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# Supporting Information

# A Chiral-at-Metal Asymmetric Catalyzed Vinylogous Michael Addition of Ortho-Methyl Aromatic Nitro Compounds for Isoxazole Derivatives Synthesis

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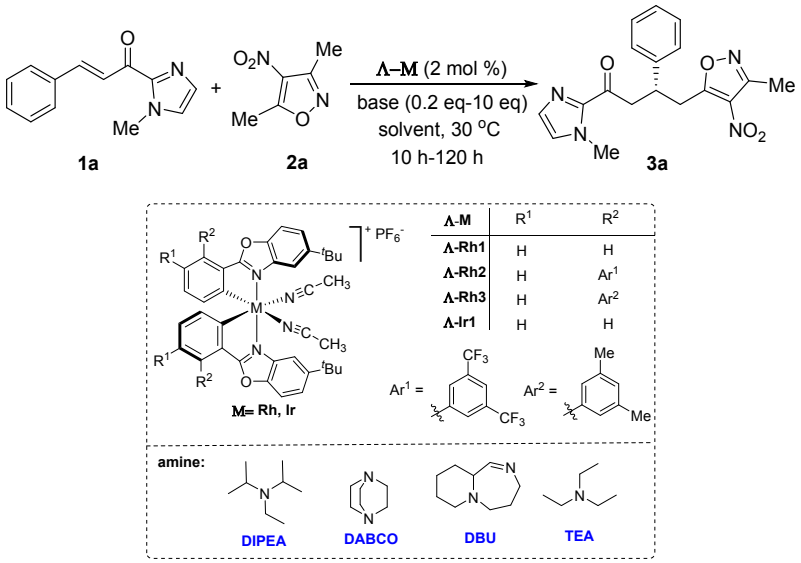
# I General Information

All reactions were performed in Schlenk tubes at 30 °C using oven-dried glassware. Commercially obtained reagents were used without further purification, unless otherwise noted. Dry 1,2-dichloroethane (DCE) was obtained from solvent distillation machine (Vigor VSPS-5) and stored under argon over 4 Å type molecular sieves. THF and toluene were distilled freshly before use over sodium and benzophenone. Dichloromethane (DCM) was distilled from $CaH_2$. Methanol was used without further purification. Reactions were checked by TLC analysis and plates were visualized with short-wave UV light (254 nm). The $^{1}H$ and $^{13}C$ NMR spectra were obtained in $CDCl_3$ using a Bruker-BioSpin AVANCE III HD NMR spectrometer at 400 and 100 MHz, respectively. Chemical shifts are reported in parts per million (δ value) calibrated against the residual solvent peak. Signal patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Coupling constants (*J*) are given in hertz (Hz). HPLC analyses of the compounds were performed on chiralcel IA-IF columns and chiralcel AD-H, AS-H, OJ-H and OD-H columns using hexane and isopropanol as eluent. The infrared spectra were recorded on a Bruker VERTEX 70 IR spectrometer as KBr pellets, with absorption reported in $cm^{-1}$. High-resolution mass spectra were recorded on a Bruker Impact II UHR TOF LC/MS Mass Spectrometry.

# II Optimization of Reaction Conditions

## Table 1. Optimization of the reaction conditions[a]




| entry | **Λ-M** (x mol %) | base (y equiv.) | solvent | time (h) | yield (%)[b] | ee(%)[c] |
|---|---|---|---|---|---|---|
| 1 | **Λ-Rh1** (2) | **DIPEA** (0.2) | DCE | 96 | 95 | 94 |
| 2 | **Λ-Rh2** (2) | **DIPEA** (0.2) | DCE | 96 | 90 | 94 |
| 3 | **Λ-Rh3** (2) | **DIPEA** (0.2) | DCE | 96 | 92 | 79 |
| 4 | **Λ-Ir1** (2) | **DIPEA** (0.2) | DCE | 120 | 70 | 92 |
| 5 | / | **DIPEA** (0.2) | DCE | 24 | NR | NR |
| 6 | **Λ-Rh1** (2) | / | DCE | 24 | trace | trace |
| 7 | **Λ-Rh1** (2) | **DIPEA** (0.2) | DCM | 96 | 75 | 93 |
| 8 | **Λ-Rh1** (2) | **DIPEA** (0.2) | THF | 96 | 86 | 90 |
| 9 | **Λ-Rh1**(2) | **DIPEA** (0.2) | $CH_3OH$ | 96 | 95 | 88 |
| 10 | **Λ-Rh1**(2) | **DIPEA** (0.2) | toluene | 96 | 85 | 78 |
| 11 | **Λ-Rh1**(2) | **DABCO** (0.2) | DCE | 96 | 68 | 93 |
| 12 | **Λ-Rh1**(2) | **DBU** (0.2) | DCE | 96 | 80 | 92 |
| 13 | **Λ-Rh1**(2) | **TEA** (0.2) | DCE | 96 | 90 | 94 |
| 15 [d] | **Λ-Rh1**(2) | **DIPEA** (0.2) | DCE | 40 | 92 | 94 |
| 16 [d] | **Λ-Rh1**(2) | **DIPEA** (0.5) | DCE | 18 | 96 | 95 |

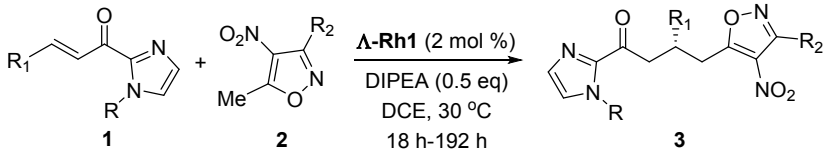
| | | | | | | |
|---|---|---|---|---|---|---|
| 17 [d] | **Λ-Rh1**(2) | **DIPEA** (2.0) | DCE | 16 | 95 | 94 |
| 18 [d] | **Λ-Rh1**(2) | **DIPEA** (5.0) | DCE | 14 | 90 | 94 |
| 19 [d] | **Λ-Rh1**(2) | **DIPEA** (10.0) | DCE | 10 | 93 | 95 |
| 20 [d] | **Λ-Rh1**(1) | **DIPEA** (0.5) | DCE | 60 | 92 | 94 |

[a]Reaction conditions: **1a** (0.20 mmol), **2a** (0.40 mmol), **Λ-M** (2 mol %), base (0.2 - 10 eq), solvent (0.5-1 mL) at 30 °C under argon atmosphere. [b]Isolated yields. [c]Determined by chiral HPLC. [d]1,2-dichloroethane (0.5 mL). DIPEA = *N,N*-Diisopropylethylamine, DABCO = Triethylenediamine, DBU= 1,8-Diazabicyclo[5.4.0]undec-7-ene, TEA= Triethylamine.

## III Experimental Section

**Λ-Rh1, Λ-Rh2, Λ-Rh3 and Λ-Ir1** were prepared according to reported procedure.[1-2] *α,β*-unsaturated 2-acyl imidazoles[3] and 3,5-disubstituted-4-nitroisoxazole substrates **2a-2f** were synthesized according to reported procedures.[4]

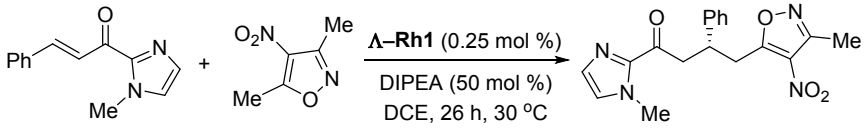
**General procedure for catalytic asymmetric synthesis of isoxazole analogues.**




**1** **2** **3**

To an oven-dried 25 mL Schlenk tube equipped with a stir bar, **Λ-Rh1** (2.0 mol %) was added along with *α,β*-unsaturated 2-acyl imidazole **1** (1 equiv., 0.2 mmol), DIPEA (50 mol %) and DCE (0.5 mL). After being stirred at room temperature for 5 min, 3,5-disubstituted-4-nitroisoxazole substrates **2** (2.0 equiv., 0.40 mmol) was added. The reaction was stirring at 30 °C until consumption of the 2-acyl imidazole (monitored by TLC). The reaction mixture was concentrated and directly purified by silica gel column chromatography (with ethyl acetate-petroleum ether as the eluent) to afford the desired products **3** or **4**.

**General procedure for gram-scale experiments with lower catalyst loading.**

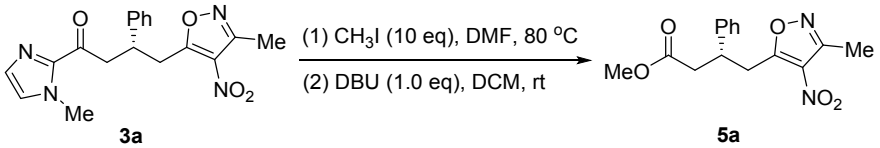



**1a** 1.10 g, 5.12 mmol **2a** 1.47 g, 10.38 mmol **3a** 1.69 g, 93% yield, 95% ee

To an oven-dried 50 mL Schlenk tube equipped with a stir bar, **Λ-Rh1** (0.25 mol%) was added along with *α,β*-unsaturated 2-acyl imidazole **1a** (1.10 g, 5.12 mmol, 1.0 equiv.), DIPEA (50 mol %) and DCE (6 mL). After being stirred at room temperature for 5 min, 3,5-dimethyl-substituted 4-nitroisoxazole **2a** (1.47 g, 10.38 mmol, 2.0 equiv.) was added. The reaction was stirring at room temperature until consumption of the 2-acyl imidazole as monitored by TLC for 26 h. The reaction mixture was

concentrated and directly purified by silica gel column chromatography (EtOAc/Petroleum ether = 1:4-1:3) to afford **3a** (white solid, 1.69 g, 93% yield, 95% ee).

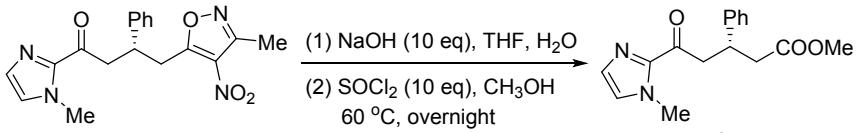
**General procedure for synthetic transformation.**




**3a**
120 mg, 95% ee

**5a**
86% yield, 95 % ee

A solution of **3a** (120 mg, 0.34 mmol, 1 equiv.) and methyl iodide (10 equiv.) in DMF (2 ml) was stirred in a sealed tube at 80 °C overnight, after **3a** was fully converted to salt (monitored by TLC), the reaction was cooled down to room temperature. The reaction mixture was concentrated and $CH_3OH$ (2 mL) was added to the mixture, and then DBU (10 equiv.) was added to the solution. The resulting mixture was stirred for 12 hours at room temperature before it was quenched with $NH_4Cl$ (20 mL, sat. aq.), the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (20 mL), dried ($Na_2SO_4$) and concentrated in vacuo. Flash column chromatography (silica gel) afforded the desired product **5a** (89 mg, 86% yield, 95% ee).

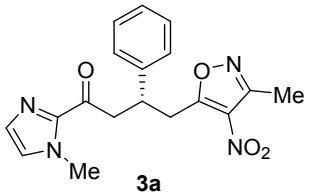



**3a**
120 mg, 95% ee

**6a**
93% yield, 90% ee

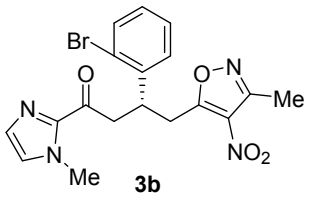
To the compound **3a** (120 mg, 0.34 mmol, 1 equiv.) in 5 mL solvent (5:1 THF/$H_2O$) was added NaOH (10 equiv.) at 0 °C. The resulting mixture was refluxed for 3 h. The reaction mixture was quenched with 4 M aqueous HCl and the solvent was removed under reduced pressure. The remaining precipitation dissolves in methanol, and then 5 mL $SOCl_2$ was added to the above reaction solution. The reaction was stirred at 60 °C overnight. After evaporation of solvent, dissolved the crude product in 20 mL

saturated sodium carbonate solution and 30 mL ethyl acetate, then the reaction was stirred under the room temperature for 120 min. The aqueous layer was extracted three times with ethyl acetate (20 mL × 3). The combined organic layer was dried over $Na_2SO_4$. The volatile solvent was removed under reduced pressure at last, the product **6a** was obtained after purified by flash column chromatography on silica gel (90 mg, 93% yield, 90% ee) as light yellow oil.



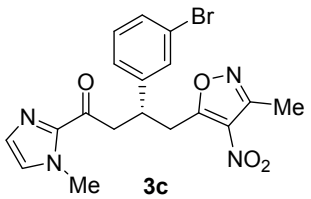

**3a**

White solid, m.p. 119.1-119.5 °C, 68 mg, 96% yield, 95% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, tr (major) = 9.50 min, tr (minor) = 10.88 min); $[\alpha]_D^{25}$ = +16.8 (c = 0.5, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 4.3 Hz, 4H), 7.20-7.18 (m, 1H), 7.13 (s, 1H), 7.01 (s, 1H), 4.01-3.92 (m, 1H), 3.91 (s, 3H), 3.74-3.62 (m, 2H), 3.58-3.50 (m, 2H), 2.47 (s, 3H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ = 189.9, 173.2, 155.4, 142.8, 141.8, 130.4, 129.2, 128.7, 127.3, 127.2, 44.5, 38.9, 36.2, 34.2, 11.7. IR (KBr): *v* ($cm^{-1}$) 2921, 2851, 2359, 1676, 1603, 1519, 1415, 1379, 1365, 1289, 1075, 985, 915, 829. HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{18}N_4NaO_4$ $[M+Na]^+$: 377.1219, found: 377.1220.




**3b**

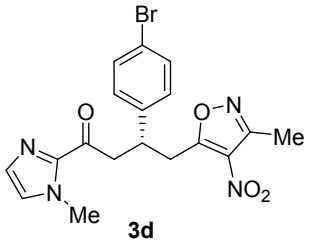
Light yellow oil, 79 mg, 92% yield, 97% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, tr (major) = 9.74 min, tr (minor) = 10.93 min); $[\alpha]_D^{25}$ = +8.4 (c = 0.5, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.26 (d, *J* = 7.8 Hz, 1H), 7.13 (s, 1H), 7.13-7.03 (m, 1H), 7.03 (s, 1H), 4.58-4.51 (m, 1H), 3.94 (s, 3H), 3.68-3.56 (m, 4H), 2.49 (s, 3H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ = 189.4, 172.5, 155.4, 142.7, 140.7, 133.3, 130.6, 129.2, 128.7, 127.9, 127.3, 124.5, 43.6, 37.4, 36.2, 32.8, 11.7. IR (KBr): *v* ($cm^{-1}$) 2922, 2852, 2361, 1675, 1603, 1519, 1413, 1379, 1365, 1289, 1155, 1023, 985, 829, 759. HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{17}BrN_4NaO_4$ $[M+Na]^+$: 455.0324, found: 455.0325.




**3c**

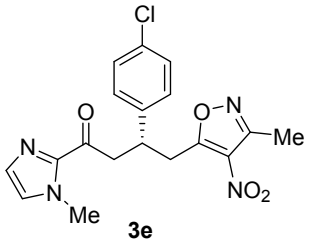
Yellow oil, 75 mg, 87% yield, 95% ee (HPLC: chiralpak IC column, 254 nm,

hexane/isopropanol = 80/20, flow rate 1.0 mL/min, tr (major) = 8.21 min, tr (minor) = 8.93 min); $[\alpha]_D^{25}$ = +12.4 (c = 0.5, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.42 (s, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.20-7.10 (m, 1H), 7.14 (s, 1H), 7.04 (s, 1H), 4.00-3.95 (m, 1H), 3.93 (s, 3H), 3.71-3.50 (m, 4H), 2.49 (s, 3H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ = 189.3, 172.6, 155.5, 144.2, 142.5, 130.5, 130.4, 130.3, 129.2, 127.4, 126.0, 122.7, 44.3, 38.5, 36.2, 34.0, 11.6. IR (KBr): *v* ($cm^{-1}$) 2923, 2360, 1676, 1615, 1519, 1413, 1383, 1289, 984. HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{17}BrN_4NaO_4$ $[M+Na]^+$: 455.0325, found: 455.0325.




**3d**

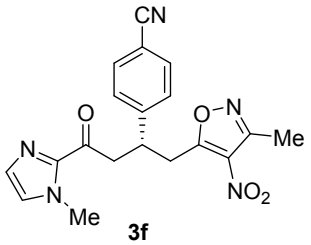
Light yellow oil, 77 mg, 89% yield, 96% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, tr (major) = 8.58 min, tr (minor) = 9.40 min); $[\alpha]_D^{25}$ = +15.9 (c = 0.5, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.13 (s, 1H), 7.03 (s, 1H), 4.01-3.96(m, 1H), 3.92 (s, 3H), 3.73-3.60 (m, 2H), 3.53-3.46 (m, 2H), 2.49 (s, 3H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ = 189.5, 172.7, 155.5, 142.7, 140.8, 131.8, 130.4, 129.3, 129.1, 127.4, 121.1, 44.3, 38.3, 36.2, 34.0, 11.7. IR (KBr): *v* ($cm^{-1}$) 2922, 2360, 1674, 1603, 1519, 1414, 1382, 1289, 985, 828. HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{17}BrN_4NaO_4$ $[M+Na]^+$: 455.0322, found: 455.0325.




**3e**

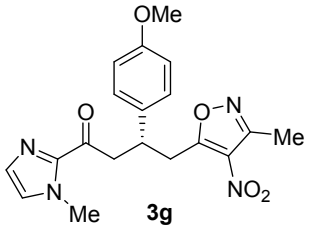
Light yellow oil, 74 mg, 95% yield, 96% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, tr (major) = 8.24 min, tr (minor) = 9.05 min); $[\alpha]_D^{25}$ = +12.1 (c = 0.5, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.22 (brs,

4H), 7.13 (s, 1H), 7.03 (s, 1H), 4.03-3.95(m, 1H), 3.92 (s, 3H), 3.73-3.60 (m, 2H), 3.54-3.47 (m, 2H), 2.49 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ = 189.5, 172.8, 155.5, 142.7, 140.3, 132.9, 130.4, 129.3, 128.9, 128.7, 127.4, 44.4, 38.3, 36.2, 34.1, 11.7. IR (KBr): *v* ($cm^{-1}$) 2922, 2360, 2340, 1674, 1603, 1519, 1492, 1415, 1380, 1092, 829. HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{17}ClN_4NaO_4$ $[M+Na]^+$: 411.0841, found: 411.0831.




**3f**

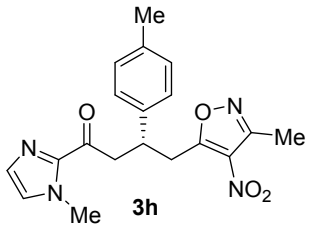
Light yellow oil, 68 mg, 90% yield, 92% ee (HPLC: chiralpak OD-H column, 254 nm, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, tr (major) = 14.08 min, tr (minor) = 16.97 min); $[\alpha]_D^{25}$ = +7.8 (c = 0.5, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.15 (s, 1H), 7.06 (s, 1H), 4.10-4.00 (m, 1H), 3.93 (s, 3H), 3.79-3.73 (m, 1H), 3.69-3.63 (m, 1H), 3.58-3.52 (m, 2H), 2.49 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ = 188.9, 172.2, 155.6, 147.3, 142.3, 132.6, 130.5, 129.2, 128.3, 127.6, 118.6, 111.3, 44.1, 38.8, 36.2, 33.7, 11.6. IR (KBr): *v* ($cm^{-1}$) 2922, 2360, 1672, 1603, 1593, 1517, 1409, 1385, 1366, 702. HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{17}N_5NaO_4$ $[M+Na]^+$: 402.1170, found: 402.1173.




**3g**

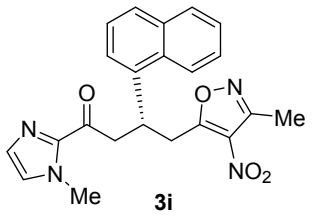
Light yellow oil, 65 mg, 85% yield, 94% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, tr (major) = 13.38 min, tr (minor) = 15.38 min); $[\alpha]_D^{25}$ = +18.0 (c = 0.5, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.18 (d, *J* = 8.5 Hz, 2H), 7.12 (s, 1H), 7.01 (s, 1H), 6.78 (d, *J* = 8.5 Hz, 2H), 3.99-3.95 (m, 1H), 3.91 (s, 3H), 3.74 (s, 3H), 3.71-3.59 (m, 2H), 3.53-3.46 (m, 2H), 2.47 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ = 190.0, 173.3, 158.5, 155.4, 142.8, 133.8, 130.4,

129.2, 128.3, 127.2, 114.0, 55.2, 44.7, 38.2, 36.1, 34.4, 11.7. IR (KBr): *v* ($cm^{-1}$) 2923, 2360, 2341, 1672, 1604, 1514, 1410, 1382, 1249, 985, 829. HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{20}N_4NaO_5$ $[M+Na]^+$: 407.1326, found: 407.1326.




**3h**

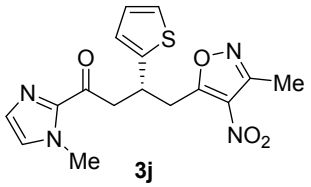
Light yellow oil, 66 mg, 90% yield, 94% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, tr (major) = 9.90 min, tr (minor) = 10.99 min); $[\alpha]_D^{25}$ = +14.3 (c = 0.5, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.15 (d, *J* = 7.9 Hz, 2H), 7.12 (s, 1H), 7.06 (d, *J* = 7.9 Hz, 2H), 7.01 (s, 1H), 3.98-3.94 (m, 1H), 3.91 (s, 3H), 3.71-3.59 (m, 2H), 3.56-3.47 (m, 2H), 2.47 (s, 3H), 2.27 (s, 3H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ = 190.0, 173.3, 155.4, 142.8, 138.8, 136.8, 130.4, 129.4, 129.2, 127.2, 127.1, 44.6, 38.5, 36.2, 34.3, 21.1, 11.7. IR (KBr): *v* ($cm^{-1}$) 2922, 2360, 2341, 1673, 1603, 1518, 1492, 1410, 1379, 1365, 985, 829. HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{20}N_4NaO_4$ $[M+Na]^+$: 391.1376, found: 391.1377.




**3i**

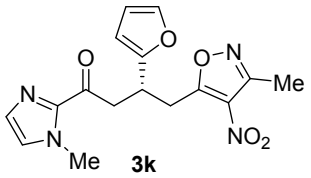
White solid, 75 mg, m.p. 130.1-130.5 °C, 93% yield, 96% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, tr (major) = 9.98 min, tr (minor) = 10.92 min); $[\alpha]_D^{25}$ = +13.2 (c = 0.5, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.56-7.39 (m, 4H), 7.13 (s, 1H), 6.99 (s, 1H), 4.98 (brs, 1H), 3.85 (s, 3H), 3.83-3.60 (m, 4H), 2.41 (s, 3H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ = 190.0, 173.0, 155.4, 142.7, 138.1, 133.9, 131.1, 130.5, 129.3, 129.0, 127.8, 127.3, 126.5, 125.7, 125.5, 123.5, 122.6, 44.5, 36.1, 33.7, 32.8, 11.6. IR (KBr): *v* ($cm^{-1}$) 2921, 2851, 2361, 2341,

1672, 1601, 1518, 1409, 1155, 829, 778. HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{20}N_4NaO_4$ $[M+Na]^+$: 427.1377, found: 427.1377.



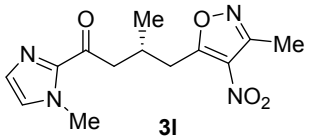
**3j**

Light yellow oil, 66 mg, 91% yield, 95% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, tr (major) = 11.20 min, tr (minor) = 12.22 min); $[\alpha]_D^{25}$ = +16.7 (c = 0.5, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.18-7.11 (m, 1H), 7.13 (s, 1H), 7.04 (s, 1H), 6.86 (t, *J* = 3.5 Hz, 2H), 4.37-4.30 (m, 1H), 3.95 (s, 3H), 3.77-3.65 (m, 2H), 3.60-3.54 (m, 2H), 2.50 (s, 3H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ = 189.3, 172.6, 155.5, 145.2, 142.6, 130.6, 129.3, 127.4, 126.8, 124.5, 124.1, 45.4, 36.2, 35.1, 34.2, 11.7. IR (KBr): *v* ($cm^{-1}$) 2361, 2341, 1675, 1603, 1519, 1414, 1378, 981, 915, 829, 703. HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{16}N_4NaO_4S$ $[M+Na]^+$: 383.0785, found: 383.0784.



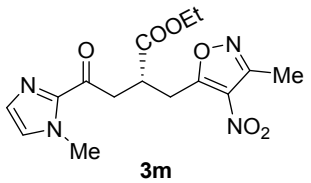
**3k**

Light yellow oil, 60 mg, 87% yield, 93% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 87/13, flow rate 1.0 mL/min, tr (major) = 16.37 min, tr (minor) = 17.80 min); $[\alpha]_D^{25}$ = +27.6 (c = 0.5, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.29 (s, 1H), 7.14 (s, 1H), 7.05 (s, 1H), 6.22 (m, 1H), 6.06 (d, *J* = 3.2 Hz, 1H), 4.14-4.06 (m, 1H), 3.97 (s, 3H), 3.73-3.64 (m, 2H), 3.58-3.47 (m, 2H), 2.52 (s, 3H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ = 189.4, 172.7, 155.5, 154.6, 142.6, 141.9, 130.5, 129.3, 127.3, 110.2, 106.0, 42.1, 36.2, 32.5, 31.9, 11.7. IR (KBr): *v* ($cm^{-1}$) 2922, 2361, 2341, 1675, 1604, 1519, 1415, 1380, 1151, 915, 830. HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{16}N_4NaO_5$ $[M+Na]^+$: 367.1013, found: 367.1013.



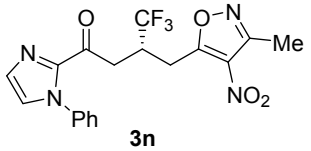
**3l**

Light yellow oil, 47 mg, 80% yield, 94% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 94/6, flow rate 1.0 mL/min, tr (major) = 21.72 min, tr (minor) = 23.38 min); $[\alpha]_D^{25}$ = +9.2 (c = 0.5, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.13 (s, 1H), 7.05 (s, 1H), 4.00 (s, 3H), 3.32-3.12 (m, 4H), 2.84-2.76 (m, 1H), 2.55 (s, 3H), 1.10 (d, *J* = 6.8 Hz, 3H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ = 191.0, 174.0, 155.6, 142.9, 130.4, 129.0, 127.2, 45.2, 36.3, 33.9, 28.6, 20.3, 11.7. IR (KBr): *v* ($cm^{-1}$) 2360, 2341, 1690, 1609, 1521, 1418, 1382, 1169, 829. HRMS (ESI, *m*/*z*) calcd for $C_{13}H_{16}N_4NaO_4$ $[M+Na]^+$: 315.1062, found: 315.1064.




**3m**

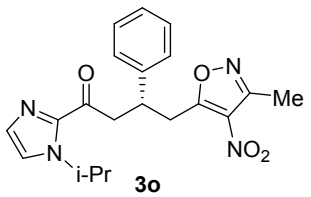
Light yellow oil, 62 mg, 89% yield, 93% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 75/25, flow rate 1.0 mL/min, tr (major) = 17.74 min, tr (minor) = 22.34 min); $[\alpha]_D^{25}$ = +5.6 (c = 0.5, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.08 (s, 1H), 6.99 (s, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 3H), 3.68-3.58(m, 2H), 3.53-3.35 (m, 3H), 2.49 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ = 188.0, 171.6, 171.5, 154.6, 141.2, 129.4, 128.2, 126.3, 60.4, 39.0, 36.8, 35.2, 28.1, 12.9, 10.6. IR (KBr): *v* ($cm^{-1}$) 2921, 2360, 2341, 1734, 1679, 1607, 1520, 1417, 1383, 1155, 829. HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{18}N_4NaO_6$ $[M+Na]^+$: 373.1120, found: 373.1119.




**3n**

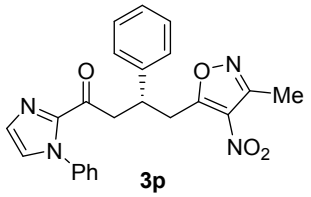
Light yellow oil, 68 mg, 83% yield, 97% ee (HPLC: chiralpak AD-H column, 254 nm, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, tr (major) = 11.74 min, tr (minor) = 9.50 min); $[\alpha]_D^{25}$ = -15.0 (c = 0.5, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.49-7.43 (m, 3H), 7.29-7.18 (m, 4H), 3.68-3.58 (m, 2H), 3.54-3.45 (m, 2H), 3.28 (dd, *J* = 14.8, 7.2 Hz, 1H), 2.50 (s, 3H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ = 185.8, 170.8, 155.7, 141.9, 137.9, 130.7, 130.1, 129.1, 129.0, 127.9, 126.8 (q, *J* = 279.7 Hz), 125.9, 37.4, 36.6 (q, *J* = 27.8 Hz), 26.6 (q, *J* = 2.8 Hz), 11.6. $^{19}F$ NMR (376.4 MHz, $CDCl_3$): δ = -

71.7. IR (KBr): *v* ($cm^{-1}$) 2360, 2341, 1690, 1608, 1521, 1418, 1382, 1168, 829. HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{15}F_3N_4NaO_4$ $[M+Na]^+$: 431.0936, found: 431.0938.



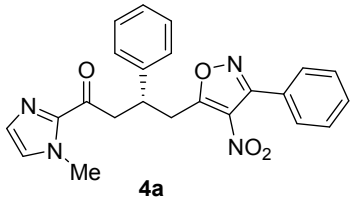

**3o**

Light yellow oil, 73 mg, 95% yield, 92% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, tr (major) = 9.19 min, tr (minor) = 8.30 min); $[\alpha]_D^{25}$ = -17.2 (c = 0.5, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.27-7.23 (m, 5H), 7.20-7.14 (m, 2H), 5.46-5.36 (m, 1H), 4.04-3.96 (m, 1H), 3.74-3.50 (m, 4H), 2.47 (s, 3H), 1.38 (d, *J* = 6.6 Hz, 3H), 1.35 (d, *J* = 6.6 Hz, 3H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ = 190.1, 173.2, 155.4, 142.0, 141.8, 130.4, 129.7, 128.7, 127.3, 127.2, 121.4, 49.2, 45.1, 39.0, 34.3, 23.6, 23.4, 11.6. IR (KBr): *v* ($cm^{-1}$) 2361, 2341, 1674, 1603, 1519, 1396, 1381, 1365, 1255, 985, 829. HRMS (ESI, *m*/*z*) calcd for $C_{20}H_{22}N_4NaO_4$ $[M+Na]^+$: 405.1531, found: 405.1533.



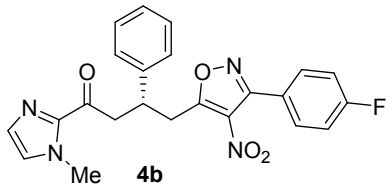

**3p**

Light yellow oil, 75 mg, 90% yield, 95% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, tr (major) = 11.63 min, tr (minor) = 14.78 min); $[\alpha]_D^{25}$ = -31.3 (c = 0.5, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.43-7.38 (m, 3H), 7.26-7.11 (m, 9H), 3.98-3.91 (m, 1H), 3.74-3.54 (m, 3H), 3.50-3.44 (m, 1H), 2.45 (s, 3H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ = 188.5, 173.1, 155.4, 142.7, 141.8, 138.1, 130.4, 129.7, 129.0, 128.8, 128.7, 127.4, 127.3, 125.8, 44.7, 38.8, 34.2, 11.7. IR (KBr): *v* ($cm^{-1}$) 2923, 2360, 2341, 1685, 1602, 1517, 1493, 1407, 1378, 1364, 829, 763, 700. HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{20}N_4NaO_4$ $[M+Na]^+$: 439.1375, found: 439.1377.



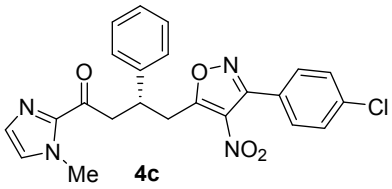

**4a**

Light yellow oil, 73 mg, 88% yield, 90% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, tr (major) = 9.39 min, tr (minor) = 10.57 min); $[\alpha]_D^{25}$ = +18.7 (c = 0.5, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.53-7.44 (m, 5H),7.31-7.18 (m, 5H), 7.14 (s, 1H), 7.01 (s, 1H), 4.10-4.03 (m, 1H), 3.91 (s, 3H), 3.78-3.57 (m, 4H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ = 189.9, 173.8, 157.6, 142.8, 141.8, 130.7, 129.8, 129.2, 128.8, 128.5, 127.3, 125.8, 44.4, 38.9, 36.2, 34.5. IR (KBr): *v* ($cm^{-1}$) 2922, 2851, 2360, 2341, 1676, 1636, 1617, 1593, 1515, 1413, 1367, 829. HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{20}N_4NaO_4$ $[M+Na]^+$: 439.1375, found: 439.1377.




**4b**

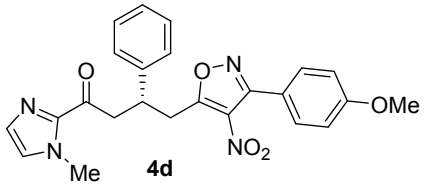
Light yellow oil, 78 mg, 90% yield, 95% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, tr (major) = 8.45 min, tr (minor) = 9.30 min); $[\alpha]_D^{25}$ = +7.9 (c = 0.5, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.55-7.51 (m, 2H), 7.31-7.26 (m, 4H), 7.21-7.12 (m, 4H), 7.01 (s, 1H), 4.09-4.02 (m, 1H), 3.90 (s, 3H), 3.78-3.57 (m, 4H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ = 189.8, 174.1, 164.2 (d, *J* = 249.9 Hz), 156.7, 142.7, 141.8, 131.5 (d, *J* = 8.7 Hz), 129.7, 129.2, 128.8, 127.3, 127.3, 121.9 (d, *J* = 3.5 Hz), 115.7 (d, *J* = 21.9 Hz), 44.5, 38.9, 36.2, 34.5. $^{19}F$ NMR (376.4 MHz, $CDCl_3$): δ = -109.2. IR (KBr): *v* ($cm^{-1}$) 2922, 2360, 2341, 1674, 1606, 1617, 1593, 1515, 1413, 1367, 828, 699. HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{19}FN_4NaO_4$ $[M+Na]^+$: 457.1283, found: 457.1283.




**4c**

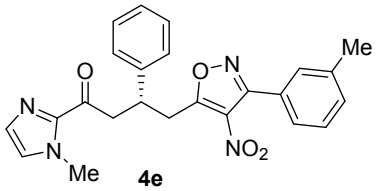
White solid, 83 mg, m.p. 128.4-128.8 °C, 92% yield, 95% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, tr (major) = 8.83

min, tr (minor) = 9.69 min); $[\alpha]_D^{25}$ = +8.0 (c = 0.5, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.48-7.41 (m, 4H), 7.31-7.25 (m, 4H), 7.21-7.18 (m, 1H), 7.13 (s, 1H), 7.01 (s, 1H), 4.10-4.02 (m, 1H), 3.90 (s, 3H), 3.77-3.57 (m, 4H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ = 189.8, 174.2, 156.7, 142.7, 141.7, 137.0, 130.7, 129.7, 129.2, 128.8, 127.6, 127.4, 127.3, 124.3, 44.5, 38.9, 36.2, 34.5. IR (KBr): *v* ($cm^{-1}$) 2918, 2849, 2360, 2341, 1671, 1604, 1521, 1507, 1409, 1384, 831, 701. HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{19}ClN_4NaO_4$ $[M+Na]^+$: 473.0983, found: 473.0987.




**4d**

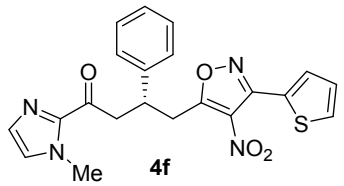
White solid, 85 mg, m.p. 126.5-126.9 °C, 95% yield, 95% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, tr (major) = 13.60 min, tr (minor) = 15.61 min); $[\alpha]_D^{25}$ = +9.1 (c = 0.5, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 8.7 Hz, 2H), 7.31-7.25 (m, 4H), 7.20 (t, *J* = 7.0 Hz, 1H), 7.13 (s, 1H), 7.00 (s, 1H), 6.96 (d, *J* = 8.7 Hz, 2H), 4.09-4.02 (m, 1H), 3.90 (s, 3H), 3.84 (s, 3H), 3.77-3.55 (m, 4H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ = 189.9, 173.8, 161.5, 157.2, 142.7, 141.9, 130.8, 129.8, 129.2, 128.8, 127.4, 127.3, 117.9, 113.9, 55.4, 44.4, 38.9, 36.2, 34.5. IR (KBr): *v* ($cm^{-1}$) 2924, 2360, 1674, 1598, 1520, 1411, 1365, 1155, 982, 827, 702. HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{22}N_4NaO_5$ $[M+Na]^+$: 469.1479, found: 469.1482.




**4e**

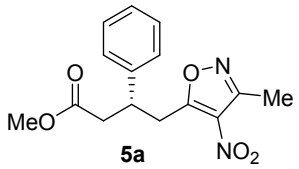
Yellow oil, 77 mg, 90% yield, 95% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, tr (major) = 8.88 min, tr (minor) = 10.15 min); $[\alpha]_D^{25}$ = +4.8 (c = 0.5, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.36-7.25 (m, 8H), 7.20 (t, *J* = 6.8 Hz, 1H), 7.13 (s, 1H), 7.00 (s, 1H), 4.10-4.02 (m, 1H), 3.90 (s, 3H), 3.78-3.55 (m, 4H), 2.40 (s, 3H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ = 189.9, 173.7, 157.7, 142.8, 141.8, 138.3, 131.4, 129.8, 129.7, 129.2, 128.8, 128.4, 127.3,

126.3, 125.7, 44.4, 38.9, 36.2, 34.5, 21.4. IR (KBr): *v* ($cm^{-1}$) 2924, 2360, 1674, 1598, 1520, 1411, 1365, 1155, 982, 702. HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{22}N_4NaO_4$ $[M+Na]^+$: 453.1532, found: 453.1533.



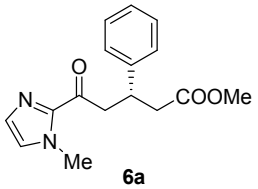
**4f**

White solid, 75 mg, m.p. 120.2-120.5 °C, 89% yield, 95% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, tr (major) = 10.75 min, tr (minor) = 11.80 min); $[\alpha]_D^{25}$ = +13.0 (c = 0.5, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.80 (t, *J* = 3.1 Hz, 1H), 7.53-7.51 (m, 1H), 7.31-7.25 (m, 4H), 7.21-7.12 (m, 3H), 7.00 (s, 1H), 4.08-4.01 (m, 1H), 3.89 (s, 3H), 3.75-3.55 (m, 4H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ = 189.9, 174.5, 151.7, 142.7, 141.8, 131.8, 129.9, 129.4, 129.2, 128.8, 127.8, 127.3, 127.2, 125.6, 44.5, 38.9, 36.2, 34.6. IR (KBr): *v* ($cm^{-1}$) 2922, 2360, 1673, 1594, 1517, 1409, 1385, 1365, 702. HRMS (ESI, *m*/*z*) calcd for $C_{21}H_{18}N_4NaO_4S$ $[M+Na]^+$: 445.0943, found: 445.0941.



