Supporting Information:

Enantioselective Dearomative [3+2] Cycloaddition of 2-Nitrobenzofurans with Aldehyde-Derived Morita−Baylis−Hillman Carbonates

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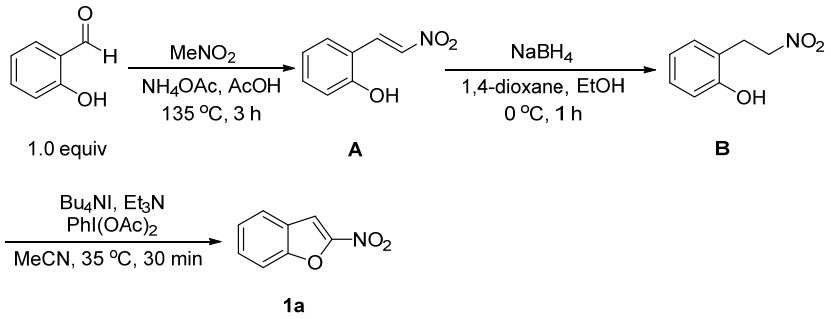
Contents

1. General information

All reactions were carried out in oven-dried Schlenk tube filled nitrogen, and monitored by thin layer chromatography (TLC). All reagents were reagent grade quality and purchased from commercial sources unless otherwise indicated. ^{1}H, $^{13}C\{1H\}$ NMR spectra were recorded on Bruker (^{1}H 600 MHz, $^{13}C\{1H\}$ 151 MHz) and Bruker (^{1}H 400 MHz, $^{13}C\{1H\}$ 101 MHz) . Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, t = triplet, q = quartet, m = multiplet). Coupling constants (*J*) are reported in Hertz (Hz). Enantiomer excesses were determined by chiral HPLC analysis on Chiralcel IA/ID/OJ-H/OD-H in comparison with the authentic racemates. Chiral HPLC analysis recorded on Thermo scientific Dionex Ultimate 3000. Optical rotations were reported as follows: $[\alpha]$DT (c: = g/100mL, in solvent). Optical rotations recorded on Autopol Automatic Polarimeter. All products were further characterized by high-resolution mass spectra (HRMS). The HRMS was obtained using a Q-TOF instrument equipped with an ESI source. $PhCH_3$ and $CHCl_3$ were freshly distilled from CaH_2. The 2-nitrobenzofurans (**1a-1h**)[1] and Morita−Baylis−Hillman carbonates (**2a-2o**)[2] were prepared according to the reported procedures.

2. Synthesis of starting materials

Synthesis of variously functionalized 2-nitrobenzofurans (1a-1h)[1]:

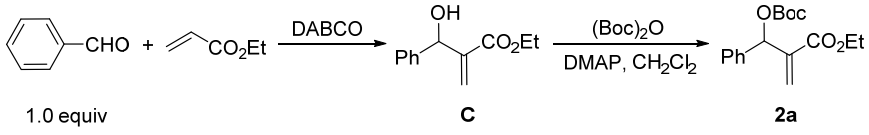


To a 25 mL flask equipped with a magnetic stir bar, nitromethane (5.0 mL), NH_4OAc (77 mg, 1.0 mmol), and acetic acid (2.0 mL) were added. The mixture was stirred at 90 °C for 15 min before addition of salicylaldehyde (0.61 g, 5.0 mmol). The reaction mixture was then heated at 135 °C for 3 h. After cooling to ambient temperature, the mixture was extracted with Et_2O (50 mL). The organic phase was washed by brine (50 mL). Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 8/1) yielded product **A** (0.58 g, 70%) as a yellow solid.

$NaBH_4$ (45 mg, 1.2 mmol) was suspended in a mixture of 1,4-dioxane and EtOH (4.0 mL, 3:1). **A** (165 mg, 1 mmol) dissolved in 1,4-dioxane (3.0 mL) was added dropwise at 0 °C. The reaction mixture was stirred at 0 °C for 1 h, quenched with saturated aqueous NH_4Cl solution (10 mL), extracted with Et_2O (3 × 25 mL). The combined organic phase was washed with brine (50 mL), and dried over Na_2SO_4. The organic phase was removed under vacuum to afford the crude **B**.

To a 25 mL flask were added crude **B**, Bu_4NI (923 mg, 2.5 mmol), NEt_3 (202 mg, 2.0 mmol), $PhI(OAc)_2$ (966 mg, 3.0 equiv), and acetonitrile (10.0 mL). The mixture was stirred at 35 °C for 30 min, extracted with Et_2O (50 mL). The organic phase was washed by brine (3 × 25 mL), dried over Na_2SO_4. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) yielded 2-nitrobenzofuran **1a** (98 mg, 60%) as a light yellow solid. **1b-1h** were synthesized in the same reaction conditions.

Synthesis of Morita−Baylis−Hillman carbonates (2a-2o)[2]:



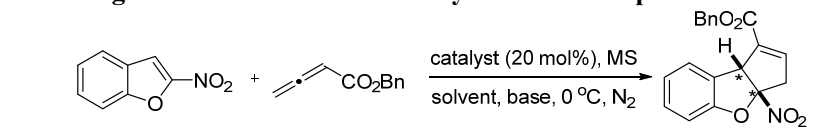
Benzaldehyde (1.0 equiv), ethyl acrylate (2.0 equiv) and DABCO (1.0 equiv) was taken in a round bottom flask. The mixture was stirred at room temperature for 5-7 days. The solution was extracted with $EtOAc/H_2O$, the organic phases were dried and concentrated. Purification by

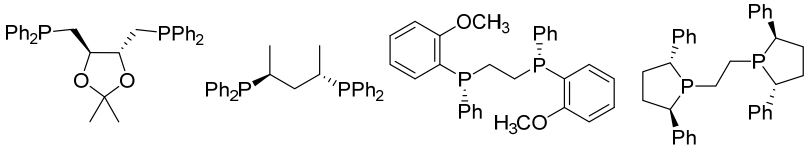
column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) yielded product **C**.

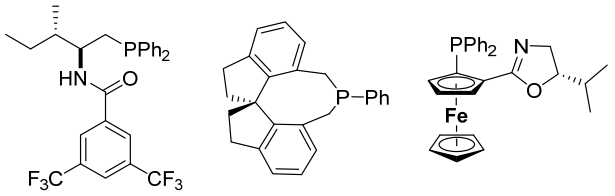
To a solution of compound **C** (1.0 equiv) in DCM were added DMAP (10 mmol%) and $(Boc)_2O$ (1.2 equiv) at room temperature. After being stirred at room temperature for 5 h, The reaction mixture was extracted with ethyl acetate, the combined organic phases were dried and concentrated. Purification by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) yielded product **2a**. **2b**-**2o** were synthesized in the same reaction conditions.

3. Optimization of reaction conditions of 2-nitrobenzofurans with allenoate.

Table S1. Screening of reaction conditions for synthesis of compound 5





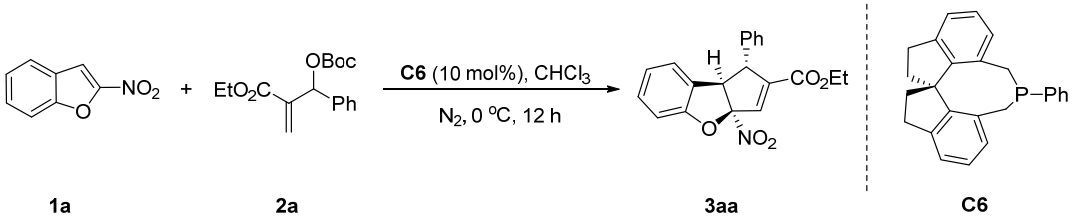


entry	cat.	solvent	MS	base	time (h)	yield[b] (%)	ee[c] (%)
1	**C1**	DCM	-	-	12	28	31
2	**C2**	DCM	-	-	12	35	0
3	**C3**	DCM	-	-	12	24	19
4	**C4**	DCM	-	-	12	37	4
5	**C5**	DCM	-	-	12	trace	11
6	**C6**	DCM	-	-	12	32	11
7	**C7**	DCM	-	-	12	NR	-
8	**C1**	DCE	-	-	12	35	33
9	**C1**	CH_3CN	-	-	12	NR	-
10	**C1**	MTBE	-	-	12	38	55
11	**C1**	toluene	-	-	12	37	68
12	**C1**	dioxane	-	-	12	NR	-
13	**C1**	toluene	3Å	-	12	35	67
14	**C1**	toluene	4Å	-	12	38	72
15	**C1**	toluene	5Å	-	12	37	69
16	**C1**	toluene	4Å	-	24	40	69
17	**C1**	toluene	4Å	Cs_2CO_3	12	24	75
18	**C1**	toluene	4Å	NEt_3	12	21	69
19	**C1**	toluene	-	Cs_2CO_3	12	19	74
20	**C1**	toluene	-	NEt_3	12	27	66
[d]21	**C1**	toluene	4Å	-	12	36	70

[a] Reaction conditions: **1a** (0.2 mmol), **4** (0.4 mmol), catalyst (20 mol%), MS (80 mg) and base (0.2 mmol) in solvent (2.0 mL), 0 °C, N_2. [b]Yields of isolated product. [c]Determined by chiral HPLC analysis. [d]The reaction was performed on 0.5 mmol scale.

4. Typical procedure for the asymmetric dearomatization cycloaddition reaction

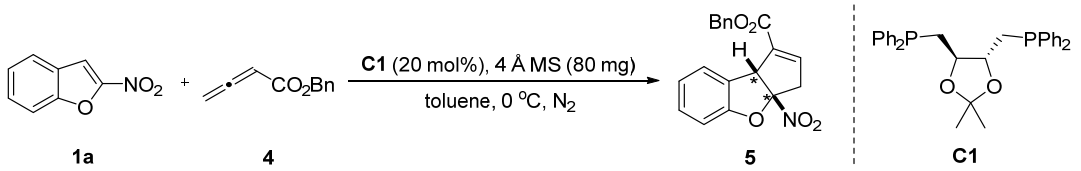
General procedure for the enantioselective preparation of dearomatized products 3 (3aa was used as a representative example)



1a **2a** **3aa** **C6**

To an oven-dried test tube equipped with a magnetic stir bar, 2-nitrobenzofuran **1a** (16.3 mg, 0.1 mmol, 1.0 equiv), **C6** (3.6 mg, 0.01 mmol, 10 mol%) and MBH carbonates **2a** (61.2 mg, 0.2 mmol, 2.0 equiv) were added. The tube was sealed with a threaded rubber stopper, evacuated and backfilled with N_2. The tube was then charged with $CHCl_3$ (1.0 mL) via syringe and the mixture was stirred at 0 ^oC for 12 h. Upon consumption of 2-nitrobenzofuran **1a** (determined by TLC), the mixture was concentrated in vacuo to give the crude product, which was then purified by preparative thin layer chromatography (eluent: petroleum ether/ethyl acetate = 15/1) to afford the cycloadduct **3aa** (32.6 mg, 93% yield, 97% ee).

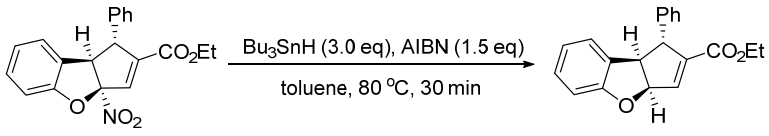
General procedure for the enantioselective preparation of dearomatized product 5



1a **4** **5** **C1**

To an oven-dried test tube equipped with a magnetic stir bar, 2-nitrobenzofuran **1a** (32.6 mg, 0.2 mmol, 1 equiv.), **C1** (20.0 mg, 0.04 mmol, 20 mol%), benzyl buta-2,3-dienoate (69.6 mg, 0.4 mmol, 2.0 equiv) and 4 Å MS (80.0 mg) were added. The tube was sealed with a threaded rubber stopper, evacuated and backfilled with N_2. The tube was then charged with $PhCH_3$ (2.0 mL) via syringe and the mixture was stirred at 0 ^oC for 12 h. concentrated in vacuo to give the crude product, which was then purified by preparative thin layer chromatography (eluent: petroleum ether/ethyl acetate = 15/1) to afford the cycloadduct **5** (25.7mg, 38% yield, 72% ee).

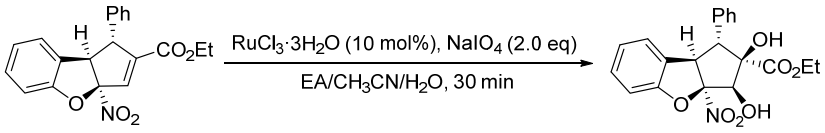
5. Transformations of product 3aa



3aa
0.2 mmol, 97% ee

6a
73% yield, 94% ee

To a solution of compound **3aa** (70 mg, 0.2 mmol, 1.0 equiv) in toluene (2.0 mL) were added tributyltin hydride (162 μL, 0.6 mmol, 3.0 equiv) and AIBN (49.2 mg, 0.3 mmol, 1.5 equiv) at room temperature. After being stirred at 80 ºC for 30 min, the reaction mixture was cooled to room temperature. The reaction mixture was quenched with saturated KF solution (10.0 mL) and extracted with ethyl acetate. The combined organic phases were dried and concentrated. The residue was purified by preparative thin layer chromatography (eluent: petroleum ether/ethyl acetate = 3/1) to afford product **6a** (44.4 mg, 73% yield, 94% ee).



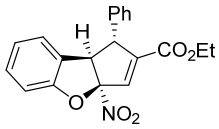
3aa
0.2 mmol, 97% ee

6b
51% yield, 3:1 dr, 96% ee

To a test tube equipped with a magnetic stir bar, $NaIO_4$ (89.2 mg, 0.4 mmol, 2.0 equiv) and H_2O (0.2 mL) were added The solution was cooled to 0 °C and $RuCl_3 \cdot 3H_2O$ (5.6 mg, 0.02 mmol, 10 mol%) was added. Then EtOAc (0.4 mL) was added. CH_3CN (0.8 mL) and a solution of substrate **3aa** (70.0 mg, 0.2 mmol, 1.0 equiv) in EtOAc (0.8 mL) was added in sequence. After being stirred at 0 ºC for 30 min, 10 % $NaHCO_3$ (2.0 mL) and saturated Na_2SO_3 solution (4.0 mL) were added. The solution was stirred for 10 min at room temperature, and extracted with EtOAc. The combined organic phases were dried and concentrated. The residue was purified by preparative thin layer chromatography (eluent: petroleum ether/ethyl acetate = 4/1) to afford product **6b** (39.1 mg, 51% yield, 3:1 dr, 96% ee).

6. Characterization of compounds

Ethyl (1*R*,3a*R*,8b*R*)-3a-nitro-1-phenyl-3a,8b-dihydro-1*H*-cyclopenta[*b*]benzofuran-2-carboxylate (3aa)



White solid. 32.6 mg, 93% yield, 97% ee.

$[\alpha]_D^{26}$ = -45.20 (c = 0.86, CH_2Cl_2).

m.p.: 80-82 ^oC

HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, temperature = 25 ^oC, λ = 250 nm, retention time: 8.883 min (major), 9.972 min (minor).

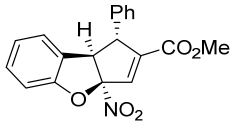
TLC: R_f = 0.33 (petroleum ether:ethyl acetate = 15:1) [UV]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.34 – 7.28 (m, 5H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 2.0 Hz, 1H), 4.40 (d, *J* = 2.8 Hz, 1H), 4.31 (t, *J* = 2.4 Hz, 1H), 4.17 – 4.01 (m, 2H), 1.13 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 157.4, 148.7, 140.7, 133.2, 130.0, 129.4, 127.9, 127.5, 126.9, 125.3, 124.8, 123.7, 111.2, 61.7, 61.5, 58.6, 14.0.

HRMS (ESI): m/z calcd. For $C_{20}H_{17}NNaO_5$ $[M+Na]^+$ 374.0999, found m/z 374.0995.

Methyl (1*R*,3a*R*,8b*R*)-3a-nitro-1-phenyl-3a,8b-dihydro-1*H*-cyclopenta[*b*]benzofuran-2-carboxylate (3ab)



White solid. 31.1 mg, 92% yield, 94% ee.

$[\alpha]_D^{26}$ = -48.20 (c = 1.00, CH_2Cl_2).

m.p.: 139-140 ^oC

HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 ^oC, λ = 256 nm, retention time: 7.057 min (major), 7.992 min (minor).

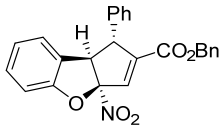
TLC: R_f = 0.28 (petroleum ether:ethyl acetate = 15:1) [UV]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H), 7.34 – 7.28 (m, 5H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 2.0 Hz, 1H), 4.39 (d, *J* = 2.8 Hz, 1H), 4.33 (t, *J* = 2.4 Hz, 1H), 3.66 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 157.4, 148.3, 140.5, 133.5, 130.1, 129.4, 128.0, 127.4, 126.9, 125.3, 124.8, 123.7, 111.2, 61.7, 58.6, 52.4.

HRMS (ESI): m/z calcd. For $C_{19}H_{15}NNaO_5$ $[M+Na]^+$ 360.0842, found m/z 360.0837.

Benzyl (1*R*,3a*R*,8b*R*)-3a-nitro-1-phenyl-3a,8b-dihydro-1*H*-cyclopenta[*b*]benzofuran-2-carboxylate (3ac)



Light yellow solid. 36.4 mg, 88% yield, 93% ee.

$[\alpha]_D^{26}$ = -32.41 (c = 0.87, CH_2Cl_2).

m.p.: 36-38 ^oC

HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, temperature = 25 ^oC, λ = 250 nm, retention time: 11.903 min (major), 14.652 min (minor).

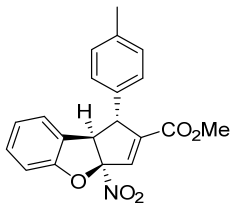
TLC: R_f = 0.27 (petroleum ether:ethyl acetate = 15:1) [UV]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7.35 – 7.23 (m, 8H), 7.08 – 7.02 (m, 4H), 7.00 (d, *J* = 8.0 Hz, 1H), 5.12 (d, *J* = 12.4 Hz, 1H), 4.96 (d, *J* = 12.4 Hz, 1H), 4.39 (d, *J* = 2.8 Hz, 1H), 4.31 (t, *J* = 2.6 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.4, 157.4, 148.3, 140.6, 135.0, 133.9, 130.1, 129.5, 128.6, 128.5, 128.2, 127.9, 127.5, 126.8, 125.1, 124.7, 123.7, 111.2, 67.2, 61.8, 58.6.

HRMS (ESI): m/z calcd. For $C_{25}H_{19}NNaO_5$ $[M+Na]^+$ 436.1155, found m/z 436.1157.

Methyl (1*R*,3a*R*,8b*R*)-3a-nitro-1-(p-tolyl)-3a,8b-dihydro-1*H*-cyclopenta[*b*]benzofuran-2-carboxylate (3ad)



Light yellow solid. 32.3 mg, 92% yield, 94% ee.

$[\alpha]_D^{26}$ = -75.71 (c = 0.87, CH_2Cl_2).

m.p.: 126-128 ^oC

HPLC CHIRALCEL IA, *n*-hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, temperature = 25 ^oC, λ = 256 nm, retention time: 7.633 min (major), 12.413 min (minor).

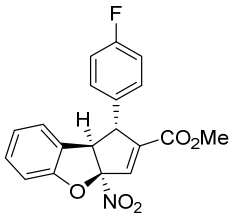
TLC: R_f = 0.28 (petroleum ether:ethyl acetate = 15:1) [UV]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 2H), 7.18 – 7.13 (m, 4H), 7.02 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 2.0 Hz, 1H), 4.32 (d, *J* = 2.8 Hz, 1H), 4.24 (t, *J* = 2.4 Hz, 1H), 3.61 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.2, 157.4, 148.3, 137.7, 137.6, 133.2, 130.1, 130.0, 127.3, 127.0, 125.3, 124.8, 123.7 , 111.1, 61.8, 58.2, 52.4, 21.3.

HRMS (ESI): m/z calcd. For $C_{20}H_{17}NNaO_5$ $[M+Na]^+$ 374.0999, found m/z 374.0999.

Methyl (1*R*,3a*R*,8b*R*)-1-(4-fluorophenyl)-3a-nitro-3a,8b-dihydro-1*H*-cyclopenta[*b*]benzofuran-2-carboxylate (3ae)



Light yellow solid. 30.9 mg, 87% yield, 94% ee.

$[\alpha]_D^{26}$ = -39.59 (c = 0.94, CH_2Cl_2).

m.p.: 42-43 ^oC

HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, temperature = 25 ^oC, λ = 256 nm, retention time: 9.032 min (major), 10.513 min (minor).

TLC: R_f = 0.24 (petroleum ether:ethyl acetate = 15:1) [UV]

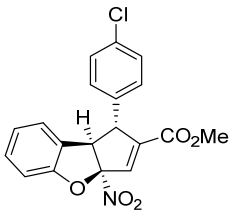
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 3H), 7.25 – 7.23 (m, 1H), 7.08 – 7.03 (m, 3H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 2.0 Hz, 1H), 4.33 (d, *J* = 2.8 Hz, 1H), 4.29 (t, *J* = 2.4 Hz, 1H), 3.64 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.0, 162.4 (d, $J_{C,F}$ = 247.6 Hz), 157.3, 148.1, 136.3 (d, $J_{C,F}$ = 3.0 Hz), 133.6, 130.2, 129.1 (d, $J_{C,F}$ = 9.1 Hz), 126.6, 125.1, 124.7, 123.8, 116.3 (d, $J_{C,F}$ = 22.7 Hz), 111.2, 61.7, 57.9, 52.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.4 (s).

HRMS (ESI): m/z calcd. For $C_{19}H_{14}FNNaO_5$ $[M+Na]^+$ 378.0748, found m/z 378.0744.

Methyl (1*R*,3a*R*,8b*R*)-1-(4-chlorophenyl)-3a-nitro-3a,8b-dihydro-1*H*-cyclopenta[*b*]benzofuran-2-carboxylate (3af)



White solid. 31.9 mg, 86% yield, 97% ee.

$[\alpha]_D^{26}$ = -88.52 (c = 0.72, CH_2Cl_2).

m.p.: 129 -130 ^oC

HPLC CHIRALCEL OJ-H, *n*-hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, temperature = 25 ^oC, λ = 250 nm, retention time: 22.777 min (major), 44.773 min (minor).

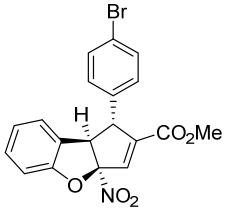
TLC: R_f = 0.26 (petroleum ether:ethyl acetate = 15:1) [UV]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H), 7.32 – 7.29 (m, 1H), 7.29 – 7.25 (m, 3H), 7.08 (t, *J* = 7.2 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.98 ((t, *J* = 1.8 Hz, 1H), 4.35 – 4.33 (m, 1H), 4.30 (t, *J* = 3.0 Hz, 1H), 3.66 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.9, 157.3, 147.9, 139.0, 133.9, 133.9, 130.2, 129.6, 128.9, 126.5, 125.1, 124.7, 123.8, 111.3, 61.6, 57.9, 52.5.

HRMS (ESI): m/z calcd. For $C_{19}H_{14}ClNNaO_5$ $[M+Na]^+$ 394.0453, found m/z 394.0453.

Methyl (1*R*,3a*R*,8b*R*)-1-(4-bromophenyl)-3a-nitro-3a,8b-dihydro-1*H*-cyclopenta[*b*]benzofuran-2-carboxylate (3ag)



White solid. 36.5mg, 88% yield, 96% ee.

$[\alpha]_D^{26}$ = -106.00 (c = 0.42, CH_2Cl_2).

m.p.: 128-129 °C

HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, temperature = 25 °C, λ = 256 nm, retention time: 9.768 min (major), 11.407 min (minor).

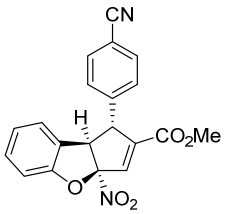
TLC: R_f = 0.24 (petroleum ether:ethyl acetate = 15:1) [UV]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 – 7.51 (m, 2H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.27 – 7.25 (m, 1H), 7.23 – 7.20 (m, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 2.4 Hz, 1H), 4.35 (d, *J* = 3.0 Hz, 1H), 4.28 (t, *J* = 2.4 Hz, 1H), 3.67 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.9, 157.3, 147.8, 139.6, 133.9, 132.6, 130.2, 129.2, 126.5, 125.1, 124.7, 123.8, 122.0, 111.3, 61.5, 58.0, 52.5.

HRMS (ESI): m/z calcd. For $C_{19}H_{14}BrNNaO_5$ $[M+Na]^+$ 437.9948, found m/z 437.9949.

Methyl (1*R*,3a*R*,8b*R*)-1-(4-cyanophenyl)-3a-nitro-3a,8b-dihydro-1*H*-cyclopenta[*b*]benzofuran-2-carboxylate (3ah)



White solid. 31.2mg, 86% yield, 96% ee.

$[\alpha]_D^{26}$ = -121.96 (c = 1.01, CH_2Cl_2).

m.p.: 121-122 °C

HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, temperature = 25 ^{o}C, λ = 256 nm, retention time: 27.635 min (major), 33.292 min (minor).

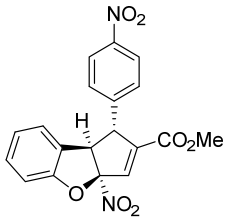
TLC: R_f = 0.28 (petroleum ether:ethyl acetate = 5:1) [UV]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 2H), 7.49 – 7.45 (m, 2H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.27 – 7.24 (m, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.06 – 7.01 (m, 2H), 4.38 – 4.34 (m, 2H), 3.67 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.7, 157.3, 147.2, 145.8, 134.7, 133.3, 130.4, 128.4, 126.1, 124.9, 124.6, 123.9, 118.6, 112.1, 111.4, 61.3, 58.4, 52.6.

HRMS (ESI): m/z calcd. For $C_{20}H_{14}N_2NaO_5$ $[M+Na]^+$ 385.0795, found m/z 385.0791.

Methyl (1*R*,3a*R*,8b*R*)-3a-nitro-1-(4-nitrophenyl)-3a,8b-dihydro-1*H*-cyclopenta[*b*]benzofuran-2-carboxylate (3ai)



White solid. 32.5mg, 85% yield, 96% ee.

$[\alpha]_D^{26}$ = -120.15 (c = 0.93, CH_2Cl_2).

m.p.: 105-106 ^{o}C

HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, temperature = 25 ^{o}C, λ = 256 nm, retention time: 24.478 min (major), 30.032 min (minor).

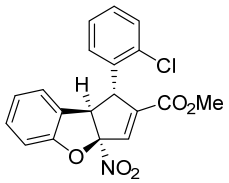
TLC: R_f = 0.32 (petroleum ether:ethyl acetate = 5:1) [UV]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.25 (m, 2H), 7.56 – 7.51 (m, 2H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.28 –7.26 (m, 1H), 7.11 (td, *J* = 7.4, 1.2 Hz, 1H), 7.07 – 7.03 (m, 2H), 4.43 (t, *J* = 2.4 Hz, 1H), 4.38 (d, *J* = 2.8 Hz, 1H), 3.68 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 157.3, 147.8, 147.7, 147.2, 134.8, 130.5, 128.5, 126.0, 124.9, 124.7, 124.6, 124.0, 111.4, 61.3, 58.2, 52.7.

HRMS (ESI): m/z calcd. For $C_{19}H_{14}N_2NaO_7$ $[M+Na]^+$ 405.0693, found m/z 405.0693.

Methyl (1*S*,3a*R*,8b*R*)-1-(2-chlorophenyl)-3a-nitro-3a,8b-dihydro-1*H*-cyclopenta[*b*]benzofuran-2-carboxylate (3aj)



White solid. 32.6mg, 88% yield, 96% ee.

$[\alpha]_D^{26}$ = -3.72 (c = 0.95, CH_2Cl_2).

m.p.: 81-82 ^{o}C

HPLC CHIRALCEL IA, *n*-hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, temperature = 25 ^{o}C, λ = 256 nm, retention time: 7.752 min (major), 8.522 min (minor).

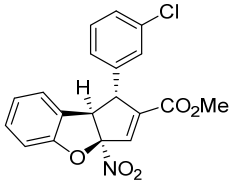
TLC: R_f = 0.30 (petroleum ether:ethyl acetate = 15:1) [UV]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.6 Hz, 1H), 7.46 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.32 – 7.22 (m, 4H), 7.09 (td, *J* = 7.4, 1.2 Hz, 1H), 7.06 (d, *J* = 1.6 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 4.96 (s, 1H), 4.30 (s, 1H), 3.66 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 157.4, 148.7, 140.7, 133.2, 130.0, 129.4, 127.9, 127.5, 126.9, 125.3, 124.8, 123.7, 111.2, 61.7, 61.5, 58.6, 14.0.

HRMS (ESI): m/z calcd. For $C_{19}H_{14}ClNNaO_5$ $[M+Na]^+$ 394.0453, found m/z 394.0458.

Methyl (1*R*,3a*R*,8b*R*)-1-(3-chlorophenyl)-3a-nitro-3a,8b-dihydro-1*H*-cyclopenta[*b*]benzofuran-2-carboxylate (3ak)



White solid. 34.1mg, 92% yield, 94% ee.

$[\alpha]_D^{26}$ = -63.09 (c = 0.88, CH_2Cl_2).

m.p.: 46-48 ^{o}C

HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, temperature = 25 ^{o}C, λ = 256 nm, retention time: 9.090 min (major), 10.503 min (minor).

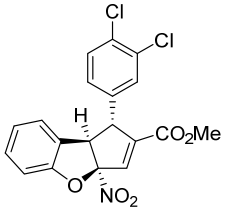
TLC: R_f = 0.24 (petroleum ether:ethyl acetate = 15:1) [UV]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 5H), 7.21 (dt, *J* = 7.2, 1.8 Hz, 1H), 7.09 (td, *J* = 7.6, 1.2 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 2.0 Hz, 1H), 4.36 (d, *J* = 2.8 Hz, 1H), 4.28 (t, *J* = 2.4 Hz, 1H), 3.68 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 157.3, 147.6, 142.5, 135.2, 134.1, 130.8, 130.3, 128.3, 127.8, 126.5, 125.5, 125.0, 124.7, 123.8, 111.3, 61.5, 58.2, 52.6.

HRMS (ESI): m/z calcd. For $C_{19}H_{14}ClNNaO_5$ $[M+Na]^+$ 394.0453, found m/z 394.0455.

Methyl (1*R*,3a*R*,8b*R*)-1-(3,4-dichlorophenyl)-3a-nitro-3a,8b-dihydro-1*H*-cyclopenta[*b*]benzofuran-2-carboxylate (3al)



Light yellow solid. 36.4mg, 90% yield, 96% ee.

$[\alpha]_D^{26}$ = -96.18 (c = 0.96, CH_2Cl_2).

m.p.: 112-114 ^oC

HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, temperature = 25 ^oC, λ = 256 nm, retention time: 9.378 min (major), 10.582 min (minor).

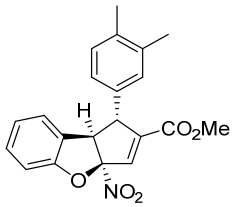
TLC: R_f = 0.25 (petroleum ether:ethyl acetate = 15:1) [UV]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 1H), 7.45 (d, *J* = 2.0 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.18 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.10 (td, *J* = 7.4, 0.8 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 2.0 Hz, 1H), 4.34 (d, *J* = 2.8 Hz, 1H), 4.27 (t, *J* = 2.6 Hz, 1H), 3.69 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 157.3, 147.4, 140.7, 134.4, 133.5, 132.3, 131.5, 130.4, 129.7, 126.7, 126.2, 124.9, 124.6, 123.9, 111.3, 61.4, 57.6, 52.6.

HRMS (ESI): m/z calcd. For $C_{19}H_{13}Cl_2NNaO_5$ $[M+Na]^+$ 428.0063, found m/z 428.0060.

Methyl (1*R*,3a*R*,8b*R*)-3a-nitro-1-(m-tolyl)-3a,8b-dihydro-1*H*-cyclopenta[*b*]benzofuran-2-carboxylate (3am)



Light yellow solid. 32.8 mg, 90% yield, 97% ee.

$[\alpha]_D^{26}$ = -66.66 (c = 0.88, CH_2Cl_2).

m.p.: 43-45 ^oC

HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 ^oC, λ = 256 nm, retention time: 6.867 min (major), 7.747 min (minor).

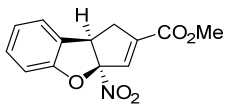
TLC: R_f = 0.29 (petroleum ether:ethyl acetate = 15:1) [UV]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.10 – 7.00 (m, 4H), 6.97 (d, *J* = 2.0 Hz, 1H), 4.37 (d, *J* = 2.8 Hz, 1H), 4.27 (t, *J* = 2.4 Hz, 1H), 3.67 (s, 3H), 2.29 (s, 3H), 2.27 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 157.4, 148.4, 138.0, 137.7, 136.3, 133.1, 130.6, 130.0, 128.6, 127.0, 125.3, 124.8, 124.7, 123.6, 111.1, 61.8, 58.2, 52.4, 20.1, 19.6.

HRMS (ESI): m/z calcd. For $C_{21}H_{19}NNaO_5$ $[M+Na]^+$ 388.1155, found m/z 388.1150.

Methyl (3a*R*,8b*R*)-3a-nitro-3a,8b-dihydro-1*H*-cyclopenta[*b*]benzofuran-2-carboxylate (3an)



White solid. 25.1 mg, 96% yield, 95% ee.

$[\alpha]_D^{26}$ = 152.19 (c = 1.29, CH_2Cl_2).

m.p.: 82-83 °C

HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 °C, λ = 256 nm, retention time: 8.762 min (major), 10.593 min (minor).

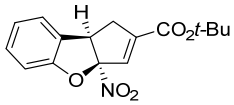
TLC: R_f = 0.19 (petroleum ether:ethyl acetate = 15:1) [UV]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.19 (m, 2H), 7.03 (td, *J* = 7.6, 1.2 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.78 (t, *J* = 2.2 Hz, 1H), 4.52 (dd, *J* = 8.8, 2.8 Hz, 1H), 3.78 (s, 3H), 3.43 (ddd, *J* = 17.6, 8.8, 2.4 Hz, 1H), 2.85 (dt, *J* = 17.6, 2.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 157.4, 146.0, 132.7, 129.8, 127.5, 126.5, 124.8, 123.5, 110.9, 52.5, 51.2, 38.8.

HRMS (ESI): m/z calcd. For $C_{13}H_{11}NNaO_5$ $[M+Na]^+$ 284.0529, found m/z 284.0523.

Tert-butyl (3a*R*,8b*R*)-3a-nitro-3a,8b-dihydro-1*H*-cyclopenta[*b*]benzofuran-2-carboxylate (3ao)



White solid. 28.4 mg, 94% yield, 96% ee.

$[\alpha]_D^{26}$ = 127.14 (c = 0.42, CH_2Cl_2).

m.p.: 133-135 °C

HPLC CHIRALCEL OJ-H, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 °C, λ = 256 nm, retention time: 6.825 min (major), 11.173 min (minor).

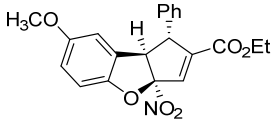
TLC: R_f = 0.34 (petroleum ether:ethyl acetate = 15:1) [UV]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.71 (t, *J* = 2.2 Hz, 1H), 4.55 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.43 (ddd, *J* = 18.0, 8.8, 2.4 Hz, 1H), 2.84 (dt, *J* = 17.6, 2.4 Hz, 1H), 1.51 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.4, 157.5, 148.1, 131.6, 129.7, 127.8, 126.8, 124.8, 123.4, 110.9, 82.5, 51.1, 38.9, 28.1.

HRMS (ESI): m/z calcd. For $C_{16}H_{17}NNaO_5$ $[M+Na]^+$ 326.0999, found m/z 326.1005.

(1*R*,3a*S*,8b*R*)-7-Methoxy-3a-nitro-1-phenyl-3a,8b-dihydro-1*H*-cyclopenta[*b*]benzofuran-2-yl propionate (3ba)



Yellow solid. 27.5mg, 72% yield, 94% ee.

$[\alpha]_D^{26}$ = -43.33 (c = 0.72, CH_2Cl_2).

m.p.: 100-101 °C

HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, temperature = 25 ^{o}C, λ = 256 nm, retention time: 12.717 min (major), 14.470 min (minor).

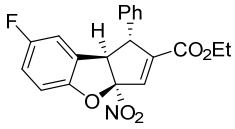
TLC: R_f = 0.28 (petroleum ether:ethyl acetate = 10:1) [UV]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 2H), 7.34 – 7.29 (m, 3H), 6.97 (d, *J* = 2.0 Hz, 1H), 6.95 – 6.91 (m, 1H), 6.84 – 6.80 (m, 2H), 4.37 (d, *J* = 2.8 Hz, 1H), 4.30 (t, *J* = 2.6 Hz, 1H), 4.16 – 4.01 (m, 2H), 3.78 (s, 3H), 1.13 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.6, 156.4, 151.3, 148.5, 140.6, 133.3, 129.4, 127.9, 127.8, 127.5, 125.7, 115.1, 111.3, 110.5, 62.1, 61.5, 58.4, 56.2, 14.0.

HRMS (ESI): m/z calcd. For $C_{21}H_{19}NNaO_6$ $[M+Na]^+$ 404.1105, found m/z 404.1106.

(1*R*,3a*S*,8b*R*)-7-Fluoro-3a-nitro-1-phenyl-3a,8b-dihydro-1*H*-cyclopenta[*b*]benzofuran-2-yl propionate (3ca)



White solid. 31.0 mg, 84% yield, 95% ee.

$[\alpha]_D^{26}$ = -46.61 (c = 0.61, CH_2Cl_2).

m.p.: 81-83 ^{o}C

HPLC CHIRALCEL IA, *n*-hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, temperature = 25 ^{o}C, λ = 256 nm, retention time: 7.027 min (major), 13.022 min (minor).

TLC: R_f = 0.21 (petroleum ether:ethyl acetate = 15:1) [UV]

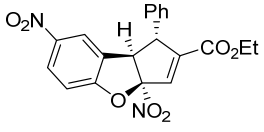
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.35 –7.28 (m, 3H), 7.05 – 6.90 (m, 4H), 4.39 (d, *J* = 2.8 Hz, 1H), 4.30 (t, *J* = 2.4 Hz, 1H), 4.17 – 4.00 (m, 2H), 1.13 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.5, 159.2 (d, $J_{C,F}$ = 241.6 Hz), 153.4, 148.8, 140.3, 133.0, 129.4, 128.2 (d, $J_{C,F}$ = 9.1 Hz), 128.0, 127.4, 125.8, 116.6 (d, $J_{C,F}$ = 24.2 Hz), 111.9 (d, $J_{C,F}$ = 25.7 Hz), 111.8 (d, $J_{C,F}$ = 9.1 Hz), 61.7, 61.6, 58.4, 14.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -119.8 (s).

HRMS (ESI): m/z calcd. For $C_{20}H_{16}FNNaO_5$ $[M+Na]^+$ 392.0905, found m/z 392.0902.

(1*R*,3a*S*,8b*R*)-3a,7-Dinitro-1-phenyl-3a,8b-dihydro-1*H*-cyclopenta[*b*]benzofuran-2-yl propionate (3da)



White solid. 26.7 mg, 67% yield, 90% ee.

$[\alpha]_D^{26}$ = -20.81 (c = 0.66, CH_2Cl_2).

m.p.: 128-129 ^{o}C

HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, temperature = 25 ^{o}C, λ = 250 nm, retention time: 17.538 min (major), 19.512 min (minor).

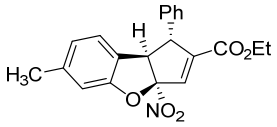
TLC: R_f = 0.43 (petroleum ether:ethyl acetate = 5:1) [UV]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 8.8, 2.4 Hz, 1H), 8.20 (dd, *J* = 2.4, 1.2 Hz, 1H), 7.45 – 7.39 (m, 2H), 7.37 – 7.30 (m, 3H), 7.14 (d, *J* = 8.8 Hz, 1H), 7.01 (d, *J* = 2.4 Hz, 1H), 4.47 (d, *J* = 2.8 Hz, 1H), 4.35 (t, *J* = 2.4 Hz, 1H), 4.18 – 4.02 (m, 2H), 1.13 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.1, 162.0, 149.6, 144.4, 139.6, 132.1, 129.6, 128.6, 128.3, 127.4, 127.1, 126.1, 121.2, 111.4, 61.8, 60.6, 58.5, 14.0.

HRMS (ESI): m/z calcd. For $C_{20}H_{16}N_2NaO_7$ $[M+Na]^+$ 419.0850, found m/z 419.0847.

(1*R*,3a*S*,8b*R*)-6-Methyl-3a-nitro-1-phenyl-3a,8b-dihydro-1*H*-cyclopenta[*b*]benzofuran-2-yl propionate (3ea)



White solid. 26.7 mg, 73% yield, 96% ee.

m.p.: 82-84 ^{o}C

$[\alpha]_D^{26}$ = -69.11 (c = 0.85, CH_2Cl_2).

HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, temperature = 25 ^{o}C, λ = 256 nm, retention time: 8.557 min (major), 10.153 min (minor).

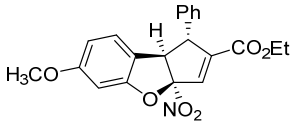
TLC: R_f = 0.26 (petroleum ether:ethyl acetate = 15:1) [UV]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.5 Hz, 2H), 7.33 – 7.29 (m, 3H), 7.16 (d, *J* = 7.8 Hz, 1H), 6.99 (s, 1H), 6.89 (d, *J* = 7.2 Hz, 1H), 6.85 (s, 1H), 4.35 (d, *J* = 2.4 Hz, 1H), 4.28 (t, *J* = 2.4 Hz, 1H), 4.15 – 4.02 (m, 2H), 2.37 (s, 3H), 1.13 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.6, 157.7, 148.6, 140.7, 140.6, 133.3, 129.3, 127.8, 127.5, 125.6, 124.4, 124.3, 124.0, 111.7, 61.6, 61.5, 58.7, 21.7, 14.0.

HRMS (ESI): m/z calcd. For $C_{21}H_{19}NNaO_5$ $[M+Na]^+$ 388.1155, found m/z 388.1148.

(1*R*,3a*S*,8b*R*)-6-Methoxy-3a-nitro-1-phenyl-3a,8b-dihydro-1*H*-cyclopenta[*b*]benzofuran-2-yl propionate (3fa)



Light yellow solid. 29.7mg, 78% yield, 90% ee.

$[\alpha]_D^{26}$ = -101.59 (c = 0.32, CH_2Cl_2).

m.p.: 42-44 ^{o}C

HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, temperature = 25 ^{o}C, λ = 256 nm, retention time: 11.303 min (major), 13.192 min (minor).

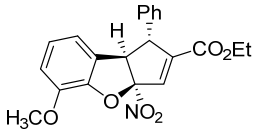
TLC: R_f = 0.30 (petroleum ether:ethyl acetate = 10:1) [UV]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.32 – 7.29 (m, 3H), 7.15 (d, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 1.8 Hz, 1H), 6.62 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.59 (d, *J* = 2.4 Hz, 1H), 4.32 (d, *J* = 2.4 Hz, 1H), 4.26 (t, *J* = 2.4 Hz, 1H), 4.15 – 4.02 (m, 2H), 3.80 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.7, 161.7, 158.7, 148.8, 140.7, 133.1, 129.3, 127.8, 127.5, 126.1, 124.9, 118.8, 109.8, 97.3, 61.5, 61.4, 58.8, 55.8, 14.0.

HRMS (ESI): m/z calcd. For $C_{21}H_{19}NNaO_6$ $[M+Na]^+$ 404.1105, found m/z 404.1108.

(1*R*,3a*S*,8b*R*)-5-Methoxy-3a-nitro-1-phenyl-3a,8b-dihydro-1*H*-cyclopenta[*b*]benzofuran-2-yl propionate (3ga)



Light yellow solid. 35.9 mg, 94% yield, >99% ee.

$[\alpha]_D^{26}$ = -54.74 (c = 1.06, CH_2Cl_2).

m.p.: 46-47 °C

HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, temperature = 25 °C, λ = 256 nm, retention time: 12.185 min (major), 13.883 min (minor).

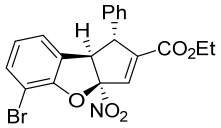
TLC: R_f = 0.23 (petroleum ether:ethyl acetate = 10:1) [UV]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 2H), 7.33 – 7.27 (m, 3H), 7.04 (t, *J* = 7.8 Hz, 1H), 7.01 (d, *J* = 2.0 Hz, 1H) 6.90 (s, 1H), 6.88 (s, 1H), 4.39 (d, *J* = 2.8 Hz, 1H), 4.31 (t, *J* = 2.6 Hz, 1H), 4.17 – 4.00 (m, 2H), 3.92 (s, 3H), 1.12 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.5, 148.7,145.6, 145.0, 140.6, 133.0, 129.3, 128.1, 127.8, 127.4, 125.4, 124.6, 116.3, 113.0, 62.2, 61.5, 58.5, 56.3, 14.0.

HRMS (ESI): m/z calcd. For $C_{21}H_{19}NNaO_6$ $[M+Na]^+$ 404.1105, found m/z 404.1104.

(1*R*,3a*S*,8b*R*)-5-Bromo-3a-nitro-1-phenyl-3a,8b-dihydro-1*H*-cyclopenta[*b*]benzofuran-2-yl propionate (3ha)



Light yellow solid. 34.7 mg, 81% yield, 97% ee.

$[\alpha]_D^{26}$ = -78.75 (c = 0.93, CH_2Cl_2).

m.p.: 42-44 °C

HPLC CHIRALCEL OD-H, *n*-hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, temperature = 25 °C, λ = 256 nm, retention time: 8.287 min (major), 13.217 min (minor).

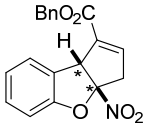
TLC: R_f = 0.23 (petroleum ether:ethyl acetate = 15:1) [UV]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.34 – 7.28 (m, 3H), 7.22 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.03 (d, *J* = 2.0 Hz, 1H), 6.97 (t, *J* = 8.0 Hz, 1H), 4.46 (d, *J* = 2.8 Hz, 1H), 4.31 (t, *J* = 2.4 Hz, 1H), 4.18 – 4.01 (m, 2H), 1.14 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.4, 154.9, 149.1, 140.3, 133.2, 132.7, 129.4, 128.2, 128.0, 127.4, 125.0, 124.7, 123.6, 103.8, 62.4, 61.6, 58.6, 14.0.

HRMS (ESI): m/z calcd. For $C_{20}H_{16}BrNNaO_5$ $[M+Na]^+$ 452.0104, found m/z 452.0112.

Benzyl 3a-nitro-3a,8b-dihydro-3*H*-cyclopenta[*b*]benzofuran-1-carboxylate (5)



Light yellow oil. 25.7 mg, 38% yield, 72% ee.

$[\alpha]_D^{26}$ = -24.76 (c = 1.93, CH_2Cl_2).

HPLC CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 0.8 mL/min, temperature = 25 ^oC, λ = 256 nm, retention time: 6.963 min (major), 7.623 min (minor).

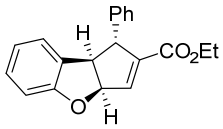
TLC: R_f = 0.26 (petroleum ether:ethyl acetate = 15:1) [UV]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.6 Hz, 1H), 7.43 – 7.35 (m, 5H), 7.28 – 7.23 (m, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.97 (td, *J* = 7.4, 1.2 Hz, 1H) 6.80 (q, *J* = 2.4 Hz, 1H), 5.30 (d, *J* = 12.4 Hz, 1H), 5.20 (d, *J* = 12.4 Hz, 1H), 5.14 (s, 1H), 3.74 (ddd, *J* = 20.0, 1.2, 1.2 Hz, 1H), 3.32 (ddd, *J* = 19.6, 2.8, 1.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 157.9, 139.5, 135.4, 134.8, 129.7, 128.8, 128.7, 128.7, 126.7, 123.9, 123.2, 121.5, 110.4, 67.0, 60.6, 44.4.

HRMS (ESI): m/z calcd. For $C_{19}H_{15}NNaO_5$ $[M+Na]^+$ 360.0842, found m/z 360.0842.

Ethyl (1*R*,3a*R*,8b*R*)-1-Phenyl-3a,8b-dihydro-1*H*-cyclopenta[*b*]benzofuran-2-carboxylate (6a)



White solid. 44.4 mg, 73% yield, 94% ee.

$[\alpha]_D^{26}$ = -150.86 (c = 0.70, CH_2Cl_2).

m.p.: 54-55 ^oC

HPLC CHIRALCEL OD-H, *n*-hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, temperature = 25 ^oC, λ = 254 nm, retention time: 9.725 min (major), 18.097 min (minor).

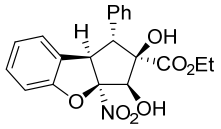
TLC: R_f = 0.32 (petroleum ether:ethyl acetate = 3:1) [UV]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 3H), 7.16 – 7.08 (m, 3H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 2.0 Hz, 1H), 6.86 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 5.83 –5.79 (m, 1H), 4.55 (t, *J* = 2.6 Hz, 1H), 4.25 – 4.08 (m, 2H), 3.66 (d, *J* = 3.2 Hz, 1H), 1.14 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 209.4, 164.4, 164.2, 153.7, 140.7, 136.7, 130.6, 129.1, 129.1, 127.4, 127.3, 124.3, 121.2, 116.7, 61.8, 61.1, 53.2, 14.0.

HRMS (ESI): m/z calcd. For $C_{20}H_{18}NaO_3$ $[M+Na]^+$ 329.1148, found m/z 329.1142.

Ethyl (1*R*,2*R*,3*R*,3a*S*,8b*R*)-2,3-dihydroxy-3a-nitro-1-phenyl-2,3,3a,8b-tetrahydro-1*H*-cyclopenta[*b*]benzofuran-2-carboxylate (6b)



White solid. 39.1 mg, 51% yield, 3:1 dr, 96% ee.

$[\alpha]_D^{26}$ = -33.67 (c = 0.98, CH_2Cl_2).

m.p.: 128-130 °C

HPLC CHIRALCEL OD-H, *n*-hexane/2-propanol = 90/10, flow rate = 0.8 mL/min, temperature = 25 °C, λ = 256 nm, retention time: 20.868 min (major), 44.990 min (minor).

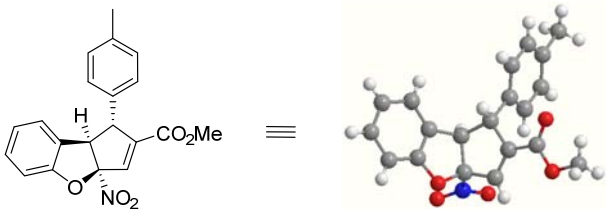
TLC: R_f = 0.20 (petroleum ether:ethyl acetate = 4:1) [UV]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H), 7.44 – 7.39 (m, 2H), 7.38 – 7.29 (m, 2H), 7.17 – 7.13 (m, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 5.80 (d, *J* = 11.6 Hz, 1H), 4.60 (d, *J* = 3.2 Hz, 1H), 3.90 – 3.81 (m, 1H), 3.77 (s, 1H), 3.63 – 3.54 (m, 1H), 3.48 (d, *J* = 3.2 Hz, 1H), 3.28 (d, *J* = 12.0 Hz, 1H), 0.80 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 157.8, 138.2, 129.8, 129.2, 128.9, 128.5, 128.3, 124.1, 123.7, 121.5, 111.1, 86.0, 77.7, 63.0, 63.0, 57.1, 14.0.

HRMS (ESI): m/z calcd. For $C_{20}H_{19}NNaO_7$ $[M+Na]^+$ 408.1054, found m/z 408.1055.

7. Crystal data of 3ad and 3ao



3ad **3ad**

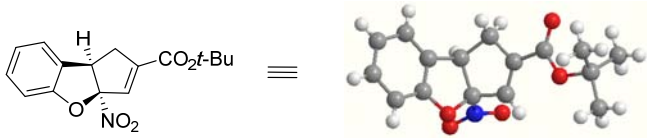
The chiral product of **3ad** was recrystallized by petroleum ether/ethyl acetate.

CCDC 1919097 (**3ad**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S3. Crystal data and structure refinement of 3ad

Identification code	**3ad**
Empirical formula	$C_{20}H_{17}NO_5$
Formula weight	351.35
Temperature/K	100.00(10)
Crystal system	tetragonal
Space group	$P4_32_12$
a/Å	9.08830(10)
b/Å	9.08830(10)
c/Å	41.3484(8)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3415.26(10)
Z	8
ρ_{calc}g/cm^3	1.367
μ/mm^{-1}	0.820
F(000)	1472.0
Crystal size/mm^3	0.11 × 0.1 × 0.08
Radiation	CuKα (λ = 1.54184)

2Θ range for data collection/°	8.554 to 147.494
Index ranges	$-11 \leq h \leq 10$, $-10 \leq k \leq 7$, $-51 \leq l \leq 51$
Reflections collected	22632
Independent reflections	3424 [R_{int} = 0.0296, R_{sigma} = 0.0155]
Data/restraints/parameters	3424/7/238
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0768, wR_2 = 0.2148
Final R indexes [all data]	R_1 = 0.0775, wR_2 = 0.2155
Largest diff. peak/hole / e $Å^{-3}$	0.70/-0.63
Flack/Hooft parameter	-0.01(5)/0.00(5)



3ao **3ao**

The chiral product of **3ao** was recrystallized by petroleum ether/ethyl acetate.

CCDC 1919105 (**3ao**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S2. Crystal data and structure refinement of 3ao

Identification code	**3ao**
Empirical formula	$C_{16}H_{17}NO_5$
Formula weight	303.30
Temperature/K	286(4)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.23380(10)
b/Å	11.66010(10)
c/Å	21.6605(2)
α/°	90
β/°	90
γ/°	90

Volume/Å^3	1574.43(3)
Z	4
ρ_{calc}g/cm^3	1.280
μ/mm^{-1}	0.798
F(000)	640.0
Crystal size/mm^3	0.38 × 0.25 × 0.18
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.164 to 142.498
Index ranges	$-5 \leq h \leq 7$, $-14 \leq k \leq 14$, $-26 \leq l \leq 26$
Reflections collected	15520
Independent reflections	3000 [R_{int} = 0.0258, R_{sigma} = 0.0200]
Data/restraints/parameters	3000/0/202
Goodness-of-fit on F^2	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0372, wR_2 = 0.0932
Final R indexes [all data]	R_1 = 0.0421, wR_2 = 0.0955
Largest diff. peak/hole / e Å^{-3}	0.12/-0.18
Flack parameter	-0.01(8)

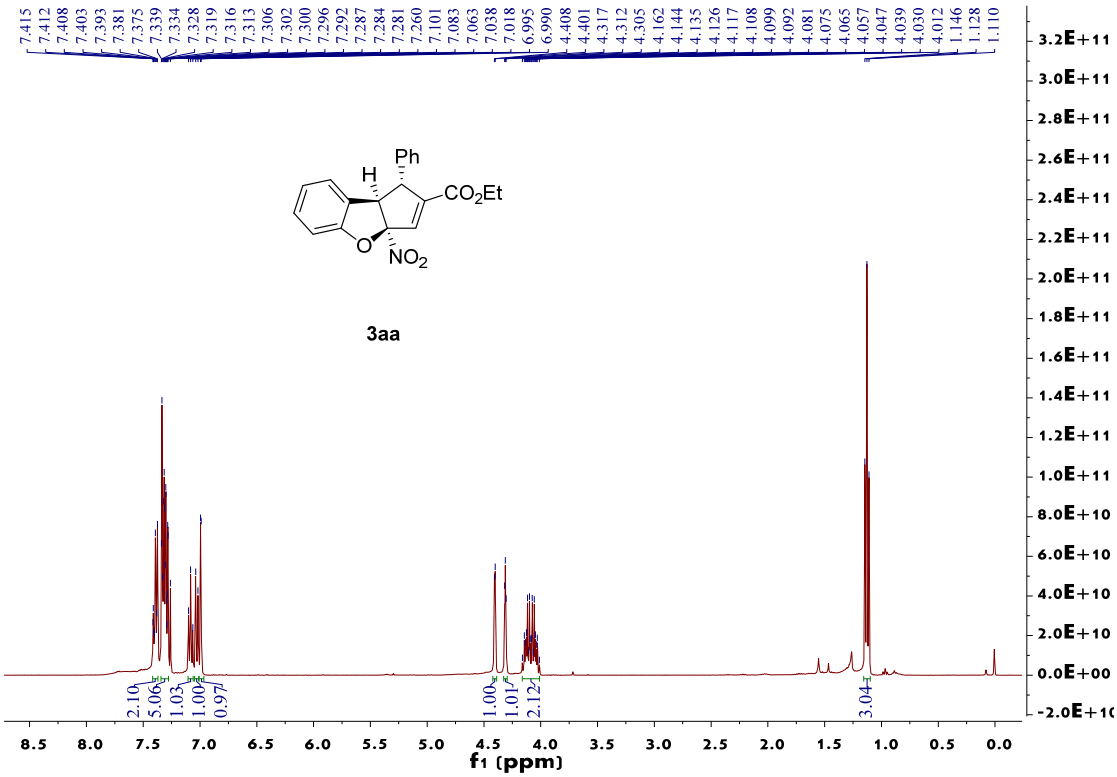
References

(1) L. Liang, H.-Y. Niu, D.-C. Wang, X.-H. Yang, G.-R. Qu and H.-M. Guo, *Chem. Commun.*, 2019, **55**, 553.

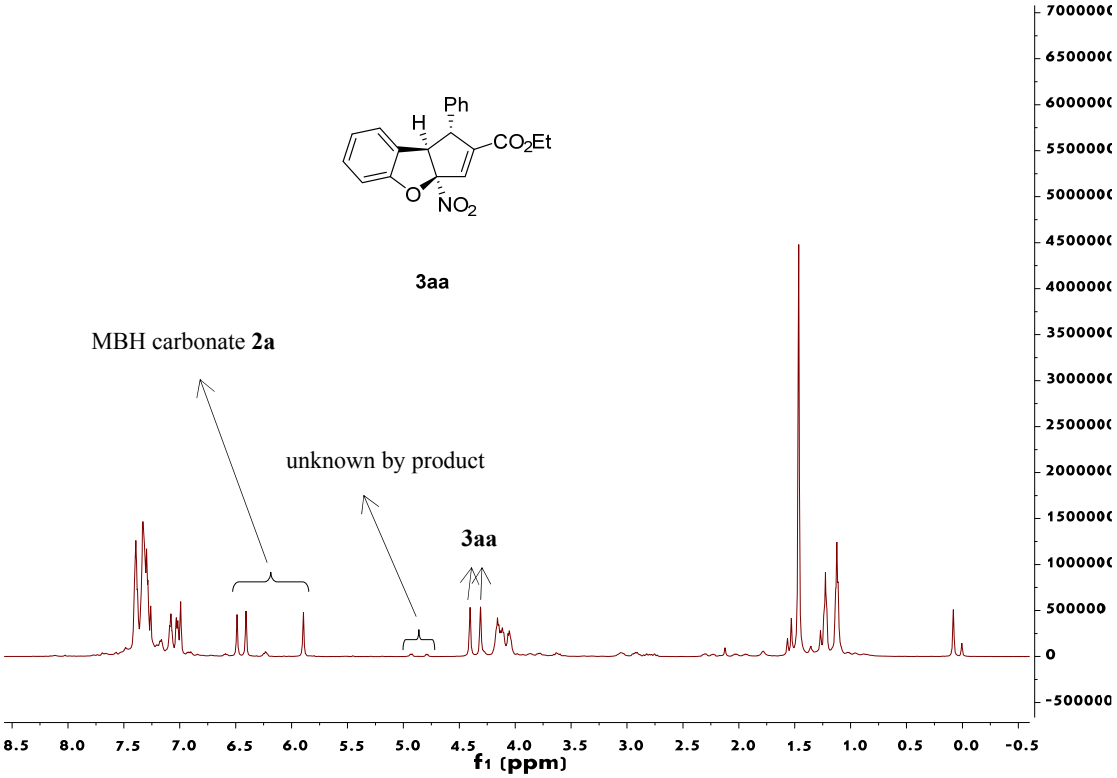
(2) S. J. S. Roy and S. Mukherjee, *Chem. Commun.*, 2014, **50**, 121.

