Electronic Supplementary Information

Hydrogen Bonding Mediated Enantioselective Organocatalysis in Brine: Significant Rate Acceleration and Enhanced Stereoselectivity in Enantioselective Michael Addition Reactions of 1,3-Dicarbonyls to β-Nitroolefins

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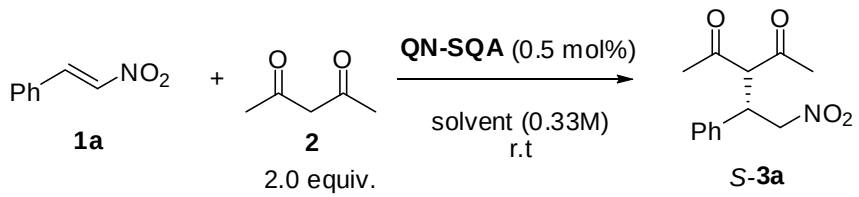
1. General

All chemicals used in this study were obtained from commercial sources and used without further purification. The organocatalysts examined in this study (**QN-TU,**[1a] **QN-SA,**[1b] **QN-SQA,**[1c,1d] **CN-SQA**[1c]) were prepared starting from the corresponding 9-*epi*-amino cinchona alkaloids according to the literature procedure. The chromatographic purification of the products was conducted by flash chromatography using Merck silica gel 60 (230–400 mesh). Thin-layer chromatography was conducted on Merck silica gel 60F plates. HPLC analyses were performed on a Varian Pro Star Series instrument equipped with an isostatic pump using a CHIRALCEL Column (250 × 4.6 mm). The ^{1}H and ^{13}C NMR spectra were recorded on Varian 300 spectrometers.

2. General procedure for the Michael Addition

2,4-Pentanedione (**2**, 103 μL, 0.5 mmol) was added to a mixture of *β*-nitrostyrene (**1a**, 75 mg, 0.5 mmol), **QN-SQA** (1.6 mg, 0.5 mol%), and brine (1.5 mL of saturated NaCl aqueous solution) in a 5 mL vial. The reaction mixture was stirred vigorously (using five magnetic bars at a stirring speed of 1000 rpm) at room temperature. After completion of the reaction, which was monitored by TLC, an aqueous HCl solution (1 N, 1 mL) was added to quench the reaction then extracted with CH_2Cl_2 (3 x 5 mL). The combined organic phase was washed with water and dried over anhydrous Na_2SO_4, and the solvent was concentrated. The obtained crude product was purified by column chromatography on silica gel to afford the Michael addition product **3a**.

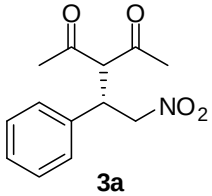
3. Solvent Screening



entry	solvent	time (h)	conv. (%)[a]	ee (%)[b]
1	CH_2Cl_2	2	>99	>99
2	DMSO	1	>99	racemic
3	Toluene	2	>99	>99
4	MeOH	96	>99	>99

[a] Determined by ^{1}H NMR. [b] Determined by HPLC analysis using chiral AD-H column.

4. Product Characterization

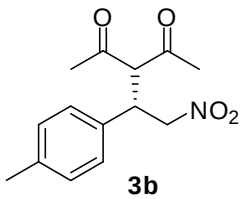


3a

Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded **3a** as a white solid (98% yield). Analytical data was matched with previously reported values.

^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 7.26-7.19 (m, 3H), 7.12-7.10 (m, 2H), 4.58-4.55 (m, 2H), 4.30 (d, 1H, *J* = 10.5 Hz), 4.21-4.17 (m, 1H), 2.23 (s, 3H), 1.87 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 201.7, 201.0, 135.9, 129.3, 128.5, 127.9, 78.1, 70.6, 42.7, 30.4, 29.6; HPLC (AD-H, Hexane : iPrOH = 90 : 10, 1.0. mL/min, 220 nm): t_{major} = 11.0 min, t_{minor} = 14.7 min; >99% ee.

Configuration assignment: The absolute stereochemistry was assigned as (*S*) by comparison of the retention time of HPLC with the literature data. [2]

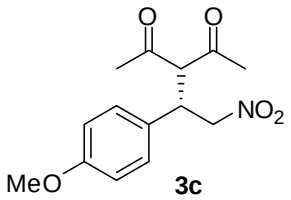


3b

Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded **3b** as a white solid (92% yield). Analytical data was matched with previously reported values.

^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 7.20-6.97(m 4H), 4.54-4.52 (m, 2H), 4.28 (d, *J* = 10.8 Hz, 1H), 4.17-4.11 (m, 1H), 2.22 (s, 3H), 2.19 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 201.8, 201.1, 138.2, 132.8, 129.9, 127.7, 78.2, 70.6, 42.4, 30.3, 29.5, 20.9; HPLC (AD-H, Hexane : iPrOH = 90 : 10, 1.0 mL/min, 220 nm): t_{major} = 10.2 min, t_{minor} = 16.6 min; 97% ee.

Configuration assignment: The absolute stereochemistry was assigned as (*S*) by comparison of the retention time of HPLC with the literature data. [1c]

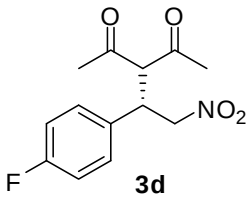


3c

Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded **3c** as a white solid (91% yield). Analytical data was matched with previously reported values.

^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 7.03 (d, *J* = 8.7 Hz, 3H), 6.76 (d, 3*J* = 8.7 Hz, 2H), 4.53-4.51 (m, 2H), 4.23 (d, *J*= 11.1 Hz, 1H), 4.16-4.08 (m, 1H), 3.69 (s, 3H), 2.19 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 201.8, 201.1, 159.4, 129.0, 127.6, 114.6, 78.4, 70.8, 55.1, 42.1, 30.3, 29.5; HPLC (AD-H, Hexane : iPrOH = 90 : 10, 1.0 mL/min, 220 nm): t_{major} = 16.2 min, t_{minor} = 25.7 min; 98% ee.

Configuration assignment: The absolute stereochemistry was assigned as (*S*) by comparison of the retention time of HPLC with the literature data.[3]



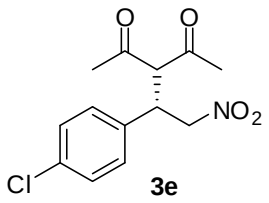
3d

Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded **3d** as a white solid (89% yield). Analytical data was matched with previously reported values.

^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 7.13 - 7.09 (m, 2H), 6.97-6.91 (m, 2H), 4.58-4.49 (m, 2H), 4.27 (d, *J* = 10.8, 1H), 4.21- 4.13 (m, 1H), 2.20 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 201.4, 200.7, 164.0, 160.7, 131.8, 131.7, 129.7, 129.6, 116.3, 116.0, 78.0, 70.4, 42.0, 30.3, 29.6; HPLC (OD-H, Hexane : iPrOH = 85 : 15, 1 mL/min, 220 nm): t_{major} = 16.9 min, t_{minor} = 18.8 min; >99% ee.

Configuration assignment: The absolute stereochemistry was assigned as (*S*) by comparison of the

retention time of HPLC with the literature data. [4]

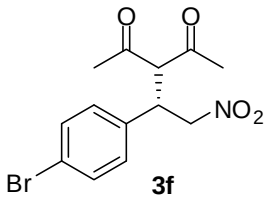


3e

Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded **3e** as a white solid (99% yield). Analytical data was matched with previously reported values.

^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 7.23 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 4.55 (d, *J* = 6.3 Hz, 2H), 4.14 (d, *J* = 10.5 Hz, 1H), 4.20-4.12 (m, 1H), 2.20 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 201.3, 200.6, 134.5, 134.3, 129.4, 129.3, 77.8, 70.3, 42.0, 30.4, 29.7; HPLC (AS-H, Hexane : iPrOH = 85 : 15, 1 mL/min, 220 nm): t_{major} = 15.2 min, t_{minor} = 28.5 min; >99% ee.

Configuration assignment: The absolute stereochemistry was assigned as (*S*) by comparison of the retention time of HPLC with the literature data. [3]

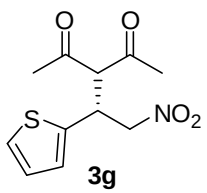


3f

Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded **3f** as a white solid (96% yield). Analytical data was matched with previously reported values.

^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 4.62 (d, *J* = 6.3 Hz, 2H), 4.25 (d, *J* = 6.0 Hz, 1H), 4.26-4.18 (m, 1H), 2.29 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): 201.3. 200.5. 135.1. 132.4. 129.6. 122.5. 77.7. 70.2, 42.1, 30.4, 29.7; HPLC (OD-H, Hexane : iPrOH = 90 : 10, 0.8 mL/min, 220 nm): t_{major} = 34.2 min, t_{minor} = 37.3 min; >99% ee.

Configuration assignment: The absolute stereochemistry was assigned as (*S*) by comparison of the retention time of HPLC with the literature data. [1c]

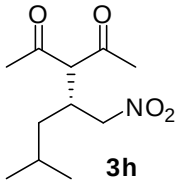


3g

Purification by column chromatography (4:1 = Hexane : EtOAc) afforded **3g** as a white solid (91% yield). Analytical data was matched with previously reported values.

^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 7.28-7.23 (m, 1H), 6.93-6.89 (m, 2H), 4.68-4.66 (m, 2H), 4.58-4.51 (m, 1H), 4.40 (d, J = 9.9 Hz, 1H), 2.29 (s, 3H), 2.07(s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 201.4, 200.6, 138.4, 127.3, 126.9, 125.6, 78.4, 70.9, 38.2, 30.5, 29.6; HPLC (AS-H, Hexanes : iPrOH = 90 : 10, 0.6 mL/min, 220 nm): t_{major} = 33.2 min, t_{minor} = 41.1 min; >99% ee.

Configuration assignment: The absolute stereochemistry was assigned as (*R*) by comparison of the retention time of HPLC with the literature data. [5]

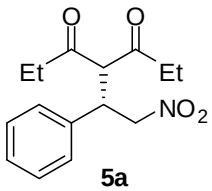


3h

Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded **3h** as a white solid (90% yield). Analytical data was matched with previously reported values.

^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 4.56-4.51 (m, 2H), 4.00 (d, *J* = 8.4 Hz, 1H), 2.96-2.85 (m, 1H), 2.29 (s, 3H), 2.26 (s, 3H), 1.78-1.64 (m, 1H), 1.42-1.32 (m, 1H), 1.05-0.95 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ202.9, 202.2, 75.6, 69.3, 38.2, 34.7, 31.0, 29.7, 24.8, 23.1, 21.1; HPLC (OD-H, Hexane : iPrOH = 96 : 4, 0.7 mL/min, 210 nm): t_{major} = 17.1 min, t_{minor} = 15.6 min; >99% ee.

Configuration assignment: The absolute stereochemistry was assigned as (*R*) by comparison of the retention time of HPLC with the literature data. [5]



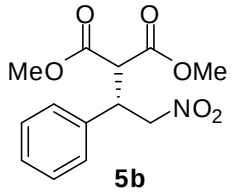
5a

Purification by column chromatography (5 : 1 = Hexane : Acetone) afforded **5a** as a white solid (96% yield). Analytical data was matched with previously reported values.

^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 7.32-7.27 (m, 3H), 7.18-7.15 (m, 2H), 4.71-4.60 (m, 2H), 4.35-4.23 (m, 2H), 2.65-2.44 (m, 2H), 2.38-2.25 (m, 1H), 2.20-2.04 (m, 1H), 1.07 (t, J = 7.2 Hz, 3H), 0.78 (t,

J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 204.4, 203.8, 136.2, 129.1, 128.3, 127.8, 77.8, 69.0, 42.9, 36.8, 36.4, 7.4, 7.2; HPLC (AD-H, Hexane : iPrOH = 90 : 10, 1.0 mL/min, 220 nm): t_{major} = 8.2 min, t_{minor} = 11.3 min; >99% ee.

Configuration assignment: The absolute stereochemistry was assigned as (*S*) by comparison of the retention time of HPLC with the literature data. [2]

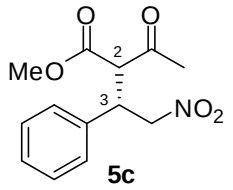


5b

Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded **5b** as a white solid (92% yield). Analytical data was matched with previously reported values.

^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 7.33-7.21 (m, 5H), 4.96-4.83 (m, 2H), 4.24 (td, *J* = 8.8, 5.7 Hz, 1H), 3.86 (d, *J* = 9.2 Hz, 1H), 3.76 (s, 3H), 3.56 (s, 3H); ^{13}C NMR (75 MHz , $CDCl_3$, Me_4Si): δ 167.7, 167.1, 136.1, 128.9, 128.3, 127.8, 77.4, 54.6, 52.9, 52.7, 42.9; HPLC (AD-H, Hexanes : iPrOH = 90 : 10, 1 mL/min, 220 nm): t_{major} = 26.4 min, t_{minor} = 16.2 min; 97 % ee.

Configuration assignment: The absolute stereochemistry was assigned as (*S*) by comparison of the retention time of HPLC with the literature data. [2]



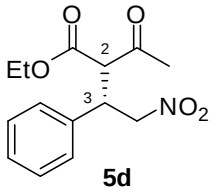
5c

Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded **5c** as a white solid (95% yield, 1 : 1 mixture of diastereomers). Analytical data was matched with previously reported values.

^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 7.33-7.25 (m, 3H), 7.21-7.18 (m, 2H), 4.83-4.81 (m, 1 H), 4.78-4.76 (m, 1 H), 4.29-4.17 (m,1 H), 4.12 (d, J = 9.6 Hz, 0.5 H), 4.03 (d, J = 9.6 Hz, 0.5 H), 3.77-3.53 (s, 3H), 2.29-2.05 (s, 3H); dr = 1 : 1 (determined by integration of ^{1}H NMR); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 200.5, 199.6, 167.4, 166.7, 135.8, 135.6, 128.5, 128.3, 127.7, 127.6, 127.2, 127.2, 76.4, 76.0,

61.2, 60.8, 52.3, 52.1, 42.0, 41.7, 29.7, 29.6; HPLC (AD-H, Hexane : iPrOH = 95 : 5, 1.0 mL/min, 220 nm): First diastereomer: t_{major} = 15.4 min, t_{minor} = 23.2 min; >99% ee; Second diastereomer : t_{major} = 28.6 min, t_{minor} = 21.7 min; >99 % ee.

Configuration assignment: The absolute stereochemistry of carbon (3) was assigned as (*S*) by comparison of the retention time of HPLC with the literature data. [2]

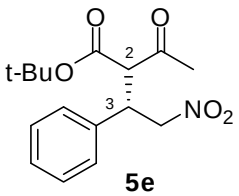


5d

Purification by column chromatography (5 : 1 = Hexane : Acetone) afforded **5d** as a white solid. Analytical data was matched with previously reported values (94% yield, 1.5:1 mixture of diastereomers).

^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 7.32-7.27 (m, 3H), 7.22-7.19 (m, 2H), 4.89-4.76 (m, 2H), 4.26-4.18 (m, 2 H), 4.12 (d, J = 9.9 Hz, 0.6H) 4.03 (d, 0.4 H, J = 9.9 Hz), 3.96 (q, 1H, *J* = 7.2 Hz), 2.30-2.05 (s, 3H), 1.28-1.00 (t, *J* = 7.2 Hz, 4H); dr = 1.5 : 1 (determined by integration of ^{1}H NMR); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 201.4, 200.5, 167.7, 167.1, 136.7, 129.4, 128.6, 128.5, 128.2, 128.1, 78.1, 78.0, 76.8, 65.4, 62.2, 62.2, 61.9, 42.8, 42.5, 30.5, 30.3, 13.9, 13.6; HPLC (AD-H, Hexanes : iPrOH = 95 : 5, 0.8 mL/min, 220 nm): First diastereomer : t_{major} = 15.6 min, t_{minor} = 26.8 min; >99% ee; Second diastereomer: t_{major} = 51.6 min, t_{minor} = 23.5 min; >99% ee.

Configuration assignment: The absolute stereochemistry of carbon (3) was assigned as (*S*) by comparison of the retention time of HPLC with the literature data. [2]



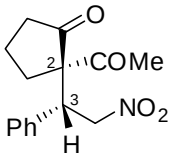
5e

Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded **5e** as a white solid (94% yield, 4.9 : 1 mixture of diastereomers). Analytical data was matched with previously reported values.

^{1}H NMR (300 MHz, $CDCl_3$ Me_4Si): δ 7.34-7.29 (m, 3H), 7.25-7.20 (m, 2H), 4.85-4.82 (m 0.4H), 4.77-4.65 (m, 2H), 4.23-4.10 (m, 1H), 4.03 (d, J = 10.2 Hz, 0.83H), 3.92 (d, J = 10.2 Hz, 0.17H) , 2.30-2.06 (s, 3H), 1.47 - 1.11 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 201.5, 200.9 166.9, 166.1, 136.9, 129.3, 129.0, 128.5, 128.4, 128.4, 128.2, 83.6, 83.1, 78.6, 78.1, 63.3, 62.9, 42.8, 42.6, 30.3, 29.9, 28.0,

27.6; dr = 4.9 : 1 (determined by integration of ^{1}H NMR); HPLC (AD-H, Hexanes : iPrOH = 95 : 5, 1 mL/min, 220 nm): First (major) diastereomer: t_{major} = 8.8 min, t_{minor} = 13.5 min ; 98 % ee; Second (minor) diastereomer: t_{major} = 24.2 min, t_{minor} = 15.2 min; 98% ee.

Configuration assignment: The absolute stereochemistry of carbon (3) was assigned as (*S*) by comparison of the retention time of HPLC with the literature data. [2]



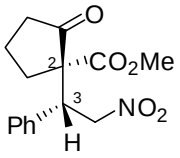
5f

(major diastereomer)

Purification by column chromatography (4 : 1 = Hexane : EtOAc) afforded **5f** as a white solid (85% yield, 7.3 : 1 mixture of diastereomers). Analytical data was matched with previously reported values.

^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 7.24-7.34(m, 5H), 5.01(dd, J = 11.1, 13.2 Hz, 0.12H) 4.86(dd, J = 11.4 Hz and J = 13.5 Hz, 0.88H), 4.60-4.51 (dd, J = 3.9 Hz and 13.2 Hz, 1H), 4.39-4.28 (dd, J = 3.9 and J = 11.1 Hz, 1H), 2.61-2.54 (m, 1H), 2.33 (s, 3H), 2.26-2.14(m, 1H), 2.03-1.93 (m, 1H), 1.80-1.65 (m, 3H); dr = 7.3 : 1 (determined by integration of ^{1}H NMR); ^{13}C NMR (75 MHz , $CDCl_3$, Me_4Si): δ 213.3, 203.0, 134.4, 129.7, 129.1, 128.7, 75.8, 71.4, 46.6, 38.9, 27.5, 26.8, 19.7; HPLC (OD-H, Hexane : iPrOH = 80 : 20, 1 mL/min, 220 nm): First (major) diastereomer: t_{major} = 13.4 min, t_{minor} = 60.9 min; 97% ee; Second (minor) diastereomer: t_{major} = 17.0 min, t_{minor} = 27.1 min; 75% ee.

Configuration assignment: The absolute stereochemistry was assigned as (*2R,3R*) by comparison of the retention time of HPLC with the literature data.[6]



5g

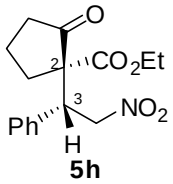
(major diastereomer)

Purification by column chromatography (4:1 = Hexane : EtOAc) afforded **5g** as a colorless oil (87% yield, 99:1 mixture of diastereomers). Analytical data was matched with previously reported values.

^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 7.31-7.23 (m, 5H), 5.17 (dd, J = 4.2 and 13.5 Hz, 1H), 5.01(dd, J = 10.8 Hz and J = 13.5Hz, 1H), 4.08 (dd, J = 3.9 Hz and 10.8 Hz, 1H), 3.75 (s, 3H), 2.40-2.32 (m, 2H), 2.05-1.82 (m, 4H) ; dr >99 : 1 (determined by integration of ^{1}H NMR); ^{13}C NMR (75MHz, $CDCl_3$, Me_4Si): δ 212.4, 170.0, 135.5, 129.5, 129.1, 128.5, 76.6, 62.7, 53.2, 46.4, 38.1, 31.4, 19.5; HPLC (OD-

H, Hexane : iPrOH = 80 : 20, 1 mL/min, 220 nm): First (major) diastereomer: t_{major} = 16.1 min, t_{minor} = 26.4 min; >99% ee; Second (minor) diastereomer: t_{major} = 13.5 min, t_{minor} = 23.1 min; 84% ee.

Configuration assignment: The absolute stereochemistry was assigned as (*2S,3R*) by comparison of the retention time of HPLC with the literature data.[1c,6]



5h

(major diastereomer)

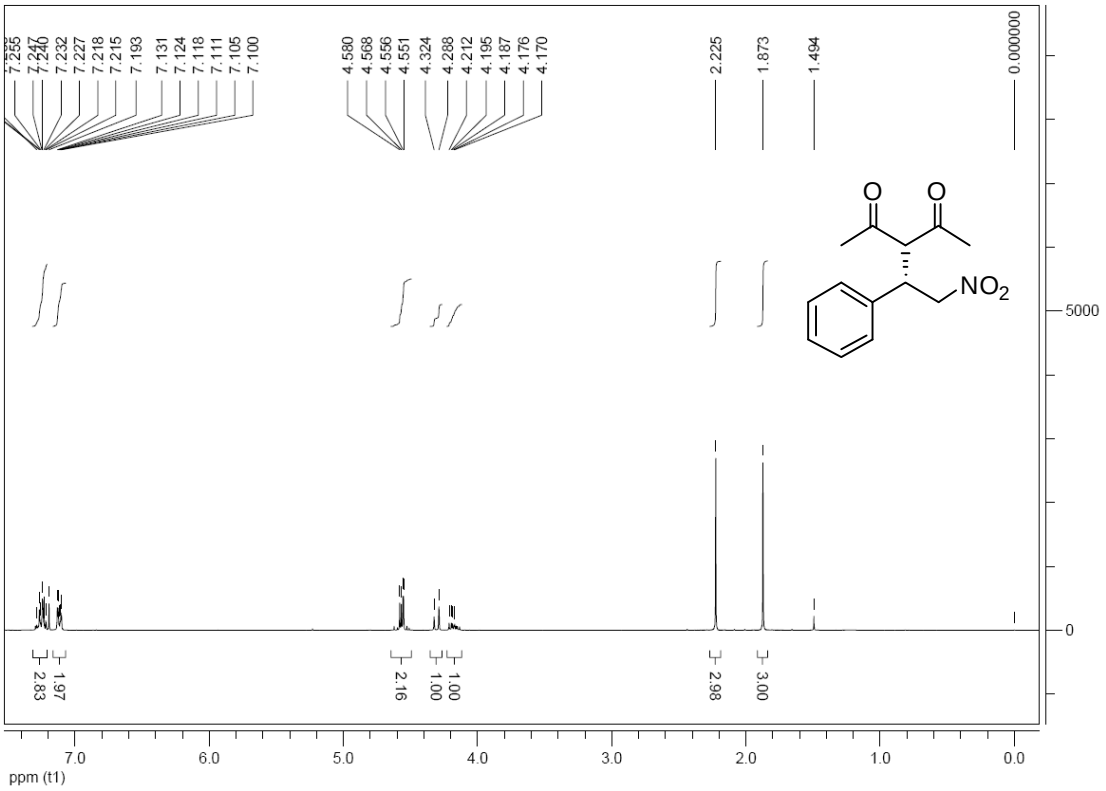
Purification by column chromatography (4:1 = Hexane : EtOAc) afforded **5h** as a colorless oil (98% yield, 99:1 mixture of diastereomers). Analytical data was matched with previously reported values.

