Supplementary Information

Recyclable organocatalysis: Highly enantioselective Michael addition of 1,3-diaryl-1,3-propanedione to nitroolefins

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General Information: Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate.

Flash chromatography was performed using Merck silica gel 60 with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use.

Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on Bruker AMX 400 spectrophotometer ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 7.26, singlet). Multiplicities were given as: s (singlet), d (doublet), t (triplet), dd (doublets of doublet) or m (multiplets). Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 77.0, triplet).

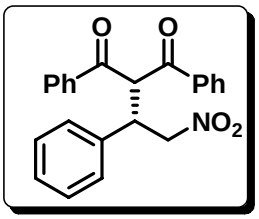
Enantioselectivities were determined by High performance liquid chromatography (HPLC) analysis employing a Daicel Chirapak AD-H or AS-H column. Optical rotations were measured in CH_2Cl_2 on a *Schmidt + Haensdch* polarimeter (Polartronic MH8) with a 10 cm cell (*c* given in g/100 mL). Absolute configuration of the products was determined by comparison with compounds previously published.

High resolution mass spectrometry (HRMS) was recorded on Finnigan MAT 95 × P spectrometer.

General experimental procedure for the Michael addition of 1,3-diphenyl-1,3-propanedione to nitroolefins:

To a solution of 1,3-diphenyl-1,3-propanedione (67.2 mg, 0.3 mmol, 3 eq) and nitroolefin (0.1 mmol, 1eq) in diethyl ether (0.3 mL) was added catalyst **VI** (**Q-NH_2**) (0.015 mmol, 0.15 eq). The resulting mixture was stirred at room temperature (23 ℃). After the reaction was complete (monitored by TLC), the products were isolated and purified either by filtration/washing with diethyl or by flash chromatography over silica gel (EtOAc:Hexane = 1:10 to 1:3).

(*S*)-2-(2-Nitro-1-phenylethyl)-1,3-diphenylpropane-1,3-dione (3a)



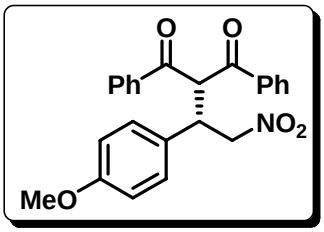
Prepared according to the general procedure to provide the title compound (96% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 7.6 Hz, 2H), 7.59-7.51 (m, 2H), 7.43-7.37 (m, 3H), 7.27-7.19 (m, 6 H), 5.85 (d, *J* = 8.0 Hz, 1H), 5.03-5.01 (m, 2H), 4.64 (dd, *J* = 7.2, 14.4 Hz, 1H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.2, 193.6, 136.8, 136.2, 135.8, 134.1, 133.8, 128.97, 128.96, 128.8, 128.8, 128.6, 128.3, 128.2, 77.3, 59.9, 44.0.
HPLC: Chiralpak AS-H (hexane/*i*-PrOH = 85/15, flow rate 1 mL/min, λ= 210 nm), t_R (major) = 20.4 min, t_R (minor) = 28.3 min; 98% ee.

$[\alpha]_D^{25}$ = 21.3 (*c* = 1.0, CH_2Cl_2).

MS (ESI, m/z): 374.3 (M+H).

(*S*)-2-(1-(4-Methoxyphenyl)-2-nitroethyl)-1,3-diphenylpropane-1,3-dione (3b)

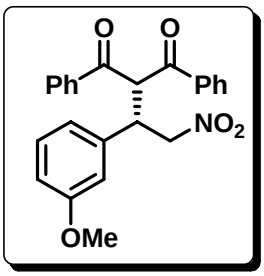


Prepared according to the general procedure to provide the title compound (92% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 2H), 7.81 (d, *J* = 7.6 Hz, 2H), 7.57-7.51 (m, 2H), 7.44-7.36 (m, 4H), 7.17 (d, *J* = 8.8 Hz, 2 H), 6.74 (d, *J* = 8.8 Hz, 2H), 5.84 (d, *J* = 8.0 Hz, 1H), 5.00-4.96 (m, 2H), 4.61 (dd, *J* = 7.2, 14.4 Hz, 1H), 3.72 (s, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.3, 193.7, 159.3, 136.2, 135.9, 134.1, 133.8, 129.4, 129.0, 128.84, 128.81, 128.6, 128.5, 114.3, 77.7, 60.1, 55.2, 43.5.
HPLC: Chiralpak AD-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ= 230 nm), t_R (major) = 10.7 min, t_R (minor) = 22.5 min; 97% ee.

$[\alpha]_D^{25}$ = 25.1 (*c* = 1.0, CH_2Cl_2).
MS (ESI, m/z): 404.1 (M+H).

(*S*)-2-(1-(3-Methoxyphenyl)-2-nitroethyl)-1,3-diphenylpropane-1,3-dione (3c)



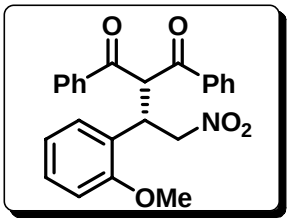
Prepared according to the general procedure to provide the title compound (91% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.59-7.52 (m, 2H), 7.44-7.37 (m, 4H), 7.16-7.12 (m, 1H), 6.85-6.71 (m, 3H), 5.85 (d, *J* = 8.0 Hz, 1H), 5.02-4.99 (m, 2H), 4.64-4.58 (m, 1H), 3.70 (s, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.3, 193.6, 159.8, 138.3, 136.2, 135.8, 134.1, 133.8, 130.0, 128.8, 128.8, 128.6, 128.1, 120.3, 114.3, 113.6, 77.2, 59.7, 55.2, 44.0.
HPLC: Chiralpak AD-H (hexane/*i*-PrOH = 85/15, flow rate 1 mL/min, λ= 220 nm), t_R (major) = 19.2 min, t_R (minor) = 32.5 min; 93% ee.

$[\alpha]_D^{25}$ = 5.1 (*c* = 1.1, CH_2Cl_2).

HRMS (EI) calcd for $C_{24}H_{21}NO_5$, m/z 403.1414, found 403.1412.

(*S*)-2-(1-(2-Methoxyphenyl)-2-nitroethyl)-1,3-diphenylpropane-1,3-dione (3d)



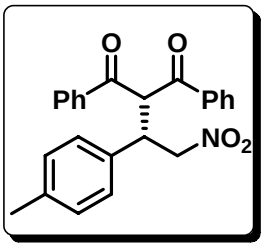
Prepared according to the general procedure to provide the title compound (94% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.91-7.87 (m, 4H), 7.55-7.51 (m, 2H), 7.43-7.37 (m, 4H), 7.20-7.13 (m, 2H), 6.81-6.76 (m, 2H), 6.09 (d, *J* = 8.0 Hz, 1H), 5.25 (dd, *J* = 9.6, 12.8 Hz, 1H), 4.94 (dd, *J* = 4.0, 13.2 Hz, 1H), 4.86-4.80 (m, H), 3.87 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.4, 194.2, 157.1, 136.4, 136.0, 133.8, 133.7, 131.0, 129.4, 128.9, 128.7, 128.6, 128.6, 124.2, 121.1, 110.9, 75.8, 57.2, 55.3, 40.9.
HPLC: Chiralpak AD-H (hexane/*i*-PrOH = 85/15, flow rate 1 mL/min, λ= 210 nm), t_R (major) = 16.7 min, t_R (minor) = 23.5 min; 99% ee.

$[\alpha]_D^{25}$ = -17.4 (*c* = 1.0, CH_2Cl_2).
HRMS (EI) calcd for $C_{24}H_{21}NO_5$, m/z 403.1414, found 403.1414.

(*S*)-2-(2-Nitro-1-*p*-tolylethyl)-1, 3-diphenylpropane-1, 3-dione (3e)

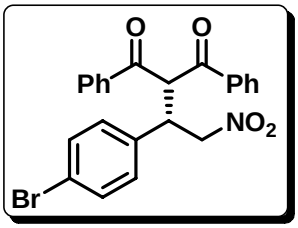


Prepared according to the general procedure to provide the title compound (93% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.6 Hz, 2H), 7.81 (d, *J* = 7.6 Hz, 2H), 7.57-7.52 (m, 2H), 7.44-7.37 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 2 H), 7.03 (d, *J* = 7.6 Hz, 2H), 5.85 (d, *J* = 8.0 Hz, 1H), 5.00-4.98 (m, 2H), 4.62 (dd, *J* = 5.2, 8.0 Hz, 1H), 2.25 (s, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.3, 193.6, 137.9, 136.2, 135.9, 134.1, 133.8, 133.7, 129.6, 129.0, 128.83, 128.81, 128.7, 128.1, 77.5, 60.1, 43.7, 21.0.
HPLC: Chiralpak AS-H (hexane/*i*-PrOH = 85/15, flow rate 1 mL/min, λ= 210 nm), t_R (major) = 18.8 min, t_R (minor) = 25.5 min; 98% ee.

$[\alpha]_D^{25}$ = 8.6 (*c* = 1.0, CH_2Cl_2).
MS (ESI, m/z): 388.3 (M+H).

(*S*)-2-(1-(4-Bromophenyl)-2-nitroethyl)-1,3-diphenylpropane-1,3-dione (3f)



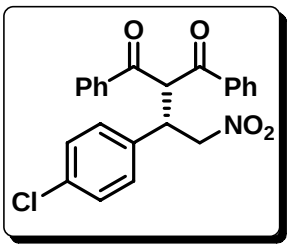
Prepared according to the general procedure to provide the title compound (96% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.87-7.85 (m, 2H), 7.77-7.74 (m, 2H), 7.59-7.52 (m, 2H), 7.54-7.47 (m, 2H), 7.41-7.29 (m, 6H), 7.11-7.08 (m, 2H), 5.78 (d, *J* = 10.8 Hz, 1H), 4.93-4.90 (m, 2H), 4.57 (dd, *J* = 7.2, 19.6 Hz, 1H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.0, 193.3, 136.0, 135.8, 135.7, 134.3, 134.0, 132.1, 130.0, 129.1, 129.0, 128.8, 128.6, 122.3, 77.2, 59.6, 43.6.

HPLC: Chiralpak AS-H (hexane/*i*-PrOH = 85/15, flow rate 1 mL/min, λ= 210 nm), t_R (major) = 23.8 min, t_R (minor) = 33.5 min; >99% ee.

$[\alpha]_D^{25}$ = 17.8 (*c* = 1.3, CH_2Cl_2).
MS (ESI, m/z): 453.3 (M+H).

(*S*)-2-(1-(4-Chlorophenyl)-2-nitroethyl)-1,3-diphenylpropane-1,3-dione (3g)

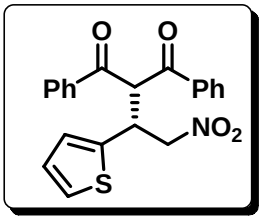


Prepared according to the general procedure to provide the title compound (97% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.88-7.85 (m, 2H), 7.77-7.74 (m, 2H), 7.54-7.48 (m, 2H), 7.41-7.32 (m, 4H), 7.15 (m, 4H), 5.78 (d, *J* = 10.8 Hz, 1H), 4.93-4.91 (m, 2H), 4.57 (dd, *J* = 7.2, 19.2 Hz, 1H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.0, 193.4, 136.0, 135.7, 135.3, 134.3, 134.1, 134.0, 129.7, 129.2, 129.1, 129.0, 128.8, 128.6, 77.3, 59.7, 43.5.
HPLC: Chiralpak AS-H (hexane/*i*-PrOH = 85/15, flow rate 1 mL/min, λ= 210 nm), t_R (major) = 22.1 min, t_R (minor) = 31.2 min; >99% ee.

$[\alpha]_D^{25}$ = 18.9 (*c* = 1.2, CH_2Cl_2).
HRMS (EI) calcd for $C_{23}H_{18}ClNO_4$, m/z 407.0919, found 407.0912.

(*R*)-2-(2-Nitro-1-(thiophen-2-yl)ethyl)-1,3-diphenylpropane-1,3-dione (3h)

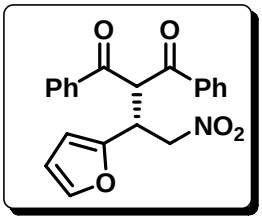


Prepared according to the general procedure to provide the title compound (92% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.91-7.87 (m, 4H), 7.60-7.56 (m, 2H), 7.45-7.41 (m, 4H), 7.15 (d, *J* = 5.2 Hz, 1 H), 6.90 (d, *J* = 3.2 Hz, 1H), 6.82 (dd, *J* = 3.6, 5.2 Hz, 1H), 5.98 (d, *J* = 7.2 Hz, 1H), 5.03-5.00 (m, 2H), 4.92 (dd, *J* = 6.8, 12.8 Hz, 1H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.0, 193.5, 139.3, 136.0, 135.6, 134.1, 134.0, 129.0, 128.96, 128.73, 128.68, 127.2, 127.1, 125.4, 78.0, 59.9, 39.5.
HPLC: Chiralpak AS-H (hexane/*i*-PrOH = 85/15, flow rate 1 mL/min, λ= 262 nm), t_R (major) = 23.4 min, t_R (minor) = 27.0 min; 97% ee.

$[\alpha]_D^{25}$ = -15.6 (*c* = 1.4, CH_2Cl_2).
MS (ESI, m/z): 380.4 (M+H).

(*R*)-2-(1-(Furan-2-yl)-2-nitroethyl)-1,3-diphenylpropane-1,3-dione (3i)

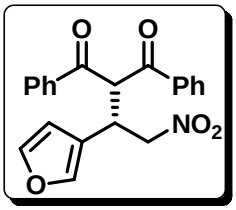


Prepared according to the general procedure to provide the title compound (91% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.89-7.85 (m, 4H), 7.58-7.55 (m, 2H), 7.45-7.39 (m, 4H), 7.23 (m, 1H), 6.13 (m, 2H), 6.04 (d, *J* = 7.6 Hz, 1H), 5.01-4.90 (m, 2H), 4.77-4.72 (m, 1H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 193.7, 149.8, 142.5, 135.9, 135.4, 134.1, 133.9, 129.0, 128.9, 128.6, 110.7, 108.9, 75.6, 56.7, 37.8.
HPLC: Chiralpak AS-H (hexane/*i*-PrOH = 85/15, flow rate 1 mL/min, λ= 210 nm), t_R (minor) = 20.7 min, t_R (major) = 25.1 min; 98% ee.

$[\alpha]_D^{25}$ = 38.5 (*c* = 1.1, CH_2Cl_2).
MS (ESI, m/z): 364.5 (M+H).

(*S*)-2-(1-(Furan-3-yl)-2-nitroethyl)-1,3-diphenylpropane-1,3-dione (3j)

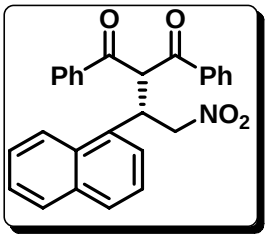


Prepared according to the general procedure to provide the title compound (91% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 2H), 7.88 (d, *J* = 7.6 Hz, 2H), 7.60-7.57 (m, 2H), 7.46-7.42 (m, 4H), 7.28-7.21 (m, 2 H), 6.32 (s, 1H), 5.88 (d, *J* = 8.0 Hz, 1H), 4.92-4.86 (m, 2H), 4.61 (dd, *J* = 6.8, 13.6 Hz, 1H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.2, 193.9, 143.6, 140.9, 136.0, 135.8, 134.1, 134.0, 129.0, 129.0, 128.7, 128.6, 121.0, 109.7, 77.5, 58.7, 35.3.
HPLC: Chiralpak AS-H (hexane/*i*-PrOH = 85/15, flow rate 1 mL/min, λ= 210 nm), t_R (major) = 24.5 min, t_R (minor) = 27.7 min; 96% ee.

$[\alpha]_D^{25}$ = 74.6 (*c* = 1.0, CH_2Cl_2).
MS (ESI, m/z): 364.4 (M+H).

(*S*)-2-(1-(Naphthalen-1-yl)-2-nitroethyl)-1,3-diphenylpropane-1,3-dione (3k)

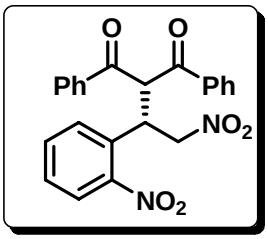


Prepared according to the general procedure to provide the title compound (88% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 7.6 Hz, 2H), 7.75-7.60 (m, 6H), 7.56-7.40 (m, 3H), 7.33-7.28 (m, 5H), 7.22-7.18 (m, 1H), 6.02 (d, *J* = 6.0 Hz, 1H), 5.66-5.61 (m, 1H), 5.31 (dd, *J* = 4.0, 14.4 Hz, 1H), 4.61 (dd, *J* = 9.2, 14.0 Hz, 1H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 195.0, 193.8, 136.2, 135.7, 134.2, 133.7, 132.8, 131.1, 129.3, 128.9, 128.8, 128.8, 128.5, 127.1, 126.1, 124.9, 122.4, 76.5, 58.5, 37.3.
HPLC: Chiralpak AS-H (hexane/*i*-PrOH = 85/15, flow rate 1 mL/min, λ= 210 nm), t_R (major) = 21.8min, t_R (minor) = 29.6 min; 96% ee.

$[\alpha]_D^{25}$ = -155.4 (*c* = 1.0, CH_2Cl_2).
HRMS (EI) calcd for $C_{27}H_{21}NO_4$, m/z 423.1465, found 423.1466.

(*S*)-2-(2-Nitro-1-(2-nitrophenyl)ethyl)-1,3-diphenylpropane-1,3-dione (3l)

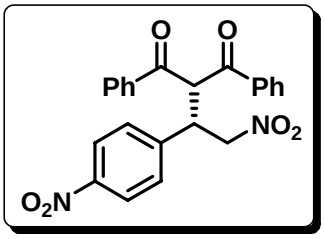


Prepared according to the general procedure to provide the title compound (92% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.89-7.84 (m, 5H), 7.60-7.52 (m, 2H), 7.43-7.36 (m, 7H), 6.28 (d, *J* = 6.0 Hz, 1H), 5.28-5.26 (m, 1H), 5.12-5.09 (m, 2H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.4, 193.4, 150.0, 136.2, 135.6, 134.3, 133.2, 131.7, 130.1, 129.1, 129.1, 128.9, 128.9, 128.6, 128.6, 125.4, 75.1, 58.0, 439.0.
HPLC: Chiralpak AS-H (hexane/*i*-PrOH = 85/15, flow rate 1 mL/min, λ= 210 nm), t_R (minor) = 16.0 min, t_R (major) = 18.0 min; 94% ee.

$[\alpha]_D^{25}$ = -81.4 (*c* = 1.1, CH_2Cl_2).
MS (ESI, m/z): 419.4 (M+H).

(*S*)-2-(2-Nitro-1-(4-nitrophenyl)ethyl)-1,3-diphenylpropane-1,3-dione (3m)

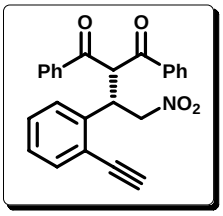


Prepared according to the general procedure to provide the title compound (86% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.93 (d, *J* = 7.6 Hz, 2H), 7.82-7.80 (m, 2H), 7.61-7.54 (m, 2H), 7.49-7.39 (m, 6H), 5.87 (d, *J* = 6.0 Hz, 1H), 5.02-5.00 (m, 2H), 4.78 (dd, *J* = 7.6 Hz, 14.0 Hz, 1H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ 193.5, 192.9, 147.6, 144.2, 135.8, 135.4, 134.5, 134.3, 129.5, 129.2, 129.1, 128.8, 128.6, 124.1, 76.8, 59.3, 43.7.
HPLC: Chiralpak AS-H (hexane/*i*-PrOH = 85/15, flow rate 1 mL/min, λ= 210 nm), t_R (major) = 20.5 min, t_R (minor) = 28.1 min; 94% ee.

$[\alpha]_D^{25}$ = 36.8 (*c* = 1.1, CH_2Cl_2).
MS (ESI, m/z): 419.4 (M+H).

2-((*S*)-1-(2-Ethynylphenyl)-2-nitroethyl)-1,3-diphenylpropane-1,3-dione (3n)

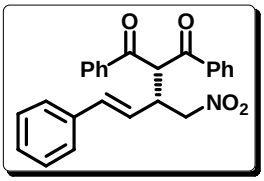


Prepared according to the general procedure to provide the title compound (87% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.5 Hz, 2H), 7.83 (d, *J* = 7.5, 2H), 7.57-7.52 (m, 3H), 7.40-7.37 (m, 4H), 7.18-7.13 (m, 3H), 6.23 (d, *J* = 7.0 Hz, 1H), 5.26 (dd, *J* = 10.5, 14.5 Hz, 1H), 5.15-5.11 (m, 2H), 3.5 (s, 1H).
^{13}C-NMR (125 MHz, $CDCl_3$) δ 194.5, 193.6, 139.1, 136.3, 135.7, 134.2, 134.1, 133.9, 129.4, 129.0, 128.8, 128.7, 128.7, 127.9, 121.5, 83.7, 81.8, 75.7, 57.7, 42.0.
HPLC: Chiralpak AD-H (hexane/*i*-PrOH = 85/15, flow rate 1 mL/min, λ= 254 nm), t_R (major) = 18.7 min, t_R (minor) = 21.5 min; 93% ee.

$[\alpha]_D^{25}$ = -45.6 (*c* = 1.0, CH_2Cl_2).
HRMS (ESI) calcd for $C_{25}H_{19}NO_4Na$, m/z 420.1212, found 420.1209.