**5a**

Light yellow oil, 88.6 mg, 86% yield, 95% ee (HPLC: chiralpak OD-H column, 254 nm, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, tr (major) = 9.88 min, tr (minor) = 15.62 min); $[\alpha]_D^{25}$ = +5.6 (c = 0.5, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.28 (t, *J* = 6.9 Hz, 2H), 7.23-7.19 (m, 3H), 3.82-3.74 (m, 1H), 3.65-3.59 (m, 1H), 3.60 (s, 3H), 3.55-3.49 (m, 1H), 2.82-2.72 (m, 2H), 2.48 (s, 3H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ = 172.8, 171.6, 155.5, 141.1, 130.4, 128.9, 127.5, 127.0, 51.9, 40.3, 39.9, 33.8, 11.6. IR (KBr): *v* ($cm^{-1}$) 2921, 2360, 1733, 1679, 1607, 1520, 1416, 1384, 1155, 829. HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{16}N_2NaO_5$ $[M+Na]^+$: 327.0949, found: 327.0951.




**6a**

Light yellow oil, 90.0 mg, 93% yield, 90% ee (HPLC: chiralpak IC column, 254 nm, hexane/isopropanol = 85/15, flow rate 1.0 mL/min, tr (major) = 11.68 min, tr (minor) = 13.53 min); $[\alpha]_D^{25}$ = +12.3 (c = 0.5, $CHCl_3$). $^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.30-7.22 (m, 4H), 7.19-7.14 (m, 1H), 7.12 (s, 1H), 7.00 (s, 1H), 3.91 (s, 3H), 3.88-3.83 (m, 1H), 3.65 (dd, *J* = 17.0, 7.7 Hz, 1H), 3.57 (s, 3H), 3.47 (dd, *J* = 17.0, 6.7 Hz, 1H), 2.77 (dd, *J* = 15.6, 7.0 Hz, 1H), 2.67 (dd, *J* = 15.6, 8.0 Hz, 1H). $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ = 190.4, 172.3, 143.2, 128.7, 128.5, 127.5, 126.9, 126.7, 51.6, 44.8, 41.0, 37.2, 36.2. IR (KBr): *v* ($cm^{-1}$) 2924, 2361 1733, 1679, 1607, 1520, 1416, 1384, 1155, 828. HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{18}N_2NaO_3$ $[M+Na]^+$: 309.1215, found: 309.1216.

## IV References

(1) (a) C. Wang, L.-A. Chen, H. Huo, X. Shen, K. Harms, L. Gong and E. Meggers, *Chem. Sci.*, 2015, **6**, 1094; (b) G.-J. Sun, J. Gong and O. Kang, *J. Org. Chem.*, 2017, **82**, 796; (c) S.-W. Li, J. Gong and Q. Kang, *Org. Lett*., 2017, **19**, 1350; (d) K. Li, Q. Wan and Q. Kang, *Org. Lett*., 2017, **19**, 3299; (e) S.-X. Lin, G.-J. Sun and Q. Kang, *Chem. Commun.*, 2017, **53**, 7665.

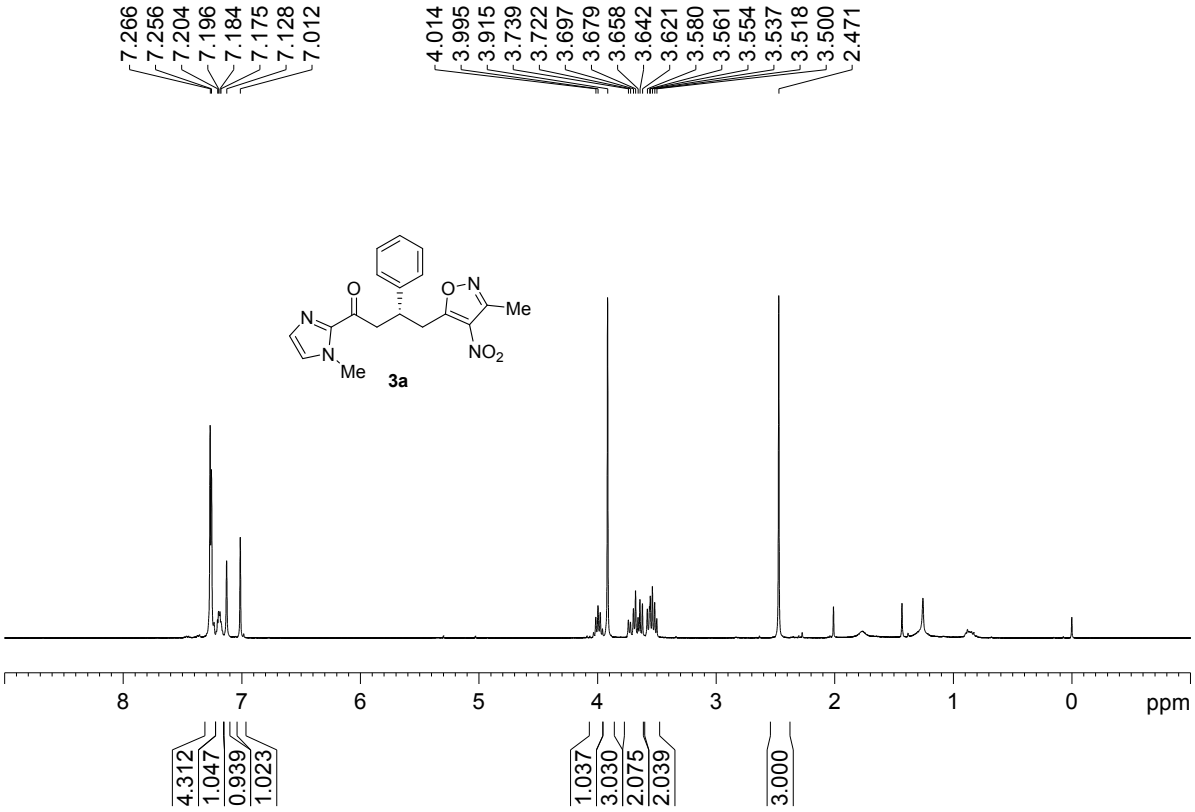
(2) H. Huo, X. Shen, C. Wang, L. Zhang, P. Rose, L.-A. Chen, K. Harms, M. Marsch, G. Hilt and E. Meggers, *Nature*, 2014, **515**, 100.

(3) H. Huo, C. Fu, K. Harms and E. Meggers, *J. Am. Chem. Soc*., 2014, **136**, 2990.

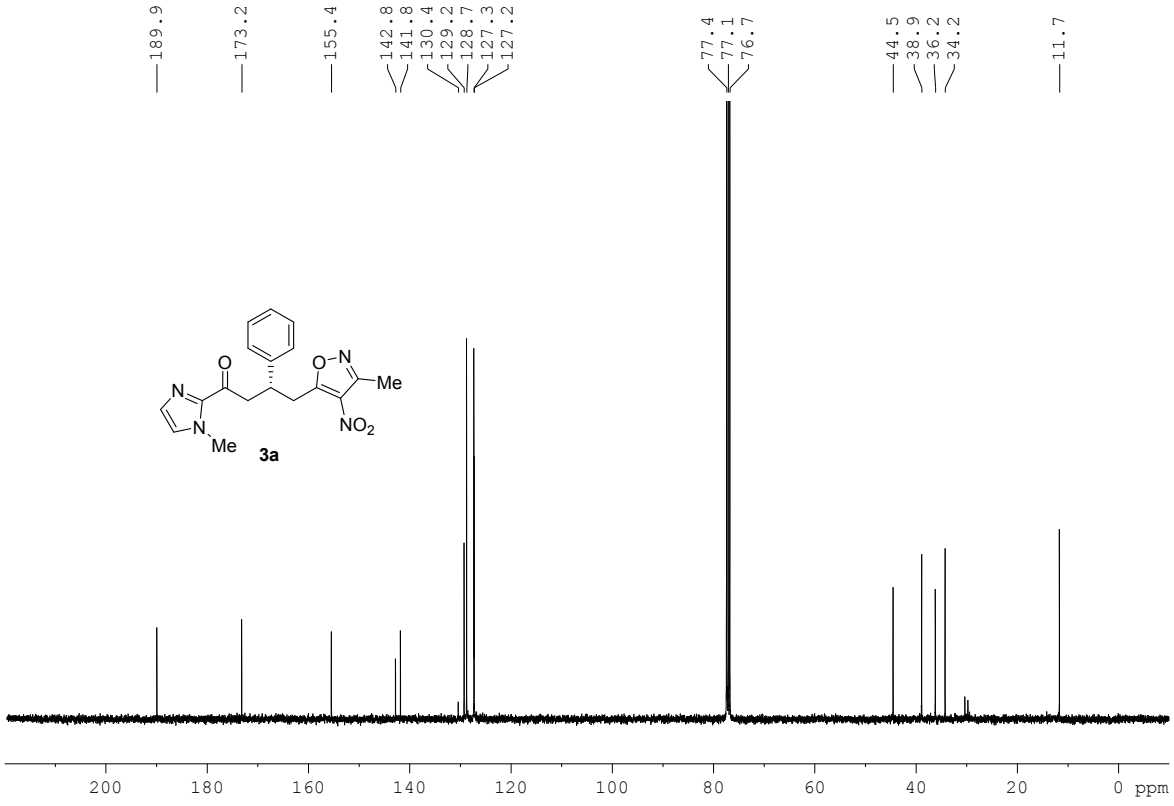
(4) (a) J.-L. Zhang, X.-H. Liu, X.-J. Ma and R. Wang, *Chem. Commun.*, 2013, **49**, 9329; (b) G. Fuller, B. Kelly and M. F. A. Adamo, *Org. Process Res. Dev.*, 2015, **19**, 1274; (c) C. Balsamini, G. Spadoni, L. Staccioli and E. Duranti, *J. Org. Chem.*, 1988, **53**, 2870; (d) S. Chimichi, P. Sarti-Fantoni, A. Buzzi, D. Giomi and R. Nesi, *Heterocycles*, 1985, **23**, 1465.

# V NMR Spectrum

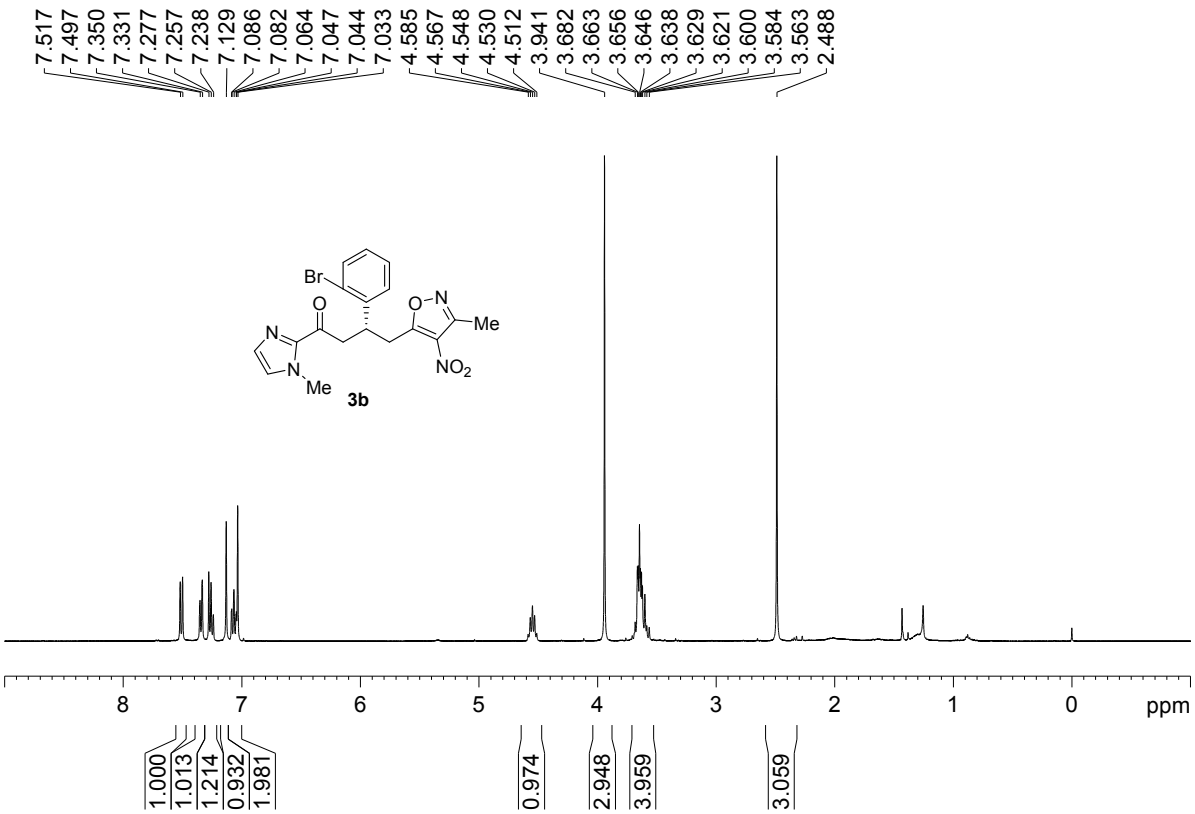
$^{1}$H NMR (400 MHz) spectra of **3a**



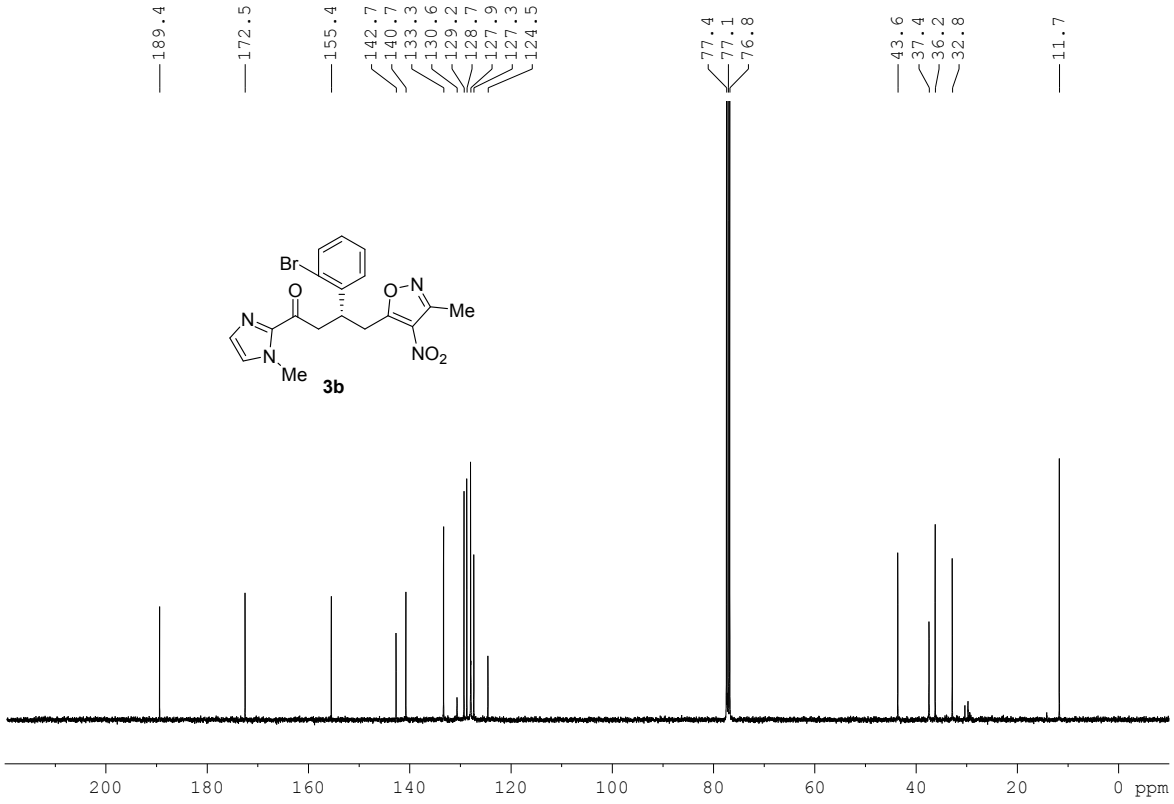

$^{13}$C NMR (100 MHz) spectra of **3a**



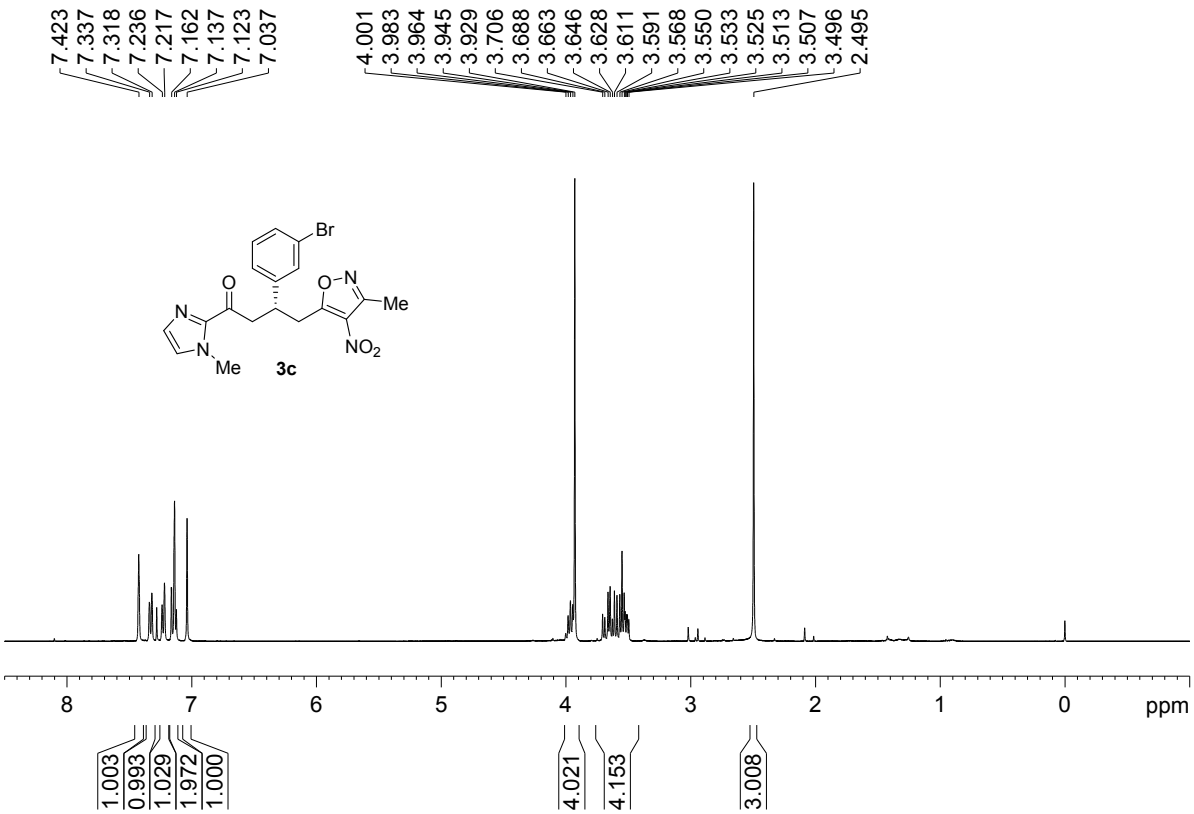
$^{1}$H NMR (400 MHz) spectra of **3b**



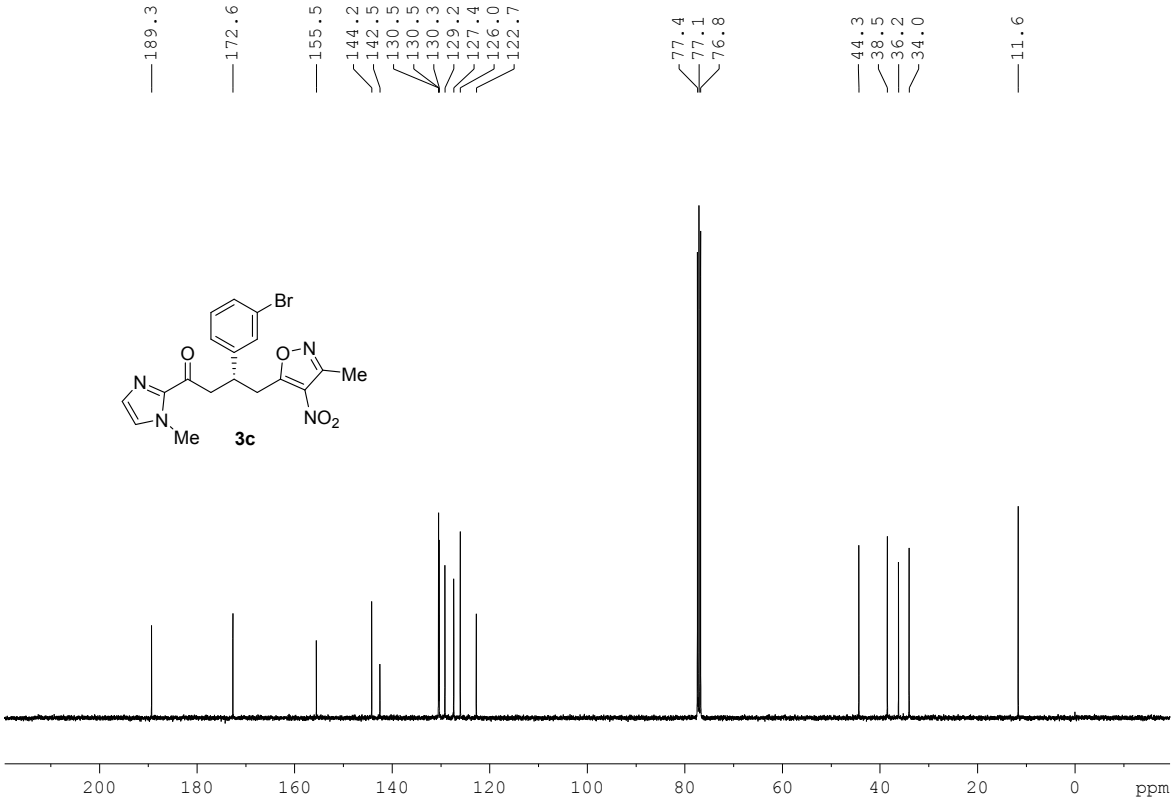

$^{13}$C NMR (100 MHz) spectra of **3b**



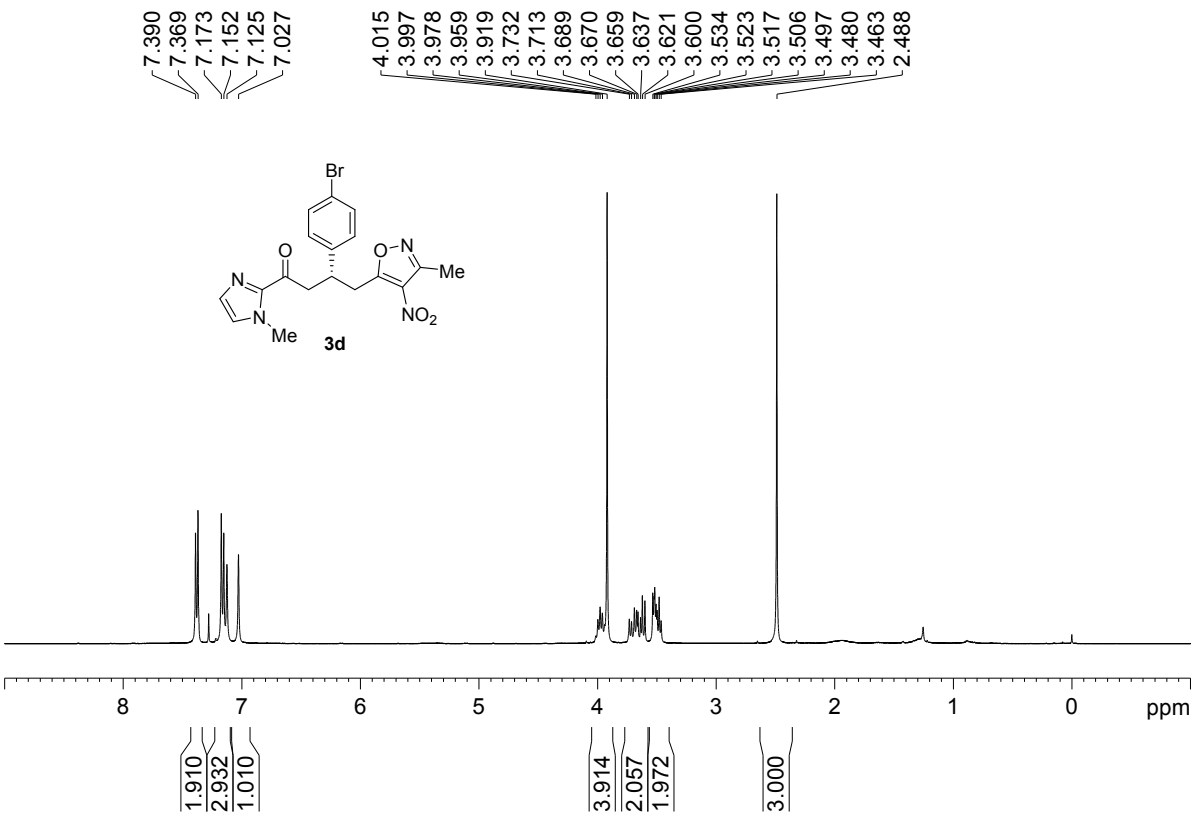
$^{1}$H NMR (400 MHz) spectra of **3c**



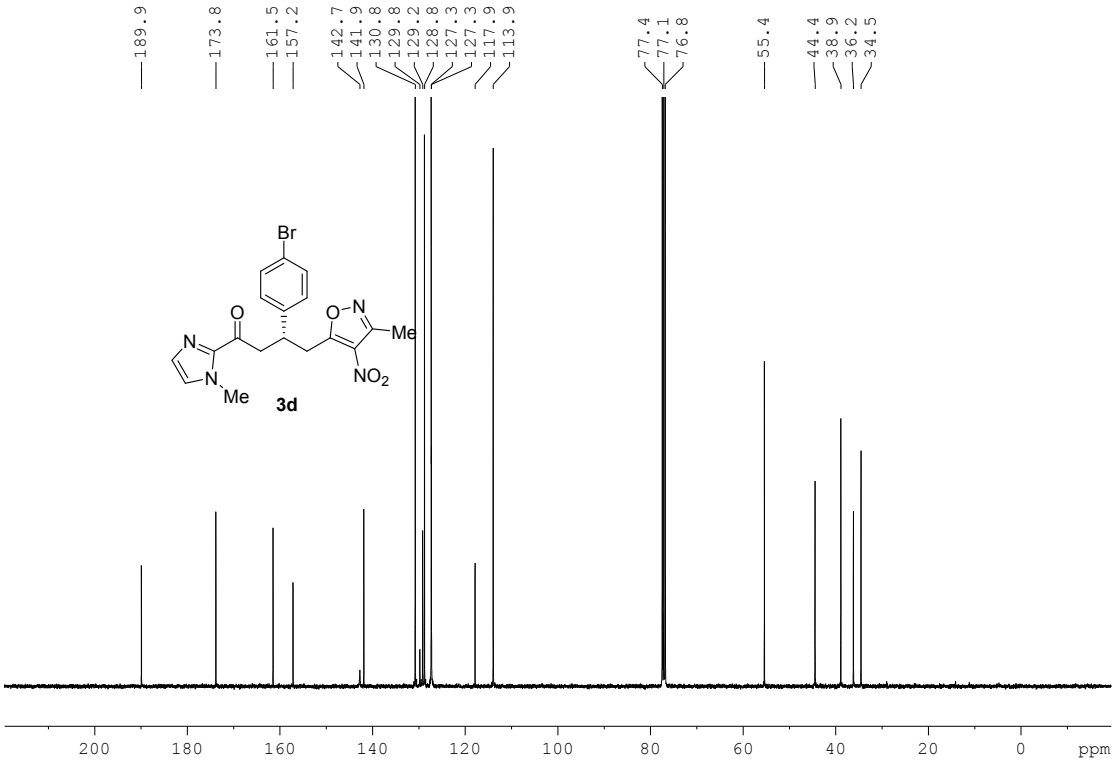

$^{13}$C NMR (100 MHz) spectra of **3c**



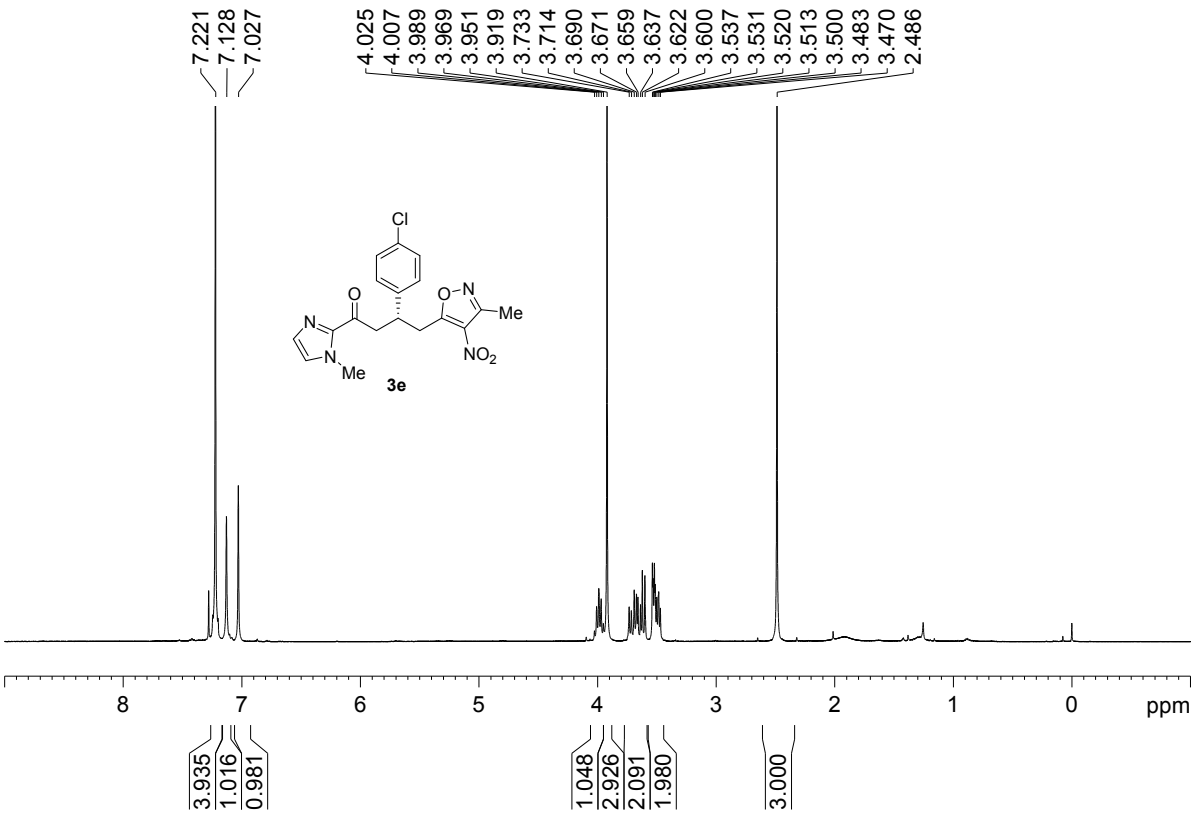
$^{1}$H NMR (400 MHz) spectra of **3d**




$^{13}$C NMR (100 MHz) spectra of **3d**



$^{1}$H NMR (400 MHz) spectra of **3e**

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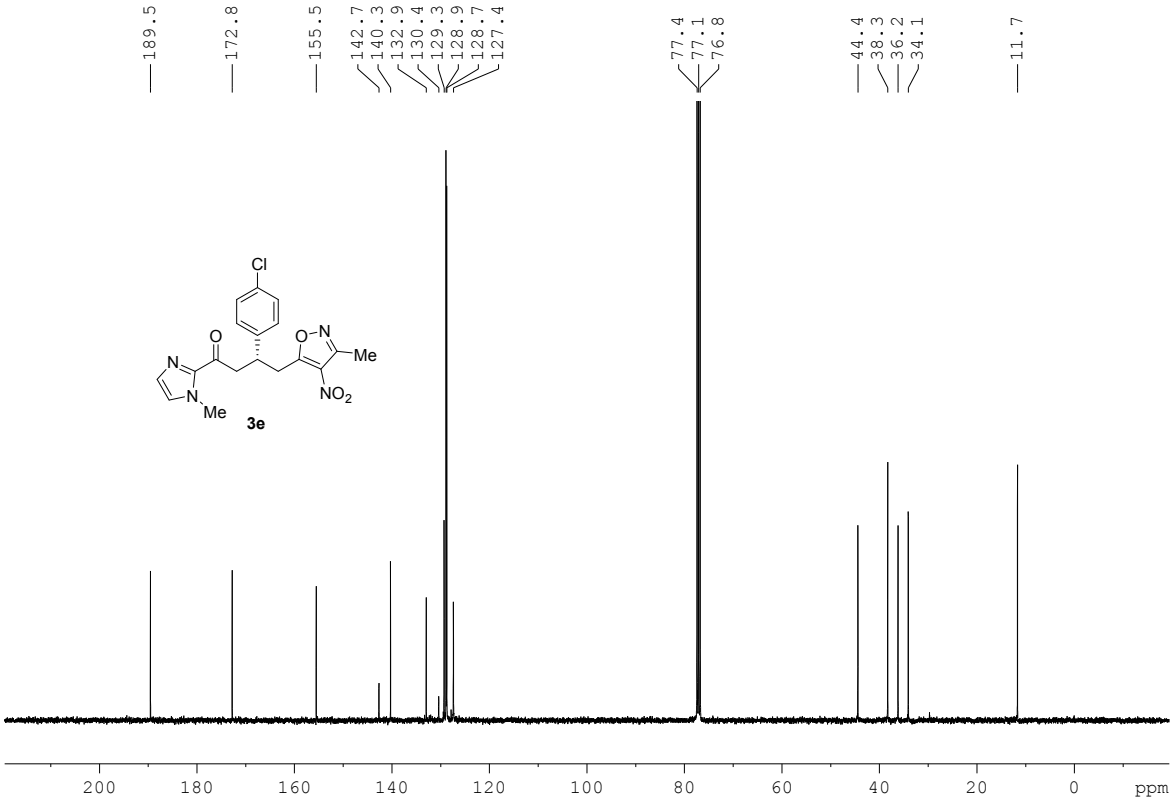
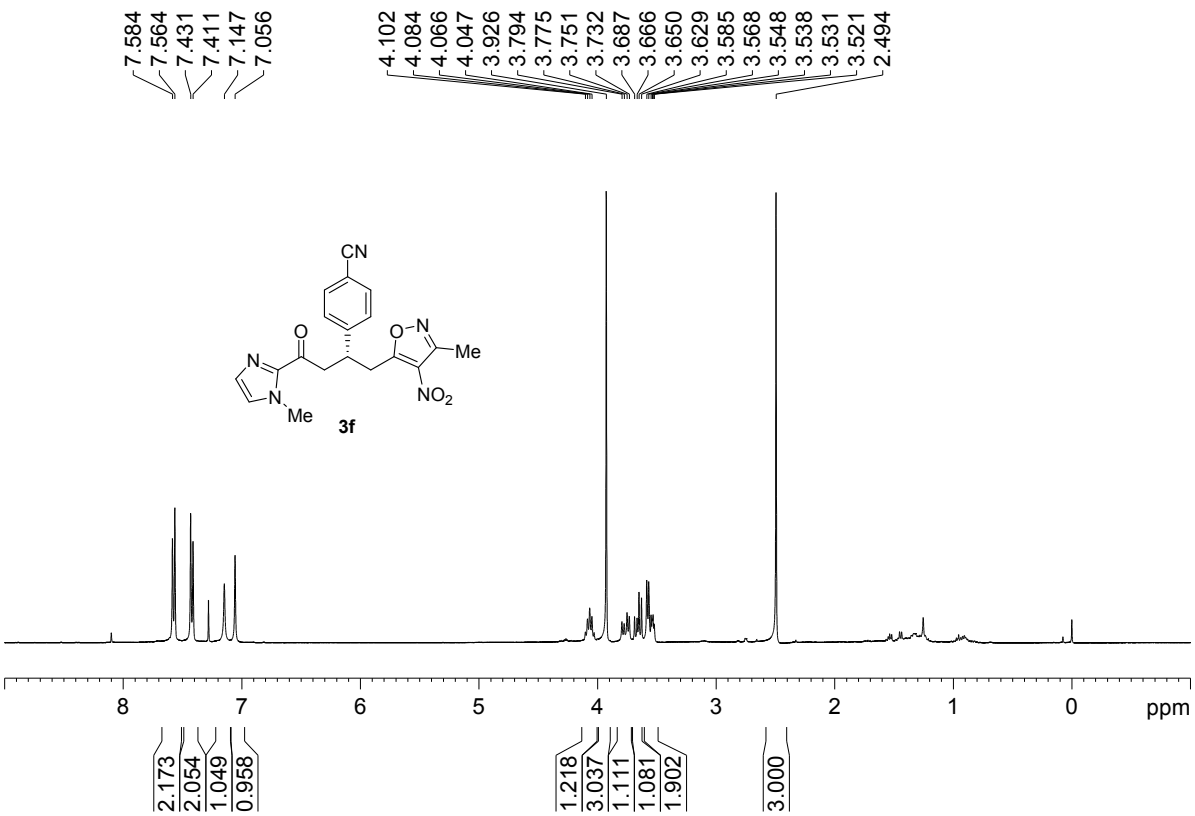
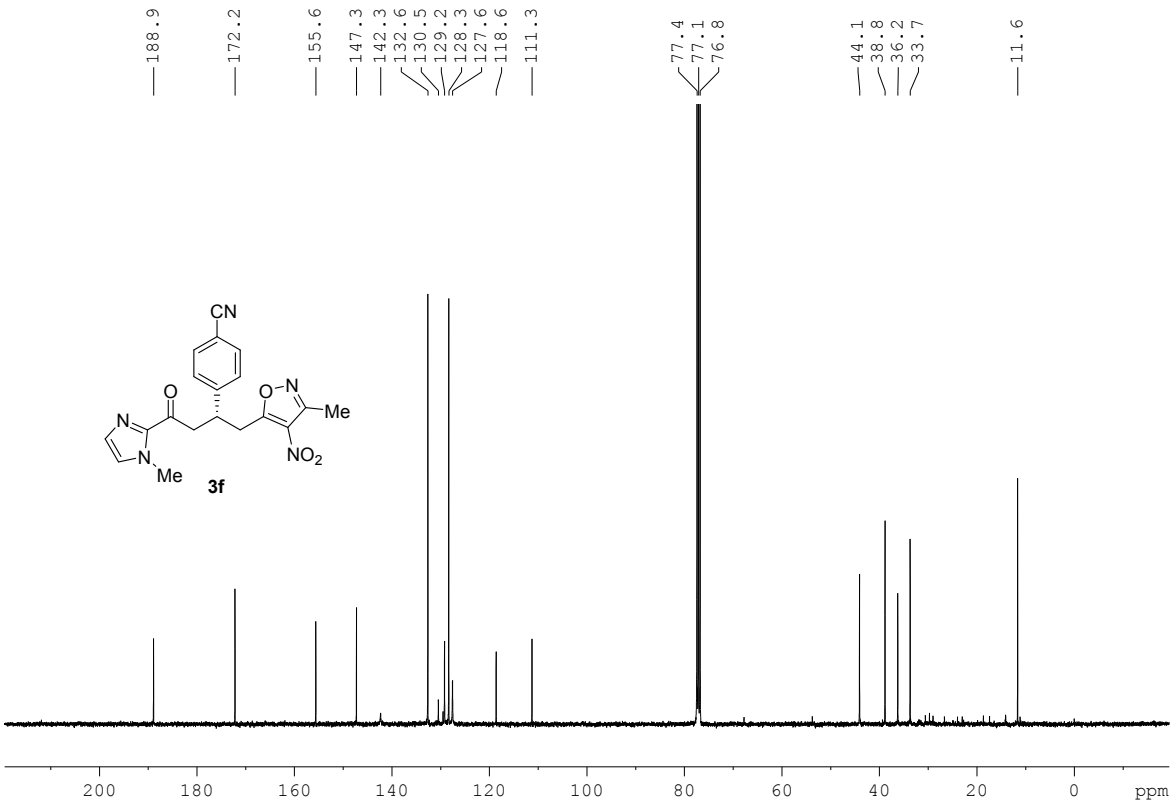


