Supporting Information
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Synthesis of Homoallylic Alcohols with Acyclic Quaternary Centers *via* Co^{III}-Catalyzed Three-Component C–H Bond Addition to Internally Substituted Dienes and Carbonyls

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Abstract: An efficient Co^{III}-catalyzed three-component strategy to prepare homoallylic alcohols containing acyclic quaternary centers is disclosed. This transformation enables introduction of two C–C σ bonds via C–H bond activation and sequential addition to internally substituted dienes and a wide range of aldehydes and activated ketones. Isoprene and other internally substituted dienes are effective inputs, with the reaction proceeding with high diastereoselectivity for those substrate combinations that result in more than one stereogenic center. Moreover, the opposite relative stereochemistry can be achieved by employed 1,2-disubstituted dienes. A mechanism for the transformation is proposed based upon the relative stereochemistry of the products and studies with isotopically labeled starting materials.

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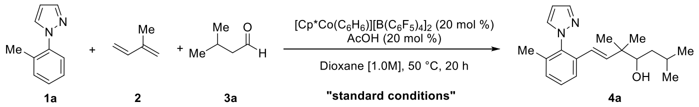
I. Supplemental Optimization Table S1



Entry[a]	Variation from the standard conditions	Recovered **1a**[b]	Yield **4a**[b]
1	None	30	65 (62) [c]
2	No catalyst	98	0
3	No AcOH	55	34
4	LiOAc (20 mol%) instead of AcOH	38	57
5	PivOH (20 mol%) instead of AcOH	48	46
6	Performed at 23 ^{0}C	76	20
7	Performed at 70 ^{0}C	28	60
8	Performed at [0.4 M]	39	56
9	In DCE	35	55
10	In toluene	32	61
11	Performed in toluene at 70 ^{0}C	11	72 (71) [c]
12	$[Cp^*Co(C_6H_6)][PF_6]_2$ instead of $[Cp^*Co(C_6H_6)][B_6F_5]_2$	87	0
13	$[Cp^*Co(MeCN)_3][SbF_6]_2$ instead of $[Cp^*Co(C_6H_6)][B_6F_5]_2$	83	17
14	$[Cp^*Rh(MeCN)_3][SbF_6]_2$ instead of $[Cp^*Co(C_6H_6)][B_6F_5]_2$	77	14

[a] Conditions: **1a** (0.2 mmol), **2a** (0.8 mmol), and **3a** (0.6 mmol) using above parameters. [b] Yields determined by crude ^{1}H NMR analysis relative to 1,3,5 trimethoxybenzene as an external standard. [c] Isolated yield from silica gel chromatography.

II. General Information

Unless otherwise noted, all Co(III)/Rh(III)-catalyzed reactions were set up in a N_2 filled glovebox, using glassware that was oven-dried (150 °C) and evacuated while hot prior to use. Unless otherwise indicated, all reactions for substrate preparation were carried out on the benchtop under a N_2 atmosphere. Solvents were sparged with argon and purified by elution through a column of activated alumina under argon before use and were stored in a N_2 filled glovebox in presence of activated 3Å molecular sieves (molecular sieves were dried at 200℃ overnight under vacuum). Unless otherwise noted, all reagents were purchased from commercial sources and used without further purification. Microwave vials and caps were purchased from Biotage with part numbers 351521 and 352298 respectively. Product purification was performed by either flash column chromatography with SiliaFlash® P60 (230-400 mesh) silica gel, reverse phase chromatography with a Teledyne Isco automated chromatography system using C-18 gold columns, or preparative thin-layer chromatography with plates from Analtech (1 mm SiO_2, 20 x 20 cm). ^1H, ^{13}C, ^{19}F, ^{31}P NMR spectra were recorded on either a 400, 500, or 600 MHz instrument. Data are reported in the following format: chemical shift in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, bs = broad singlet, m = multiplet, dd = doublet of doublets, etc.), coupling constant *J* in Hz, and integration. $CDCl_3$ was used as received. NMR chemical shifts are reported in ppm relative to $CDCl_3$ (7.26 ppm ^1H and 77.2 ppm ^{13}C). Partial IR spectra are reported. Melting points are reported uncorrected. High-resolution mass spectra (HRMS) were obtained using electrospray ionization (ESI) on a time of flight (TOF) mass spectrometer.

III. Preparation of Starting Materials

Catalysts:
$[Cp^*RhCl_2]_2$[1], $[Cp^*Co(C_6H_6)][B(C_6F_5)_4]_2$[2], $[Cp^*Co(C_6H_6)][PF_6]_2$[3], $[Cp^*Co(MeCN)_3][SbF_6]_2$[4], $[Cp^*Rh(MeCN)_3][SbF_6]_2$[5] were each synthesized according to literature procedures.

Substrates:
1-(*m*-Tolyl)-1*H*-pyrazole[6], 1-(*o*-tolyl)-1*H*-pyrazole[6], 2-(*m*-tolyl)pyridine[7], phenyl(pyrrolidin-1-yl)methanone[8], *N*-isopropylbenzamide[9], 2-methyl-3,4-dihydroisoquinolin-1(2*H*)-one[10], 1-methylindoline-2,3-dione[11], 3-methyleneoct-1-ene[12], 2-phenyl-1,3-butadiene[13], 3-methyl-1,3-hexadiene[14], 6-chloro-1-methylindoline-2,3-dione[15], and indantrione[16] were each synthesized according to literature procedures. 5-Methyl-3-methylene-hex-1-ene[14] was made according to the literature procedure and the characterization data matched those reported in the literature.[17] Isoprene was purified by washing with dilute NaOH and water prior to fractional distillation[18] and was stored in a freezer in a glove box. 3-Methyleneoct-1-ene, 2-phenyl-1,3-butadiene, 3-methyl 1,3-hexadiene, and 5-methyl-3-methylene-hex-1-ene were stored in a microwave vial under N_2 and stored in a -78 °C freezer. All other substrates were purchased from commercial sources and used without further purification.

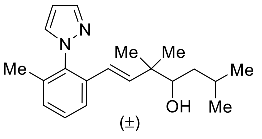
IV. Procedures for Co(III)-Catalyzed Three-Component Synthesis

General Procedure A for C–H Bond Substrate, Aldehyde and Ketone Scope
In a N_2-filled glove box, a 2.0–5.0 mL Biotage® microwave vial with a triangular stir bar (1 x 0.5 cm) was charged with the indicated C–H bond partner (0.200 mmol, 1.00 equiv) and $[Cp^*Co(C_6H_6)][B(C_6F_5)_4]_2$ (65.2 mg, 0.0400 mmol, 0.200 equiv). Following this, 67 µL of a [0.6 M] stock solution of acetic acid in 1,4-dioxane followed by 133 µL of 1,4-dioxane were added. The corresponding aldehyde or ketone (0.600 mmol, 3.00 equiv) and isoprene (0.800 mmol, 4.00 equiv) were added successively. The reaction vial was then sealed and taken outside the glove box. The reaction mixture was stirred in a preheated oil bath at 50 °C for 20 h. The reaction vial was then cooled to room temperature and uncapped. The reaction was quenched with saturated $NaHCO_3$ (10 mL), and the resulting mixture was then extracted with ethyl acetate (5 x 3 mL). The organic layers were combined and dried over Na_2SO_4. After filtering the mixture through a celite plug using ethyl acetate as the eluent, the resulting mixture was then concentrated and purified by the corresponding chromatographic method to afford the desired product.

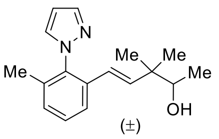
General Procedure B for C–H Bond Substrate, Aldehyde and Ketone Scope
In a N_2-filled glove box, a 2.0–5.0 mL Biotage® microwave vial with a triangular stir bar (1 x 0.5 cm) was charged with the indicated C–H bond partner (0.200 mmol, 1.00 equiv) and $[Cp^*Co(C_6H_6)][B(C_6F_5)_4]_2$ (65.2 mg, 0.0400 mmol, 0.200 equiv). Following this, 67 µL of a [0.6 M] stock solution of acetic acid in 1,4-dioxane followed by 133 µL of 1,4-dioxane were added. The corresponding aldehyde or ketone (0.600 mmol, 3.00 equiv) and corresponding diene (0.400 mmol, 2.00 equiv) were added successively. The reaction vial was then sealed and taken outside the glove box. The reaction mixture was stirred in a preheated oil bath at 50 °C for 20 h. The reaction vial was then cooled to room temperature and uncapped. The reaction was quenched with saturated $NaHCO_3$ (5 mL), and the resulting mixture was then extracted with ethyl acetate (5 x 3 mL). The organic layers were combined and dried over Na_2SO_4. After filtering the mixture through a celite plug using ethyl acetate as the eluent, the resulting mixture was then concentrated and purified by the corresponding chromatographic method to afford the desired product.

General Procedure C for C–H Bond Substrate, and Aldehyde Scope
In a N_2-filled glove box, a 2.0–5.0 mL Biotage® microwave vial with a triangular stir bar (1 x 0.5 cm) was charged with the indicated C–H bond partner (0.200 mmol, 1.00 equiv) and $[Cp^*Co(C_6H_6)][B(C_6F_5)_4]_2$ (65.2 mg, 0.0400 mmol, 0.200 equiv). Following this, 67 µL of

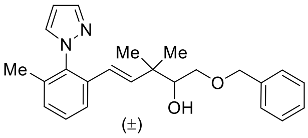
a [0.6 M] stock solution of acetic acid in 1,4-dioxane followed by 133 µL of 1,4-dioxane were added. The corresponding aldehyde (0.600 mmol, 3.00 equiv) and corresponding diene (0.400 mmol, 2.00 equiv) were added successively. The reaction vial was then sealed and taken outside the glove box. The reaction mixture was stirred in a preheated oil bath at 70 °C for 40 h. The reaction vial was then cooled to room temperature and uncapped. The reaction was quenched with saturated $NaHCO_3$ (5 mL), and the resulting mixture was then extracted with ethyl acetate (5 x 3 mL). The organic layers were combined and dried over Na_2SO_4. After filtering the mixture through a celite plug using ethyl acetate as the eluent, the resulting mixture was then concentrated and purified by the corresponding chromatographic method to afford the desired product.



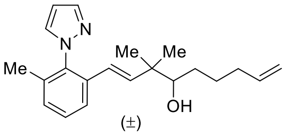
(*E*)-3,3,6-Trimethyl-1-(3-methyl-2-(1*H*-pyrazol-1-yl)phenyl)hept-1-en-4-ol (4a): The general procedure A was modified using 1-*o*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv) and 3-methylbutanal (51.7 mg, 0.600 mmol, 3.00 equiv) in toluene at 70 °C. Purification by silica gel chromatography (40% ethyl acetate in hexane) provided the product **4a** (38.7 mg, 71% yield) as a colorless oil. IR (neat): 3380, 2956, 2868, 1517, 1467, 1393, 1366 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (m, 1H), 7.45 (m, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 6.45 (m, 1H), 5.98 (d, *J* = 16.3 Hz, 1H), 5.73 (d, *J* = 16.3 Hz, 1H), 3.35-3.24 (m, 1H), 2.04 (s, 3H), 1.79-1.73 (m, 1H), 1.57-1.35 (bs, 1H), 1.23-1.12 (m, 2H), 0.94-0.91 (m, 9H), 0.86 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 140.5, 140.2, 137.6, 136.5, 136.2, 131.4, 129.2, 129.1, 129.0, 123.9, 106.0, 76.3, 41.3, 40.7, 24.9, 24.1, 23.4, 22.4, 21.3, 17.3. HRMS (ESI/$[M+H]^+$) calcd. for $C_{20}H_{29}N_2O^+$, 313.2280. Found $[M+H]^+$, 313.2274.



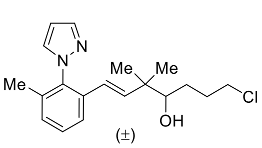
(*E*)-3,3-Dimethyl-5-(3-methyl-2-(1*H*-pyrazol-1-yl)phenyl)pent-4-en-2-ol (4b): The general procedure A was followed using 1-*o*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv) and acetaldehyde (26.4 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (40% ethyl acetate in hexane) provided the product **4b** (54.1 mg, 74% yield) as a colorless oil. IR (neat): 3360, 2967, 1647, 1594, 1515, 1469, 1392 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (m, 1H), 7.45 (m, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.2 Hz, 1H), 6.45 (m, 1H), 5.99 (d, *J* = 16.3 Hz, 1H), 5.74 (d, *J* = 16.3 Hz, 1H), 3.44 (m, 1H), 2.04 (s, 3H), 1.76-1.72 (bs, 1H), 1.05 (d, *J* = 5 Hz, 3H), 0.93 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 140.3, 140.2, 136.4, 136.2, 131.4, 129.2, 129.0, 124.0, 123.94, 123.90, 106.0, 74.2, 41.4, 23.5, 21.8, 17.6, 17.3. HRMS (ESI/$[M+H]^+$) calcd. for $C_{17}H_{23}N_2O^+$, 271.1810. Found $[M+H]^+$, 271.1802.



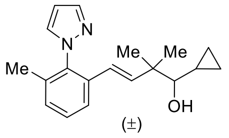
(*E*)-1-(Benzyloxy)-3,3-dimethyl-5-(3-methyl-2-(1*H*-pyrazol-1-yl)phenyl)pent-4-en-2-ol (4c): The general procedure A was followed using 1-*o*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv) and 2-(benzyloxy)acetaldehyde (91.1 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (40% ethyl acetate in hexane) provided the product **4c** (64.0 mg, 85% yield) as a colorless oil. IR (neat): 3318, 2964, 1719, 1516, 1470, 1393 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, *J* = 1.5 Hz, 1H), 7.40-7.37 (m, 2H), 7.34-7.26 (m, 6H), 7.17 (d, *J* = 7.3 Hz, 1H), 6.43 (t, *J* = 2.1 Hz, 1H), 6.13 (d, *J* = 16.3 Hz, 1H), 5.70 (d, *J* = 16.3 Hz, 1H), 4.51 (s, 2H), 3.56-3.51 (m, 2H), 3.31 (m, 1H), 2.59-2.43 (bs, 1H), 2.04 (s, 3H), 0.99 (s, 3H), 0.97 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 140.1, 139.6, 138.0, 137.6, 136.34, 136.28, 131.5, 129.2, 129.0, 128.4, 127.74, 127.70, 123.7, 122.9, 106.0, 76.8, 73.3, 71.6, 39.7, 23.9, 23.0, 17.3. HRMS (ESI/$[M+H]^+$) calcd. for $C_{24}H_{29}N_2O_2^+$, 377.2229. Found $[M+H]^+$, 377.2238.



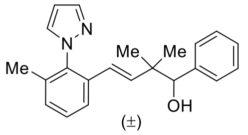
(*E*)-3,3-Dimethyl-1-(3-methyl-2-(1*H*-pyrazol-1-yl)phenyl)nona-1,8-dien-4-ol (4d): The general procedure A was followed using 1-*o*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv) and (*E*)-hex-4-enal (58.9 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (40% ethyl acetate in hexane) provided the product **4d** (27.9 mg, 43% yield) as a colorless oil. IR (neat): 3343, 2929, 1641, 1517, 1469, 1393 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (m, 1H), 7.45 (d, *J* = 2.0 Hz, 1H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 6.45 (m, 1H), 5.98 (d, *J* = 16.3 Hz, 1H), 5.83-5.77 (m, 1H), 5.73 (d, *J* = 16.3 Hz, 1H), 5.00 (d, *J* = 17.1 Hz, 1H), 4.94 (d, *J* = 10.1 Hz, 1H), 3.20 (m, 1H), 2.04 (s, 3H), 2.07-1,93 (m, 2H), 1.65-1.56 (m, 2H), 1.46 (dt, *J* = 14.2, 8.2 Hz, 1H), 1.36 (m, 1H), 1.22-1.14 (m, 1H), 0.94 (s, 3H), 0.91 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 140.5, 140.2, 138.8, 137.6, 136.4, 136.2, 131.4, 129.2, 129.0, 123.88, 123.87, 114.5, 106.0, 78.4, 41.5, 33.7, 31.0, 26.2, 23.3, 22.5, 17.3. HRMS (ESI/$[M+H]^+$) calcd. for $C_{21}H_{29}N_2O^+$, 325.2280. Found $[M+H]^+$, 325.2299.



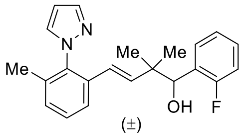
(*E*)-7-Chloro-3,3-dimethyl-1-(3-methyl-2-(1*H*-pyrazol-1-yl)phenyl)hept-1-en-4-ol (4e): The general procedure A was followed using 1-*o*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv) and 4-chlorobutanal (63.9 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (30% ethyl acetate in hexane) provided the product **4e** (34.0 mg, 51% yield) as a colorless oil. IR (neat): 3343, 2961, 2867, 1648, 1516, 1468, 1393 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (m, 1H), 7.46 (d, *J* = 2.1 Hz, 1H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 6.46 (m, 1H), 5.95 (d, *J* = 16.3 Hz, 1H), 5.74 (d, *J* = 16.3 Hz, 1H), 3.62-3.49 (m, 2H), 3.20 (m, 1H), 2.04 (s, 3H), 2.04-1.91 (m, 1H), 1.78-1.72 (m, 1H), 1.68-1.62 (m, 1H), 1.30-1.24 (m, 1H), 0.95 (s, 3H), 0.93 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 140.20, 140.17, 136.4, 136.2, 131.5, 129.3, 129.1, 124.28, 124.25, 124.0, 106.1, 77.8, 45.3, 41.5, 30.0, 28.7, 23.4, 22.3, 17.3. HRMS (ESI/$[M+H]^+$) calcd. for $C_{19}H_{26}ClN_2O^+$, 333.1734. Found $[M+H]^+$, 333.1751.



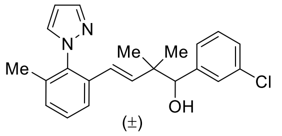
(*E*)-1-Cyclopropyl-2,2-dimethyl-4-(3-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-en-1-ol (4f): The general procedure A was modified using 1-*o*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv) and cyclopropanecarbaldehyde (42.1 mg, 0.600 mmol, 3.00 equiv) in toluene at 70 °C. Purification by silica gel chromatography (30% ethyl acetate in hexane) provided the product **4f** (32.2 mg, 62% yield) as a colorless oil. IR (neat): 3354, 2960, 1647, 1594, 1515, 1468, 1393 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.74 (m, 1H), 7.45 (m, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 6.45 (m, 1H), 6.18 (d, *J* = 16.3 Hz, 1H), 5.75 (d, *J* = 16.3 Hz, 1H), 2.54 (d, *J* = 8.8 Hz, 1H), 2.04 (s, 3H), 1.67-1.57 (bs, 1H), 1.03 (s, 3H), 1.00 (s, 3H), 0.86-0.81 (m, 1H), 0.56-0.53 (m, 1H), 0.45-0.42 (m, 1H), 0.26-0.21 (m, 2H). ^{13}C NMR (126 MHz, CDCl$_3$): δ 140.5, 140.2, 137.6, 136.6, 136.2, 131.5, 129.1, 129.0, 123.7, 123.3, 105.9, 83.2, 42.2, 24.3, 22.7, 17.3, 13.6, 4.9, 1.7. HRMS (ESI/[M+H]$^+$) calcd. for $C_{19}H_{25}N_2O^+$, 297.1967. Found [M+H]$^+$, 297.1995.



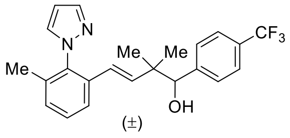
(*E*)-2,2-Dimethyl-4-(3-methyl-2-(1*H*-pyrazol-1-yl)phenyl)-1-phenylbut-3-en-1-ol (4g): The general procedure A was followed using 1-*o*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv) and benzaldehyde (63.7 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (40% ethyl acetate in hexane) provided the product **4g** (40.6 mg, 61% yield) as a colorless oil. IR (neat): 3352, 2969, 1703, 1595, 1516, 1469, 1393 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.72 (m, 1H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.37 (m, 1H), 7.32-7.23 (m, 6H), 7.19 (d, *J* = 7.5 Hz, 1H), 6.40 (m, 1H), 6.09 (d, *J* = 16.3 Hz, 1H), 5.70 (d, *J* = 16.3 Hz, 1H), 4.35 (s, 1H), 2.44-2.23 (bs, 1H), 2.05 (s, 3H), 0.96 (s, 3H), 0.87 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$): δ 141.0, 140.2, 140.0, 137.6, 136.3, 136.1, 131.6, 129.3, 129.0, 127.7, 127.5, 127.3, 124.1, 123.8, 106.0, 81.0, 42.0, 24.4, 21.9, 17.4. HRMS (ESI/[M+H]$^+$) calcd. for $C_{22}H_{25}N_2O^+$, 333.1967. Found [M+H]$^+$, 333.1990.



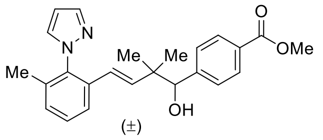
(*E*)-1-(2-Fluorophenyl)-2,2-dimethyl-4-(3-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-en-1-ol (4h): The general procedure A was followed using 1-*o*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv) and 2-fluorobenzaldehyde (74.5 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (40% ethyl acetate in hexane) provided the product **4h** (52.6 mg, 75% yield) as a yellow oil. IR (neat): 3322, 2967, 1587, 1470, 1393, 1221 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.71 (m, 1H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.37-7.35 (m, 2H), 7.31 (t, *J* = 7.7 Hz, 1 H), 7.22-7.18 (m, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.40 (m, 1H), 6.11 (d, *J* = 16.3 Hz, 1H), 5.69 (d, *J* = 16.2 Hz, 1H), 4.78 (s, 1H), 2.54-2.29 (bs, 1H), 2.05 (s, 3H), 0.98 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$): δ 160.0 (d, *J* = 245.0 Hz), 140.2, 139.5, 136.3, 136.0, 131.6, 129.3, 129.2 (d, *J* = 3.1 Hz), 129.1, 128.6 (d, *J* = 8.4 Hz), 128.4 (d, *J* = 13.0 Hz), 124.3 (d, *J* = 4.9 Hz), 124.2, 123.9, 123.6 (d, *J* = 3.2 Hz), 114.8 (d, *J* = 23.0 Hz), 106.0, 73.2, 42.5, 23.8, 21.7, 17.4. ^{19}F NMR (470 MHz, CDCl$_3$): δ -115.7. HRMS (ESI/[M+H]$^+$) calcd. for $C_{22}H_{24}FN_2O^+$, 351.1873. Found [M+H]$^+$, 351.1889.



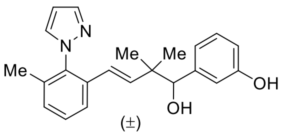
(*E*)-1-(3-Chlorophenyl)-2,2-dimethyl-4-(3-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-en-1-ol (4i) The general procedure A was followed using 1-*o*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv) and 3-chlorobenzaldehyde (83.3 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (40% ethyl acetate in hexane) provided the product **4i** (59.4 mg, 81% yield) as a yellow oil. IR (neat): 3319, 2966, 1596, 1517, 1469, 1427, 1393 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.72 (m, 1H), 7.39-7.38 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.26-7.19 (m, 4H), 7.10 (d, *J* = 7.0 Hz, 1H), 6.42 (m, 1H), 6.01 (d, *J* = 16.3 Hz, 1H), 5.69 (d, *J* = 16.3 Hz, 1H), 4.29 (s, 1H), 2.56-2.37 (bs, 1H), 2.04 (s, 3H), 0.94 (s, 3H), 0.85 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$): δ 143.1, 140.2, 139.7, 137.6, 136.2, 136.1, 133.4, 131.6, 129.4, 129.1, 128.7, 127.8, 127.4, 125.9, 124.5, 123.9, 106.0, 80.2, 42.0, 24.4, 21.5, 17.4. HRMS (ESI/[M+H]$^+$) calcd. for $C_{22}H_{24}ClN_2O^+$, 367.1577. Found [M+H]$^+$, 367.1594.



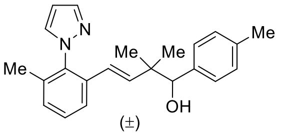
(*E*)-2,2-Dimethyl-4-(3-methyl-2-(1*H*-pyrazol-1-yl)phenyl)-1-(4-(trifluoromethyl)phenyl)but-3-en-1-ol (4j): The general procedure A was followed using 1-*o*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv) and 4-(trifluoromethyl)benzaldehyde (104 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (20% ethyl acetate in hexane) provided the product **4j** (64.9 mg, 81% yield) as a yellow solid (mp: 122 °C). IR (neat): 3263, 2965, 1706, 1618, 1518, 1469, 1417 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.17 (m, 1H), 7.70 (m, 1H), 7.54 (dd, *J* = 8.2, 2.4 Hz, 1H), 7.40-7.34 (m, 2H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.26-7.17 (m, 3H), 6.42 (m, 1H), 5.98 (d, *J* = 16.3 Hz, 1H), 5.64 (d, *J* = 16.3 Hz, 1H), 4.32 (s, 1H), 3.02-2.62 (bs, 1H), 2.03 (s, 3H), 0.93 (s, 3H), 0.83 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$): δ 144.9, 140.3, 139.3, 137.6, 136.2, 136.1, 131.5, 129.49 (q, *J* = 32.8 Hz), 129.51, 129.1, 128.0, 124.8, 124.4 (q, *J* = 3.6 Hz), 124.2 (q, *J* = 272.2 Hz), 123.9, 106.1, 80.0, 42.0, 24.4, 21.6, 17.4. ^{19}F NMR (470 MHz, CDCl$_3$): δ -62.4. HRMS (ESI/[M+H]$^+$) calcd. for $C_{23}H_{24}F_3N_2O^+$, 401.1841. Found [M+H]$^+$, 401.1848.



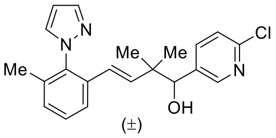
Methyl (*E*)-4-(1-hydroxy-2,2-dimethyl-4-(3-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-en-1-yl) benzoate (4k): The general procedure A was followed using 1-*o*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv) and methyl 4-formylbenzoate (98.5 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (40% ethyl acetate in hexane) provided the product **4k** (63.3 mg, 81% yield) as a white solid (mp: 91-93 °C). IR (neat): 3335, 2964, 1718, 1611, 1516, 1436, 1415 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.69 (m, 1H), 7.37 (m, 2H), 7.29-7.26 (m, 3H), 7.18 (d, *J* = 7.5 Hz, 1H), 6.38 (m, 1H), 6.01 (d, *J* = 16.3 Hz, 1H), 5.66 (d, *J* = 16.3 Hz, 1H), 4.34 (s, 1H), 3.90 (s, 3H), 2.86-2.68 (bs, 1H), 2.02 (s, 3H), 0.93 (s, 3H), 0.84 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$): δ 167.1, 146.3, 140.2, 139.5, 137.5, 136.2, 136.1, 131.5, 129.4, 129.1, 128.7, 127.7, 124.50, 124.46, 123.8, 106.0, 80.5, 52.1, 42.0, 24.3, 21.7, 17.3. HRMS (ESI/[M+H]$^+$) calcd. for $C_{24}H_{27}N_2O_3^+$, 391.2022. Found [M+H]$^+$, 391.2030.



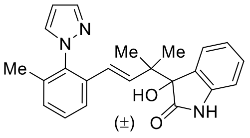
(*E*)-3-(1-Hydroxy-2,2-dimethyl-4-(3-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-en-1-yl)phenol (4l): The general procedure A was followed using 1-*o*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv) and 3-hydroxybenzaldehyde (73.3 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (40% ethyl acetate in hexane) provided the product **4l** (34.9 mg, 50% yield) as a yellow oil. IR (neat): 3280, 2967, 1590, 1517, 1465, 1394 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (m, 1H), 7.41 (m, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 7.3 Hz, 1H), 7.06 -7.03 (m, 1H), 6.68-6.62 (m, 3H), 6.42 (m, 1H), 6.02 (d, *J* = 16.3 Hz, 1H), 5.64 (d, *J* = 16.3 Hz, 1H), 4.18 (s, 1H), 2.01 (s, 3H), 0.96 (s, 3H), 0.79 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 155.8, 142.6, 140.3, 140.1, 136.5, 136.2, 131.8, 129.3, 129.2, 128.5, 124.1, 123.8, 123.7, 119.8, 119.7, 114.8, 106.2, 81.3, 41.7, 24.6, 22.7, 17.3. HRMS (ESI/[M+H]$^+$) calcd. for $C_{22}H_{25}N_2O_2^+$, 349.1916. Found [M+H]$^+$, 349.1934.



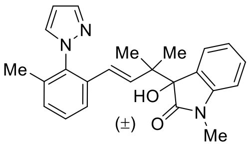
(*E*)-2,2-Dimethyl-4-(3-methyl-2-(1*H*-pyrazol-1-yl)phenyl)-1-(*p*-tolyl)but-3-en-1-ol (4m): The general procedure A was followed using 1-*o*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv) and 4-methylbenzaldehyde (72.1 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (40% ethyl acetate in hexane) provided the product **4m** (43.0 mg, 62% yield) as a colorless oil. IR (neat): 3249, 2965, 1516, 1470, 1393 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (m, 1H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.22 (m, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.96 (m, 4H), 6.25 (m, 1H), 5.94 (d, *J* = 16.3 Hz, 1H), 5.54 (d, *J* = 16.3 Hz, 1H), 4.18 (s, 1H), 2.18 (s, 3H), 2.06-1.98 (bs, 1H), 1.90 (s, 3H), 0.80 (s, 3H), 0.72 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 140.0, 139.9, 137.9, 137.5, 136.8, 136.2, 136.0, 131.4, 129.1, 128.9, 128.1, 127.4, 123.8, 123.7, 105.8, 80.8, 41.9, 24.3, 21.8, 20.9, 17.2. HRMS (ESI/[M+H]$^+$) calcd. for $C_{23}H_{27}N_2O^+$, 347.2123. Found [M+H]$^+$, 347.2142.



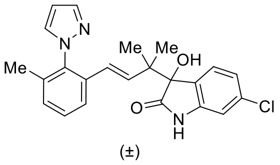
(*E*)-1-(6-Chloropyridin-3-yl)-2,2-dimethyl-4-(3-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-en-1-ol (4n): The general procedure A was followed using 1-*o*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv) and 6-chloronicotinaldehyde (84.9 mg, 0.600 mmol, 3.00 equiv). Purified by silica gel chromatography (30% ethyl acetate in hexane) provided the product **4n** (69.2 mg, 94% yield) as a white solid (mp: 72-74 °C). IR (neat): 3198, 3047, 2971, 2931, 1570, 1506, 1459 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (m, 1H), 7.66 (s, 1H), 7.49 (dd, *J* = 8.2, 8.5 Hz, 1H), 7.35-7.34 (m, 2H), 7.28 (t, *J* = 7.7 Hz, 1H), 7.18 (m, 2H), 6.39 (m, 1H), 5.99 (d, *J* = 16.3 Hz, 1H), 5.56 (d, *J* = 16.3 Hz, 1H), 4.22 (s, 1H), 3.63-3.47 (bs, 1H), 1.98 (s, 3H), 0.88 (s, 3H), 0.79 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.0, 148.8, 140.1, 138.9, 138.0, 137.4, 136.1, 136.0, 135.7, 131.6, 129.5, 129.2, 124.7, 123.8, 123.2, 106.1, 77.8, 41.9, 24.0, 21.7, 17.3. HRMS (ESI/[M+H]$^+$) calcd. for $C_{21}H_{23}ClN_3O^+$, 368.1530. Found [M+H]$^+$, 368.1547.



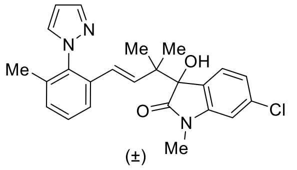
(*E*)-3-Hydroxy-3-(2-methyl-4-(3-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-en-2-yl)indolin-2-one (4o): The general procedure A was followed using 1-*o*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv) and isatin (88.3 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (15% ethyl acetate in dichloromethane) provided the product **4o** (38.1 mg, 51% yield) as a pale yellow solid (mp: 101-103 °C). IR (neat): 3264, 2973, 1712, 1620, 1470, 1393 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (bs, 1H), 7.69 (m, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.40 (m, 1H), 7.29-7.24 (m, 2H), 7.21 (t, *J* = 7.9 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 7.7 Hz, 1H), 6.38 (m, 2H), 5.73 (d, *J* = 16.3 Hz, 1H), 2.03 (s, 3H), 1.07 (s, 3H), 1.03 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 180.1, 141.3, 140.1, 137.49, 137.45, 136.9, 136.1, 135.9, 131.7, 129.4, 129.3, 129.1, 126.0, 125.0, 123.9, 122.1, 109.9, 106.0, 80.9, 43.2, 22.1, 20.2, 17.3. HRMS (ESI/[M+H]$^+$) calcd. for $C_{23}H_{24}N_3O_2^+$ 374.1869. Found [M+H]$^+$, 374.1879.



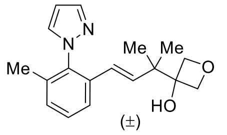
(*E*)-3-Hydroxy-1-methyl-3-(2-methyl-4-(3-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-en-2-yl)indolin-2-one (4p): The general procedure A was followed using 1-*o*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv) and 1-methylisatin (96.7 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (20% ethyl acetate in dichloromethane) provided the product **4p** (37.2 mg, 48% yield) as a pale yellow solid (mp: 152-155 °C). IR (neat): 3399, 2980, 1705, 1612, 1464, 1352 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (m, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.41 (m, 1H), 7.31-7.26 (m, 3H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 7.7 Hz, 1H), 6.45-6.41 (m, 2H), 5.73 (d, *J* = 16.3 Hz, 1H), 3.13 (s, 3H), 2.91 (s, 1H), 2.04 (s, 3H), 1.03 (s, 3H), 1.00 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 177.6, 144.1, 140.2, 137.7, 136.9, 136.1, 136.0, 131.6, 129.53, 129.52, 129.1, 128.5, 125.6, 125.4, 123.9, 122.4, 107.9, 106.0, 80.5, 43.3, 26.1, 22.1, 20.3, 17.4. HRMS (ESI/[M+H]$^+$) calcd. for $C_{24}H_{26}N_3O_2^+$, 388.2025. Found [M+H]$^+$, 388.2027.



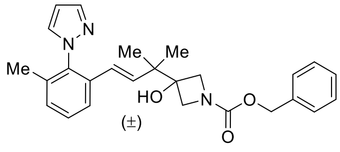
(*E*)-6-Chloro-3-hydroxy-3-(2-methyl-4-(3-methyl-2-(1H-pyrazol-1-yl)phenyl)but-3-en-2-yl) indolin-2-one (4q): The general procedure A was modified using 1-o-tolyl-1H-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv) and 6-chloroisatin (109 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (40% ethyl acetate in hexane) provided yellow oil. This material was further purified by another silica gel chromatography (20% ethyl acetate in dichloromethane) to provide the product **4q** (36.3 mg, 49% yield) as a white solid (mp: 146-148 °C). IR (neat): 3378, 2969, 1706, 1610, 1466, 1391 cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.31 (s, 1H), 7.66 (m, 2H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.74 (m, 1H), 6.42 (d, *J* = 2.1 Hz, 1H), 6.37 (d, *J* = 16.3 Hz, 1H), 6.00 (s, 1H), 5.40 (d, *J* = 16.3 Hz, 1H), 1.93 (s, 3H), 1.05 (s, 3H), 0.80 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 178.5, 143.6, 139.8, 137.6, 135.8, 135.5, 133.0, 132.2, 129.8, 129.17, 129.15, 126.9, 123.1, 122.4, 120.6, 109.0, 105.8, 79.0, 42.5, 21.3, 20.2, 16.9 (2 aromatic peaks overlap). HRMS (ESI/[M+H]$^+$) calcd. for $C_{23}H_{23}ClN_3O_2^+$, 408.1473. Found [M+H]$^+$, 408.1480.



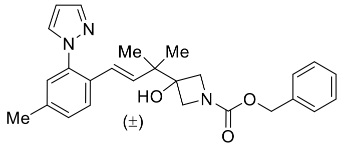
(*E*)-6-Chloro-3-hydroxy-1-methyl-3-(2-methyl-4-(3-methyl-2-(1H-pyrazol-1-yl)phenyl)but-3-en-2-yl)indolin-2-one (4r): The general procedure A was modified using 1-o-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv) and 6-chloro-1-methylisatin (117 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (40% ethyl acetate in hexane) provided yellow oil. This material was further purified by another silica gel chromatography (20% ethyl acetate in dichloromethane) to provide the product **4r** (40.5 mg, 52% yield) as a white solid (mp: 168-170 °C). IR (neat): 3392, 2964, 1704, 1608, 1462, 1380 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (m, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.41 (m, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.21-7.14 (m, 2H), 7.03-6.95 (m, 1H), 6.76 (m, 1H), 6.42 (t, *J* = 2.1 Hz, 1H), 6.36 (d, *J* = 16.3 Hz, 1H), 5.72 (d, *J* = 16.3 Hz, 1H), 3.10 (s, 3H), 2.04 (s, 3H), 1.02 (s, 3H), 0.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.6, 145.4, 140.4, 137.8, 136.6, 136.3, 136.0, 135.4, 131.7, 129.8, 129.3, 127.0, 126.7, 125.8, 124.0, 122.3, 108.7, 106.2, 80.3, 43.4, 26.3, 22.2, 20.4, 17.5. HRMS (ESI/[M+H]$^+$) calcd. for $C_{24}H_{25}ClN_3O_2^+$, 422.1630. Found [M+H]$^+$, 422.1640.



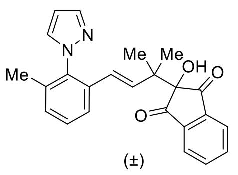
(*E*)-3-(2-Methyl-4-(3-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-en-2-yl)oxetan-3-ol (4s): The general procedure A was followed using 1-*o*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv) and benzyl oxetan-3-one (43.2 mg, 0.600 mmol, 3.00 equiv). Purified by silica gel chromatography (30% ethyl acetate in hexane) provided the product **4s** (46.5 mg, 78% yield) as a white solid (mp: 83-86 °C). IR (neat): 3309, 2962, 2881, 1645, 1511, 1469, 1396 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (m, 1H), 7.31 (m, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.3 Hz, 1H), 6.31 (m, 1H), 5.85 (d, *J* = 16.2 Hz, 1H), 5.65 (d, *J* = 16.2 Hz, 1H), 4.39 (d, *J* = 6.8 Hz, 2H), 4.25 (d, *J* = 6.8 Hz, 2H), 2.84-2.66 (bs, 1H), 1.88 (s, 3H), 0.88 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 140.1, 137.4, 137.3, 136.0, 135.9, 131.3, 129.4, 129.0, 125.3, 124.0, 106.1, 80.0, 78.3, 40.5, 21.1, 17.2. HRMS (ESI/[M+H]$^+$) calcd. for $C_{18}H_{23}N_2O_2^+$ 299.1760. Found [M+H]$^+$, 299.1769.



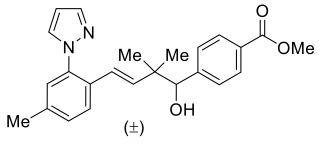
Benzyl (*E*)-3-hydroxy-3-(2-methyl-4-(3-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-en-2-yl) azetidine-1-carboxylate (4t): The general procedure A was followed using 1-*o*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv) and benzyl 3-oxoazetidine-1-carboxylate (123 mg, 0.600 mmol, 3.00 equiv). Purified by silica gel chromatography (30% ethyl acetate in hexane) provided the product **4t** (80.3 mg, 93% yield) as a yellow oil. IR (neat): 3295, 2963, 1701, 1417, 1393, 1354 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (m, 1H), 7.44 (m, 1H), 7.33-7.26 (m, 7H), 7.19 (d, *J* = 7.2 Hz, 1H), 6.44 (m, 1H), 5.93 (d, *J* = 16.2 Hz, 1H), 5.79 (d, *J* = 16.2 Hz, 1H), 5.03 (s, 2H), 3.97 (d, *J* = 9.3 Hz, 2H), 3.66 (d, *J* = 9.3 Hz, 2H), 3.42-3.20 (bs, 1H), 2.03 (s, 3H), 0.97 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 156.3, 140.3, 137.4, 137.1, 136.5, 136.1, 135.9, 131.6, 129.7, 129.3, 128.5, 128.0, 127.9, 125.8, 124.1, 106.3, 75.2, 66.8, 58.5, 58.1, 41.3, 21.1, 17.3. HRMS (ESI/[M+H]$^+$) calcd. for $C_{26}H_{30}N_3O_3^+$, 432.2287. Found [M+H]$^+$, 432.2294.



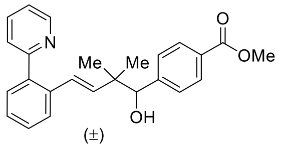
Benzyl (*E*)-3-hydroxy-3-(2-methyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-en-2-yl) azetidine-1-carboxylate (4u): The general procedure A was followed using 1-*m*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv) and benzyl 3-oxoazetidine-1-carboxylate (123 mg, 0.600 mmol, 3.00 equiv). Purified by silica gel chromatography (30% ethyl acetate in hexane) provided the product **4u** (81.1 mg, 94% yield) as a yellow oil. IR (neat): 3385, 2965, 1702, 1454, 1416, 1354 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (m, 1H), 7.62 (m, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.33-7.29 (m, 5H), 7.15 (m, 2H), 6.43 (m, 1H), 6.26 (d, *J* = 16.2 Hz, 1H), 5.95 (d, *J* = 16.2 Hz, 1H), 5.06 (s, 2H), 4.06 (d, *J* = 9.3 Hz, 2H), 3.75 (d, *J* = 9.5 Hz, 2H), 3.57-3.34 (bs, 1H), 2.37 (s, 3H), 1.07 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 156.4, 140.7, 138.3, 137.9, 136.6, 135.9, 130.9, 130.4, 129.2, 128.5, 128.0, 127.9, 127.3, 127.0, 126.0, 106.6, 75.4, 66.7, 58.8, 58.2, 41.3, 29.3, 21.4, 20.9. HRMS (ESI/[M+H]$^+$) calcd. for $C_{26}H_{30}N_3O_3^+$, 432.2287. Found [M+H]$^+$, 432.2267.



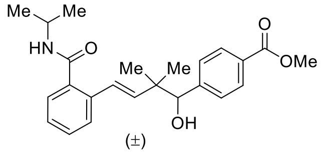
(*E*)-2-Hydroxy-2-(2-methyl-4-(3-methyl-2-(1H-pyrazol-1-yl)phenyl)but-3-en-2-yl)-1H-indene-1,3(2H)-dione (4v): The general procedure A was modified using 1-o-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv) and indantrione (96.1 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (40% ethyl acetate in hexane) to provide the product **4v** (26.7 mg, 35% yield) as a white solid (mp: 153-155 °C). IR (neat): 3152, 2974, 1742, 1708, 1596, 1462, 1396 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95-7.93 (m, 2H), 7.86-7.84 (m, 2H), 7.72 (d, *J* = 1.9 Hz, 1H), 7.43 (d, *J* = 1.9 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.7, 1.5 Hz, 1H), 6.43 (m, 1H), 5.99 (d, *J* = 16.1 Hz, 1H), 5.70 (d, *J* = 16.1 Hz, 1H), 2.01 (s, 3H), 1.00 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.5, 141.6, 140.5, 137.8, 136.5, 136.4, 136.2, 135.8, 131.7, 129.8, 129.1, 125.8, 123.8, 123.3, 106.2, 81.8, 43.7, 22.4, 17.4. HRMS (ESI/[M+H]$^+$) calcd. for $C_{24}H_{23}N_2O_3^+$, 387.1703. Found [M+H]$^+$, 387.1696.