2-((*R*,*E*)-1-Nitro-4-phenylbut-3-en-2-yl)-1,3-diphenylpropane-1,3-dione (3o)

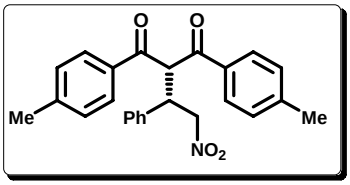


To a solution of 1,3-diphenyl-1,3-propanedione (67.2 mg, 0.3 mmol, 3 eq) and nitroolefin **2o** (0.1 mmol, 1eq) in diethyl ether (0.2 mL) was added catalyst **VI** (**Q-NH$_2$**) (0.03 mmol, 0.3 eq). The resulting mixture was stirred at room temperature (23 ℃) for 30 hours. The products were isolated and purified with diethyl or by flash chromatography over silica gel (EtOAc:Hexane = 1:10 to 1:5) to provide the title compound (81% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.00-7.97 (m, 4H), 7,62 (t, *J* = 7.0 Hz, 2H), 7.51-7.47 (dd, *J* = 7.5, 13.5 Hz, 4H), 7.29-7.16 (m, 5H), 6.48 (d, *J* = 15.5 Hz, 1H), 6.20 (dd, *J* = 9.5, 15.5Hz, 1H), 5.81 (d, *J* = 7.0 Hz, 1H), 4.88-4.80 (m, 2H), 4.06-4.01 (s, 1H).
^{13}C-NMR (125 MHz, $CDCl_3$) δ 194.5, 194.3, 136.0, 135.9, 135.3, 134.1, 134.0, 129.2, 129.1, 128.7, 128.7, 128.5, 128.1, 126.6, 124.3, 77.6, 57.4, 42.4.
HPLC: Chiralpak AS-H (hexane/*i*-PrOH = 85/15, flow rate 1 mL/min, λ= 254 nm), t_R (major) = 16.4 min, t_R (minor) = 42.0 min; 90% ee.

$[\alpha]_D^{25}$ = 141.1 (*c* = 0.8, CH_2Cl_2).
HRMS (ESI) calcd for $C_{25}H_{21}NO_4Na$, m/z 422.1368, found 422.1363.

2-((*S*)-2-Nitro-1-phenylethyl)-1,3-dip-tolylpropane-1,3-dione (3p)



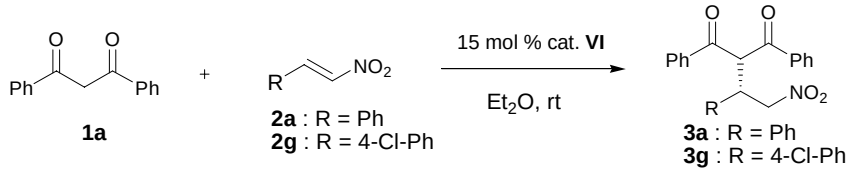
To a solution of dione **1b** (0.1 mmol, 1 eq) and *trans*-β-nitrostyrene **2a** (0.2 mmol, 2eq) in diethyl ether (0.2 mL) was added catalyst **VI** (**Q-NH$_2$**) (0.015 mmol, 0.15 eq). The resulting mixture was stirred at room temperature (23 ℃) for 24 hours. The product was purified by flash chromatography over silica gel (EtOAc:Hexane = 1:10 to 1:5) to provide the title compound (85% yield).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.28-7.16 (m, 9H), 5.80 (d, *J* = 8.0 Hz, 1H), 5.01 (d, *J* = 6.8 Hz, 2H), 4.64 (dd, *J* = 7.6, 14.4 Hz, 1H), 2.39 (s. 3H), 2.37 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 193.8, 193.1, 145.2, 144.9, 137.0, 133.8, 133.3, 129.7, 129.5, 128.96, 128.93, 128.8, 128.3, 128.1, 59.7, 44.1, 21.7, 21.7.
HPLC: Chiralpak AD-H (hexane/*i*-PrOH = 70/30, flow rate 1 mL/min, λ= 254 nm), t_R (major) = 10.7 min, t_R (minor) = 28.0 min; 97% ee.

$[\alpha]_D^{25}$ = -2.6 (*c* = 1.0, CH_2Cl_2).
HRMS (ESI) calcd for $C_{25}H_{24}NO_4$, m/z 402.1705, found 402.1692.

The procedure for the recycling of the Michael addition of 1,3-diphenyl-1,3-propanedione to *trans*-β-nitrostyrene (1a) and 1-chloro-4-((*E*)-2-nitrovinyl)benzene (1g)



cycle	R = Ph (**3a**)			R = 4-Cl-Ph (**3g**)		
	t (h)	Yield	ee (%)	t (h)	Yield	ee (%)
1	8	74	98	8	76	>99
2	9	83	97	10	82	99
3	10	110	97	11	108	98
4	12	95	96	13	96	97
5	15	109	96	16	114	96
6	19	94	95	19	97	96
7	30	101	94	23	97	95

To *trans*-β-nitrostyrene (2a):

To a solution of 1,3-diphenyl-1,3-propanedione (**1a**) (67.2 mg, 0.3 mmol, 3 eq) and *trans*-β-nitrostyrene (**1a**) (14.9 mg, 0.1 mmol, 1eq) in diethyl ether (0.3 mL) was added catalyst **VI** (**Q-NH_2)** (0.015 mmol, 0.15 eq). The resulting mixture was stirred at room temperature (23 ℃). After the reaction was complete (monitored by TLC), the product **3a** was isolated and purified by centrifuge / washing with diethyl ether (0.5 mL). All the catalyst **VI** (0.15 eq) and 2 equivalents of the excess the dione **1a** were retained in the filtrate. The combined ethereal filtrate was evaporated to 0.3 mL before the dione **1a** (1 equiv) and nitrostryene **2a** (1 eq) were added again to the solution for the next round of the Michael reaction. This was to ensure that the reaction condition for each cycle was almost the same as the previous one. The excellent yields (96% in average) and enantioselectivities (>99-95% ee) were achieved in seven cycles.

To 1-chloro-4-((*E*)-2-nitrovinyl)benzene (2g):

To a solution of 1,3-diphenyl-1,3-propanedione (**1a**) (0.3 mmol, 3 eq) and 1-chloro-4-((*E*)-2-nitrovinyl)benzene (**2g**) (0.1 mmol, 1eq) in diethyl ether (0.3 mL) was added catalyst **VI (Q-NH_2)** (0.015 mmol, 0.15 eq). The resulting mixture was stirred at room temperature (23 ℃). After the reaction was complete (monitored by TLC), the product **3g** was isolated and purified by centrifuge / washing with diethyl ether (0.3 mL). All the catalyst **VI** (0.15 equiv) and 2 equivalents of the excess the dione **1a** were retained in the filtrate. The combined ethereal filtrate was evaporated to 0.3 mL before the dione **1a** (1 eq) and **2g** (1 eq) were added again to the solution for the next round of the Michael reaction. This was to ensure that the reaction condition for each cycle was almost the same as the previous one. The excellent yields (96% in average) and enantioselectivities (98-94% ee) were achieved in seven cycles.

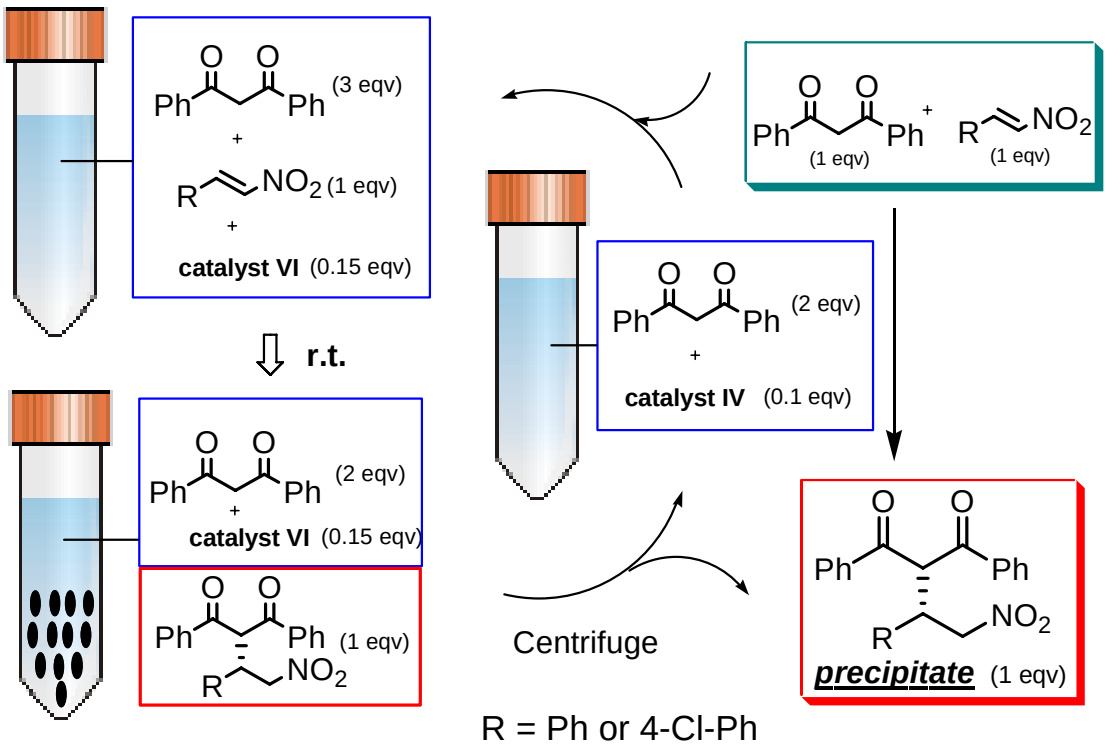
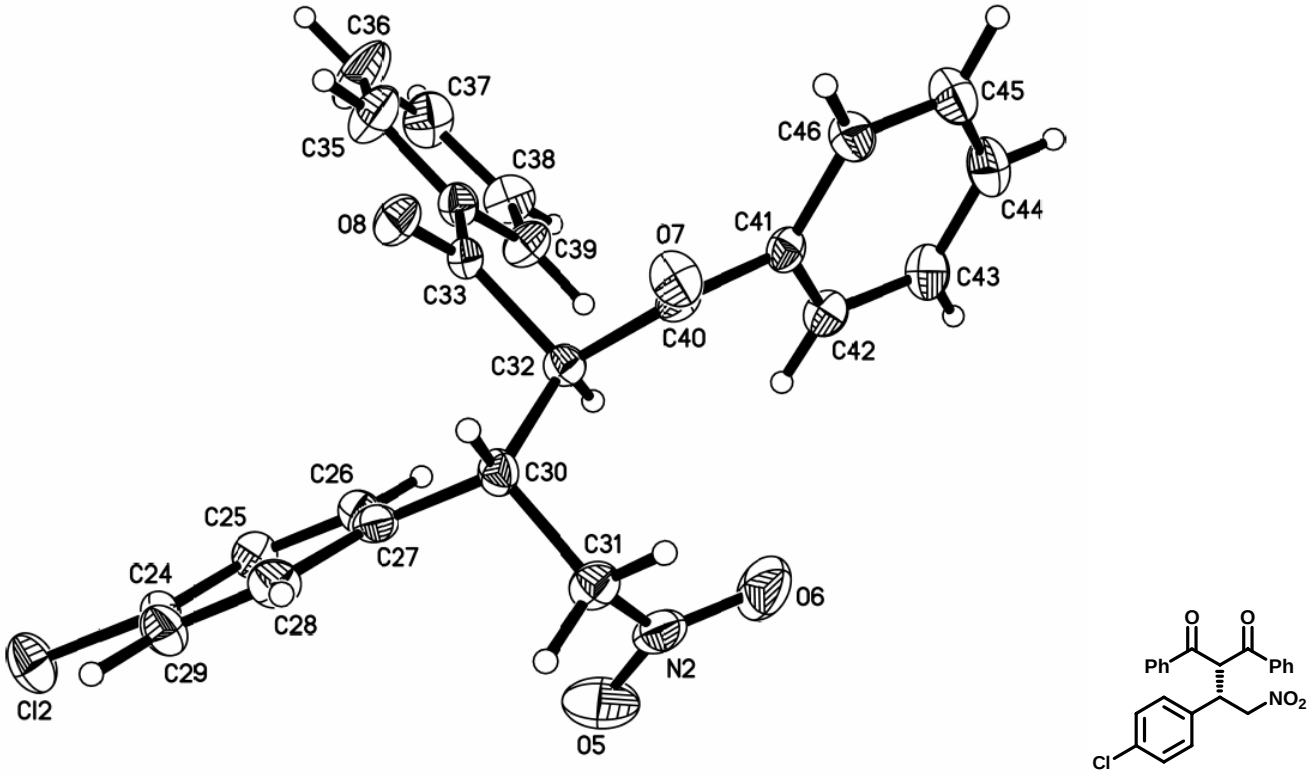


Figure S4 Recycling strategy for the organocatalytic asymmetric Michael addition

The stereochemistry of the Michael addition was determined by X-ray crystallography to be *S*:

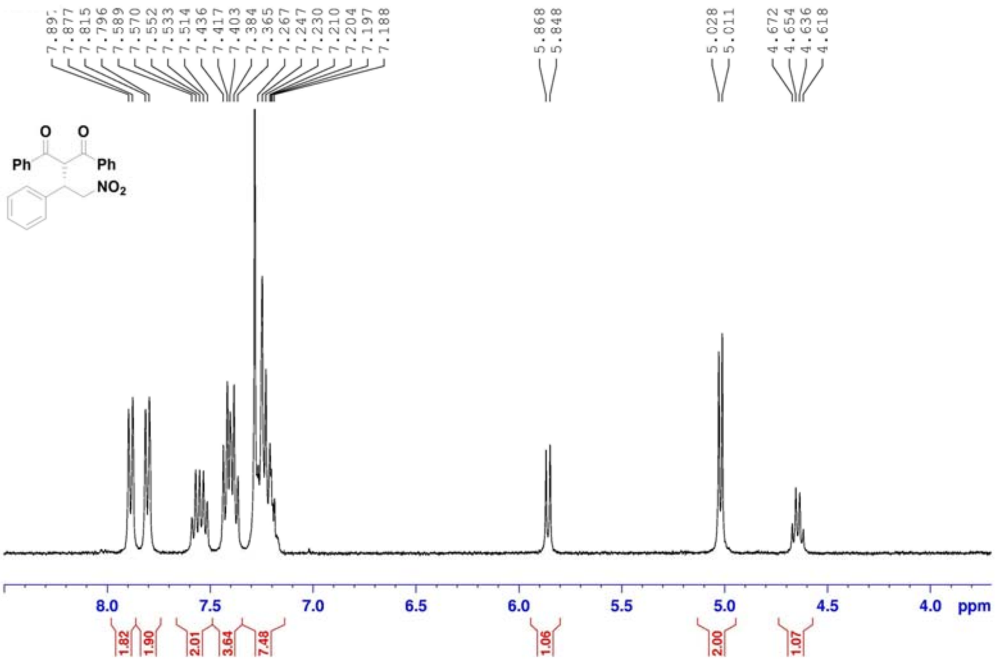
The absolute configuration of one product **3g** was determined by X-ray crystallography to be ***S***.



The X-ray crystal structure of product **3g** (ORTEP)

For the X-ray crystallography data of the product **3g**, see the CIF file (zgf21.cif) which was deposited at the Cambridge Crystallographic Data Centre (CCDC) and its deposition number is CCDC 658642.

