Organocatalytic Asymmetric Michael/Acyl Transfer Reaction between α-Nitroketones and 4-Arylidene-pyrrolidine-2,3-diones

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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, 500MHz and 600 MHz spectrometer. ^{13}C NMR spectra were recorded on 100 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 (chloroform δ 7.260), carbon (chloroform δ 77.23). 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 IA, IF, ID and AD-H Column. For visualizing the products UV light and I_2 were used. Silica gel (60-120 mesh size) was used for the column chromatography. Reactions were monitored by TLC on silica gel 60 F254 (0.25 mm).

2. General procedure for the synthesis of *γ*-hydroxyenones:[1]

γ-hydroxyenones was prepared according to reported procedures.

3. General procedure for the synthesis of *α*-nitro ketone:[1]

α-nitro ketone was prepared according to reported procedures.

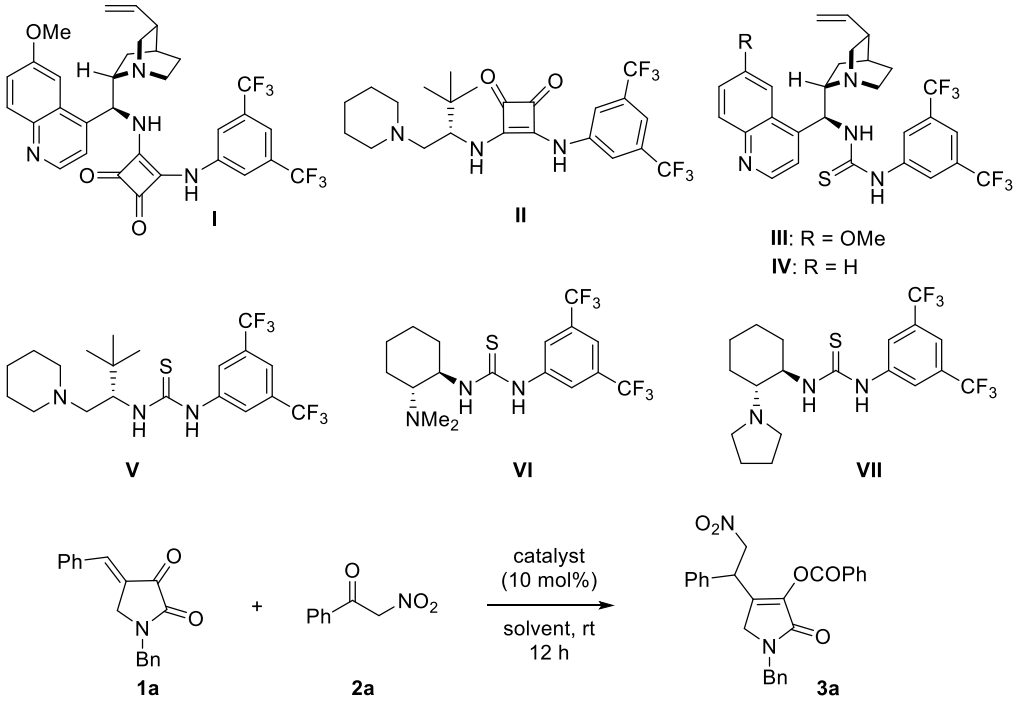
4. General procedure for the synthesis of catalyst VII:

The catalyst (**VII**) was prepared according to reported procedures.[2]

5. General procedure for the synthesis of compound 3:

In an oven dried round bottom flask, **1a** (27.7 mg, 0.1 mmol), **2a** (16.5 mg, 0.1 mmol) and 10 mol% of catalyst (**VII**) were taken. 0.6 mL 1,2-DCE of was added to the reaction mixture and stirred at room temperature for 12h. Completion of reaction was checked by TLC. After the completion of reaction, solvent was concentrated and reaction mixture was directly purified by column chromatography on silica gel eluting with hexane/ethyl acetate (10-12%) to afford desired product **3a-w**.

6. Catalyst optimization for (R)-1-benzyl-4-(2-nitro-1-phenylethyl)-2-oxo-2,5-dihydro-1H-pyrrol-3-yl benzoate



entry[a]	catalyst	solvent	yield[b]	ee[c]
1	**I**	CH_2Cl_2	70	20
2	**II**	CH_2Cl_2	73	34
3	**III**	CH_2Cl_2	76	55
4	**IV**	CH_2Cl_2	78	52
5	**V**	CH_2Cl_2	80	74
6	**VI**	CH_2Cl_2	75	50
7	**VII**	CH_2Cl_2	80	80
8	**VII**	$PhCF_3$	78	78
9	**VII**	THF	80	80
10	**VII**	$CHCl_3$	80	86
11	**VII**	$(CH_2Cl)_2$	80	90

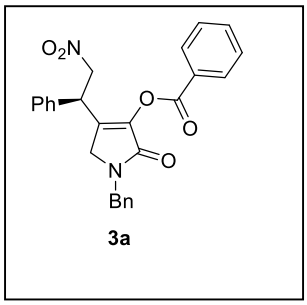
[a]Reactions were carried out with 0.1 mmol of **1a** and 0.1 mmol of **2a** in 0.6 mL solvent at rt for 12 hours; [b]Isolated yield after silica gel column chromatography; [c]Determined by HPLC.

7. References:

1. Mondal, B.; Pan, S. C. *J. Org. Chem.* **2018**, *83*, 5301–5312.
2. Mitchell, J. M.; Finney, N. S. *TetrahedronLett.* **2000**, *41*, 8431.
3. Fofana, m.; Dudognon, Y.; Bertrand, L.; Constantieux, T.; Rodriguez, J.; Ndiaye, I.; Bonne, D.; Bugaut, X. *Eur. J. Org. Chem.* **2020**, 3486–3490.

8. Characterisation of the products:

(*R*)-1-benzyl-4-(2-nitro-1-phenylethyl)-2-oxo-2,5-dihydro-1H-pyrrol-3-yl benzoate (3a)



3a

Yellow sticky, 80% (35mg) yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.21 – 8.15 (m, 2H), 7.70 – 7.64 (m, 1H), 7.53 (t, J = 7.8 Hz, 2H), 7.37 – 7.27 (m, 6H), 7.22 (ddd, J = 7.8, 3.7, 1.6 Hz, 4H), 4.99 (dd, J = 13.5, 8.0 Hz, 1H), 4.78 (dd, J = 13.5, 8.0 Hz, 1H), 4.66 (d, J = 15.1 Hz, 1H), 4.60 (t, J = 7.9 Hz, 1H), 4.52 (d, J = 15.1 Hz, 1H), 3.70 (s, 2H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.44, 163.89, 140.87, 136.49, 136.16, 135.91, 134.56, 130.90, 129.78, 129.12, 128.97, 128.88, 128.26, 128.07, 127.99, 127.86, 77.00, 48.96, 46.99, 42.76.

ESI HRMS: calcd. For $C_{26}H_{22}N_2O_5$ $[M+H]^+$ 443.1601, found 443.1601.

HPLC Analysis: ee = 90%, IF Column, *n*-Hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 220 nm (t_{major}= 20.9 min, t_{minor} = 23.3 min).

From literature study, the optical rotation of the compound (S) **3a** is $[\alpha]_D^{20}$ = 30.69 (c 1.03, $CHCl_3$, 25.1 °C).[3]

This sample was measured on an Autopol I, Serial #35386
Manufactured by Rudolph Research Analytical, Hackettstown, NJ, USA.

Measurement Date : Friday, 12-MAR-2021

Set Temperature : OFF

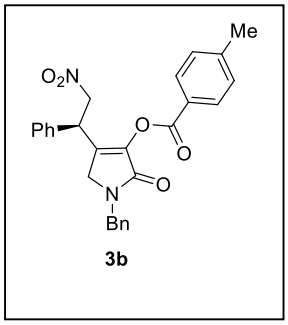
Time Delay : Disabled

n	Average	Std.Dev.	% RSD	Maximum	Minimum
5	-35.00	3.70	-10.57	-31.67	-41.11

S.No	Sample ID	Time	Result	Scale	OR °Arc	WLG.nm	Lg.mm	Temp.
1	mm acyl1	02:30 PM	-41.11	SR	-0.074	589	100.00	27.5
2	mm acyl1	02:30 PM	-33.89	SR	-0.061	589	100.00	27.5
3	mm acyl1	02:30 PM	-32.78	SR	-0.059	589	100.00	27.5
4	mm acyl1	02:30 PM	-31.67	SR	-0.057	589	100.00	27.5
5	mm acyl1	02:31 PM	-35.56	SR	-0.064	589	100.00	27.5

$[\alpha]_D^{20}$ = -35.00 (c 1.03, $CHCl_3$, 27.5 °C)

(*R*)-1-benzyl-4-(2-nitro-1-phenylethyl)-2-oxo-2,5-dihydro-1H-pyrrol-3-yl 4-methylbenzoate(3b). light orange sticky, 80% (36mg) yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.07 (d, J = 8.2 Hz, 2H), 7.41 – 7.26 (m, 8H), 7.26 – 7.15 (m, 4H), 4.98 (dd, J = 13.5, 7.9 Hz, 1H), 4.77 (dd, J = 13.5, 8.0 Hz, 1H), 4.67 (d, J = 15.1 Hz, 1H), 4.57 (t, J = 8.0 Hz, 1H), 4.51 (d, J = 15.1 Hz, 1H), 3.69 (d, J = 3.0 Hz, 2H), 2.46 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.51, 163.95, 145.62, 140.87, 136.51, 136.00, 135.95, 130.98, 129.78, 129.70, 129.11, 128.88, 128.26, 128.06, 127.88, 125.16, 76.91, 48.96, 46.95, 42.81, 22.08.

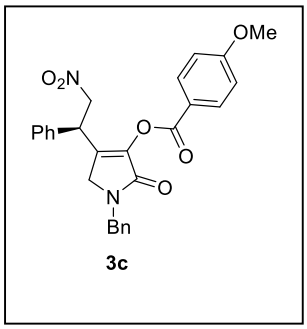


3b

ESI HRMS: calcd. For $C_{27}H_{24}N_2O_5$ $[M+H]^+$ 457.1758, found 457.1758.

HPLC Analysis: ee = 88%, IF Column, *n*-Hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 220 nm (t_{major}= 24.6 min, t_{minor} = 26.5 min).

(*R*)-1-benzyl-4-(2-nitro-1-phenylethyl)-2-oxo-2,5-dihydro-1H-pyrrol-3-yl 4-methoxybenzoate (3c).



3c

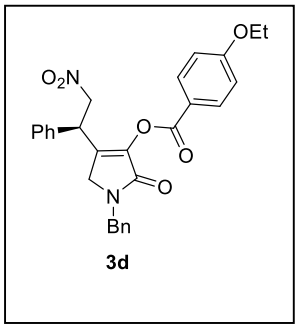
Colourless sticky solid, 82% (38mg) yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.13 (d, J = 8.9 Hz, 2H), 7.42 – 7.27 (m, 6H), 7.22 (dt, J = 10.5, 4.1 Hz, 4H), 7.04 – 6.96 (m, 2H), 4.99 (dd, J = 13.5, 7.9 Hz, 1H), 4.77 (dd, J = 13.5, 8.0 Hz, 1H), 4.67 (d, J = 15.0 Hz, 1H), 4.57 (t, J = 8.0 Hz, 1H), 4.50 (d, J = 15.1 Hz, 1H), 3.91 (s, 3H), 3.68 (d, J = 3.1 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.74, 164.61, 163.59, 140.88, 136.51, 135.97, 135.95, 133.15, 129.75, 129.09, 128.85, 128.25, 128.04, 127.89, 120.14, 114.28, 76.91, 55.79, 48.95, 46.93, 42.80.

ESI HRMS: calcd. For $C_{27}H_{24}N_2O_6$ $[M+H]^+$ 473.1707, found 473.1707.

HPLC Analysis: ee = 80%, Chiralpak IA Column, *n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 43.5 min, t_{minor} = 47.4 min).

(*R*)-1-benzyl-4-(2-nitro-1-phenylethyl)-2-oxo-2,5-dihydro-1H-pyrrol-3-yl 4-ethoxybenzoate (3d)

Pale yellow semi solid, 78% (38mg) yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.12 (d, J = 8.9 Hz, 2H), 7.38 – 7.26 (m, 6H), 7.25 – 7.18 (m, 4H), 6.98 (d, J = 8.9 Hz, 2H), 4.96 (s, 1H), 4.78 (s, 1H), 4.65 (s, 1H), 4.57 (s, 1H), 4.52 (s, 1H), 4.13 (d, J = 7.0 Hz, 2H), 3.68 (d, J = 3.4 Hz, 2H), 1.46 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.64, 164.18, 163.64, 140.90, 136.52, 135.99, 135.93, 133.15, 129.76, 129.09, 128.85, 128.25, 128.04, 127.90, 119.88, 114.70, 76.91, 64.11, 48.95, 46.94, 42.82, 14.85.

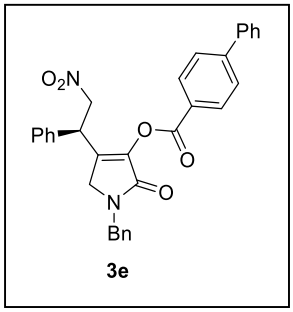


3d

ESI HRMS: calcd. For $C_{28}H_{26}N_2O_6$ $[M+H]^+$ 487.1864, found 487.1863.

HPLC Analysis: ee = 80%, Chiralpak IA Column, *n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 38.6 min, t_{minor} = 44.5 min).

(*R*)-1-benzyl-4-(2-nitro-1-phenylethyl)-2-oxo-2,5-dihydro-1H-pyrrol-3-yl [1,1'-biphenyl]-4-carboxylate (3e)



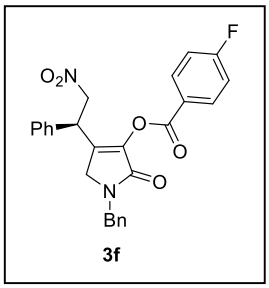
3e

Light yellow sticky solid, 82% (42mg) yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.28 – 8.23 (m, 2H), 7.78 – 7.73 (m, 2H), 7.67 (dd, J = 5.2, 3.3 Hz, 2H), 7.54 – 7.47 (m, 2H), 7.46 – 7.41 (m, 1H), 7.37 – 7.28 (m, 6H), 7.23 (dt, J = 10.8, 4.1 Hz, 4H), 5.01 (dd, J = 13.5, 8.0 Hz, 1H), 4.79 (dd, J = 13.5, 7.9 Hz, 1H), 4.68 (d, J = 15.1 Hz, 1H), 4.61 (t, J = 8.0 Hz, 1H), 4.53 (d, J = 15.1 Hz, 1H), 3.71 (d, J = 2.2 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.51, 163.82, 147.36, 140.88, 139.94, 136.48, 136.11, 135.90, 131.46, 129.81, 129.23, 129.13, 128.92, 128.68, 128.27, 128.09, 127.89, 127.64, 127.61, 126.58, 77.43, 48.98, 46.98, 42.80.

ESI HRMS: calcd. For $C_{32}H_{26}N_2O_5$ $[M+H]^+$ 519.1914, found 519.1914.

HPLC Analysis: ee = 82%, Chiralpak IA Column, *n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 45.7 min, t_{minor} = 51.5 min).

(*R*)-1-benzyl-4-(2-nitro-1-phenylethyl)-2-oxo-2,5-dihydro-1H-pyrrol-3-yl 4-fluorobenzoate (3f)



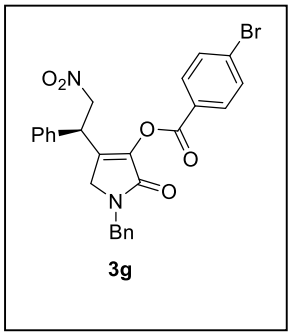
3f

Yellow semi solid, 79% (36mg) yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.26 – 8.12 (m, 2H), 7.38 – 7.27 (m, 6H), 7.26 – 7.14 (m, 6H), 4.97 (dd, J = 13.5, 8.3 Hz, 1H), 4.76 (dd, J = 13.5, 7.6 Hz, 1H), 4.67 (d, J = 15.0 Hz, 1H), 4.61 (d, J = 8.0 Hz, 1H), 4.52 (d, J = 15.1 Hz, 1H), 3.70 (s, 2H).**^{13}C NMR (100 MHz, $CDCl_3$)** 13C NMR (101 MHz, CDCl3) δ 168.12, 165.57, 164.34, 162.92, 140.73, 136.41, 136.20, 135.77, 133.69, 133.59, 129.82, 129.14, 128.94, 128.25, 128.11, 127.84, 124.22, 124.19, 116.40, 116.18, 77.43, 48.94, 46.98, 42.70.

ESI HRMS: calcd. For $C_{26}H_{21}FN_2O_5$ $[M+H]^+$ 461.1507, found 461.1506.

HPLC Analysis: ee = 90%, Chiralpak IF Column, *n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 39.3 min, t_{minor} = 42.7 min).

(*R*)-1-benzyl-4-(2-nitro-1-phenylethyl)-2-oxo-2,5-dihydro-1H-pyrrol-3-yl 4-bromobenzoate (3g)



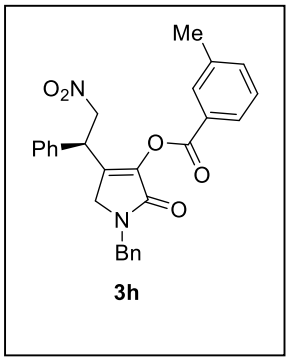
3g

Light yellow sticky solid, 78% (40mg) yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.03 (d, J = 8.6 Hz, 2H), 7.68 (d, J = 8.6 Hz, 2H), 7.38 – 7.26 (m, 6H), 7.21 (d, J = 6.9 Hz, 4H), 4.96 (dd, J = 13.5, 8.4 Hz, 1H), 4.75 (dd, J = 13.5, 7.5 Hz, 1H), 4.66 (d, J = 15.0 Hz, 1H), 4.60 (t, J = 8.0 Hz, 1H), 4.52 (d, J = 15.1 Hz, 1H), 3.70 (s, 2H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.26, 163.23, 140.72, 136.41, 136.27, 135.75, 132.40, 132.30, 130.03, 129.83, 129.15, 128.96, 128.26, 128.12, 127.83, 126.88, 77.43, 48.95, 47.01, 42.69.

ESI HRMS: calcd. For $C_{26}H_{21}BrN_2O_5$ $[M+H]^+$ 521.0707, found 521.0708.

HPLC Analysis: ee = 90%, Chiralpak IA Column, *n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 43.6 min, t_{minor} = 47.9 min).

(*R*)-1-benzyl-4-(2-nitro-1-phenylethyl)-2-oxo-2,5-dihydro-1H-pyrrol-3-yl 3-methylbenzoate (3h)



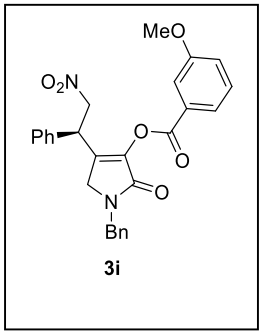
3h

Yellow sticky, 70% (32mg) yield. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.01 – 7.96 (m, 2H), 7.48 (d, J = 7.4 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.36 – 7.27 (m, 6H), 7.24 – 7.19 (m, 4H), 4.99 (dd, J = 13.5, 7.9 Hz, 1H), 4.78 (dd, J = 13.5, 8.1 Hz, 1H), 4.67 (d, J = 15.1 Hz, 1H), 4.58 (t, J = 8.0 Hz, 1H), 4.51 (d, J = 15.1 Hz, 1H), 3.70 (d, J = 5.5 Hz, 2H), 2.45 (s, 3H).**^{13}C NMR (150 MHz, $CDCl_3$)** δ 164.45, 164.10, 140.79, 138.84, 136.46, 136.07, 135.87, 135.38, 131.41, 129.76, 129.09, 128.87, 128.85, 128.24, 128.05, 127.86, 127.78,76.98, 48.94, 46.93, 42.76, 21.49.

ESI HRMS: calcd. For $C_{27}H_{24}N_2O_5$ $[M+H]^+$ 457.1758, found 457.1757.

HPLC Analysis: ee = 72%, Chiralpak IF Column, *n*-Hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 21.0 min, t_{minor} = 23.3 min).

(*R*)-1-benzyl-4-(2-nitro-1-phenylethyl)-2-oxo-2,5-dihydro-1H-pyrrol-3-yl 3-methoxybenzoate (3i)



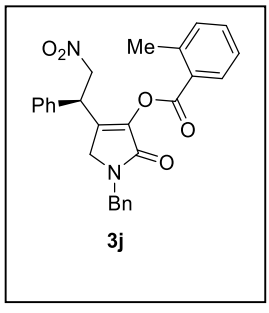
3i

Orange semi solid 72% (34mg) yield. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.79 (dt, J = 7.6, 1.2 Hz, 1H), 7.68 (dd, J = 2.7, 1.6 Hz, 1H), 7.43 (t, J = 8.0 Hz, 1H), 7.36 – 7.27 (m, 6H), 7.22 (ddd, J = 6.8, 4.6, 2.5 Hz, 5H), 5.00 (dd, J = 13.6, 8.3 Hz, 1H), 4.76 (dd, J = 13.6, 7.7 Hz, 1H), 4.68 (d, J = 15.1 Hz, 1H), 4.58 (t, J = 8.0 Hz, 1H), 4.51 (d, J = 15.1 Hz, 1H), 3.89 (s, 3H), 3.70 (d, J = 4.8 Hz, 2H).**^{13}C NMR (150 MHz, $CDCl_3$)** δ 164.37, 163.79, 159.93, 140.79, 136.43, 136.07, 135.78, 129.98, 129.79, 129.10, 129.06, 128.90, 128.23, 128.06, 127.85, 123.36, 121.52, 114.82, 76.96, 55.76, 48.96, 46.93, 42.76.

ESI HRMS: calcd. For $C_{27}H_{24}N_2O_6$ $[M+H]^+$ 473.1707, found 473.1714.

HPLC Analysis: ee = 66%, Chiralpak IA Column, *n*-Hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 22.4 min, t_{minor} = 18.5 min).

(*R*)-1-benzyl-4-(2-nitro-1-phenylethyl)-2-oxo-2,5-dihydro-1H-pyrrol-3-yl 2-methylbenzoate (3j)



3j

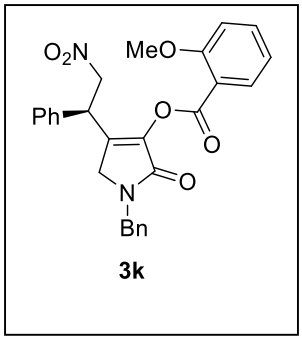
Pale yellow semi solid, 65% (29mg) yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.14 (dd, J = 8.2, 1.5 Hz, 1H), 7.51 (td, J = 7.5, 1.5 Hz, 1H), 7.41 – 7.26 (m, 8H), 7.22 (ddd, J = 7.7, 4.0, 1.6 Hz, 4H), 5.00 (dd, J = 13.4, 7.8 Hz, 1H), 4.79 (dd, J = 13.4, 8.1 Hz, 1H), 4.67 (d, J = 15.1 Hz, 1H), 4.59 (t, J = 7.9 Hz, 1H), 4.53 (d, J = 15.0 Hz, 1H), 3.70 (d, J = 2.0 Hz, 2H),

2.70 (s, 3H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.57, 164.15, 142.43, 140.91, 136.46, 136.00, 135.96, 133.71, 132.25, 131.94, 129.77, 129.12, 128.88, 128.27, 128.08, 127.85, 126.94, 126.31,77.43, 48.97, 46.98, 42.71, 22.17.

ESI HRMS: calcd. For $C_{27}H_{24}N_2O_5$ $[M+H]^+$ 457.1758, found 457.1757.

HPLC Analysis: ee = 68%, Chiralpak ADH Column, *n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 15.9 min, t_{minor} = 14.9 min).

(*R*)-1-benzyl-4-(2-nitro-1-phenylethyl)-2-oxo-2,5-dihydro-1H-pyrrol-3-yl 2-methoxybenzoate (3k)



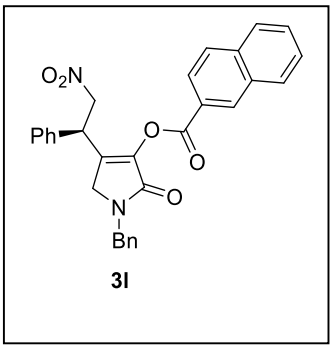
3k

Yellow sticky solid, 68% (32mg) yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.04 (dd, J = 7.8, 1.8 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.35 – 7.27 (m, 8H), 7.23 – 7.19 (m, 2H), 7.09 – 7.03 (m, 2H), 5.10 (dd, J = 13.5, 6.9 Hz, 1H), 4.94 (dd, J = 13.6, 9.0 Hz, 1H), 4.68 (d, J = 15.0 Hz, 1H), 4.56 – 4.47 (m, 2H), 3.96 (s, 3H), 3.68 (d, J = 10.5 Hz, 2H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.56, 163.34, 160.16, 136.57, 136.31, 135.98, 135.33, 133.27, 129.72, 129.09, 128.83, 128.24, 128.03, 128.00, 120.68, 117.58, 112.26, 77.43, 56.21, 49.10, 46.91, 42.98.

ESI HRMS: calcd. For $C_{27}H_{24}N_2O_6$ $[M+H]^+$ 473.1707, found 473.1711.

HPLC Analysis: ee = 70%, Chiralpak ID Column, *n*-Hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 59.0 min, t_{minor} = 72.9 min).

(*R*)-1-benzyl-4-(2-nitro-1-phenylethyl)-2-oxo-2,5-dihydro-1H-pyrrol-3-yl 2-naphthoate (3l)



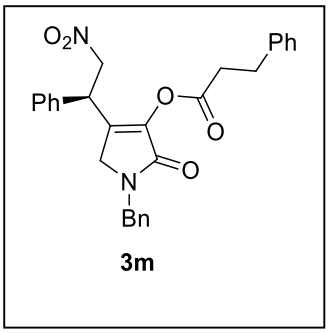
3l

White sticky solid, 75% (37mg) yield. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.78 (s, 1H), 8.15 (dd, J = 8.6, 1.8 Hz, 1H), 8.02 (d, J = 8.1 Hz, 1H), 7.97 (d, J = 8.6 Hz, 1H), 7.93 (d, J = 8.1 Hz, 1H), 7.66 (ddd, J = 8.1, 6.8, 1.3 Hz, 1H), 7.60 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 7.34 (td, J = 7.8, 7.3, 1.7 Hz, 4H), 7.30 (dd, J = 7.4, 2.0 Hz, 2H), 7.24 (ddd, J = 11.1, 6.9, 1.8 Hz, 4H), 5.03 (dd, J = 13.6, 8.1 Hz, 1H), 4.79 (dd, J = 13.6, 7.9 Hz, 1H), 4.69 (d, J = 15.1 Hz, 1H), 4.63 (t, J = 8.0 Hz, 1H), 4.53 (d, J = 15.1 Hz, 1H), 3.73 (d, J = 4.2 Hz, 2H).**^{13}C NMR (150 MHz, $CDCl_3$)** δ 164.49, 164.11, 140.85, 136.45, 136.33, 136.20, 135.84, 133.11, 132.60, 129.90, 129.79, 129.27, 129.12, 128.89, 128.83, 128.26, 128.08, 127.88, 127.21, 125.70, 125.03, 76.98, 48.97, 46.95, 42.77.

ESI HRMS: calcd. For $C_{30}H_{24}N_2O_5$ $[M+H]^+$ 493.1758, found 493.1767.

HPLC Analysis: ee = 80%, Chiralpak IF Column, *n*-Hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 35.9 min, t_{minor} = 40.3 min).

(*R*)-1-benzyl-4-(2-nitro-1-phenylethyl)-2-oxo-2,5-dihydro-1H-pyrrol-3-yl 3-phenylpropanoate (3m)



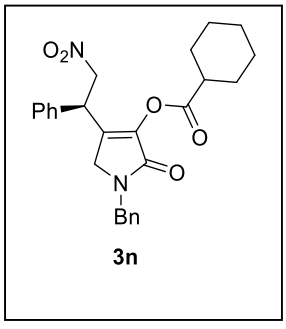
3m

Colourless semi solid, 65% (31mg) yield. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.33 – 7.27 (m, 10H), 7.21 – 7.16 (m, 3H), 7.11 – 7.07 (m, 2H), 4.62 (dtd, J = 21.6, 13.5, 8.0 Hz, 3H), 4.50 – 4.40 (m, 2H), 3.60 (d, J = 8.6 Hz, 2H), 3.09 (t, J = 7.6 Hz, 2H), 3.00 – 2.95 (m, 2H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.14, 164.41, 140.40, 139.97, 136.38, 135.85, 135.82, 129.71, 129.11, 128.89, 128.86, 128.59, 128.20, 128.08, 127.81, 126.81, 77.44, 48.85, 46.91, 42.58, 35.47, 30.79.

ESI HRMS: calcd. For $C_{28}H_{26}N_2O_5$ $[M+H]^+$ 479.1914, found 479.1915.

HPLC Analysis: ee = 72%, Chiralpak IF Column, *n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 37.3 min, t_{minor} = 35.4 min).

(*R*)-1-benzyl-4-(2-nitro-1-phenylethyl)-2-oxo-2,5-dihydro-1H-pyrrol-3-yl cyclohexanecarboxylate (3n)



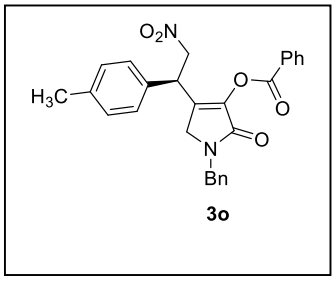
3n

Pale yellow semi solid, 70% (31mg) yield. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.36 – 7.29 (m, 5H), 7.28 – 7.26 (m, 1H), 7.21 – 7.14 (m, 4H), 4.95 – 4.87 (m, 1H), 4.80 – 4.73 (m, 1H), 4.66 – 4.58 (m, 1H), 4.54 – 4.45 (m, 2H), 3.67 – 3.56 (m, 2H), 2.68 – 2.60 (m, 1H), 2.15 – 2.07 (m, 2H), 1.89 – 1.80 (m, 2H), 1.72 – 1.65 (m, 2H), 1.43 – 1.27 (m, 4H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 173.28, 164.47, 140.72, 136.44, 136.00, 135.48, 129.74, 129.08, 128.85, 128.20, 128.03, 127.83, 48.84, 46.88, 42.92, 42.64, 29.05, 25.81, 25.43.

ESI HRMS: calcd. For $C_{26}H_{28}N_2O_5$ $[M+H]^+$ 449.2071, found 449.2072.

HPLC Analysis: ee = 72%, Chiralpak IA Column, *n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 220 nm (t_{major} = 16.7 min, t_{minor} = 15.5 min).

(*R*)-1-benzyl-4-(2-nitro-1-(p-tolyl)ethyl)-2-oxo-2,5-dihydro-1H-pyrrol-3-yl benzoate (3o)



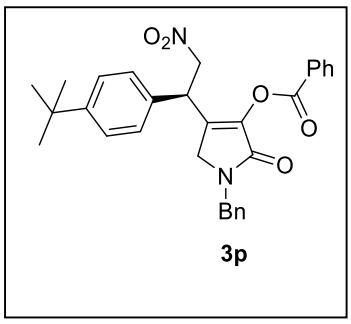
3o

Light yellow semi solid, 83% (38mg) yield. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.17 (dd, J = 8.3, 1.2 Hz, 2H), 7.72 – 7.64 (m, 1H), 7.53 (dd, J = 10.8, 4.8 Hz, 2H), 7.36 – 7.29 (m, 3H), 7.23 – 7.19 (m, 4H), 7.06 – 6.99 (m, 2H), 4.97 (dd, J = 13.4, 7.7 Hz, 1H), 4.77 – 4.65 (m, 2H), 4.59 – 4.49 (m, 2H), 3.69 (d, J = 5.2 Hz, 2H), 1.60 (s, 3H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.30, 163.93, 140.90, 136.38, 135.81, 134.69, 131.66, 131.63, 130.90, 129.69, 129.61, 129.14, 129.01, 128.28, 128.13, 127.80, 116.93, 116.71, 77.02, 48.90, 46.98, 42.09.

ESI HRMS: calcd. For $C_{27}H_{24}N_2O_5$ $[M+H]^+$ 457.1758, found 457.1766.

HPLC Analysis: ee = 72%, Chiralpak IA Column, *n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 24.5 min, t_{minor} = 21.4 min).

(*R*)-1-benzyl-4-(1-(4-(tert-butyl)phenyl)-2-nitroethyl)-2-oxo-2,5-dihydro-1H-pyrrol-3-yl benzoate (3p)



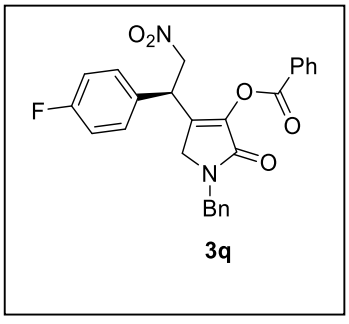
3p

White semi solid, 72% (40mg) yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.21 – 8.15 (m, 2H), 7.71 – 7.62 (m, 1H), 7.53 (t, J = 7.8 Hz, 2H), 7.38 – 7.27 (m, 5H), 7.24 – 7.19 (m, 2H), 7.14 (d, J = 8.3 Hz, 2H), 4.97 (dd, J = 13.5, 8.2 Hz, 1H), 4.75 (dd, J = 13.5, 7.7 Hz, 1H), 4.67 (d, J = 15.1 Hz, 1H), 4.55 (dd, J = 19.1, 11.5 Hz, 2H), 3.73 (s, 2H), 1.27 (s, 10H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.50, 163.86, 151.91, 140.68, 136.54, 136.42, 134.51, 132.67, 130.89, 129.09, 128.94, 128.27, 128.04, 127.99, 127.51, 126.67, 77.07, 49.00, 46.94, 42.28, 31.38.

ESI HRMS: calcd. For $C_{30}H_{30}N_2O_5$ $[M+H]^+$ 499.2227, found 499.2228.

HPLC Analysis: ee = 72%, Chiralpak ADH Column, *n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 10.5 min, t_{minor} = 11.8 min).

(*R*)-1-benzyl-4-(1-(4-fluorophenyl)-2-nitroethyl)-2-oxo-2,5-dihydro-1H-pyrrol-3-yl benzoate (3q)



3q

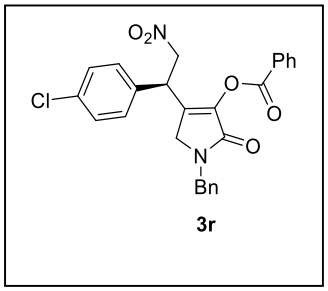
Pale Yellow semi solid, 80% (37mg) yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.21 – 8.14 (m, 2H), 7.71 – 7.65 (m, 1H), 7.54 (t, J = 7.8 Hz, 2H), 7.38 – 7.27 (m, 3H), 7.25 – 7.17 (m, 4H), 7.10 – 6.96 (m, 2H), 4.97 (dd, J = 13.4, 7.6 Hz, 1H), 4.75 (dd, J = 13.4, 8.3 Hz, 1H), 4.68 (d, J = 15.0 Hz, 1H), 4.57 (t, J = 8.0 Hz, 1H), 4.52 (d, J = 15.0 Hz, 1H), 3.75 – 3.63 (m, 2H).**^{13}C NMR (125 MHz,**

$CDCl_3$) δ 164.10, 163.73, 163.67, 161.70, 140.77, 136.21, 135.60, 134.46, 131.51, 131.48, 130.70, 129.49, 129.42, 128.95, 128.81, 128.09, 127.94, 127.68, 116.71, 116.54, 48.71, 46.82, 41.92, 29.71.

ESI HRMS: calcd. For $C_{26}H_{21}FN_2O_5$ $[M+H]^+$ 461.1507, found 461.1513.