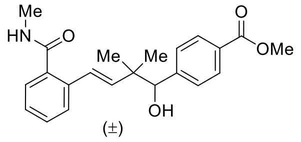
Methyl (*E*)-4-(1-hydroxy-2,2-dimethyl-4-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)but-3-en-1-yl) benzoate (4w): The general procedure A was followed using 1-*m*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv) and methyl 4-formylbenzoate (98.5 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (40% ethyl acetate in hexane) provided the product **4w** (55.4 mg, 73% yield) as a white solid (mp: 115-117 °C). IR (neat): 3220, 3119, 2969, 1709, 1610, 1515, 1406 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.8 Hz, 2H), 7.69 (m, 1H), 7.49 (m, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.19-7.16 (m, 2H), 6.36 (m, 1H), 6.18 (d, *J* = 16.3 Hz, 1H), 6.00 (d, *J* = 16.3 Hz, 1H), 4.47 (s, 1H), 3.90 (s, 3H), 3.07-2.90 (bs, 1H), 2.38 (s, 3H), 1.04 (s, 3H), 0.95 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.0, 146.4, 140.6, 138.4, 138.1, 138.0, 130.9 130.3, 129.1, 129.0, 128.8, 127.8, 127.2, 126.0, 125.7, 106.4, 80.8, 52.0, 42.1, 24.6, 22.1, 20.9. HRMS (ESI/[M+H]$^+$) calcd. for $C_{24}H_{27}N_2O_3^+$, 391.2022. Found [M+H]$^+$, 391.2025.



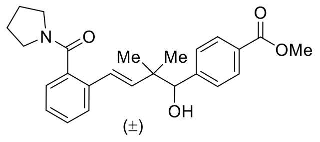
Methyl (*E*)-4-(1-hydroxy-2,2-dimethyl-4-(2-(pyridin-2-yl)phenyl)but-3-en-1-yl) benzoate (4x): The general procedure A was followed using 2-phenylpyridine (31.0 mg, 0.200 mmol, 1.00 equiv) and methyl 4-formylbenzoate (98.5 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (40% ethyl acetate in hexane) provided the product **4x** (73.6 mg, 95% yield) as a yellow oil. IR (neat): 3368, 2956, 1718, 1610, 1588, 1461, 1435 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.68 (m, 1H), 7.96 (d, *J* = 7.4 Hz, 2H), 7.69 (t, *J* = 7.7 Hz, 1H), 7.49 (d, *J* = 7.2 Hz, 2H), 7.40-7.34 (m, 5H), 7.25-7.19 (m, 1H), 6.52 (d, *J* = 16.2 Hz, 1H), 6.00 (d, *J* = 16.2 Hz, 1H), 4.48 (s, 1H), 3.90 (s, 3H), 3.77-3.43 (bs, 1H), 1.06 (s, 3H), 0.95 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.1, 158.8, 149.1, 146.5, 138.3, 138.0, 136.7, 136.4, 130.0, 129.8, 129.0, 128.8, 128.7, 127.8, 127.4, 127.1, 124.4, 121.9, 80.7, 52.0, 42.2, 24.9, 21.8. HRMS (ESI/[M+H]$^+$) calcd. for $C_{25}H_{26}NO_3^+$, 388.1913. Found [M+H]$^+$, 388.1919.



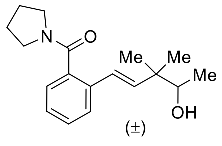
Methyl (*E*)-4-(1-hydroxy-4-(2-(isopropylcarbamoyl)phenyl)-2,2-dimethylbut-3-en-1-yl) benzoate (4y): The general procedure A was followed using *N*-isopropylbenzamide (32.6 mg, 0.200 mmol, 1.00 equiv) and methyl 4-formylbenzoate (98.5 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (20% methyl *tert*-butyl ether in hexane) provided the product **4y** (35.6 mg, 45% yield) as a colorless oil. IR (neat): 3346, 2971, 1718, 1631, 1531, 1436 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.9 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.38-7.33 (m, 3H), 7.25 (d, *J* = 6.7 Hz, 1H), 6.63 (d, *J* = 16.2 Hz, 1H), 6.08 (d, *J* = 16.2 Hz, 1H), 5.83-5.67 (bs, 1H), 4.47 (s, 1H), 4.31-4.16 (m, 1H), 3.89 (s, 3H), 3.27-2.78 (bs, 1H), 1.17 (d, *J* = 6.4 Hz, 6H), 1.08 (s, 3H), 1.02 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.6, 167.0, 146.4, 139.5, 136.0, 135.2, 130.1, 129.2, 128.8, 127.8, 127.5, 127.2, 127.1, 126.7, 80.7, 52.1, 42.2, 41.9, 24.8, 22.7, 21.7. HRMS (ESI/[M+H]$^+$) calcd. for $C_{24}H_{30}NO_4^+$, 396.2175. Found [M+H]$^+$, 396.2191.



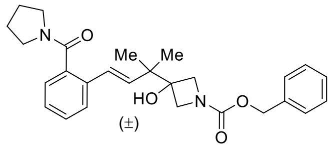
Methyl (*E*)-4-(1-hydroxy-2,2-dimethyl-4-(2-(methylcarbamoyl)phenyl)but-3-en-1-yl)benzoate (4z): The general procedure A was modified using *N*-methylbenzamide (27.0 mg, 0.200 mmol, 1.00 equiv) and methyl 4-formylbenzoate (98.5 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (40% ethyl acetate in hexane) provided the product **4z** (36.0 mg, 49% yield) as a colorless oil. IR (neat): 3351, 2963, 2881, 1700, 1608, 1453, 1423 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.43-7.42 (m, 1H), 7.40-7.46 (m, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.26-7.22 (m, 1H), 6.59 (d, *J* = 16.3 Hz, 1H), 6.03 (d, *J* = 16.3 Hz, 1H), 6.03 (s, 1H), 4.48 (s, 1H), 3.88 (s, 3H), 3.16 (bs, 1H), 2.84 (s, 3H), 1.91 (bs, 1H), 1.09 (s, 3H), 1.01 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.0, 167.0, 146.5, 139.7, 136.4, 134.6, 130.3, 129.1, 128.7, 127.8, 127.6, 127.5, 127.2, 127.0, 80.7, 52.1, 42.1, 26.7, 24.8, 21.9. HRMS (ESI/[M+Na]$^+$) calcd. for $C_{22}H_{26}NNaO_4^+$, 390.1681. Found [M+Na]$^+$, 390.1662.



Methyl (*E*)-4-(1-hydroxy-2,2-dimethyl-4-(2-(pyrrolidine-1-carbonyl)phenyl)but-3-en-1-yl) benzoate (4aa): The general procedure A was followed using phenyl(pyrrolidin-1-yl)methanone (35.0 mg, 0.200 mmol, 1.00 equiv) and methyl 4-formylbenzoate (98.5 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (65% ethyl acetate in hexane) provided the product **4aa** (48.9 mg, 60% yield) as a colorless oil. IR (neat): 3359, 2955, 2876, 1718, 1609, 1454, 1434 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.9 Hz, 2H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.36-7.31 (m, 3H), 7.26-7.22 (m, 2H), 6.36 (d, *J* = 16.2 Hz, 1H), 6.22 (d, *J* = 16.2 Hz, 1H), 4.51 (s, 1H), 3.90 (s, 3H), 3.59 (t, *J* = 6.5 Hz, 2H), 3.03 (m, 2H), 2.67-2.49 (bs, 1H), 1.87 (m, 2H), 1.77 (m, 2H), 1.07 (s, 3H), 1.01 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 169.7, 167.0, 146.4, 139.4, 136.4, 134.0, 129.12, 129.09, 128.7, 127.8, 127.3, 126.2, 126.0, 125.7, 80.7, 52.1, 48.2, 45.5, 42.1, 25.9, 24.6, 24.5, 22.2. HRMS (ESI/[M+H]$^+$) calcd. for $C_{25}H_{30}NO_4^+$, 408.2175. Found [M+H]$^+$, 408.2184.

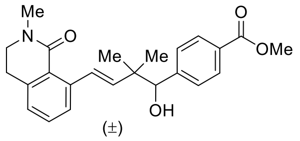


(*E*)-(2-(4-Hydroxy-3,3-dimethylpent-1-en-1-yl)phenyl)(pyrrolidin-1-yl)methanone (4ab): The general procedure A was modified using phenyl(pyrrolidin-1-yl)methanone (35.0 mg, 0.200 mmol, 1.00 equiv) and acetaldehyde (26.4 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (60% ethyl acetate in hexane) provided the product **4ab** (24.1 mg, 42% yield) as a colorless oil. IR (neat): 3411, 2970, 2875, 1608, 1452, 1426 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, *J* = 7.8 Hz, 1H), 7.33-7.29 (m, 1H), 7.24-7.23 (m, 2H), 6.42 (d, *J* = 16.3 Hz, 1H), 6.16 (d, *J* = 16.3 Hz, 1H), 3.64 (t, *J* = 7.0 Hz, 2H), 3.57 (q, *J* = 6.4 Hz, 1H), 3.11 (t, *J* = 6.8 Hz, 2H), 1.96-1.90 (m, 2H), 1.86-1.80 (m, 3H), 1.12 (d, *J* = 6.4 Hz, 3H), 1.07 (s, 3H), 1.06 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 169.8, 140.4, 136.4, 134.2, 129.0, 127.2, 126.3, 126.2, 125.6, 74.5, 48.2, 45.6, 41.5, 26.0, 24.6, 23.8, 22.1, 17.8. HRMS (ESI/[M+H]$^+$) calcd. for $C_{18}H_{26}NO_2^+$, 288.1964. Found [M+H]$^+$, 288.1978.

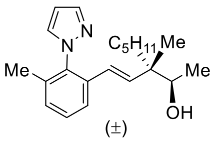


Benzyl (*E*)-3-hydroxy-3-(2-methyl-4-(2-(pyrrolidine-1-carbonyl)phenyl)but-3-en-2-yl)azetidine-1-carboxylate (4ac): The general procedure A was modified using phenyl(pyrrolidin-1-yl)methanone (35.0 mg, 0.200 mmol, 1.00 equiv) and benzyl 3-oxoazetidine-1-carboxylate (123 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (40% ethyl acetate in hexane) provided the product **4ac** (26.9 mg, 30% yield) as a colorless oil. IR (neat): 3361, 2963, 1716, 1633, 1536, 1436, 1411 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.8 Hz, 1H), 7.34-7.29 (m, 5H), 7.27-7.22 (m, 3H), 6.50 (d, *J* = 16.2 Hz, 1H), 6.10 (d, *J* = 16.2 Hz, 1H), 5.05, (s, 2H), 4.08 (d, *J* = 9.4 Hz, 2H), 3.77 (d, *J* = 9.4 Hz, 2H), 3.62 (t, *J* = 7.0 Hz, 2H), 3.10 (t, *J* = 6.8 Hz, 2H), 1.93-1.90 (m, 2H), 1.83-1.80 (m, 2H), 1.13 (s, 6H). ^{13}C NMR (126 MHz,

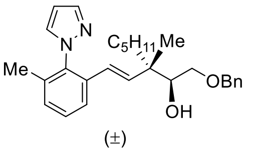
$CDCl_3$): δ 169.7, 156.4, 137.2, 136.5, 136.2, 134.1, 129.2, 128.5, 128.0, 127.9, 127.5, 127.4, 126.6, 126.3, 75.3, 66.8, 58.8, 58.2, 48.5, 45.6, 41.4, 26.0, 24.6, 21.4. HRMS (ESI/$[M+H]^+$) calcd. for $C_{27}H_{33}N_2O_4^+$, 449.2440. Found $[M+H]^+$, 449.2427.



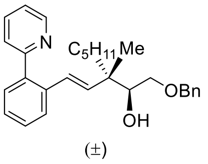
Methyl (*E*)-4-(1-hydroxy-2,2-dimethyl-4-(2-methyl-1-oxo-1,2,3,4-tetrahydroisoquinolin-8-yl)but-3-en-1-yl)benzoate (4ad): The general procedure A was modified using 2-methyl-3,4-dihydroisoquinolin-1(2H)-one (32.2 mg, 0.200 mmol, 1.00 equiv) and methyl 4-formylbenzoate (98.5 mg, 0.600 mmol, 3.00 equiv) in toluene at 70 °C. Purification by silica gel chromatography (40% ethyl acetate in hexane) provided the product **4ad** (29.1 mg, 42% yield) as a yellow oil. IR (neat): 3395.8, 2953.1, 1717.5, 1630.1, 1489.1, 1435.3, 1275.6 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 6.9 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 7.4 Hz, 1H), 5.65 (d, *J* = 16.3 Hz, 1H), 4.54 (s, 1H), 4.43-4.16 (bs, 1H), 3.89 (s, 3H), 3.55 (t, *J* = 6.1 Hz, 2H), 3.16 (s, 3H), 2.98 (t, *J* = 6.4 Hz, 2H), 1.13 (s, 3H), 1.05 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.2, 164.8, 146.6, 140.9, 139.2, 137.3, 132.7, 131.1, 128.8, 128.6, 128.0, 127.6, 126.6, 126.2, 80.6, 52.0, 47.9, 42.0, 35.4, 29.0, 25.8, 21.3. HRMS (ESI/$[M^+H]^+$) calcd. for $C_{24}H_{28}NO_4^+$, 394.2018. Found $[M^+H]^+$, 394.2031.



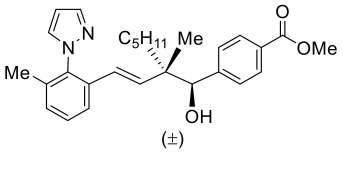
(±)-(2*R*,3*S*)-3-Methyl-3-((*E*)-3-methyl-2-(1*H*-pyrazol-1-yl)styryl)octan-2-ol (6a): The general procedure A was followed using 1-*o*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv), 3-methyleneoct-1-ene (49.7 mg, 0.400 mmol, 2.00 equiv) and acetaldehyde (26.4 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (20% ethyl acetate in hexane) provided the product **6a** (40.5 mg, 62% yield, >20:1 *dr*) as a clear oil. IR (neat): 3367, 2957, 2930, 2859, 1516, 1488, 1392, 1087 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.74-7.69 (m, 1H), 7.46-7.41 (m, 1H), 7.37-7.35 (m, 1H), 7.29-7.24 (m, 1H), 7.16-7.14 (m, 1H), 6.44-6.42 (m, 1H), 5.89 (d, *J* = 16.4 Hz, 1H), 5.69 (d, *J* = 16.4 Hz, 1H), 3.44 (q, *J* = 6.3 Hz, 1H), 2.02 (s, 3H), 1.83 (bs, 1H), 1.33-1.04 (m, 8H), 1.02 (d, *J* = 6.3 Hz, 3H), 0.84 (t, *J* = 7.1 Hz, 3H), 0.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 139.6, 137.4, 136.5, 136.1, 131.4, 129.2, 129.0, 125.4, 124.0, 106.1, 73.3, 44.8, 37.6, 32.6, 23.8, 22.6, 17.3, 17.1, 17.0, 14.1. HRMS (ESI/$[M+H]^+$) calcd. for $C_{21}H_{31}N_2O^+$, 327.2431. Found $[M+H]^{+,}$ 327.2441.



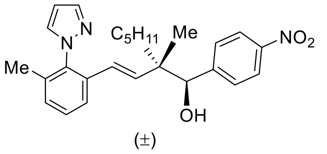
(±)-(*E*)-1-(Benzyloxy)-3-methyl-3-(3-methyl-2-(1H-pyrazol-1-yl)styryl)octan-2-ol (6b): The general procedure B was followed using 1-*o*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv), 3-methyleneoct-1-ene (49.7 mg, 0.400 mmol, 2.00 equiv) and 2-benzyloxyacetaldehyde (90.1 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (20% ethyl acetate in hexane) provided the product **6b** (56.9 mg, 66% yield, >20:1 *dr*) as a clear oil. IR (neat): 3431, 2928, 2860, 1469, 1392, 1088 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.75-7.72 (m, 1H), 7.40-7.39 (m, 2H), 7.36-7.26 (m, 6H), 7.18-7.17 (m, 1H), 6.44-6.42 (m, 1H), 6.13 (d, *J* = 16.4 Hz, 1H), 5.65 (d, *J* = 16.4 Hz, 1H), 4.53 (d, *J* = 11.6 Hz. 1H), 4.49 (d, *J* = 11.6 Hz, 1H)3.60 (dd, *J* = 8.9, 2.7 Hz, 1H), 3.53 (dd, *J* = 8.9, 2.7 Hz, 1H), 3.30 (t, *J* = 8.9 Hz, 1H), 2.45 (bs, 1H), 2.04 (s, 3H), 1.45-1.39 (m, 2H), 1.31-1.23 (m, 2H), 1.23-1.13 (m, 3H), 1.11-1.02 (m, 1H), 0.92-0.81 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.1, 138.6, 138.0, 137.5, 136.5, 136.2, 131.5, 129.11, 129.05, 128.4, 127.73, 127.70, 124.0, 123.8, 105.9, 76.1, 73.3, 71.4, 42.7, 37.3, 32.6, 23.4, 22.7, 19.0, 17.3, 14.1. HRMS (ESI/$[M+H]^+$) calcd. for $C_{28}H_{37}N_2O_2^+$, 433.2850. Found $[M+H]^+$, 433.2856.



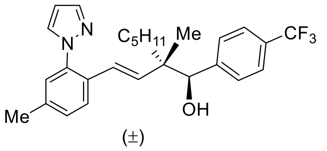
(±)-(2*S*,3*S*)-1-(Benzyloxy)-3-methyl-3-((E)-2-(pyridin-2-yl)styryl)octan-2-ol (6c): The general procedure B was followed using 2-phenylpyridine (31.0 mg, 0.200 mmol, 1.00 equiv), 3-methyleneoct-1-ene (49.7 mg, 0.400 mmol, 2.00 equiv) and 2-benzyloxyacetaldehyde (90.1 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (20% ethyl acetate in hexane) provided the product **6c** (44.0 mg, 51% yield, >20:1 *dr*) as a yellow oil. IR (neat): 3411, 2928, 2859, 1585, 1454, 1424, 1091 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.71-8.70 (m, 1H), 7.70 (td, *J* = 7.7, 1.9 Hz, 1H), 7.53-7.50 (m, 2H), 7.46-7.43 (m, 1H), 7.37-7.29 (m, 7H), 7.26-7.22 (m, 1H), 6.43 (d, *J* = 16.3 Hz, 1H), 6.13 (d, *J* = 16.3 Hz, 1H), 4.58 (d, *J* = 11.8 Hz, 1H), 4.53 (d, *J* = 11.8 Hz, 1H) 3.70-3.62 (m, 2H), 3.43 (*t*, 8.9 Hz, 1H), 2.74 (bs, 1H), 1.50-1.47 (m, 2H), 1.33-1.20 (m, 6H), 0.97 (s, 3H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 149.5, 138.8, 138.2, 137.4, 136.8, 136.0, 129.9, 128.7, 128.5, 127.8, 127.3, 127.0, 124.9, 121.9, 76.5, 73.5, 71.6, 43.1, 37.7, 32.7, 23.8, 22.8, 19.2, 14.2 (2 aromatic peaks overlap). HRMS (ESI/$[M+H]^+$) calcd. for $C_{29}H_{36}NO_2^+$, 430.2741. Found $[M+H]^+$, 430.2727.



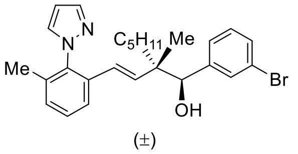
(±)-Methyl 4-((1*S*,2*S*)-1-hydroxy-2-methyl-2-((*E*)-3-methyl-2-(1H-pyrazol-1-yl)styryl)heptyl)-benzoate (6d): The general procedure B was followed using 1-*o*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv), 3-methyleneoct-1-ene (49.7 mg, 0.400 mmol, 2.00 equiv) and methyl 4-formylbenzoate (26.4 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (20% ethyl acetate in hexane) provided the product **6d** (58.5 mg, 55% yield, >20:1 *dr*) as a clear oil. IR (neat): 3413, 2962, 2931, 2858, 1720, 1468, 1275,1104, 1018 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.92-7.89 (m, 2H), 7.69-6.63 (m, 1H), 7.37-7.32 (m, 2H), 7.31-7.21 (m, 3H), 7.17-7.15 (m, 1H), 6.39-6.33 (m, 1H), 5.93 (d, *J* = 16.3 Hz, 1H), 5.61 (d, *J* = 16.3 Hz, 1H), 4.31 (s, 1H), 3.87 (s, 3H), 2.74 (bs, 1H), 2.00 (s, 3H), 1.42-1.32 (m, 1H), 1.25-1.05 (m, 7H), 0.81 (t, *J* = 7.2, 3H), 0.71 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 146.2, 140.2, 138.7, 137.4, 136.3, 136.1, 131.5, 129.4, 129.1, 129.0, 128.6, 128.0, 125.9, 123.9, 106.0, 80.1, 52.0, 45.5, 37.6, 32.5, 23.8, 22.6, 17.4, 17.3, 14.1. HRMS (ESI/$[M+H]^+$) calcd. for $C_{28}H_{35}N_2O_3^+$, 447.2642. Found $[M+H]^+$, 447.2645.



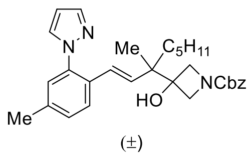
(±)-(1*S*,2*S*)-2-Methyl-2-((*E*)-3-methyl-2-(1H-pyrazol-1-yl)styryl)-1-(4-nitrophenyl)heptan-1-ol (6e): The general procedure B was followed using 1-*o*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv), 3-methyleneoct-1-ene (49.7 mg, 0.400 mmol, 2.00 equiv) and 4-nitrobenzaldehyde (90.7 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (30% ethyl acetate in hexane) provided the product **6e** (52.0 mg, 60% yield, >20:1 *dr*) as a yellow oil. IR (neat): 3290, 2930, 2560, 1515, 1466, 1294, 1048 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.10 (d, *J* = 8.4 Hz, 2H), 7.70-7.68 (m, 1H), 7.40-7.35 (m, 4H), 7.33-7.30 (m, 1H), 7.21-7.19 (m, 1H), 6.43-6.39 (m, 1H), 5.92 (d, *J* = 16.4 Hz, 1H), 5.64 (d, *J* = 16.4 Hz, 1H), 4.37 (s, 1H), 2.02 (s, 3H), 1.42-1.36 (m, 1H), 1.26-1.09 (m, 7H), 0.84 (t, *J* = 7.0 Hz, 3H), 0.73 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 148.2, 147.2, 140.3, 138.2, 137.5, 136.11, 136.09, 131.4, 129.6, 129.2, 128.8, 126.8, 124.0, 122.6, 106.2, 79.7, 45.7, 37.8, 32.5, 23.8, 22.6, 17.3, 17.1, 14.0. HRMS (ESI/[M+H]$^+$) calcd. for $C_{26}H_{32}N_3O_3^+$, 434.2438. Found [M+H]$^+$, 434.2428.



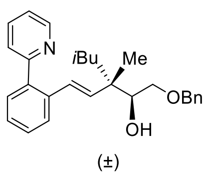
(±)-(1*S*,2*S*)-2-Methyl-2-((*E*)-4-methyl-2-(1H-pyrazol-1-yl)styryl)-1-(4-(trifluoromethyl) phenyl) heptan-1-ol (6f): The general procedure B was followed using 1-*m*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv), 3-methyleneoct-1-ene (49.7 mg, 0.400 mmol, 2.00 equiv) and 4-(trifluoromethyl)benzaldehyde (104 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (20% ethyl acetate in hexane) provided the product **6f** (50.2 mg, 55% yield, >20:1 *dr*) as a clear oil. IR (neat): 3390, 2927, 2859, 1323, 1122, 1066 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.70-7.66 (m, 1H), 7.54-7.50 (m, 3H), 7.44-7.37 (m, 3H), 7.19-7.17 (m, 2H), 6.37 (t, *J* = 2.1 Hz, 1H), 6.14 (d, *J* = 16.3 Hz, 1H), 5.97 (d, *J* = 16.3 Hz, 1H), 4.44 (s, 1H), 3.23 (bs, 1H), 2.39 (s, 3H), 1.56-1.46 (m, 1H), 1.30-1.16 (s, 7H), 0.92-0.81 (m, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 145.3, 140.8, 138.2, 138.0, 137.7, 130.9, 130.6, 129.5 (q, *J* = 32.6 Hz), 129.2, 128.4, 127.4, 127.2, 126.1, 124.38 (q, *J* = 3.76 Hz), 124.35 (q, *J* = 269.8 Hz), 106.6, 80.3, 45.7, 38.1, 32.7, 24.1, 22.8, 21.1, 17.8, 14.2. ^{19}F NMR (470 MHz, CDCl$_3$) δ -62.4. HRMS (ESI/[M+H]$^+$) calcd. for $C_{27}H_{32}F_3N_2O^+$, 457.2467. Found [M+H]$^+$, 457.2483.



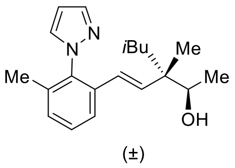
(±)-(1*S*,2*S*)-1-(3-Bromophenyl)-2-methyl-2-((*E*)-3-methyl-2-(1H-pyrazol-1-yl)styryl)heptan-1-ol (6g): The general procedure B was followed using 1-*o*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv), 3-methyleneoct-1-ene (49.7 mg, 0.400 mmol, 2.00 equiv) and 3-bromobenzaldehyde (111 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (30% ethyl acetate in hexane) provided the product **6g** (50.5 mg, 54% yield, >20:1 *dr*) as a white solid (mp: 52-54 °C). IR (neat): 3311, 2929, 2856, 1738, 1467, 1228, 1045 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.73-7.71 (m, 1H), 7.41-7.31 (m, 5H), 7.21-7.13 (m, 3H), 6.43-4.37 (m, 1H), 5.95 (d, *J* = 16.4 Hz, 1H), 5.66 (d, *J* = 16.4 Hz, 1H), 4.26 (s, 1H), 2.54 (bs, 1H), 2.05 (s, 3H), 1.41-1.35 (m, 1H), 1.26-1.16 (m, 7H), 0.85 (t, *J* = 7.1 Hz, 3H), 0.75 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 143.3, 140.4, 138.9, 137.6, 136.5, 136.2, 131.6, 131.1, 130.5, 129.6, 129.3, 129.1, 126.8, 126.2, 124.2, 121.8, 106.2, 80.0, 45.7, 37.8, 32.7, 24.0, 22.8, 17.5, 17.4, 14.2. HRMS (ESI/[M+H]$^+$) calcd. for $C_{26}H_{32}BrN_2O^+$, 467.1693. Found [M+H]$^+$, 467.1722.



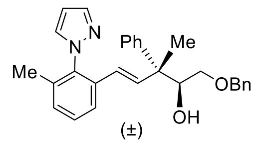
(±)-Benzyl-(*E*)-3-hydroxy-3-(3-methyl-1-(4-methyl-2-(1H-pyrazol-1-yl)phenyl)oct-1-en-3-yl) azetidine-1- carboxylate (6h): The general procedure B was followed using 1-*m*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv), 3-methyleneoct-1-ene (49.7 mg, 0.400 mmol, 2.00 equiv) and benzyl 3-oxoazetidine-1-carboxylate (123 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (35% ethyl acetate in hexane) provided the product **6h** (80.0 mg, 82% yield) as a yellow oil. IR (neat): 3400, 2955, 1704, 1417, 1353, 1096 cm^{-1}. ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.71-7.70 (m, 1H), 7.61-7.60 (m, 1H), 7.37-7.27 (m, 6H), 7.16-7.15 (m, 2H), 6.42 (t, *J* = 2.2 Hz, 1H), 6.22 (d, *J* = 16.2 Hz, 1H), 5.86 (d, *J* = 16.2 Hz, 1H), 5.06 (s, 2H), 4.13-4.05 (m, 2H), 3.76-3.72 (m, 2H), 3.47 (bs, 1H), 2.37 (s, 3H), 1.55-1.48 (m, 1H), 1.43-1.38 (m, 1H), 1.33-1.13 (m, 6H), 0.99 (s, 3H), 0.87 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 156.4, 140.8, 138.4, 137.9, 136.7, 135.0, 131.0, 130.6, 129.3, 128.5, 128.3, 128.1, 128.0, 127.4, 126.1, 106.7, 75.9, 66.8, 59.2 and 58.9 (two carbamate conformers), 58.5 and 58.3 (two carbamate conformers), 44.7, 34.4, 32.7, 24.2, 22.7, 21.0, 16.9, 14.2. HRMS (ESI/[M+H]$^+$) calcd. for $C_{30}H_{38}N_3O^+$, 488.2908. Found [M+H]$^+$, 488.2922.



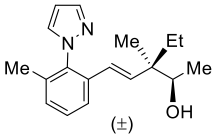
(±)- (2*S*,3*S*)-1-(Benzyloxy)-3,5-dimethyl-3-((E)-2-(pyridin-2-yl)styryl)hexan-2-ol (6i): The general procedure C was followed using 2-phenylpyridine (31.0 mg, 0.200 mmol, 1.00 equiv), 5-methyl-3-methylene-hex-1-ene (44.1 mg, 0.400 mmol, 2.00 equiv) and 2-benzyloxyacetaldehyde (90.1 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (20% ethyl acetate in hexane) provided the product **6i** (40.2 mg, 49% yield, >20:1 *dr*) as a yellow oil. IR(neat): 3434, 2951, 2866, 1584, 1460,1090 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.73-8.69 (m, 1H), 7.69 (td, *J* = 7.7, 1.8 Hz, 1H), 7.50 (dd, *J* = 7.2, 1.9 Hz, 2H), 7.44-7.42 (m, 7H), 7.37-7.28 (m, 1H), 7.26-7.22 (m, 1H), 6.42 (d, *J* = 16.3 Hz, 1H), 6.14 (d, *J* = 16.3 Hz, 0.94H, major), 6.04 (d, *J* = 16.3 Hz, 0.06H, minor), 4.58 (d, *J* = 11.8 Hz, 1H), 4.53 (d, *J* = 11.8 Hz, 1H), 3.65-3.61 (m, 2H), 3.41 (t, *J* = 9.9 Hz, 1H) 2.79 (bs, 1H), 1.71-1.62 (m, 1H), 1.52-1.38 (m, 2H), 1.00 (s, 3H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.88 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 159.0, 149.5, 138.8, 138.2, 138.0, 136.8, 136.1, 129.9, 128.8, 128.6, 127.8, 127.3, 126.9, 124.8, 121.9, 77.3, 73.5, 71.5, 46.6, 43.8, 25.5, 25.1, 24.5, 19.0 (2 aromatic peaks overlap). HRMS (ESI/[M+H]$^+$) calcd. for $C_{28}H_{34}NO_2^+$, 416.2584. Found [M+H]$^+$, 416.2591.



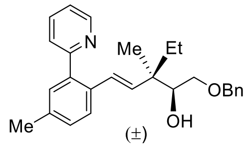
(±)-(2*R*,3*S*)-3,5-Dimethyl-3-((E)-3-methyl-2-(1H-pyrazol-1-yl)styryl)hexan-2-ol (6j): The general procedure C was followed using 1-*o*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv), 5-methyl-3-methylene-hex-1-ene (44.1 mg, 0.400 mmol, 2.00 equiv) and acetaldehyde (26.4 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (20% ethyl acetate in hexane) provided the product **6j** as a mixture of diastereomers (26.8 mg, 43% yield, 3:1 *dr*) as a yellow oil. IR(neat): 3394, 2952, 2866, 1467, 1392 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.74-7.73 (m, 1H), 7.46-7.45 (m, 1H), 7.38-7.35 (m, 1H), 7.32-7.29 (m, 1H), 7.19-7.17 (m, 1H), 6.46 (t, *J* = 2.1 Hz, 1H), 5.96 (d, *J* = 16.3 Hz, 0.25H, minor) 5.95 (d, *J* = 16.3 Hz, 0.75H, major), 5.72 (d, *J* = 16.3 Hz, 0.75H, major), 5.68 (d, *J* = 16.3 Hz, 0.25H, minor) 3.41 (q, *J* = 6.3 Hz, 1H), 2.04 (s, 3H), 1.81 (bs, 1H), 1.60-1.53 (m, 1H), 1.31-1.22 (m, 2H), 1.04 (d, *J* = 6.4 Hz, 3H), 0.93-0.79 (m, 9H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 140.30, 140.28, 139.6, 137.5, 136.7, 136.6, 136.2, 136.1, 131.4, 129.24, 129.16, 129.1, 125.2, 124.6, 123.9, 123.8, 106.11, 106.09, 74.9, 73.9, 46.7, 46.4, 45.3, 44.9, 25.3, 25.2, 24.8, 24.58, 24.54, 24.46, 18.3, 18.2 17.3, 16.9, 16.7. HRMS (ESI/[M+H]$^+$) calcd. for $C_{20}H_{29}N_2O^+$, 313.2274. Found [M+H]$^+$, 313.2269.



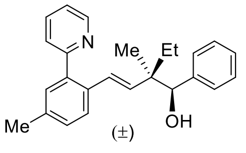
(±)-(2*S*,3*R*,*E*)-1-(Benzyloxy)-3-methyl-5-(3-methyl-2-(1H-pyrazol-1-yl)phenyl)-3-phenylpent-4-en-2-ol (6k): The general procedure C was followed using 1-*o*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv), 2-phenyl-1,3-butadiene (52.1 mg, 0.400 mmol, 2.00 equiv) and 2-benzyloxyacetaldehyde (90.1 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (35% ethyl acetate in hexane) provided the product **6k** as a mixture of diastereomers (28.0 mg, 35% yield, 3:1 *dr*) as a yellow oil. IR(neat): 3425, 3030, 2921, 1681, 1453, 1110 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.73-7.71 (m, 1H), 7.48-7.26 (m, 12H), 7.23-7.19 (m, 2H), 6.56 (d, *J* = 16.4 Hz, 0.75H, major) and 6.34 (d, *J* = 16.4 Hz, 0.25 H, minor), 6.40 (m, 1H), 5.85 (d, *J* = 16.4 Hz, 0.25H, minor), 5.81 (d, *J* = 16.3 Hz, 0.75H, major), 4.50-4.45 (m, 2H), 4.28-4.22 (m, 0.75H, major), 4.18-4.13 (m, 0.25H, minor), 3.57-3.52 (m, 0.25H, minor), 3.46-3.42 (m, 0.75H, major), 3.33 (q, *J* = 9.3 Hz, 0.25H, minor), 3.31 (q, *J* = 9.3 Hz, 0.75H, major), 2.38 (bs, 1H), 2.06 (s, 2.25H, major), 2.05(s, 0.75H, minor), 1.35 (s, 0.75H, minor) and 1.26 (s, 2.25H, major). ^{13}C NMR (126 MHz, CDCl$_3$) δ 145.2, 145.1, 140.4, 140.3, 138.11, 138.07, 137.93, 137.86, 137.84, 137.82, 136.5, 136.43, 136.39, 136.3, 131.62, 131.59, 129.6, 129.5, 129.3, 129.2, 128.54, 128.52, 128.4, 127.84, 127.80, 127.1, 127.0, 126.55, 126.50, 125.2, 124.8, 124.1, 124.0, 106.2, 106.1, 76.3, 75.8, 73.47 , 73.46, 71.8, 71.6, 47.9, 47.7, 21.7, 21.3, 17.5 (both diastereomers listed). HRMS (ESI/[M+H]$^+$) calcd. for $C_{29}H_{31}N_2O_2^+$, 439.2380. Found [M+H]$^+$, 439.2366.



(±)-(2*R*,3*R*,E)-3-Ethyl-3-methyl-5-(3-methyl-2-(1H-pyrazol-1-yl)phenyl)pent-4-en-2-ol (8a): The general procedure C was followed using 1-*o*-tolyl-1*H*-pyrazole (31.6 mg, 0.200 mmol, 1.00 equiv), 3-methyl-1,3-pentadiene (32.9 mg, 0.400 mmol, 2.00 equiv) and acetaldehyde (26.4 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (20% ethyl acetate in hexane) provided the product **8a** (28.0 mg, 49% yield, >20:1 *dr*) as a clear oil. IR (neat): 3377, 2967, 2877, 1515, 1471, 1392 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.75-7.73 (m, 1H), 7.45-7.44 (m, 1H), 7.40-7.38 (m, 1H), 7.31-7.28 (m, 1H), 7.19-7.17 (m, 1H), 6.46-6.44 (m, 1H), 5.88 (d, *J* = 16.5 Hz, 1H), 5.70 (d, *J* = 16.5 Hz, 1H), 3.50 (q, *J* = 6.4 Hz, 1H), 2.04 (s, 3H), 1.78 (bs, 1H), 1.46-1.32 (m, 2H), 1.05 (d, *J* = 6.4 Hz, 3H), 0.86 (s, 3H), 0.75 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 140.3, 138.8, 137.6, 136.8, 136.4, 131.6, 129.3, 129.2, 125.4, 124.0, 106.2, 74.0, 44.9, 29.5, 18.3, 17.8, 17.4, 8.5. HRMS (ESI/[M+H]$^+$) calcd. for $C_{18}H_{25}N_2O^+$, 285.1961. Found [M+H]$^+$, 285.1960.

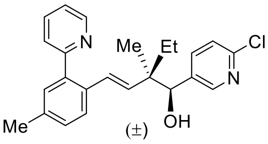


(±)-Methyl 4-((1*S*,2*R*,*E*)-2-ethyl-1-hydroxy-2-methyl-4-(4-methyl-2-(pyridin-2-yl)phenyl)but-3-en-1-yl)benzoate (8b): The general procedure C was followed using 2-(3-methylphenyl)pyridine (33.8 mg, 0.200 mmol, 1.00 equiv), 3-methyl-1,3-pentadiene (32.9 mg, 0.400 mmol, 2.00 equiv), and 2-benzyloxyacetaldehyde (90.1 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (20% ethyl acetate in hexane) provided a yellow oil containing the product. This material was further purified by using a C-18-reverse phase column, with a gradient of 0 to 40% acetonitrile buffered with 0.1% of TFA in H_2O buffered with 0.1% of TFA. Fractions containing the product were combined and diluted with sat. aq. $NaHCO_3$ (50 mL) and extracted with ethyl acetate (3 × 40 mL). The combined organic layers were then washed with brine (50 mL), dried over Na_2SO_4, and concentrated to afford product **8b** (55.2 mg, 69% yield, 93:7 *dr*) as a yellow oil. IR (neat): 3402, 2965, 1718, 1586, 1453, 1377, 1077 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.72-8.71 (m, 1H), 7.70-7.66 (m, 1H), 7.44-7.29 (m, 8H), 7.25-7.22 (m, 1H), 7.19-7.17 (m, 1H), 6.40 (d, *J* = 16.2 Hz, 1H), 6.08 (d, *J* = 16.2 Hz, 0.07H), 5.96 (d, *J* = 16.2 Hz, 0.93H), 4.53 (s, 2H), 3.70 (dd, *J* = 9.6, 2.6 Hz, 1H), 3.62 (dd, *J* = 9.6, 2.6 Hz, 1H), 3.43 (t, *J* = 9.0 Hz, 1H), 2.80 (bs, 1H), 2.40 (s, 3H), 1.59-1.50 (m, 2H), 0.98 (s, 2.79H, major), 0.94 (s, 0.21H, minor), 0.84 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 158.9, 149.3, 138.5, 138.2, 137.1, 136.2, 136.0, 133.8, 130.6, 129.5, 128.54, 128.47, 127.81, 127.78, 126.8, 125.1, 121.9, 76.2, 73.5, 71.9, 43.2, 30.7, 21.2, 17.9, 8.4. HRMS (ESI/[M+H]$^+$) calcd. for $C_{27}H_{32}NO_2^+$, 402.2428. Found [M+H]$^+$, 402.2439.

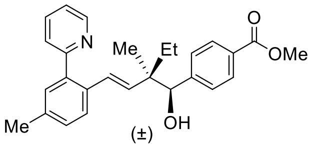


(±)-(1*S*,2*R*,*E*)-2-Ethyl-2-methyl-4-(4-methyl-2-(pyridin-2-yl)phenyl)-1-phenylbut-3-en-1-ol (8c): The general procedure C was followed using 2-(3-methylphenyl)pyridine (33.8 mg, 0.200 mmol, 1.00 equiv), 3-methyl-1,3-pentadiene (32.9 mg, 0.400 mmol, 2.00 equiv) and benzaldehyde (63.7 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (20% ethyl acetate in hexane) provided the product **8c** (41.3 mg, 58% yield, 88:12 *dr*) as a yellow oil. IR (neat): 3382, 2965, 1736, 1587, 1462, 1240, 1040 cm^{-1}. ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.68-8.67 (m, 1H), 7.65 (td, *J* = 7.7, 1.8 Hz, 0.12H, minor), 7.62 (td, *J* = 7.7, 1.8 Hz, 0.88H), 7.45-7.44 (m, 0.12H, minor), 7.39-7.38 (m, 0.88H), 7.35-7.34 (m, 1H), 7.31- 7.18 (m, 8H), 6.43 (d, *J* = 16.3 Hz, 0.12H, minor), 6.38 (d, *J* = 16.3 Hz, 0.88H, major), 5.98 (d, *J* = 16.3 Hz, 0.12H, minor), 5.86 (d, *J* = 16.3 Hz, 0.88H, major), 4.48 (s, 1H), 3.12 (bs, 1H), 2.39 (s, 3H), 1.48- 1.35 (m, 2H), 1.06 (s, 2.64H, major), 0.85 (s, 0.36H, minor), 0.82 (t, J = 7.5 Hz, 0.36H, minor), 0.81 (t, *J* = 7.5 Hz, 2.64H, major). ^{13}C NMR (151

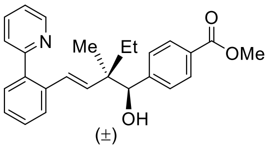
MHz, $CDCl_3$) δ 158.6, 149.2, 141.8, 138.0, 137.1, 136.2, 135.4, 134.1, 130.7, 130.4, 129.5, 128.1, 127.8, 127.5, 127.11, 127.08, 124.6, 121.8, 81.5, 45.7, 29.7, 21.2, 19.2, 8.7. HRMS (ESI/$[M+H]^+$) calcd. for $C_{25}H_{28}NO^+$, 358.2165. Found $[M+H]^+$, 358.2160.



