Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.


# Organocatalytic Enantioselective Aminoalkylation of Pyrazol-3-ones with Aldimines Generated in Situ from α-Amido Sulfones.

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## General Experimental Methods

Commercial reagents were used as purchased. Reactions were monitored by TLC (thin layer chromatography) analysis using Merck Silica Gel 60 F-254 thin layer plates. Flash column chromatography was performed on Merck silica gel 60, 0.040–0.063 mm. Melting points were determined in capillary tubes. NMR spectra were run in a Bruker DPX300 spectrometer (Bruker, Billerica, MA, USA) at 300 MHz for $^{1}H$ and at 75 MHz for $^{13}C$ using residual non-deuterated solvent as internal standard ($CHCl_3$: δ 7.26 for $^{1}H$ and 77.0 ppm for $^{13}C$; DMSO-$d_6$ δ 2.50 for $^{1}H$ and 39.52 ppm for $^{13}C$). Chemical shifts are given in ppm. The carbon type was determined by DEPT (Distortionless Enhancement by Polarization Transfer) experiments. High resolution mass spectra (ESI) were recorded on a TRIPLETO$^{FT}$5600 spectrometer (AB Sciex, Warrington, UK) equipped with an electrospray source with a capillary voltage of 4.5 kV (ESI). Specific optical rotations were measured using sodium light (D line 589 nm). Chiral HPLC (High performance liquid chromatography) analyses were performed in a chromatograph equipped with a UV diode-array detector using chiral stationary columns from Daicel. α-amidosulfones **1** derivatives were prepared as described in the literature.[1] Pyrazolone derivatives **2** were prepared as described in the literature.[2]

## General procedure for the racemic reaction with α-amidosulfones 1 and pyrazolones 2.

In a 5 mL vial, α-amidosulfone (**1**, 0.2 mmol), pyrazolone (**2**, 0.1 mmol), $Na_2CO_3$ (0.15 mmol) and achiral catalyst (3-((3,5-bis(trifluoromethyl)phenyl)amino)-4-((2-(dimethylamino)ethyl)amino)ciclobut-3-e-1,2-dione) (**K**, 10 mol %, 4.1 mg) in DCM (1 mL):$H_2O$ (0.5 mL). The mixture was stirred at room temperatura until completion (TLC). The mixture was extracted with DCM (3x20 mL), the combined organic layers were dried over $MgSO_4$ (anh.) and solvent was removed under reduced pressure. The residue was purified by column chromatography being eluted with hexane/$Et_2O$ 50:50 to hexane/$Et_2O$ 20:80, affording the non-acetilated intermediate, which was subjected to acetylation with $Ac_2O$ (0.2 mmols, 19 μL) and $Et_3N$ (30 mol %, 0.03 mmols, 5μL) in DCM (2 mL) at room temperature. The resulting product was purified by column chromatography being eluted with hexane/$Et_2O$ 50:50 to hexane/$Et_2O$ 20:80.

## Procedure for the enantioselective reaction with α-amidosulfones 1 and pyrazolones 2.

In a 5 mL vial, α-amidosulfone (**1**, 0.3 mmol), pyrazolone (**2**, 0.2 mmol), $Na_2CO_3$ (0.3 mmol) and catalyst (**E**, 6.2 mg, 5 mol %) in DCM (1 mL):$H_2O$ (0.5 mL). The mixture was stirred at 4 °C until completion (TLC). The mixture was extracted with DCM (3x20 mL), the combined organic layers were dried over $MgSO_4$ (anh.) and solvent was removed under reduced pressure. The residue was purified by column chromatography being eluted with hexane/$Et_2O$ 50:50 to hexane/$Et_2O$ 20:80, affording the non-acetilated intermediate, which was subjected to acetylation with $Ac_2O$ (0.4 mmols, 38 μL) and $Et_3N$ (30 mol %, 0.06 mmols, 9μL) in DCM (2 mL) at room temperature. The resulting product

was purified by column chromatography being eluted with hexane/$Et_2O$ 50:50 to hexane/$Et_2O$ 20:80.

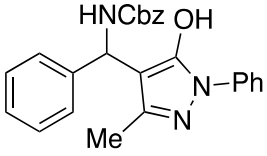
## References


1- J. B. F. N. Engberts, J. Strating, *Recl. Trav. Chim. Pays-Bas.* **1964**, *83*, 733.

2-. (a) L. Carpino, *J. Am. Chem. Soc*. **1958**, *80*, 599; (b) J. Sun, C. –G. Yan, Y. Han, *Synthetic Commun*., **2001**, *31*, 151; (c) A. Mazzanti, T. Calbet, M.Font-Bardia, A. Moyano, R. Rios, *Org. Biomol. Chem*., **2012**, *10*, 1645.

**Characterization data for compounds 3**

**Benzyl ((5-hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)(phenyl)methyl)carbamate**

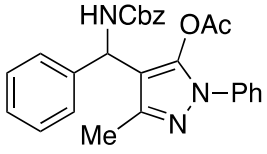



**3a**

Enantiomeric excess (98%) was determined by chiral HPLC (Chiralpak® IC), hexane-iPrOH 80:20, 1.0 mL/min, major enantiomer $t_r$ = 23.97 min, minor enantiomer $t_r$ = 13.70 min. Yellow Oil; $[\alpha_D^{20}]$ = +4.5 (*c* 1.33, $CHCl_3$).

**$^1$H NMR** (300 MHz, MeOD) δ 7.66-7.56 (m, 2H), 7.45 (t, *J* = 7.9 Hz, 2H), 7.42-7.17 (m, 11H), 5.83 (s, 1H), 5.10 (s, 2H), 2.09 (s, 3H). **$^{13}$C NMR** (75 MHz, MeOD) δ 159.0 (C), 148.8 (C), 143.6 (C), 139.1 (C), 138.3 (C), 135.8 (C), 131.1 (CH), 130.4 (CH), 130.3 (CH), 129.8 (CH), 129.6 (CH), 129.0 (CH), 128.5 (CH), 128.4 (CH), 123.3 (CH), 107.5 (C), 68.6 ($CH_2$), 51.7 (CH), 12.2 ($CH_3$). **HRMS** (ESI) m/z 414.1820 $[M+H]^+$, $C_{25}H_{24}N_3O_3$ requires 414.1812.

**4-((((Benzyloxy)carbonyl)amino)(phenyl)methyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-yl acetate**

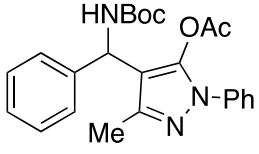



**3aa**

Enantiomeric excess (96%) was determined by chiral HPLC (Chiralpak® IC), hexane-iPrOH 80:20, 1.0 mL/min, major enantiomer $t_r$ = 16.67 min, minor enantiomer $t_r$ = 14.63 min. Yellow Oil; $[\alpha_D^{20}]$ = -88,3 (*c* 1.1, $CHCl_3$).

**$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.51-7.20 (m, 15H), 6.10 (d, *J* = 8.8 Hz, 1H), 5.58 (d, *J* = 8.6 Hz, 1H), 5.17 (s, 2H), 2.27 (s, 3H), 1.74 (s, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 167.9 (C), 155.7 (C), 148.1 (C), 141.5 (C), 139.3 (C), 137.6 (C), 136.4 (C), 129.1 (CH), 128.5 (CH), 128.4 (CH), 128.1 (CH), 127.4 (CH), 127.2 (CH), 126.2 (CH), 123.0 (CH), 109.1 (C), 67.0 ($CH_2$), 48.9 (CH), 19.8 ($CH_3$), 13.1 ($CH_3$). **HRMS** (ESI) m/z 456.1898 $[M+H]^+$, $C_{27}H_{26}N_3O_4$ requires 456.1918.

**4-(((*tert*-Butoxycarbonyl)amino)(phenyl)methyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-yl acetate**



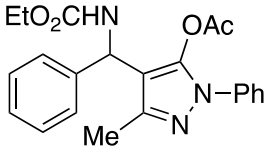

**3da**

Enantiomeric excess (66%) was determined by chiral HPLC (Chiralpak® IC), hexane-iPrOH 80:20, 1.0 mL/min, major enantiomer $t_r$ = 7.62 min, minor enantiomer $t_r$ = 6.27

min. White Solid; mp = 123-125 °C; $[\alpha_D^{20}]$ = +4.0 (*c* 1.12, MeOH).

**$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.46-7.36 (m, 4H), 7.35-7.23 (m, 6H), 6.03 (d, *J* = 8.4 Hz, 1H), 5.29 (d, *J* = 8.8 Hz, 1H), 2.27 (s, 3H), 1.76 (s, 3H), 1.48 (s, 9H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 168.0 (C), 155.1 (C), 148.2 (C), 141.4 (C), 139.8 (C), 137.6 (C), 129.1 (CH), 128.4 (CH), 127.3 (CH), 127.1 (CH), 126.3 (CH), 122.9 (CH), 109.5 (C), 79.7 (C), 48.4 (CH), 28.4 ($CH_3$), 19.9 ($CH_3$), 13.1 ($CH_3$). **HRMS** (ESI) m/z 422.2070 $[M+H]^+$ $C_{24}H_{28}N_3O_4$ requires 422.2074.

**Ethyl N-((5-hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)(phenyl)methyl)methanimidoperoxoate**

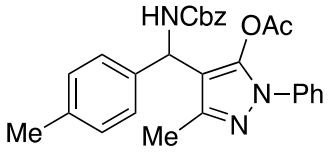



**3ea**

Enantiomeric excess (88%) was determined by chiral HPLC (Chiralpak® IC), hexane-iPrOH 80:20, 1.0 mL/min, major enantiomer $t_r$ = 15.13 min, minor enantiomer $t_r$ = 12.97 min. White Solid; mp = 135-137 °C; $[\alpha_D^{20}]$ = +1.0 (*c* 1.3, MeOH).

**$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.46-7.38 (m, 4H), 7.37-7.23 (m, 6H), 6.07 (d, *J* = 8.7 Hz, 1H), 5.48 (d, *J* = 8.4 Hz, 1H), 4.17 (q, **J** = 7.1 Hz, 2H), 2.28 (s, 3H), 1.76 (s, 3H), 1.27 (t, J = 7.2 Hz, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 168.0 (C), 156.0 (C), 148.2 (C), 141.5 (C), 139.6 (C), 137.6 (C), 129.2 (CH), 128.5 (CH), 127.5 (CH), 127.2 (CH), 126.3 (CH), 123.0 (CH), 109.4 (C), 61.2 ($CH_2$), 48.8 (CH), 19.9 ($CH_3$), 14.6 ($CH_3$), 13.1 ($CH_3$). **HRMS** (ESI) m/z 394.1754 $[M+H]^+$ $C_{22}H_{24}N_3O_4$ requires 394.1761.

**4-((((Benzyloxy)carbonyl)amino)(*p*-tolyl)methyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-yl acetate**

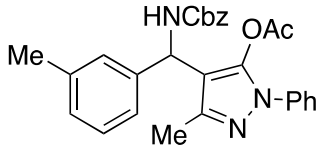



**3fa**

Enantiomeric excess (86%) was determined by chiral HPLC (Chiralpak® ADH), hexane-iPrOH 80:20, 1.0 mL/min, major enantiomer $t_r$ = 9.46 min, minor enantiomer $t_r$ = 6.97 min. White Solid; mp = 124-126 °C; $[\alpha_D^{20}]$ = -67.9 (*c* 0.93, MeOH).

**$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.49-7.26 (m, 10H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.06 (d, *J* = 8.6 Hz, 1H), 5.57 (d, *J* = 8.6 Hz, 1H), 5.17 (s, 2H), 2.34 (s, 3H), 2.26 (s, 3H), 1.78 (s, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 167.9 (C), 155.6 (C), 148.0 (C), 141.4 (C), 137.6 (C), 136.7 (C), 136.4 (C), 136.3 (C), 129.1 (CH), 128.4 (CH), 128.1 (CH), 128.09 (CH), 127.3 (CH), 126.1 (CH), 122.9 (CH), 109.2 (C), 66.9 ($CH_2$), 48.8 (CH), 21.0 ($CH_3$), 19.8 ($CH_3$), 13.1 ($CH_3$). **HRMS** (ESI) m/z 470.2065 [M+H]+, $C_{28}H_{28}N_3O_4$ requires 470.2074.

**4-((((Benzyloxy)carbonyl)amino)(*m*-tolyl)methyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-yl acetate**

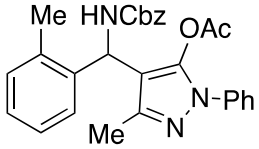



**3ga**

Enantiomeric excess (94%) was determined by chiral HPLC (Chiralpak® IC), hexane-iPrOH 80:20, 1.0 mL/min, major enantiomer $t_r$ = 21,43 min, minor enantiomer $t_r$ = 14,45min. Yellow Oil; $[\alpha_D^{20}]$ = -85,9 (*c* 0.96, MeOH).

**$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.49-7.17 (m, 12H), 7.16-7.00 (m, 2H), 6.06 (d, *J* = 8.8 Hz, 1H), 5.57 (d, *J* = 8.8 Hz, 1H), 5.18 (s, 2H), 2.34 (s, 3H), 2.28 (s, 3H), 1.76 (s, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 167.9 (C), 155.7 (C), 148.1 (C), 141.5 (C), 139.2 (C), 138.0 (C), 137.6 (C), 136.4 (C), 129.1 (CH), 129.0 (CH), 128.5 (CH), 128.3 (CH), 128.1 (CH), 127.9 (CH), 127.4 (CH), 126.9 (CH), 123.3 (CH), 122.9 (CH), 109.2 (C), 66.9 ($CH_2$), 48.9 (CH), 21.4 ($CH_3$), 19.8 ($CH_3$), 13.0 ($CH_3$). **HRMS** (ESI) m/z 470.2079 [M+H]+, $C_{28}H_{28}N_3O_4$ requires 470.2074.

**4-((((Benzyloxy)carbonyl)amino)(*o*-tolyl)methyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-yl acetate**

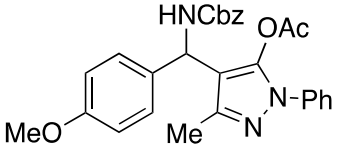



**3ha**

Enantiomeric excess (74%) was determined by chiral HPLC (Chiralpak® ADH), hexane-iPrOH 80:20, 1.0 mL/min, major enantiomer $t_r$ = 11.67 min, minor enantiomer $t_r$ = 18.00 min. Orange Oil; $[\alpha_D^{20}]$ = -102.5 (*c* 0.95, MeOH).

**$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.42-7.24 (m, 12H), 7.22-7.16 (m, 2H), 6.07 (d, *J* = 8.5 Hz, 1H), 5.63 (d, *J* = 8.5 Hz, 1H), 5.19 (d, *J* = 12.3 Hz, 1H), 5.12 (d, *J* = 12.2 Hz, 1H), 2.31 (s, 3H), 2.19 (s, 3H), 1.72 (s, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 167.9 (C), 155.3 (C), 148.1 (C), 141.4 (C), 137.44 (C), 137.37 (C), 136.4 (C), 135.6 (C), 130.8 (CH), 129.0 (CH), 128.4 (CH), 128.1 (CH), 127.4 (CH), 127.3 (CH), 125.7 (CH), 124.8 (CH), 122.9 (CH), 107.8 (C), 66.9 ($CH_2$), 47.2 (CH), 19.9 ($CH_3$), 19.1 ($CH_3$), 12.8 ($CH_3$). **HRMS** (ESI) m/z 470.2063 $[M+H]^+$, $C_{28}H_{28}N_3O_4$ requires 470.2074.

**4-((((Benzyloxy)carbonyl)amino)(4-methoxyphenyl)methyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-yl acetate**



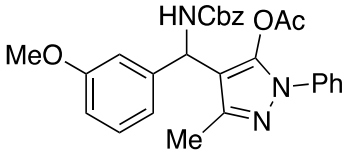

**3ia**

Enantiomeric excess (27%) was determined by chiral HPLC (Chiralpak® IC), hexane-

iPrOH 80:20, 1.0 mL/min, major enantiomer $t_r$ = 27.57 min, minor enantiomer $t_r$ = 25.21 min. White Solid; mp = 113-115 °C; $[\alpha_D^{20}]$ = -8.3 (*c* 0.95, MeOH).

**$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.48-7.27 (m, 10H), 7.23 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.03 (d, *J* = 8.7 Hz, 1H), 5.57 (d, *J* = 8.7 Hz, 1H), 5.17 (s, 2H), 3.79 (s, 3H), 2.24 (s, 3H), 1.81 (s, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 168.0 (C), 158.8 (C), 155.7 (C), 148.1 (C), 141.5 (C), 137.7 (C), 136.5 (C), 131.5 (C), 129.2 (CH), 128.6 (CH), 128.2 (CH), 128.2 (CH), 127.5 (CH), 127.5 (CH), 123.0 (CH), 113.9 (CH), 109.3 (C), 67.0 ($CH_2$), 55.4 ($CH_3$), 48.7 (CH), 20.0 ($CH_3$), 13.2 ($CH_3$). **HRMS** (ESI) m/z 486.2030 $[M+H]^+$, $C_{28}H_{28}N_3O_5$ requires 486.2023.

**4-((((Benzyloxy)carbonyl)amino)(3-methoxyphenyl)methyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-yl acetate**

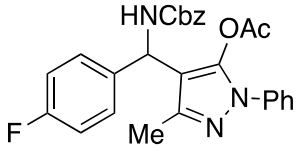



**3ja**

Enantiomeric excess (99%) was determined by chiral HPLC (Chiralpak® IC), hexane-iPrOH 80:20, 1.0 mL/min, major enantiomer $t_r$ = 33.99 min, minor enantiomer $t_r$ = 24.67 min. Yellow Oil; $[\alpha_D^{20}]$ = -19,7 (*c* 0,67, $CHCl_3$).

**$^1$H NMR** (400 MHz, $CHCl_3$) δ 7.47 -7.27 (m, 10H), 7.24 (d, *J* = 8.0 Hz, 1H), 6.94-6.87 (m, 1H), 6.86 (d, *J* = 1.5 Hz, 1H), 6.80 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.05 (d, *J* = 8.7 Hz, 1H), 5.57 (d, *J* = 8.7 Hz, 1H), 5.17 (s, 2H), 3.77 (s, 3H), 2.27 (s, 3H), 1.80 (s, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 168.0 (C), 159.7 (C), 155.6 (C), 148.0 (C), 141.5 (C), 141.1 (C), 137.5 (C), 136.4 (C), 129.5 (CH), 129.1 (CH), 128.5 (CH), 128.12 (CH), 128.06 (CH), 127.4 (CH), 122.9 (CH), 118.5 (CH), 112.6 (CH), 112.0 (CH), 109.1 (C), 66.9 ($CH_2$), 55.2 ($CH_3$), 48.9 (CH), 19.8 ($CH_3$), 13.0 ($CH_3$). **HRMS** (ESI) m/z 486.2028 $[M+H]^+$, $C_{28}H_{28}N_3O_5$ requires 486.2023.

**4-((((Benzyloxy)carbonyl)amino)(4-fluorophenyl)methyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-yl acetate**



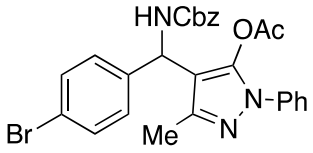

**3ka**

Enantiomeric excess (91%) was determined by chiral HPLC (Chiralpak® IC), hexane-iPrOH 80:20, 1.0 mL/min, major enantiomer $t_r$ = 14.09 min, minor enantiomer $t_r$ = 10.35 min. White Solid; mp = 100-102 °C; $[\alpha_D^{20}]$ = -34.6 (*c* 0.92, MeOH).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.47-7.28 (m, 12H), 7.03 (t, *J* = 8.6 Hz, 2H), 6.05 (d, *J* = 8.6 Hz, 1H), 5.55 (d, *J* = 8.7 Hz, 1H), 5.17 (s, 2H), 2.25 (s, 3H), 1.81 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 167.8 (C), 161.95 (d, $J_{C-F}$ = 245.9 Hz, C), 155.7 (C), 147.9 (C), 141.4 (C), 137.5 (C), 136.3 (C), 135.2 (C), 129.1 (CH), 128.5 (CH), 128.2 (CH), 128.1 (CH), 127.9 (d, $J_{C-F}$ = 8.0 Hz, CH), 127.5 (CH), 123.0 (CH), 115.25 (d, $J_{C-F}$ = 21.3 Hz,

CH), 109.01 (C), 67.1 ($CH_2$), 48.5 (CH), 19.9 ($CH_3$), 13.1 ($CH_3$). **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ -115.52 (s). **HRMS** (ESI) m/z 479.1731 $[M+H]^+$, $C_{27}H_{25}FN_3O_4$ requires 479.1724.

**4-((((Benzyloxy)carbonyl)amino)(4-bromophenyl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-yl acetate**

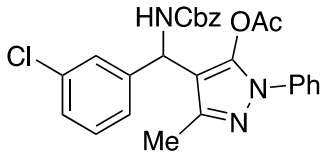



**3la**

Enantiomeric excess (88%) was determined by chiral HPLC (Chiralpak® IC), hexane-iPrOH 80:20, 1.0 mL/min, major enantiomer $t_r$ = 16.57 min, minor enantiomer $t_r$ = 12.43 min. White Solid; mp = 129-130 °C; $[\alpha_D^{20}]$ = -27.4 (*c* 0.94, MeOH).

**$^1$H NMR (**300 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.43-7.28 (m, 10H), 7.20 (d, *J* = 7.9 Hz, 2H), 6.03 (d, *J* = 8.5 Hz, 1H), 5.58 (d, *J* = 8.6 Hz, 1H), 5.17 (s, 2H), 2.25 (s, 3H), 1.81 (s, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 167.8 (C), 155.6 (C), 147.9 (C), 141.4 (C), 138.6 (C), 137.4 (C), 136.2 (C), 131.4 (CH), 129.1 (CH), 128.5 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.5 (CH), 122.9 (CH), 121.0 (C), 108.7 (C), 67.1 ($CH_2$), 48.5 (CH), 19.9 ($CH_3$), 13.0 ($CH_3$). **HRMS** (ESI) m/z 534.1002 $[M+H]^+$, $C_{27}H_{25}BrN_3O_4$ requires 534.1023.

**4-((((Benzyloxy)carbonyl)amino)(3-chlorophenyl)methyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-yl acetate**

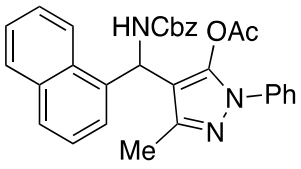



**3ma**

Enantiomeric excess (96%) was determined by chiral HPLC (Chiralcel® ADH), hexane-iPrOH 80:20, 0.7 mL/min, major enantiomer $t_r$ = 23.81 min, minor enantiomer $t_r$ = 25.51 min. Colorless Oil; $[\alpha_D^{20}]$ = -93.3 (*c* 1.84, $CHCl_3$).

**$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.44-7.26 (m, 13H), 7.22-7.15 (m, 1H), 6.05 (d, *J* = 8.5 Hz, 1H), 5.61 (d, *J* = 8.5 Hz, 1H), 5.17 (s, 2H), 2.27 (s, 3H), 1.82 (s, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 167.9 (C), 155.6 (C), 147.9 (C), 141.8 (C), 141.4 (C), 137.4 (C), 136.2 (C), 134.4 (C), 129.7 (CH), 129.1 (CH), 128.5 (CH), 128.2 (CH), 128.1 (CH), 127.5 (CH), 127.4 (CH), 126.2 (CH), 124.6 (CH), 123.0 (CH), 108.7 (C), 67.1 ($CH_2$), 48.5 (CH), 19.8 ($CH_3$), 13.0 ($CH_3$). **HRMS** (ESI) m/z 490.1521 $[M+H]^+$, $C_{27}H_{25}ClN_3O_4$ requires 490.1528.

**4-((((Benzyloxy)carbonyl)amino)(naphthalen-1-yl)methyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-yl acetate**

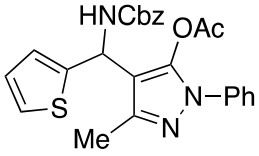



**3na**

Enantiomeric excess (56%) was determined by chiral HPLC (Chiralcel® ODH), hexane-iPrOH 80:20, 1.0 mL/min, major enantiomer $t_r$ = 16,16 min, minor enantiomer $t_r$ = 9,87 min. White Solid; mp =64-66 °C; $[\alpha_D^{20}]$ = +99.6 (*c* 1.84, $CHCl_3$).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.84-7.65 (m, 3H), 7.49-7.26 (m, 11H), 7.25-7.17 (m, 3H), 6.59 (d, *J* = 8.5 Hz, 1H), 5.62 (d, *J* = 8.5 Hz, 1H), 5.14 (d, *J* = 12.3 Hz, 1H), 5.08 (d, *J* = 12.2 Hz, 1H), 2.31 (s, 3H), 1.58 (s, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 168.1 (C), 155.4 (C), 147.8 (C), 141.5 (C), 137.4 (C), 136.4 (C), 134.8 (C), 133.9 (C), 130.5 (C), 129.0 (CH), 128.7 (CH), 128.52 (CH), 128.50 (CH), 128.4 (CH), 128.1 (CH), 127.4 (CH), 126.4 (CH), 125.8 (CH), 124.9 (CH), 123.4 (CH), 123.0 (CH), 122.9 (CH), 108.9 (C), 67.0 ($CH_2$), 47.1 (CH), 19.9 ($CH_3$), 13.0 ($CH_3$). **HRMS** (ESI) m/z 506.2081 $[M+H]^+$, $C_{31}H_{28}N_3O_4$ requires 506.2074.

**4-((((Benzyloxy)carbonyl)amino)(thiophen-3-yl)methyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-yl acetate**

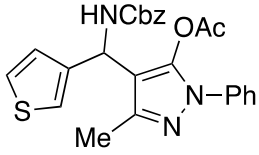



**3oa**

Enantiomeric excess (94%) was determined by chiral HPLC (Chiralpak® IC), hexane-iPrOH 80:20, 1.0 mL/min, major enantiomer $t_r$ = 24,65 min, minor enantiomer $t_r$ = 16,96 min. White Solid; mp = 124-126 °C; $[\alpha_D^{20}]$ = -1.3 (*c* 1,05, $CHCl_3$).

**$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.56-7.27 (m, 10H), 7.24 (d, *J* = 4.5 Hz, 1H), 7.04-6.82 (m, 2H), 6.25 (d, *J* = 8.9 Hz, 1H), 5.72 (d, *J* = 8.9 Hz, 1H), 5.17 (s, 2H), 2.29 (s, 3H), 1.90 (s, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 168.0 (C), 155.6 (C), 147.7 (C), 144.3 (C), 141.6 (C), 137.6 (C), 136.3 (C), 129.2 (CH), 128.6 (CH), 128.23 (CH), 128.20 (CH), 127.6 (CH), 126.9 (CH), 124.9 (CH), 124.6 (CH), 123.1 (CH), 108.9 (C), 67.17 ($CH_2$), 46.1 (CH), 20.0 ($CH_3$), 13.1 ($CH_3$). **HRMS** (ESI) m/z 462.1486 $[M+H]^+$, $C_{25}H_{24}N_3O_4S$ requires 462.1482.

**4-((((Benzyloxy)carbonyl)amino)(thiophen-2-yl)methyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-yl acetate**

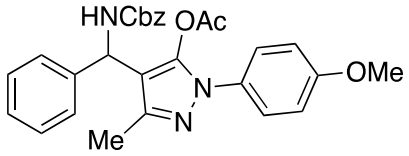



**3pa**

Enantiomeric excess (54%) was determined by chiral HPLC (Chiralpak® IC), hexane-iPrOH 80:20, 1.0 mL/min, major enantiomer $t_r$ = 26,96 min, minor enantiomer $t_r$ = 15,43 min. White Solid; mp = 133-134 °C; $[\alpha_D^{20}]$ = + 48.3 (*c* 1.74, $CHCl_3$).

**$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.51-7.20 (m, 11H), 7.11 (s, 1H), 6.94 (dd, *J* = 5.0, 0.9 Hz, 1H), 6.07 (d, *J* = 8.7 Hz, 1H), 5.64 (d, *J* = 8.4 Hz, 1H), 5.17 (s, 2H), 2.28 (s, 3H), 1.86 (s, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 168.1 (C), 155.7 (C), 147.9 (C), 141.5 (C), 141.2 (C), 137.6 (C), 136.4 (C), 129.2 (CH), 128.6 (CH), 128.2 (CH), 127.5 (CH), 126.8 (CH), 126.3 (CH), 123.02 (CH), 123.02 (CH), 120.9 (CH), 108.7 (C), 67.1 ($CH_2$), 46.2 (CH), 19.9 ($CH_3$), 13.1 ($CH_3$). **HRMS** (ESI) m/z 462.1489 $[M+H]^+$, $C_{25}H_{24}N_3O_4S$ requires 462.1482.

**4-((((Benzyloxy)carbonyl)amino)(phenyl)methyl)-1-(4-methoxyphenyl)-3-methyl-1*H*-pyrazol-5-yl acetate**

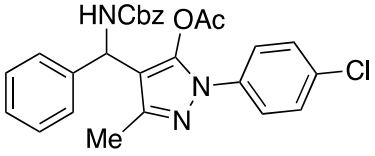



**3ab**

Enantiomeric excess (88%) was determined by chiral HPLC (Chiralcel® ODH), hexane-iPrOH 80:20, 1.0 mL/min, major enantiomer $t_r$ = 12,55 min, minor enantiomer $t_r$ = 11,10 min. White Solid; mp = 44-45 °C; $[\alpha_D^{20}]$ = - 81.0 (*c* 1.03, $CHCl_3$).

**$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.49-7.13 (m, 12H), 6.90 (d, *J* = 9.1 Hz, 2H), 6.08 (d, *J* = 8.6 Hz, 1H), 5.57 (d, *J* = 8.6 Hz, 1H), 5.17 (s, 2H), 3.81 (s, 3H), 2.26 (s, 3H), 1.72 (s, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 168.1 (C), 159.0 (C), 155.8 (C), 147.7 (C), 141.5 (C), 139.5 (C), 136.5 (C), 130.6 (C), 128.58 (CH), 128.55 (CH), 128.48 (CH), 128.2 (CH), 127.2 (CH), 126.3 (CH), 124.9 (CH), 114.3 (CH), 108.7 (C), 67.0 ($CH_2$), 55.5 ($CH_3$), 49.0 (CH), 19.8 ($CH_3$), 13.1 ($CH_3$). **HRMS** (ESI) m/z 486.2019 $[M+H]^+$, $C_{28}H_{28}N_3O_5$ requires 486.2023.

**4-((((Benzyloxy)carbonyl)amino)(phenyl)methyl)-1-(4-chlorophenyl)-3-methyl-1*H*-pyrazol-5-yl acetate**



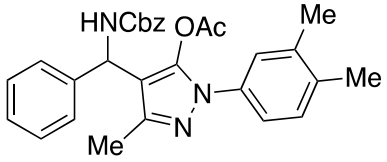

**3ac**

Enantiomeric excess (84%) was determined by chiral HPLC (Chiralpak® ADH), hexane-iPrOH 80:20, 1.0 mL/min, major enantiomer $t_r$ = 19,87 min, minor enantiomer $t_r$ = 24,71 min. White Solid; mp = 142-144 °C; $[\alpha_D^{20}]$ = -72.6 (*c* 1.07, $CHCl_3$).

**$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.39-7.13 (m, 14H), 6.00 (d, *J* = 8.7 Hz, 1H), 5.47 (d, *J* = 8.6 Hz, 1H), 5.09 (s, 2H), 2.17 (s, 3H), 1.67 (s, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 167.8 (C), 155.7 (C), 148.5 (C), 141.5 (C), 139.1 (C), 136.3 (C), 136.1 (C), 133.0 (C), 129.7 (CH), 129.3 (CH), 128.5 (CH), 128.2 (CH), 128.1 (CH), 127.3 (CH), 126.2 (CH), 124.0

(CH), 109.5 (C), 67.0 ($CH_2$), 48.9 (CH), 19.8 ($CH_3$), 13.1 ($CH_3$). **HRMS** (ESI) m/z 490.1521 $[M+H]^+$, $C_{27}H_{25}ClN_3O_4$ requires 490.1528.

**4-((((Benzyloxy)carbonyl)amino)(phenyl)methyl)-1-(3,4-dimethylphenyl)-3-methyl-1*H*-pyrazol-5-yl acetate**

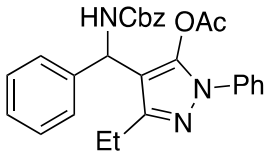



**3ad**

Enantiomeric excess (94%) was determined by chiral HPLC (Chiralcel® ODH), hexane-iPrOH 80:20, 1.0 mL/min, major enantiomer $t_r$ = 9,58 min, minor enantiomer $t_r$ = 7,57 min. White Solid; mp = 83-84 °C; $[\alpha_D^{20}]$ = -72.1 (*c* 1.02, $CHCl_3$).

**$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.39-7.22 (m, 11H), 7.15-7.07 (m, 2H), 6.10 (d, *J* = 8.7 Hz, 1H), 5.64 (d, *J* = 8.6 Hz, 1H), 5.20 (d, *J* = 12 Hz, 1H), 5.15 (d, *J* = 12 Hz, 1H), 2.26 (s, 9H), 1.74 (s, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 167.9 (C), 155.7 (C), 147.6 (C), 141.3 (C), 139,4 (C), 137.7 (C), 136.3 (C), 136.0 (C), 135.2 (C), 129.9 (CH), 128.4 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 127.1 (CH), 126.2 (CH), 124.2 (CH), 120.0 (CH), 108.8 (C), 66.9 ($CH_2$), 48.9 (CH), 19.74 ($CH_3$), 19.70 ($CH_3$), 19.3 ($CH_3$), 13.0 ($CH_3$). **HRMS** (ESI) m/z 484.2236 $[M+H]^+$, $C_{29}H_{30}N_3O_4$ requires 484.2231.

**4-((((Benzyloxy)carbonyl)amino)(phenyl)methyl)-3-ethyl-1-phenyl-1*H*-pyrazol-5-yl acetate**

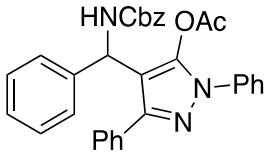



**3ae**

Enantiomeric excess (96%) was determined by chiral HPLC (Chiralcel® ODH), hexane-iPrOH 80:20, 1.0 mL/min, major enantiomer $t_r$ = 7,69 min, minor enantiomer $t_r$ = 6,59 min. White Solid; mp = 102-103 °C; $[\alpha_D^{20}]$ = -95.7 (*c* 1.2, $CHCl_3$).

**$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.47-7.20 (m, 15H), 6.13 (d, *J* = 8.7 Hz, 1H), 5.65 (d, *J* = 8.8 Hz, 1H), 5.21 (d, *J* = 12.0 Hz, 1H), 5.15 (d, *J* = 11.9 Hz, 1H), 2.75-2.62 (m, 2H), 1.72 (s, 3H), 1.28 (t, *J* = 7.5 Hz, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 168.0 (C), 155.6 (C), 153.2 (C), 141.3 (C), 139.5 (C), 137.6 (C), 136.4 (C), 129.1 (CH), 128.5 (CH), 128.4 (CH), 128.12 (CH), 128.10 (CH), 127.3 (CH), 127.1 (CH), 126.1 (CH), 123,0 (CH), 108.6 (C), 66.9 ($CH_2$), 48.6 (CH), 20.8 ($CH_2$), 19.8 ($CH_3$), 13.1 ($CH_3$). **HRMS** (ESI) m/z 470.2069 $[M+H]^+$, $C_{28}H_{27}N_3O_4$ requires 470.2074.

**4-((((Benzyloxy)carbonyl)amino)(phenyl)methyl)-1,3-diphenyl-1*H*-pyrazol-5-yl acetate**

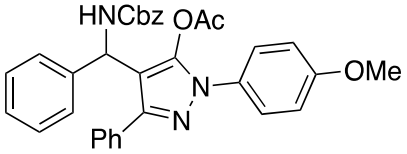



**3af**

Enantiomeric excess (91%) was determined by chiral HPLC (Chiralpak® IC), hexane-iPrOH 80:20, 1.0 mL/min, major enantiomer $t_r$ = 19,49 min, minor enantiomer $t_r$ = 30,45 min. White Solid; mp = 53-54 °C; $[\alpha_D^{20}]$ = -43.9 (*c* 1.01, $CHCl_3$).

**$^1$H NMR** (300 MHz, $CDCl_3$) 7.68 (dd, *J* = 6.3, 2.8 Hz, 2H), 7.61-7.28 (m, 18H), 6.24 (d, *J* = 8.5 Hz, 1H), 5.81 (d, *J* = 8.4 Hz, 1H), 5.11 (d, *J* = 12.0 Hz, 1H), 5.06 (d, *J* = 12.1 Hz, 1H), 1.79 (s, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 167.8 (C), 155.3 (C), 150.7 (C), 142.2 (C), 139.8 (C), 137.5 (C), 136.6 (C), 132.6 (C), 129.1 (CH), 128.6 (CH), 128.4 (CH), 128.4 (CH), 128.13 (CH), 128,08 (CH), 127.8 (CH), 127.1 (CH), 126.1 (CH), 123.2 (CH), 108.9 (C), 66.9 ($CH_2$), 49.2 (CH), 19.9 ($CH_3$). **HRMS** (ESI) m/z 518.2069 $[M+H]^+$, $C_{32}H_{28}N_3O_4$ requires 518.2074.