HPLC Analysis: ee = 84%, Chiralpak IF Column, *n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 33.3 min, t_{minor} = 42.0 min).

(*R*)-1-benzyl-4-(1-(4-chlorophenyl)-2-nitroethyl)-2-oxo-2,5-dihydro-1H-pyrrol-3-yl benzoate (3r)



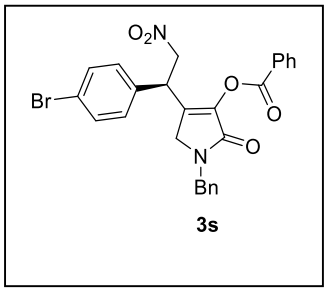
3r

Yellow semi solid, 79% (38mg) yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.16 (dd, J = 8.2, 1.0 Hz, 2H), 7.68 (dd, J = 10.6, 4.3 Hz, 1H), 7.53 (t, J = 7.8 Hz, 2H), 7.37 – 7.28 (m, 5H), 7.25 – 7.14 (m, 4H), 4.96 (dd, J = 13.5, 7.6 Hz, 1H), 4.75 (dd, J = 13.5, 8.3 Hz, 1H), 4.67 (d, J = 15.0 Hz, 1H), 4.60 – 4.49 (m, 2H), 3.69 (d, J = 4.4 Hz, 2H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.26, 163.91, 141.07, 136.35, 135.51, 135.00, 134.71, 134.33, 130.89, 130.00, 129.25, 129.16, 129.02, 128.30, 128.16, 76.79, 48.88, 47.01, 42.15.

ESI HRMS: calcd. For $C_{26}H_{21}ClN_2O_5$ $[M+H]^+$ 477.1212, found 477.1224.

HPLC Analysis: ee = 76%, Chiralpak ADH Column, *n*-Hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 12.7 min, t_{minor} = 14.8 min).

(*R*)-1-benzyl-4-(1-(4-bromophenyl)-2-nitroethyl)-2-oxo-2,5-dihydro-1H-pyrrol-3-yl benzoate (3s)



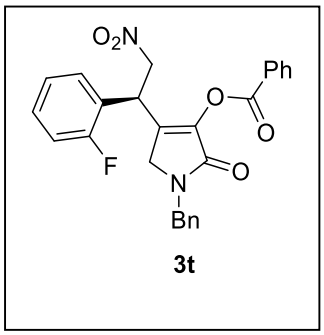
3s

Yellow semi solid, 82% (76mg) yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.20 – 8.13 (m, 2H), 7.68 (t, J = 7.5 Hz, 1H), 7.54 (t, J = 7.8 Hz, 2H), 7.49 – 7.42 (m, 2H), 7.39 – 7.28 (m, 3H), 7.25 – 7.19 (m, 2H), 7.11 (d, J = 8.4 Hz, 2H), 4.96 (dd, J = 13.5, 7.6 Hz, 1H), 4.75 (dd, J = 13.5, 8.3 Hz, 1H), 4.67 (d, J = 15.0 Hz, 1H), 4.59 – 4.49 (m, 2H), 3.69 (d, J = 4.4 Hz, 2H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.24, 163.90, 141.10, 136.34, 135.40, 134.84, 134.72, 132.97, 130.90, 129.55, 129.17, 129.03, 128.30, 128.17, 127.75, 123.10, 76.71, 48.88, 47.00, 42.22.

ESI HRMS: calcd. For $C_{26}H_{21}BrN_2O_5$ $[M+H]^+$ 521.0707, found 521.0726.

HPLC Analysis: ee = 76%, Chiralpak ADH Column, *n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 25.6 min, t_{minor} = 21.3 min).

(*S*)-1-benzyl-4-(1-(2-fluorophenyl)-2-nitroethyl)-2-oxo-2,5-dihydro-1H-pyrrol-3-yl benzoate (3t)



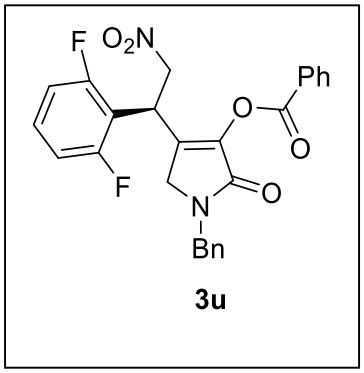
3t

Yellow semi solid, 79% (36mg) yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.15 (dd, J = 8.3, 1.1 Hz, 2H), 7.70 – 7.63 (m, 1H), 7.52 (t, J = 7.8 Hz, 2H), 7.38 – 7.27 (m, 4H), 7.26 – 7.19 (m, 3H), 7.12 – 7.03 (m, 2H), 5.01 (dd, J = 11.4, 6.1 Hz, 1H), 4.91 – 4.80 (m, 2H), 4.67 (d, J = 15.0 Hz, 1H), 4.56 (d, J = 15.0 Hz, 1H), 3.78 (s, 2H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.30, 163.63, 161.82, 159.36, 141.37, 136.44, 134.97, 134.54, 130.87, 130.80, 130.72, 129.62, 129.58, 129.14, 128.93, 128.27, 128.10, 127.90, 125.45, 125.41, 122.78, 122.64, 116.71, 116.49, 75.41, 75.38, 48.95, 46.99, 36.80, 36.77.

ESI HRMS: calcd. For $C_{26}H_{21}FN_2O_5$ $[M+H]^+$ 461.1507, found 461.1516.

HPLC Analysis: ee = 86%, Chiralpak ID Column, *n*-Hexane/*i*-PrOH = 75/25, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 56.1 min, t_{minor} = 68.1 min).

(*S*)-1-benzyl-4-(1-(2,6-difluorophenyl)-2-nitroethyl)-2-oxo-2,5-dihydro-1H-pyrrol-3-yl benzoate (3u)



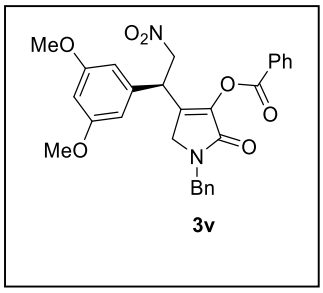
3u

White sticky solid, 78% (37mg) yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.18 – 8.09 (m, 2H), 7.70 – 7.64 (m, 1H), 7.52 (t, J = 7.8 Hz, 2H), 7.39 – 7.28 (m, 3H), 7.26 – 7.18 (m, 3H), 6.88 – 6.78 (m, 2H), 5.02 – 4.93 (m, 1H), 4.82 (dq, J = 15.5, 7.7 Hz, 2H), 4.67 (d, J = 15.0 Hz, 1H), 4.56 (d, J = 15.0 Hz, 1H), 3.77 (d, J = 4.3 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.96, 163.45, 141.32, 136.16, 134.43, 134.36, 130.65, 130.33, 130.27, 128.96, 128.77, 128.10, 127.95, 127.59, 118.51, 112.65, 112.44, 105.22, 104.96, 104.71, 75.12, 48.69, 46.81, 36.19, 36.17, 29.70.

ESI HRMS: calcd. For $C_{26}H_{20}F_2N_2O_5$ $[M+H]^+$ 479.1413, found 479.1424.

HPLC Analysis: ee = 72%, Chiralpak ADH Column, *n*-Hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 11.4 min, t_{minor} = 10.1 min).

(*R*)-1-benzyl-4-(1-(3,5-dimethoxyphenyl)-2-nitroethyl)-2-oxo-2,5-dihydro-1H-pyrrol-3-yl benzoate (3v) light yellow semi solid, 80% (40mg) yield. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.20 – 8.15 (m, 2H), 7.68 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.8 Hz, 2H), 7.33 (t, J = 7.2 Hz, 2H), 7.29 (dd, J = 8.5, 6.0 Hz, 1H), 7.22 (d, J = 7.0 Hz, 2H), 6.80 – 6.72 (m, 3H), 4.98 (dd, J = 13.5, 8.1 Hz, 1H), 4.73 (dd, J = 13.5, 7.9 Hz, 1H), 4.68 (d, J = 15.1 Hz, 1H), 4.55 – 4.48 (m, 2H), 3.83 (d, J = 3.0 Hz, 6H), 3.71 (d, J = 4.6 Hz, 2H).**^{13}C NMR (150 MHz, $CDCl_3$)** δ 164.48, 164.07, 149.94, 149.37, 140.63, 136.54, 136.48, 134.63, 130.85, 129.11, 129.00, 128.22, 128.08, 127.90, 119.98, 111.81, 110.71, 77.26, 56.20, 56.11, 49.05, 46.94, 42.55.

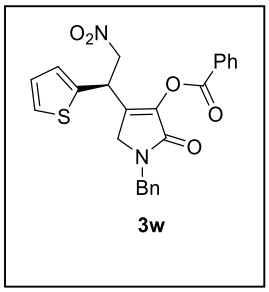


3v

ESI HRMS: calcd. For $C_{28}H_{26}N_2O_7$ $[M+H]^+$ 503.1813, found 503.1814.

HPLC Analysis: ee = 72%, Chiralpak ADH Column, *n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 37.1 min, t_{minor} = 32.4 min).

(*R*)-1-benzyl-4-(2-nitro-1-(thiophen-2-yl)ethyl)-2-oxo-2,5-dihydro-1H-pyrrol-3-yl benzoate (3w) light brown semi solid, 81% (36mg) yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.24 – 8.14 (m, 2H), 7.67 (dd, J = 10.6, 4.3 Hz, 1H), 7.53 (t, J = 7.8 Hz, 2H), 7.38 – 7.29 (m, 3H), 7.27 – 7.22 (m, 3H), 6.94 (d, J = 3.4 Hz, 2H), 4.98 – 4.91 (m, 2H), 4.85 – 4.79 (m, 1H), 4.63 (d, J = 3.4 Hz, 2H), 3.81 (d, J = 5.0 Hz, 2H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.28, 163.57, 140.87, 137.77, 136.42, 135.52, 134.58, 130.92, 130.38, 129.15, 128.97, 128.66, 128.25, 128.11, 127.90, 127.74, 126.70, 126.31, 77.32, 48.63, 47.00, 37.39.

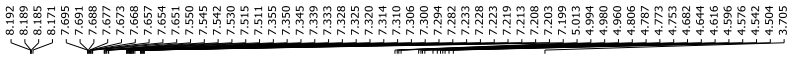


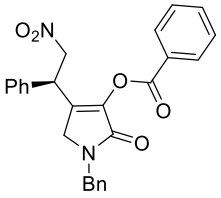
3w

ESI HRMS: calcd. For $C_{24}H_{20}N_2O_5S$ $[M+H]^+$ 449.1166, found 449.1167.

HPLC Analysis: ee = 82%, Chiralpak IA Column, *n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 34.1 min, t_{minor} = 36.9 min).

9. NMR spectra of the products:





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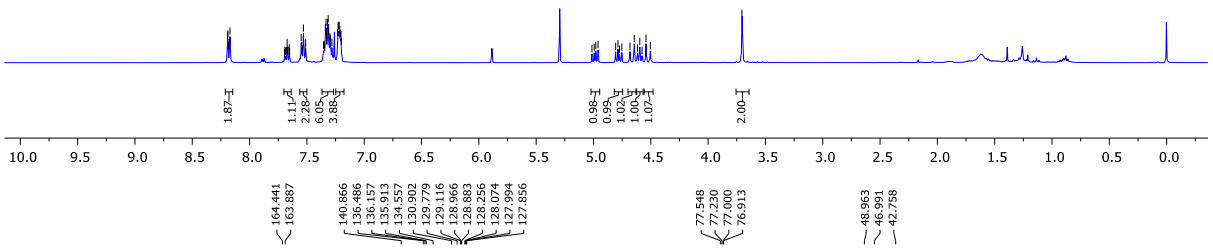

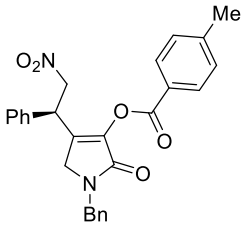

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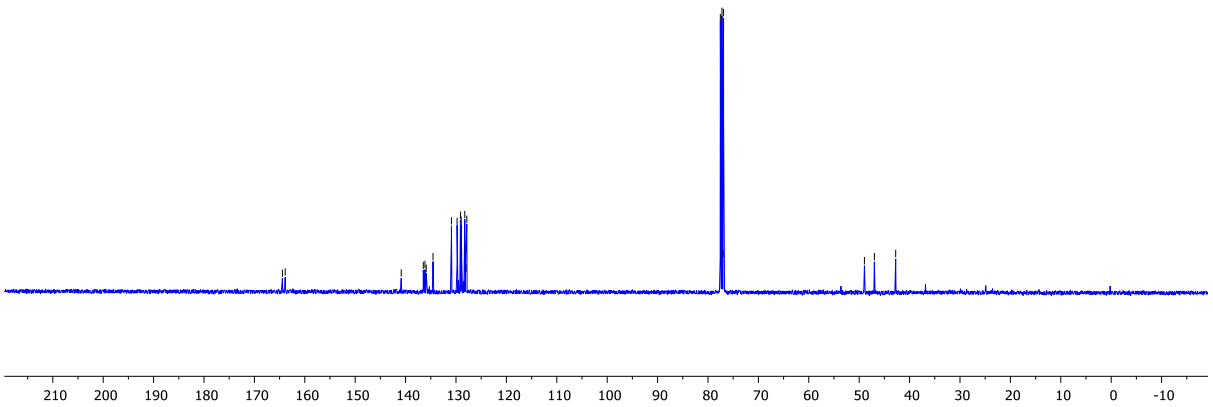


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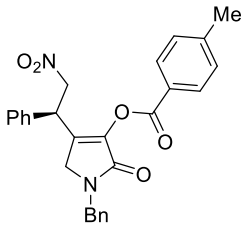
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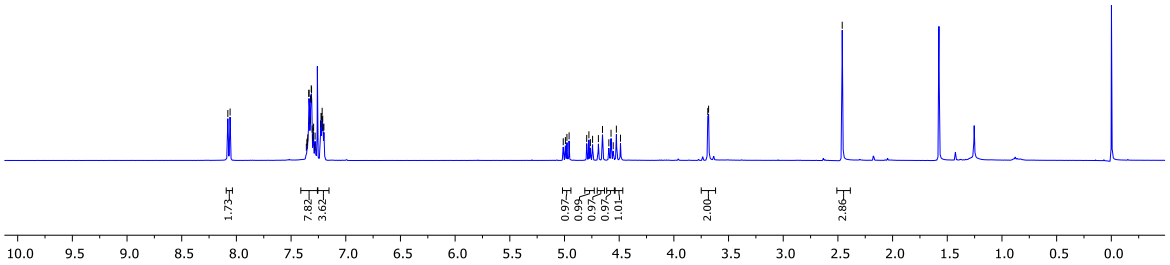
Bn

3b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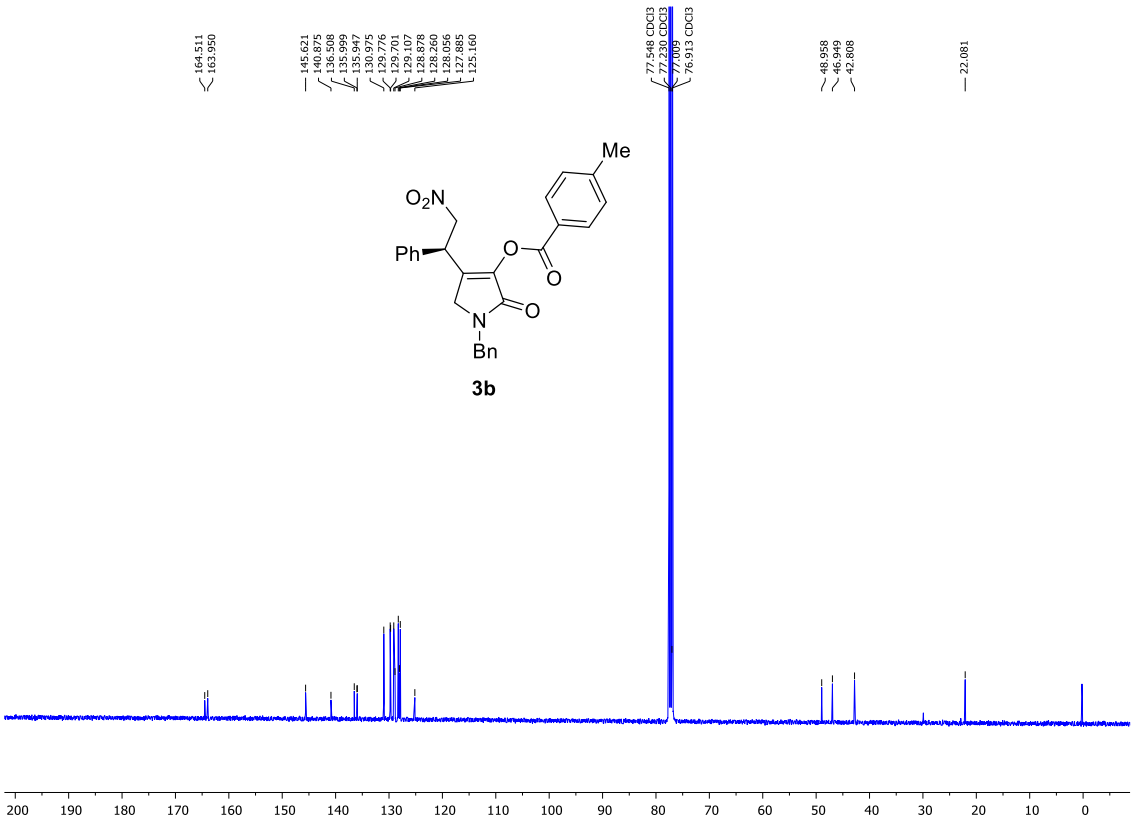
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46.949
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22.081
200
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180
170
160
150
140
130
120
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100
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Me
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Ph
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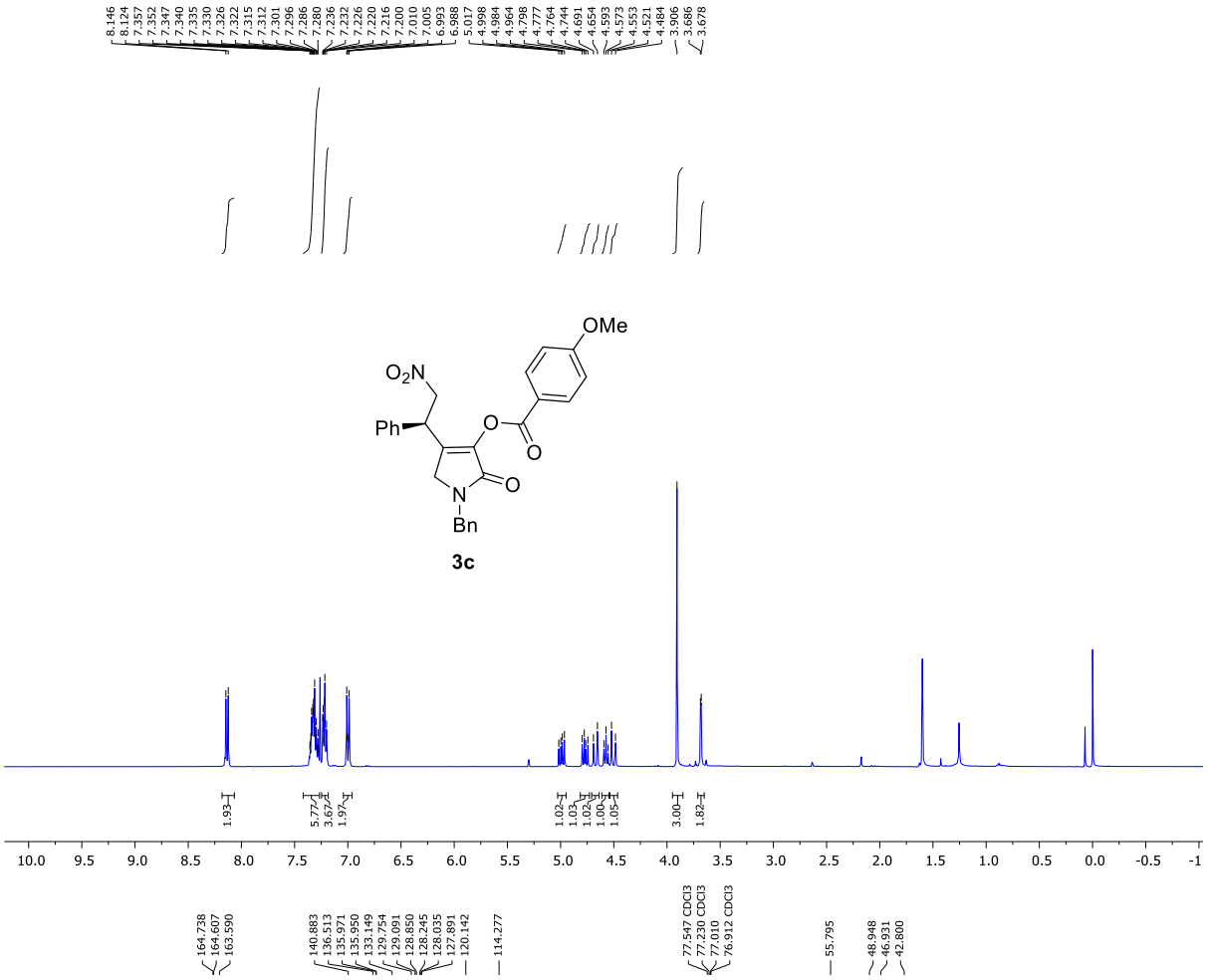
N
Bn