8. Copies of ^{1}H and ^{13}C NMR spectra

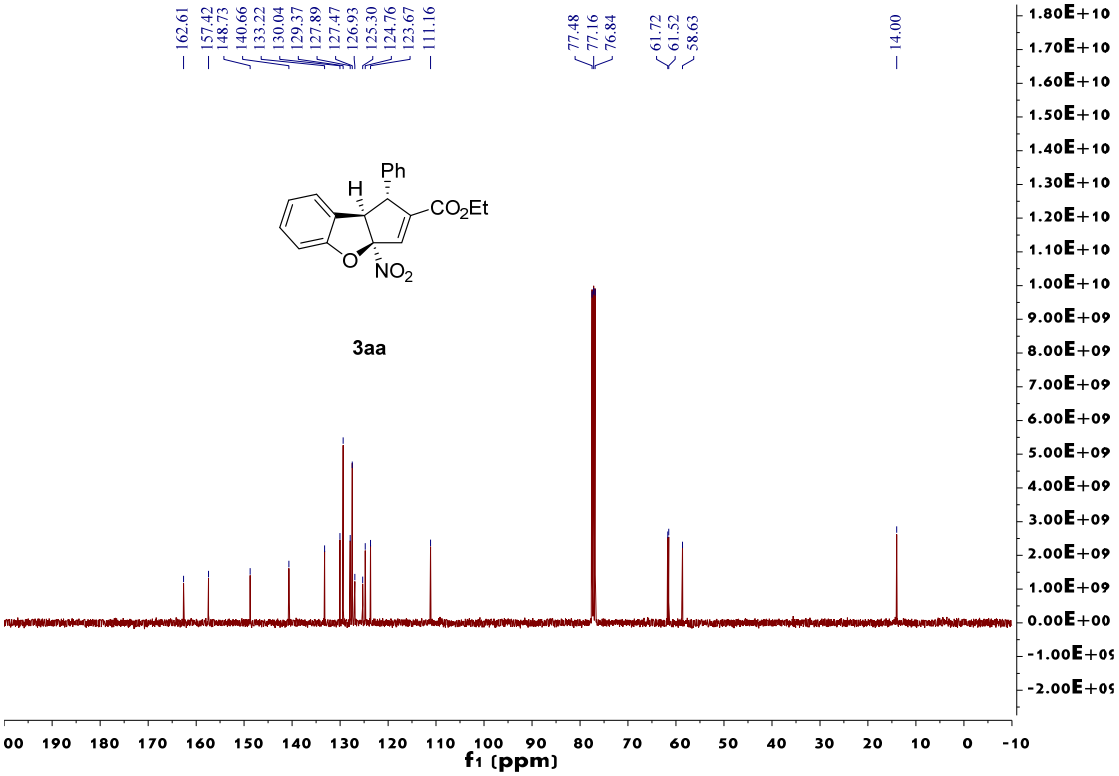
^{1}H NMR of 3aa



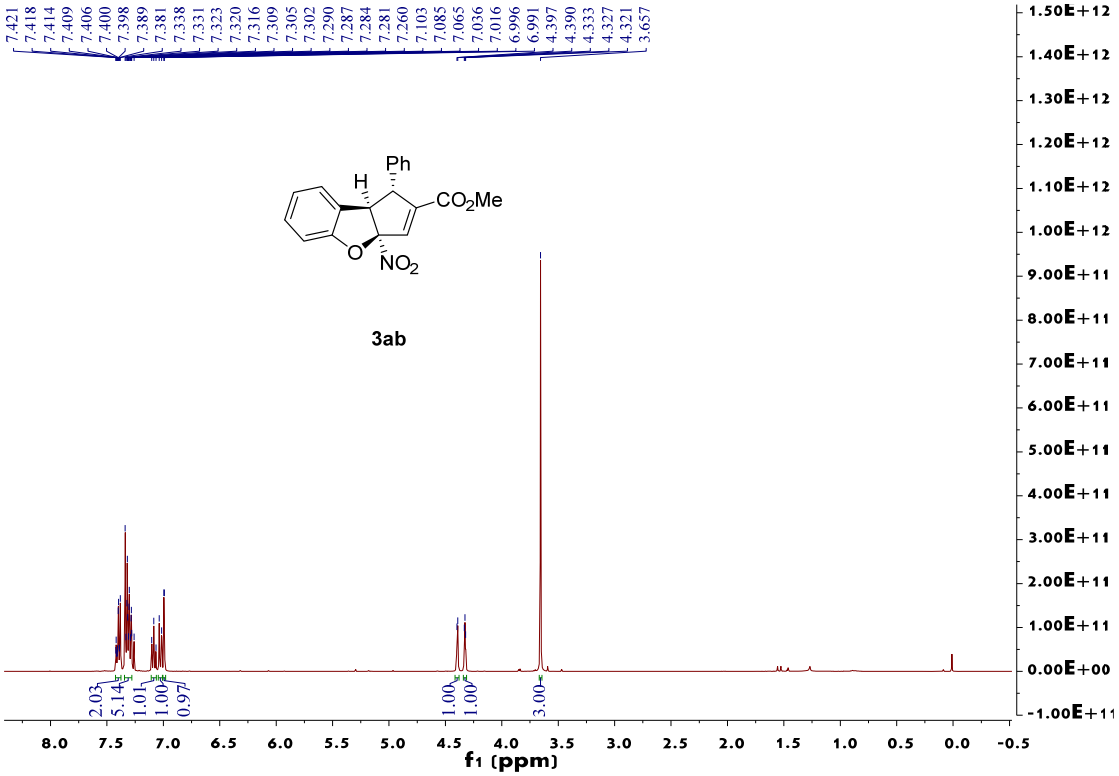
Crude NMR of 3aa



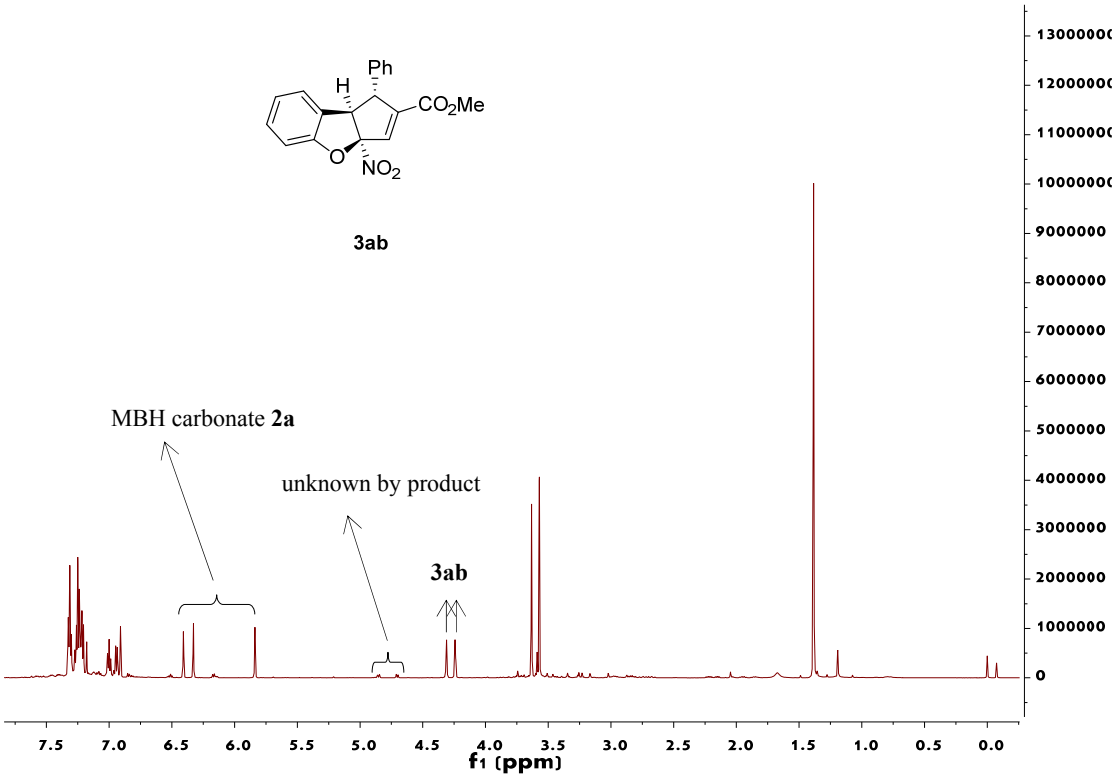
^{13}C NMR of 3aa



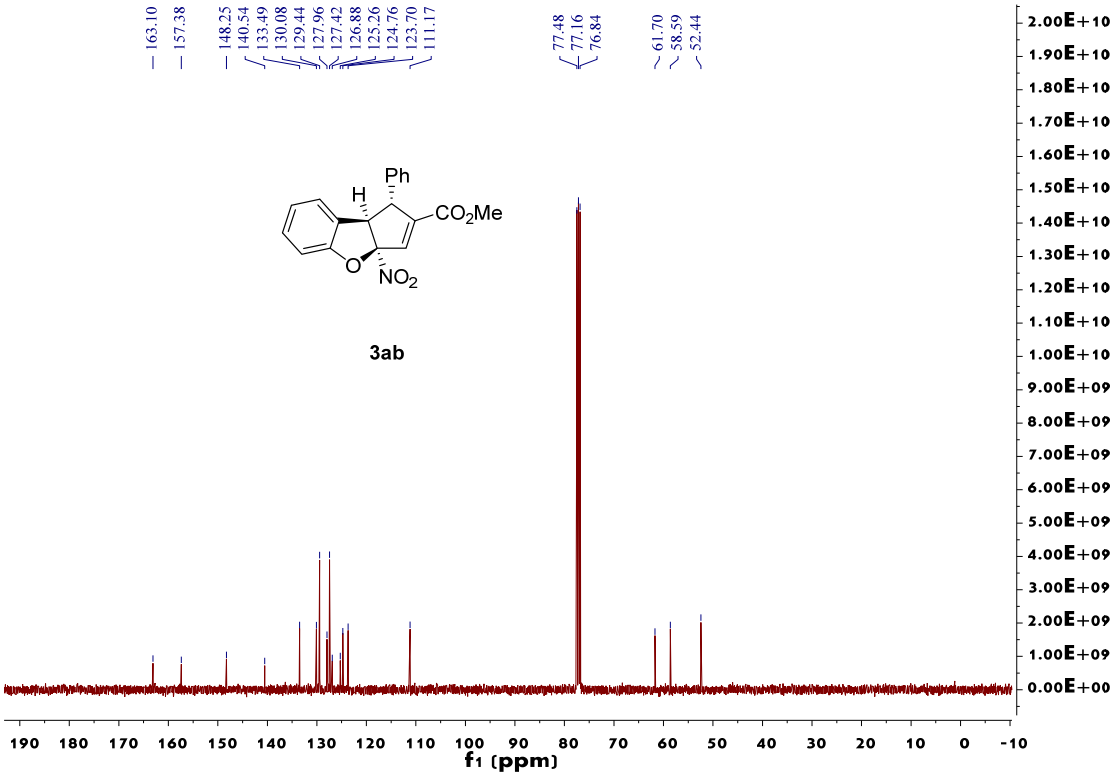
^{1}H NMR of 3ab



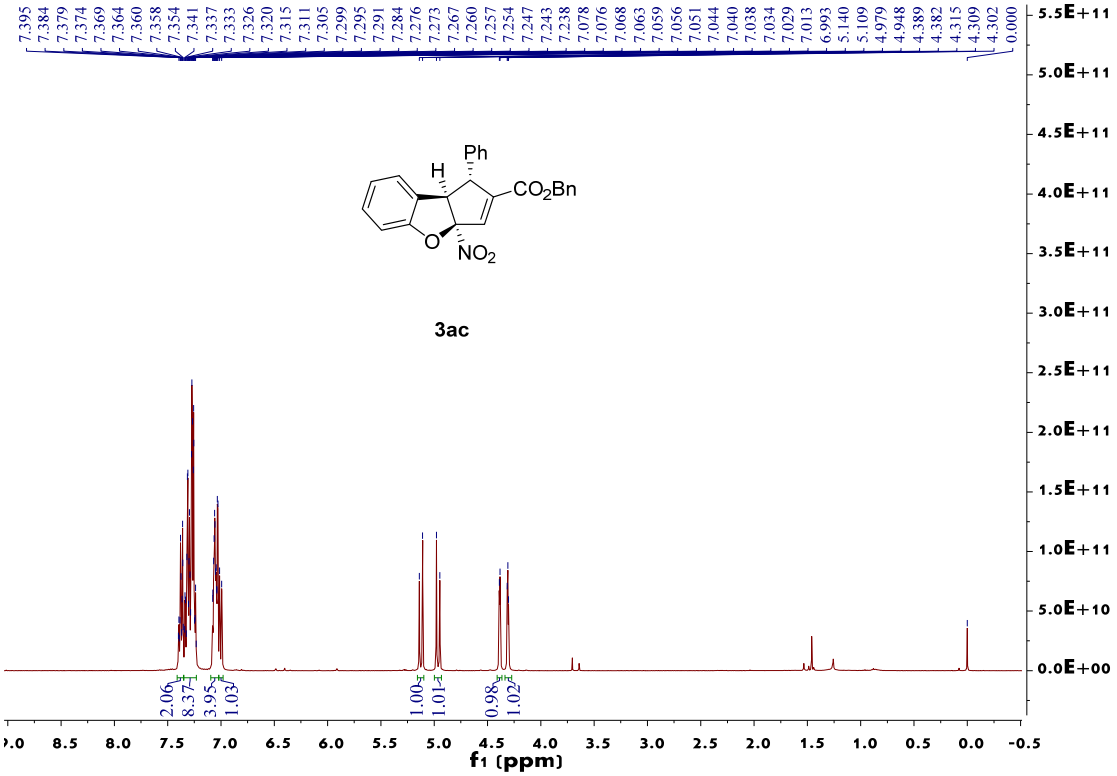
Crude NMR of 3ab



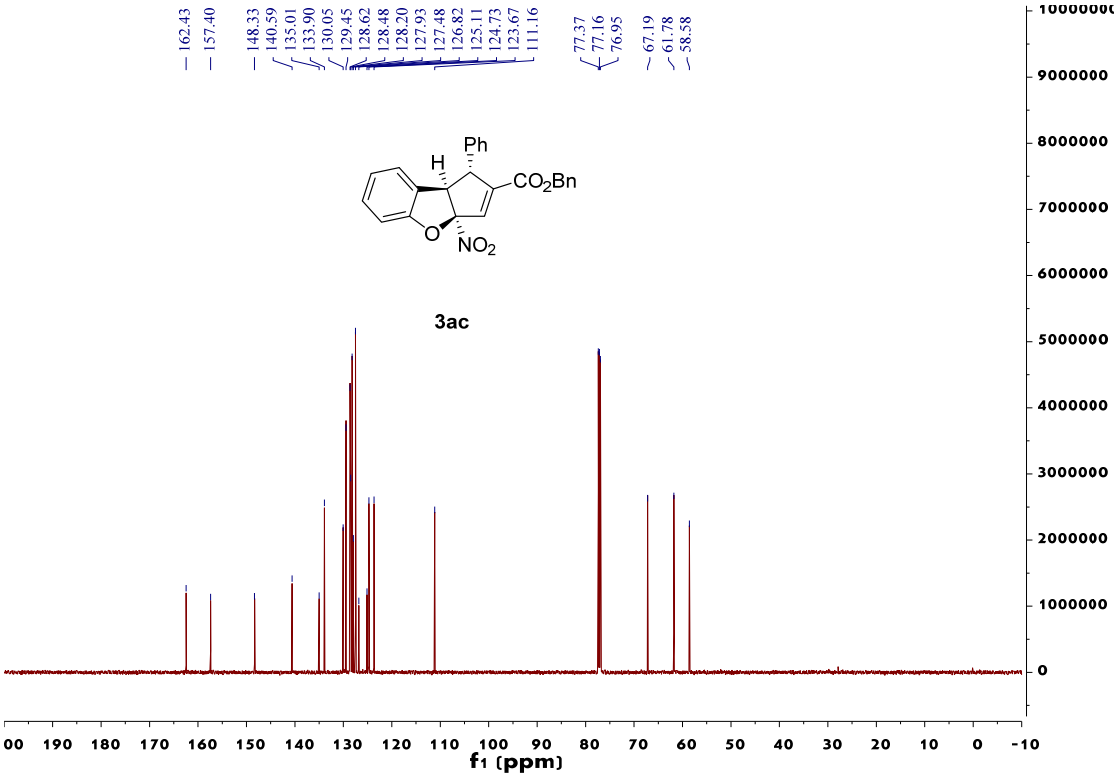
^{13}C NMR of 3ab



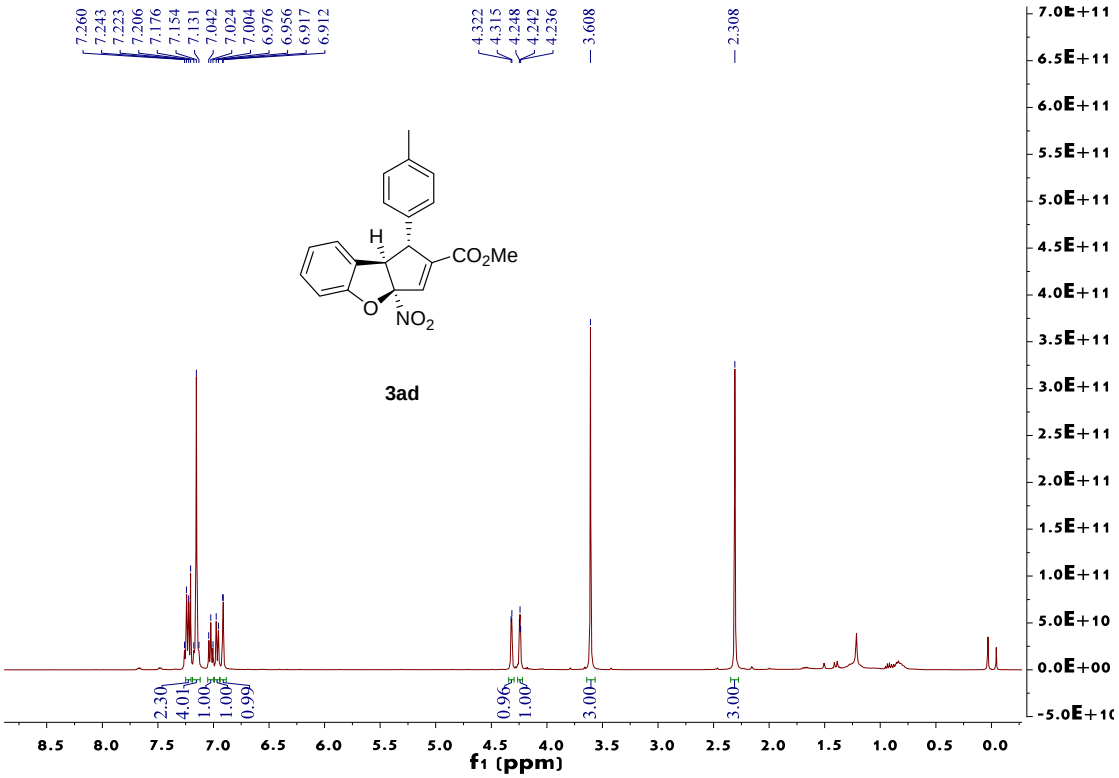
^{1}H NMR of 3ac



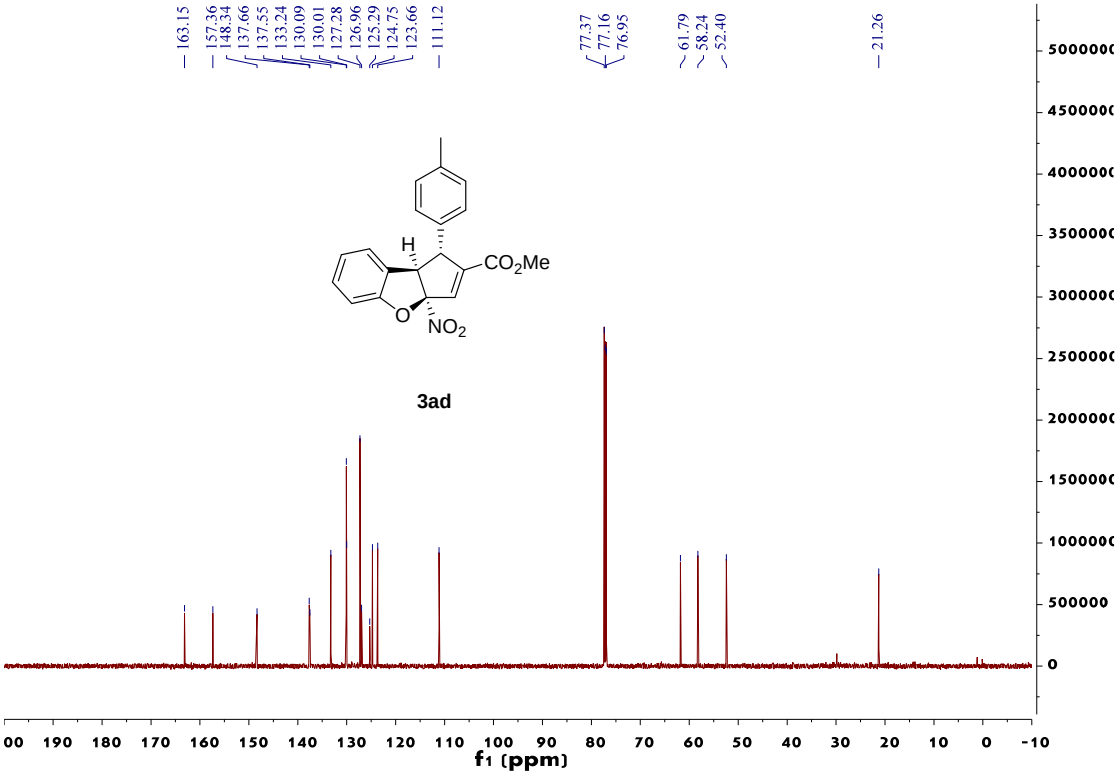
^{13}C NMR of 3ac



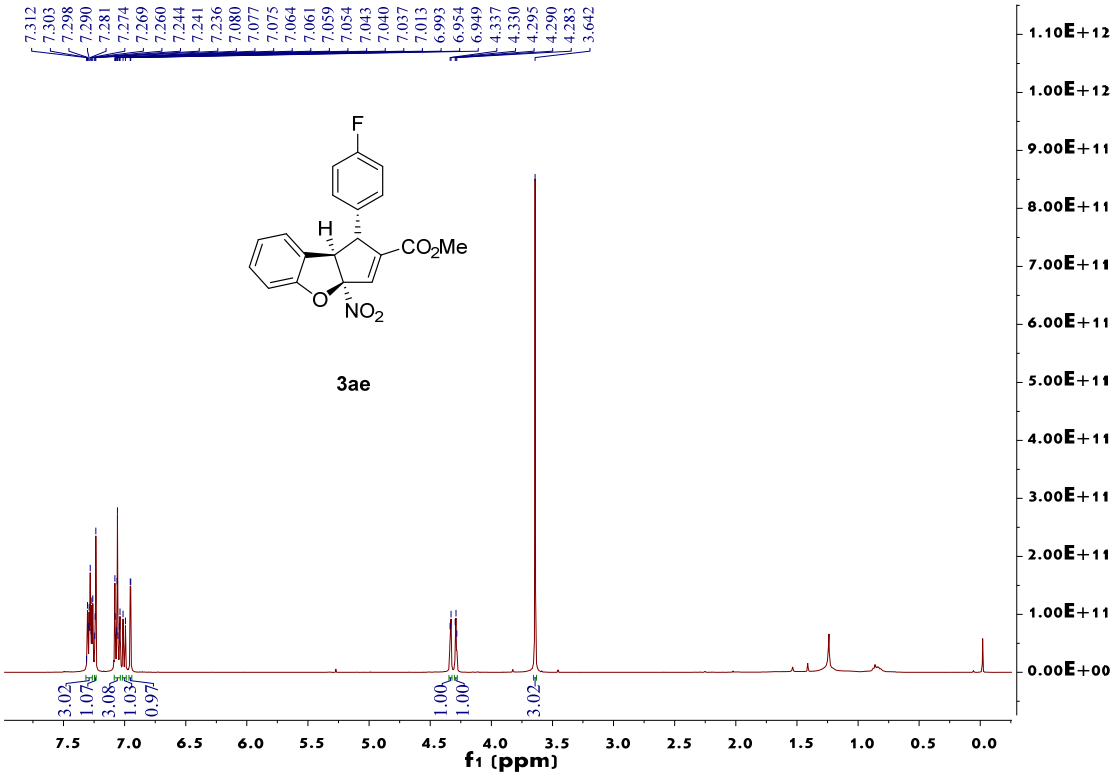
^{1}H NMR of **3ad**



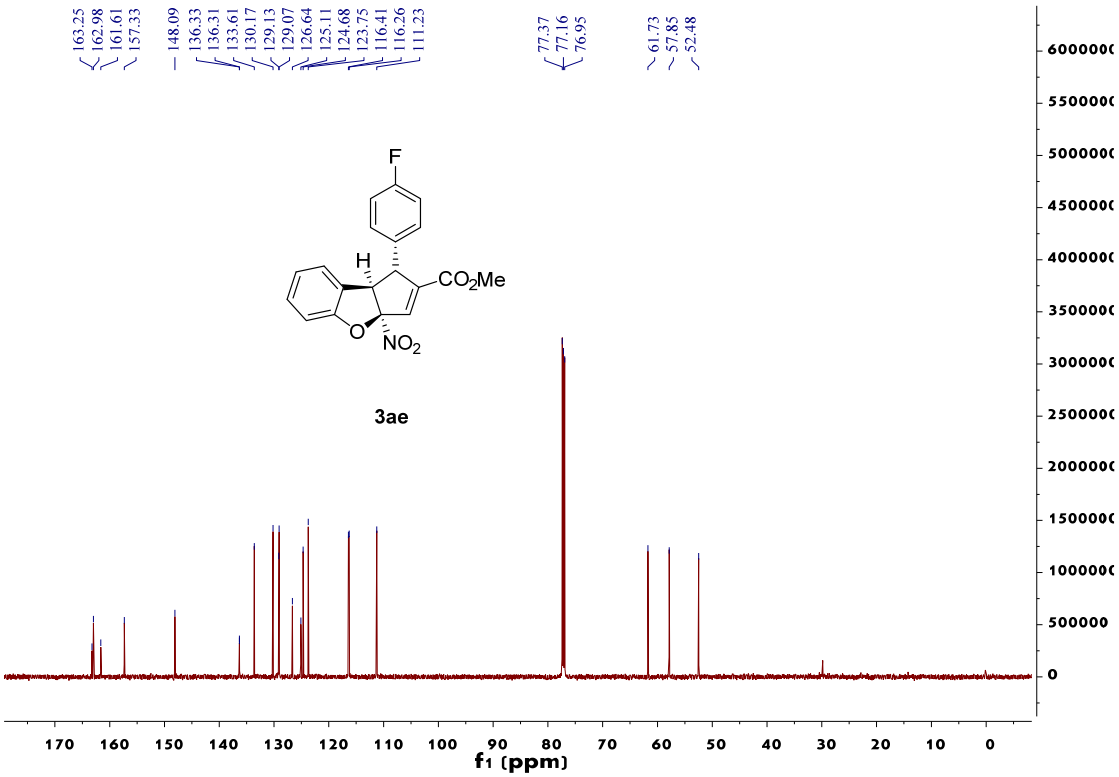
^{13}C NMR of **3ad**



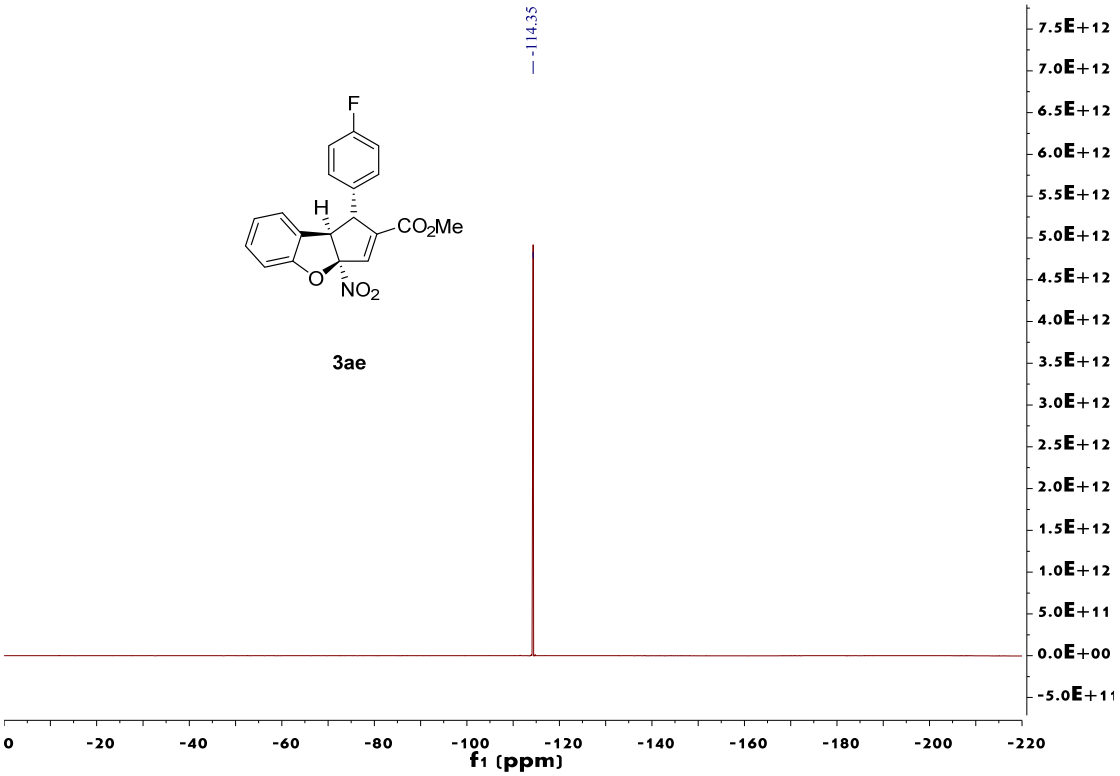
^{1}H NMR of 3ae



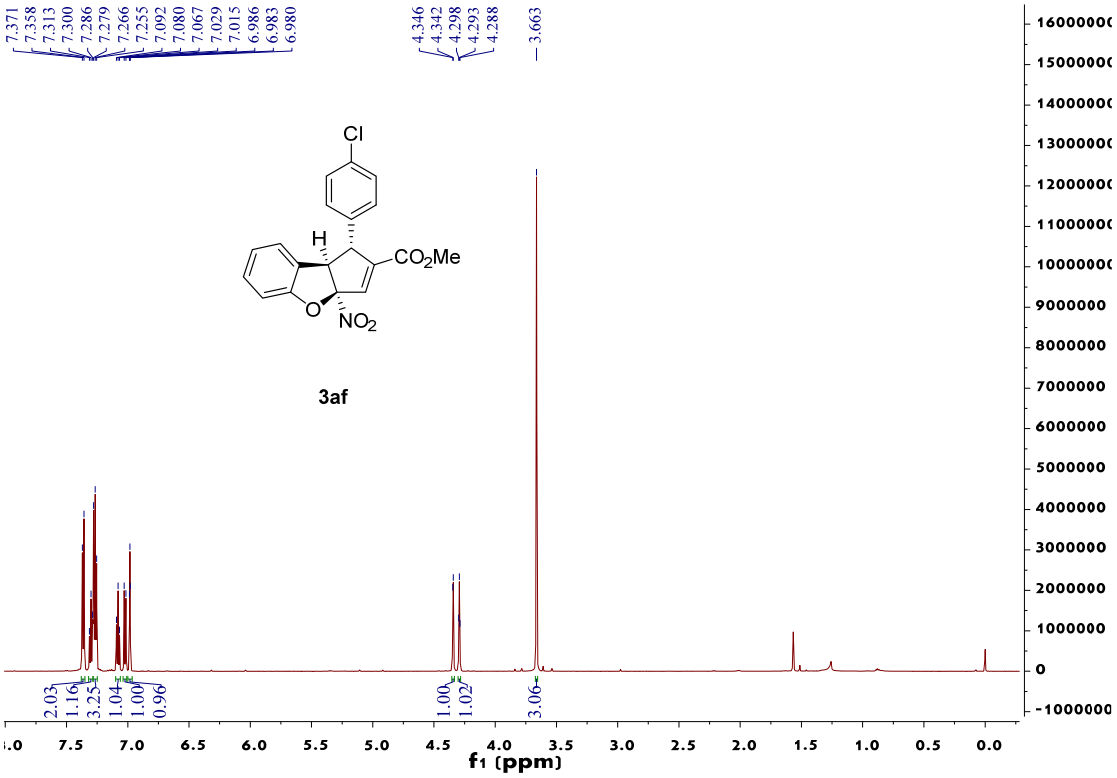
^{13}C NMR of 3ae



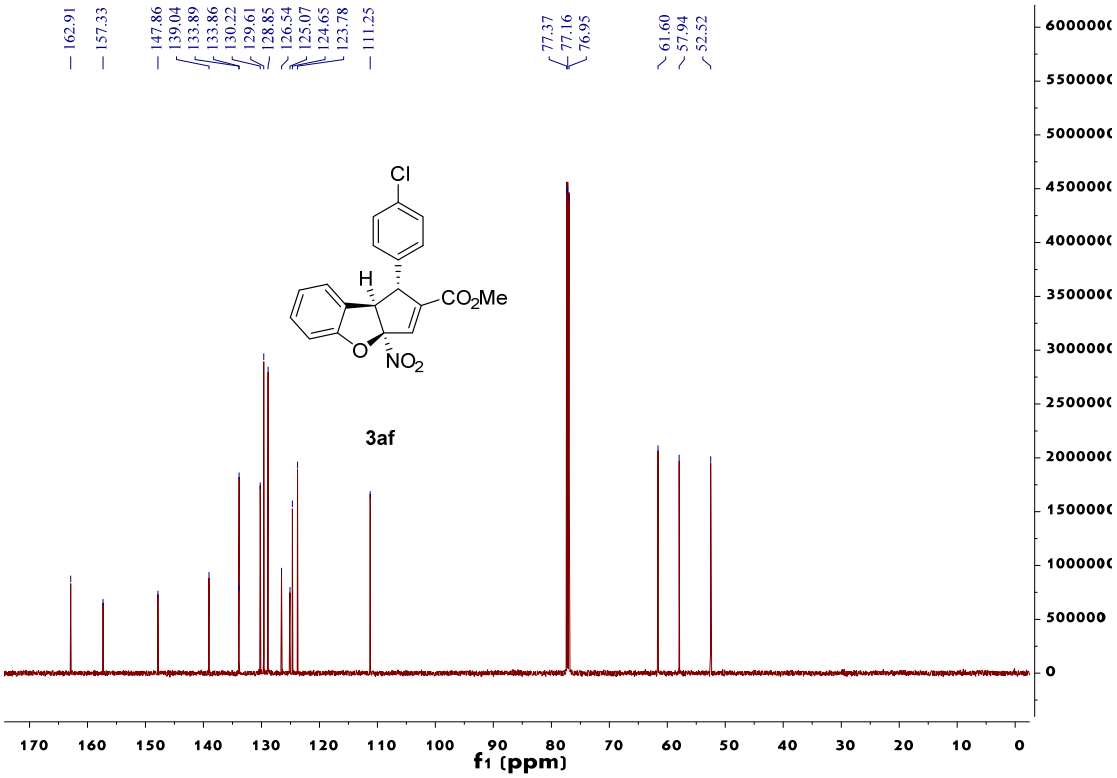
^{19}F NMR of 3ae



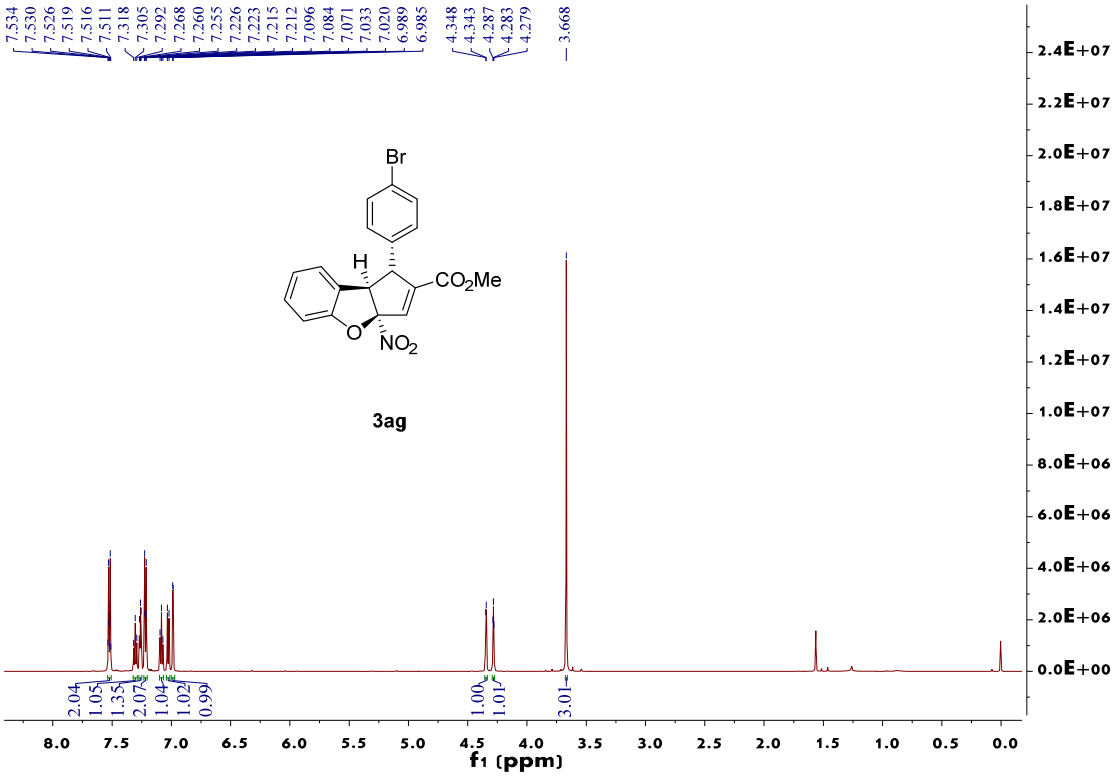