**4-((((Benzyloxy)carbonyl)amino)(phenyl)methyl)-1-(4-methoxyphenyl)-3-phenyl-1*H*-pyrazol-5-yl acetate**

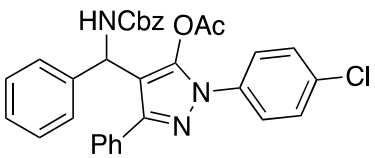



**3ag**

Enantiomeric excess (96%) was determined by chiral HPLC (Chiralpak® IC), hexane-iPrOH 80:20, 1.0 mL/min, major enantiomer $t_r$ = 16,45 min, minor enantiomer $t_r$ = 37,91 min. White Solid; mp = 46-48 °C; $[\alpha_D^{20}]$ = -4.4 (*c* 0.88, $CHCl_3$).

**$^1$H NMR** (300 MHz, $CDCl_3$) 7.73-7.62 (m, 2H), 7.48-7.21 (m, 15H), 6.94 (d, *J* = 9.0 Hz, 2H), 6.23 (d, *J* = 8.4 Hz, 1H), 5.82 (d, *J* = 8.4 Hz, 1H), 5.15 (d, *J* = 12.3 Hz, 1H), 5.03 (d, *J* = 12.0 Hz, 1H), 3.82 (s, 3H), 1.77 (s, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 167.9 (C), 159.2 (C), 155.4 (C), 150.3 (C), 142.2 (C), 140.0 (C), 136.7 (C), 132.7 (C), 130.6 (C), 128.7 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.24 (CH), 128.20 (CH), 128.2 (CH), 127.2 (CH), 126.2 (CH), 125.1 (CH), 114.3 (CH), 108.5 (C), 66.9 ($CH_2$), 55.5 ($CH_3$), 49.3 (CH), 19.9 ($CH_3$). **HRMS** (ESI) m/z 548.2171 $[M+H]^+$, $C_{33}H_{30}N_3O_5$ requires 548.2180.

**4-((((Benzyloxy)carbonyl)amino)(phenyl)methyl)-1-(4-chlorophenyl)-3-phenyl-1*H*-pyrazol-5-yl acetate**



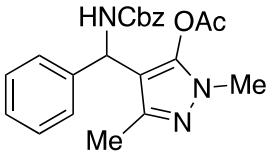

**3ah**

Enantiomeric excess (87%) was determined by chiral HPLC (Chiralpak® IC), hexane-

iPrOH 80:20, 1.0 mL/min, major enantiomer $t_r$ = 9,23 min, minor enantiomer $t_r$ = 19,57 min. White Solid; mp = 58-59 °C; $[\alpha_D^{20}]$ = -65.0 (*c* 1.76, $CHCl_3$).

**$^1$H NMR** (300 MHz, $CDCl_3$) 7.64 (dd, *J* = 6.5, 2.8 Hz, 2H), 7.52-7.18 (m, 17H), 6.21 (d, *J* = 8.5 Hz, 1H), 5.76 (d, *J* = 8.4 Hz, 1H), 5.23 (d, *J* = 12.3 Hz, 1H), 5.11 (d, *J* = 12.0 Hz, 1H), 1.80 (s, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 167.6 (C), 155.3 (C), 151.0 (C), 142.2 (C), 139.7 (C), 136.5 (C), 136.1 (C), 133.5 (C), 132.3 (C), 129.3 (CH), 128.7 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.2 (CH), 128.1 (CH), 128.1 (CH), 127.2 (CH), 126.1 (CH), 124.3 (CH), 109.2 (C), 66.9 ($CH_2$), 49.2 (CH), 19.9 ($CH_3$). **HRMS** (ESI) m/z 552.1677 $[M+H]^+$, $C_{32}H_{27}ClN_3O_4$ requires 552.1685.

**4-((((Benzyloxy)carbonyl)amino)(phenyl)methyl)-1,3-dimethyl-1*H*-pyrazol-5-yl acetate**

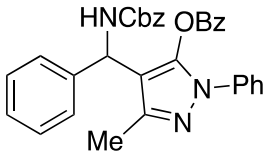



**3ai**

Enantiomeric excess (94%) was determined by chiral HPLC (Chiralpak® ADH), hexane-iPrOH 80:20, 1.0 mL/min, major enantiomer $t_r$ = 23.43 min, minor enantiomer $t_r$ = 55.50 min. Yellow Oil; $[\alpha_D^{20}]$ = -60.9 (*c* 0.89, $CHCl_3$).

**$^1$H NMR** (300 MHz, $CDCl_3$) 7.42-7.17 (m, 10H), 6.00 (d, *J* = 8.7 Hz, 1H), 5.48 (d, *J* = 8.7 Hz, 1H), 5.14 (s, 2H), 3.53 (s, 3H), 2.17 (s, 3H), 1.83 (s, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 167.9 (C), 155.7 (C), 146.2 (C), 142.1 (C), 139.6 (C), 136.4 (C), 128.5 (CH), 128.5 (CH), 128.2 (CH), 127.2 (CH), 126.3 (CH), 107.3 (C), 66.9 ($CH_2$), 49.0 (CH), 34.4 ($CH_3$), 19.8 ($CH_3$), 12.9 ($CH_3$). **HRMS** (ESI) m/z 394.1748 $[M+H]^+$, $C_{22}H_{24}N_3O_4$ requires 394.1761.

**4-((((benzyloxy)carbonyl)amino)(phenyl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-yl benzoate**



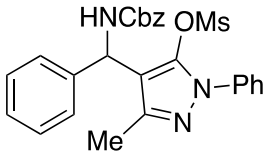

**5**

Enantiomeric excess (95%) was determined by chiral HPLC (Chiralpak® ADH), hexane-iPrOH 80:20, 1.0 mL/min, major enantiomer $t_r$ = 17,54 min, minor enantiomer $t_r$ = 19,84 min. Colorless Oil; $[\alpha_D^{20}]$ = - 54.2 (*c* 1.09, $CHCl_3$).

**$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.74 (d, *J* = 6.9 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.42-7.17 (m, 12H), 7.11 (t, *J* = 7.4 Hz, 2H), 7.01 (t, *J* = 7.0 Hz, 1H), 6.14 (d, *J* = 8.6 Hz, 1H), 5.71 (d, *J* = 8.7 Hz, 1H), 5.14 (s, 2H), 2.34 (s, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 163.8 (C), 155.7 (C), 148.2 (C), 141.6 (C), 139.2 (C), 137.6 (C), 136.4 (C), 134.3 (C), 130.3 (CH), 129.1 (CH), 128.5 (CH), 128.44 (CH), 128.40 (CH), 128.3 (CH), 128.1 (CH), 127.3 (CH), 127.0 (CH), 126.9 (CH), 126.1 (CH), 122.8 (CH), 109.46 (C), 66.9 ($CH_2$), 49.1 (CH), 13.1 ($CH_3$). **HRMS** (ESI) m/z 518.2082 $[M+H]^+$,

$C_{32}H_{28}N_3O_4$ requires 518.2074.

**4-((((benzyloxy)carbonyl)amino)(phenyl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-yl methanesulfonate**

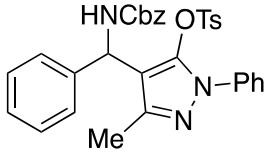



**6**

Enantiomeric excess (96%) was determined by chiral HPLC (Phenomenex® Amilose1), hexane- iPrOH 80:20, 1.0 mL/min, major enantiomer $t_r$ = 30,69 min, minor enantiomer $t_r$ = 29,13 min. White Solid; m.p = 56-57 ºC; $[\alpha_D^{20}]$ = - 45.6 (*c* 1.07, $CHCl_3$).

**$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.7 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.40-7.27 (m, 11H), 6.18 (d, *J* = 9.0 Hz, 1H), 5.85 (d, *J* = 9.1 Hz, 1H), 5.18 (s, 2H), 2.67 (s, 3H), 2.20 (s, 3H). **$^{13}$C NMR (75 MHz, $CDCl_3$)** δ 155.8 (C) 148.4 (C), 139.3 (C), 138.7 (C), 137.4 (C), 136.4 (C), 129.2 (C), 128.47 (CH), 128.46 (CH), 128.1 (CH), 126.6 (CH), 126.4 (CH), 124.0 (CH), 111.1 (CH), 67.0 ($CH_2$), 49.0 (CH), 38.6 ($CH_3$), 13.4 ($CH_3$). **HRMS** (ESI) m/z 492.1583 $[M+H]^+$, $C_{26}H_{26}N_3O_5S$ requires 492.1588.

**4-((((benzyloxy)carbonyl)amino)(phenyl)methyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-yl 4-methylbenzenesulfonate**

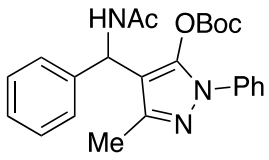



**7**

Enantiomeric excess (94%) was determined by chiral HPLC (Chiralpak® ADH), hexane-iPrOH 80:20, 1.0 mL/min, major enantiomer $t_r$ = 23.08 min, minor enantiomer $t_r$ = 20.54 min. Colorless Oil, $[\alpha_D^{20}]$ = -24.4 (*c* 0.99, $CHCl_3$).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.44-7.26 (m, 11H), 7.23-7.17 (m, 5H), 6.95 (d, *J* = 8.1 Hz, 2H), 6.18 (d, *J* = 9.2 Hz, 1H), 6.06 (d, *J* = 9.3 Hz, 1H), 5.20 (s, 2H), 2.32 (s, 3H), 2.21 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 155.8 (C), 148.4 (C), 146.1 (C), 139.6 (C), 139.3 (C), 137.4 (C), 136.6 (C), 130.8 (C), 129.6 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 127.3 (CH), 127.0 (CH), 123.4 (CH), 126.7 (CH), 111.4 (C), 66.9 ($CH_2$), 49.2 (CH), 21.6 ($CH_3$), 13.5 ($CH_3$). **HRMS** (ESI) m/z 568.1897 $[M+H]^+$, $C_{32}H_{30}N_3O_5S$ requires 568.1901.

**4-(acetamido(phenyl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-yl tert-butyl carbonate**

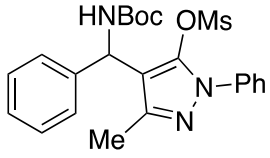



**8**

Enantiomeric excess (86%) was determined by chiral HPLC (Chiralpak® IC), hexane-iPrOH 80:20, 1.0 mL/min, major enantiomer $t_r$ = 12.95 min, minor enantiomer $t_r$ = 19,49 min. Colorless Oil, $[\alpha_D^{20}]$ = -29.4 (*c* 0.57, $CHCl_3$).

**$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.58-7.53 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.40-7.27 (m, 6H), 6.10 (d, *J* = 9.1 Hz, 1H), 5.52 (d, *J* = 8.9 Hz, 1H), 2.71 (s, 3H), 2.19 (s, 3H), 1.48 (s, 9H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 169.1 (C), 149.2 (C), 147.9 (C), 141.9 (C), 139.4 (C), 137.6 (C), 129.1 (CH), 128.5 (CH), 127.4 (CH), 127.2 (CH), 126.2 (CH), 122.8 (CH), 109.1 (C), 85.7 (C), 47.1 (CH), 27.2 ($CH_3$), 23.3 ($CH_3$), 13.1 ($CH_3$). **HRMS** (ESI) m/z 422.2079 $[M+H]^+$ $C_{24}H_{28}N_3O_4$ requires 422.2074.

**4-(((tert-butoxycarbonyl)amino)(phenyl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-yl methanesulfonate**

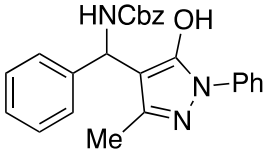



**9**

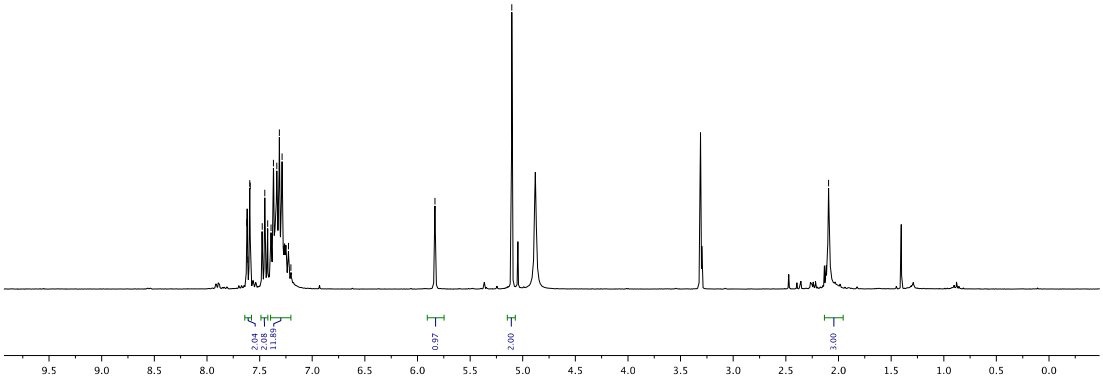
Enantiomeric excess (95%) was determined by chiral HPLC (Chiralpak® ADH), hexane-iPrOH 80:20, 1.0 mL/min, major enantiomer $t_r$ = 11,23 min, minor enantiomer $t_r$ = 8,67 min. Colorless Oil, $[\alpha_D^{20}]$ = -22.8 (*c* 0.72, $CHCl_3$).

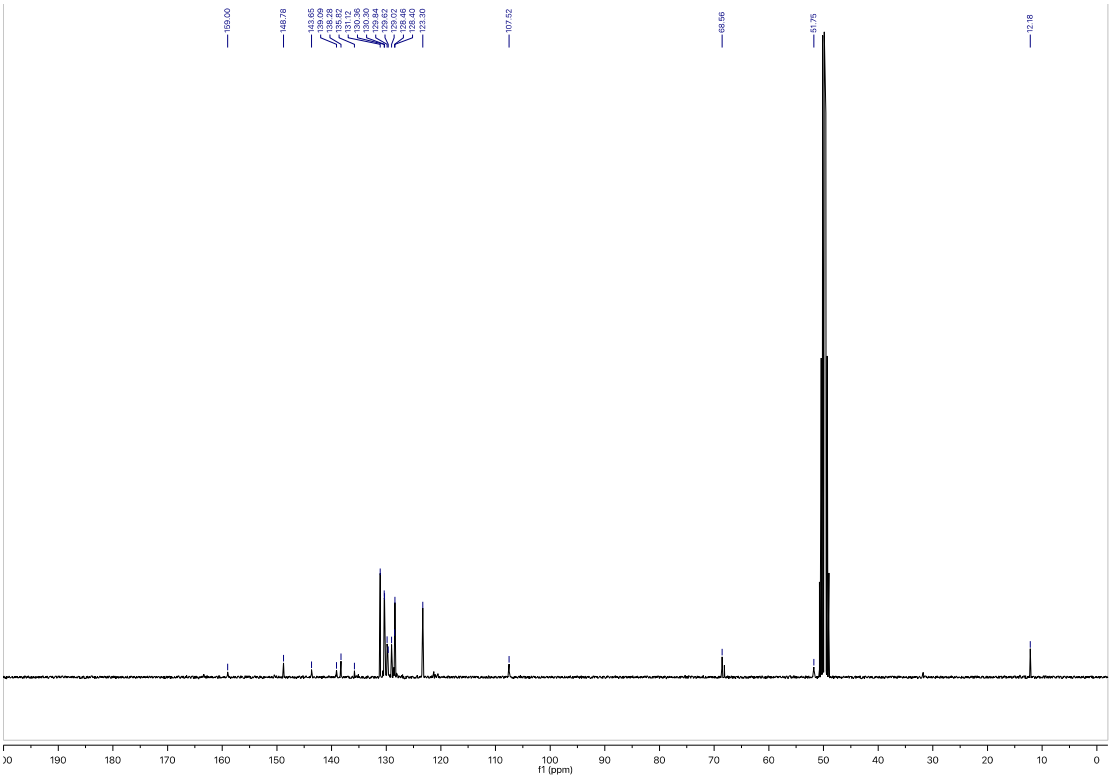
**$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.58-7.53 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.40-7.27 (m, 6H), 6.10 (d, *J* = 9.1 Hz, 1H), 5.52 (d, *J* = 8.9 Hz, 1H), 2.71 (s, 3H), 2.19 (s, 3H), 1.48 (s, 9H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 155.2 (C), 148.5 (C), 139.8 (C), 138.8 (C), 137.5 (C), 129.3 (CH), 128.4 (CH), 128.1 (CH), 127.3 (CH), 126.6 (CH), 124.0 (CH), 111.4 (C), 79.8 (C), 48.4 (CH), 38.6 ($CH_3$), 28.3 ($CH_3$), 13.5 ($CH_3$). **HRMS** (ESI) m/z 458.1737 $[M+H]^+$, $C_{23}H_{28}N_3O_5S$ requires 458.1744.

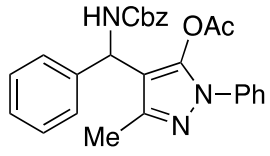
## $^{1}$H-NMR and $^{13}$C-NMR SPECTRA




**3a**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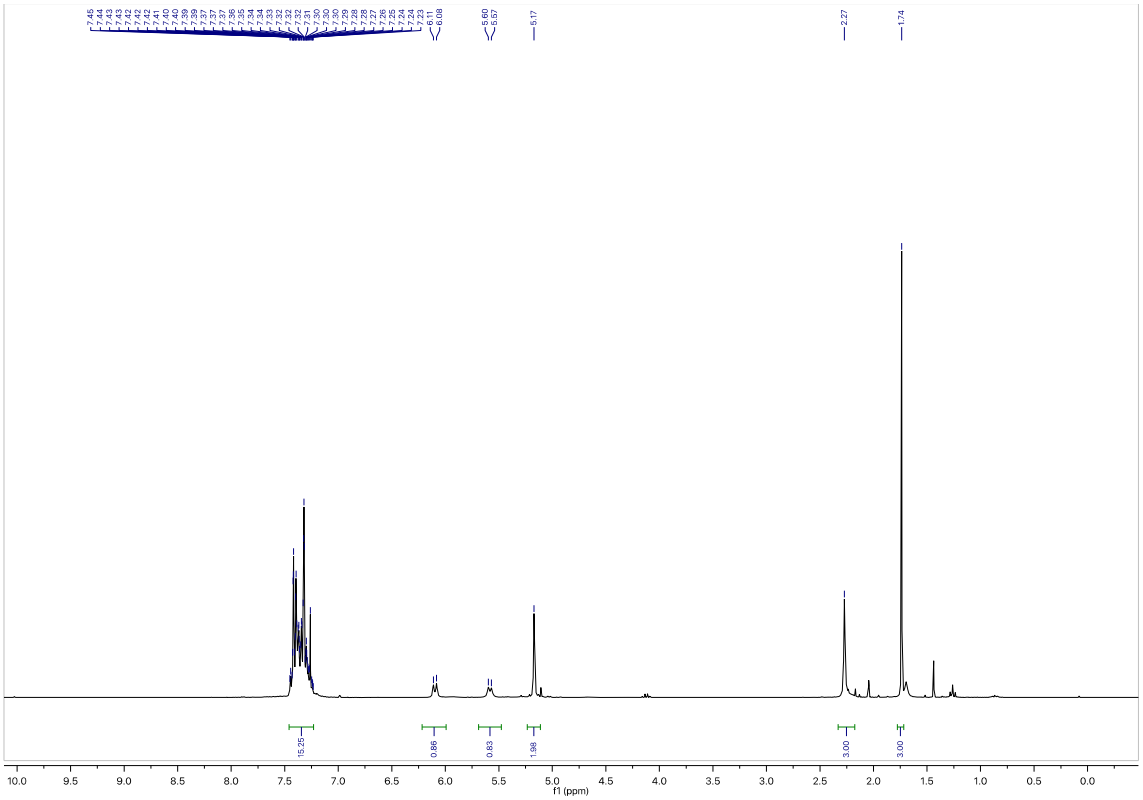
N
Me

**3aa**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7.25
7.24
7.23
7.23
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6.08
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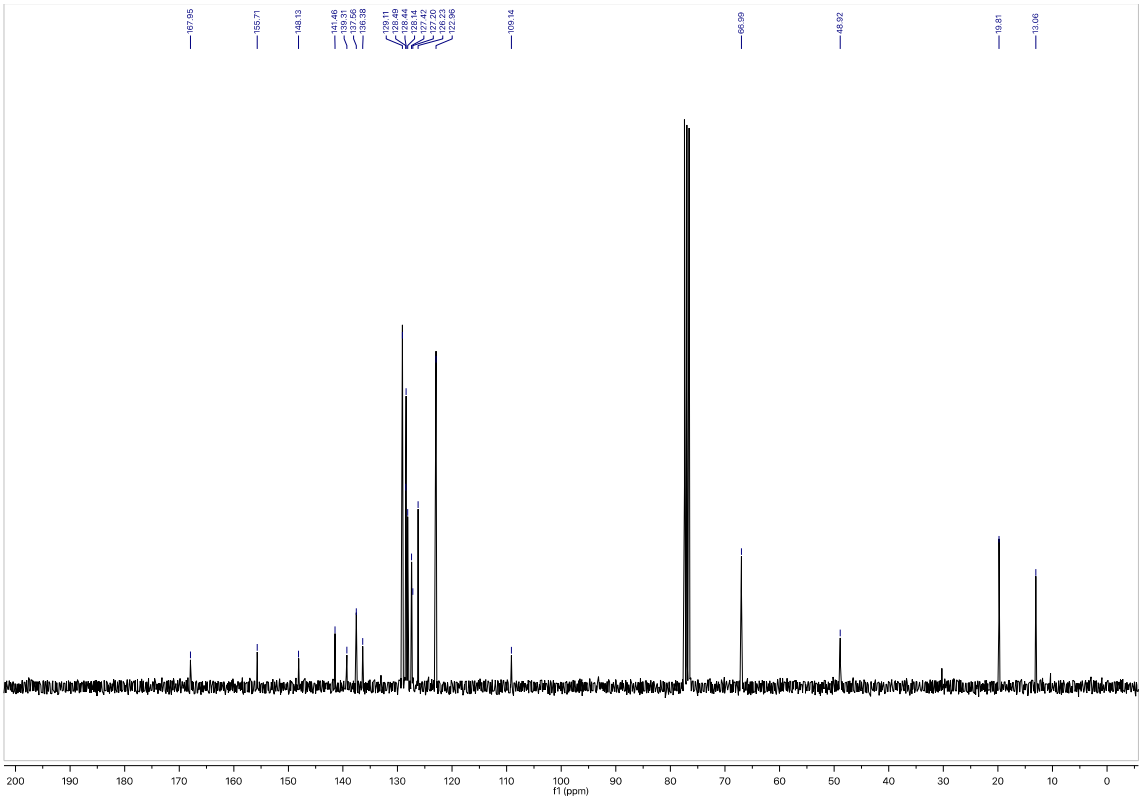
3.00
f1 (ppm)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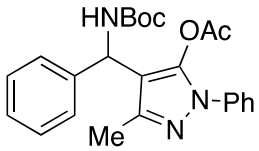
f1 (ppm)


HNBoc
OAc
N-Ph
Me
N

**3da**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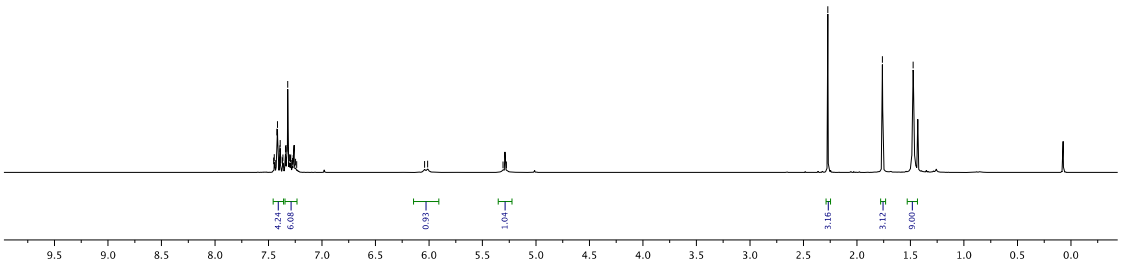
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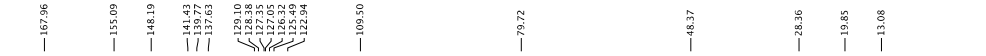
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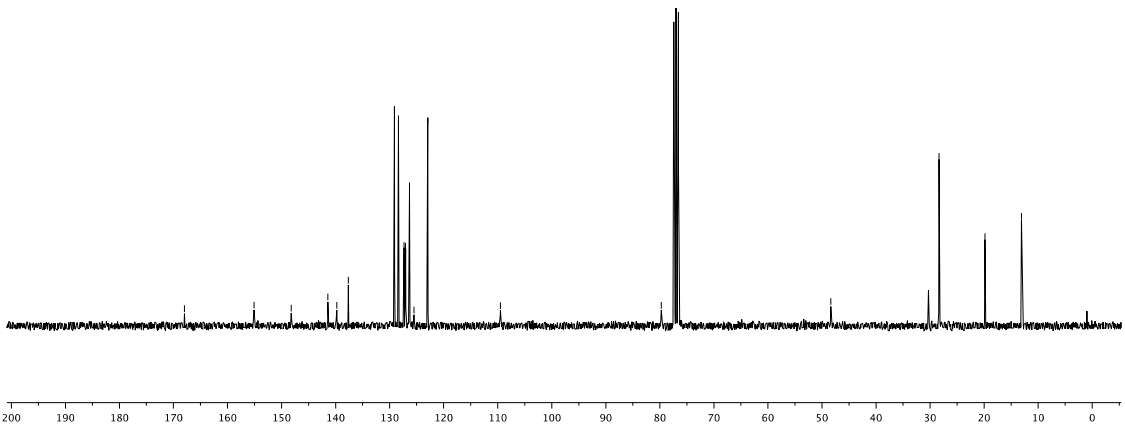
13.08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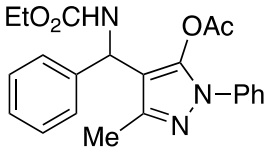
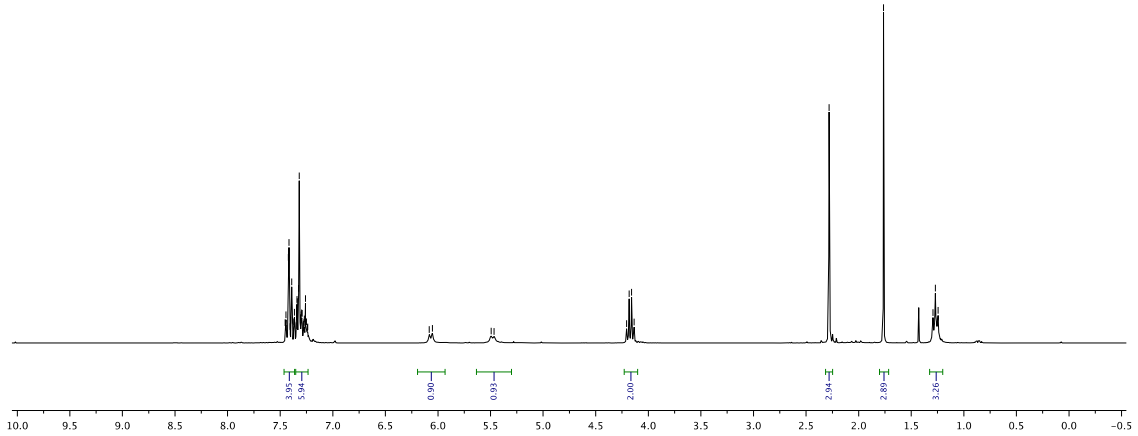
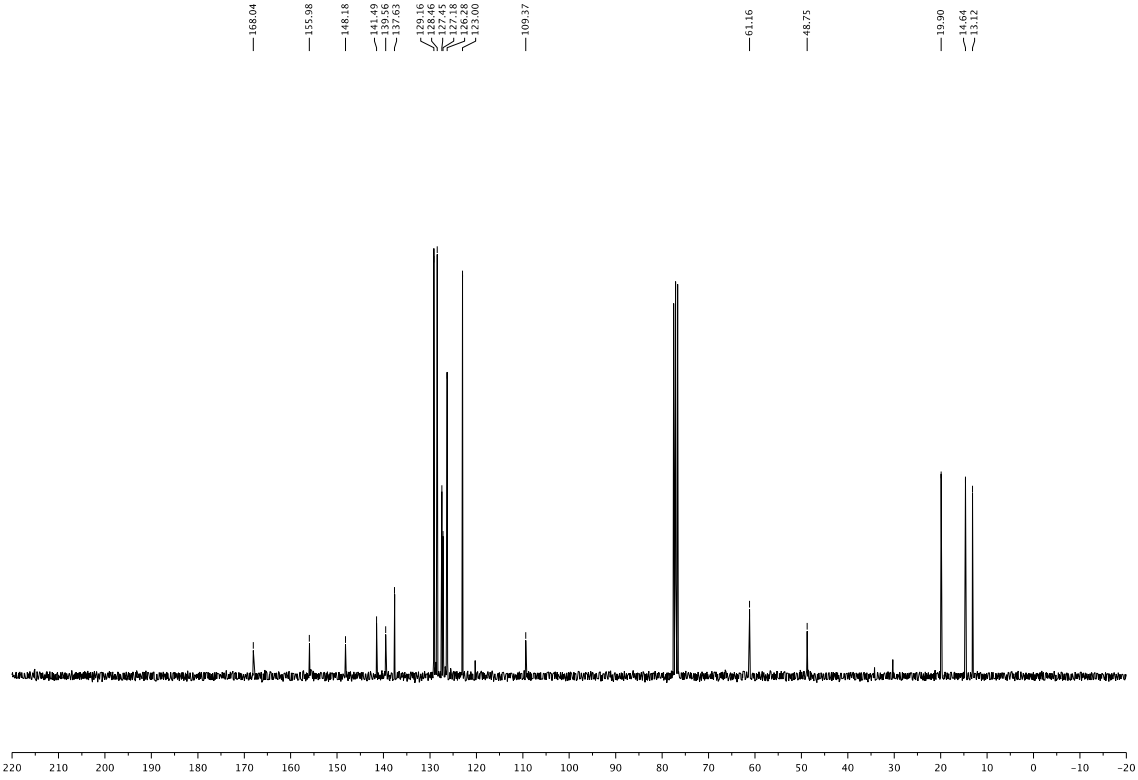
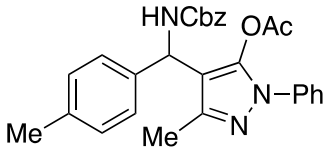



**3ea**



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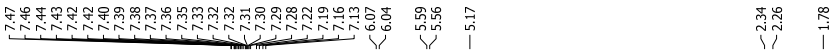
Me
Me
N

**3fa**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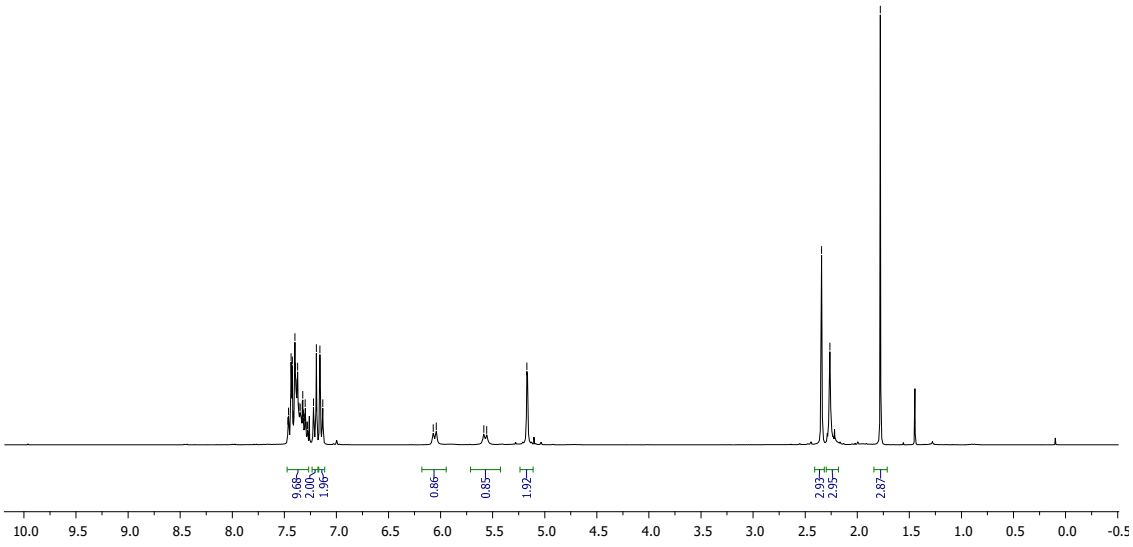
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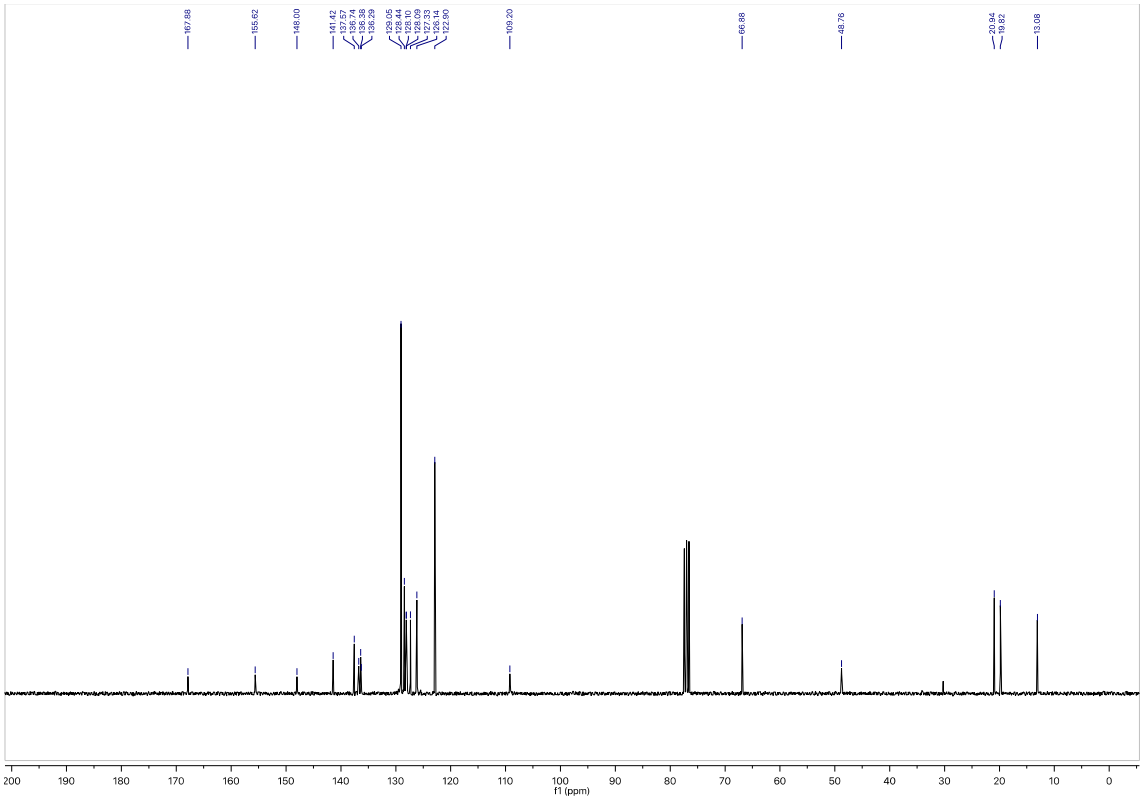
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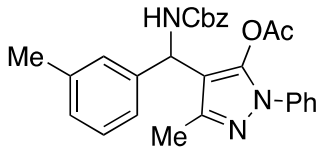
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N-Ph
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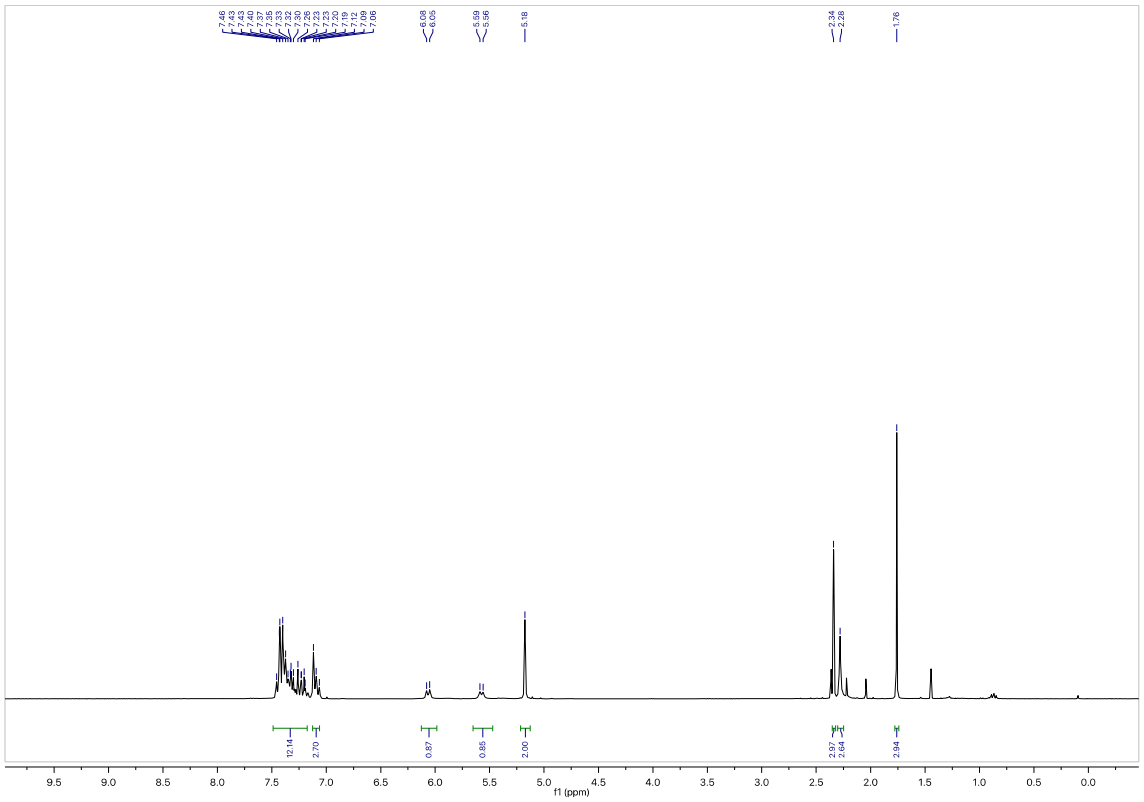
N

