Supporting Information

Organocatalytic Asymmetric Synthesis of Compounds Bearing both Isoxazole and Pyrazole Moieties *via* 1,6-Addition of Pyrazol-5-ones to 3-Methyl-4-nitro-5-alkenylisoxazoles

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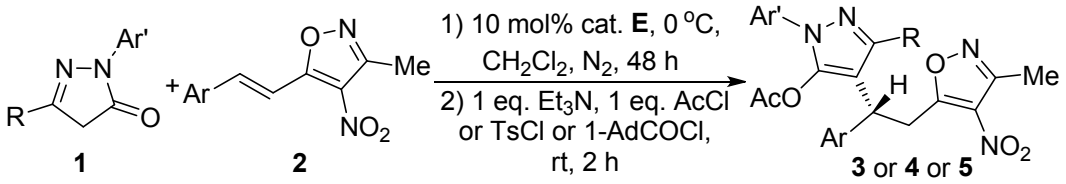
General information:

^{1}H, ^{13}C, and ^{19}F were recorded at Bruker 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR), as well as 376 MHz (^{19}F NMR). Chemical shifts were reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm, 77.0 ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br (broad). Coupling constants were reported in Hertz (Hz). Infrared spectra were obtained with a AVATAR 360 FT-IR spectrometer. Melting points were measured with a XT-4 melting point apparatus without correction. X-ray structural analysis was conducted on the XtaLAB mini. The enantiomeric excesses of the products were determined by chiral HPLC using an Agilent 1260 infinity instrument with commercial ChiralPak columns and hexane and isopropyl alcohol as eluents. The high resolution ESI-MS spectra were obtained with a Bruker APEX IV Fourier transformmass spectrometer.

Materials: All commercially available reagents and solvent were used without further purification. Analytical thin layer chromatography was performed on 0.25 mm silica gel plates. Silica gel (200-300 mesh) was used for flash chromatography.

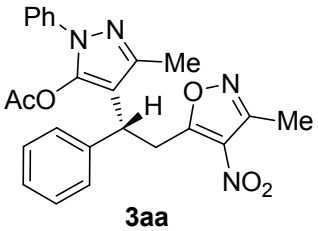
General Procedure for Organocatalytic Asymmetric 1,6-Addition of Pyrazol-5-ones to 3-Methyl-4-nitro-5-alkenylisoxazoles:



To a 10 mL Schlenk charged with pyrazol-5-ones **1** (0.1 mmol), 3-methyl-4-nitro-5-alkenylisoxazoles **2** (0.12 mmol) and thiourea Cat. **E** (4.5 mg, 0.01 mmol) was purged with N_2. Then, 1.0 mL CH_2Cl_2 was added and the mixture was stirred at 0 °C for 48 h. After the reaction was complete, the reaction mixture was warmed to room temperature. Then, Et_3N (0.1 mmol) and AcCl or TsCl or 1-AdCOCl (0.1 mmol) were added and the reaction mixture was stirred for additional 2 h. Finally, the reaction

mixture was concentrated and directly purified by silica gel column chromatography, using petroleum ether:EtOAc (15:5) as eluent to afford the desired products **3**.

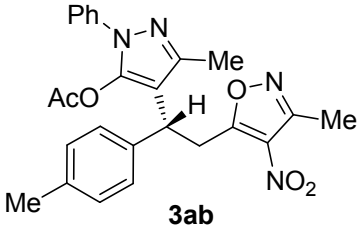
3-methyl-4-(2-(3-methyl-4-nitroisoxazol-5-yl)-1-phenylethyl)-1-phenyl-1H-pyrazol-5-yl acetate (3aa):



3aa

White solid; 84% yield; 92% ee, [Determined by HPLC analysis Chiralcel AD-H column, Hexane/*i*-PrOH = 90/10, Flow rate: 1.0 mL/min, UV detection at 254 nm, Retention time: t_{major}= 10.708 min, t_{minor}= 12.668 min]; $[\alpha]_D^{20}$ = 19.6° (*c* = 0.1 g/100 mL, CH_2Cl_2); mp 71–73 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.11 (s, 3H), 2.16 (s, 3H), 2.48 (s, 3H), 3.88 (dd, *J* = 14.4 Hz, 8.8 Hz, 1H), 3.96 (dd, *J* = 14.8 Hz, 8.0 Hz, 1H), 4.60 (t, *J* = 8.0 Hz, 1H), 7.19–7.24 (m, 1H), 7.25–7.34 (m, 5H), 7.35–7.46 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.6, 167.2, 155.5, 147.3, 141.4, 140.1, 137.6, 130.5, 129.1, 128.6, 127.3, 127.2, 127.0, 122.7, 109.0, 37.1, 31.5, 20.0, 13.3, 11.5; **IR** (KBr) ν 3420, 2925, 1790, 1598, 1505, 1432, 1379, 1365, 1166, 1126, 877, 828, 754, 618 cm^{-1}; **HRMS** (ESI): *m/z* calcd. for $C_{24}H_{23}N_4O_5$ $[M+H]^+$ 447.1663, found 447.1665.

3-methyl-4-(2-(3-methyl-4-nitroisoxazol-5-yl)-1-(p-tolyl)ethyl)-1-phenyl-1H-pyrazol-5-yl acetate (3ab):

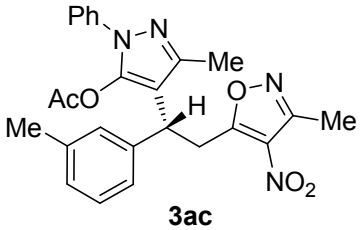


3ab

White solid; 83% yield; 91% ee, [Determined by HPLC analysis Chiralcel OD-H column, Hexane/*i*-PrOH = 95/5, Flow rate: 1.0 mL/min, UV detection at 254 nm, Retention time: t_{major}= 20.386 min, t_{minor}= 16.809 min]; $[\alpha]_D^{20}$ = 37.3° (*c* = 0.1 g/100 mL, CH_2Cl_2); mp 89–91 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.12 (s, 3H), 2.17 (s, 3H),

2.30 (s, 3H), 2.48 (s, 3H), 3.88 (dd, *J* = 14.4 Hz, 8.8 Hz, 1H), 3.96 (dd, *J* = 14.8 Hz, 7.6 Hz, 1H), 4.57 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 6.4 Hz, 2H), 7.19 (d, *J* = 6.8 Hz, 2H), 7.24–7.34 (m, 1H), 7.35–7.47 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 167.3, 155.5, 147.3, 141.4, 137.6, 137.1, 136.6, 130.4, 129.2, 128.0, 127.3, 127.1, 122.7, 109.1, 36.8, 31.7, 20.9, 20.1, 13.4, 11.5; **IR** (KBr) ν 3419, 2926, 1790, 1598, 1506, 1432, 1378, 1167, 1128, 876, 757, 618 cm^{-1}; **HRMS** (ESI): *m/z* calcd. for $C_{25}H_{25}N_4O_5$ $[M+H]^+$ 461.1819, found 461.1824.

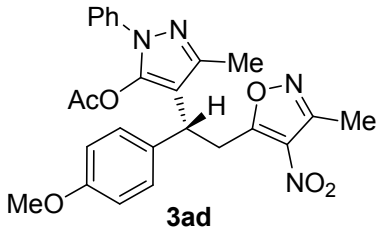
3-methyl-4-(2-(3-methyl-4-nitroisoxazol-5-yl)-1-(m-tolyl)ethyl)-1-phenyl-1H-pyrazol-5-yl acetate (3ac):



3ac

White solid; 82% yield; 90% ee, [Determined by HPLC analysis Chiralcel OD-H column, Hexane/*i*-PrOH = 95/5, Flow rate: 1.0 mL/min, UV detection at 254 nm, Retention time: t_{major}= 18.249 min, t_{minor}= 15.938 min]; $[\alpha]_D^{20}$ = -93.7° (*c* = 0.1 g/100 mL, CH_2Cl_2); mp 78–80 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.11 (s, 3H), 2.18 (s, 3H), 2.32 (s, 3H), 2.49 (s, 3H), 3.80–4.00 (m, 2H), 4.56 (t, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 6.4 Hz, 1H), 7.08–7.14 (m, 2H), 7.19 (t, *J* = 6.8 Hz, 1H), 7.29 (t, *J* = 6.4 Hz, 1H), 7.35–7.48 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 167.2, 155.5, 147.3, 141.5, 140.1, 138.2, 137.7, 130.5, 129.1, 128.4, 128.1, 127.8, 127.3, 124.1, 122.7, 109.0, 64.3, 37.1, 31.6, 31.4, 20.1, 13.4, 11.5; **IR** (KBr) ν 3420, 2924, 1789, 1601, 1505, 1419, 1379, 1261, 1167, 1128, 758, 617 cm^{-1}; **HRMS** (ESI): *m/z* calcd. for $C_{25}H_{25}N_4O_5$ $[M+H]^+$ 461.1819, found 461.1823.

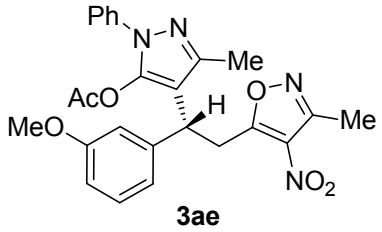
4-(1-(4-methoxyphenyl)-2-(3-methyl-4-nitroisoxazol-5-yl)ethyl)-3-methyl-1-phenyl-1H-pyrazol-5-yl acetate (3ad):



3ad

White solid; 80% yield; 83% ee, [Determined by HPLC analysis Chiralcel OD-H column, Hexane/*i*-PrOH = 85/15, Flow rate: 1.0 mL/min, UV detection at 254 nm, Retention time: t_{major}= 15.293 min, t_{minor}= 12.359 min]; $[\alpha]_D^{20}$ = -22.7° (*c* = 0.1 g/100 mL, CH_2Cl_2); mp 141–143 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.07 (s, 3H), 2.08 (s, 3H), 2.42 (s, 3H), 3.69 (s, 3H), 3.76 (dd, *J* = 14.4 Hz, 8.0 Hz, 1H), 3.87 (dd, *J* = 14.8 Hz, 8.0 Hz, 1H), 4.47 (t, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 7.2 Hz, 2H), 7.14 (d, *J* = 7.6 Hz, 2H), 7.18–7.26 (m, 1H), 7.29–7.39 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 167.4, 158.4, 155.5, 147.3, 141.4, 137.7, 132.2, 130.5, 129.1, 128.3, 127.3, 122.8, 113.9, 109.3, 55.1, 36.5, 31.8, 20.1, 13.4, 11.5; **IR** (KBr) ν 3419, 2924, 1790, 1598, 1506, 1432, 1378, 1365, 1167, 1128, 876, 828, 757, 618 cm^{-1}; **HRMS** (ESI): *m/z* calcd. for $C_{25}H_{25}N_4O_6$ $[M+H]^+$ 477.1769, found 477.1767.

4-(1-(3-methoxyphenyl)-2-(3-methyl-4-nitroisoxazol-5-yl)ethyl)-3-methyl-1-phenyl-1H-pyrazol-5-yl acetate (3ae):

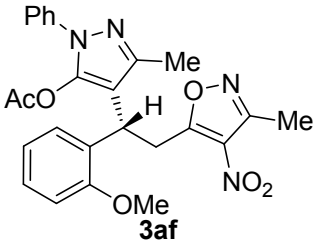


3ae

White solid; 81% yield; 93% ee, [Determined by HPLC analysis Chiralcel OD-H column, Hexane/*i*-PrOH = 85/15, Flow rate: 1.0 mL/min, UV detection at 254 nm, Retention time: t_{major}= 20.444 min, t_{minor}= 15.976 min]; $[\alpha]_D^{20}$ = -41.2° (*c* = 0.1 g/100 mL, CH_2Cl_2); mp 69–72 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.13 (s, 3H), 2.18 (s, 3H), 2.49 (s, 3H), 3.76 (s, 3H), 3.87 (dd, *J* = 13.2 Hz, 8.4 Hz, 1H), 3.95 (dd, *J* = 13.6 Hz, 7.2 Hz, 1H), 4.57 (t, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 6.82–6.96 (m, 2H), 7.22 (t, *J* = 6.8 Hz, 1H), 7.24–7.33 (m, 1H), 7.34–7.50 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.6, 167.3, 159.6, 155.5, 147.3, 141.8, 141.4, 137.6, 130.5, 129.5, 129.1,

127.3, 122.7, 119.5, 113.3, 112.1, 108.9, 55.1, 37.2, 31.6, 20.1, 13.3, 11.5; **IR** (KBr) ν 3441, 2926, 1790, 1599, 1517, 1434, 1378, 1264, 1168, 1047, 877, 828, 759, 618 cm^{-1}; **HRMS** (ESI): *m/z* calcd. for $C_{25}H_{25}N_4O_6$ $[M+H]^+$ 477.1769, found 477.1775.

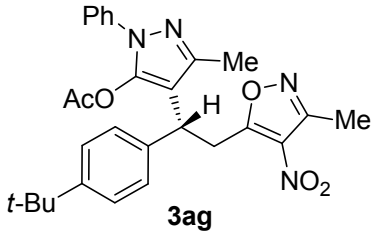
4-(1-(2-methoxyphenyl)-2-(3-methyl-4-nitroisoxazol-5-yl)ethyl)-3-methyl-1-phenyl-1H-pyrazol-5-yl acetate (3af):



3af

White solid; 82% yield; 89% ee, [Determined by HPLC analysis Chiralcel AD-H column, Hexane/*i*-PrOH = 95/5, Flow rate: 1.0 mL/min, UV detection at 254 nm, Retention time: t_{major}= 18.641 min, t_{minor}= 20.589 min]; $[\alpha]_D^{20}$ = -17.3° (*c* = 0.1 g/100 mL, CH_2Cl_2); mp 121–123 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.08 (s, 3H), 2.23 (s, 3H), 2.49 (s, 3H), 3.76 (s, 3H), 3.90 (d, *J* = 7.6 Hz, 2H), 4.95 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.91 (t, *J* = 6.4 Hz, 1H), 7.20 (t, *J* = 6.8 Hz, 1H), 7.24–7.30 (m, 1H), 7.32 (d, *J* = 6.8 Hz, 1H), 7.35–7.49 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.0, 167.0, 156.6, 155.3, 147.6, 141.6, 137.7, 130.3, 129.0, 128.3, 128.2, 127.1, 127.0, 122.6, 120.2, 110.5, 108.4, 55.2, 31.1, 30.5, 20.1, 13.0, 11.5; **IR** (KBr) ν 3416, 2955, 1790, 1598, 1562, 1505, 1435, 1378, 1246, 1167, 1110, 1047, 828, 756, 618 cm^{-1}; **HRMS** (ESI): *m/z* calcd. for $C_{25}H_{25}N_4O_6$ $[M+H]^+$ 477.1769, found 477.1777.

4-(1-(4-(tert-butyl)phenyl)-2-(3-methyl-4-nitroisoxazol-5-yl)ethyl)-3-methyl-1-phenyl-1H-pyrazol-5-yl acetate (3ag):

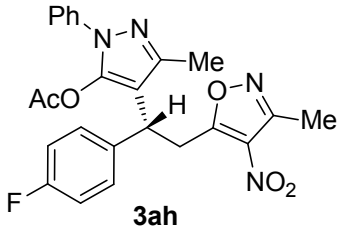


3ag

White solid; 78% yield; 93% ee, [Determined by HPLC analysis Chiralcel OD-H

column, Hexane/*i*-PrOH = 85/15, Flow rate: 1.0 mL/min, UV detection at 254 nm, Retention time: t_{major}= 10.185 min, t_{minor}= 12.222 min]; $[\alpha]_D^{20}$ = -9.8° (*c* = 0.1 g/100 mL, CH_2Cl_2); mp 97–99 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.20 (s, 9H), 2.01 (s, 3H), 2.10 (s, 3H), 2.40 (s, 3H), 3.72–3.92 (m, 2H), 4.50 (t, *J* = 7.6 Hz, 1H), 7.10–7.21 (m, 3H), 7.24 (d, *J* = 7.2 Hz, 2H), 7.27–7.38 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 167.1, 155.4, 149.8, 147.3, 141.4, 137.6, 137.1, 130.4, 129.0, 127.2, 126.8, 125.4, 122.7, 109.0, 36.6, 34.3, 31.6, 31.1, 20.0, 13.4, 11.5; **IR** (KBr) ν 3439, 2961, 1791, 1599, 1564, 1506, 1432, 1378, 1170, 1126, 828, 759, 617 cm^{-1}; **HRMS** (ESI): *m/z* calcd. for $C_{28}H_{31}N_4O_5$ $[M+H]^+$ 503.2289, found 503.2289.

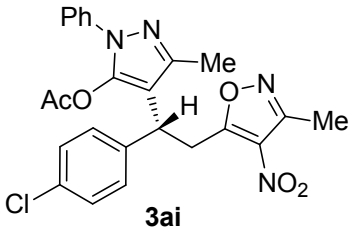
4-(1-(4-fluorophenyl)-2-(3-methyl-4-nitroisoxazol-5-yl)ethyl)-3-methyl-1-phenyl-1H-pyrazol-5-yl acetate (3ah):



3ah

White solid; 87% yield; 91% ee, [Determined by HPLC analysis Chiralcel OD-H column, Hexane/*i*-PrOH = 95/5, Flow rate: 1.0 mL/min, UV detection at 254 nm, Retention time: t_{major}= 22.646 min, t_{minor}= 26.587 min]; $[\alpha]_D^{20}$ = -156.2° (*c* = 0.1 g/100 mL, CH_2Cl_2); mp 103–105 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.06 (s, 6H), 2.42 (s, 3H), 3.78 (dd, *J* = 13.6 Hz, 8.0 Hz, 1H), 3.86 (dd, *J* = 14.8 Hz, 7.6 Hz, 1H), 4.50 (t, *J* = 7.6 Hz, 1H), 6.91 (t, *J* = 7.6 Hz, 2H), 7.12–7.27 (m, 3H), 7.28–7.41 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.4, 167.3, 161.6 (d, $J_{C\text{-}F}$ = 244.6 Hz), 155.5, 147.2, 141.4, 137.6, 136.0 (d, $J_{C\text{-}F}$ = 3.0 Hz), 130.5, 129.1, 128.9 (d, $J_{C\text{-}F}$ = 8.0 Hz), 127.4, 122.8, 115.4 (d, $J_{C\text{-}F}$ = 21.2 Hz), 108.8, 36.6, 31.7, 20.1, 13.4, 11.5; **IR** (KBr) ν 3423, 2962, 1790, 1598, 1507, 1433, 1382, 1260, 1164, 1127, 750, 618 cm^{-1}; **HRMS** (ESI): *m/z* calcd. for $C_{24}H_{22}N_4O_5$ $[M+H]^+$ 465.1569, found 465.1570.

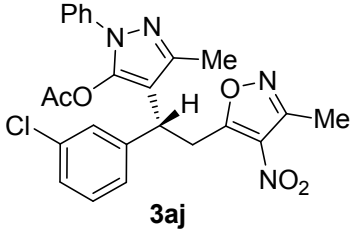
4-(1-(4-chlorophenyl)-2-(3-methyl-4-nitroisoxazol-5-yl)ethyl)-3-methyl-1-phenyl-1H-pyrazol-5-yl acetate (3ai):



3ai

White solid; 88% yield; 91% ee, [Determined by HPLC analysis Chiralcel OD-H column, Hexane/*i*-PrOH = 95/5, Flow rate: 1.0 mL/min, UV detection at 254 nm, Retention time: t_{major}= 15.453 min, t_{minor}= 11.727 min]; $[\alpha]_D^{20}$ = -6.8° (*c* = 0.1 g/100 mL, CH_2Cl_2); mp 115–117 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.07 (s, 6H), 2.42 (s, 3H), 3.77 (dd, *J* = 13.2 Hz, 8.0 Hz, 1H), 3.85 (dd, *J* = 14.4 Hz, 7.6 Hz, 1H), 4.49 (t, *J* = 7.6 Hz, 1H), 7.10–7.27 (m, 5H), 7.27–7.40 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2, 167.3, 155.5, 147.2, 141.4, 138.7, 137.5, 132.8, 130.5, 129.1, 128.8, 128.7, 127.4, 122.8, 108.6, 36.6, 31.5, 20.1, 13.4, 11.5; **IR** (KBr) ν 3431, 2928, 1790, 1598, 1519, 1433, 1378, 1137, 828, 760, 617 cm^{-1}; **HRMS** (ESI): *m/z* calcd. for $C_{24}H_{22}ClN_4O_5$ $[M+H]^+$ 481.1273, found 481.1266.

4-(1-(3-chlorophenyl)-2-(3-methyl-4-nitroisoxazol-5-yl)ethyl)-3-methyl-1-phenyl-1H-pyrazol-5-yl acetate (3aj):

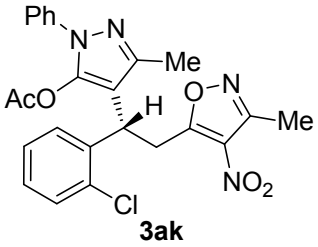


3aj

White solid; 89% yield; 87% ee, [Determined by HPLC analysis Chiralcel OD-H column, Hexane/*i*-PrOH = 95/5, Flow rate: 1.0 mL/min, UV detection at 254 nm, Retention time: t_{major}= 28.675 min, t_{minor}= 24.018 min]; $[\alpha]_D^{20}$ = 59.9° (*c* = 0.1 g/100 mL, CH_2Cl_2); mp 109–110 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.06 (s, 3H), 2.09 (s, 3H), 2.42 (s, 3H), 3.62–3.93 (m, 2H), 4.50 (t, *J* = 8.0 Hz, 1H), 7.07–7.19 (m, 3H), 7.20–7.27 (m, 2H), 7.28–7.41 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1, 167.2, 155.6, 147.1, 142.3, 141.5, 137.5, 134.4, 130.6, 129.9, 129.1, 127.5, 127.4, 127.3, 125.6, 122.8, 108.3, 36.9, 31.4, 20.1, 13.3, 11.5; **IR** (KBr) ν 3424, 2955, 1790, 1597, 1563, 1505, 1431, 1379, 1166, 1128, 876, 828, 618 cm^{-1}; **HRMS** (ESI): *m/z* calcd. for

$C_{24}H_{22}ClN_4O_5$ $[M+H]^+$ 481.1273, found 481.1274.

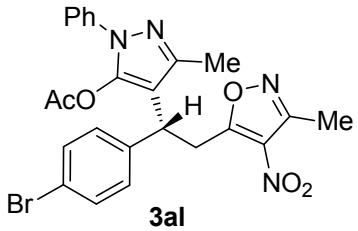
4-(1-(2-chlorophenyl)-2-(3-methyl-4-nitroisoxazol-5-yl)ethyl)-3-methyl-1-phenyl-1H-pyrazol-5-yl acetate (3ak):



3ak

White solid; 86% yield; 92% ee, [Determined by HPLC analysis Chiralcel OD-H column, Hexane/*i*-PrOH = 95/5, Flow rate: 1.0 mL/min, UV detection at 254 nm, Retention time: t_{major}= 24.001 min, t_{minor}= 18.430 min]; $[\alpha]_D^{20}$ = 18.8° (*c* = 0.1 g/100 mL, CH_2Cl_2); mp 120–122 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.00 (s, 3H), 2.14 (s, 3H), 2.42 (s, 3H), 3.78 (dd, *J* = 14.8 Hz, 8.4 Hz, 1H), 3.87 (dd, *J* = 14.4 Hz, 7.6 Hz, 1H), 4.97 (t, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 7.2 Hz, 1H), 7.15–7.24 (m, 2H), 7.25–7.38 (m, 5H), 7.41 (d, *J* = 7.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.0, 167.1, 155.5, 147.5, 141.7, 137.6, 137.5, 133.8, 130.5, 130.0, 129.1, 128.4, 127.4, 126.9, 122.8, 107.6, 34.4, 31.3, 20.1, 13.2, 11.5; **IR** (KBr) ν 3427, 2925, 1790, 1598, 1505, 1473, 1378, 1167, 1045, 876, 828, 756, 618 cm^{-1}; **HRMS** (ESI): *m/z* calcd. for $C_{24}H_{22}ClN_4O_5$ $[M+H]^+$ 481.1273, found 481.1271.

4-(1-(4-bromophenyl)-2-(3-methyl-4-nitroisoxazol-5-yl)ethyl)-3-methyl-1-phenyl-1H-pyrazol-5-yl acetate (3al):

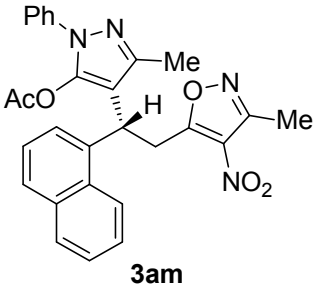


3al

White solid; 90% yield; 90% ee, [Determined by HPLC analysis Chiralcel OD-H column, Hexane/*i*-PrOH = 85/15, Flow rate: 1.0 mL/min, UV detection at 254 nm, Retention time: t_{major}= 16.907 min, t_{minor}= 12.243 min]; $[\alpha]_D^{20}$ = -17.1° (*c* = 0.1 g/100

mL, CH_2Cl_2); mp 109–110 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.14 (s, 3H), 2.15 (s, 3H), 2.50 (s, 3H), 3.84 (dd, *J* = 14.8 Hz, 8.4 Hz, 1H), 3.93 (dd, *J* = 14.8 Hz, 8.0 Hz, 1H), 4.55 (t, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.27–7.34 (m, 1H), 7.35–7.69 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2, 167.3, 155.6, 147.2, 141.4, 139.3, 137.5, 131.7, 130.5, 129.1, 129.0, 127.5, 122.8, 121.0, 108.5, 36.7, 31.5, 20.1, 13.4, 11.5; **IR** (KBr) ν 3029, 1786, 1666, 1519, 1433, 1378, 1166, 1009, 828, 763, 617 cm^{-1}; **HRMS** (ESI): *m/z* calcd. for $C_{24}H_{22}BrN_4O_5$ $[M+H]^+$ 525.0768, found 525.0760.

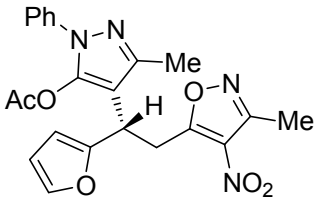
3-methyl-4-(2-(3-methyl-4-nitroisoxazol-5-yl)-1-(naphthalen-1-yl)ethyl)-1-phenyl-1H-pyrazol-5-yl acetate (3am):



3am

White solid; 72% yield; 89% ee, [Determined by HPLC analysis Chiralcel OD-H column, Hexane/*i*-PrOH = 85/15, Flow rate: 1.0 mL/min, UV detection at 254 nm, Retention time: t_{major}= 19.050 min, t_{minor}= 12.762 min]; $[\alpha]_D^{20}$ = 7.8° (*c* = 0.1 g/100 mL, CH_2Cl_2); mp 94–96 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.05 (s, 3H), 2.19 (s, 3H), 2.49 (s, 3H), 3.98 (dd, *J* = 14.8 Hz, 8.4 Hz, 1H), 4.11 (dd, *J* = 14.4 Hz, 8.0 Hz, 1H), 4.78 (t, *J* = 8.0 Hz, 1H), 7.30 (t, *J* = 6.0 Hz, 1H), 7.36–7.52 (m, 7H), 7.72–7.85 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.6, 167.3, 155.6, 147.4, 141.6, 137.6, 137.5, 133.1, 132.3, 130.6, 129.1, 128.5, 127.7, 127.5, 127.4, 126.3, 126.1, 126.0, 125.1, 122.8, 108.8, 37.3, 31.5, 20.0, 13.4, 11.5; **IR** (KBr) ν 3423, 2924, 1637, 1560, 1421, 1384, 1117, 856, 618 cm^{-1}; **HRMS** (ESI): *m/z* calcd. for $C_{28}H_{25}N_4O_5$ $[M+H]^+$ 497.1819, found 497.1819.

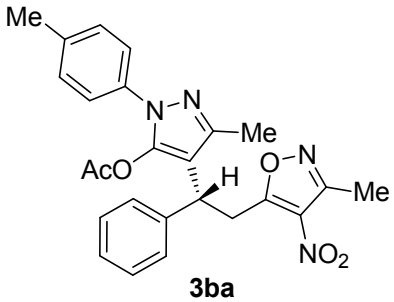
4-(1-(furan-2-yl)-2-(3-methyl-4-nitroisoxazol-5-yl)ethyl)-3-methyl-1-phenyl-1H-pyrazol-5-yl acetate (3an):



3an

White solid; 82% yield; 90% ee, [Determined by HPLC analysis Chiralcel AD-H column, Hexane/*i*-PrOH = 80/20, Flow rate: 0.1 mL/min, UV detection at 254 nm, Retention time: t_{major}= 71.889 min, t_{minor}= 76.526 min]; $[\alpha]_D^{20}$ = -35.1° (*c* = 0.1 g/100 mL, CH_2Cl_2); mp 43–45 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.16 (s, 3H), 2.26 (s, 3H), 2.52 (s, 3H), 3.80 (dd, *J* = 12.4 Hz, 8.0 Hz, 1H), 3.93 (dd, *J* = 14.4 Hz, 8.0 Hz, 1H), 4.61 (t, *J* = 5.6 Hz, 1H), 6.13 (s, 1H), 6.29 (s, 1H), 7.27–7.35 (m, 2H), 7.36–7.50 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1, 167.2, 155.6, 153.0, 147.2, 142.0, 141.7, 137.7, 130.6, 129.1, 127.4, 122.8, 110.3, 106.8, 106.4, 31.7, 30.7, 20.1, 13.2, 11.6; **IR** (KBr) ν 3442, 2924, 1792, 1637, 1565, 1505, 1420, 1382, 1170, 1126, 742, 618 cm^{-1}; **HRMS** (ESI): *m/z* calcd. for $C_{22}H_{21}N_4O_6$ $[M+H]^+$ 437.1456, found 437.1456.

3-methyl-4-(2-(3-methyl-4-nitroisoxazol-5-yl)-1-phenylethyl)-1-(p-tolyl)-1H-pyrazol-5-yl acetate (3ba):

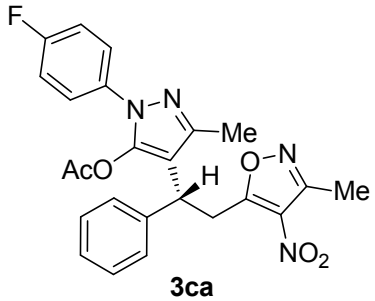


3ba

White solid; 81% yield; 91% ee, [Determined by HPLC analysis Chiralcel AD-H column, Hexane/*i*-PrOH = 90/10, Flow rate: 1.0 mL/min, UV detection at 254 nm, Retention time: t_{major}= 11.737 min, t_{minor}= 14.704 min]; $[\alpha]_D^{20}$ = 19.2° (*c* = 0.1 g/100 mL, CH_2Cl_2); mp 106–108 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.11 (s, 3H), 2.16 (s, 3H), 2.34 (s, 3H), 2.48 (s, 3H), 3.88 (dd, *J* = 14.4 Hz, 8.4 Hz, 1H), 3.96 (dd, *J* = 14.8 Hz, 7.6 Hz, 1H), 4.59 (t, *J* = 7.6 Hz, 1H), 7.13–7.25 (m, 3H), 7.25–7.36 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.6, 167.3, 155.5, 147.0, 141.4, 140.2, 137.2, 135.1,

130.5, 129.6, 128.5, 127.2, 127.0, 122.7, 108.7, 37.2, 31.6, 20.9, 20.1, 13.3, 11.5; **IR** (KBr) ν 3241, 2926, 1788, 1601, 1518, 1418, 1364, 1168, 1126, 827, 701, 619 cm^{-1}; **HRMS** (ESI): *m/z* calcd. for $C_{25}H_{25}N_4O_5$ $[M+H]^+$ 461.1819, found 461.1822.

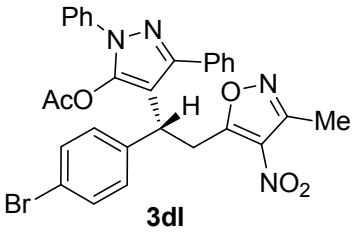
1-(4-fluorophenyl)-3-methyl-4-(2-(3-methyl-4-nitroisoxazol-5-yl)-1-phenylethyl)-1H-pyrazol-5-yl acetate (3ca):



3ca

White solid; 80% yield; 94% ee, [Determined by HPLC analysis Chiralcel AD-H column, Hexane/*i*-PrOH = 90/10, Flow rate: 1.0 mL/min, UV detection at 254 nm, Retention time: t_{major}= 12.471 min, t_{minor}= 14.765 min]; $[\alpha]_D^{20}$ = 18.9° (*c* = 0.1 g/100 mL, CH_2Cl_2); mp 87–89 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.11 (s, 3H), 2.15 (s, 3H), 2.49 (s, 3H), 3.88 (dd, *J* = 14.0 Hz, 8.4 Hz, 1H), 3.95 (dd, *J* = 14.4 Hz, 7.6 Hz, 1H), 4.59 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 2H), 7.18–7.25 (m, 1H), 7.27–7.35 (m, 4H), 7.35–7.44 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.6, 167.2, 161.5 (d, $J_{C\text{-}F}$ = 246.3 Hz), 155.5, 147.4, 141.5, 140.1, 133.8 (d, $J_{C\text{-}F}$ = 3.1 Hz), 130.5, 128.6, 127.2, 127.1, 124.9 (d, $J_{C\text{-}F}$ = 8.6 Hz), 116.0 (d, $J_{C\text{-}F}$ = 22.8 Hz), 108.9, 37.2, 31.6, 20.0, 13.3, 11.5; **IR** (KBr) ν 3431, 2925, 1790, 1602, 1562, 1518, 1453, 1378, 1365, 1168, 1127, 828, 618 cm^{-1}; **HRMS** (ESI): *m/z* calcd. for $C_{24}H_{22}FN_4O_5$ $[M+H]^+$ 465.1569, found 465.1572.

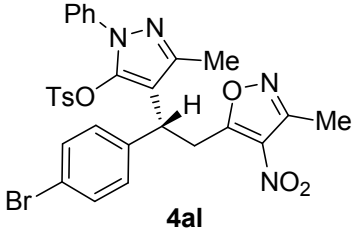
4-(1-(4-bromophenyl)-2-(3-methyl-4-nitroisoxazol-5-yl)ethyl)-1,3-diphenyl-1H-pyrazol-5-yl acetate (3dl):



3dl

White solid; 85% yield; 93% ee, [Determined by HPLC analysis Chiralcel OD-H column, Hexane/*i*-PrOH = 97/3, Flow rate: 1.0 mL/min, UV detection at 254 nm, Retention time: t_{major}= 31.849 min, t_{minor}= 23.631 min]; $[\alpha]_D^{20}$ = 39.5° (*c* = 0.1 g/100 mL, CH_2Cl_2); mp 87–88 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.07 (s, 3H), 2.43 (s, 3H), 3.76 (dd, *J* = 14.4 Hz, 8.8 Hz, 1H), 3.90 (dd, *J* = 14.4 Hz, 7.2 Hz, 1H), 4.83 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 7.32–7.48 (m, 10H), 7.52 (d, *J* = 6.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1, 167.0, 155.4, 150.6, 142.1, 139.7, 137.5, 131.7, 130.5, 129.2, 129.1, 128.5, 128.4, 127.9, 123.2, 121.0, 108.3, 36.7, 32.0, 20.1, 11.5; **IR** (KBr) ν 3424, 2925, 1637, 1560, 1437, 1383, 1118, 990, 876, 618 cm^{-1}; **HRMS** (ESI): *m/z* calcd. for $C_{29}H_{24}BrN_4O_5$ $[M+H]^+$ 587.0925, found 587.0933.