^{1}H NMR of 3af



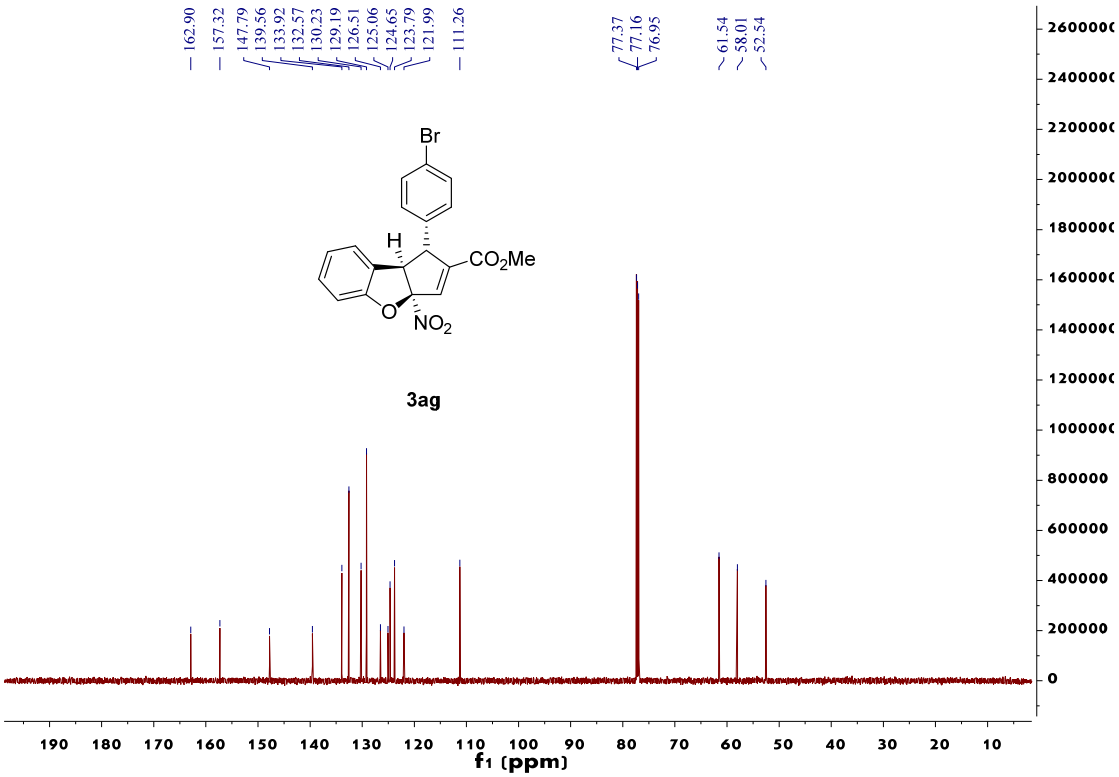
^{13}C NMR of 3af



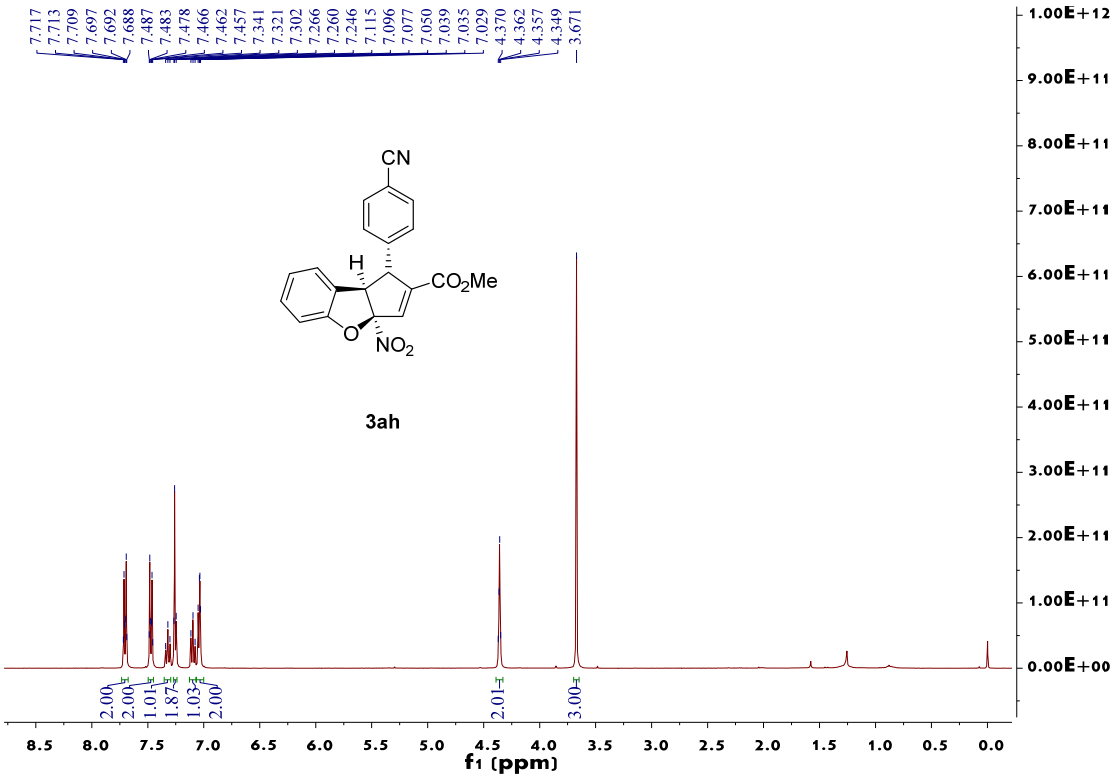
^{1}H NMR of 3ag



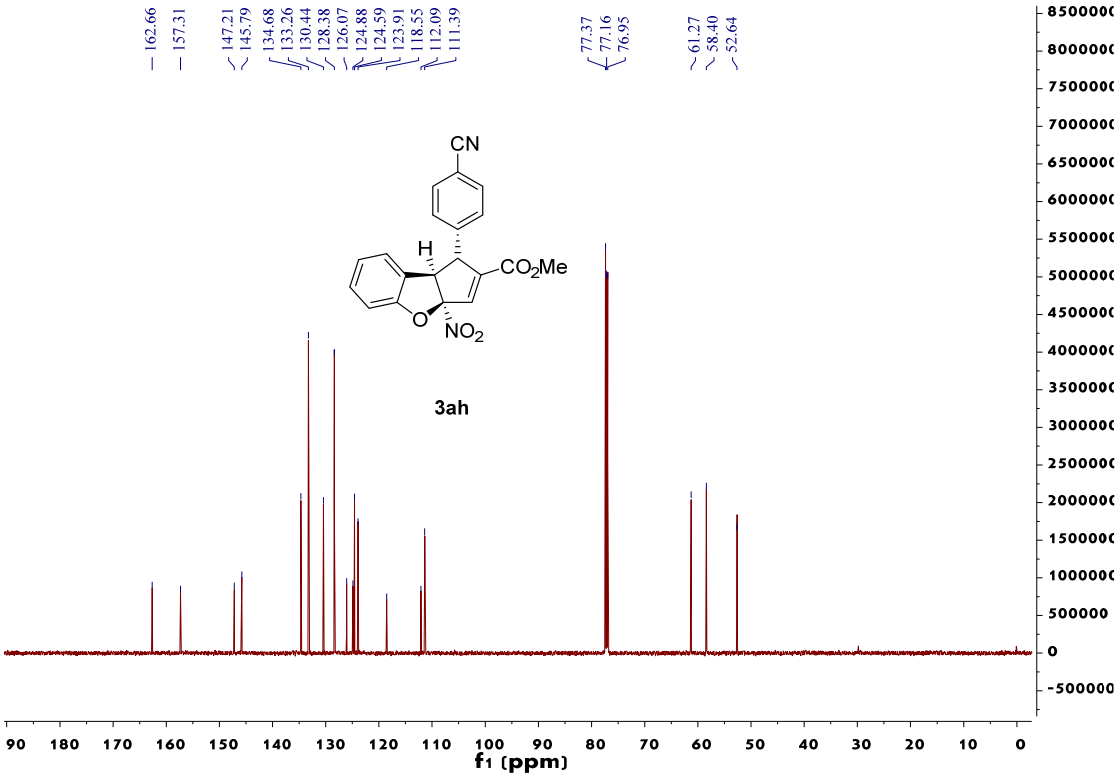
^{13}C NMR of 3ag



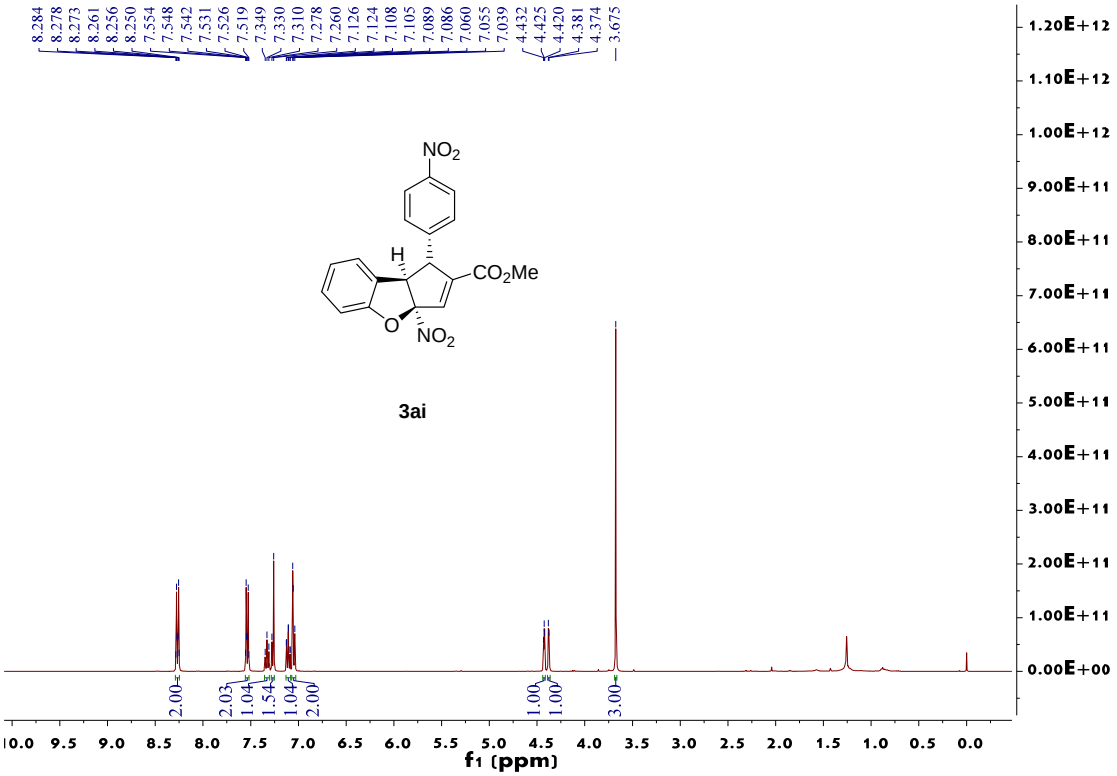
^{1}H NMR of 3ah



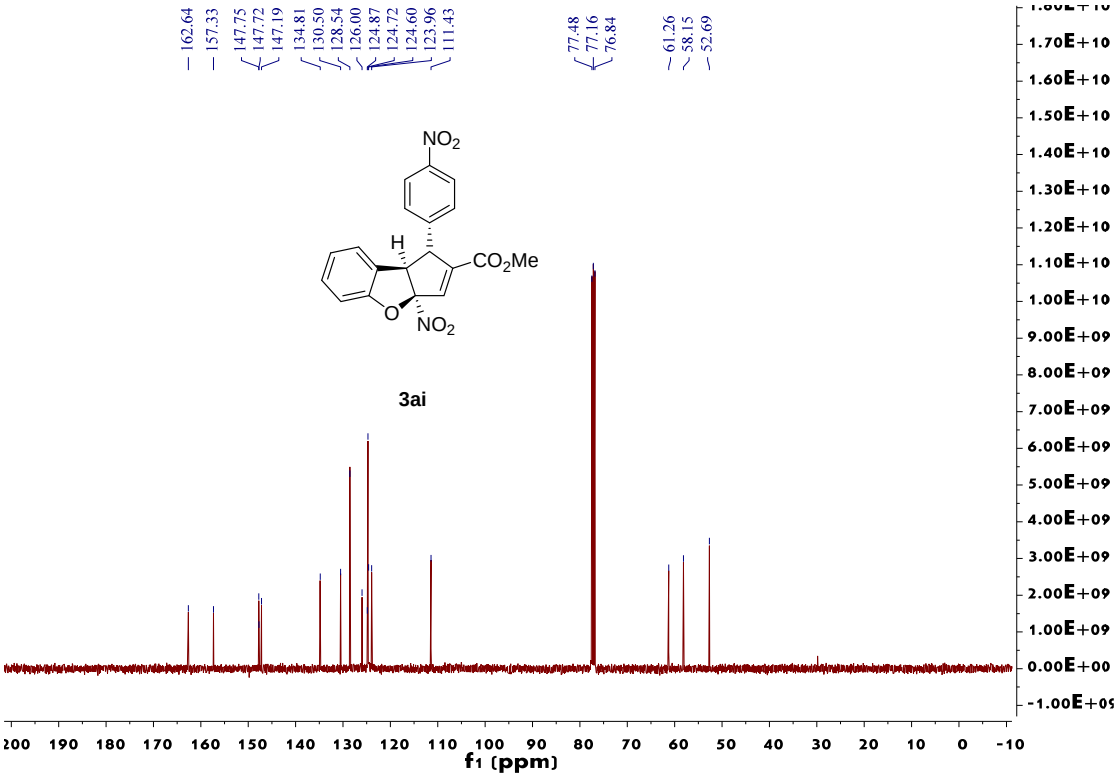
^{13}C NMR of 3ah



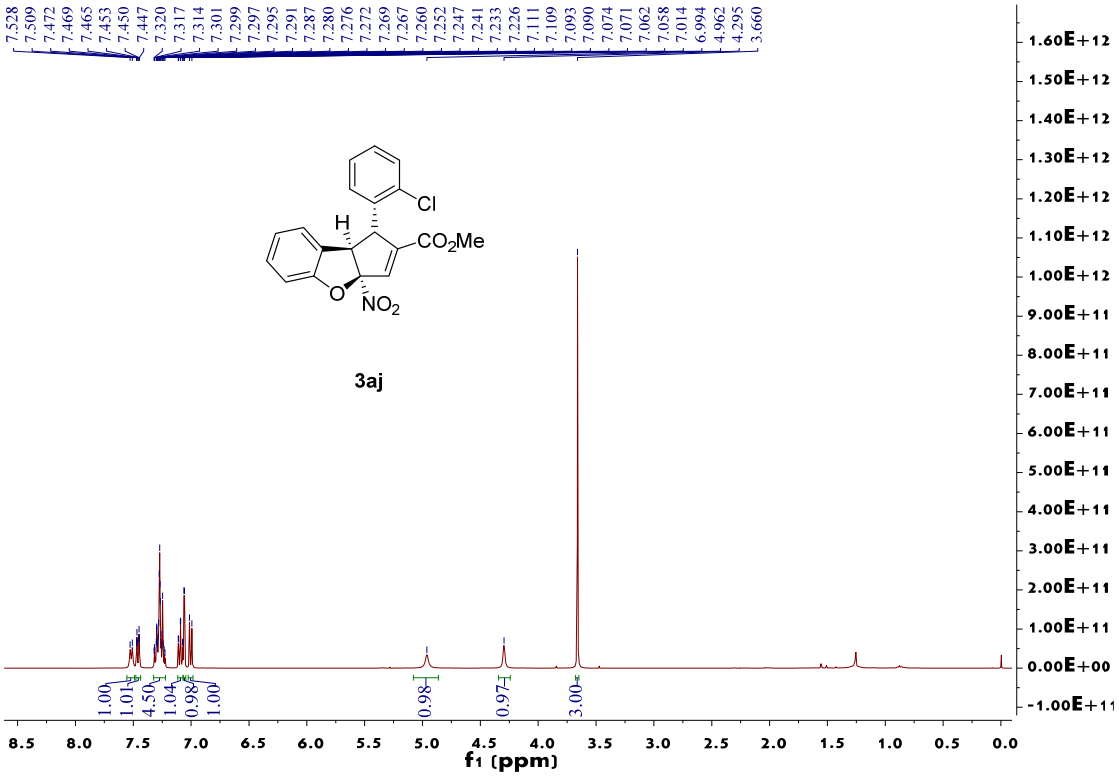
^{1}H NMR of 3ai



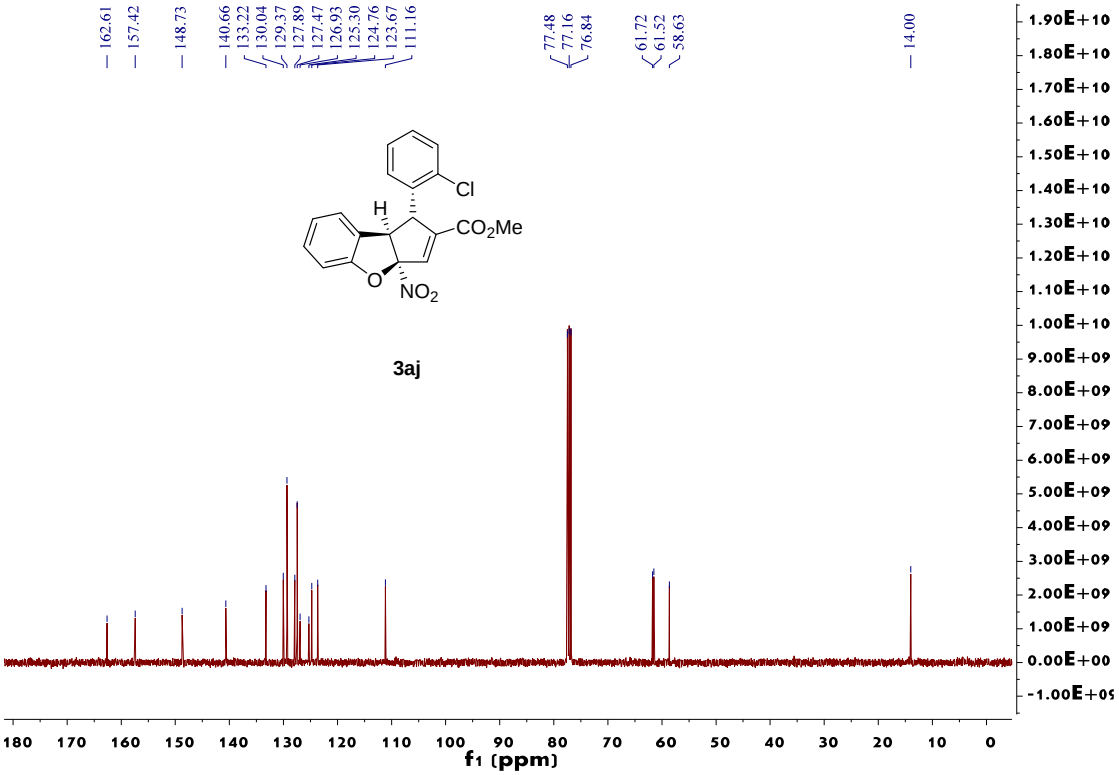
^{13}C NMR of 3ai



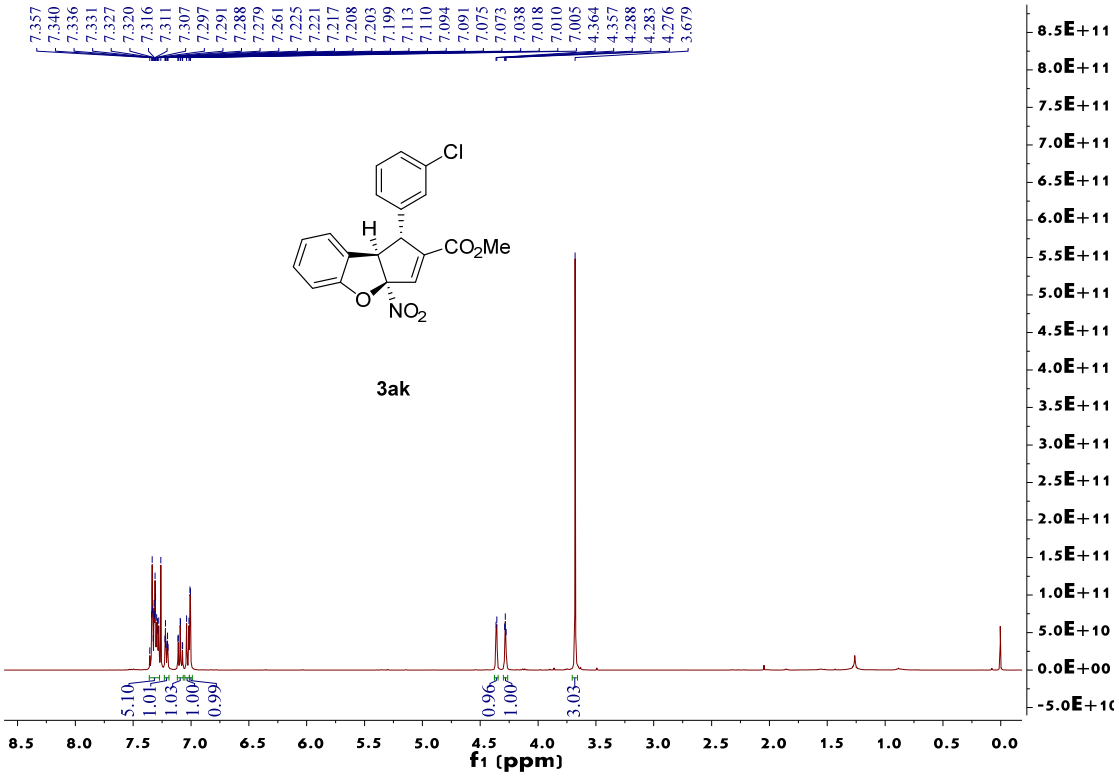
^{1}H NMR of 3aj



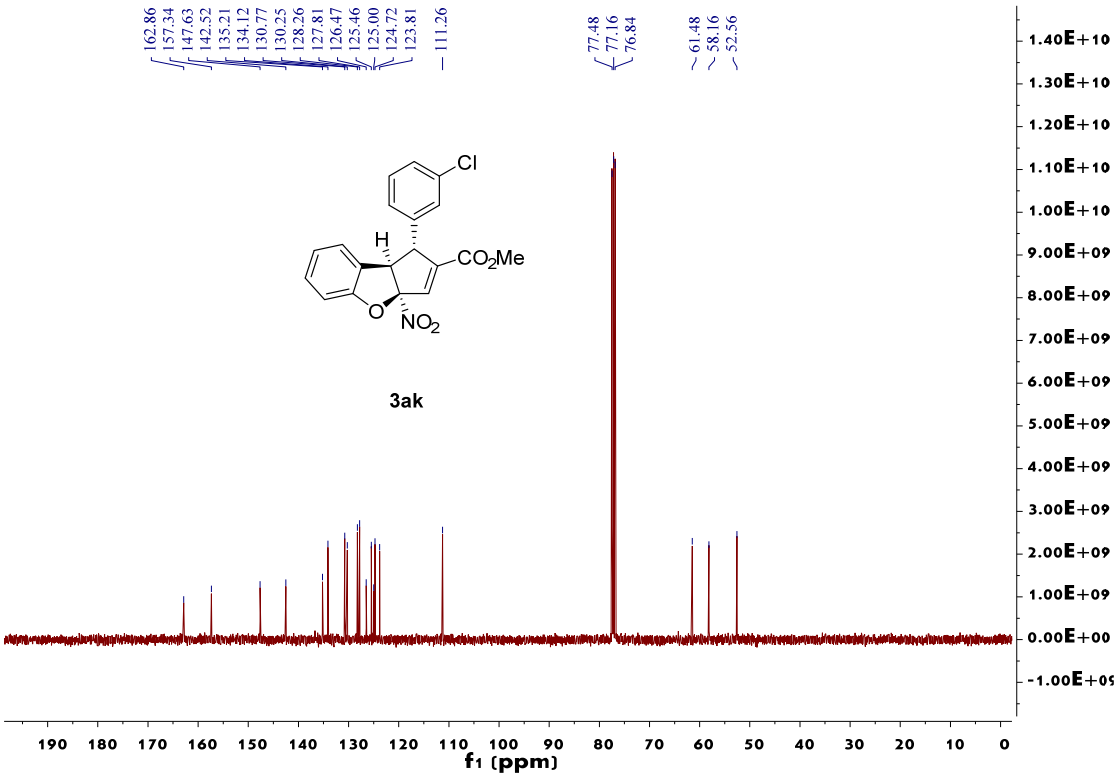
^{13}C NMR of 3aj



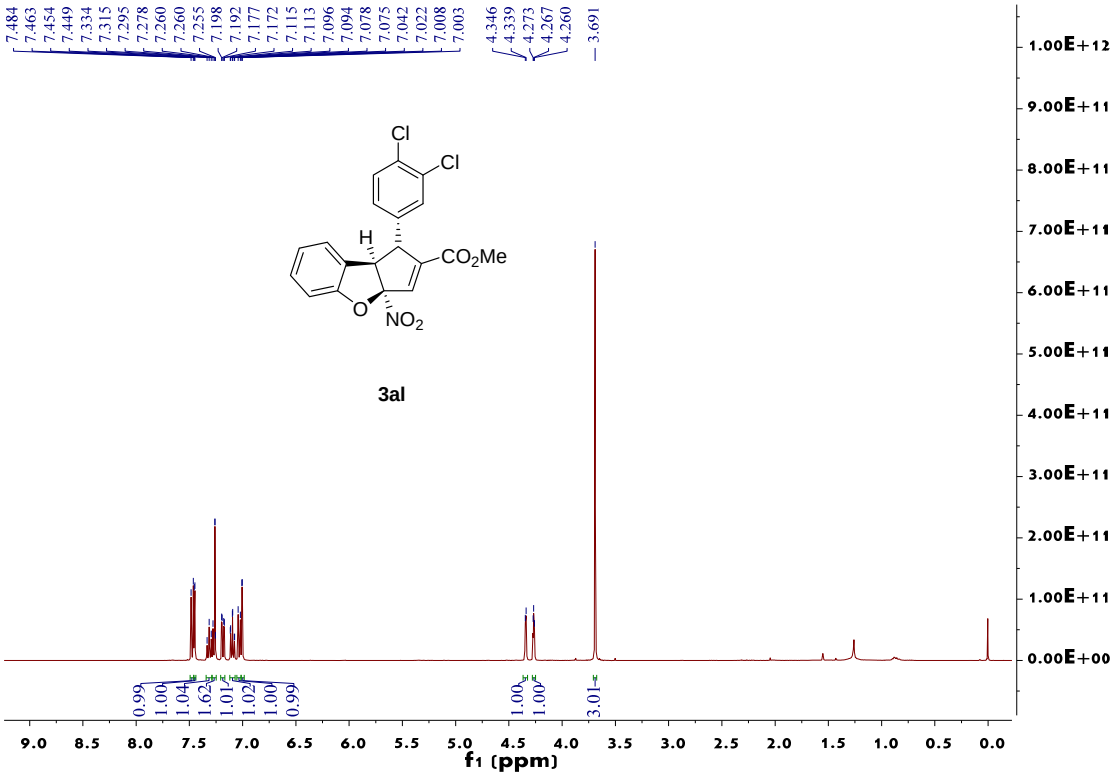
^{1}H NMR of 3ak



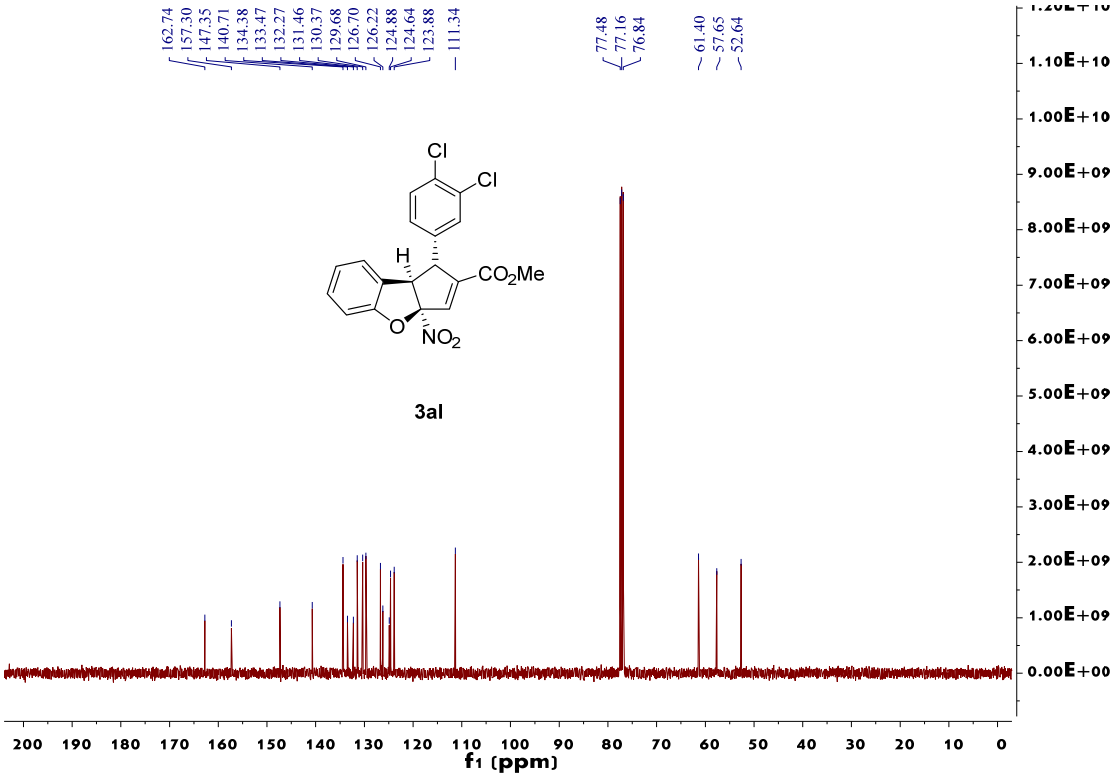
^{13}C NMR of 3ak



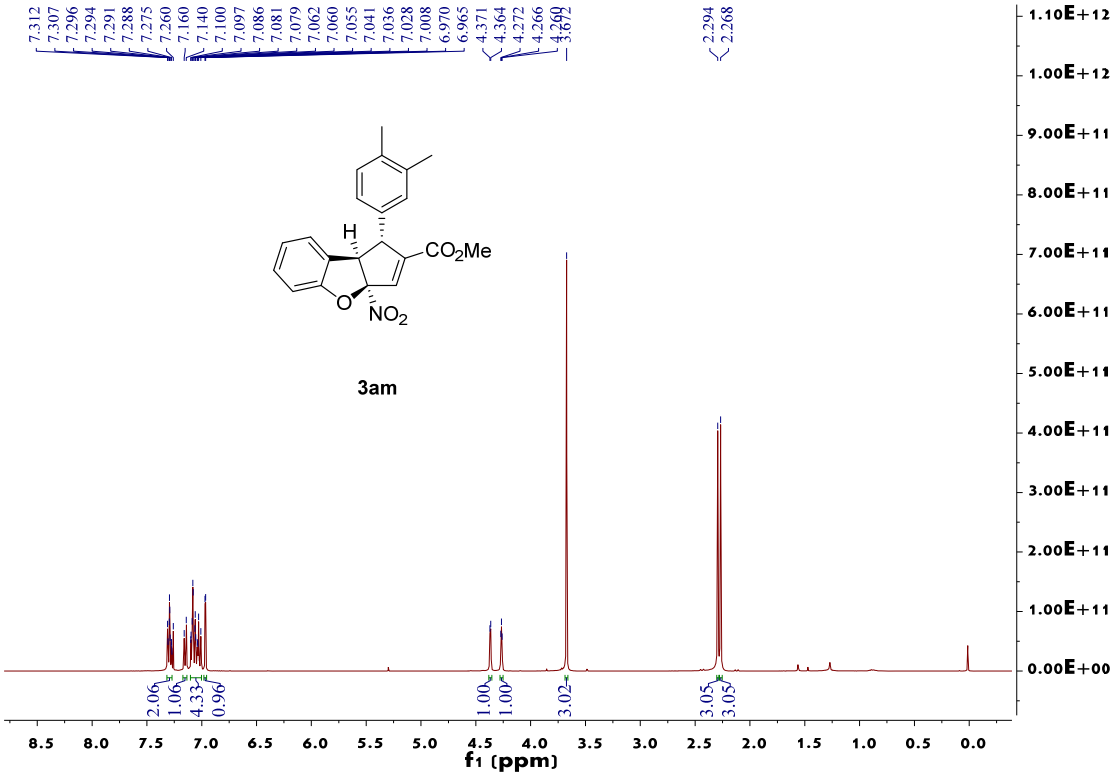
^{1}H NMR of 3al



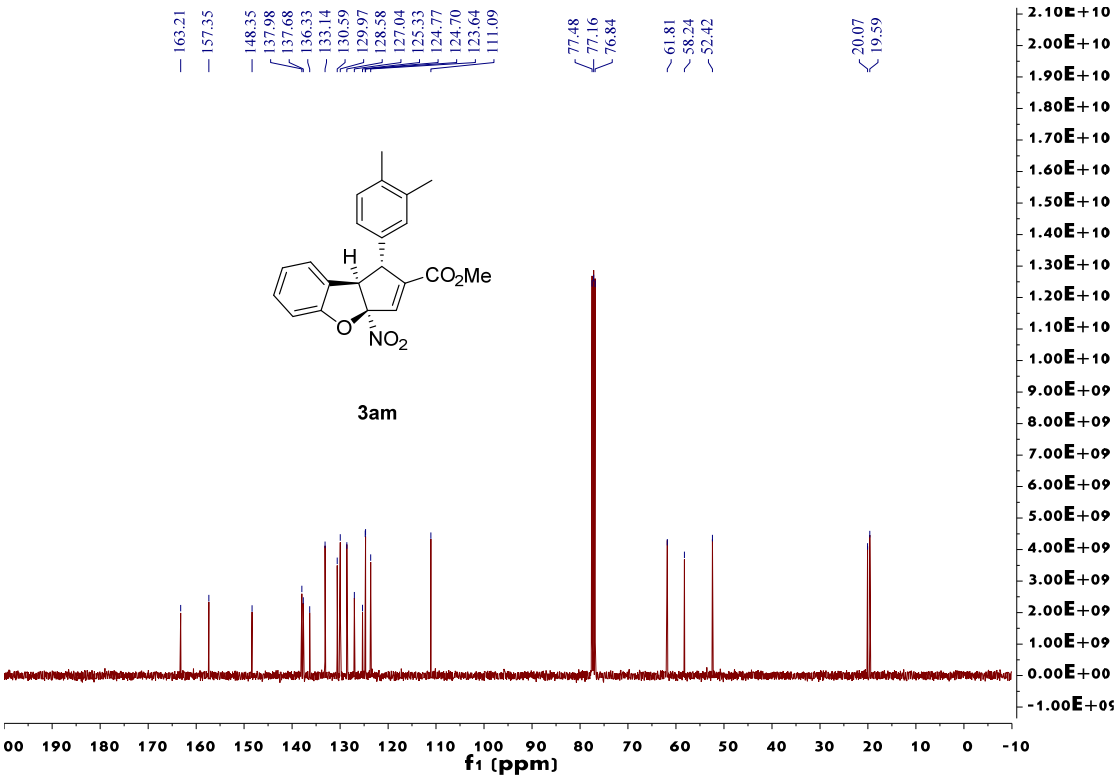
^{13}C NMR of 3al



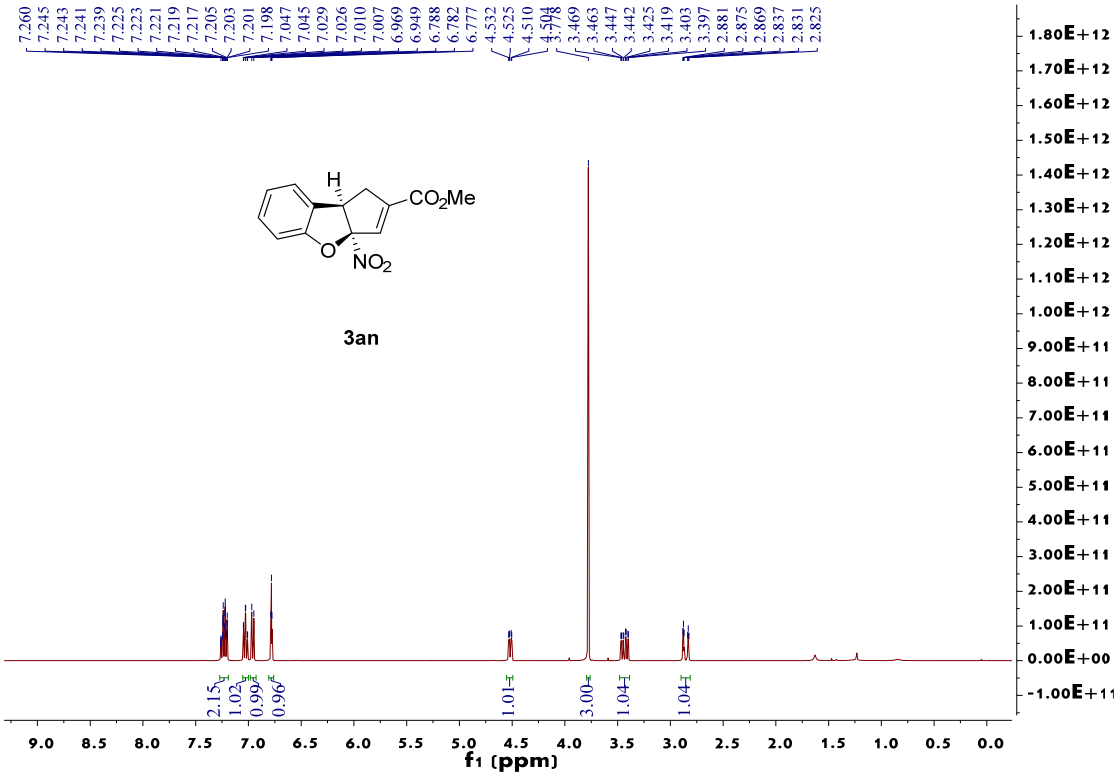
^{1}H NMR of 3am



