Continuous Flow, Highly Enantioselective Michael Additions Catalyzed by a PS-Supported Squaramide

Supporting Information

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General Methods

Unless otherwise stated, all commercial reagents were used as received and solvents were used from solvent drying system, all reactions were carried out directly under open air. Merrifield resin (1% DVB, f = 0.53 mmol Cl g^{-1} resin) was obtained from Novabiochem. All flash chromatography was carried out using 60 mesh silica gel and dry-packed columns. The ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz and 500 MHz for ^{1}H or at 100 MHz and 125 MHz for ^{13}C, respectively. TMS was used as internal standard for ^{1}H NMR and $CDCl_3$ for ^{13}C NMR. Chemical shifts are reported in ppm referred to TMS. FT-IR measurements carried out on a FTIR spectrometer equipped with a DTGS detector, KBr beamsplitter at 4 cm^{-1} resolution. Elemental analyses were performed on a CHNS 932 micro-analyzer. Specific optical rotation measurement was carried out on a polarimeter equipped with a PMT detector using the Sodium line at 589 nm. High performance liquid chromatography (HPLC) was performed by using Chiralpak IA, and IC columns and guard columns. Racemic standard products were prepared using DABCO (20 mol%) as catalyst in order to establish HPLC conditions. Catalyst **PS-SQ** was synthesized according to the reported procedures.[1]

General procedure for the Michael reaction

To a solution of squaramide organocatalyst **PS-SQ** (11.5 mg, 0.004 mmol, 2 mol%, f = 0.38 $mmol \cdot g^{-1}$) in CH_2Cl_2 (0.5 mL) was added nitroolefin (0.2 mmol) and 2-hydroxy-1,4-naphthoquinone (0.2 mmol). Reactions were monitored by TLC until the consumption of starting compounds, and then the reaction mixture was directly purified by column chromatography on silica gel to afford the Michael product.

General procedure for the recycling reactions in batch conditions

To a solution of squaramide organocatalyst **PS-SQ** (23.0 mg, 0.008 mmol, 4 mol%, f = 0.38 $mmol \cdot g^{-1}$) in CH_2Cl_2 (0.5 mL) was added nitroolefin (0.2 mmol) and 2-hydroxy-1,4-naphthoquinone (0.2 mmol). Reactions were monitored by TLC until the consumption of starting compounds. Then the reaction mixture was filtered, and washed with 15 ml of CH_2Cl_2. After that the filtrate was concentrated at reduced pressure and purified by column chromatography on silica gel to afford the Michael product.

Description of the experimental setup for the continuous flow process

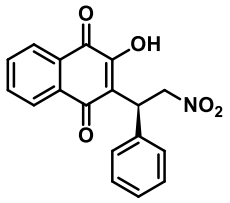
The packed bed reactor consisted of a vertically mounted and fritted low-pressure glass chromatography column (10 mm bore size and up to maximal 70 mm of adjustable bed height)

loaded with **PS-SQ** (0.25 g, 0.095 mmol, f = 0.38 mmol·g^{-1}). At the start, CH_2Cl_2/THF (10:1) was flushed for half an hour at 0.2 ml·min^{-1} flow rate to swell the resin. After that, the solvent channel was switched to a solution of 2-hydroxy-1,4-naphthoquinone (27.0 mmol, 4.79 g) and *trans*-β-nitrostyrene (32.4 mmol, 4.83 g) in 270 ml CH_2Cl_2/THF (10:1) of this solution were pumped to the reactor with a flow rate 0.2 ml·min^{-1}. The reactor outlet was connected to a receiving flask where the product was collected. After 22 h flow was stopped and **PS-SQ** washed with CH_2Cl_2/THF (10:1) solvent system for an hour. Conversion and enantioselectivity of the formed product were determined by ^{1}H NMR and HPLC analysis of periodically collected samples. In the end, collected solution was concentrated at reduced pressure and purified by flash chromatography on silica gel.

Description of the experimental setup for the continuous flow process with different substrates

The packed bed reactor was loaded with swollen resin **PS-SQ** (0.50 g, 0.19 mmol, f = 0.38 mmol·g^{-1}) in CH_2Cl_2/THF (10:1) and flushed half an hour with the same solvent mixture at 0.2 ml·min^{-1} flow rate. After the resin was conditioned, the solvent channel was switched to a solution of 2-hydroxy-1,4-naphthoquinone (1.80 mmol) and the corresponding nitroalkene (1.80 mmol) in 18 ml CH_2Cl_2/THF (10:1) and pumped through the reactor with a flow rate of 0.2 ml·min^{-1}. The reactor outlet was connected to a receiving flask where the product was collected. After 1 h, the flow was switched to a washing solvent CH_2Cl_2/THF (10:1) to clean the resin for half an hour. This process was repeated for each nitroalkene. Conversion and enantioselectivity of the product were determined by ^{1}H NMR and HPLC analysis of periodically collected samples. In the end, collected solutions were concentrated at reduced pressure and purified by flash chromatography on silica gel.

Physical and spectroscopical data of Michael adducts 3a-m

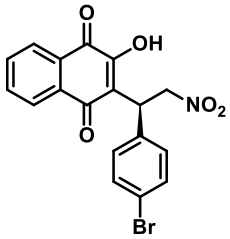


(S)-2-Hydroxy-3-(2-nitro-1-phenylethyl)naphthalene-1,4-dione (3a)[2]

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.14 (dd, *J* = 6.9, 13.4 Hz, 1H), 5.31 (dd, *J* = 6.8, 9.1 Hz, 1H), 5.47 (dd, *J* = 9.1, 13.4 Hz, 1H), 7.24-7.32 (m, 3H), 7.46 (d, *J* = 7.2 Hz, 2H), 7.68 (dt, *J* = 1.3, 7.5 Hz, 1H), 7.76 (dt, *J* = 1.3, 7.5 Hz, 1H), 8.05 (d, *J* = 7.6 Hz, 1H), 8.11 (d, *J* = 7.6 Hz, 1H) ppm.

^{13}C NMR (100 MHz, CDCl3): 39.7, 76.4, 120.8, 126.3, 127.2, 127.8, 128.3 (×2), 129.0 (×3), 132.6, 133.3, 135.4, 137.5, 153.2, 181.1, 183.7.

HPLC analysis: Chiralpak IA Column, Hexane (0.1% TFA)/Dichloromethane/Ethanol (90:5:5), flow rate = 1.0 mL/min, wavelength = 254 nm, r_t = 17.8 (major), 23.9 min (minor).

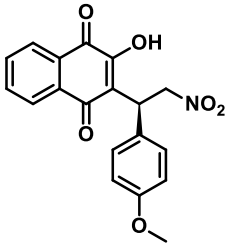


(S)-2-(1-(4-Fluorophenyl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione (3b)[2]

^{1}H NMR (400 MHz, DMSO-d_6): δ 5.17 (t, *J* = 7.7 Hz, 1H), 5.33-5.28 (m, 1H), 5.45 (dd, *J* = 8.3, 13.7 Hz, 1H), 7.34(d, *J* = 8.5Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.76 (t, *J* = 7.4 Hz, 1H), 7.82 (t, *J* = 7.4 Hz, 1H), 7.97-7.94 (m, 2H) ppm.

^{13}C NMR (100 MHz, DMSO-d_6): 38.5, 76.9, 120.1, 120.6, 126.2, 126.4, 130.3, 130.5, 131.8, 132.5, 133.6, 135.2, 138.8, 158.6, 181.8, 183.6.

HPLC analysis: Chiralpak IA Column, Hexane (0.1% TFA)/Dichloromethane/Ethanol (85:14:1), flow rate = 1.0 mL/min, wavelength = 254 nm, r_t = 25.6 (major), 26.6 min (minor).

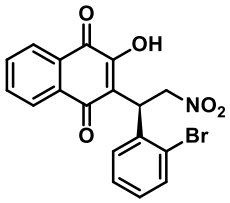


(S)-2-Hydroxy-3-(1-(4-methoxyphenyl)-2-nitroethyl)naphthalene-1,4-dione (3c)[2]

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.76 (s, 3H), 5.11 (dd, *J* = 6.9, 13.3 Hz, 1H), 5.25 (dd, *J* = 7.0, 9.0 Hz, 1H), 5.43 (dd, *J* = 9.0, 13.3 Hz, 1H), 6.84 (d, *J* = 8.9 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 7.69 (dt, *J* = 1.3, 7.6 Hz, 1H), 7.77 (dt, *J* = 1.3, 7.6 Hz, 1H), 8.06 (d, *J* = 7.6 Hz, 1H), 8.11 (d, *J* = 7.6 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): 39.0, 55.3, 76.6, 114.3, 121.1, 126.3, 127.3, 129.0, 129.4, 129.5, 132.7, 133.3, 135.4, 152.9, 159.2, 181.2, 183.3.

HPLC analysis: Chiralpak IA Column, Hexane (0.1% TFA)/Dichloromethane/Ethanol (92:4:4), flow rate = 0.6 mL/min, wavelength = 254 nm, r_t = 68.4 (major), 70.4 min (minor).

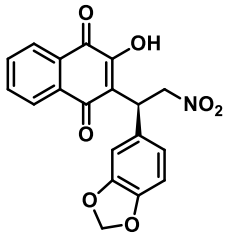


(R)-2-(1-(2-Bromophenyl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione (3d)[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.91 (dd, *J* = 5.8, 13.7 Hz, 1H), 5.42 (dd, *J* = 10.4, 13.9 Hz, 1H), 5.70 (dd, *J* = 5.7, 10.4 Hz, 1H), 7.13 (dt, *J* = 1.5, 7.8 Hz, 1H), 7.27-7.23 (m, 1H), 7.41 (dd, *J* = 1.6, 7.8 Hz, 1H), 7.60 (dd, *J* = 1.2, 7.9 Hz, 1H), 7.80-7.69 (m, 2H), 8.13-8.09 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): 39.9, 74.9, 119.6, 124.6, 126.4, 127.3, 127.9, 129.0, 129.4, 129.6, 132.7, 133.3, 133.6, 135.6, 136.2, 154.0, 181.0, 183.8.

HPLC analysis: Chiralpak IA Column, Hexane (0.1% TFA)/Dichloromethane/Ethanol (90:9:1), flow rate = 1.0 mL/min, wavelength = 254 nm, r_t = 23.2 (major), 24.1 min (minor).



(S)-2-(1-(Benzo[d][1,3]dioxol-5-yl)-2-nitroethyl)-3hydroxy-naphthalene-1,4-dione (3e)

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.13 (dd, *J* = 7.1, 13.1 Hz, 1H), 5.22 (t, *J* = 7.1, 15.6 Hz, 1H), 5.38 (dd, *J* = 8.4, 13.1 Hz, 1H), 5.90 (dd, *J* = 1.2, 4.0 Hz, 2H), 6.72 (d, *J* = 8.1 Hz, 1H). 6.93 (dd, *J* = 2.1, 7.8 Hz, 1H), 6.97 (d, *J* = 1.7 Hz, 1H), 7.67 (dt, *J* = 1.3, 7.5 Hz, 1H), 7.79-7.75 (m, 2H), 8.05 (dd, *J* = 1.4, 7.6 Hz, 1H), 8.10 (dd, *J* = 1.4, 7.8 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): 39.5, 76.6, 101.2, 108.6, 108.7, 120.9, 121.8, 126.3, 127.2, 129.0, 131.1, 132.6, 133.3, 135.4, 147.2, 148.0, 153.0, 181.1, 183.7.

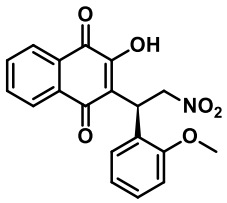
HRMS (ESI): *m*/*z* calcd. for $C_{19}H_{12}NO_7$ $[M - H]^-$ 366.0621, found 366.0619.

$[\alpha]_D^{26}$ = +2.29 (*c* 7.40, $CHCl_3$)

m.p. 136-138 °C.

IR (ATR): ν = 3229, 2891, 1673, 1635, 1546, 1271, 1235, 1038, 790.

HPLC analysis: Chiralpak IA Column, Hexane (0.1% TFA)/Dichloromethane/Ethanol (88:6:6), flow rate = 1.0 mL/min, wavelength = 254 nm, r_t = 29.9 (major), 49.8 min (minor).

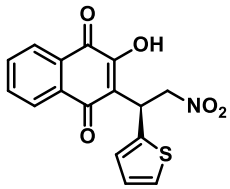


(S)-2-Hydroxy-3-(1-(2-methoxyphenyl)-2-nitroethyl)naphthalene-1,4-dione (3f)[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.87 (s, 3H), 4.96 (dd, *J* = 5.6, 13.6 Hz, 1H), 5.41 (dd, *J* = 10.2, 13.6 Hz, 1H), 5.65 (dd, *J* = 5.6, 10.2 Hz, 1H), 6.90-6.86 (m, 2H), 7.26-7.22 (m, 2H), 7.68 (dt, *J* = 1.3, 6.2 Hz, 1H), 7.71 (s, 1H), 7.76 (dt, *J* = 1.4, 6.2 Hz, 1H), 8.11- 8.07 (m, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): 34.2, 55.6, 75.4, 110.9, 120.5, 120.7, 124.9, 126.3, 127.2, 128.8, 129.0, 129.1, 132.9, 133.1, 135.3, 154.0, 156.9, 181.2, 183.8.

HPLC analysis: Chiralpak IC Column, Hexane (0.1% TFA)/Dichloromethane/Ethanol (75:23:2), flow rate = 0.7 mL/min, wavelength = 254 nm, r_t = 13.7 (major), 14.4 min (minor).

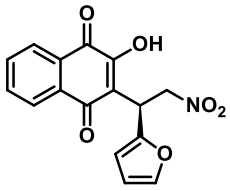


(S)-2-Hydroxy-3-(2-nitro-1-(thiophen-2-yl)ethyl)naphthalene-1,4-dione (3g)[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.13 (dd, *J* = 6.8, 13.5 Hz, 1H), 5.43 (dd, *J* = 8.9, 13.5 Hz, 1H), 5.61 (dd, *J* = 6.6, 9.0 Hz, 1H), 6.93 (dd, *J* = 3.5, 5.1 Hz, 1H), 7.10-7.11 (m, 1H), 7.20 (dd, *J* = 1.2, 5.1 Hz, 1H), 7.71 (dt, *J* = 1.3, 7.6 Hz, 1H), 7.81-7.77 (m, 2H), 8.08 (d, *J* = 7.5 Hz, 1H), 8.14 (d, *J* = 7.5 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): 34.8, 76.7, 119.9, 125.4, 126.4, 126.6, 127.0, 127.2, 129.0, 132.6, 133.4, 135.6, 139.0, 153.1, 181.0, 183.3.

HPLC analysis: Chiralpak IA Column, Hexane (0.1% TFA)/Dichloromethane/Ethanol (90:5:5), flow rate = 1.0 mL/min, wavelength = 254 nm, r_t = 21.2 (major), 22.9 min (minor).

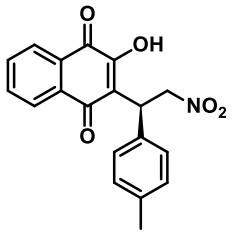


(S)-2-(1-(Furan-2-yl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione (3h)[2]

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.19 (dd, *J* = 6.9, 13.5 Hz, 1H), 5.27 (dd, *J* = 8.6, 13.5 Hz, 1H), 5.47 (t, *J* = 8.7 Hz, 1H), 6.23 (d, *J* = 3.3 Hz, 1H), 6.30 (dd, *J* = 1.8, 3.3 Hz, 1H), 7.32 (dd, *J* = 0.7, 1.8 Hz, 1H), 7.71 (dt, *J* =1.2, 7.6 Hz, 1H), 7.81-7.78 (m, 2H), 8.09 (dd, *J* = 1.4, 7.7 Hz, 1H), 8.14 (dd, *J* = 1.4, 7.7 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): 33.4, 74.7, 107.4, 110.7, 118.0, 126.4, 127.3, 129.0, 132.6, 133.4, 135.6, 142.3, 149.8, 153.9, 181.0, 183.2.

HPLC analysis: Chiralpak IA Column, Hexane (0.1% TFA)/Dichloromethane/Ethanol (92:4:4), flow rate = 1.0 mL/min, wavelength = 254 nm, r_t = 24.1 (major), 27.5 min (minor).

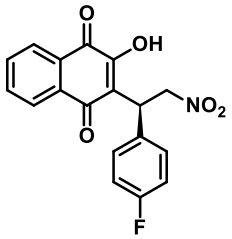


(S)-2-Hydroxy-3-(2-nitro-1-(p-tolyl)ethyl)naphthalene-1,4-dione (3i)[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.29 (s, 3H), 5.12 (dd, *J* = 6.8, 13.3 Hz, 1H), 5.28 (dd, *J* = 6.8, 10.4 Hz, 1H), 5.46 (dd, *J* = 9.0, 13.3 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.66-7.78 (m, 3H), 8.06 (d, *J* = 7.6 Hz, 1H), 8.11 (d, *J* = 7.6 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): 21.0, 39.3, 76.4, 121.0, 126.3, 127.2, 128.1, 129.0, 129.7, 132.7, 133.2, 134.5, 135.4, 137.7, 153.1, 181.2, 183.7.

HPLC analysis: Chiralpak IA Column, Hexane (0.1% TFA)/Dichloromethane/Ethanol (90:5:5), flow rate = 1.0 mL/min, wavelength = 254 nm, r_t = 20.9 (major), 25.8 min (minor).

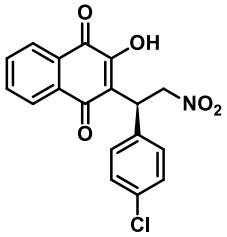


(S)-2-(1-(4-Fluorophenyl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione (3j)[2]

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.15 (dd, *J* = 6.8, 12.7 Hz, 1H), 5.29 (t, *J* = 15.2 Hz, 1H), 5.40 (dd, *J* = 8.4, 12.7 Hz, 1H), 6.99 (t, *J* = 8.7 Hz, 2H), 7.45 (dd, *J* = 5.2, 8.8 Hz, 2H), 7.70 (dt, *J* = 1.4, 7.6 Hz, 1H), 7.78 (dt, *J* = 1.4, 7.6 Hz, 1H), 8.07 (d, *J* = 7.6 Hz, 1H), 8.11 (d, *J* = 7.7 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): 39.0, 76.4, 115.9 (d, *J* = 21.3 Hz), 120.6, 126.4, 127.2, 128.9, 130.0 (d, *J* = 8.3 Hz), 130.1, 132.6, 133.3, 133.4, 135.6, 153.3, 162.2 (d, *J* = 246.9 Hz), 181.1, 183.7.