NMR Spectra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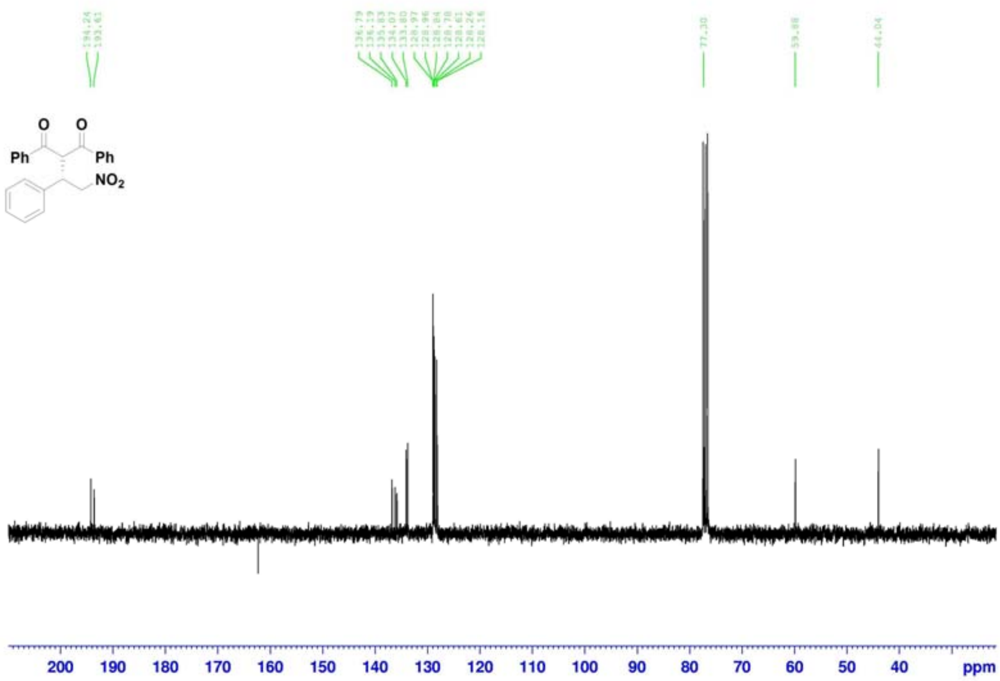
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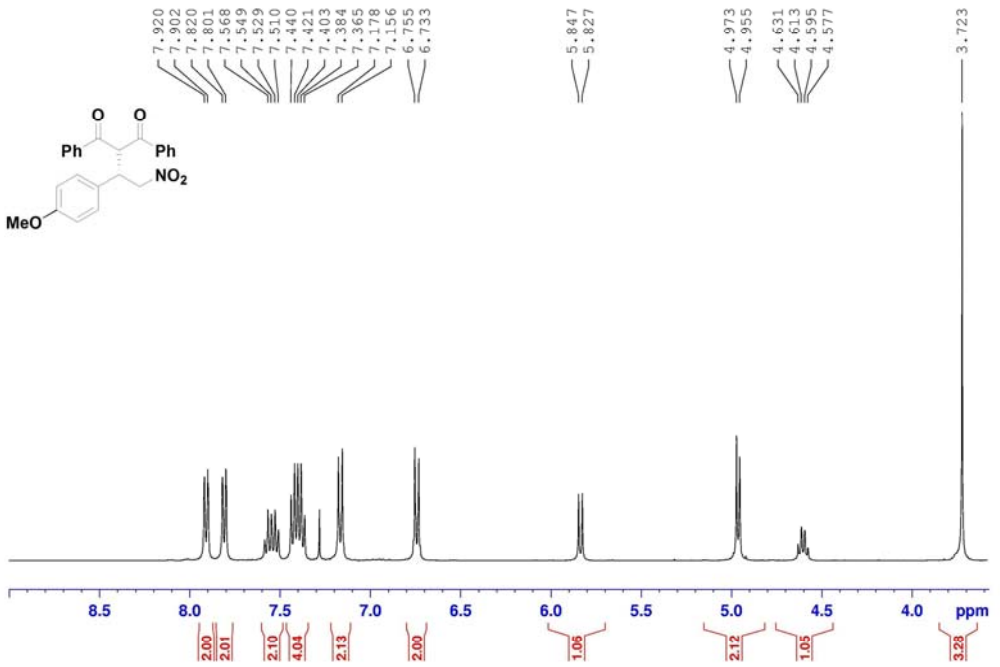
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7.178
7.156
6.755
6.733
5.847
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4.595
4.577
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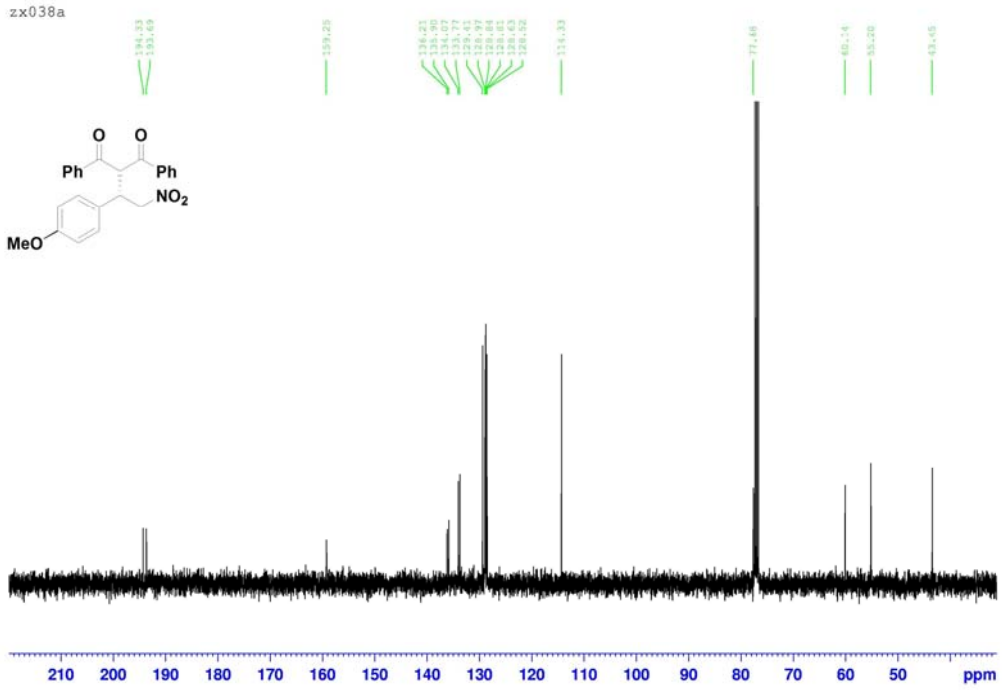
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Ph
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MeO
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60
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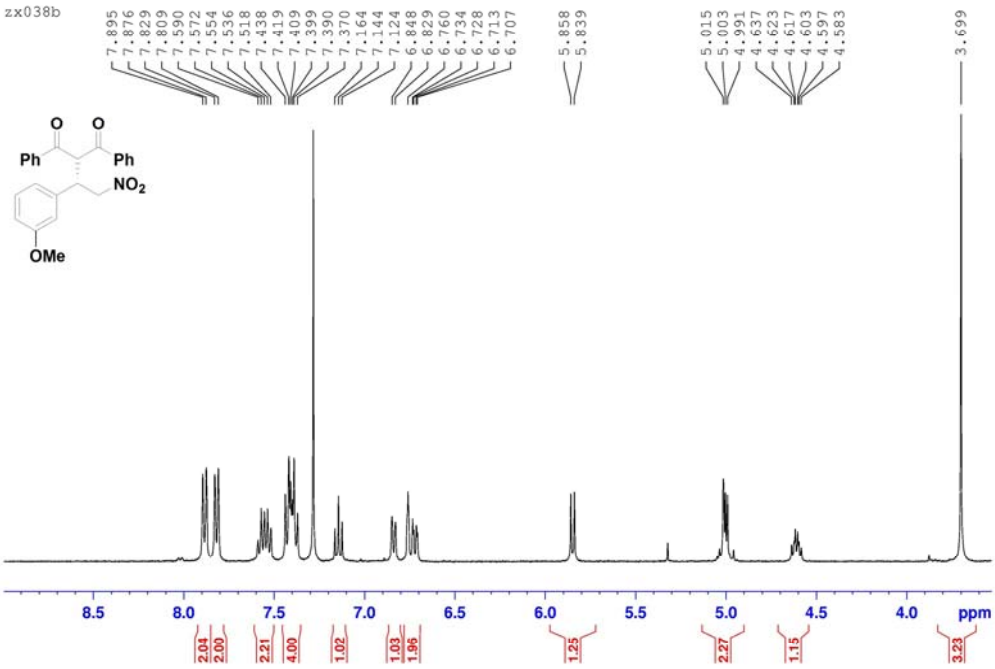
ppm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7.144
7.124
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6.829
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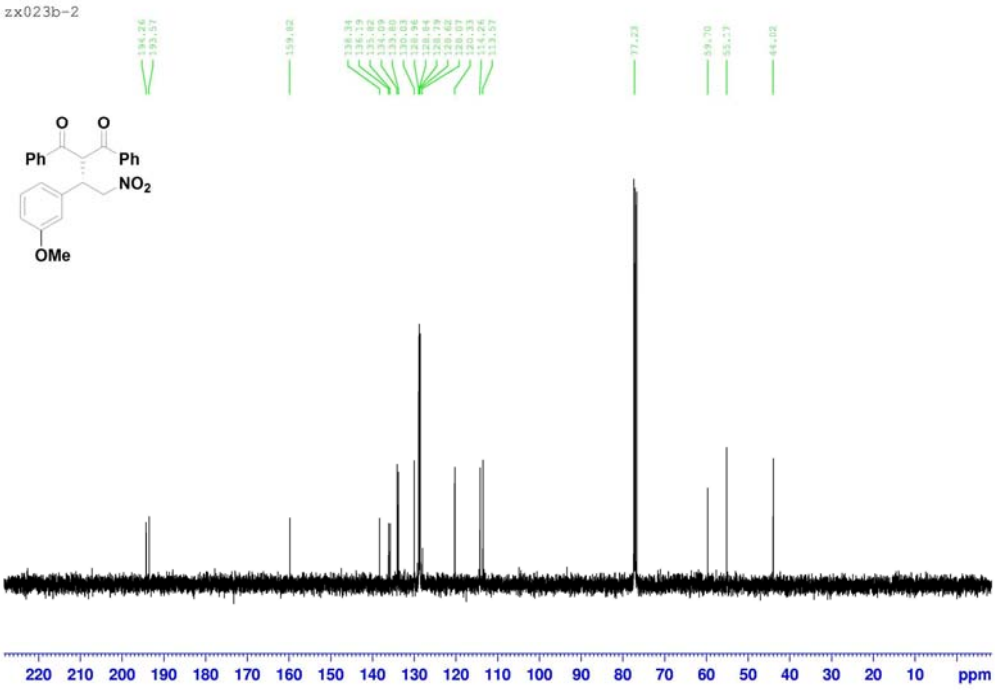
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OMe
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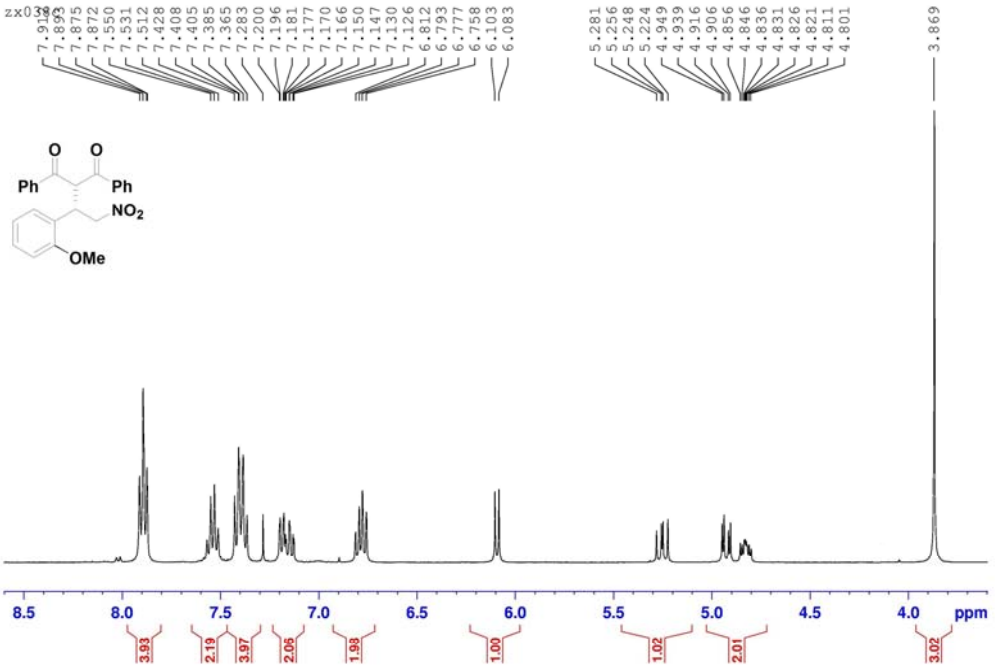
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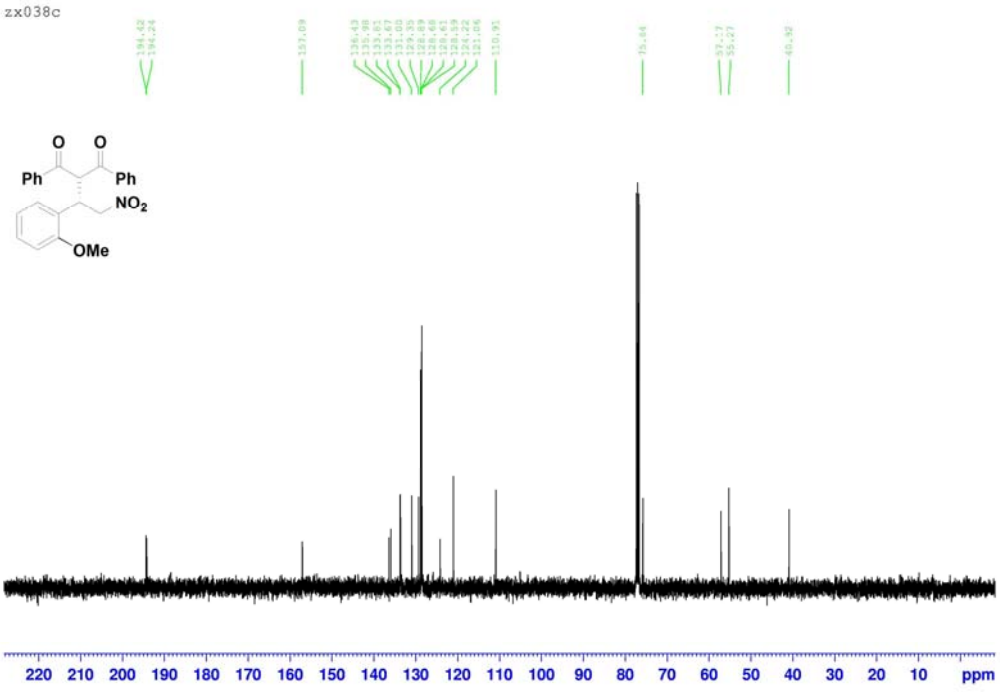
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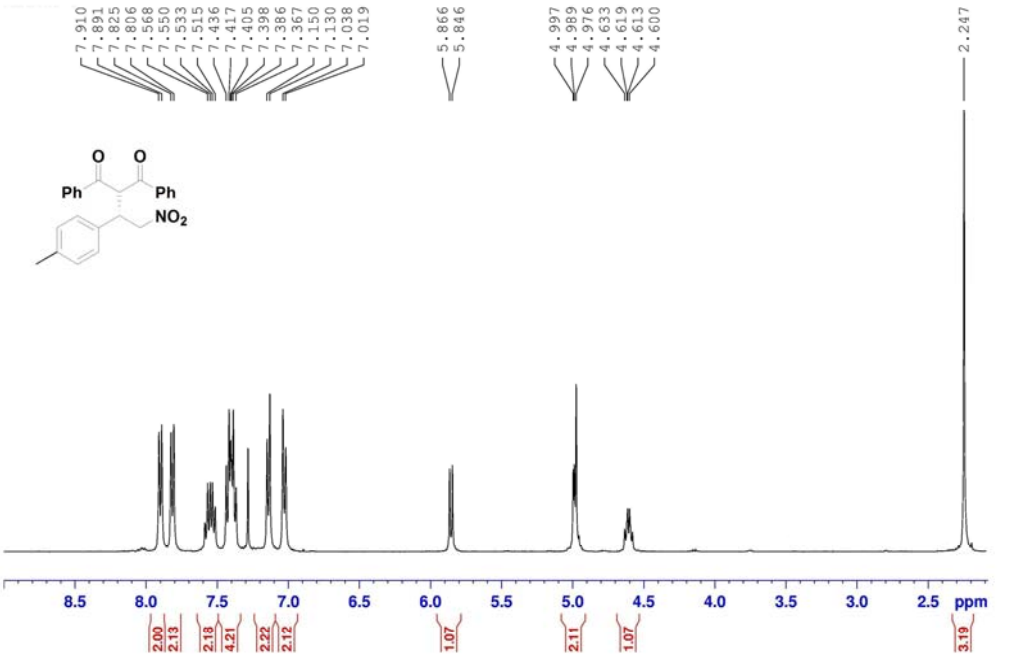
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7.150
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4.613
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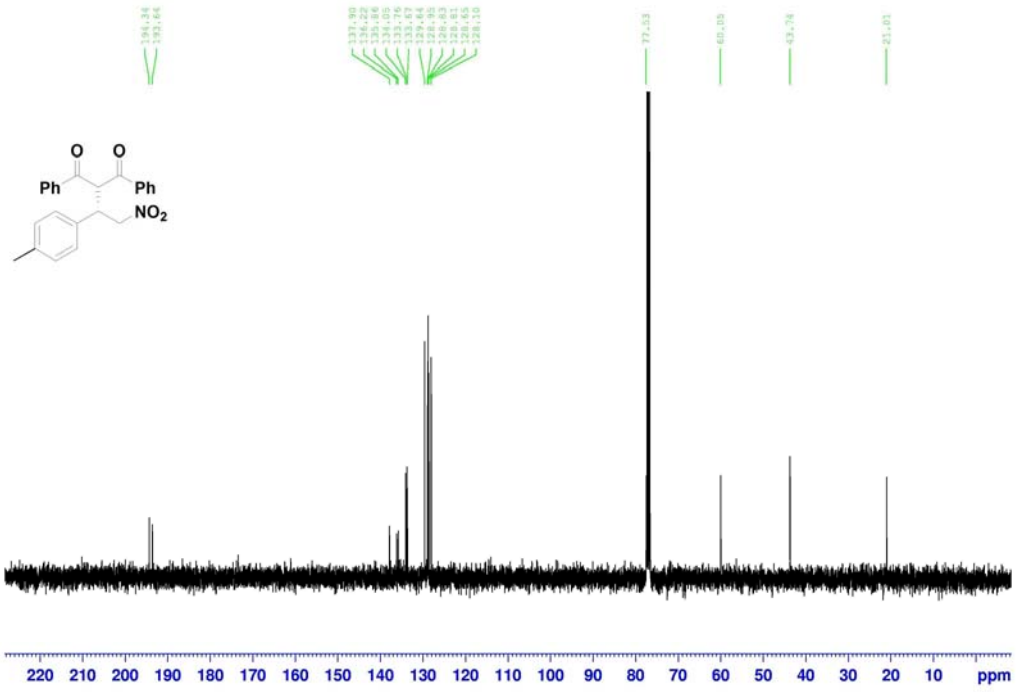
1.07
3.19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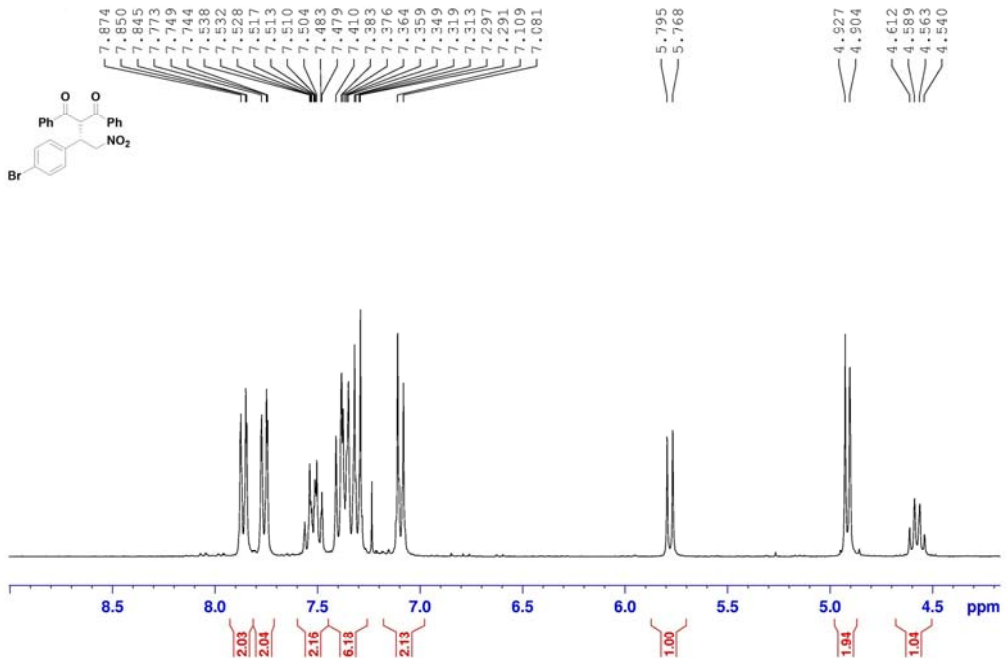
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7.0
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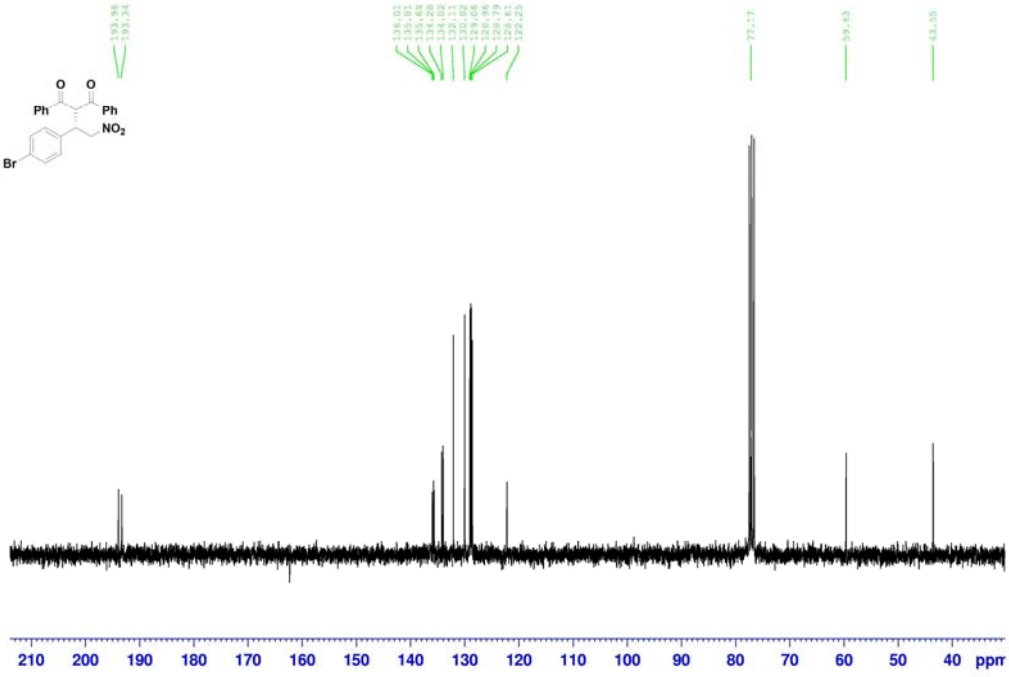
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77.17
59.43
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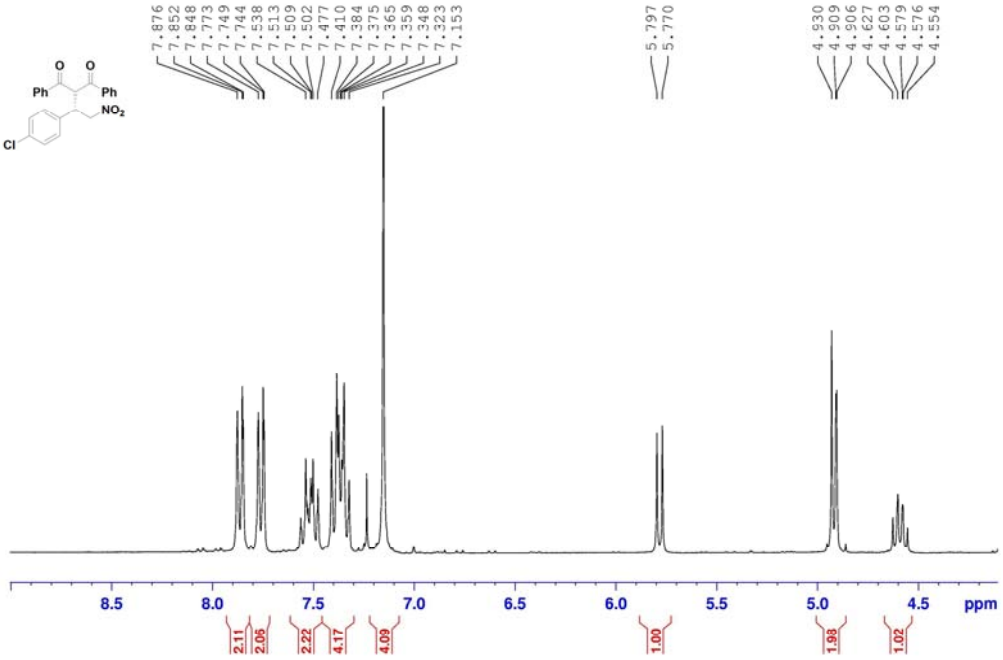
ppm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Cl
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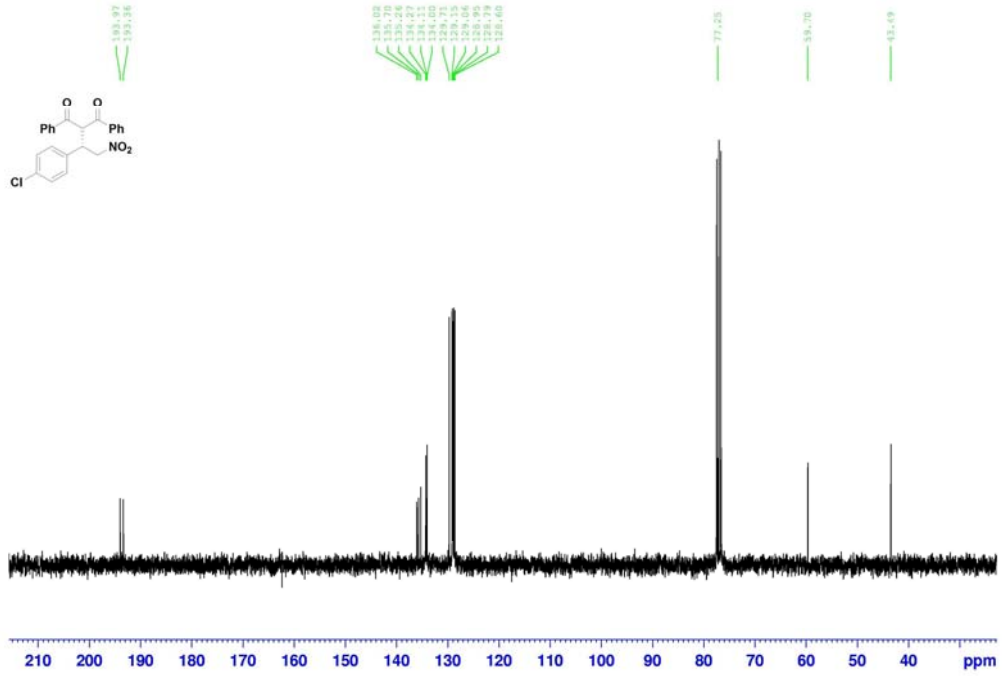
1.02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128.60
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Ph
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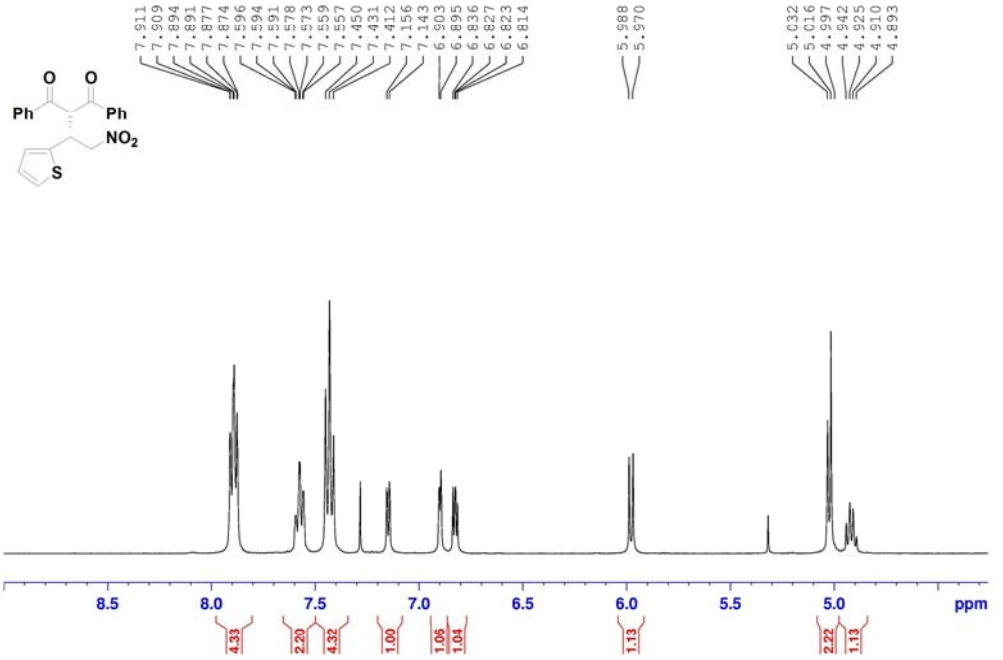
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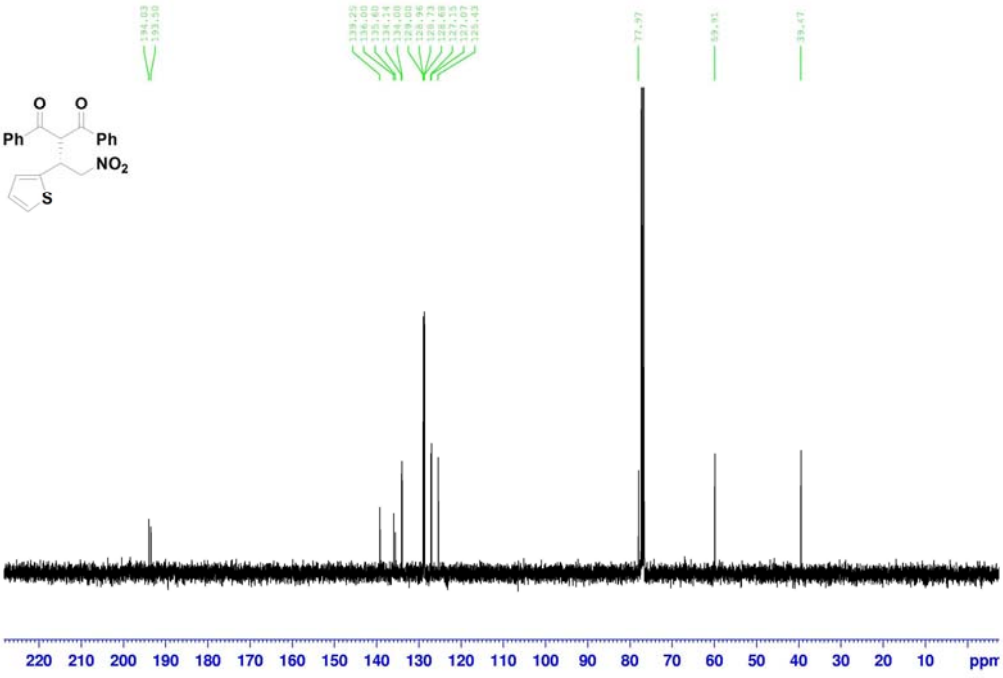
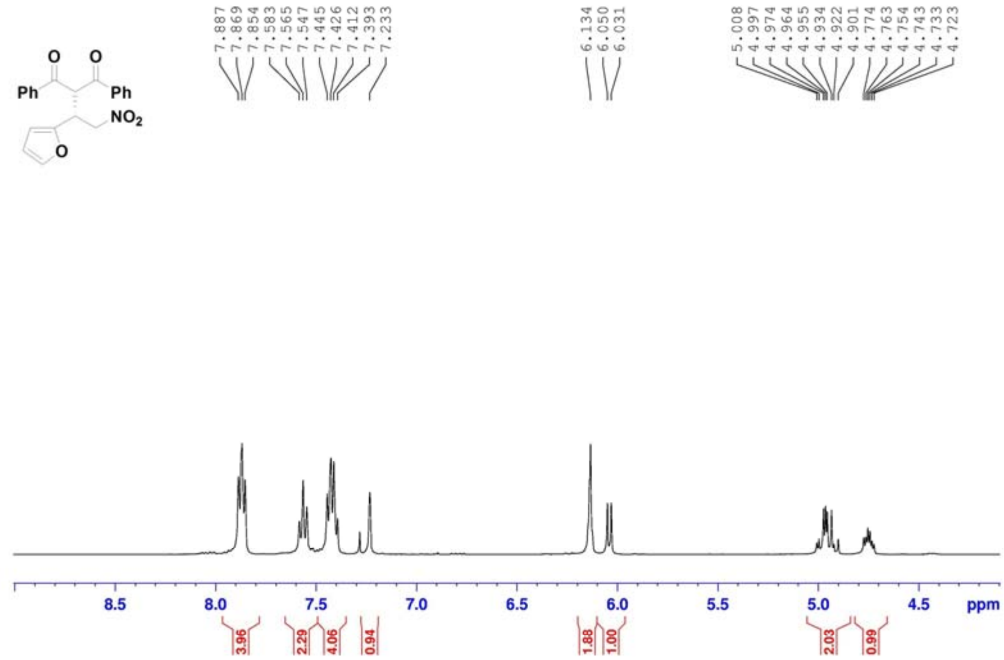
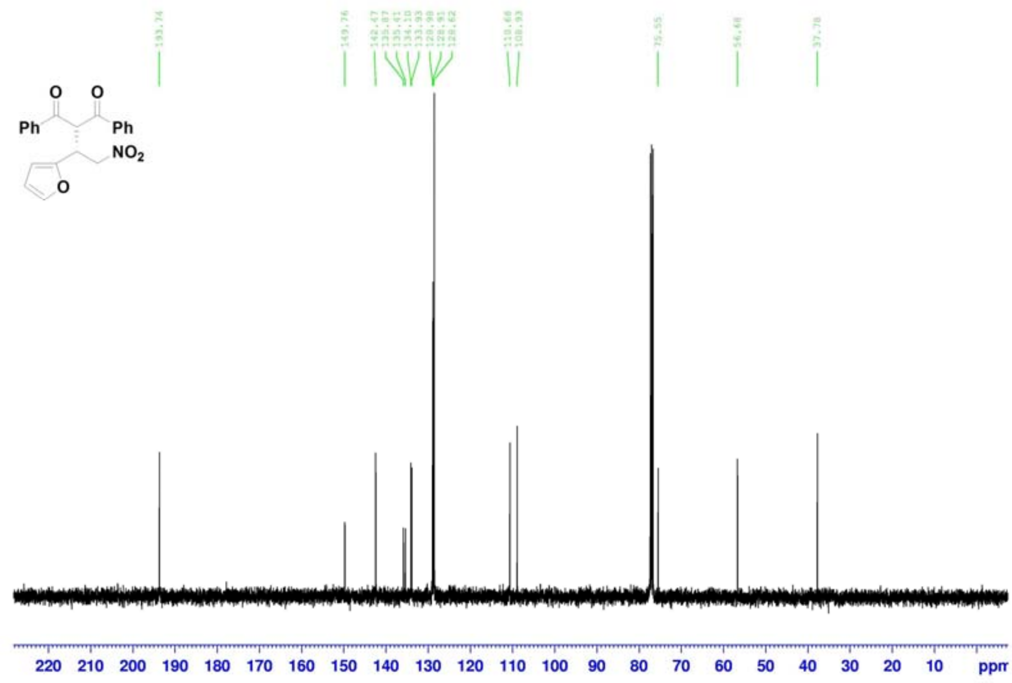
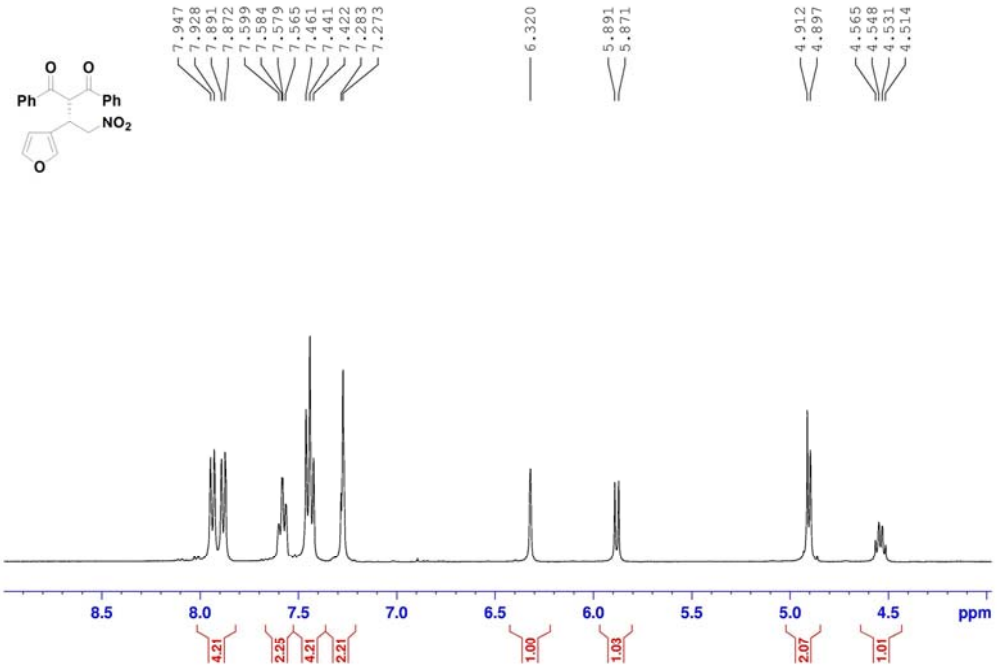
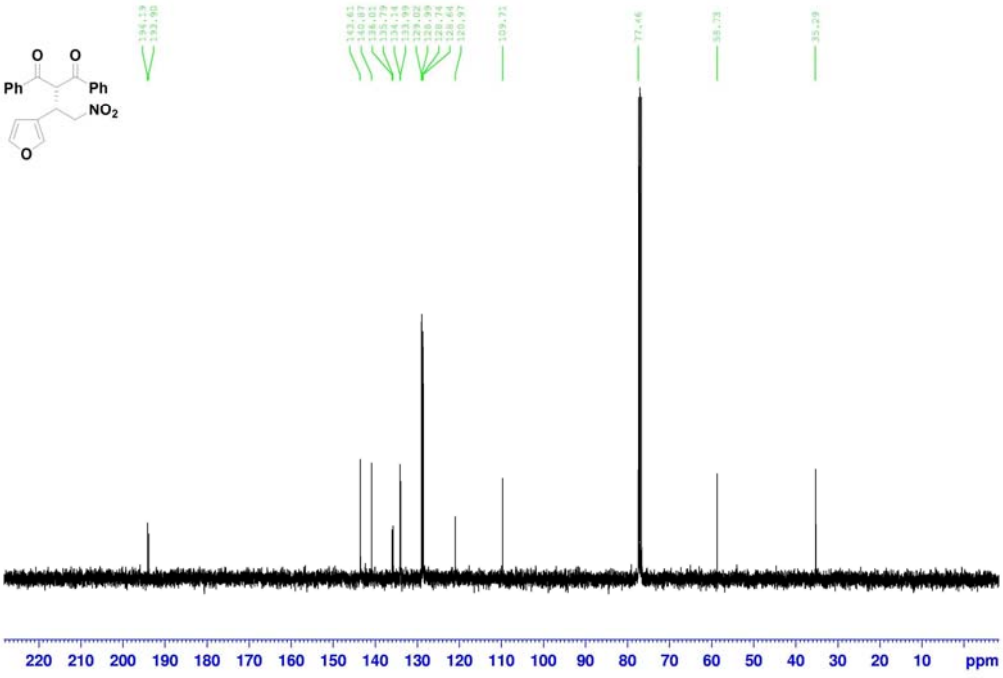
7.5
7.0
6.5
6.0
5.5
5.0
ppm
4.33
2.20
4.32
1.00
1.06
1.04
1.13
2.22
1.13