3b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Bn
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1.02
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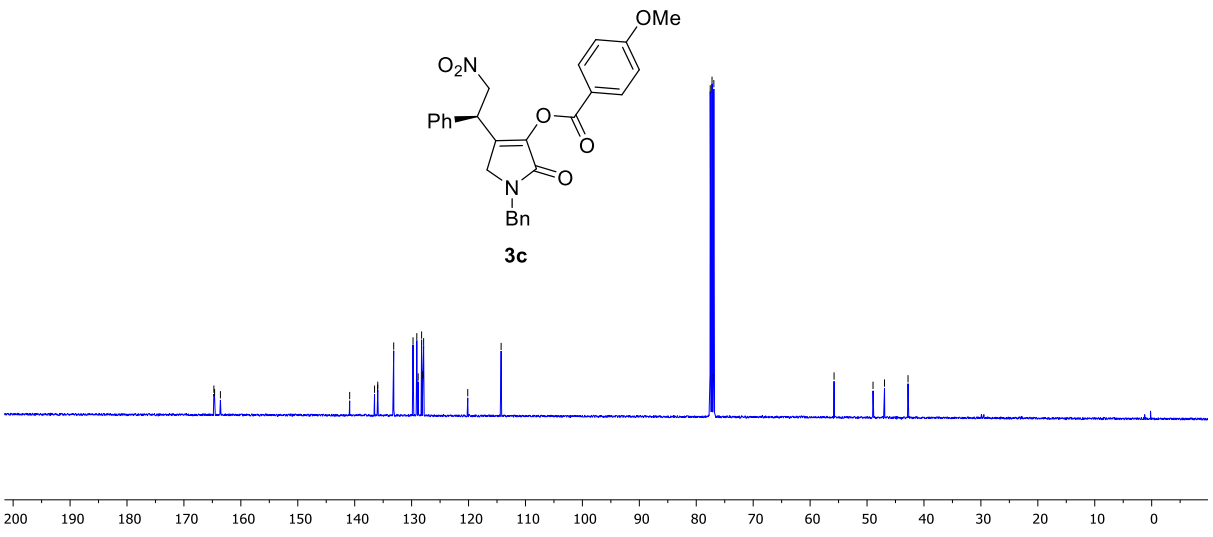
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O2N
Ph
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N
Bn
3c
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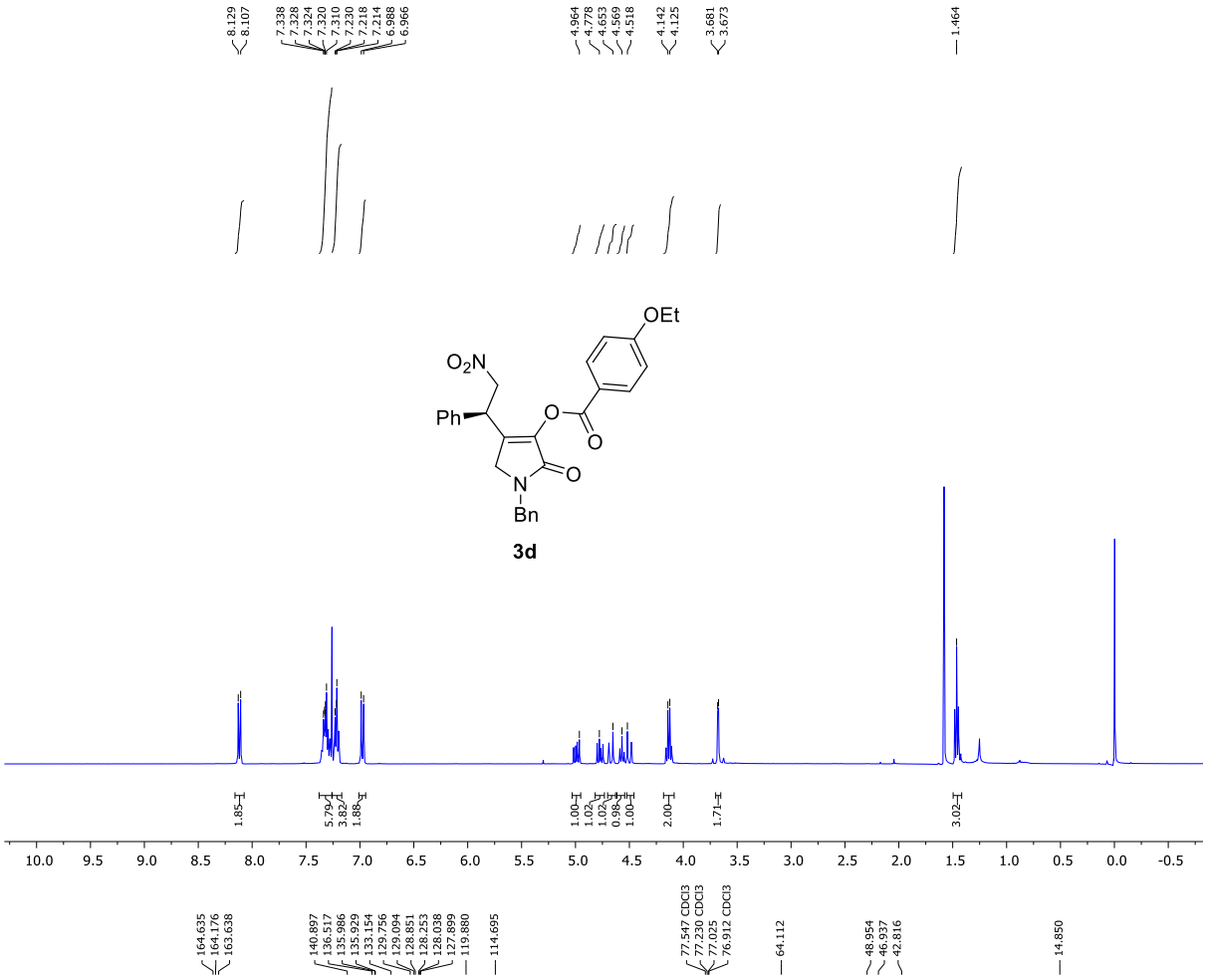
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3.673
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O2N
Ph
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O
O
N
Bn
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1.02
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2.00
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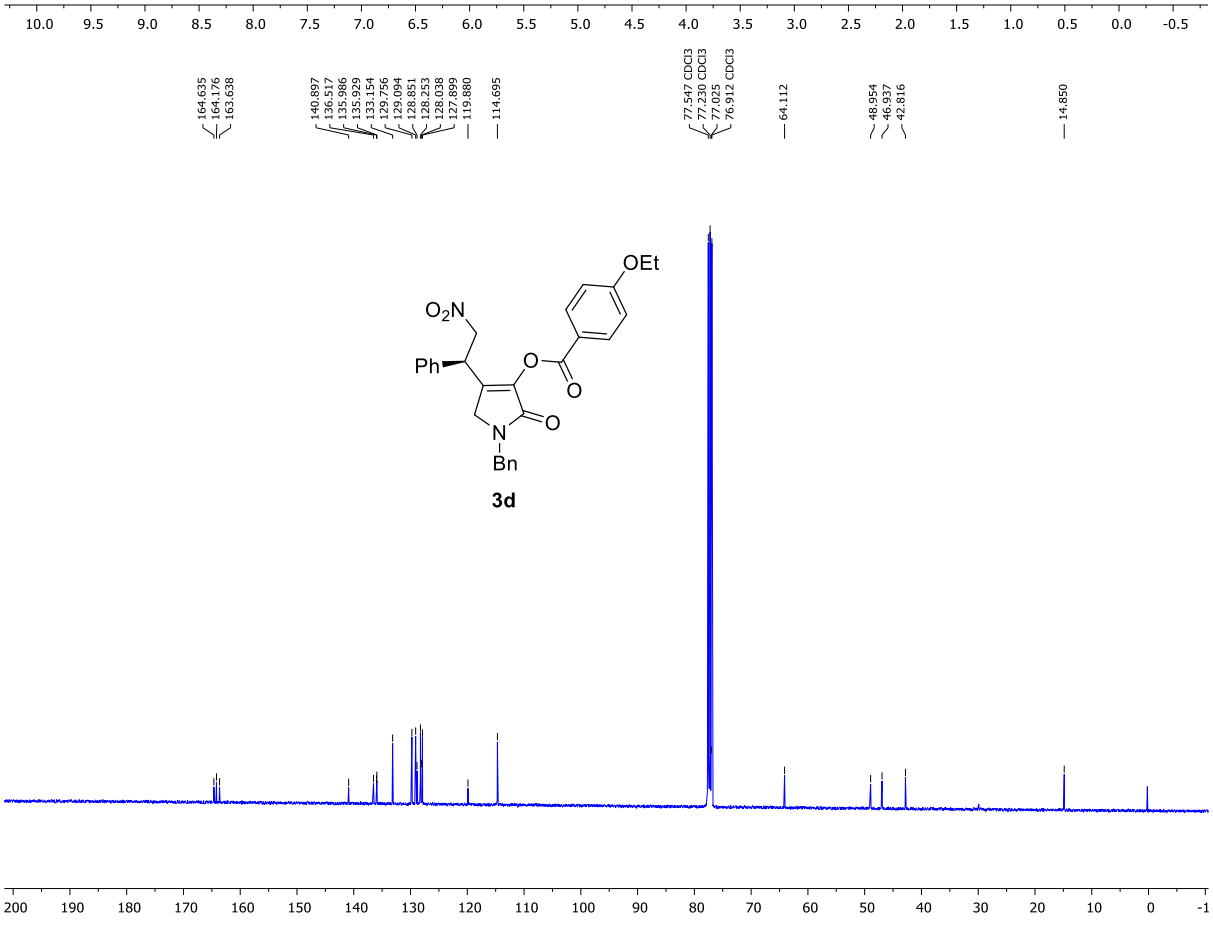
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119.880
114.695
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77.025
76.912 CDCl3
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48.954
46.937
42.816
14.850
OEt
O2N
Ph
O
O
O
N
Bn
200
190
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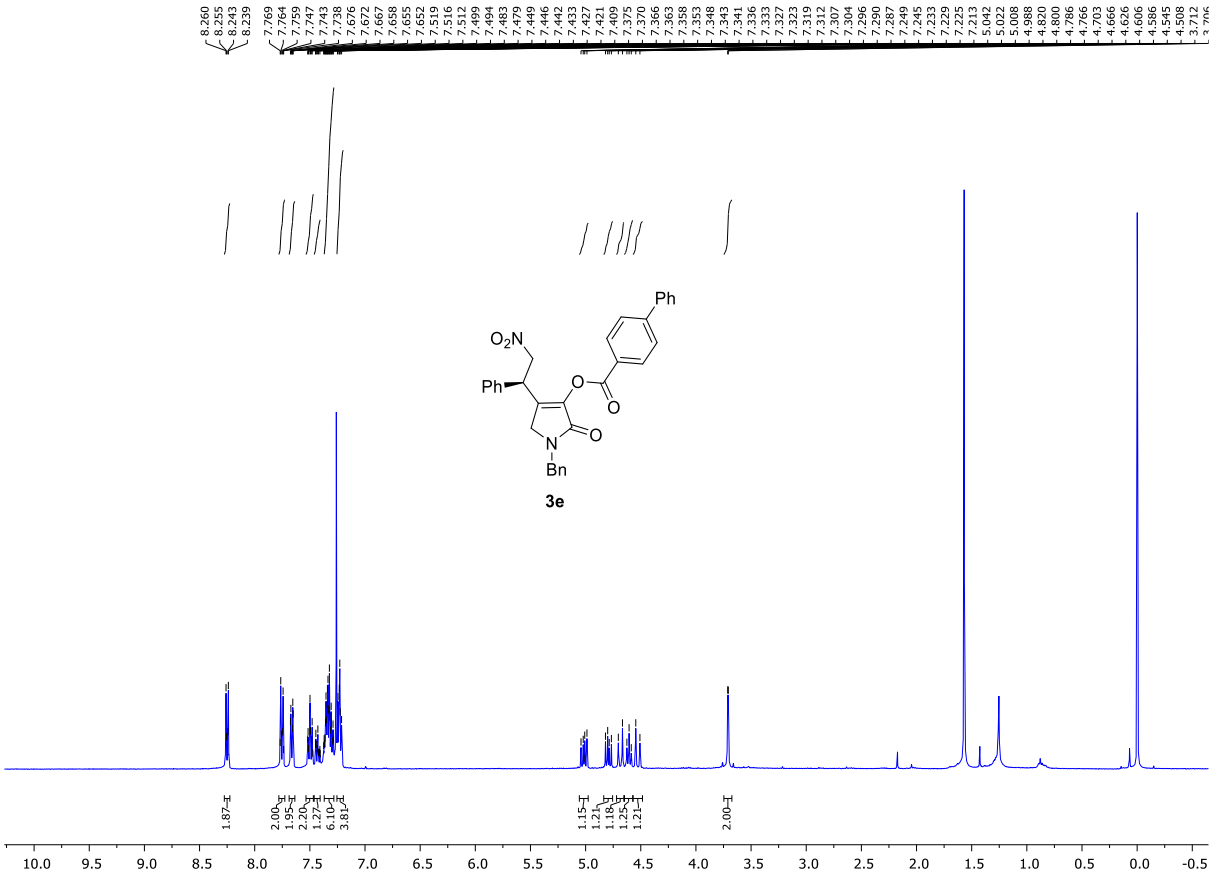
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Bn
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1.22
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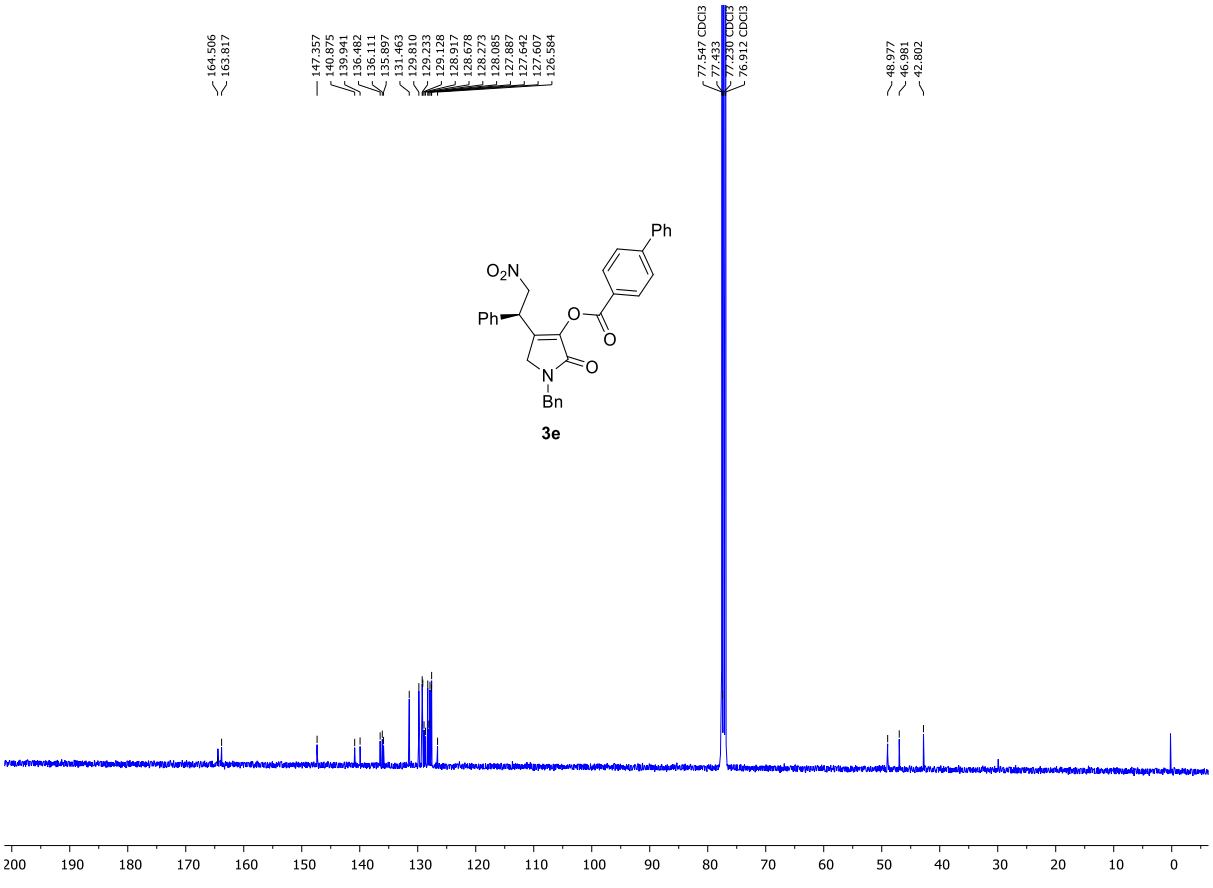
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Ph
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N
O
Bn
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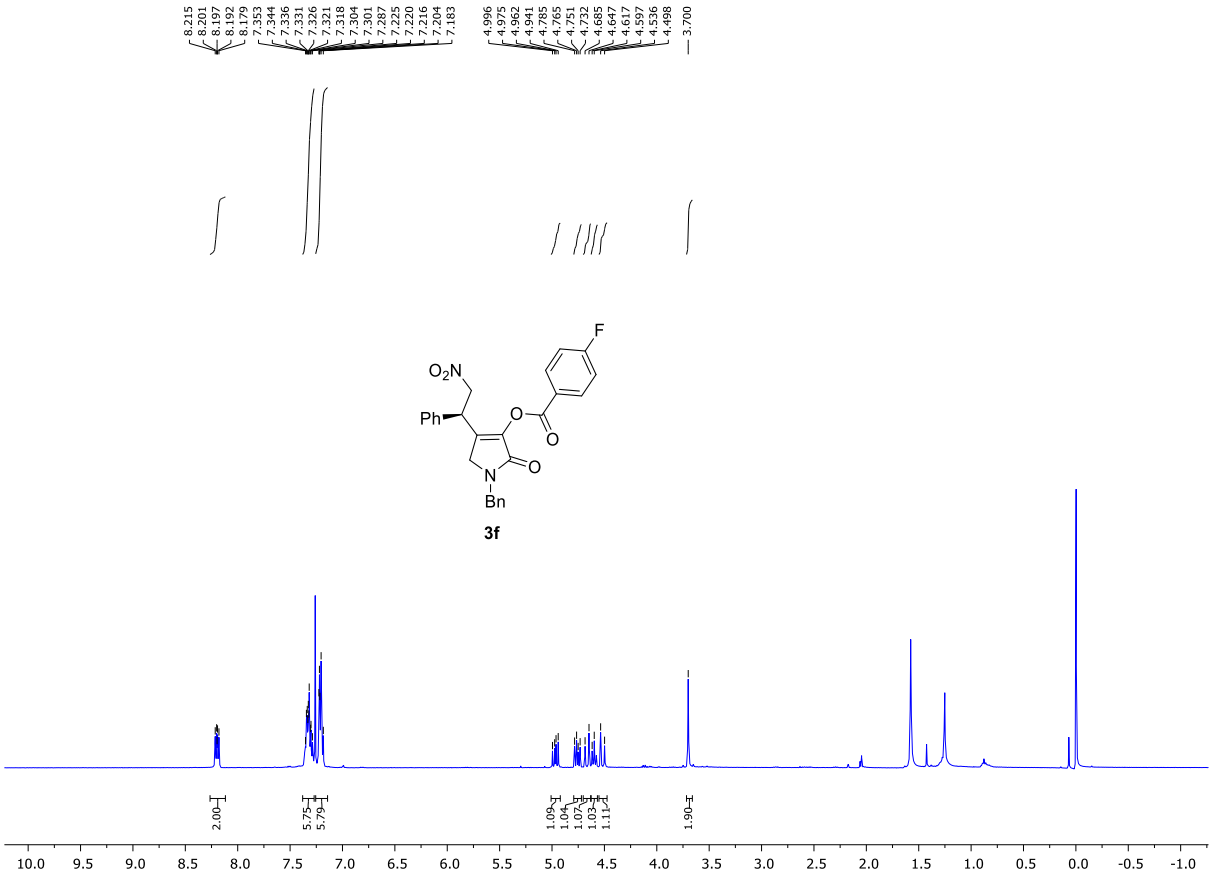
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3.700
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Ph
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O
O
N
Bn
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5.79
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1.04
1.07
1.03
1.11
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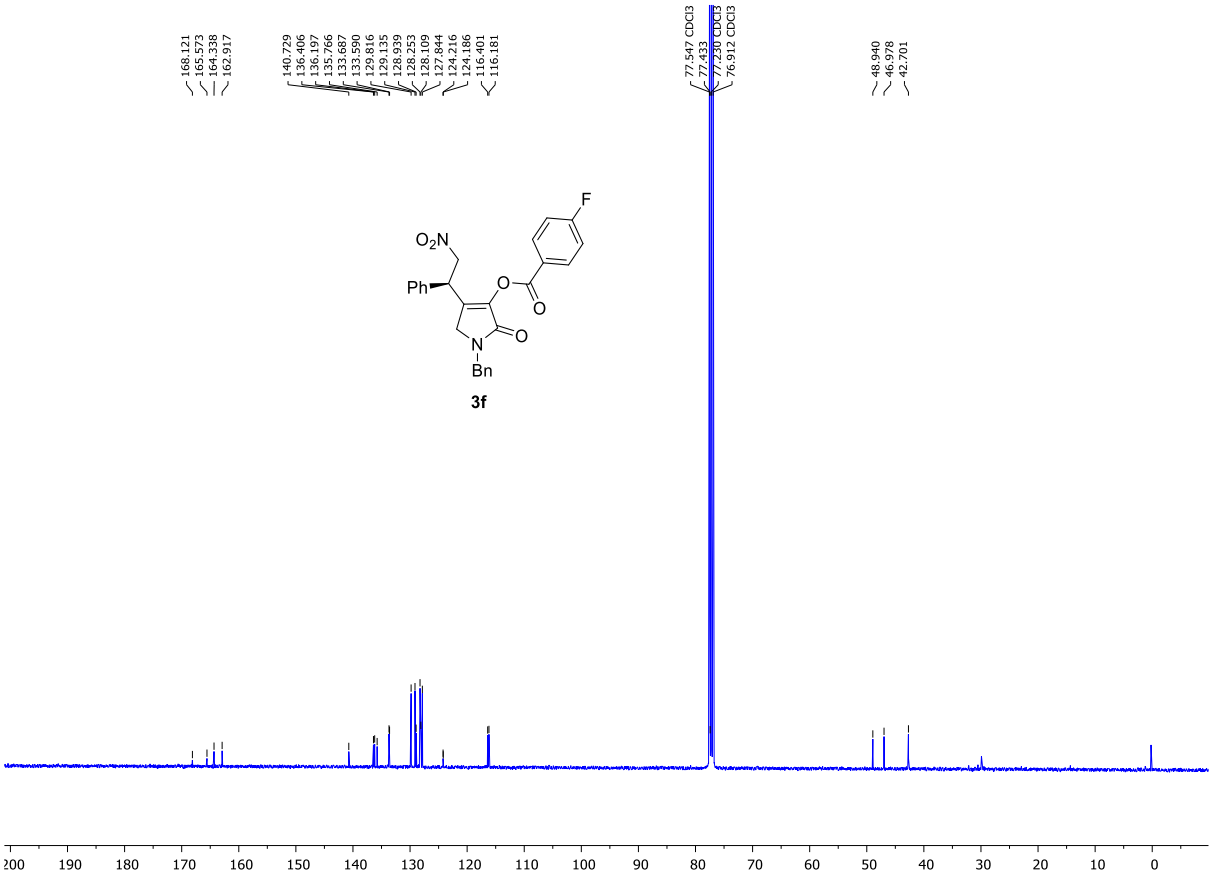
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76.912 CDCl3
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42.701
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Ph
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O
O
N
Bn
3f
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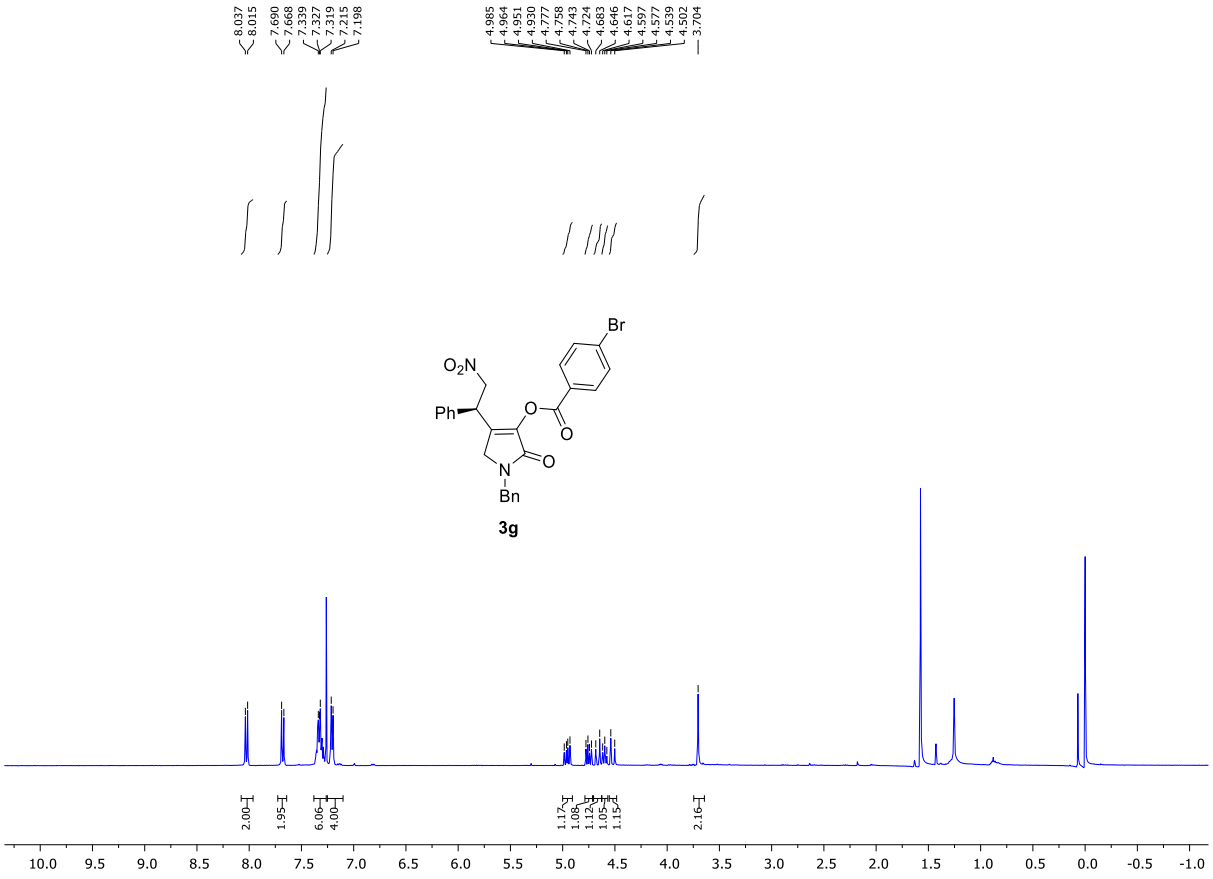
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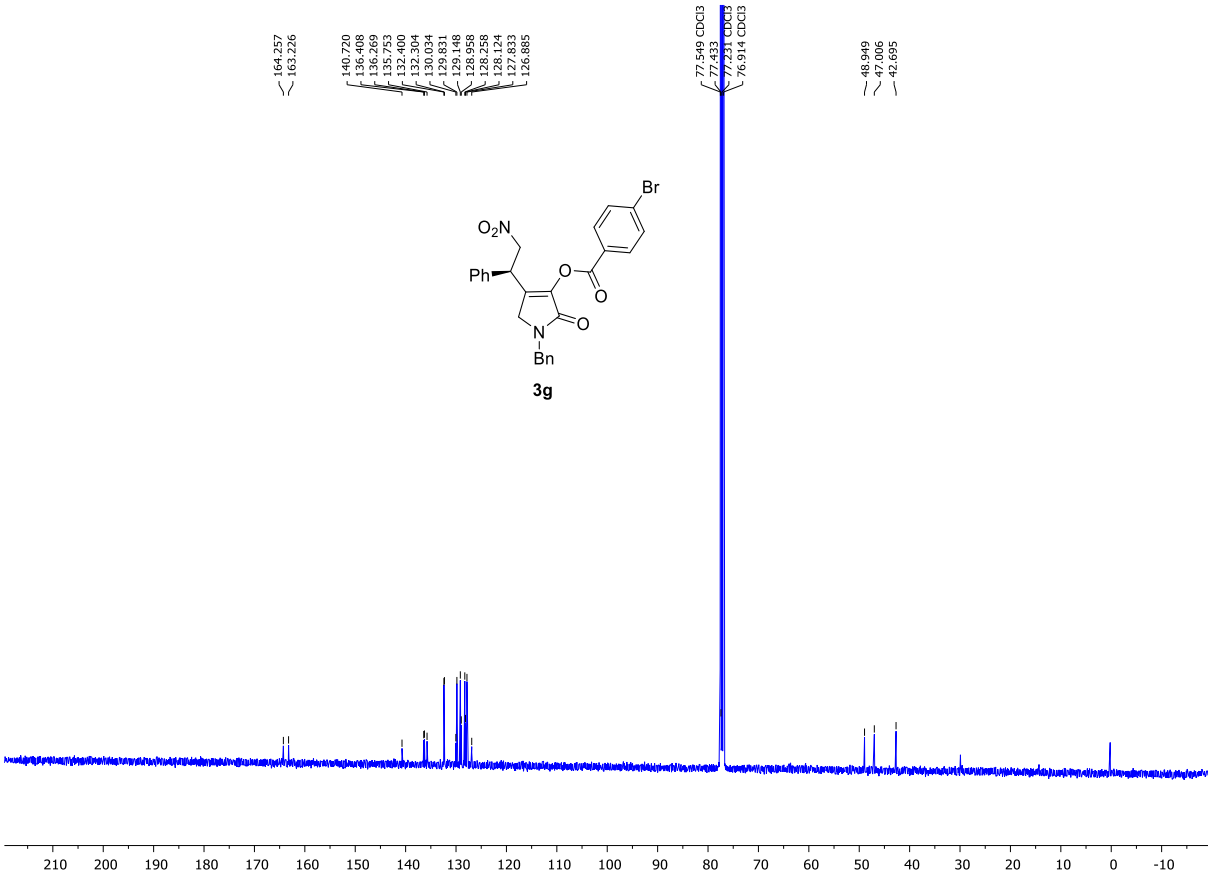
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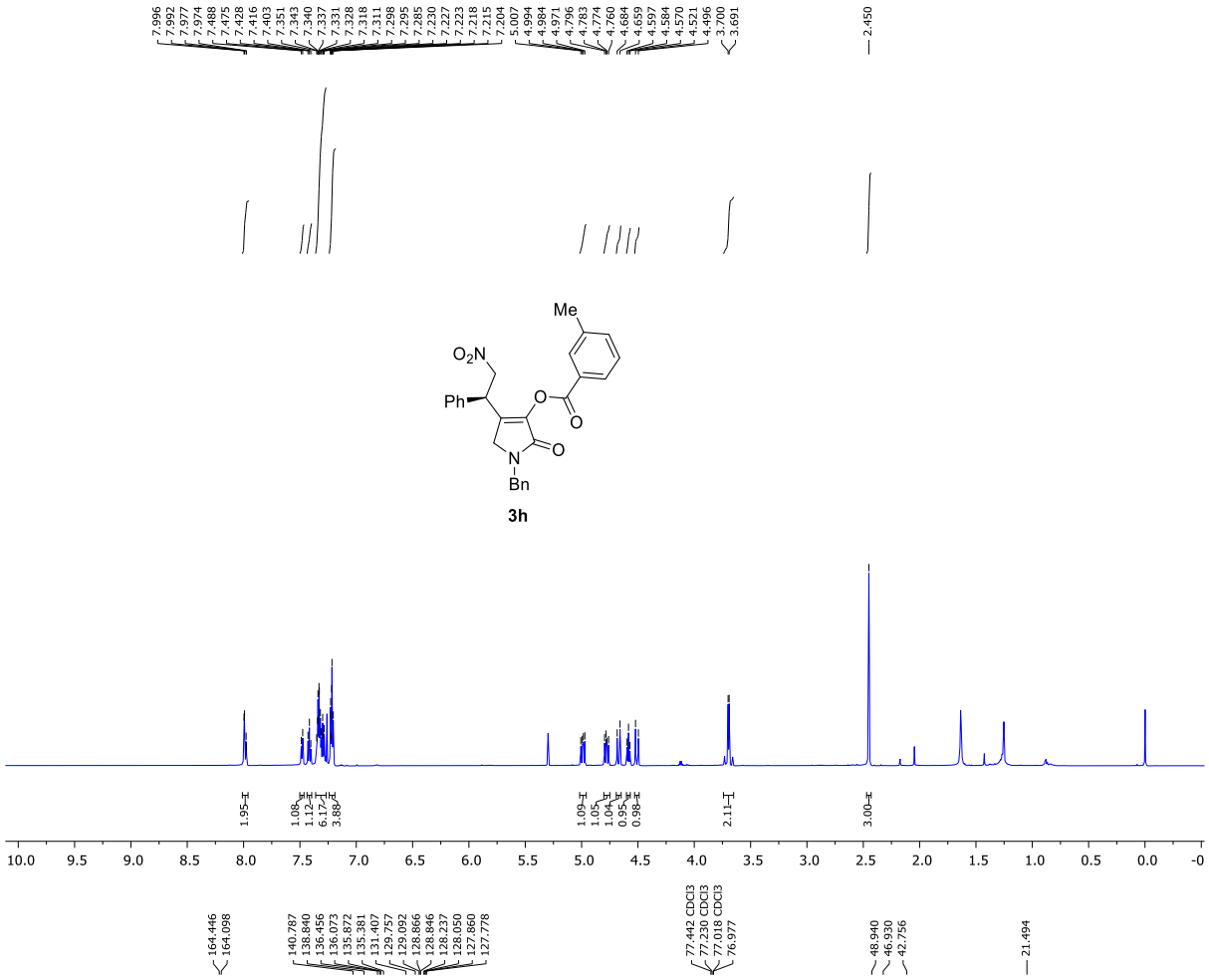
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Ph
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Bn
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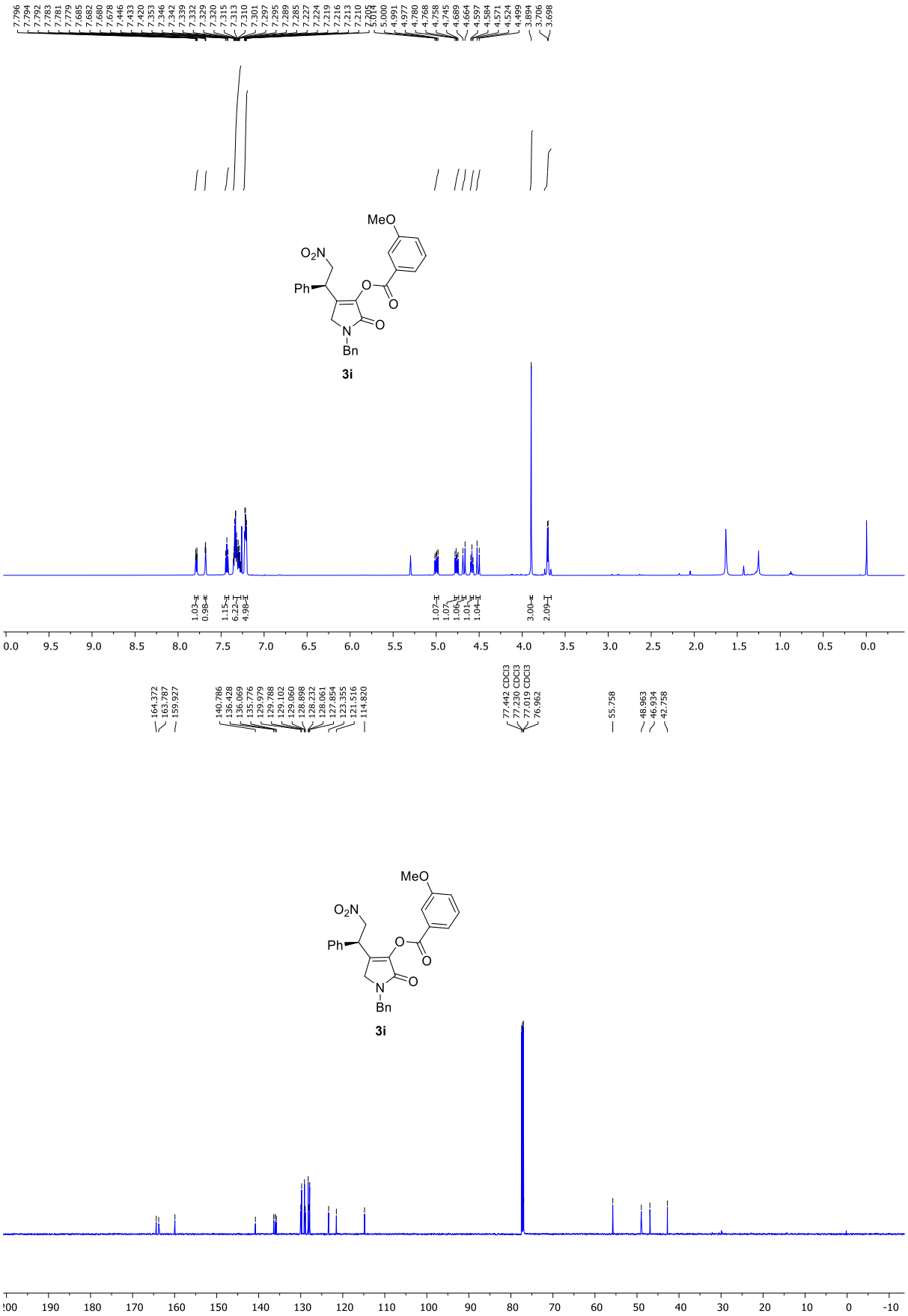
3h

3h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1.06
1.04
1.04
3.00
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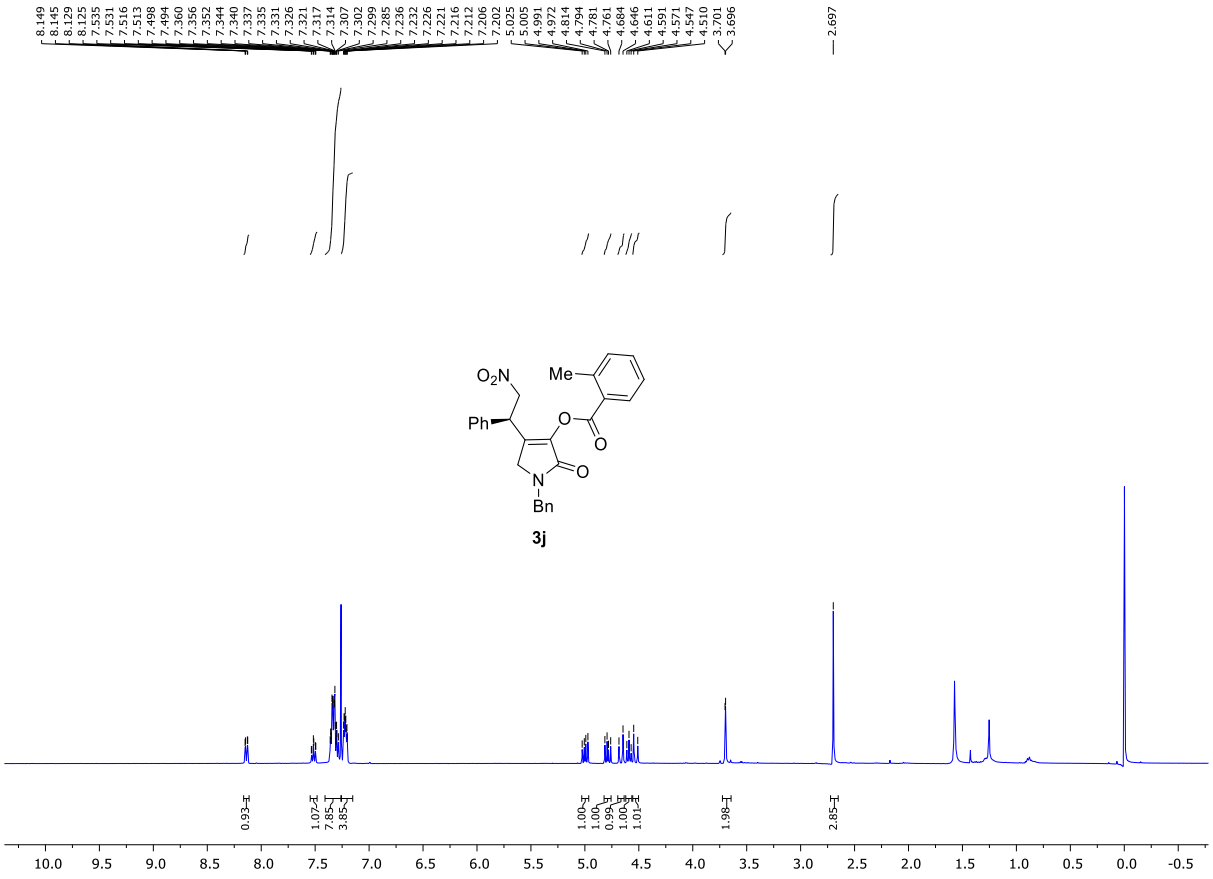
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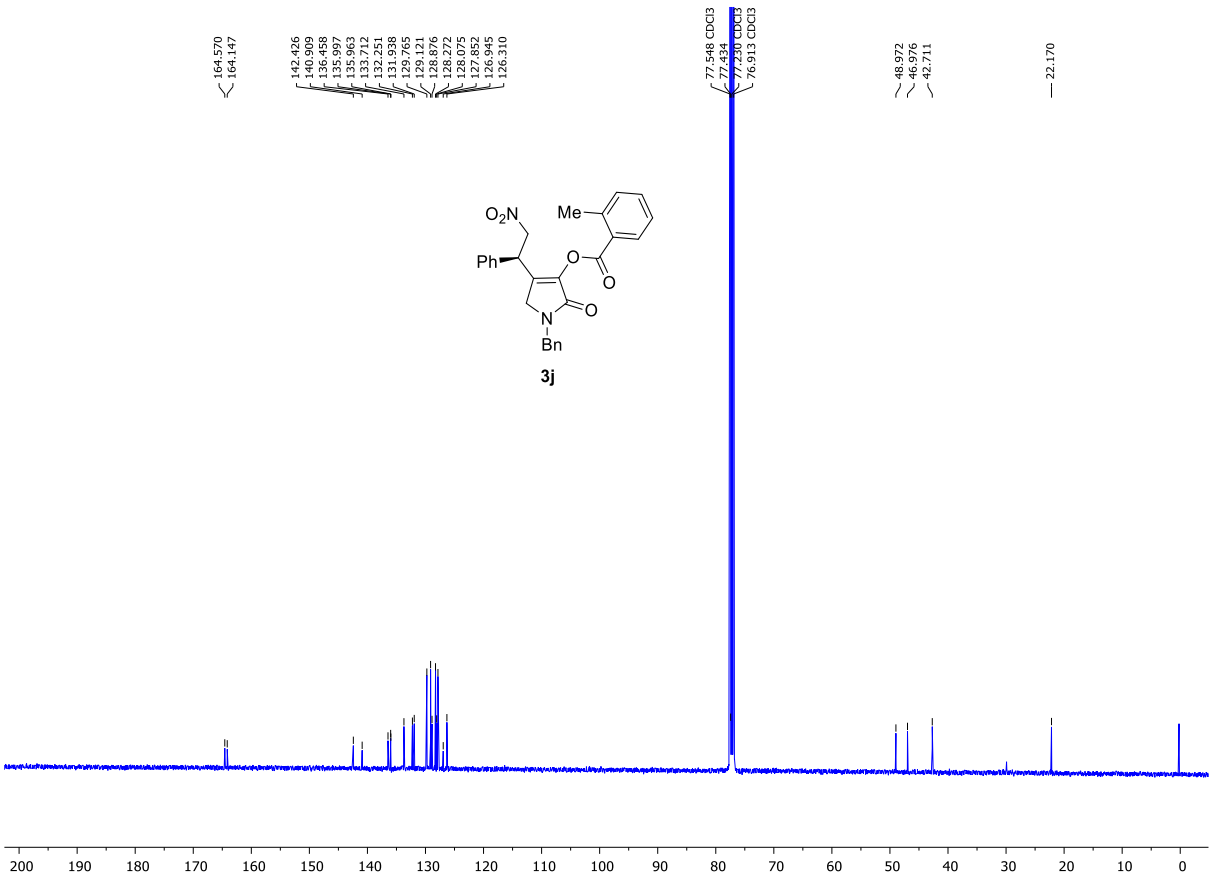
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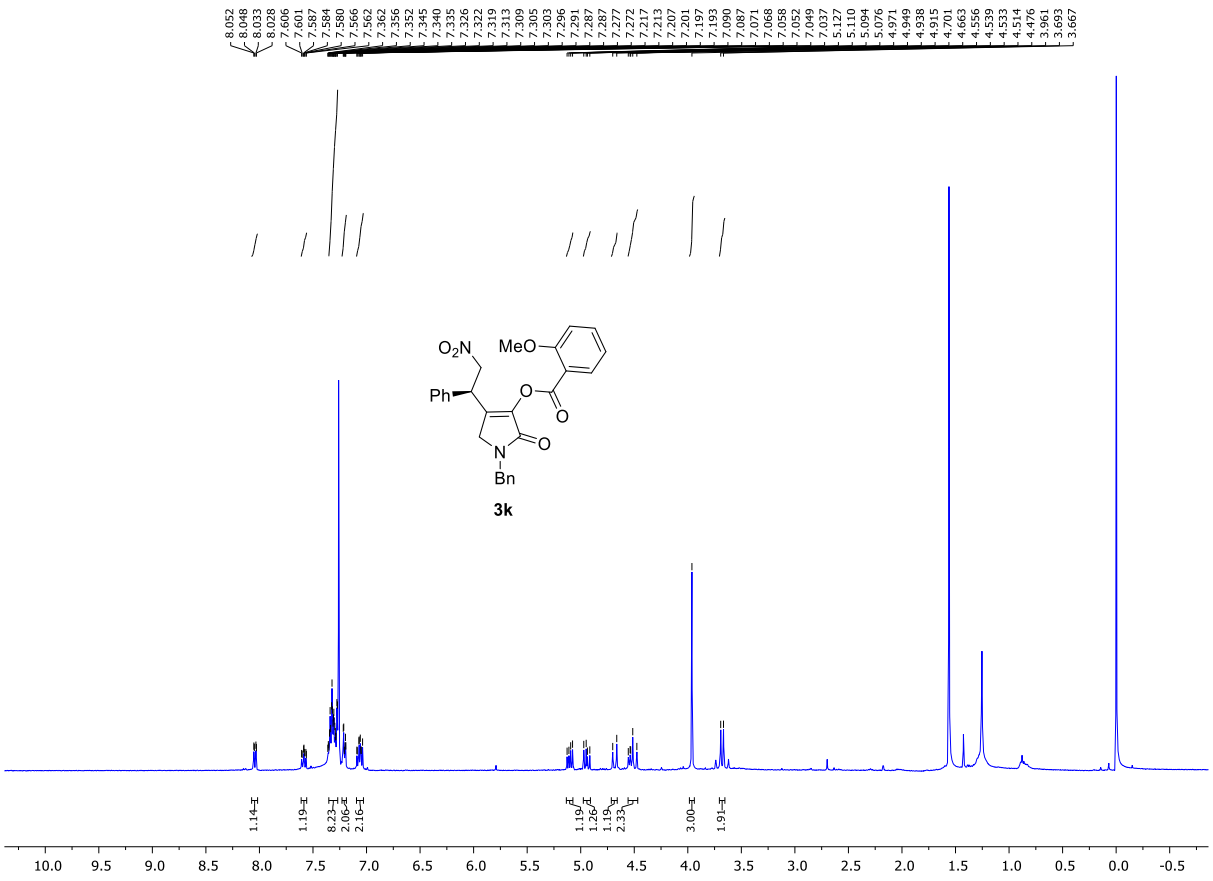
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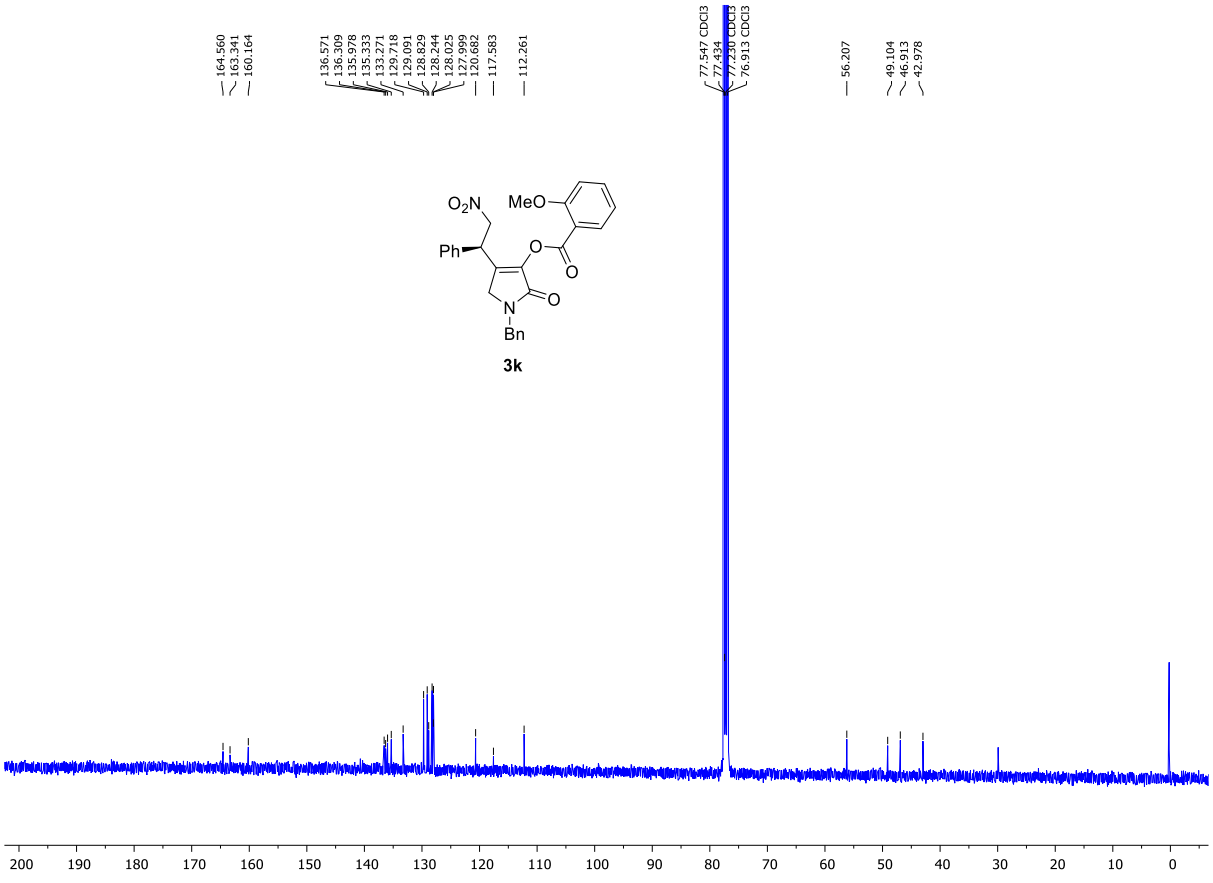
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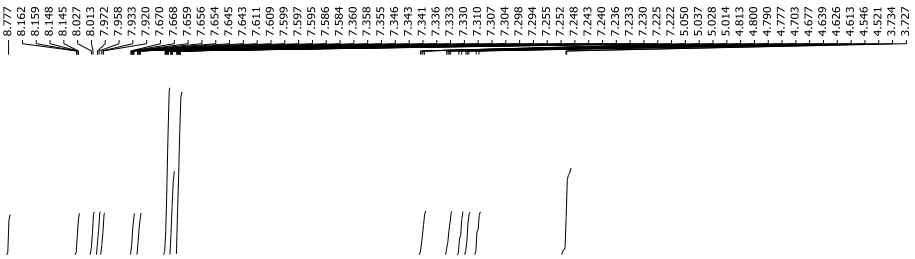

