Supporting Information for:

Low catalyst loading enabled organocatalytic synthesis of chiral *bis*-heterocyclic frameworks containing pyrazole and isoxazole

Banni Preet Kaur[a], Vivek Sharma[a], Subhash Chandra Sahoo[b], Swapandeep Singh Chimni[a]

[a] *Department of Chemistry, U.G.C. Centre of Advance Studies in Chemistry, Guru Nanak Dev University, Amritsar-143001, India; E-mail: sschimni@yahoo.com, sschimni.chem@gndu.ac.in.*

[b] *Department of Chemistry, Panjab University, Chandigarh-160014.*

Table of Contents

General Information

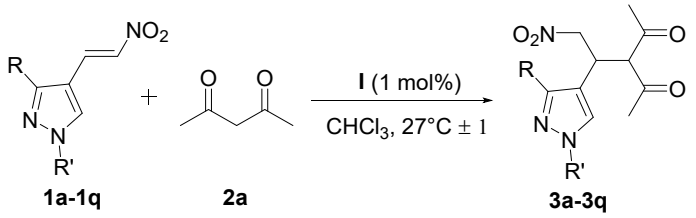
All the reactions were performed in oven-dried glassware. All solvents and commercially available chemicals were used without further purification. Pyrazolyl nitroalkenes were prepared according to the literature procedure.[1] Cinchona derived squaramide catalysts were prepared according to the procedure.[2] The column chromatography was carried out on a column packed with silica gel 60-120 mesh. ^{1}H NMR and spectra were recorded in $CDCl_3$ on a Bruker Avance III (500 MHz) and JEOL (400 MHz) spectrometer. ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker Avance III (125 MHz) and JEOL (100 MHz) spectrometer. Chemical shifts (δ) are expressed in ppm downfield from internal TMS. HRMS were recorded on micrOTOF-Q II 10356 Mass Spectrometer. Optical rotation was determined with Anton Paar MCP-150 polarimeter at 25°C using sodium D light. HPLC analyses were performed on a Shimadzu LC-20AD using Daicel Chiralpak IA, IB, IC and IE columns.

References:

1 P. Rathelot, N. Azas, H. E. Kashef, F. Delmas, C. D. Giorgio, P. T-. David, J. Maldonado and P. Vanelle, *Eur. J. Med. Chem.,* 2002, **37**, 671-679.

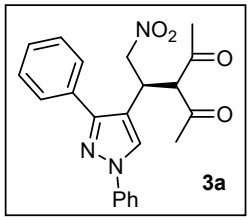
2 J. P. Malerich, K. Hagihara and V. H. Rawal, *J. Am. Chem. Soc*., 2008, **130**, 14416-14417.

General procedure for the reaction of pyrazolyl nitroalkenes with acetyl acetone



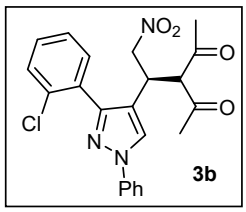
To a stirred solution of (*E*)-4-(2-nitrovinyl)-1,3-diphenyl-1*H*-pyrazole **1** (0.25 mmol) and organocatalyst **I** (1 mol%) in $CHCl_3$ (1.25 mL) was added acetyl acetone **2** (0.3 mmol, 1.2 equiv.) at 27 °C. The reaction was stirred for 12 h, and progress of the reaction was monitored at regular intervals by thin layer chromatography. The crude reaction mixture was purified by column chromatography on silica gel (mesh 60–120) using *n*-hexane:ethyl acetate (85:15) as the eluents to obtain the pure product **3**.

3-(1-(1,3-diphenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)pentane-2,4-dione (3a)



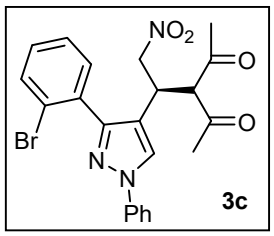
Light-yellow solid; 87% yield; mp. 95-96°C; $[\alpha]_D^{25}$= +170.00 (c 0.10, $CHCl_3$); 94% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 13.44 min (minor) and t_R = 23.90 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.70 – 7.67 (m, 2H), 7.64 – 7.62 (m, 2H), 7.53 – 7.49 (m, 2H), 7.47 – 7.42 (m, 3H), 7.31 – 7.28 (m, 1H), 4.75 (dd, *J* = 12.5, 5.9 Hz, 1H), 4.59 (dd, *J* = 12.4, 4.3 Hz, 1H), 4.43 – 4.39 (m, 1H), 4.35 (d, *J* = 9.4 Hz, 1H), 2.21 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 201.4, 151.7, 139.4, 132.3, 129.4, 129.0, 128.7, 128.4, 126.9, 126.6, 119.1, 115.9, 77.5, 70.0, 32.9, 30.7, 28.7; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{21}N_3O_4$ $[M+Na]^+$ 414.1424; found 414.1449.

3-(1-(3-(2-chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)pentane-2,4-dione (3b)



Pale-yellow solid; 76% yield; mp. 71-73°C; $[\alpha]_D^{25}$= +130.00 (c 0.10, $CHCl_3$); 96% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 8.18 min (minor) and t_R = 10.93 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.69 – 7.67 (m, 2H), 7.56 – 7.54 (m, 1H), 7.47 – 7.43 (m, 5H), 7.33 – 7.29 (m, 1H), 4.77 (dd, *J* = 12.6, 5.8 Hz, 1H), 4.60 (dd, *J* = 12.6, 4.6 Hz, 1H), 4.40 (d, *J* = 8.7 Hz, 1H), 3.99 – 3.94 (m, 1H), 2.23 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.8, 201.9, 149.9, 139.4, 133.9, 132.5, 131.4, 130.6, 129.9, 129.4, 127.2, 127.0, 126.4, 119.2, 117.3, 76.9, 69.5, 33.2, 30.9, 28.7; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{20}ClN_3O_4$ $[M+H]^+$ 426.1215; found 426.1226.

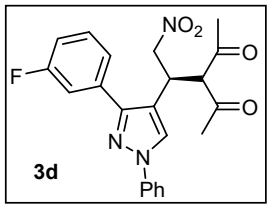
3-(1-(3-(2-bromophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)pentane-2,4-dione (3c)



Pale-yellow solid; 74% yield; mp. 98-99°C; $[\alpha]_D^{25}$= +113.33 (c 0.15, $CHCl_3$); 92% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 12.11 min (minor) and t_R = 18.84 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.73 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.71 – 7.67 (m, 2H), 7.49 – 7.42 (m, 4H), 7.38 – 7.34 (m, 1H), 7.32 – 7.28 (m, 1H), 4.80 (dd, *J* = 12.8, 6.0 Hz, 1H), 4.63 (dd, *J* = 12.7, 4.5 Hz, 1H), 4.41 (d, *J* = 8.4 Hz, 1H), 3.97 – 3.92 (m, 1H), 2.22 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.8, 201.9, 151.4, 139.5, 133.5, 133.1, 132.5, 130.8, 129.4, 127.7, 127.0, 126.3,

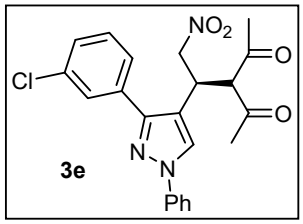
124.0, 119.2, 117.2, 76.9, 69.4, 33.2, 31.0, 29.0; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{20}BrN_3O_4$ $[M+Na]^+$ 492.0529; found 492.0509.

3-(1-(3-(3-fluorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)pentane-2,4-dione (3d)



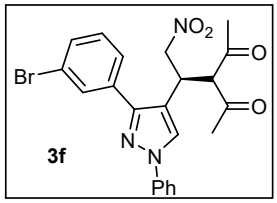
Pale-yellow solid; 74% yield; mp. 48-49°C; $[\alpha]_D^{25}$= +166.67 (c 0.15, $CHCl_3$); 94% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 12.55 min (minor) and t_R = 18.62 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.69 – 7.67 (m, 2H), 7.52 – 7.43 (m, 4H), 7.42 – 7.38 (m, 1H), 7.34 – 7.30 (m, 1H), 7.19 – 7.14 (m, 1H), 4.79 – 4.74 (m, 1H), 4.59 (dd, *J* = 12.5, 4.0 Hz, 1H), 4.43 – 4.36 (m, 2H), 2.24 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 201.2, 163.0 (*J* = 245.7 Hz), 150.4, 139.3, 134.4 (d, *J* = 7.9 Hz), 130.6 (d, *J* = 8.4 Hz), 129.5, 127.1, 126.8, 123.9 (d, *J* = 2.6 Hz), 119.2, 116.0, 115.8, 115.6, 115.4, 77.5, 70.1, 32.8, 30.8, 29.0; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{20}FN_3O_4$ $[M+Na]^+$ 432.1330; found 432.1293.

3-(1-(3-(3-chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)pentane-2,4-dione (3e)



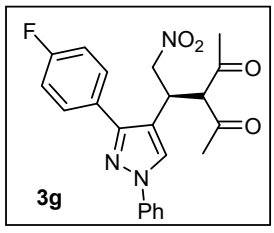
Brown semi-solid; 65% yield; $[\alpha]_D^{25}$= +110.00 (c 0.10, $CHCl_3$); 94% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 11.93 min (minor) and t_R = 16.13 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.69 – 7.66 (m, 3H), 7.55 – 7.52 (m, 1H), 7.47 – 7.42 (m, 4H), 7.34 – 7.30 (m, 1H), 4.80 – 4.75 (m, 1H), 4.60 – 4.57 (m, 1H), 4.41 – 4.35 (m, 2H), 2.23 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 201.2, 150.3, 139.3, 134.9, 134.1, 130.2, 129.5, 128.8, 128.6, 127.2, 126.8, 126.3, 119.2, 116.2, 77.5, 70.0, 32.8, 30.8, 29.1; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{20}ClN_3O_4$ $[M+H]^+$ 426.1215; found 426.1226.

3-(1-(3-(3-bromophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)pentane-2,4-dione (3f)



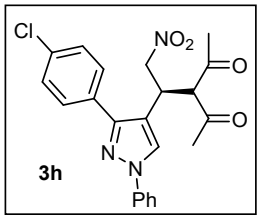
Light-yellow solid; 74% yield; mp. 43-44°C; $[\alpha]_D^{25}$= +106.67 (c 0.225, $CHCl_3$); 96% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 9.91 min (minor) and t_R = 14.94 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.84 – 7.82 (m, 1H), 7.69 – 7.67 (m, 2H), 7.61 – 7.57 (m, 2H), 7.48 – 7.44 (m, 2H), 7.42 –7.38 (m, 1H), 7.35 – 7.30 (m, 1H), 4.81 – 4.76 (m, 1H), 4.61 – 4.57 (m, 1H), 4.38 – 4.37 (m, 2H), 2.25 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 201.3, 150.2, 139.3, 134.3, 131.8, 131.5, 130.5, 129.5, 127.2, 126.8, 126.7, 123.1, 119.2, 116.1, 77.5, 70.0, 32.8, 30.9, 29.1; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{20}BrN_3O_4$ $[M+H]^+$ 470.0710; found 470.0728.

3-(1-(3-(4-fluorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)pentane-2,4-dione (3g)



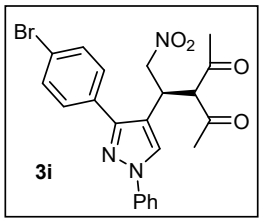
Light-brown semi-solid; 70% yield; $[\alpha]_D^{25}$= +130.00 (c 0.10, $CHCl_3$); 90% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 9.19 min (minor) and t_R = 15.43 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.68 – 7.61 (m, 4H), 7.48 – 7.44 (m, 2H), 7.33 – 7.30 (m, 1H), 7.24 – 7.19 (m, 2H), 4.76 – 4.72 (m, 1H), 4.59 – 4.55 (m, 1H), 4.39 – 4.33 (m, 2H), 2.24 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 201.3, 163.0 (d, *J* = 247.2 Hz), 150.9, 139.4, 130.3 (d, *J* = 8.4 Hz), 129.5, 128.4, 127.1, 126.6, 119.2, 116.21, 116.0, 115.9, 77.6, 70.1, 32.9, 30.8, 29.0; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{20}FN_3O_4$ $[M+H]^+$ 410.1511; found 410.1497.

3-(1-(3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)pentane-2,4-dione (3h)



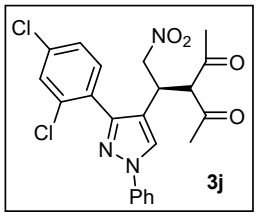
Light-brown solid; 62% yield; mp. 44-45°C; $[\alpha]_D^{25}$= +100.00 (c 0.10, $CHCl_3$); 95% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 9.73 min (minor) and t_R = 19.60 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.68 – 7.66 (m, 2H), 7.61 – 7.59 (m, 2H), 7.51 – 7.48 (m, 2H), 7.46 – 7.44 (m, 2H), 7.34 – 7.30 (m, 1H), 4.76 – 4.72 (m, 1H), 4.59 – 4.55 (m, 1H), 4.40 – 4.35 (m, 2H), 2.24 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 201.2, 150.6, 139.3, 134.9, 130.8, 129.7, 129.5, 129.3, 127.1, 126.8, 119.2, 116.0, 77.6, 70.1, 32.9, 30.8, 29.1; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{20}ClN_3O_4$ $[M+Na]^+$ 448.1035 found 448.1012.

3-(1-(3-(4-bromophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)pentane-2,4-dione (3i)



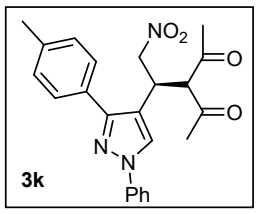
Light-yellow solid; 60% yield; mp. 51-52°C; $[\alpha]_D^{25}$= +120.00 (c 0.10, $CHCl_3$); 94% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 14.32 min (minor) and t_R = 31.56 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.68 – 7.65 (m, 4H), 7.55 – 7.52 (m, 2H), 7.49 – 7.44 (m, 2H), 7.34 – 7.30 (m, 1H), 4.76 – 4.72 (m, 1H), 4.59 – 4.55 (m, 1H), 4.40 – 4.36 (m, 2H), 2.25 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 201.2, 150.6, 139.3, 132.2, 131.3, 130.0, 129.5, 127.2, 126.8, 123.1, 119.2, 115.9, 77.6, 70.1, 32.9, 30.9, 29.1; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{20}BrN_3O_4$ $[M+H]^+$ 470.0710; found 470.0684.

3-(1-(3-(2,4-dichlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)pentane-2,4-dione (3j)

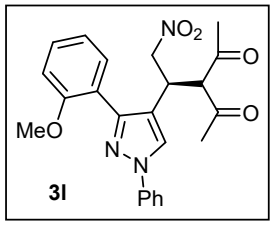


Pale-yellow solid; 71% yield; mp. 56-57°C; $[\alpha]_D^{25}$= +95.00 (c 0.20, $CHCl_3$); 97% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 10.02 min (minor) and t_R = 14.01 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.67 (d, J = 7.8 Hz, 2H), 7.58 (d, J = 1.4 Hz, 1H), 7.48 – 7.40 (m, 4H), 7.34 – 7.30 (m, 1H), 4.76 (dd, J = 12.7, 5.9 Hz, 1H), 4.59 (dd, J = 12.7, 4.5 Hz, 1H), 4.41 (d, J = 8.8 Hz, 1H), 3.95 – 3.91 (m, 1H), 2.24 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.5, 201.6, 148.9, 139.3, 136.0, 134.6, 133.30, 129.9, 129.7, 129.5, 127.6, 127.2, 126.5, 119.2, 117.4, 77.0, 69.5, 33.1, 31.0, 29.1; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{19}Cl_2N_3O_4$ $[M+Na]^+$ 482.0645; found 482.0607.

3-(2-nitro-1-(1-phenyl-3-(*p*-tolyl)-1*H*-pyrazol-4-yl)ethyl)pentane-2,4-dione (3k)



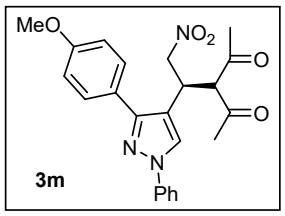
Light-yellow solid; 83% yield; mp. 53-54°C; $[\alpha]_D^{25}$= +155.00 (c 0.20, $CHCl_3$); 92% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 12.93 min (minor) and t_R = 29.67 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.69 – 7.67 (m, 2H), 7.52 – 7.50 (m, 2H), 7.46 – 7.42 (m, 2H), 7.33 – 7.27 (m, 3H), 4.75 (dd, J = 12.4, 5.5 Hz, 1H), 4.59 (dd, J = 12.4, 4.2 Hz, 1H), 4.40 – 4.35 (m, 2H), 2.43 (s, 3H), 2.22 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.5, 201.6, 151.8, 139.5, 138.7, 129.7, 129.4, 129.4, 128.3, 128.3, 128.3, 126.9, 126.6, 119.1, 119.1, 115.8, 77.5, 70.1, 33.0, 30.8, 28.6, 21.4; HRMS (ESI-TOF) m/z: calcd. for $C_{23}H_{23}N_3O_4$ $[M+Na]^+$ 428.1581; found 428.1580.



3-(1-(3-(2-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl) pentane-2,4-dione (3l)

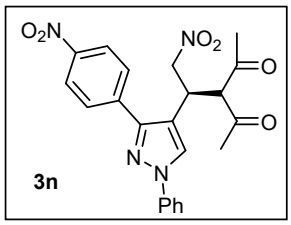
Light brown solid; 68% yield; mp. 43-45°C; $[\alpha]_D^{25}$= +120.00 (c 0.15, $CHCl_3$); 95% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 8.33 min (minor) and t_R = 12.99 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.69 – 7.66 (m, 2H), 7.48 – 7.41 (m, 4H), 7.29 – 7.26 (m, 1H), 7.11 – 7.04 (m, 2H), 4.71 (dd, *J* = 12.1, 5.0 Hz, 1H), 4.60 (dd, *J* = 12.1, 5.3 Hz, 1H), 4.36 (d, *J* = 9.6 Hz, 1H), 4.12 – 4.07 (m, 1H), 3.85 (s, 3H), 2.19 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 202.3, 156.9, 149.7, 139.5, 132.0, 130.7, 129.3, 126.6, 126.4, 121.3, 121.1, 119.0, 117.4, 111.1, 77.1, 69.9, 55.4, 33.5, 30.5, 27.9; HRMS (ESI-TOF) m/z: calcd. for $C_{23}H_{23}N_3O_5$ $[M+Na]^+$ 444.1530; found 444.1493.

3-(1-(3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl) pentane-2,4-dione (3m)



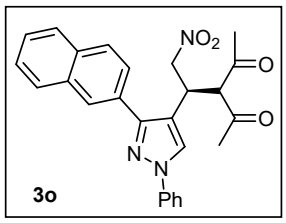
Brown solid; 75% yield; mp. 41-42°C; $[\alpha]_D^{25}$= +140.00 (c 0.20, $CHCl_3$); 90% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 19.04 min (minor) and t_R = 38.82 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.69 – 7.67 (m, 2H), 7.57 – 7.55 (m, 2H), 7.46 – 7.42 (m, 2H), 7.31 – 7.26 (m, 1H), 7.06 – 7.02 (m, 2H), 4.74 (dd, *J* = 12.4, 5.7 Hz, 1H), 4.59 (dd, *J* = 12.4, 4.2 Hz, 1H), 4.42 – 4.34 (m, 2H), 3.87 (s, 3H), 2.22 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 201.5, 160.0, 151.6, 139.5, 129.7, 129.4, 126.8, 126.6, 124.7, 119.1, 115.8, 114.5, 77.5, 70.1, 55.3, 33.0, 30.8, 28.7; HRMS (ESI-TOF) m/z: calcd. For $C_{23}H_{23}N_3O_5$ $[M+H]^+$ 422.1710; found 422.1691.

3-(2-nitro-1-(3-(4-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)ethyl)pentane-2,4-dione (3n)



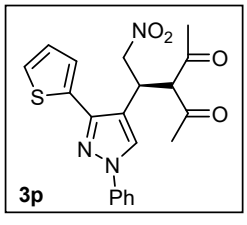
Yellow solid; 70% yield; mp. 92-94°C; $[\alpha]_D^{25}$= +20.00 (c 0.10, $CHCl_3$); 95% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 31.25 min (minor) and t_R = 45.95 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 – 8.38 (m, 2H), 7.93 – 7.89 (m, 3H), 7.70 – 7.68 (m, 2H), 7.51 – 7.47 (m, 2H), 7.38 – 7.34 (m, 1H), 4.75 (dd, *J* = 12.6, 6.1 Hz, 1H), 4.58 (dd, *J* = 12.6, 4.1 Hz, 1H), 4.48 – 4.39 (m, 2H), 2.29 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.7, 200.8, 149.4, 147.8, 139.1, 138.9, 129.6, 129.1, 127.6, 127.0, 124.2, 119.3, 116.7, 77.7, 70.1, 32.8, 30.9, 29.8; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{20}N_4O_6$ $[M+Na]^+$ 459.1275; found 459.1220.

3-(1-(3-(naphthalen-2-yl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)pentane-2,4-dione (3o)



Light-brown solid; 60% yield; mp. 53-54°C; $[\alpha]_D^{25}$= +140.00 (c 0.10, $CHCl_3$); 93% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 10.49 min (minor) and t_R = 16.23 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 0.8 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.97 – 7.91 (m, 2H), 7.90 (s, 1H), 7.77 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.73 – 7.71 (m, 2H), 7.57 – 7.55 (m, 2H), 7.49 – 7.45 (m, 2H), 7.34 – 7.30 (m, 1H), 4.80 (dd, *J* = 12.4, 6.1 Hz, 1H), 4.64 (dd, *J* = 12.4, 4.6 Hz, 1H), 4.55 – 4.50 (m, 1H), 4.38 (d, *J* = 9.2 Hz, 1H), 2.21 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 201.6, 151.6, 139.5, 133.4, 133.2, 129.8, 129.5, 128.9, 128.4, 127.8, 127.6, 127.0, 126.9, 126.7, 126.6, 126.0, 119.2, 116.2, 77.5, 70.0, 33.0, 30.9, 28.8; HRMS (ESI-TOF) m/z: calcd. for $C_{26}H_{23}N_3O_4$ $[M+Na]^+$ 464.1581; found 464.1566.

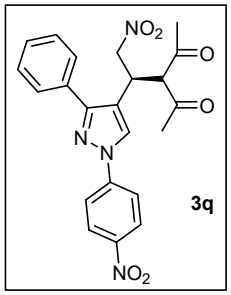
3,5-dimethyl-4-(2-nitro-1-(1-phenyl-3-(thiophen-2-yl)-1*H*-pyrazol-4-yl)ethyl)pentane-2,4-dione (3p)



Brown semi-solid; 69% yield; $[\alpha]_D^{25}$= +66.67 (c 0.15, $CHCl_3$); 97% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 9.97 min (minor) and t_R = 12.21 min (major)]; ^{1}H

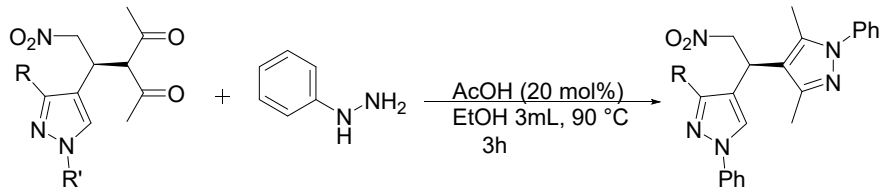
NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.69 – 7.66 (m, 2H), 7.47 – 7.42 (m, 4H), 7.33 – 7.29 (m, 1H), 7.18 (dd, J = 5.1, 3.6 Hz, 1H), 4.80 (dd, J = 12.4, 5.9 Hz, 1H), 4.68 (dd, J = 12.4, 4.7 Hz, 1H), 4.59 – 4.54 (m, 1H), 4.44 (d, J = 9.4 Hz, 1H), 2.27 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.5, 201.5, 145.5, 139.2, 133.7, 129.5, 127.9, 127.2, 127.1, 126.4, 125.9, 119.2, 115.6, 77.3, 70.0, 33.0, 30.8, 28.4; HRMS (ESI-TOF) m/z: calcd. for $C_{20}H_{19}N_3O_4S$ $[M+Na]^+$ 420.0988; found 420.0985.

3-(2-nitro-1-(1-(4-nitrophenyl)-3-phenyl-1*H*-pyrazol-4-yl)ethyl)pentane-2,4-dione (3q)



Yellow brown solid; 55% yield; mp. 72-74°C; $[\alpha]_D^{25}$= +60.00 (c 0.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.33 (m, 2H), 7.98 (s, 1H), 7.90 – 7.88 (m, 2H), 7.64 – 7.62 (m, 2H), 7.58 – 7.51 (m, 3H), 4.80 (dd, J = 12.6, 5.9 Hz, 1H), 4.60 (dd, J = 12.6, 4.4 Hz, 1H), 4.43 – 4.33 (m, 2H), 2.23 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.3, 201.5, 153.5, 145.7, 143.6, 131.5, 129.4, 129.2, 128.4, 127.1, 125.4, 118.7, 117.9, 77.2, 69.7, 32.8, 30.8, 28.8; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{20}N_4O_6$ $[M+Na]^+$ 437.1456; found 437.1433.

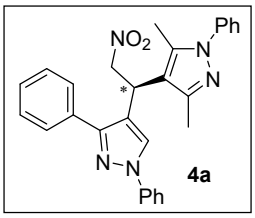
General procedure for the synthesis of *bis*-pyrazole derivatives 4



3a-q **7** **4a-q**

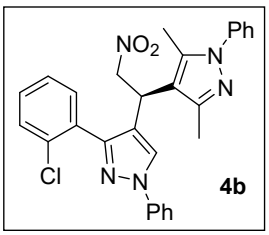
To a stirred solution of compound **3** (0.1 mmol) in 2 mL ethanol was added phenyl hydrazine **7** (0.11 mmol, 1.2 equiv.) and 20 mol% glacial acetic acid. The reaction mixture was refluxed at 90 °C for 3h, after which the solvent was reduced under pressure, and the crude reaction mixture was purified by column chromatography on silica gel (mesh 60–120) using *n*-hexane:ethyl acetate (85:15) as the eluents to obtain **4** as the pure product.

4-(1-(1,3-diphenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-3,5-dimethyl-1-phenyl-1*H*-pyrazole (4a)



Reddish brown semi-solid, 81% yield, $[\alpha]_D^{25}$ = +45.00 (c 0.2, $CHCl_3$); 99% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 7.97 min (minor) and t_R = 13.00 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 0.4 Hz, 1H), 7.73 – 7.70 (m, 2H), 7.58 – 7.55 (m, 2H), 7.48 – 7.42 (m, 7H), 7.38 – 7.36 (m, 1H), 7.32 – 7.29 (m, 3H), 5.07 (dd, J = 9.0, 7.4 Hz, 1H), 4.90 (dd, J = 12.4, 7.1 Hz, 1H), 4.78 (dd, J = 12.4, 9.4 Hz, 1H), 2.23 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 146.9, 139.7, 139.3, 137.4, 133.0, 129.5, 129.1, 128.6, 128.5, 128.2, 127.8, 126.7, 125.8, 125.2, 119.0, 118.6, 113.7, 77.4, 31.2, 13.2, 10.9; HRMS (ESI-TOF) m/z: calcd. for $C_{28}H_{25}N_5O_2$ $[M+H]^+$ 464.2081; found 464.2065.

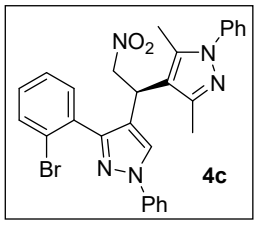
4-(1-(3-(2-chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-3,5-dimethyl-1-phenyl-1*H*-pyrazole (4b)



Reddish brown semi-solid; 57% yield; $[\alpha]_D^{25}$ = +76.00 (c = 0.5, $CHCl_3$); 97% *ee*, HPLC [Chiralpak IA, hexane/*i*-PrOH 85:15, 1ml/min, 254 nm, t_R = 7.82 min (minor) and t_R = 13.61 min (major)]; ^{1}H

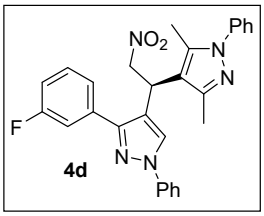
NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 0.8 Hz, 1H), 7.73 – 7.71 (m, 2H), 7.49 – 7.44 (m, 4H), 7.42 – 7.40 (m, 2H), 7.36 – 7.29 (m, 4H), 7.24 – 7.21 (m, 2H), 4.96 – 4.91 (m, 2H), 4.82 (dd, J =14.4, 11.8 Hz, 1H), 2.07 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 146.8, 139.7, 139.4, 137.5, 134.1, 132.3, 131.6, 130.1, 129.5, 129.4, 129.0, 127.7, 126.8, 126.7, 125.1, 124.2, 120.5, 119.0, 113.5, 77.4, 31.0, 12.8, 10.4; HRMS (ESI-TOF) m/z: calcd. for $C_{28}H_{24}ClN_5O_2$ $[M+H]^+$ 498.1691; found 498.1744.

4-(1-(3-(2-bromophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-3,5-dimethyl-1-phenyl-1*H*-pyrazole (4c)



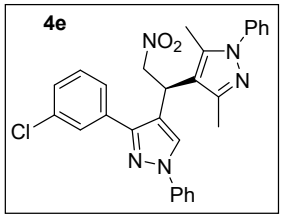
Reddish brown semi-solid; 60% yield; $[\alpha]_D^{25}$ = +110.00 (c = 0.5, $CHCl_3$); 93% *ee*, HPLC [Chiralpak IA, hexane/*i*-PrOH 85:15, 1ml/min, 254 nm, t_R = 10.25 min (minor) and t_R = 18.14 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.73 – 7.71 (m, 2H), 7.64 (dd, J = 7.8, 1.3 Hz, 1H), 7.48 – 7.43 (m, 3H), 7.42 – 7.40 (m, 2H), 7.36 – 7.32 (m, 2H), 7.30 – 7.27 (m, 1H), 7.23 – 7.21 (m, 2H), 7.19 – 7.17 (m, 1H), 4.98 – 4.87 (m, 2H), 4.82 (dd, J = 9.7, 7.3 Hz, 1H), 2.07 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 146.8, 139.6, 139.4, 137.5, 134.3, 132.5, 131.6, 130.2, 129.5, 129.0, 127.6, 127.3, 126.7, 125.1, 124.1, 124.0, 120.2, 119.0, 113.5, 77.1, 31.0, 12.8, 10.4; HRMS (ESI-TOF) m/z: calcd. for $C_{28}H_{24}BrN_5O_2$ $[M+H]^+$ 542.1186; found 542.1187.

4-(1-(3-(3-fluorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-3,5-dimethyl-1-phenyl-1*H*-pyrazole (4d)



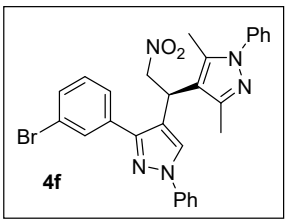
Reddish brown semi-solid; 71% yield; $[\alpha]_D^{25}$ = +74.00 (c = 0.5, $CHCl_3$); 97% *ee*, HPLC [Chiralpak IA, hexane/*i*-PrOH 85:15, 1ml/min, 254 nm, t_R = 7.55 min (minor) and t_R = 10.32 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 0.6 Hz, 1H), 7.73 – 7.70 (m, 2H), 7.50 – 7.48 (m, 2H), 7.45 – 7.43 (m, 2H), 7.39 – 7.27 (m, 7H), 7.11 – 7.06 (m, 1H), 5.06 – 5.02 (m, 1H), 4.93 (dd, J = 12.3, 7.6 Hz, 1H), 4.79 (dd, J = 12.3, 8.9 Hz, 1H), 2.22 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, J = 245.4 Hz), 150.6, 146.8, 139.6, 139.3, 137.4, 135.1 (d, J = 7.9 Hz), 130.2 (d, J = 8.4 Hz), 129.6, 129.1, 127.9, 127.0, 125.9, 125.2, 123.8, 119.1, 118.6, 115.4, 115.2, 113.6, 77.6, 31.3, 13.2, 10.9; HRMS (ESI-TOF) m/z: calcd. for $C_{28}H_{24}FN_5O_2$ $[M+Na]^+$ 504.1806; found 504.1741.

4-(1-(3-(3-chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-3,5-dimethyl-1-phenyl-1*H*-pyrazole (4e)



Reddish brown semi-solid; 67% yield; $[\alpha]_D^{25}$ = +34.00 (c = 0.5, $CHCl_3$); 95% *ee*, HPLC [Chiralpak IA, hexane/*i*-PrOH 85:15, 1ml/min, 254 nm, t_R = 9.17 min (minor) and t_R = 12.68 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 0.7 Hz, 1H), 7.73 – 7.70 (m, 2H), 7.51 – 7.49 (m, 2H), 7.48 – 7.46 (m, 3H), 7.44 – 7.42 (m, 2H), 7.39 – 7.38 (m, 1H), 7.35 – 7.34 (m, 2H), 7.31 – 7.29 (m, 2H), 5.04 – 5.00 (m, 1H), 4.95 (dd, J = 12.1, 7.7 Hz, 1H), 4.78 (dd, J = 12.1, 8.3 Hz, 1H), 2.19 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 146.9, 139.6, 139.3, 137.4, 134.8, 134.4, 129.8, 129.6, 129.1, 128.5, 128.3, 127.9, 127.0, 126.3, 125.7, 125.3, 119.2, 118.7, 113.6, 77.7, 31.3, 13.2, 10.9; HRMS (ESI-TOF) m/z: calcd. for $C_{28}H_{24}ClN_5O_2$ $[M+H]^+$ 498.1691; found 498.1746.

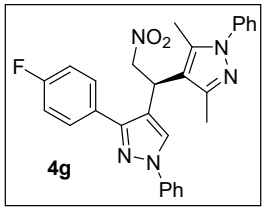
4-(1-(3-(3-bromophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-3,5-dimethyl-1-phenyl-1*H*-pyrazole (4f)



Reddish brown semi-solid; 70% yield; $[\alpha]_D^{25}$ = +72.00 (c = 0.5, $CHCl_3$); 98% *ee*, HPLC [Chiralpak IA, hexane/*i*-PrOH 85:15, 1ml/min, 254 nm, t_R = 7.84 min (minor) and t_R = 10.44 min

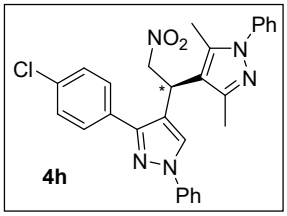
(major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 0.5 Hz, 1H), 7.73 – 7.71 (m, 2H), 7.66 – 7.65 (m, 1H), 7.51 – 7.46 (m, 5H), 7.45 – 7.43 (m, 2H), 7.39-7.37 (m, 1H), 7.33 – 7.30 (m, 3H), 5.04 – 5.00 (m, 1H), 4.95 (dd, J = 12.0, 7.8 Hz, 1H), 4.78 (dd, J = 12.0, 8.2 Hz, 1H), 2.19 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 146.8, 139.5, 139.3, 137.4, 135.0, 131.4, 131.2, 130.1, 129.6, 129.1, 127.9, 127.0, 126.8, 125.7, 125.3, 122.5, 119.1, 118.7, 113.5, 77.7, 31.3, 13.2, 11.0; HRMS (ESI-TOF) m/z: calcd. for $C_{28}H_{24}BrN_5O_2$ $[M+H]^+$ 542.1186; found 542.1100.

4-(1-(3-(4-fluorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-3,5-dimethyl-1-phenyl-1*H*-pyrazole (4g)



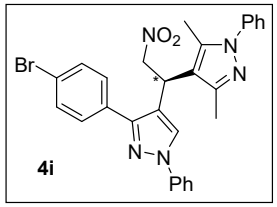
Reddish brown semi-solid; 76% yield; $[\alpha]_D^{25}$ = +52.00 (c = 0.5, $CHCl_3$); 91% *ee*, HPLC [Chiralpak IA, hexane/*i*-PrOH 85:15, 1ml/min, 254 nm, t_R = 9.23 min (minor) and t_R = 16.36 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 0.9 Hz, 1H), 7.72 – 7.69 (m, 2H), 7.54 – 7.49 (m, 3H), 7.47 (d, J = 1.2 Hz, 1H), 7.45 – 7.43 (m, 2H), 7.39 – 7.37 (m, 1H), 7.34 – 7.31 (m, 1H), 7.31 – 7.28 (m, 2H), 7.14 – 7.10 (m, 2H), 5.03 – 4.99 (m, 1H), 4.91 (dd, J = 12.3, 7.4 Hz, 1H), 4.81 – 4.76 (m, 1H), 2.21 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 146.8, 139.6, 139.3, 137.3, 130.1, 130.0, 129.5, 129.1, 127.9, 126.8, 125.7, 125.2, 119.1, 118.5, 115.7, 115.5, 113.7, 77.5, 31.2, 13.2, 11.0; HRMS (ESI-TOF) m/z: calcd. for $C_{28}H_{24}FN_5O_2$ $[M+H]^+$ 482.1987; found 482.1984.

4-(1-(3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-3,5-dimethyl-1-phenyl-1*H*-pyrazole (4h)



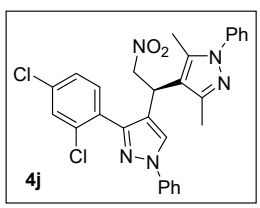
Reddish brown semi-solid, 65% yield, $[\alpha]_D^{25}$ = +48.00 (c 0.5, $CHCl_3$); 96% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH 85:15, 1 mL/min, 254 nm; t_R = 8.71 min (minor) and t_R = 15.59 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.71 – 7.69 (m, 2H), 7.51 – 7.44 (m, 7H), 7.41 – 7.3 (m, 3H), 7.30 – 7.28 (m, 2H), 5.04 – 5.00 (m, 1H), 4.92 (dd, J = 12.4, 7.4 Hz, 1H), 4.79 (d, J = 12.3, 9 Hz, 1H), 2.21 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 146.8, 139.6, 139.3, 137.4, 134.5, 131.5, 129.6, 129.5, 129.1, 128.8, 127.9, 126.9, 125.9, 125.2, 119.1, 118.6, 113.6, 77.5, 31.3, 13.2, 11.0; HRMS (ESI-TOF) m/z: calcd. for $C_{28}H_{24}ClN_5O_2$ $[M+H]^+$ 498.1691; found 498.1607.

4-(1-(3-(4-bromophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-3,5-dimethyl-1-phenyl-1*H*-pyrazole (4i)



Reddish brown semi-solid, 79% yield, $[\alpha]_D^{25}$ = +32.00 (c 0.5, $CHCl_3$); 86% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH 85:15, 1 mL/min, 254 nm; t_R = 9.24 min (minor) and t_R = 17.22 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 0.7 Hz, 1H), 7.72 – 7.69 (m, 2H), 7.56 – 7.54 (m, 2H), 7.49 – 7.45 (m, 4H), 7.44 – 7.42 (m, 2H), 7.40 – 7.32 (m, 2H), 7.30 – 7.27 (m, 2H), 5.04 – 5.00 (m, 1H), 4.92 (dd, J = 12.3, 7.4 Hz, 1H), 4.78 (dd, J = 12.3, 8.9 Hz, 1H), 2.20 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 146.8, 139.6, 139.2, 137.4, 132.0, 131.7, 129.8, 129.6, 129.1, 127.9, 126.9, 125.9, 125.3, 122.7, 119.1, 118.6, 113.6, 77.5, 31.3, 13.2, 11.0; HRMS (ESI-TOF) m/z: calcd. for $C_{28}H_{24}BrN_5O_2$ $[M+Na]^+$ 564.1006; found 564.1010.

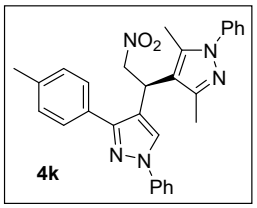
4-(1-(3-(2,4-dichlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-3,5-dimethyl-1-phenyl-1*H*-pyrazole (4j)



Reddish brown semi-solid, 60% yield, $[\alpha]_D^{25}$ = +46.00 (c 0.5, $CHCl_3$); 94% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH 85:15, 1 mL/min, 254 nm; t_R = 10.08 min (minor) and t_R = 20.70 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.72 – 7.70 (m, 2H), 7.48 – 7.46 (m, 3H), 7.44 – 7.42 (m,

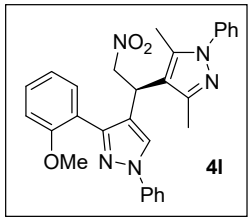
2H), 7.38 – 7.33 (m, 2H), 7.24 – 7.18 (m, 3H), 7.13 (d, J = 8.2 Hz, 1H), 4.99 – 4.89 (m, 2H), 4.81 (dd, J = 11.0, 8.2 Hz, 1H), 2.04 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 146.7, 139.5, 139.2, 137.5, 135.3, 134.8, 132.3, 131.0, 129.6, 129.1, 129.0, 127.8, 127.1, 127.0, 125.1, 124.2, 120.7, 119.1, 113.4, 77.2, 31.0, 12.9, 10.5; HRMS (ESI-TOF) m/z: calcd. for $C_{28}H_{23}Cl_2N_5O_2$ $[M+H]^+$ 532.1302; found 532.1323.

3,5-dimethyl-4-(2-nitro-1-(1-phenyl-3-(*p*-tolyl)-1*H*-pyrazol-4-yl)ethyl)-1-phenyl-1*H*-pyrazole (4k)



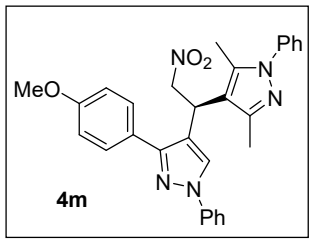
Reddish brown semi-solid; 64% yield; $[\alpha]_D^{25}$ = +30.00 (c = 0.5, $CHCl_3$); 84% *ee*, HPLC [Chiralpak IA, hexane/*i*-PrOH 85:15, 1ml/min, 254 nm, t_R = 7.78 min (minor) and t_R = 12.72 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 0.8 Hz, 1H), 7.72 – 7.69 (m, 2H), 7.49 – 7.43 (m, 7H), 7.39 – 7.35 (m, 1H), 7.33 – 7.32 (m, 1H), 7.31 – 7.30 (m, 1H), 7.25 – 7.23 (m, 2H), 5.10 – 5.05 (m, 1H), 4.89 (dd, J = 12.4, 6.9 Hz, 1H), 4.77 (dd, J = 12.4, 9.6 Hz, 1H), 2.39 (s, 3H), 2.25 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 146.9, 139.7, 139.4, 138.3, 137.5, 130.1, 129.5, 129.4, 129.1, 128.0, 127.8, 126.6, 126.0, 125.2, 119.0, 118.4, 113.8, 77.2, 31.3, 21.3, 13.3, 11.1; HRMS (ESI-TOF) m/z: calcd. for $C_{29}H_{27}N_5O_2$ $[M+H]^+$ 478.2238; found 478.2193.

4-(1-(3-(2-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-3,5-dimethyl-1-phenyl-1*H*-pyrazole (4l)



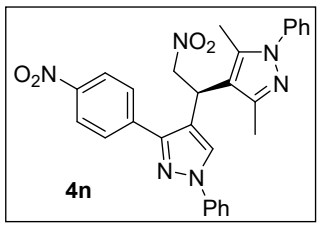
Reddish brown semi-solid; 68% yield; $[\alpha]_D^{25}$ = +28.00 (c = 0.5, $CHCl_3$); 96% *ee*, HPLC [Chiralpak IA, hexane/*i*-PrOH 85:15, 1ml/min, 254 nm, t_R = 8.13 min (minor) and t_R = 14.92 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 0.7 Hz, 1H), 7.71 – 7.69 (m, 2H), 7.46 – 7.41 (m, 5H), 7.39 – 7.35 (m, 3H), 7.29 – 7.26 (m, 1H), 7.28 – 7.27 (m, 1H), 7.03 – 6.99 (m, 1H), 6.98 (d, J = 8.3 Hz, 1H), 5.08 – 5.04 (m, 1H), 4.79 – 4.75 (m, 2H), 3.88 (s, 3H), 2.19 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 149.6, 147.0, 139.8, 139.5, 137.4, 131.3, 130.3, 129.4, 129.0, 127.6, 126.5, 125.1, 125.0, 122.0, 120.9, 120.7, 118.9, 114.0, 110.6, 77.23, 55.5, 31.4, 13.1, 10.7; HRMS (ESI-TOF) m/z: calcd. for $C_{29}H_{27}N_5O_3$ $[M+H]^+$ 494.2187; found 494.2286.

4-(1-(3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-3,5-dimethyl-1-phenyl-1*H*-pyrazole (4m)



Reddish brown semi-solid; 56% yield; $[\alpha]_D^{25}$ = +22.50 (c = 0.4, $CHCl_3$); 92% *ee*, HPLC [Chiralpak IA, hexane/*i*-PrOH 85:15, 1ml/min, 254 nm, t_R = 13.16 min (minor) and t_R = 24.11 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 0.8 Hz, 1H), 7.71 – 7.69 (m, 2H), 7.51 – 7.49 (m, 2H), 7.47 – 7.43 (m, 4H), 7.39 – 7.34 (m, 1H), 7.33 – 7.29 (m, 3H), 6.97 – 6.95 (m, 2H), 5.07 – 5.03 (m, 1H), 4.90 (dd, J = 12.4, 7.0 Hz, 1H), 4.78 (dd, J = 12.4, 9.5 Hz, 1H), 3.84 (s, 3H), 2.24 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 151.6, 146.9, 139.8, 139.4, 137.5, 129.5, 129.4, 129.1, 127.8, 126.6, 125.8, 125.4, 125.2, 119.0, 118.4, 114.1, 113.9, 77.4, 55.3, 31.4, 13.3, 11.0; HRMS (ESI-TOF) m/z: calcd. for $C_{29}H_{27}N_5O_3$ $[M+H]^+$ 494.2187; found 494.2241.

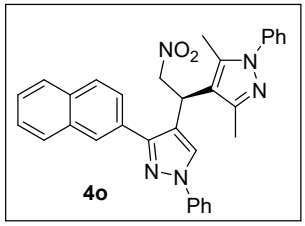
3,5-dimethyl-4-(2-nitro-1-(3-(4-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)ethyl)-1-phenyl-1*H*-pyrazole (4n)



Reddish brown semi-solid; 63% yield; $[\alpha]_D^{25}$ = +7.50 (c = 0.4, $CHCl_3$); 95% *ee*, HPLC [Chiralpak IA, hexane/*i*-PrOH 85:15, 1ml/min, 254 nm, t_R = 13.60 min (minor) and t_R = 24.69

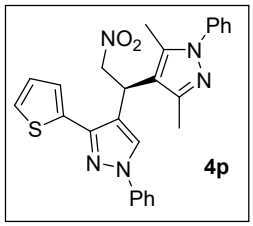
min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.26 (m, 2H), 7.95 (s, 1H), 7.78 – 7.76 (m, 2H), 7.74 – 7.72 (m, 2H), 7.52 – 7.48 (m, 2H), 7.45 – 7.43 (m, 2H), 7.40 – 7.35 (m, 2H), 7.27 – 7.25 (m, 2H), 5.10 – 5.06 (m, 1H), 4.95 (dd, *J* = 12.4, 7.8 Hz, 1H), 4.81 (dd, *J* = 12.4, 8.3 Hz, 1H), 2.20 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 147.5, 146.7, 139.6, 139.4, 139.1, 137.3, 129.7, 129.2, 128.8, 128.0, 127.4, 126.3, 125.1, 123.7, 119.2, 113.4, 77.7, 31.4, 13.2, 11.1; HRMS (ESI-TOF) m/z: calcd. for $C_{28}H_{24}N_6O_4$ $[M+Na]^+$ 531.1751; found 531.1744.

3,5-dimethyl-4-(1-(3-(naphthalen-2-yl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-1-phenyl-1*H*-pyrazole (4o)



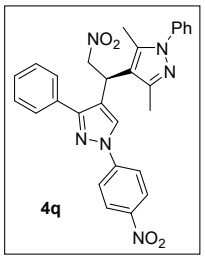
Reddish brown semi-solid; 75% yield; $[\alpha]_D^{25}$= +4.00 (c = 0.5, $CHCl_3$); 98% *ee*, HPLC [Chiralpak IA, hexane/*i*-PrOH 85:15, 1ml/min, 254 nm, t_R = 10.07 min (minor) and t_R = 14.57 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.91 – 7.84 (m, 5H), 7.76 – 7.72 (m, 3H), 7.53 – 7.52 (m, 1H), 7.49 – 7.47 (m, 2H), 7.39 – 7.38 (m, 2H), 7.36 – 7.33 (m, 2H), 7.17 – 7.15 (m, 2H), 5.17 (dd, *J* = 8.6, 7.6 Hz, 1H), 4.96 (dd, *J* = 12.4, 7.2 Hz, 1H), 4.80 (dd, *J* = 12.4, 9.2 Hz, 1H), 2.24 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 146.9, 139.8, 139.3, 137.5, 133.2, 133.1, 130.5, 129.6, 129.0, 128.3, 128.2, 127.8, 127.3, 126.8, 126.5, 126.4, 126.0, 125.9, 125.2, 119.1, 118.9, 113.8, 77.6, 31.5, 13.3, 11.0; HRMS (ESI-TOF) m/z: calcd. for $C_{32}H_{27}N_5O_2$ $[M+H]^+$ 514.2238; found 514.2297.

3,5-dimethyl-4-(2-nitro-1-(1-phenyl-3-(thiophen-2-yl)-1*H*-pyrazol-4-yl)ethyl)-1-phenyl-1*H*-pyrazole (4p)



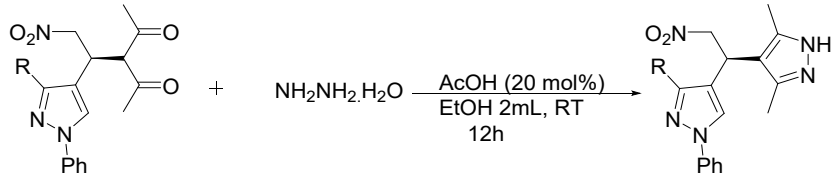
Reddish brown semi-solid; 66% yield; $[\alpha]_D^{25}$ = +18.00 (c = 0.5, $CHCl_3$); 95% *ee*, HPLC [Chiralpak IA, hexane/*i*-PrOH 85:15, 1ml/min, 254 nm, t_R = 8.86 min (minor) and t_R = 11.87 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 0.8 Hz, 1H), 7.71 – 7.68 (m, 2H), 7.48 – 7.44 (m, 5H), 7.38 – 7.37 (m, 2H), 7.35 – 7.33 (m, 2H), 7.33 – 7.29 (m, 1H), 7.12 (dd, *J* = 5.1, 3.6 Hz, 1H), 5.14 (dd, *J* = 9.6, 6.7 Hz, 1H), 4.98 (dd, *J* = 12.5, 6.7 Hz, 1H), 4.85 (dd, *J* = 12.5, 9.6 Hz, 1H), 2.33 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 145.6, 139.5, 139.3, 137.6, 134.5, 129.5, 129.1, 127.8, 127.7, 126.9, 126.7, 126.2, 125.7, 125.3, 119.1, 118.3, 113.5, 77.1, 31.6, 13.4, 11.1; HRMS (ESI-TOF) m/z: calcd. for $C_{26}H_{23}N_5O_2S$ $[M+Na]^+$ 492.1465; found 492.1410.

3,5-dimethyl-4-(2-nitro-1-(1-(4-nitrophenyl)-3-phenyl-1*H*-pyrazol-4-yl)ethyl)-1-phenyl-1*H*-pyrazole (4q)



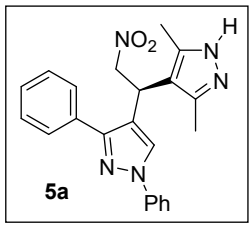
Reddish brown semi-solid; 52% yield; $[\alpha]_D^{25}$ = +75.00 (c = 0.2, $CHCl_3$); 74% *ee*, HPLC [Chiralpak IA, hexane/*i*-PrOH 85:15, 1ml/min, 254 nm, t_R = 20.40 min (minor) and t_R = 23.98 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.34 (m, 2H), 7.94 (d, *J* = 0.9 Hz, 1H), 7.92 – 7.90 (m, 2H), 7.56 – 7.53 (m, 2H), 7.46 – 7.42 (m, 5H), 7.39 – 7.38 (m, 1H), 7.29 – 7.27 (m, 2H), 5.09 – 5.04 (m, 1H), 4.92 (dd, *J* = 12.5, 7.5 Hz, 1H), 4.78 (dd, *J* = 12.5, 8.9 Hz, 1H), 2.22 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 146.7, 145.5, 143.9, 139.3, 137.5, 132.2, 129.1, 129.0, 128.8, 128.2, 127.9, 125.8, 125.5, 125.2, 122.0, 120.8, 118.4, 113.3, 113.2, 77.2, 31.3, 13.3, 10.9; HRMS (ESI-TOF) m/z: calcd. for $C_{28}H_{24}N_6O_4$ $[M+H]^+$ 509.1932; found 509.1919.

General procedure for the synthesis of 5



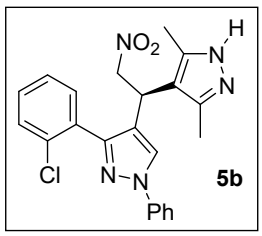
To a stirred solution of compound **3** (0.1 mmol) in 2 mL ethanol was added hydrazine hydrate (0.15 mmol, 1.5 equiv.) and 20 mol% glacial acetic acid. The reaction mixture was run for 12 h at 28 °C, after which the solvent was reduced under pressure, and the crude reaction mixture was purified by column chromatography on silica gel (mesh 60–120) using *n*-hexane:ethyl acetate (75:25) as the eluents to procure the final product **5**.

4-(1-(3,5-dimethyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-1,3-diphenyl-1*H*-pyrazole (5a)



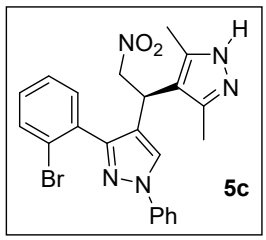
Off-white solid; 66% yield; mp. 78-79°C; $[\alpha]_D^{25}$ = +40.00 (c = 0.15, $CHCl_3$); 87% *ee*, HPLC [Chiralpak IE, hexane/*i*-PrOH 85:15, 1ml/min, 254 nm, t_R = 13.89 min (minor) and t_R = 14.86 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.70 – 7.68 (m, 2H), 7.58 – 7.56 (m, 2H), 7.46 – 7.37 (m, 5H), 7.31 – 7.27 (m, 1H), 6.46 (s, 1H), 5.02 (dd, *J* = 9.4, 7.2 Hz, 1H), 4.81 (dd, *J* = 12.4, 7.0 Hz, 1H), 4.70 (dd, *J* = 12.3, 9.6 Hz, 1H), 2.15 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 142.4, 139.6, 132.8, 129.5, 128.7, 128.5, 128.1, 126.7, 126.1, 119.0, 118.5, 111.7, 77.4, 30.8, 11.5; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{21}N_5O_2$ $[M+Na]^+$ 410.1587; found 410.1525.

3-(2-chlorophenyl)-4-(1-(3,5-dimethyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-1-phenyl-1*H*-pyrazole (5b)



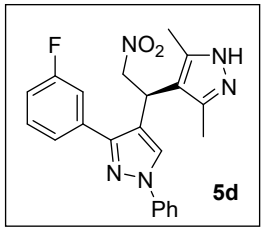
Off-white solid; 72% yield; mp. 87-89°C; $[\alpha]_D^{25}$ = +75.00 (c 0.2, $CHCl_3$); 98% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 80:20, 1 mL/min, 254 nm, t_R = 12.84 min (minor) and t_R = 25.43 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.70 – 7.68 (m, 2H), 7.47 – 7.43 (m, 3H), 7.34 – 7.28 (m, 2H), 7.26 – 7.20 (m, 2H), 7.13 (s, 1H), 4.86 (dd, *J* = 9.8, 6.7 Hz, 1H), 4.81 – 4.70 (m, 2H), 2.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 142.2, 139.6, 134.0, 132.1, 131.6, 130.2, 129.5, 129.5, 126.8, 126.8, 124.6, 120.4, 119.0, 111.6, 77.2, 30.5, 11.1; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{20}ClN_5O_2$ $[M+H]^+$ 422.1378; found 422.1397.

3-(2-bromophenyl)-4-(1-(3,5-dimethyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-1-phenyl-1*H*-pyrazole (5c)



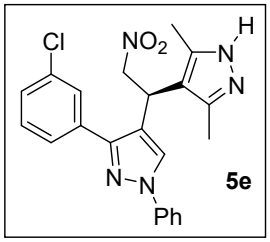
Off-white solid; 73% yield; mp. 96-97°C; $[\alpha]_D^{25}$ = +70.00 (c 0.1, $CHCl_3$); 90% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 80:20, 1 mL/min, 254 nm, t_R = 13.28 min (minor) and t_R = 22.47 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.71 – 7.69 (m, 2H), 7.65 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.48 – 7.44 (m, 2H), 7.33 – 7.29 (m, 2H), 7.25 – 7.23 (m, 1H), 7.18 (dd, *J* = 7.3, 1.9 Hz, 1H), 4.87 – 4.72 (m, 3H), 4.34 (s, 1H), 2.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 142.5, 139.6, 134.16, 132.72, 131.67, 130.33, 129.50, 127.4, 126.8, 124.5, 124.1, 120.1, 119.0, 111.6, 77.2, 30.5, 11.2; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{20}BrN_5O_2$ $[M+H]^+$ 466.0873; found 466.0878.

4-(1-(3,5-dimethyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-3-(3-fluorophenyl)-1-phenyl-1*H*-pyrazole (5d)



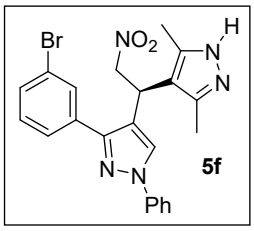
Off-white solid; 82% yield; mp. 88-90°C; $[\alpha]_D^{25}$ = +60.00 (c 0.2, $CHCl_3$); 96% *ee*; HPLC [Chiralpak IE, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 13.63 min (minor) and t_R = 19.42 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.71 – 7.68 (m, 2H), 7.48 – 7.44 (m, 2H), 7.42 – 7.28 (m, 4H), 7.10 – 7.05 (m, 1H), 5.72 (s, 1H), 5.02 – 4.97 (m, 1H), 4.85 (dd, *J* = 12.4, 7.4 Hz, 1H), 4.72 (dd, *J* = 12.3, 9.1 Hz, 1H), 2.16 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, *J* = 244.9 Hz), 150.3, 142.4, 139.5, 134.9 (d, *J* = 8.3 Hz), 130.3 (d, *J* = 8.3 Hz), 129.5, 126.9, 126.1, 123.6, 119.1, 118.5, 115.5, 115.3, 115.1, 111.6, 77.6, 30.8, 11.6; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{20}FN_5O_2$ $[M+H]^+$ 406.1674; found 406.1680.

3-(3-chlorophenyl)-4-(1-(3,5-dimethyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-1-phenyl-1*H*-pyrazole (5e)



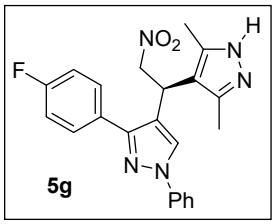
Off-white solid; 71% yield; mp. 84-85°C; $[\alpha]_D^{25}$ = +73.33 (c 0.15, $CHCl_3$); 98% *ee*; HPLC [Chiralpak IE, hexane/*i*-PrOH, 90:10, 1 mL/min, 254 nm, t_R = 15.62 min (minor) and t_R = 19.39 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.71 – 7.68 (m, 2H), 7.51 – 7.43 (m, 4H), 7.34 – 7.29 (m, 3H), 6.38 (s, 1H), 4.99 – 4.95 (m, 1H), 4.85 (dd, *J* = 12.3, 7.6 Hz, 1H), 4.71 (dd, *J* = 12.3, 8.8 Hz, 1H), 2.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 142.4, 139.6, 134.7, 134.5, 130.0, 129.6, 128.5, 128.3, 127.0, 126.2, 126.1, 119.2, 118.7, 111.6, 77.8, 30.9, 11.6; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{20}ClN_5O_2$ $[M+Na]^+$ 444.1198; found 444.1188.

3-(3-bromophenyl)-4-(1-(3,5-dimethyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-1-phenyl-1*H*-pyrazole (5f)



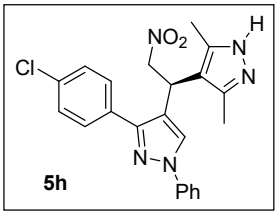
Off-white solid; 52% yield; mp. 91-92°C; $[\alpha]_D^{25}$ = + 60.00 (c 0.15, $CHCl_3$); >99% *ee*; HPLC [Chiralpak IE, hexane/*i*-PrOH, 90:10, 1 mL/min, 254 nm, t_R = 18.14 min (minor) and t_R = 24.19 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 0.68 Hz, 1H), 7.71 – 7.69 (m, 2H), 7.65 (t, *J* = 1.76 Hz, 1H), 7.51 – 7.45 (m, 4H), 7.34 – 7.25 (m, 2H), 4.98 – 4.94 (m, 1H), 4.86 (dd, *J* = 12.3, 7.7 Hz, 1H), 4.71 (dd, *J* = 12.3, 8.7 Hz, 1H), 2.15 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 139.5, 134.9, 131.4, 131.1, 130.1, 129.5, 127.0, 126.61, 125.9, 122.6, 119.1, 118.6, 111.5, 77.7, 30.8, 11.6; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{20}BrN_5O_2$ $[M+Na]^+$ 488.0693; found 488.0732.

3-(4-fluorophenyl)-4-(1-(3,5-dimethyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-1-phenyl-1*H*-pyrazole (5g)



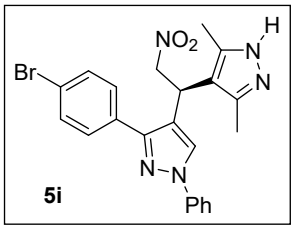
Off-white solid; 66% yield; mp. 86-87°C; $[\alpha]_D^{25}$ = + 50.00 (c 0.2, $CHCl_3$); >99% *ee*; HPLC [Chiralpak IE, hexane/*i*-PrOH, 90:10, 0.5 mL/min, 254 nm, t_R = 41.25 min (minor) and t_R = 44.21 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.67 – 7.67 (m, 2H), 7.52 – 7.49 (m, 2H), 7.46 – 7.42 (m, 2H), 7.31 – 7.25 (m, 1H), 7.11 – 7.07 (m, 2H), 4.95 (dd, *J* = 8.6, 7.8 Hz, 1H), 4.82 (dd, *J* = 12.3, 7.4 Hz, 1H), 4.70 (dd, *J* = 12.3, 9.2 Hz, 1H), 2.12 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 161.5, 150.7, 142.2, 139.6, 129.9 (d, *J* = 32.2), 129.5, 129.0 (d, *J* = 11.8), 126.8, 125.9, 119.0, 118.5, 115.7, 115.5, 111.6, 77.5, 30.8, 11.4; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{20}FN_5O_2$ $[M+H]^+$ 406.1674; found 406.1680.

3-(4-chlorophenyl)-4-(1-(3,5-dimethyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-1-phenyl-1*H*-pyrazole (5h)



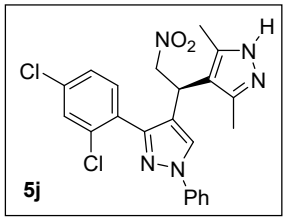
Off-white solid; 50% yield; mp. 95-96°C; $[\alpha]_D^{25}$= + 25.00 (c 0.2, $CHCl_3$); 98% *ee*; HPLC [Chiralpak IE, hexane/*i*-PrOH, 90:10, 1 mL/min, 254 nm, t_R = 15.43 min (minor) and t_R = 17.38 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.69 – 7.67 (m, 2H), 7.51 – 7.48 (m, 2H), 7.47 – 7.43 (m, 2H), 7.40 – 7.37 (m, 2H), 7.32 – 7.29 (m, 1H), 5.84 (s, 1H), 4.99 – 4.94 (m, 1H), 4.82 (dd, J = 12.3, 7.4 Hz, 1H), 4.70 (dd, J = 12.3, 9.1 Hz, 1H), 2.15 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 142.4, 139.6, 134.5, 131.4, 129.5, 129.4, 128.9, 126.9, 126.1, 119.1, 118.5, 111.7, 77.5, 30.9, 11.6; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{20}ClN_5O_2$ $[M+H]^+$ 422.1378; found 422.1326.

3-(4-bromophenyl)-4-(1-(3,5-dimethyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-1-phenyl-1*H*-pyrazole (5i)



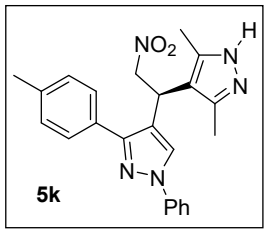
White solid; 75% yield; mp. 84-85°C; $[\alpha]_D^{25}$= + 20.00 (c 0.1, $CHCl_3$); 93% *ee*; HPLC [Daicel Chiralpak IE, hexane/*i*-PrOH, 90:10, 1 mL/min, 254 nm, t_R = 16.38 min (minor) and t_R = 19.86 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.69 – 7.67 (m, 2H), 7.57 – 7.54 (m, 2H), 7.48 – 7.42 (m, 4H), 7.33 – 7.29 (m, 1H), 5.00 – 4.94 (m, 1H), 4.83 (dd, J = 12.4, 7.4 Hz, 1H), 4.71 (dd, J = 12.4, 9.1 Hz, 1H), 4.33 (br s, 1H), 2.15 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 142.4, 139.6, 131.8, 129.6, 129.5, 126.9, 126.1, 122.7, 119.1, 118.5, 111.7, 77.5, 30.9, 11.6; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{20}BrN_5O_2$ $[M+H]^+$ 466.0873; found 466.0836.

3-(2,4-dichlorophenyl)-4-(1-(3,5-dimethyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-1-phenyl-1*H*-pyrazole (5j)



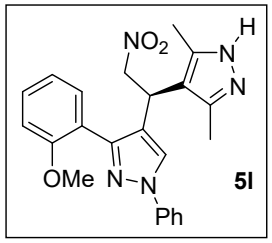
Dirty white solid; 62% yield; mp. 99-100°C; $[\alpha]_D^{25}$= + 46.67 (c 0.15, $CHCl_3$); 90% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 80:20, 1 mL/min, 254 nm, t_R = 11.78 min (minor) and t_R = 23.00 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 0.4 Hz, 1H), 7.69 – 7.67 (m, 2H), 7.48 – 7.44 (m, 3H), 7.34 – 7.29 (m, 1H), 7.24 (dd, J = 8.2, 2.1 Hz, 1H), 7.14 – 7.08 (m, 2H), 4.96 (s, 1H), 4.86 – 4.79 (m, 2H), 4.76 – 4.70 (m, 1H), 2.01 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 142.2, 139.5, 135.4, 134.2, 132.4, 130.7, 129.5, 129.3, 127.1, 127.0, 125.8, 124.6, 120.5, 119.1, 111.7, 77.2, 30.5, 19.7, 11.2; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{19}Cl_2N_5O_2$ $[M+H]^+$ 456.0989; found 456.0991.

4-(1-(3,5-dimethyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-1-phenyl-3-(*p*-tolyl)-1*H*-pyrazole (5k)



Off-white solid; 81% yield; mp. 93-94°C; $[\alpha]_D^{25}$= +26.67 (c 0.15, $CHCl_3$); 95% *ee*; HPLC [Chiralpak IE, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 16.13 min (minor) and t_R = 17.65 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.69 – 7.67 (m, 2H), 7.50 – 7.48 (m, 2H), 7.45 – 7.41 (m, 2H), 7.30 – 7.28 (m, 1H), 7.26 – 7.23 (m, 2H), 6.53 (s, 1H), 5.02 (dd, J = 9.7, 6.9 Hz, 1H), 4.80 (dd, J = 12.4, 6.8 Hz, 1H), 4.69 (dd, J = 12.3, 9.8 Hz, 1H), 2.38 (s, 3H), 2.18 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 142.4, 139.7, 138.3, 129.9, 129.4, 127.8, 126.6, 126.2, 118.9, 118.3, 111.8, 77.2, 30.8, 21.3, 11.6; HRMS (ESI-TOF) m/z: calcd. for $C_{23}H_{23}N_5O_2$ $[M+H]^+$ 402.1925; found 402.1934.

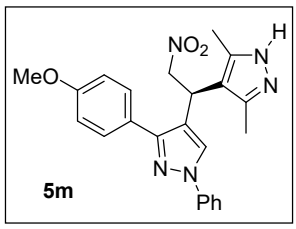
4-(1-(3,5-dimethyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-3-(2-methoxyphenyl)-1-phenyl-1*H*-pyrazole (5l)



Off-white solid; 71% yield; mp. 89-90°C; $[\alpha]_D^{25}$= +10.00 (c 0.2, $CHCl_3$); 91% *ee*; HPLC [Chiralpak IC, hexane/*i*-PrOH, 75:25, 1 mL/min, 254 nm, t_R = 30.38 min (minor) and t_R = 59.62 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.66 (m, 2H), 7.63 (d, J = 0.8 Hz, 1H), 7.45 – 7.38 (m, 4H), 7.29 – 7.24 (m, 1H), 7.04 – 6.98 (m, 2H), 5.04 – 5.00 (m, 1H), 4.71 – 4.64 (m, 2H), 3.90 (s, 3H),

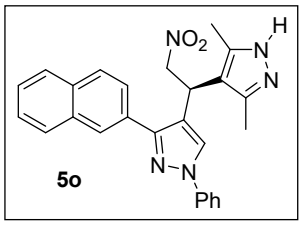
3.36 (s, 1H), 2.12 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 149.4, 142.5, 139.8, 131.4, 130.4, 129.4, 126.4, 125.5, 121.9, 121.0, 120.7, 118.9, 110.7, 77.2, 55.5, 31.0, 11.4; HRMS (ESI-TOF) m/z: calcd. for $C_{23}H_{23}N_5O_3$ $[M+H]^+$ 418.1874; found 418.1880.

4-(1-(3,5-dimethyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazole (5m)



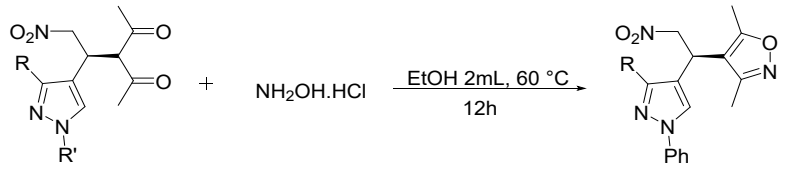
Off-white solid; 63% yield; mp. 82-83°C; $[\alpha]_D^{25}$= +10.00 (c 0.1, $CHCl_3$); 94% *ee*; HPLC [Chiralpak IE, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 25.17 min (minor) and t_R = 29.68 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.69 – 7.67 (m, 2H), 7.52 – 7.50 (m, 2H), 7.46 – 7.42 (m, 2H), 7.30 – 7.28 (m, 1H), 6.97 – 6.95 (m, 2H), 6.36 (s, 1H), 5.00 (dd, *J* = 9.5, 7.0 Hz, 1H), 4.81 (dd, *J* = 12.4, 6.9 Hz, 1H), 4.69 (dd, *J* = 12.3, 9.7 Hz, 1H), 3.84 (s, 3H), 2.18 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 151.3, 142.4, 139.7, 129.4, 129.3, 126.6, 126.1, 125.3, 118.9, 118.2, 114.2, 111.8, 77.2, 55.3, 30.9, 29.7, 11.6; HRMS (ESI-TOF) m/z: calcd. for $C_{23}H_{23}N_5O_3$ $[M+H]^+$ 418.1874; found 418.1880.

4-(1-(3,5-dimethyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-3-(naphthalen-2-yl)-1-phenyl-1*H*-pyrazole (5o)



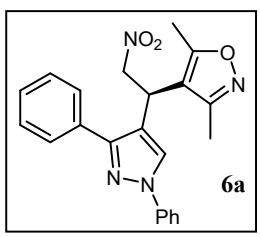
White solid; 77% yield; mp. 98-100°C; $[\alpha]_D^{25}$= + 6.7 (c 0.15, $CHCl_3$); 92% *ee*; HPLC [Chiralpak IE, hexane/*i*-PrOH, 90:10, 1 mL/min, 254 nm, t_R = 23.58 min (minor) and t_R = 28.56 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.90 (d, *J* = 8.5 Hz, 1H), 7.86 – 7.82 (m, 2H), 7.80 (s, 1H), 7.77 – 7.75 (m, 1H), 7.74 – 7.71 (m, 2H), 7.52 – 7.48 (m, 3H), 7.47 – 7.44 (m, 2H), 7.33 – 7.29 (m, 1H), 5.12 (dd, *J* = 8.9, 7.4 Hz, 1H), 4.86 (dd, *J* = 12.4, 7.2 Hz, 1H), 4.70 (dd, *J* = 12.4, 9.3 Hz, 1H), 2.15 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 142.5, 139.7, 133.3, 133.1, 130.3, 129.5, 128.4, 128.2, 127.7, 127.1, 126.8, 126.5, 126.3, 125.8, 119.1, 118.7, 111.9, 77.5, 31.1, 11.6; HRMS (ESI-TOF) m/z: calcd. for $C_{26}H_{23}N_5O_2$ $[M+H]^+$ 438.1925; found 438.1923.

General procedure for the synthesis of 6



To a stirred solution of **3** (0.1 mmol) in ethanol was added hydroxyl amine hydrochloride (0.15 mmol, 1.5 equiv.). The reaction mixture was carried out at 60 °C for 12h, after which the solvent was reduced under pressure, and the crude reaction mixture was purified by column chromatography on silica gel (mesh 60–120) using *n*-hexane:ethyl acetate (85:15) as the eluents to afford the final adduct **6**.

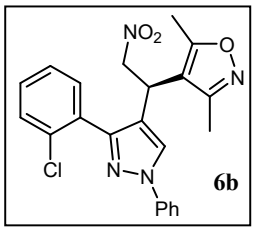
4-(1-(1,3-diphenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-3,5-dimethylisoxazole (6a)



Off-white solid; 63% yield; mp. 124-126°C; $[\alpha]_D^{25}$= +53.33 (c 0.15, $CHCl_3$); 99% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 9.97 min (minor) and t_R = 14.53 min

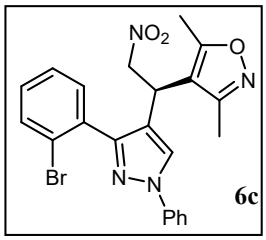
(major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.71 – 7.68 (m, 2H), 7.52 – 7.40 (m, 7H), 7.34 – 7.30 (m, 1H), 4.94 (dd, J = 9.6, 6.9 Hz, 1H), 4.84 (dd, J = 12.5, 6.9 Hz, 1H), 4.70 (dd, J = 12.6, 9.5 Hz, 1H), 2.20 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 158.5, 151.7, 139.5, 132.5, 129.5, 128.8, 128.7, 128.1, 127.0, 125.5, 119.1, 117.1, 110.6, 76.8, 29.9, 11.4, 10.8; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{20}N_4O_3$ $[M+Na]^+$ 411.1428; found 411.1307.

4-(1-(3-(2-chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-3,5-dimethylisoxazole (6b)



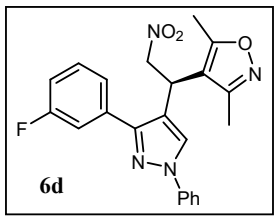
Off-white solid; 72% yield; mp. 138-140°C; $[\alpha]_D^{25}$= +53.33 (c 0.15, $CHCl_3$); 91% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 11.89 min (minor) and t_R = 17.98 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.71 – 7.69 (m, 2H), 7.49 – 7.45 (m, 3H), 7.39 – 7.28 (m, 3H), 7.23 (dd, J = 7.6, 1.7 Hz, 1H), 4.88 – 4.78 (m, 2H), 4.74 (dd, J = 9.5, 7.7 Hz, 1H), 2.05 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 158.3, 149.9, 139.4, 133.9, 131.7, 131.6, 130.5, 129.7, 129.6, 127.1, 127.0, 124.3, 119.1, 118.8, 110.3, 76.6, 29.7, 10.9, 10.6; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{19}ClN_4O_3$ $[M+Na]^+$ 423.1218; found 423.1242.

4-(1-(3-(2-bromophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-3,5-dimethylisoxazole (6c)



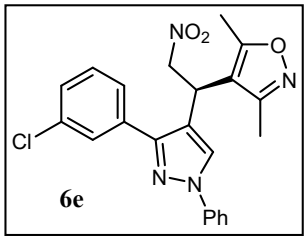
Off-white solid; 80% yield; mp. 74-75°C; $[\alpha]_D^{25}$= +113.33 (c 0.15, $CHCl_3$); 91% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 10.65 min (minor) and t_R = 14.84 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.72 – 7.69 (m, 2H), 7.68 – 7.66 (m, 1H), 7.49 – 7.45 (m, 2H), 7.37 – 7.27 (m, 3H), 7.19 (dd, J = 7.4, 1.9 Hz, 1H), 4.90 – 4.72 (m, 3H), 2.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 158.3, 151.4, 139.5, 133.8, 132.8, 131.6, 130.6, 129.6, 127.6, 127.0, 124.2, 123.9, 119.1, 118.5, 110.3, 76.6, 29.7, 10.9, 10.6; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{19}BrN_4O_3$ $[M+Na]^+$ 489.0533; found 489.0561.

4-(1-(3-(3-fluorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-3,5-dimethylisoxazole (6d)



Off-white solid; 75% yield; mp. 85-86°C; $[\alpha]_D^{25}$= +70.00 (c 0.1, $CHCl_3$); 95% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 11.25 min (minor) and t_R = 15.34 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.71 – 7.68 (m, 2H), 7.50 – 7.46 (m, 2H), 7.44 – 7.39 (m, 1H), 7.36 – 7.29 (m, 2H), 7.28 – 7.24 (m, 1H), 7.14 – 7.08 (m, 1H), 4.94 (dd, J = 8.9, 7.3 Hz, 1H), 4.87 (dd, J = 12.5, 7.1 Hz, 1H), 4.72 (dd, J = 12.5, 9.1 Hz, 1H), 2.24 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 164.0, 161.6, 158.4, 150.3, 139.3, 134.6 (d, J = 8.0 Hz), 130.4 (d, J = 8.5 Hz), 129.6, 127.2, 125.7, 123.6 (d, J = 2.7 Hz), 119.1, 117.1, 115.8, 115.6, 115.1, 110.4, 76.9, 29.9, 11.4, 10.9; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{19}FN_4O_3$ $[M+H]^+$ 407.1514; found 407.1544.

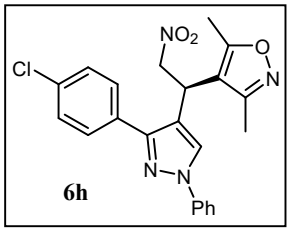
4-(1-(3-(3-chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-3,5-dimethylisoxazole (6e)



Off-white solid; 62% yield; mp. 125-126°C; $[\alpha]_D^{25}$= +53.33 (c 0.30, $CHCl_3$); 88% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 9.72 min (minor) and t_R = 12.83 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.71 – 7.68 (m, 2H), 7.51 – 7.46 (m, 3H), 7.42 – 7.32 (m, 4H), 4.95 – 4.85 (m, 2H), 4.72 (dd, J = 11.9, 8.5 Hz, 1H), 2.24 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 158.3, 150.3, 139.4, 134.7, 134.2, 130.1, 129.6,

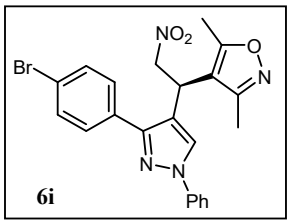
128.8, 128.2, 127.2, 126.1, 125.6, 119.2, 117.1, 110.4, 76.97, 29.9, 11.4, 10.8; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{19}ClN_4O_3$ $[M+H]^+$ 423.1218; found 423.1200.

4-(1-(3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-3,5-dimethylisoxazole (6h)



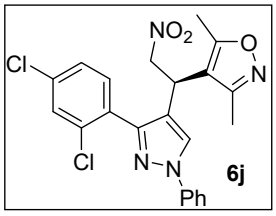
Light-yellow solid; 56% yield; mp. 136-137°C; $[\alpha]_D^{25}$= +30.00 (c 0.10, $CHCl_3$); 97% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 11.56 min (minor) and t_R = 26.32 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 0.7 Hz, 1H), 7.70 – 7.67 (m, 2H), 7.50 – 7.41 (m, 6H), 7.36 – 7.32 (m, 1H), 4.93 – 4.82 (m, 2H), 4.71 (dd, J = 12.3, 9.1 Hz, 1H), 2.24 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 158.4, 150.5, 139.4, 134.9, 131.0, 129.6, 129.4, 129.1, 127.2, 125.7, 119.1, 117.1, 110.5, 76.8, 29.9, 11.5, 10.9; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{19}ClN_4O_3$ $[M+Na]^+$ 445.1038 found 445.1061.

4-(1-(3-(4-bromophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-3,5-dimethylisoxazole (6i)



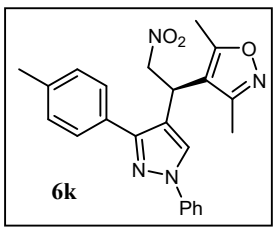
Pale-yellow solid; 70% yield; mp. 146-148°C; $[\alpha]_D^{25}$= +13.33 (c 0.15, $CHCl_3$); 93% *ee*; HPLC [Chiralpak IE, hexane/*i*-PrOH, 90:10, 1 mL/min, 254 nm, t_R = 15.99 min (minor) and t_R = 17.97 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 0.5 Hz, 1H), 7.69 – 7.67 (m, 2H), 7.59 – 7.57 (m, 2H), 7.50 – 7.45 (m, 2H), 7.41 – 7.39 (m, 2H), 7.36 – 7.31 (m, 1H), 4.93 – 4.82 (m, 2H), 4.71 (dd, J = 12.3, 9.1 Hz, 1H), 2.23 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 158.4, 150.5, 139.4, 132.0, 131.4, 129.6, 127.2, 125.8, 123.0, 119.1, 117.0, 110.5, 76.8, 29.9, 11.5, 10.9; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{19}BrN_4O_3$ $[M+Na]^+$ 489.0533; found 489.0515.

4-(1-(3-(2,4-dichlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-3,5-dimethylisoxazole (6j)



Off-white solid; 73% yield; mp. 160-161°C; $[\alpha]_D^{25}$= +70.00 (c 0.20, $CHCl_3$); 95% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 80:20, 1 mL/min, 254 nm, t_R = 8.28 min (minor) and t_R = 11.98 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.70 – 7.68 (m, 2H), 7.51 – 7.46 (m, 3H), 7.36 – 7.32 (m, 1H), 7.30 (dd, J = 8.2, 2.0 Hz, 1H), 7.17 (d, J = 8.2 Hz, 1H), 4.88 – 4.71 (m, 3H), 2.09 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 158.2, 148.8, 139.3, 135.8, 134.7, 132.3, 130.3, 129.6, 129.5, 127.4, 127.2, 124.5, 119.1, 118.8, 110.2, 76.6, 29.7, 10.9, 10.6; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{18}Cl_2N_4O_3$ $[M+H]^+$ 457.0829; found 457.0830.

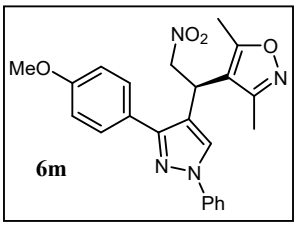
3,5-dimethyl-4-(2-nitro-1-(1-phenyl-3-(*p*-tolyl)-1*H*-pyrazol-4-yl)ethyl)isoxazole (6k)



Off-white solid; 73% yield; mp. 146-147°C; $[\alpha]_D^{25}$= +33.33 (c 0.15, $CHCl_3$); 90% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 12.68 min (minor) and t_R = 26.26 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.70 – 7.67 (m, 2H), 7.49 – 7.44 (m, 2H), 7.44 – 7.41 (m, 2H), 7.33 – 7.29 (m, 1H), 7.27 – 7.25 (m, 2H), 4.95 (dd, J = 9.9, 6.6 Hz, 1H), 4.83

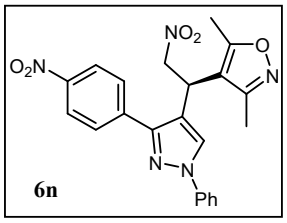
(dd, J = 12.6, 6.7 Hz, 1H), 4.69 (dd, J = 12.6, 9.8 Hz, 1H), 2.40 (s, 3H), 2.24 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 158.6, 151.7, 139.5, 138.7, 129.5, 127.9, 126.9, 125.6, 119.0, 116.9, 110.6, 77.2, 29.9, 21.3, 11.5, 10.9; HRMS (ESI-TOF) m/z: calcd. for $C_{23}H_{22}N_4O_3$ $[M+H]^+$ 403.1765; found 403.1750.

4-(1-(3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl)-3,5-dimethylisoxazole (6m)



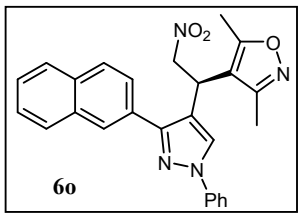
Pale yellow solid; 63% yield; mp. 136-138°C; $[\alpha]_D^{25}$= +32.00 (c 0.125, $CHCl_3$); 96% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 80:20, 1 mL/min, 254 nm, t_R = 10.73 min (minor) and t_R = 18.52 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.69 – 7.67 (m, 2H), 7.48 – 7.44 (m, 4H), 7.33 – 7.29 (m, 1H), 6.99 – 6.96 (m, 2H), 4.93 (dd, J = 9.5, 6.8 Hz, 1H), 4.84 (dd, J = 12.6, 6.8 Hz, 1H), 4.69 (dd, J = 12.5, 9.6 Hz, 1H), 3.85 (s, 3H), 2.24 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 160.0, 158.5, 151.5, 139.5, 129.5, 129.3, 126.9, 125.5, 124.8, 119.0, 116.8, 114.3, 110.7, 76.8, 55.3, 29.96, 11.5, 10.9; HRMS (ESI-TOF) m/z: calcd. For $C_{23}H_{22}N_4O_4$ $[M+Na]^+$ 441.1533; found 441.1511.

3,5-dimethyl-4-(2-nitro-1-(3-(4-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)ethyl)isoxazole (6n)



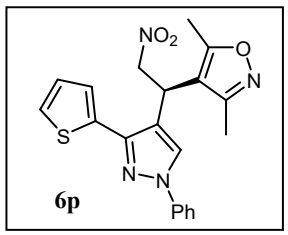
Yellowish solid; 58% yield; mp. 208-210°C; $[\alpha]_D^{25}$= +26.67 (c 0.15, $CHCl_3$); 89% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 13.28 min (minor) and t_R = 29.57 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 – 8.29 (m, 2H), 7.88 (s, 1H), 7.76 – 7.74 (m, 2H), 7.72 – 7.70 (m, 2H), 7.53 – 7.49 (m, 2H), 7.40 – 7.36 (m, 1H), 4.99 – 4.95 (m, 1H), 4.88 (dd, J = 12.5, 7.4 Hz, 1H), 4.74 (dd, J = 12.5, 8.7 Hz, 1H), 2.26 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 158.3, 149.1, 147.7, 139.2, 139.0, 129.7, 128.6, 127.6, 126.2, 124.0, 119.3, 117.6, 110.3, 76.9, 30.0, 11.6, 11.0; HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{19}N_5O_5$ $[M+H]^+$ 434.1459; found 434.1446.

3,5-dimethyl-4-(1-(3-(naphthalen-2-yl)-1-phenyl-1*H*-pyrazol-4-yl)-2-nitroethyl) isoxazole (6o)



Off-white solid; 51% yield; mp. 105-107°C; $[\alpha]_D^{25}$= +20.00 (c 0.15, $CHCl_3$); 96% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 80:20, 1 mL/min, 254 nm, t_R = 10.11 min (minor) and t_R = 15.30 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 1.1 Hz, 1H), 7.92 (d, J = 8.6 Hz, 1H), 7.89 – 7.85 (m, 2H), 7.81 (d, J = 0.8 Hz, 1H), 7.74 – 7.72 (m, 2H), 7.69 (dd, J = 8.5, 1.7 Hz, 1H), 7.54 – 7.46 (m, 4H), 7.36 – 7.32 (m, 1H), 5.07 – 5.03 (m, 1H), 4.88 (dd, J = 12.6, 6.9 Hz, 1H), 4.71 (dd, J = 12.6, 9.5 Hz, 1H), 2.21 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 158.5, 151.5, 139.5, 133.2, 133.1, 129.9, 129.6, 128.7, 128.2, 127.8, 127.2, 127.1, 126.7, 125.8, 125.6, 119.1, 117.2, 110.7, 76.9, 30.2, 11.5, 10.9; HRMS (ESI-TOF) m/z: calcd. for $C_{26}H_{22}N_4O_3$ $[M+Na]^+$ 461.1584; found 461.1593.

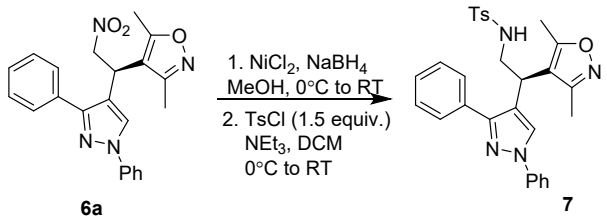
3,5-dimethyl-4-(2-nitro-1-(1-phenyl-3-(thiophen-2-yl)-1*H*-pyrazol-4-yl)ethyl)isoxazole (6p)



Light yellowish solid; 59% yield; mp. 119-120°C; $[\alpha]_D^{25}$= +20.00 (c 0.2, $CHCl_3$); 93% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 85:15, 1 mL/min, 254 nm, t_R = 11.81 min (minor) and t_R = 16.06 min (major)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.69 – 7.67 (m, 2H), 7.49 – 7.45 (m, 2H), 7.39 (dd, J = 5.1, 0.9 Hz, 1H), 7.35 – 7.31 (m, 1H), 7.29 (dd, J = 3.6, 0.9 Hz, 1H), 7.13 (dd, J = 5.0, 3.6 Hz, 1H), 5.01 (dd, J = 9.6, 6.5 Hz, 1H), 4.93 (dd, J = 12.7, 6.6 Hz, 1H), 4.76 (dd, J = 12.6, 9.6 Hz, 1H), 2.32 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 158.7, 145.6, 139.3, 133.9, 129.6, 127.8,

127.2, 126.5, 126.2, 125.8, 119.1, 116.9, 110.4, 76.6, 30.2, 11.8, 11.0; HRMS (ESI-TOF) m/z: calcd. for $C_{20}H_{18}N_4O_3S$ $[M+H]^+$ 395.1172; found 395.1161.

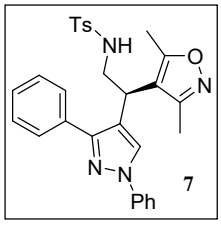
General procedure for synthesis of 7



6a **7**

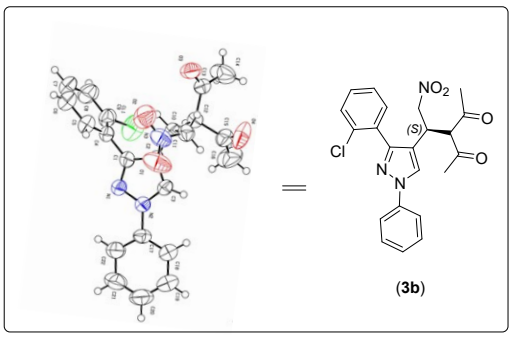
To a suspension of **6a** (0.1 mmol, 1 equiv.) and nickel chloride hexahydrate (0.1 mmol, 1 equiv.) in methanol (5 mL) was added sodium borohydride (1.2 mmol, 12 equiv.) at 0 °C and the mixture was stirred at room temperature for 1 h, after which the mixture was quenched with sat. NH_4Cl at 0 °C and extracted with dichloromethane. The combined organic layers were washed with brine and dried over Na_2SO_4 and concentrated under vacuum to give the corresponding amine. The crude amine was then dissolved in CH_2Cl_2 (5 mL) at 0 °C followed by adding of Et_3N (0.1 mmol, 14 uL). The resulting mixture was stirred at 0 °C for 10 min, then a solution of TsCl (0.15 mmol, 28.6 mg) in dry CH_2Cl_2 (1.0 mL) was added dropwise. The resulting solution was stirred at 0 °C for 30 min, then was allowed to warm to room temperature; stirring was then continued for about 4 h. The reaction mixture was concentrated under vacuum and purified by column chromatography on silica gel (mesh 60–120) using *n*-hexane:ethyl acetate (85:15) as the eluents to afford **7.**

***N*-(2-(3,5-dimethylisoxazol-4-yl)-2-(1,3-diphenyl-1*H*-pyrazol-4-yl)ethyl)-4-methylbenzenesulfonamide (7)**



Pale-yellow solid; 60% yield; mp. 70-71°C; $[\alpha]_D^{25}$ = +6.67 (c 0.15, $CHCl_3$); 99% *ee*; HPLC [Chiralpak IA, hexane/*i*-PrOH, 75:25, 1 mL/min, 254 nm, t_R = 21.99 min (minor) and t_R = 26.28 min (major)]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.68 (m, 2H), 7.60 (s, 1H), 7.58 – 7.56 (m, 2H), 7.54 – 7.51 (m, 2H), 7.46 – 7.43 (m, 2H), 7.42 - 7.38(m, 2H), 7.31 – 7.27 (m, 1H), 4.29 – 4.26 (m, 1H), 4.22 – 4.17 (m, 1H), 3.88 (dd, J = 10.6, 3.2 Hz, 1H), 2.38 (s, 3H), 2.35 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 150.7, 145.1, 143.2, 139.6, 139.1, 135.3, 132.7, 130.1, 129.5, 128.9, 128.1, 127.1, 126.7, 125.6, 123.3, 122.1, 118.8, 58.0, 36.3, 23.5, 21.6, 15.6; HRMS (ESI-TOF) m/z: calcd. for $C_{29}H_{28}N_4O_3S$ $[M+H]^+$ 513.1955; found 513.1850.