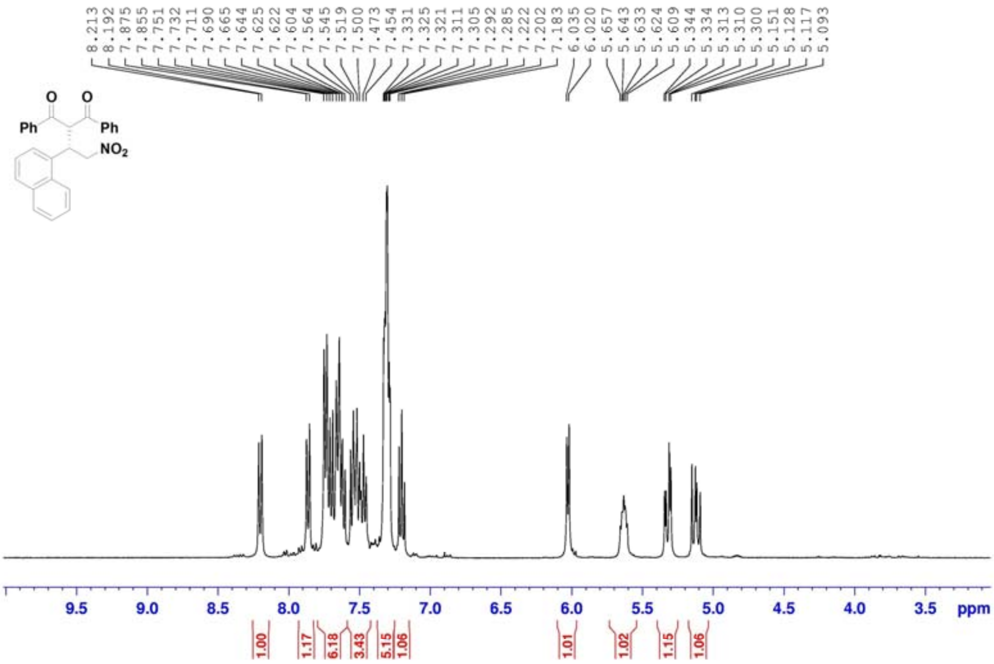

O
O
Ph
Ph
NO2
S
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

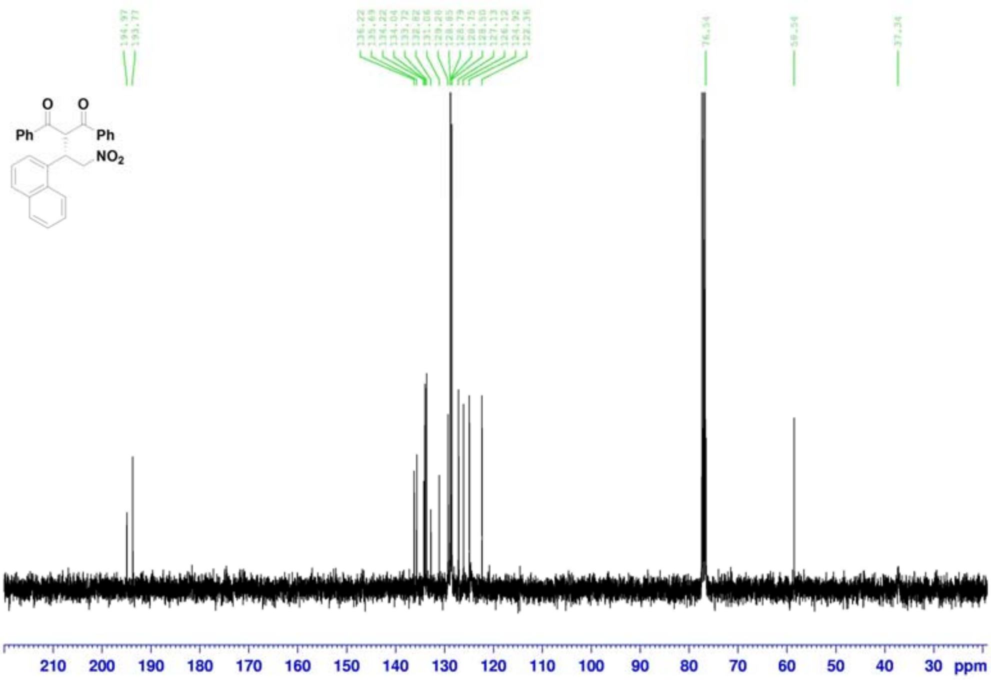

7.887
7.869
7.854
7.583
7.565
7.547
7.445
7.426
7.412
7.393
7.233
6.134
6.050
6.031
5.008
4.997
4.974
4.964
4.955
4.934
4.922
4.901
4.774
4.763
4.754
4.743
4.733
4.723
Ph
Ph
O
O
NO2
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
ppm
3.96
2.29
4.06
0.94
1.88
1.00
2.03
0.99

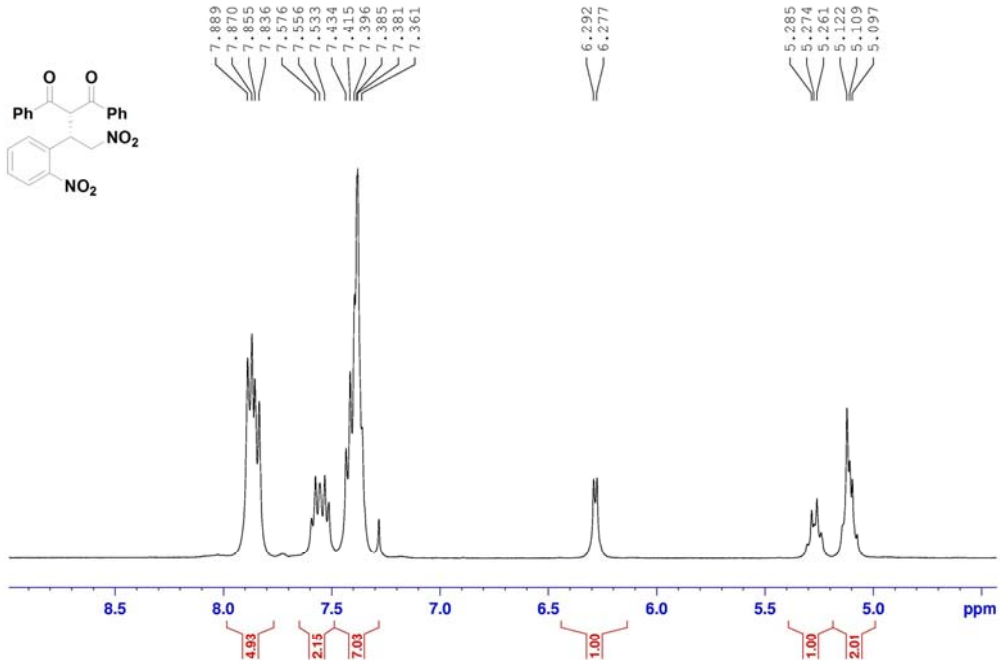

Ph
Ph
O
O
NO2
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

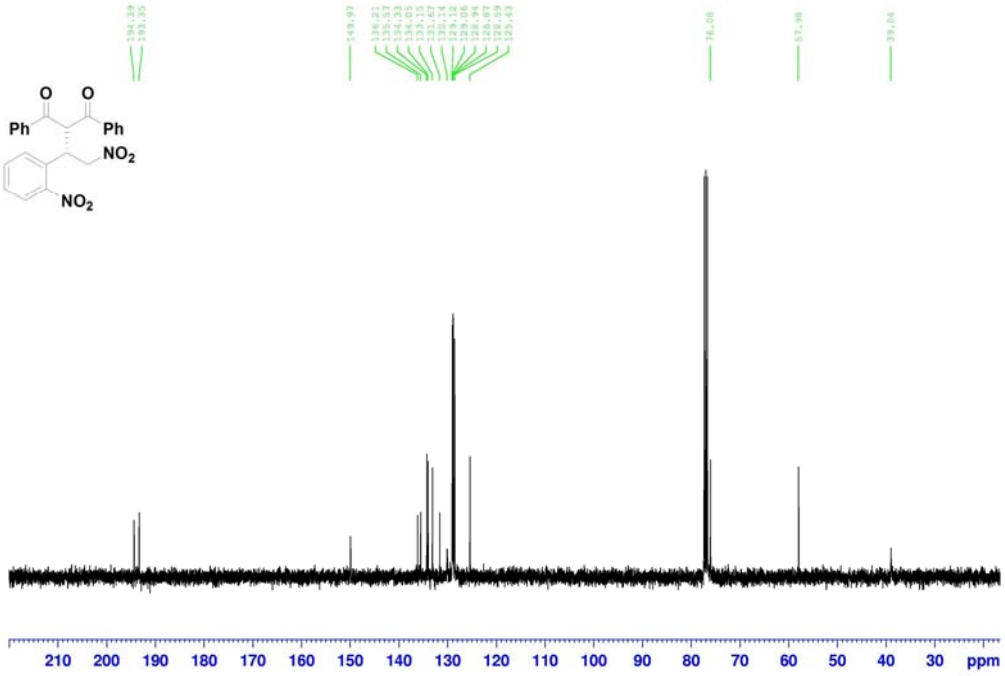

7.947
7.928
7.891
7.872
7.599
7.584
7.579
7.565
7.461
7.441
7.422
7.283
7.273
6.320
5.891
5.871
4.912
4.897
4.565
4.548
4.531
4.514
Ph
Ph
NO2
O
O
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
ppm
4.21
2.25
4.21
2.21
1.00
1.03
2.07
1.01