4-(1-(4-bromophenyl)-2-(3-methyl-4-nitroisoxazol-5-yl)ethyl)-3-methyl-1-phenyl-1H-pyrazol-5-yl 4-methylbenzenesulfonate (4al):

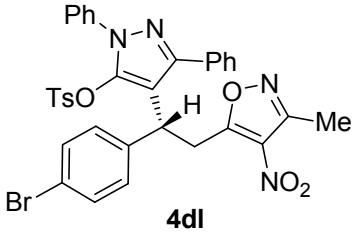


4al

White solid; 89% yield; 92% ee, [Determined by HPLC analysis Chiralcel AD-H column, Hexane/*i*-PrOH = 90/10, Flow rate: 1.0 mL/min, UV detection at 254 nm, Retention time: t_{major}= 26.542 min, t_{minor}= 30.094 min]; $[\alpha]_D^{20}$ = 60.1° (*c* = 0.1 g/100 mL, CH_2Cl_2); mp 78–80 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.17 (s, 3H), 2.34 (s, 3H), 2.53 (s, 3H), 3.87 (dd, *J* = 12.4 Hz, 9.6 Hz, 1H), 3.90 (dd, *J* = 14.8 Hz, 6.0 Hz, 1H), 4.85 (t, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 6.8 Hz, 2H), 7.08–7.15 (m, 2H), 7.16–7.22 (m, 2H), 7.23–7.34 (m, 5H), 7.48 (d, *J* = 6.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.5, 155.6, 147.7, 146.2, 139.7, 139.4, 137.3, 131.7, 130.8, 130.6, 129.6, 129.2, 128.6, 128.1, 127.0, 123.3, 120.9, 110.2, 36.4, 31.4, 21.6, 14.7, 11.6; **IR** (KBr) ν 3440,

2925, 1636, 1561, 1427, 1384, 1116, 992, 875, 617 cm^{-1}; **HRMS** (ESI): *m/z* calcd. for $C_{29}H_{26}BrN_4O_6S$ $[M+H]^+$ 637.0751, found 637.0750.

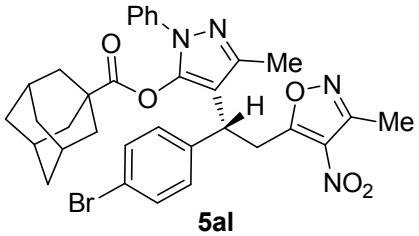
4-(1-(4-bromophenyl)-2-(3-methyl-4-nitroisoxazol-5-yl)ethyl)-1,3-diphenyl-1H-pyrazol-5-yl 4-methylbenzenesulfonate (4dl):



4dl

White solid; 87% yield; 93% ee, [Determined by HPLC analysis Chiralcel OD-H column, Hexane/*i*-PrOH = 97/3, Flow rate: 1.0 mL/min, UV detection at 254 nm, Retention time: t_{major}= 41.189 min, t_{minor}= 35.785 min]; $[\alpha]_D^{20}$ = 60.2° (*c* = 0.1 g/100 mL, CH_2Cl_2); mp 77–79 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 2.46 (s, 3H), 3.88 (dd, *J* = 14.4 Hz, 9.6 Hz, 1H), 4.04 (dd, *J* = 14.4 Hz, 6.0 Hz, 1H), 4.95 (t, *J* = 7.2 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 2H), 7.17 (d, *J* = 7.2 Hz, 2H), 7.21–7.28 (m, 5H), 7.29–7.38 (m, 7H), 7.41 (d, *J* = 8.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 155.7, 151.4, 146.2, 140.1, 139.9, 137.5, 133.1, 131.5, 131.2, 130.5, 129.7, 129.3, 129.0, 128.7, 128.6, 128.3, 128.2, 127.4, 123.8, 120.9, 110.8, 36.6, 31.5, 21.6, 11.5; **IR** (KBr) ν 3440, 2922, 1636, 1562, 1428, 1384, 1119, 990, 876, 618 cm^{-1}; **HRMS** (ESI): *m/z* calcd. for $C_{34}H_{28}BrN_4O_6S$ $[M+H]^+$ 699.0907, found 699.0910.

1-(4-bromophenyl)-2-(3-methyl-4-nitroisoxazol-5-yl)ethyl)-3-methyl-1-phenyl-1H-pyrazol-5-yl adamantane-1-carboxylate (5al):

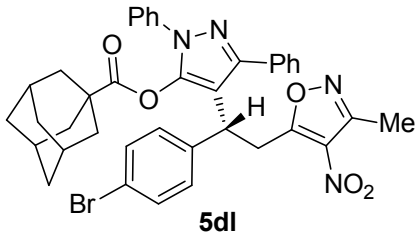


5al

White solid; 86% yield; 92% ee, [Determined by HPLC analysis Chiralcel OD-H column, Hexane/*i*-PrOH = 90/10, Flow rate: 1.0 mL/min, UV detection at 254 nm, Retention time: t_{major}= 13.151 min, t_{minor}= 8.741 min]; $[\alpha]_D^{20}$ = 21.9° (*c* = 0.1 g/100

mL, CH_2Cl_2); mp 57–59 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.62–1.74 (m, 6H), 1.80 (s, 6H), 2.00 (s, 3H), 2.16 (s, 3H), 2.50 (s, 3H), 3.80 (dd, *J* = 12.4 Hz, 9.2 Hz, 1H), 3.93 (dd, *J* = 14.0 Hz, 5.6 Hz, 1H), 4.44 (t, *J* = 7.2 Hz, 1H), 7.17 (d, *J* = 6.0 Hz, 2H), 7.28–7.33 (m, 1H), 7.34–7.41 (m, 4H), 7.43 (d, *J* = 6.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.0, 172.4, 155.6, 147.2, 142.0, 139.7, 137.3, 131.7, 130.5, 129.0, 128.9, 127.7, 123.8, 120.9, 108.1, 40.9, 38.2, 36.8, 36.0, 31.6, 27.5, 13.7, 11.6; **IR** (KBr) ν 3443, 2926, 1636, 1564, 1425, 1387, 1116, 829, 618 cm^{-1}; **HRMS** (ESI): *m/z* calcd. for $C_{33}H_{34}BrN_4O_5$ $[M+H]^+$ 645.1707, found 645.1709.

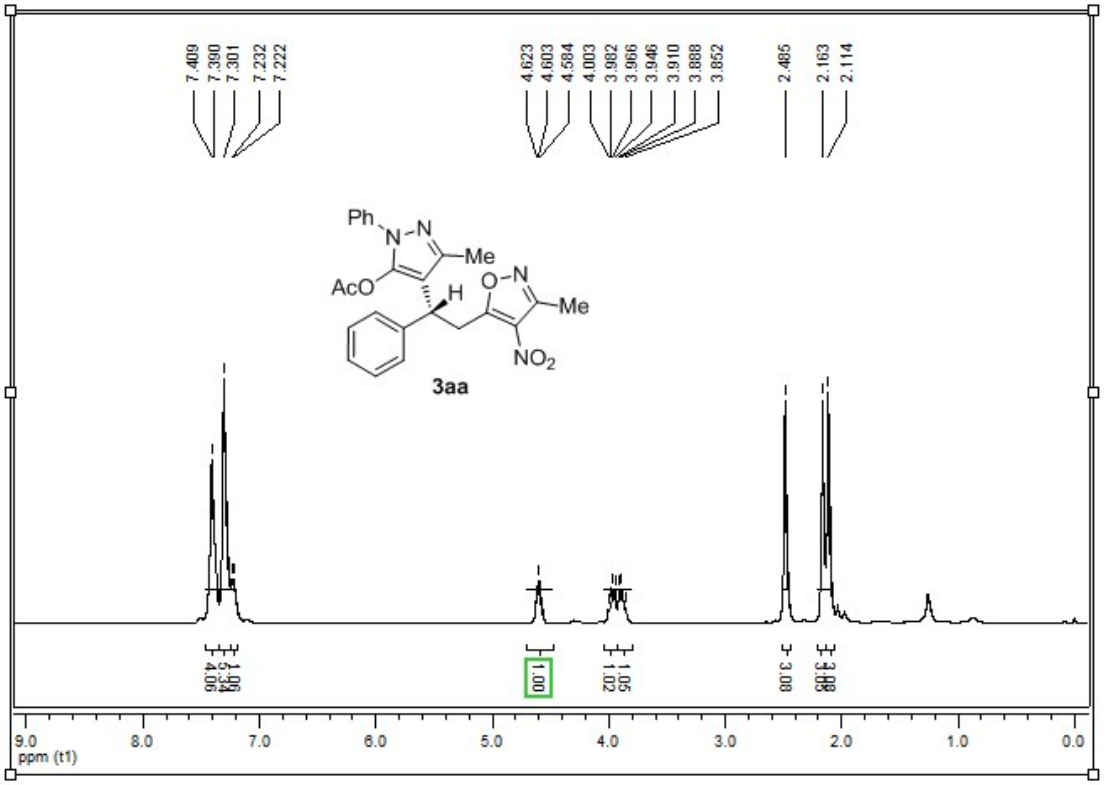
1-(4-bromophenyl)-2-(3-methyl-4-nitroisoxazol-5-yl)ethyl)-1,3-diphenyl-1H-pyrazol-5-yl adamantane-1-carboxylate (5dl):

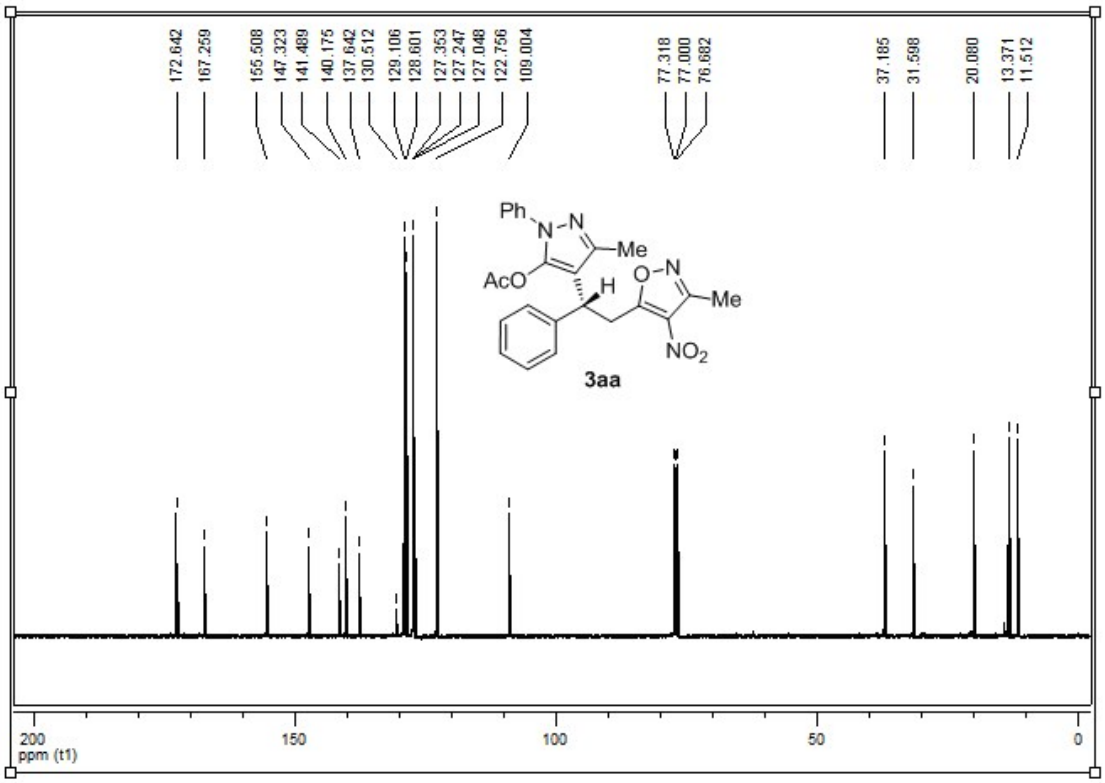


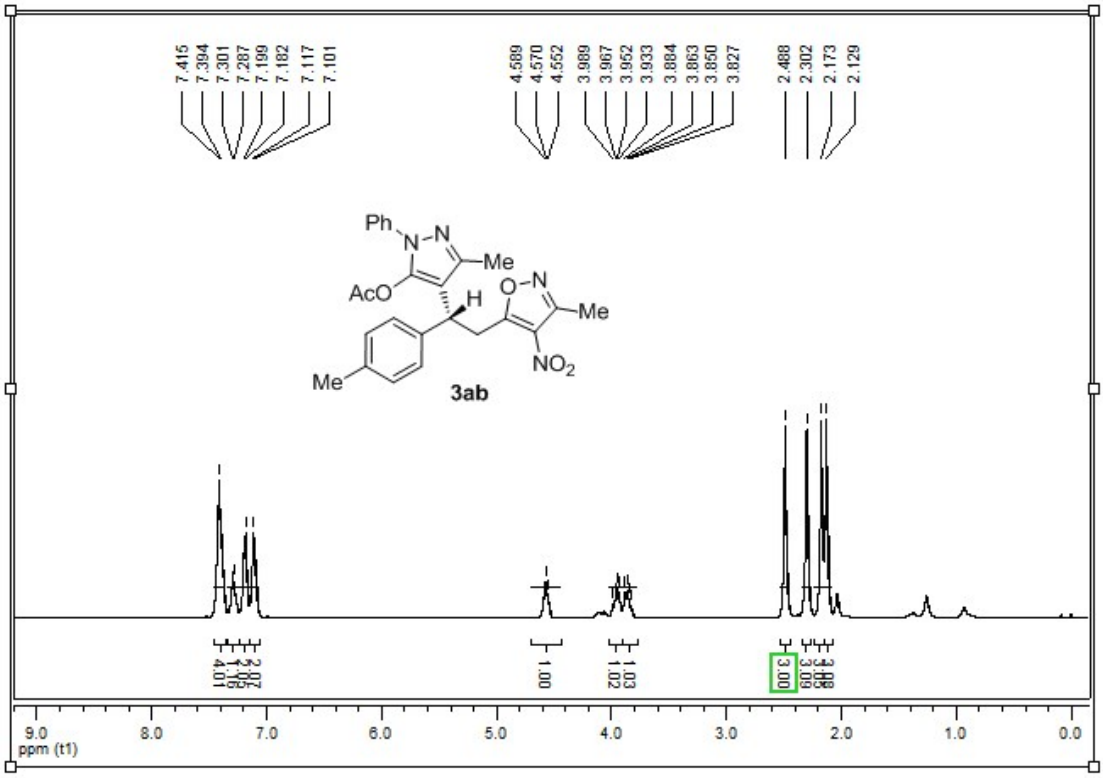
5dl

White solid; 82% yield; 93% ee, [Determined by HPLC analysis Chiralcel AD-H column, Hexane/*i*-PrOH = 90/10, Flow rate: 1.0 mL/min, UV detection at 254 nm, Retention time: t_{major}= 7.531 min, t_{minor}= 9.021 min]; $[\alpha]_D^{20}$ = 31.1° (*c* = 0.1 g/100 mL, CH_2Cl_2); mp 66–68 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.72 (s, 10H), 1.90 (s, 1H), 1.99 (s, 4H), 2.45 (s, 3H), 3.70 (dd, *J* = 12.4 Hz, 9.6 Hz, 1H), 3.91 (dd, *J* = 14.0 Hz, 6.8 Hz, 1H), 4.73 (t, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 6.0 Hz, 2H), 7.29–7.39 (m, 6H), 7.40–7.47 (m, 4H), 7.49 (d, *J* = 6.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.5, 172.3, 155.4, 150.8, 142.7, 140.1, 137.4, 132.7, 131.7, 130.4, 129.0, 128.9, 128.5, 128.4, 128.1, 124.3, 120.9, 108.0, 40.8, 38.2, 36.8, 36.0, 32.3, 27.4, 11.5; **IR** (KBr) ν 3439, 2908, 1772, 1603, 1565, 1517, 1451, 1377, 1172, 1130, 1018, 827, 764, 617 cm^{-1}; **HRMS** (ESI): *m/z* calcd. for $C_{38}H_{36}BrN_4O_5$ $[M+H]^+$ 707.1864, found 707.1871.

Copies of NMR spectra of the products:



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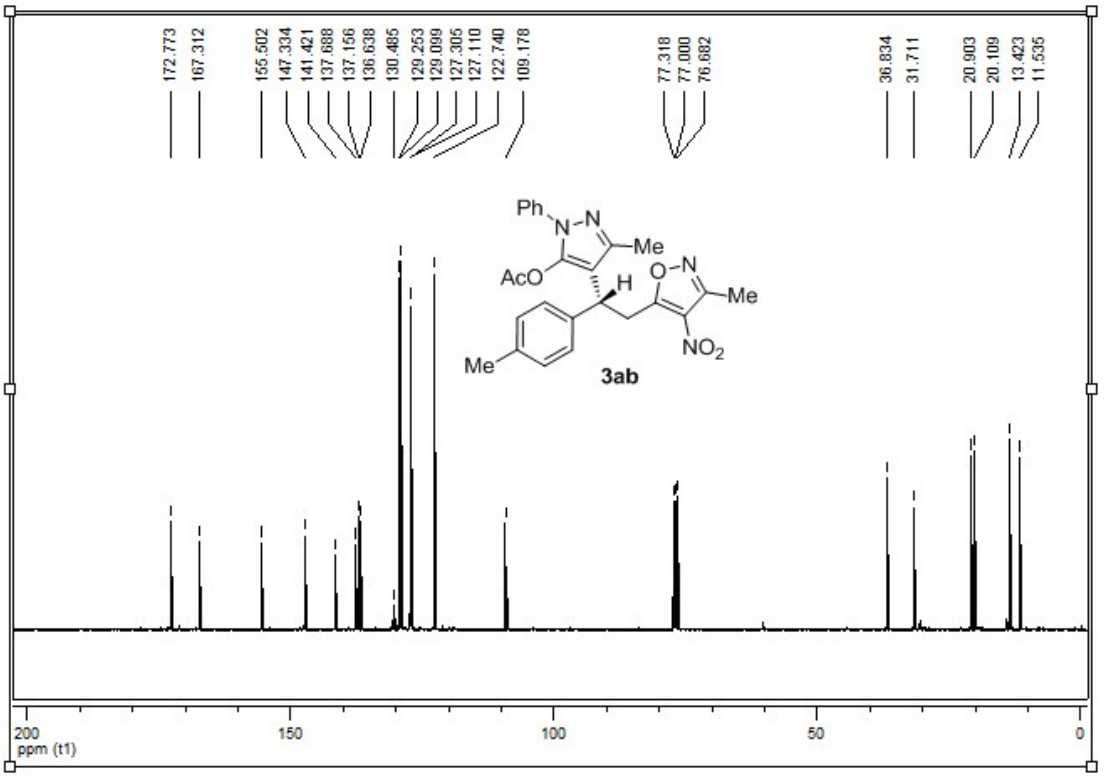
7.394
7.301
7.287
7.199
7.182
7.117
7.101
4.589
4.570
4.552
3.989
3.967
3.952
3.933
3.884
3.863
3.850
3.827
2.488
2.302
2.173
2.129
Ph
N-N
Me
AcO
H
O-N
Me
NO2
Me
3ab
4.01
1.76
2.18
2.02
1.00
1.02
3.00
3.09
3.08
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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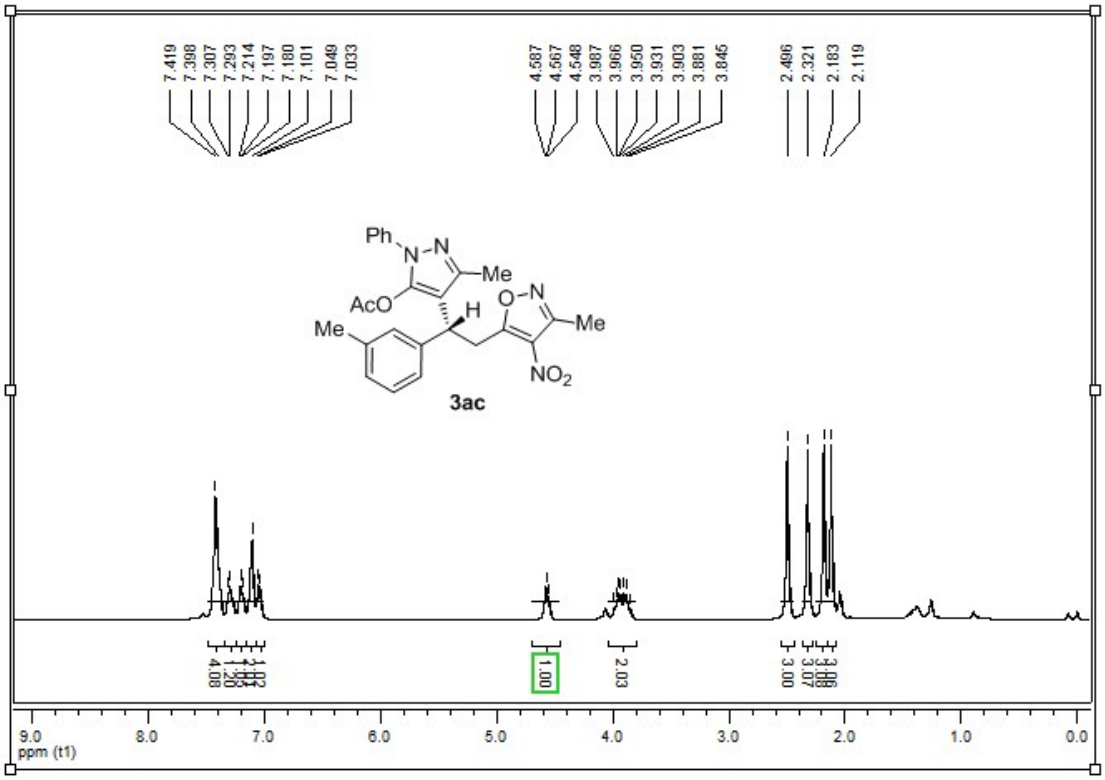
137.688
137.156
136.638
130.485
129.253
129.099
127.305
127.110
122.740
109.178
77.318
77.000
76.682
36.834
31.711
20.903
20.109
13.423
11.535
Ph
N-N
Me
AcO
H
O-N
Me
NO2
Me
3ab
200
150
100
50
0
ppm (t1)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7.197
7.180
7.101
7.049
7.033
4.587
4.567
4.548
3.987
3.966
3.950
3.931
3.903
3.881
3.845
2.496
2.321
2.183
2.119
Ph
N-N
Me
AcO
H
O-N
Me
Me
NO2
3ac
4.08
2.20
1.43
1.00
2.03
3.00
3.07
3.08
9.0
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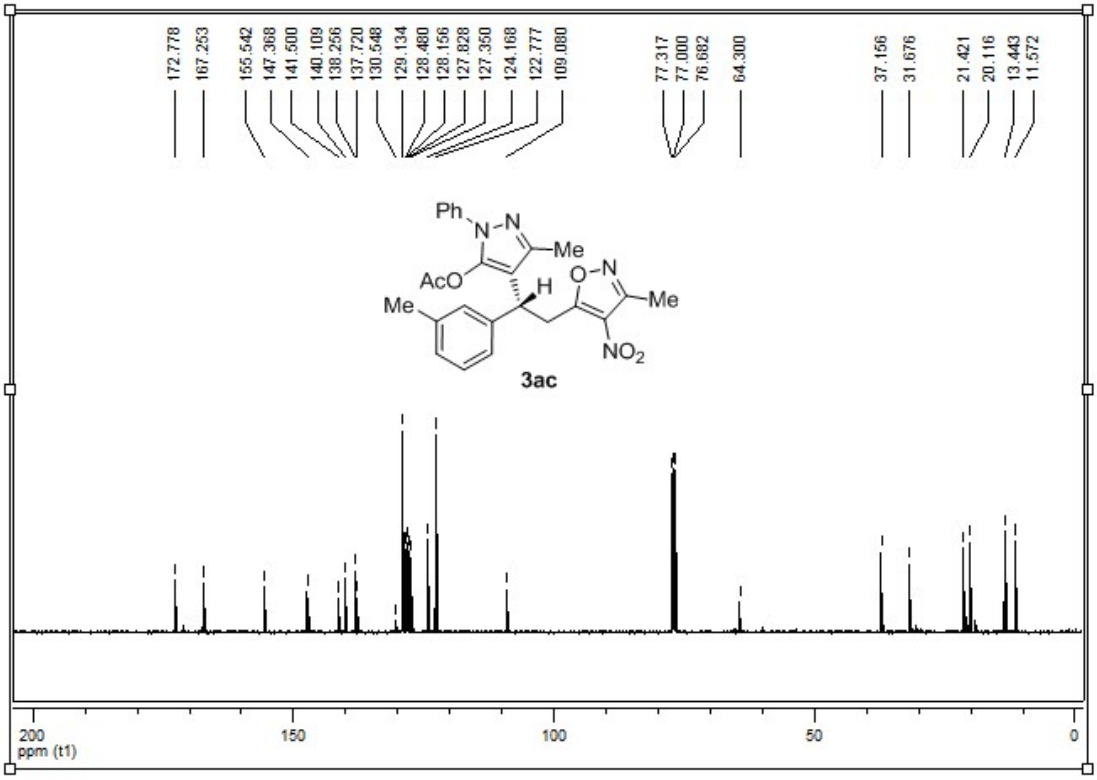
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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137.720
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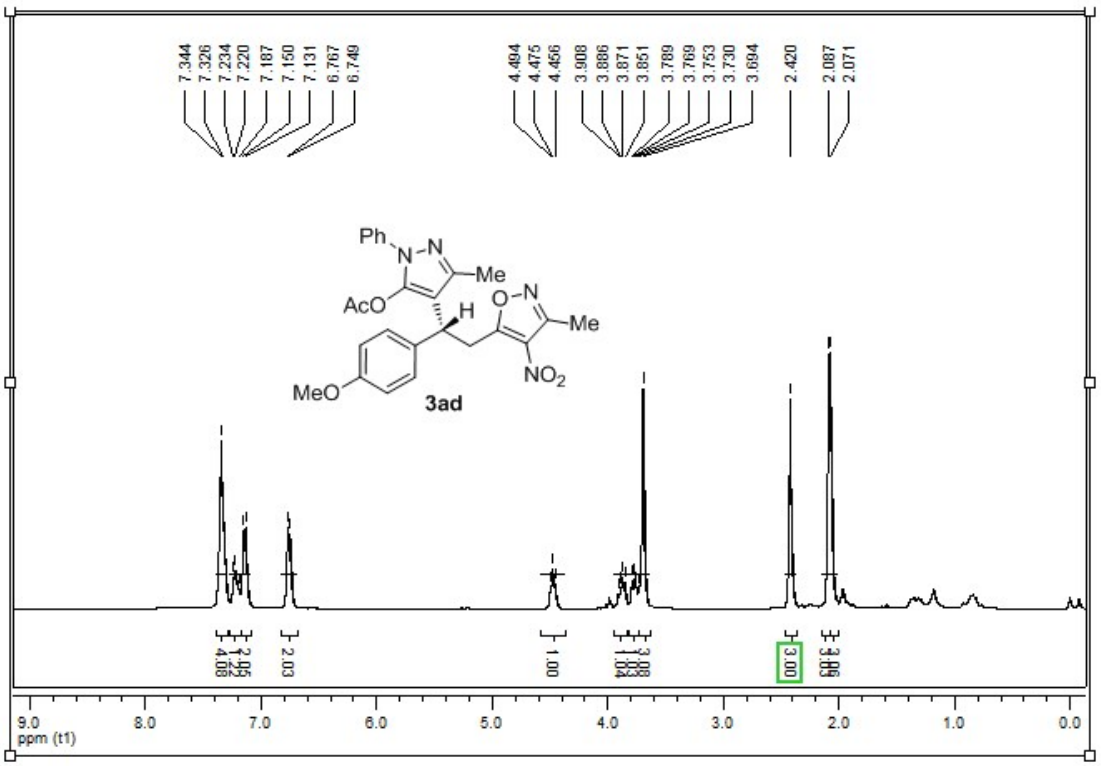
129.134
128.480
128.156
127.828
127.350
124.168
122.777
109.080
77.317
77.000
76.682
64.300
37.156
31.676
21.421
20.116
13.443
11.572
Ph
N-N
Me
AcO
H
O-N
Me
Me
NO2
3ac
200
150
100
50
0
ppm (t1)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7.234
7.220
7.187
7.150
7.131
6.767
6.749
4.494
4.475
4.456
3.908
3.886
3.871
3.851
3.789
3.769
3.753
3.730
3.694
2.420
2.087
2.071
Ph
N-N
Me
AcO
H
O-N
Me
NO2
MeO
3ad
4.06
2.95
2.03
1.00
3.08
1.04
3.00
3.09
9.0
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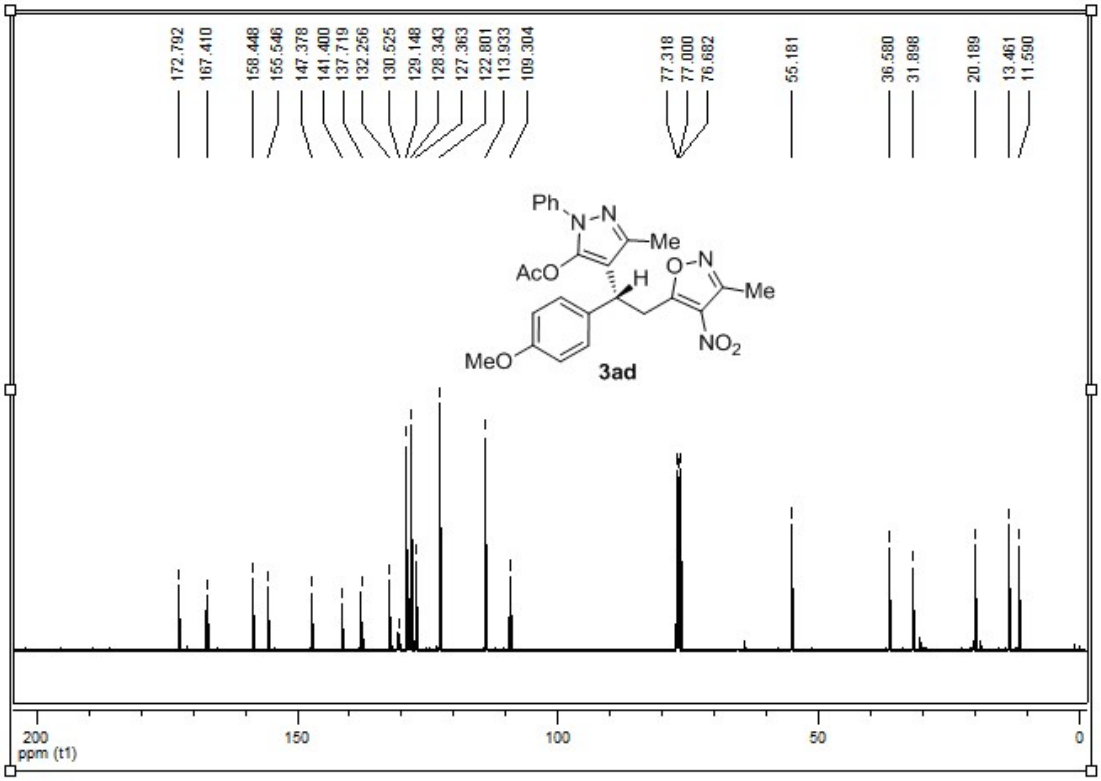
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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155.546
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132.256
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127.363
122.801
113.933
109.304
77.318
77.000
76.682
55.181
36.580
31.898
20.189
13.461
11.590
Ph
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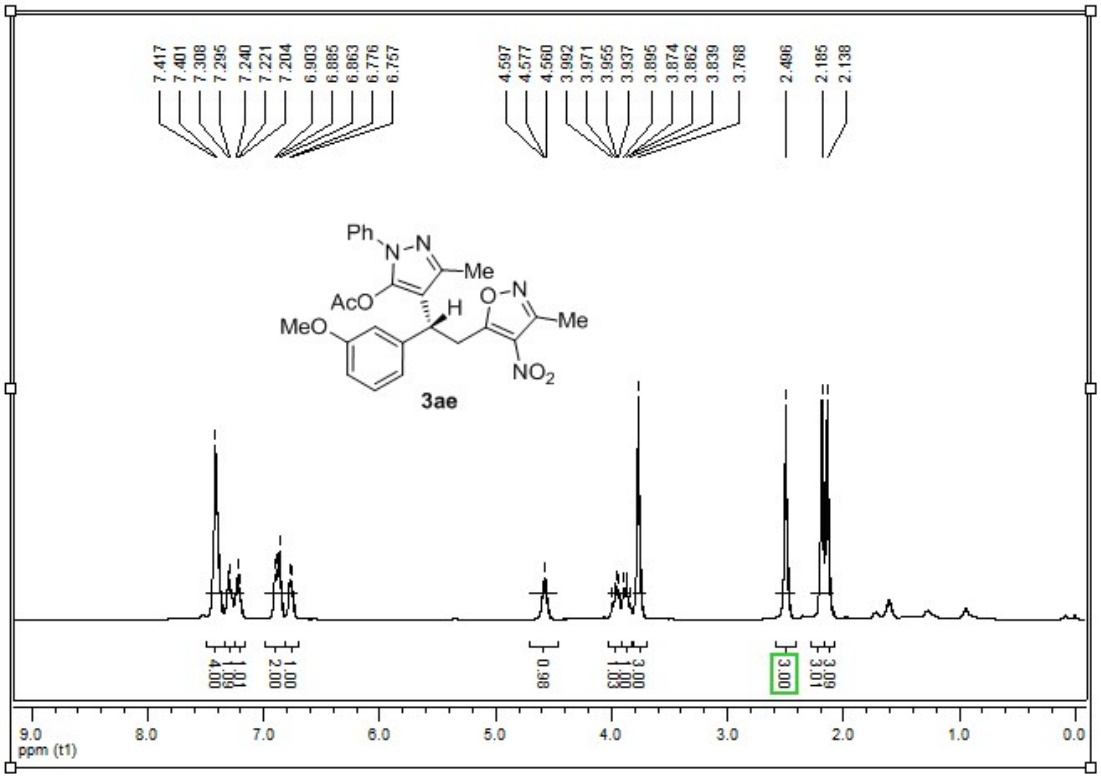
Me
AcO
H
O-N
Me
NO2
MeO
3ad
200
150
100
50
0
ppm (t1)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7.401
7.308
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7.240
7.221
7.204
6.903
6.885
6.863
6.776
6.757
4.597
4.577
4.560
3.992
3.971
3.955
3.937
3.895
3.874
3.862
3.839
3.768
2.496
2.185
2.138
Ph
N-N
Me
AcO
H
O-N
Me
MeO
NO2
3ae
4.00
1.09
1.01
1.00
2.00
0.98
3.00
1.08
1.00
3.00
3.01
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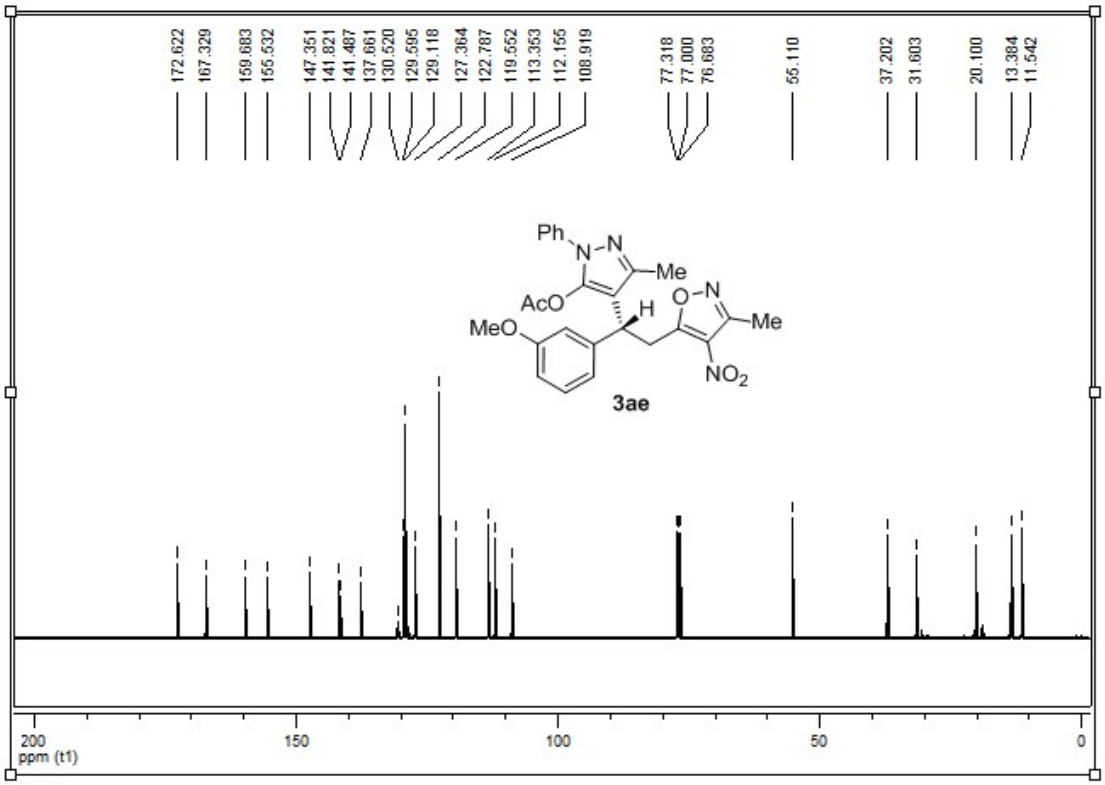
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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159.683
155.532
147.351
141.821
141.487
137.661
130.520
129.595
129.118
127.364
122.787
119.552
113.353
112.155
108.919
77.318
77.000
76.683
55.110
37.202
31.603
20.100
13.384
11.542
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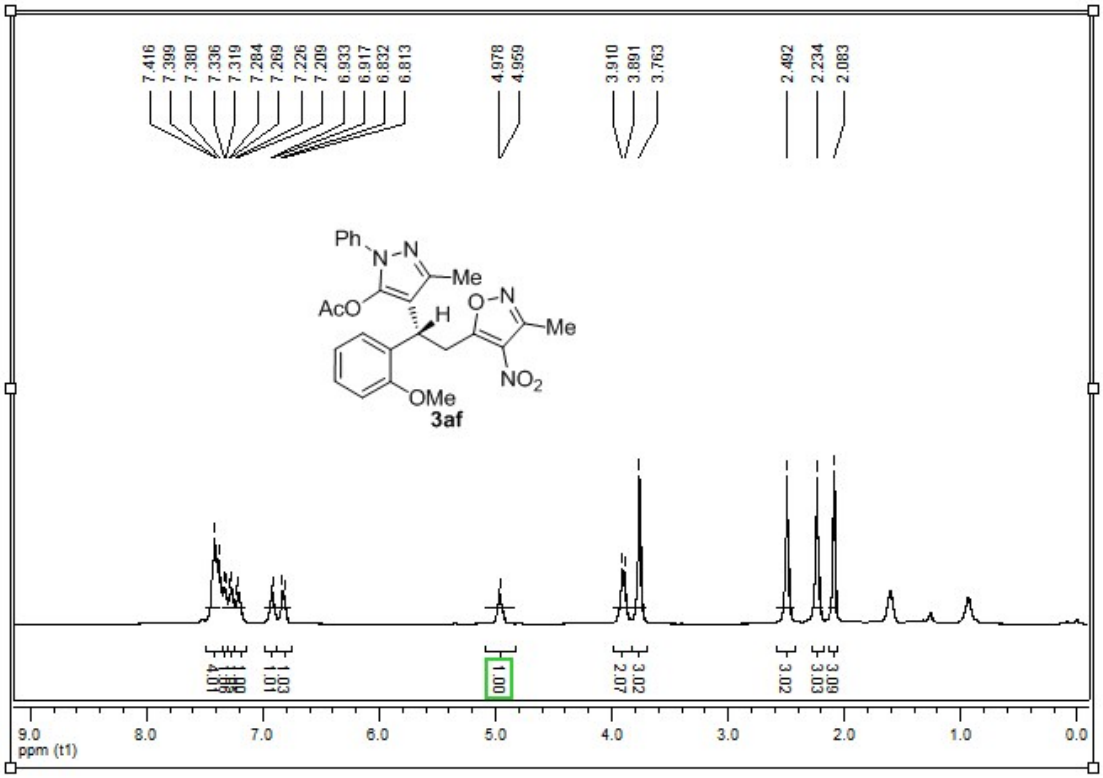
Me
AcO
H
O-N
Me
MeO
NO2
3ae
200
150
100
50
0
ppm (t1)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7.380
7.336
7.319
7.284
7.269
7.226
7.209
6.933
6.917
6.832
6.813
4.978
4.959
3.910
3.891
3.763
2.492
2.234
2.083
Ph
N-N
Me
AcO
H
O-N
Me
NO2
OMe
3af
4.07
1.88
1.03
1.01
1.00
2.07
3.02
3.02
3.03
3.09
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7.0
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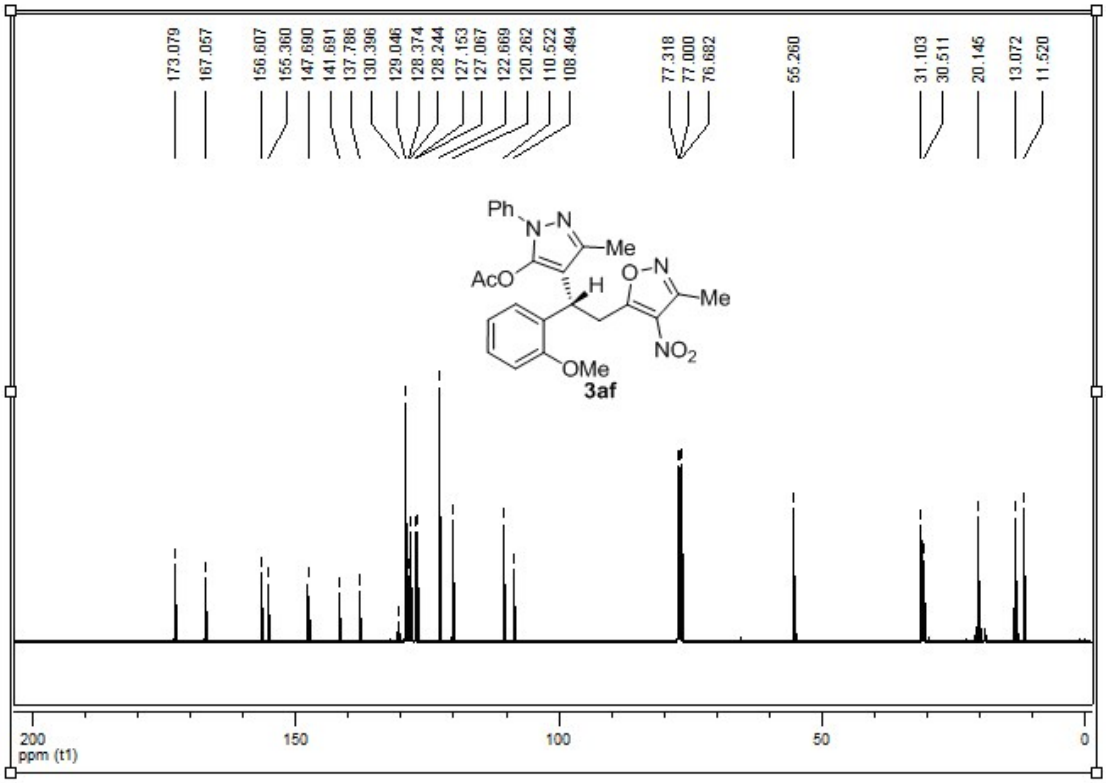
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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156.607
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141.691
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130.396
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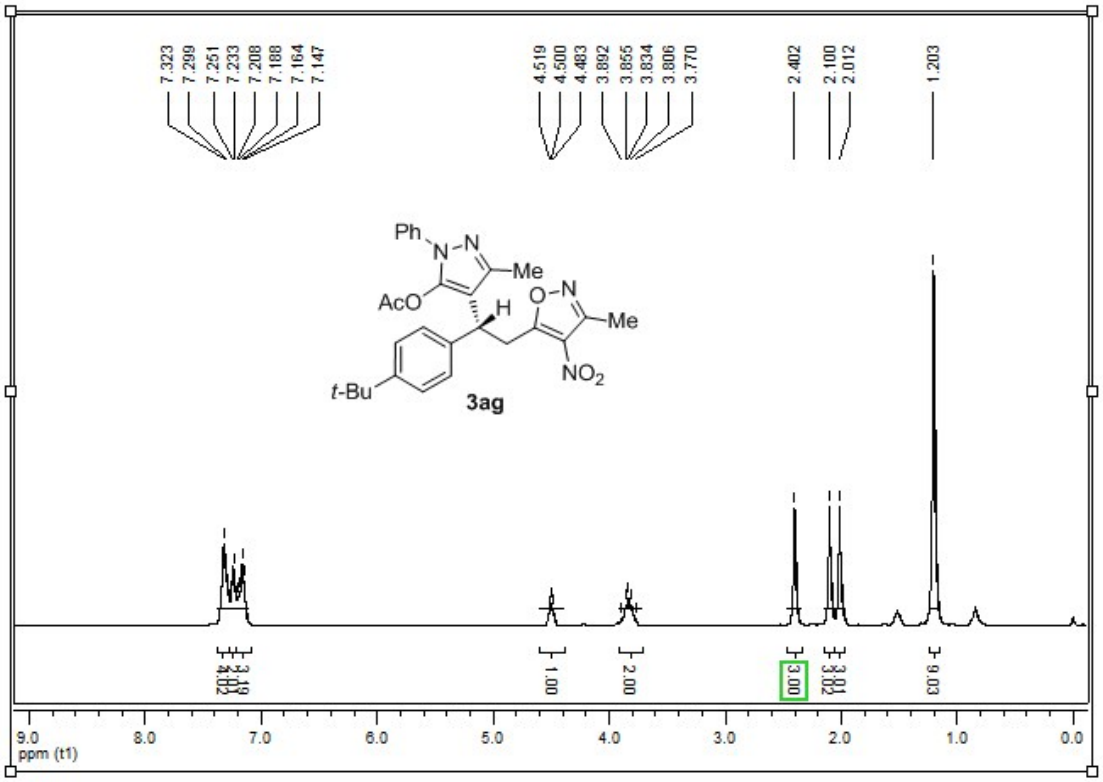
128.374
128.244
127.153
127.067
122.669
120.262
110.522
108.494
77.318
77.000
76.682
55.260
31.103
30.511
20.145
13.072
11.520
Ph
N-N
Me
AcO
H
O-N
Me
NO2
OMe
3af
200
150
100
50
0
ppm (t1)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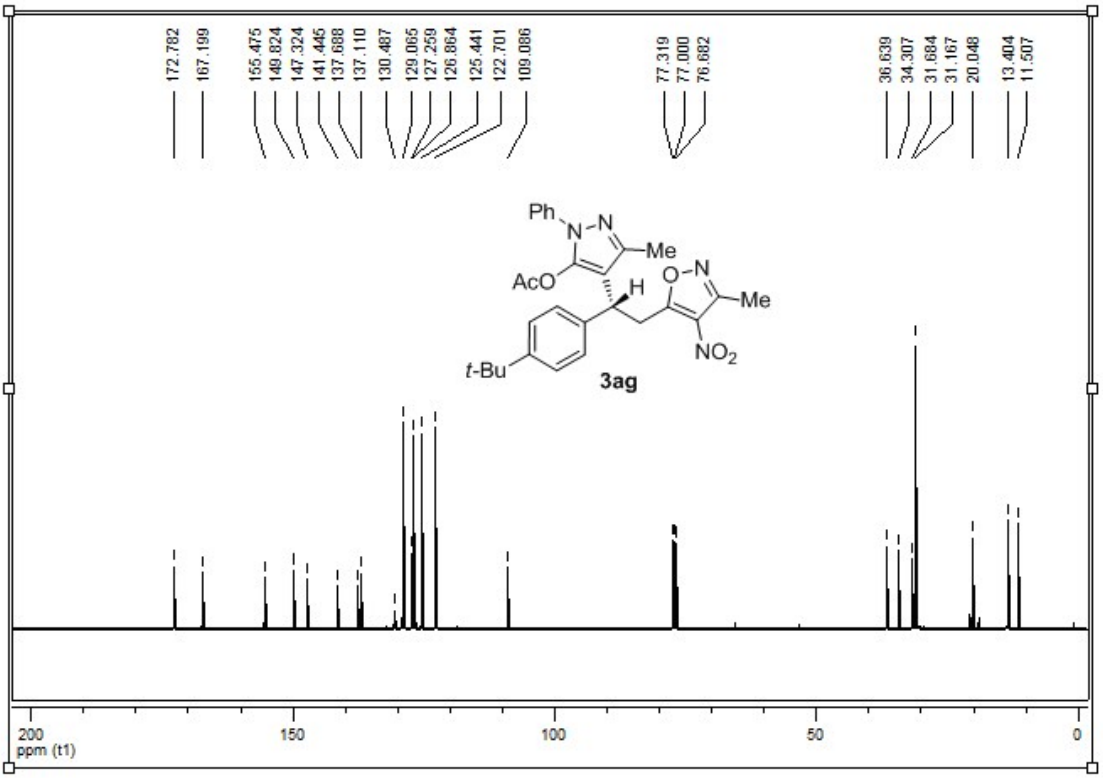
7.299
7.251
7.233
7.208
7.188
7.164
7.147
4.519
4.500
4.483
3.892
3.855
3.834
3.806
3.770
2.402
2.100
2.012
1.203
Ph
N
N
Me
AcO
H
O
N
Me
NO2
t-Bu
3ag
3.19
4.02
1.00
2.00
3.00
3.02
9.03
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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137.110
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129.065
127.259
126.864
125.441
122.701
109.086
77.319
77.000
76.682
36.639
34.307
31.684
31.167
20.048
13.404
11.507
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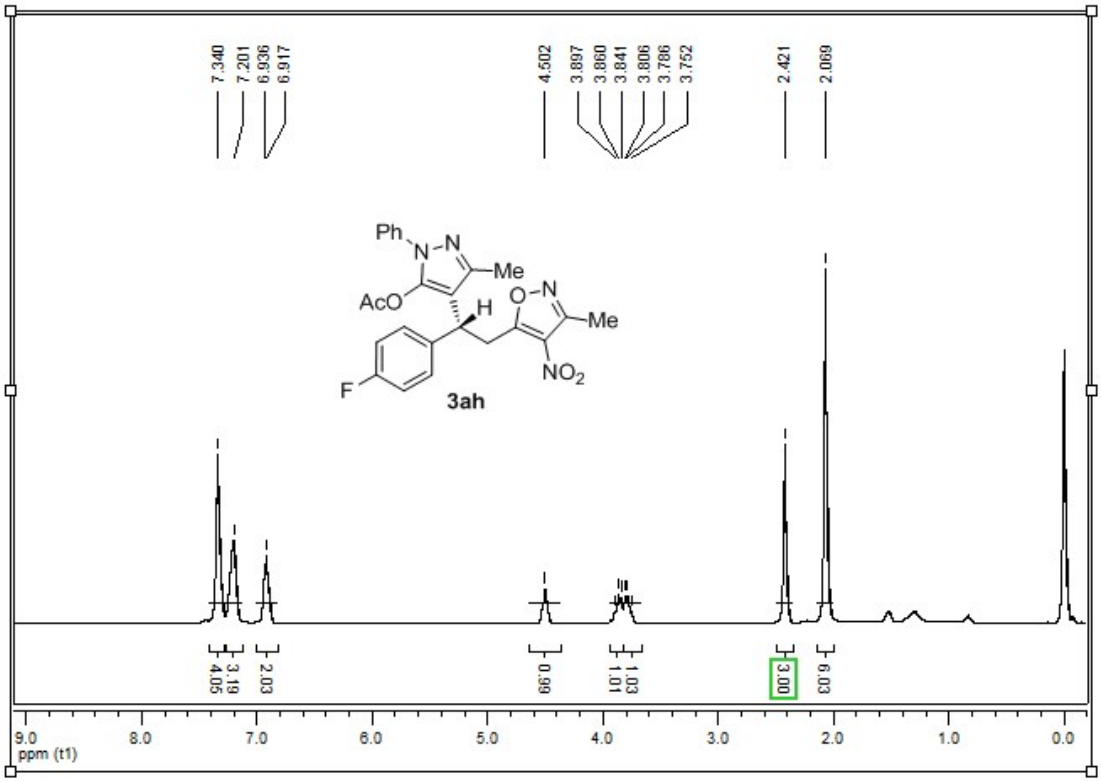
N
Me
AcO
H
O
N
Me
NO2
t-Bu
3ag
200
150
100
50
0
ppm (t1)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6.917
4.502
3.897
3.860
3.841
3.806
3.786
3.752
2.421
2.069
Ph
N
N
Me
AcO
H
O
N
Me
NO2
F
3ah
4.06
3.19
2.03
0.99
1.03
1.01
3.00
6.03
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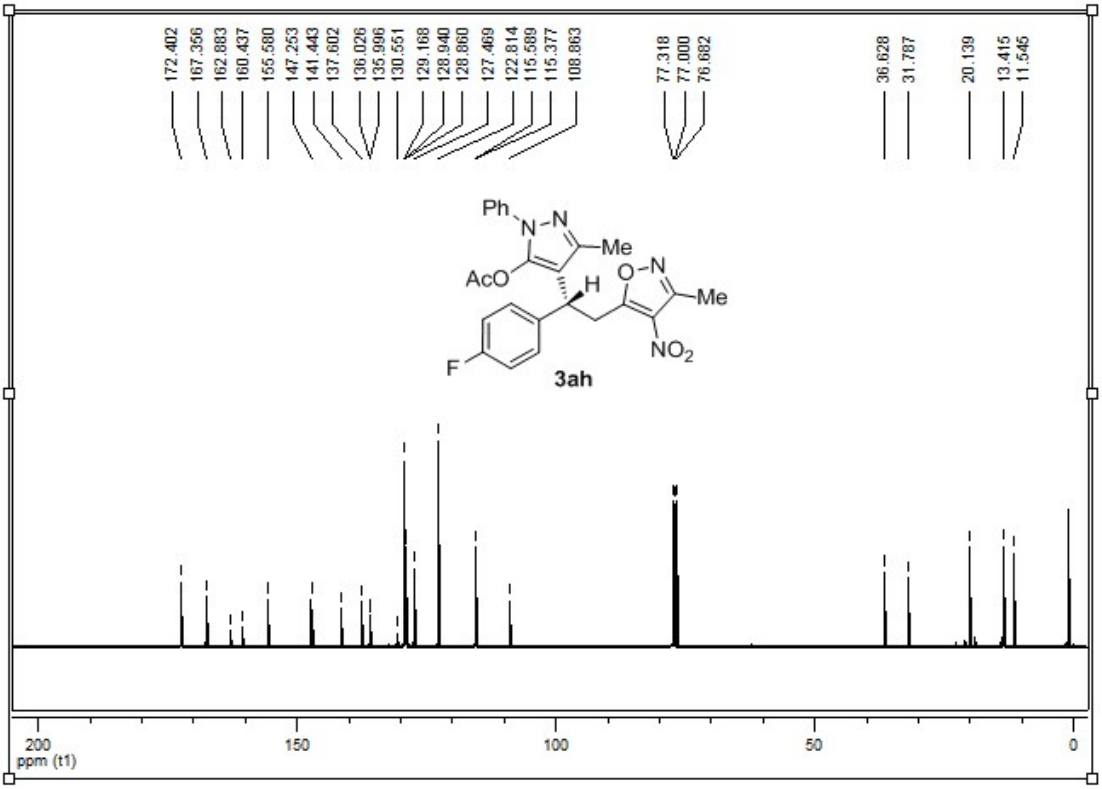
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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136.026
135.996
130.551
129.168
128.940
128.860
127.469
122.814
115.589
115.377
108.863
77.318
77.000
76.682
36.628
31.787
20.139
13.415
11.545
Ph
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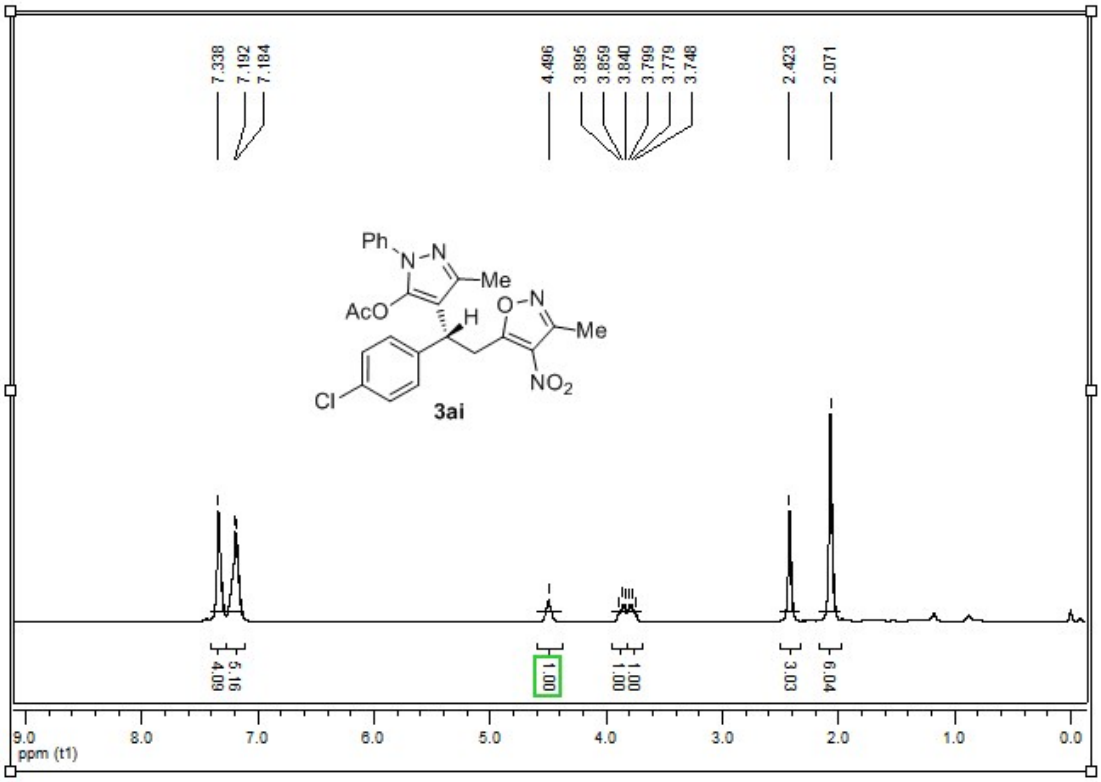
Me
AcO
H
O
N
Me
NO2
F
3ah
200
150
100
50
0
ppm (t1)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3.799
3.779
3.748
2.423
2.071
Ph
N-N
Me
AcO
H
O-N
Me
NO2
Cl
3ai
4.09
5.16
1.00
1.00
1.00
3.03
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7.0
6.0
5.0
4.0
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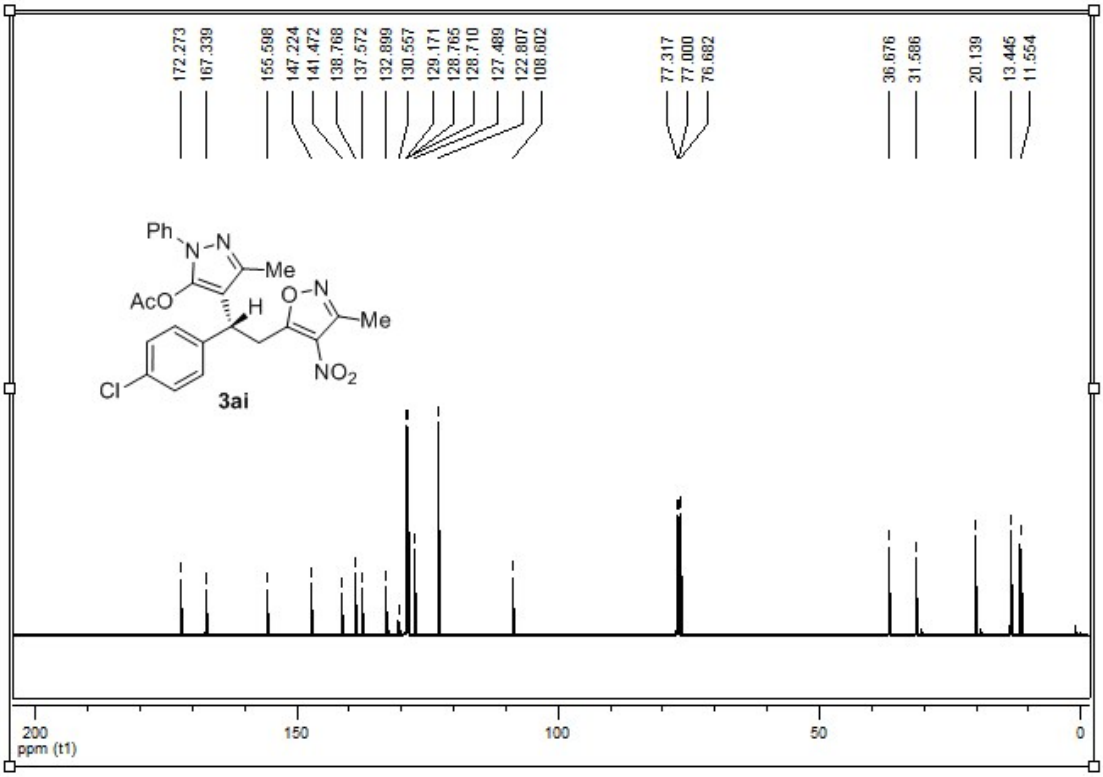
2.0
1.0
0.0
ppm (t1)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147.224
141.472
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137.572
132.899
130.557
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128.765
128.710
127.489
122.807
108.602
77.317
77.000
76.682
36.676
31.586
20.139
13.445
11.554
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Me
AcO
H
O-N
Me
NO2
Cl
3ai
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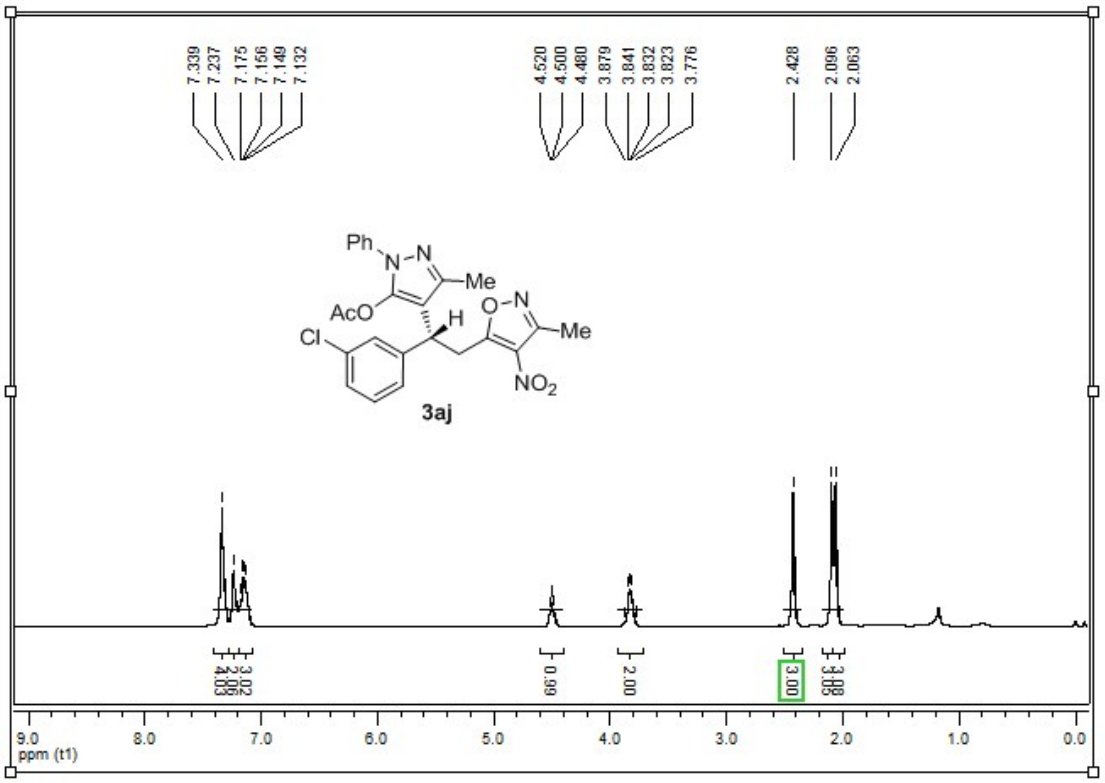
100
50
0
ppm (t1)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7.156
7.149
7.132
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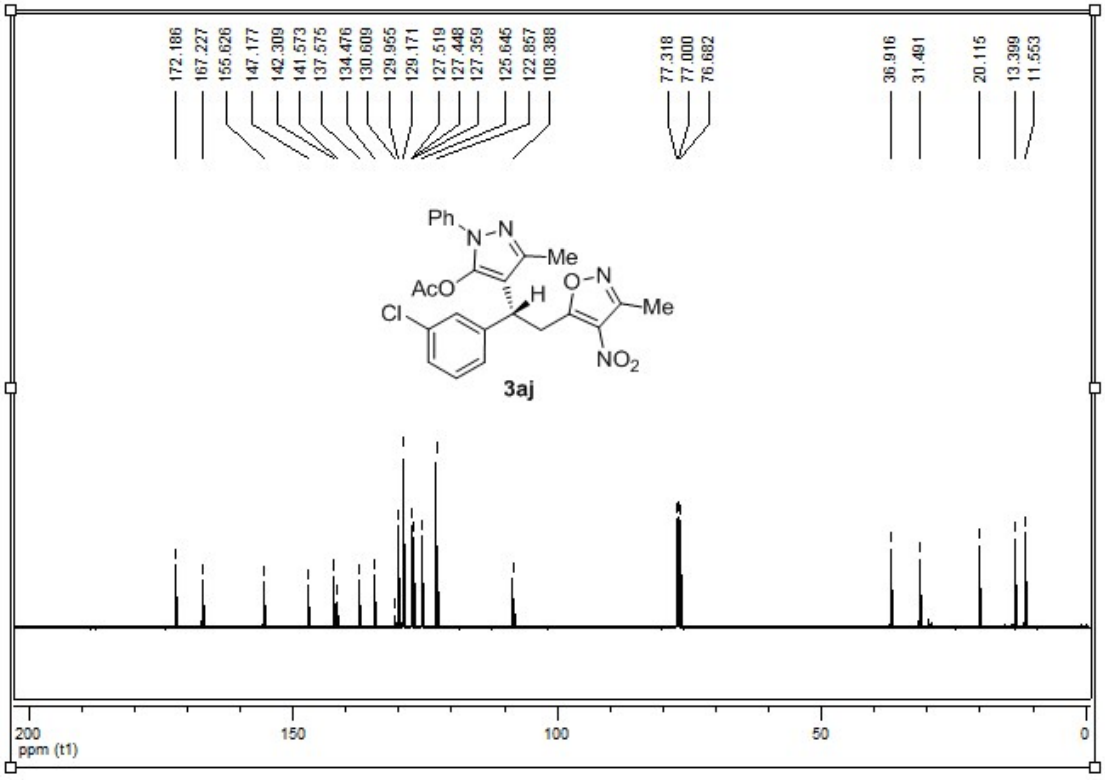
4.500
4.480
3.879
3.841
3.832
3.823
3.776
2.428
2.096
2.063
Ph
N
N
Me
AcO
H
O
N
Me
Cl
NO2
3aj
4.08
3.03
2.02
0.99
2.00
3.00
3.08
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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129.955
129.171
127.519
127.448
127.359
125.645
122.857
108.388
77.318
77.000
76.682
36.916
31.491
20.115
13.399
11.553
Ph
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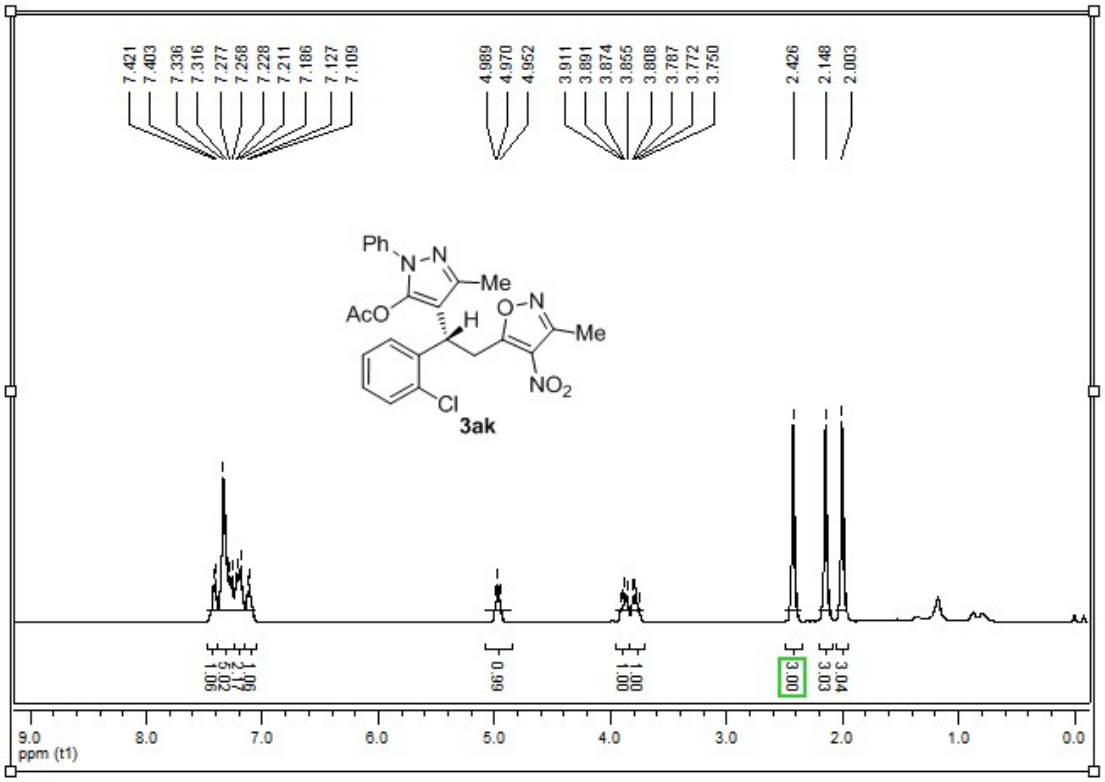
N
Me
AcO
H
O
N
Me
Cl
NO2
3aj
200
150
100
50
0
ppm (t1)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7.258
7.228
7.211
7.186
7.127
7.109
4.989
4.970
4.952
3.911
3.891
3.874
3.855
3.808
3.787
3.772
3.750
2.426
2.148
2.003
Ph
N-N
Me
AcO
H
O-N
Me
NO2
Cl
3ak
1.06
5.02
1.09
1.17
0.99
1.00
1.00
3.00
3.03
3.04
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7.0
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5.0
4.0
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2.0
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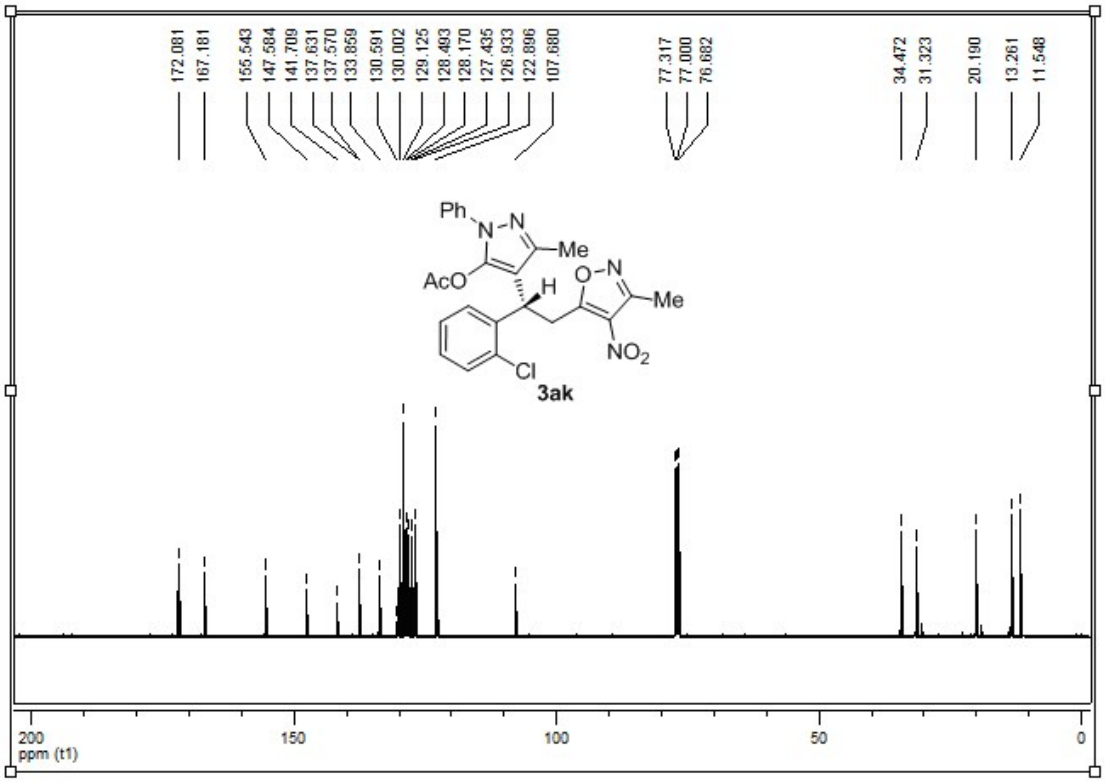
ppm (t1)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137.570
133.859
130.591
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129.125
128.493
128.170
127.435
126.933
122.896
107.680
77.317
77.000
76.682
34.472
31.323
20.190
13.261
11.548
Ph
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AcO
H
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Me
NO2
Cl
3ak
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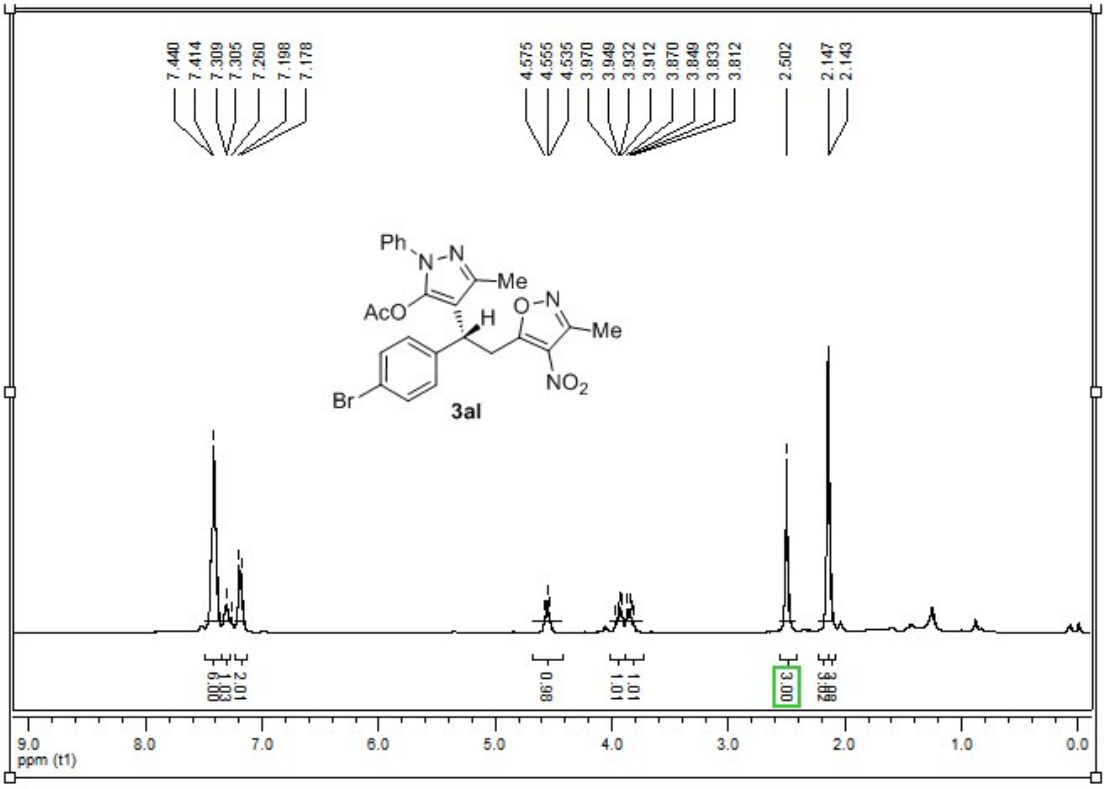
150
100
50
0
ppm (t1)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4.555
4.535
3.970
3.949
3.932
3.912
3.870
3.849
3.833
3.812
2.502
2.147
2.143
Ph
N-N
Me
AcO
H
O-N
Me
NO2
Br
3al
2.01
1.03
6.00
0.98
1.01
1.01
3.00
3.02
3.08
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7.0
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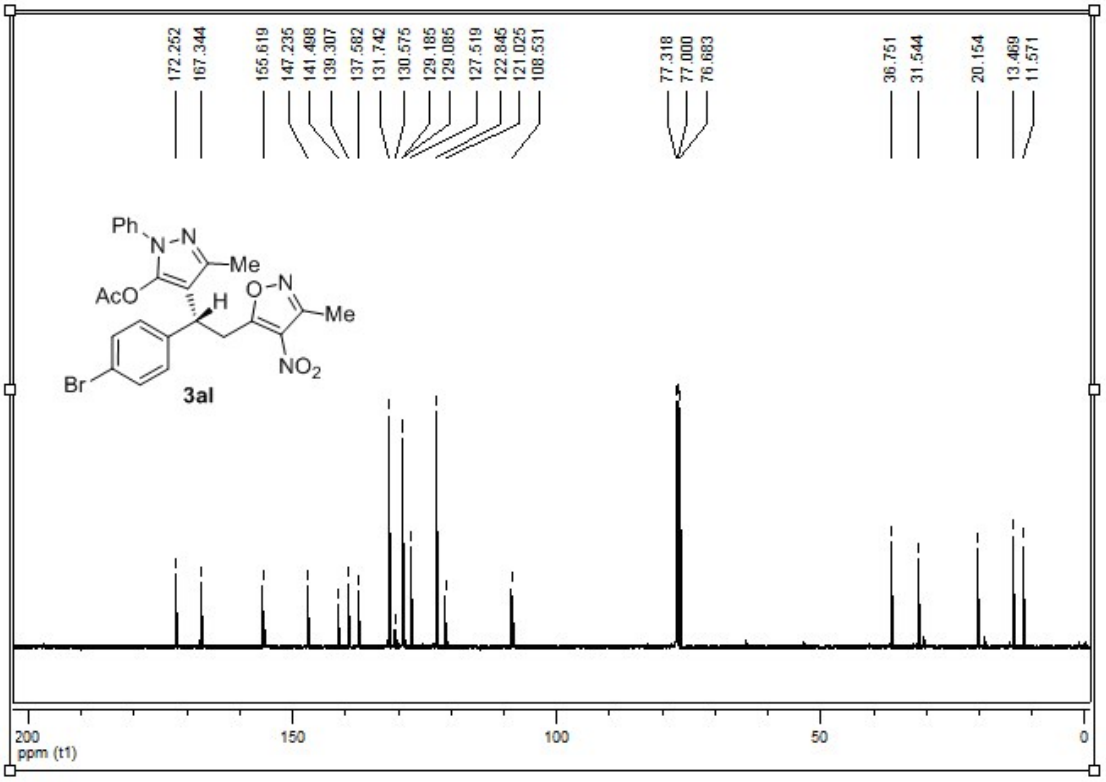
2.0
1.0
0.0
ppm (t1)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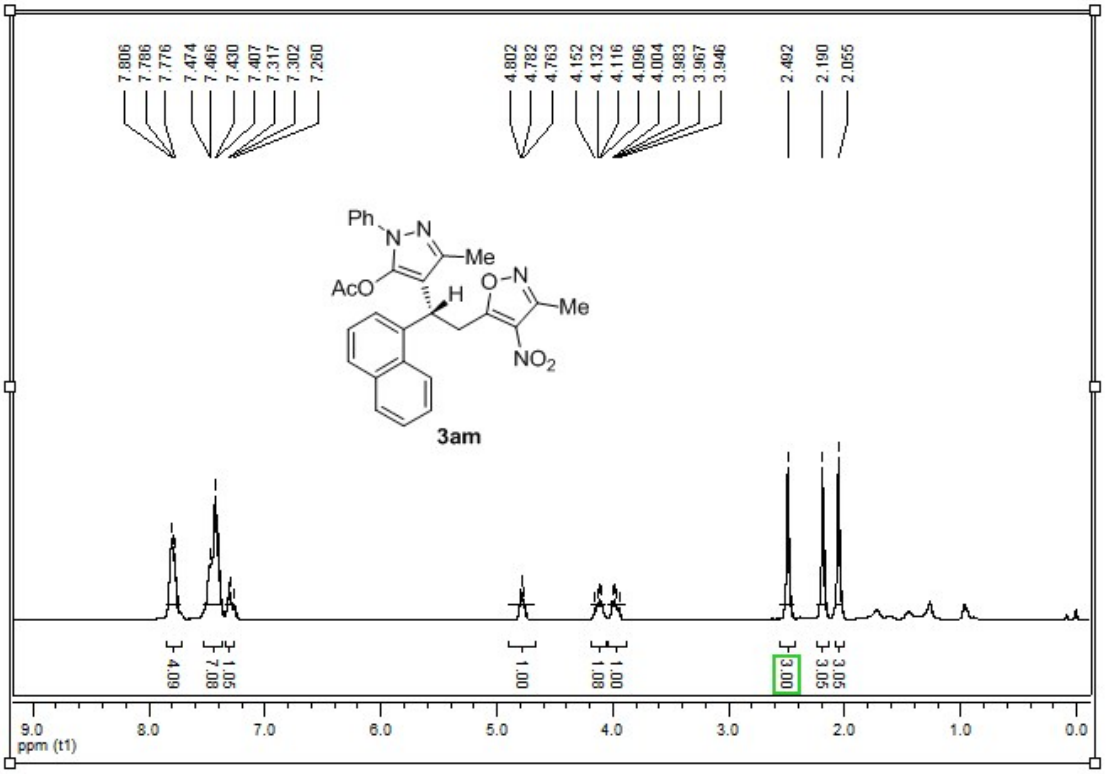
167.344
155.619
147.235
141.498
139.307
137.582
131.742
130.575
129.185
129.085
127.519
122.845
121.025
108.531
77.318
77.000
76.683
36.751
31.544
20.154
13.469
11.571
Ph
N-N
Me
AcO
H
O-N
Me
NO2
Br
3al
200
150
100
50
0
ppm (t1)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7.466
7.430
7.407
7.317
7.302
7.260
4.802
4.782
4.763
4.152
4.132
4.116
4.096
4.004
3.983
3.967
3.946
2.492
2.190
2.055
Ph
N
N
Me
AcO
H
O
N
Me
NO2
3am
4.09
7.08
1.06
1.00
1.08
1.00
3.00
3.06
3.06
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7.0
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4.0
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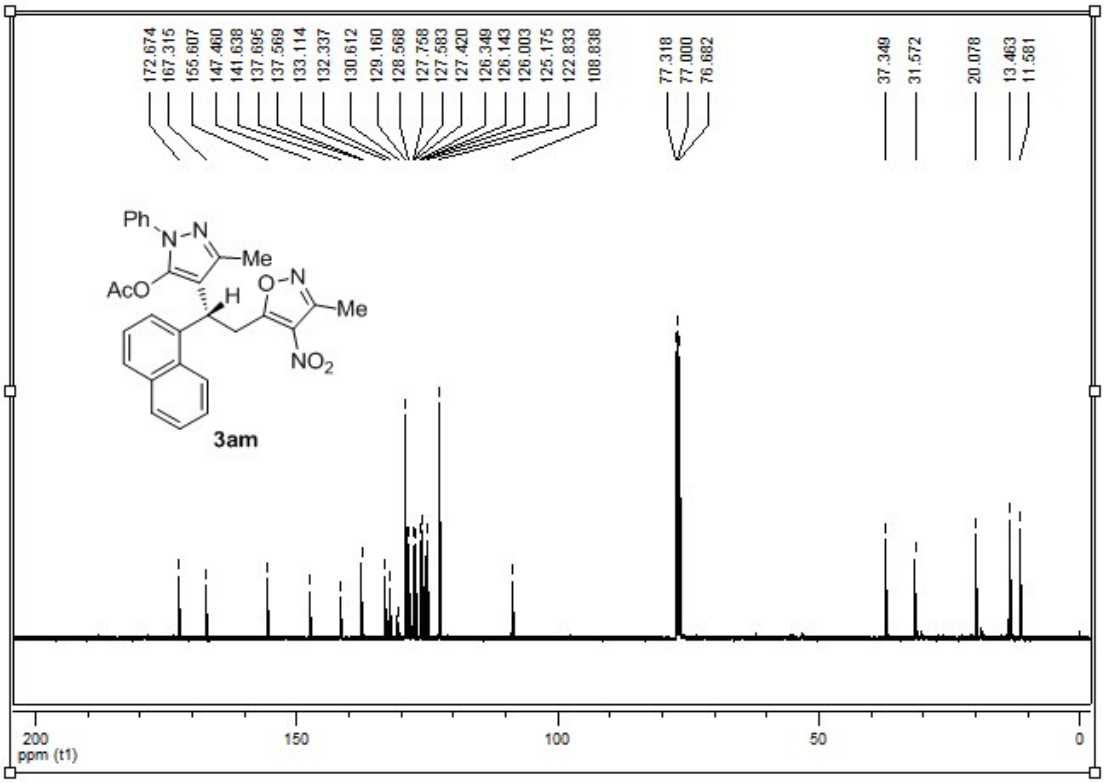
2.0
1.0
0.0
ppm (t1)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133.114
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130.612
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127.758
127.583
127.420
126.349
126.143
126.003
125.175
122.833
108.838
77.318
77.000
76.682
37.349
31.572
20.078
13.463
11.581
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H
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N
Me
NO2
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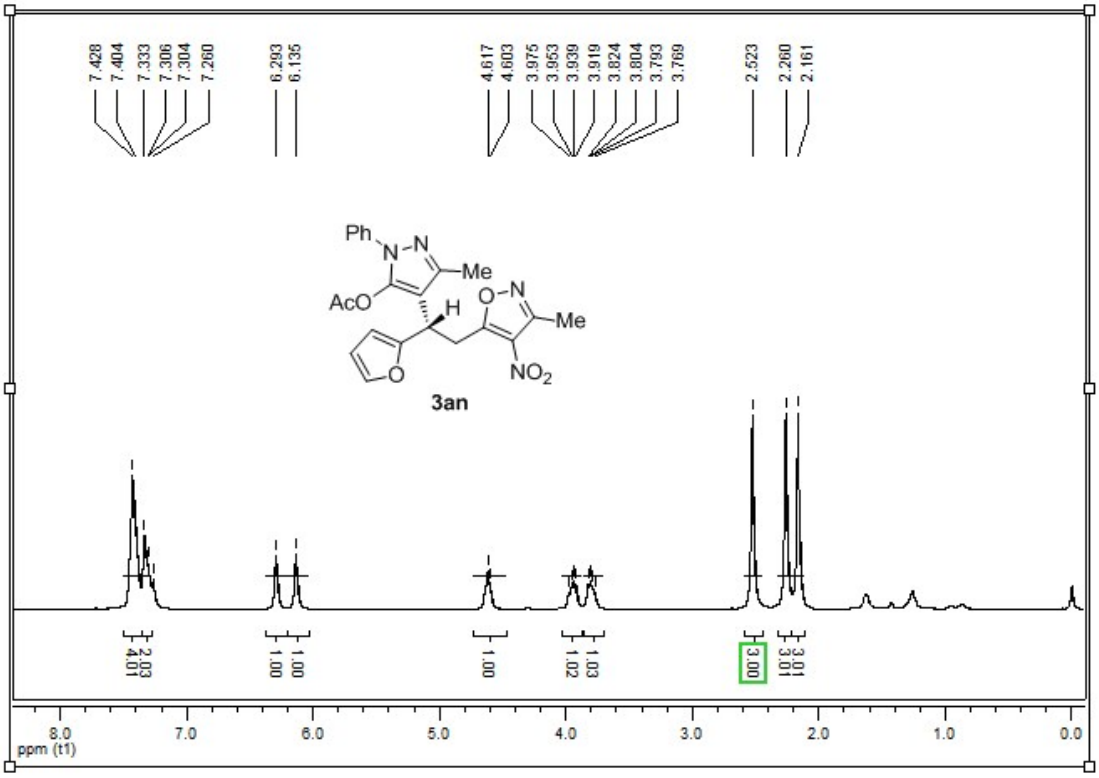
200
150
100
50
0
ppm (t1)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7.260
6.293
6.135
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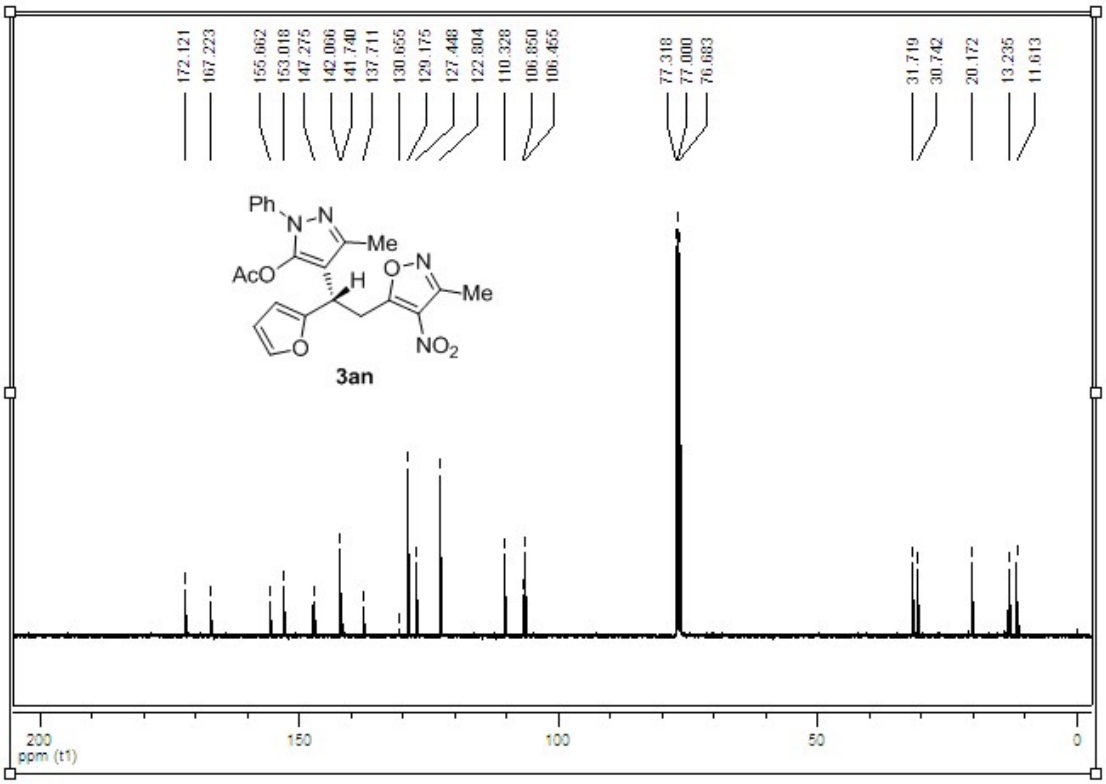
4.603
3.975
3.953
3.939
3.919
3.824
3.804
3.793
3.769
2.523
2.260
2.161
Ph
N-N
Me
AcO
H
O-N
Me
NO2
O
3an
4.10
2.03
1.00
1.00
1.00
1.02
1.03
3.00
3.01
3.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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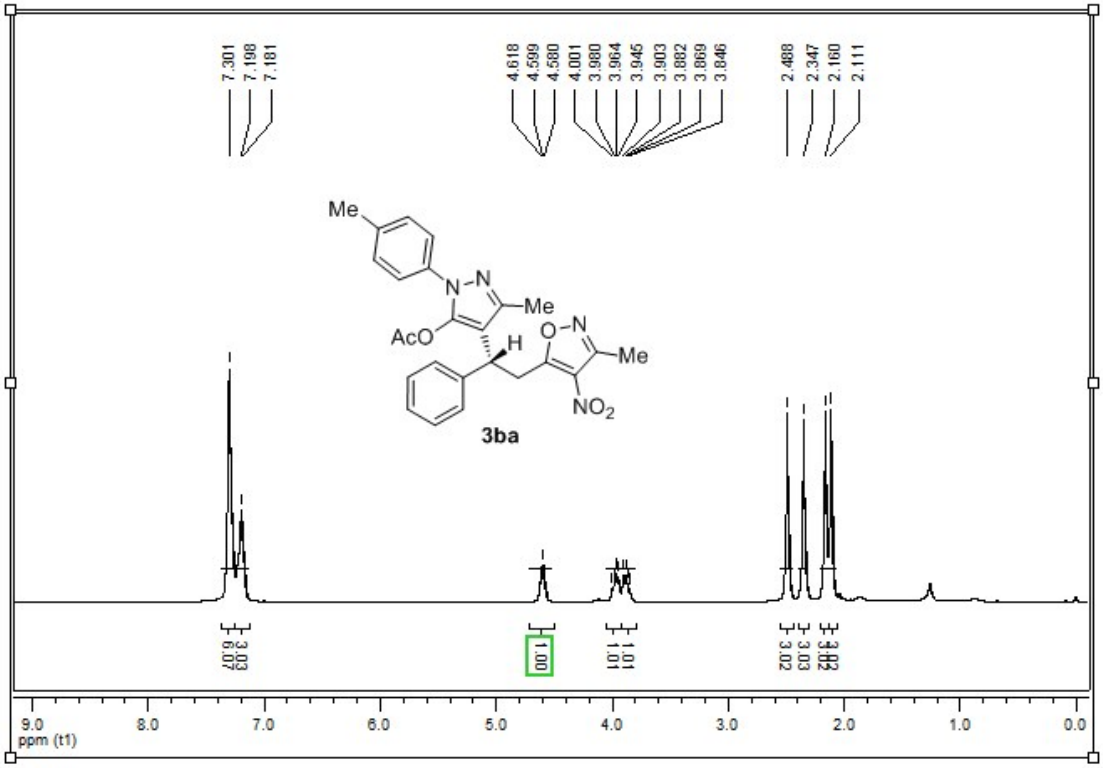
153.018
147.275
142.066
141.740
137.711
130.655
129.175
127.448
122.804
110.328
106.850
106.455
77.318
77.000
76.683
31.719
30.742
20.172
13.235
11.613
Ph
N-N
Me
AcO
H
O-N
Me
NO2
O
3an
200
150
100
50
0
ppm (t1)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7.198
7.181
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4.599
4.580
4.001
3.980
3.964
3.945
3.903
3.882
3.869
3.846
2.488
2.347
2.160
2.111
Me
N-N
Me
AcO
H
O-N
Me
NO2
3ba
3.09
6.07
1.00
1.01
1.01
3.02
3.03
3.82
3.82
9.0
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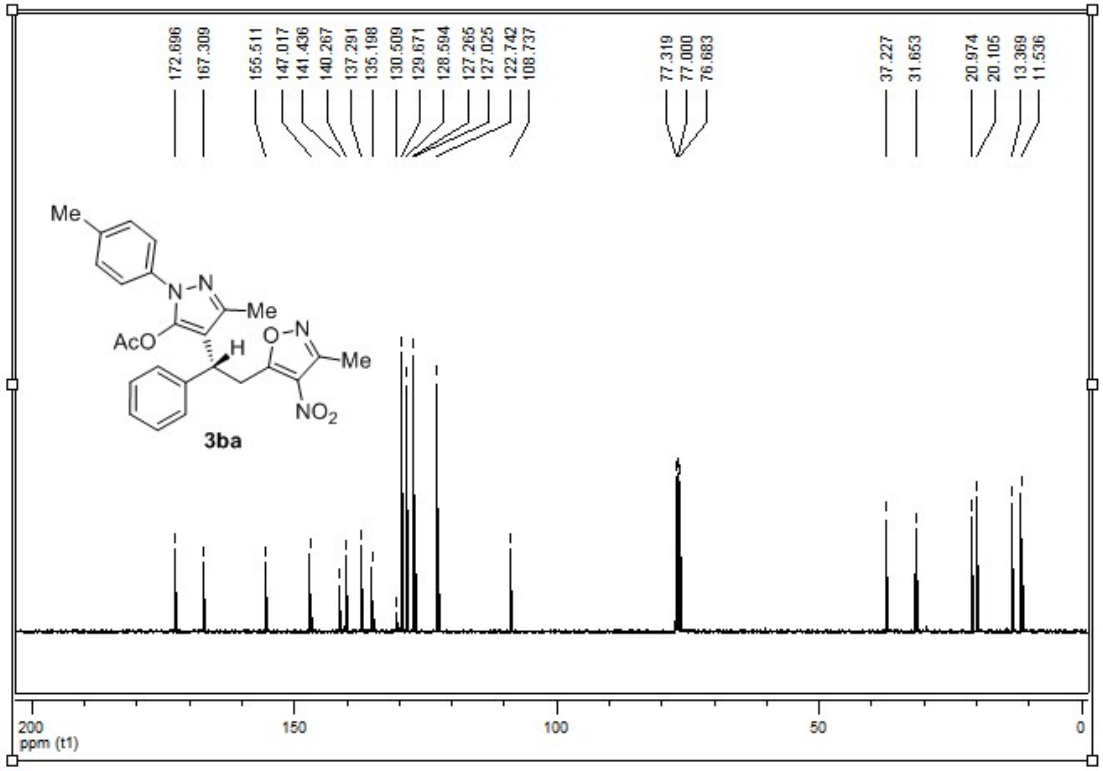
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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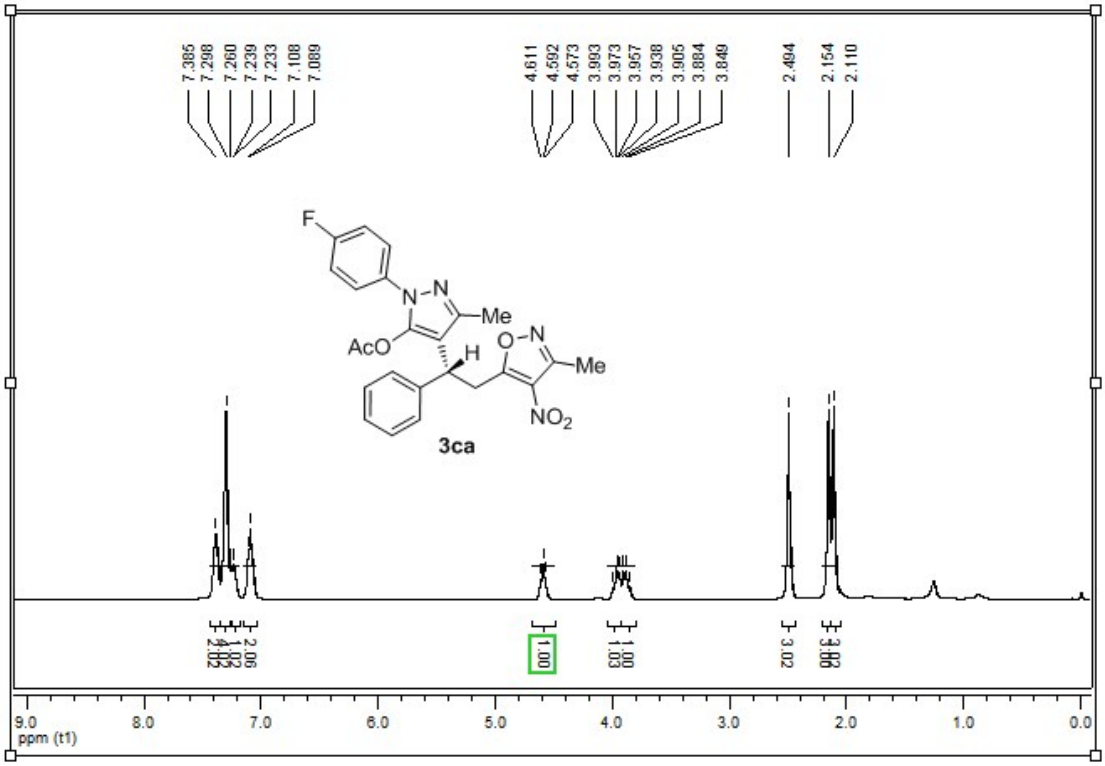
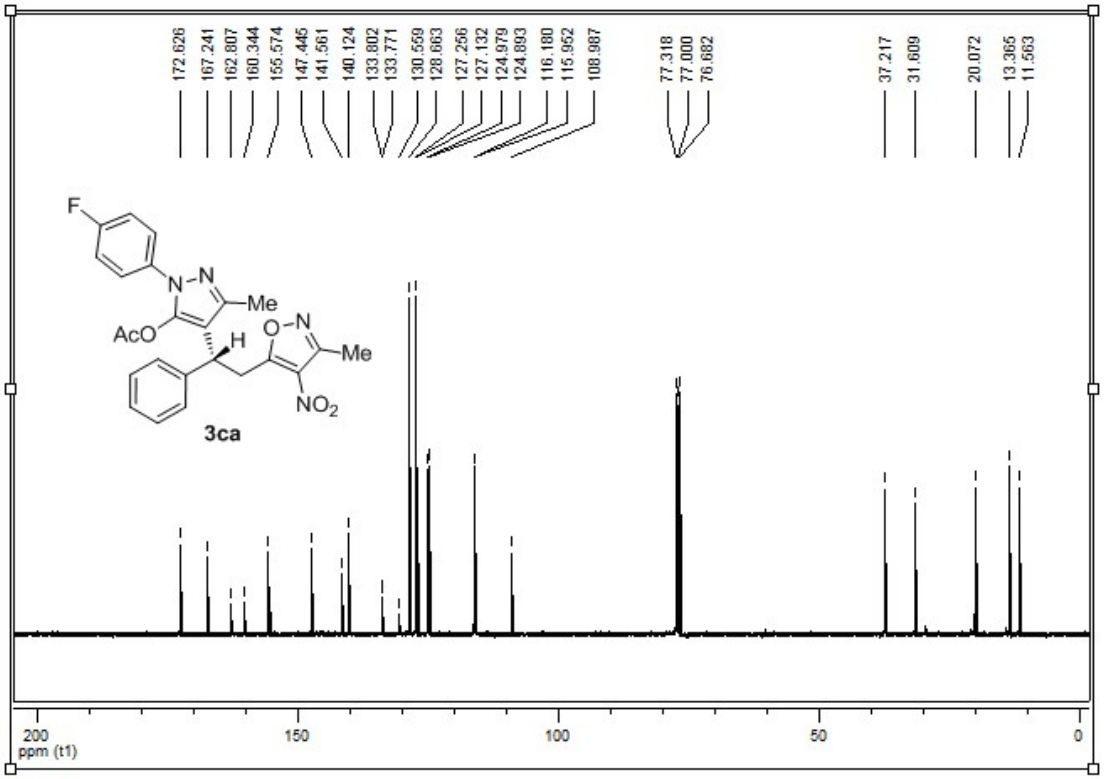
155.511
147.017
141.436
140.267
137.291
135.198
130.509
129.671
128.594
127.265
127.025
122.742
108.737
77.319
77.000
76.683
37.227
31.653
20.974
20.105
13.369
11.536
Me
N-N
Me
AcO
H
O-N
Me
NO2
3ba
200
150
100
50
0
ppm (t1)