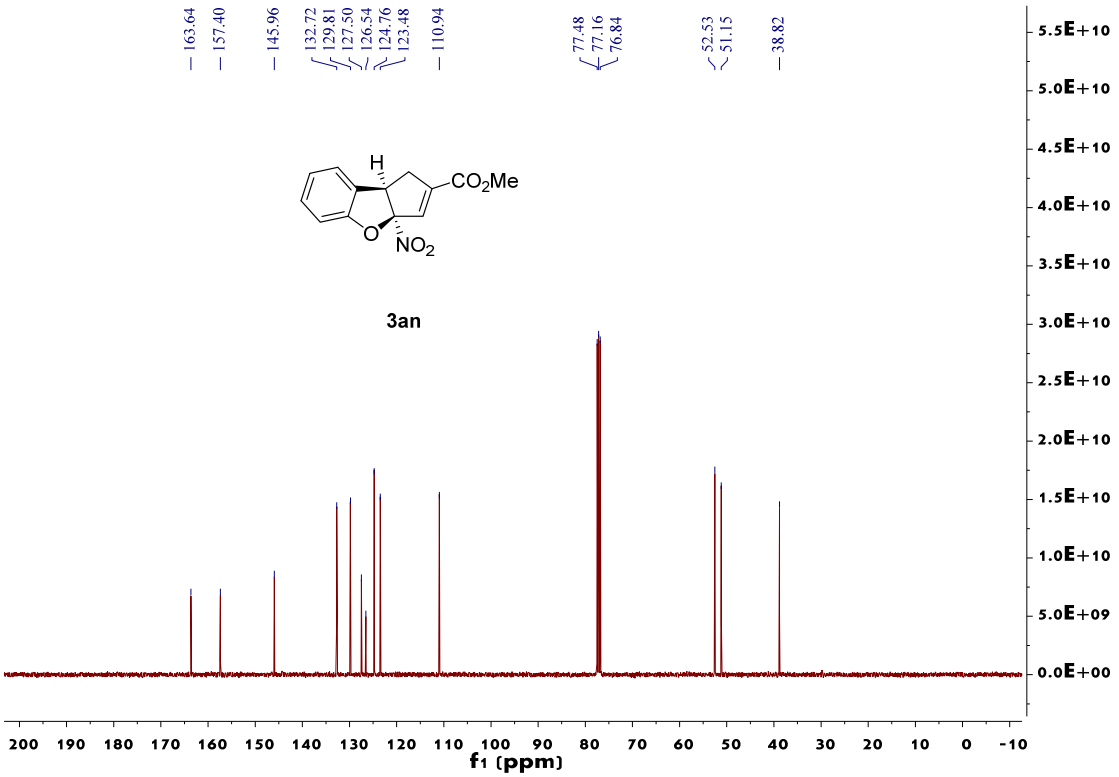
^{13}C NMR of 3am



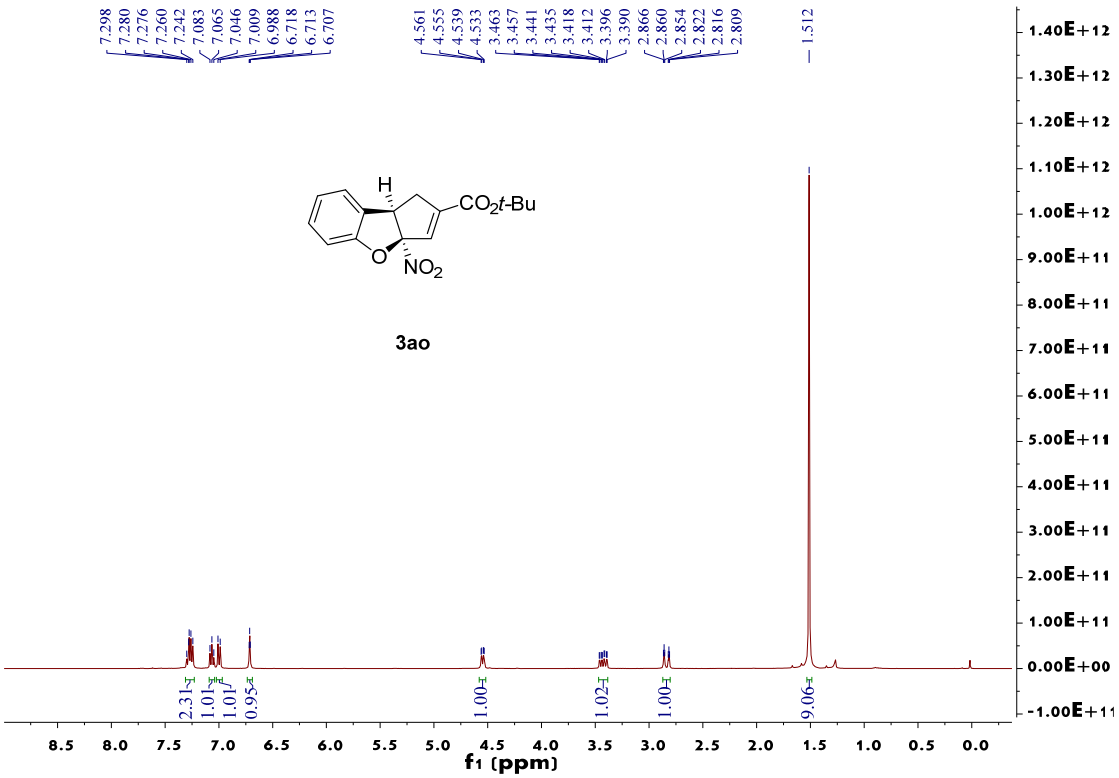
^{1}H NMR of 3an



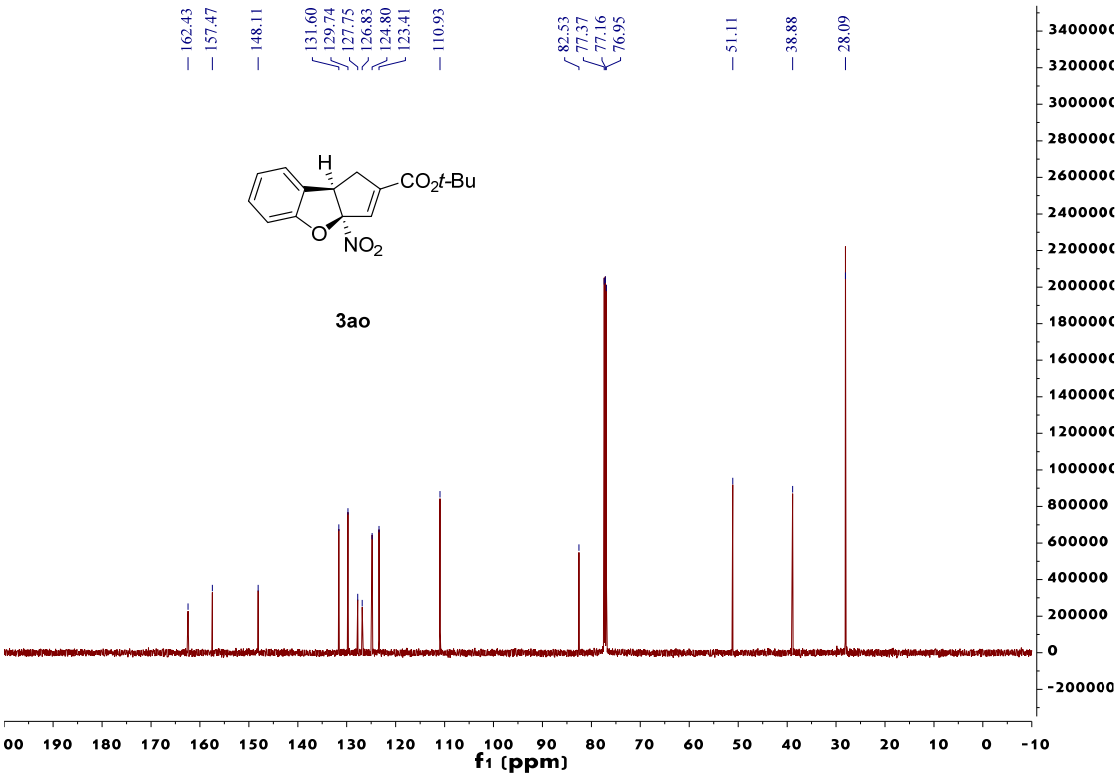
^{13}C NMR of 3an



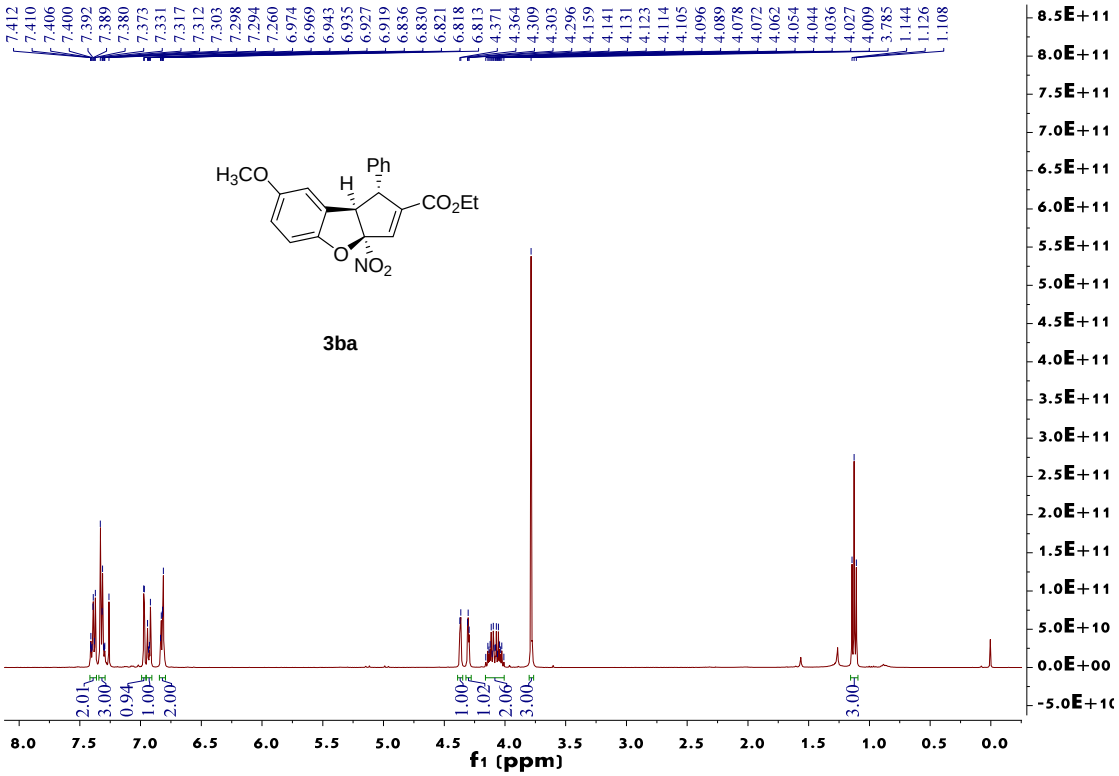
^{1}H NMR of 3ao



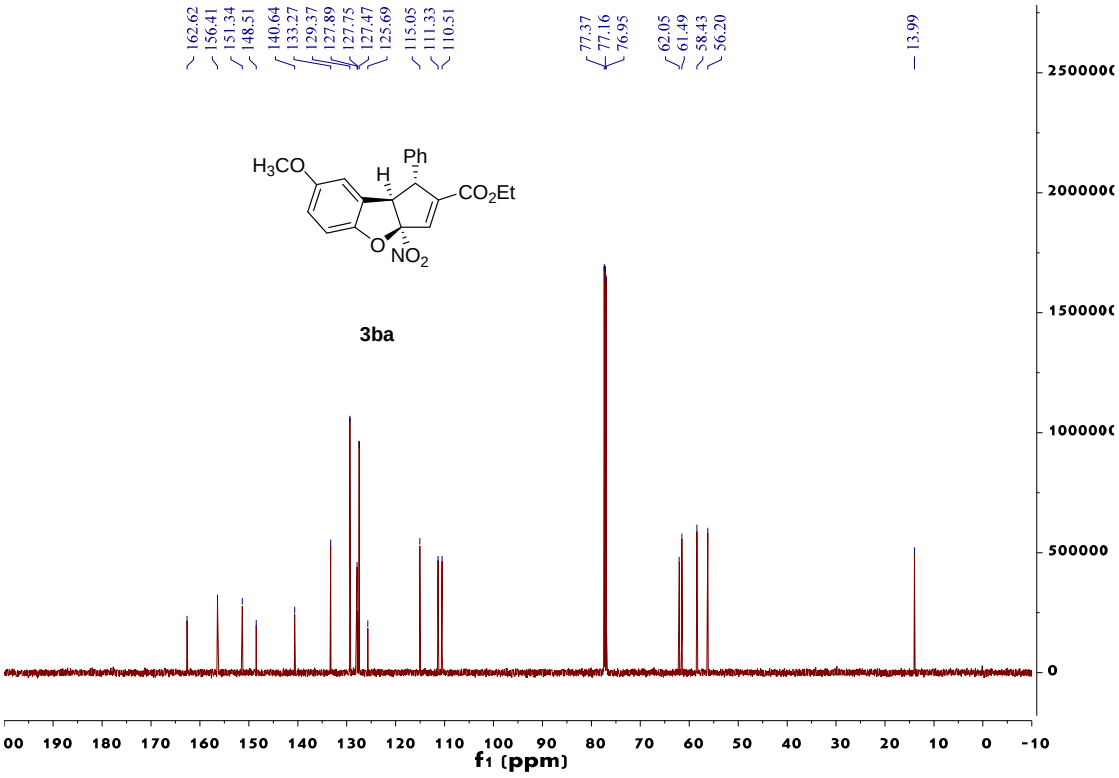
^{13}C NMR of 3ao



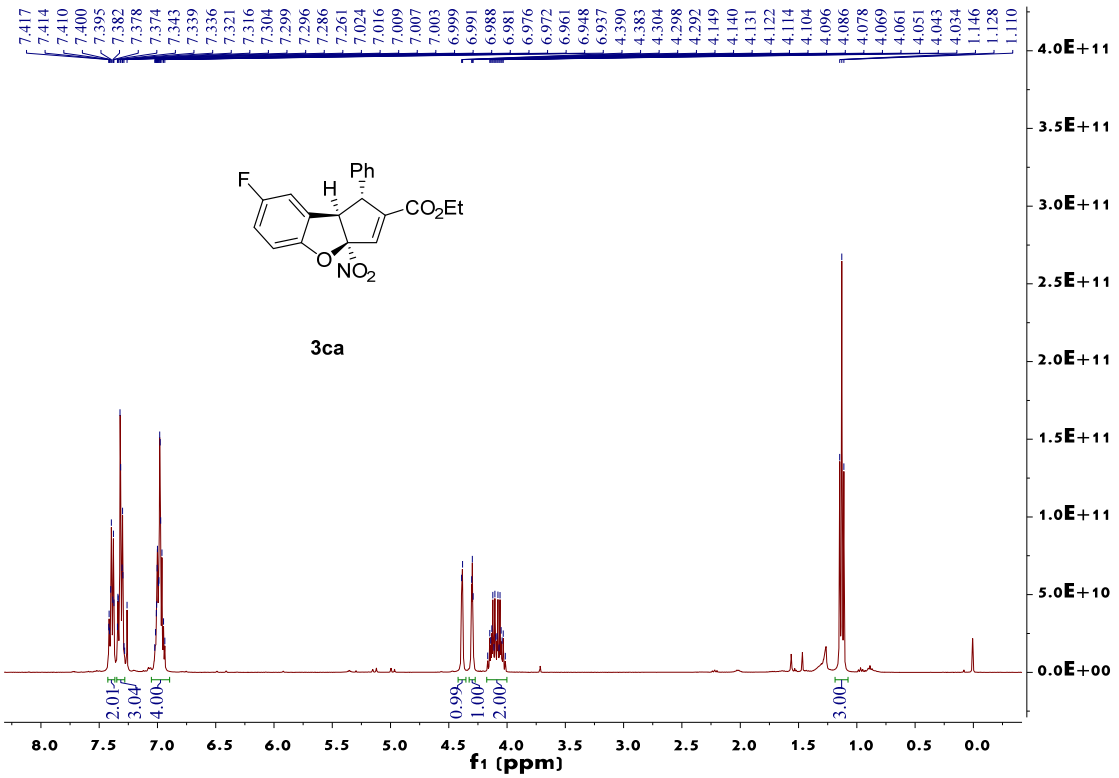
^{1}H NMR of 3ba



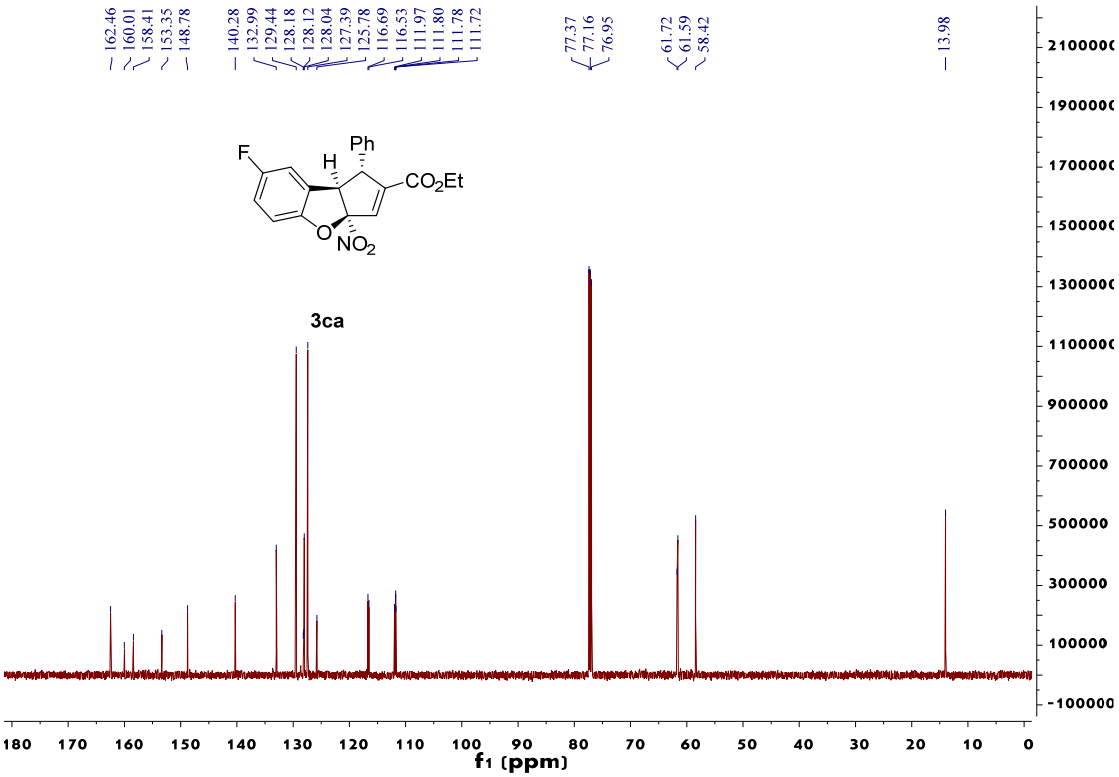
^{13}C NMR of 3ba



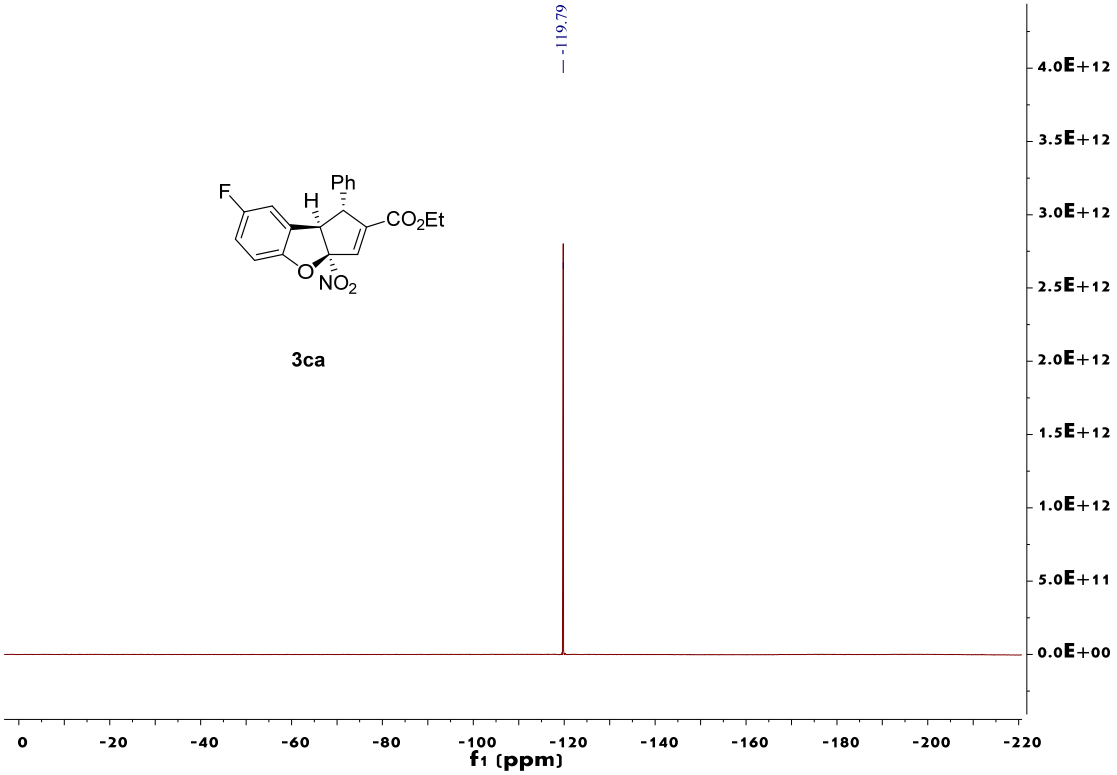
^{1}H NMR of 3ca



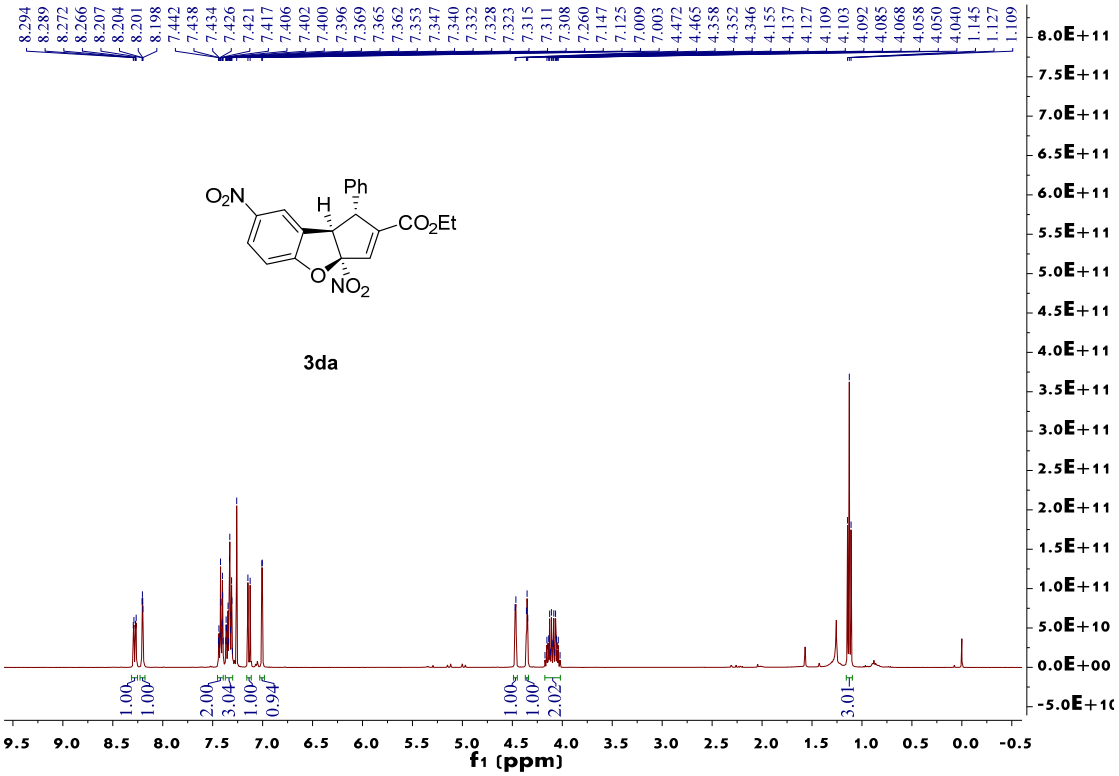
^{13}C NMR of 3ca



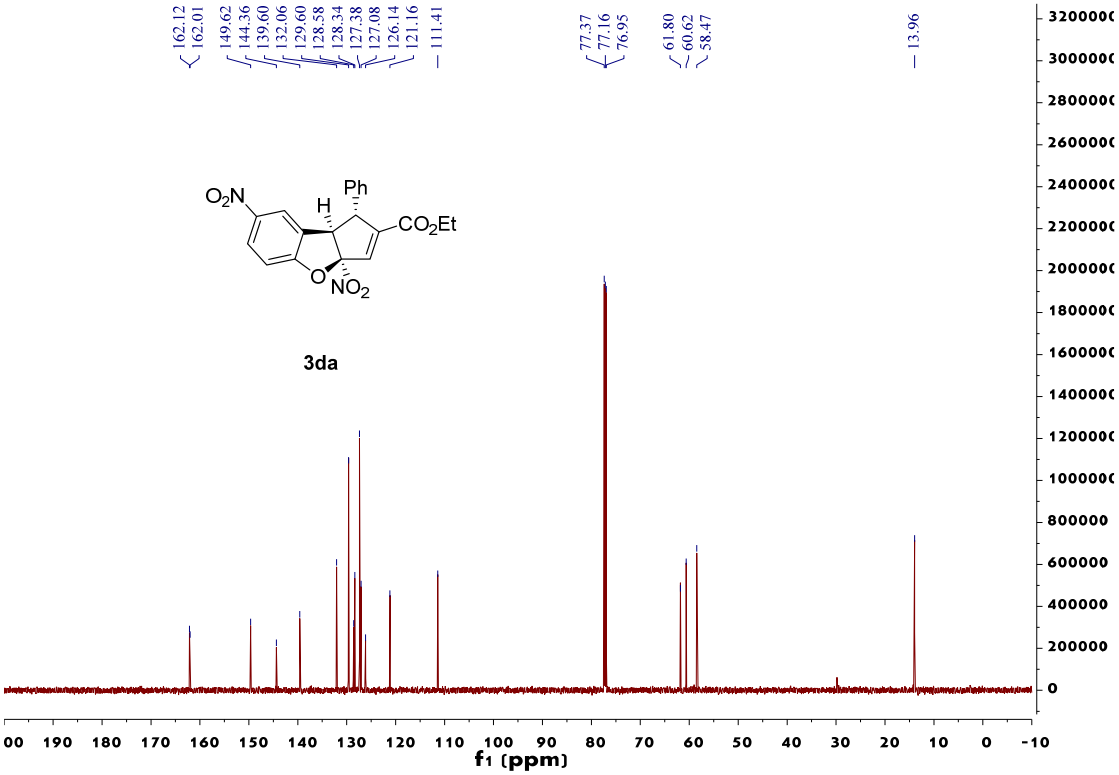
^{19}F NMR of 3ca



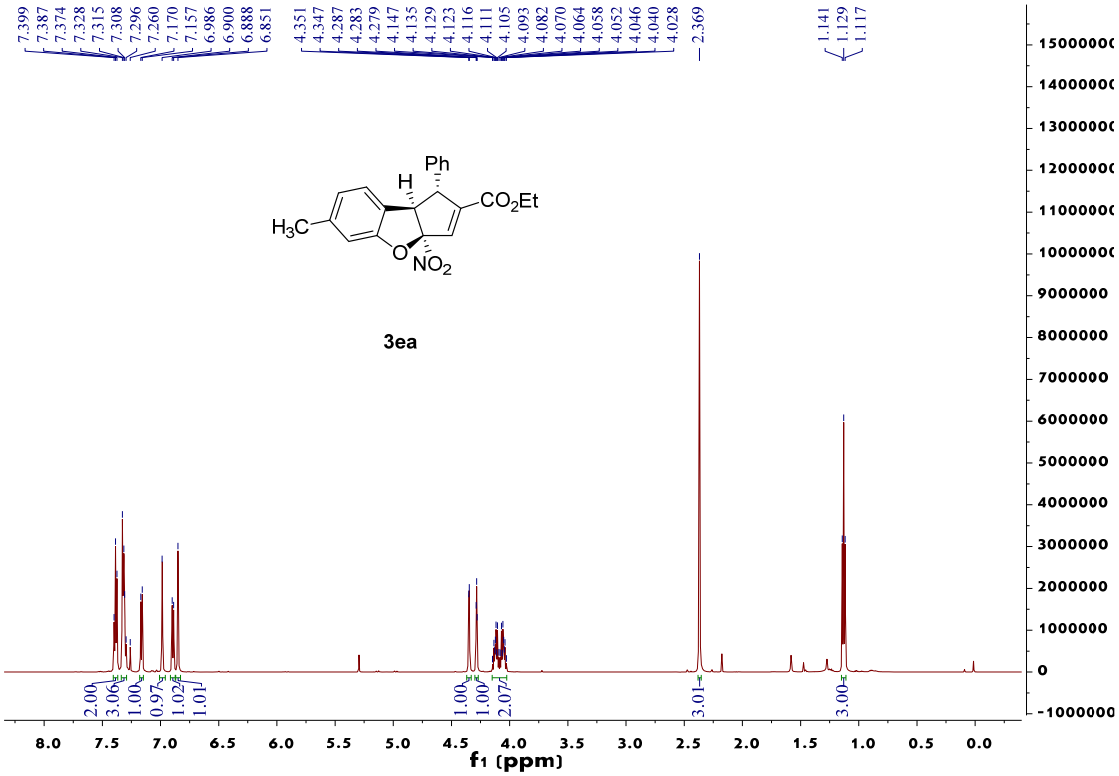
^{1}H NMR of 3da



^{13}C NMR of 3da



^{1}H NMR of 3ea



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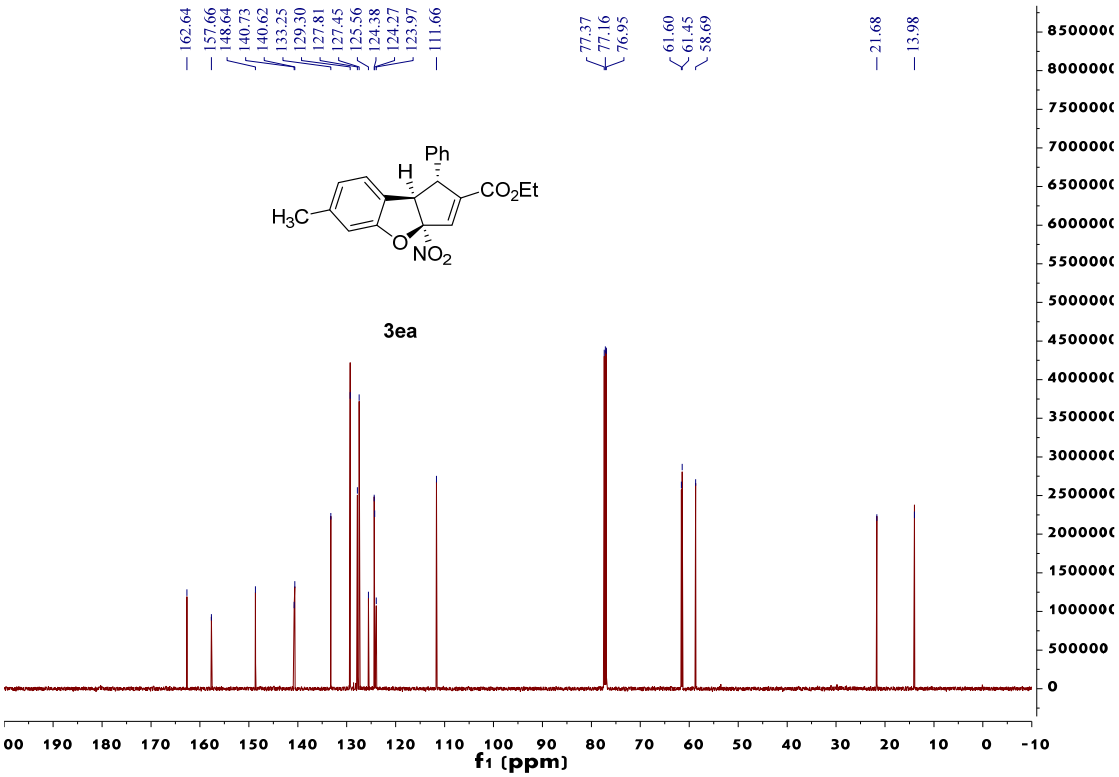
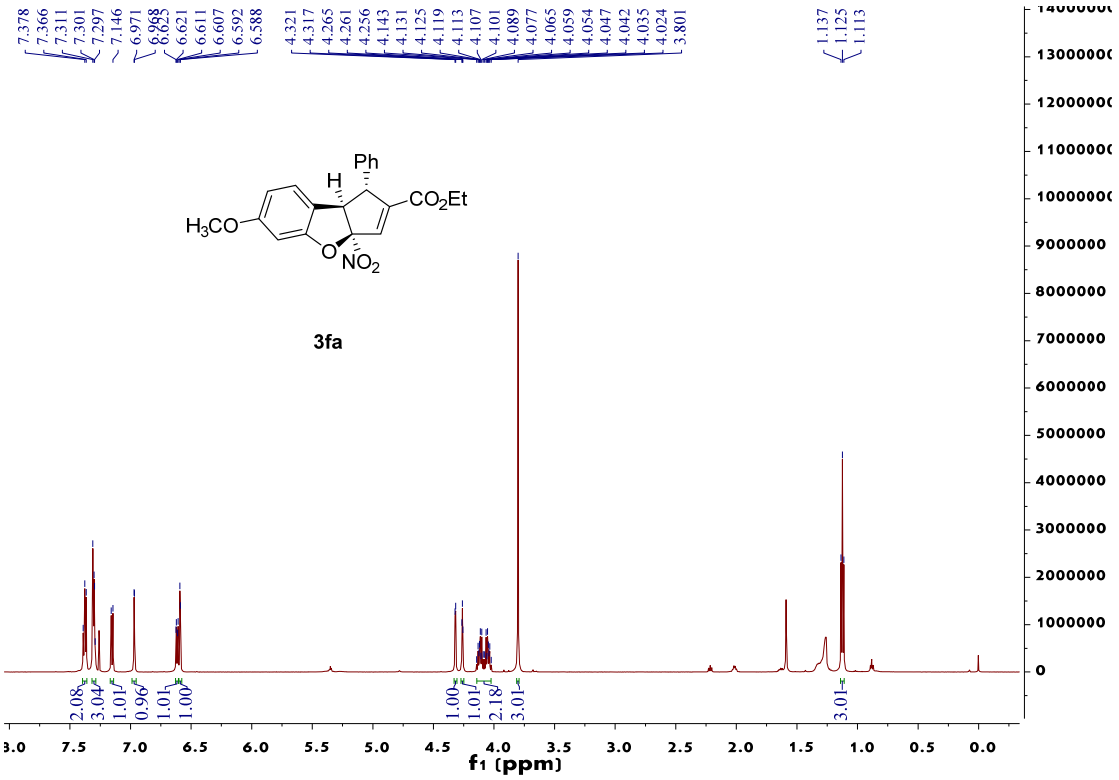
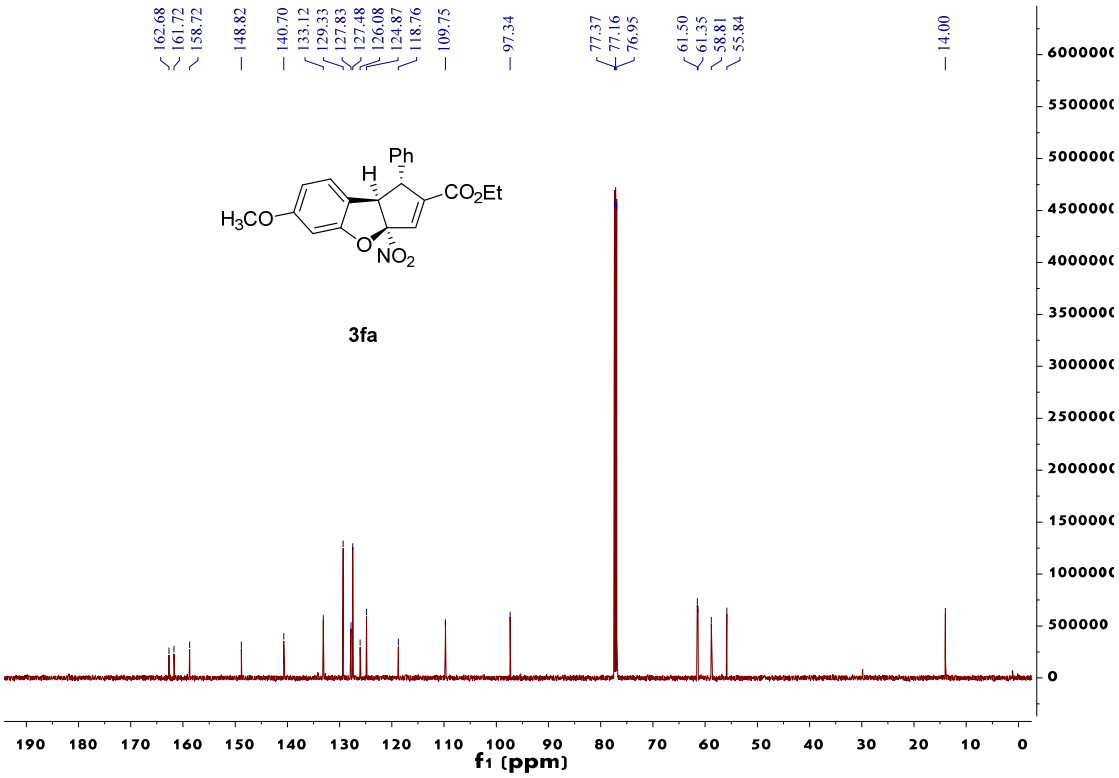