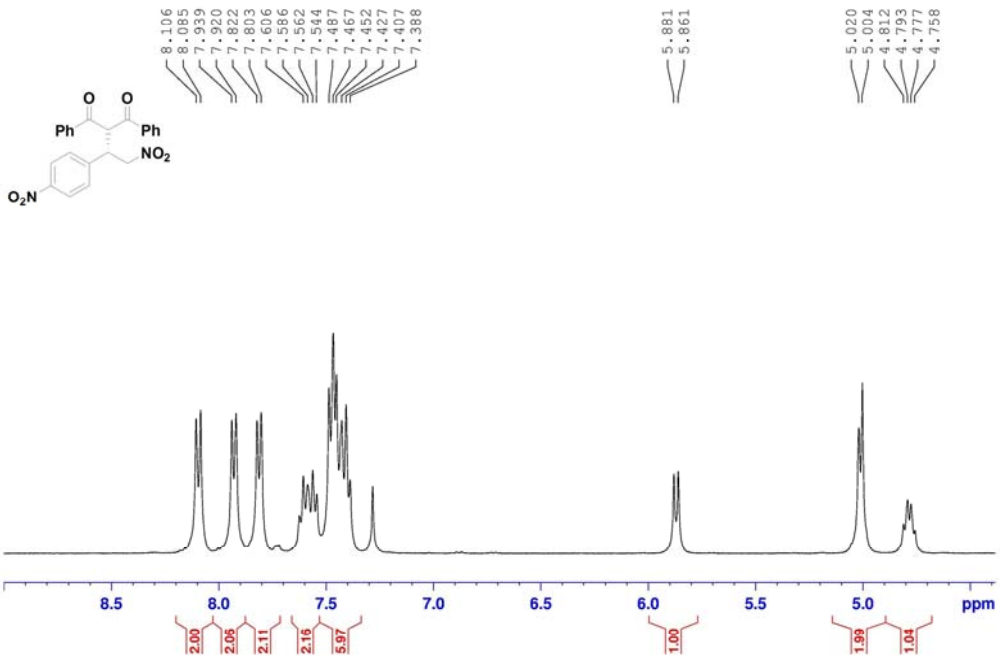

Ph
Ph
NO2
O
O
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

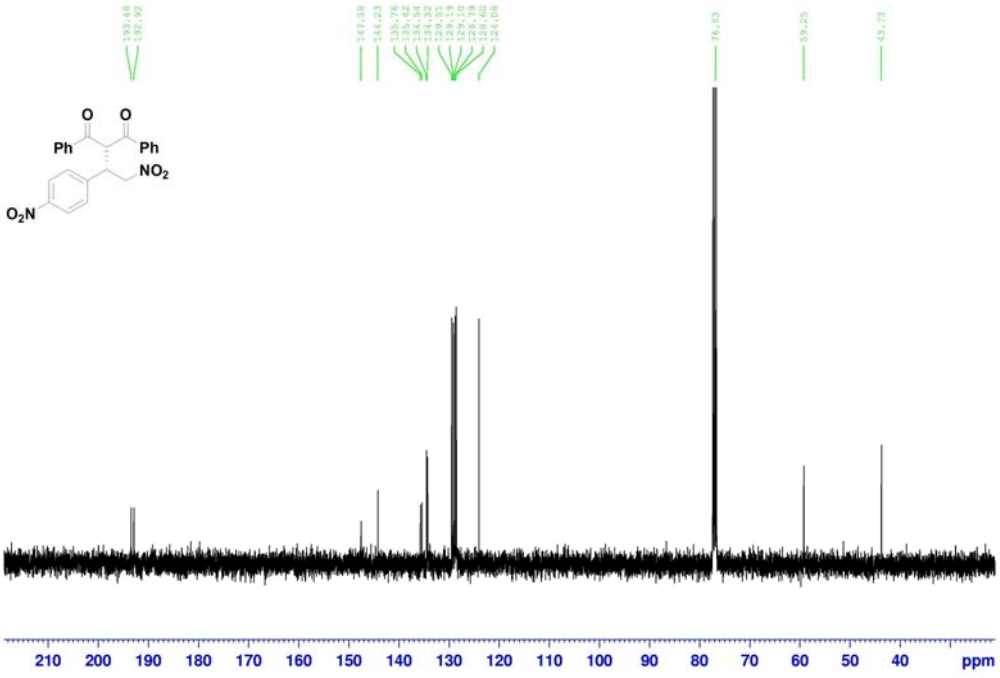

8.213
8.192
7.875
7.855
7.751
7.732
7.711
7.690
7.665
7.644
7.625
7.622
7.604
7.564
7.545
7.519
7.500
7.473
7.454
7.331
7.325
7.321
7.311
7.305
7.292
7.285
7.222
7.202
7.183
6.035
6.020
5.657
5.643
5.633
5.624
5.609
5.344
5.334
5.313
5.310
5.300
5.151
5.128
5.117
5.093
O
O
Ph
Ph
NO_2
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 ppm
1.00
1.17
6.18
3.43
5.15
1.06
1.01
1.02
1.15
1.06

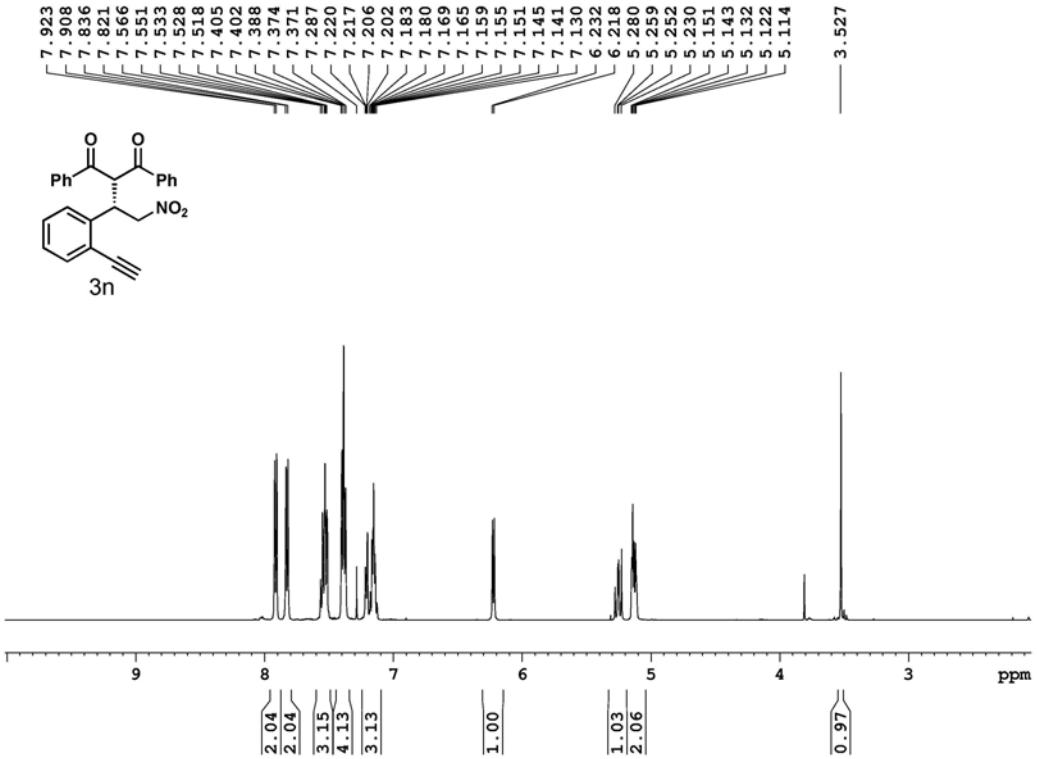

194.97
193.77
136.22
135.69
134.22
134.04
133.72
132.82
131.06
129.26
128.85
128.79
128.75
128.50
127.13
126.12
124.92
122.36
76.54
58.54
37.34
O
O
Ph
Ph
NO_2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

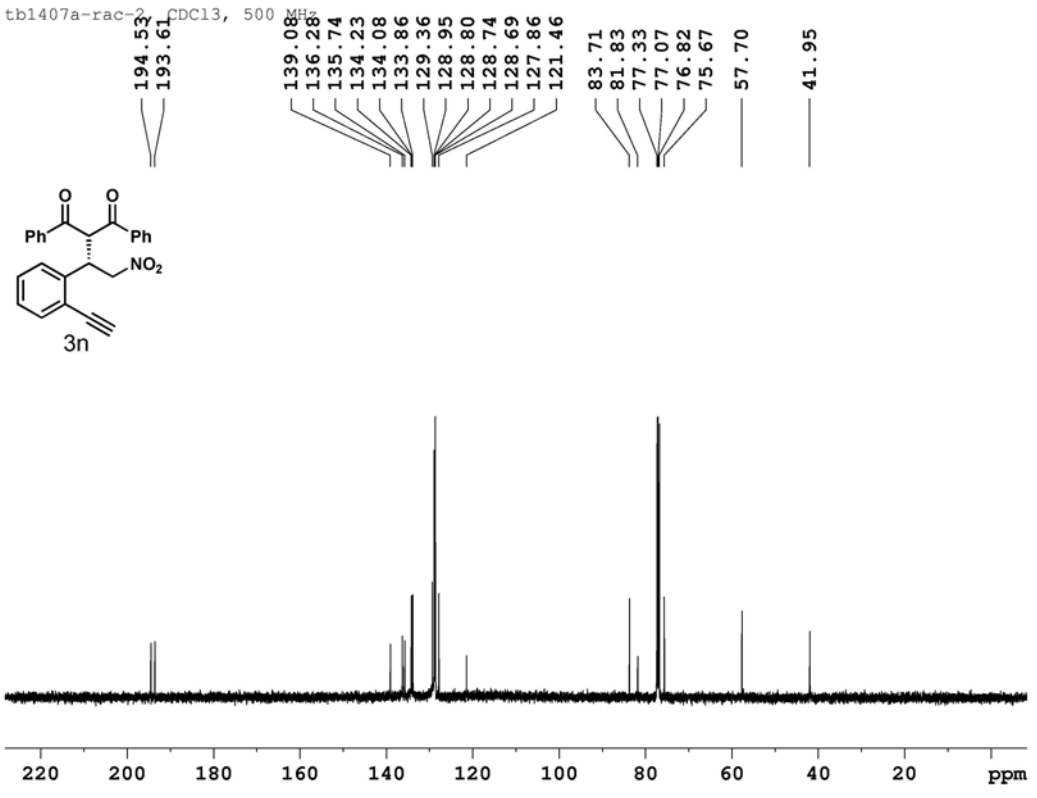

7.889
7.870
7.855
7.836
7.576
7.556
7.533
7.434
7.415
7.396
7.385
7.381
7.361
6.292
6.277
5.285
5.274
5.261
5.122
5.109
5.097
O
O
Ph
Ph
NO2
NO2
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
ppm
4.93
2.15
7.03
1.00
1.00
2.01

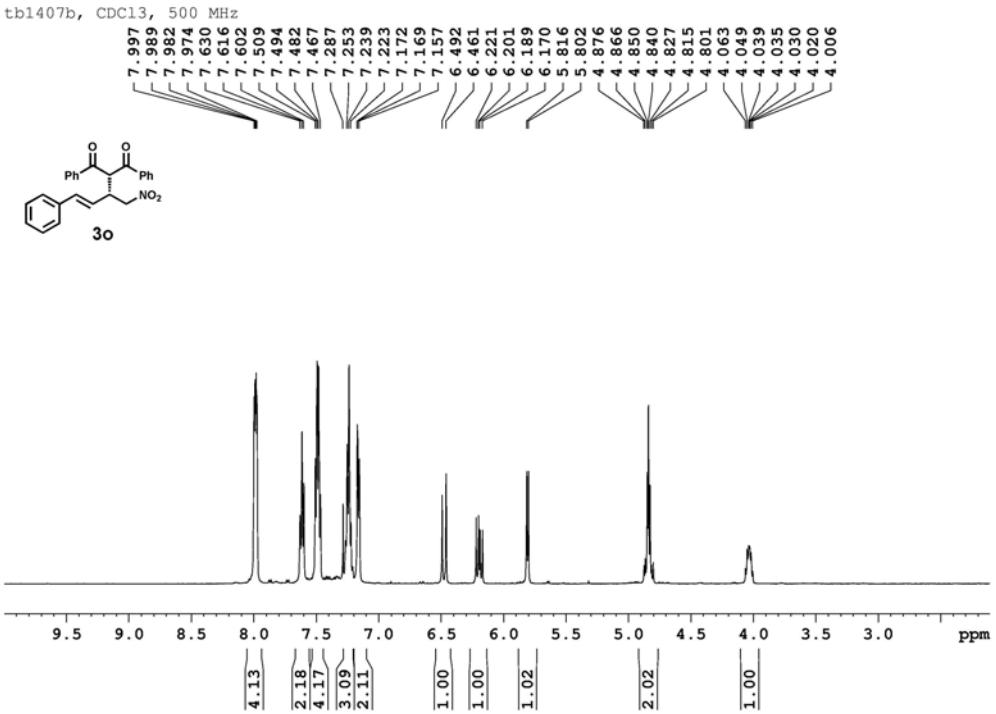

O
O
Ph
Ph
NO2
NO2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

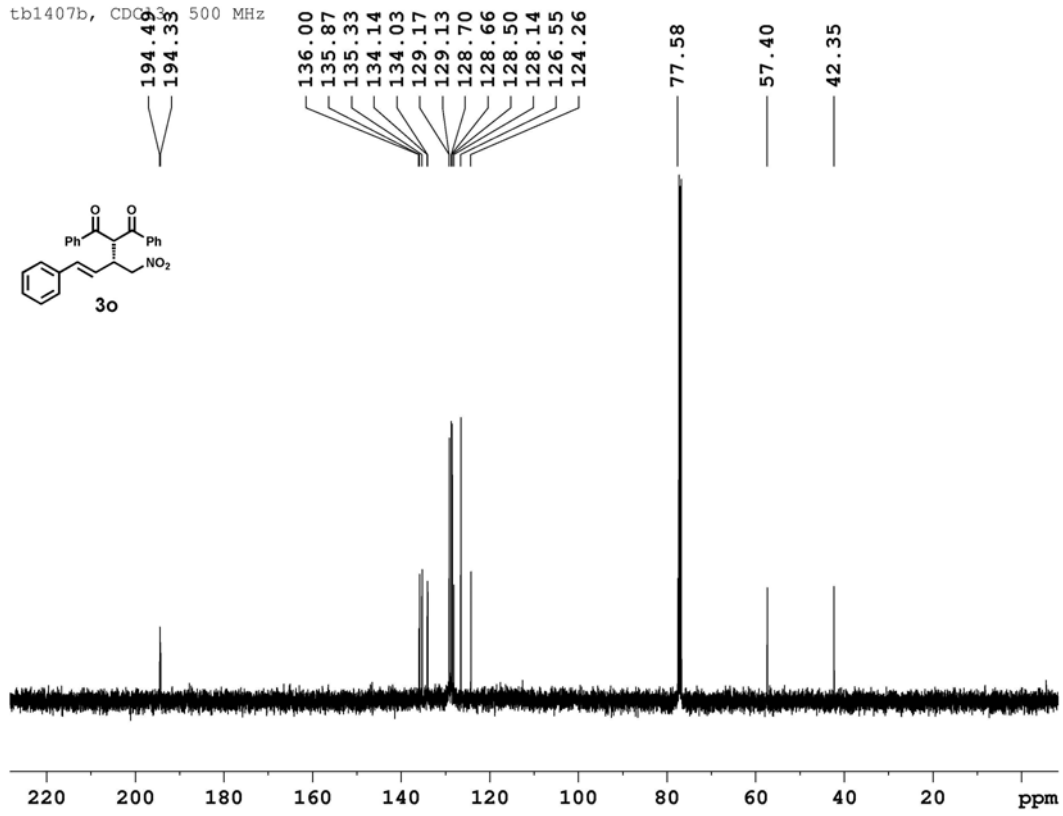

8.106
8.085
7.939
7.920
7.822
7.803
7.606
7.586
7.562
7.544
7.487
7.467
7.452
7.427
7.407
7.388
5.881
5.861
5.020
5.004
4.812
4.793
4.777
4.758
Ph
Ph
NO2
O2N
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
ppm
2.00
2.06
2.11
2.16
5.97
1.00
1.99
1.04

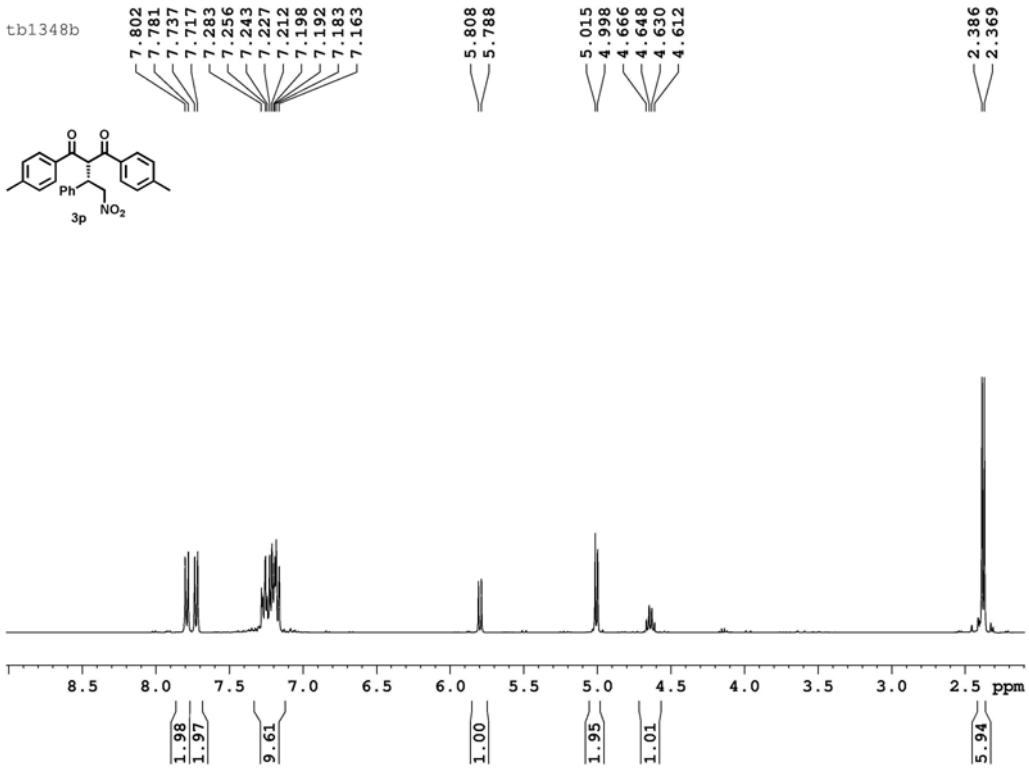

Ph
Ph
NO2
O2N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

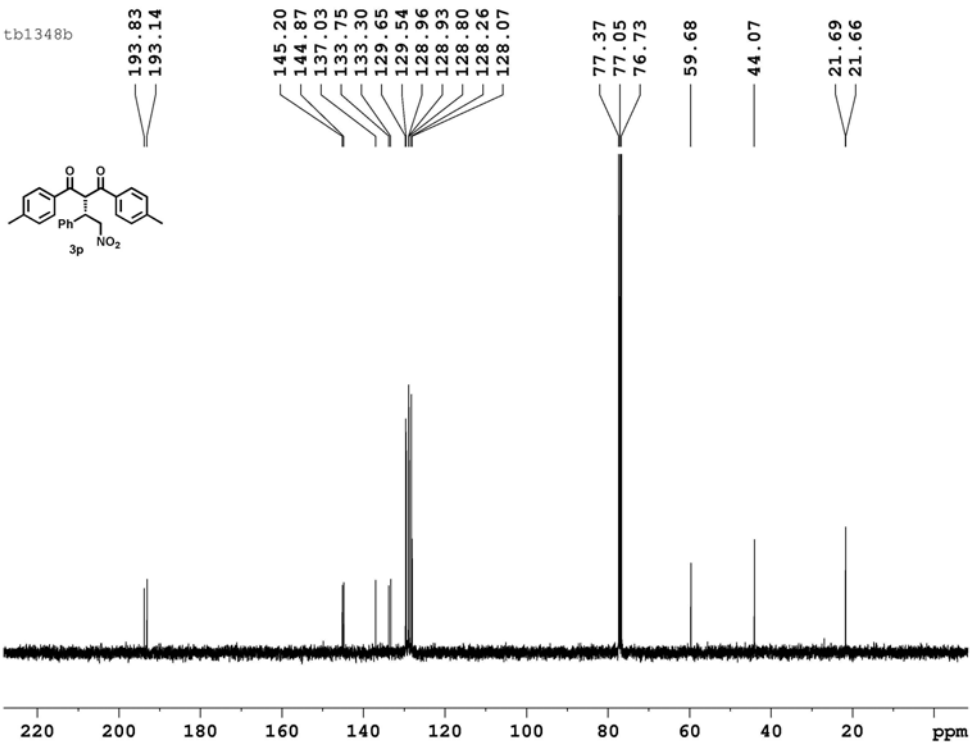

7.923
7.908
7.836
7.821
7.566
7.551
7.533
7.528
7.518
7.405
7.402
7.388
7.374
7.371
7.287
7.220
7.217
7.206
7.202
7.183
7.180
7.169
7.165
7.159
7.155
7.151
7.145
7.141
7.130
6.232
6.218
5.280
5.259
5.252
5.230
5.151
5.143
5.132
5.122
5.114
3.527
Ph
Ph
NO2
3n
9
8
7
6
5
4
3
ppm
2.04
2.04
3.15
4.13
3.13
1.00
1.03
2.06
0.97


tb1407a-rac-2, CDCl3, 500 MHz
194.53
193.61
139.08
136.28
135.74
134.23
134.08
133.86
129.36
128.95
128.80
128.74
128.69
127.86
121.46
83.71
81.83
77.33
77.07
76.82
75.67
57.70
41.95
Ph
Ph
NO2
3n
220
200
180
160
140
120
100
80
60
40
20
ppm