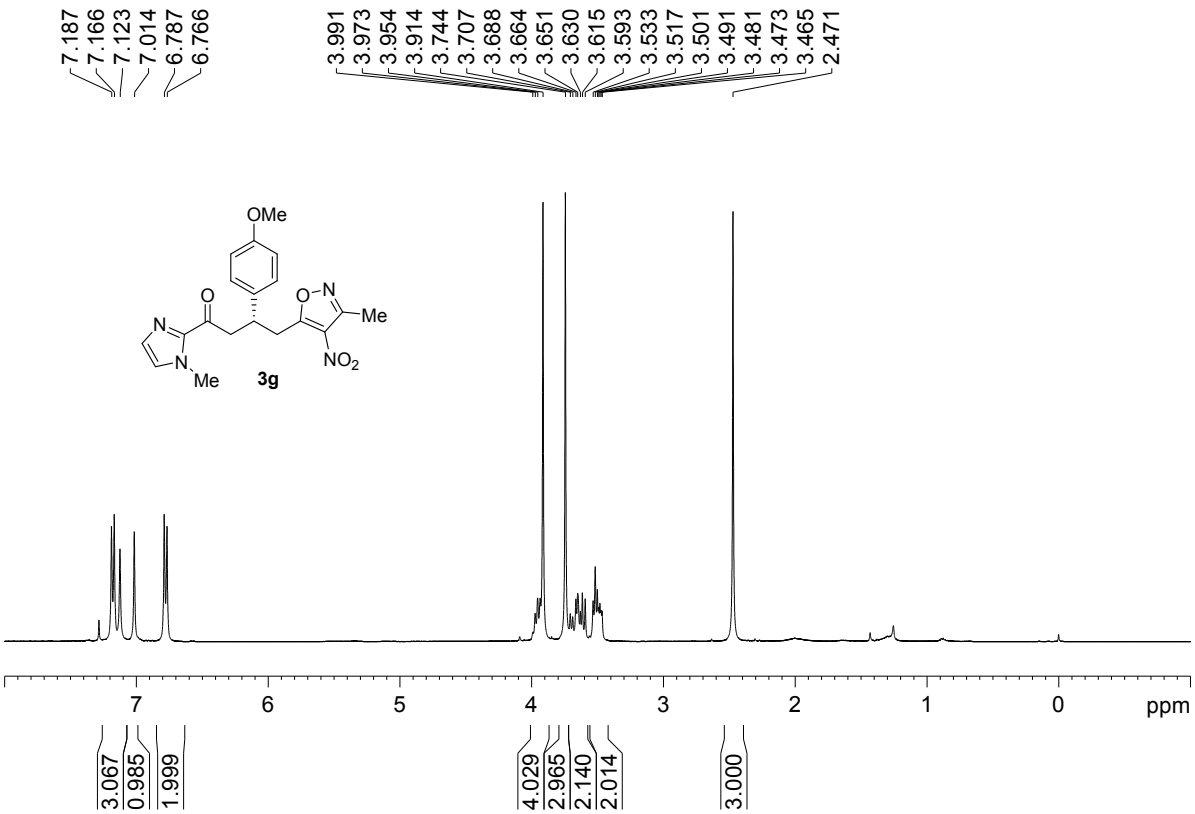
$^{1}$H NMR (400 MHz) spectra of **3f**




$^{13}$C NMR (100 MHz) spectra of **3f**



$^{1}$H NMR (400 MHz) spectra of **3g**

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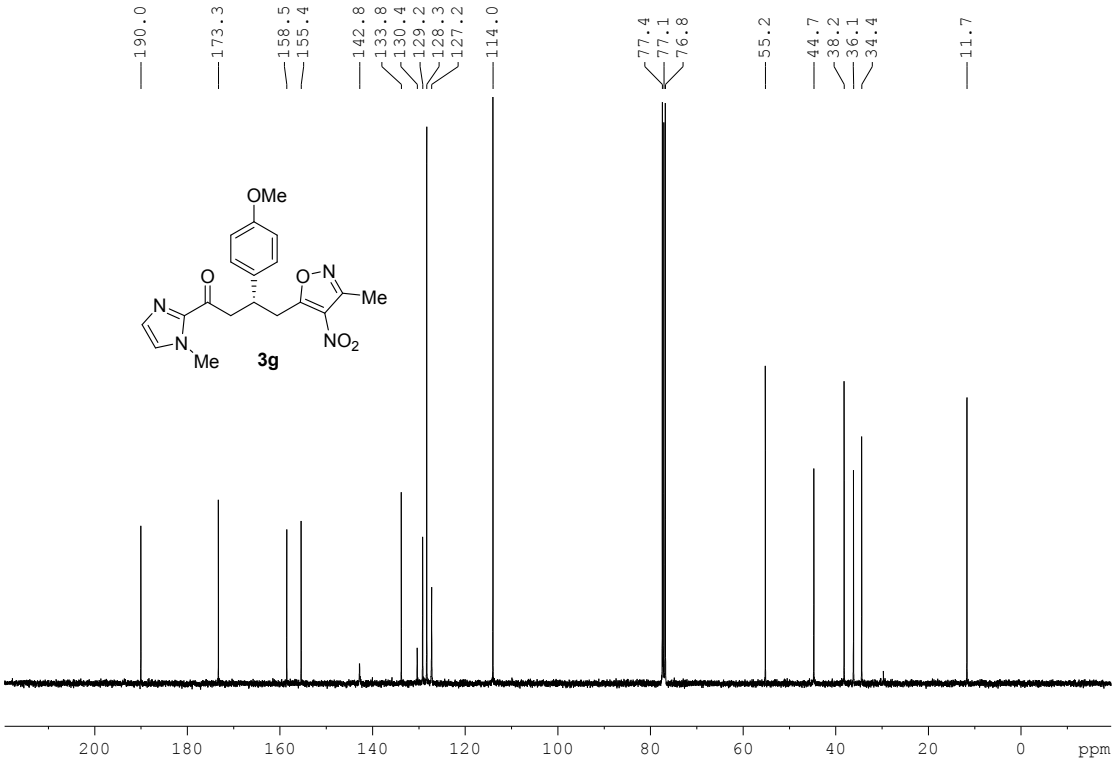

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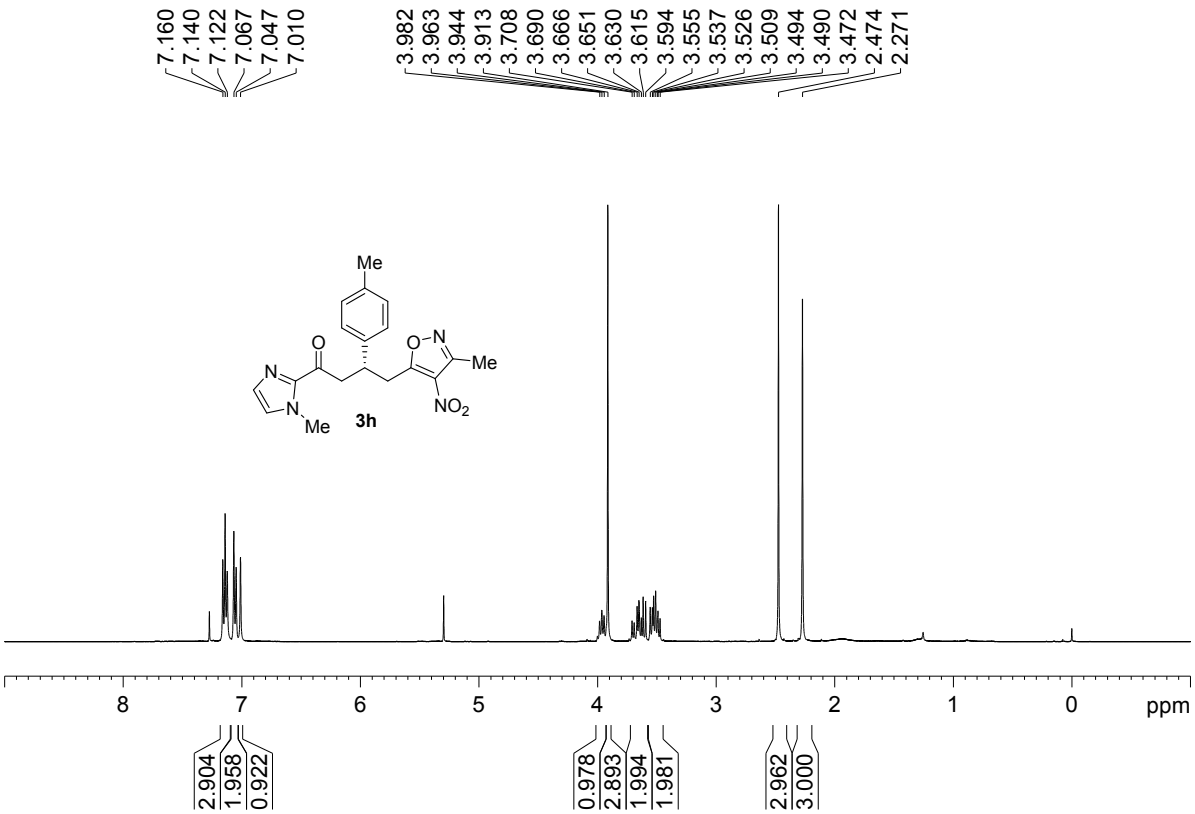


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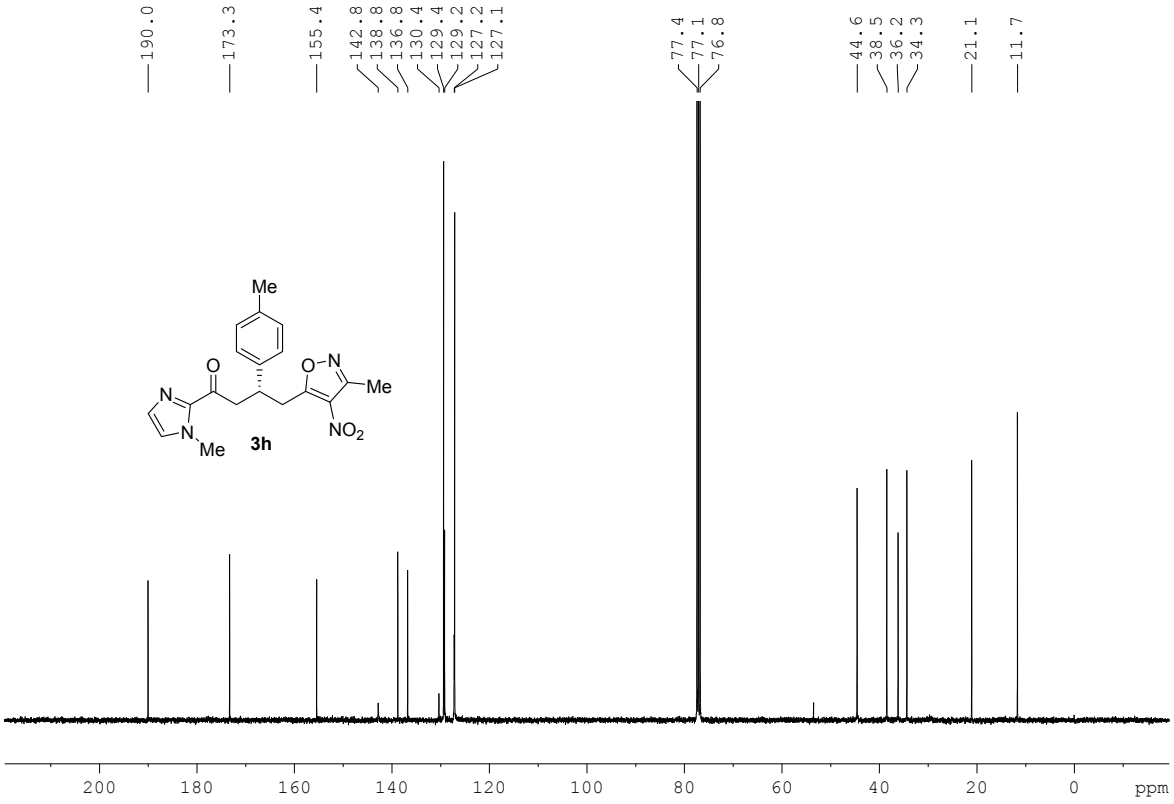
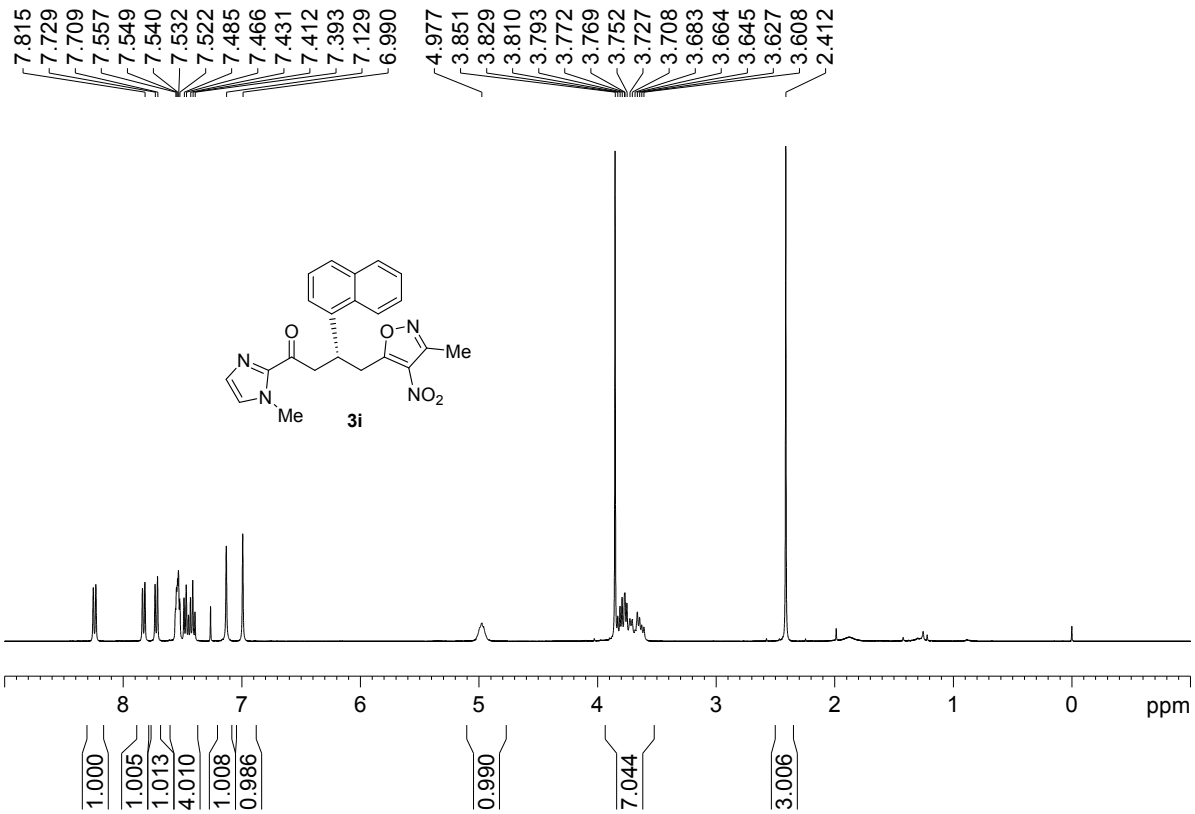


$^{1}$H NMR (400 MHz) spectra of **3i**

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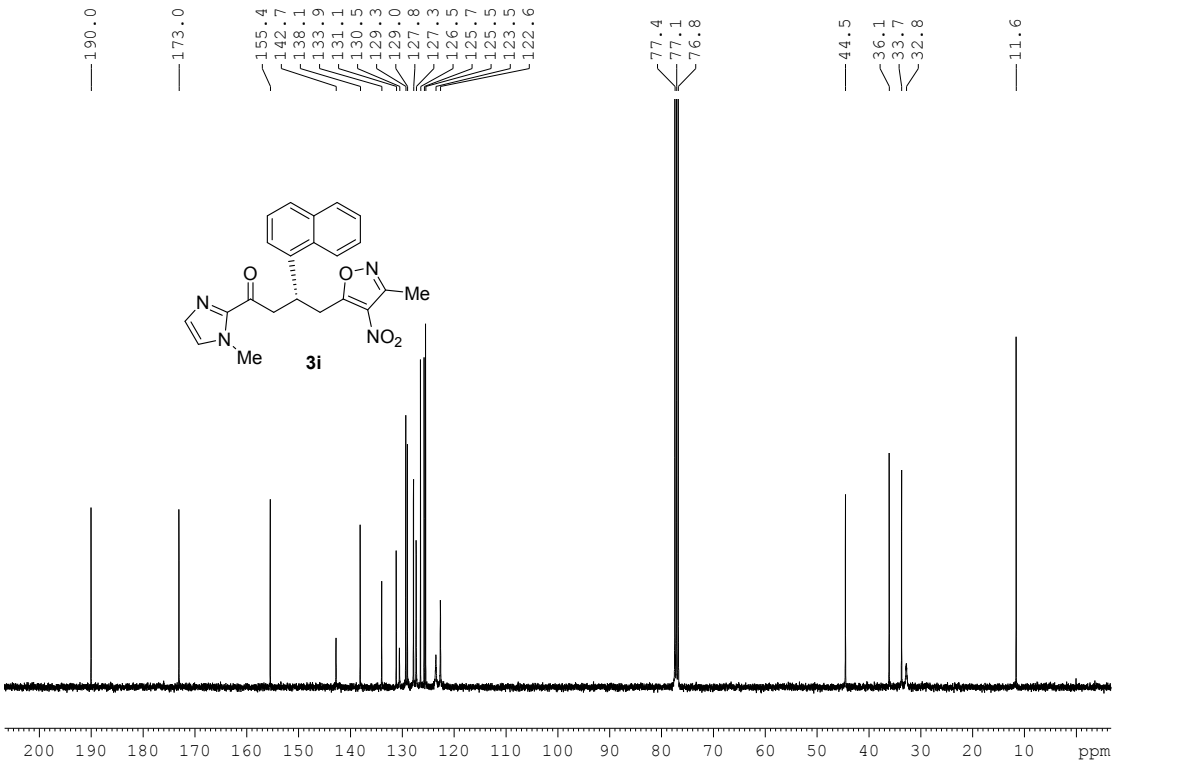

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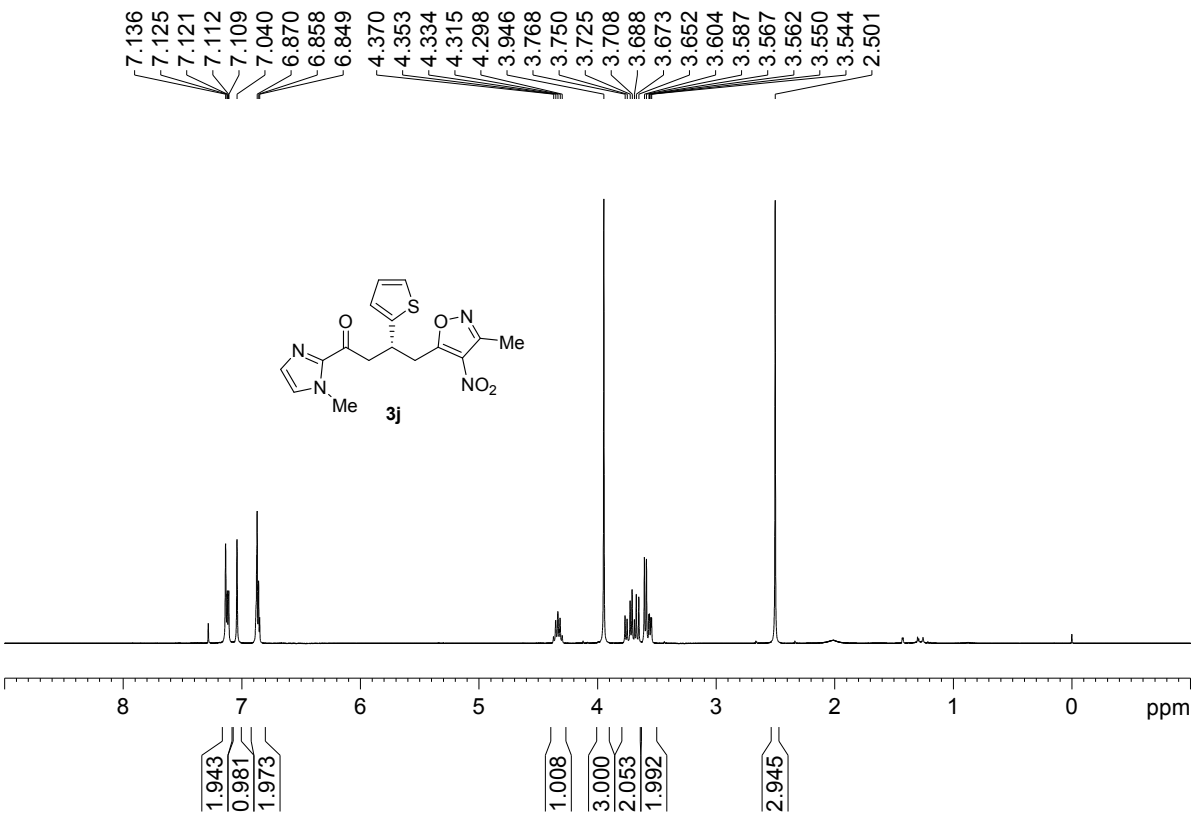


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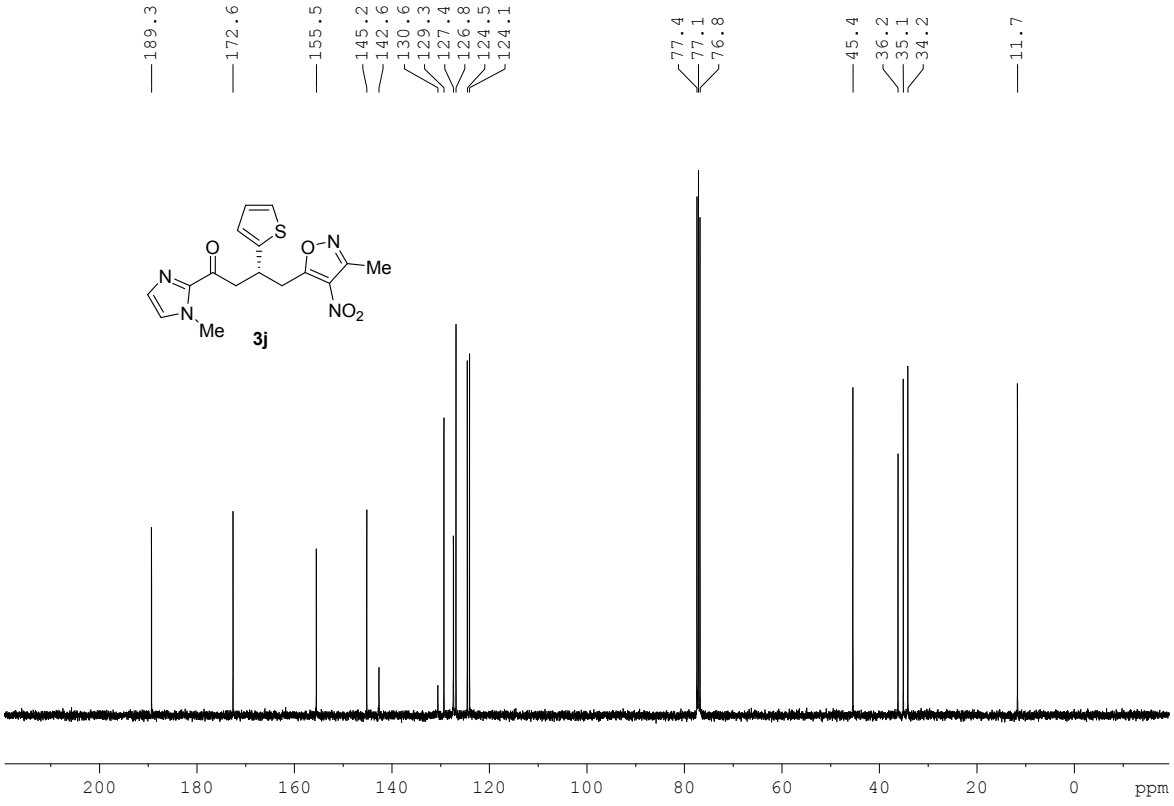

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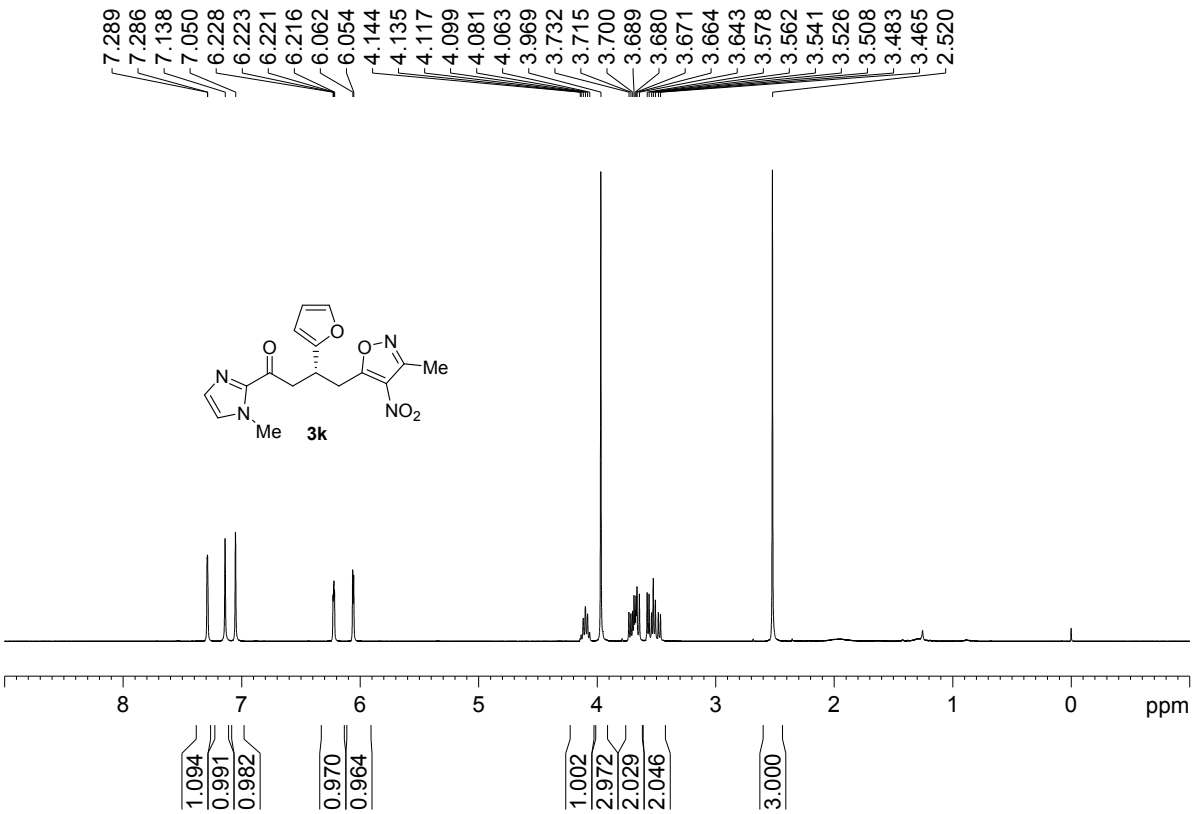


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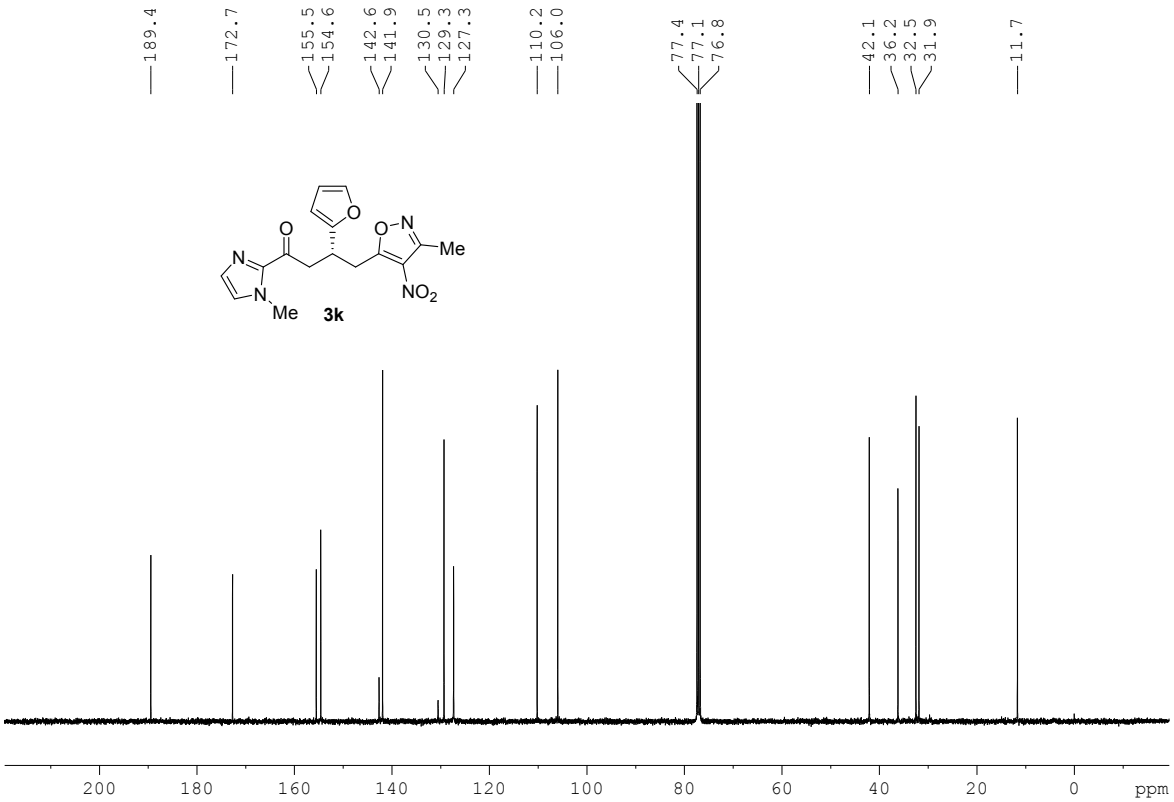

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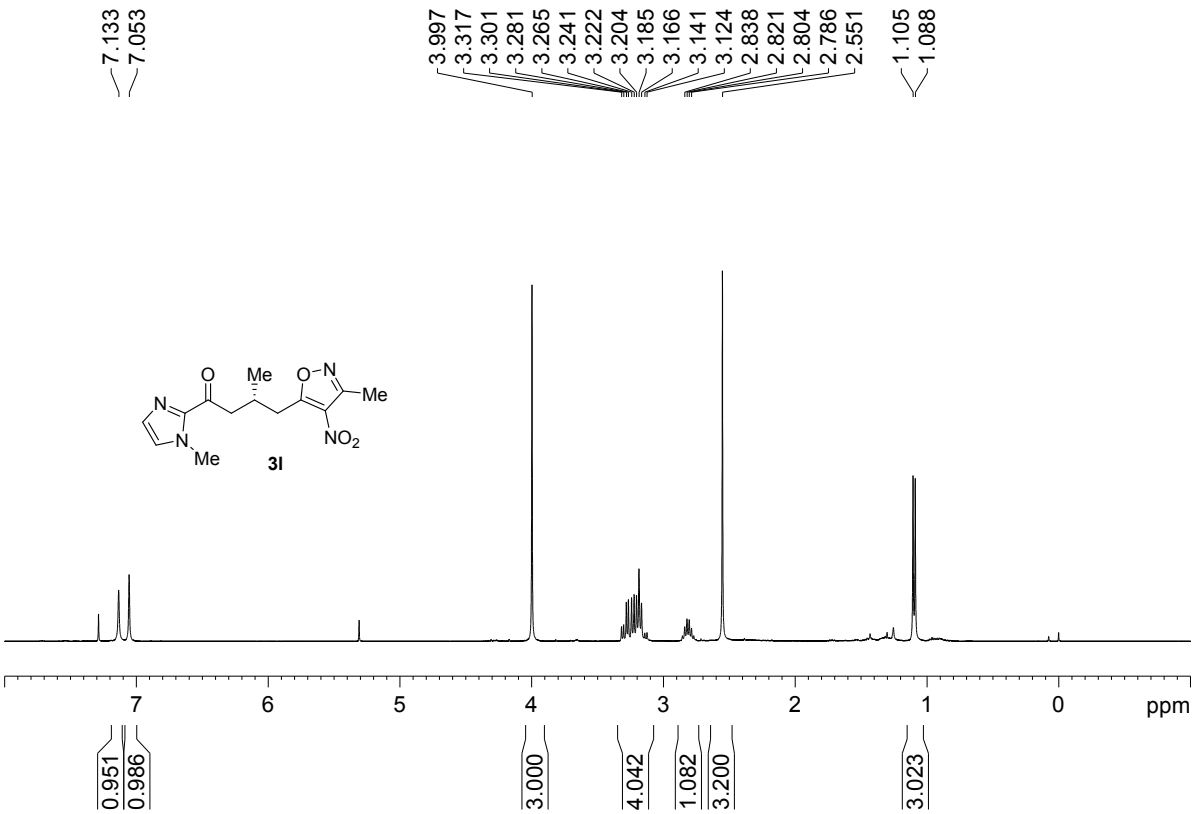


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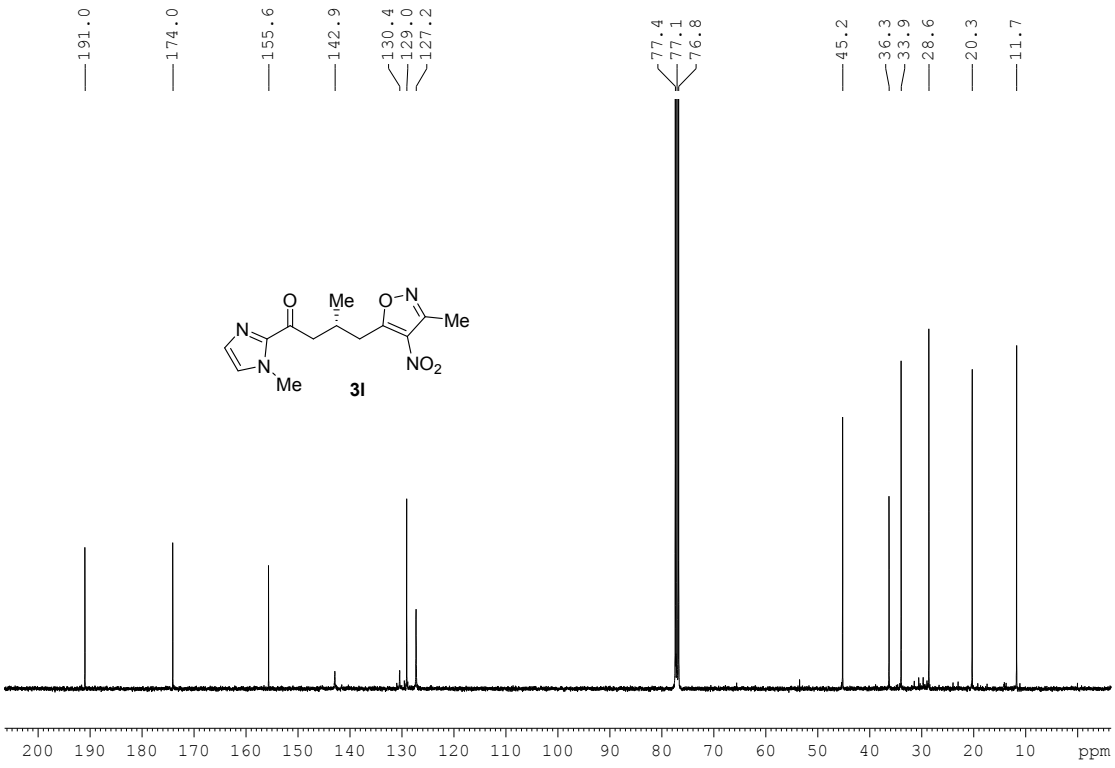
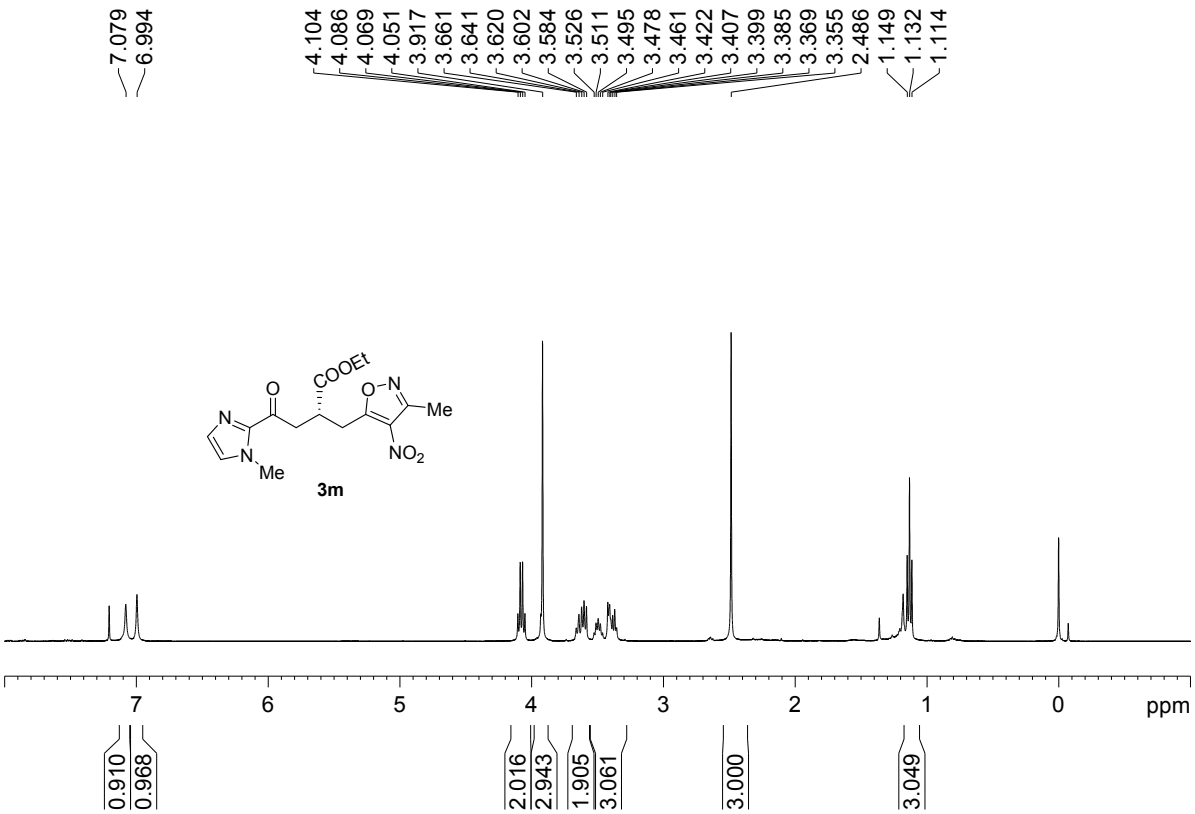


