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Organocatalytic Asymmetric Michael/Hemiketalization/Acyl Transfer Reaction of 1,3-Propanediones with (*E*)-2-(2-nitrovinyl)phenols

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1. General Information:

Chemicals and solvents were purchased from commercial suppliers and used as received. ^{1}H NMR spectra are recorded on 600 MHz spectrometer. ^{13}C NMR spectra were recorded on 151 MHz. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak is used as an internal reference: proton (chloroform δ 7.260), carbon (chloroform δ 77.23). Multiplicity is indicated as follows**:** s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), brs (broad singlet). Coupling constants are reported in Hertz (Hz). High-resolution mass spectra (HRMS) were recorded in Q-TOF electron spray ionization (ESI). Enantiomeric ratios were determined by HPLC analysis performed on Chiral Columns using a Daicel Chiralpak IA/ IC 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 (*E*)-2-(2-nitrovinyl)phenols:

(*E*)-2-(2-nitrovinyl)phenols are prepared according to reported procedure.[1]

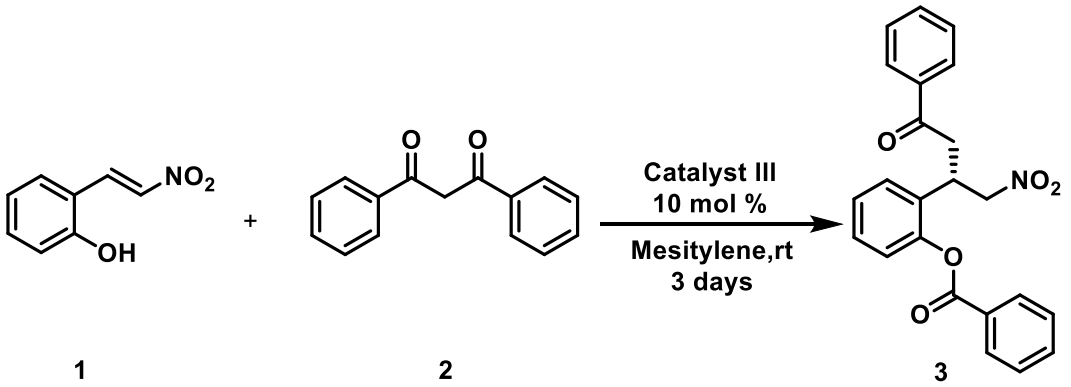
3. General procedure for the synthesis of 1,3-propanediones:

1,3-propanediones are prepared according to reported procedures.[2]

4. General procedure for the synthesis of catalyst:

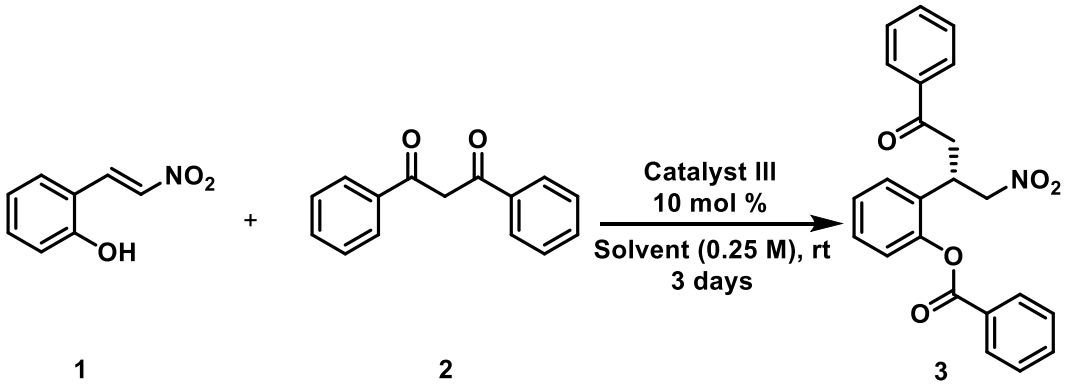
The catalyst (**I, II** and **III**) was prepared according to reported procedures.[3]

5. General procedure for the synthesis of compound 3:



In an oven dried round bottom flask, **1** (16.5 mg, 0.1 mmol), **2** (24.6. mg, 0.11 mmol), 10 mol% of catalyst (**III**) were taken. 0.4 mL of mesitylene was added to the reaction mixture and stirred at rt for 3 days. 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 %) to afford desired product **3a-r.**

6. Solvent optimization for Phenyl benzoates:

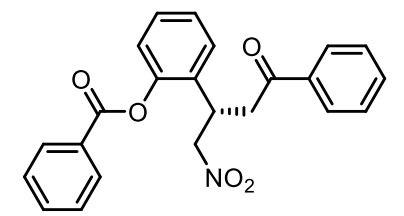


Entry[a]	Solvent	Yield[b]	ee[c]
1	DCM	71	92
2	Toluene	73	94

3	**Mesitylene**	**73**	**96**
4	$PhCF_3$	68	94
5	Xylene	72	94
6	$CHCl_3$	70	92
7	MTBE	75	92

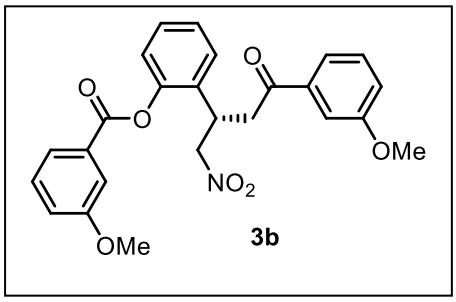
[a]Reaction condition: 0.05 mmol of **1a** and 0.055 mmol of **2a** in 0.2 mL solvent using 10 mol% catalyst **III**. [b]Isolated yield after silica gel column chromatography. [c]Determined by HPLC.

7. Characterisation of the products:

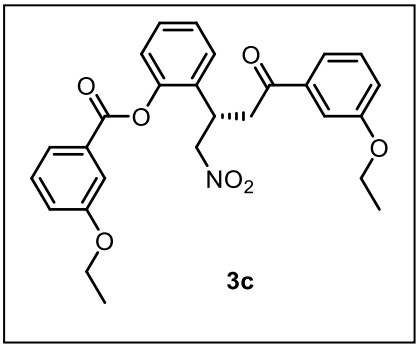


3a

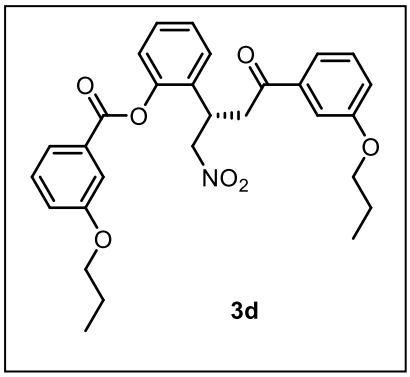
((S)-2-(1-nitro-4-oxo-4phenylbutan2-yl)phenyl benzoate) (3a); Brownish yellow sticky compound in 73% yield (28.4 mg) after column chromatography.**^{1}H NMR (600 MHz, Chloroform-*d*)** δ 8.23 (d, *J* = 7.1 Hz, 2H), 7.86 (d, *J* = 7.2 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 3H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 8.1 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 1H), 4.81 (dd, *J* = 12.7, 6.8 Hz, 1H), 4.76 (dd, *J* = 12.7, 7.4 Hz, 1H), 4.50 – 4.44 (m, 1H), 3.49 (dd, *J* = 17.5, 6.0 Hz, 1H), 3.42 (dd, *J* = 17.5, 7.9 Hz, 1H).**^{13}C NMR (151 MHz, Chloroform-*d*):** δ 196.9, 165.48, 149.0, 136.3, 134.2, 133.7, 131.4, 130.4, 129.1, 129.0, 129.0, 129.0, 128.8, 128.2, 126.9, 123.5, 78.6, 40.9, 33.6, 33.5, 29.8, 29.5.**HPLC Analysis:** ee = 96%, Chiralpak IA Column, n-Hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 22.4 min, t_{minor} = 23.6 min). **HRMS (+ESI-TOF) m/z:** calcd. For $C_{23}H_{20}NO_5[M+H]^+$ 390.1336, found 390.1339.



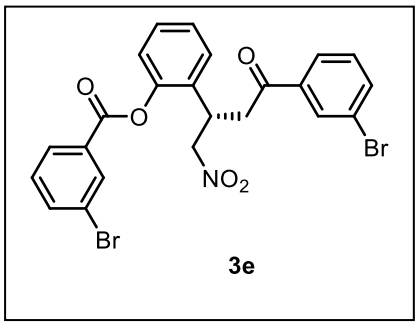
((S)-2-(4-(3-methoxyphenyl)-1-nitro-4-oxobutan-2-yl)phenyl 3-methoxybenzoate) (3b); was obtained as light yellow viscous compound in 75% (33.6 mg) yield after column chromatography. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 7.82 (d, *J* = 7.7 Hz, 1H), 7.74 (dd, *J* = 2.4, 1.6 Hz, 1H), 7.44 (t, *J* = 7.9 Hz, 2H), 7.39 – 7.33 (m, 3H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.24 – 7.19 (m, 2H), 7.10 – 7.06 (m, 1H), 4.78 (qd, *J* = 12.6, 7.1 Hz, 2H), 4.51 – 4.42 (m, 1H), 3.90 (s, 3H), 3.81 (s, 3H), 3.43 (qd, *J* = 17.5, 6.9 Hz, 2H)**^{13}C NMR (101 MHz, Chloroform-*d*)** δ 196.7, 165.3, 160.1, 149.0, 137.7, 131.4, 130.3, 130.0, 129.8, 129.1, 128.3, 126.9, 123.6, 122.9, 120.9, 120.8, 120.3, 114.7, , 112.3, 78.7, 55.7, 55.6, 41.0, 33.8. **HPLC Analysis:** ee = 95%, Chiralpak IC Column, n-Hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 34.6 min, t_{minor} = 37.3 min). **HRMS (+ESI-TOF) m/z:** calcd. For $C_{25}H_{24}NO_7$ $[M+H]^+$ 450.1547, found 450.1542.



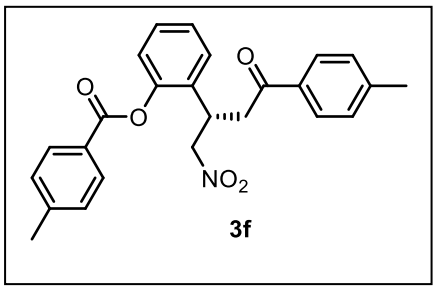
((S)-2-(4-(3-ethoxyphenyl)-1-nitro-4-oxobutan-2yl)phenyl 3-ethoxybenzoate) (3c);was obtained as a light yellow sticky compound in 68% (32.4 mg) yield after column chromatography. **^{1}H NMR (600 MHz, Chloroform-*d*):** δ 7.83 (d, *J* = 7.7 Hz, 1H), 7.75 – 7.73 (m, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.41 – 7.37 (m, 3H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.25 – 7.21 (m, 2H), 7.10 (dd, *J* = 8.2, 2.5 Hz, 1H), 4.83 (dd, *J* = 12.7, 6.9 Hz, 1H), 4.77 (dd, *J* = 12.7, 7.5 Hz, 1H), 4.50 – 4.44 (m, 1H), 4.14 (q, *J* = 7.0 Hz, 2H), 4.05 (tq, *J* = 6.7, 2.1 Hz, 2H), 3.49 (dd, *J* = 17.6, 6.1 Hz, 1H), 3.42 (dd, *J* = 17.6, 7.9 Hz, 1H), 1.48 (t, *J* = 7.0 Hz, 3H), 1 .43 (t, *J* = 7.0 Hz, 3H).**13C NMR (151 MHz, Chloroform-*d*):** δ 196.7, 165.4, 159.3, 149.0, 137.6, 131.3, 130.2, 130.0, 129.8, 129.1, 128.3, 126.9, 123.6, 122.7, 121.4, 120.7, 120.6, 115.2, 112.9, 78.6, 64.0, 63.8, 41.0, 33.7, 14.9, 14.9. **HPLC Analysis:** ee = 94%, Chiralpak IA Column, n-Hexane/i-PrOH = 93/7, flow rate 0.8 mL/min, λ = 254 nm (t_{major} = 38.3 min, t_{minor} = 35.0 min). **HRMS (+ESI-TOF) m/z:** calcd. For $C_{27}H_{28}NO_7$ $[M+H]^+$ 478.1860, found 478.1865.



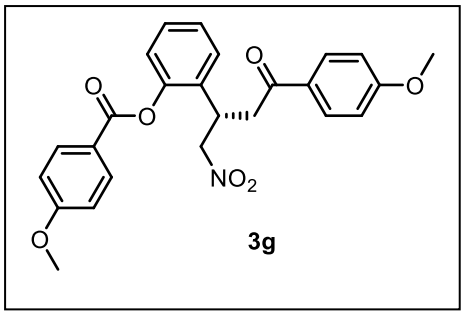
((S)-2-(1-nitro-4-oxo-4-(3-propoxyphenyl)butan-2-yl)phenyl 3-propoxybenzoate) (3d); was obtained as a colorless viscous compound in 66% (33.4 mg) yield after column chromatography. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.80 (d, *J* = 7.7 Hz, 1H), 7.74 – 7.71 (m, 1H), 7.42 (t, *J* = 7.9 Hz, 2H), 7.39 – 7.33 (m, 3H), 7.29 (dd, *J* = 7.7, 5.8 Hz, 2H), 7.23 – 7.18 (m, 2H), 7.07 (dd, *J* = 8.2, 1.8 Hz, 1H), 4.78 (qd, *J* = 12.6, 7.1 Hz, 2H), 4.50 – 4.38 (m, 1H), 4.01 (t, *J* = 6.5 Hz, 2H), 3.92 (t, *J* = 6.6 Hz, 2H), 3.43 (qd, *J* = 17.6, 6.9 Hz, 2H), 1.89 – 1.75 (m, 4H), 1.04 (dt, *J* = 13.4, 7.4 Hz, 6H).**^{13}C NMR (101 MHz Chloroform-*d*):** δ 196.8, 165.4, 159.6, 149.1, 137.7, 131.4, 130.3, 130.0, 129.8, 129.1, 128.3, 126.9, 123.6, 122.7, 121.4, 120.7, 120.6, 115.4, 113.1, 78.6, 70.0, 69.9, 41.0, 33.9, 22.7, 22.7, 10.7, 10.6. **HPLC Analysis:** ee = 90%, Chiralpak IA Column, n-Hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 16.7 min, t_{minor} = 15.5 min). **HRMS (+ESI-TOF) m/z:** calcd. For $C_{29}H_{32}NO_7$ $[M+H]^+$ 506.2173, found 506.2177.



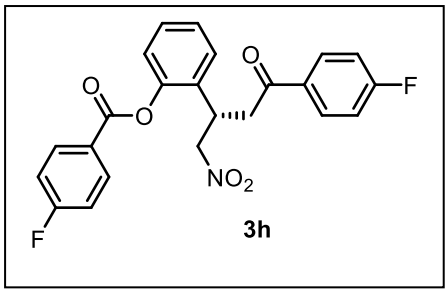
((S)-2-(4-(3-bromophenyl)-1-nitro-4-oxobutan-2-yl)phenyl 3-bromobenzoate) (3e); was obtained as a whitish sticky compound in 78% (42.4 mg) yield after column chromatography. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 8.35 (s, 1H), 8.17 (d, *J* = 7.9 Hz, 1H), 7.98 (s, 1H), 7.82 – 7.76 (m, 2H), 7.68 (d, *J* = 8.9 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 1H), 7.36 (dd, *J* = 12.4, 4.7 Hz, 2H), 7.30 (t, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 1H), 4.75 (qd, *J* = 12.7, 7.2 Hz, 2H), 4.43 (p, *J* = 7.1 Hz, 1H), 3.42 (qd, *J* = 17.6, 6.9 Hz, 2H).**^{13}C NMR (101 MHz, Chloroform-*d*):** δ 195.4, 164.2, 148.8, 137.2, 136.6, 133.4, 131.3, 130.6, 130.5, 129.3, 129.0, 128.0, 127.2, 126.7, 123.5, 78.6, 41.1, 33.2.**HPLC Analysis:** ee = 95%, Chiralpak IC Column, n-Hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 18.4 min, t_{minor} = 17.0 min). **HRMS (+ESI-TOF) m/z:** calcd. For $C_{23}H_{18}Br_2NO_5$ $[M+H]^+$545.9546, found 545.9543.



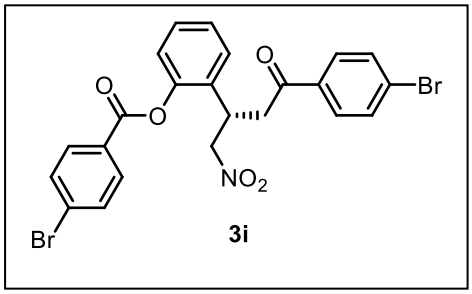
((S)-2-(1-nitro-4-oxo-4-(p-tolyl)butan-2-yl)phenyl-4-methylbenzoate) (3f); was obtained as a yellow sticky compound in 77% (32.2 mg) yield after column chromatography. **^{1}H NMR (600 MHz, Chloroform-*d*):**δ 8.12 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.35 (dd, *J* = 14.3, 7.6 Hz, 4H), 7.26 (dd, *J* = 8.7, 6.0 Hz, 1H), 7.20 (t, *J* = 8.8 Hz, 3H), 4.80 (dd, *J* = 12.7, 6.8 Hz, 1H), 4.75 (dd, *J* = 12.7, 7.5 Hz, 1H), 4.48 – 4.39 (m, 1H), 3.45 (dd, *J* = 17.4, 5.8 Hz, 1H), 3.37 (dd, *J* = 17.4, 8.1 Hz, 1H), 2.47 (s, 3H), 2.38 (s, 3H).**^{13}C NMR (151 MHz, Chloroform-*d*):** δ 196.5, 165.5, 149.1, 145.1, 144.6, 133.9, 131.5, 130.5, 129.7, 129.5, 129.0, 128.3, 128.3, 126.7, 126.3, 123.6, 78.6, 77.4, 77.2, 77.0, 40.7, 33.9, 22.0, 21.8. **HPLC Analysis:** ee = 81%, Chiralpak IC Column, n-Hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 47.5 min, t_{minor} = 38.1 min). **HRMS (+ESI-TOF) m/z:** calcd. For $C_{25}H_{24}NO_5$ $[M+H]^+$ 418.1649, found 418.1649.



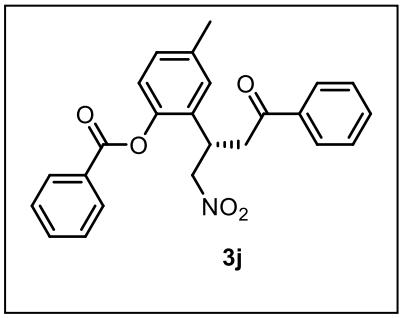
((S)-2-(4-(4-methoxyphenyl)-1-nitro-4-oxobutan-2-yl)phenyl 4-methoxybenzoate) (3g); was obtained as a light yellow sticky compound in 65% (29.2 mg) yield after column chromatography. **^{1}H NMR (600 MHz, Chloroform-*d*):** δ 8.19 (dd, *J* = 9.3, 2.3 Hz, 2H), 7.86 (d, *J* = 8.9 Hz, 2H), 7.37 (t, *J* = 7.1 Hz, 2H), 7.28 (s, 3H), 7.24 – 7.21 (m, 1H), 7.03 (d, *J* = 8.9 Hz, 2H), 6.88 (d, *J* = 8.9 Hz, 2H), 4.84 (dd, *J* = 12.7, 6.7 Hz, 1H), 4.78 (dd, *J* = 12.7, 7.6 Hz, 1H), 4.45 (p, *J* = 7.4 Hz, 1H), 3.93 (s, 3H), 3.87 (s, 3H), 3.44 (dd, *J* = 17.1, 5.8 Hz, 1H), 3.36 (dd, *J* = 17.2, 8.2 Hz, 1H).**^{13}C NMR (151 MHz, Chloroform-*d*):** δ 195.5, 165.2, 164.4, 163.9, 149.1, 132.7, 130.6, 129.0, 12 6.7, 123.7, 114.3, 114.0, 78.6, 55.8, 55.7, 40.5, 33.9.**HPLC Analysis:** ee = 74%, Chiralpak IA Column, n-Hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 43.8 min, t_{minor} = 55.7 min). **HRMS (+ESI-TOF) m/z:** calcd. For $C_{25}H_{24}NO_7$ $[M+H]^+$ 450.1547, found 450.1552.



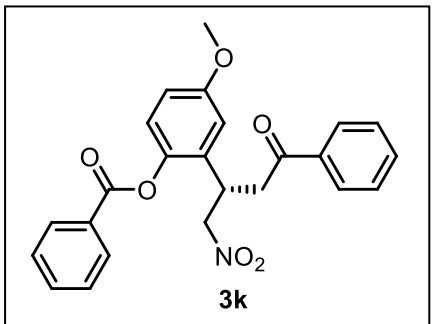
((S)-2-(4-(4-fluorophenyl)-1-nitro-4-oxobutan-2-yl)phenyl 4-fluorobenzoate) (3h); was obtained as a yellow sticky compound in 73% (31.0 mg) yield after column chromatography. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 8.27 – 8.22 (m, 2H), 7.92 – 7.86 (m, 2H), 7.39 – 7.33 (m, 2H), 7.29 (d, *J* = 6.5 Hz, 1H), 7.24 – 7.18 (m, 3H), 7.11 – 7.05 (m, 2H), 4.76 (qd, *J* = 12.7, 7.1 Hz, 2H), 4.48 – 4.39 (m, 1H), 3.41 (qd, *J* = 17.4, 6.9 Hz, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*):** ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.2, 167.9, 167.4, 165.3, 164.9, 164.5, 148.9, 133.2, 133.1, 131.4, 131.0, 130.9, 129.2, 127.9, 127.0, 125.3, 123.6, 116.4, 116.1, 115.9, 78.6, 40.9, 33.4. **HPLC Analysis:** ee = 78%, Chiralpak IA Column, n-Hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 26.9 min, t_{minor} = 33.5 min). **HRMS (+ESI-TOF) m/z:** calcd. For $C_{23}H_{18}F_2NO_5$ $[M+H]^+$ 426.1148, found 426.1150.



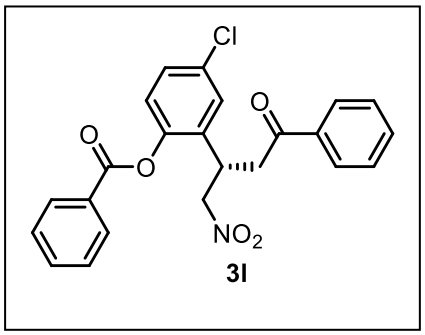
((S)-2-(4-(4-bromophenyl)-1-nitro-4-oxobutan-2-yl)phenyl 4-bromobenzoate)(3i); was obtained as a brownish yellow sticky compound in 76% (41.2 mg) yield after column chromatography. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 8.09 – 8.03 (m, 2H), 7.74 – 7.66 (m, 4H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.40 – 7.28 (m, 3H), 7.22 – 7.19 (m, 1H), 4.74 (qd, *J* = 12.7, 7.2 Hz, 2H), 4.42 (p, *J* = 7.1 Hz, 1H), 3.39 (qd, *J* = 17.4, 6.9 Hz, 2H).**^{13}C NMR (101 MHz, Chloroform-*d*):** δ 195.8, 164.8, 148.8, 135.0, 132.4, 132.2, 131.9, 131.2, 129.7, 129.6, 129.3, 129.0, 127.9, 127.9, 127.1, 123.5, 78.6, 41.0, 33.3. **HPLC Analysis:** ee = 86%, Chiralpak IA Column, n-Hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 41.5 min, t_{minor} = 56.0 min). **HRMS (+ESI-TOF) m/z:** calcd. For $C_{23}H_{18}Br_2NO_5$ $[M+H]^+$ 545.9546, found 545.9549.



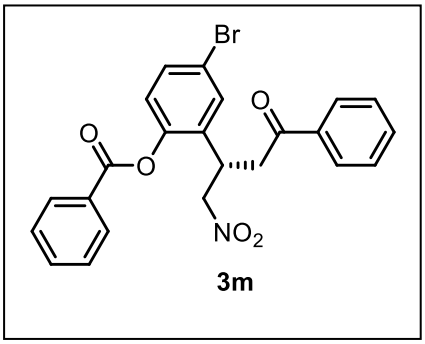
((S)-4-methyl-2-(2-nitro-4-oxo-4-phenylbutan-2-yl)phenyl benzoate) (3j) ; was obtained as a light yellow sticky compound in 75% (30.2 mg) yield after column chromatography. **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 8.24 – 8.19 (m, 2H), 7.89 – 7.85 (m, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.54 (q, *J* = 7.7 Hz, 3H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.17 – 7.13 (m, 2H), 7.09 (d, *J* = 8.1 Hz, 1H), 4.77 (ddd, *J* = 31.7, 12.7, 7.2 Hz, 2H), 4.44 – 4.36 (m, 1H), 3.43 (ddd, *J* = 25.6, 17.5, 7.0 Hz, 2H), 2.36 (s, 3H).**^{13}C NMR (151 MHz, Chloroform-*d*)** δ 197.0, 165.7, 146.7, 136.6, 136.3, 134.1, 133.7, 130.9, 130.5, 129.8, 129.1, 129.0, 128.9, 128.7, 128.2, 123.2, 78.6, 40.9, 33.6, 21.2. **HPLC Analysis:** ee = 83%, Chiralpak IA Column, n-Hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 29.5 min, t_{minor} = 27.3 min). **HRMS (+ESI-TOF) m/z:** calcd. For $C_{24}H_{22}NO_5$ $[M+H]^+$ 404.1492, found 404.1488.



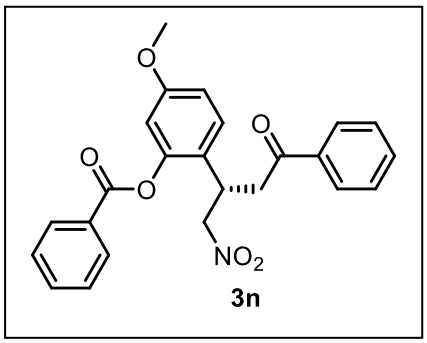
(S)-4-methoxy-2-(1-nitro-4-oxo-4-phenylbutan-2-yl)phenyl benzoate (3k); was obtained as a pale yellow sticky liquid in 75% (31.4 mg) yield after column chromatography. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 8.23 – 8.14 (m, 2H), 7.83 (d, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51 (dd, *J* = 14.1, 6.2 Hz, 3H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 9.2 Hz, 1H), 6.86 – 6.81 (m, 2H), 4.75 (dd, *J* = 13.9, 6.8 Hz, 2H), 4.39 – 4.34 (m, 1H), 3.78 (s, 3H), 3.40 (dd, *J* = 21.2, 6.9 Hz, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*):** δ 196.9, 165.9, 157.9, 142.5, 134.1, 133.7, 130.5, 129.0, 128.9, 128.2, 124.3, 114.1, 113.6, 78.5, 55.8, 40.9, 34.0. **HPLC Analysis:** ee = 86%, Chiralpak IA Column Column, n-Hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 40.5 min, t_{minor} = 37.5 min). **HRMS (+ESI-TOF) m/z:** calcd. For $C_{24}H_{22}NO_6$ $[M+H]^+$ 420.1442, found 420.1444.



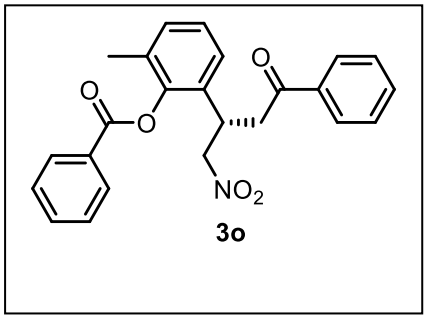
((S)-4-chloro-2-(1-nitro-4-oxo-4-phenylbutan-2-yl)phenyl benzoate) (3l);was obtained as a brownish sticky compound in 78% (33.0 mg) yield after column chromatography: **^{1}H NMR (600 MHz, Chloroform-*d*):** δ 8.22 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.89 – 7.86 (m, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.56 (dt, *J* = 11.8, 7.6 Hz, 3H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.36 – 7.31 (m, 2H), 7.18 (d, *J* = 8.3 Hz, 1H), 4.80 (dd, *J* = 12.9, 6.7 Hz, 1H), 4.73 (dd, *J* = 12.9, 7.6 Hz, 1H), 4.47 – 4.40 (m, 1H), 3.47 (dd, *J* = 17.7, 6.1 Hz, 1H), 3.41 (dd, *J* = 17.8, 7.8 Hz, 1H).**^{13}C NMR (151 MHz, Chloroform-*d*):** δ 196.4, 165.3, 147.5, 136.2, 134.4, 133.9, 133.4, 132.2, 130.5, 129.2, 129.1, 128.9, 128.7, 128.3, 128.2, 125.0, 78.3, 40.7, 33.4.**HPLC Analysis:** ee = 81%, Chiralpak IA Column, n-Hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 26.2 min, t_{minor} = 28.7min). **HRMS (+ESI-TOF) m/z:** calcd. For $C_{23}H_{19}ClNO_5$ $[M+H]^+$ 424.0946, found 424.0944.



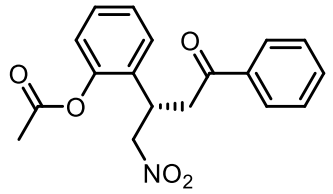
((S)-4-bromol-2-(1-nitro-4-oxo-4-phenylbutan-2-yl)phenyl benzoate)(3m); was obtained as a yellow sticky compound in 72% (33.6 mg) yield after column chromatography. **^{1}H NMR (600 MHz, Chloroform-*d*):** δ 8.22 (d, *J* = 7.3 Hz, 2H), 7.87 (d, *J* = 7.4 Hz, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.56 (dt, *J* = 12.5, 7.6 Hz, 3H), 7.50 – 7.46 (m, 2H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 1H), 4.80 (dd, *J* = 12.9, 6.7 Hz, 1H), 4.72 (dd, *J* = 12.9, 7.6 Hz, 1H), 4.46 – 4.39 (m, 1H), 3.46 (dd, *J* = 17.7, 6.1 Hz, 1H), 3.40 (dd, *J* = 17.8, 7.8 Hz, 1H).**^{13}C NMR (151 MHz, Chloroform-*d*):** δ 196.4, 165.2, 148.1, 136.2, 134.4, 133.9, 132.2, 131.2, 130.5, 129.1, 128.9, 128.7, 128.2, 125.3, 119.9, 78.3, 40.7, 33.4. **HPLC Analysis:** ee = 81%, Chiralpak IA Column, n-Hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 31.3 min, t_{minor} = 28.1 min). **HRMS (+ESI-TOF) m/z:** calcd. For $C_{23}H_{19}BrNO_5$ $[M+H]^+$ 468.0441, found 468.0446.



((S)-5-methoxy-2-(1-nitro-4-oxo-4-phenylbutan-2-yl)phenyl benzoate)(3n); was obtained as a yellow sticky compound in 70% (29.2 mg) yield after column chromatography. **^{1}H NMR (600 MHz, Chloroform-*d*):** δ 8.23 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.89 – 7.86 (m, 2H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.55 (dd, *J* = 10.9, 4.6 Hz, 3H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 1.5 Hz, 1H), 6.84 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.77 (d, *J* = 2.6 Hz, 1H), 4.78 (dd, *J* = 12.5, 6.9 Hz, 1H), 4.73 (dd, *J* = 12.5, 7.4 Hz, 1H), 4.40 – 4.35 (m, 1H), 3.80 (s, 3H), 3.47 (dd, *J* = 17.4, 6.2 Hz, 1H), 3.40 (dd, *J* = 17.4, 7.9 Hz, 1H). **^{13}C NMR (151 MHz Chloroform-*d*):** δ 197.1, 165.4, 159.9, 149.7, 136.3, 134.2, 133.7, 130.5, 129.0, 128.9, 128.8, 128.7, 128.2, 123.1, 113.1, 108.9, 78.8, 55.7, 41.0, 33.2. **HPLC Analysis:** ee = 92%, Chiralpak IC Column, n-Hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 35.4 min, t_{minor} = 40.5 min). **HRMS (+ESI-TOF) m/z:** calcd. For $C_{24}H_{22}NO_6$ [M+H] $^{+}$ 420.1442, found 420.1446.

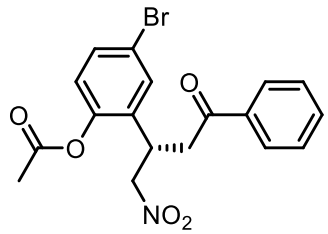


((S)-2-methyl-6-(1-nitro-4-oxo-4-phenylbutan-2-yl)phenyl benzoate) (3o); was obtained as a brownish sticky compound in 73% (29.4 mg) yield after column chromatography.**^{1}H NMR (600 MHz, Chloroform-*d*):** δ 8.22 (d, *J* = 7.2 Hz, 2H), 7.87 (d, *J* = 7.3 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.54 (q, *J* = 7.6 Hz, 3H), 7.43 – 7.38 (m, 2H), 7.18 – 7.12 (m, 2H), 7.09 (d, *J* = 8.1 Hz, 1H), 4.80 (dd, *J* = 12.7, 6.8 Hz, 1H), 4.75 (dd, *J* = 12.7, 7.5 Hz, 1H), 4.43 – 4.37 (m, 1H), 3.47 (dd, *J* = 17.5, 5.9 Hz, 1H), 3.40 (dd, *J* = 17.5, 8.1 Hz, 1H), 2.36 (s, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*):** δ 196.9, 165.7, 146.7, 136.6, 136.3, 134.1, 133.7, 130.9, 130.5, 129.8, 129.1, 129.0, 128.9, 128.7, 128.2, 123.2, 78.6, 40.9, 33.6, 21.2. **HPLC Analysis:** ee = 97%, Chiralpak IA Column, n-Hexane/i-PrOH = 95/5, flow rate 0.7 mL/min, λ = 254 nm (t_{major} = 31.7 min, t_{minor} = 34.2 min). **HRMS (+ESI-TOF) m/z:** calcd. For $C_{24}H_{22}NO_5$ [M+H] $^{+}$ 404.1492, found 404.1504.