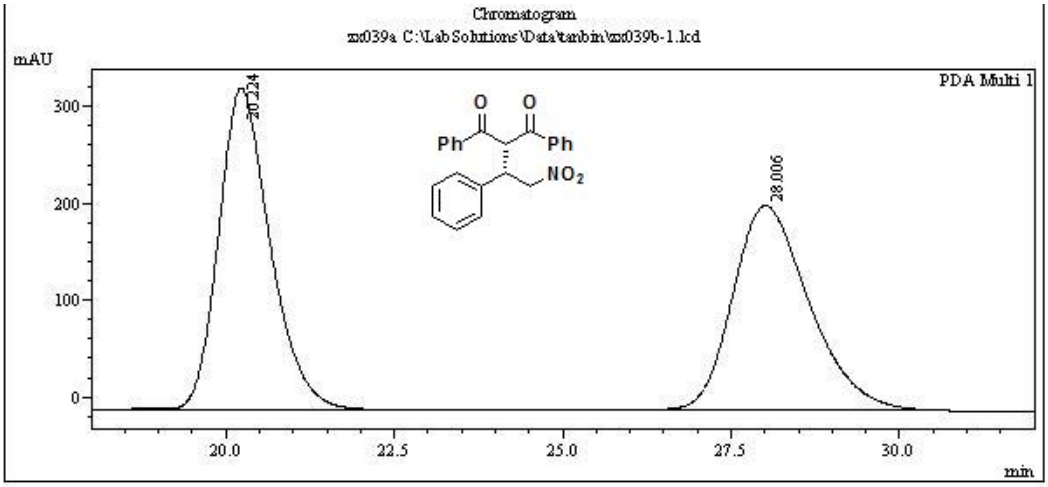

tb1407b, CDCl3, 500 MHz
7.997
7.989
7.982
7.974
7.630
7.616
7.602
7.509
7.494
7.482
7.467
7.287
7.253
7.239
7.223
7.172
7.169
7.157
6.492
6.461
6.221
6.201
6.189
6.170
5.816
5.802
4.876
4.866
4.850
4.840
4.827
4.815
4.801
4.063
4.049
4.039
4.035
4.030
4.020
4.006
Ph
Ph
NO2
3o
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
4.13
2.18
4.17
3.09
2.11
1.00
1.00
1.02
2.02
1.00


tb1407b, CDCl3, 500 MHz
194.49
194.33
136.00
135.87
135.33
134.14
134.03
129.17
129.13
128.70
128.66
128.50
128.14
126.55
124.26
77.58
57.40
42.35
Ph
Ph
NO2
3o
220
200
180
160
140
120
100
80
60
40
20
ppm


tb1348b
7.802
7.781
7.737
7.717
7.283
7.256
7.243
7.227
7.212
7.198
7.192
7.183
7.163
5.808
5.788
5.015
4.998
4.666
4.648
4.630
4.612
2.386
2.369
Ph
NO2
3p
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
ppm
1.98
1.97
9.61
1.00
1.95
1.01
5.94


tb1348b
193.83
193.14
145.20
144.87
137.03
133.75
133.30
129.65
129.54
128.96
128.93
128.80
128.26
128.07
77.37
77.05
76.73
59.68
44.07
21.69
21.66
Ph
NO2
3p
220
200
180
160
140
120
100
80
60
40
20
ppm

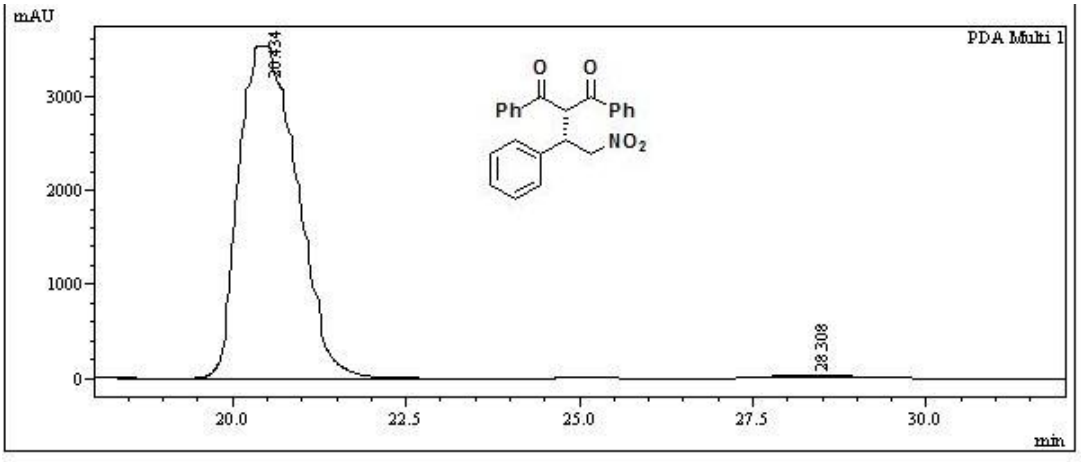
HPLC Spectra



PeakTable

PDA Ch1 210nm 4nm

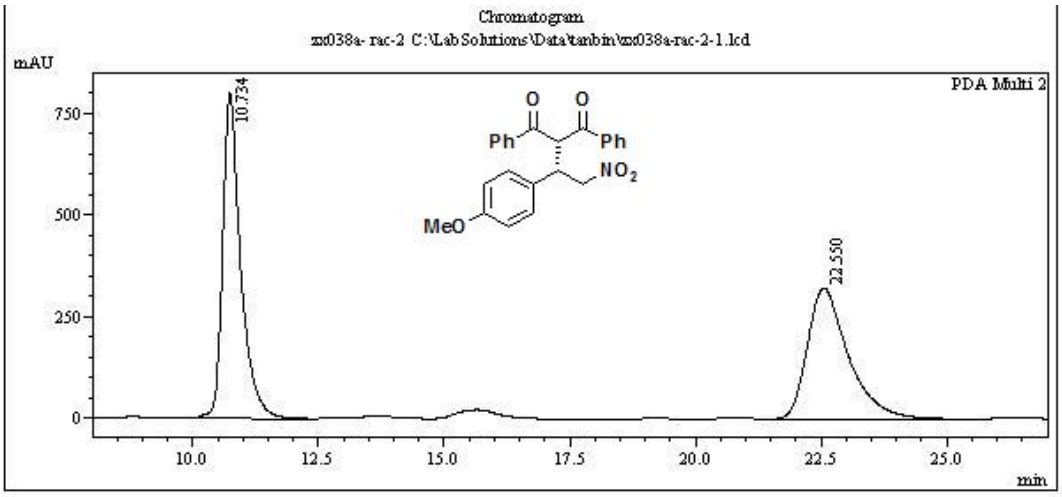
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.224	17610461	331998	51.382	61.138
2	28.006	16663391	211033	48.618	38.862
Total		34273852	543031	100.000	100.000



PeakTable

PDA Ch1 210nm 4nm

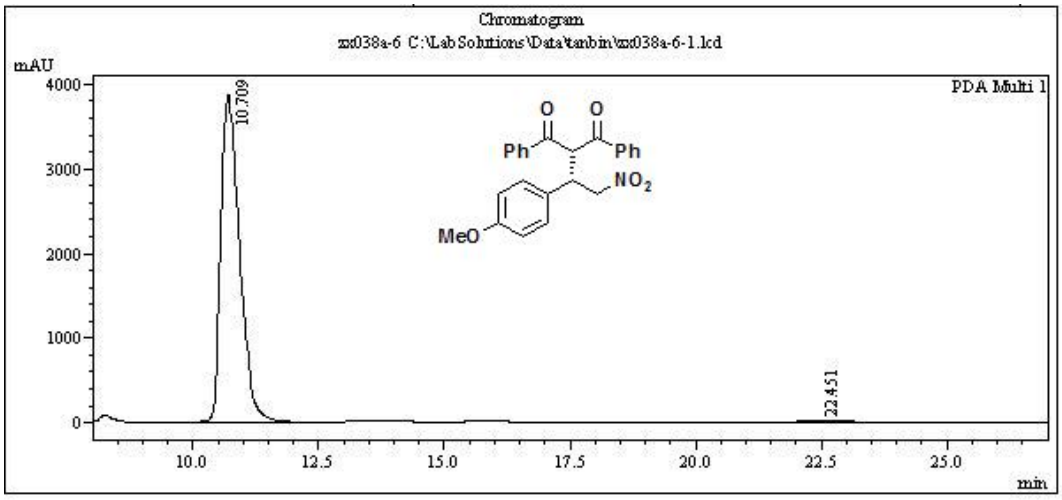
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.434	206272333	3532167	98.901	99.024
2	28.308	2291766	34797	1.099	0.976
Total		208564099	3566964	100.000	100.000



PeakTable

PDA Ch2 230nm 4nm

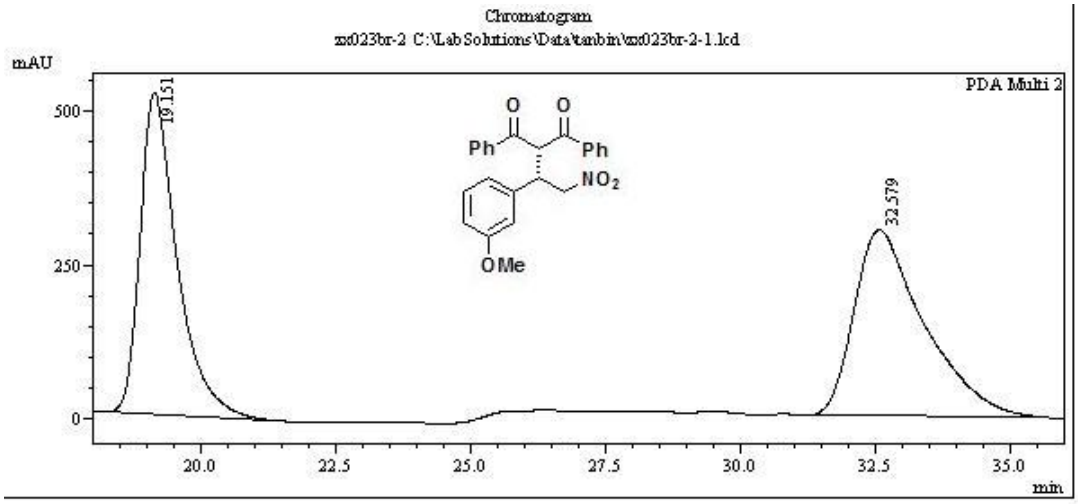
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.734	19890097	802102	52.254	71.395
2	22.550	18173973	321362	47.746	28.605
Total		38064070	1123464	100.000	100.000



PeakTable

PDA Ch1 210nm 4nm

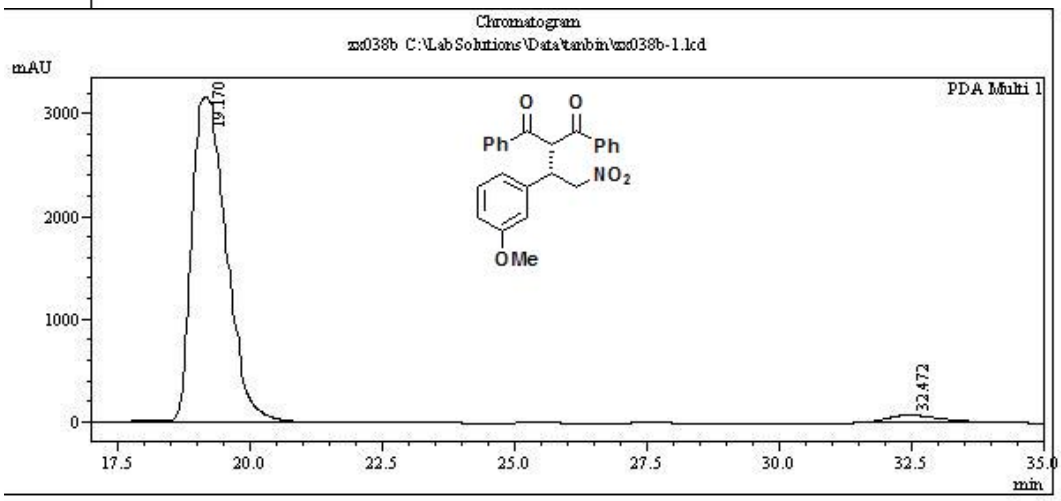
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.709	101060917	3870196	98.560	99.297
2	22.451	1476306	27385	1.440	0.703
Total		102537222	3897581	100.000	100.000



PeakTable

PDA Ch2 230nm 4nm

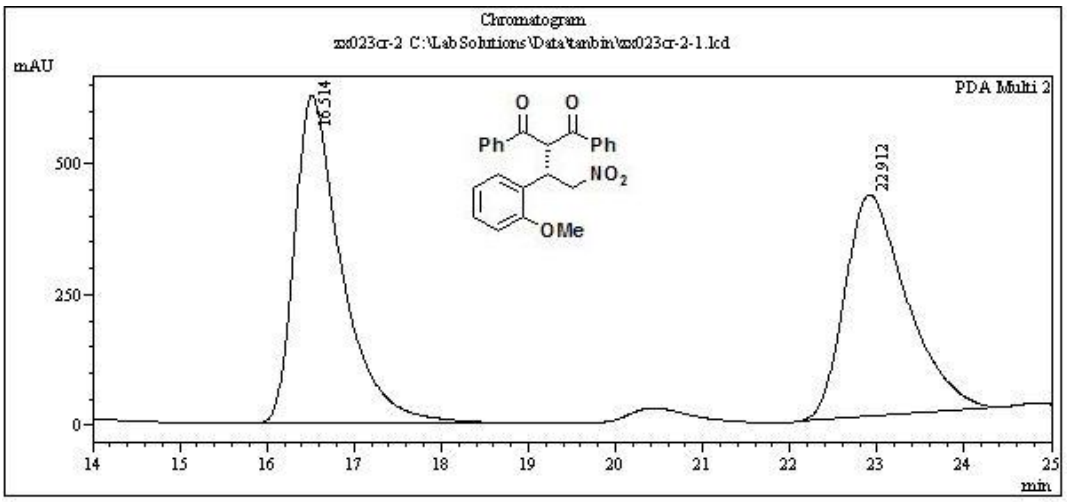
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.151	25001049	523123	48.074	63.418
2	32.579	27004392	301757	51.926	36.582
Total		52005441	824880	100.000	100.000



PeakTable

PDA Ch1 210nm 4nm

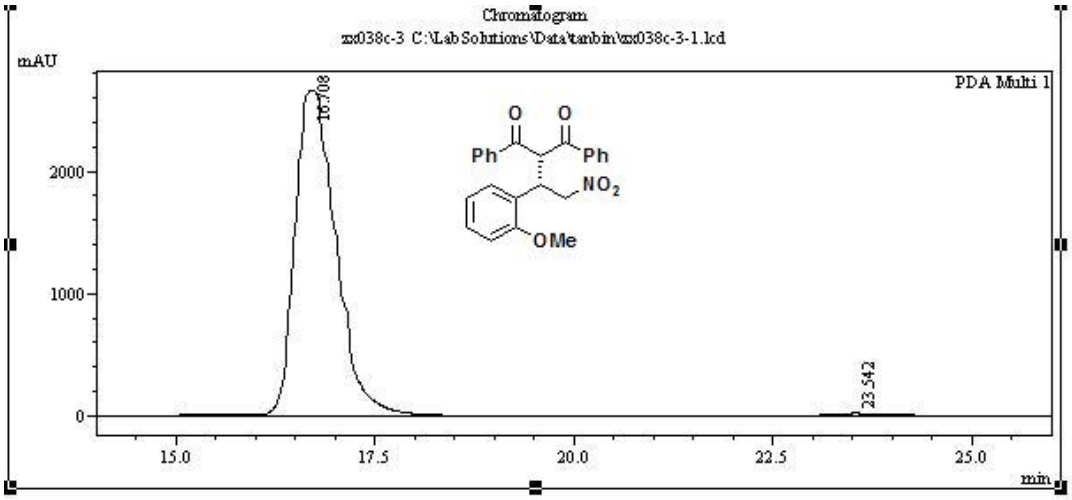
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.170	144405516	3167707	96.414	97.747
2	32.472	5370597	73018	3.586	2.253
Total		149776113	3240725	100.000	100.000



PeakTable

PDA Ch2 230nm 4nm

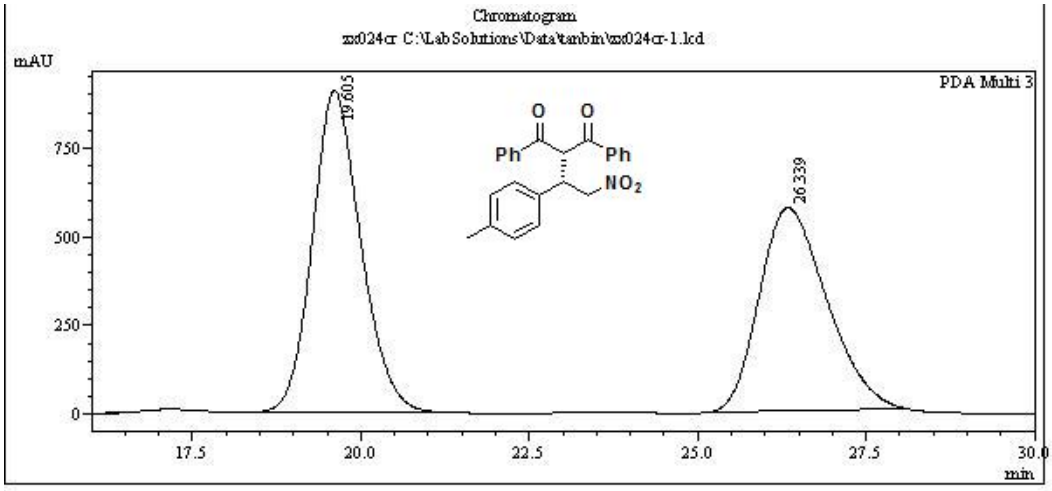
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.514	23522601	627534	52.696	59.665
2	22.912	21115835	424228	47.304	40.335
Total		44638436	1051761	100.000	100.000



PeakTable

PDA Ch1 210nm 4nm

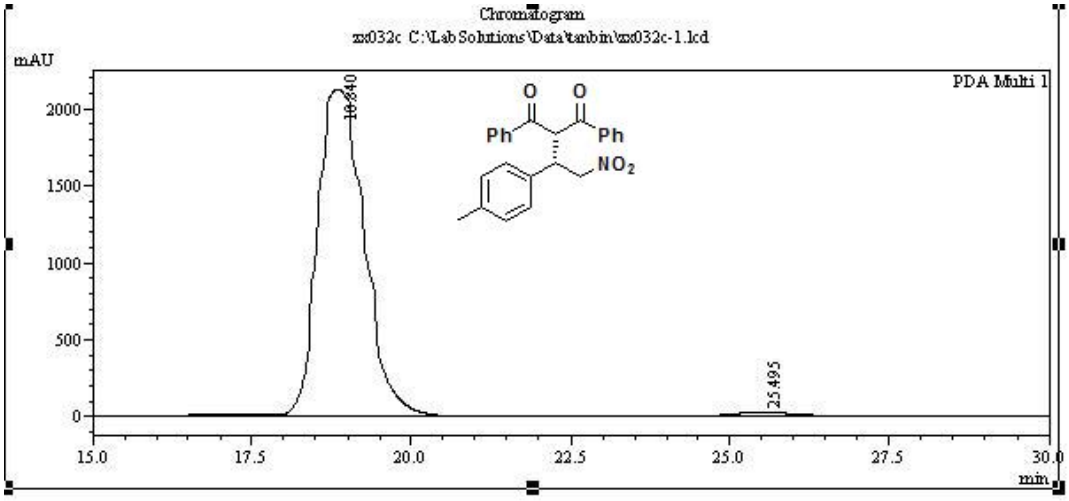
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.708	95435887	2662474	98.912	99.266
2	23.542	1049872	19697	1.088	0.734
Total		96485759	2682170	100.000	100.000



PeakTable

PDA Ch3 254nm 4nm

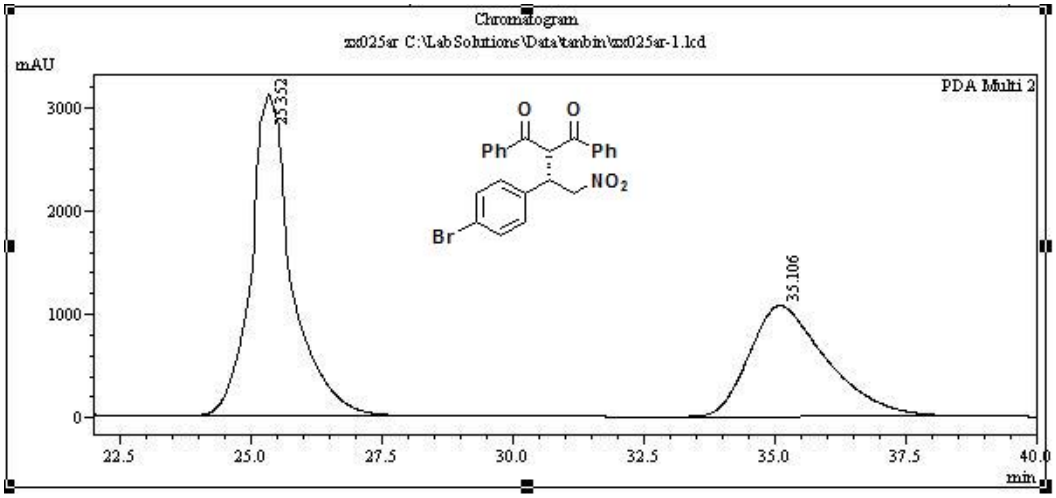
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.605	45384920	907571	53.069	61.308
2	26.339	40136050	572775	46.931	38.692
Total		85520969	1480346	100.000	100.000