7.385
7.298
7.260
7.239
7.233
7.108
7.089
4.611
4.592
4.573
3.993
3.973
3.957
3.938
3.905
3.884
3.849
2.494
2.154
2.110
F
N-N
Me
AcO
H
O-N
Me
NO2
3ca
2.06
4.23
2.02
1.00
1.03
3.02
3.66
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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167.241
162.807
160.344
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141.561
140.124
133.802
133.771
130.559
128.663
127.256
127.132
124.979
124.893
116.180
115.952
108.987
77.318
77.000
76.682
37.217
31.609
20.072
13.365
11.563
F
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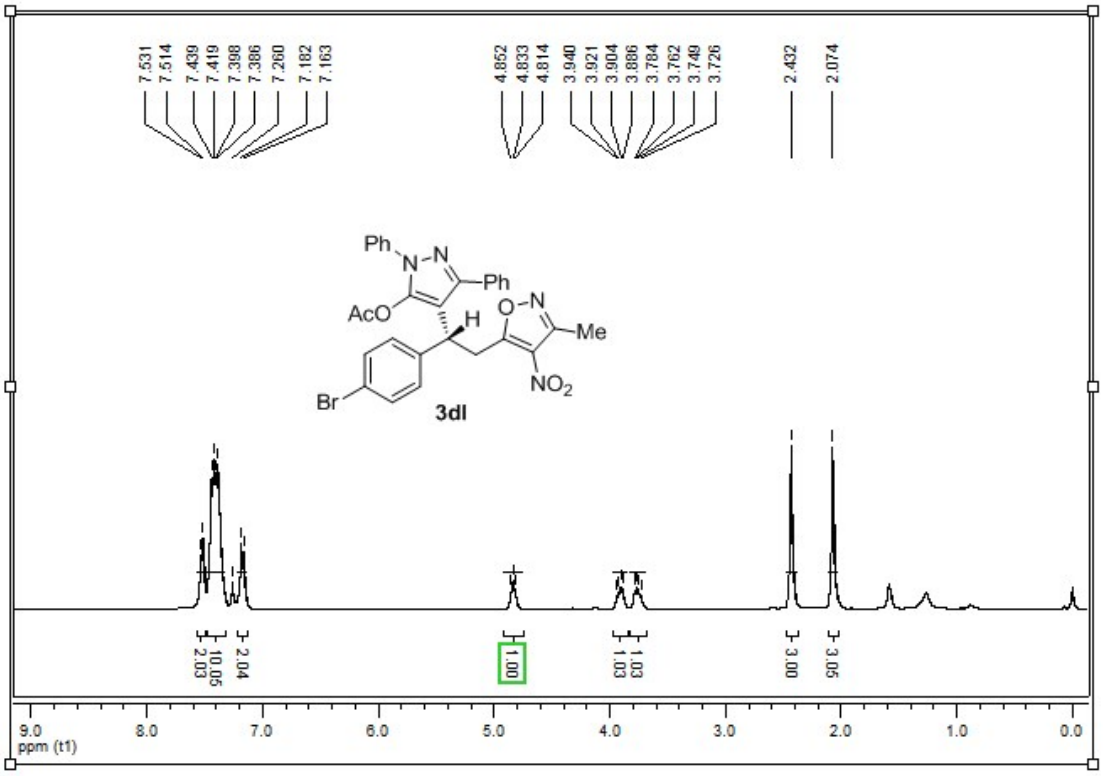
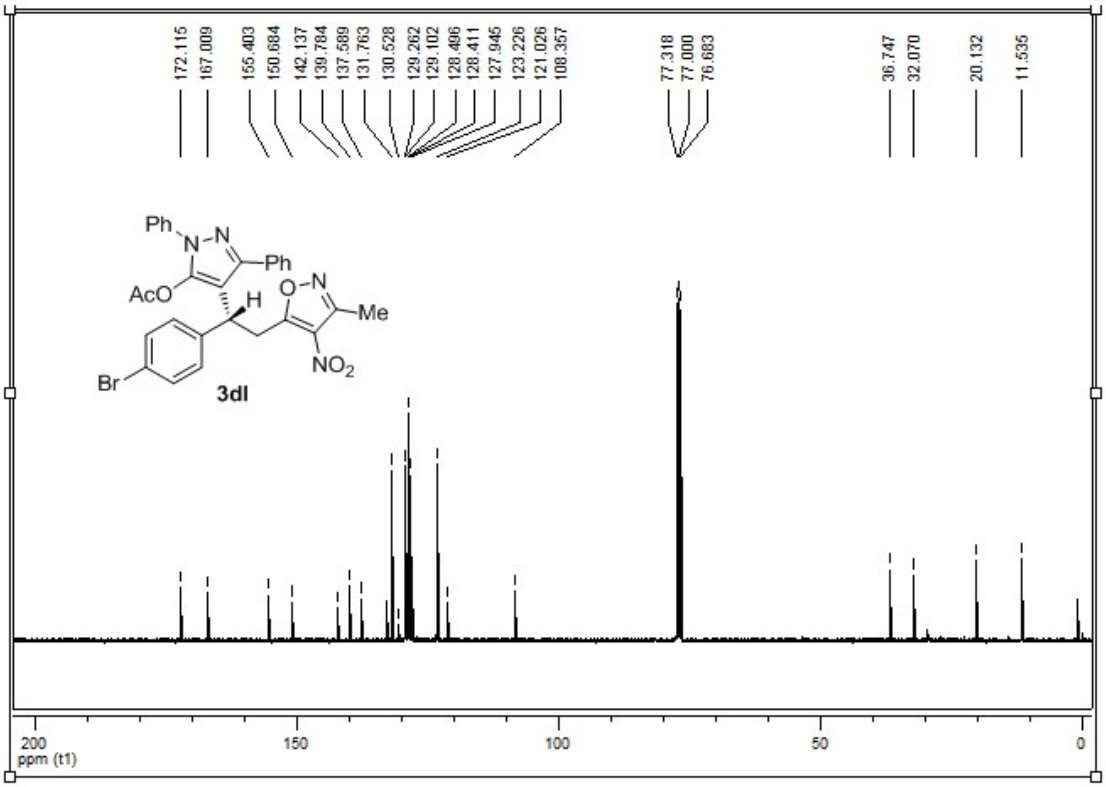
Me
AcO
H
O-N
Me
NO2
3ca
200
150
100
50
0
ppm (t1)