Single crystal X-ray diffraction analysis and crystal data of (3b)



Empirical formula	$C_{22}H_{20}ClN_3O_4$
Formula weight	425.86
Temperature/K	293.15K
Crystal system	monoclinic
Space group	P21
a/Å	7.7803(2)
b/Å	9.3559(3)
c/Å	14.8204(4)
α/°	90
β/°	90.009 (3)
γ/°	90
Volume/Å^3	1078.80 (5)
Z	2
ρcalcg/cm^3	1.311
μ/mm^{-1}	0.210
F(000)	444.0
Crystal size/mm^3	0.25 × 0.12 × 0.10
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.812 to 54.934
Index ranges	$-10 \le h \le 9$, $-12 \le k \le 11$, $-19 \le l \le 15$
Reflections collected	14001
Independent reflections	4537 [R_{int} = 0.0838, R_{sigma} = 0.0518]
Data/restraints/parameters	4537/1/273
Goodness-of-fit on F2	1.087
Final R indexes [I>=2σ (I)]	R1 = 0.0561, wR2 = 0.1366
Final R indexes [all data]	R1 = 0.0806, wR2 = 0.1700
Largest diff. peak/hole / e Å^{-3}	0.15/-0.28
Flack parameter	0.14 (7)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for sub-GNDU2. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl1	6643.5(18)	2760(2)	907(1)	107.6(6)
O3	9420(4)	1430(4)	3851(2)	77.5(9)
N2	5525(4)	6873(4)	2292(2)	54.0(8)
N1	6587(4)	6500(4)	1606(2)	56.7(8)
N3	9675(6)	5801(5)	4250(3)	73.8(11)
C13	7911(5)	1344(5)	3709(3)	58.7(10)
O1	9199(6)	7014(4)	4342(3)	111.9(14)
C3	5810(5)	6094(5)	3040(3)	56.3(10)
C2	7123(5)	5165(4)	2854(2)	50.5(9)
C1	7554(5)	5468(5)	1949(2)	52.8(9)
C17	4258(5)	7963(5)	2160(3)	56.4(9)
C12	6855(5)	2665(5)	3467(2)	52.1(9)
C4	8937(5)	4785(5)	1418(2)	54(1)
O4	5476(5)	2810(7)	4877(3)	112.7(15)
O2	11120(6)	5478(5)	4035(3)	108.9(14)
C10	7930(5)	4038(5)	3433(2)	49.9(9)
C5	10584(6)	5343(6)	1422(3)	73.4(13)
C15	5282(5)	2747(6)	4082(4)	71.7(12)
C9	8664(6)	3565(6)	917(3)	68.2(12)
C18	2970(5)	8134(5)	2783(3)	71.3(13)
C20	1837(8)	10043(7)	1918(4)	96.3(17)
C11	8392(5)	4619(5)	4372(3)	58.3(10)
C19	1758(7)	9184(7)	2651(4)	91.1(16)
C22	4336(7)	8811(7)	1409(3)	85.4(16)
C6	11895(7)	4734(8)	931(4)	93.1(19)
C8	9980(8)	2928(8)	417(3)	91.1(17)
C21	3099(9)	9867(8)	1295(4)	106(2)
C7	11590(8)	3549(8)	434(4)	94.0(19)
C14	7026(8)	-41(7)	3724(6)	112(2)
C16	3557(6)	2727(10)	3631(5)	115(2)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for sub-GNDU2.

The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U11	U22	U33	U23	U13	U12
Cl1	100.3(10)	128.2(14)	94.3(9)	-42.4(9)	11.3(7)	-24(1)
O3	58.3(18)	64(2)	110(2)	-0.7(18)	2.1(16)	12.2(15)
N2	56.3(17)	54(2)	51.8(16)	3.3(15)	7.1(14)	8.3(15)
N1	58.7(18)	62(2)	49.4(16)	4.8(16)	8.2(14)	11.2(17)
N3	83(3)	58(3)	81(2)	1(2)	-17(2)	-2(2)
C13	56(2)	54(2)	66(2)	0(2)	8.2(19)	8(2)
O1	136(3)	52(2)	147(4)	-5(2)	-42(3)	1(2)
C3	59(2)	60(3)	50.0(19)	-0.9(19)	12.3(17)	11.9(19)
C2	50.5(19)	54(2)	47.3(18)	1.1(17)	7.3(15)	6.1(17)
C1	56(2)	54(2)	48.1(18)	1.6(18)	6.7(16)	2.5(19)
C17	61(2)	46(2)	62(2)	-5.1(18)	-0.6(17)	12.3(18)
C12	51.5(19)	53(2)	51.5(19)	0.6(18)	2.6(15)	1.9(18)
C4	57(2)	61(3)	44.1(17)	5.9(19)	10.5(16)	10.5(19)
O4	87(2)	173(5)	79(2)	-6(3)	35.6(18)	-11(3)
O2	86(3)	95(3)	145(4)	-7(3)	20(2)	-20(2)
C10	51.0(19)	53(2)	45.7(18)	4.2(17)	7.3(15)	10.0(17)
C5	62(3)	81(3)	77(3)	5(3)	18(2)	4(2)
C15	55(2)	72(3)	88(3)	4(3)	13(2)	1(2)
C9	71(3)	80(3)	53(2)	-3(2)	8(2)	8(2)
C18	63(3)	71(3)	79(3)	2(3)	11(2)	13(2)
C20	99(4)	86(4)	104(4)	-4(4)	0(3)	42(3)
C11	62(2)	60(3)	53(2)	2.0(19)	0.2(18)	1(2)
C19	79(3)	87(4)	107(4)	-3(4)	18(3)	29(3)
C22	100(4)	86(4)	70(3)	14(3)	15(2)	38(3)
C6	70(3)	106(5)	103(4)	15(4)	28(3)	17(3)
C8	110(4)	92(4)	71(3)	-17(3)	21(3)	25(4)
C21	131(5)	99(5)	89(4)	28(3)	6(4)	53(4)
C7	85(4)	108(5)	89(4)	16(4)	40(3)	33(4)
C14	90(4)	60(4)	186(7)	18(4)	-15(4)	-9(3)
C16	50(3)	128(6)	168(6)	0(5)	-1(3)	8(3)

Table 4 Bond Lengths for sub-GNDU2.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C9	1.743(5)	C17	C22	1.369(7)
O3	C13	1.195(5)	C12	C10	1.533(6)
N2	N1	1.356(4)	C12	C15	1.528(6)
N2	C3	1.346(5)	C4	C5	1.384(6)
N2	C17	1.432(5)	C4	C9	1.378(7)
N1	C1	1.325(5)	O4	C15	1.189(6)
N3	O1	1.201(6)	C10	C11	1.536(6)
N3	O2	1.206(6)	C5	C6	1.377(7)
N3	C11	1.501(6)	C15	C16	1.499(7)
C13	C12	1.527(6)	C9	C8	1.397(7)
C13	C14	1.467(8)	C18	C19	1.376(7)
C3	C2	1.369(5)	C20	C19	1.353(9)
C2	C1	1.411(5)	C20	C21	1.358(9)
C2	C10	1.498(6)	C22	C21	1.389(8)
C1	C4	1.479(5)	C6	C7	1.352(10)
C17	C18	1.372(6)	C8	C7	1.381(9)

Table 5 Bond Angles for sub-GNDU2.

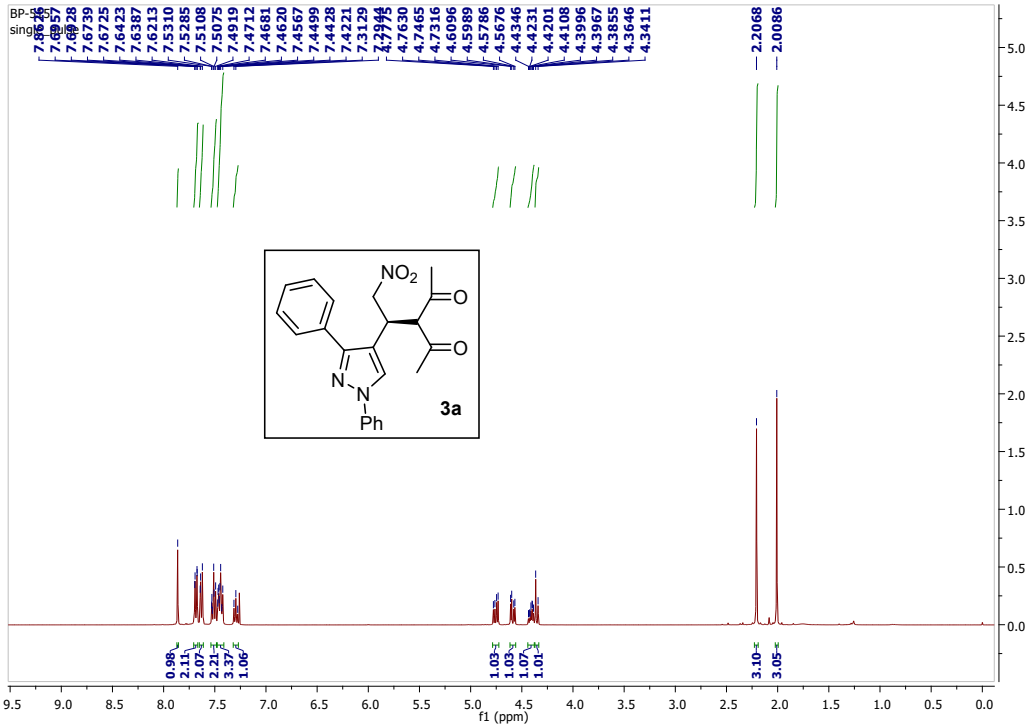
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	N2	C17	120.1(3)	C5	C4	C1	120.5(4)
C3	N2	N1	112.2(3)	C9	C4	C1	122.2(4)
C3	N2	C17	127.7(3)	C9	C4	C5	117.3(4)
C1	N1	N2	104.2(3)	C2	C10	C12	112.3(3)
O1	N3	O2	123.6(5)	C2	C10	C11	111.6(4)
O1	N3	C11	118.5(5)	C12	C10	C11	113.3(3)
O2	N3	C11	117.9(4)	C6	C5	C4	121.8(6)
O3	C13	C12	121.0(4)	O4	C15	C12	119.4(4)
O3	C13	C14	121.2(4)	O4	C15	C16	123.8(5)
C14	C13	C12	117.8(4)	C16	C15	C12	116.8(5)
N2	C3	C2	107.5(3)	C4	C9	Cl1	120.1(3)
C3	C2	C1	103.9(3)	C4	C9	C8	121.7(5)
C3	C2	C10	130.1(3)	C8	C9	Cl1	118.2(4)
C1	C2	C10	125.9(3)	C17	C18	C19	119.2(5)
N1	C1	C2	112.1(3)	C19	C20	C21	120.4(5)
N1	C1	C4	121.5(3)	N3	C11	C10	107.9(3)
C2	C1	C4	126.3(4)	C20	C19	C18	120.5(5)
C18	C17	N2	119.6(4)	C17	C22	C21	118.7(5)
C22	C17	N2	119.5(4)	C7	C6	C5	119.8(6)
C22	C17	C18	120.9(4)	C7	C8	C9	118.4(6)
C13	C12	C10	113.1(3)	C20	C21	C22	120.4(6)
C13	C12	C15	109.3(3)	C6	C7	C8	120.9(5)
C15	C12	C10	114.5(4)				

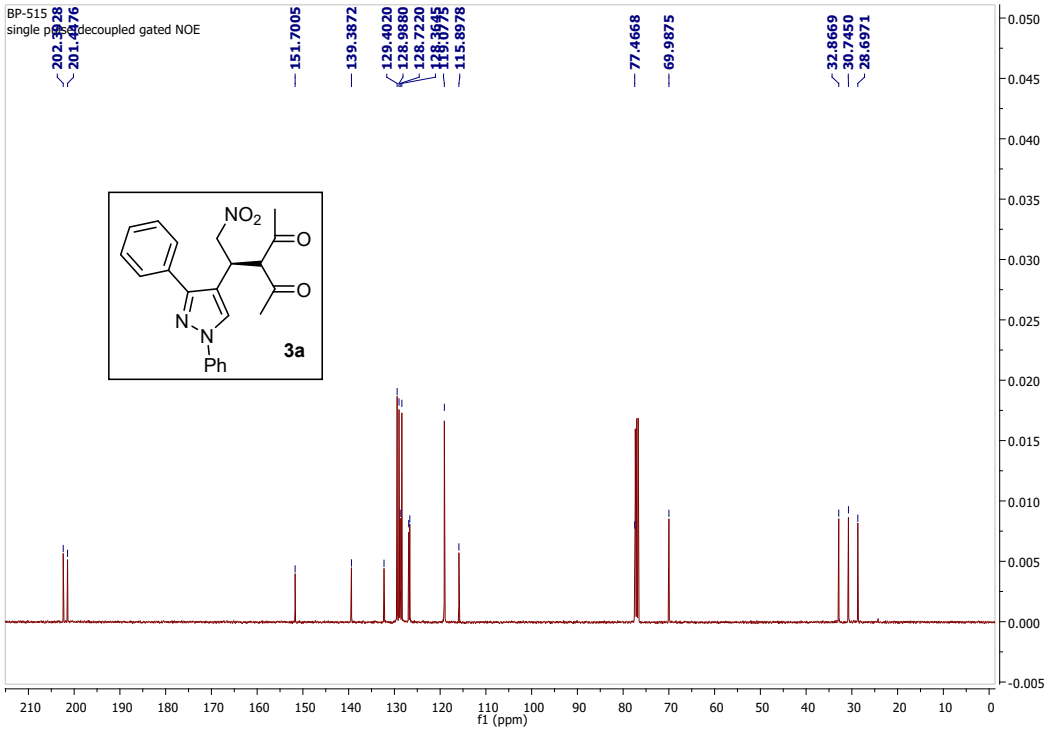
Table 6 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for sub- GNDU2.

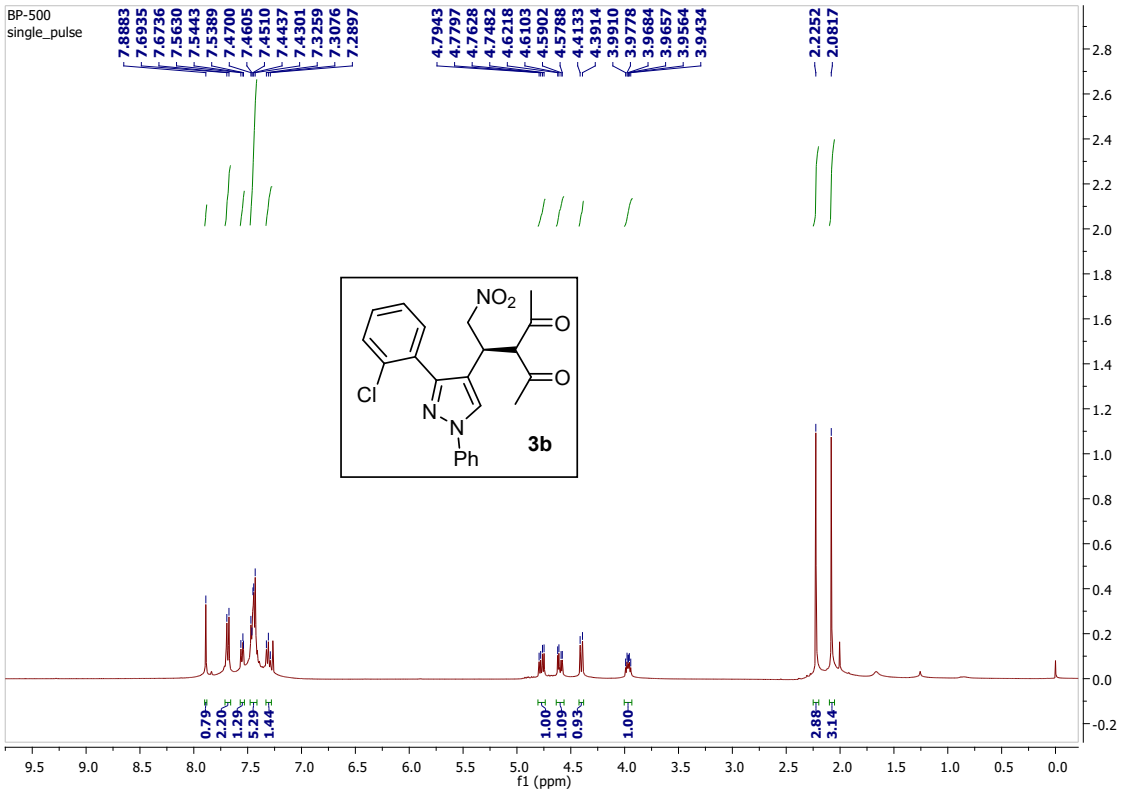
Atom	*x*	*y*	*z*	U(eq)
H3	5223.06	6171.57	3584.08	68
H12	6419.72	2509.02	2853.92	63
H10	9019.08	3782.72	3142.74	60
H5	10811.29	6152.68	1766.66	88
H18	2917.75	7547.14	3289.12	86
H20	1021	10759.13	1839.59	116
H11A	7370.29	4979.17	4669.95	70
H11B	8879.31	3864.37	4740.51	70
H19	877.47	9304.47	3068.6	109
H22	5199.67	8682.85	982.46	103
H6	12988.07	5135.76	941.98	112
H8	9776.6	2104.76	82.01	109
H21	3136.61	10456.48	790.4	128
H7	12475.91	3147.75	97.69	113
H14A	7857.75	-794.69	3772.43	168
H14B	6378.35	-156.95	3177.64	168
H14C	6261.92	-76.89	4232.43	168
H16A	3555.9	3389.85	3136.08	173
H16B	2688.32	2997.15	4057.97	173
H16C	3322.95	1782.92	3409.69	173

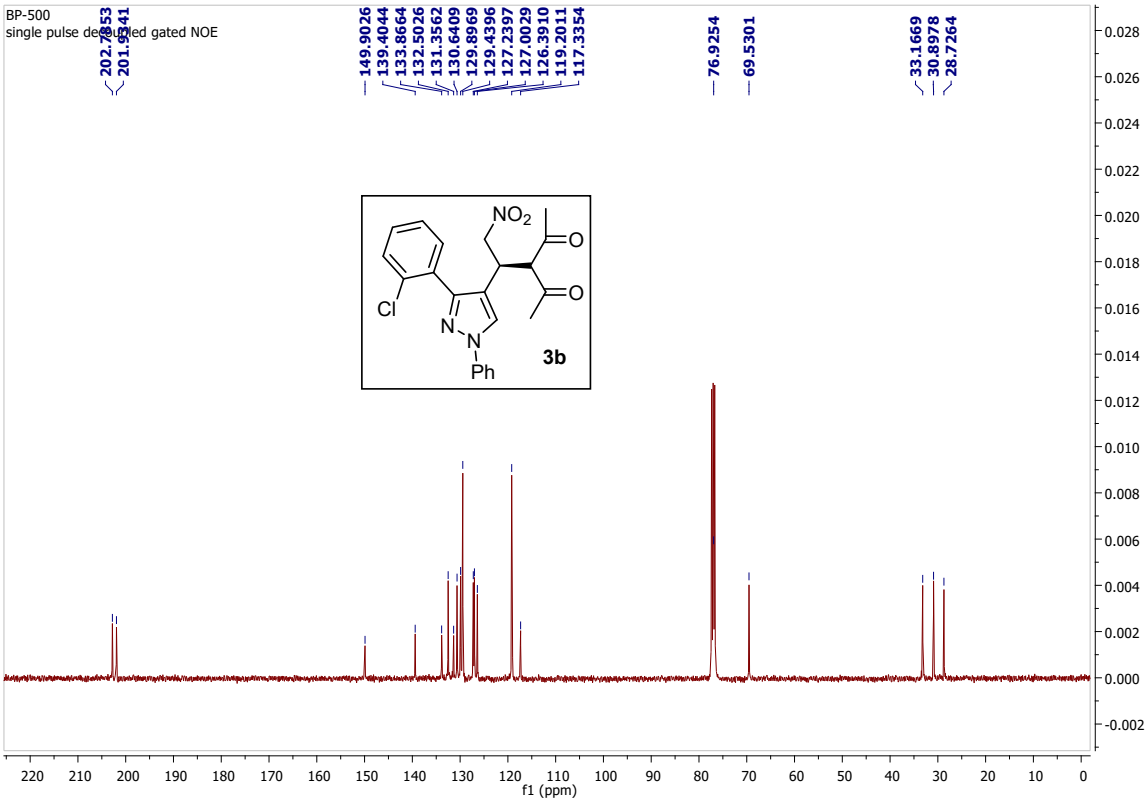
^{1}H and ^{13}C NMR spectra

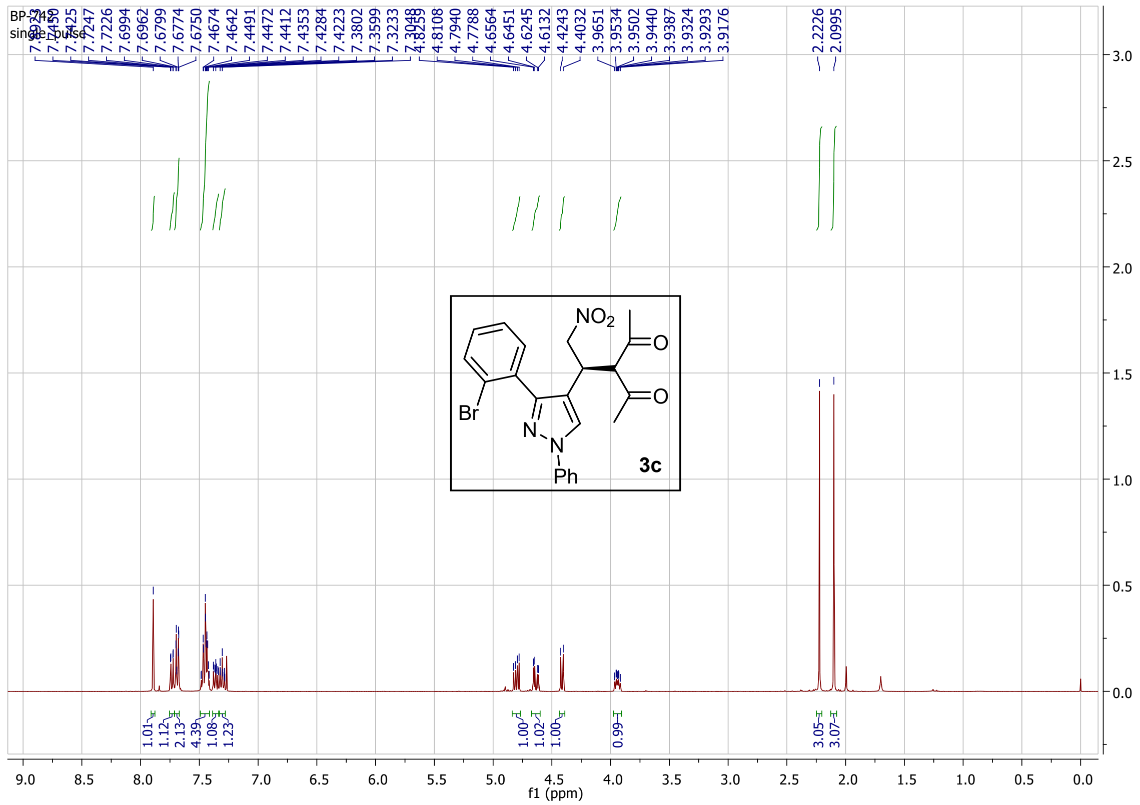
^{1}H and ^{13}C NMR spectra of Michael adduct 3a-3q

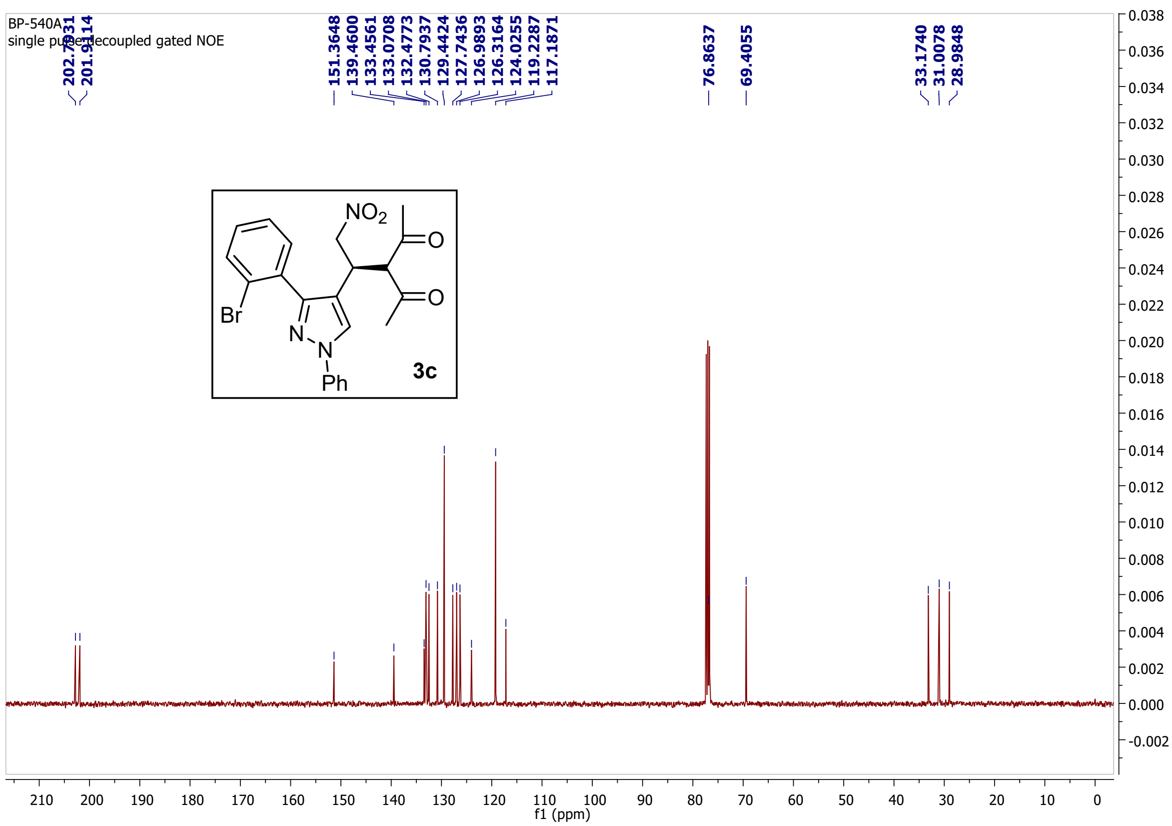


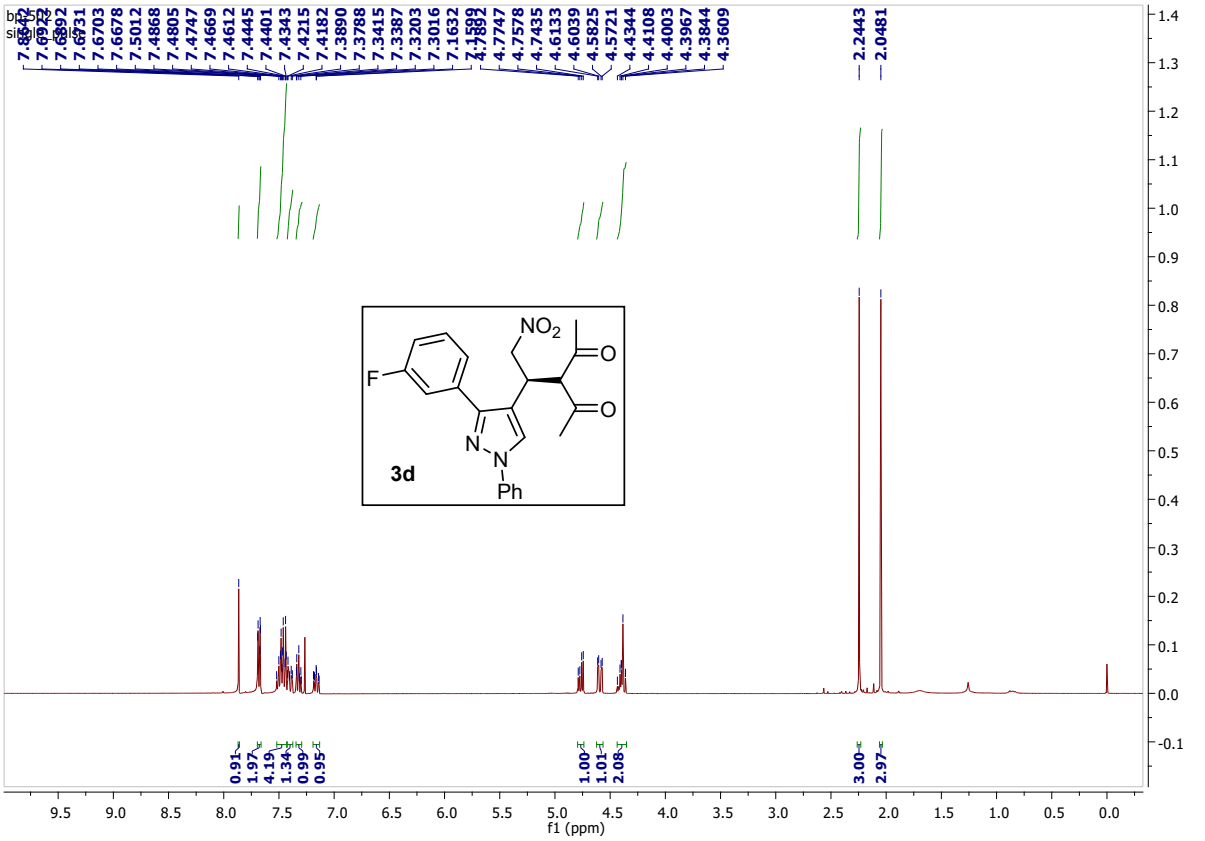


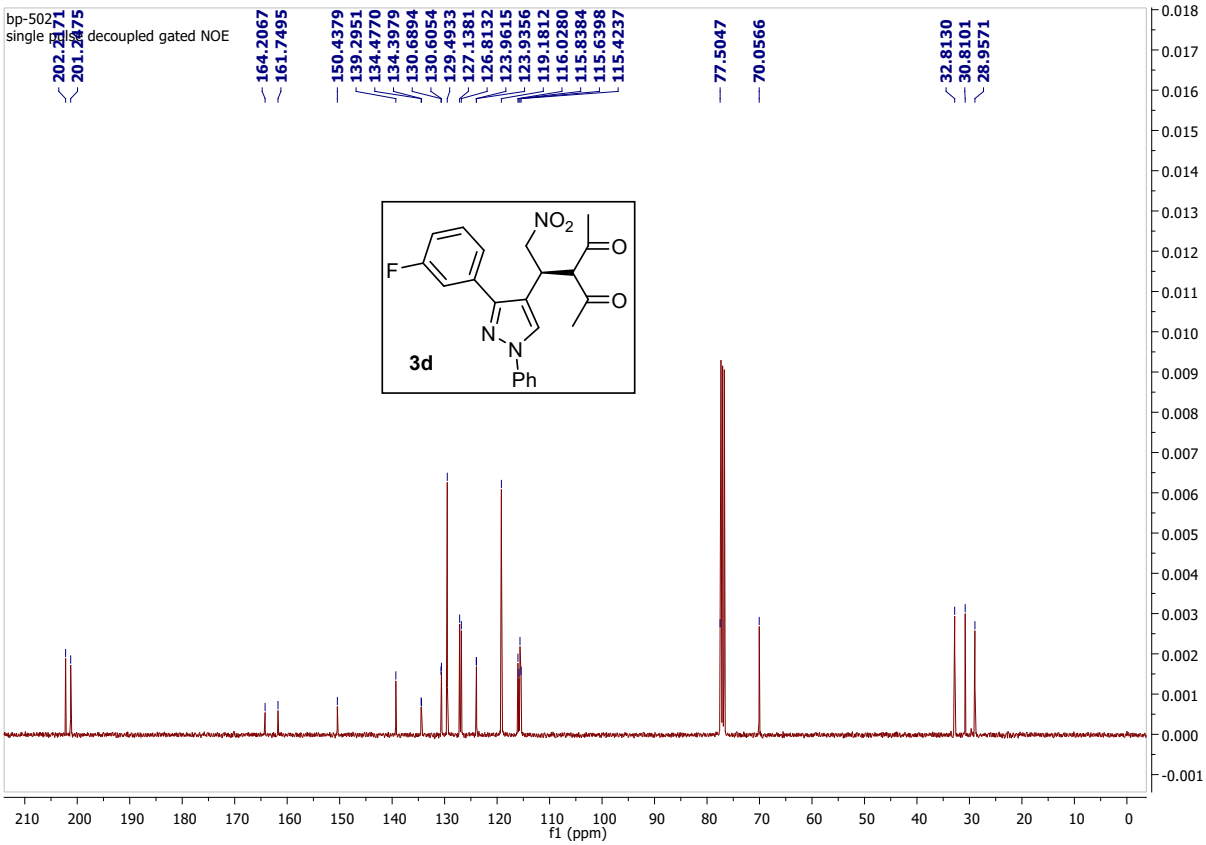

BP-500
single_pulse
7.8883
7.6935
7.6736
7.5630
7.5443
7.5389
7.4700
7.4605
7.4510
7.4437
7.4301
7.3259
7.3076
7.2897
4.7943
4.7797
4.7628
4.7482
4.6218
4.6103
4.5902
4.5788
4.4133
4.3914
3.9910
3.9778
3.9684
3.9657
3.9564
3.9434
2.2252
2.0817
NO2
O
O
Cl
N
N
Ph
3b
0.79
2.20
1.29
5.29
1.44
1.00
1.09
0.93
1.00
2.88
3.14
f1 (ppm)

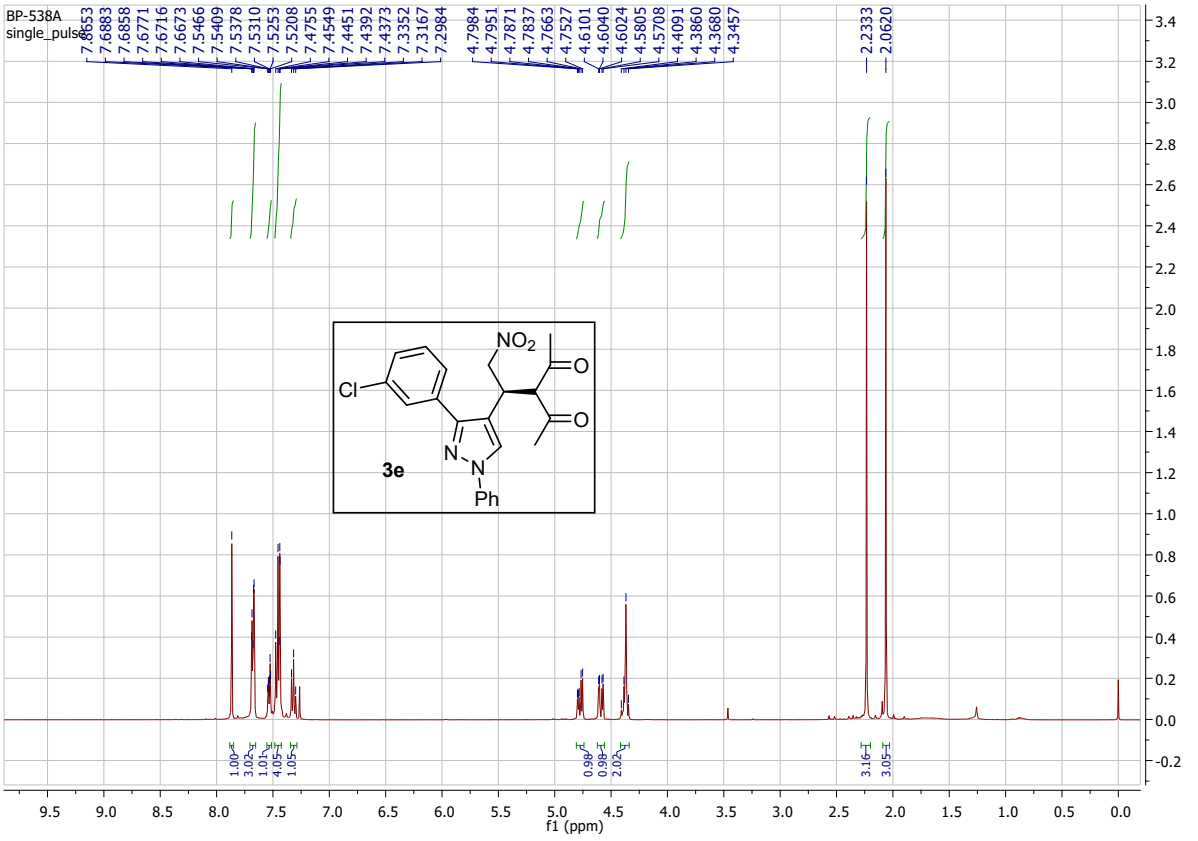

BP-500
single pulse decoupled gated NOE
202.7853
201.9741
149.9026
139.4044
133.8664
132.5026
131.3562
130.6409
129.8969
129.4396
127.2397
127.0029
126.3910
119.2011
117.3354
76.9254
69.5301
33.1669
30.8978
28.7264
NO2
O
O
Cl
N
N
Ph
3b
f1 (ppm)

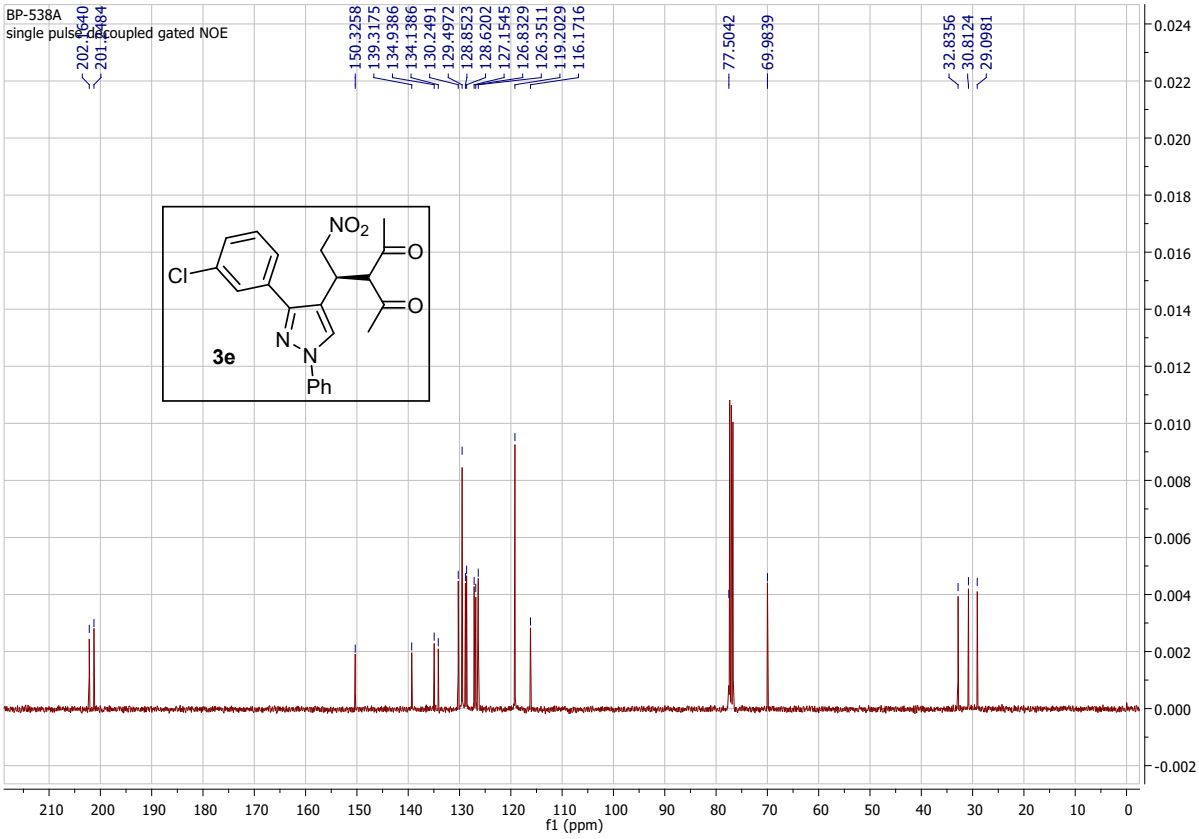

single_pulse
7.7425
7.7247
7.7226
7.6994
7.6962
7.6799
7.6774
7.6750
7.4674
7.4642
7.4491
7.4472
7.4412
7.4353
7.4284
7.4223
7.3802
7.3599
7.3233
4.8108
4.7940
4.7788
4.6564
4.6451
4.6245
4.6132
4.4243
4.4032
3.9651
3.9534
3.9502
3.9440
3.9387
3.9324
3.9293
3.9176
2.2226
2.0995
NO_2
O
O
Br
N
N
Ph
3c
1.01
1.12
2.13
4.39
1.08
1.23
1.00
1.02
1.00
0.99
3.05
3.07
f1 (ppm)

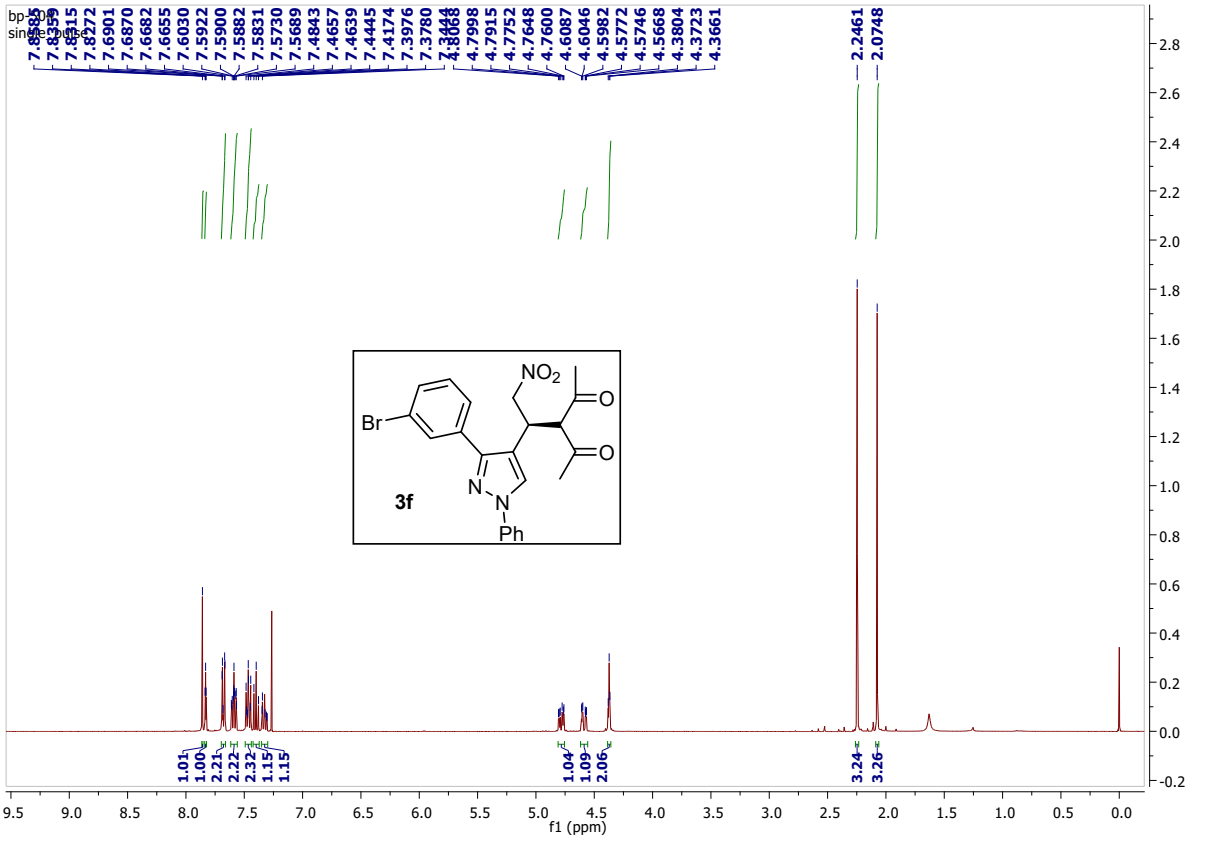

BP-540A
single pulse decoupled gated NOE
151.3648
139.4600
133.4561
133.0708
132.4773
130.7937
129.4424
127.7436
126.9893
126.3164
124.0255
119.2287
117.1871
76.8637
69.4055
33.1740
31.0078
28.9848
NO_2
O
O
Br
N
N
Ph
3c
f1 (ppm)

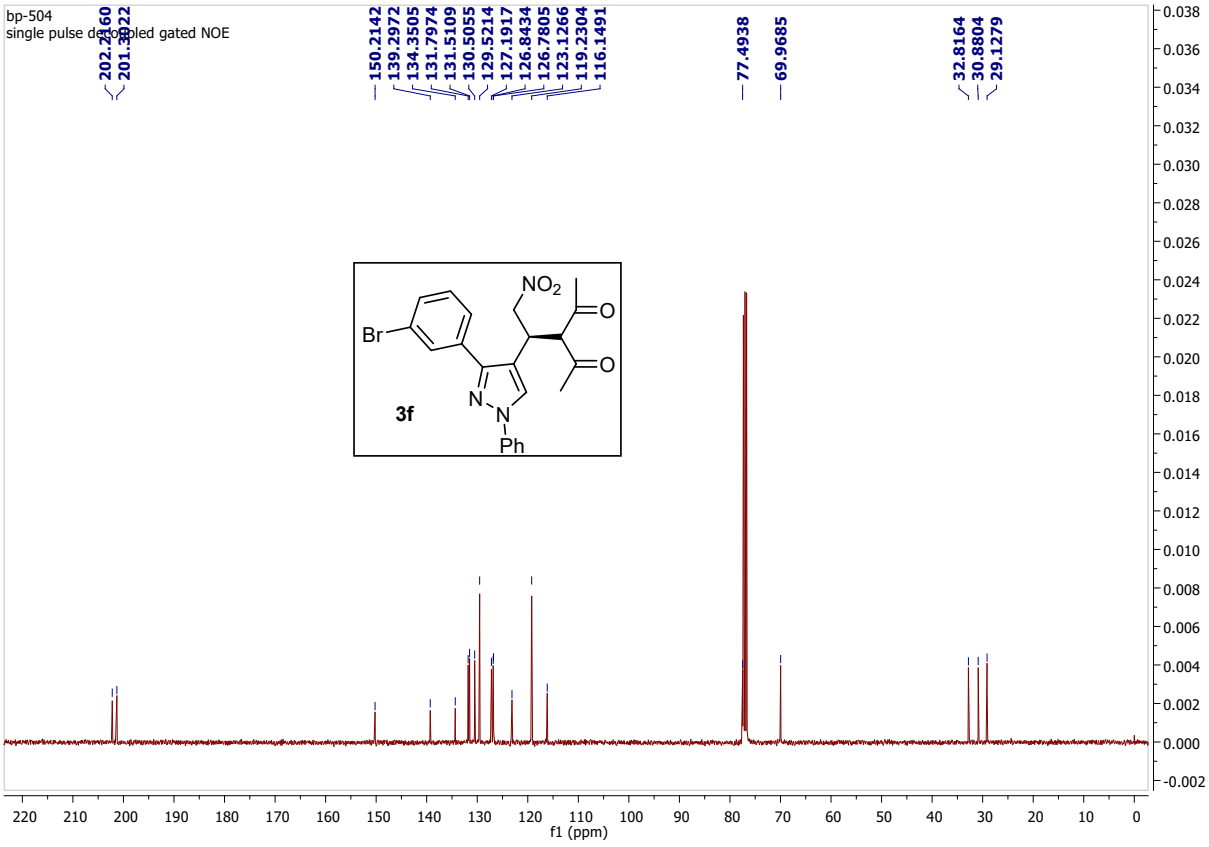

bp-502
single pulse
7.8412
7.6972
7.6892
7.6731
7.6703
7.6678
7.5012
7.4868
7.4805
7.4747
7.4669
7.4612
7.4445
7.4401
7.4343
7.4215
7.4182
7.3890
7.3788
7.3415
7.3387
7.3203
7.3016
7.1632
7.1599
7.1592
4.7747
4.7578
4.7435
4.6133
4.6039
4.5825
4.5721
4.4344
4.4108
4.4003
4.3967
4.3844
4.3609
2.2443
2.0481
NO2
O
O
F
N
N
Ph
3d
0.91
1.97
4.19
1.34
0.99
0.95
1.00
1.01
2.08
3.00
2.97
f1 (ppm)

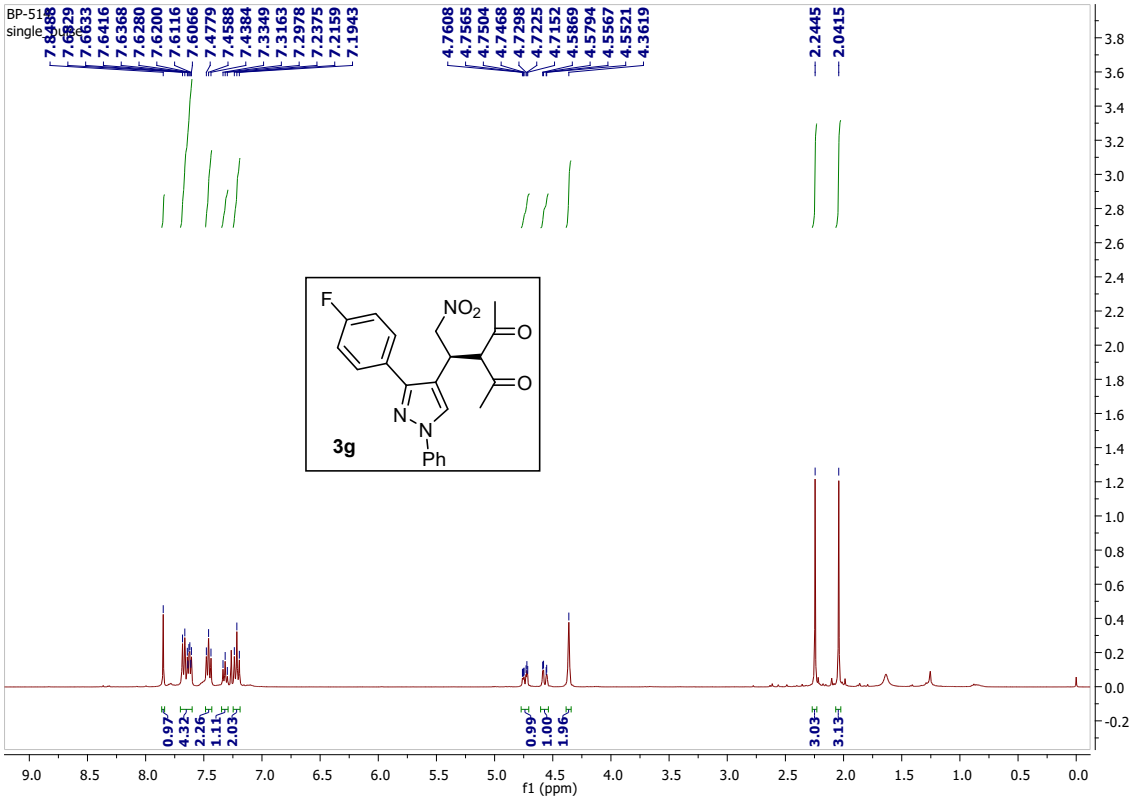

bp-502
single pulse decoupled gated NOE
202.2171
201.7475
164.2067
161.7495
150.4379
139.2951
134.4770
134.3979
130.6894
130.6054
129.4933
127.1381
126.8132
123.9615
123.9356
119.1812
116.0280
115.8384
115.6398
115.4237
77.5047
70.0566
32.8130
30.8101
28.9571
NO2
O
O
F
N
N
Ph
3d
f1 (ppm)

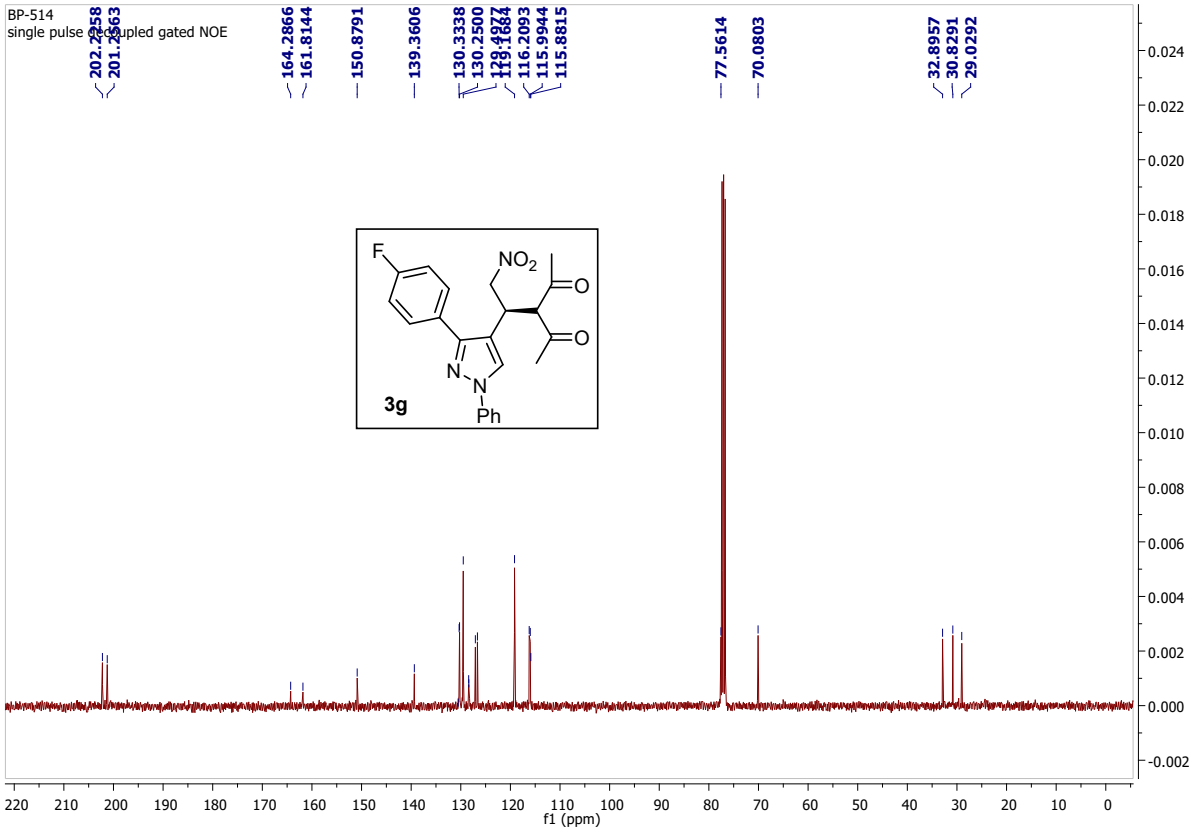

BP-538A
single_pulse
7.8653
7.6883
7.6858
7.6771
7.6716
7.6673
7.5466
7.5409
7.5378
7.5310
7.5253
7.5208
7.4755
7.4549
7.4451
7.4392
7.4373
7.3352
7.3167
7.2984
4.7984
4.7951
4.7871
4.7837
4.7663
4.7527
4.6101
4.6040
4.6024
4.5805
4.5708
4.4091
4.3860
4.3680
4.3457
2.2333
2.0620
NO2
O
O
Cl
N
N
Ph
3e
1.00
3.02
1.01
4.05
1.05
0.99
0.98
2.02
3.16
3.05
f1 (ppm)

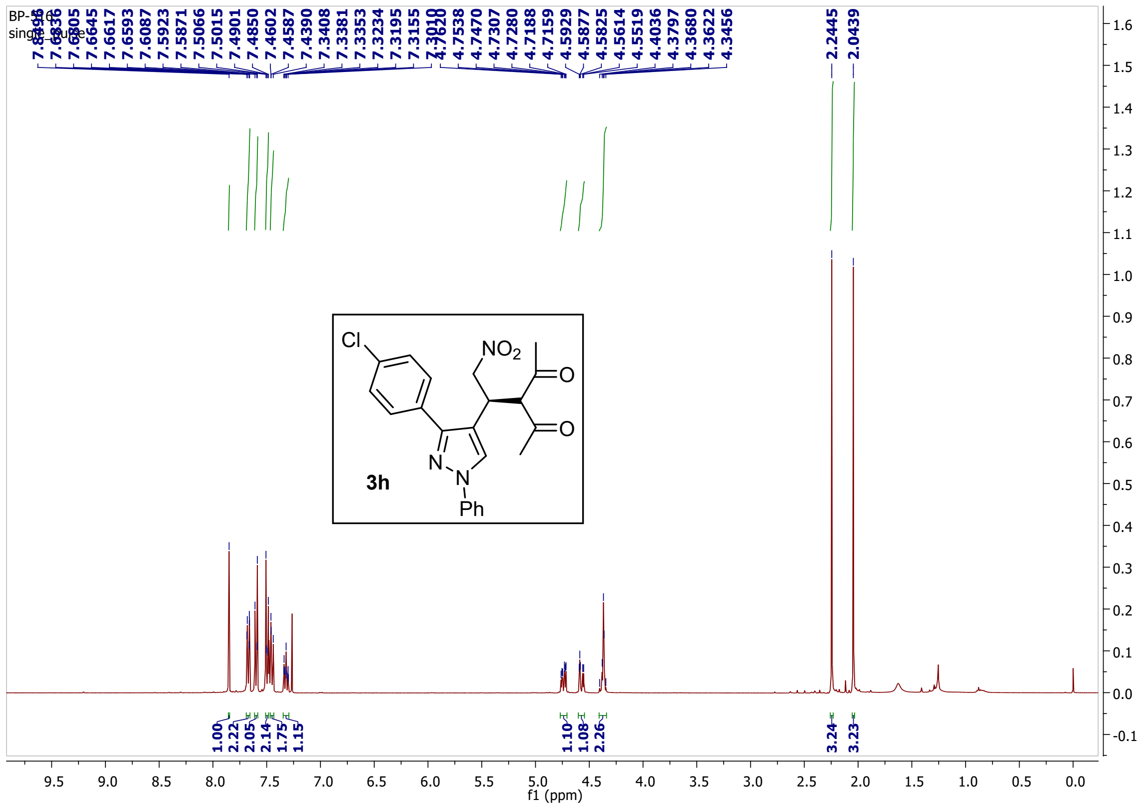

BP-538A
single pulse decoupled gated NOE
202.1640
201.3484
150.3258
139.3175
134.9386
134.1386
130.2491
129.4972
128.8523
128.6202
127.1545
126.8329
126.3511
119.2029
116.1716
77.5042
69.9839
32.8356
30.8124
29.0981
NO2
O
O
Cl
N
N
Ph
3e
f1 (ppm)

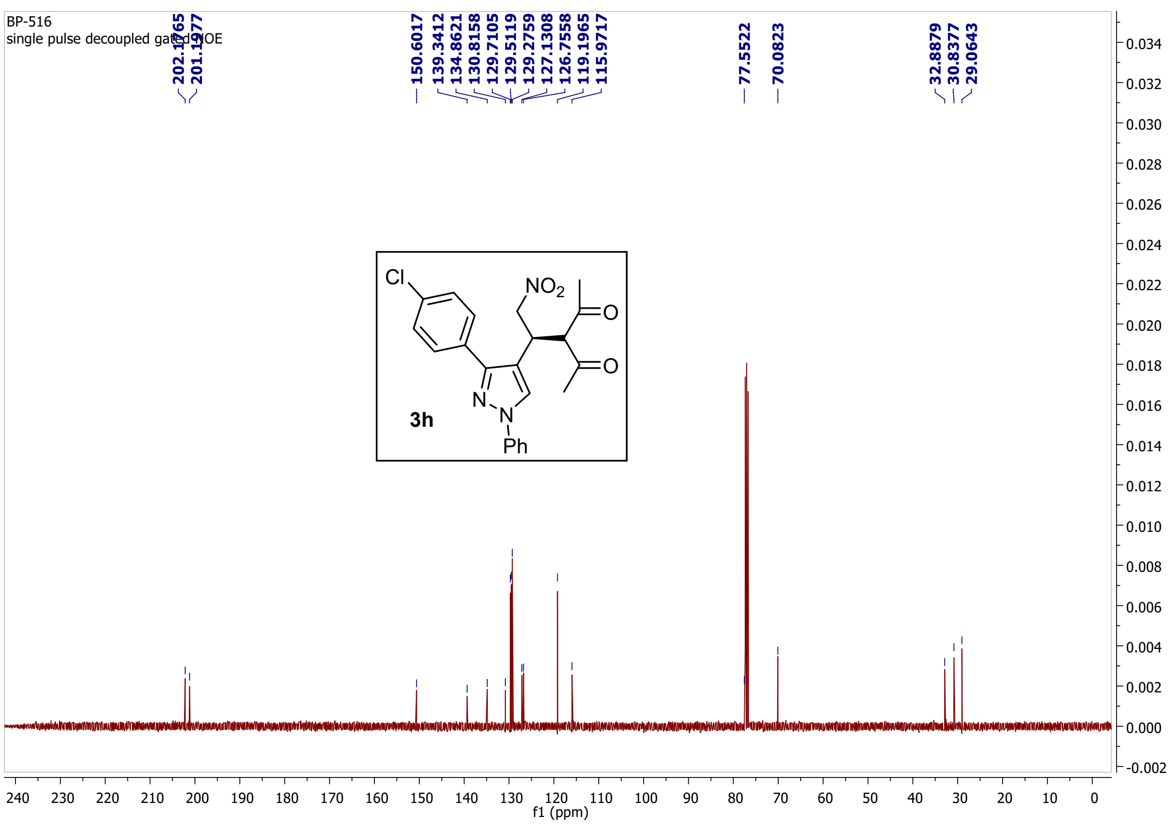

bp-504
single pulse
7.8825
7.8599
7.8415
7.8272
7.6901
7.6870
7.6682
7.6655
7.6030
7.5922
7.5900
7.5882
7.5831
7.5730
7.5689
7.4843
7.4657
7.4639
7.4445
7.4174
7.3976
7.3780
4.8068
4.7998
4.7915
4.7752
4.7648
4.7600
4.6087
4.6046
4.5982
4.5772
4.5746
4.5668
4.3804
4.3723
4.3661
2.2461
2.0748
1.01
1.00
2.21
2.22
2.32
1.15
1.15
1.04
1.09
2.06
3.24
3.26
f1 (ppm)
3f
Br
NO2
O
O
N
N
Ph

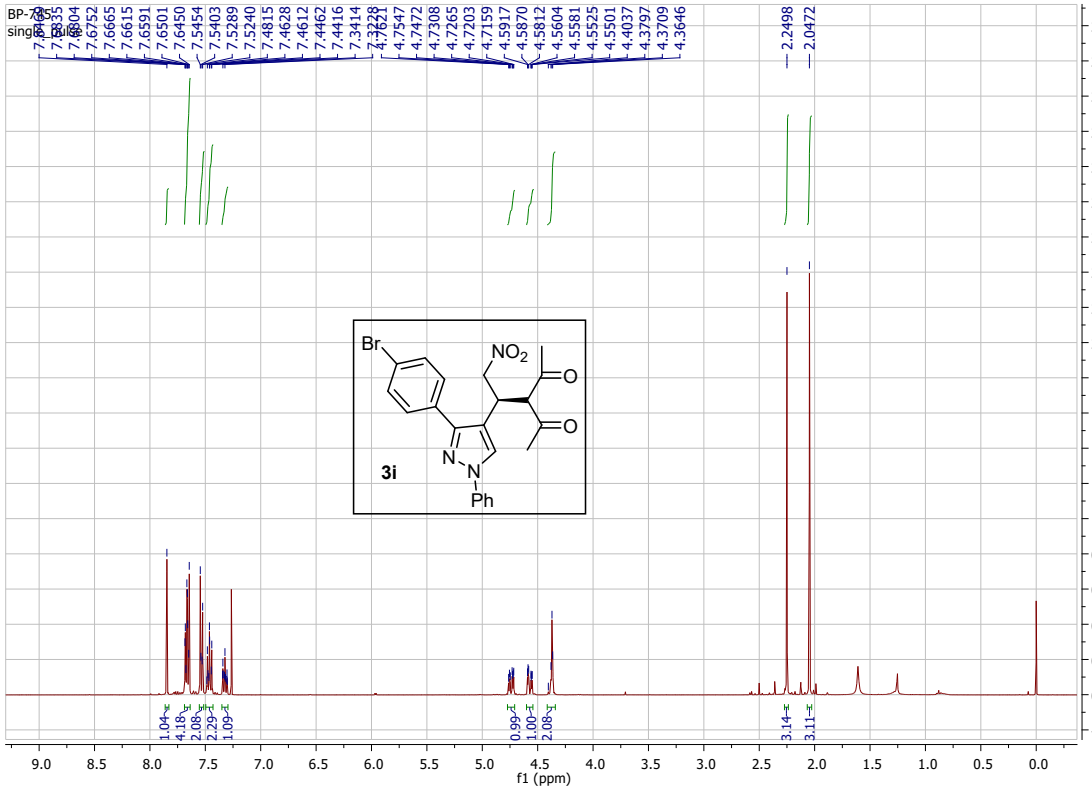

bp-504
single pulse decoupled gated NOE
202.2160
201.3922
150.2142
139.2972
134.3505
131.7974
131.5109
130.5055
129.5214
127.1917
126.8434
126.7805
123.1266
119.2304
116.1491
77.4938
69.9685
32.8164
30.8804
29.1279
f1 (ppm)
3f
Br
NO2
O
O
N
N
Ph

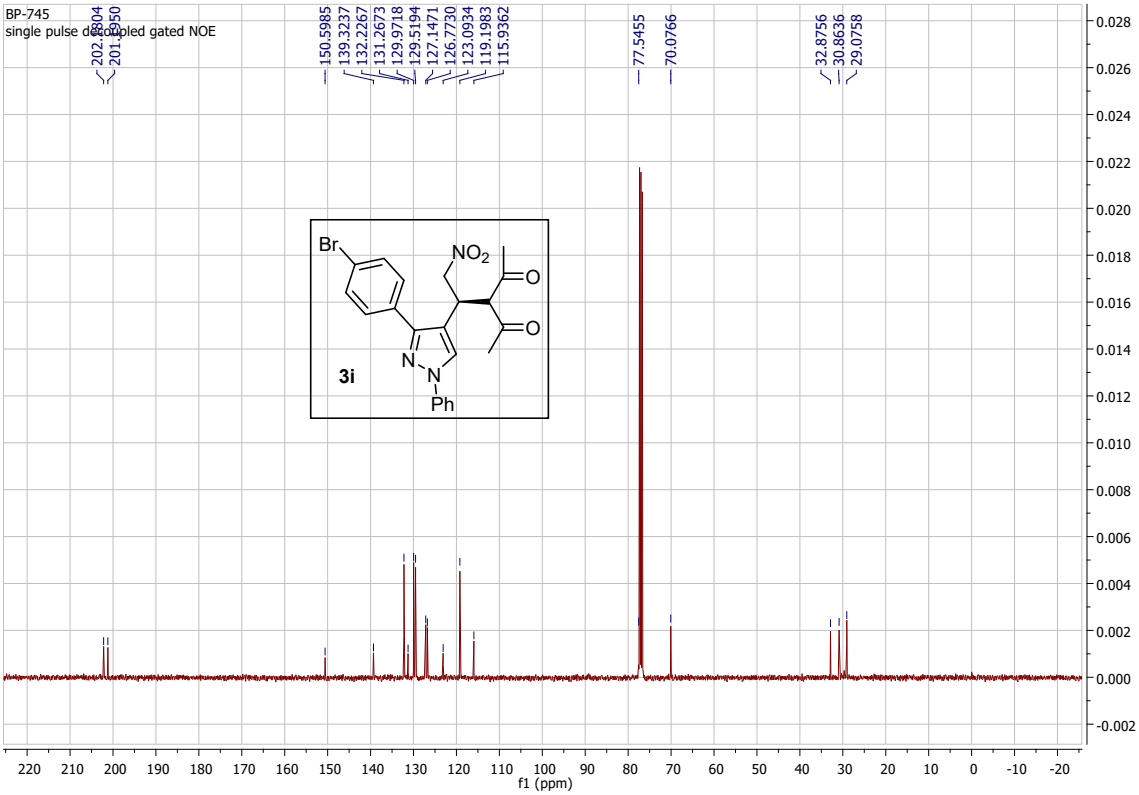

BP-514
single pulse
7.8488
7.6829
7.6633
7.6416
7.6368
7.6280
7.6200
7.6116
7.6066
7.4779
7.4588
7.4384
7.3349
7.3163
7.2978
7.2375
7.2159
7.1943
4.7608
4.7565
4.7504
4.7468
4.7298
4.7225
4.7152
4.5869
4.5794
4.5567
4.5521
4.3619
2.2445
2.0415
F
NO2
O
O
N
N
Ph
3g
0.97
4.32
2.26
1.11
2.03
0.99
1.00
1.96
3.03
3.13
f1 (ppm)

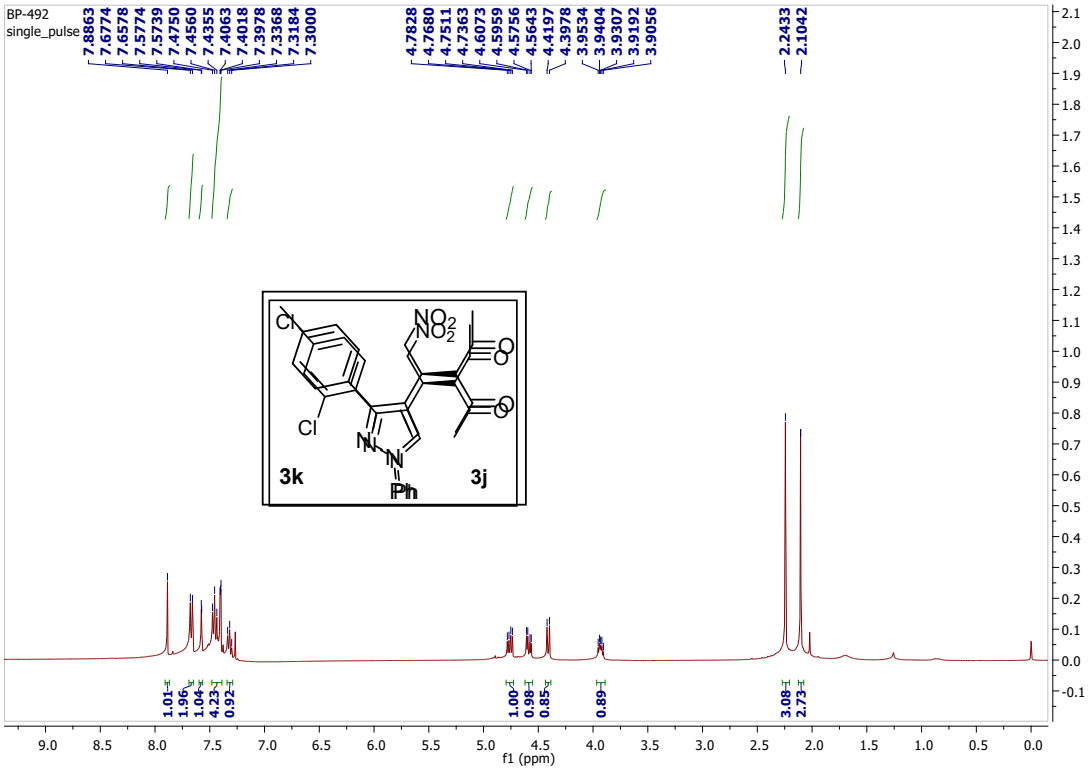

BP-514
single pulse decoupled gated NOE
202.2258
201.2363
164.2866
161.8144
150.8791
139.3606
130.3338
130.2500
129.4877
129.1684
116.2093
115.9944
115.8815
77.5614
70.0803
32.8957
30.8291
29.0292
F
NO2
O
O
N
N
Ph
3g
f1 (ppm)

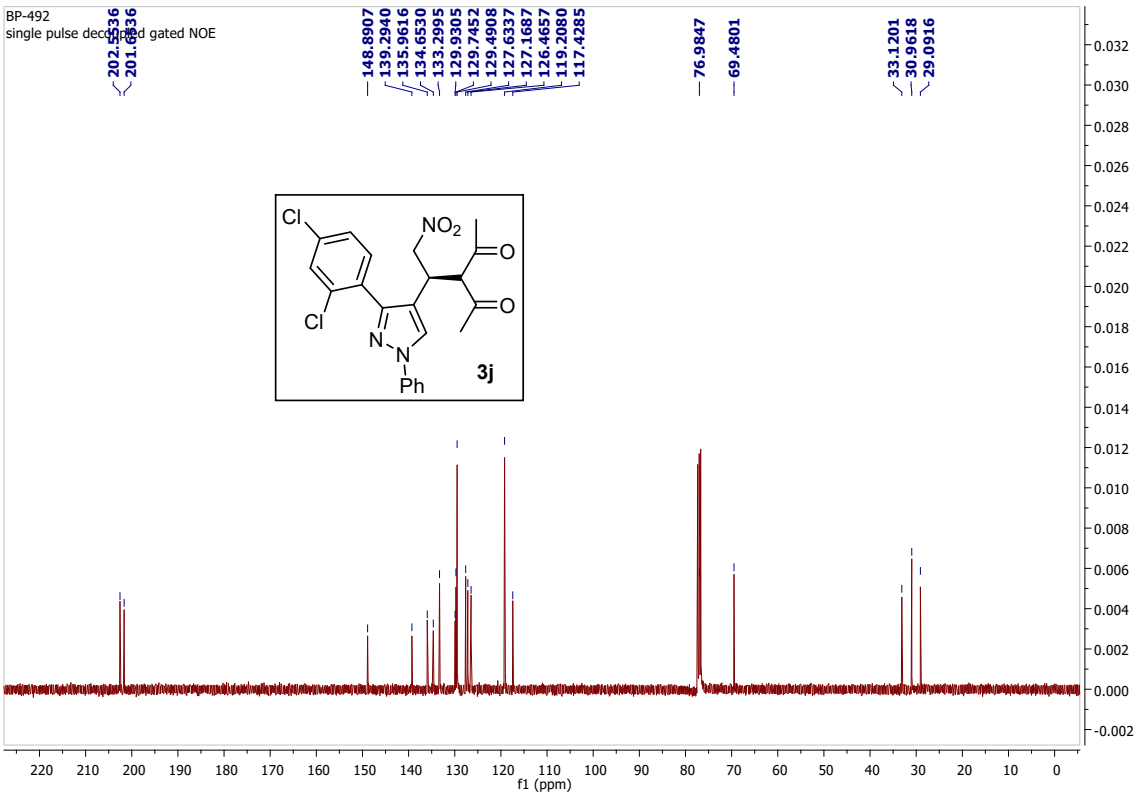

BP-516
3h
f1 (ppm)

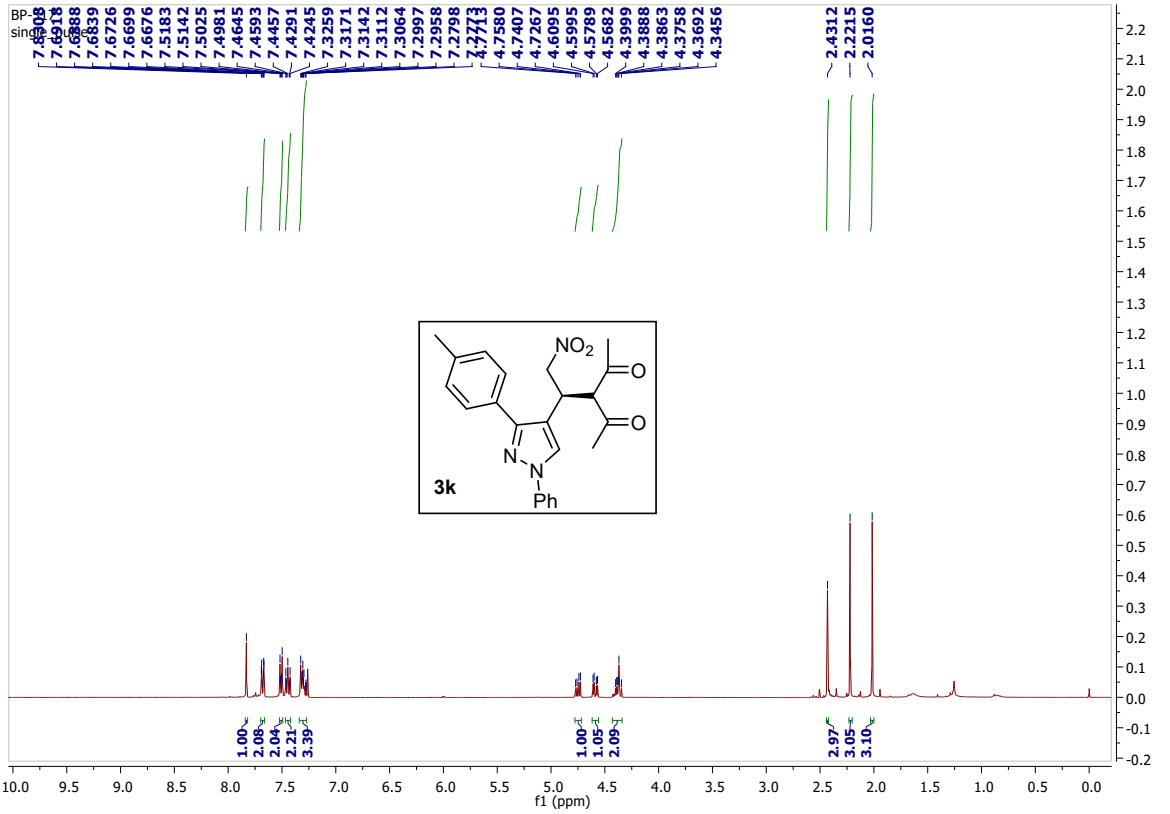

BP-516
single pulse decoupled gated NOE
3h
f1 (ppm)

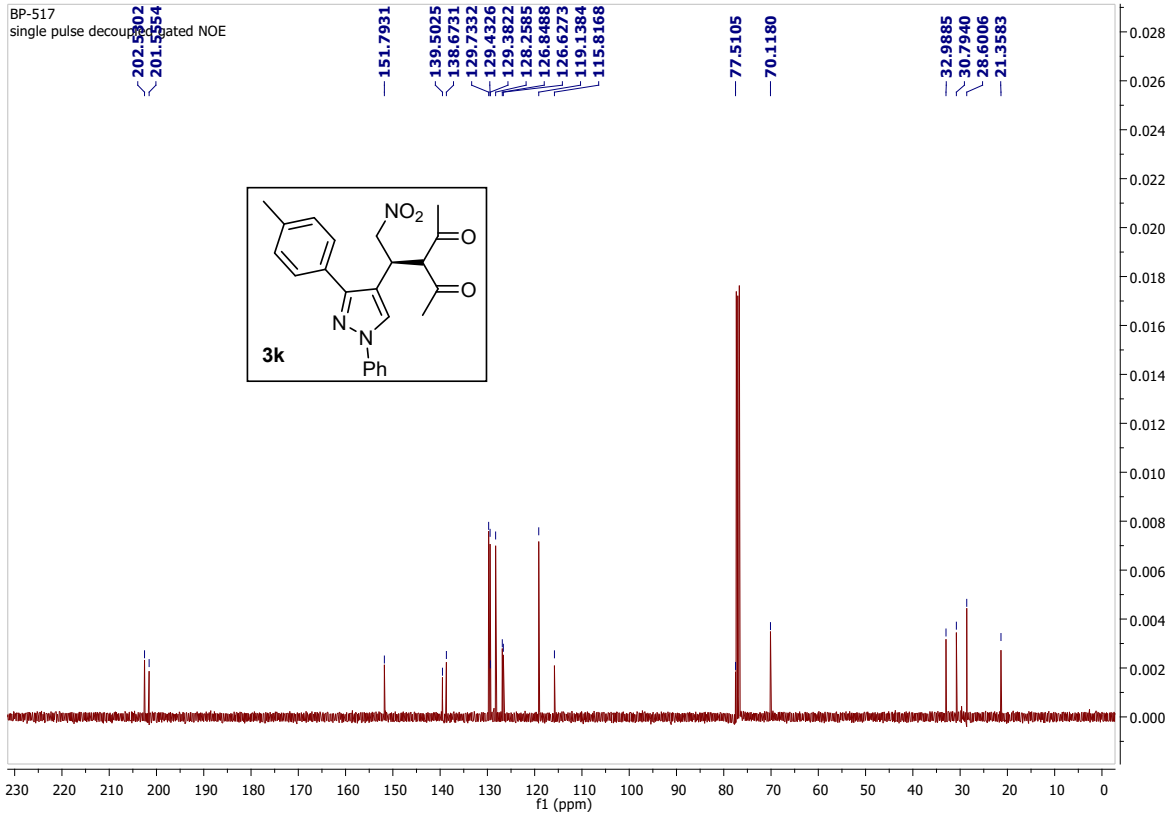

BP-745
single pulse
Br
NO2
O
O
N
N
Ph
3i
2.2498
2.0472
f1 (ppm)

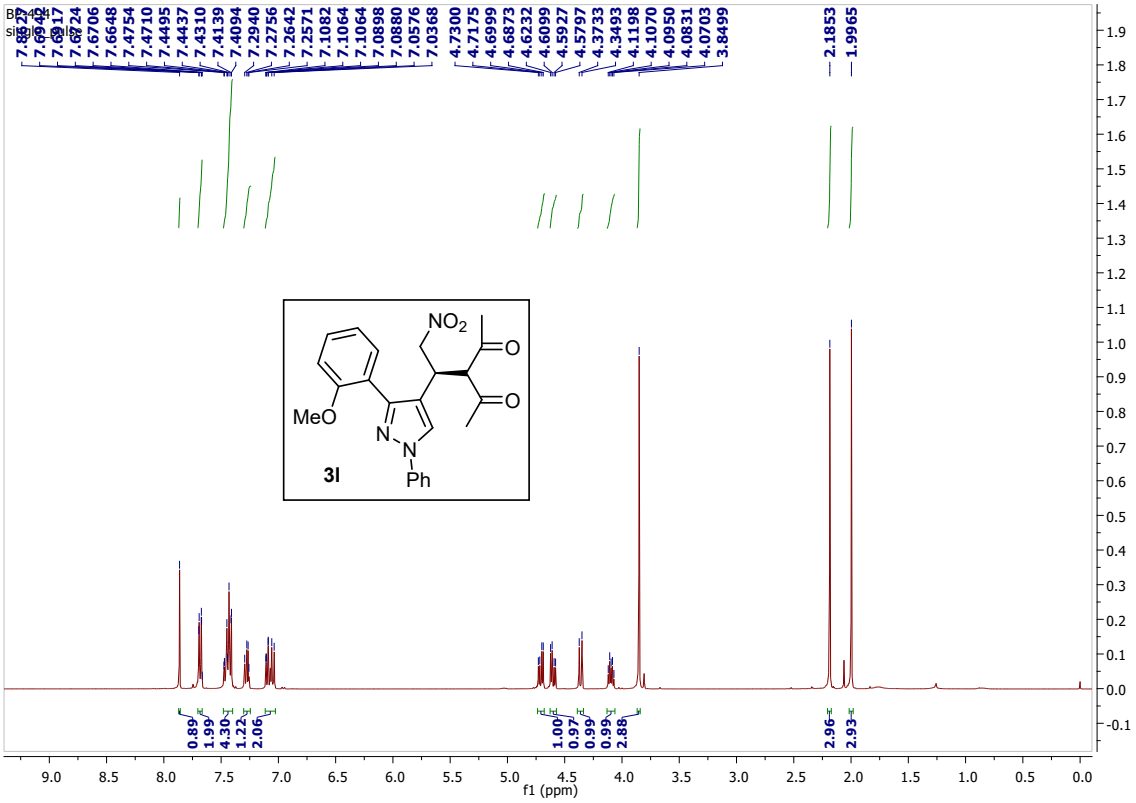

BP-745
single pulse decoupled gated NOE
202.8204
201.2950
150.5985
139.3237
132.2267
131.2673
129.9718
129.5194
127.1471
126.7730
123.0934
119.1983
115.9362
77.5455
70.0766
32.8756
30.8636
29.0758
Br
NO2
O
O
N
N
Ph
3i
f1 (ppm)

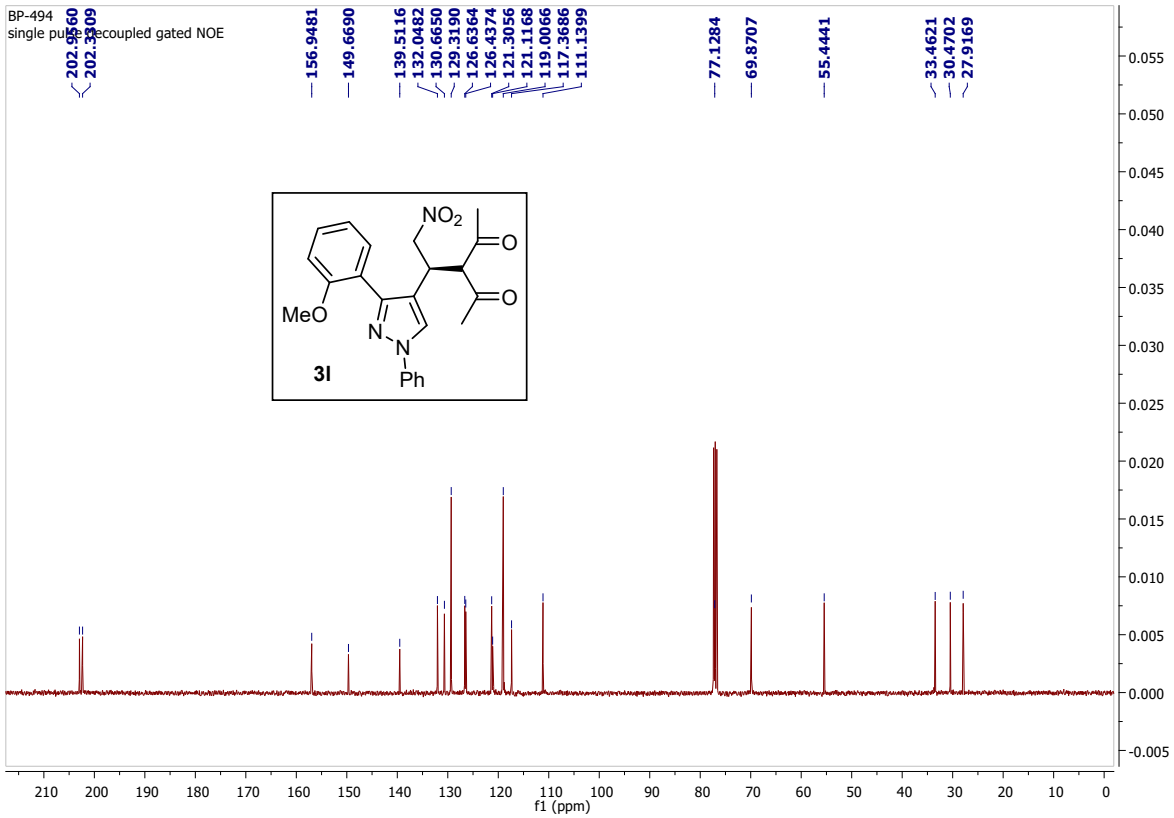

BP-492
single_pulse
7.8863
7.6774
7.6578
7.5774
7.5739
7.4750
7.4560
7.4355
7.4063
7.4018
7.3978
7.3368
7.3184
7.3000
4.7828
4.7680
4.7511
4.7363
4.6073
4.5959
4.5756
4.5643
4.4197
4.3978
3.9534
3.9404
3.9307
3.9192
3.9056
2.2433
2.1042
3k
3j
1.01
1.96
1.04
4.23
0.92
1.00
0.98
0.85
0.89
3.08
2.73
f1 (ppm)

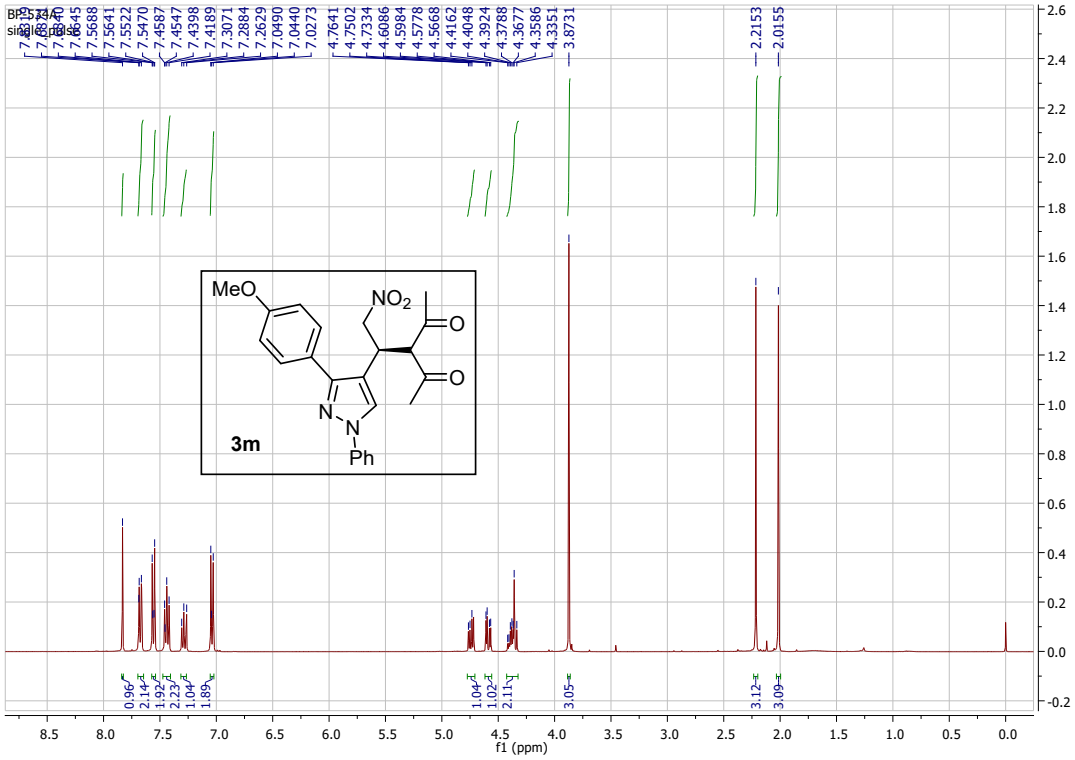

BP-492
single pulse decoupled gated NOE
202.2336
201.6336
148.8907
139.2940
135.9616
134.6530
133.2995
129.9305
129.7452
129.4908
127.6337
127.1687
126.4657
119.2080
117.4285
76.9847
69.4801
33.1201
30.9618
29.0916
3j
f1 (ppm)

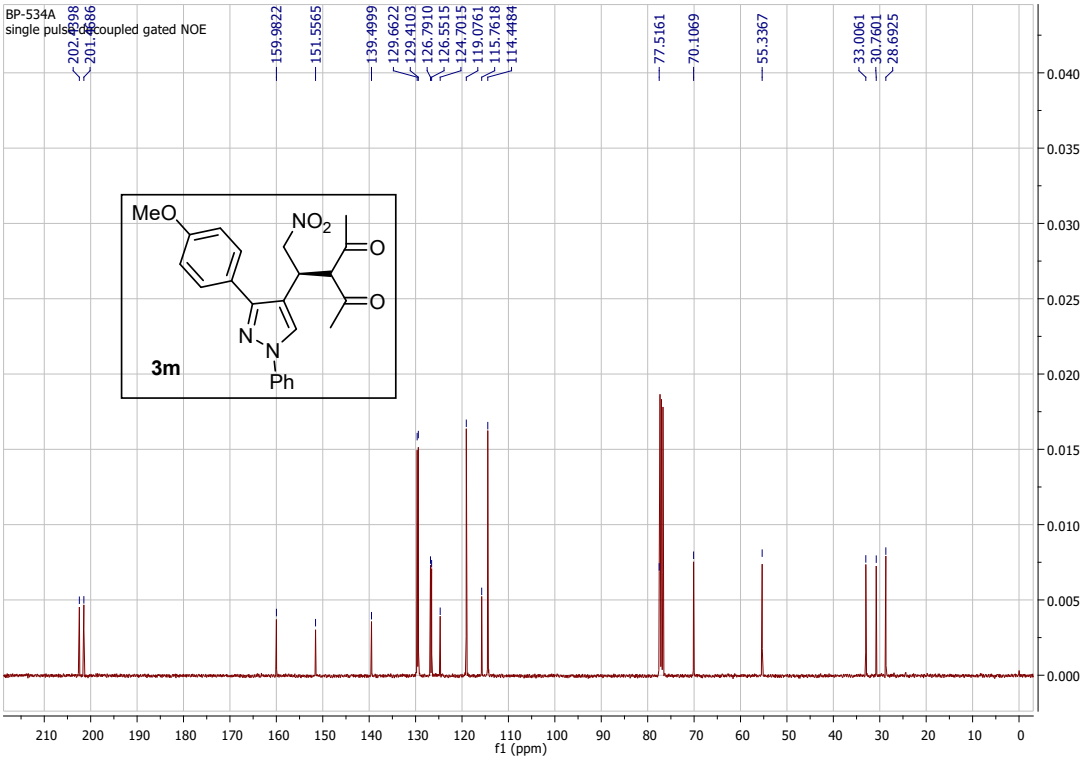

BP-
single pulse
7.8108
7.6918
7.6888
7.6839
7.6726
7.6699
7.6676
7.5183
7.5142
7.5025
7.4981
7.4645
7.4593
7.4457
7.4291
7.4245
7.3259
7.3171
7.3142
7.3112
7.3064
7.2997
7.2958
7.2798
7.2778
4.7713
4.7580
4.7407
4.7267
4.6095
4.5995
4.5789
4.5682
4.3999
4.3888
4.3863
4.3758
4.3692
4.3456
2.4312
2.2215
2.0160
NO2
O
O
N
N
Ph
3k
1.00
2.08
2.04
2.21
3.39
1.00
1.05
2.09
2.97
3.05
3.10
f1 (ppm)

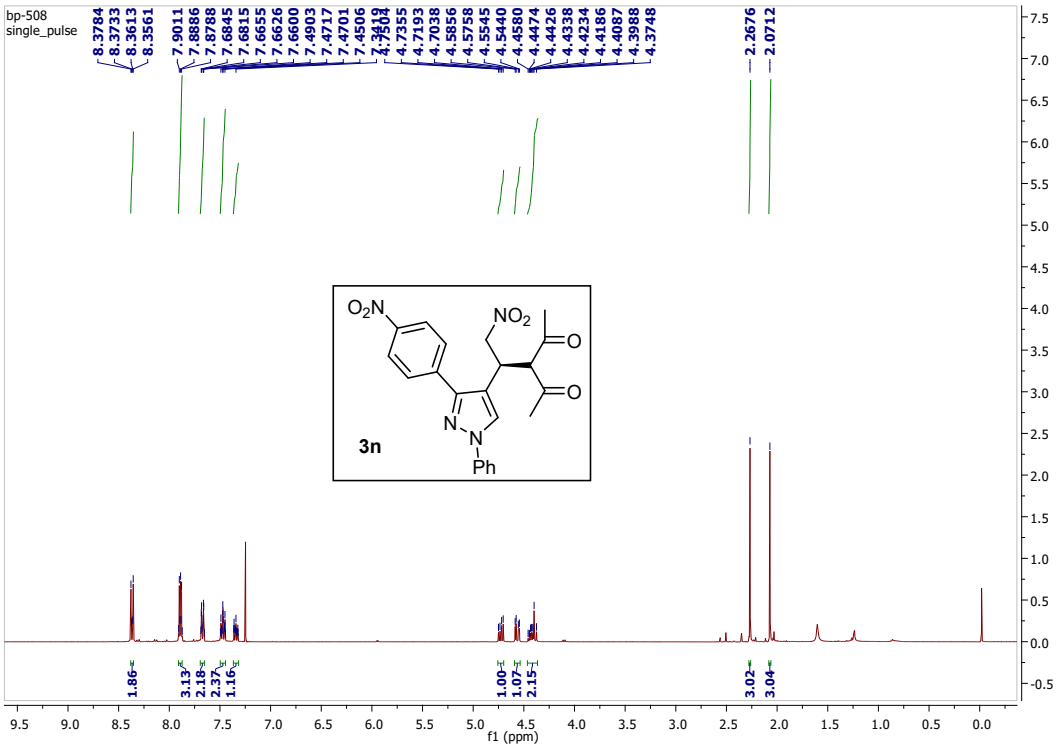

BP-517
single pulse decoupled gated NOE
202.5302
201.5554
151.7931
139.5025
138.6731
129.7332
129.4326
129.3822
128.2585
126.8488
126.6273
119.1384
115.8168
77.5105
70.1180
32.9885
30.7940
28.6006
21.3583
NO2
O
O
N
N
Ph
3k
f1 (ppm)