3p

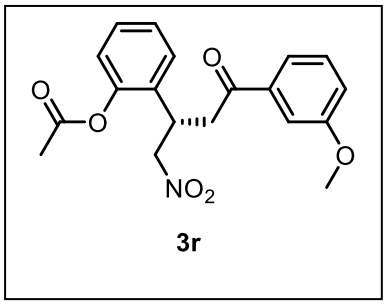
((S)-2-(1-nitro-4-oxo-4-phenylbutan-2-yl)phenyl acetate) (3p); was obtained as a yellow sticky liquid 60% (19.6 mg) yield after column chromatography. **^{1}H NMR (600 MHz, Chloroform-*d*):** δ 7.93 – 7.90 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.25 – 7.21 (m, 1H), 7.13 – 7.10 (m, 1H), 4.77 (dd, *J* = 12.6, 7.2 Hz, 1H), 4.69 (dd, *J* = 12.6, 7.0 Hz, 1H), 4.44 – 4.37 (m, 1H), 3.46 – 3.43 (m, 2H), 2.38 (s, 3H).**^{13}C NMR (151 MHz, Chloroform-*d*):** δ 196.8, 196.8, 169.8, 148.7, 136.3, 133.8, 131.3, 129.0, 128.9, 128.8, 128.2, 127.6, 126.8, 123.4, 78.6, 40.9, 33.0, 21.2. **HPLC Analysis:** ee = 79%, Chiralpak IA Column n-Hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 18.6 min, t_{minor} = 26.5 min). **HRMS (+ESI-TOF) m/z:** calcd. For $C_{18}H_{18}NO_5$ $[M+H]^+$ 328.1179, found 328.1285.



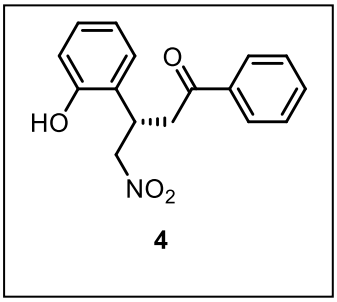
3q

((S)-4-bromo-2-(1-nitro-4-oxo-4-phenylbutan-2-yl)phenyl acetate) (3q); was obtained as a pale yellow sticky compound in 56% (22.6 mg) yield after column chromatography. **^{1}H NMR (600 MHz, Chloroform-*d*):** δ 7.92 (d, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.43 – 7.40 (m, 2H), 7.02 (d, *J* = 8.5 Hz, 1H), 4.75 (dd, *J* = 12.8, 7.0 Hz, 1H), 4.65 (dd, *J* = 12.8, 7.2 Hz, 1H), 4.41 – 4.35 (m, 1H), 3.42 (d, *J* = 6.9 Hz, 2H), 2.39 (s, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*):** δ 196.2, 169.3, 147.6, 135.9, 133.8, 133.5, 131.8, 130.5, 128.8, 128.0, 125.0, 119.7, 78.1, 40.6, 32.5, 20.9.

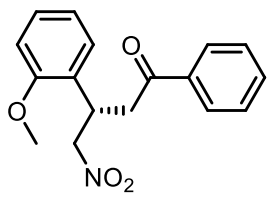
HPLC Analysis: ee = 78%, Chiralpak IA Column, n-Hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 18.6 min, t_{minor} = 17.1 min). **HRMS (+ESI-TOF) m/z:** calcd. For $C_{18}H_{17}BrNO_5$ $[M+H]^+$ 406.0285, found 406.0289.



((S)-2-(1-nitro-4-oxo-4-(m-tolyl)lbutan-2-yl)phenyl acetate)(3r); was obtained as a colorless sticky compound in 46% (16.4 mg) yield after column chromatography. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.46 (d, *J* = 7.8 Hz, 1H), 7.42 – 7.39 (m, 1H), 7.33 (t, *J* = 7.9 Hz, 1H), 7.30 – 7.24 (m, 2H), 7.20 (dd, *J* = 10.7, 4.3 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 2H), 4.69 (ddd, *J* = 29.7, 12.6, 7.1 Hz, 2H), 4.38 (p, *J* = 7.0 Hz, 1H), 3.80 (s, 3H), 3.40 (dd, *J* = 6.9, 3.9 Hz, 2H), 2.35 (s, 3H).**^{13}C NMR (101 MHz, Chloroform-*d*):** δ 196.7, 169.7, 160.1, 148.7, 137.7, 131.3, 129.9, 128.9, 127.6, 126.8, 123.4, 120.8, 120.3, 112.4, 78.6, , 55.6, 41.1, 33.2, 21.1**. HPLC Analysis:** ee = 70%, Chiralpak IA Column, n-Hexane/i-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 12.6 min, t_{minor} = 25.1 min). **HRMS (+ESI-TOF) m/z:** calcd. For $C_{19}H_{20}NO_6$ $[M+H]^+$ 358.1285, found 358.1283.



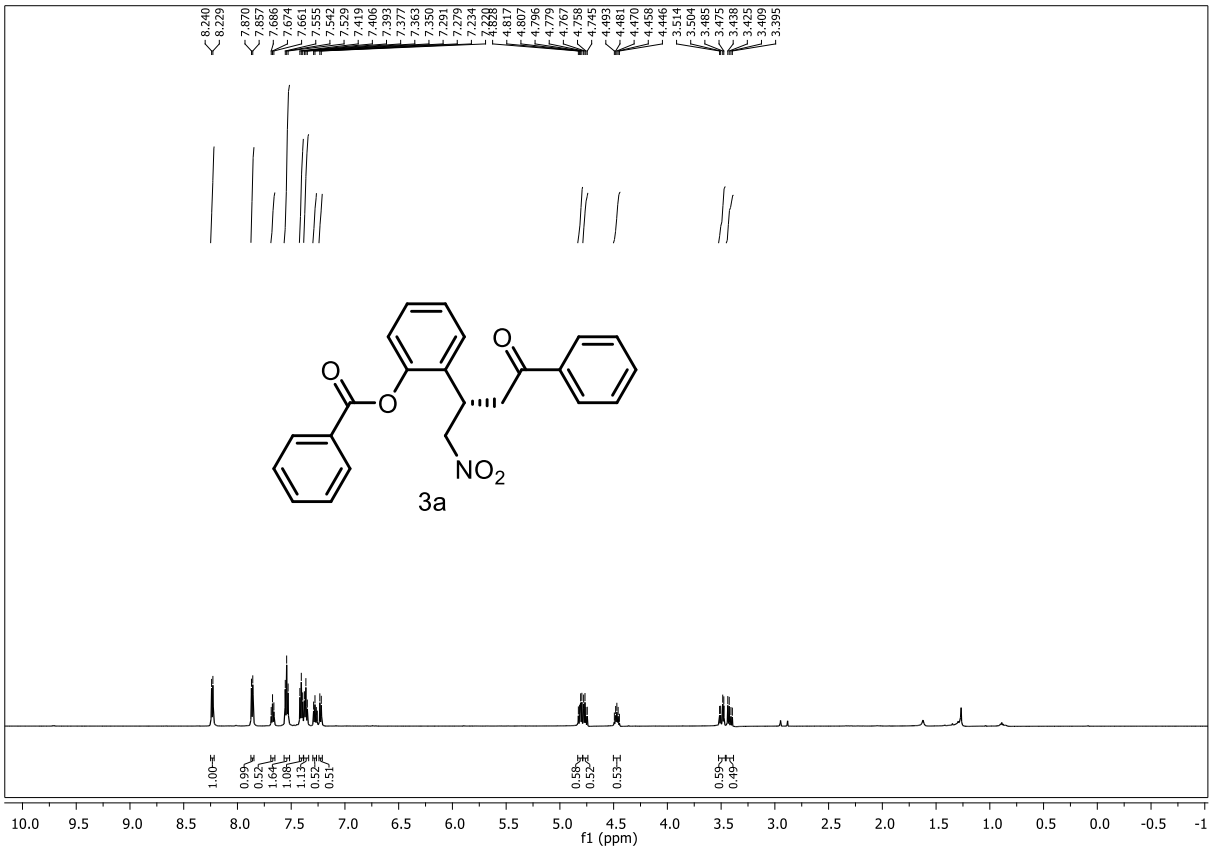
((S)-3-(2-hydroxyphenyl)-4-nitro-1-phenylbutan-1-one)(4); was obtained as a brownish sticky compound in 40% (29.9 mg) yield after column chromatography. **^{1}H NMR (600 MHz, Chloroform-*d*):** δ 7.94 (d, *J* = 7.3 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.16 – 7.11 (m, 2H), 6.90 (td, *J* = 7.6, 0.8 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.40 (s, 1H), 4.88 (dd, *J* = 12.7, 7.9 Hz, 1H), 4.82 (dd, *J* = 12.7, 6.9 Hz, 1H), 4.47 – 4.41 (m, 1H), 3.61 (dd, *J* = 18.0, 7.9 Hz, 1H), 3.53 (dd, *J* = 18.0, 5.6 Hz, 1H). **^{13}C NMR (151 MHz, Chloroform-*d*):** δ 198.8, 154.0, 136.2, 134.0, 129.1, 128.9, 128.4, 125.5, 121.4, 117.3, 78.2, 77.4, 41.1, 34.7.**HPLC Analysis:** ee = 93%, Chiralpak IA Column, n-Hexane/i-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm (t_{major} = 38.5 min, t_{minor} = 41.2 min). **HRMS (+ESI-TOF) m/z:** calcd. For $C_{16}H_{16}NO_4$ $[M+H]^+$ 286.1074, found 286.1070.

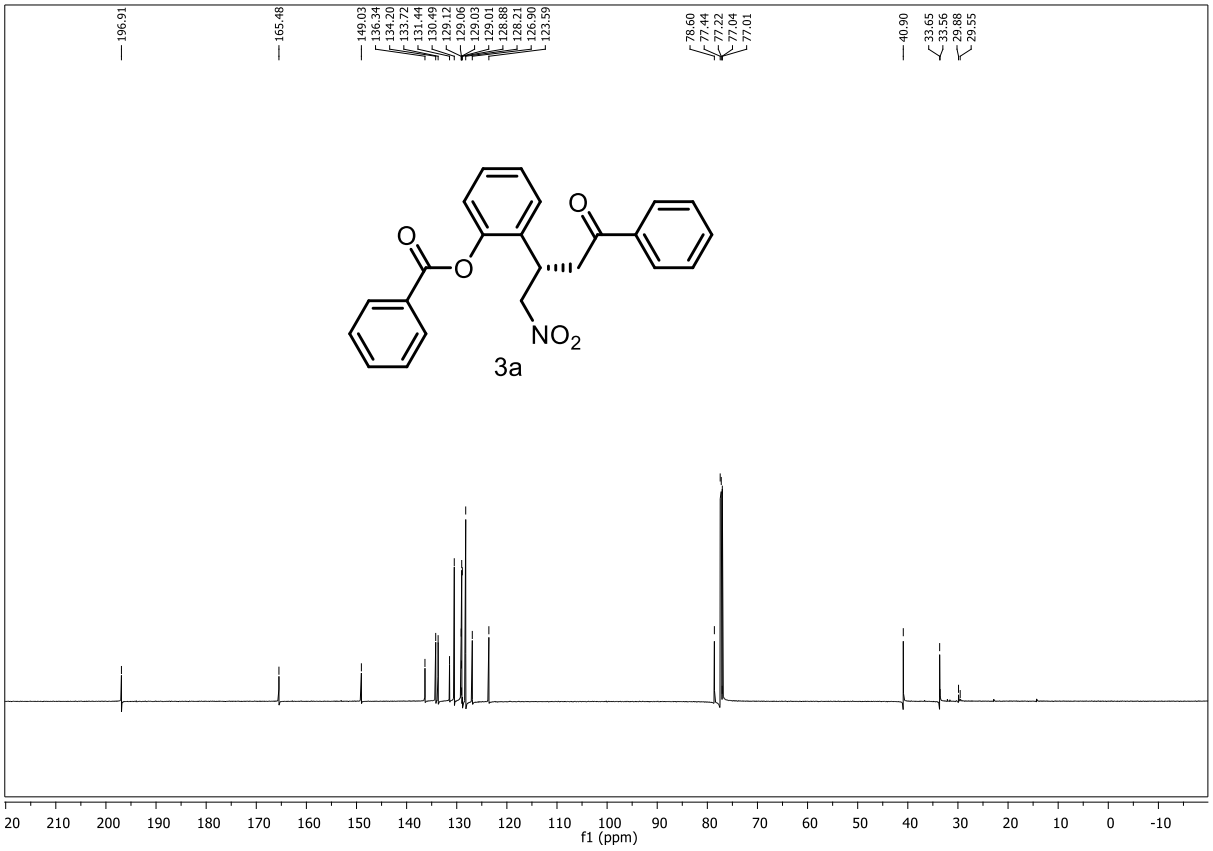


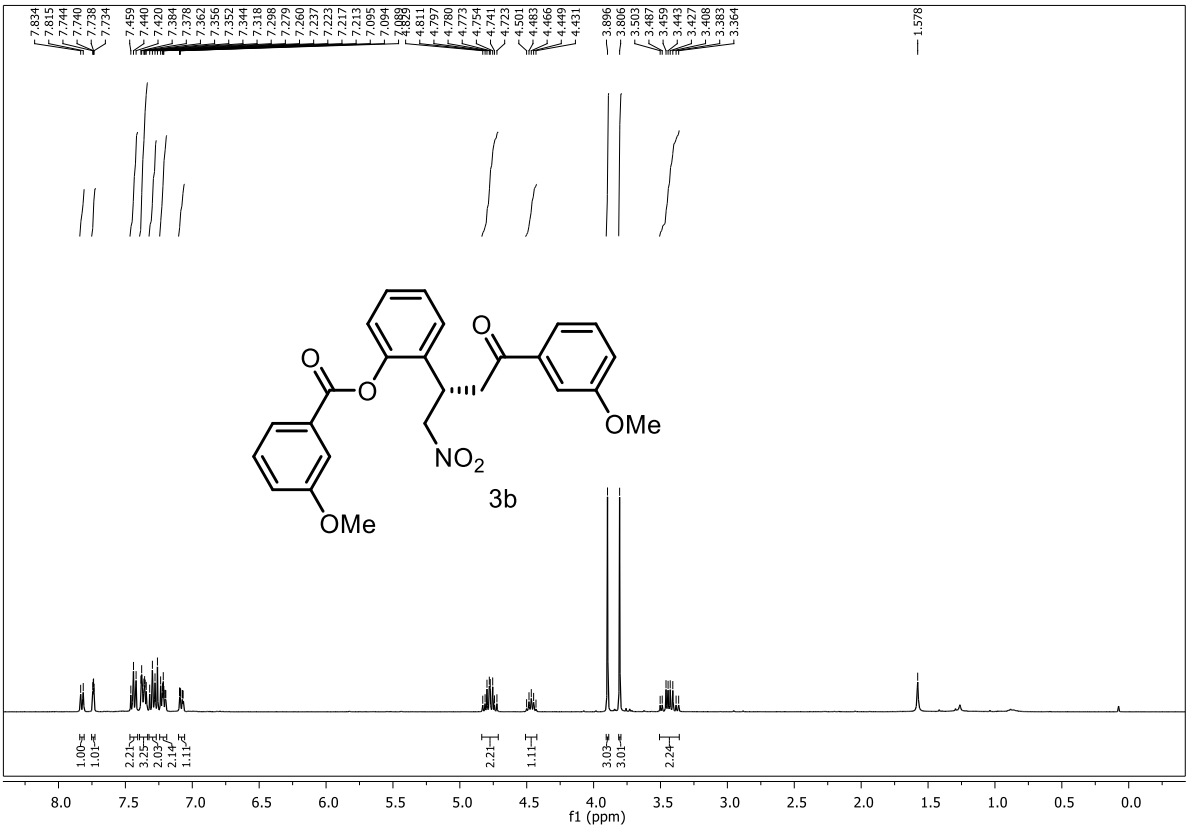
5

((S)-3-(2-methoxyphenyl)-4-nitro-1-phenylbutan-1-one) (5); was obtained as a colourless sticky compound in 55% (16.4 mg) yield after column chromatography. **^{1}H NMR (600 MHz, Chloroform-*d*)**: δ 7.95 – 7.92 (m, 2H), 7.58 – 7.55 (m, 2H), 7.48 – 7.44 (m, 3H), 6.92 – 6.87 (m, 2H), 4.86 (dd, *J* = 7.0, 2.2 Hz, 2H), 4.43 – 4.41 (m, 1H), 3.87 (s, 3H), 3.54 (d, *J* = 6.9 Hz, 2H). **^{13}C NMR (151 MHz, Chloroform-*d*)**: δ 197.8, 157.3, 136.7, 133.6, 129.7, 129.1, 128.8, 128.2, 126.8, 121.1, 111.2, 78.0, 55.5, 39.9, 36.1.**HPLC Analysis:** ee = 93%, Chiralpak IC Column, n-Hexane/i-PrOH = 75/25, flow rate 1.0 mL/min, λ = 225 nm (t_{major} = 11.5 min, t_{minor} = 10.7 min). **ESI HRMS**: calcd. For $C_{17}H_{18}NO_4$ $[M+H]^+$ 300.1230, found 300.1242.

8. NMR spectra of the products:



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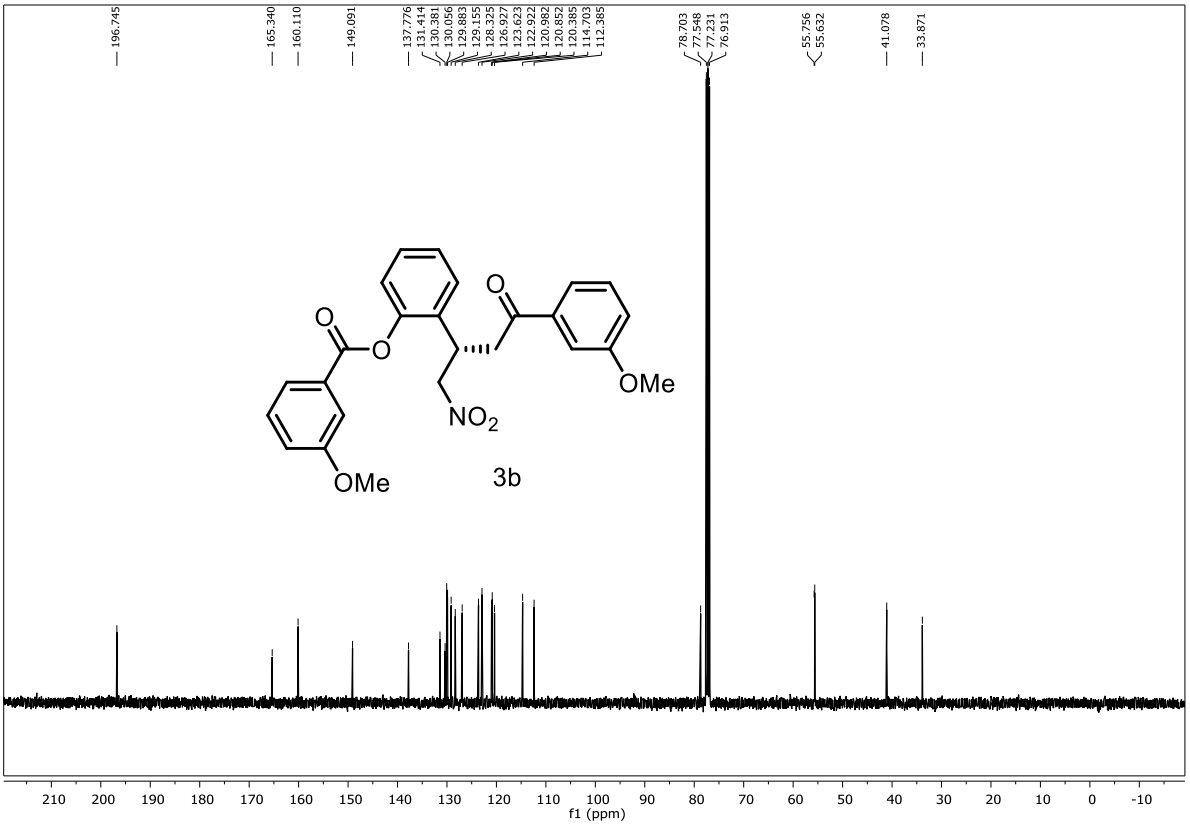
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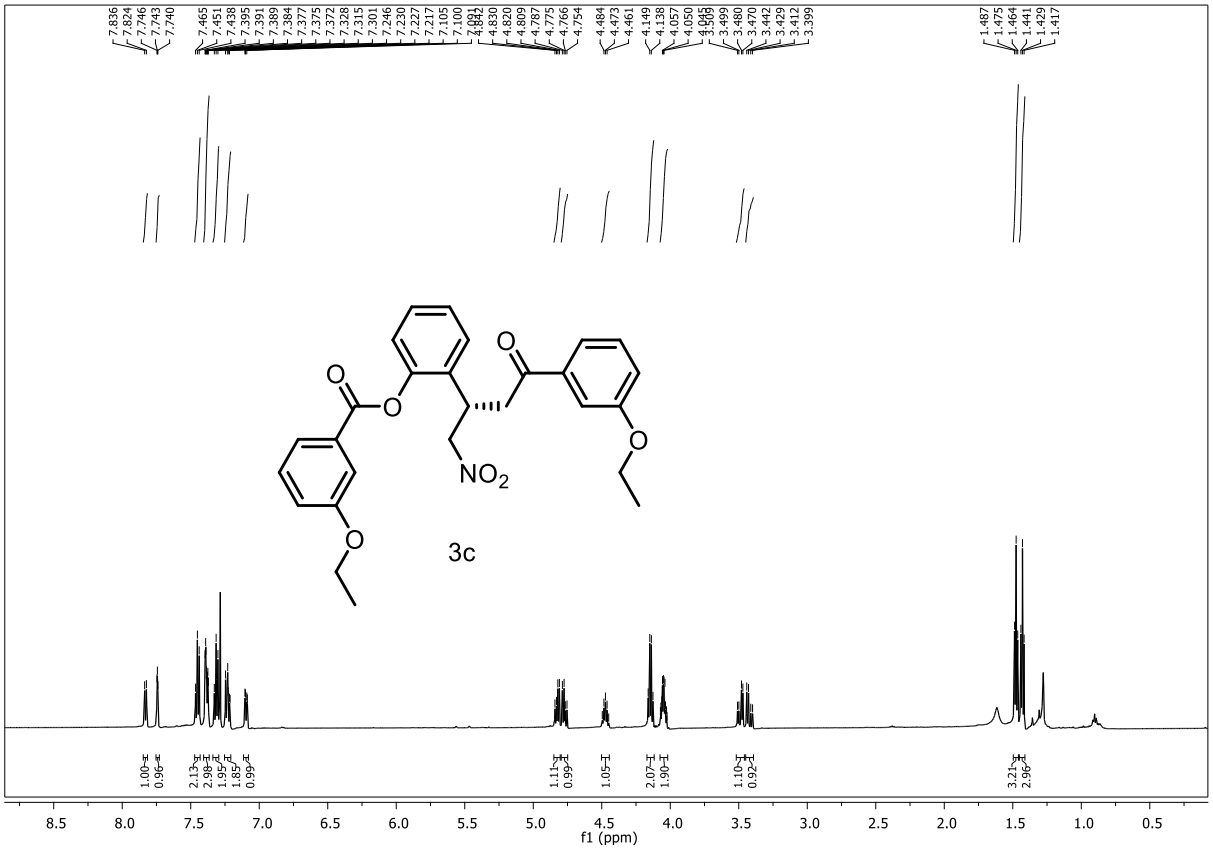
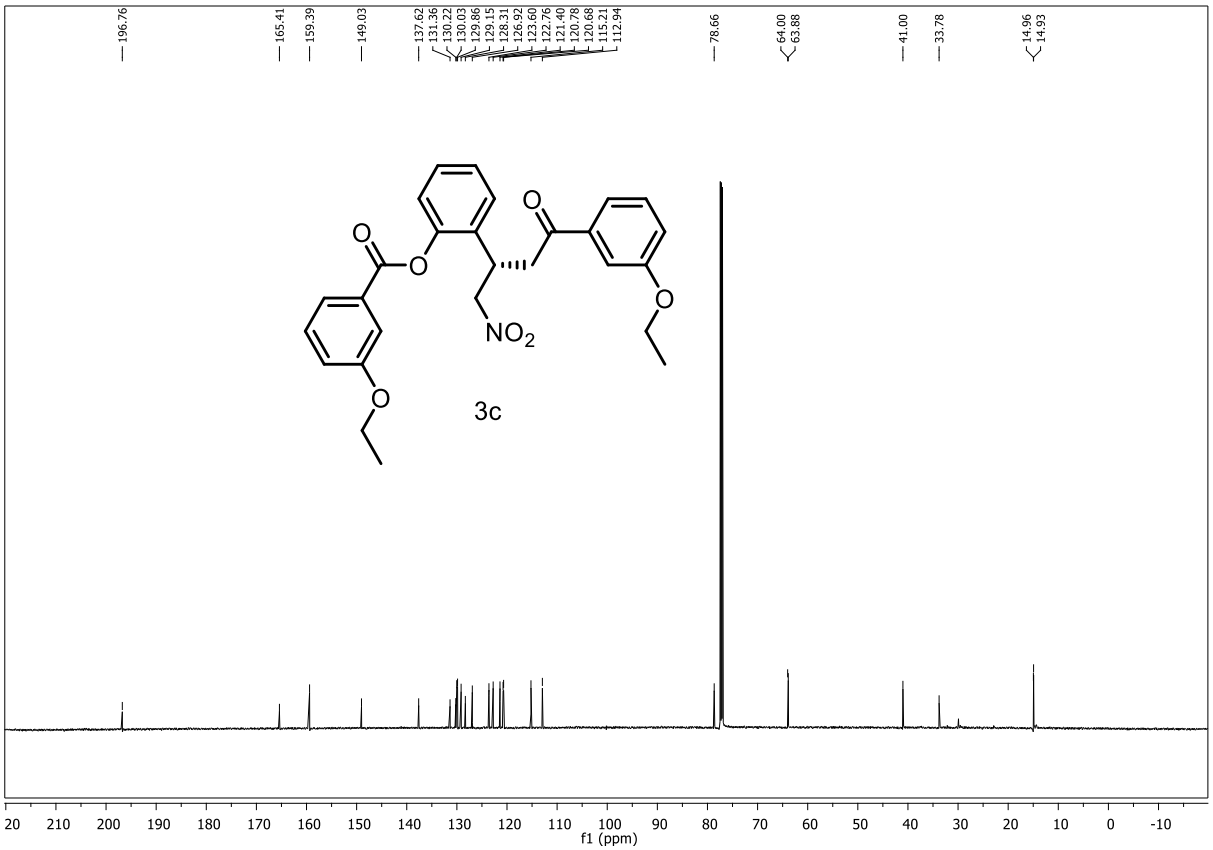
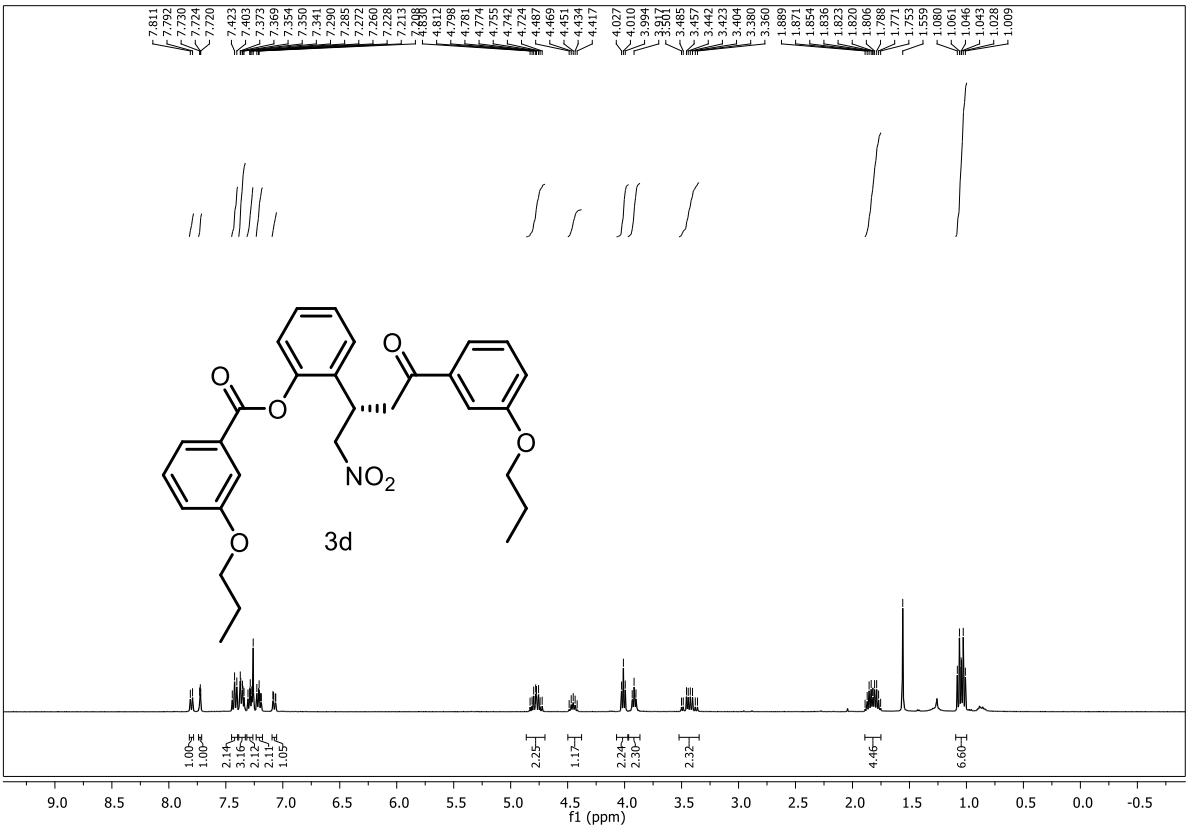
f1 (ppm)


3c
f1 (ppm)


3c
f1 (ppm)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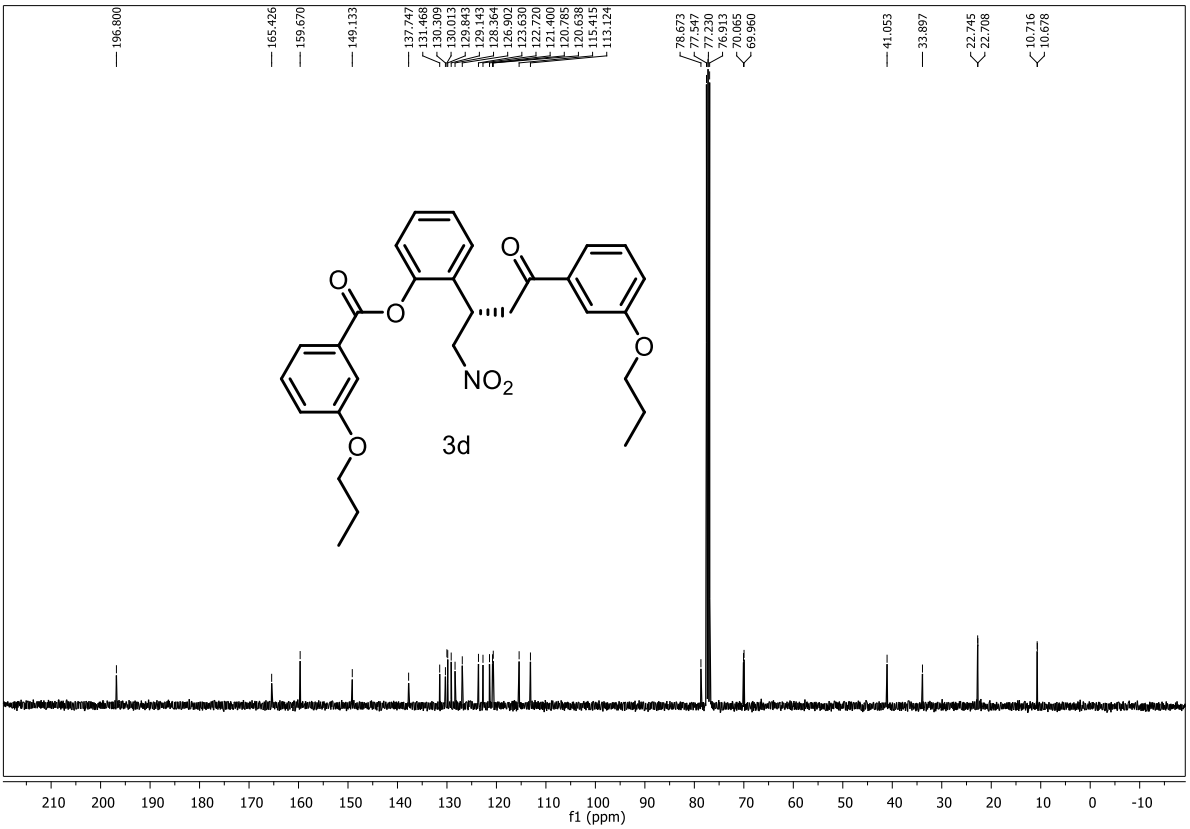
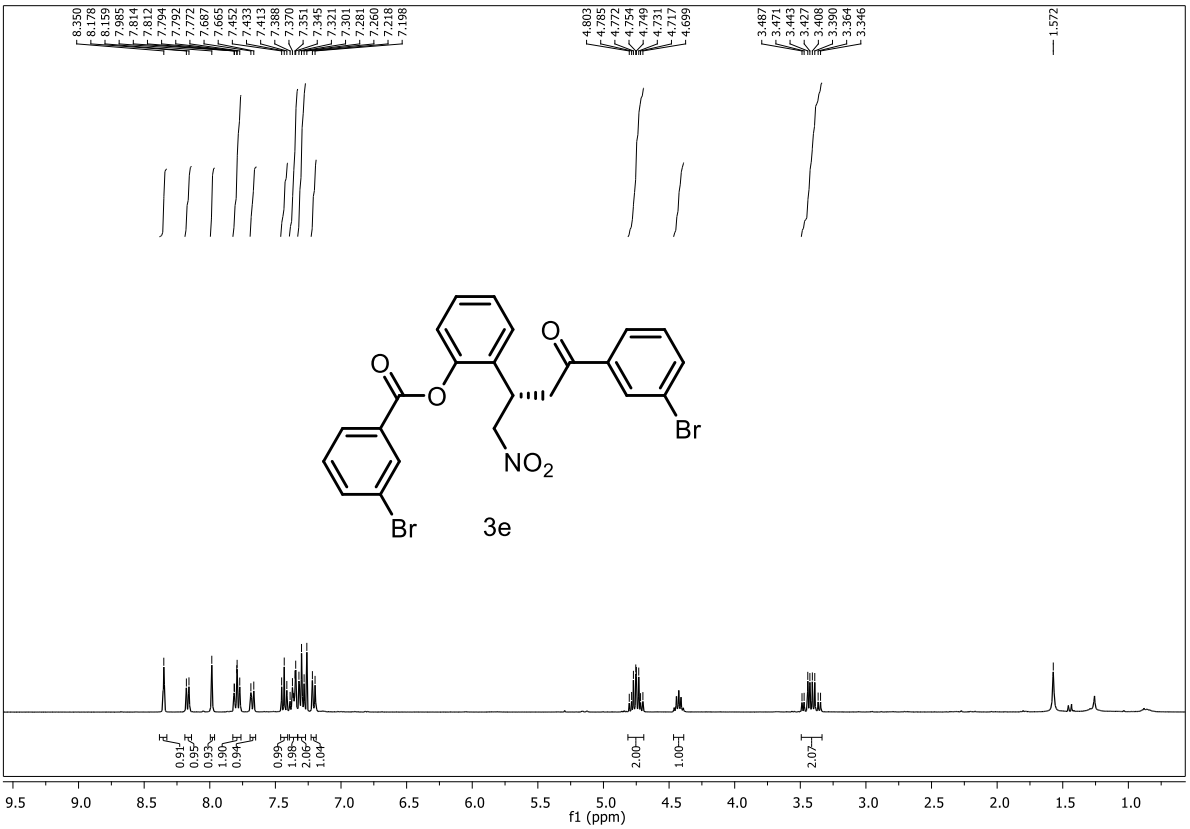
O
O
O
O
NO2
O
3d
1.00 1.00 2.14 3.16 2.12 2.11 1.05 2.25 1.17 2.24 2.30 2.32 4.46 6.60
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