7.531
7.514
7.439
7.419
7.398
7.386
7.260
7.182
7.163
4.852
4.833
4.814
3.940
3.921
3.904
3.886
3.784
3.762
3.749
3.726
2.432
2.074
Ph
N-N
Ph
AcO
H
O-N
Me
NO2
Br
3dl
10.05
2.04
1.00
1.03
1.03
3.00
3.06
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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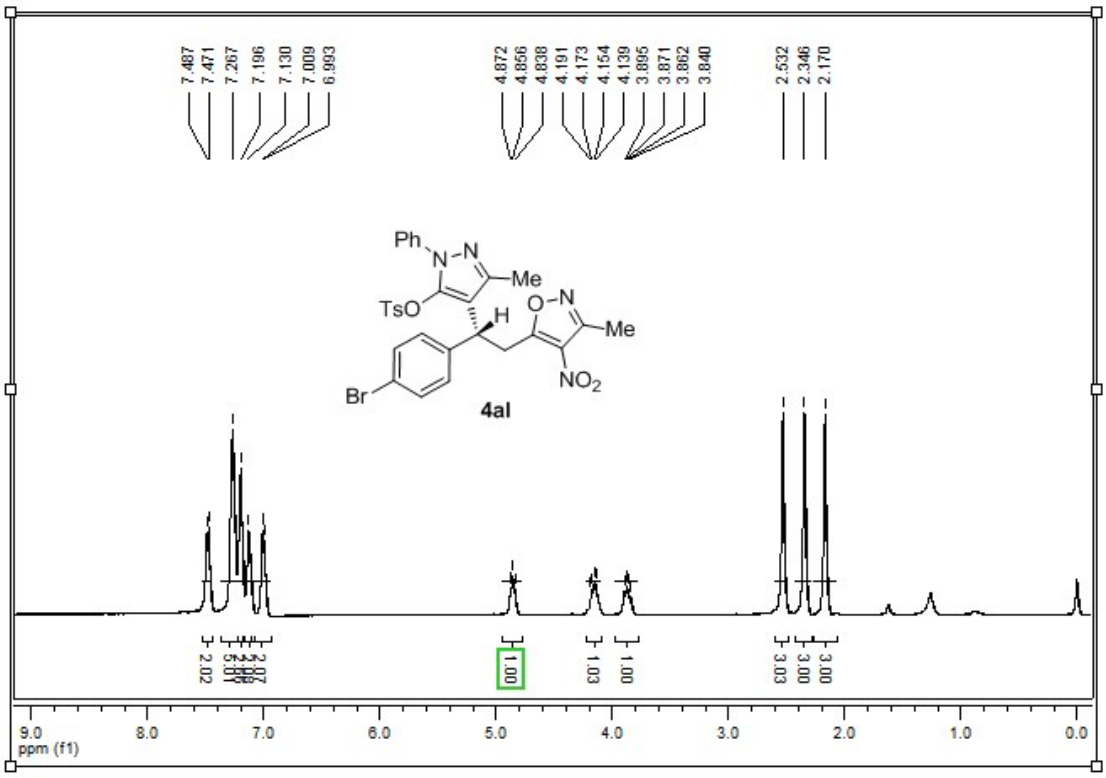
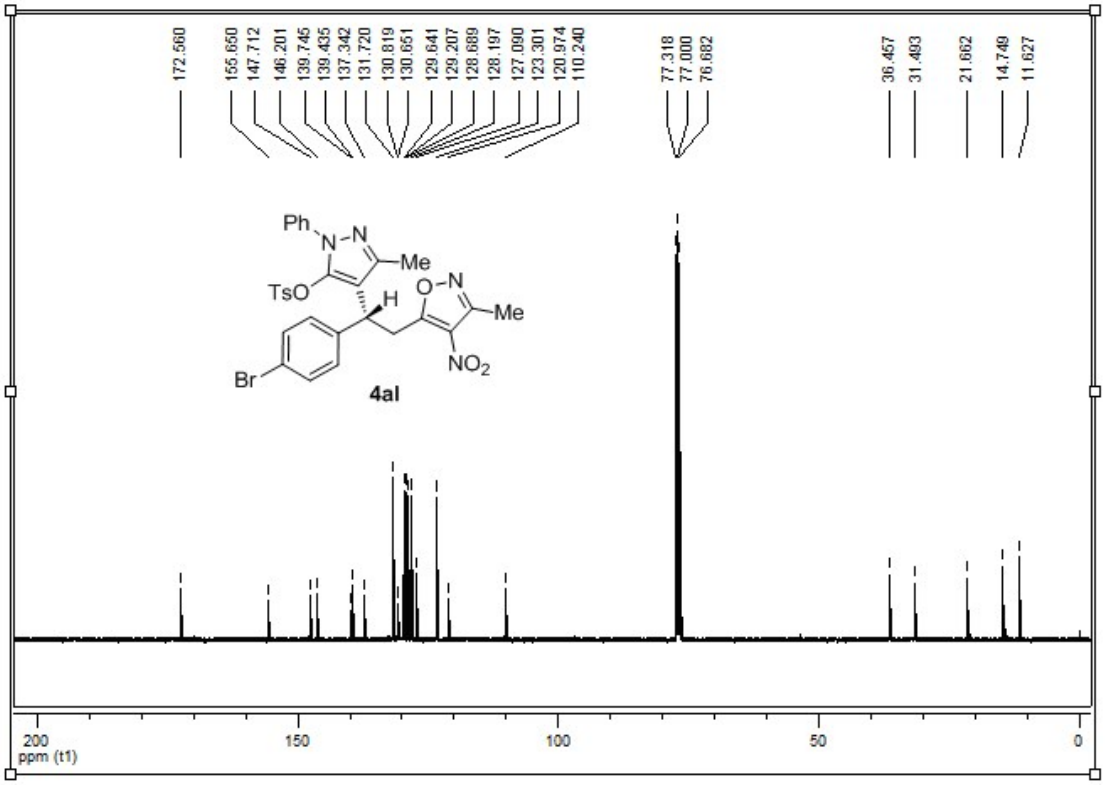
155.403
150.684
142.137
139.784
137.589
131.763
130.528
129.262
129.102
128.496
128.411
127.945
123.226
121.026
108.357
77.318
77.000
76.683
36.747
32.070
20.132
11.535
Ph
N-N
Ph
AcO
H
O-N
Me
NO2
Br
3dl
200
150
100
50
0
ppm (t1)


7.487
7.471
7.267
7.196
7.130
7.009
6.993
4.872
4.856
4.838
4.191
4.173
4.154
4.139
3.895
3.871
3.862
3.840
2.532
2.346
2.170
Ph
N-N
Me
TsO
H
O-N
Me
NO2
Br
4al
2.02
1.00
1.03
1.00
3.03
3.00
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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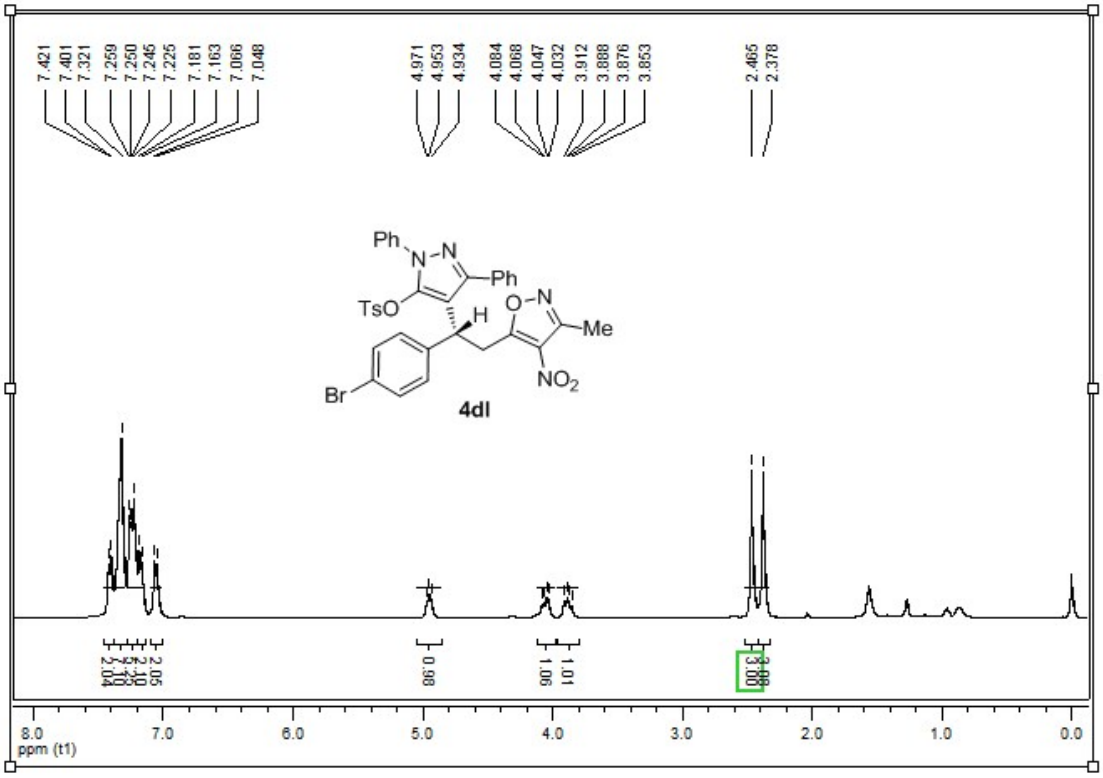
147.712
146.201
139.745
139.435
137.342
131.720
130.819
130.651
129.641
129.207
128.689
128.197
127.090
123.301
120.974
110.240
77.318
77.000
76.682
36.457
31.493
21.662
14.749
11.627
Ph
N-N
Me
TsO
H
O-N
Me
NO2
Br
4al
200
150
100
50
0
ppm (t1)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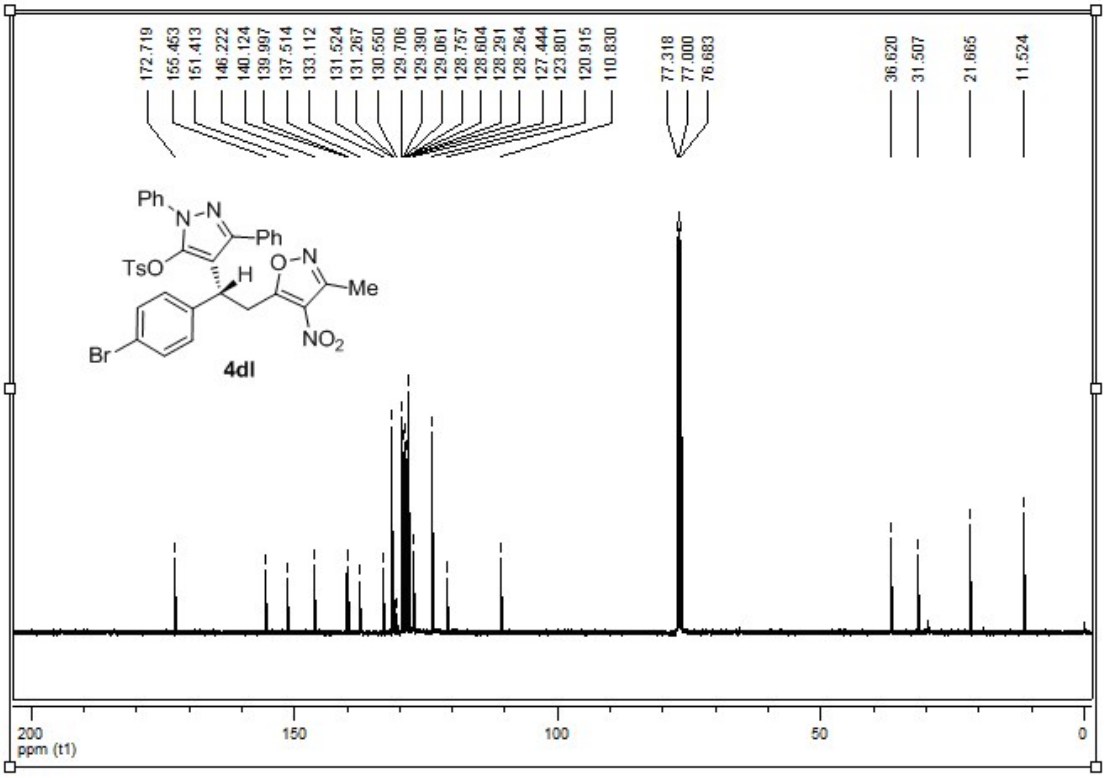
7.401
7.321
7.259
7.250
7.245
7.225
7.181
7.163
7.066
7.048
4.971
4.953
4.934
4.084
4.068
4.047
4.032
3.912
3.888
3.876
3.853
2.465
2.378
Ph
N
N
Ph
TsO
H
O
N
Me
NO2
Br
4dl
2.06
0.98
1.06
1.01
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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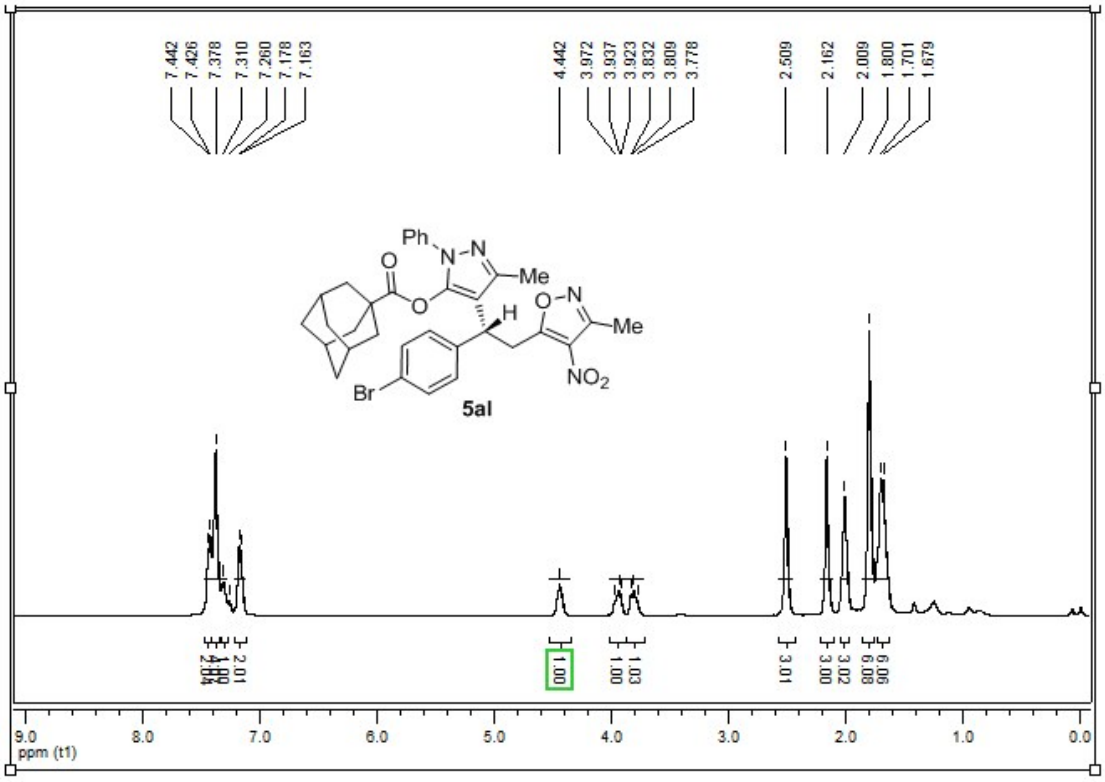
151.413
146.222
140.124
139.997
137.514
133.112
131.524
131.267
130.550
129.706
129.390
129.061
128.757
128.604
128.291
128.264
127.444
123.801
120.915
110.830
77.318
77.000
76.683
36.620
31.507
21.665
11.524
Ph
N
N
Ph
TsO
H
O
N
Me
NO2
Br
4dl
200
150
100
50
0
ppm (t1)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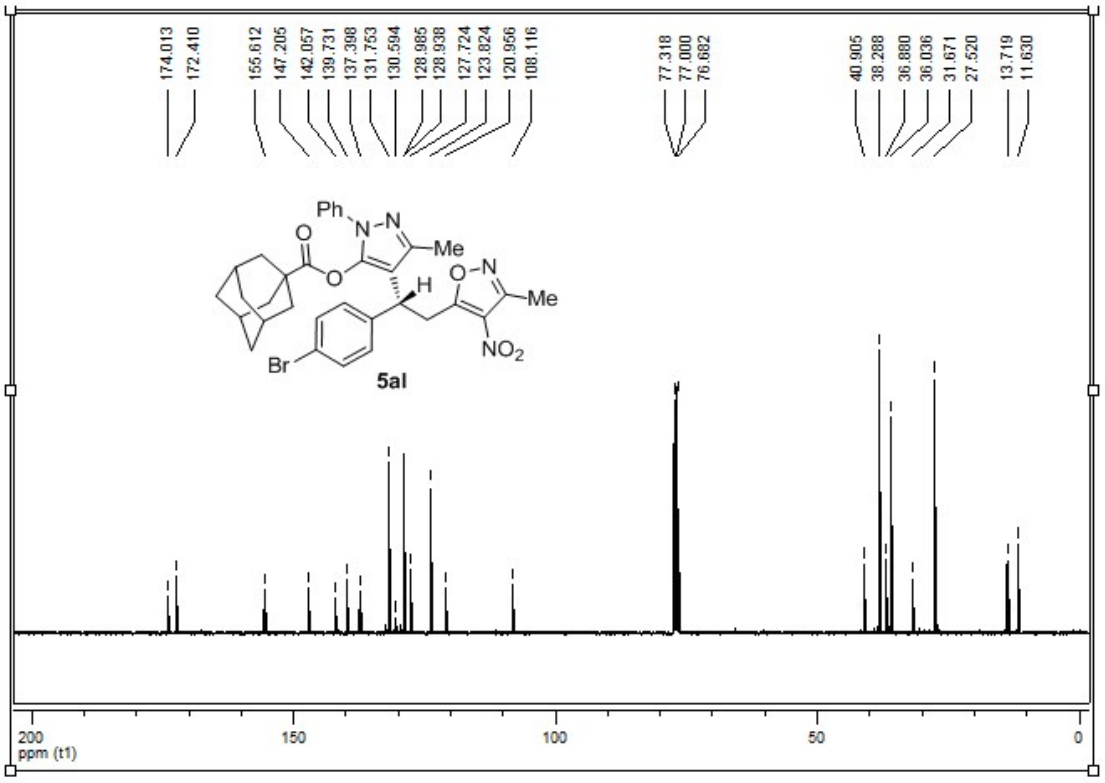
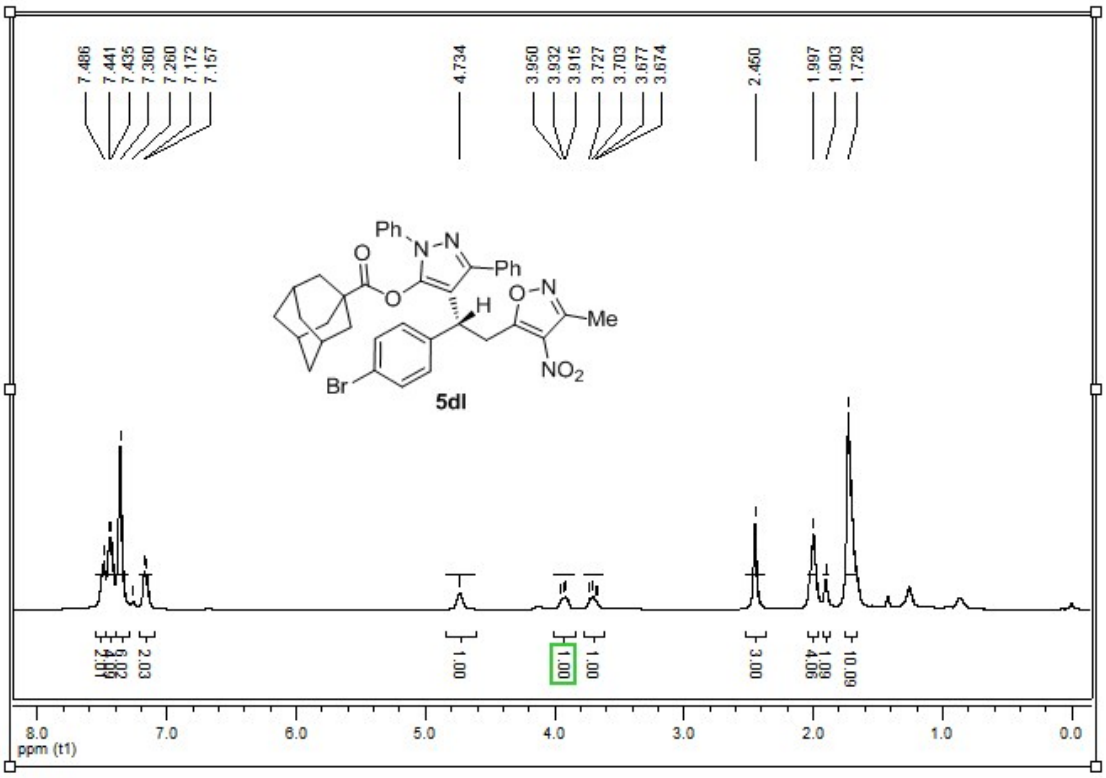
7.260
7.178
7.163
4.442
3.972
3.937
3.923
3.832
3.809
3.778
2.509
2.162
2.009
1.800
1.701
1.679
Ph
N
N
O
O
Me
O
N
H
Me
Br
NO2
5aI
2.01
4.08
2.01
1.00
1.03
1.00
3.01
3.00
3.02
6.08
6.06
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


174.013
172.410
155.612
147.205
142.057
139.731
137.398
131.753
130.594
128.985
128.938
127.724
123.824
120.956
108.116
77.318
77.000
76.682
40.905
38.288
36.880
36.036
31.671
27.520
13.719
11.630
Ph
N
N
O
O
Me
O
N
H
Me
Br
NO2
5aI
200
150
100
50
0
ppm (t1)


7.486
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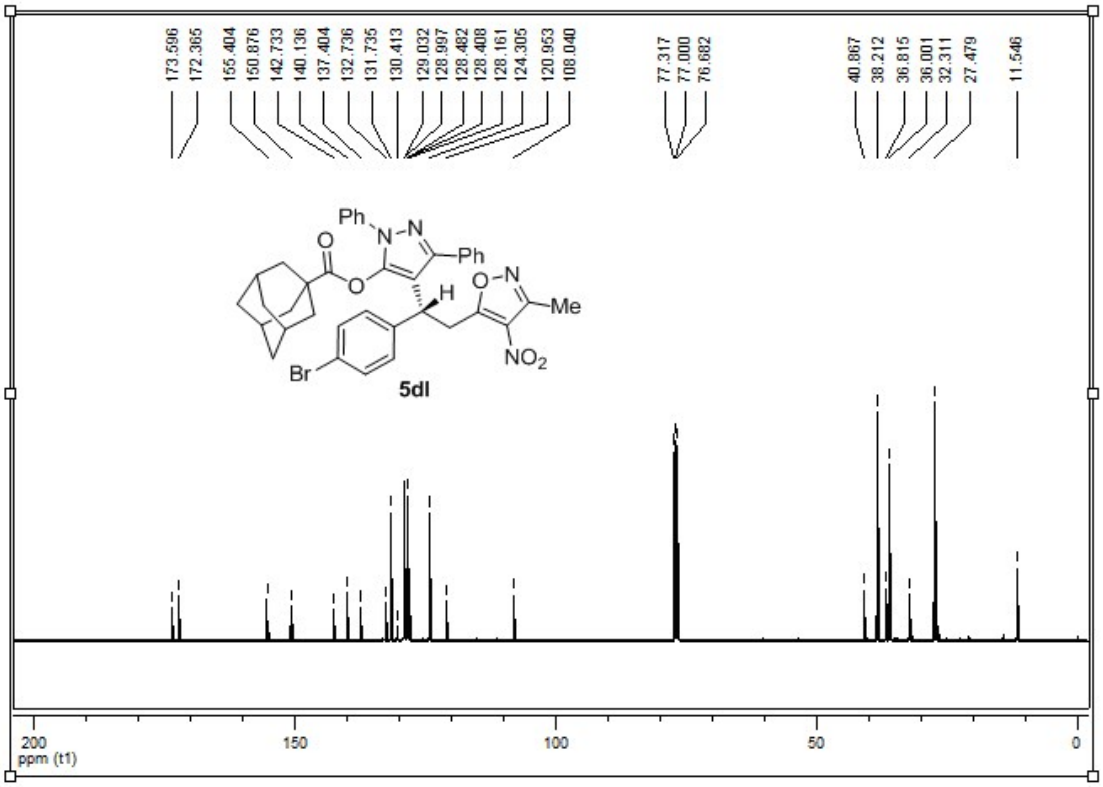
7.435
7.360
7.260
7.172
7.157
4.734
3.950
3.932
3.915
3.727
3.703
3.677
3.674
2.450
1.997
1.903
1.728
Ph
N-N
Ph
O
O
H
O-N
Me
NO2
Br
5dl
2.03
1.00
1.00
1.00
3.00
4.09
4.06
10.09
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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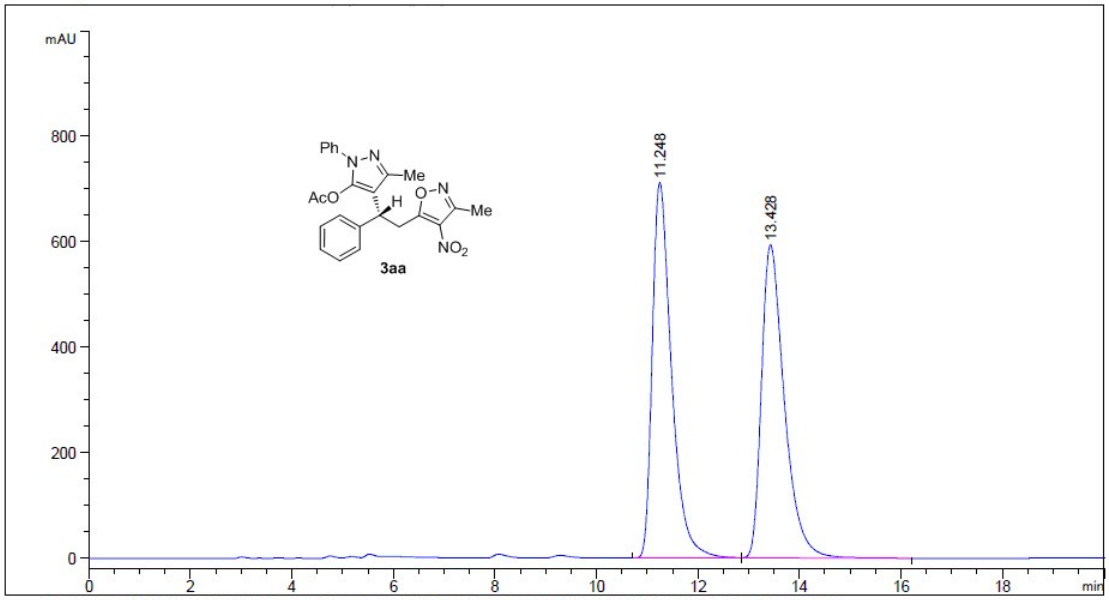
137.404
132.736
131.735
130.413
129.032
128.997
128.482
128.408
128.161
124.305
120.953
108.040
77.317
77.000
76.682
40.867
38.212
36.815
36.001
32.311
27.479
11.546
Ph
N-N
Ph
O
O
H
O-N
Me
NO2
Br
5dl
200
150
100
50
0
ppm (t1)

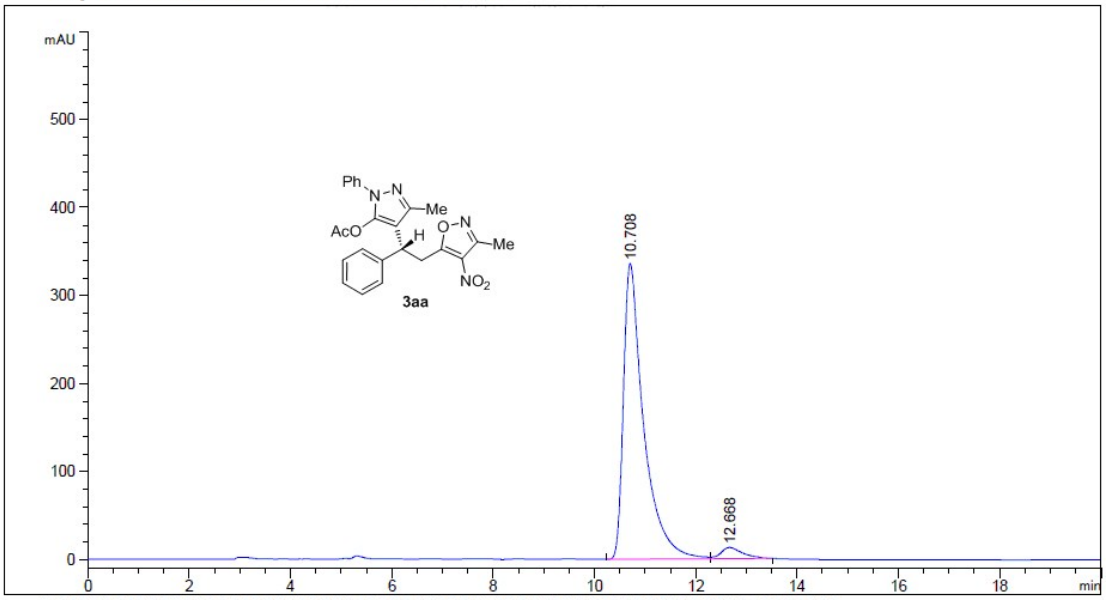
Copies of HPLC spectra of the products:

Sample Info: 254nm, AD-H, i-PrOH : Hexane = 10 : 90, 1.0 mL/min



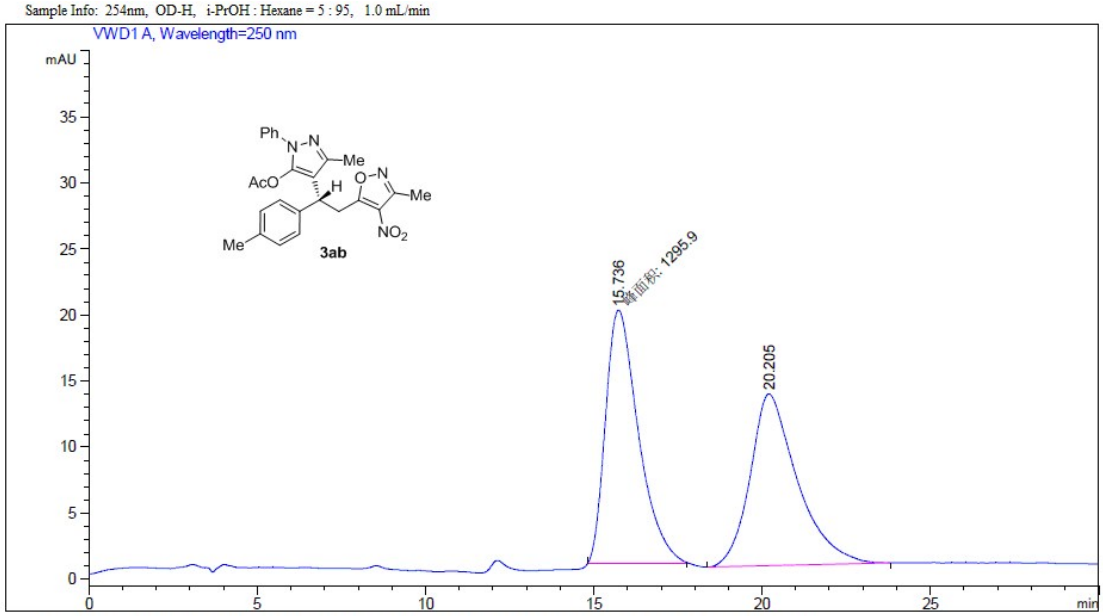
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.248	BB	0.3974	1.86920e4	711.64044	50.2138
2	13.428	BB	0.4732	1.85328e4	593.74060	49.7862

Sample Info: 254nm, AD-H, i-PrOH : Hexane = 10 : 90, 1.0 mL/min



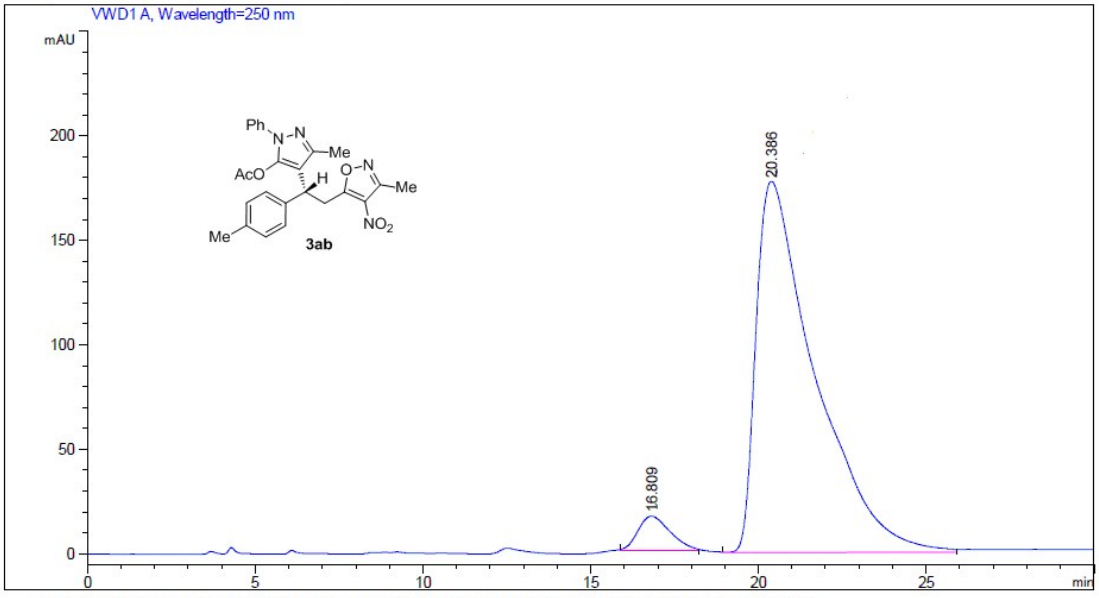
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.708	BV	0.3980	9304.08301	336.07257	96.1248
2	12.668	VBA	0.4306	375.08884	12.73541	3.8752