PeakTable

PDA Ch1 210nm 4nm

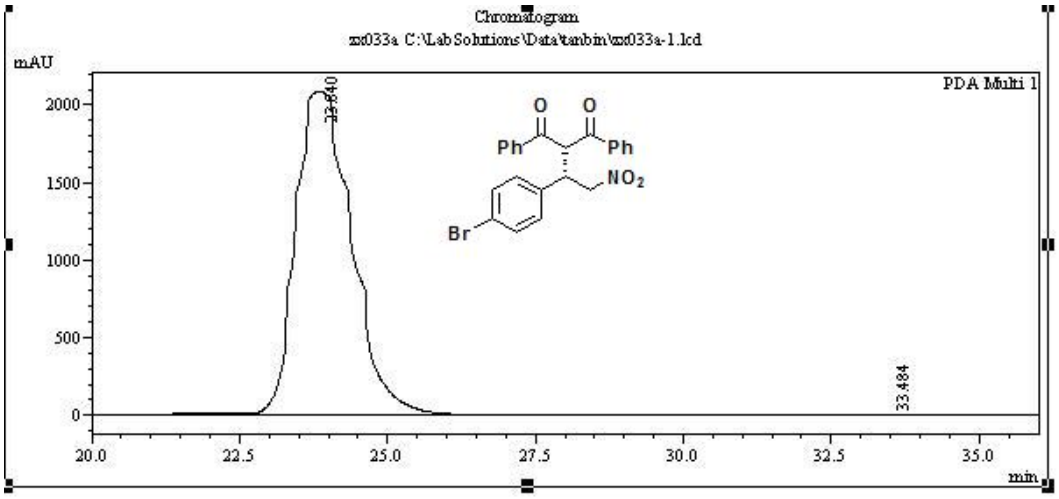
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.840	108580063	2125767	98.480	98.845
2	25.495	1676289	24834	1.520	1.155
Total		110256352	2150601	100.000	100.000



PeakTable

PDA Ch2 230nm 4nm

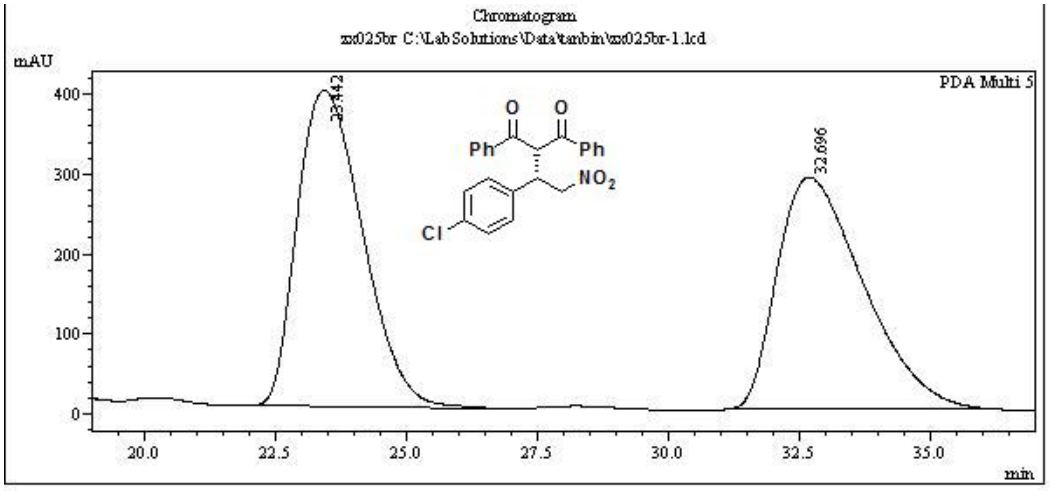
Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.352	167998430	3112430	60.488	74.439
2	35.106	109738788	1068767	39.512	25.561
Total		277737217	4181197	100.000	100.000



PeakTable

PDA Ch1 210nm 4nm

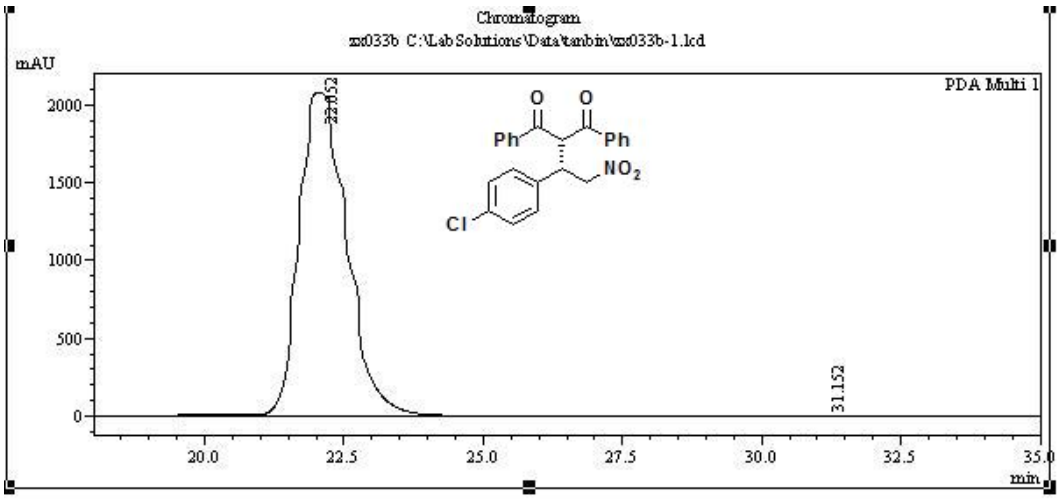
Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.840	137360056	2085064	99.655	99.726
2	33.484	475123	5721	0.345	0.274
Total		137835179	2090785	100.000	100.000



PeakTable

PDA Ch5 280nm 4nm

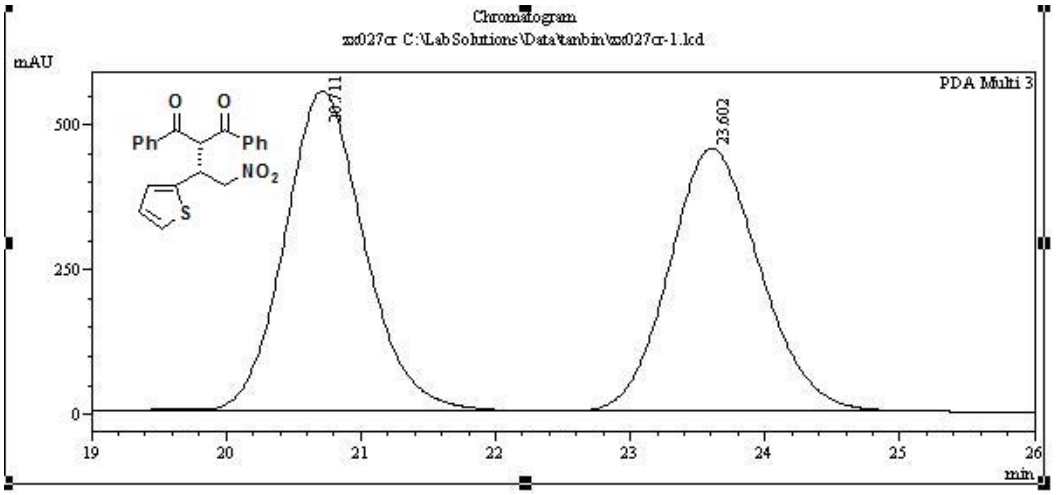
Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.442	34315639	395286	50.911	57.734
2	32.696	33088131	289385	49.089	42.266
Total		67403770	684672	100.000	100.000



PeakTable

PDA Ch1 210nm 4nm

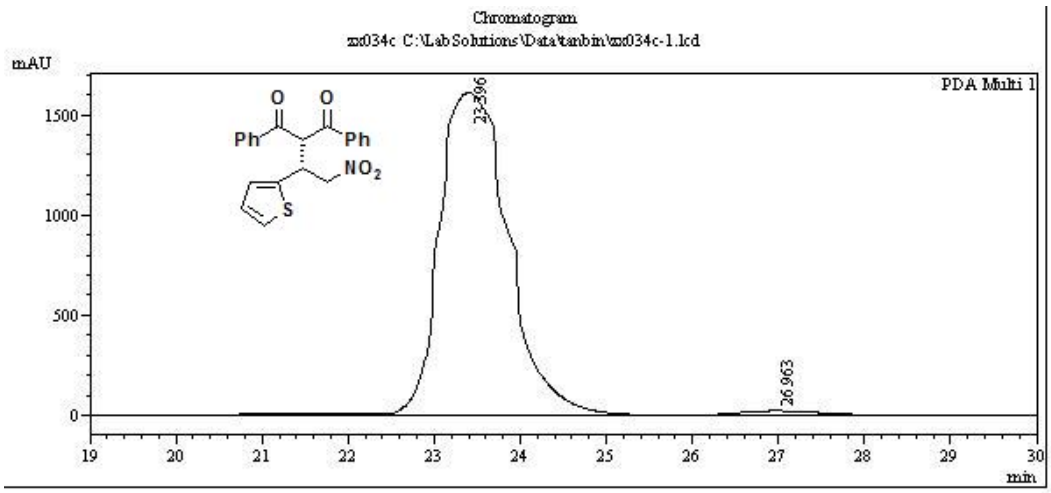
Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.052	124042959	2079693	99.713	99.793
2	31.152	356953	4305	0.287	0.207
Total		124399912	2083998	100.000	100.000



PeakTable

PDA Ch3 254nm 4nm

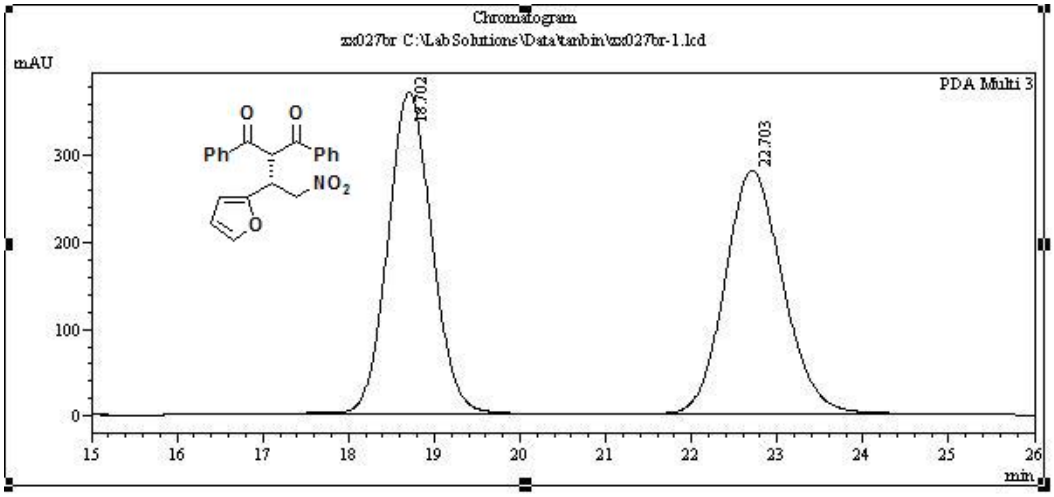
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.711	22717082	552787	51.634	54.920
2	23.602	21279480	453738	48.366	45.080
Total		43996562	1006525	100.000	100.000



PeakTable

PDA Ch1 210nm 4nm

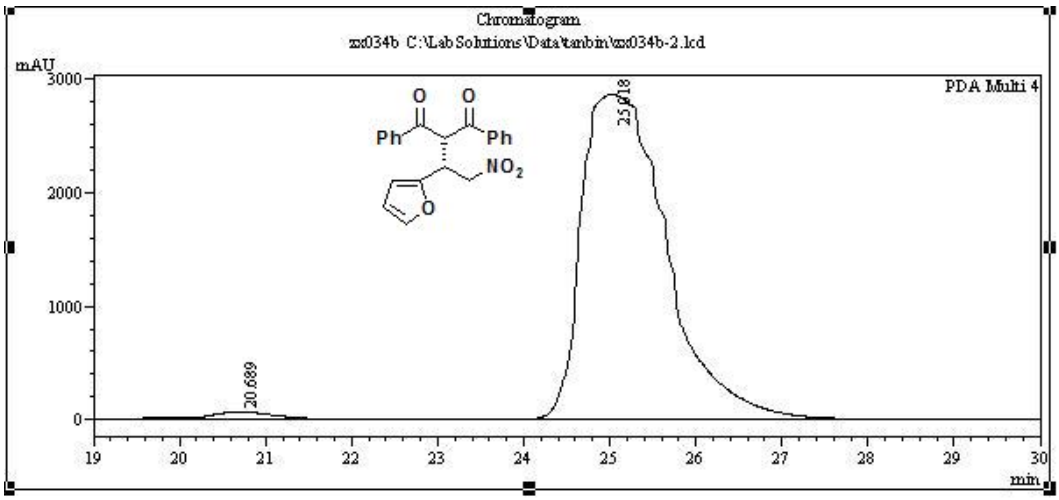
Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.396	89704827	1612541	98.417	98.644
2	26.963	1443068	22172	1.583	1.356
Total		91147895	1634713	100.000	100.000



PeakTable

PDA Ch3 254nm 4nm

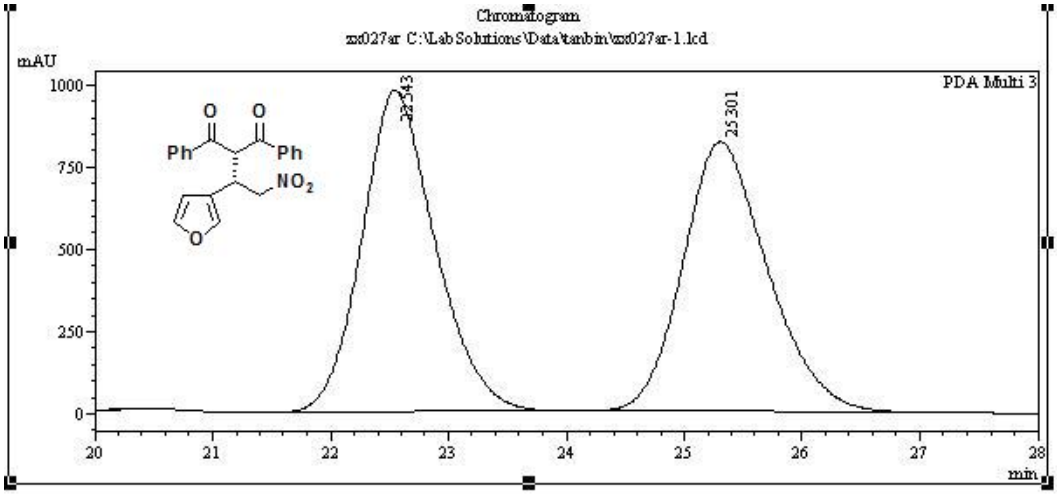
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.702	13252250	370920	50.206	56.972
2	22.703	13143716	280136	49.794	43.028
Total		26395966	651056	100.000	100.000



PeakTable

PDA Ch4 262nm 4nm

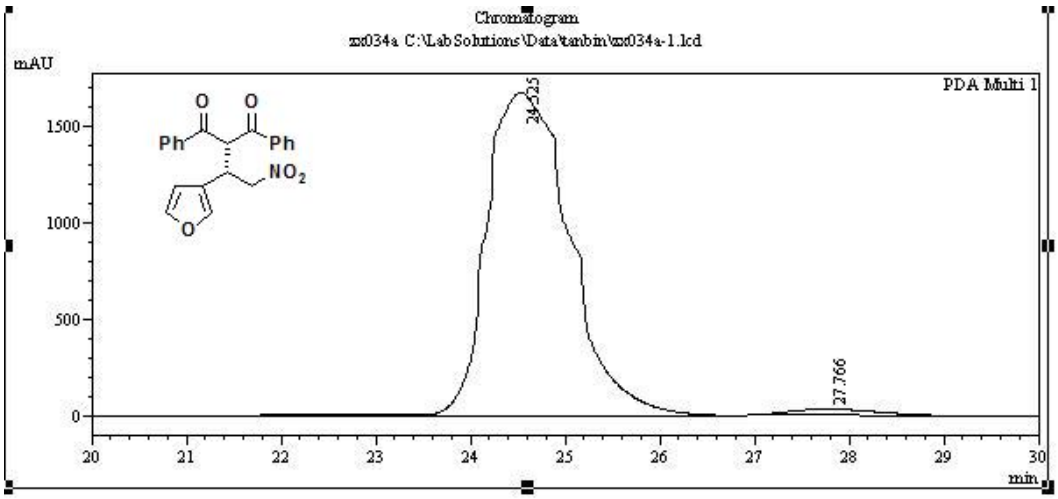
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.689	2538169	58257	1.269	1.990
2	25.018	197422001	2869522	98.731	98.010
Total		199960170	2927779	100.000	100.000



PeakTable

PDA Ch3 254nm 4nm

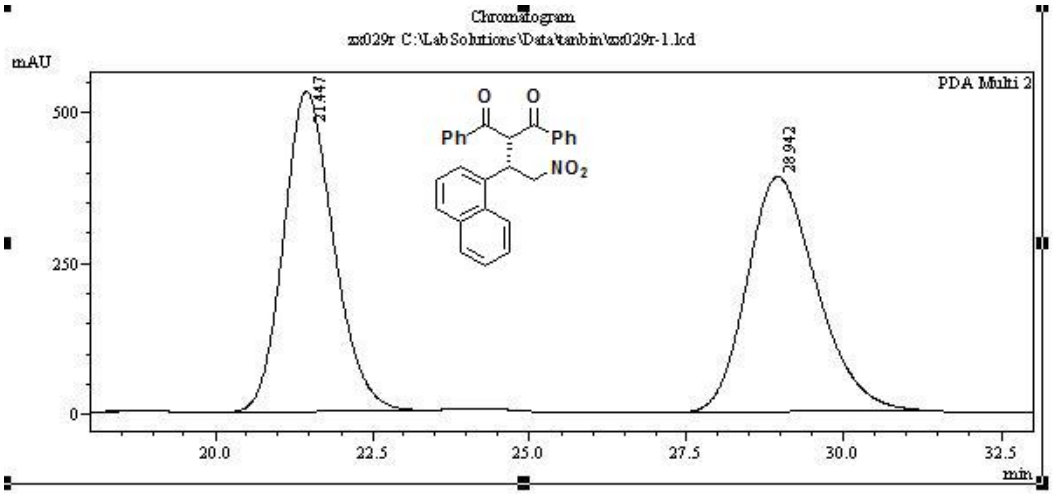
Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.543	42273906	977519	50.719	54.393
2	25.301	41075274	819613	49.281	45.607
Total		83349180	1797131	100.000	100.000



PeakTable

PDA Ch1 210nm 4nm

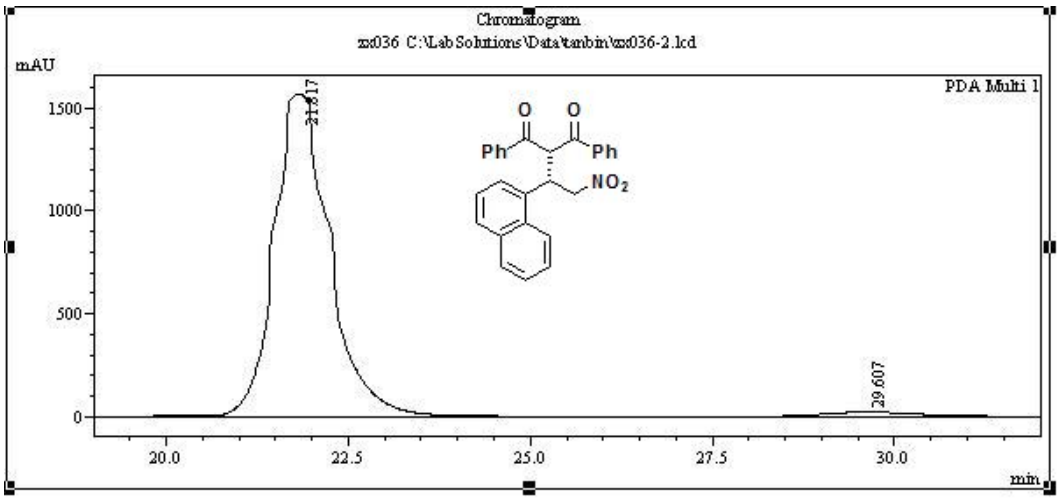
Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.525	101778041	1672455	98.266	98.245
2	27.766	1796403	29868	1.734	1.755
Total		103574444	1702324	100.000	100.000