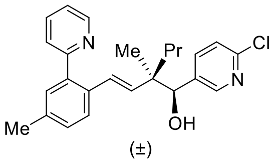
(±)-(1*S*,2*R*,*E*)-1-(6-Chloropyridin-3-yl)-2-ethyl-2-methyl-4-(4-methyl-2-(pyridin-2-yl)phenyl)but-3-en-1-ol (8d): The general procedure C was followed using 2-(3-methylphenyl)pyridne (33.8 mg, 0.200 mmol, 1.00 equiv), 3-methyl-1,3-pentadiene (32.9 mg, 0.400 mmol, 2.00 equiv) and 6-chloronicotinaldehyde (84.9 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (20% ethyl acetate in hexane) provided the product **8d** (70.0 mg, 90% yield, 94:6 *dr*) as a yellow oil. IR (neat): 3338, 2967, 2328, 1736, 1585, 1455, 1373, 1204, cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 8.66-8.64 (m, 1H), 8.28 (d, *J* = 2.4 Hz, 1H), 7.76-7.73 (m, 1H), 7.59 (dd, *J* = 8.3, 2.5 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.33-7.31 (m, 1H), 7.27-7.25 (m, 1H), 7.23-7.19 (m, 2H), 6.49 (d, *J* = 16.3 Hz, 1H), 5.86 (d, *J* = 16.3 Hz, 0.06H, minor), 5.72 (d, *J* = 16.3 Hz, 0.94H, major), 4.49 (s, 1H), 3.87 (bs, 1H), 2.41 (s, 3H), 1.45-1.29 (m, 2H), 1.07 (s, 3H), 0.83 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.8, 150.2, 149.1, 149.0, 138.2, 137.7, 137.5, 136.9, 136.3, 134.4, 134.1, 132.5, 130.6, 129.8, 127.3, 124.5, 123.4, 122.1, 78.9, 45.7, 29.2, 21.3, 19.6, 8.7. HRMS (ESI/$[M+H]^+$) calcd. for $C_{24}H_{26}ClN_2O^+$, 393.1728. Found $[M+H]^+$, 393.1719.



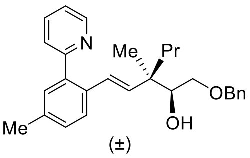
(±)-Methyl 4-((1*S*,2*R*,*E*)-2-ethyl-1-hydroxy-2-methyl-4-(4-methyl-2-(pyridin-2-yl)phenyl)but-3-en-1-yl)benzoate (8e): The general procedure C was followed using 2-(3-methylphenyl)pyridine (33.8 mg, 0.200 mmol, 1.00 equiv), 3-methyl-1,3-pentadiene (32.9 mg, 0.400 mmol, 2.00 equiv), and methyl 4-formylbenzoate (98.5 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (20% ethyl acetate in hexane) provided a yellow oil containing the product. This material was further purified by using a C-18-reverse phase column, with a gradient of 0 to 40% acetonitrile buffered with 0.1% of TFA in H_2O buffered with 0.1% of TFA. Fractions containing the product were combined and diluted with sat. aq. $NaHCO_3$ (50 mL) and extracted with ethyl acetate (3 × 40 mL). The combined organic layers were then washed with brine (50 mL), dried over Na_2SO_4, and concentrated to afford product **8e** (64.1 mg, 77% yield, 88:12 *dr*) as a yellow oil. IR (neat): 3310, 2965, 2324, 1718, 1609, 1587, 1434, 1275, 1103 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.65-8.63 (m, 1H), 7.92-7.89 (m, 2H), 7.63-7.59 (m, 1H), 7.36-7.26 (m, 5H), 7.21-7.16 (m, 2H), 6.37 (d, *J* = 16.4 Hz, 1H), 5.92 (d, *J* = 15.5 Hz, 0.12H), 5.78 (d, *J* = 16.4 Hz, 0.88H), 4.48 (s, 1H), 3.86 (s, 3H), 2.37 (s, 3H), 1.44-1.32 (m, 2H), 1.02 (s, 3H), 0.79 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 158.6, 149.0, 147.2, 137.8, 137.1, 136.3, 135.0, 134.0, 130.9, 130.4, 129.6, 128.9, 128.7, 127.8, 127.0, 124.5, 121.9, 81.0, 52.0, 45.7, 29.5, 21.1, 19.2, 8.6. HRMS (ESI/$[M+H]^+$) calcd. for $C_{27}H_{30}NO_3^+$, 416.2220. Found $[M+H]^+$, 416.2220.



(±)-Methyl 4-((1*S*, 2*R*, *E*)-2-ethyl-1-hydroxy-2-methyl-4-(2-(pyridin-2-yl)phenyl)but-3-en-1-yl)benzoate (8f): The general procedure C was followed using 2-phenylpyridine (31.0 mg, 0.200 mmol, 1.00 equiv), 3-methyl-1,3-pentadiene (32.9 mg, 0.400 mmol, 2.00 equiv) and methyl 4-formylbenzoate (98.5 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (20% ethyl acetate in hexane) provided the product as a yellow oil. This material was further purified by using a C-18-reverse phase column, with a gradient of 0 to 40% acetonitrile buffered with 0.1% of TFA in H_2O buffered with 0.1% of TFA. Fractions containing the product were combined and diluted with sat. aq. $NaHCO_3$ (50 mL) and extracted with ethyl acetate (3 × 40 mL). The combined organic layers were then washed with brine (50 mL), dried over Na_2SO_4, and concentrated to afford product **8f** (50.0 mg, 62% yield, 93:7 *dr*) as a yellow oil. IR (neat): 3482, 2965, 1718, 1609, 1585, 1460,1286,1103 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.68-8.66 (m, 1H), 7.94-7.92 (m, 2H), 7.69-7.65 (m, 1H), 7.52-7.46 (m, 2H), 7.41-7.33 (m, 5H), 7.25-7.21 (m, 1H), 6.47 (d, *J* = 16.2 Hz, 1H), 5.95 (d, *J* = 16.2 Hz, 0.07H, minor), 5.83 (d, *J* = 16.2 Hz, 0.93H, major), 4.52 (s, 1H), 3.89 (s, 3H), 3.80 (bs, 1H), 1.48-1.30 (m, 2H), 1.07 (s, 3H), 0.81 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 158.7, 149.1, 147.2, 138.0, 137.0, 136.6, 136.0, 131.5, 129.9, 129.03, 128.96, 128.8, 127.9, 127.5, 127.3, 124.6, 122.1, 81.2, 52.2, 45.9, 29.5, 19.5, 8.8. HRMS (ESI/$[M+H]^+$) calcd. for $C_{26}H_{28}NO_3^+$, 402.2064. Found $[M+H]^+$, 402.2063.



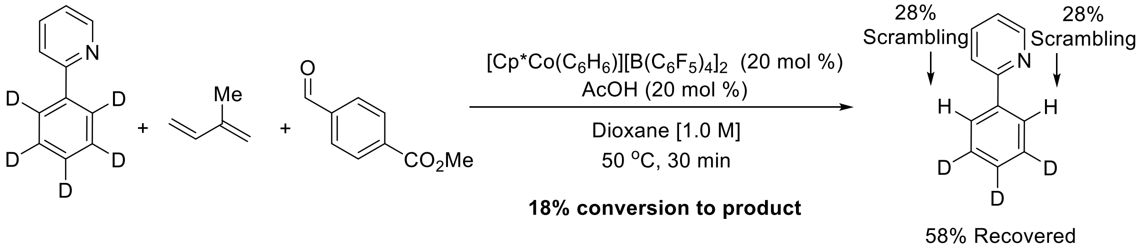
(±)-(1*S*,2*R*)-1-(6-Chloropyridin-3-yl)-2-methyl-2-((*E*)-4-methyl-2-(pyridin-2-yl)styryl)pentan-1-ol (8g): The general procedure C was followed using 2-(3-methylphenyl)pyridine (33.8 mg, 0.200 mmol, 1.00 equiv), 3-methyl-1,3-hexadiene (38.5 mg, 0.400 mmol, 2.00 equiv) and 6-chloronicotinaldehyde (84.9 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography from gradient of 0% to 40% ethylacetate/hexane gave a yellow oil containing the product. This material was further purified by using a C-18-reverse phase column, with a gradient of 0 to 40% acetonitrile buffered with 0.1% of TFA in H_2O buffered with 0.1% of TFA. Fractions containing the product were combined and diluted with sat. aq. $NaHCO_3$ (50 mL) and extracted with ethyl acetate (3 × 40 mL). The combined organic layers were then washed with brine (50 mL), dried over Na_2SO_4, and concentrated to afford product **8g** (49.8 mg, 61%, >20:1 *dr*) as a yellow oil. IR (neat): 3242, 2959, 2869, 1585, 1454, 1100 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.65-8.63 (m, 1H), 8.25 (d, *J* = 2.4 Hz, 1H), 7.73 (td, *J* = 7.7, 1.8 Hz, 1H), 7.57 (dd, *J* = 8.3, 2.5 Hz, 1H), 7.39-7.30 (m, 3H), 7.26-7.18 (m, 3H), 6.44 (d, *J* = 16.3 Hz, 1H), 5.74 (d, *J* = 16.3 Hz, 1H), 4.44 (s, 1H), 3.26 (bs, 1H), 2.40 (s, 3H), 1.37-1.23 (m, 4H), 1.06 (s, 3H), 0.89-0.79 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 150.1, 149.1, 149.0, 138.2, 137.9, 137.5, 136.8, 136.3, 134.8, 134.0, 131.7, 130.6, 129.8, 127.2, 124.5, 123.4, 122.1, 78.9, 45.5, 39.2, 21.3, 20.1, 17.7, 15.0. HRMS (ESI/$[M+H]^+$) calcd. for $C_{25}H_{28}ClN_2O^+$, 407.1885. Found $[M+H]^+$, 407.1884.



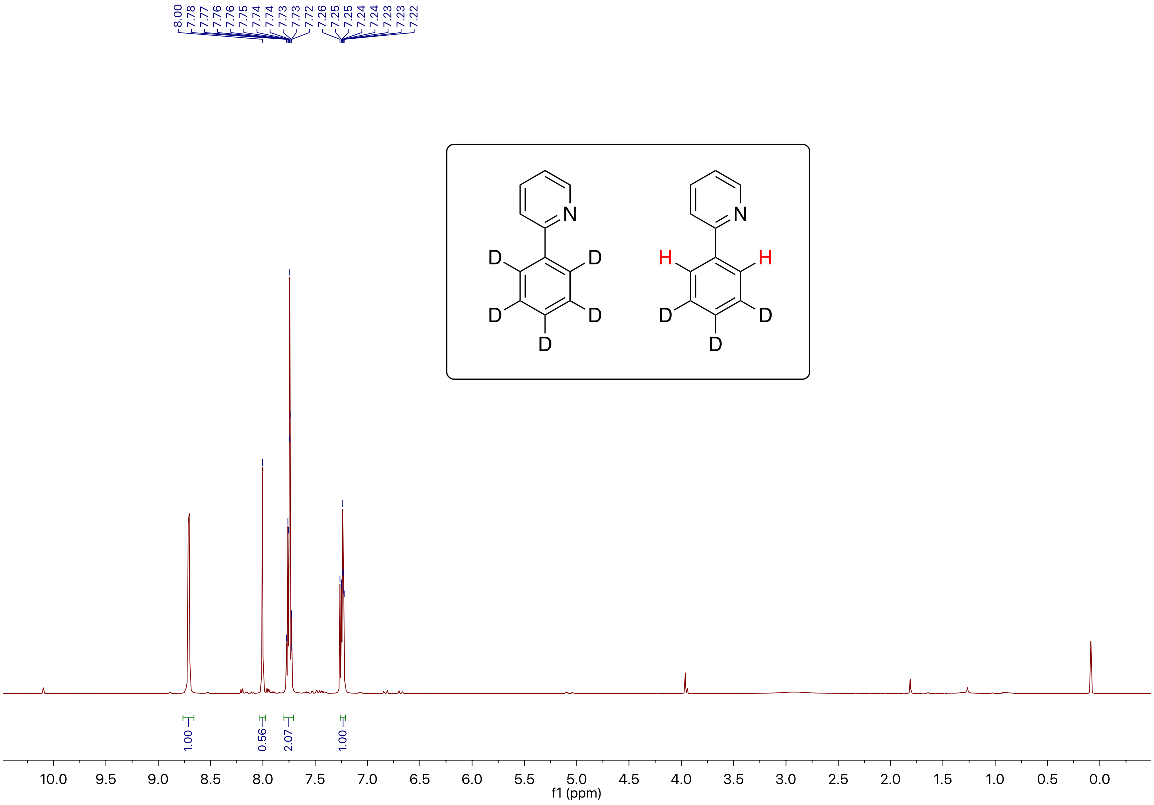
(±)-(2*S*,3*R*)-1-(Benzyloxy)-3-methyl-3-((*E*)-4-methyl-2-(pyridin-2-yl)styryl)hexan-2-ol (8h): The general procedure C was followed using 2-(3-methylphenyl)pyridine (33.8 mg, 0.200 mmol, 1.00 equiv), 3-methyl-1,3-hexadiene (38.5 mg, 0.400 mmol, 2.00 equiv), and 2-benzyloxyacetaldehyde (90.1 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography from gradient of 0% to 40% ethyl acetate in hexane gave a green oil containing the product. This material was further purified by using a C-18-reverse phase column, with a gradient of 0 to 60% acetonitrile buffered with 0.1% of TFA in H_2O buffered with 0.1% of TFA. Fractions containing the product were combined and diluted with sat. aq. $NaHCO_3$ (50 mL) and extracted with ethyl acetate (3 × 40 mL). The combined organic layers were then washed with brine (50 mL), dried over Na_2SO_4, and concentrated to afford product **8h** (45.0 mg, 54%, 93:7 *dr*) as a green oil. IR (neat): 3404, 2927, 2868, 1585, 1453 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.71-8.70 (m, 1H), 7.71-7.66 (m, 1H), 7.41-7.22 (m, 9H), 7.19-7.16 (m, 1H), 6.37 (d, *J* = 16.2 Hz, 1H), 6.08 (d, *J* = 16.2 Hz, 0.07), 5.97 (d, *J* = 16.2 Hz, 0.93H), 4.53 (s, 2H), 3.67 (dd, *J* = 9.0, 2.6 Hz, 1H), 3.61 (dd, *J* = 9.0, 2.6 Hz, 1H), 3.42 (t, *J* = 9.0 Hz, 1H), 2.59 (bs, 1H), 2.39 (s, 3H), 1.48-1.41 (m, 2H), 1.31-1.21 (m, 2H), 0.99 (s, 2.79H, major), 0.96 (s. 0.21H, minor), 0.87 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 149.4, 138.5, 138.1, 137.1, 136.5, 136.0, 133.7, 130.6, 129.6, 128.6, 128.2, 127.84, 127.81, 126.7, 125.0, 121.9, 76.5, 73.5, 71.9, 43.2, 40.7, 21.2, 18.5, 17.3, 15.0. HRMS (ESI/[M+H]$^+$) calcd. for $C_{28}H_{34}NO_2^+$, 416.2584. Found [M+H]$^+$, 416.2570.

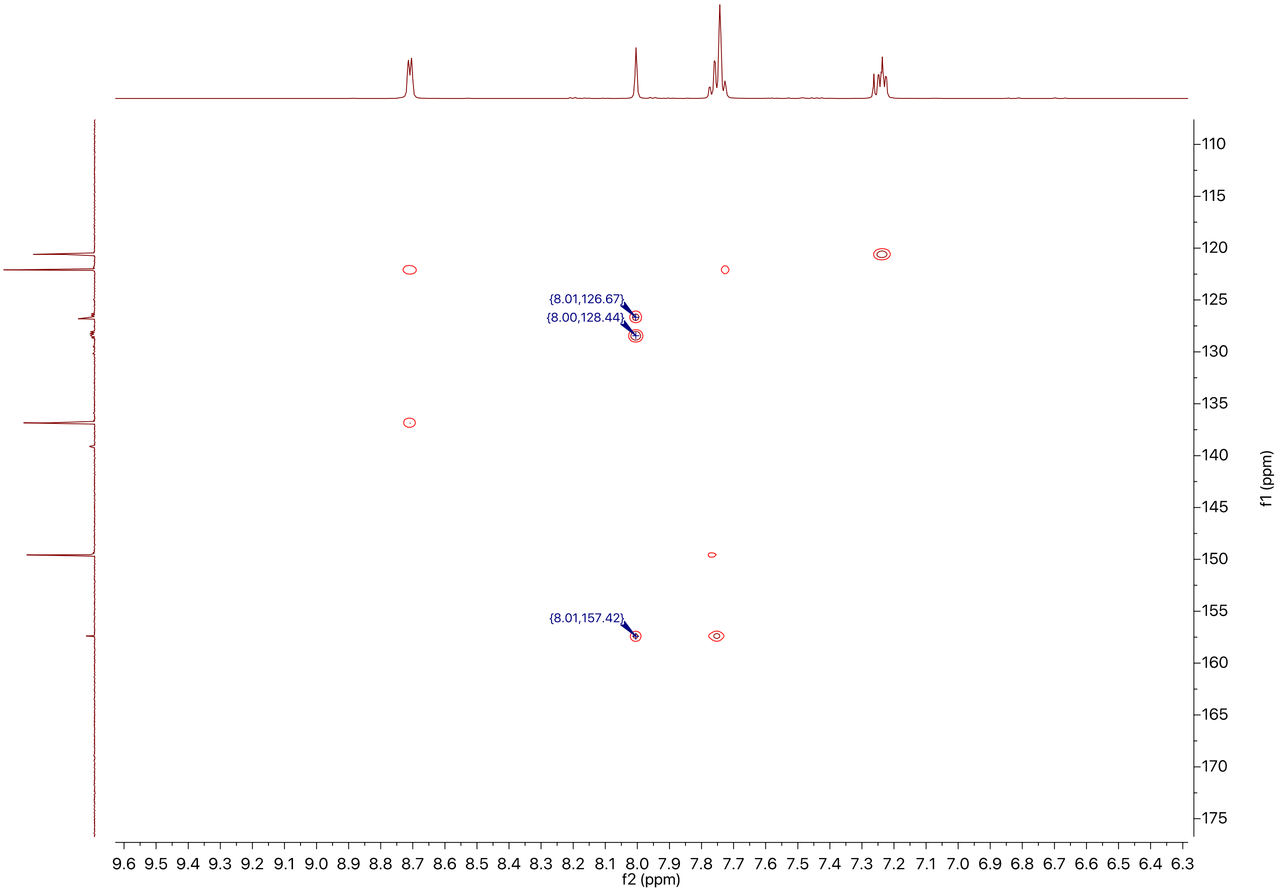
V. Mechanism Experiments

A. Reversibility of C–H bond activation step



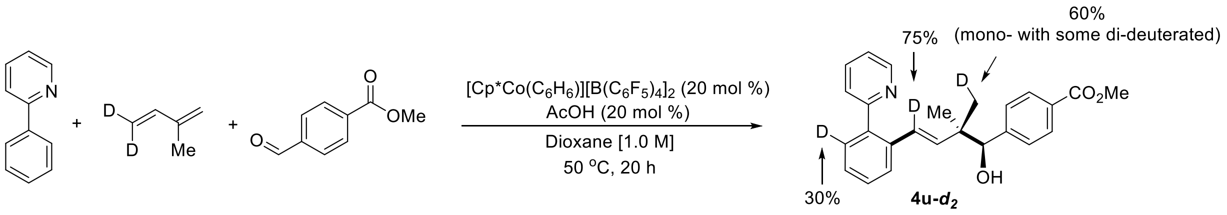
In order to investigate the reversibility of the C–H bond activation step, studies were conducted with 2-(phenyl-d_5)pyridine, which was made according to the literature procedure[7] and the characterization data matched those reported in the literature.[19]In a N_2-filled glove box, a 2.0–5.0 mL Biotage® microwave vial with a triangular stir bar (1 x 0.5 cm) was charged with 2-(phenyl-d_5)pyridine (32.1 mg, 0.200 mmol, 1.00 equiv) and [Cp*Co(C_6H_6)][B(C_6F_5)$_4$]$_2$ (65.2 mg, 0.0400 mmol, 0.200 equiv). Following this, 67 µL of a [0.6 M] stock solution of acetic acid in 1,4-dioxane followed by 133 µL of 1,4-dioxane were added. Methyl 4-formylbenzoate (32.1 mg, 0.600 mmol, 3.00 equiv) and isoprene (54.5 mg, 0.800 mmol, 4.00 equiv) were added successively. The reaction vial was then sealed and taken outside the glove box. The reaction mixture was stirred in a preheated oil bath at 50 °C for 30 min. The reaction vial was then cooled to room temperature and uncapped. The reaction was quenched with saturated $NaHCO_3$ (5 mL), and the resulting mixture was then extracted with ethyl acetate (5 x 3 mL). The organic layers were combined and dried over Na_2SO_4. The mixture was filtered through a celite plug using ethyl acetate as the eluent, and the resulting mixture was then concentrated. The NMR yield (18%) of the alcohol product was determined relative to 1,3,5-trimethoxybenzene as an external standard. The starting material C–H bond substrate was recovered by silica gel chromatography as a yellow oil (18.5 mg, 58% recovery). Approximately 28% H/D exchange at the ortho positions was observed by ^{1}H NMR, indicating reversible C–H activation. The site of H/D exchange was further confirmed by HMBC experiments of the recovered C–H bond substrate mixture. The spectra are shown below.


8.00
7.78
7.77
7.76
7.76
7.75
7.74
7.74
7.73
7.73
7.72
7.26
7.25
7.25
7.24
7.24
7.23
7.23
7.22
N
D
D
D
D
D
N
H
H
D
D
D
1.00
0.56
2.07
1.00
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
f1 (ppm)


{8.01,126.67}
{8.00,128.44}
{8.01,157.42}
110
115
120
125
130
135
140
145
150
155
160
165
170
175
f1 (ppm)
9.6 9.5 9.4 9.3 9.2 9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3
f2 (ppm)

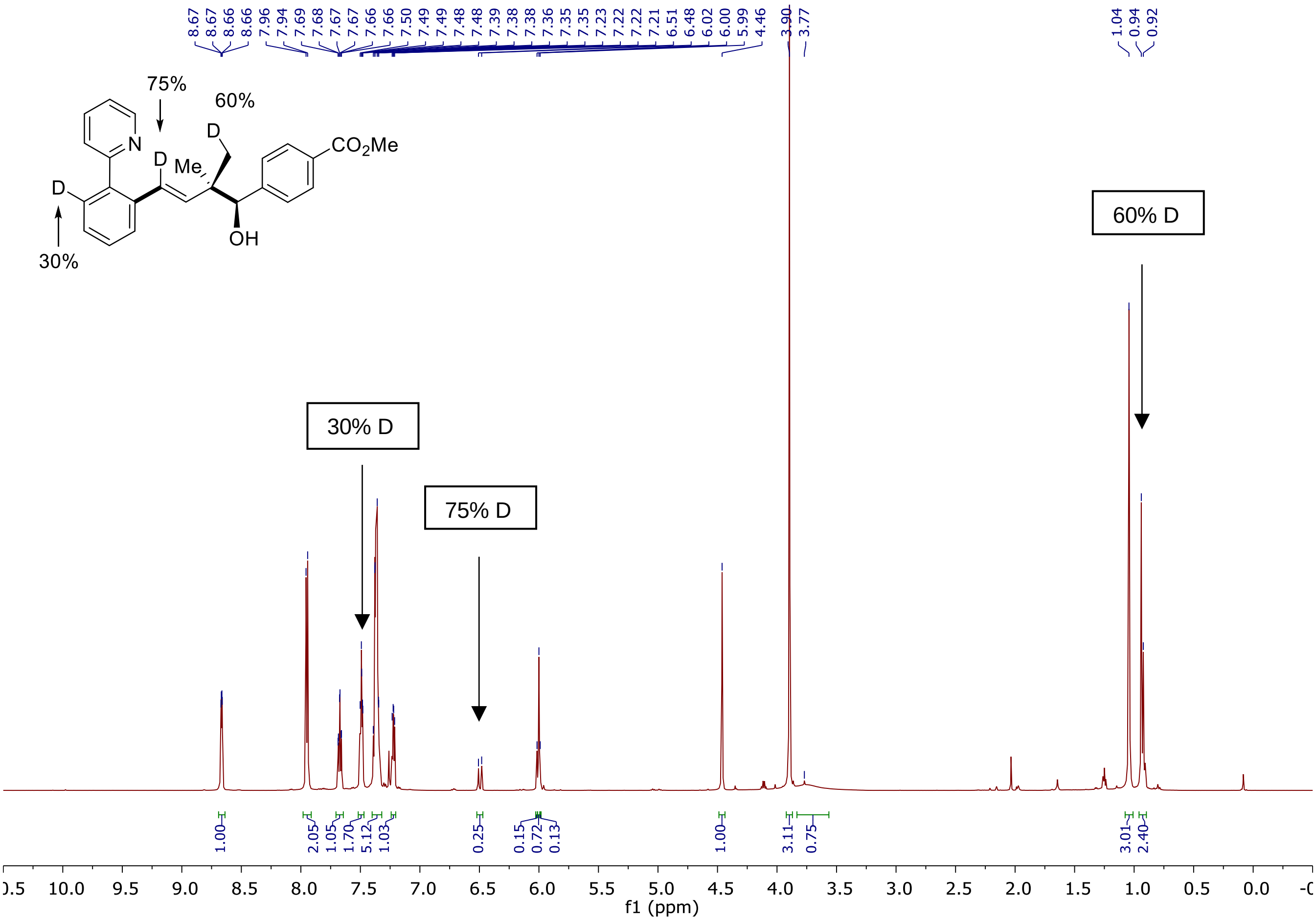
B. Investigation of 1,4-Deuterium Migration

Preparation of PPh_3CD_3I: PPh_3CD_3I was prepared by the following modified procedure based on the literature.[20] In a 250 three neck flask equipped with a reflux condenser under the N_2 atmosphere, Ph_3P (8.47 g, 32.3 mmol, 1.00 equiv) and THF (60 mL) was added. To the mixture was added CD_3I (2.4 mL, 38.6 mmol, 1.20 equiv) dropwise via a syringe over 5 min. The flask was placed in a preheated oil bath and was refluxed for 2 h. After 2 h, the reaction mixture was cooled to rt. The mixture was vacuum filtered and washed with diethyl ether. The white solid (12.5 g, 95%) was dried under vacuum overnight prior to use (100%-*d*$_3$). The spectroscopic properties of this compound were consistent with the data available in the literature.[20]



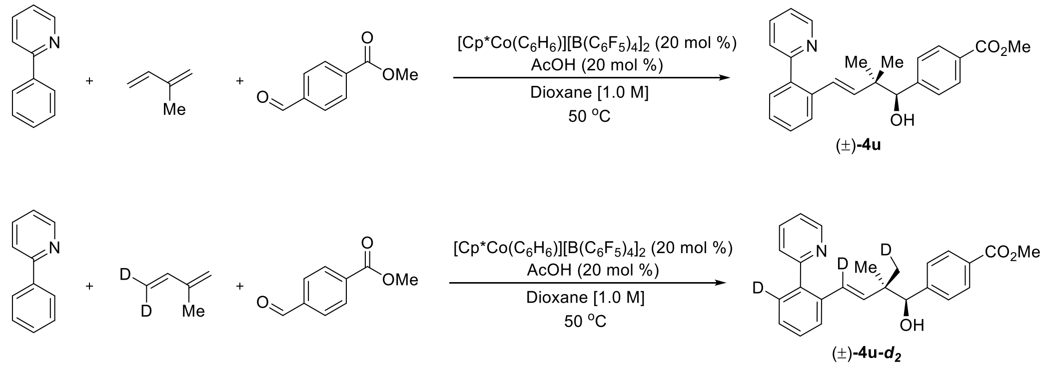
4u-*d*$_2$

Methyl 4-((1S,2R,E)-1-hydroxy-2-methyl-2-(methyl-d)-4-(2-(pyridin-2-yl)phenyl)but-3-en-1-yl-4-d)benzoate (4u-*d*$_2$): Isoprene-*d*$_2$ was prepared based on the literature procedure.[21] The general procedure A was followed using 2-phenylpyridine (31.0 mg, 0.200 mmol, 1.00 equiv), Isoprene-*d*$_2$ (56.2 mg, 0.800 mmol, 4.00 equiv) and methyl 4-formylbenzoate (98.5 mg, 0.600 mmol, 3.00 equiv). Purification by silica gel chromatography (40% ethyl acetate in hexane) provided the product **4u-*d*$_2$** (55.4 mg, 71% yield) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.67-8.66 (m, 1H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.69-7.66 (m, 1H), 7.50-7.48 (m, 1.70H), 7.40-7.34 (m, 5H), 7.25-7.19 (m, 1H), 6.50 (d, *J* = 16.2 Hz, 0.25H), 6.00 (d, *J* = 16.2 Hz, 0.28H), 6.00 (m, 0.72H) 4.46 (s, 1H), 3.90 (s, 3H), 3.77 (bs, 1H), 1.03 (s, 3H), 0.94-0.92 (m, 2.40H).



C. KIE experiments

Parallel kinetic experiments at early conversion



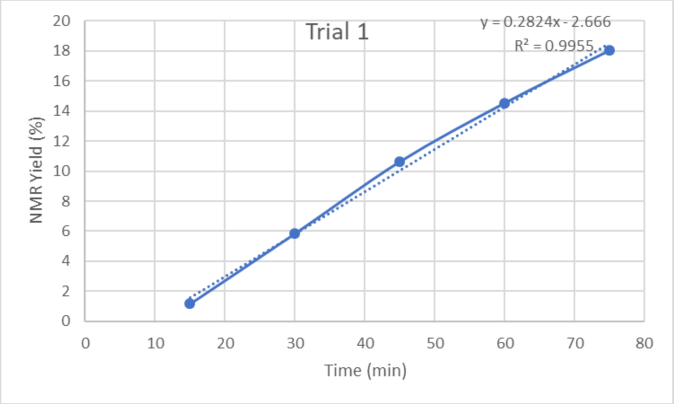
K_H/K_D =0.97 ± 0.08

In a N_2-filled glove box, equipped with a stir bar was charged 2-phenylpyridine (31.0 mg, 0.200 mmol, 1.00 equiv) and $[Cp^*Co(C_6H_6)][B(C_6F_5)_4]_2$ (65.2 mg, 0.0400 mmol, 0.200 equiv). Following this, 67 μL of a [0.6 M] stock solution of acetic acid in 1,4-dioxane followed by 133 μL of 1,4-dioxane were added. Methyl 4-formylbenzoate (0.600 mmol, 3.00 equiv) and trimethoxybenzene (11.2 mg, 0.200 mol, 1.00 equiv) was added. Next, either isoprene **2** (54.5 mg, 0.800 mmol, 4.00 equiv) or isoprene-*d₂*, **2- *d₂*** (56.2 mg, 0.800 mmol, 4.00 equiv) were added successively. The reaction vial was then sealed and taken outside the glove box. The reaction mixture was stirred in a preheated oil bath at 50 °C. At the designated time, an aliquot of approximately 0.02 mL was taken out and worked up with 1 mL of saturated $NaHCO_3$ and 1 mL of diethyl ether. The combined organic layer was dried under Na_2SO_4 and filtered through celite. At each time point, this was repeated, and the yield of **4u** and **4u-*d₂*** was analyzed by crude NMR yield relative to the trimethoxybenzene peak.

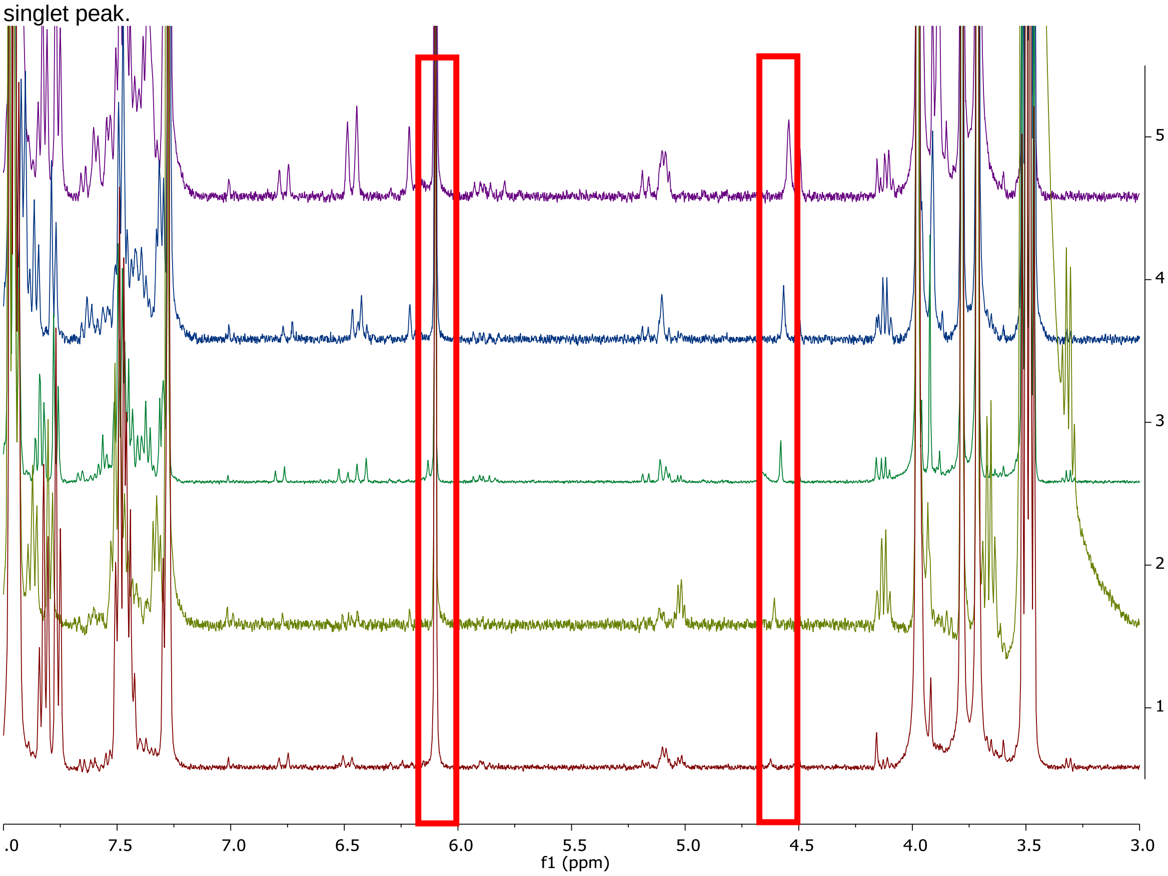
C-1. Initial Rates for 4u

Trial 1		Trial 2	
Time (min)	NMR Yield (%)	Time (min)	NMR Yield (%)
15	1.18	15	1.12
30	5.85	30	4.79
45	10.63	45	8.42
60	14.53	60	12.84
75	18.02	75	16.95

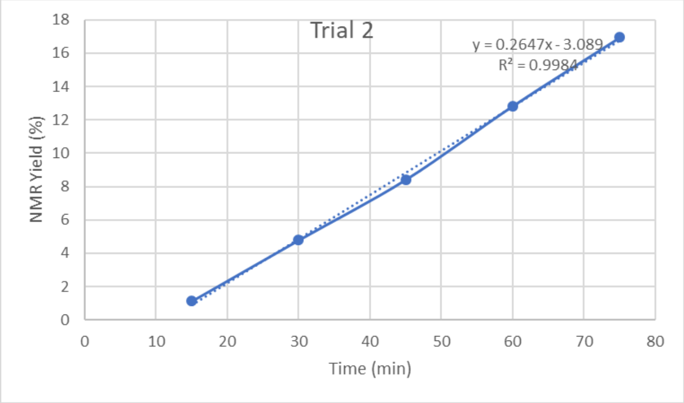
Trial 1. **4u** yield (%) plotted against each time point (min).



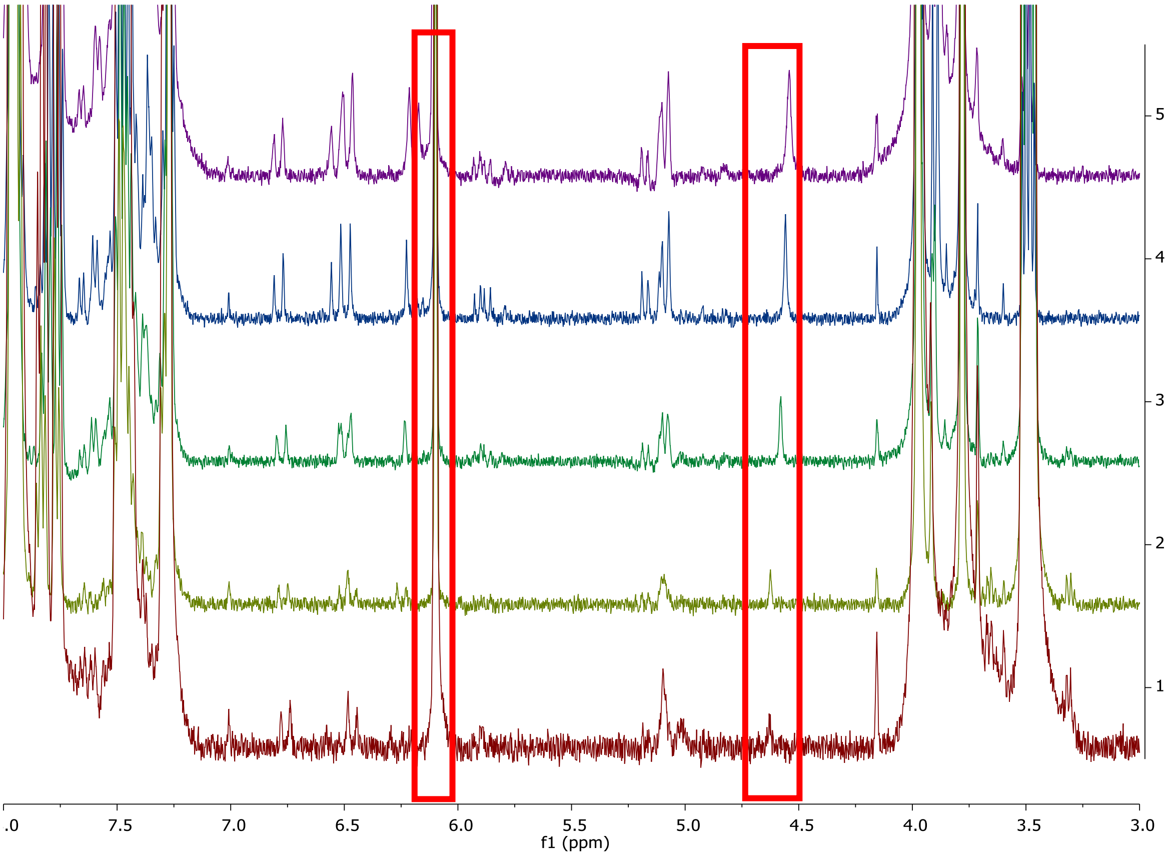
Trial 1. ^{1}H NMR stacked at each time points (at 15, 30, 45, 60, 75 min), comparing trimethoxy benzene (6.1 ppm) and the product **4u** singlet peak.



Trial 2. **4u** yield (%) plotted against each time point (min).



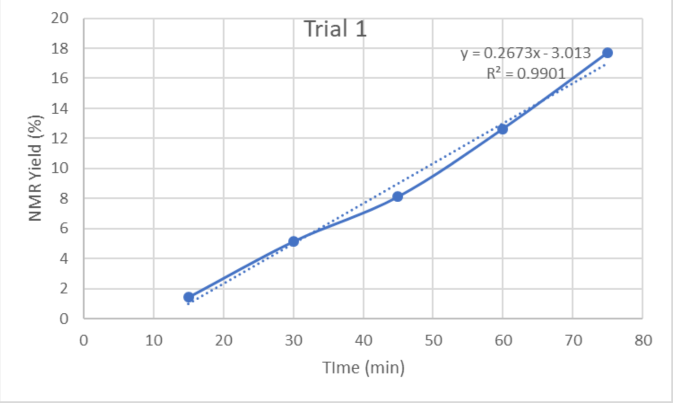
Trial 2. ^{1}H NMR stacked at each time points (at 15, 30, 45, 60, 75 min), comparing trimethoxy benzene (6.1 ppm) and the product **4u** singlet peak.



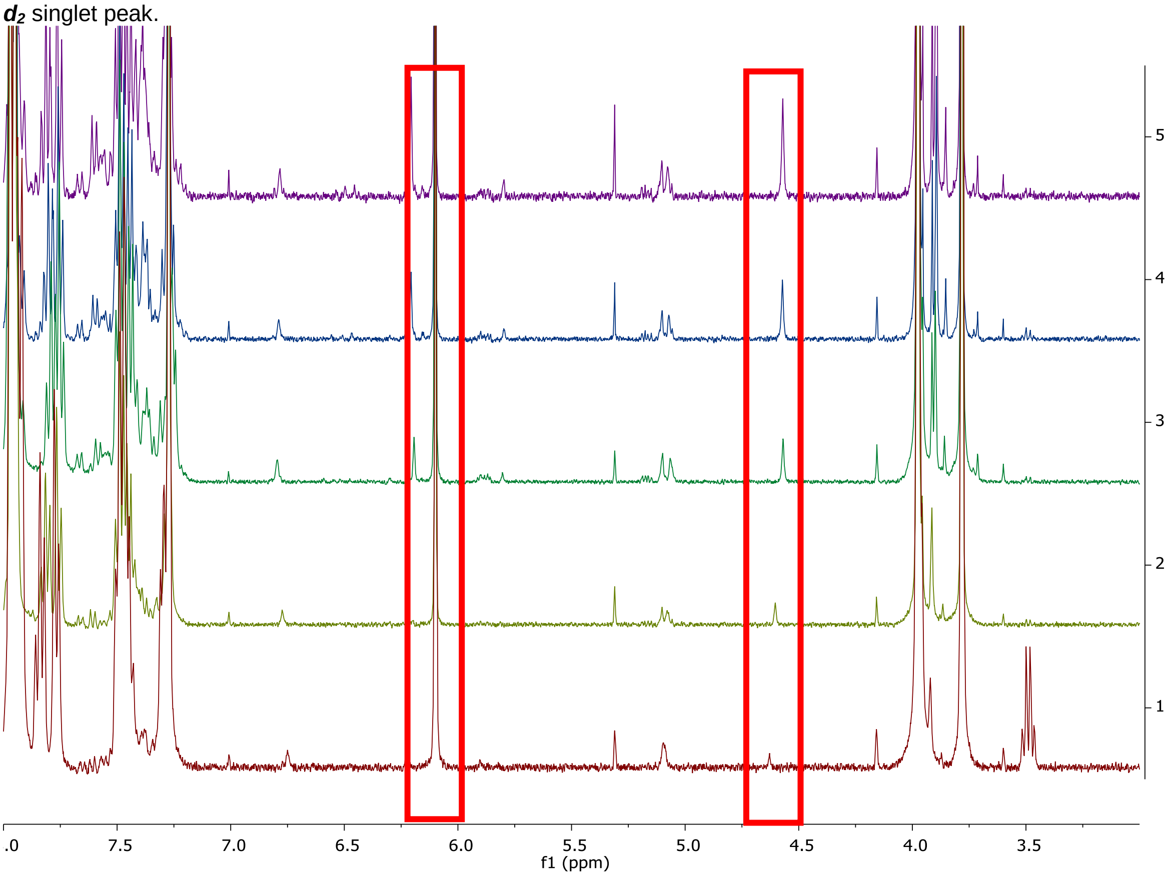
C-2. Initial Rates for 4u-d_2

Trial 1		Trial 2	
Time (min)	NMR Yield (%)	Time (min)	NMR Yield (%)
15	1.43	15	1.67
30	5.14	30	6.27
45	8.13	45	11.17
60	12.65	60	15.45
75	17.72	75	19.27

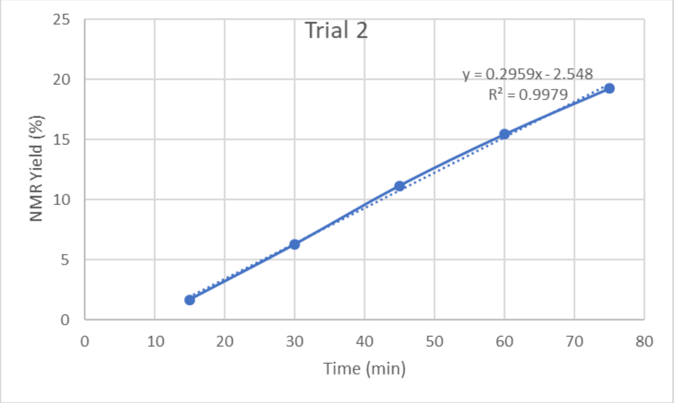
Trial 1. **4u-d_2** yield (%) plotted against each time point (min).