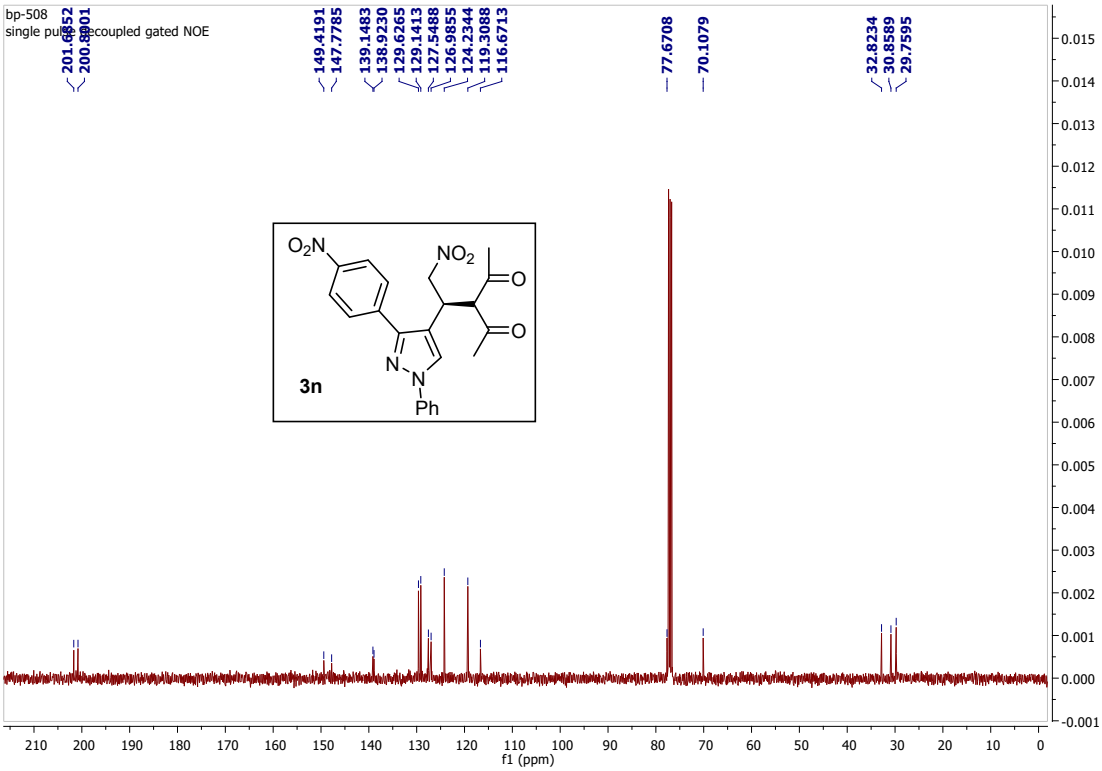

7.8527
7.6944
7.6917
7.6724
7.6706
7.6648
7.4754
7.4710
7.4495
7.4437
7.4310
7.4139
7.4094
7.2940
7.2756
7.2642
7.2571
7.1082
7.1064
7.1064
7.0898
7.0880
7.0576
7.0368
4.7300
4.7175
4.6999
4.6873
4.6232
4.6099
4.5927
4.5797
4.3733
4.3493
4.1198
4.1070
4.0950
4.0831
4.0703
3.8499
2.1853
1.9965
NO2
O
O
MeO
N
N
Ph
3l
0.89
1.99
4.30
1.22
2.06
1.00
0.97
0.99
2.88
2.96
2.93
f1 (ppm)

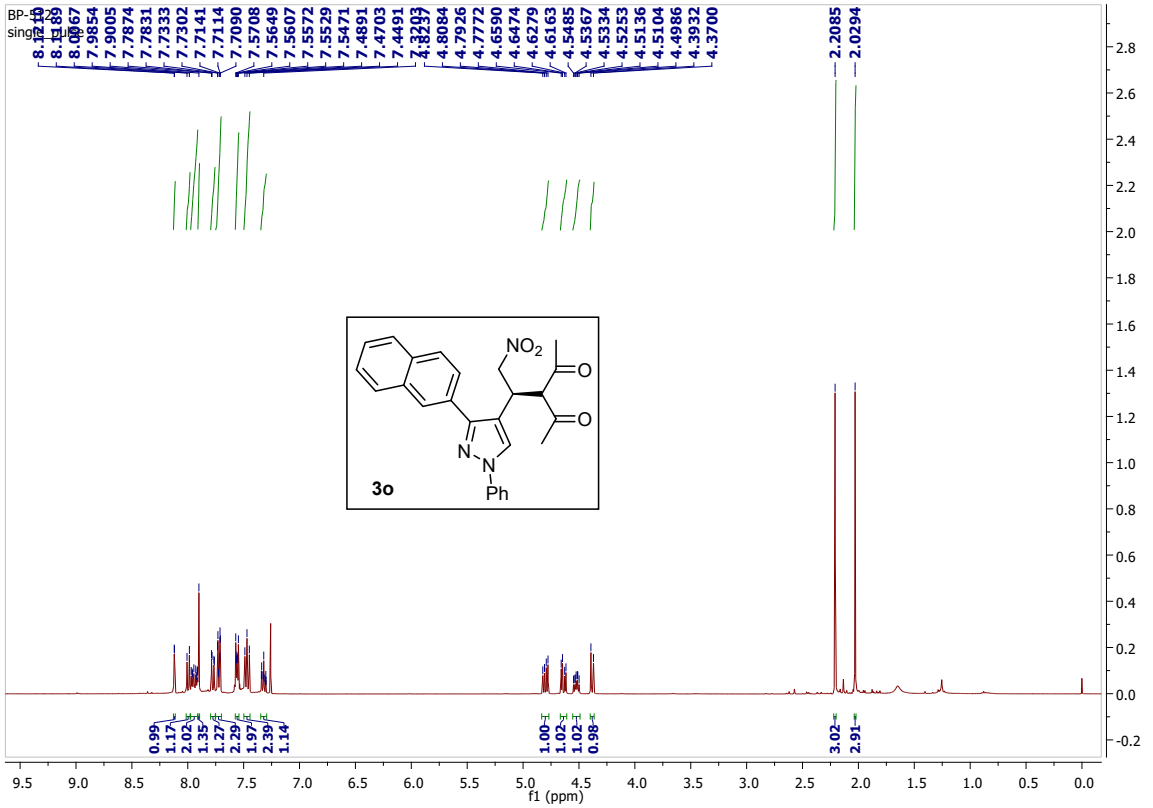

BP-494
single pulse decoupled gated NOE
202.9560
202.3309
156.9481
149.6690
139.5116
132.0482
130.6650
129.3190
126.6364
126.4374
121.3056
121.1168
119.0066
117.3686
111.1399
77.1284
69.8707
55.4441
33.4621
30.4702
27.9169
NO2
O
O
MeO
N
N
Ph
3l
f1 (ppm)

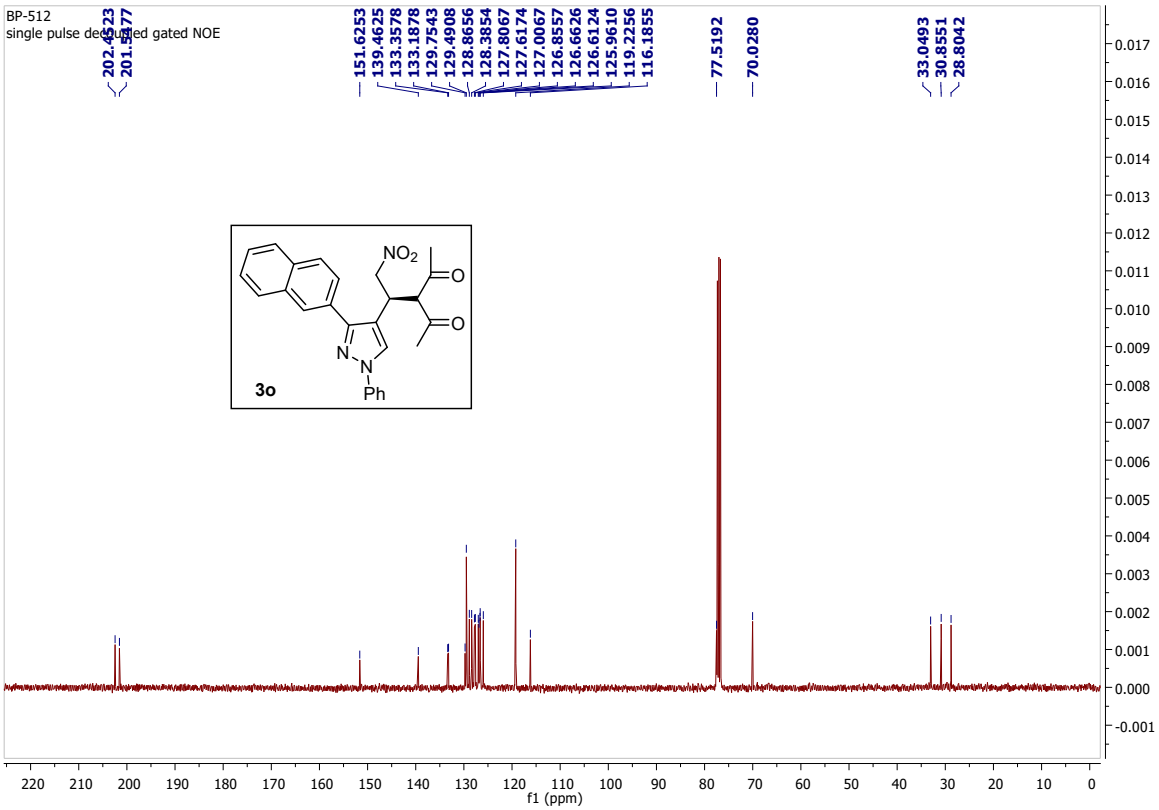

MeO
NO2
O
O
N
N
Ph
3m
f1 (ppm)

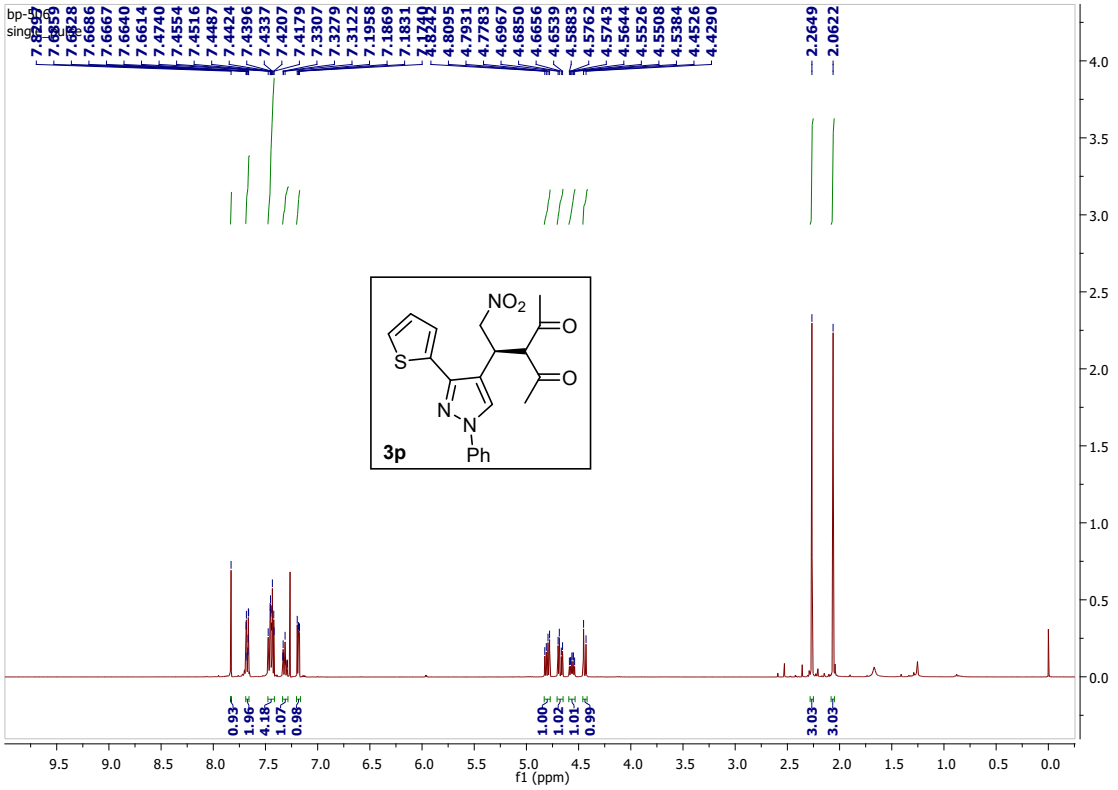

BP-534A
single pulse decoupled gated NOE
MeO
NO2
O
O
N
N
Ph
3m
f1 (ppm)

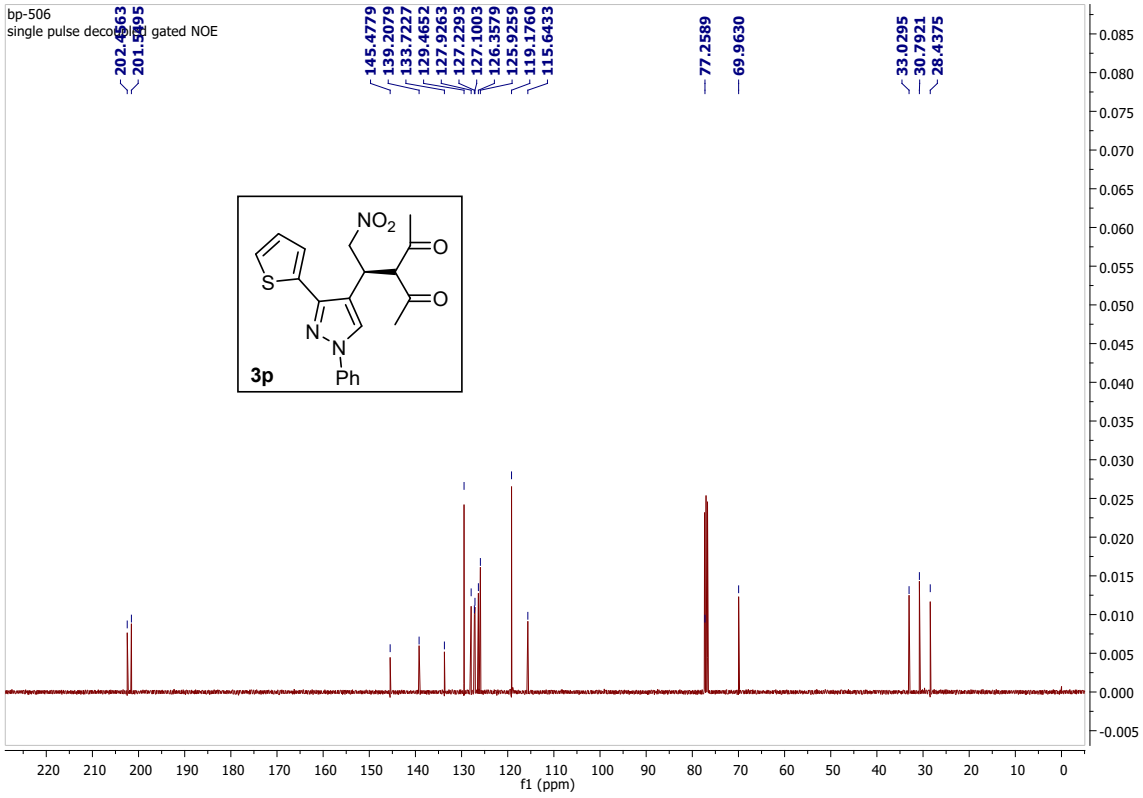

bp-508
single_pulse
8.3784
8.3733
8.3613
8.3561
7.9011
7.8886
7.8788
7.6845
7.6815
7.6655
7.6626
7.6600
7.4903
7.4717
7.4701
7.4506
7.3419
7.3304
4.7355
4.7193
4.7038
4.5856
4.5758
4.5545
4.5440
4.4580
4.4474
4.4426
4.4338
4.4234
4.4186
4.4087
4.3988
4.3748
2.2676
2.0712
1.86
3.13
2.18
2.37
1.16
1.00
1.07
2.15
3.02
3.04
3n
f1 (ppm)

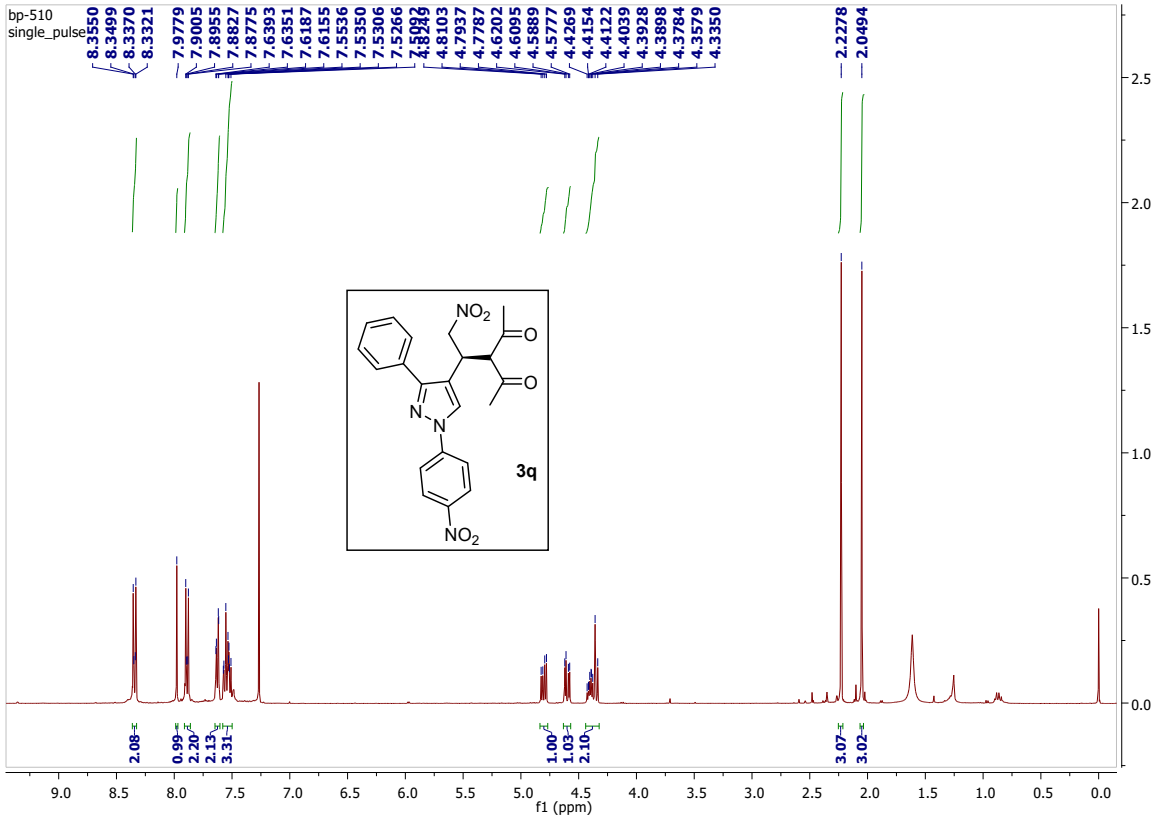

bp-508
single pulse decoupled gated NOE
201.6852
200.8901
149.4191
147.7785
139.1483
138.9230
129.6265
129.1413
127.5488
126.9855
124.2344
119.3088
116.6713
77.6708
70.1079
32.8234
30.8589
29.7595
3n
f1 (ppm)

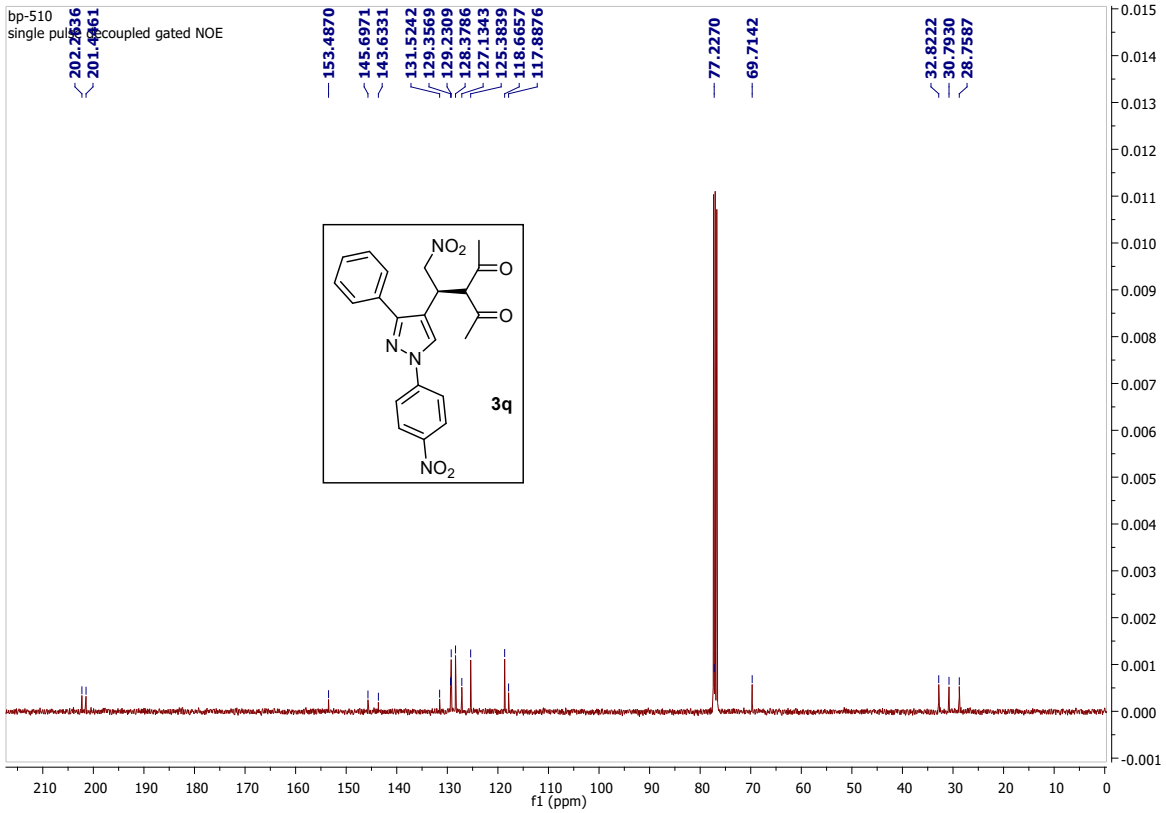

BP-512
single pulse
8.1289
8.0067
7.9854
7.9005
7.7874
7.7831
7.7333
7.7302
7.7141
7.7114
7.7090
7.5708
7.5649
7.5607
7.5572
7.5529
7.5471
7.4891
7.4703
7.4491
4.8084
4.7926
4.7772
4.6590
4.6474
4.6279
4.6163
4.5485
4.5367
4.5334
4.5253
4.5136
4.5104
4.4986
4.3932
4.3700
2.2085
2.0294
0.99
1.17
2.02
1.35
1.27
2.29
1.97
2.39
1.14
1.00
1.02
1.02
0.98
3.02
2.91
NO2
O
O
N
N
Ph
3o
f1 (ppm)


BP-512
single pulse decoupled gated NOE
202.4523
201.5377
151.6253
139.4625
133.3578
133.1878
129.7543
129.4908
128.8656
128.3854
127.8067
127.6174
127.0067
126.8557
126.6626
126.6124
125.9610
119.2256
116.1855
77.5192
70.0280
33.0493
30.8551
28.8042
NO2
O
O
N
N
Ph
3o
f1 (ppm)

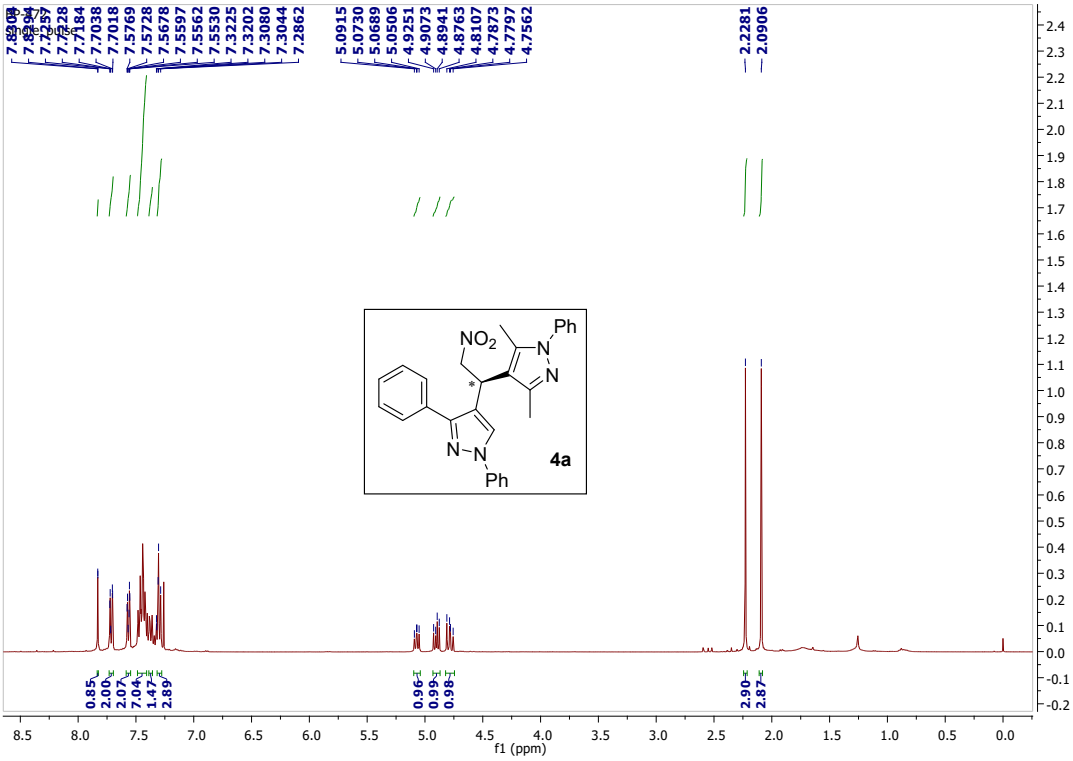

bp-506
single pulse decoupled gated NOE
7.6859
7.6828
7.6686
7.6667
7.6640
7.6614
7.4740
7.4554
7.4516
7.4487
7.4424
7.4396
7.4337
7.4207
7.4179
7.3307
7.3279
7.3122
7.1958
7.1869
7.1831
4.8095
4.7931
4.7783
4.6967
4.6850
4.6656
4.6539
4.5883
4.5762
4.5743
4.5644
4.5526
4.5508
4.5384
4.4526
4.4290
2.2649
2.0622
NO2
O
O
S
N
N
Ph
3p
0.93
1.96
4.18
1.07
0.98
1.00
1.02
1.01
0.99
3.03
3.03
f1 (ppm)

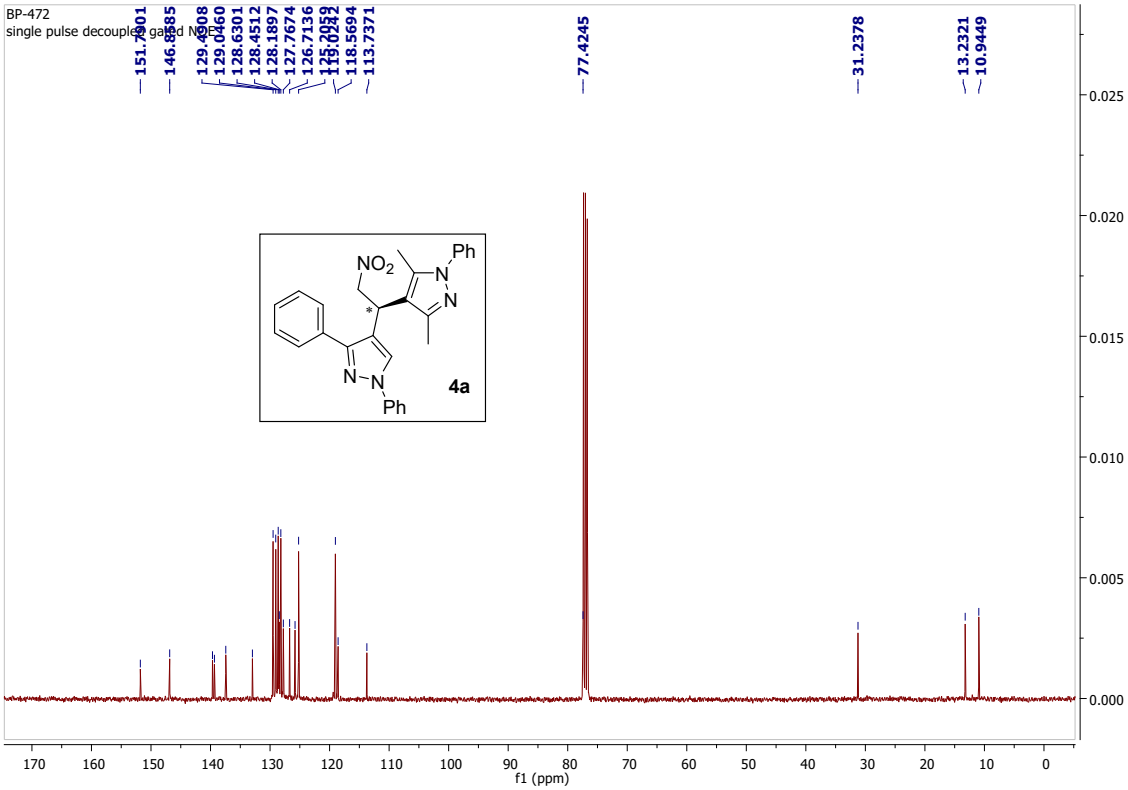

bp-506
single pulse decoupled gated NOE
202.4963
201.5895
145.4779
139.2079
133.7227
129.4652
127.9263
127.2293
127.1003
126.3579
125.9259
119.1760
115.6433
77.2589
69.9630
33.0295
30.7921
28.4375
NO2
O
O
S
N
N
Ph
3p
f1 (ppm)

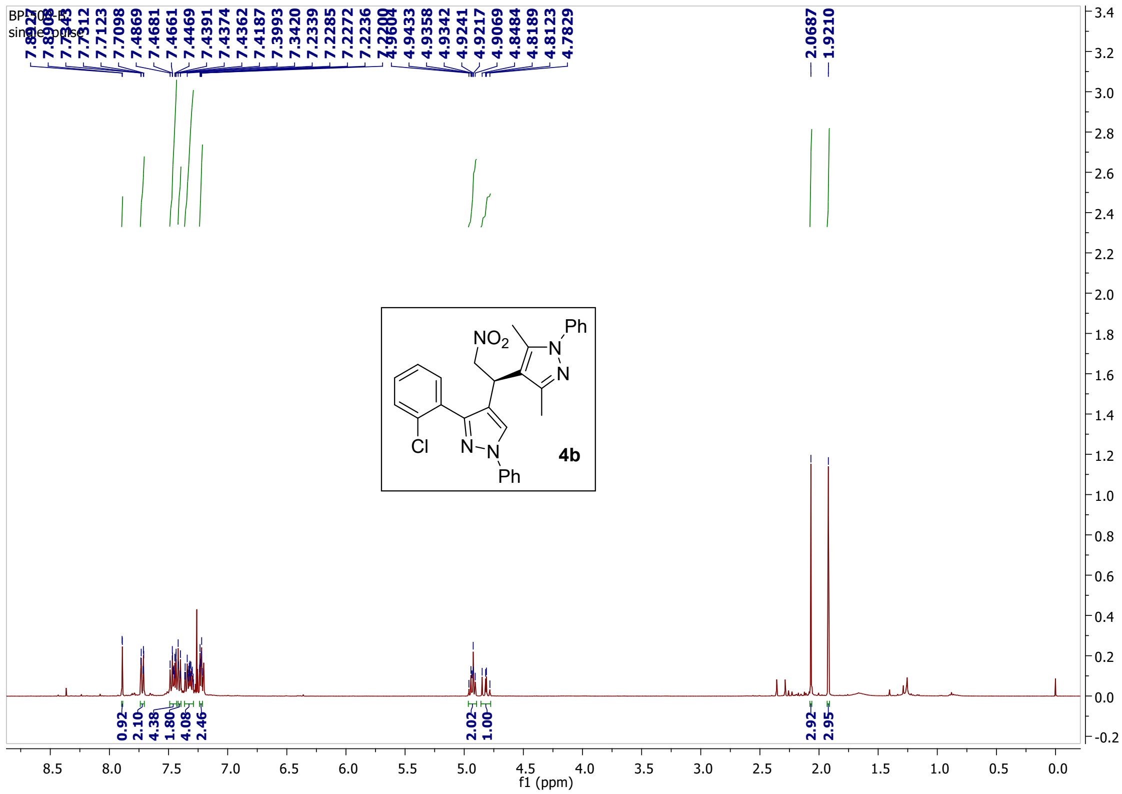

bp-510
single_pulse
8.3550
8.3499
8.3370
8.3321
7.9779
7.9005
7.8955
7.8827
7.8775
7.6393
7.6351
7.6187
7.6155
7.5536
7.5350
7.5306
7.5266
4.8103
4.7937
4.7787
4.6202
4.6095
4.5889
4.5777
4.4269
4.4154
4.4122
4.4039
4.3928
4.3898
4.3784
4.3579
4.3350
2.2278
2.0494
NO2
O
O
N
N
3q
NO2
2.08
0.99
2.20
2.13
3.31
1.00
1.03
2.10
3.07
3.02
f1 (ppm)


bp-510
single pulse decoupled gated NOE
202.2636
201.4461
153.4870
145.6971
143.6331
131.5242
129.3569
129.2309
128.3786
127.1343
125.3839
118.6657
117.8876
77.2270
69.7142
32.8222
30.7930
28.7587
NO2
O
O
N
N
3q
NO2
f1 (ppm)

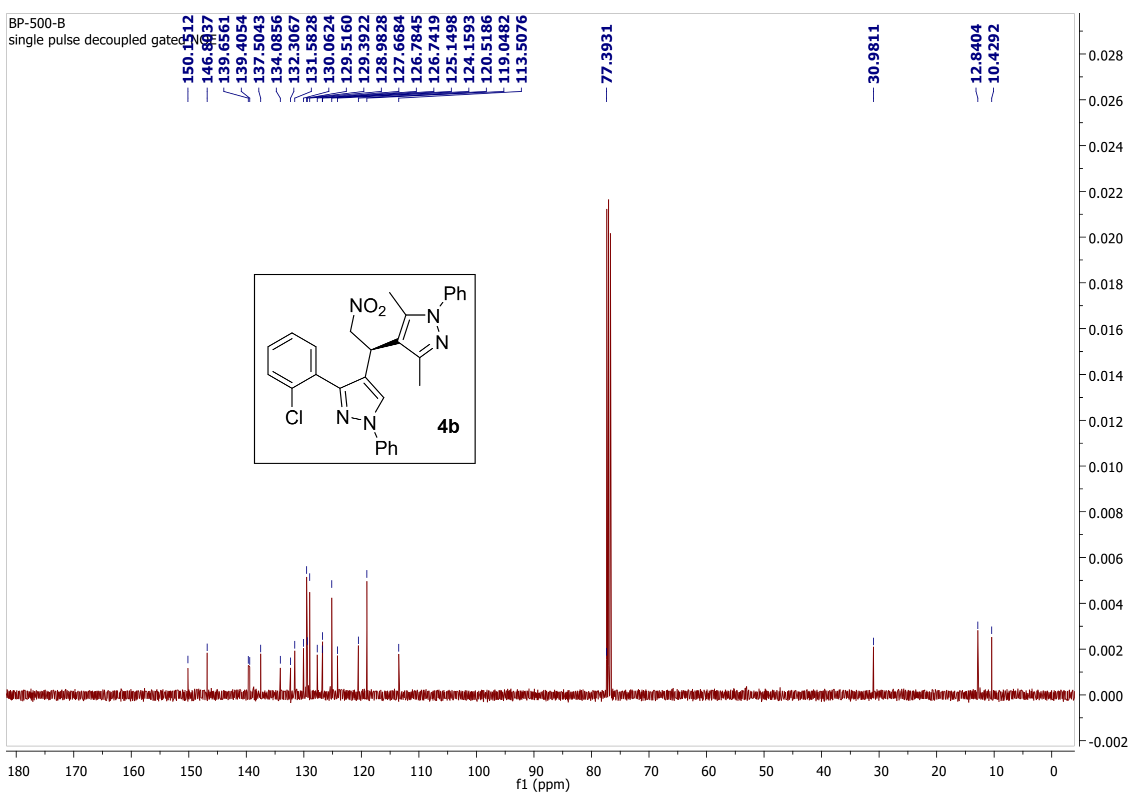
^{1}H and ^{13}C NMR spectra of series 4



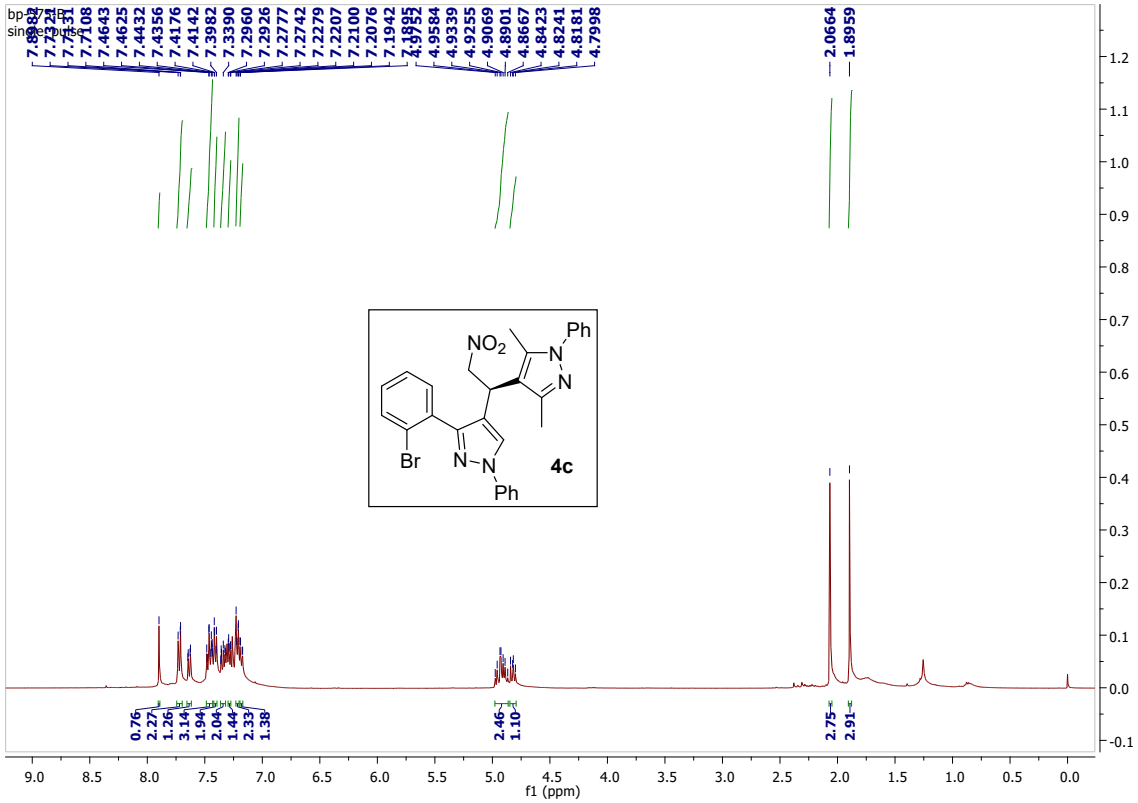


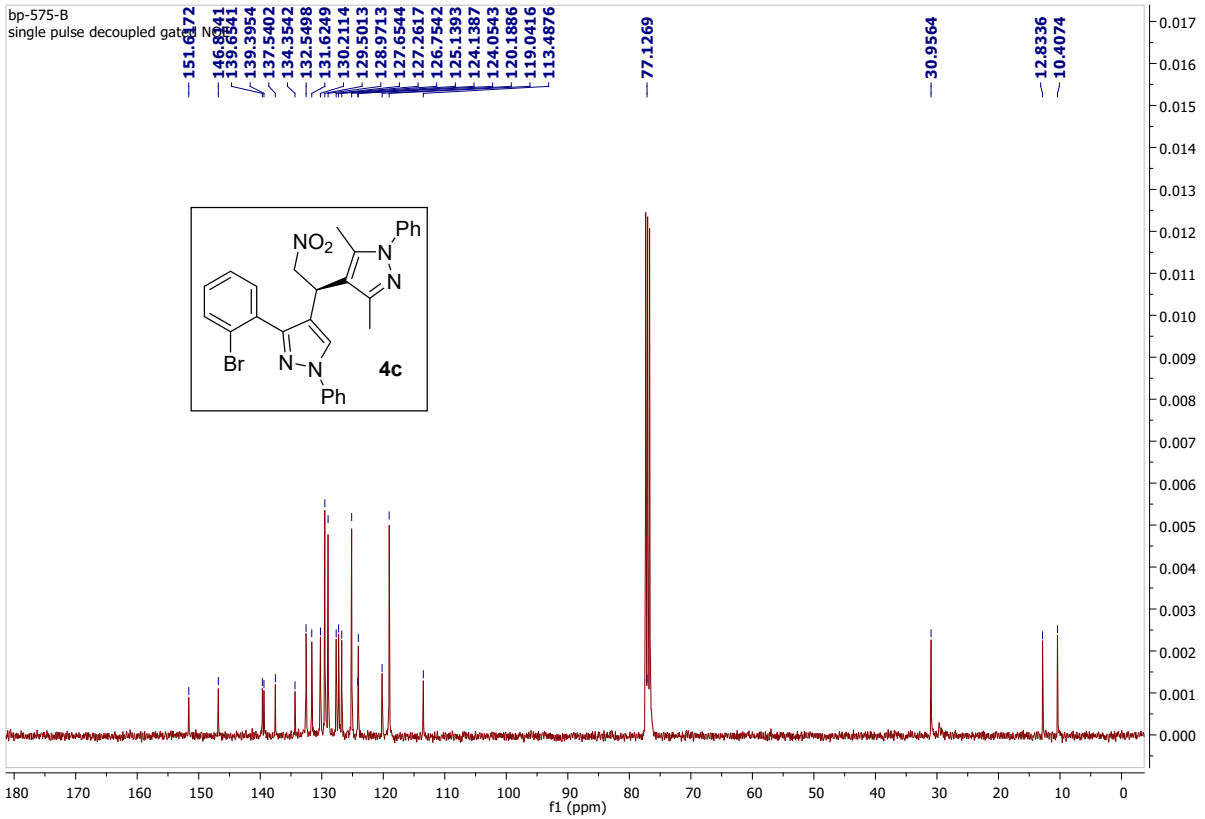


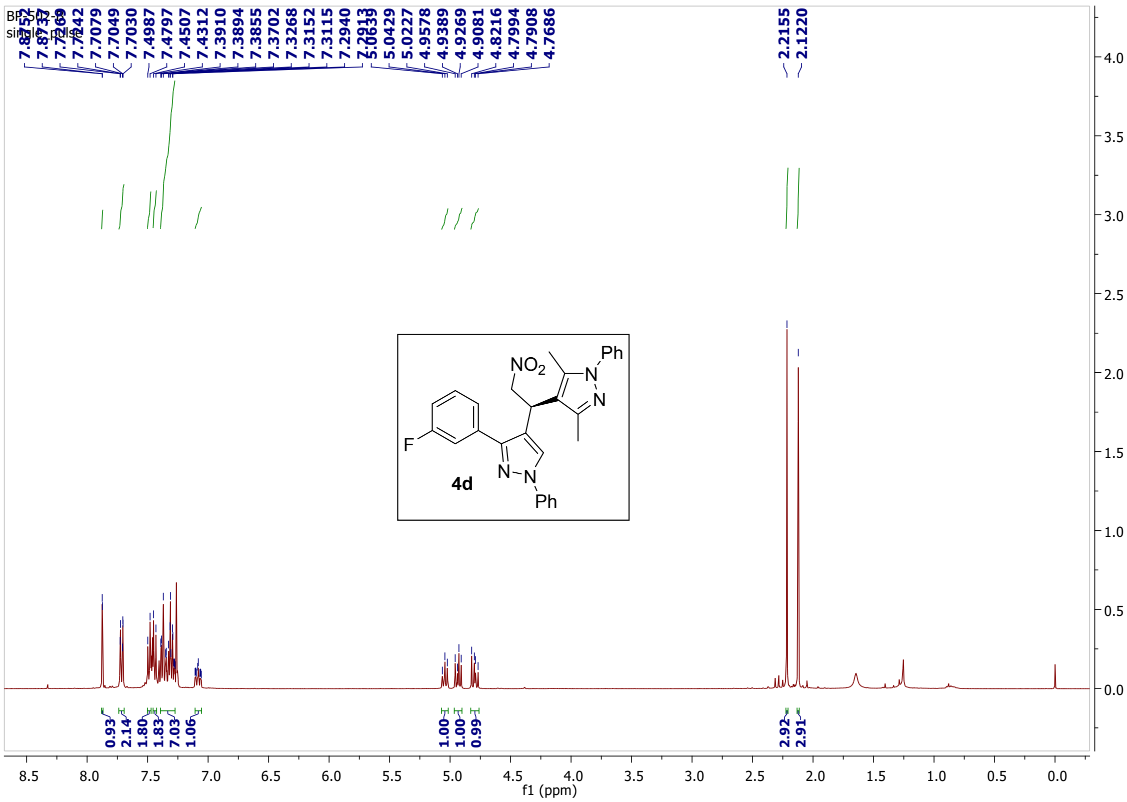
single pulse
7.7312
7.7123
7.7098
7.4869
7.4681
7.4661
7.4469
7.4391
7.4374
7.4362
7.4187
7.3993
7.3420
7.2339
7.2285
7.2272
7.2236
4.9433
4.9358
4.9342
4.9241
4.9217
4.9069
4.8484
4.8189
4.8123
4.7829
2.0687
1.9210
NO2
Ph
N
N
Cl
N
N
Ph
4b
0.92
2.10
4.38
1.80
4.08
2.46
2.02
1.00
2.92
2.95
f1 (ppm)

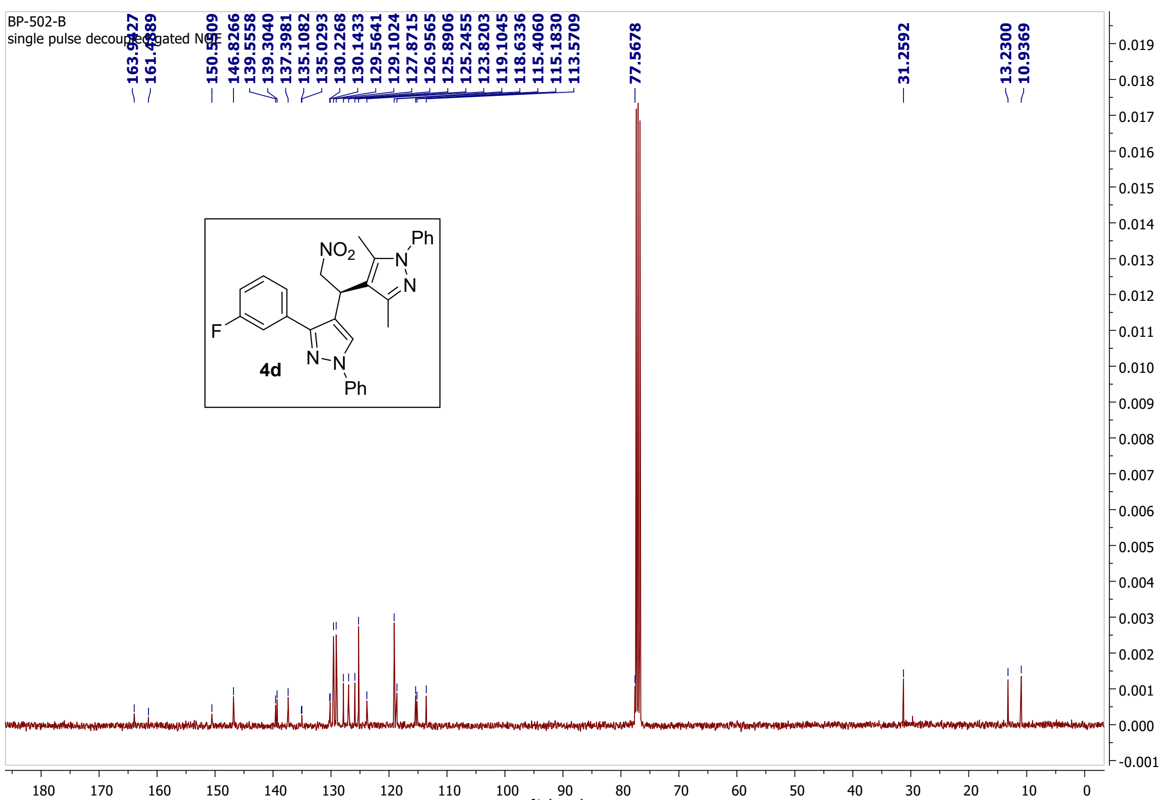


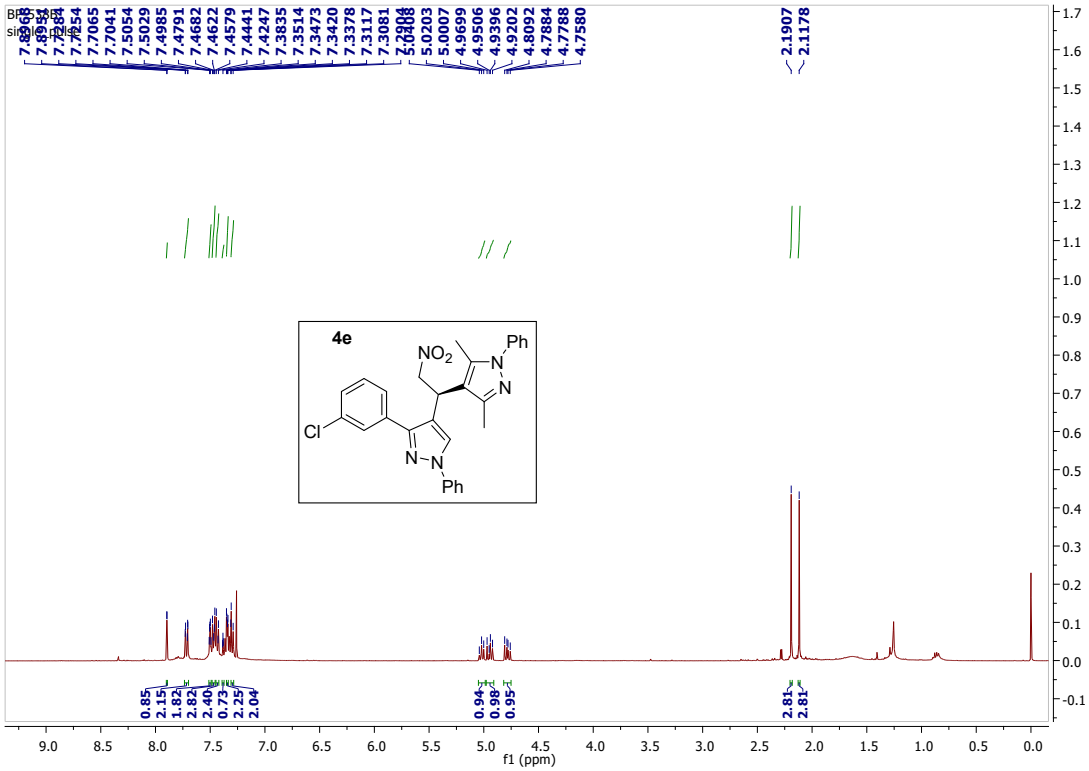
BP-500-B
single pulse decoupled gated NOE
150.1512
146.8937
139.6561
139.4054
137.5043
134.0856
132.3067
131.5828
130.0624
129.5160
129.3922
128.9828
127.6684
126.7845
126.7419
125.1498
124.1593
120.5186
119.0482
113.5076
77.3931
30.9811
12.8404
10.4292
NO2
Ph
N
N
Cl
N
N
Ph
4b
f1 (ppm)

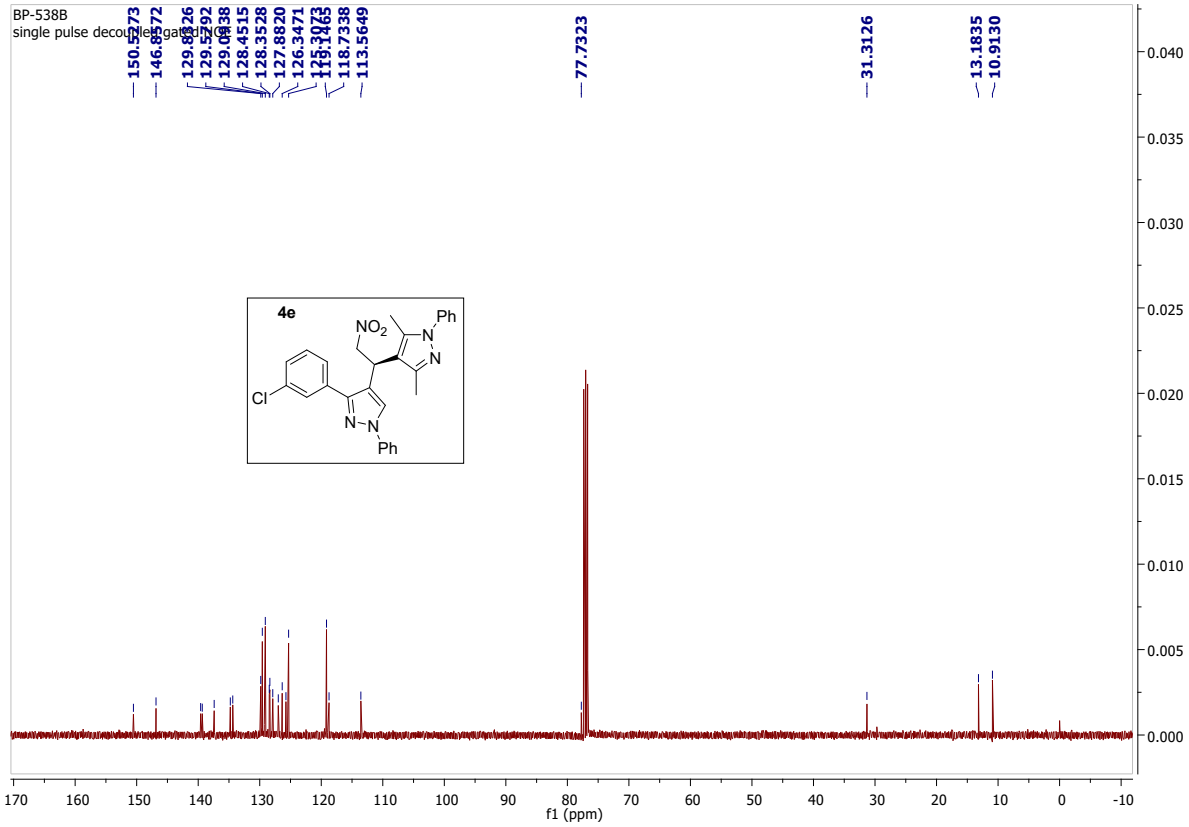

NO2
Ph
N
N
Br
N
N
Ph
4c
f1 (ppm)

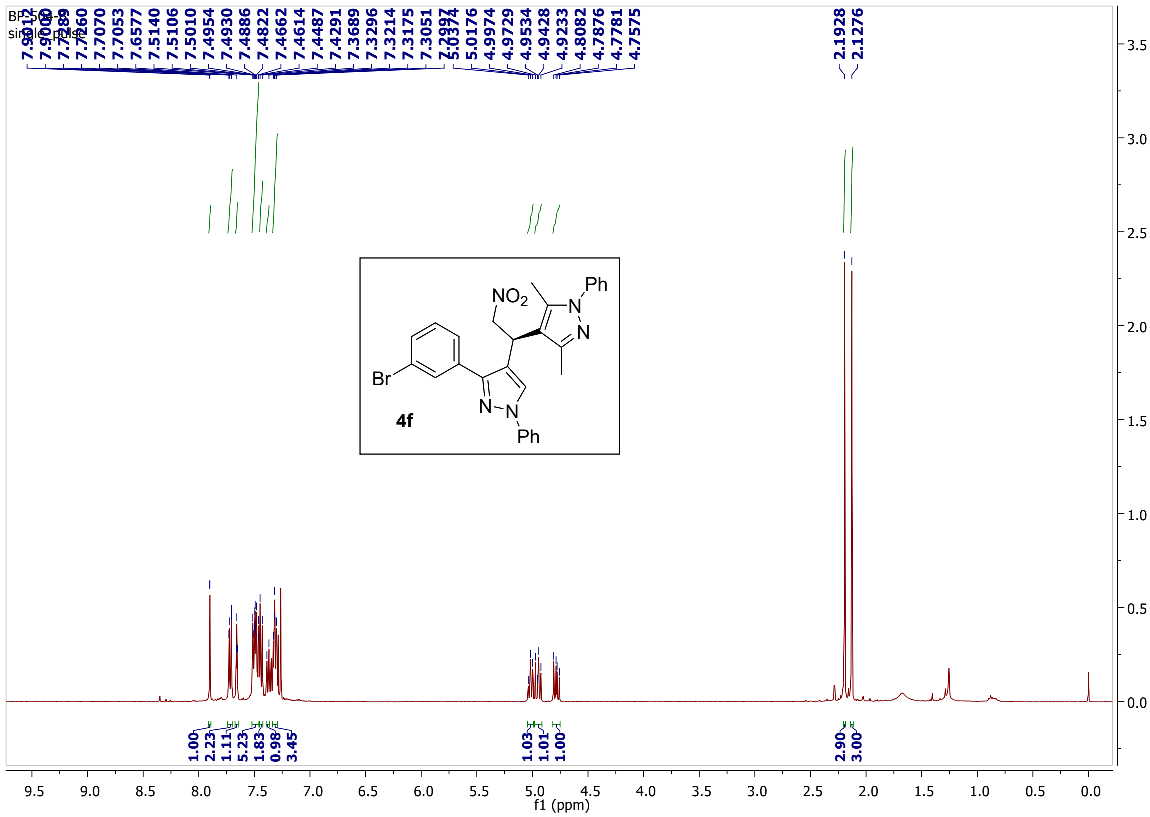

NO2
Ph
N
N
Br
N
N
Ph
4c
f1 (ppm)

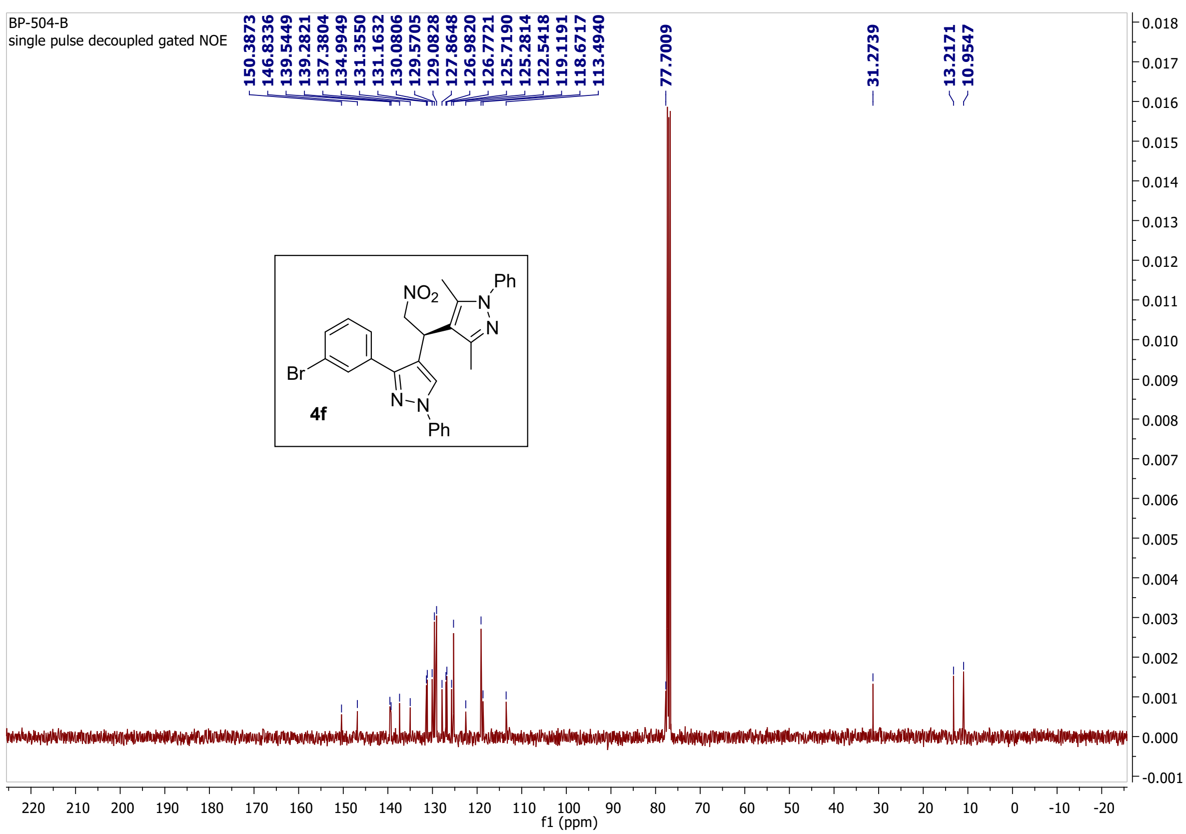

BP-502-B
single pulse
2.2155
2.1220
4d
f1 (ppm)

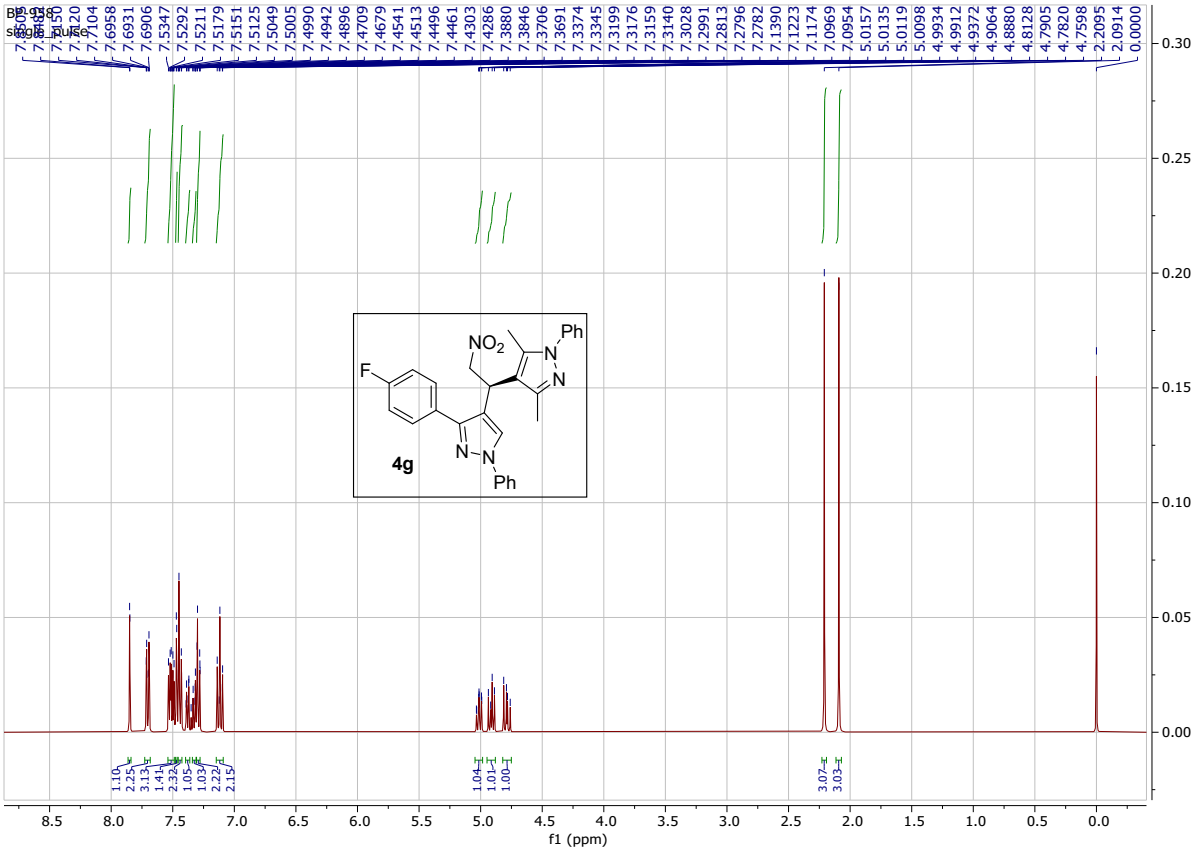

BP-502-B
single pulse decoupled gated NOE
163.9227
150.5509
146.8266
139.5558
139.3040
137.3981
135.1082
135.0293
130.2268
130.1433
129.5641
129.1024
127.8715
126.9565
125.8906
125.2455
123.8203
119.1045
118.6336
115.4060
115.1830
113.5709
77.5678
31.2592
13.2300
10.9369
4d
f1 (ppm)

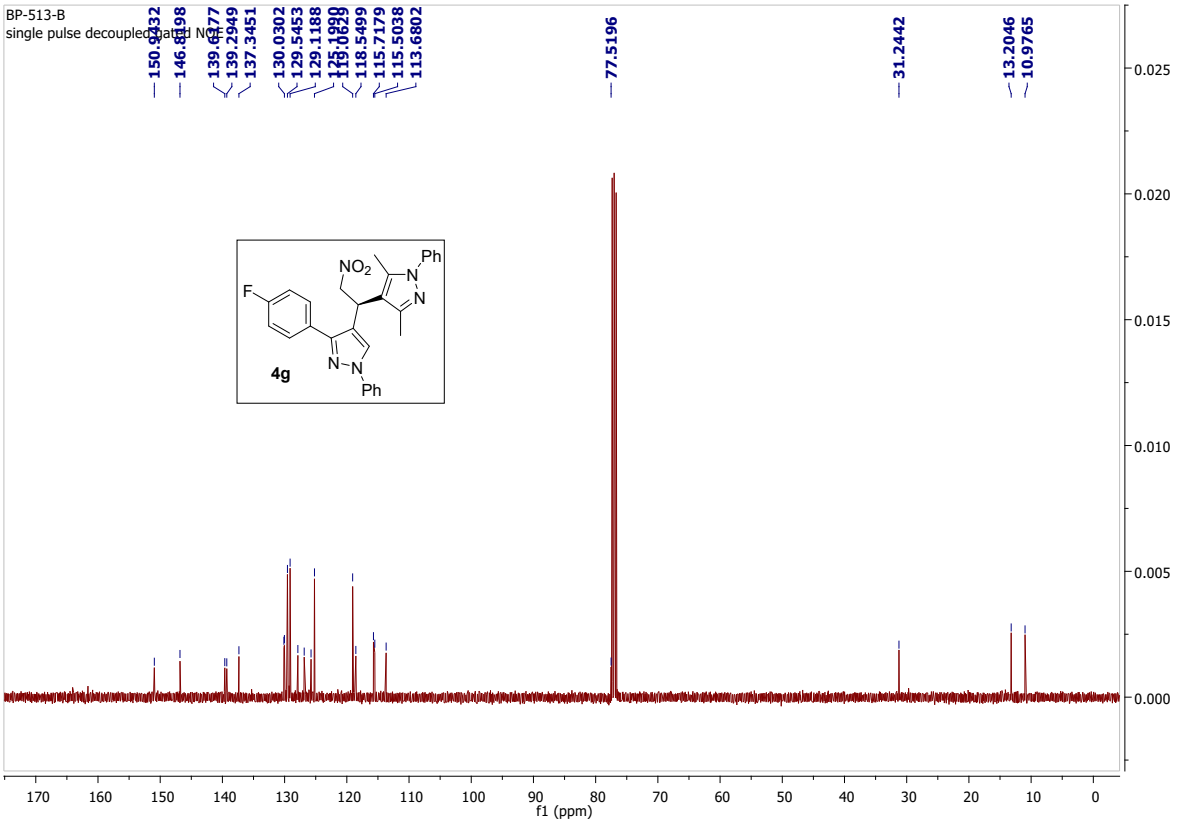

4e
NO2
Ph
N
N
Cl
N
N
Ph
f1 (ppm)

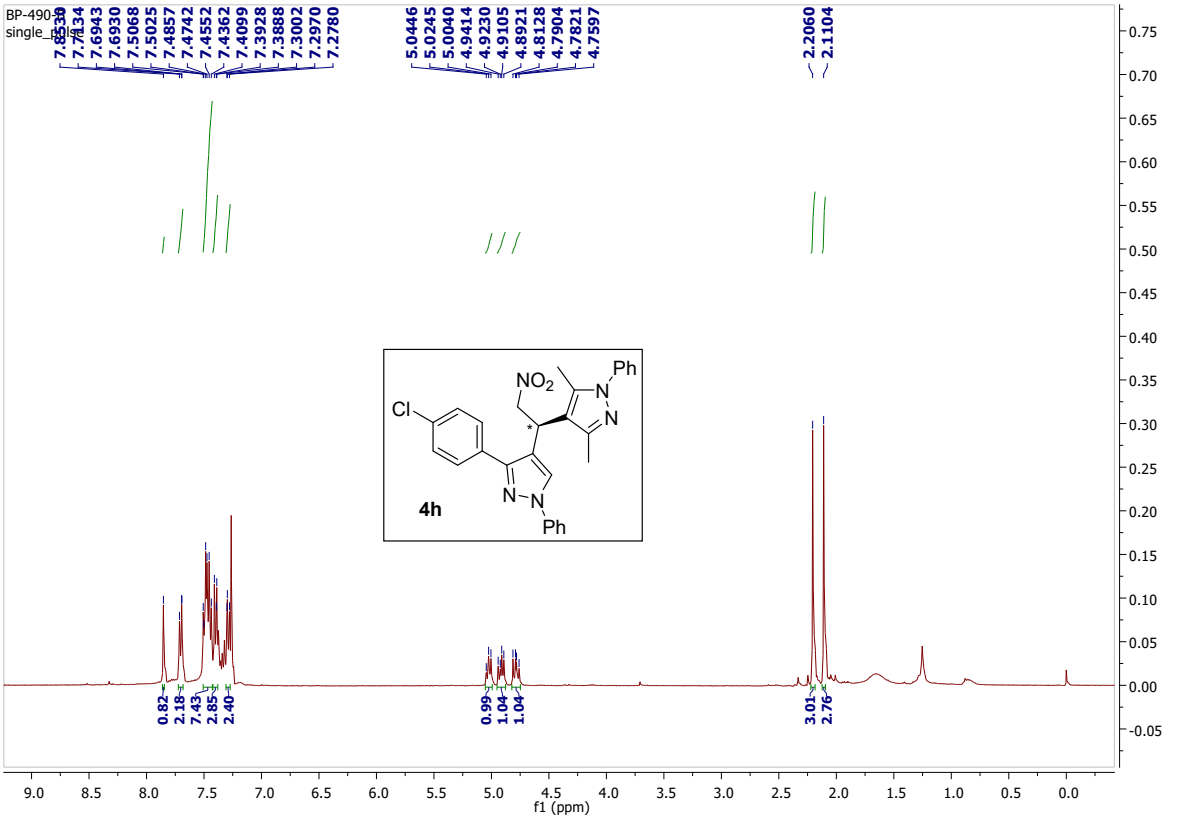

BP-538B
single pulse decoupled gated
4e
NO2
Ph
N
N
Cl
N
N
Ph
f1 (ppm)

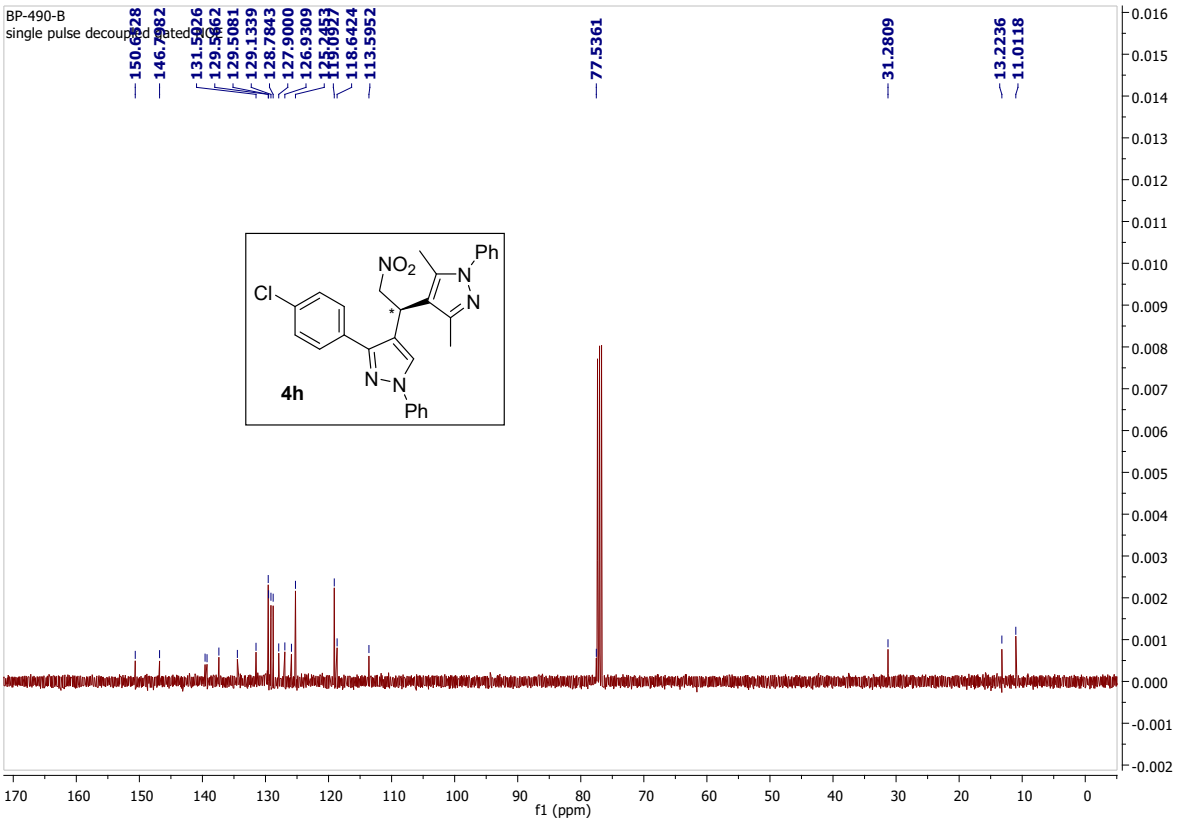

BP-504-B
single pulse
4f
NO2
Ph
Br
Ph
f1 (ppm)

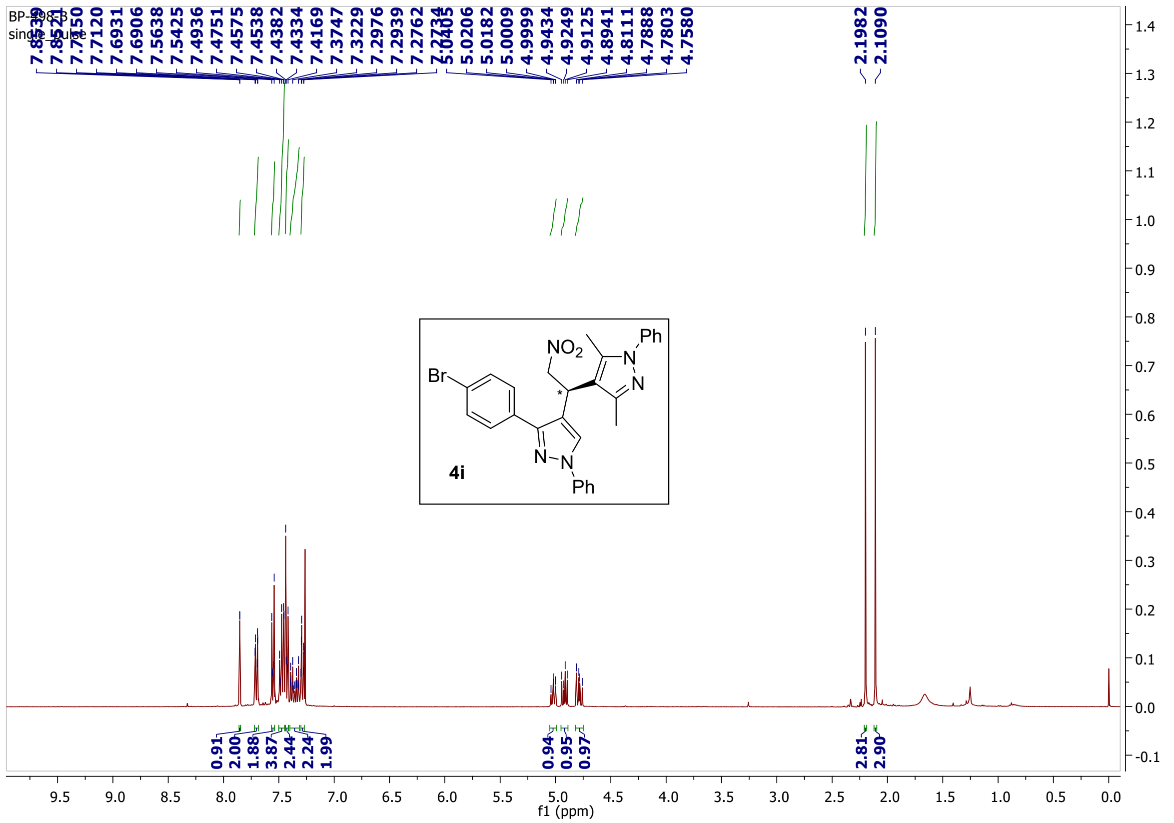

BP-504-B
single pulse decoupled gated NOE
150.3873
146.8336
139.5449
139.2821
137.3804
134.9949
131.3550
131.1632
130.0806
129.5705
129.0828
127.8648
126.9820
126.7721
125.7190
125.2814
122.5418
119.1191
118.6717
113.4940
77.7009
31.2739
13.2171
10.9547
4f
f1 (ppm)

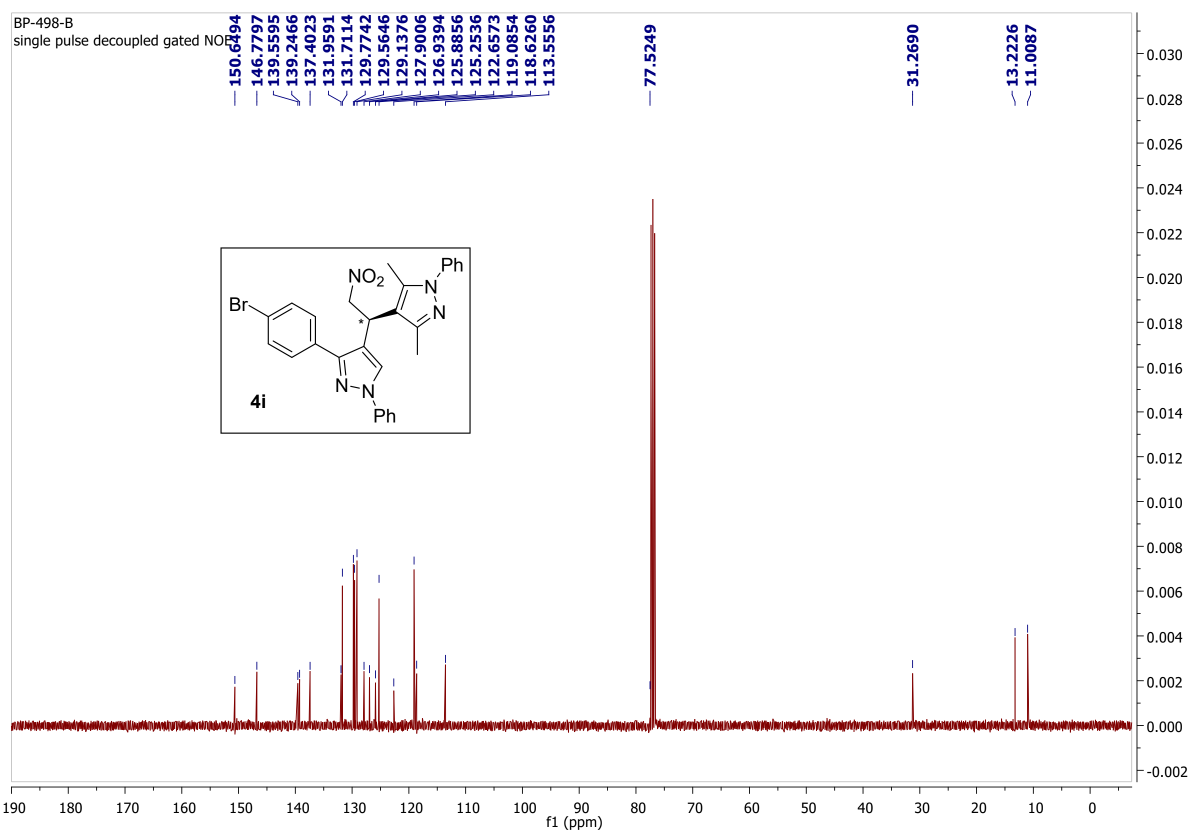

BP-513-B
single pulse
4g
f1 (ppm)

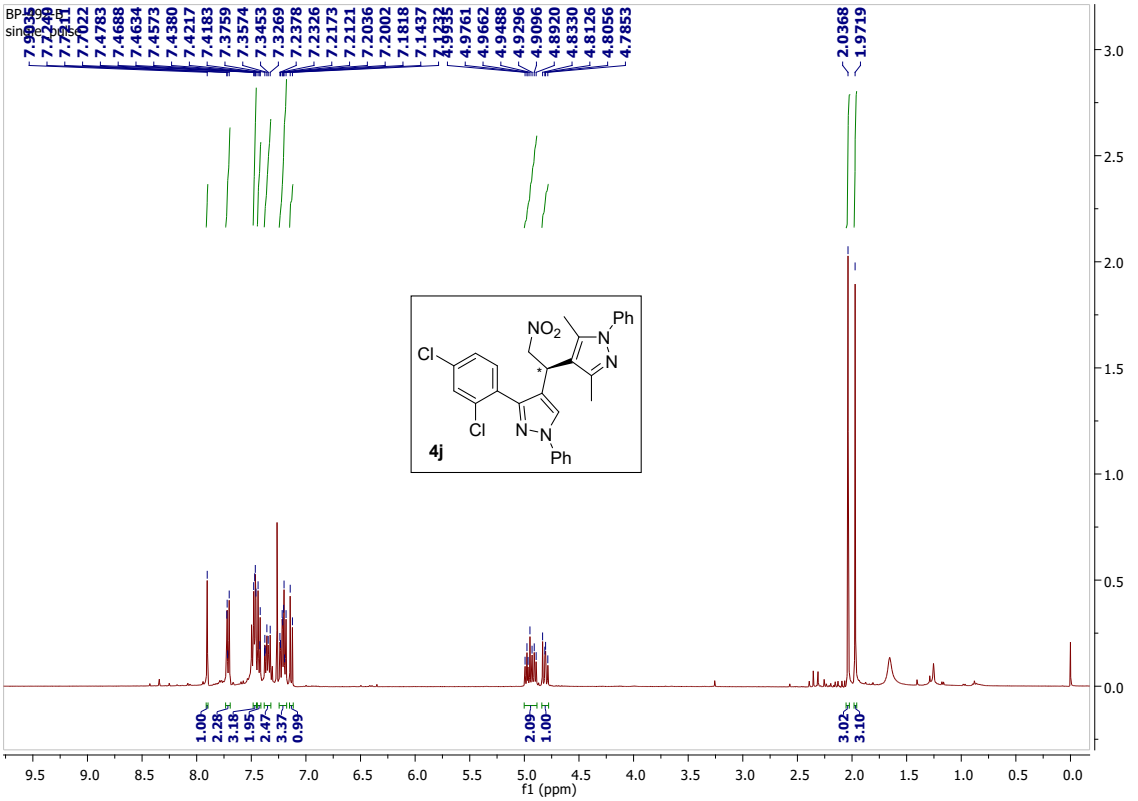

BP-513-B
single pulse decoupled gated NOE
150.9332
146.8498
139.6477
139.2949
137.3451
130.0302
129.5453
129.1188
118.5499
115.7179
115.5038
113.6802
77.5196
31.2442
13.2046
10.9765
4g
f1 (ppm)

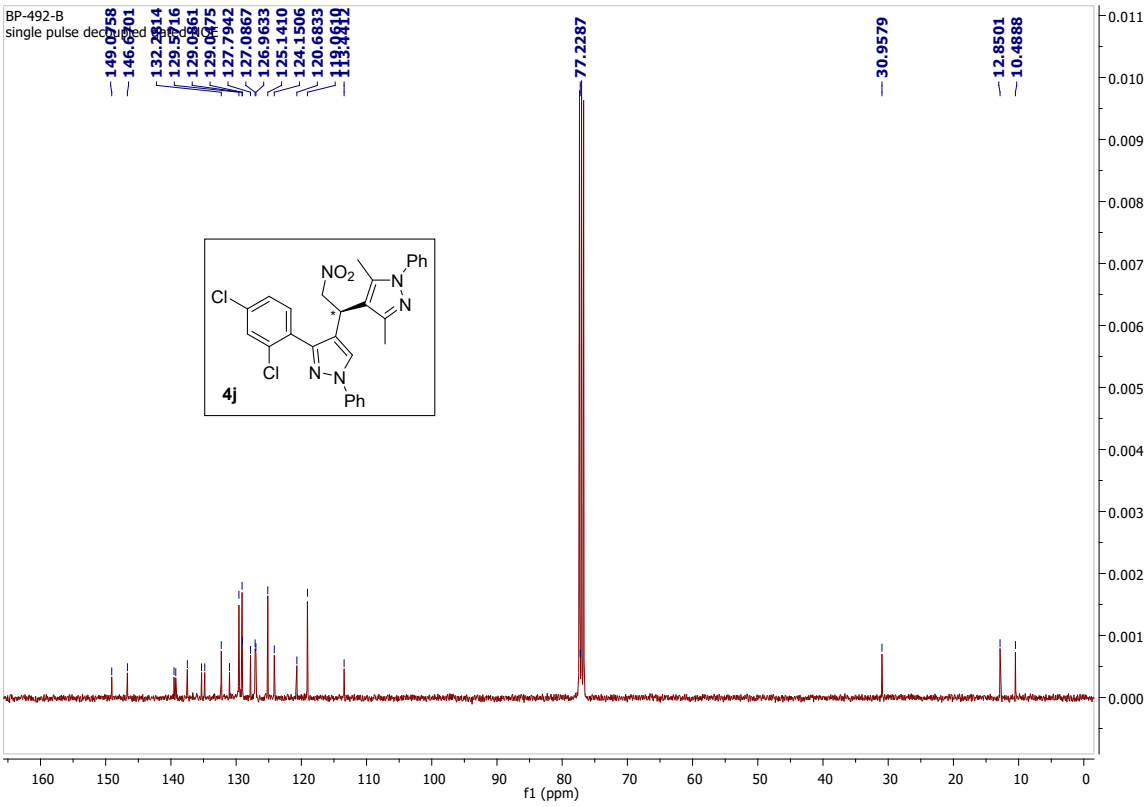

BP-490-B
single_pulse
7.8339
7.7734
7.6943
7.6930
7.5068
7.5025
7.4857
7.4742
7.4552
7.4362
7.4099
7.3928
7.3888
7.3002
7.2970
7.2780
5.0446
5.0245
5.0040
4.9414
4.9230
4.9105
4.8921
4.8128
4.7904
4.7821
4.7597
2.2060
2.1104
NO2
Ph
N
N
Cl
N
N
Ph
4h
0.82
2.18
7.43
2.85
2.40
0.99
1.04
1.04
3.01
2.76
f1 (ppm)

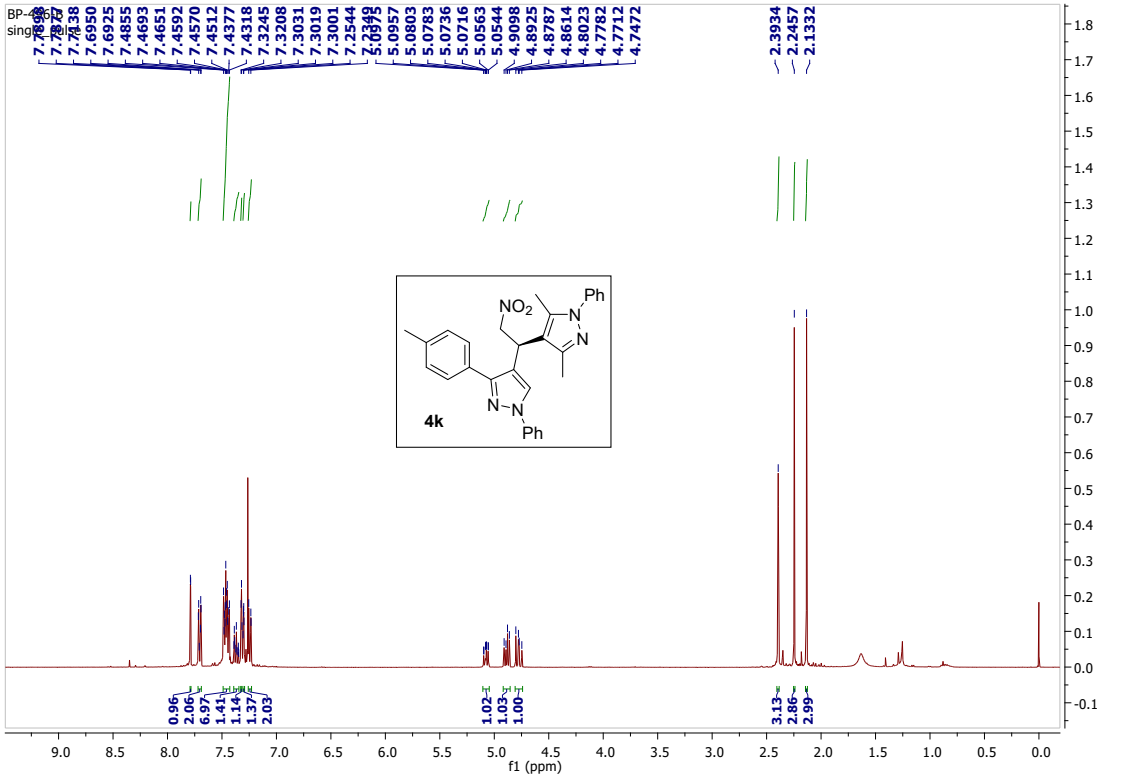

BP-490-B
single pulse decoupled gated
150.6628
146.7982
131.5926
129.5462
129.5081
129.1339
128.7843
127.9000
126.9309
118.6424
113.5952
77.5361
31.2809
13.2236
11.0118
NO2
Ph
N
N
Cl
N
N
Ph
4h
f1 (ppm)

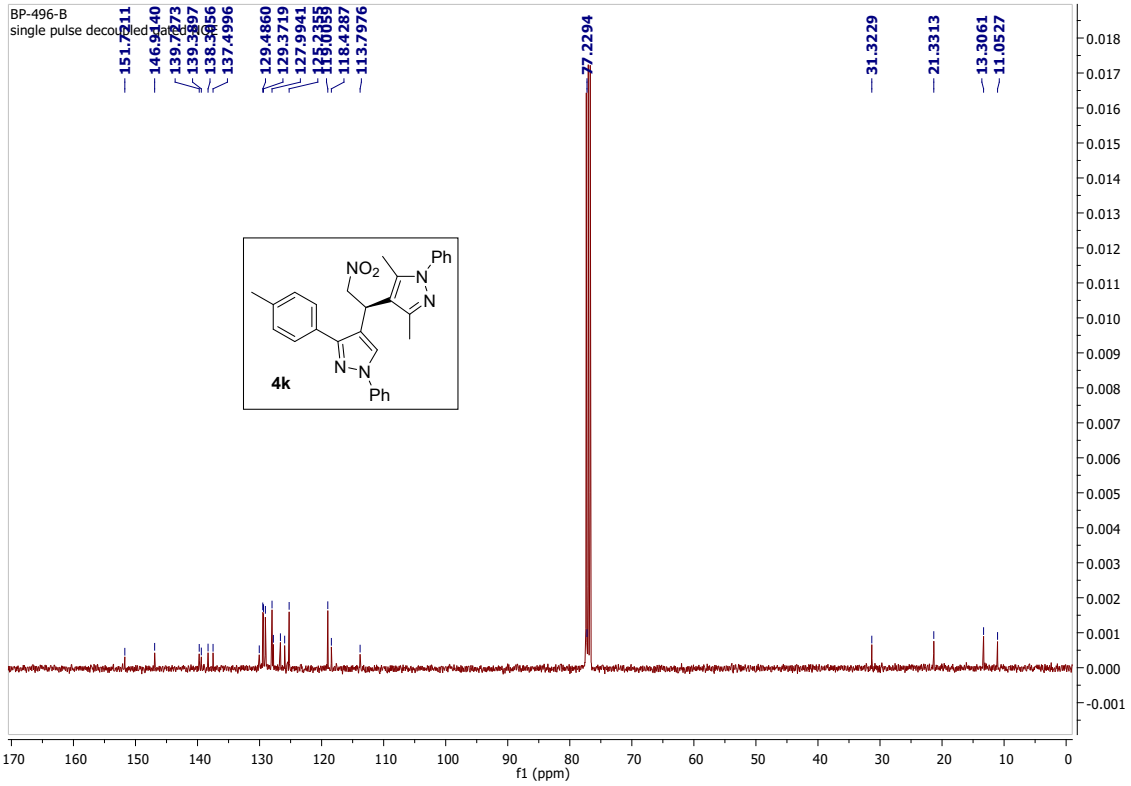

BP-498-B
single pulse
7.8539
7.8521
7.7150
7.7120
7.6931
7.6906
7.5638
7.5425
7.4936
7.4751
7.4575
7.4538
7.4382
7.4334
7.4169
7.3747
7.3229
7.2976
7.2939
7.2762
7.2734
5.0405
5.0206
5.0182
4.9999
4.9434
4.9249
4.9125
4.8941
4.8111
4.7888
4.7803
4.7580
2.1982
2.1090
NO2
Ph
Br
N
N
N
N
Ph
4i
0.91
2.00
1.88
3.87
2.44
2.24
1.99
0.94
0.95
0.97
2.81
2.90
f1 (ppm)