$^{1}$H NMR (400 MHz) spectra of **3m**

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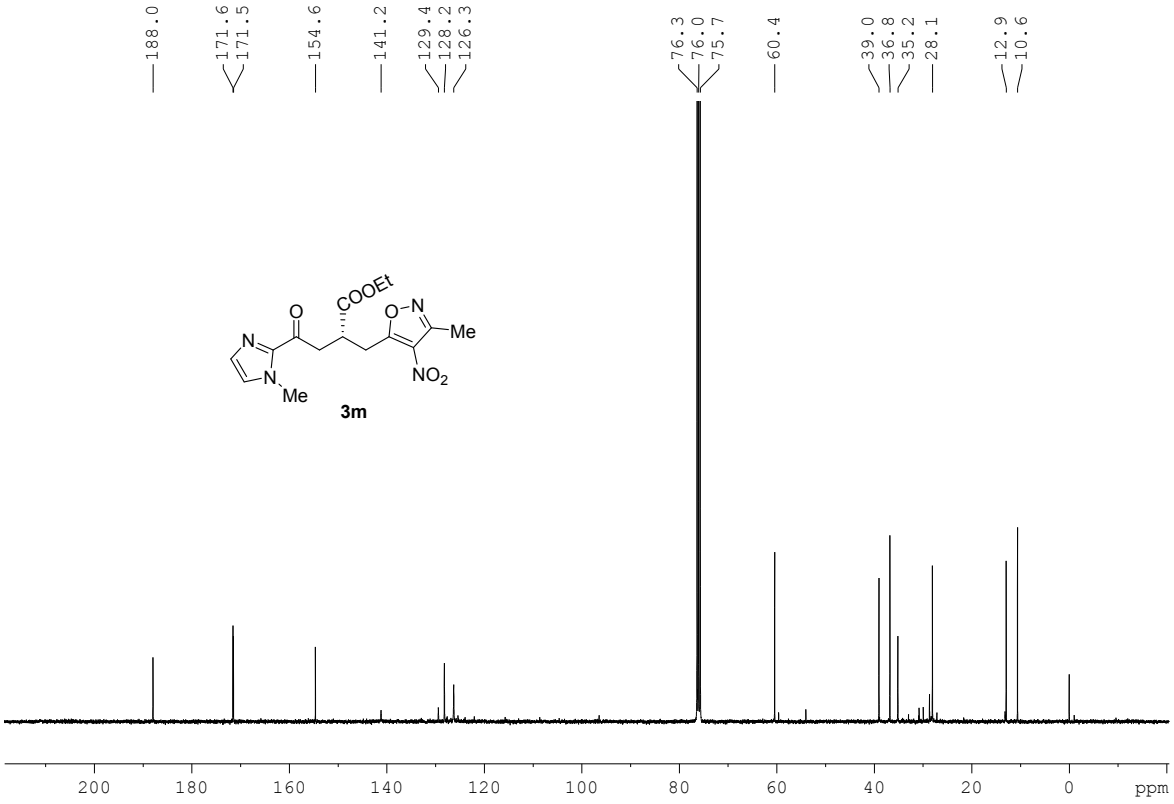
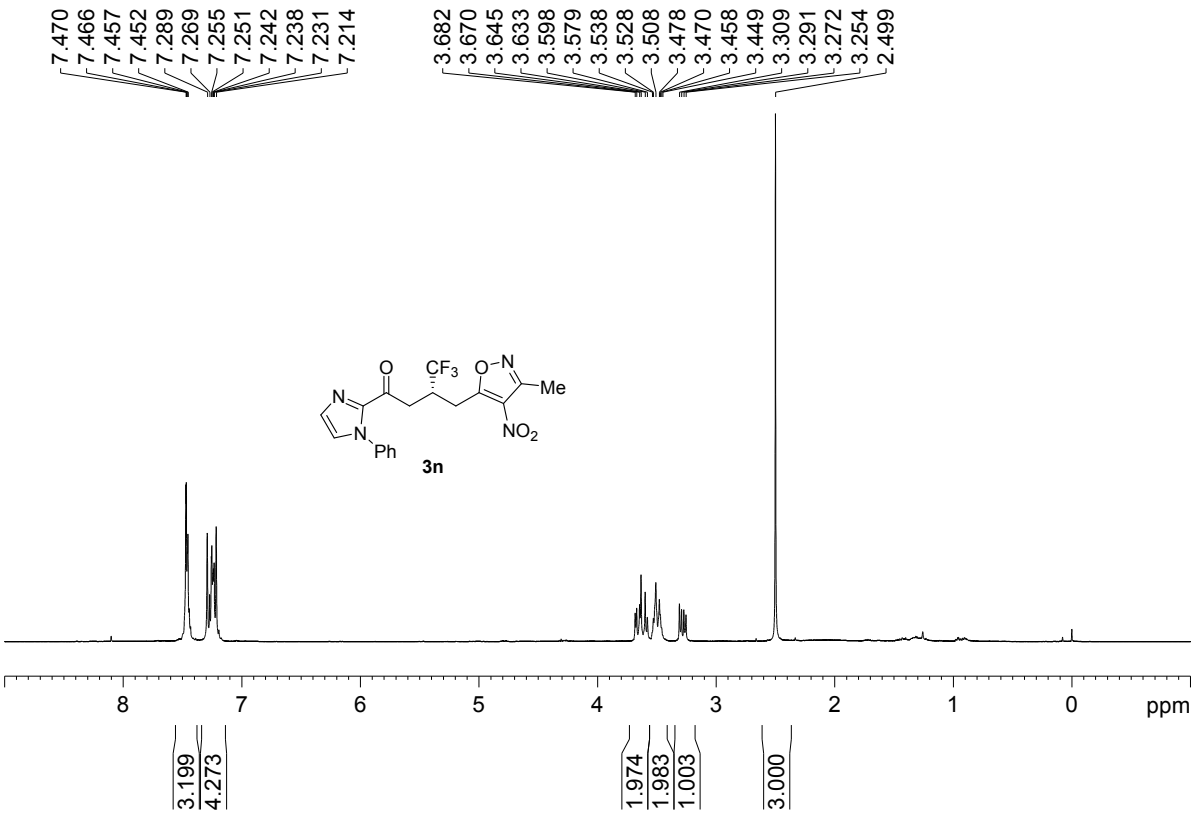
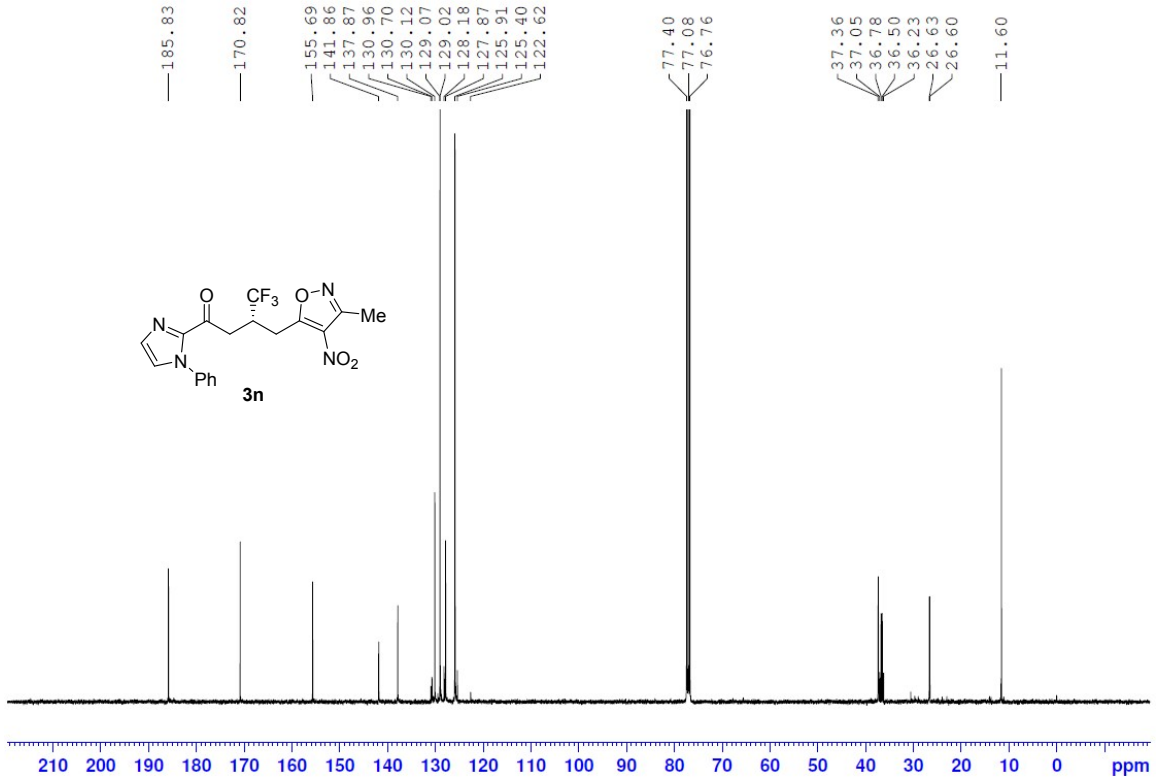


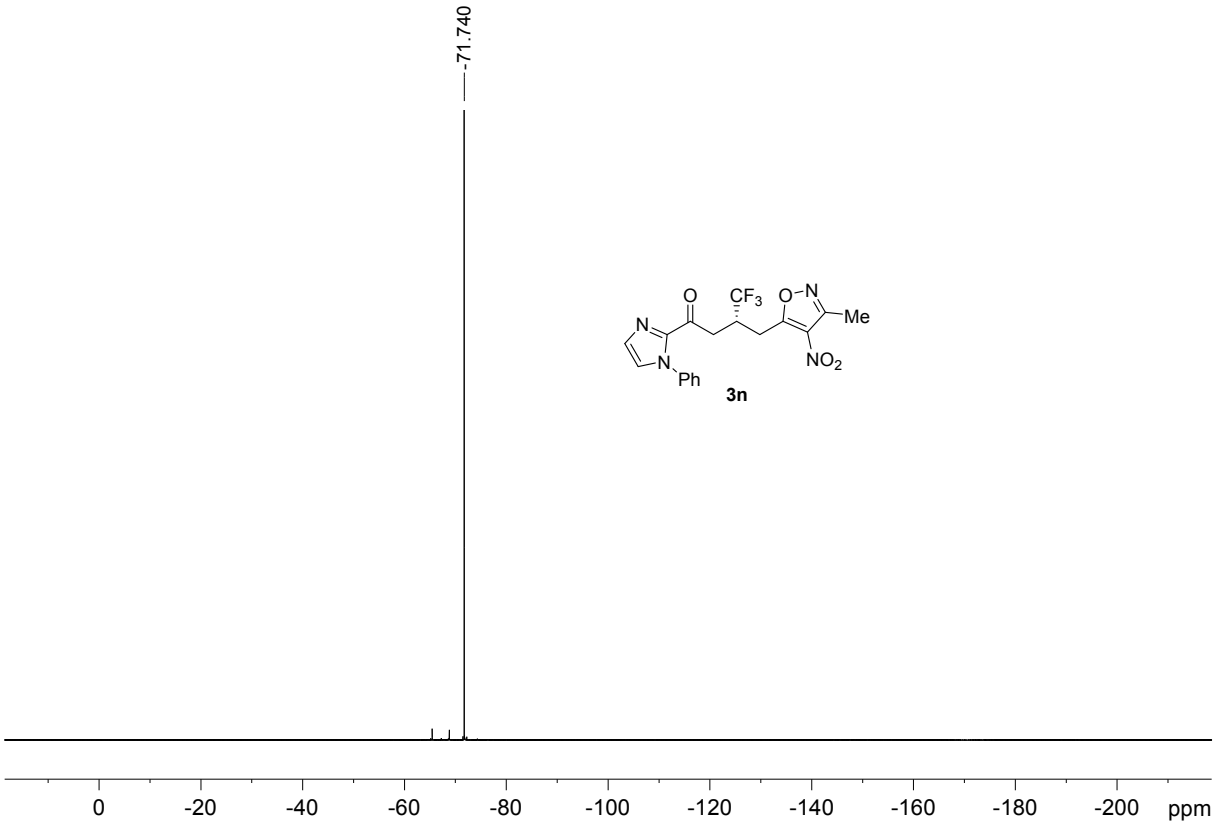
$^{1}$H NMR (400 MHz) spectra of **3n**



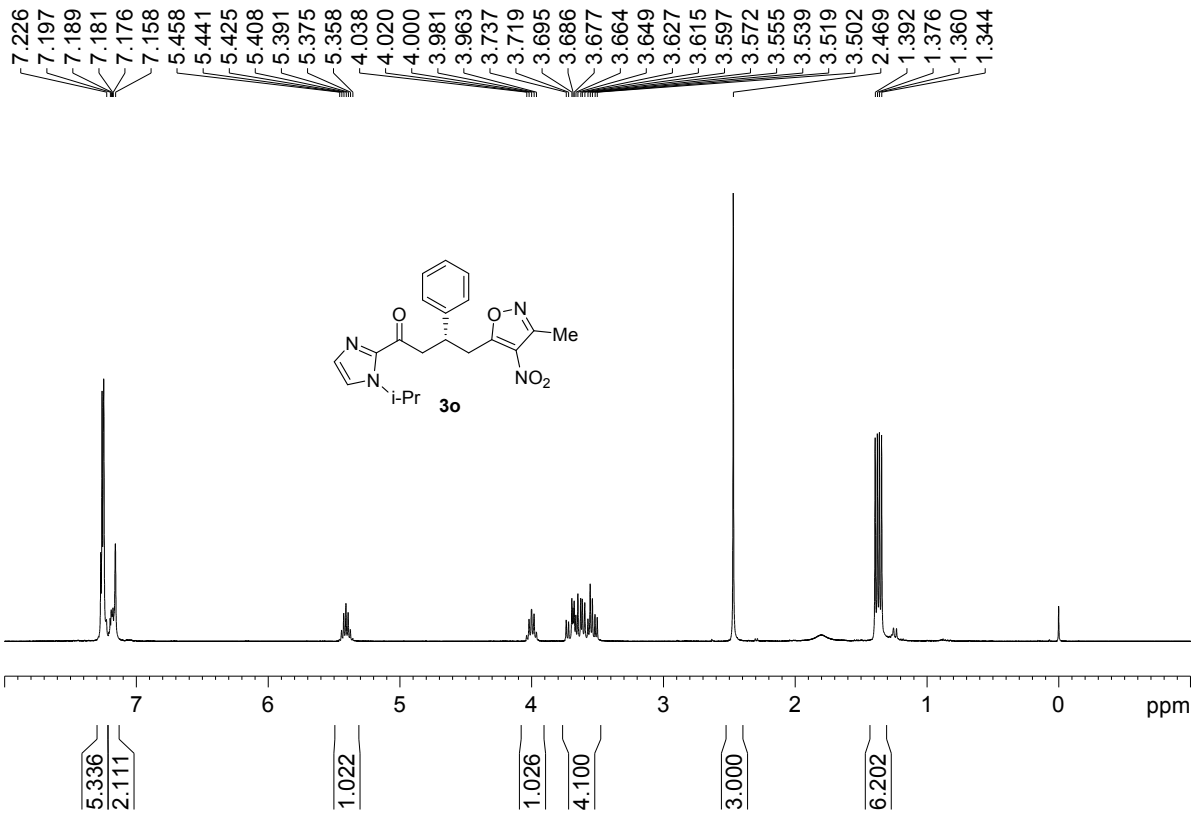

$^{13}$C NMR (100 MHz) spectra of **3n**



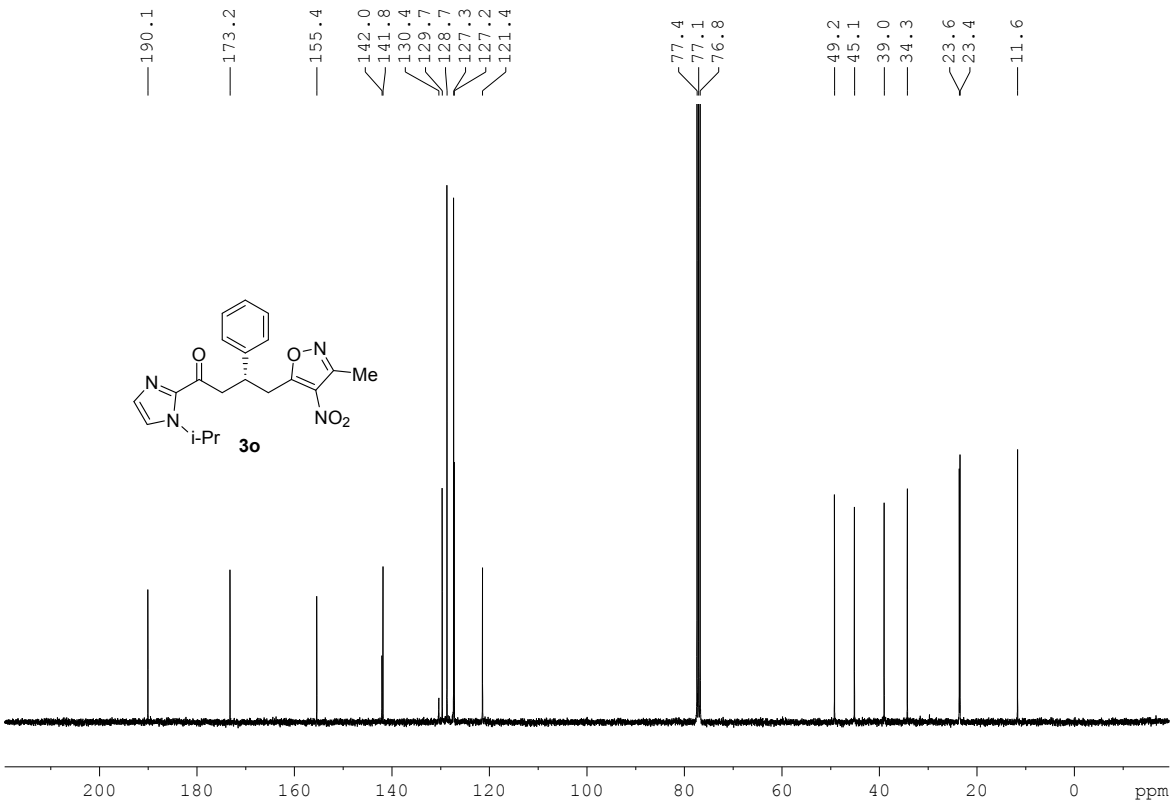
$^{19}$F NMR (376.4 MHz) spectra of **3n**