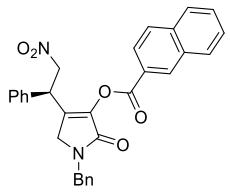

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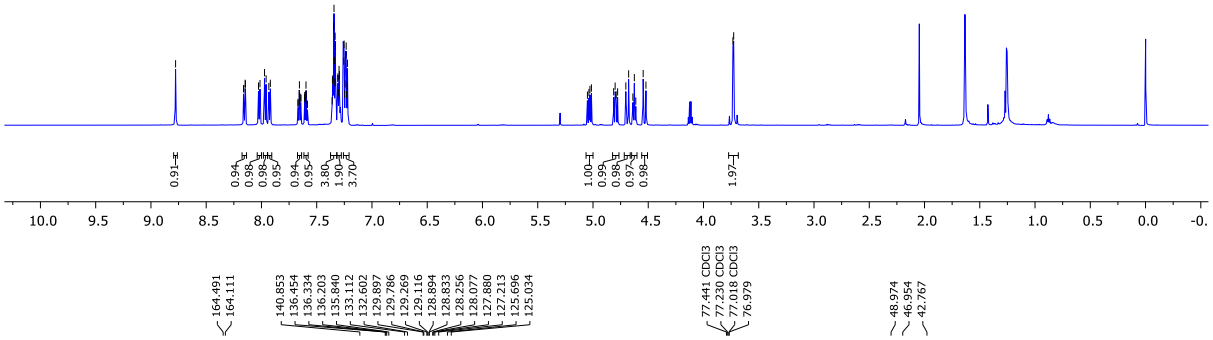

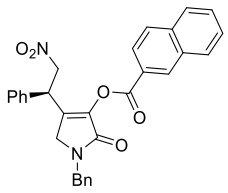

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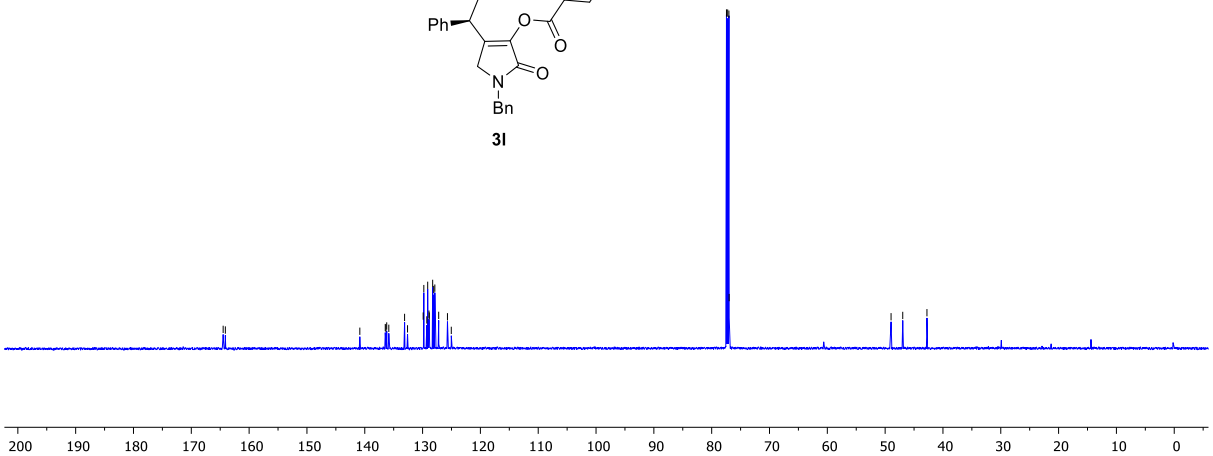

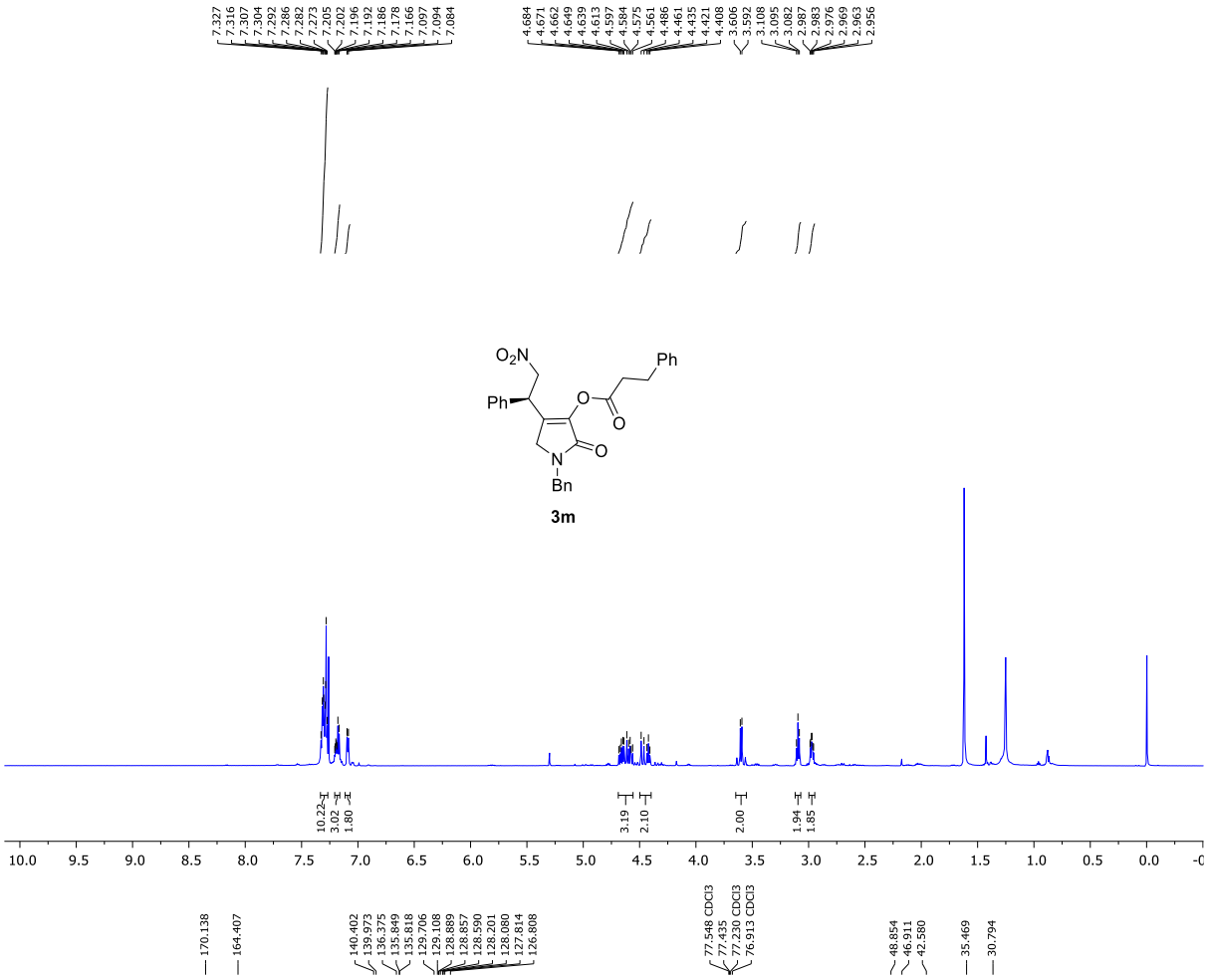
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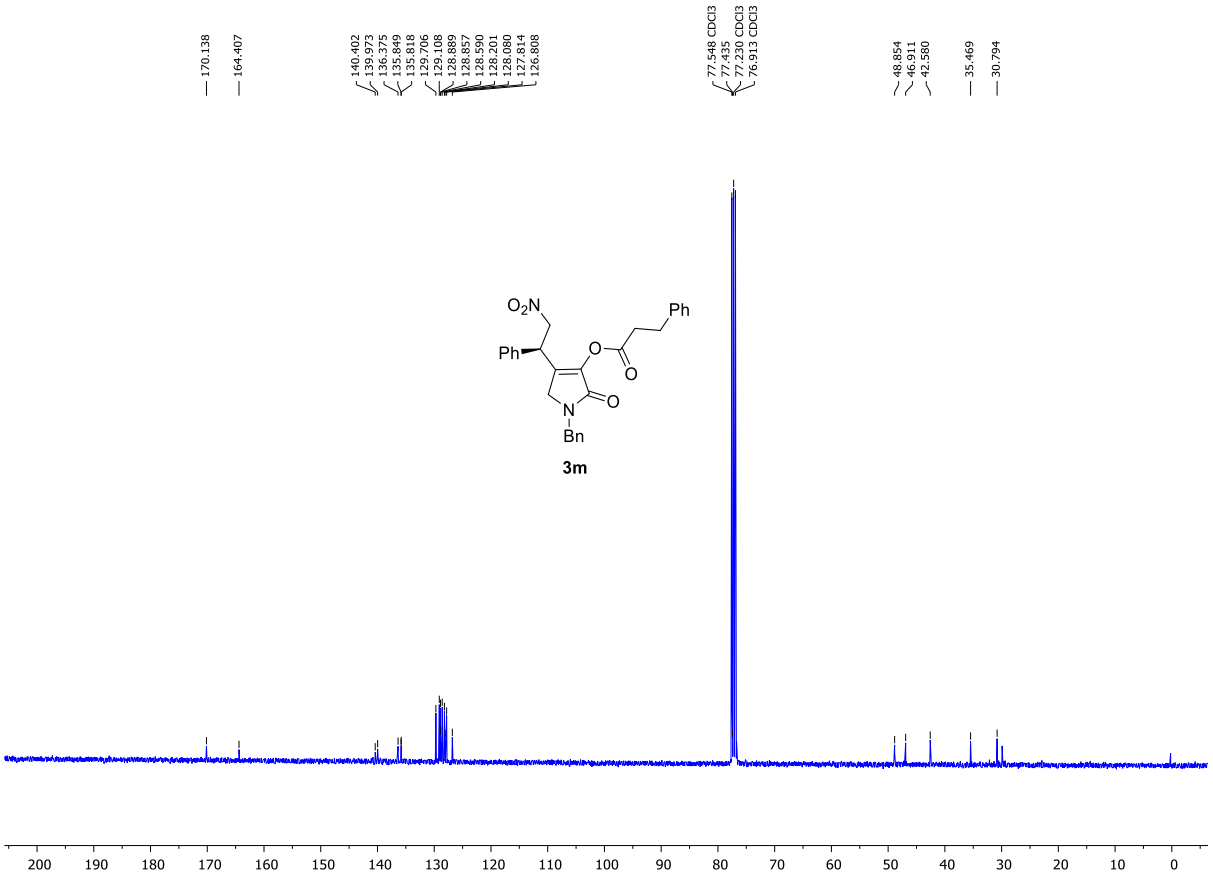
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77.435
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76.913 CDCl3
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Ph
Ph
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O
N
Bn
3m
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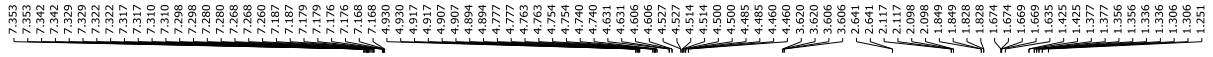

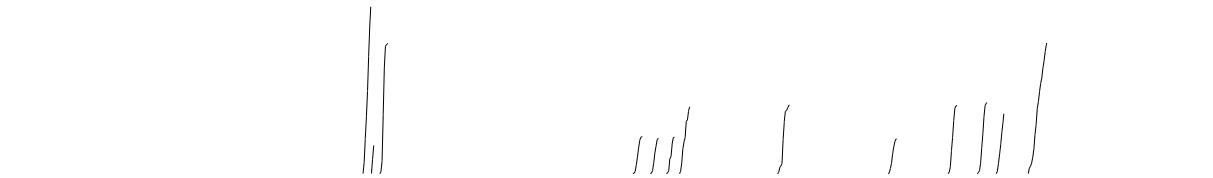

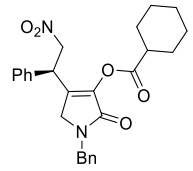
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Bn

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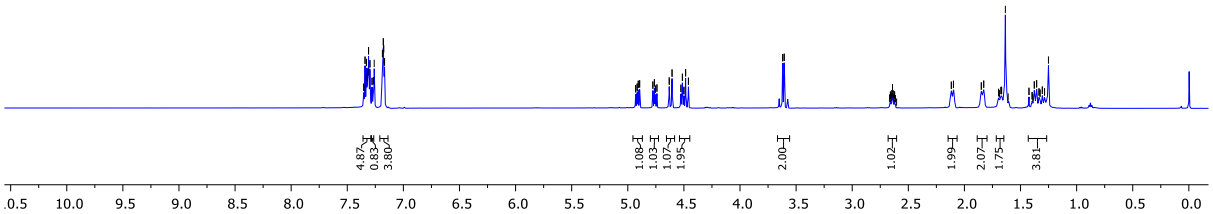
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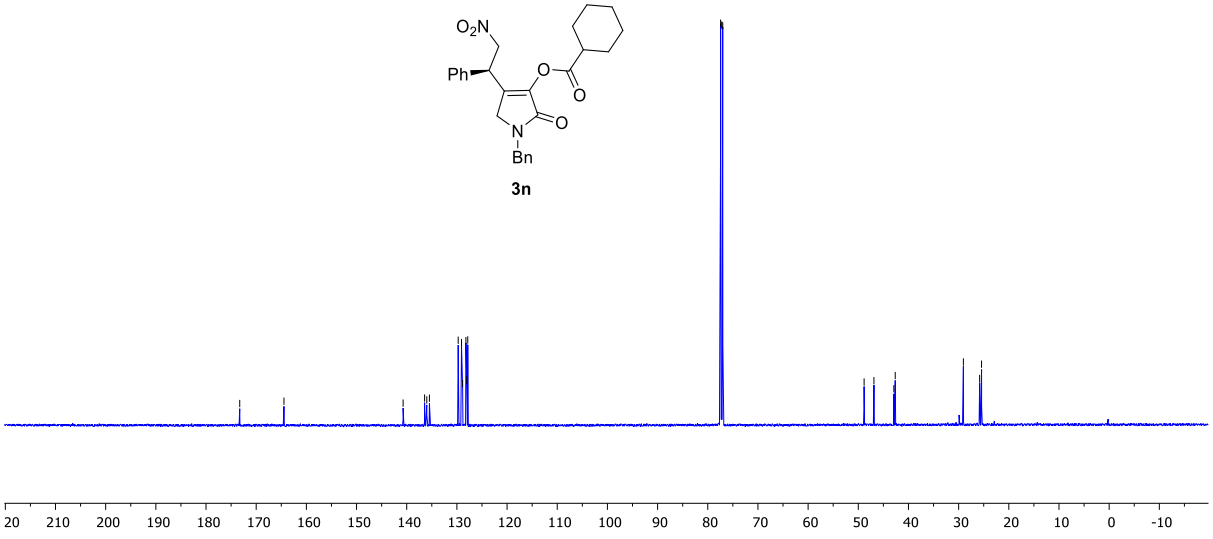
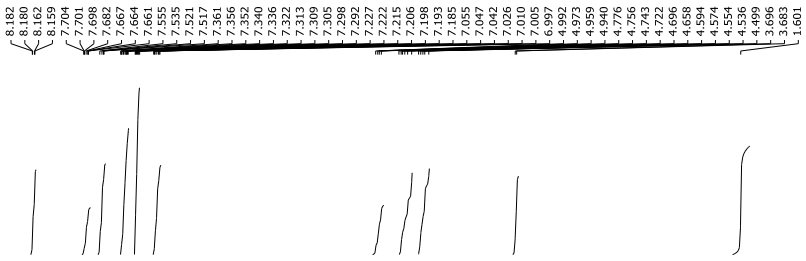
N
Bn

3n

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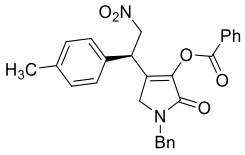
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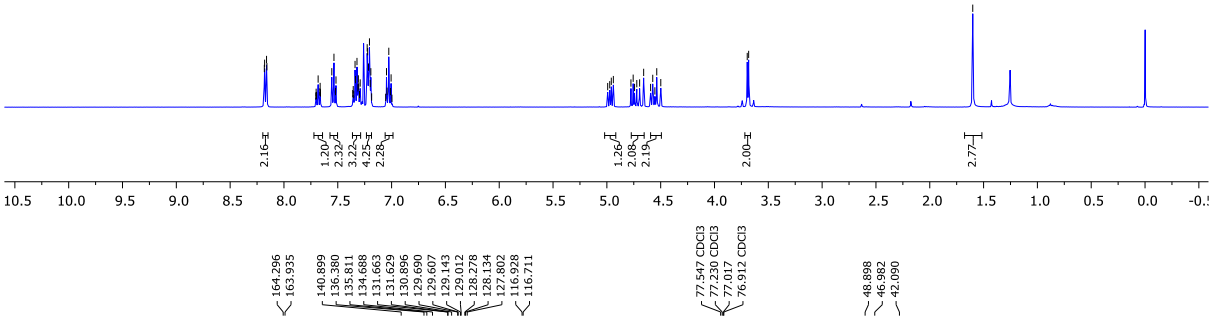
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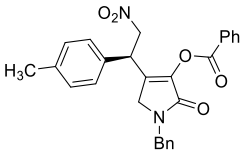
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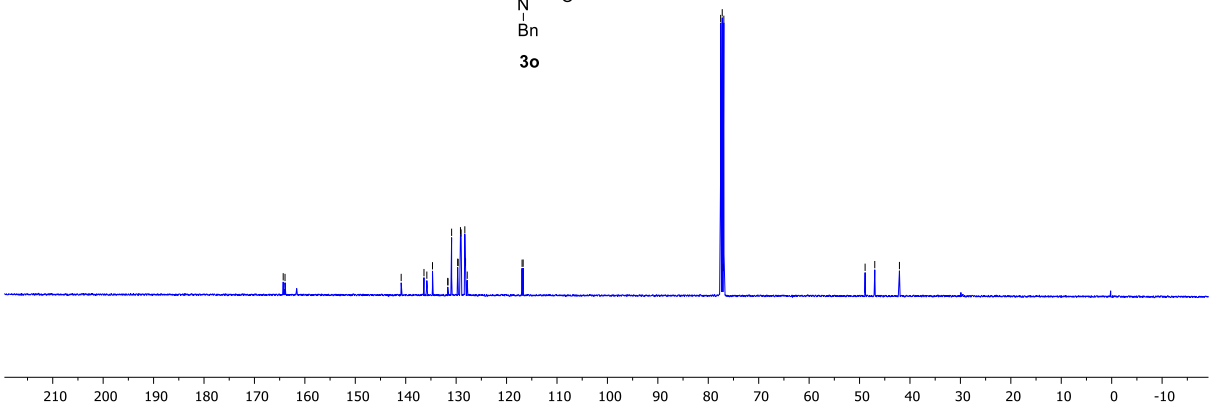
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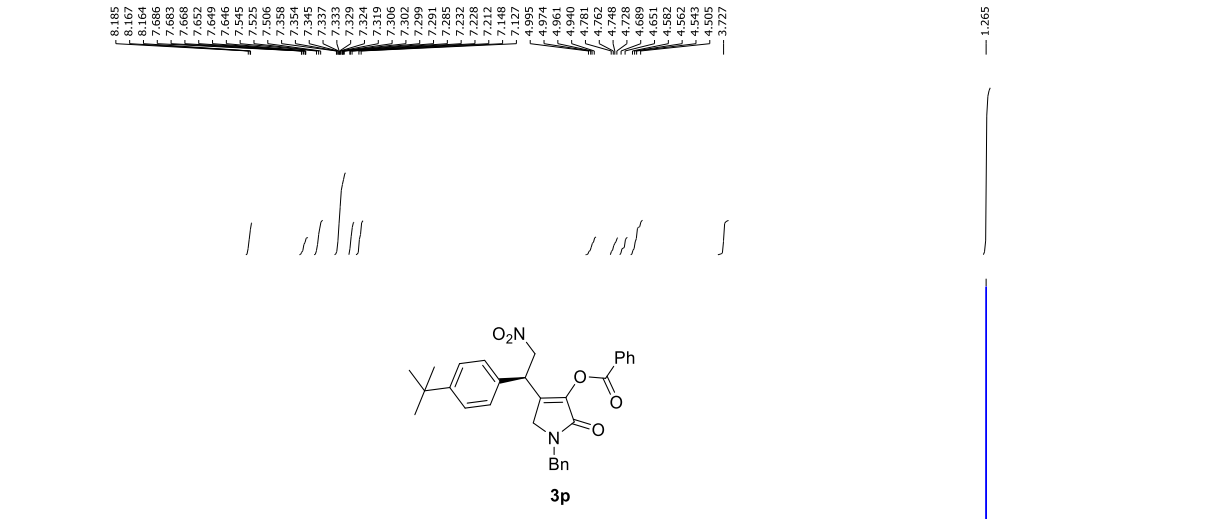
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Bn

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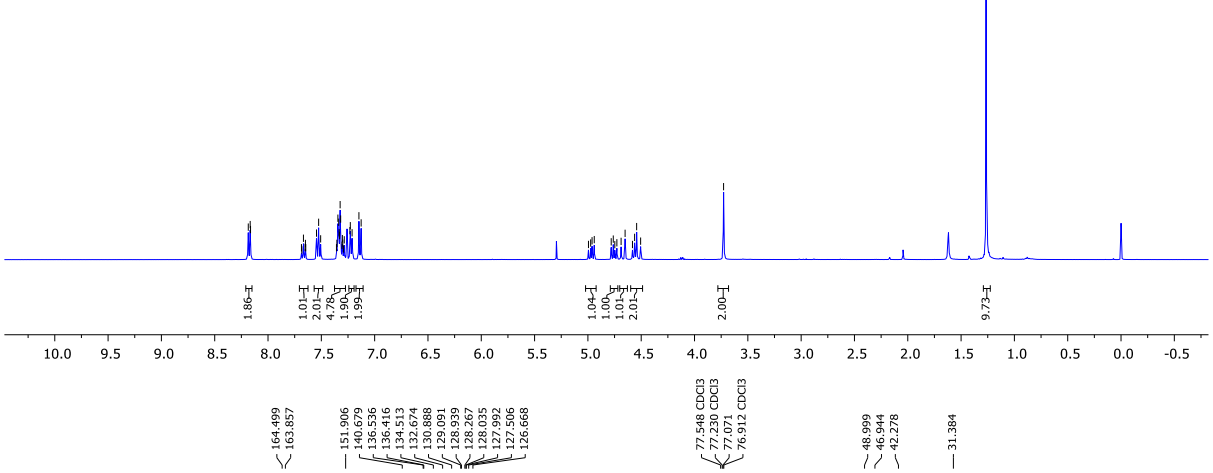
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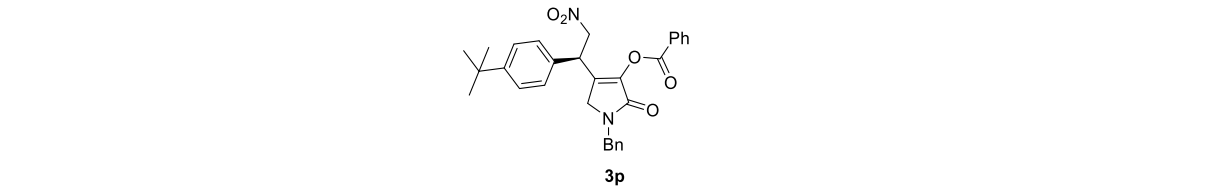
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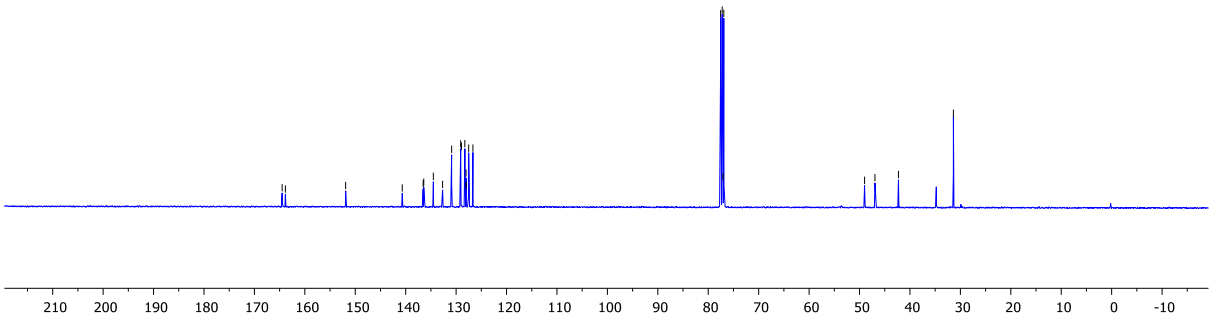
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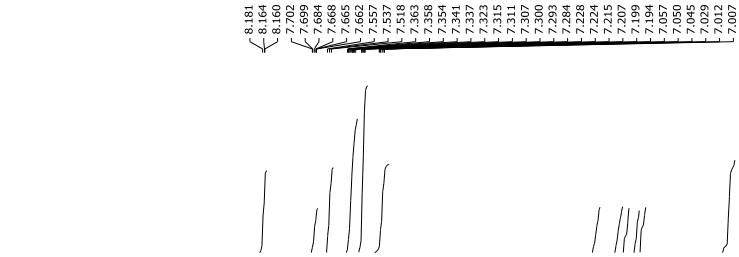
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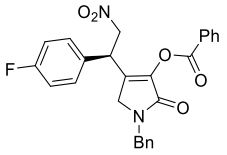
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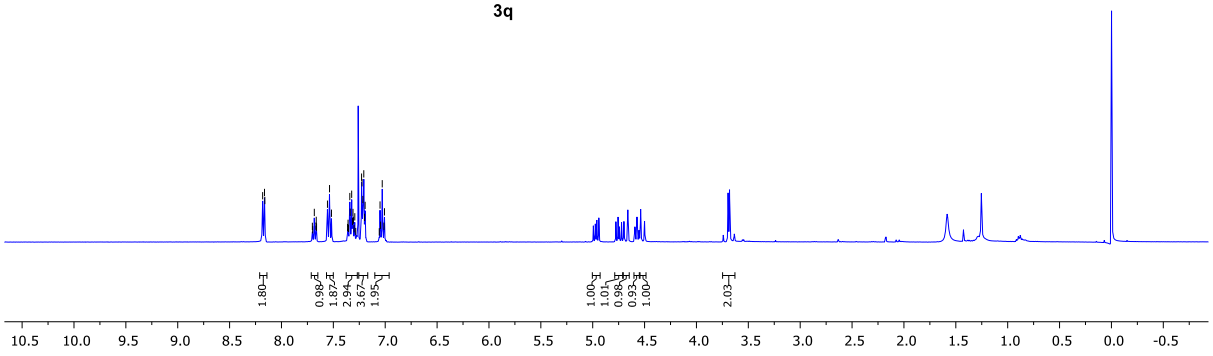
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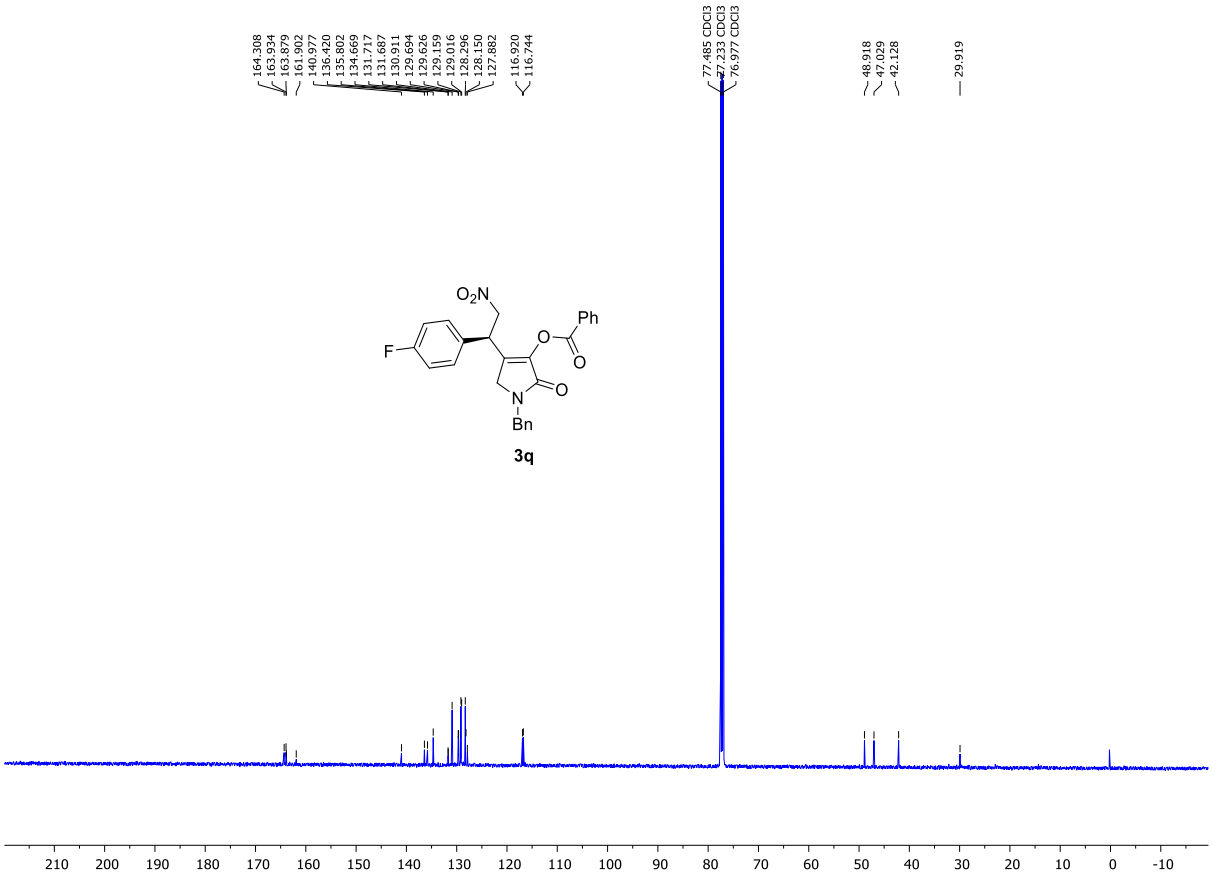
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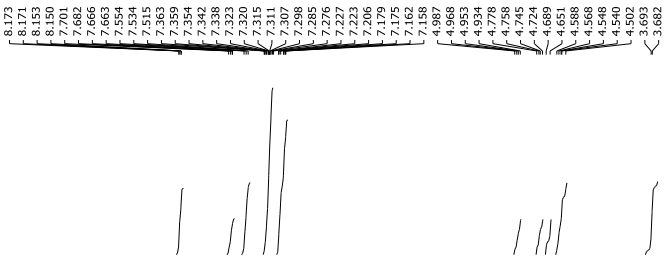
Bn

3q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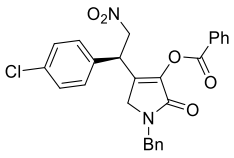
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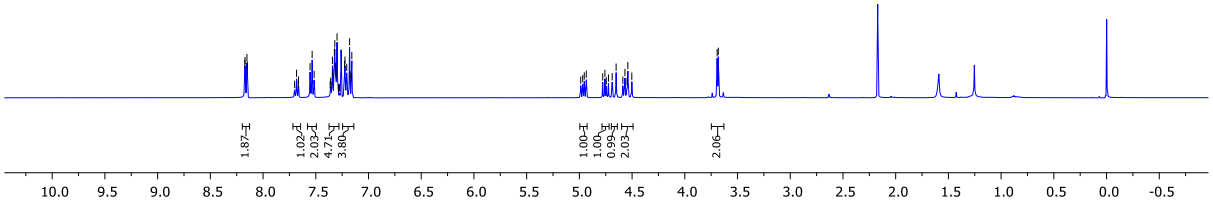
Bn