PeakTable

PDA Ch2 230nm 4nm

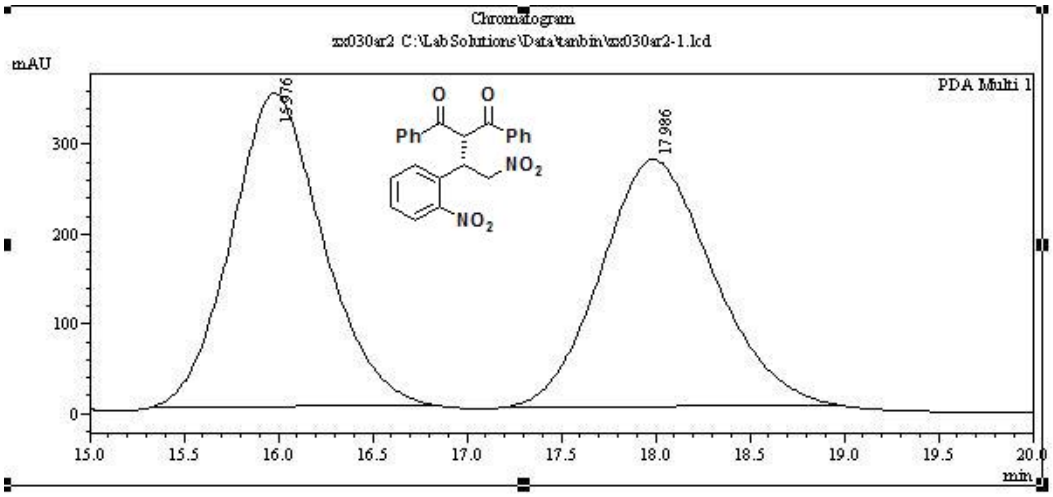
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.447	29360366	530521	49.391	57.673
2	28.942	30084101	389357	50.609	42.327
Total		59444467	919878	100.000	100.000



PeakTable

PDA Ch1 210nm 4nm

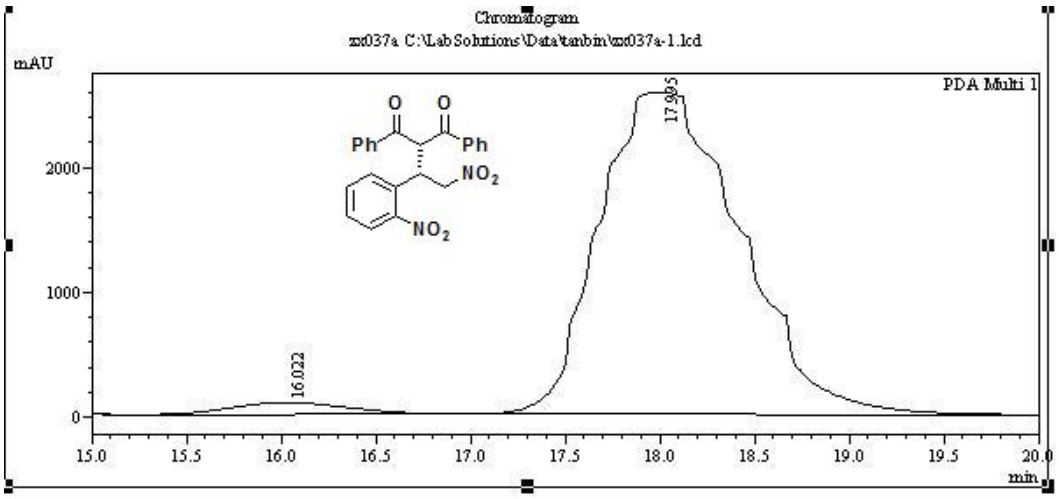
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.817	82888677	1563593	97.800	98.677
2	29.607	1864962	20959	2.200	1.323
Total		84753639	1584552	100.000	100.000



PeakTable

PDA Ch1 210nm 4nm

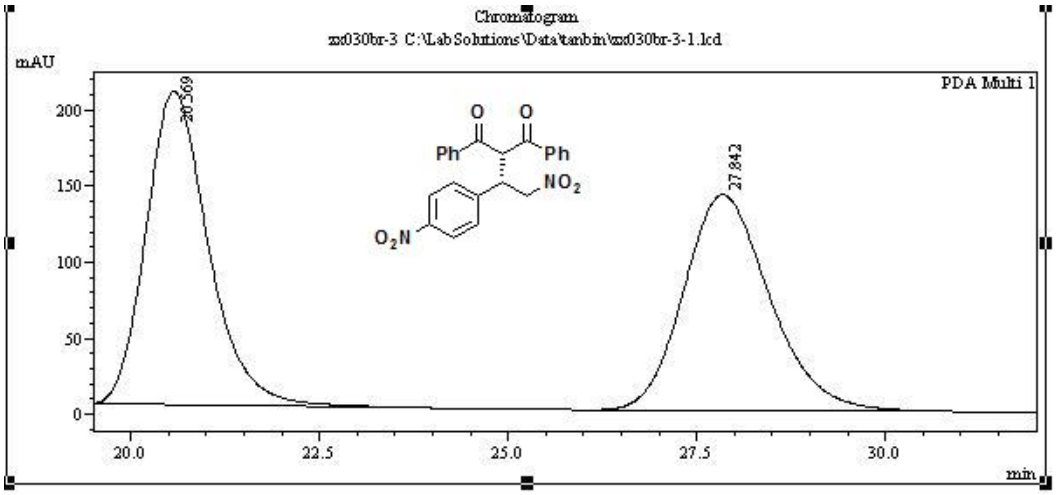
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.976	11828961	349824	50.872	55.982
2	17.986	11423521	275063	49.128	44.018
Total		23252482	624887	100.000	100.000



PeakTable

PDA Ch1 210nm 4nm

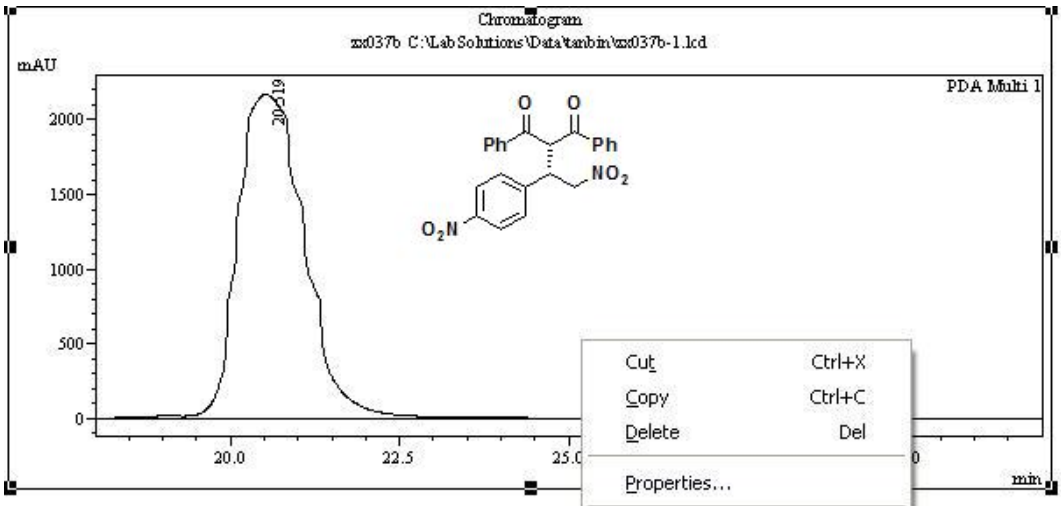
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.022	3854099	92546	2.810	3.463
2	17.995	133303629	2579997	97.190	96.537
Total		137157728	2672543	100.000	100.000



PeakTable

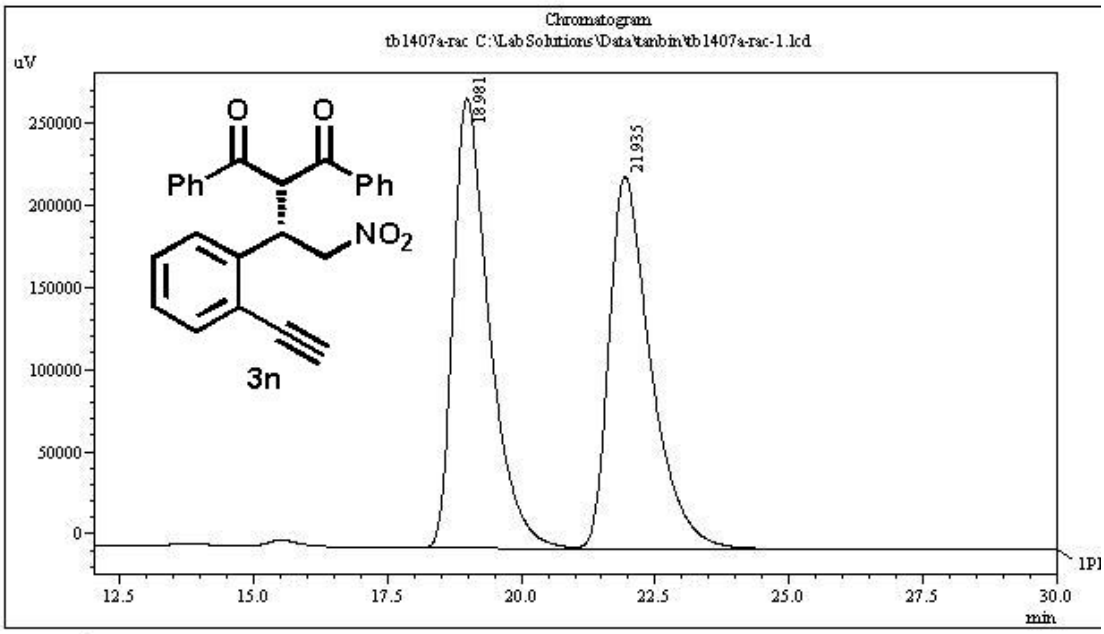
PDA Ch1 210nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.569	11853055	206417	51.384	59.289
2	27.842	11214340	141735	48.616	40.711
Total		23067394	348152	100.000	100.000



PDA Ch1 210nm 4nm

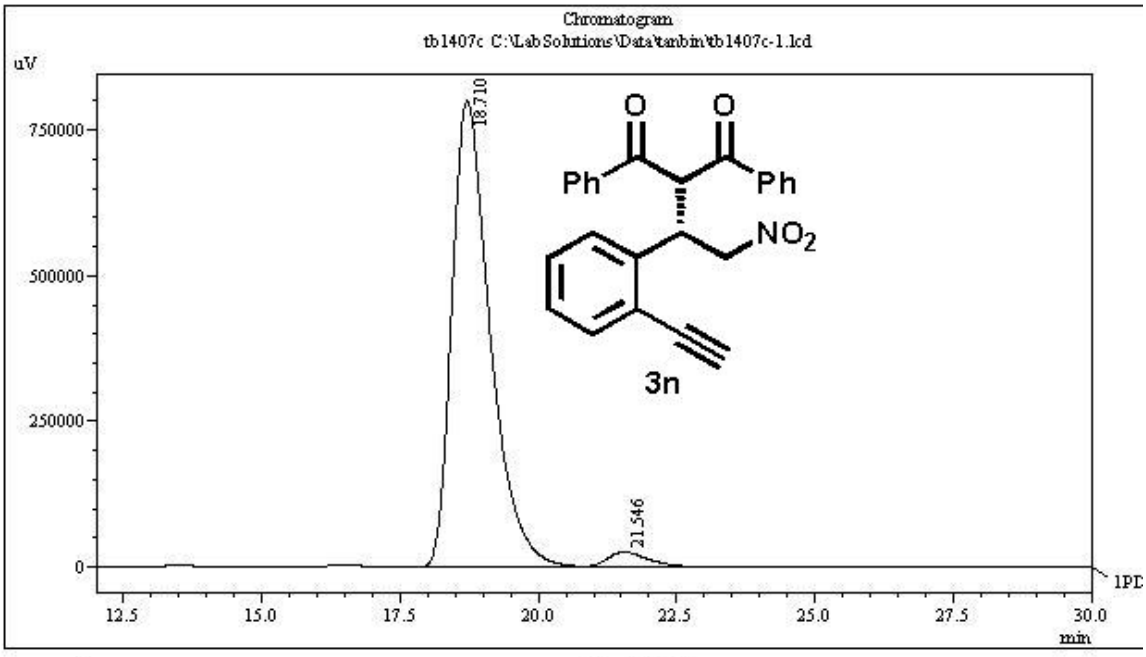
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.519	148699430	2170976	96.974	97.643
2	28.072	4639921	52403	3.026	2.357
Total		153339351	2223380	100.000	100.000



PeakTable

PDA Ch3 254nm 4nm

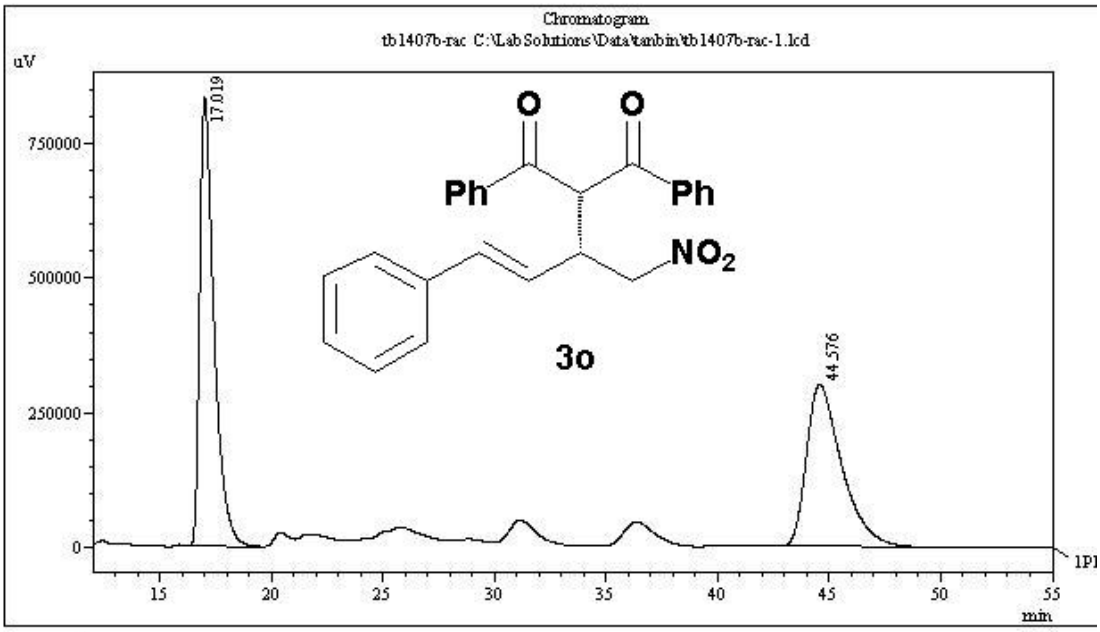
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.981	12809014	273536	51.044	54.727
2	21.935	12284927	226284	48.956	45.273
Total		25093941	499820	100.000	100.000



PeakTable

PDA Ch3 254nm 4nm

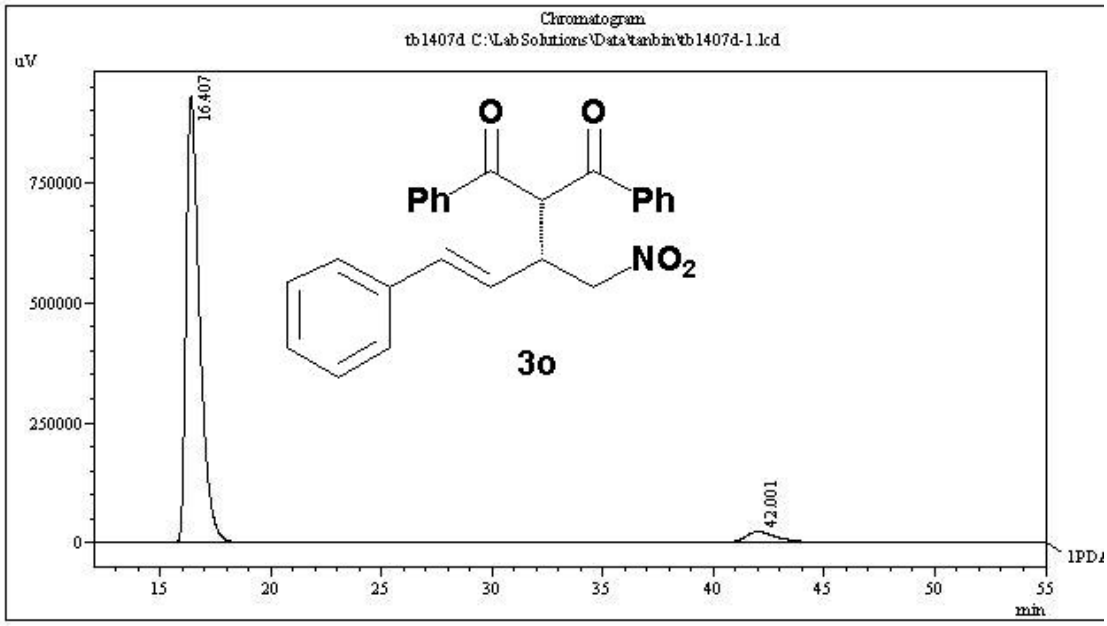
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.710	38574258	800006	96.476	96.822
2	21.546	1409093	26260	3.524	3.178
Total		39983351	826266	100.000	100.000



PeakTable

PDA Ch3 254nm 4nm

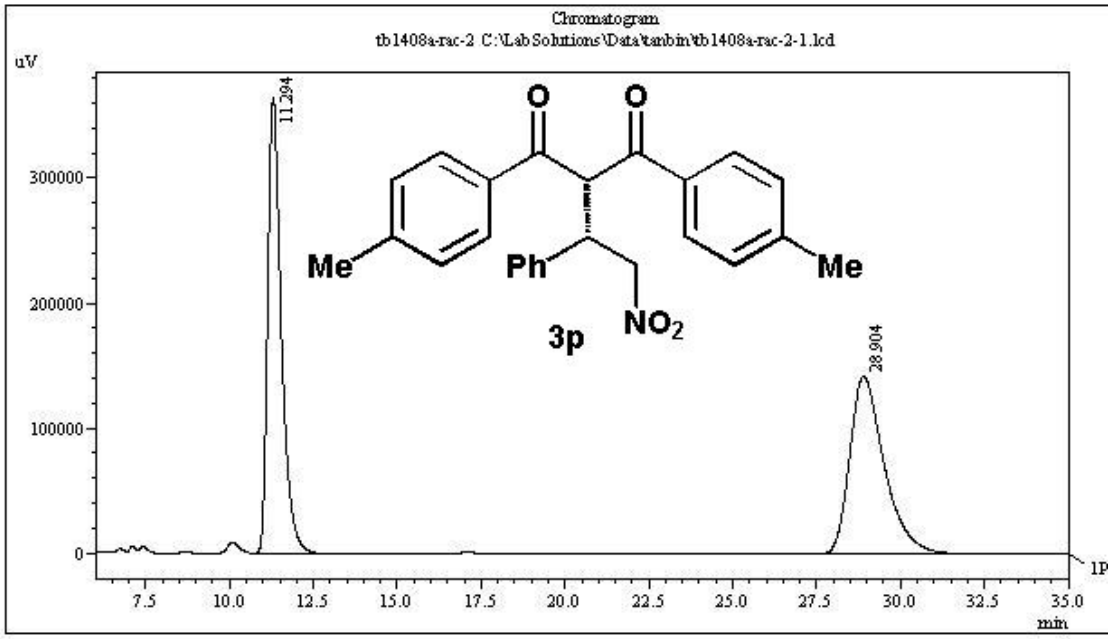
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.019	37270388	832111	52.910	73.460
2	44.576	33170070	300622	47.090	26.540
Total		70440458	1132733	100.000	100.000



PeakTable

PDA Ch3 254nm 4nm

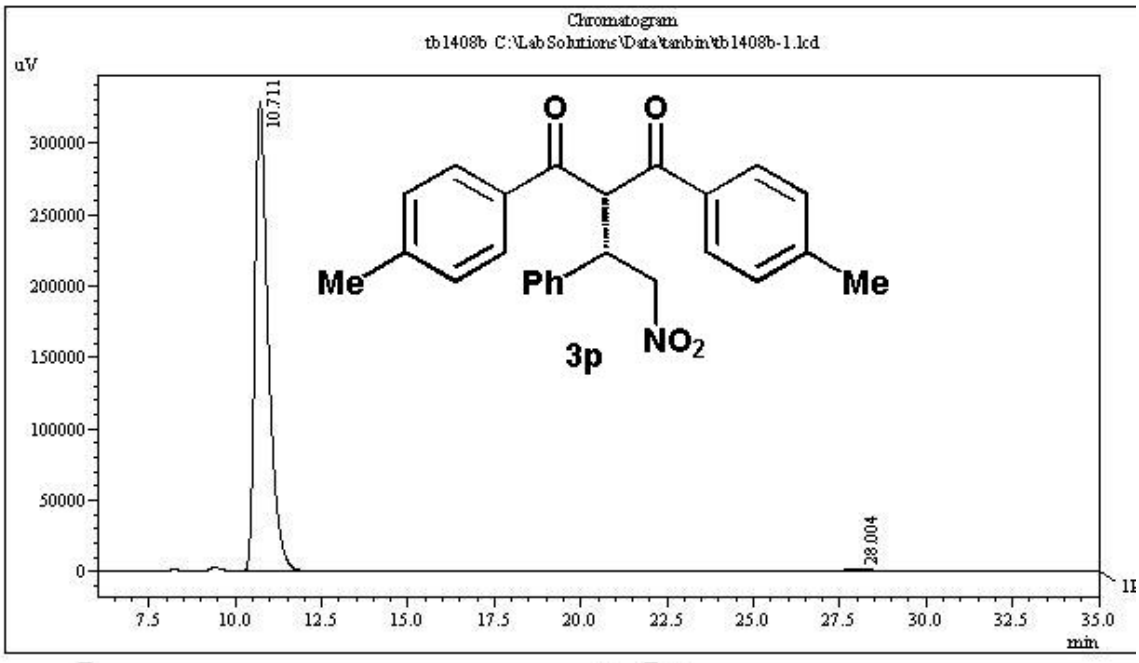
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.407	39559867	928211	94.875	97.685
2	42.001	2136889	21997	5.125	2.315
Total		41696756	950208	100.000	100.000



PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.294	10314045	363990	50.225	71.889
2	28.904	10221447	142334	49.775	28.111
Total		20535492	506325	100.000	100.000



PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.711	8920310	328043	98.690	99.492
2	28.004	118436	1676	1.310	0.508
Total		9038746	329718	100.000	100.000