HPLC analysis: Chiralpak IA Column, Hexane (0.1% TFA)/Dichloromethane/Ethanol (90:5:5), flow rate = 1.0 mL/min, wavelength = 254 nm, r_t = 20.5 (major), 23.4 min (minor).

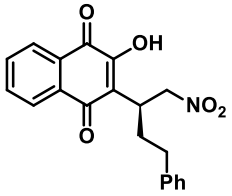


(S)-2-(1-(4-Chlorophenyl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione (3k)[2]

^{1}H NMR (400 MHz, DMSO-d_6): δ 5.19 (t, *J* = 7.8 Hz, 1H), 5.32 (dd, *J* = 7.5, 13.9 Hz, 1H), 5.43 (dd, *J* = 8.2, 13.8 Hz, 1H), 7.41-7.35 (m, 4H), 7.79 (dt, *J* = 1.4, 7.4 Hz, 1H), 7.85 (dt, *J* = 1.4, 7.4 Hz, 1H), 8.00-7.97 (m, 2H) ppm.

^{13}C NMR (100 MHz, DMSO-d_6): 38.3, 76.9, 120.8, 126.3, 126.4, 129.0 (×2), 130.2 (×3), 130.4, 132.2, 133.9, 135.3, 138.0, 157.1, 181.3, 184.2.

HPLC analysis: Chiralpak IA Column, Hexane (0.1% TFA)/Dichloromethane/Ethanol (90:5:5), flow rate = 1.0 mL/min, wavelength = 254 nm, r_t = 20.4 (major), 21.8 min (minor).

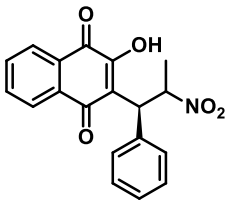


(S)-2-Hydroxy-3-(1-nitro-4-phenylbutan-2-yl)naphthalene-1,4-dione (3l)[2]

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.04-1.97 (m, 1H), 2.33-2.25 (m, 1H), 2.61-2.55 (m, 1H), 2.72-2.66 (m, 1H), 4.13-4.07 (m, 1H), 4.71 (dd, *J* = 12.6, 6.2 Hz, 1H), 4.96 (dd, *J* = 12.7, 9.1 Hz, 1H), 7.10-7.04 (m, 3H), 7.17-7.14 (m, 2H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.78 (t, *J* = 7.5 Hz, 1H), 8.06 (d, *J* = 7.6 Hz, 1H), 8.11 (d, *J* = 7.6 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): 31.7, 33.8, 34.8, 77.1, 120.4, 126.1, 126.3, 127.1, 128.2, 128.3, 129.1, 132.8, 133.2, 135.3, 140.9, 153.9, 180.7, 183.9.

HPLC analysis: Chiralpak IA Column, Hexane (0.1% TFA)/Dichloromethane/Ethanol (90:9:1), flow rate = 1.0 mL/min, wavelength = 254 nm, r_t = 23.8 (major), 25.4 min (minor).



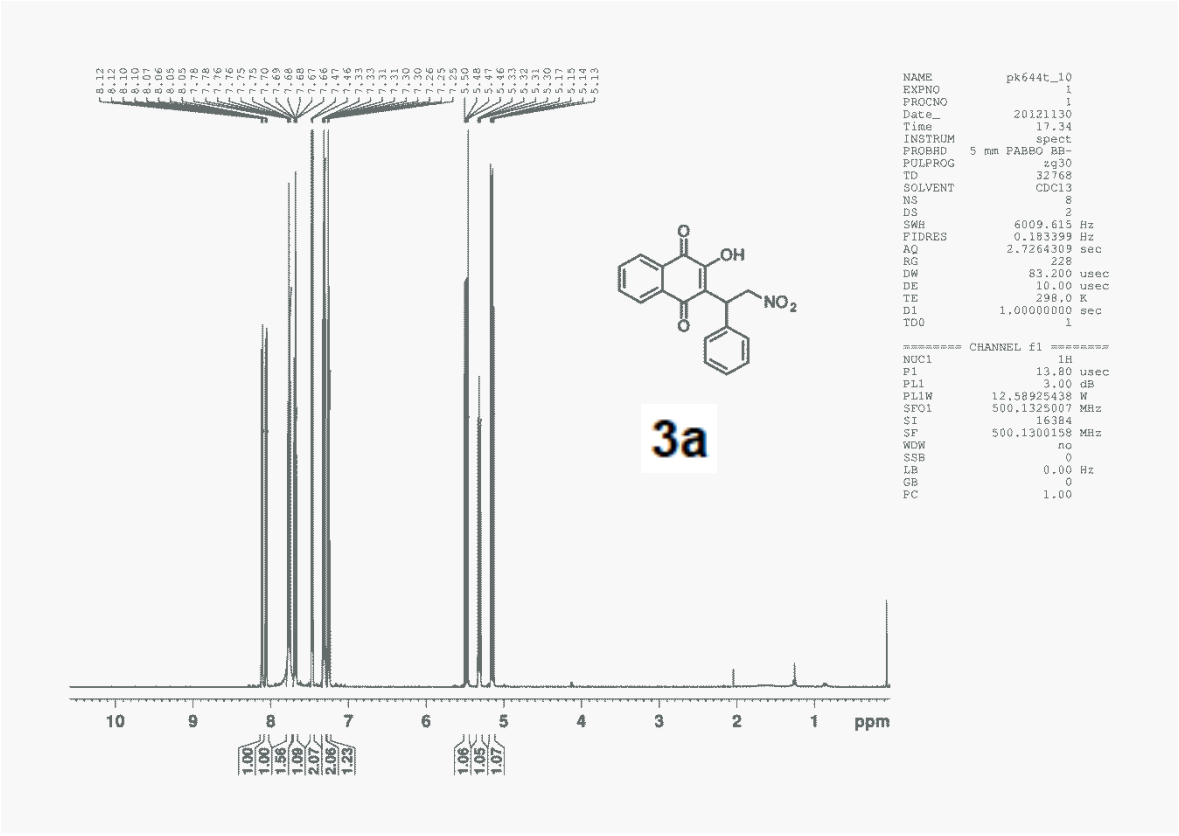
2-Hydroxy-3-((1S)-2-nitro-1-phenylpropyl)naphthalene-1,4-dione (3m)[3]

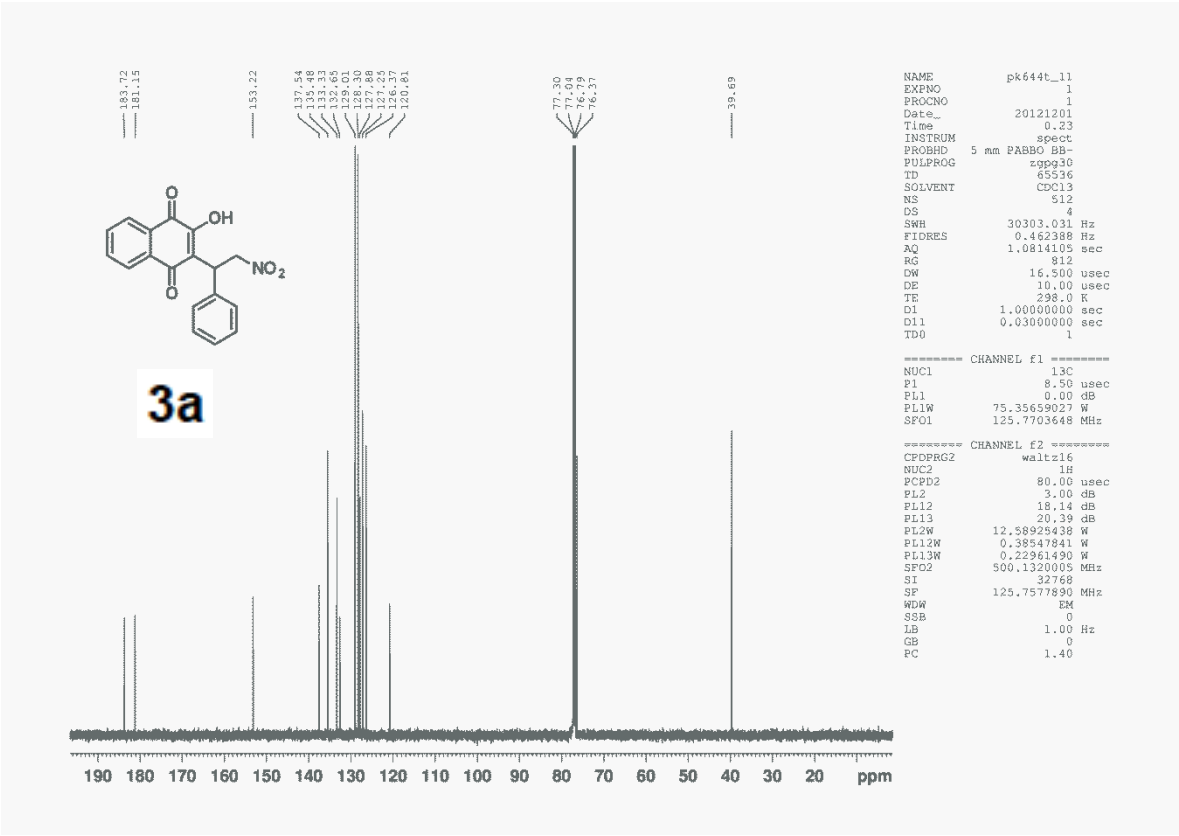
^{1}H NMR (500 MHz, $CDCl_3$): δ 1.53 (d, *J* = 6.7 Hz, 3H), 4.93 (d, *J* = 11.6 Hz, 1H), 6.05-6.12 (m, 1H), 7.24-7.33 (m, 3H), 7.52-7.54 (m, 2H), 7.64 (dt, *J* = 1.2, 7.5 Hz, 1H), 7.73 (dt, *J* = 1.3, 7.5 Hz, 1H), 7.78 (s, 1H), 8.01 (dd, *J* = 1.3, 7.6 Hz, 1H), 8.10 (dd, *J* = 1.0, 7.6 Hz, 1H) ppm.

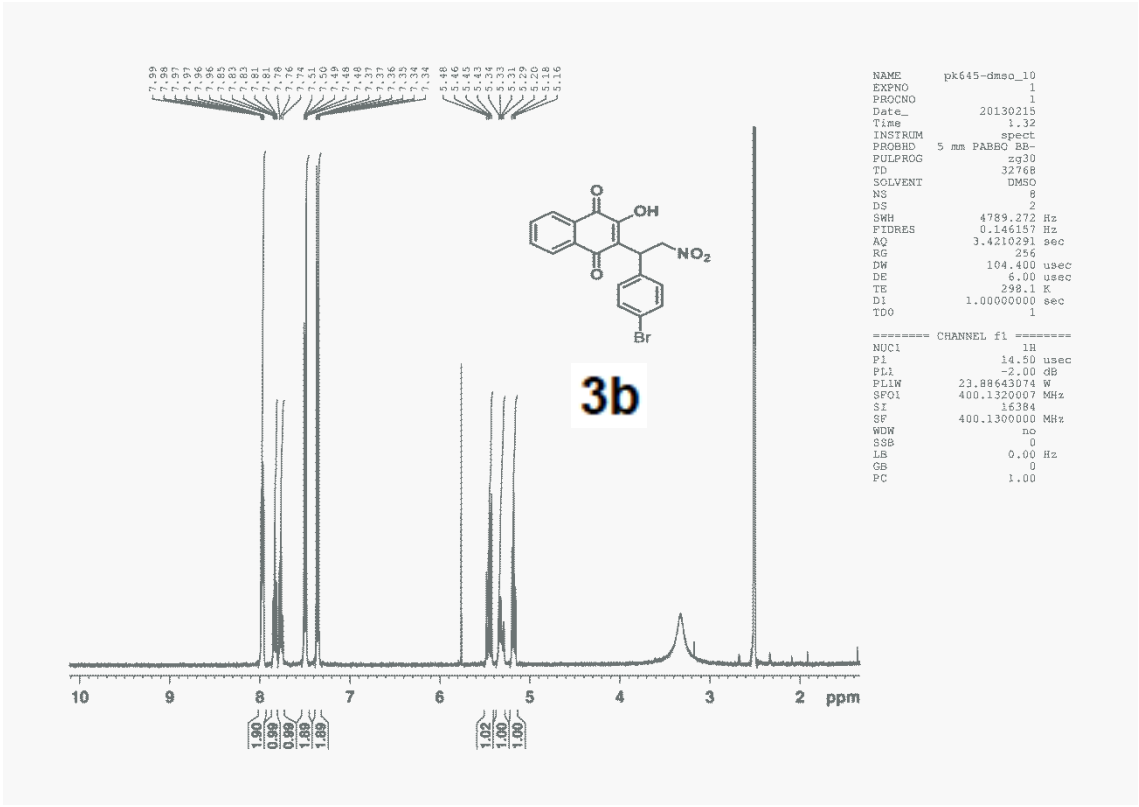
^{13}C NMR (100 MHz, $CDCl_3$): 19.7, 46.6, 83.4, 121.2, 126.2, 127.2, 127.9, 129.1, 129.2, 129.9, 132.7, 133.1, 135.3, 137.3, 152.8, 181.1, 183.6.

HPLC analysis: Chiralpak IA Column, Hexane (0.1% TFA)/Dichloromethane/Ethanol (90:5:5), flow rate = 1.0 mL/min, wavelength = 254 nm, r_t = 15.2 (major), 23.9 min (minor).