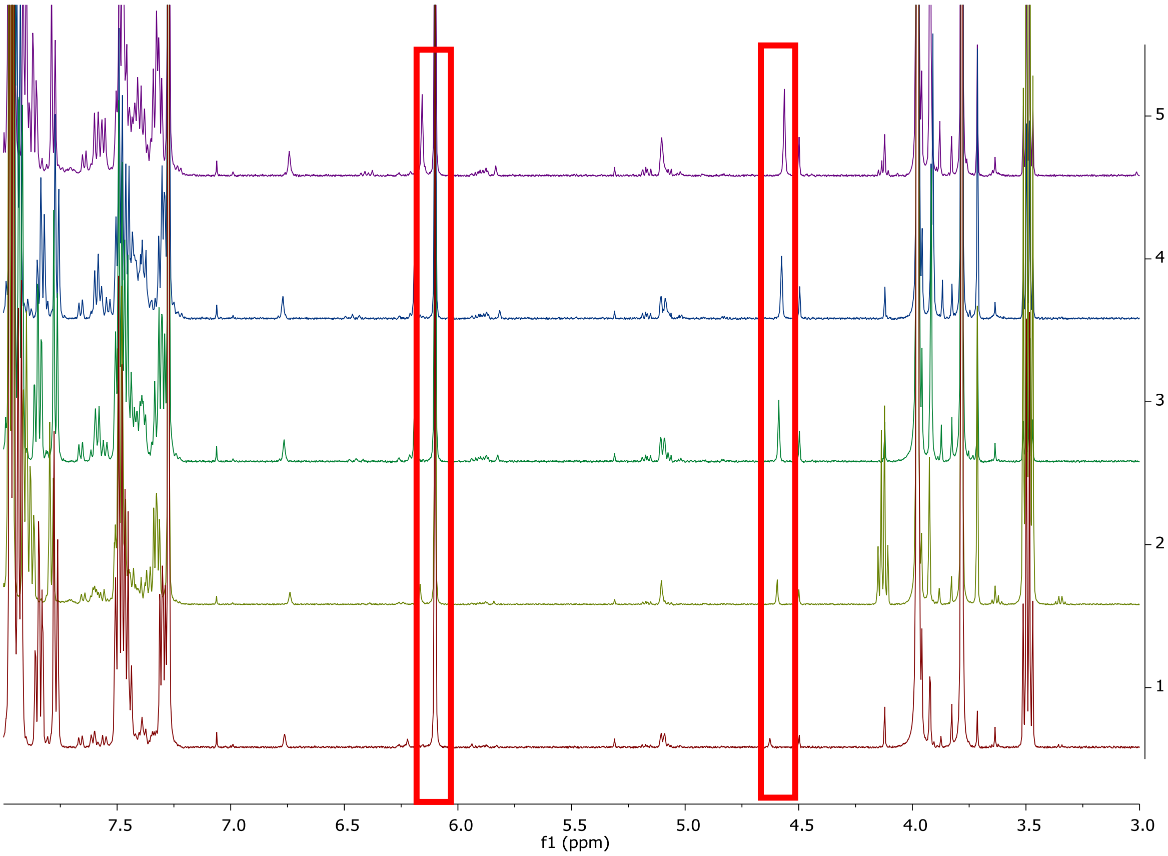
Trial 1. ^{1}H NMR stacked at each time points (at 15, 30, 45, 60, 75 min), comparing trimethoxy benzene (6.1 ppm) and the product **4u-d_2** singlet peak.



Trial 2. **4u-*d*$_2$** yield (%) plotted against each time point (min).



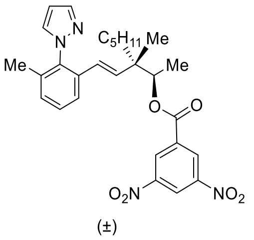
Trial 2. ^{1}H NMR stacked at each time points (at 15, 30, 45, 60, 75 min), comparing trimethoxy benzene (6.1 ppm) and the product **4u-*d*$_2$** singlet peak.



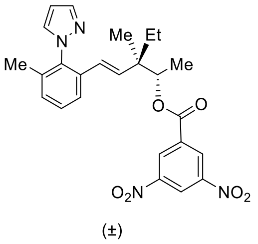
C-3. K_H/K_D Value

Initial Rates for **4u**	
Slope of 1st Run	0.2824
Slope of 2nd Run	0.2647
Average Slope	0.2736
Std Deviation	0.0126
Initial Rates for **4u-*d₂***	
Slope of 1st Run	0.2673
Slope of 2nd Run	0.2959
Average Slope	0.2816
Std Deviation	0.0202
K_H/K_D	0.97 ± 0.08

VI. 3,5-Dinitrobenzoylated Derivatives of 6a and 8a



(±)-(2*R*,3*S*)-3-Methyl-3-((*E*)-3-methyl-2-(1H-pyrazol-1-yl)styryl)octan-2-yl 3,5-dinitrobenzoate: To an oven-dried microwave vial equipped with a stir bar was added 3,5-dinitrobenzoyl chloride (16.9 mg, 0.0735 mmol, 2.00 equiv). The vial was then capped with a microwave cap and equipped with a N_2-inlet. Pyridine (0.3 mL) was then added, and the solution was cooled to 0 °C. Then **6a** (12.0 mg, 0.0368 mmol, 1.00 equiv) dissolved in pyridine (0.5 mL) was transferred to the reaction vial via a syringe (total pyridine: 0.8 mL). The vial was kept at 0 °C for 10 min and then allowed to warm to rt, and the reaction mixture was stirred at rt for 5 h. The reaction was quenched with water followed by addition of a saturated solution of $CuSO_4\cdot 5H_2O$ (2 mL), and the resulting mixture was extracted with ethyl acetate (3 x 4 mL). The organic extract was dried over Na_2SO_4 and concentrated under reduced pressure. The product was purified by silica gel chromatography (30% ethyl acetate in hexane) to afford the 3,5-dinitrobenzoylated derivative of **6a** (16.8 mg, 88% yield) as a white solid (mp: 128-130 °C). IR (neat): 2935, 2870, 2359, 1726, 1546, 1347, 1275 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.20 (t, *J* = 2.1 Hz, 1H), 9.05 (d, *J* = 2.1 Hz, 2H), 7.68-7.67 (m, 1H), 7.40-7.37 (m, 2H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 7.2 Hz, 1H), 6.41 (t, *J* = 2.1 Hz, 1H), 6.03 (d, *J* = 16.3 Hz, 1H), 5.70 (d, *J* = 16.3 Hz, 1H), 5.15 (q, *J* = 6.4 Hz, 1H), 1.99 (s, 3H), 1.40-1.35 (m, 2H), 1.28 (d, *J* = 6.5 Hz, 3H), 1.26-1.24 (m, 2H), 1.23-1.11 (m, 4H) 0.98 (s, 3H), 0.86 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.1, 148.8, 140.3, 137.7, 137.5, 136.7, 136.0, 134.5, 131.5, 129.6, 129.44, 129.35, 125.2, 123.7, 122.4, 106.1, 79.3, 44.2, 37.8, 32.6, 23.8, 22.7, 18.2, 17.4, 15.2, 14.2. HRMS (ESI/[M+H]$^+$) calcd. for $C_{28}H_{33}N_4O_6^+$, 521.2395. Found [M+H]$^+$, 521.2408.



(±)-(2*R*,3*R*,*E*)-3-Ethyl-3-methyl-5-(3-methyl-2-(1H-pyrazol-1-yl)phenyl)pent-4-en-2-yl 3,5-dinitrobenzoate : To an oven-dried microwave vial equipped with a stir bar was added 3,5-dinitrobenzoyl chloride 3,5-dinitrobenzoyl chloride (81.1 mg, 0.352 mmol, 2.00 equiv). The vial was then capped with a microwave cap and equipped with a N_2-inlet. Pyridine (0.8 mL) was then added, and the solution was cooled to 0 °C. Then **8a** (50.0 mg, 0.176 mmol, 1.00 equiv) dissolved in pyridine (1 mL) was transferred to the reaction vial via a syringe (total pyridine: 1.8 mL). The vial was kept at 0 °C for 10 min and then allowed to warm to rt, and the reaction mixture was stirred at rt for 5h. The reaction was quenched with water followed by addition of a saturated solution of $CuSO_4\cdot 5H_2O$ (2 mL), and the resulting mixture was extracted with ethyl acetate (3 x 4 mL). The organic extract was dried over Na_2SO_4 and concentrated under reduced pressure. The product was isolated by silica gel chromatography (30% ethyl acetate in hexane) to afford the 3,5-dinitrobenzoylated derivative of **8a** (68.3 mg, 81%) as a white solid (mp: 124-126 °C). IR (neat): 3115, 2926, 1740, 1545, 1346, 1276 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.23-9.21 (m, 1H), 9.10-9.09 (m, 2H), 7.73-7.71 (m, 1H), 7.46-7.45 (m, 1H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 6.45-6.43 (m, 1H), 5.93 (d, *J* = 16.4 Hz, 1H), 5.78 (d, *J* = 16.4 Hz, 1H), 5.15 (q, *J* = 6.4 Hz, 1H), 2.04 (s, 3H), 1.47-1.41 (m, 2H), 1.26 (d, *J* = 6.9 Hz, 3H), 1.01 (s, 3H), 0.77 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.1, 148.8, 140.3, 137.8, 136.7, 136.6, 136.2, 134.5, 131.6, 129.7, 129.5, 129.4, 125.8, 123.9, 122.4, 106.2, 79.3, 44.0, 30.1, 17.9, 17.4, 15.5, 8.4. HRMS (ESI/[M+H]$^+$) calcd. for $C_{25}H_{27}N_4O_6^+$, 479.1925. Found [M+H]$^+$, 479.1935.

VII. X-Ray Crystallographic Data for 3,5-dinitrobenzoylated derivatives of 6a and 8a

Experimental for 3,5-dinitrobenzoylated derivative of 6a

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα (λ = 1.54178 Å) for the structure of 3,5-dinitrobenzoylated derivative of **6a**. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The atoms C1 to C7 and O1 are disordered over two positions. The site occupancies are freely refined to converged values of 0.55/0.45. The major and minor orientations are distinguished by the suffixes "A" and "B". All chemically similar bond distances are restrained to be similar. No additional restraints or constraints were needed for a stable refinement. The full numbering scheme of compound 3,5-dinitrobenzoylated derivative of **6a** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 1917393 (007b-19035) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

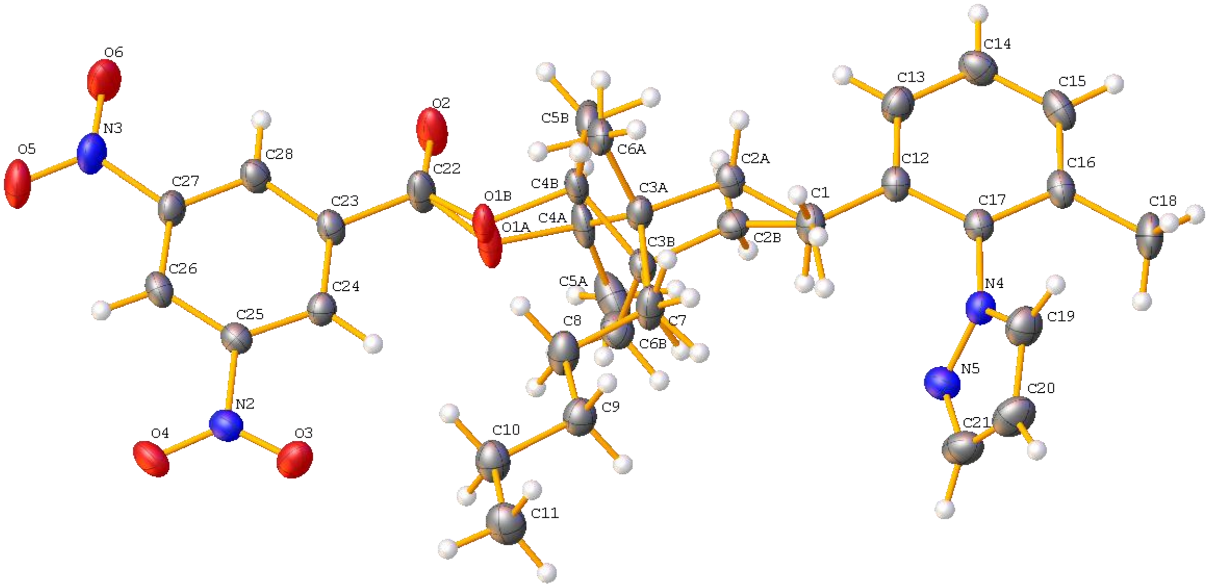


Figure S1. The complete numbering scheme of 3,5-dinitrobenzoylated derivative of **6a** with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.

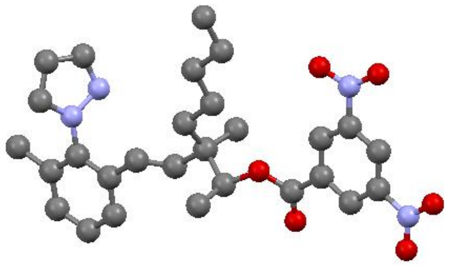


Figure S2. Another perspective of thecrystal structure showing the indicated relative stereochemistry. The hydrogen atoms are omitted for clarity.

Table S2. Crystal data and structure refinement for 3,5-dinitrobenzoylated derivative of **6a**.

Identification code	007b-19035	
Empirical formula	C28 H34 N4 O6	
Formula weight	522.59	
Temperature	93(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 7.7273(2) Å	α= 90°.
	b = 31.6878(6) Å	β= 99.883(2)°.
	c = 10.8702(2) Å	γ= 90°.
Volume	2622.19(10) Å^3	
Z	4	
Density (calculated)	1.324 Mg/m^3	
Absorption coefficient	0.771 mm^{-1}	
F(000)	1112	
Crystal size	0.200 x 0.200 x 0.200 mm^3	
Crystal color and habit	Colorless Block	
Diffractometer	Rigaku Saturn 944+ CCD	
Theta range for data collection	2.789 to 66.594°.	
Index ranges	-9<=h<=9, -37<=k<=37, -12<=l<=12	
Reflections collected	89834	
Independent reflections	4612 [R(int) = 0.0547]	
Observed reflections (I > 2sigma(I))	4214	
Completeness to theta = 66.594°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.73443	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	4612 / 10 / 405	
Goodness-of-fit on F^2	1.063	
Final R indices [I>2sigma(I)]	R1 = 0.0478, wR2 = 0.1276	
R indices (all data)	R1 = 0.0515, wR2 = 0.1306	
Extinction coefficient	0.0061(4)	
Largest diff. peak and hole	0.534 and -0.507 e.Å^{-3}	

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 3,5-dinitrobenzoylated derivative of **6a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1B)	7956(9)	6620(3)	5406(7)	29(2)
O(1A)	7353(8)	6639(2)	5431(6)	37(2)
O(2)	8115(2)	7323(1)	5791(1)	45(1)
O(3)	8027(2)	5643(1)	8791(1)	40(1)
O(4)	8851(2)	5850(1)	10702(1)	35(1)
O(5)	11901(2)	7184(1)	11413(1)	42(1)
O(6)	11766(2)	7630(1)	9889(1)	53(1)
N(2)	8603(2)	5909(1)	9575(1)	28(1)
N(3)	11415(2)	7291(1)	10328(1)	35(1)
N(4)	3502(2)	5816(1)	-836(1)	26(1)
N(5)	2422(2)	5740(1)	7(1)	32(1)
C(1)	5442(2)	6332(1)	1087(2)	30(1)
C(2B)	5494(7)	6547(1)	2144(3)	25(1)
C(2A)	6510(6)	6559(1)	1969(3)	24(1)
C(3B)	6033(5)	6401(1)	3493(3)	25(1)
C(3A)	7273(4)	6410(1)	3282(3)	25(1)
C(4B)	7583(7)	6684(1)	4033(3)	25(1)
C(4A)	6487(6)	6716(1)	4141(3)	32(1)
C(5B)	9247(16)	6610(3)	3543(13)	37(2)
C(5A)	4558(9)	6689(2)	4105(6)	45(1)
C(6B)	4445(9)	6499(2)	4153(7)	31(1)
C(6A)	9279(12)	6471(2)	3444(10)	31(2)
C(7)	6680(3)	5933(1)	3494(2)	35(1)
C(8)	7248(3)	5742(1)	4799(2)	35(1)
C(9)	7326(2)	5261(1)	4789(2)	31(1)
C(10)	7893(3)	5079(1)	6095(2)	34(1)
C(11)	8024(3)	4601(1)	6121(2)	39(1)
C(12)	4845(2)	6498(1)	-179(2)	24(1)
C(13)	5176(2)	6914(1)	-495(2)	30(1)
C(14)	4606(2)	7066(1)	-1686(2)	33(1)
C(15)	3689(2)	6807(1)	-2593(2)	32(1)
C(16)	3324(2)	6391(1)	-2330(2)	27(1)
C(17)	3914(2)	6241(1)	-1120(2)	24(1)

C(18)	2254(3)	6118(1)	-3318(2)	37(1)
C(19)	3910(2)	5455(1)	-1390(2)	35(1)
C(20)	3083(3)	5132(1)	-898(2)	41(1)
C(21)	2192(2)	5325(1)	-40(2)	37(1)
C(22)	8132(3)	6962(1)	6138(2)	34(1)
C(23)	8763(2)	6829(1)	7459(2)	25(1)
C(24)	8403(2)	6429(1)	7887(2)	24(1)
C(25)	9010(2)	6329(1)	9116(2)	24(1)
C(26)	9998(2)	6602(1)	9948(2)	26(1)
C(27)	10340(2)	6993(1)	9482(2)	26(1)
C(28)	9746(2)	7116(1)	8262(2)	26(1)

Table S4. Bond lengths [Å] and angles [°] for 3,5-dinitrobenzoylated derivative of **6a**.

O(1B)-C(22)	1.339(8)
O(1B)-C(4B)	1.485(8)
O(1A)-C(22)	1.359(7)
O(1A)-C(4A)	1.467(7)
O(2)-C(22)	1.203(2)
O(3)-N(2)	1.2267(19)
O(4)-N(2)	1.2210(18)
O(5)-N(3)	1.2232(19)
O(6)-N(3)	1.224(2)
N(2)-C(25)	1.473(2)
N(3)-C(27)	1.471(2)
N(4)-C(19)	1.355(2)
N(4)-N(5)	1.362(2)
N(4)-C(17)	1.429(2)
N(5)-C(21)	1.328(2)
C(1)-C(2B)	1.332(4)
C(1)-C(2A)	1.359(4)
C(1)-C(12)	1.472(2)
C(1)-H(1AA)	0.9900
C(1)-H(1AB)	0.9900
C(1)-H(1BC)	0.9900
C(1)-H(1BD)	0.9900
C(2B)-C(3B)	1.525(5)
C(2B)-H(2BA)	0.9900
C(2B)-H(2BB)	0.9900
C(2A)-C(3A)	1.522(4)
C(2A)-H(2AA)	0.9900
C(2A)-H(2AB)	0.9900
C(3B)-C(4B)	1.530(6)
C(3B)-C(6B)	1.555(8)
C(3B)-C(7)	1.567(4)
C(3A)-C(4A)	1.541(5)
C(3A)-C(6A)	1.542(10)
C(3A)-C(7)	1.609(3)
C(4B)-C(5B)	1.492(12)
C(4B)-H(4B)	1.0000

C(4A)-C(5A)	1.487(8)
C(4A)-H(4A)	1.0000
C(5B)-H(5BA)	0.9800
C(5B)-H(5BB)	0.9800
C(5B)-H(5BC)	0.9800
C(5A)-H(5AA)	0.9800
C(5A)-H(5AB)	0.9800
C(5A)-H(5AC)	0.9800
C(6B)-H(6BA)	0.9800
C(6B)-H(6BB)	0.9800
C(6B)-H(6BC)	0.9800
C(6A)-H(6AA)	0.9800
C(6A)-H(6AB)	0.9800
C(6A)-H(6AC)	0.9800
C(7)-C(8)	1.535(2)
C(7)-H(7BC)	0.9900
C(7)-H(7BD)	0.9900
C(7)-H(7AA)	0.9900
C(7)-H(7AB)	0.9900
C(8)-C(9)	1.526(2)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.524(2)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-C(11)	1.518(2)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-C(13)	1.396(2)
C(12)-C(17)	1.405(2)
C(13)-C(14)	1.380(3)
C(13)-H(13)	0.9500
C(14)-C(15)	1.381(3)
C(14)-H(14)	0.9500
C(15)-C(16)	1.388(2)

C(15)-H(15)	0.9500
C(16)-C(17)	1.399(2)
C(16)-C(18)	1.510(2)
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-C(20)	1.364(3)
C(19)-H(19)	0.9500
C(20)-C(21)	1.391(3)
C(20)-H(20)	0.9500
C(21)-H(21)	0.9500
C(22)-C(23)	1.496(2)
C(23)-C(28)	1.392(2)
C(23)-C(24)	1.393(2)
C(24)-C(25)	1.375(2)
C(24)-H(24)	0.9500
C(25)-C(26)	1.382(2)
C(26)-C(27)	1.382(2)
C(26)-H(26)	0.9500
C(27)-C(28)	1.382(2)
C(28)-H(28)	0.9500

C(22)-O(1B)-C(4B)	117.9(7)
C(22)-O(1A)-C(4A)	120.0(6)
O(4)-N(2)-O(3)	124.54(14)
O(4)-N(2)-C(25)	118.14(14)
O(3)-N(2)-C(25)	117.31(13)
O(5)-N(3)-O(6)	124.51(15)
O(5)-N(3)-C(27)	118.22(14)
O(6)-N(3)-C(27)	117.26(14)
C(19)-N(4)-N(5)	111.42(14)
C(19)-N(4)-C(17)	128.43(14)
N(5)-N(4)-C(17)	119.84(13)
C(21)-N(5)-N(4)	104.12(15)
C(2B)-C(1)-C(12)	125.5(2)
C(2A)-C(1)-C(12)	121.61(19)
C(2B)-C(1)-H(1AA)	106.0
C(12)-C(1)-H(1AA)	106.0

C(2B)-C(1)-H(1AB)	106.0
C(12)-C(1)-H(1AB)	106.0
H(1AA)-C(1)-H(1AB)	106.3
C(2A)-C(1)-H(1BC)	106.9
C(12)-C(1)-H(1BC)	106.9
C(2A)-C(1)-H(1BD)	106.9
C(12)-C(1)-H(1BD)	106.9
H(1BC)-C(1)-H(1BD)	106.7
C(1)-C(2B)-C(3B)	129.6(3)
C(1)-C(2B)-H(2BA)	104.9
C(3B)-C(2B)-H(2BA)	104.9
C(1)-C(2B)-H(2BB)	104.9
C(3B)-C(2B)-H(2BB)	104.9
H(2BA)-C(2B)-H(2BB)	105.8
C(1)-C(2A)-C(3A)	126.0(3)
C(1)-C(2A)-H(2AA)	105.8
C(3A)-C(2A)-H(2AA)	105.8
C(1)-C(2A)-H(2AB)	105.8
C(3A)-C(2A)-H(2AB)	105.8
H(2AA)-C(2A)-H(2AB)	106.2
C(2B)-C(3B)-C(4B)	104.9(3)
C(2B)-C(3B)-C(6B)	106.1(4)
C(4B)-C(3B)-C(6B)	109.5(4)
C(2B)-C(3B)-C(7)	108.8(3)
C(4B)-C(3B)-C(7)	109.0(3)
C(6B)-C(3B)-C(7)	117.8(3)
C(2A)-C(3A)-C(4A)	104.1(2)
C(2A)-C(3A)-C(6A)	106.7(5)
C(4A)-C(3A)-C(6A)	110.2(4)
C(2A)-C(3A)-C(7)	110.5(2)
C(4A)-C(3A)-C(7)	110.7(3)
C(6A)-C(3A)-C(7)	114.0(3)
O(1B)-C(4B)-C(5B)	107.9(7)
O(1B)-C(4B)-C(3B)	108.0(4)
C(5B)-C(4B)-C(3B)	116.0(5)
O(1B)-C(4B)-H(4B)	108.3
C(5B)-C(4B)-H(4B)	108.3
C(3B)-C(4B)-H(4B)	108.3

O(1A)-C(4A)-C(5A)	107.9(4)
O(1A)-C(4A)-C(3A)	108.2(4)
C(5A)-C(4A)-C(3A)	116.5(4)
O(1A)-C(4A)-H(4A)	108.0
C(5A)-C(4A)-H(4A)	108.0
C(3A)-C(4A)-H(4A)	108.0
C(4B)-C(5B)-H(5BA)	109.5
C(4B)-C(5B)-H(5BB)	109.5
H(5BA)-C(5B)-H(5BB)	109.5
C(4B)-C(5B)-H(5BC)	109.5
H(5BA)-C(5B)-H(5BC)	109.5
H(5BB)-C(5B)-H(5BC)	109.5
C(4A)-C(5A)-H(5AA)	109.5
C(4A)-C(5A)-H(5AB)	109.5
H(5AA)-C(5A)-H(5AB)	109.5
C(4A)-C(5A)-H(5AC)	109.5
H(5AA)-C(5A)-H(5AC)	109.5
H(5AB)-C(5A)-H(5AC)	109.5
C(3B)-C(6B)-H(6BA)	109.5
C(3B)-C(6B)-H(6BB)	109.5
H(6BA)-C(6B)-H(6BB)	109.5
C(3B)-C(6B)-H(6BC)	109.5
H(6BA)-C(6B)-H(6BC)	109.5
H(6BB)-C(6B)-H(6BC)	109.5
C(3A)-C(6A)-H(6AA)	109.5
C(3A)-C(6A)-H(6AB)	109.5
H(6AA)-C(6A)-H(6AB)	109.5
C(3A)-C(6A)-H(6AC)	109.5
H(6AA)-C(6A)-H(6AC)	109.5
H(6AB)-C(6A)-H(6AC)	109.5
C(8)-C(7)-C(3B)	114.48(18)
C(8)-C(7)-C(3A)	117.32(16)
C(8)-C(7)-H(7BC)	108.0
C(3A)-C(7)-H(7BC)	108.0
C(8)-C(7)-H(7BD)	108.0
C(3A)-C(7)-H(7BD)	108.0
H(7BC)-C(7)-H(7BD)	107.2
C(8)-C(7)-H(7AA)	108.6

C(3B)-C(7)-H(7AA)	108.6
C(8)-C(7)-H(7AB)	108.6
C(3B)-C(7)-H(7AB)	108.6
H(7AA)-C(7)-H(7AB)	107.6
C(9)-C(8)-C(7)	113.13(14)
C(9)-C(8)-H(8A)	109.0
C(7)-C(8)-H(8A)	109.0
C(9)-C(8)-H(8B)	109.0
C(7)-C(8)-H(8B)	109.0
H(8A)-C(8)-H(8B)	107.8
C(10)-C(9)-C(8)	112.16(14)
C(10)-C(9)-H(9A)	109.2
C(8)-C(9)-H(9A)	109.2
C(10)-C(9)-H(9B)	109.2
C(8)-C(9)-H(9B)	109.2
H(9A)-C(9)-H(9B)	107.9
C(11)-C(10)-C(9)	113.72(15)
C(11)-C(10)-H(10A)	108.8
C(9)-C(10)-H(10A)	108.8
C(11)-C(10)-H(10B)	108.8
C(9)-C(10)-H(10B)	108.8
H(10A)-C(10)-H(10B)	107.7
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(13)-C(12)-C(17)	117.44(15)
C(13)-C(12)-C(1)	121.83(15)
C(17)-C(12)-C(1)	120.73(14)
C(14)-C(13)-C(12)	121.11(16)
C(14)-C(13)-H(13)	119.4
C(12)-C(13)-H(13)	119.4
C(13)-C(14)-C(15)	120.36(16)
C(13)-C(14)-H(14)	119.8
C(15)-C(14)-H(14)	119.8
C(14)-C(15)-C(16)	120.90(16)

C(14)-C(15)-H(15)	119.5
C(16)-C(15)-H(15)	119.5
C(15)-C(16)-C(17)	118.12(15)
C(15)-C(16)-C(18)	120.20(15)
C(17)-C(16)-C(18)	121.63(15)
C(16)-C(17)-C(12)	122.06(15)
C(16)-C(17)-N(4)	118.28(14)
C(12)-C(17)-N(4)	119.62(14)
C(16)-C(18)-H(18A)	109.5
C(16)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(16)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
N(4)-C(19)-C(20)	107.39(17)
N(4)-C(19)-H(19)	126.3
C(20)-C(19)-H(19)	126.3
C(19)-C(20)-C(21)	104.66(16)
C(19)-C(20)-H(20)	127.7
C(21)-C(20)-H(20)	127.7
N(5)-C(21)-C(20)	112.42(17)
N(5)-C(21)-H(21)	123.8
C(20)-C(21)-H(21)	123.8
O(2)-C(22)-O(1B)	126.1(4)
O(2)-C(22)-O(1A)	124.0(3)
O(2)-C(22)-C(23)	123.68(15)
O(1B)-C(22)-C(23)	108.9(4)
O(1A)-C(22)-C(23)	111.6(3)
C(28)-C(23)-C(24)	120.15(15)
C(28)-C(23)-C(22)	118.00(15)
C(24)-C(23)-C(22)	121.85(15)
C(25)-C(24)-C(23)	118.74(15)
C(25)-C(24)-H(24)	120.6
C(23)-C(24)-H(24)	120.6
C(24)-C(25)-C(26)	123.22(15)
C(24)-C(25)-N(2)	118.72(14)
C(26)-C(25)-N(2)	118.06(14)
C(27)-C(26)-C(25)	116.18(15)

C(27)-C(26)-H(26)	121.9
C(25)-C(26)-H(26)	121.9
C(26)-C(27)-C(28)	123.41(15)
C(26)-C(27)-N(3)	117.99(15)
C(28)-C(27)-N(3)	118.60(15)
C(27)-C(28)-C(23)	118.28(15)
C(27)-C(28)-H(28)	120.9
C(23)-C(28)-H(28)	120.9

Symmetry transformations used to generate equivalent atoms:

Table S5. Anisotropic displacement parameters (Å^{2}x 10^3) for 3,5-dinitrobenzoylated derivative of **6a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1B)	47(4)	23(2)	13(2)	0(1)	-6(2)	-2(3)
O(1A)	70(4)	20(2)	16(2)	0(1)	-9(2)	6(3)
O(2)	81(1)	23(1)	25(1)	3(1)	-9(1)	-4(1)
O(3)	50(1)	31(1)	35(1)	4(1)	-6(1)	-13(1)
O(4)	43(1)	40(1)	24(1)	10(1)	9(1)	-1(1)
O(5)	59(1)	38(1)	22(1)	-4(1)	-10(1)	-1(1)
O(6)	87(1)	36(1)	31(1)	-2(1)	-4(1)	-27(1)
N(2)	29(1)	29(1)	26(1)	5(1)	4(1)	-2(1)
N(3)	48(1)	31(1)	24(1)	-6(1)	-1(1)	-6(1)
N(4)	28(1)	25(1)	23(1)	0(1)	1(1)	-2(1)
N(5)	33(1)	32(1)	30(1)	4(1)	6(1)	-3(1)
C(1)	34(1)	30(1)	22(1)	-1(1)	-2(1)	6(1)
C(2B)	22(2)	27(2)	26(2)	1(2)	4(2)	-1(2)
C(2A)	31(2)	20(1)	20(2)	-1(1)	3(1)	4(1)
C(3B)	30(3)	29(2)	17(2)	-1(1)	2(2)	0(2)
C(3A)	33(2)	21(2)	19(2)	0(1)	-2(1)	-1(1)
C(4B)	39(3)	21(2)	14(2)	1(1)	-1(2)	0(2)
C(4A)	50(3)	30(2)	13(2)	2(1)	-4(2)	10(2)
C(5B)	36(3)	55(7)	19(3)	-6(4)	0(2)	-4(4)
C(5A)	49(3)	62(4)	23(2)	6(3)	6(2)	22(3)
C(6B)	31(2)	37(3)	26(3)	-4(3)	8(2)	2(3)
C(6A)	33(2)	38(4)	19(3)	2(3)	-3(2)	-4(3)
C(7)	54(1)	24(1)	24(1)	-2(1)	-7(1)	1(1)
C(8)	48(1)	28(1)	26(1)	-2(1)	-4(1)	4(1)
C(9)	34(1)	28(1)	29(1)	-2(1)	2(1)	1(1)
C(10)	43(1)	29(1)	29(1)	-2(1)	2(1)	5(1)
C(11)	49(1)	31(1)	37(1)	4(1)	6(1)	3(1)
C(12)	26(1)	26(1)	21(1)	-1(1)	2(1)	3(1)
C(13)	34(1)	26(1)	28(1)	-4(1)	1(1)	-2(1)
C(14)	42(1)	25(1)	33(1)	6(1)	9(1)	2(1)
C(15)	39(1)	36(1)	22(1)	7(1)	5(1)	8(1)
C(16)	28(1)	33(1)	19(1)	-1(1)	2(1)	5(1)
C(17)	25(1)	24(1)	21(1)	0(1)	3(1)	2(1)

C(18)	40(1)	45(1)	21(1)	-4(1)	-6(1)	4(1)
C(19)	39(1)	29(1)	35(1)	-6(1)	4(1)	0(1)
C(20)	44(1)	25(1)	50(1)	-2(1)	1(1)	-3(1)
C(21)	37(1)	30(1)	43(1)	7(1)	2(1)	-6(1)
C(22)	58(1)	22(1)	20(1)	-2(1)	0(1)	0(1)
C(23)	34(1)	23(1)	18(1)	-1(1)	4(1)	3(1)
C(24)	26(1)	23(1)	22(1)	-3(1)	3(1)	0(1)
C(25)	25(1)	24(1)	22(1)	2(1)	5(1)	1(1)
C(26)	30(1)	30(1)	17(1)	1(1)	4(1)	3(1)
C(27)	34(1)	25(1)	20(1)	-6(1)	2(1)	-1(1)
C(28)	36(1)	22(1)	21(1)	-1(1)	5(1)	1(1)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for 3,5-dinitrobenzoylated derivative of **6a**.

	x	y	z	U(eq)
H(1AA)	4709	6080	1162	35
H(1AB)	6651	6226	1096	35
H(1BC)	4376	6262	1437	35
H(1BD)	6048	6061	992	35
H(2BA)	4294	6662	2100	30
H(2BB)	6255	6793	2062	30
H(2AA)	5864	6822	2076	29
H(2AB)	7529	6642	1582	29
H(4B)	7224	6984	3866	30
H(4A)	6773	7010	3912	38
H(5BA)	10132	6816	3912	56
H(5BB)	9027	6642	2633	56
H(5BC)	9675	6324	3762	56
H(5AA)	4267	6416	4437	67
H(5AB)	3951	6718	3240	67
H(5AC)	4186	6916	4613	67
H(6BA)	3452	6318	3806	47
H(6BB)	4108	6796	4019	47
H(6BC)	4775	6445	5050	47
H(6AA)	9810	6415	4314	46
H(6AB)	9539	6762	3228	46
H(6AC)	9764	6275	2893	46
H(7BC)	5382	5920	3291	42
H(7BD)	7143	5750	2886	42
H(7AA)	5722	5758	3031	42
H(7AB)	7683	5919	3039	42
H(8A)	8422	5853	5161	42
H(8B)	6413	5833	5342	42
H(9A)	6153	5148	4430	37
H(9B)	8163	5169	4249	37
H(10A)	9051	5199	6459	41
H(10B)	7040	5168	6627	41

H(11A)	6870	4479	5796	59
H(11B)	8413	4506	6981	59
H(11C)	8873	4510	5601	59
H(13)	5804	7096	121	36
H(14)	4845	7350	-1882	39
H(15)	3304	6915	-3410	38
H(18A)	3038	5929	-3676	55
H(18B)	1614	6298	-3977	55
H(18C)	1416	5951	-2941	55
H(19)	4639	5432	-2007	42
H(20)	3110	4841	-1097	49
H(21)	1496	5176	456	45
H(24)	7751	6230	7341	29
H(26)	10417	6525	10791	31
H(28)	10002	7389	7979	31

Table S7. Torsion angles [°] for 3,5-dinitrobenzoylated derivative of **6a**.

C(19)-N(4)-N(5)-C(21)	0.39(19)
C(17)-N(4)-N(5)-C(21)	174.43(15)
C(12)-C(1)-C(2B)-C(3B)	177.9(3)
C(12)-C(1)-C(2A)-C(3A)	-177.0(3)
C(1)-C(2B)-C(3B)-C(4B)	120.0(5)
C(1)-C(2B)-C(3B)-C(6B)	-124.1(5)
C(1)-C(2B)-C(3B)-C(7)	3.5(6)
C(1)-C(2A)-C(3A)-C(4A)	-117.5(4)
C(1)-C(2A)-C(3A)-C(6A)	125.9(4)
C(1)-C(2A)-C(3A)-C(7)	1.4(5)
C(22)-O(1B)-C(4B)-C(5B)	103.0(6)
C(22)-O(1B)-C(4B)-C(3B)	-131.0(5)
C(2B)-C(3B)-C(4B)-O(1B)	169.0(4)
C(6B)-C(3B)-C(4B)-O(1B)	55.5(5)
C(7)-C(3B)-C(4B)-O(1B)	-74.6(5)
C(2B)-C(3B)-C(4B)-C(5B)	-69.9(7)
C(6B)-C(3B)-C(4B)-C(5B)	176.7(7)
C(7)-C(3B)-C(4B)-C(5B)	46.5(7)
C(22)-O(1A)-C(4A)-C(5A)	-107.6(5)
C(22)-O(1A)-C(4A)-C(3A)	125.6(5)
C(2A)-C(3A)-C(4A)-O(1A)	-171.6(4)
C(6A)-C(3A)-C(4A)-O(1A)	-57.4(6)
C(7)-C(3A)-C(4A)-O(1A)	69.6(4)
C(2A)-C(3A)-C(4A)-C(5A)	66.8(4)
C(6A)-C(3A)-C(4A)-C(5A)	-179.0(5)
C(7)-C(3A)-C(4A)-C(5A)	-52.0(4)
C(2B)-C(3B)-C(7)-C(8)	-179.4(3)
C(4B)-C(3B)-C(7)-C(8)	66.7(3)
C(6B)-C(3B)-C(7)-C(8)	-58.8(4)
C(2A)-C(3A)-C(7)-C(8)	-176.5(2)
C(4A)-C(3A)-C(7)-C(8)	-61.7(3)
C(6A)-C(3A)-C(7)-C(8)	63.2(5)
C(3B)-C(7)-C(8)-C(9)	162.2(2)
C(3A)-C(7)-C(8)-C(9)	-155.9(2)
C(7)-C(8)-C(9)-C(10)	180.00(16)
C(8)-C(9)-C(10)-C(11)	-178.75(16)

C(2B)-C(1)-C(12)-C(13)	36.3(4)
C(2A)-C(1)-C(12)-C(13)	-7.4(3)
C(2B)-C(1)-C(12)-C(17)	-143.8(3)
C(2A)-C(1)-C(12)-C(17)	172.5(2)
C(17)-C(12)-C(13)-C(14)	0.1(2)
C(1)-C(12)-C(13)-C(14)	-179.98(16)
C(12)-C(13)-C(14)-C(15)	0.1(3)
C(13)-C(14)-C(15)-C(16)	0.0(3)
C(14)-C(15)-C(16)-C(17)	-0.2(3)
C(14)-C(15)-C(16)-C(18)	177.41(16)
C(15)-C(16)-C(17)-C(12)	0.4(2)
C(18)-C(16)-C(17)-C(12)	-177.18(15)
C(15)-C(16)-C(17)-N(4)	178.44(14)
C(18)-C(16)-C(17)-N(4)	0.9(2)
C(13)-C(12)-C(17)-C(16)	-0.4(2)
C(1)-C(12)-C(17)-C(16)	179.74(15)
C(13)-C(12)-C(17)-N(4)	-178.37(14)
C(1)-C(12)-C(17)-N(4)	1.7(2)
C(19)-N(4)-C(17)-C(16)	58.3(2)
N(5)-N(4)-C(17)-C(16)	-114.59(17)
C(19)-N(4)-C(17)-C(12)	-123.60(18)
N(5)-N(4)-C(17)-C(12)	63.5(2)
N(5)-N(4)-C(19)-C(20)	-0.2(2)
C(17)-N(4)-C(19)-C(20)	-173.56(16)
N(4)-C(19)-C(20)-C(21)	-0.1(2)
N(4)-N(5)-C(21)-C(20)	-0.5(2)
C(19)-C(20)-C(21)-N(5)	0.4(2)
C(4B)-O(1B)-C(22)-O(2)	-4.4(7)
C(4B)-O(1B)-C(22)-C(23)	-171.6(4)
C(4A)-O(1A)-C(22)-O(2)	2.8(7)
C(4A)-O(1A)-C(22)-C(23)	173.8(4)
O(2)-C(22)-C(23)-C(28)	-15.3(3)
O(1B)-C(22)-C(23)-C(28)	152.2(4)
O(1A)-C(22)-C(23)-C(28)	173.7(3)
O(2)-C(22)-C(23)-C(24)	165.16(19)
O(1B)-C(22)-C(23)-C(24)	-27.3(4)
O(1A)-C(22)-C(23)-C(24)	-5.9(4)
C(28)-C(23)-C(24)-C(25)	1.1(2)

C(22)-C(23)-C(24)-C(25)	-179.40(15)
C(23)-C(24)-C(25)-C(26)	-1.4(2)
C(23)-C(24)-C(25)-N(2)	178.94(14)
O(4)-N(2)-C(25)-C(24)	-166.49(14)
O(3)-N(2)-C(25)-C(24)	13.2(2)
O(4)-N(2)-C(25)-C(26)	13.9(2)
O(3)-N(2)-C(25)-C(26)	-166.43(15)
C(24)-C(25)-C(26)-C(27)	0.8(2)
N(2)-C(25)-C(26)-C(27)	-179.58(14)
C(25)-C(26)-C(27)-C(28)	0.2(2)
C(25)-C(26)-C(27)-N(3)	-178.82(15)
O(5)-N(3)-C(27)-C(26)	-2.6(2)
O(6)-N(3)-C(27)-C(26)	177.15(17)
O(5)-N(3)-C(27)-C(28)	178.31(16)
O(6)-N(3)-C(27)-C(28)	-1.9(2)
C(26)-C(27)-C(28)-C(23)	-0.5(3)
N(3)-C(27)-C(28)-C(23)	178.53(15)
C(24)-C(23)-C(28)-C(27)	-0.2(2)
C(22)-C(23)-C(28)-C(27)	-179.69(15)

Symmetry transformations used to generate equivalent atoms:

Experimental for 3,5-dinitrobenzoylated derivative of 8a

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα (λ = 1.54178 Å) for the structure of 3,5-dinitrobenzoylated derivative of **8a**. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The full numbering scheme of compound 3,5-dinitrobenzoylated derivative of **8a** can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 1917394 (007b-19053) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

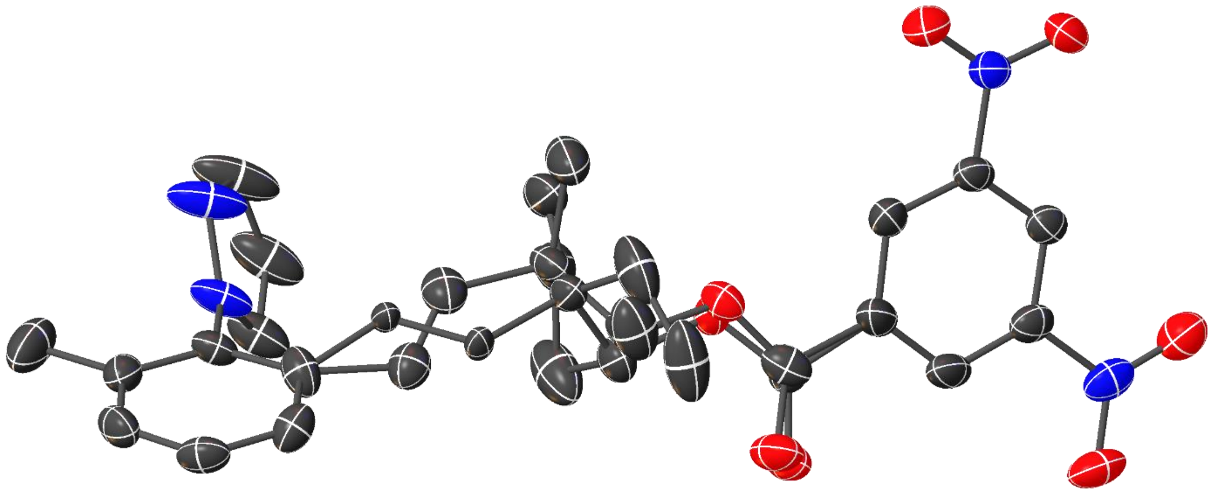


Figure S3. The complete model of **3,5-dinitrobenzoylated derivative of 8a** with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.