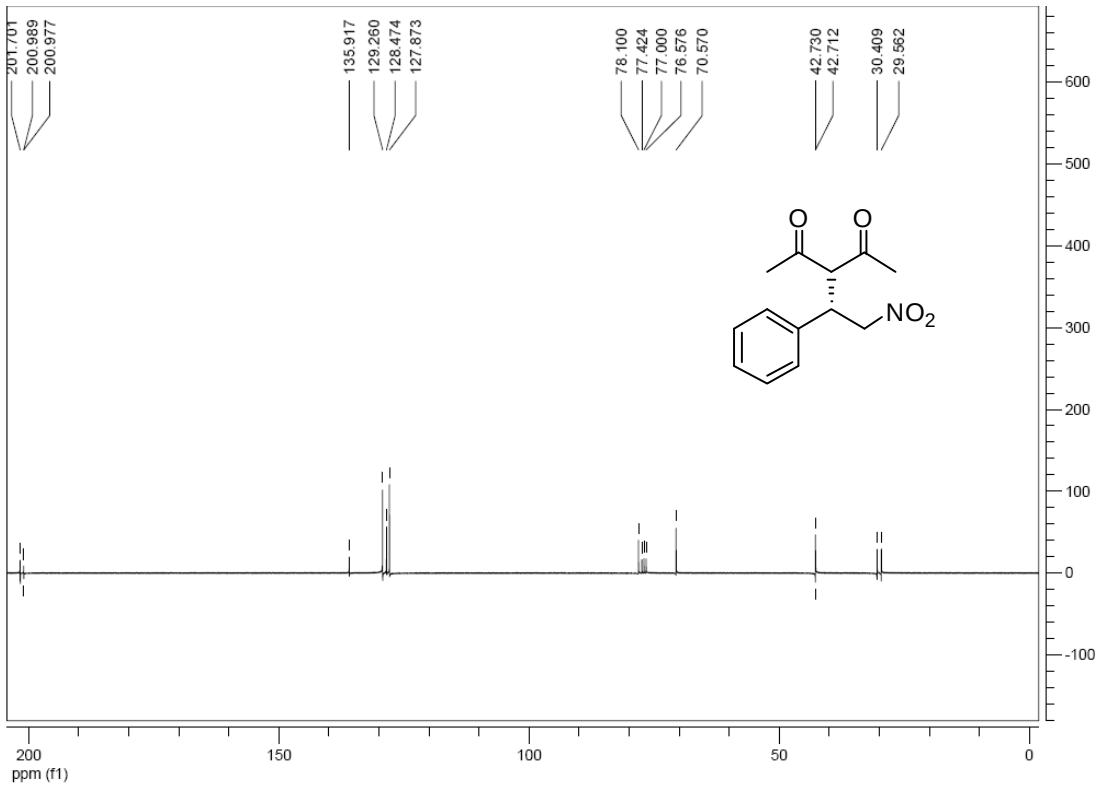
^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 7.34-7.27 (m, 5H), 5.18 (dd, J = 3.9 and 13.6 Hz, 1H), 5.01 (dd, J = 10.9 and 13.5Hz, 1H), 4.24-4.17 (m, 1H), 4.08 (dd, J = 3.9 and 10.9Hz, 1H), 2.40-2.32 (m, 2H), 2.07-1.74 (m, 4H), 1.27 (t, J = 7.1Hz, 1H); dr >99 : 1 (determined by integration of ^{1}H NMR); ^{13}C NMR (75MHz, $CDCl_3$, Me_4Si): δ 212.3, 169.3, 135.3, 129.3, 128.7, 128.2, 76.4, 62.4, 62.1, 46.1, 37.8, 31.1, 19.3, 13.9; HPLC (OD-H, Hexane : iPrOH = 90 : 10, 0.5 mL/min, 215 nm): First (major) diastereomer: t_{major} = 23.0 min, t_{minor} = 33.5 min; >99% ee ; Second (minor) diastereomer: t_{major} = 19.6 min, t_{minor} = 29.2 min; 78% ee.

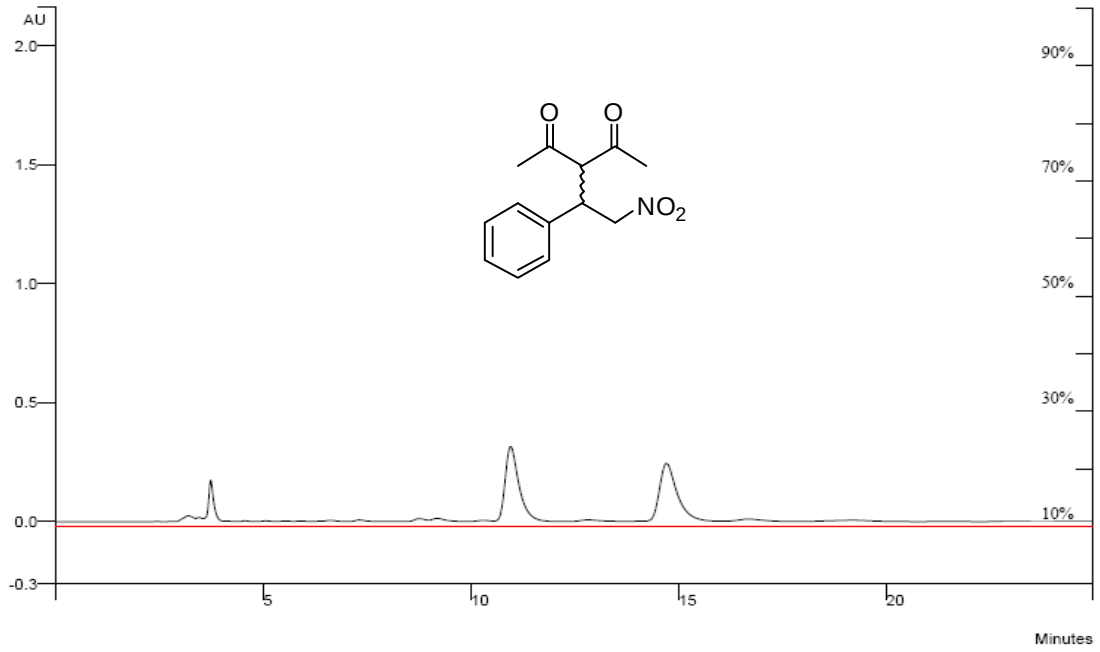
Configuration assignment: The absolute stereochemistry was assigned as (*2S,3R*) by comparison of the retention time of HPLC with the literature data. [7]

5. ^{1}H NMR, ^{13}C NMR and HPLC Spectra for Table 2

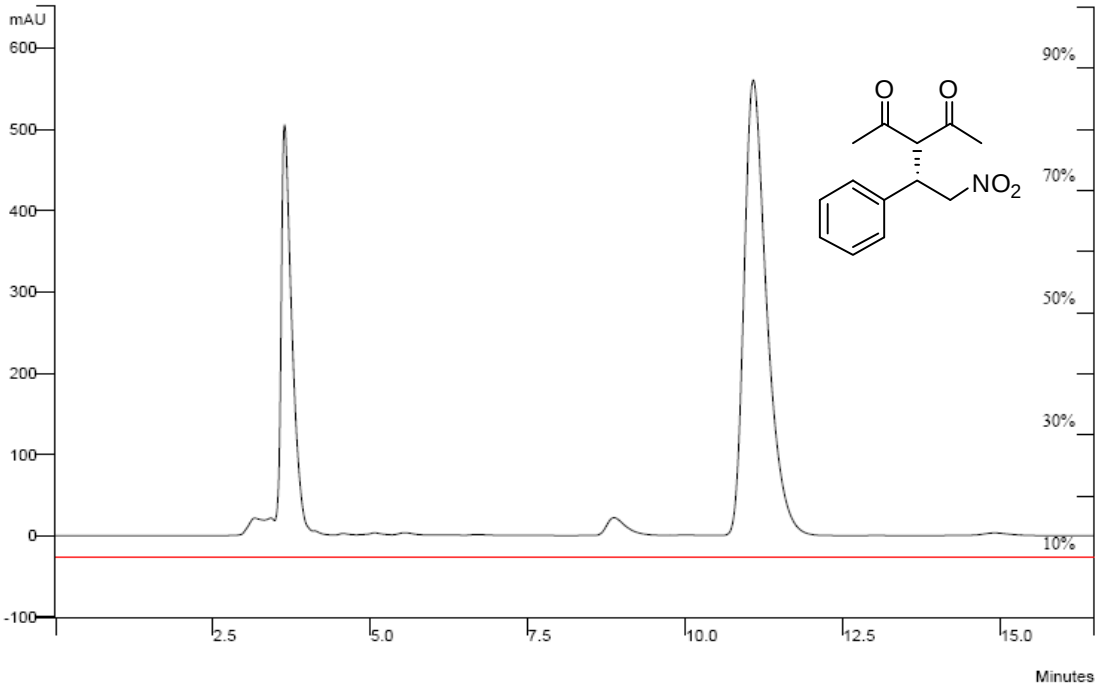
3a (Entry 2, Table 2)


7.255
7.247
7.240
7.232
7.227
7.218
7.215
7.193
7.131
7.124
7.118
7.111
7.105
7.100
4.580
4.568
4.556
4.551
4.324
4.288
4.212
4.195
4.187
4.176
4.170
2.225
1.873
1.494
0.000000
O
O
NO2
5000
0
2.83
1.97
2.16
1.00
1.00
2.98
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


201.701
200.989
200.977
135.917
129.260
128.474
127.873
78.100
77.424
77.000
76.576
70.570
42.730
42.712
30.409
29.562
O
O
NO2
600
500
400
300
200
100
0
-100
200
150
100
50
0
ppm (f1)

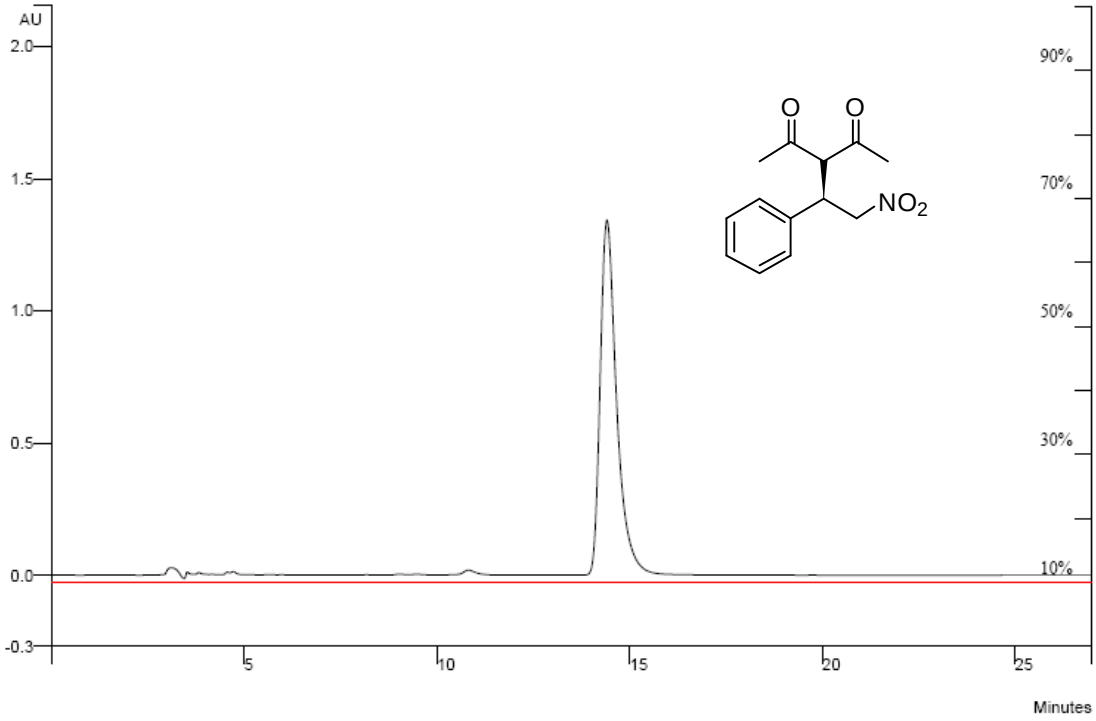


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		50.1789	10.960	0.000	71975616	0.00	BB	20.3		0
2		49.8211	14.716	0.000	71462376	0.00	BB	25.8		0
	Totals	**100.0000**		**0.000**	**143437984**					



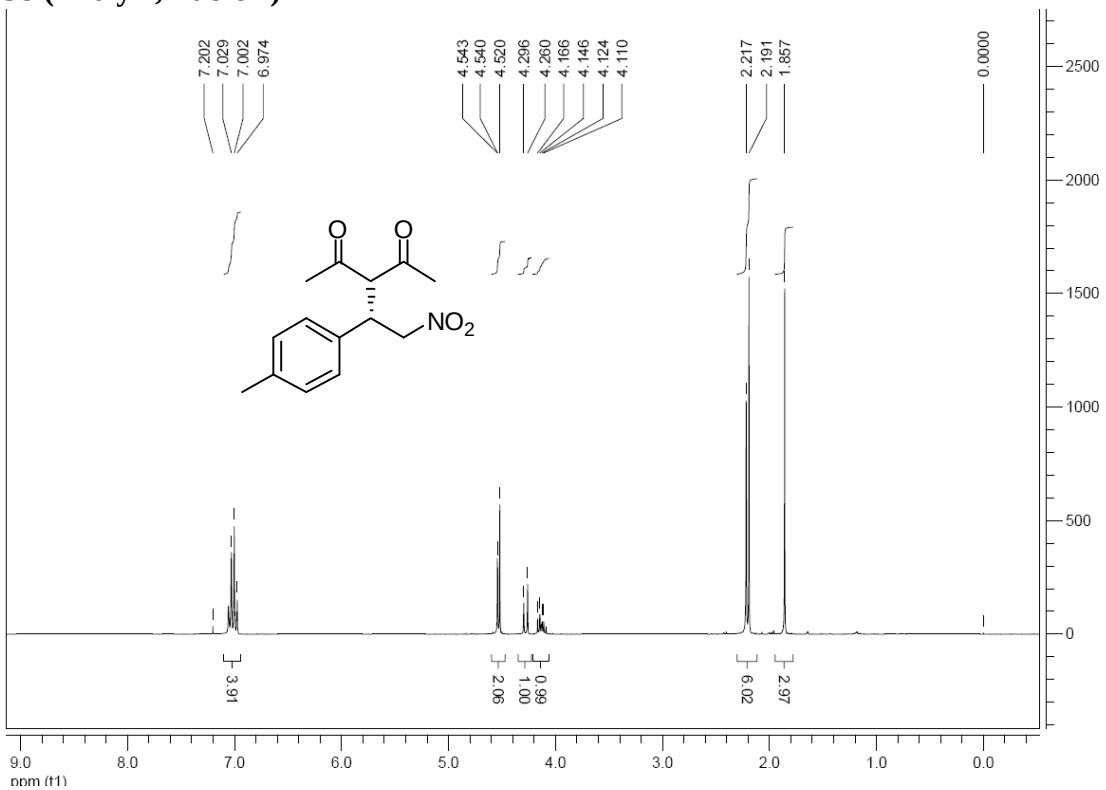
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		99.5284	11.080	0.000	140049344	0.00	BB	22.5		0
2		0.4716	14.913	0.000	663585	0.00	BB	23.0		0
	Totals	**100.0000**		**0.000**	**140712928**					

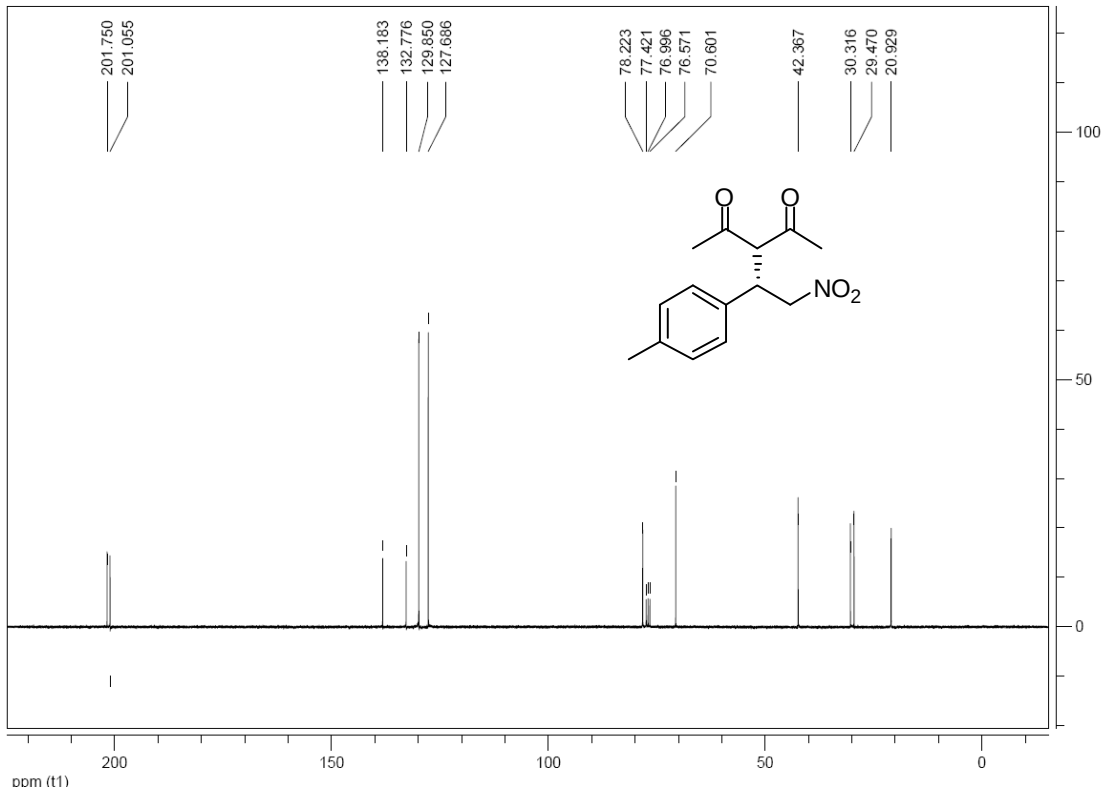
3a (using **CN-SQA**:[1c] 98% ee (*R*); Entry 11, Table 1**)**

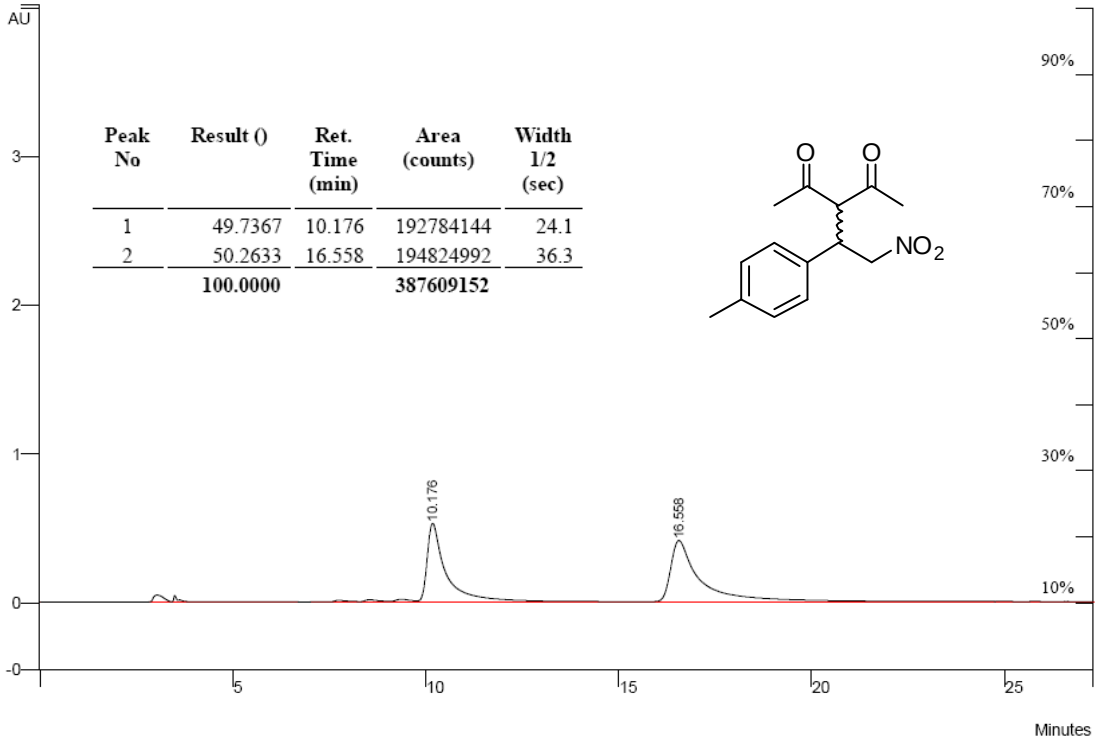


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		1.1130	10.821	0.000	4499929	0.00	BB	20.0		0
2		98.8870	14.416	0.000	399819680	0.00	BB	26.1		0
	Totals	**100.0000**		**0.000**	**404319616**					

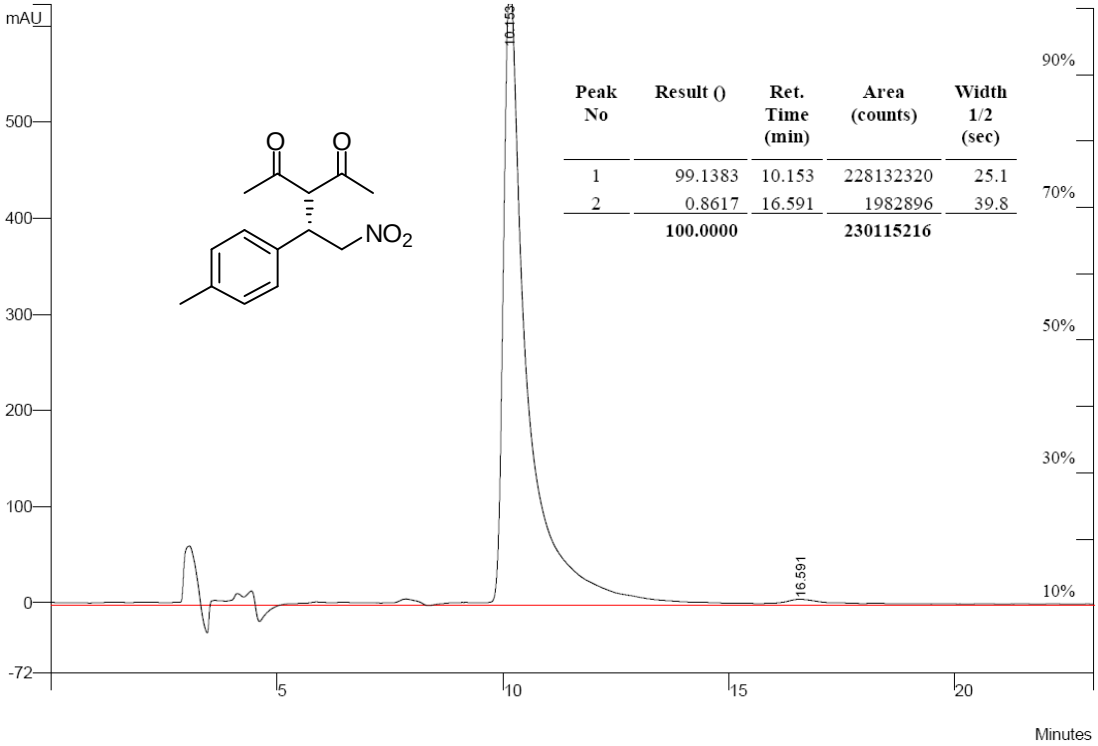
3b (Entry 4, Table 2)