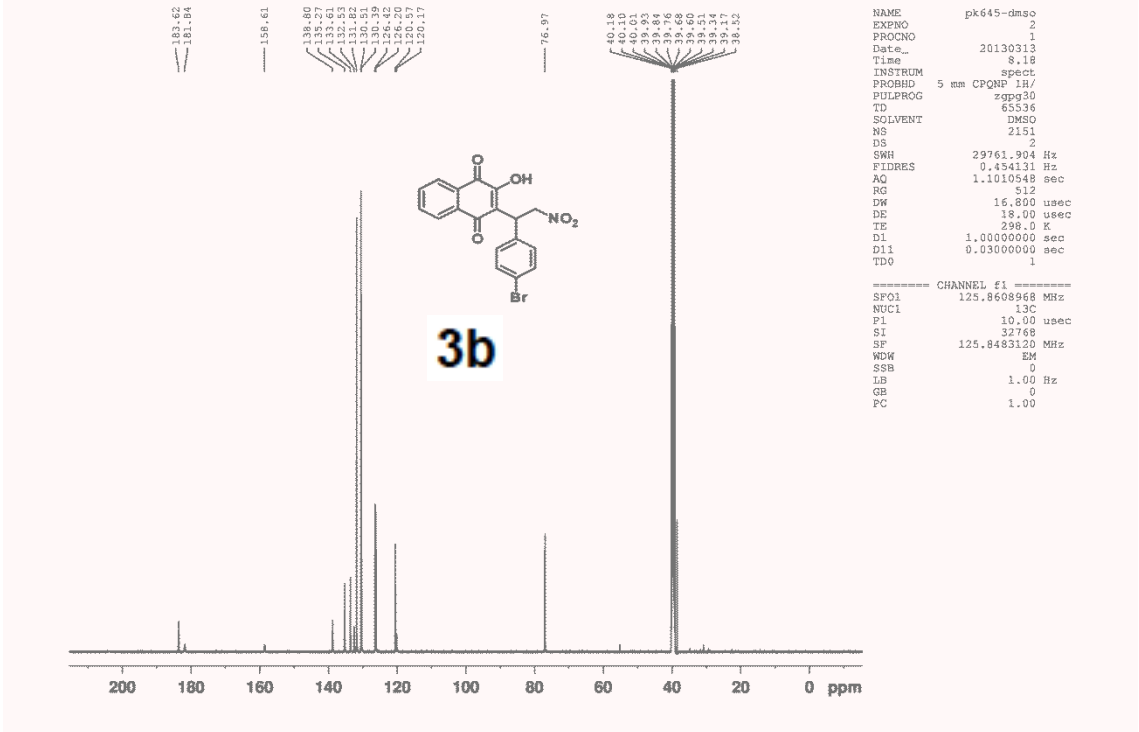
^{1}H and ^{13}C NMR spectra of 3a-m



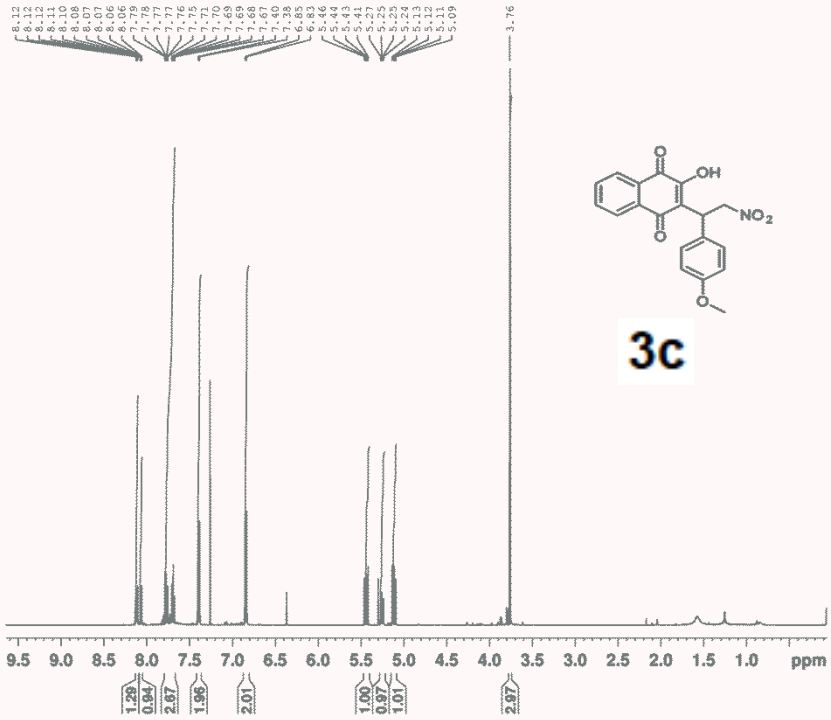




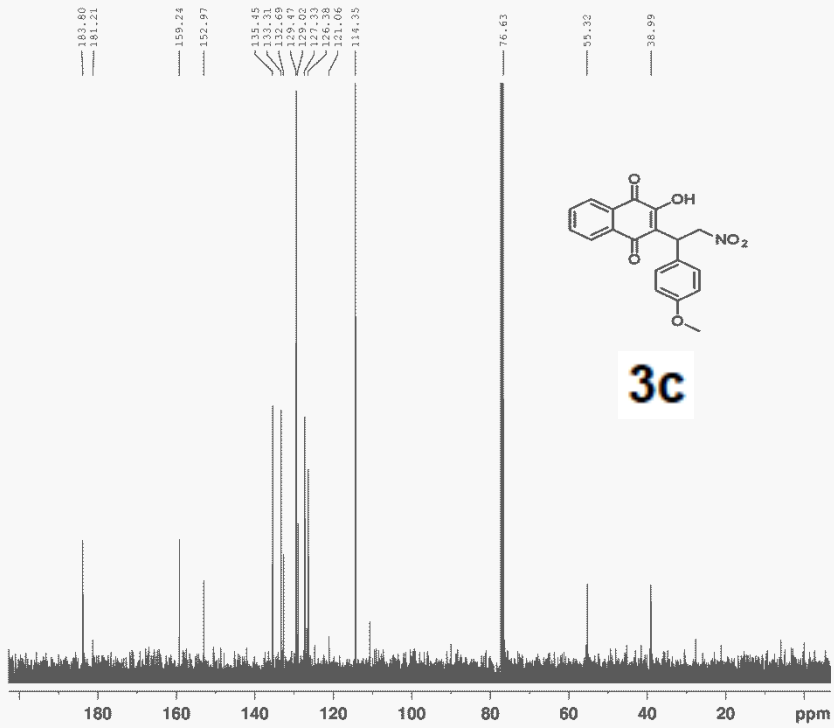

```
NAME        pk645-dmso_10
EXPNO                  1
PROCNO                 1
Date_           20130215
Time                1.32
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT             DMSO
NS                     8
DS                     2
SWH             4789.272 Hz
FIDRES          0.146157 Hz
AQ              3.4210291 sec
RG                   256
DW                104.400 usec
DE                  6.00 usec
TE                298.1 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.50 usec
PL1                -2.00 dB
PL1W         23.88643074 W
SFO1         400.1320007 MHz
SI                 16384
SF           400.1300000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```



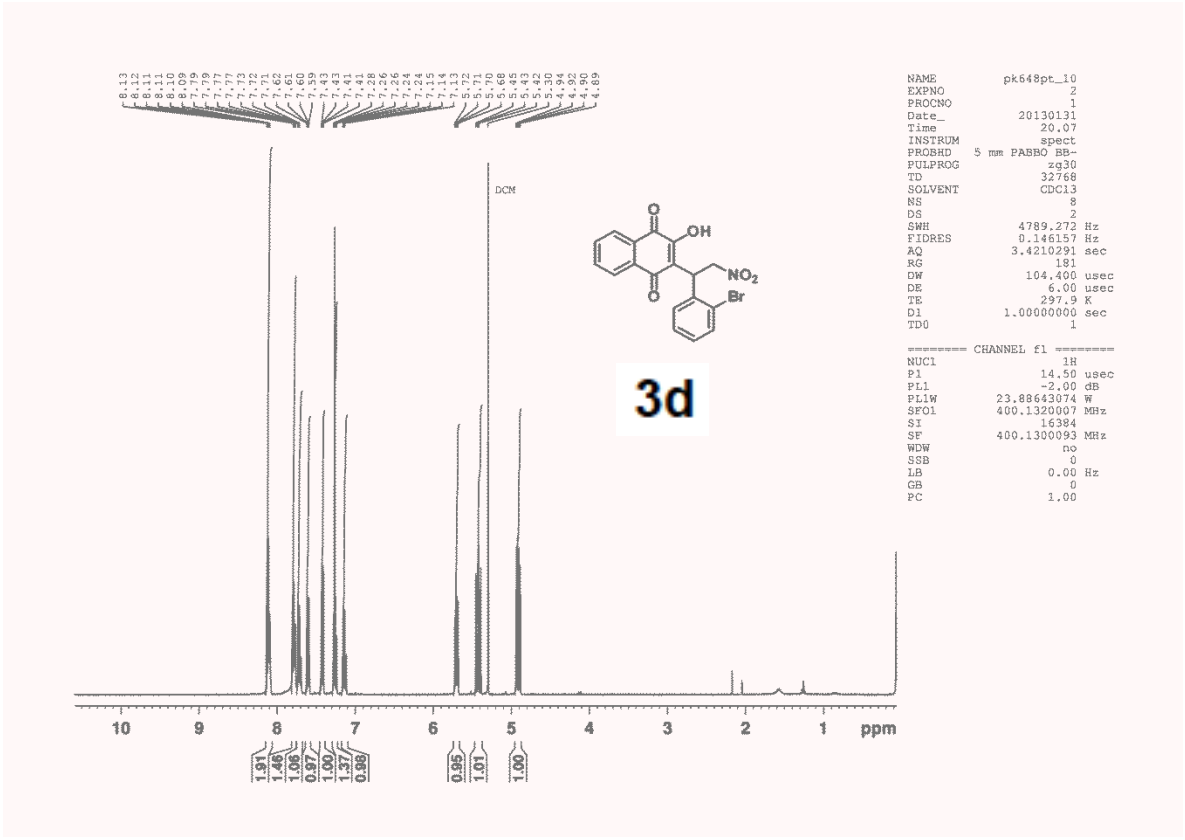

```
NAME          pk645-dmso
EXPNO                  2
PROCNO                 1
Date_           20130313
Time                8.18
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG          zgpg30
TD                 65536
SOLVENT             DMSO
NS                  2151
DS                     2
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ              1.1010548 sec
RG                   512
DW                16.800 usec
DE                 18.00 usec
TE                298.0 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         125.8608968 MHz
NUC1                  13C
P1                 10.00 usec
SI                 32768
SF           125.8483120 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.00
```

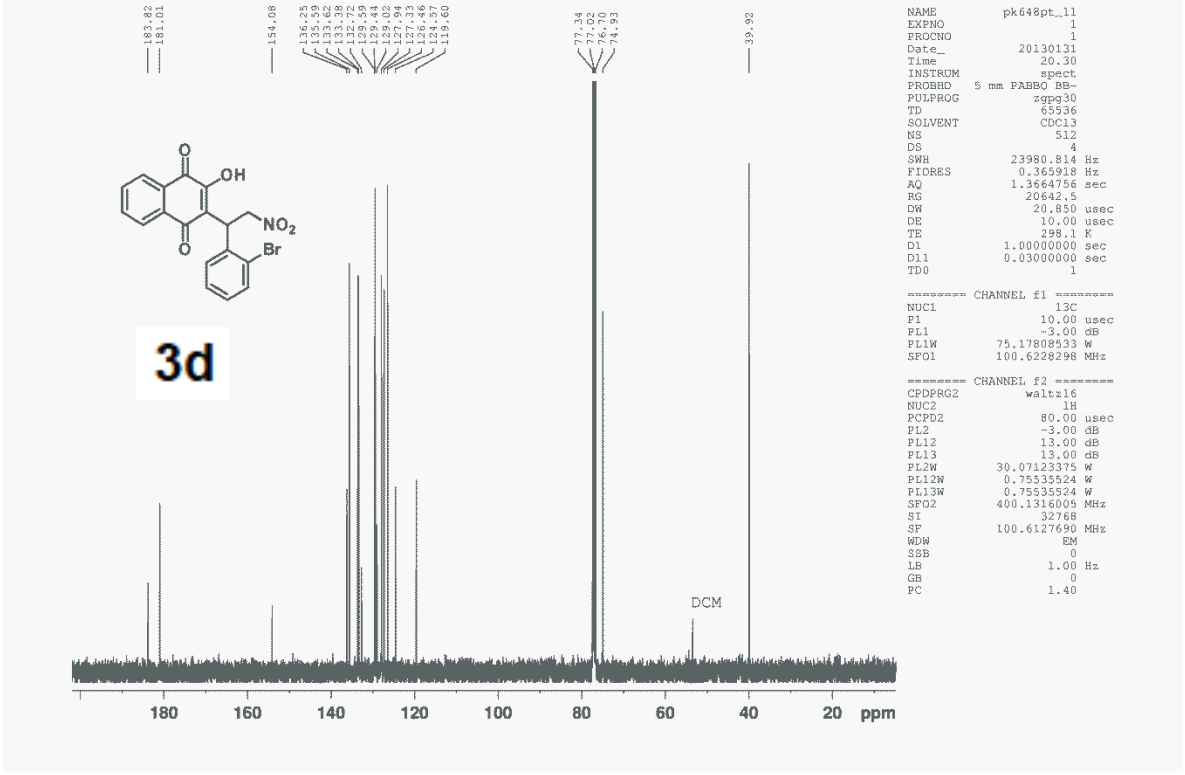


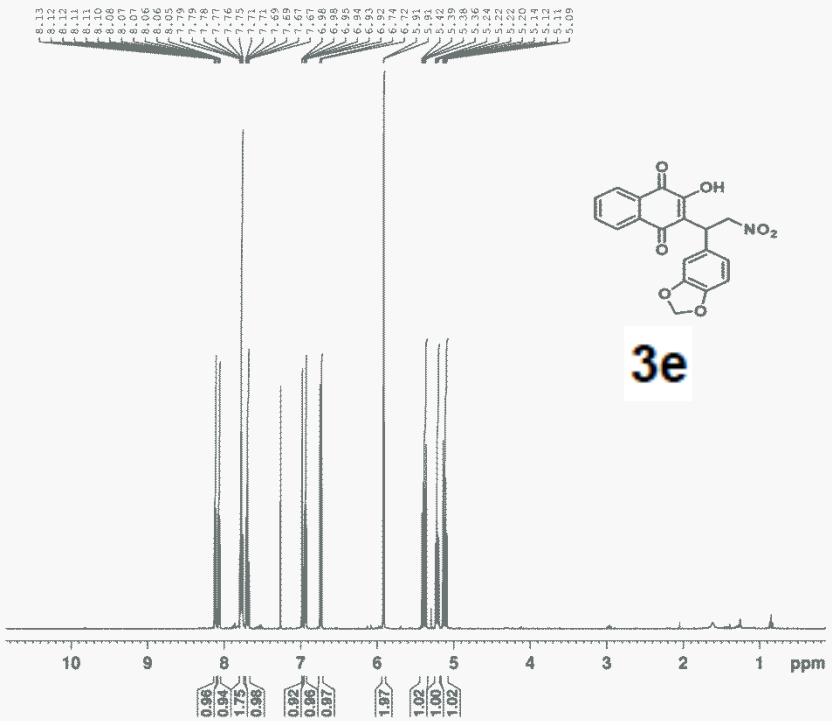

```
NAME           pk647p_10
EXPNO                  2
PROCNO                 1
Date_           20121122
Time                4.25
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             6009.615 Hz
FIDRES          0.183399 Hz
AQ              2.7264309 sec
RG                   203
DW                83.200 usec
DE                10.00 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1

========= CHANNEL f1 =========
NUC1                  1H
P1                 13.80 usec
PL1                 3.00 dB
PL1W          12.58925438 W
SFO1          500.1325007 MHz
SI                 16384
SF            500.1300139 MHz
WDW                   no
SSB                    0
LB                 0.00 Hz
GB                     0
PC                  1.00
```



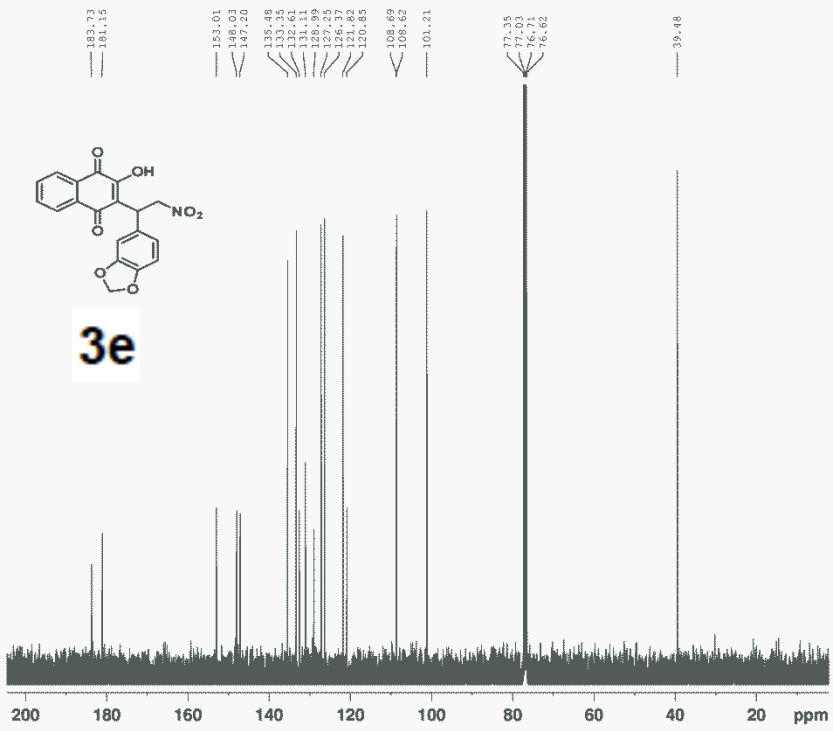

```
NAME           pk647p_11
EXPNO                  1
PROCNO                 1
Date_           20121122
Time                4.45
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     4
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ              1.0814105 sec
RG                   812
DW                16.500 usec
DE                10.00 usec
TE                297.9 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 8.50 usec
PL1                0.00 dB
PL1W          75.35659027 W
SFO1          125.7703648 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                3.00 dB
PL12               18.14 dB
PL13               20.39 dB
PL2W          12.58925438 W
PL12W          0.38547841 W
PL13W          0.22961490 W
SFO2          500.1320005 MHz
SI                 32768
SF            125.7577890 MHz
WDW                   no
SSB                    0
LB                 0.00 Hz
GB                     0
PC                  1.40
```


8.13
8.12
8.11
8.11
8.10
8.09
7.79
7.79
7.77
7.77
7.73
7.72
7.71
7.62
7.60
7.59
7.43
7.41
7.41
7.28
7.26
7.25
7.24
7.15
7.14
7.13
5.72
5.71
5.70
5.68
5.45
5.43
5.42
5.10
4.94
4.92
4.90
4.89
DCM
OH
NO2
Br
3d
10
9
8
7
6
5
4
3
2
1
ppm
1.91
1.46
1.06
0.97
1.00
1.37
0.98
0.95
1.01
1.00
NAME pk648pt_10
EXPNO 2
PROCNO 1
Date_ 20130131
Time 20.07
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 2
SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 181
DW 104.400 usec
DE 6.00 usec
TE 297.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.50 usec
PL1 -2.00 dB
PL1W 23.88643074 W
SFO1 400.1320007 MHz
SI 16384
SF 400.1300093 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

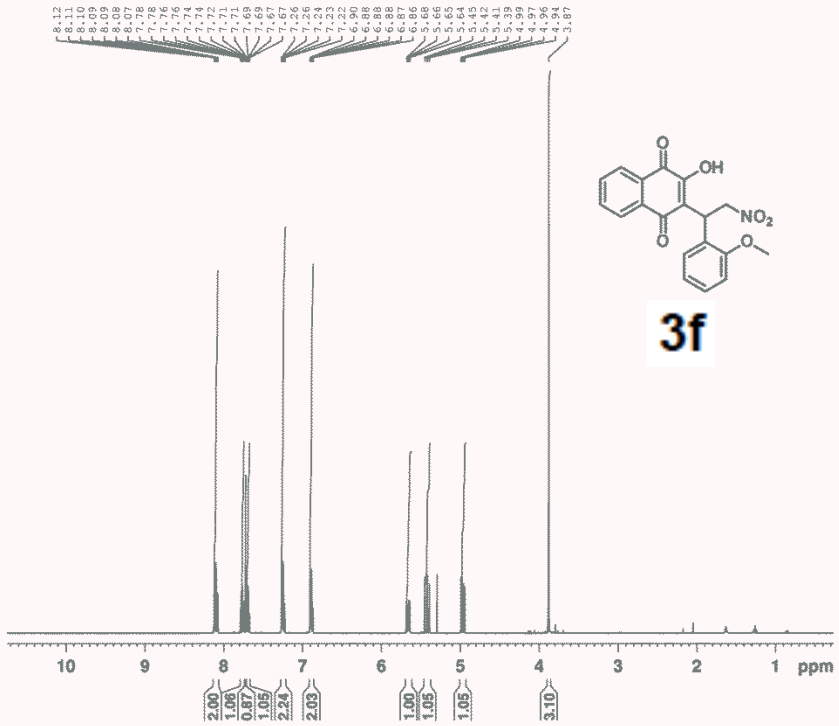

183.82
181.01
154.08
136.25
135.59
133.62
133.38
132.72
129.59
129.44
129.02
127.94
127.33
126.46
124.57
119.60
77.34
77.02
76.70
74.93
39.92
OH
NO2
Br
3d
DCM
180
160
140
120
100
80
60
40
20
ppm
NAME pk648pt_11
EXPNO 1
PROCNO 1
Date_ 20130131
Time 20.30
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 20642.5
DW 20.850 usec
DE 10.00 usec
TE 298.1 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -3.00 dB
PL1W 75.17808533 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 13.00 dB
PL13 13.00 dB
PL2W 30.07123375 W
PL12W 0.75535524 W
PL13W 0.75535524 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



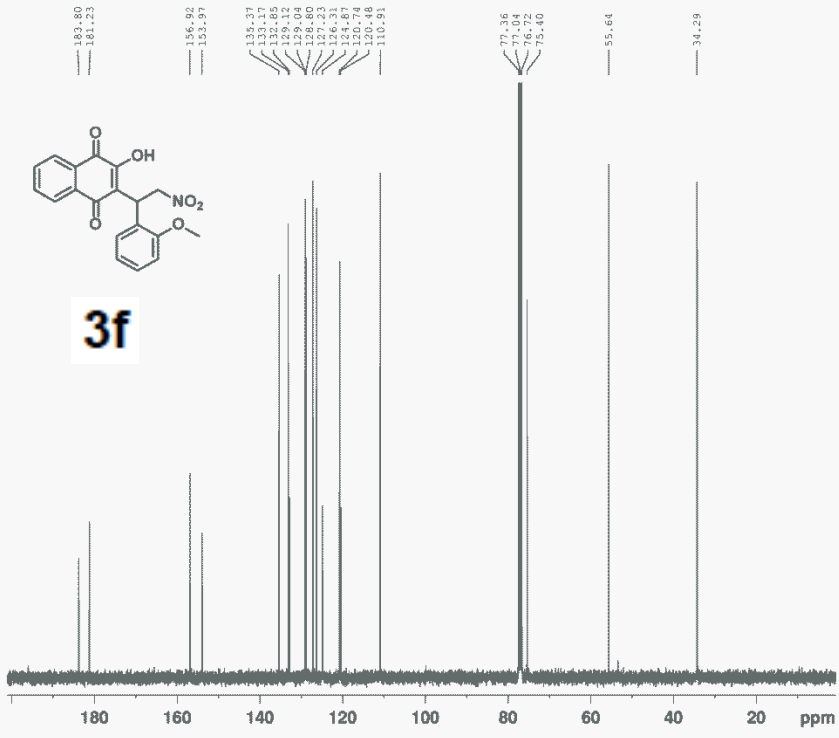

