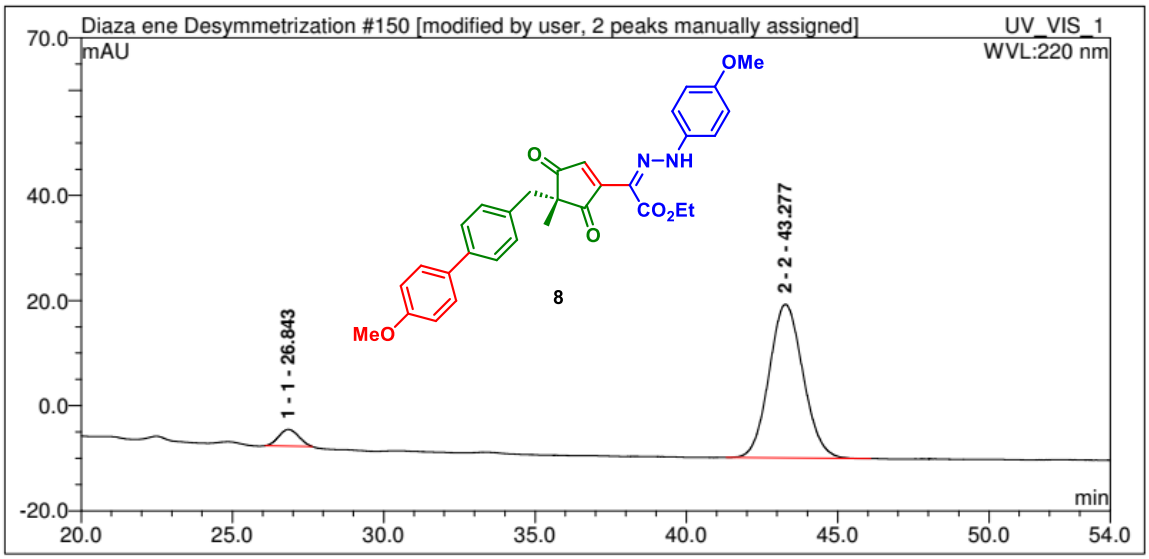
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	19.89	53.99944	50.41928421	71.79981	n.a.
2	2	23.34	53.101	49.58071579	59.182	n.a.



No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	19.87	6.845243	91.60155323	9.0644	n.a.
2	2	23.37	0.628	8.398446773	1.014	n.a.



No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	25.70166667	77.99993	49.48386764	98.1337	n.a.
2	2	41.15	79.62706	50.51613236	65.73893	n.a.



No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	26.84333333	2.435218	6.013064036	3.18454	n.a.
2	2	43.27666667	38.06356	93.98693596	29.24711	n.a.

14. References:

[1] a) M. Fernández, U. Uria, J. L. Vicario, L. Reyes, L. Carrillo, *J. Am. Chem. Soc.* 2012, **134**, 11872; b) N. Zabaleta, U. Uria, E. Reyes, L. Carrillo, J. L. Vicario, *Chem. Commun.* 2018, **54**, 8905-8908

[2] a) S. Zhou, T. Zhu, L. Zhou, C. Mou, H. Chai, Y. Lu, L. Pan, Z. Jin, Y. R. Chi, *Angew. Chem. Int. Ed*. 2019, **58**, 1784-1788; b) M. S. Manna, R. Sarkar, S. Mukherjee, *Chem.-Eur. J.* 2016, **22**, 14912. c) M. S. Manna, S. Mukherjee, *J. Am. Chem. Soc*. **2015**, *137*, 130; d) M. S. Manna, S. Mukherjee, *Chem. Sci*. 2014, **5**, 1627.

[3] S. Müller, M. J. Webber, B. List, *J. Am. Chem. Soc*. 2011, **133**, 18534.