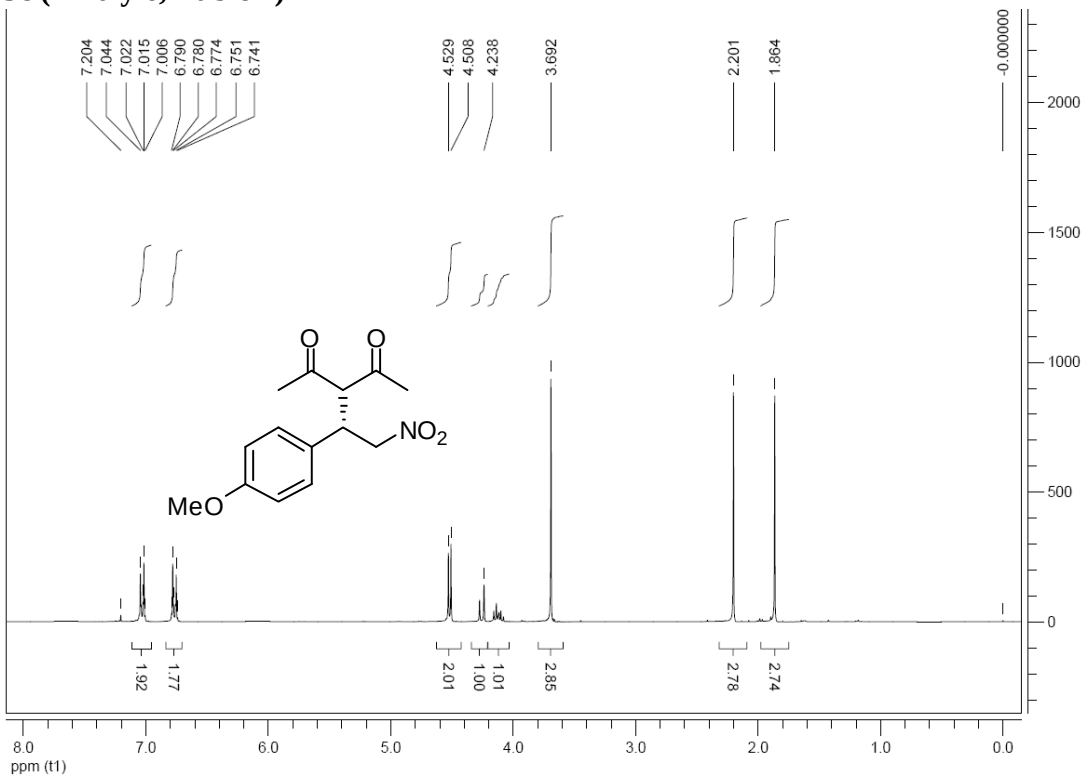


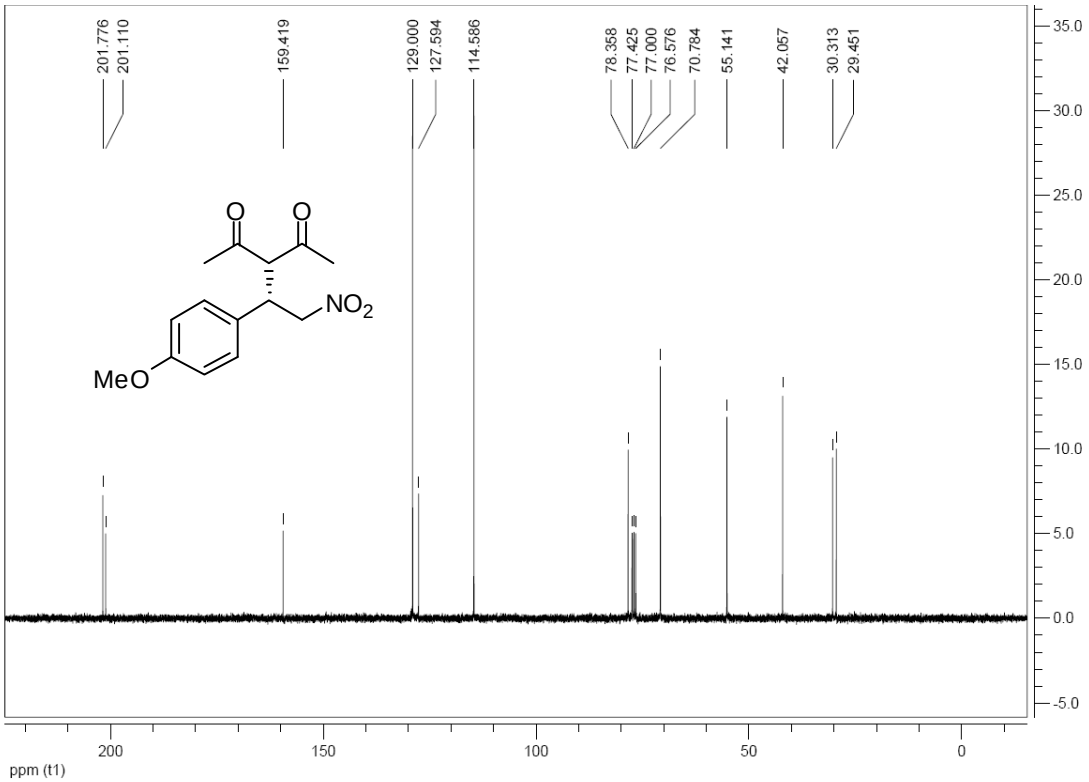
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	49.7367	10.176	192784144	24.1
2	50.2633	16.558	194824992	36.3
	100.0000		**387609152**	

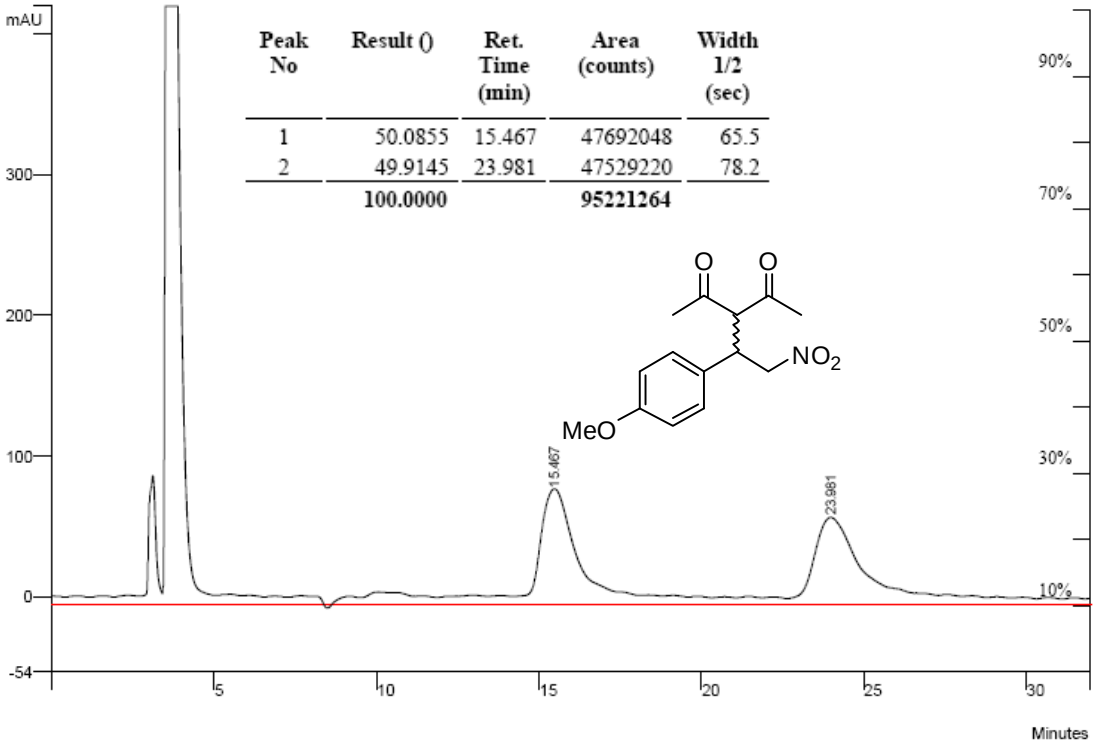


Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	99.1383	10.153	228132320	25.1
2	0.8617	16.591	1982896	39.8
	100.0000		**230115216**	

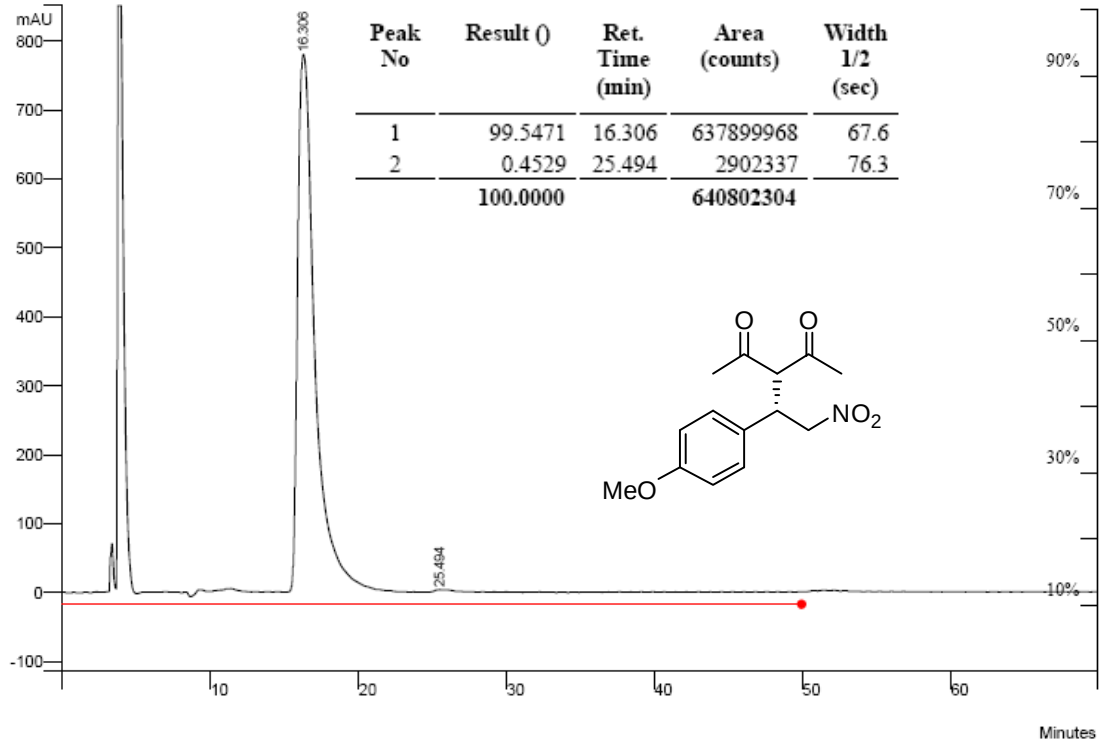
3c (Entry 6, Table 2)





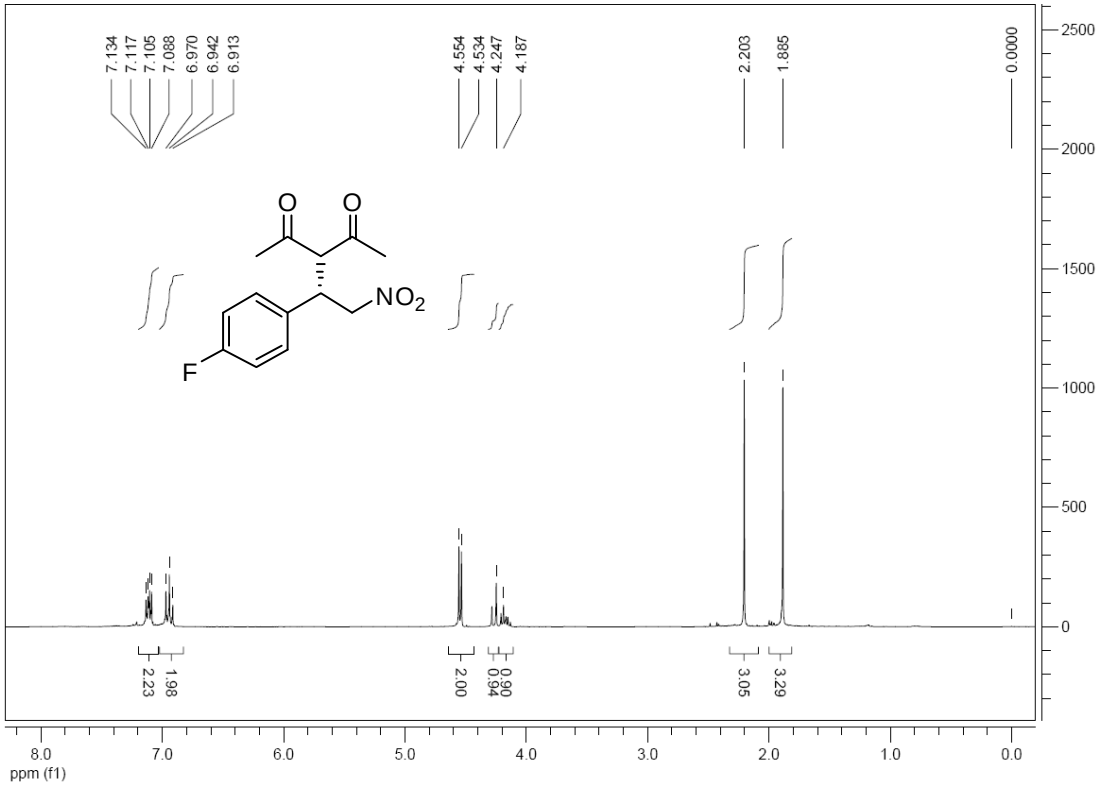


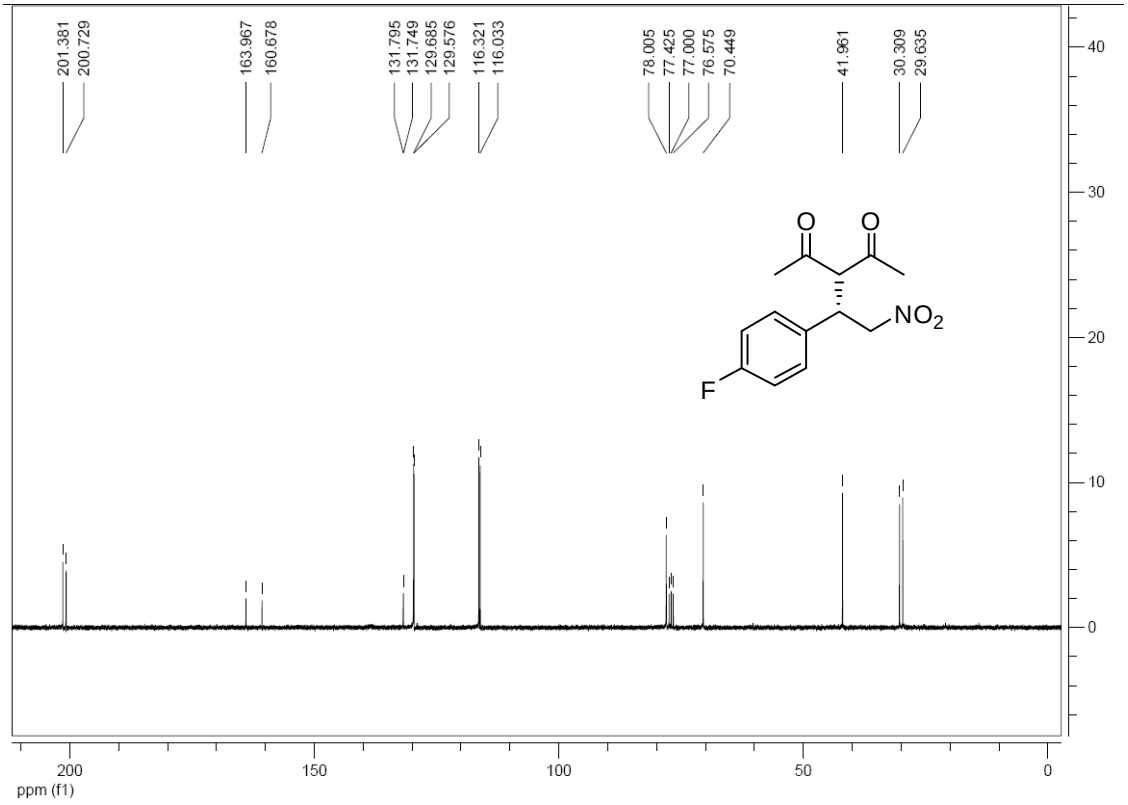
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	50.0855	15.467	47692048	65.5
2	49.9145	23.981	47529220	78.2
	100.0000		**95221264**	

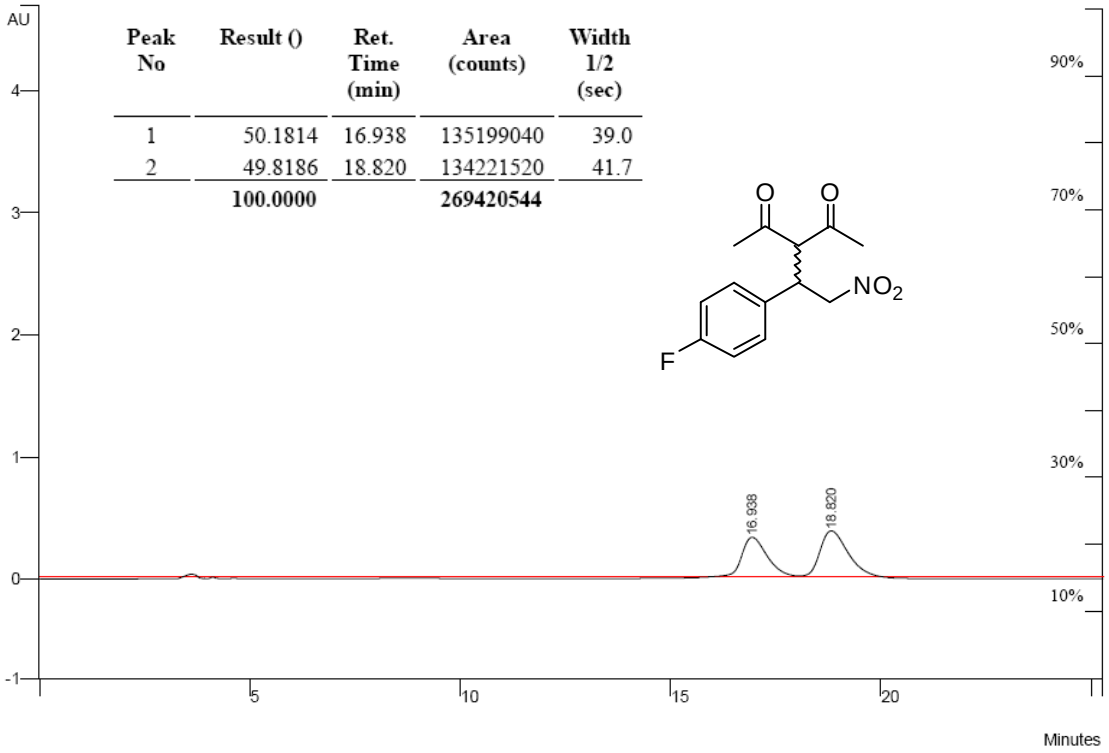


Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	99.5471	16.306	637899968	67.6
2	0.4529	25.494	2902337	76.3
	100.0000		**640802304**	

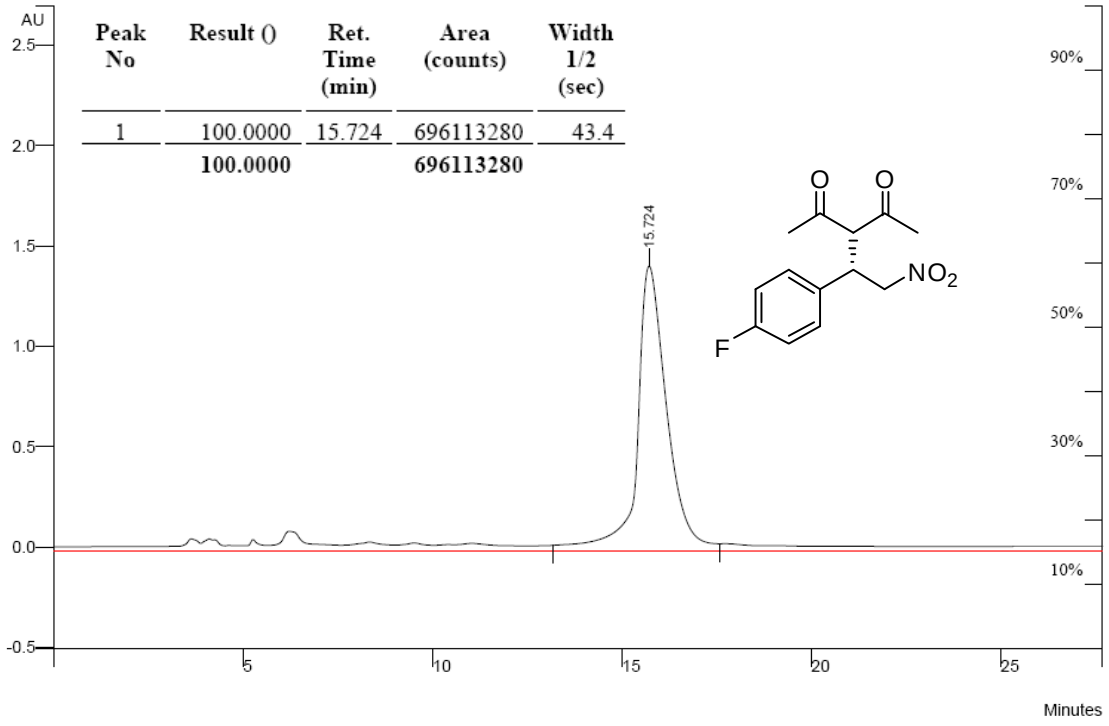
3d (Entry 8, Table 2)





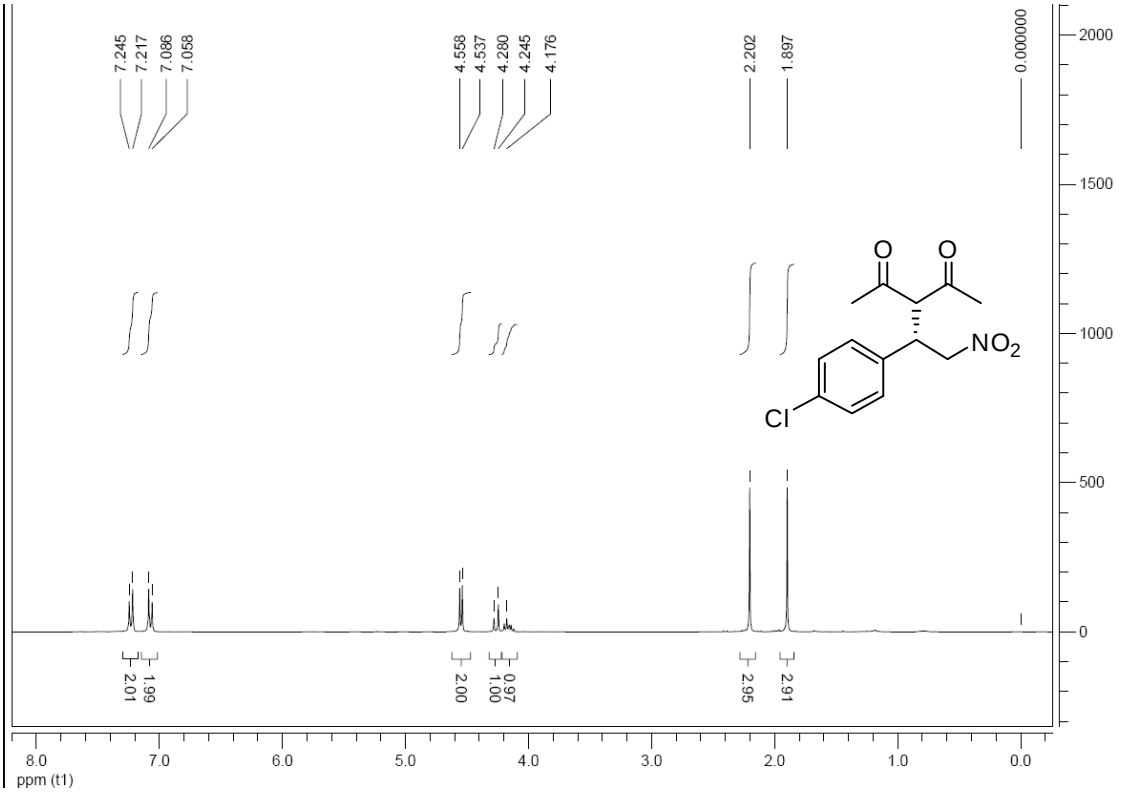


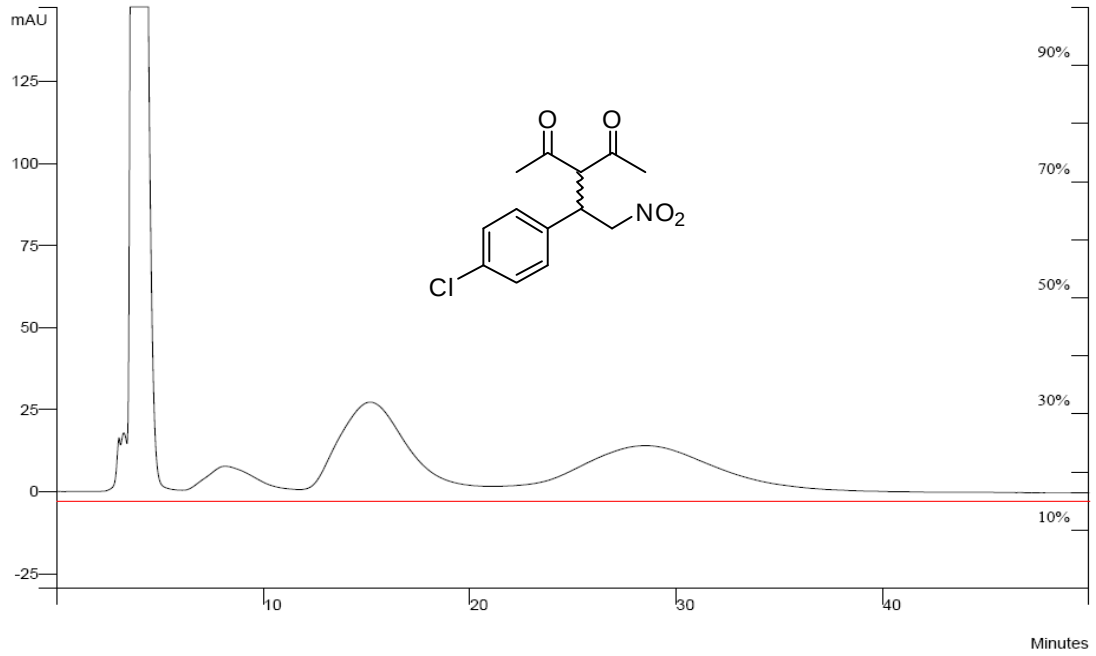
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	50.1814	16.938	135199040	39.0
2	49.8186	18.820	134221520	41.7
	100.0000		**269420544**	