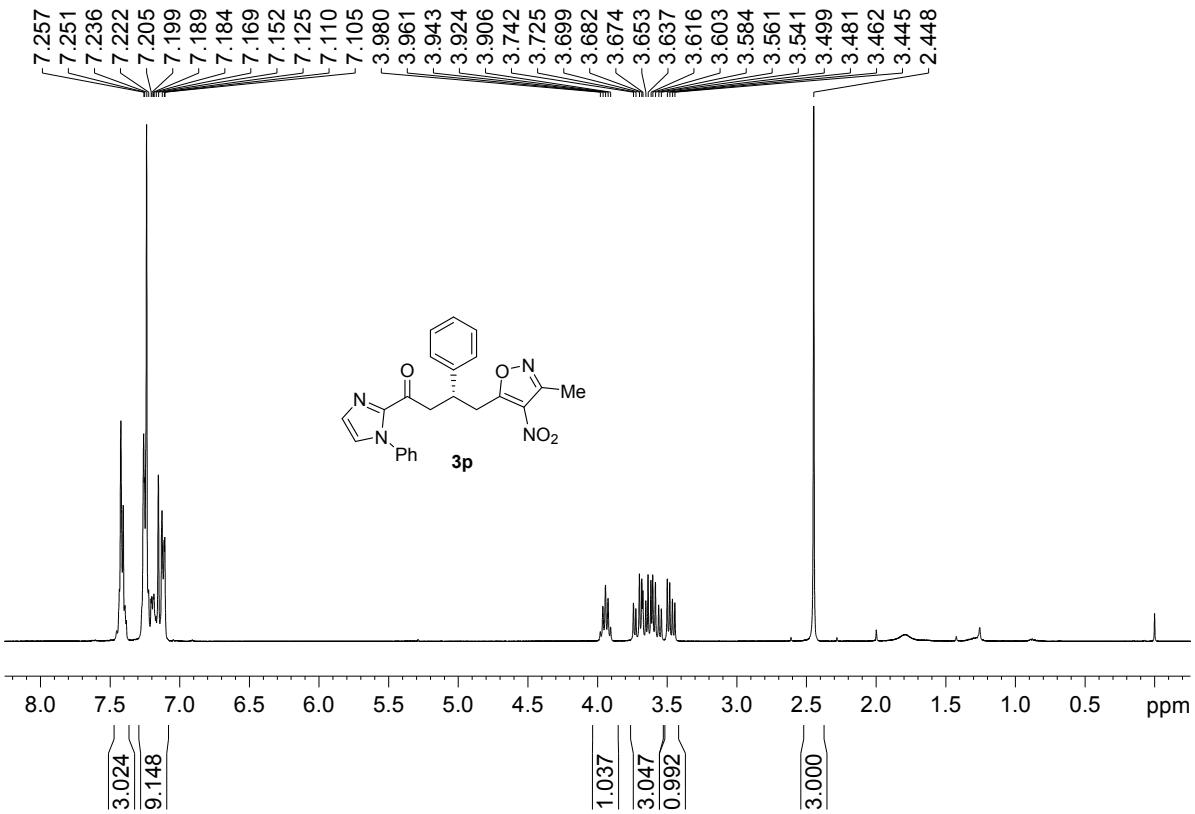
$^{1}$H NMR (400 MHz) spectra of **3o**



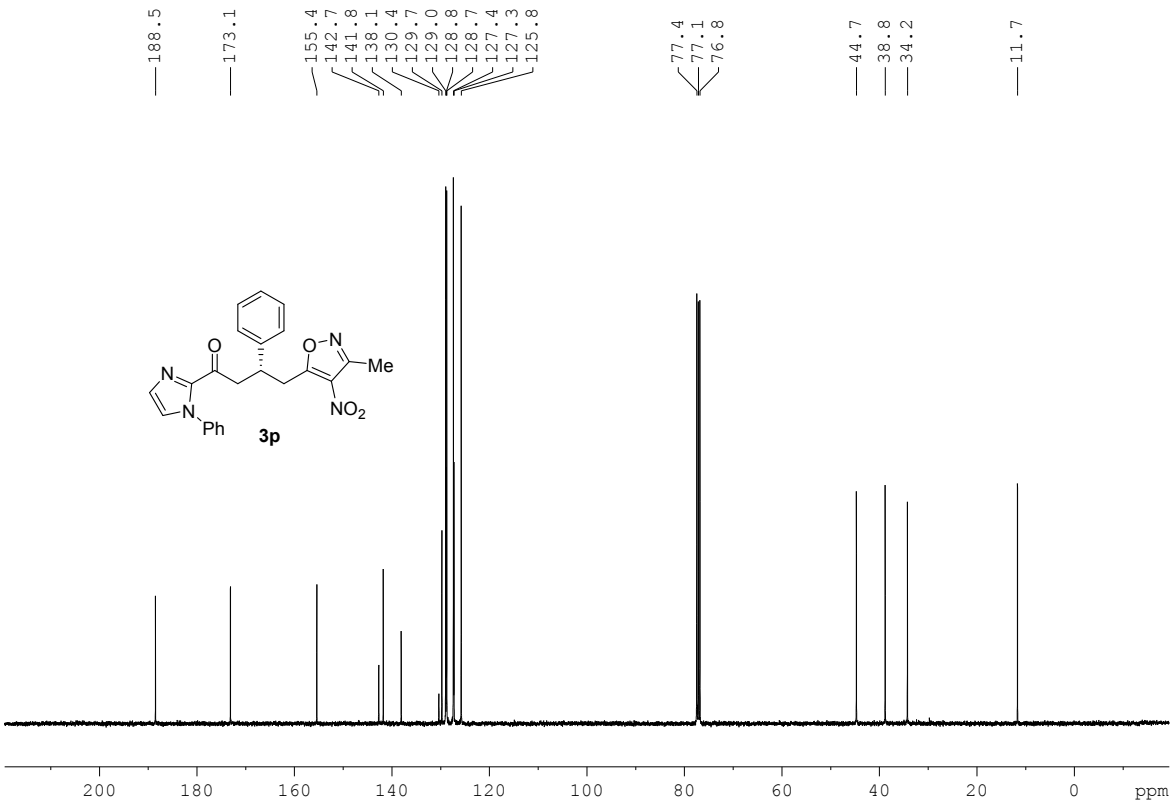

$^{13}$C NMR (100 MHz) spectra of **3o**



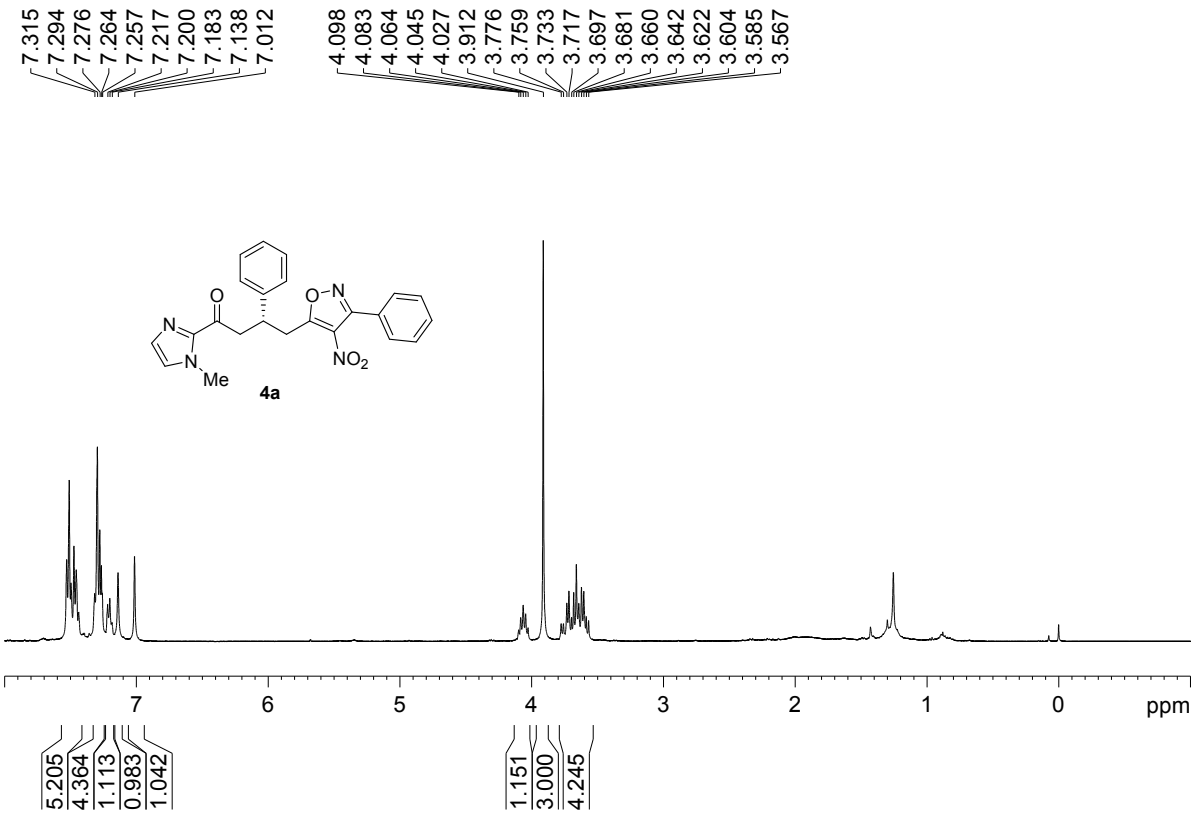
$^{1}$H NMR (400 MHz) spectra of **3p**



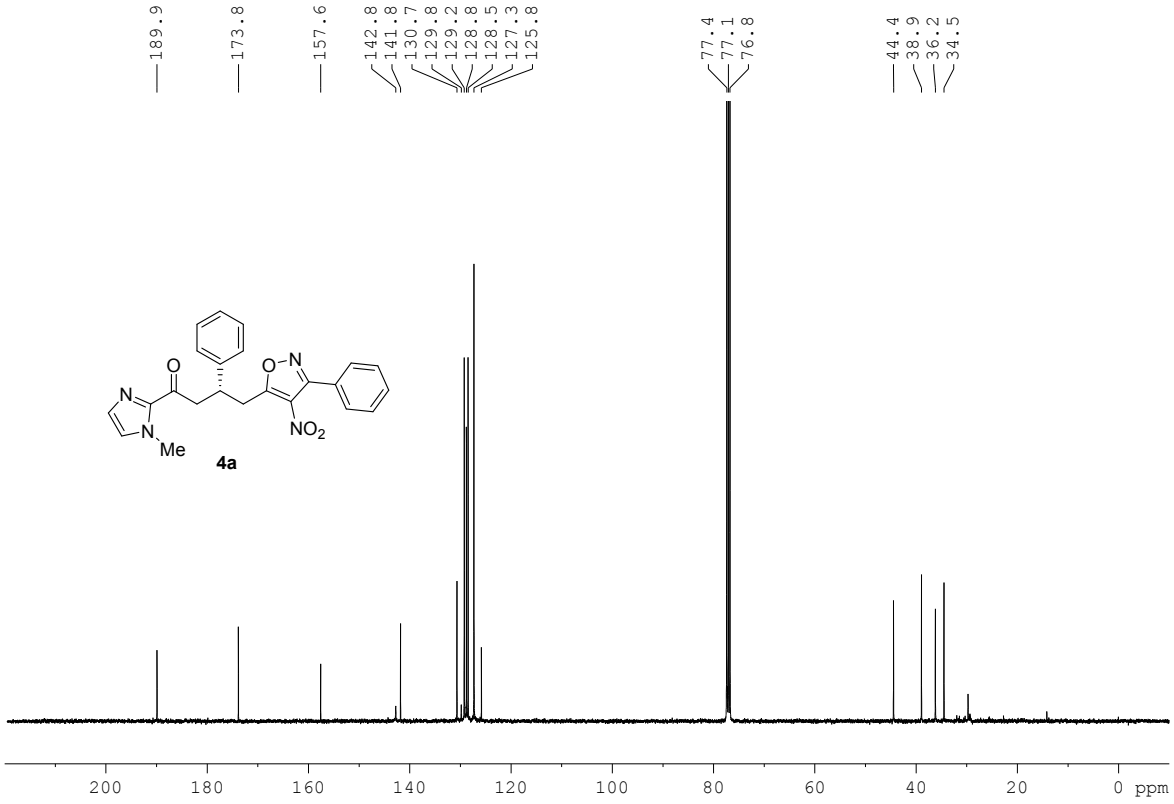

$^{13}$C NMR (100 MHz) spectra of **3p**



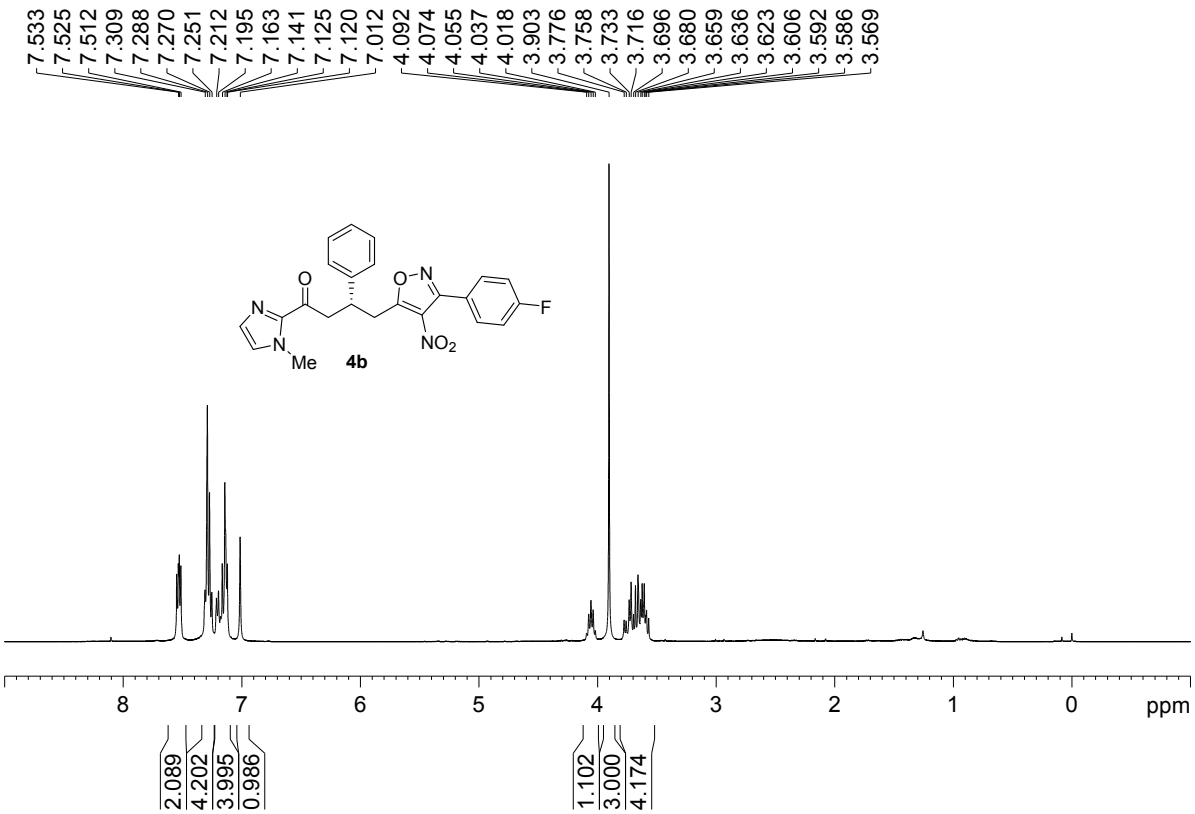
$^{1}$H NMR (400 MHz) spectra of **4a**



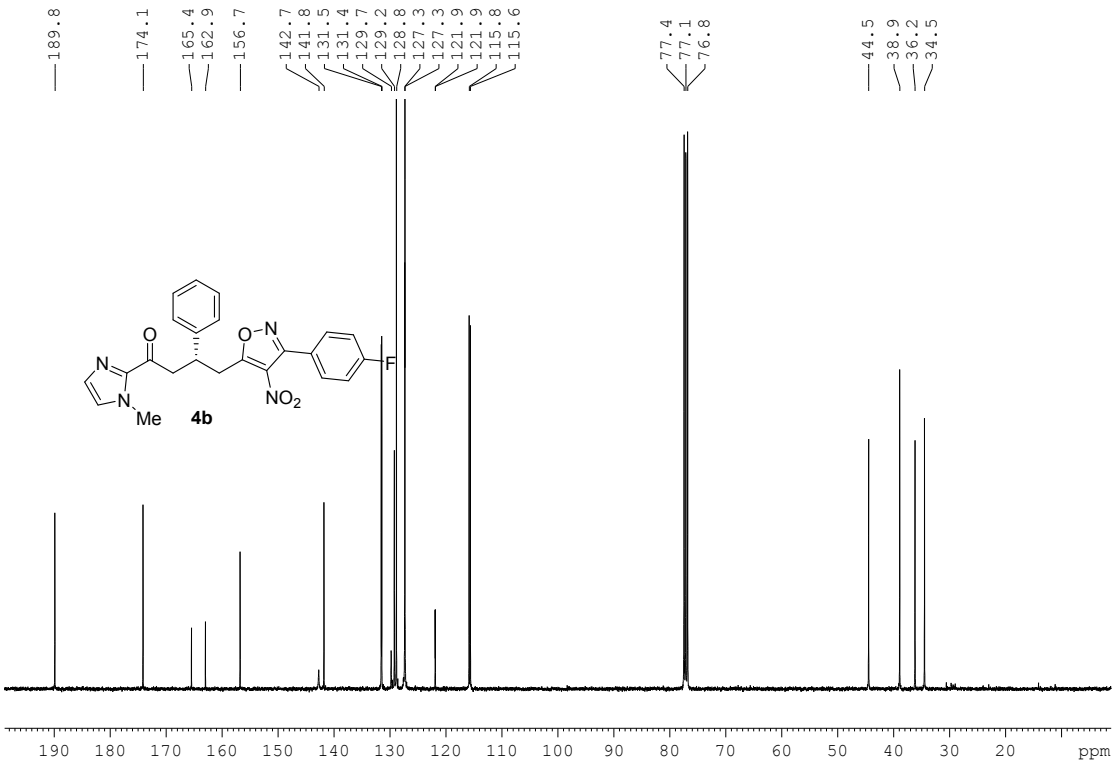

$^{13}$C NMR (100 MHz) spectra of **4a**



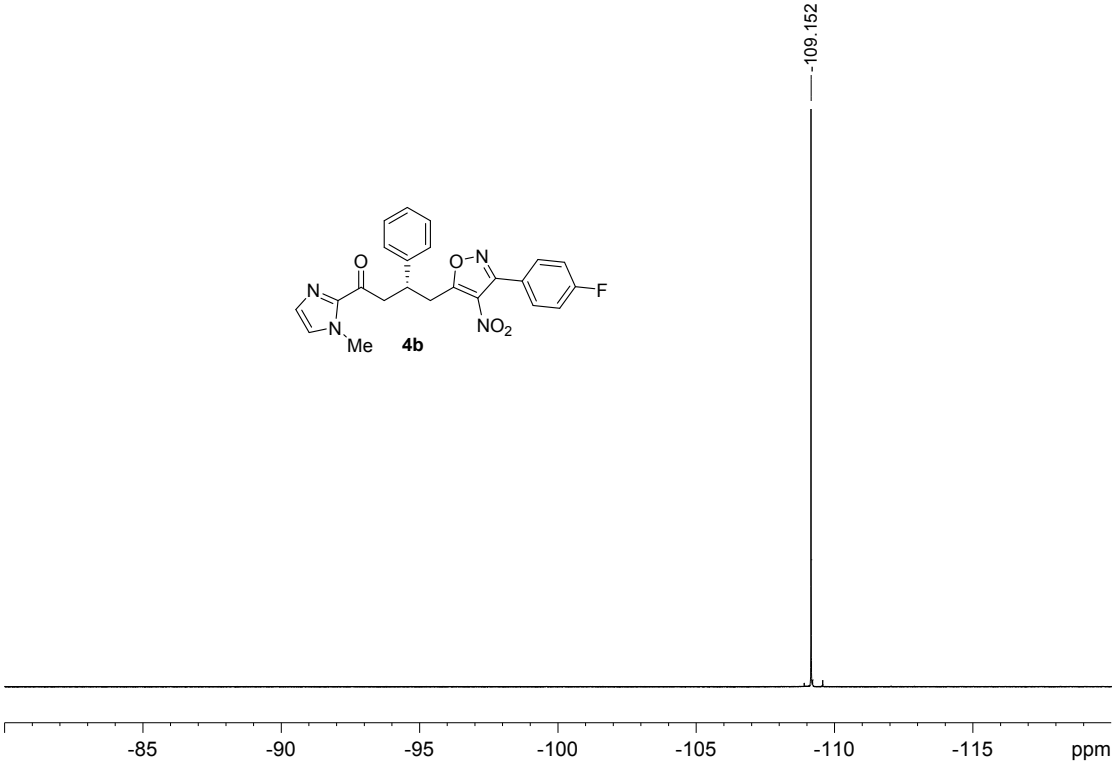
$^{1}$H NMR (400 MHz) spectra of **4b**



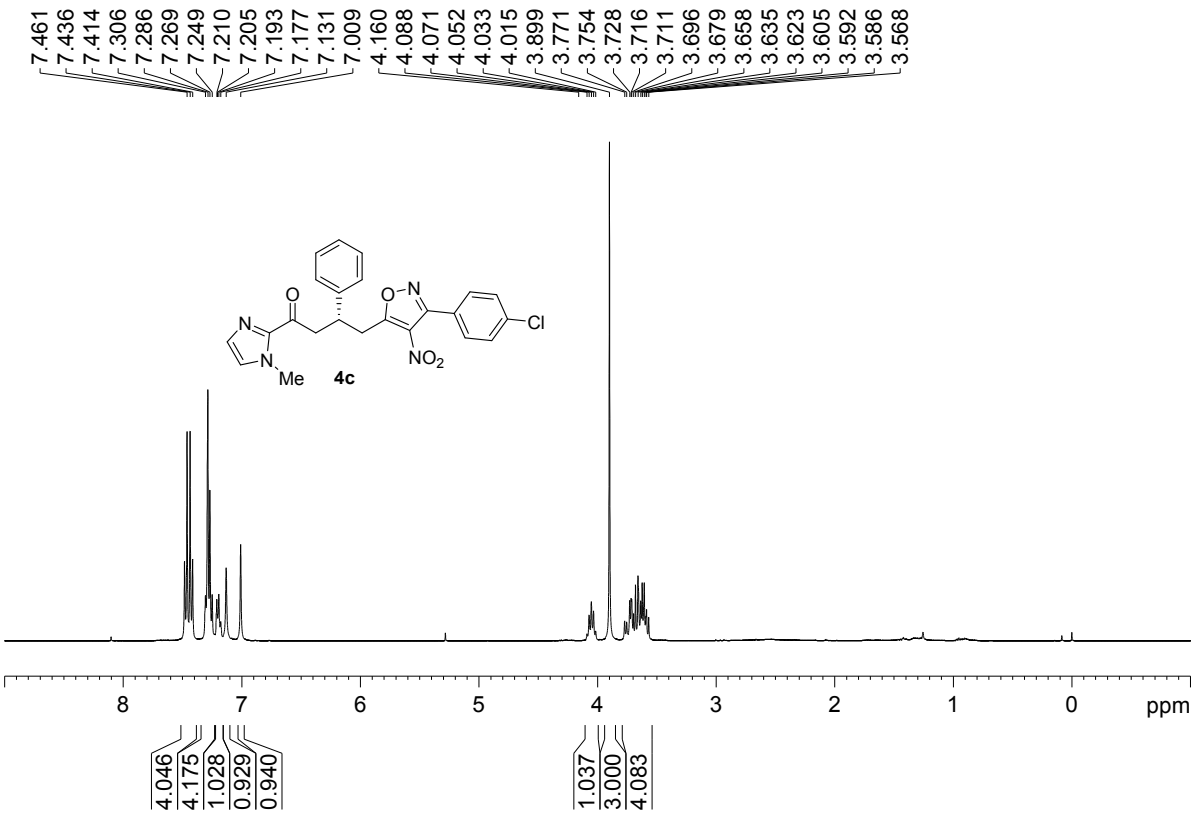

$^{13}$C NMR (100 MHz) spectra of **4b**



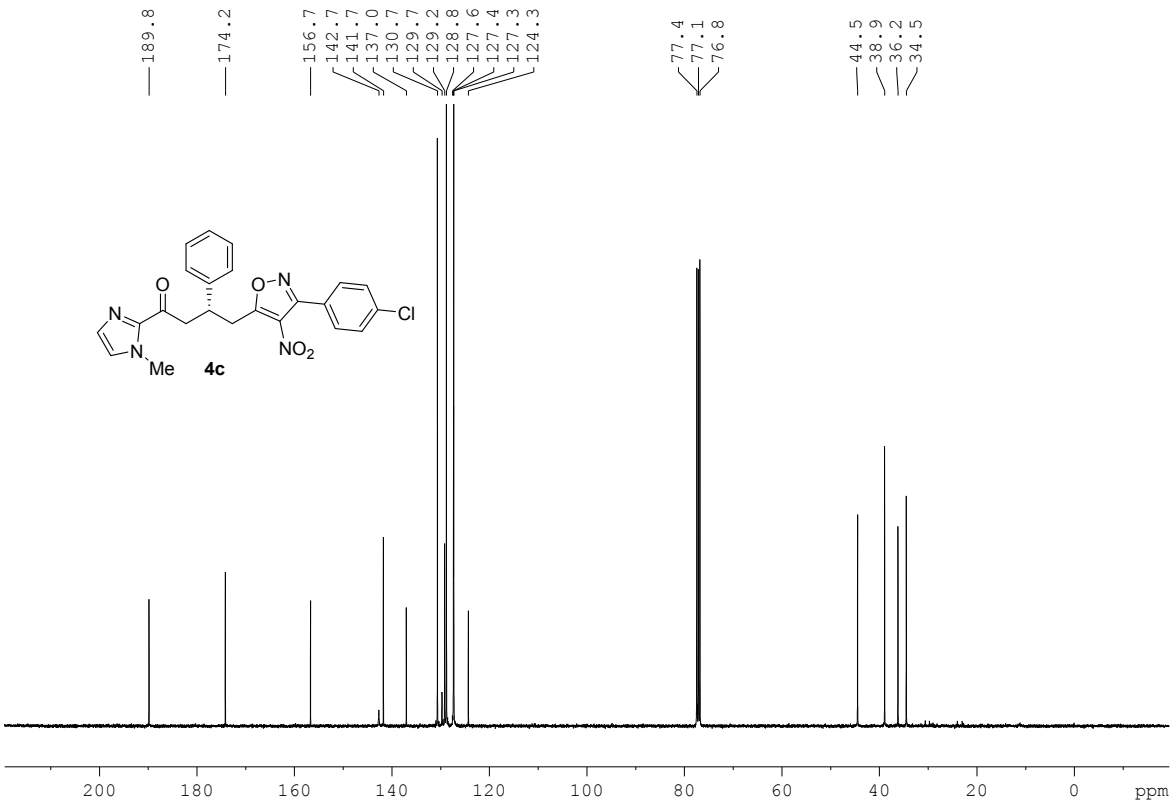
$^{19}$F NMR (376.4 MHz) spectra of **4b**



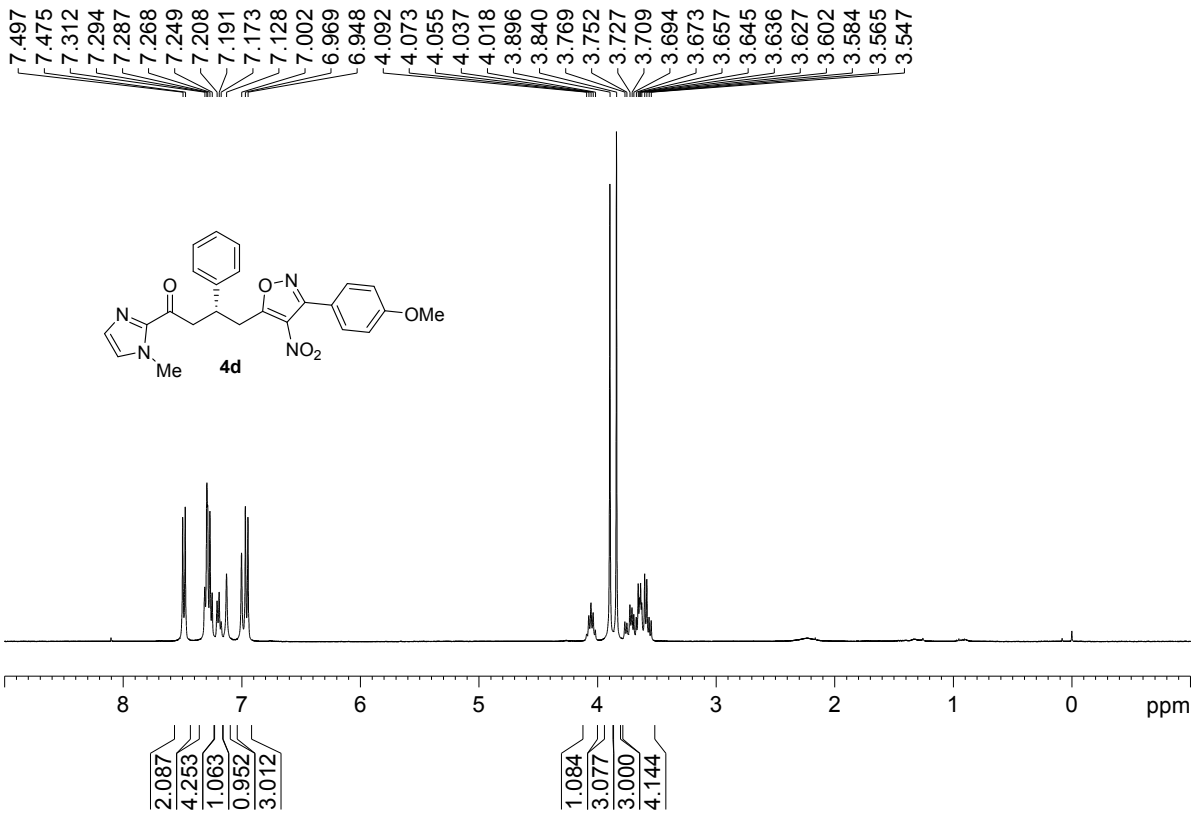
$^{1}$H NMR (400 MHz) spectra of **4c**




$^{13}$C NMR (100 MHz) spectra of **4c**



$^{1}$H NMR (400 MHz) spectra of **4d**

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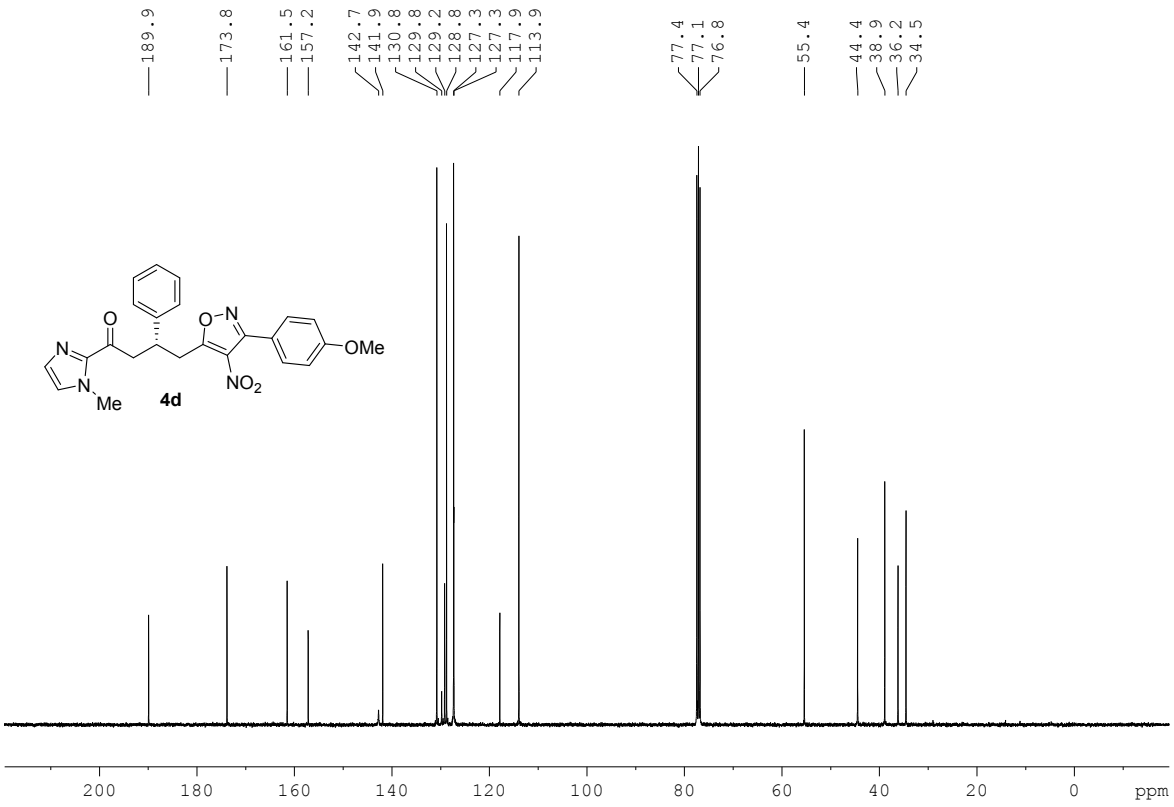

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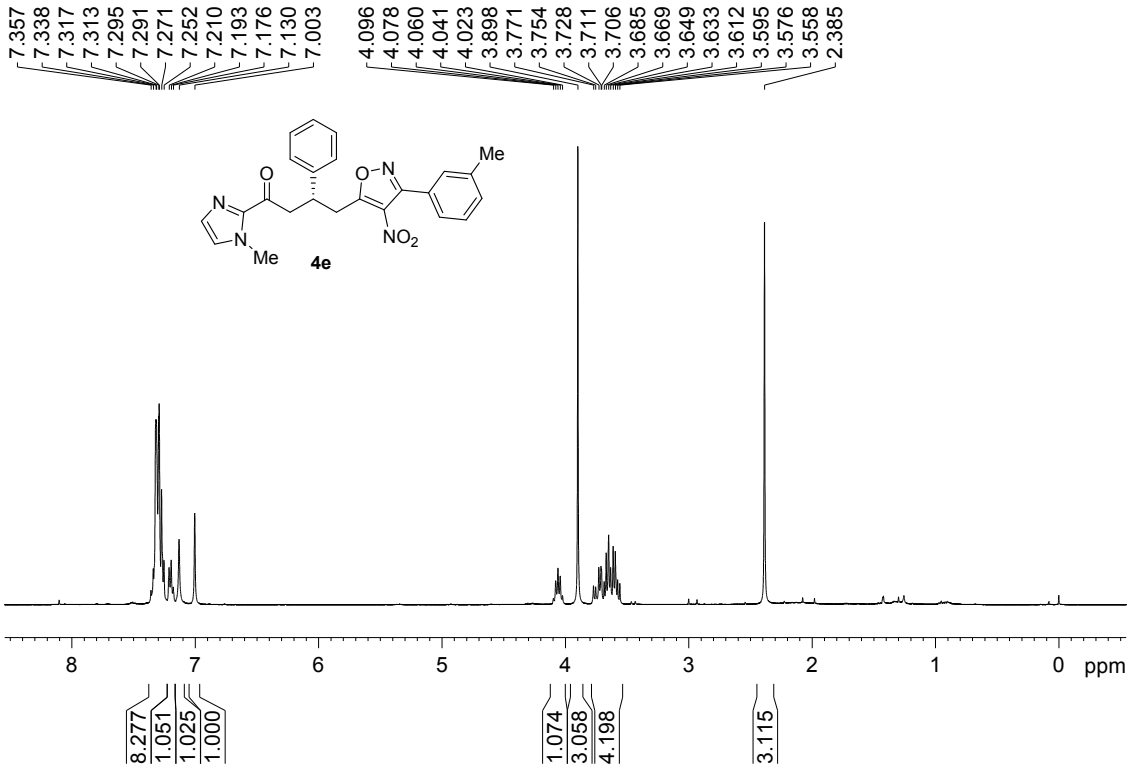


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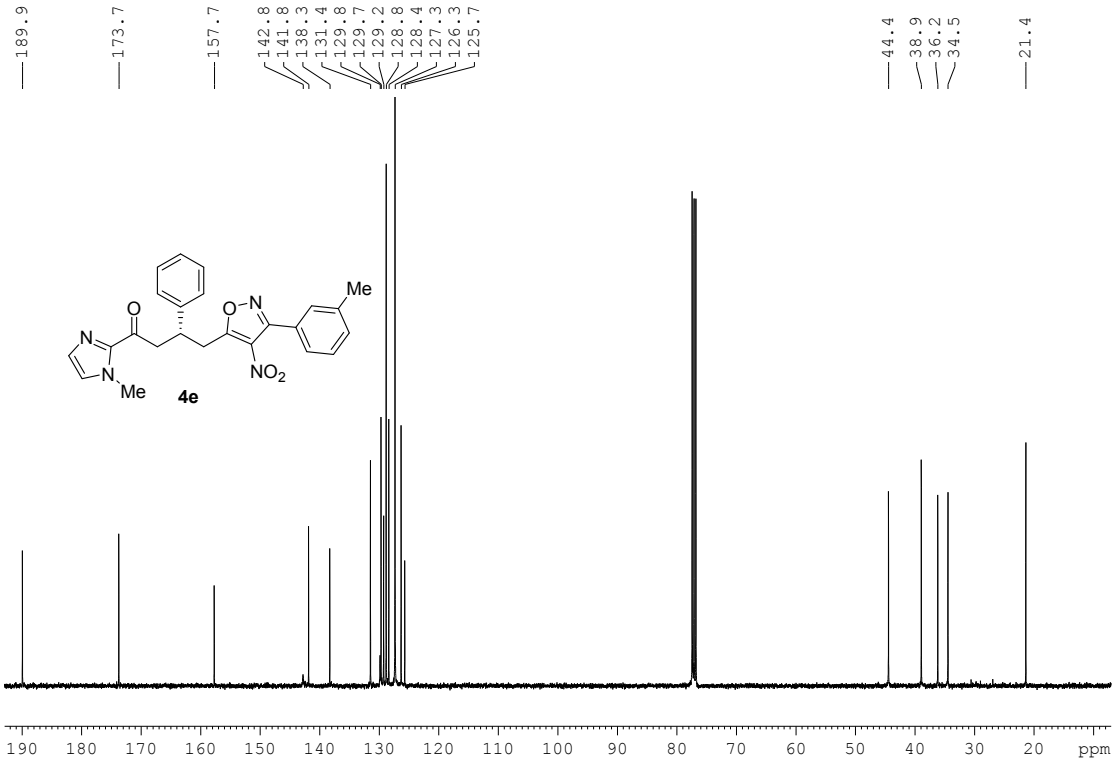
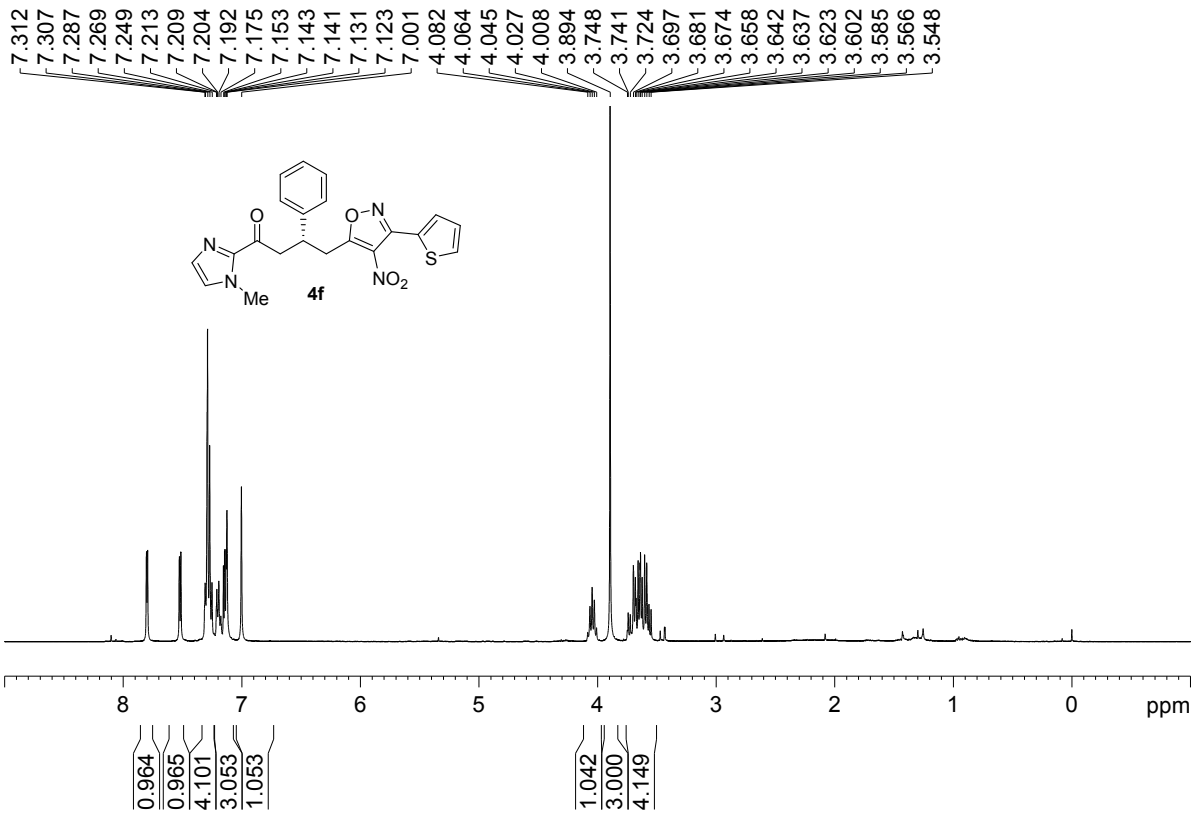


$^{1}$H NMR (400 MHz) spectra of **4f**

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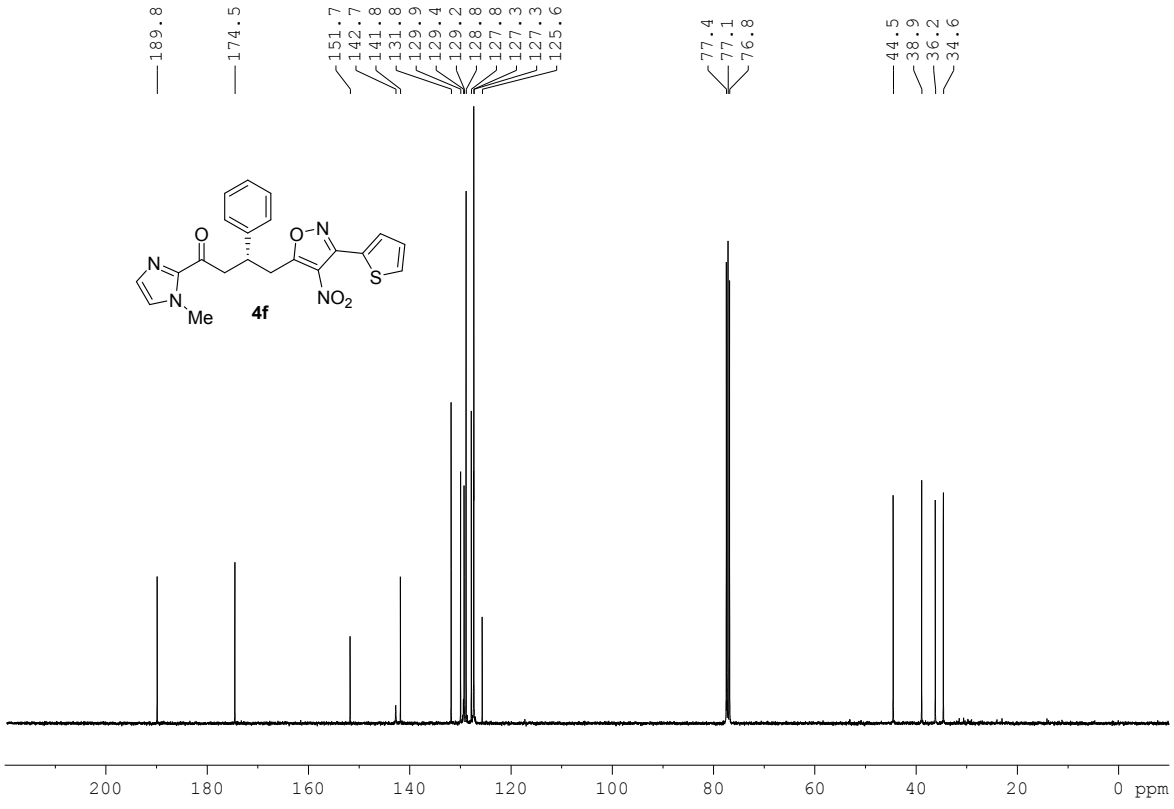
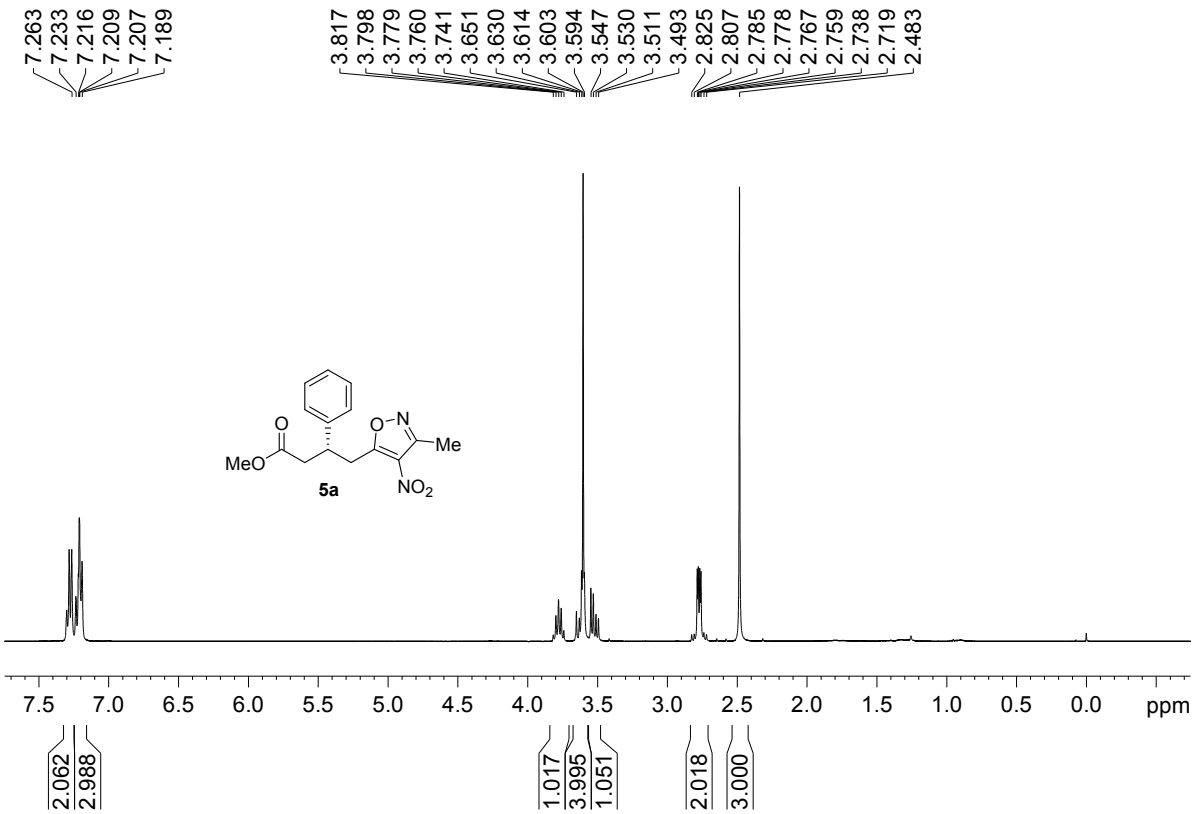
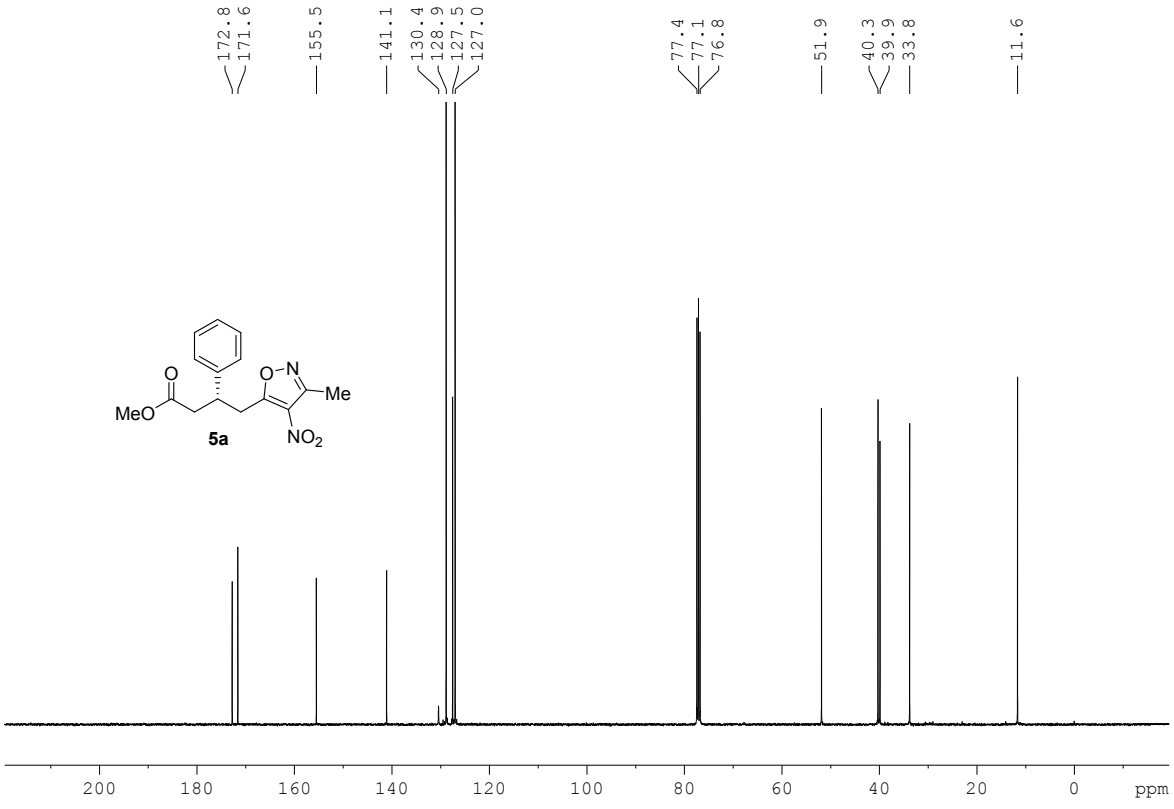


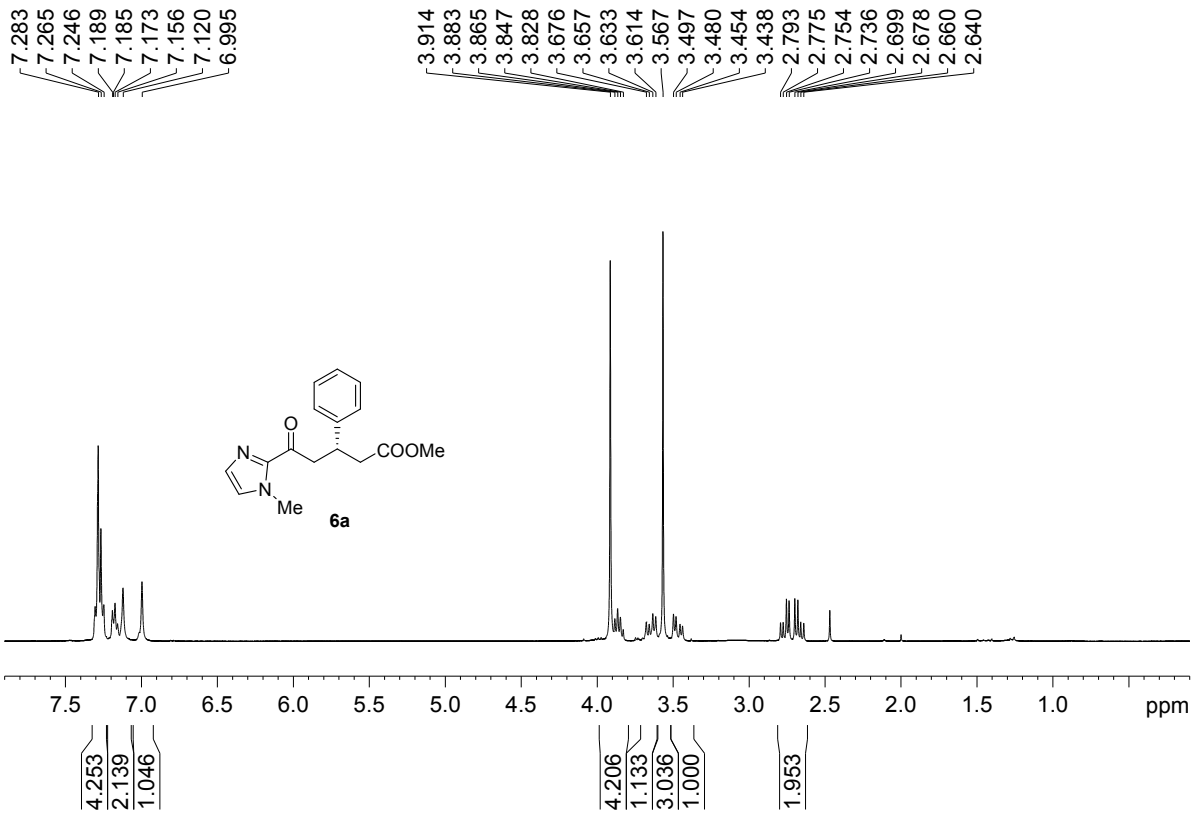
$^{1}$H NMR (400 MHz) spectra of **5a**



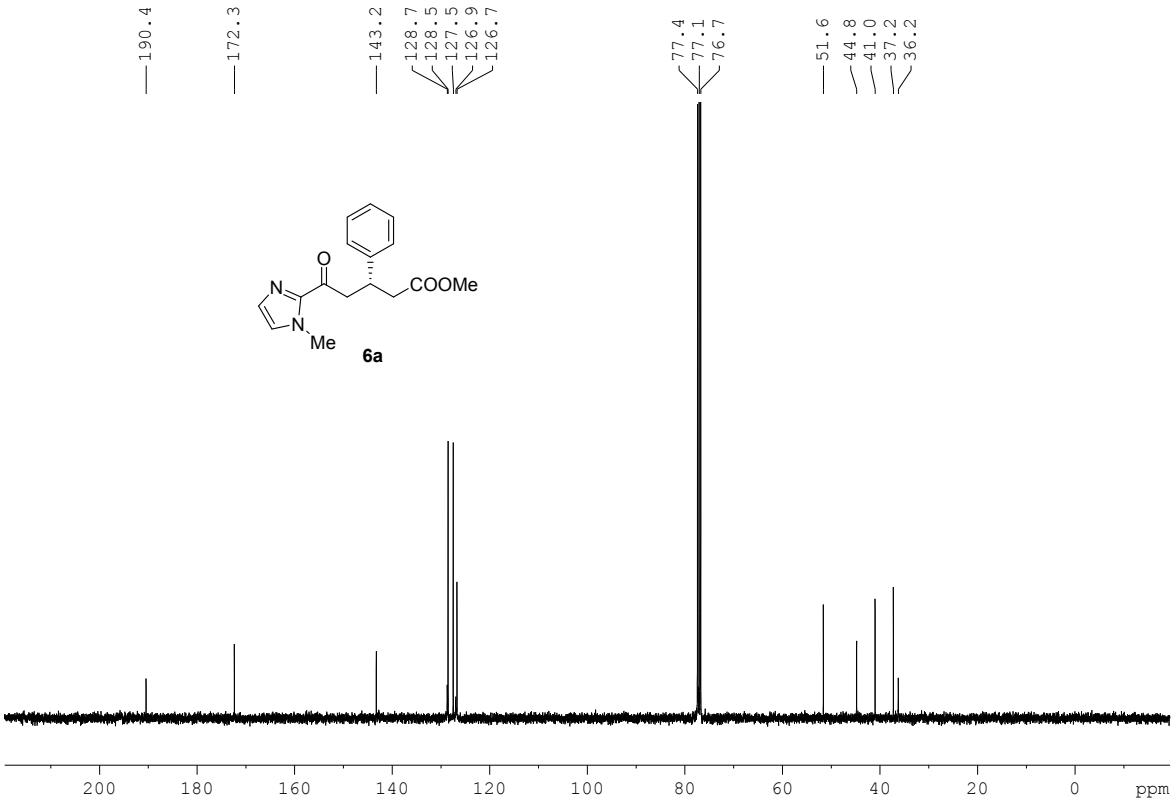

$^{13}$C NMR (100 MHz) spectra of **5a**



$^{1}$H NMR (400 MHz) spectra of **6a**

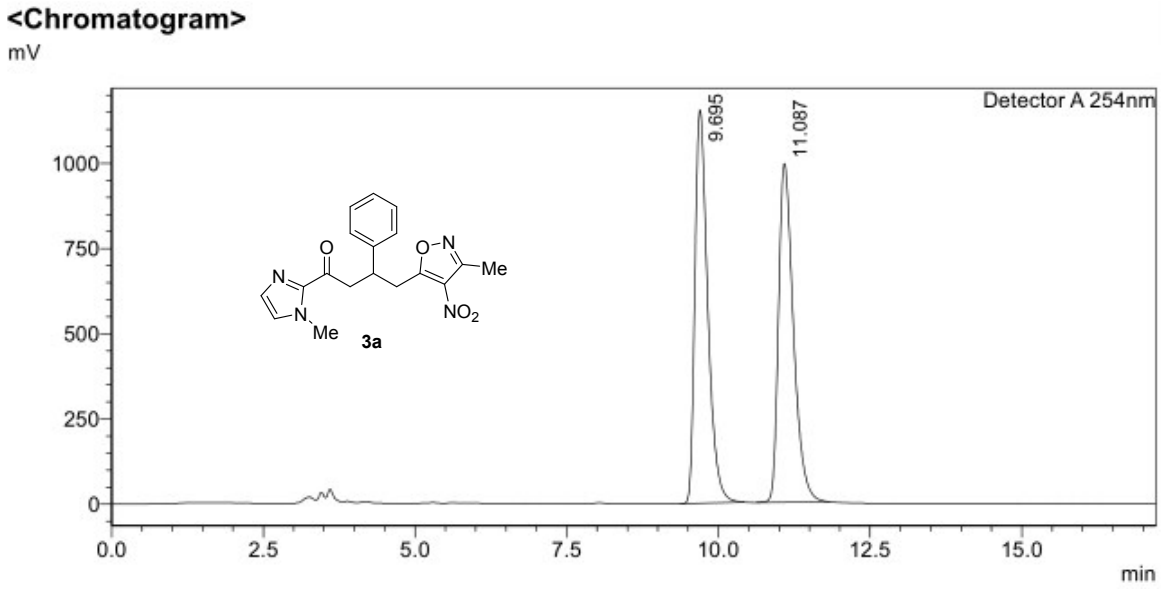



$^{13}$C NMR (100 MHz) spectra of **6a**



## VI Chiral HPLC trace analysis

Racemic **3a**

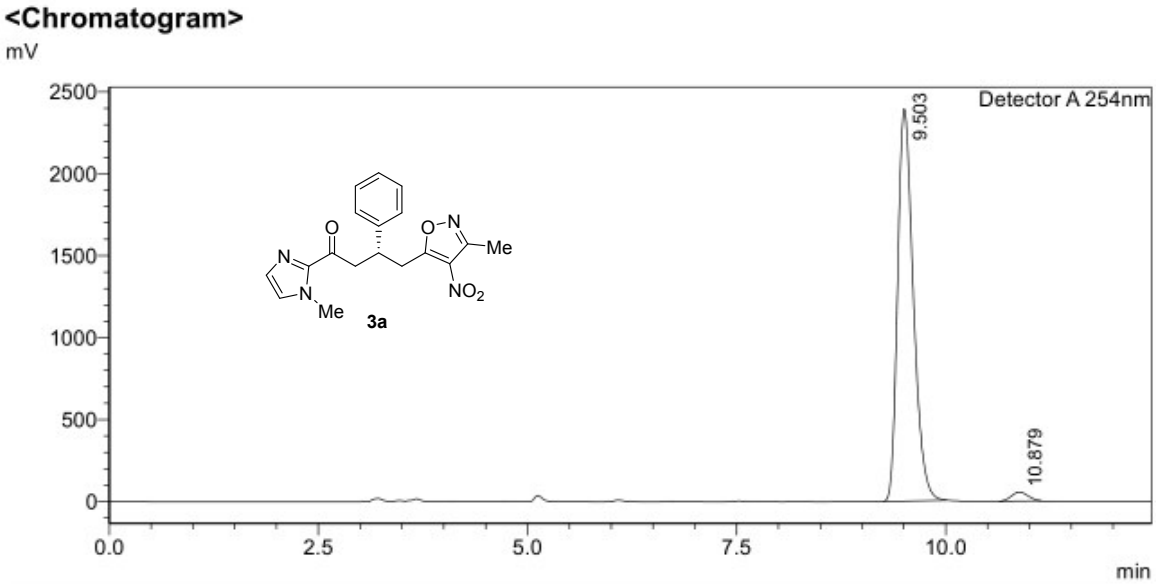



<Peak Table>

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 9.695 | 16955282 | 1153931 | 49.995 | | M | |
| 2 | 11.087 | 16958842 | 993837 | 50.005 | | M | |
| Total | | 33914124 | 2147769 | | | | |

Chiral **3a**:




<Peak Table>

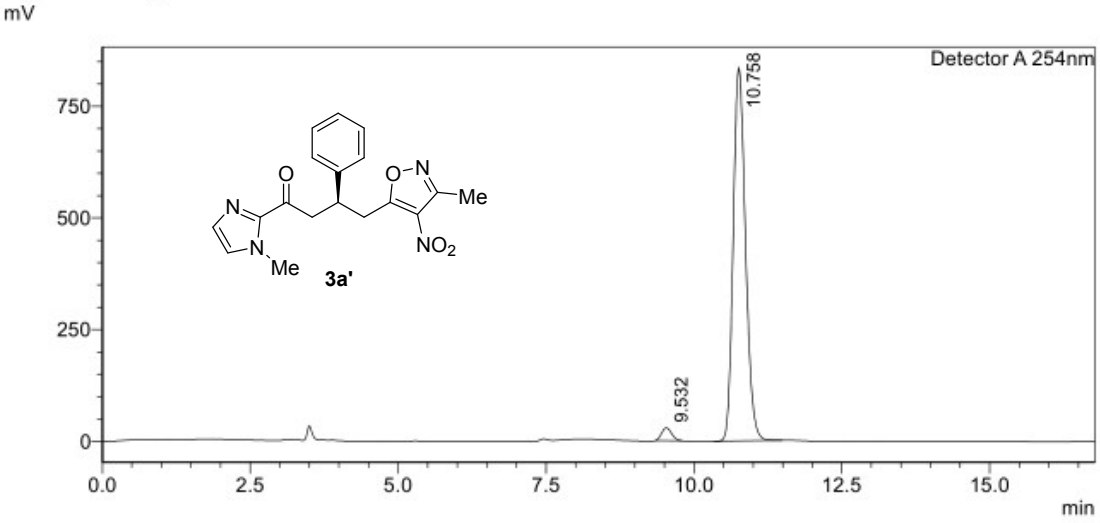
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 9.503 | 31145211 | 2391785 | 97.624 | | M | |
| 2 | 10.879 | 757906 | 54922 | 2.376 | | M | |
| Total | | 31903117 | 2446707 | | | | |

HPLC traces of racemic **3a** and chiral **3a**. Area integration = 95% ee.