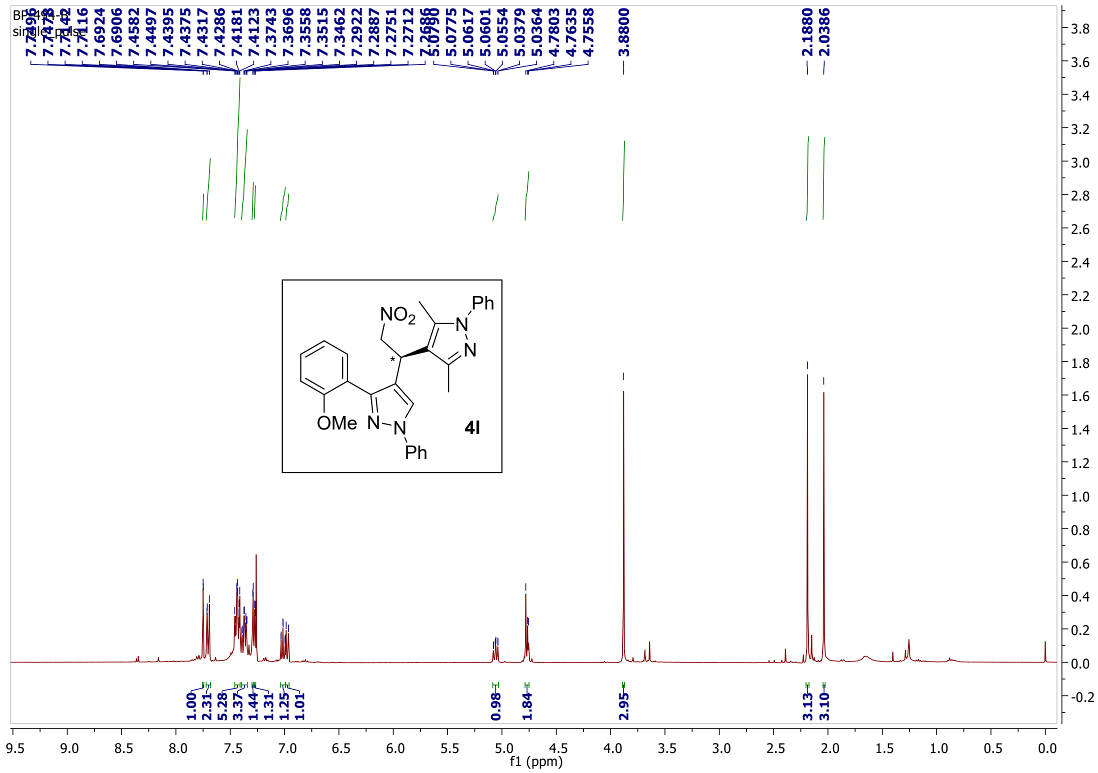

BP-498-B
single pulse decoupled gated NOE
150.6494
146.7797
139.5595
139.2466
137.4023
131.9591
131.7114
129.7742
129.5646
129.1376
127.9006
126.9394
125.8856
125.2536
122.6573
119.0854
118.6260
113.5556
77.5249
31.2690
13.2226
11.0087
NO2
Ph
Br
N
N
N
N
Ph
4i
f1 (ppm)


BP-492-B
single pulse
7.9935
7.7749
7.7711
7.7022
7.4783
7.4688
7.4634
7.4573
7.4380
7.4217
7.4183
7.3759
7.3574
7.3453
7.3269
7.2378
7.2326
7.2173
7.2121
7.2036
7.2002
7.1818
7.1437
4.9761
4.9662
4.9488
4.9296
4.9096
4.8920
4.8330
4.8126
4.8056
4.7853
2.0368
1.9719
NO2
Ph
N
N
Cl
Cl
N
N
Ph
4j
1.00
2.28
3.18
1.95
2.47
3.37
0.99
2.09
1.00
3.02
3.10
f1 (ppm)

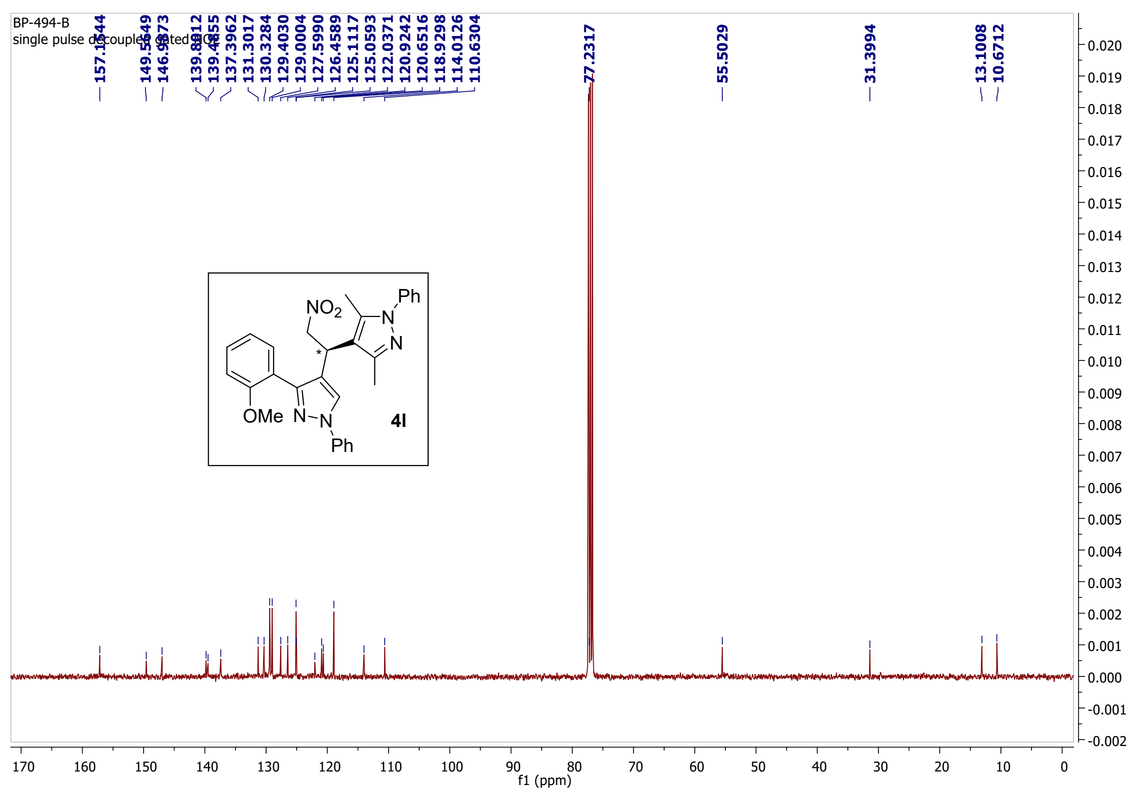

BP-492-B
single pulse decoupled gated
149.0758
146.6701
132.2814
129.5716
129.0861
129.0475
127.7942
127.0867
126.9633
125.1410
124.1506
120.6833
113.0610
113.0412
77.2287
30.9579
12.8501
10.4888
NO2
Ph
N
N
Cl
Cl
N
N
Ph
4j
f1 (ppm)


f1 (ppm)
4k

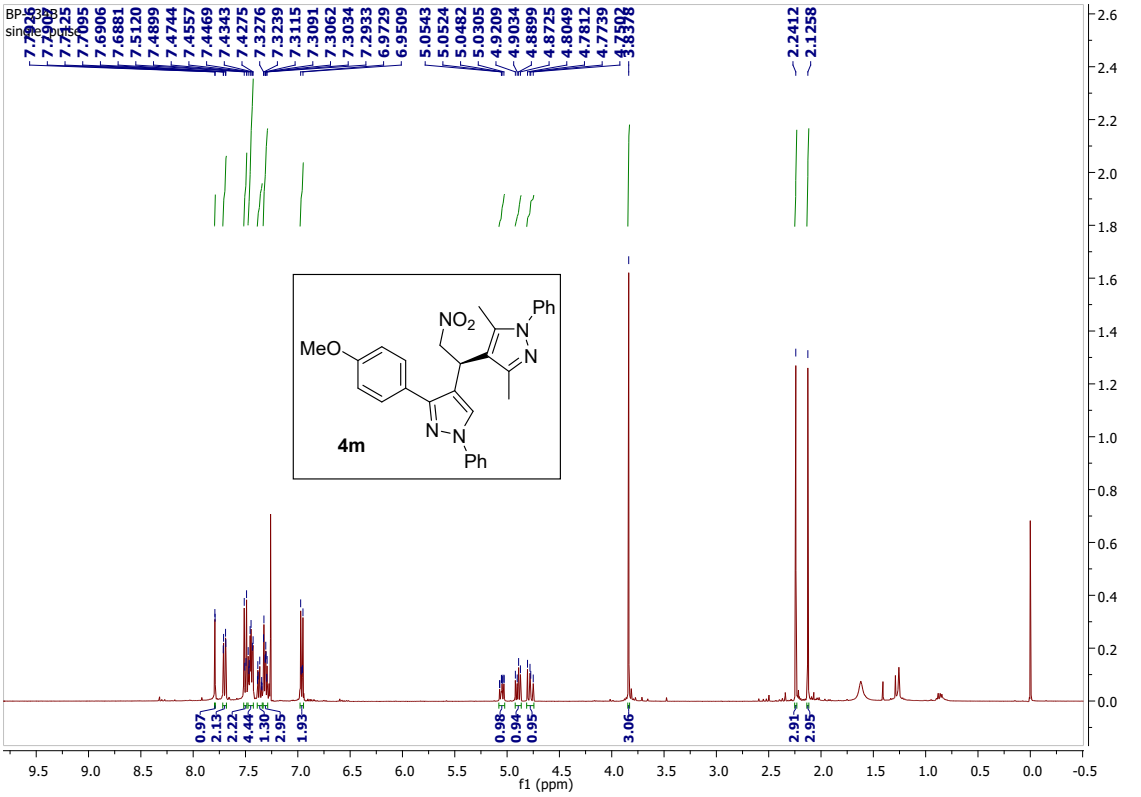

BP-496-B
single pulse decoupled carbon
f1 (ppm)
4k

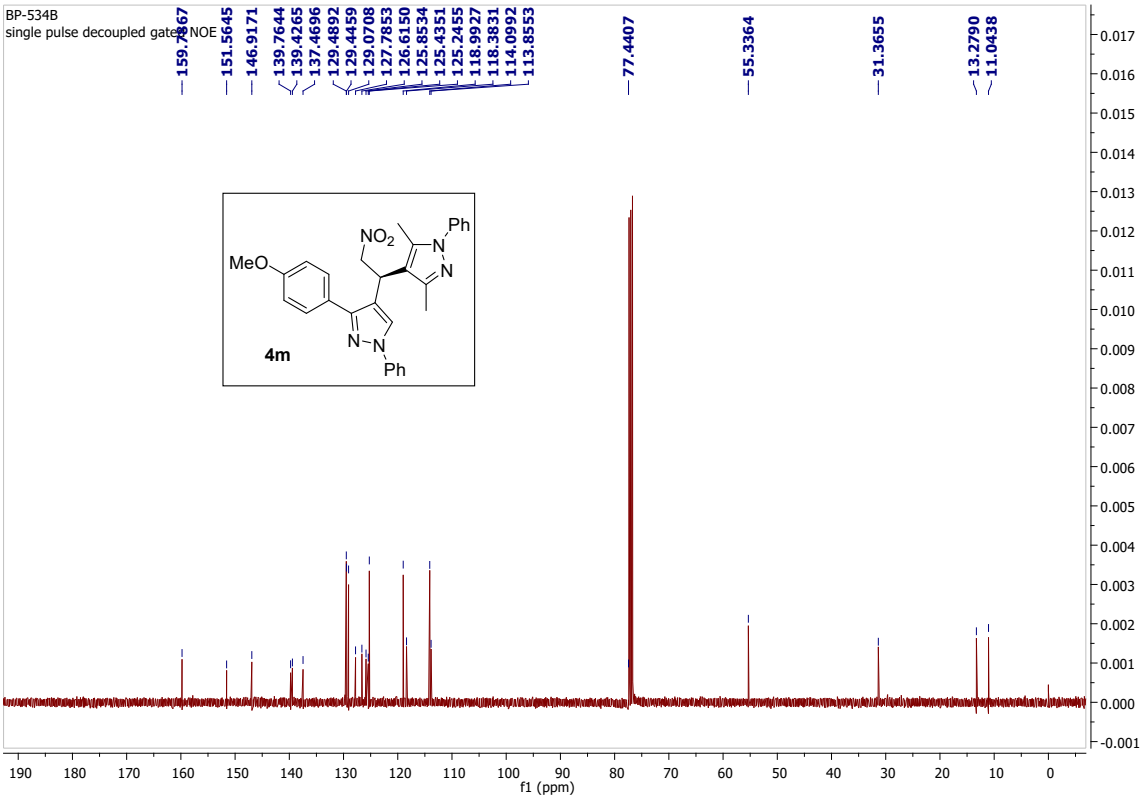


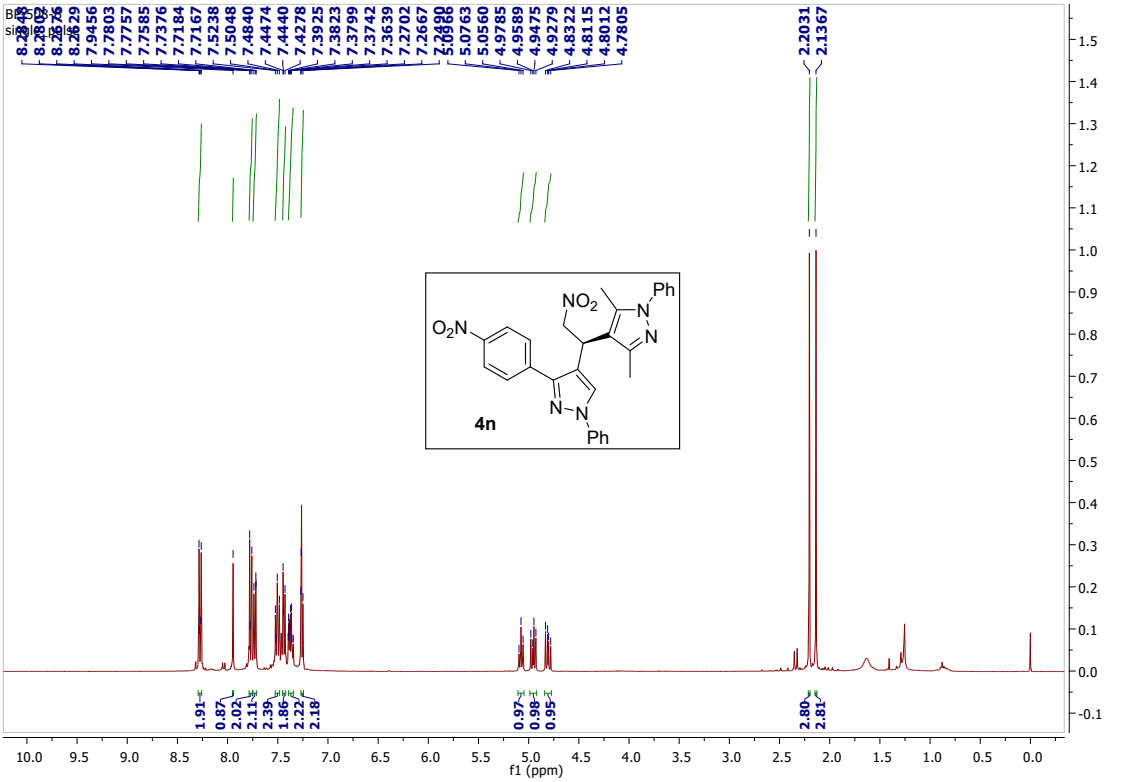
7.7116
7.6924
7.6906
7.4582
7.4497
7.4395
7.4375
7.4317
7.4286
7.4181
7.4123
7.3743
7.3696
7.3558
7.3515
7.3462
7.2922
7.2887
7.2751
7.2712
5.0775
5.0617
5.0601
5.0554
5.0379
5.0364
4.7803
4.7635
4.7558
3.8800
2.1880
2.0386
NO2
Ph
N
N
OMe
N
N
Ph
4l
1.00
2.31
5.28
3.37
1.44
1.31
1.25
1.01
0.98
1.84
2.95
3.13
3.10
f1 (ppm)

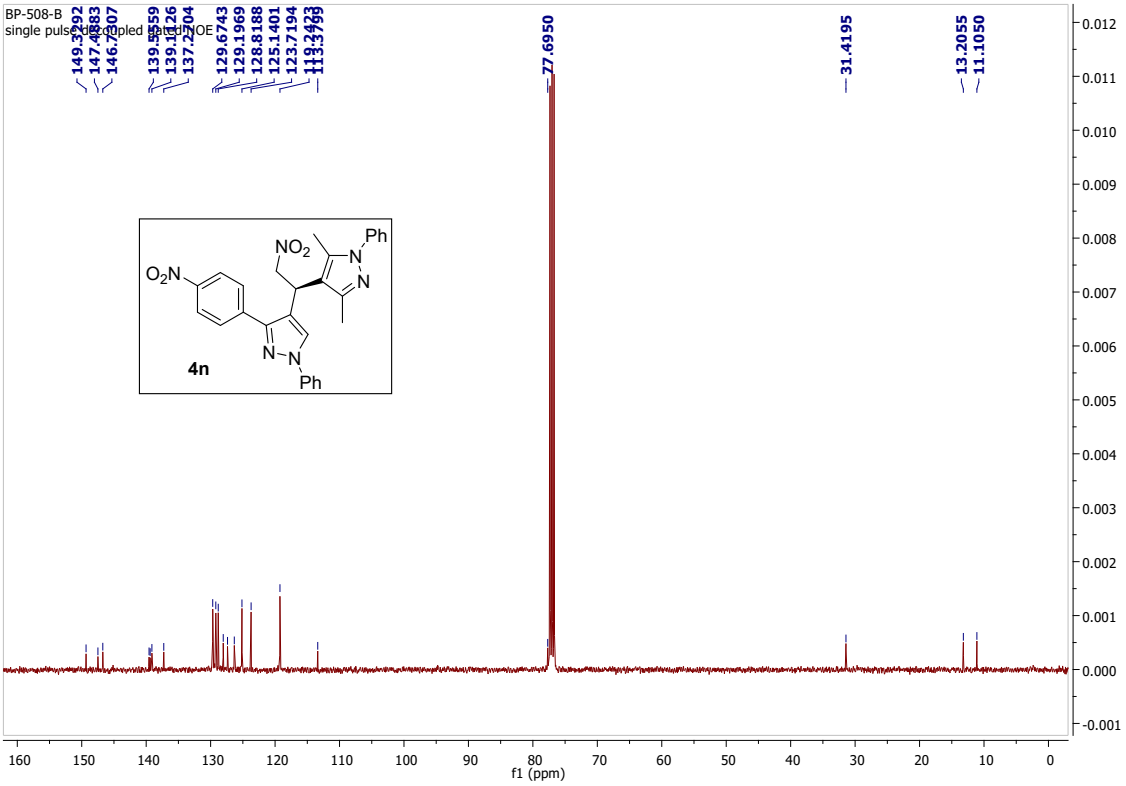


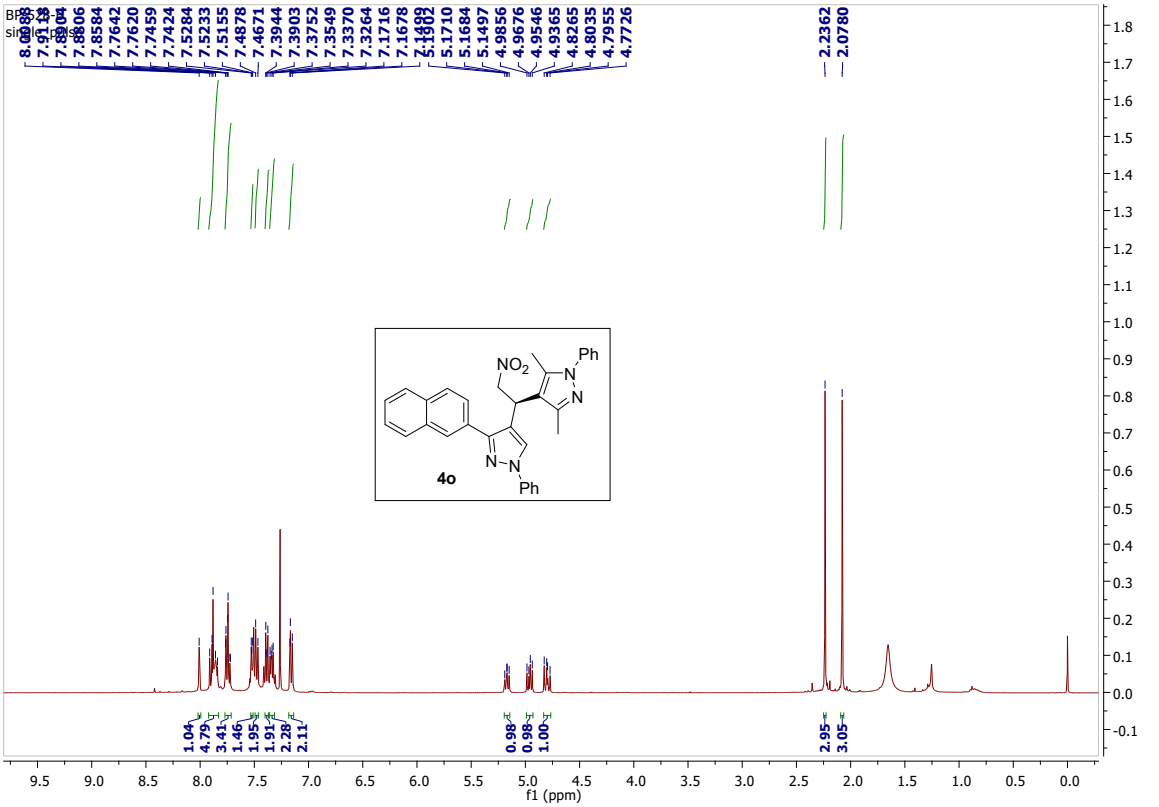
BP-494-B
137.3962
131.3017
130.3284
129.4030
129.0004
127.5990
126.4589
125.1117
125.0593
122.0371
120.9242
120.6516
118.9298
114.0126
110.6304
77.2317
55.5029
31.3994
13.1008
10.6712
NO2
Ph
N
N
OMe
N
N
Ph
4l
f1 (ppm)

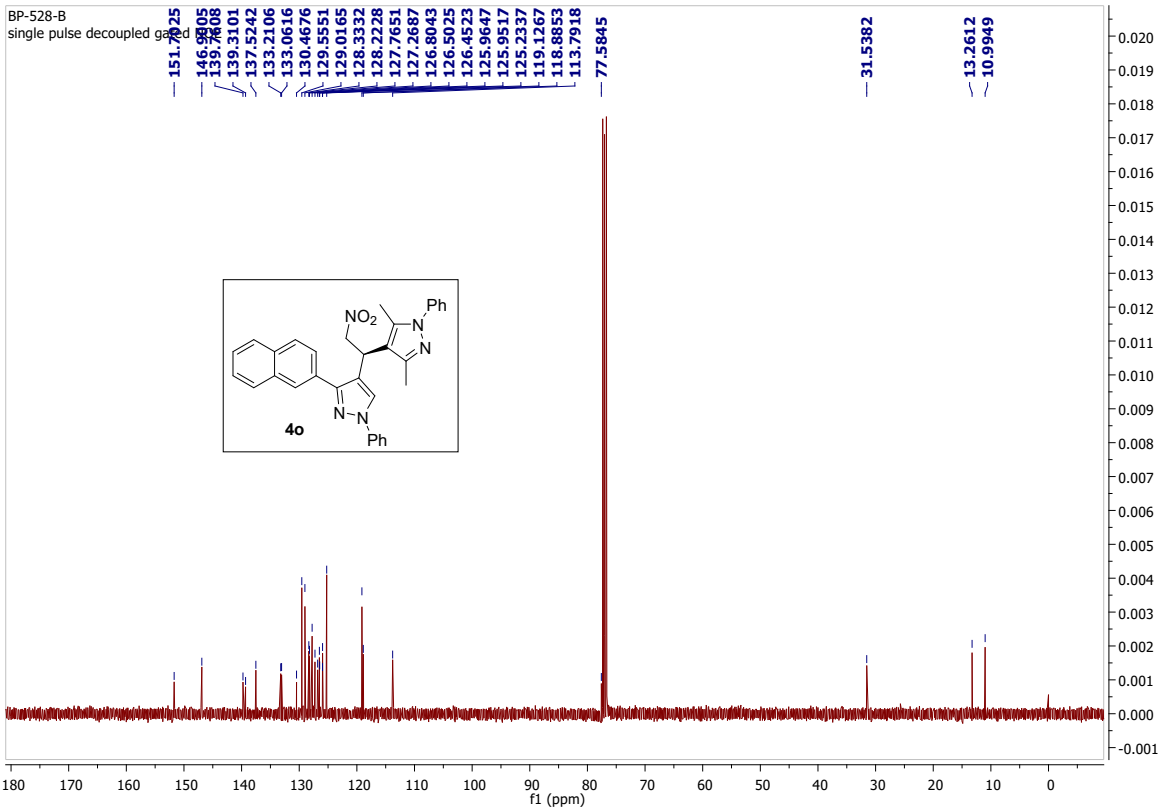

BP-534B
single pulse
7.7622
7.7508
7.7225
7.7095
7.6906
7.6881
7.5120
7.4899
7.4744
7.4557
7.4469
7.4343
7.4275
7.3276
7.3239
7.3115
7.3091
7.3062
7.3034
7.2933
6.9729
6.9509
5.0543
5.0524
5.0482
5.0305
4.9209
4.9034
4.8899
4.8725
4.8049
4.7812
4.7739
4.7502
3.8378
2.2412
2.1258
NO2
Ph
N
N
MeO
N
N
Ph
4m
0.97
2.13
2.22
4.44
1.30
2.95
1.93
0.98
0.94
0.95
3.06
2.91
2.95
f1 (ppm)

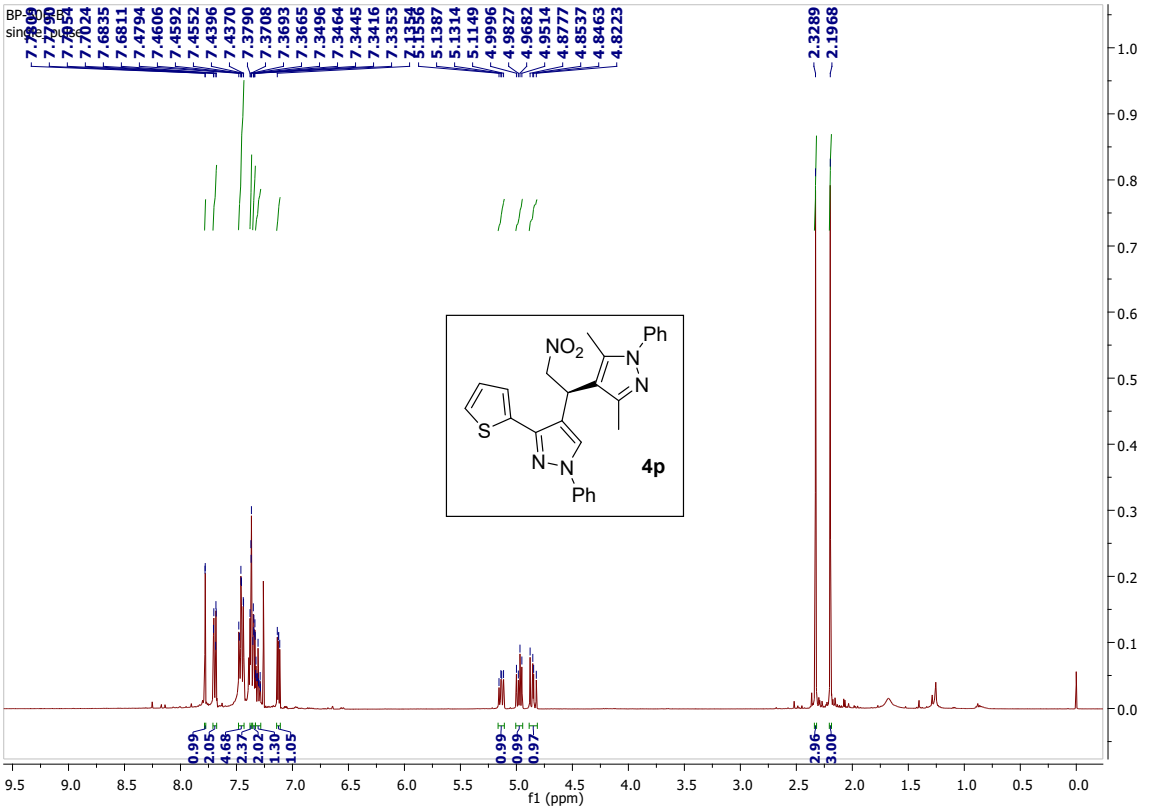

BP-534B
single pulse decoupled gated NOE
159.7867
151.5645
146.9171
139.7644
139.4265
137.4696
129.4892
129.4459
129.0708
127.7853
126.6150
125.8534
125.4351
125.2455
118.9927
118.3831
114.0992
113.8553
77.4407
55.3364
31.3655
13.2790
11.0438
NO2
Ph
N
N
MeO
N
N
Ph
4m
f1 (ppm)

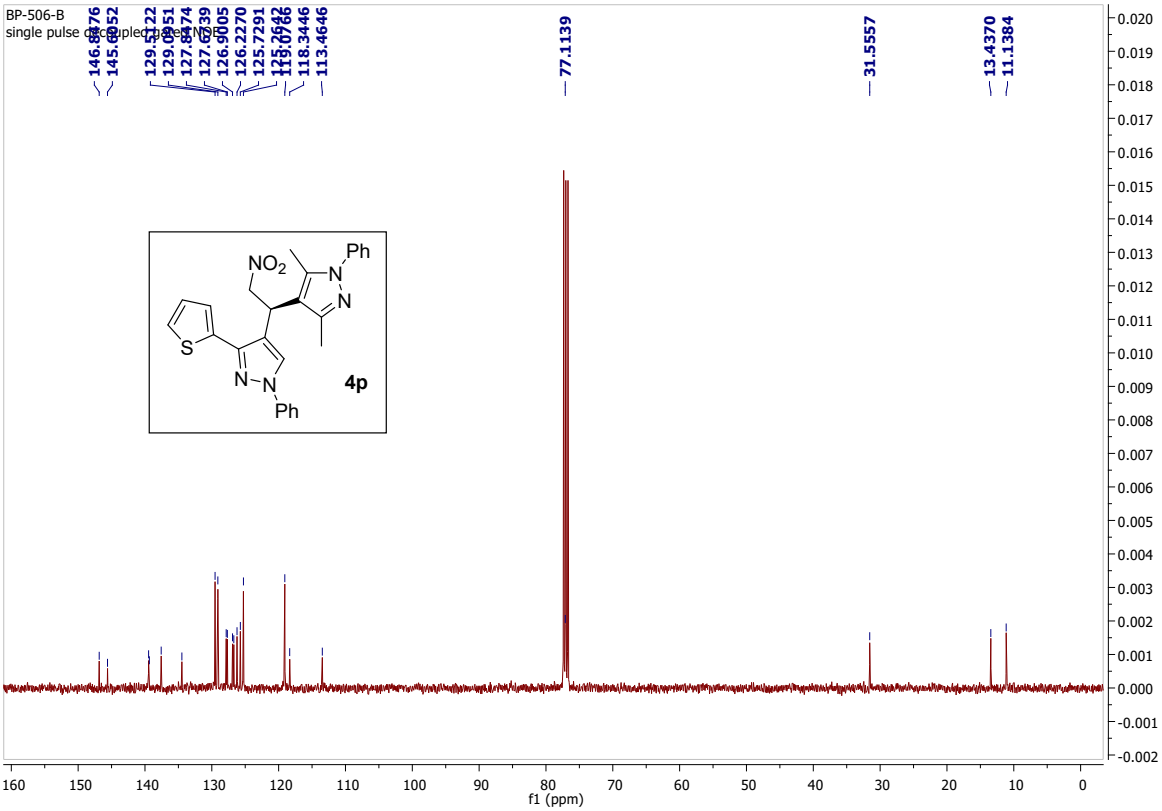

4n

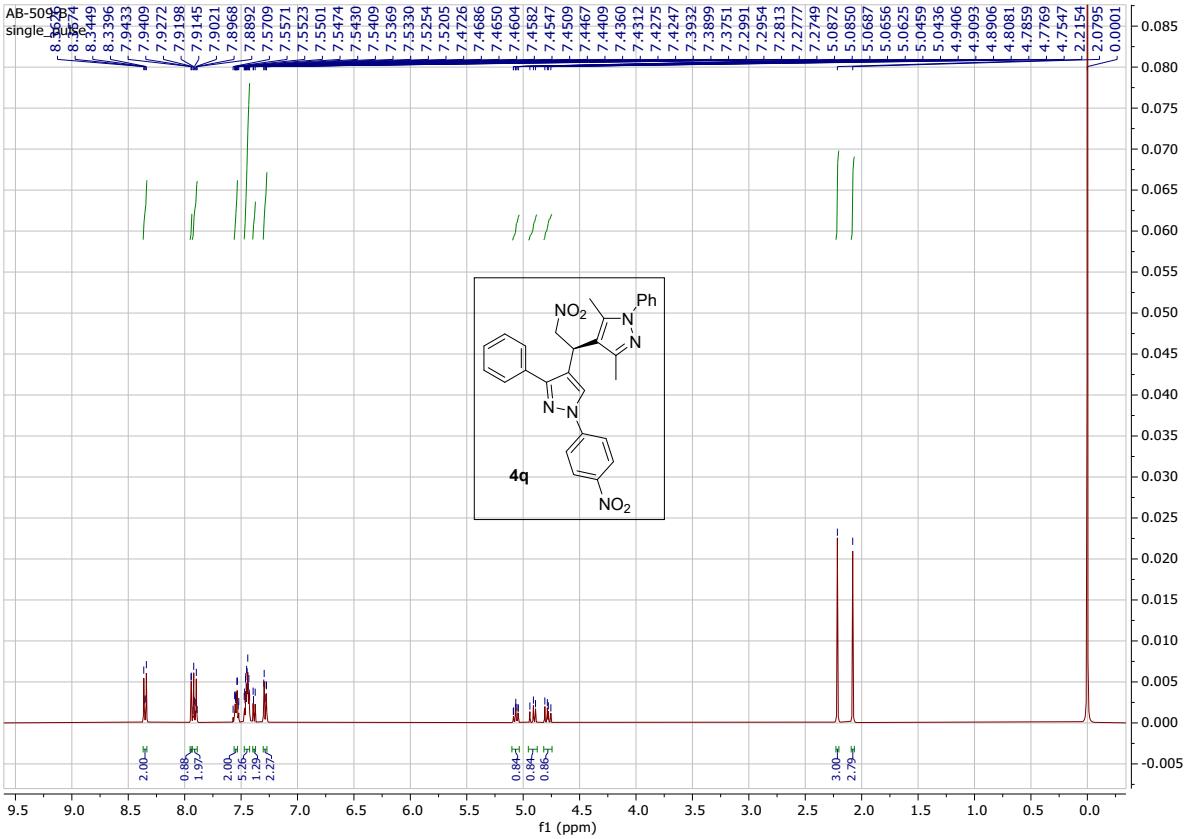

4n

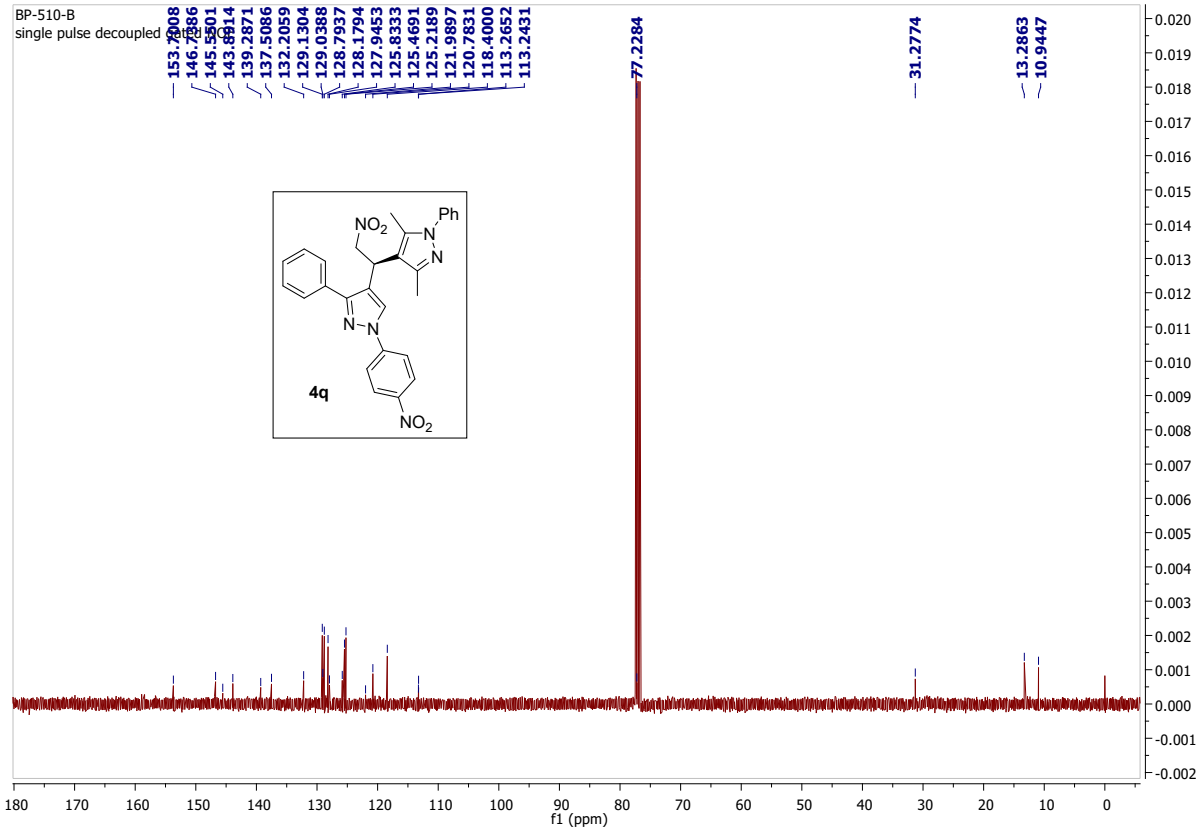

4o
f1 (ppm)


BP-528-B
single pulse decoupled gated
4o
f1 (ppm)

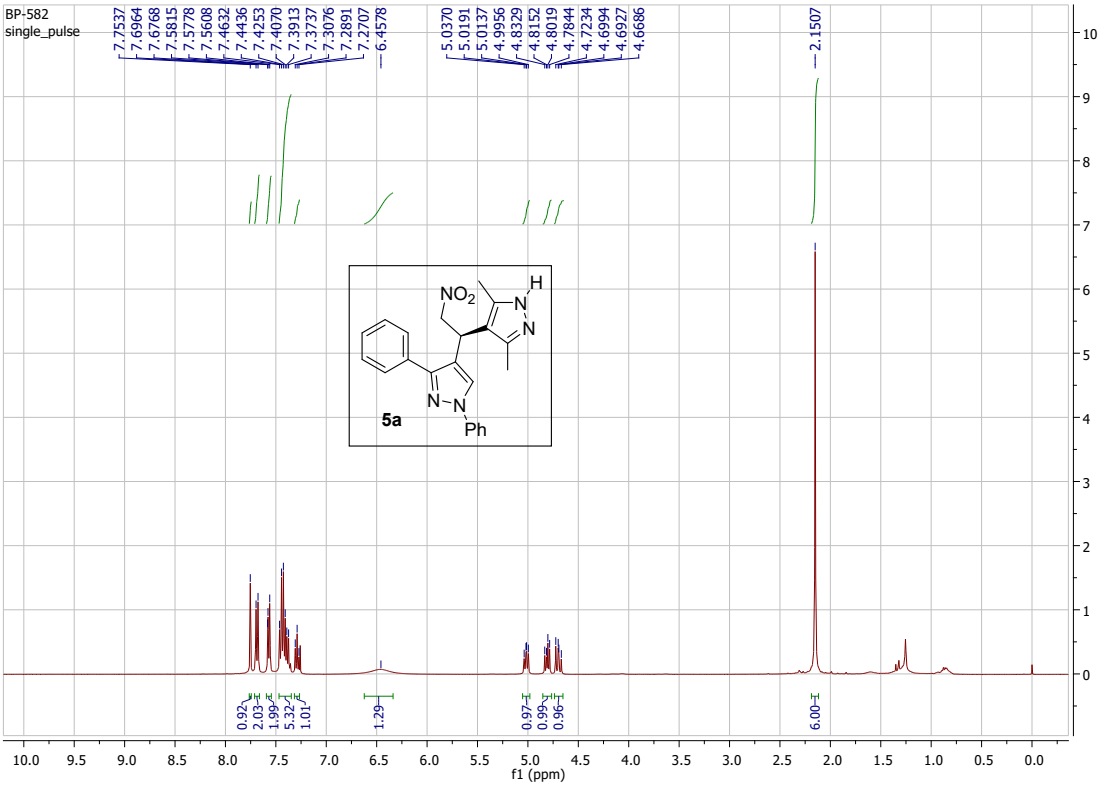

BP-506-B
single pulse
7.7900
7.7754
7.7024
7.6835
7.6811
7.4794
7.4606
7.4592
7.4552
7.4396
7.4370
7.3790
7.3708
7.3693
7.3665
7.3496
7.3464
7.3445
7.3416
7.3353
5.1556
5.1387
5.1314
5.1149
4.9996
4.9827
4.9682
4.9514
4.8777
4.8537
4.8463
4.8223
2.3289
2.1968
0.99
2.05
4.68
2.37
2.02
1.30
1.05
0.99
0.99
0.97
2.96
3.00
NO2
Ph
N
N
S
N
N
Ph
4p
f1 (ppm)

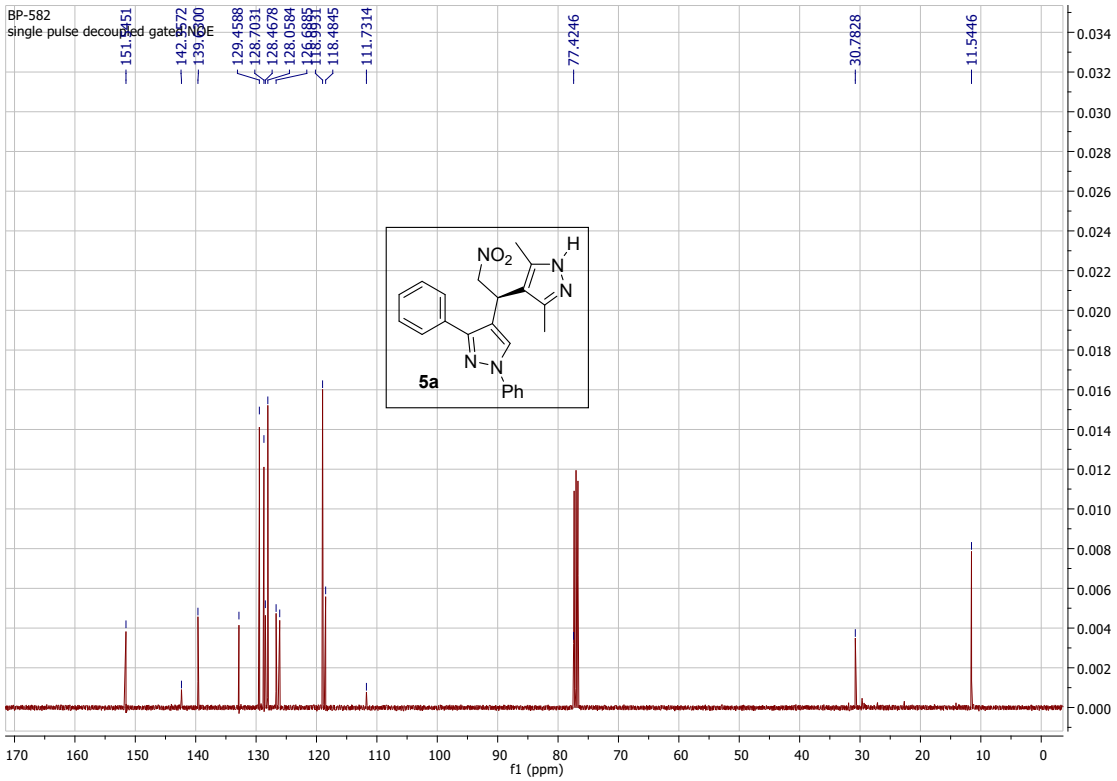

BP-506-B
single pulse decoupled gated NMR
146.6476
145.6852
129.4222
129.0351
127.8474
127.5339
126.9005
126.2270
125.7291
118.3446
113.4646
77.1139
31.5557
13.4370
11.1384
NO2
Ph
N
N
S
N
N
Ph
4p
f1 (ppm)

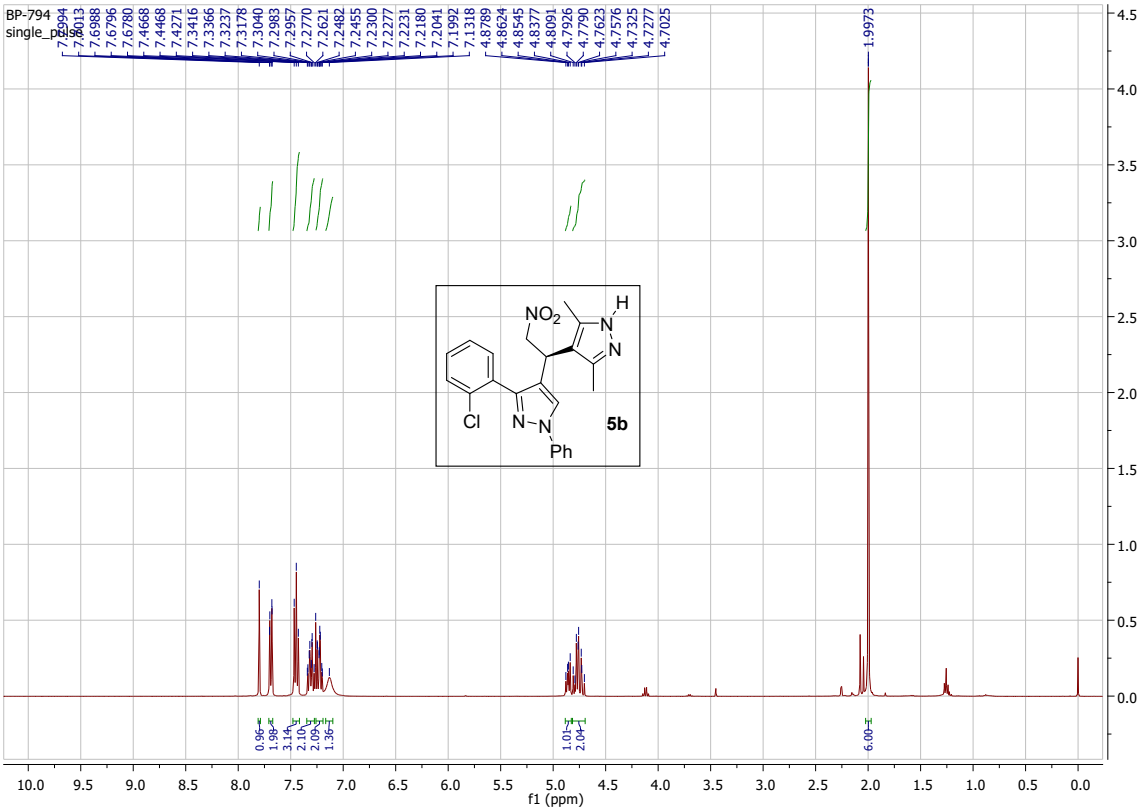

AB-5099-B
single_pulse
4q
f1 (ppm)

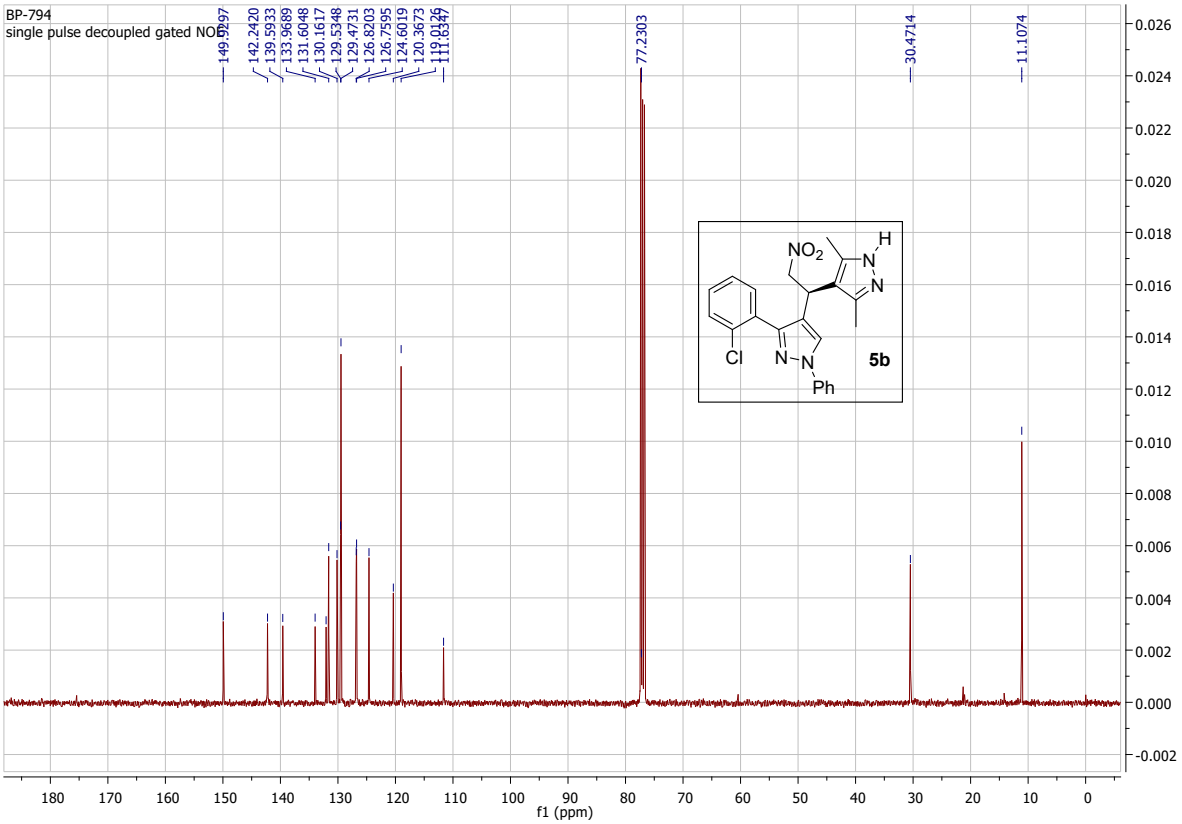

BP-510-B
single pulse decoupled refined
153.7008
146.7586
145.5501
143.8914
139.2871
137.5086
132.2059
129.1304
129.0388
128.7937
128.1794
127.9453
125.8333
125.4691
125.2189
121.9897
120.7831
118.4000
113.2652
113.2431
77.2284
31.2774
13.2863
10.9447
4q
f1 (ppm)

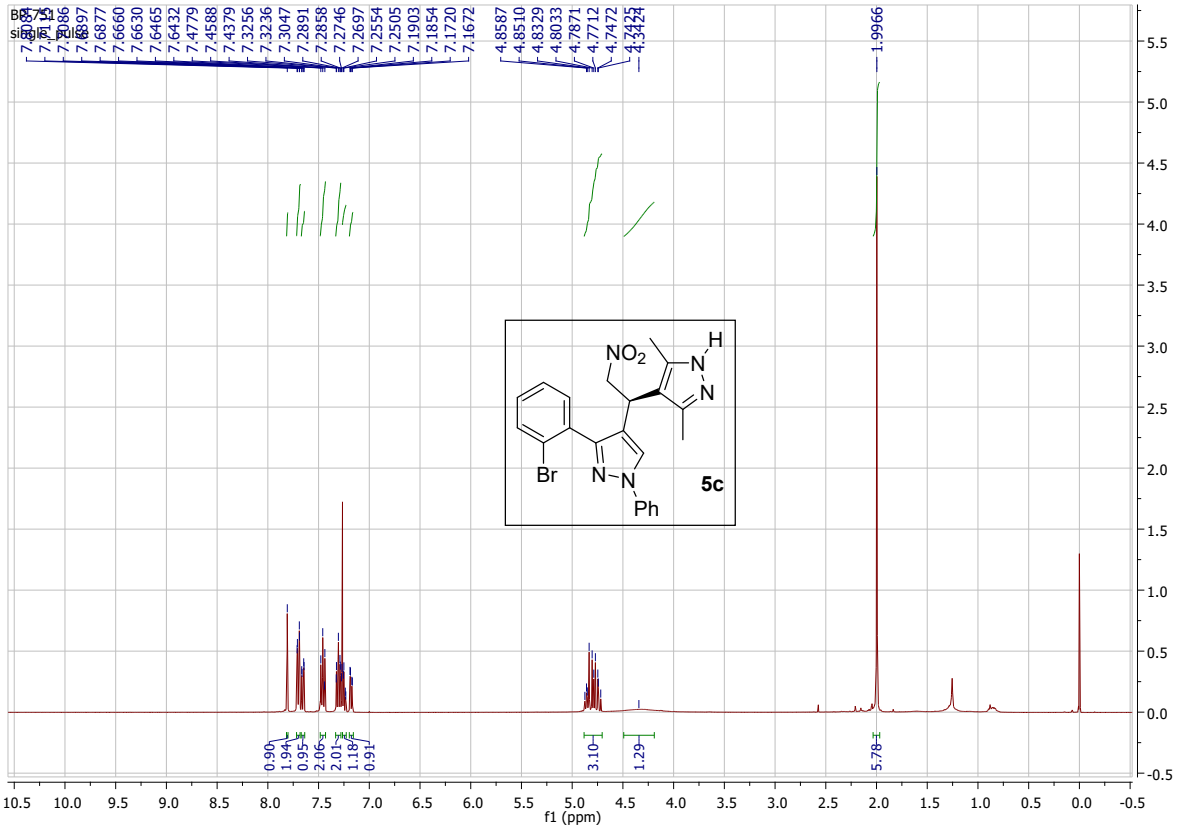
^{1}H and ^{13}C NMR spectra of 5

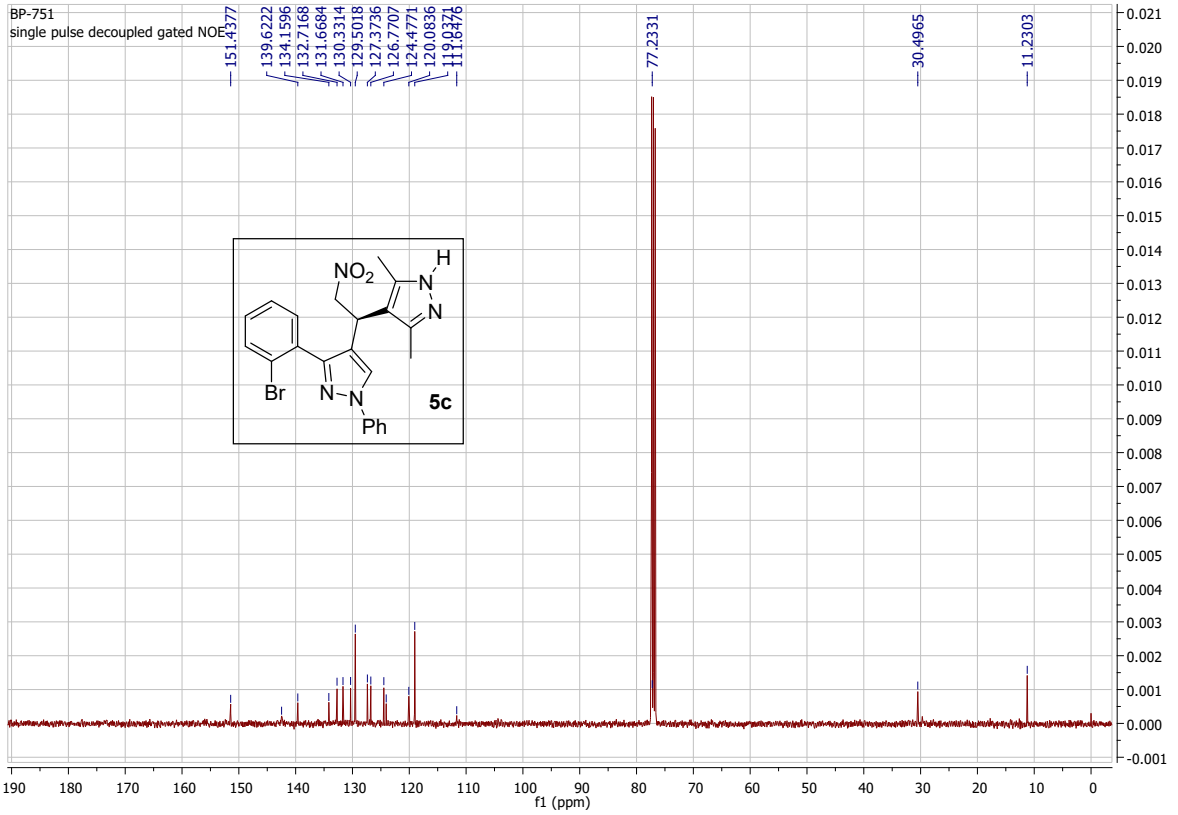


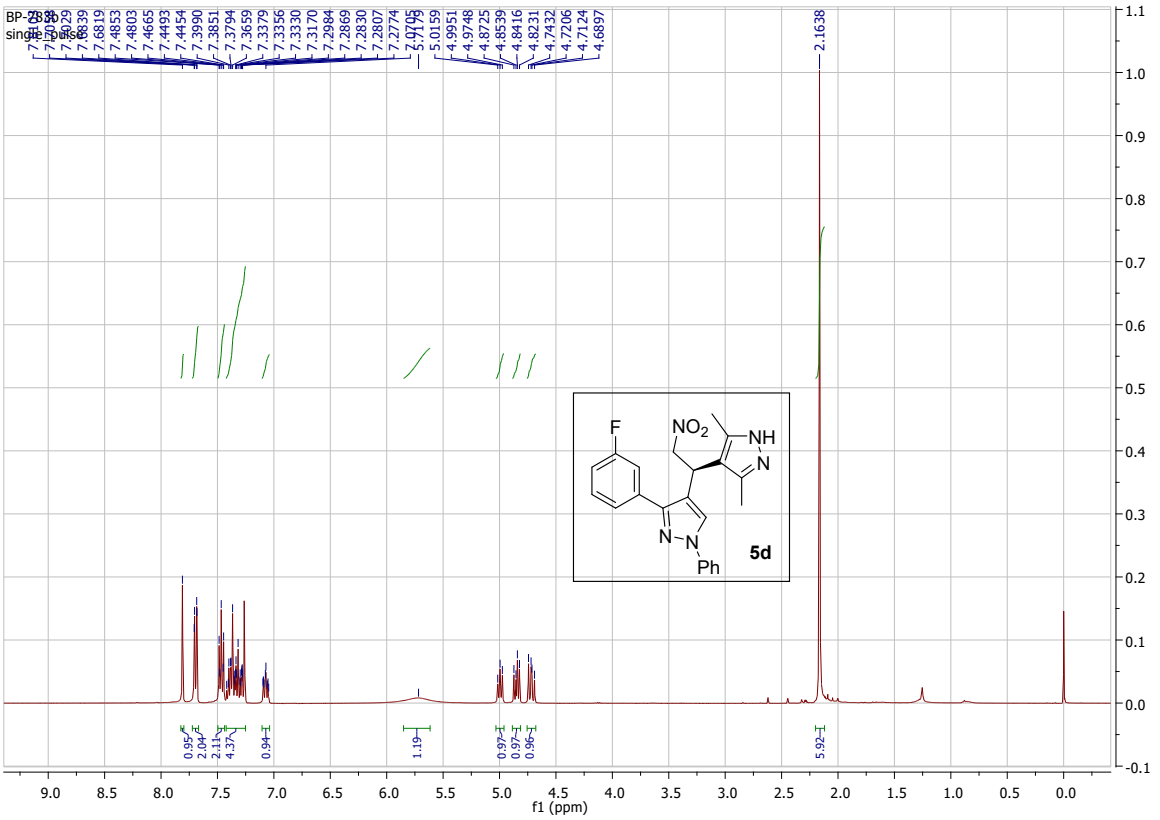


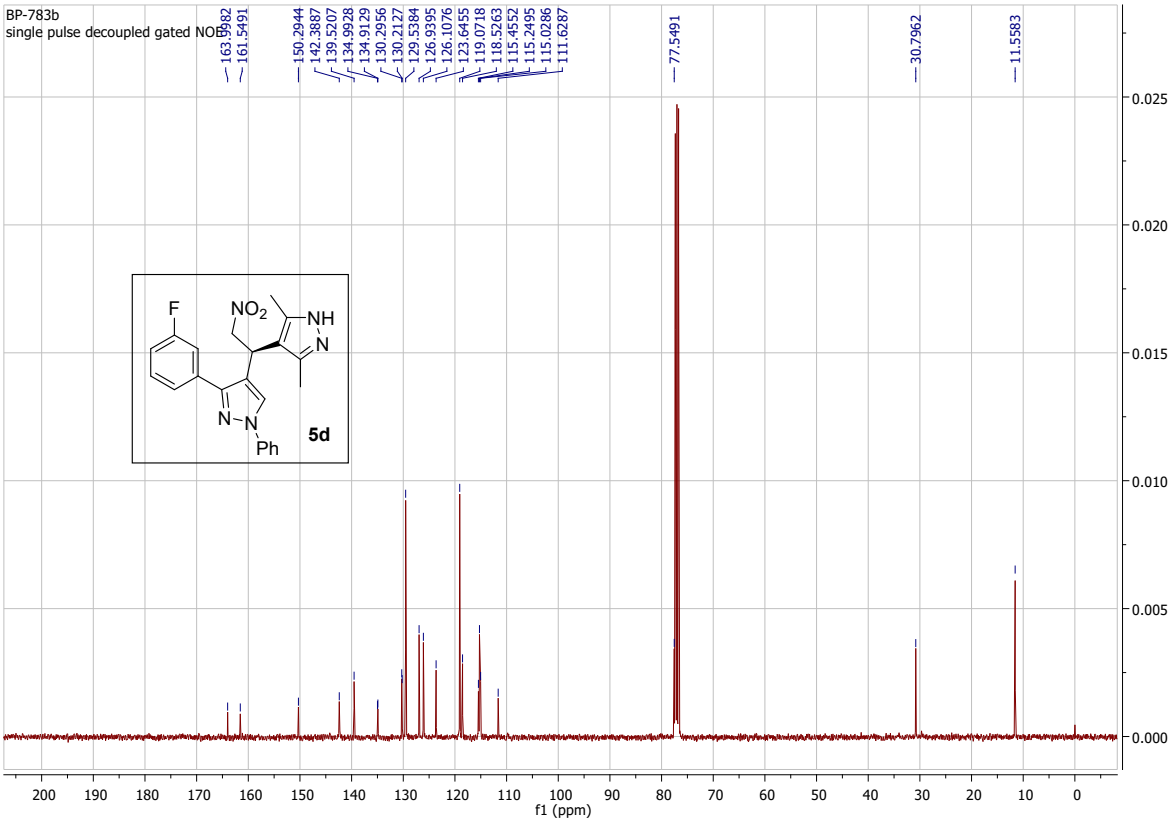

BP-794
single_pulse
NO2
H
N
N
Cl
N
N
Ph
5b
f1 (ppm)

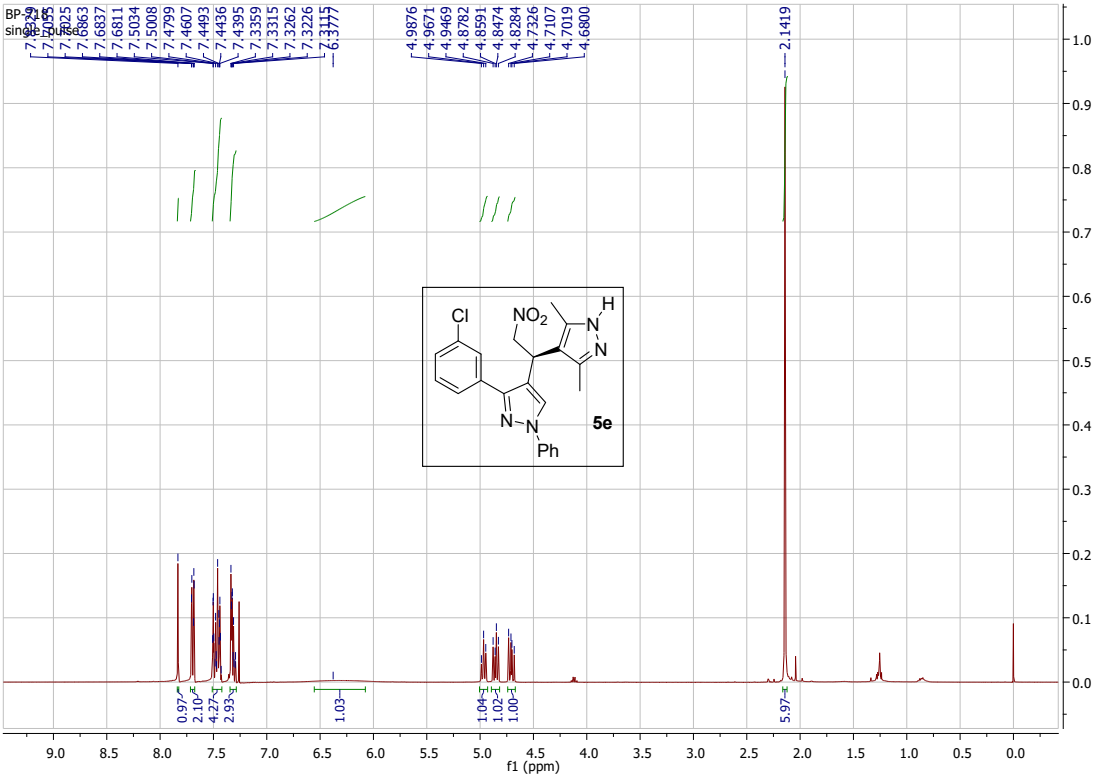

BP-794
single pulse decoupled gated NOE
77.2303
30.4714
11.1074
NO2
H
N
N
Cl
N
N
Ph
5b
f1 (ppm)

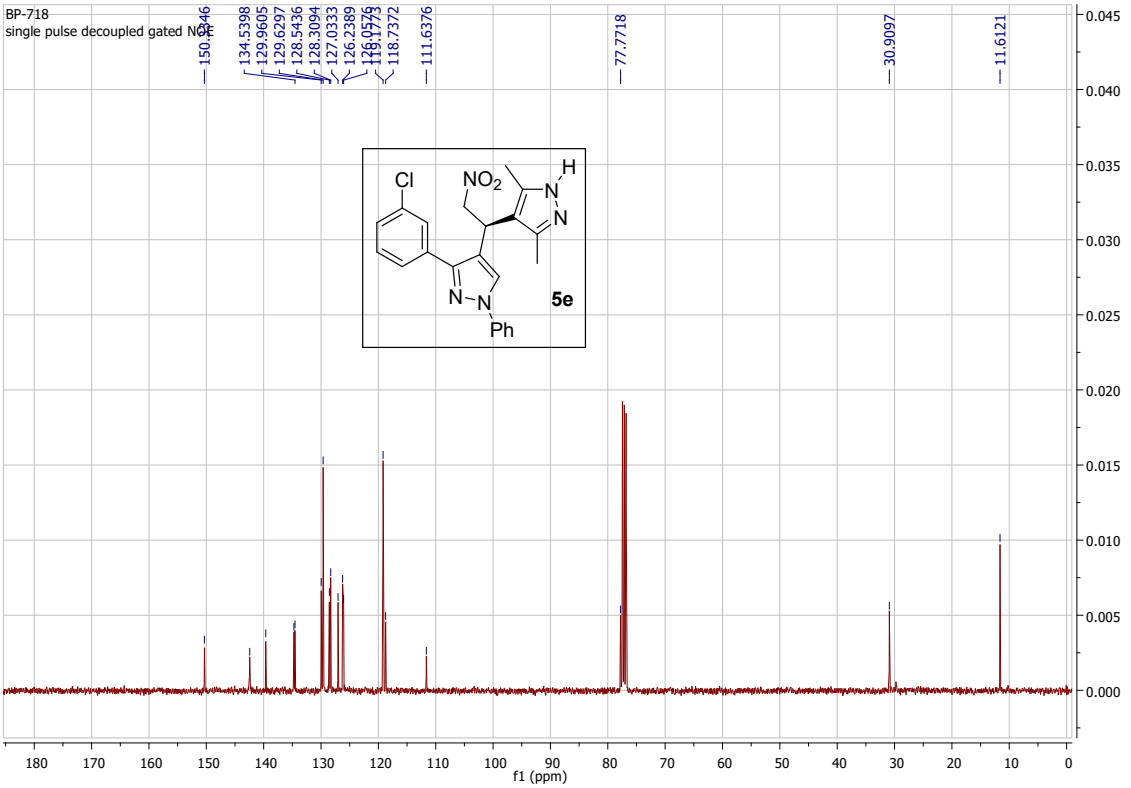

BP-751
single pulse
1.9966
0.90
1.94
0.95
2.06
2.01
1.18
0.91
3.10
1.29
5.78
f1 (ppm)
NO2
H
N
N
Br
N
N
Ph
5c

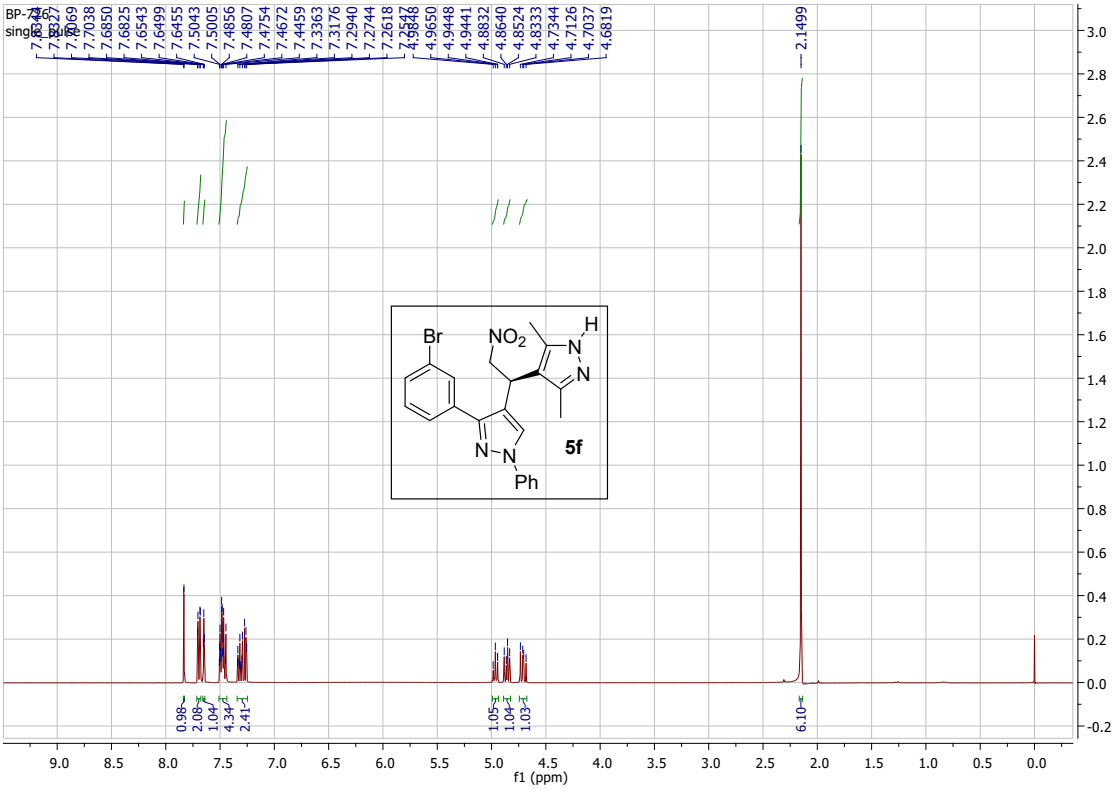

BP-751
single pulse decoupled gated NOE
151.4377
139.6222
134.1596
132.7168
131.6684
130.3314
129.5018
127.3736
126.7707
124.4771
120.0836
119.0321
111.8476
77.2331
30.4965
11.2303
f1 (ppm)
NO2
H
N
N
Br
N
N
Ph
5c

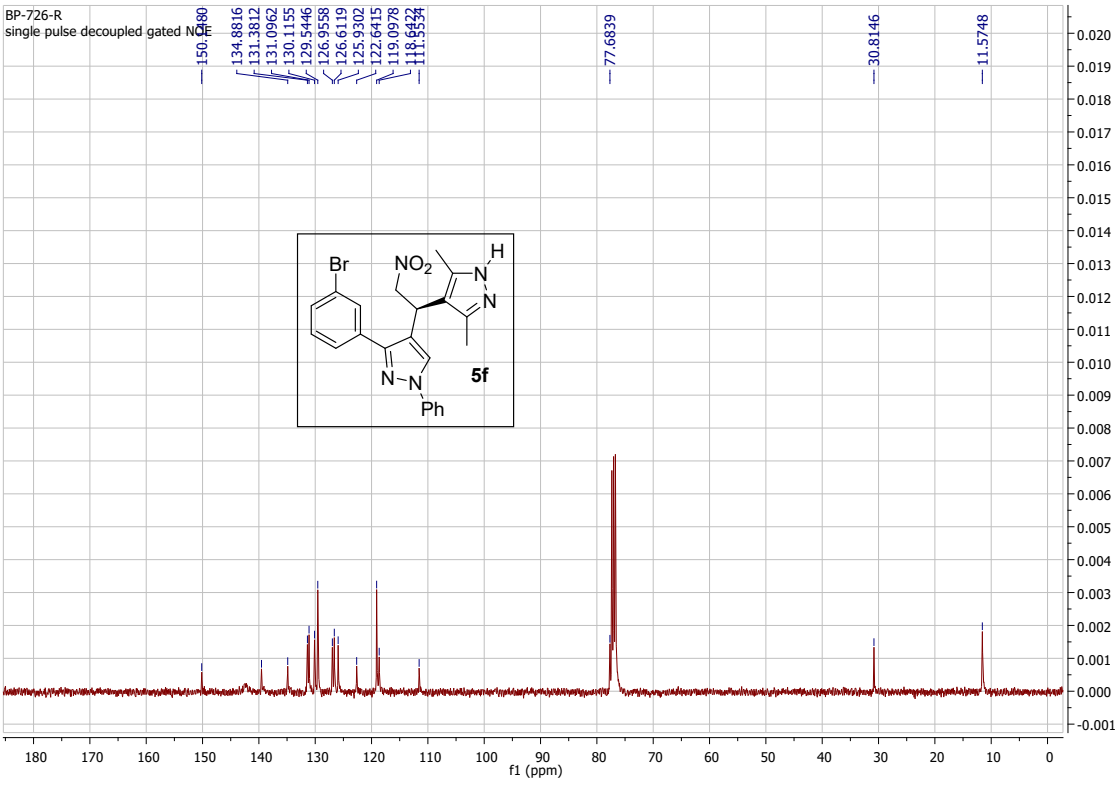

BP-783
single pulse
2.1638
f1 (ppm)
5d

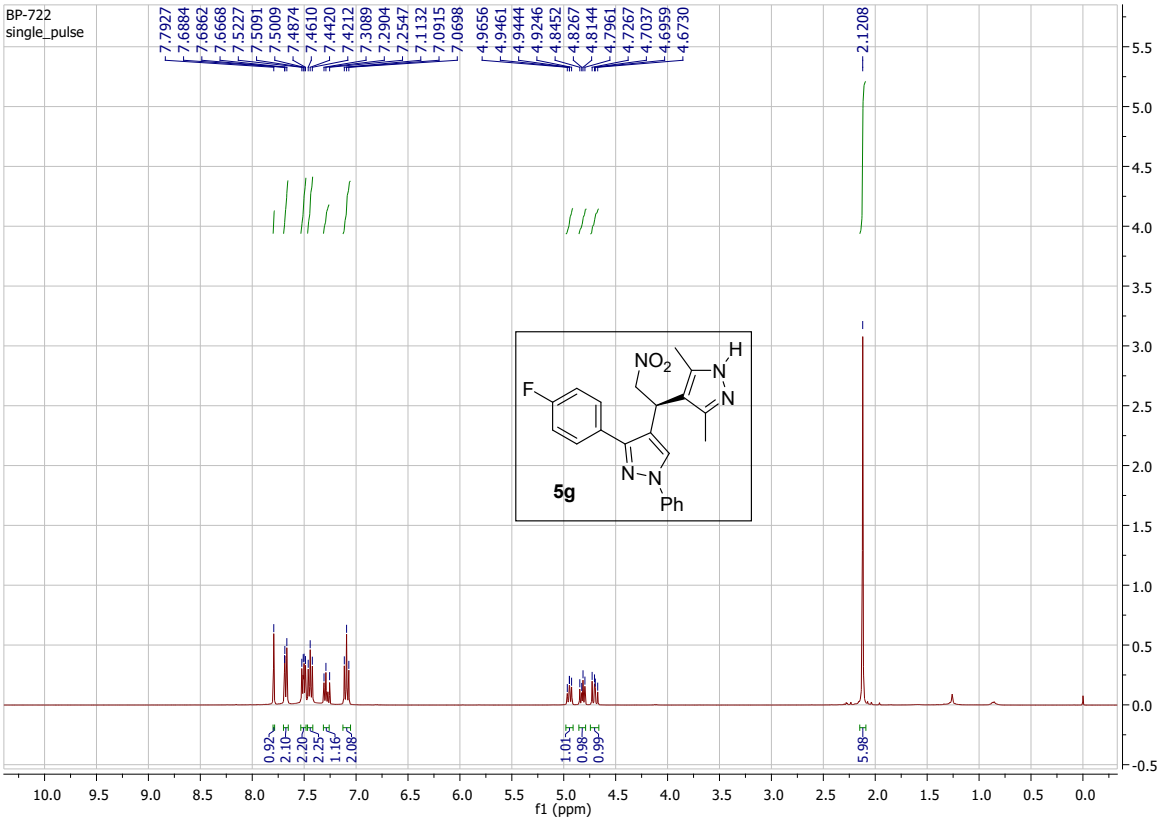

BP-783b
single pulse decoupled gated NOE
163.9982
161.5491
150.2944
142.3887
139.5207
134.9928
134.9129
130.2956
130.2127
129.5384
126.9395
126.1076
123.6455
119.0718
118.5263
115.4552
115.2495
115.0286
111.6287
77.5491
30.7962
11.5583
f1 (ppm)
5d

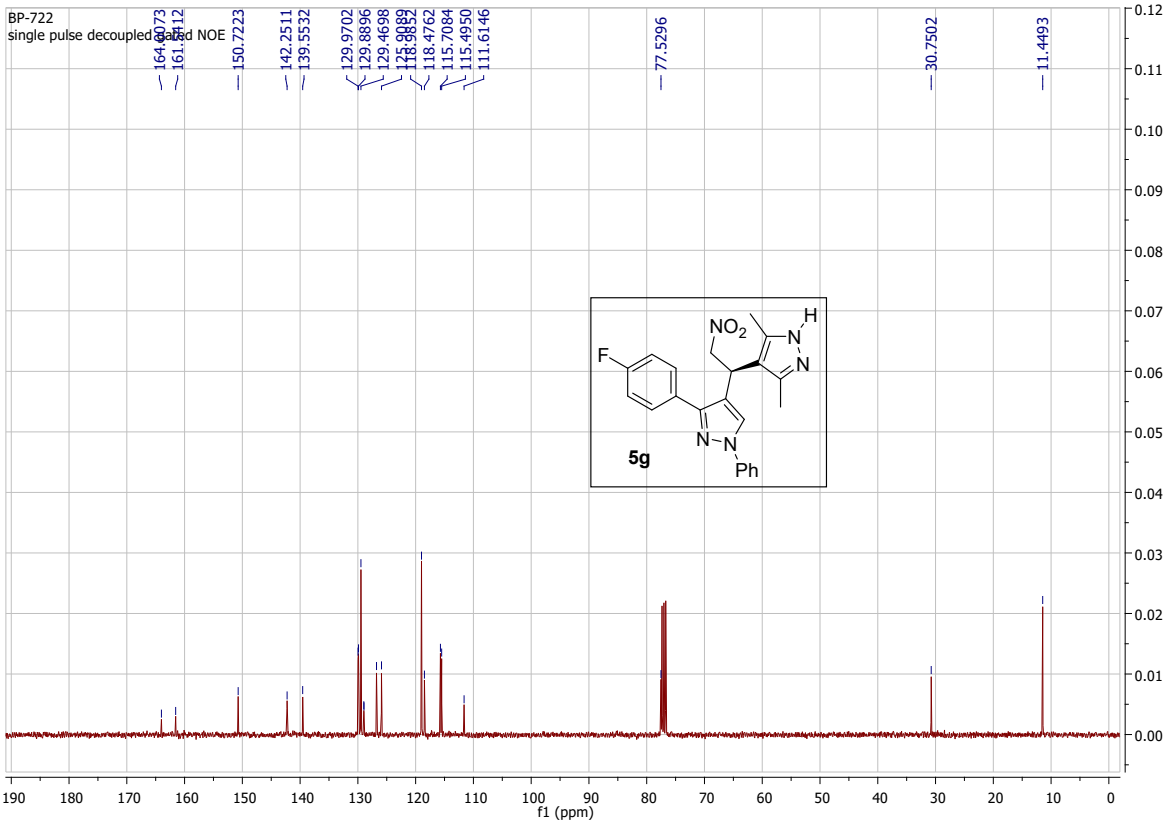

BP-718
single pulse
4.9876
4.9671
4.9469
4.8782
4.8591
4.8474
4.8284
4.7326
4.7107
4.7019
4.6800
2.1419
Cl
NO2
H
N
N
N
N
Ph
5e
0.97
2.10
4.27
2.93
1.03
1.04
1.02
1.00
5.97
f1 (ppm)

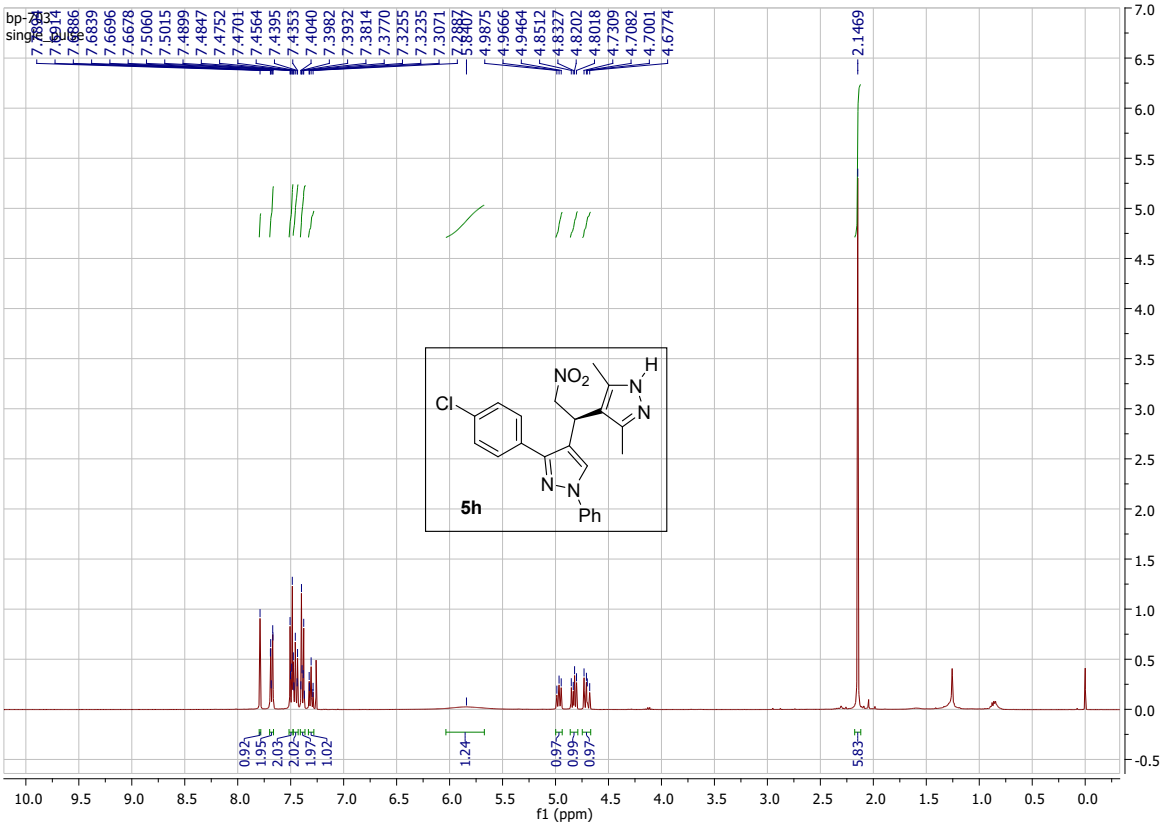

BP-718
single pulse decoupled gated NOE
150.4946
134.5398
129.9605
129.6297
128.5436
128.3094
127.0333
126.2389
126.0576
119.1773
118.7372
111.6376
77.7718
30.9097
11.6121
Cl
NO2
H
N
N
N
N
Ph
5e
f1 (ppm)

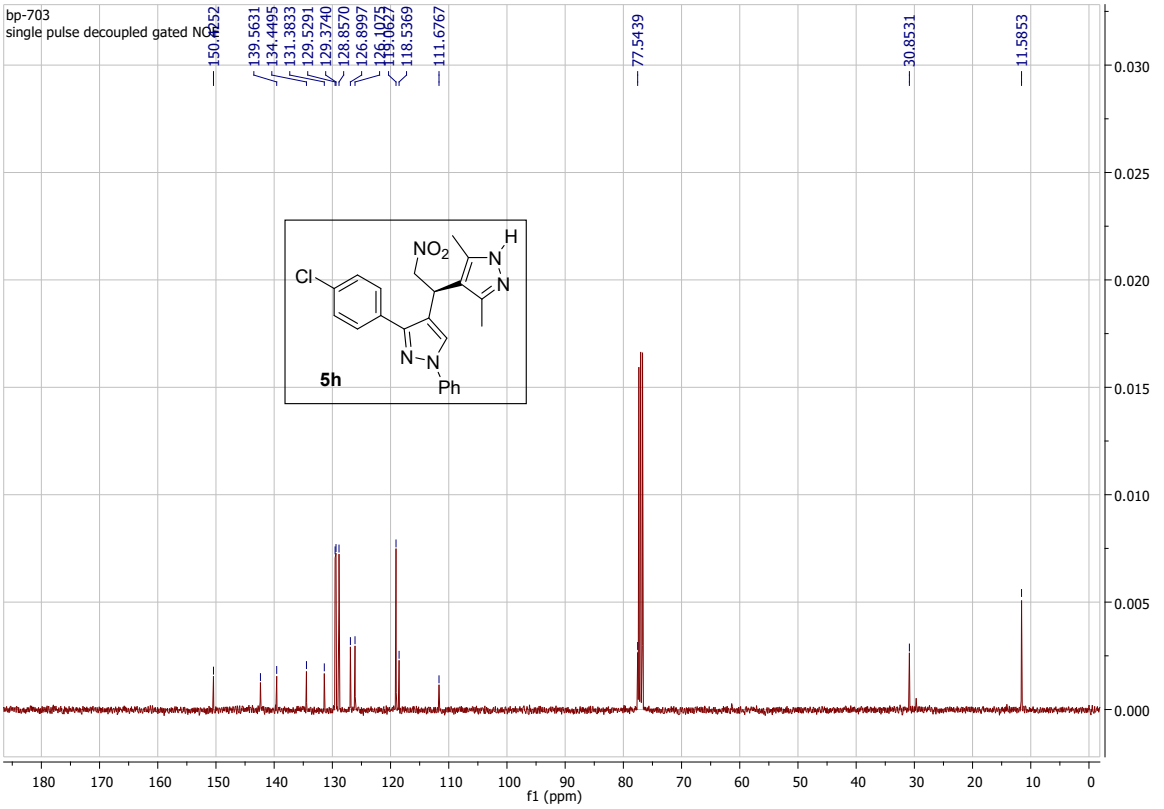

BP-726
single_pulse
Br
NO2
H
N
N
N
N
Ph
5f
2.1499
0.98
2.08
1.04
4.34
2.41
1.05
1.04
1.03
6.10
f1 (ppm)

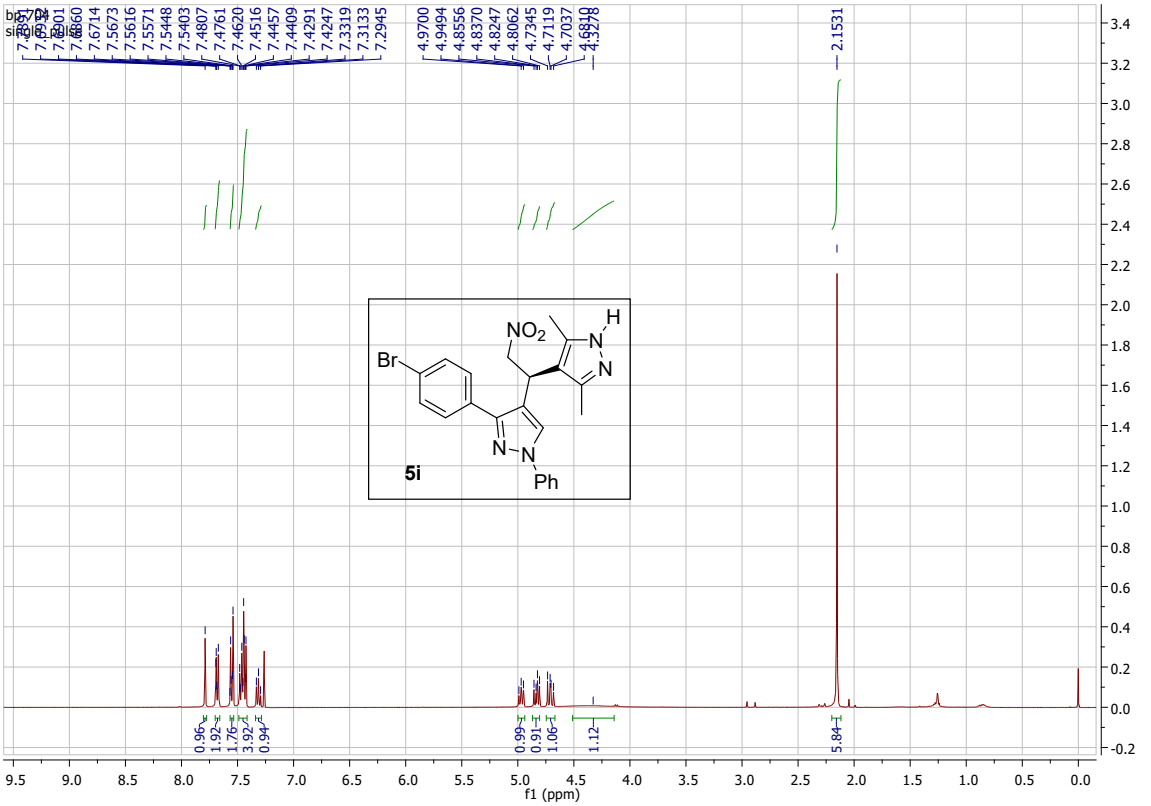

BP-726-R
single pulse decoupled gated NOE
150.1880
134.8816
131.3812
131.0962
130.1155
129.5446
126.9558
126.6119
125.9302
122.6415
119.0978
77.6839
30.8146
11.5748
Br
NO2
H
N
N
N
N
Ph
5f
f1 (ppm)

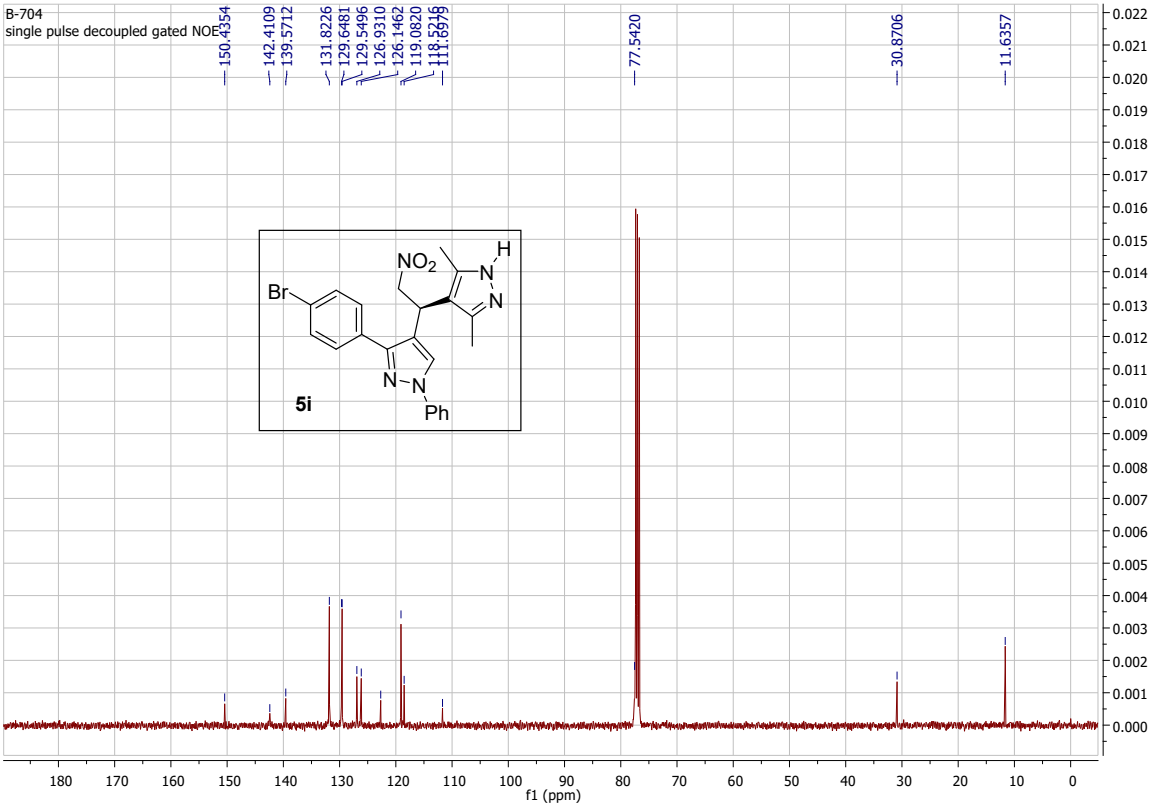

BP-722
single_pulse
7.7927
7.6884
7.6862
7.6668
7.5227
7.5091
7.5009
7.4874
7.4610
7.4420
7.4212
7.3089
7.2904
7.2547
7.1132
7.0915
7.0698
4.9656
4.9461
4.9444
4.9246
4.8452
4.8267
4.8144
4.7961
4.7267
4.7037
4.6959
4.6730
2.1208
0.92
2.10
2.20
2.25
1.16
2.08
1.01
0.98
0.99
5.98
NO2
H
N
N
F
N
N
Ph
5g
f1 (ppm)