**3ga**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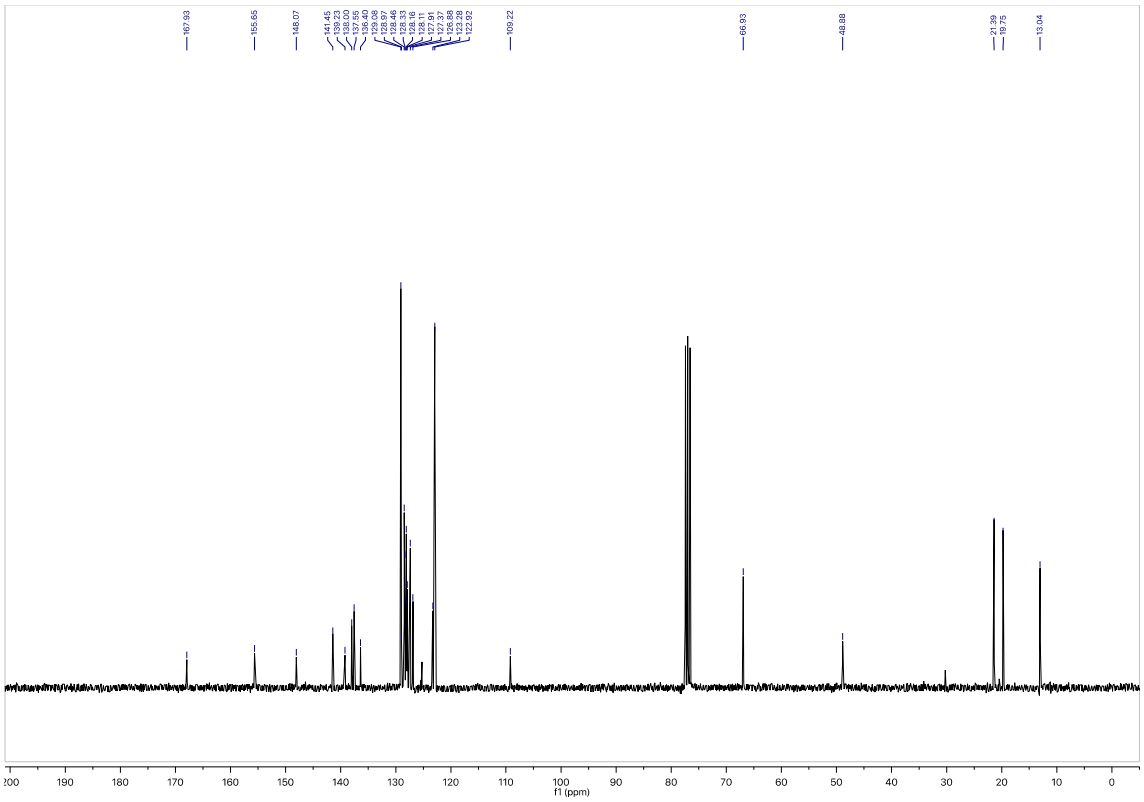
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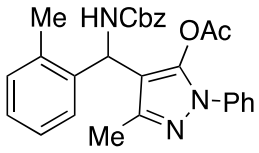
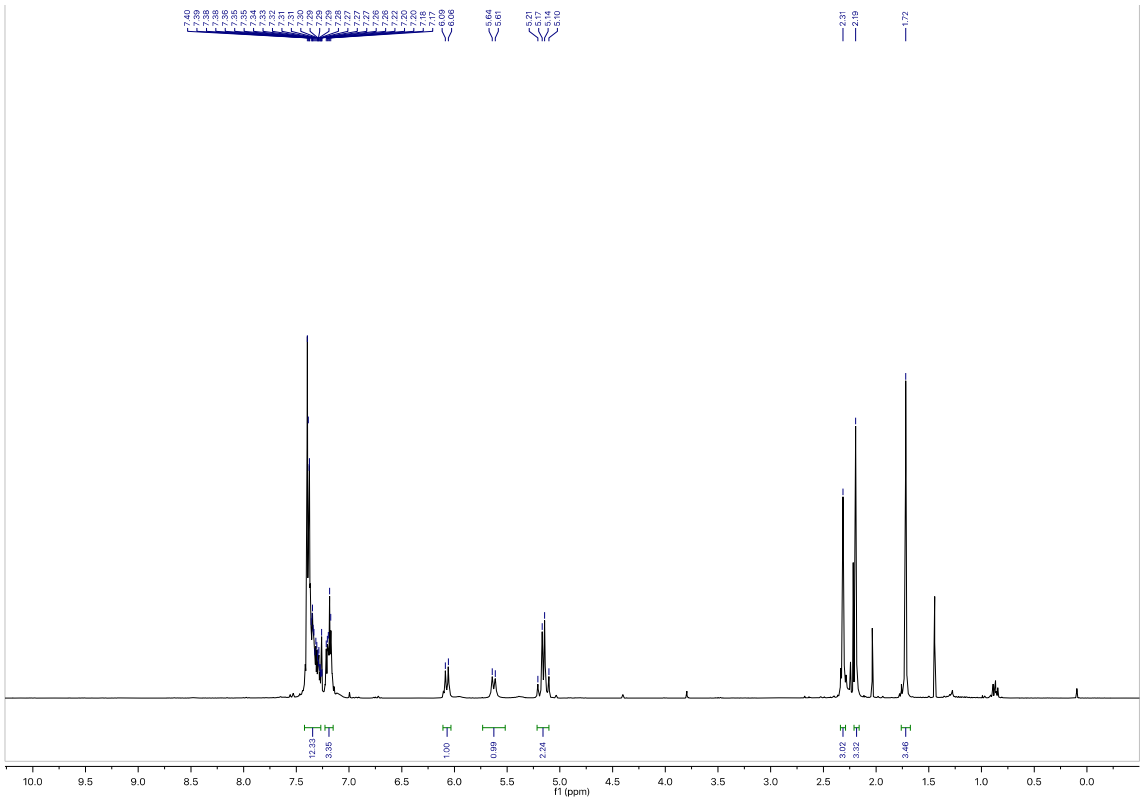
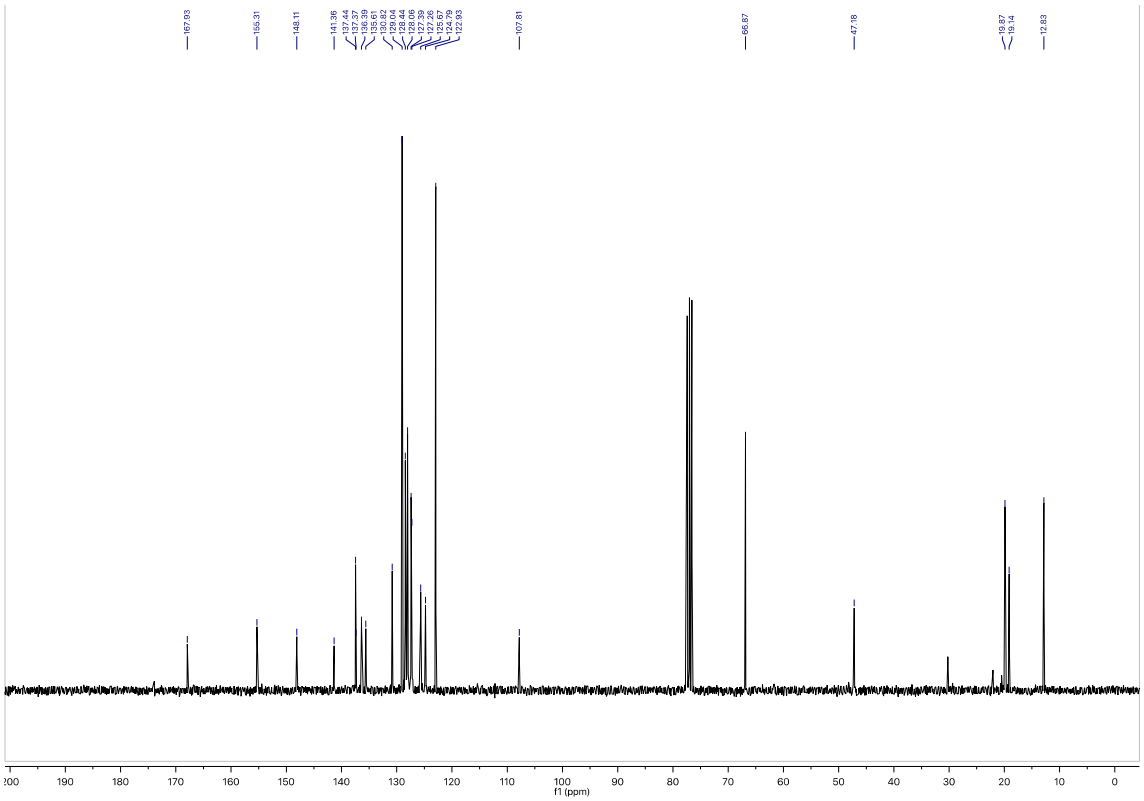
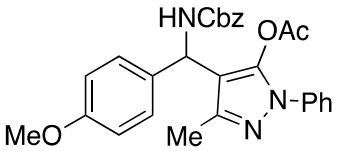



**3ha**



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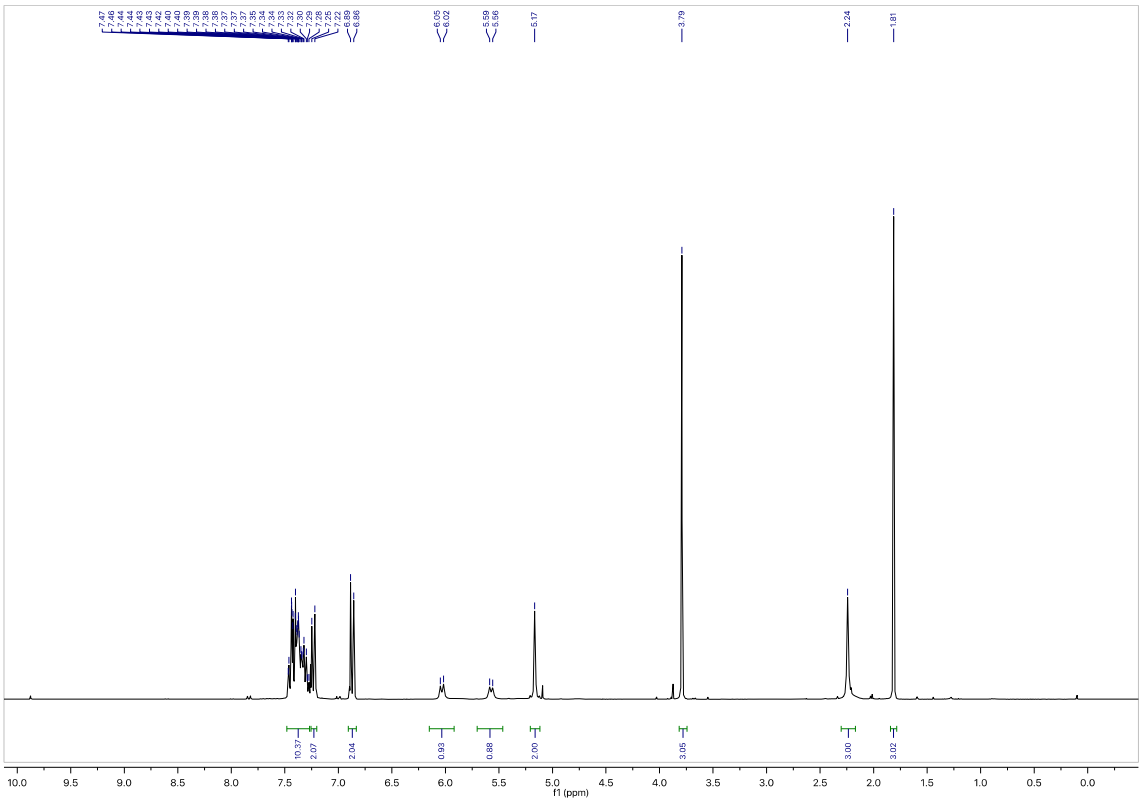
OAc
N-Ph
MeO
Me
N

**3ia**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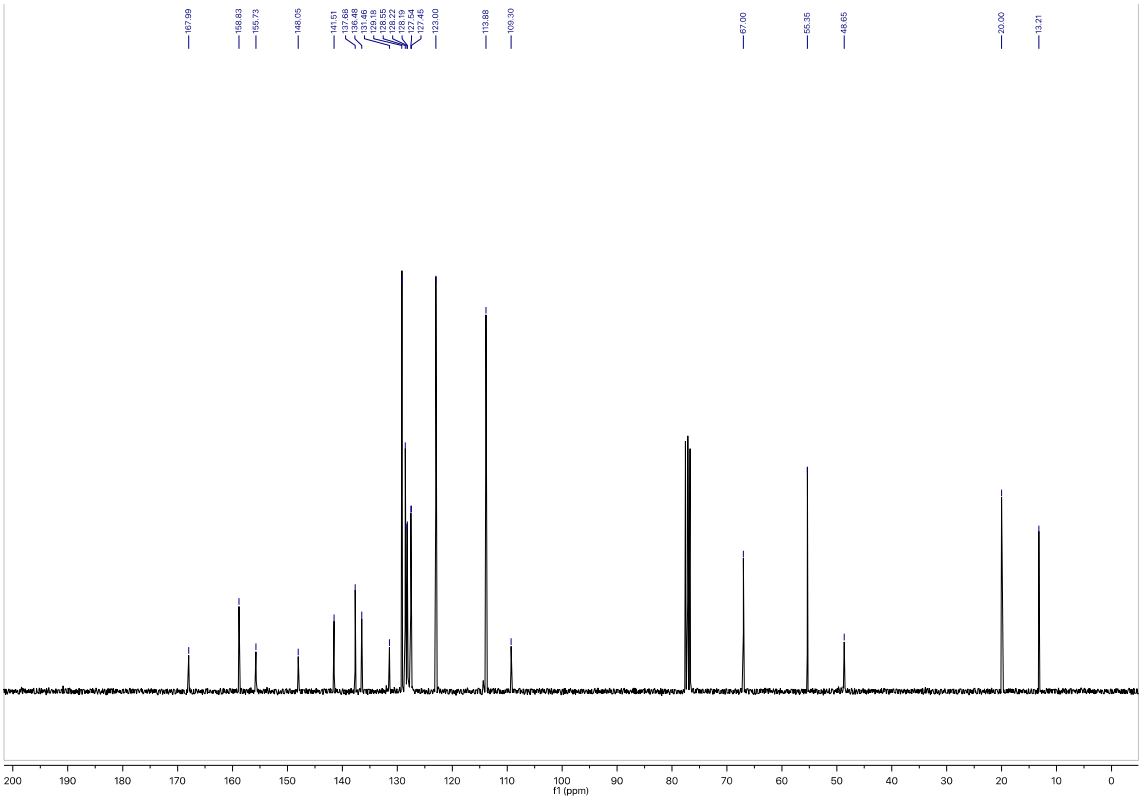
f1 (ppm)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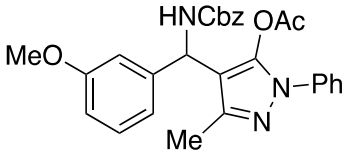
48.65
20.00
13.21
f1 (ppm)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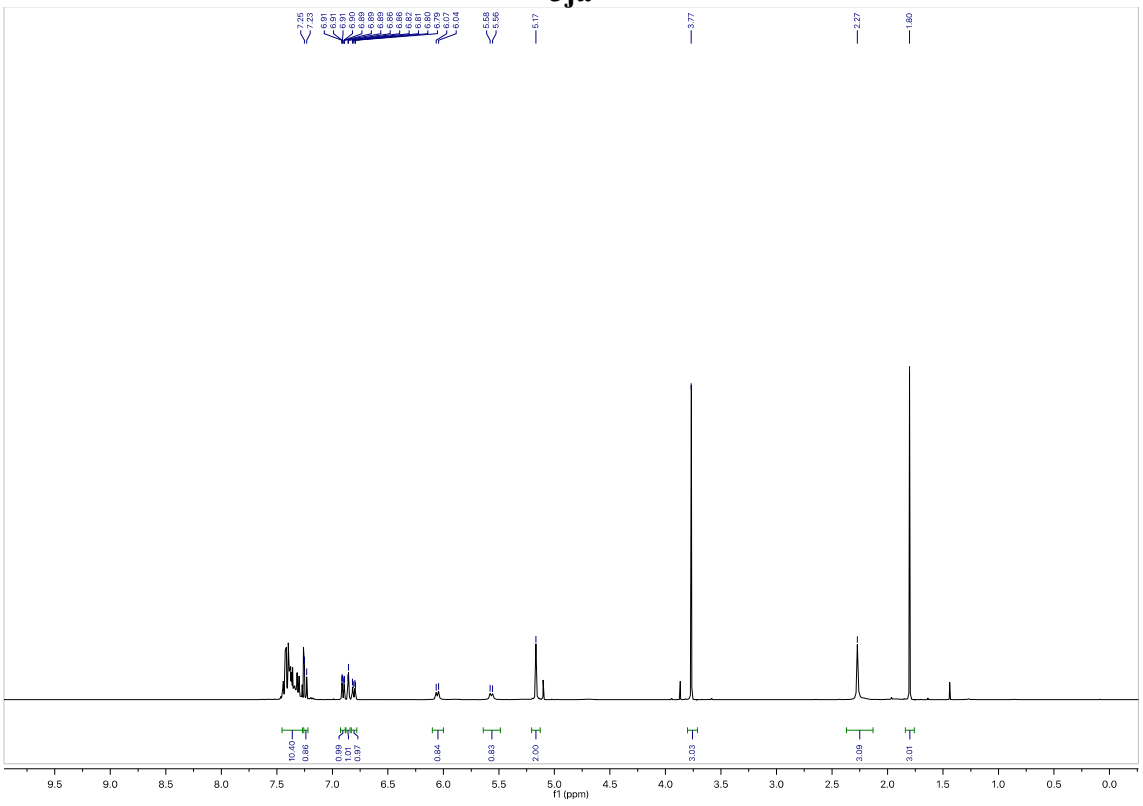
OAc
MeO
N–Ph
N
Me

**3ja**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6.89
6.88
6.88
6.86
6.82
6.81
6.80
6.79
6.07
6.04
5.58
5.56
5.17
3.77
2.27
1.80
10.40
0.86
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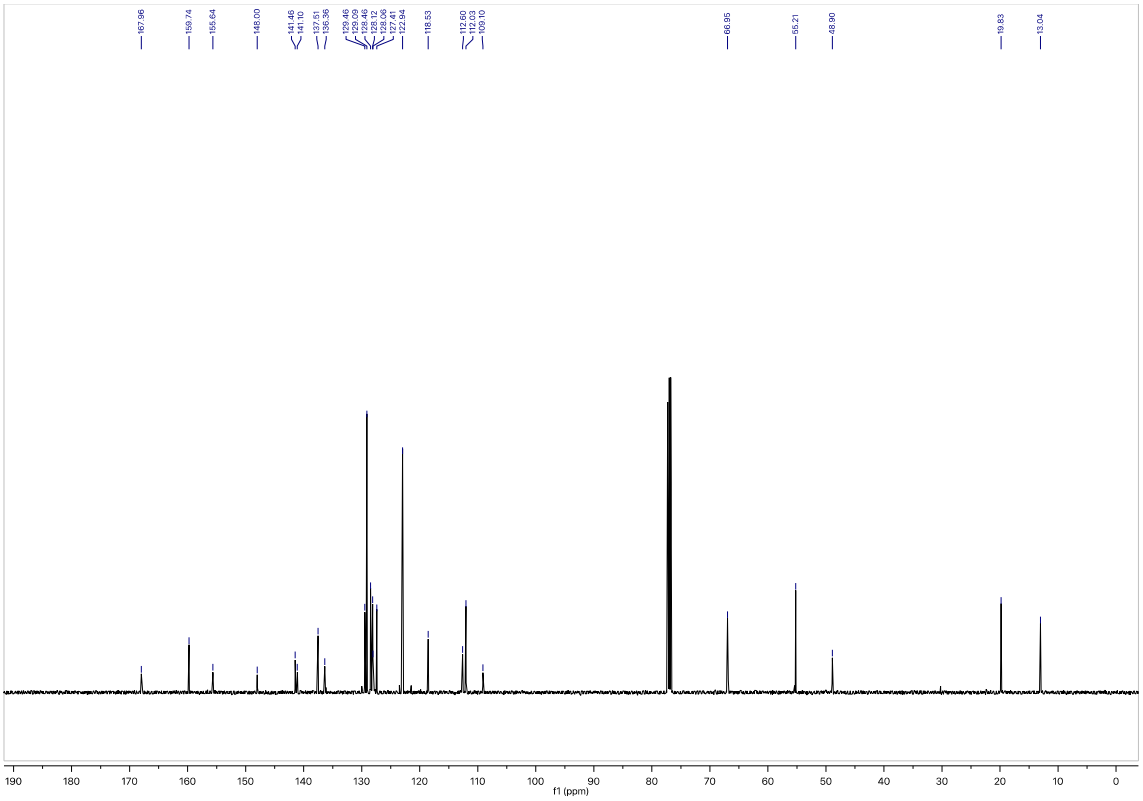
1.01
0.97
0.84
0.83
2.00
3.03
3.09
3.01
f1 (ppm)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159.74
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141.46
141.10
137.51
136.36
129.46
129.09
128.46
128.12
128.06
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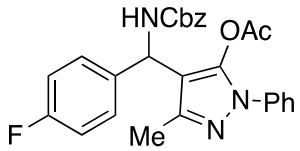
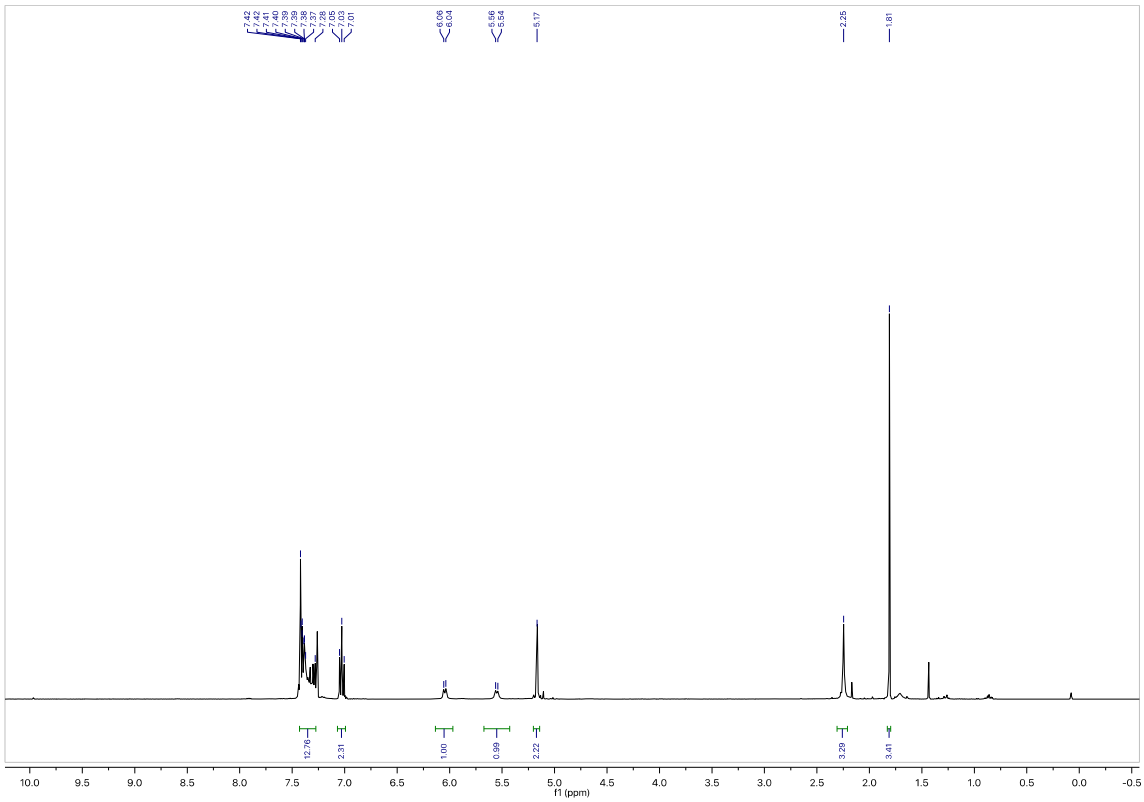
112.03
109.10
66.95
55.21
48.80
19.83
13.04
f1 (ppm)


HNCbz
OAc
N-Ph
F
Me
N

**3ka**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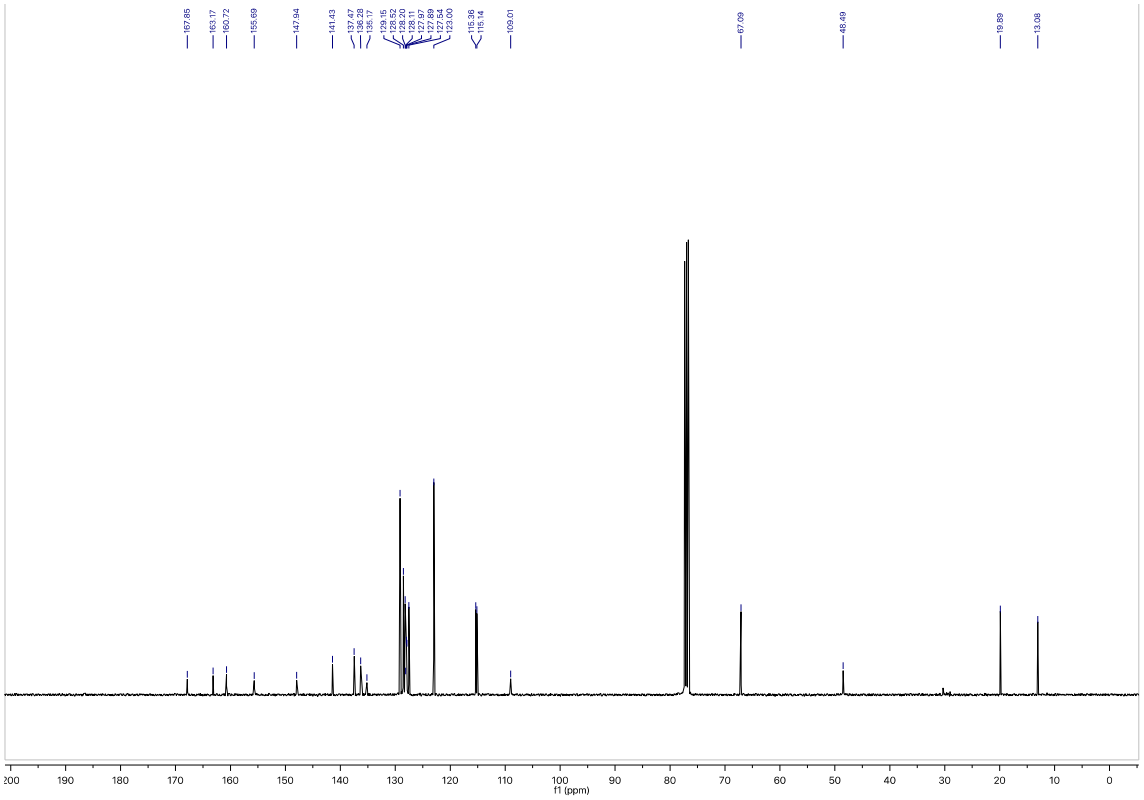
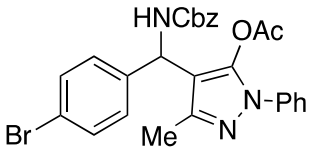
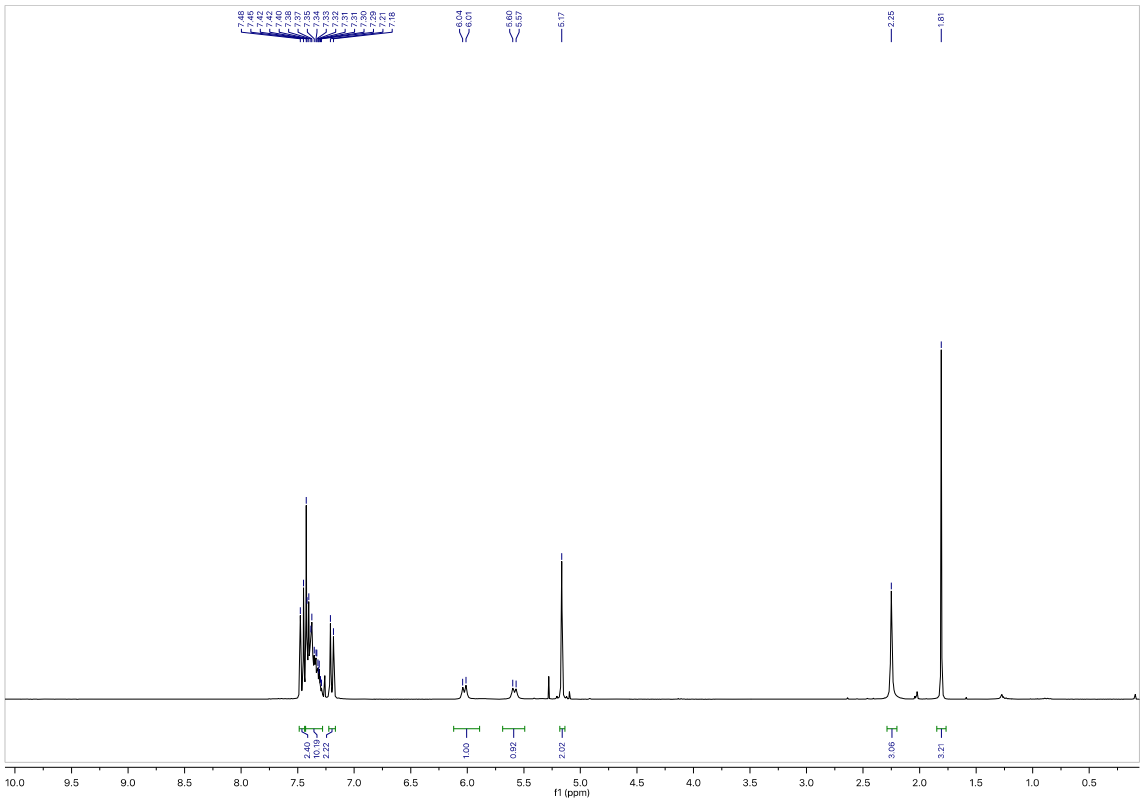
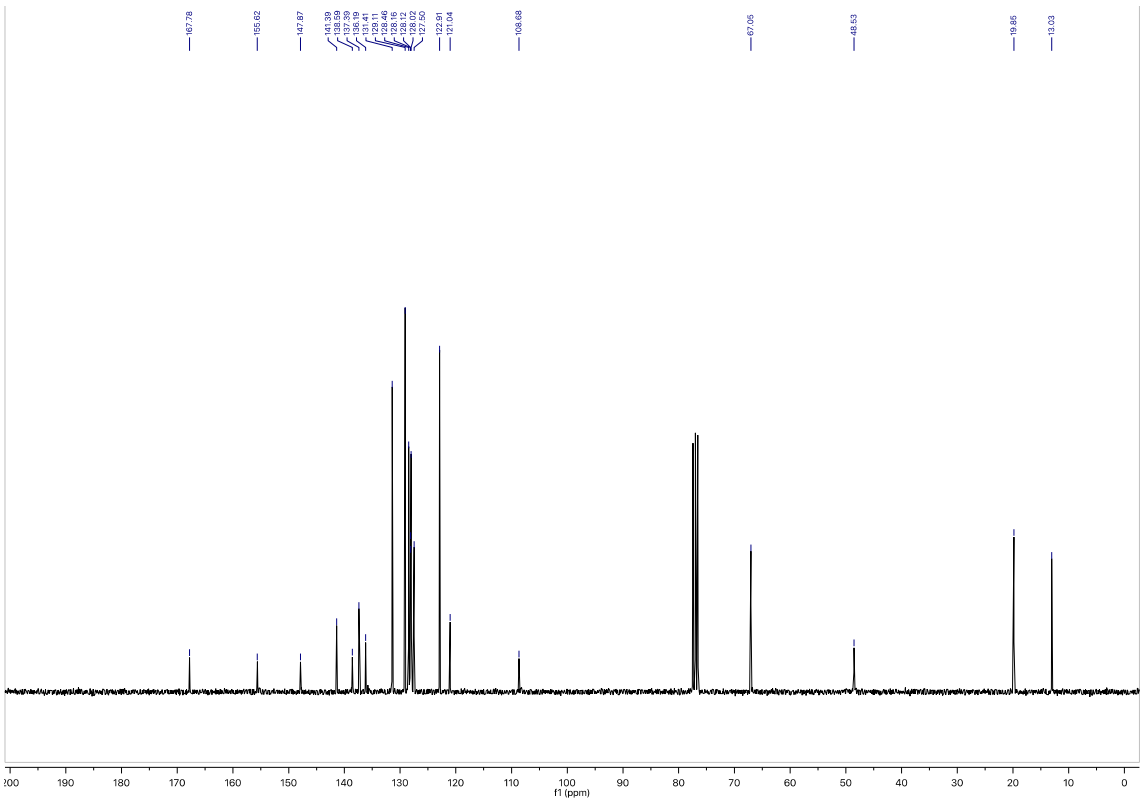
7.42
7.41
7.40
7.39
7.39
7.38
7.37
7.36
7.05
7.03
7.01
6.06
6.04
5.56
5.54
5.17
2.25
1.81
12.76
2.31
1.00
0.99
2.22
3.29
3.41
f1 (ppm)

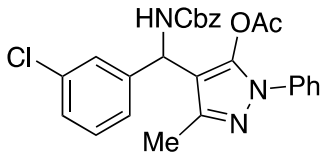

167.85
163.17
160.72
155.69
147.94
141.43
137.47
136.28
136.17
129.15
128.52
128.20
128.11
127.97
127.89
127.54
123.00
115.36
115.14
109.01
67.09
48.49
19.89
13.08
f1 (ppm)