196.800 165.426 159.670 149.133 137.747 131.468 130.309 130.013 129.843 129.143 128.364 126.902 123.630 122.720 121.400 120.785 120.638 115.415 113.124 78.673 77.547 77.230 76.913 70.065 69.960 41.053 33.897 22.745 22.708 10.716 10.678
O
O
O
O
NO2
O
3d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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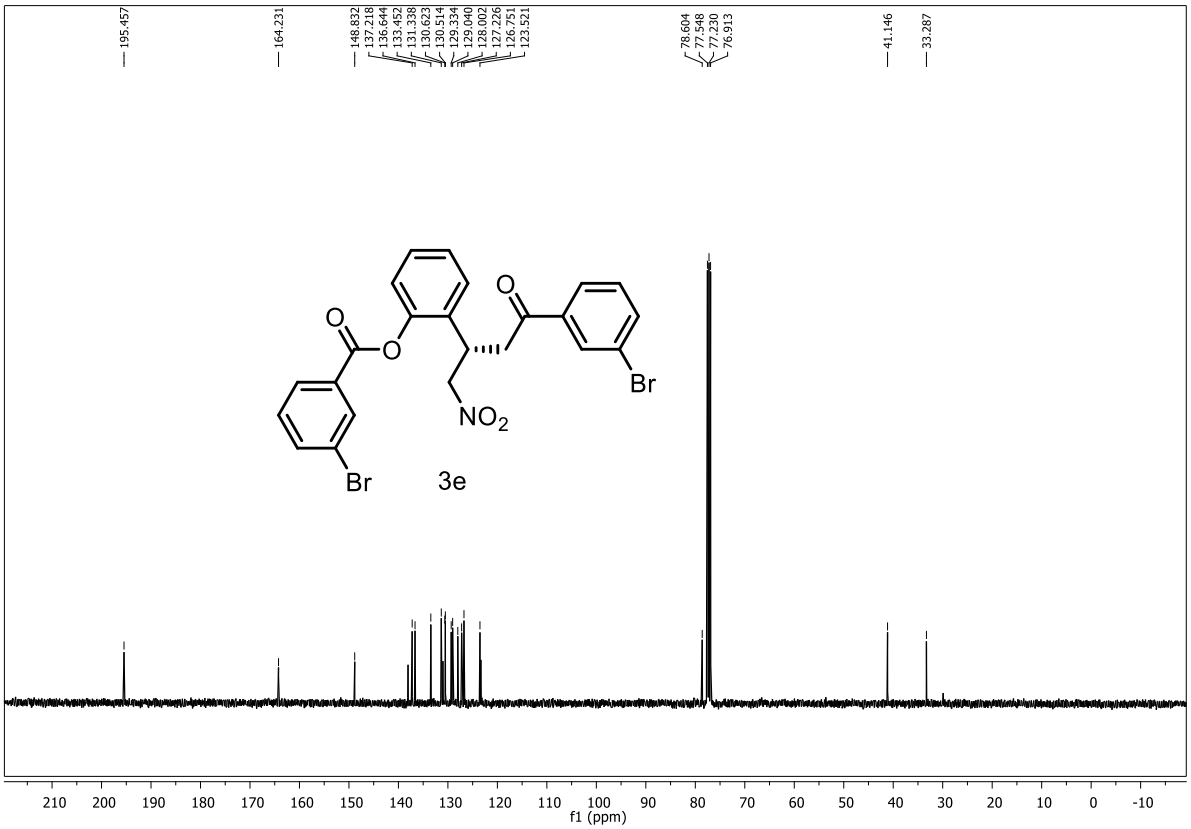
7.792
7.772
7.687
7.665
7.452
7.433
7.413
7.388
7.370
7.351
7.345
7.321
7.301
7.281
7.260
7.218
7.198
4.803
4.785
4.772
4.754
4.749
4.731
4.717
4.699
3.487
3.471
3.443
3.427
3.408
3.390
3.364
3.346
1.572
O
O
O
Br
NO2
Br
3e
0.91
0.95
0.93
1.90
0.94
0.99
1.98
2.06
1.04
2.00
1.00
2.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)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137.218
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130.623
130.514
129.334
129.040
128.002
127.226
126.751
123.521
78.604
77.548
77.230
76.913
41.146
33.287
O
O
O
Br
NO2
Br
3e
210
200
190
180
170
160
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140
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120
110
100
90
80
70
60
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40
30
20
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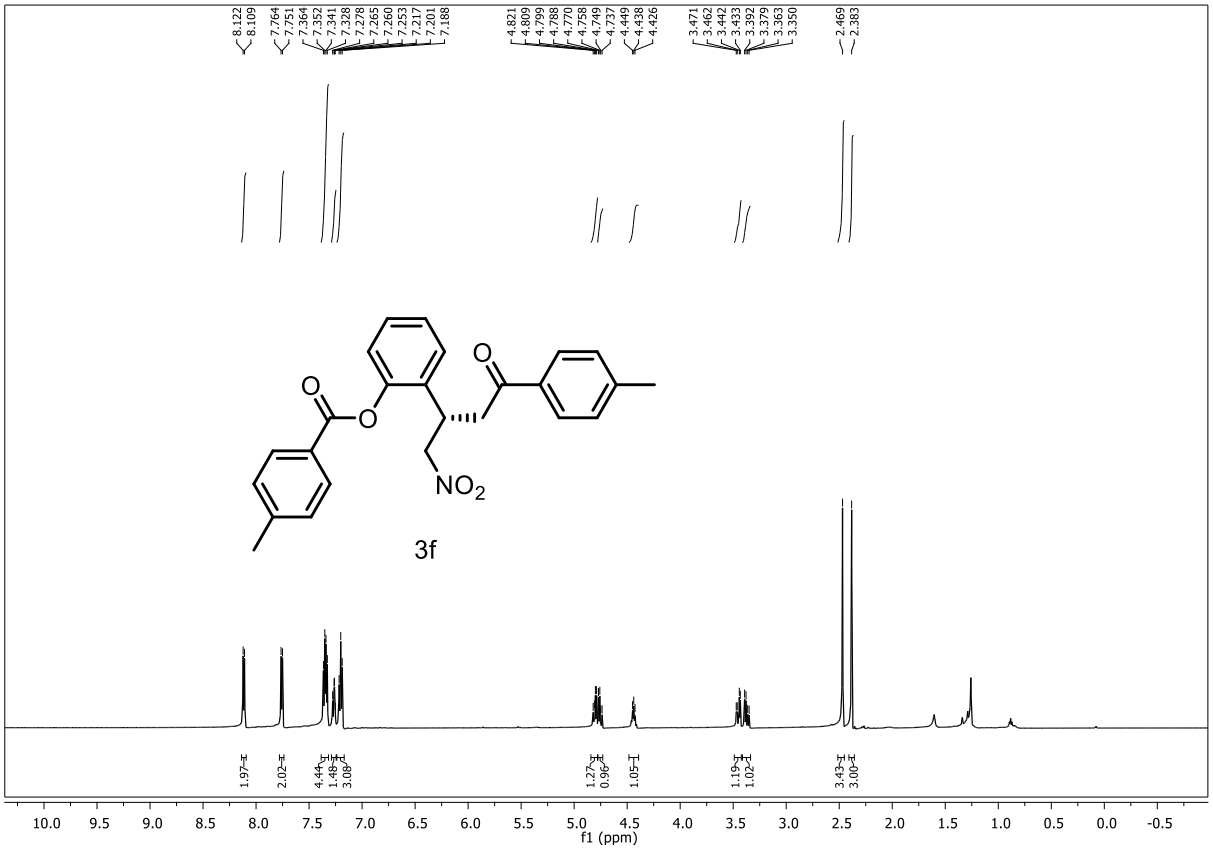
0
-10
f1 (ppm)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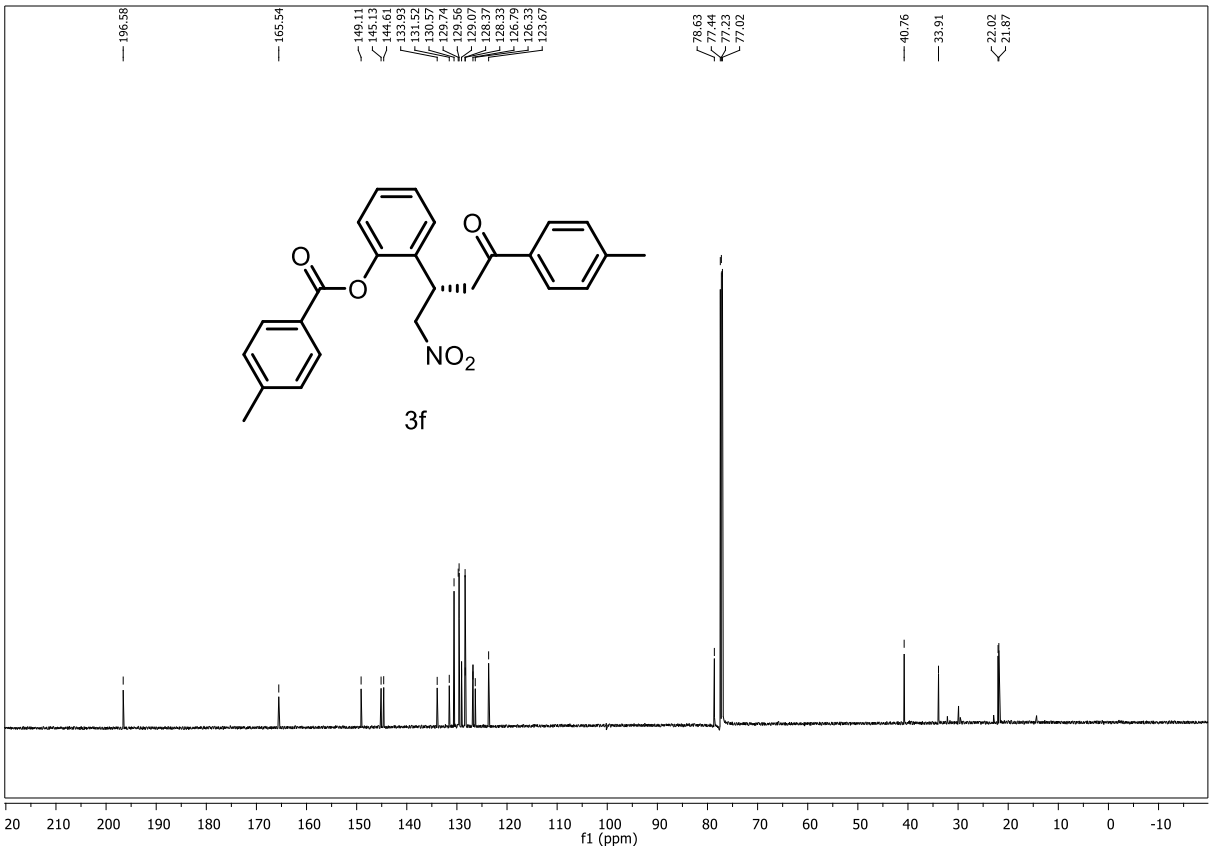
7.751
7.364
7.352
7.341
7.328
7.278
7.265
7.260
7.253
7.217
7.201
7.188
4.821
4.809
4.799
4.788
4.770
4.758
4.749
4.737
4.449
4.438
4.426
3.471
3.462
3.442
3.433
3.392
3.379
3.363
3.350
2.469
2.383
O
O
O
NO2
3f
1.97
2.02
4.44
1.48
3.08
1.27
0.96
1.05
1.19
1.02
3.43
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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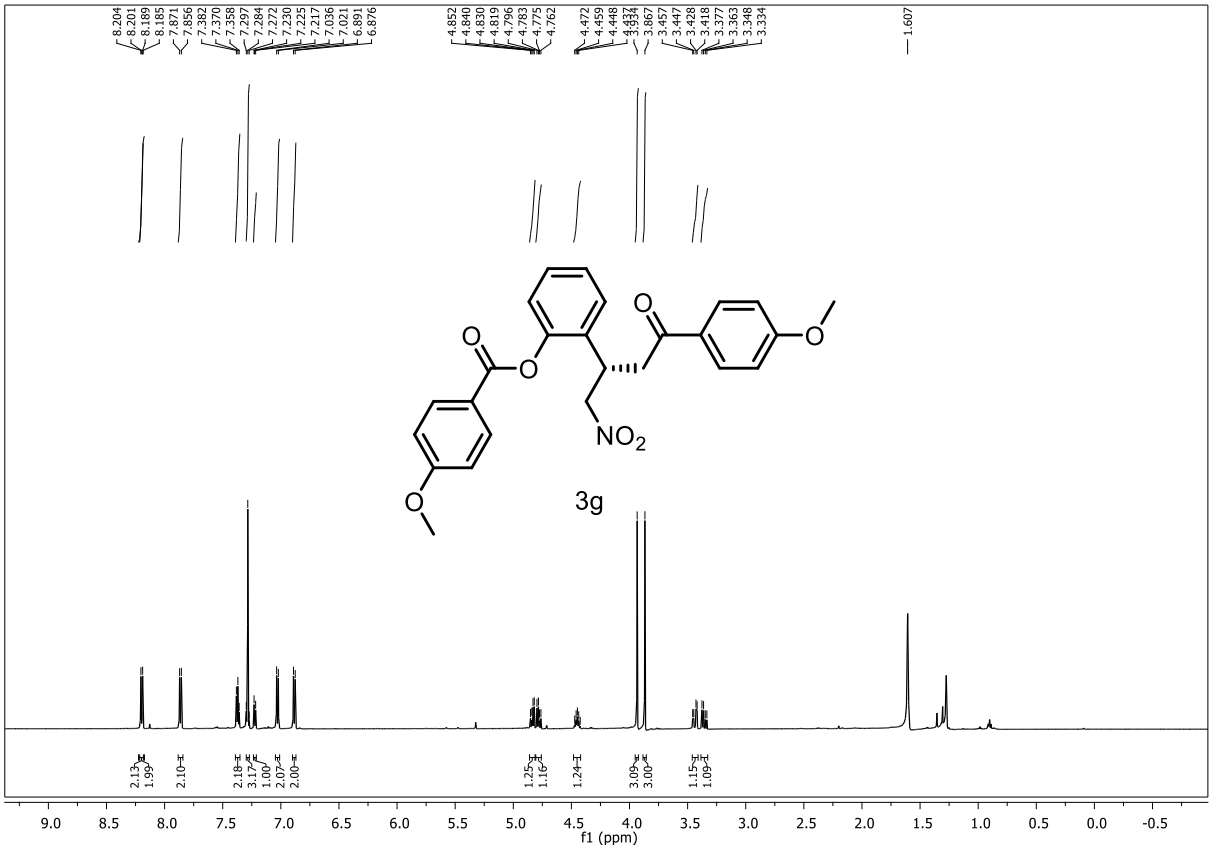
145.13
144.61
133.93
131.52
130.57
129.74
129.56
129.07
128.37
128.33
126.79
126.33
123.67
78.63
77.44
77.23
77.02
40.76
33.91
22.02
21.87
O
O
O
NO2
3f
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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8.189
8.185
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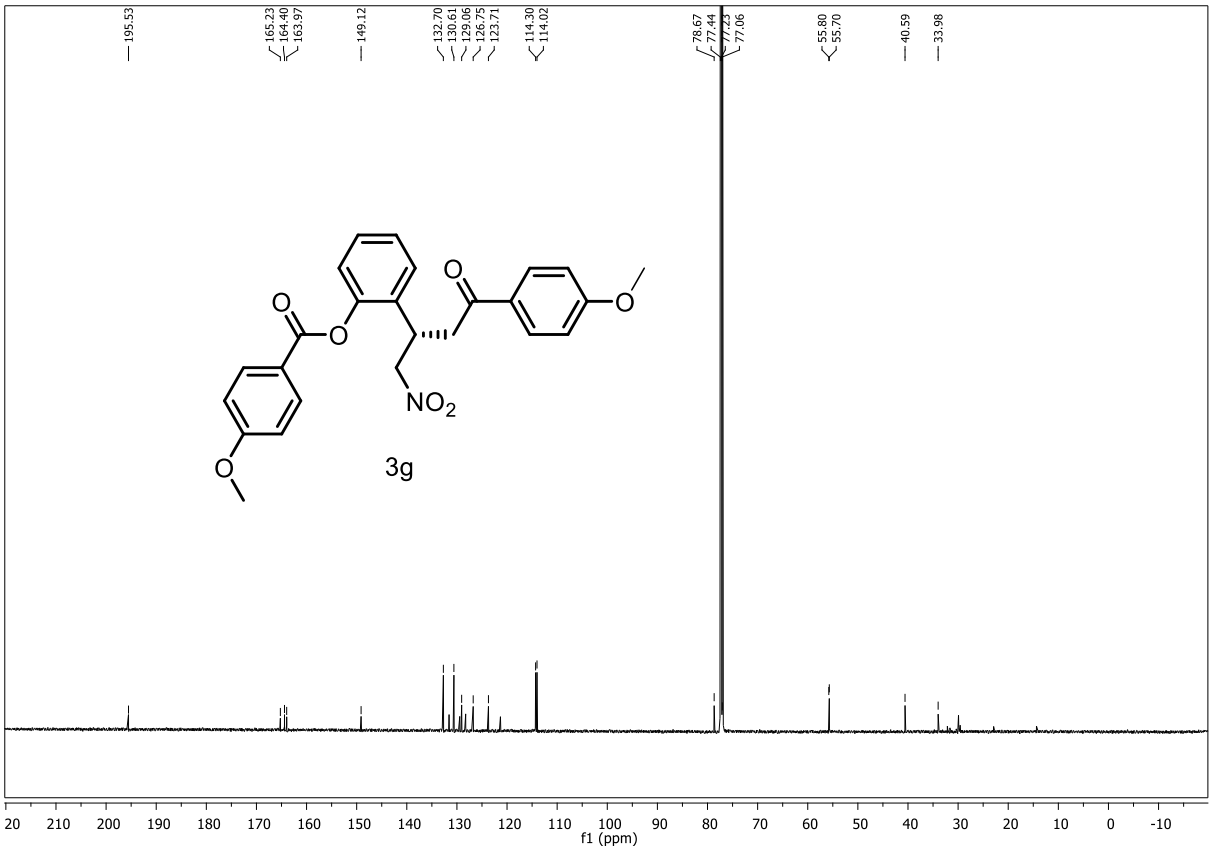
7.856
7.382
7.370
7.358
7.297
7.284
7.272
7.230
7.225
7.217
7.036
7.021
6.891
6.876
4.852
4.840
4.830
4.819
4.796
4.783
4.775
4.762
4.472
4.459
4.448
3.867
3.457
3.447
3.428
3.418
3.377
3.363
3.348
3.334
1.607
O
O
O
O
NO2
O
3g
2.13
1.99
2.10
2.18
3.17
1.00
2.07
2.00
1.25
1.16
1.24
3.09
3.00
1.15
1.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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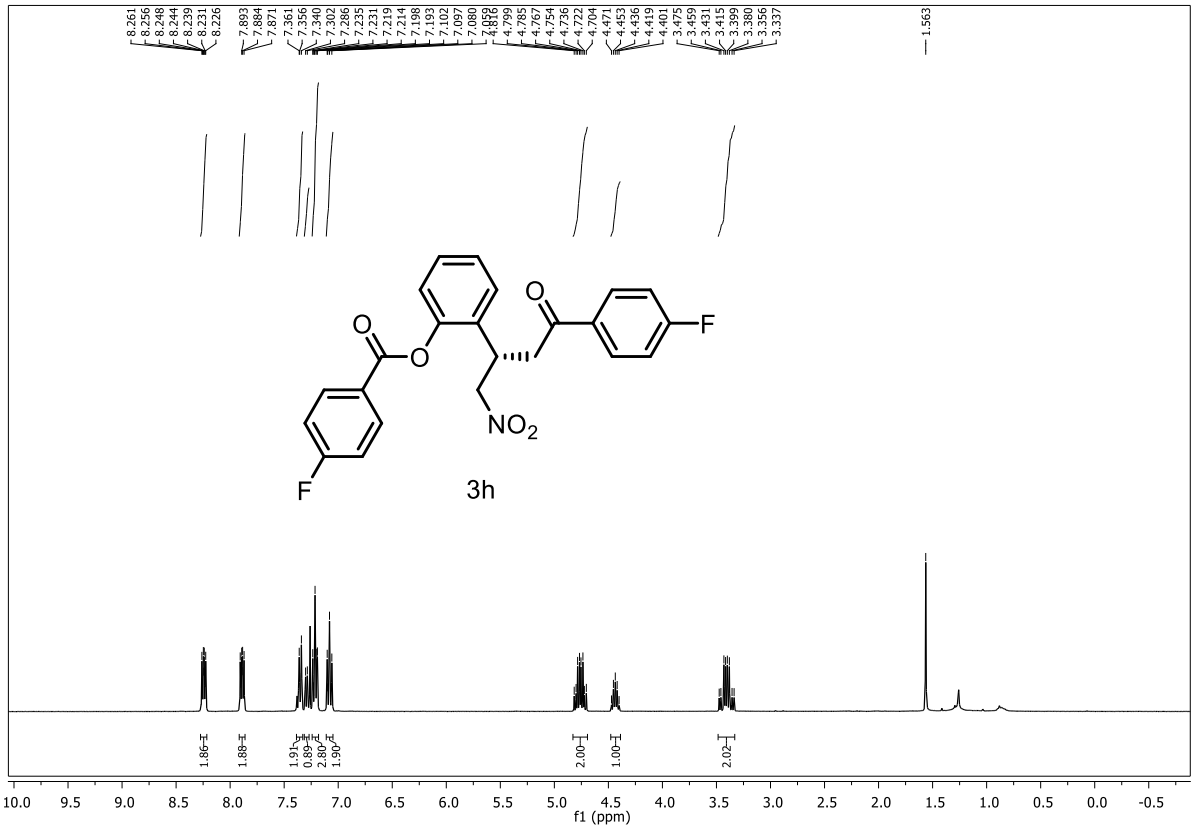
165.23
164.40
163.97
149.12
132.70
130.61
129.06
126.75
123.71
114.30
114.02
78.67
77.44
77.23
77.06
55.80
55.70
40.59
33.98
O
O
O
O
NO2
3g
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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8.239
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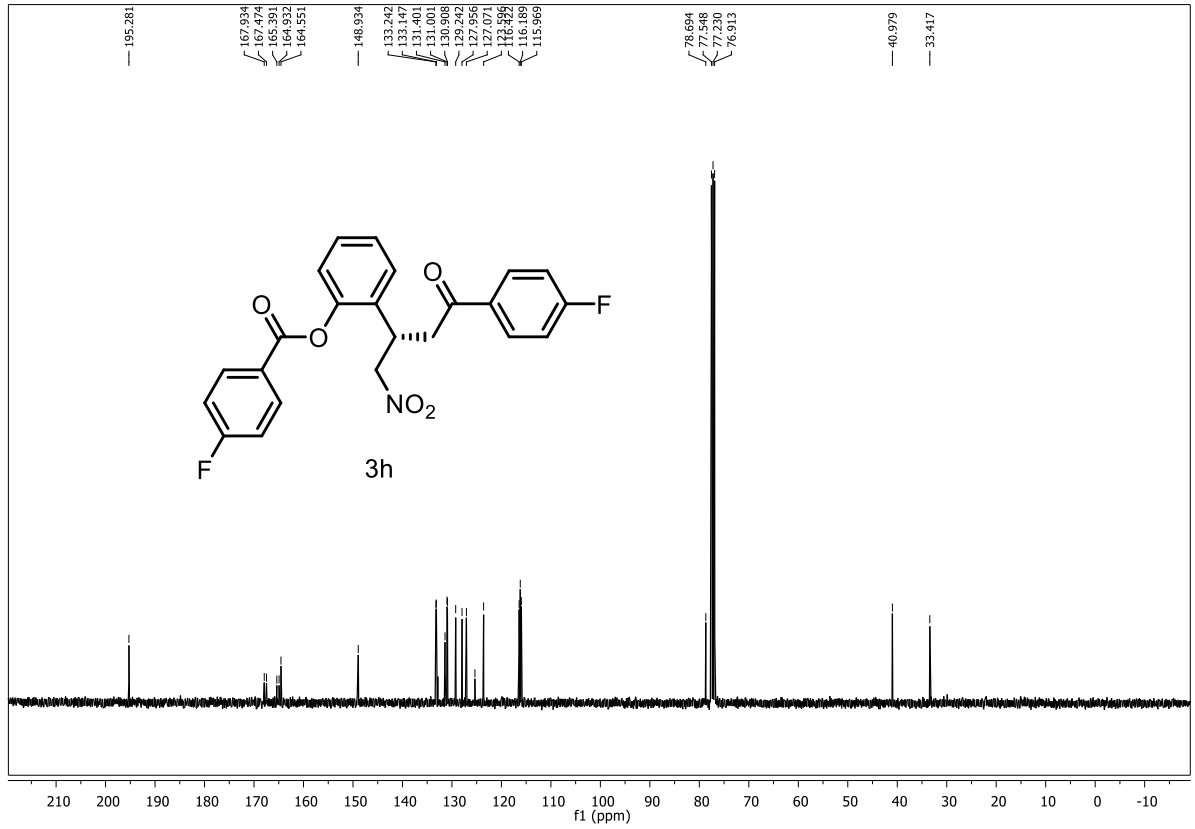
7.893
7.884
7.871
7.361
7.356
7.340
7.302
7.286
7.235
7.231
7.219
7.214
7.198
7.193
7.102
7.097
7.080
4.799
4.785
4.767
4.754
4.736
4.722
4.704
4.471
4.453
4.436
4.419
4.401
3.475
3.459
3.431
3.415
3.399
3.380
3.356
3.337
1.563
O
O
O
F
F
NO2
3h
1.86
1.88
1.91
0.89
2.89
1.90
2.00
1.00
2.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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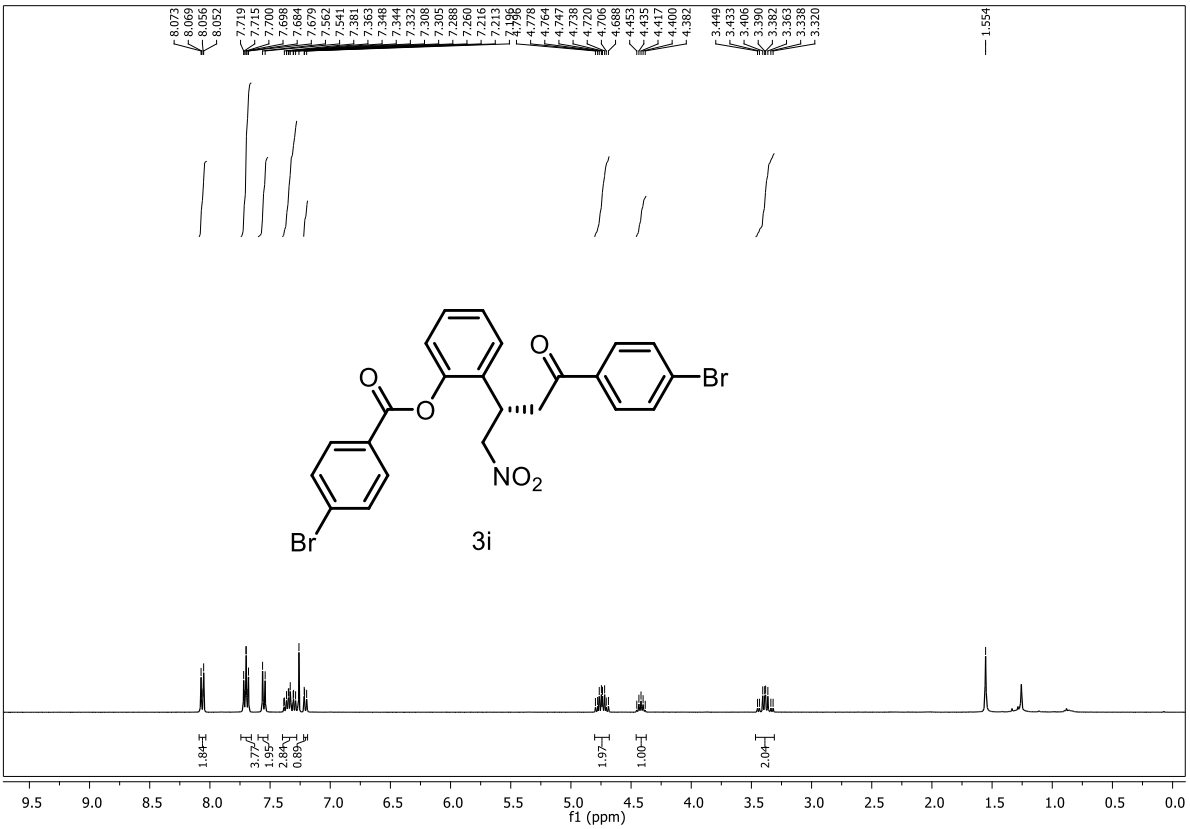
167.474
165.391
164.932
164.551
148.934
133.242
133.147
131.401
131.001
130.908
129.242
127.956
127.071
123.596
116.422
116.189
115.969
78.694
77.548
77.230
76.913
40.979
33.417
O
O
O
F
F
NO2
3h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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8.052
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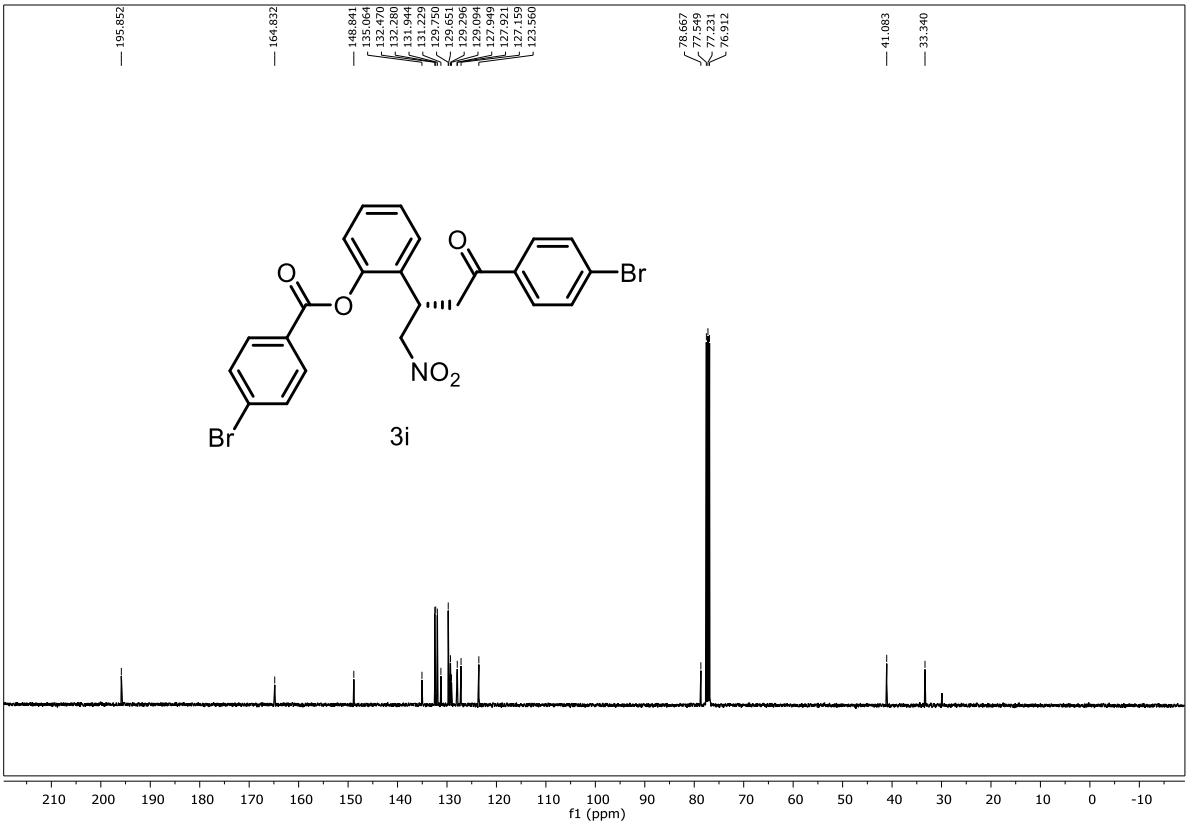
7.715
7.700
7.698
7.684
7.679
7.562
7.541
7.381
7.363
7.348
7.344
7.332
7.308
7.305
7.288
7.260
7.216
7.213
7.196
4.778
4.764
4.747
4.738
4.720
4.706
4.688
4.453
4.435
4.417
4.400
4.382
3.449
3.433
3.406
3.390
3.382
3.363
3.338
3.320
1.554
O
O
O
Br
NO2
Br
3i
1.84
3.77
1.95
2.84
0.89
1.97
1.00
2.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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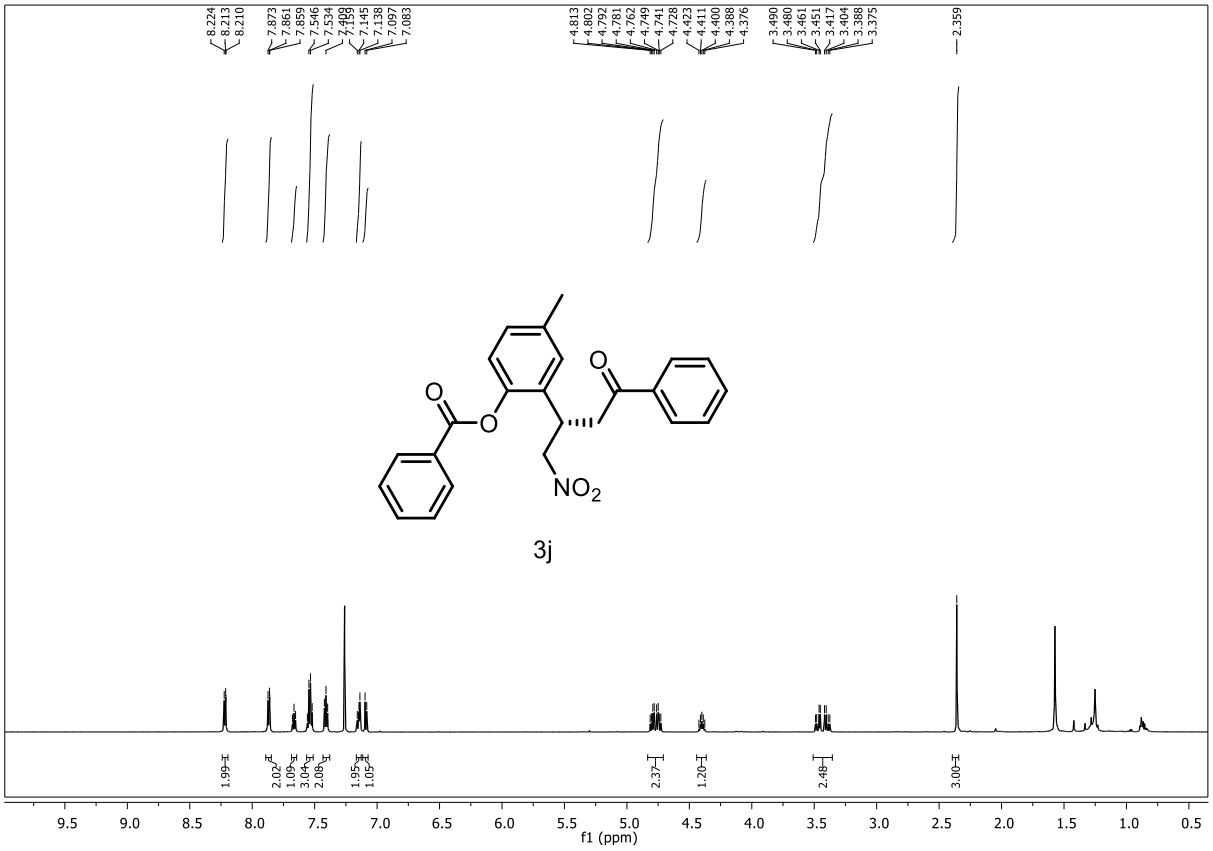
131.229
129.750
129.651
129.296
129.094
127.949
127.921
127.159
123.560
78.667
77.549
77.231
76.912
41.083
33.340
O
O
O
Br
NO2
Br
3i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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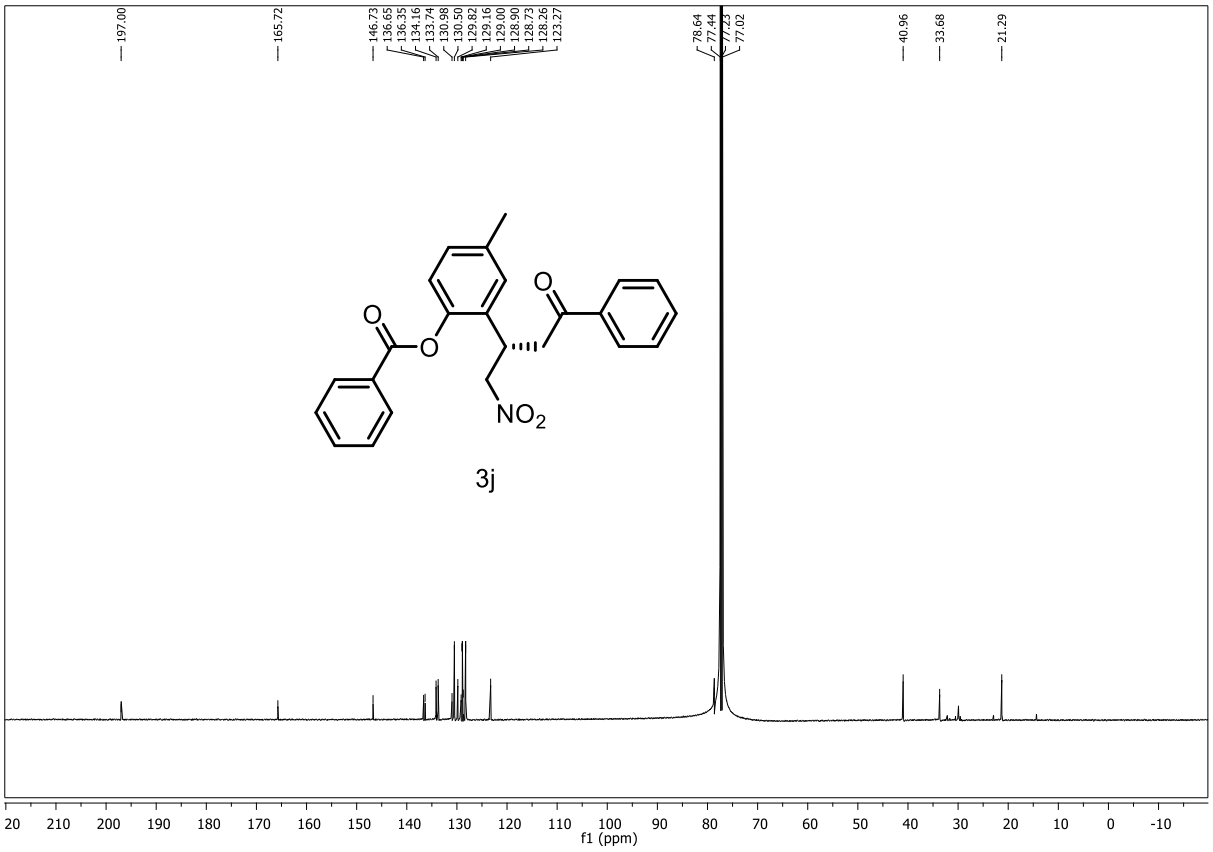
7.409
7.159
7.145
7.138
7.097
7.083
4.813
4.802
4.792
4.781
4.762
4.749
4.741
4.728
4.423
4.411
4.400
4.388
4.376
3.490
3.480
3.461
3.451
3.417
3.404
3.388
3.375
2.359
O
O
O
NO2
3j
1.99
2.02
1.09
3.04
2.08
1.95
1.05
2.37
1.20
2.48
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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130.98
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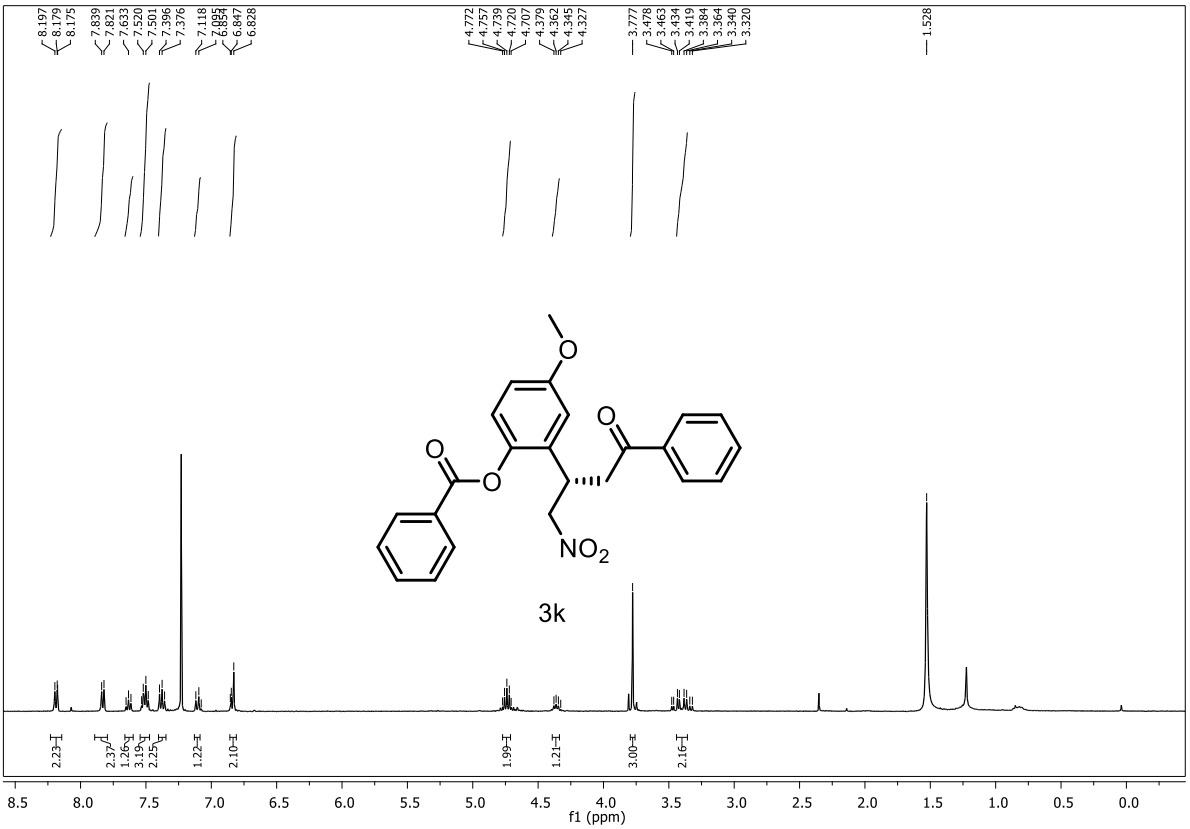
129.82
129.16
129.00
128.90
128.73
128.26
123.27
78.64
77.44
77.23
77.02
40.96
33.68
21.29
O
O
O
NO2
3j
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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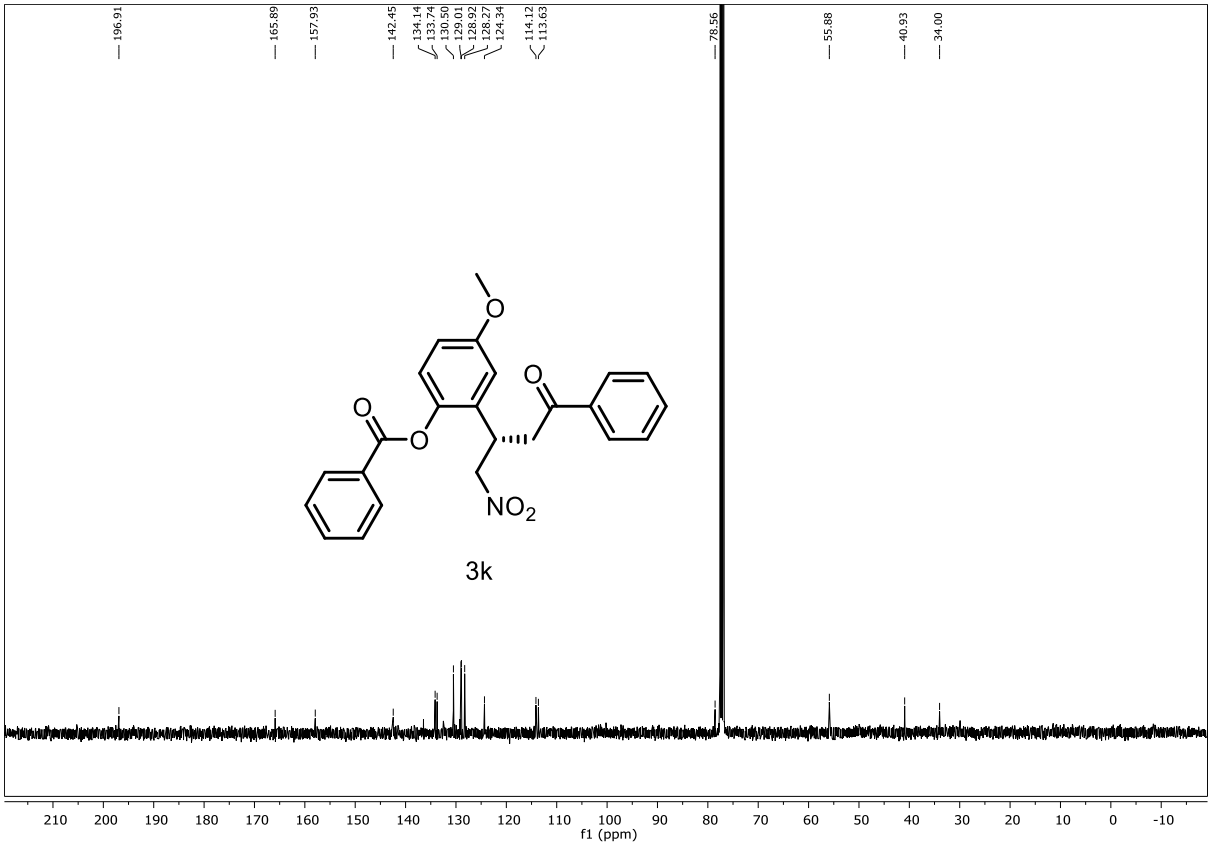
7.396
7.376
7.118
7.095
6.854
6.847
6.828
4.772
4.757
4.739
4.720
4.707
4.379
4.362
4.345
4.327
3.777
3.478
3.463
3.434
3.419
3.384
3.364
3.340
3.320
1.528
O
O
O
O
NO2
3k
2.23
2.37
1.26
3.19
2.25
1.22
2.10
1.99
1.21
3.00
2.16
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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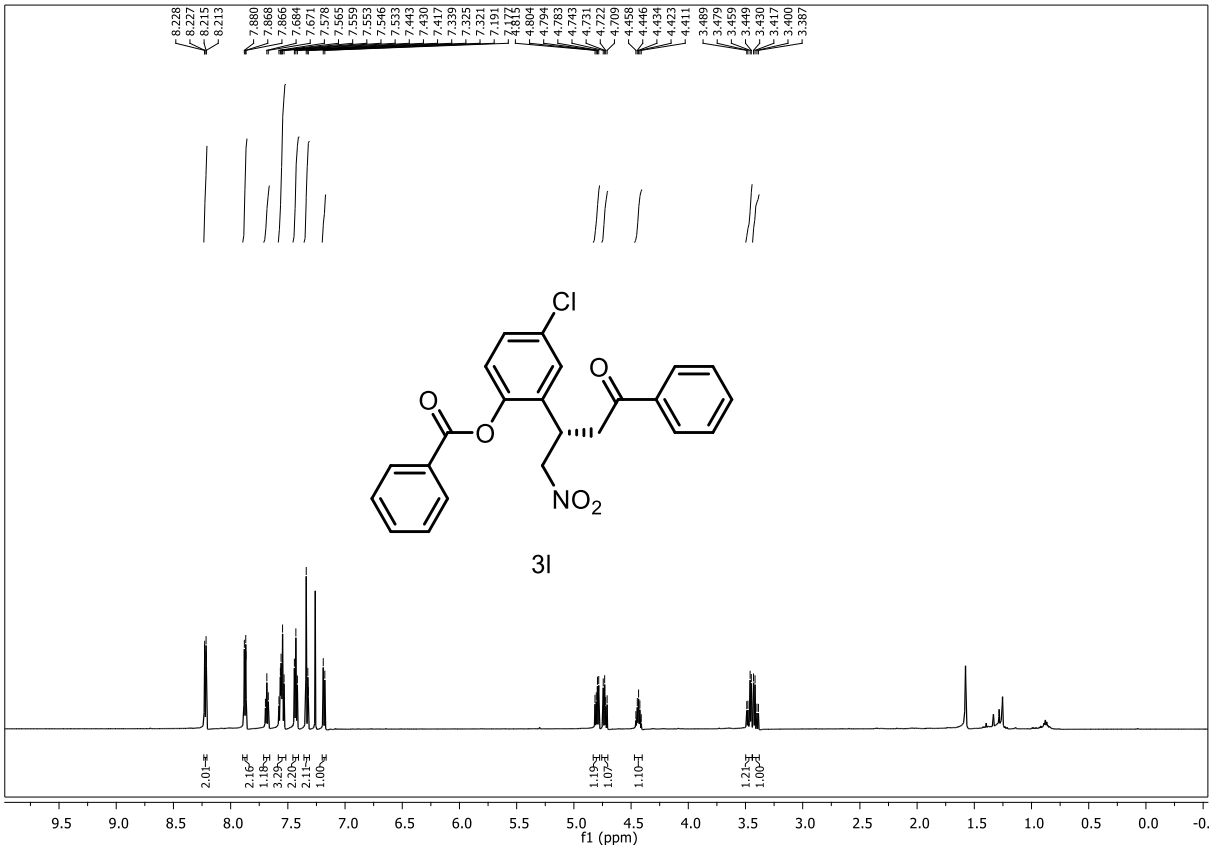
134.14
133.74
130.50
129.01
128.92
128.27
124.34
114.12
113.63
78.56
55.88
40.93
34.00
O
O
O
O
NO2
3k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.684
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7.565
7.559
7.553
7.546
7.533
7.443
7.430
7.417
7.339
7.325
7.321
7.191
7.177
4.815
4.804
4.794
4.783
4.743
4.731
4.722
4.709
4.458
4.446
4.434
4.423
4.411
3.489
3.479
3.459
3.449
3.430
3.417
3.400
3.387
Cl
O
O
O
NO2
3l
2.01
2.16
1.18
3.29
2.20
2.11
1.00
1.19
1.07
1.10
1.21
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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3.5
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2.5
2.0
1.5
1.0
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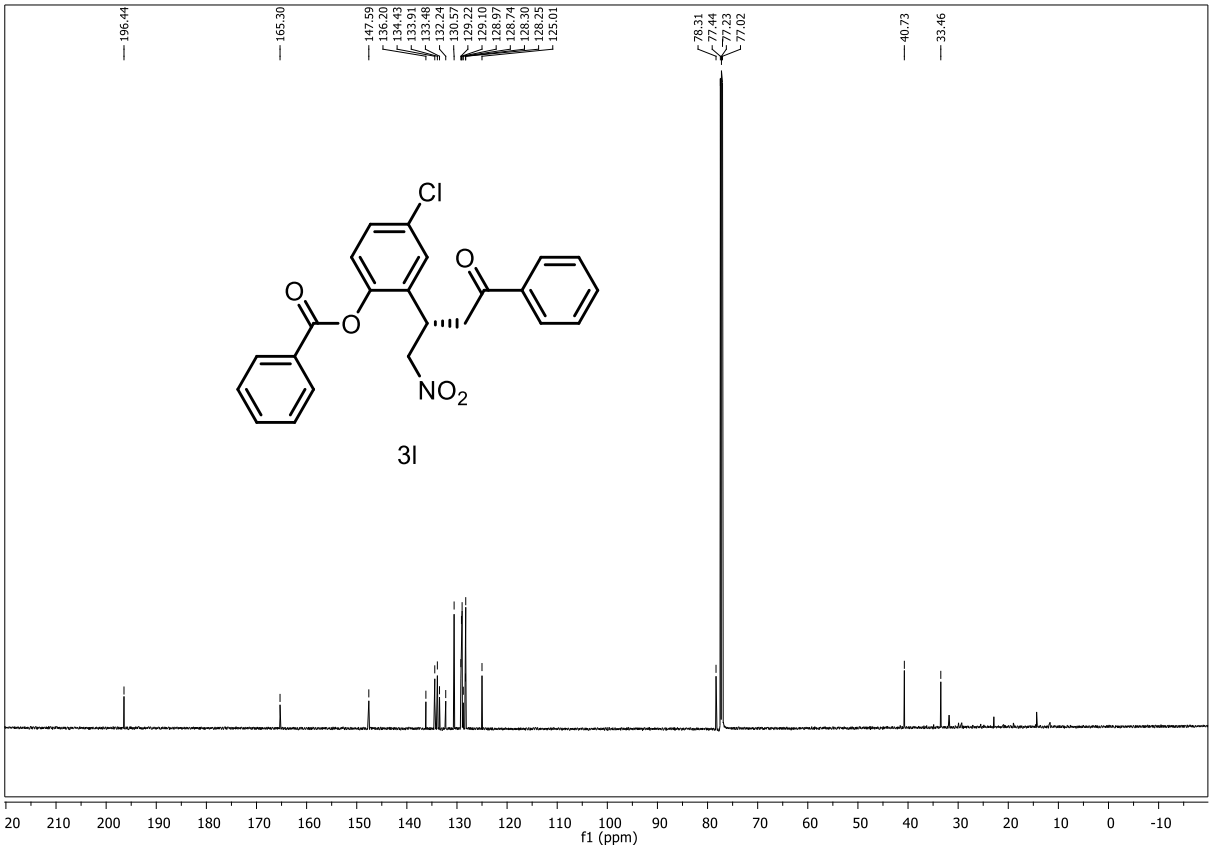
0.0
f1 (ppm)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136.20
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133.91
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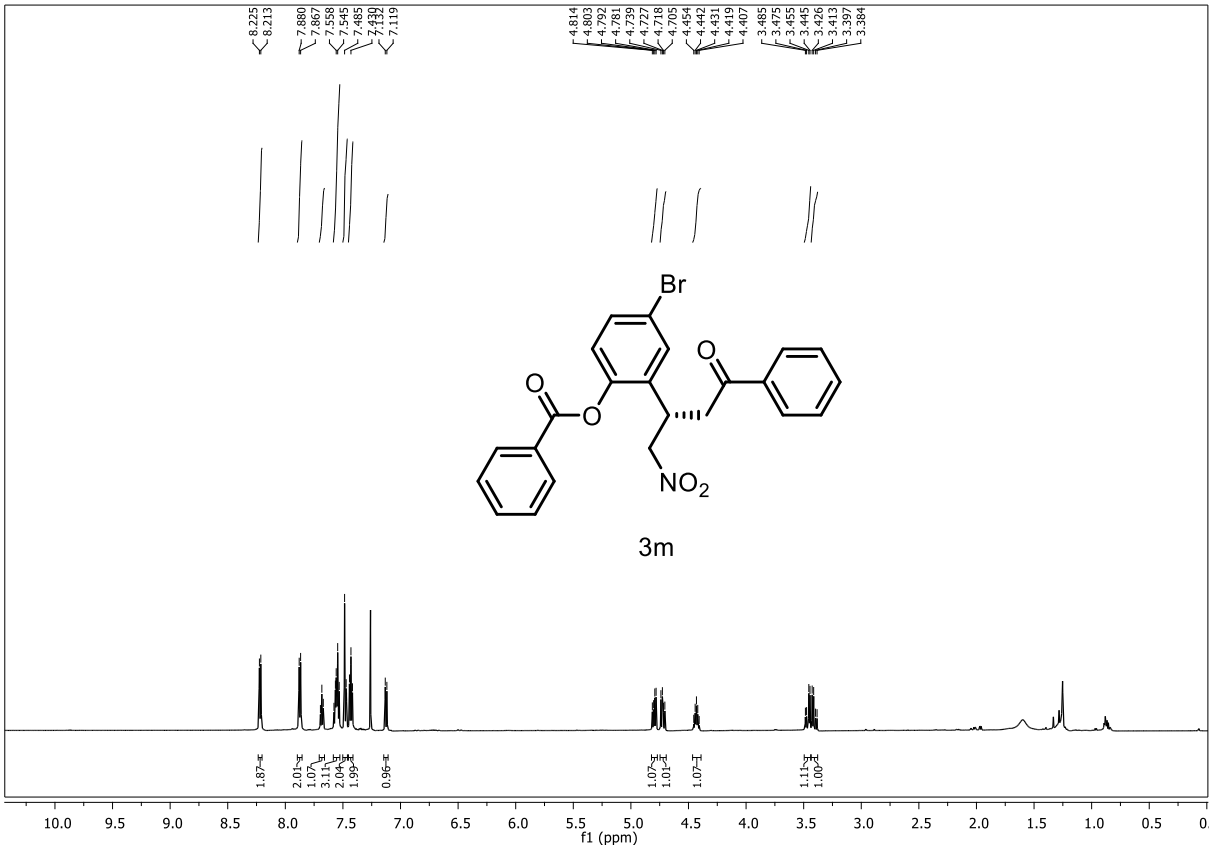
132.24
130.57
129.22
129.10
128.97
128.74
128.30
128.25
125.01
78.31
77.44
77.23
77.02
40.73
33.46
Cl
O
O
O
NO2
3l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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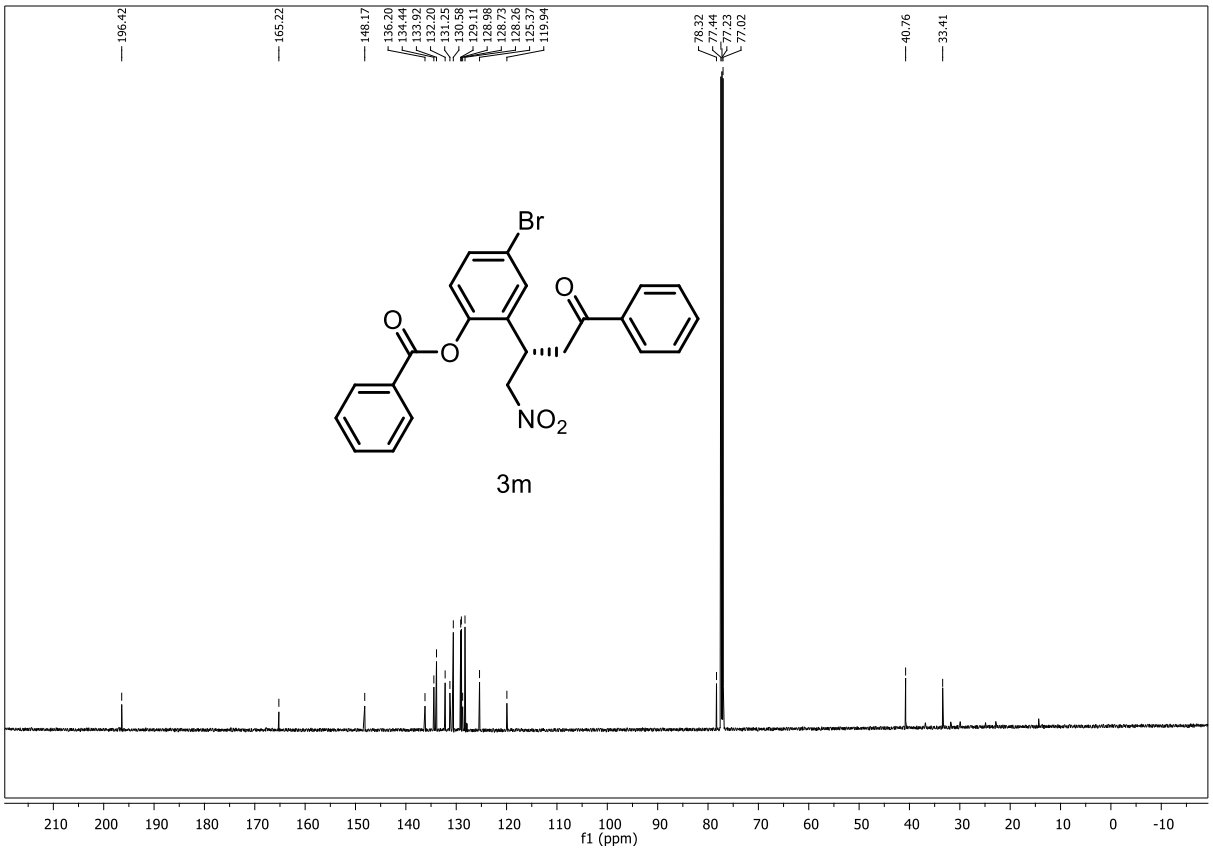
7.470
7.432
7.119
4.814
4.803
4.792
4.781
4.739
4.727
4.718
4.705
4.454
4.442
4.431
4.419
4.407
3.485
3.475
3.455
3.445
3.426
3.413
3.397
3.384
Br
O
O
O
NO2
3m
1.87
2.01
1.07
3.11
2.04
1.99
0.96
1.07
1.01
1.07
1.11
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)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131.25
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129.11
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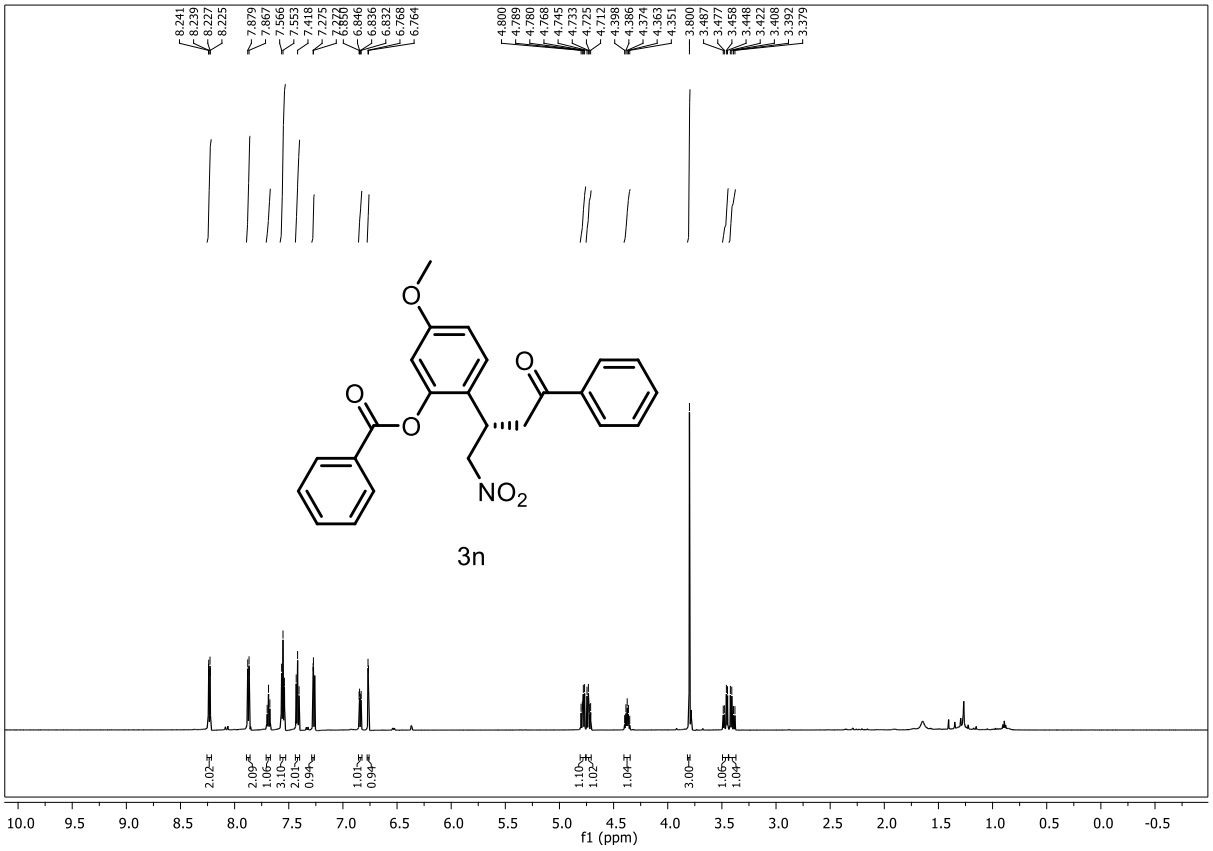
128.73
128.26
125.37
119.94
78.32
77.44
77.23
77.02
40.76
33.41
Br
O
O
O
NO2
3m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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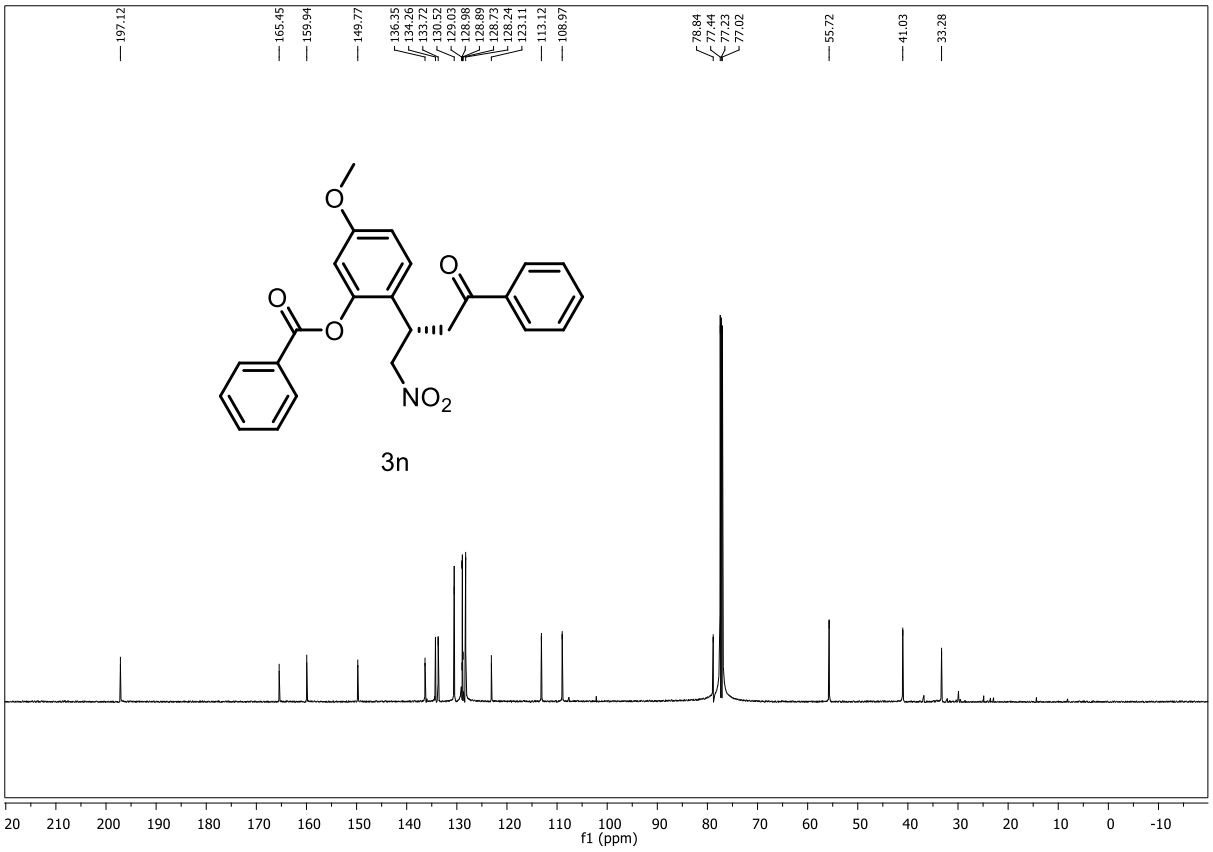
6.836
6.832
6.768
6.764
4.800
4.789
4.780
4.768
4.745
4.733
4.725
4.712
4.398
4.386
4.374
4.363
4.351
3.800
3.487
3.477
3.458
3.448
3.422
3.408
3.392
3.379
O
O
O
O
NO2
3n
2.02
2.09
1.06
3.10
2.01
0.94
1.01
0.94
1.10
1.02
1.04
3.00
1.06
1.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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128.24
123.11
113.12
108.97
78.84
77.44
77.23
77.02
55.72
41.03
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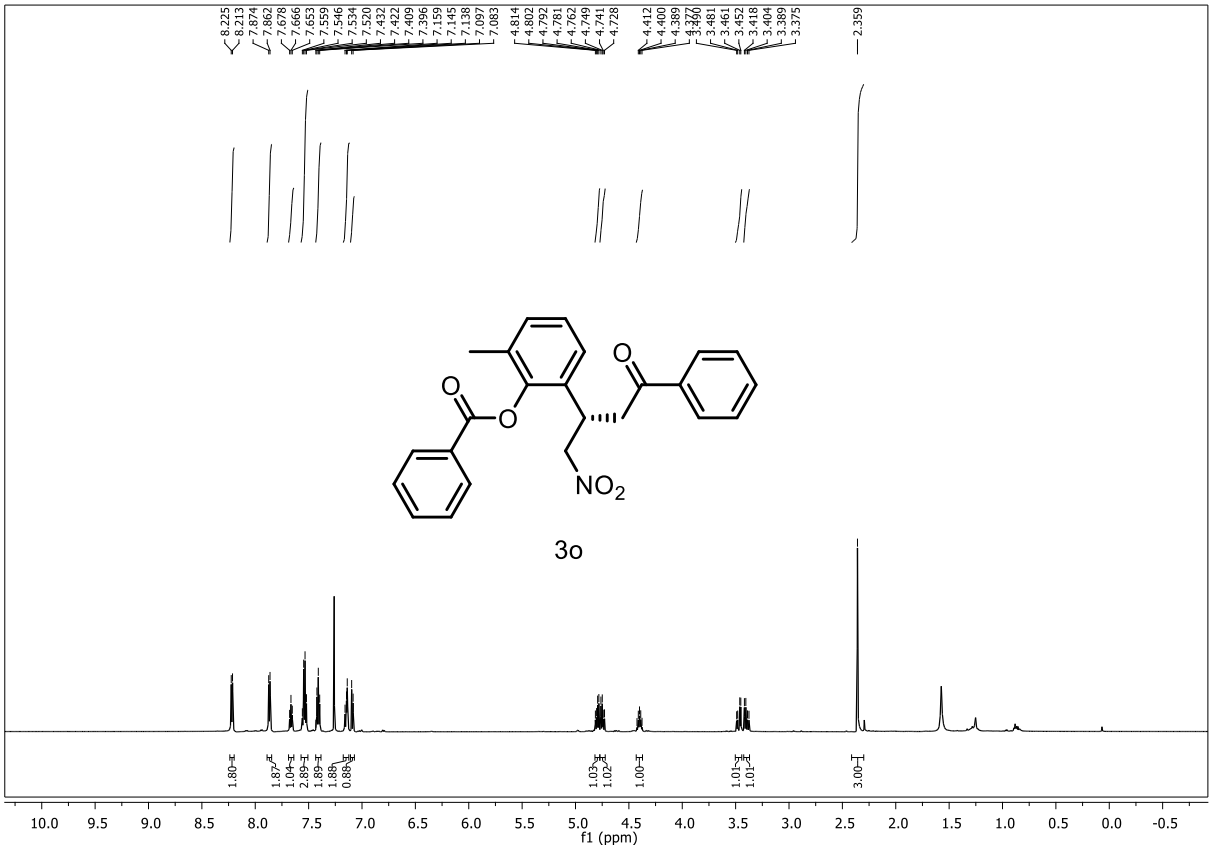
O
O
O
O
NO2
3n
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.546
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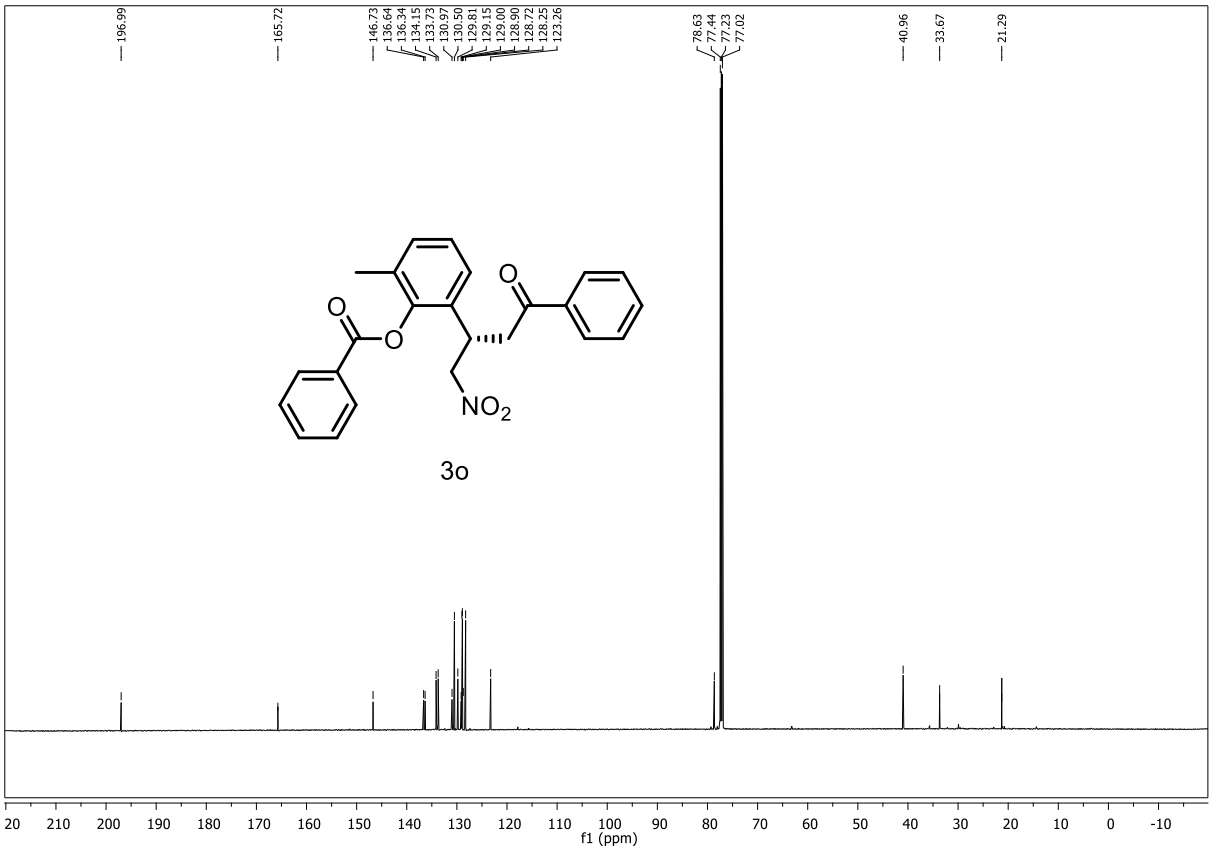
7.422
7.409
7.396
7.159
7.145
7.138
7.097
7.083
4.814
4.802
4.792
4.781
4.762
4.749
4.741
4.728
4.412
4.400
4.389
4.377
4.490
3.481
3.461
3.452
3.418
3.404
3.389
3.375
2.359
O
O
O
NO2
3o
1.80
1.87
1.04
2.89
1.89
1.88
0.88
1.03
1.02
1.00
1.01
1.01
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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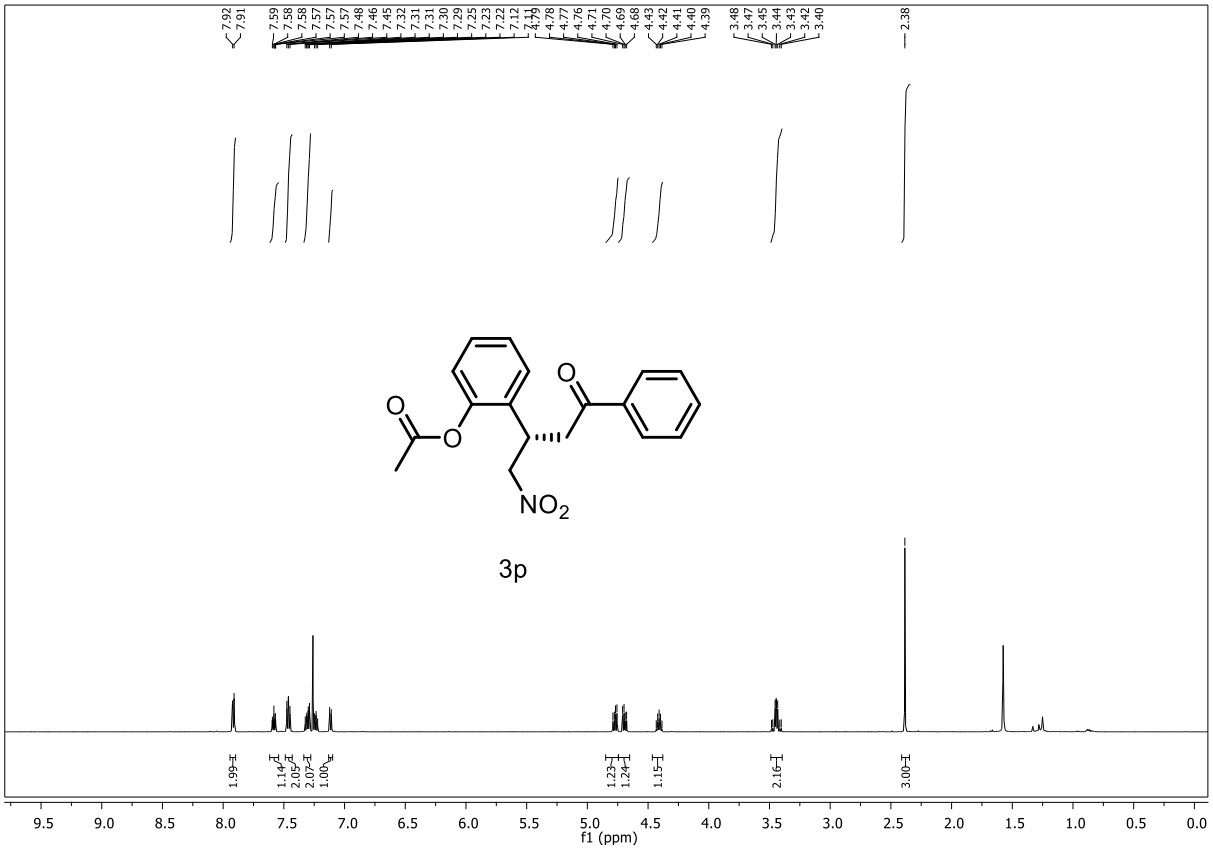
129.00
128.90
128.72
128.25
123.26
78.63
77.44
77.23
77.02
40.96
33.67
21.29
O
O
O
NO2
3o
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.58
7.58
7.57
7.57
7.57
7.48
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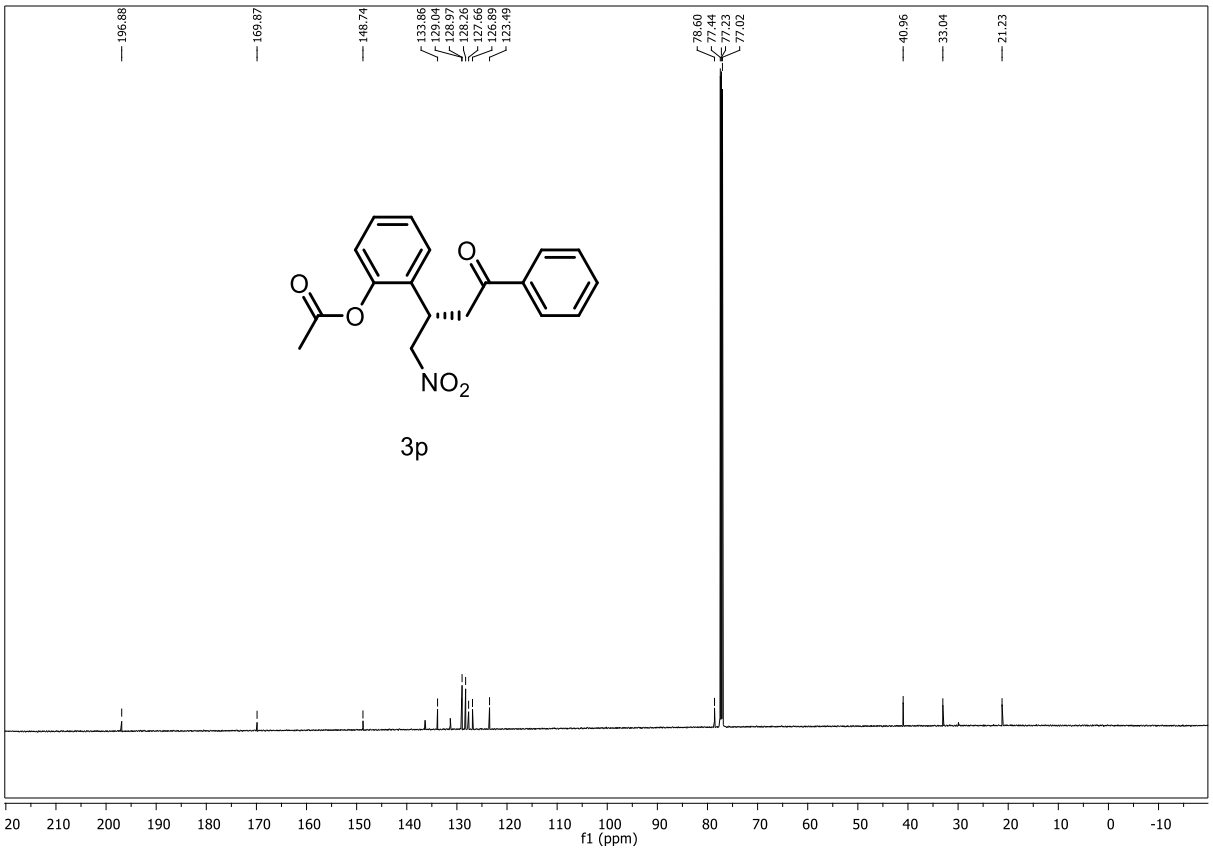
7.45
7.32
7.31
7.31
7.30
7.29
7.25
7.23
7.22
7.12
4.78
4.77
4.76
4.71
4.70
4.69
4.68
4.43
4.42
4.41
4.40
4.39
3.48
3.47
3.45
3.44
3.43
3.42
3.40
2.38
O
O
O
NO2
3p
1.99
1.14
2.05
2.07
1.00
1.23
1.24
1.15
2.16
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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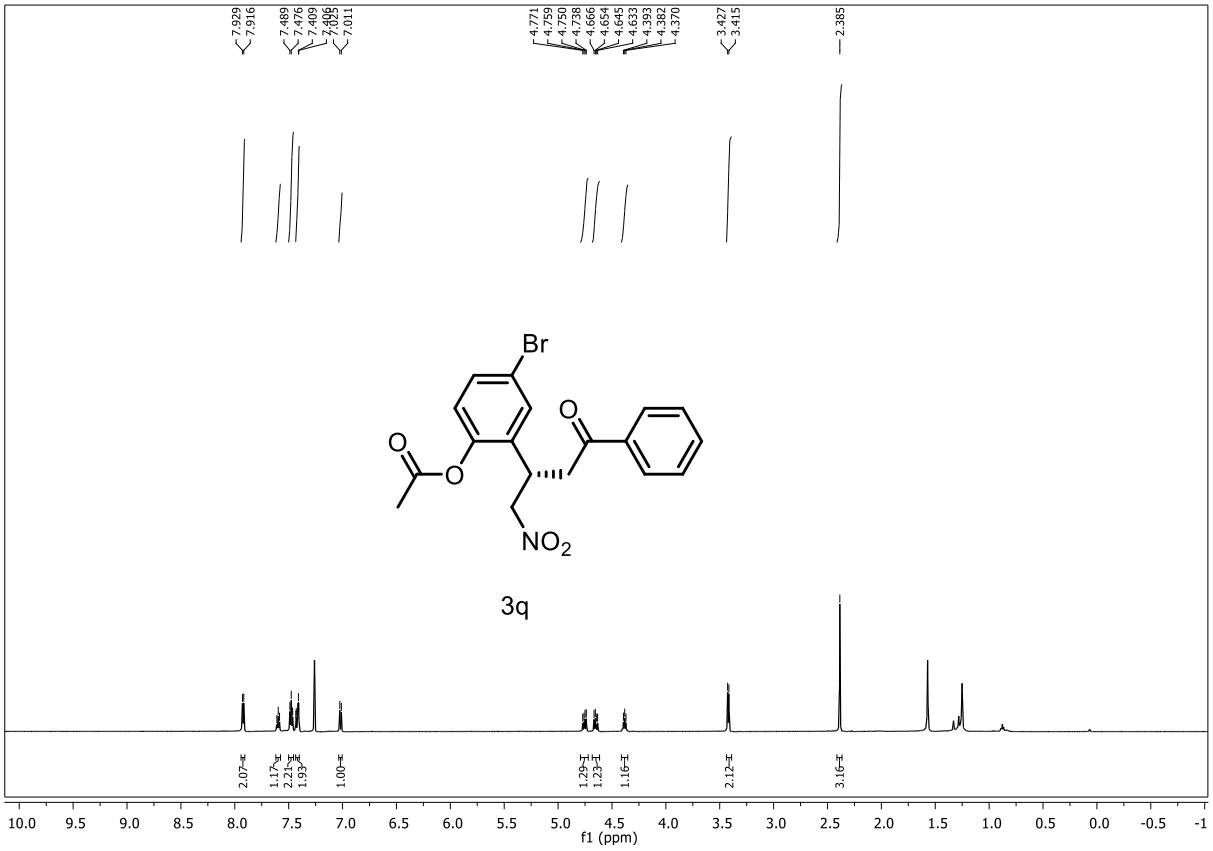
128.26
127.66
126.89
123.49
78.60
77.44
77.23
77.02
40.96
33.04
21.23
O
O
O
NO2
3p
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.409
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7.011
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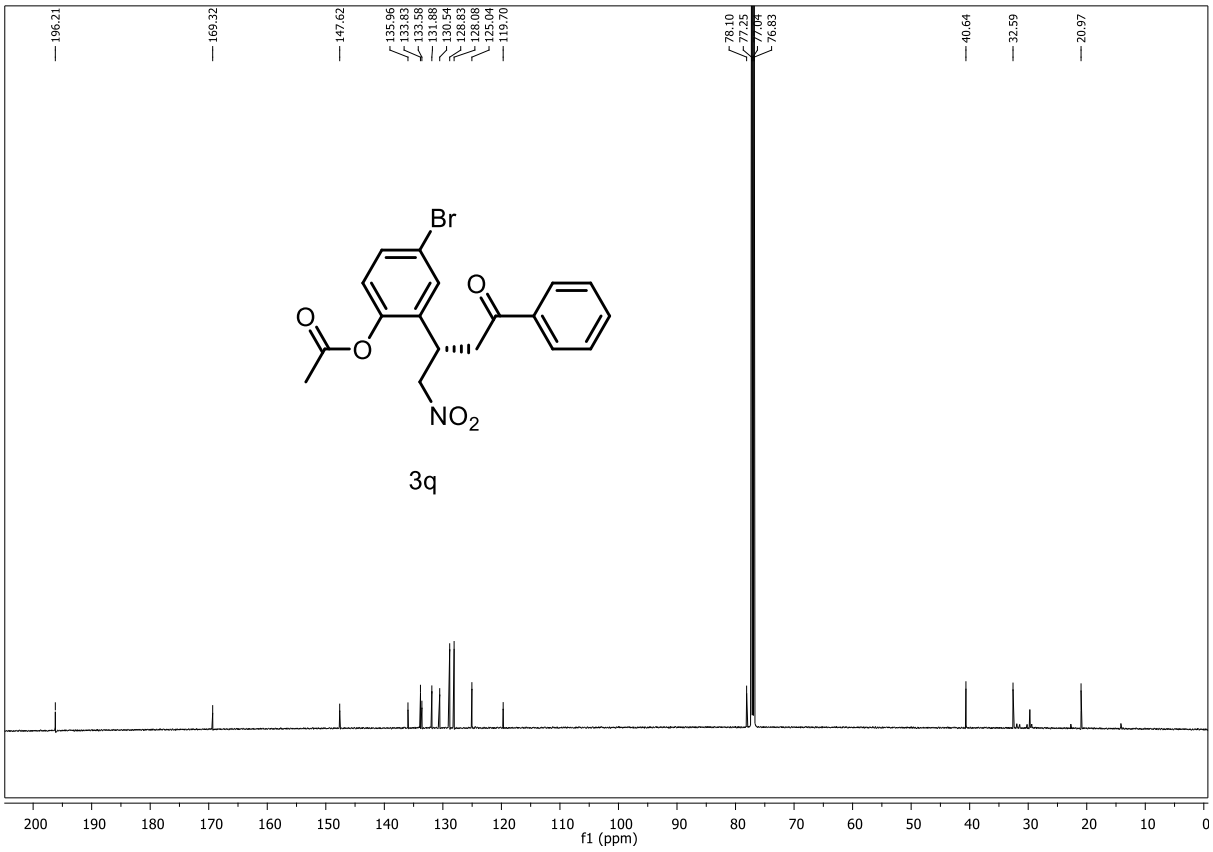
4.759
4.750
4.738
4.666
4.654
4.645
4.633
4.393
4.382
4.370
3.427
3.415
2.385
Br
O
O
O
NO2
3q
2.07
1.17
2.21
1.99
1.00
1.29
1.23
1.16
2.12
3.16
f1 (ppm)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135.96
133.83
133.58
131.88
130.54
128.83
128.08
125.04
119.70
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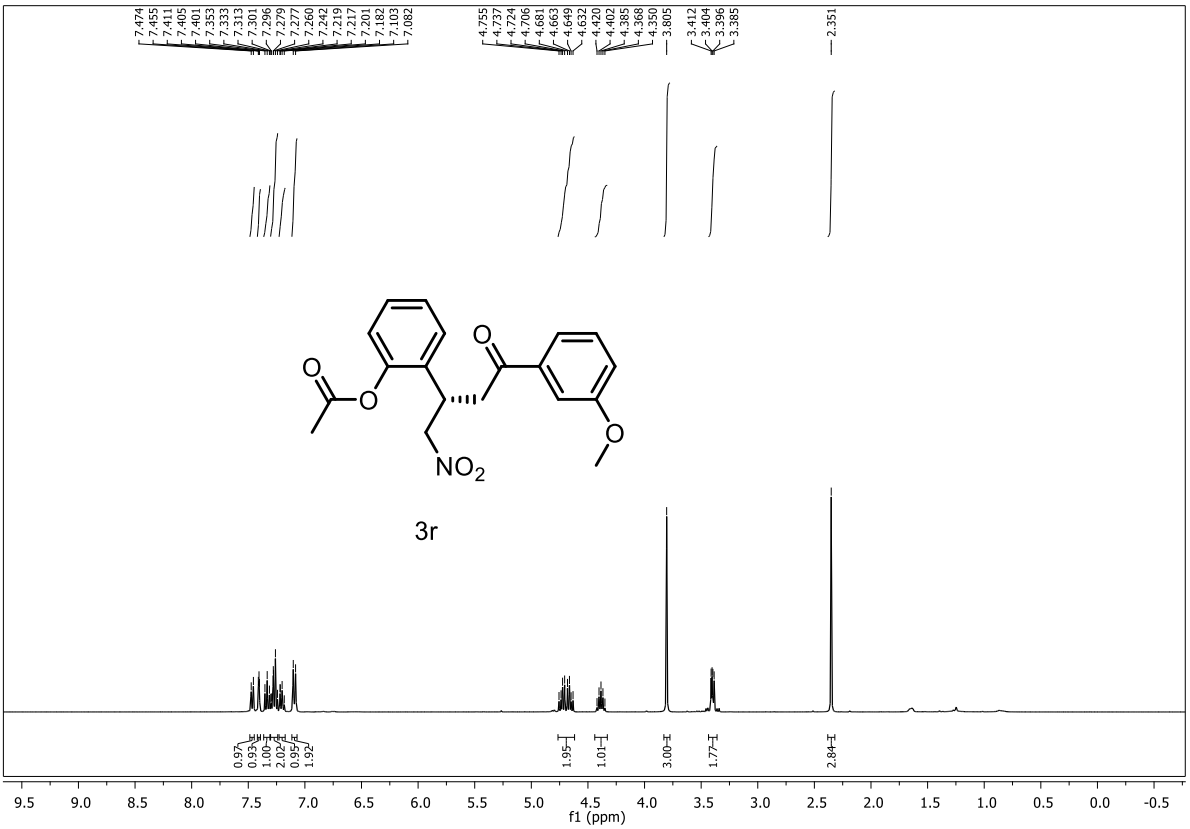
77.25
77.04
76.83
40.64
32.59
20.97
Br
O
O
O
NO2
3q
f1 (ppm)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7.353
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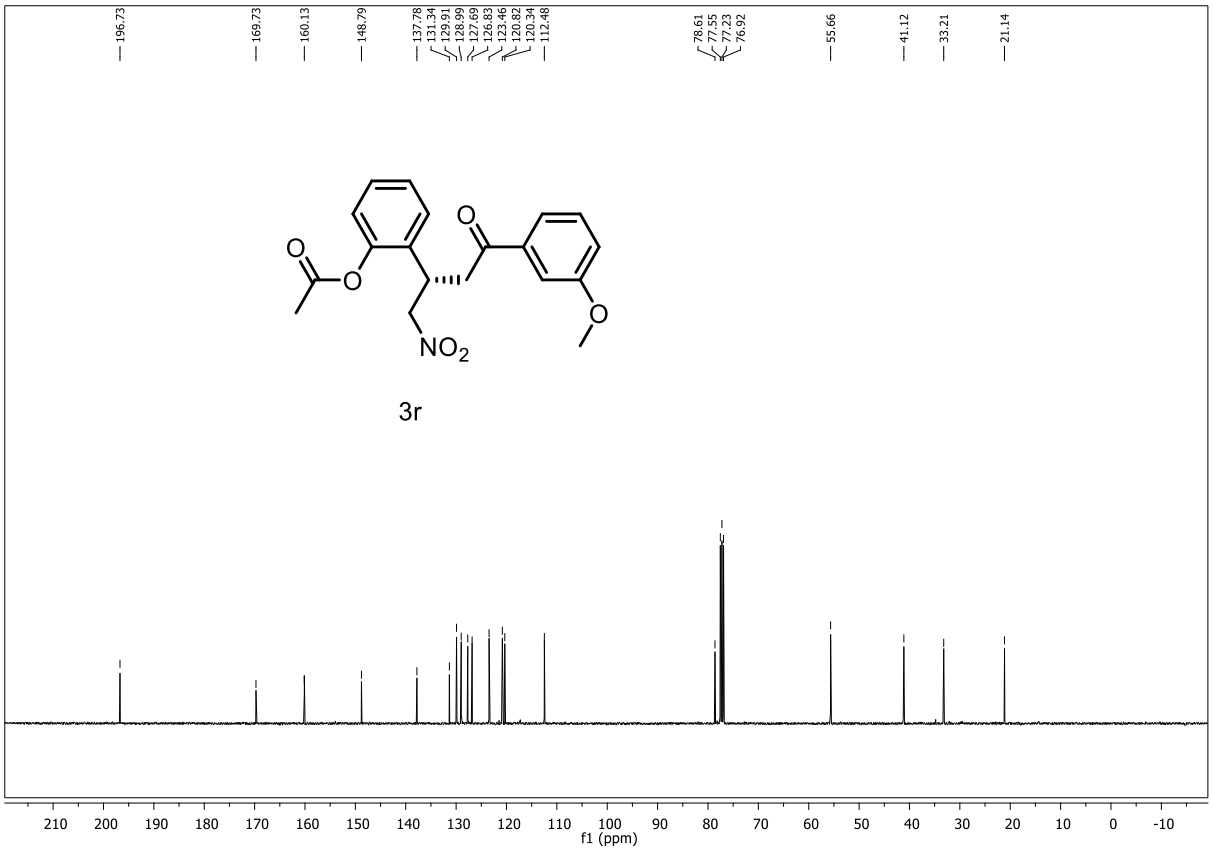
7.296
7.279
7.277
7.260
7.242
7.219
7.217
7.201
7.182
7.103
7.082
4.755
4.737
4.724
4.706
4.681
4.663
4.649
4.632
4.420
4.402
4.385
4.368
4.350
3.805
3.412
3.404
3.396
3.385
2.351
O
O
O
O
NO2
3r
0.97
0.93
1.00
2.02
0.95
1.92
1.95
1.01
3.00
1.77
2.84
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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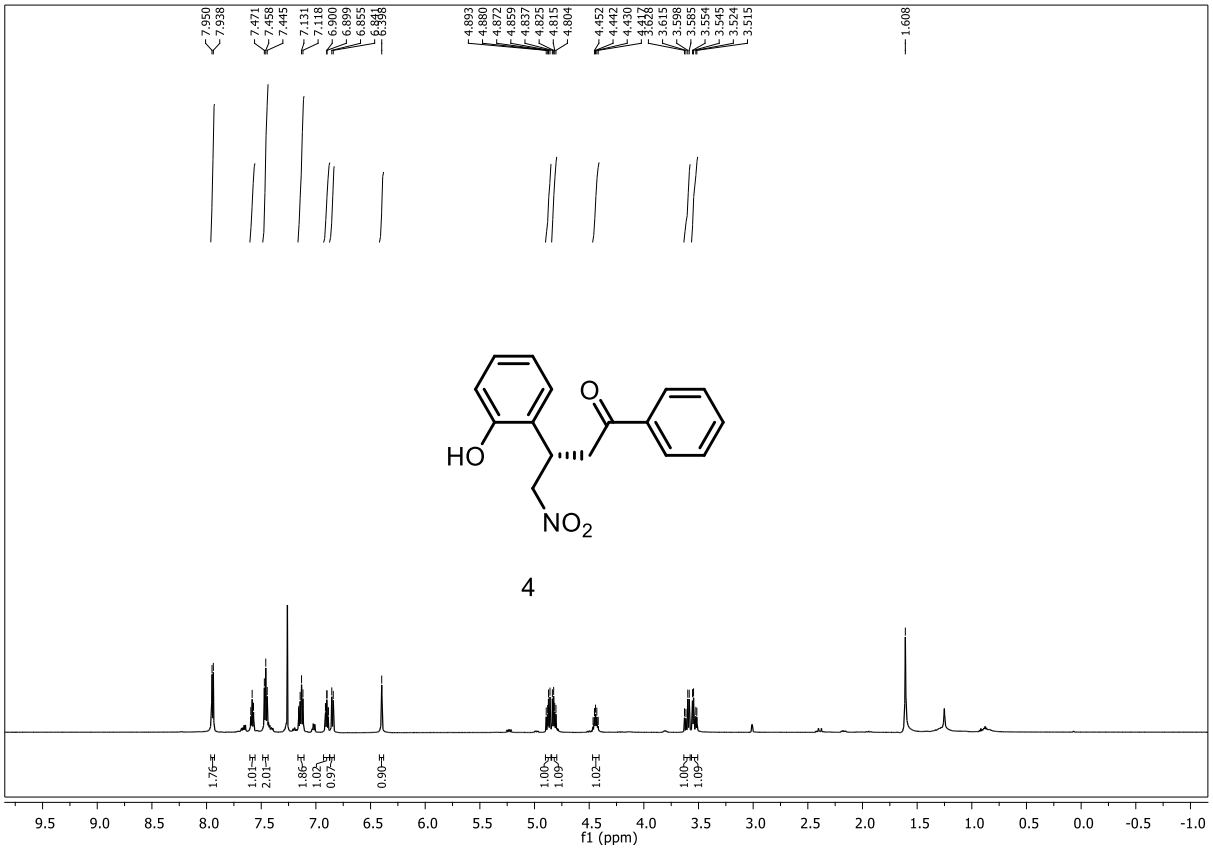
128.99
127.69
126.83
123.46
120.82
120.34
112.48
78.61
77.55
77.23
76.92
55.66
41.12
33.21
21.14
O
O
O
O
NO2
3r
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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6.855
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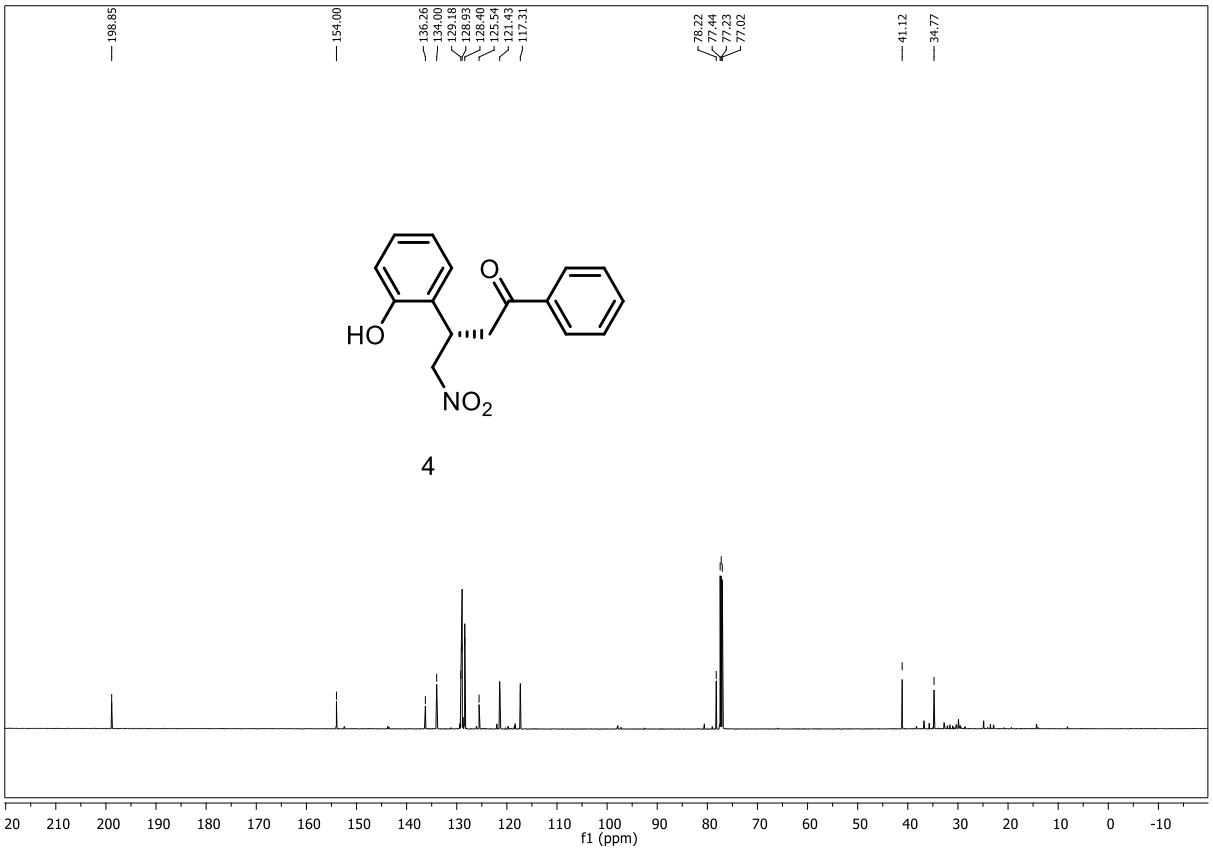
6.398
4.893
4.880
4.872
4.859
4.837
4.825
4.815
4.804
4.452
4.442
4.430
4.417
3.628
3.615
3.598
3.585
3.554
3.545
3.524
3.515
1.608
HO
O
NO2
4
1.76
1.01
2.01
1.86
1.02
0.97
0.90
1.00
1.09
1.02
1.00
1.09
f1 (ppm)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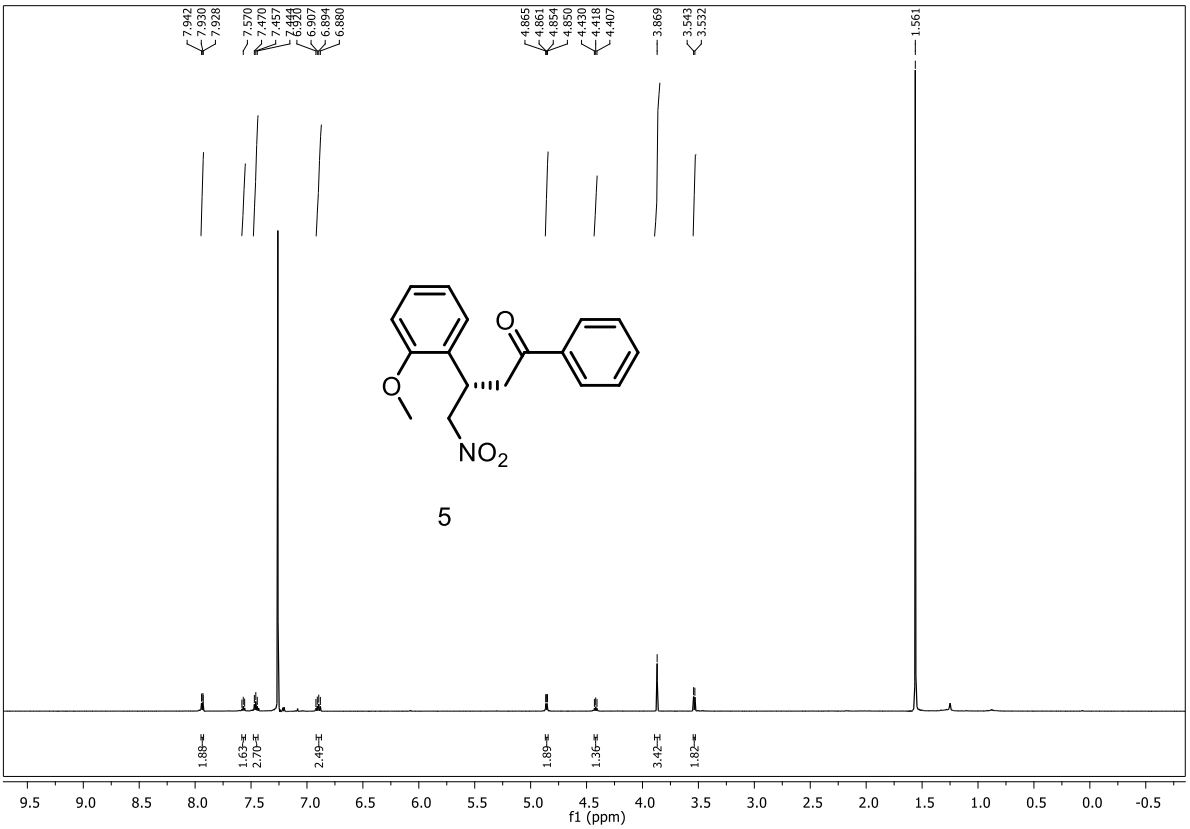
134.00
129.18
128.93
128.40
125.54
121.43
117.31
78.22
77.44
77.23
77.02
41.12
34.77
HO
O
NO2
4
f1 (ppm)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7.470
7.457
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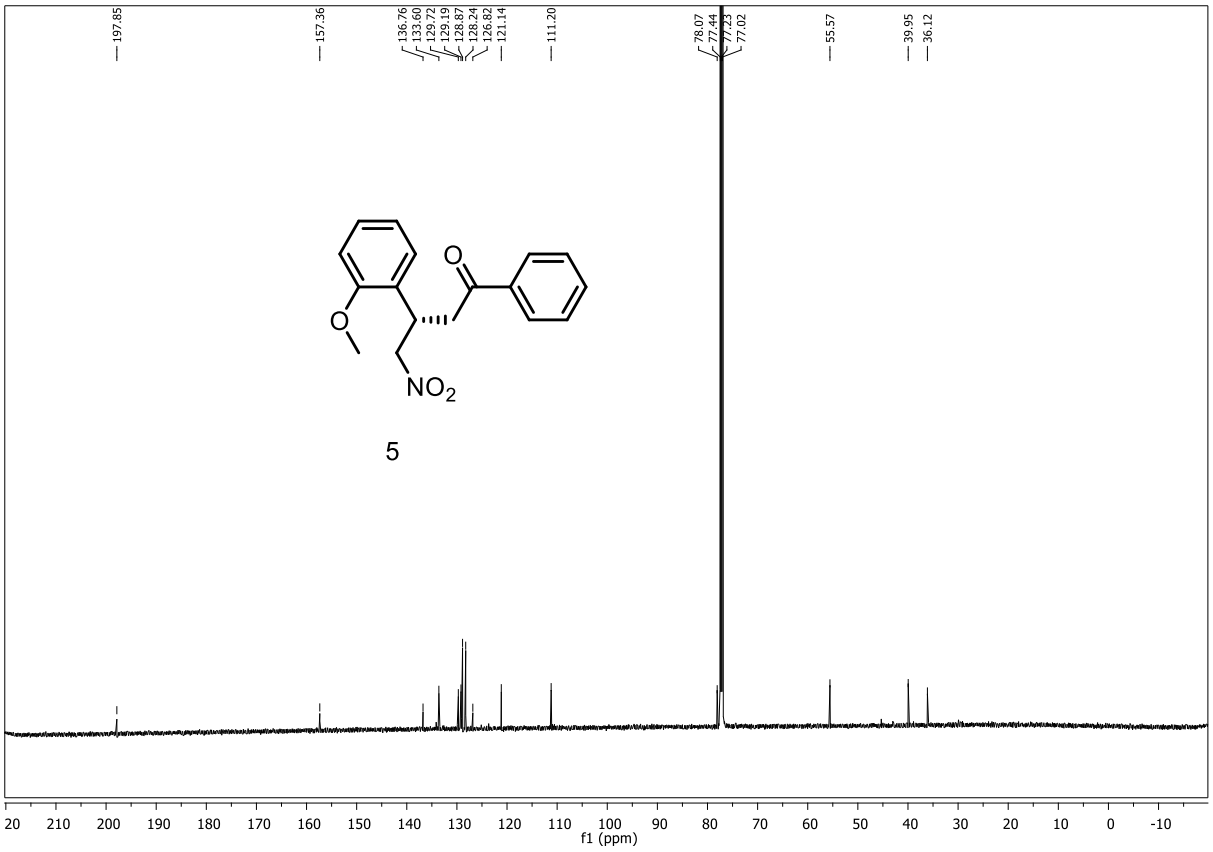
6.894
6.880
4.865
4.861
4.854
4.850
4.430
4.418
4.407
3.869
3.543
3.532
1.561
O
O
NO2
5
1.88
1.63
2.70
2.49
1.89
1.36
3.42
1.82
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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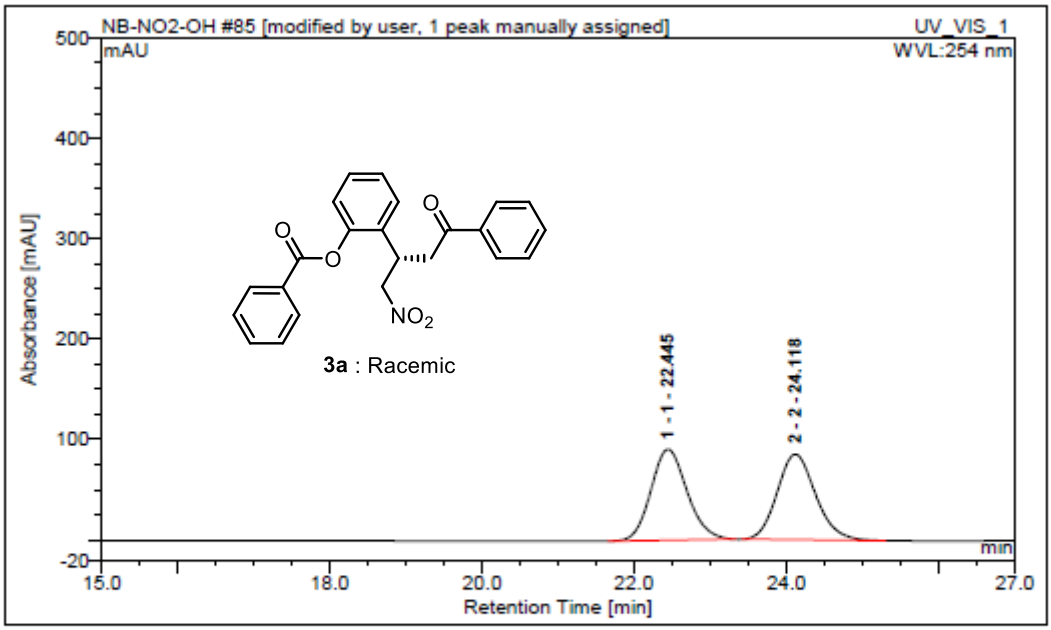
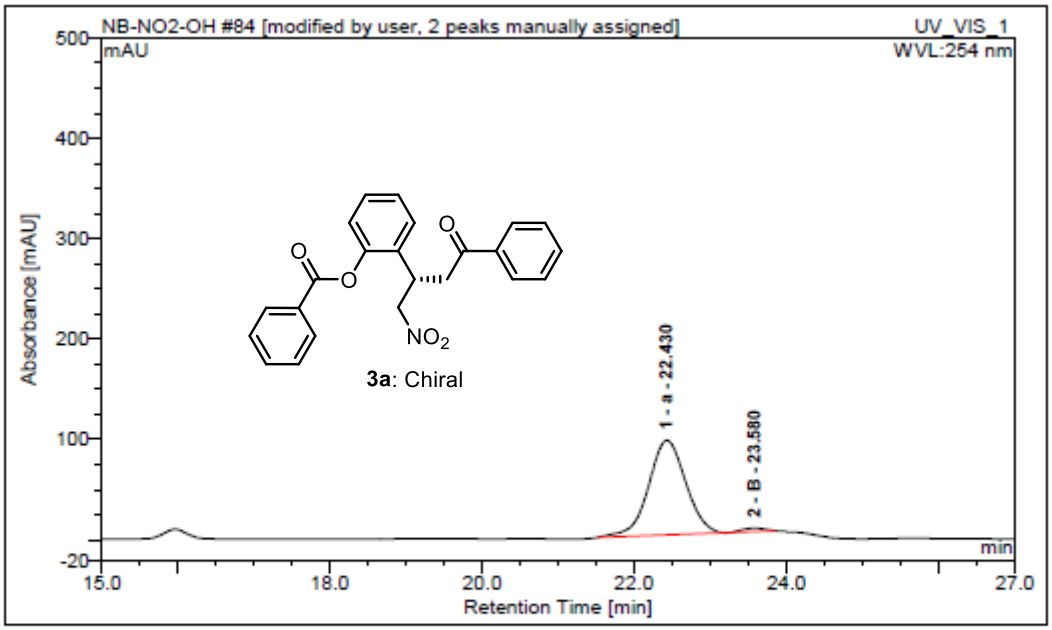
157.36
136.76
133.60
129.72
129.19
128.87
128.24
126.82
121.14
111.20
78.07
77.44
77.23
77.02
55.57
39.95
36.12
O
O
NO2
5
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