Sample Info: 254nm, OD-H, i-PrOH : Hexane = 5 : 95, 1.0 mL/min



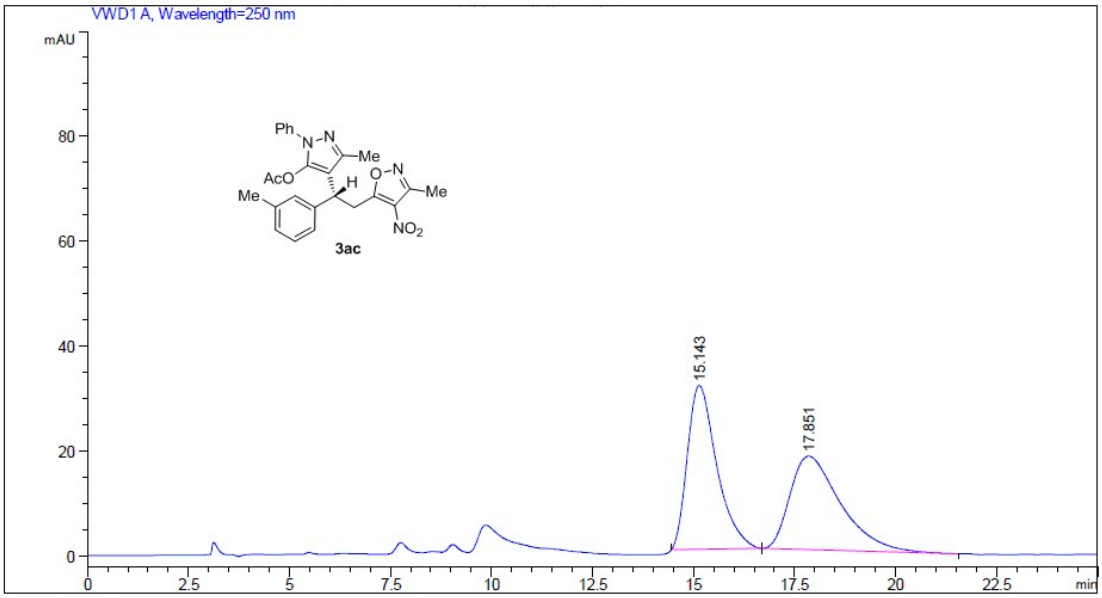
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.736	MM	1.1282	1295.90112	19.14345	50.5521
2	20.205	BB	1.3382	1267.59473	13.00397	49.4479

Sample Info: 254nm, OD-H, i-PrOH : Hexane = 5 : 95, 1.0 mL/min



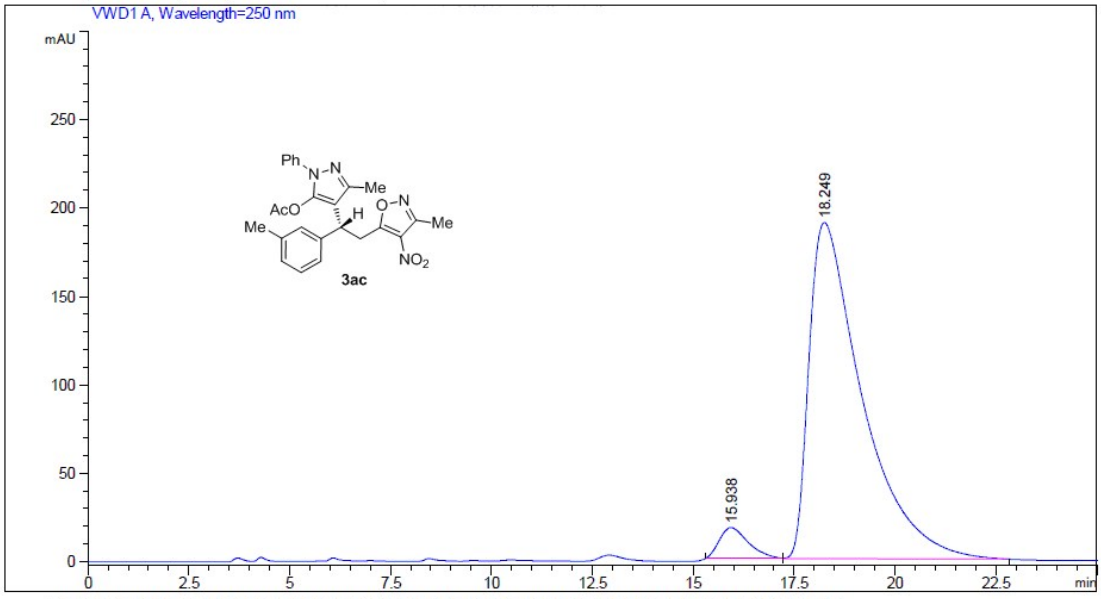
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.809	MM	1.0975	1061.89111	16.12643	4.6708
2	20.386	MM	2.0344	2.16729e4	177.54965	95.3292

Sample Info: 254nm, OD-H, i-PrOH : Hexane = 5 : 95, 1.0 mL/min



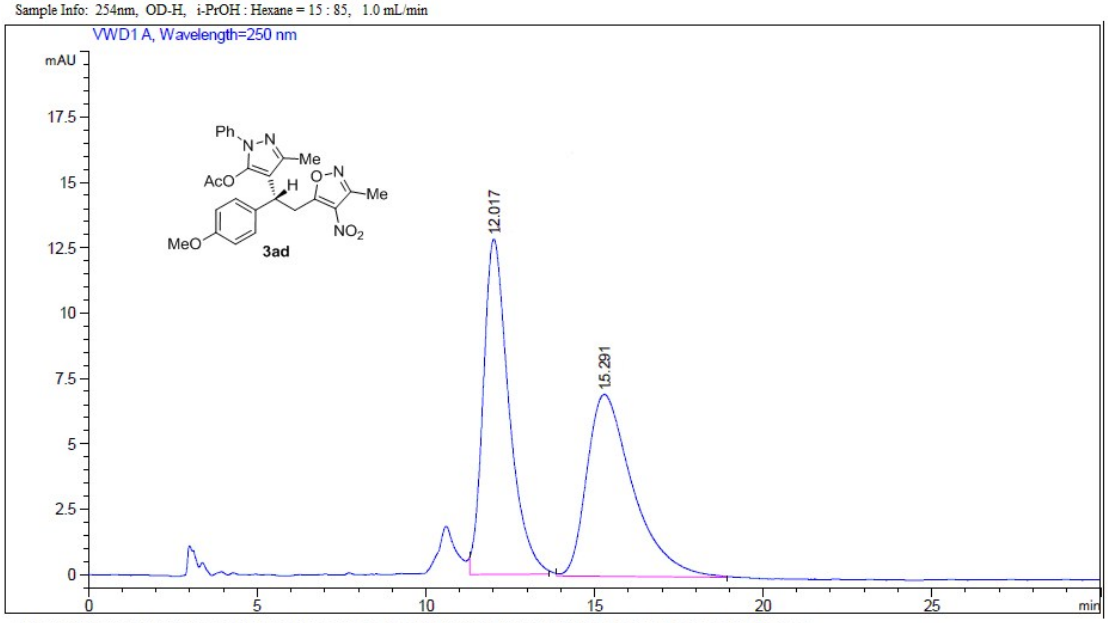
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.143	BB	0.7667	1578.66895	31.23101	50.4927
2	17.851	BB	1.2822	1547.85815	17.82287	49.5073

Sample Info: 254nm, OD-H, i-PrOH : Hexane = 5 : 95, 1.0 mL/min



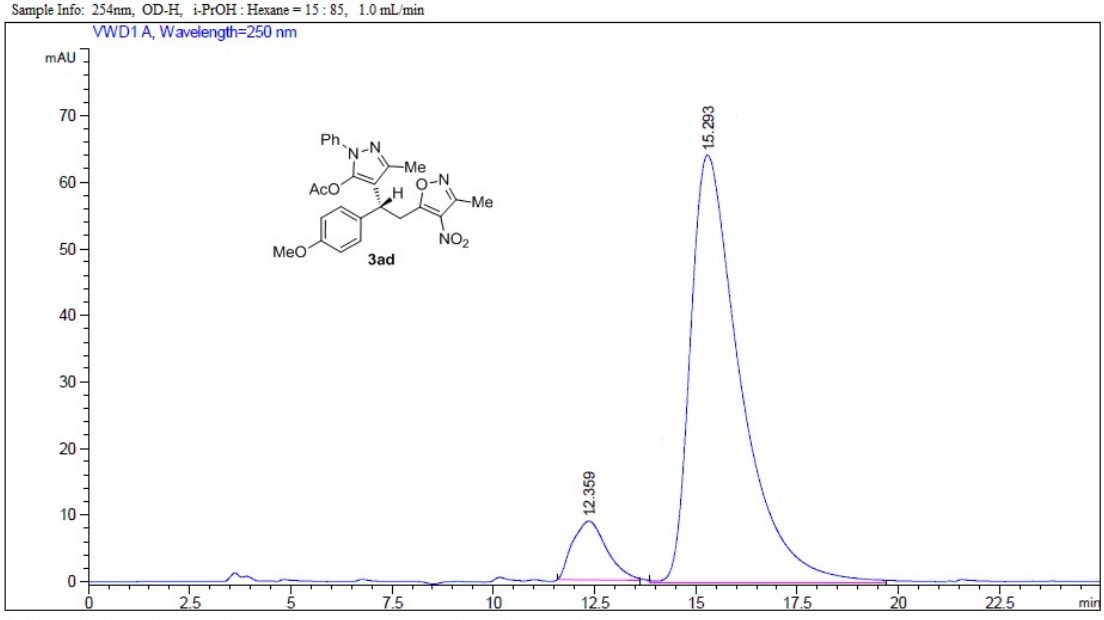
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.938	BV	0.7613	885.67694	17.56371	4.8389
2	18.249	VBA	1.3350	1.74176e4	190.08414	95.1611

Sample Info: 254nm, OD-H, i-PrOH : Hexane = 15 : 85, 1.0 mL/min



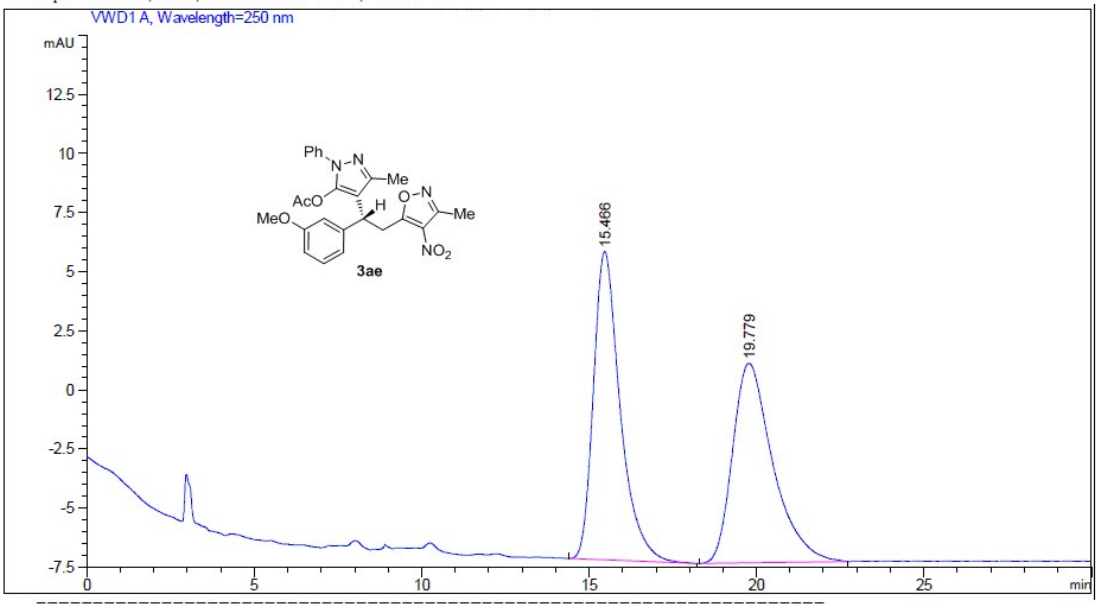
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.017	MM	0.8845	680.58630	12.82501	50.7628
2	15.291	MM	1.5821	660.13269	6.95397	49.2372

Sample Info: 254nm, OD-H, i-PrOH : Hexane = 15 : 85, 1.0 mL/min



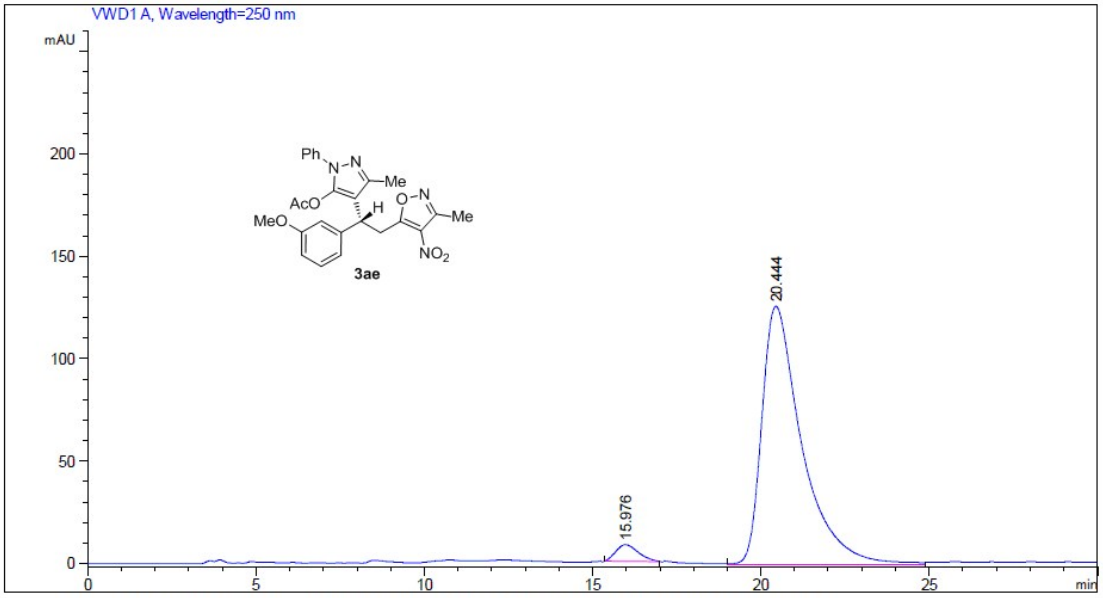
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.359	MM	0.9746	516.70654	8.83638	8.6033
2	15.293	MM	1.4242	5489.20361	64.23738	91.3967

Sample Info: 254nm, OD-H, i-PrOH : Hexane = 15 : 85, 1.0 mL/min



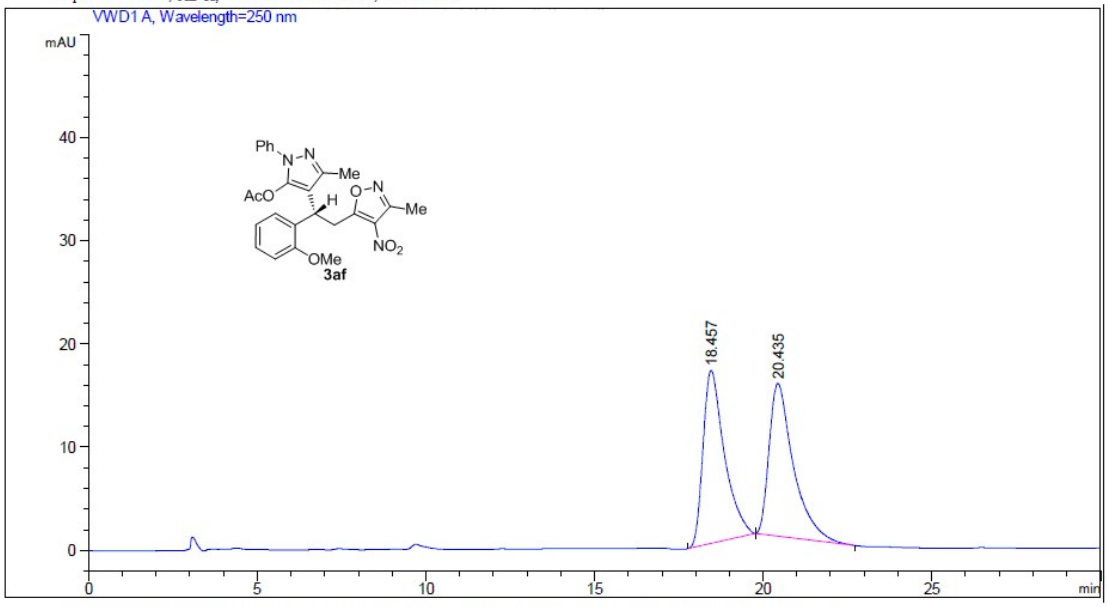
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.466	BB	0.8227	723.53558	13.03263	50.6154
2	19.779	BBA	1.2118	705.94220	8.44062	49.3846

Sample Info: 254nm, OD-H, i-PrOH : Hexane = 15 : 85, 1.0 mL/min



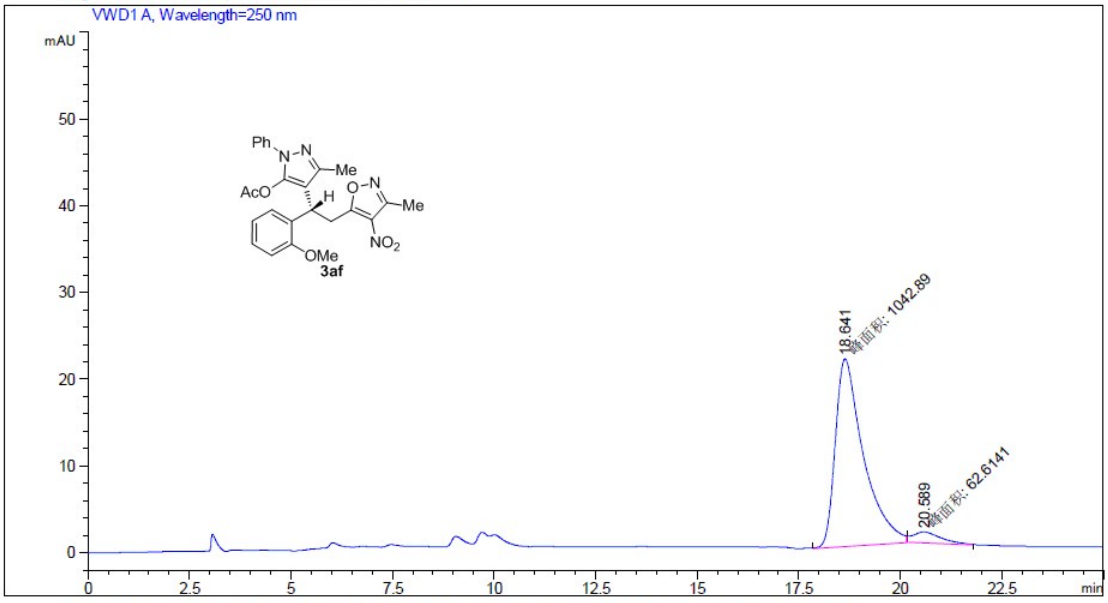
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.976	BBA	0.7171	376.88205	8.11134	3.4866
2	20.444	MM	1.3773	1.04325e4	126.24329	96.5134

Sample Info: 254nm, AD-H, i-PrOH : Hexane = 5 : 95, 1.0 mL/min



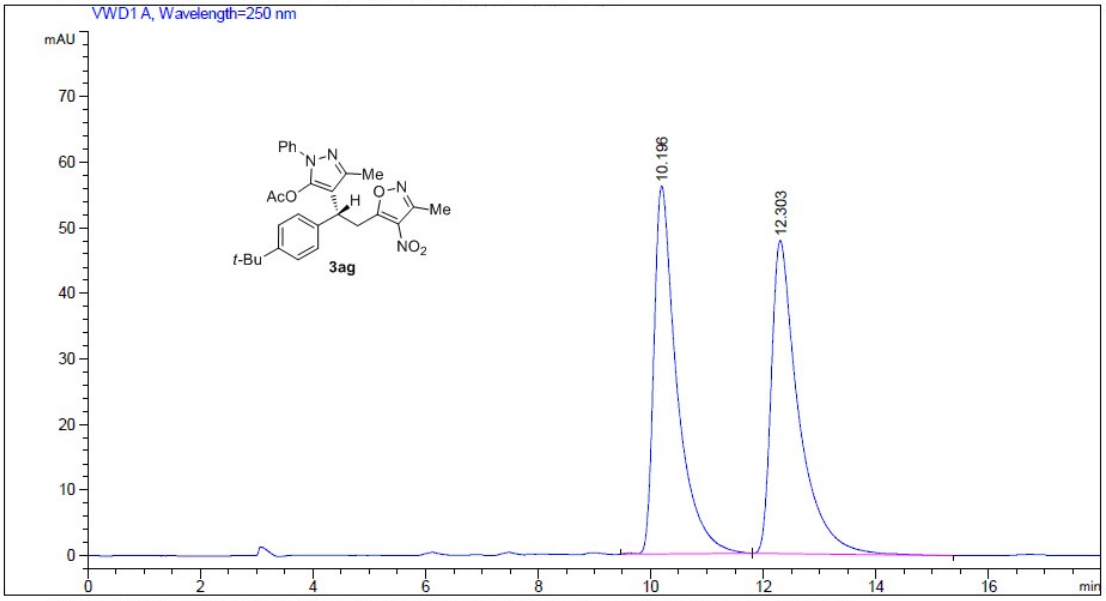
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.457	BB	0.6486	737.15063	16.74382	49.8479
2	20.435	BB	0.7344	741.64874	14.80564	50.1521

Sample Info: 254nm, AD-H, i-PrOH : Hexane = 5 : 95, 1.0 mL/min



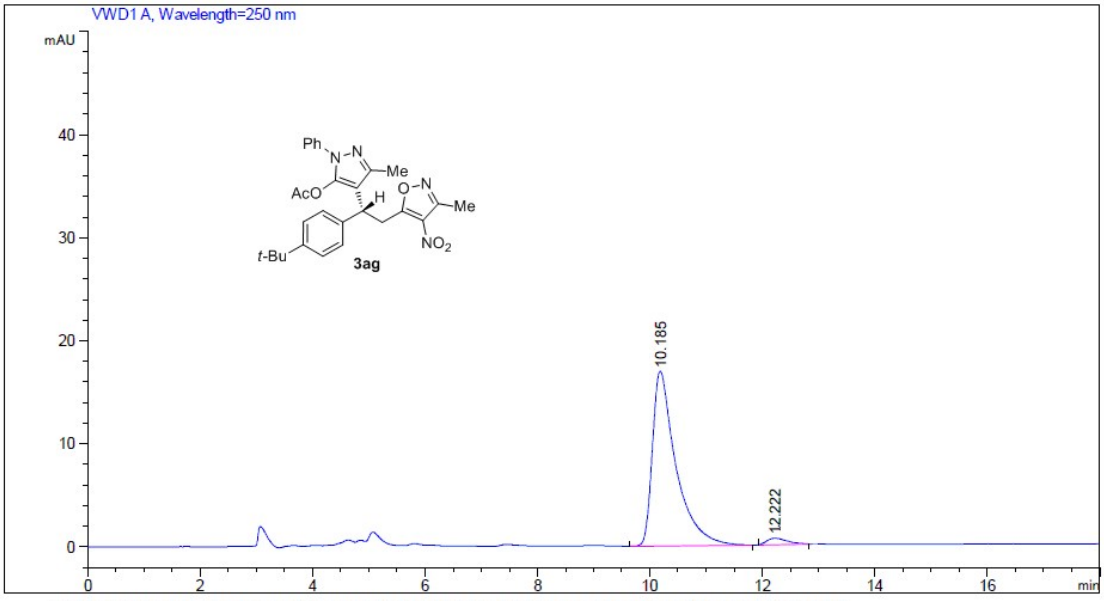
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.641	MM	0.8044	1042.88904	21.60686	94.3361
2	20.589	MM	0.8342	62.61412	1.25103	5.6639

Sample Info: 254nm, AD-H, i-PrOH : Hexane = 5 : 95, 1.0 mL/min



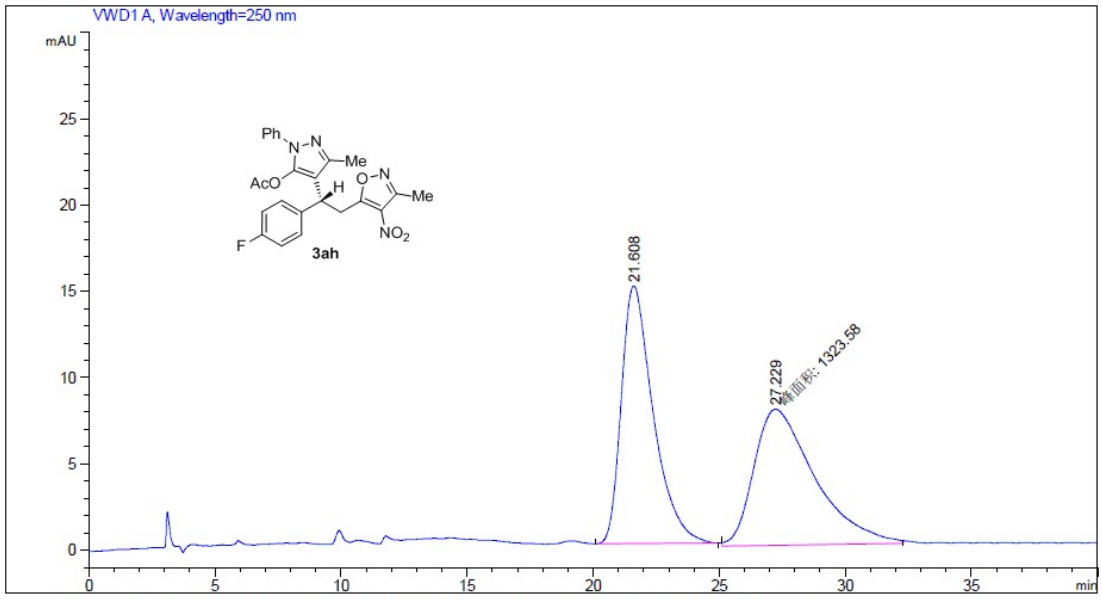
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.196	BB	0.4121	1598.17493	56.13903	49.9236
2	12.303	BB	0.4827	1603.06641	47.74142	50.0764

Sample Info: 254nm, AD-H, i-PrOH : Hexane = 5 : 95, 1.0 mL/min



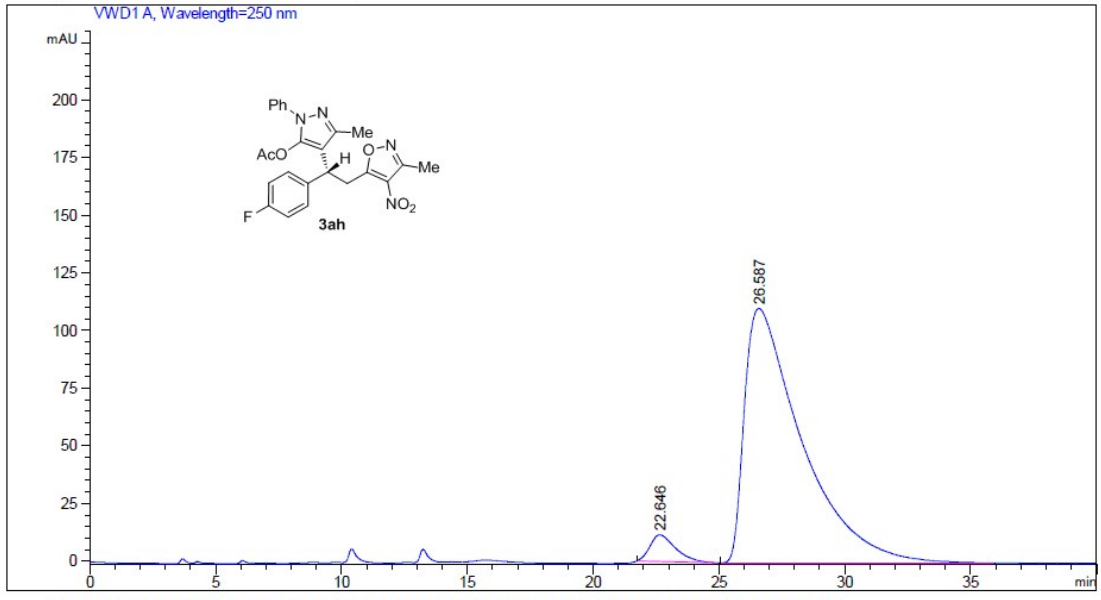
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.185	BB	0.4197	493.83569	16.96252	96.8074
2	12.222	MM	0.4261	16.28621	6.37065e-1	3.1926

Sample Info: 254nm, OD-H, i-PrOH : Hexane = 5 : 95, 1.0 mL/min



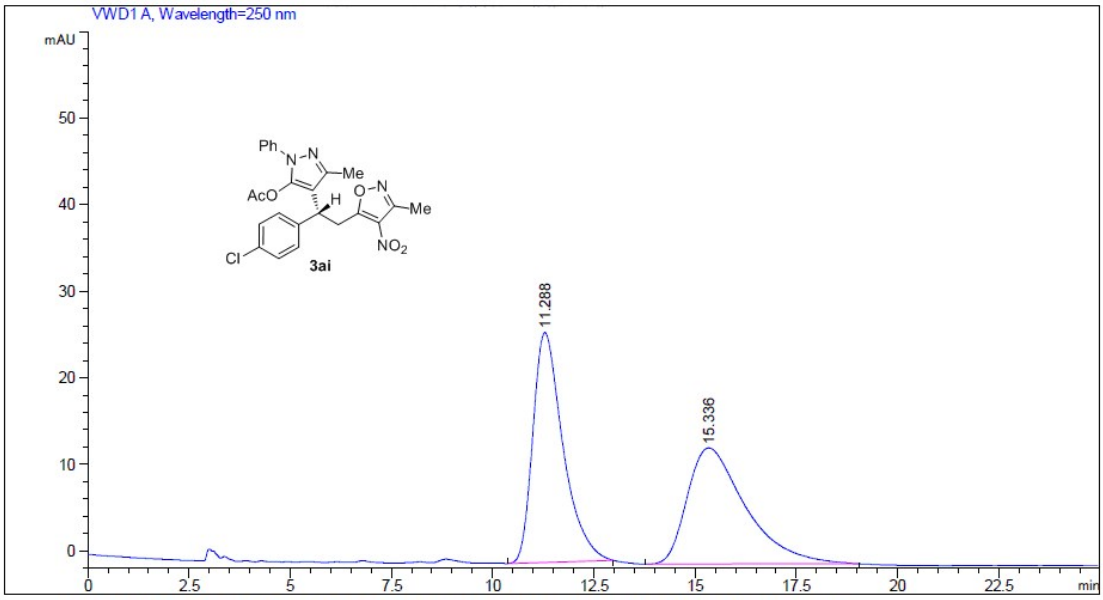
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.608	BB	1.2604	1315.10535	14.93361	49.8393
2	27.229	MM	2.7940	1323.58423	7.89528	50.1607

Sample Info: 254nm, OD-H, i-PrOH : Hexane = 5 : 95, 1.0 mL/min



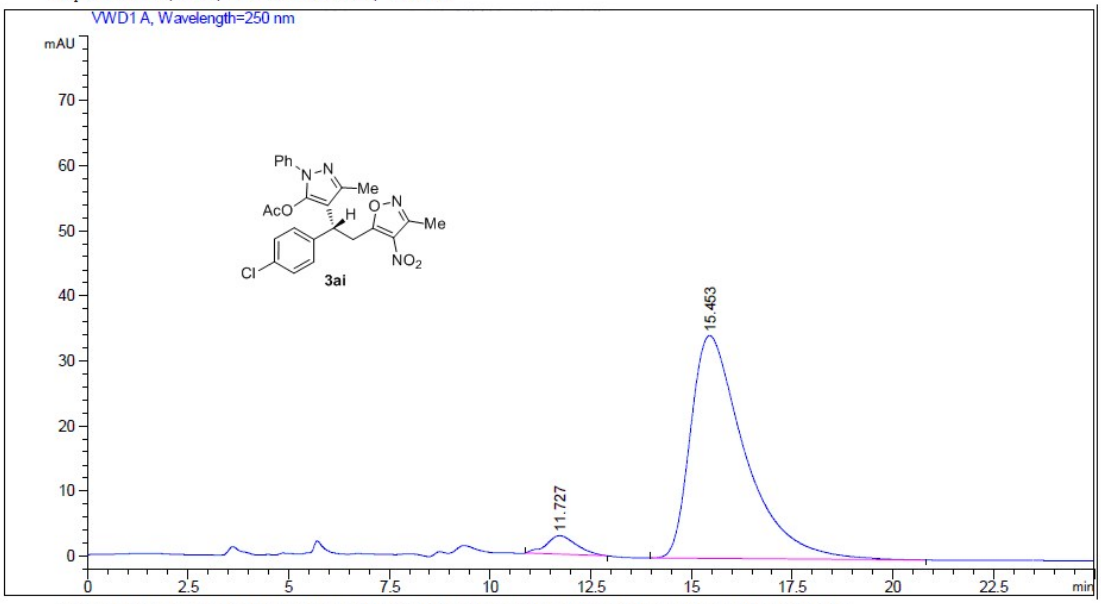
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.646	BB	1.0342	829.22607	11.62543	4.5305
2	26.587	BB	2.2720	1.74738e4	110.37421	95.4695

Sample Info: 254nm, OD-H, i-PrOH : Hexane = 5 : 95, 1.0 mL/min



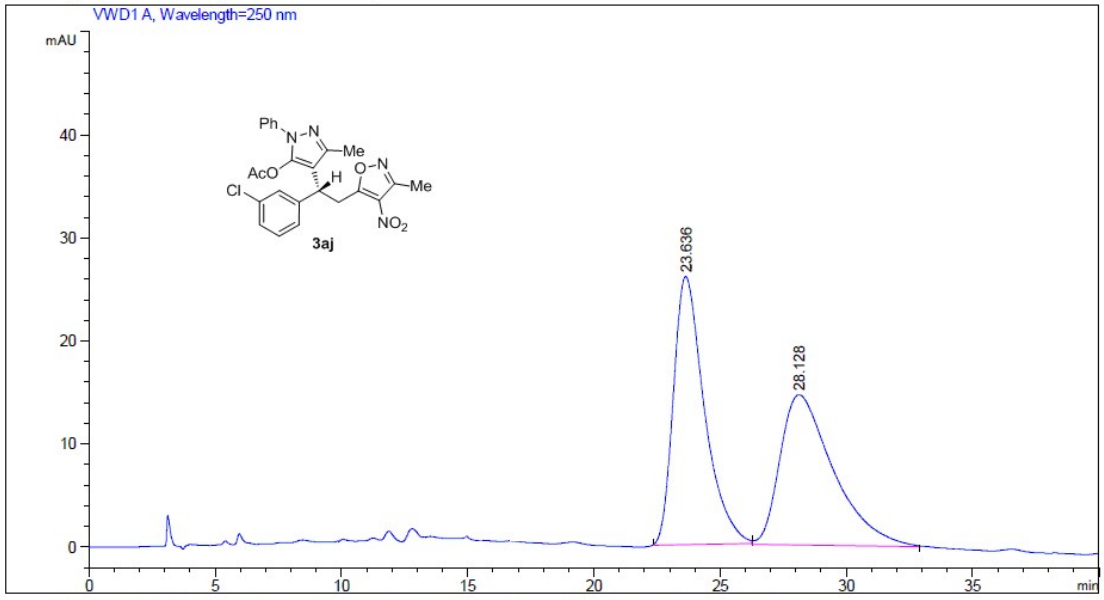
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.288	BBA	0.7776	1376.56287	26.56420	50.6509
2	15.336	BBA	1.4254	1341.18433	13.41504	49.3491

Sample Info: 254nm, OD-H, i-PrOH : Hexane = 5 : 95, 1.0 mL/min



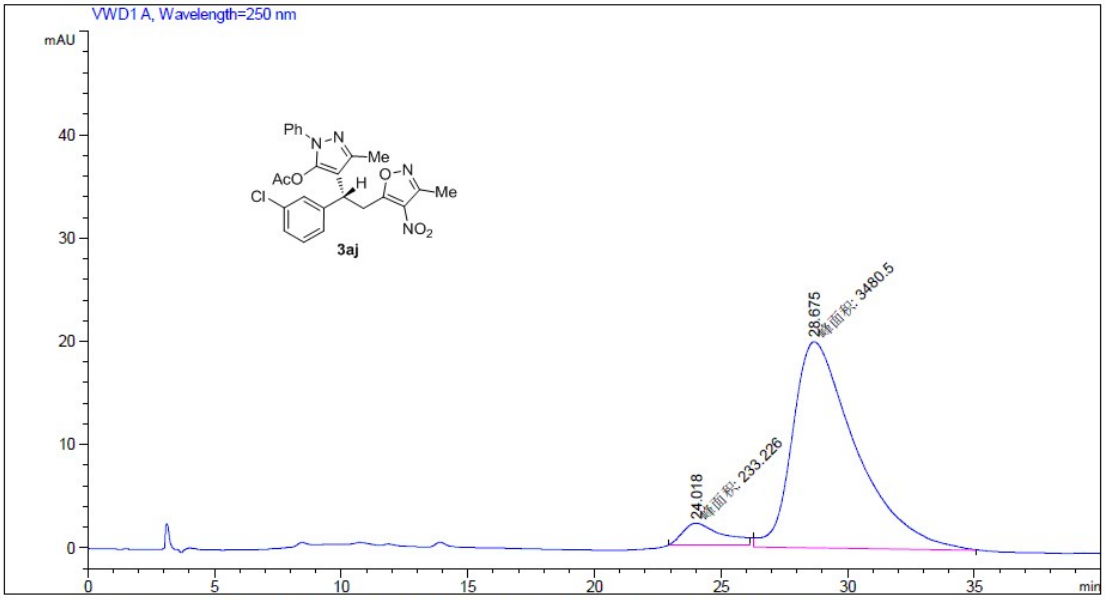
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.727	BBA	0.7475	149.44789	2.85594	4.4634
2	15.453	BB	1.3701	3198.87280	34.23636	95.5366