3r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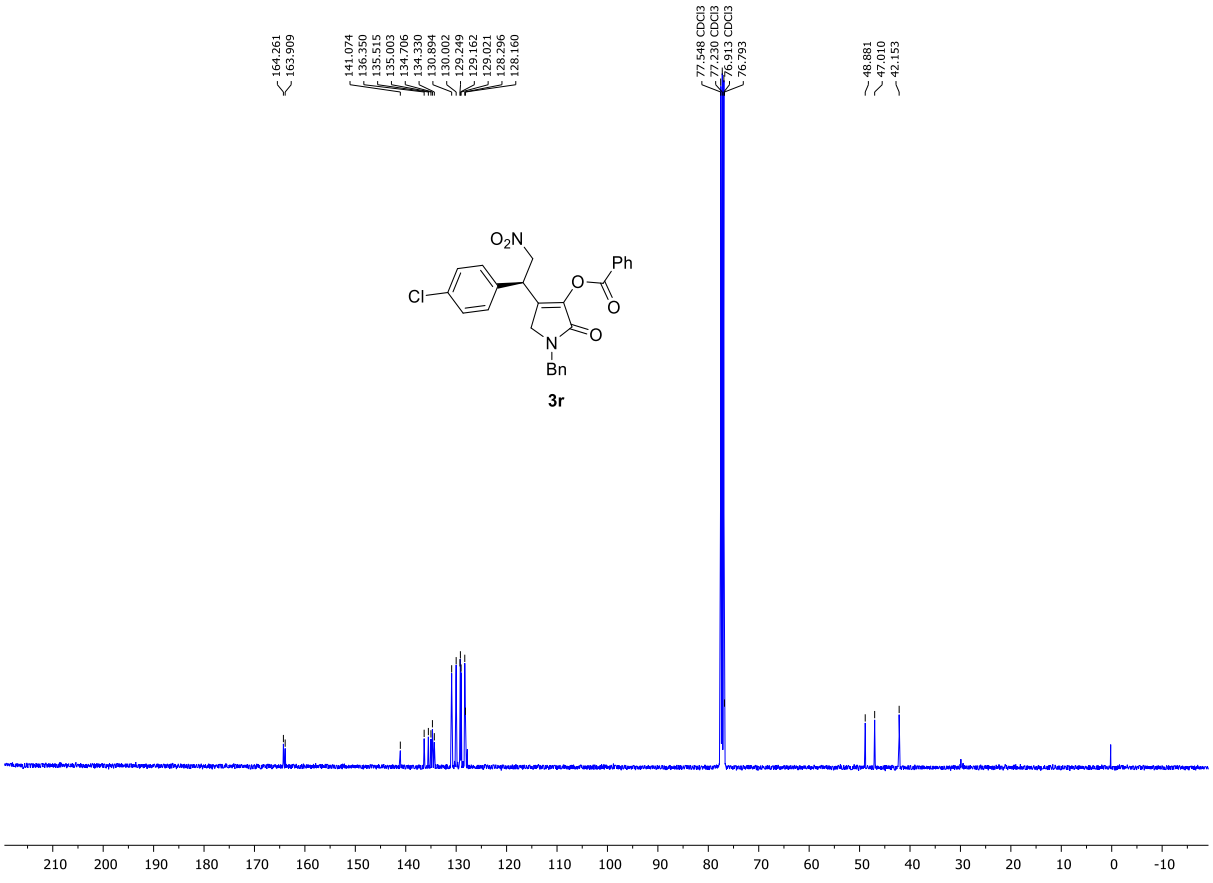
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47.010
42.153
210
200
190
180
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140
130
120
110
100
90
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O2N
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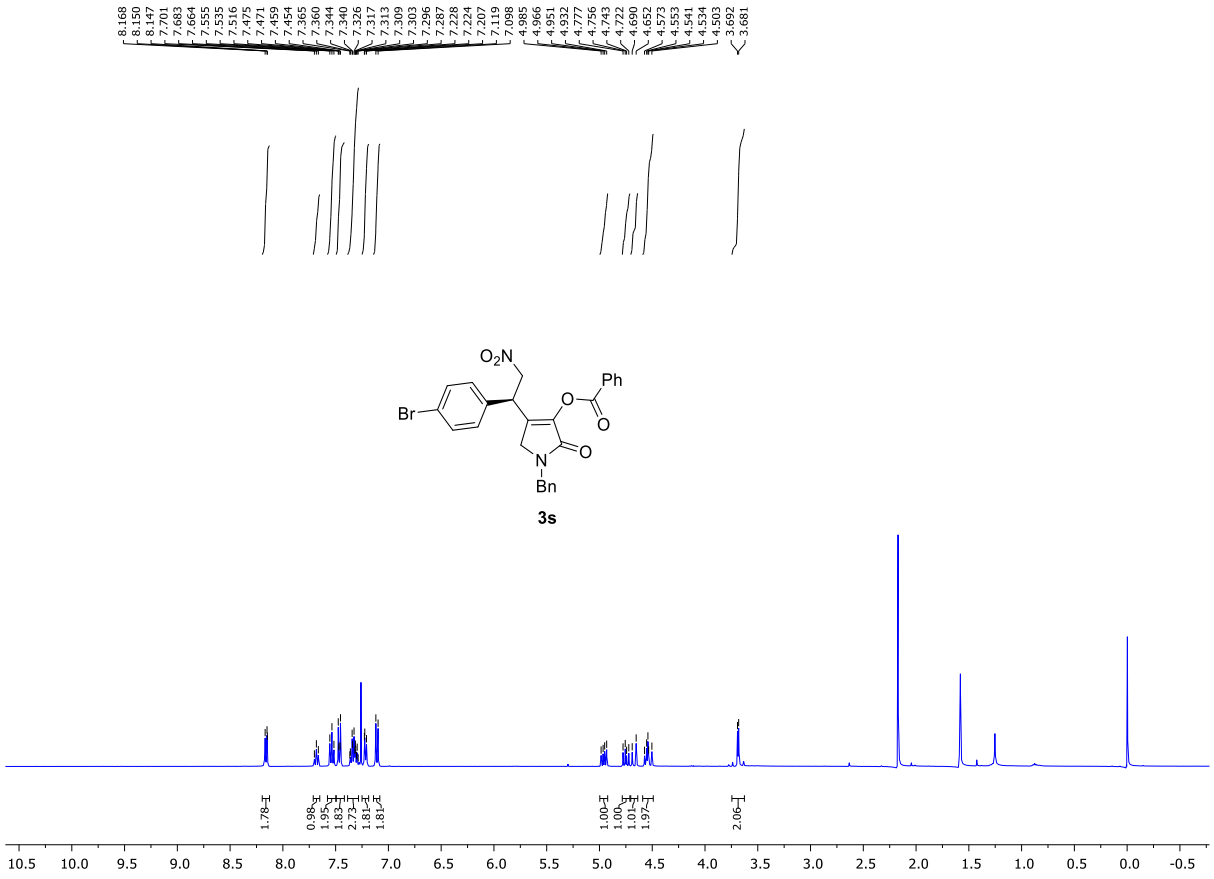
3r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2.06
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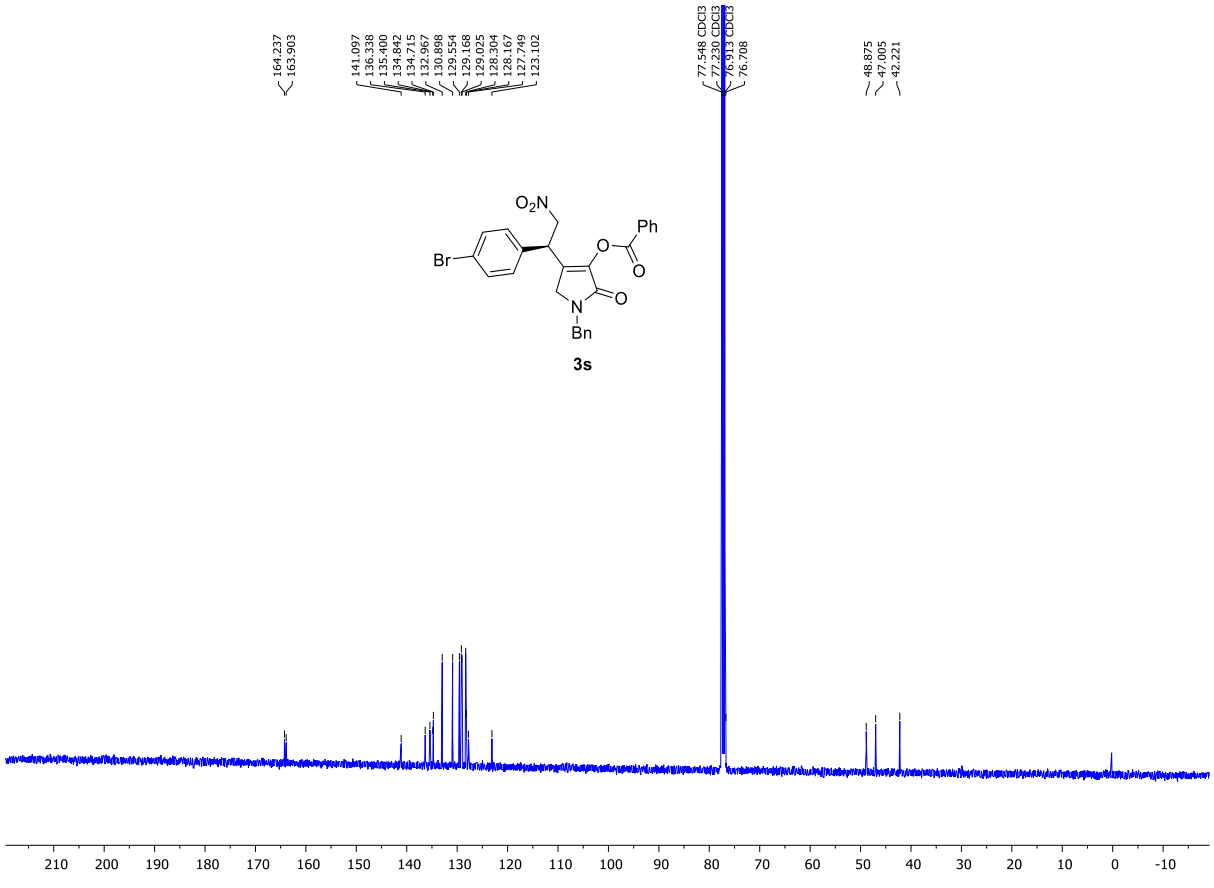
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77.230 CDCl3
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48.875
47.005
42.221
O2N
Ph
Br
O
O
O
N
Bn
3s
210
200
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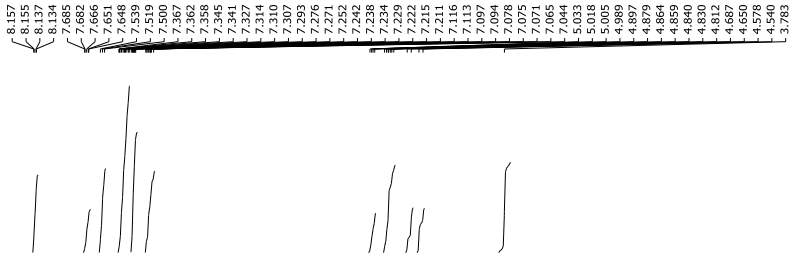

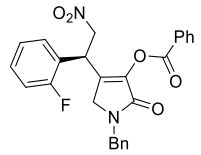

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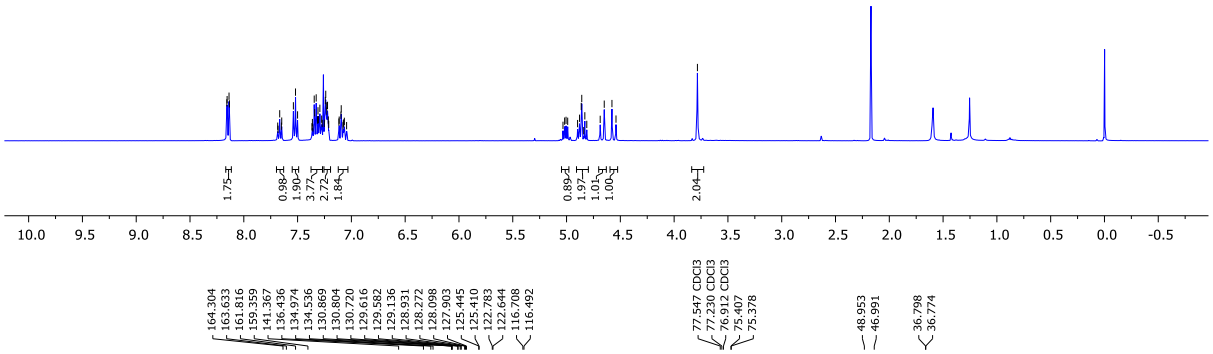

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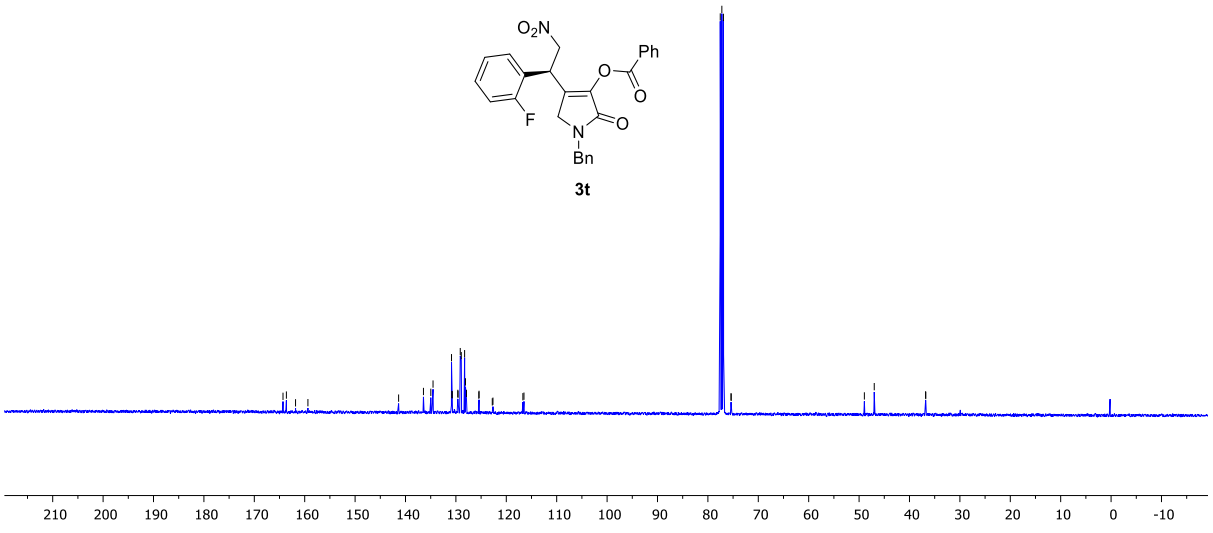


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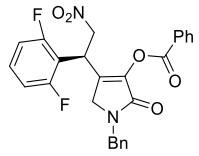
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Ph
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F
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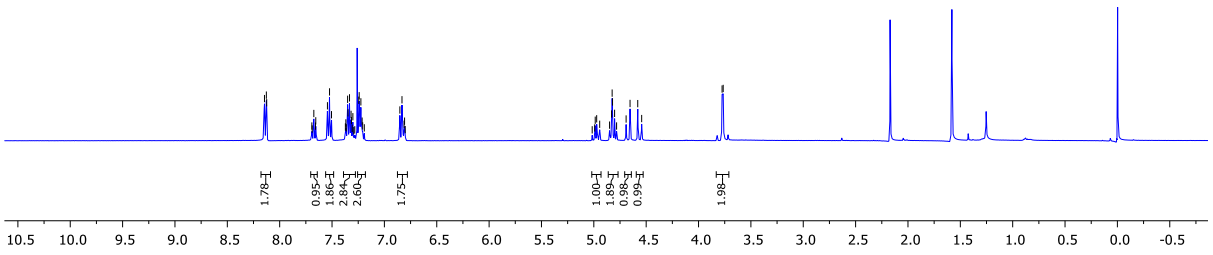
N
Bn

3u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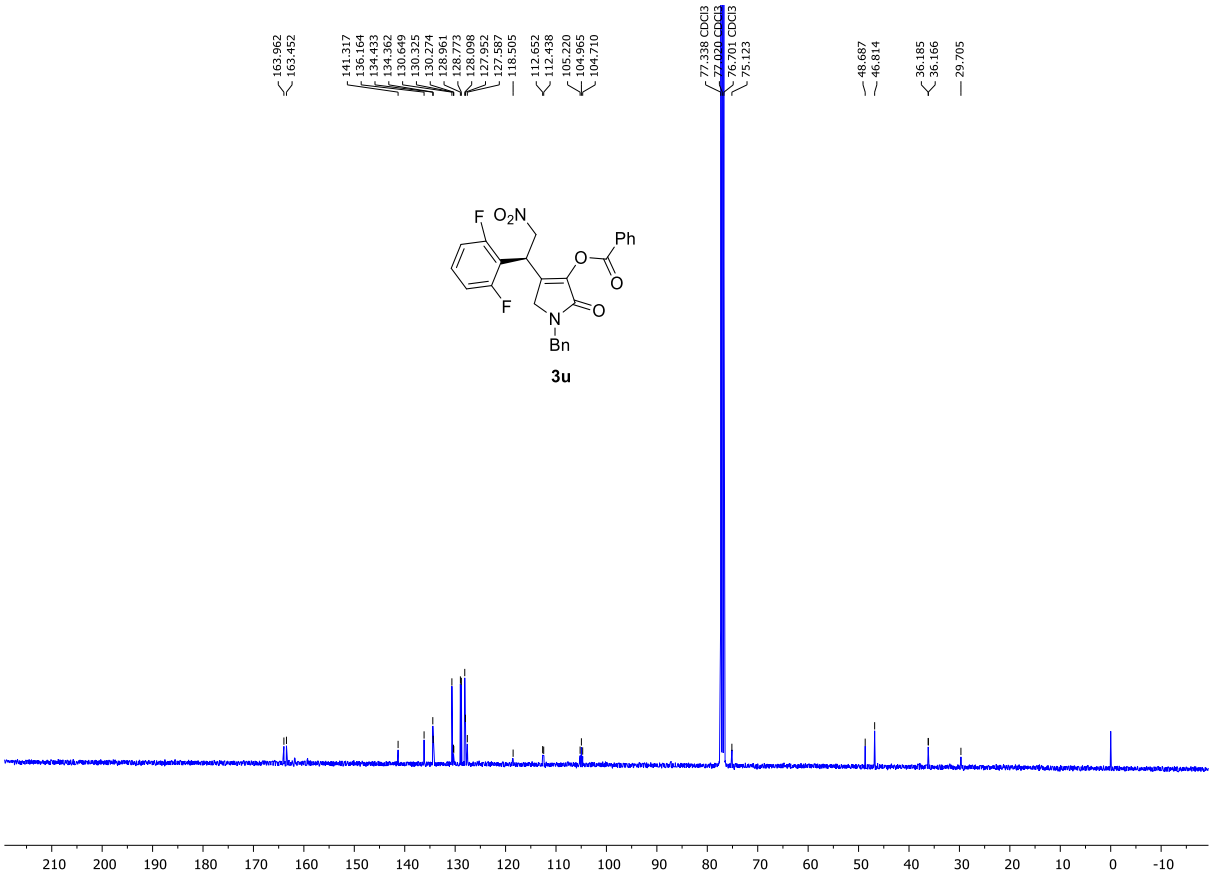
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77.020 CDCl3
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F
O2N
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F
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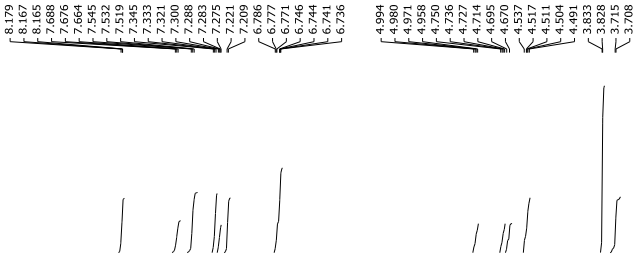
N
Bn

3u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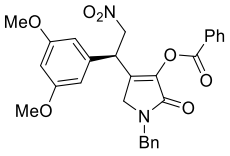
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O2N
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MeO
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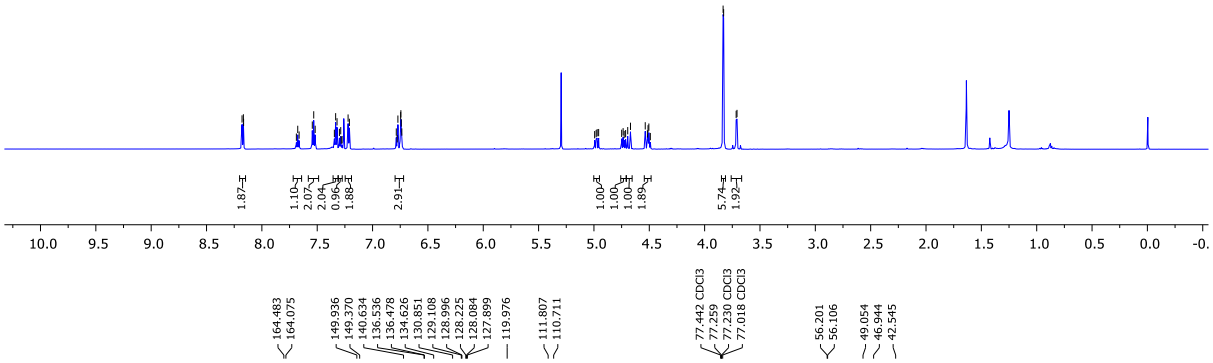
Bn

3v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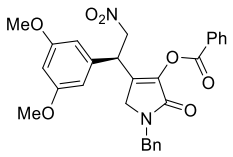
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MeO
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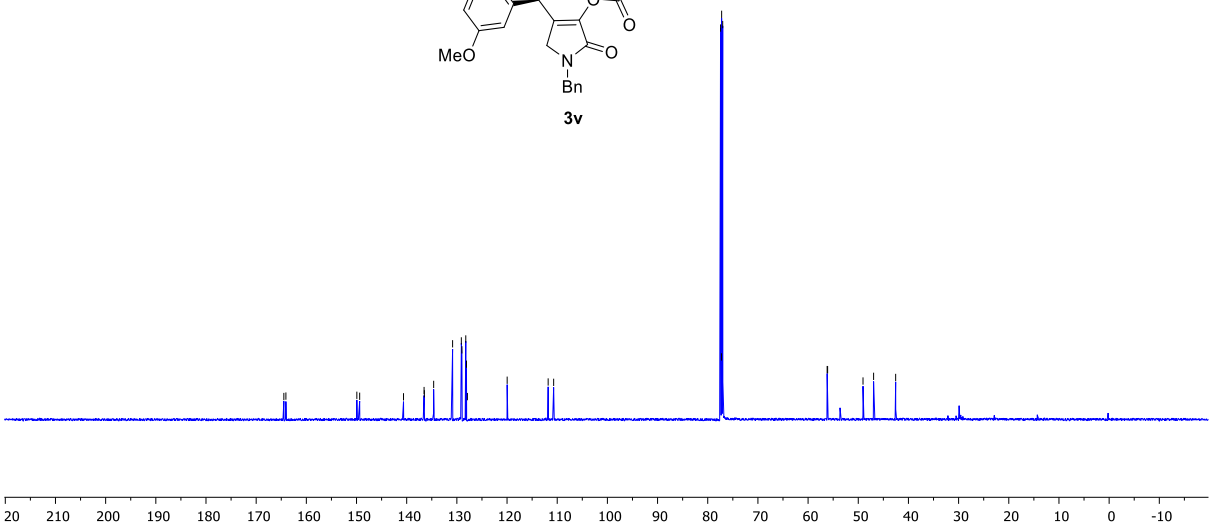
Bn

3v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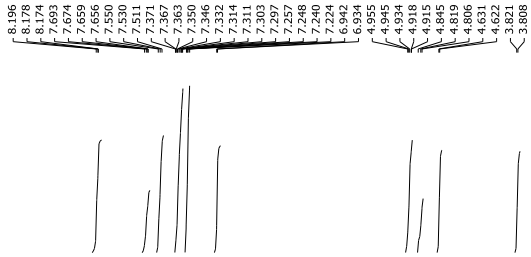
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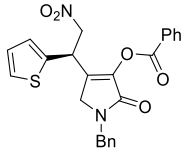
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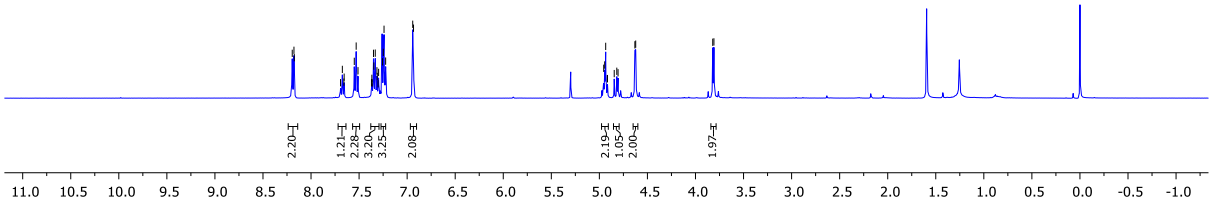
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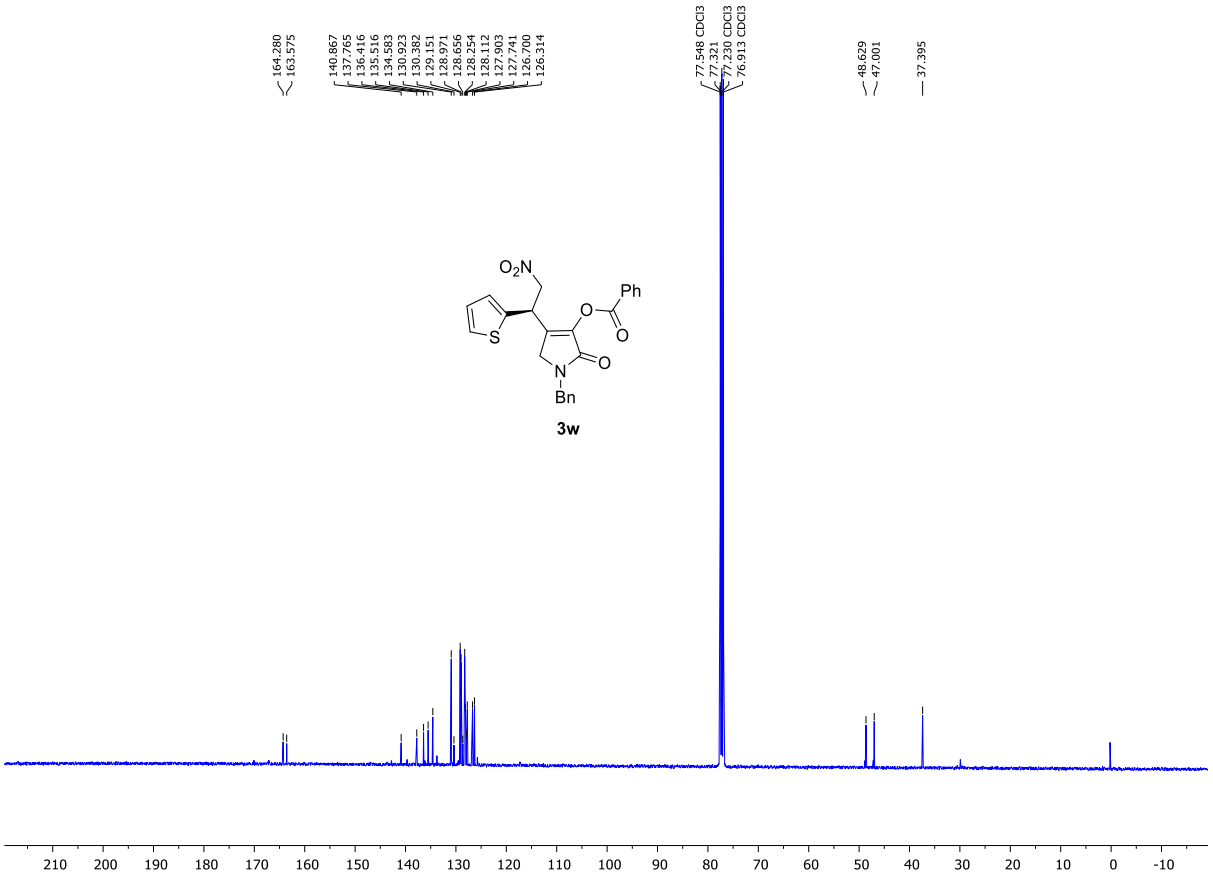
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127.741
126.700
126.314
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76.913 CDCl3
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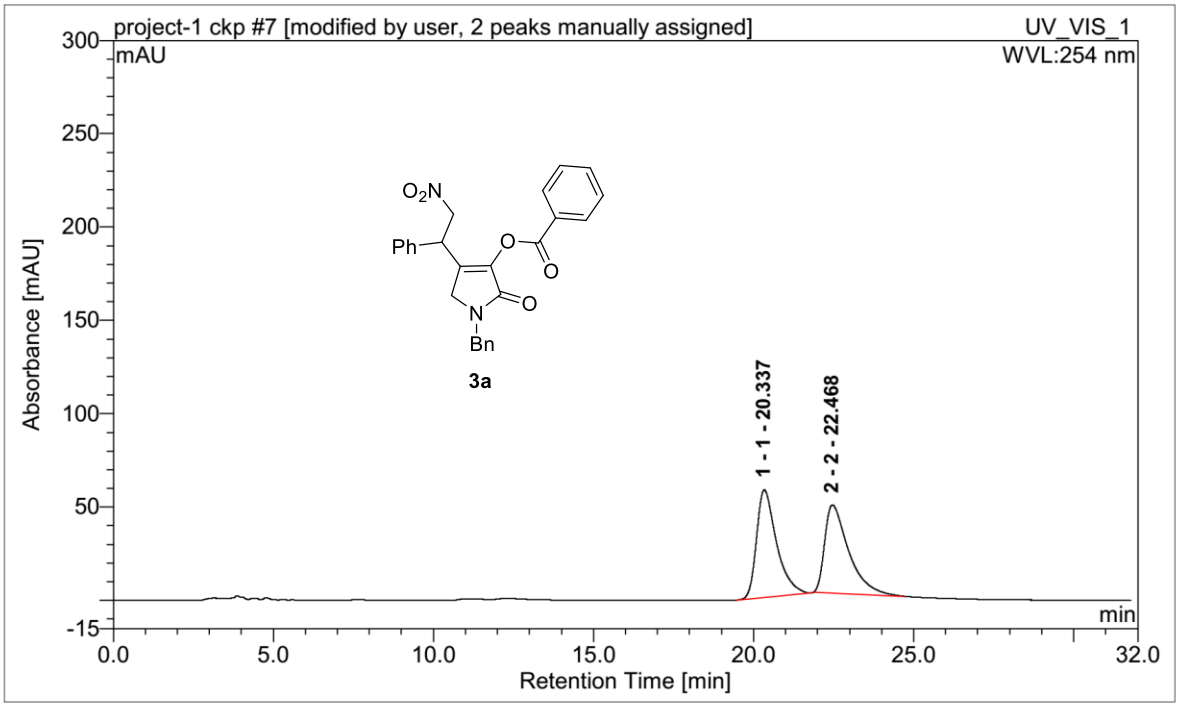
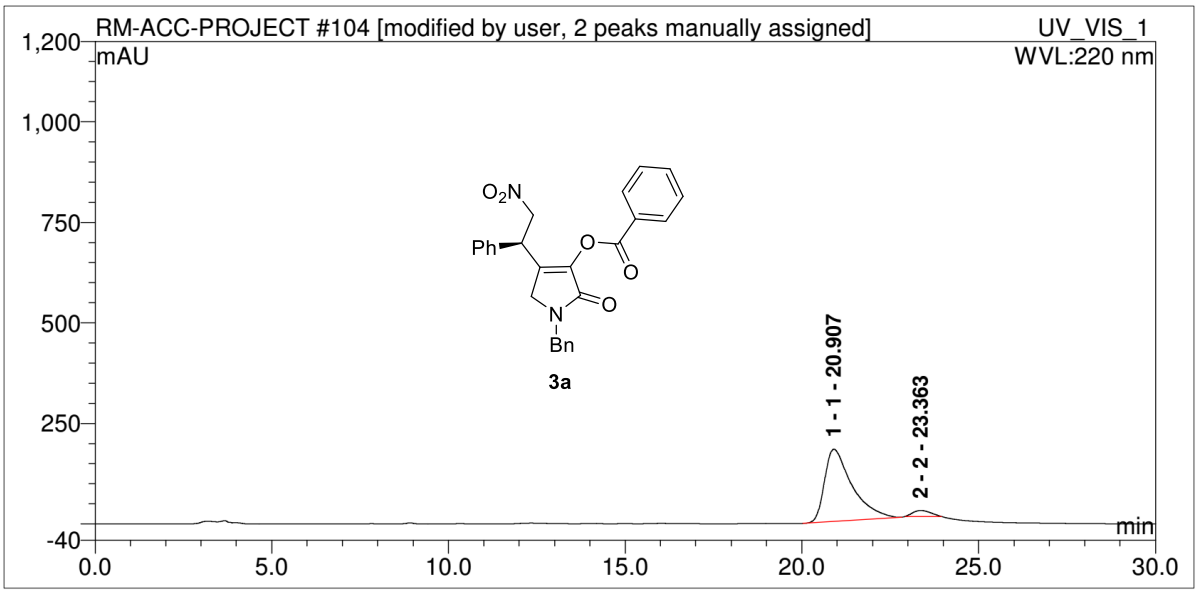
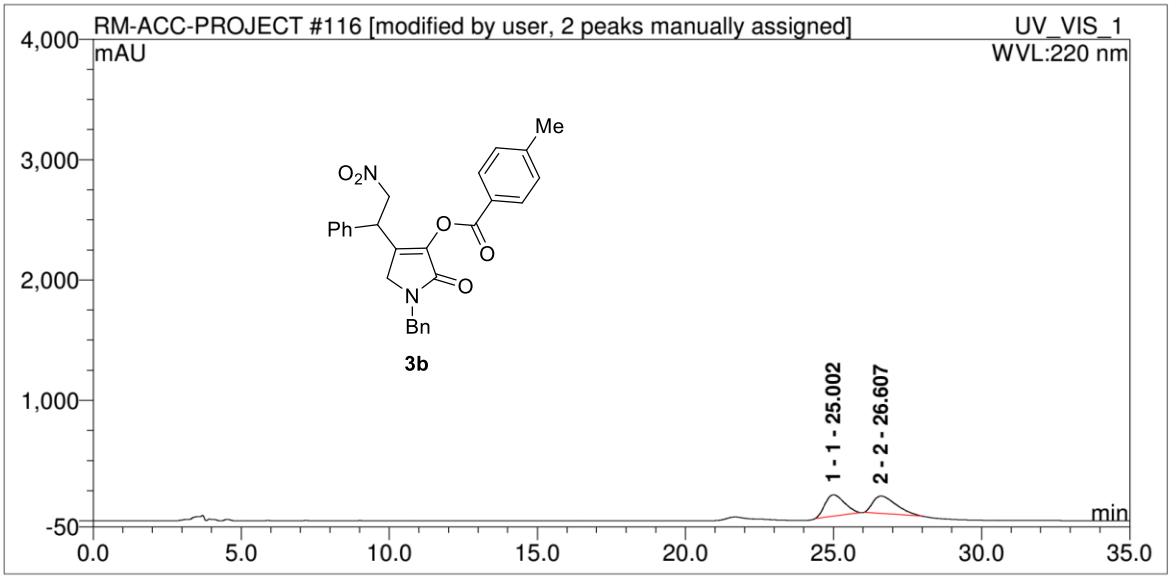
10. HPLC spectra of the products:



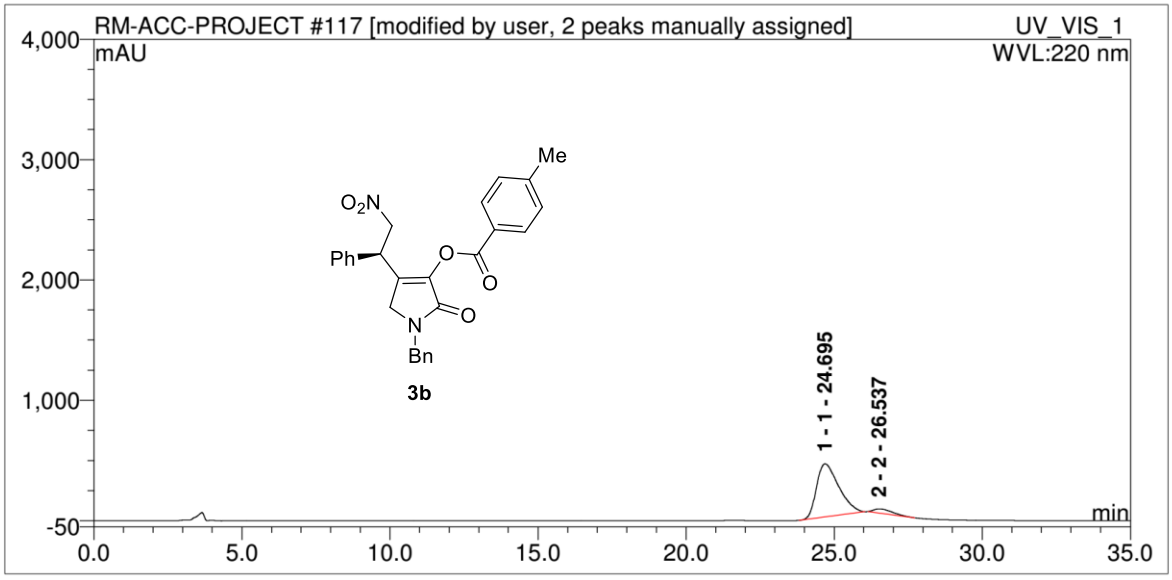
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	20.34	41.85811	50.38787979	57.64804	n.a.
2	2	22.47	41.214	49.61212021	47.394	n.a.