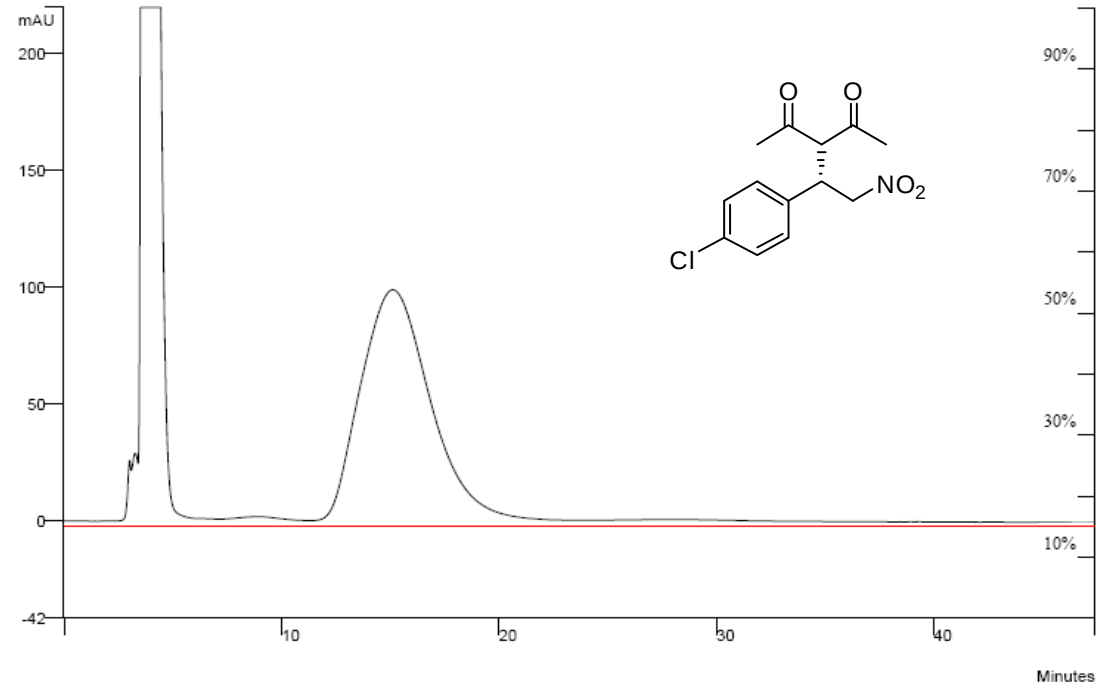
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	100.0000	15.724	696113280	43.4
	100.0000		**696113280**	

3e (Entry 10, Table 2)



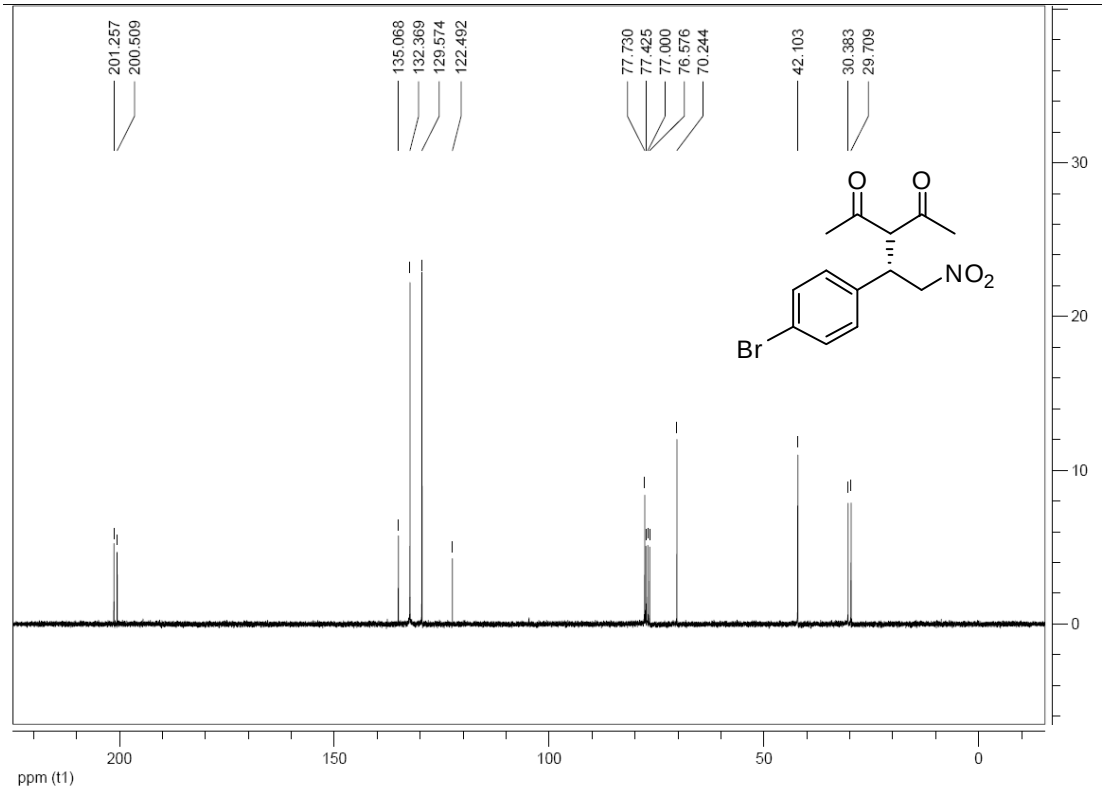


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		50.6397	15.171	0.000	56614508	0.00	BB	210.5		0
2		49.3603	28.500	0.000	55184232	0.00	BB	383.0		0
	Totals	**100.0000**		**0.000**	**111798736**					

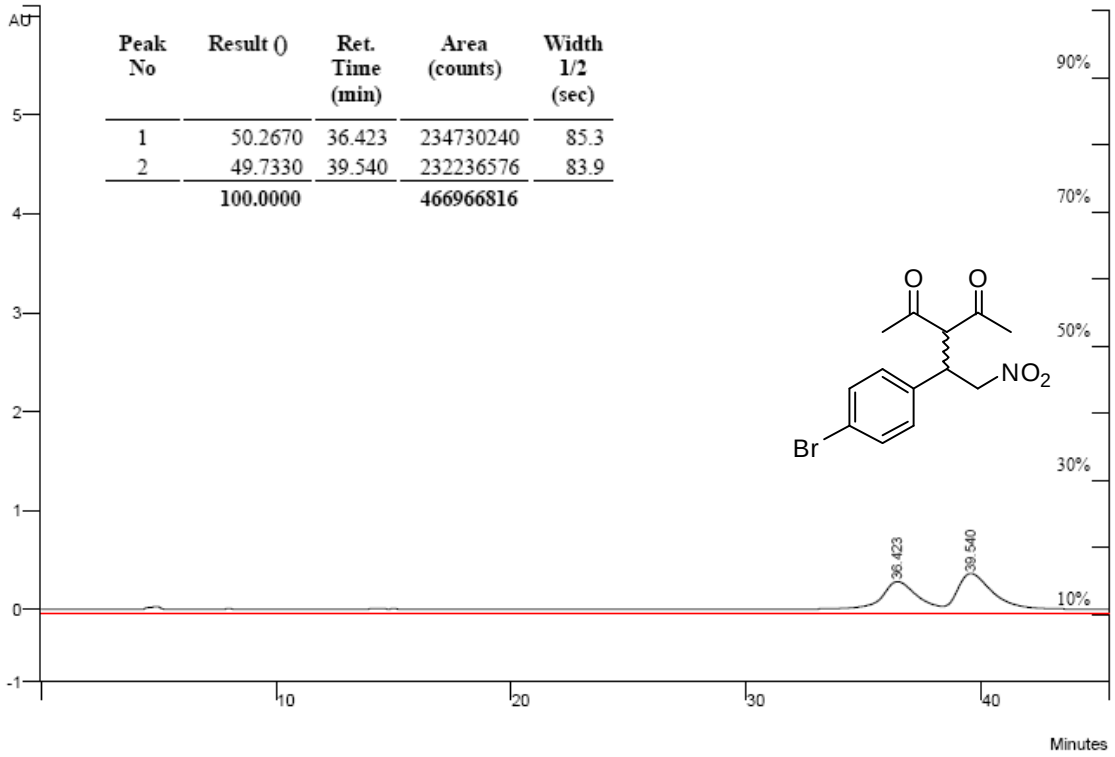


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		99.5330	15.125	0.000	217833344	0.00	BB	208.1		0
2		0.4670	28.021	0.000	1022017	0.00	BB	207.9		0
	Totals	**100.0000**		**0.000**	**218855360**					

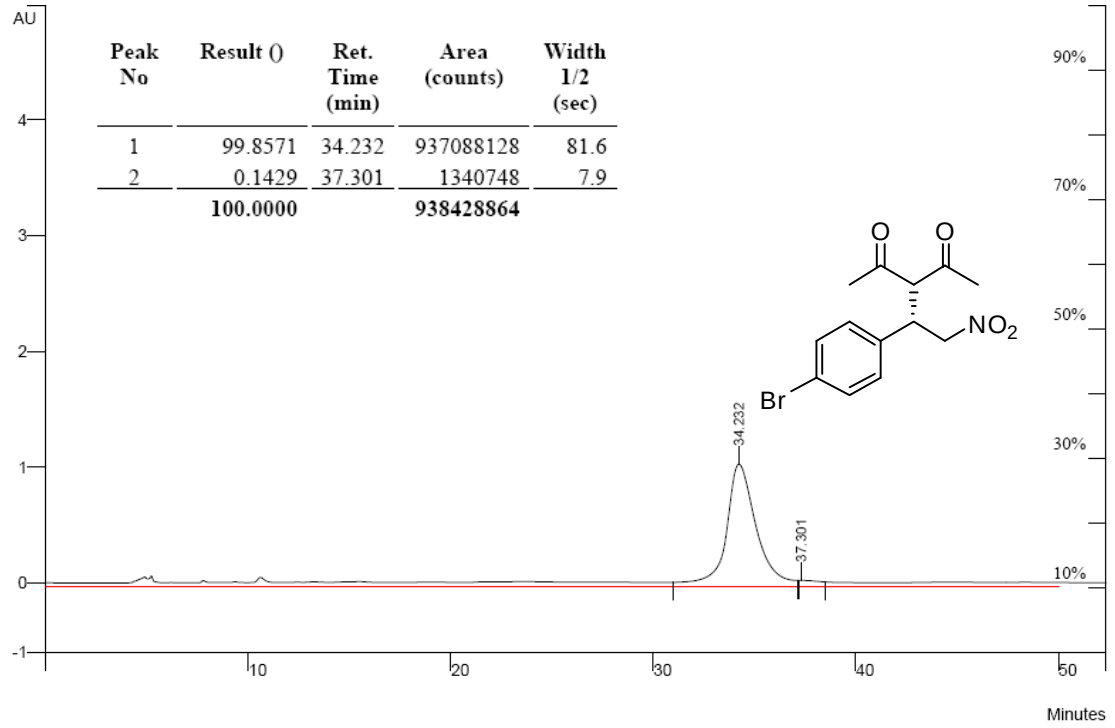
3f (Entry 12, Table 2)



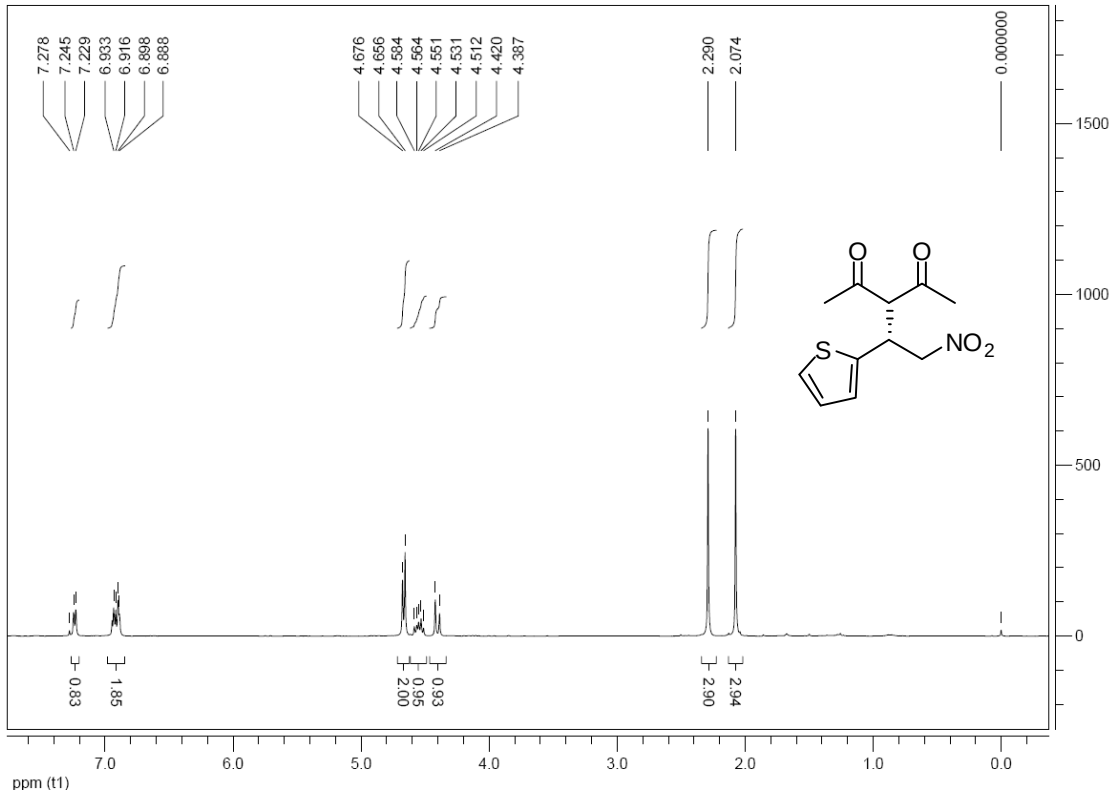
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	50.2670	36.423	234730240	85.3
2	49.7330	39.540	232236576	83.9
	100.0000		**466966816**	

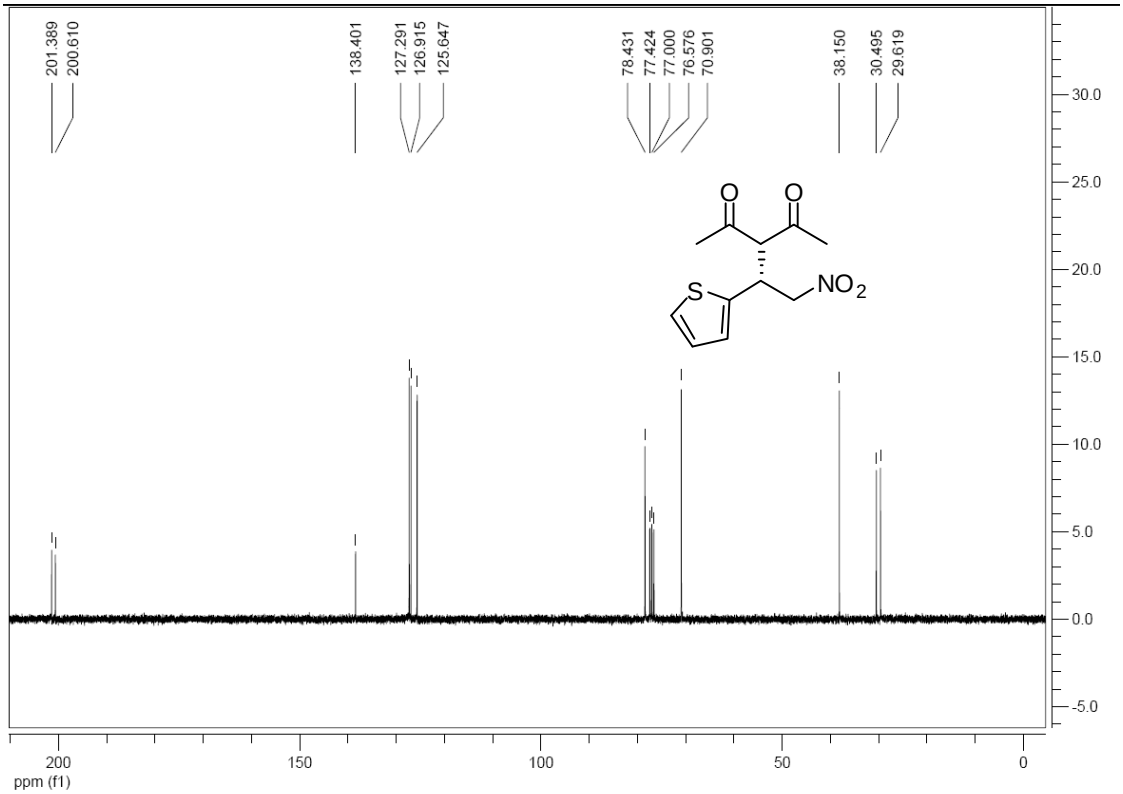


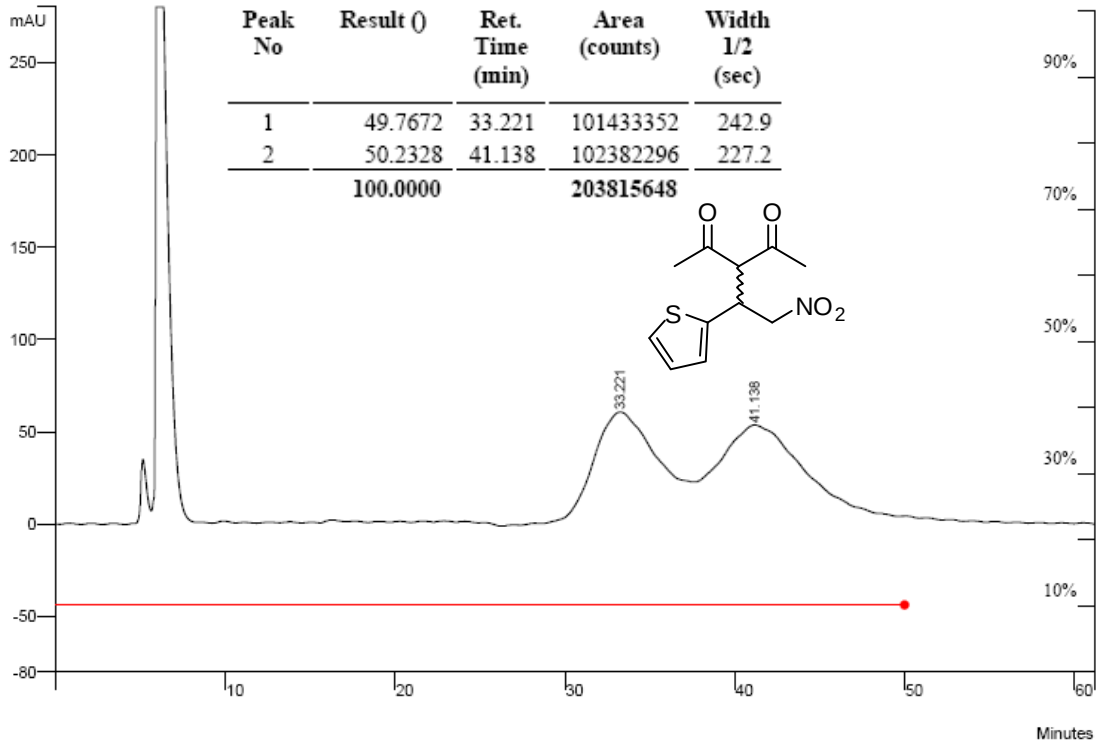
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	99.8571	34.232	937088128	81.6
2	0.1429	37.301	1340748	7.9
	100.0000		**938428864**	



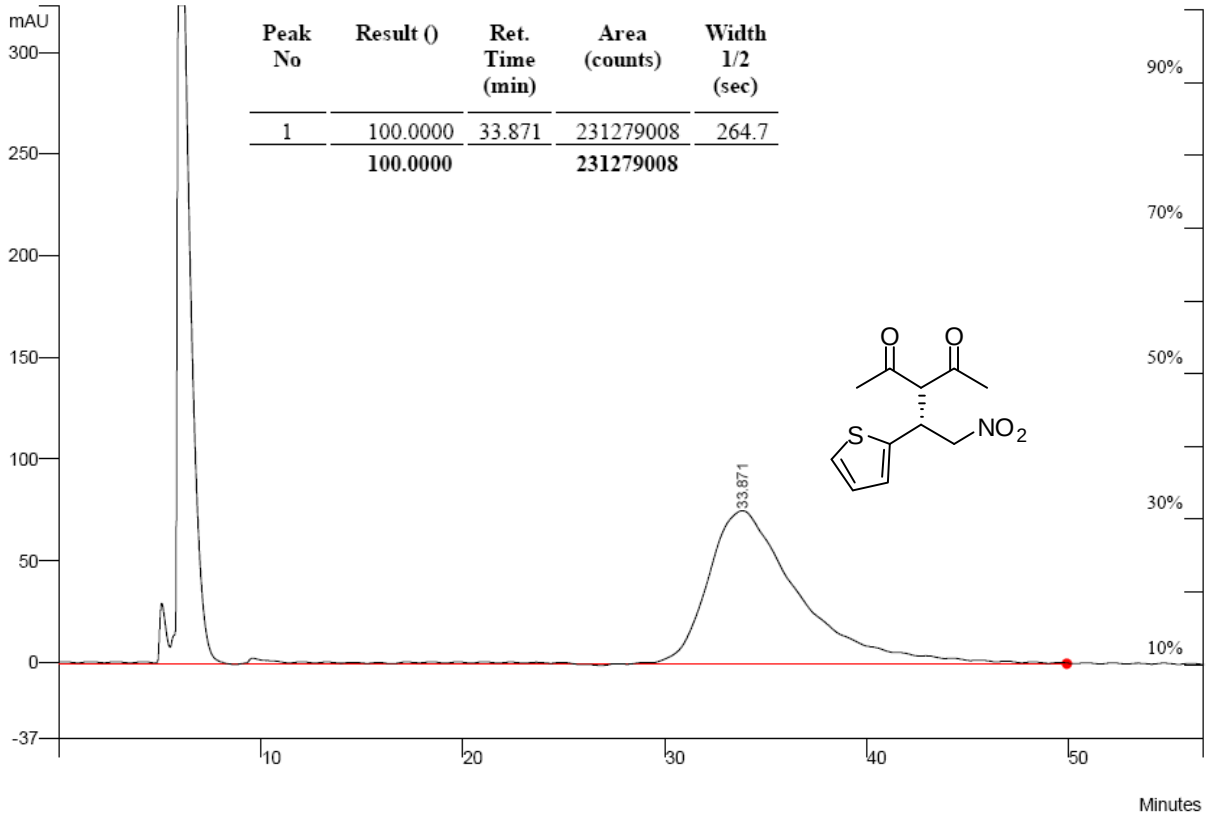
3g (Entry 14, Table 2)