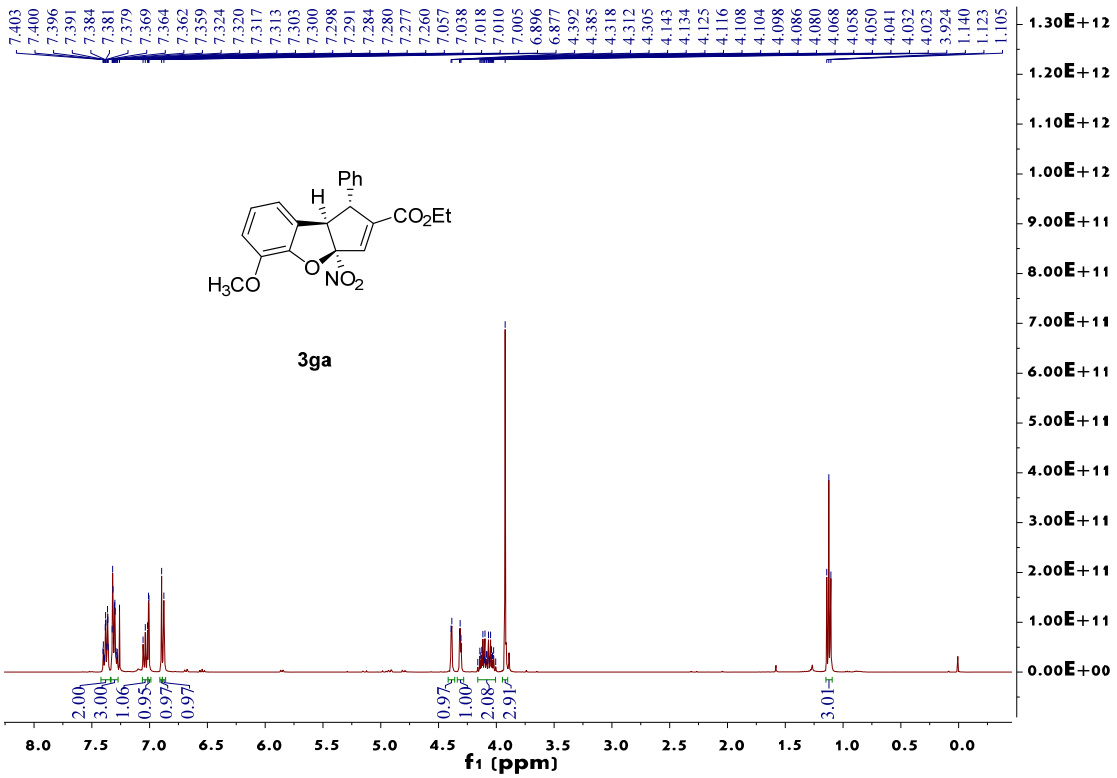
^{1}H NMR of 3fa



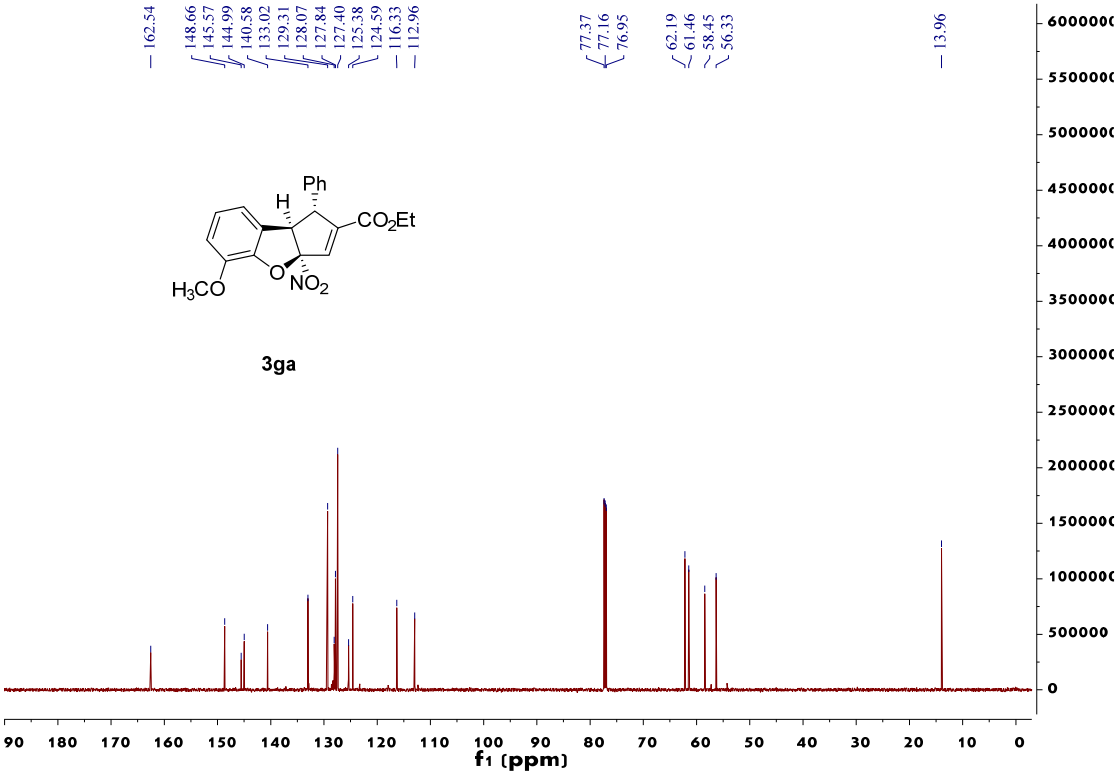
^{13}C NMR of 3fa



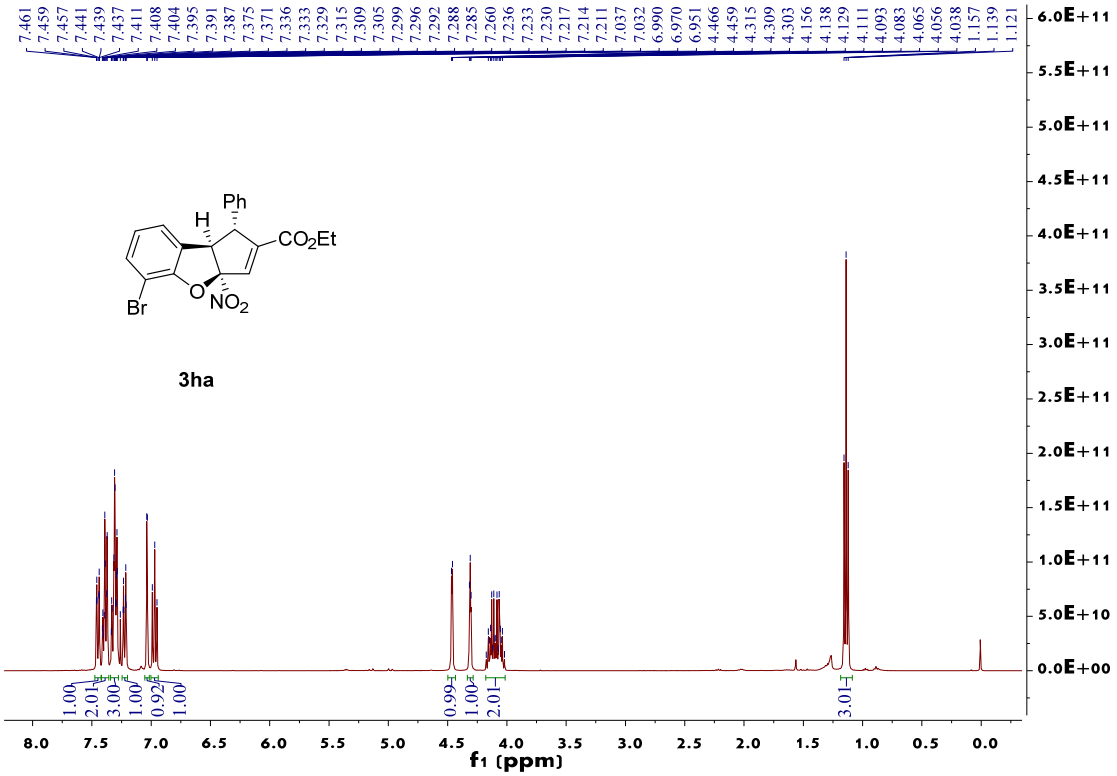
^{1}H NMR of 3ga



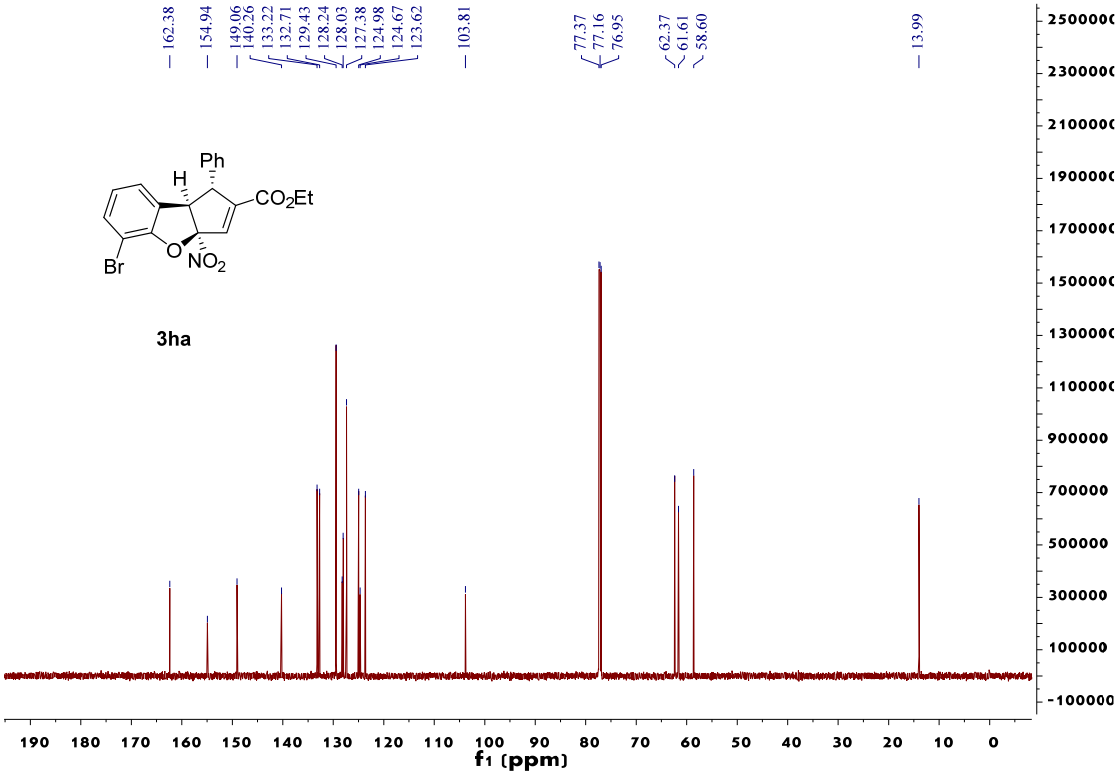
^{13}C NMR of 3ga



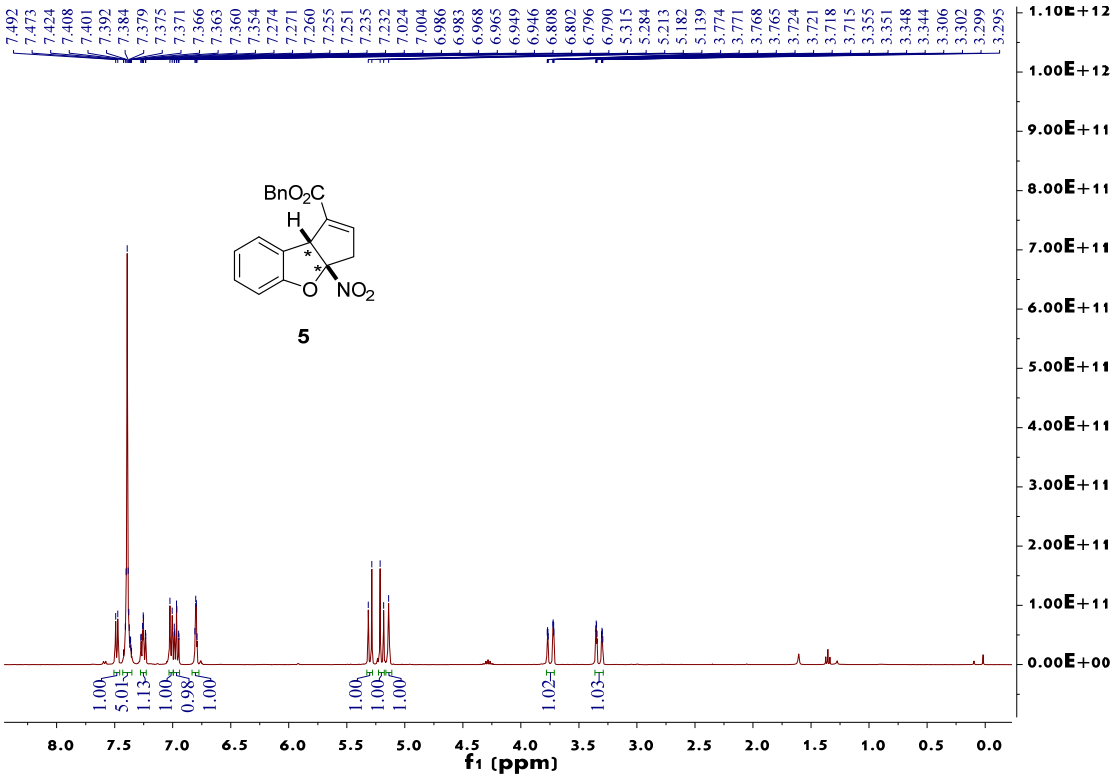
^{1}H NMR of 3ha



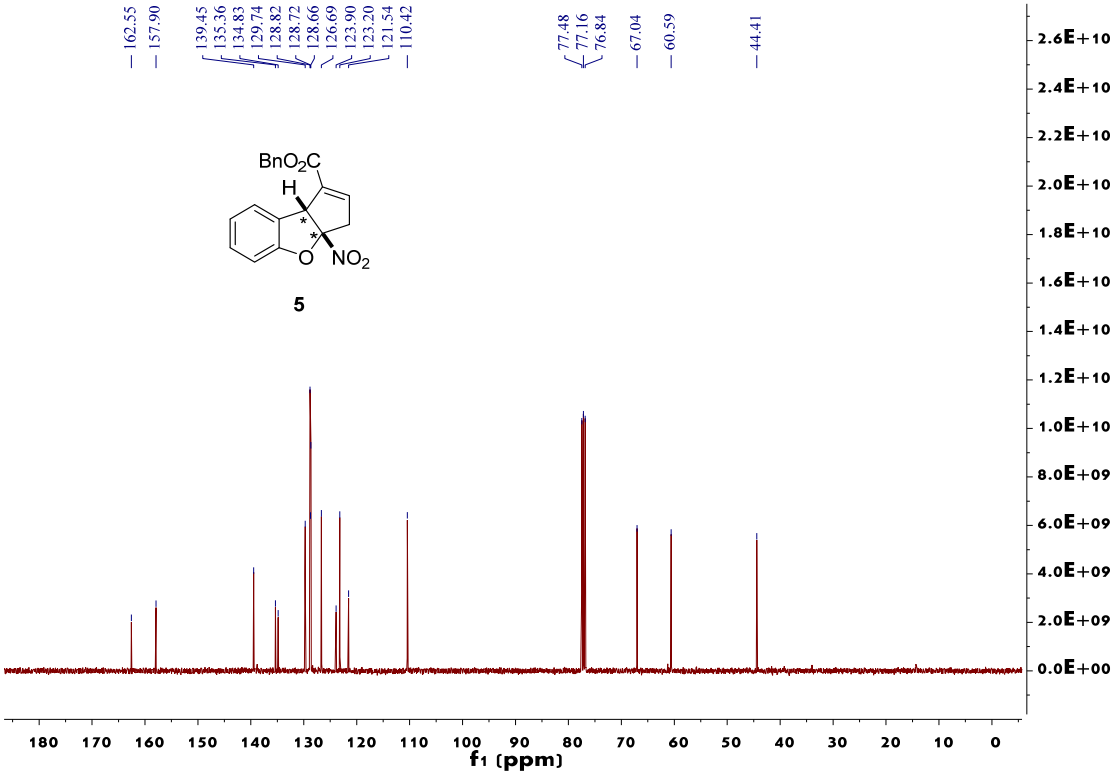
^{13}C NMR of 3ha



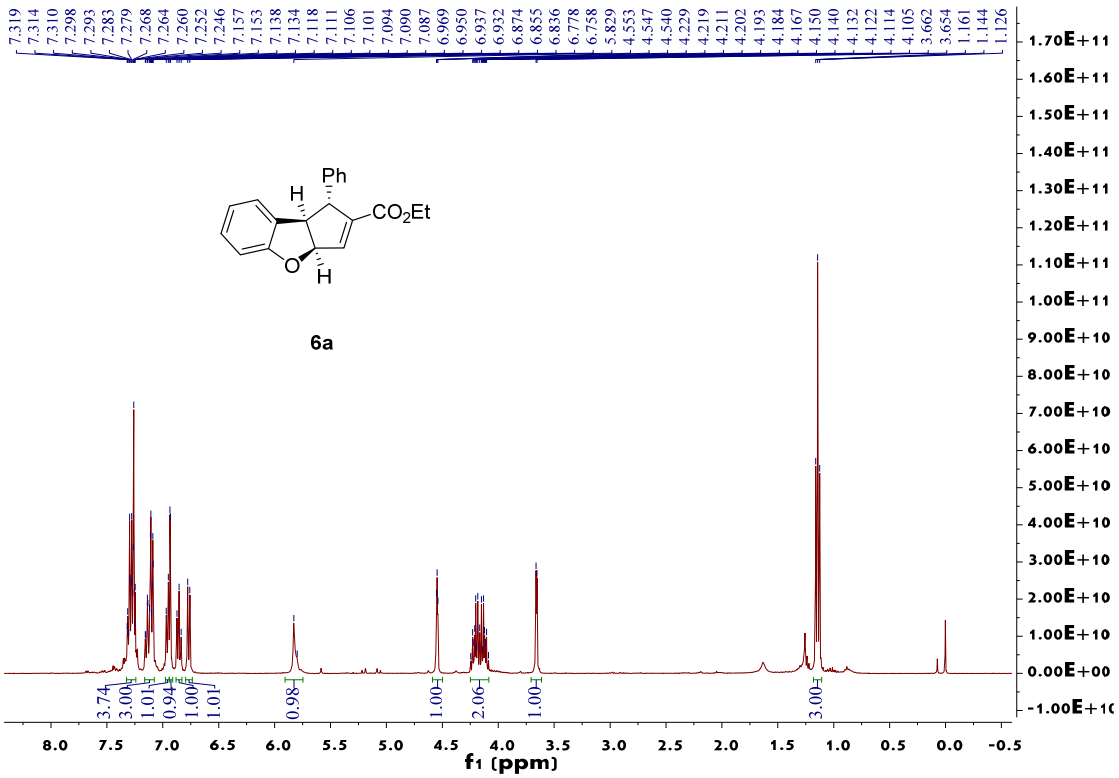
^{1}H NMR of 5



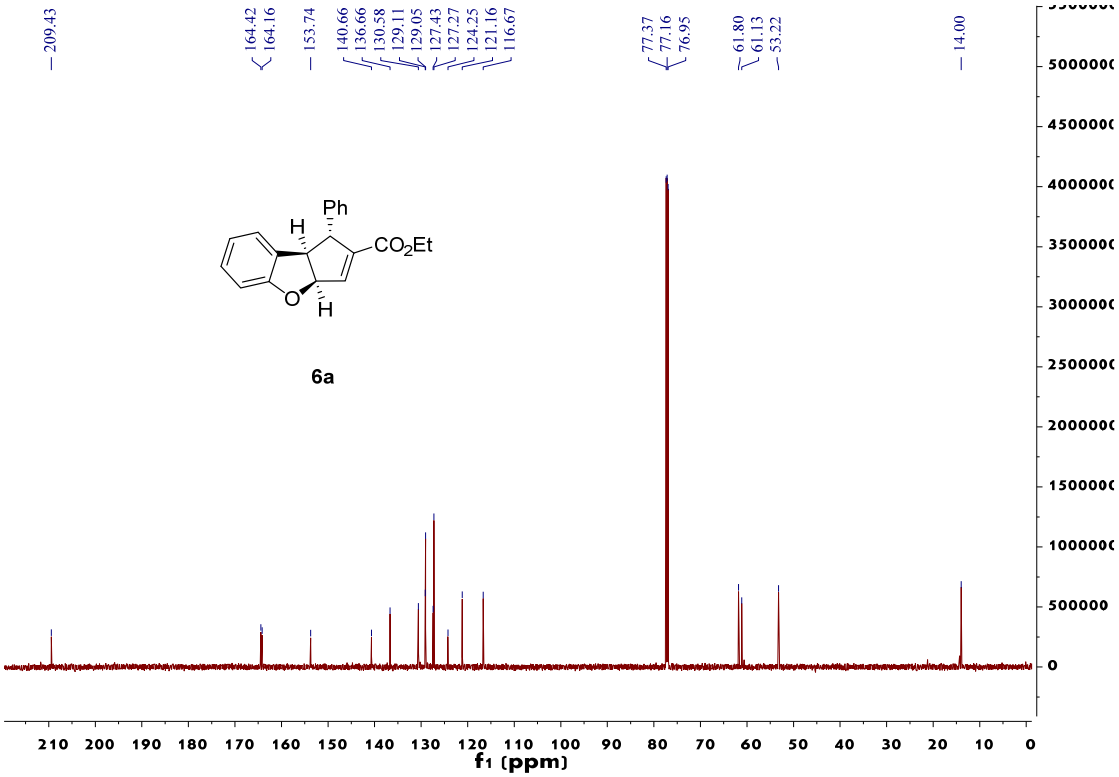
^{13}C NMR of 5



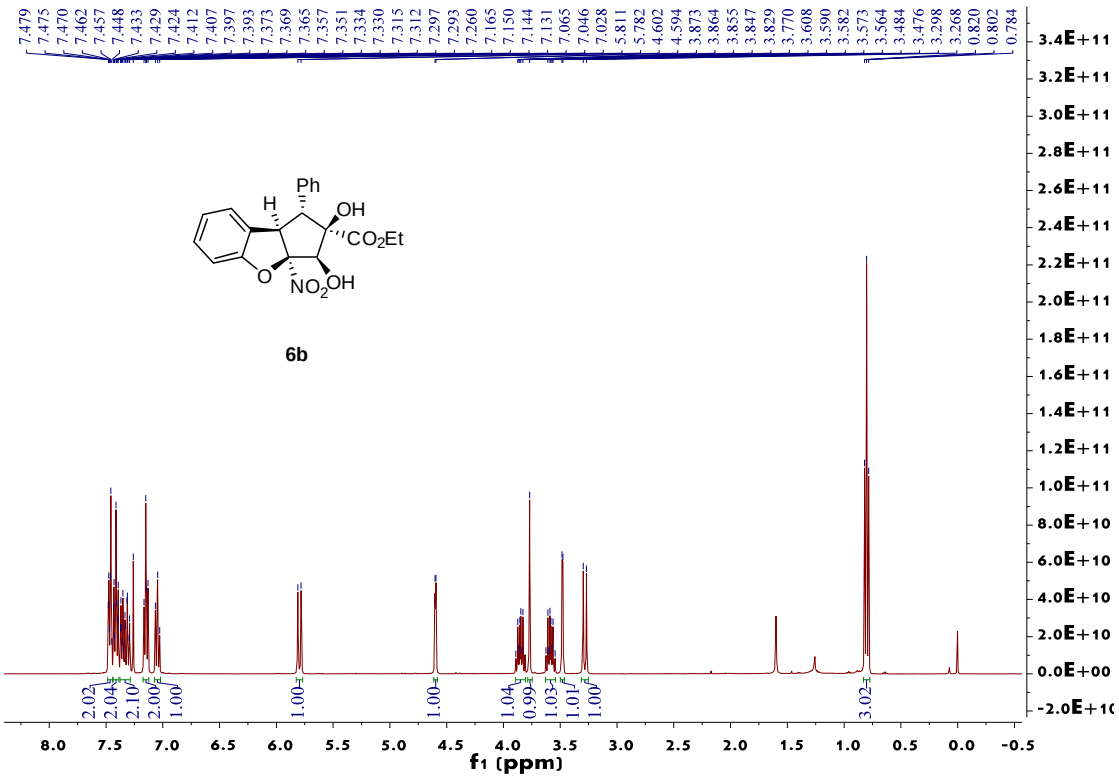
^{1}H NMR of 6a



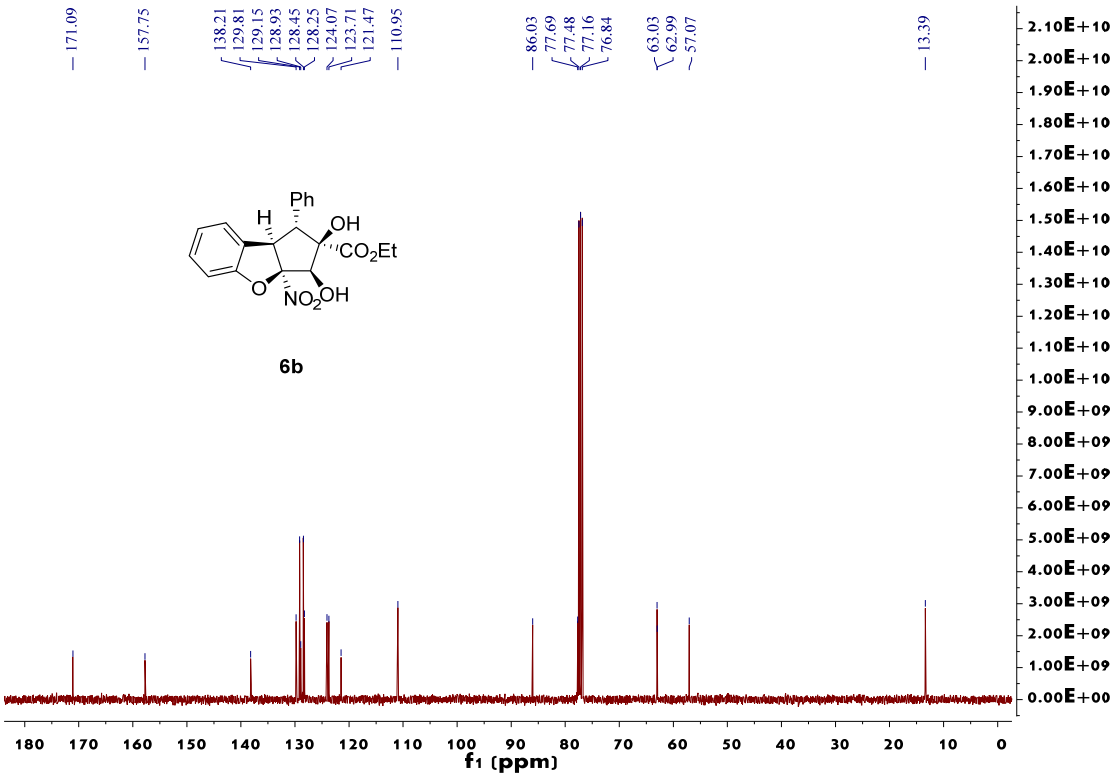
^{13}C NMR of 6a



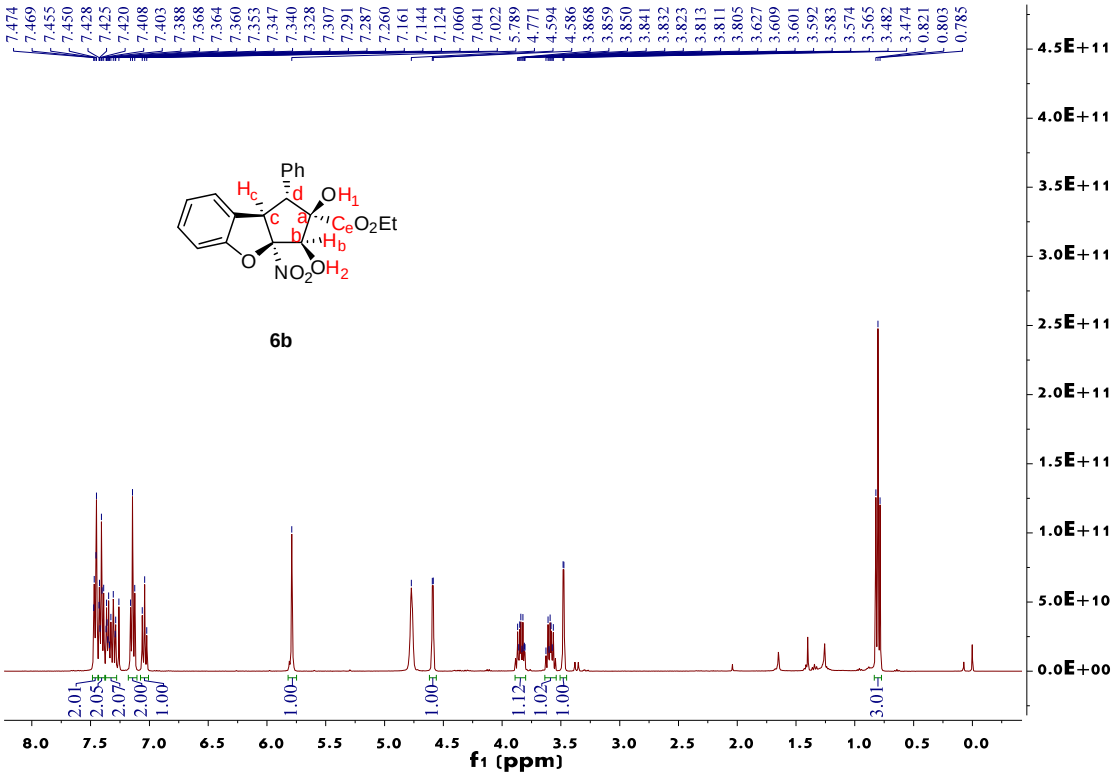
^{1}H NMR of 6b



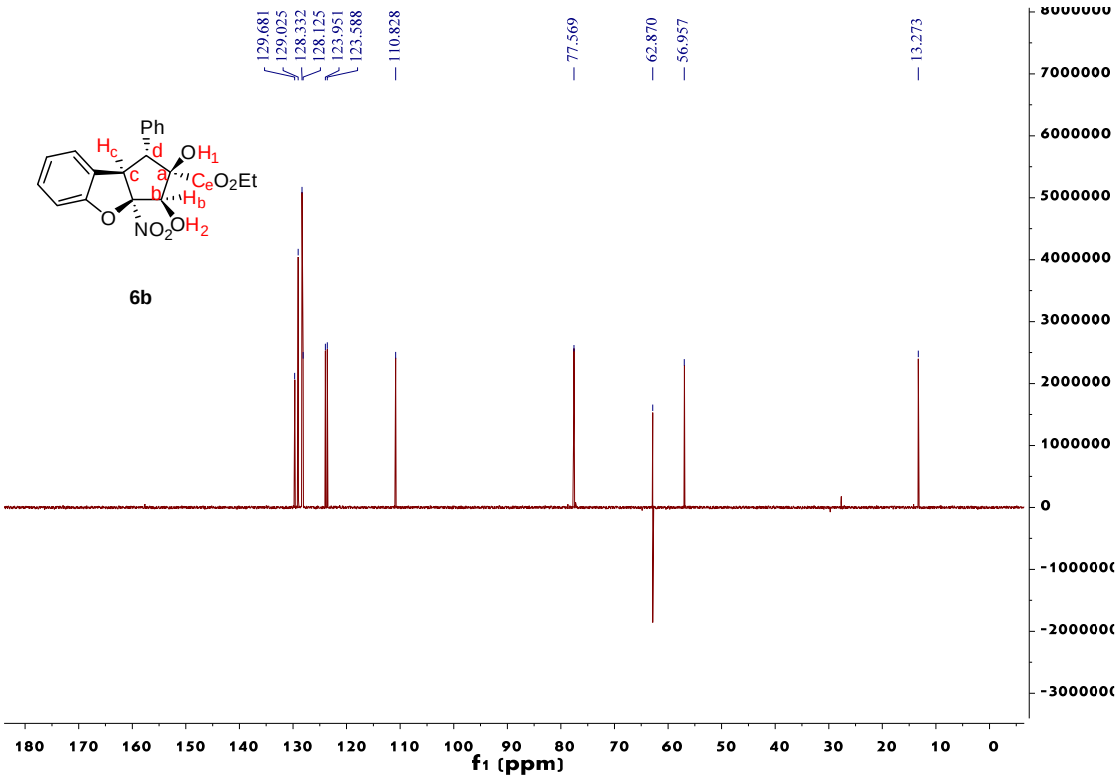
^{13}C NMR of 6b



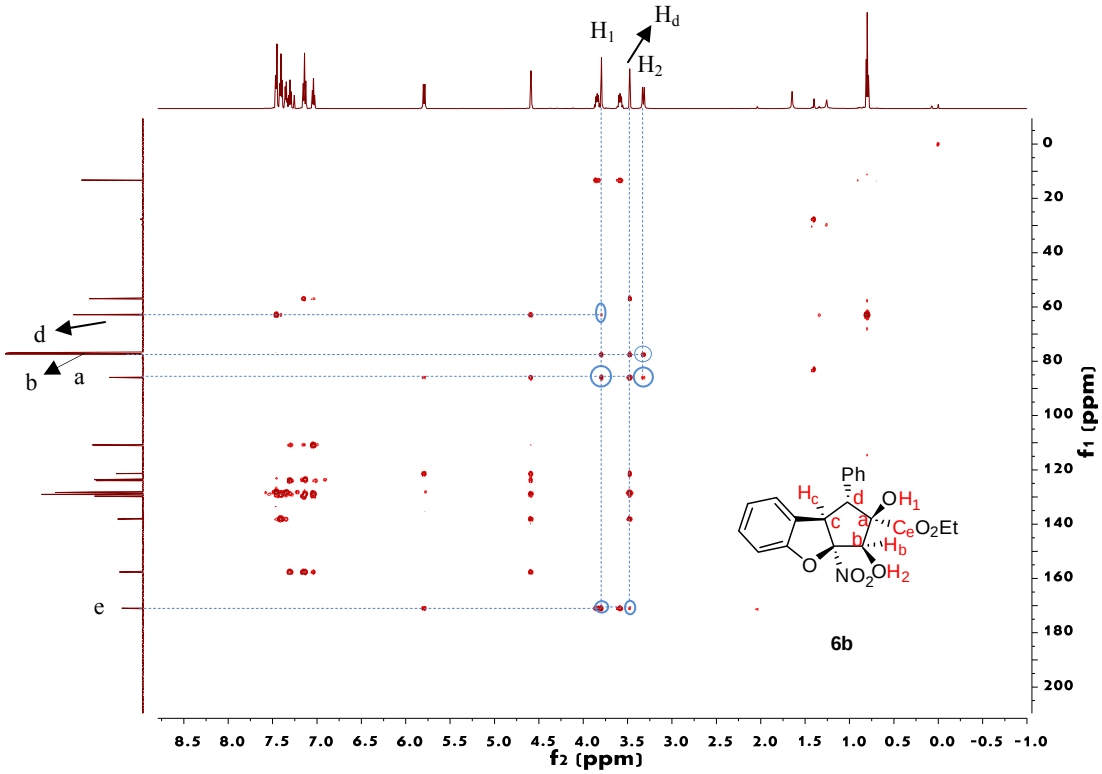
Deuteration Experiment of 6b



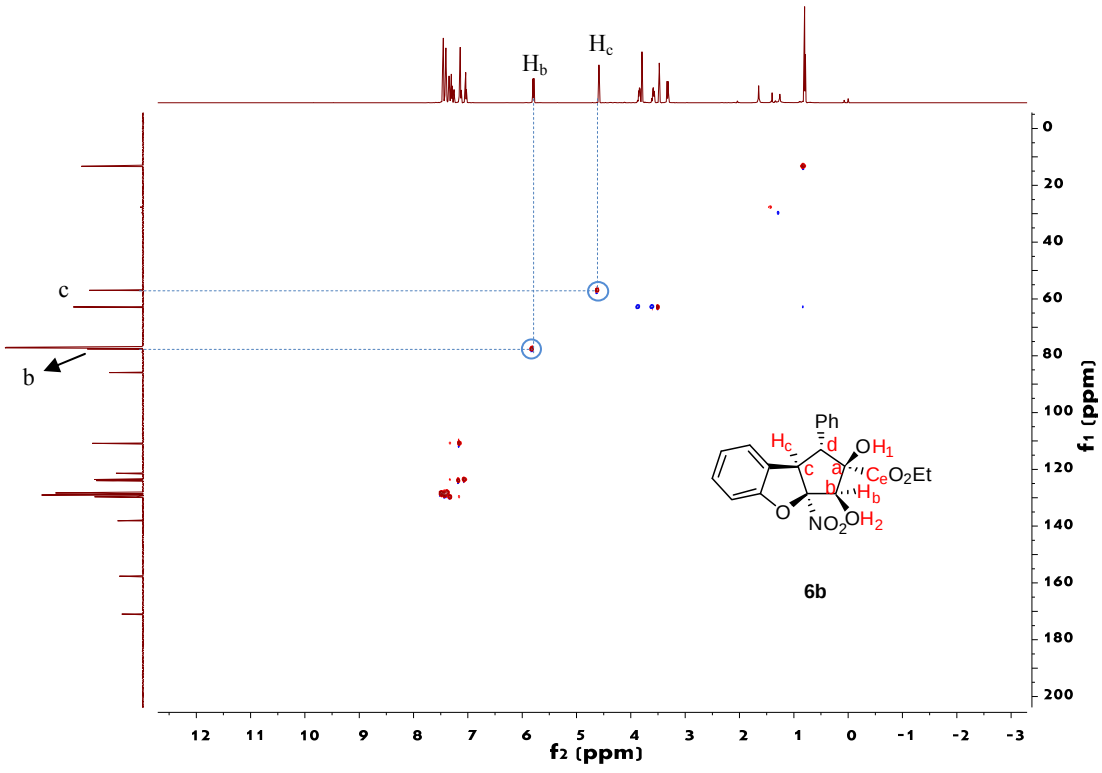
DEPT 135 of 6b



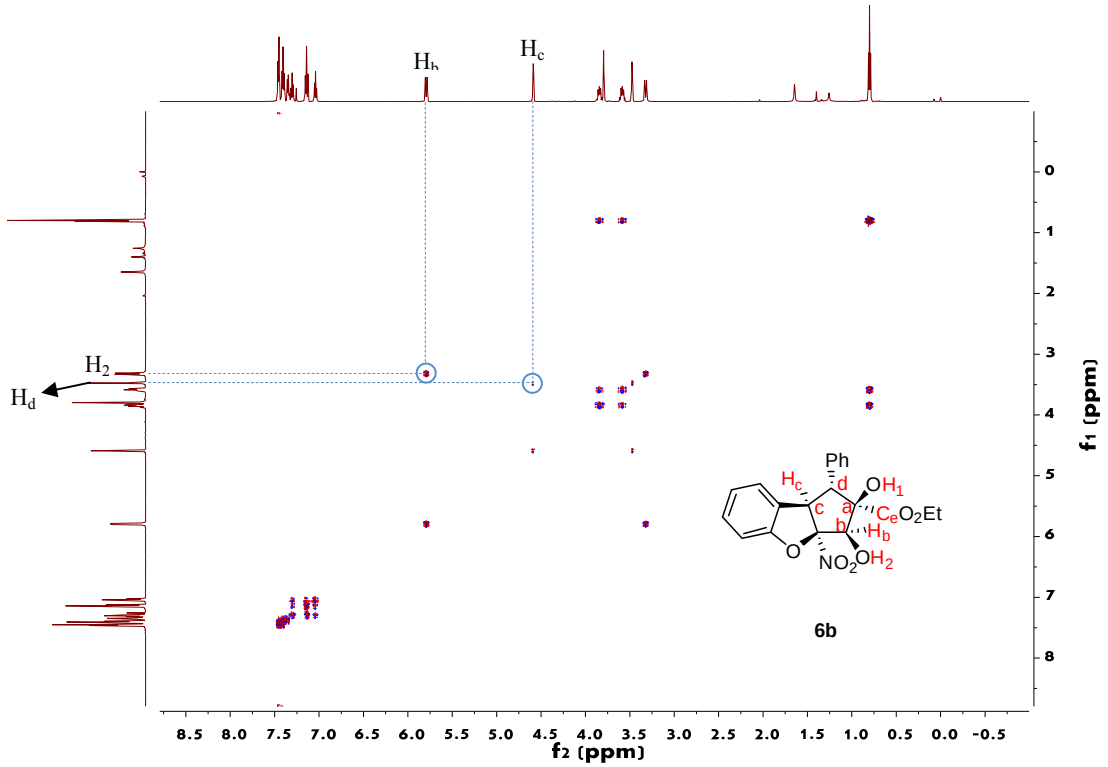
HMBC of 6b



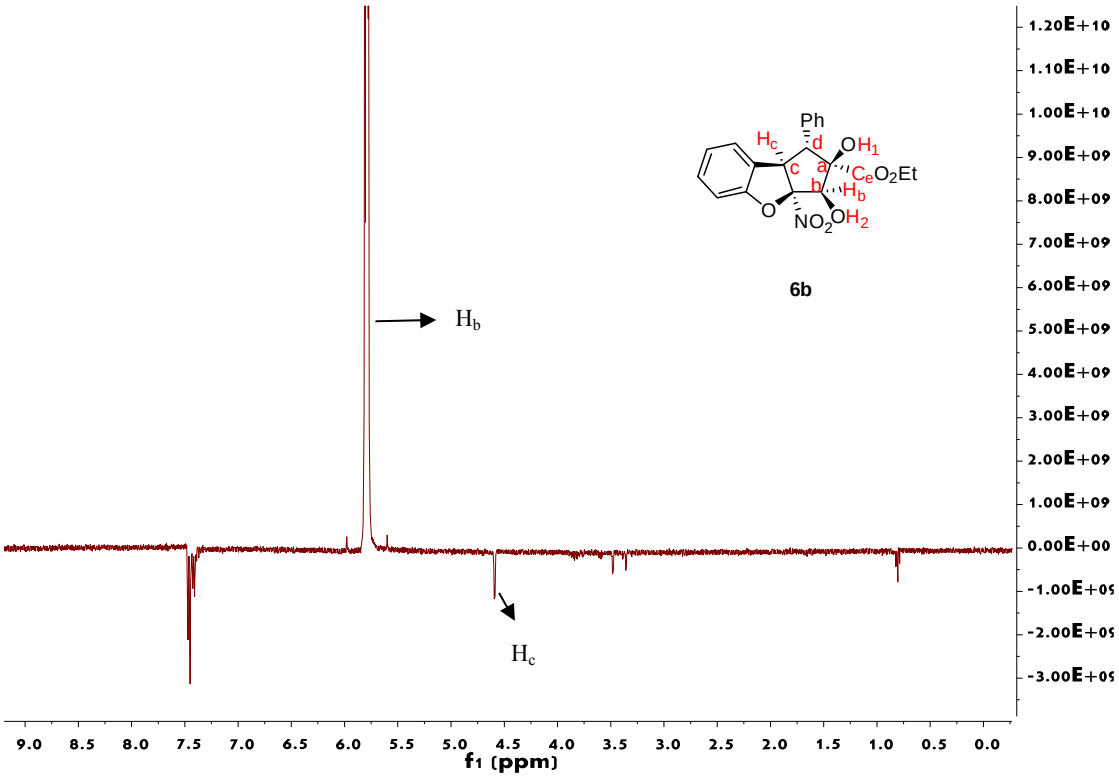
HSQC of 6b



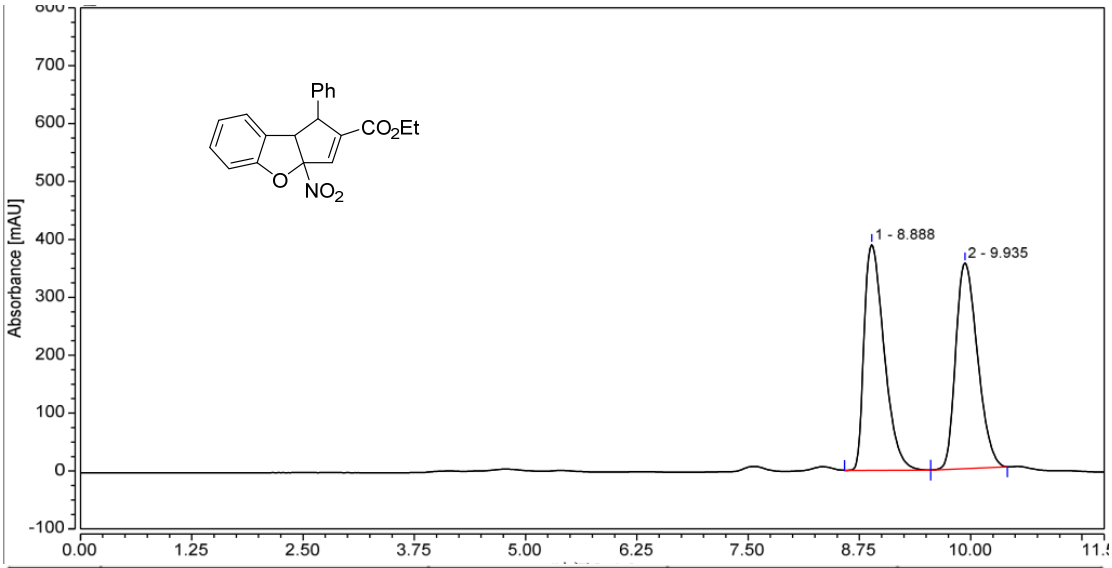
COSY of 6b



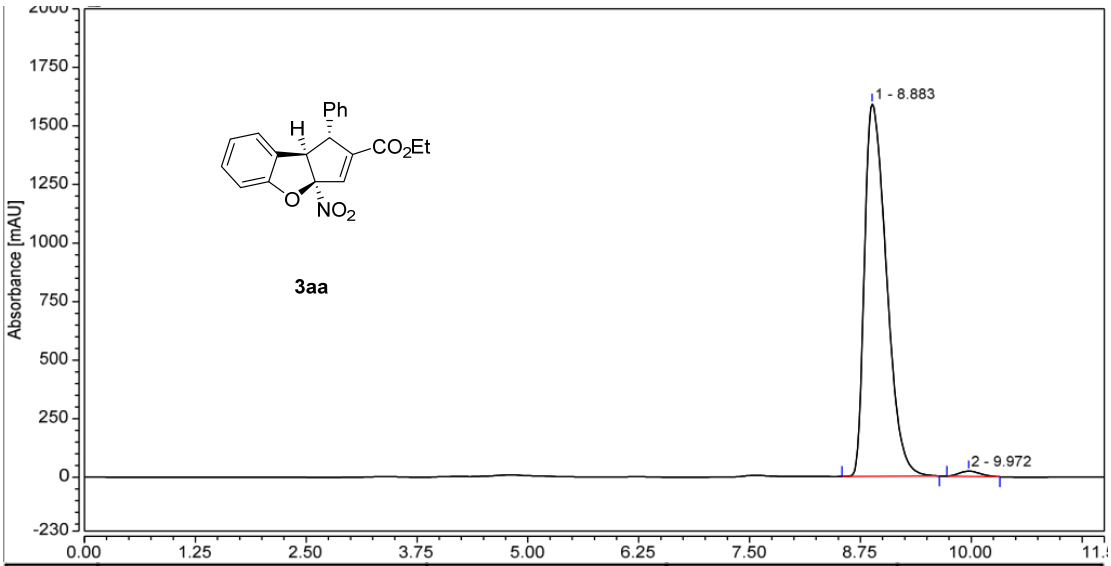
Selective Gradient NOESY of 6b



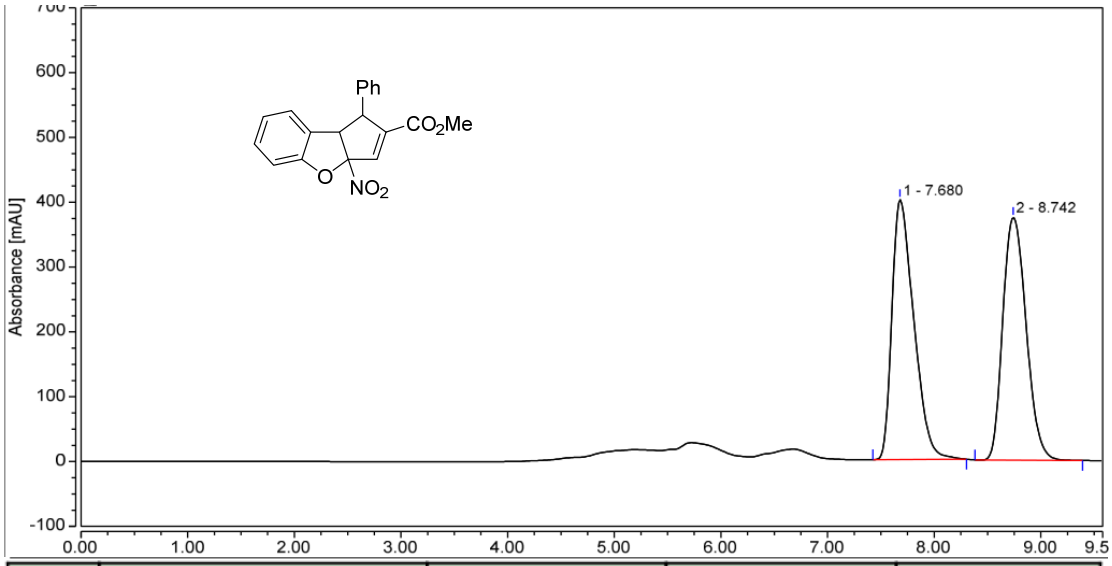
9. Copies of HPLC spectra for products



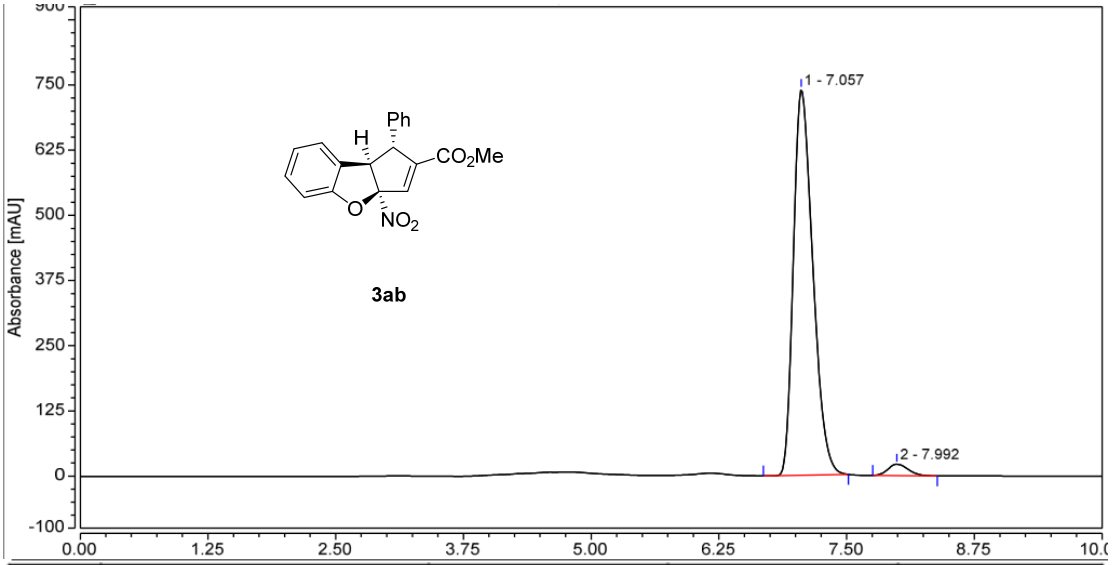
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	8.888	101.786	389.782	50.13
2	9.935	101.240	355.519	49.87
Total:		**203.027**	**745.301**	**100.00**



Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	8.883	456.061	1589.846	98.67
2	9.972	6.152	22.738	1.33
Total:		**462.213**	**1612.585**	**100.00**

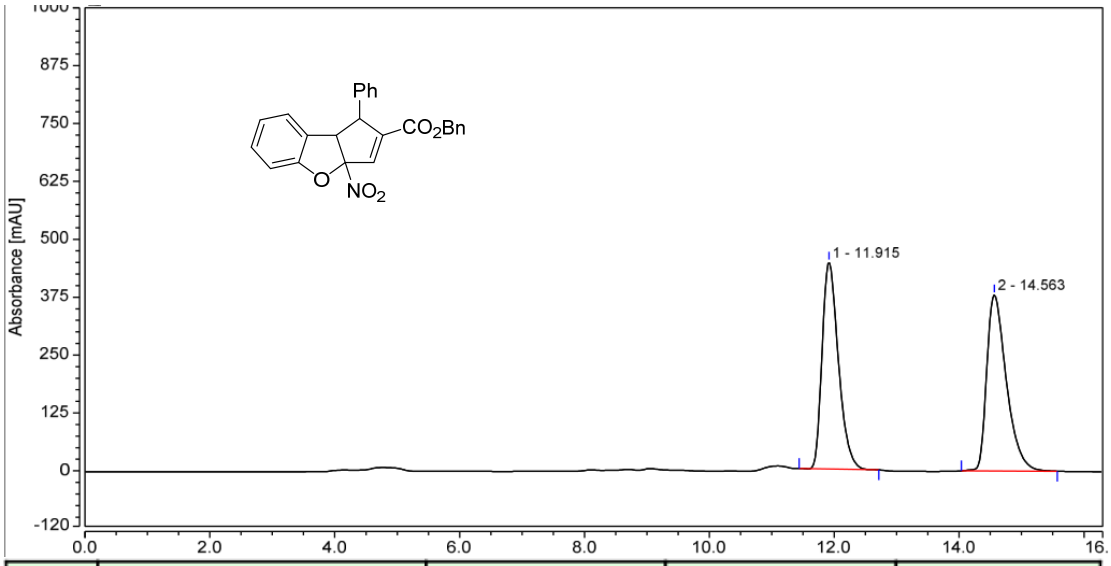


Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	7.680	95.230	401.113	50.04
2	8.742	95.080	374.176	49.96
Total:		**190.310**	**775.289**	**100.00**

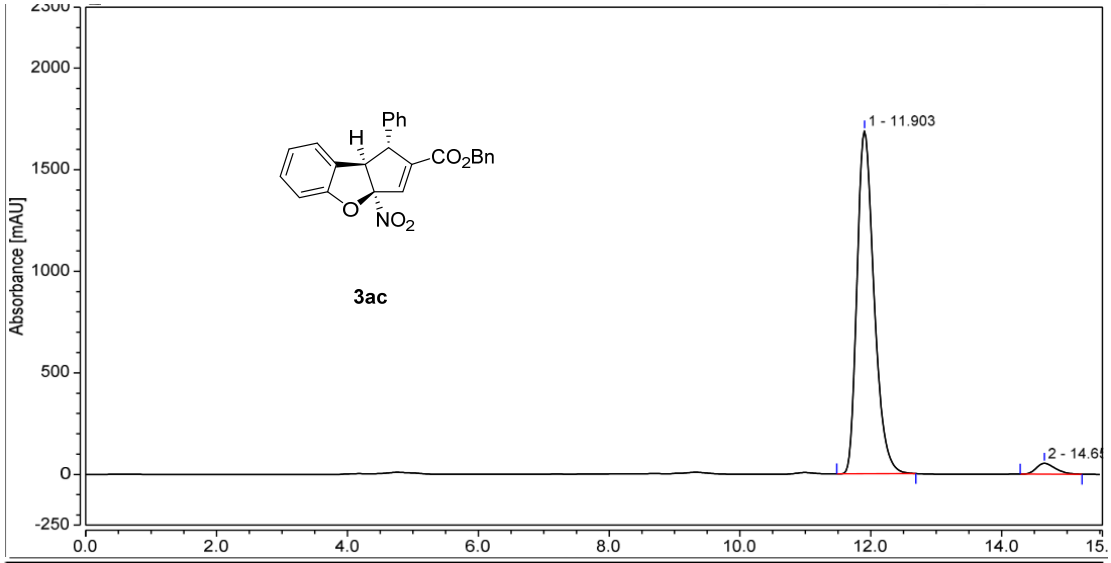


3ab

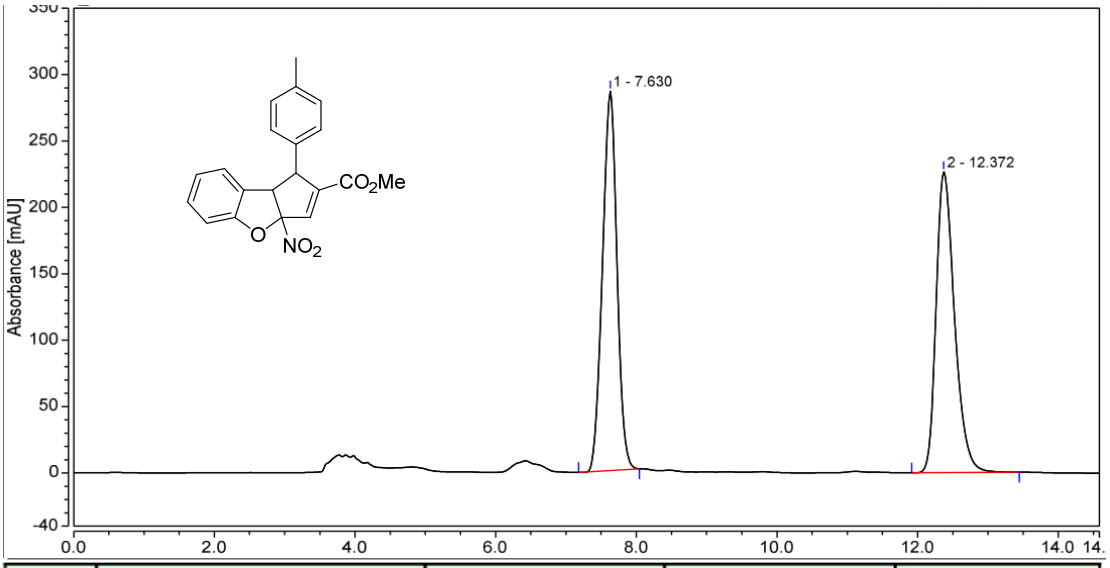
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	7.057	163.032	740.000	97.01
2	7.992	5.024	21.899	2.99
Total:		**168.057**	**761.898**	**100.00**



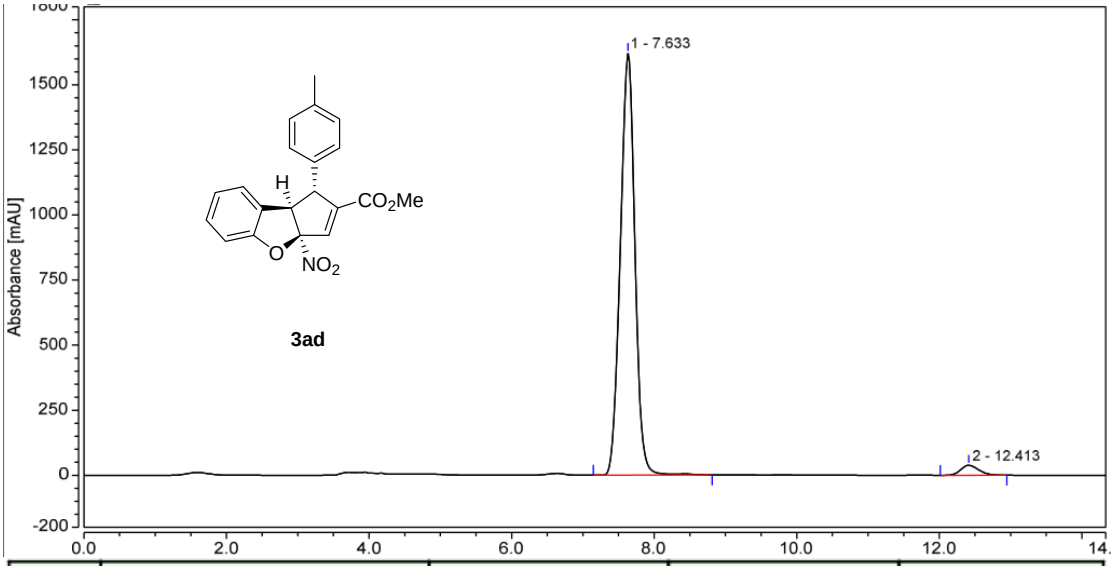
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	11.915	134.850	446.918	49.31
2	14.563	138.644	380.441	50.69
Total:		**273.494**	**827.358**	**100.00**



Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	11.903	509.882	1688.298	96.57
2	14.652	18.104	53.405	3.43
Total:		**527.986**	**1741.702**	**100.00**

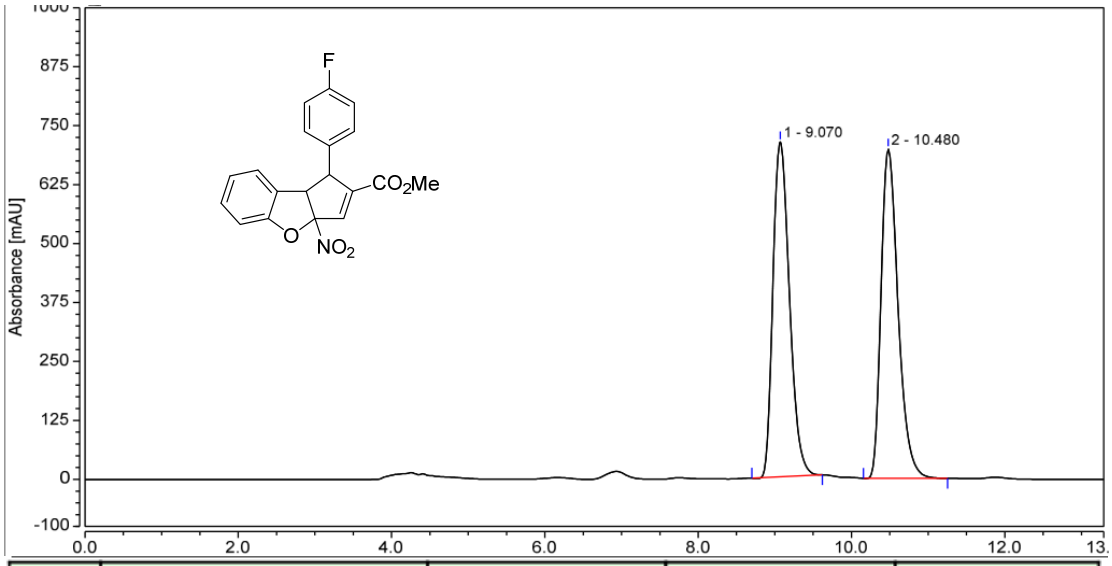


Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	7.630	68.194	285.692	49.90
2	12.372	68.465	226.531	50.10
Total:		**136.658**	**512.223**	**100.00**

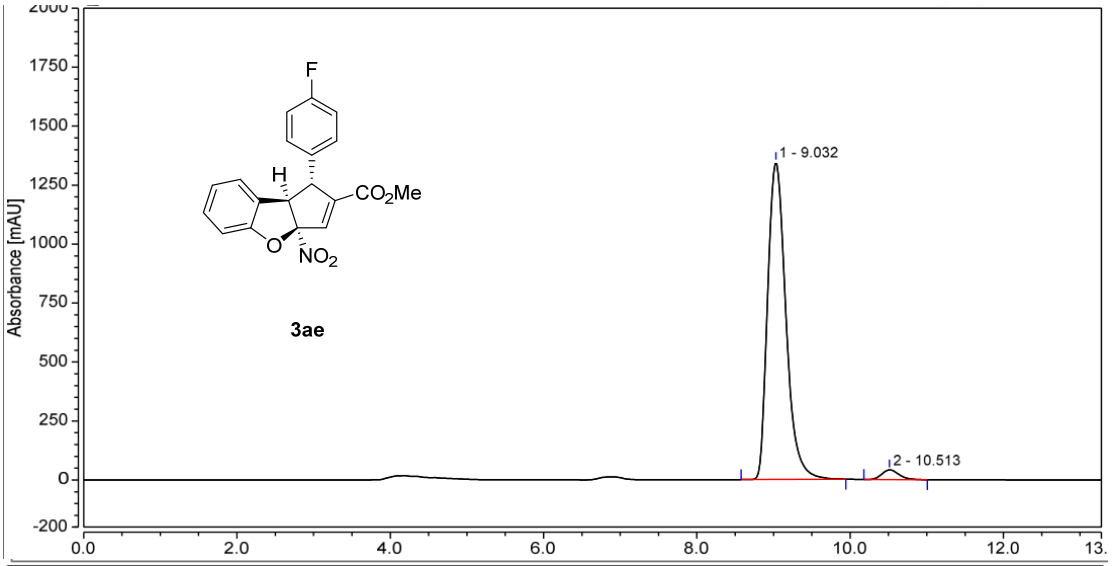


3ad

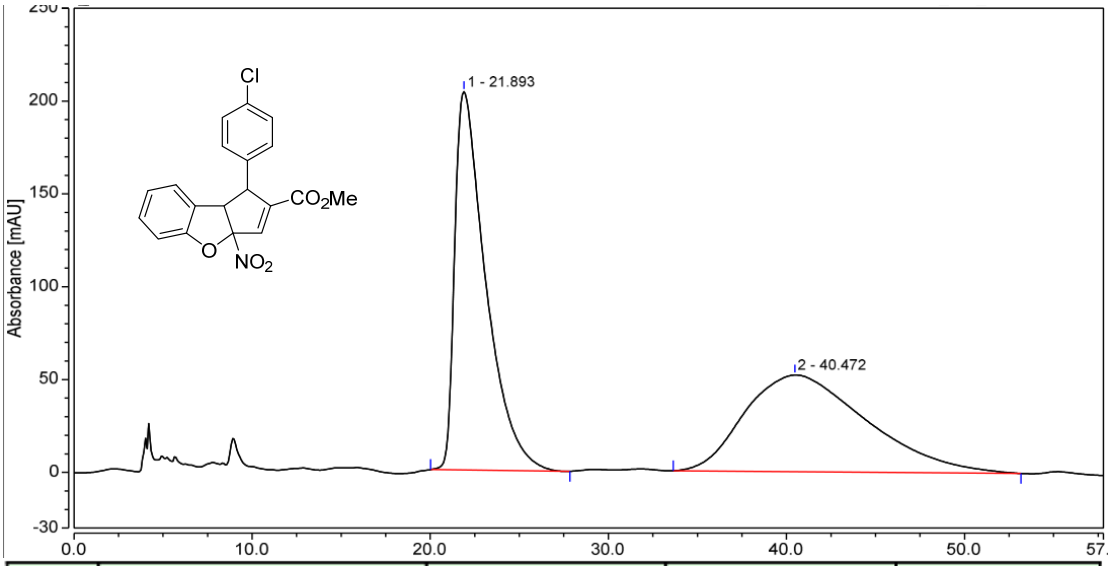
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	7.633	382.796	1620.215	97.11
2	12.413	11.400	38.544	2.89
Total:		**394.196**	**1658.759**	**100.00**



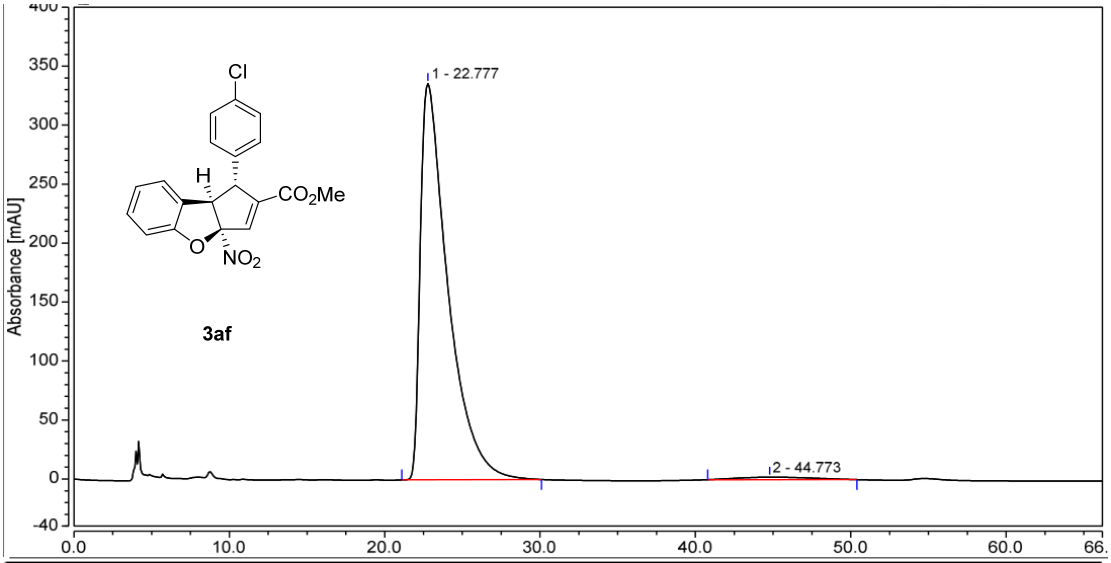
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	9.070	177.018	710.506	49.64
2	10.480	179.588	698.703	50.36
Total:		**356.606**	**1409.209**	**100.00**