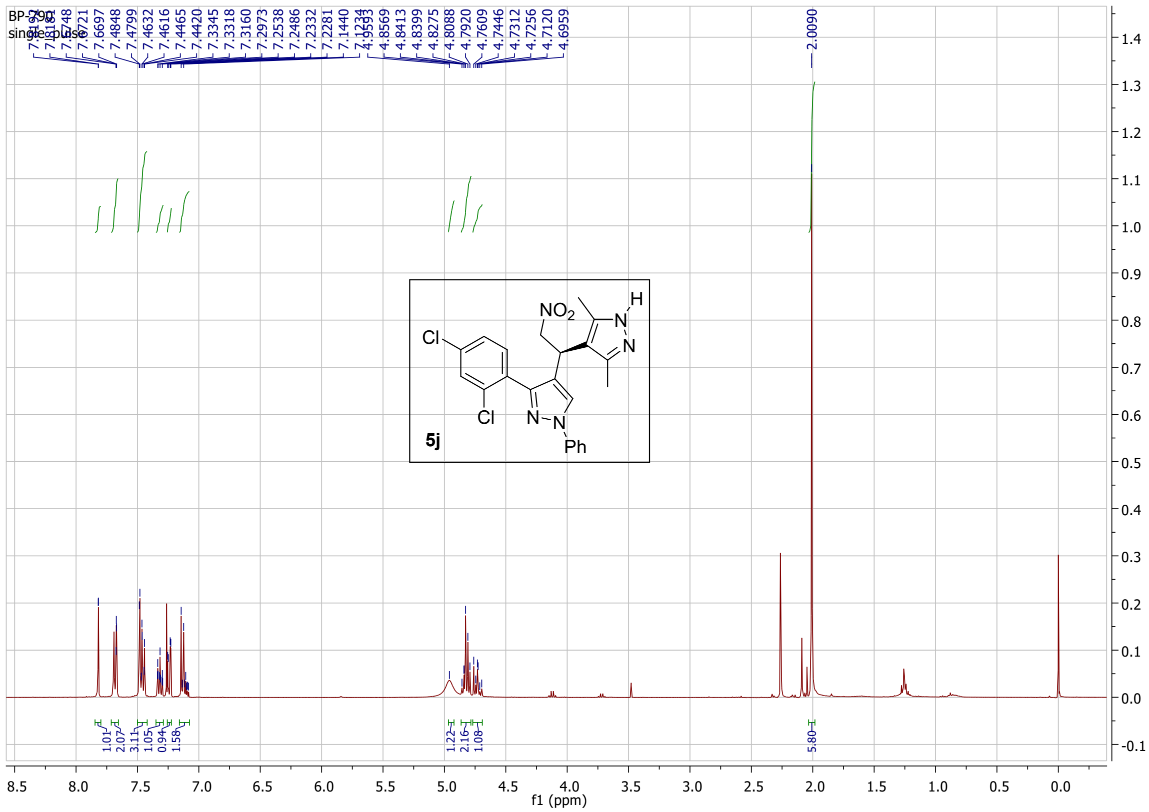

BP-722
single pulse decoupled gated NOE
164.0073
161.7112
150.7223
142.2511
139.5532
129.9702
129.8896
129.4698
125.9089
118.9852
118.4762
115.7084
115.4950
111.6146
77.5296
30.7502
11.4493
NO2
H
N
N
F
N
N
Ph
5g
f1 (ppm)

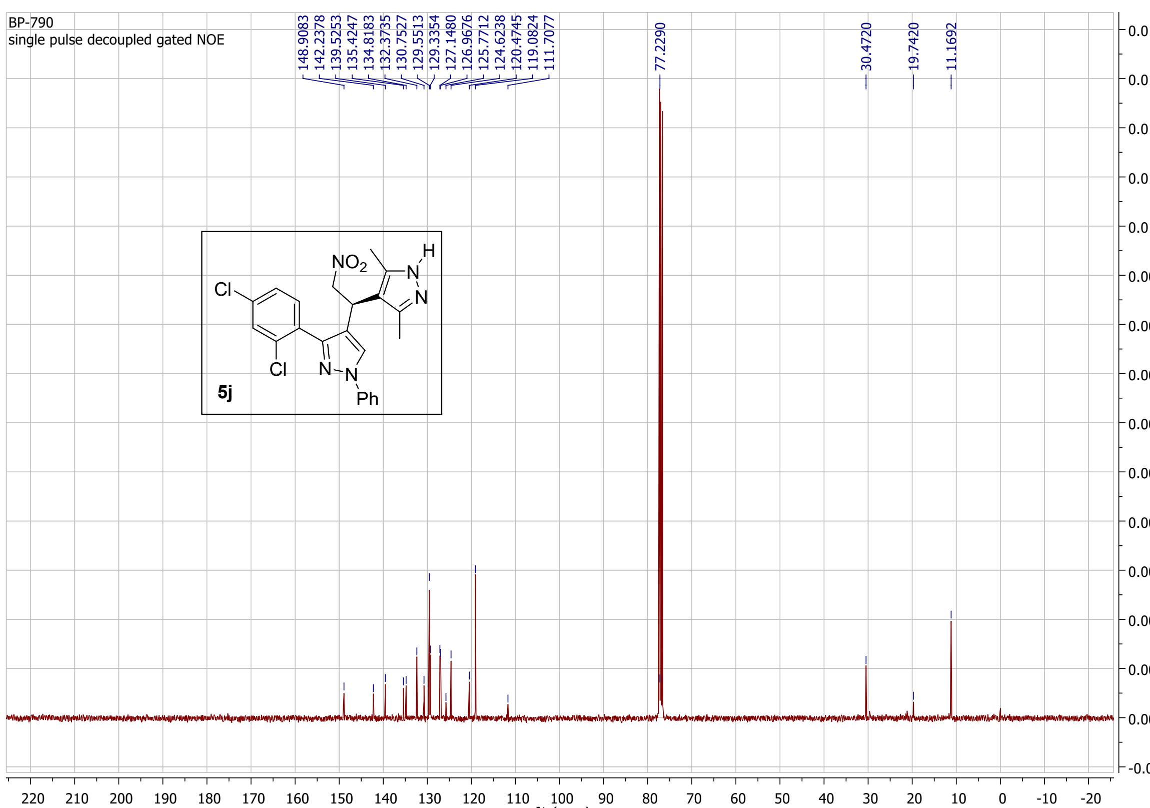

bp-703
single pulse
7.9014
7.8886
7.6839
7.6696
7.6678
7.5060
7.5015
7.4899
7.4847
7.4752
7.4701
7.4564
7.4395
7.4353
7.4040
7.3982
7.3932
7.3814
7.3770
7.3255
7.3235
7.3071
7.2887
5.8307
4.9875
4.9666
4.9464
4.8512
4.8327
4.8202
4.8018
4.7309
4.7082
4.7001
4.6774
2.1469
NO2
H
N
N
Cl
N
N
Ph
5h
0.92
1.95
2.03
2.02
1.97
1.02
1.24
0.97
0.99
0.97
5.83
f1 (ppm)

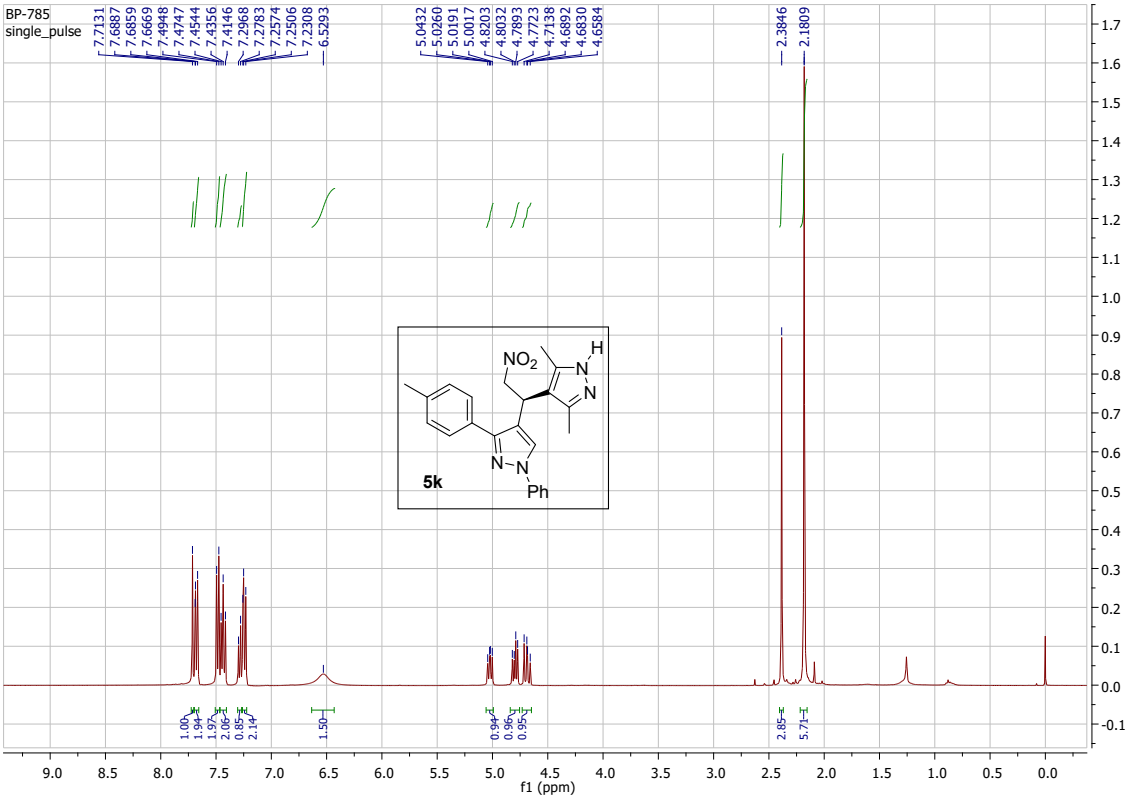

bp-703
single pulse decoupled gated NOE
150.4252
139.5631
134.4495
131.3833
129.5291
129.3740
128.8570
126.8997
126.1075
125.0627
118.5369
111.6767
77.5439
30.8531
11.5853
NO2
H
N
N
Cl
N
N
Ph
5h
f1 (ppm)

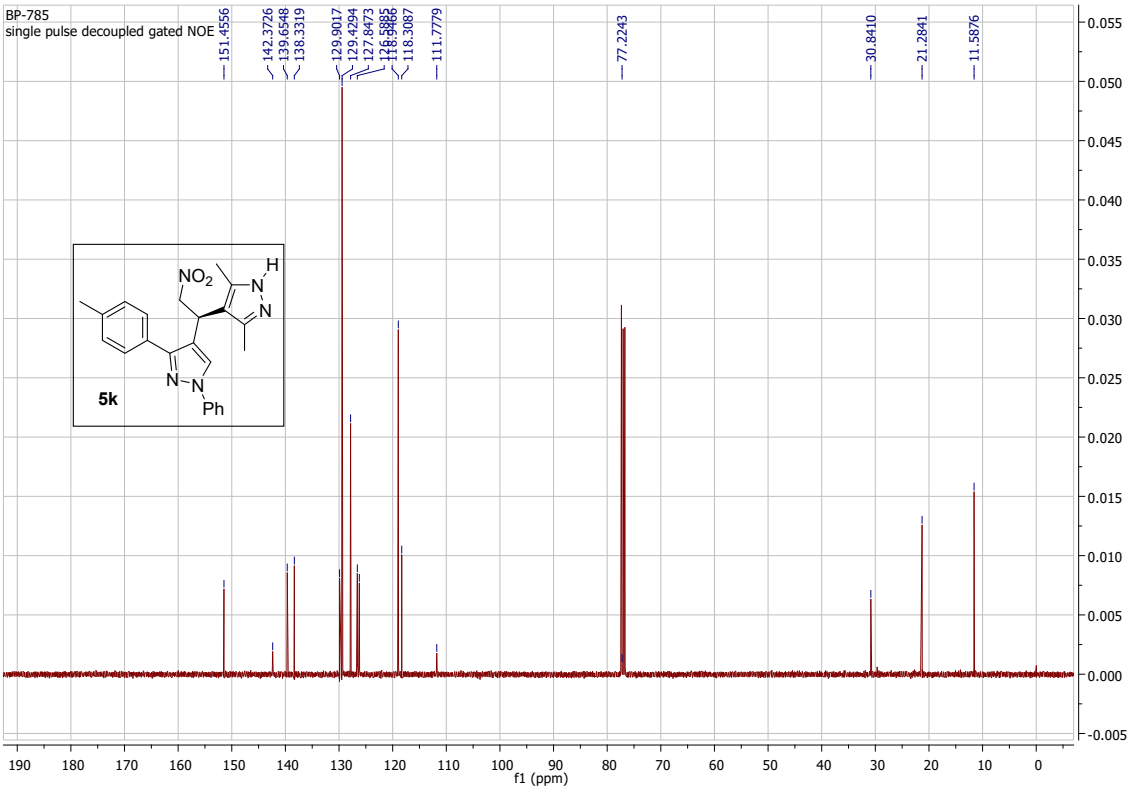

b-704
single pulse
7.7901
7.7860
7.6714
7.5673
7.5616
7.5571
7.5448
7.5403
7.4807
7.4761
7.4620
7.4516
7.4457
7.4409
7.4291
7.4247
7.3319
7.3133
7.2945
4.9700
4.9494
4.8556
4.8370
4.8247
4.8062
4.7345
4.7119
4.7037
2.1531
0.96
1.92
1.76
3.92
0.94
0.99
0.91
1.06
1.12
5.84
Br
NO2
H
N
N
N
N
Ph
5i
f1 (ppm)

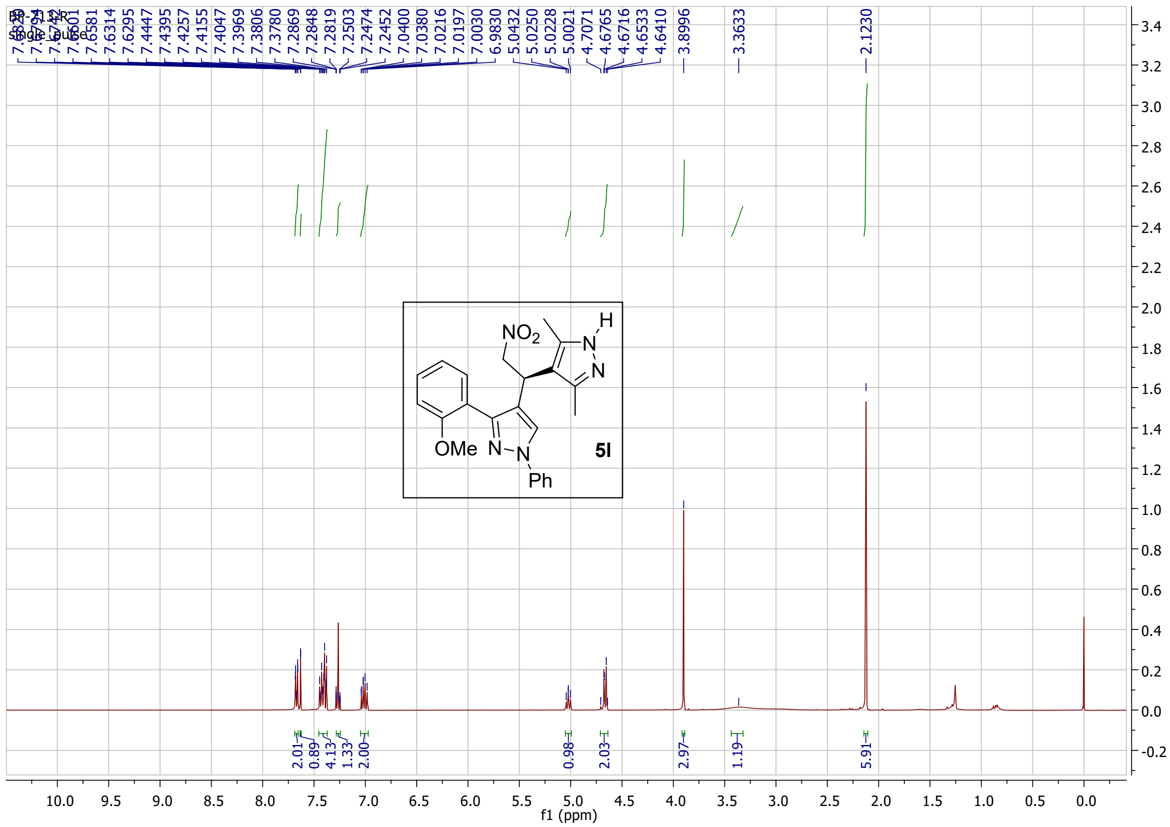

B-704
single pulse decoupled gated NOE
150.4354
142.4109
139.5712
131.8226
129.6481
129.5496
126.9310
126.1462
119.0820
77.5420
30.8706
11.6357
Br
NO2
H
N
N
N
N
Ph
5i
f1 (ppm)

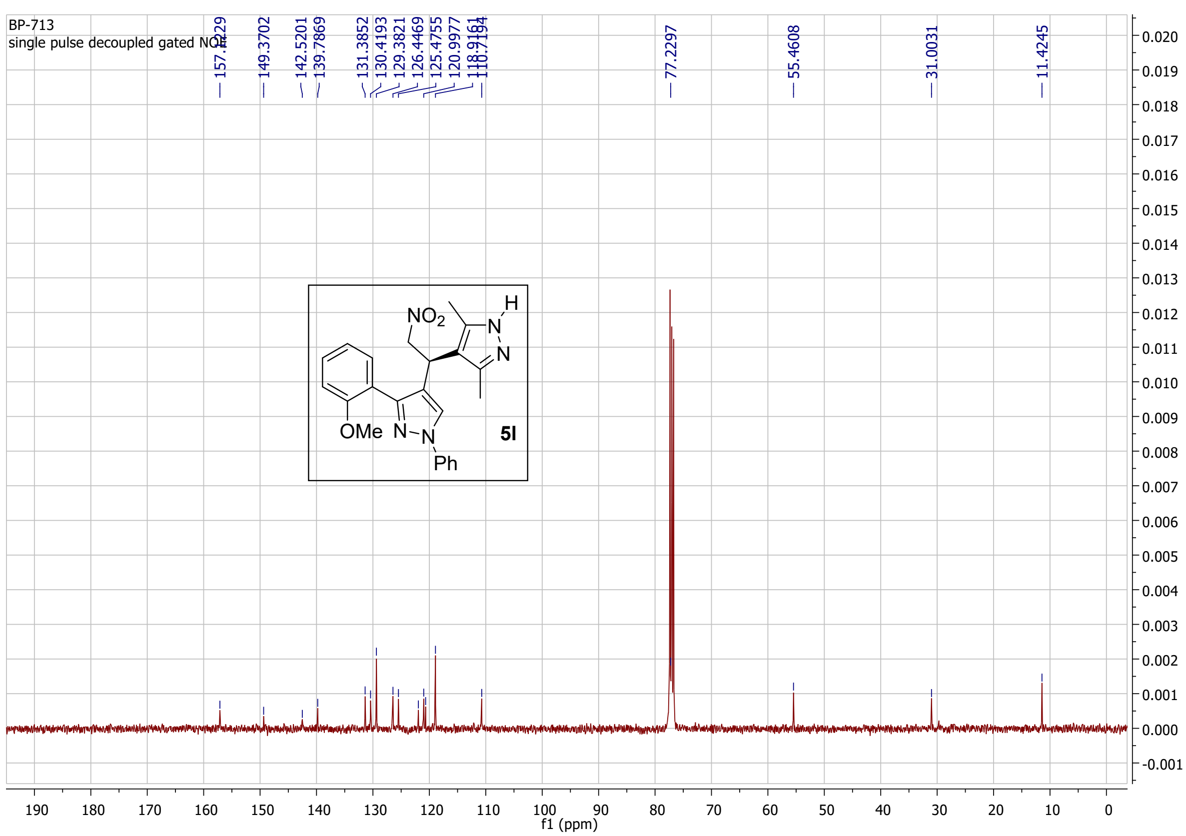

BP-790
single pulse
7.6697
7.4848
7.4799
7.4632
7.4616
7.4465
7.4420
7.3345
7.3318
7.3160
7.2973
7.2538
7.2486
7.2332
7.2281
7.1440
4.8569
4.8413
4.8399
4.8275
4.8088
4.7920
4.7609
4.7446
4.7312
4.7256
4.7120
4.6959
2.0090
NO2
H
Cl
N
N
Cl
N
N
Ph
5j
1.01
2.07
3.11
1.05
0.94
1.58
1.22
2.16
1.08
5.80
f1 (ppm)

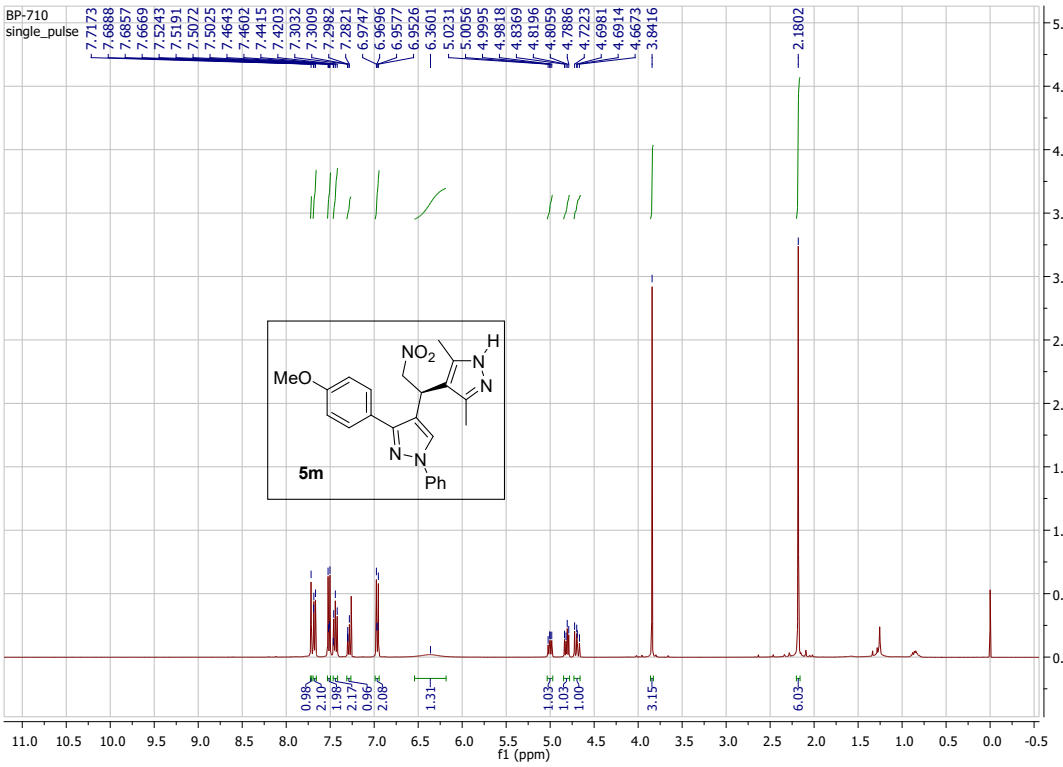

BP-790
single pulse decoupled gated NOE
148.9083
142.2378
139.5253
135.4247
134.8183
132.3735
130.7527
129.5513
129.3354
127.1480
126.9676
125.7712
124.6238
120.4745
119.0824
111.7077
77.2290
30.4720
19.7420
11.1692
NO2
H
Cl
N
N
Cl
N
N
Ph
5j
f1 (ppm)

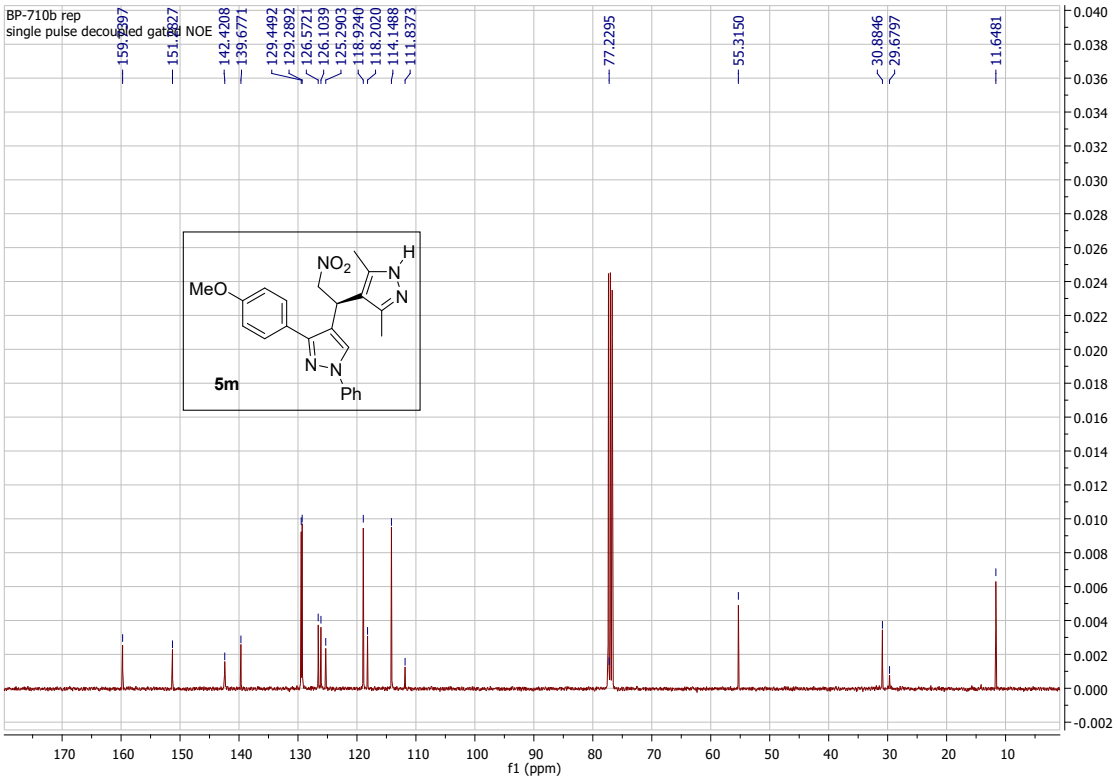

BP-785
single_pulse
7.7131
7.6887
7.6859
7.6669
7.4948
7.4747
7.4544
7.4356
7.4146
7.2968
7.2783
7.2574
7.2506
7.2308
6.5293
5.0432
5.0260
5.0191
5.0017
4.8203
4.8032
4.7893
4.7723
4.7138
4.6892
4.6830
4.6584
2.3846
2.1809
NO2
H
N
N
N
N
Ph
5k
f1 (ppm)

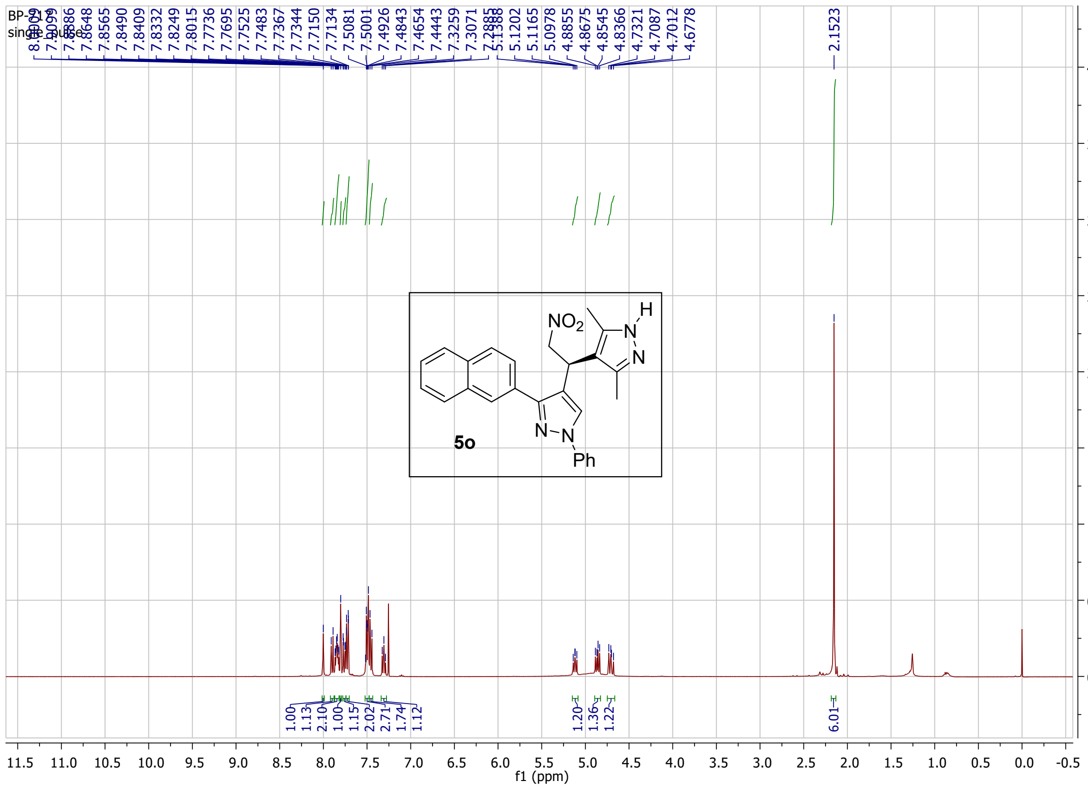

BP-785
single pulse decoupled gated NOE
151.4556
142.3726
139.6548
138.3319
129.9017
129.4294
127.8473
126.5885
118.9466
118.3087
111.7779
77.2243
30.8410
21.2841
11.5876
NO2
H
N
N
N
N
Ph
5k
f1 (ppm)

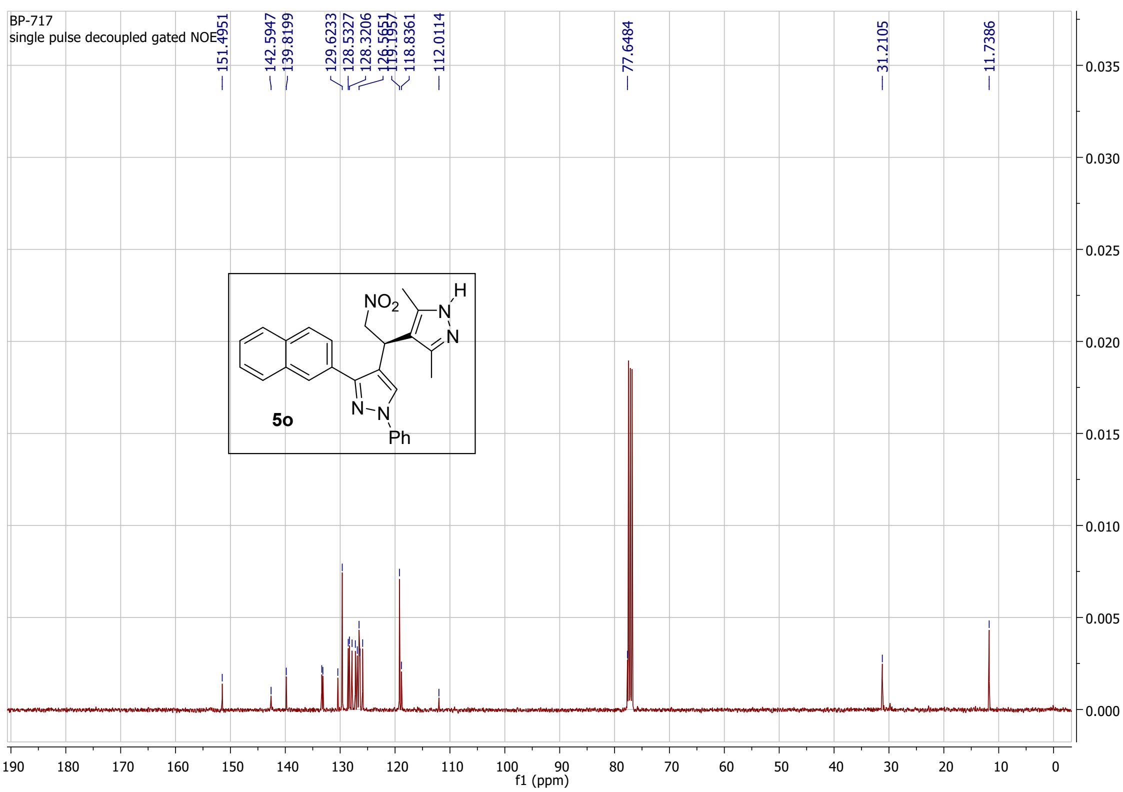

BP-712-R
single_pulse
5l
f1 (ppm)


BP-713
single pulse decoupled gated NOE
157.4229
149.3702
142.5201
139.7869
131.3852
130.4193
129.3821
126.4469
125.4755
120.9977
118.9161
110.7194
77.2297
55.4608
31.0031
11.4245
5l
f1 (ppm)

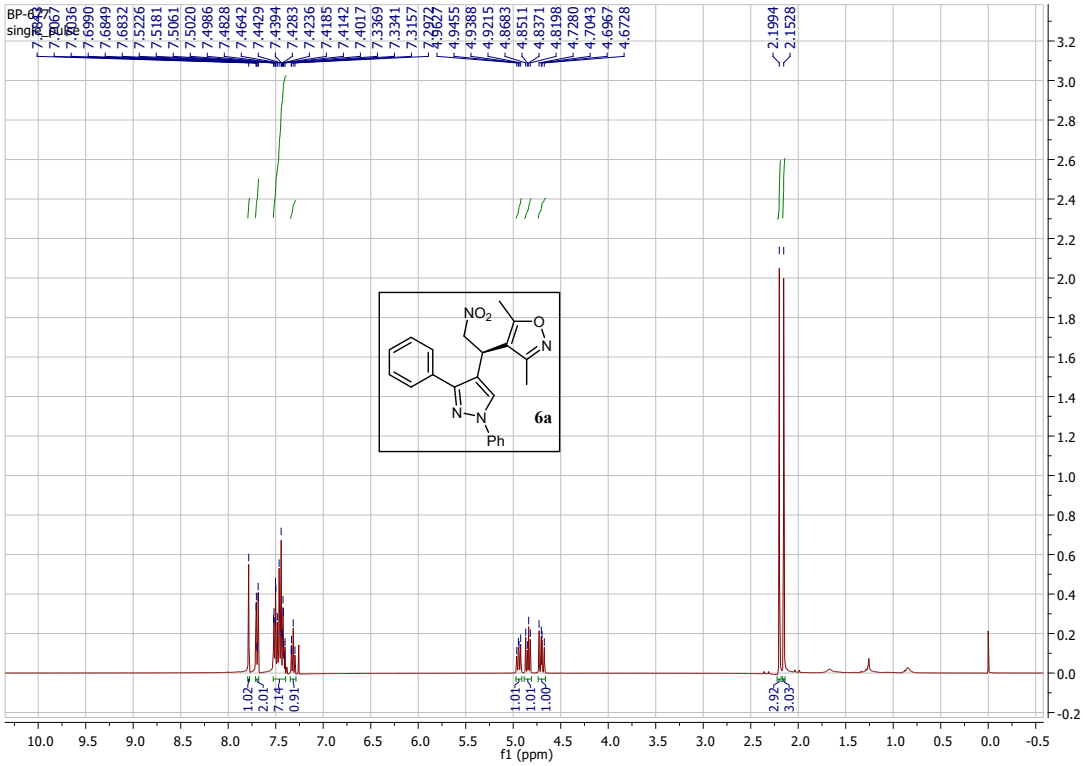

BP-710
single_pulse
7.7173
7.6888
7.6857
7.6669
7.5243
7.5191
7.5072
7.5025
7.4643
7.4602
7.4415
7.4203
7.3032
7.3009
7.2982
7.2821
6.9747
6.9696
6.9577
6.9526
6.3601
5.0231
5.0056
4.9995
4.9818
4.8369
4.8196
4.8059
4.7886
4.7223
4.6981
4.6914
4.6673
3.8416
2.1802
NO2
H
N
N
MeO
N
N
Ph
5m
0.98
2.10
1.98
2.17
0.96
2.08
1.31
1.03
1.03
1.00
3.15
6.03
f1 (ppm)

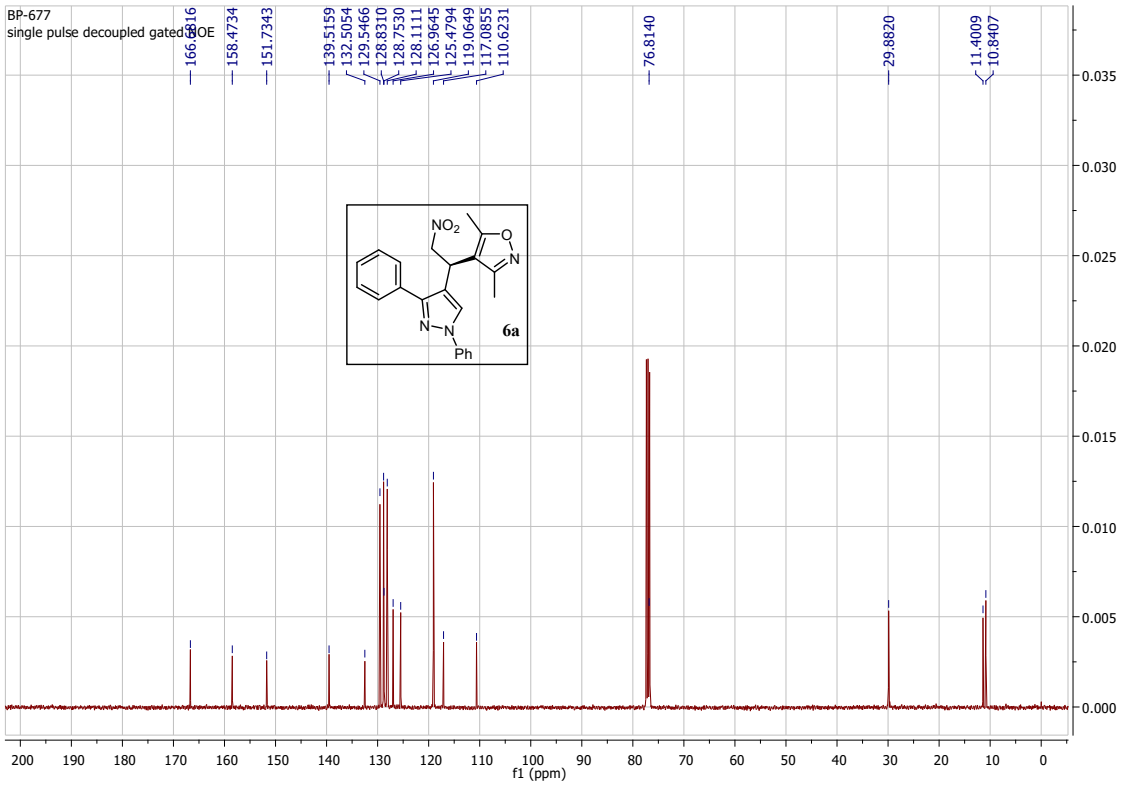

BP-710b rep
single pulse decoupled gated NOE
159.4997
151.8827
142.4208
139.6771
129.4492
129.2892
126.5721
126.1039
125.2903
118.9240
118.2020
114.1488
111.8373
77.2295
55.3150
30.8846
29.6797
11.6481
NO2
H
N
N
MeO
N
N
Ph
5m
f1 (ppm)

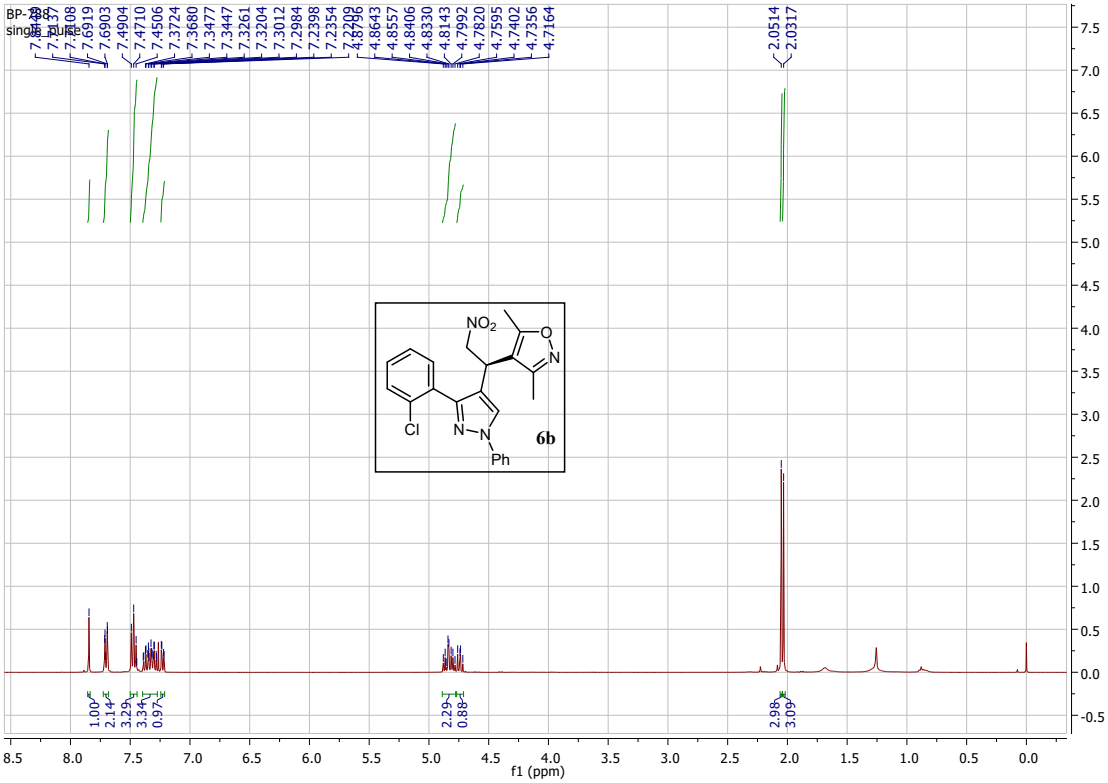

BP-719
single pulse
2.1523
NO2
H
N
N
N
N
5o
Ph
f1 (ppm)
1.00
1.13
2.10
1.00
1.15
2.02
2.71
1.74
1.12
1.20
1.36
1.22
6.01

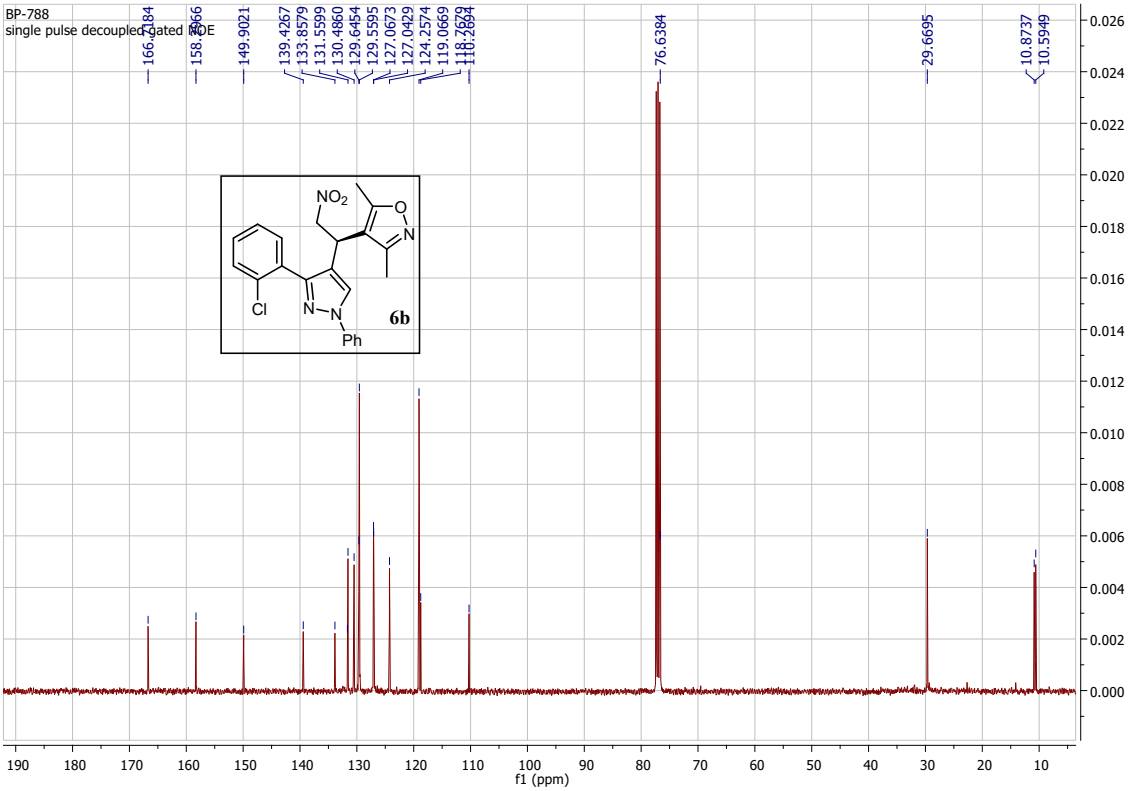

BP-717
single pulse decoupled gated NOE
151.4951
142.5947
139.8199
129.6233
128.5327
128.3206
118.8361
112.0114
77.6484
31.2105
11.7386
NO2
H
N
N
N
N
5o
Ph
f1 (ppm)

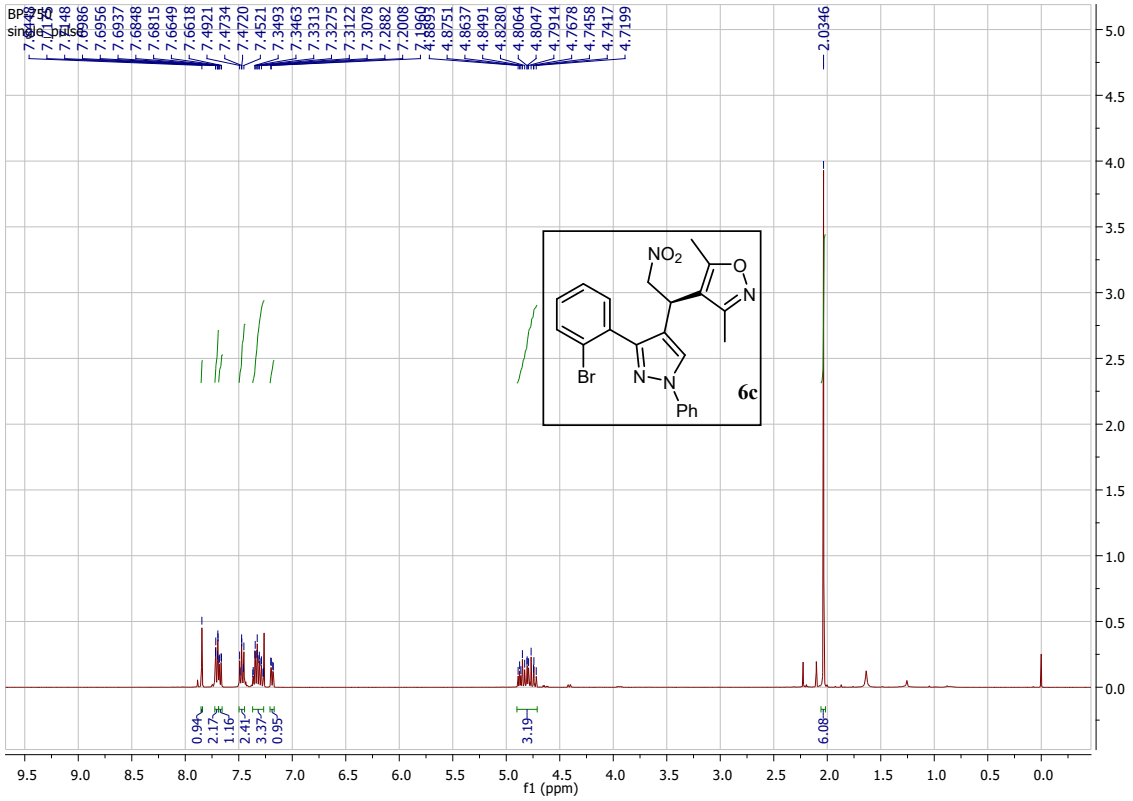
^{1}H and ^{13}C NMR spectra of 6

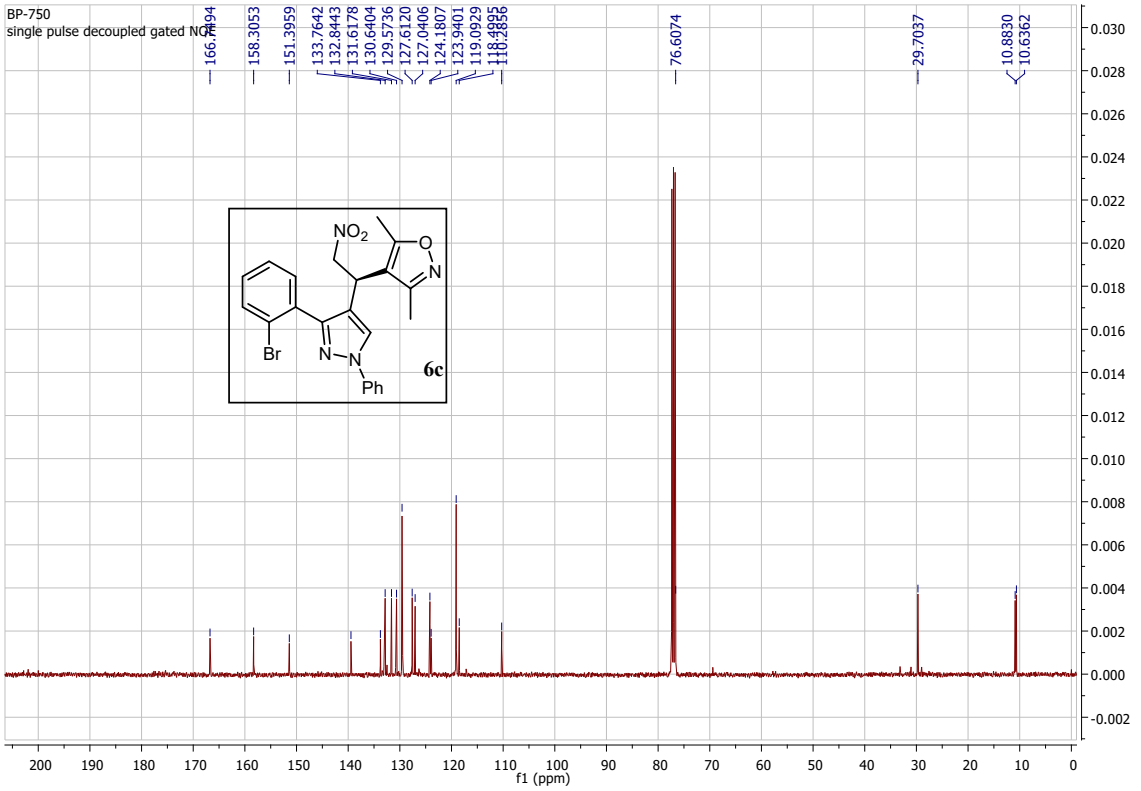


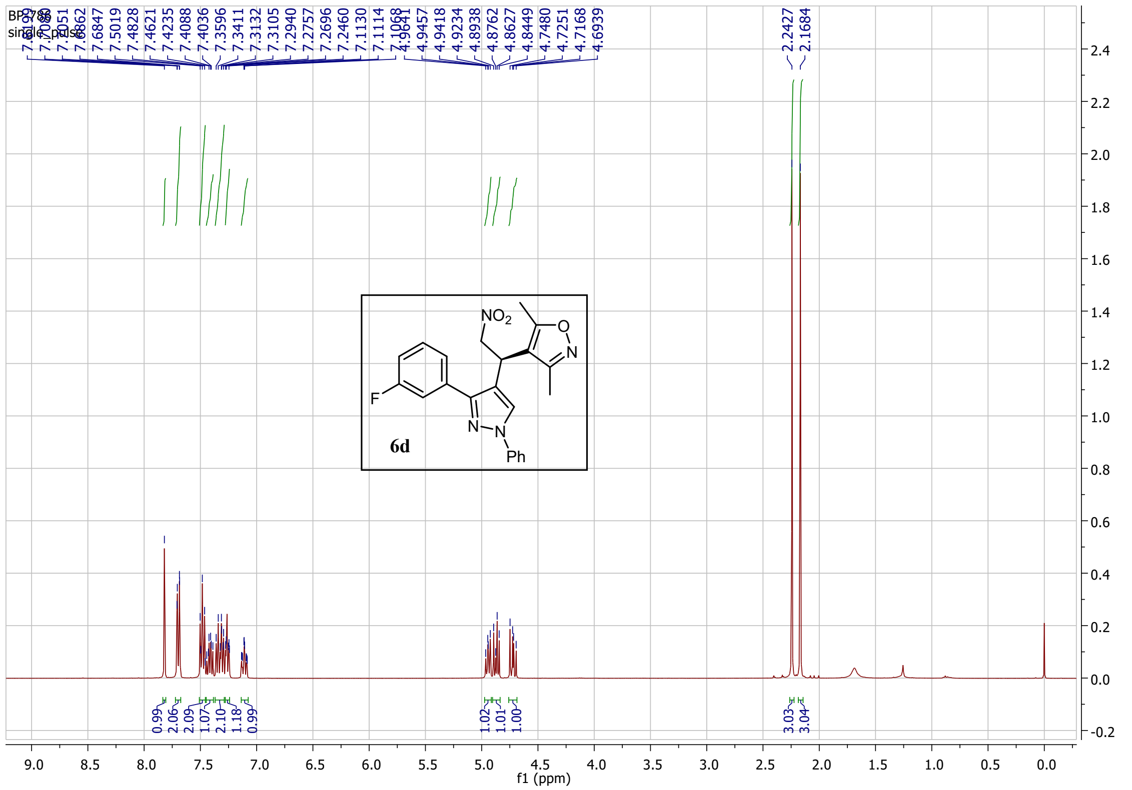


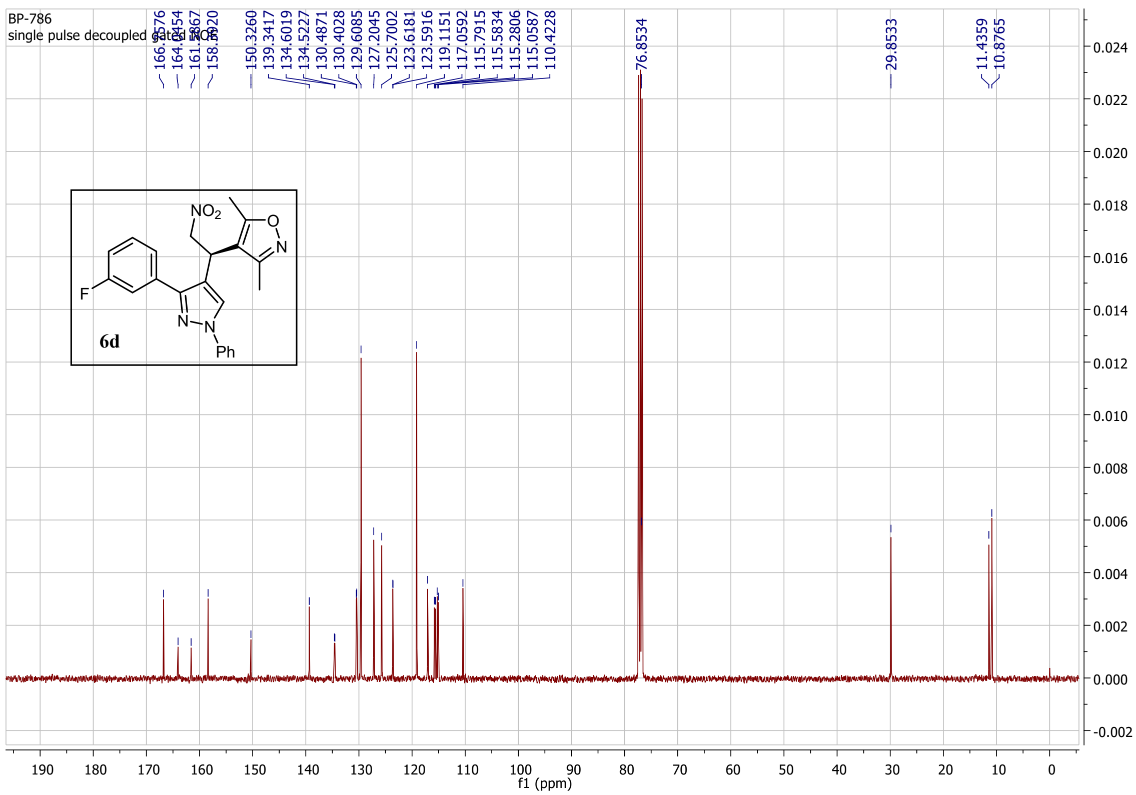

BP-788
single pulse
2.0514
2.0317
6b
f1 (ppm)

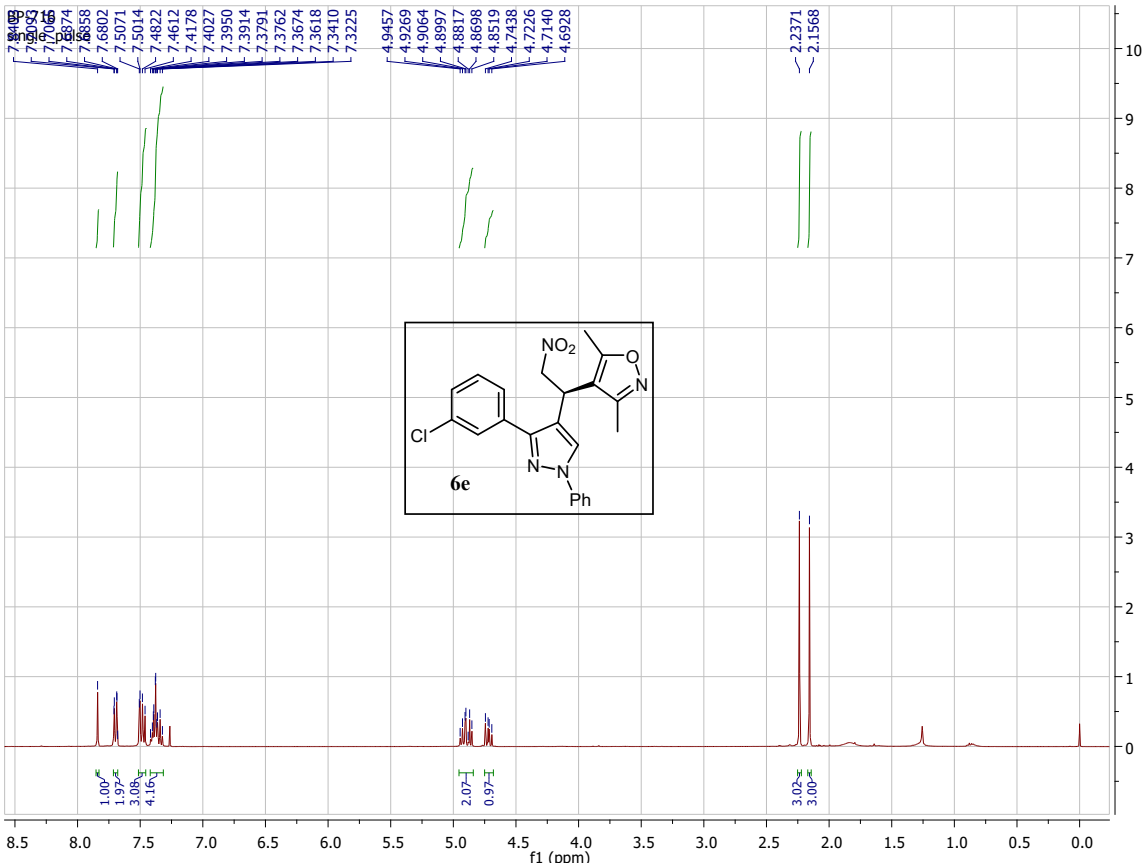

BP-788
single pulse decoupled gated NOE
166.4384
158.4566
149.9021
139.4267
133.8579
131.5599
130.4860
129.6454
129.5595
127.0673
127.0429
124.2574
119.0669
118.2679
118.2694
76.6384
29.6695
10.8737
10.5949
6b
f1 (ppm)

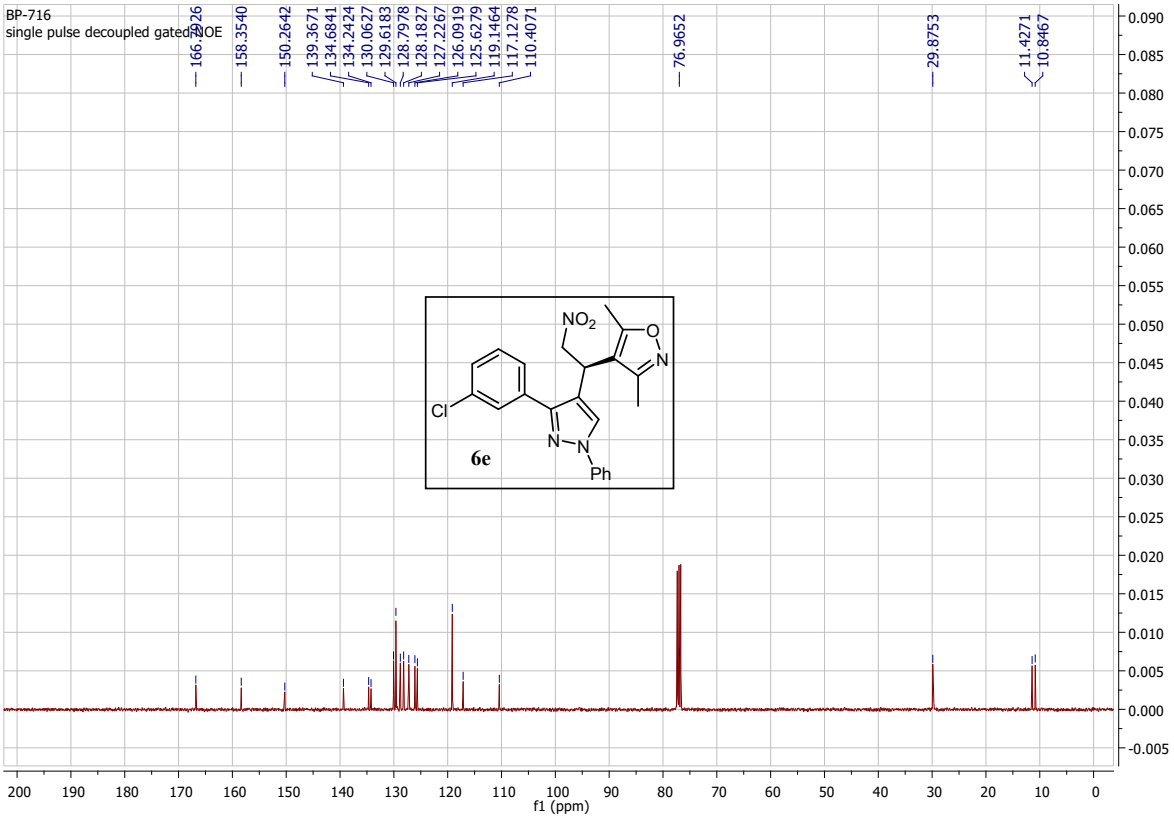

BP-750
single pulse
7.7199
4.7199
2.0346
NO2
O
N
Br
N
N
Ph
6c
0.94
2.17
1.16
2.41
3.37
0.95
3.19
6.08
f1 (ppm)


BP-750
single pulse decoupled gated NOE
166.4194
158.3053
151.3959
133.7642
132.8443
131.6178
130.6404
129.5736
127.6120
127.0406
124.1807
123.9401
119.0929
118.4895
110.2856
76.6074
29.7037
10.8830
10.6362
NO2
O
N
Br
N
N
Ph
6c
f1 (ppm)

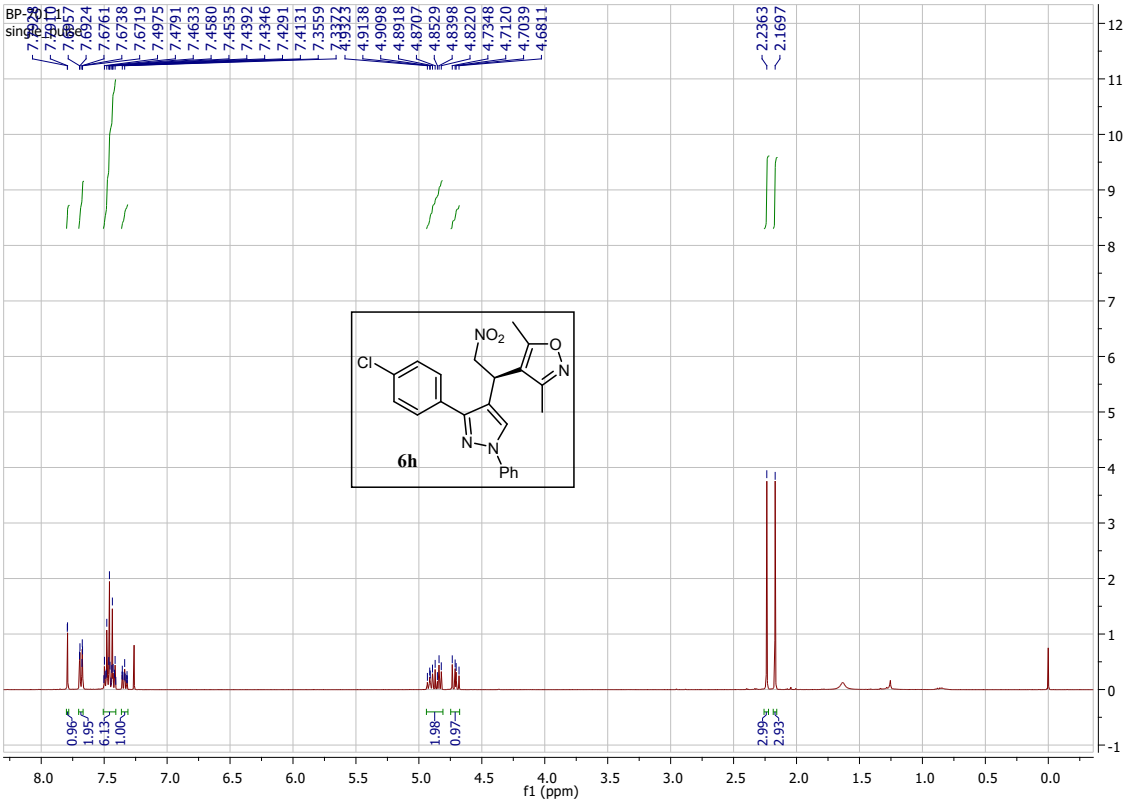

BP-786
single pulse
6d
f1 (ppm)

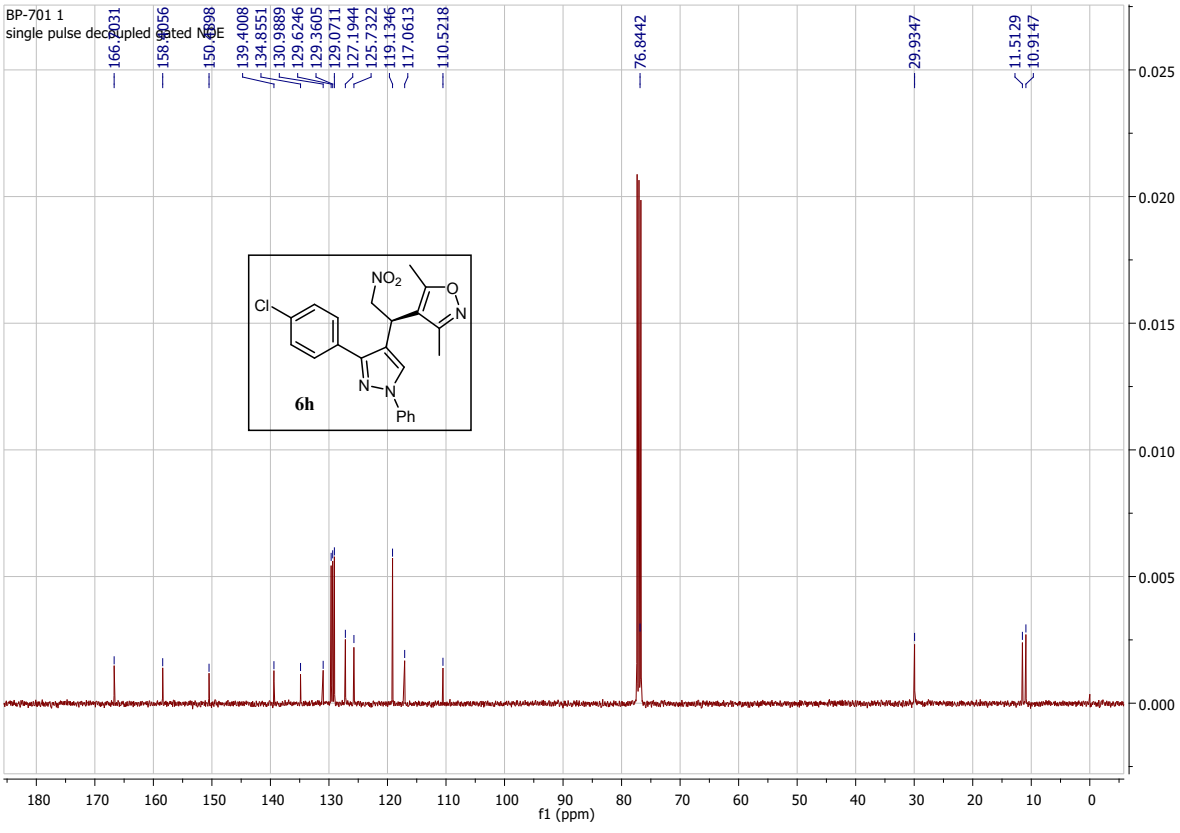

BP-786
single pulse decoupled gated NOE
6d
f1 (ppm)

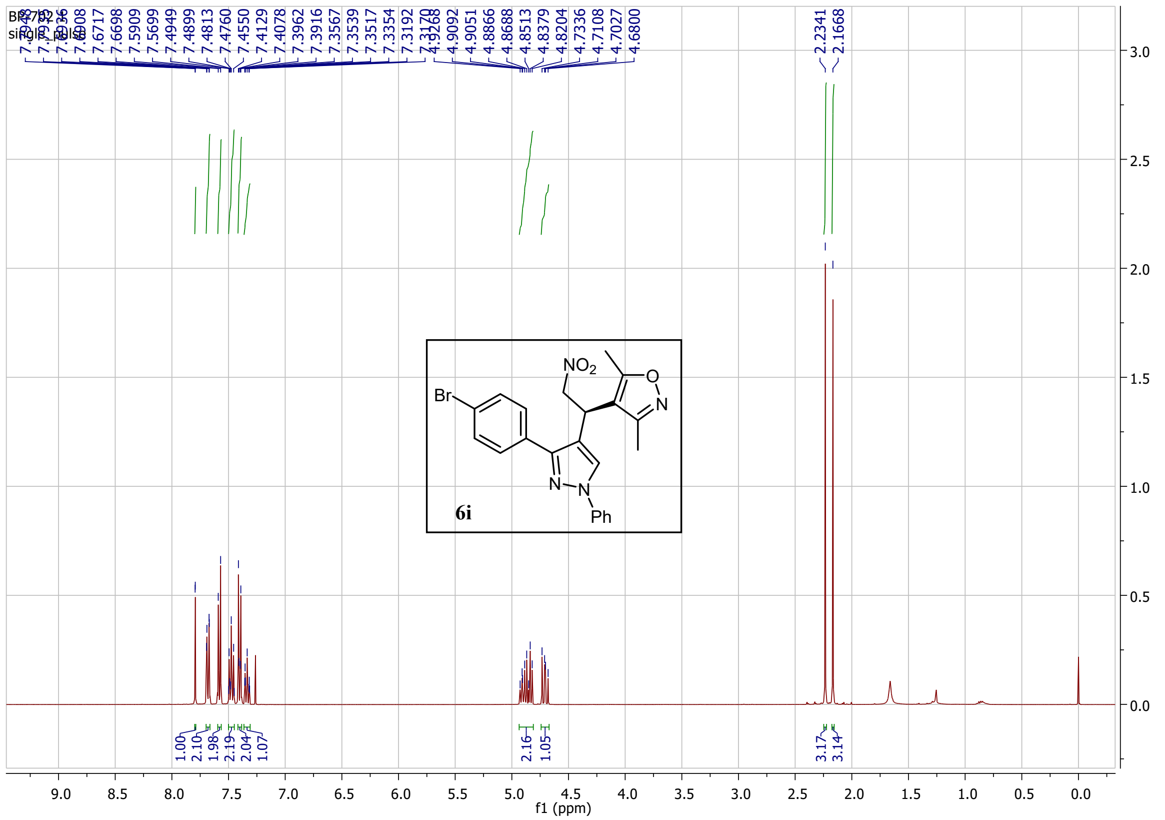

BP-716
single pulse
7.6802
7.5071
7.5014
7.4822
7.4612
7.4178
7.4027
7.3950
7.3914
7.3791
7.3762
7.3674
7.3618
7.3410
7.3225
4.9457
4.9269
4.9064
4.8997
4.8817
4.8698
4.8519
4.7438
4.7226
4.7140
4.6928
2.2371
2.1568
NO2
O
N
Cl
N
N
Ph
6e
1.00
1.97
3.08
4.16
2.07
0.97
3.02
3.00
f1 (ppm)

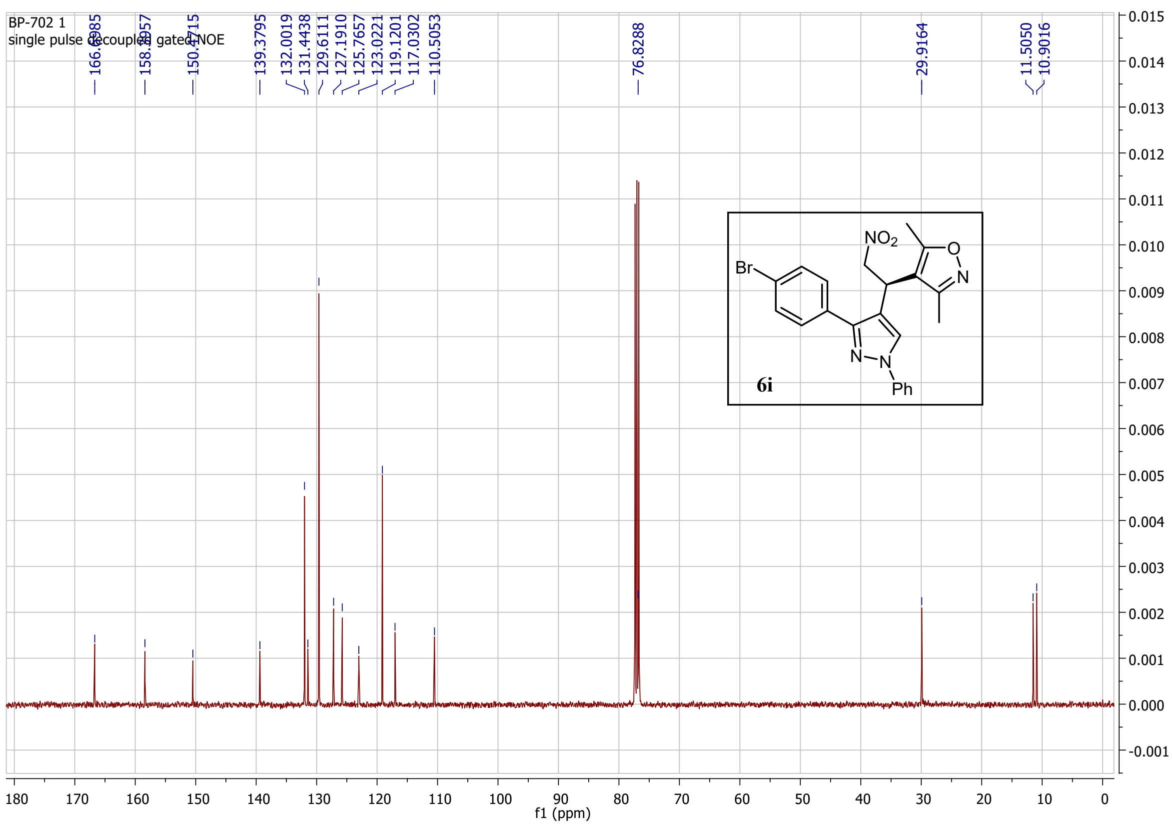

BP-716
single pulse decoupled gated NOE
166.4026
158.3540
150.2642
139.3671
134.6841
134.2424
130.0627
129.6183
128.7978
128.1827
127.2267
126.0919
125.6279
119.1464
117.1278
110.4071
76.9652
29.8753
11.4271
10.8467
NO2
O
N
Cl
N
N
Ph
6e
f1 (ppm)

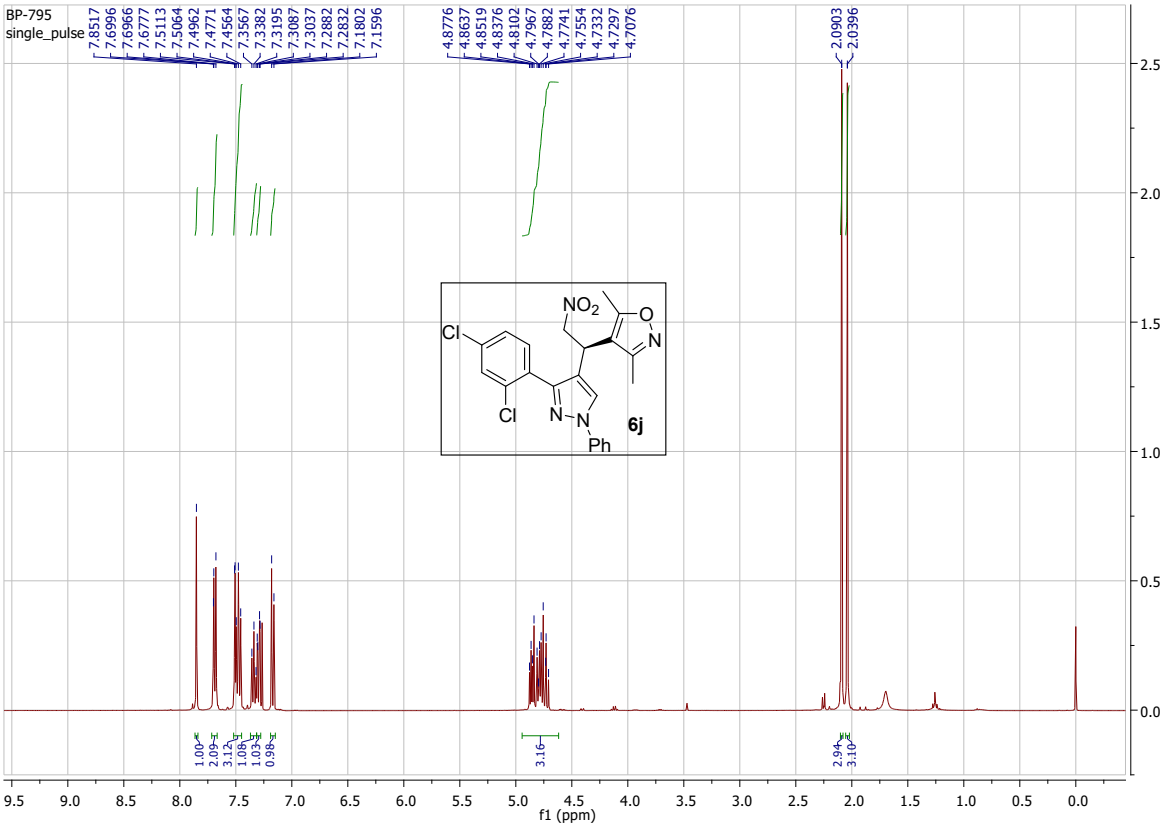
f

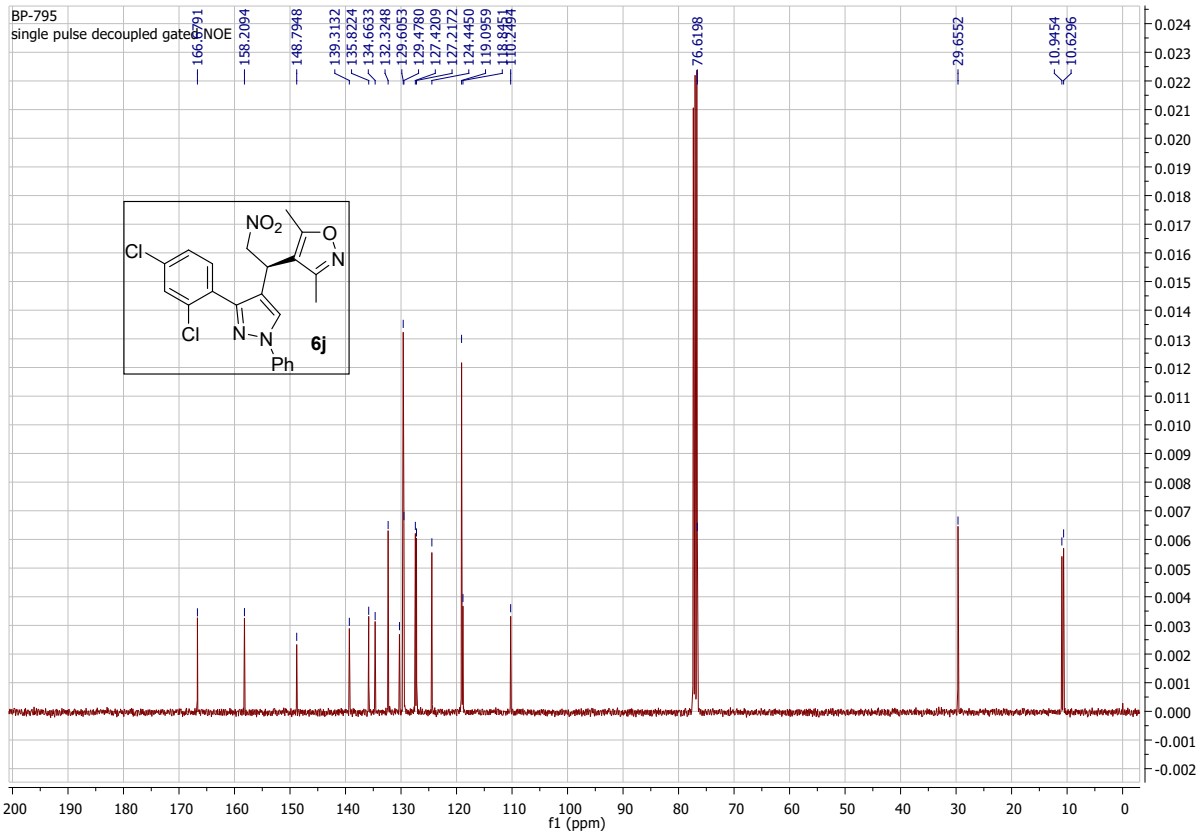

BP-701 1
single pulse
7.7200
7.7057
7.6924
7.6761
7.6738
7.6719
7.4975
7.4791
7.4633
7.4580
7.4535
7.4392
7.4346
7.4291
7.4131
7.3559
4.9138
4.9098
4.8918
4.8707
4.8529
4.8398
4.8220
4.7348
4.7120
4.7039
4.6811
2.2363
2.1697
NO2
O
N
Cl
N
N
Ph
6h
0.96
1.95
6.13
1.00
1.98
0.97
2.99
2.93
f1 (ppm)

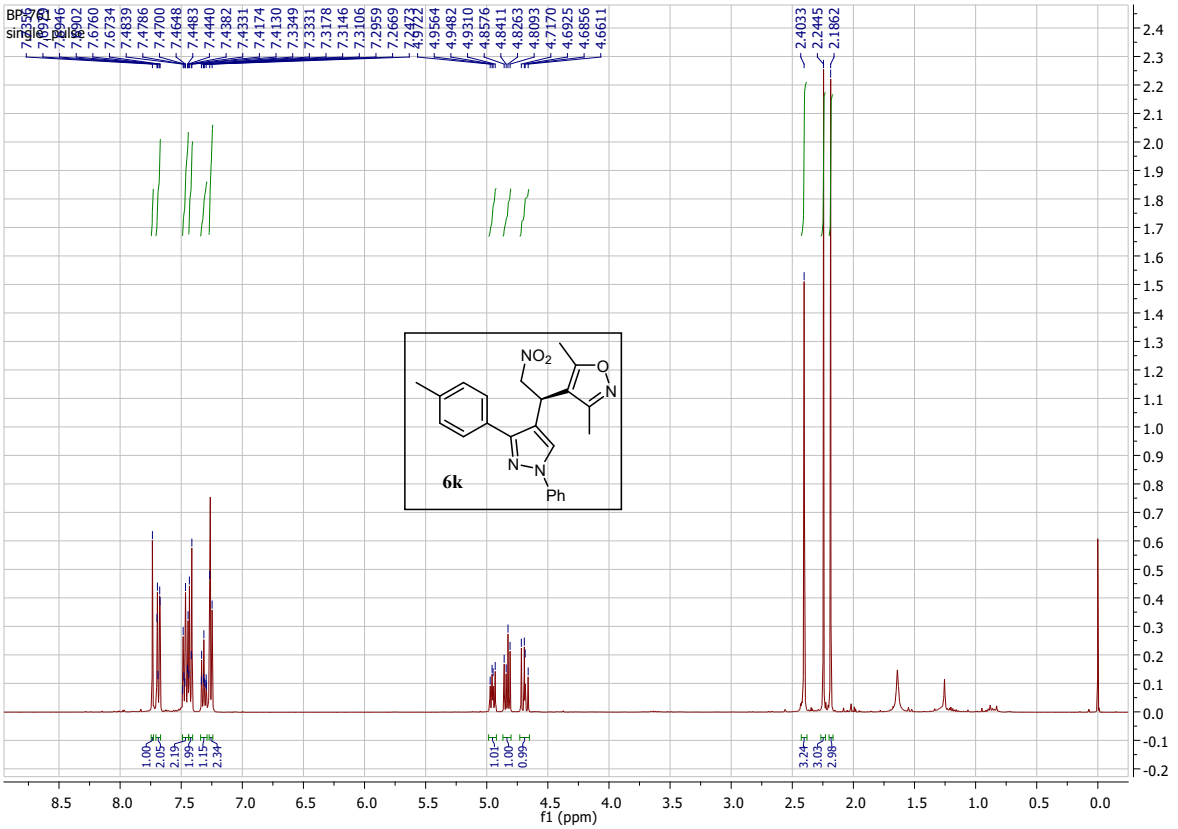

BP-701 1
single pulse decoupled gated NOE
166.8031
158.8056
150.8398
139.4008
134.8551
130.9889
129.6246
129.3605
129.0711
127.1944
125.7322
119.1346
117.0613
110.5218
76.8442
29.9347
11.5129
10.9147
NO2
O
N
Cl
N
N
Ph
6h
f1 (ppm)

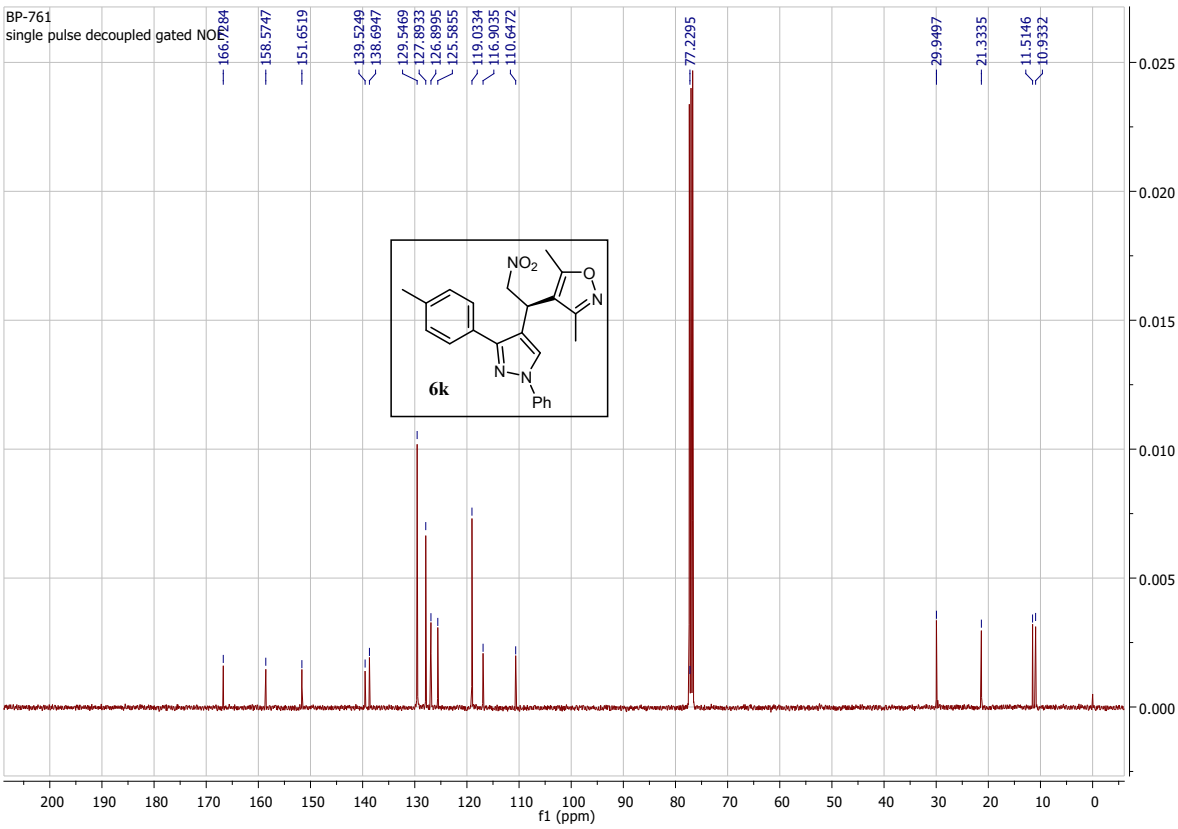

single_pulse
7.6717
7.6698
7.5909
7.5699
7.4949
7.4899
7.4813
7.4760
7.4550
7.4129
7.4078
7.3962
7.3916
7.3567
7.3539
7.3517
7.3354
7.3192
4.9268
4.9092
4.9051
4.8866
4.8688
4.8513
4.8379
4.8204
4.7336
4.7108
4.7027
4.6800
2.2341
2.1668
1.00
2.10
1.98
2.19
2.04
1.07
2.16
1.05
3.17
3.14
f1 (ppm)
NO2
Br
O
N
N
N
Ph
6i

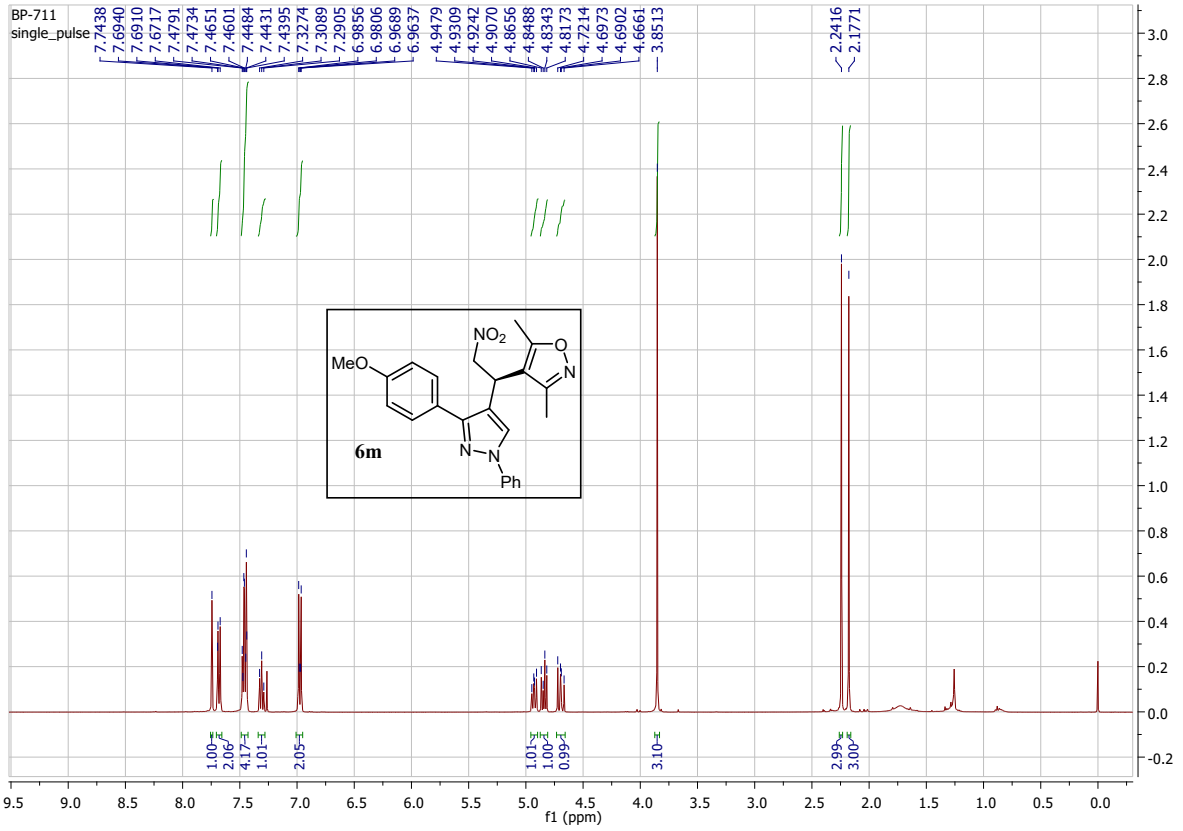

BP-702 1
single pulse decoupled gated NOE
166.6985
158.3957
150.4215
139.3795
132.0019
131.4438
129.6111
127.1910
125.7657
123.0221
119.1201
117.0302
110.5053
76.8288
29.9164
11.5050
10.9016
f1 (ppm)
NO2
Br
O
N
N
N
Ph
6i

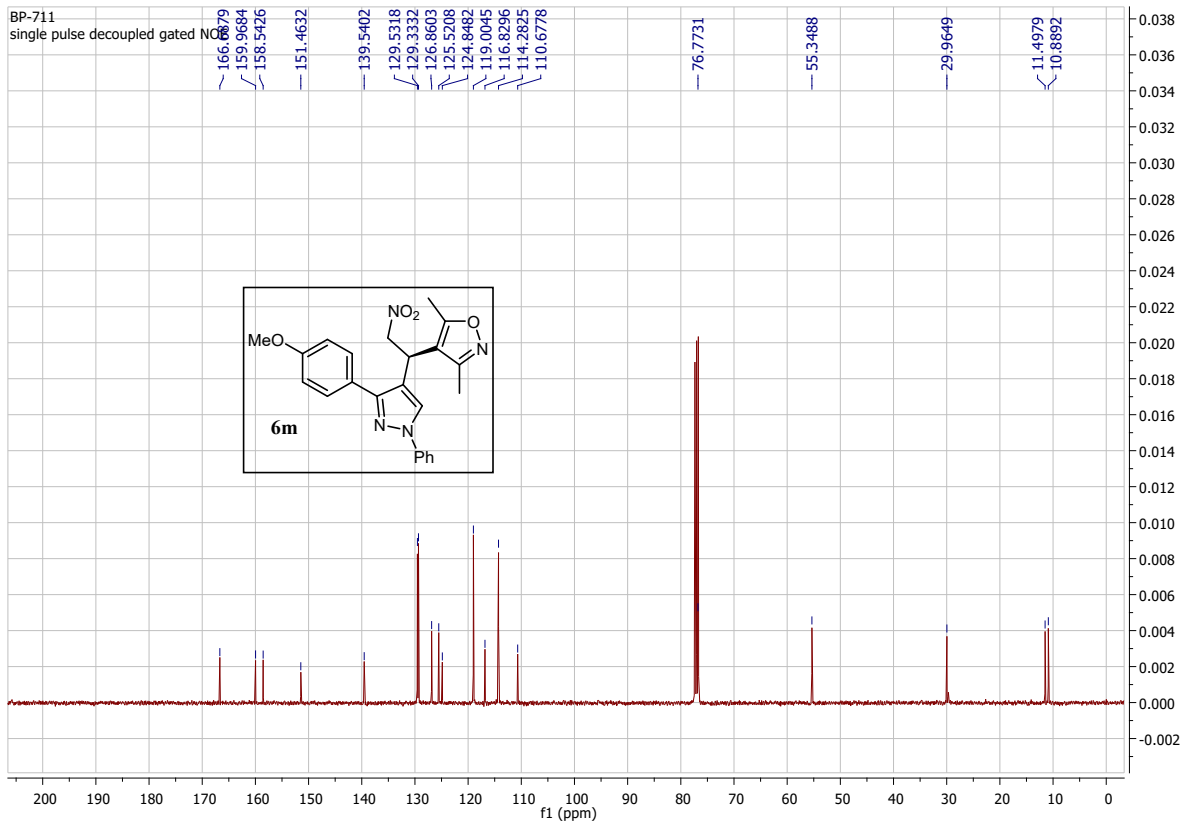

BP-795
single_pulse
7.8517
7.6996
7.6966
7.6777
7.5113
7.5064
7.4962
7.4771
7.4564
7.3567
7.3382
7.3195
7.3087
7.3037
7.2882
7.2832
7.1802
7.1596
4.8776
4.8637
4.8519
4.8376
4.8102
4.7967
4.7882
4.7741
4.7554
4.7332
4.7297
4.7076
2.0903
2.0396
NO2
O
N
Cl
Cl
N
N
Ph
6j
1.00
2.09
3.12
1.06
1.03
0.98
3.16
2.94
3.10
f1 (ppm)