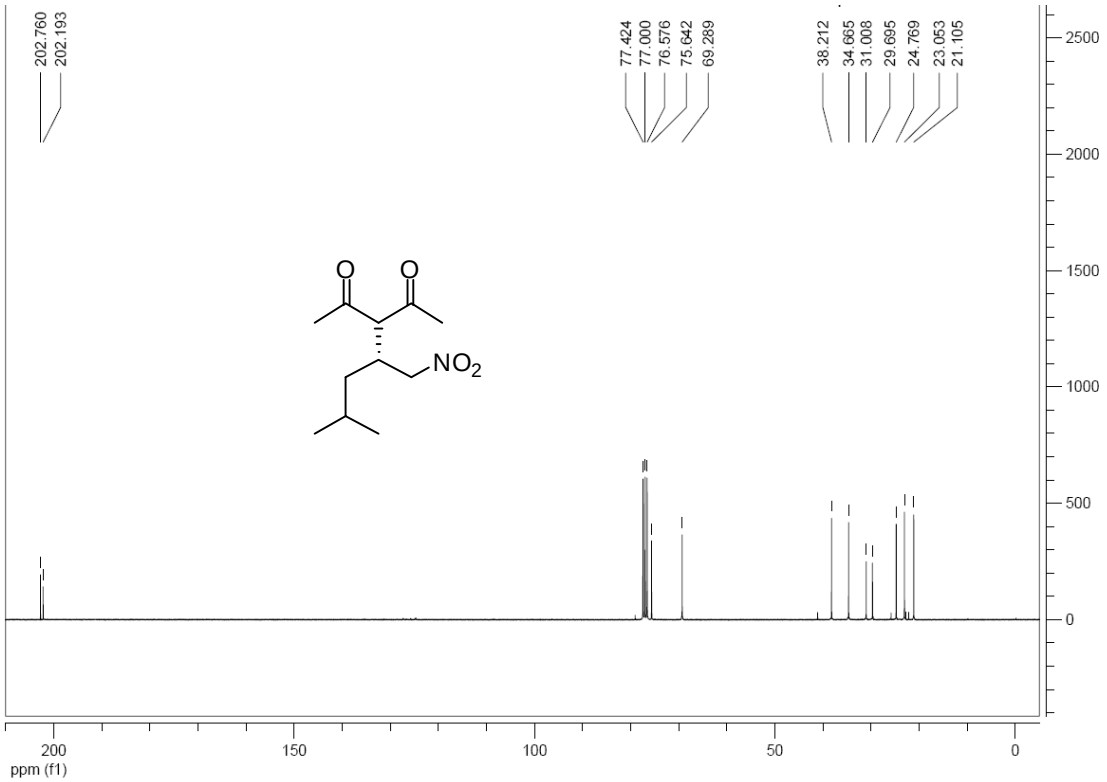
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	49.7672	33.221	101433352	242.9
2	50.2328	41.138	102382296	227.2
	100.0000		**203815648**	

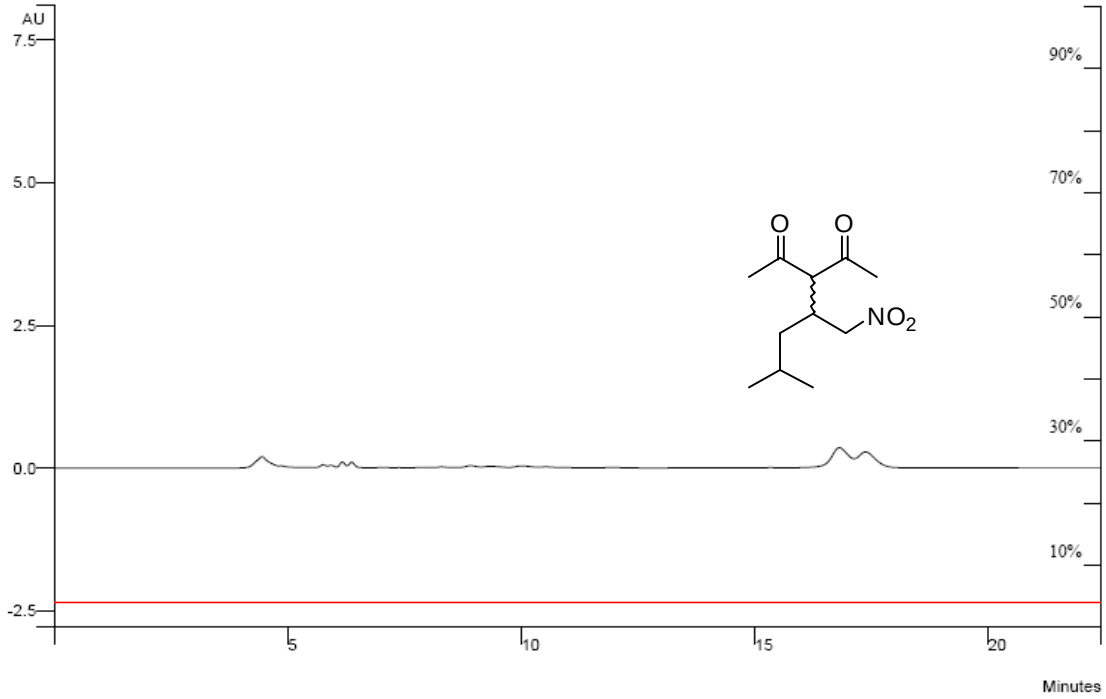


Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	100.0000	33.871	231279008	264.7
	100.0000		**231279008**	

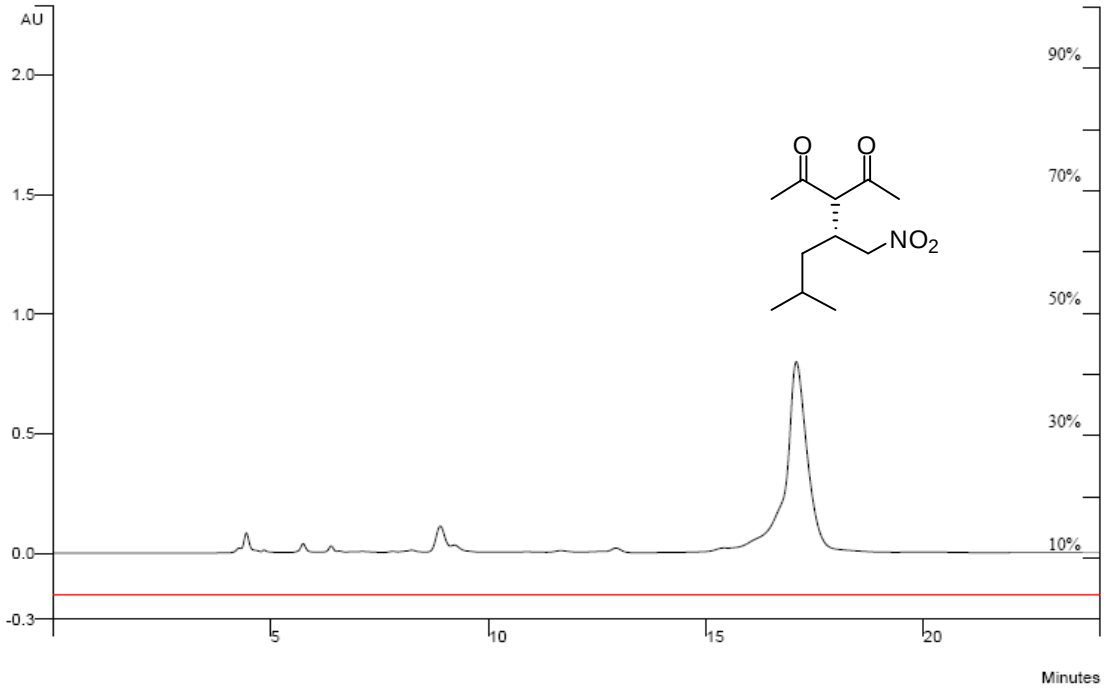
3h (Entry 16, Table 2)


7.277
4.527
4.523
4.513
4.507
4.018
3.990
2.944
2.928
2.915
2.911
2.900
2.896
2.882
2.867
2.292
2.264
1.717
1.710
1.702
1.419
1.385
1.371
1.355
1.337
1.321
1.051
1.036
1.020
1.004
0.989
0.931
O
O
NO2
15000
10000
5000
0
2.14
1.00
1.03
3.08
1.29
1.12
6.12
1.33
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


202.760
202.193
77.424
77.000
76.576
75.642
69.289
38.212
34.665
31.008
29.695
24.769
23.053
21.105
O
O
NO2
2500
2000
1500
1000
500
0
200
150
100
50
0
ppm (f1)



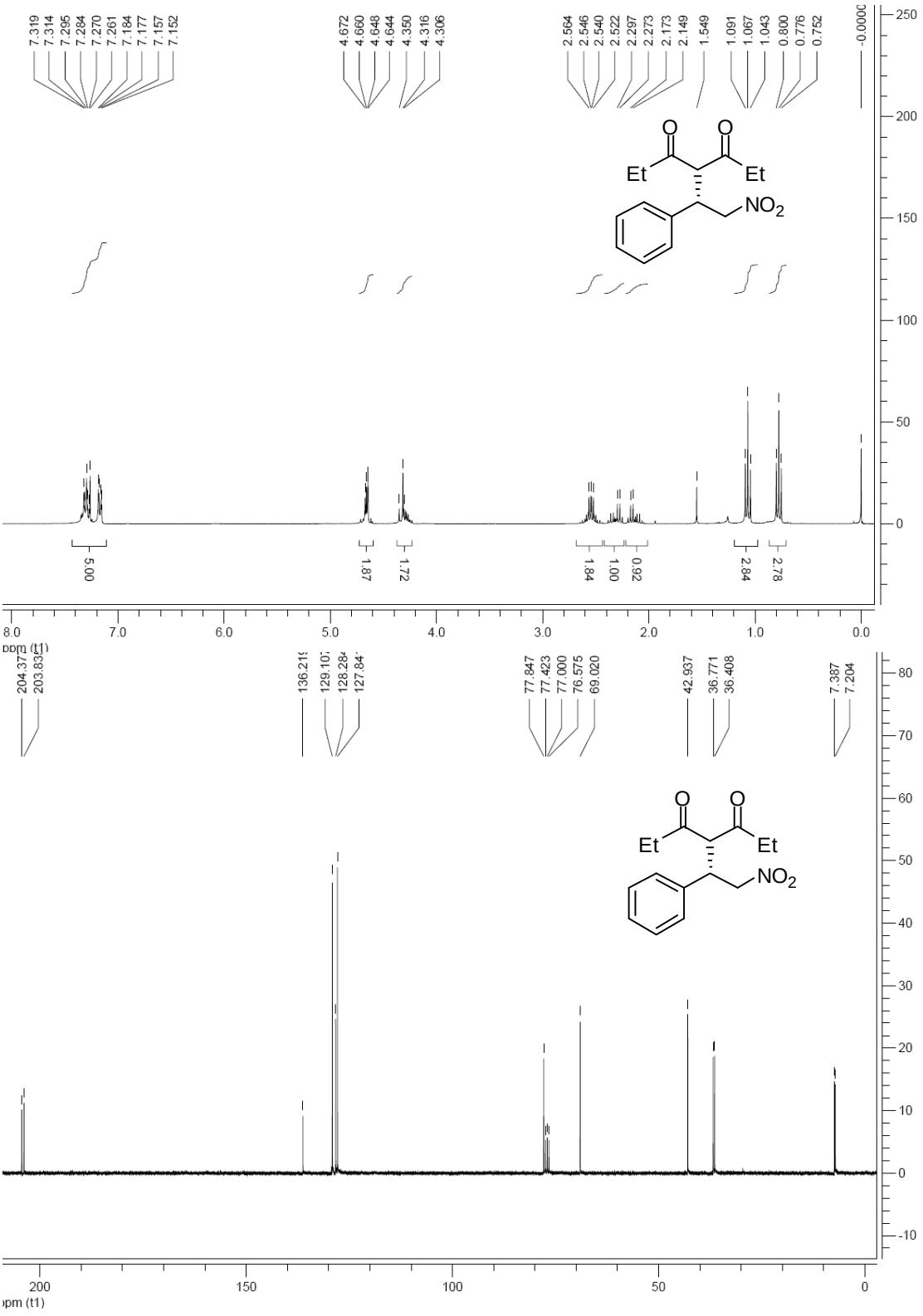
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		50.9359	16.817	0.000	32931208	0.00	BB	16.9		0
2		49.0641	17.378	0.000	31721068	0.00	BB	14.7		0
	Totals	**100.0000**		**0.000**	**64652276**					

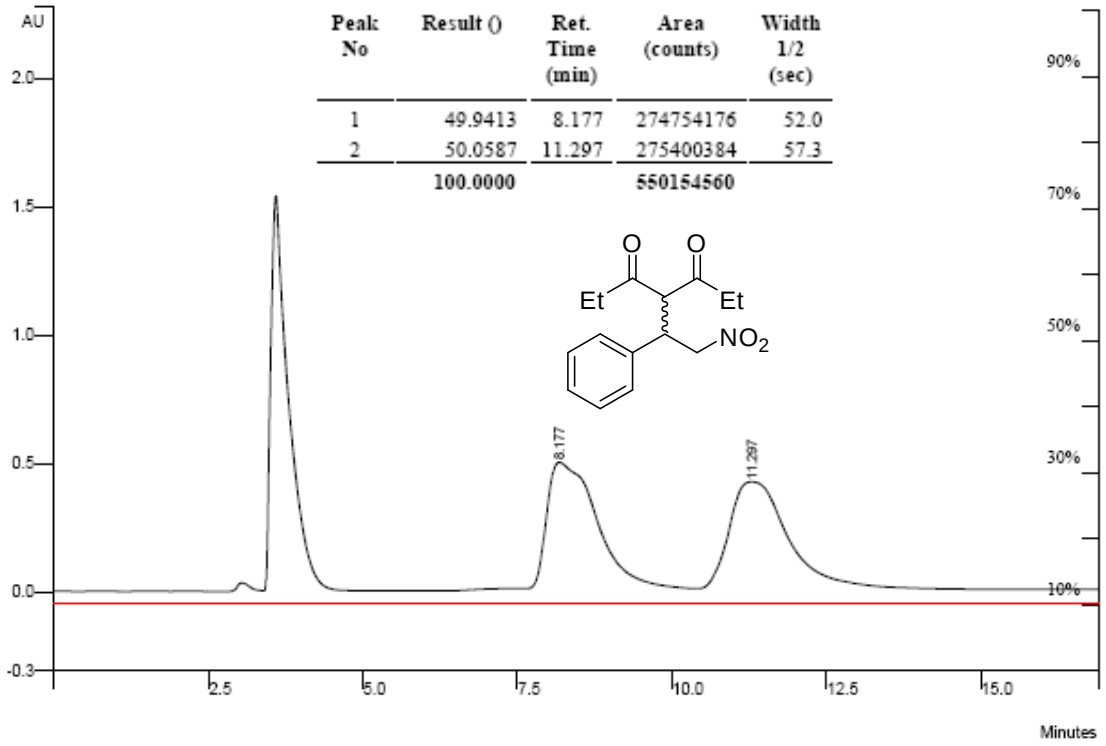


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		0.2532	15.576	0.000	681472	0.00	BB	-9.4		0
2		99.7468	17.079	0.000	268452704	0.00	BB	25.7		0
	Totals	**100.0000**		**0.000**	**269134176**					

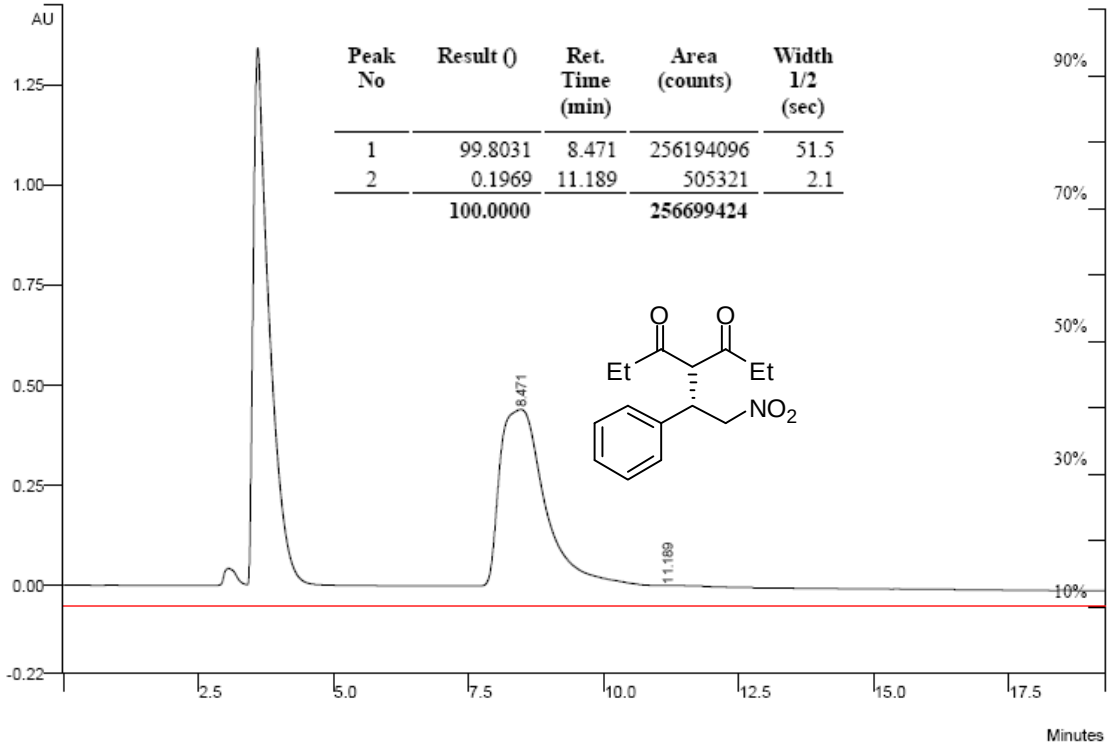
6. ^{1}H NMR, ^{13}C NMR and HPLC Spectra for Table 3

5a (Entry 2, Table 3)



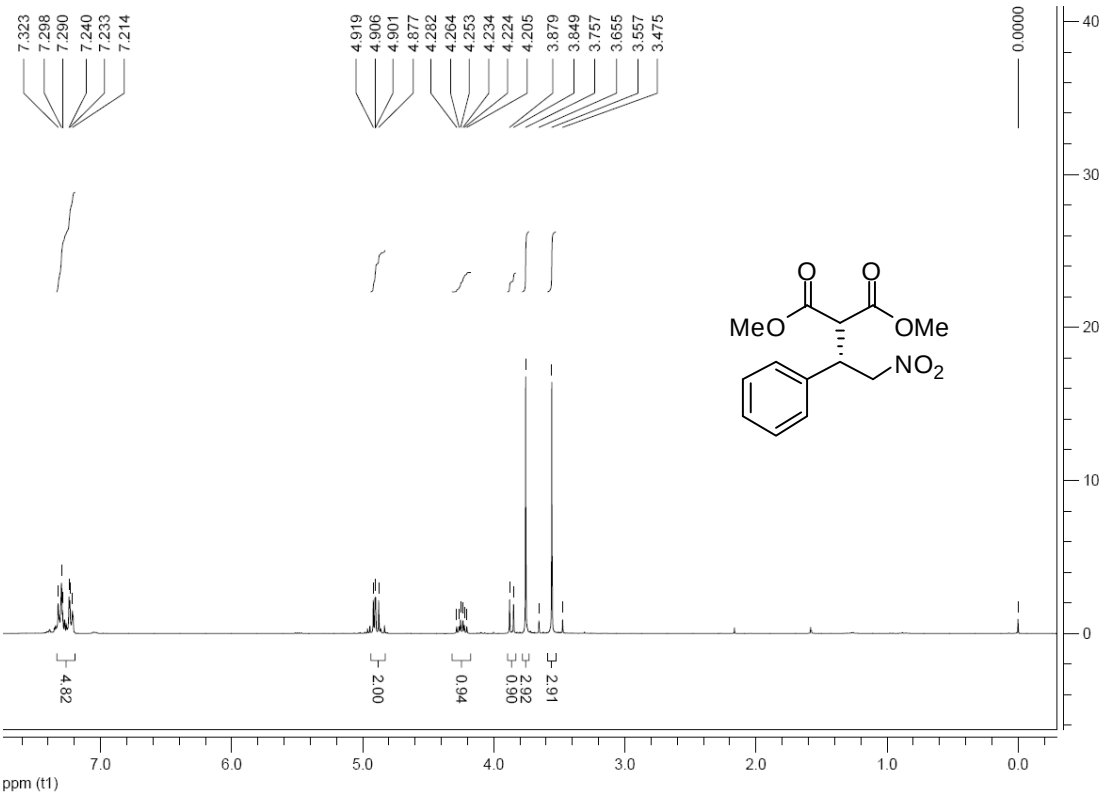


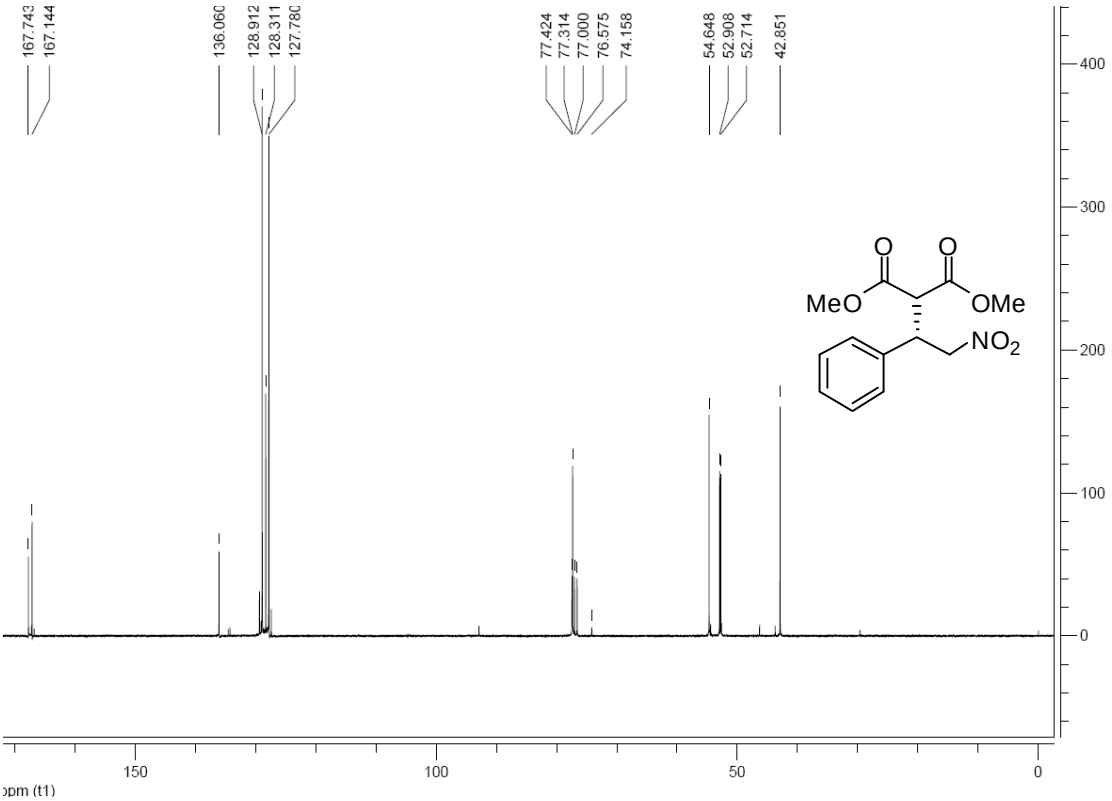
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	49.9413	8.177	274754176	52.0
2	50.0587	11.297	275400384	57.3
	100.0000		**550154560**	