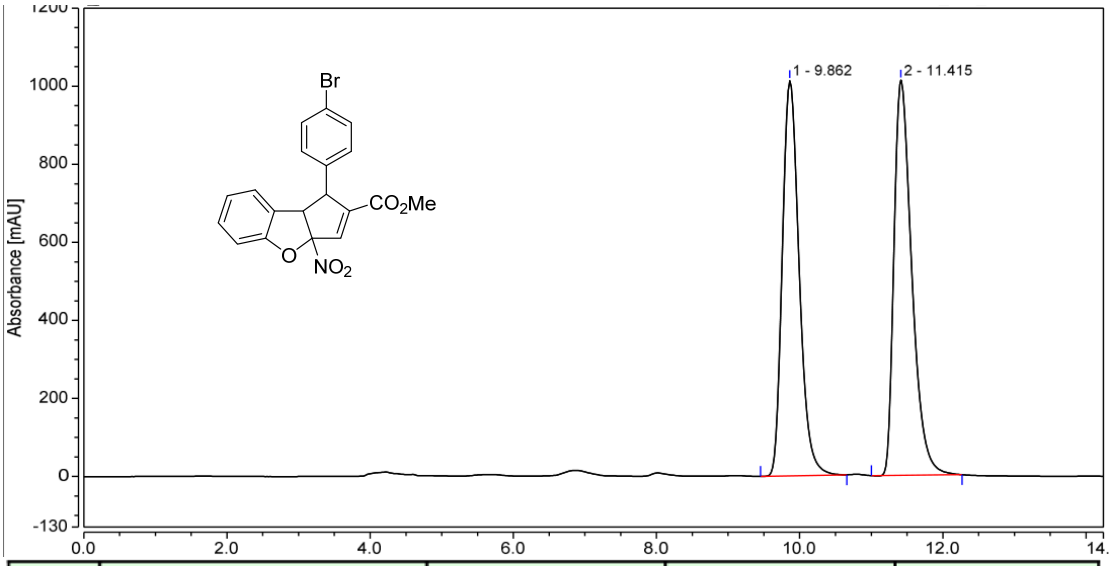
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	9.032	369.244	1344.442	97.16
2	10.513	10.812	41.422	2.84
Total:		**380.056**	**1385.865**	**100.00**



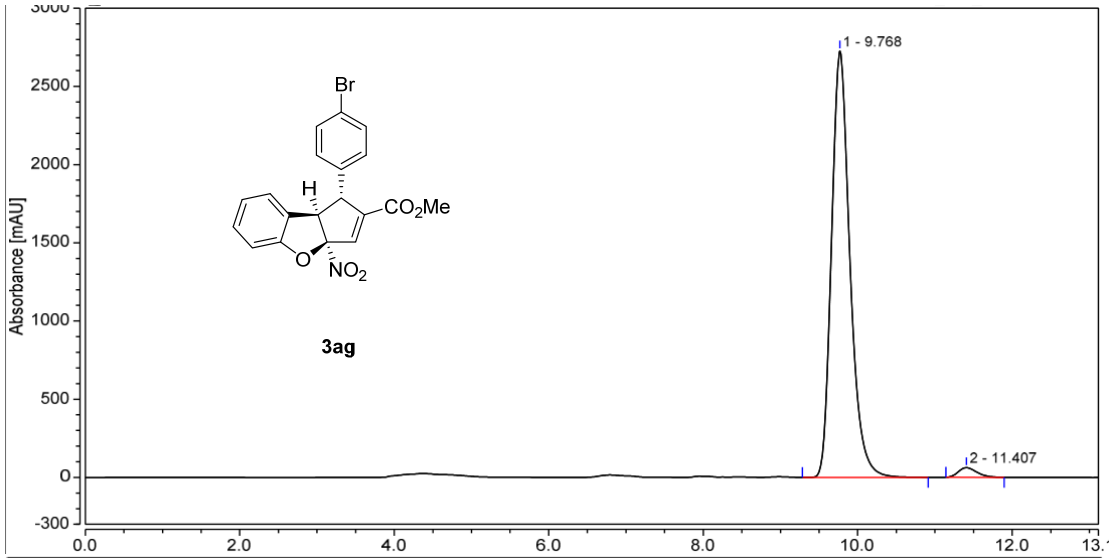
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	21.893	412.947	203.848	50.00
2	40.472	412.980	52.093	50.00
Total:		**825.927**	**255.941**	**100.00**



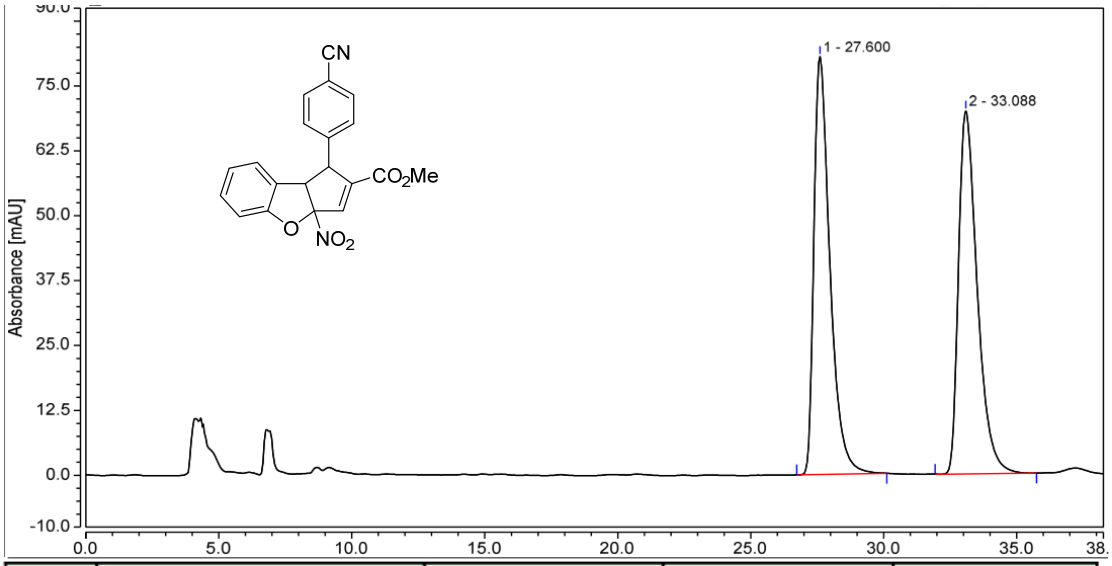
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	22.777	691.314	336.116	98.31
2	44.773	11.872	2.152	1.69
Total:		**703.186**	**338.268**	**100.00**



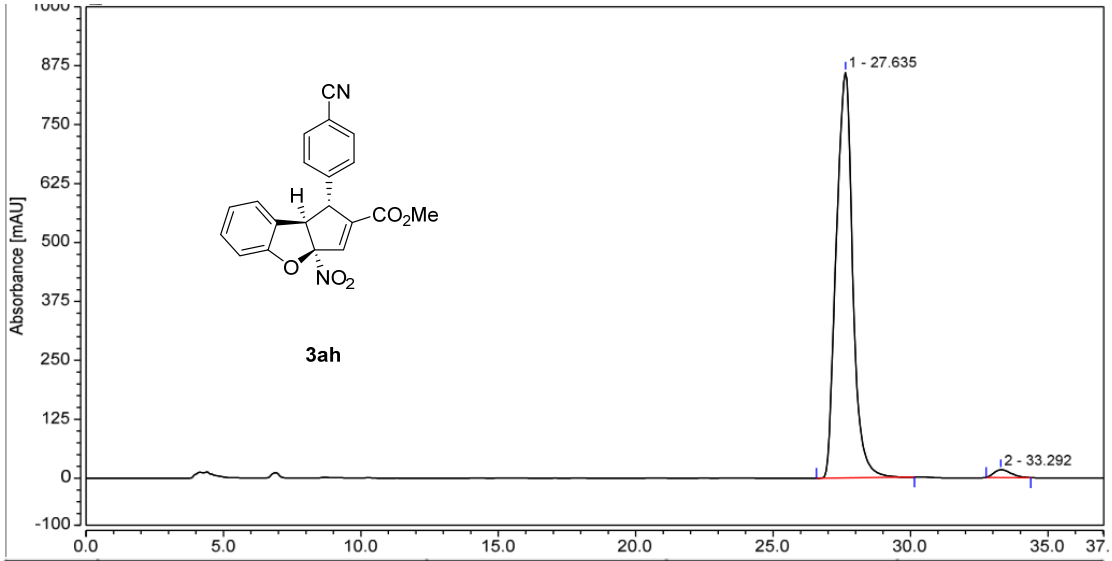
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	9.862	276.181	1013.227	48.64
2	11.415	291.677	1012.693	51.36
Total:		**567.857**	**2025.920**	**100.00**



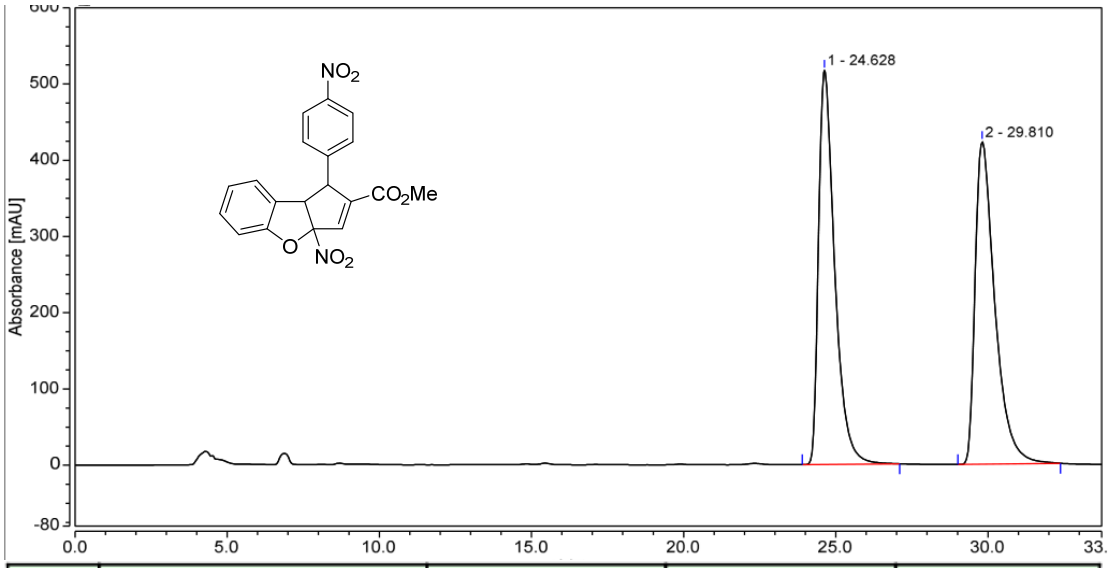
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	9.768	753.740	2726.456	97.77
2	11.407	17.189	61.411	2.23
Total:		**770.929**	**2787.868**	**100.00**



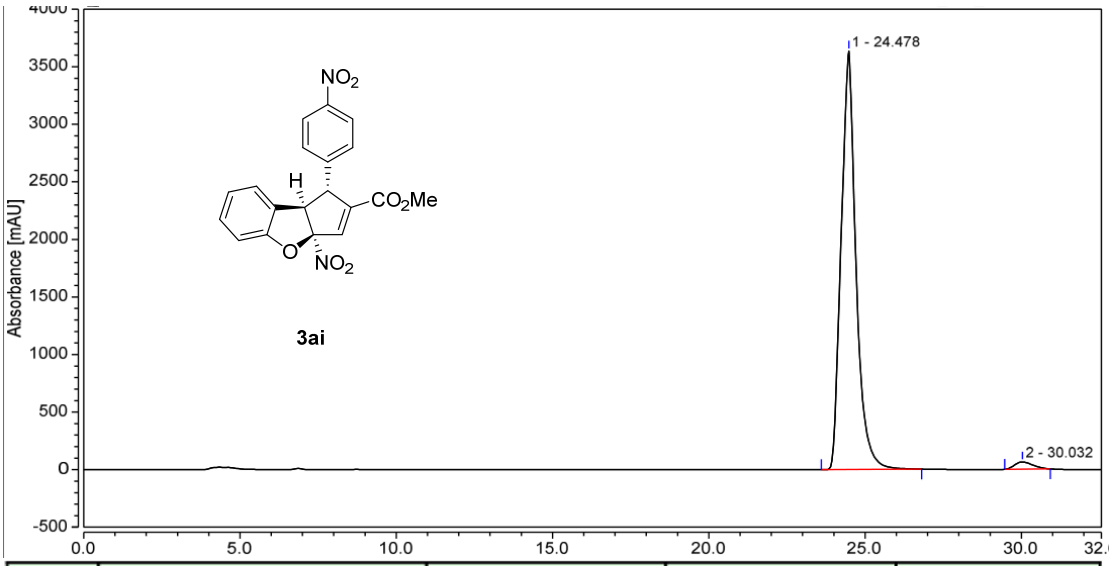
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	27.600	56.208	80.550	49.63
2	33.088	57.053	69.916	50.37
Total:		**113.261**	**150.466**	**100.00**



Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	27.635	596.802	860.536	98.03
2	33.292	11.967	16.574	1.97
Total:		**608.768**	**877.110**	**100.00**

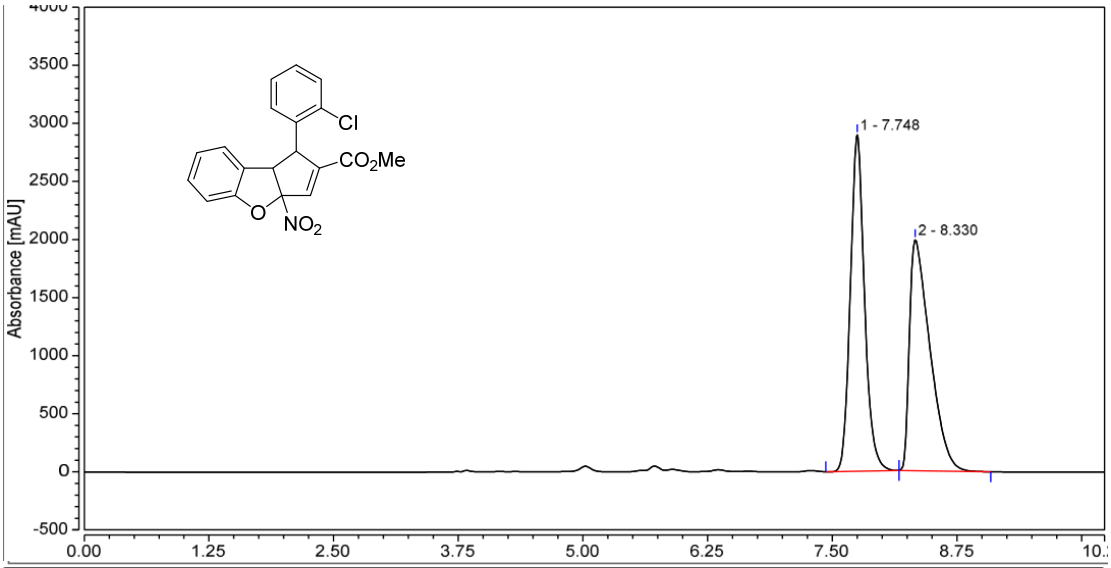


Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	24.628	317.327	516.969	49.91
2	29.810	318.439	423.322	50.09
Total:		**635.766**	**940.291**	**100.00**

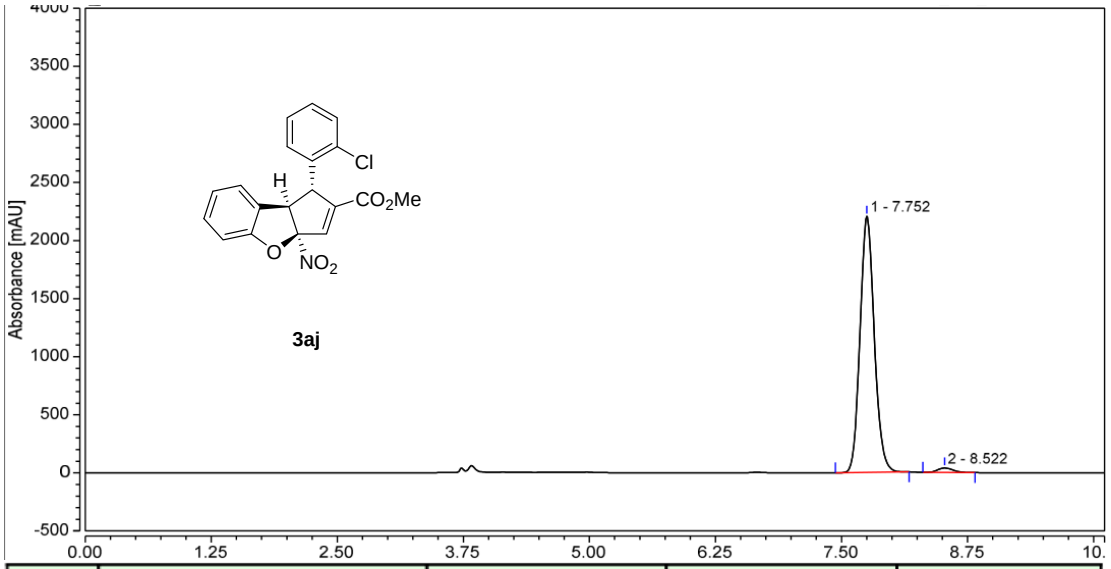


3ai

Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	24.478	1992.779	3634.984	97.92
2	30.032	42.380	62.534	2.08
Total:		**2035.160**	**3697.518**	**100.00**

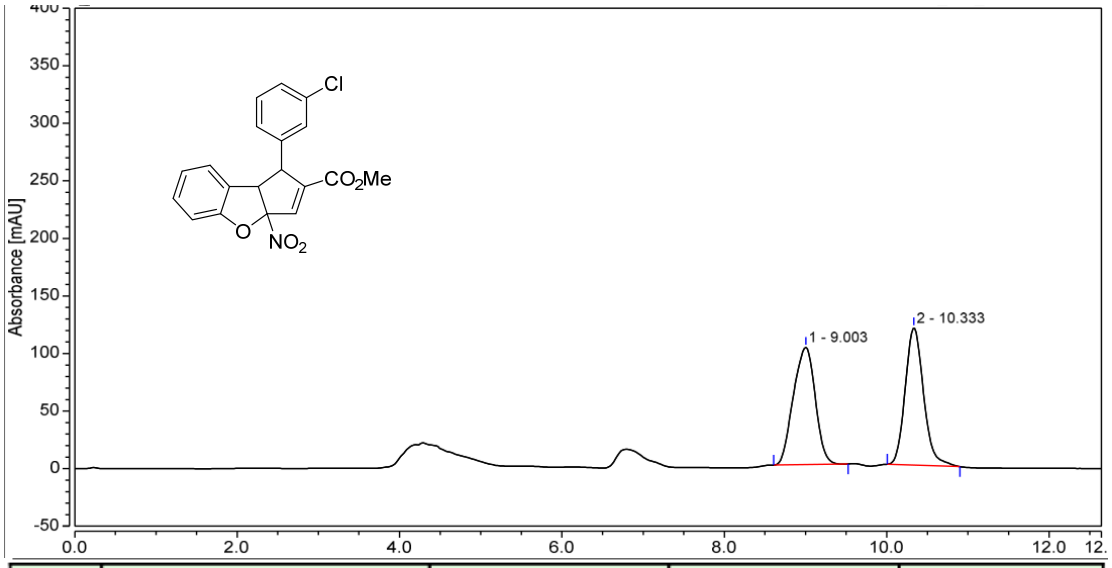


Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	7.748	477.882	2896.756	50.30
2	8.330	472.232	1989.245	49.70
Total:		**950.114**	**4886.001**	**100.00**

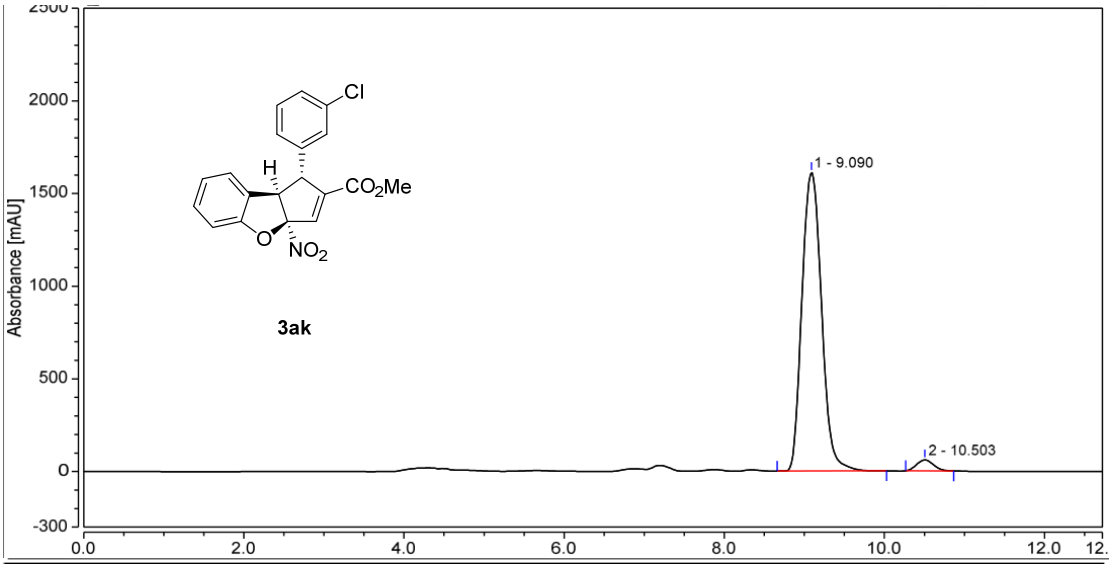


3aj

Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	7.752	361.394	2206.375	98.13
2	8.522	6.881	38.800	1.87
Total:		**368.275**	**2245.175**	**100.00**

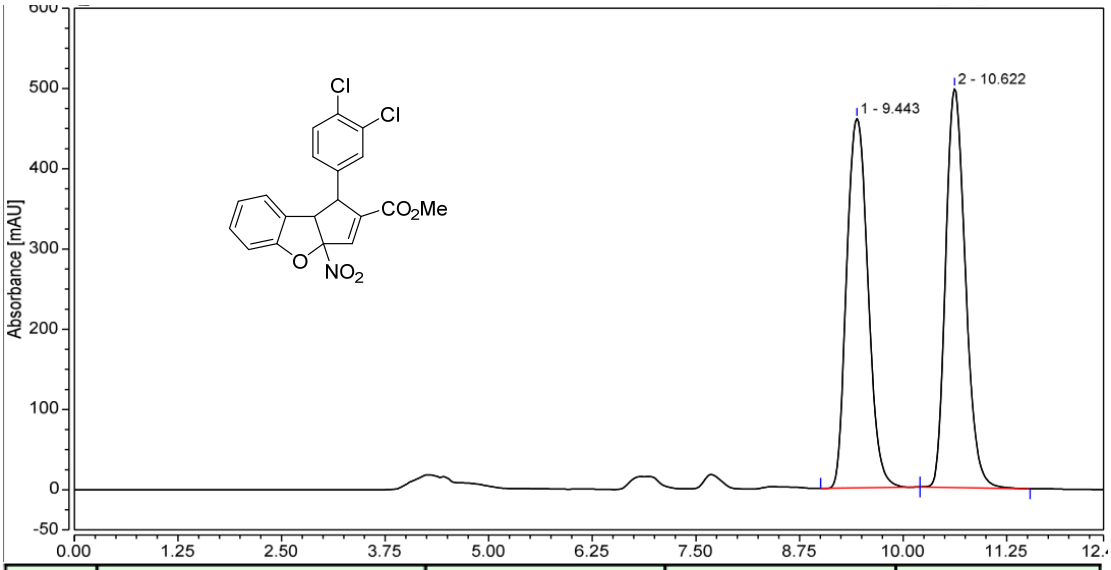


Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	9.003	31.859	101.816	50.35
2	10.333	31.417	119.237	49.65
Total:		**63.275**	**221.053**	**100.00**

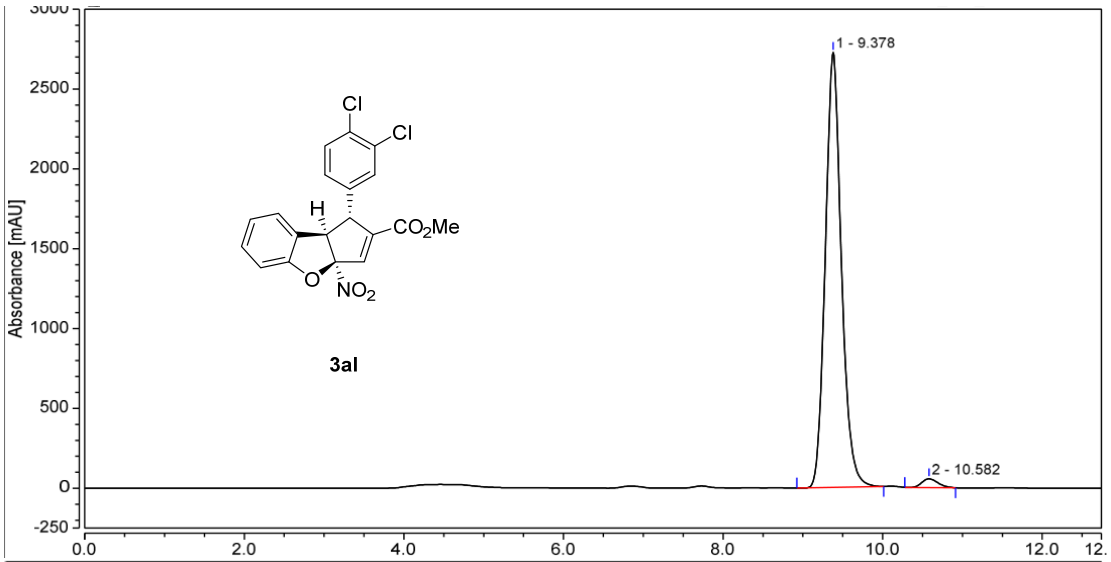


3ak

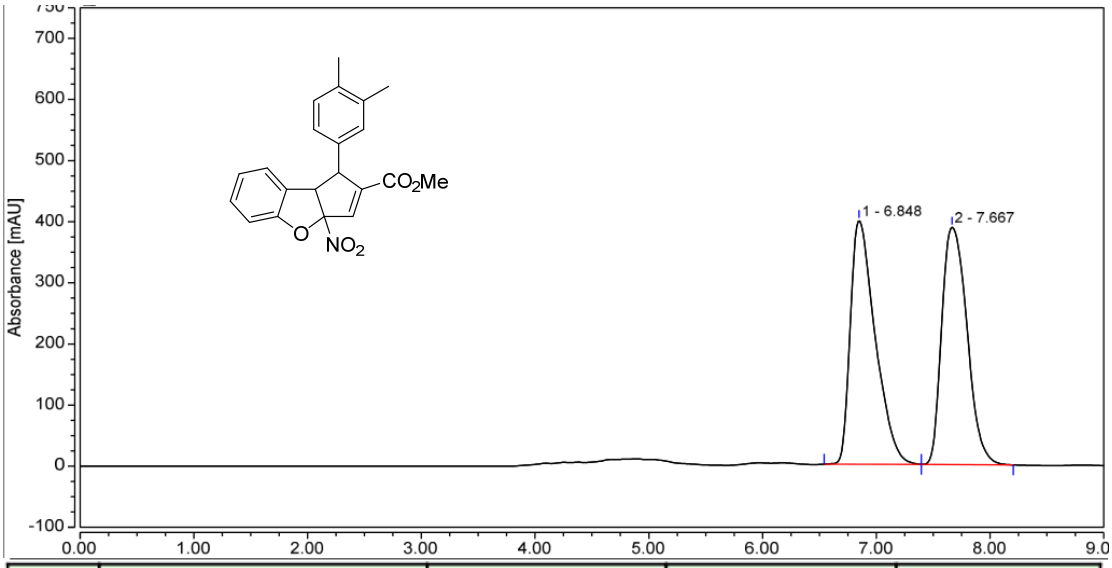
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	9.090	456.577	1611.025	96.95
2	10.503	14.381	58.989	3.05
Total:		**470.958**	**1670.014**	**100.00**



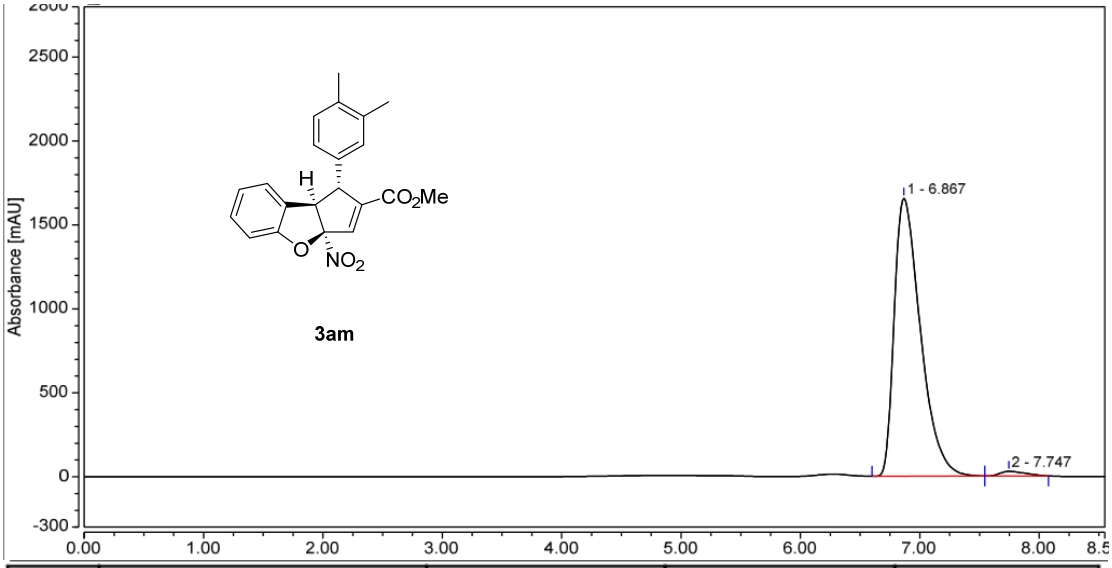
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	9.443	137.115	460.263	49.99
2	10.622	137.163	497.263	50.01
Total:		**274.277**	**957.525**	**100.00**



Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	9.378	637.149	2724.941	98.04
2	10.582	12.748	54.799	1.96
Total:		**649.897**	**2779.740**	**100.00**

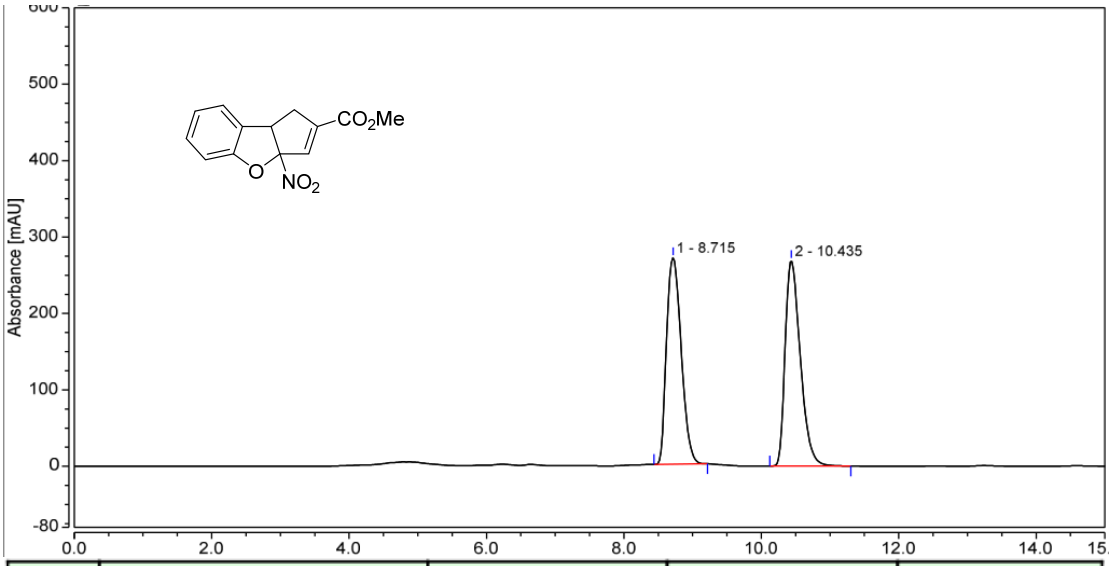


Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	6.848	101.009	398.845	50.22
2	7.667	100.129	388.195	49.78
Total:		**201.138**	**787.040**	**100.00**

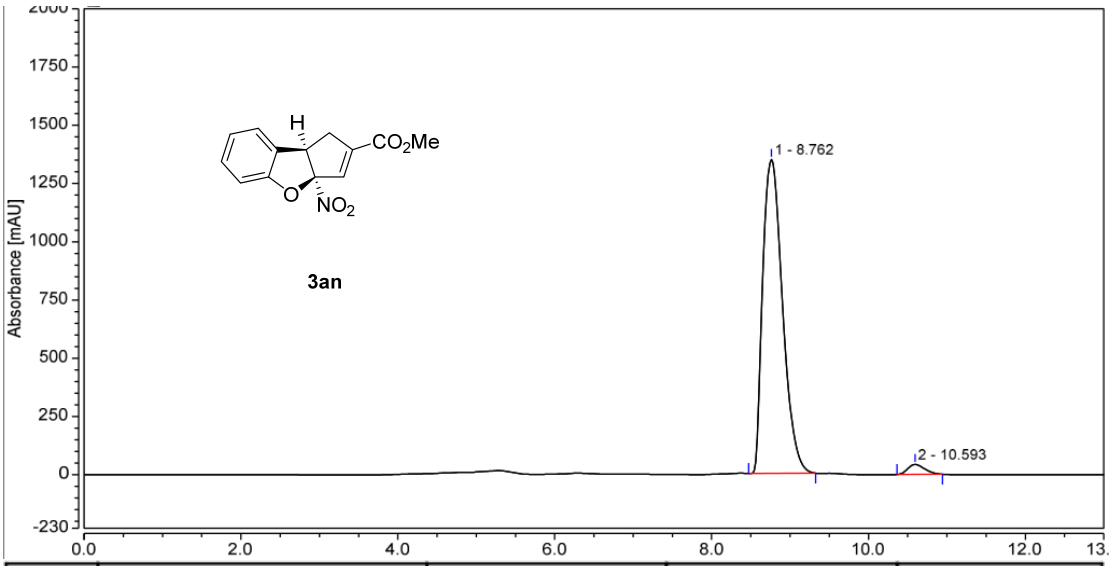


3am

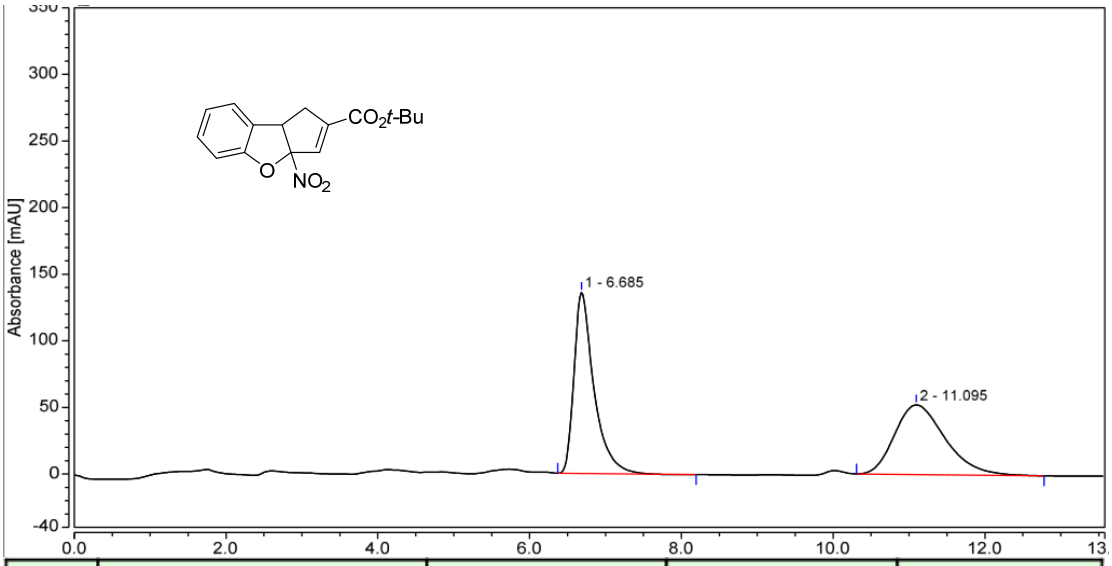
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	6.867	421.847	1656.961	98.41
2	7.747	6.833	28.267	1.59
Total:		**428.680**	**1685.228**	**100.00**



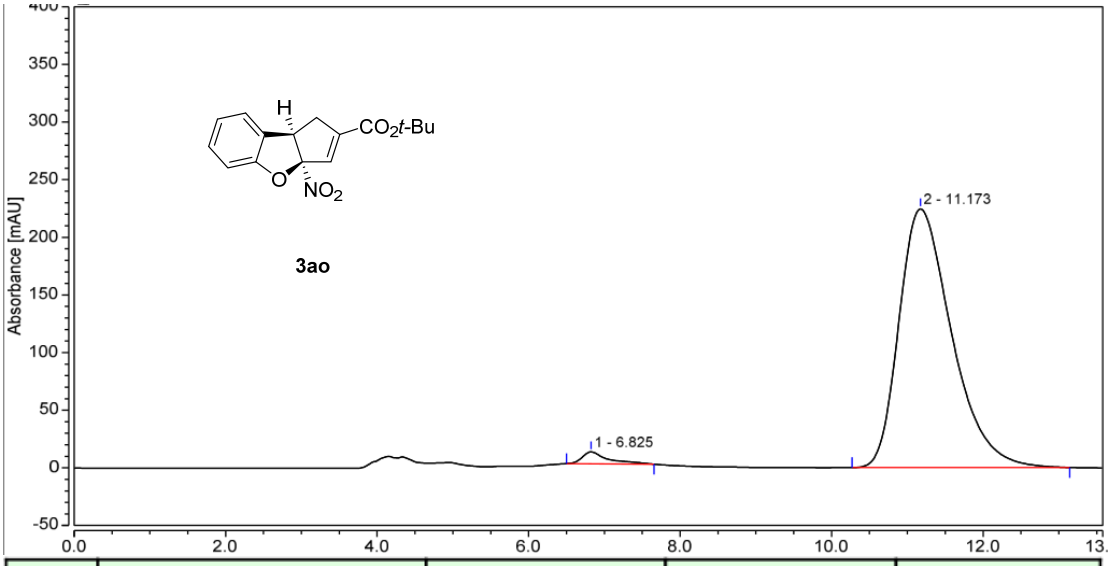
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	8.715	67.045	270.105	49.37
2	10.435	68.769	268.984	50.63
Total:		**135.813**	**539.090**	**100.00**



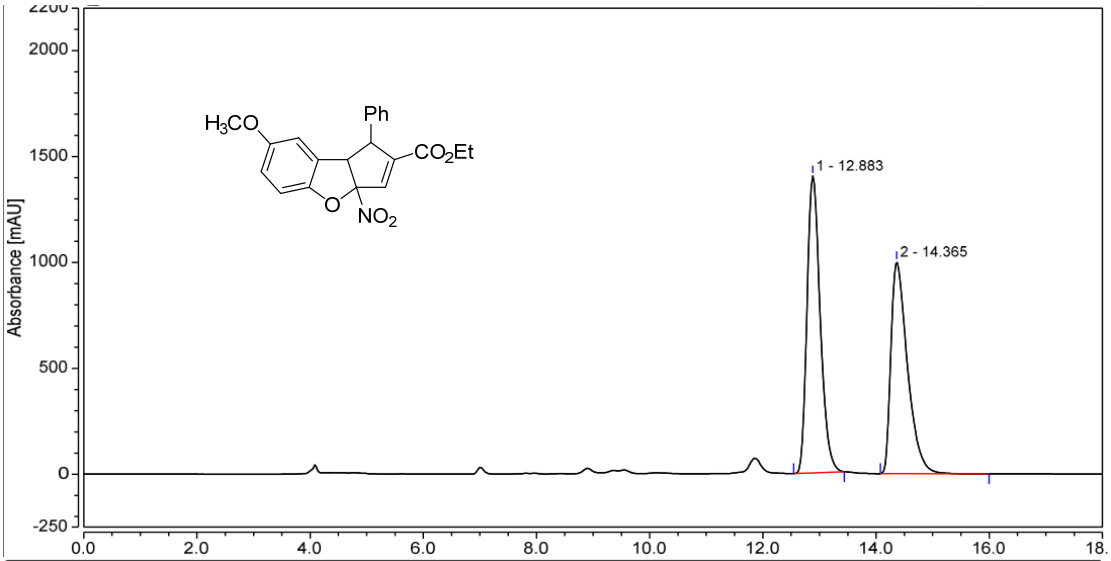
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	8.762	393.546	1348.347	97.34
2	10.593	10.764	42.867	2.66
Total:		**404.310**	**1391.213**	**100.00**