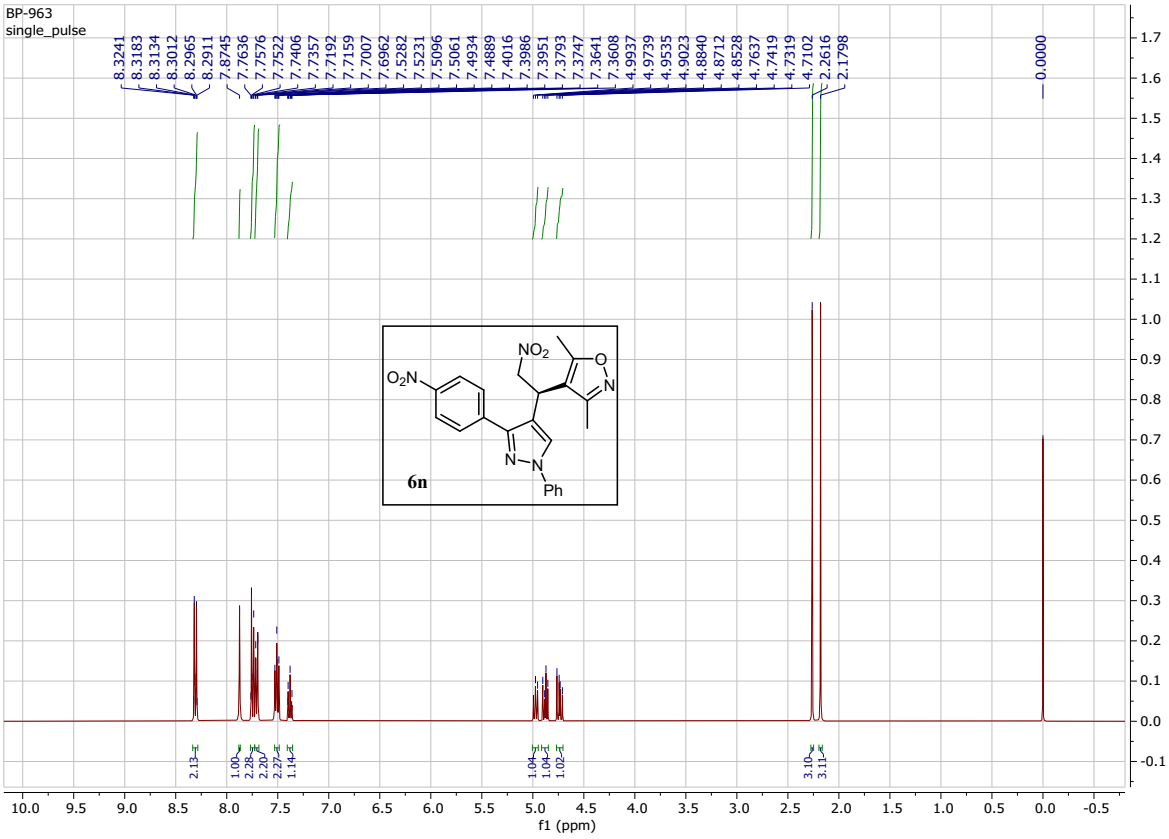

BP-795
single pulse decoupled gated-NOE
166.4791
158.2094
148.7948
139.3132
135.8224
134.6633
132.3248
129.6053
129.4780
127.4209
127.2172
124.4450
119.0959
118.8451
110.2494
76.6198
29.6552
10.9454
10.6296
NO2
O
N
Cl
Cl
N
N
Ph
6j
f1 (ppm)

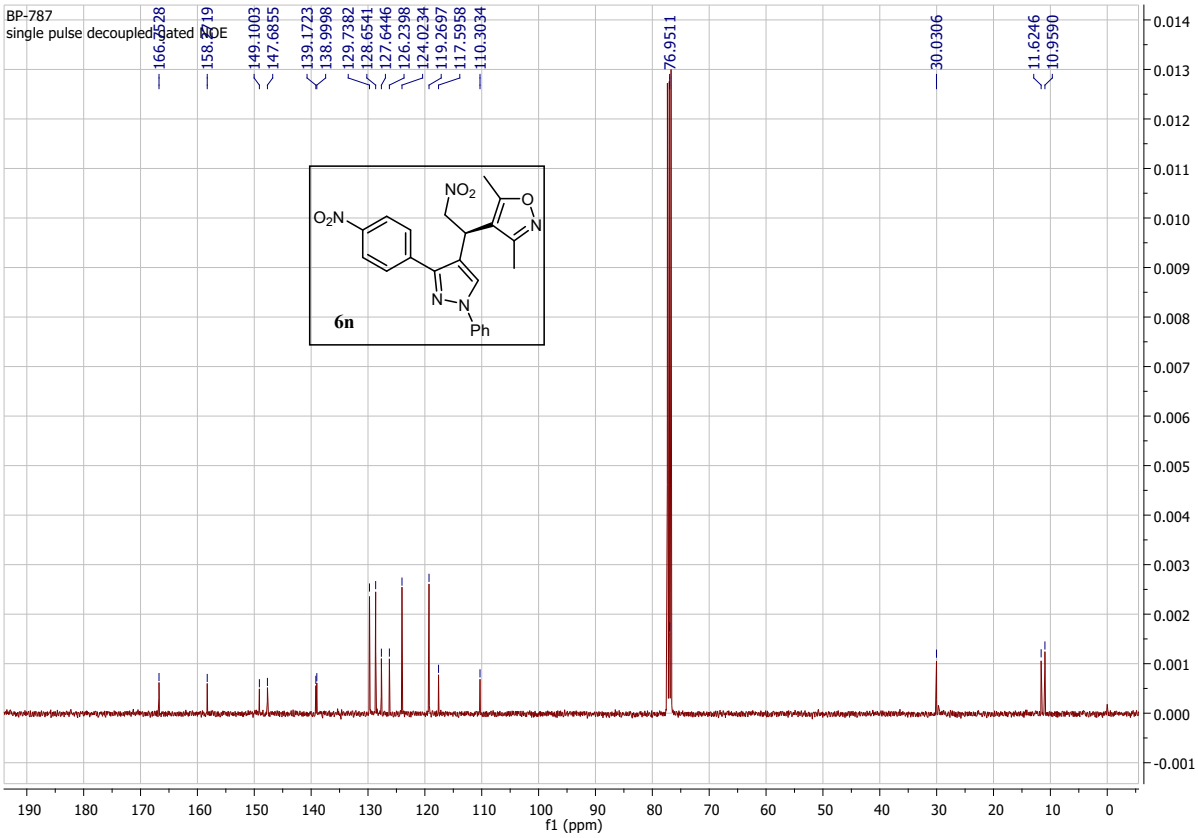

BP-761
single pulse
2.4033
2.2445
2.1862
6k
f1 (ppm)

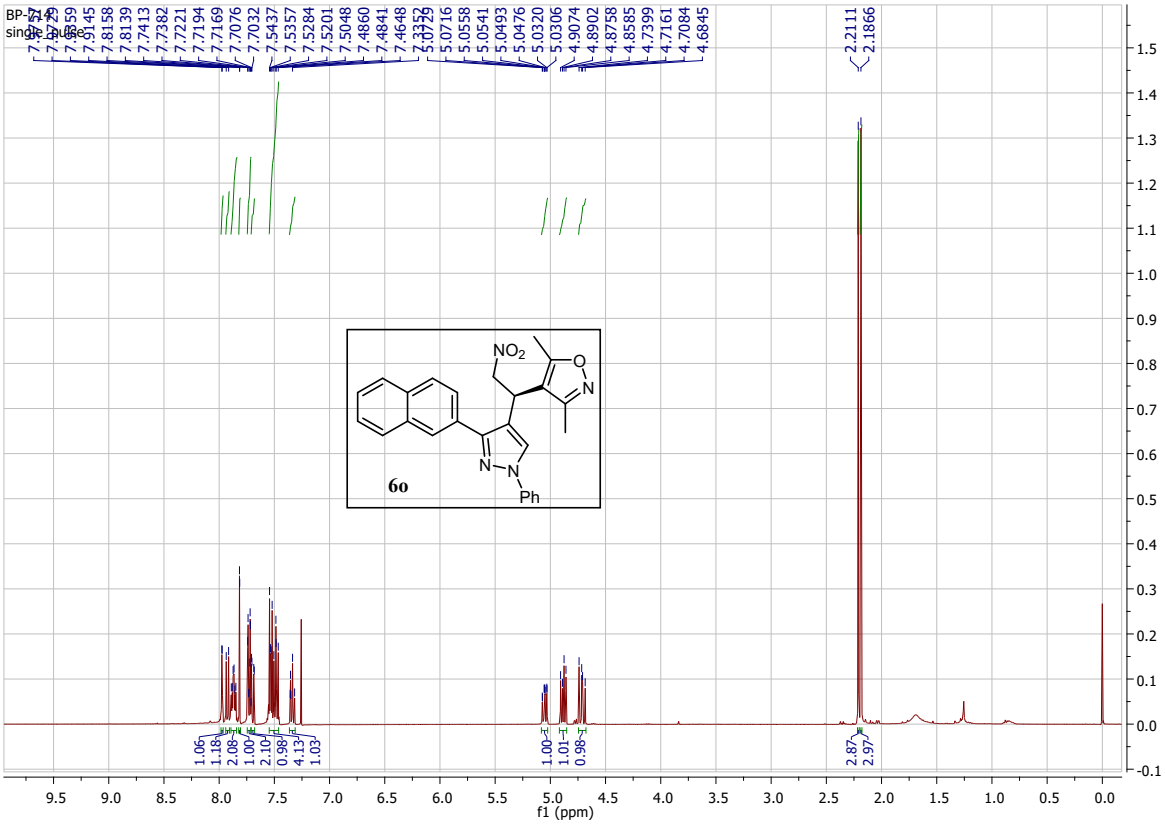

BP-761
single pulse decoupled gated NOE
166.7284
158.5747
151.6519
139.5249
138.6947
129.5469
127.8933
126.8995
125.5855
119.0334
116.9035
110.6472
77.2295
29.9497
21.3335
11.5146
10.9332
6k
f1 (ppm)

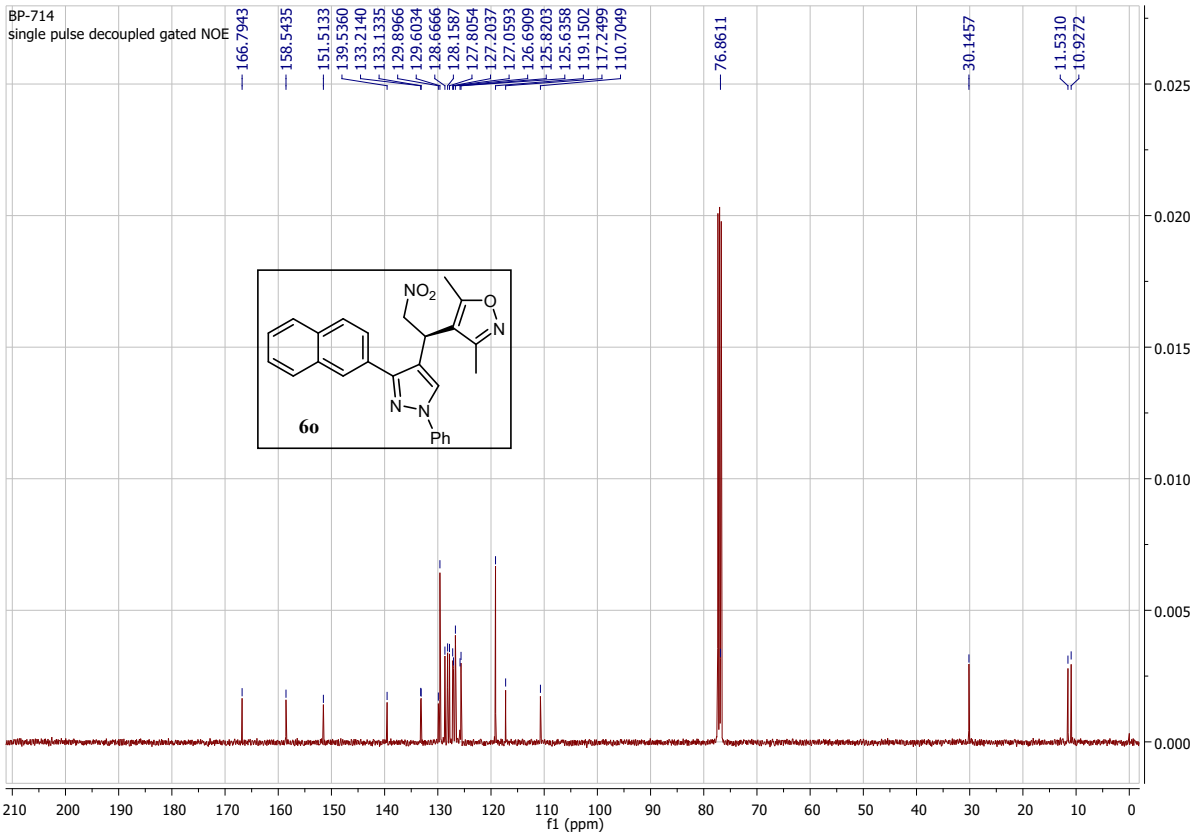

BP-711
single_pulse
7.7438
7.6940
7.6910
7.6717
7.4791
7.4734
7.4651
7.4601
7.4484
7.4431
7.4395
7.3274
7.3089
7.2905
6.9856
6.9806
6.9689
6.9637
4.9479
4.9309
4.9242
4.9070
4.8656
4.8488
4.8343
4.8173
4.7214
4.6973
4.6902
4.6661
3.8513
2.2416
2.1771
MeO
NO2
O
N
N
N
Ph
6m
1.00
2.06
4.17
1.01
2.05
1.01
1.00
0.99
3.10
2.99
3.00
f1 (ppm)

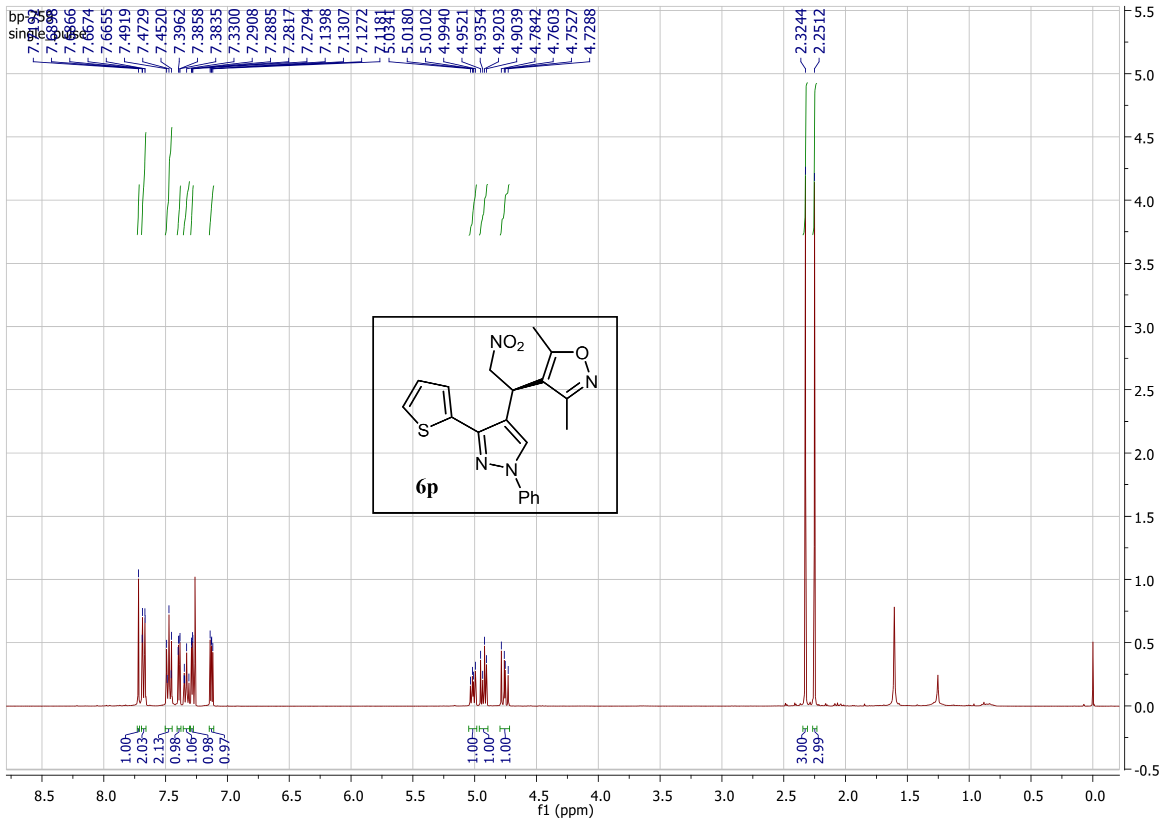

BP-711
single pulse decoupled gated NOE
166.6879
159.9684
158.5426
151.4632
139.5402
129.5318
129.3332
126.8603
125.5208
124.8482
119.0045
116.8296
114.2825
110.6778
76.7731
55.3488
29.9649
11.4979
10.8892
MeO
NO2
O
N
N
N
Ph
6m
f1 (ppm)

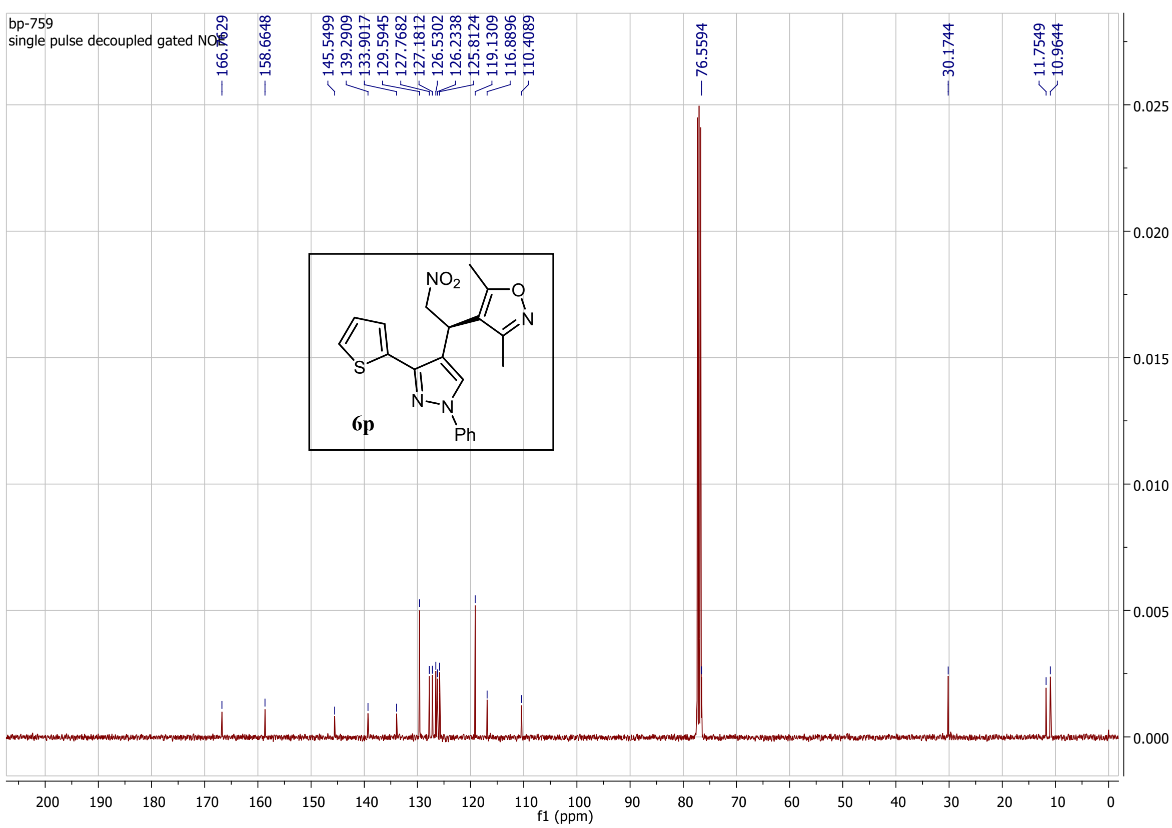

BP-963
single_pulse
8.3241
8.3183
8.3134
8.3012
8.2965
8.2911
7.8745
7.7636
7.7576
7.7522
7.7406
7.7357
7.7192
7.7159
7.7007
7.6962
7.5282
7.5231
7.5096
7.5061
7.4934
7.4889
7.4016
7.3986
7.3951
7.3793
7.3747
7.3641
7.3608
4.9937
4.9739
4.9535
4.9023
4.8840
4.8712
4.8528
4.7637
4.7419
4.7319
4.7102
2.2616
2.1798
0.0000
6n
f1 (ppm)

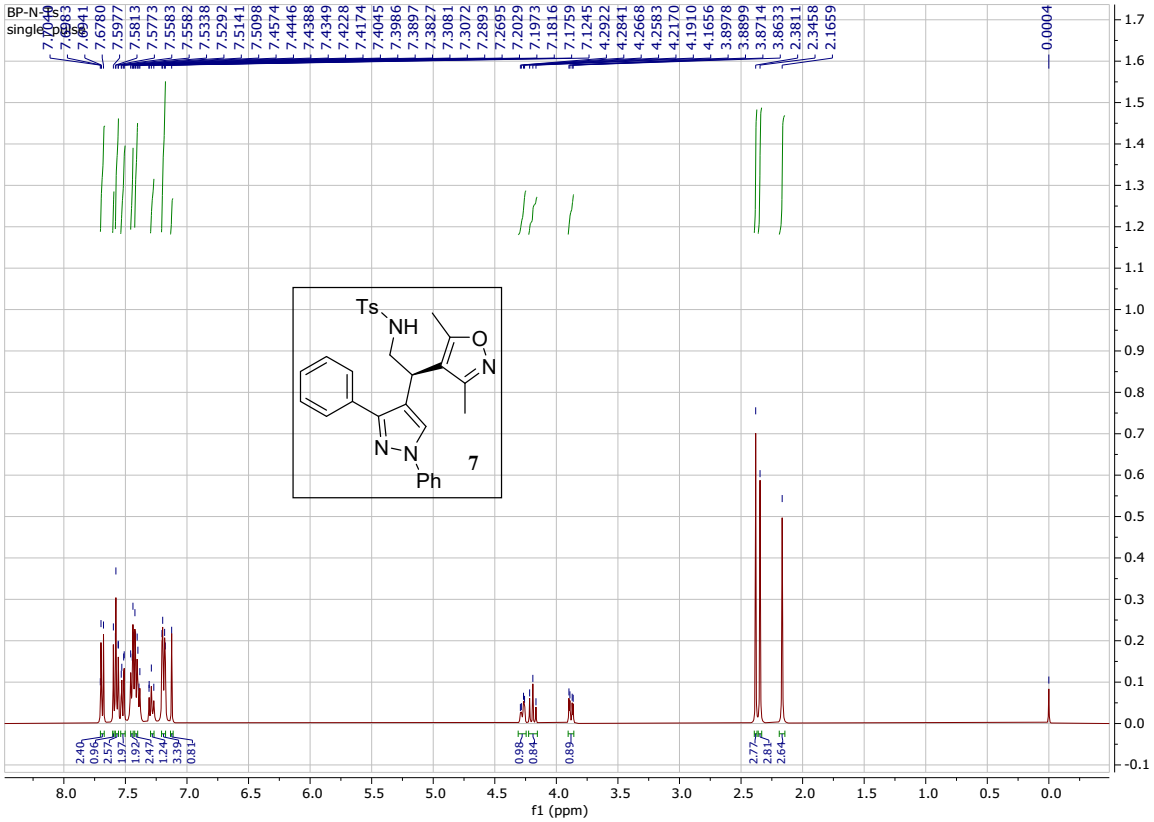

BP-787
single pulse decoupled gated NOE
166.4528
158.4719
149.1003
147.6855
139.1723
138.9998
129.7382
128.6541
127.6446
126.2398
124.0234
119.2697
117.5958
110.3034
76.9511
30.0306
11.6246
10.9590
6n
f1 (ppm)

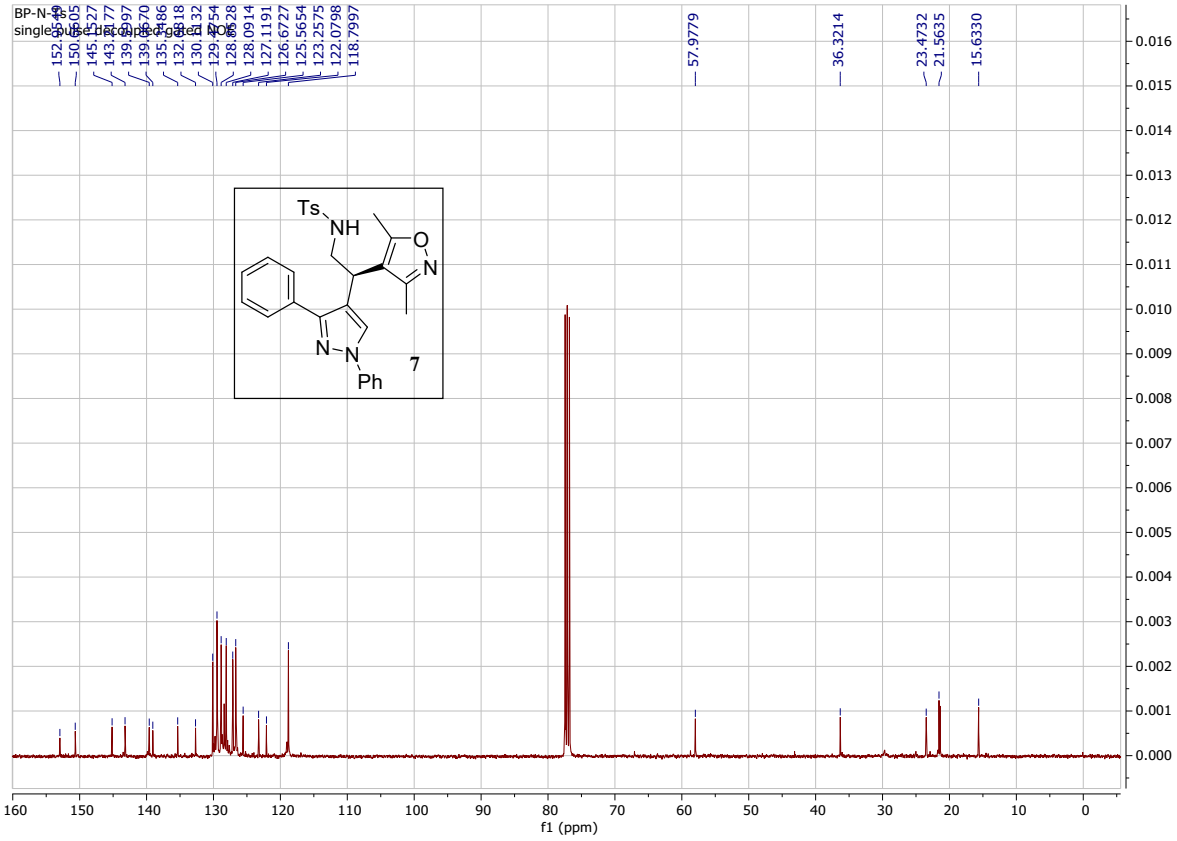

BP-714
single pulse
7.9145
7.8158
7.8139
7.7413
7.7382
7.7221
7.7194
7.7169
7.7076
7.7032
7.5437
7.5357
7.5284
7.5201
7.5048
7.4860
7.4841
7.4648
5.0716
5.0558
5.0541
5.0493
5.0476
5.0320
5.0306
4.9074
4.8902
4.8758
4.8585
4.7399
4.7161
4.7084
4.6845
2.2111
2.1866
1.06
1.18
2.08
1.00
2.10
0.98
4.13
1.03
1.00
1.01
0.98
2.87
2.97
NO2
O
N
N
N
Ph
6o
f1 (ppm)


BP-714
single pulse decoupled gated NOE
166.7943
158.5435
151.5133
139.5360
133.2140
133.1335
129.8966
129.6034
128.6666
128.1587
127.8054
127.2037
127.0593
126.6909
125.8203
125.6358
119.1502
117.2499
110.7049
76.8611
30.1457
11.5310
10.9272
NO2
O
N
N
N
Ph
6o
f1 (ppm)


bp-759
single pulse
7.6674
7.6655
7.4919
7.4729
7.4520
7.3962
7.3858
7.3835
7.3300
7.2908
7.2885
7.2817
7.2794
7.1398
7.1307
7.1272
5.0180
5.0102
4.9940
4.9521
4.9354
4.9203
4.9039
4.7842
4.7603
4.7527
4.7288
2.3244
2.2512
1.00
2.03
2.13
0.98
1.06
0.98
0.97
1.00
1.00
1.00
3.00
2.99
NO2
O
N
S
N
N
Ph
6p
f1 (ppm)

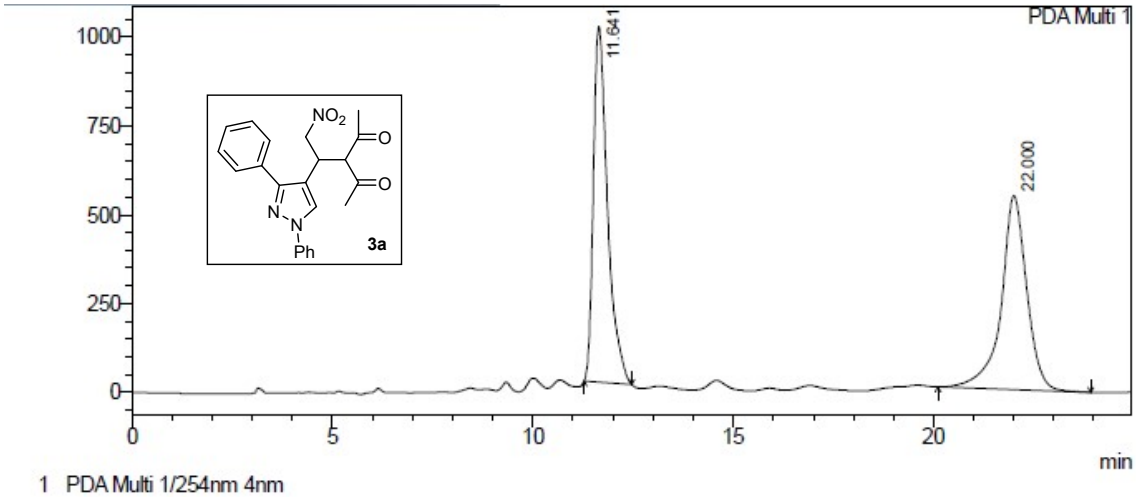

bp-759
single pulse decoupled gated NOE
158.6648
145.5499
139.2909
133.9017
129.5945
127.7682
127.1812
126.5302
126.2338
125.8124
119.1309
116.8896
110.4089
76.5594
30.1744
11.7549
10.9644
NO2
O
N
S
N
N
Ph
6p
f1 (ppm)


BP-N-Ts
single_pulse
Ts
NH
O
N
N
N
Ph
7
f1 (ppm)


BP-N-Ts
single_pulse_decoupled_400
Ts
NH
O
N
N
N
Ph
7
f1 (ppm)

HPLC chromatograms

HPLC chromatogram of Michael adducts 3a-3q

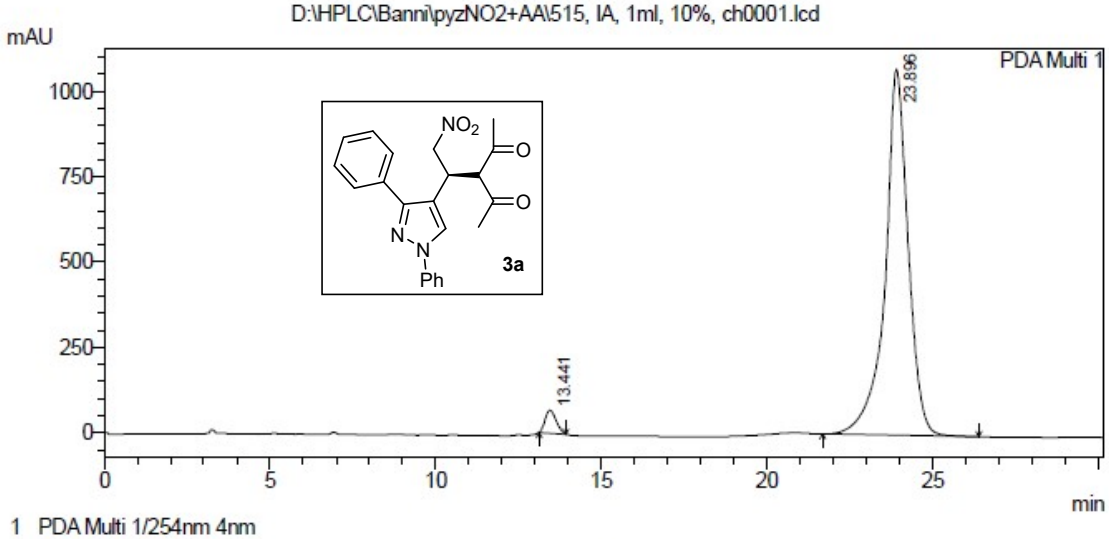


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.641	24744062	1001842	50.480	64.721
2	22.000	24273784	546106	49.520	35.279
Total		49017846	1547948	100.000	100.000

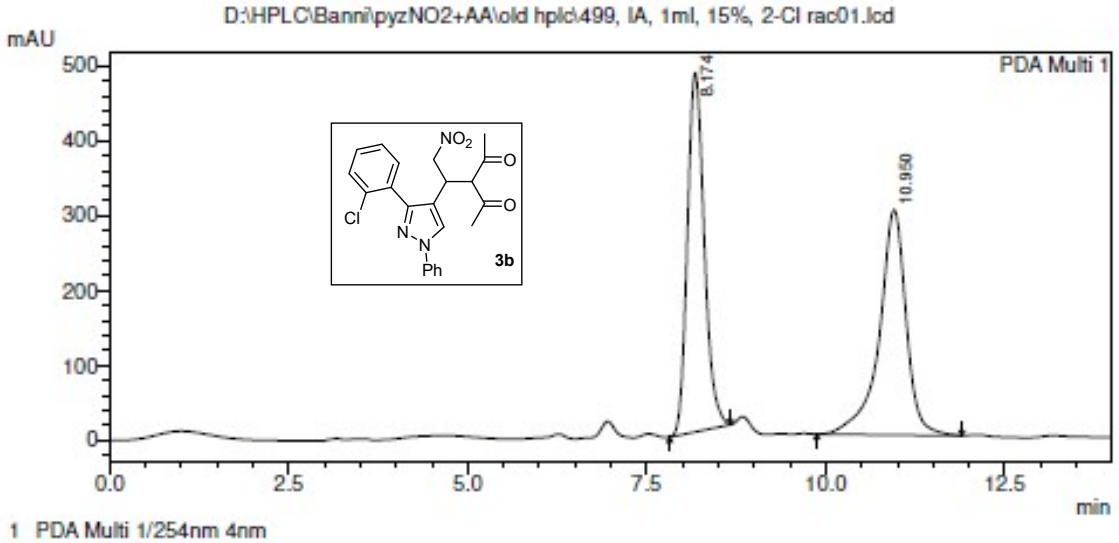


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.441	1548691	67178	2.893	5.896
2	23.896	51992736	1072131	97.107	94.104
Total		53541428	1139310	100.000	100.000

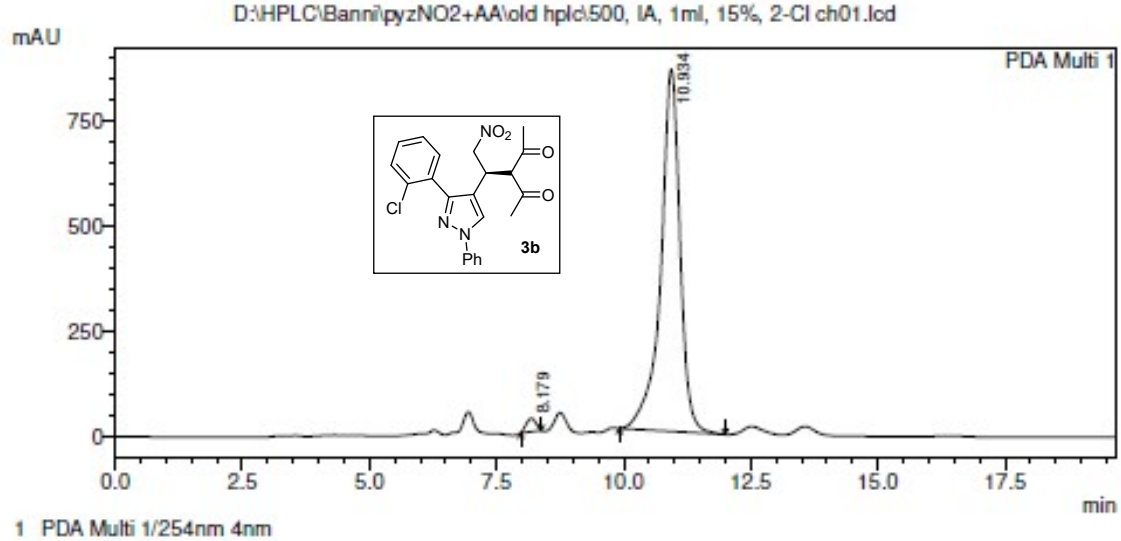


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.174	7885171	479780	50.046	61.473
2	10.950	7870631	300690	49.954	38.527
Total		15755803	780470	100.000	100.000

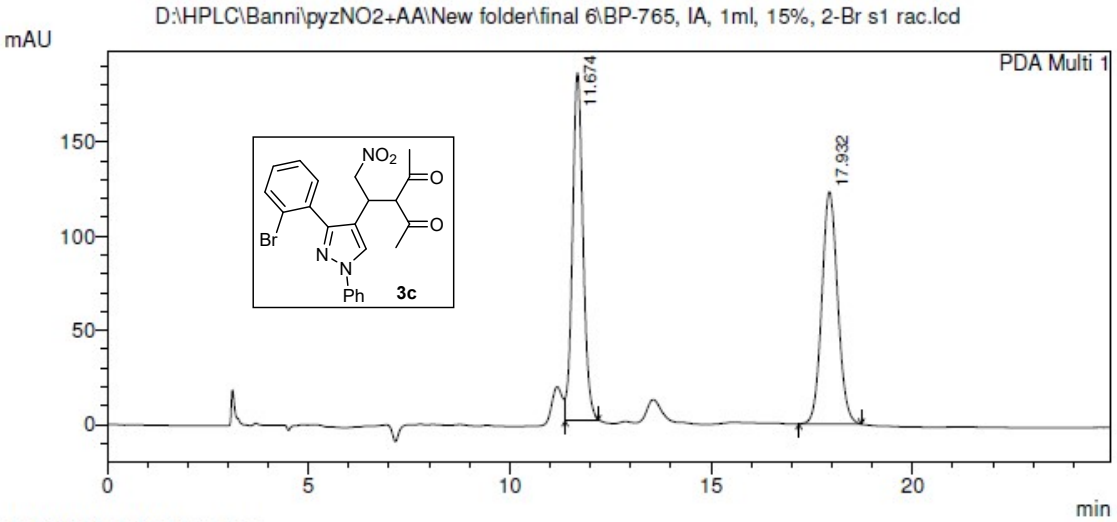


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.179	419791	31466	1.818	3.529
2	10.934	22672258	860275	98.182	96.471
Total		23092049	891741	100.000	100.000

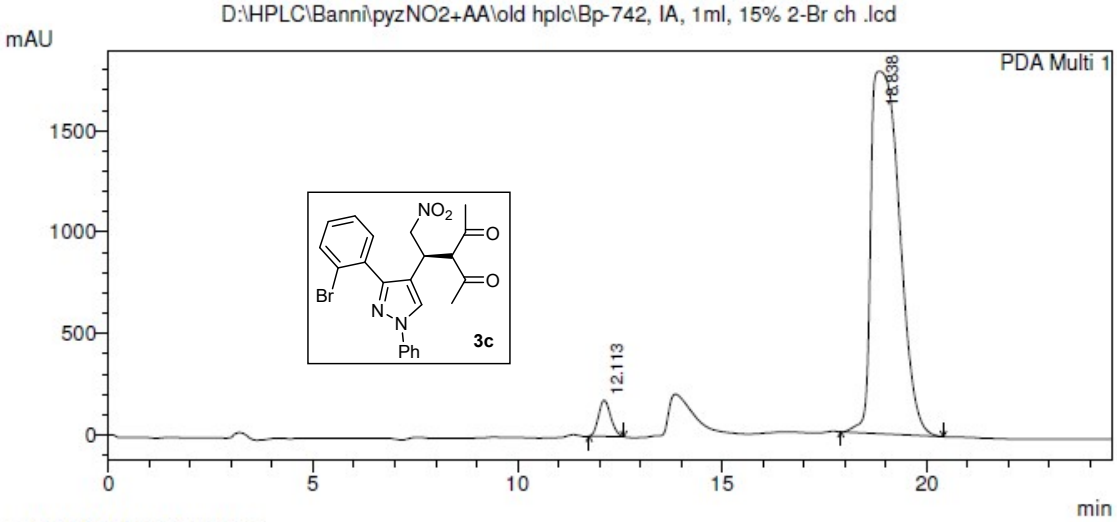


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.674	3374260	184889	50.080	59.989
2	17.932	3363453	123317	49.920	40.011
Total		6737713	308206	100.000	100.000

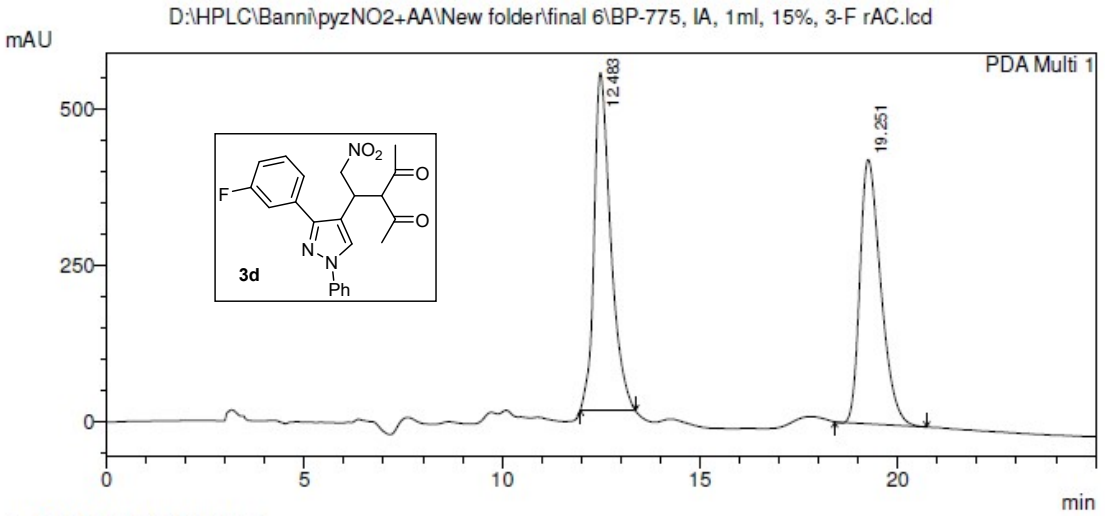


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.113	3710613	178516	4.097	9.084
2	18.838	86857086	1786644	95.903	90.916
Total		90567699	1965160	100.000	100.000

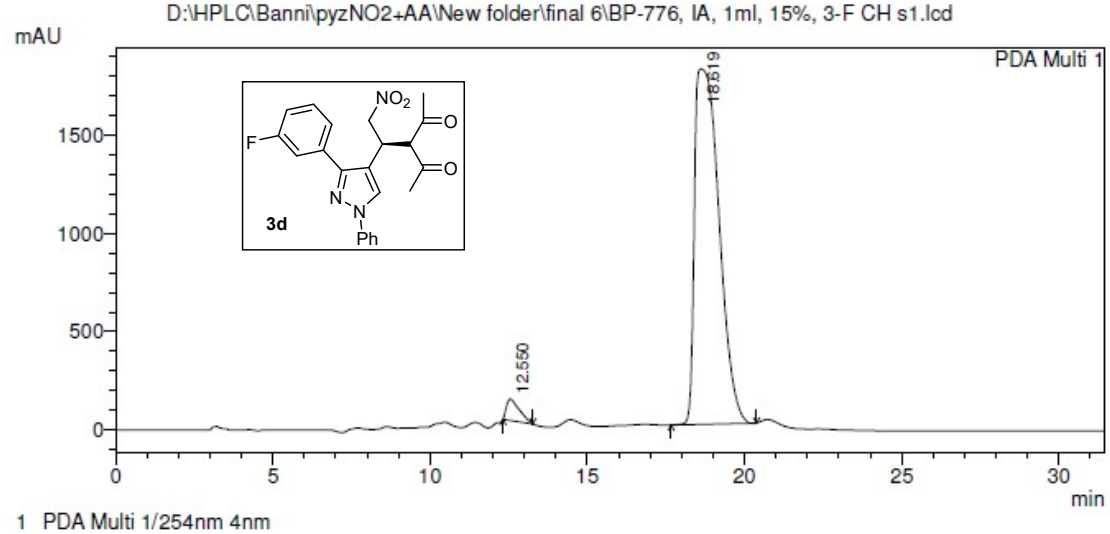


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.483	15873802	539875	50.664	56.083
2	19.251	15457995	422752	49.336	43.917
Total		31331796	962627	100.000	100.000

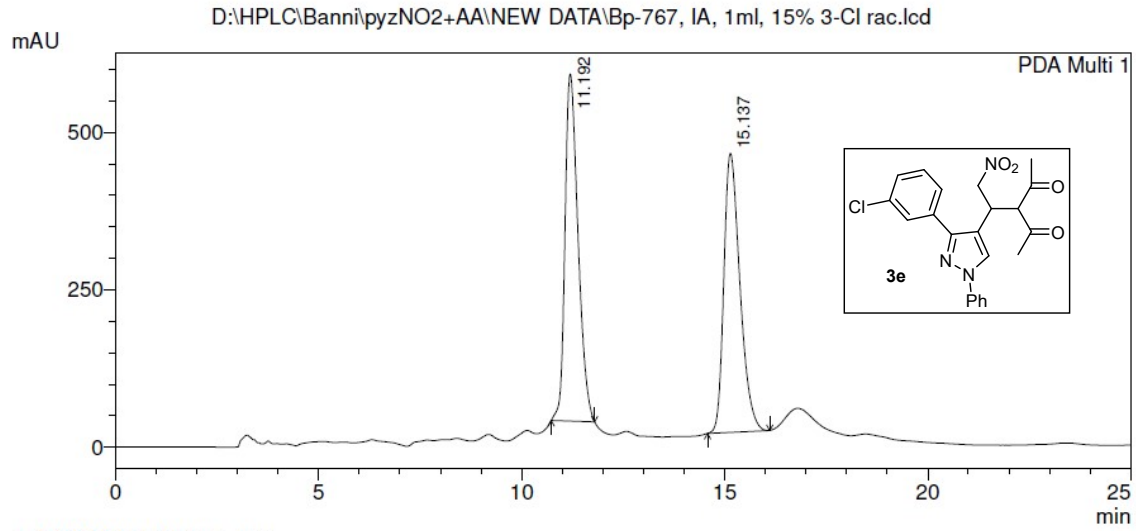


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.550	3111856	109601	3.078	5.710
2	18.619	98003108	1809904	96.922	94.290
Total		101114964	1919505	100.000	100.000

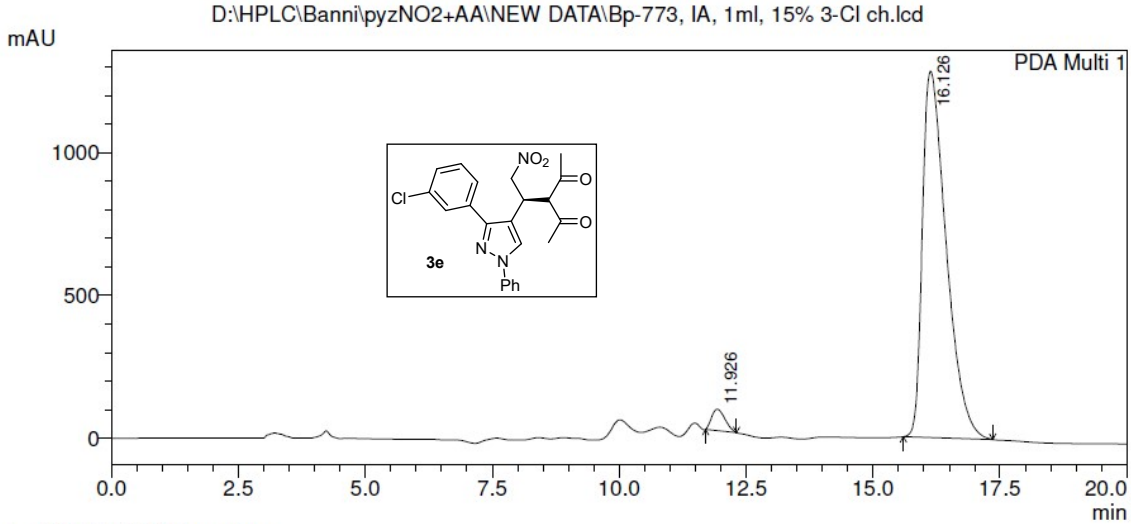


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.192	12277351	551320	50.152	55.443
2	15.137	12202993	443076	49.848	44.557
Total		24480345	994396	100.000	100.000

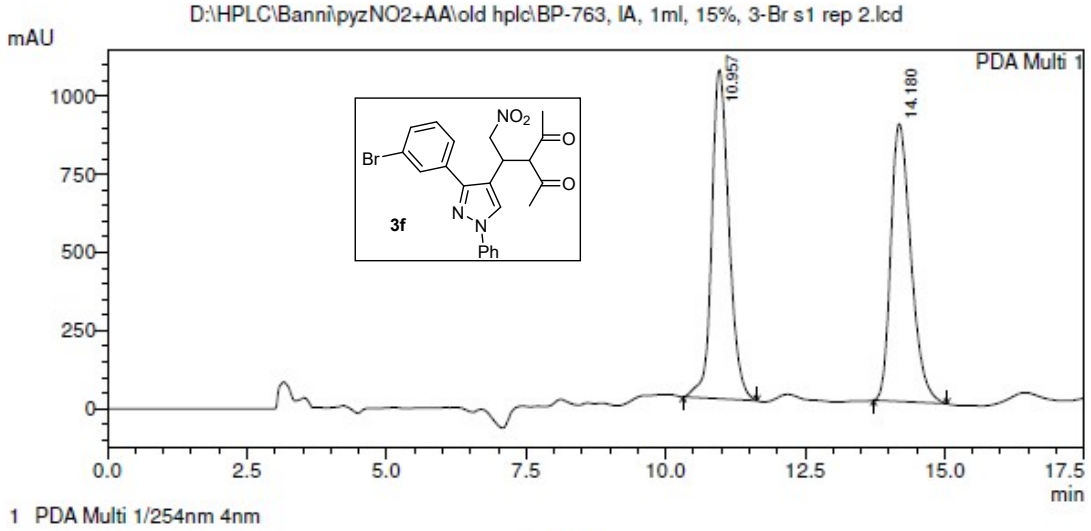


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.926	1352056	74560	3.129	5.495
2	16.126	41859087	1282185	96.871	94.505
Total		43211143	1356744	100.000	100.000

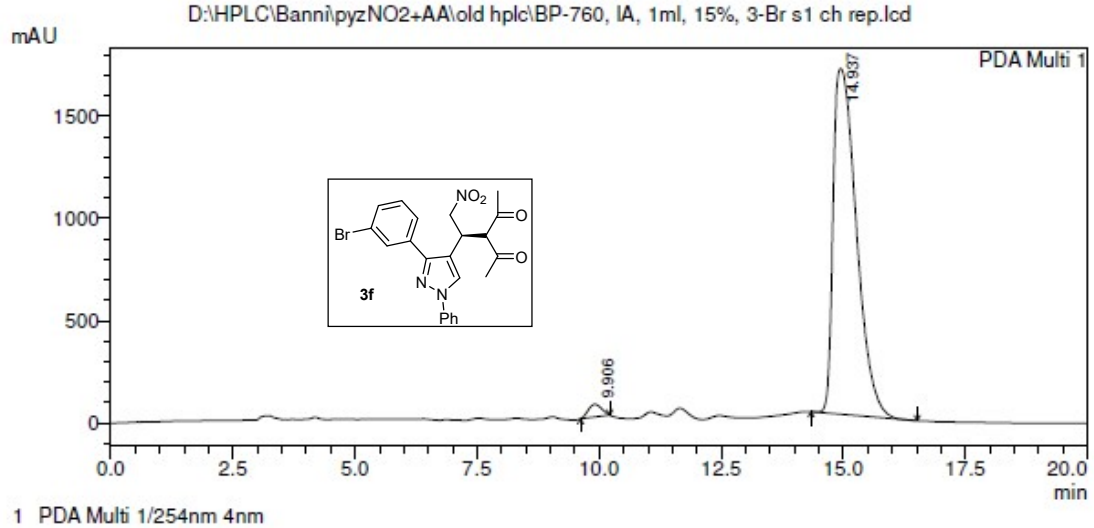


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.957	22593042	1053220	50.265	54.232
2	14.180	22354714	888856	49.735	45.768
Total		44947756	1942076	100.000	100.000

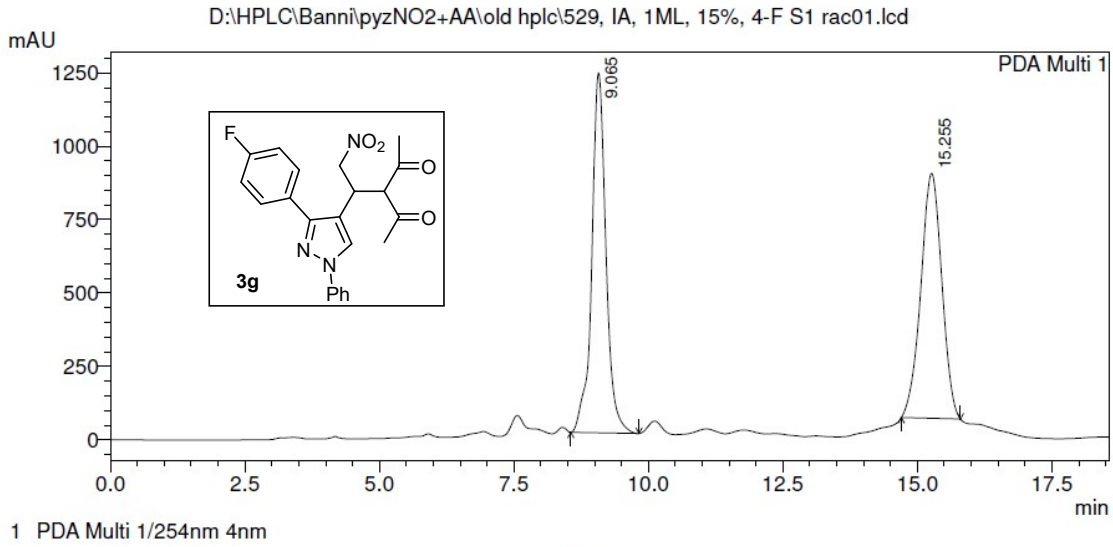


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.906	1178372	61741	2.067	3.524
2	14.937	55841723	1690043	97.933	96.476
Total		57020095	1751785	100.000	100.000

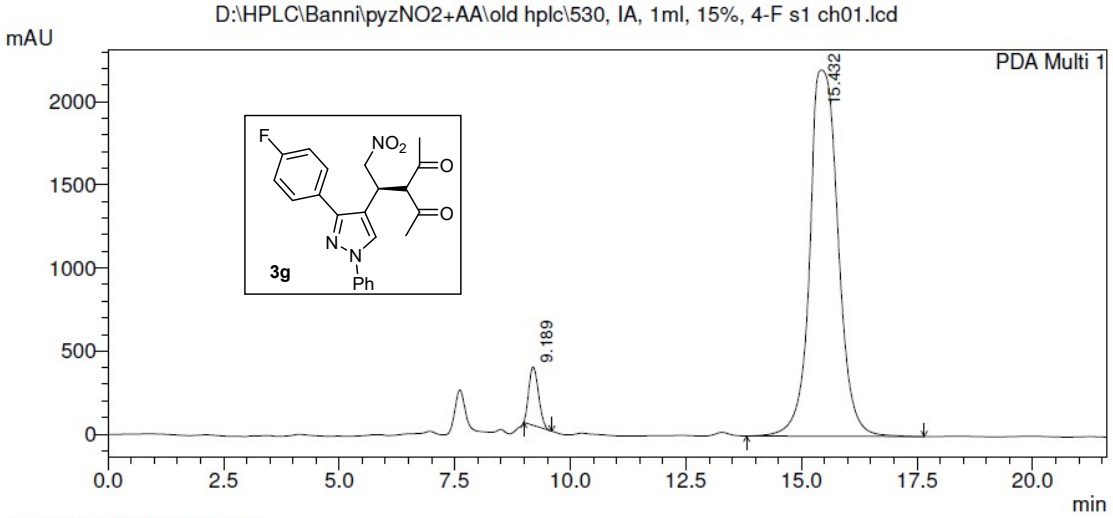


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.065	22453408	1226254	49.814	59.505
2	15.255	22621160	834514	50.186	40.495
Total		45074568	2060768	100.000	100.000

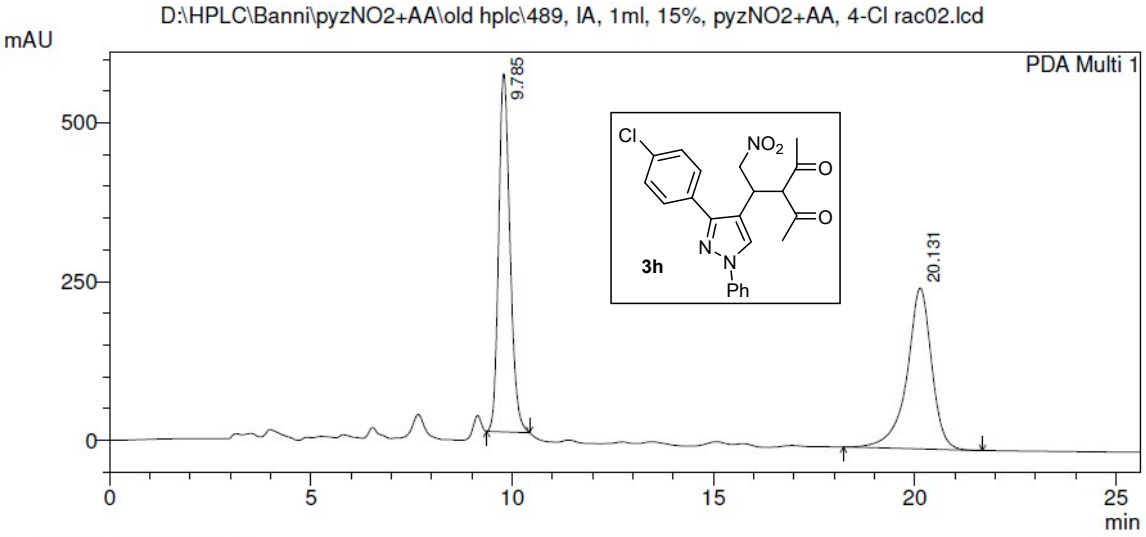


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.189	5139200	351525	5.172	13.769
2	15.432	94233537	2201463	94.828	86.231
Total		99372738	2552988	100.000	100.000

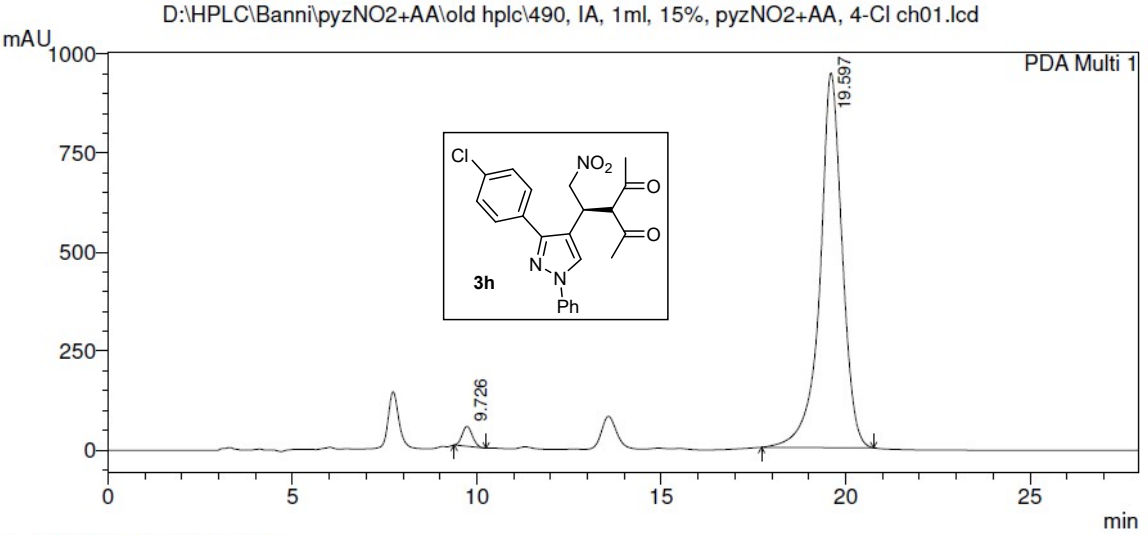


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.785	11061522	564117	50.566	69.015
2	20.131	10814105	253261	49.434	30.985
Total		21875627	817378	100.000	100.000

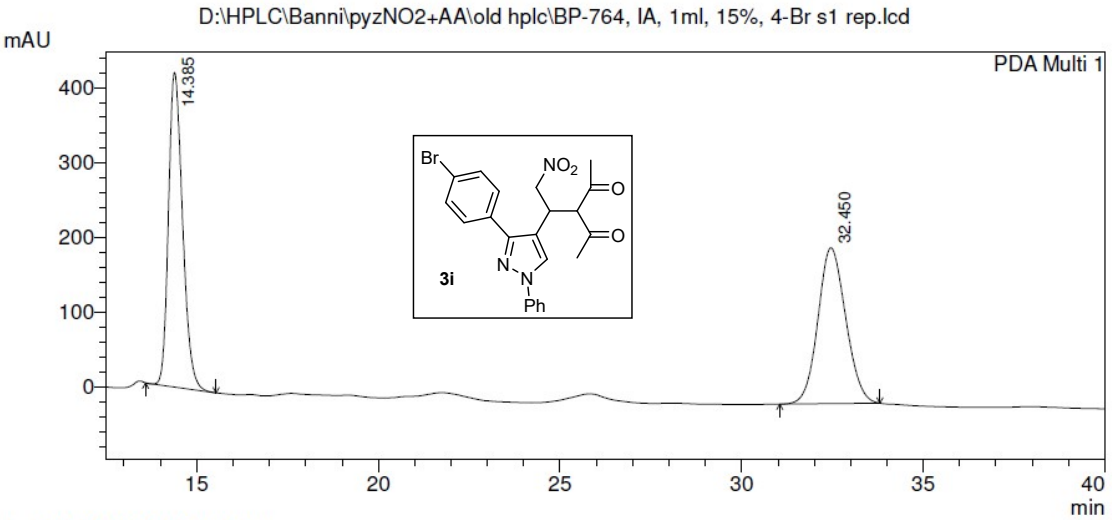


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.726	976950	50367	2.401	5.056
2	19.597	39717651	945760	97.599	94.944
Total		40694601	996127	100.000	100.000

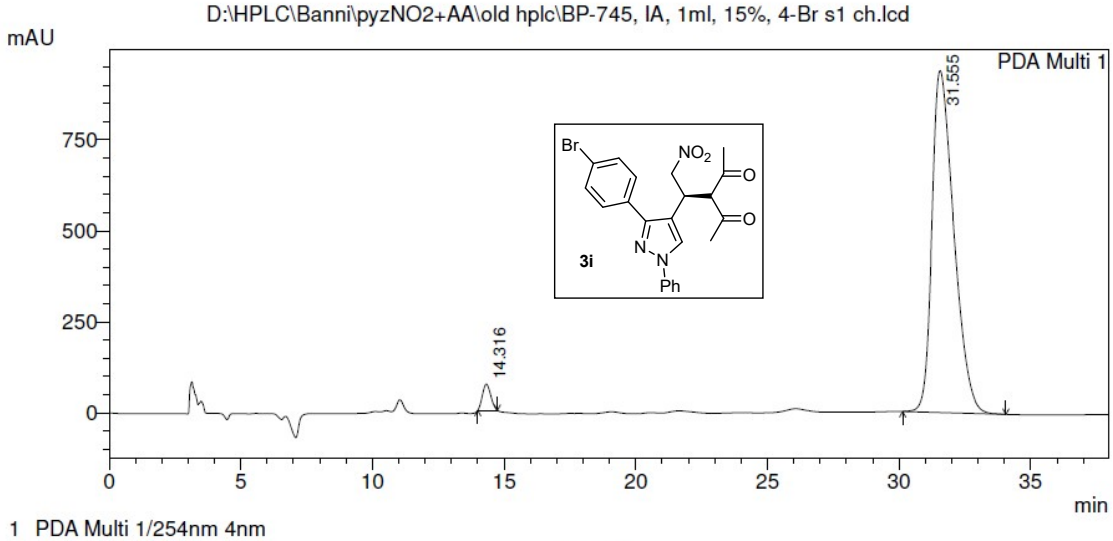


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.385	11323743	420477	50.475	66.857
2	32.450	11110407	208447	49.525	33.143
Total		22434150	628924	100.000	100.000

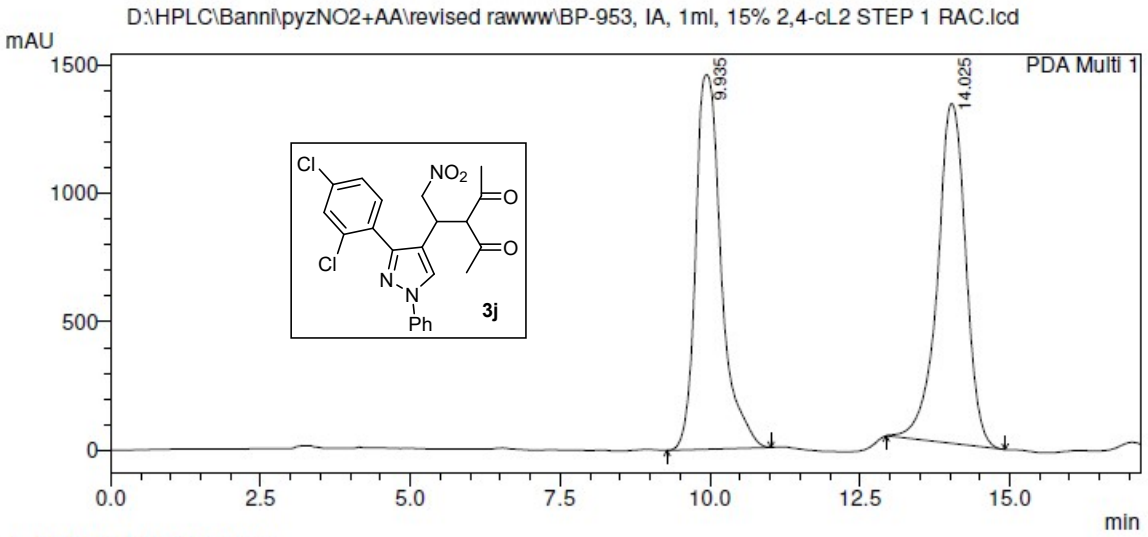


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.316	1594865	72402	2.856	7.156
2	31.555	54246832	939398	97.144	92.844
Total		55841696	1011800	100.000	100.000

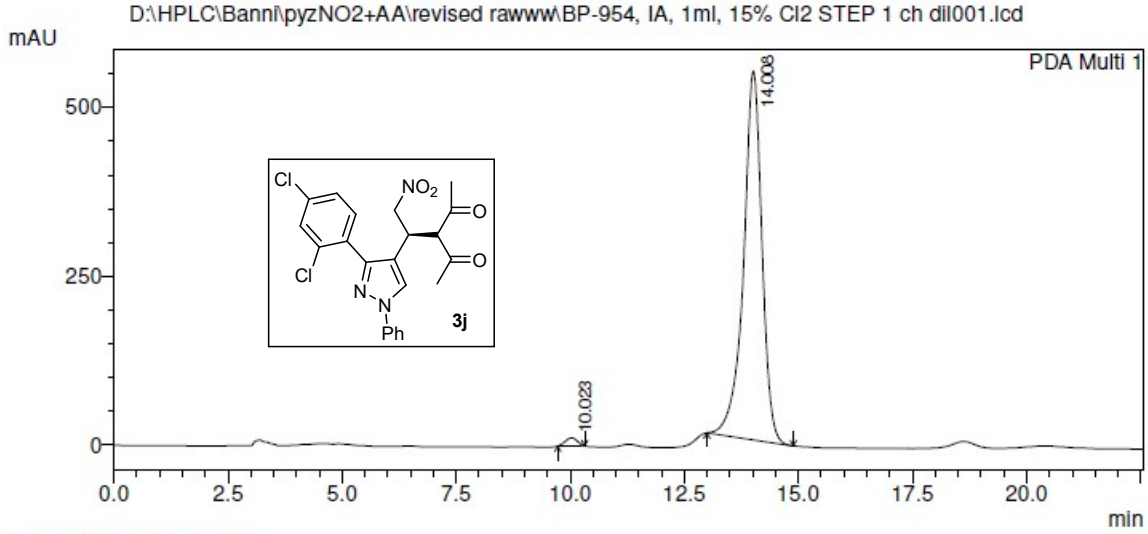


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.935	43322120	1458763	49.876	52.450
2	14.025	43537565	1322482	50.124	47.550
Total		86859686	2781245	100.000	100.000

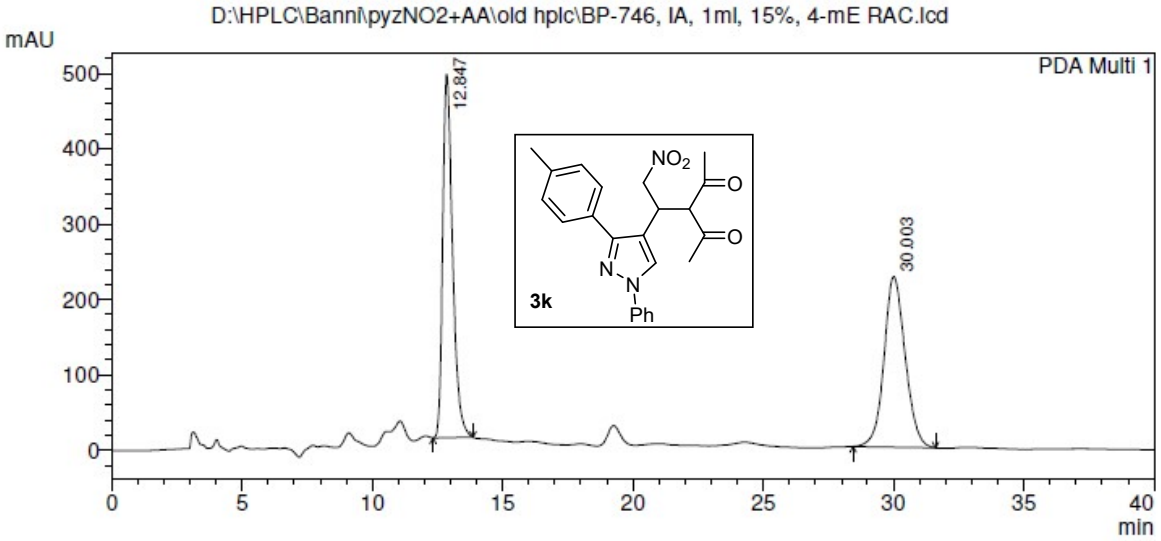


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.023	214243	11837	1.379	2.123
2	14.008	15322125	545656	98.621	97.877
Total		15536368	557493	100.000	100.000

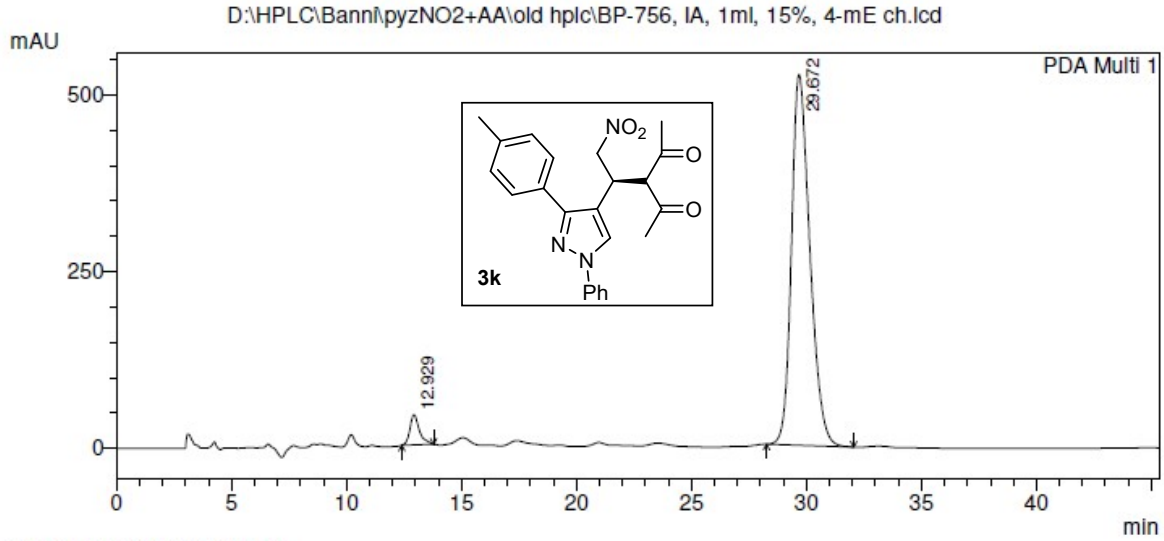


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.847	12687559	482270	49.804	68.042
2	30.003	12787349	226507	50.196	31.958
Total		25474908	708777	100.000	100.000

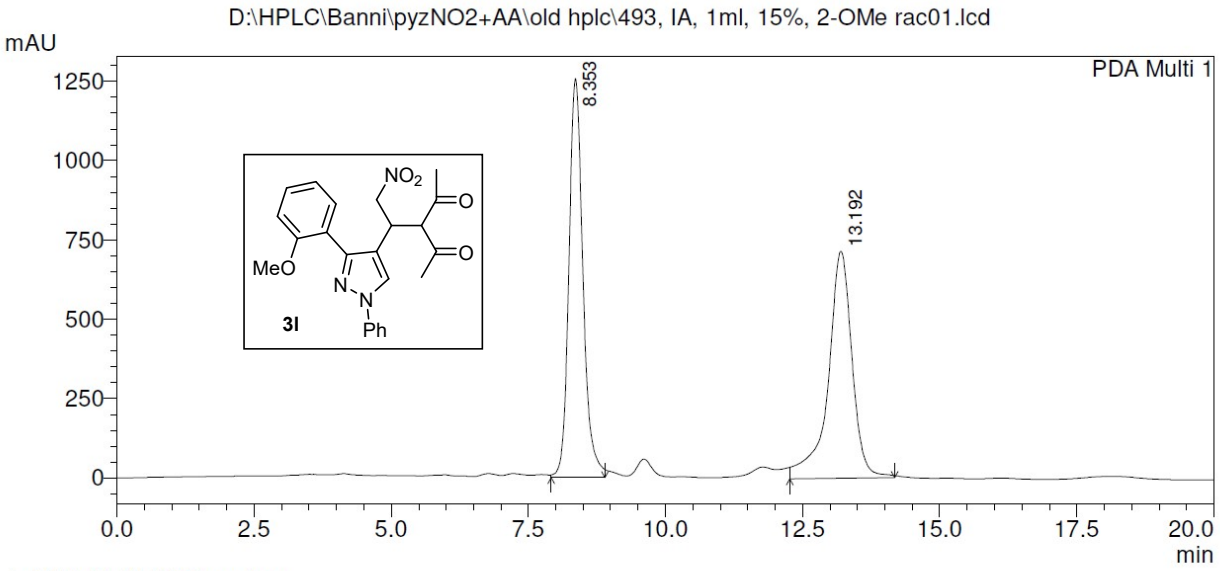


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.929	1217709	42613	4.003	7.517
2	29.672	29202678	524303	95.997	92.483
Total		30420387	566916	100.000	100.000

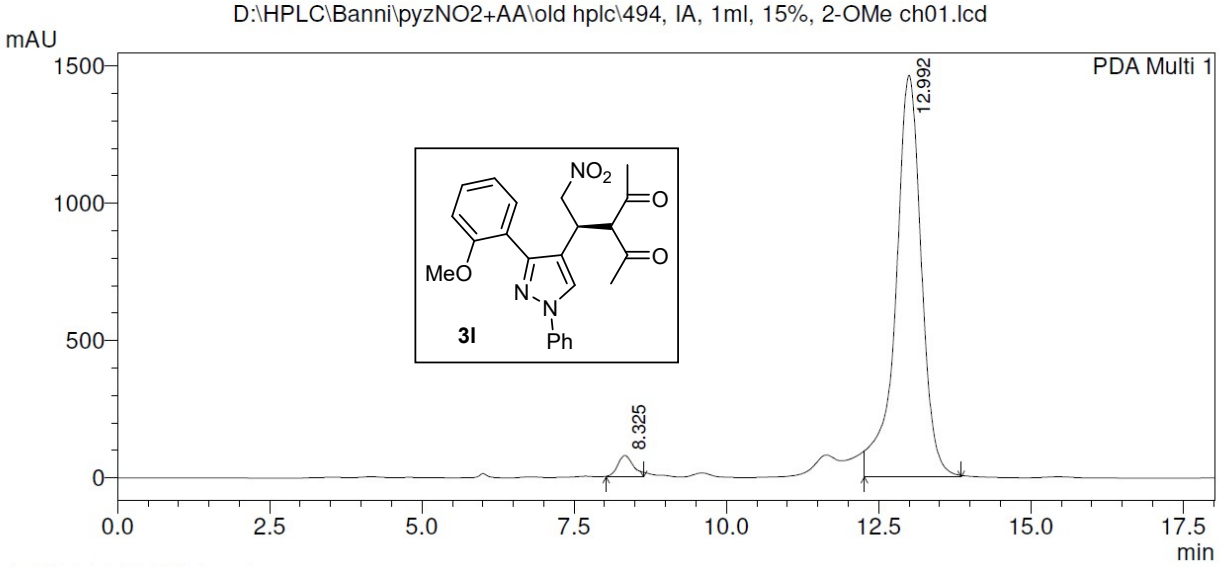


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.353	22404004	1257347	50.675	63.729
2	13.192	21807109	715597	49.325	36.271
Total		44211113	1972944	100.000	100.000

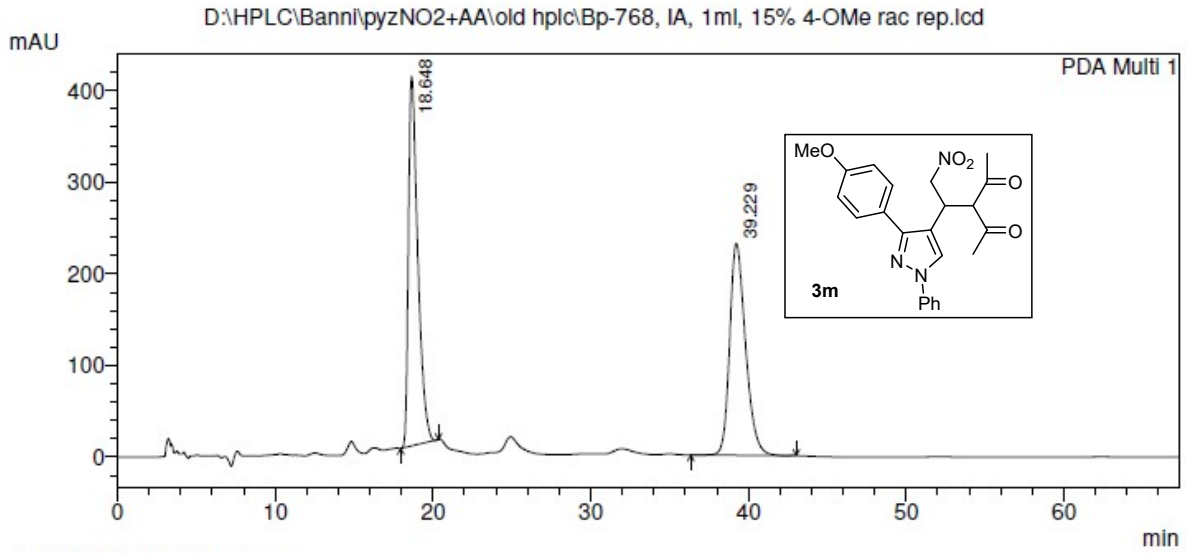


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.325	1033519	67932	2.355	4.442
2	12.992	42846372	1461474	97.645	95.558
Total		43879891	1529405	100.000	100.000

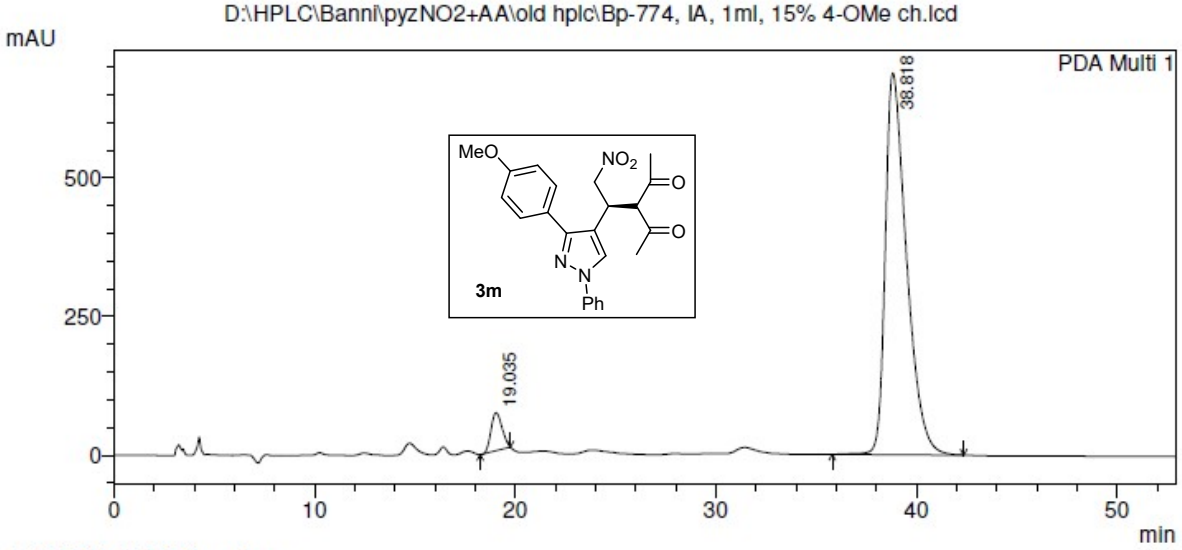


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.648	16569654	403471	50.597	63.566
2	39.229	16178615	231257	49.403	36.434
Total		32748269	634728	100.000	100.000

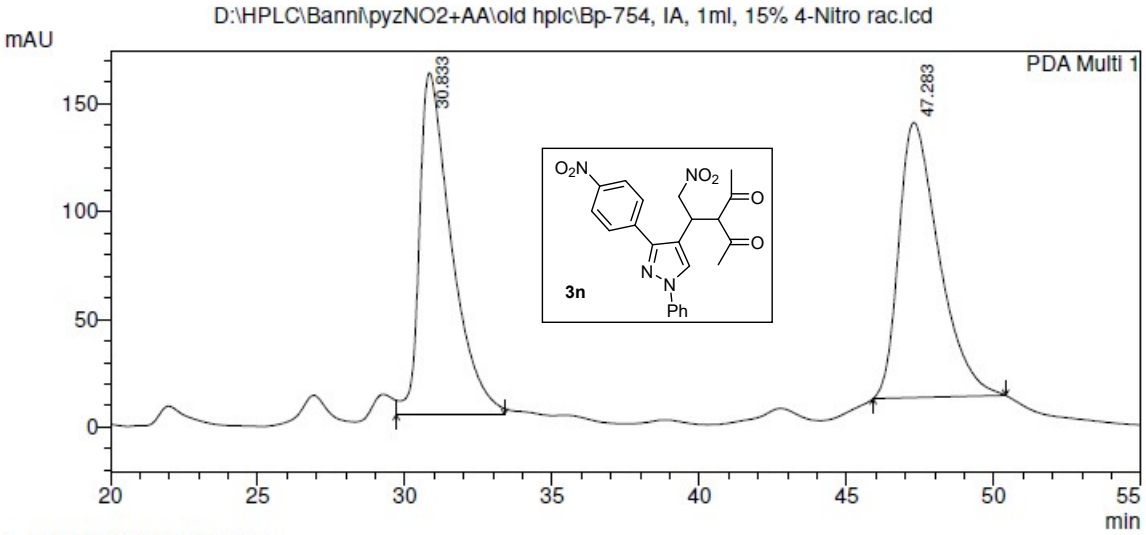


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.035	2618432	68810	4.913	9.082
2	38.818	50676460	688820	95.087	90.918
Total		53294892	757630	100.000	100.000

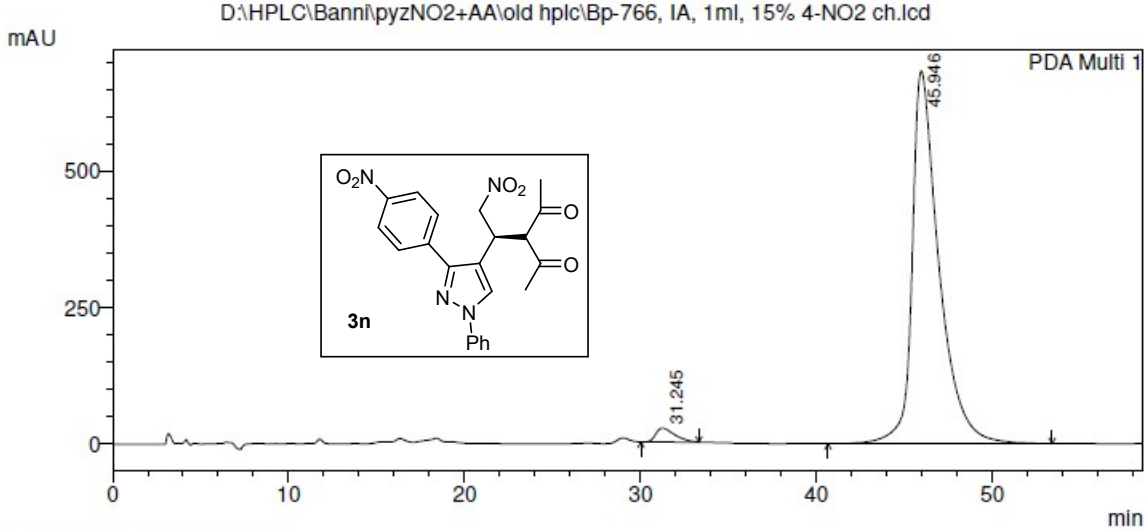


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.833	11950170	158273	49.623	55.397
2	47.283	12131540	127435	50.377	44.603
Total		24081710	285708	100.000	100.000

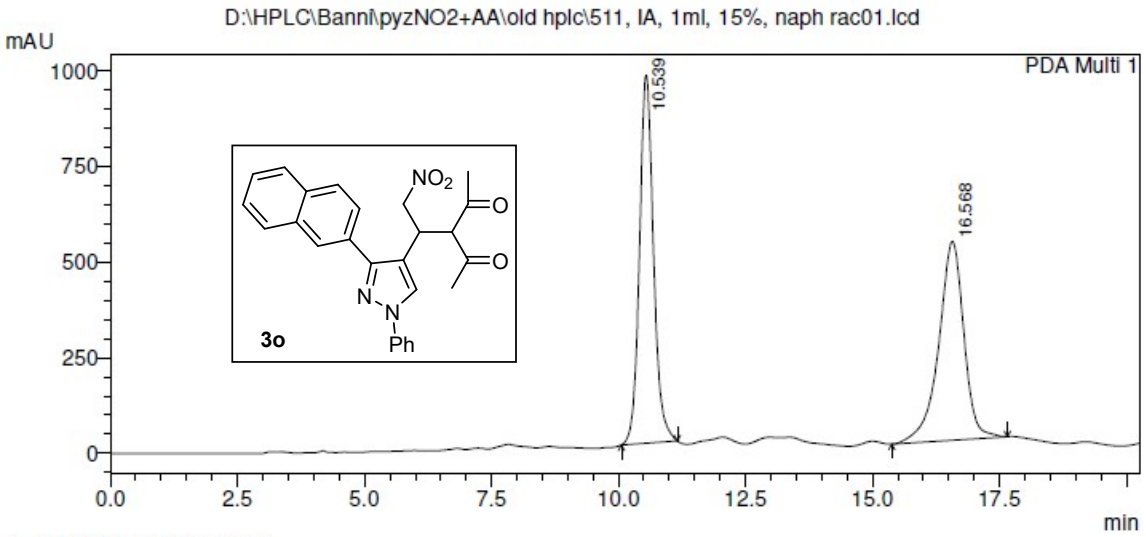


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.245	1912858	25715	2.564	3.626
2	45.946	72686868	683499	97.436	96.374
Total		74599726	709214	100.000	100.000

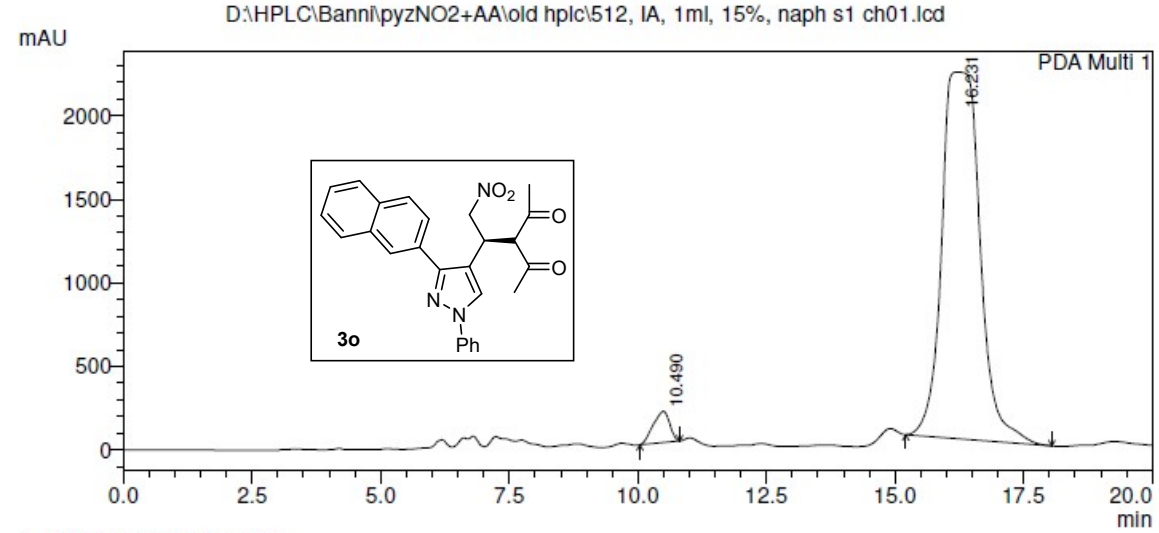


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.539	18477473	961949	50.760	64.924
2	16.568	17923905	519694	49.240	35.076
Total		36401378	1481643	100.000	100.000

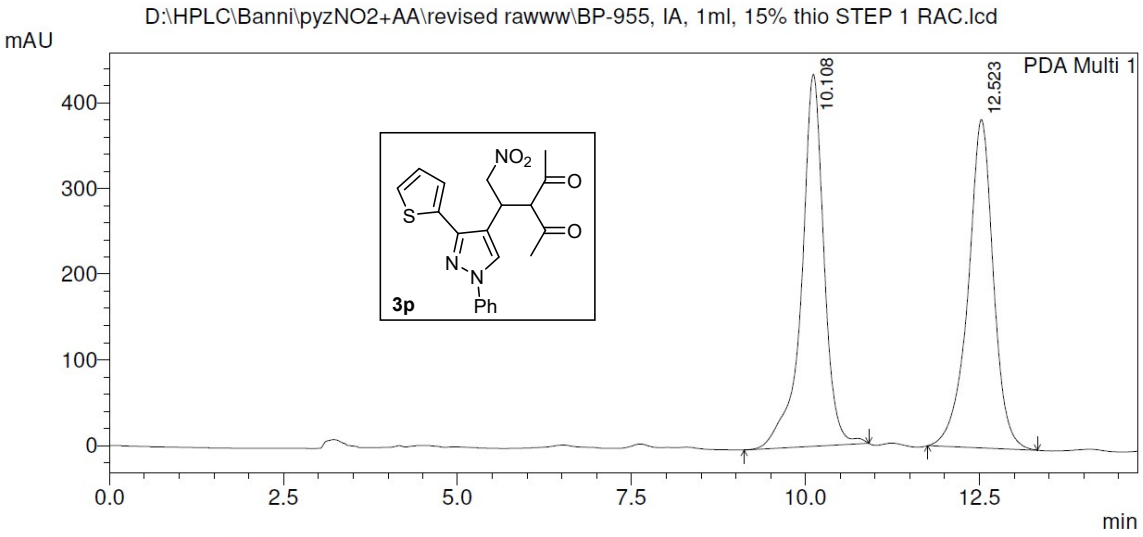


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.490	4160715	186779	3.547	7.842
2	16.231	113126302	2195010	96.453	92.158
Total		117287017	2381789	100.000	100.000