Sample Info: 254nm, OD-H, i-PrOH : Hexane = 5 : 95, 1.0 mL/min



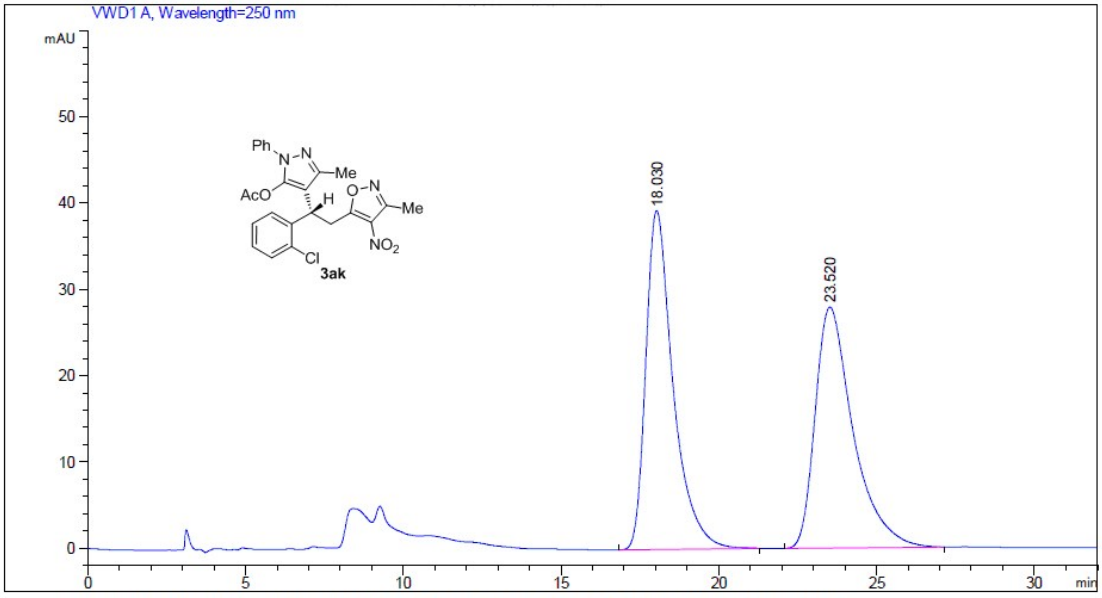
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.636	MM	1.4241	2222.67676	26.01279	50.9808
2	28.128	MM	2.4432	2137.15308	14.57867	49.0192

Sample Info: 254nm, OD-H, i-PrOH : Hexane = 5 : 95, 1.0 mL/min



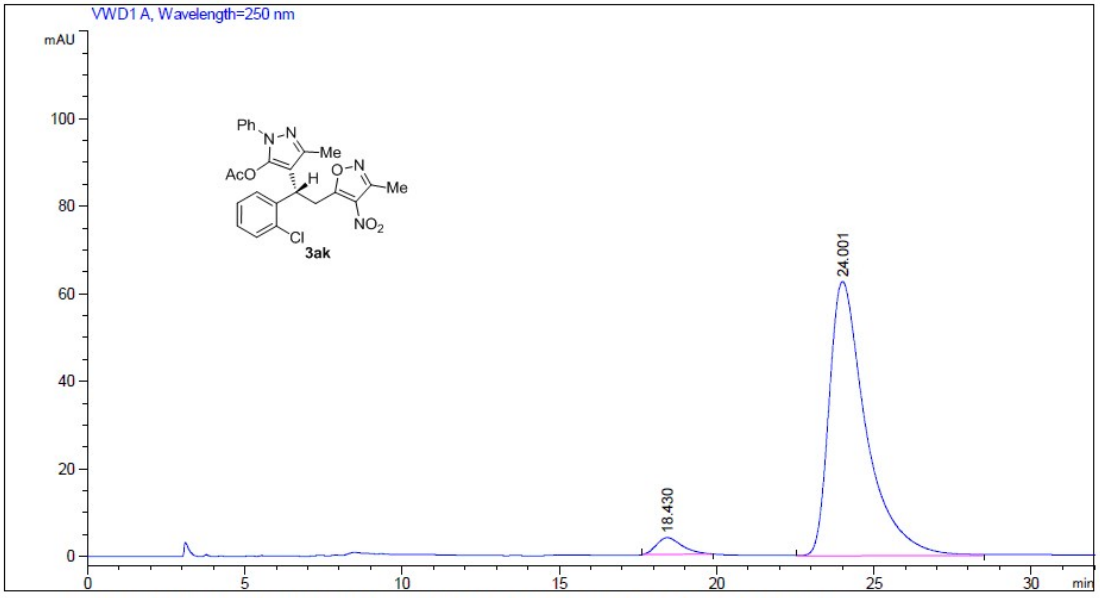
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.018	MM	1.8118	233.22597	2.14540	6.2801
2	28.675	MM	2.9023	3480.50000	19.98712	93.7199

Sample Info: 254nm, OD-H, i-PrOH : Hexane = 5 : 95, 1.0 mL/min



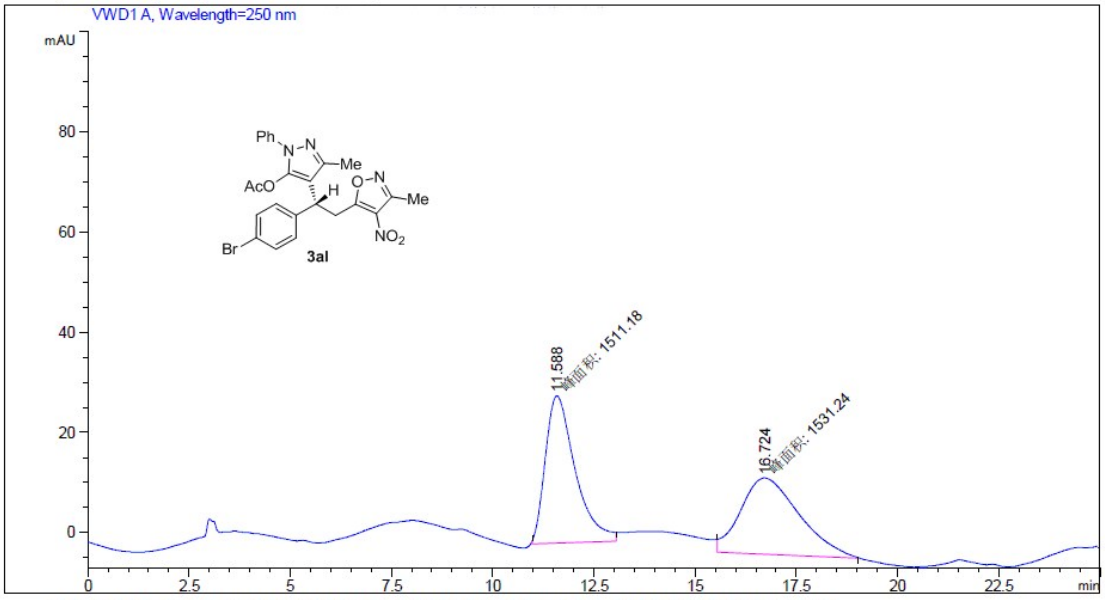
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.030	BB	0.8965	2366.79907	39.30566	50.3622
2	23.520	BB	1.2390	2332.75293	27.94303	49.6378

Sample Info: 254nm, OD-H, i-PrOH : Hexane = 5 : 95, 1.0 mL/min



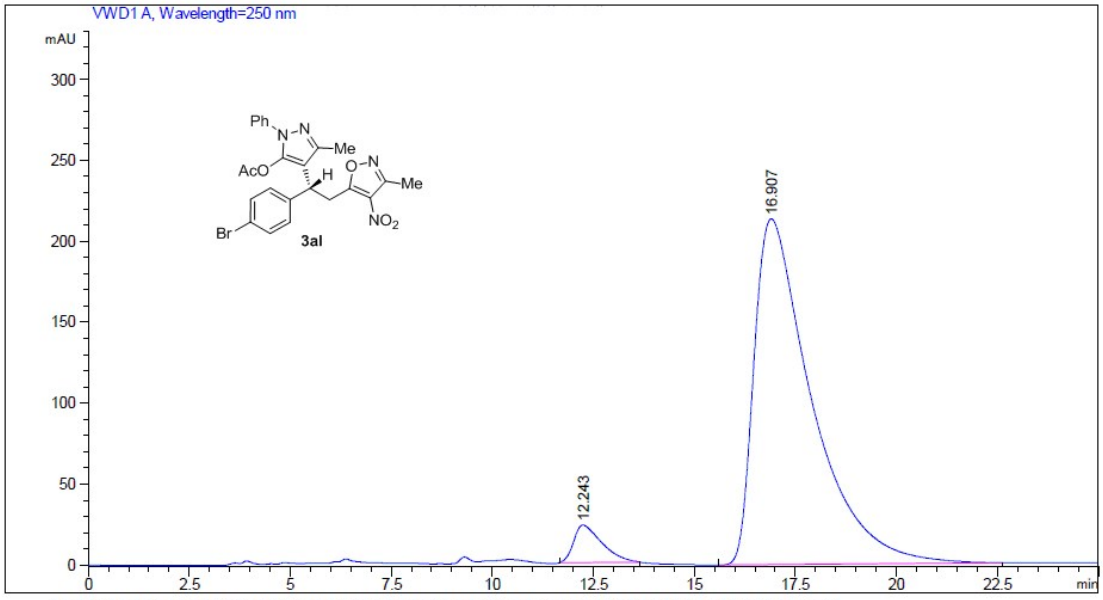
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.430	BBA	0.8042	218.26270	3.83392	4.0931
2	24.001	MM	1.3594	5114.16846	62.70169	95.9069

Sample Info: 254nm, OD-H, i-PrOH : Hexane = 15 : 85, 1.0 mL/min



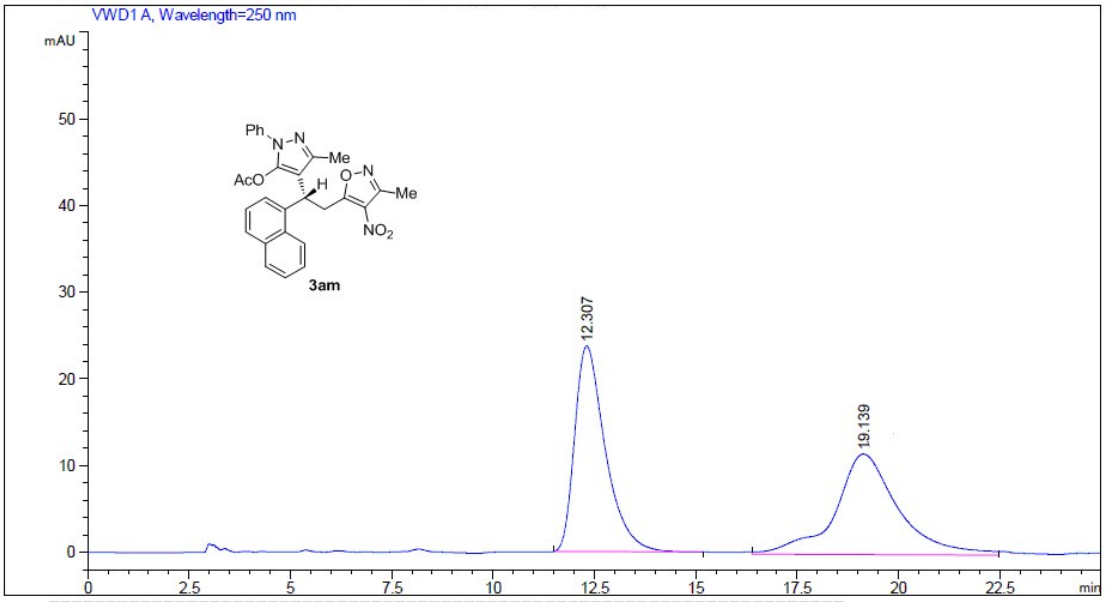
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.588	MM	0.8567	1511.18372	29.40044	49.6705
2	16.724	MM	1.6804	1531.23535	15.18731	50.3295

Sample Info: 254nm, OD-H, i-PrOH : Hexane = 15 : 85, 1.0 mL/min



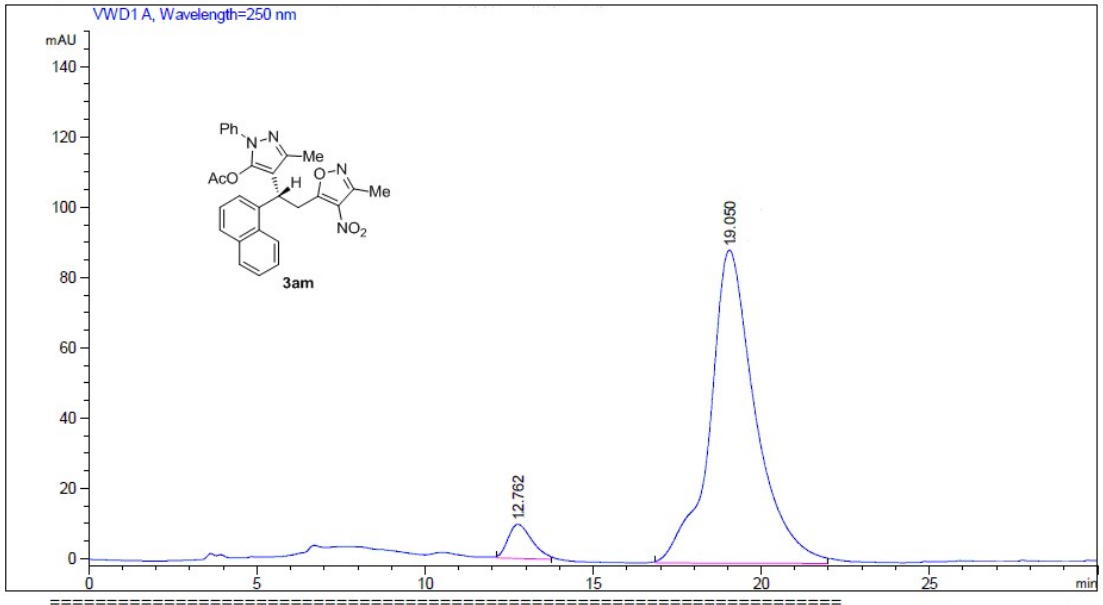
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.243	BBA	0.7188	1113.74951	23.12798	5.0123
2	16.907	BB	1.4446	2.11066e4	213.64935	94.9877

Sample Info: 254nm, OD-H, i-PrOH : Hexane = 15 : 85, 1.0 mL/min



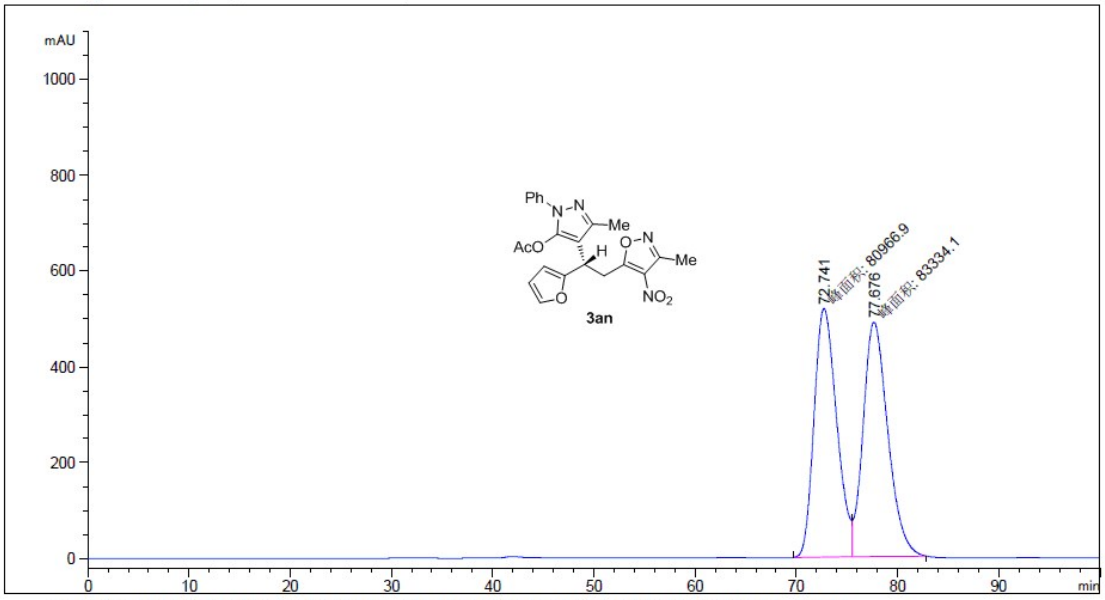
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.307	BB	0.7903	1249.31897	23.72508	49.9259
2	19.139	MM	1.8011	1253.02832	11.59515	50.0741

Sample Info: 254nm, OD-H, i-PrOH : Hexane = 15 : 85, 1.0 mL/min



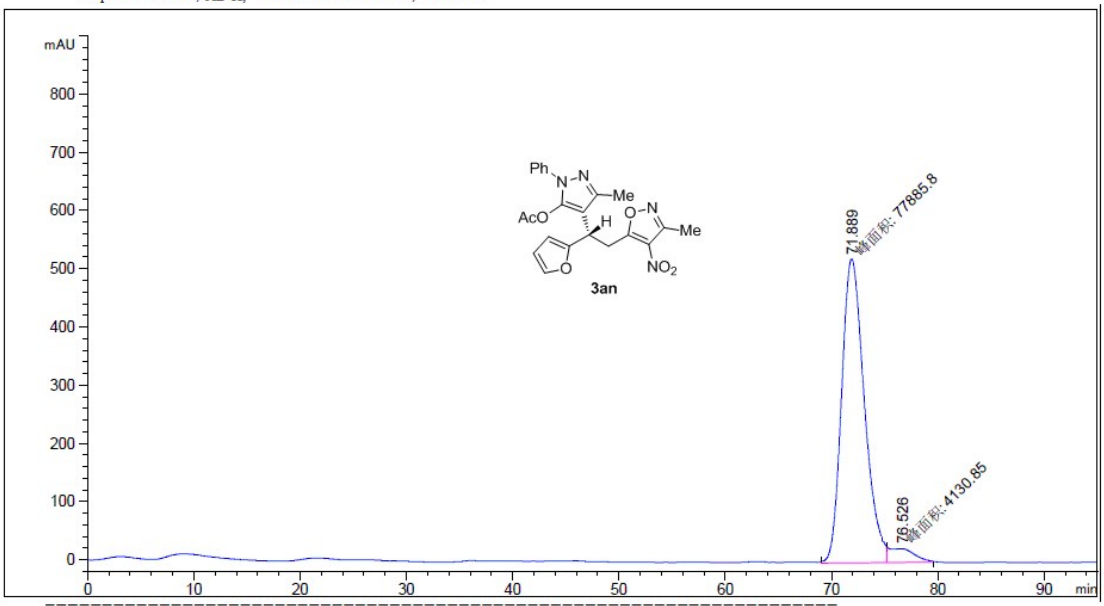
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.762	MM	0.8219	479.58234	9.72538	5.4063
2	19.050	MM	1.5696	8391.25684	89.10047	94.5937

Sample Info: 254nm, AD-H, i-PrOH : Hexane = 20 : 80, 0.1mL/min



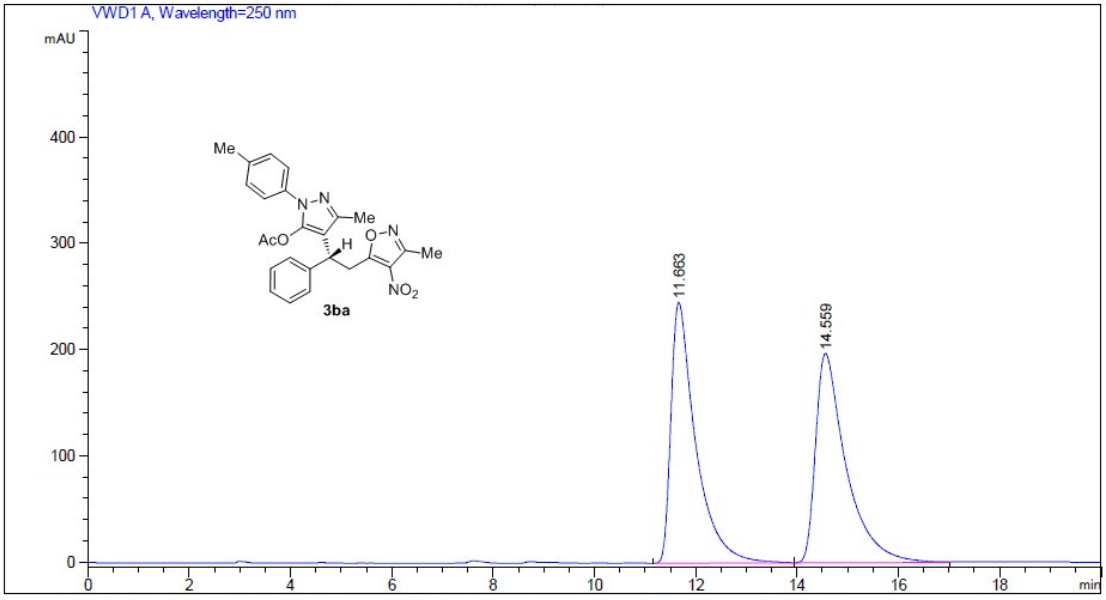
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	72.741	MM	2.5983	8.09669e4	519.35486	49.2796
2	77.676	MM	2.8336	8.33341e4	490.14713	50.7204

Sample Info: 254nm, AD-H, i-PrOH : Hexane = 20 : 80, 0.1mL/min



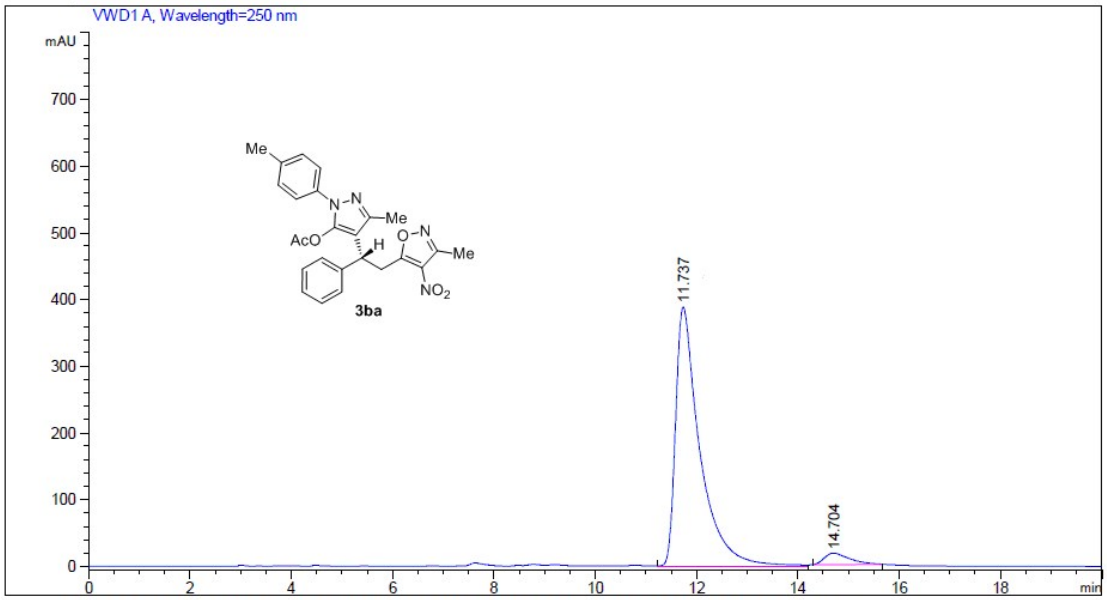
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	71.889	MM	2.4831	7.78858e4	522.76422	94.9634
2	75.197	MM	2.1023	4130.84521	27.66851	5.0366

Sample Info: 254nm, AD-H, i-PrOH : Hexane = 10 : 90, 1.0 mL/min



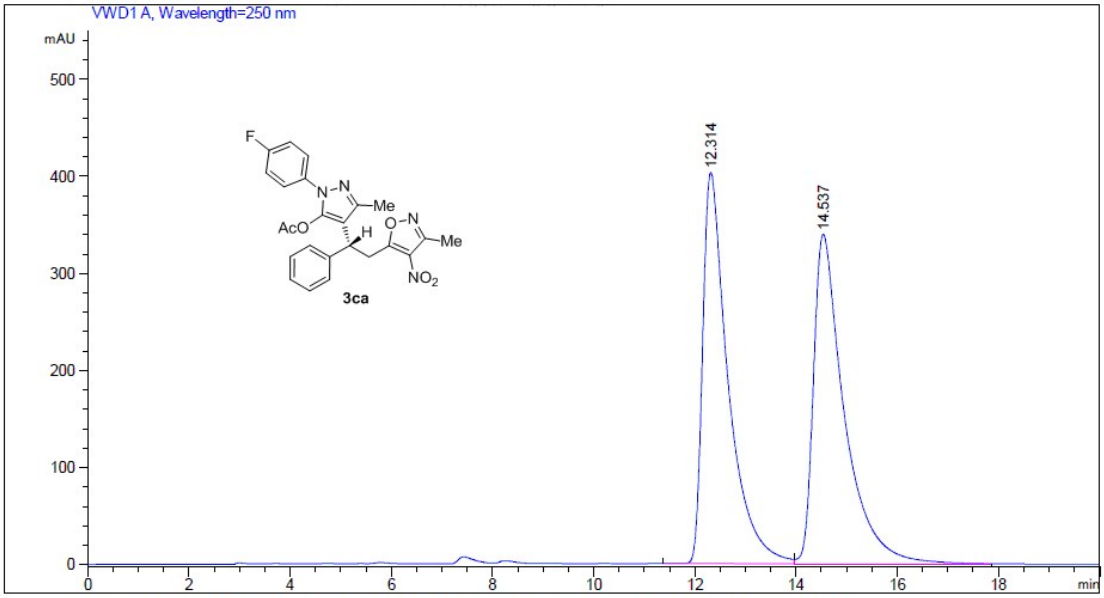
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.663	BB	0.4888	8295.71680	245.16788	50.2422
2	14.559	BBA	0.6041	8215.72852	196.78899	49.7578

Sample Info: 254nm, AD-H, i-PrOH : Hexane = 10 : 90, 1.0 mL/min



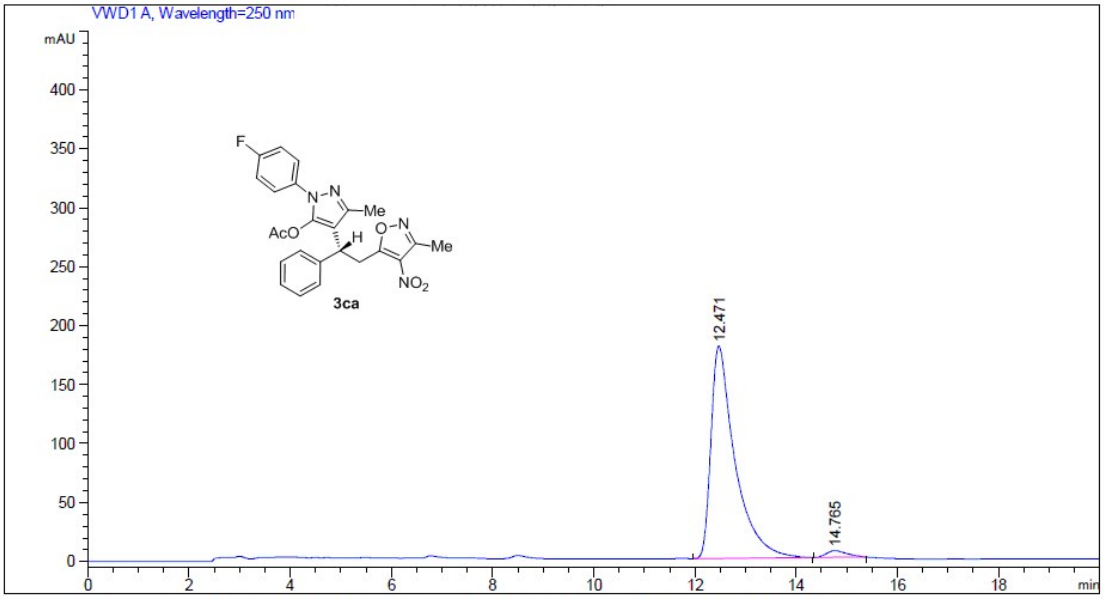
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.737	MM	0.5522	1.28607e4	388.18747	95.6343
2	14.704	BBA	0.5058	587.09552	17.13404	4.3657

Sample Info: 254nm, AD-H, i-PrOH : Hexane = 10 : 90, 1.0 mL/min



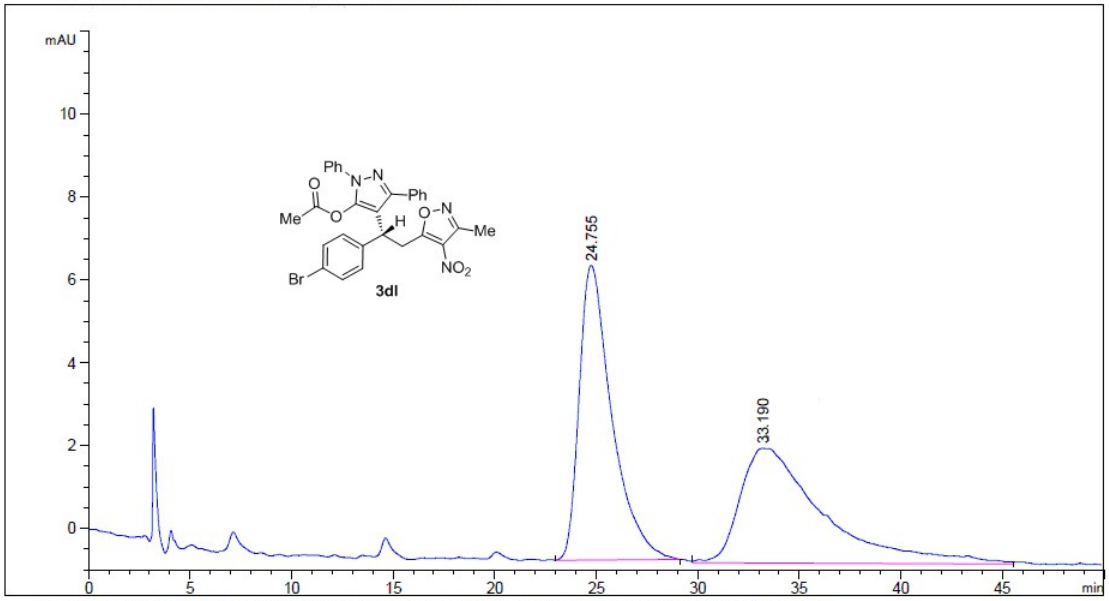
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.314	BV	0.5068	1.40721e4	402.61700	49.5727
2	14.537	VBA	0.6085	1.43147e4	339.11917	50.4273

Sample Info: 254nm, AD-H, i-PrOH : Hexane = 10 : 90, 1.0 mL/min



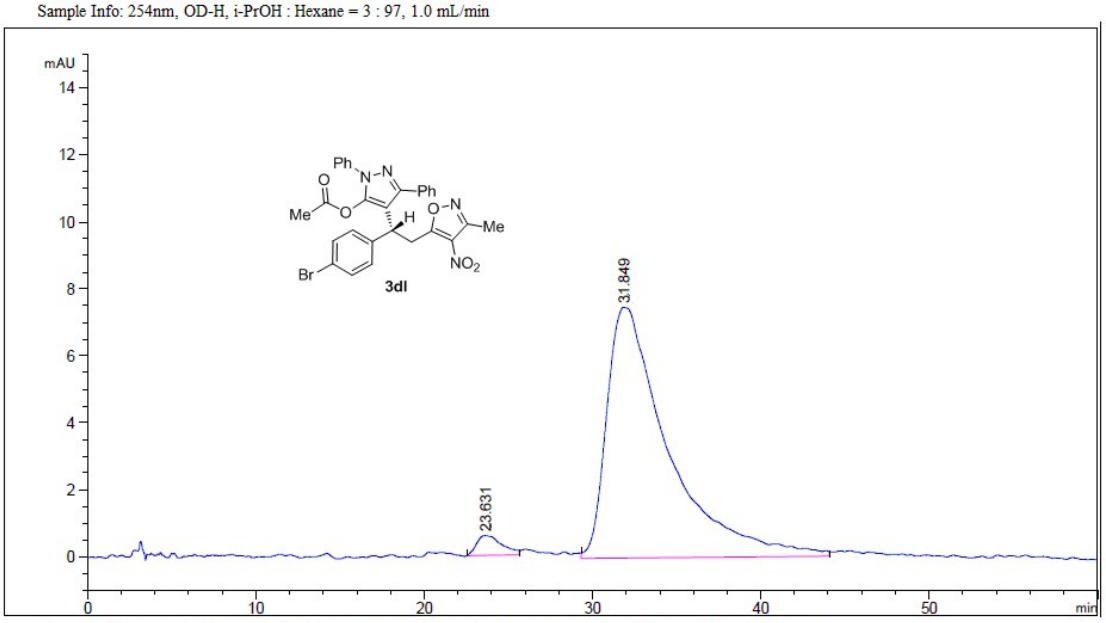
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.471	BB	0.4741	5943.90039	180.08514	97.4090
2	14.765	BBA	0.4321	158.10571	5.60519	2.5910

Sample Info: 254nm, OD-H, i-PrOH : Hexane = 3 : 97, 1.0 mL/min



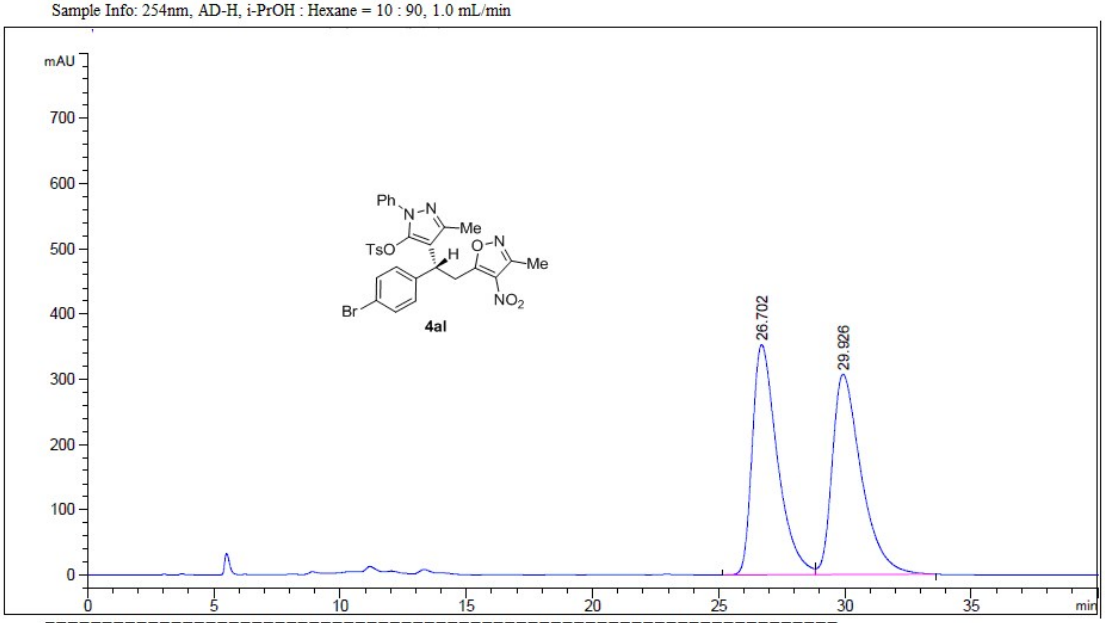
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.755	BB	1.3467	795.20685	7.11087	50.2892
2	33.190	MM	4.7318	786.05927	2.76871	49.7108