```
NAME            pk699a_10
EXPNO                   3
PROCNO                  1
Date_            20130206
Time                 8.00
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                      8
DS                      2
SWH             4789.272 Hz
FIDRES          0.146157 Hz
AQ              3.4210291 sec
RG                  161.3
DW                104.400 usec
DE                  6.00 usec
TE                  298.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.50 usec
PL1                 -2.00 dB
PL1W           23.88643074 W
SFO1          400.1320007 MHz
SI                  16384
SF            400.1300090 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```



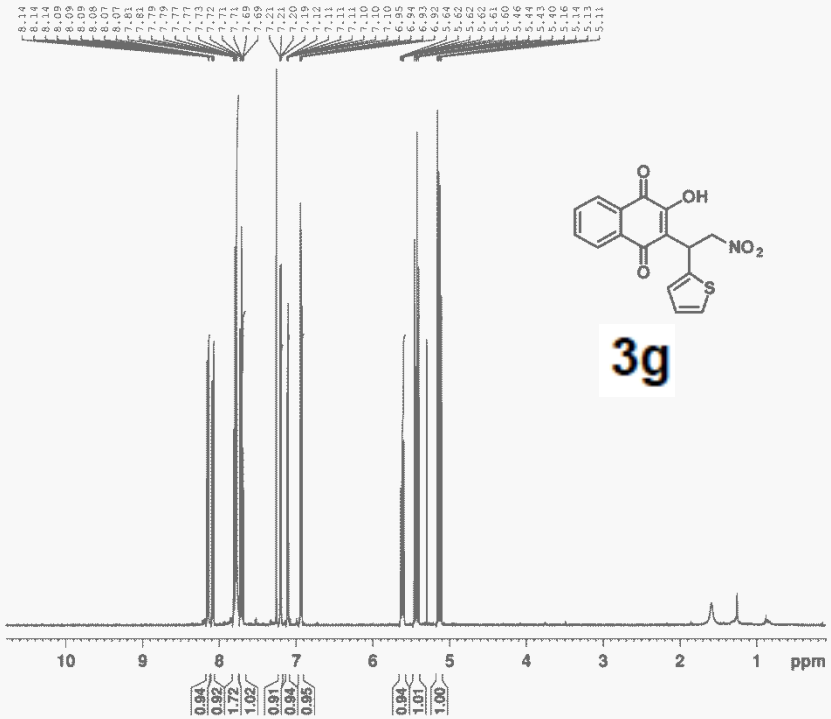

```
NAME            pk699a_11
EXPNO                   3
PROCNO                  1
Date_            20130206
Time                16.25
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG          zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     76
DS                      4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ              1.3664756 sec
RG                  32768
DW                20.850 usec
DE                  10.00 usec
TE                  298.2 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   13C
P1                  10.00 usec
PL1                 -3.00 dB
PL1W           75.17808533 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                 -3.00 dB
PL12                13.00 dB
PL13                13.00 dB
PL2W           30.07123375 W
PL12W           0.75535524 W
PL13W           0.75535524 W
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127690 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



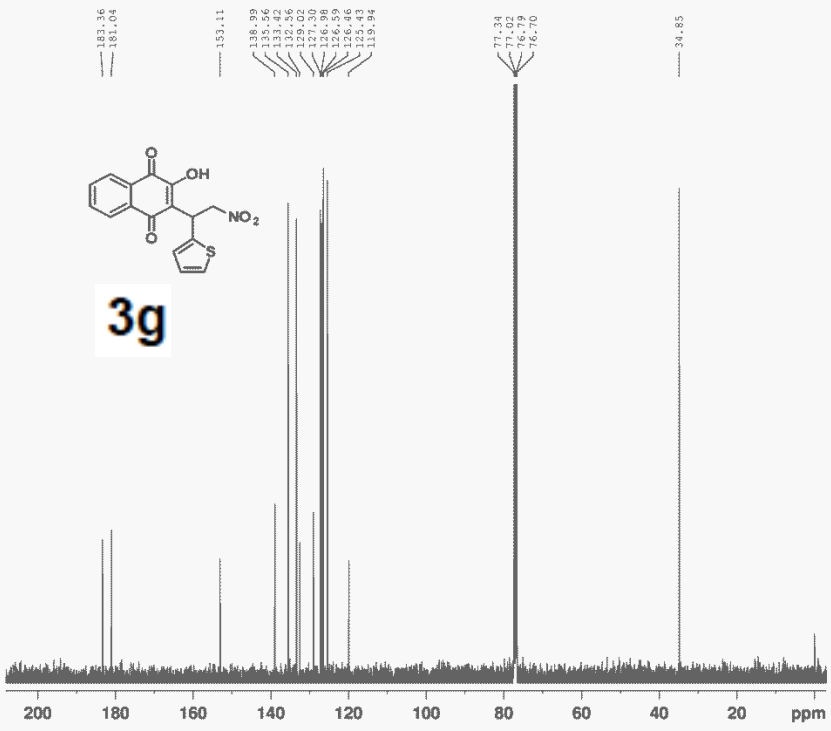

```
NAME            pk700p_10
EXPNO                   2
PROCNO                  1
Date_            20130205
Time                3.13
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              4789.272 Hz
FIDRES           0.146157 Hz
AQ               3.4210291 sec
RG                    128
DW                104.400 usec
DE                  6.00 usec
TE                 297.9 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.50 usec
PL1                 -2.00 dB
PL1W           23.88643074 W
SFO1          400.1320007 MHz
SI                    16384
SF            400.1300105 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00
```



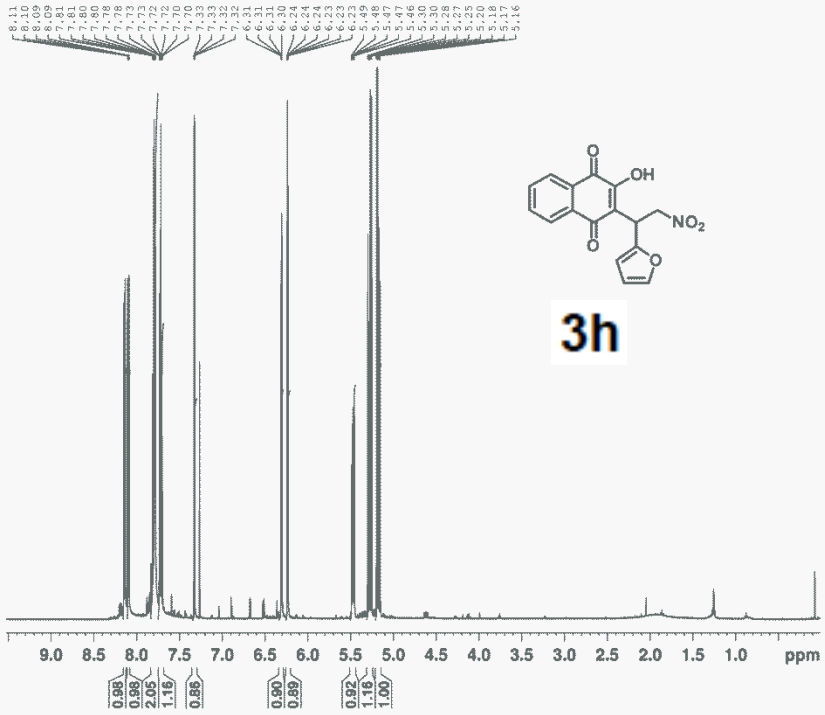

```
NAME            pk700p_11
EXPNO                   1
PROCNO                  1
Date_            20130205
Time                3.35
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    512
DS                      4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ               1.3664756 sec
RG                  26008
DW                20.850 usec
DE                  10.00 usec
TE                 298.0 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.00 usec
PL1                 -3.00 dB
PL1W           75.17808533 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                 -3.00 dB
PL12                13.00 dB
PL13                13.00 dB
PL2W           30.07123375 W
PL12W           0.75535524 W
PL13W           0.75535524 W
SFO2          400.1316005 MHz
SI                    32768
SF            100.6127690 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```



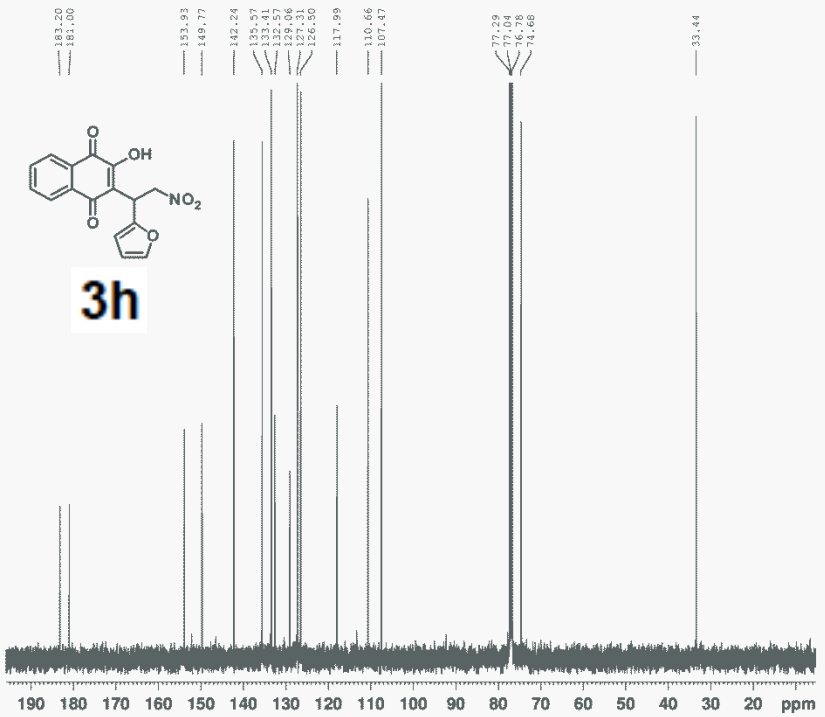

```
NAME          pk658pt_10
EXPNO                  2
PROCNO                 1
Date_           20130201
Time                1.17
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     8
DS                     2
SWH           4789.272 Hz
FIDRES        0.146157 Hz
AQ            3.4210291 sec
RG                   181
DW              104.400 usec
DE                6.00 usec
TE                297.9 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.50 usec
PL1                -2.00 dB
PL1W        23.88643074 W
SFO1        400.1320007 MHz
SI                 16384
SF          400.1300097 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```



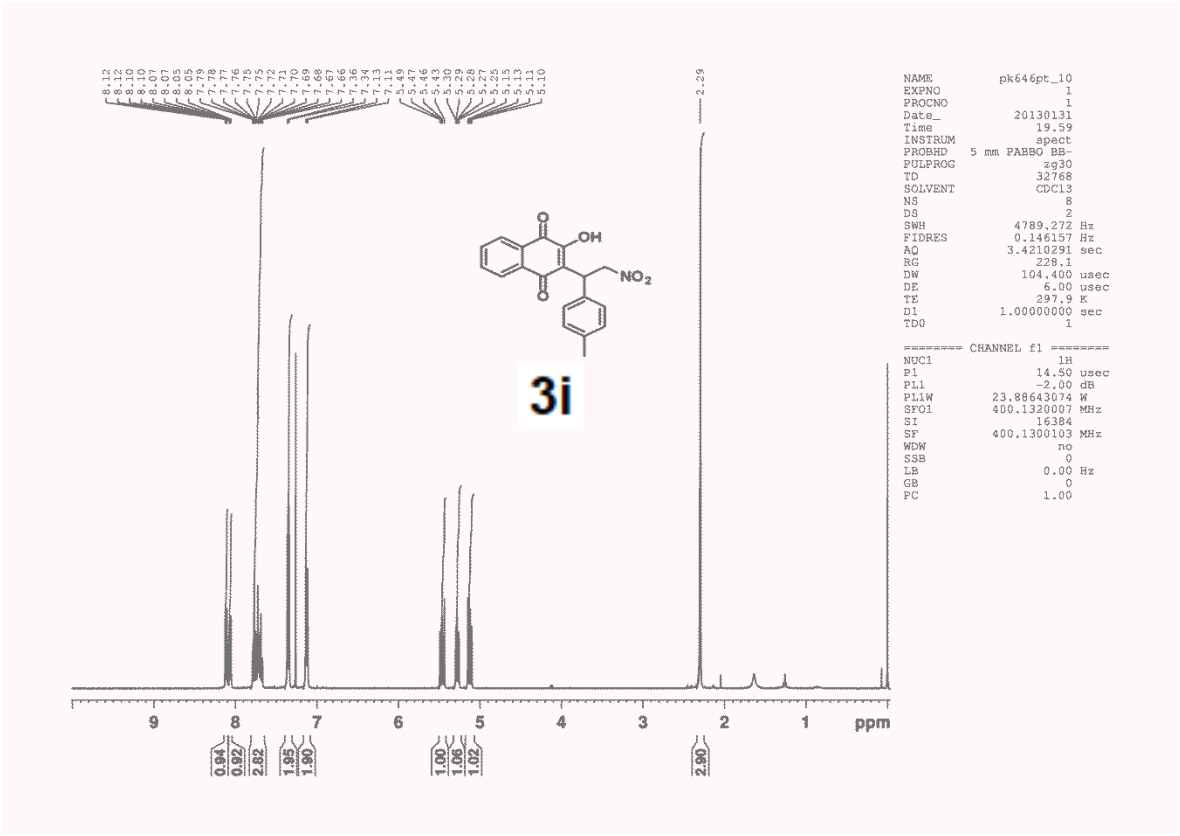

```
NAME          pk658pt_11
EXPNO                  1
PROCNO                 1
Date_           20130201
Time                1.40
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     4
SWH          23980.814 Hz
FIDRES        0.365918 Hz
AQ            1.3664756 sec
RG                 23170.5
DW                20.850 usec
DE                10.00 usec
TE                298.1 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 10.00 usec
PL1                -3.00 dB
PL1W        75.17808533 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               13.00 dB
PL13               13.00 dB
PL2W        30.07123375 W
PL12W        0.75535524 W
PL13W        0.75535524 W
SFO2        400.1316005 MHz
SI                 32768
SF          100.6127690 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



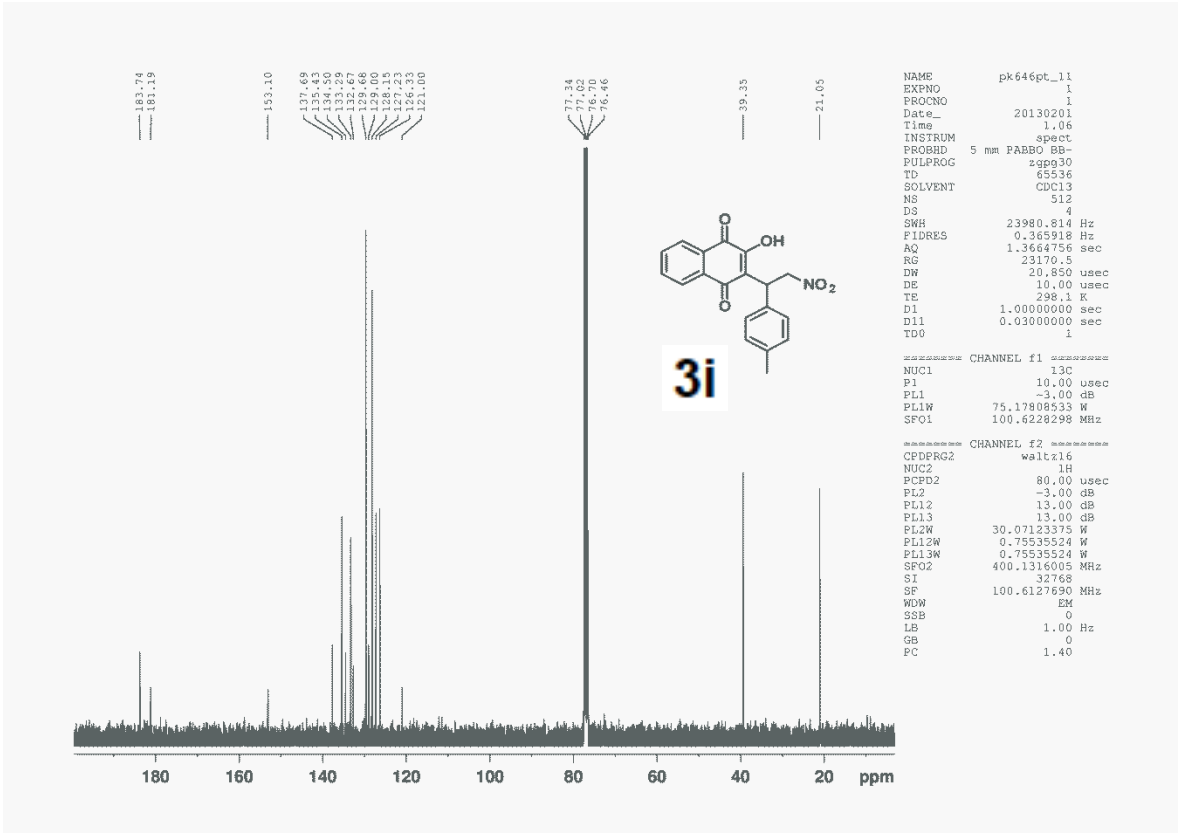

```
NAME            pk649p_10
EXPNO                   1
PROCNO                  1
Date_            20121121
Time                1.46
INSTRUM            spect
PROBHD    5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                      8
DS                      2
SWH             6009.615 Hz
FIDRES          0.183399 Hz
AQ              2.7264309 sec
RG                    256
DW                83.200 usec
DE                10.00 usec
TE                298.0 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  1H
P1                 13.80 usec
PL1                 3.00 dB
PL1W          12.58925438 W
SFO1          500.1325007 MHz
SI                  16384
SF            500.1300117 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```



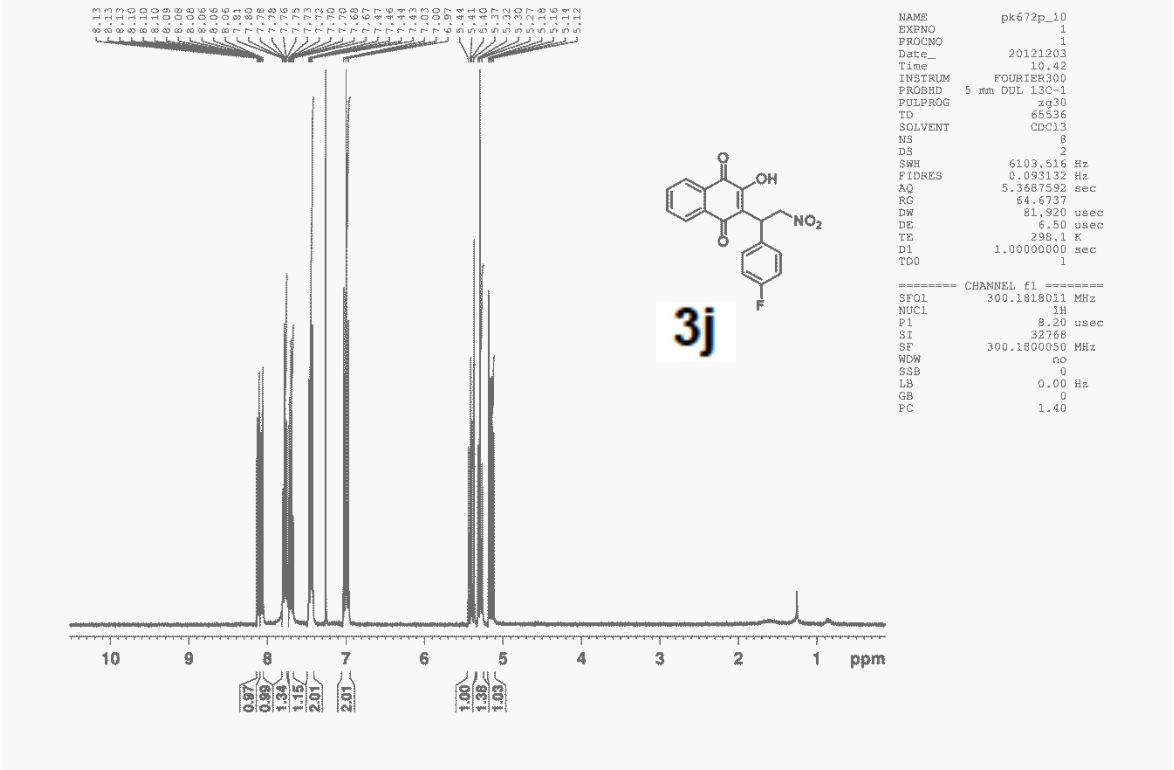