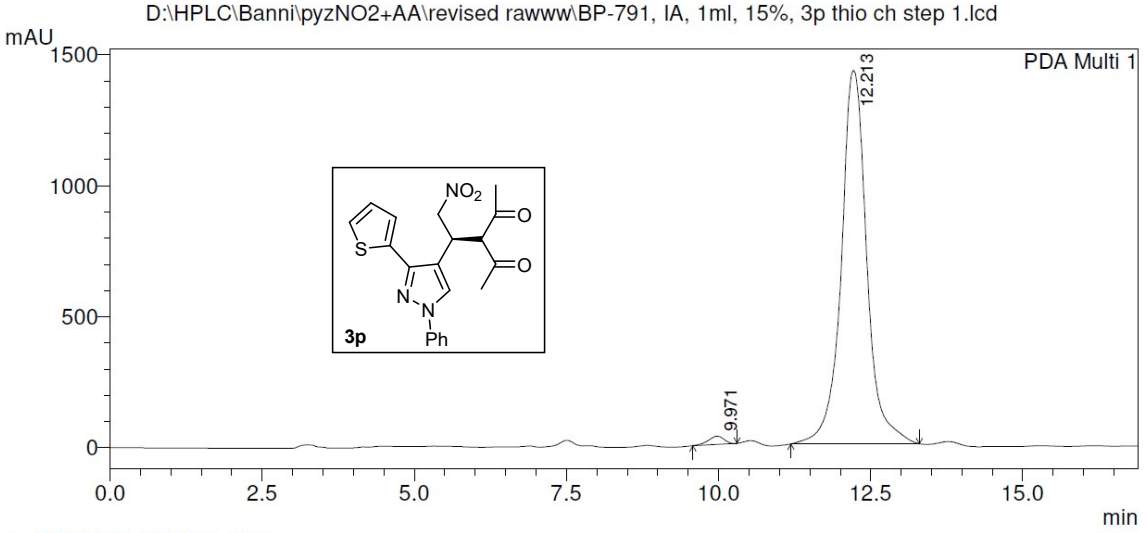


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.108	9731702	434304	50.022	53.120
2	12.523	9722992	383282	49.978	46.880
Total		19454693	817586	100.000	100.000



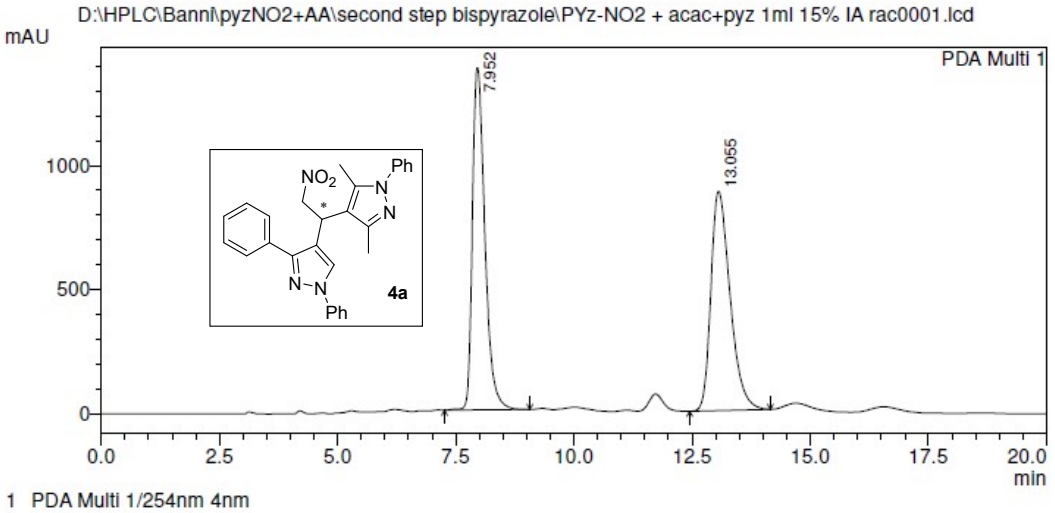
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.971	556848	31115	1.318	2.136
2	12.213	41680458	1425566	98.682	97.864
Total		42237306	1456681	100.000	100.000

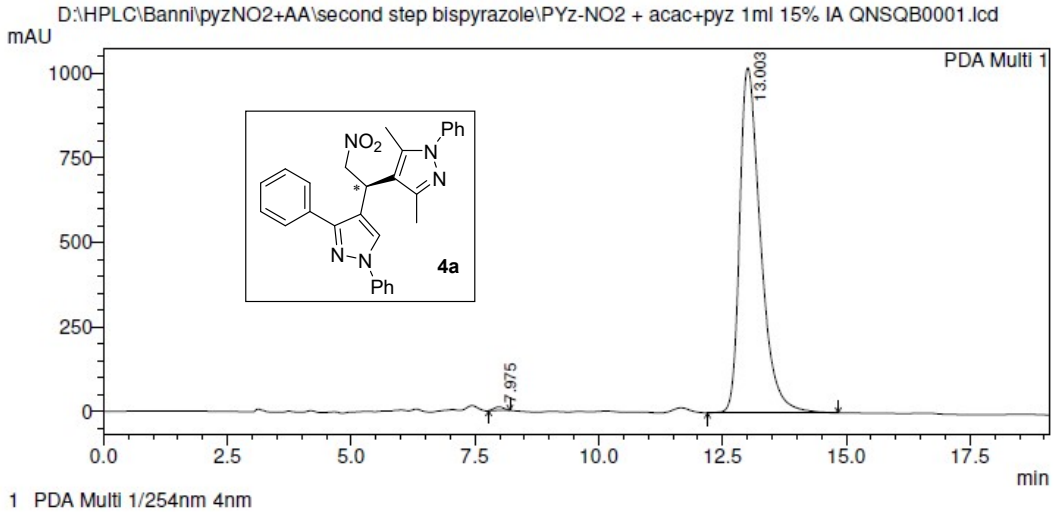
HPLC chromatogram of *bis*-pyrazole derivatives 4



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.952	25273842	1379238	50.352	60.952
2	13.055	24920189	883585	49.648	39.048
Total		50194031	2262823	100.000	100.000

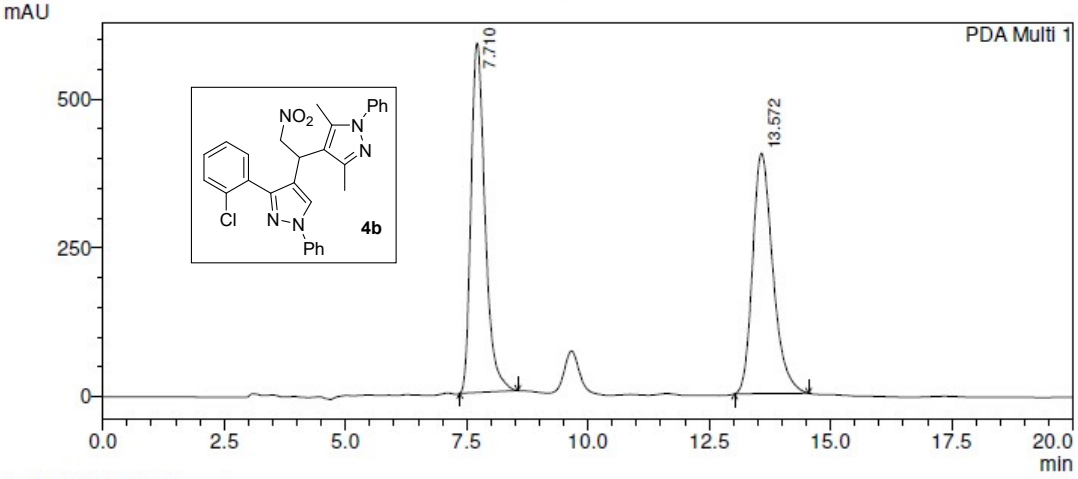


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.975	148301	10918	0.493	1.059
2	13.003	29912724	1020175	99.507	98.941
Total		30061025	1031093	100.000	100.000

D:\...\Banni\pyzNO2+AA\second step bispyrazole\subs scope\465, IA, 1ml, 15%, pyzNO2+AA+PH, 2-Cl rac01.lcd



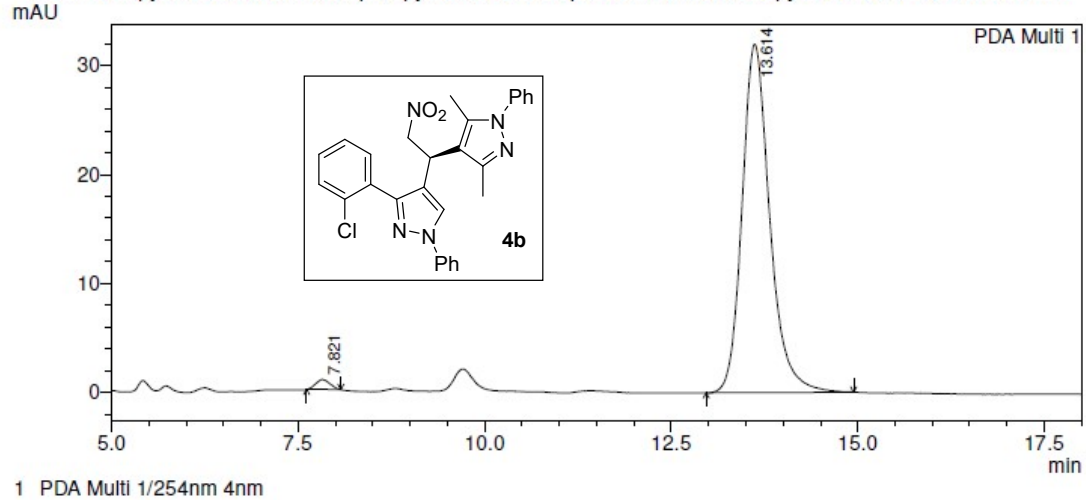
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.710	11859501	587160	50.220	59.235
2	13.572	11755368	404078	49.780	40.765
Total		23614869	991237	100.000	100.000

D:\...\Banni\pyzNO2+AA\second step bispyrazole\subs scope\466, IA, 1ml, 15%, pyzNO2+AA+PH, 2-Cl ch01.lcd



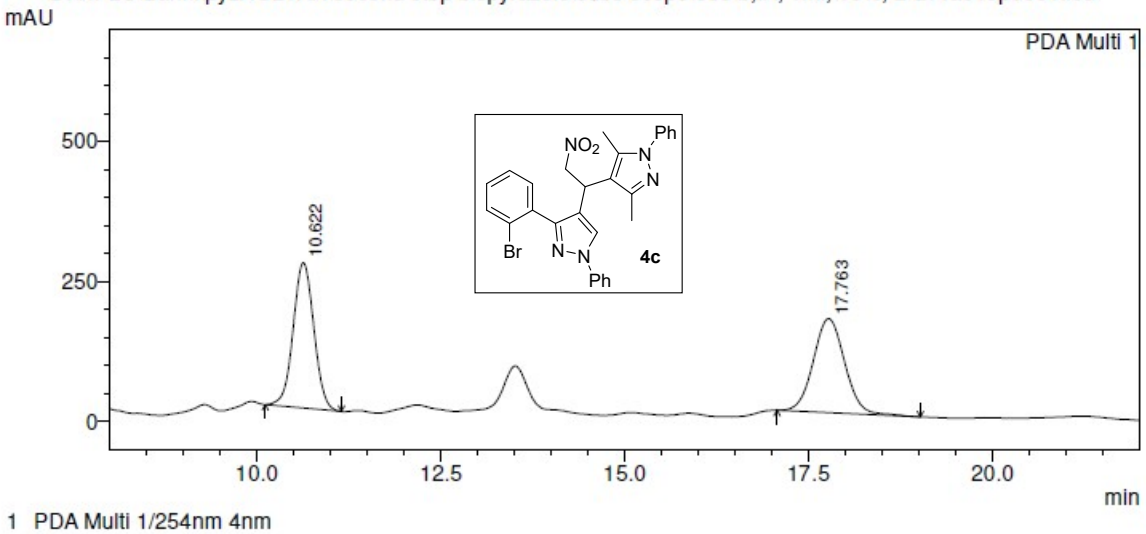
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.821	12115	912	1.446	2.770
2	13.614	825938	32019	98.554	97.230
Total		838053	32931	100.000	100.000

D:\HPLC\Banni\pyzNO2+AA\second step bispyrazole\subs scope\539 b,IA, 1ml, 15%, 2-Br rac rep0001.lcd



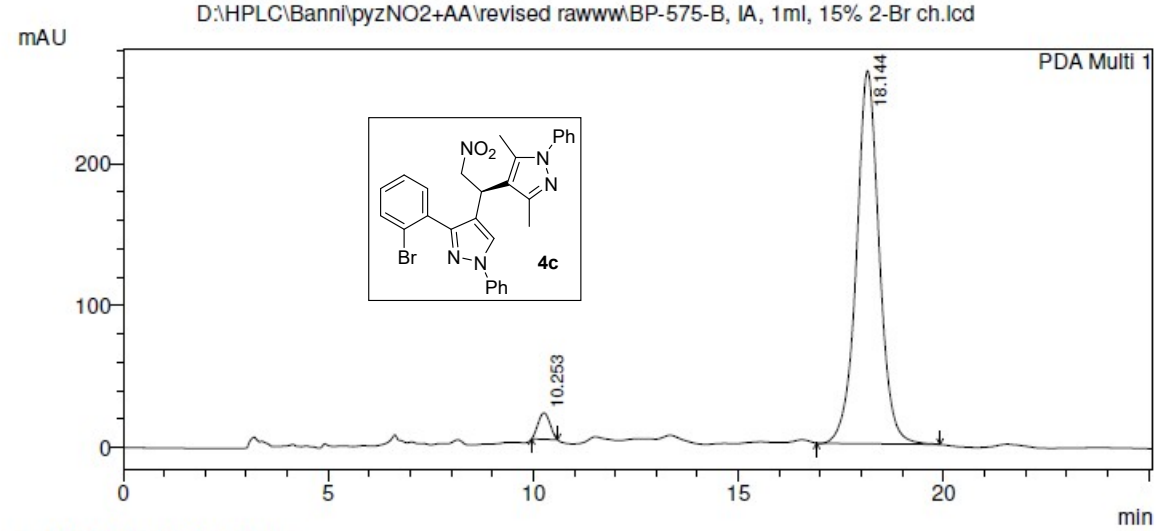
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.622	5088668	259699	50.464	60.725
2	17.763	4995088	167966	49.536	39.275
Total		10083756	427665	100.000	100.000

D:\HPLC\Banni\pyzNO2+AA\revised rawww\BP-575-B, IA, 1ml, 15% 2-Br ch.lcd



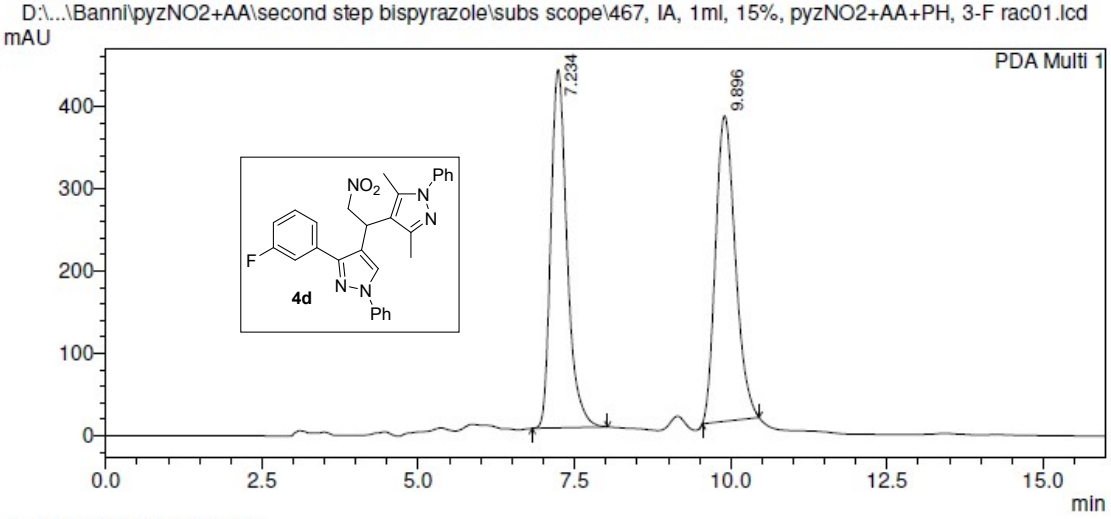
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.253	368845	18493	3.502	6.572
2	18.144	10163742	262909	96.498	93.428
Total		10532586	281402	100.000	100.000

D:\...\Banni\pyzNO2+AA\second step bispyrazole\subs scope\467, IA, 1ml, 15%, pyzNO2+AA+PH, 3-F rac01.lcd



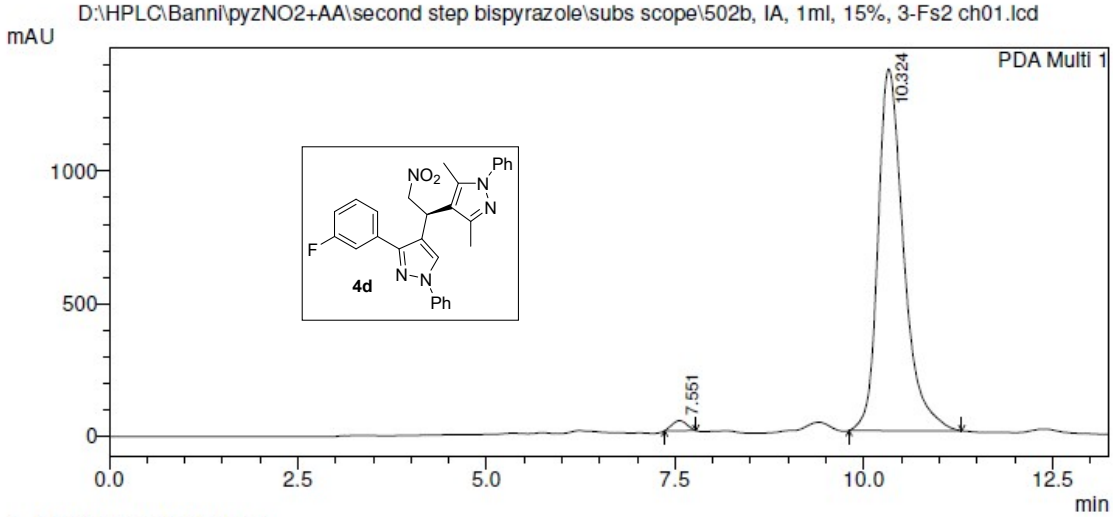
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.234	7859310	435093	49.022	53.960
2	9.896	8172739	371229	50.978	46.040
Total		16032049	806323	100.000	100.000

D:\HPLC\Banni\pyzNO2+AA\second step bispyrazole\subs scope\502b, IA, 1ml, 15%, 3-Fs2 ch01.lcd



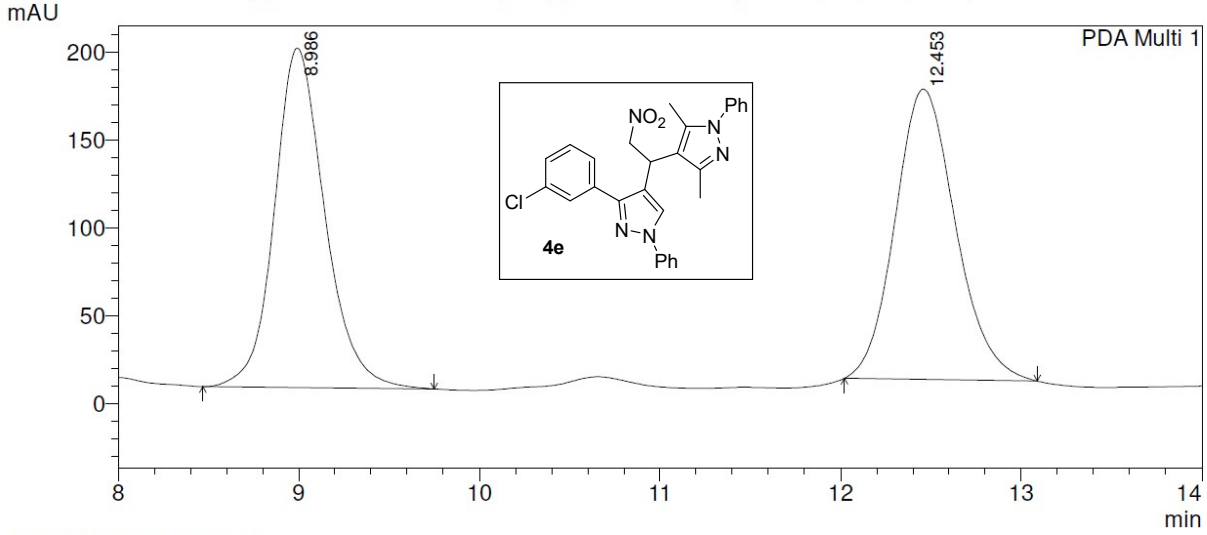
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.551	521467	38135	1.588	2.720
2	10.324	32326008	1363693	98.412	97.280
Total		32847474	1401828	100.000	100.000

D:\HPLC\Banni\pyzNO2+AA\second step bispyrazole\subs scope\537B, IA, 1ml, 15%,3-Cl s2 rac.lcd



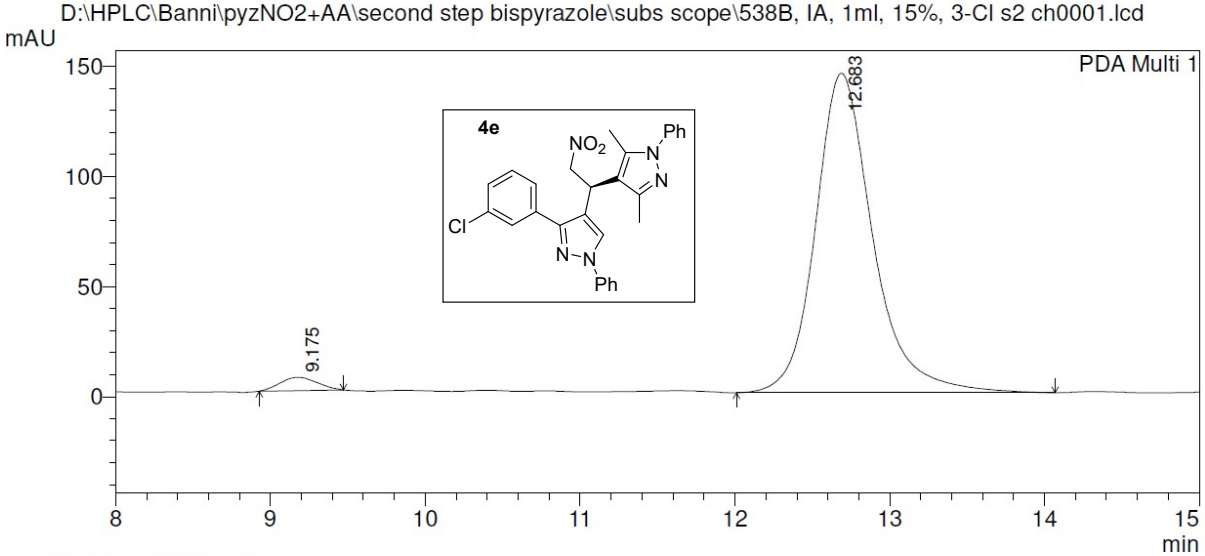
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.986	3747827	193123	49.360	53.896
2	12.453	3845002	165202	50.640	46.104
Total		7592830	358325	100.000	100.000

D:\HPLC\Banni\pyzNO2+AA\second step bispyrazole\subs scope\538B, IA, 1ml, 15%, 3-Cl s2 ch0001.lcd



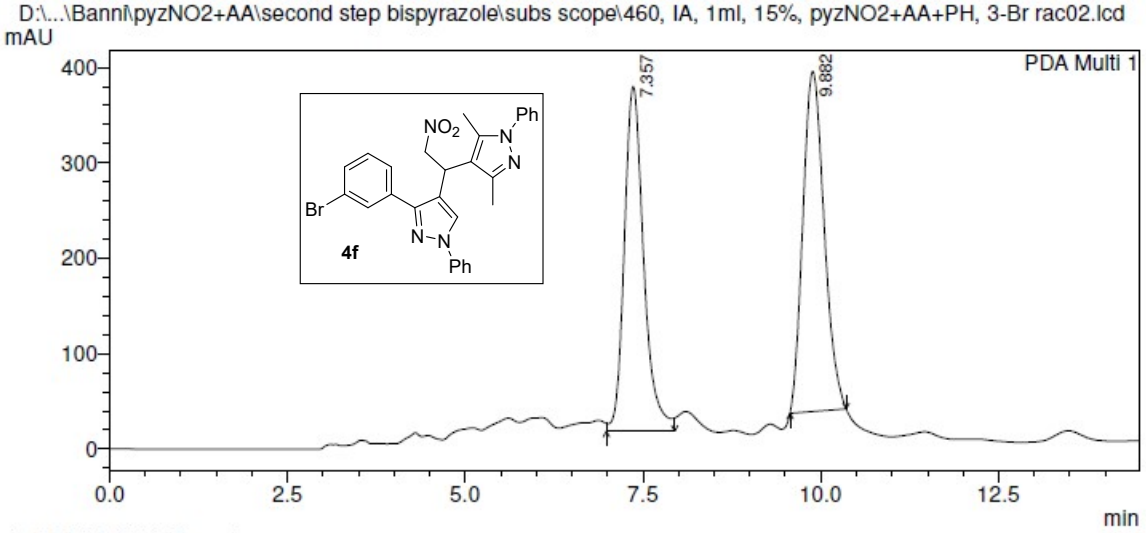
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.175	99330	6031	2.591	3.991
2	12.683	3734916	145085	97.409	96.009
Total		3834246	151117	100.000	100.000

D:\...\Banni\pyzNO2+AA\second step bispyrazole\subs scope\460, IA, 1ml, 15%, pyzNO2+AA+PH, 3-Br rac02.lcd



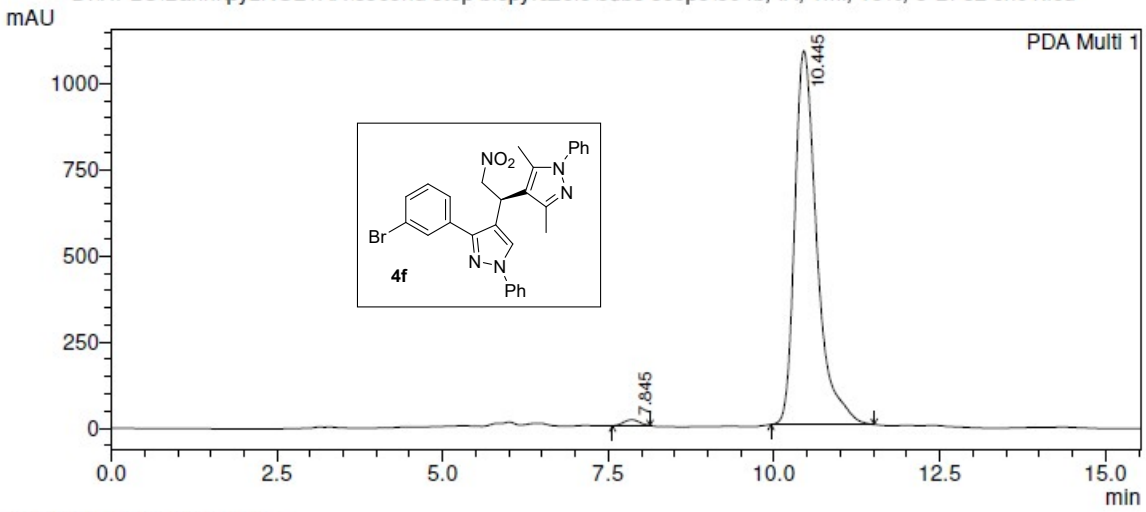
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.357	6868655	361393	48.152	50.337
2	9.882	7395959	356552	51.848	49.663
Total		14264614	717944	100.000	100.000

D:\HPLC\Banni\pyzNO2+AA\second step bispyrazole\subs scope\504b, IA, 1ml, 15%, 3-Br s2 ch01.lcd



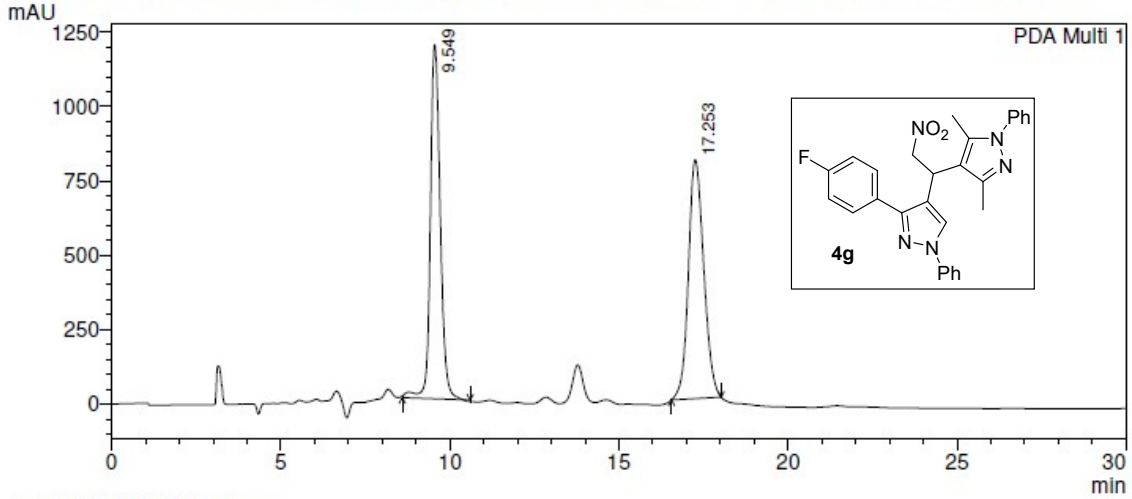
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.845	293770	17685	1.152	1.604
2	10.445	25198287	1084642	98.848	98.396
Total		25492057	1102327	100.000	100.000

D:\HPLC\Banni\pyzNO2+AA\second step bispyrazole\subs scope\554 b, IA, 1ml, 15%, 4-F s2 rac0001.lcd



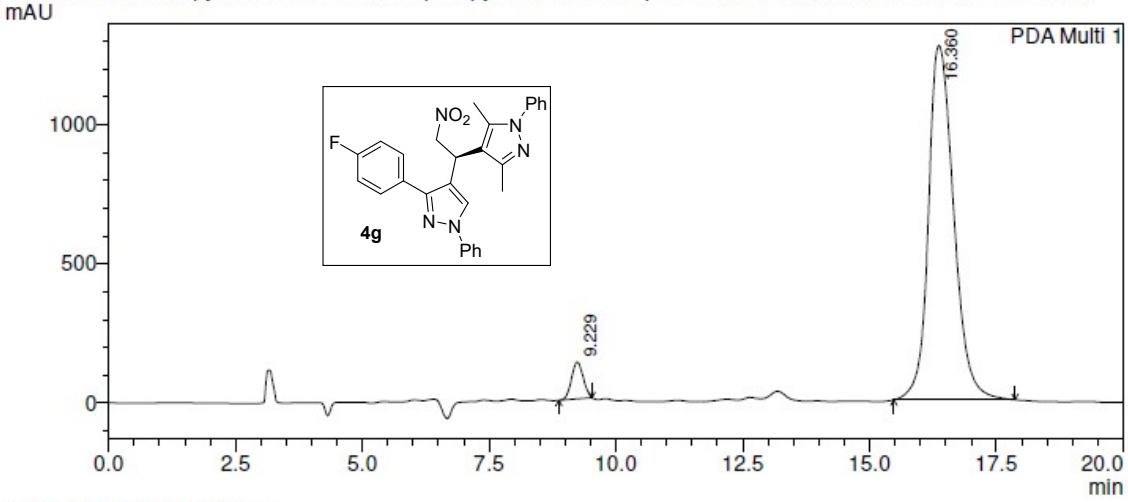
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.549	24188331	1190397	48.774	59.725
2	17.253	25404328	802722	51.226	40.275
Total		49592659	1993119	100.000	100.000

D:\HPLC\Banni\pyzNO2+AA\second step bispyrazole\subs scope\555 b, IA, 1ml, 15%, 4-F s2 ch ree0001.lcd

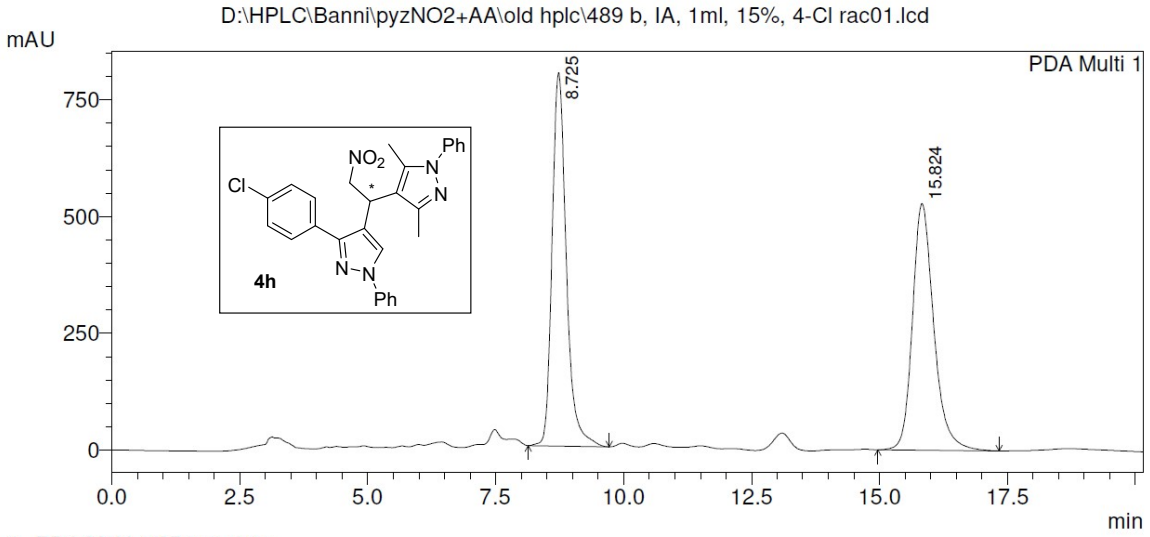


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.229	2117026	132305	4.559	9.405
2	16.360	44322065	1274377	95.441	90.595
Total		46439091	1406682	100.000	100.000

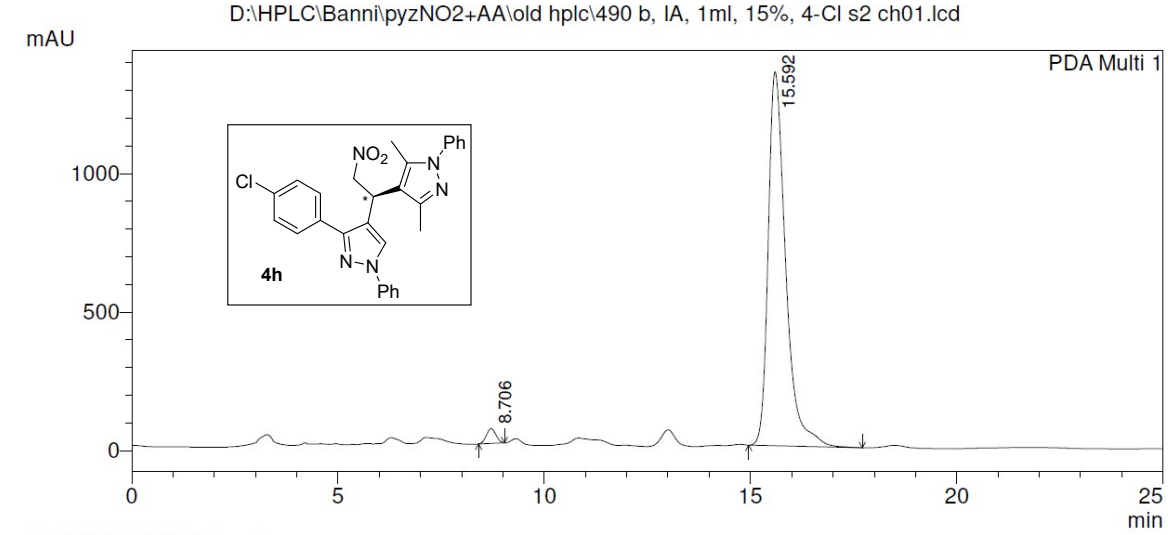


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.725	15456374	799475	50.234	60.214
2	15.824	15312161	528253	49.766	39.786
Total		30768535	1327728	100.000	100.000



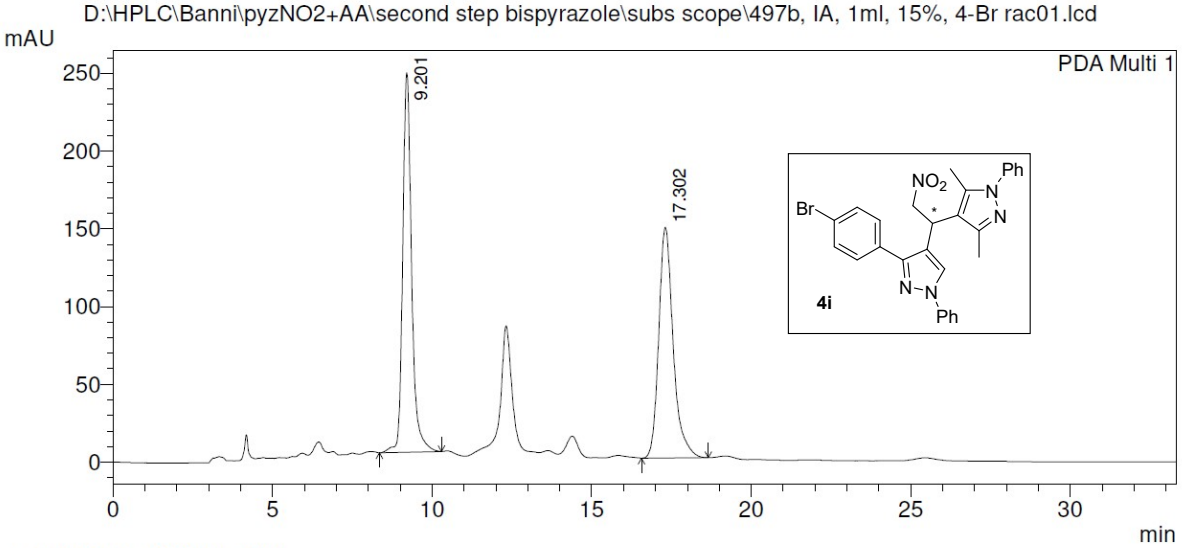
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.706	856843	53645	2.113	3.820
2	15.592	39687098	1350681	97.887	96.180
Total		40543941	1404326	100.000	100.000

D:\HPLC\Banni\pyzNO2+AA\second step bispyrazole\subs scope\497b, IA, 1ml, 15%, 4-Br rac01.lcd



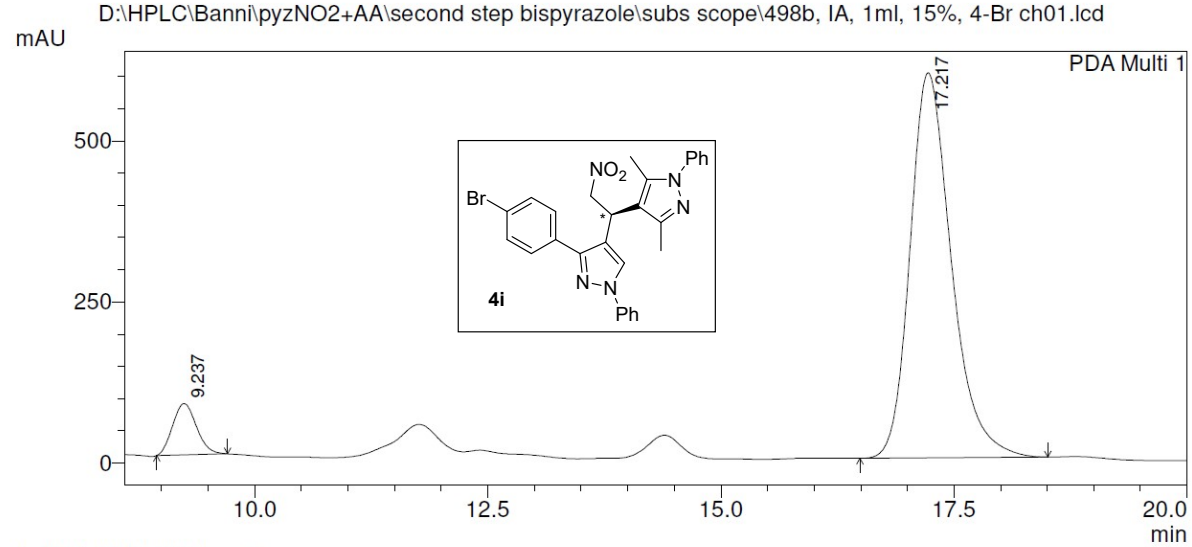
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.201	4748000	244046	50.448	62.196
2	17.302	4663682	148333	49.552	37.804
Total		9411681	392379	100.000	100.000

D:\HPLC\Banni\pyzNO2+AA\second step bispyrazole\subs scope\498b, IA, 1ml, 15%, 4-Br ch01.lcd

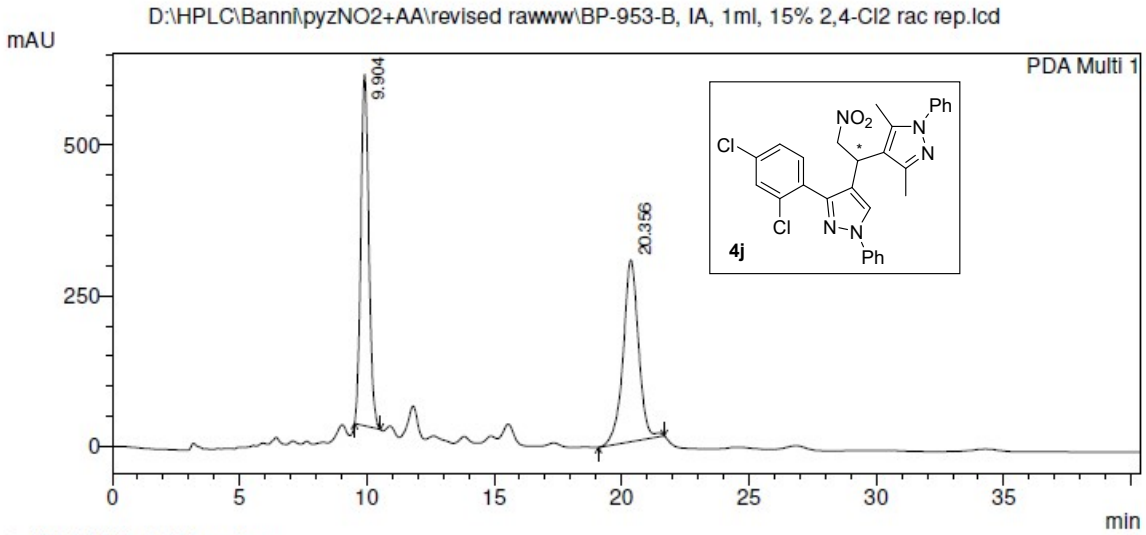


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.237	1418817	79586	7.145	11.744
2	17.217	18439804	598073	92.855	88.256
Total		19858622	677659	100.000	100.000

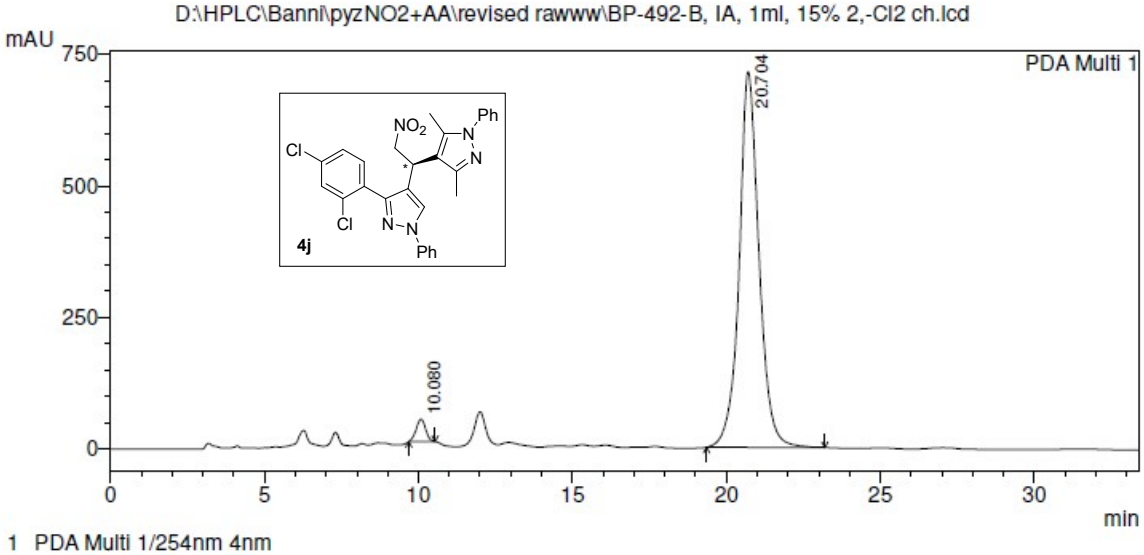


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.904	12682695	582721	50.107	65.909
2	20.356	12628339	301406	49.893	34.091
Total		25311035	884127	100.000	100.000



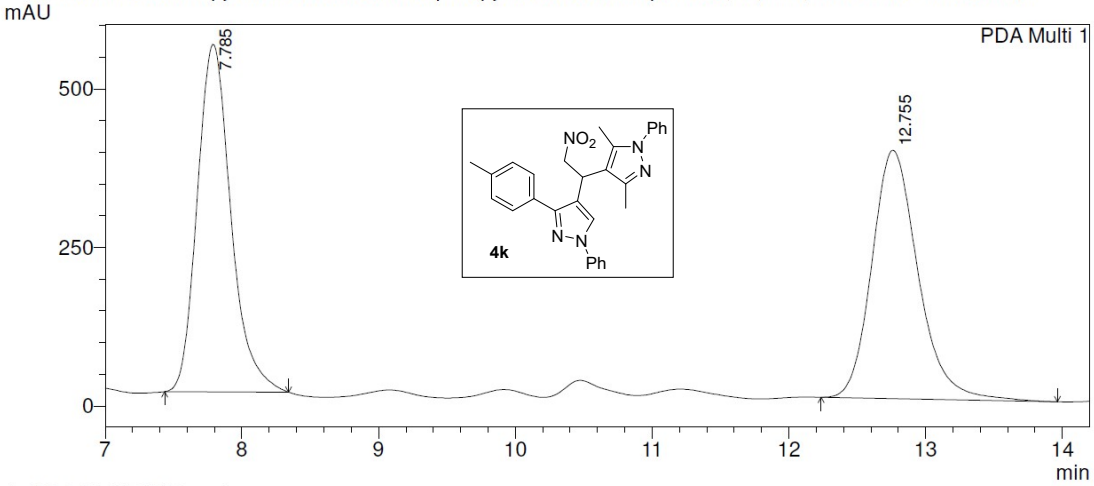
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.080	909185	42612	2.769	5.636
2	20.704	31925344	713385	97.231	94.364
Total		32834529	755997	100.000	100.000

D:\HPLC\Banni\pyzNO2+AA\second step bispyrazole\subs scope\495b, IA, 1ml, 15% 4-Me s2 rac02.lcd



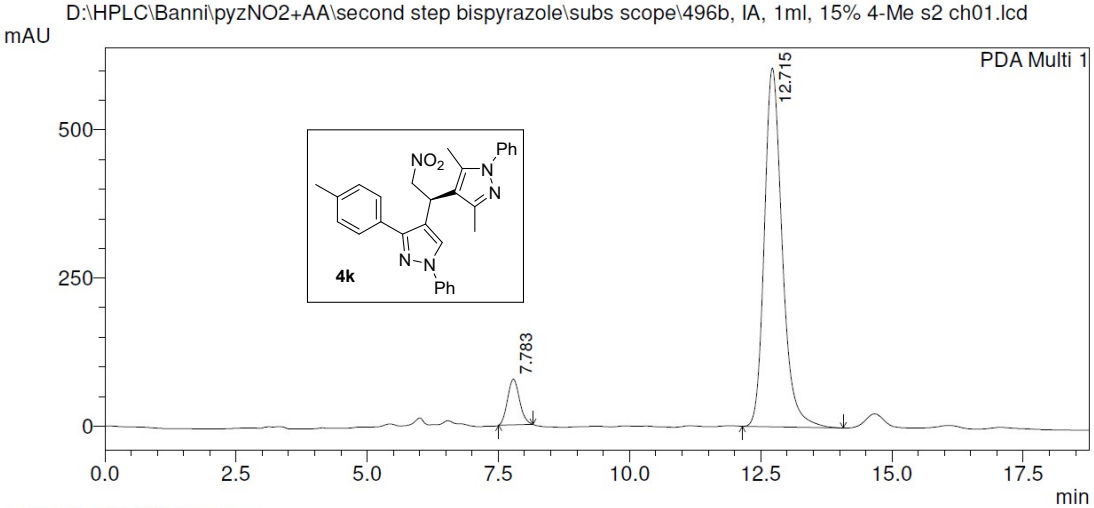
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.785	9378511	547991	50.470	58.323
2	12.755	9203981	391591	49.530	41.677
Total		18582492	939582	100.000	100.000

D:\HPLC\Banni\pyzNO2+AA\second step bispyrazole\subs scope\496b, IA, 1ml, 15% 4-Me s2 ch01.lcd



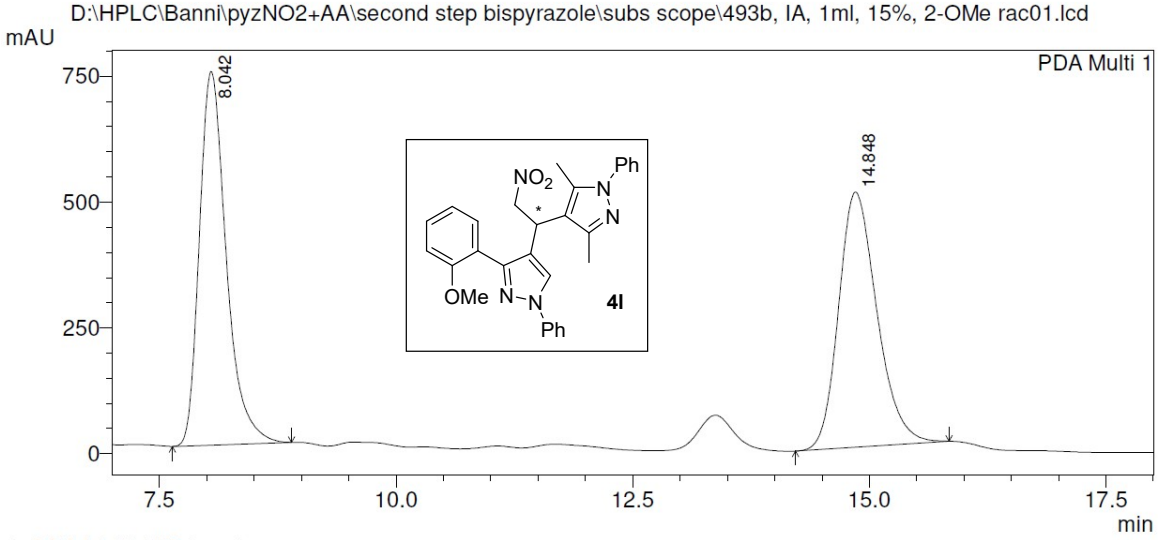
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.783	1230199	77264	7.904	11.306
2	12.715	14333706	606144	92.096	88.694
Total		15563905	683408	100.000	100.000

D:\HPLC\Banni\pyzNO2+AA\second step bispyrazole\subs scope\493b, IA, 1ml, 15%, 2-OMe rac01.lcd



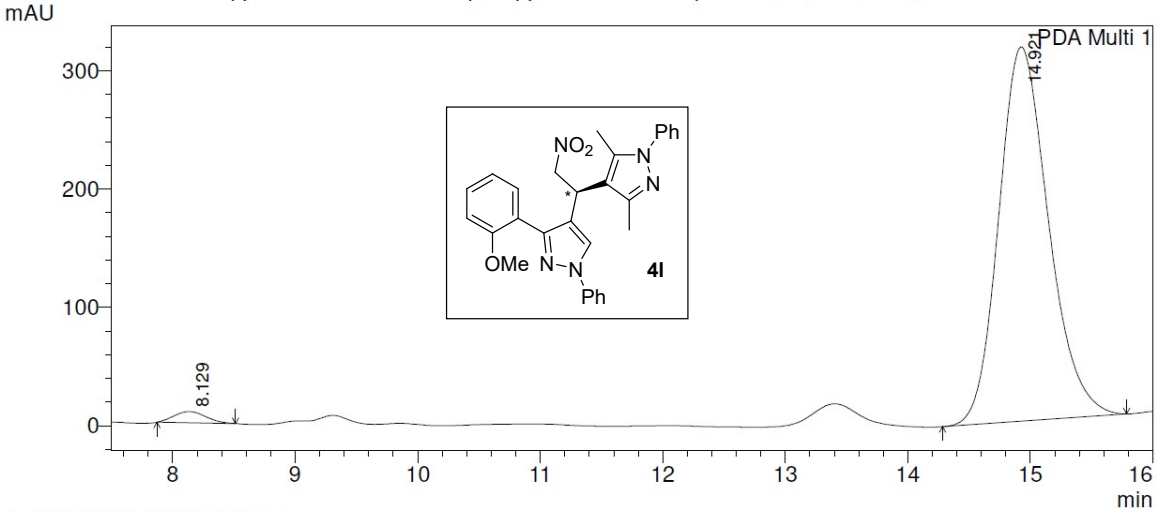
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.042	14664437	742369	50.637	59.418
2	14.848	14295443	507032	49.363	40.582
Total		28959881	1249401	100.000	100.000

D:\HPLC\Banni\pyzNO2+AA\second step bispyrazole\subs scope\494b, IA, 1ml, 15%, 2-OMe ch01.lcd



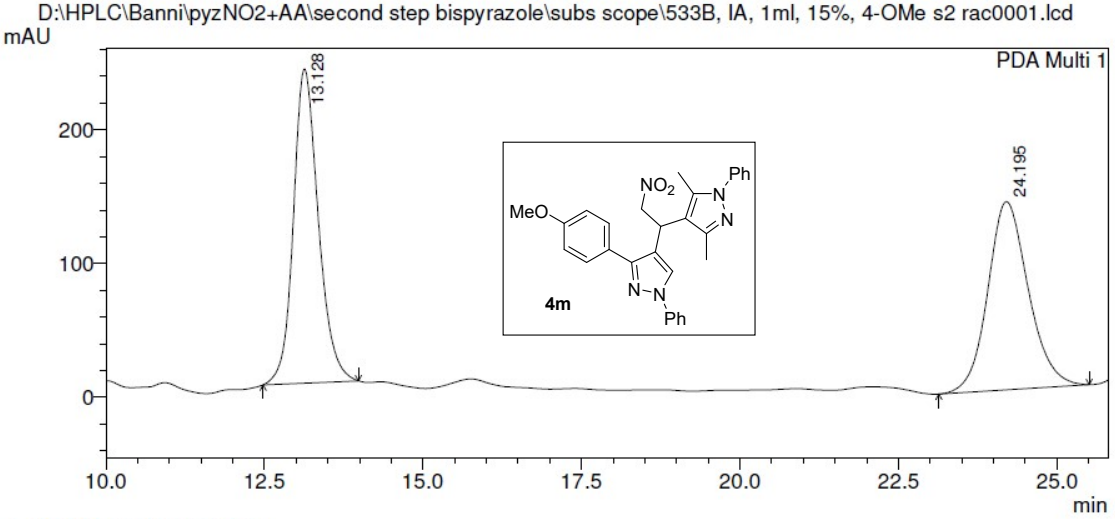
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.129	170514	9440	1.874	2.898
2	14.921	8928878	316295	98.126	97.102
Total		9099392	325735	100.000	100.000

D:\HPLC\Banni\pyzNO2+AA\second step bispyrazole\subs scope\533B, IA, 1ml, 15%, 4-OMe s2 rac0001.lcd



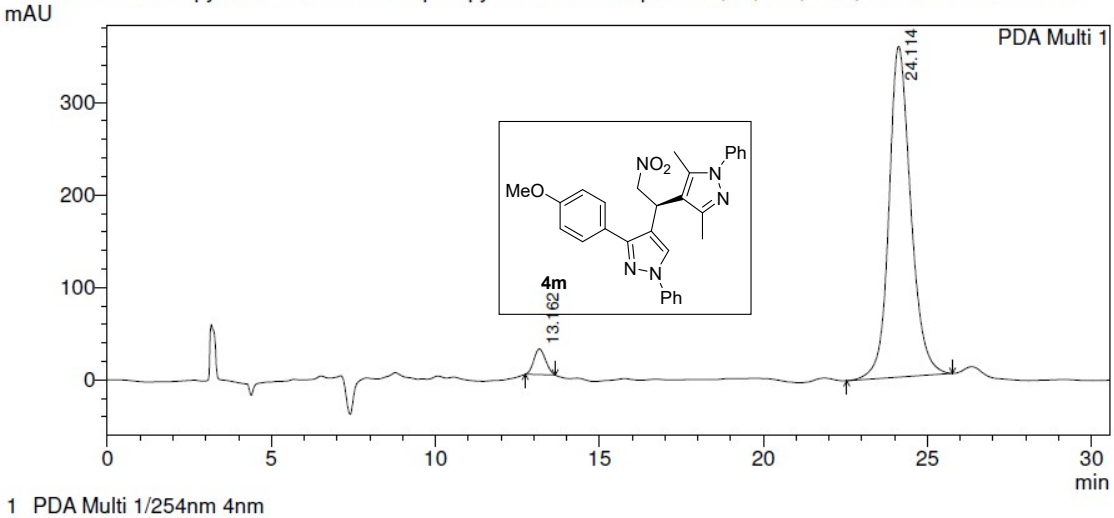
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.128	6441336	235023	50.687	62.514
2	24.195	6266722	140930	49.313	37.486
Total		12708058	375953	100.000	100.000

D:\HPLC\Banni\pyzNO2+AA\second step bispyrazole\subs scope\534B, IA, 1ml, 15%, 4-OMe s2 ch0001.lcd



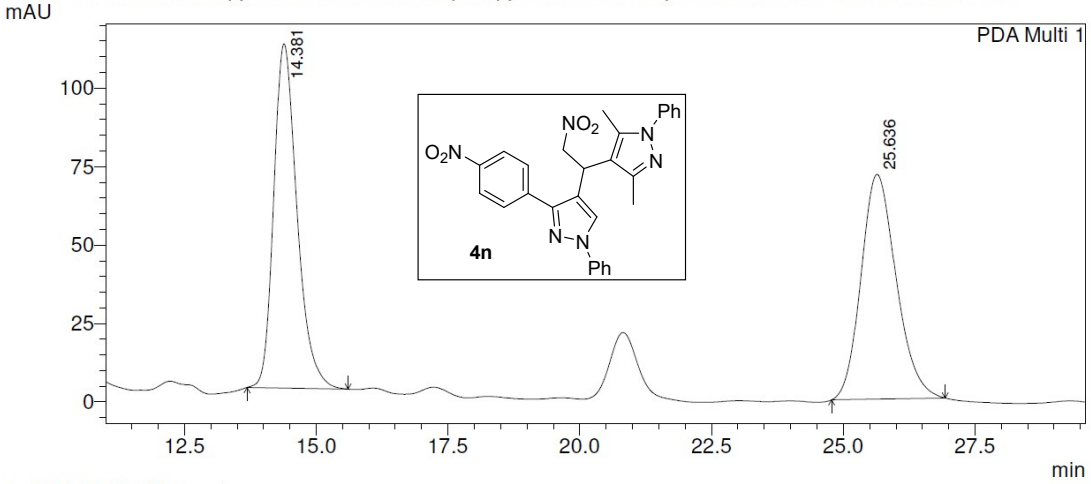
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.162	692785	27819	4.010	7.216
2	24.114	16585264	357718	95.990	92.784
Total		17278049	385537	100.000	100.000

D:\HPLC\Banni\pyzNO2+AA\second step bispyrazole\subs scope\507b, IA, 1ml, 15%, s2 racB01.lcd



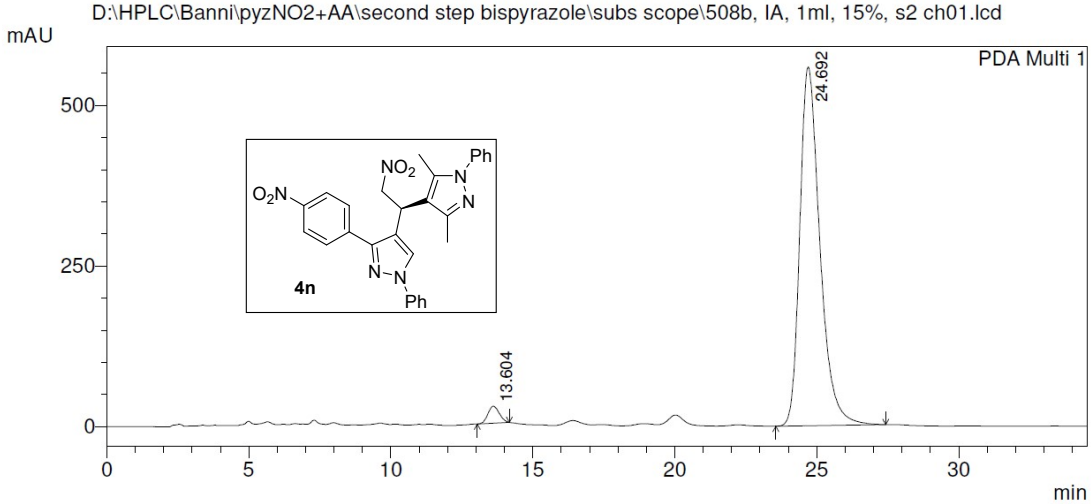
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.381	3371621	109653	50.320	60.494
2	25.636	3328763	71610	49.680	39.506
Total		6700384	181264	100.000	100.000

D:\HPLC\Banni\pyzNO2+AA\second step bispyrazole\subs scope\508b, IA, 1ml, 15%, s2 ch01.lcd



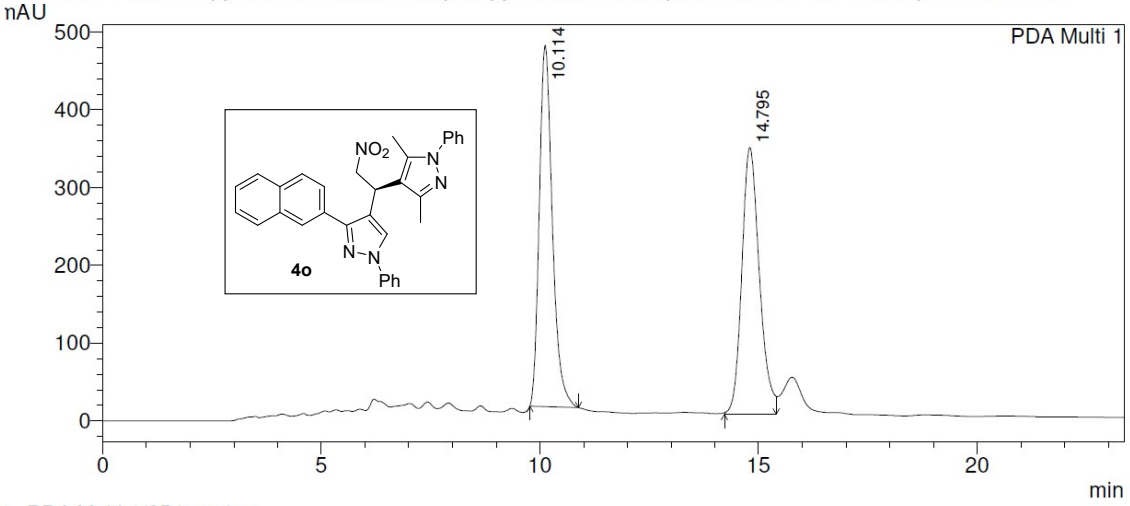
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.604	737440	26424	2.609	4.515
2	24.692	27525839	558849	97.391	95.485
Total		28263278	585273	100.000	100.000

D:\HPLC\Banni\pyzNO2+AA\second step bispyrazole\subs scope\511b, IA, 1ml, 15%, naph s2 rac01.lcd



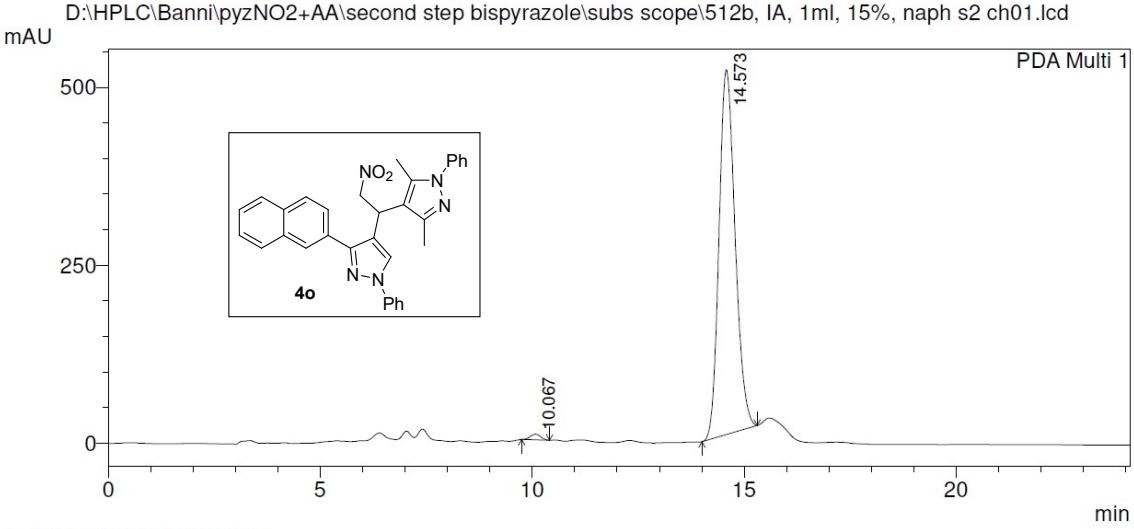
l PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.114	9666777	464245	50.245	57.522
2	14.795	9572339	342826	49.755	42.478
Total		19239116	807070	100.000	100.000

D:\HPLC\Banni\pyzNO2+AA\second step bispyrazole\subs scope\512b, IA, 1ml, 15%, naph s2 ch01.lcd



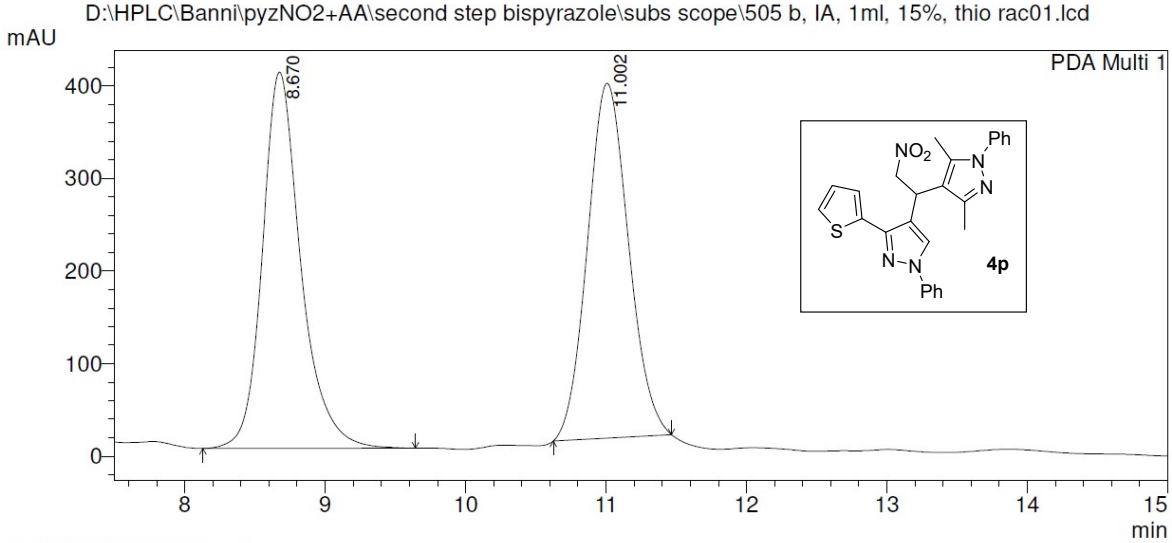
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.067	136161	7824	0.997	1.504
2	14.573	13517629	512377	99.003	98.496
Total		13653791	520201	100.000	100.000

D:\HPLC\Banni\pyzNO2+AA\second step bispyrazole\subs scope\505 b, IA, 1ml, 15%, thio rac01.lcd



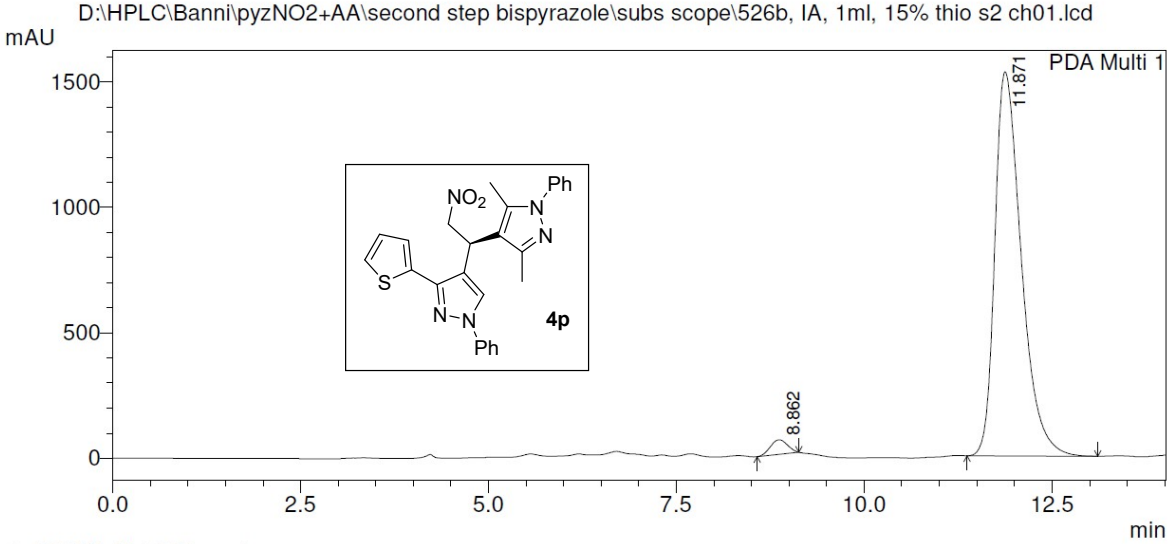
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.670	7778071	406777	49.974	51.469
2	11.002	7786146	383562	50.026	48.531
Total		15564217	790339	100.000	100.000

D:\HPLC\Banni\pyzNO2+AA\second step bispyrazole\subs scope\526b, IA, 1ml, 15% thio s2 ch01.lcd



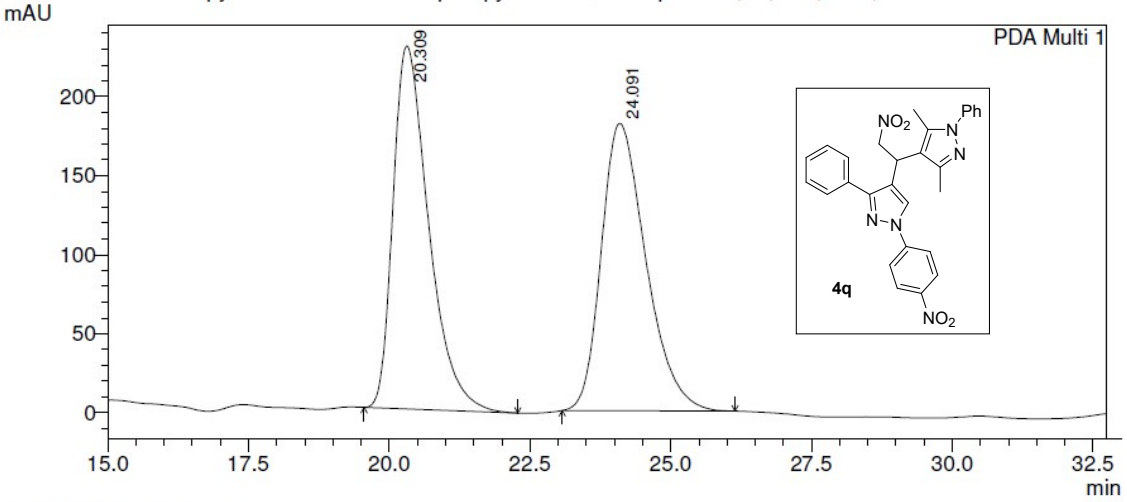
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.862	922121	58211	2.404	3.665
2	11.871	37442683	1530288	97.596	96.335
Total		38364805	1588499	100.000	100.000

D:\HPLC\Banni\pyzNO2+AA\second step bispyrazole\subs scope\509b, IA, 1ml, 15%, 4-NO2 s2 rac02.lcd



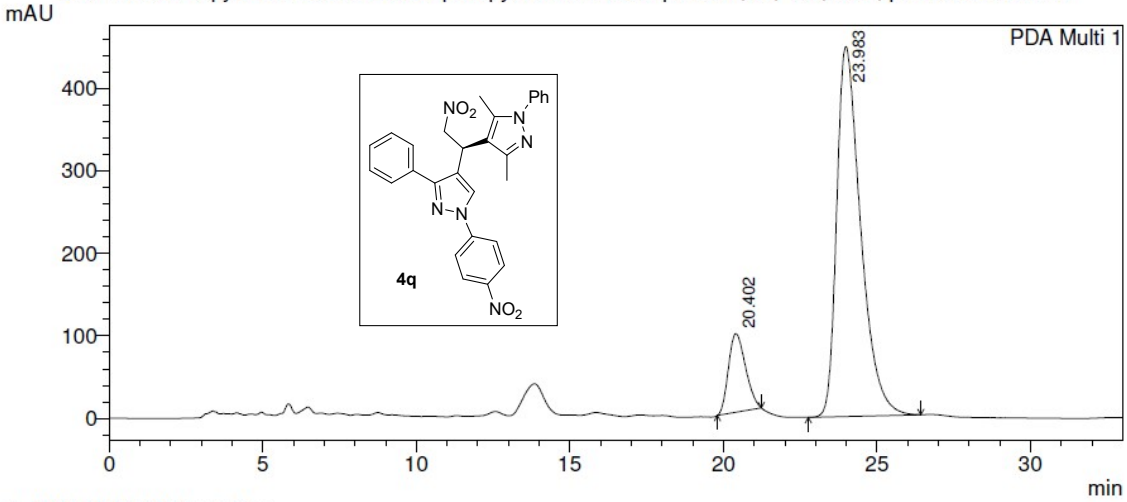
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.309	10102902	229553	50.182	55.802
2	24.091	10029684	181821	49.818	44.198
Total		20132586	411375	100.000	100.000

D:\HPLC\Banni\pyzNO2+AA\second step bispyrazole\subs scope\510b, IA, 1ml, 15%, p-NO2 s2 ch01.lcd



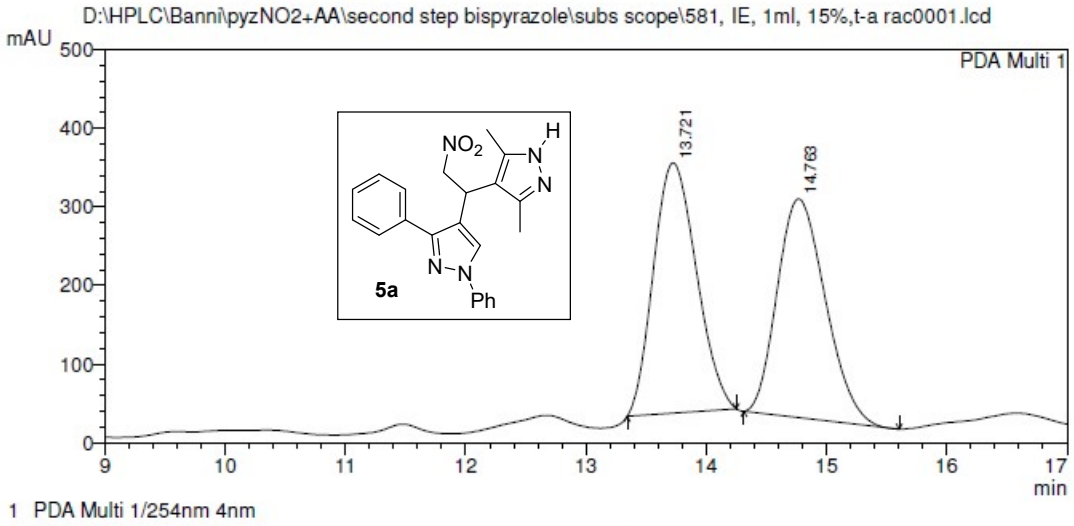
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.402	3690829	95311	13.160	17.526
2	23.983	24354337	448505	86.840	82.474
Total		28045166	543816	100.000	100.000

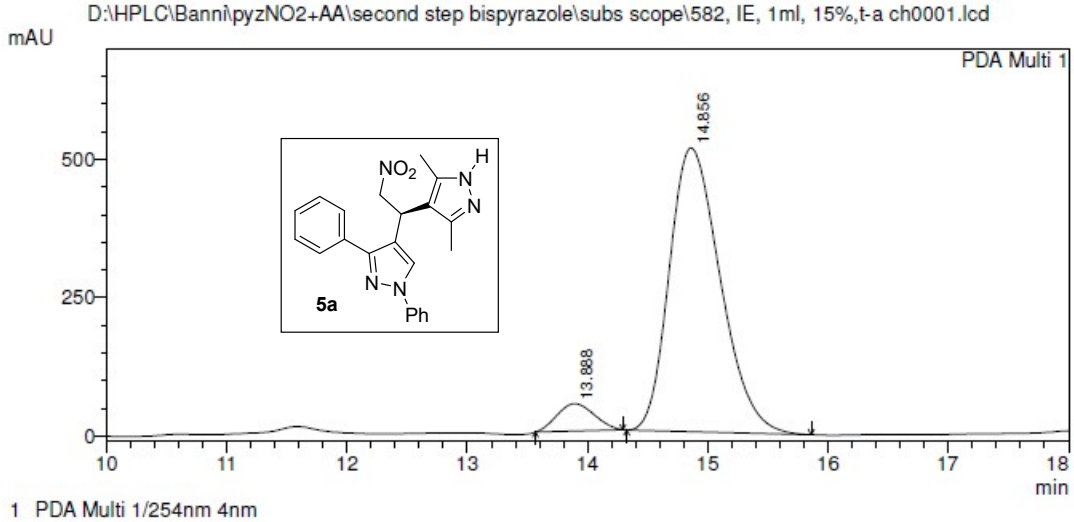
HPLC chromatogram of series 5



PeakTable

PDA Ch1 254nm 4nm

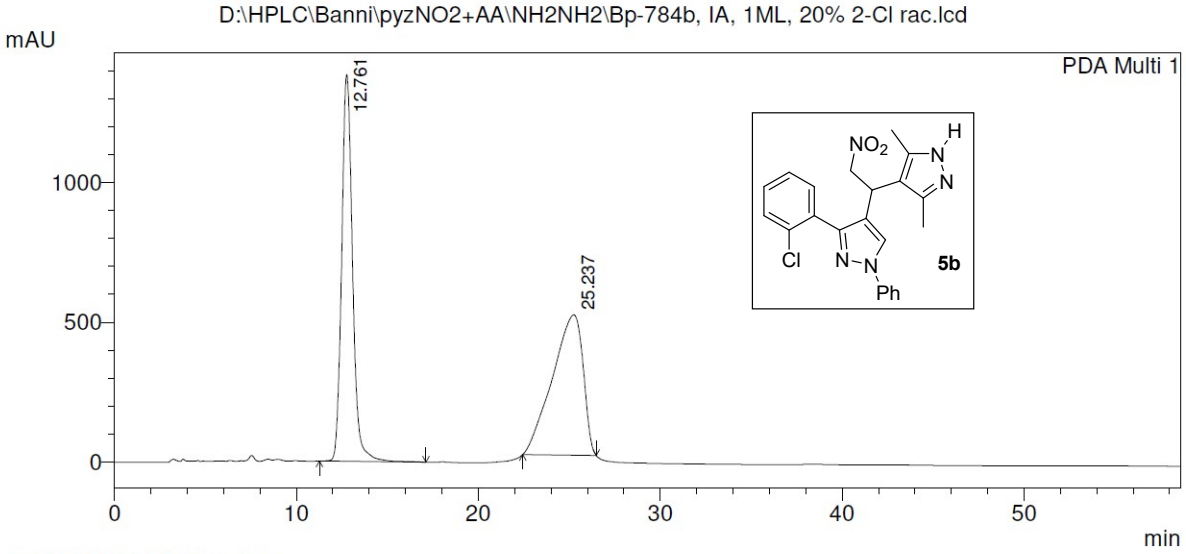
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.721	7906560	318507	50.527	53.386
2	14.763	7741479	278100	49.473	46.614
Total		15648039	596607	100.000	100.000



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.888	1066999	49412	6.587	8.789
2	14.856	15130633	512825	93.413	91.211
Total		16197632	562237	100.000	100.000

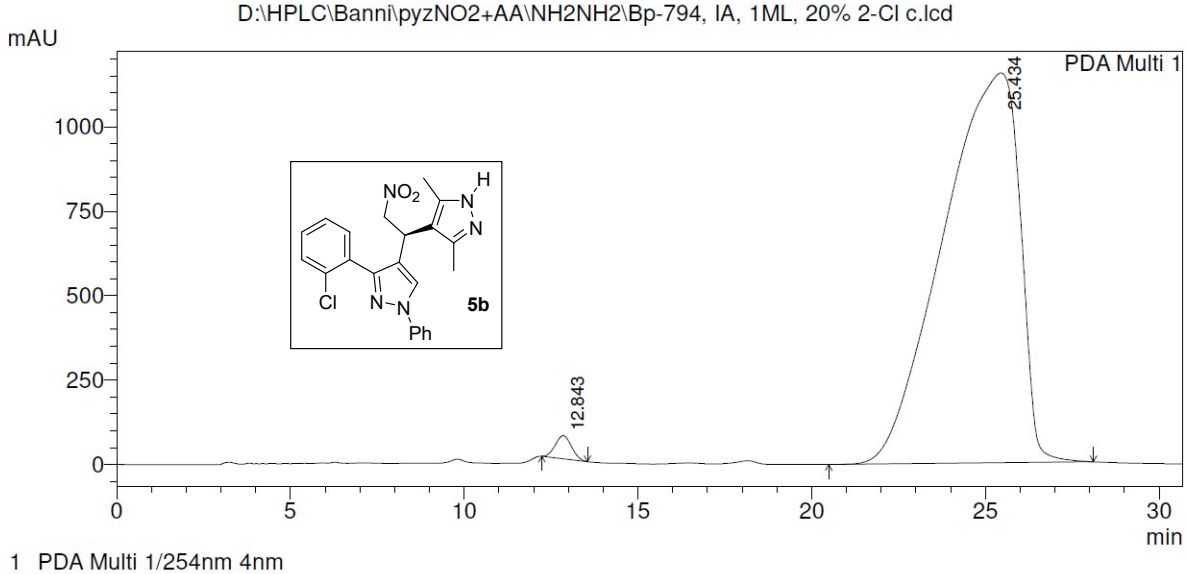


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.761	57511425	1383271	49.358	73.354
2	25.237	59006694	502482	50.642	26.646
Total		116518119	1885753	100.000	100.000

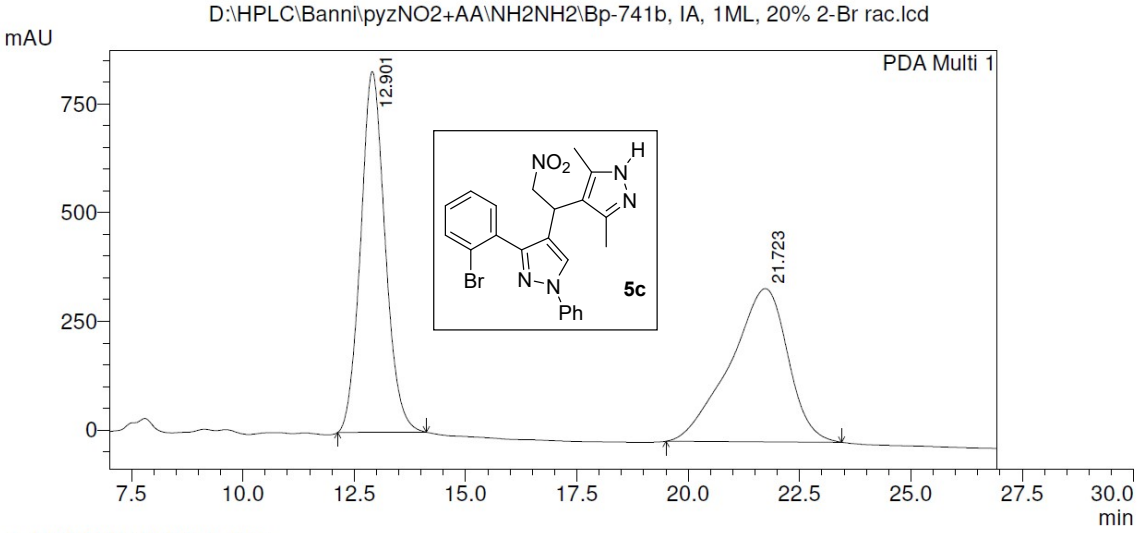


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.843	2218388	68166	1.233	5.578
2	25.434	177689642	1153993	98.767	94.422
Total		179908030	1222159	100.000	100.000

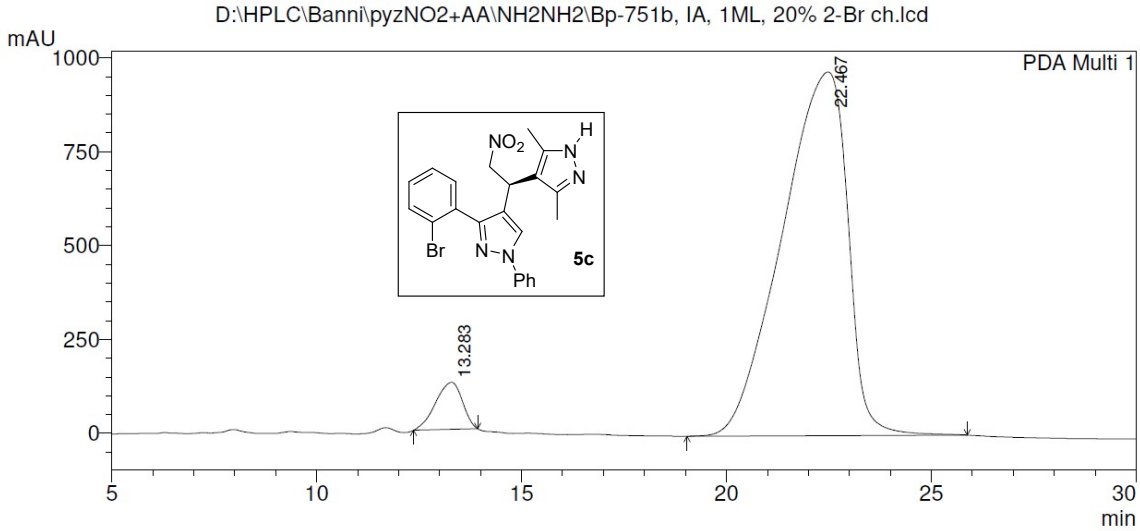


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.901	31779687	829310	50.018	70.197
2	21.723	31756960	352091	49.982	29.803
Total		63536647	1181401	100.000	100.000

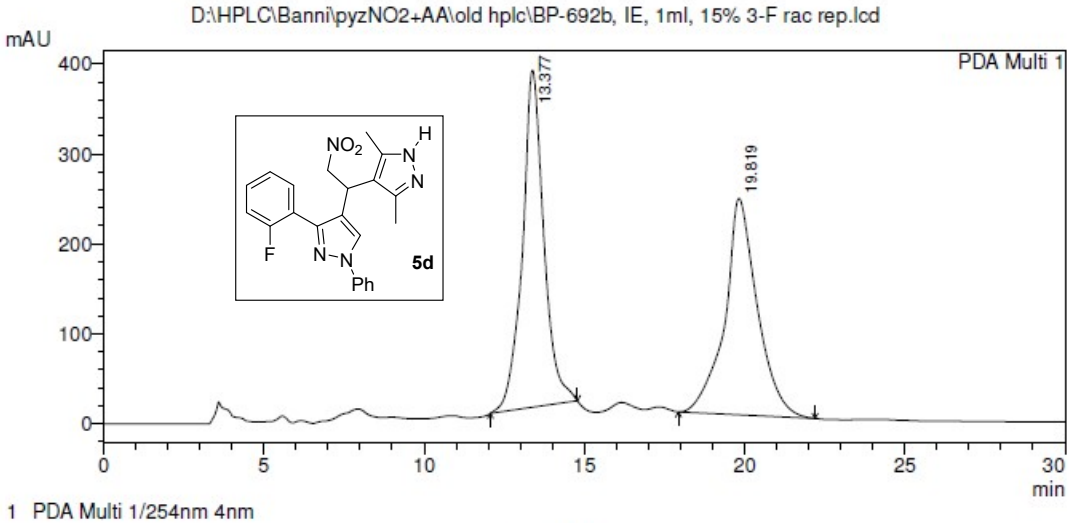


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.283	5731381	125525	5.048	11.474
2	22.467	107811150	968507	94.952	88.526
Total		113542532	1094032	100.000	100.000

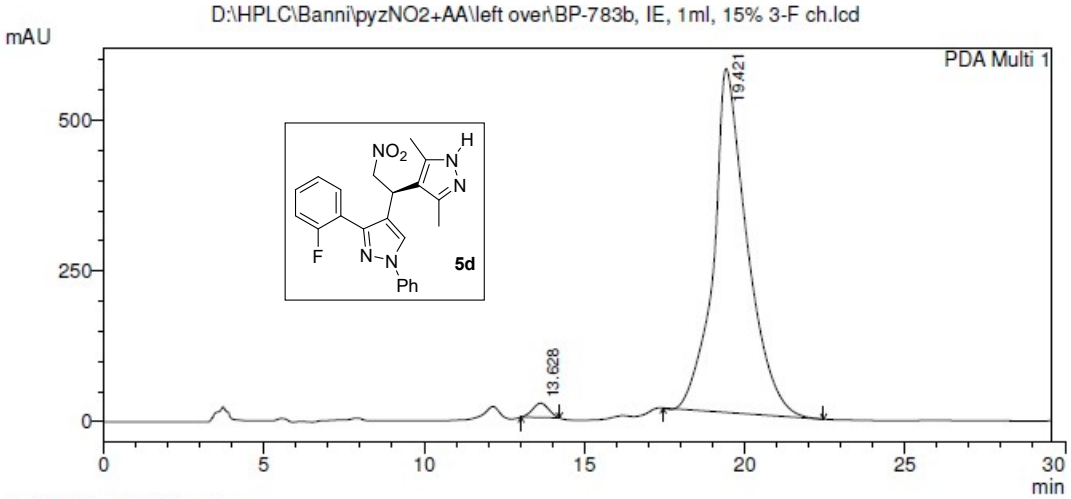


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.377	17464732	374898	50.638	60.903
2	19.819	17024968	240672	49.362	39.097
Total		34489700	615570	100.000	100.000

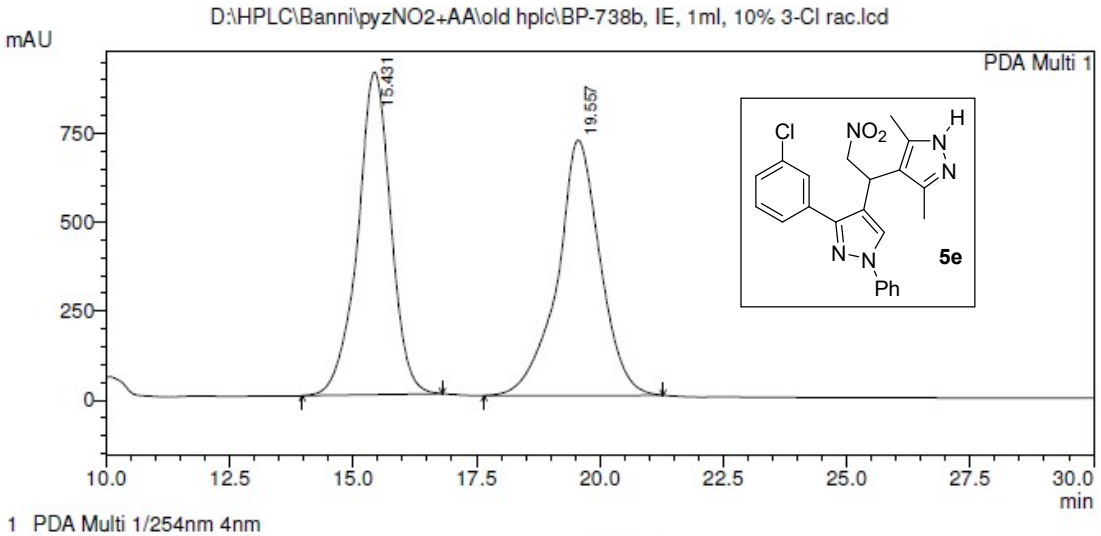


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.628	830431	23875	1.949	4.019
2	19.421	41768669	570130	98.051	95.981
Total		42599101	594005	100.000	100.000

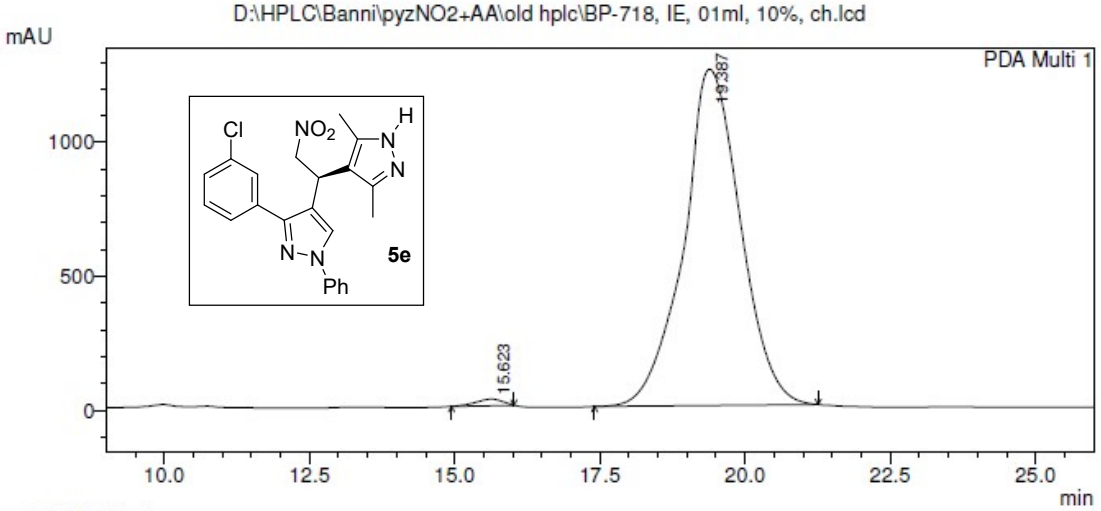


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.431	42416008	905512	49.429	55.813
2	19.557	43395670	716878	50.571	44.187
Total		85811678	1622389	100.000	100.000