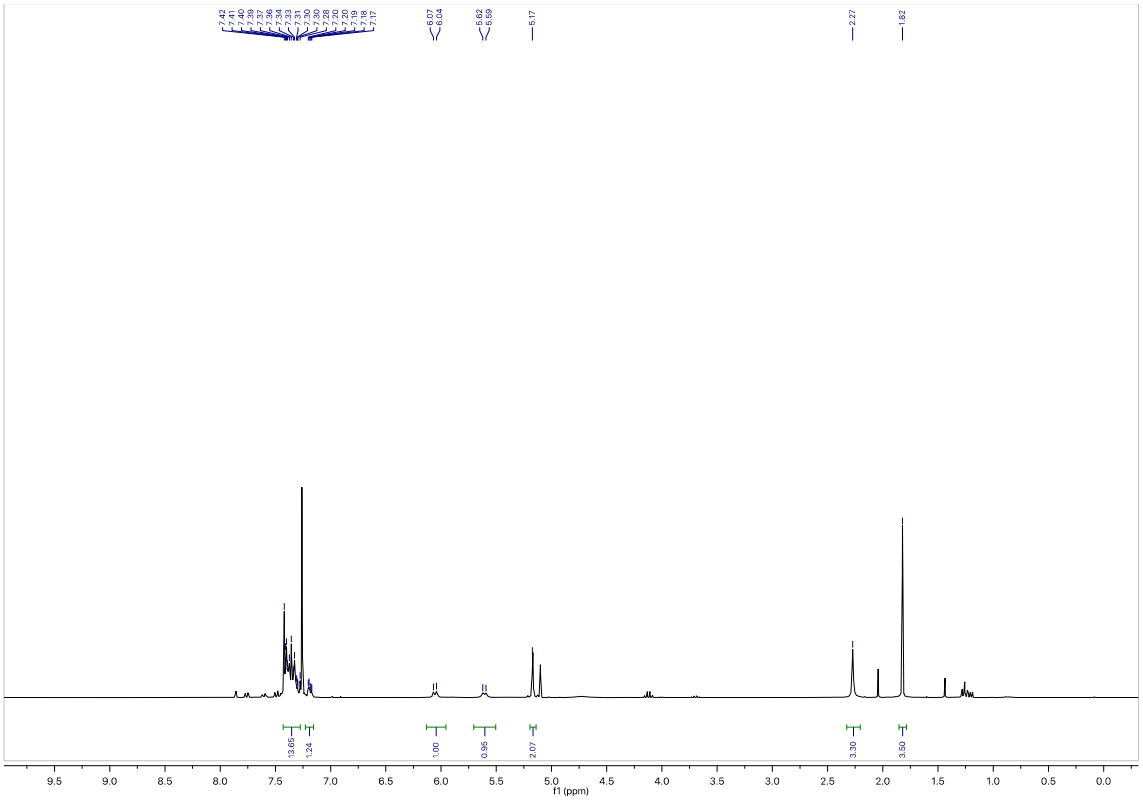

**3la**






HNCbz
OAc
Cl
N–Ph
N
Me

**3ma**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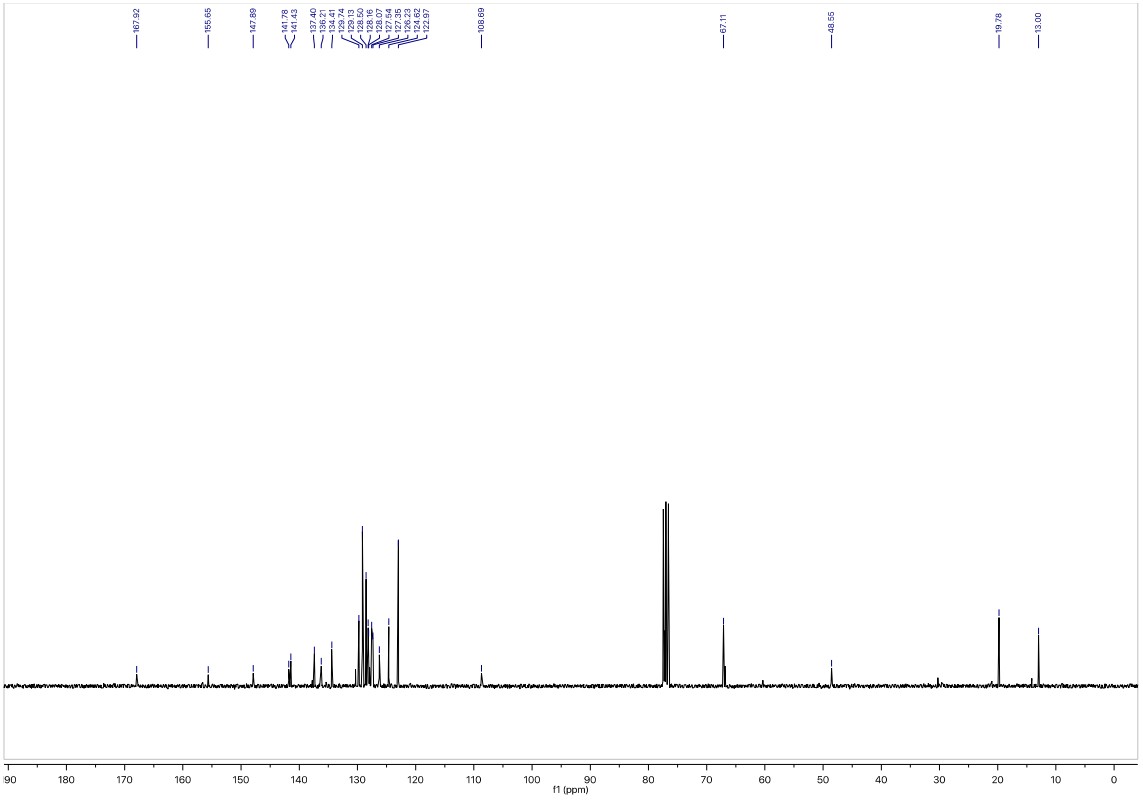
7.41
7.40
7.39
7.37
7.36
7.34
7.33
7.31
7.30
7.28
7.20
7.19
7.18
7.17
6.07
6.04
5.62
5.59
5.17
2.27
1.82
13.65
1.24
1.00
0.96
2.07
3.30
3.50
f1 (ppm)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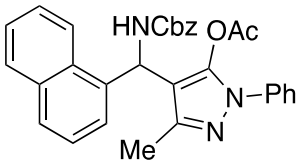
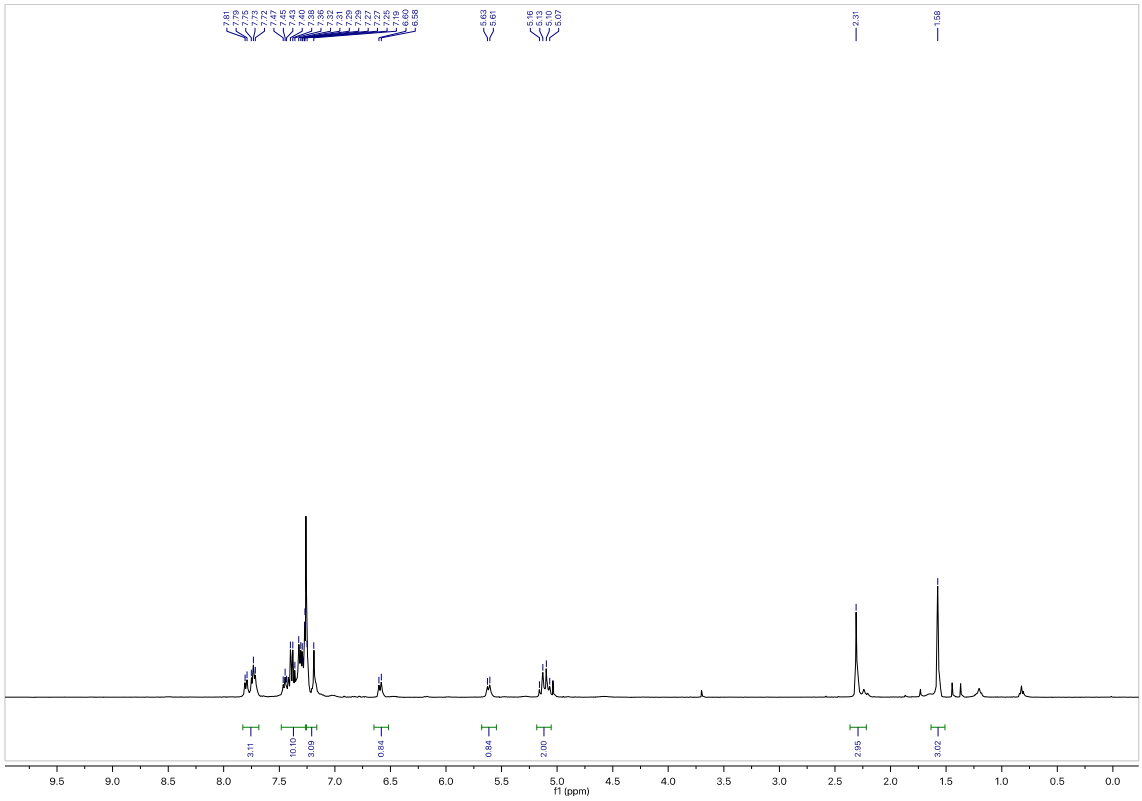
155.65
147.89
141.78
141.43
137.40
136.71
134.41
129.74
129.33
128.50
128.16
128.07
127.54
127.35
126.73
124.62
122.97
108.69
87.11
48.55
19.78
13.00
f1 (ppm)


HNCbz
OAc
N–Ph
N
Me

**3na**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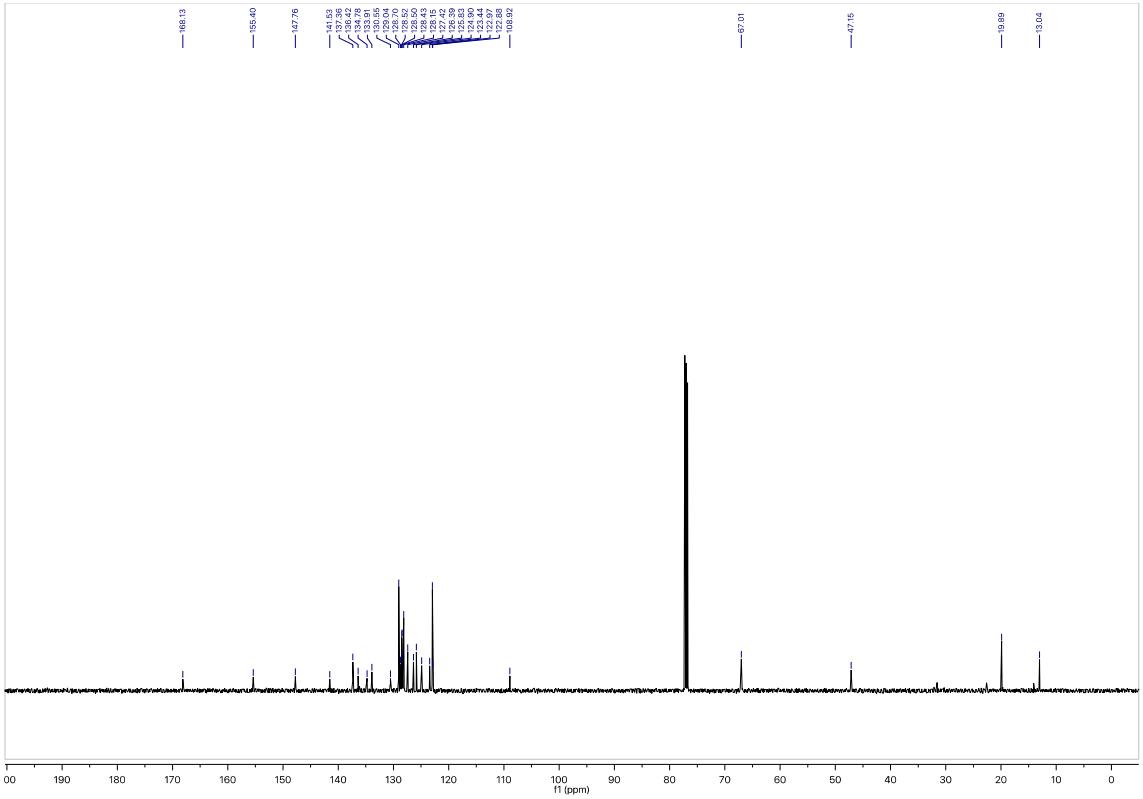
7.79
7.75
7.73
7.72
7.47
7.45
7.43
7.40
7.38
7.36
7.32
7.31
7.30
7.29
7.27
7.26
7.25
7.19
7.00
6.98
6.63
5.61
5.16
5.13
5.10
5.07
2.31
1.58
3.11
10.10
3.09
0.84
0.84
2.00
2.95
3.02
f1 (ppm)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155.40
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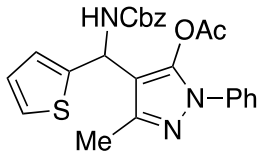
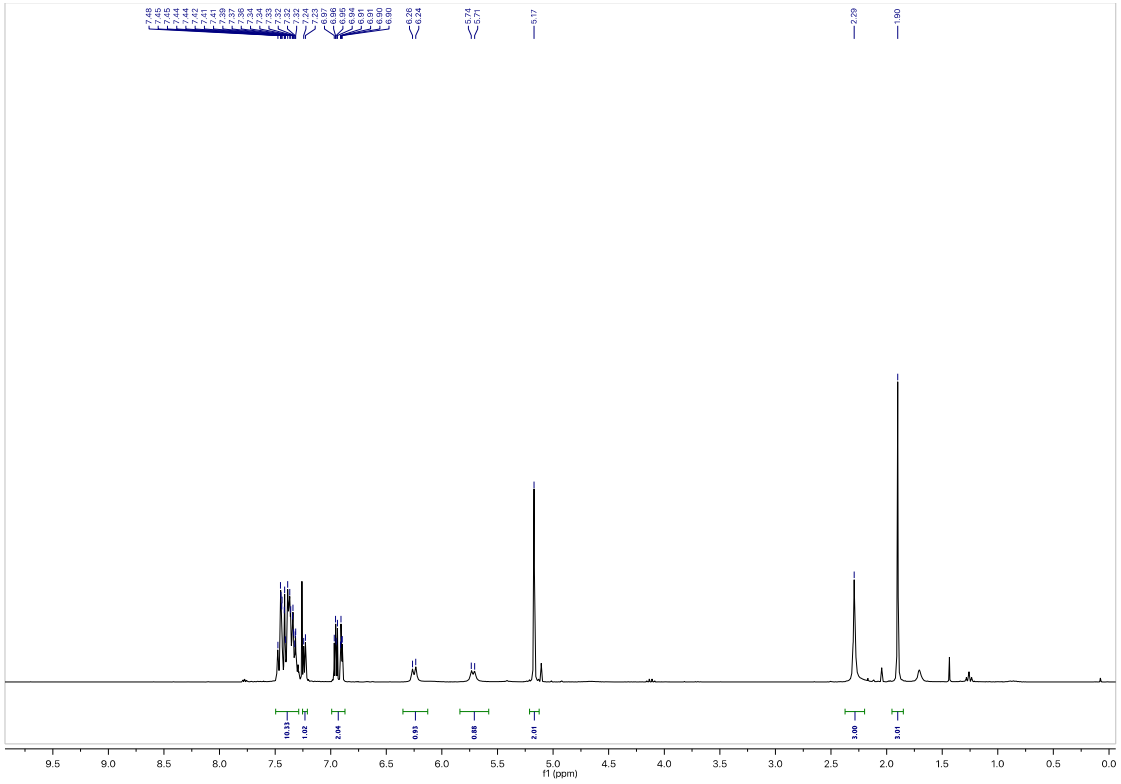
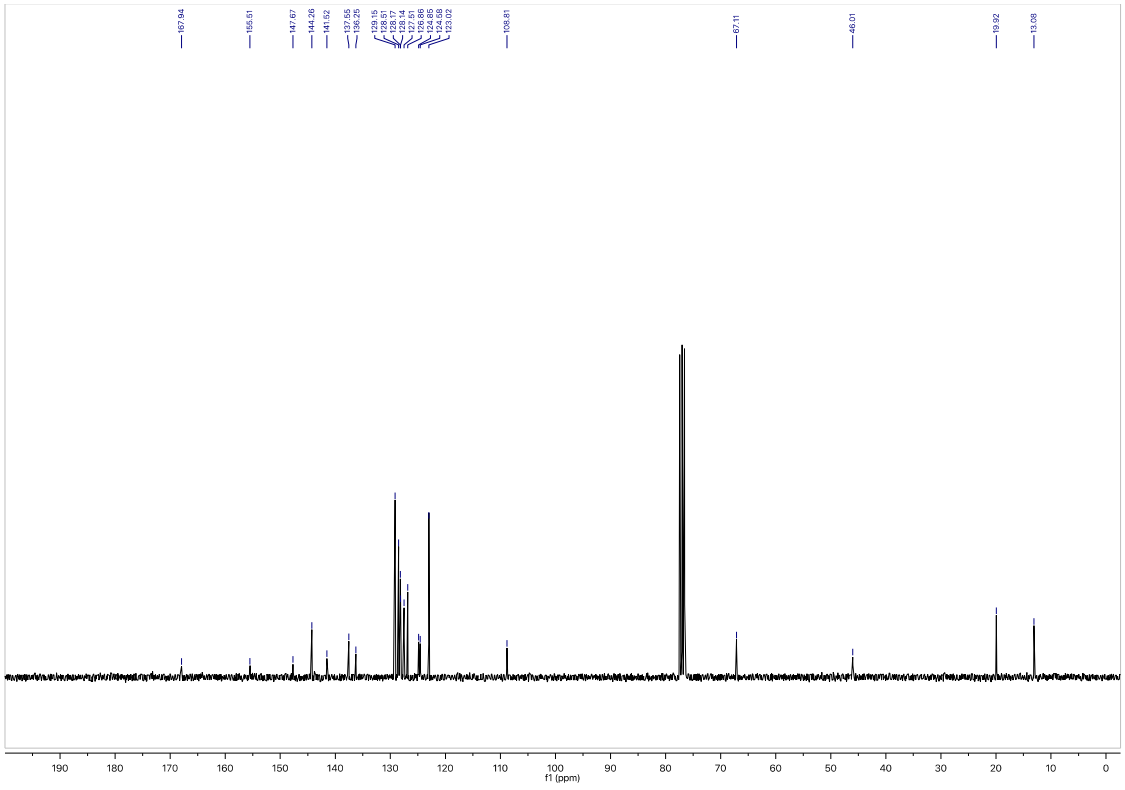
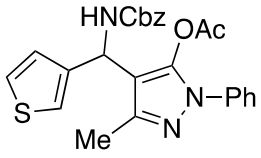
141.53
137.35
136.42
134.78
133.61
130.51
129.04
128.70
128.52
128.50
128.43
128.15
127.42
126.39
125.83
124.90
123.44
122.97
122.88
108.92
67.01
47.15
19.89
13.04
f1 (ppm)




**3oa**

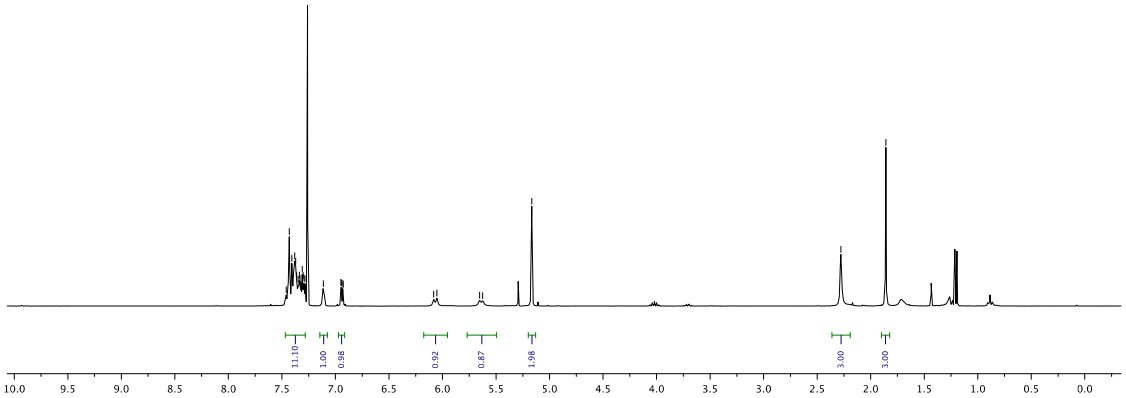





HNCbz
OAc
N–Ph
S
N
Me

**3pa**


7.46
7.43
7.41
7.38
7.37
7.36
7.35
7.34
7.33
7.32
7.32
7.31
7.30
7.29
7.28
7.26
7.11
6.95
6.94
6.93
6.93
6.08
6.05
5.65
5.62
5.17
2.28
1.86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1.00
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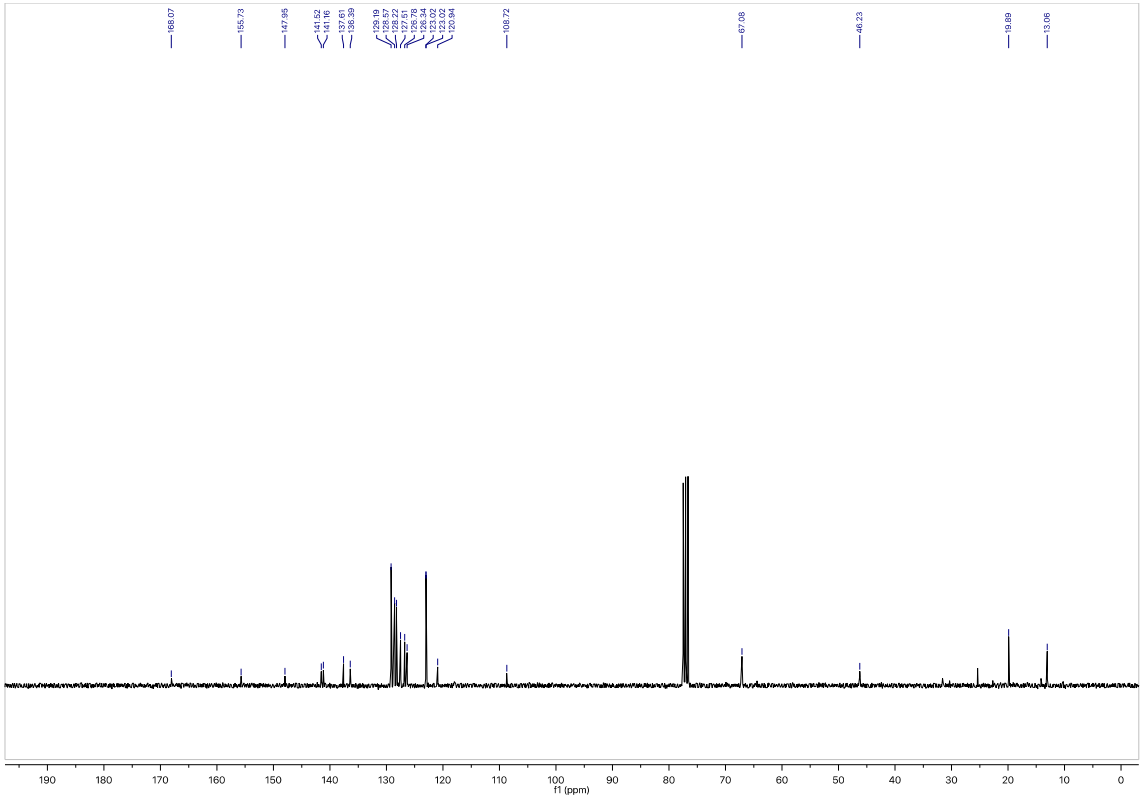
0.92
0.87
1.98
3.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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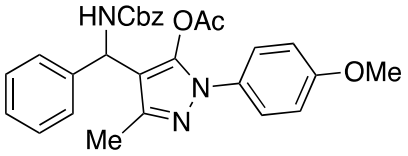
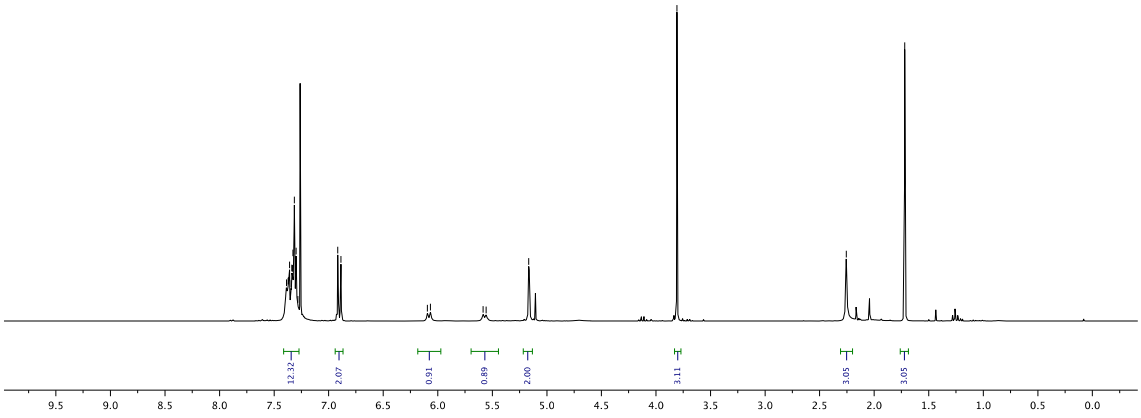
141.16
137.61
136.99
129.19
128.57
128.27
127.61
126.78
125.34
123.52
123.02
120.94
108.72
67.08
46.23
19.89
13.06
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HNCbz
OAc
N
N
OMe
Me

**3ab**


7.39
7.37
7.37
7.36
7.34
7.34
7.33
7.31
7.30
7.28
6.92
6.89
6.10
6.07
5.58
5.56
5.17
3.81
2.26
1.72


12.32
2.07
0.91
0.89
2.00
3.11
3.05
3.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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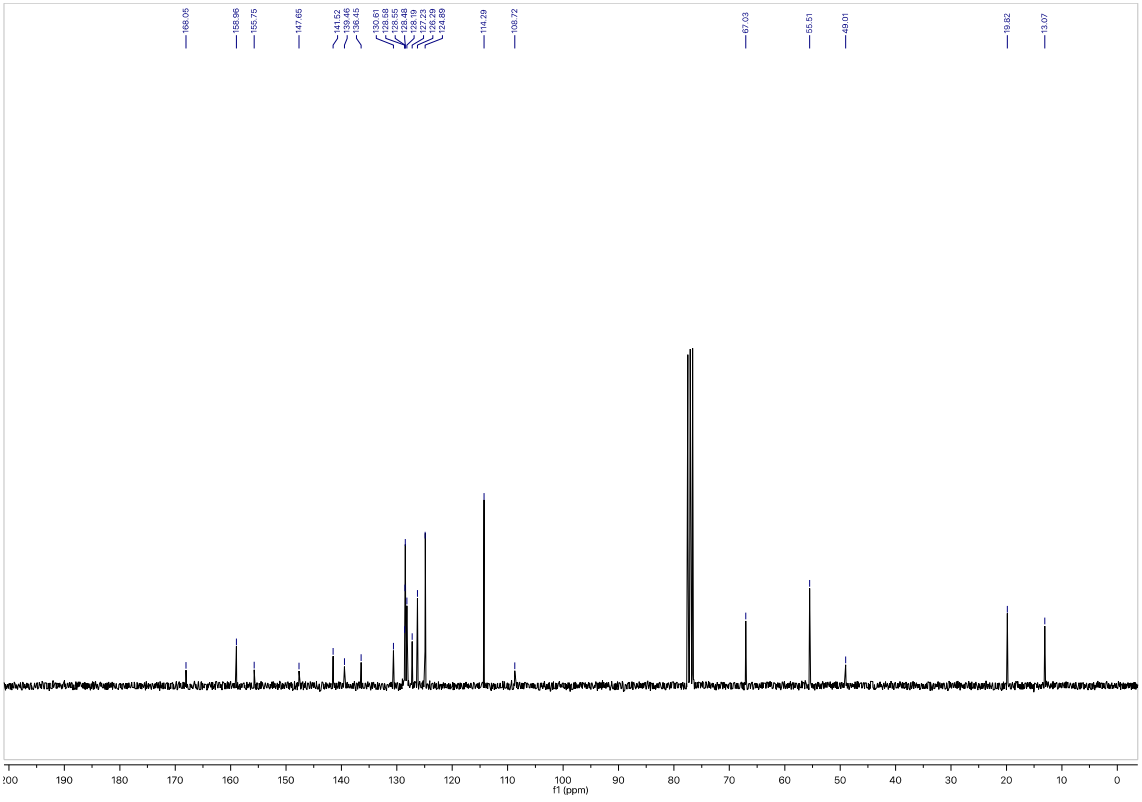
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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130.61
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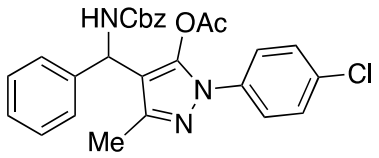
128.45
128.44
128.19
127.23
126.93
124.89
114.29
108.72
67.03
55.51
49.01
19.82
13.07
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HNCbz
OAc
N
N
Cl
Me

**3ac**


7.33
7.30
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7.27
7.26
7.25
7.24
7.23
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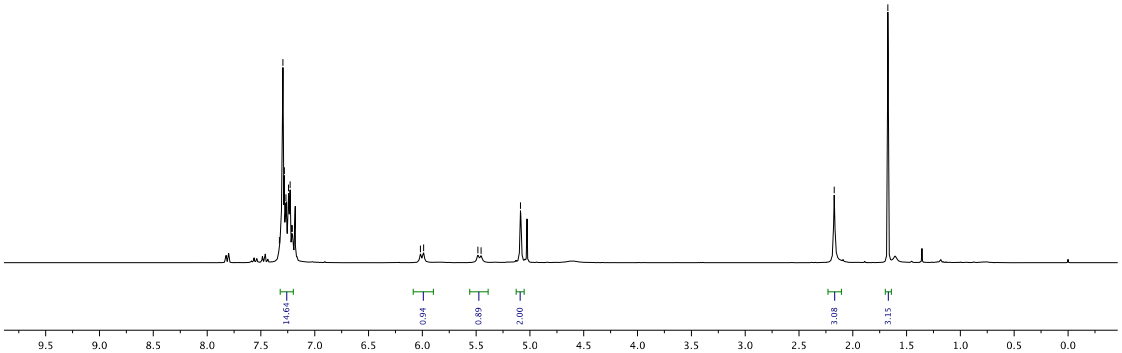
7.21
7.21
7.21
6.02
5.99
5.48
5.45
5.09
2.17
1.67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8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


167.78
155.67
148.53
141.49
139.15
136.33
136.13
133.04
129.72
129.28
128.49
128.17
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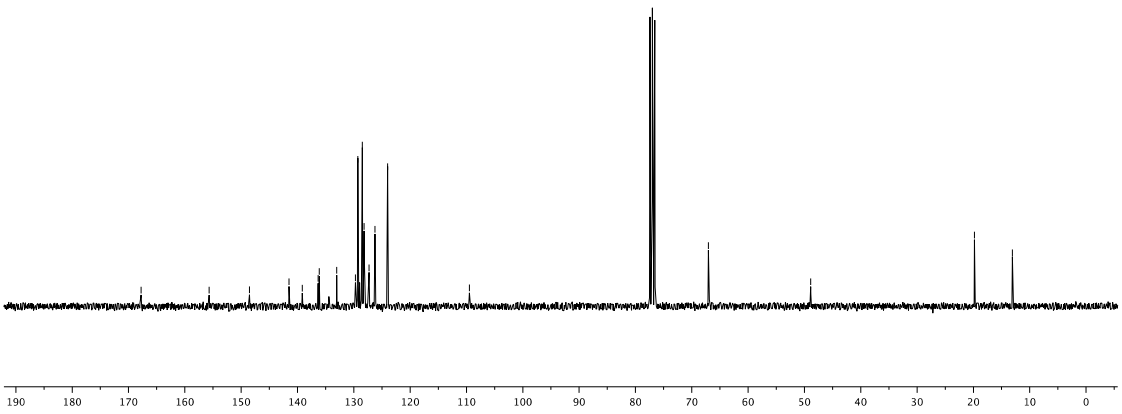
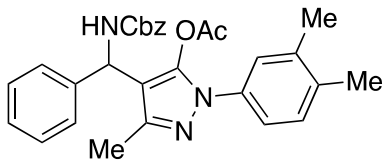
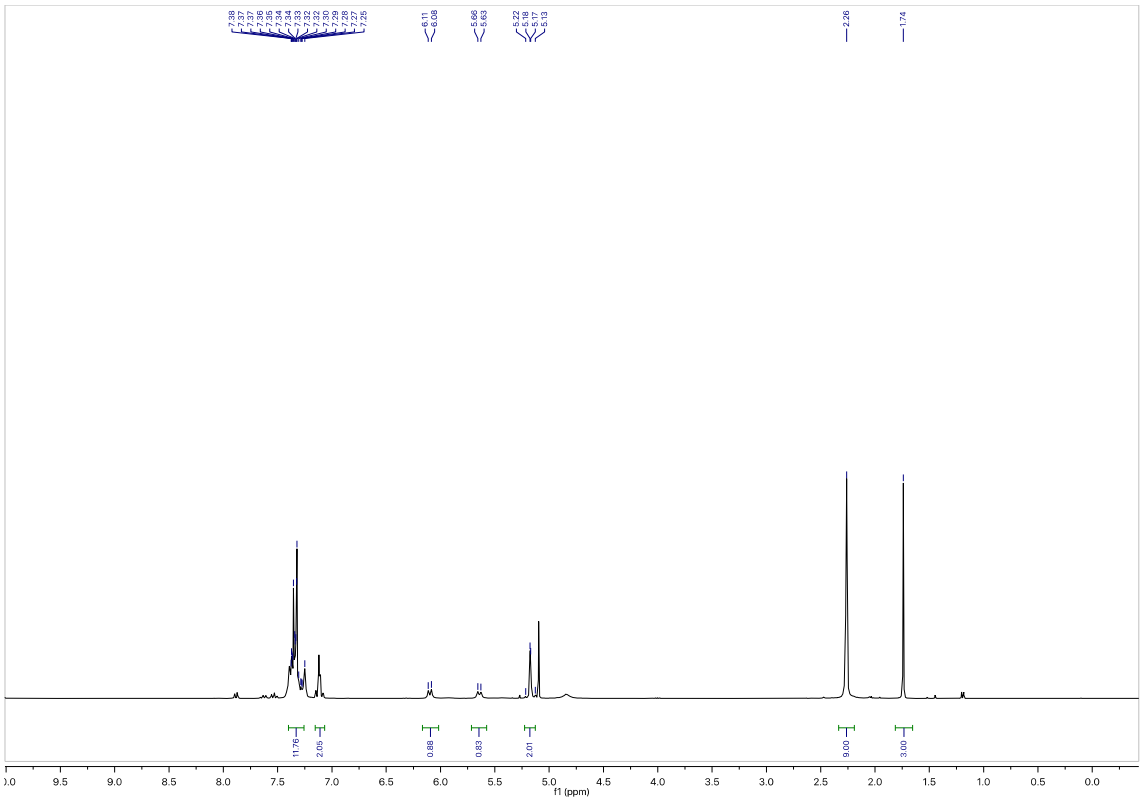
124.00
109.48
67.03
48.89
19.81
13.07


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


HNCbz
OAc
Me
Me
N
N
Me

**3ad**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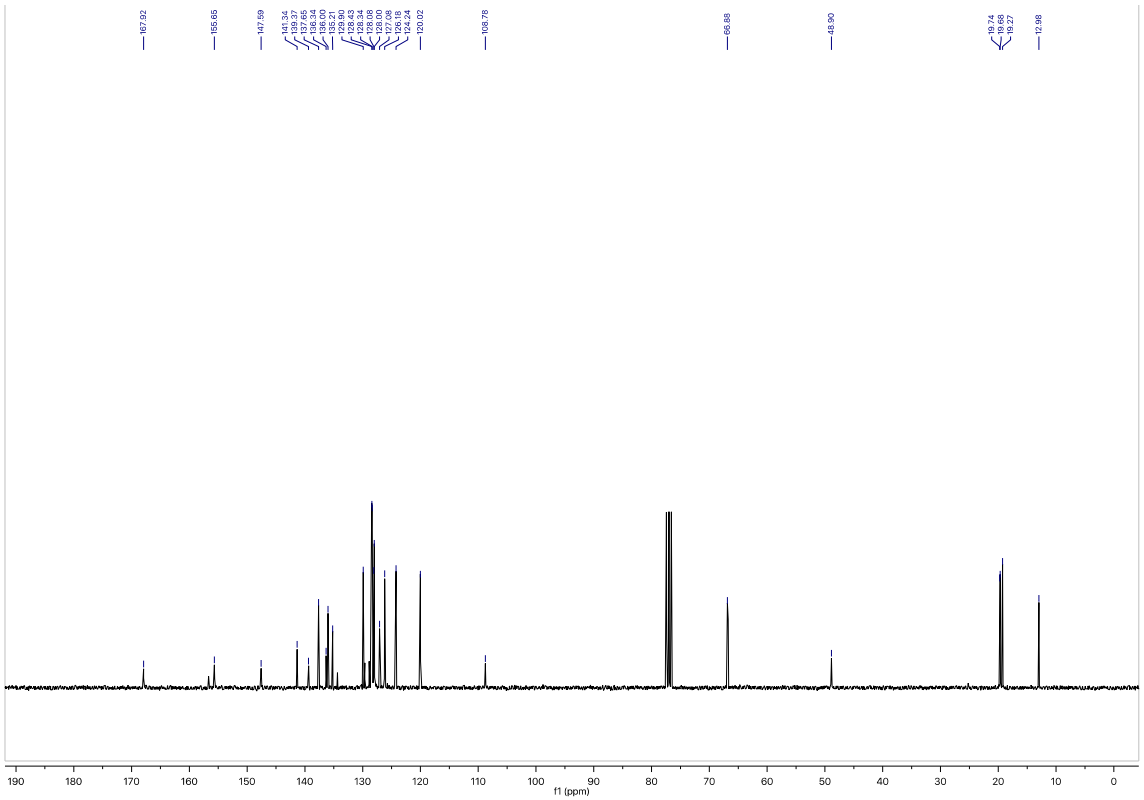
7.32
7.30
7.29
7.28
7.27
7.26
6.11
6.08
5.66
5.63
5.22
5.18
5.17
5.13
2.26
1.74
11.76
2.05
0.88
0.83
2.01
9.00
3.00
f1 (ppm)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139.27
137.65
136.34
135.60
135.21
129.90
129.45
128.34
128.08
128.00
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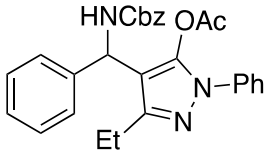
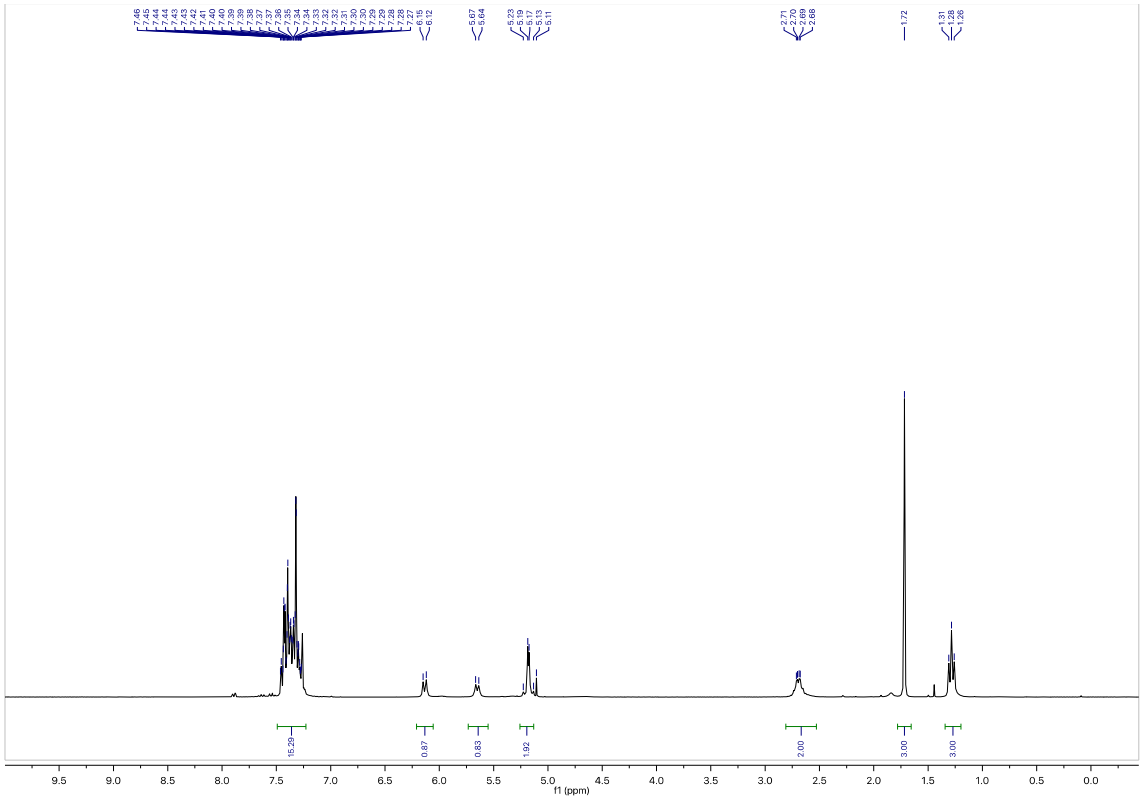
19.74
19.68
19.27
12.98
f1 (ppm)