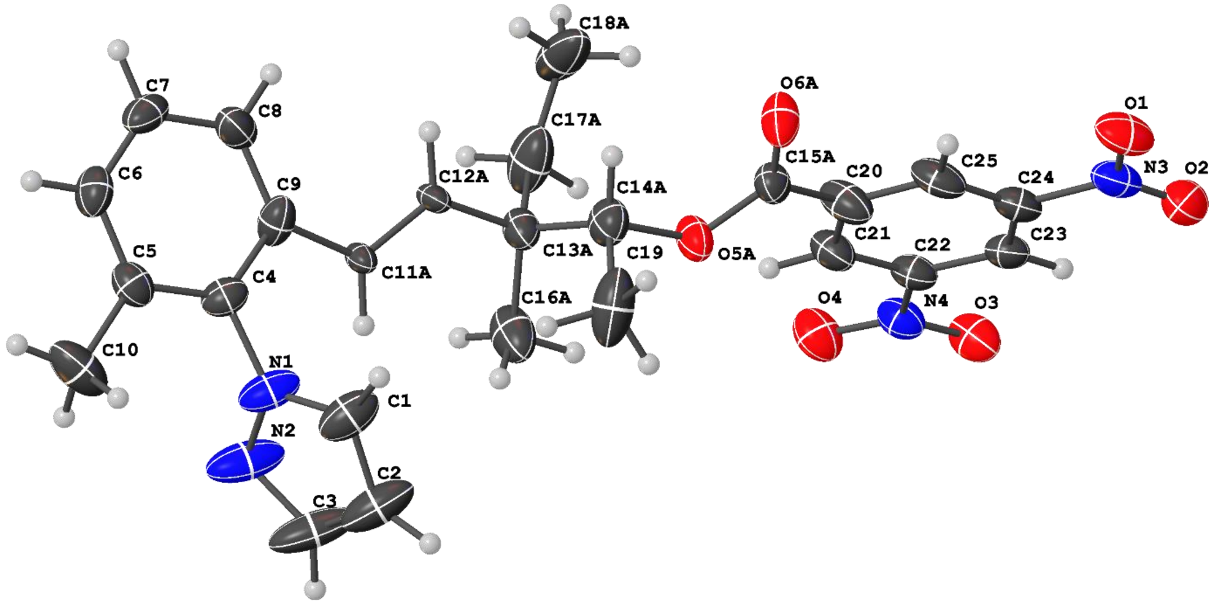


Figure S4. The complete numbering scheme of **3,5-dinitrobenzoylated derivative of 8a** part 1 with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.

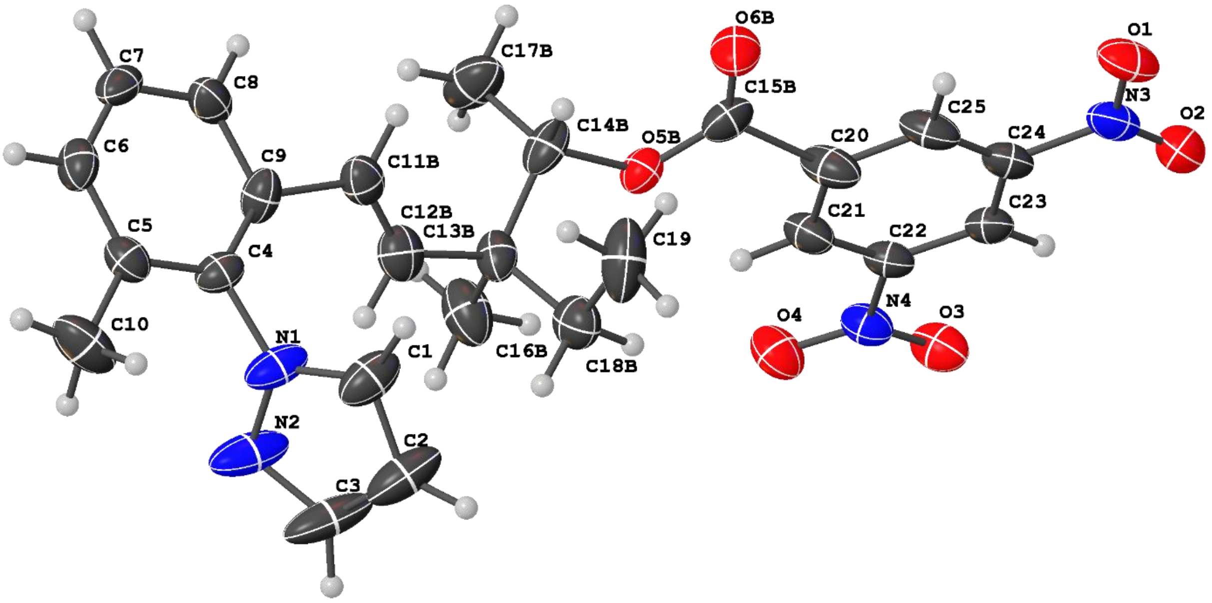


Figure S5. The complete numbering scheme of 3,5-dinitrobenzoylated derivative of **8a** part 2 with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.

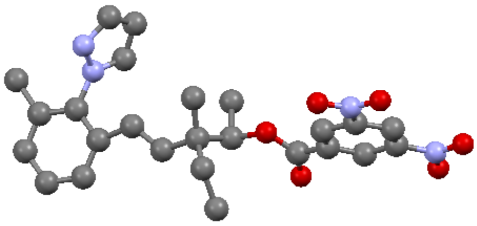


Figure S6. Another perspective of thecrystal structure showing the indicated relative stereochemistry. The hydrogen atoms are omitted for clarity.

Table S8. Crystal data and structure refinement for 3,5-dinitrobenzoylated derivative of **8a**.

Identification code	007b-19053	
Empirical formula	C25 H26 N4 O6	
Formula weight	478.50	
Temperature	93(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.8001(2) Å	α= 90°.
	b = 12.4294(2) Å	β= 98.830(2)°.
	c = 17.9310(3) Å	γ = 90°.
Volume	2378.51(7) Å^3	
Z	4	
Density (calculated)	1.336 Mg/m^3	
Absorption coefficient	0.804 mm^{-1}	
F(000)	1008	
Crystal size	0.220 x 0.210 x 0.040 mm^3	
Crystal color and habit	Colorless Block	
Diffractometer	Rigaku Saturn 944+ CCD	
Theta range for data collection	4.345 to 66.597°.	
Index ranges	-12<=h<=12, -14<=k<=14, -21<=l<=21	
Reflections collected	82818	
Independent reflections	4203 [R(int) = 0.0521]	
Observed reflections (I > 2sigma(I))	3977	
Completeness to theta = 66.597°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.75370	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	4203 / 84 / 414	
Goodness-of-fit on F^2	1.140	
Final R indices [I>2sigma(I)]	R1 = 0.0579, wR2 = 0.1419	
R indices (all data)	R1 = 0.0603, wR2 = 0.1435	
Extinction coefficient	0.0117(5)	
Largest diff. peak and hole	0.465 and -0.277 e.Å^{-3}	

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 3,5-dinitrobenzoylated derivative of **8a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	7333(2)	6016(1)	612(1)	53(1)
O(2)	7177(2)	4872(1)	-312(1)	50(1)
O(3)	4534(2)	1780(1)	-326(1)	47(1)
O(4)	3519(2)	1485(1)	606(1)	50(1)
N(1)	4062(2)	2118(2)	6409(1)	47(1)
N(2)	3817(2)	1058(2)	6284(2)	67(1)
N(3)	6944(2)	5172(2)	301(1)	43(1)
N(4)	4251(2)	2005(1)	292(1)	38(1)
C(1)	5244(2)	2373(2)	6311(2)	53(1)
C(2)	5806(3)	1447(3)	6127(2)	67(1)
C(3)	4893(3)	669(3)	6110(2)	78(1)
C(4)	3076(2)	2860(2)	6487(1)	34(1)
C(5)	2653(2)	2941(2)	7180(1)	36(1)
C(6)	1758(2)	3709(2)	7251(1)	40(1)
C(7)	1306(2)	4385(2)	6657(1)	40(1)
C(8)	1728(2)	4280(2)	5970(1)	40(1)
C(9)	2606(2)	3496(2)	5867(1)	39(1)
C(10)	3173(3)	2232(2)	7835(2)	63(1)
C(19)	5706(3)	3625(3)	4240(2)	72(1)
C(20)	5033(3)	4180(2)	1718(1)	48(1)
C(21)	4533(2)	3235(2)	1379(1)	39(1)
C(22)	4826(2)	2967(2)	680(1)	34(1)
C(23)	5624(2)	3572(2)	319(1)	34(1)
C(24)	6112(2)	4496(2)	679(1)	36(1)
C(25)	5818(2)	4819(2)	1368(1)	43(1)
O(5A)	4626(4)	3723(2)	2891(2)	40(1)
O(6A)	5102(5)	5466(7)	2681(4)	46(1)
C(11A)	3003(4)	3078(4)	5159(2)	23(1)
C(12A)	2900(3)	3684(3)	4521(2)	25(1)
C(13A)	3271(6)	3334(5)	3786(3)	35(1)
C(14A)	4399(4)	3964(4)	3665(2)	42(1)
C(15A)	4968(6)	4538(4)	2485(3)	32(1)
C(16A)	3587(7)	2122(5)	3770(3)	59(2)

C(17A)	2145(5)	3549(7)	3147(3)	66(2)
C(18A)	1895(6)	4748(7)	2955(4)	74(2)
O(5B)	3720(4)	3809(3)	2706(2)	35(1)
O(6B)	4605(7)	5439(8)	2708(6)	49(2)
C(11B)	2951(5)	3699(7)	5085(3)	40(1)
C(12B)	3211(5)	2927(5)	4688(4)	44(1)
C(13B)	3501(7)	2907(7)	3874(4)	37(2)
C(14B)	3248(5)	3994(5)	3427(3)	42(1)
C(15B)	4371(7)	4565(6)	2430(4)	38(2)
C(16B)	2774(8)	1992(6)	3469(4)	58(2)
C(17B)	1845(7)	4233(8)	3266(4)	59(2)
C(18B)	4916(5)	2639(5)	3958(3)	48(1)

Table S10. Bond lengths [Å] and angles [°] for 3,5-dinitrobenzoylated derivative of **8a**.

O(1)-N(3)	1.230(2)
O(2)-N(3)	1.224(3)
O(3)-N(4)	1.227(2)
O(4)-N(4)	1.223(2)
N(1)-C(1)	1.353(3)
N(1)-N(2)	1.355(3)
N(1)-C(4)	1.432(3)
N(2)-C(3)	1.339(4)
N(3)-C(24)	1.469(3)
N(4)-C(22)	1.472(3)
C(1)-C(2)	1.365(4)
C(1)-H(1)	0.9500
C(2)-C(3)	1.377(5)
C(2)-H(2)	0.9500
C(3)-H(3)	0.9500
C(4)-C(5)	1.392(3)
C(4)-C(9)	1.394(3)
C(5)-C(6)	1.378(3)
C(5)-C(10)	1.507(3)
C(6)-C(7)	1.386(3)
C(6)-H(6)	0.9500
C(7)-C(8)	1.384(3)
C(7)-H(7)	0.9500
C(8)-C(9)	1.392(3)
C(8)-H(8)	0.9500
C(9)-C(11A)	1.495(5)
C(9)-C(11B)	1.526(6)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(19)-C(18B)	1.535(6)
C(19)-C(14A)	1.669(6)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(19)-H(19D)	0.9800

C(19)-H(19E)	0.9800
C(19)-H(19F)	0.9800
C(20)-C(25)	1.381(4)
C(20)-C(21)	1.392(3)
C(20)-C(15A)	1.458(6)
C(20)-C(15B)	1.628(7)
C(21)-C(22)	1.380(3)
C(21)-H(21)	0.9500
C(22)-C(23)	1.378(3)
C(23)-C(24)	1.382(3)
C(23)-H(23)	0.9500
C(24)-C(25)	1.381(3)
C(25)-H(25)	0.9500
O(5A)-C(15A)	1.331(6)
O(5A)-C(14A)	1.478(5)
O(6A)-C(15A)	1.208(9)
C(11A)-C(12A)	1.360(6)
C(11A)-H(11A)	0.9500
C(12A)-C(13A)	1.499(7)
C(12A)-H(12A)	0.9500
C(13A)-C(14A)	1.492(8)
C(13A)-C(16A)	1.546(7)
C(13A)-C(17A)	1.562(9)
C(14A)-H(14A)	1.0000
C(16A)-H(16A)	0.9800
C(16A)-H(16B)	0.9800
C(16A)-H(16C)	0.9800
C(17A)-C(18A)	1.544(10)
C(17A)-H(17A)	0.9900
C(17A)-H(17B)	0.9900
C(18A)-H(18A)	0.9800
C(18A)-H(18B)	0.9800
C(18A)-H(18C)	0.9800
O(5B)-C(15B)	1.315(9)
O(5B)-C(14B)	1.478(6)
O(6B)-C(15B)	1.206(11)
C(11B)-C(12B)	1.253(10)
C(11B)-H(11B)	0.9500

C(12B)-C(13B)	1.539(10)
C(12B)-H(12B)	0.9500
C(13B)-C(16B)	1.504(10)
C(13B)-C(18B)	1.548(10)
C(13B)-C(14B)	1.574(9)
C(14B)-C(17B)	1.528(9)
C(14B)-H(14B)	1.0000
C(16B)-H(16D)	0.9800
C(16B)-H(16E)	0.9800
C(16B)-H(16F)	0.9800
C(17B)-H(17C)	0.9800
C(17B)-H(17D)	0.9800
C(17B)-H(17E)	0.9800
C(18B)-H(18D)	0.9900
C(18B)-H(18E)	0.9900

C(1)-N(1)-N(2)	111.7(2)
C(1)-N(1)-C(4)	126.3(2)
N(2)-N(1)-C(4)	120.88(19)
C(3)-N(2)-N(1)	103.6(2)
O(2)-N(3)-O(1)	124.3(2)
O(2)-N(3)-C(24)	117.71(18)
O(1)-N(3)-C(24)	118.0(2)
O(4)-N(4)-O(3)	124.33(18)
O(4)-N(4)-C(22)	117.89(18)
O(3)-N(4)-C(22)	117.78(18)
N(1)-C(1)-C(2)	107.3(3)
N(1)-C(1)-H(1)	126.4
C(2)-C(1)-H(1)	126.4
C(1)-C(2)-C(3)	104.7(2)
C(1)-C(2)-H(2)	127.6
C(3)-C(2)-H(2)	127.6
N(2)-C(3)-C(2)	112.6(2)
N(2)-C(3)-H(3)	123.7
C(2)-C(3)-H(3)	123.7
C(5)-C(4)-C(9)	122.76(19)
C(5)-C(4)-N(1)	119.0(2)
C(9)-C(4)-N(1)	118.27(19)

C(6)-C(5)-C(4)	117.6(2)
C(6)-C(5)-C(10)	121.0(2)
C(4)-C(5)-C(10)	121.4(2)
C(5)-C(6)-C(7)	121.2(2)
C(5)-C(6)-H(6)	119.4
C(7)-C(6)-H(6)	119.4
C(8)-C(7)-C(6)	120.2(2)
C(8)-C(7)-H(7)	119.9
C(6)-C(7)-H(7)	119.9
C(7)-C(8)-C(9)	120.5(2)
C(7)-C(8)-H(8)	119.8
C(9)-C(8)-H(8)	119.8
C(8)-C(9)-C(4)	117.65(19)
C(8)-C(9)-C(11A)	130.3(3)
C(4)-C(9)-C(11A)	111.3(2)
C(8)-C(9)-C(11B)	105.9(3)
C(4)-C(9)-C(11B)	135.6(3)
C(5)-C(10)-H(10A)	109.5
C(5)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(5)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(14A)-C(19)-H(19A)	109.5
C(14A)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(14A)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(18B)-C(19)-H(19D)	109.5
C(18B)-C(19)-H(19E)	109.5
H(19D)-C(19)-H(19E)	109.5
C(18B)-C(19)-H(19F)	109.5
H(19D)-C(19)-H(19F)	109.5
H(19E)-C(19)-H(19F)	109.5
C(25)-C(20)-C(21)	120.8(2)
C(25)-C(20)-C(15A)	112.0(3)
C(21)-C(20)-C(15A)	126.7(3)

C(25)-C(20)-C(15B)	124.1(3)
C(21)-C(20)-C(15B)	113.7(3)
C(22)-C(21)-C(20)	118.1(2)
C(22)-C(21)-H(21)	120.9
C(20)-C(21)-H(21)	120.9
C(23)-C(22)-C(21)	122.83(19)
C(23)-C(22)-N(4)	118.09(18)
C(21)-C(22)-N(4)	119.07(19)
C(22)-C(23)-C(24)	117.1(2)
C(22)-C(23)-H(23)	121.4
C(24)-C(23)-H(23)	121.4
C(25)-C(24)-C(23)	122.3(2)
C(25)-C(24)-N(3)	119.16(19)
C(23)-C(24)-N(3)	118.5(2)
C(20)-C(25)-C(24)	118.7(2)
C(20)-C(25)-H(25)	120.6
C(24)-C(25)-H(25)	120.6
C(15A)-O(5A)-C(14A)	117.3(3)
C(12A)-C(11A)-C(9)	121.7(4)
C(12A)-C(11A)-H(11A)	119.2
C(9)-C(11A)-H(11A)	119.2
C(11A)-C(12A)-C(13A)	125.4(4)
C(11A)-C(12A)-H(12A)	117.3
C(13A)-C(12A)-H(12A)	117.3
C(14A)-C(13A)-C(12A)	108.0(5)
C(14A)-C(13A)-C(16A)	108.8(5)
C(12A)-C(13A)-C(16A)	112.9(5)
C(14A)-C(13A)-C(17A)	111.4(5)
C(12A)-C(13A)-C(17A)	108.2(5)
C(16A)-C(13A)-C(17A)	107.6(5)
O(5A)-C(14A)-C(13A)	106.7(4)
O(5A)-C(14A)-C(19)	106.4(3)
C(13A)-C(14A)-C(19)	114.2(4)
O(5A)-C(14A)-H(14A)	109.8
C(13A)-C(14A)-H(14A)	109.8
C(19)-C(14A)-H(14A)	109.8
O(6A)-C(15A)-O(5A)	126.7(5)
O(6A)-C(15A)-C(20)	123.0(5)

O(5A)-C(15A)-C(20)	109.9(4)
C(13A)-C(16A)-H(16A)	109.5
C(13A)-C(16A)-H(16B)	109.5
H(16A)-C(16A)-H(16B)	109.5
C(13A)-C(16A)-H(16C)	109.5
H(16A)-C(16A)-H(16C)	109.5
H(16B)-C(16A)-H(16C)	109.5
C(18A)-C(17A)-C(13A)	114.7(6)
C(18A)-C(17A)-H(17A)	108.6
C(13A)-C(17A)-H(17A)	108.6
C(18A)-C(17A)-H(17B)	108.6
C(13A)-C(17A)-H(17B)	108.6
H(17A)-C(17A)-H(17B)	107.6
C(17A)-C(18A)-H(18A)	109.5
C(17A)-C(18A)-H(18B)	109.5
H(18A)-C(18A)-H(18B)	109.5
C(17A)-C(18A)-H(18C)	109.5
H(18A)-C(18A)-H(18C)	109.5
H(18B)-C(18A)-H(18C)	109.5
C(15B)-O(5B)-C(14B)	119.6(4)
C(12B)-C(11B)-C(9)	120.2(7)
C(12B)-C(11B)-H(11B)	119.9
C(9)-C(11B)-H(11B)	119.9
C(11B)-C(12B)-C(13B)	130.3(7)
C(11B)-C(12B)-H(12B)	114.8
C(13B)-C(12B)-H(12B)	114.8
C(16B)-C(13B)-C(12B)	107.7(6)
C(16B)-C(13B)-C(18B)	108.5(6)
C(12B)-C(13B)-C(18B)	104.7(5)
C(16B)-C(13B)-C(14B)	111.5(6)
C(12B)-C(13B)-C(14B)	115.2(6)
C(18B)-C(13B)-C(14B)	109.0(5)
O(5B)-C(14B)-C(17B)	109.3(5)
O(5B)-C(14B)-C(13B)	104.8(4)
C(17B)-C(14B)-C(13B)	110.7(6)
O(5B)-C(14B)-H(14B)	110.6
C(17B)-C(14B)-H(14B)	110.6
C(13B)-C(14B)-H(14B)	110.6

O(6B)-C(15B)-O(5B)	125.3(7)
O(6B)-C(15B)-C(20)	120.0(7)
O(5B)-C(15B)-C(20)	114.2(5)
C(13B)-C(16B)-H(16D)	109.5
C(13B)-C(16B)-H(16E)	109.5
H(16D)-C(16B)-H(16E)	109.5
C(13B)-C(16B)-H(16F)	109.5
H(16D)-C(16B)-H(16F)	109.5
H(16E)-C(16B)-H(16F)	109.5
C(14B)-C(17B)-H(17C)	109.5
C(14B)-C(17B)-H(17D)	109.5
H(17C)-C(17B)-H(17D)	109.5
C(14B)-C(17B)-H(17E)	109.5
H(17C)-C(17B)-H(17E)	109.5
H(17D)-C(17B)-H(17E)	109.5
C(19)-C(18B)-C(13B)	110.5(5)
C(19)-C(18B)-H(18D)	109.5
C(13B)-C(18B)-H(18D)	109.5
C(19)-C(18B)-H(18E)	109.5
C(13B)-C(18B)-H(18E)	109.5
H(18D)-C(18B)-H(18E)	108.1

Symmetry transformations used to generate equivalent atoms:

Table S11. Anisotropic displacement parameters ($Å^2$x 10^3) for 3,5-dinitrobenzoylated derivative of **8a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	57(1)	27(1)	72(1)	5(1)	-1(1)	-6(1)
O(2)	52(1)	41(1)	59(1)	6(1)	16(1)	1(1)
O(3)	70(1)	37(1)	33(1)	-7(1)	2(1)	-3(1)
O(4)	62(1)	39(1)	47(1)	-1(1)	7(1)	-16(1)
N(1)	37(1)	40(1)	60(1)	-26(1)	-5(1)	8(1)
N(2)	46(1)	41(1)	105(2)	-35(1)	-16(1)	11(1)
N(3)	40(1)	29(1)	57(1)	10(1)	1(1)	3(1)
N(4)	50(1)	29(1)	34(1)	-1(1)	0(1)	-2(1)
C(1)	38(1)	60(2)	59(2)	-28(1)	-1(1)	6(1)
C(2)	42(1)	76(2)	77(2)	-42(2)	-10(1)	21(1)
C(3)	50(2)	60(2)	113(3)	-52(2)	-25(2)	26(1)
C(4)	35(1)	30(1)	37(1)	-12(1)	2(1)	2(1)
C(5)	45(1)	32(1)	32(1)	1(1)	3(1)	-8(1)
C(6)	47(1)	44(1)	34(1)	-10(1)	16(1)	-7(1)
C(7)	36(1)	28(1)	58(1)	-9(1)	14(1)	1(1)
C(8)	35(1)	42(1)	44(1)	13(1)	6(1)	1(1)
C(9)	32(1)	58(1)	29(1)	-4(1)	7(1)	0(1)
C(10)	72(2)	55(2)	56(2)	22(1)	-8(1)	-12(1)
C(19)	55(2)	115(3)	49(2)	-19(2)	21(1)	-29(2)
C(20)	82(2)	28(1)	32(1)	-1(1)	4(1)	1(1)
C(21)	59(1)	28(1)	32(1)	2(1)	7(1)	0(1)
C(22)	43(1)	24(1)	32(1)	0(1)	-2(1)	2(1)
C(23)	40(1)	27(1)	34(1)	1(1)	2(1)	6(1)
C(24)	41(1)	25(1)	40(1)	5(1)	-2(1)	3(1)
C(25)	64(2)	23(1)	37(1)	0(1)	-6(1)	-1(1)
O(5A)	61(2)	32(2)	31(2)	-1(1)	20(2)	-3(1)
O(6A)	61(4)	38(2)	45(2)	-13(2)	27(3)	-17(3)
C(11A)	36(2)	16(2)	19(2)	1(2)	9(1)	2(2)
C(12A)	39(2)	18(2)	20(2)	4(1)	7(1)	6(1)
C(13A)	50(3)	27(3)	31(2)	-3(2)	15(2)	-2(2)
C(14A)	51(3)	45(2)	32(2)	-5(2)	14(2)	0(2)
C(15A)	35(3)	29(2)	32(2)	-1(2)	10(3)	-5(3)
C(16A)	97(5)	43(3)	42(3)	-10(2)	31(3)	-9(3)

C(17A)	55(3)	109(5)	35(2)	-7(3)	13(2)	1(3)
C(18A)	66(4)	115(6)	43(3)	17(4)	13(3)	51(4)
O(5B)	33(2)	38(2)	35(2)	-9(1)	8(2)	1(2)
O(6B)	60(5)	34(3)	57(3)	-14(2)	22(4)	-8(4)
C(11B)	34(3)	44(4)	40(4)	5(3)	5(2)	-3(2)
C(12B)	37(3)	52(4)	41(3)	-3(2)	4(2)	-11(2)
C(13B)	44(3)	38(4)	33(3)	-11(3)	13(2)	-11(3)
C(14B)	37(3)	55(3)	36(3)	-23(2)	10(2)	-1(2)
C(15B)	28(3)	40(3)	44(3)	-11(2)	0(3)	7(3)
C(16B)	75(4)	63(4)	39(3)	-7(3)	15(3)	-25(3)
C(17B)	61(4)	73(5)	43(4)	4(4)	5(3)	28(4)
C(18B)	61(3)	50(3)	34(3)	0(2)	15(2)	0(2)

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 3,5-dinitrobenzoylated derivative of **8a**.

	x	y	z	U(eq)
H(1)	5614	3068	6360	63
H(2)	6641	1358	6033	81
H(3)	5014	-63	5988	94
H(6)	1446	3775	7716	49
H(7)	706	4922	6722	48
H(8)	1415	4747	5565	49
H(10A)	2979	1478	7706	94
H(10B)	2795	2431	8279	94
H(10C)	4084	2325	7948	94
H(19A)	6148	3064	4001	107
H(19B)	5490	3355	4717	107
H(19C)	6248	4258	4338	107
H(19D)	5602	4184	3849	107
H(19E)	6591	3418	4351	107
H(19F)	5431	3903	4699	107
H(21)	4004	2787	1622	47
H(23)	5830	3363	-156	41
H(25)	6150	5468	1597	52
H(11A)	3336	2371	5154	28
H(12A)	2566	4388	4543	30
H(14A)	4232	4751	3714	50
H(16A)	4231	1947	4200	88
H(16B)	3899	1951	3299	88
H(16C)	2830	1699	3802	88
H(17A)	2303	3171	2684	79
H(17B)	1380	3233	3299	79
H(18A)	1129	4815	2587	111
H(18B)	2603	5047	2741	111
H(18C)	1796	5142	3416	111
H(11B)	2969	4414	4899	47
H(12B)	3232	2244	4927	52
H(14B)	3710	4600	3712	51

H(16D)	1877	2156	3403	88
H(16E)	2939	1331	3766	88
H(16F)	3034	1892	2973	88
H(17C)	1704	4897	2971	89
H(17D)	1521	4320	3744	89
H(17E)	1410	3636	2980	89
H(18D)	5112	2038	4319	57
H(18E)	5126	2408	3464	57

Table S13. Torsion angles [°] for 3,5-dinitrobenzoylated derivative of **8a**.

C(1)-N(1)-N(2)-C(3)	0.4(3)
C(4)-N(1)-N(2)-C(3)	169.3(2)
N(2)-N(1)-C(1)-C(2)	-1.1(3)
C(4)-N(1)-C(1)-C(2)	-169.2(2)
N(1)-C(1)-C(2)-C(3)	1.2(3)
N(1)-N(2)-C(3)-C(2)	0.4(4)
C(1)-C(2)-C(3)-N(2)	-1.1(4)
C(1)-N(1)-C(4)-C(5)	-111.5(3)
N(2)-N(1)-C(4)-C(5)	81.3(3)
C(1)-N(1)-C(4)-C(9)	66.7(3)
N(2)-N(1)-C(4)-C(9)	-100.5(3)
C(9)-C(4)-C(5)-C(6)	-2.0(3)
N(1)-C(4)-C(5)-C(6)	176.07(19)
C(9)-C(4)-C(5)-C(10)	179.3(2)
N(1)-C(4)-C(5)-C(10)	-2.6(3)
C(4)-C(5)-C(6)-C(7)	-0.7(3)
C(10)-C(5)-C(6)-C(7)	178.0(2)
C(5)-C(6)-C(7)-C(8)	1.7(3)
C(6)-C(7)-C(8)-C(9)	0.1(3)
C(7)-C(8)-C(9)-C(4)	-2.7(3)
C(7)-C(8)-C(9)-C(11A)	166.0(3)
C(7)-C(8)-C(9)-C(11B)	-173.9(3)
C(5)-C(4)-C(9)-C(8)	3.7(3)
N(1)-C(4)-C(9)-C(8)	-174.41(19)
C(5)-C(4)-C(9)-C(11A)	-167.0(2)
N(1)-C(4)-C(9)-C(11A)	14.9(3)
C(5)-C(4)-C(9)-C(11B)	171.5(4)
N(1)-C(4)-C(9)-C(11B)	-6.5(5)
C(25)-C(20)-C(21)-C(22)	-1.1(4)
C(15A)-C(20)-C(21)-C(22)	-171.9(4)
C(15B)-C(20)-C(21)-C(22)	166.0(3)
C(20)-C(21)-C(22)-C(23)	2.4(3)
C(20)-C(21)-C(22)-N(4)	-176.6(2)
O(4)-N(4)-C(22)-C(23)	-178.18(19)
O(3)-N(4)-C(22)-C(23)	1.5(3)
O(4)-N(4)-C(22)-C(21)	0.8(3)

O(3)-N(4)-C(22)-C(21)	-179.52(19)
C(21)-C(22)-C(23)-C(24)	-1.6(3)
N(4)-C(22)-C(23)-C(24)	177.35(18)
C(22)-C(23)-C(24)-C(25)	-0.5(3)
C(22)-C(23)-C(24)-N(3)	-178.65(18)
O(2)-N(3)-C(24)-C(25)	-179.24(19)
O(1)-N(3)-C(24)-C(25)	-1.2(3)
O(2)-N(3)-C(24)-C(23)	-1.0(3)
O(1)-N(3)-C(24)-C(23)	177.09(19)
C(21)-C(20)-C(25)-C(24)	-0.8(4)
C(15A)-C(20)-C(25)-C(24)	171.2(3)
C(15B)-C(20)-C(25)-C(24)	-166.5(3)
C(23)-C(24)-C(25)-C(20)	1.6(3)
N(3)-C(24)-C(25)-C(20)	179.8(2)
C(8)-C(9)-C(11A)-C(12A)	25.7(5)
C(4)-C(9)-C(11A)-C(12A)	-165.1(3)
C(9)-C(11A)-C(12A)-C(13A)	-179.9(4)
C(11A)-C(12A)-C(13A)-C(14A)	-110.5(5)
C(11A)-C(12A)-C(13A)-C(16A)	9.9(8)
C(11A)-C(12A)-C(13A)-C(17A)	128.8(5)
C(15A)-O(5A)-C(14A)-C(13A)	139.6(5)
C(15A)-O(5A)-C(14A)-C(19)	-98.2(5)
C(12A)-C(13A)-C(14A)-O(5A)	-171.7(4)
C(16A)-C(13A)-C(14A)-O(5A)	65.4(5)
C(17A)-C(13A)-C(14A)-O(5A)	-53.0(6)
C(12A)-C(13A)-C(14A)-C(19)	71.1(5)
C(16A)-C(13A)-C(14A)-C(19)	-51.8(5)
C(17A)-C(13A)-C(14A)-C(19)	-170.2(4)
C(14A)-O(5A)-C(15A)-O(6A)	-0.7(9)
C(14A)-O(5A)-C(15A)-C(20)	-174.5(4)
C(25)-C(20)-C(15A)-O(6A)	29.5(7)
C(21)-C(20)-C(15A)-O(6A)	-159.0(5)
C(25)-C(20)-C(15A)-O(5A)	-156.4(4)
C(21)-C(20)-C(15A)-O(5A)	15.0(6)
C(14A)-C(13A)-C(17A)-C(18A)	-47.3(7)
C(12A)-C(13A)-C(17A)-C(18A)	71.3(6)
C(16A)-C(13A)-C(17A)-C(18A)	-166.5(5)
C(8)-C(9)-C(11B)-C(12B)	-146.2(5)

C(4)-C(9)-C(11B)-C(12B)	44.9(7)
C(9)-C(11B)-C(12B)-C(13B)	175.6(5)
C(11B)-C(12B)-C(13B)-C(16B)	-134.8(7)
C(11B)-C(12B)-C(13B)-C(18B)	109.8(7)
C(11B)-C(12B)-C(13B)-C(14B)	-9.9(9)
C(15B)-O(5B)-C(14B)-C(17B)	104.0(6)
C(15B)-O(5B)-C(14B)-C(13B)	-137.4(5)
C(16B)-C(13B)-C(14B)-O(5B)	-62.9(6)
C(12B)-C(13B)-C(14B)-O(5B)	174.1(5)
C(18B)-C(13B)-C(14B)-O(5B)	56.8(6)
C(16B)-C(13B)-C(14B)-C(17B)	54.8(7)
C(12B)-C(13B)-C(14B)-C(17B)	-68.2(7)
C(18B)-C(13B)-C(14B)-C(17B)	174.6(5)
C(14B)-O(5B)-C(15B)-O(6B)	-1.9(10)
C(14B)-O(5B)-C(15B)-C(20)	169.9(4)
C(25)-C(20)-C(15B)-O(6B)	-3.8(9)
C(21)-C(20)-C(15B)-O(6B)	-170.3(7)
C(25)-C(20)-C(15B)-O(5B)	-176.1(4)
C(21)-C(20)-C(15B)-O(5B)	17.4(6)
C(16B)-C(13B)-C(18B)-C(19)	170.0(5)
C(12B)-C(13B)-C(18B)-C(19)	-75.3(6)
C(14B)-C(13B)-C(18B)-C(19)	48.4(6)

Symmetry transformations used to generate equivalent atoms:

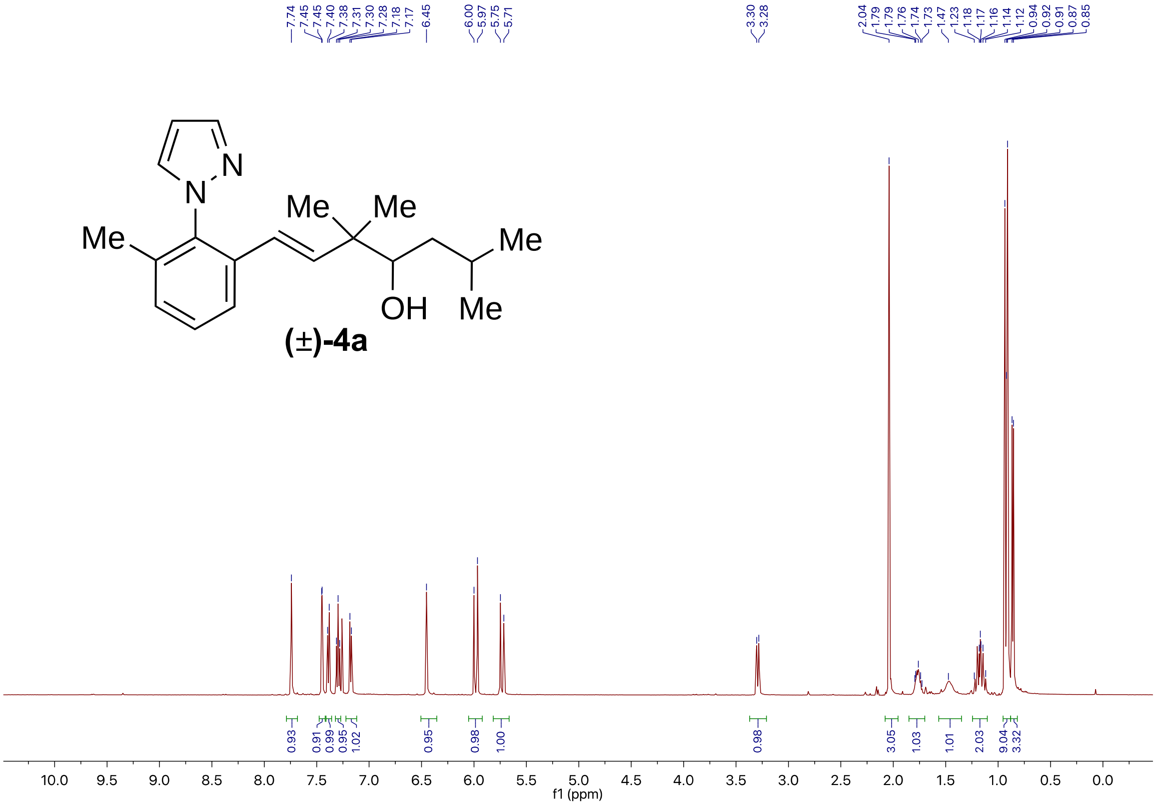
VIII. Author Contributions

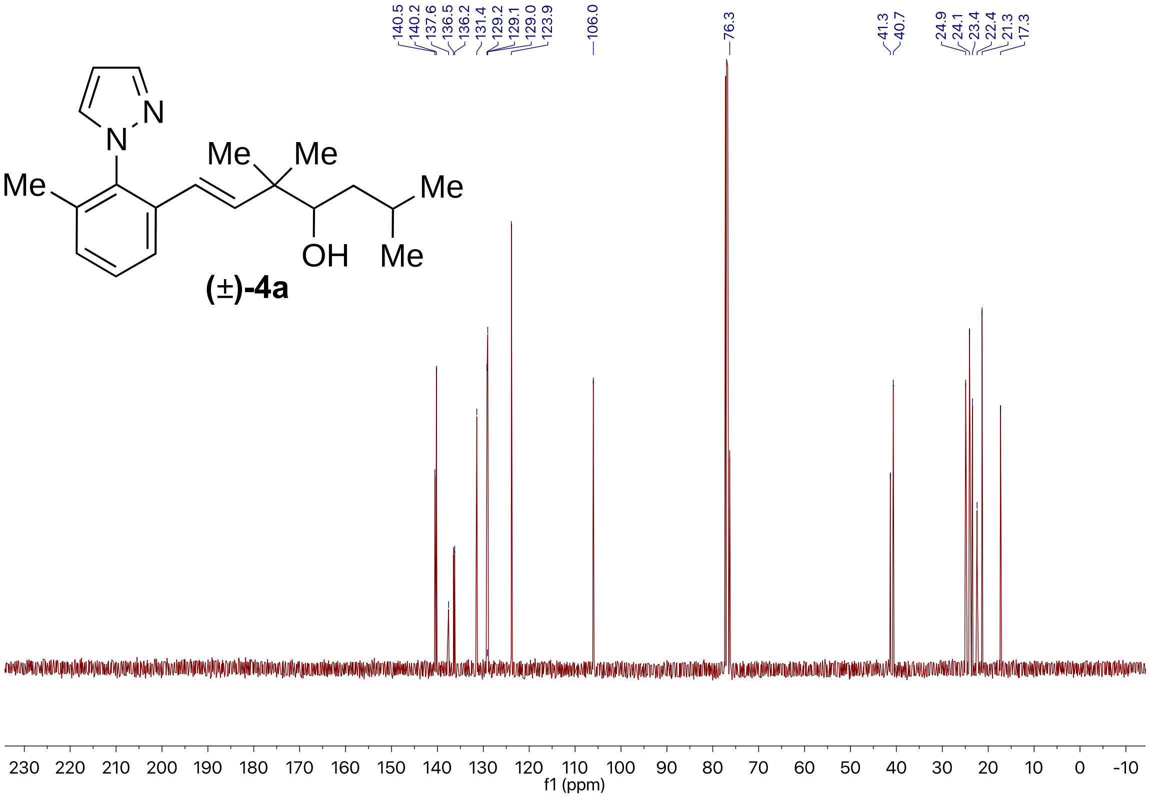
S.D. and Z.S. co-conceived the concept, developed the reaction conditions, completed the scope and mechanistic experiments and co-wrote the original draft. J.A.E. co-conceived the concept, co-wrote the manuscript with feedback from S.D. and Z.S., and acquired funding for the project.