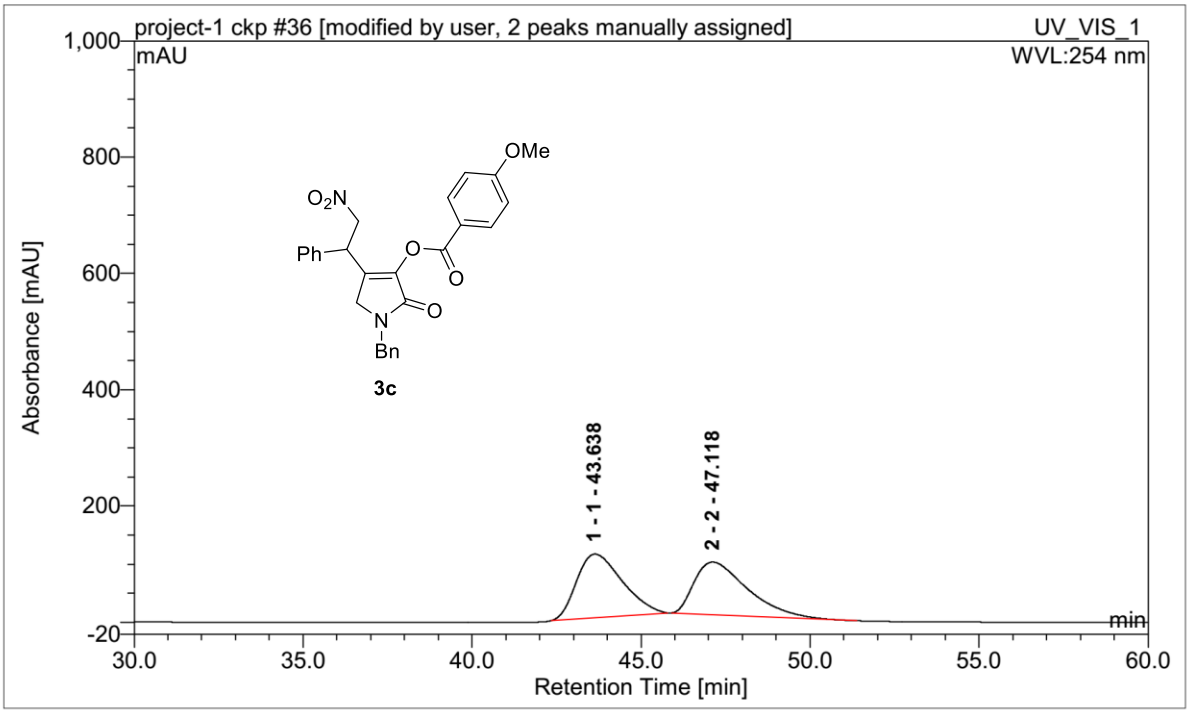
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	20.91	161.7176	94.83129978	179.7468	n.a.
2	2	23.36	8.814	5.168700222	14.981	n.a.



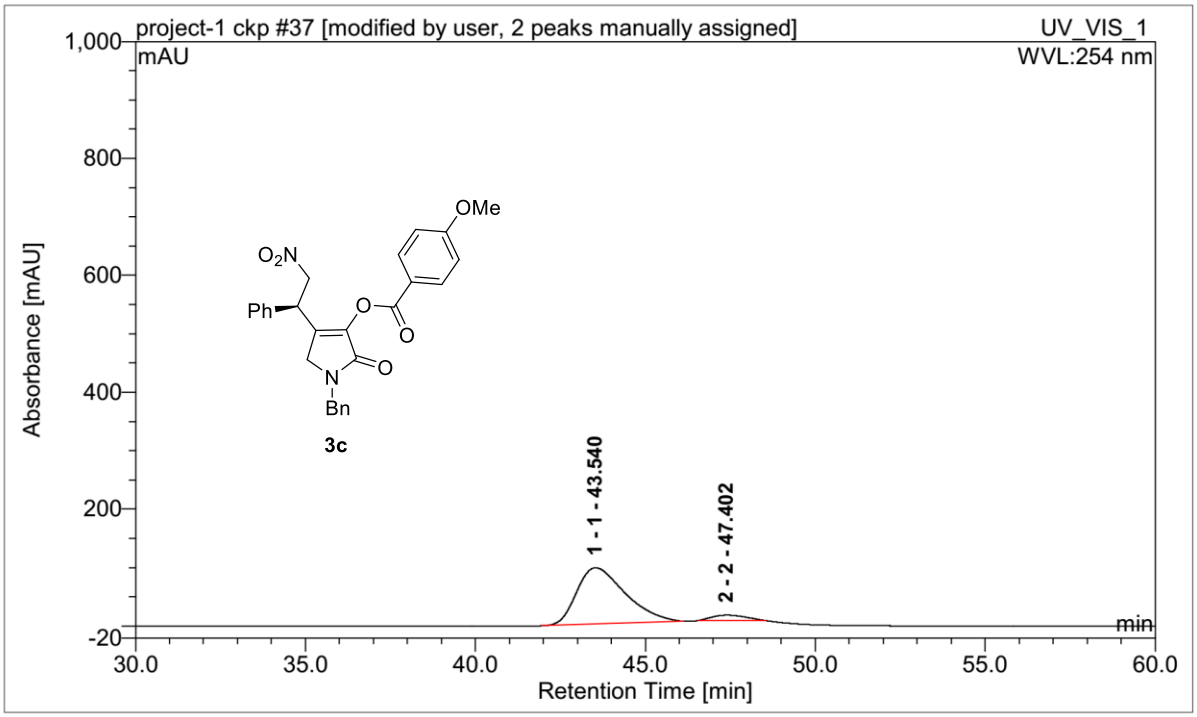
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	25.00	134.1507	50.49742646	177.5183	n.a.
2	2	26.61	131.508	49.50257354	143.190	n.a.



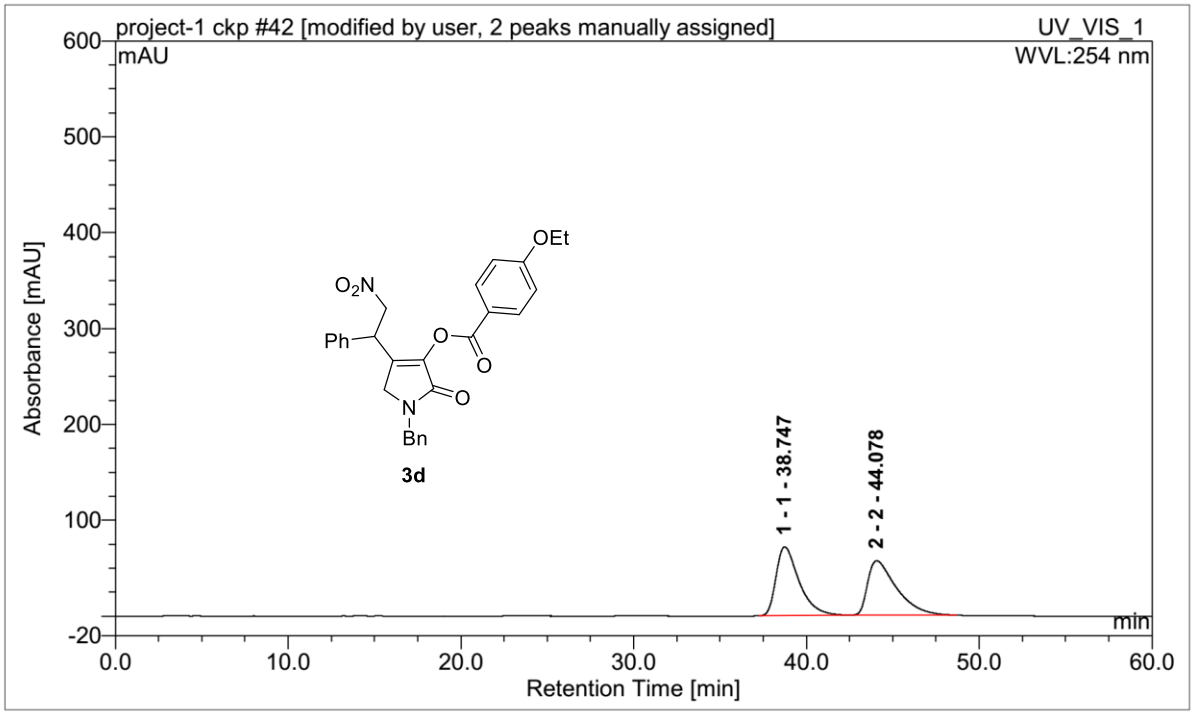
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	24.70	384.0506	93.66713089	440.6287	n.a.
2	2	26.54	25.966	6.332869113	34.231	n.a.



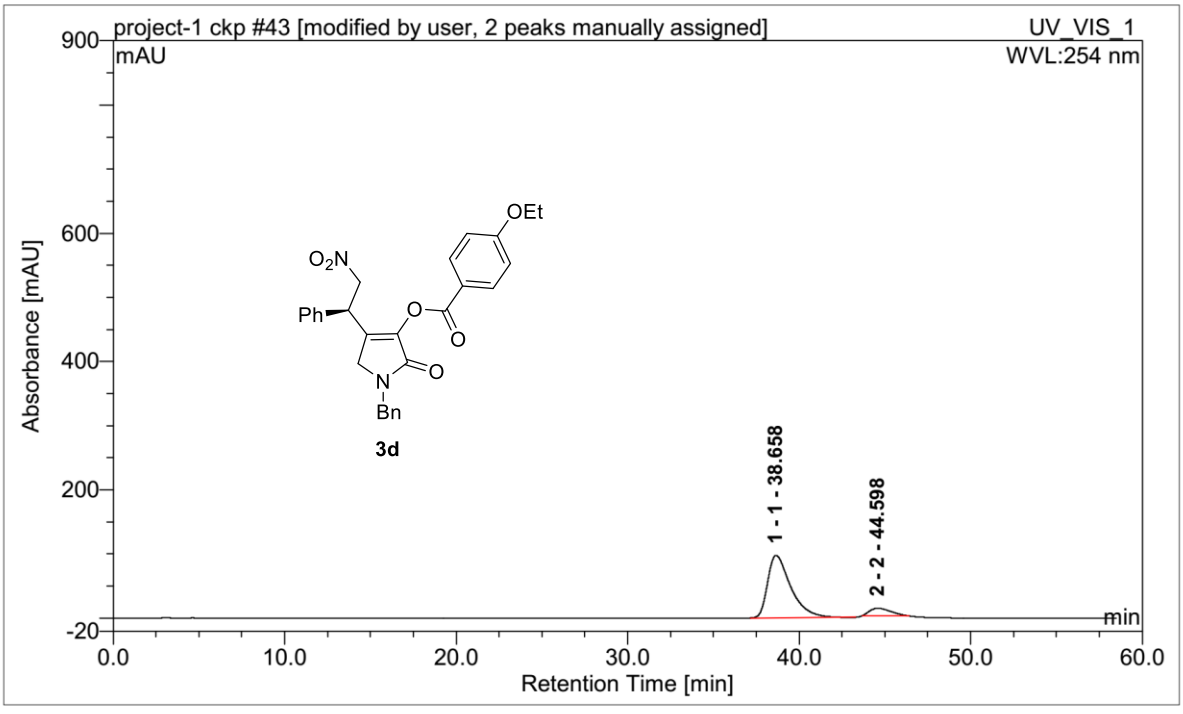
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	43.64	170.4751	50.71063113	109.3246	n.a.
2	2	47.12	165.697	49.28936887	90.290	n.a.



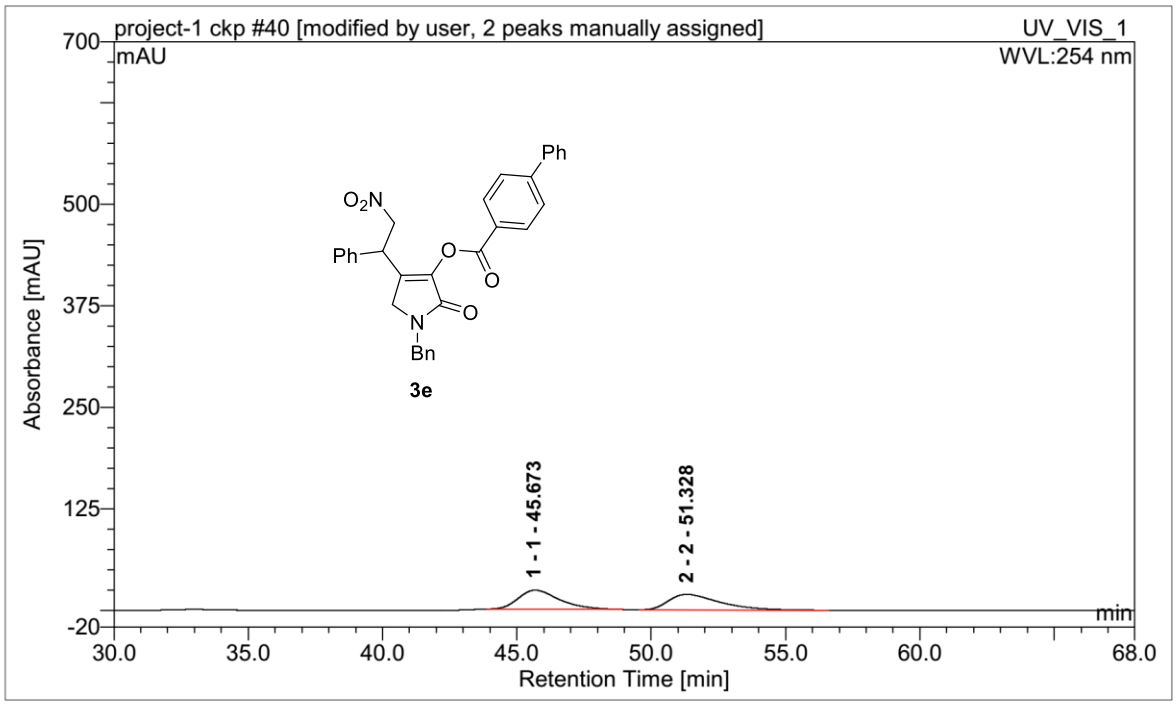
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	43.54	159.3508	93.55762674	96.30458	n.a.
2	2	47.40	10.973	6.442373257	9.368	n.a.



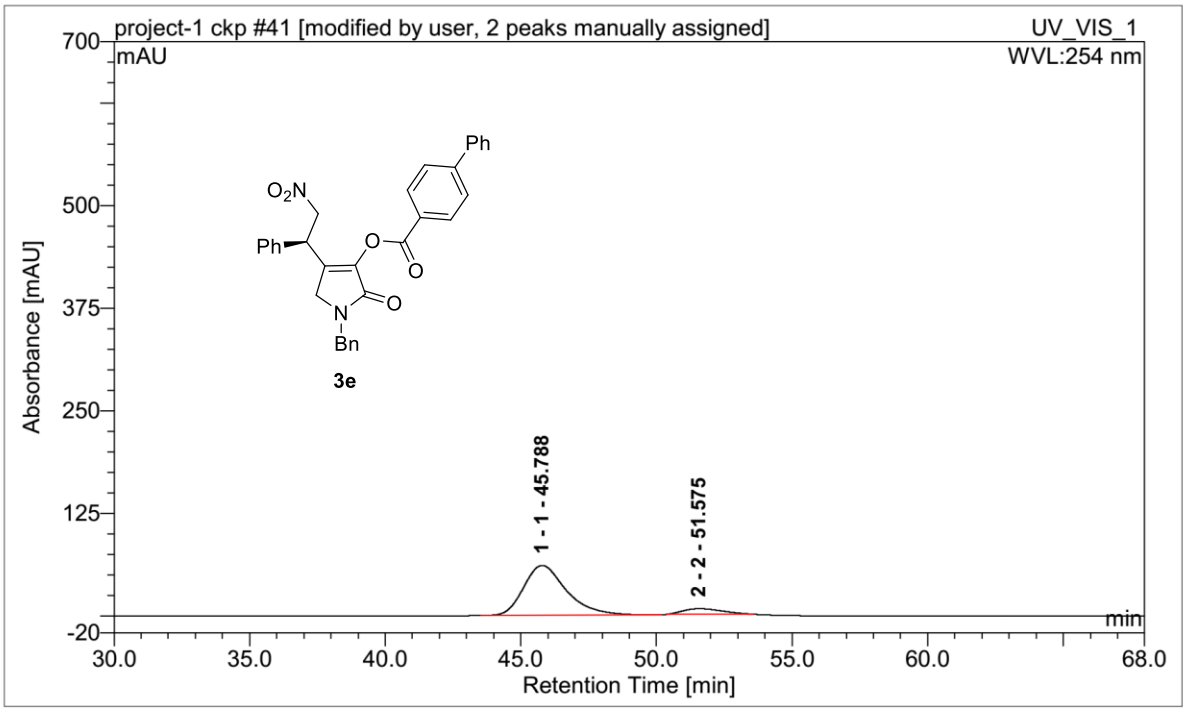
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	38.75	110.3236	50.23289711	71.69794	n.a.
2	2	44.08	109.301	49.76710289	56.554	n.a.



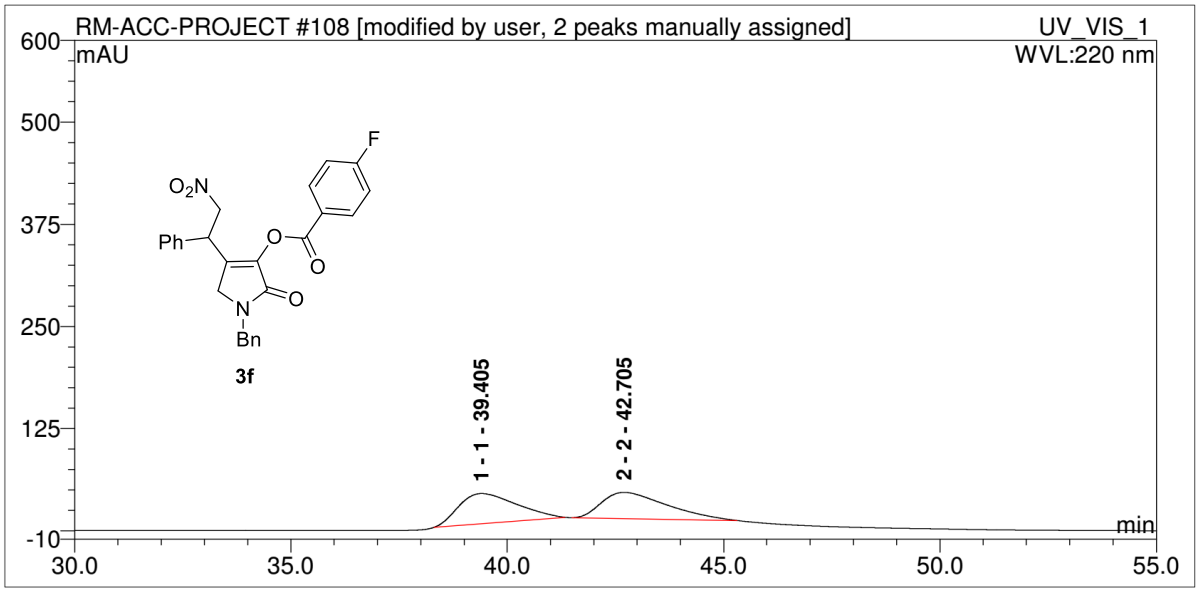
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	38.66	151.6129	89.74085595	97.43533	n.a.
2	2	44.60	17.332	10.25914405	11.910	n.a.



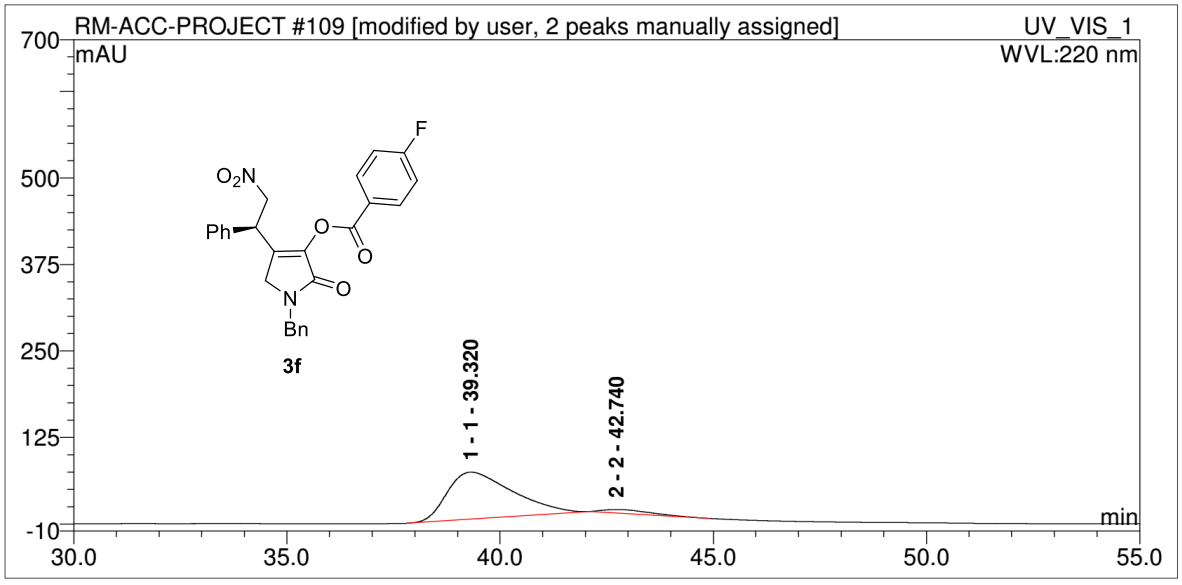
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	45.67	42.00401	49.96577891	23.43344	n.a.
2	2	51.33	42.062	50.03422109	19.054	n.a.



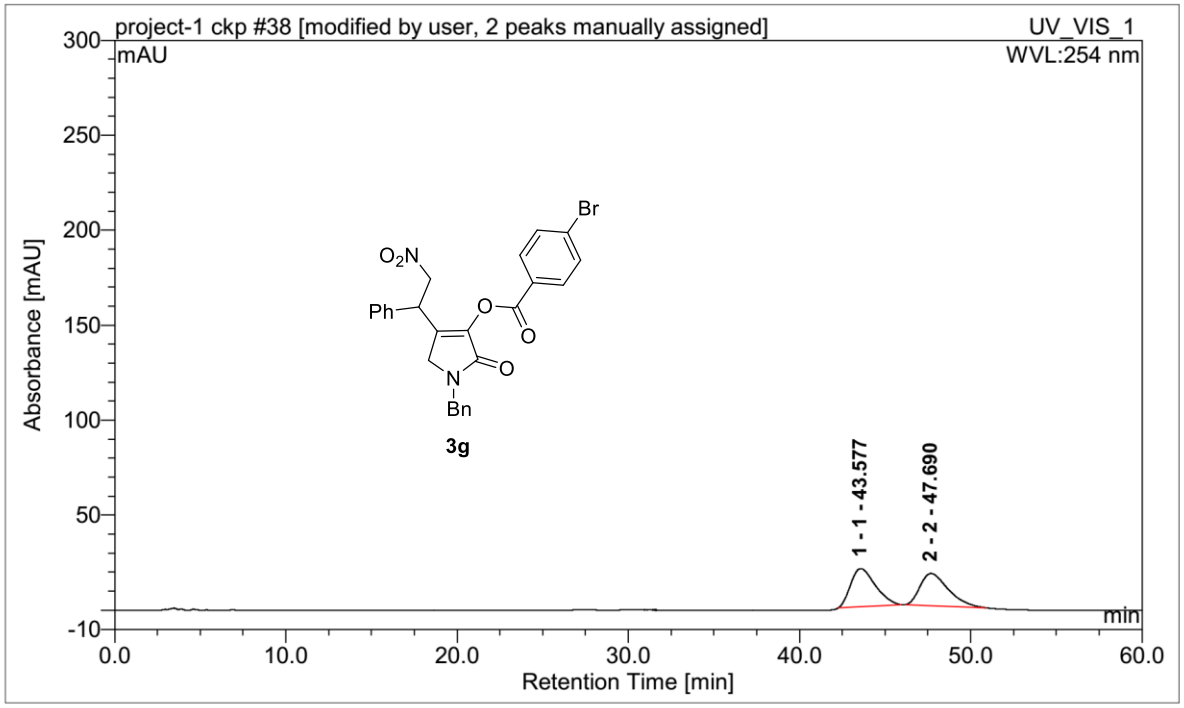
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	45.79	110.8823	90.50385156	60.79811	n.a.
2	2	51.58	11.634	9.496148443	6.870	n.a.



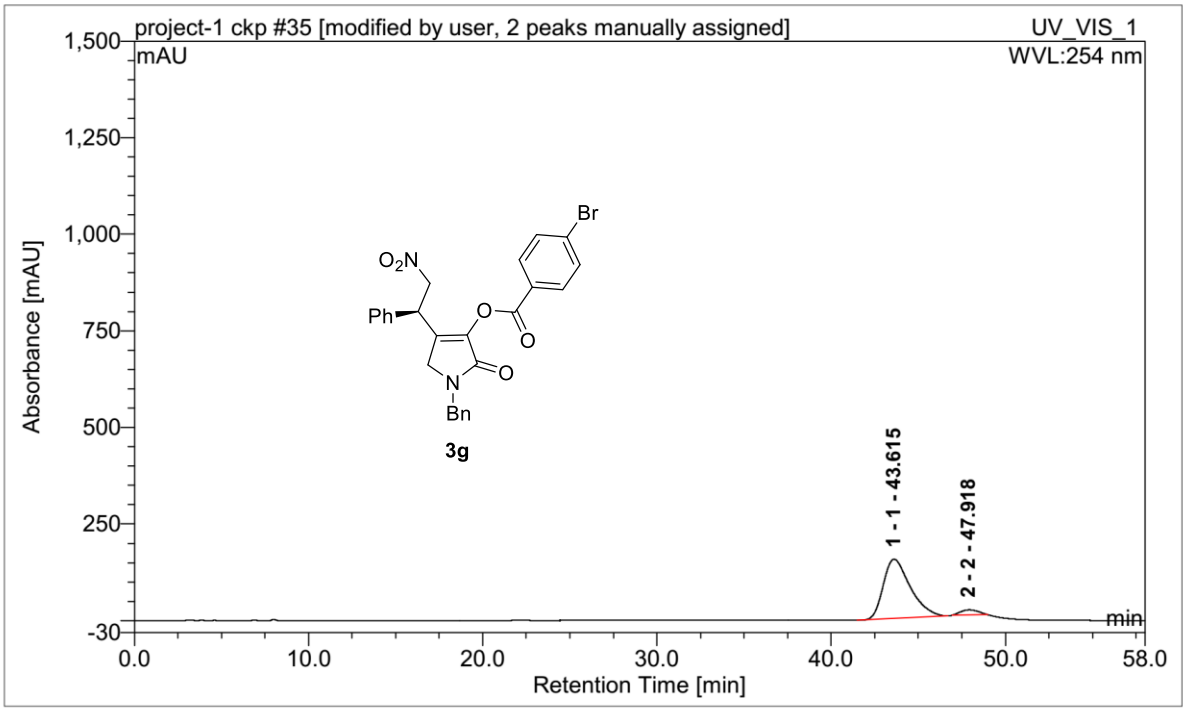
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	39.41	57.21393	50.46393603	36.941	n.a.
2	2	42.71	56.162	49.53606397	32.017	n.a.



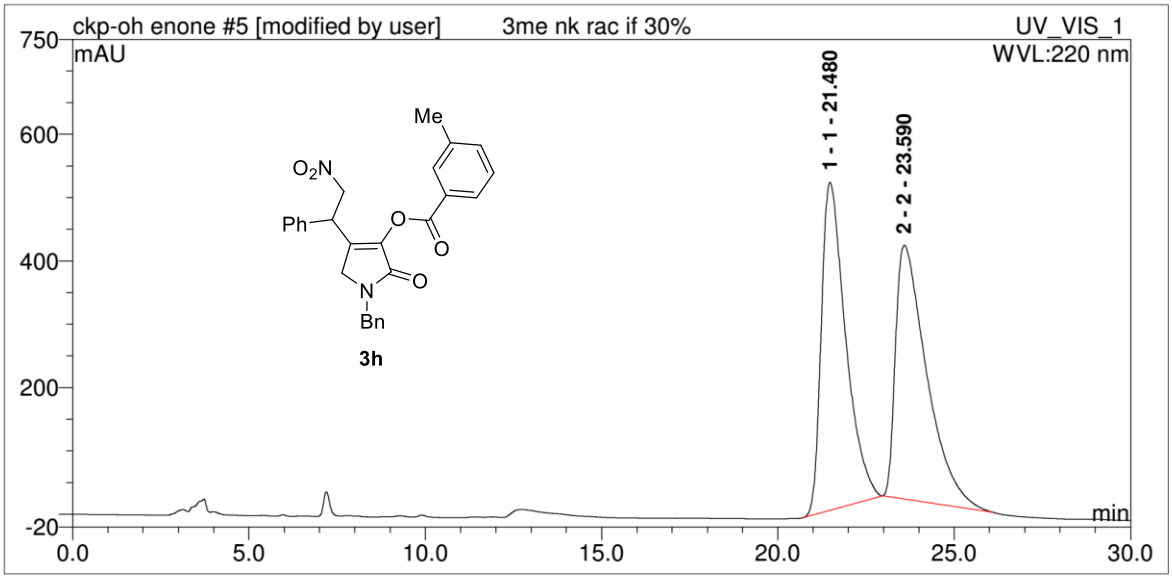
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	39.32	119.8521	94.53301927	67.85756	n.a.
2	2	42.74	6.931	5.466980731	5.153	n.a.



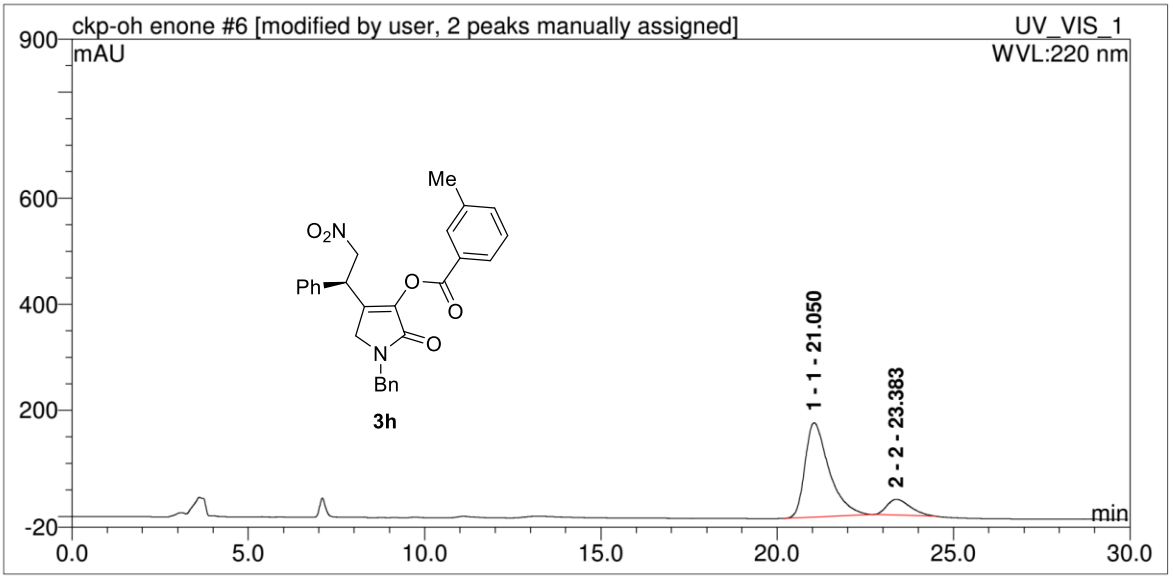
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	43.58	33.53818	50.82017884	20.08853	n.a.
2	2	47.69	32.456	49.17982116	16.978	n.a.



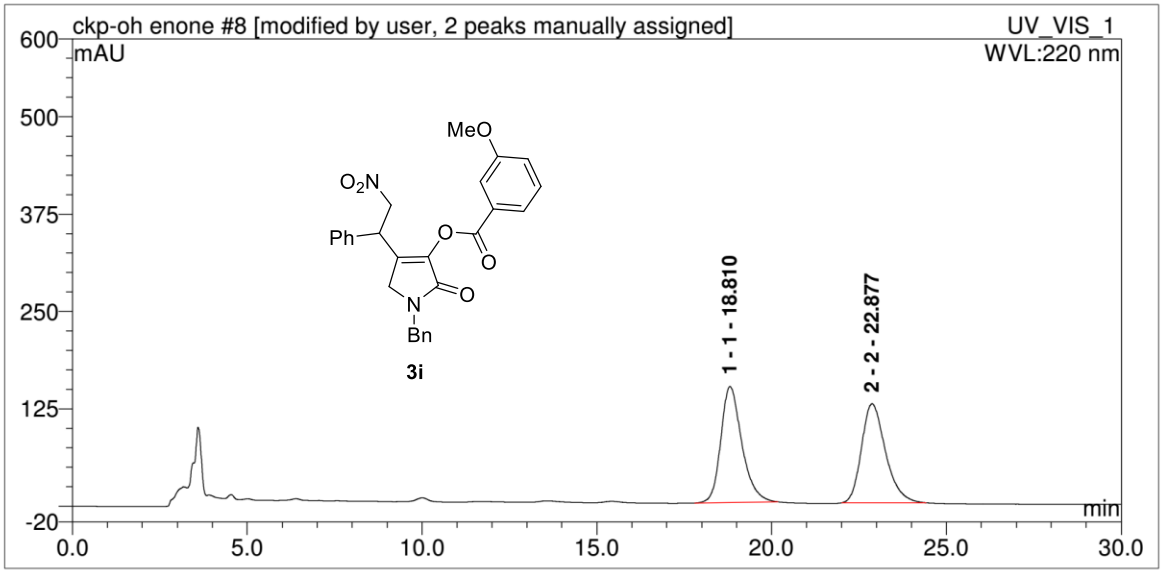
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	43.62	275.2487	94.52827747	153.6061	n.a.
2	2	47.92	15.933	5.47172253	13.348	n.a.



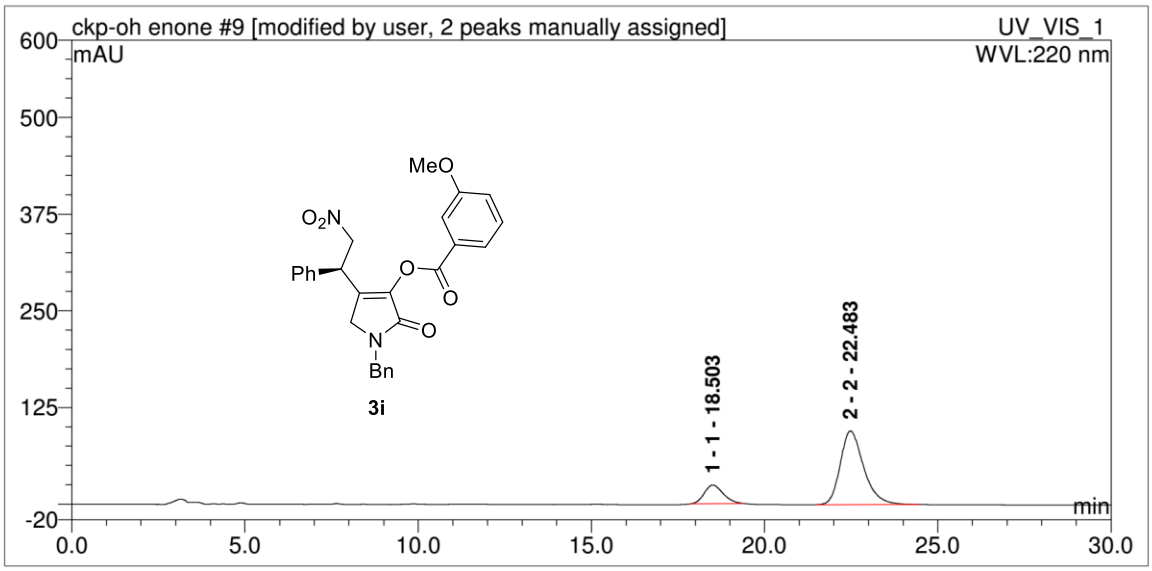
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	21.48	414.3443	50.20578505	518.0697	n.a.
2	2	23.59	410.948	49.79421495	400.873	n.a.