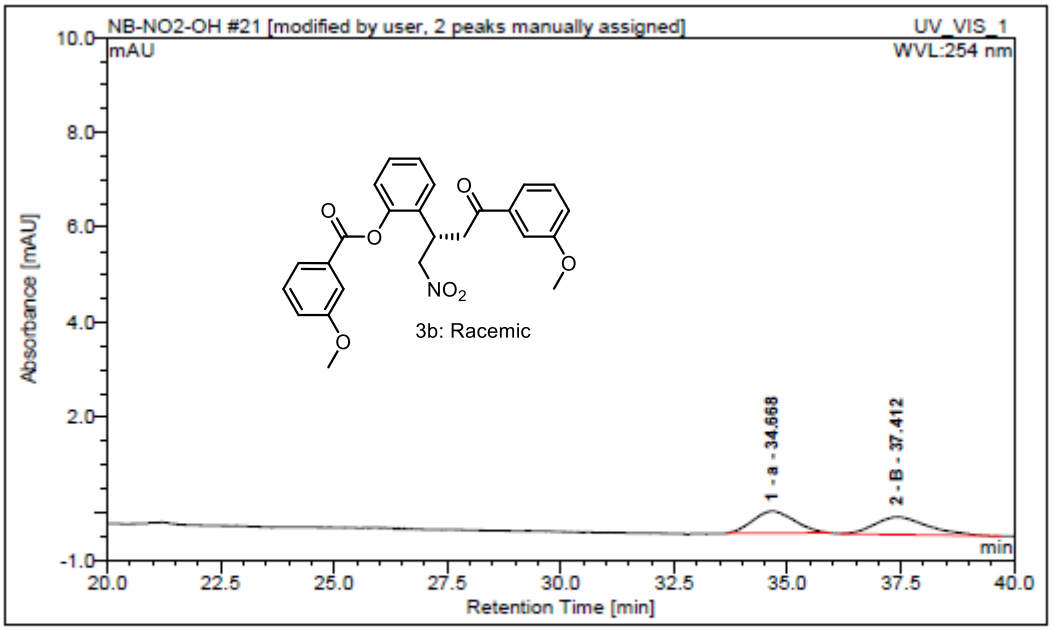
9. HPLC spectra of the products:



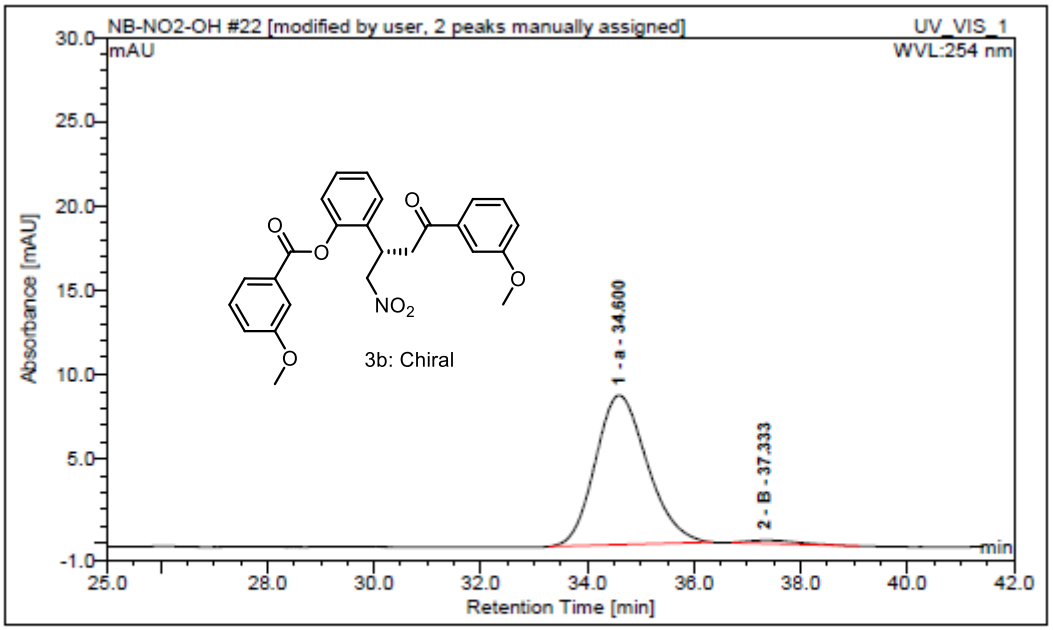
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	22.45	49.9214	49.97441389	90.62098	n.a.
2	2	24.12	49.973	50.02558611	85.225	n.a.