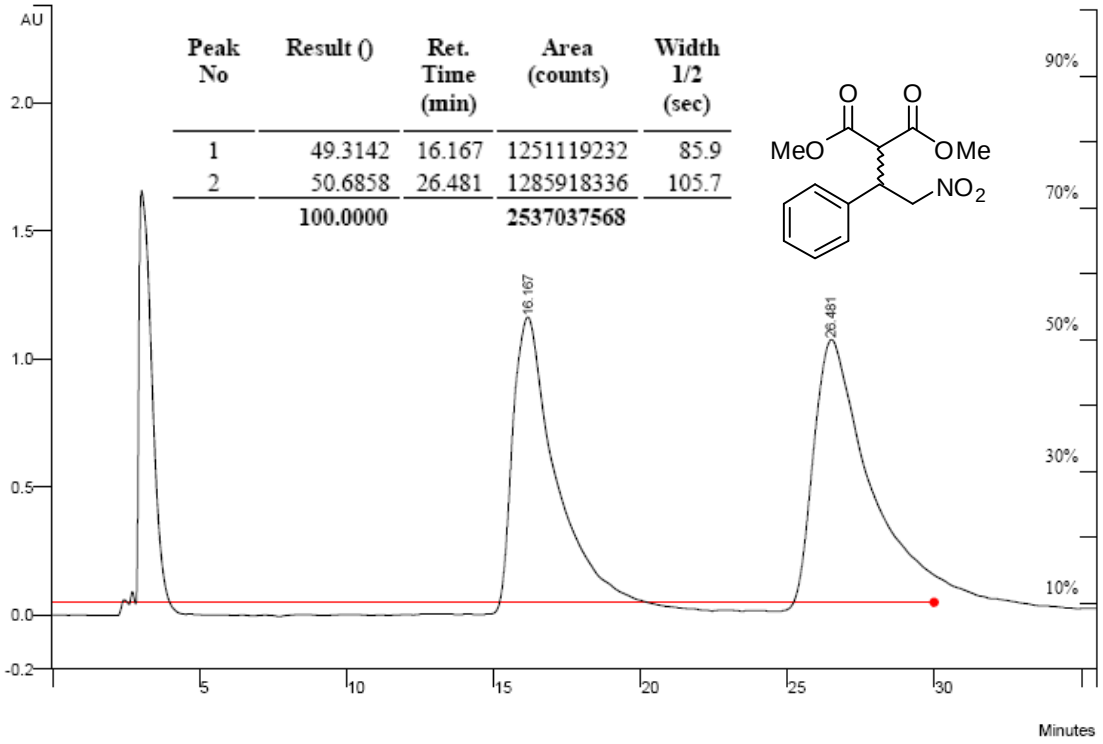


Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	99.8031	8.471	256194096	51.5
2	0.1969	11.189	505321	2.1
	100.0000		**256699424**	

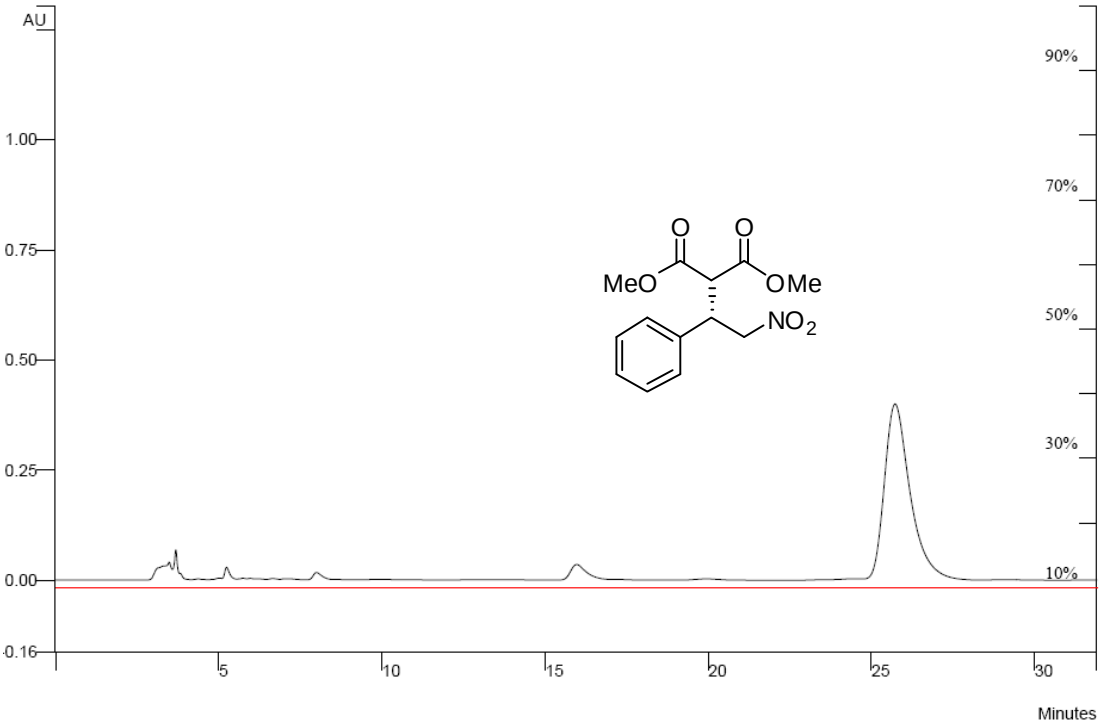
5b (Entry 4, Table 3)





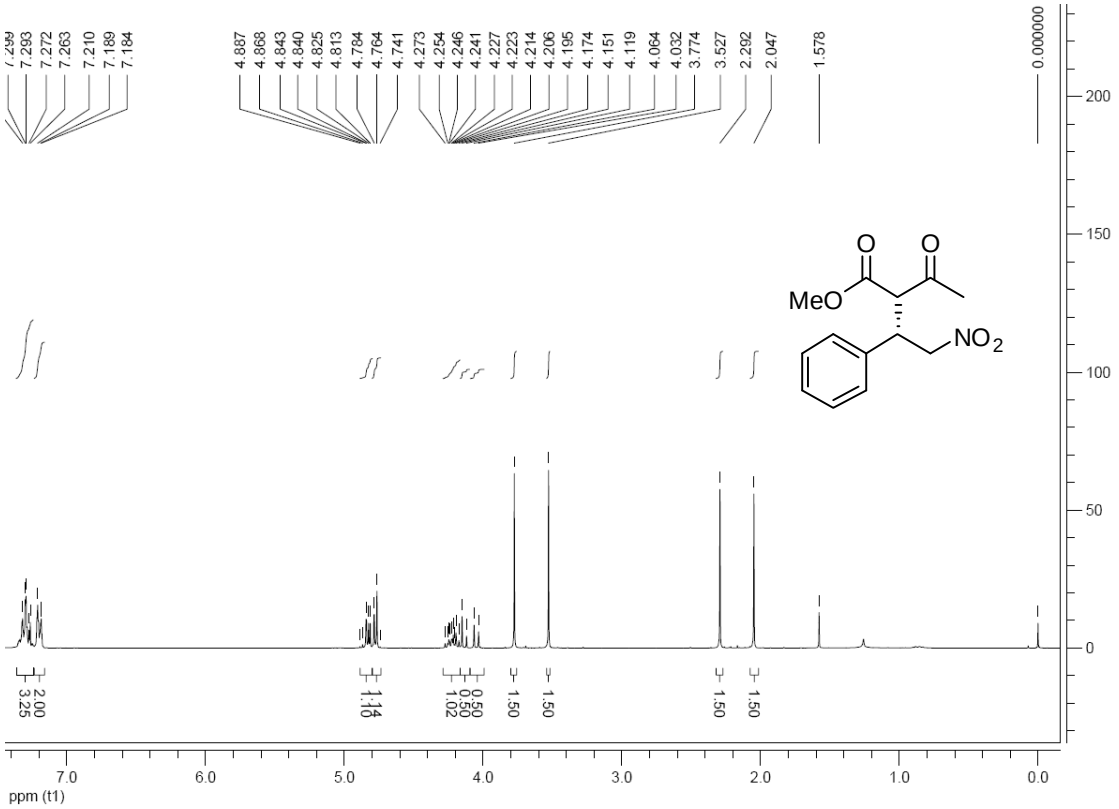


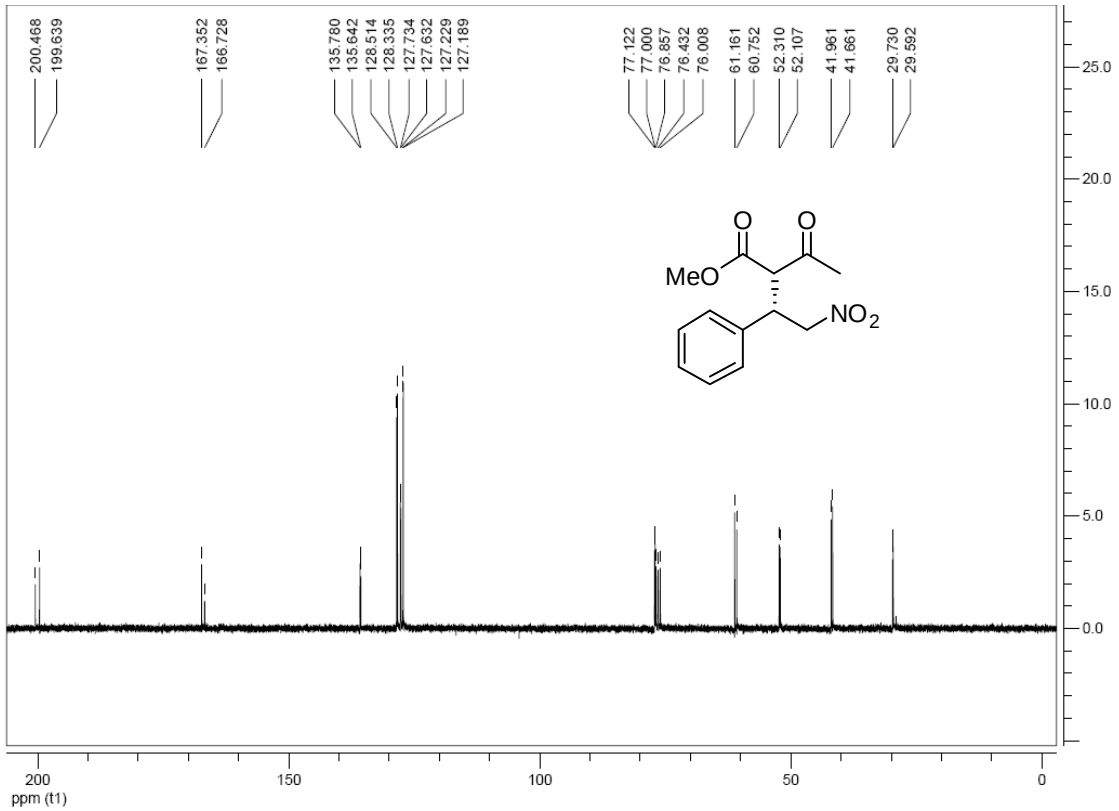
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	49.3142	16.167	1251119232	85.9
2	50.6858	26.481	1285918336	105.7
	100.0000		**2537037568**	



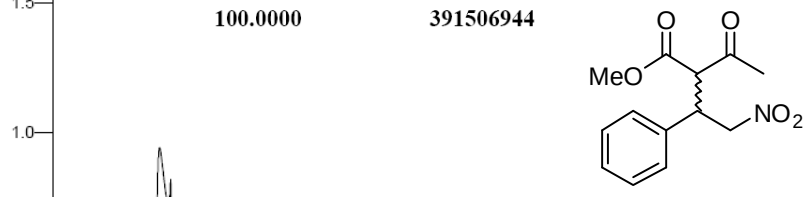
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		5.0450	15.970	0.000	11553186	0.00	BB	30.7		0
2		94.9550	25.729	0.000	217450880	0.00	BB	48.5		0
	Totals	**100.0000**		**0.000**	**229004064**					

5c (Entry 6, Table 3)

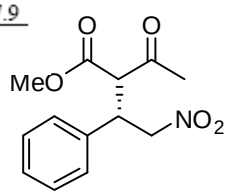

7.299
7.293
7.272
7.263
7.210
7.189
7.184
4.887
4.868
4.843
4.840
4.825
4.813
4.784
4.764
4.741
4.273
4.254
4.246
4.241
4.227
4.223
4.214
4.206
4.195
4.174
4.151
4.119
4.064
4.032
3.774
3.527
2.292
2.047
1.578
0.000000
MeO
NO2
3.25
2.00
1.14
1.10
1.02
0.50
0.50
1.50
1.50
1.50
1.50
ppm (t1)


200.468
199.639
167.352
166.728
135.780
135.642
128.514
128.335
127.734
127.632
127.229
127.189
77.122
77.000
76.857
76.432
76.008
61.161
60.752
52.310
52.107
41.961
41.661
29.730
29.592
MeO
NO2
ppm (t1)

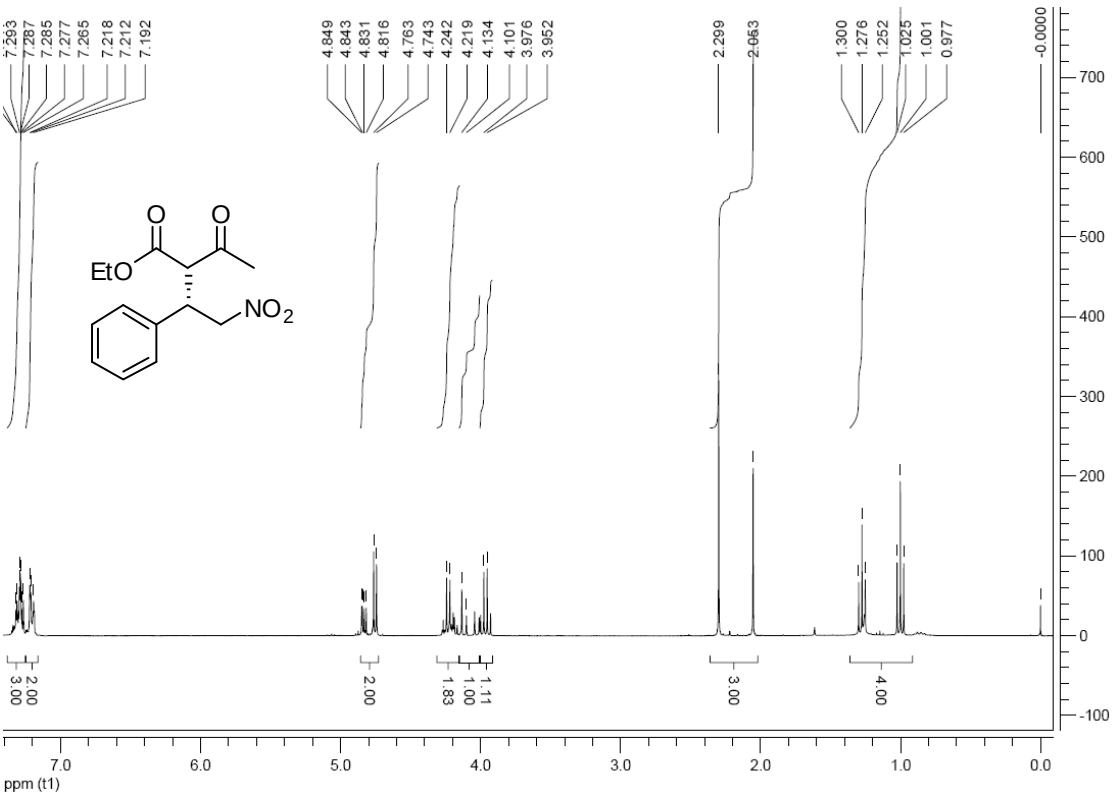
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	39.1568	15.212	153301504	57.8
2	8.4276	21.334	32994470	213.1
3	13.8384	22.401	54178448	43.1
4	38.5772	28.536	151032528	86.1
	100.0000		**391506944**	

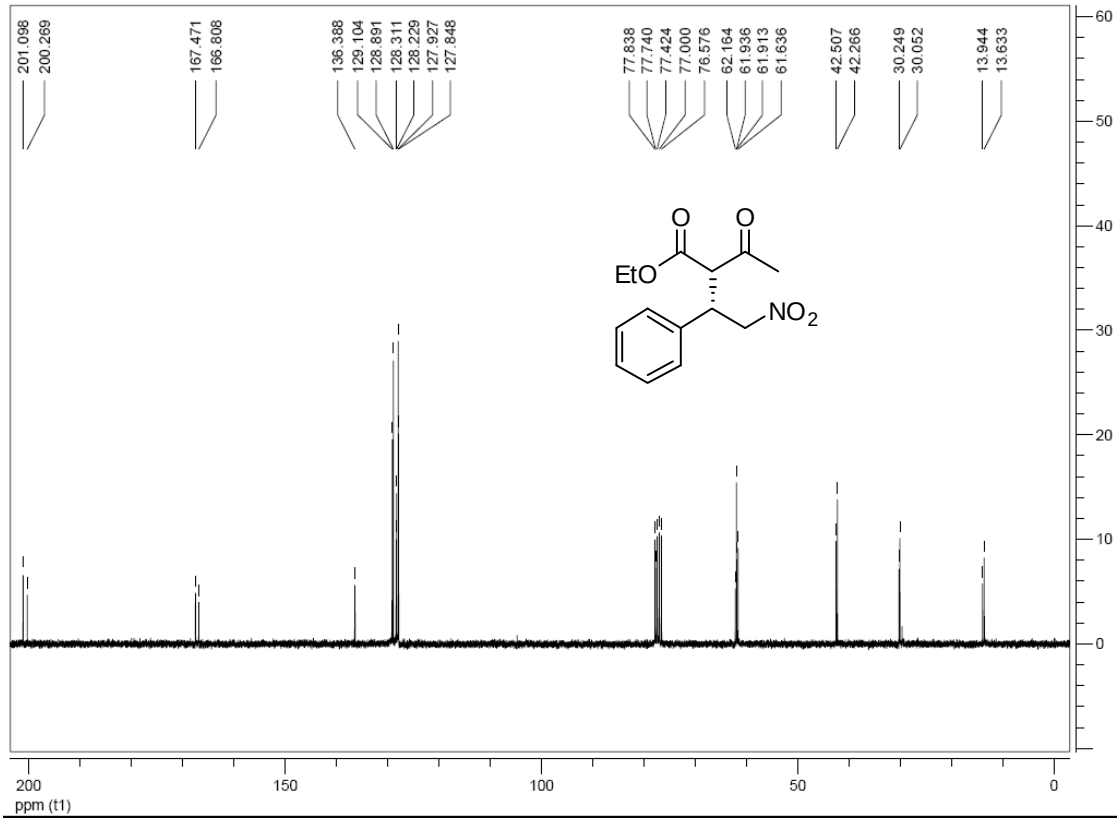


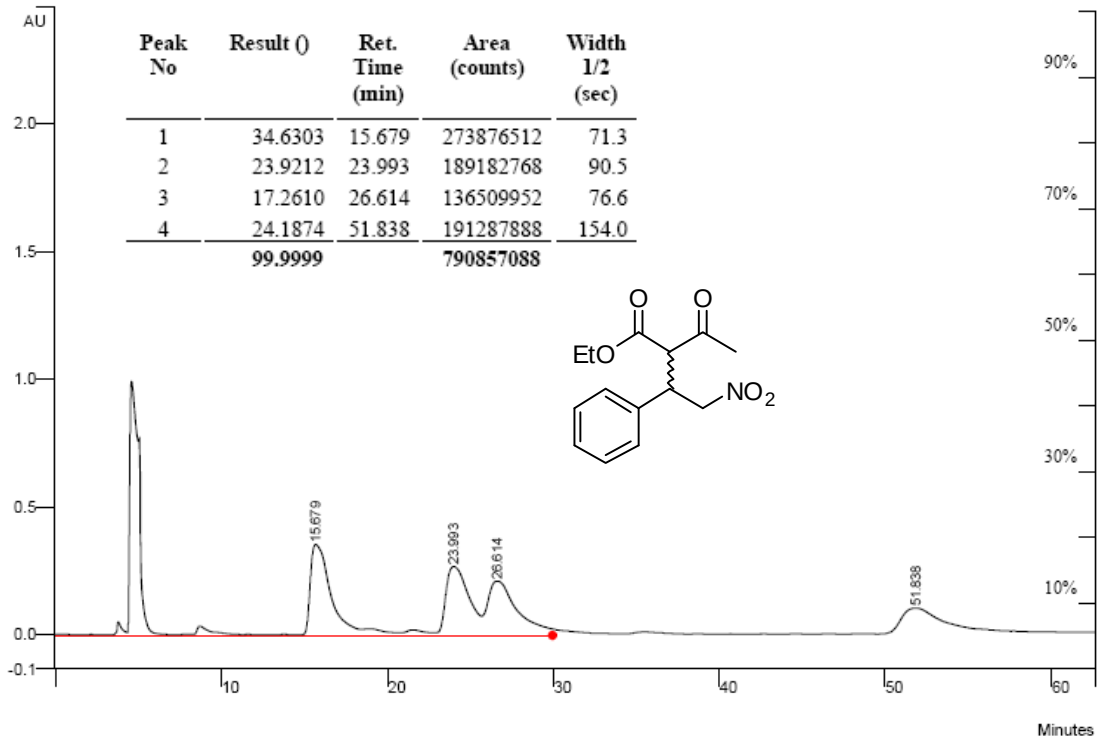
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	51.2595	15.431	499147520	60.4
2	0.1427	21.741	1389176	32.5
3	0.0781	23.233	760437	15.7
4	48.5198	28.641	472469056	87.9
	100.0001		**973766208**	



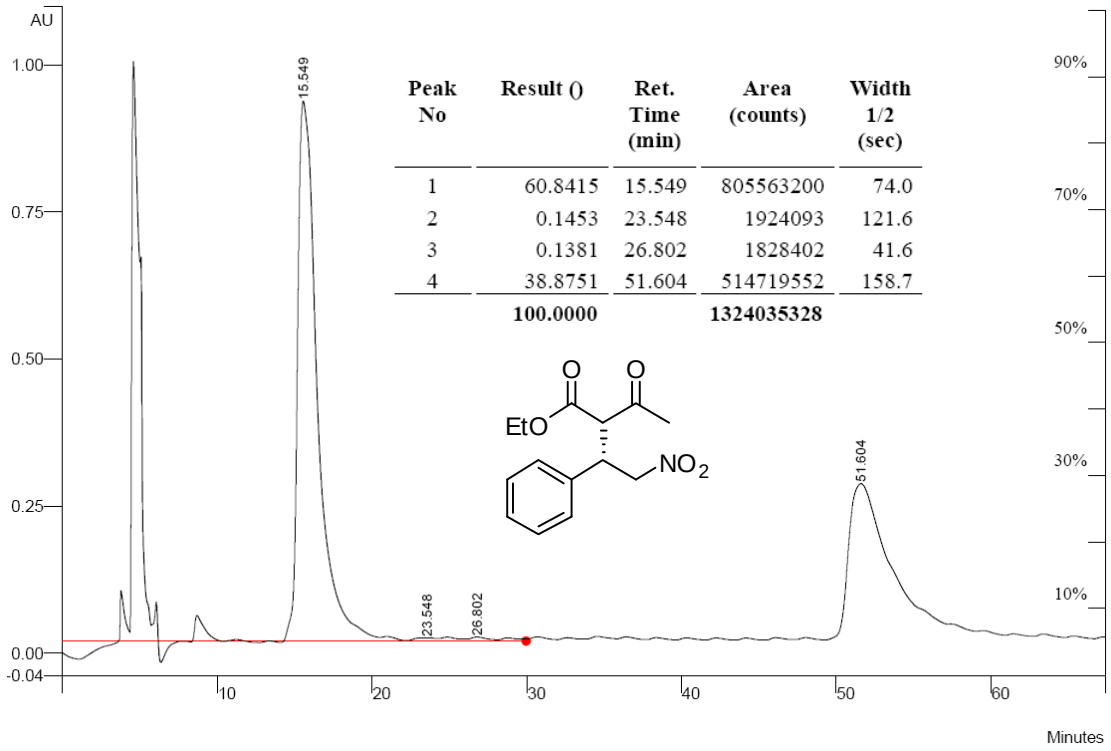
5d (Entry 8, Table 3)