HNCbz
OAc
N–Ph
N
Et

**3ae**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7.34
7.34
7.33
7.32
7.32
7.31
7.30
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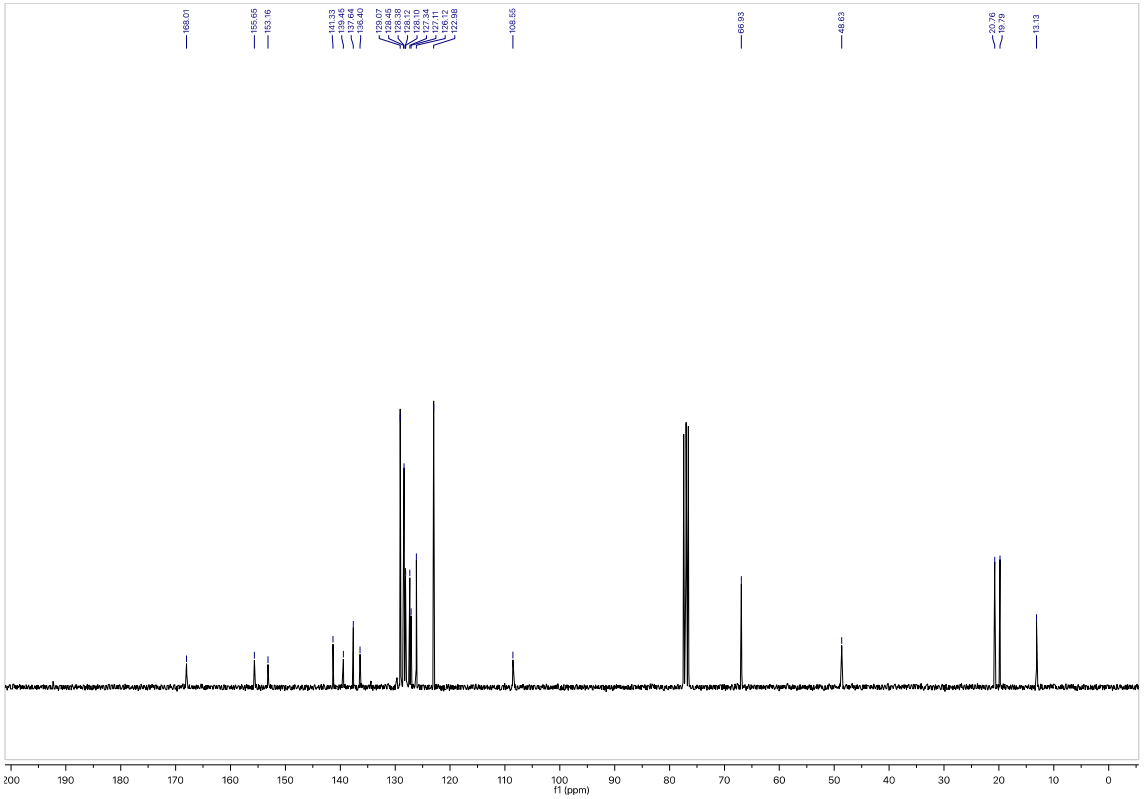
7.29
7.29
7.28
7.28
7.27
6.15
6.12
5.67
5.64
5.23
5.19
5.17
5.13
5.11
2.71
2.70
2.69
2.68
1.72
1.31
1.28
1.26
15.29
0.97
0.83
1.92
2.00
3.00
3.00
f1 (ppm)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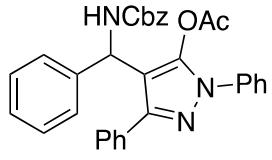
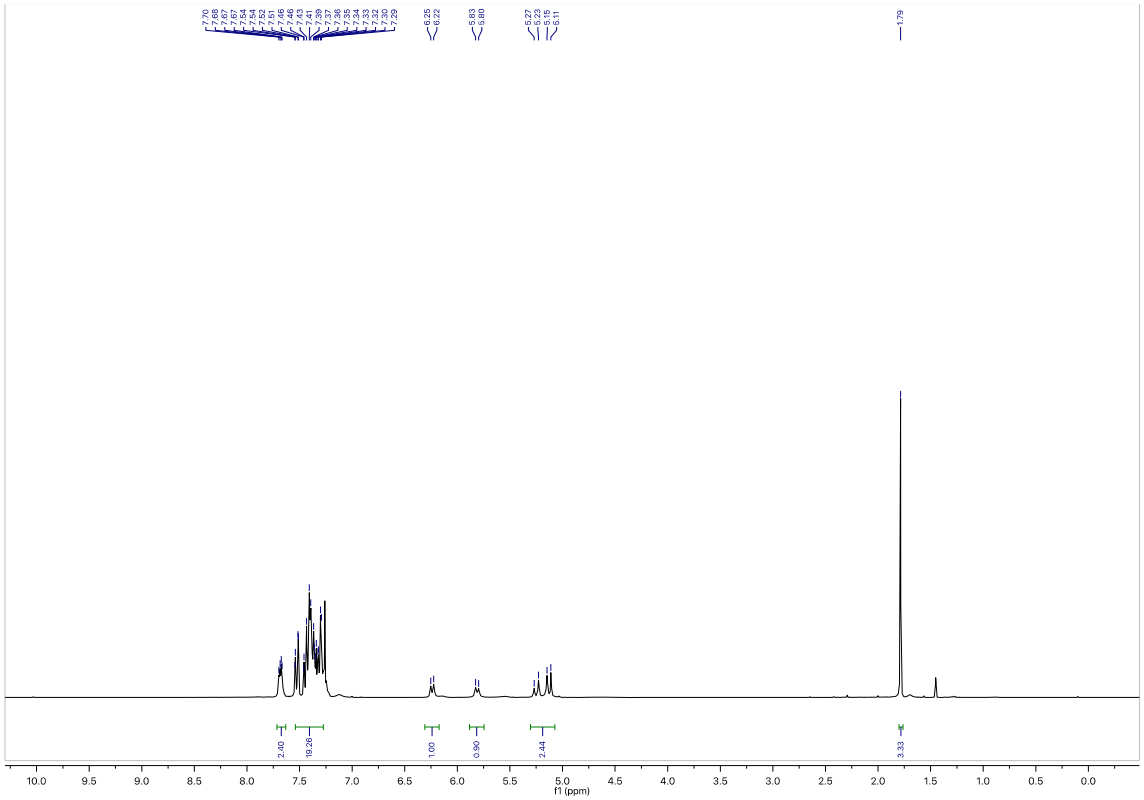
139.45
137.44
136.40
129.07
128.45
128.38
128.32
128.10
127.34
127.11
126.12
122.98
108.55
66.93
48.63
20.76
19.79
13.13
f1 (ppm)


HNCbz
OAc
N–Ph
N
Ph

**3af**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7.67
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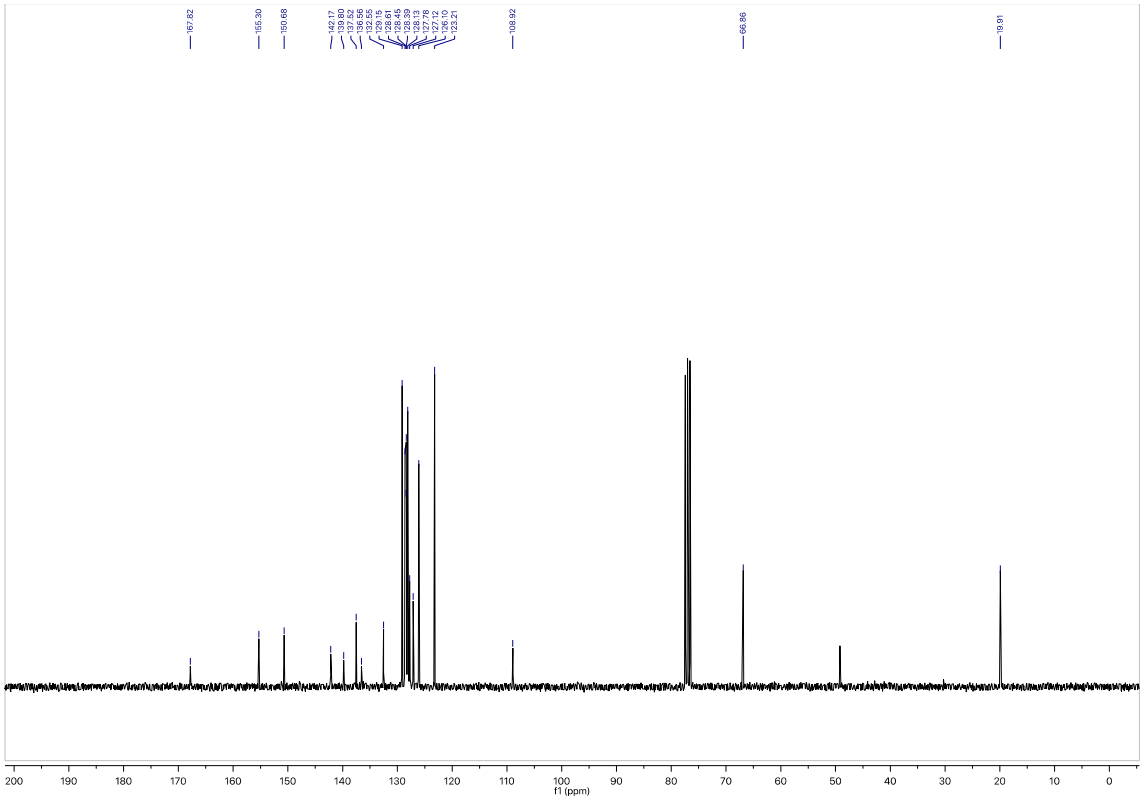
7.54
7.52
7.51
7.46
7.43
7.41
7.39
7.37
7.36
7.35
7.34
7.33
7.32
7.30
7.29
8.25
8.22
5.83
5.80
5.27
5.23
5.15
5.11
1.79
2.40
19.26
1.00
0.90
2.44
3.33
f1 (ppm)


167.82
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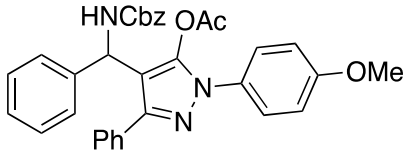
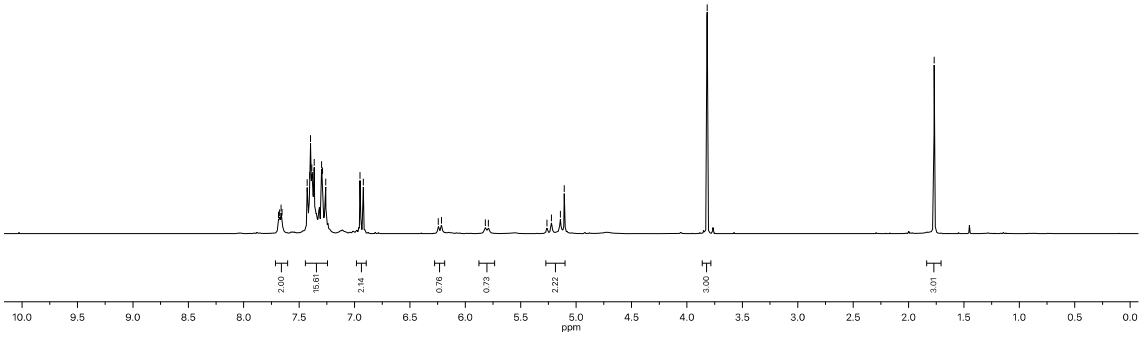
150.68
142.17
139.80
137.82
136.56
132.55
129.15
128.81
128.45
128.39
128.13
127.78
127.71
126.10
123.21
108.92
66.86
19.91
f1 (ppm)

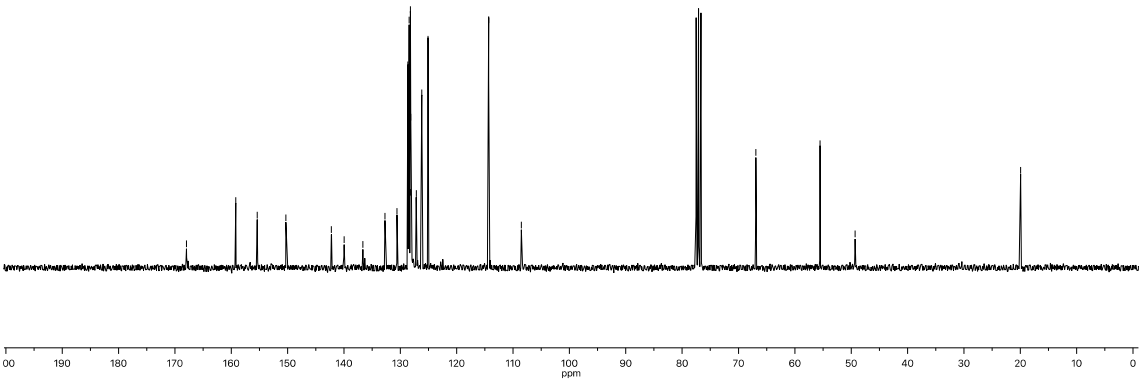

HNCbz
OAc
N
N
OMe
Ph

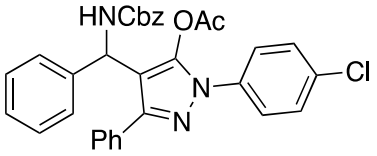
**3ag**


7.69
7.68
7.66
7.65
7.43
7.40
7.40
7.38
7.38
7.37
7.35
7.30
7.29
7.26
6.95
6.92
6.24
6.22
5.82
5.79
5.36
5.22
5.14
5.11
3.82
1.77


2.00
15.61
2.14
0.76
0.73
2.22
3.00
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

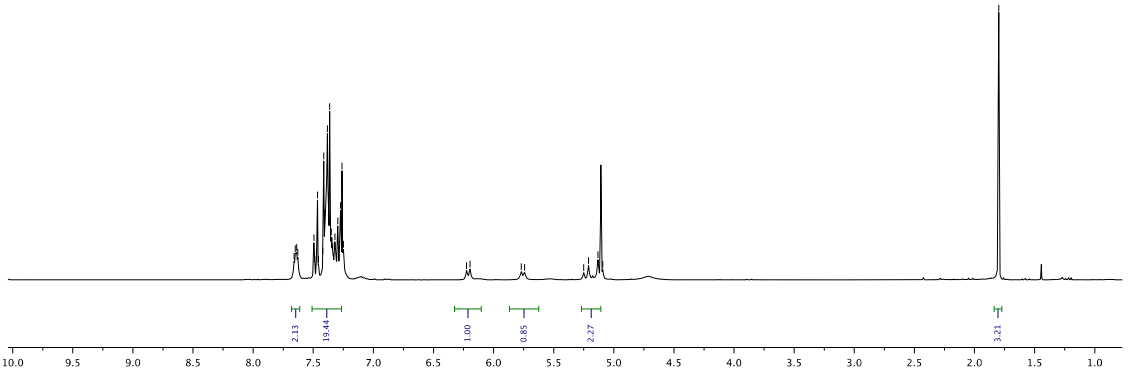

167.95
159.22
155.39
150.31
143.24
140.00
136.96
132.74
130.61
128.68
128.65
128.53
128.45
128.24
128.20
128.16
127.76
127.30
125.10
114.35
108.54
66.92
55.54
49.31
19.95

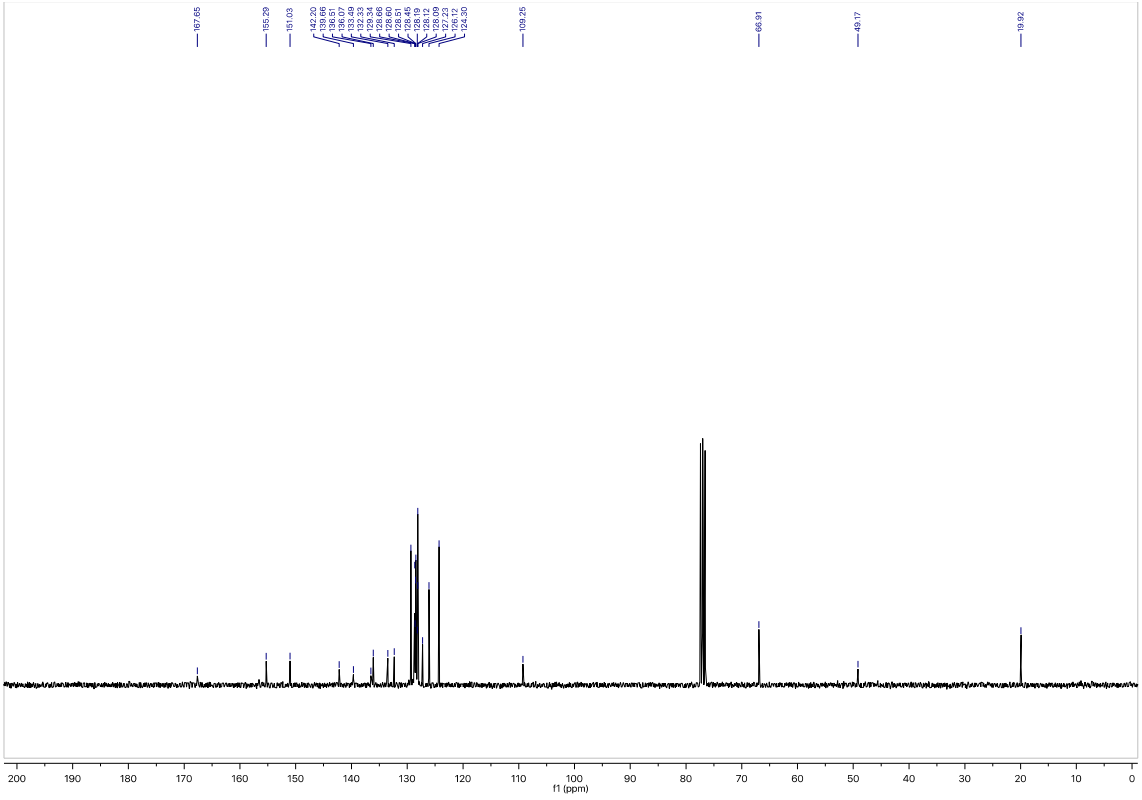

00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

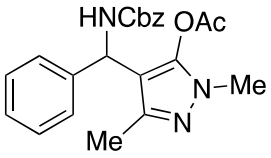

HNCbz
OAc
N
N
Cl
Ph

**3ah**

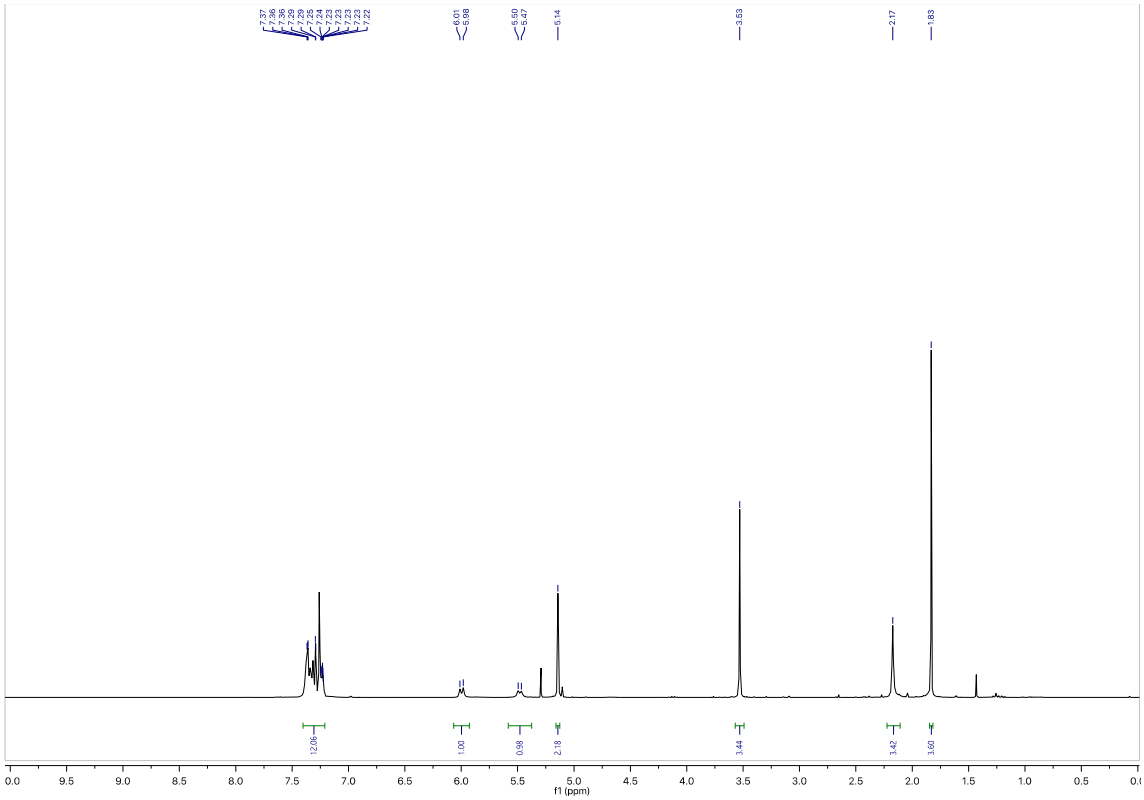

7.66
7.65
7.64
7.63
7.49
7.47
7.46
7.42
7.41
7.40
7.38
7.36
7.35
7.34
7.34
7.32
7.30
7.27
7.26
7.25
6.22
6.20
5.77
5.74
5.25
5.21
5.13
5.09
1.80

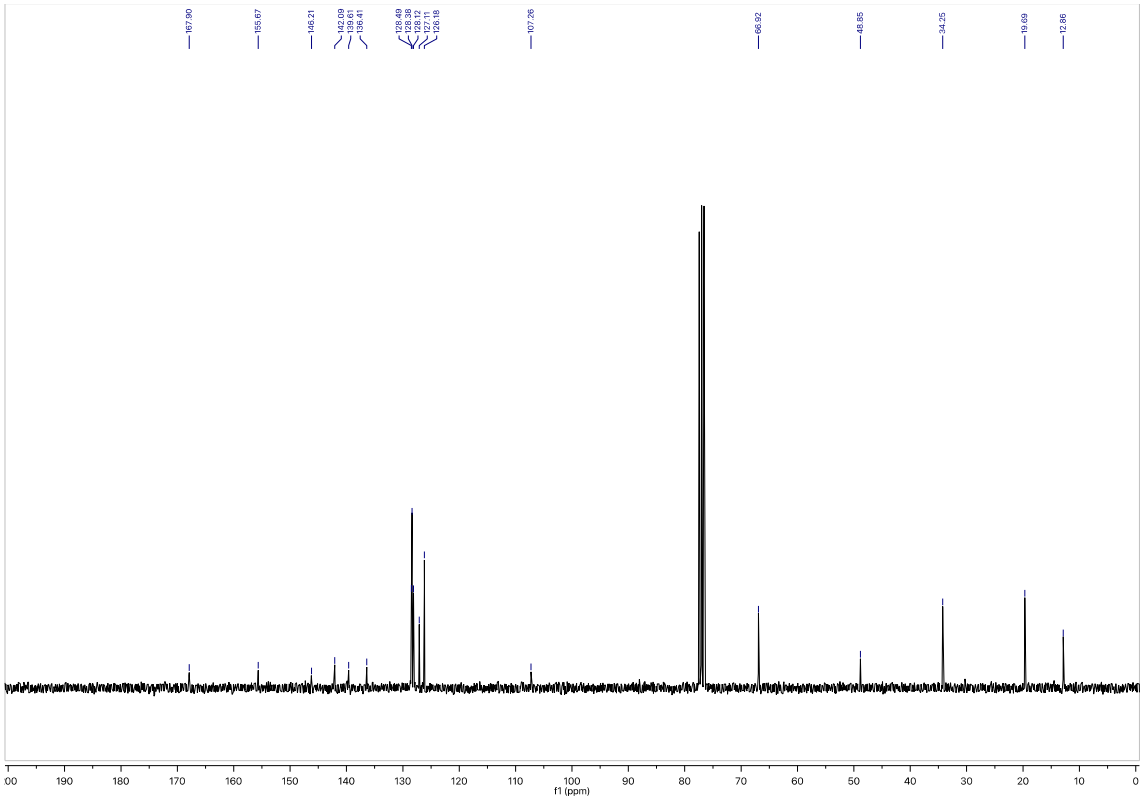

2.13
19.44
1.00
0.85
2.27
3.21
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

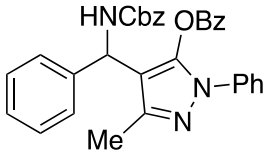

167.65
155.29
151.03
142.20
139.65
136.51
136.07
133.49
132.33
129.34
128.66
128.60
128.51
128.46
128.19
128.12
128.09
127.23
126.12
124.30
109.25
66.91
49.17
19.92
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HNCbz
OAc
N–Me
N
Me

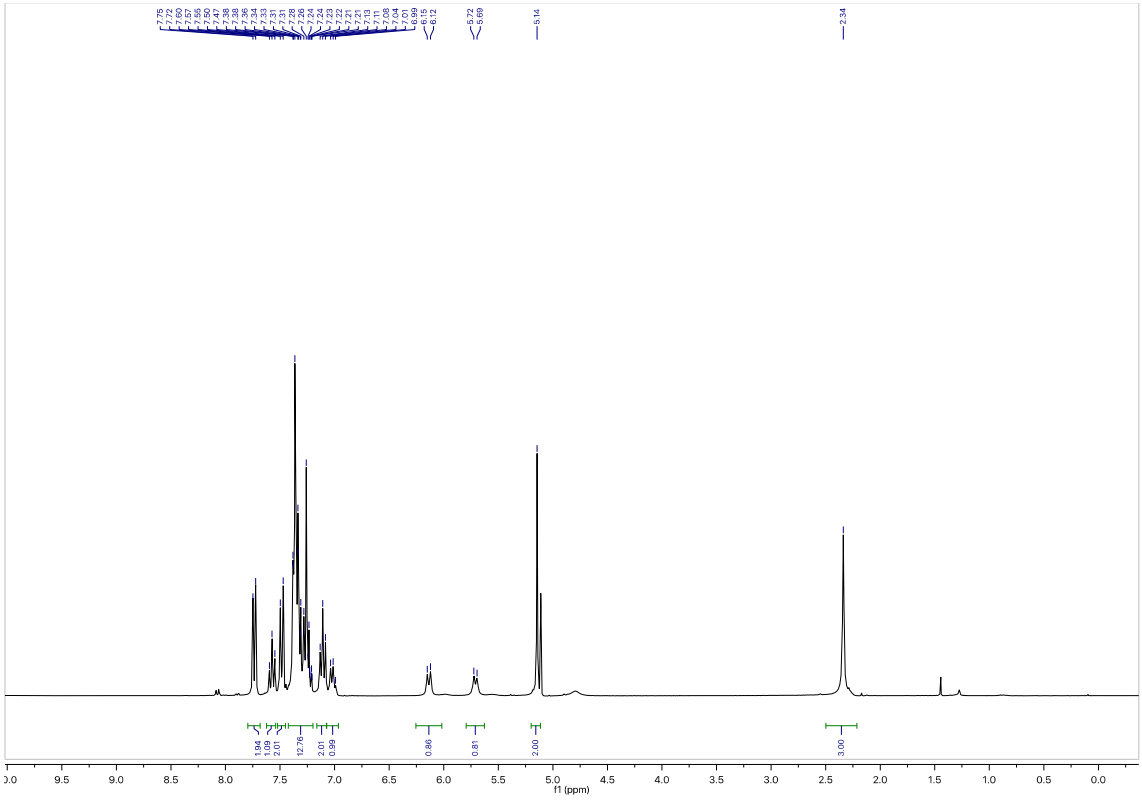
**3ai**

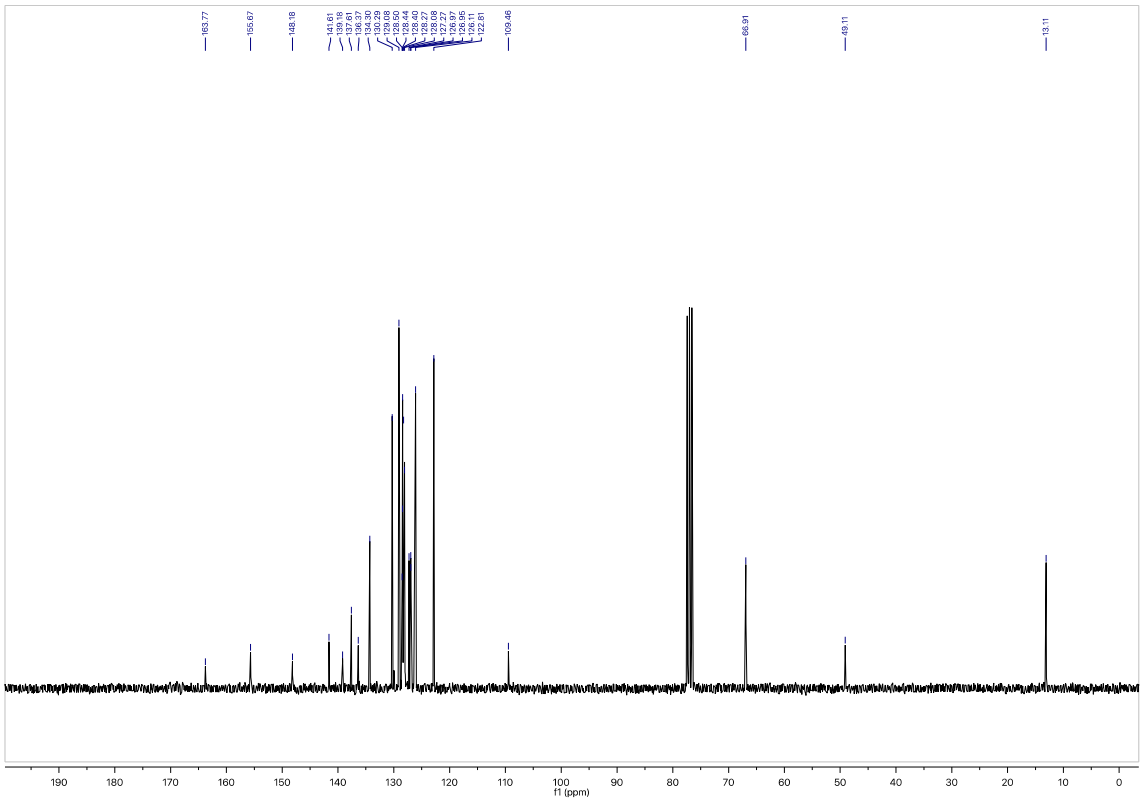

7.37
7.36
7.36
7.29
7.25
7.24
7.23
7.23
7.23
7.22
6.01
5.98
5.50
5.47
5.14
3.53
2.17
1.83
12.06
1.00
0.98
2.18
3.44
3.42
3.60
f1 (ppm)

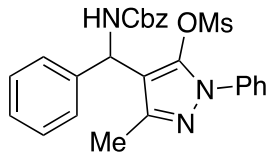

167.90
155.67
146.21
142.09
139.65
136.41
128.49
128.36
128.12
127.11
126.18
107.26
66.92
48.85
34.25
19.69
12.86
f1 (ppm)