```
NAME            pk649p_11
EXPNO                   1
PROCNO                  1
Date_            20121121
Time                2.06
INSTRUM            spect
PROBHD    5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    512
DS                      4
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ              1.0814105 sec
RG                    812
DW                16.500 usec
DE                10.00 usec
TE                297.9 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  8.50 usec
PL1                 0.00 dB
PL1W         75.35659027 W
SFO1         125.7703648 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 3.00 dB
PL12               18.14 dB
PL13               20.39 dB
PL2W          12.58925438 W
PL12W          0.38547841 W
PL13W          0.22961490 W
SFO2          500.1320005 MHz
SI                  32768
SF            125.7577890 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



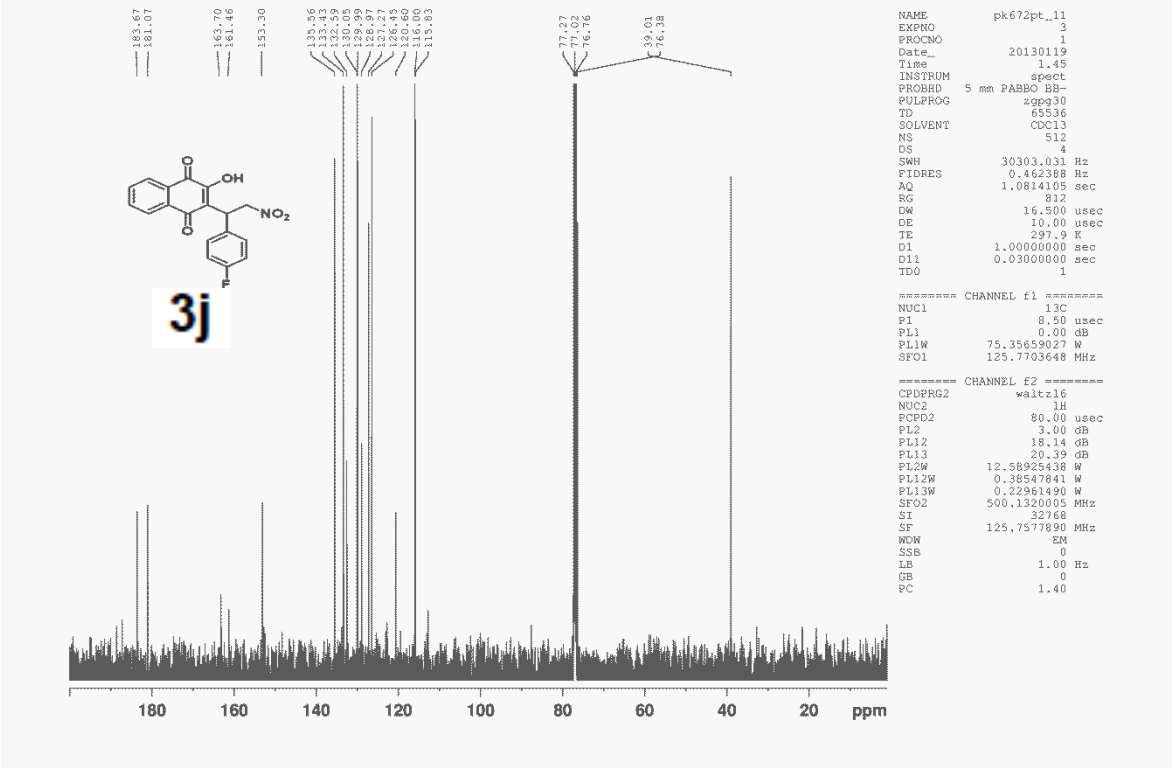

```
NAME          pk646pt_10
EXPNO                  1
PROCNO                 1
Date_           20130131
Time               19.59
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             4789.272 Hz
FIDRES          0.146157 Hz
AQ              3.4210291 sec
RG                 228.1
DW                104.400 usec
DE                  6.00 usec
TE                297.9 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.50 usec
PL1                -2.00 dB
PL1W           23.88643074 W
SFO1           400.1320007 MHz
SI                 16384
SF             400.1300103 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```



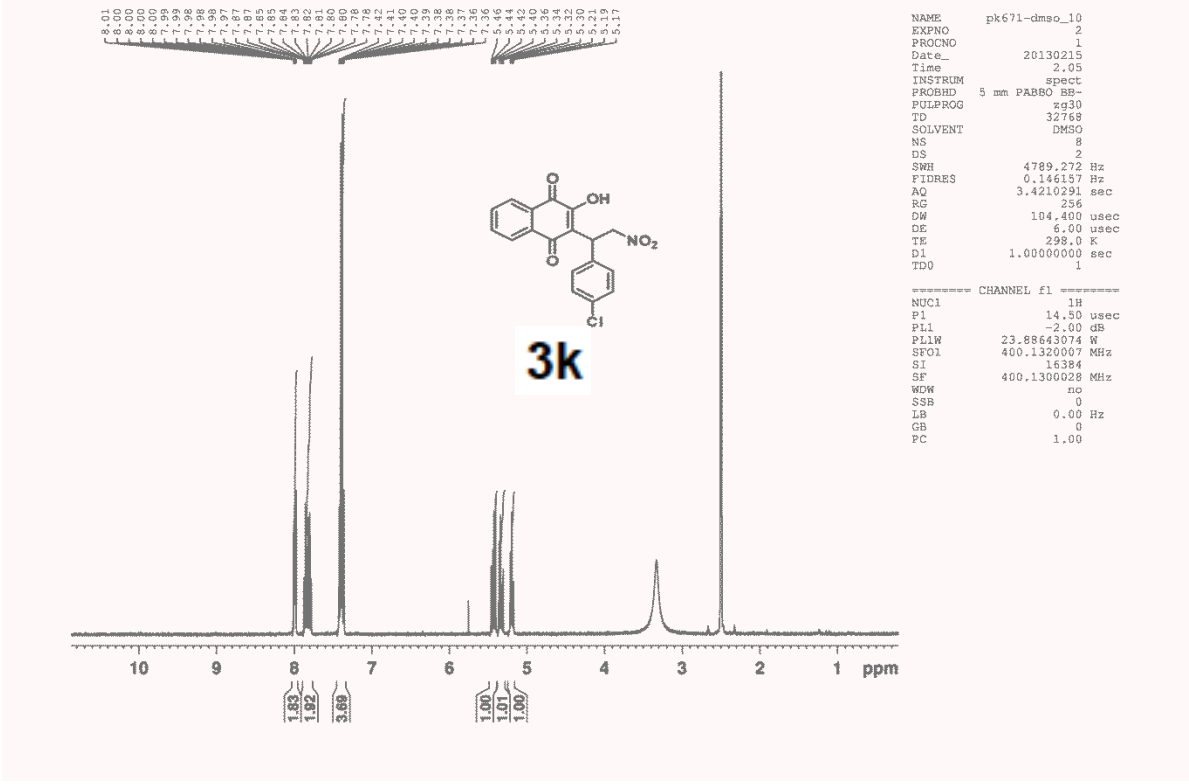

```
NAME          pk646pt_11
EXPNO                  1
PROCNO                 1
Date_           20130201
Time               1.06
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ              1.3664756 sec
RG                 23170.5
DW                 20.850 usec
DE                 10.00 usec
TE                298.1 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 10.00 usec
PL1                -3.00 dB
PL1W           75.17808533 W
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               13.00 dB
PL13               13.00 dB
PL2W           30.07123375 W
PL12W           0.75535524 W
PL13W           0.75535524 W
SFO2           400.1316005 MHz
SI                 32768
SF             100.6127690 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



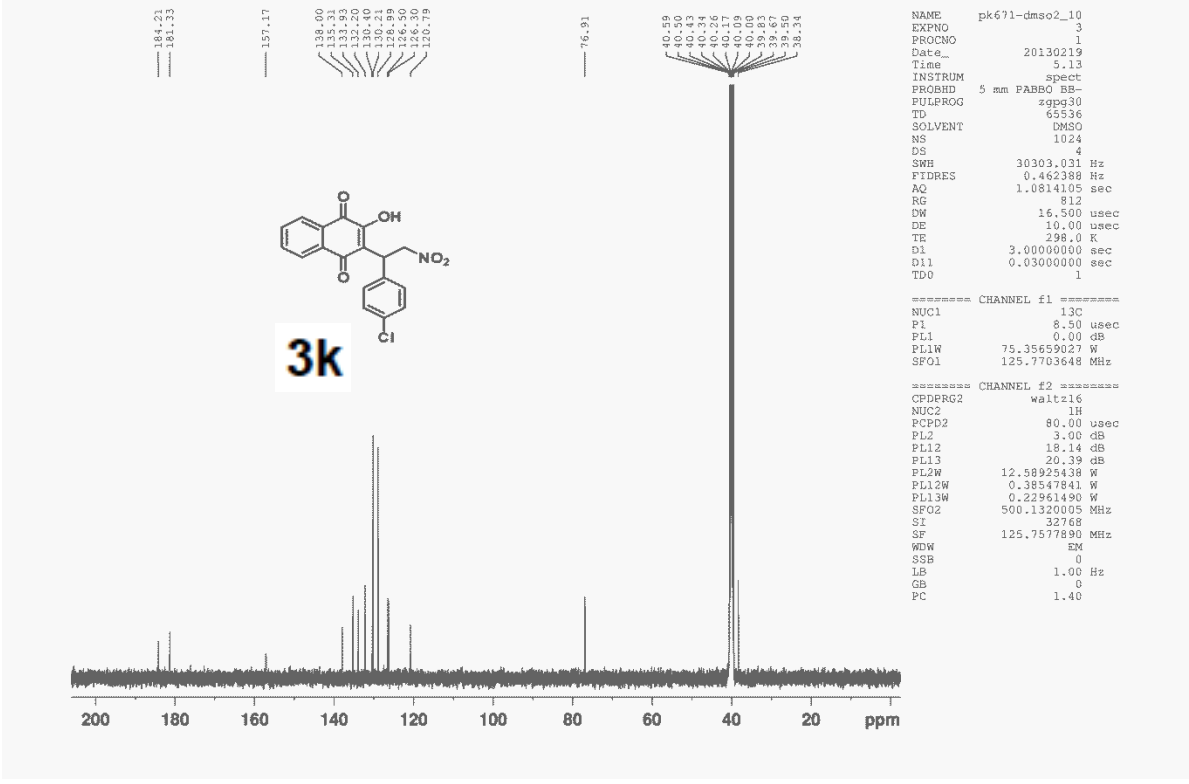

```
NAME            pk672p_10
EXPNO                   1
PROCNO                  1
Date_            20121203
Time                10.42
INSTRUM       FOURIER300
PROBHD    5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT             CDCl3
NS                      8
DS                      2
SWH             6103.516 Hz
FIDRES          0.093132 Hz
AQ              5.3687592 sec
RG                 64.6737
DW                 81.920 usec
DE                  6.50 usec
TE                 298.1 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         300.1818011 MHz
NUC1                   1H
P1                  8.20 usec
SI                 32768
SF           300.1800050 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.40
```



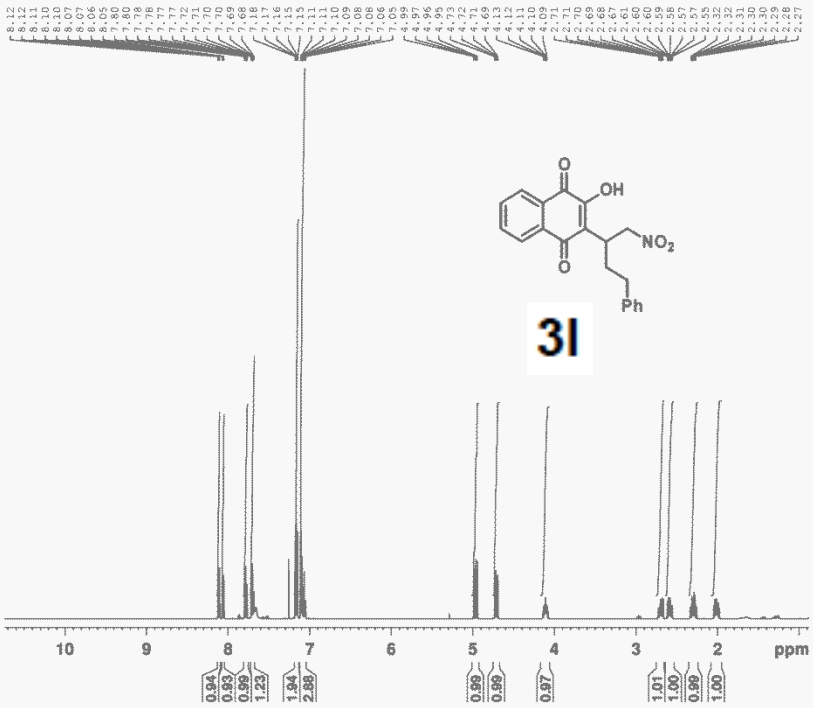

```
NAME            pk672pt_11
EXPNO                   3
PROCNO                  1
Date_            20130119
Time                 1.45
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG            zgpg30
TD                 65536
SOLVENT             CDCl3
NS                    512
DS                      4
SWH             30303.031 Hz
FIDRES          0.462388 Hz
AQ              1.0814105 sec
RG                    812
DW                 16.500 usec
DE                 10.00 usec
TE                 297.9 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   13C
P1                  8.50 usec
PL1                 0.00 dB
PL1W         75.35659027 W
SFO1        125.7703648 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                   1H
PCPD2              80.00 usec
PL2                 3.00 dB
PL12               18.14 dB
PL13               20.39 dB
PL2W         12.58925438 W
PL12W         0.38547841 W
PL13W         0.22961490 W
SFO2        500.1320005 MHz
SI                 32768
SF          125.7577890 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



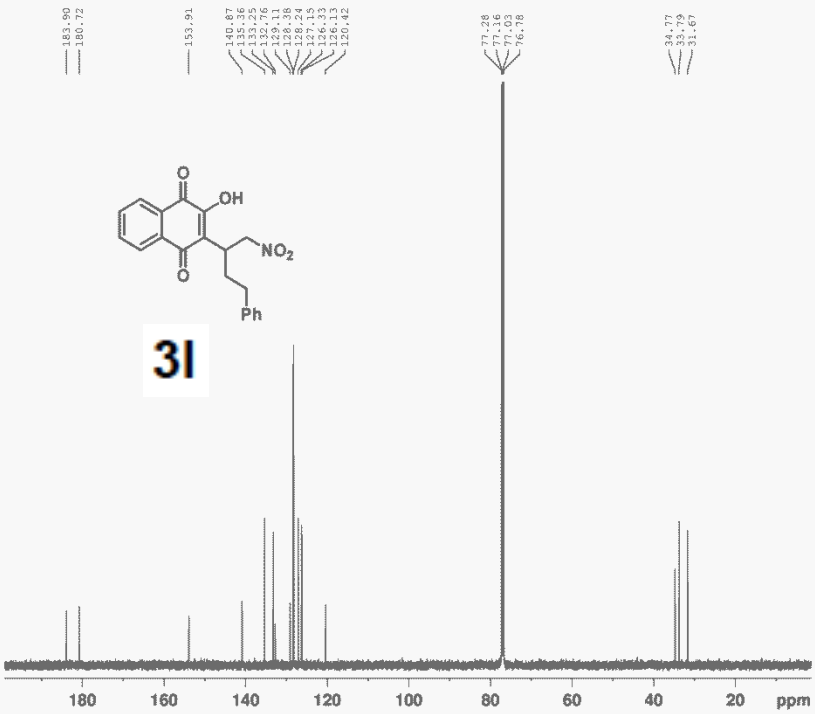

```
NAME          pk671-dmso_10
EXPNO                    2
PROCNO                   1
Date_             20130215
Time                 2.05
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT              DMSO
NS                      8
DS                      2
SWH              4789.272 Hz
FIDRES           0.146157 Hz
AQ               3.4210291 sec
RG                    256
DW                104.400 usec
DE                  6.00 usec
TE                 298.0 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.50 usec
PL1                 -2.00 dB
PL1W           23.88643074 W
SFO1           400.1320007 MHz
SI                   16384
SF             400.1300028 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```