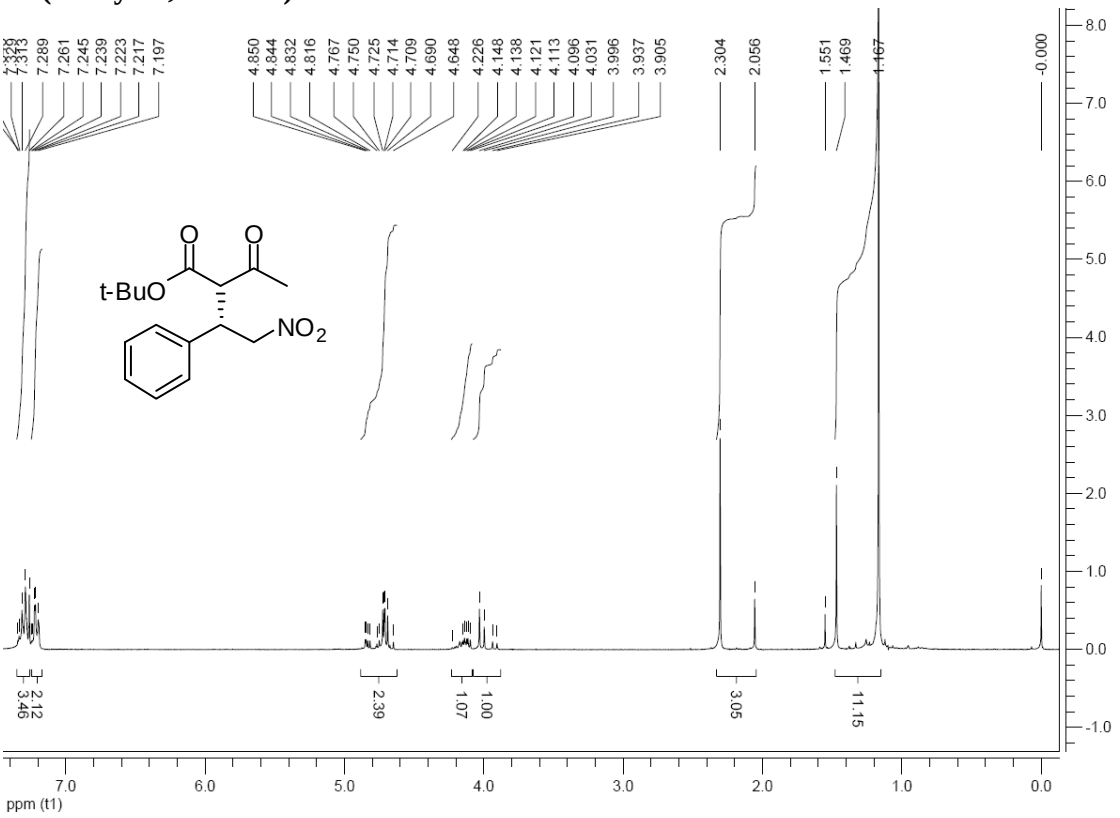


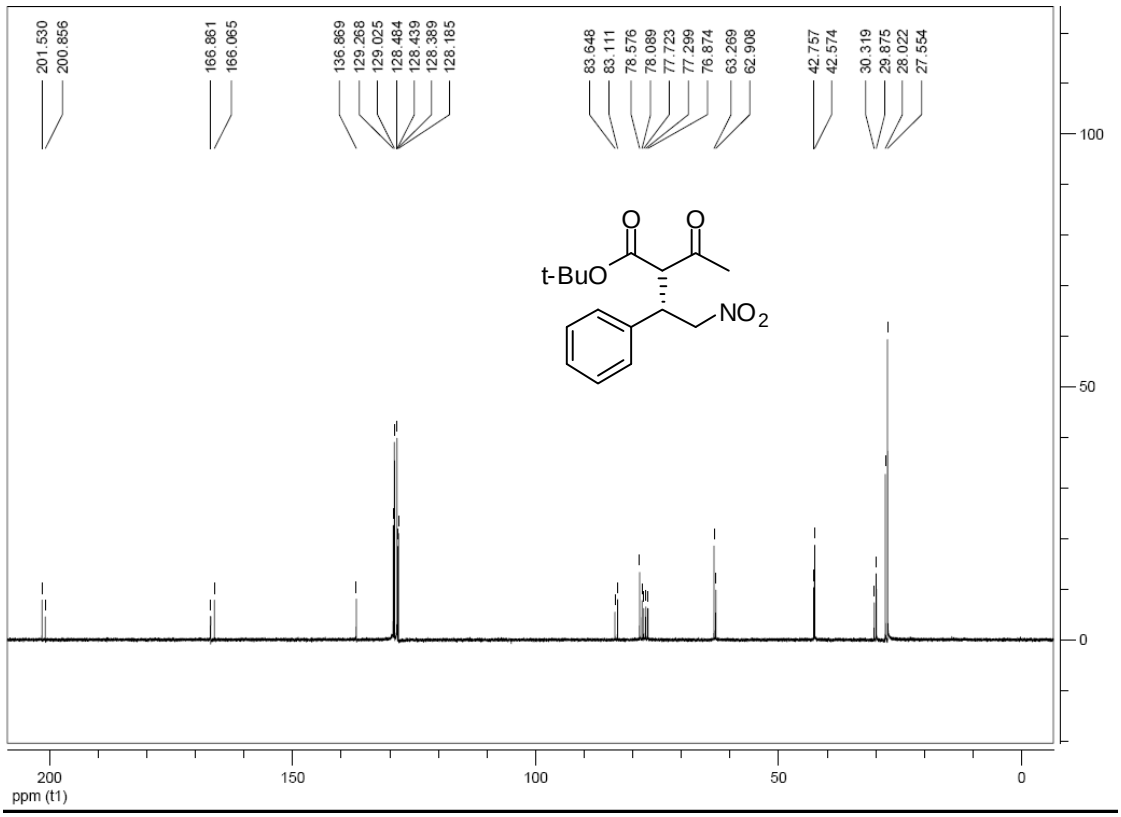
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	34.6303	15.679	273876512	71.3
2	23.9212	23.993	189182768	90.5
3	17.2610	26.614	136509952	76.6
4	24.1874	51.838	191287888	154.0
	99.9999		**790857088**	

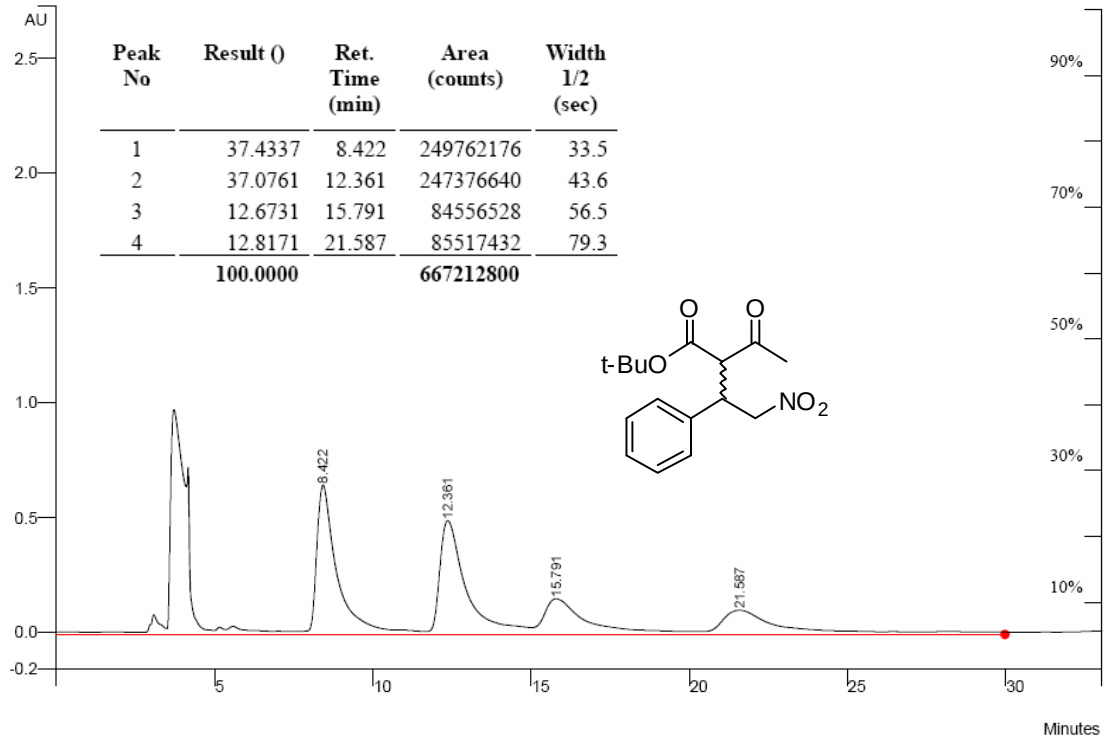


Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	60.8415	15.549	805563200	74.0
2	0.1453	23.548	1924093	121.6
3	0.1381	26.802	1828402	41.6
4	38.8751	51.604	514719552	158.7
	100.0000		**1324035328**	

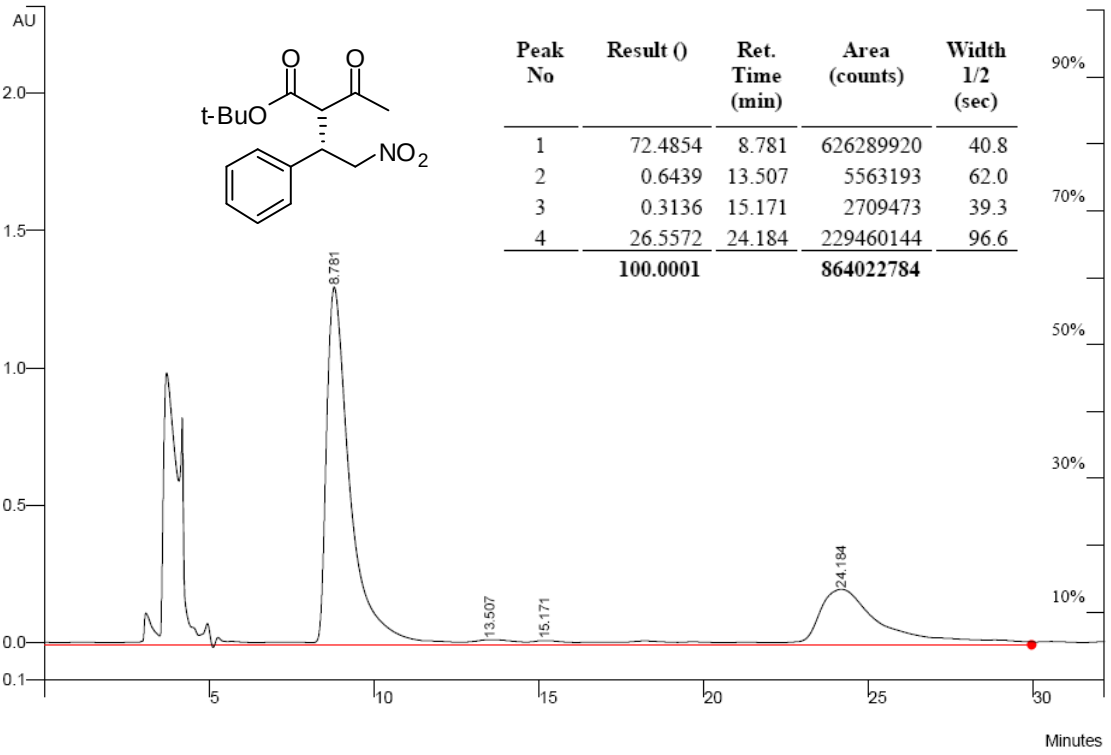
5e (Entry 10, Table 3)





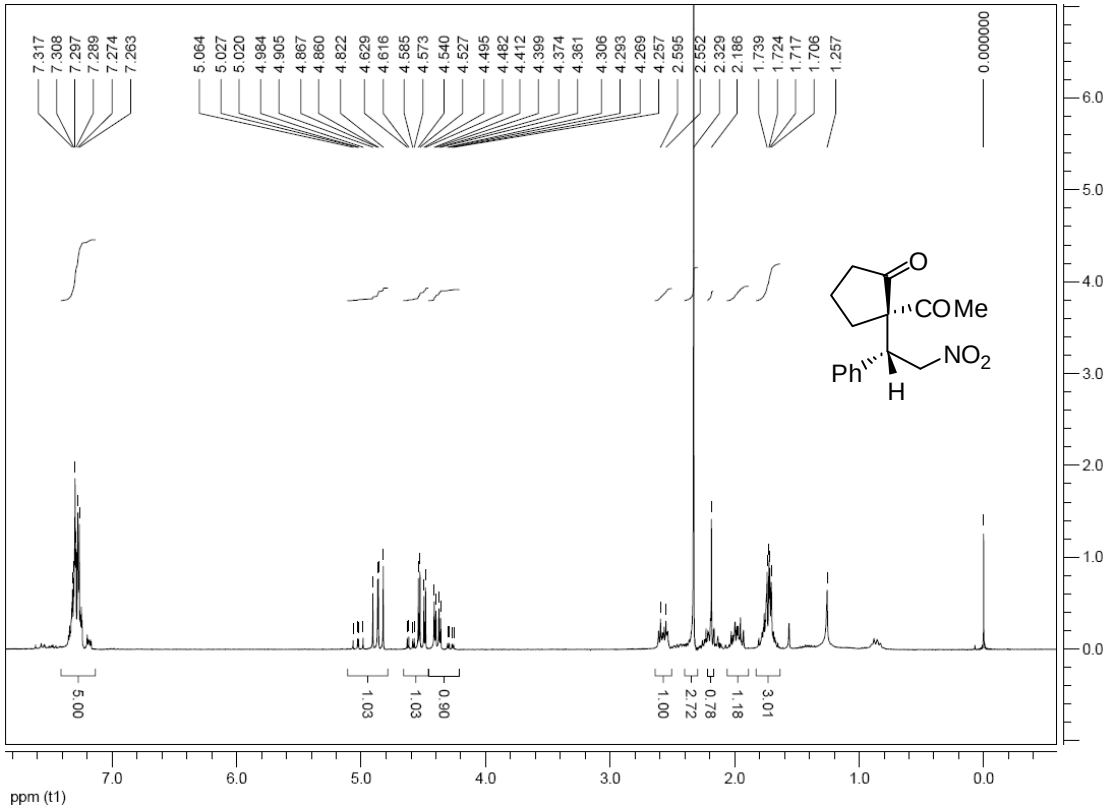


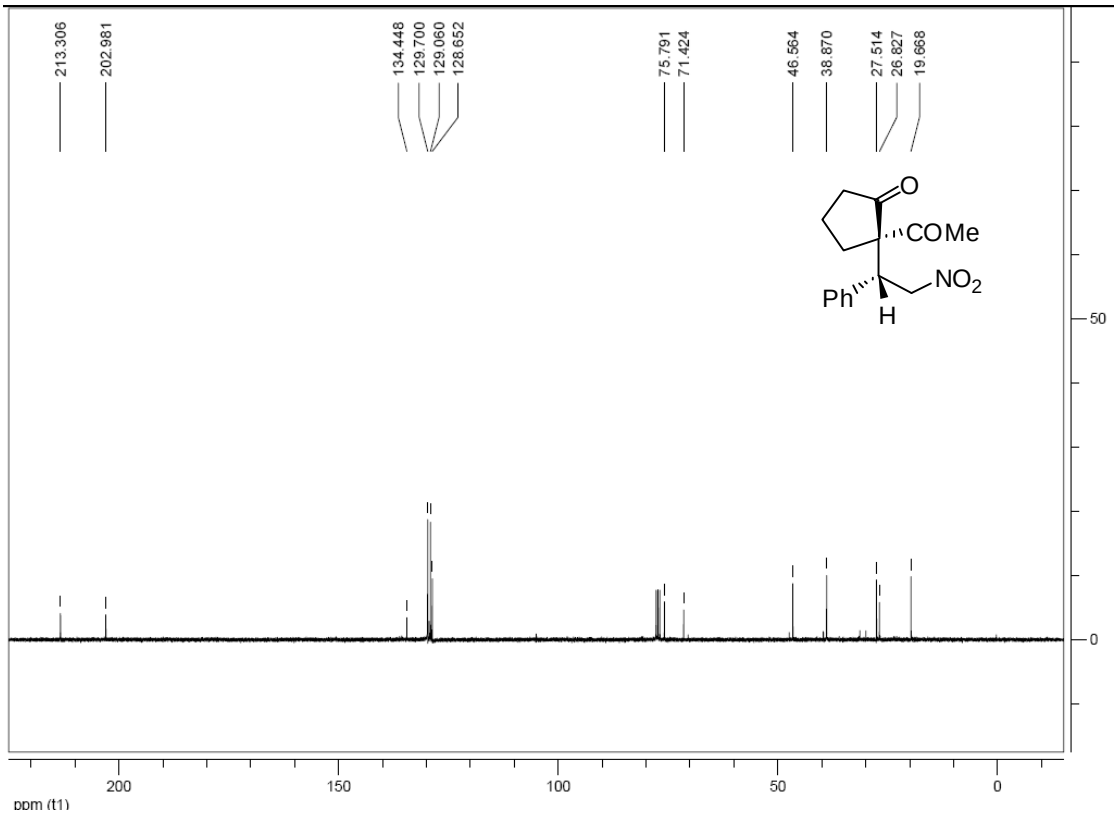
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	37.4337	8.422	249762176	33.5
2	37.0761	12.361	247376640	43.6
3	12.6731	15.791	84556528	56.5
4	12.8171	21.587	85517432	79.3
	100.0000		**667212800**	

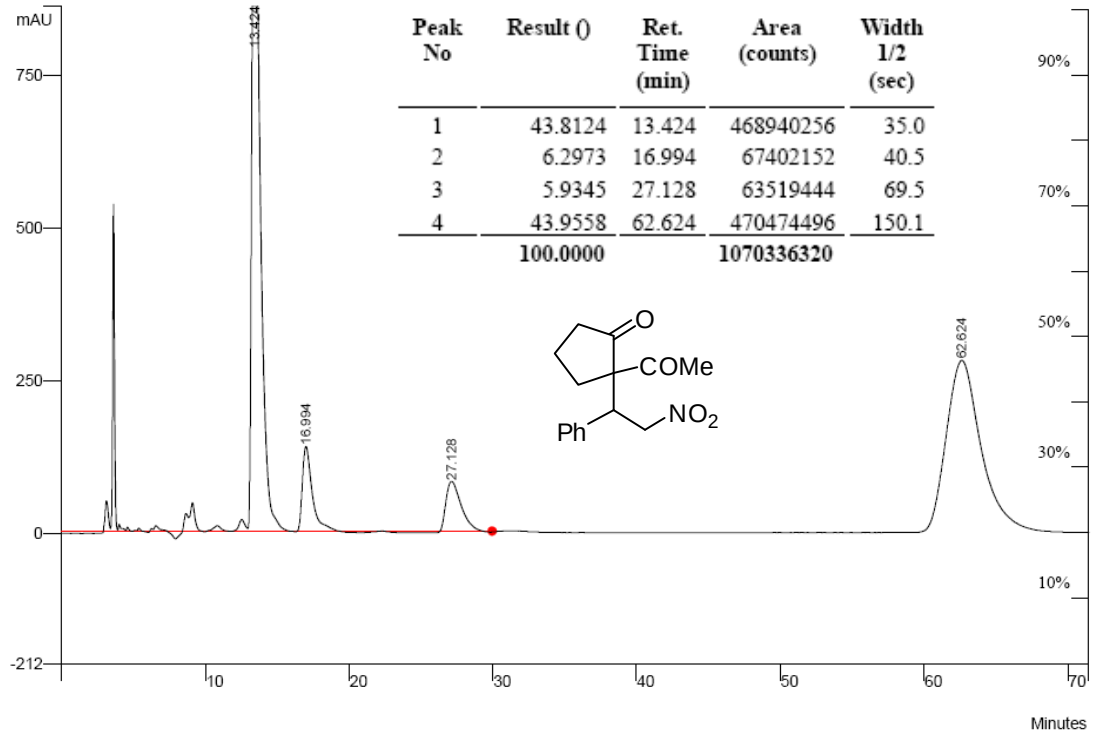


Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	72.4854	8.781	626289920	40.8
2	0.6439	13.507	5563193	62.0
3	0.3136	15.171	2709473	39.3
4	26.5572	24.184	229460144	96.6
	100.0001		**864022784**	

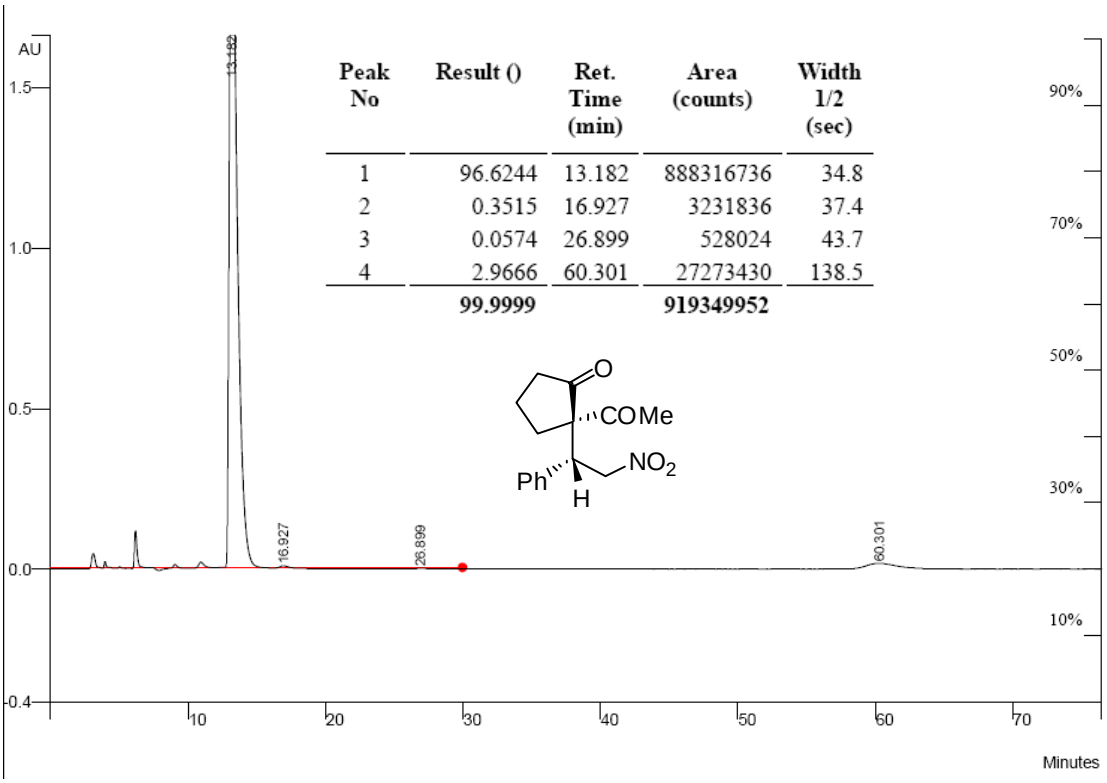
5f (Entry 12, Table 3)