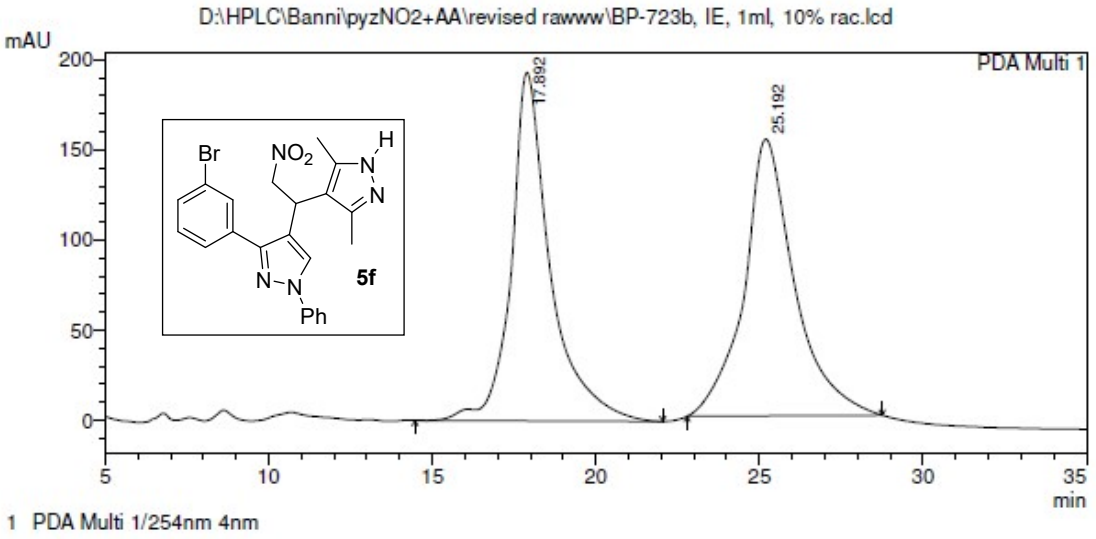


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.623	776782	24311	0.900	1.901
2	19.387	85546387	1254817	99.100	98.099
Total		86323170	1279127	100.000	100.000

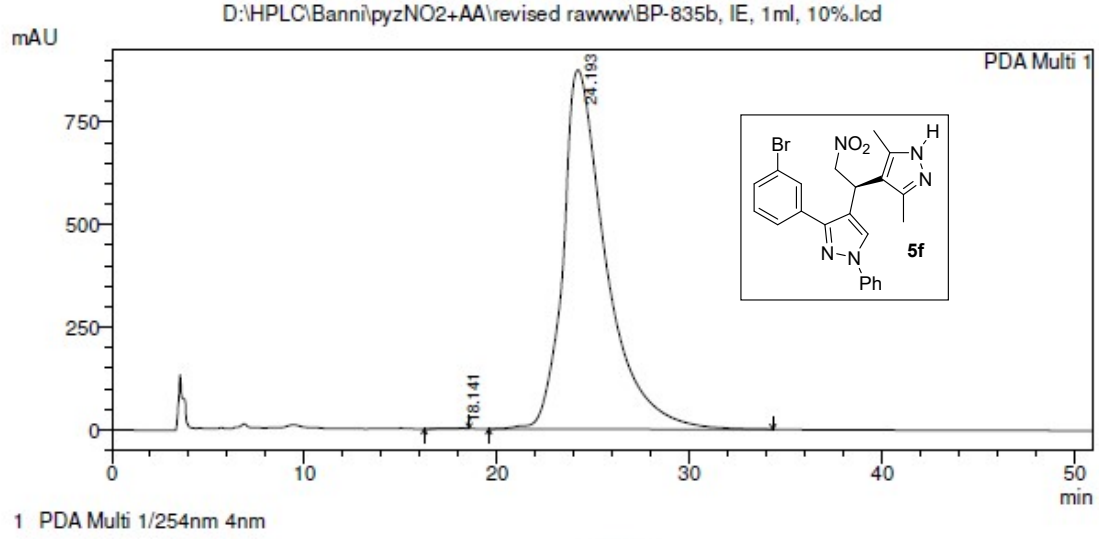


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.892	15992995	193114	49.179	55.724
2	25.192	16526858	153439	50.821	44.276
Total		32519853	346553	100.000	100.000

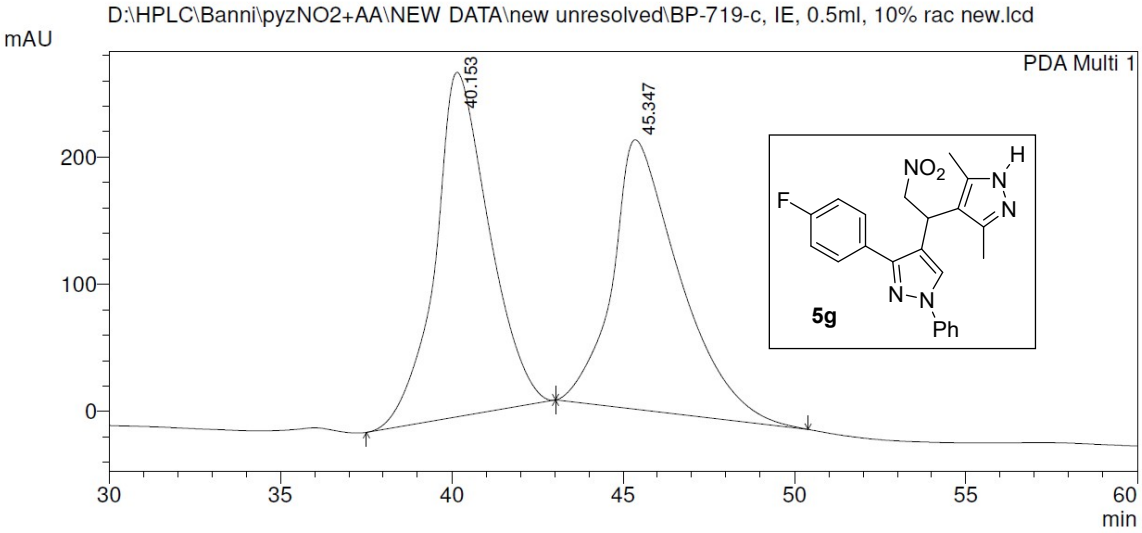


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.141	72791	880	0.053	0.100
2	24.193	136086909	875382	99.947	99.900
Total		136159700	876262	100.000	100.000

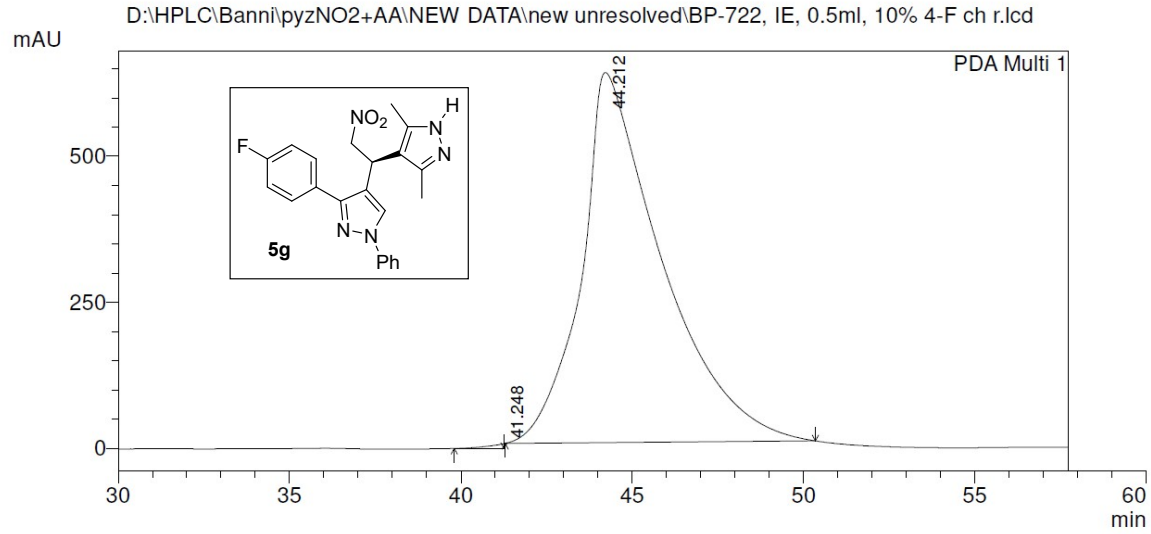


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	40.153	29699920	271003	50.419	56.114
2	45.347	29205905	211946	49.581	43.886
Total		58905826	482949	100.000	100.000

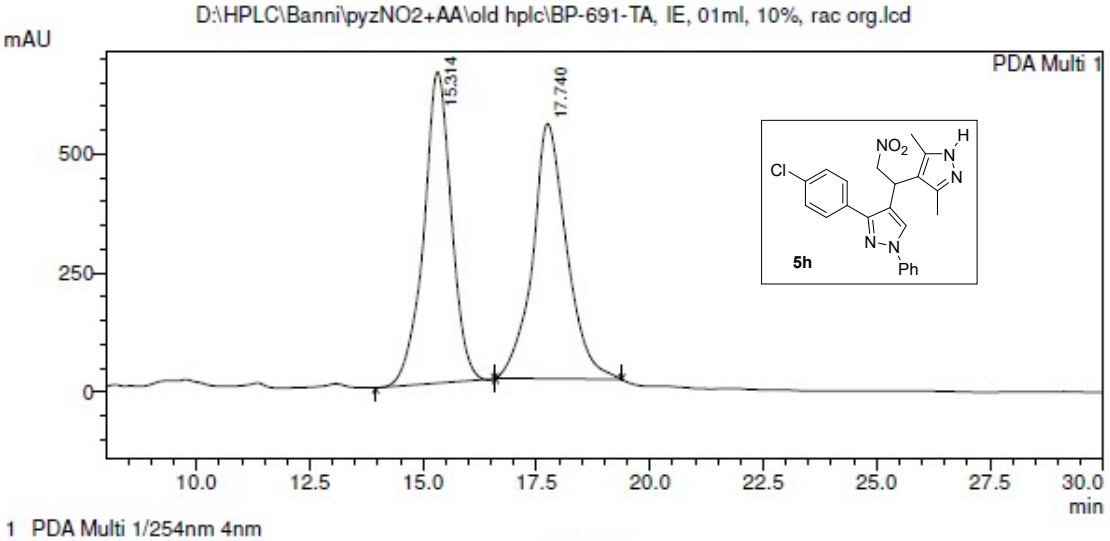


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	41.248	233616	7854	0.225	1.225
2	44.212	103518276	633202	99.775	98.775
Total		103751892	641055	100.000	100.000

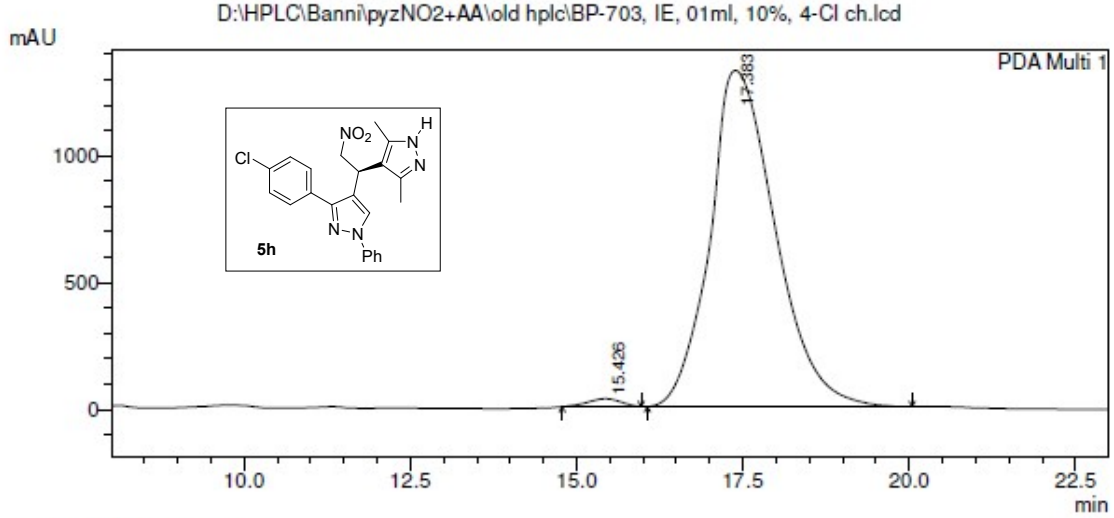


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.314	27735568	653727	49.635	54.955
2	17.740	28143385	535843	50.365	45.045
Total		55878953	1189571	100.000	100.000

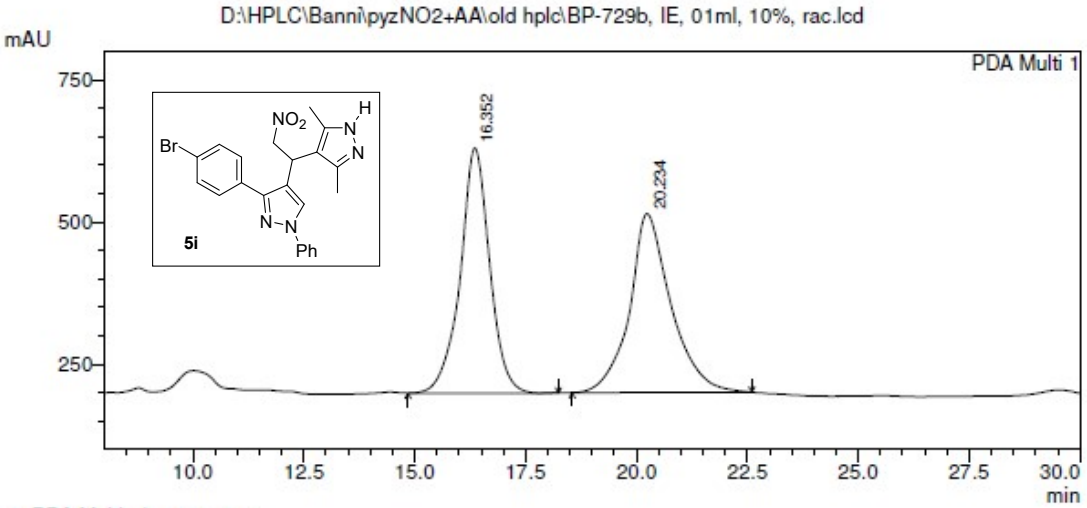


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.426	1091090	31241	1.190	2.304
2	17.383	90573588	1324722	98.810	97.696
Total		91664678	1355963	100.000	100.000

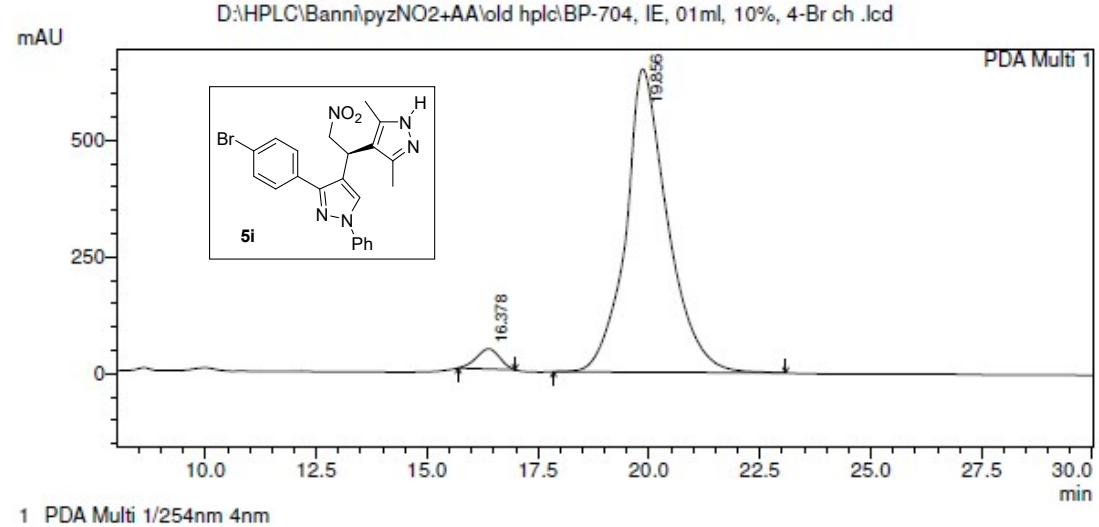


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.352	19889055	430768	49.318	57.806
2	20.234	20438794	314433	50.682	42.194
Total		40327849	745201	100.000	100.000

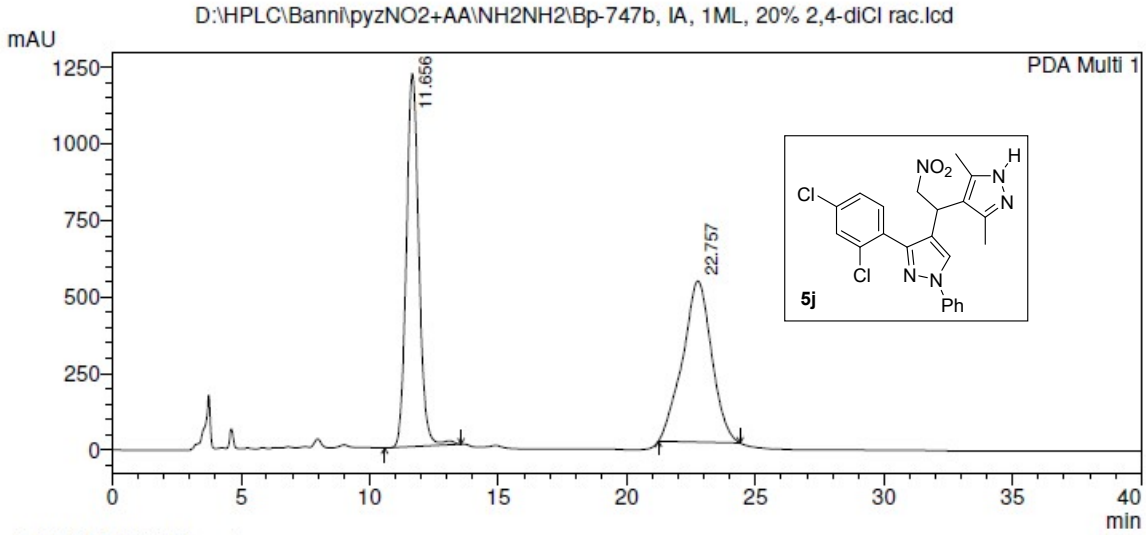


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

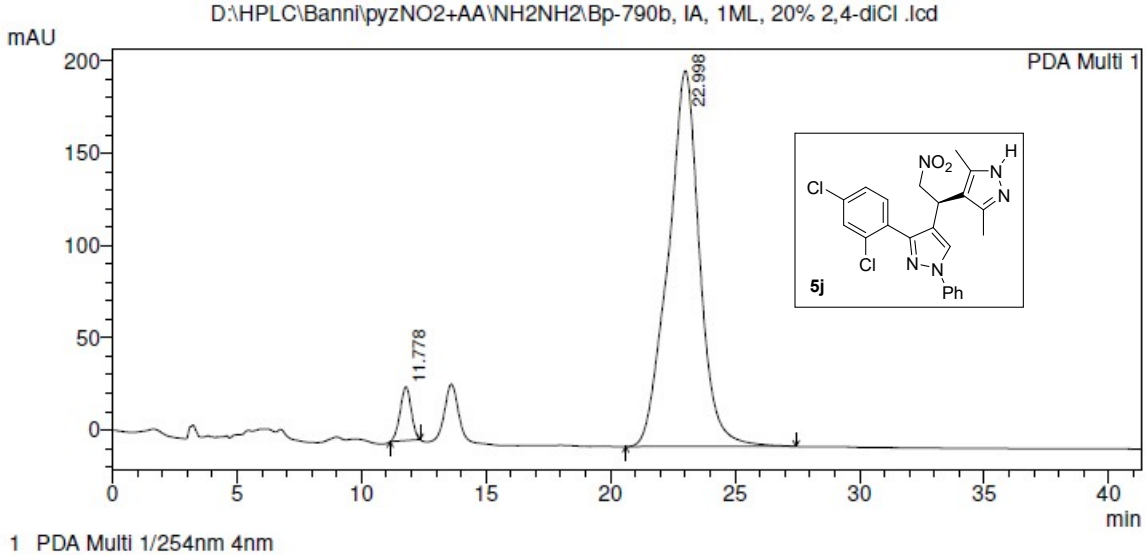
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.378	1556706	43053	3.507	6.215
2	19.856	42827016	649659	96.493	93.785
Total		44383722	692712	100.000	100.000



PeakTable

PDA Ch1 254nm 4nm

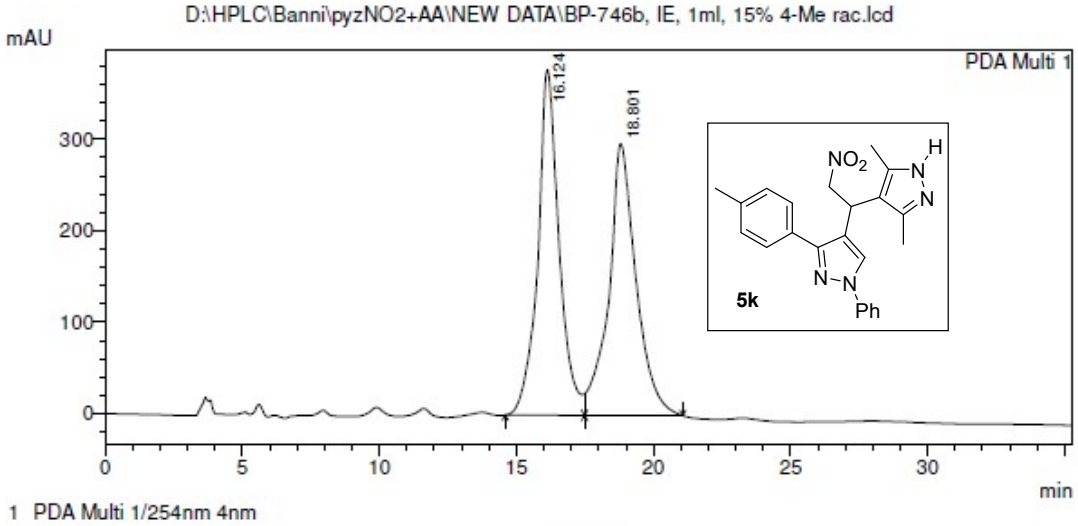
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.656	41173464	1219215	49.848	69.850
2	22.757	41424628	526272	50.152	30.150
Total		82598092	1745488	100.000	100.000



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.778	903067	29099	4.820	12.510
2	22.998	17833632	203508	95.180	87.490
Total		18736700	232607	100.000	100.000

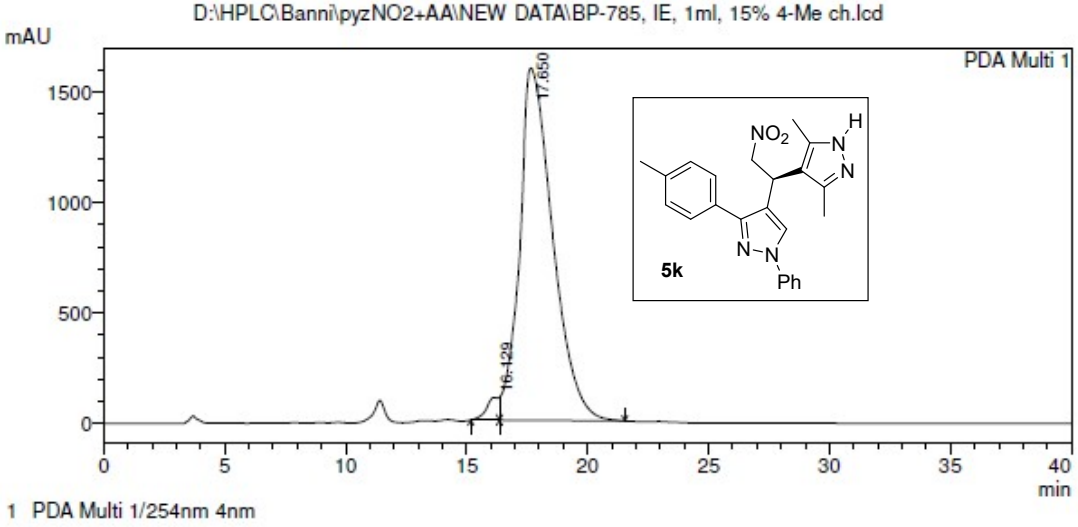


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.124	20440497	377904	49.812	55.969
2	18.801	20594867	297296	50.188	44.031
Total		41035363	675199	100.000	100.000

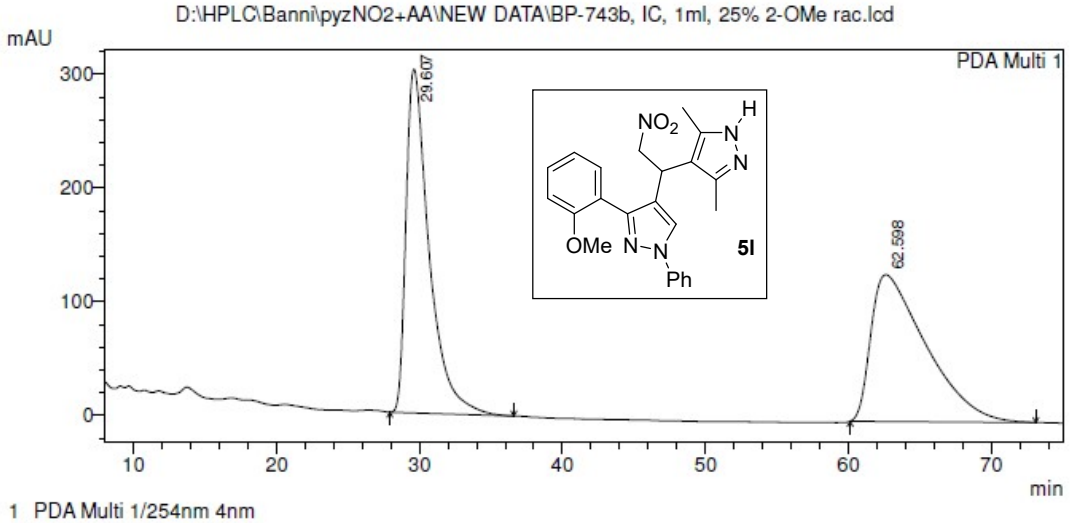


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.129	3640251	102891	2.332	6.057
2	17.650	152438515	1595722	97.668	93.943
Total		156078766	1698612	100.000	100.000

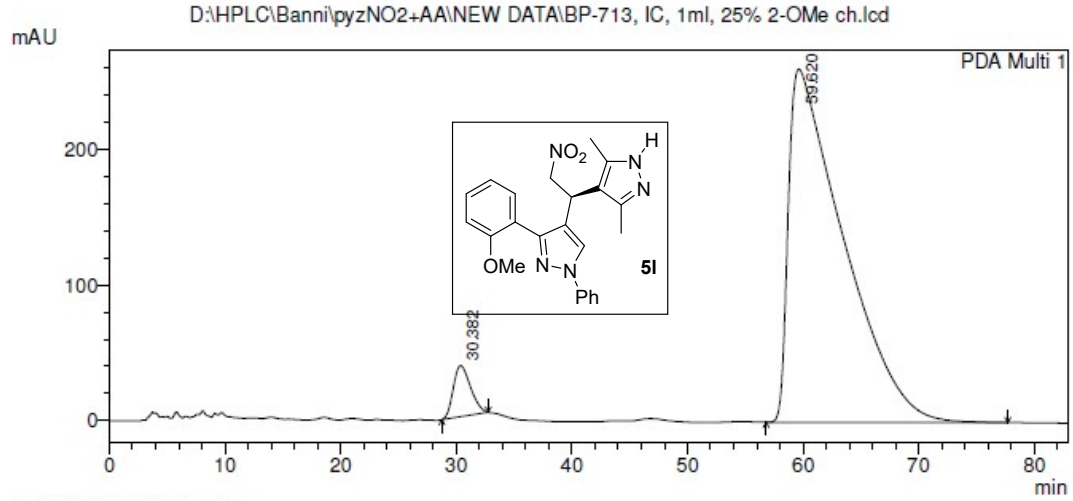


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.607	33996580	302395	49.623	70.077
2	62.598	34513061	129122	50.377	29.923
Total		68509640	431517	100.000	100.000

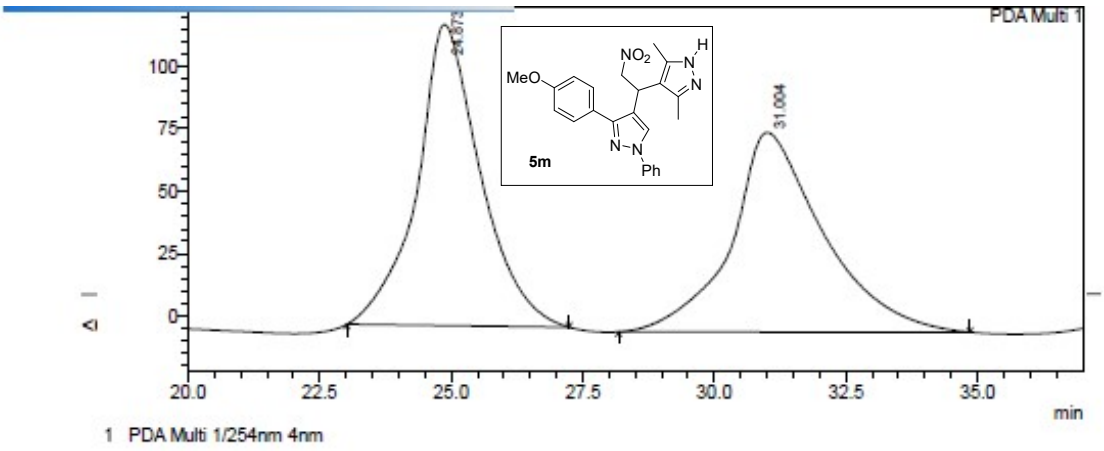


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.382	3903815	37636	4.353	12.635
2	59.620	85772822	260243	95.647	87.365
Total		89676637	297878	100.000	100.000

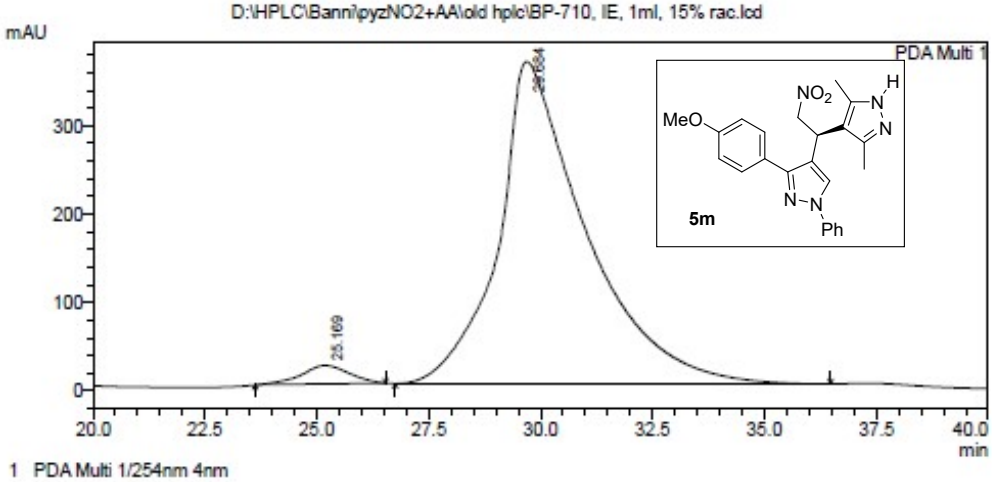


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.873	10131107	120557	50.944	60.148
2	31.004	9755512	79876	49.056	39.852
Total		19886619	200433	100.000	100.000

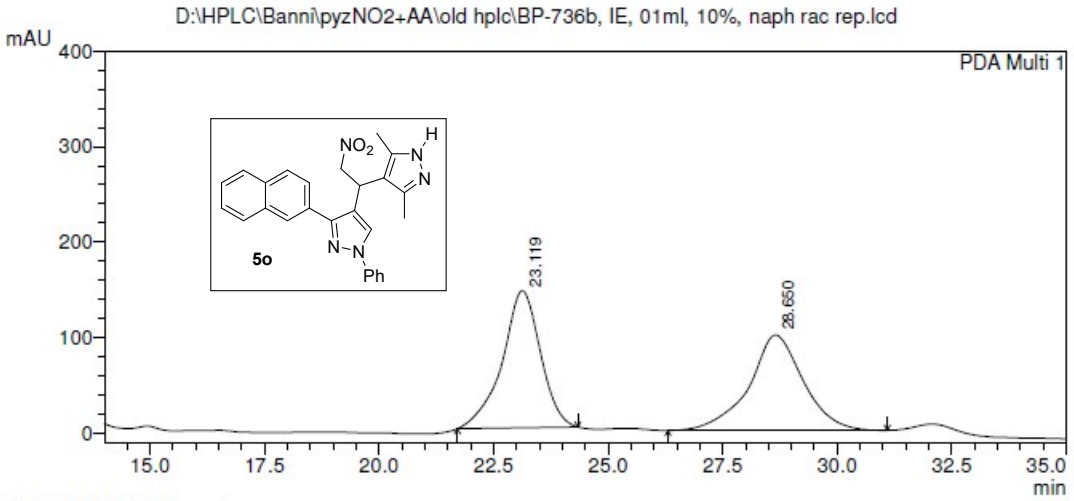


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.169	1550774	20826	3.032	5.403
2	29.684	49587870	364598	96.968	94.597
Total		51138645	385424	100.000	100.000

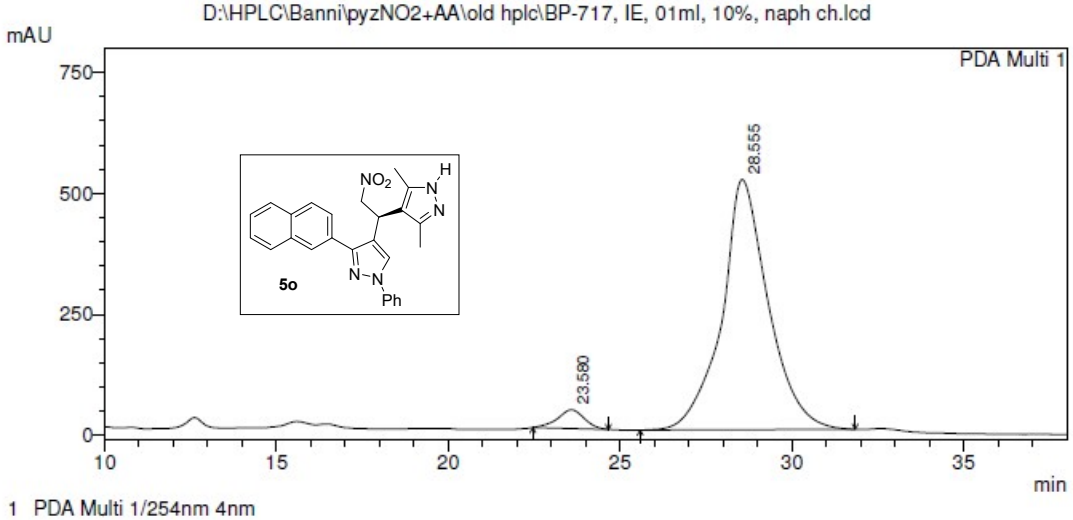


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.119	8336004	143118	50.346	58.956
2	28.650	8221462	99637	49.654	41.044
Total		16557467	242754	100.000	100.000



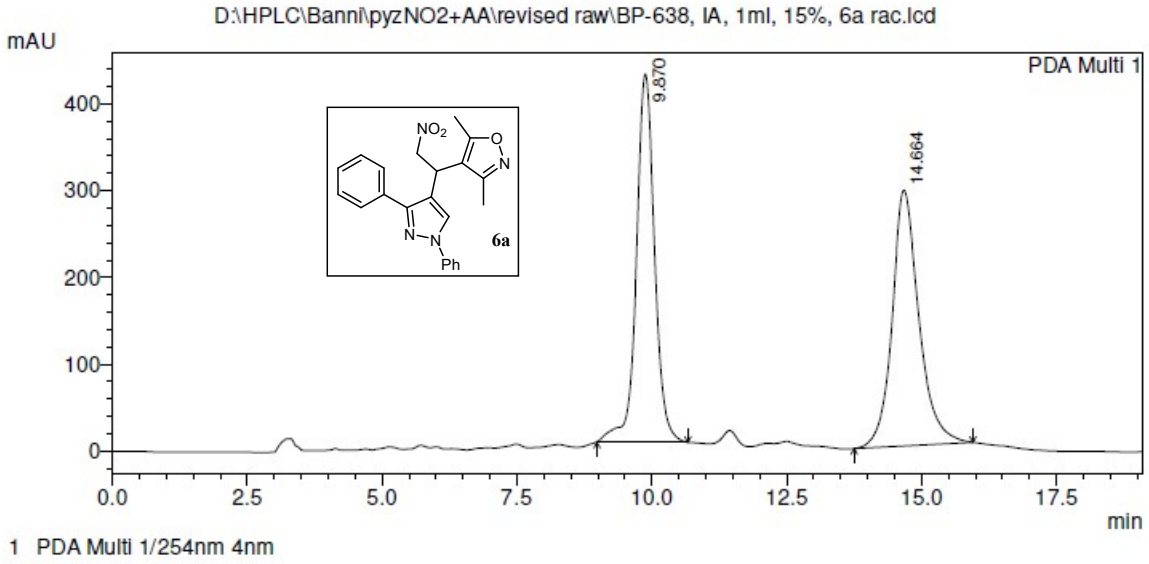
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.580	2081930	38439	4.107	6.929
2	28.555	48614890	516341	95.893	93.071
Total		50696820	554780	100.000	100.000

HPLC chromatogram of series 6

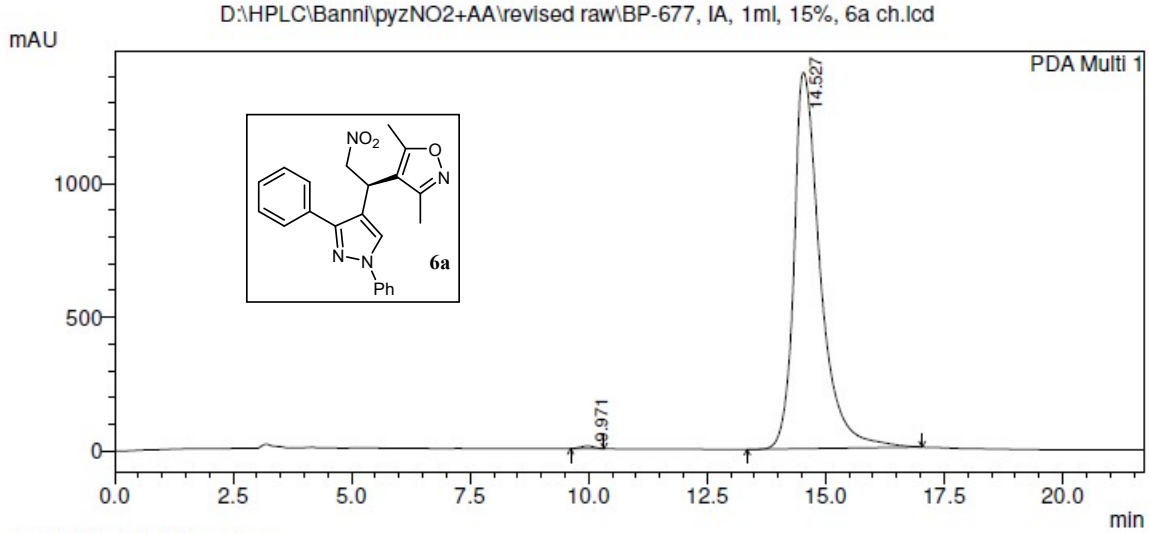


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.870	10006861	424046	49.659	59.009
2	14.664	10144095	294567	50.341	40.991
Total		20150956	718613	100.000	100.000

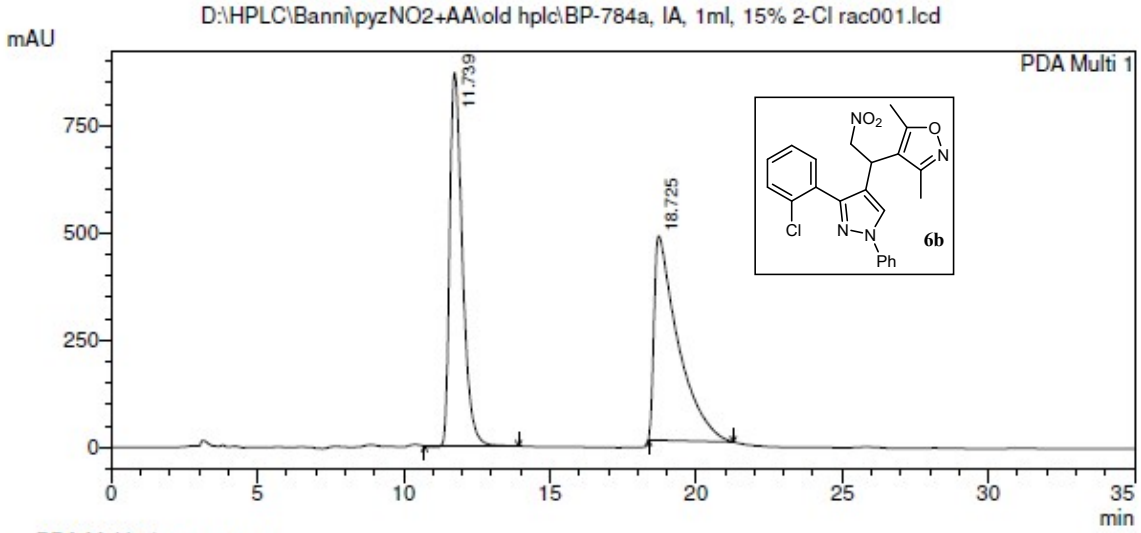


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.971	203527	10187	0.373	0.720
2	14.527	54398967	1405393	99.627	99.280
Total		54602494	1415580	100.000	100.000

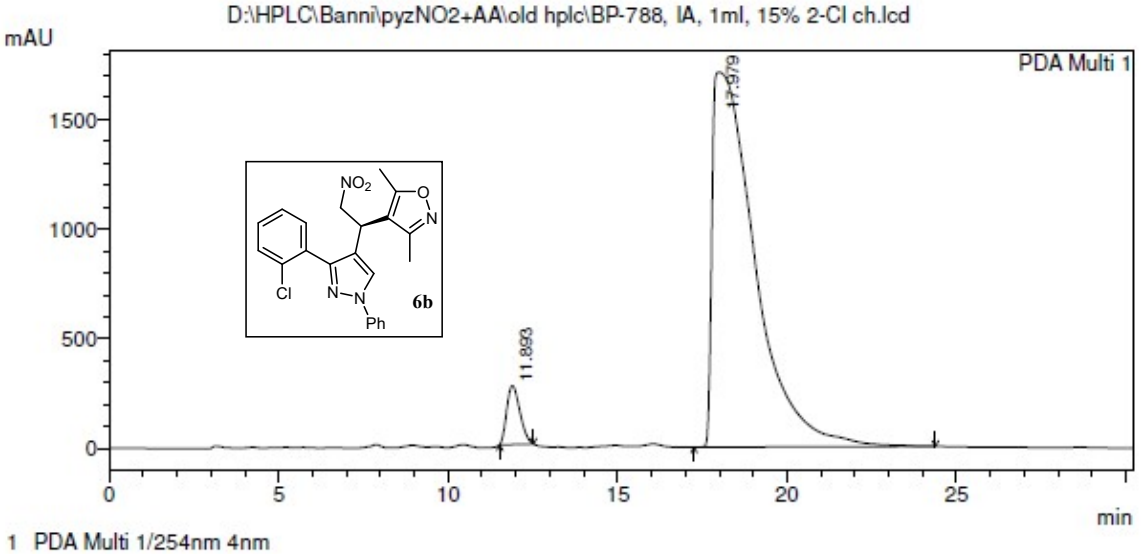


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.739	26195821	870609	49.045	64.660
2	18.725	27216021	475823	50.955	35.340
Total		53411842	1346432	100.000	100.000

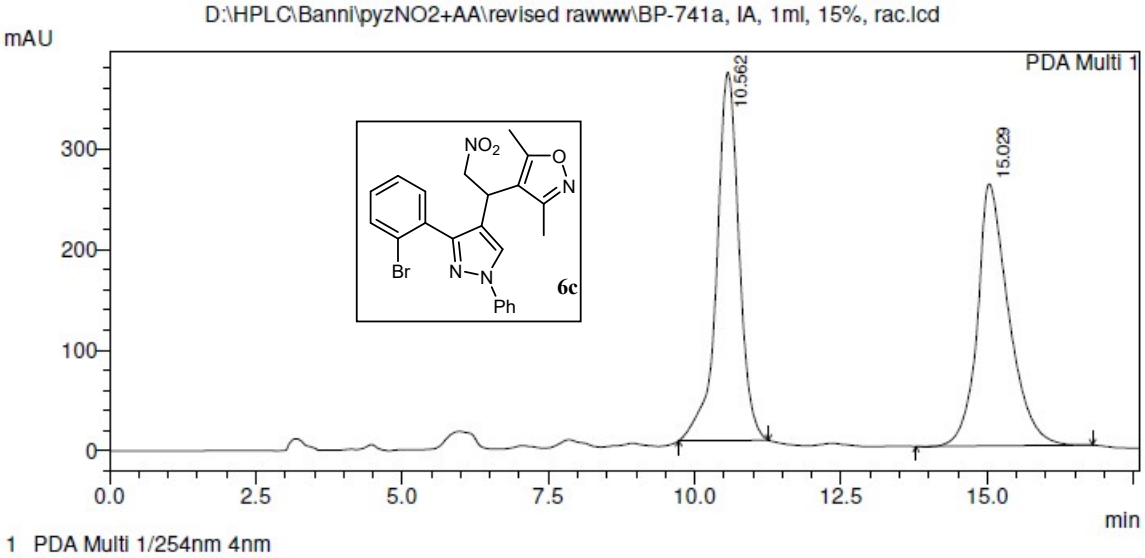


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.893	7248667	268129	4.602	13.557
2	17.979	150245700	1709674	95.398	86.443
Total		157494367	1977802	100.000	100.000

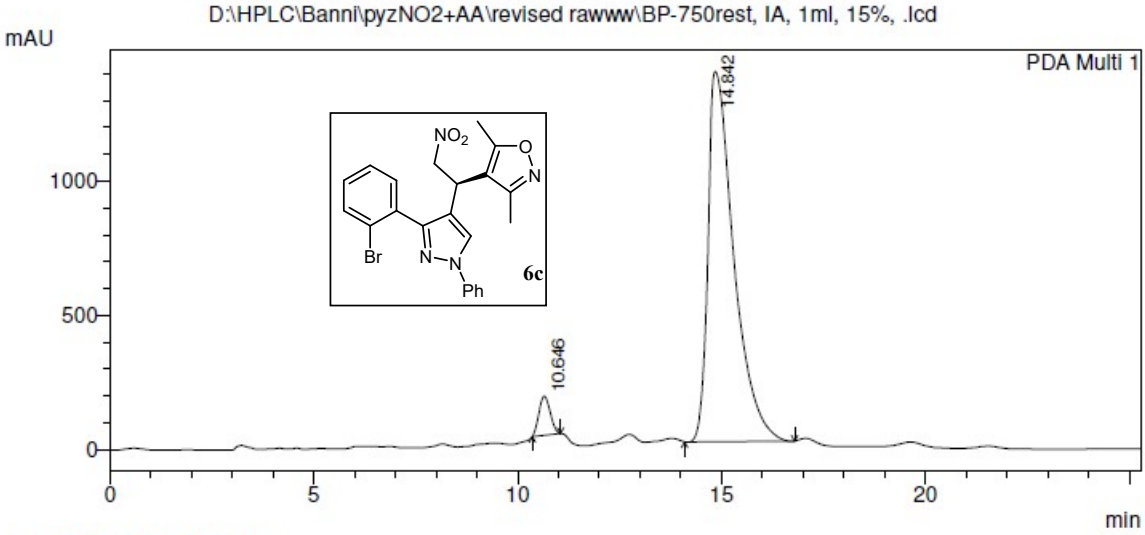


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.562	9743306	365947	50.138	58.431
2	15.029	9689837	260342	49.862	41.569
Total		19433142	626289	100.000	100.000

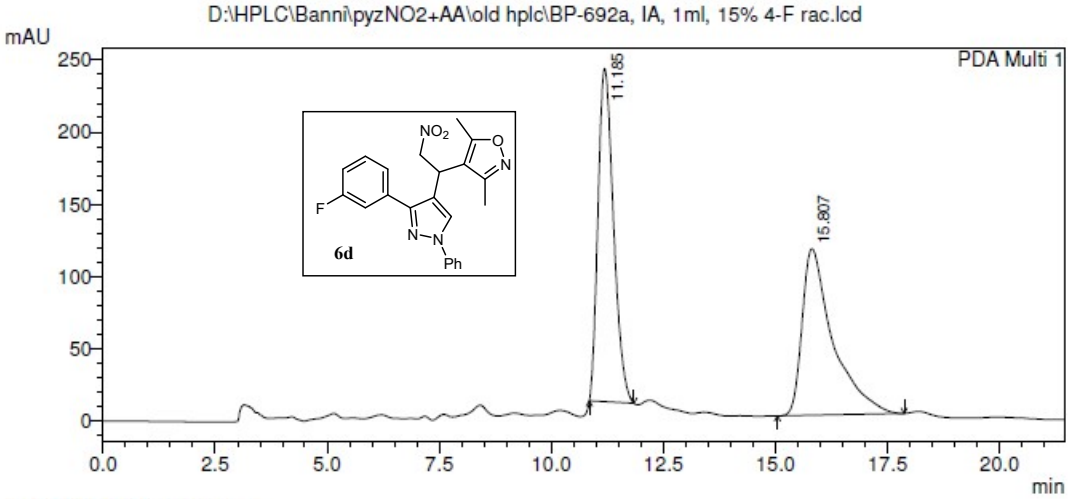


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.646	2799354	145093	4.406	9.535
2	14.842	60728672	1376520	95.594	90.465
Total		63528025	1521613	100.000	100.000

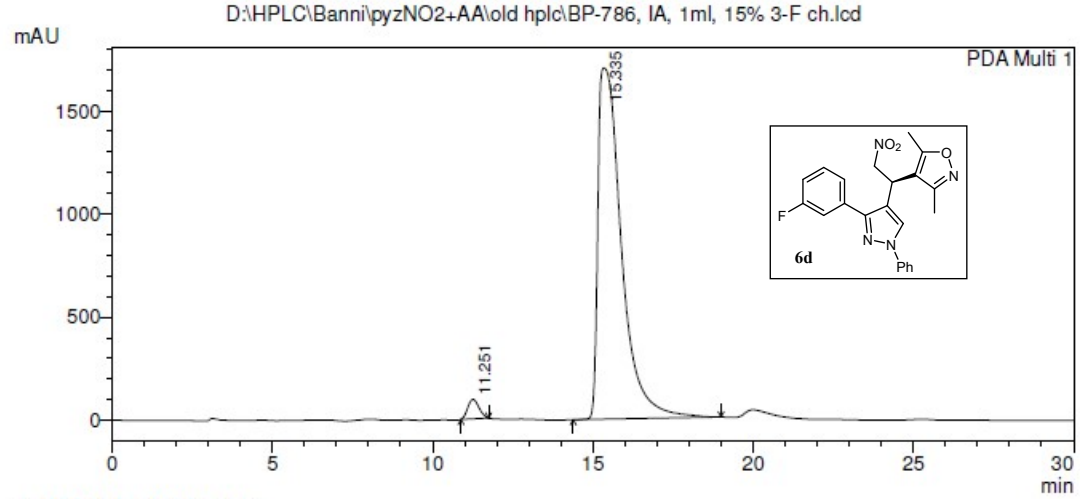


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.185	5549648	230324	50.222	66.656
2	15.807	5500612	115216	49.778	33.344
Total		11050260	345540	100.000	100.000

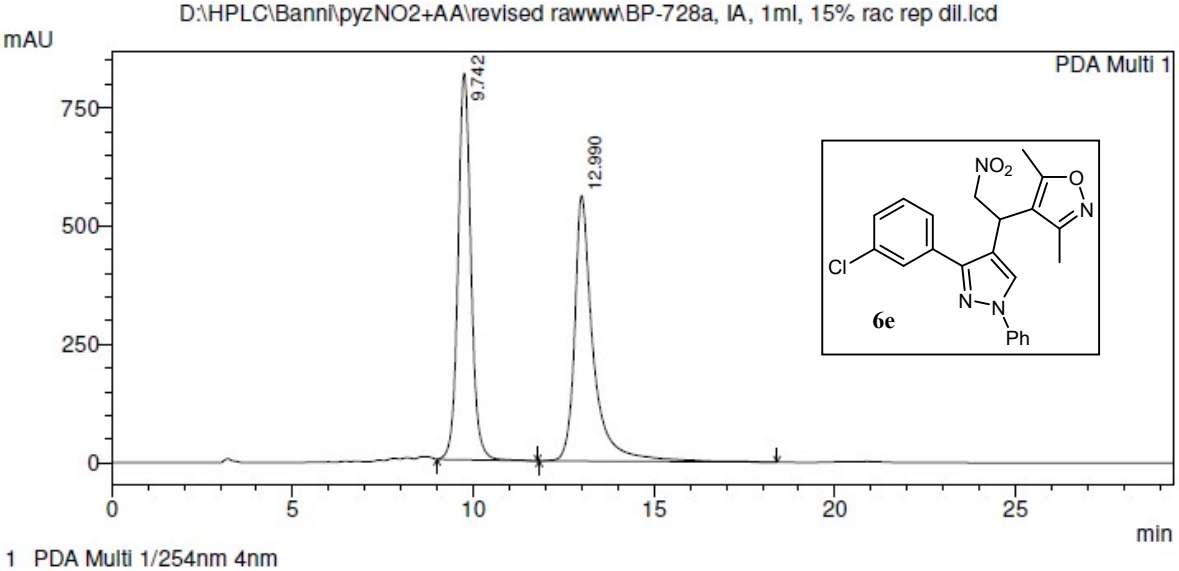


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

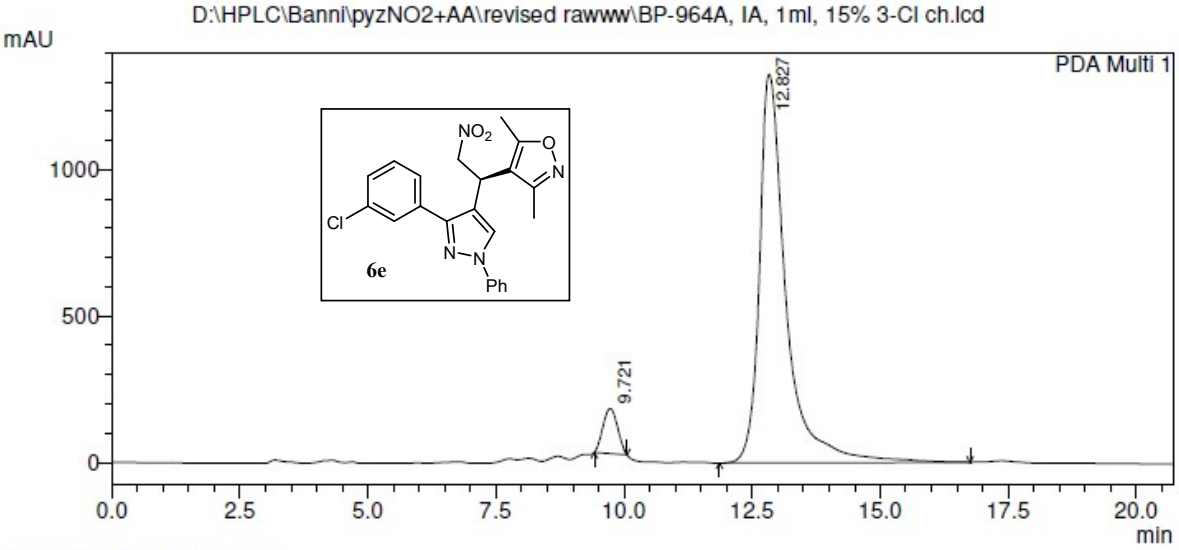
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.251	2279569	93885	2.561	5.228
2	15.335	86744839	1701968	97.439	94.772
Total		89024408	1795853	100.000	100.000



PeakTable

PDA Ch1 254nm 4nm

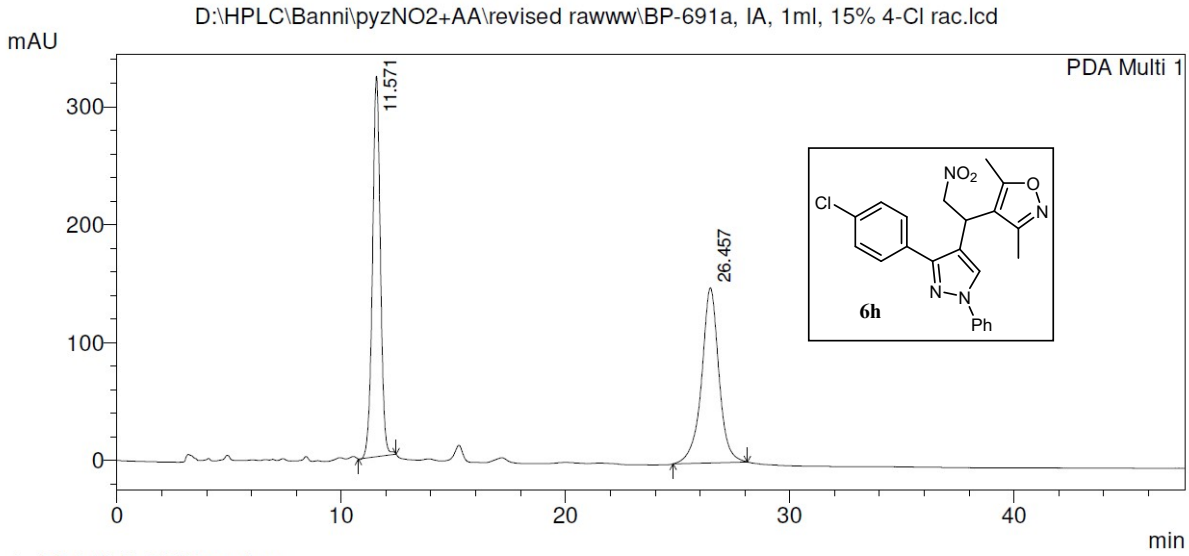
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.742	20324302	816991	50.166	59.265
2	12.990	20189988	561537	49.834	40.735
Total		40514290	1378527	100.000	100.000



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.721	3045128	153690	5.950	10.366
2	12.827	48133054	1328934	94.050	89.634
Total		51178182	1482623	100.000	100.000

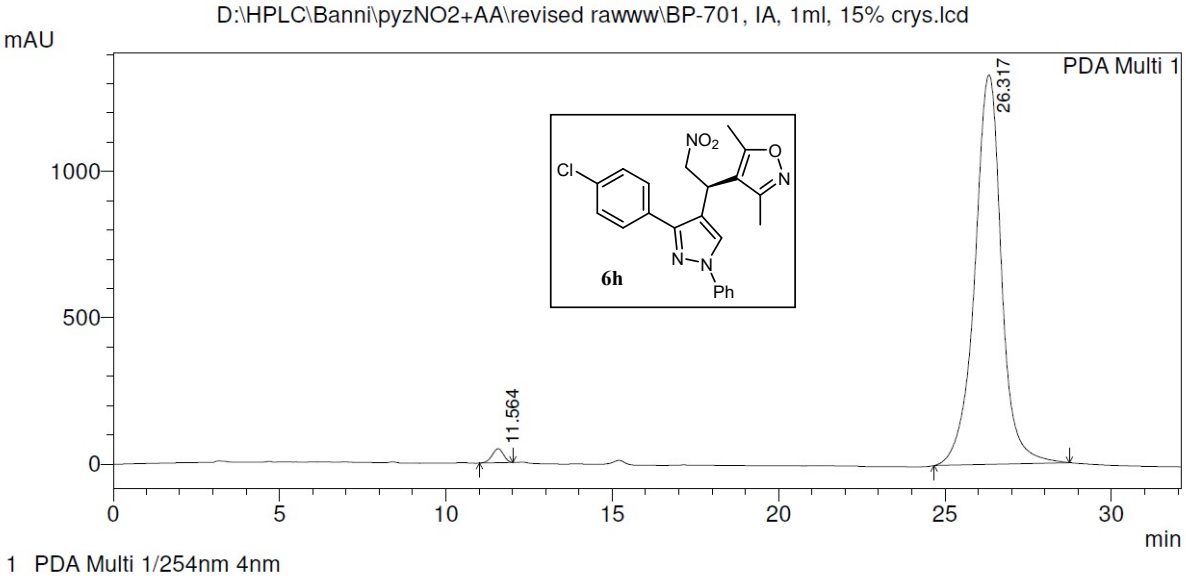


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.571	7869937	322549	49.774	68.479
2	26.457	7941395	148467	50.226	31.521
Total		15811332	471015	100.000	100.000

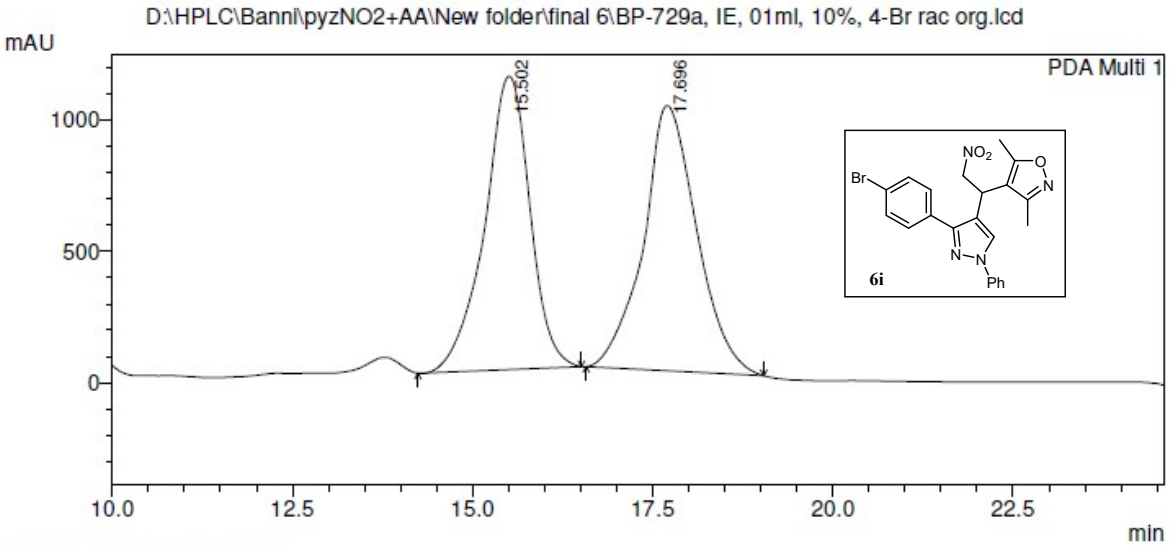


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.564	1135964	47598	1.512	3.455
2	26.317	74004318	1330245	98.488	96.545
Total		75140282	1377843	100.000	100.000

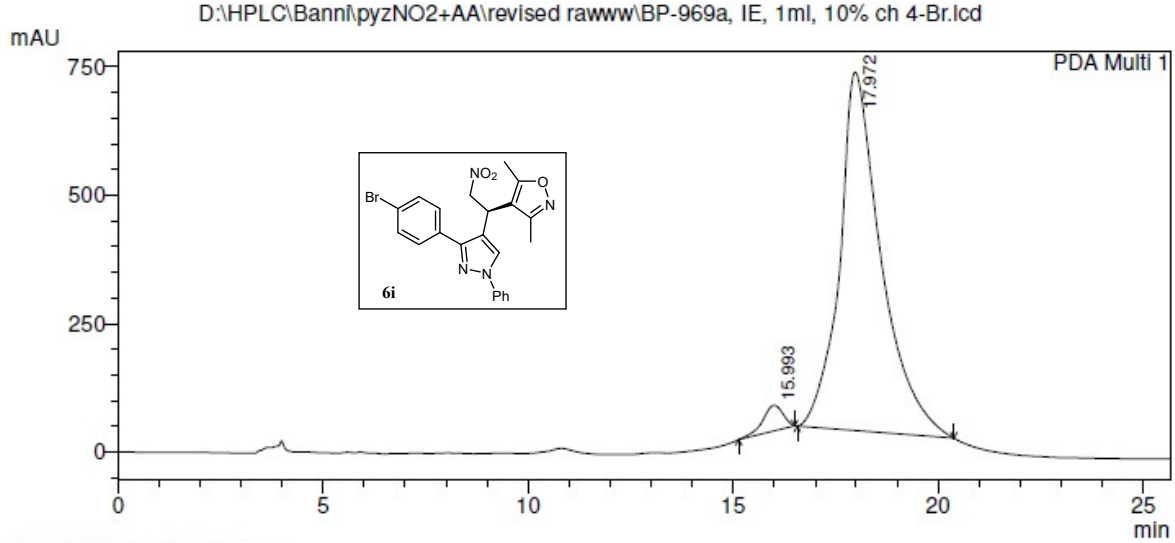


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.502	48844406	1115346	48.368	52.508
2	17.696	52141127	1008817	51.632	47.492
Total		100985532	2124163	100.000	100.000

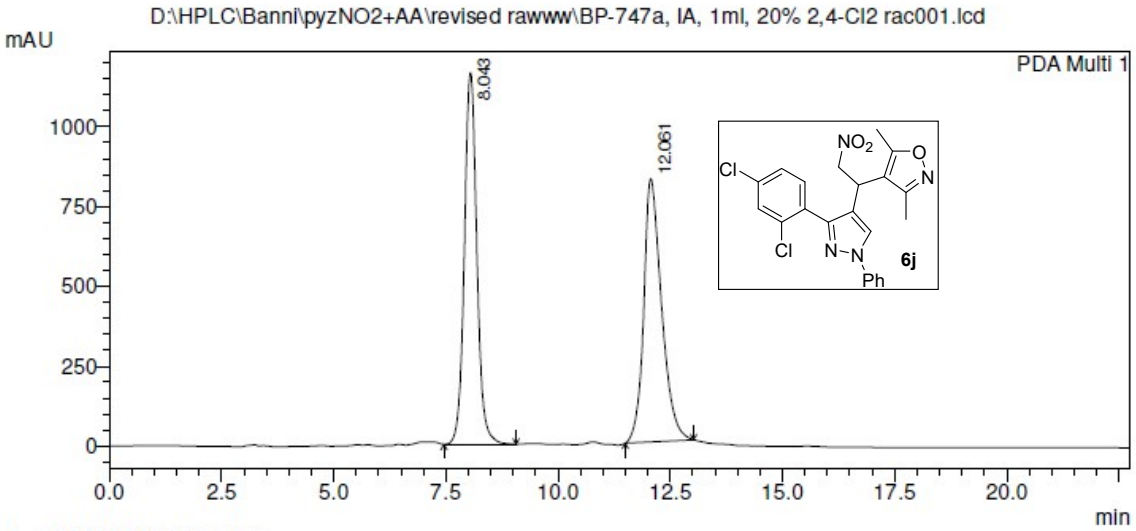


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.993	1731336	50013	3.385	6.696
2	17.972	49418413	696899	96.615	93.304
Total		51149749	746912	100.000	100.000

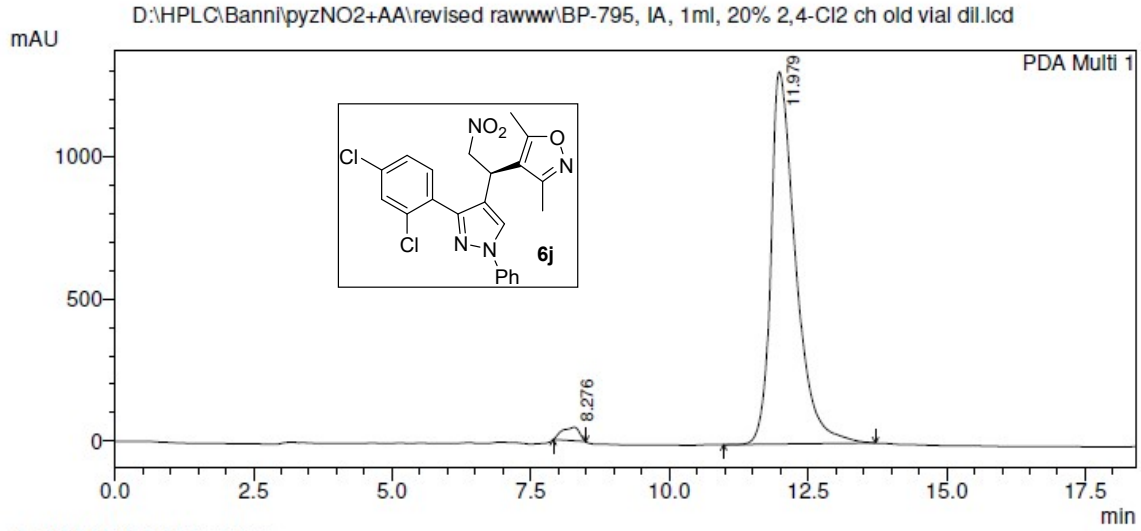


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.043	22518009	1161885	49.671	58.520
2	12.061	22815871	823555	50.329	41.480
Total		45333879	1985440	100.000	100.000

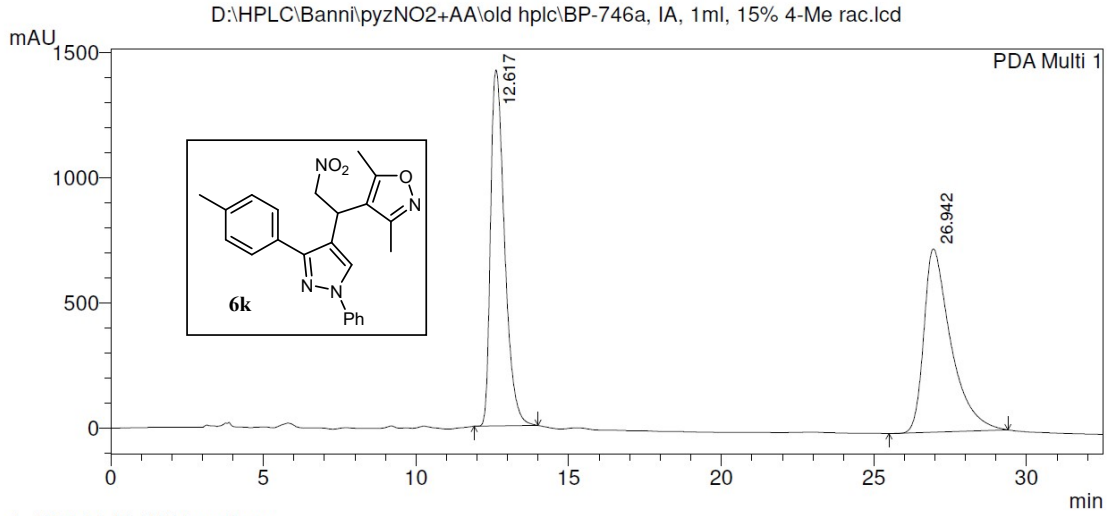


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.276	1032869	47438	2.477	3.503
2	11.979	40670646	1306802	97.523	96.497
Total		41703515	1354240	100.000	100.000

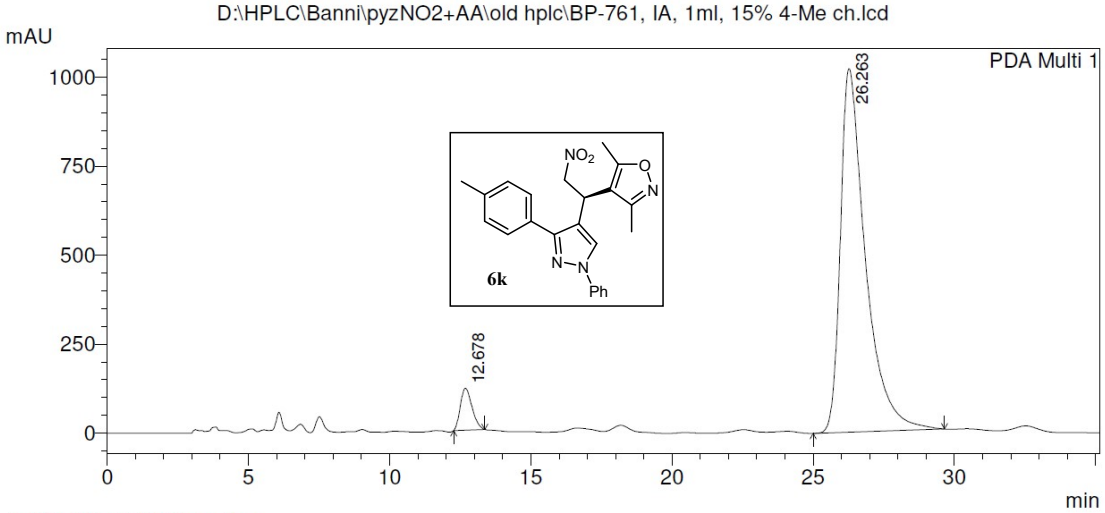


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.617	45441373	1423485	50.171	66.016
2	26.942	45132048	732802	49.829	33.984
Total		90573421	2156286	100.000	100.000

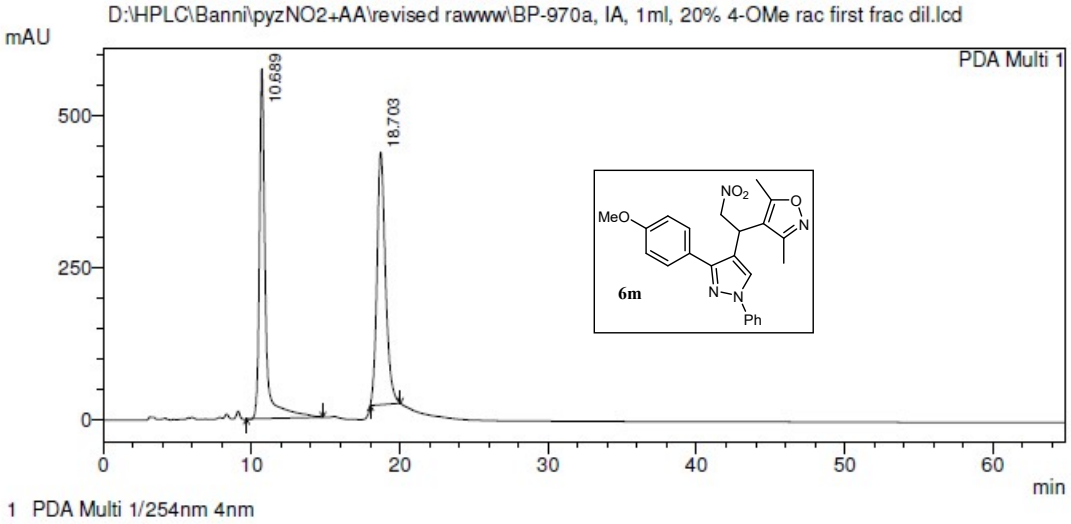


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.678	3395432	117706	5.115	10.338
2	26.263	62988646	1020902	94.885	89.662
Total		66384078	1138608	100.000	100.000

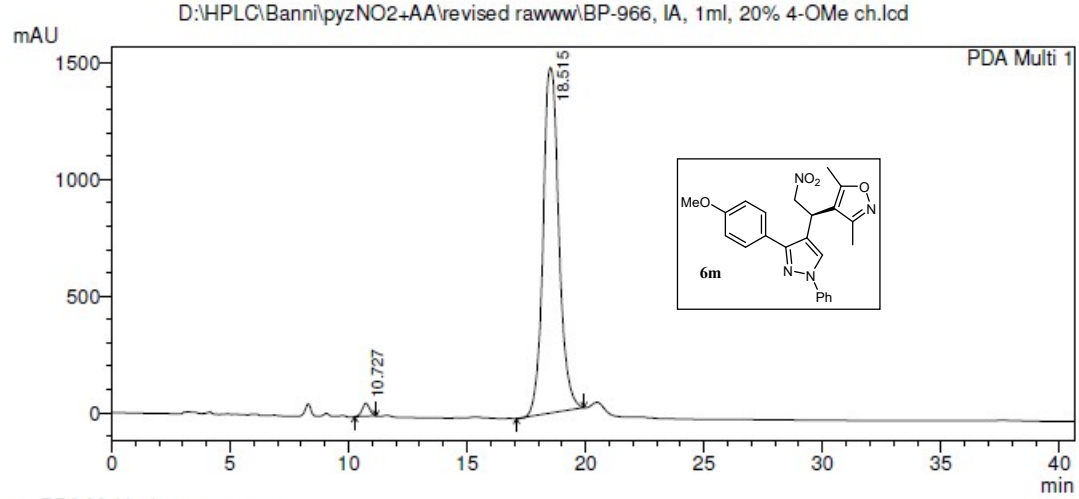


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.689	16314991	575372	49.586	58.088
2	18.703	16587695	415138	50.414	41.912
Total		32902686	990510	100.000	100.000

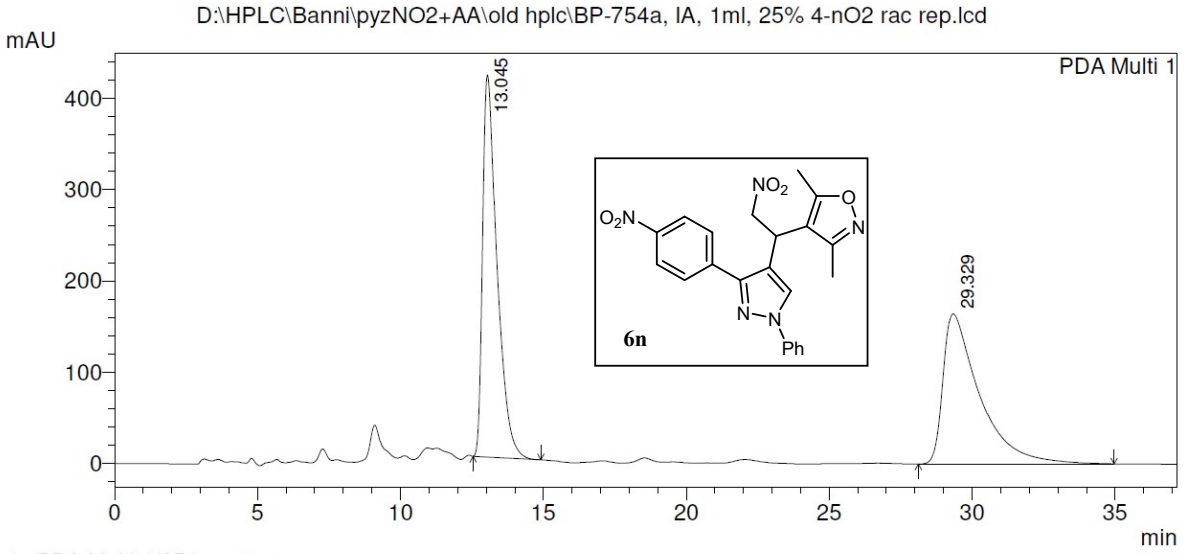


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.727	1213902	55146	1.738	3.587
2	18.515	68638423	1482084	98.262	96.413
Total		69852325	1537230	100.000	100.000

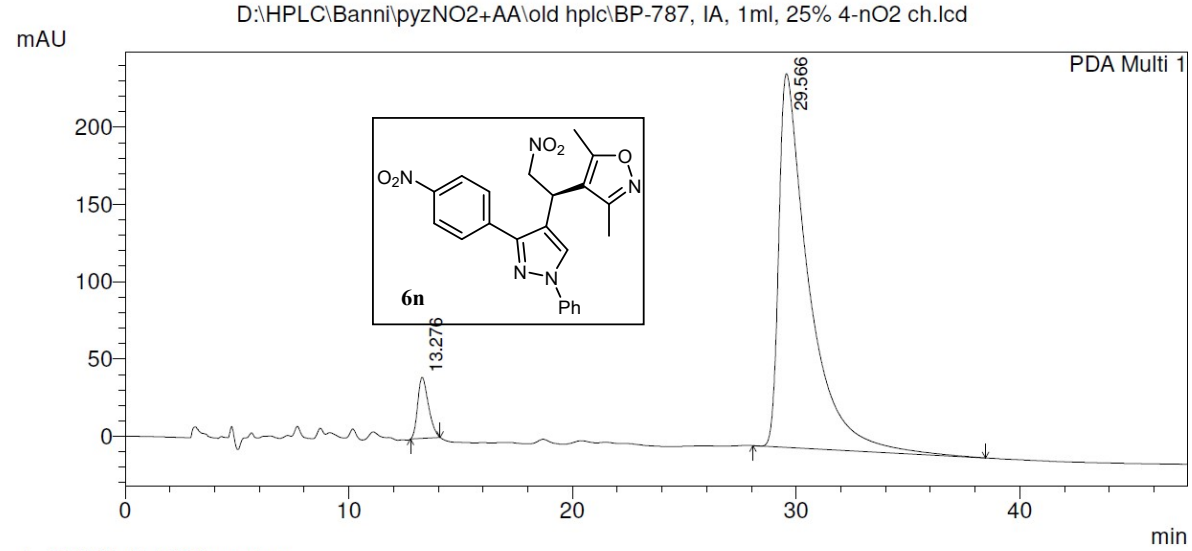


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.045	14594339	418119	50.015	71.783
2	29.329	14585738	164360	49.985	28.217
Total		29180077	582478	100.000	100.000

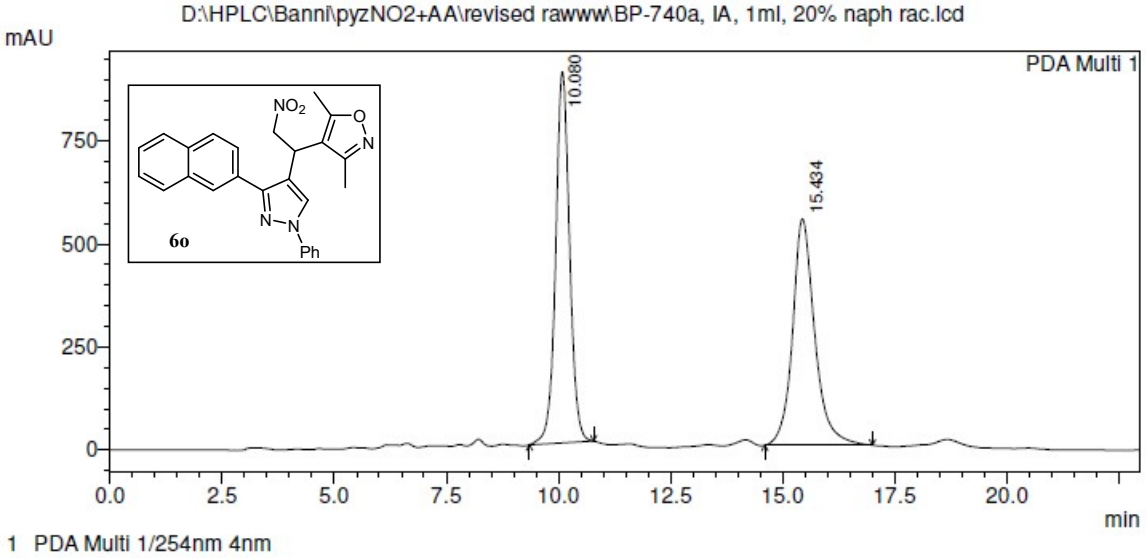


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.276	1325697	39580	5.590	14.063
2	29.566	22388263	241862	94.410	85.937
Total		23713960	281442	100.000	100.000

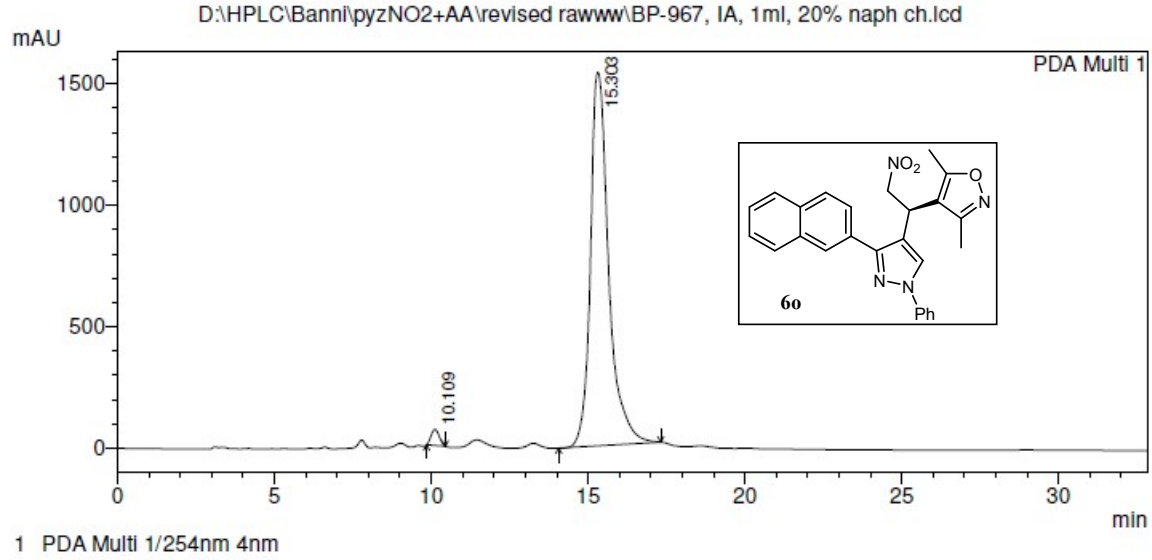


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.080	19486532	900681	50.697	62.098
2	15.434	18950848	549730	49.303	37.902
Total		38437380	1450410	100.000	100.000

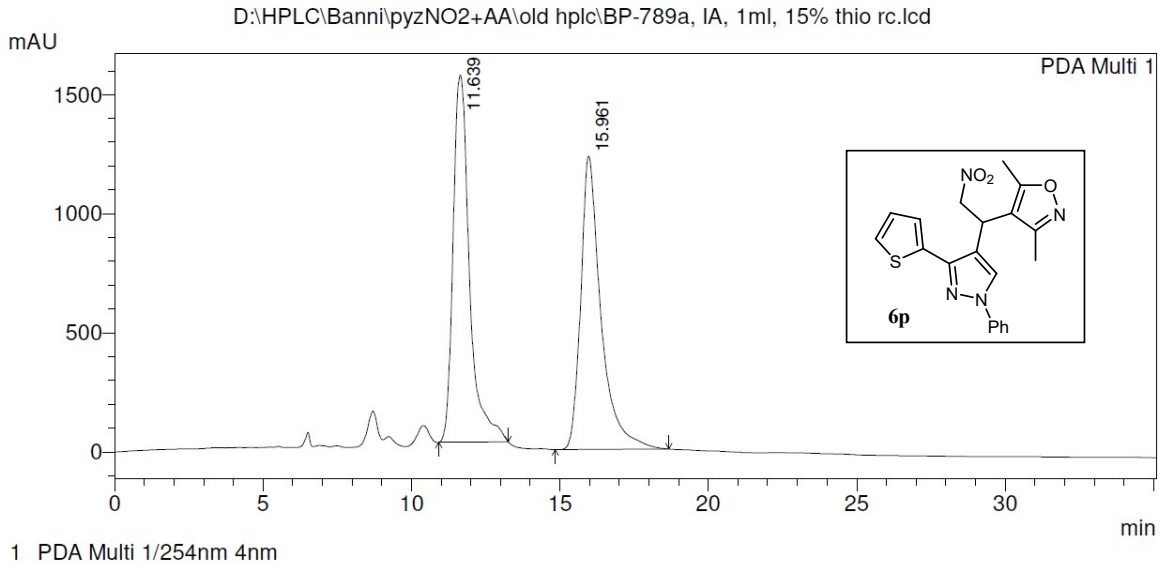


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.109	1190287	66180	1.881	4.131
2	15.303	62101187	1535816	98.119	95.869
Total		63291474	1601996	100.000	100.000

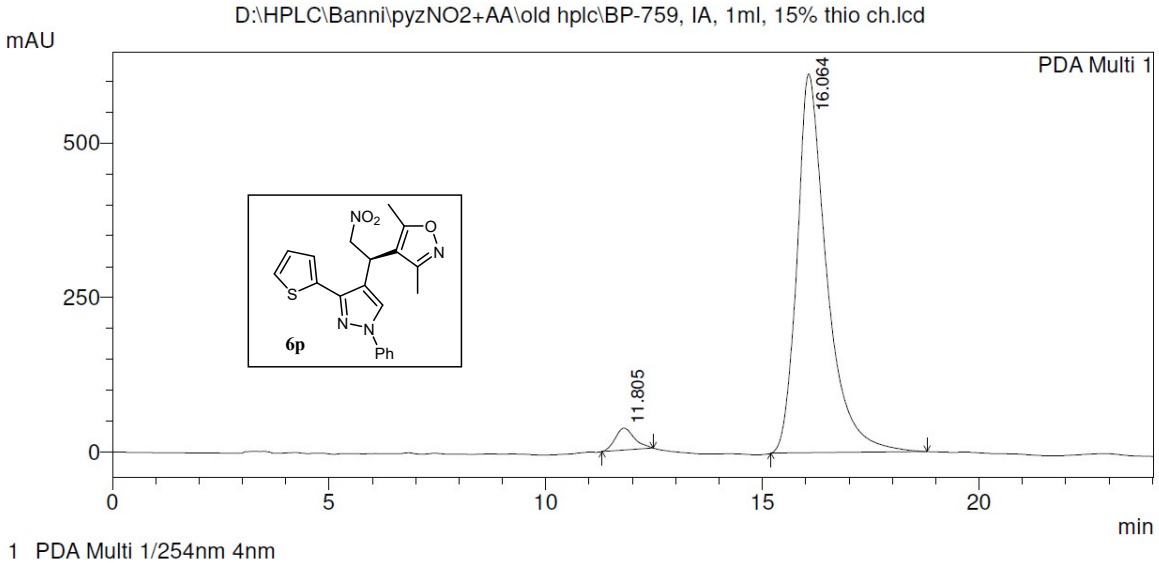


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.639	59216370	1540756	50.279	55.586
2	15.961	58560213	1231069	49.721	44.414
Total		117776583	2771825	100.000	100.000

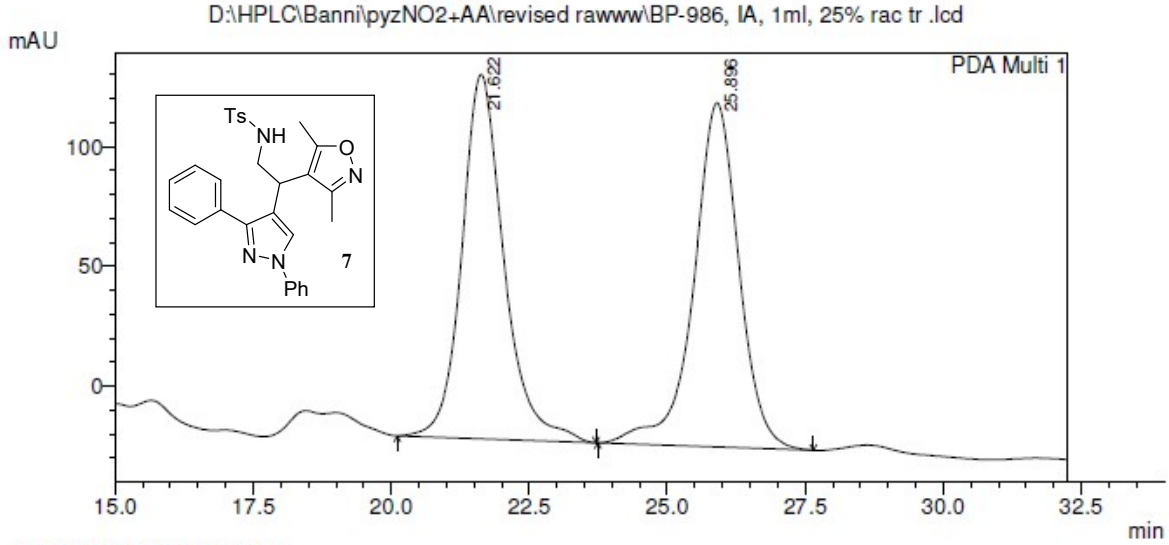


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.805	1087696	35432	3.586	5.466
2	16.064	29241832	612826	96.414	94.534
Total		30329528	648258	100.000	100.000

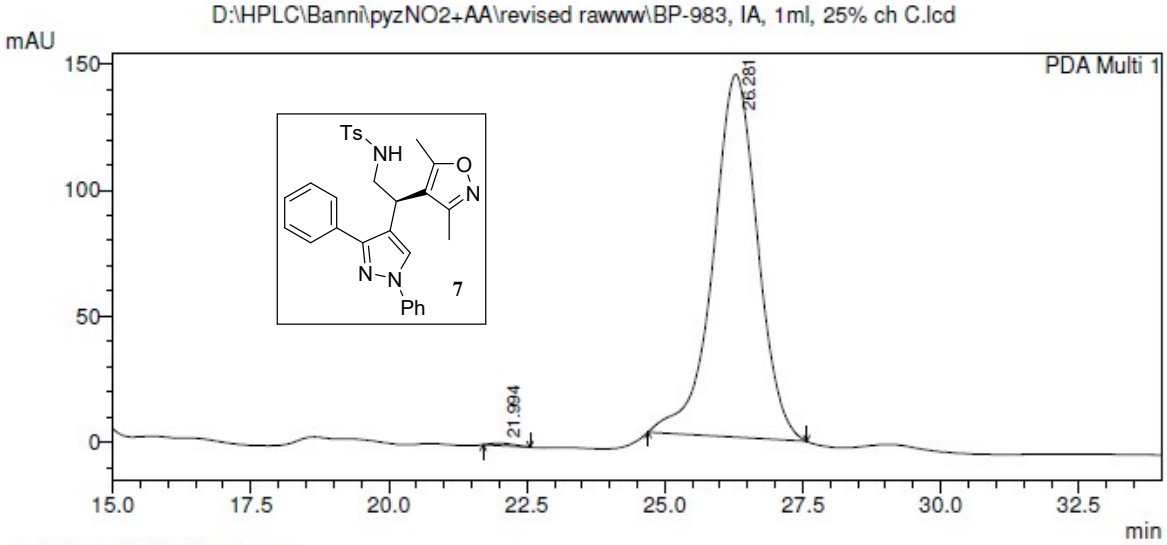


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.622	8067307	151933	49.597	51.421
2	25.896	8198418	143535	50.403	48.579
Total		16265726	295469	100.000	100.000



1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.994	27530	925	0.340	0.639
2	26.281	8066095	143847	99.660	99.361
Total		8093625	144772	100.000	100.000