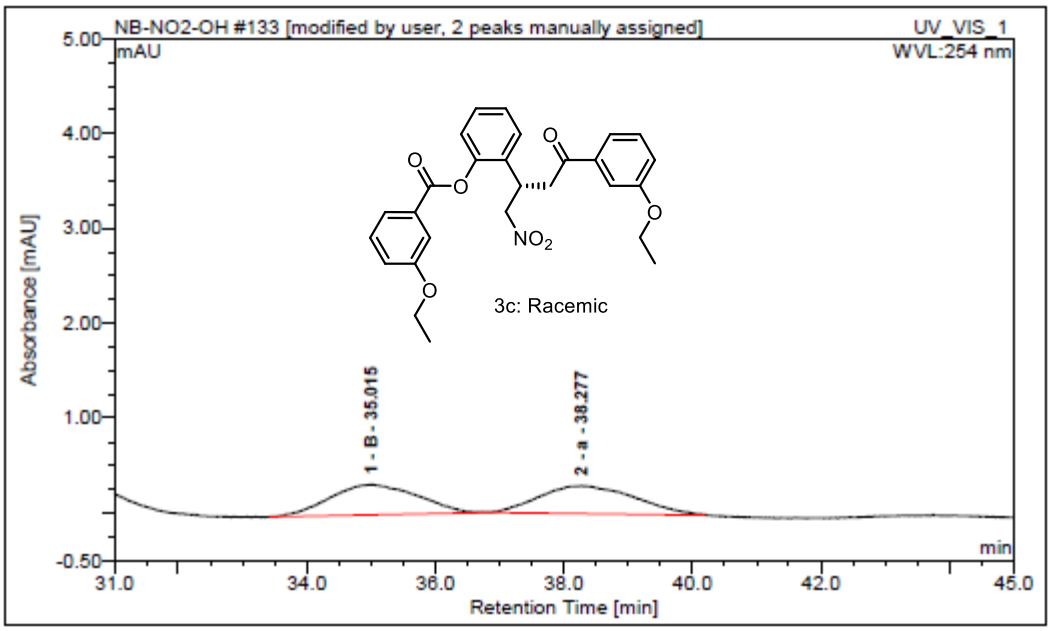
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	22.43	52.96288	97.94421359	93.98245	n.a.
2	B	23.58	1.112	2.055786408	3.381	n.a.



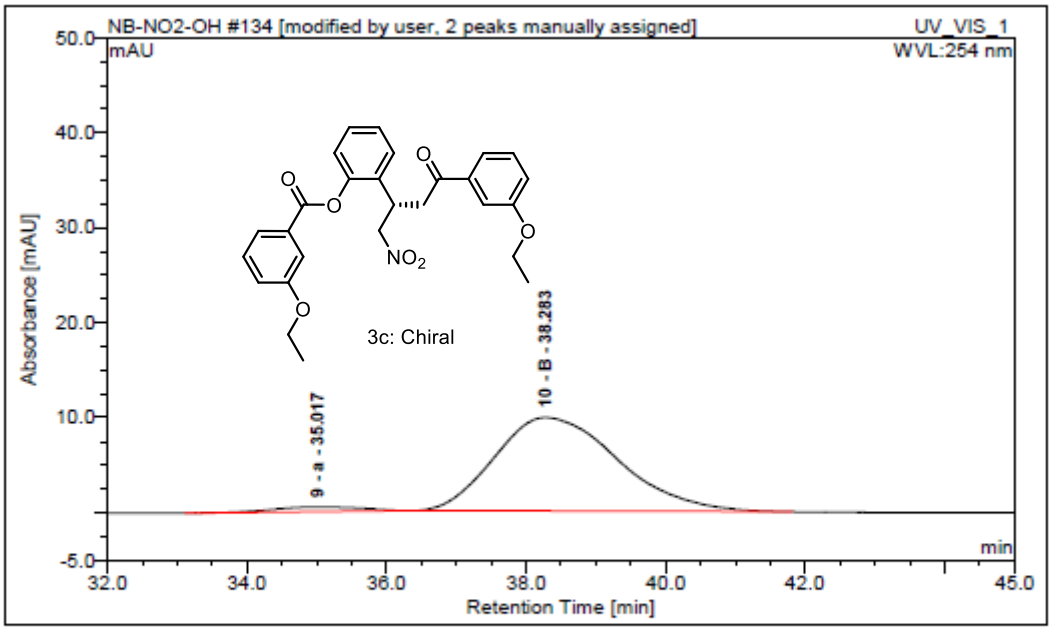
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	34.67	0.48875	49.57814687	0.46271	n.a.
2	B	37.41	0.497	50.42185313	0.367	n.a.



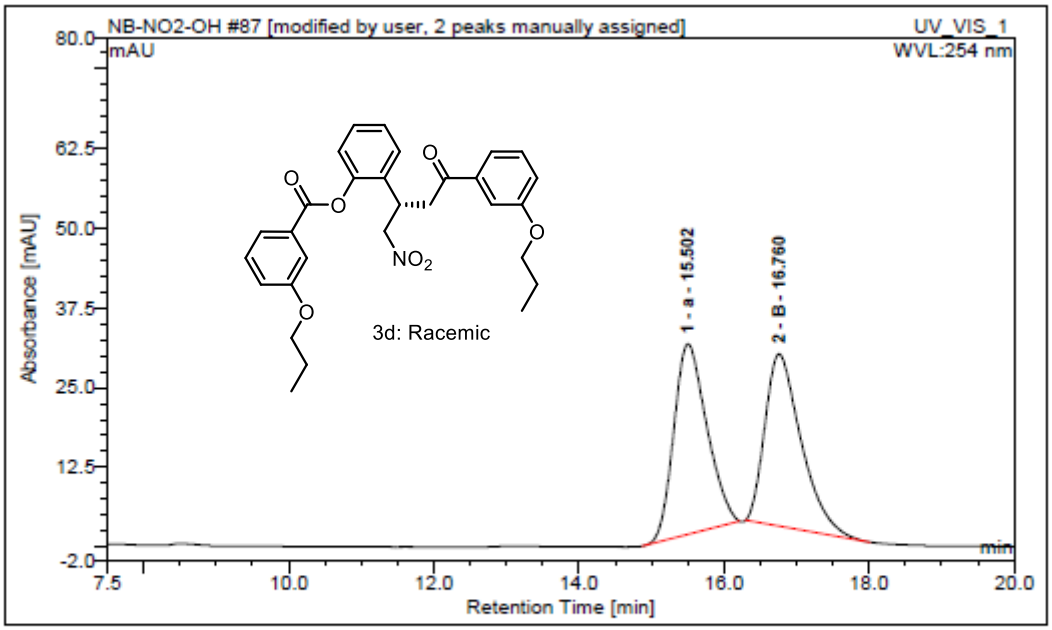
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	34.60	9.998164	97.9753208	8.86157	n.a.
2	B	37.33	0.207	2.024679195	0.200	n.a.



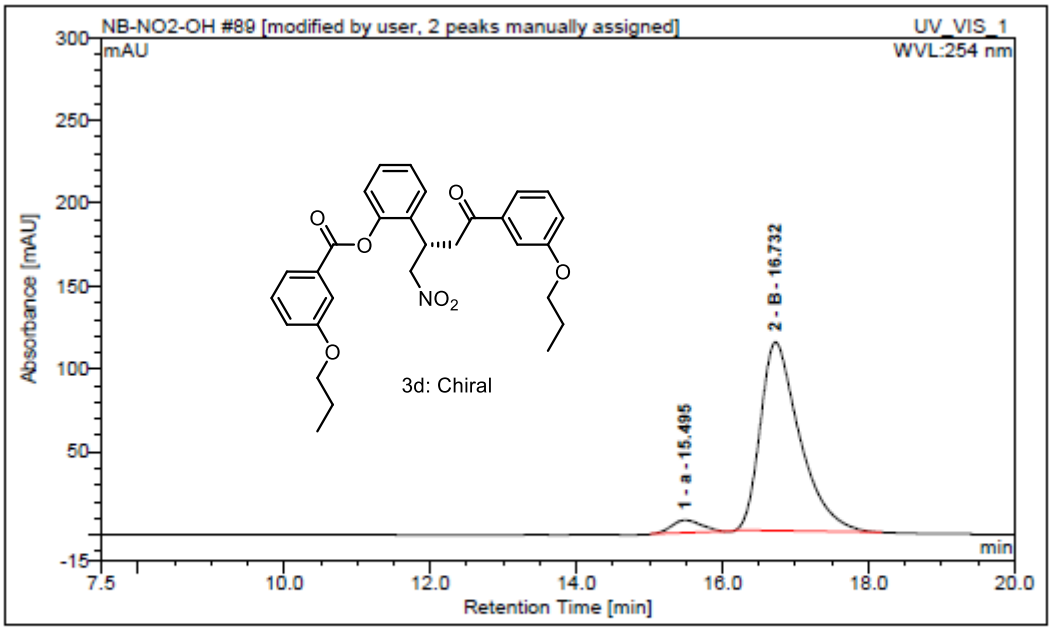
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	B	35.02	0.501621	50.27835622	0.32035	n.a.
2	a	38.28	0.496	49.72164378	0.291	n.a.



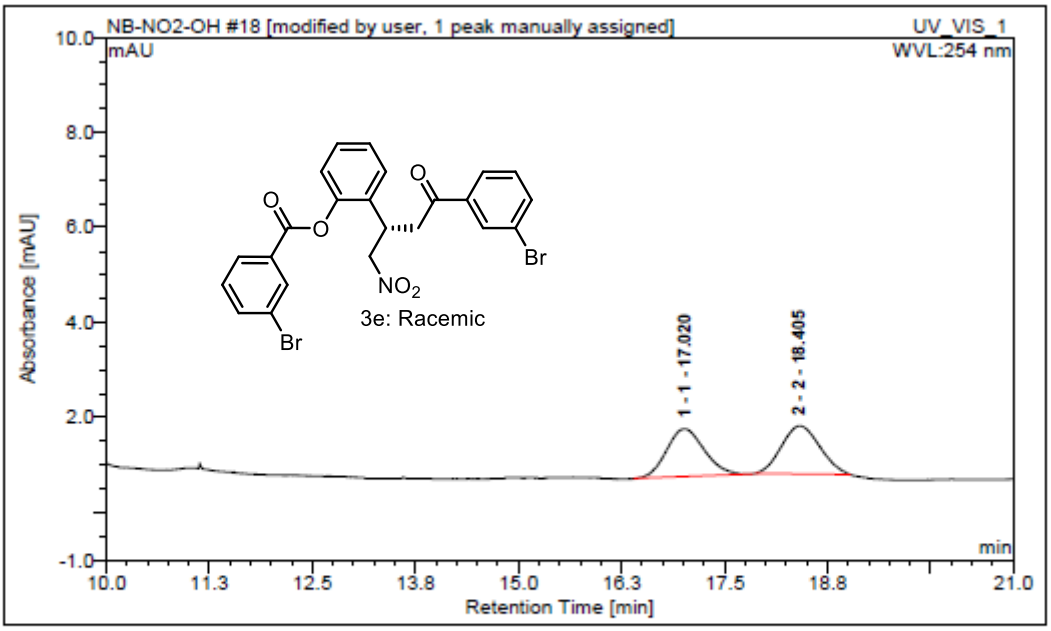
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
9	a	35.02	0.651011	3.132951539	0.46628	n.a.
10	B	38.28	20.128	96.86704846	9.813	n.a.



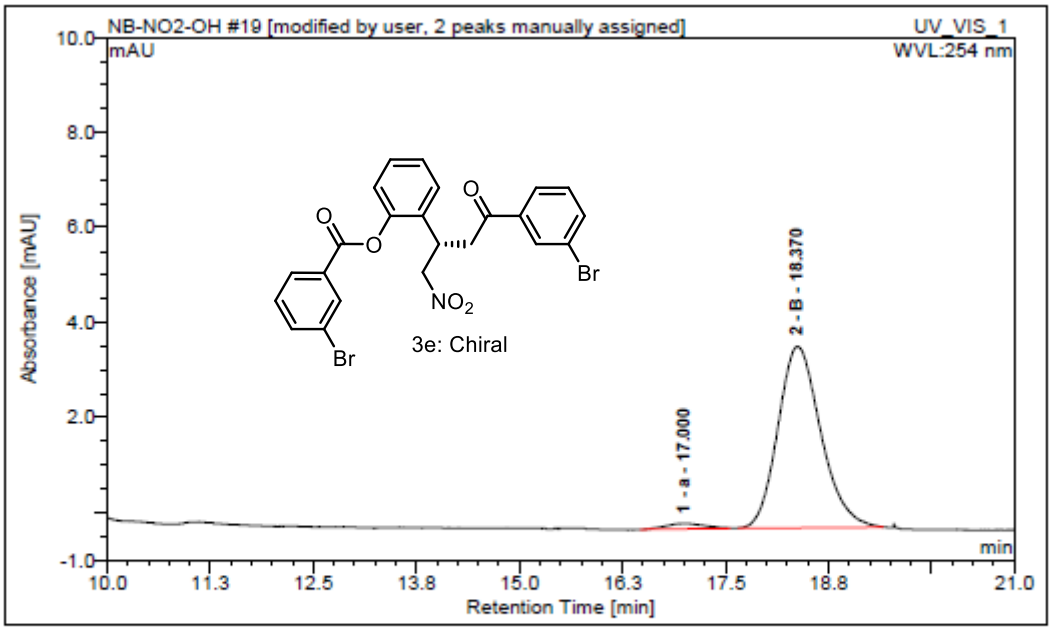
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	15.50	15.72823	50.1237301	29.89812	n.a.
2	B	16.76	15.651	49.8762699	26.980	n.a.



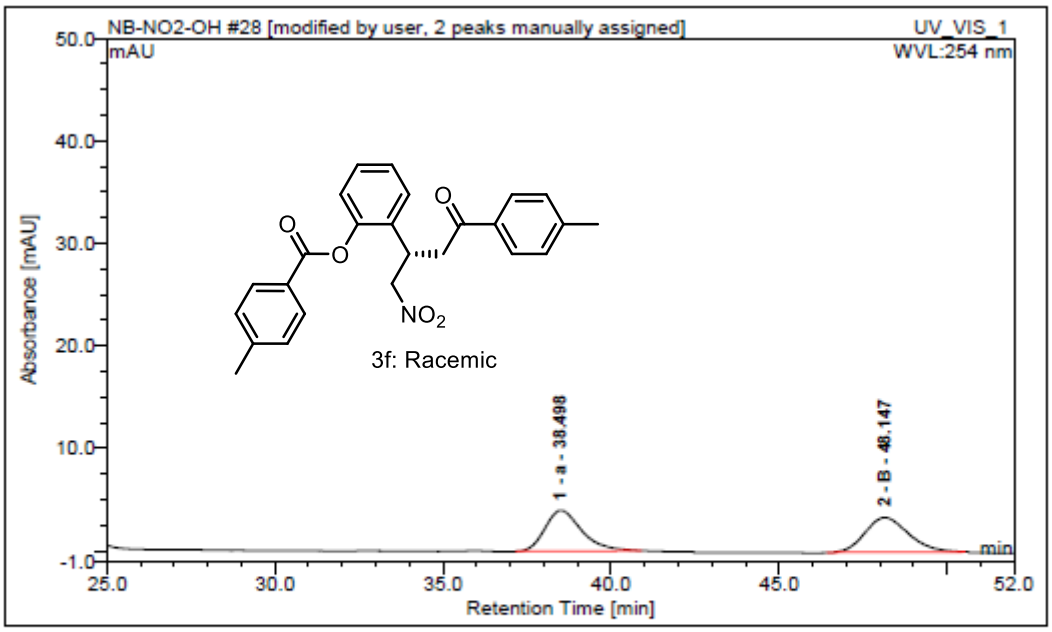
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	15.50	3.596717	4.8230348	7.61724	n.a.
2	B	16.73	70.977	95.1769652	113.493	n.a.