Sample Info: 254nm, OD-H, i-PrOH : Hexane = 3 : 97, 1.0 mL/min



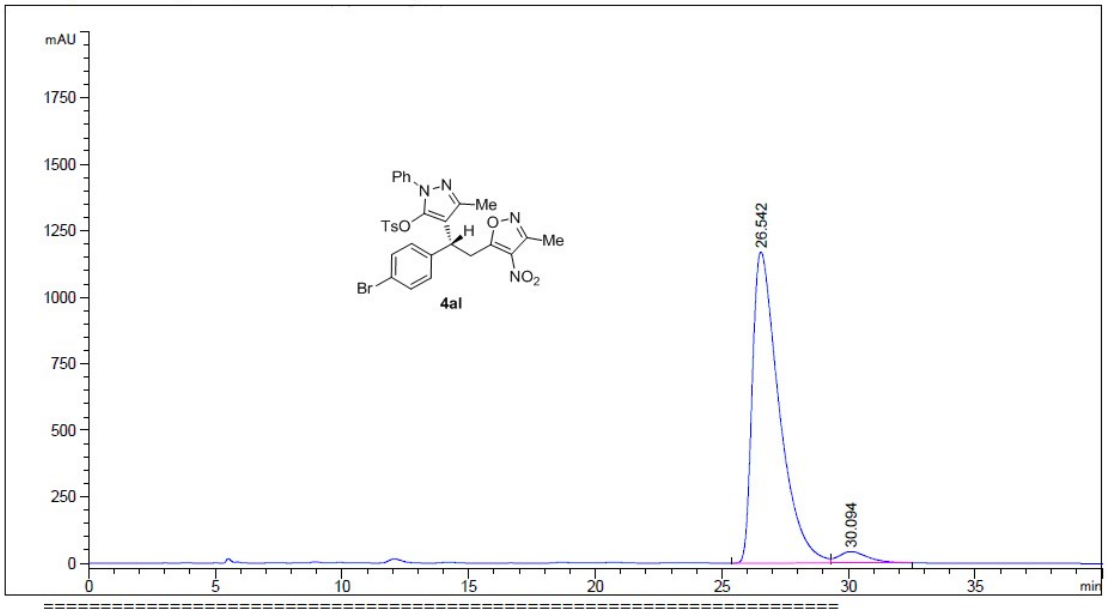
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.631	MM	1.7544	62.17023	5.90627e-1	3.1676
2	31.849	MM	4.2259	1900.50818	7.49545	96.8324

Sample Info: 254nm, AD-H, i-PrOH : Hexane = 10 : 90, 1.0 mL/min



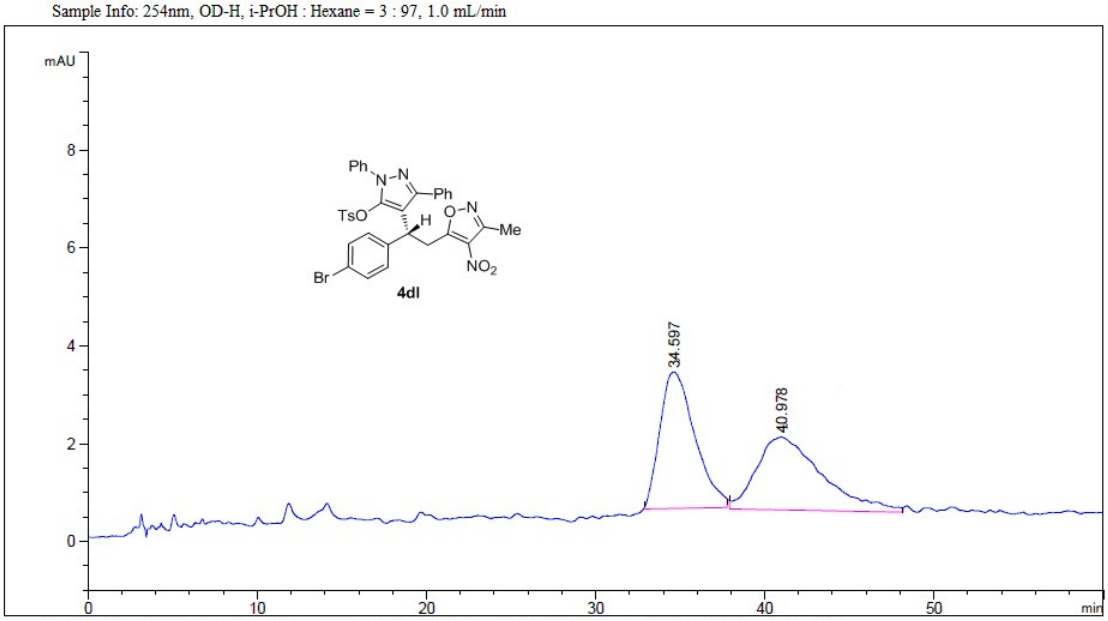
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.702	BV	1.0437	2.43750e4	352.53018	49.8056
2	29.926	VBA	1.2076	2.45652e4	306.97049	50.1944

Sample Info: 254nm, AD-H, i-PrOH : Hexane = 10 : 90, 1.0 mL/min



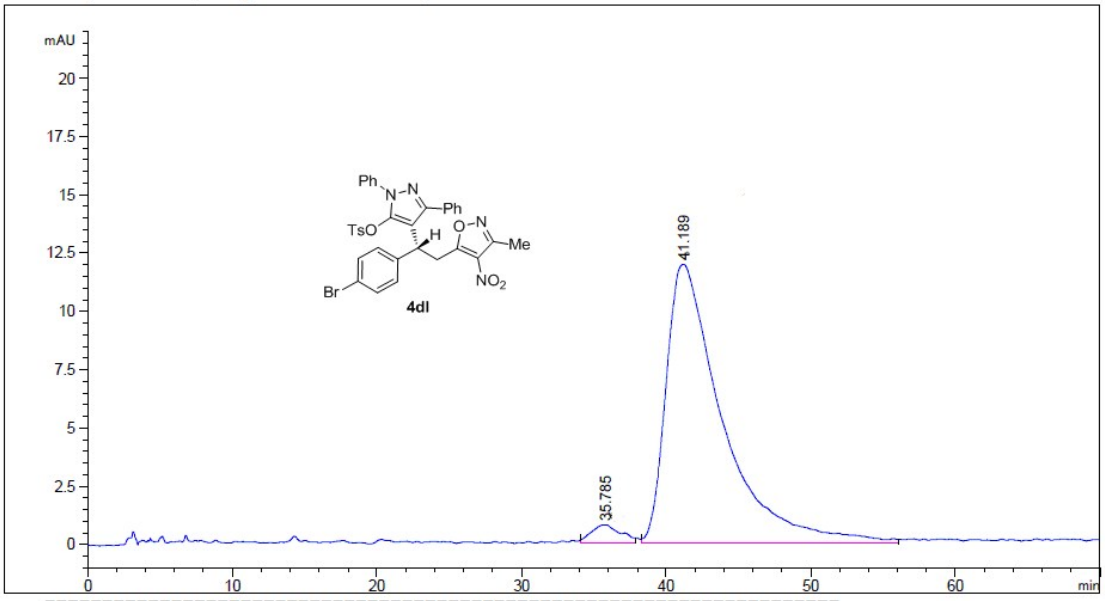
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.542	BV	1.1046	8.60096e4	1170.08411	96.0645
2	30.094	VBA	1.2088	3523.60327	43.14694	3.9355

Sample Info: 254nm, OD-H, i-PrOH : Hexane = 3 : 97, 1.0 mL/min



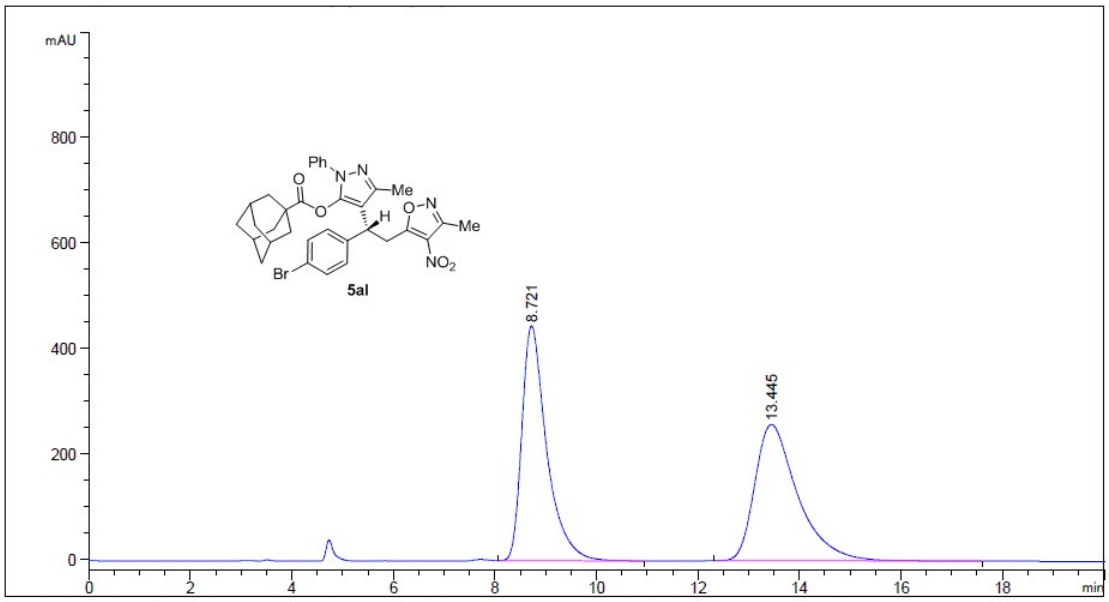
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.597	MM	2.3928	401.22696	2.79472	50.1145
2	40.978	MM	4.4628	399.39310	1.49156	49.8855

Sample Info: 254nm, OD-H, i-PrOH : Hexane = 3 : 97, 1.0 mL/min



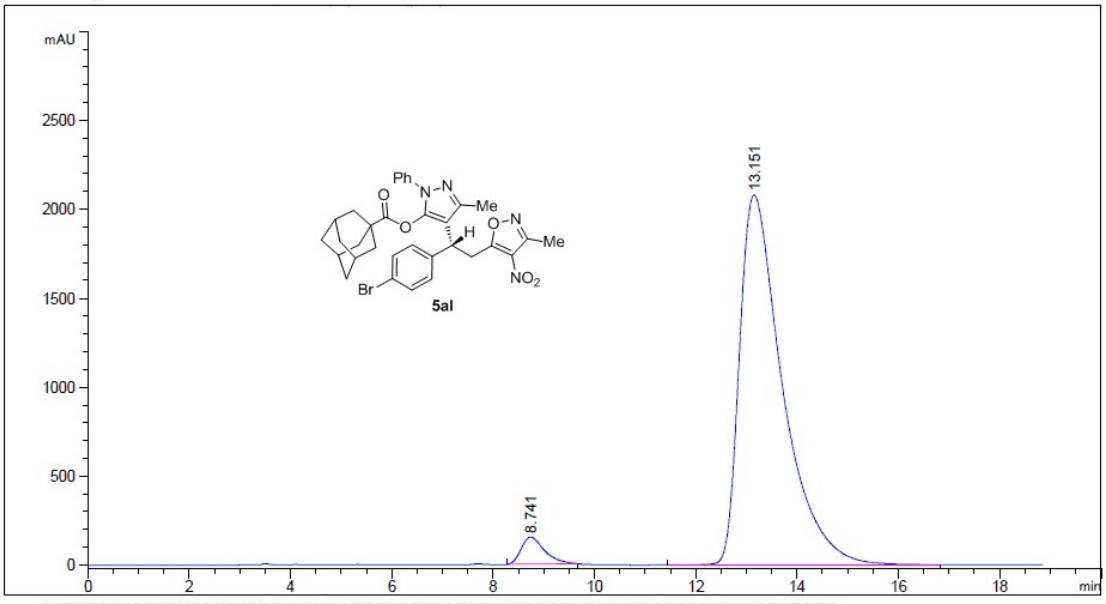
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.785	MM	2.3349	105.19222	7.50861e-1	3.1827
2	41.189	MM	4.4685	3199.94043	11.93509	96.8173

Sample Info: 254nm, OD-H, i-PrOH : Hexane = 10 : 90, 1.0 mL/min



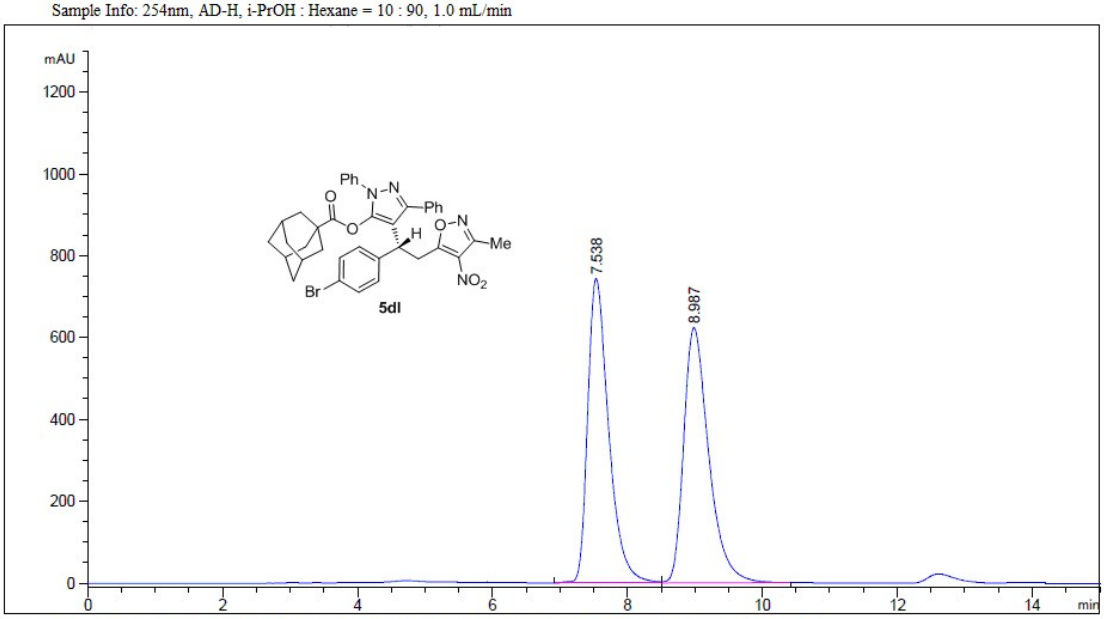
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.721	BB	0.5071	1.51070e4	444.97076	49.9204
2	13.445	BB	0.8479	1.51552e4	258.52753	50.0796

Sample Info: 254nm, OD-H, i-PrOH : Hexane = 10 : 90, 1.0 mL/min



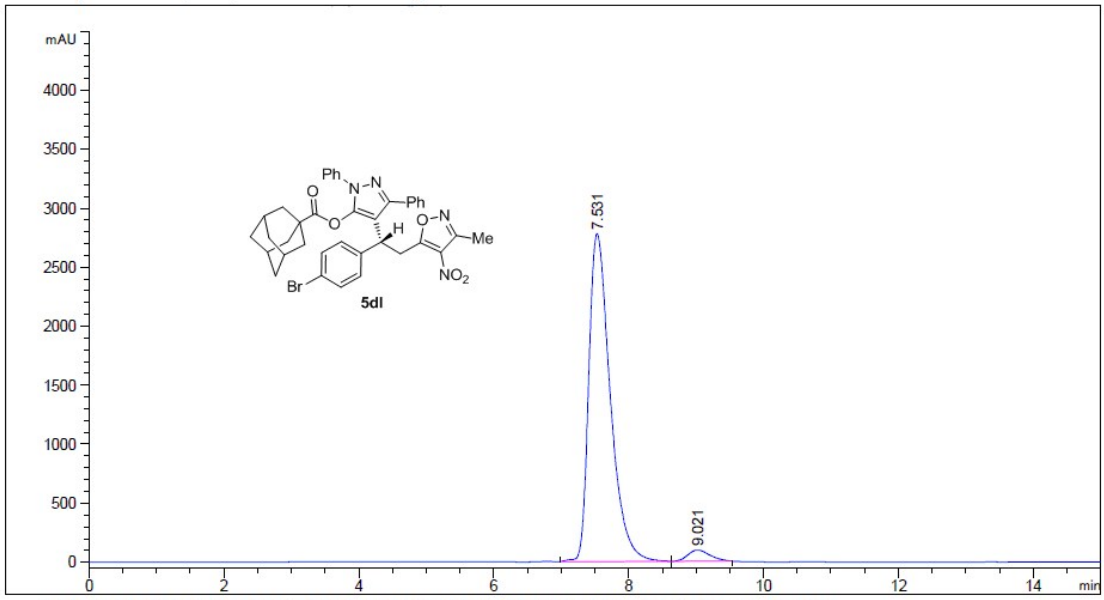
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.741	BBA	0.4838	4873.62549	152.10226	3.8389
2	13.151	BBA	0.8772	1.22079e5	2078.60327	96.1611

Sample Info: 254nm, AD-H, i-PrOH : Hexane = 10 : 90, 1.0 mL/min



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.538	BV	0.3277	1.60287e4	743.08453	49.9739
2	8.987	VB	0.3915	1.60455e4	622.90344	50.0261

Sample Info: 254nm, AD-H, i-PrOH : Hexane = 10 : 90, 1.0 mL/min



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.531	BV	0.3351	6.12501e4	2779.59058	96.6130
2	9.021	VBA	0.3522	2147.24438	94.11405	3.3870

X-Ray Analysis for the product 3dl:

CCDC 1564733 contains the supplementary crystallographic data for the product **3dl**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

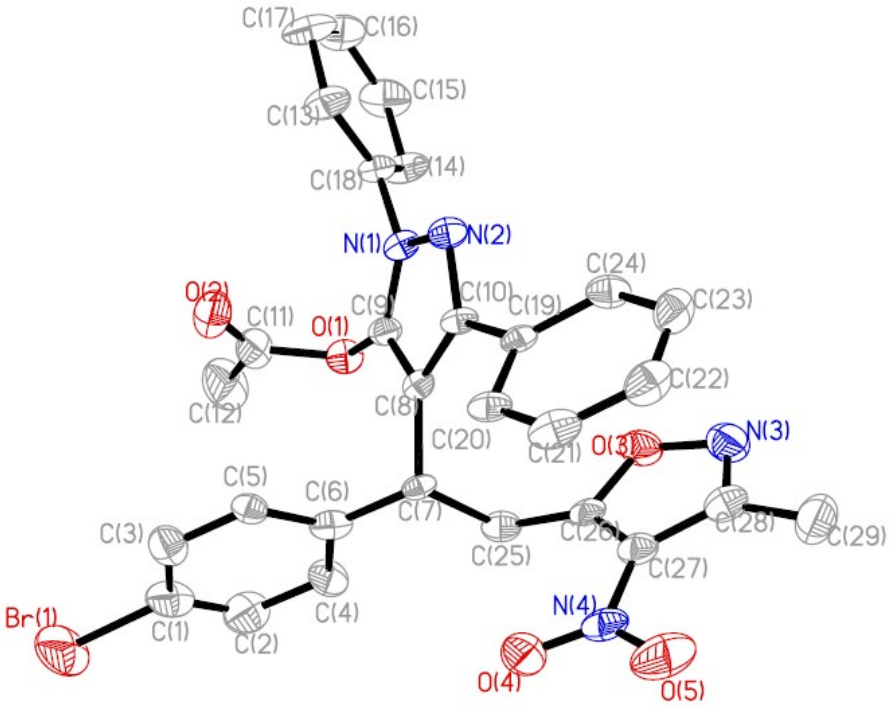


Table 1. Crystal data and structure refinement for 130703A.

Empirical formula	C29 H25 Br N4 O6
Formula weight	605.44
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system, space group	MONOCLINIC, C2/c
Unit cell dimensions	a = 14.443(9) A alpha = 90 deg. b = 6.804(4) A beta = 112.801(15) deg. c = 17.163(10) A gamma = 90 deg.
Volume	1554.8(16) Å ^{3}
Z, Calculated density	2, 1.293 Mg/m^3
Absorption coefficient	1.366 mm^{-1}
F(000)	620

Crystal size	0.17 x 0.14 x 0.05 mm
Theta range for data collection	3.06 to 25.00 deg.
Limiting indices	-17<=h<=17, -8<=k<=8, -20<=l<=20
Reflections collected / unique	21199 / 5412 [R(int) = 0.1491]
Completeness to theta = 25.03	99.4%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5412 / 1 / 373
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0866, wR2 = 0.2282
R indices (all data)	R1 = 0.1584, wR2 = 0.2537
Extinction coefficient	0.07(2)
Largest diff. peak and hole	0.721 and -0.527 $e.A^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 1_a. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	9890(1)	8765(3)	5727(1)	118(1)
N(1)	5594(5)	3786(9)	1695(4)	41(1)
C(1)	8562(7)	8304(18)	4946(7)	72(3)
O(1)	6701(4)	6508(8)	2193(3)	46(1)
O(3)	3248(5)	8238(9)	1896(3)	58(2)
C(18)	6249(8)	1145(13)	1113(6)	62(3)
C(3)	8185(7)	6426(15)	4906(6)	59(2)
N(3)	2217(7)	7924(12)	1725(5)	69(2)
O(2)	7840(5)	4169(13)	2869(4)	76(2)
N(2)	4832(5)	2879(8)	1812(4)	41(2)
C(2)	7983(9)	9758(17)	4453(8)	76(3)
O(4)	4207(6)	8262(11)	4449(4)	74(2)
N(4)	3335(7)	8039(9)	3988(5)	54(2)
C(4)	6962(7)	9381(13)	3917(6)	60(2)
O(5)	2635(7)	7818(11)	4208(5)	92(3)
C(5)	7203(6)	6042(11)	4382(5)	42(2)

C(7)	5499(6)	6973(10)	3374(5)	32(2)
C(6)	6583(7)	7508(12)	3880(6)	51(2)
C(9)	5938(6)	5300(11)	2220(5)	40(2)
C(8)	5408(5)	5458(10)	2722(4)	33(2)
C(11)	7684(7)	5782(18)	2599(6)	60(3)
C(10)	4713(5)	3913(10)	2440(4)	33(2)
C(13)	5945(6)	3019(10)	1067(5)	41(2)
C(12)	8407(9)	7270(20)	2607(9)	101(4)
C(15)	6255(8)	3519(18)	-182(6)	75(3)
C(16)	6519(9)	1623(18)	-159(6)	76(3)
C(17)	6531(9)	378(14)	478(7)	73(3)
C(19)	3876(5)	3412(9)	2704(4)	35(2)
C(20)	4022(6)	3333(10)	3548(5)	42(2)
C(21)	3215(8)	2977(12)	3762(6)	55(2)
C(22)	2287(8)	2697(13)	3172(7)	59(2)
C(23)	2133(7)	2725(13)	2326(7)	59(3)
C(24)	2925(7)	3092(11)	2090(5)	49(2)
C(25)	4836(6)	8755(12)	3012(5)	47(2)
C(26)	3780(6)	8355(10)	2737(5)	40(2)
C(27)	3095(6)	8060(11)	3101(5)	46(2)
C(28)	2153(8)	7814(12)	2459(7)	61(3)
C(29)	1139(8)	7508(18)	2506(10)	100(4)
O(7A)	8749(15)	6600(50)	313(8)	159(12)
O(7B)	9091(9)	3150(30)	1332(8)	96(7)
C(14)	5958(8)	4295(11)	430(5)	55(2)

able 3. Bond lengths [A] and angles [deg] for 1_a.

Br(1)-C(1)	1.892(10)
N(1)-C(9)	1.331(10)
N(1)-N(2)	1.343(9)
N(1)-C(13)	1.454(9)
C(1)-C(2)	1.358(16)
C(1)-C(3)	1.381(15)
O(1)-C(9)	1.390(9)
O(1)-C(11)	1.407(12)
O(3)-C(26)	1.349(9)
O(3)-N(3)	1.417(11)
C(18)-C(13)	1.340(11)
C(18)-C(17)	1.403(13)
C(18)-H(18)	0.9300
C(3)-C(5)	1.379(12)
C(3)-H(3)	0.9300
N(3)-C(28)	1.300(12)

O(2)-C(11)	1.179(12)
N(2)-C(10)	1.353(9)
C(2)-C(4)	1.427(14)
C(2)-H(2)	0.9300
O(4)-N(4)	1.210(10)
N(4)-O(5)	1.219(10)
N(4)-C(27)	1.423(11)
C(4)-C(6)	1.379(12)
C(4)-H(4)	0.9300
C(5)-C(6)	1.392(12)
C(5)-H(5)	0.9300
C(7)-C(8)	1.489(10)
C(7)-C(6)	1.512(12)
C(7)-C(25)	1.520(11)
C(7)-H(7)	0.9800
C(9)-C(8)	1.361(10)
C(8)-C(10)	1.403(10)
C(11)-C(12)	1.450(16)
C(10)-C(19)	1.487(10)
C(13)-C(14)	1.402(11)
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(15)-C(16)	1.341(16)
C(15)-C(14)	1.384(12)
C(15)-H(15)	0.9300
C(16)-C(17)	1.378(15)
C(16)-H(16)	0.9300
C(17)-H(17)	0.9300
C(19)-C(20)	1.381(10)
C(19)-C(24)	1.386(11)
C(20)-C(21)	1.372(12)
C(20)-H(20)	0.9300
C(21)-C(22)	1.344(14)
C(21)-H(21)	0.9300
C(22)-C(23)	1.381(14)
C(22)-H(22)	0.9300
C(23)-C(24)	1.376(12)
C(23)-H(23)	0.9300
C(24)-H(24)	0.9300
C(25)-C(26)	1.437(11)
C(25)-H(25A)	0.9700
C(25)-H(25B)	0.9700
C(26)-C(27)	1.374(11)

C(27)-C(28)	1.390(13)
C(28)-C(29)	1.512(15)
C(29)-H(29A)	0.9600
C(29)-H(29B)	0.9600
C(29)-H(29C)	0.9600
C(14)-H(14)	0.9300
C(9)-N(1)-N(2)	111.5(6)
C(9)-N(1)-C(13)	129.3(6)
N(2)-N(1)-C(13)	119.1(6)
C(2)-C(1)-C(3)	120.5(9)
C(2)-C(1)-Br(1)	122.1(8)
C(3)-C(1)-Br(1)	117.4(10)
C(9)-O(1)-C(11)	116.0(7)
C(26)-O(3)-N(3)	110.4(6)
C(13)-C(18)-C(17)	119.7(9)
C(13)-C(18)-H(18)	120.2
C(17)-C(18)-H(18)	120.2
C(5)-C(3)-C(1)	119.6(10)
C(5)-C(3)-H(3)	120.2
C(1)-C(3)-H(3)	120.2
C(28)-N(3)-O(3)	105.7(7)
N(1)-N(2)-C(10)	104.1(5)
C(1)-C(2)-C(4)	120.2(9)
C(1)-C(2)-H(2)	119.9
C(4)-C(2)-H(2)	119.9
O(4)-N(4)-O(5)	126.2(8)
O(4)-N(4)-C(27)	117.4(8)
O(5)-N(4)-C(27)	116.4(9)
C(6)-C(4)-C(2)	119.2(9)
C(6)-C(4)-H(4)	120.4
C(2)-C(4)-H(4)	120.4
C(3)-C(5)-C(6)	121.3(8)
C(3)-C(5)-H(5)	119.3
C(6)-C(5)-H(5)	119.3
C(8)-C(7)-C(6)	111.6(6)
C(8)-C(7)-C(25)	112.8(6)
C(6)-C(7)-C(25)	113.0(6)
C(8)-C(7)-H(7)	106.3
C(6)-C(7)-H(7)	106.3
C(25)-C(7)-H(7)	106.3
C(4)-C(6)-C(5)	119.1(9)
C(4)-C(6)-C(7)	123.5(8)
C(5)-C(6)-C(7)	117.2(7)
N(1)-C(9)-C(8)	109.6(7)

N(1)-C(9)-O(1)	121.8(6)
C(8)-C(9)-O(1)	128.5(7)
C(9)-C(8)-C(10)	103.0(6)
C(9)-C(8)-C(7)	128.5(6)
C(10)-C(8)-C(7)	128.4(6)
O(2)-C(11)-O(1)	121.5(8)
O(2)-C(11)-C(12)	128.3(11)
O(1)-C(11)-C(12)	110.2(11)
N(2)-C(10)-C(8)	111.8(6)
N(2)-C(10)-C(19)	119.5(6)
C(8)-C(10)-C(19)	128.6(6)
C(18)-C(13)-C(14)	122.1(7)
C(18)-C(13)-N(1)	119.8(7)
C(14)-C(13)-N(1)	118.0(7)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(16)-C(15)-C(14)	120.8(9)
C(16)-C(15)-H(15)	119.6
C(14)-C(15)-H(15)	119.6
C(15)-C(16)-C(17)	122.0(8)
C(15)-C(16)-H(16)	119.0
C(17)-C(16)-H(16)	119.0
C(16)-C(17)-C(18)	118.0(9)
C(16)-C(17)-H(17)	121.0
C(18)-C(17)-H(17)	121.0
C(20)-C(19)-C(24)	119.7(7)
C(20)-C(19)-C(10)	121.1(7)
C(24)-C(19)-C(10)	119.1(6)
C(21)-C(20)-C(19)	119.1(8)
C(21)-C(20)-H(20)	120.5
C(19)-C(20)-H(20)	120.5
C(22)-C(21)-C(20)	121.8(8)
C(22)-C(21)-H(21)	119.1
C(20)-C(21)-H(21)	119.1
C(21)-C(22)-C(23)	119.8(8)
C(21)-C(22)-H(22)	120.1
C(23)-C(22)-H(22)	120.1
C(24)-C(23)-C(22)	120.0(9)
C(24)-C(23)-H(23)	120.0
C(22)-C(23)-H(23)	120.0

C(23)-C(24)-C(19)	119.7(8)
C(23)-C(24)-H(24)	120.2
C(19)-C(24)-H(24)	120.2
C(26)-C(25)-C(7)	113.8(6)
C(26)-C(25)-H(25A)	108.8
C(7)-C(25)-H(25A)	108.8
C(26)-C(25)-H(25B)	108.8
C(7)-C(25)-H(25B)	108.8
H(25A)-C(25)-H(25B)	107.7
O(3)-C(26)-C(27)	105.4(7)
O(3)-C(26)-C(25)	117.1(7)
C(27)-C(26)-C(25)	137.5(7)
C(26)-C(27)-C(28)	108.2(8)
C(26)-C(27)-N(4)	124.6(8)
C(28)-C(27)-N(4)	127.2(8)
N(3)-C(28)-C(27)	110.3(9)
N(3)-C(28)-C(29)	119.6(10)
C(27)-C(28)-C(29)	130.1(10)
C(28)-C(29)-H(29A)	109.5
C(28)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
C(28)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
C(15)-C(14)-C(13)	117.2(8)
C(15)-C(14)-H(14)	121.4
C(13)-C(14)-H(14)	121.4

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 1_a. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

U11	U22	U33	U23	U13	U12
Br(1)	60(1)	167(2)	118(1)	-53(1)	26(1)	-42(1)
N(1)	50(4)	34(3)	45(3)	-1(3)	27(3)	3(3)
C(1)	54(6)	84(8)	90(7)	-40(7)	41(6)	-35(6)
O(1)	52(4)	41(3)	51(3)	2(2)	27(3)	-8(2)
O(3)	76(4)	54(4)	39(3)	2(3)	18(3)	4(3)
C(18)	89(7)	51(6)	59(6)	-6(4)	44(6)	8(5)
C(3)	51(6)	80(7)	48(5)	-1(5)	22(5)	-3(5)

N(3)	77(6)	58(5)	57(5)	-5(4)	8(4)	8(4)
O(2)	64(4)	88(6)	76(5)	13(4)	28(4)	18(4)
N(2)	55(4)	27(3)	47(4)	0(3)	26(3)	-5(3)
C(2)	64(7)	64(7)	109(9)	-21(6)	42(7)	-22(6)
O(4)	79(5)	86(5)	48(4)	-1(4)	17(4)	15(4)
N(4)	79(6)	28(4)	59(5)	-5(3)	32(5)	7(4)
C(4)	55(6)	47(6)	70(6)	-12(4)	17(5)	-18(4)
O(5)	122(7)	85(5)	107(6)	-15(4)	86(6)	-9(5)
C(5)	47(5)	35(4)	43(4)	-8(3)	15(4)	-8(3)
C(7)	42(4)	20(3)	42(4)	-5(3)	25(4)	-3(3)
C(6)	66(6)	41(5)	54(5)	-13(4)	32(5)	-7(4)
C(9)	46(5)	33(4)	41(4)	-4(4)	18(4)	2(4)
C(8)	40(4)	30(4)	33(4)	5(3)	18(3)	5(3)
C(11)	41(5)	87(8)	62(6)	-6(6)	30(5)	-5(5)
C(10)	53(4)	17(3)	34(4)	3(3)	24(3)	-1(3)
C(13)	59(5)	29(4)	41(4)	-4(3)	28(4)	-1(3)
C(12)	64(8)	131(11)	106(10)	-7(8)	31(7)	-27(7)
C(15)	116(8)	84(8)	45(5)	-2(5)	53(6)	-10(7)
C(16)	99(9)	93(9)	54(6)	-21(6)	50(6)	5(6)
C(17)	115(9)	45(5)	87(7)	-20(6)	69(7)	-4(5)
C(19)	46(4)	18(4)	45(4)	-5(3)	21(4)	0(3)
C(20)	64(5)	18(4)	48(4)	-3(3)	25(4)	-3(3)
C(21)	83(7)	36(4)	62(6)	3(4)	46(6)	0(4)
C(22)	61(6)	49(5)	85(7)	-1(5)	49(6)	-6(4)
C(23)	43(5)	49(5)	93(8)	-7(5)	34(5)	-9(4)
C(24)	64(6)	34(4)	54(5)	-7(4)	28(5)	-9(4)
C(25)	60(5)	27(4)	54(5)	-6(4)	24(4)	-6(4)
C(26)	59(5)	19(4)	42(4)	-1(3)	19(4)	12(3)
C(27)	60(5)	28(4)	50(5)	-3(3)	22(4)	4(3)
C(28)	72(7)	25(4)	80(7)	-5(4)	24(6)	11(4)
C(29)	55(7)	80(8)	159(13)	-42(8)	34(8)	-1(5)
O(7A)	88(13)	340(30)	16(7)	16(12)	-16(7)	-50(17)
O(7B)	27(7)	177(18)	64(9)	-56(10)	-4(6)	-27(8)
C(14)	99(7)	31(4)	57(5)	4(4)	53(5)	-3(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 1_a.

	x	y	z	U(eq)
H(18)	6272	358	1563	74
H(3)	8590	5425	5232	71

H(2)	8254	11003	4464	92
H(4)	6556	10387	3596	71
H(5)	6949	4778	4362	51
H(7)	5249	6361	3772	38
H(12A)	8221	7806	2050	152
H(12B)	9063	6686	2784	152
H(12C)	8417	8296	2993	152
H(15)	6272	4323	-615	90
H(16)	6700	1133	-586	91
H(17)	6720	-931	488	88
H(20)	4659	3517	3966	51
H(21)	3313	2930	4330	66
H(22)	1750	2484	3333	70
H(23)	1496	2497	1917	71
H(24)	2823	3125	1520	58
H(25A)	5015	9777	3439	56
H(25B)	4970	9253	2537	56
H(29A)	625	7534	1947	150
H(29B)	1019	8536	2839	150
H(29C)	1130	6259	2764	150
H(14)	5774	5608	419	66