Chiral **3a'**:

**<Chromatogram>**



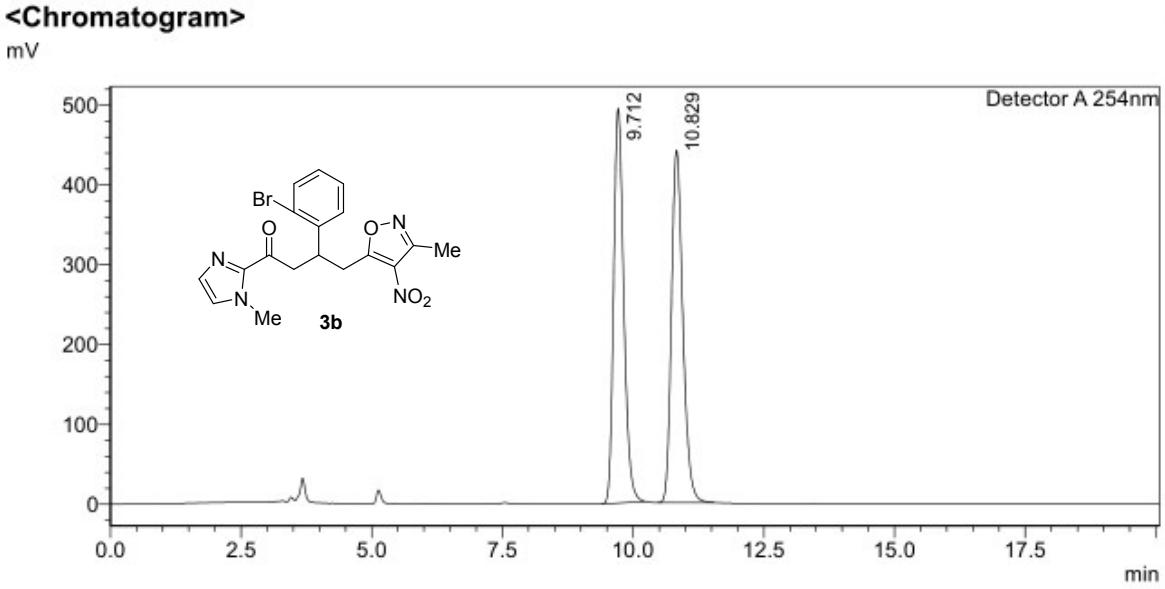

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 9.532 | 337843 | 28631 | 2.729 | | M | |
| 2 | 10.758 | 12040221 | 835239 | 97.271 | | M | |
| Total | | 12378064 | 863870 | | | | |

HPLC traces of racemic **3a** and chiral **3a'**. Area integration = 95% ee.

Racemic **3b**

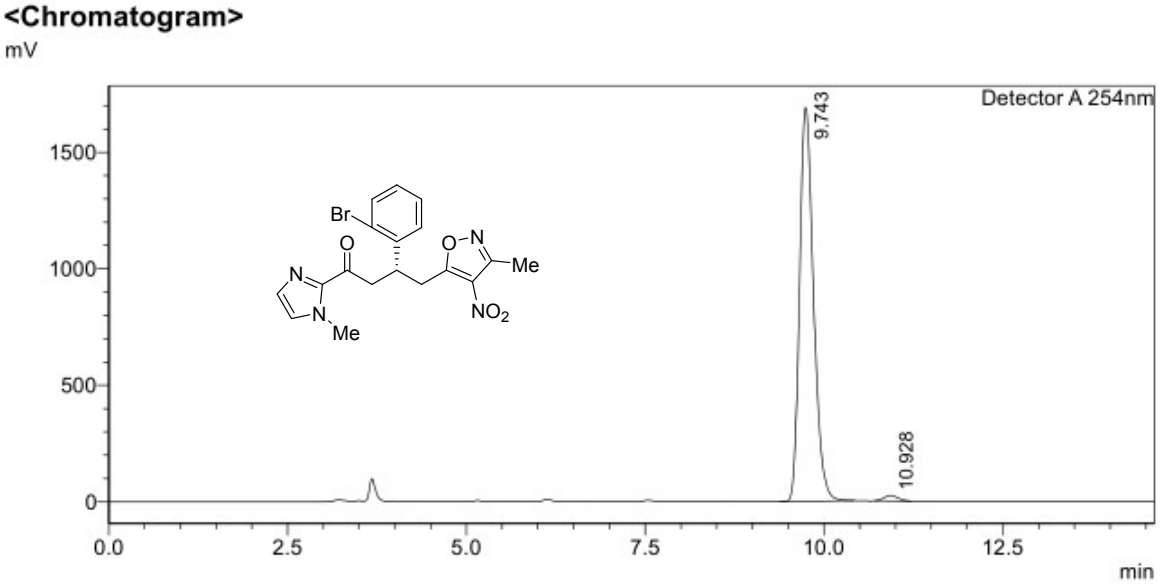



**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 9.712 | 6653930 | 494288 | 49.835 | | M | |
| 2 | 10.829 | 6698012 | 441259 | 50.165 | | M | |
| Total | | 13351942 | 935547 | | | | |

Chiral **3b**:




**<Peak Table>**

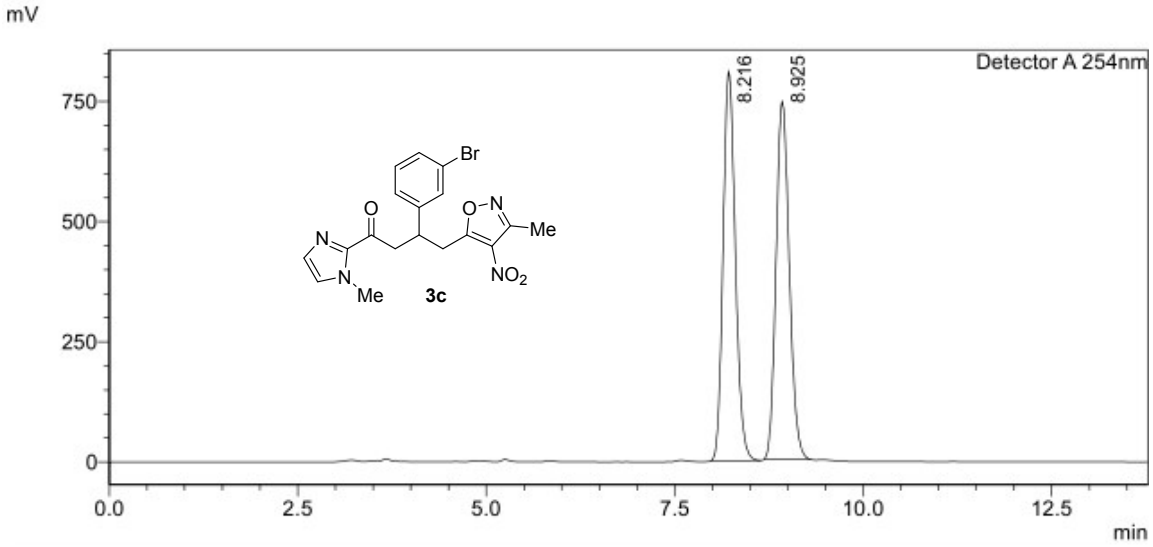
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 9.743 | 22915072 | 1689189 | 98.624 | | M | |
| 2 | 10.928 | 319774 | 22953 | 1.376 | | M | |
| Total | | 23234846 | 1712142 | | | | |

HPLC traces of racemic **3b** and chiral **3b**. Area integration = 97% ee.

Racemic **3c**

**<Chromatogram>**



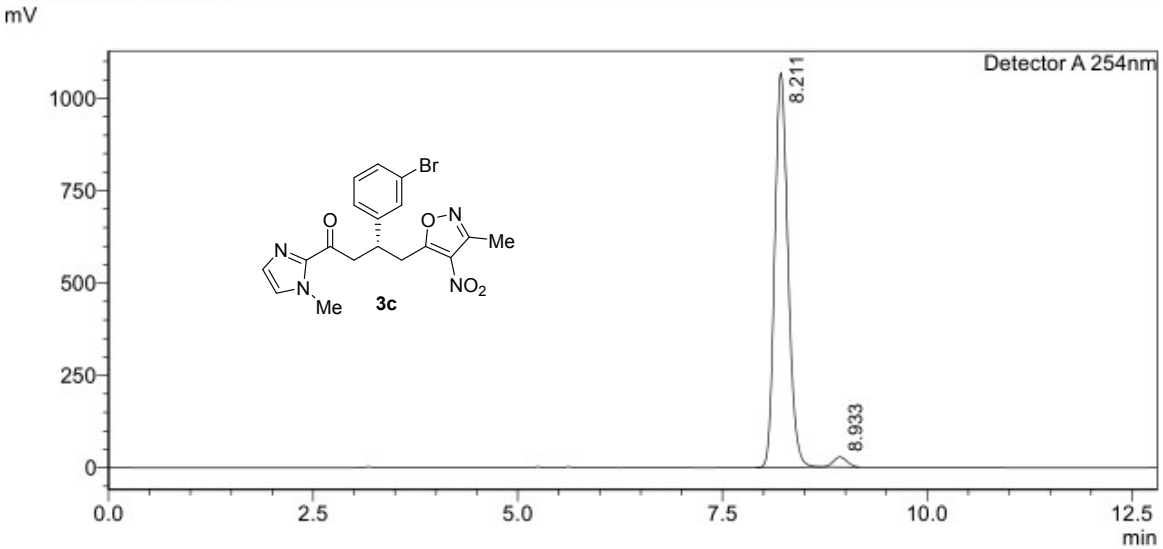

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 8.216 | 9177025 | 809348 | 50.162 | | M | |
| 2 | 8.925 | 9117879 | 743878 | 49.838 | | M | |
| Total | | 18294904 | 1553226 | | | | |

Chiral **3c**:

**<Chromatogram>**



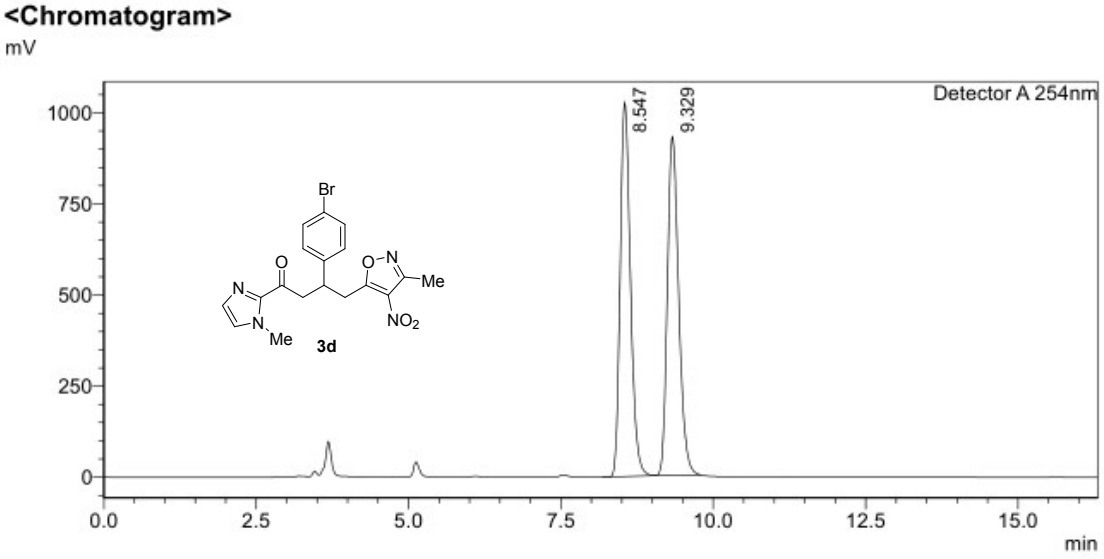

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 8.211 | 12042807 | 1067304 | 97.495 | | M | |
| 2 | 8.933 | 309397 | 26922 | 2.505 | | M | |
| Total | | 12352204 | 1094225 | | | | |

HPLC traces of racemic **3c** and chiral **3c**. Area integration = 95% ee.

Racemic **3d**

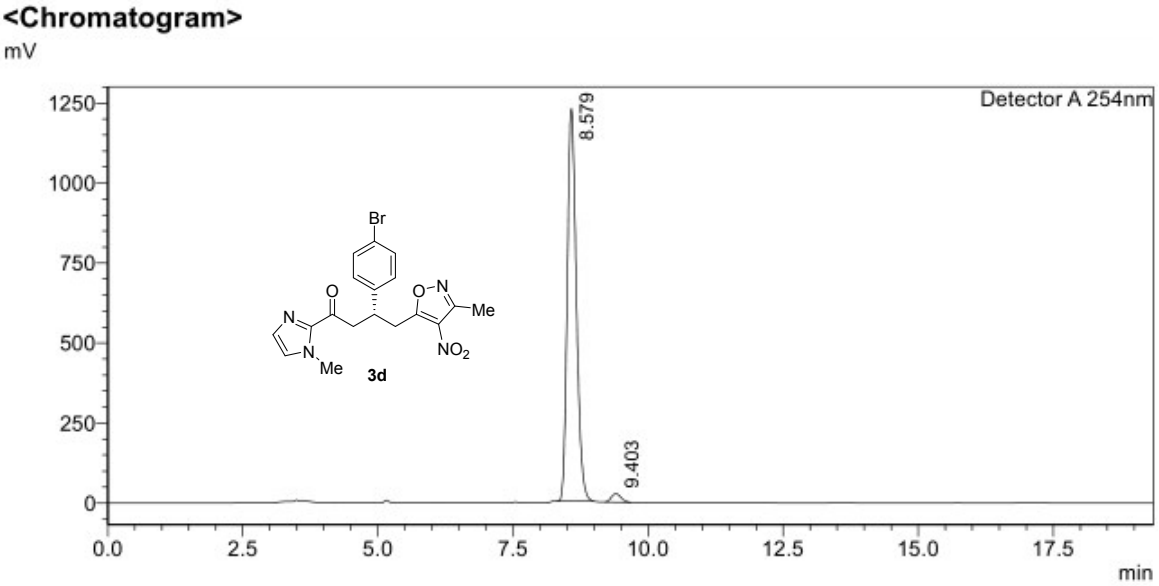



<Peak Table>

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 8.547 | 12041027 | 1026400 | 50.112 | | M | |
| 2 | 9.329 | 11987310 | 929522 | 49.888 | | M | |
| Total | | 24028337 | 1955923 | | | | |

Chiral **3d**:




<Peak Table>

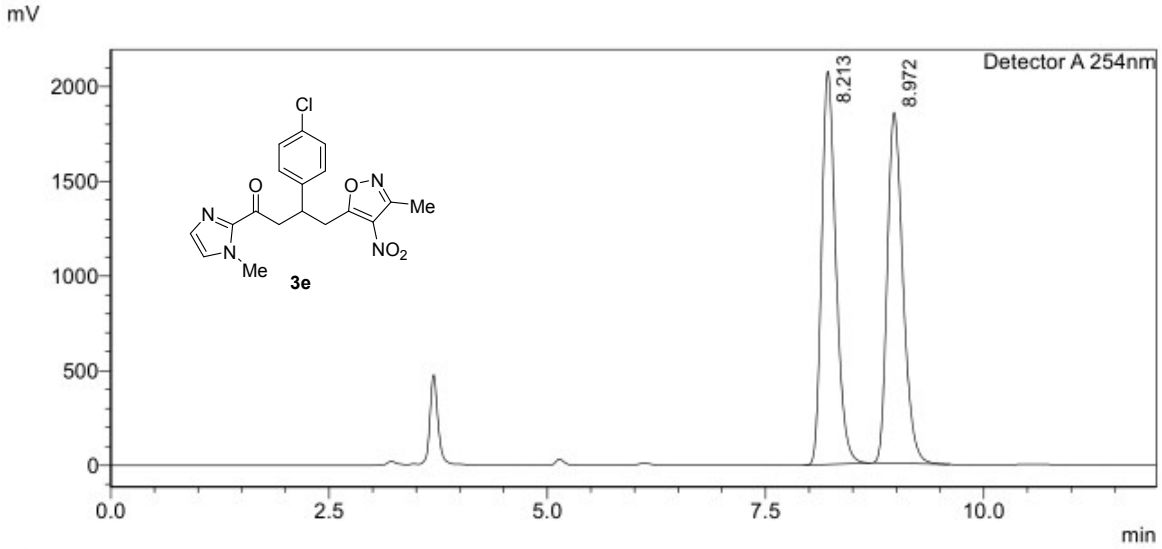
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 8.579 | 14272337 | 1225708 | 97.779 | | M | |
| 2 | 9.403 | 324251 | 26514 | 2.221 | | M | |
| Total | | 14596588 | 1252221 | | | | |

HPLC traces of racemic **3d** and chiral **3d**. Area integration = 96% ee.

Racemic **3e**

**<Chromatogram>**



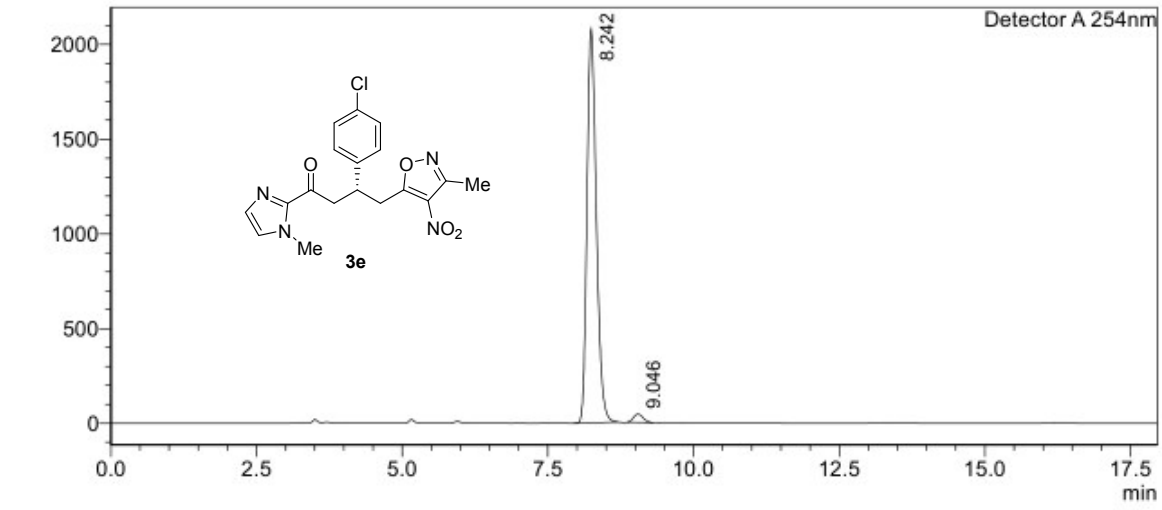

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 8.213 | 23522410 | 2074775 | 50.446 | | M | |
| 2 | 8.972 | 23106479 | 1850310 | 49.554 | | M | |
| Total | | 46628889 | 3925085 | | | | |

Chiral **3e**:

**<Chromatogram>**



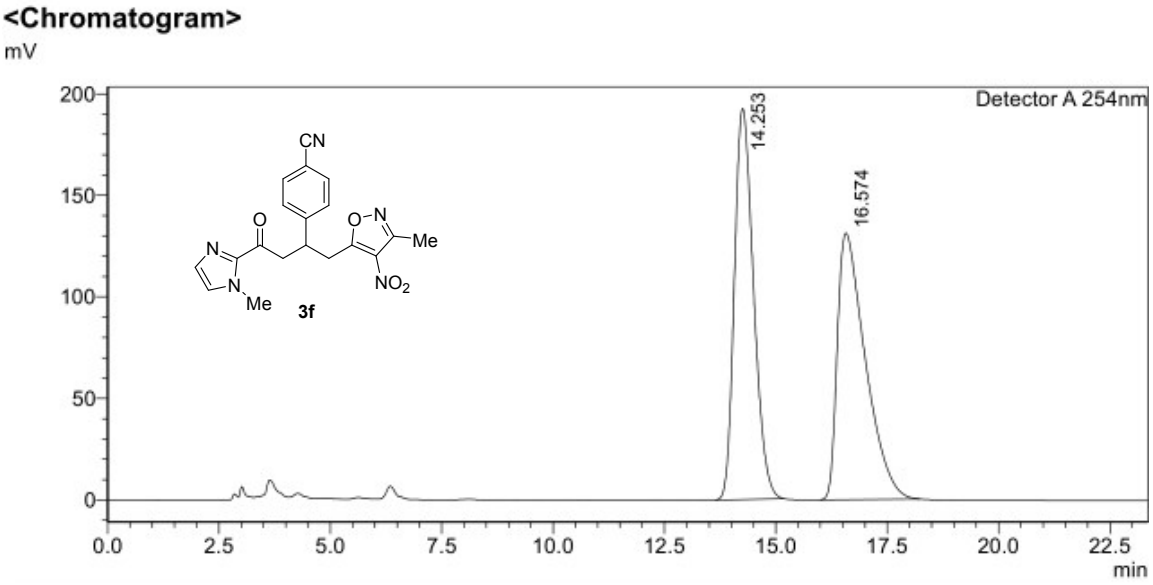

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 8.242 | 23252587 | 2077797 | 97.879 | | M | |
| 2 | 9.046 | 503940 | 43597 | 2.121 | | M | |
| Total | | 23756527 | 2121394 | | | | |

HPLC traces of racemic **3e** and chiral **3e**. Area integration = 96% ee.

Racemic **3f**

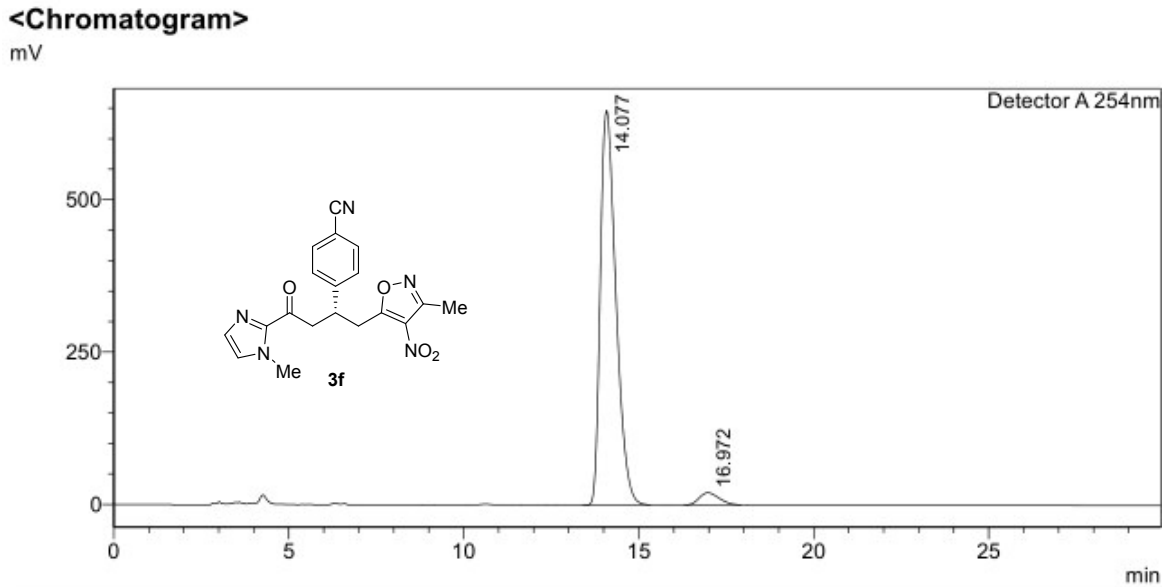



**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 14.253 | 5754970 | 192435 | 50.040 | | M | |
| 2 | 16.574 | 5745712 | 131208 | 49.960 | | M | |
| Total | | 11500682 | 323643 | | | | |

Chiral **3f**:




**<Peak Table>**

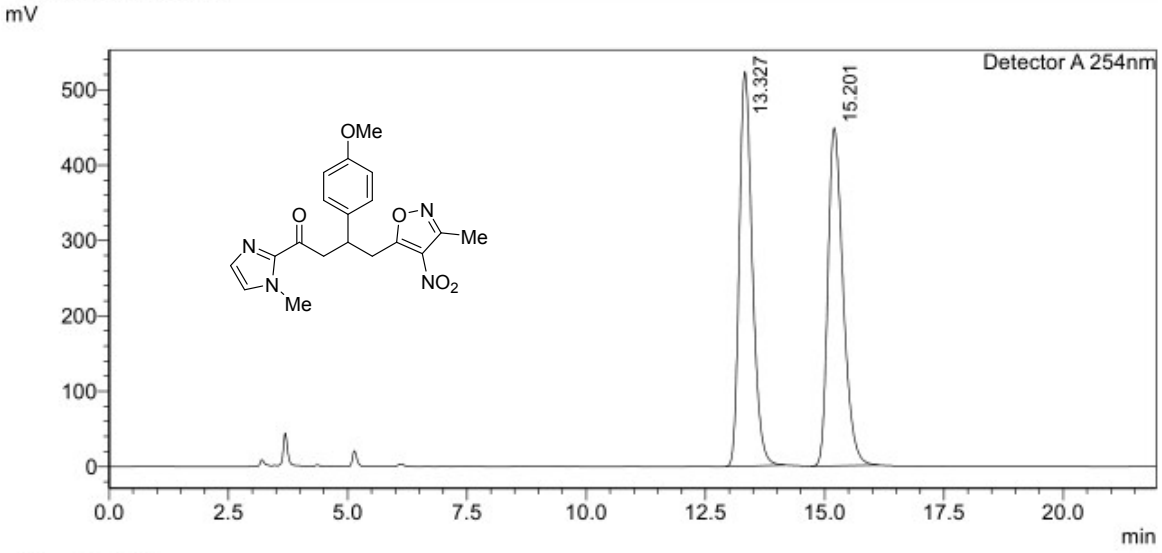
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 14.077 | 19971644 | 647547 | 96.146 | | M | |
| 2 | 16.972 | 800481 | 20071 | 3.854 | | M | |
| Total | | 20772126 | 667618 | | | | |

HPLC traces of racemic **3f** and chiral **3f**. Area integration = 92% ee.

Racemic **3g**

**<Chromatogram>**



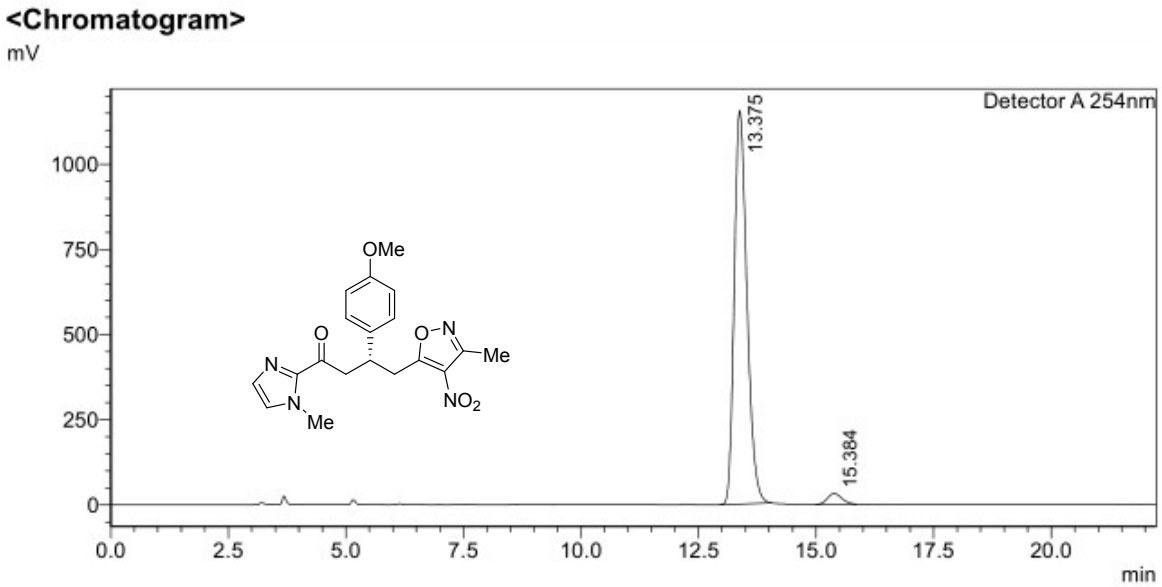

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 13.327 | 9922123 | 522787 | 49.955 | | M | |
| 2 | 15.201 | 9940127 | 447939 | 50.045 | | M | |
| Total | | 19862249 | 970726 | | | | |

Chiral **3g**:

**<Chromatogram>**




**<Peak Table>**

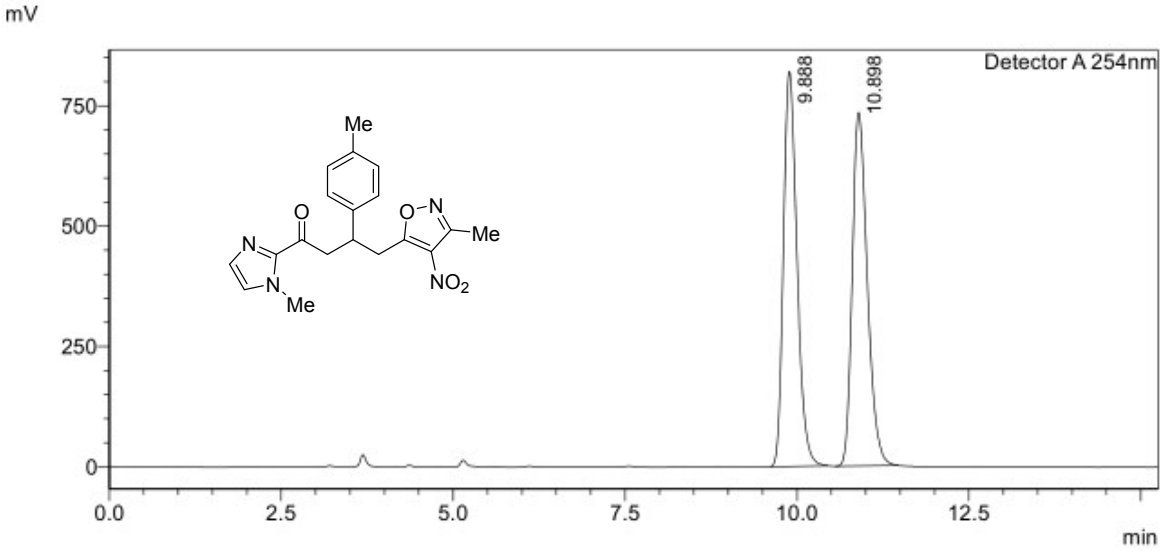
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 13.375 | 21695310 | 1155453 | 96.959 | | M | |
| 2 | 15.384 | 680473 | 31750 | 3.041 | | M | |
| Total | | 22375782 | 1187202 | | | | |

HPLC traces of racemic **3g** and chiral **3g**. Area integration = 94% ee.

Racemic **3h**

**<Chromatogram>**



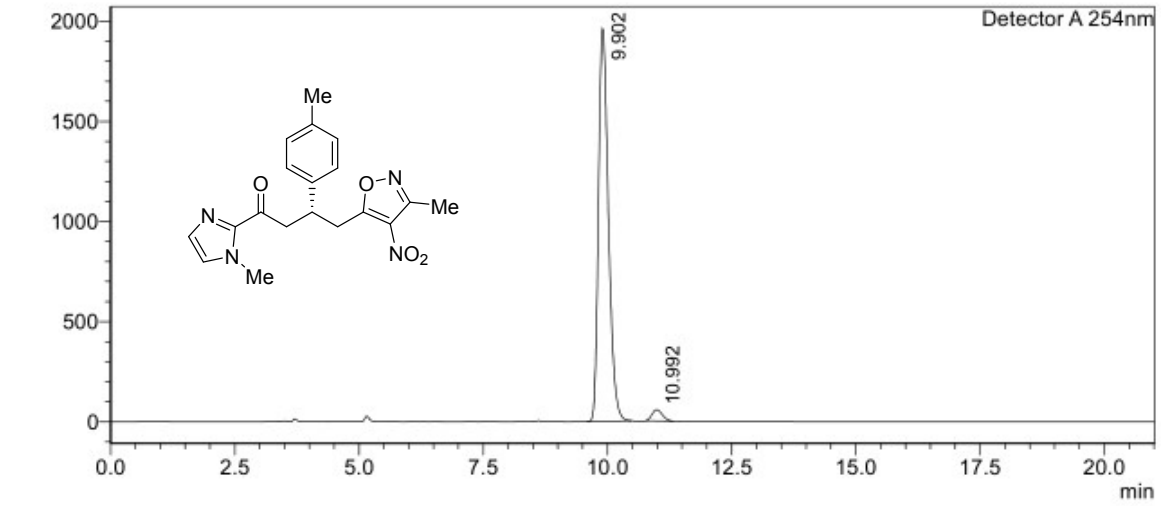

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 9.888 | 11186002 | 819737 | 49.981 | | M | |
| 2 | 10.898 | 11194686 | 734463 | 50.019 | | M | |
| Total | | 22380688 | 1554200 | | | | |

Chiral **3h**:

**<Chromatogram>**



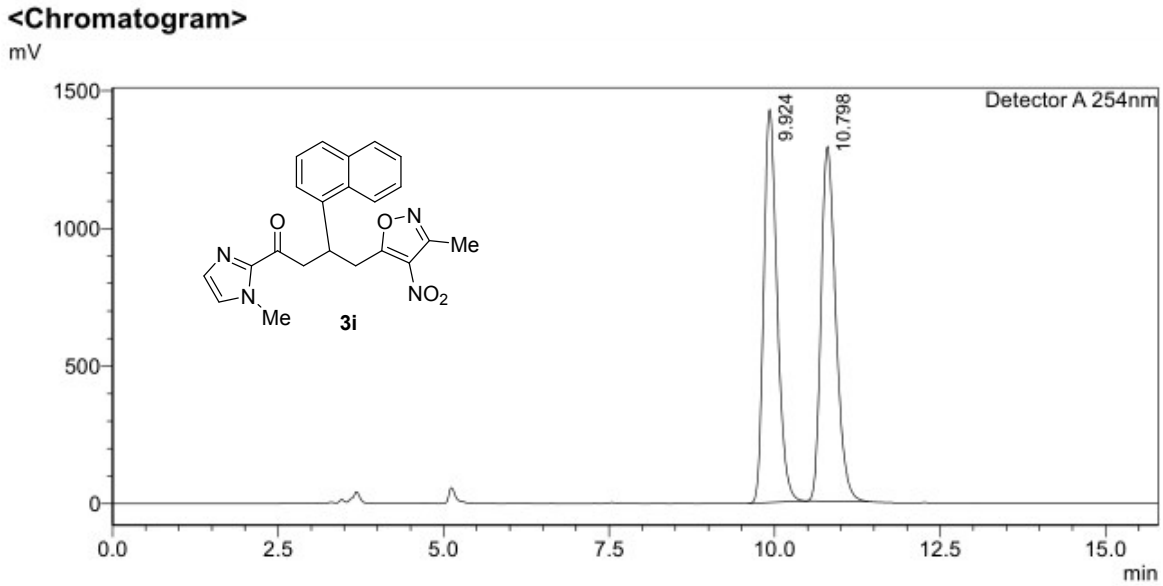

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 9.902 | 27122716 | 1960924 | 97.116 | | M | |
| 2 | 10.992 | 805399 | 55903 | 2.884 | | M | |
| Total | | 27928115 | 2016827 | | | | |

HPLC traces of racemic **3h** and chiral **3h**. Area integration = 94% ee.