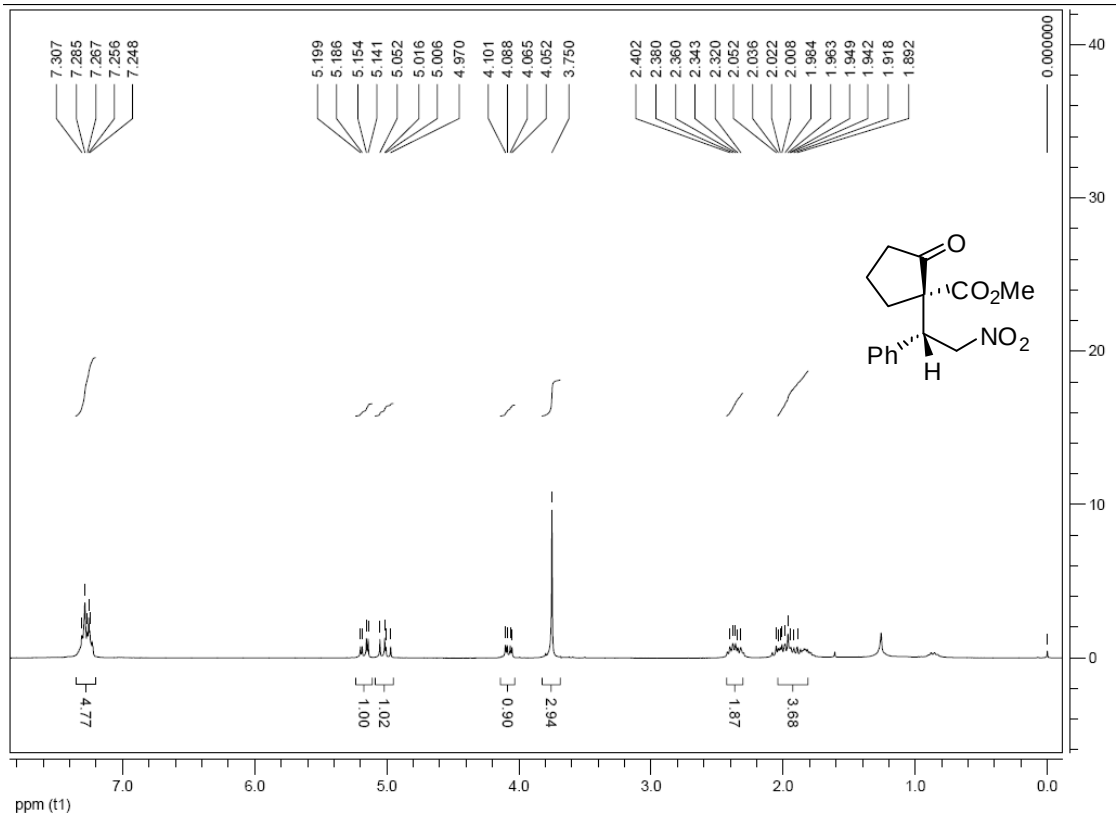


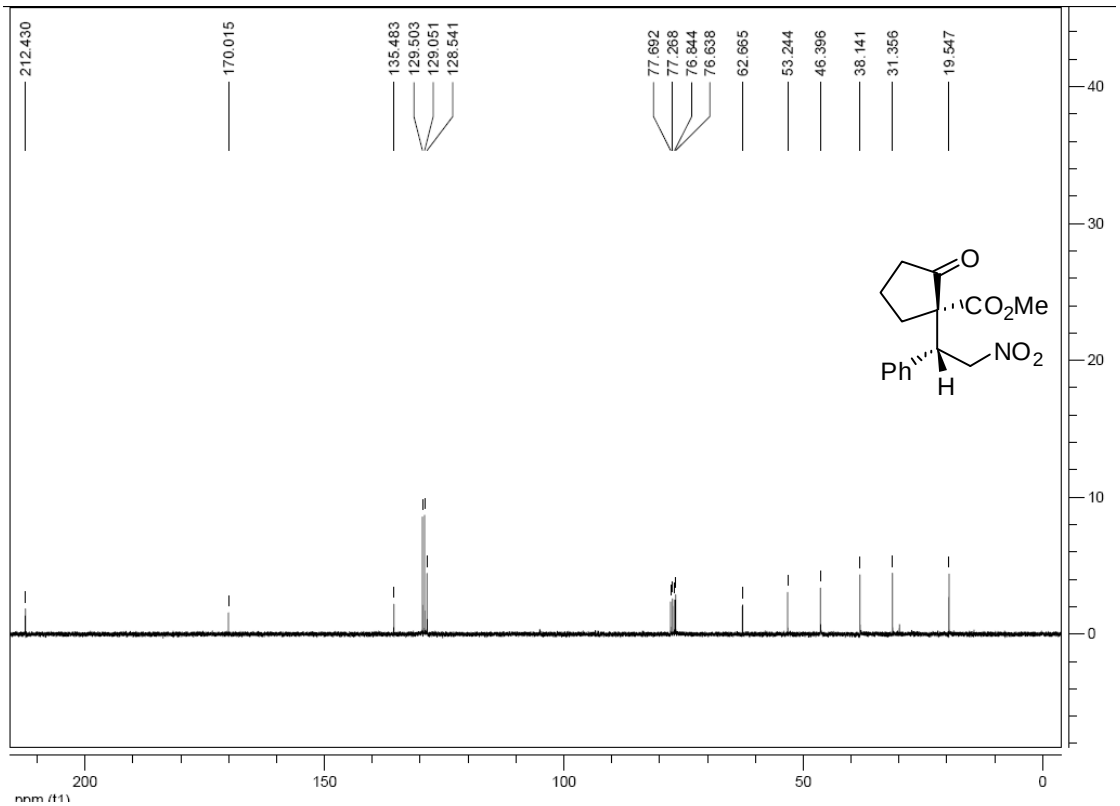
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	43.8124	13.424	468940256	35.0
2	6.2973	16.994	67402152	40.5
3	5.9345	27.128	63519444	69.5
4	43.9558	62.624	470474496	150.1
	100.0000		**1070336320**	

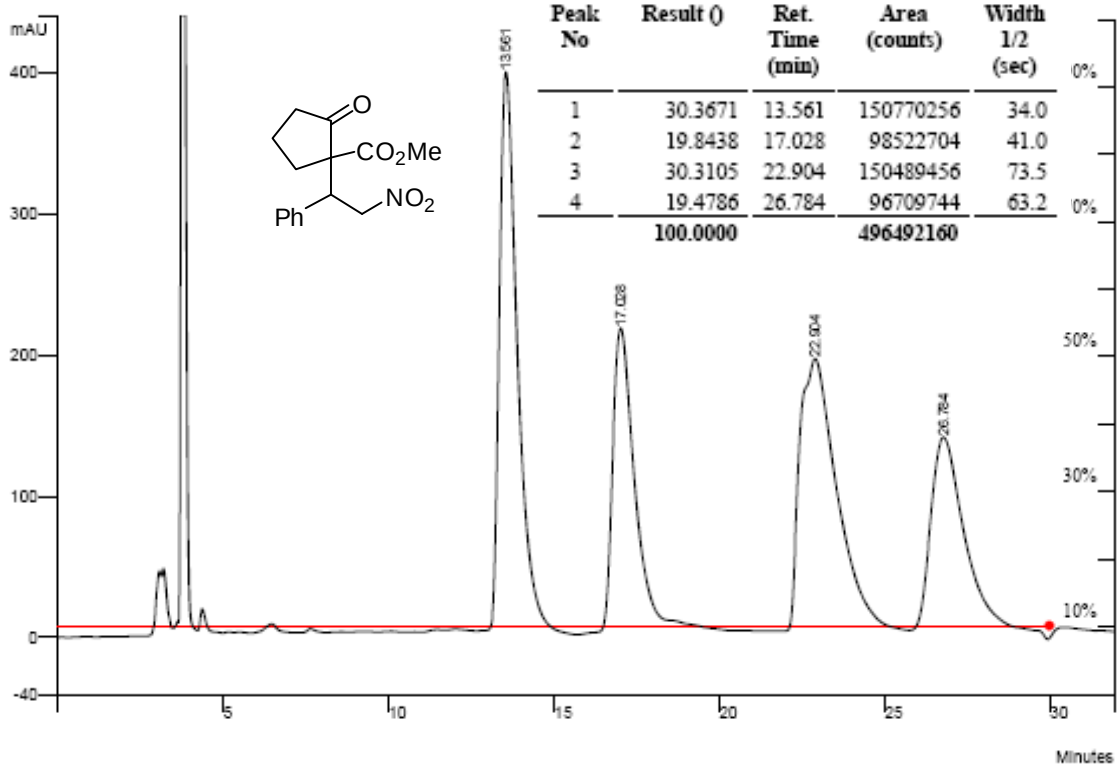


Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	96.6244	13.182	888316736	34.8
2	0.3515	16.927	3231836	37.4
3	0.0574	26.899	528024	43.7
4	2.9666	60.301	27273430	138.5
	99.9999		**919349952**	

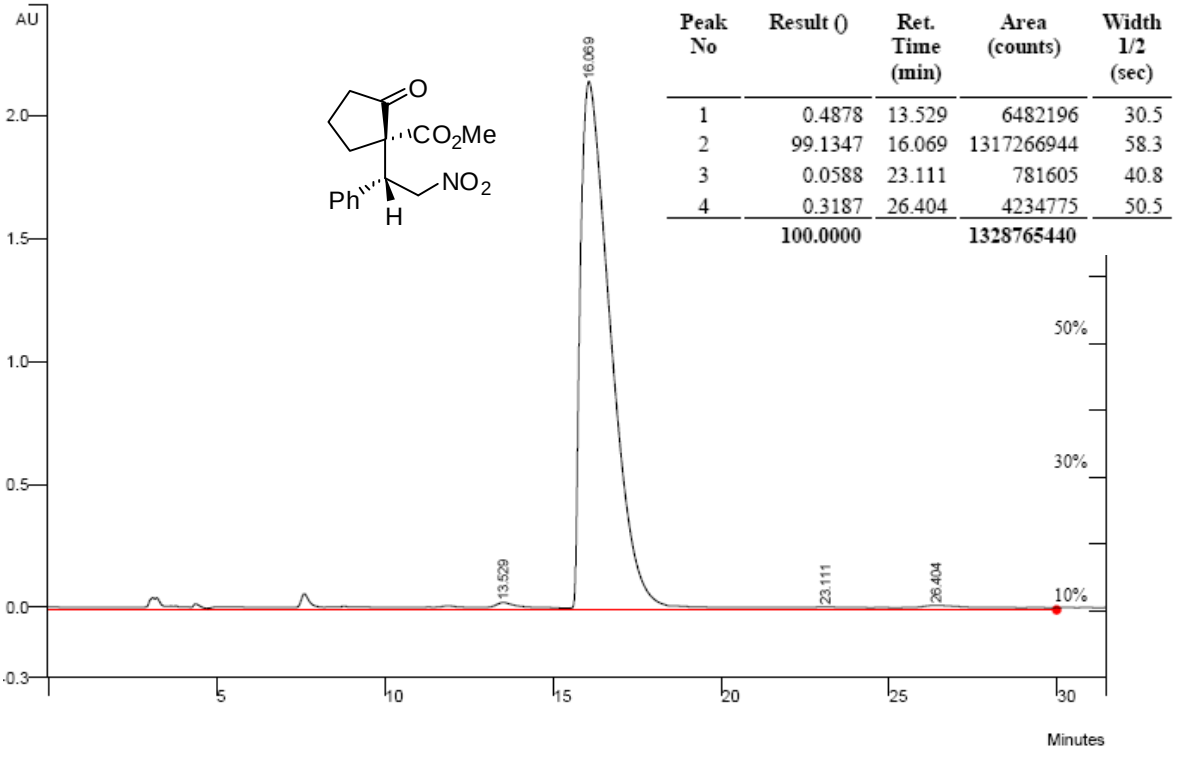
5g (Entry 14, Table 3)


7.307
7.285
7.267
7.256
7.248
5.199
5.186
5.154
5.141
5.052
5.016
5.006
4.970
4.101
4.088
4.065
4.052
3.750
2.402
2.380
2.360
2.343
2.320
2.052
2.036
2.022
2.008
1.984
1.963
1.949
1.942
1.918
1.892
0.000000
4.77
1.00
1.02
0.90
2.94
1.87
3.68
O
CO2Me
NO2
Ph
H
ppm (t1)


212.430
170.015
135.483
129.503
129.051
128.541
77.692
77.268
76.844
76.638
62.665
53.244
46.396
38.141
31.356
19.547
O
CO2Me
NO2
Ph
H

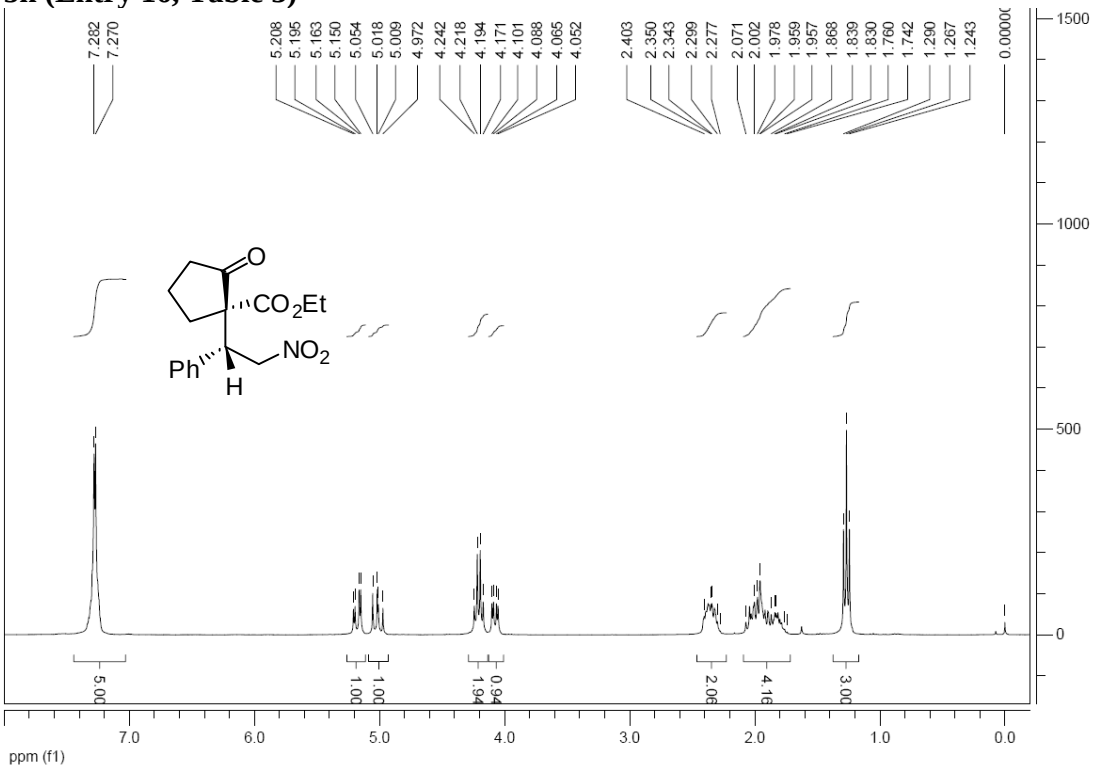


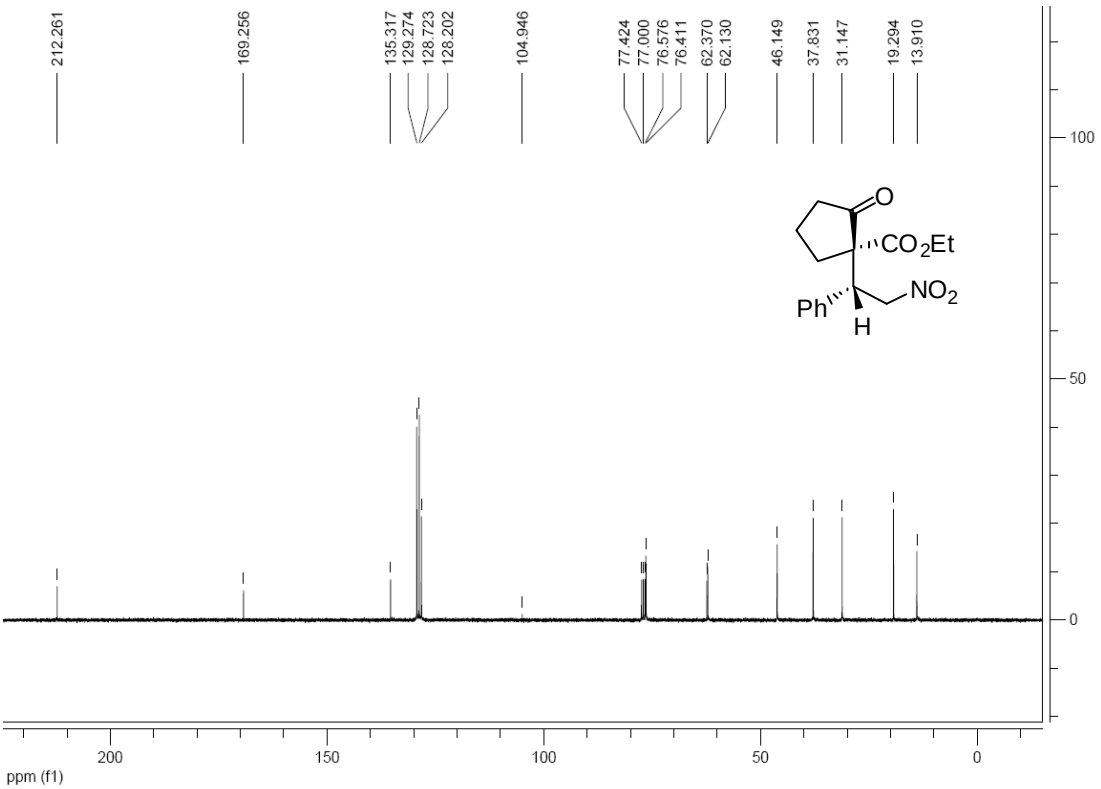
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	30.3671	13.561	150770256	34.0
2	19.8438	17.028	98522704	41.0
3	30.3105	22.904	150489456	73.5
4	19.4786	26.784	96709744	63.2
	100.0000		**496492160**	

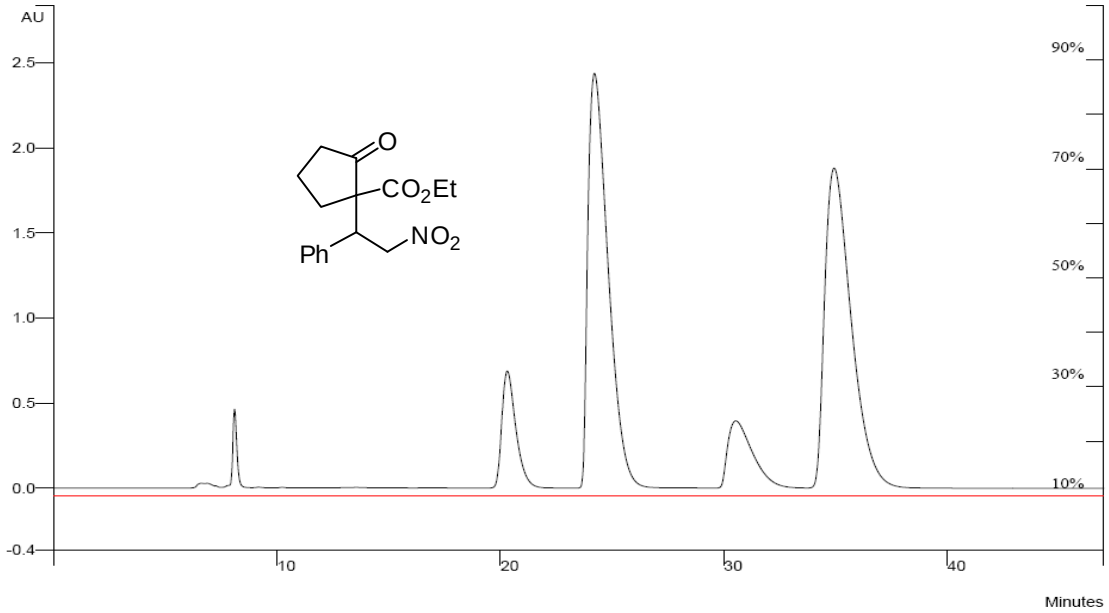


Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	0.4878	13.529	6482196	30.5
2	99.1347	16.069	1317266944	58.3
3	0.0588	23.111	781605	40.8
4	0.3187	26.404	4234775	50.5
	100.0000		**1328765440**	

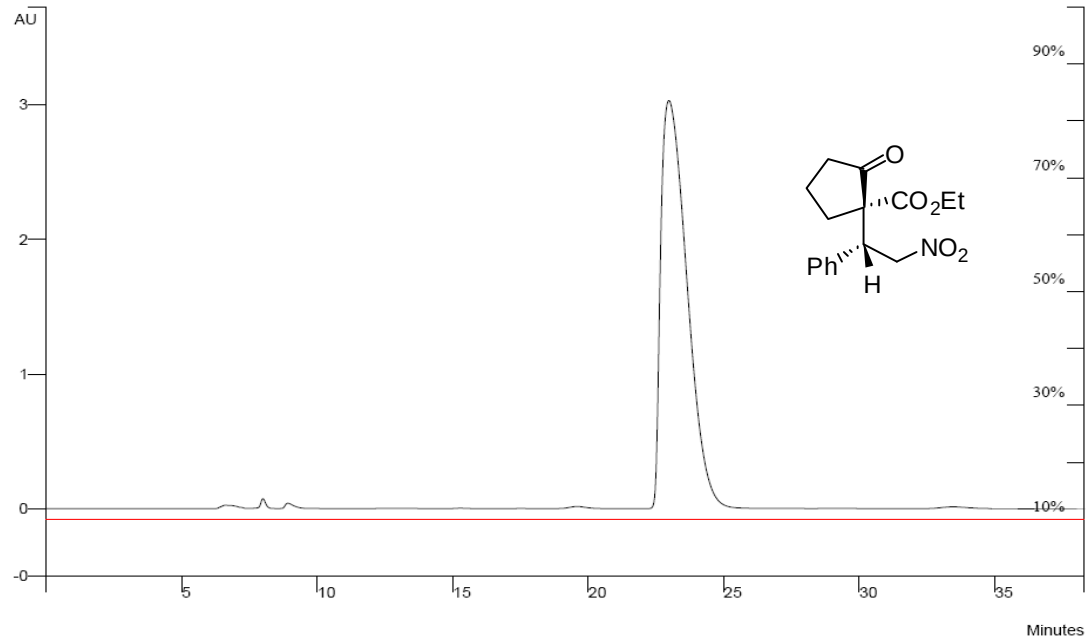
5h (Entry 16, Table 3)







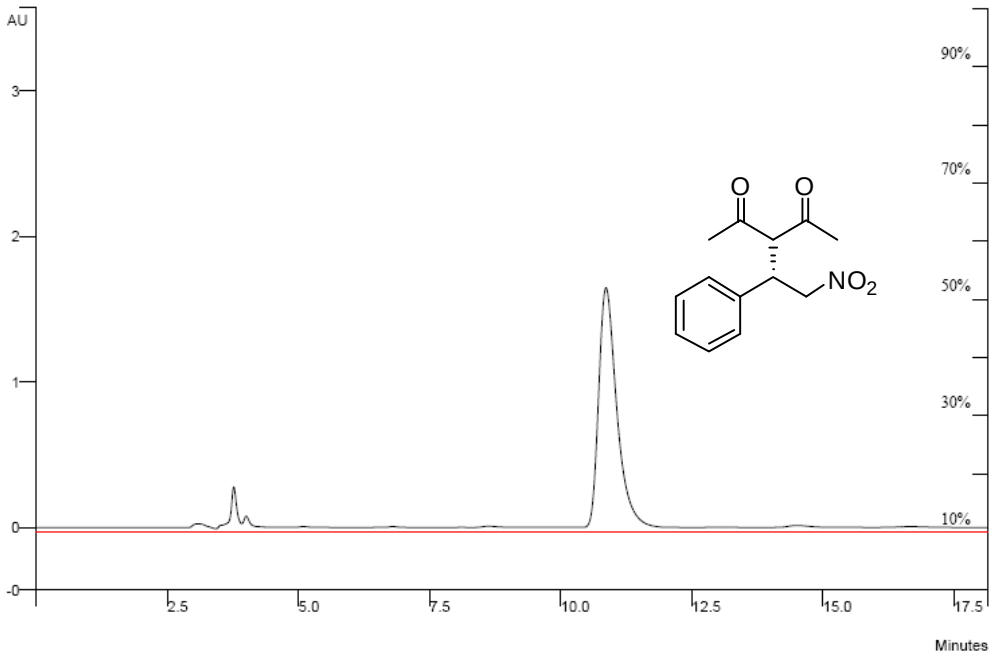
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		8.1695	20.309	0.000	300867264	0.00	BB	39.7		0
2		41.5159	24.211	0.000	1528955136	0.00	BB	59.3		0
3		8.1995	30.538	0.000	301974016	0.00	BB	72.2		0
4		42.1150	34.940	0.000	1551018112	0.00	BB	76.5		0
	Totals	**99.9999**		**0.000**	**3682814464**					



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		0.3494	19.593	0.000	7198742	0.00	BB	39.3		0
2		99.0946	22.980	0.000	2041376768	0.00	BB	64.5		0
3		0.0598	29.227	0.000	1231525	0.00	BB	49.8		0
4		0.4962	33.468	0.000	10220963	0.00	BB	66.7		0
	Totals	**100.0000**		**0.000**	**2060027904**					

7. Scale-up Experiment

2,4-Pentanedione (**2**, 10.3 mL, 100 mmol) was added to a mixture of *β*-nitrostyrene (**1a**, 7.5 g, 50 mmol) and **QN-SQA** (160 mg, 0.5 mol%) in brine (150 mL of saturated NaCl aqueous solution). The reaction mixture was mixed vigorously at 25°C. After completion of the reaction, an aqueous HCl solution (1 N, 20 mL) was added to quench the reaction. The reaction mixture was filtered and washed with water to afford the Michael addition product **3a** (11.9 g; 95 % yield; >99%ee(*S*)).



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		99.6378	10.869	0.000	395962688	0.00	BB	21.3		0
2		0.3622	14.513	0.000	1439543	0.00	BB	18.5		0
	Totals	**100.0000**		**0.000**	**397402240**					

8. References

1. (a) S. H. McCooey and S. J. Connon, *Angew. Chem. Int. Ed*., 2005, **44**, 6367-6370.; (b) S. H. Oh, H. S. Rho, J. W. Lee, J. E. Lee, S. H. Youk, J. Chin and C. E. Song, *Angew. Chem. Int. Ed.,* 2008, **47**, 7872 –7875.; (c) J. P. Malerich, K. Hagihara and V. H. Rawal, *J. Am. Chem. Soc.*, 2008, **130**, 14416-14417.; (d) H. Jiang, M. W. Paixa˜o, D. Monge and K. A. Jørgensen, *J. Am. Chem. Soc.,* 2010, **132**, 2775-2783.

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