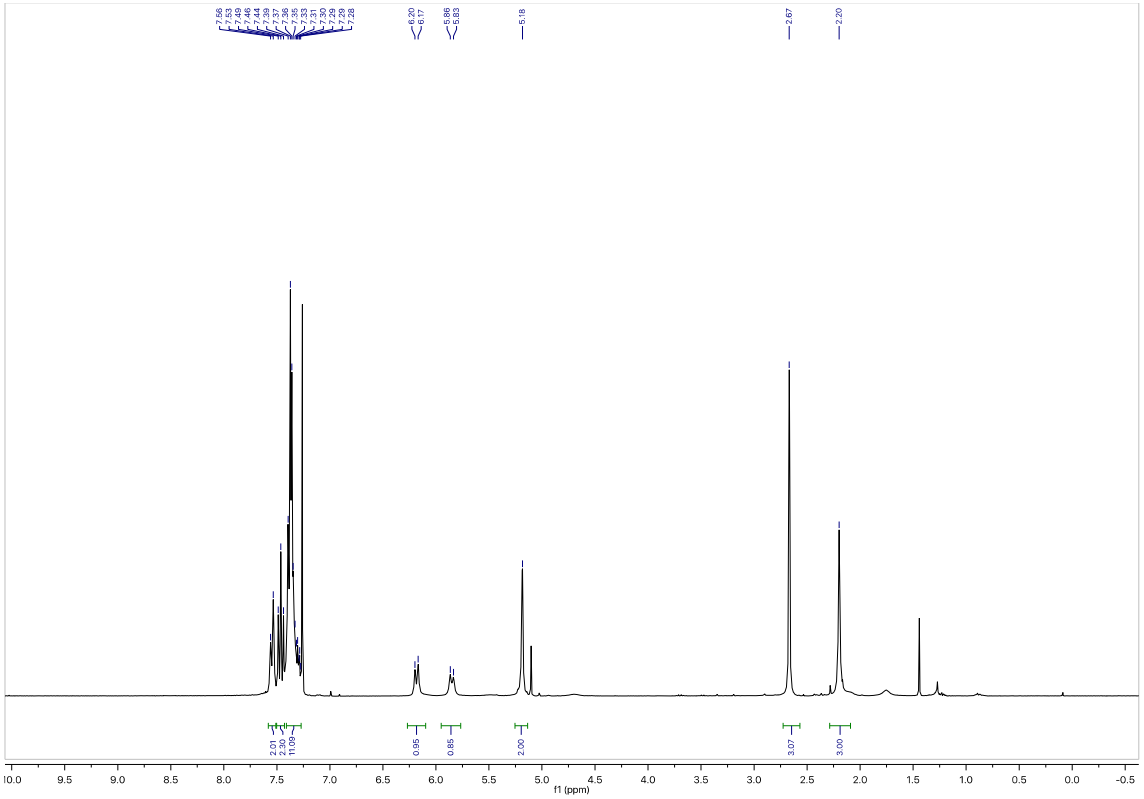

**5**

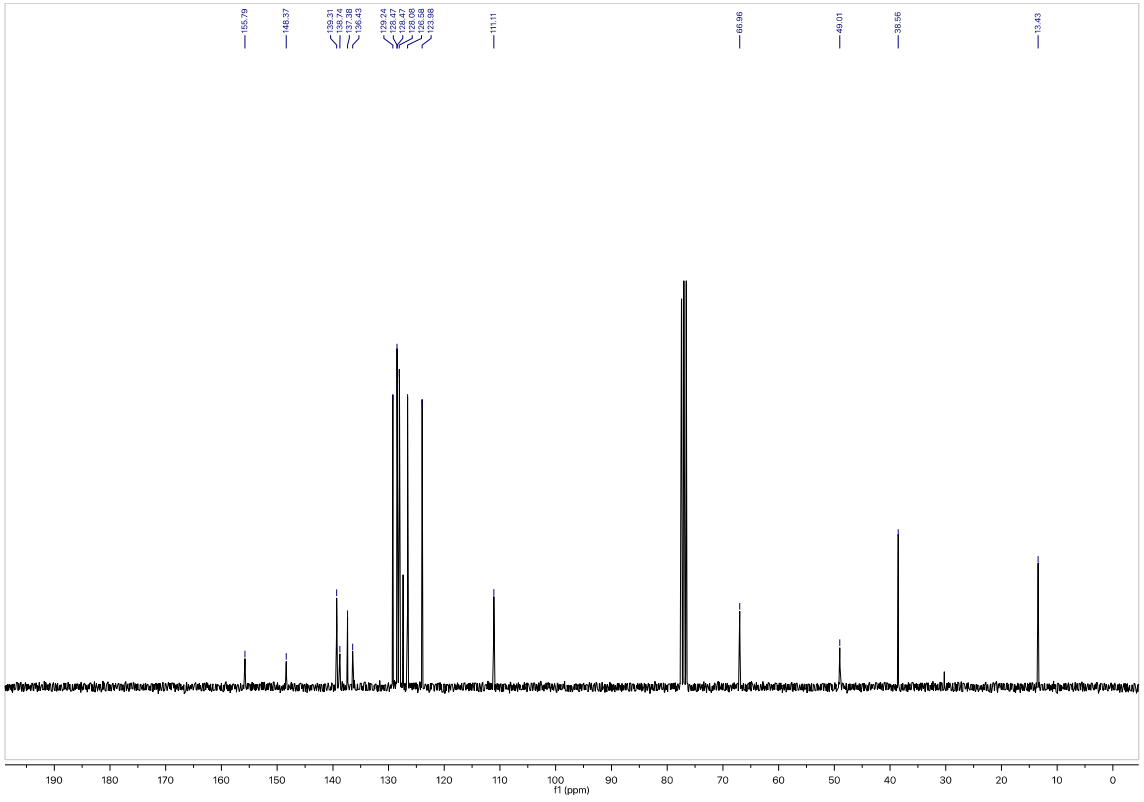


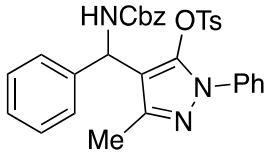




HNCbz
OMs
N–Ph
N
Me

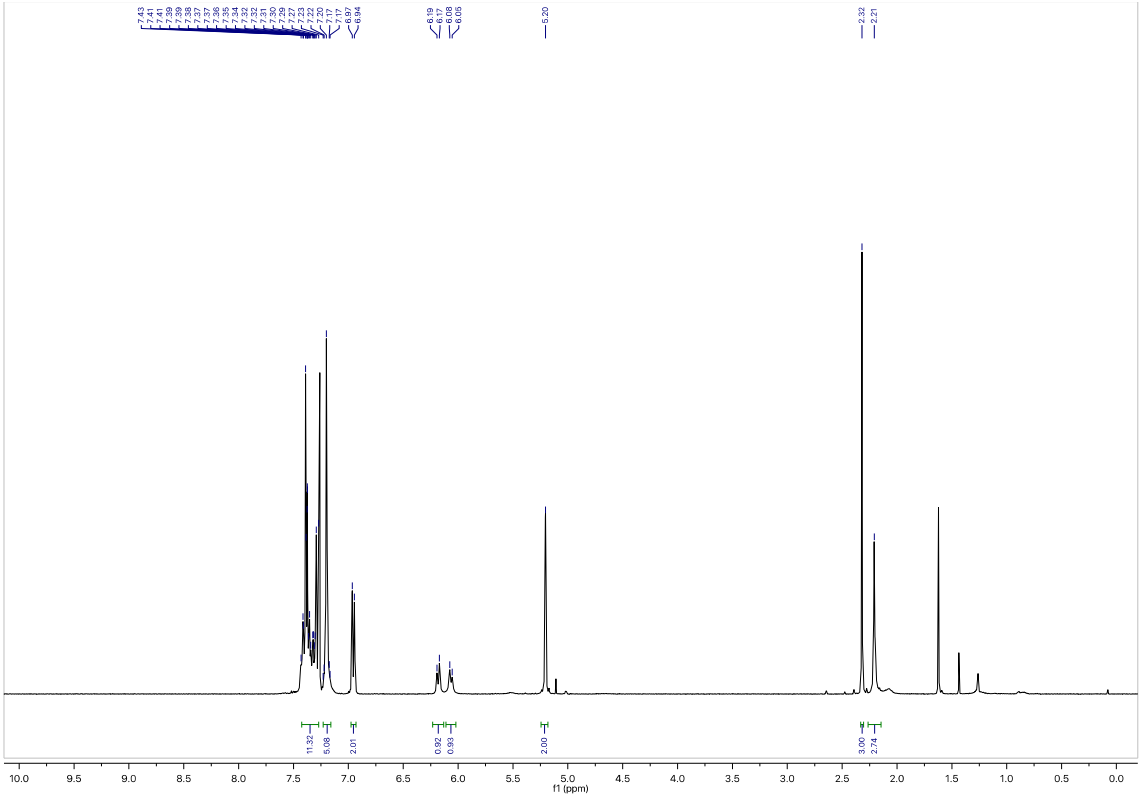
**6**

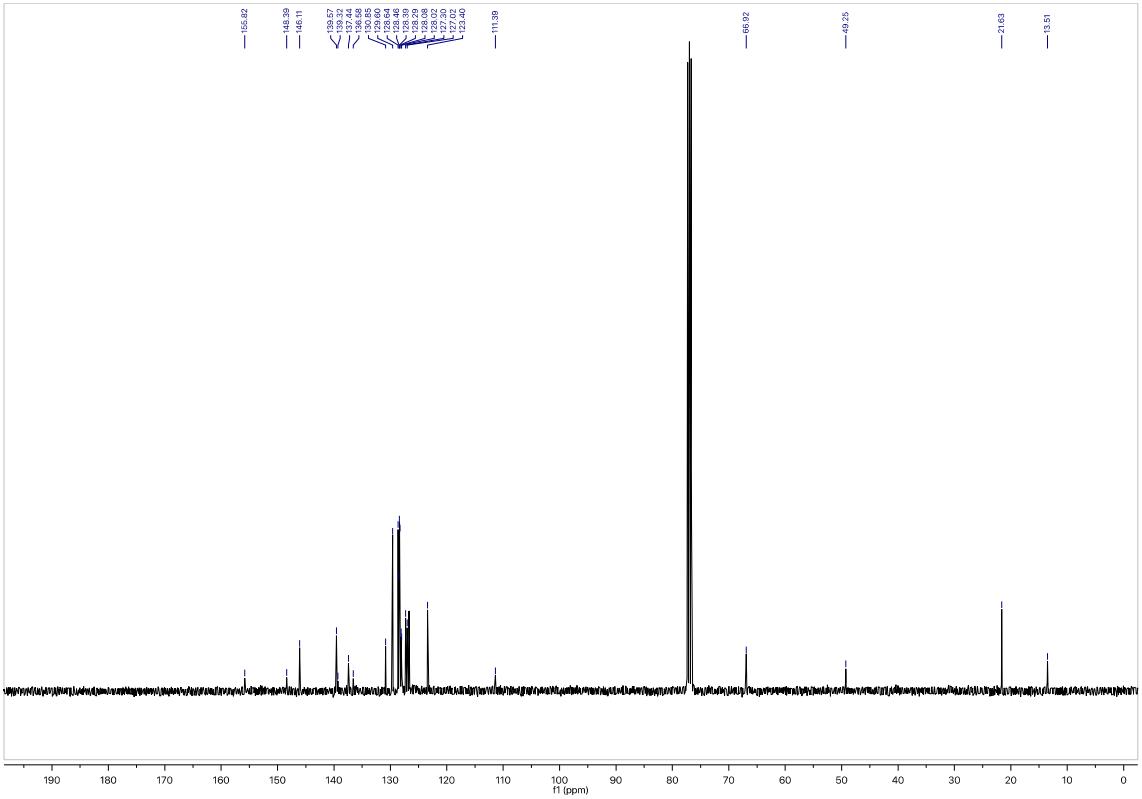

7.66
7.63
7.49
7.46
7.44
7.39
7.37
7.36
7.35
7.33
7.31
7.30
7.29
7.29
7.28
6.20
6.17
5.86
5.83
5.18
2.67
2.20
2.01
2.00
11.09
0.95
0.85
2.00
3.07
3.00
f1 (ppm)

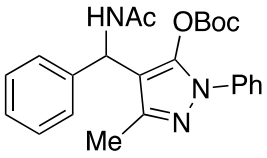

155.79
148.37
139.31
138.74
137.38
136.43
129.24
128.47
128.47
128.08
126.69
123.98
111.11
66.96
49.01
38.56
13.43
f1 (ppm)


HNCbz
OTs
N–Ph
N
Me

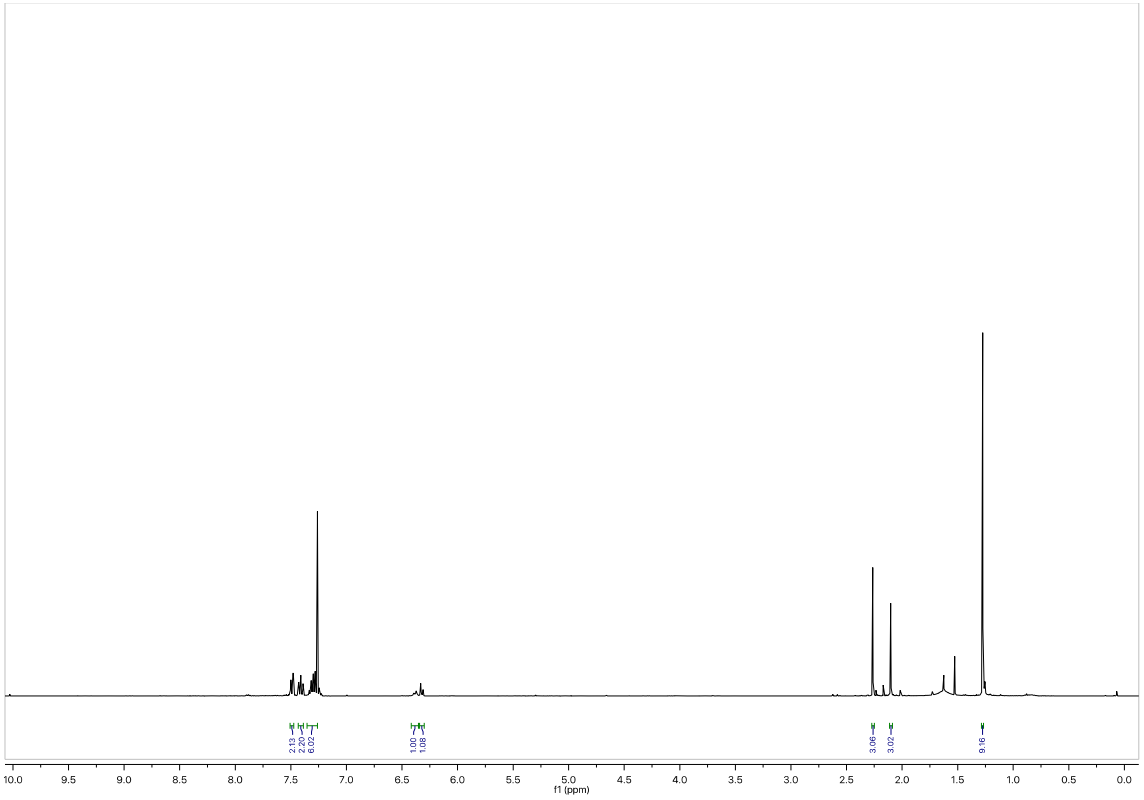
**7**

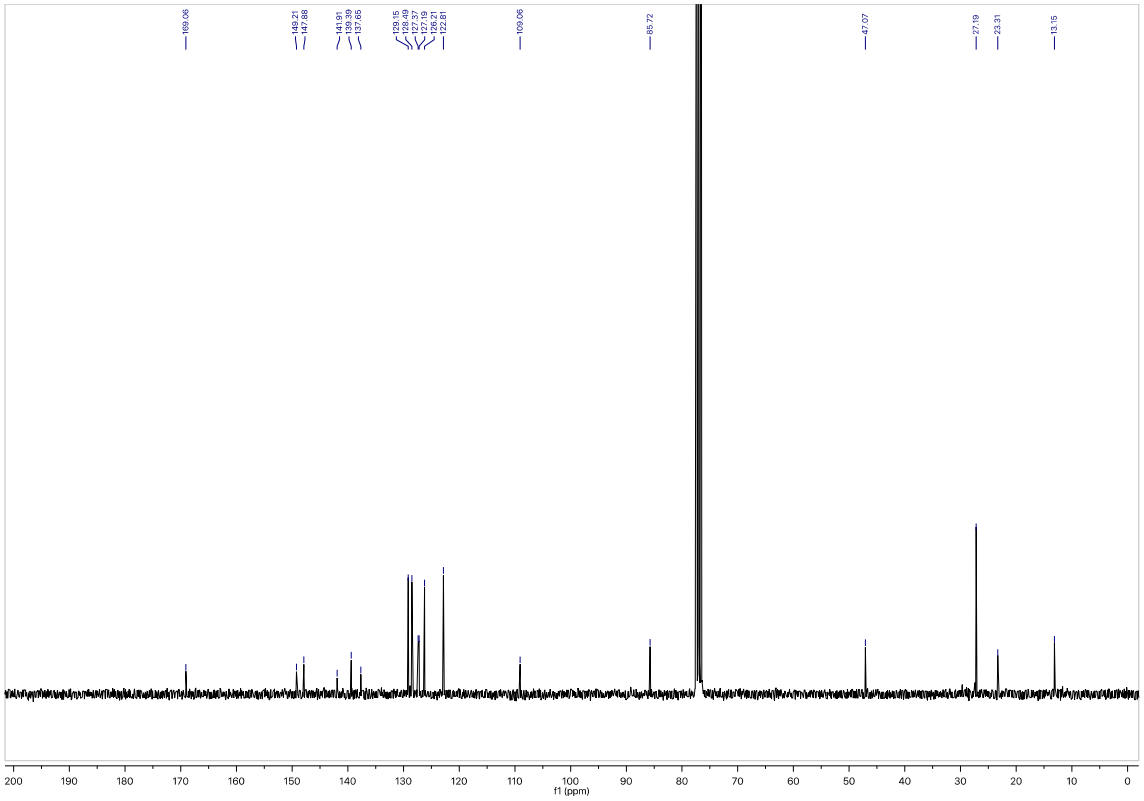

7.43
7.41
7.39
7.38
7.37
7.36
7.35
7.34
7.32
7.31
7.30
7.29
7.23
7.22
7.20
7.17
7.11
6.97
6.94
6.19
6.17
6.08
6.05
5.20
2.32
2.21
11.32
5.08
2.01
0.92
0.93
2.00
3.00
2.74
f1 (ppm)

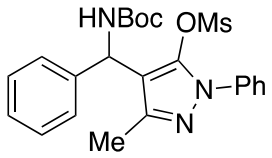

155.82
148.39
146.11
139.57
139.32
137.44
136.88
130.85
130.60
128.64
128.46
128.39
128.29
128.08
128.02
127.30
127.02
123.40
111.39
66.92
49.25
21.63
13.51
f1 (ppm)


HNAc
OBoc
N–Ph
N
Me

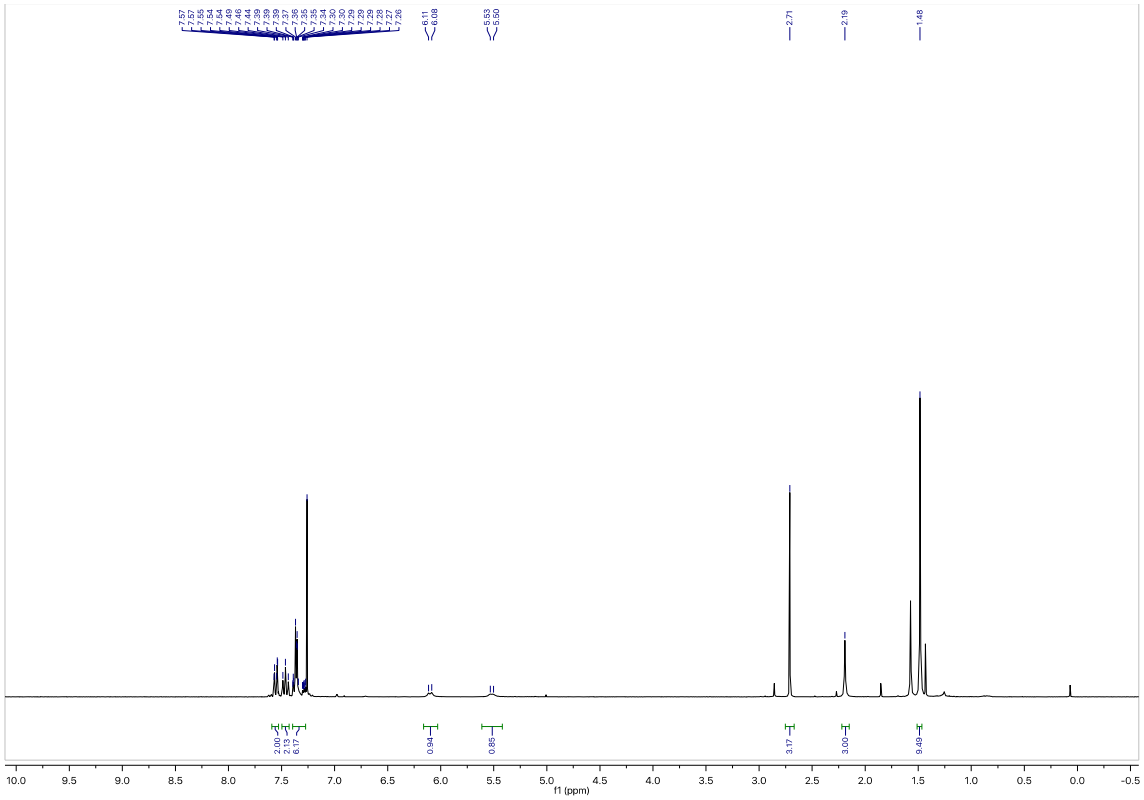
**8**

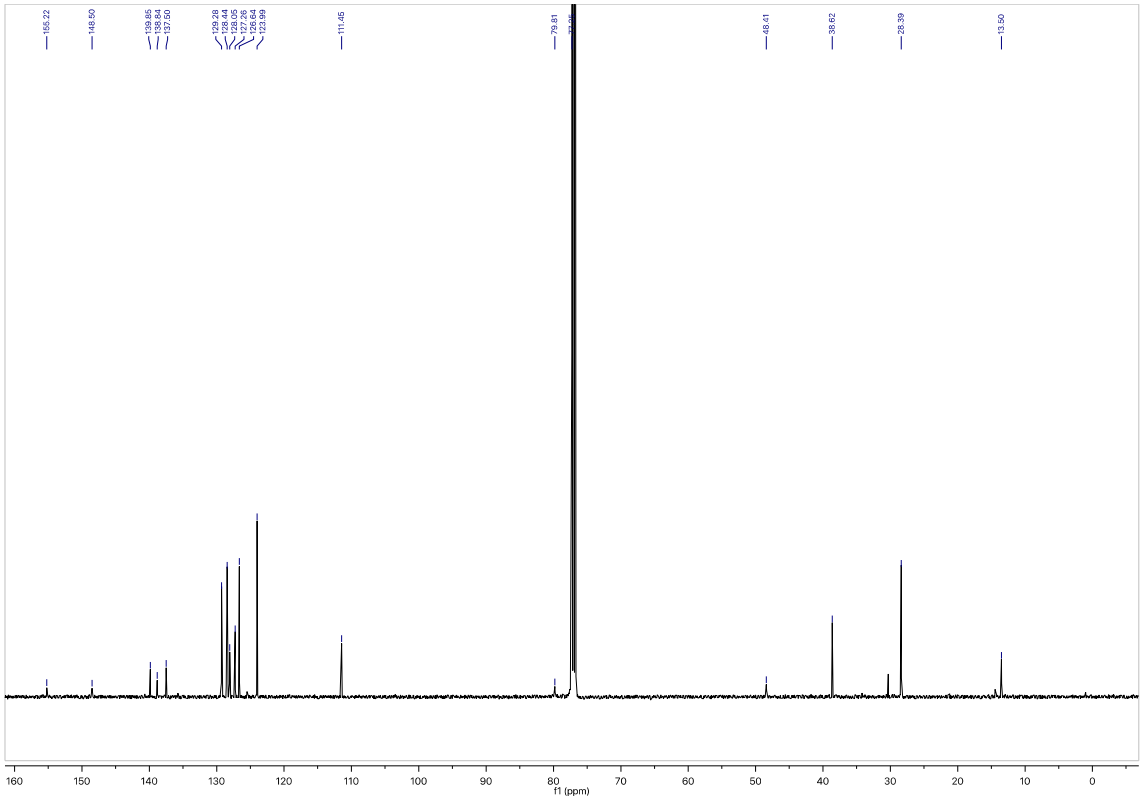

2.13
2.20
6.02
1.00
1.08
3.06
3.02
9.16
f1 (ppm)


169.06
149.21
147.88
141.91
139.39
137.65
129.15
128.49
127.37
127.19
126.71
122.81
109.06
85.72
47.07
27.19
23.31
13.15
f1 (ppm)

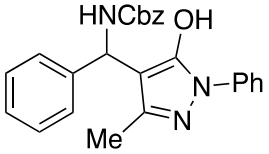

HNBoc
OMs
N–Ph
N
Me

**9**


7.57
7.57
7.55
7.54
7.54
7.49
7.46
7.44
7.39
7.39
7.37
7.36
7.35
7.35
7.34
7.30
7.30
7.29
7.29
7.29
7.28
7.27
7.26
6.11
6.08
5.53
5.50
2.71
2.19
1.48
2.00
2.13
6.17
0.94
0.85
3.17
3.00
9.49
f1 (ppm)

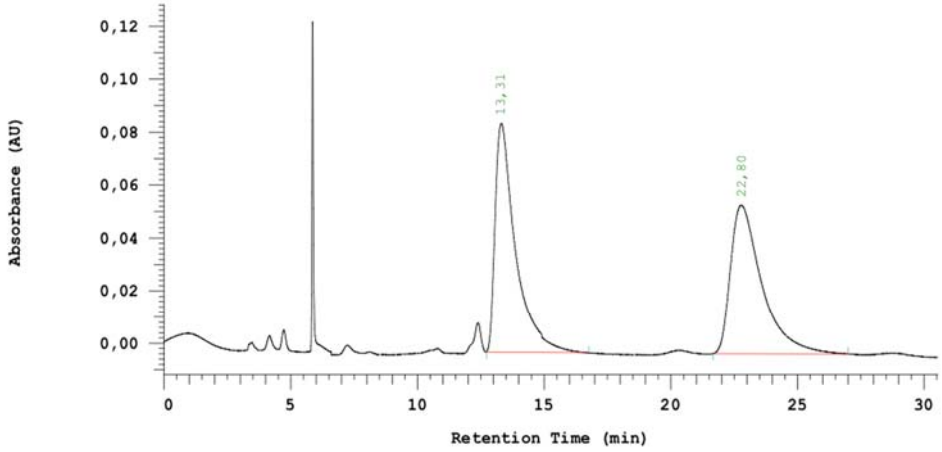

155.22
148.50
139.85
138.84
137.50
129.28
128.44
128.05
127.26
126.64
123.99
111.45
79.81
48.41
38.62
28.39
13.50
f1 (ppm)

## HPLC CHROMATOGRAMS



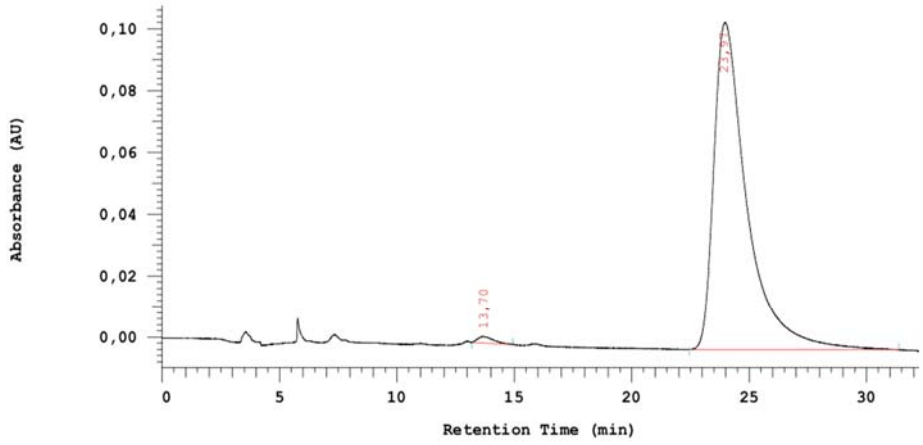

**3a**

Sample Name: CV-509 IC 8020 1mL Vial Number: 1

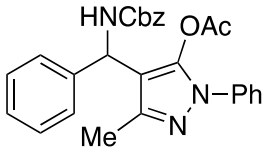



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 13,31 | 2430170 | 49,960 | |
| 2 | 22,80 | 2434100 | 50,040 | enant. (+) |
| | | 4864270 | 100,000 | |

Sample Name: LC-104bis IC 8020 1mL Vial Number: 1

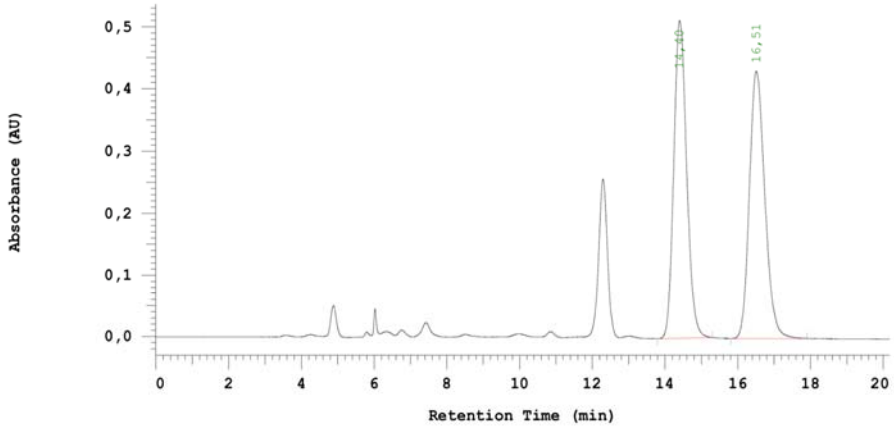



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 13,70 | 47805 | 0,913 | |
| 2 | 23,97 | 5190070 | 99,087 | enant. (+) |
| | | 5237875 | 100,000 | |



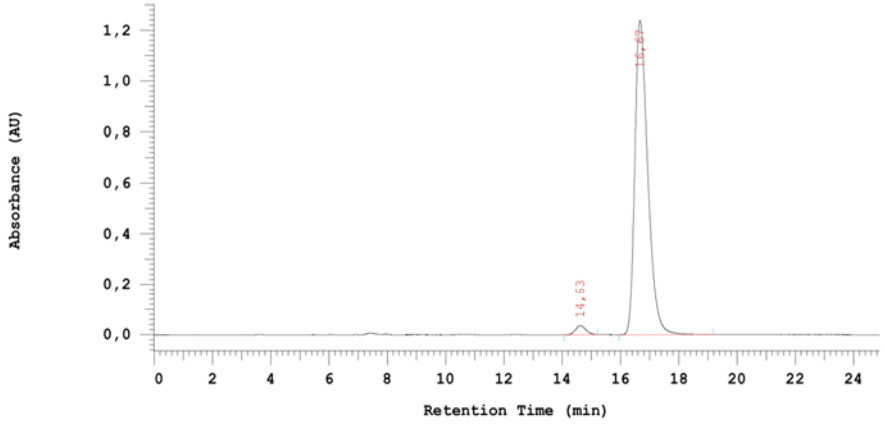

**3aa**

Sample Name: LC-114 IC 8020 1mL Vial Number: 1

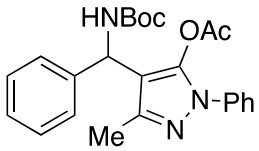



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 14,40 | 6331190 | 49,764 | |
| 2 | 16,51 | 6391150 | 50,236 | |
| | | 12722340 | 100,000 | |

Sample Name: LC-120Acetilat IC 8020 1mL Vial Number: 1

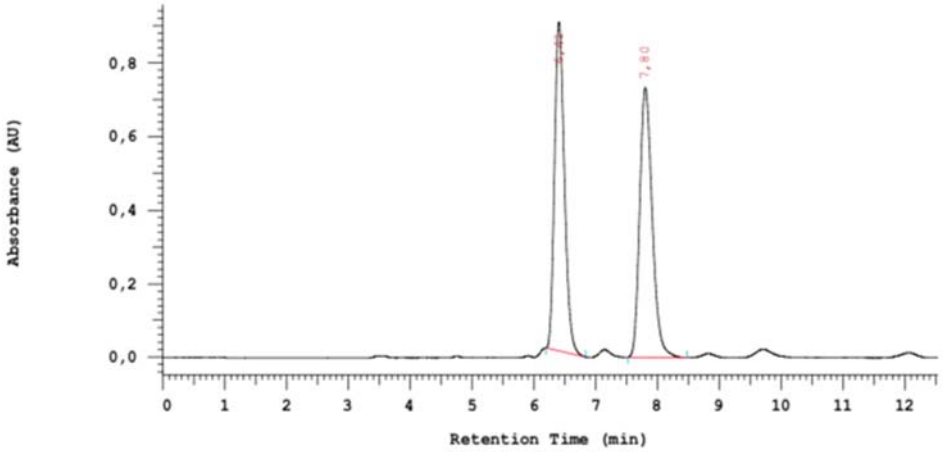



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 14,63 | 429040 | 2,186 | |
| 2 | 16,67 | 19195360 | 97,814 | |
| | | 19624400 | 100,000 | |



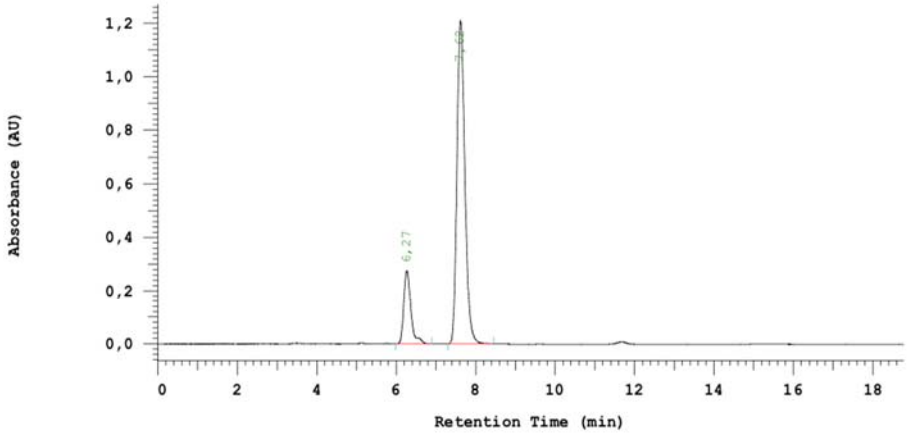

**3da**

Sample Name: LC-118Acetilada IC 8020 1mL Vial Number: 1

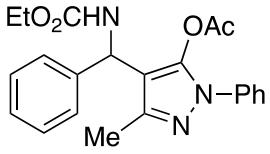



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 6,41 | 4946800 | 49,020 | |
| 2 | 7,80 | 5144690 | 50,980 | |
| | | 10091490 | 100,000 | |

Sample Name: LC-122 IC 8020 1mL Vial Number: 1

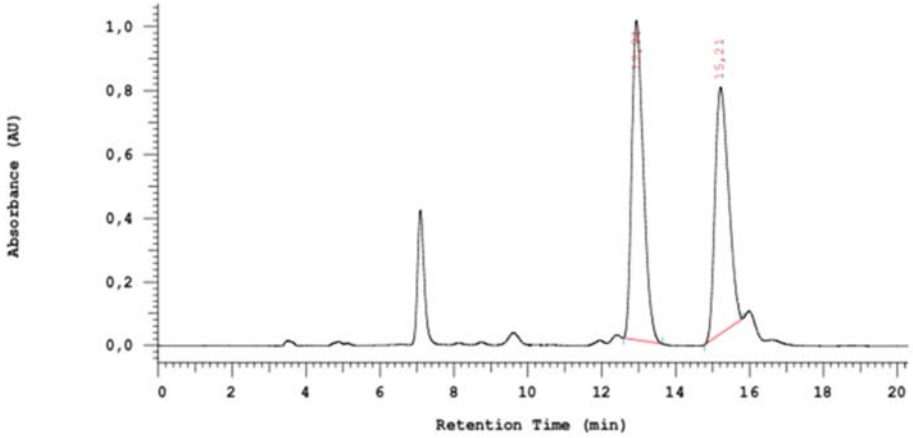



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 6,27 | 1724185 | 17,091 | |
| 2 | 7,62 | 8364200 | 82,909 | |
| | | 10088385 | 100,000 | |



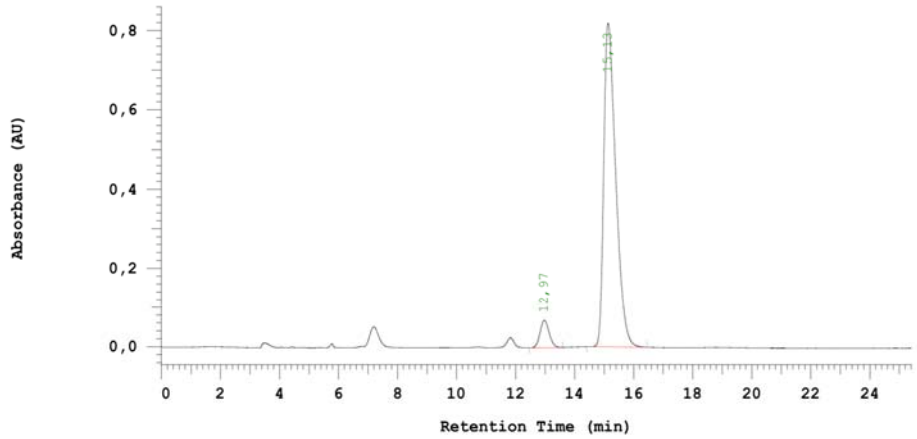

**3ea**

Sample Name: LC-106Acetilada IC 8020 1mL Vial Number: 1

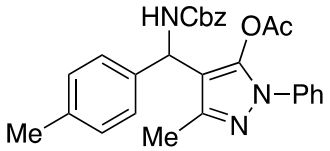



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 12,94 | 10881209 | 52,584 | |
| 2 | 15,21 | 9811849 | 47,416 | |
| | | 20693058 | 100,000 | |

Sample Name: LC-123 IC 8020 1mL Vial Number: 1

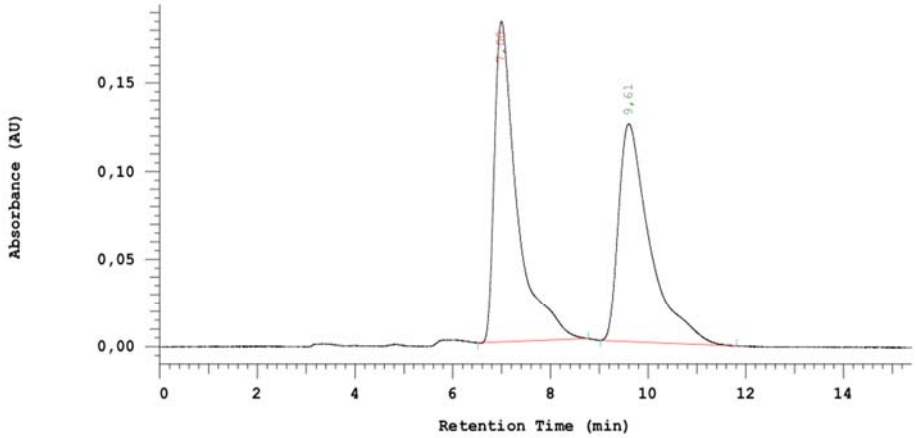



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 12,97 | 731330 | 5,974 | |
| 2 | 15,13 | 11511160 | 94,026 | |
| | | 12242490 | 100,000 | |



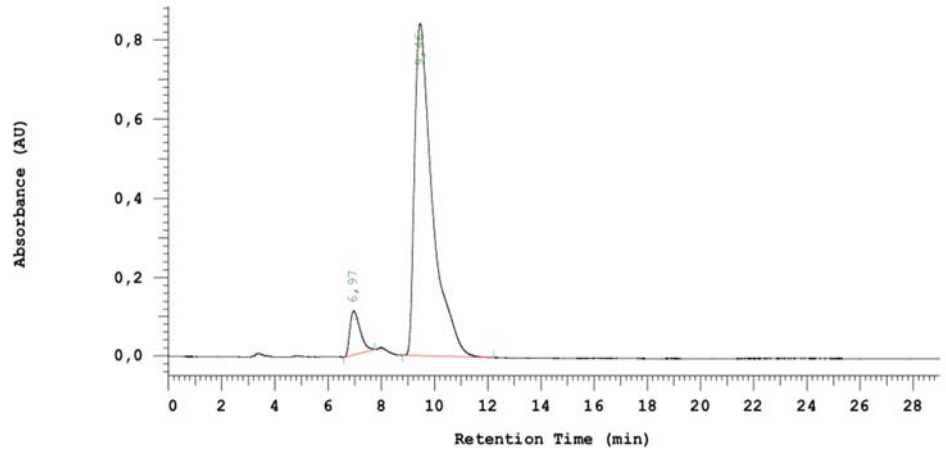

**3fa**

Sample Name: LC-127 ADH 8020 1mL Vial Number: 1

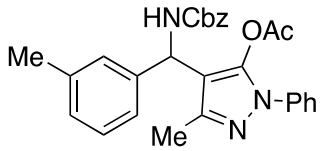



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 7,00 | 2956910 | 51,520 | |
| 2 | 9,61 | 2782420 | 48,480 | |
| | | 5739330 | 100,000 | |