Racemic **3i**

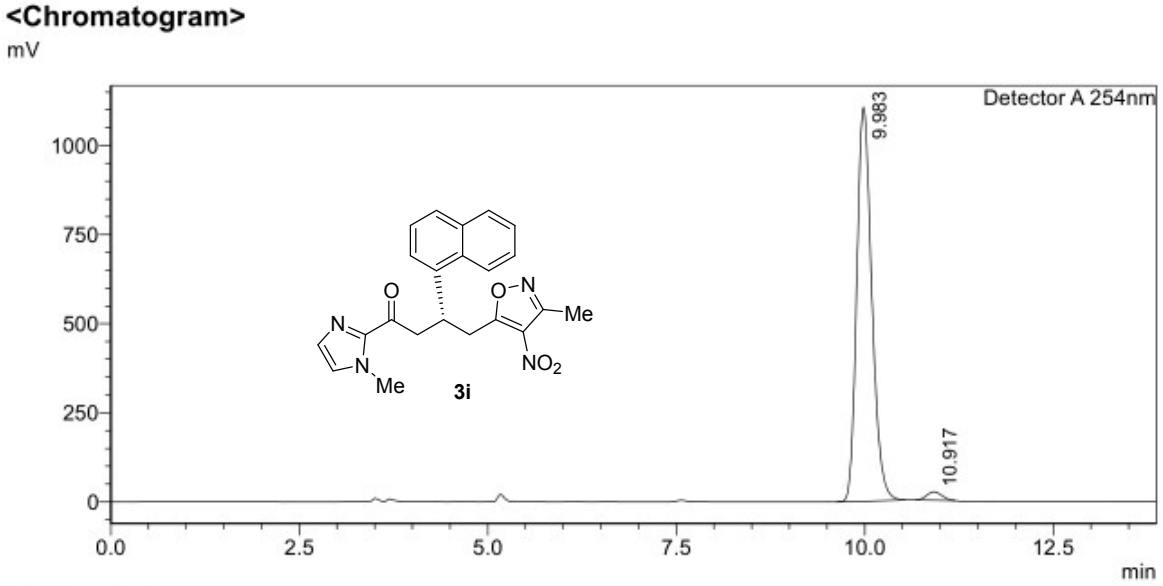



**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 9.924 | 20026174 | 1427749 | 50.043 | | M | |
| 2 | 10.798 | 19991830 | 1288658 | 49.957 | | M | |
| Total | | 40018004 | 2716407 | | | | |

Chiral **3i**:



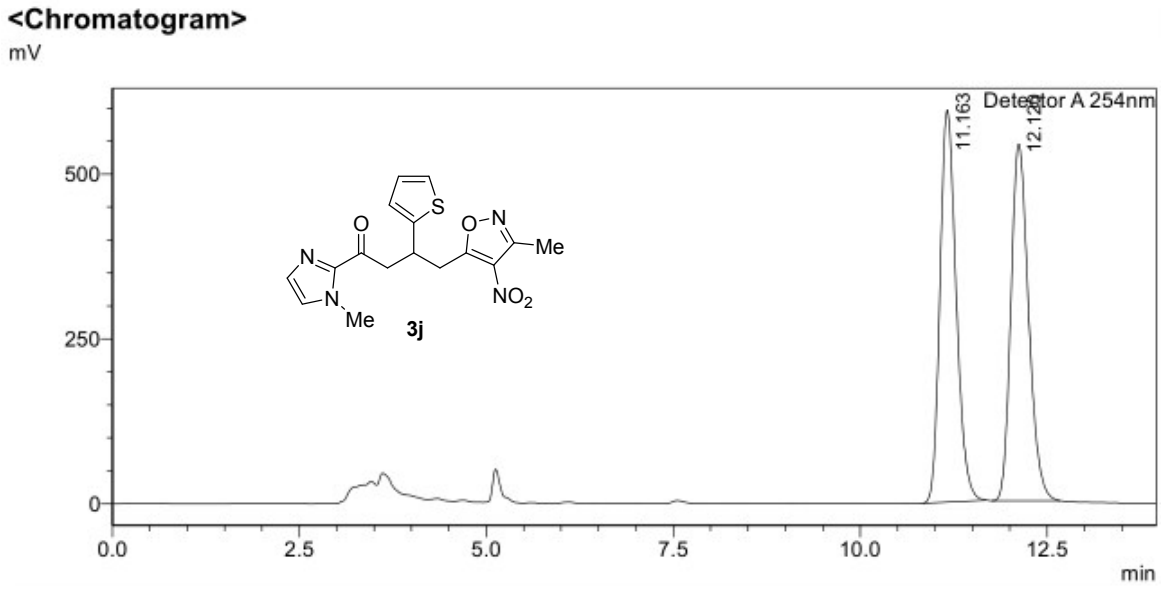

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 9.983 | 15347054 | 1104425 | 97.845 | | M | |
| 2 | 10.917 | 338001 | 23830 | 2.155 | | M | |
| Total | | 15685055 | 1128255 | | | | |

HPLC traces of racemic **3i** and chiral **3i**. Area integration = 96% ee.

Racemic **3j**

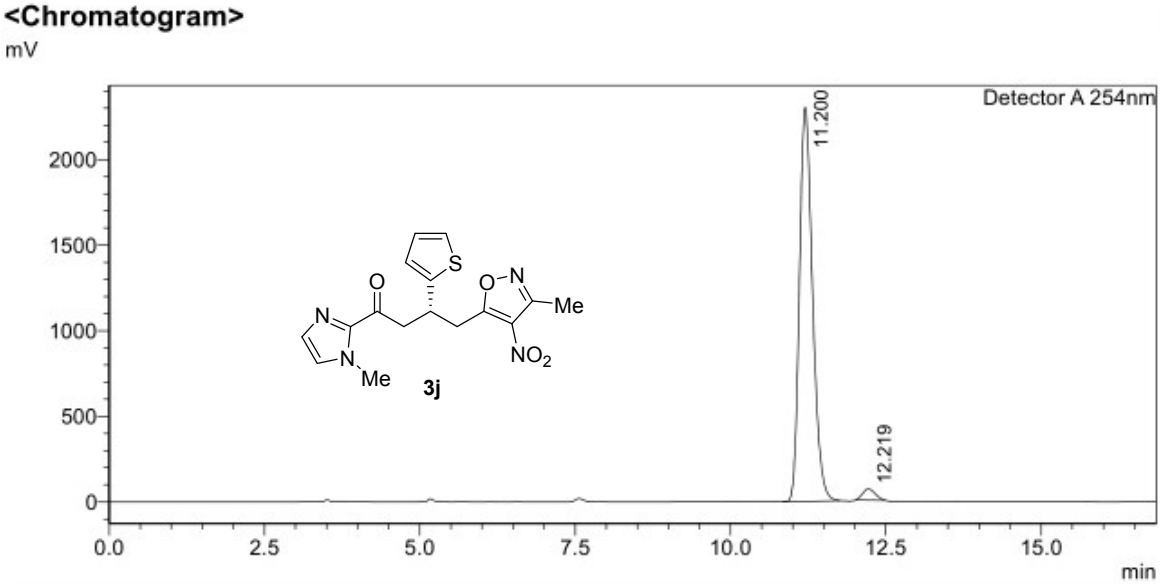



<Peak Table>

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 11.163 | 8937292 | 594584 | 50.129 | | M | |
| 2 | 12.120 | 8891338 | 541169 | 49.871 | | M | |
| Total | | 17828630 | 1135753 | | | | |

Chiral **3j**:



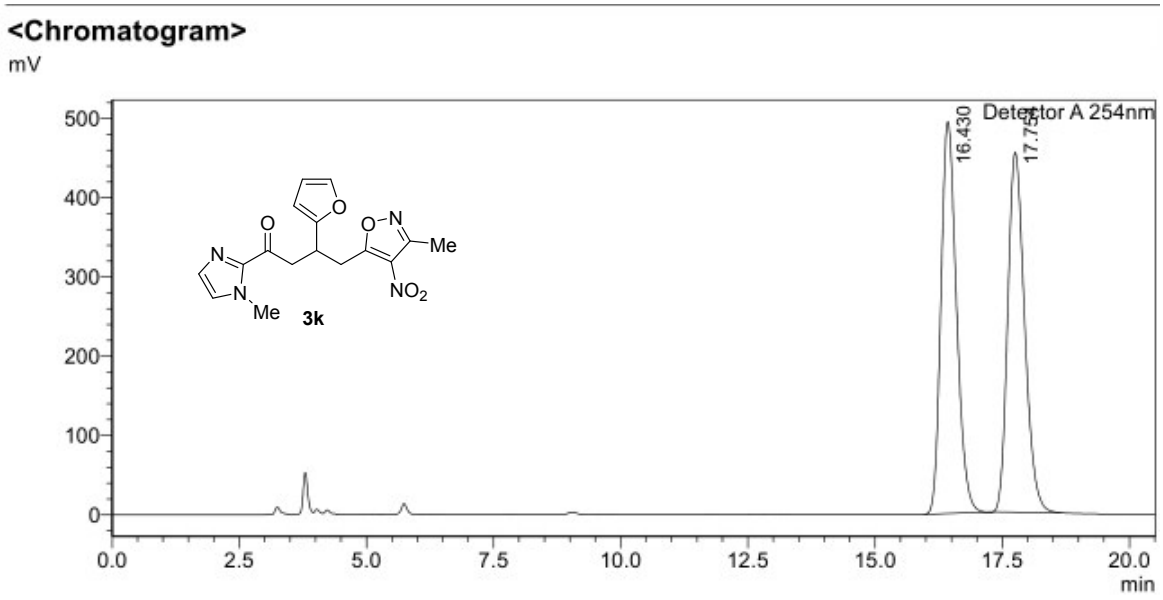

<Peak Table>

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 11.200 | 33729975 | 2300888 | 97.302 | | M | |
| 2 | 12.219 | 935358 | 65509 | 2.698 | | M | |
| Total | | 34665333 | 2366396 | | | | |

HPLC traces of racemic **3j** and chiral **3j**. Area integration = 95% ee.

Racemic **3k**

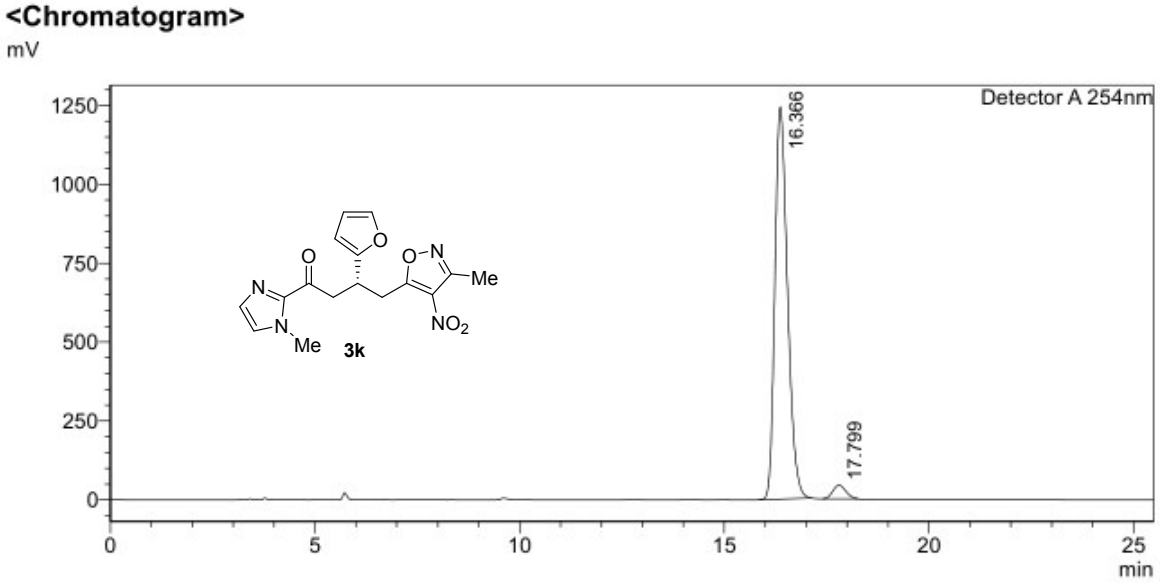



<Peak Table>

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 16.430 | 10483783 | 494062 | 50.059 | | M | |
| 2 | 17.754 | 10459034 | 453586 | 49.941 | | M | |
| Total | | 20942816 | 947648 | | | | |

Chiral **3k**:



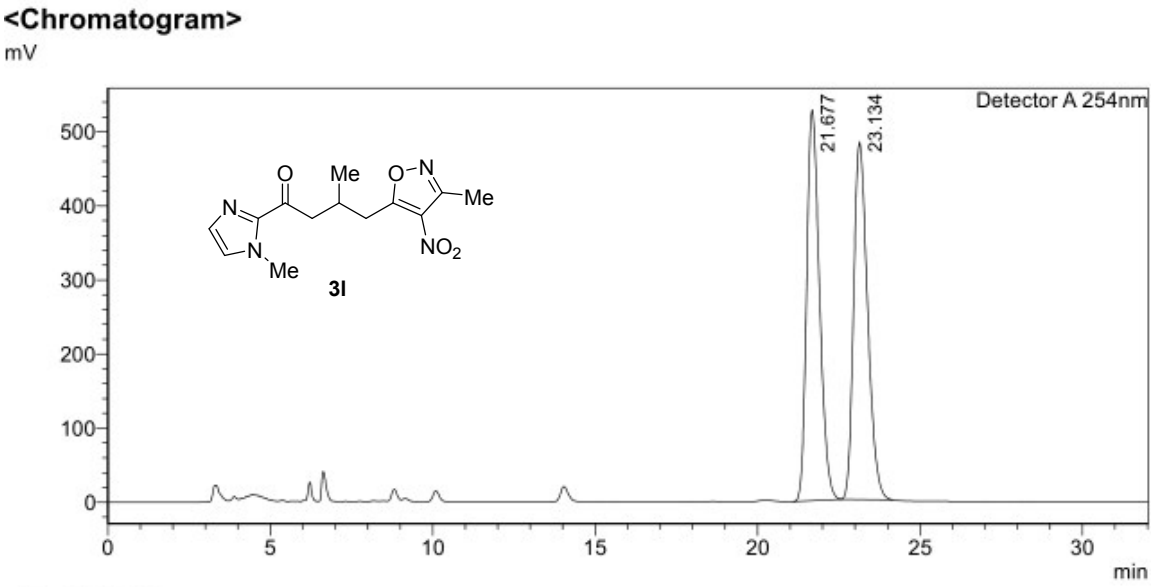

<Peak Table>

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 16.366 | 26696099 | 1242572 | 96.521 | | M | |
| 2 | 17.799 | 962190 | 43305 | 3.479 | | M | |
| Total | | 27658289 | 1285877 | | | | |

HPLC traces of racemic **3k** and chiral **3k**. Area integration = 93% ee.

Racemic **3l**

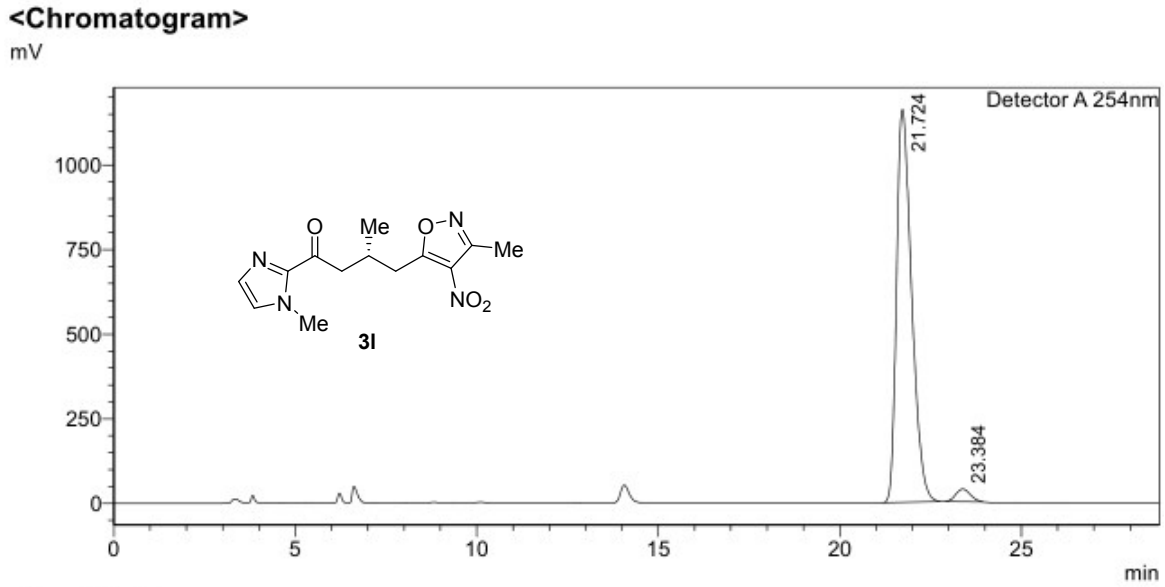



<Peak Table>

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 21.677 | 14421247 | 527230 | 50.086 | | M | |
| 2 | 23.134 | 14371569 | 481769 | 49.914 | | M | |
| Total | | 28792816 | 1008999 | | | | |

Chiral **3l**:




<Peak Table>

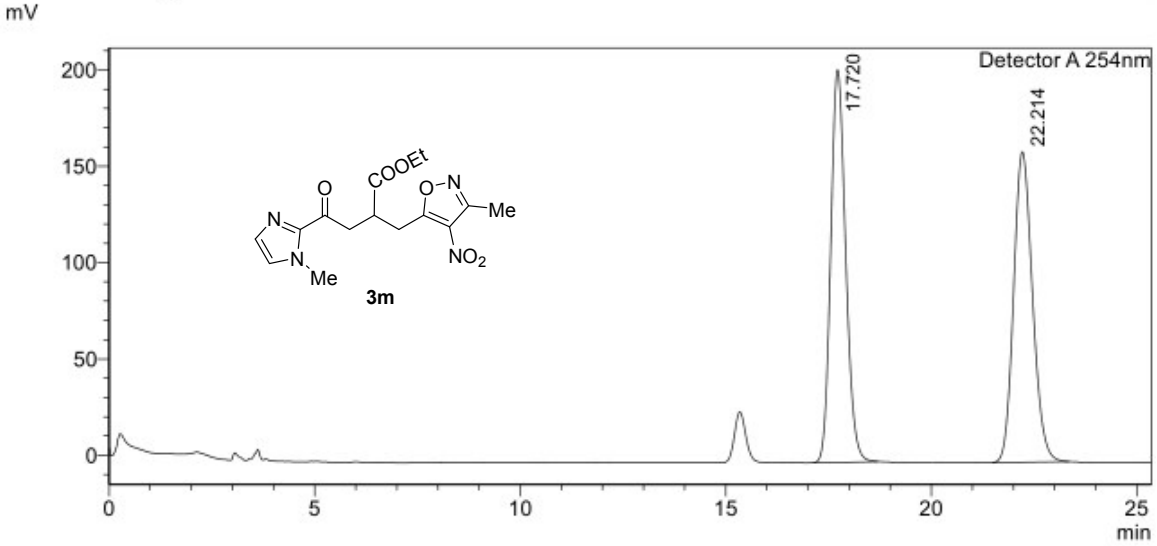
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 21.724 | 33507590 | 1160794 | 96.989 | | M | |
| 2 | 23.384 | 1040204 | 37068 | 3.011 | | M | |
| Total | | 34547794 | 1197862 | | | | |

HPLC traces of racemic **3l** and chiral **3l**. Area integration = 94% ee.

Racemic **3m**

**<Chromatogram>**



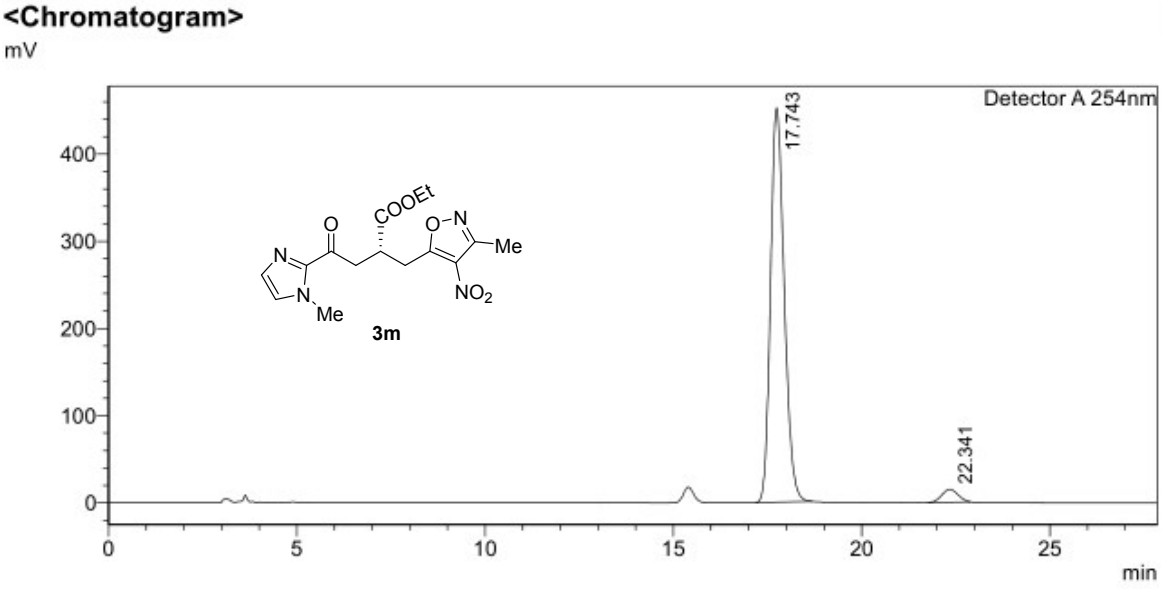

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 17.720 | 5138844 | 203634 | 50.007 | | M | |
| 2 | 22.214 | 5137369 | 161020 | 49.993 | | M | |
| Total | | 10276212 | 364654 | | | | |

Chiral **3m**:

**<Chromatogram>**




**<Peak Table>**

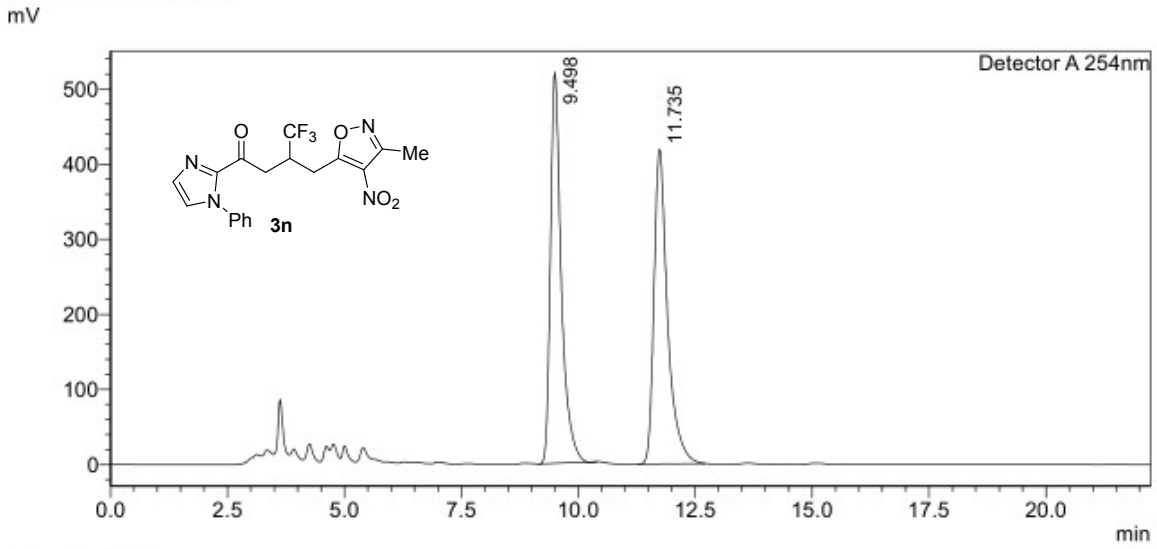
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 17.743 | 11458044 | 452001 | 96.304 | | M | |
| 2 | 22.341 | 439773 | 14684 | 3.696 | | M | |
| Total | | 11897817 | 466685 | | | | |

HPLC traces of racemic **3m** and chiral **3m**. Area integration = 93% ee.

Racemic **3n**

**<Chromatogram>**



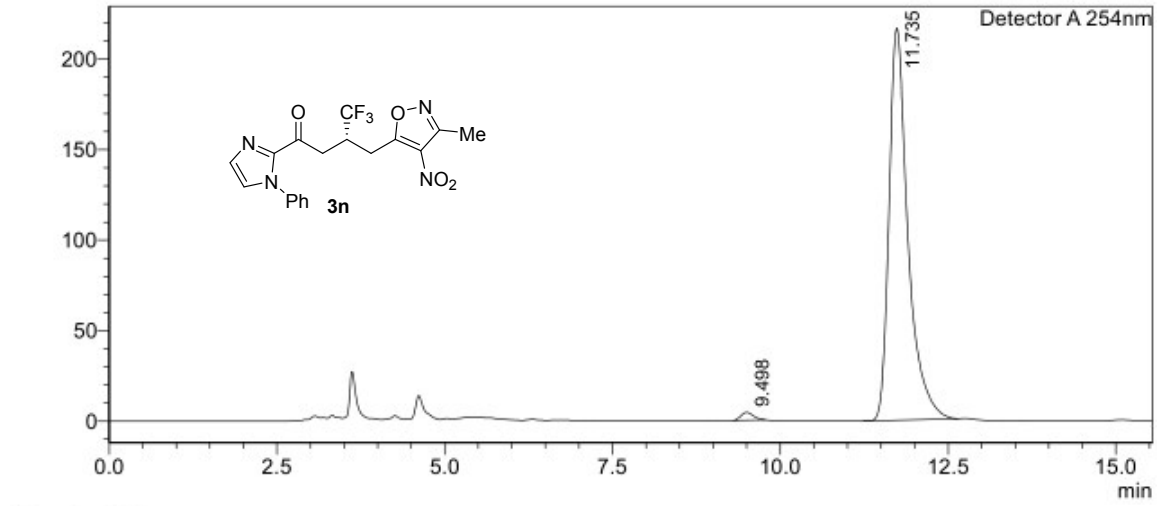

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 9.498 | 8356380 | 519836 | 49.780 | | M | |
| 2 | 11.735 | 8430089 | 419047 | 50.220 | | M | |
| Total | | 16786469 | 938884 | | | | |

Chiral **3n**:

**<Chromatogram>**




**<Peak Table>**

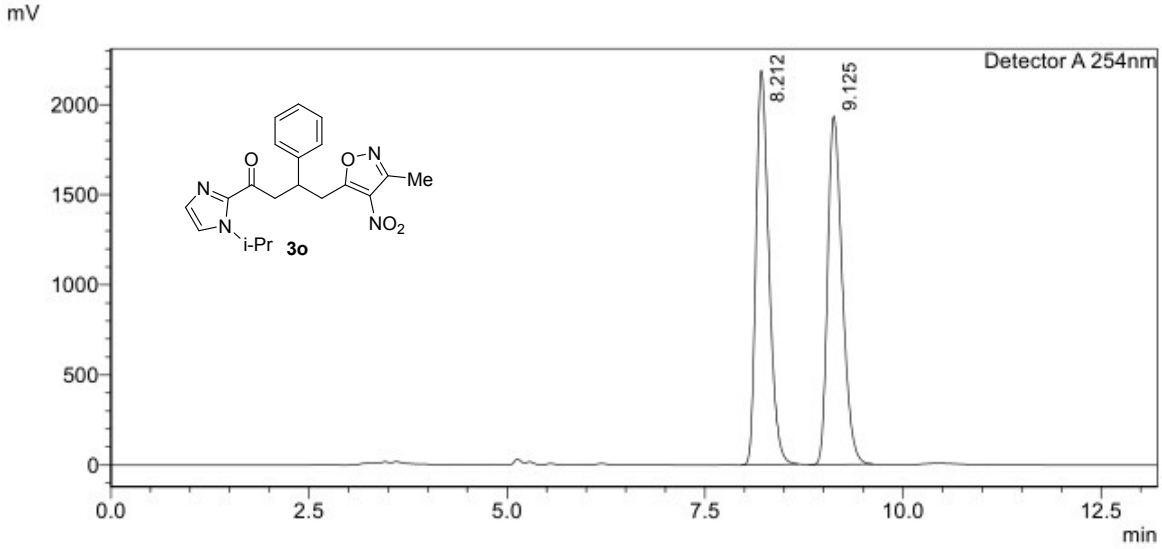
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 9.498 | 56546 | 4334 | 1.315 | | M | |
| 2 | 11.735 | 4241944 | 216661 | 98.685 | | M | |
| Total | | 4298490 | 220995 | | | | |

HPLC traces of racemic **3n** and chiral **3n**. Area integration = 97% ee.

Racemic **3o**

**<Chromatogram>**



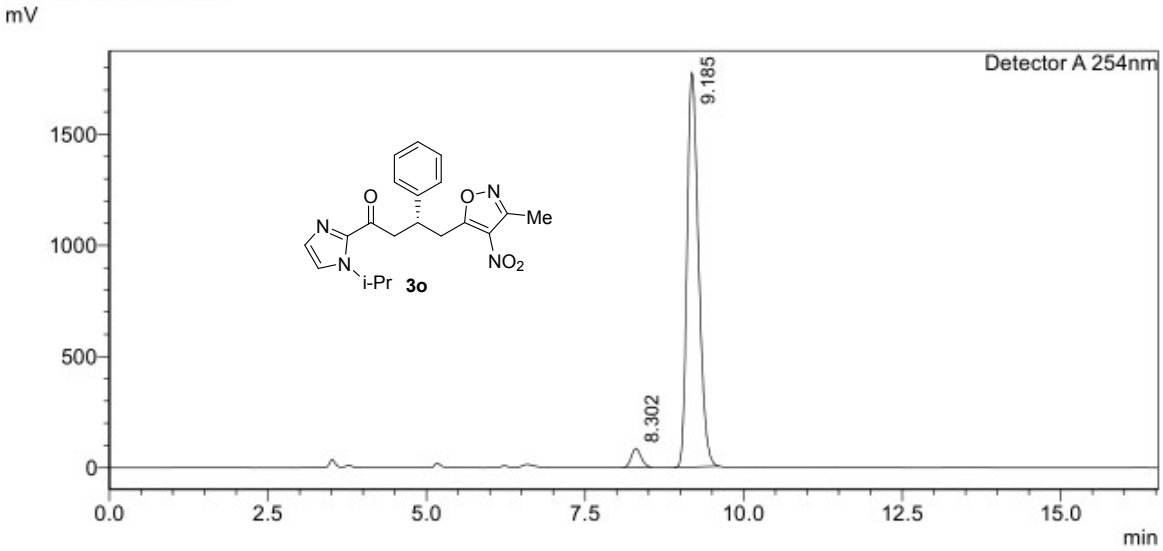

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 8.212 | 24757215 | 2186058 | 49.977 | | M | |
| 2 | 9.125 | 24780101 | 1932033 | 50.023 | | M | |
| Total | | 49537316 | 4118091 | | | | |

Chiral **3o**:

**<Chromatogram>**




**<Peak Table>**

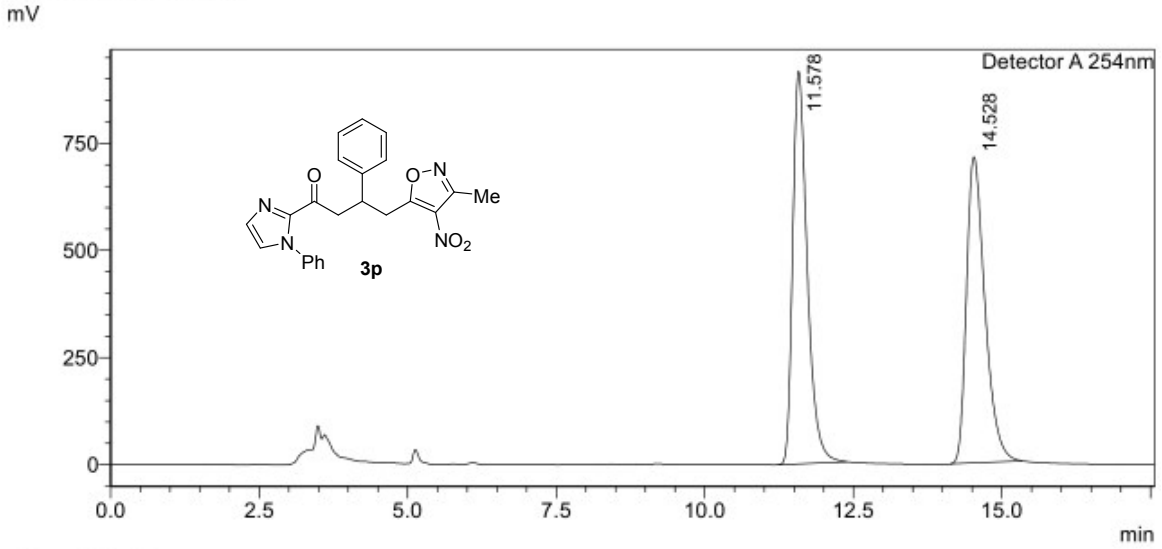
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 8.302 | 908655 | 84546 | 3.907 | | M | |
| 2 | 9.185 | 22346885 | 1774020 | 96.093 | | M | |
| Total | | 23255540 | 1858566 | | | | |

HPLC traces of racemic **3o** and chiral **3o**. Area integration = 92% ee.

Racemic **3p**

**<Chromatogram>**



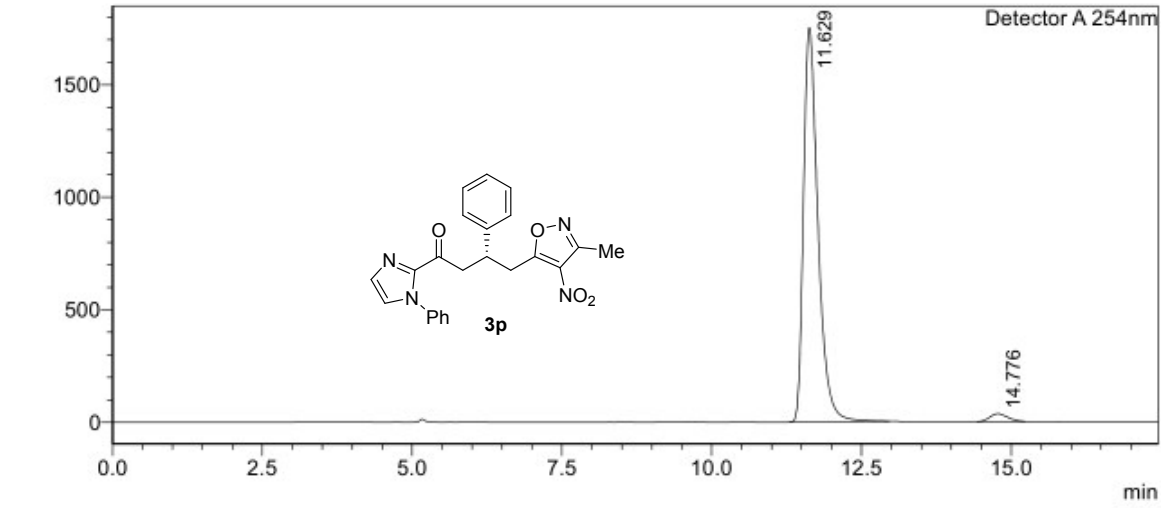

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 11.578 | 15534464 | 915869 | 50.150 | | M | |
| 2 | 14.528 | 15441811 | 713729 | 49.850 | | M | |
| Total | | 30976275 | 1629598 | | | | |

Chiral **3p**:

**<Chromatogram>**




**<Peak Table>**

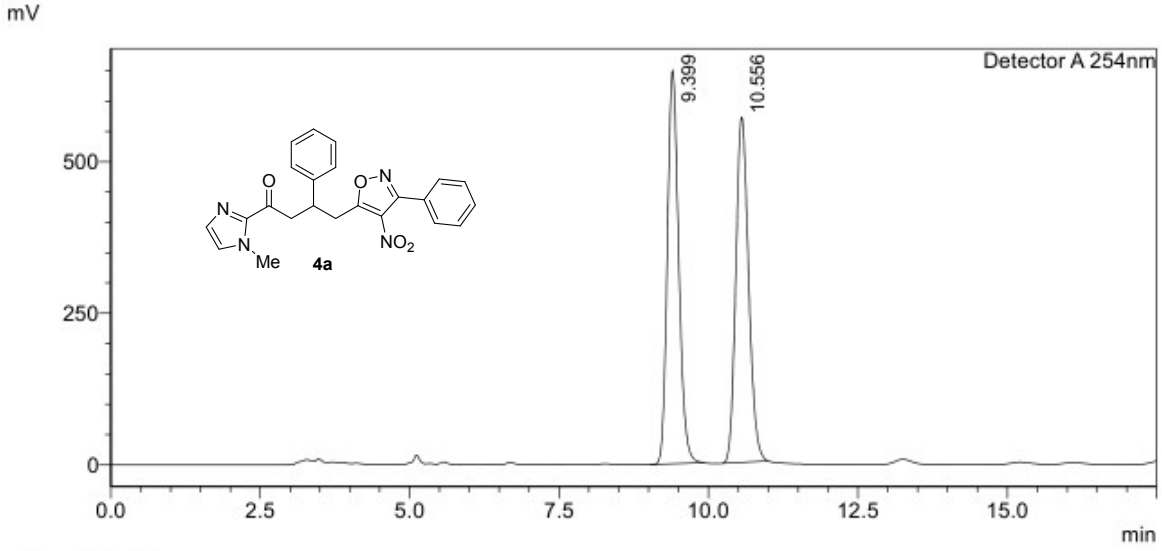
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 11.629 | 29400503 | 1751578 | 97.575 | | M | |
| 2 | 14.776 | 730556 | 34795 | 2.425 | | M | |
| Total | | 30131059 | 1786373 | | | | |

HPLC traces of racemic **3p** and chiral **3p**. Area integration = 95% ee.