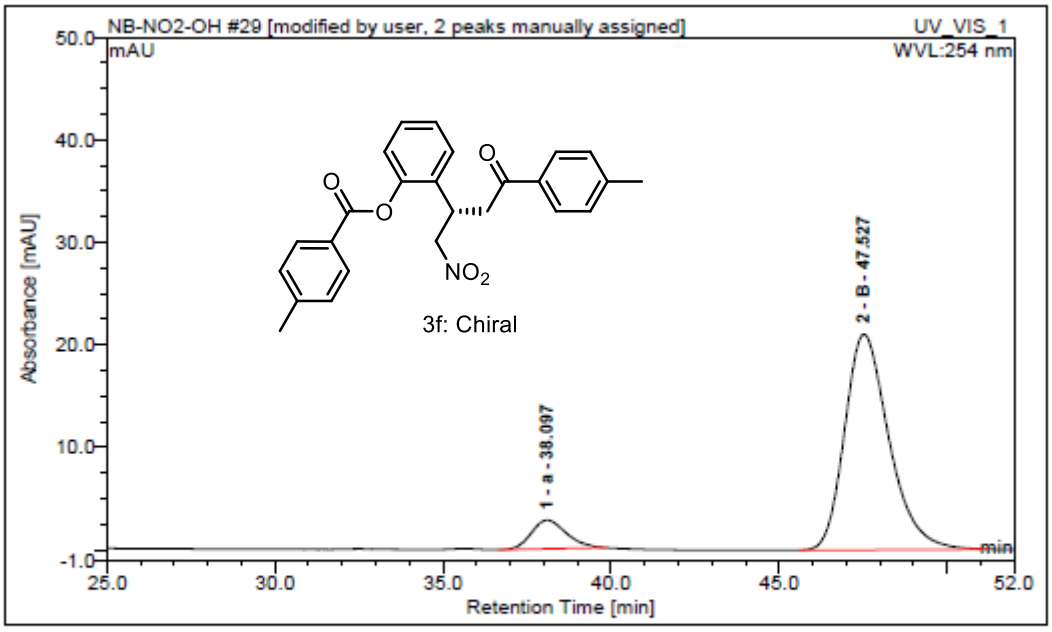
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	17.02	0.529733	49.43791528	1.00444	n.a.
2	2	18.41	0.542	50.56208472	1.005	n.a.



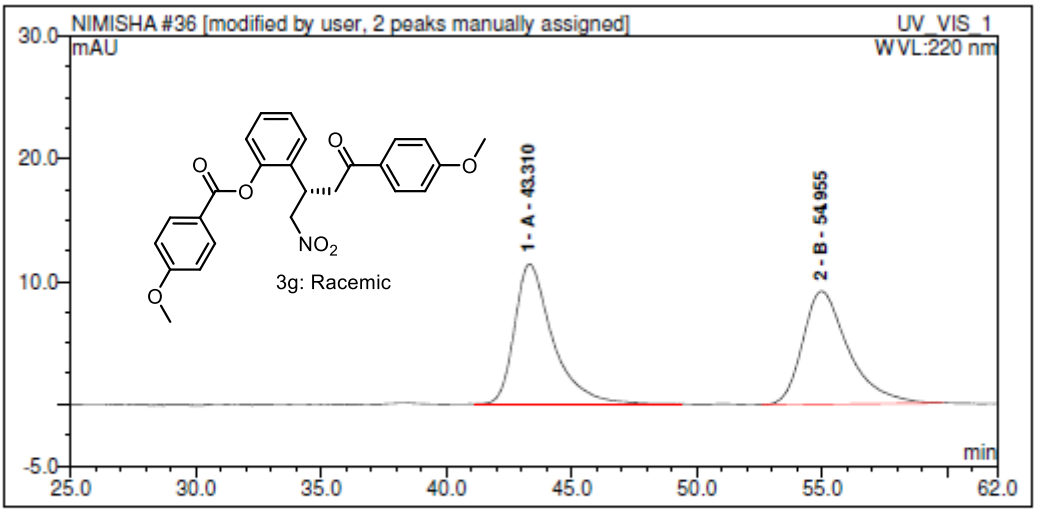
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	17.00	0.059784	2.538790787	0.11922	n.a.
2	B	18.37	2.295	97.46120921	3.815	n.a.



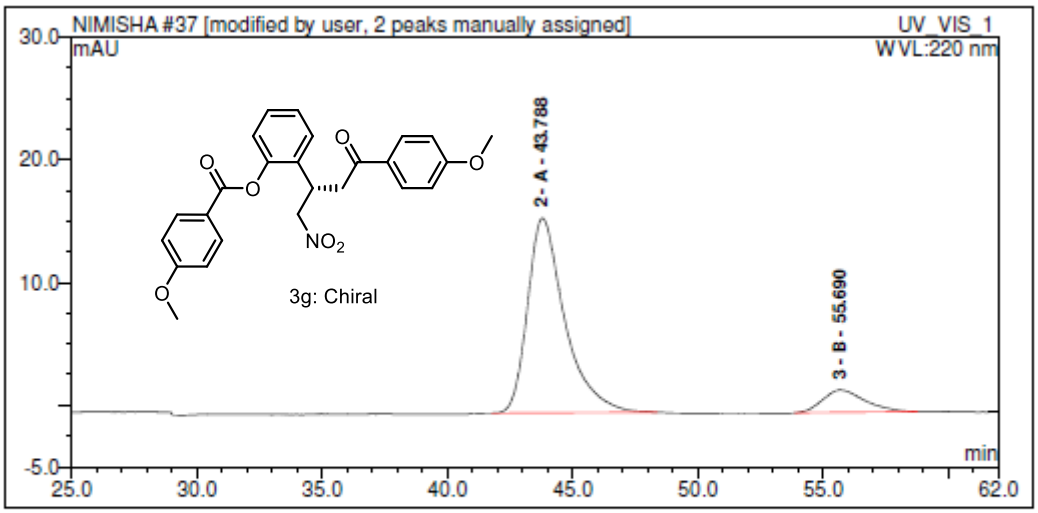
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	38.50	5.08361	49.66395578	3.98532	n.a.
2	B	48.15	5.152	50.33604422	3.396	n.a.



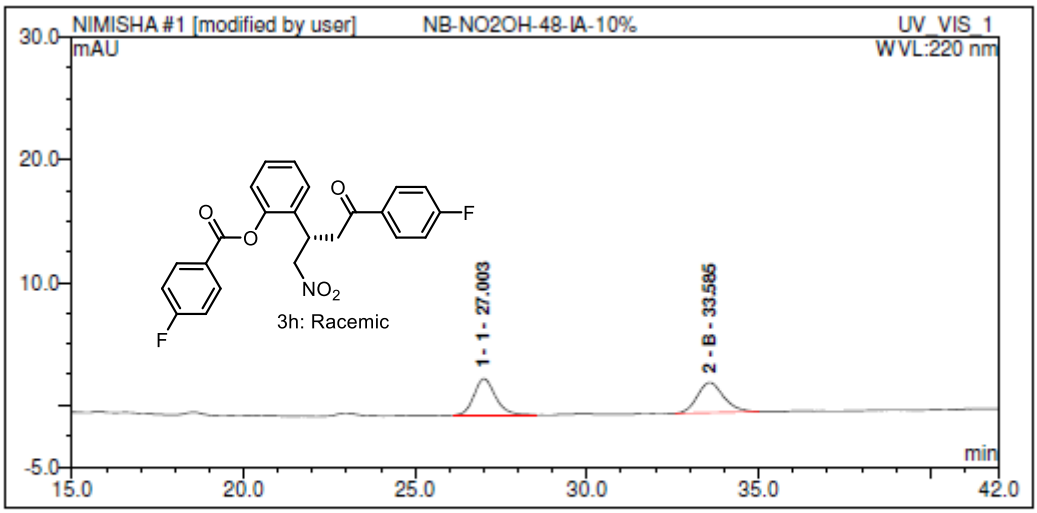
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	38.10	3.386418	9.490398605	2.79863	n.a.
2	B	47.53	32.296	90.5096014	21.052	n.a.



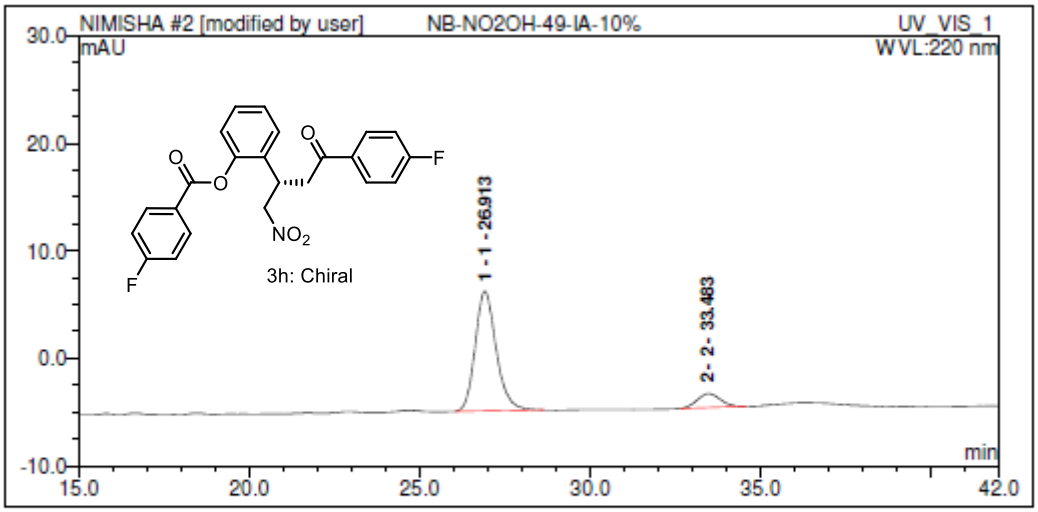
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	A	43.31	20.13327	50.77870591	11.41048	n.a.
2	B	54.96	19.516	49.22129409	9.204	n.a.



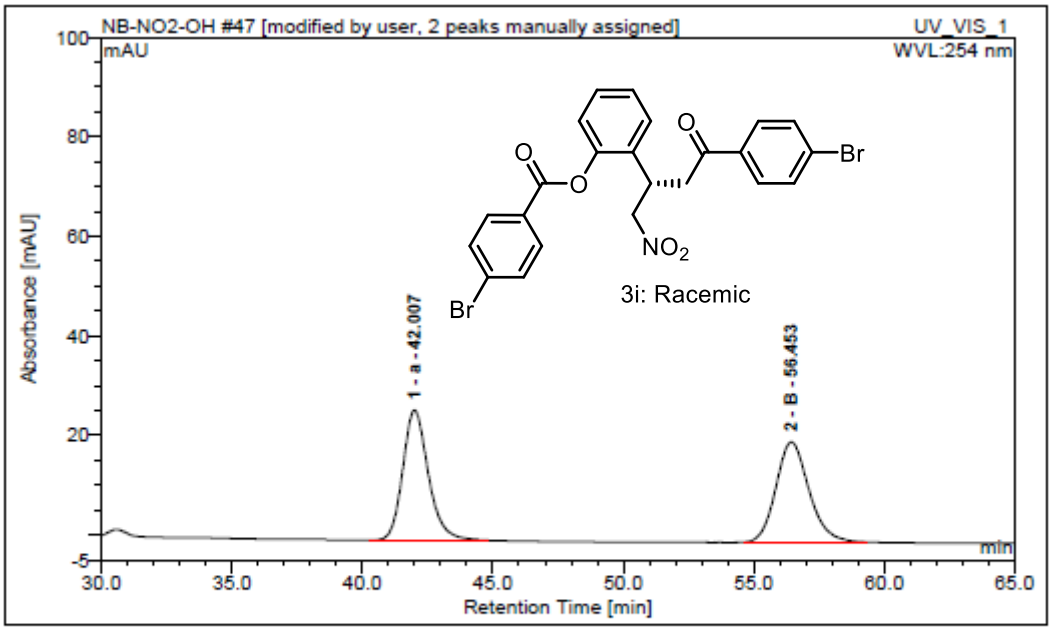
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
2	A	43.79	27.33546	88.48701989	15.85786	n.a.
3	B	55.69	3.557	11.51298011	1.825	n.a.



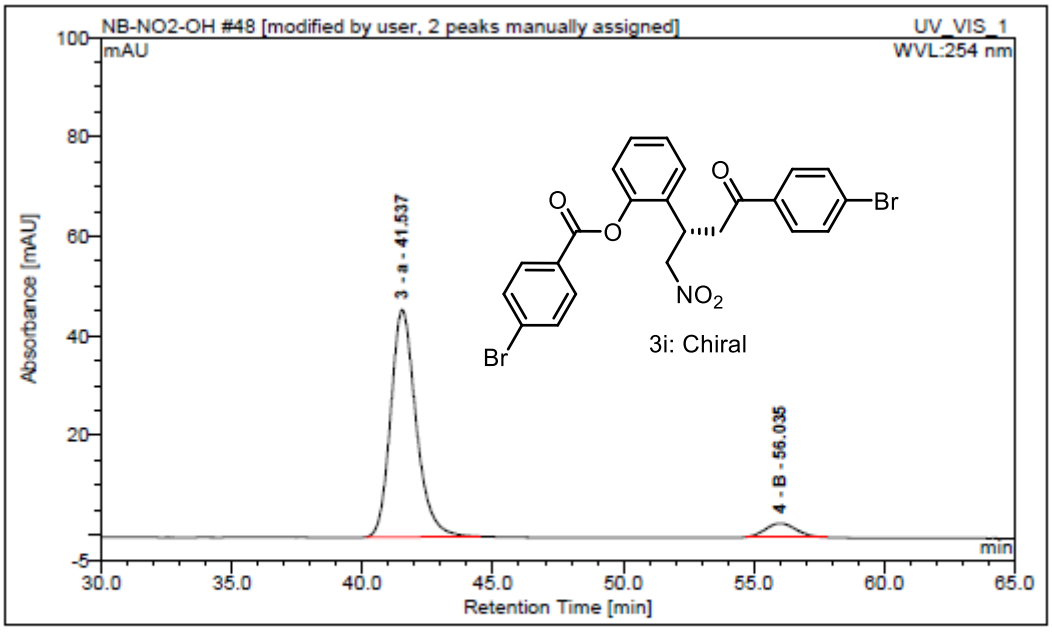
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	27.00	2.13362	49.32930985	2.95361	n.a.
2	B	33.59	2.192	50.67069015	2.456	n.a.



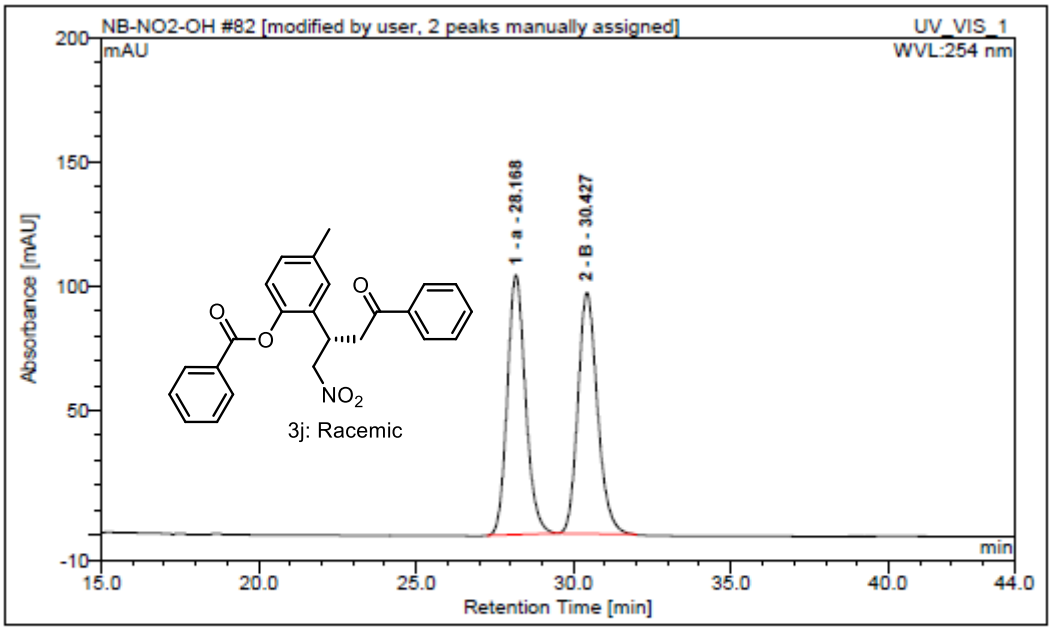
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	26.91	7.994059	88.7335943	11.14964	n.a.
2	2	33.48	1.015	11.2664057	1.286	n.a.



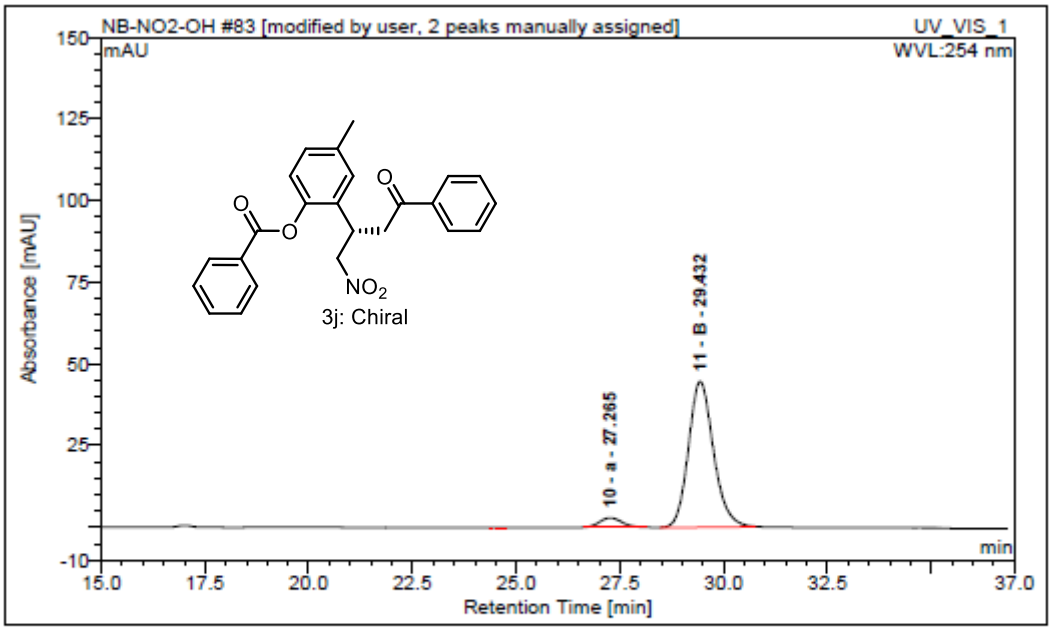
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	42.01	29.67807	50.23468072	26.10695	n.a.
2	B	56.45	29.401	49.76531928	20.059	n.a.



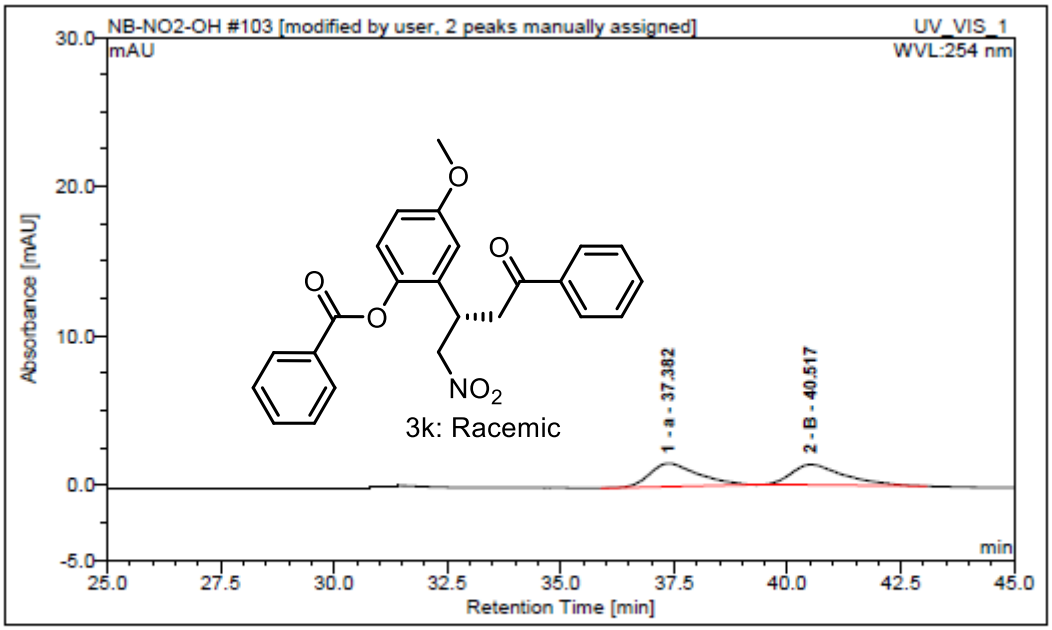
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
3	a	41.54	51.40621	93.12411073	45.58039	n.a.
4	B	56.04	3.796	6.875889271	2.809	n.a.



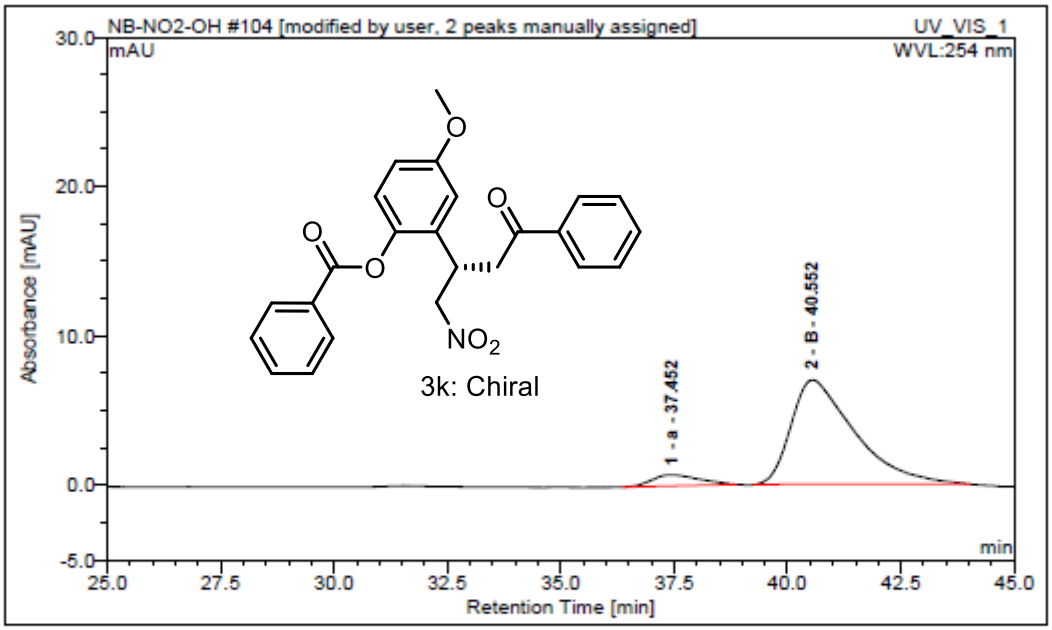
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	28.17	70.00816	49.97447352	104.2762	n.a.
2	B	30.43	70.080	50.02552648	96.936	n.a.



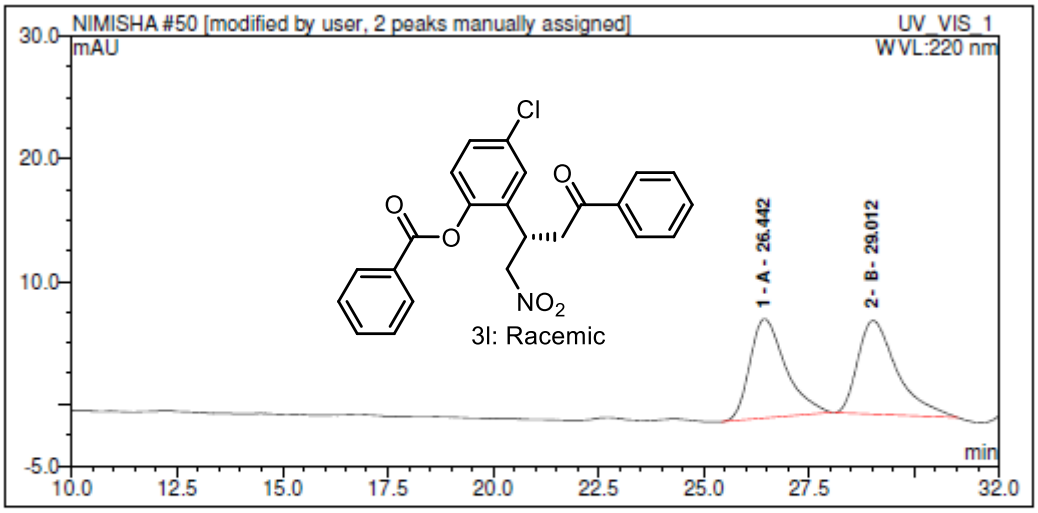
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
10	a	27.27	1.856309	5.621281089	2.98343	n.a.
11	B	29.43	31.167	94.37871891	44.621	n.a.



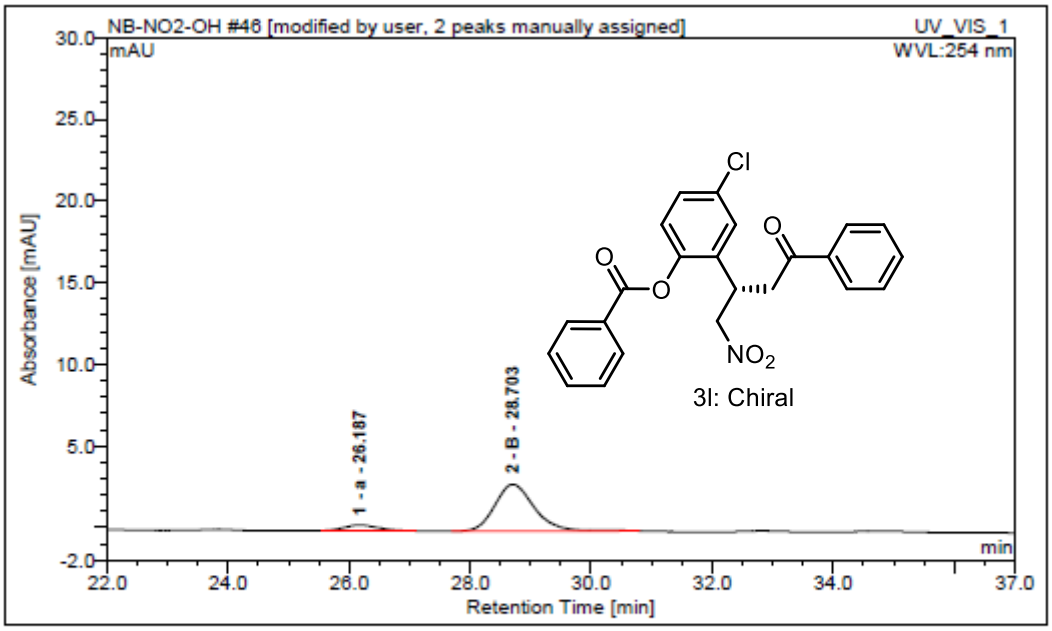
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	37.38	1.901482	50.78480587	1.55391	n.a.
2	B	40.52	1.843	49.21519413	1.362	n.a.



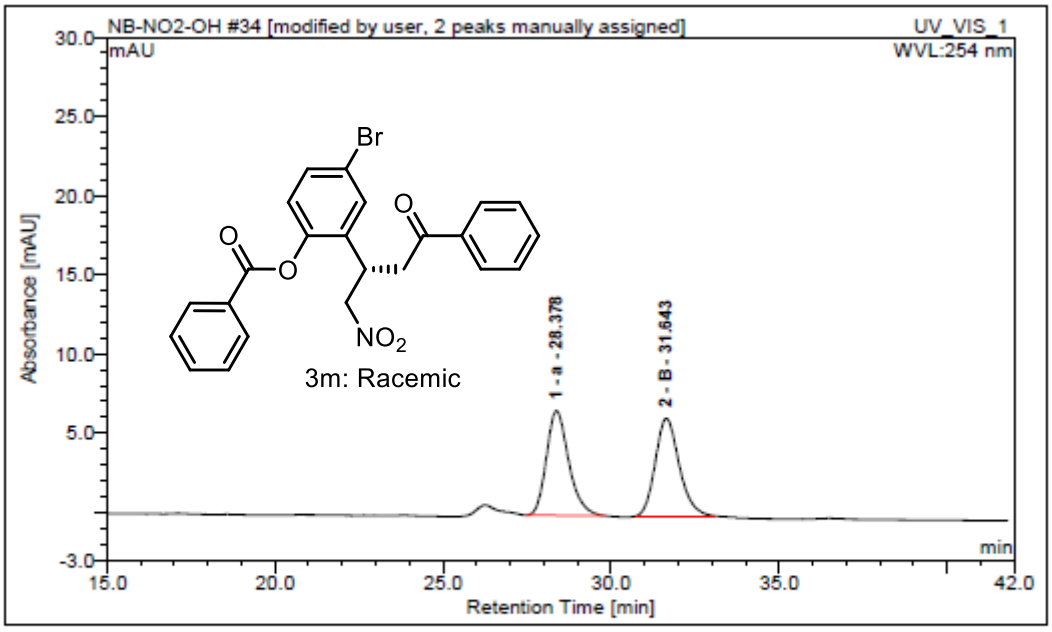
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	37.45	0.88079	7.19494079	0.74335	n.a.
2	B	40.55	11.361	92.80505921	6.992	n.a.



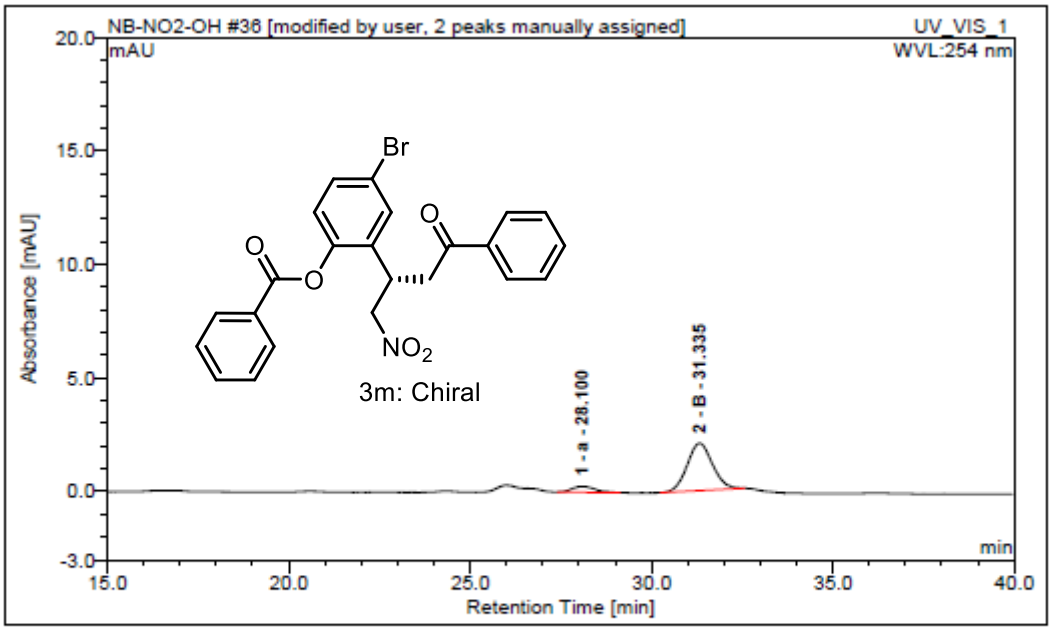
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	A	26.44	7.943625	49.12919805	8.07972	n.a.
2	B	29.01	8.225	50.87080195	7.623	n.a.



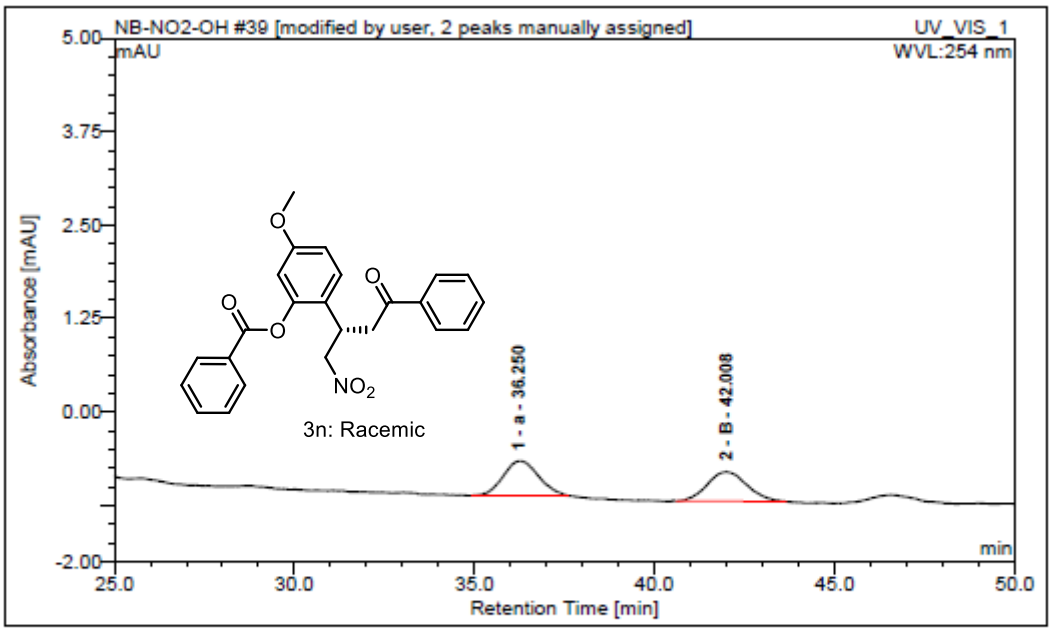
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	26.19	0.232303	9.575890377	0.34922	n.a.
2	B	28.70	2.194	90.42410962	2.874	n.a.