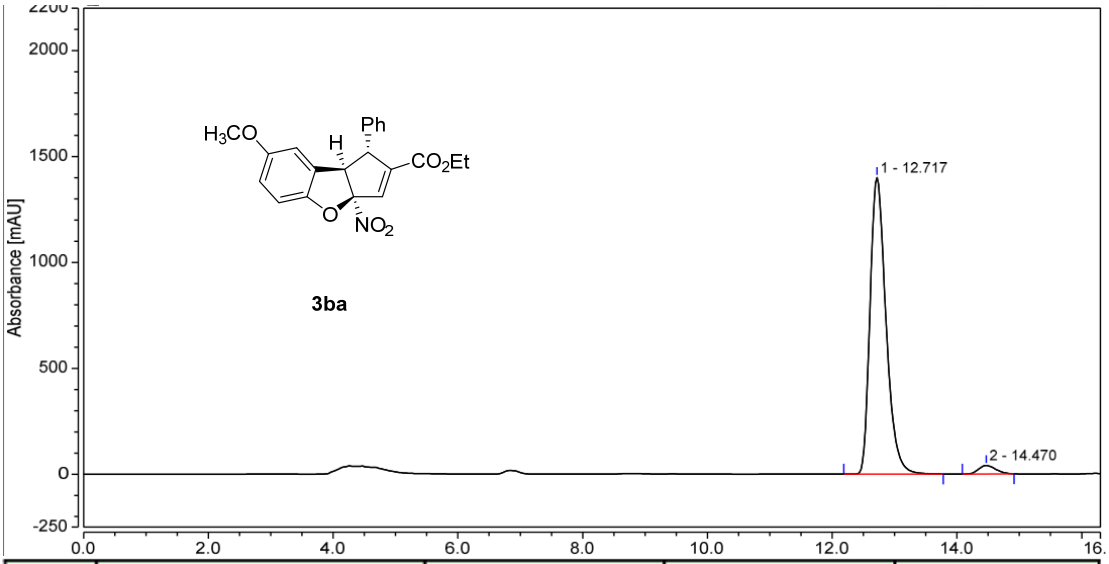
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	6.685	41.484	135.973	50.72
2	11.095	40.307	52.252	49.28
Total:		**81.791**	**188.225**	**100.00**



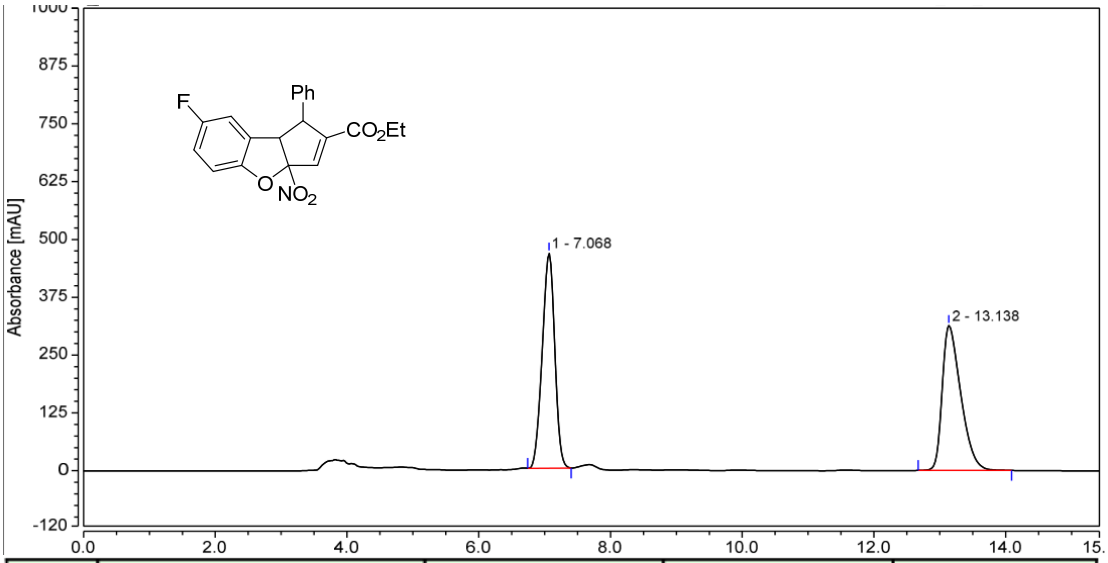
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	6.825	4.033	10.319	2.19
2	11.173	180.407	224.460	97.81
Total:		**184.440**	**234.778**	**100.00**



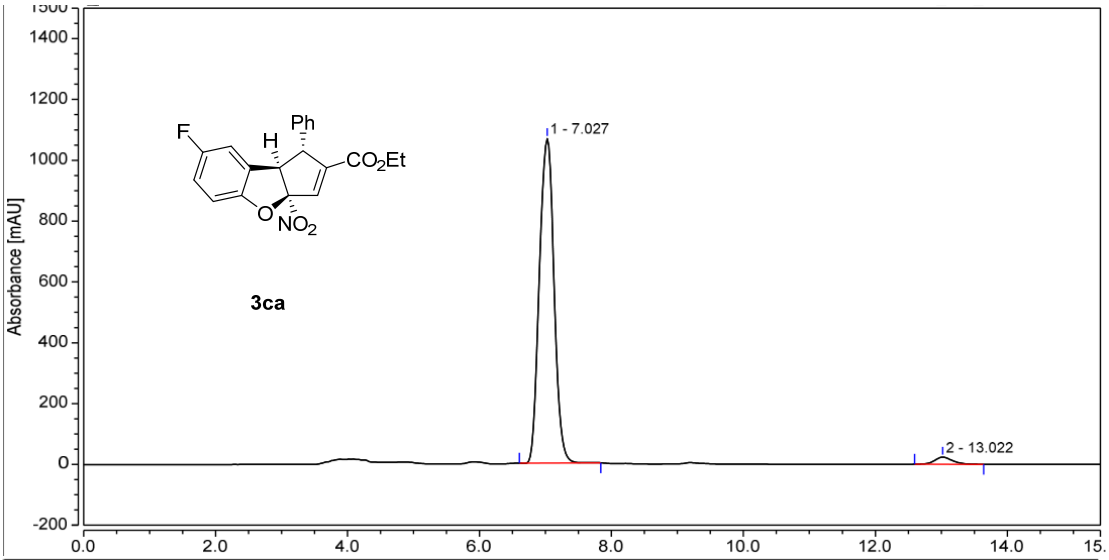
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	12.883	377.210	1402.463	52.74
2	14.365	337.969	1000.609	47.26
Total:		**715.178**	**2403.072**	**100.00**



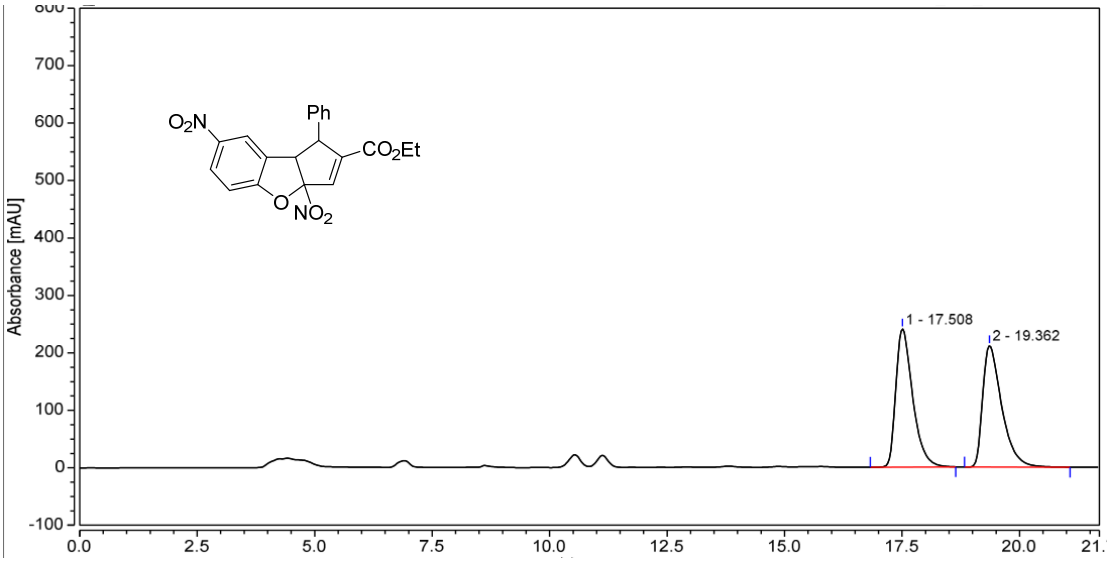
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	12.717	413.980	1400.315	97.00
2	14.470	12.811	40.095	3.00
Total:		**426.791**	**1440.410**	**100.00**



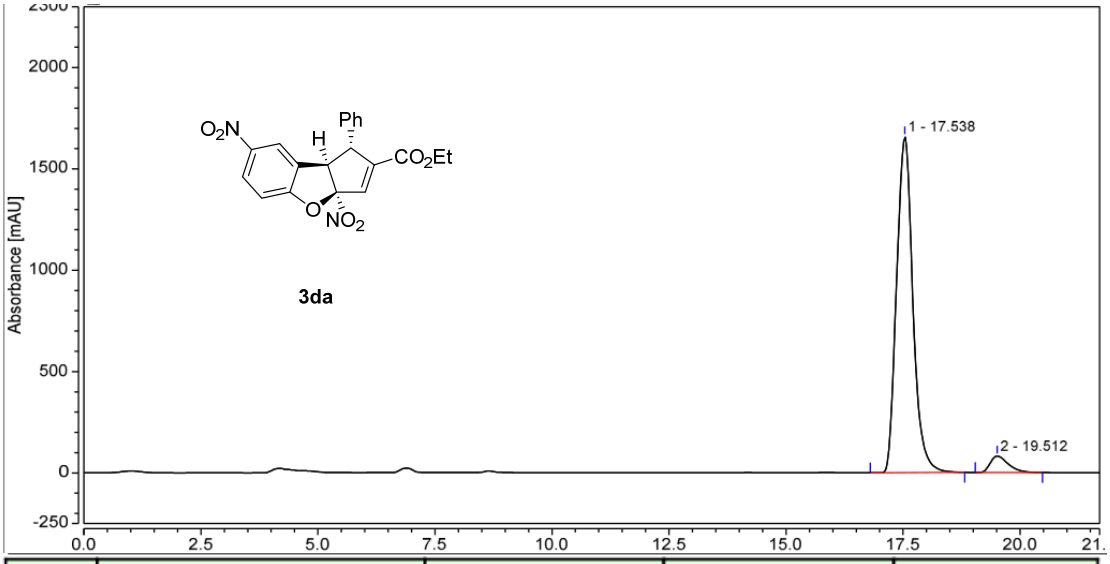
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	7.068	102.021	464.993	49.78
2	13.138	102.918	313.601	50.22
Total:		**204.939**	**778.594**	**100.00**



Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	7.027	276.371	1067.164	97.40
2	13.022	7.364	23.450	2.60
Total:		**283.735**	**1090.614**	**100.00**

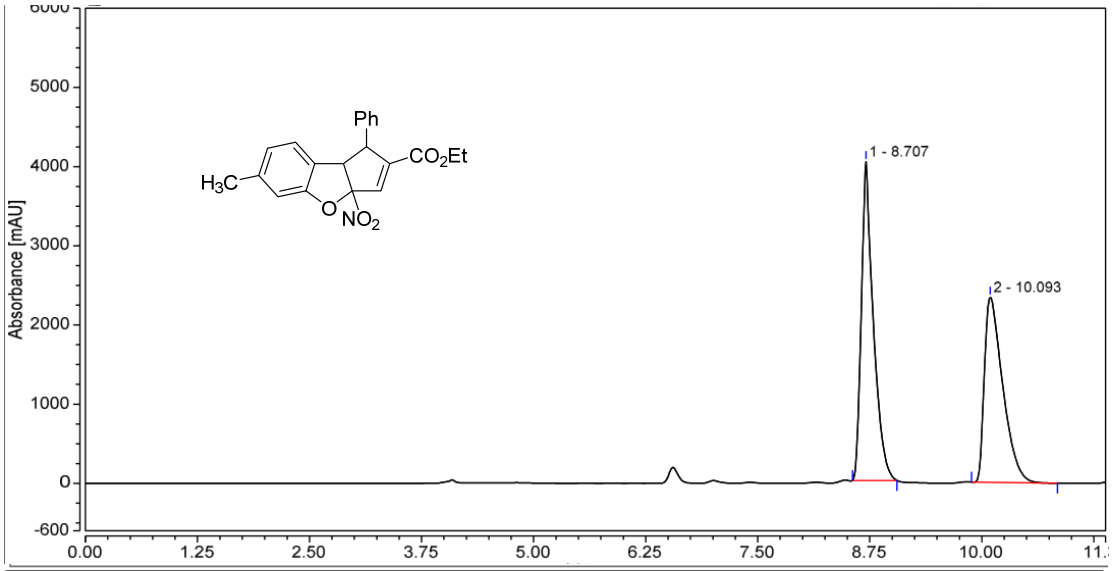


Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	17.508	100.521	240.642	50.26
2	19.362	99.488	211.171	49.74
Total:		**200.010**	**451.813**	**100.00**

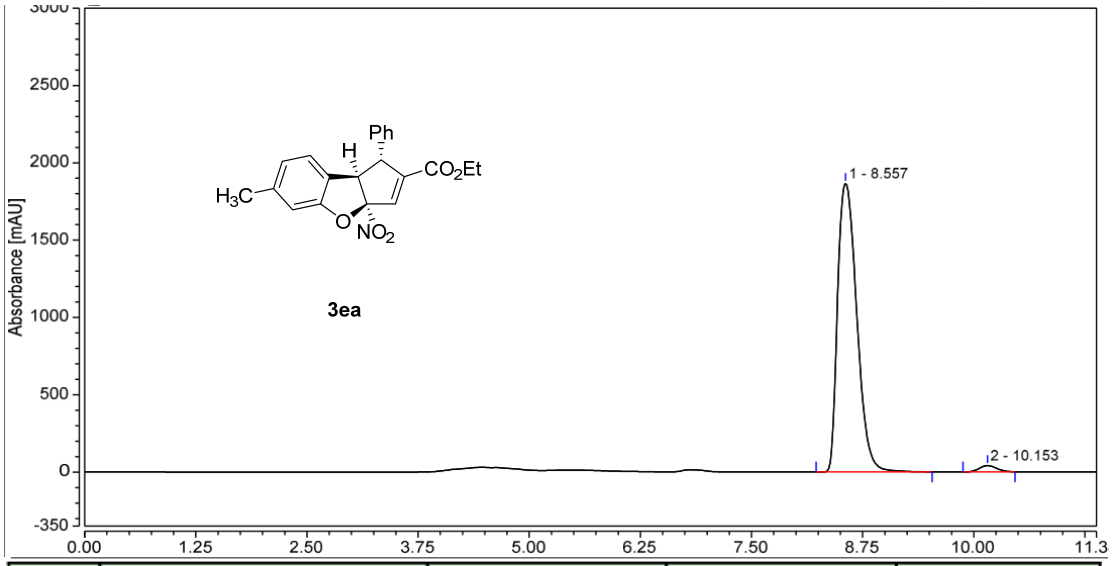


3da

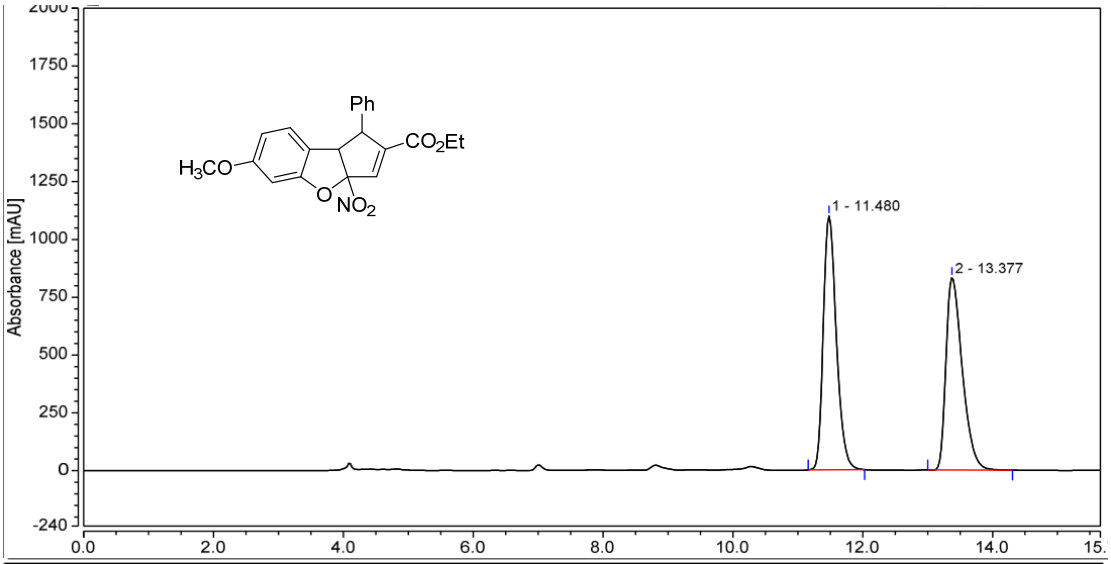
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	17.538	668.944	1657.780	94.81
2	19.512	36.594	81.267	5.19
Total:		**705.538**	**1739.047**	**100.00**



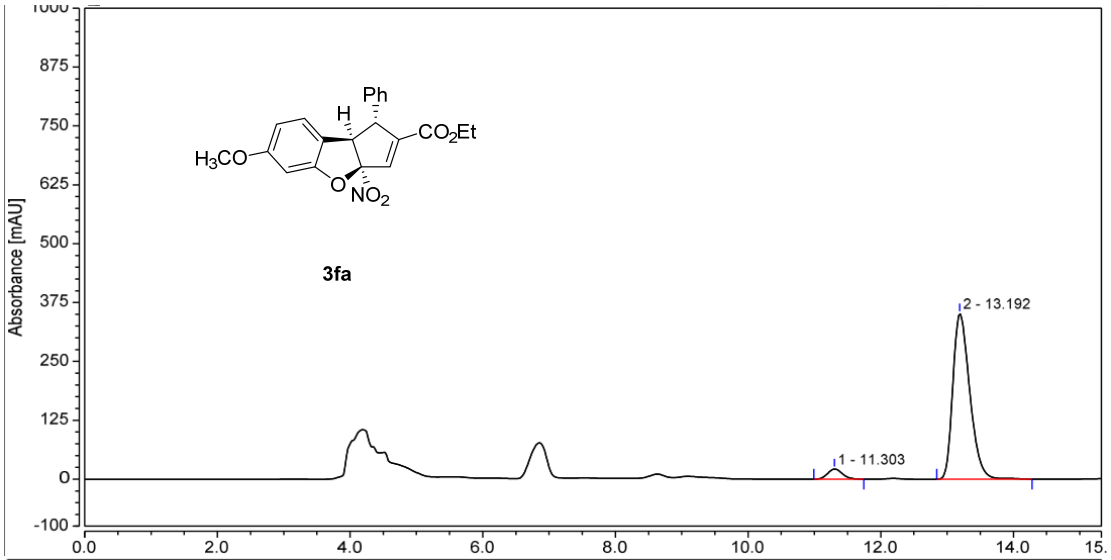
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	8.707	619.948	4028.090	52.75
2	10.093	555.346	2340.575	47.25
Total:		**1175.294**	**6368.664**	**100.00**



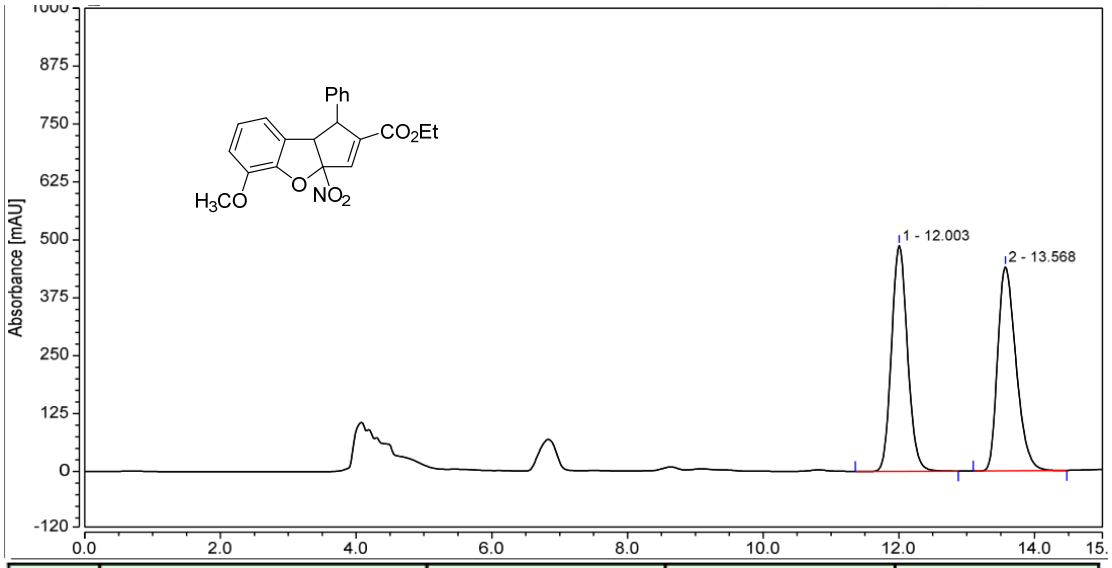
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	8.557	465.110	1866.021	98.03
2	10.153	9.361	40.937	1.97
Total:		**474.471**	**1906.958**	**100.00**



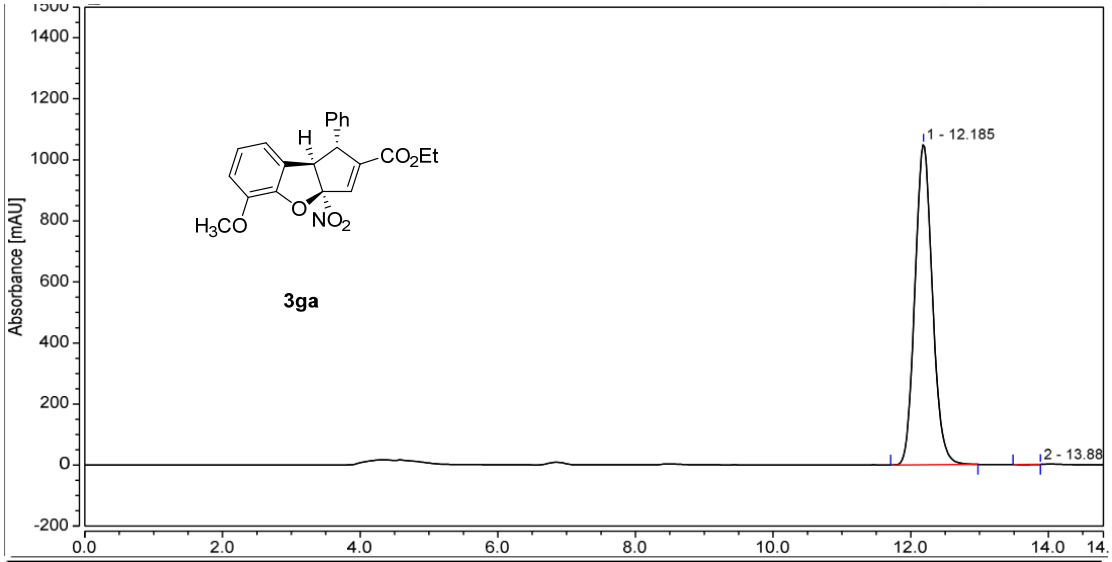
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	11.480	256.477	1098.409	51.40
2	13.377	242.499	832.248	48.60
Total:		**498.976**	**1930.657**	**100.00**



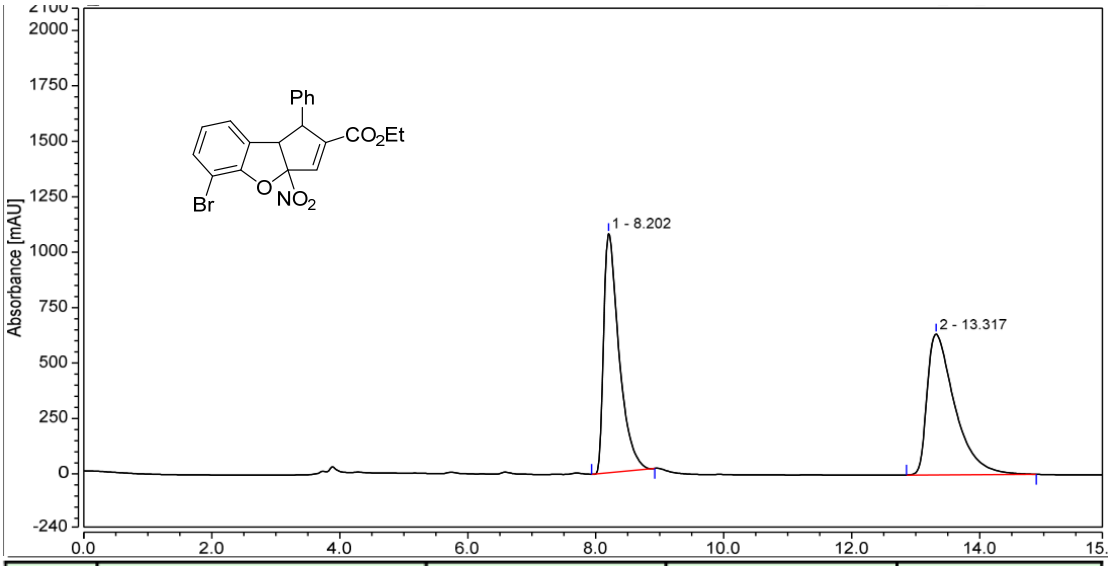
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	11.303	5.629	21.690	5.13
2	13.192	104.103	351.339	94.87
Total:		**109.733**	**373.030**	**100.00**



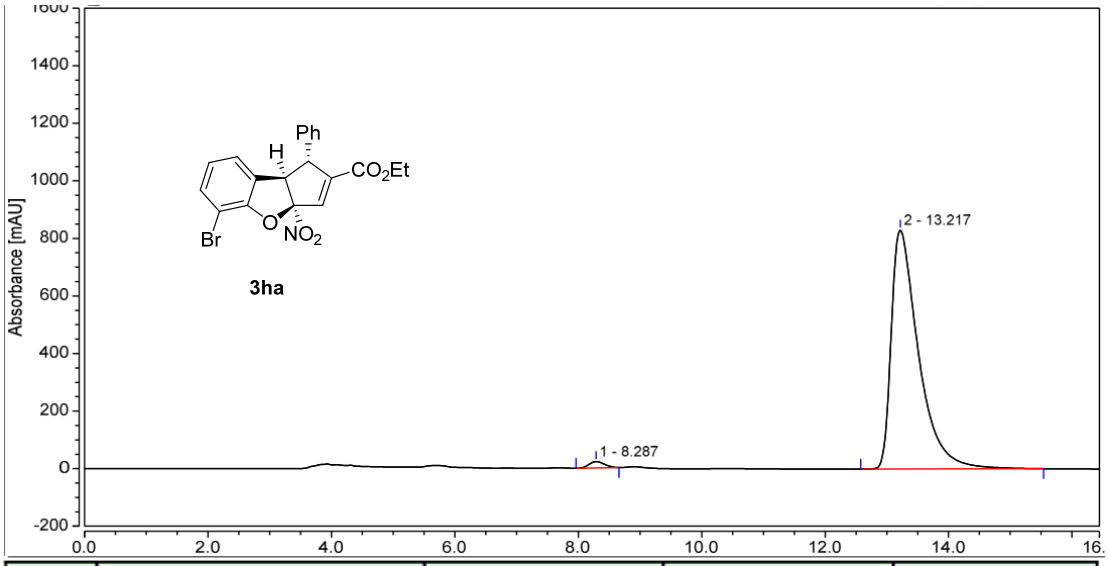
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	12.003	133.112	487.748	49.08
2	13.568	138.125	440.627	50.92
Total:		**271.237**	**928.375**	**100.00**



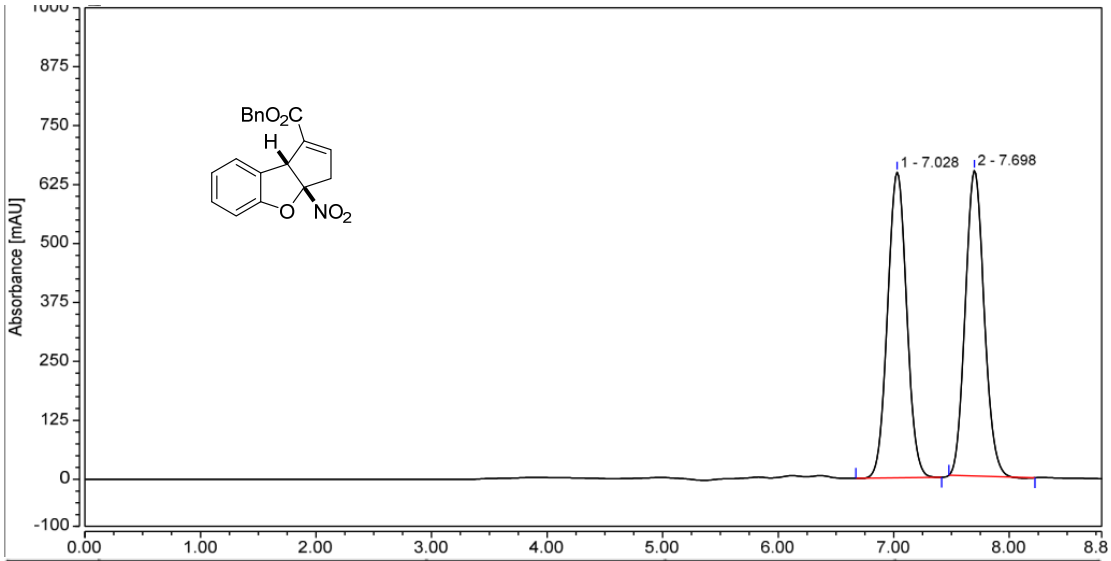
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	12.185	308.594	1050.530	99.96
2	13.883	0.137	0.000	0.04
Total:		**308.732**	**1050.530**	**100.00**



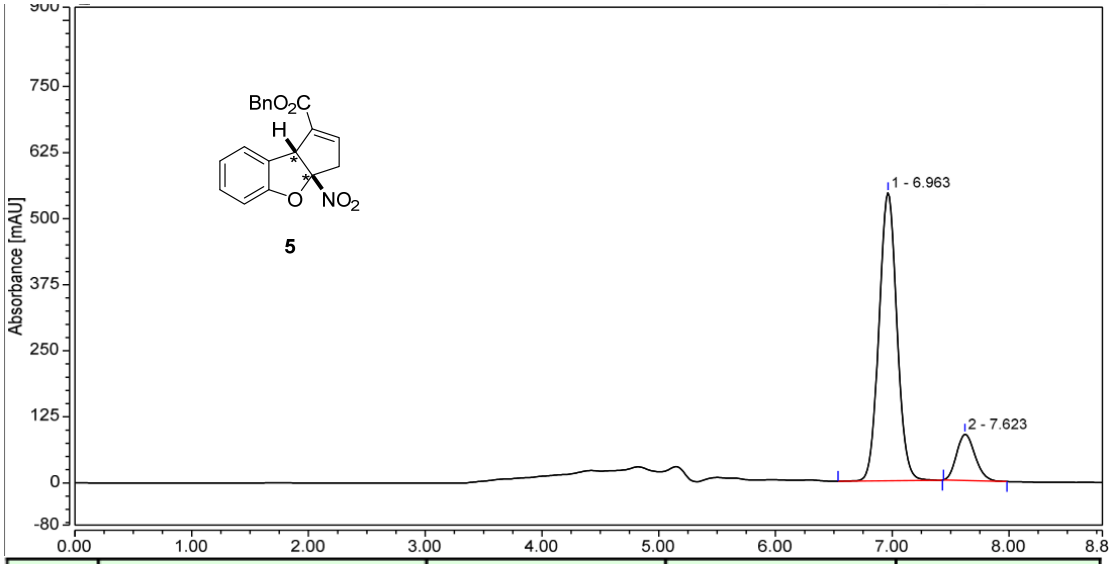
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	8.202	300.003	1078.445	48.51
2	13.317	318.480	635.223	51.49
Total:		**618.483**	**1713.668**	**100.00**



Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	8.287	6.543	22.364	1.52
2	13.217	424.631	830.357	98.48
Total:		**431.174**	**852.721**	**100.00**

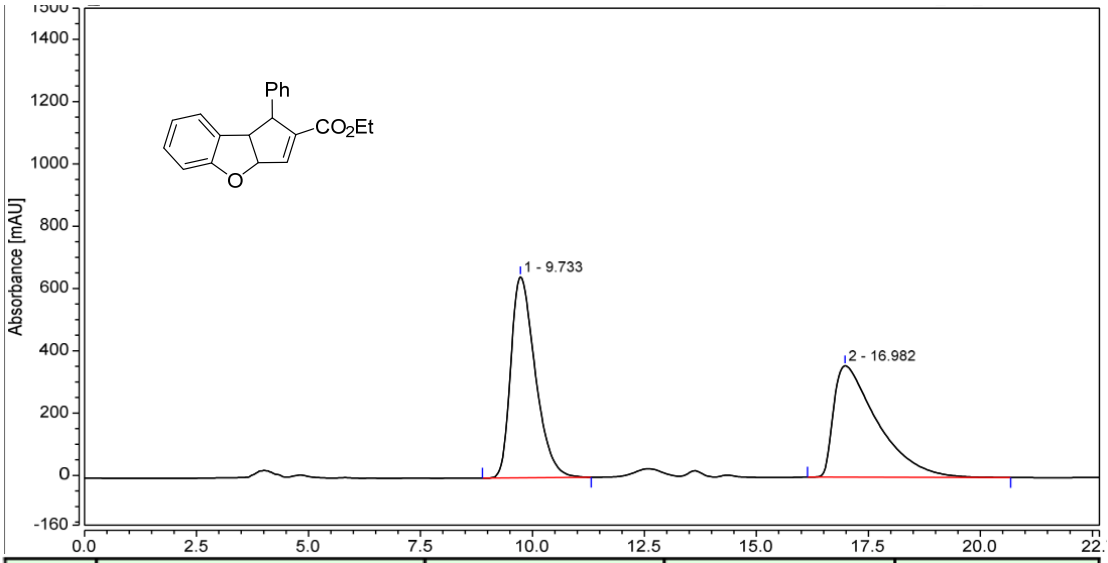


Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	7.028	124.208	648.518	50.19
2	7.698	123.273	648.356	49.81
Total:		**247.481**	**1296.874**	**100.00**

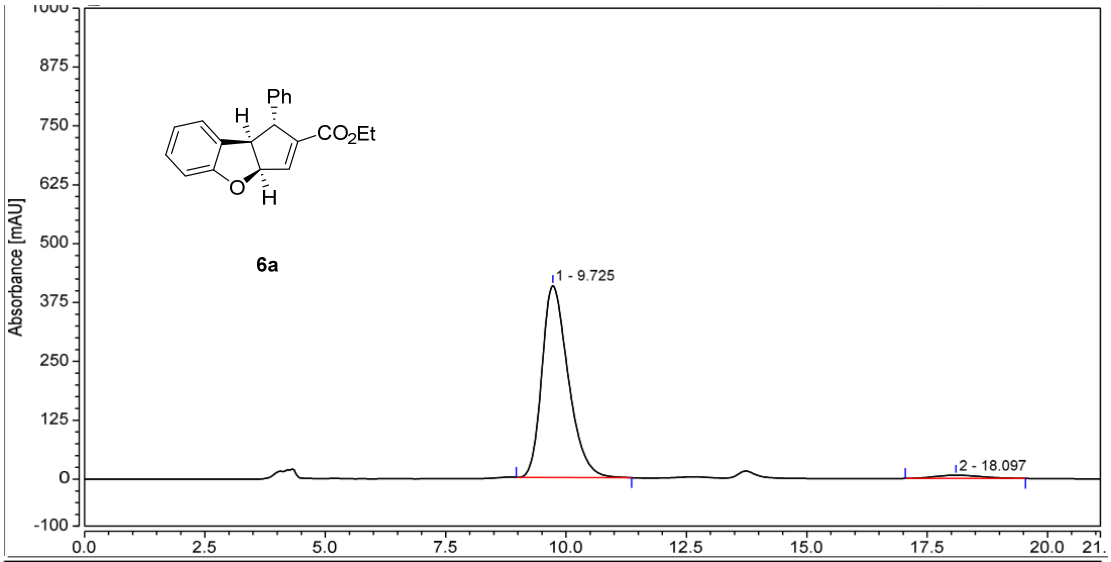


5

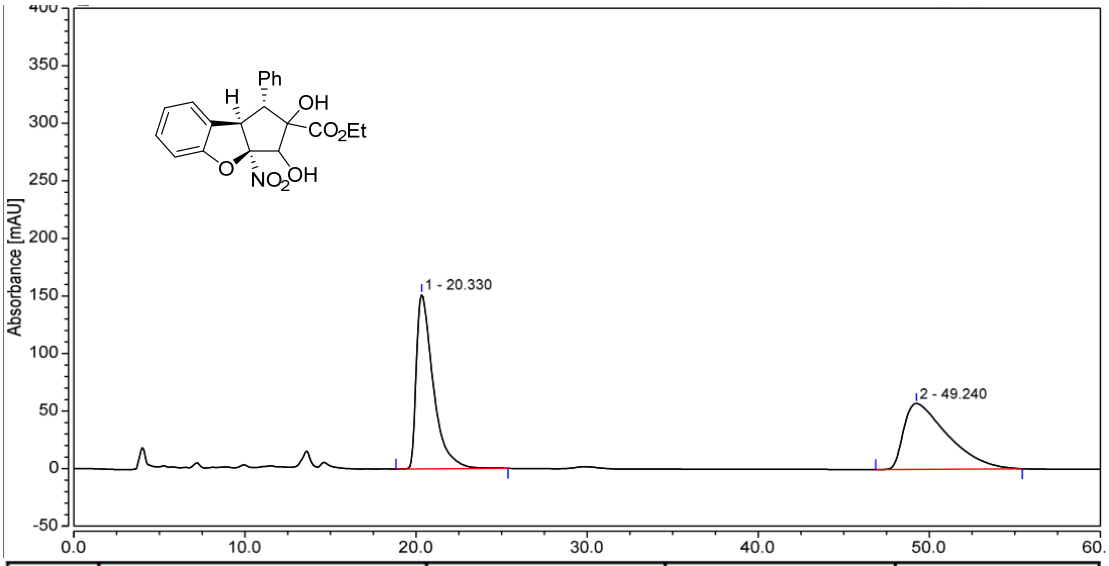
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	6.963	96.925	545.095	85.81
2	7.623	16.023	87.780	14.19
Total:		**112.949**	**632.874**	**100.00**



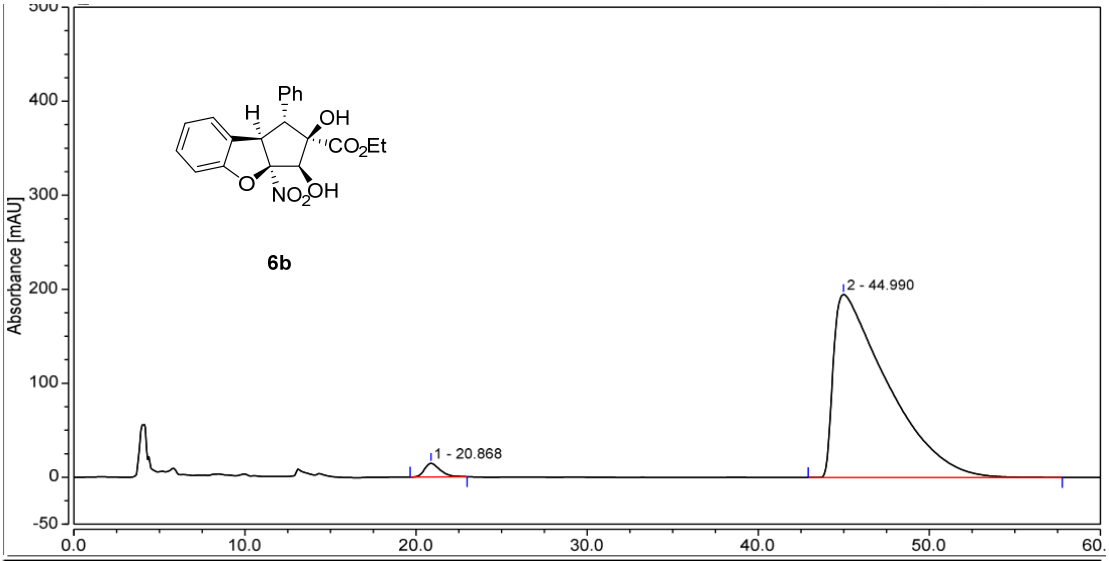
Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	9.733	409.042	645.826	50.17
2	16.982	406.224	357.429	49.83
Total:		**815.266**	**1003.255**	**100.00**



Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	9.725	258.282	407.366	97.02
2	18.097	7.936	7.008	2.98
Total:		**266.218**	**414.374**	**100.00**



Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	20.330	173.147	151.459	50.51
2	49.240	169.678	57.211	49.49
Total:		**342.824**	**208.670**	**100.00**



6b

Peak	Retention Time min	Area mAU*min	Height mAU	Area %
1	20.868	15.265	14.368	2.09
2	44.990	716.186	194.638	97.91
Total:		**731.451**	**209.006**	**100.00**