Racemic **4a**

**<Chromatogram>**



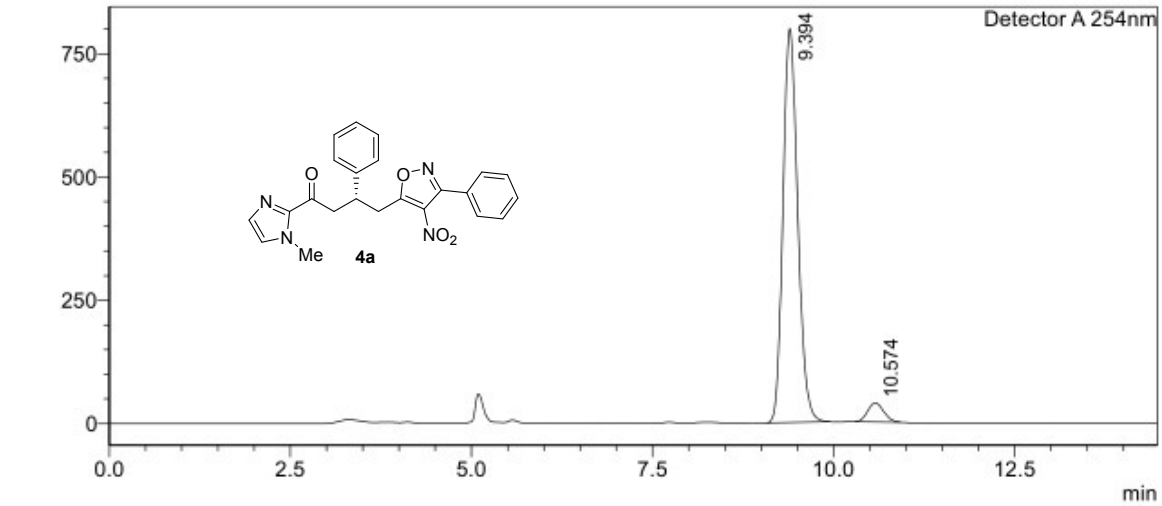

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 9.399 | 8544594 | 648449 | 50.291 | | M | |
| 2 | 10.556 | 8445820 | 569130 | 49.709 | | M | |
| Total | | 16990414 | 1217579 | | | | |

Chiral **4a**:

**<Chromatogram>**



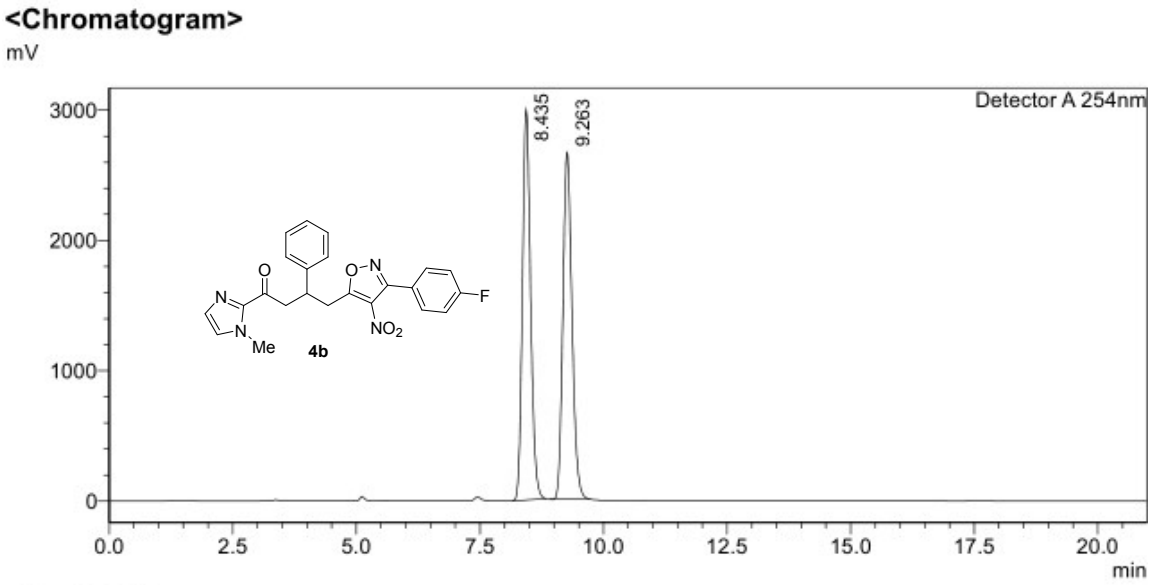

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 9.394 | 11305455 | 798357 | 95.014 | | M | |
| 2 | 10.574 | 593249 | 38521 | 4.986 | | M | |
| Total | | 11898704 | 836878 | | | | |

HPLC traces of racemic **4a** and chiral **4a**. Area integration = 90% ee.

Racemic **4b**

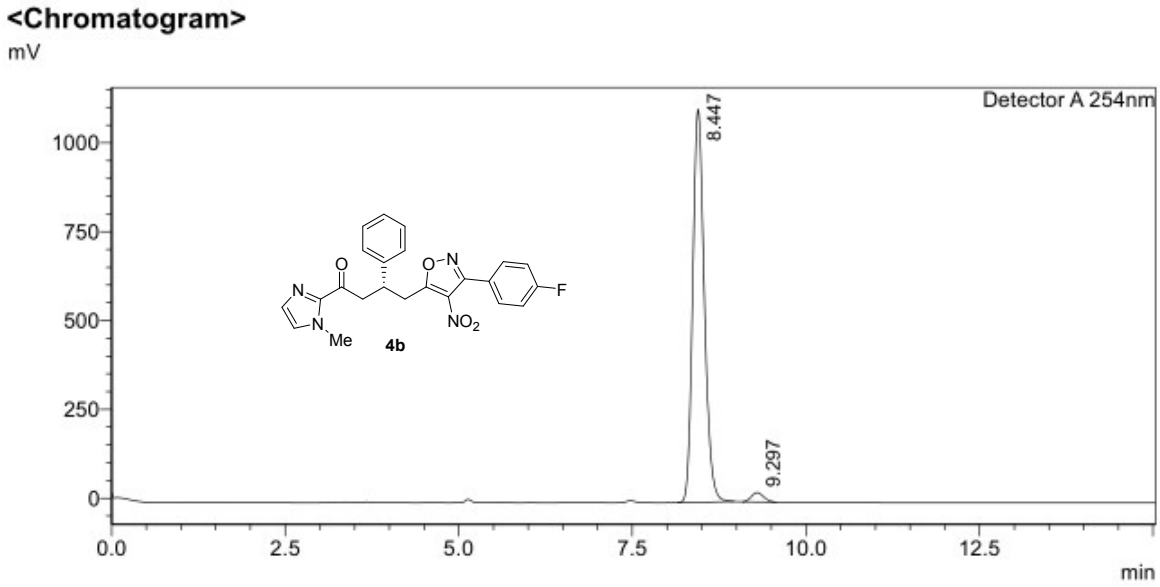



**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 8.435 | 34328716 | 2994168 | 50.170 | | M | |
| 2 | 9.263 | 34095892 | 2664272 | 49.830 | | M | |
| Total | | 68424607 | 5658440 | | | | |

Chiral **4b**:



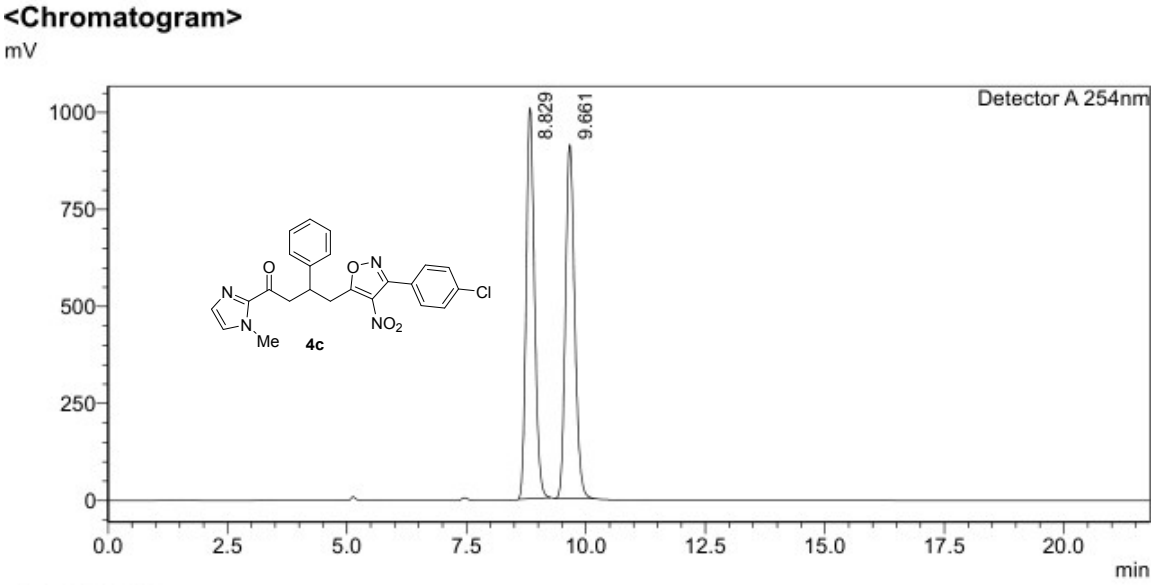

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 8.447 | 12822034 | 1105791 | 97.536 | | M | |
| 2 | 9.297 | 323950 | 26181 | 2.464 | | M | |
| Total | | 13145984 | 1131973 | | | | |

HPLC traces of racemic **4b** and chiral **4b**. Area integration = 95% ee.

Racemic **4c**

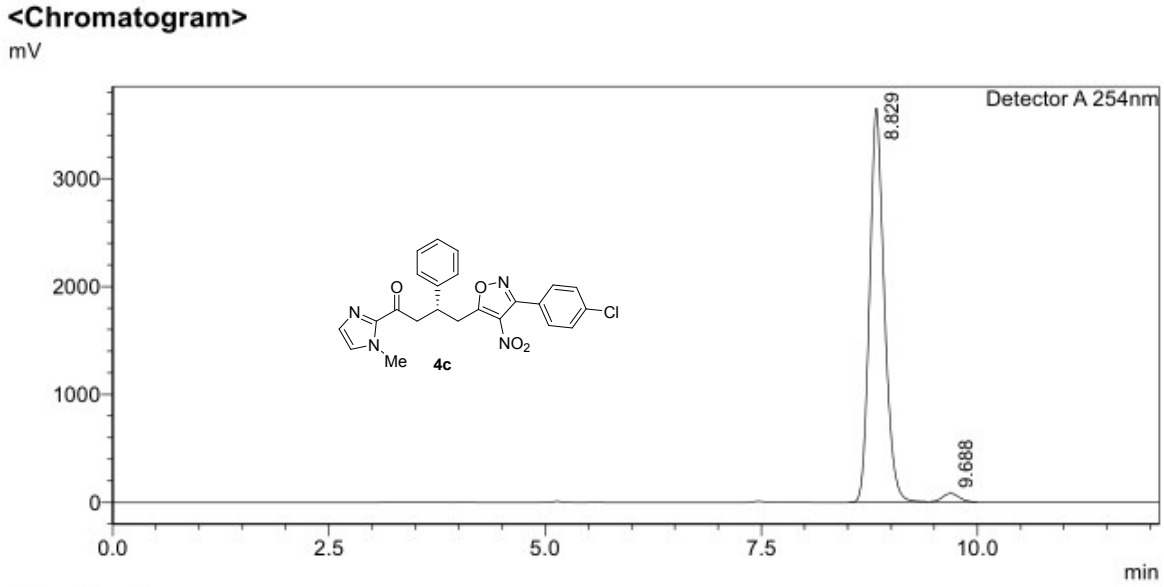



**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 8.829 | 12209382 | 1006916 | 49.896 | | M | |
| 2 | 9.661 | 12260227 | 911600 | 50.104 | | M | |
| Total | | 24469609 | 1918516 | | | | |

Chiral **4c**:




**<Peak Table>**

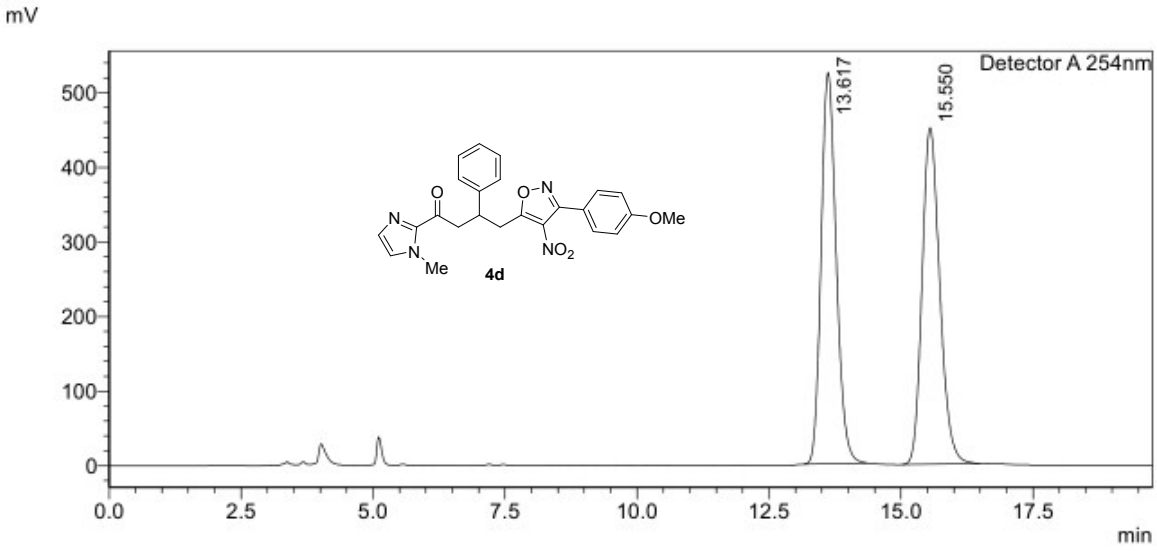
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 8.829 | 42962531 | 3644639 | 97.641 | | | |
| 2 | 9.688 | 1038158 | 78082 | 2.359 | | M | |
| Total | | 44000689 | 3722721 | | | | |

HPLC traces of racemic **4c** and chiral **4c**. Area integration = 95% ee.

Racemic **4d**

<Chromatogram>



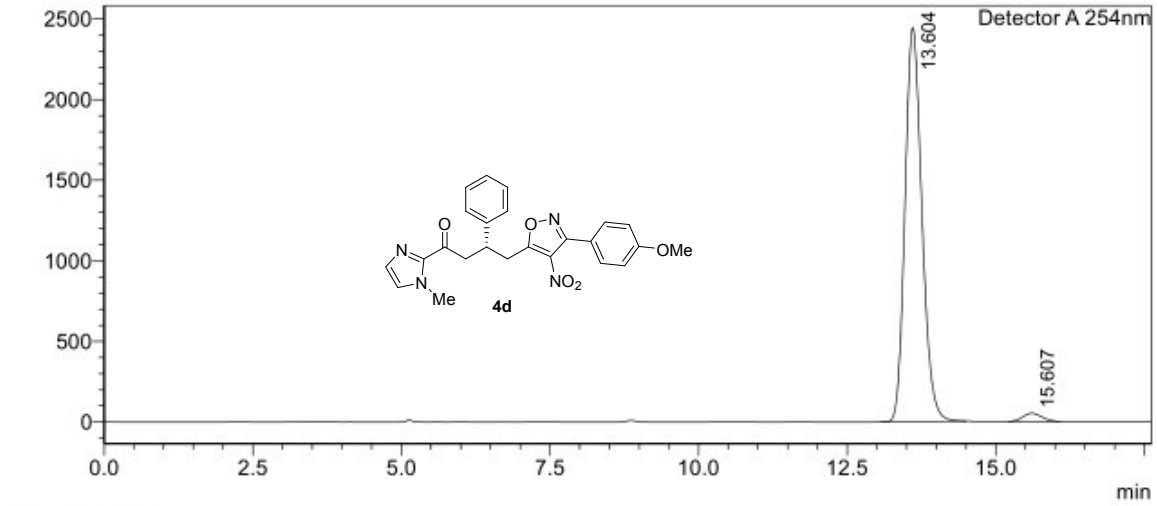

<Peak Table>

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 13.617 | 10410507 | 523983 | 49.814 | | M | |
| 2 | 15.550 | 10488264 | 450753 | 50.186 | | M | |
| Total | | 20898772 | 974736 | | | | |

Chiral **4d**:

<Chromatogram>




<Peak Table>

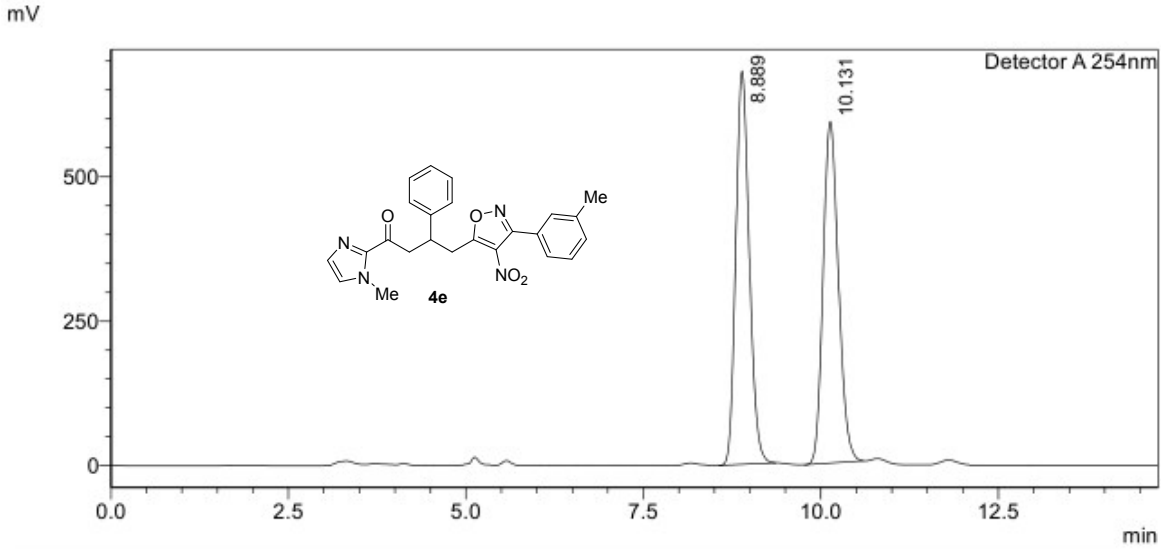
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 13.604 | 48249351 | 2444097 | 97.658 | | M | |
| 2 | 15.607 | 1157216 | 51417 | 2.342 | | M | |
| Total | | 49406567 | 2495514 | | | | |

HPLC traces of racemic **4d** and chiral **4d**. Area integration = 95% ee.

Racemic **4e**

**<Chromatogram>**



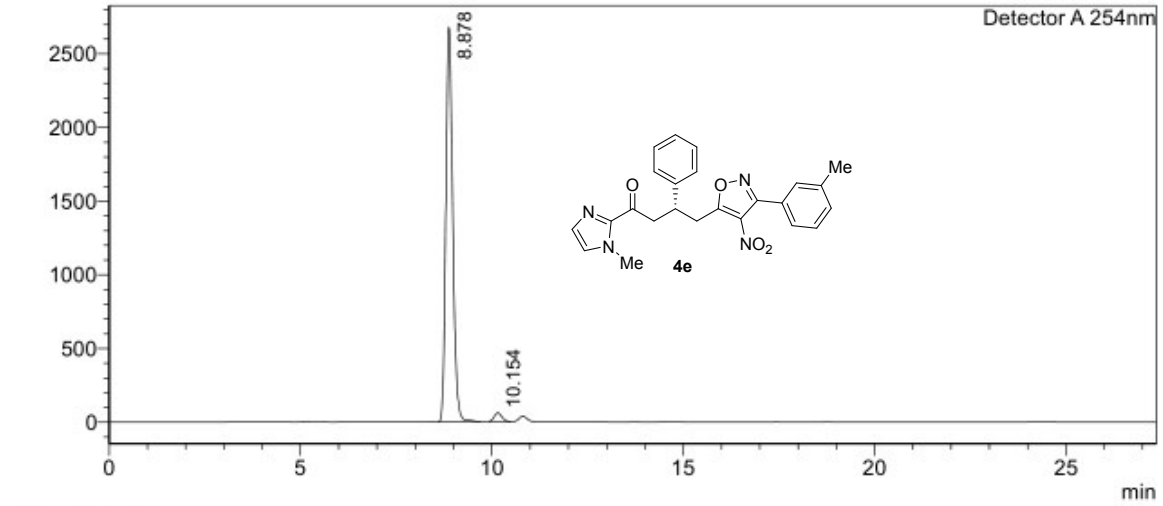

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 8.889 | 8982493 | 679657 | 50.273 | | M | |
| 2 | 10.131 | 8884810 | 590707 | 49.727 | | M | |
| Total | | 17867303 | 1270364 | | | | |

Chiral **4e**:

**<Chromatogram>**




**<Peak Table>**

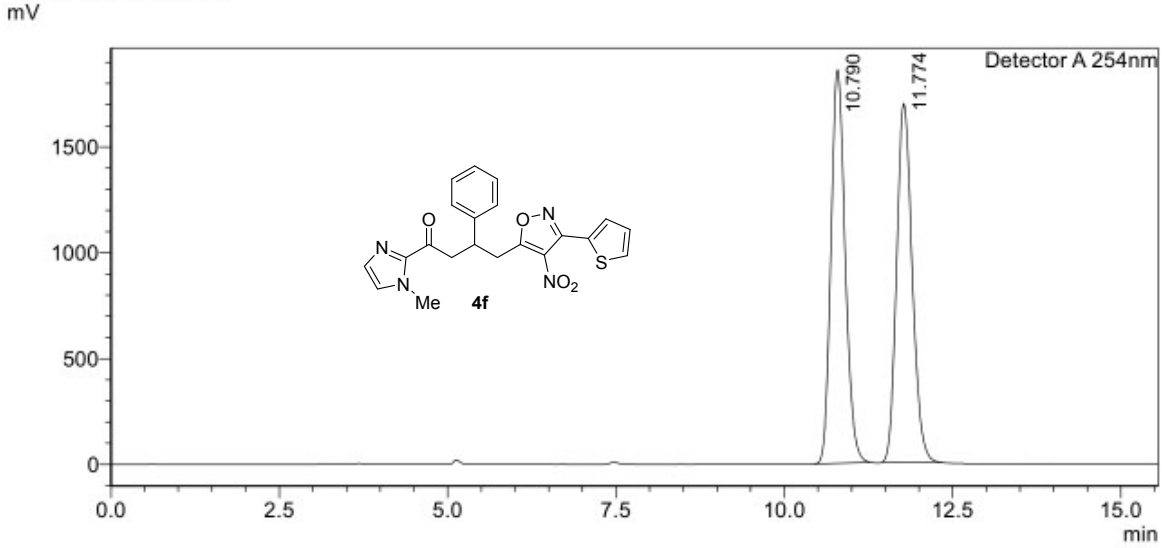
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 8.878 | 33472472 | 2676927 | 97.592 | | M | |
| 2 | 10.154 | 825896 | 58752 | 2.408 | | M | |
| Total | | 34298368 | 2735678 | | | | |

HPLC traces of racemic **4e** and chiral **4e**. Area integration = 95% ee.

Racemic **4f**

**<Chromatogram>**



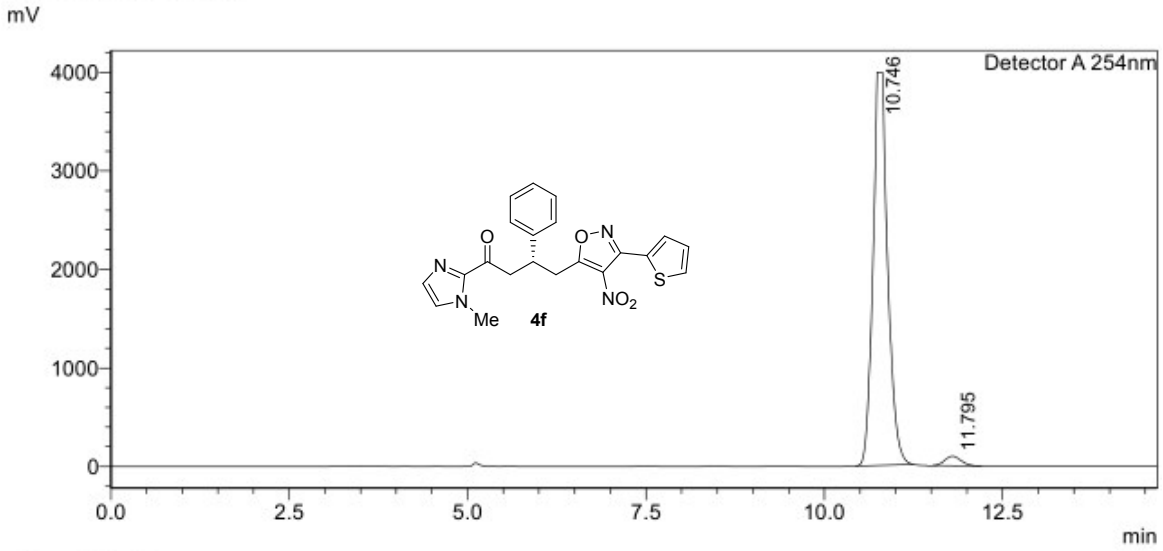

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 10.790 | 27332141 | 1858620 | 50.074 | | M | |
| 2 | 11.774 | 27251763 | 1693892 | 49.926 | | M | |
| Total | | 54583904 | 3552513 | | | | |

Chiral **4f**:

**<Chromatogram>**




**<Peak Table>**

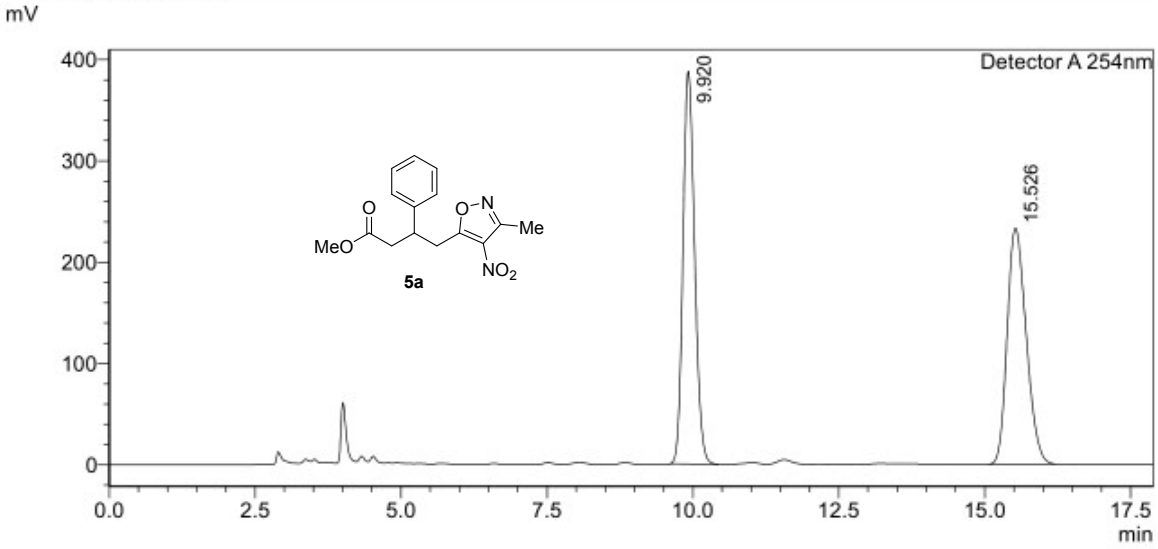
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 10.746 | 57174480 | 3988903 | 97.354 | | M | |
| 2 | 11.795 | 1553883 | 97673 | 2.646 | | M | |
| Total | | 58728364 | 4086576 | | | | |

HPLC traces of racemic **4f** and chiral **4f**. Area integration = 95% ee.

Racemic **5a**

**<Chromatogram>**



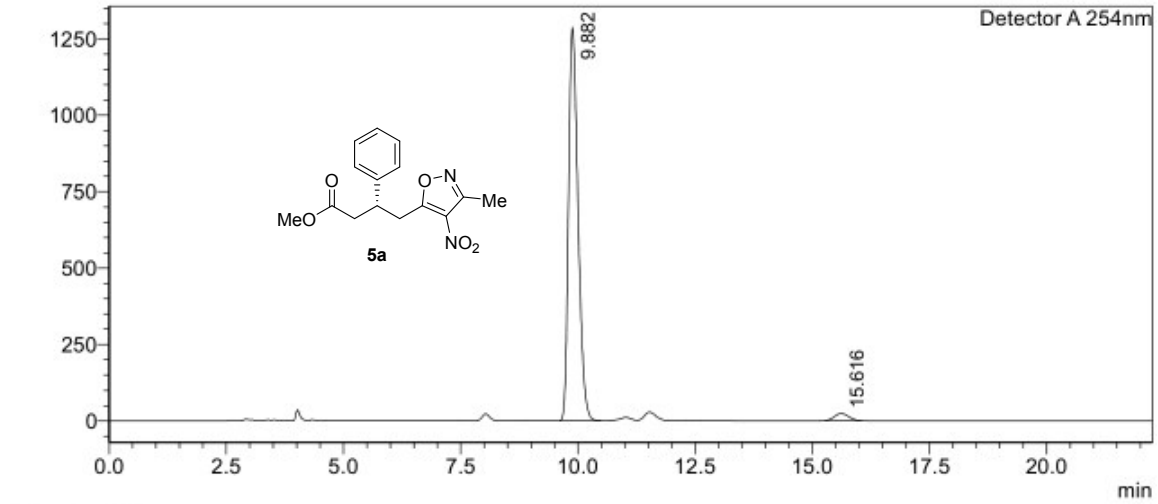

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 9.920 | 5369427 | 387537 | 50.483 | | M | |
| 2 | 15.526 | 5266774 | 232719 | 49.517 | | M | |
| Total | | 10636202 | 620256 | | | | |

Chiral **5a**:

**<Chromatogram>**



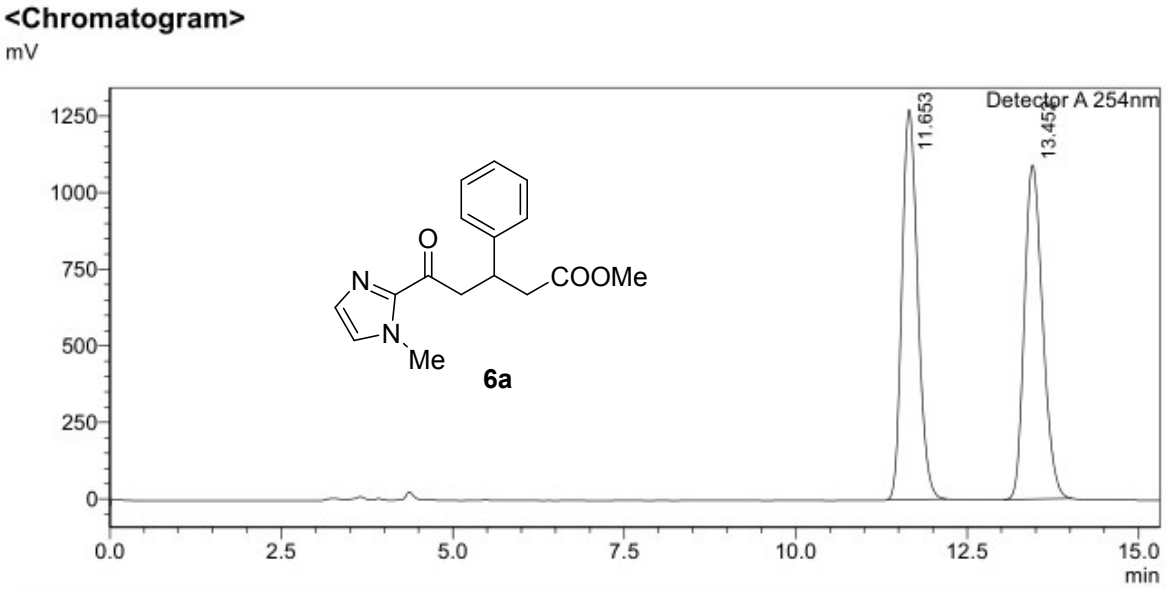

**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 9.882 | 18122350 | 1284357 | 97.397 | | M | |
| 2 | 15.616 | 484276 | 23255 | 2.603 | | M | |
| Total | | 18606626 | 1307612 | | | | |

HPLC traces of racemic **5a** and chiral **5a**. Area integration = 95% ee.

Racemic **6a**

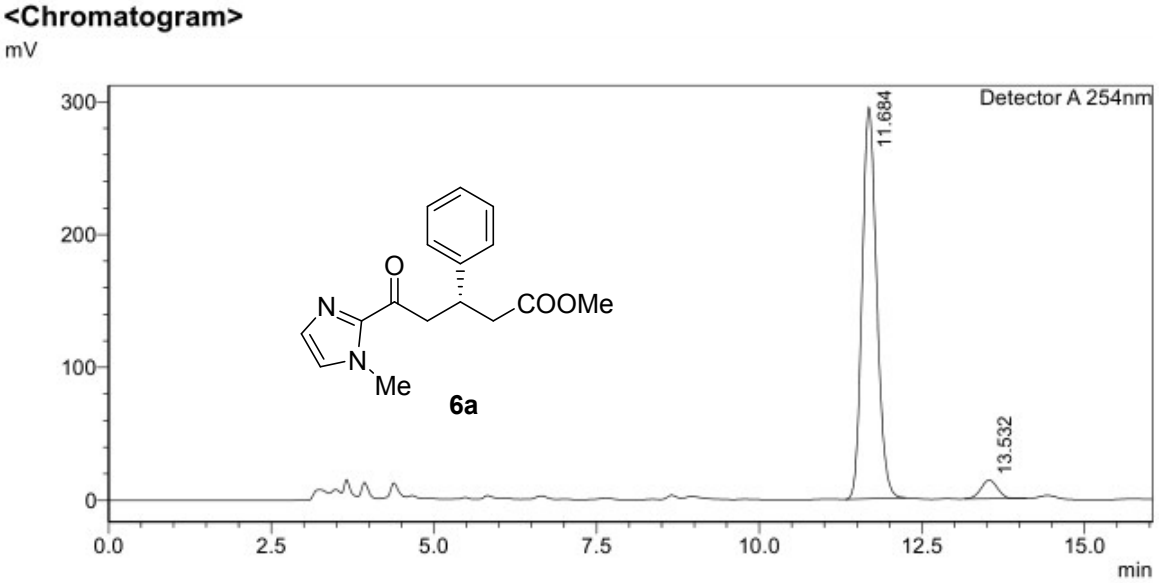



**<Peak Table>**

Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 11.653 | 20262375 | 1272560 | 50.081 | | M | |
| 2 | 13.452 | 20196793 | 1090887 | 49.919 | | M | |
| Total | | 40459169 | 2363447 | | | | |

Chiral **6a**:




**<Peak Table>**

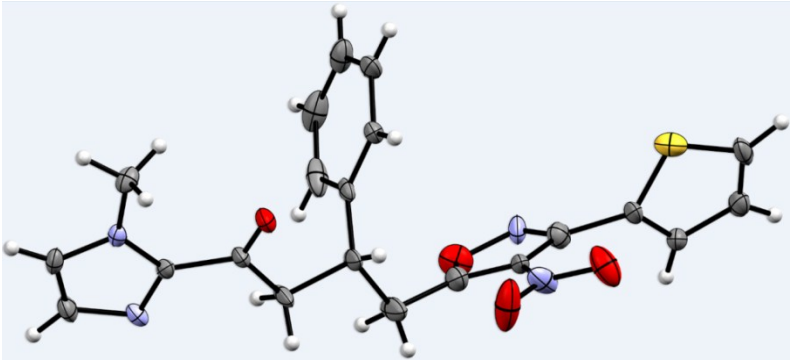
Detector A 254nm

| Peak# | Ret. Time | Area | Height | Conc. | Unit | Mark | Name |
|---|---|---|---|---|---|---|---|
| 1 | 11.684 | 4586840 | 294511 | 94.928 | | M | |
| 2 | 13.532 | 245064 | 13960 | 5.072 | | M | |
| Total | | 4831904 | 308471 | | | | |

HPLC traces of racemic **6a** and chiral **6a**. Area integration = 90% ee.

# VII. Single Crystal X-Ray Diffraction of 4f

## Table 1. Crystal data and structure refinement for 4f.



**CCDC** 1903727.

**Table 1.** Crystal data and structure refinement for **4f**.

| | | |
|---|---|---|
| Identification code | compound-**4f** | |
| Empirical formula | $C_{21}H_{18}N_4O_4S$ | |
| Formula weight | 422.45 | |
| Temperature (K) | 127(2) | |
| Wavelength (Å) | 1.54184 | |
| Crystal system | orthorhombic | |
| Space group | $P2_12_12_1$ | |
| Unit cell dimensions (Å, °) | $a$ = 6.0211(2) | α = 90 |
| | $b$ = 16.1241(5) | β = 90 |
| | $c$ = 20.6340(5) | γ = 90 |
| Volume (Å) | 2003.25(10) | |
| $Z$ | 4 | |
| Calculated density (g cm$^{-3}$) | 1.401 | |
| Absorption coefficient (mm$^{-1}$) | 1.753 | |
| $F_{000}$ | 880 | |
| Crystal size (mm$^3$) | 0.6 × 0.4 × 0.3 | |
| θ range for data collection (°) | 3.479 to 67.079 | |
| Miller index ranges | $-7 \le h \le 7$, $-16 \le k \le 19$, $-23 \le l \le 24$ | |
| Reflections collected | 16910 | |
| Independent reflections | 3543 [$R_{int}$ = 0.0657] | |
| Completeness to $\theta_{max}$ (%) | 0.987 | |
| Max. and min. transmission | 0.3203 and 0.7521 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3543 / 15 / 272 | |

| | |
|---|---|
| Goodness-of-fit on $F^2$ | 1.064 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R1$ = 0.0916, $wR2$ = 0.2275 |
| R indices (all data) | $R1$ = 0.1040, $wR2$ = 0.2394 |
| Largest diff. peak and hole (e Å$^{-3}$) | 1.320 and -0.460 |
| Absolute structure parameter | .018(13) |