Sample Name: LC-127 ADH 8020 1mL Vial Number: 1

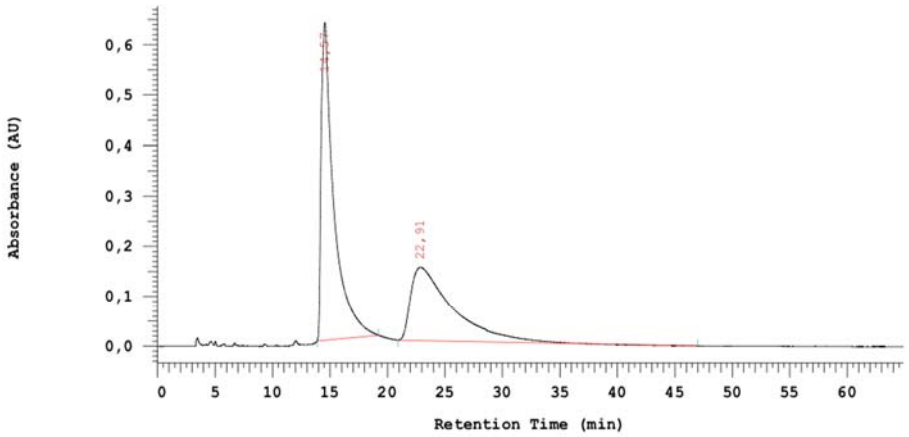



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 6,97 | 1472740 | 6,957 | |
| 2 | 9,46 | 19697174 | 93,043 | |
| | | 21169914 | 100,000 | |



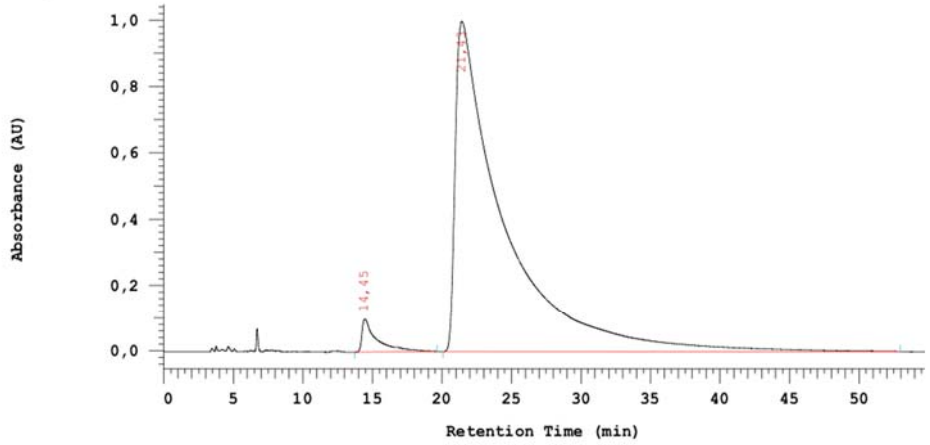

**3ga**

Sample Name: LC-119 IC 8020 1mL Vial Number: 1

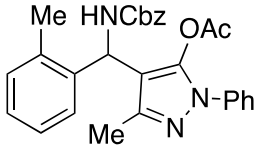



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 14,57 | 23958320 | 56,442 | |
| 2 | 22,91 | 18489139 | 43,558 | enant. (+) |
| | | 42447459 | 100,000 | |

Sample Name: LC-125bis IC 8020 1mL Vial Number: 1

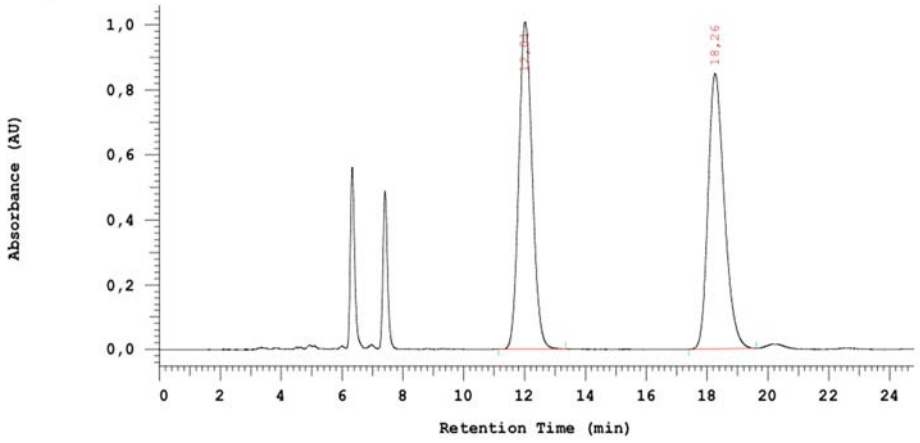



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 14,45 | 3713410 | 2,963 | |
| 2 | 21,43 | 1,215E+08 | 97,037 | |
| | | 1,253E+08 | 100,000 | |



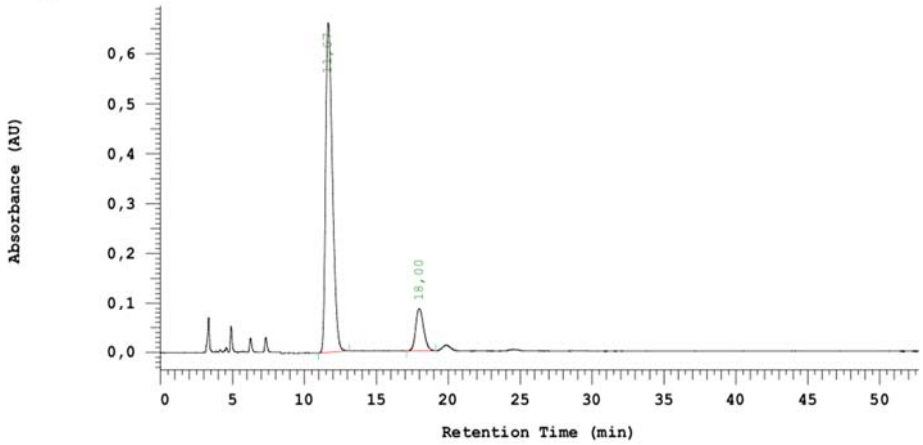

**3ha**

Sample Name: LC-118bis ADH 8020 1mL Vial Number: 1

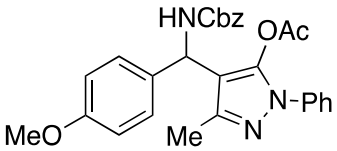



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 12,01 | 15412030 | 49,541 | |
| 2 | 18,26 | 15697740 | 50,459 | |
| | | 31109770 | 100,000 | |

Sample Name: LC-124bis ADH 8020 1mL Vial Number: 1

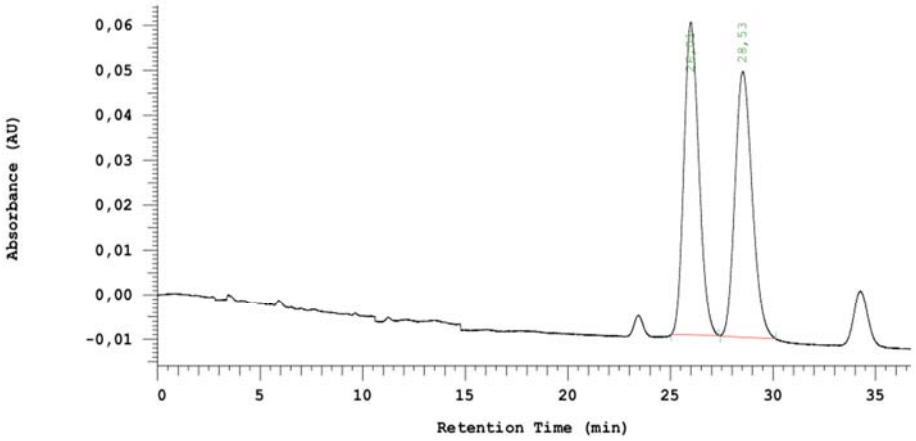



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 11,67 | 10710855 | 87,044 | |
| 2 | 18,00 | 1594300 | 12,956 | |
| | | 12305155 | 100,000 | |



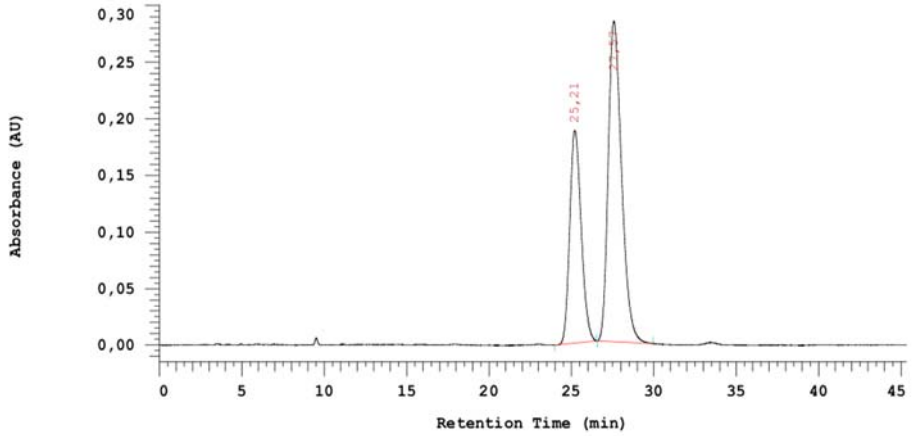

**3ia**

Sample Name: LC-128 IC 8020 1mL Vial Number: 1

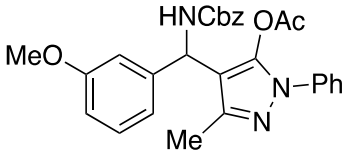



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 26,01 | 1754400 | 50,335 | enant. (+) |
| 2 | 28,53 | 1731050 | 49,665 | enanti (-) |
| | | 3485450 | 100,000 | |

Sample Name: LC-128 IC 8020 1mL Vial Number: 1

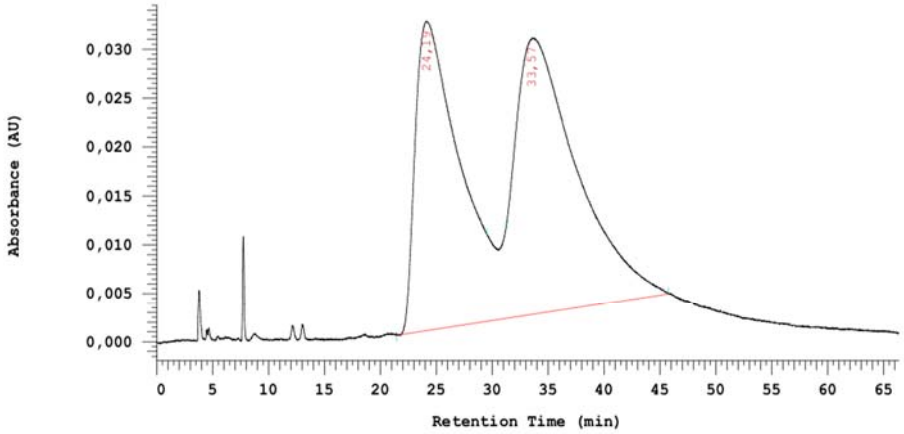



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 25,21 | 4529540 | 36,303 | enant. (+) |
| 2 | 27,57 | 7947569 | 63,697 | enanti (-) |
| | | 12477109 | 100,000 | |



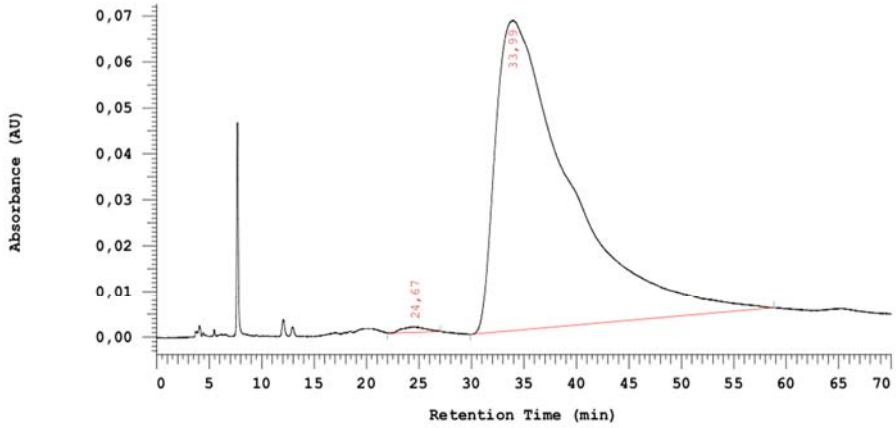

**3ja**

Sample Name: LC-160bis IC 8020 1mL Vial Number: 1

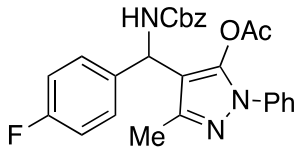



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 24,19 | 4191734 | 43,854 | enant. (+) |
| 2 | 33,57 | 5366744 | 56,146 | |
| | | 9558478 | 100,000 | |

Sample Name: LC-160 IC 8020 1mL Vial Number: 1

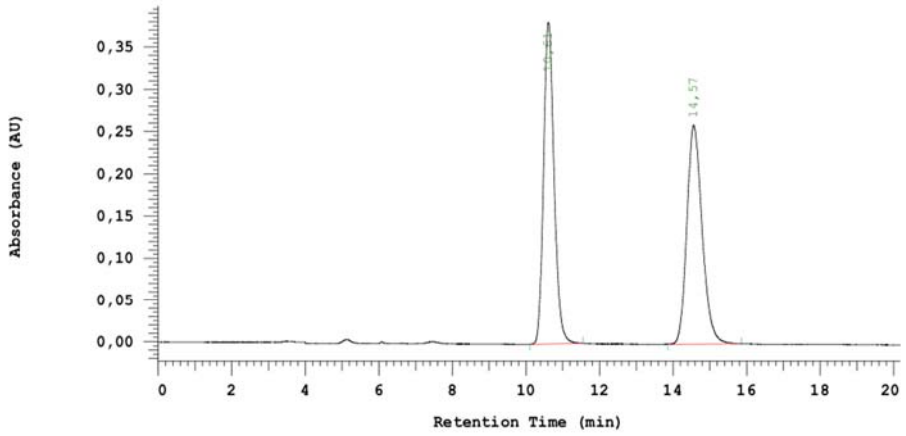



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 24,67 | 86520 | 0,514 | enant. (+) |
| 2 | 33,99 | 16761974 | 99,486 | |
| | | 16848494 | 100,000 | |



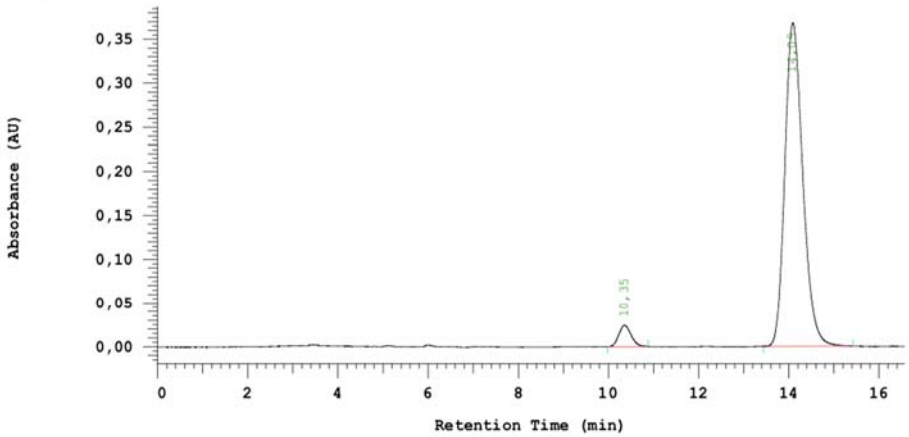

**3ka**

Sample Name: LC-132 IC 8020 1mL Vial Number: 1

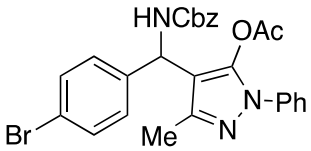



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 10,61 | 3792495 | 50,123 | |
| 2 | 14,57 | 3773870 | 49,877 | |
| | | 7566365 | 100,000 | |

Sample Name: LC-135 IC 8020 1mL Vial Number: 1

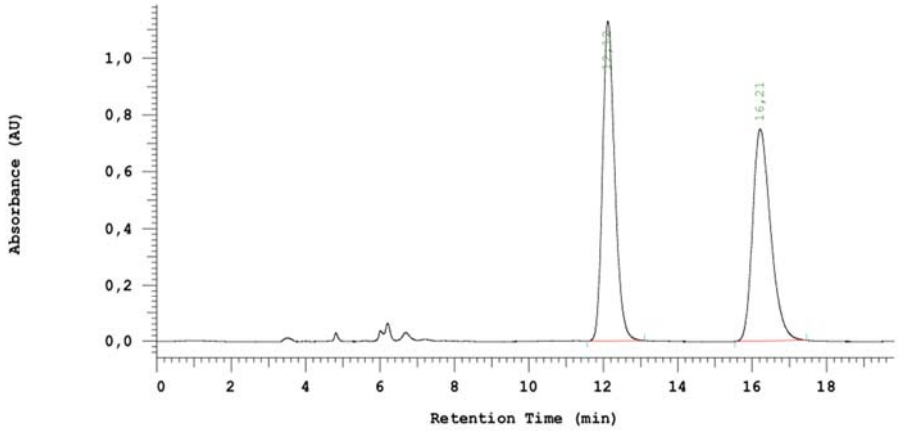



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 10,35 | 227190 | 4,275 | |
| 2 | 14,09 | 5086995 | 95,725 | |
| | | 5314185 | 100,000 | |



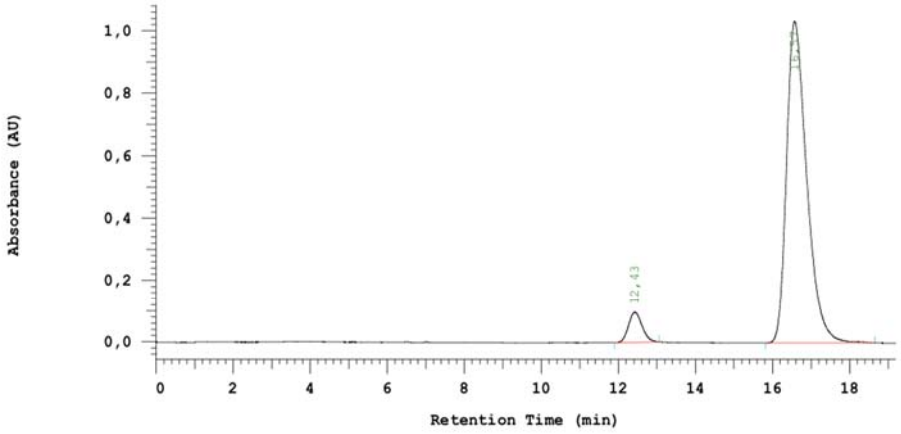

**3la**

Sample Name: LC-134 IC 8020 1mL Vial Number: 1

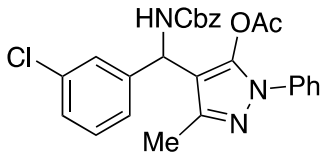



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 12,12 | 12971480 | 50,584 | |
| 2 | 16,21 | 12671800 | 49,416 | |
| | | 25643280 | 100,000 | |

Sample Name: LC-136 IC 8020 1mL Vial Number: 1

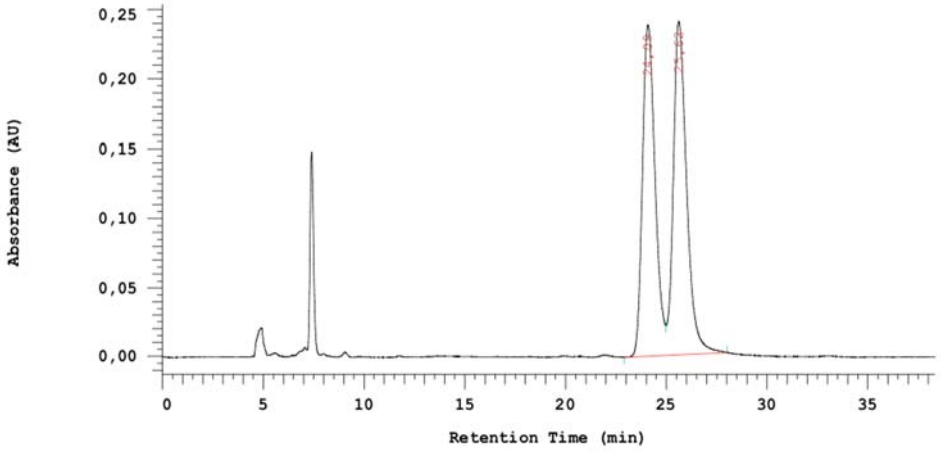



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 12,43 | 1180760 | 5,895 | |
| 2 | 16,57 | 18849420 | 94,105 | |
| | | 20030180 | 100,000 | |



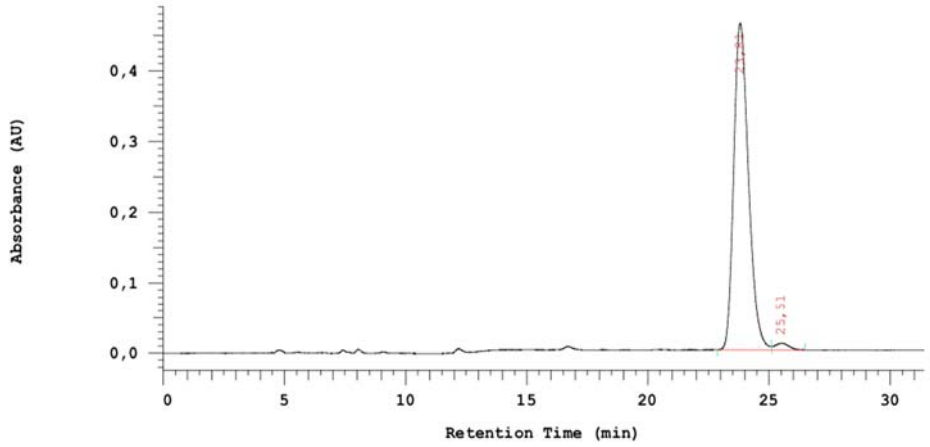

**3ma**

Sample Name: LC-158 ADH 8020 0.7mL Vial Number: 1

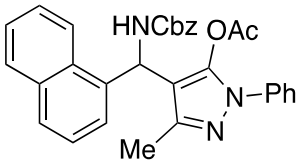



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 24,09 | 5153338 | 48,254 | enant. (+) |
| 2 | 25,62 | 5526171 | 51,746 | enanti (-) |
| | | 10679509 | 100,000 | |

Sample Name: LC-159 ADH 8020 0.7mL Vial Number: 1

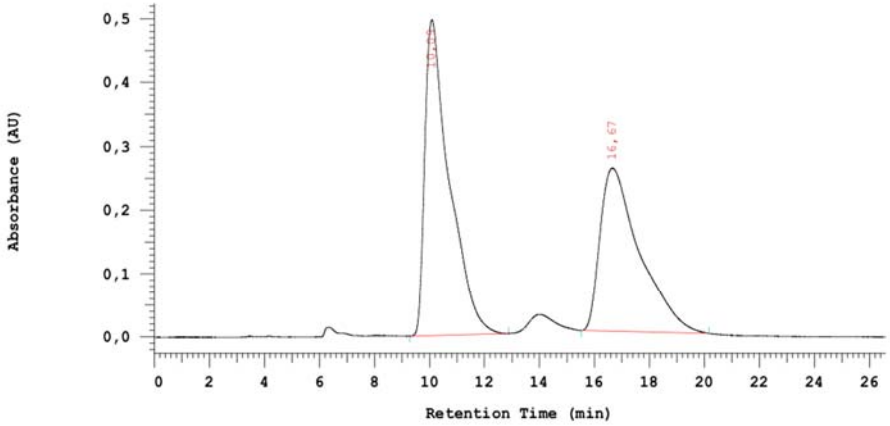



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 23,81 | 9718180 | 98,183 | enant. (+) |
| 2 | 25,51 | 179871 | 1,817 | enanti (-) |
| | | 9898051 | 100,000 | |



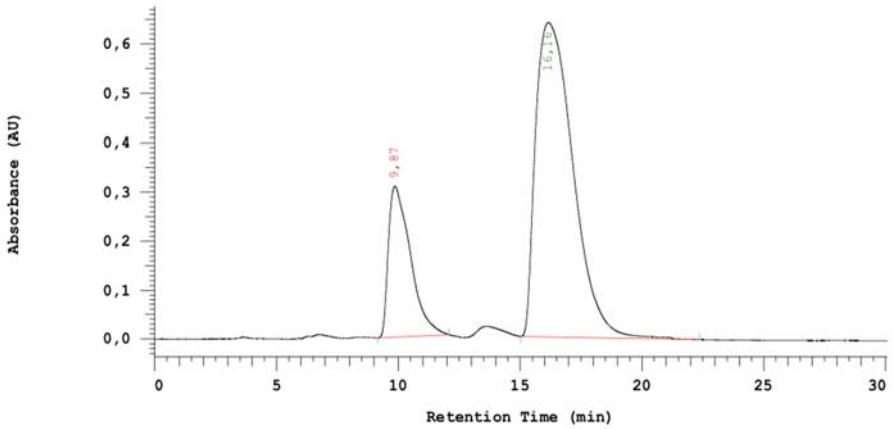

**3na**

Sample Name: LC-162 ODH 8020 1mL Vial Number: 1

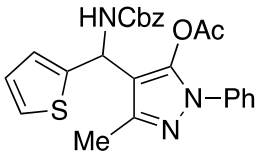



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 10,09 | 15396760 | 54,465 | |
| 2 | 16,67 | 12872420 | 45,535 | |
| | | 28269180 | 100,000 | |

Sample Name: LC-163 ODH 8020 1mL Vial Number: 1

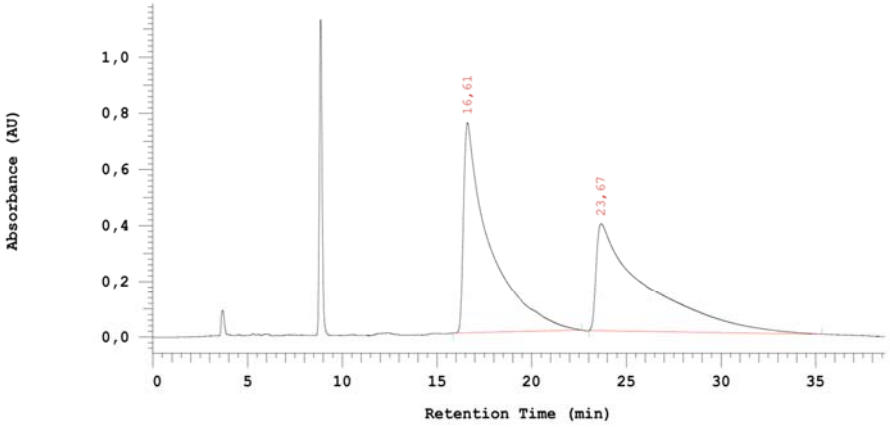



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 9,87 | 9682200 | 22,059 | |
| 2 | 16,16 | 34209724 | 77,941 | |
| | | 43891924 | 100,000 | |



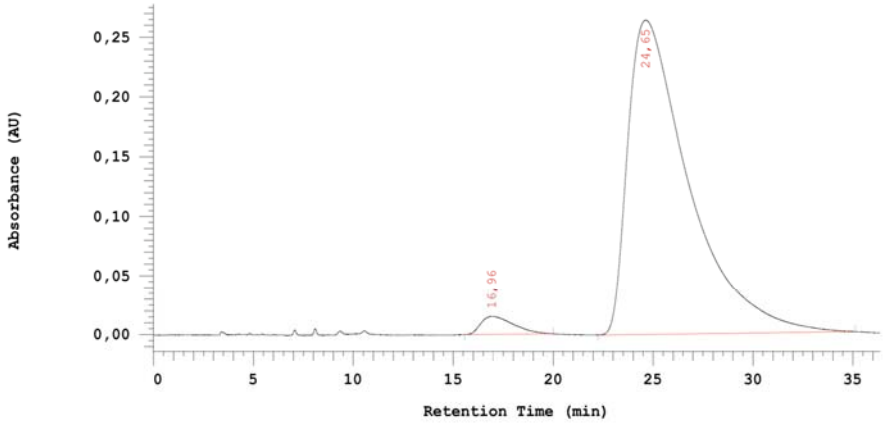

**3oa**

Sample Name: LC-151 IC 8020 1mL Vial Number: 1

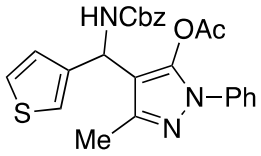



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 16,61 | 36269891 | 50,791 | |
| 2 | 23,67 | 35139760 | 49,209 | enant. (+) |
| | | 71409651 | 100,000 | |

Sample Name: LC-152 IC 8020 1mL Vial Number: 1

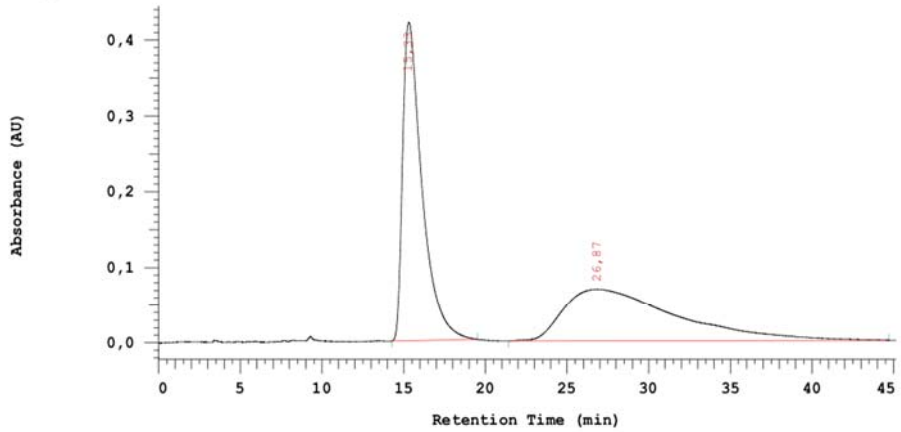



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 16,96 | 851550 | 2,938 | |
| 2 | 24,65 | 28130195 | 97,062 | enant. (+) |
| | | 28981745 | 100,000 | |



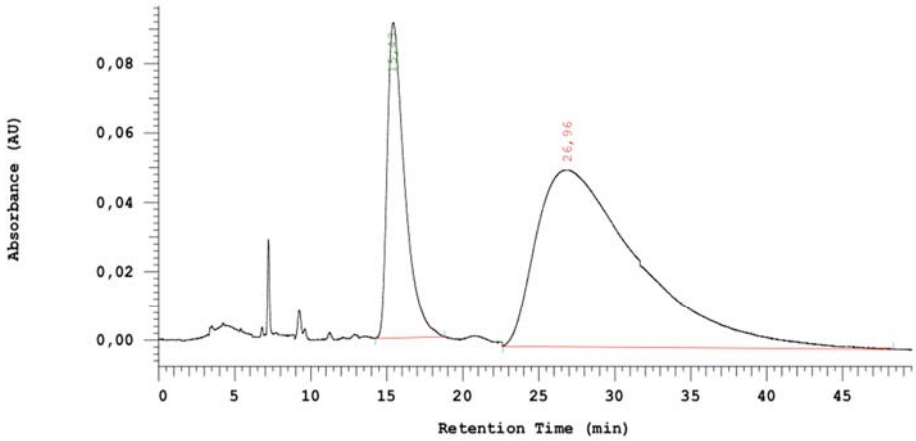

**3pa**

Sample Name: LC-156 IC 8020 1mL Vial Number: 1

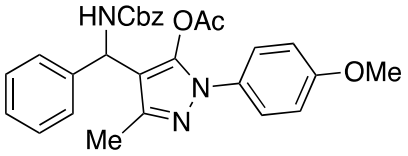



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 15,33 | 17336540 | 51,508 | |
| 2 | 26,87 | 16321369 | 48,492 | enanti (-) |
| | | 33657909 | 100,000 | |

Sample Name: LC-157 IC 8020 1mL Vial Number: 1

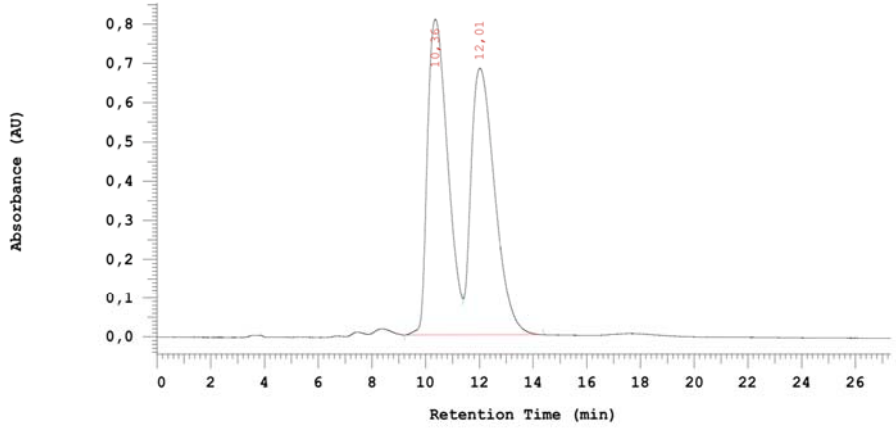



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 15,43 | 3637450 | 23,107 | |
| 2 | 26,96 | 12104350 | 76,893 | enanti (-) |
| | | 15741800 | 100,000 | |



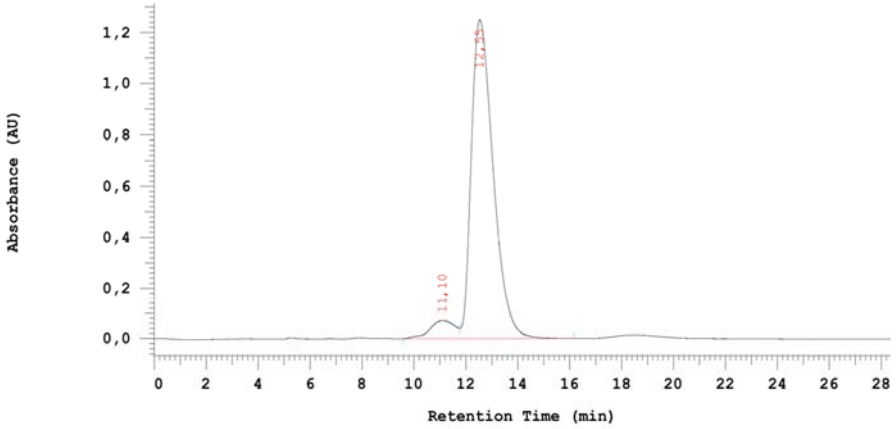

**3ab**

Sample Name: LC-176 ODH 8020 1mL Vial Number: 1

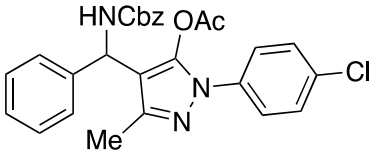



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 10,36 | 21200481 | 49,999 | |
| 2 | 12,01 | 21201182 | 50,001 | |
| | | 42401663 | 100,000 | |

Sample Name: LC-177 ODH 8020 1mL Vial Number: 1

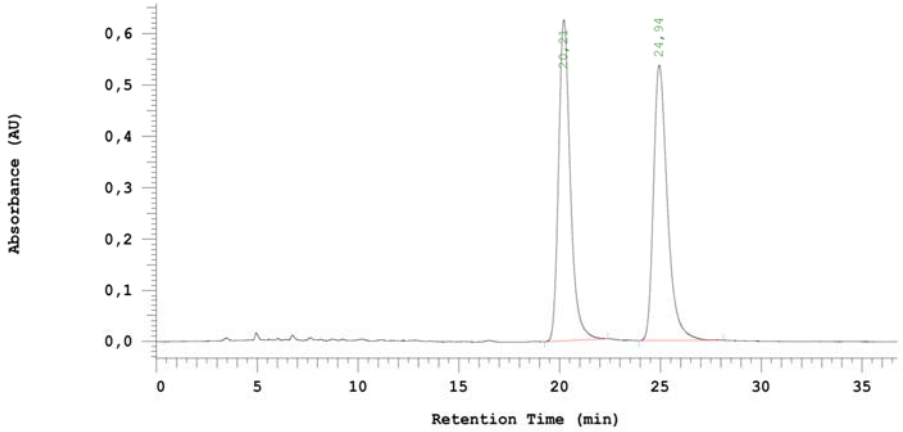



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 11,10 | 2365036 | 6,042 | |
| 2 | 12,55 | 36775782 | 93,958 | |
| | | 39140818 | 100,000 | |