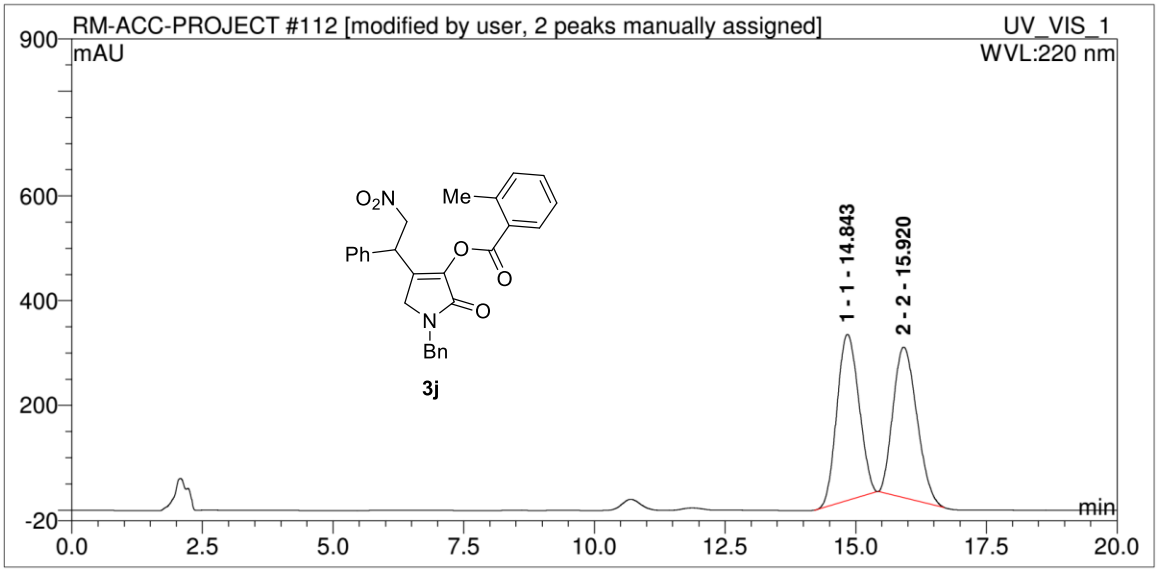
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	21.05	140.9552	86.09649053	177.7406	n.a.
2	2	23.38	22.763	13.90350947	29.591	n.a.



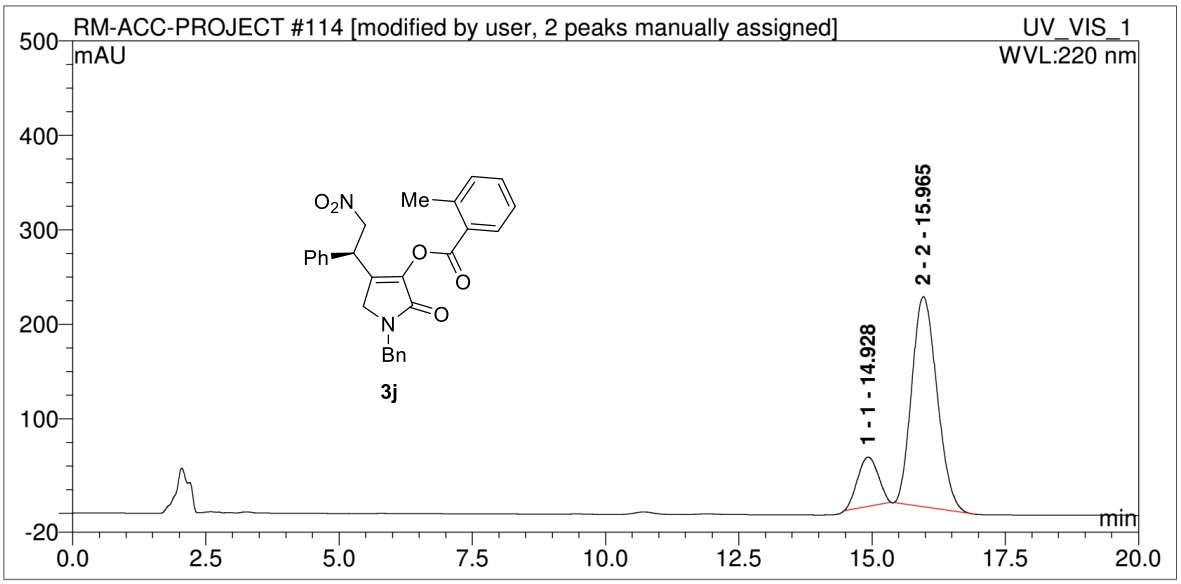
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	18.81	104.2595	50.75992276	148.9903	n.a.
2	2	22.88	101.138	49.24007724	127.020	n.a.



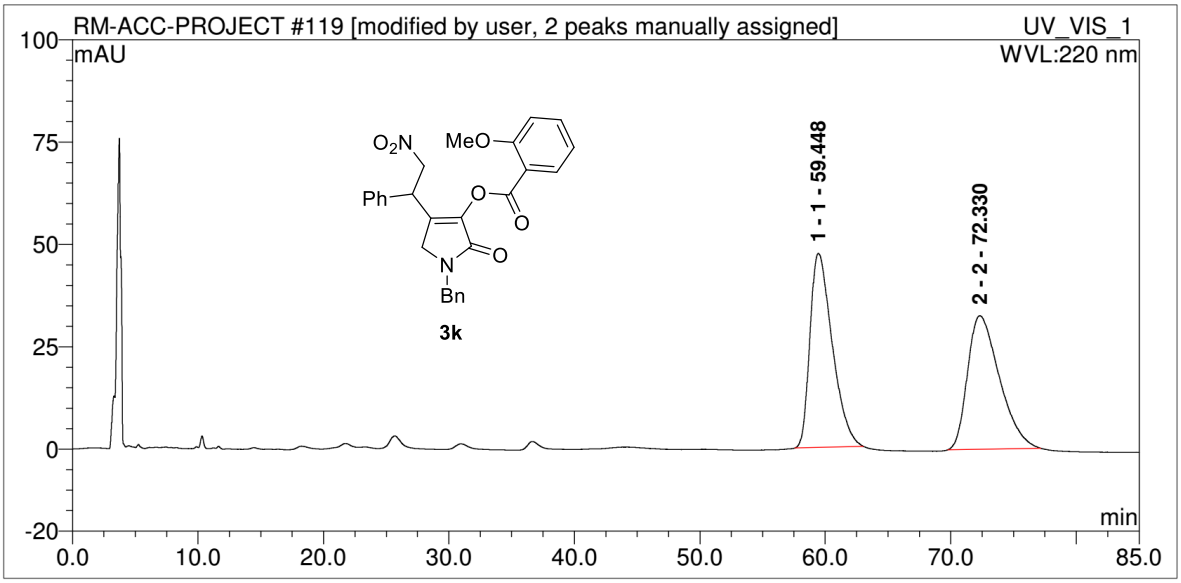
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	18.50	15.2793	17.00958056	24.15859	n.a.
2	2	22.48	74.548	82.99041944	95.068	n.a.



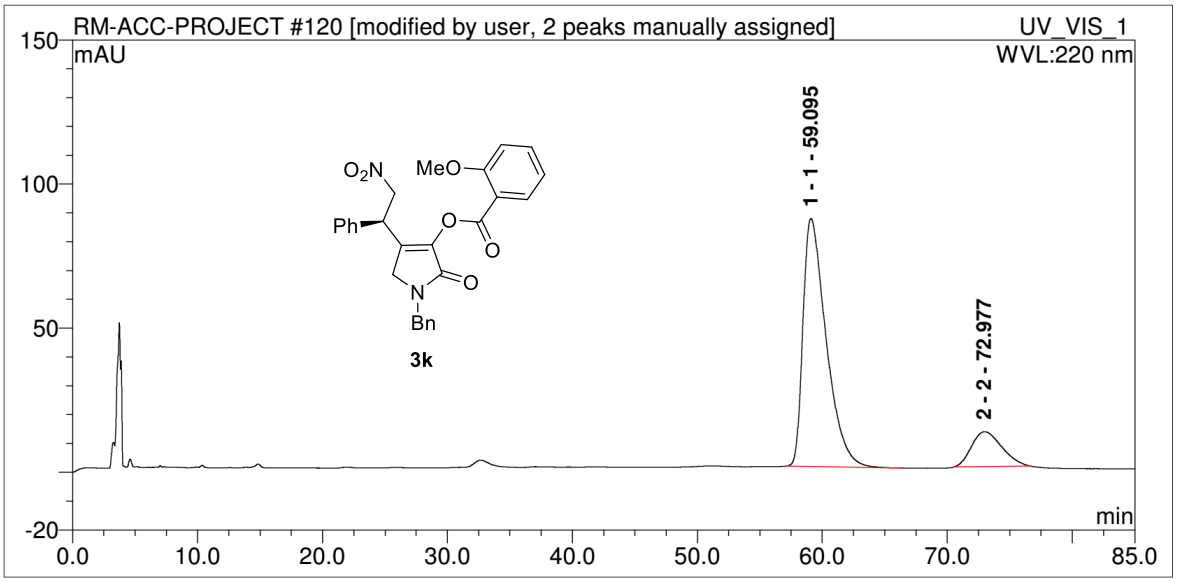
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	14.84	154.1613	50.35579852	316.8359	n.a.
2	2	15.92	151.983	49.64420148	287.411	n.a.



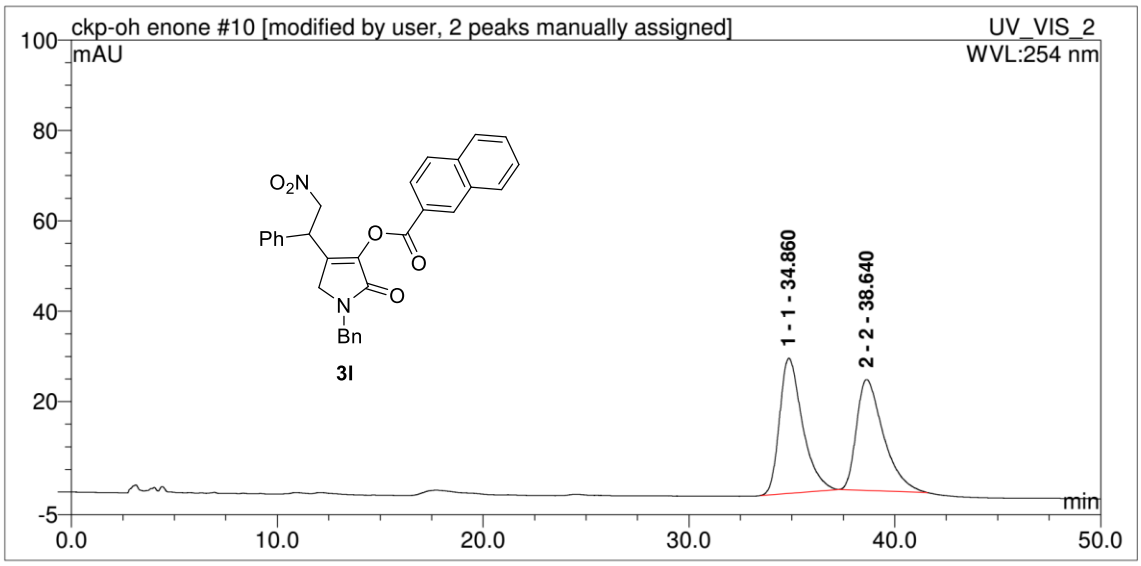
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	14.93	23.30586	16.01132578	52.02937	n.a.
2	2	15.97	122.253	83.98867422	222.411	n.a.



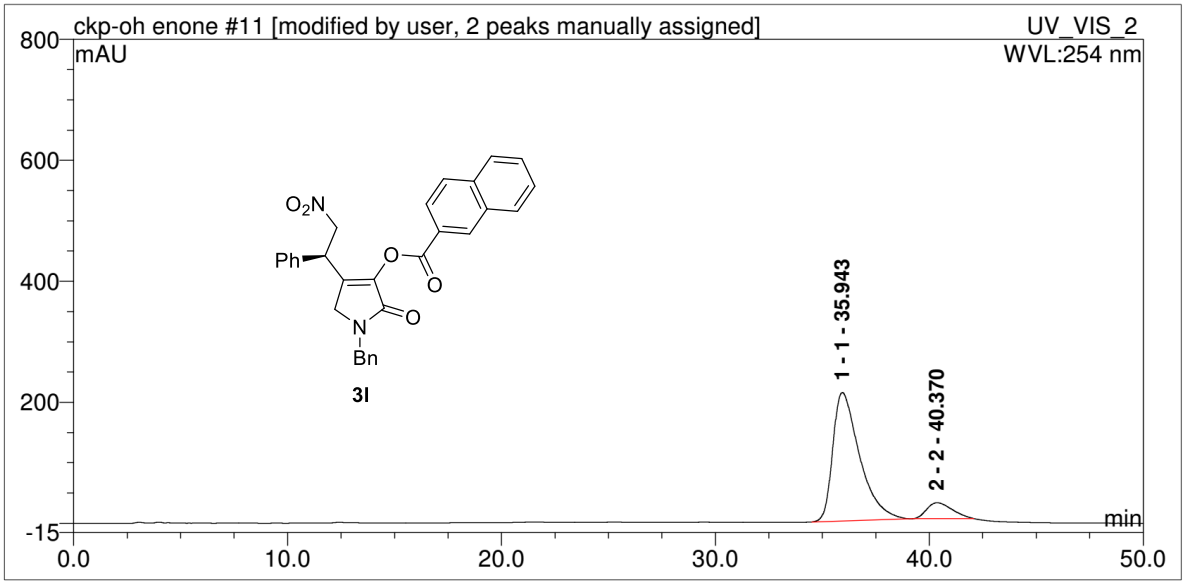
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	59.45	97.71814	50.42766045	47.38599	n.a.
2	2	72.33	96.061	49.57233955	32.610	n.a.



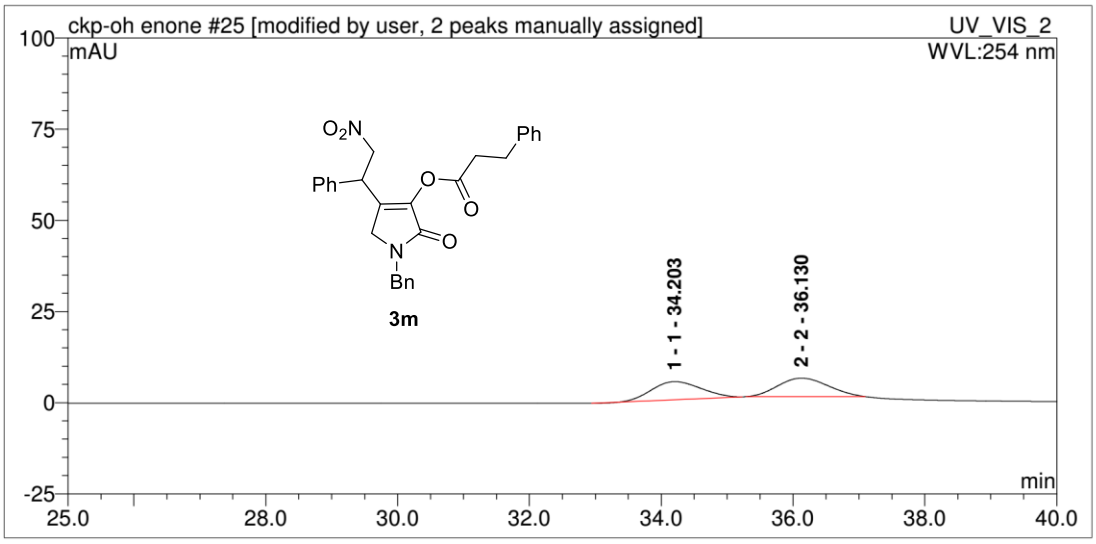
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	59.10	184.8975	84.49419517	86.0416	n.a.
2	2	72.98	33.931	15.50580483	12.084	n.a.



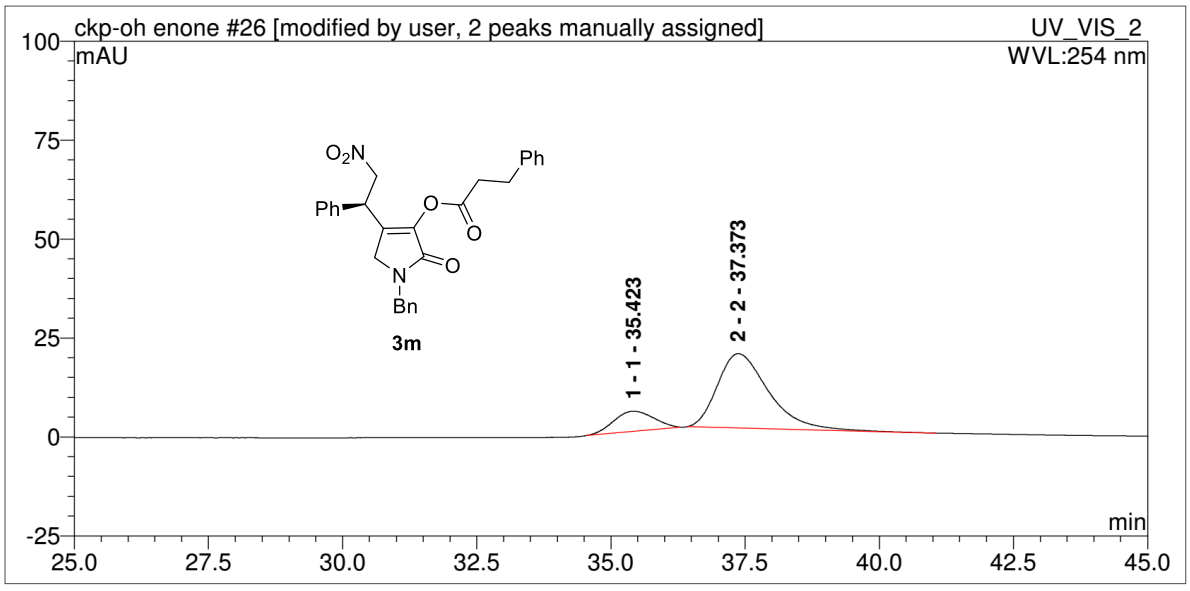
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	34.86	38.71484	50.95594947	29.89739	n.a.
2	2	38.64	37.262	49.04405053	24.533	n.a.



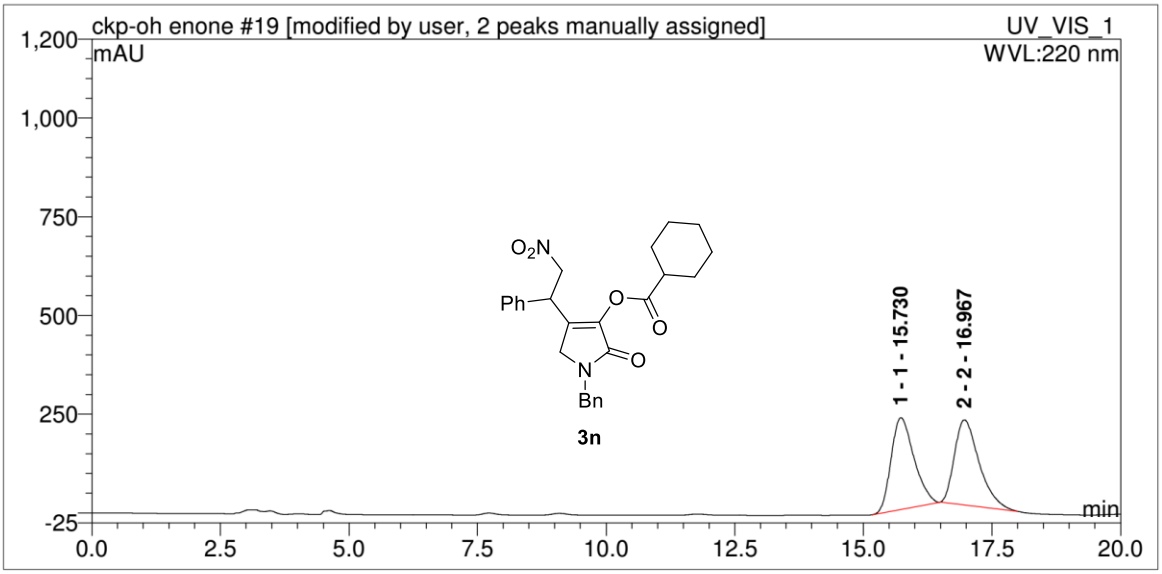
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	35.94	308.0256	89.59628812	212.0375	n.a.
2	2	40.37	35.767	10.40371188	26.049	n.a.



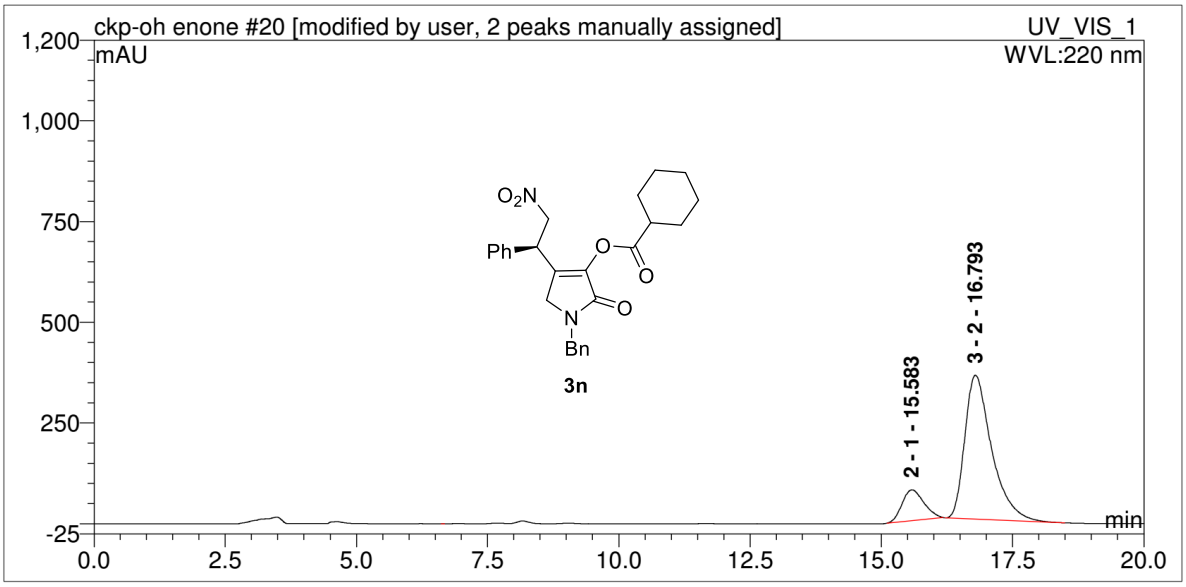
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	34.20	4.301127	48.88141027	4.97301	n.a.
2	2	36.13	4.498	51.11858973	5.077	n.a.



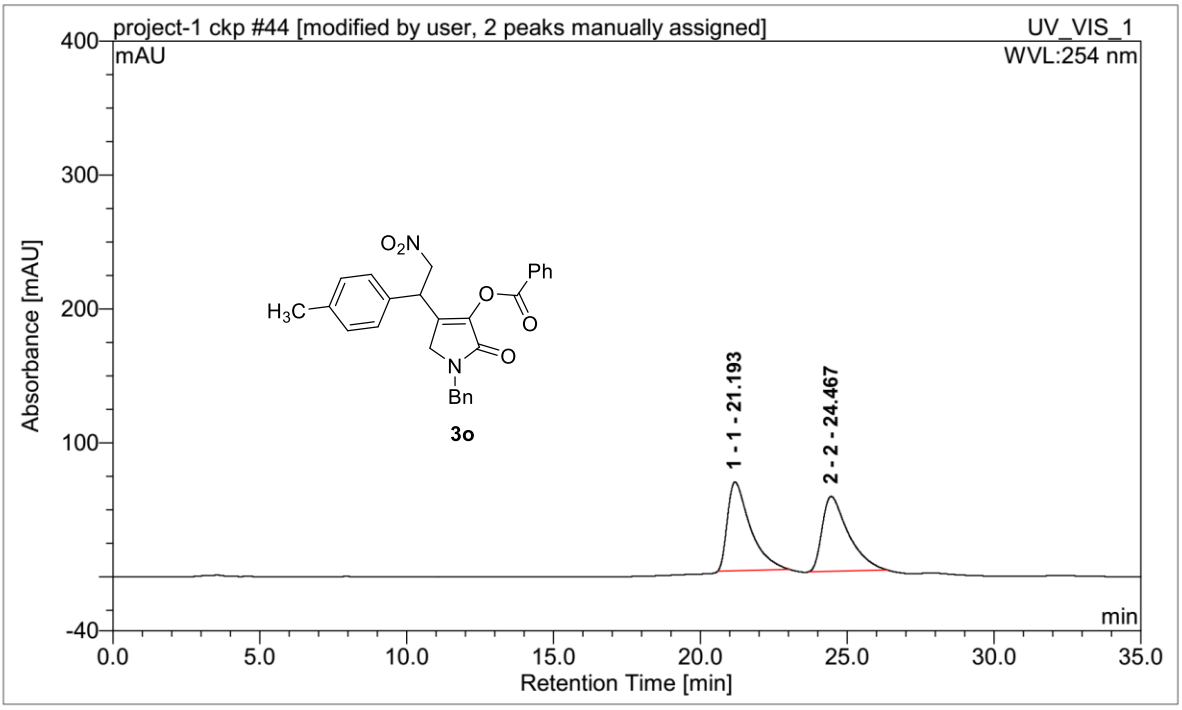
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	35.42	4.353664	17.34777353	5.06511	n.a.
2	2	37.37	20.743	82.65222647	18.790	n.a.



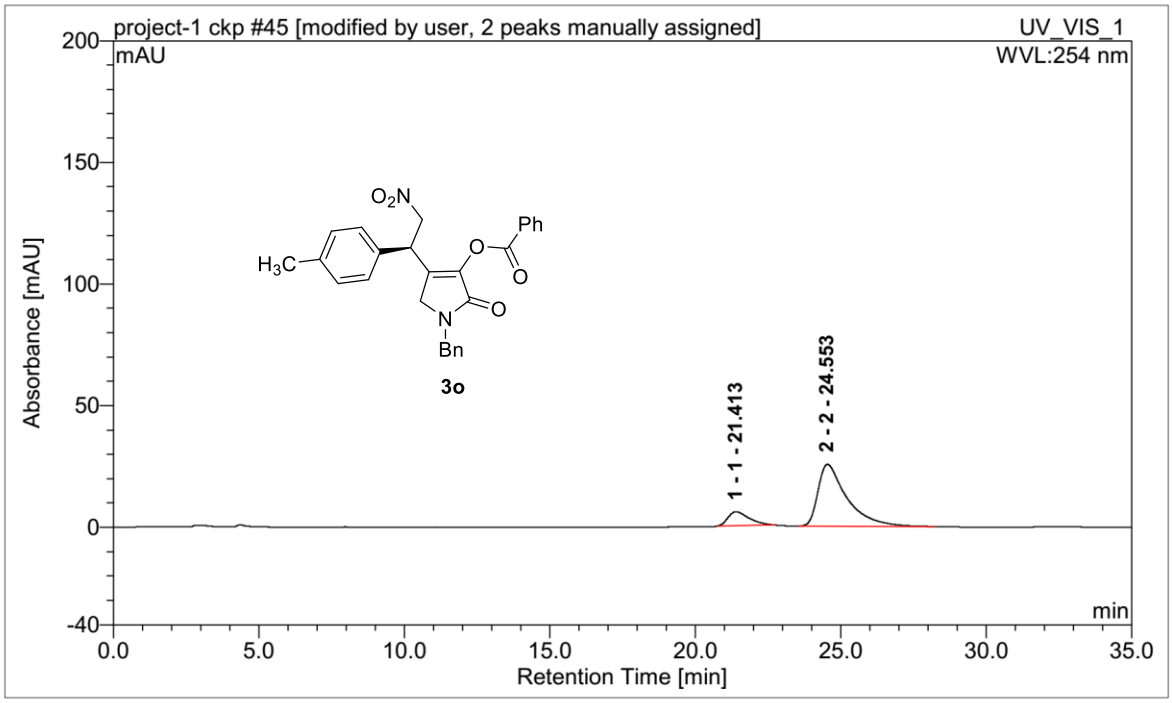
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	15.73	119.8505	49.94137103	232.0696	n.a.
2	2	16.97	120.132	50.05862897	215.356	n.a.



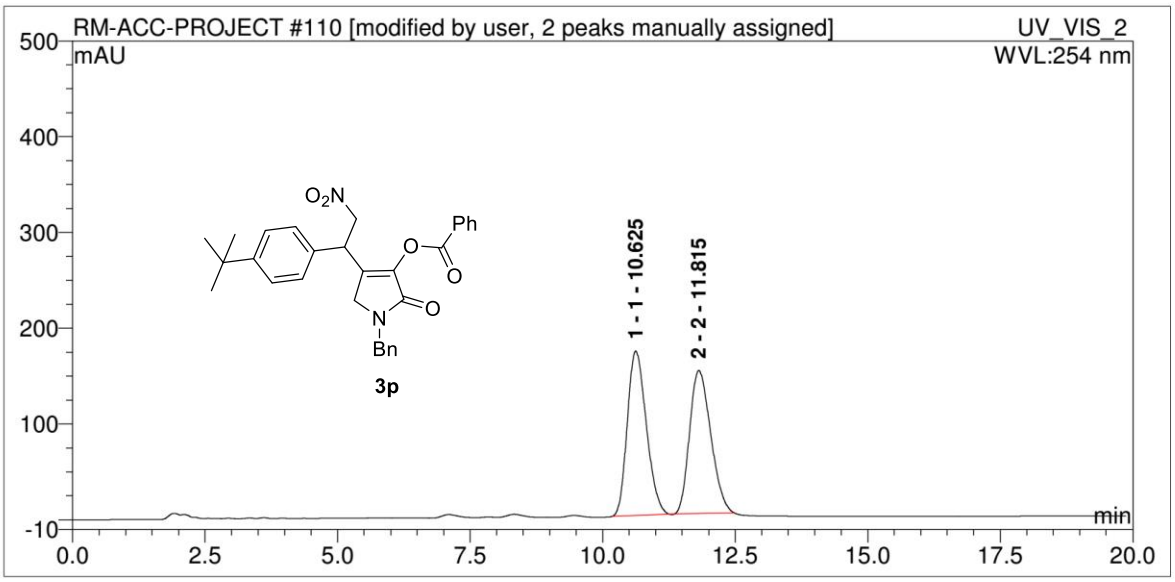
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
2	1	15.58	36.74058	14.74907585	76.5934	n.a.
3	2	16.79	212.364	85.25092415	357.231	n.a.



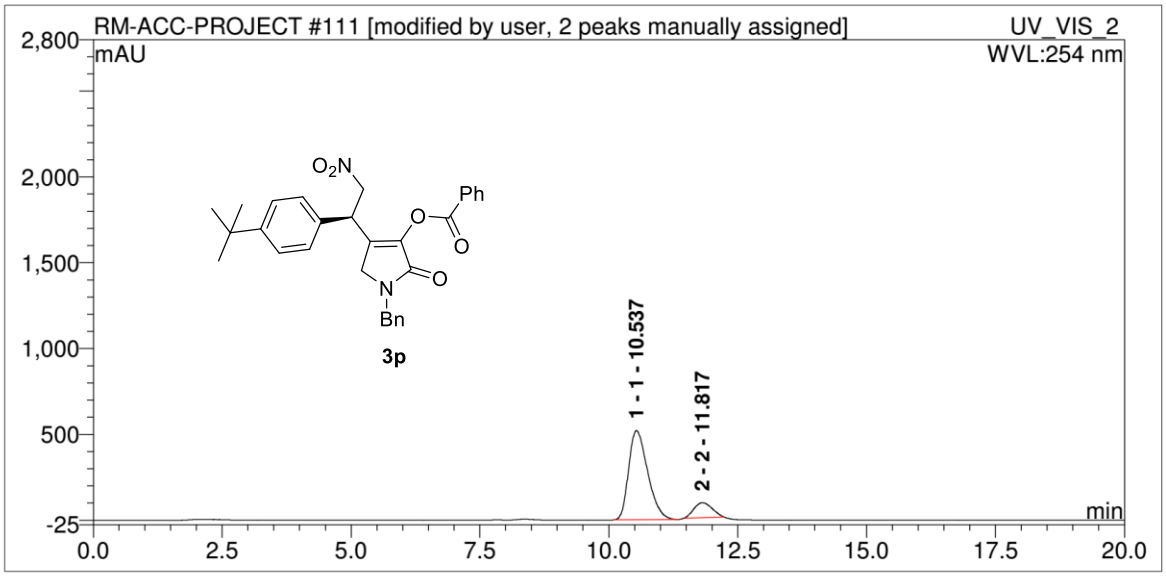
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	21.19	59.658	50.73121424	66.10262	n.a.
2	2	24.47	57.938	49.26878576	55.881	n.a.



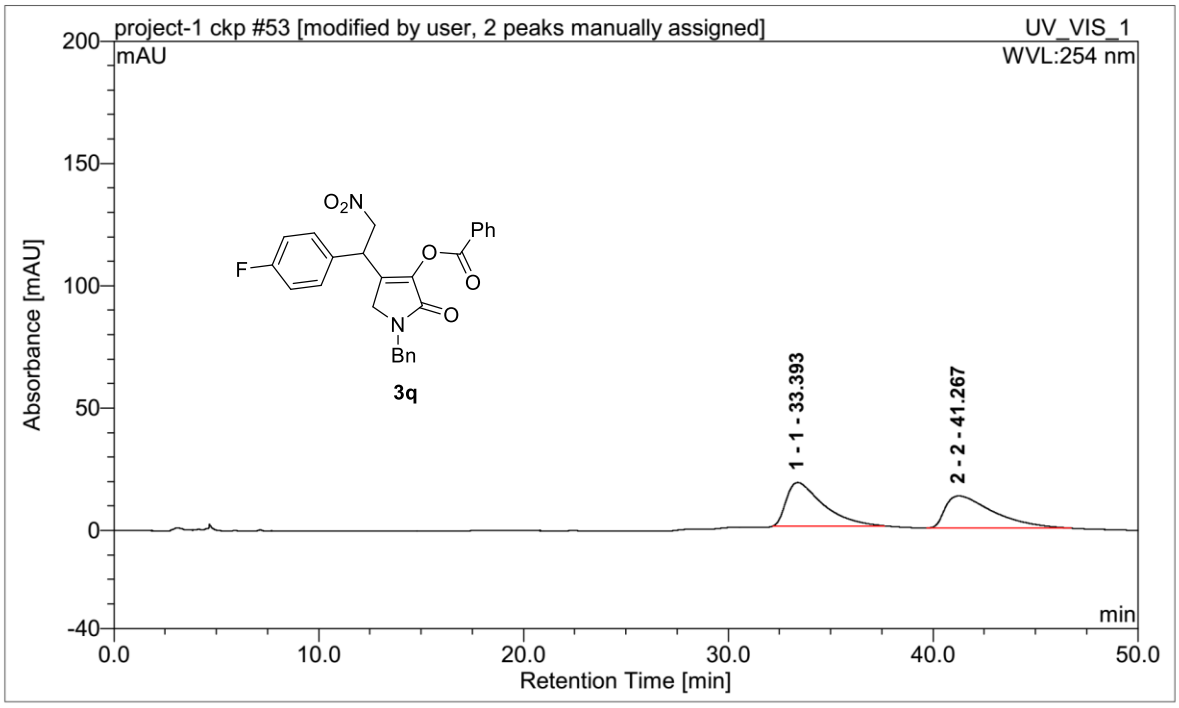
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	21.41	4.852714	14.22543367	5.73675	n.a.
2	2	24.55	29.260	85.77456633	25.409	n.a.