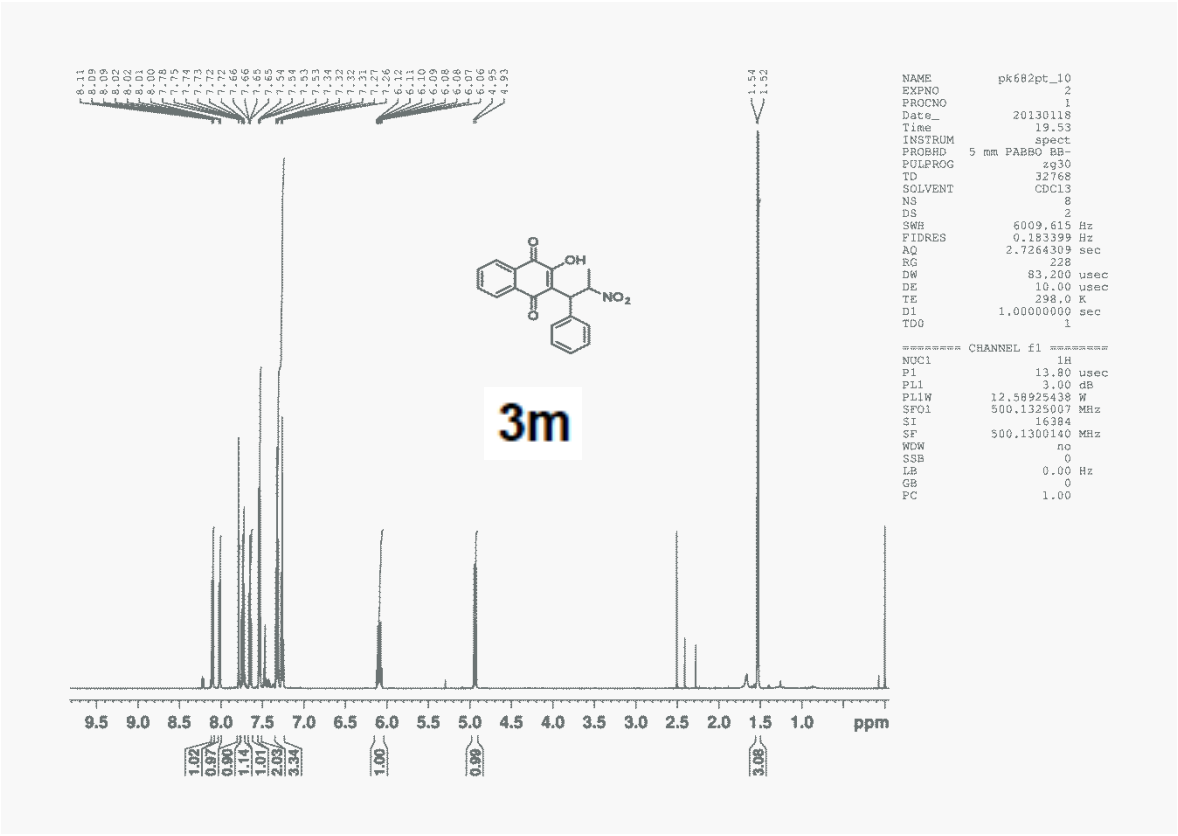

```
NAME          pk671-dmso2_10
EXPNO                    3
PROCNO                   1
Date_             20130219
Time                 5.13
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT              DMSO
NS                   1024
DS                      4
SWH             30303.031 Hz
FIDRES           0.462388 Hz
AQ               1.0814105 sec
RG                    812
DW                16.500 usec
DE                  10.00 usec
TE                 298.0 K
D1              3.00000000 sec
D11             0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.50 usec
PL1                  0.00 dB
PL1W          75.35659027 W
SFO1          125.7703648 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  3.00 dB
PL12                18.14 dB
PL13                20.39 dB
PL2W          12.58925438 W
PL12W          0.38547841 W
PL13W          0.22961490 W
SFO2          500.1320005 MHz
SI                   32768
SF            125.7577890 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



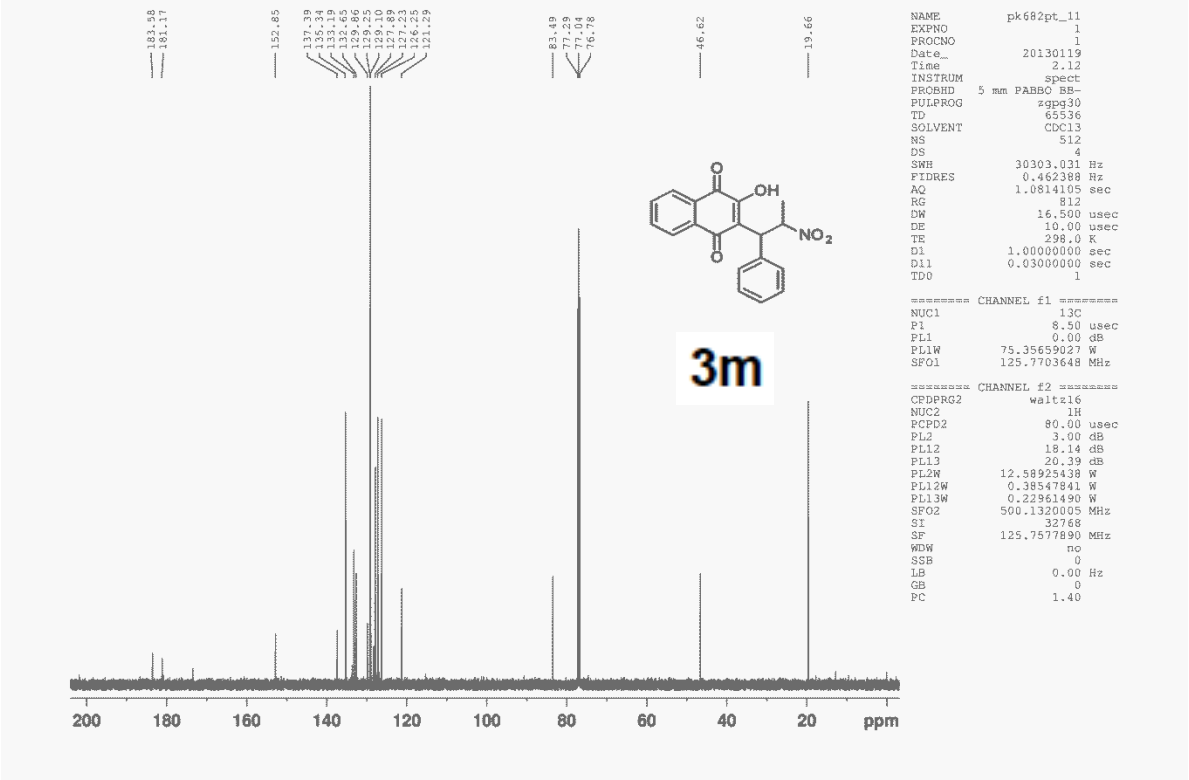

```
NAME            pk715t_10
EXPNO                   1
PROCNO                  1
Date_           20130222
Time                19.51
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT             CDCl3
NS                      8
DS                      2
SWH             6009.615 Hz
FIDRES          0.183399 Hz
AQ              2.7264309 sec
RG                    101
DW                93.200 usec
DE                10.00 usec
TE                298.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  1H
P1                13.80 usec
PL1                3.00 dB
PL1W         12.58925438 W
SFO1         500.1325007 MHz
SI                  16384
SF           500.1300161 MHz
WDW                    no
SSB                     0
LB                 0.00 Hz
GB                      0
PC                   1.00
```




```
NAME            pk715_11
EXPNO                   1
PROCNO                  1
Date_           20130220
Time                20.20
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT             CDCl3
NS                    512
DS                      4
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ              1.0814105 sec
RG                    812
DW                16.500 usec
DE                10.00 usec
TE                298.0 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                 13C
P1                 8.50 usec
PL1                0.00 dB
PL1W         75.35659027 W
SFO1         125.7703648 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             80.00 usec
PL2                3.00 dB
PL12              18.14 dB
PL13              20.39 dB
PL2W         12.58925438 W
PL12W         0.38547841 W
PL13W         0.22961490 W
SFO2         500.1320005 MHz
SI                  32768
SF           125.7577890 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                   1.40
```



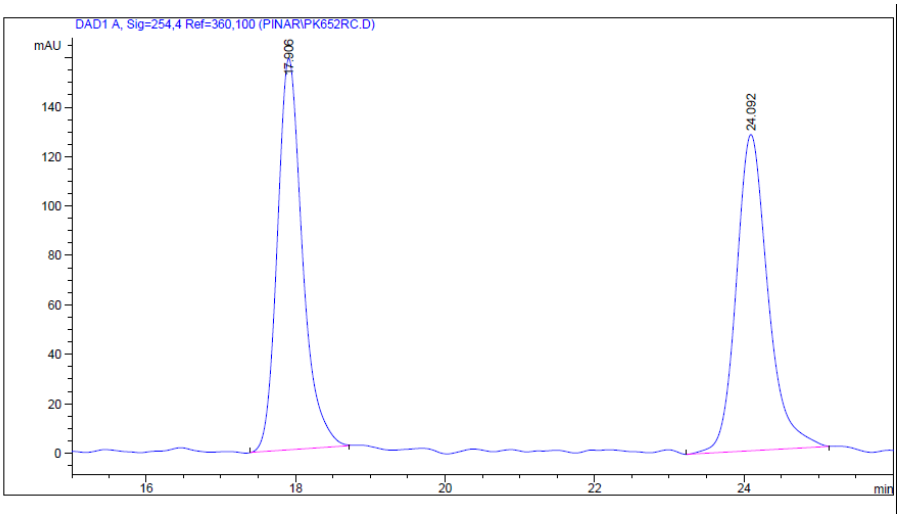

```
NAME          pk682pt_10
EXPNO                  2
PROCNO                 1
Date_           20130118
Time               19.53
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             6009.615 Hz
FIDRES          0.183399 Hz
AQ              2.7264309 sec
RG                   228
DW                83.200 usec
DE                10.00 usec
TE                298.0 K
D1              1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 13.80 usec
PL1                3.00 dB
PL1W          12.58925438 W
SFO1          500.1325007 MHz
SI                 16384
SF            500.1300140 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```




```
NAME          pk682pt_11
EXPNO                  1
PROCNO                 1
Date_           20130119
Time               2.12
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     4
SWH            30303.031 Hz
FIDRES          0.462388 Hz
AQ              1.0814105 sec
RG                   812
DW                16.500 usec
DE                10.00 usec
TE                298.0 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 8.50 usec
PL1                0.00 dB
PL1W          75.35659027 W
SFO1          125.7703648 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                3.00 dB
PL12               18.14 dB
PL13               20.39 dB
PL2W          12.58925438 W
PL12W          0.38547841 W
PL13W          0.22961490 W
SFO2          500.1320005 MHz
SI                 32768
SF            125.7577890 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.40
```

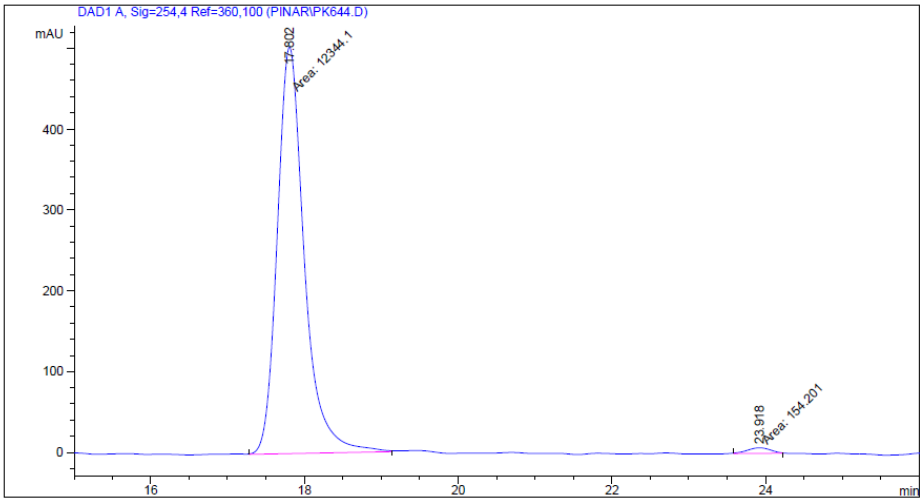
HPLC chromatograms of 3a-m

Racemic **3a**



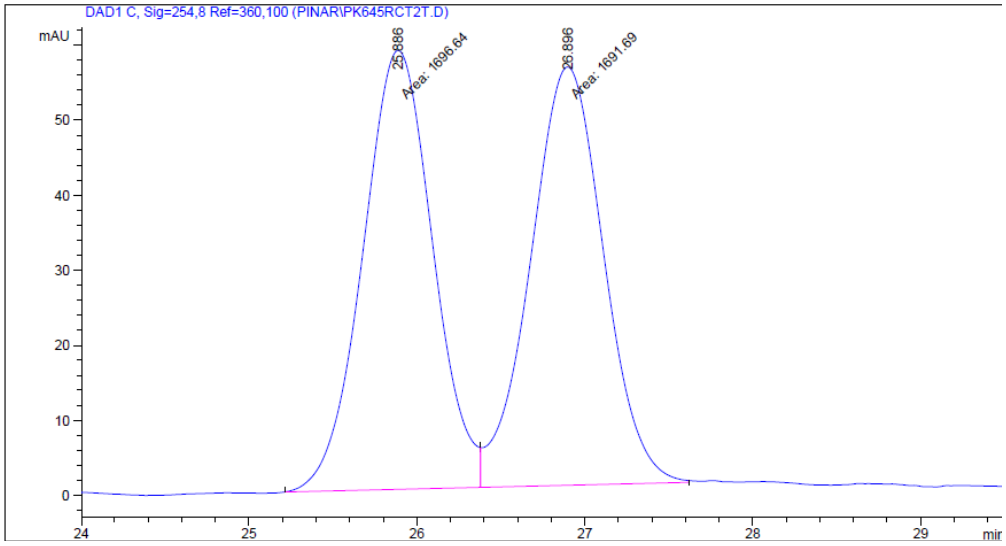
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.906	BB	0.3546	3704.31226	158.51859	49.4876
2	24.092	VB	0.4464	3781.01489	128.08470	50.5124

Enantioenriched **3a**



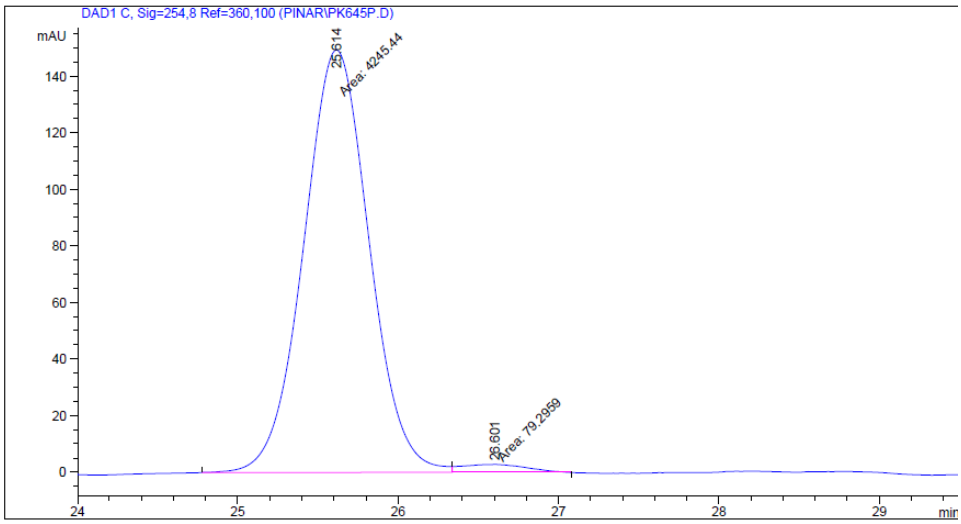
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.802	MM	0.4089	1.23441e4	503.11310	98.7662
2	23.918	MM	0.3580	154.20116	7.17821	1.2338

Racemic **3b**



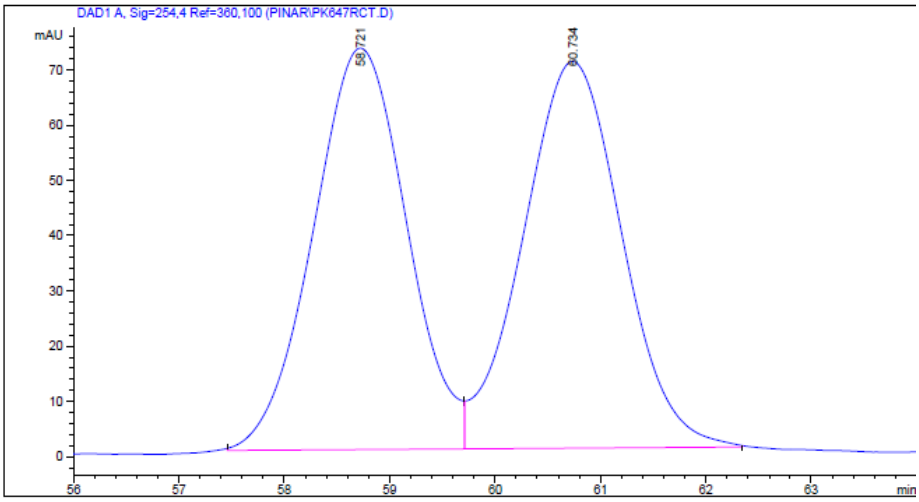
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.886	MF	0.4832	1696.63599	58.51677	50.0730
2	26.896	FM	0.5055	1691.68848	55.77486	49.9270

Enantioenriched **3b**



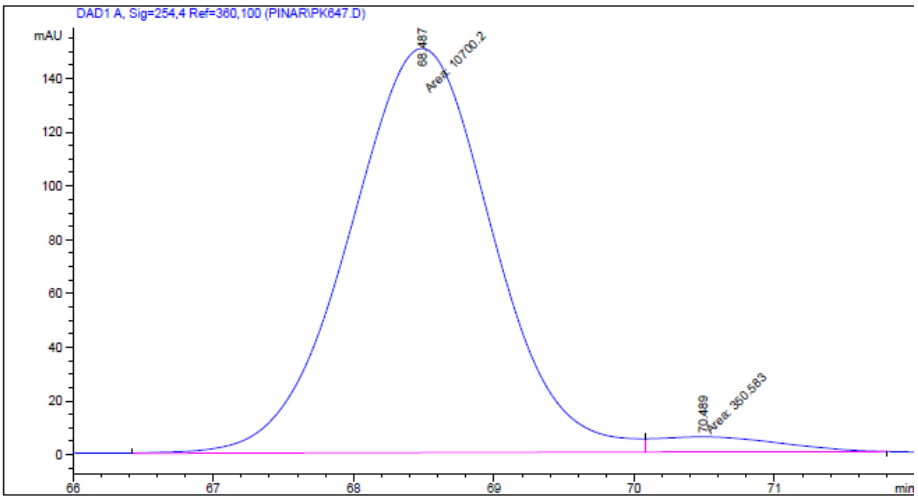
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.614	MF	0.4735	4245.44092	149.44862	98.1665
2	26.601	FM	0.4632	79.29591	2.85333	1.8335