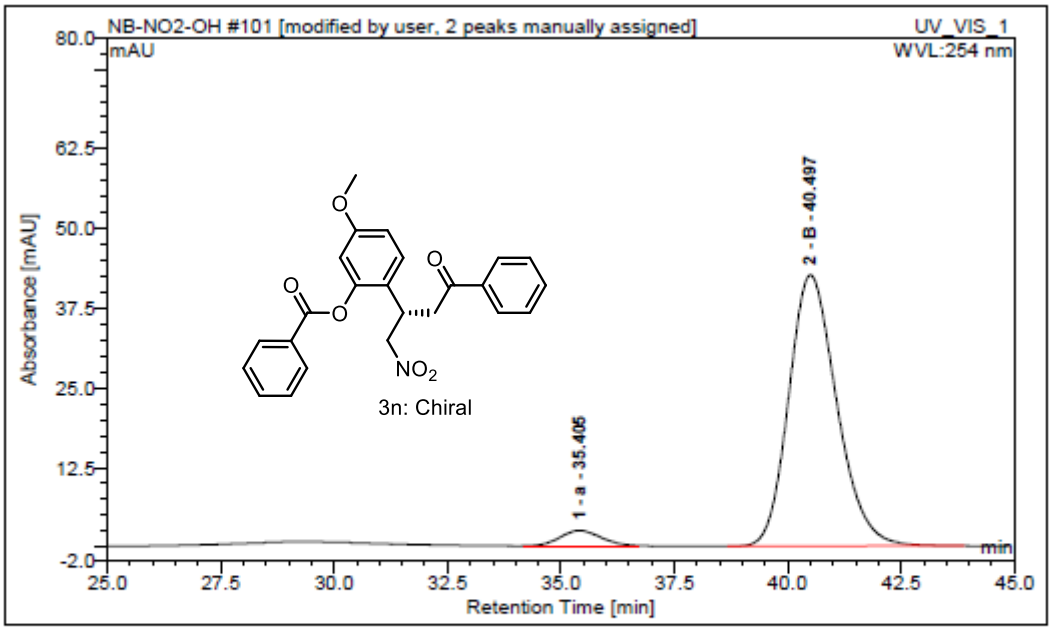
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	28.38	5.099163	50.03966933	6.60927	n.a.
2	B	31.64	5.091	49.96033067	6.159	n.a.



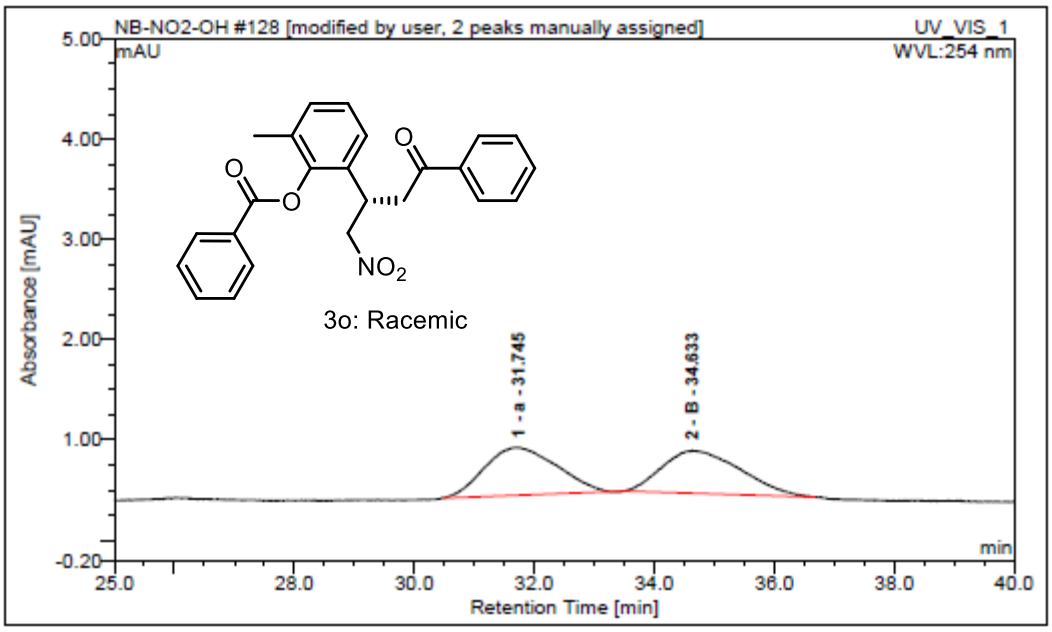
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	28.10	0.182176	9.725877471	0.25617	n.a.
2	B	31.34	1.691	90.27412253	2.083	n.a.



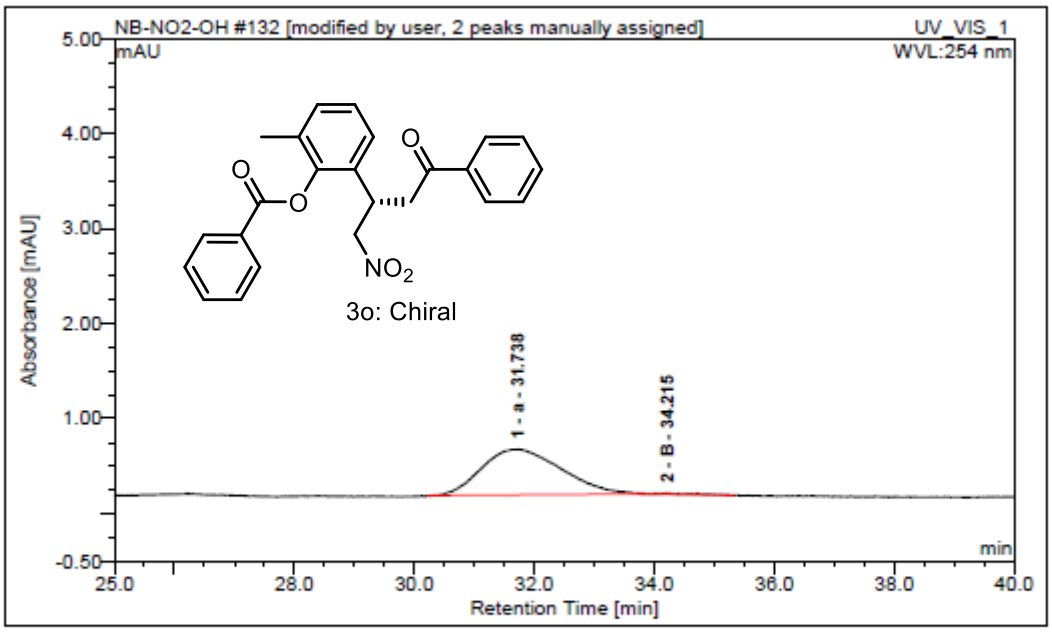
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	36.25	0.522935	50.72827631	0.46474	n.a.
2	B	42.01	0.508	49.27172369	0.398	n.a.



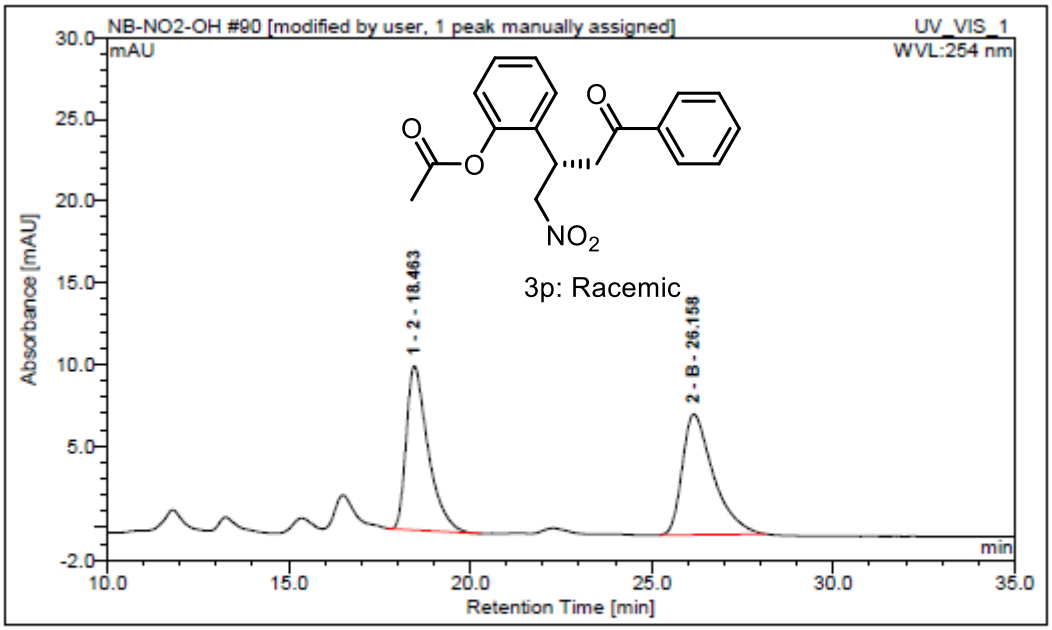
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	35.41	2.467578	4.510493061	2.38358	n.a.
2	B	40.50	52.240	95.48950694	42.539	n.a.



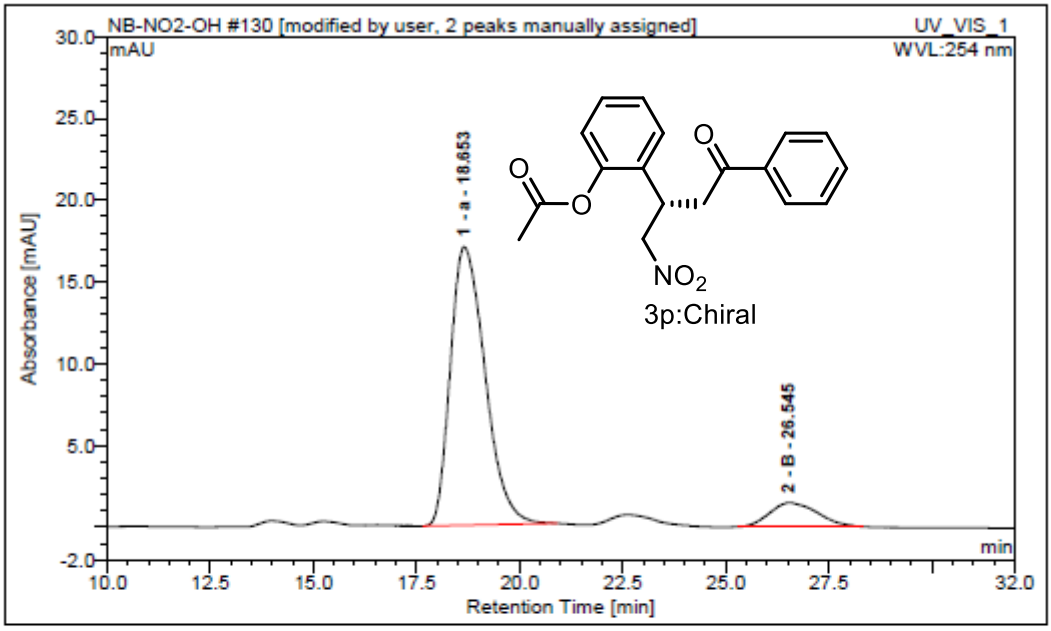
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	31.75	0.66362	50.8109133	0.47601	n.a.
2	B	34.63	0.642	49.1890867	0.424	n.a.



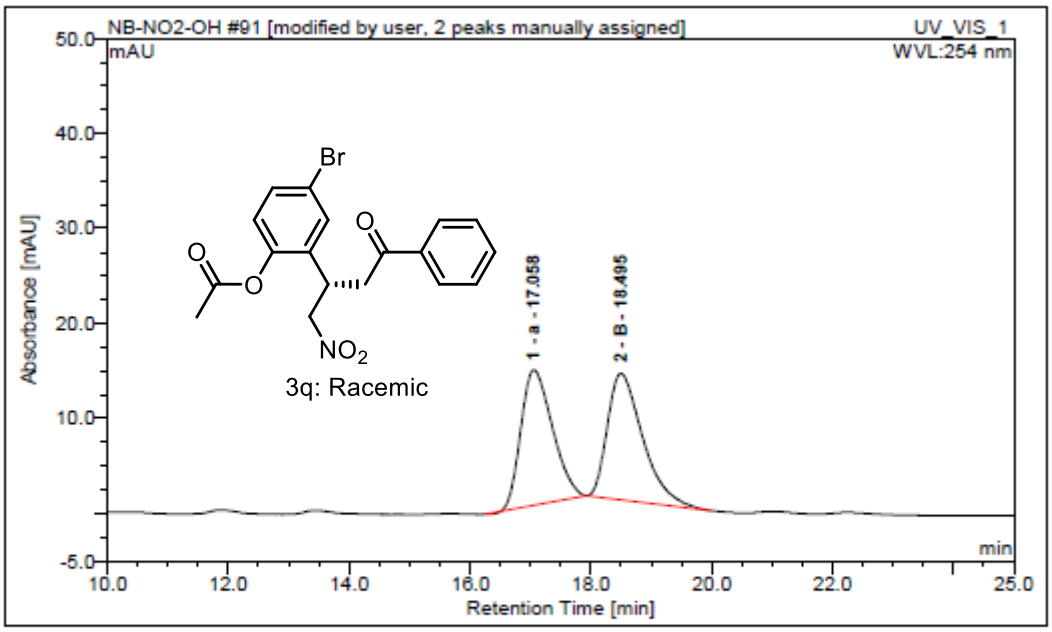
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	31.74	0.741526	98.73335071	0.48389	n.a.
2	B	34.22	0.010	1.266649291	0.011	n.a.



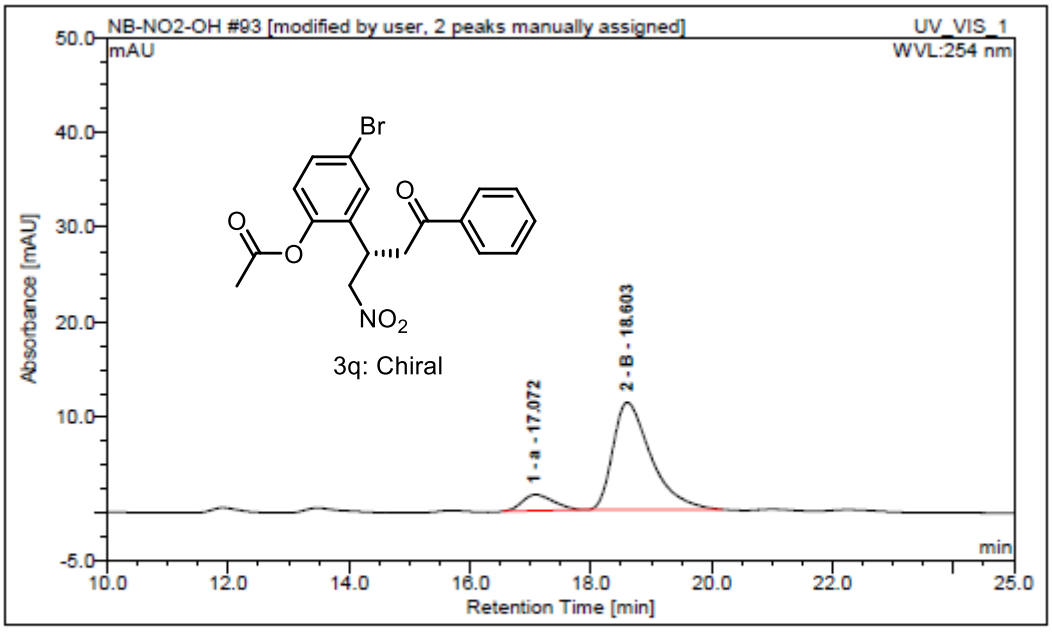
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	2	18.46	7.004031	48.8147866	10.03156	n.a.
2	B	26.16	7.344	51.1852134	7.382	n.a.



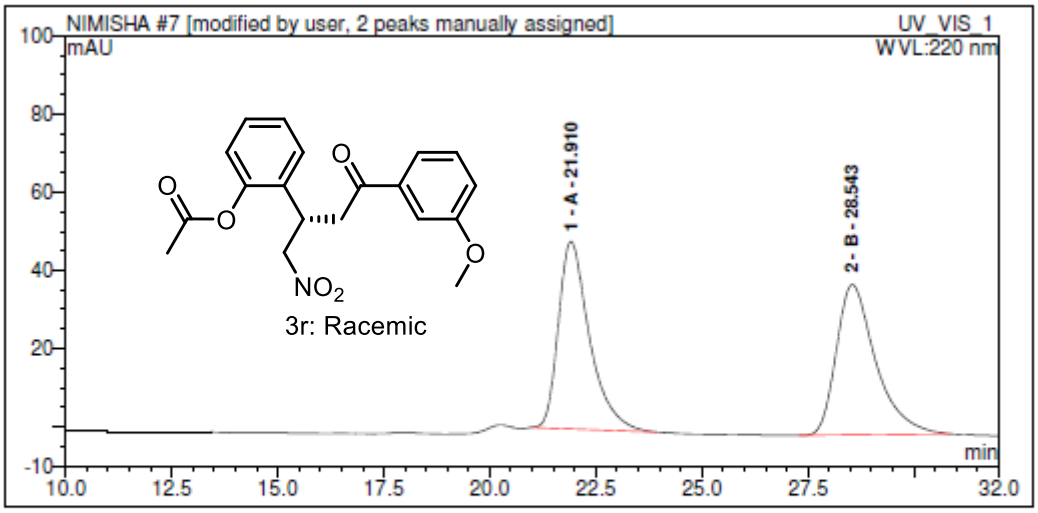
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	18.65	16.60404	89.53028364	17.02096	n.a.
2	B	26.55	1.942	10.46971636	1.458	n.a.



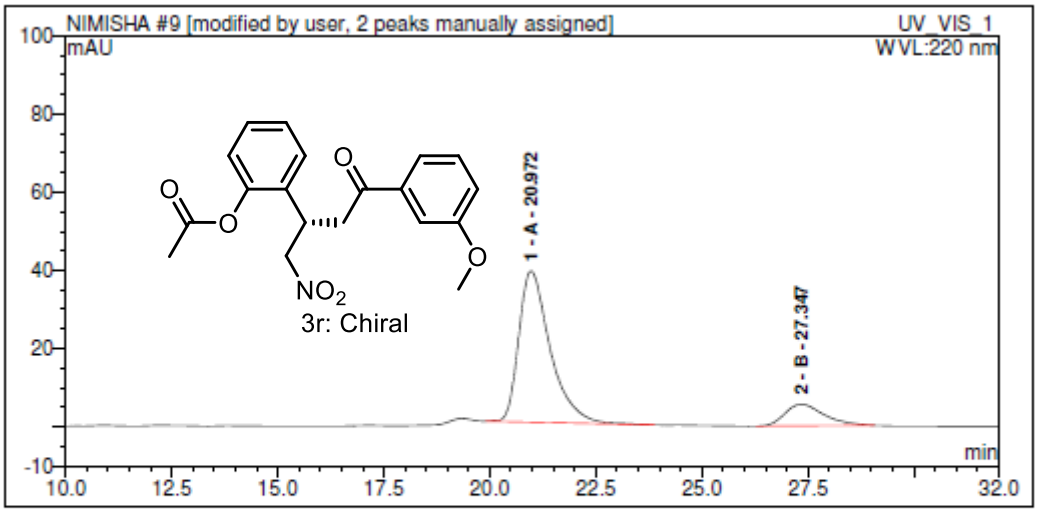
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	17.06	8.620793	48.90465071	14.24302	n.a.
2	B	18.50	9.007	51.09534929	13.309	n.a.



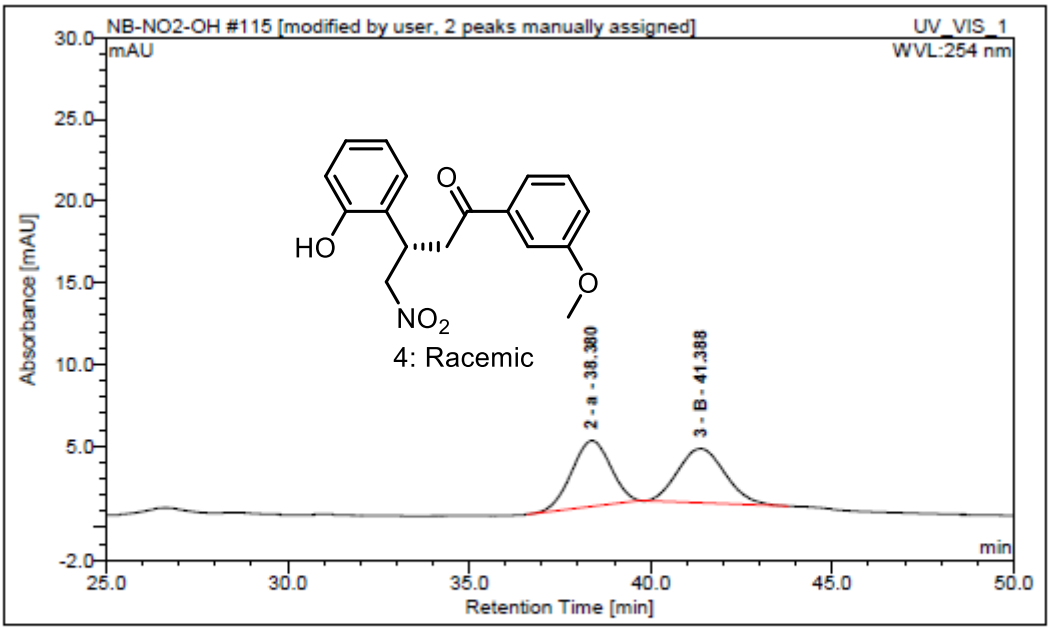
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	17.07	1.014848	10.95334925	1.68636	n.a.
2	B	18.60	8.250	89.04665075	11.283	n.a.



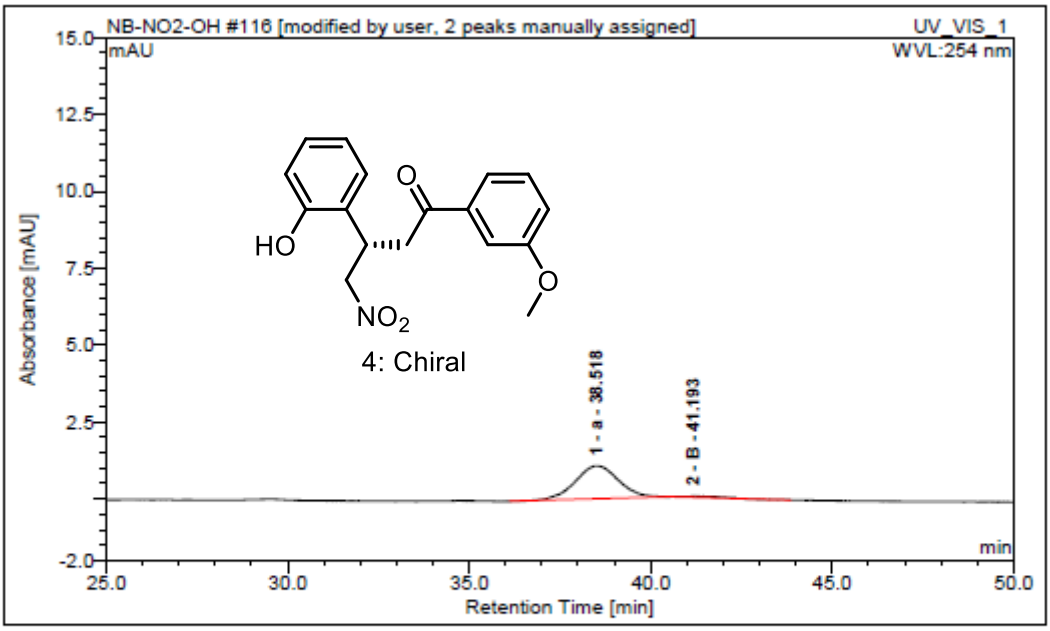
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	A	21.91	40.80966	49.61557828	48.01112	n.a.
2	B	28.54	41.442	50.38442172	38.510	n.a.



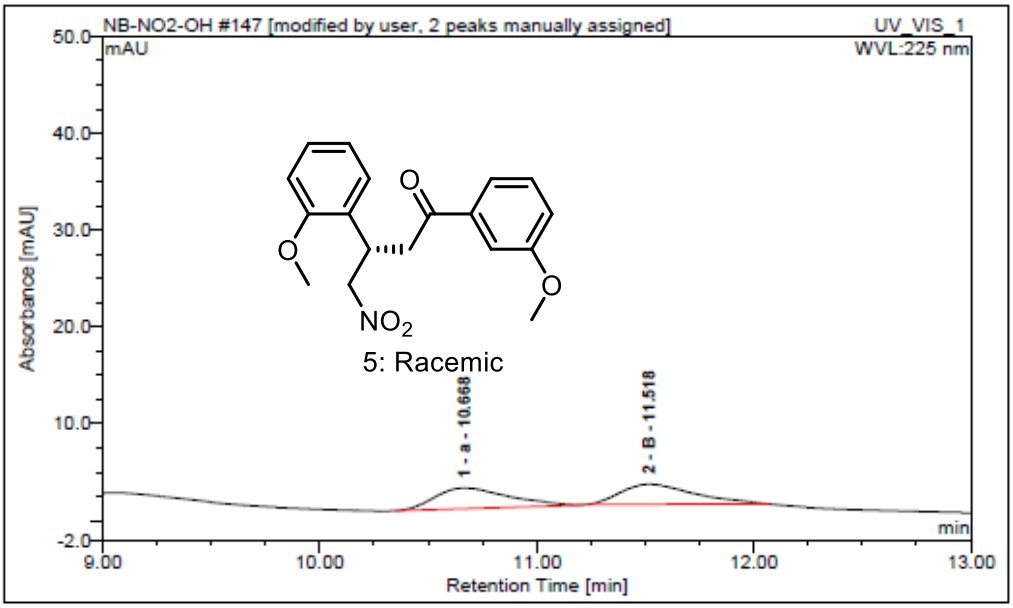
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	A	20.97	33.36697	85.03614339	38.76309	n.a.
2	B	27.35	5.872	14.96385661	5.508	n.a.



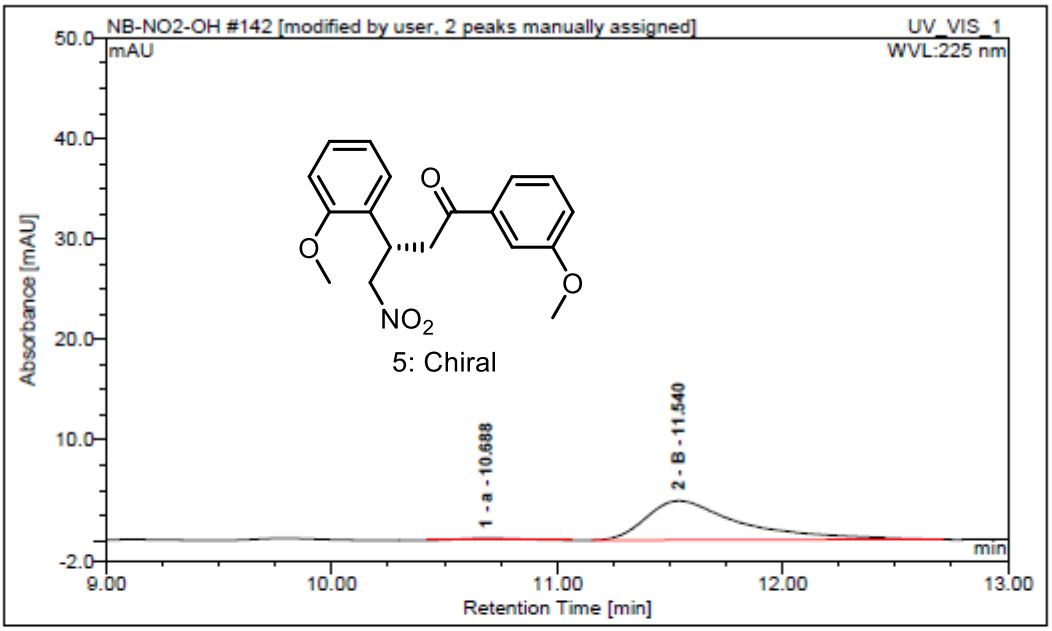
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
2	a	38.38	5.002279	49.83390493	4.01806	n.a.
3	B	41.39	5.036	50.16609507	3.329	n.a.



No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	38.52	1.505511	96.69194574	1.08123	n.a.
2	B	41.19	0.052	3.308054256	0.041	n.a.



No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	10.67	0.82577	50.41942921	2.11733	n.a.
2	B	11.52	0.812	49.58057079	2.044	n.a.

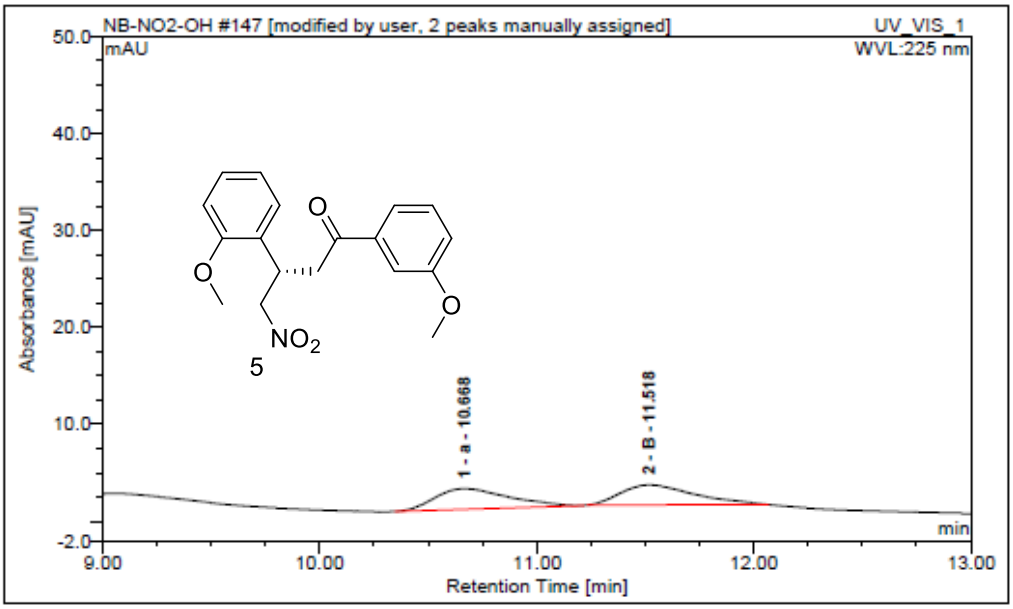


No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	10.69	0.063407	3.27133483	0.20508	n.a.
2	B	11.54	1.875	96.72866517	3.883	n.a.

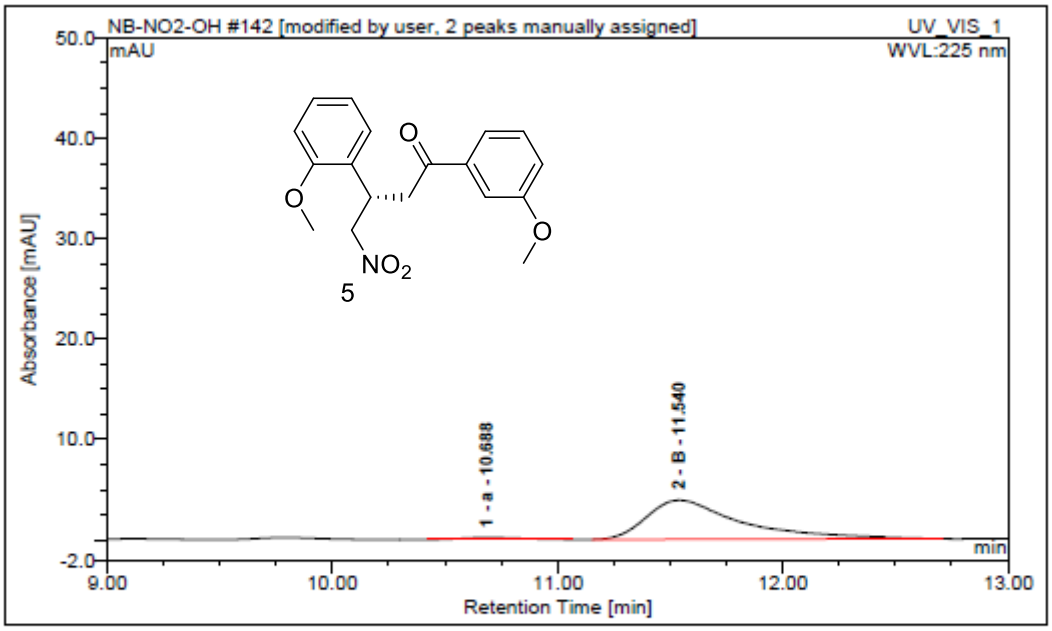
10. Structure determination:

The stereochemistry has been determined by comparing known compounds.[4] The HPLC data of compound **5** was measured according to the reported compound (**3e**) and the result obtained is the reverse of the reported compound. So the absolute stereochemistry is confirmed to be **S.**

HPLC data of compound 5:

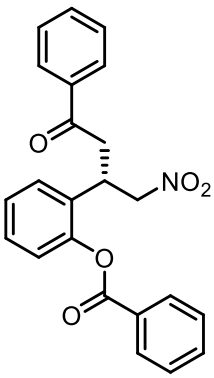


No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	10.67	0.82577	50.41942921	2.11733	n.a.
2	B	11.52	0.812	49.58057079	2.044	n.a.



No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	10.69	0.063407	3.27133483	0.20508	n.a.
2	B	11.54	1.875	96.72866517	3.883	n.a.

Hence, the structure of 3a is confirmed to be as:



14. References:

1. D. B. Ramachary, R. Sakthidevi, *Org. Biomol. Chem.*, 2010, **8**, 4259.
2. R. Balamurugan, S. Manojveer, *Chem. Commun*., 2011, **47**, 11143.
3. A. Berkessel, S. Mukherjee, T. N. Muller, F. Cleemann, K. Roland, M. Brandenburg, J. M. Neudorfl, J. Lex *Org. Biomol. Chem*., 2006, **4**, 4319.
4. A. Cholewiak, K. Adamczyk, M. Kopyt, A. Kasztelan, P. Kwiatkowski, *Org. Biomol. Chem*., 2018, **16**, 4365.