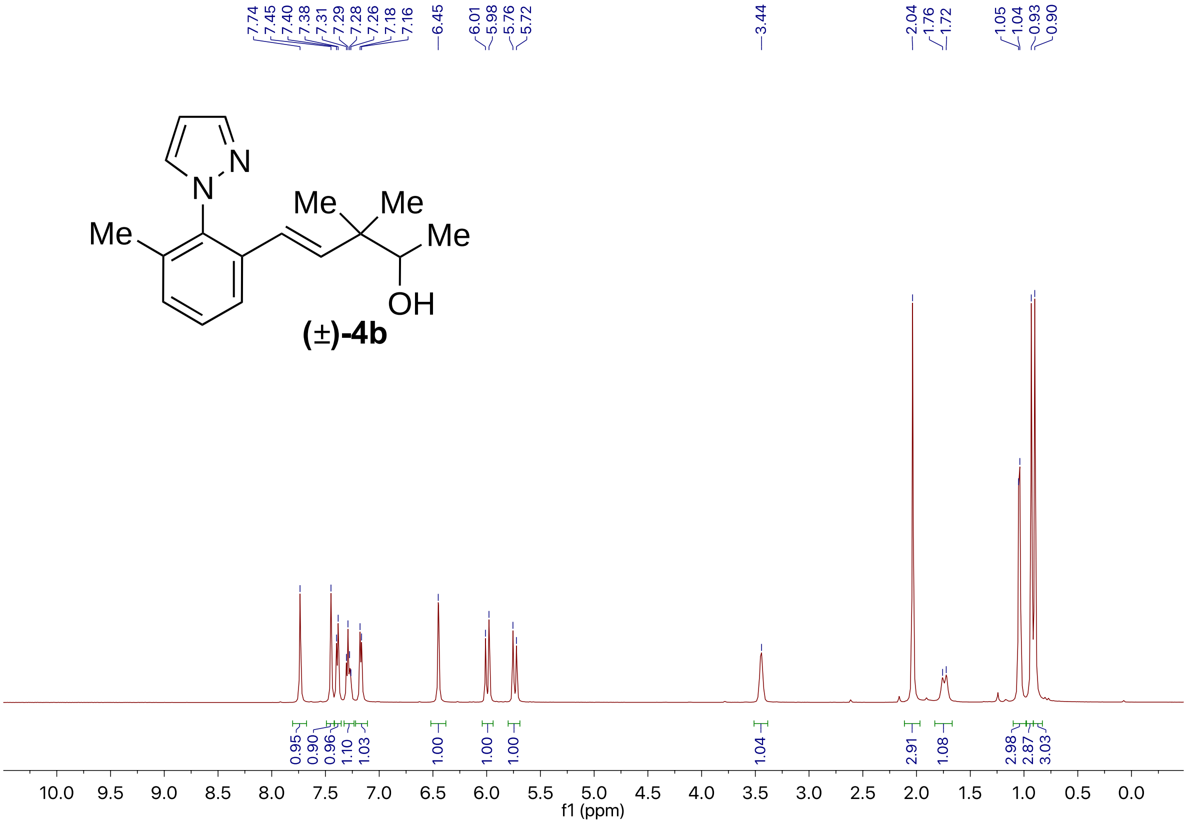
IX. References

[1] K.-I. Fujita, Y. Takahashi, M. Owaki, K. Yamamoto, R. Yamaguchi, *Org. Lett.* **2004**, *6*, 2785-2788.
[2] J. R. Hummel, J. A. Ellman, *J. Am. Chem. Soc.* **2015**, *137*, 490-498.
[3] T. Yoshino, H. Ikemoto, S. Matsunaga, M. Kanai, *Angew. Chem., Int. Ed.* **2013**, *52*, 2207-2211.
[4] J. A. Boerth, J. A. Ellman, *Angew. Chem., Int. Ed.* **2017**, *56*, 9976-9980
[5] Y. Park, K. T. Park, J. G. Kim, S. Chang. *J. Am. Chem. Soc*. **2015**, *137*, 4534-4542.
[6] P. M. Liu, C. G. Frost, *Org. Lett.* **2013**, *15*, 5862-5865.
[7] C. Liu, W. Yang, *Chem. Commun.* **2009**, *41*, 6267-6269.
[8] K. D. Hesp, R. G. Bergman, J. A. Ellman, *Org. Lett*. **2012**, *14*, 2304-2307.
[9] T. Stopka, P. Alder, G. Hagn, H. Zhang, V. Tona, N. Maulide, *Synthesis*, **2019**, *51*, 194-202.
[10] P. C. Too, G. H. Chan, Y. L. Tnay, H. Hirao, S. Chiba, *Angew. Chem., Int. Ed.* **2016**, *55*, 3719-3723.
[11] H. Ryu, J. Seo, H. M. Ko, *J. Org. Chem*. **2018**, *83*, 14102-14109.
[12] A. Sen, A. Singh, A. M. Sieburth, *J. Org. Chem.* **2009**, *74*, 2884-2886.
[13] S. Fustero, P. Bello, J. Miró, A. Simón, C. del Pozo, *Chem. Eur. J.* **2012**, *18*, 10991-10997.
[14] A. S. Kende, J. S. Mendoza, Y. Fujii, *Tetrahedron* **1993**, *49*, 8015-8038.
[15] Y. Liu, S. Duan, R. Zhang, Y. Liu, J. Chen, W. Xiao. *Org. Biomol. Chem.* **2016**, *23*, 5224-5228.
[16] I. Takayoshi, T. Jiro, T. Hideo, *Bull. Chem. Soc. Jpn*. **2009**, *82*, 475-481.
[17] H. Leicht, I. Göttker-Schnetmann, S. Mecking, *J. Am. Chem. Soc.* **2017**, *139*, 6823-6826.
[18] W. L. F. Armarego, C. Chai. in *Purification of Laboratory Chemicals* (6th edition), Butterworth-Heinemann, **2009**, pp. 154.
[19] J. Thongpaen, T. E. Schmid, L. Toupet, V. Dorcet, M. Mauduit, O. Basle. *Chem. Commun*. **2018**, *59*, 8202-8205.
[20] M. H. Shaw, R. A. Croft, W. G. Whittingham, J. F. Bower, *J. Am. Chem. Soc*. **2015**, *137*, 8054-8057.
[21] J. J. Gajewski, K. B. Peterson, J. R. Kagel, Y. C. J. Huang, *J. Am. Chem. Soc.* **1989**, *111*, 9078-9081.

X. NMR Spectra



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5.98
5.76
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3.44
2.04
1.76
1.72
1.05
1.04
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Me
Me
Me
Me
OH
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0.90
0.96
1.10
1.03
1.00
1.00
1.00
1.04
2.91
1.08
2.98
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3.03
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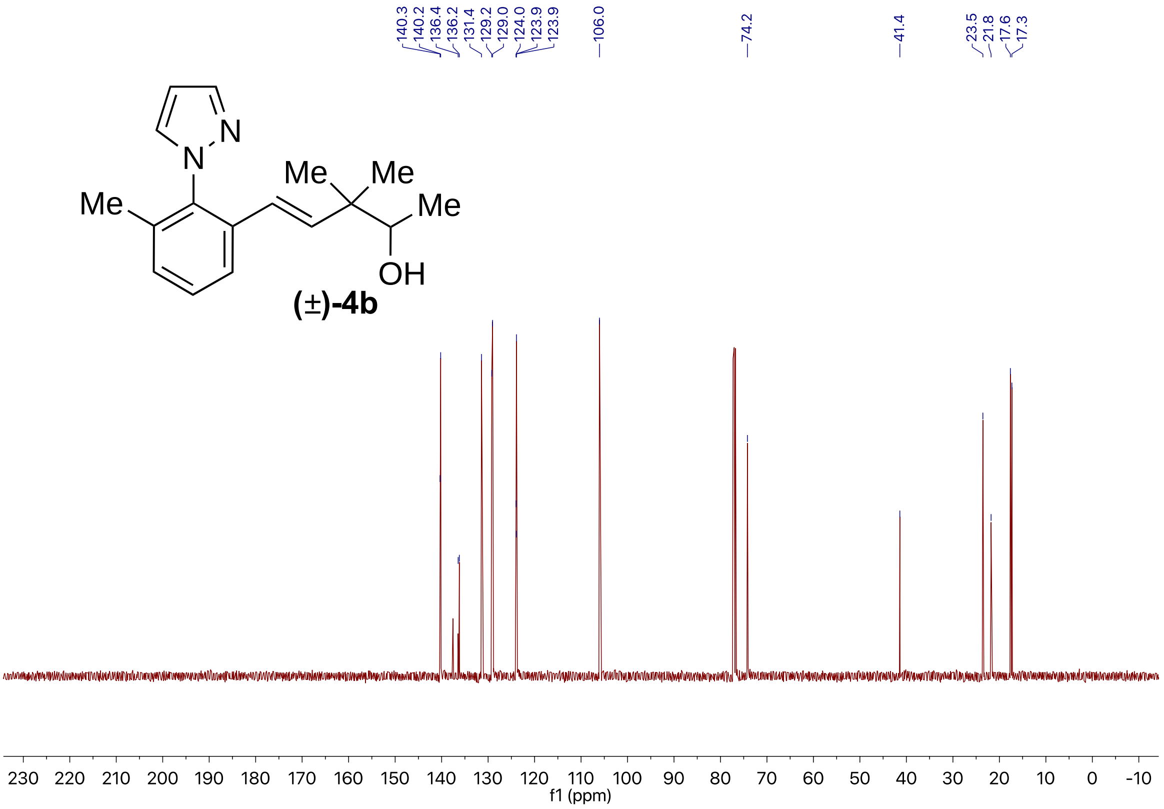
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21.8
17.6
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Me
Me
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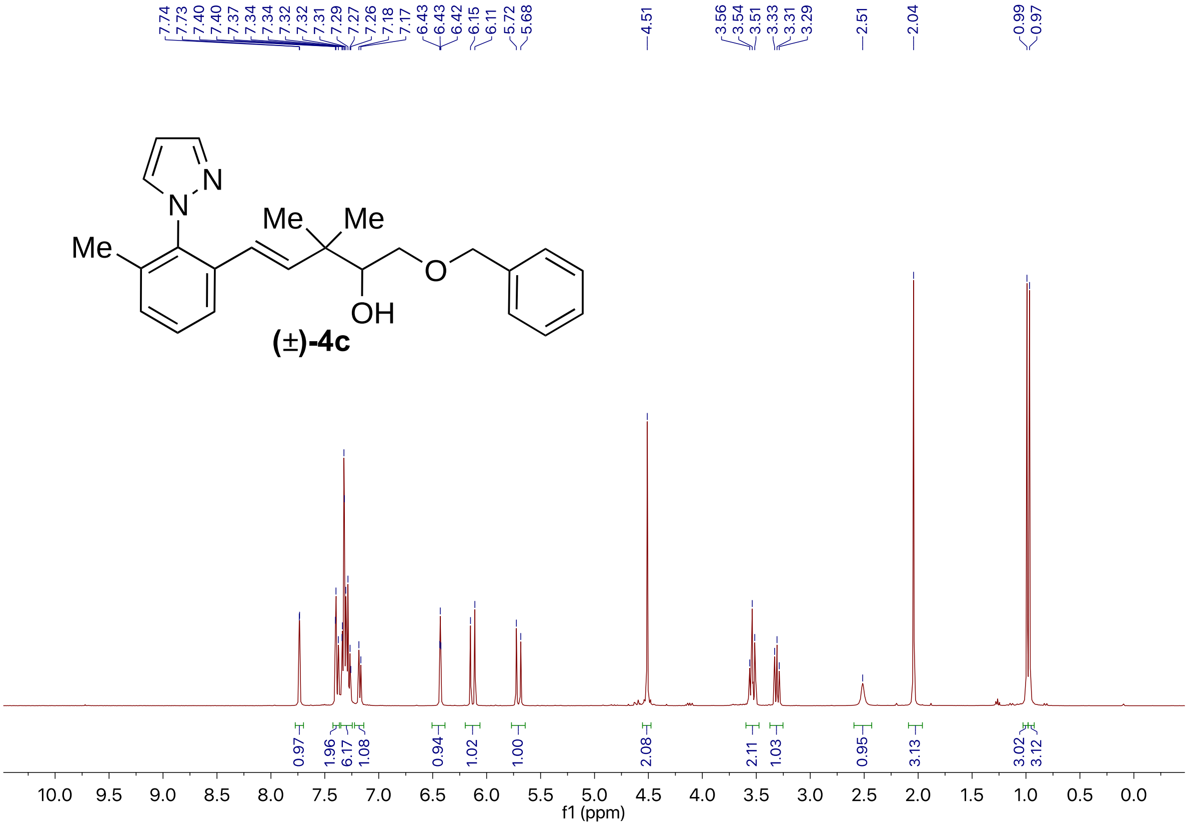
f1 (ppm)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Me
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1.02
1.00
2.08
2.11
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3.02
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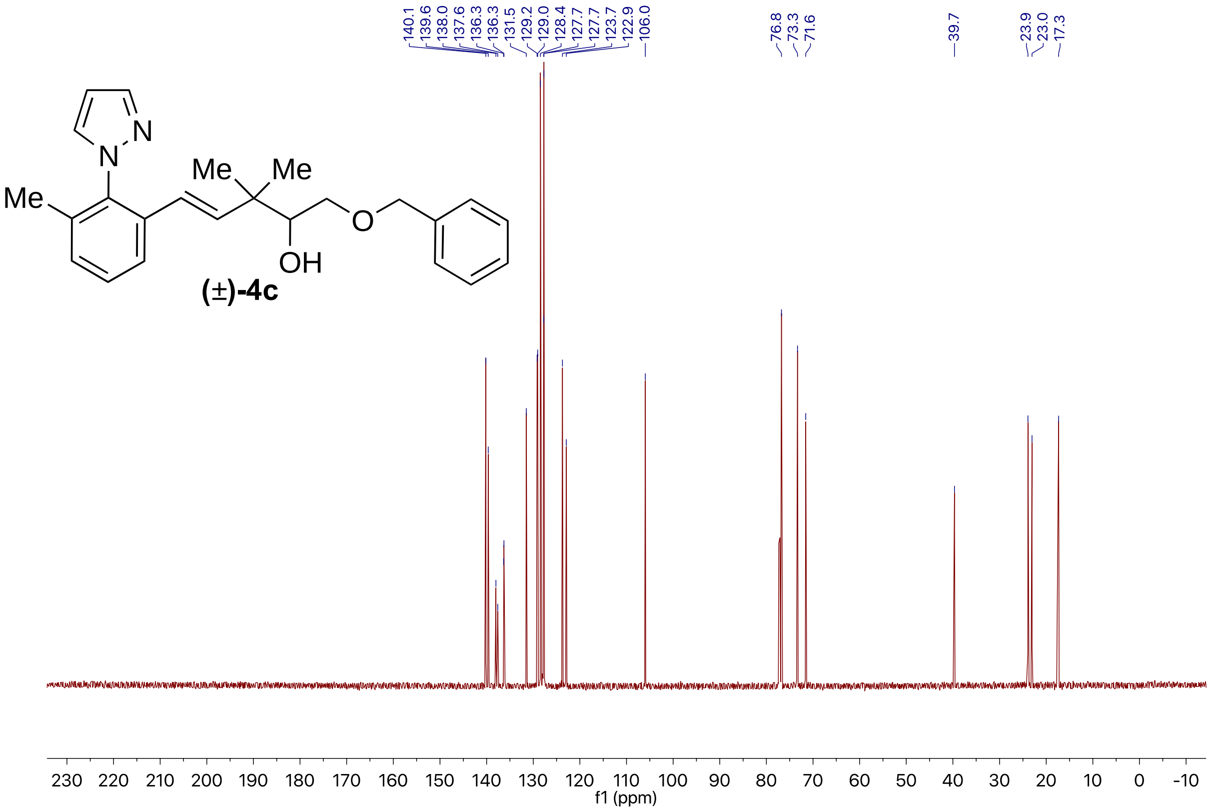
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23.0
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Me
Me
Me
O
OH
(±)-4c
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200
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180
170
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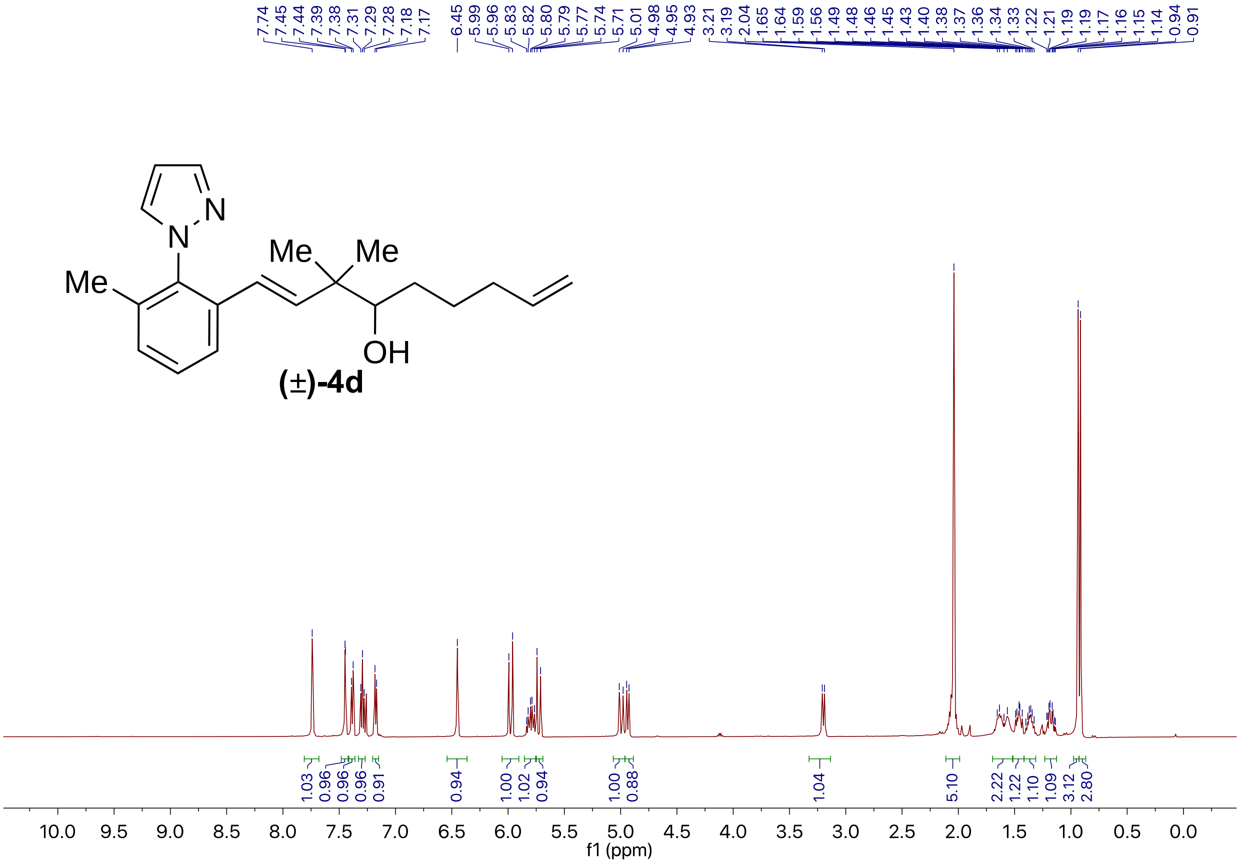

(±)-4d

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2.04
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1.38
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1.33
1.22
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1.19
1.19
1.17
1.16
1.15
1.14
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Me
Me
N
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OH
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0.96
0.96
0.91
0.94
1.00
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0.94
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6.5
6.0
5.5
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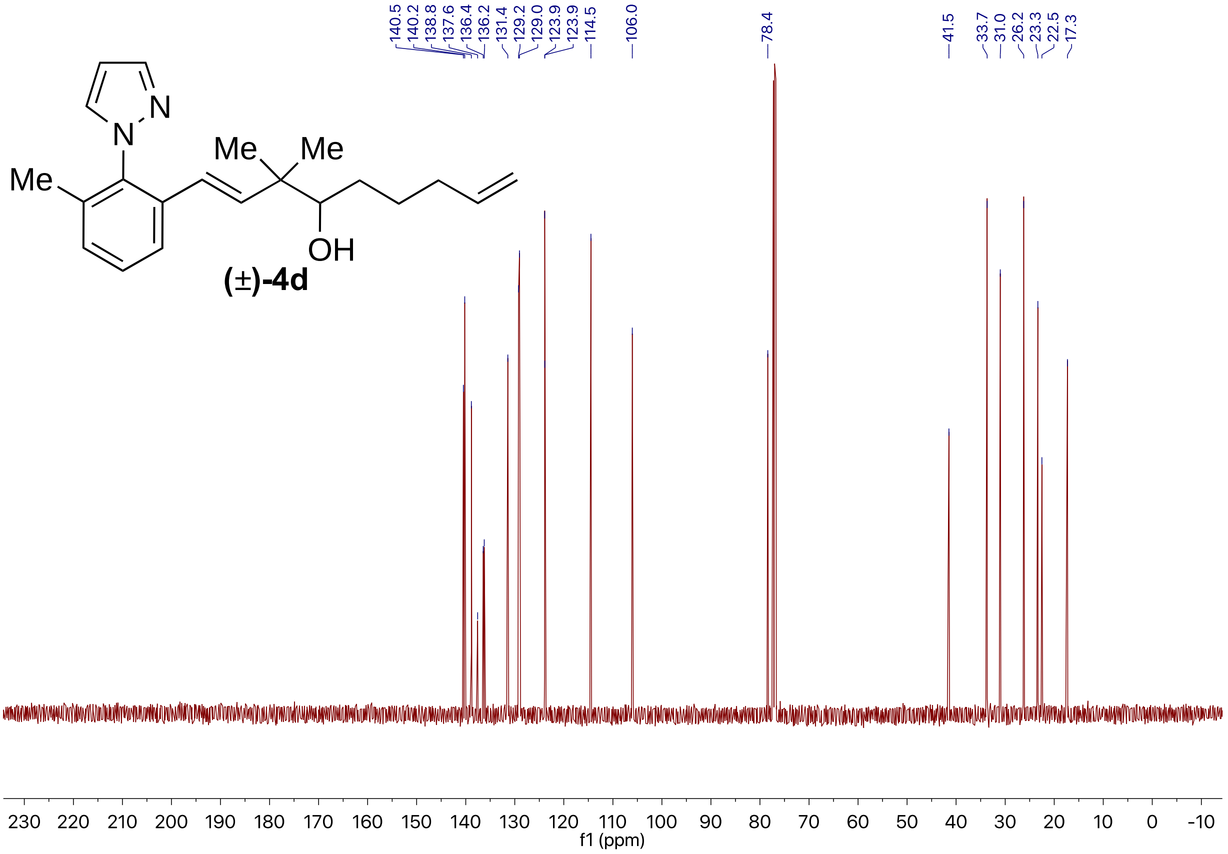

(±)-4d

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123.9
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33.7
31.0
26.2
23.3
22.5
17.3
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Me
Me
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N
OH
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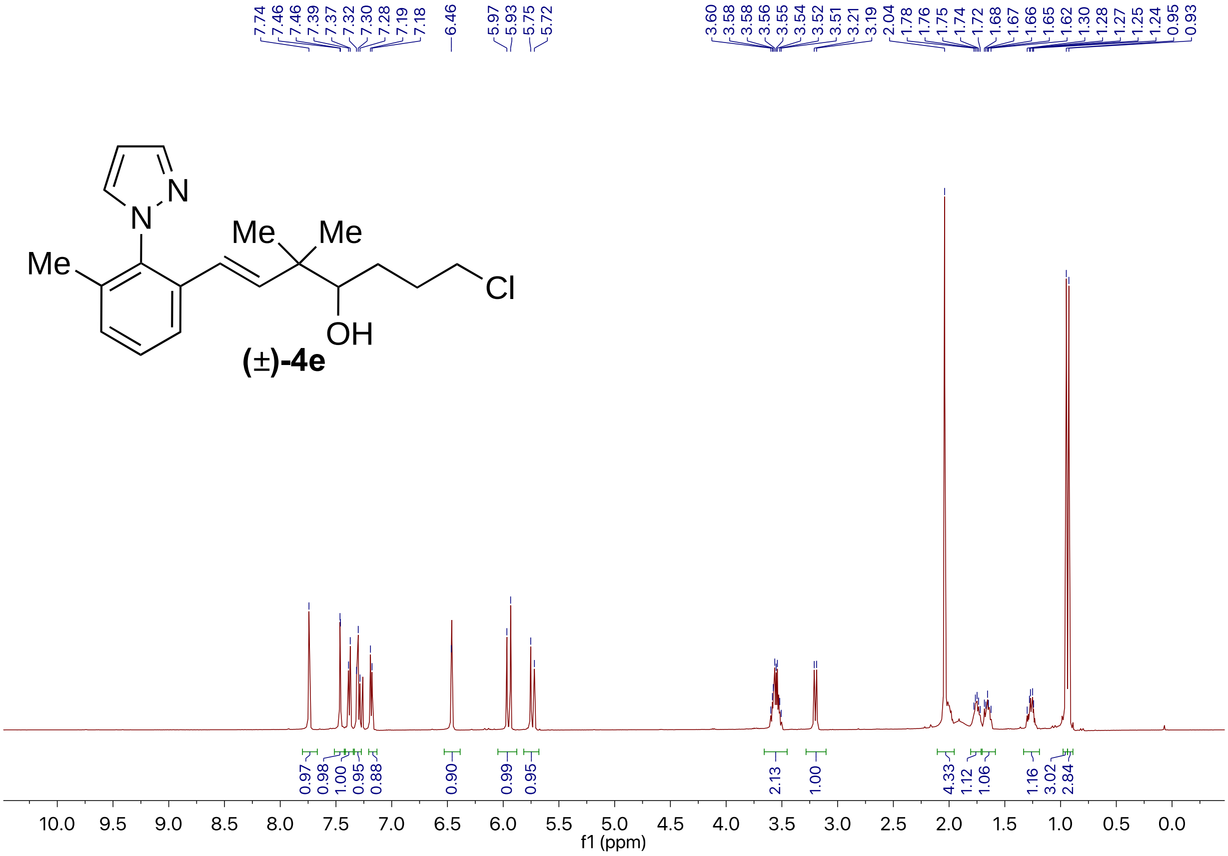
f1 (ppm)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N
N
Me
Me
Me
Cl
OH
(±)-4e
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0.98
1.00
0.95
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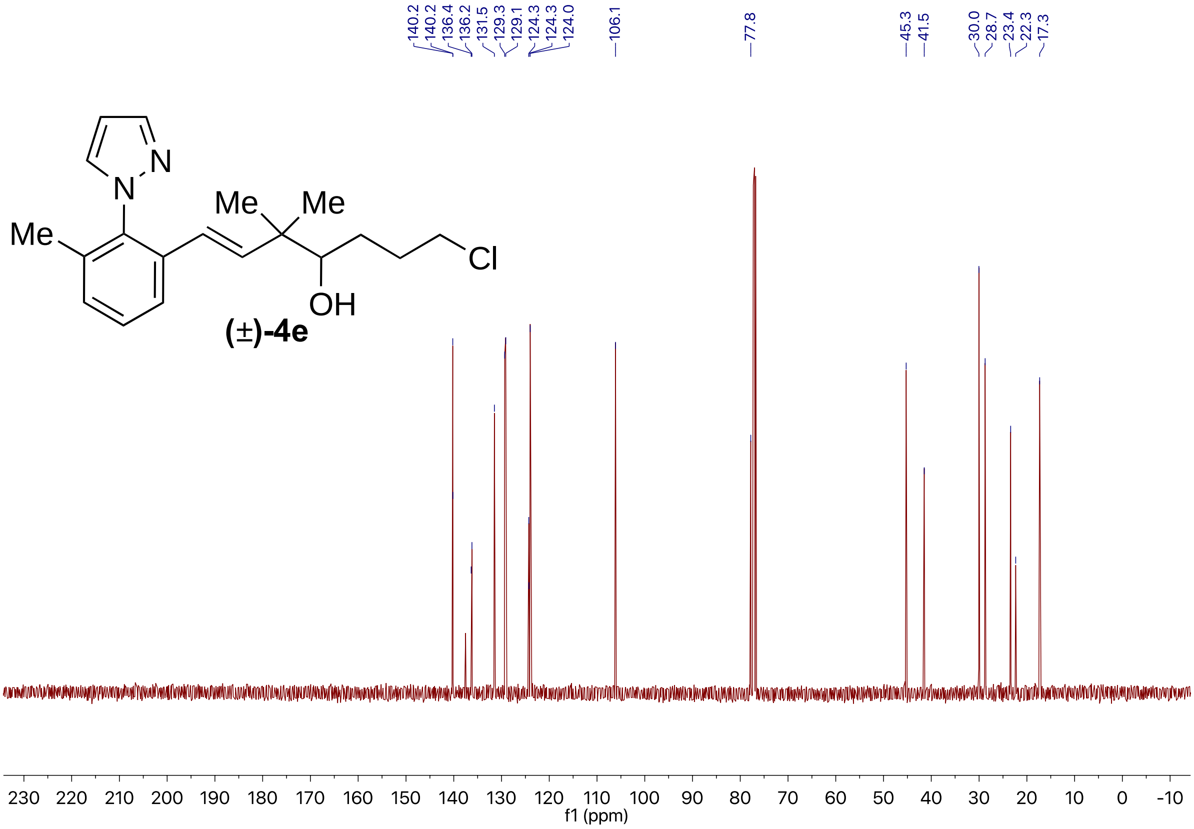
f1 (ppm)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Me
Me
Me
Cl
OH
(±)-4e
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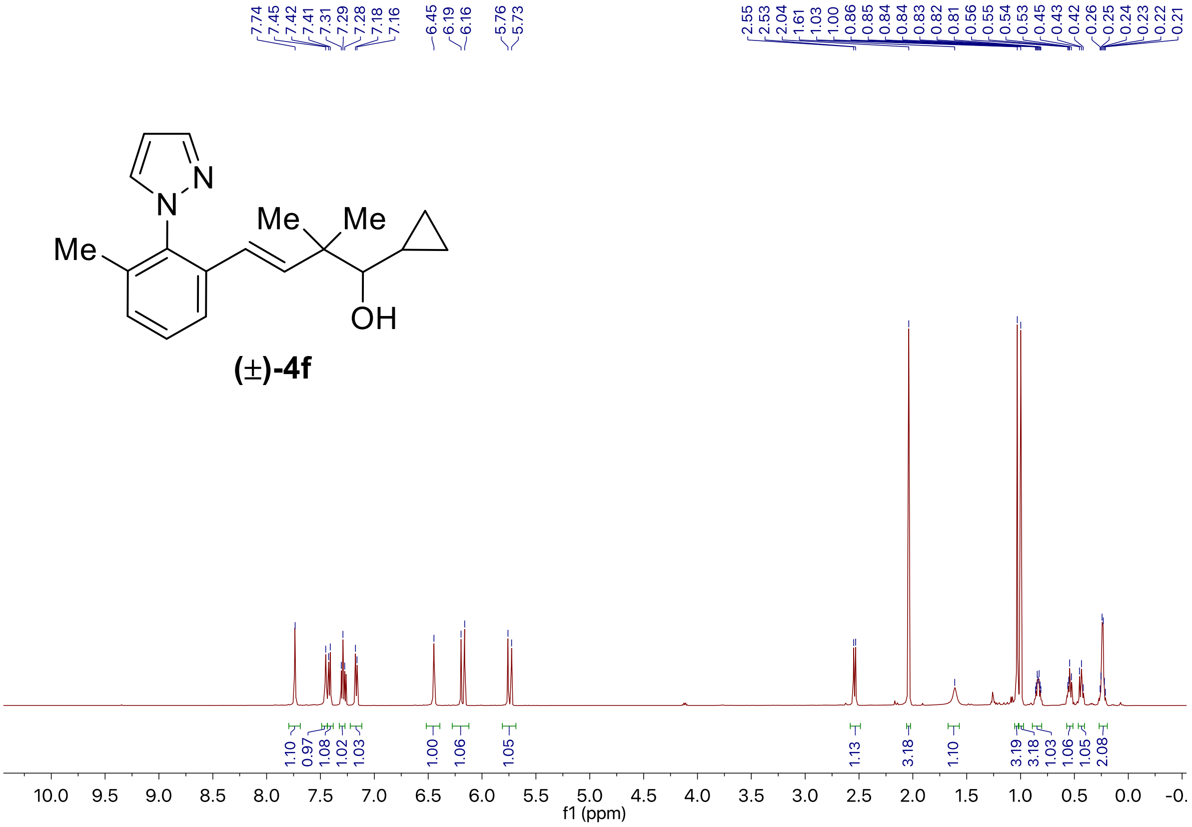
f1 (ppm)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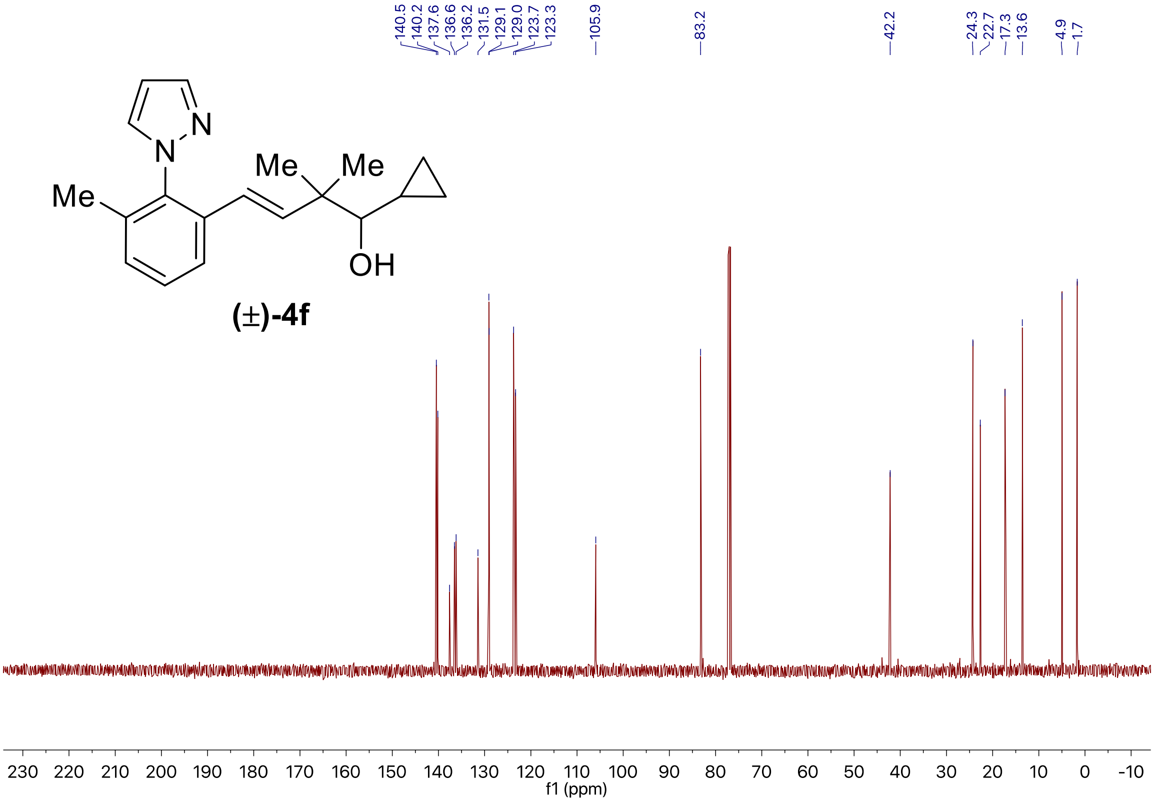
f1 (ppm)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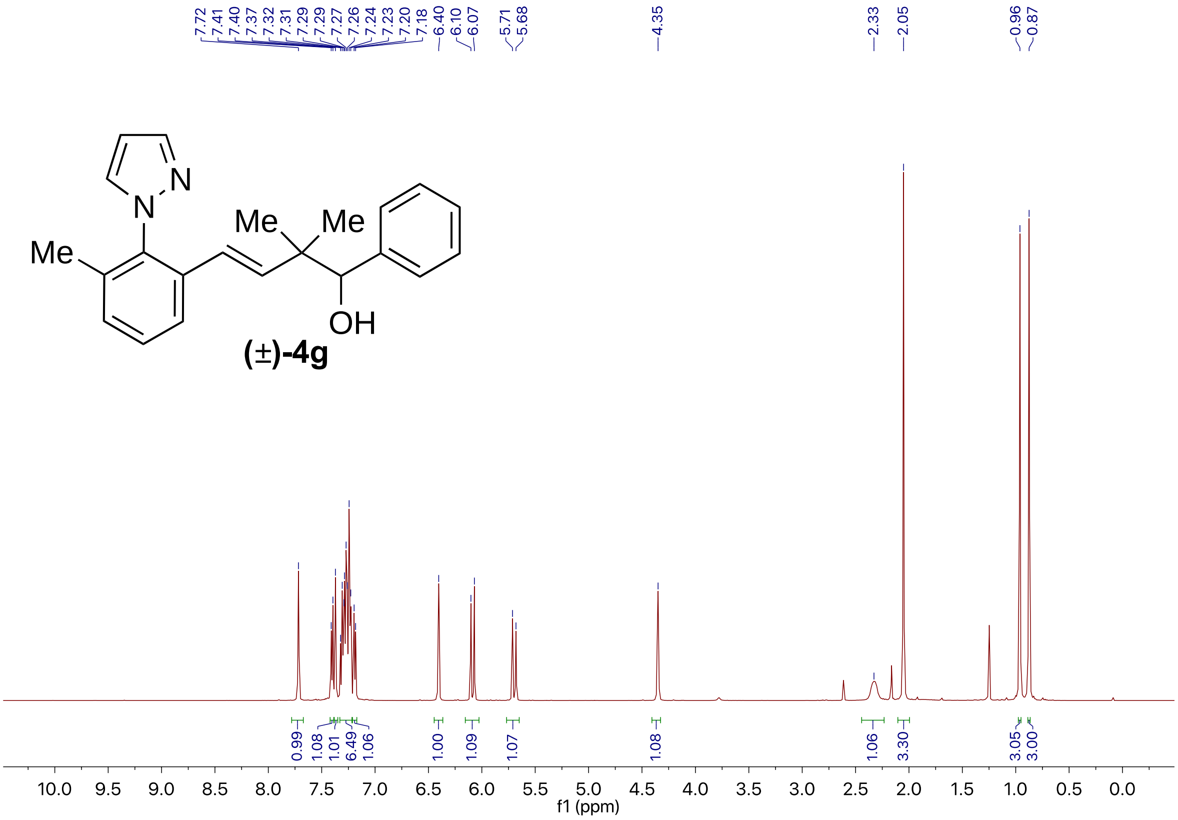
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3.00
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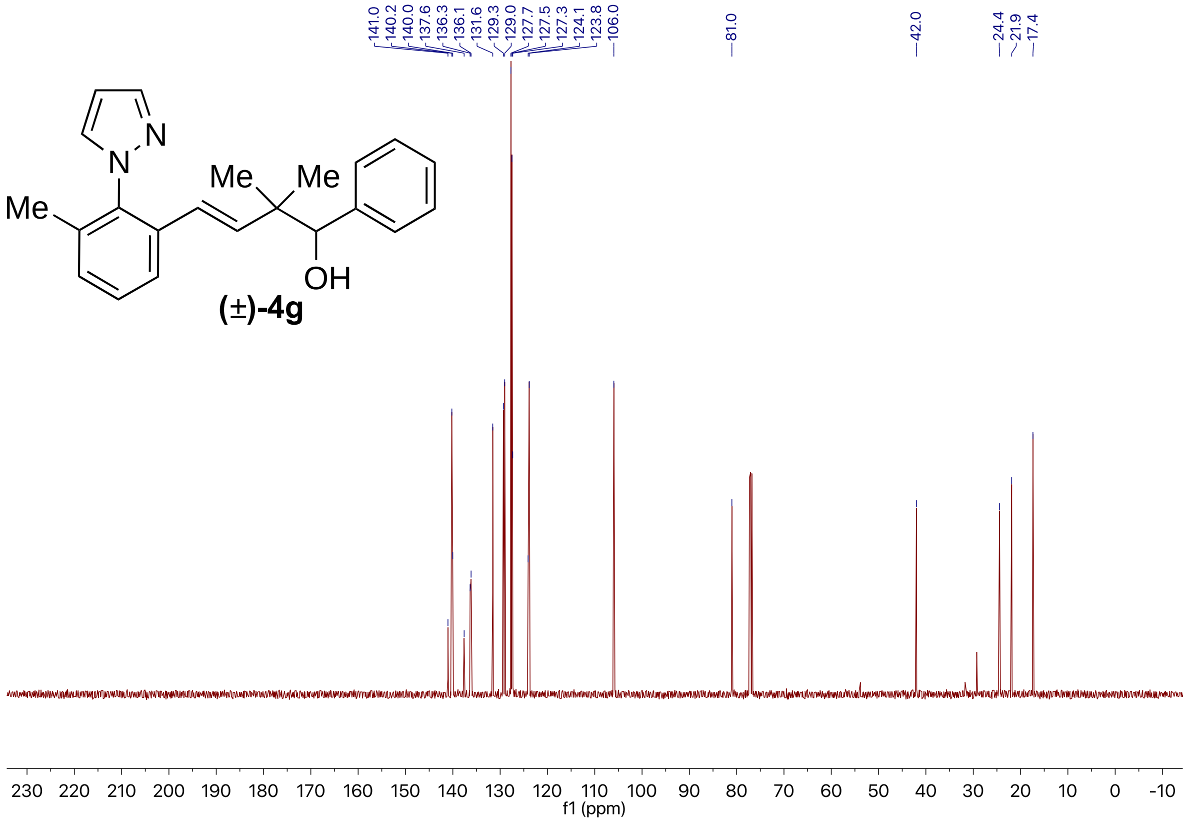
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106.0
81.0
42.0
24.4
21.9
17.4
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Me
Me
N
N
OH
(±)-4g
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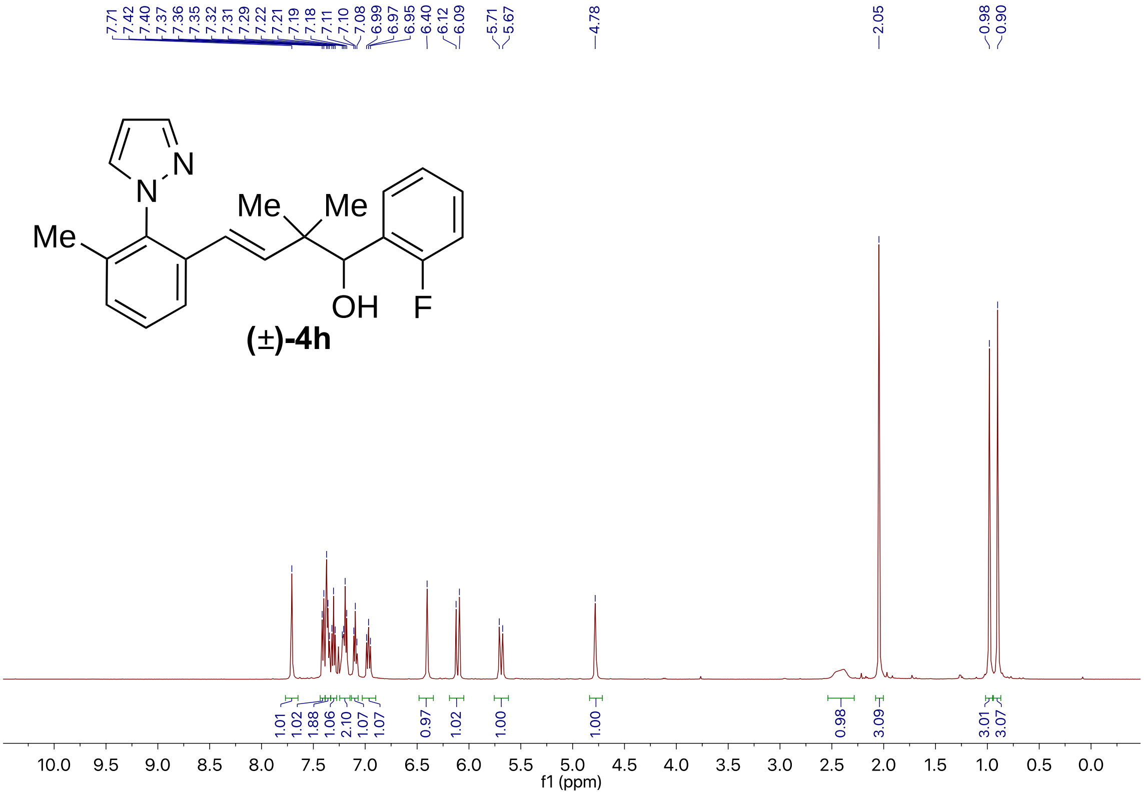
f1 (ppm)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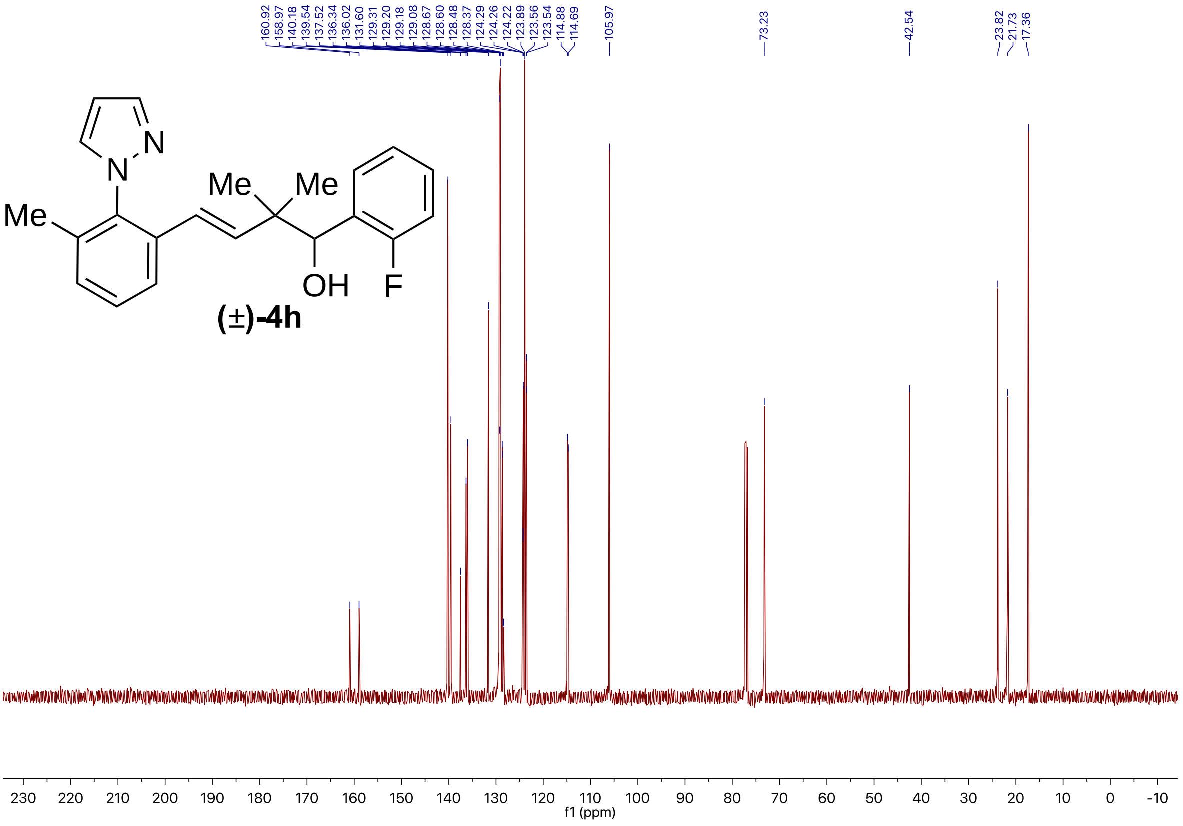
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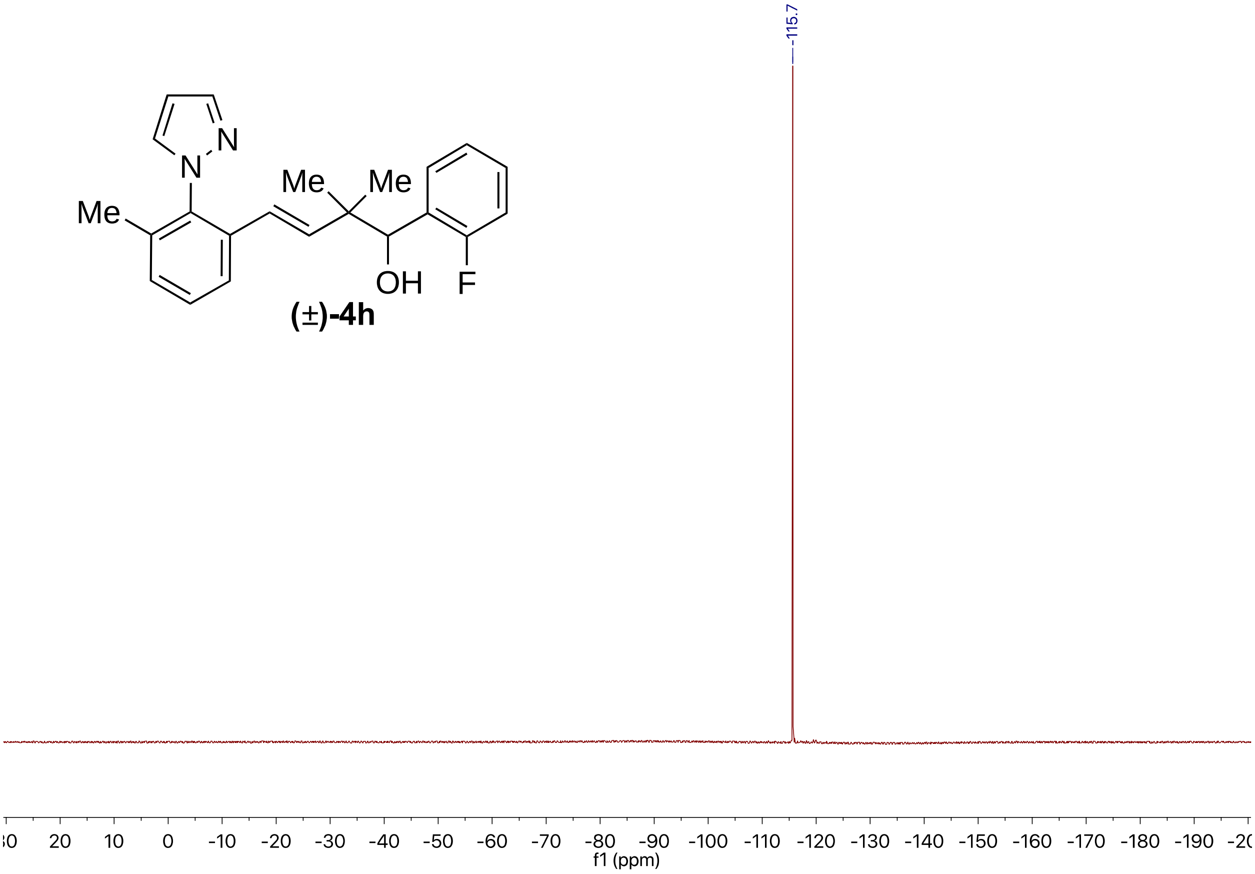
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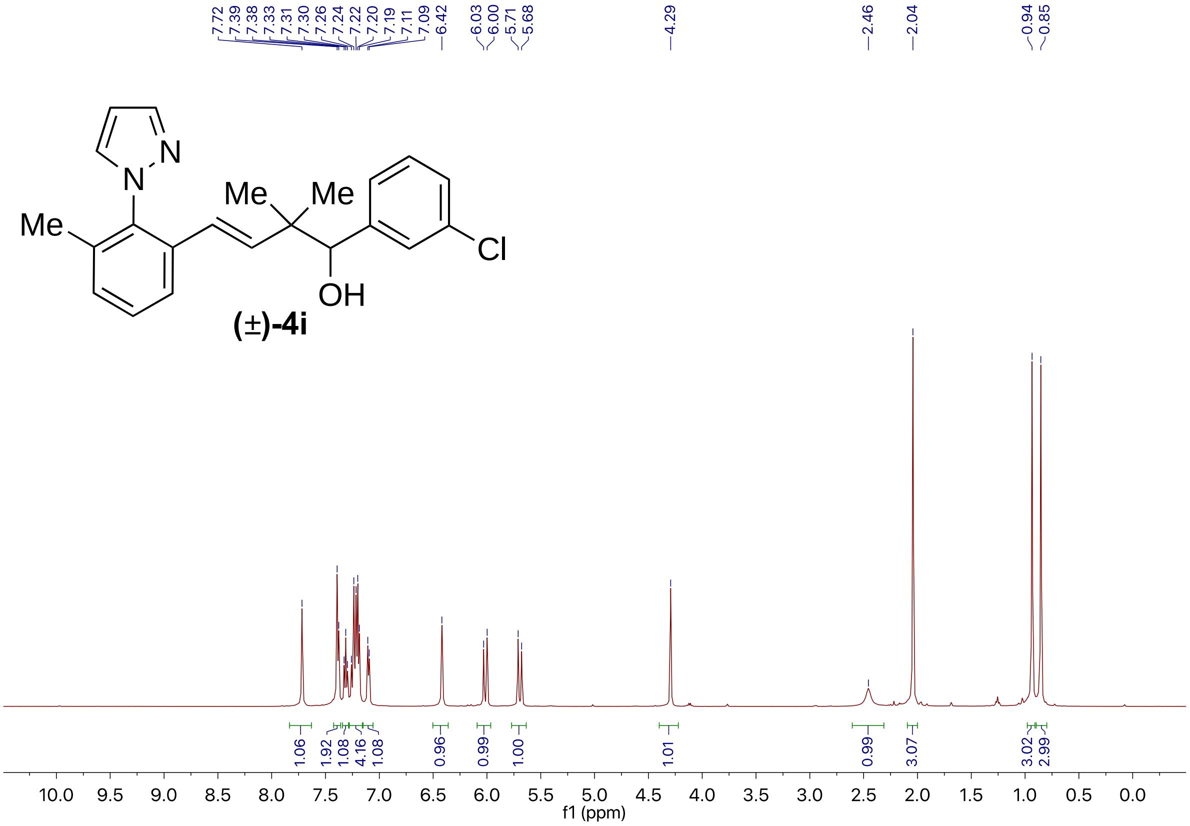
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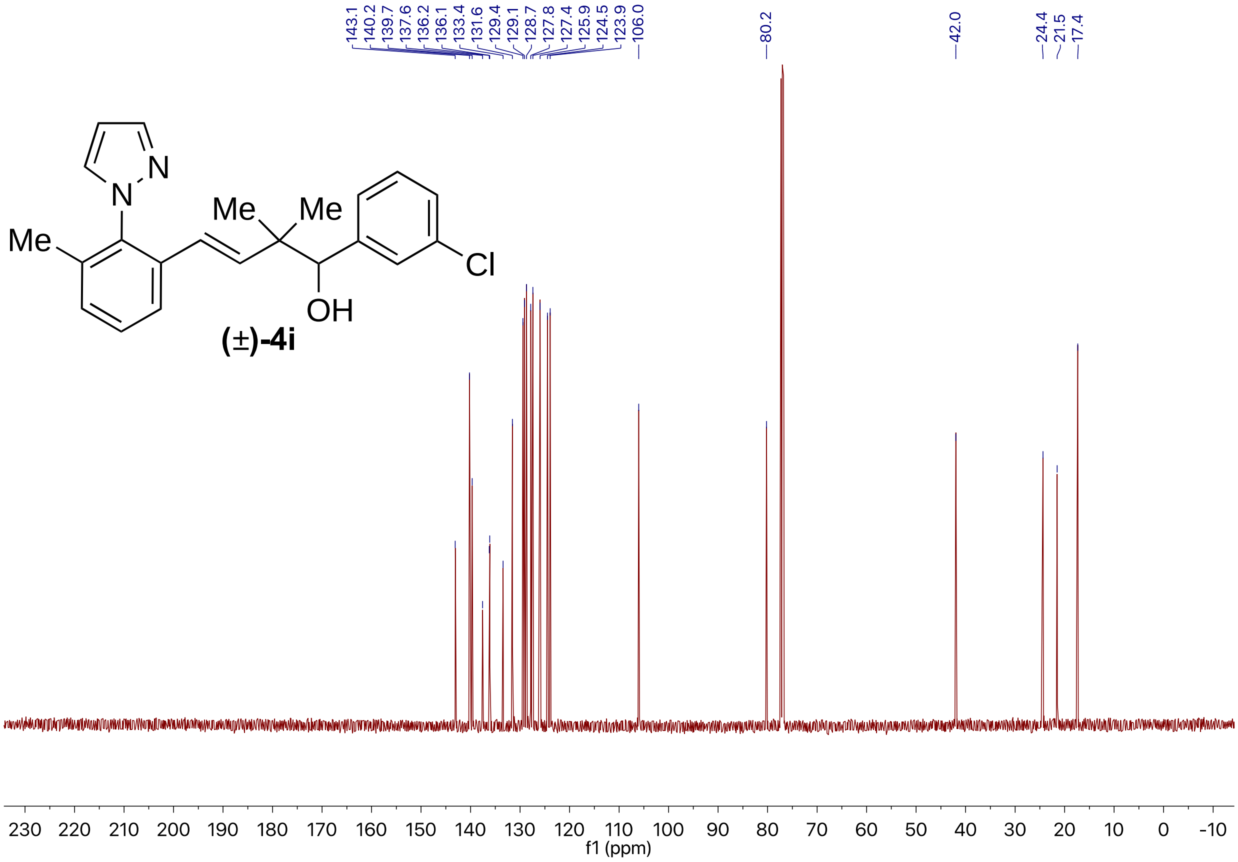
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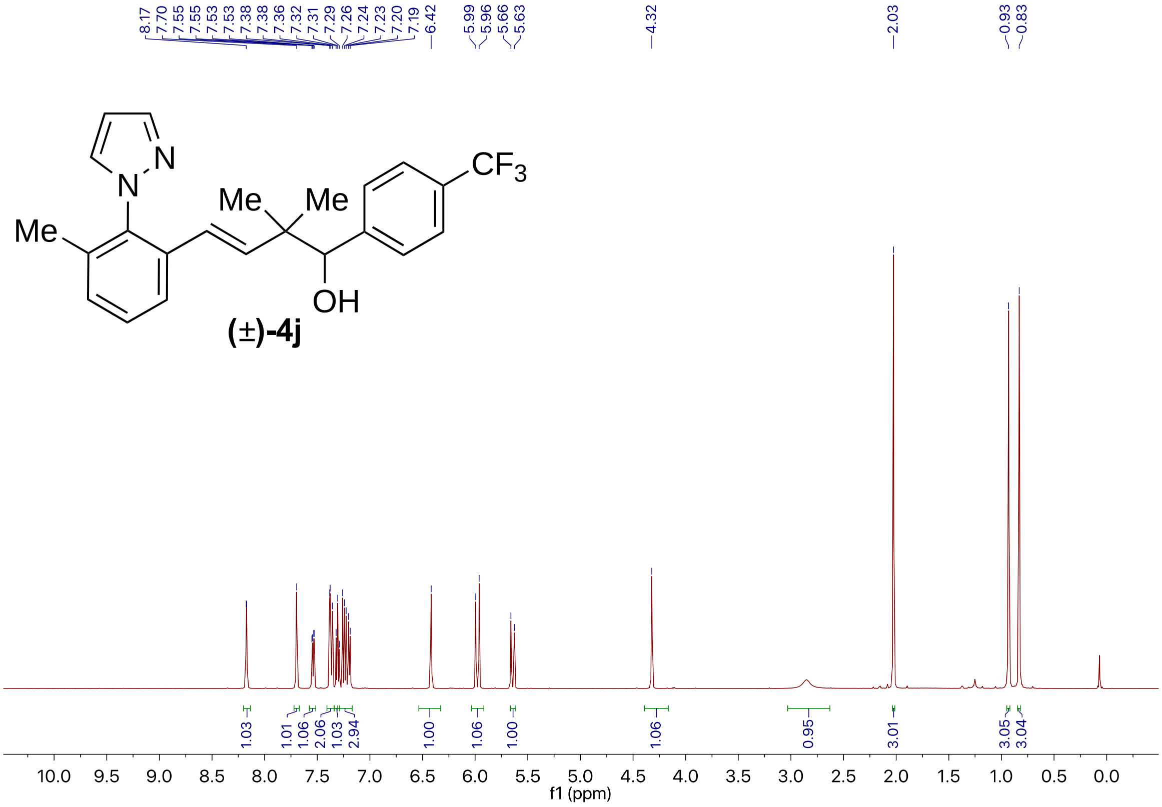
f1 (ppm)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1.00
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0.95
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3.04
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0.5
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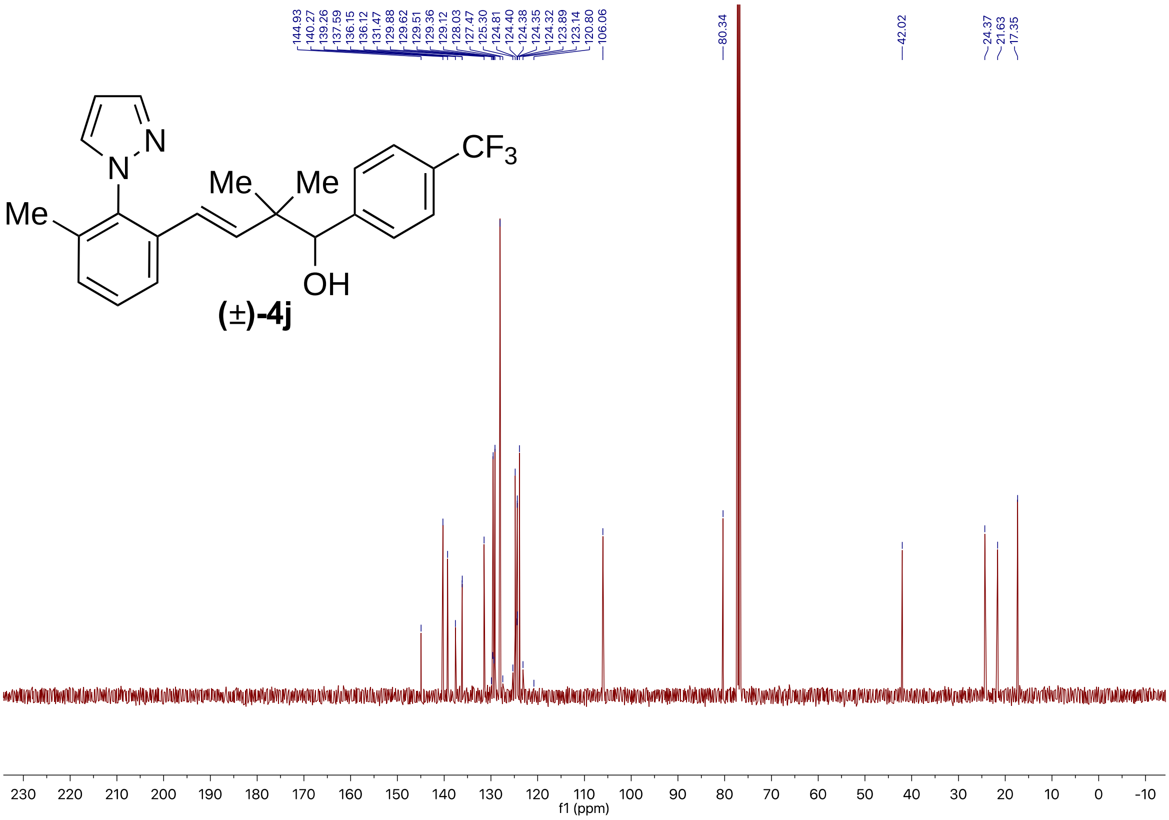
f1 (ppm)