Racemic **3c** [4]



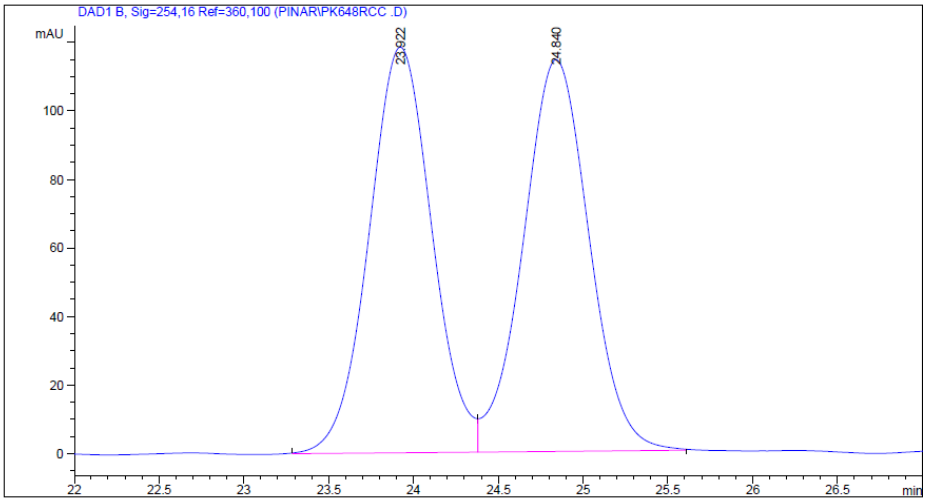
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	58.721	BV	0.9519	4486.43896	72.70438	49.5231
2	60.734	VB	1.0038	4572.84912	70.03064	50.4769

Enantioenriched **3c**



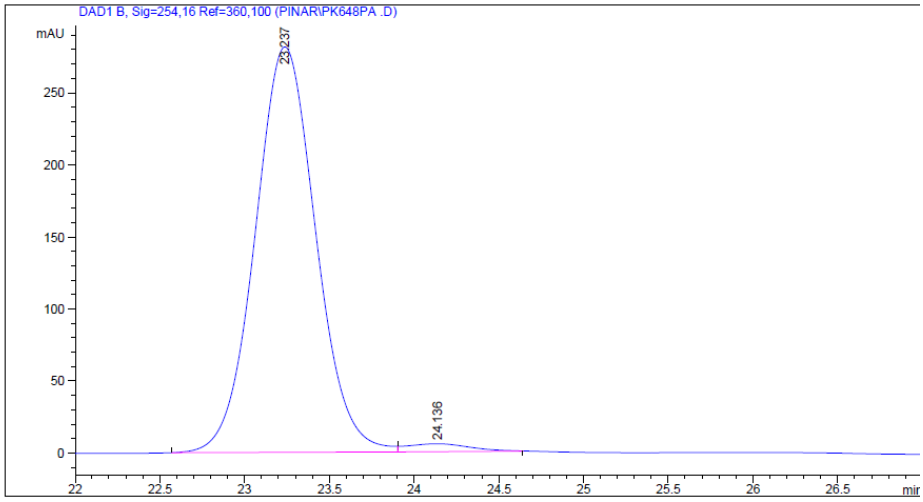
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	68.487	MF	1.1854	1.07002e4	150.44484	96.8275
2	70.489	FM	1.0188	350.58313	5.73535	3.1725

Racemic **3d**



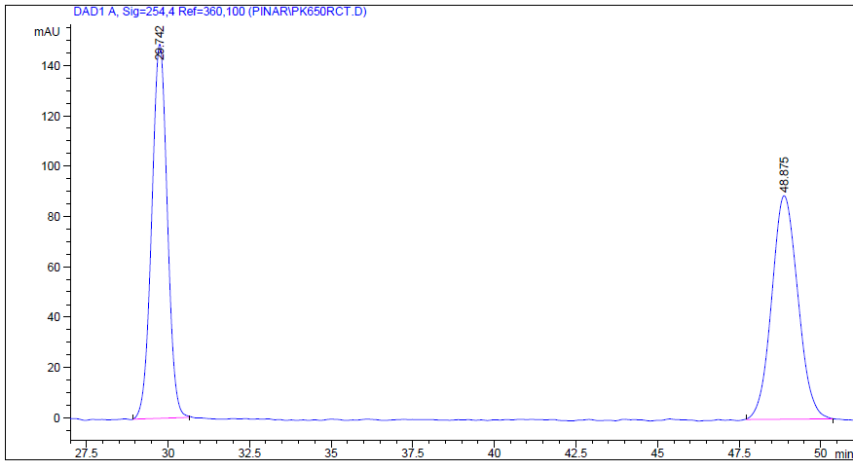
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.922	BV	0.3987	3051.84570	118.41208	49.7101
2	24.840	VB	0.4191	3087.43848	114.32726	50.2899

Enantioenriched **3d**



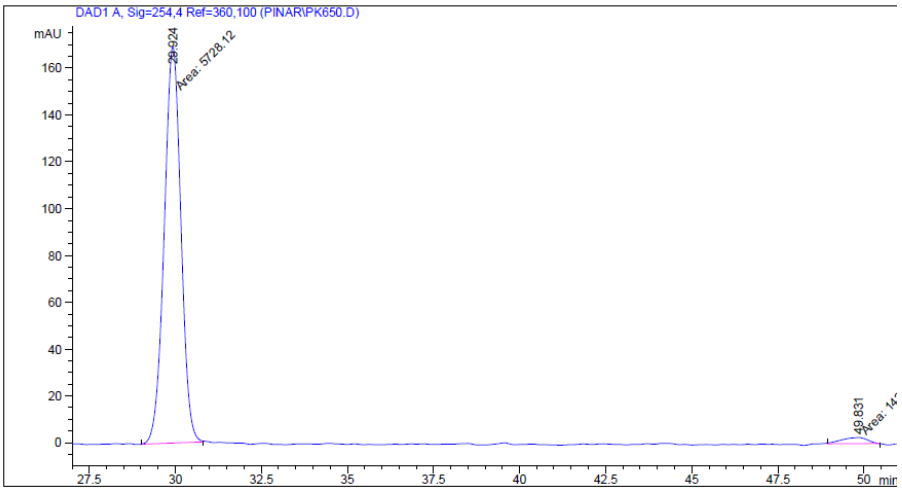
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.237	BB	0.3844	7013.01660	281.79114	97.9397
2	24.136	BB	0.3789	147.52817	5.64431	2.0603

Racemic **3e**



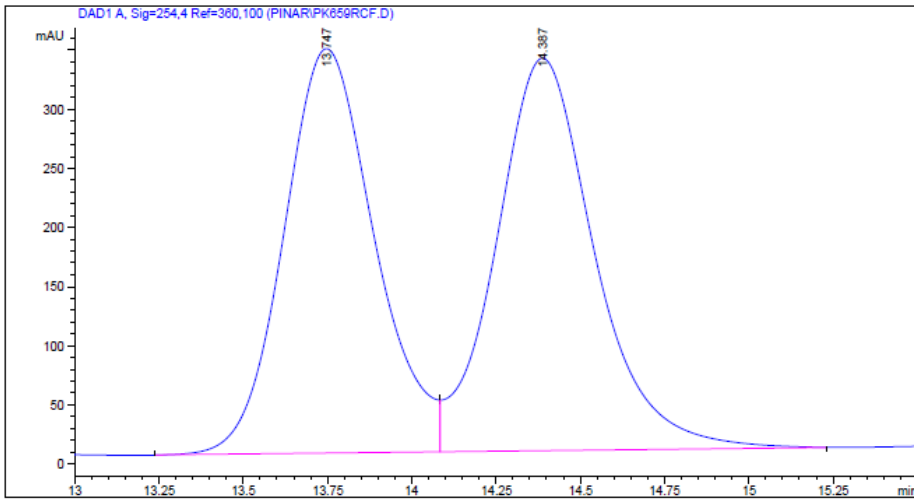
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.742	BB	0.5158	4947.71191	148.83781	49.8746
2	48.875	BB	0.8779	4972.58984	88.98877	50.1254

Enantioenriched **3e**



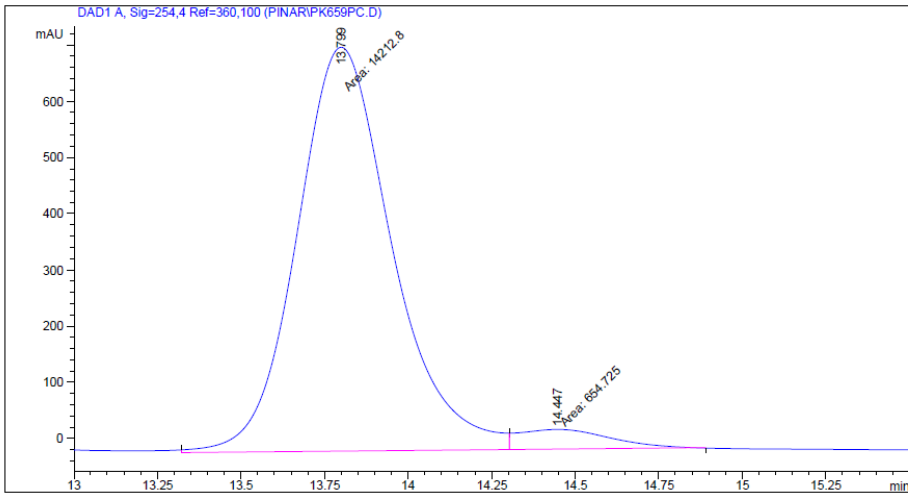
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.924	MM	0.5640	5728.11670	169.28139	97.5633
2	49.831	MM	0.8819	143.06218	2.70373	2.4367

Racemic **3f**



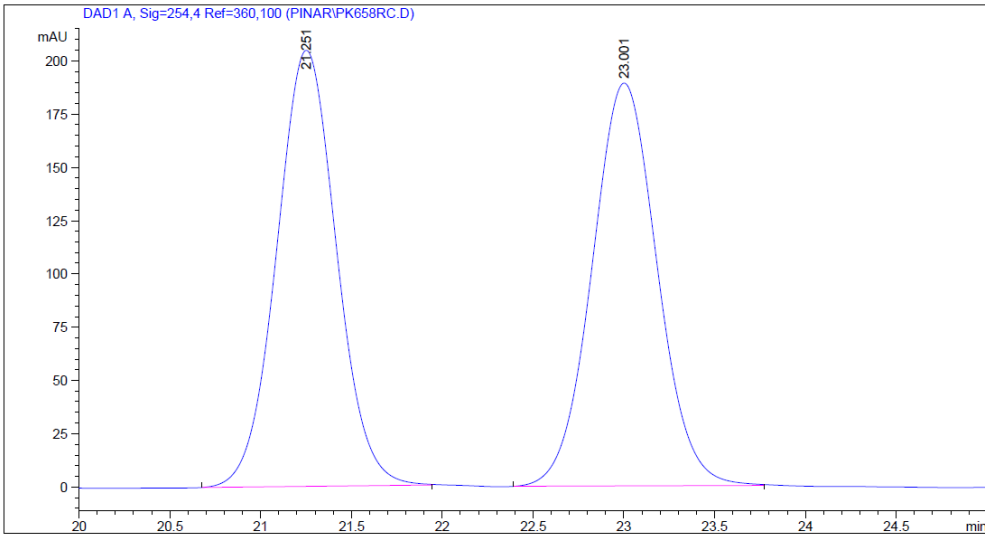
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.747	BV	0.2839	6386.39697	341.98383	48.6776
2	14.387	VB	0.3047	6733.39502	331.94006	51.3224

Enantioenriched **3f**



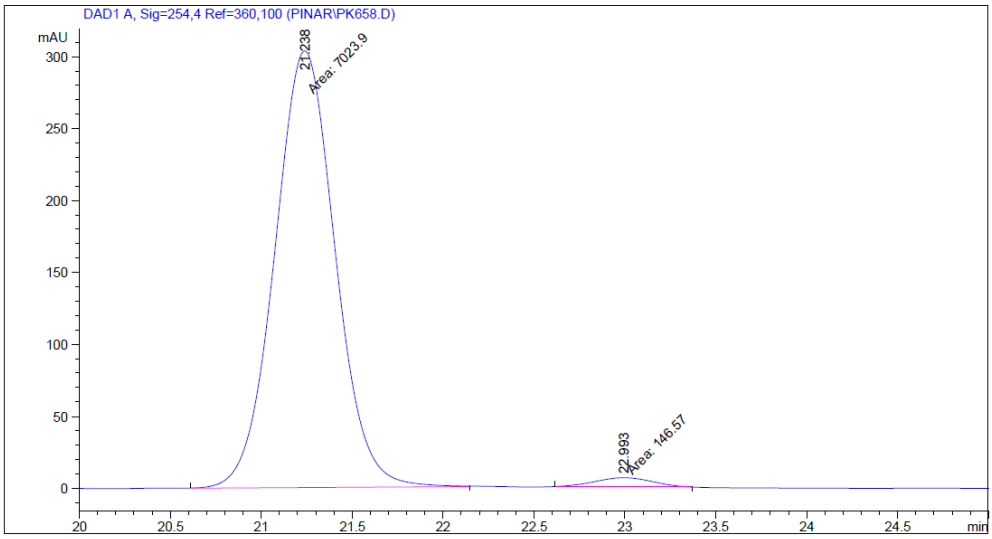
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.799	MF	0.3295	1.42128e4	718.94635	95.5963
2	14.447	FM	0.3105	654.72528	35.14039	4.4037

Racemic **3g**



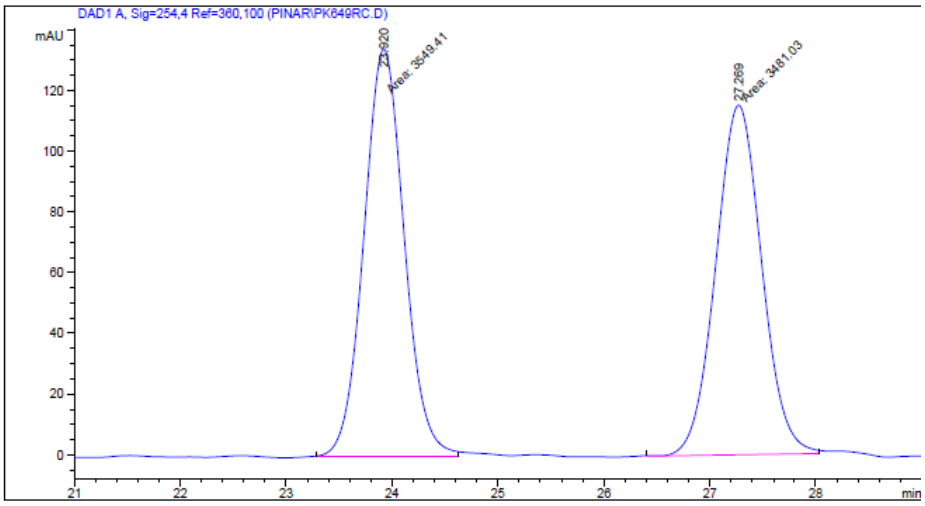
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.251	BB	0.3556	4697.72656	204.80247	49.8956
2	23.001	BB	0.3870	4717.39258	189.12001	50.1044

Enantioenriched **3g**



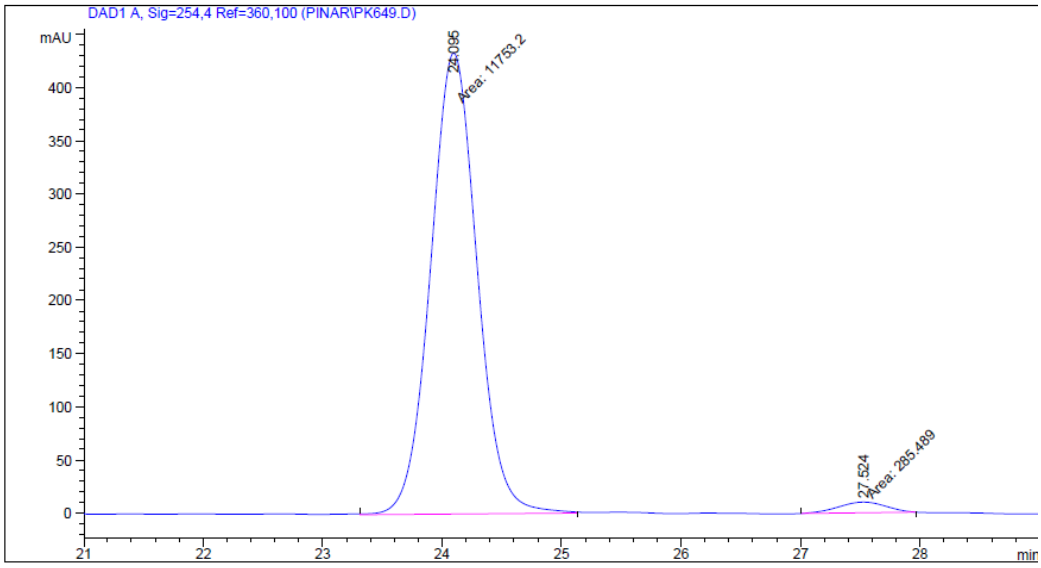
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.238	MM	0.3854	7023.89551	303.71033	97.9559
2	22.993	MM	0.3748	146.57024	6.51727	2.0441

Racemic **3h**



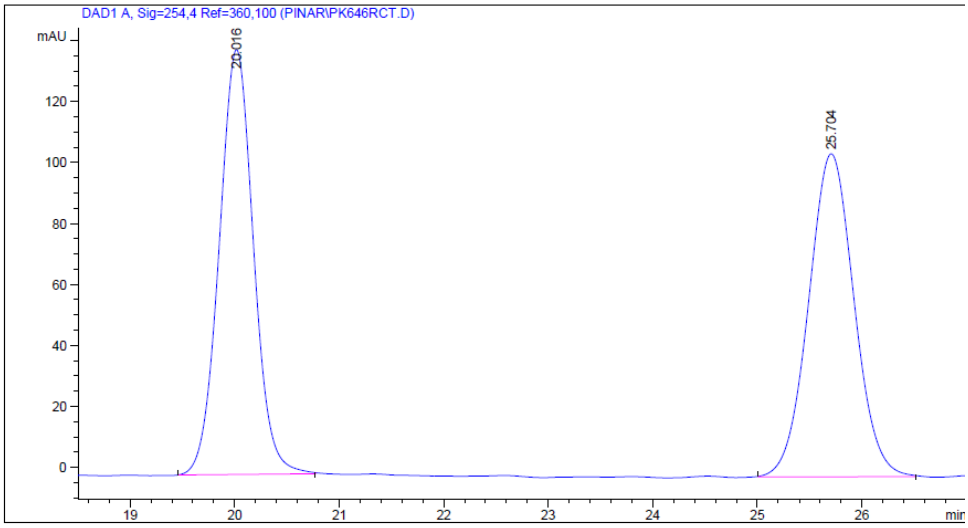
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.920	MM	0.4411	3549.41138	134.11685	50.4863
2	27.269	MM	0.5037	3481.03223	115.18871	49.5137