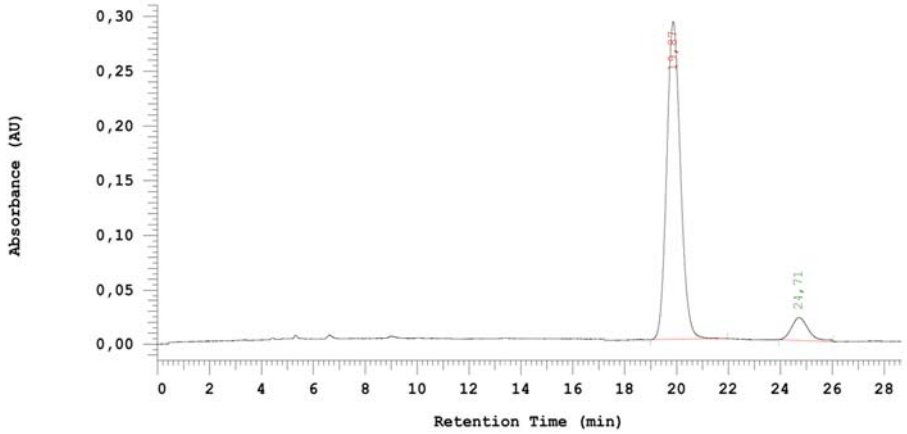

**3ac**

Sample Name: LC-174 ADH 8020 1mL Vial Number: 1

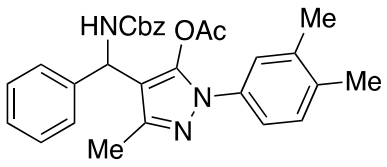



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 20,21 | 12665635 | 49,713 | |
| 2 | 24,94 | 12812049 | 50,287 | enant. (+) |
| | | 25477684 | 100,000 | |

Sample Name: FC-32 EN ASH 8020 1mL Vial Number: 1

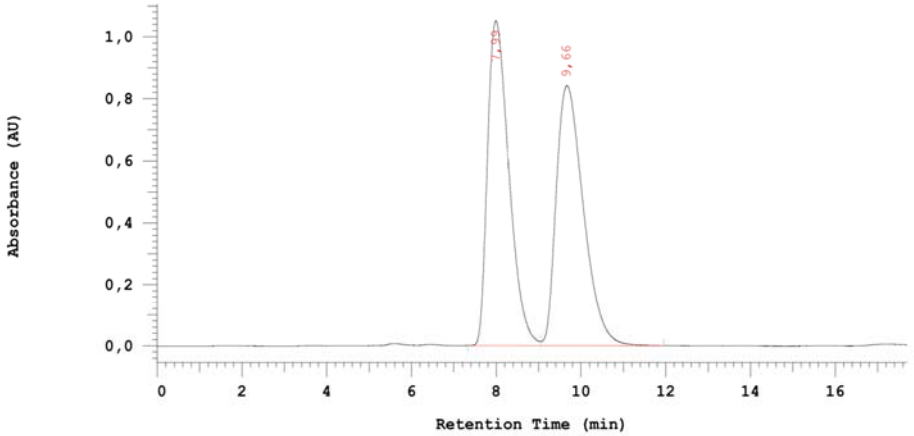



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 19,87 | 5339830 | 91,965 | |
| 2 | 24,71 | 466560 | 8,035 | enant. (+) |
| | | 5806390 | 100,000 | |



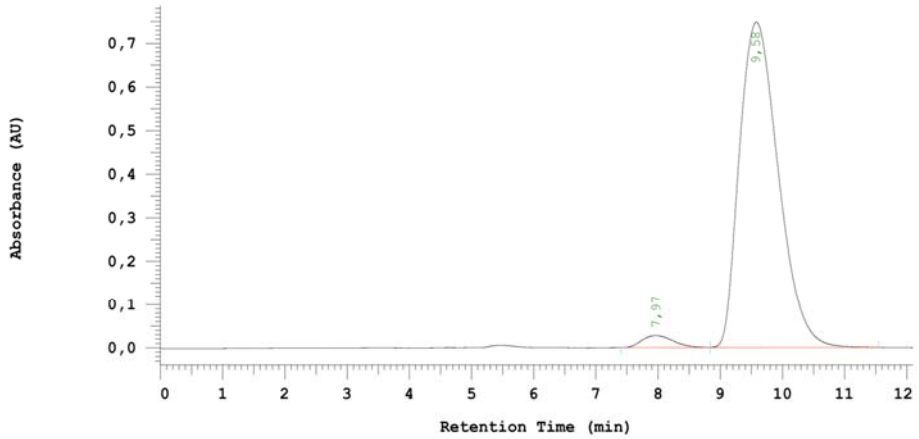

**3ad**

Sample Name: LC-180 ODH 8020 1mL Vial Number: 1

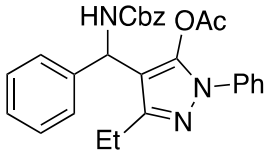



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 7,99 | 18575299 | 49,691 | |
| 2 | 9,66 | 18806489 | 50,309 | |
| | | 37381788 | 100,000 | |

Sample Name: LC-180 ODH 8020 1mL Vial Number: 1

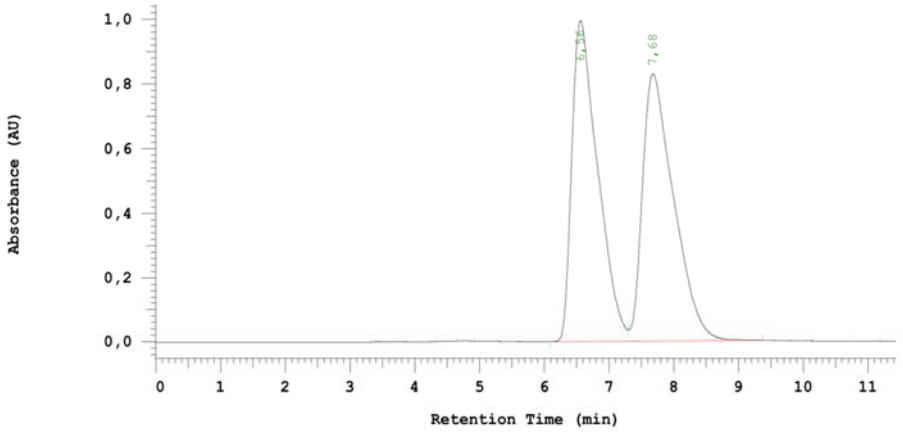



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 7,97 | 487571 | 2,905 | |
| 2 | 9,58 | 16295784 | 97,095 | |
| | | 16783355 | 100,000 | |



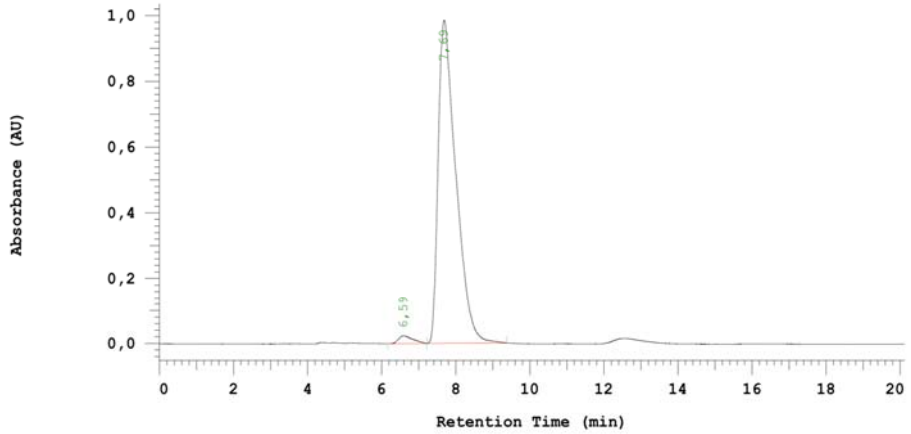

**3ae**

Sample Name: LC-178 ODH 8020 1mL Vial Number: 1

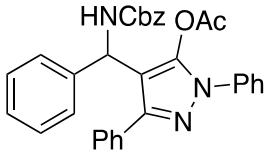



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 6,56 | 13827811 | 49,772 | |
| 2 | 7,68 | 13954414 | 50,228 | |
| | | 27782225 | 100,000 | |

Sample Name: LC-179 ODH 8020 1mL Vial Number: 1

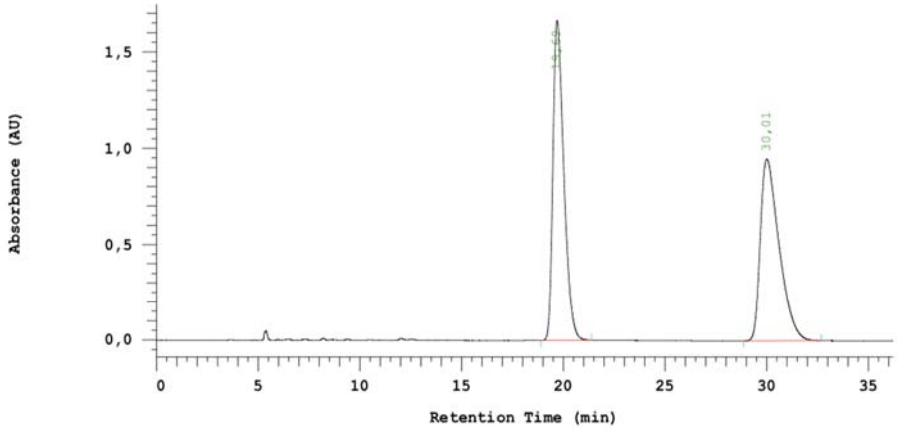



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 6,59 | 318154 | 1,900 | |
| 2 | 7,69 | 16426056 | 98,100 | |
| | | 16744210 | 100,000 | |



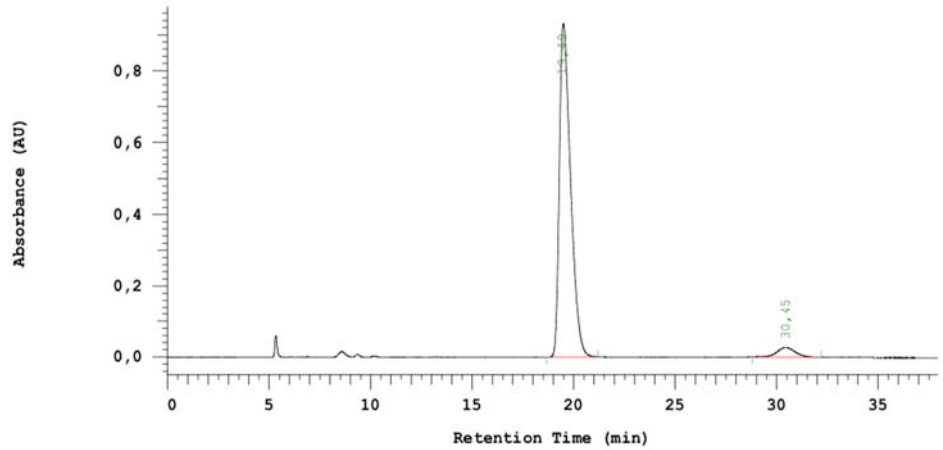

**3af**

Sample Name: LC-139 ADH 8020 1mL Vial Number: 1

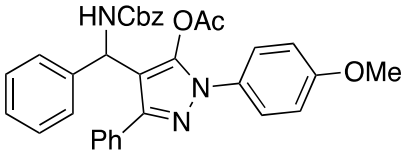



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 19,69 | 30805289 | 50,342 | |
| 2 | 30,01 | 30386265 | 49,658 | enanti (-) |
| | | 61191554 | 100,000 | |

Sample Name: LC-140 ADH 8020 1mL Vial Number: 1

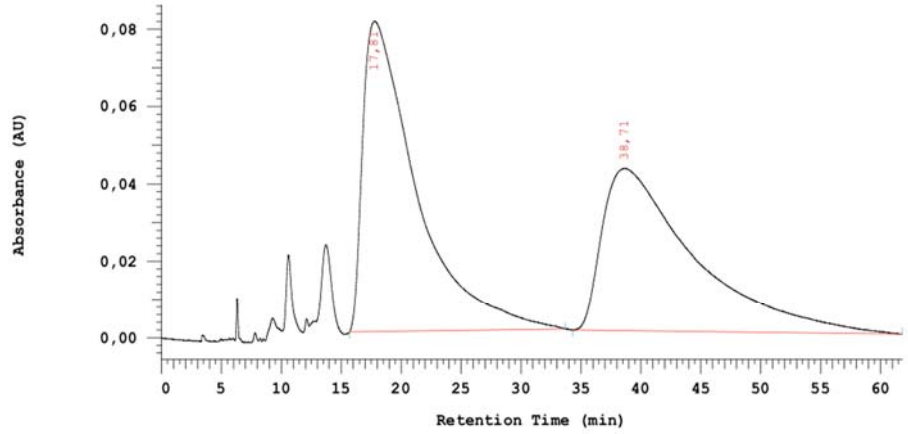



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 19,49 | 17651950 | 95,474 | |
| 2 | 30,45 | 836740 | 4,526 | enanti (-) |
| | | 18488690 | 100,000 | |



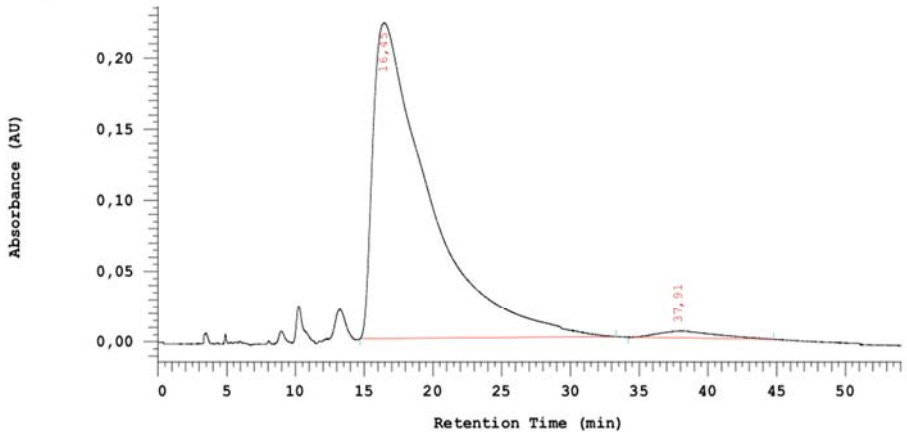

**3ag**

Sample Name: LC-148bis IC 8020 1mL Vial Number: 1

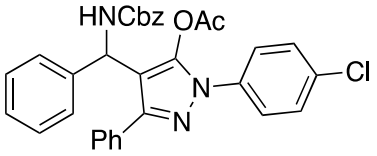



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 17,81 | 12530060 | 52,705 | |
| 2 | 38,71 | 11243664 | 47,295 | |
| | | 23773724 | 100,000 | |

Sample Name: LC-149 IC 8020 1mL Vial Number: 1

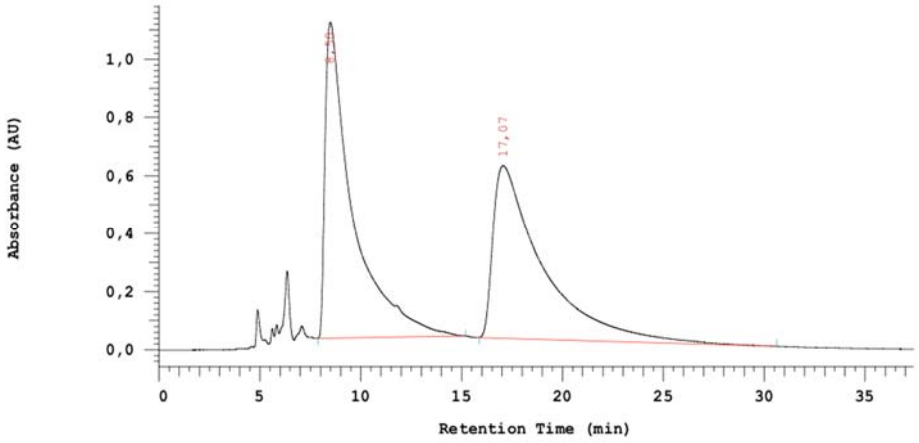



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 16,45 | 31679993 | 97,862 | |
| 2 | 37,91 | 692055 | 2,138 | |
| | | 32372048 | 100,000 | |



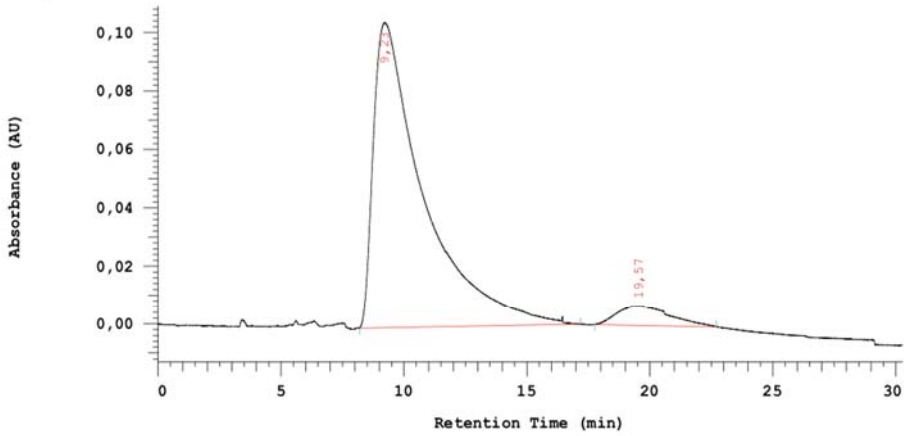

**3ah**

Sample Name: LC-142 IC 8020 1mL Vial Number: 1

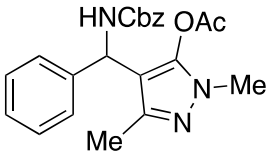



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 8,50 | 51275449 | 50,384 | |
| 2 | 17,07 | 50493411 | 49,616 | |
| | | 1,017E+08 | 100,000 | |

Sample Name: LC-143-bis IC 8020 1mL Vial Number: 1

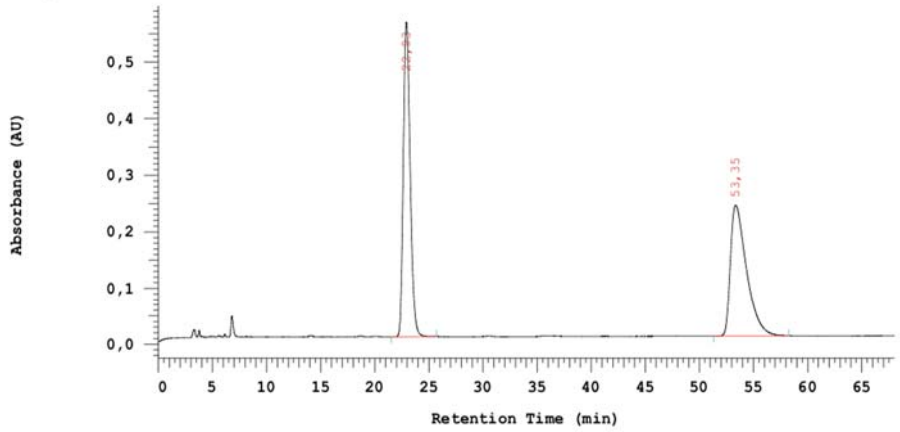



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 9,23 | 7407270 | 93,638 | |
| 2 | 19,57 | 503265 | 6,362 | |
| | | 7910535 | 100,000 | |



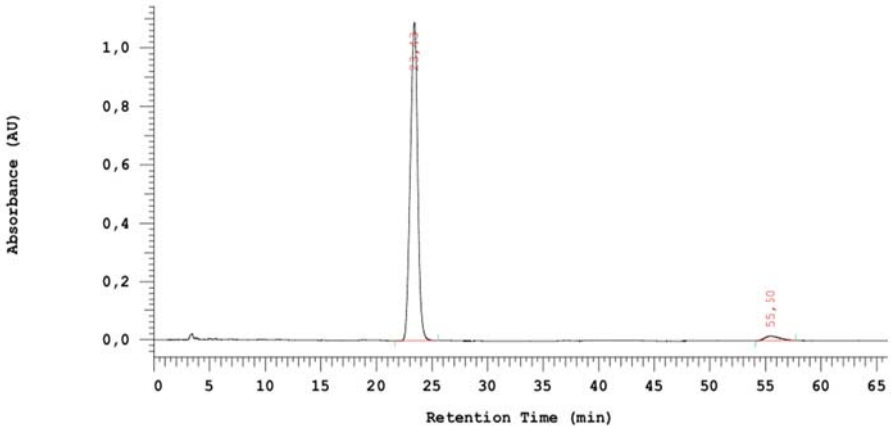

**3ai**

Sample Name: LC-141bis ADH 8020 1mL Vial Number: 1

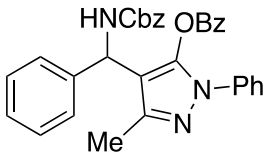



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 22,93 | 11992324 | 50,007 | enant. (+) |
| 2 | 53,35 | 11989009 | 49,993 | |
| | | 23981333 | 100,000 | |

Sample Name: LC-144bis ADH 8020 1mL Vial Number: 1

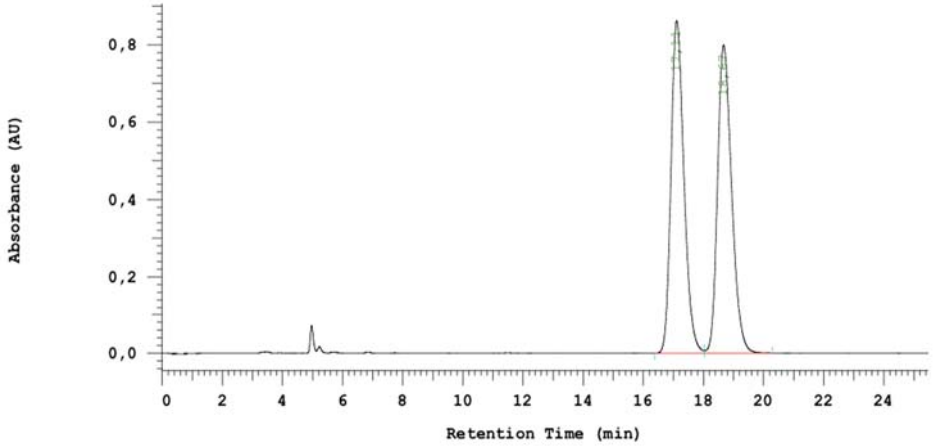



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 23,43 | 24546510 | 97,070 | enant. (+) |
| 2 | 55,50 | 740795 | 2,930 | |
| | | 25287305 | 100,000 | |



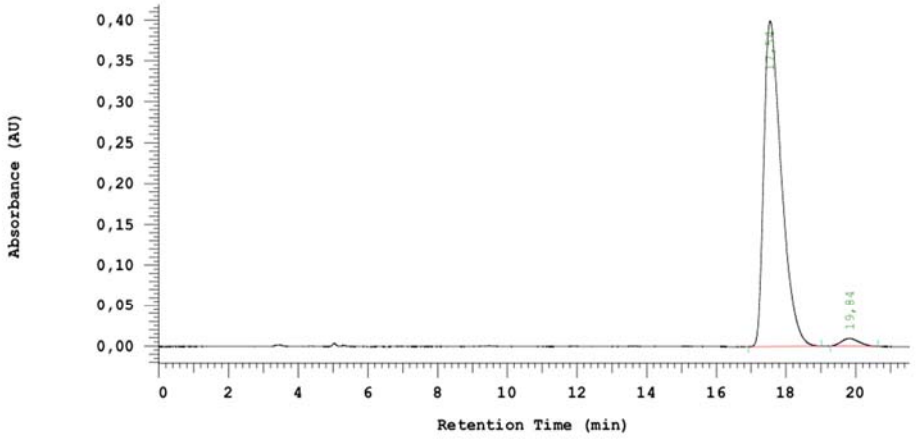

**5**

Sample Name: LC-184c ADH 8020 1mL Vial Number: 1

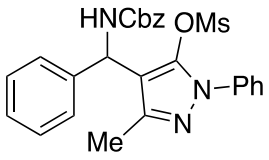



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 17,11 | 12941508 | 49,906 | |
| 2 | 18,67 | 12990432 | 50,094 | |
| | | 25931940 | 100,000 | |

Sample Name: LC-185 ADH 8020 1mL Vial Number: 1

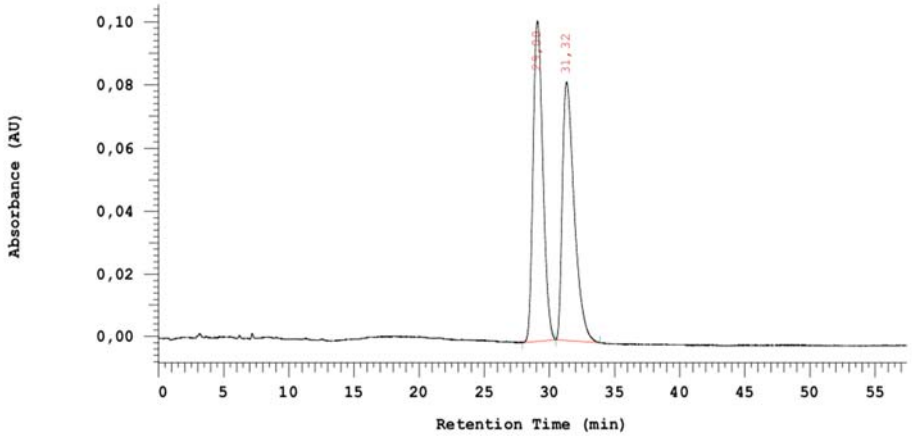



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 17,54 | 7034790 | 97,698 | |
| 2 | 19,84 | 165780 | 2,302 | |
| | | 7200570 | 100,000 | |



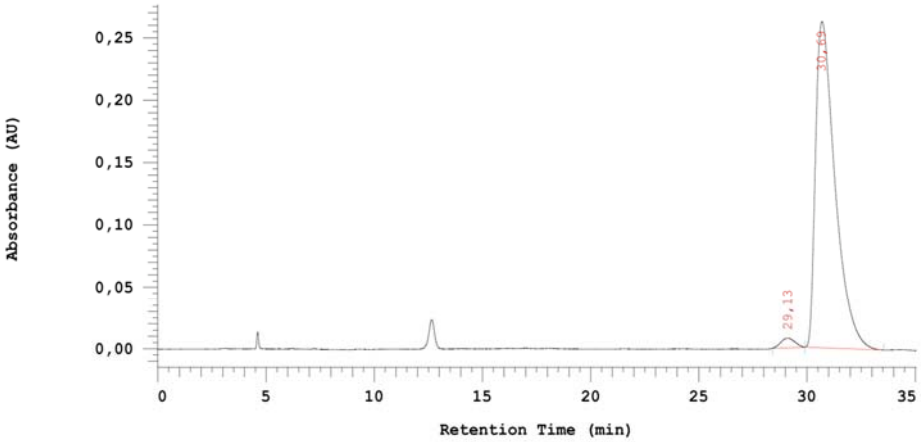

**6**

Sample Name: LC-184b Amilose1 8020 1mL Vial Number: 1

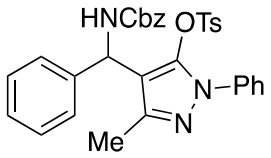



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 29,08 | 2625440 | 50,307 | enanti (-) |
| 2 | 31,32 | 2593375 | 49,693 | |
| | | 5218815 | 100,000 | |

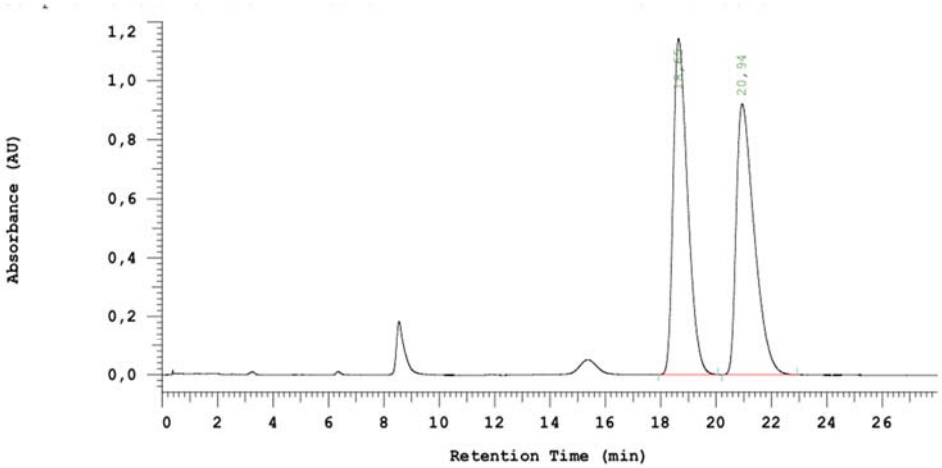
Sample Name: LC-186 Amilose1 8020 1mL Vial Number: 1




| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 29,13 | 172575 | 2,053 | enanti (-) |
| 2 | 30,69 | 8231889 | 97,947 | |
| | | 8404464 | 100,000 | |

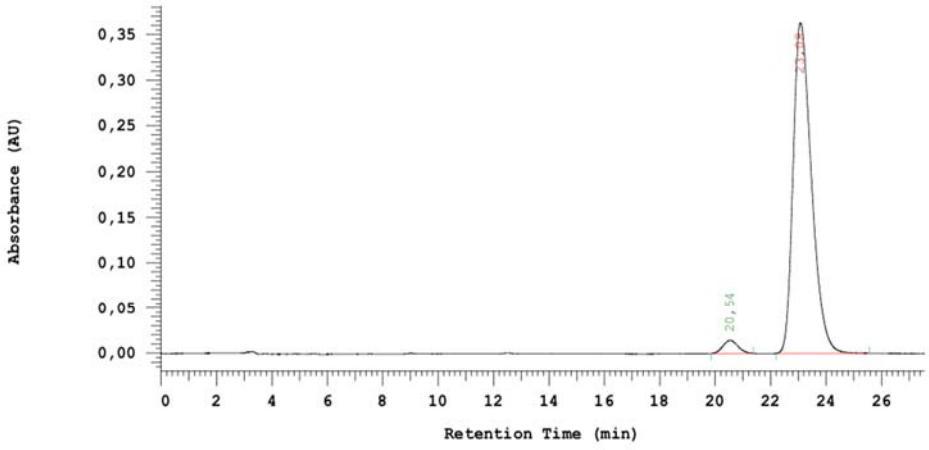



7

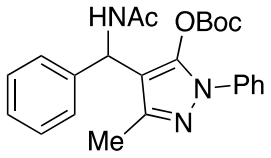



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 18,65 | 20786590 | 49,976 | |
| 2 | 20,94 | 20806289 | 50,024 | |
| | | 41592879 | 100,000 | |

Sample Name: LC-196 ADH 8020 1mL Vial Number: 1

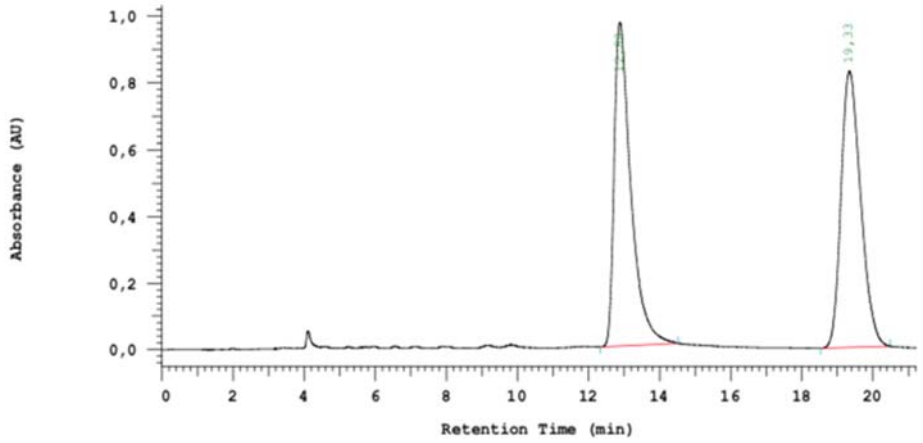



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 20,54 | 265270 | 3,069 | |
| 2 | 23,08 | 8378510 | 96,931 | enant. (+) |
| | | 8643780 | 100,000 | |



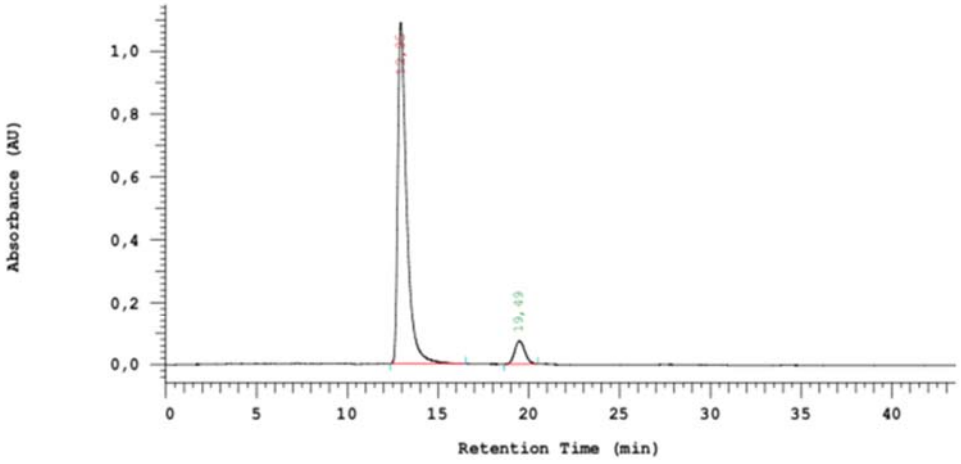

**8**

Sample Name: LC-189 IC 8020 1mL Vial Number: 1

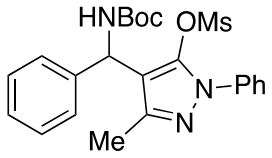



| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 12,88 | 15920220 | 50,051 | |
| 2 | 19,33 | 15887875 | 49,949 | |
| | | 31808095 | 100,000 | |

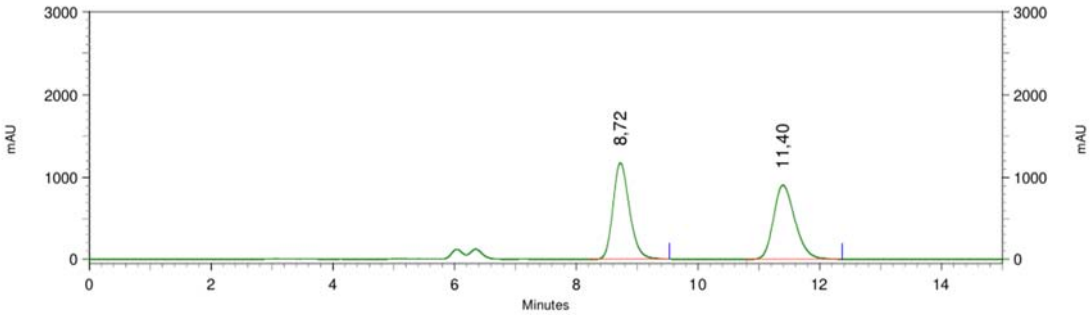
Sample Name: LC-189 IC 8020 1mL Vial Number: 1




| No. | RT | Area | Area % | Name |
|---|---|---|---|---|
| 1 | 12,95 | 18180979 | 92,832 | |
| 2 | 19,49 | 1403770 | 7,168 | |
| | | 19584749 | 100,000 | |

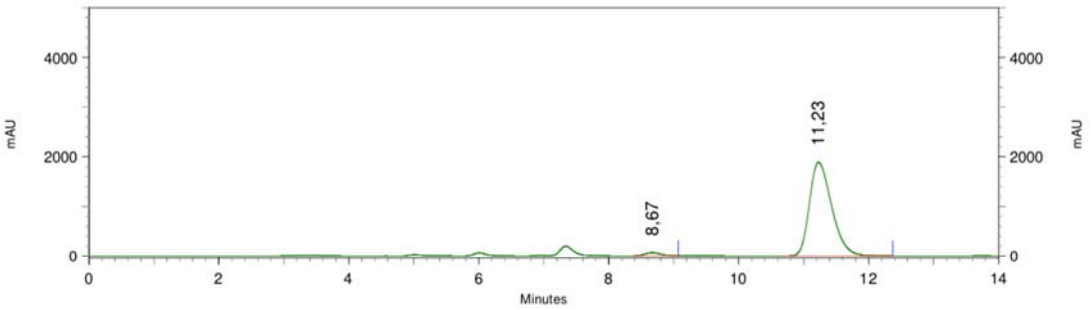



**9**




11: 252 nm, 4 nm
Results

| Retention Time | Area | Area Percent |
|---|---|---|
| 8,72 | 88647130 | 49,937 |
| 11,40 | 88870454 | 50,063 |




11: 252 nm, 4 nm
Results

| Retention Time | Area | Area Percent |
|---|---|---|
| 8,67 | 4714475 | 2,554 |
| 11,23 | 179870537 | 97,446 |