(±)-4j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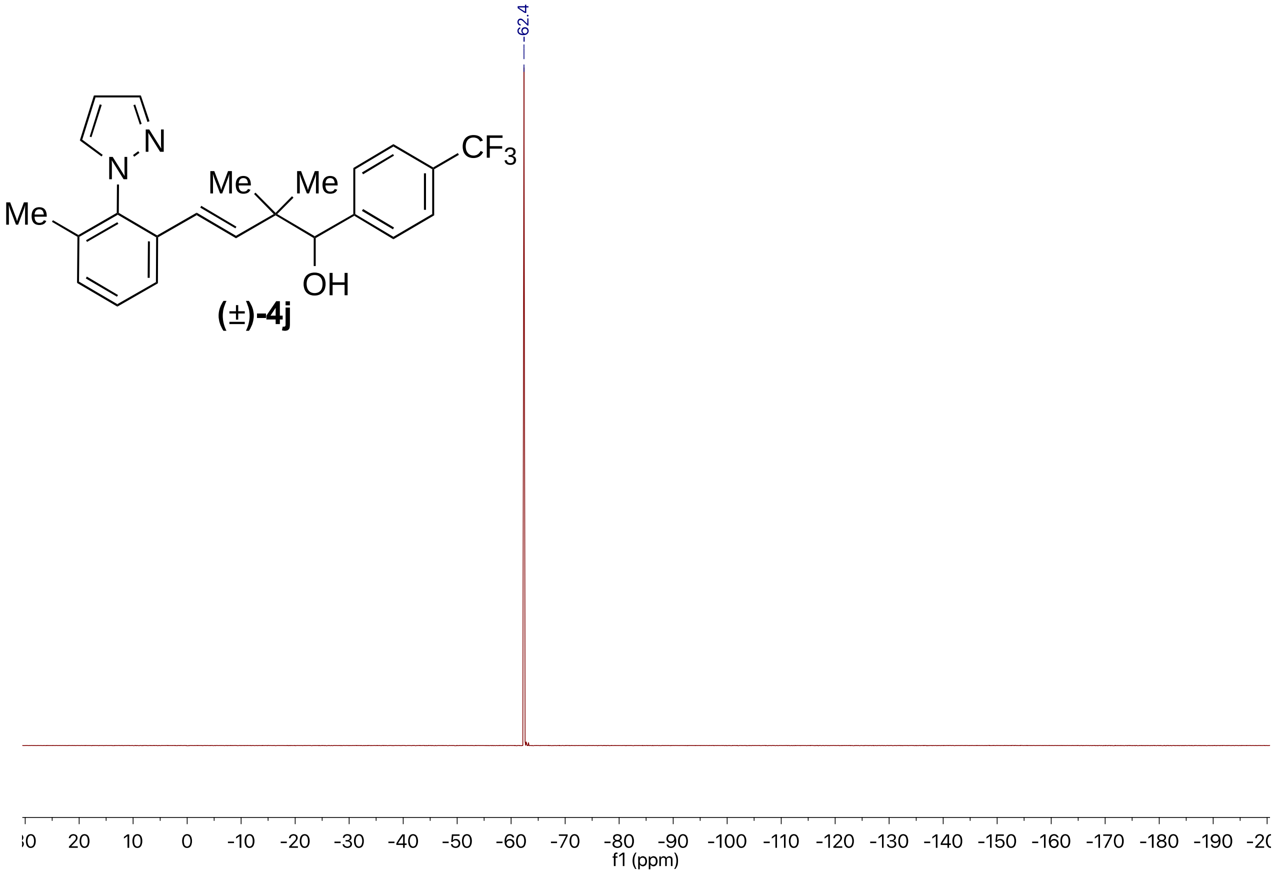
124.40
124.38
124.35
124.32
123.89
123.14
120.80
106.06
80.34
42.02
24.37
21.63
17.35
N
N
CF$_3$
Me
Me
Me
OH
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

(±)-4j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Me
Me
Me
CF3
OH
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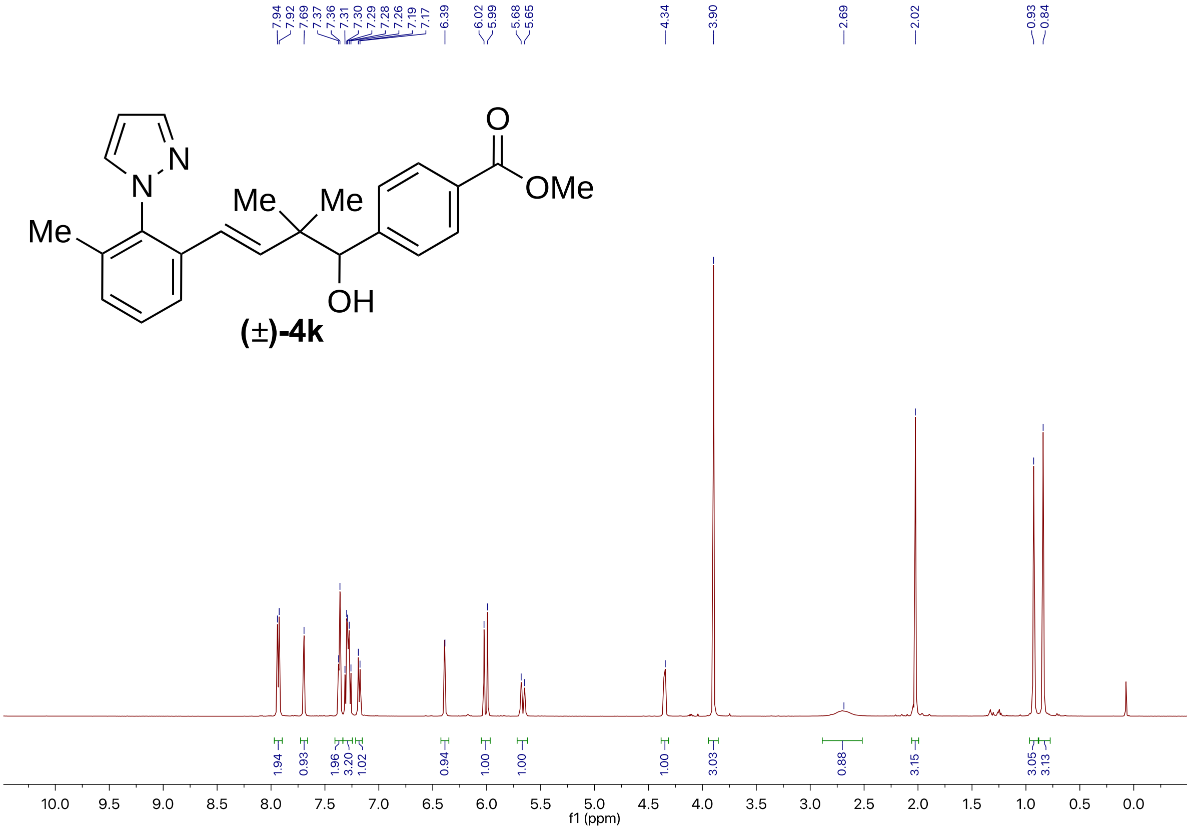
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

(±)-4j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7.92
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7.30
7.29
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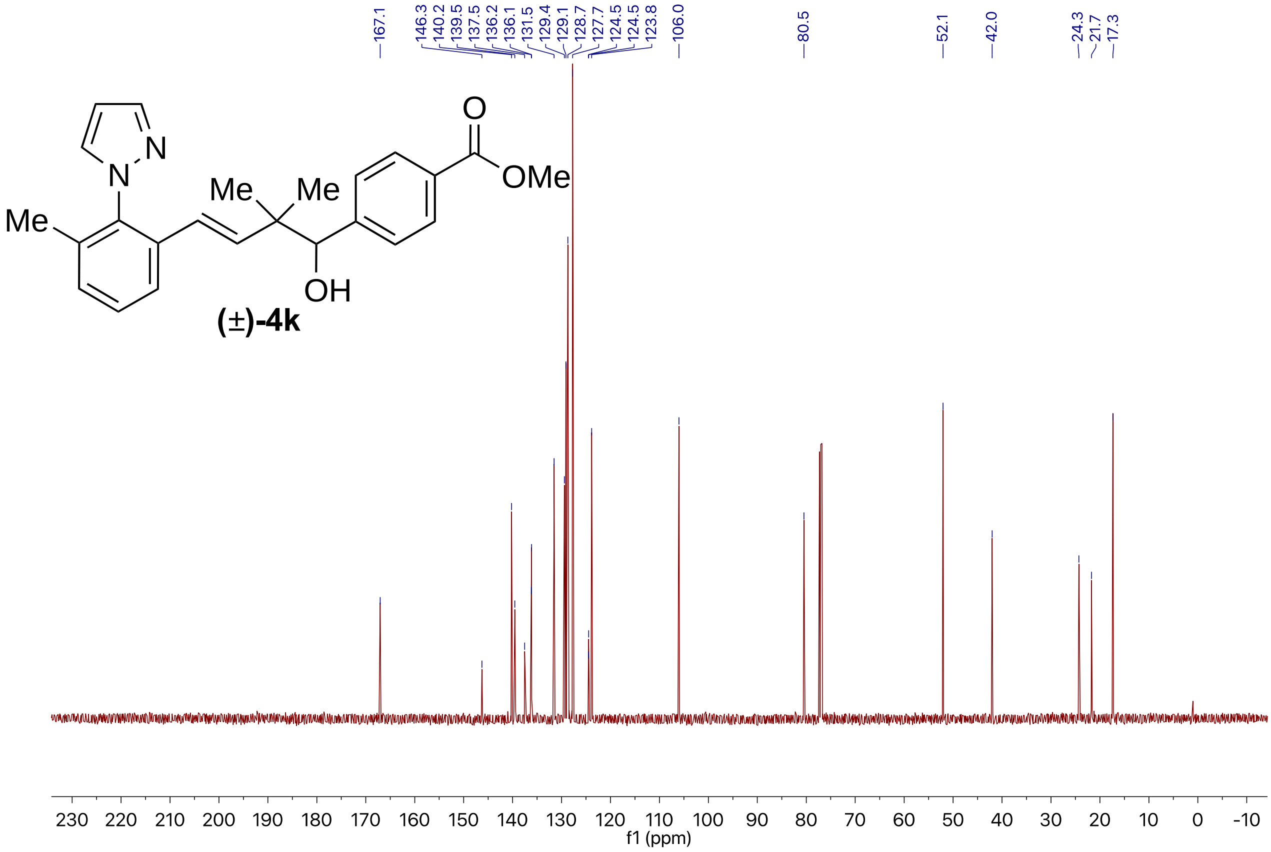
7.26
7.19
7.17
6.39
6.02
5.99
5.68
5.65
4.34
3.90
2.69
2.02
0.93
0.84
Me
N
N
Me
Me
O
OMe
OH
(±)-4k
1.94
0.93
1.96
3.20
1.02
0.94
1.00
1.00
1.00
3.03
0.88
3.15
3.05
3.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


167.1
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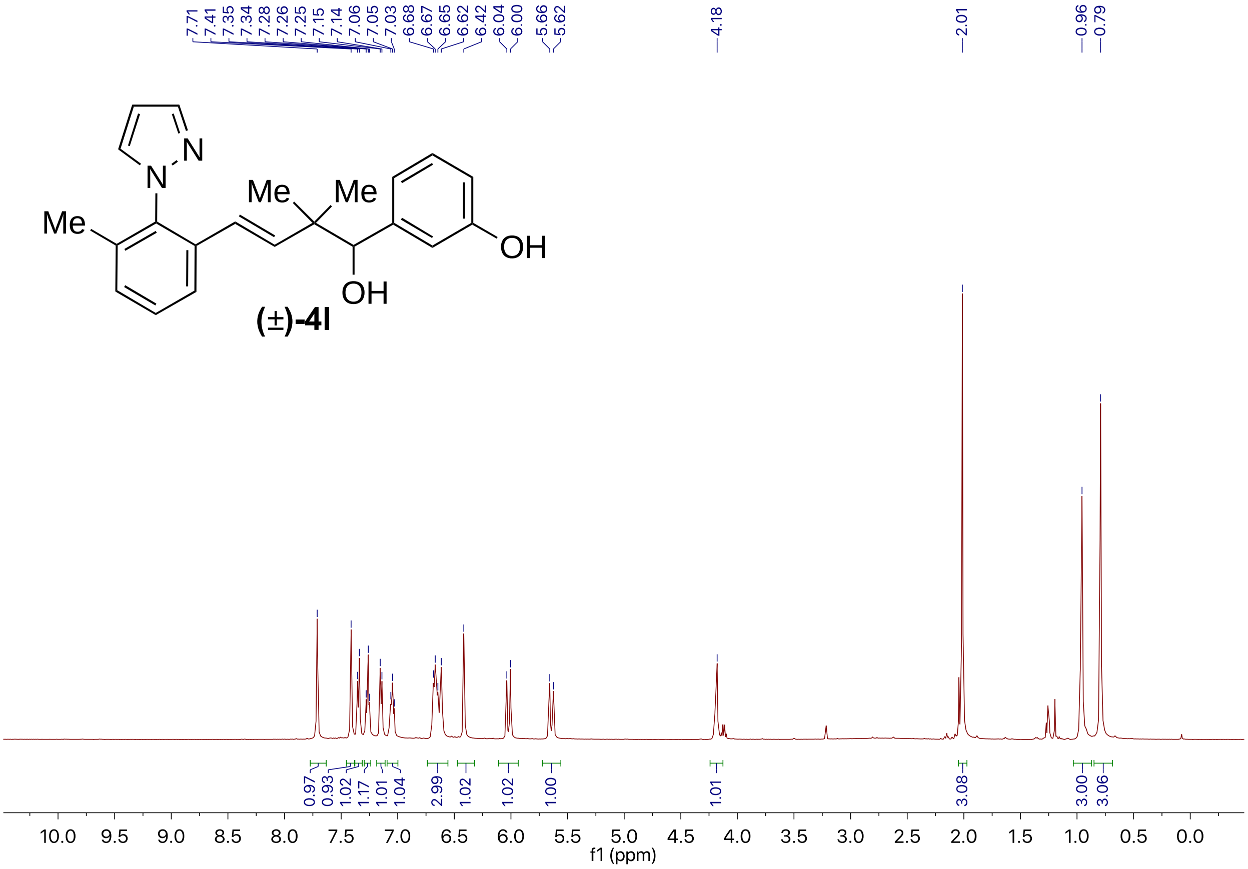
140.2
139.5
137.5
136.2
136.1
131.5
129.4
129.1
128.7
127.7
124.5
124.5
123.8
106.0
80.5
52.1
42.0
24.3
21.7
17.3
Me
N
N
Me
Me
O
OMe
OH
(±)-4k
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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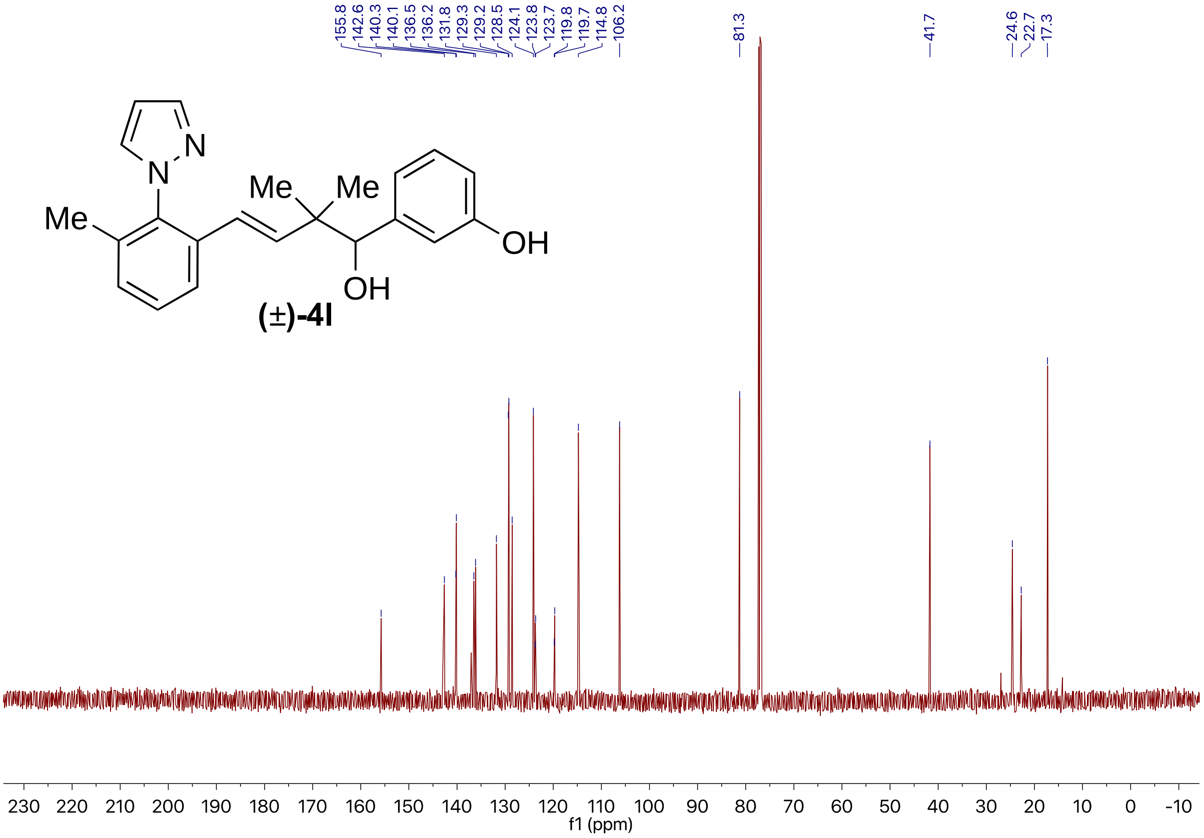
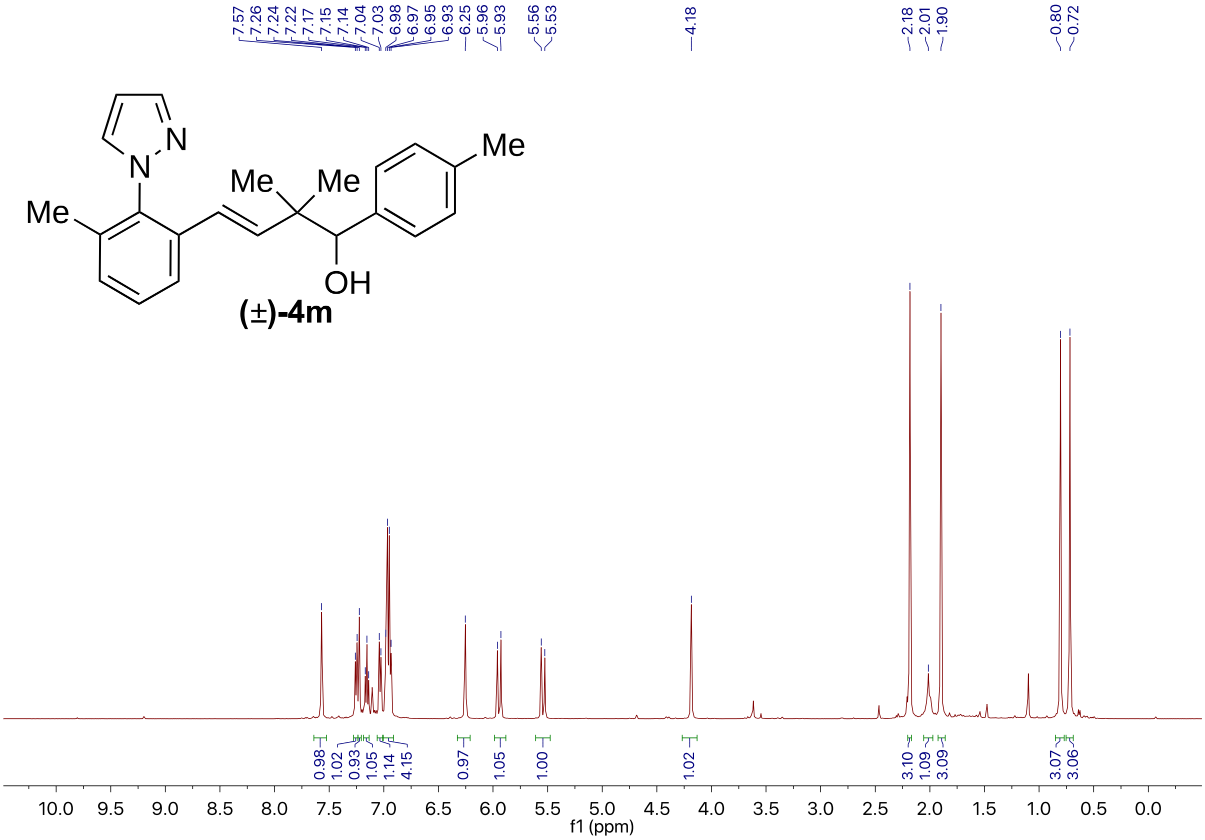
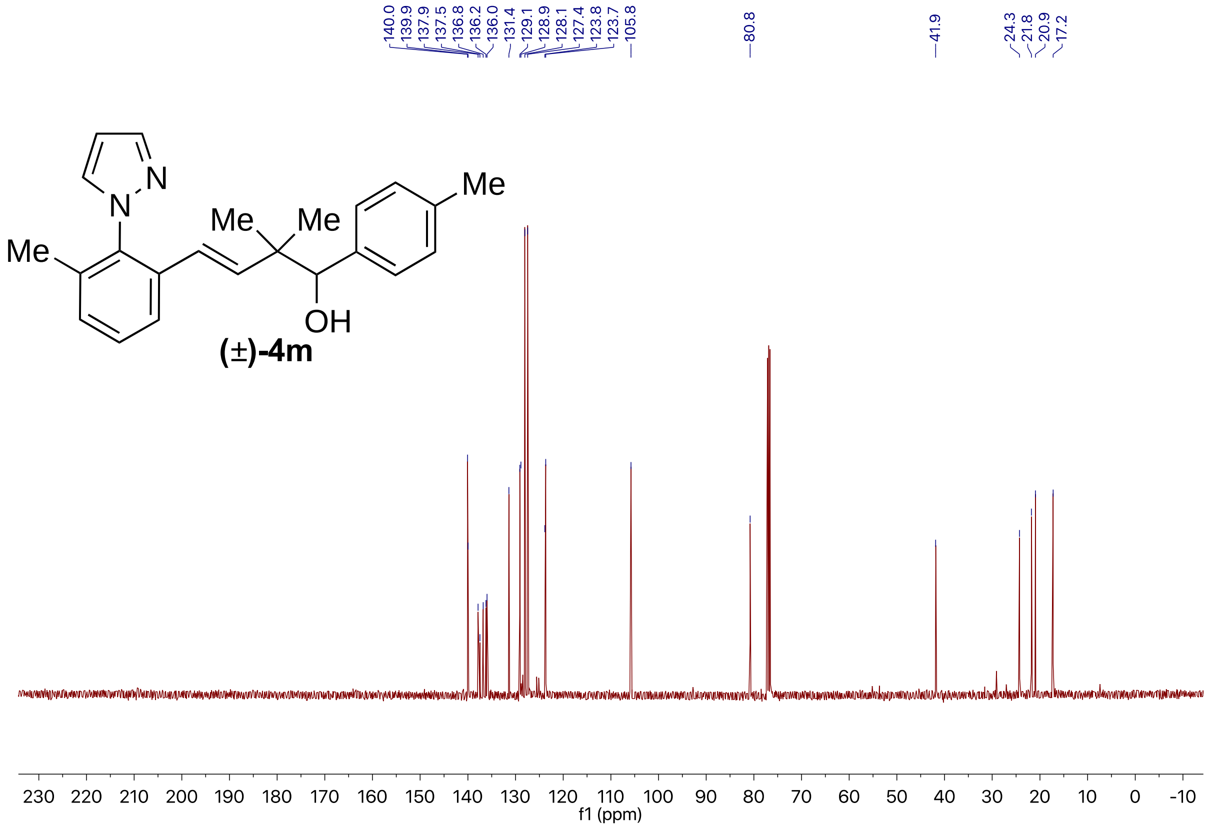
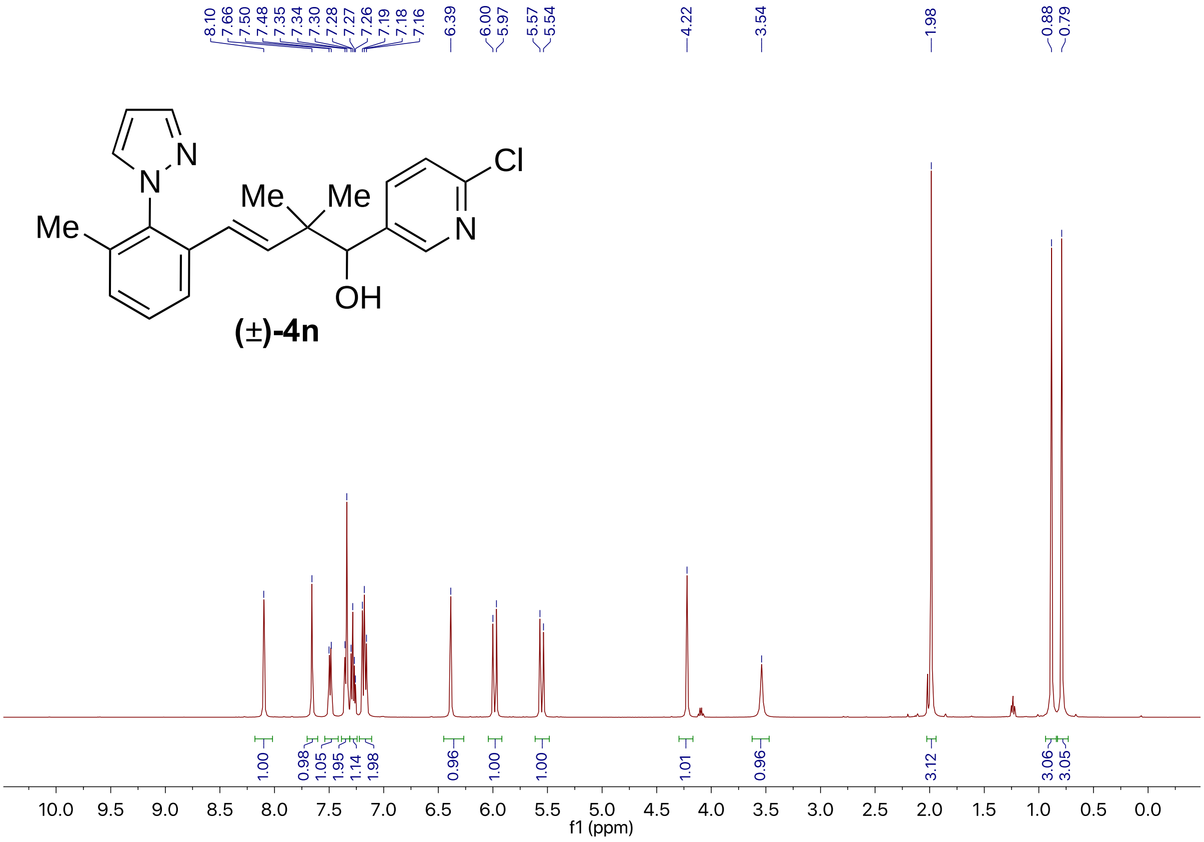
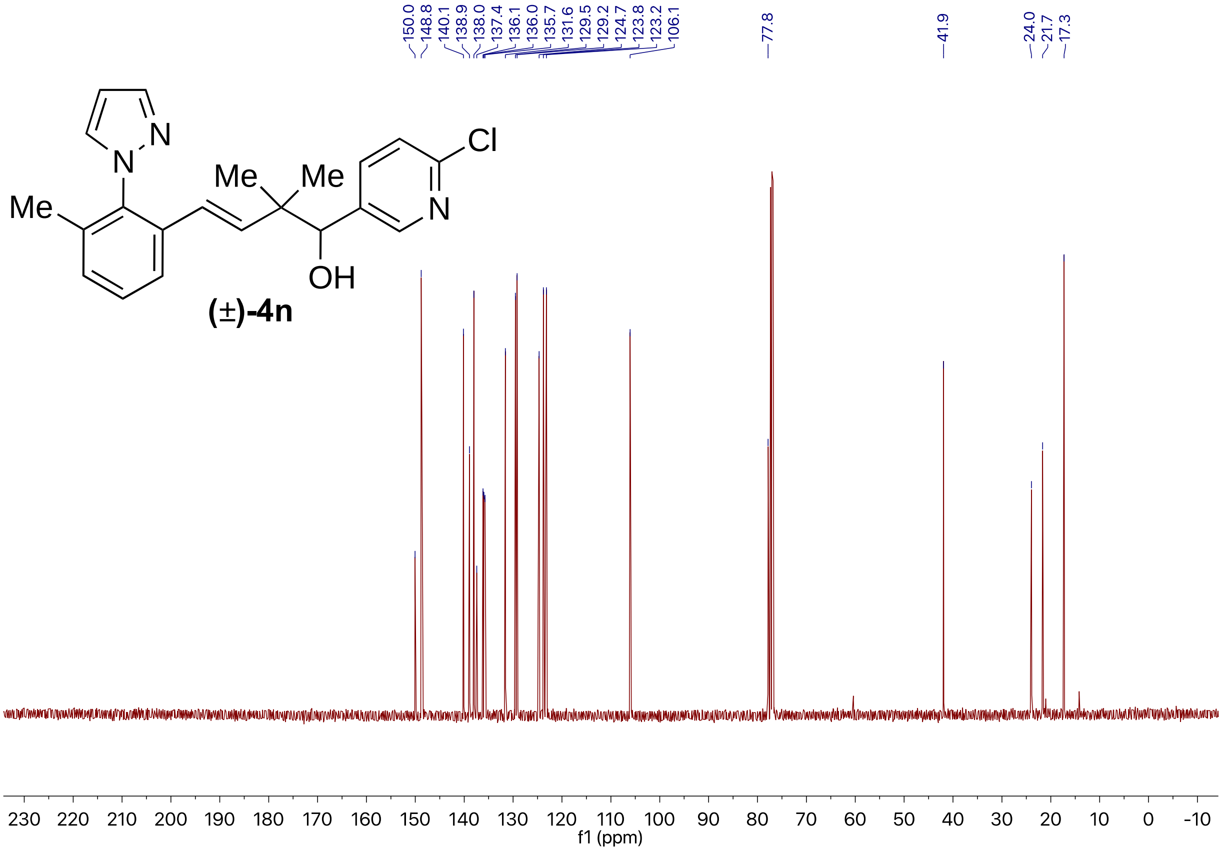
7.25
7.15
7.14
7.06
7.05
7.03
6.68
6.67
6.65
6.62
6.42
6.04
6.00
5.66
5.62
4.18
2.01
0.96
0.79
N
N
Me
Me
Me
OH
OH
(±)-4l
0.97
0.93
1.02
1.17
1.01
1.04
2.99
1.02
1.02
1.00
1.01
3.08
3.00
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