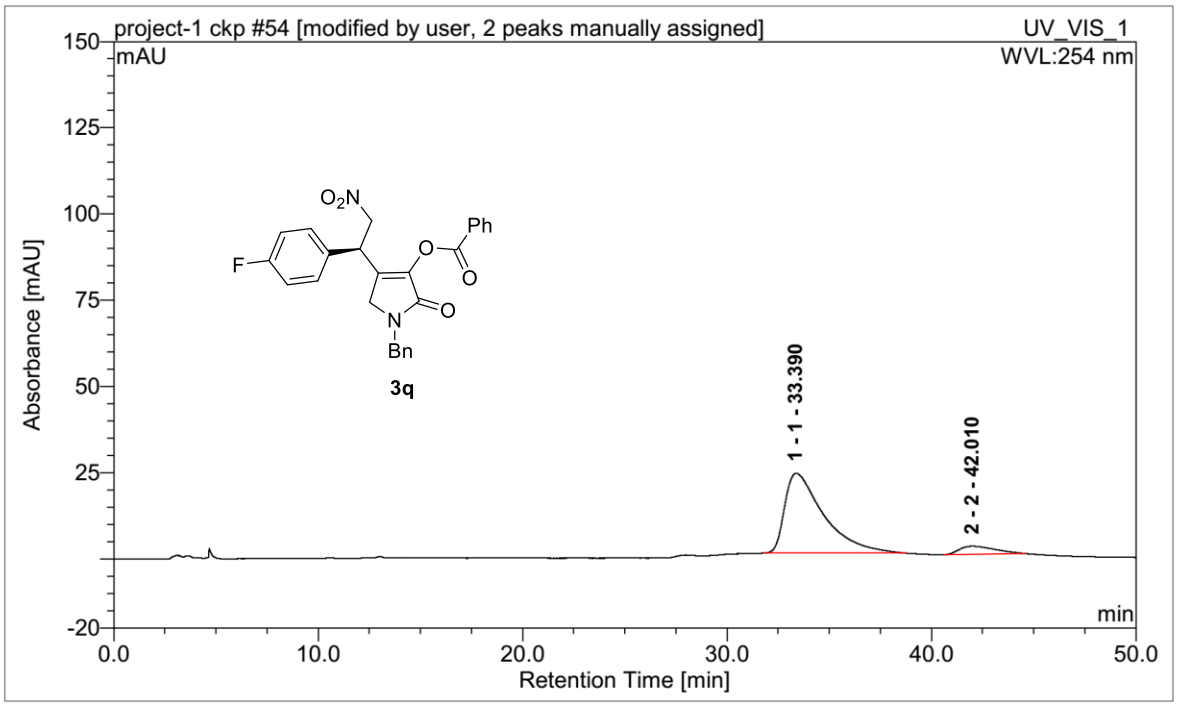
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	10.63	71.40227	50.73228303	171.5064	n.a.
2	2	11.82	69.341	49.26771697	149.375	n.a.



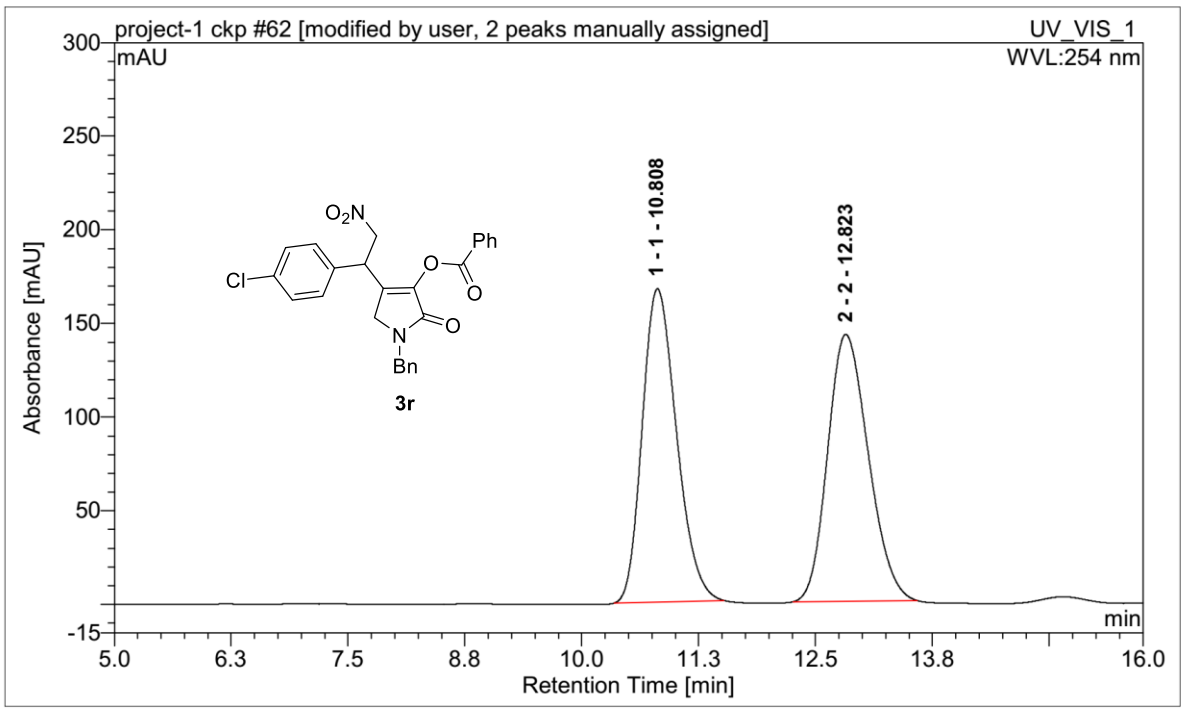
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	10.54	221.7415	86.06534162	519.0157	n.a.
2	2	11.82	35.902	13.93465838	87.205	n.a.



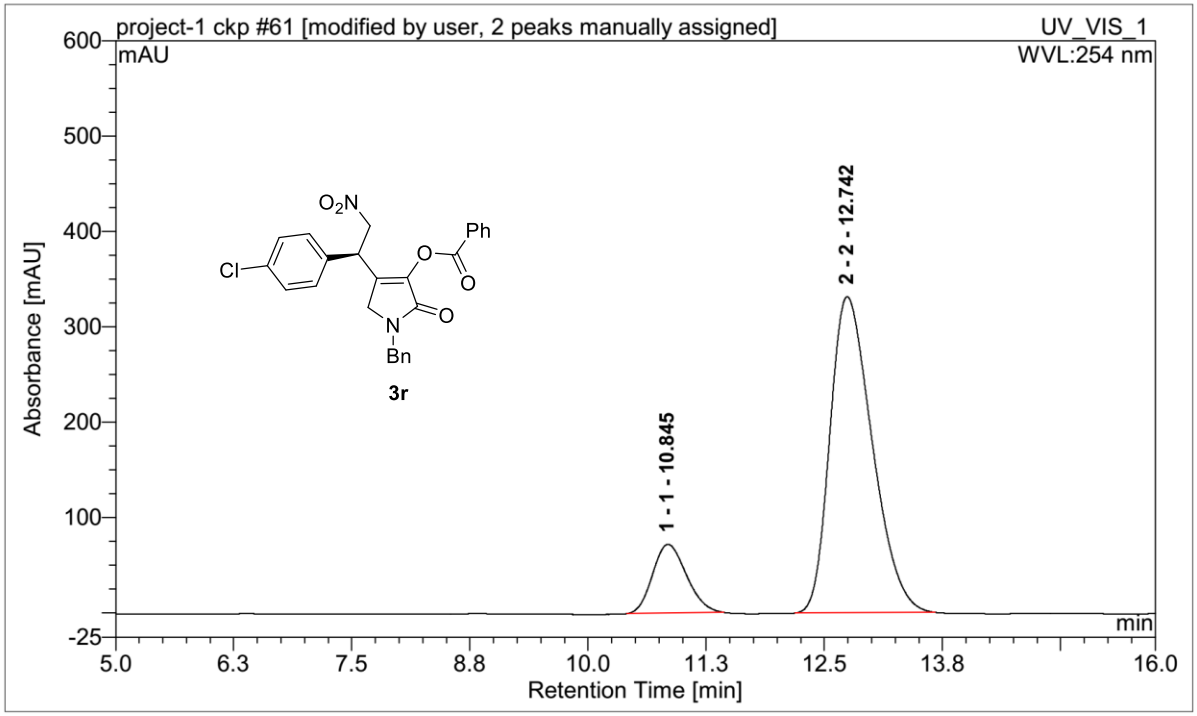
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	33.39	37.02522	50.80098629	17.79302	n.a.
2	2	41.27	35.858	49.19901371	13.123	n.a.



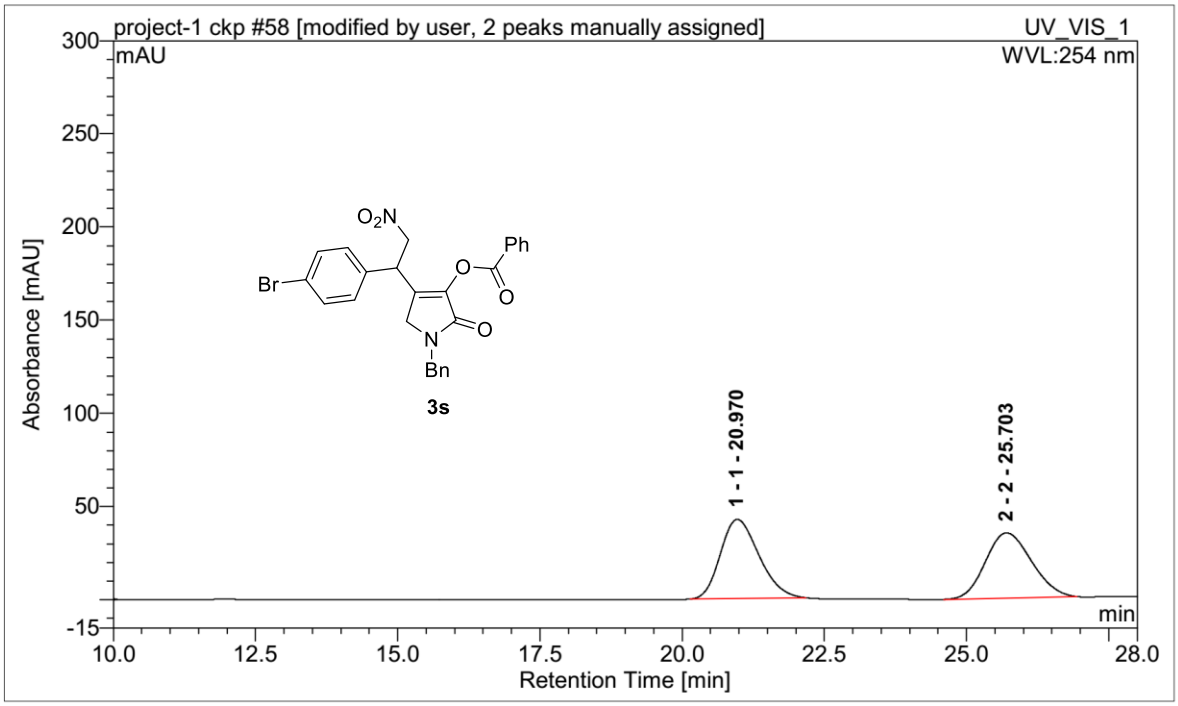
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	33.39	51.21042	91.49628513	23.13561	n.a.
2	2	42.01	4.760	8.503714867	2.337	n.a.



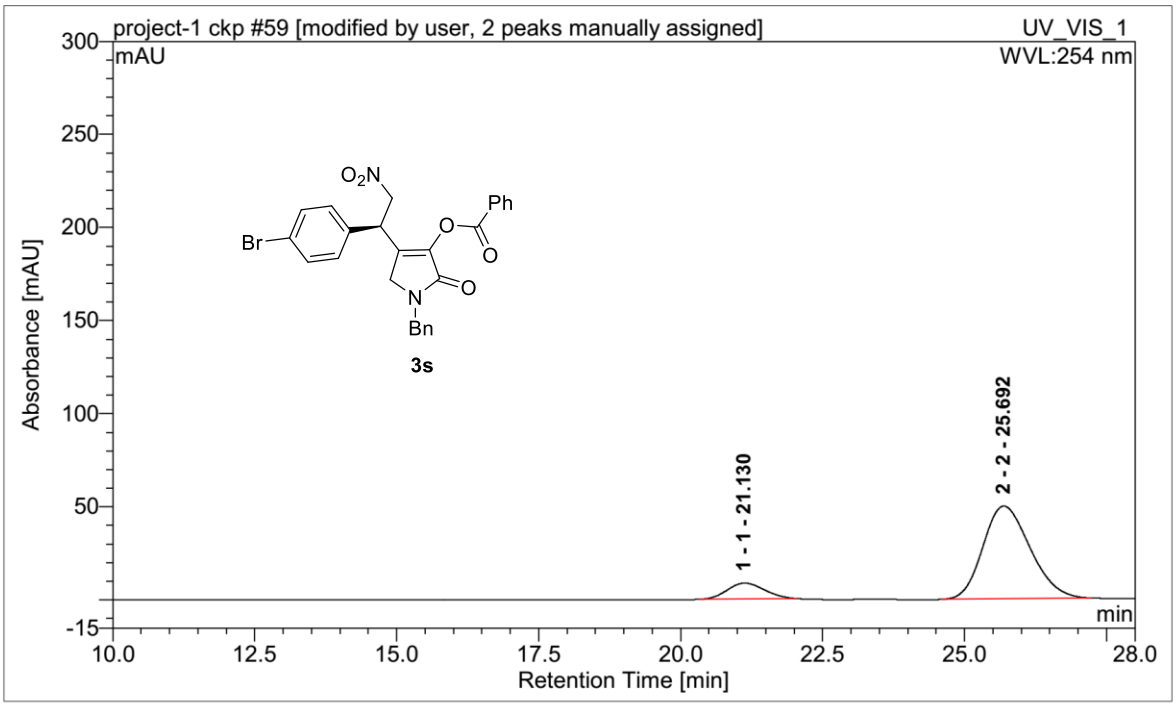
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	10.81	71.01245	49.72081463	167.281	n.a.
2	2	12.82	71.810	50.27918537	142.475	n.a.



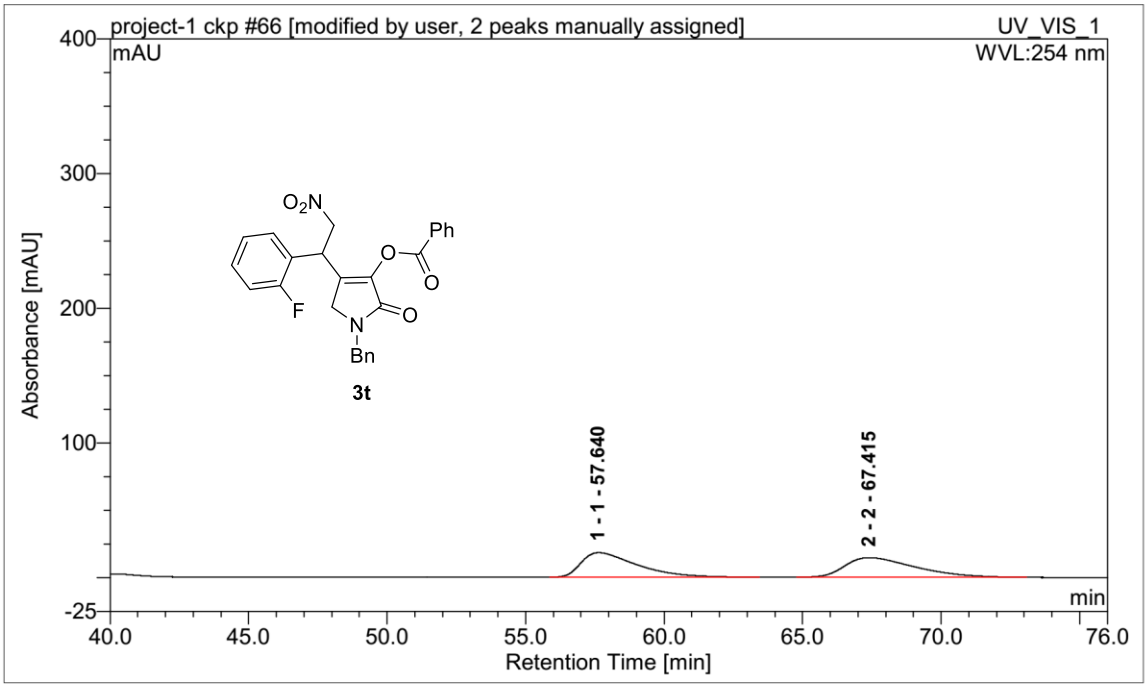
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	10.85	29.90189	14.84916038	72.00904	n.a.
2	2	12.74	171.469	85.15083962	331.303	n.a.



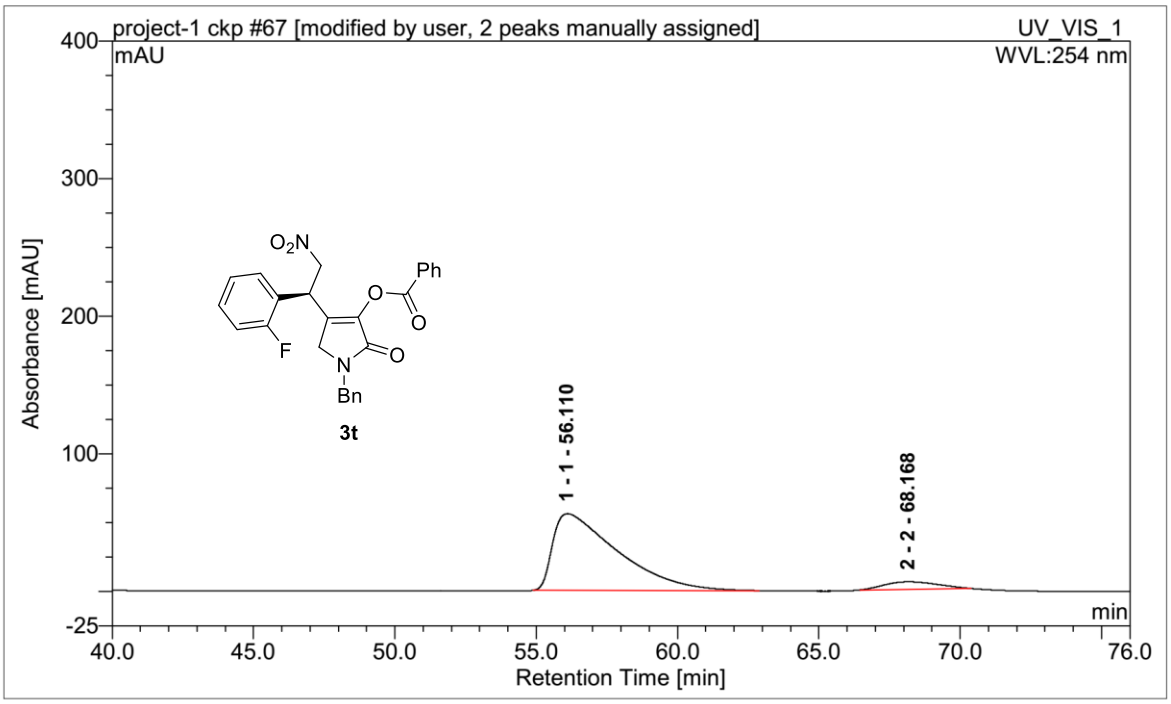
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	20.97	33.38294	50.47388693	42.41479	n.a.
2	2	25.70	32.756	49.52611307	34.960	n.a.



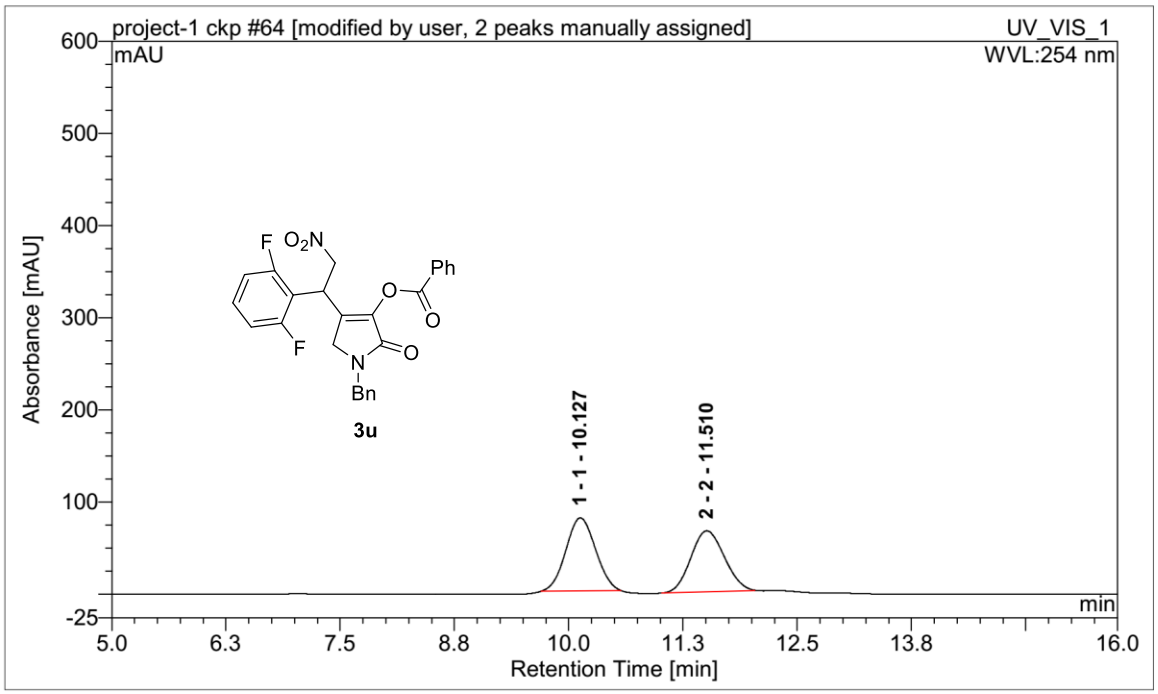
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	21.13	6.446094	11.86378467	8.49178	n.a.
2	2	25.69	47.888	88.13621533	49.821	n.a.



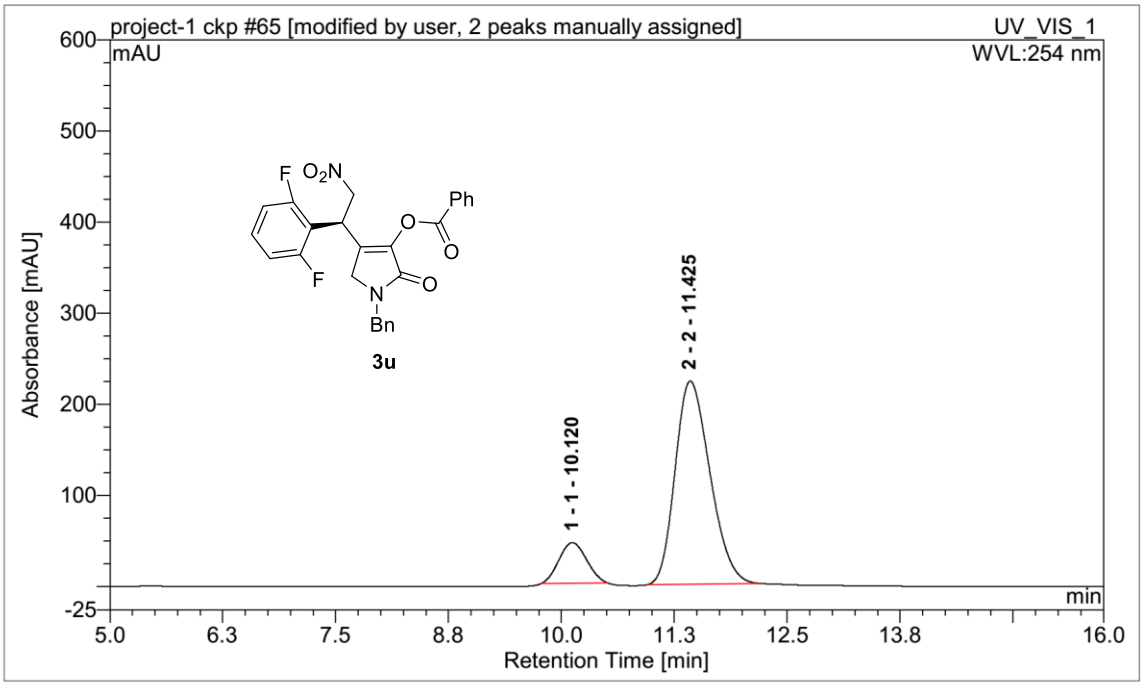
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	57.64	42.78868	50.11148574	18.26297	n.a.
2	2	67.42	42.598	49.88851426	14.589	n.a.



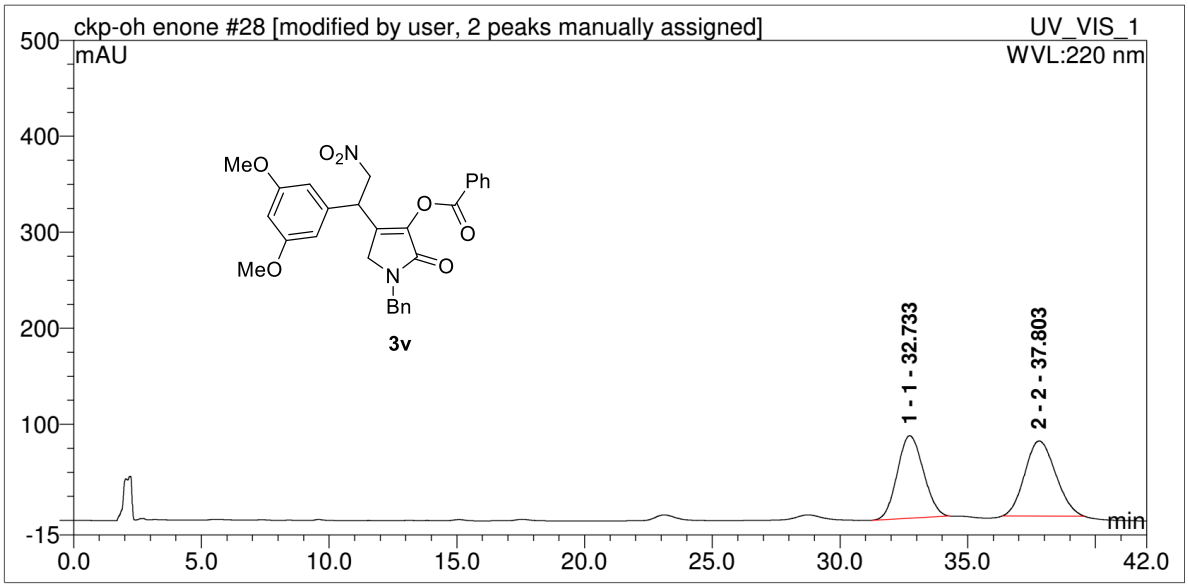
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	56.11	147.7052	92.5039058	55.76729	n.a.
2	2	68.17	11.969	7.496094196	5.467	n.a.



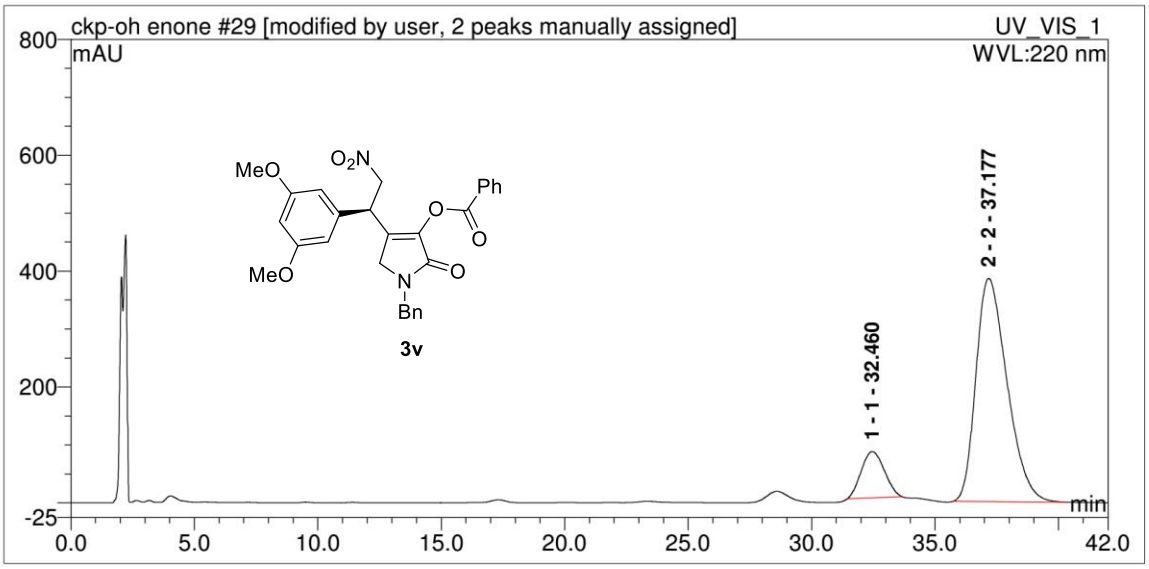
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	10.13	29.83827	51.55143988	79.08016	n.a.
2	2	11.51	28.042	48.44856012	66.056	n.a.



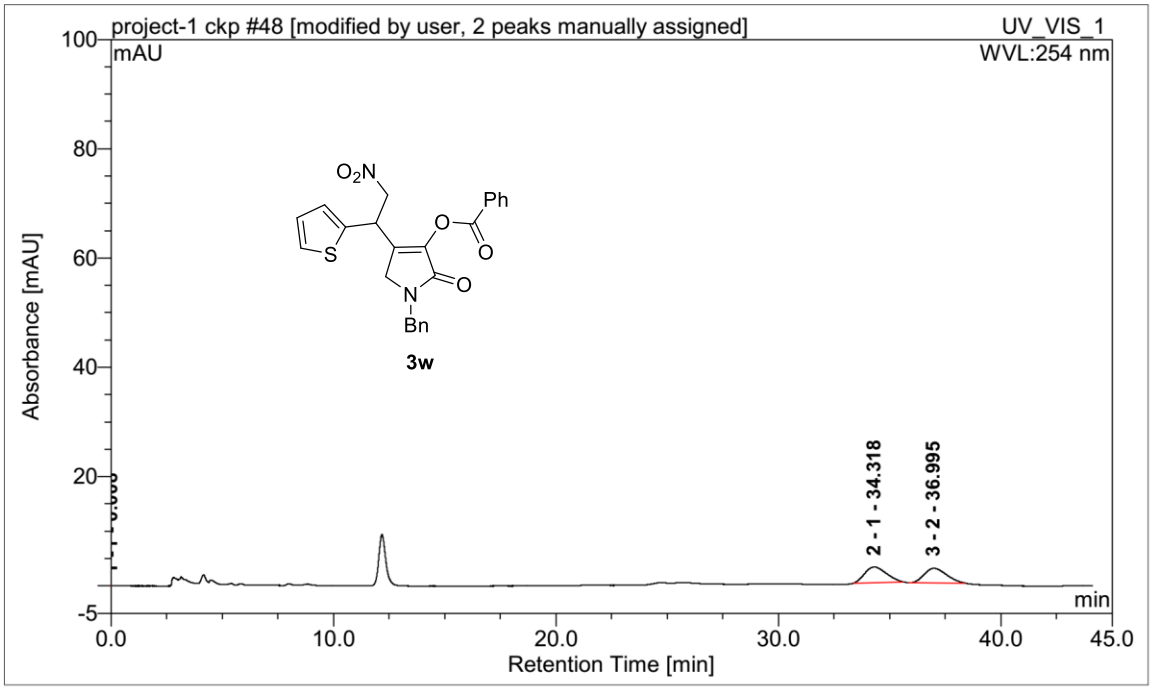
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	10.12	15.70124	13.6428715	44.45621	n.a.
2	2	11.43	99.386	86.3571285	222.589	n.a.



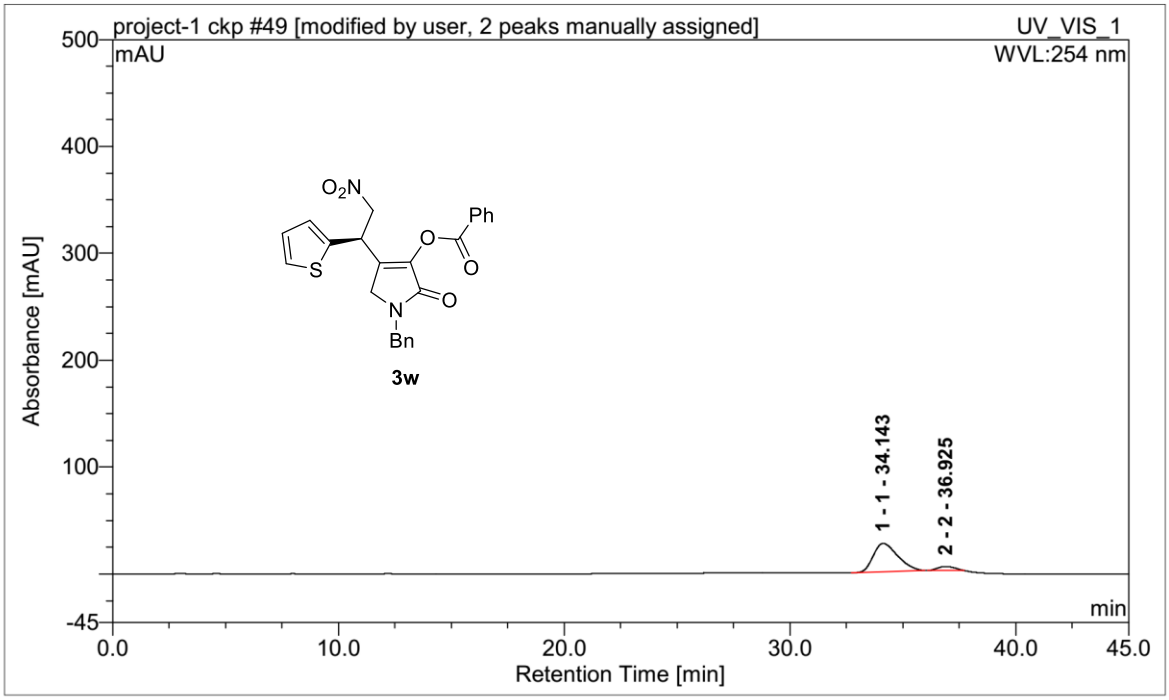
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	32.73	101.7329	48.11551612	85.81185	n.a.
2	2	37.80	109.702	51.88448388	78.151	n.a.



No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	32.46	86.86257	13.3890642	79.82599	n.a.
2	2	37.18	561.895	86.6109358	385.027	n.a.



No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
2	1	34.32	3.167195	50.68666617	2.82844	n.a.
3	2	37.00	3.081	49.31293107	2.667	n.a.



No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	34.14	33.43863	90.59762485	26.51936	n.a.
2	2	36.93	3.470	9.402375147	3.852	n.a.