Enantioenriched **3h**



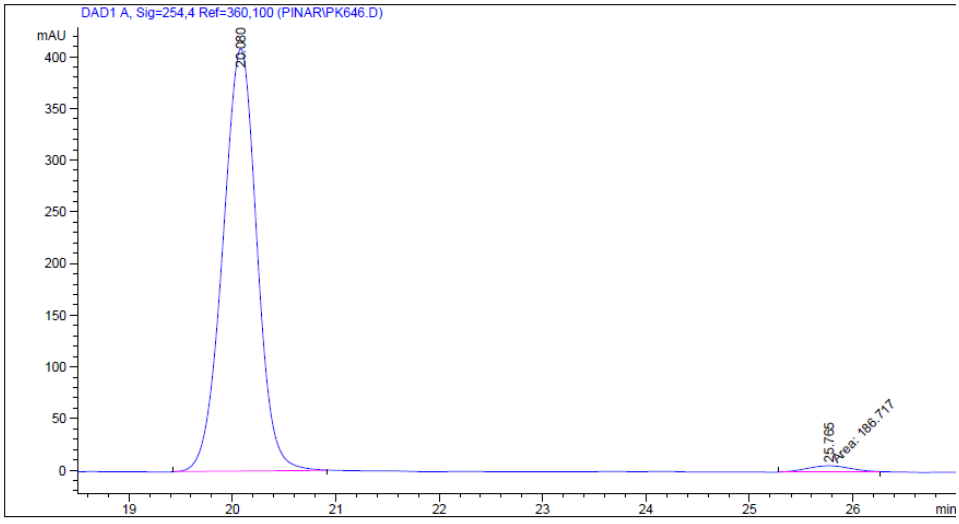
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.095	MM	0.4520	1.17532e4	433.41428	97.6286
2	27.524	MM	0.4689	285.48889	10.14751	2.3714

Racemic **3i**



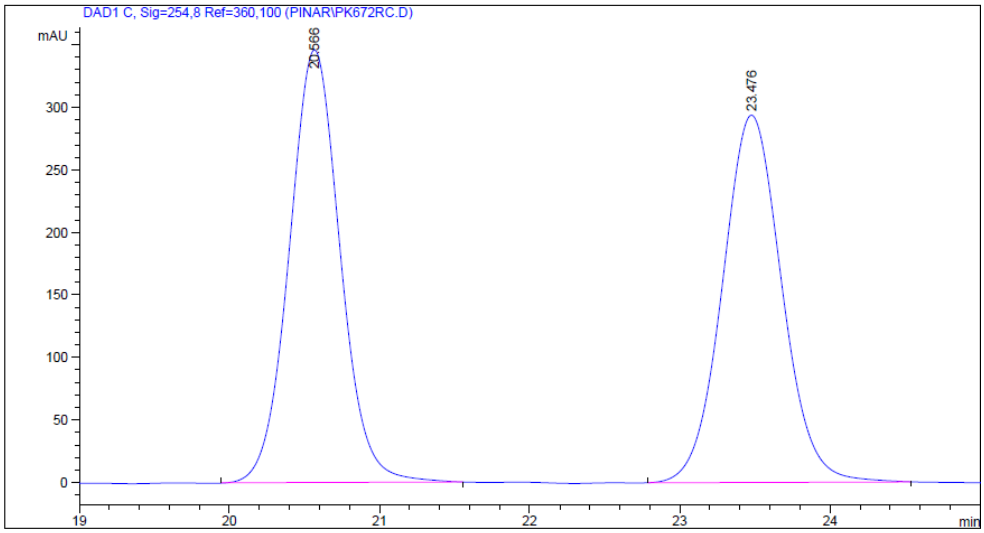
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.016	BB	0.3520	3181.97534	139.53908	49.8061
2	25.704	BB	0.4666	3206.75098	106.10830	50.1939

Enantioenriched **3i**



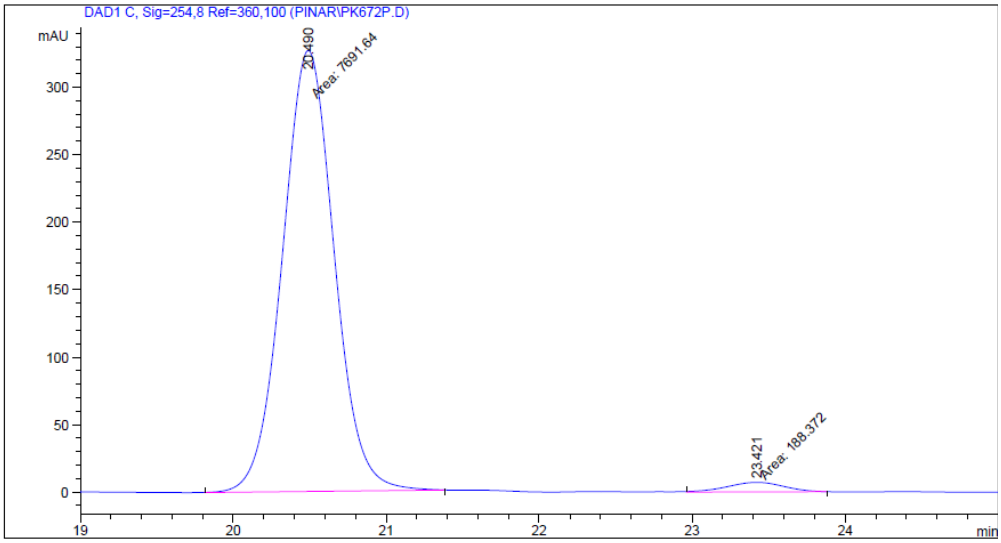
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.080	BB	0.3533	9366.82715	408.79440	98.0456
2	25.765	MM	0.5020	186.71684	6.19931	1.9544

Racemic **3j**



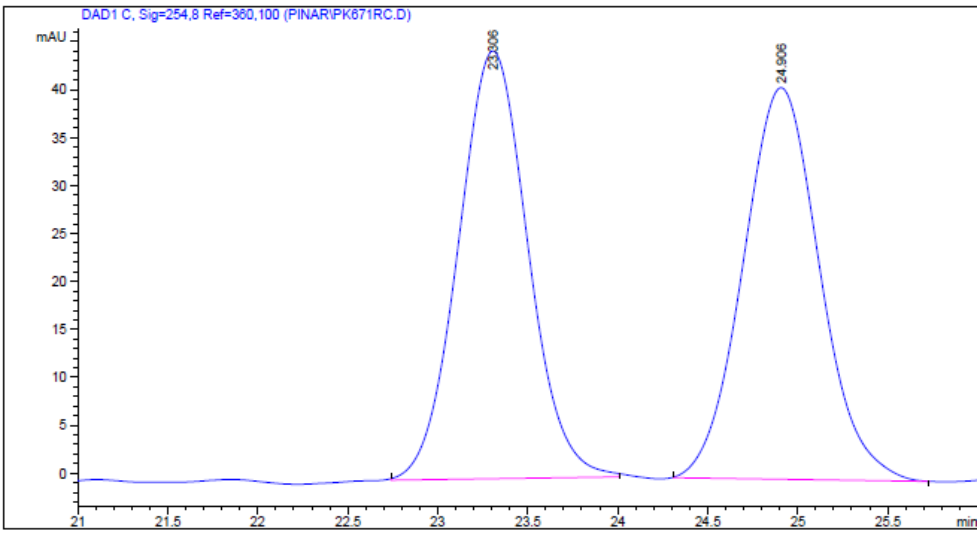
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.566	BB	0.3638	8186.64111	346.32211	50.3370
2	23.476	BB	0.4246	8077.02148	293.88864	49.6630

Enantioenriched **3j**



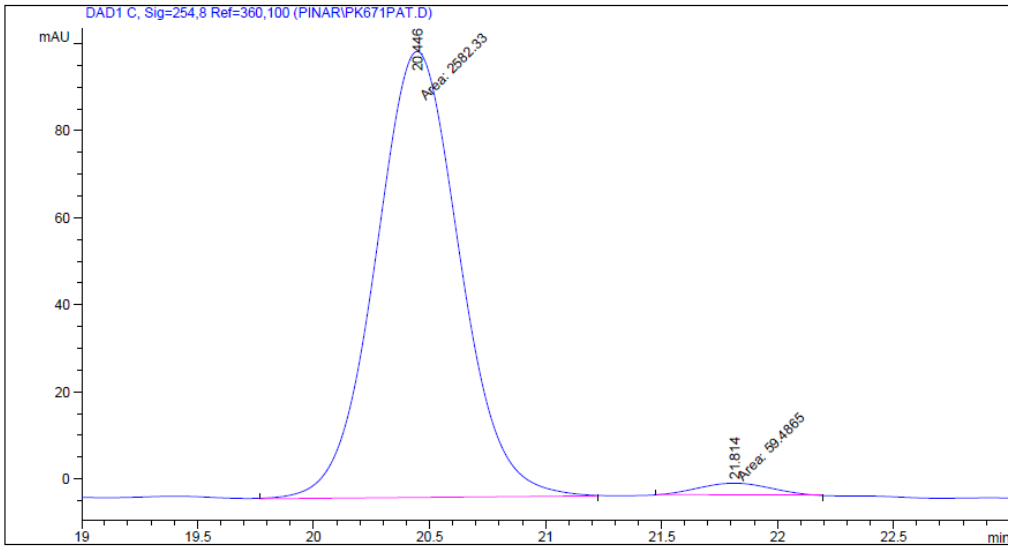
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.490	MM	0.3923	7691.63916	326.79651	97.6095
2	23.421	MM	0.4365	188.37187	7.19243	2.3905

Racemic **3k**



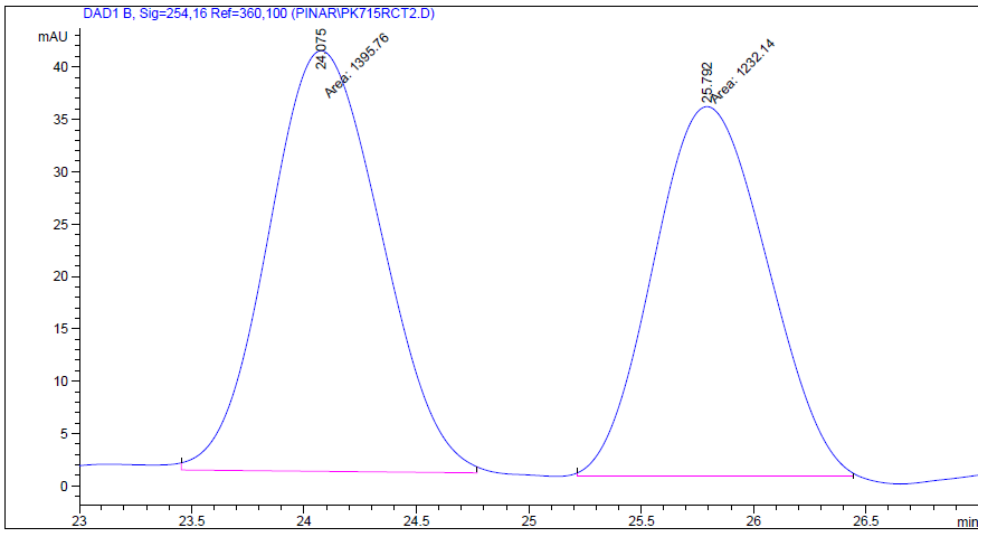
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.306	BB	0.4180	1201.36890	44.63844	49.8550
2	24.906	BB	0.4611	1208.35754	40.84908	50.1450

Enantioenriched **3k**



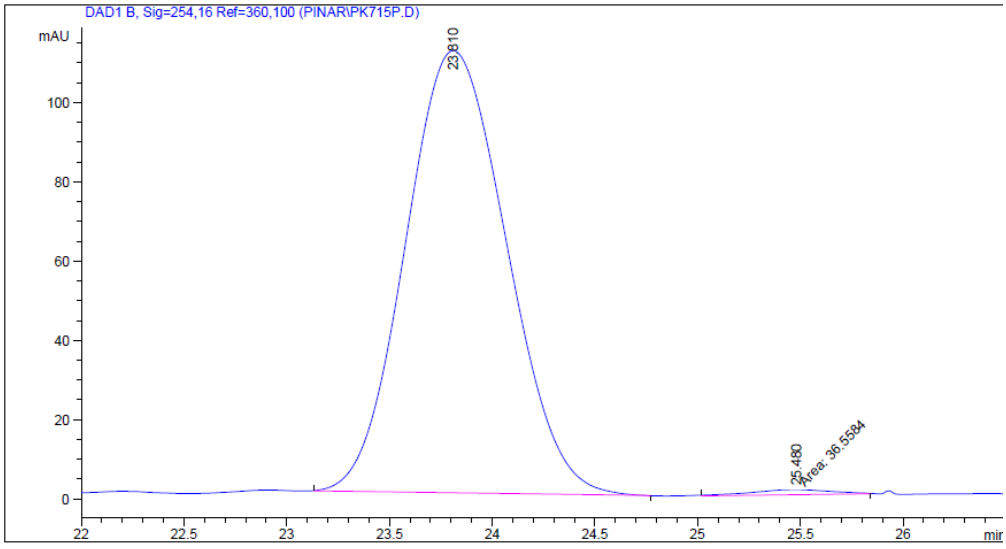
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.446	MM	0.4199	2582.33276	102.49802	97.7483
2	21.814	MM	0.3618	59.48645	2.74052	2.2517

Racemic **3l**



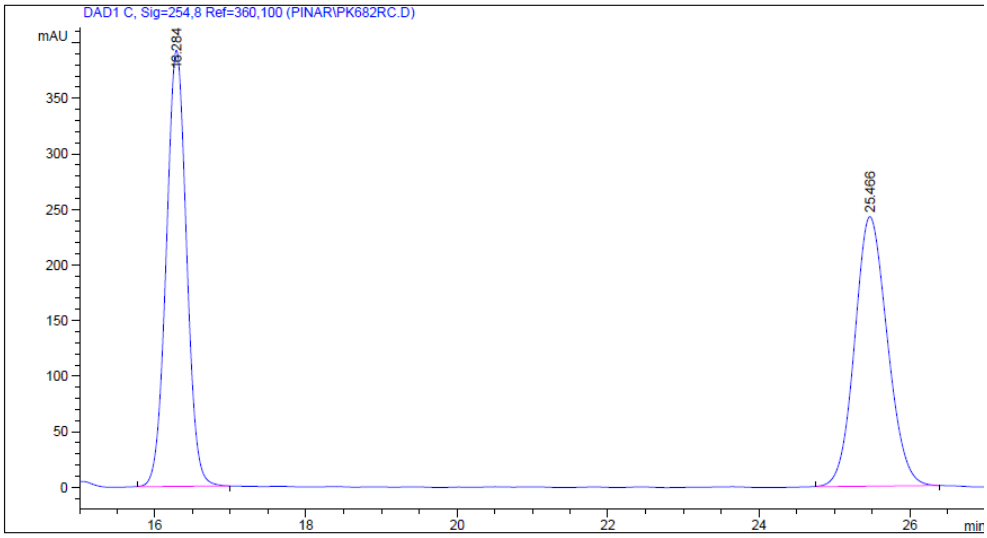
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.075	MM	0.5789	1395.75574	40.18335	53.1130
2	25.792	MM	0.5826	1232.14429	35.25049	46.8870

Enantioenriched **3l**



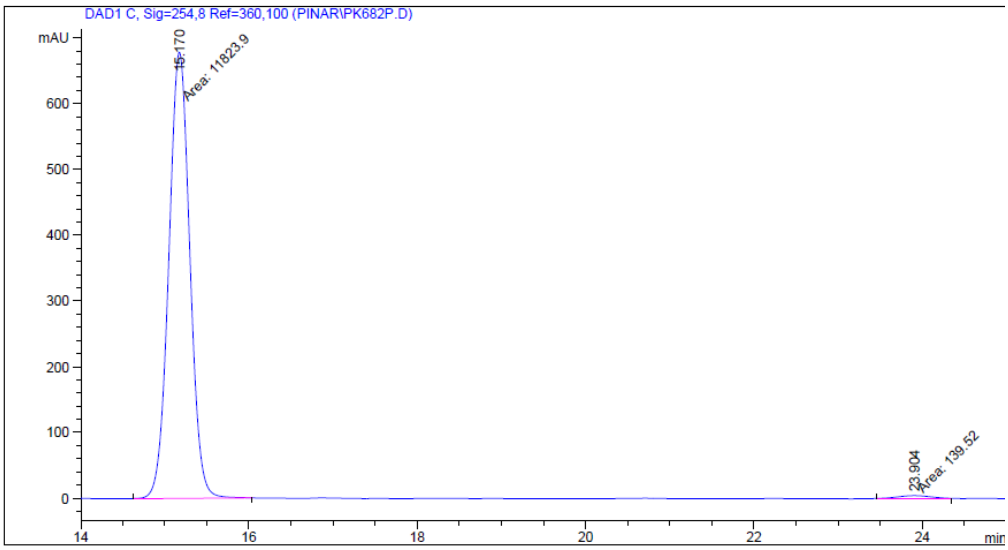
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.810	BB	0.5423	3808.82153	111.57813	99.0493
2	25.480	MM	0.4555	36.55839	1.33774	0.9507

Racemic **3m**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.284	BB	0.2902	7346.96924	392.85043	50.1074
2	25.466	BB	0.4654	7315.48438	242.84973	49.8926

Enantioenriched **3m**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.170	MM	0.2901	1.18239e4	679.20148	98.8338
2	23.904	MM	0.4884	139.51962	4.76158	1.1662

References

1. Kasaplar, P.; Riente, P.; Hartmann, C.; Pericàs, M. A., *Adv. Synth. Catal.* **2012,** *354*, 2905.
2. Zhou, W.-M.; Liu, H.; Du, D.-M., *Org. Lett.* **2008,** *10*, 2817.
3. Wu, R.; Chang, X.; Lu, A.; Wang, Y.; Wu, G.; Song, H.; Zhou, Z.; Tang, C., *Chem. Commun.* **2011,** *47*, 5034.
4. For racemic samples, HPLC flow was 0.7 ml/min.