155.8
142.6
140.3
140.1
136.5
136.2
131.8
129.3
129.2
128.5
124.1
123.8
123.7
119.8
119.7
114.8
106.2
81.3
41.7
24.6
22.7
17.3
N
N
Me
Me
Me
OH
OH
(±)-4l
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.57
7.26
7.24
7.22
7.17
7.15
7.14
7.04
7.03
6.98
6.97
6.95
6.93
6.25
5.96
5.93
5.56
5.53
4.18
2.18
2.01
1.90
0.80
0.72
N
N
Me
Me
Me
Me
OH
(±)-4m
0.98
1.02
0.93
1.05
1.14
4.15
0.97
1.05
1.00
1.02
3.10
1.09
3.09
3.07
3.06
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
f1 (ppm)


140.0
139.9
137.9
137.5
136.8
136.2
136.0
131.4
129.1
128.9
128.1
127.4
123.8
123.7
105.8
80.8
41.9
24.3
21.8
20.9
17.2
N
N
Me
Me
Me
Me
OH
(±)-4m
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.10
7.66
7.50
7.48
7.35
7.34
7.30
7.28
7.27
7.26
7.19
7.18
7.16
6.39
6.00
5.97
5.57
5.54
4.22
3.54
1.98
0.88
0.79
N
N
Me
Me
Me
Cl
N
OH
(±)-4n
1.00
0.98
1.05
1.95
1.14
1.98
0.96
1.00
1.00
1.01
0.96
3.12
3.06
3.05
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
f1 (ppm)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148.8
140.1
138.9
138.0
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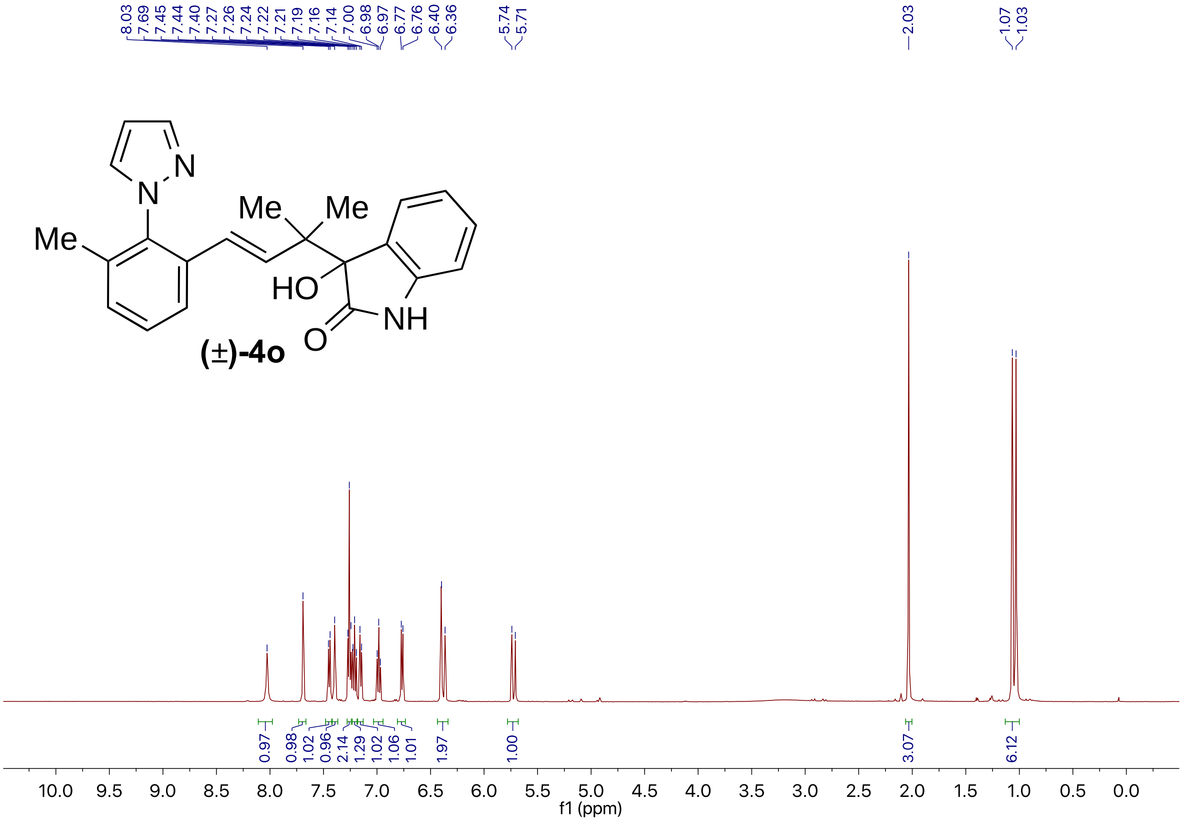
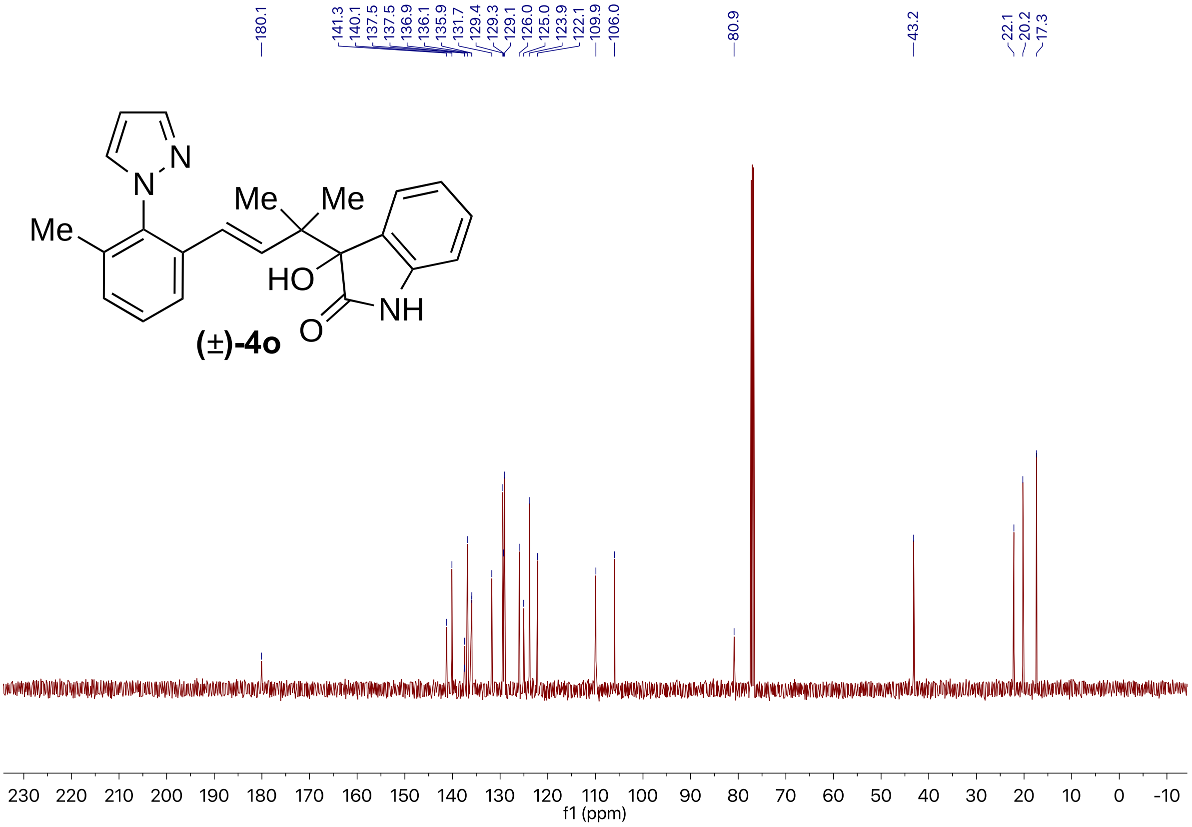
136.1
136.0
135.7
131.6
129.5
129.2
124.7
123.8
123.2
106.1
77.8
41.9
24.0
21.7
17.3
N
N
Me
Me
Me
Cl
N
OH
(±)-4n
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.03
7.69
7.45
7.44
7.40
7.27
7.26
7.24
7.22
7.21
7.19
7.16
7.14
7.00
6.98
6.97
6.77
6.76
6.40
6.36
5.74
5.71
2.03
1.07
1.03
Me
N
N
Me
Me
HO
NH
O
(±)-4o
0.97
0.98
1.02
0.96
2.14
1.29
1.02
1.06
1.01
1.97
1.00
3.07
6.12
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
f1 (ppm)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140.1
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137.5
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135.9
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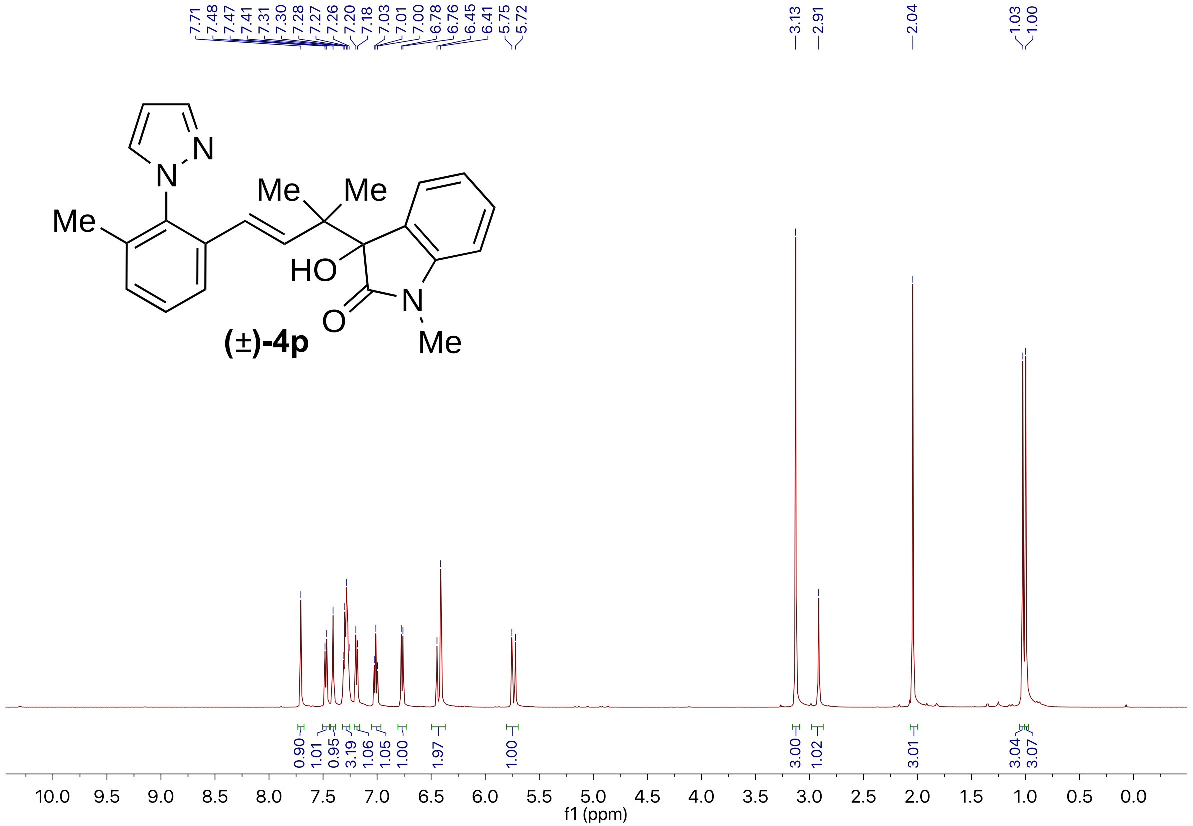
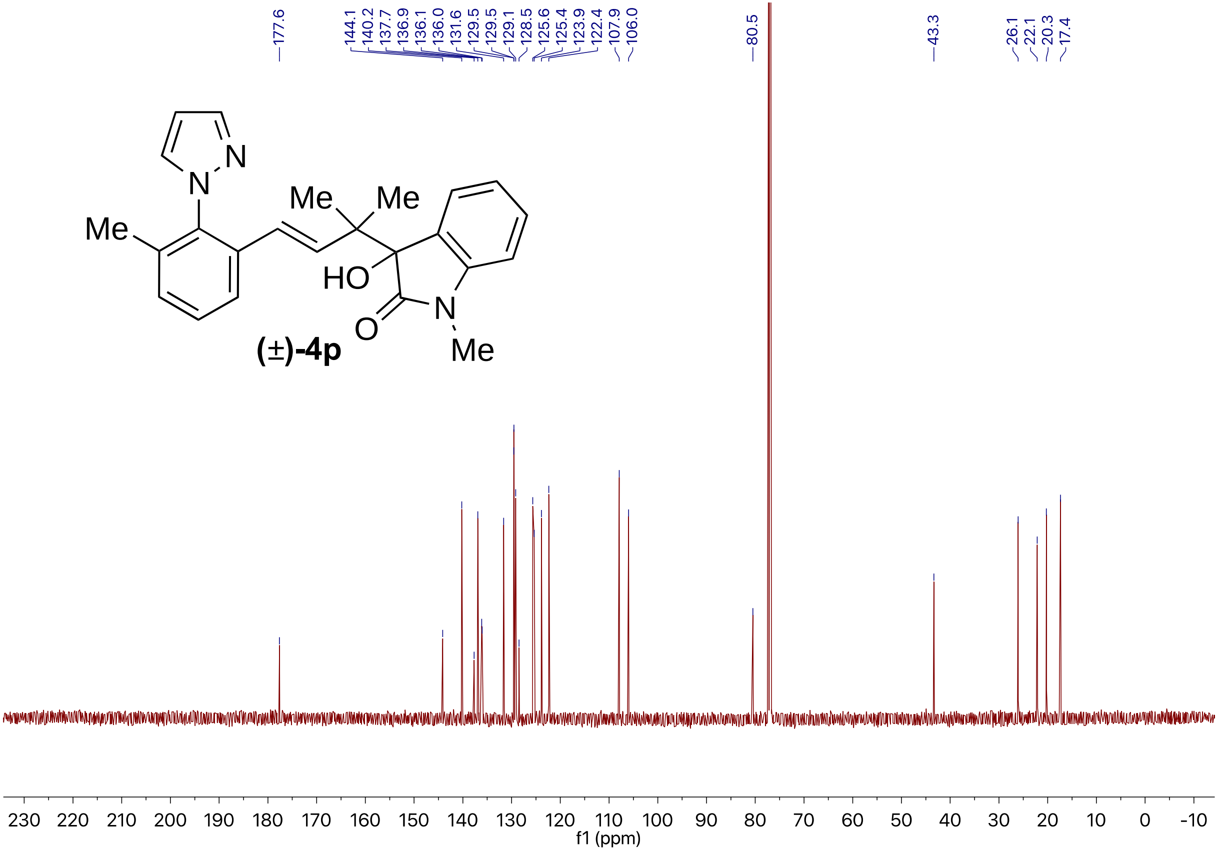
129.4
129.3
129.1
126.0
125.0
123.9
122.1
109.9
106.0
80.9
43.2
22.1
20.2
17.3
Me
N
N
Me
Me
HO
NH
O
(±)-4o
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.71
7.48
7.47
7.41
7.31
7.30
7.28
7.27
7.26
7.20
7.18
7.03
7.01
7.00
6.78
6.76
6.45
6.41
5.75
5.72
3.13
2.91
2.04
1.03
1.00
N
N
Me
Me
Me
HO
O
N
Me
(±)-4p
0.90
1.01
0.95
3.19
1.06
1.05
1.00
1.97
1.00
3.00
1.02
3.01
3.04
3.07
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
f1 (ppm)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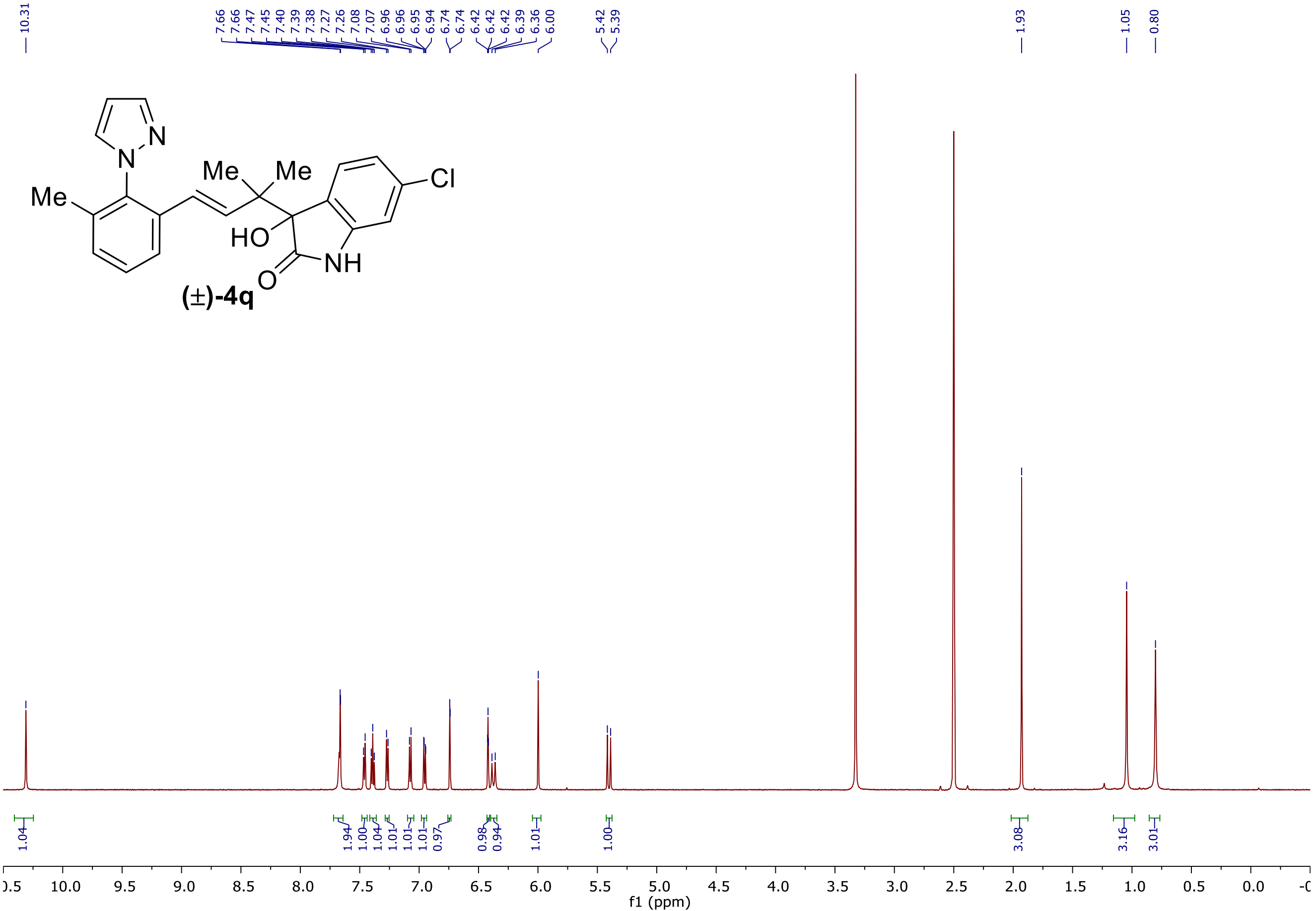
140.2
137.7
136.9
136.1
136.0
131.6
129.5
129.5
129.1
128.5
125.6
125.4
123.9
122.4
107.9
106.0
80.5
43.3
26.1
22.1
20.3
17.4
N
N
Me
Me
Me
HO
O
N
Me
(±)-4p
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.66
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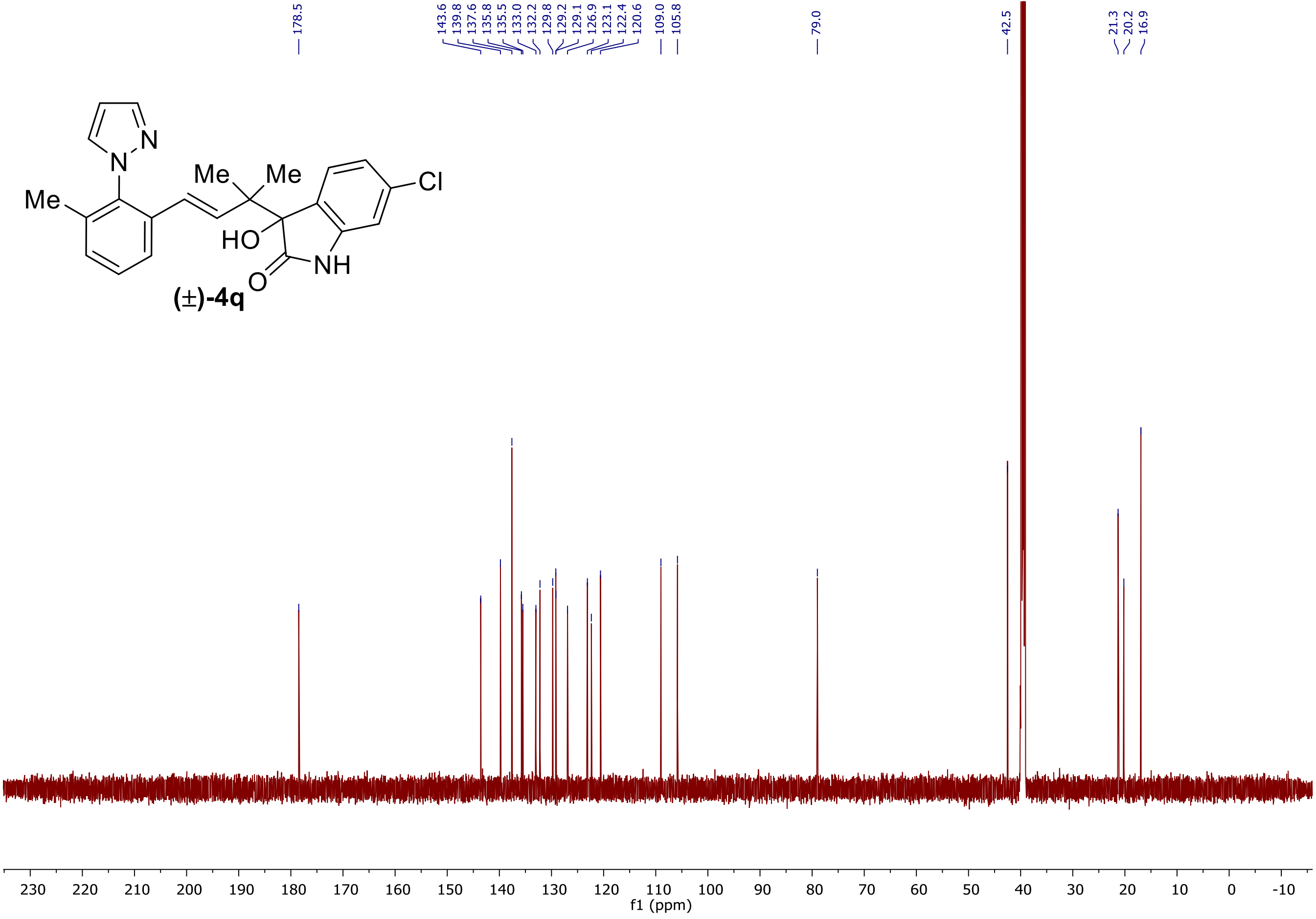
7.40
7.39
7.38
7.27
7.26
7.08
7.07
6.96
6.96
6.95
6.94
6.74
6.74
6.42
6.42
6.42
6.39
6.36
6.00
5.42
5.39
1.93
1.05
0.80
Me
N
N
Me
Me
Cl
HO
NH
O
(±)-4q
1.04
1.94
1.00
1.04
1.01
1.01
1.01
0.97
0.98
0.94
1.01
1.00
3.08
3.16
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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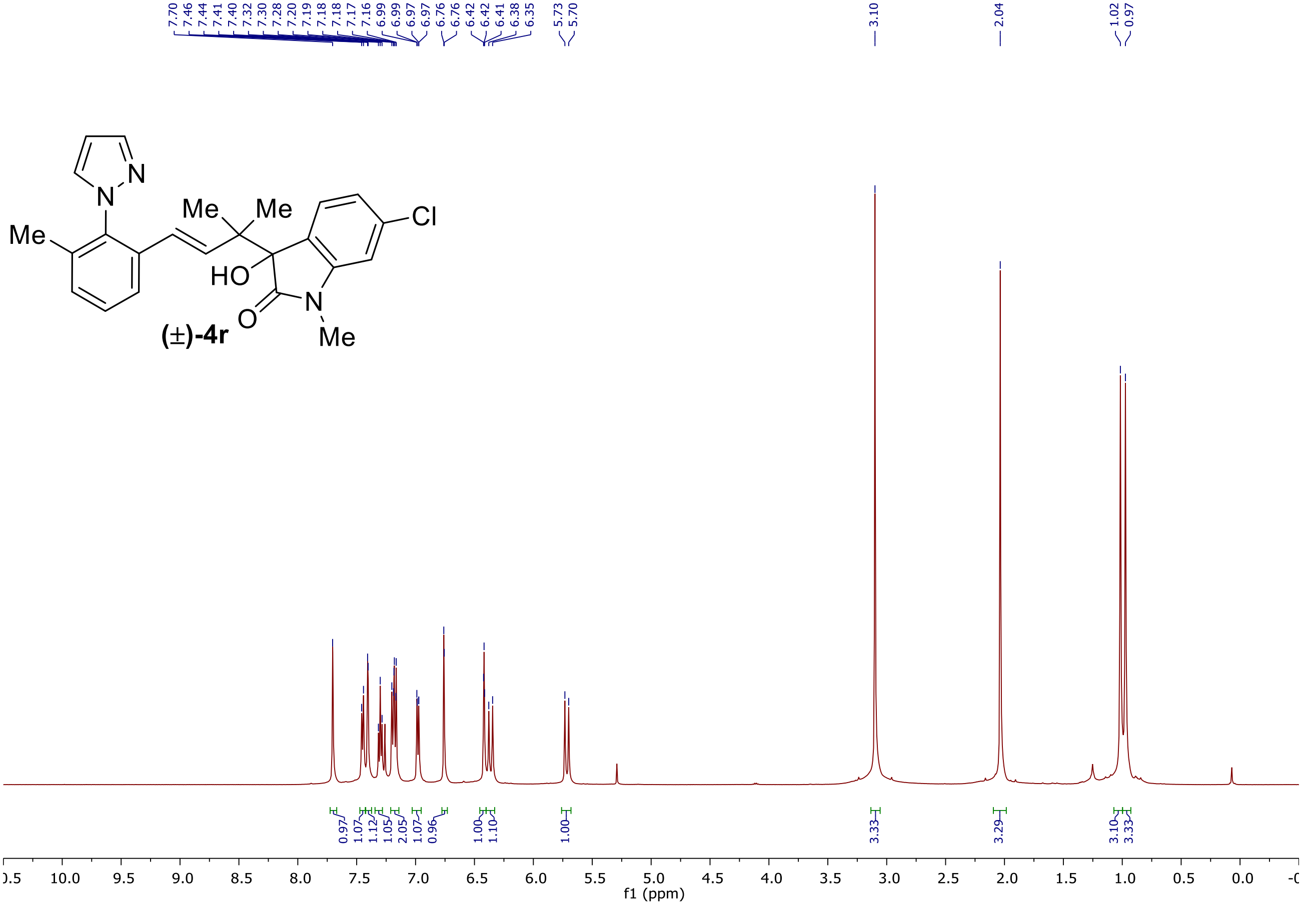
139.8
137.6
135.8
135.5
133.0
132.2
129.8
129.2
129.1
126.9
123.1
122.4
120.6
109.0
105.8
79.0
42.5
21.3
20.2
16.9
Me
N
N
Me
Me
Cl
HO
NH
O
(±)-4q
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.32
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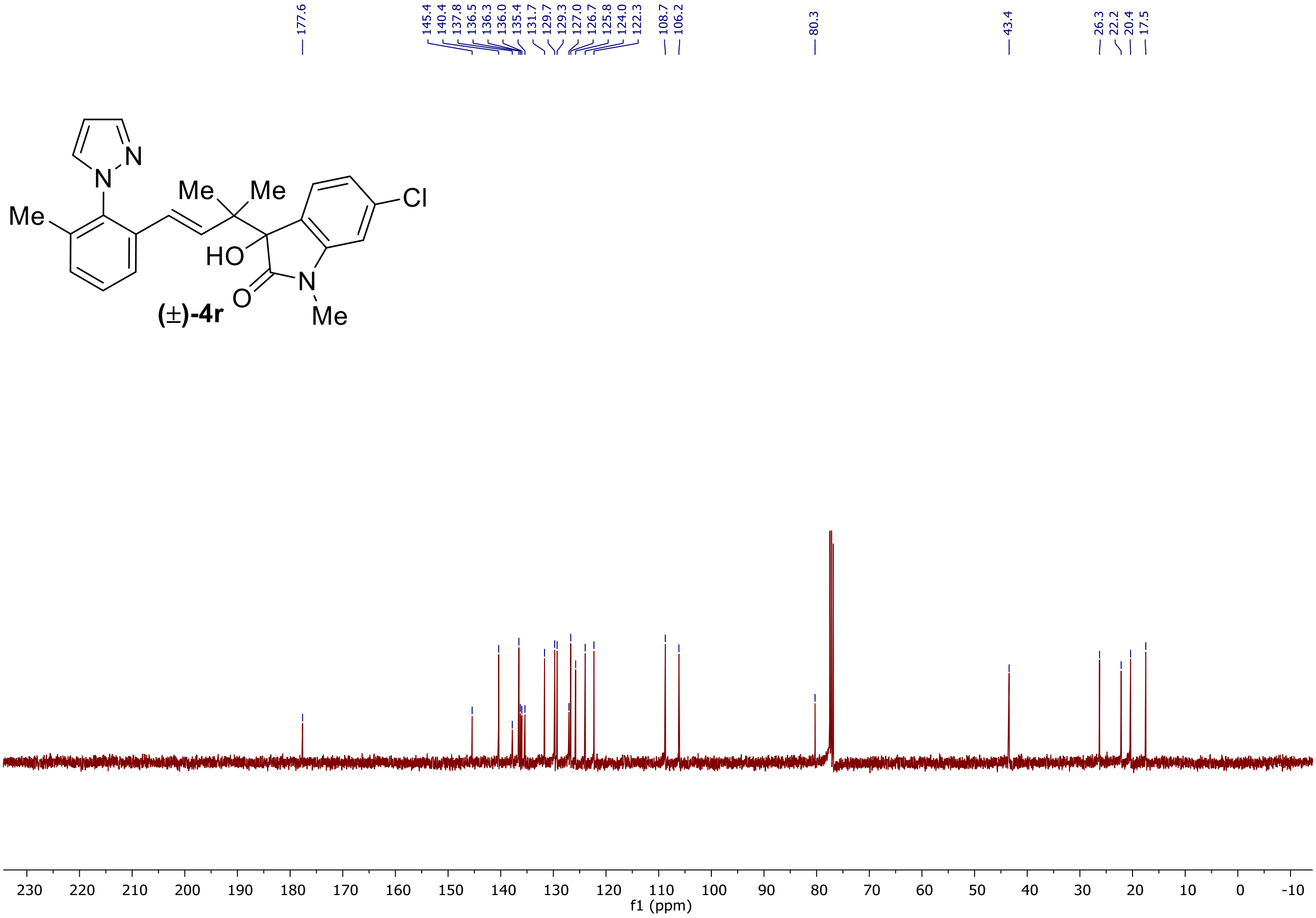
7.28
7.20
7.19
7.18
7.17
7.16
6.99
6.99
6.97
6.97
6.76
6.76
6.42
6.42
6.41
6.38
6.35
5.73
5.70
3.10
2.04
1.02
0.97
N
N
Me
Me
Me
Cl
HO
O
N
Me
(±)-4r
0.97
1.07
1.12
1.05
2.05
1.07
0.96
1.00
1.10
1.00
3.33
3.29
3.10
3.33
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


177.6
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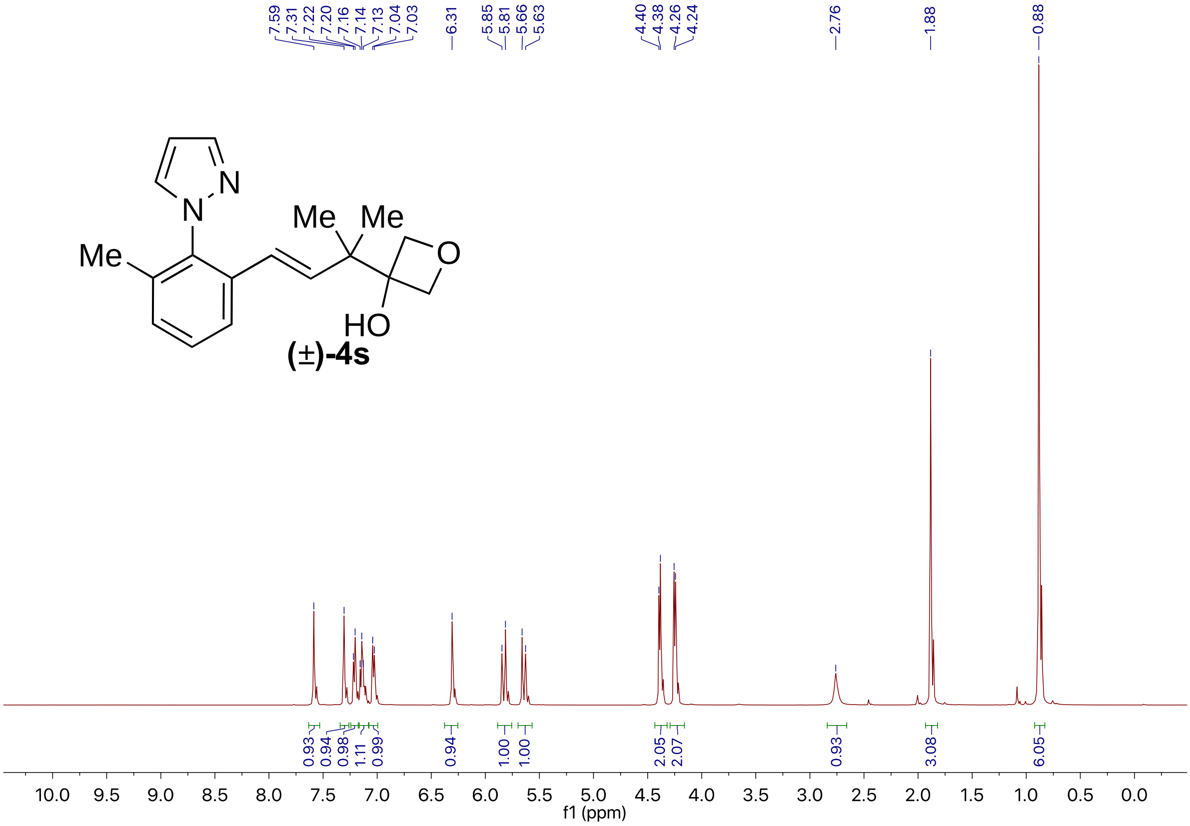
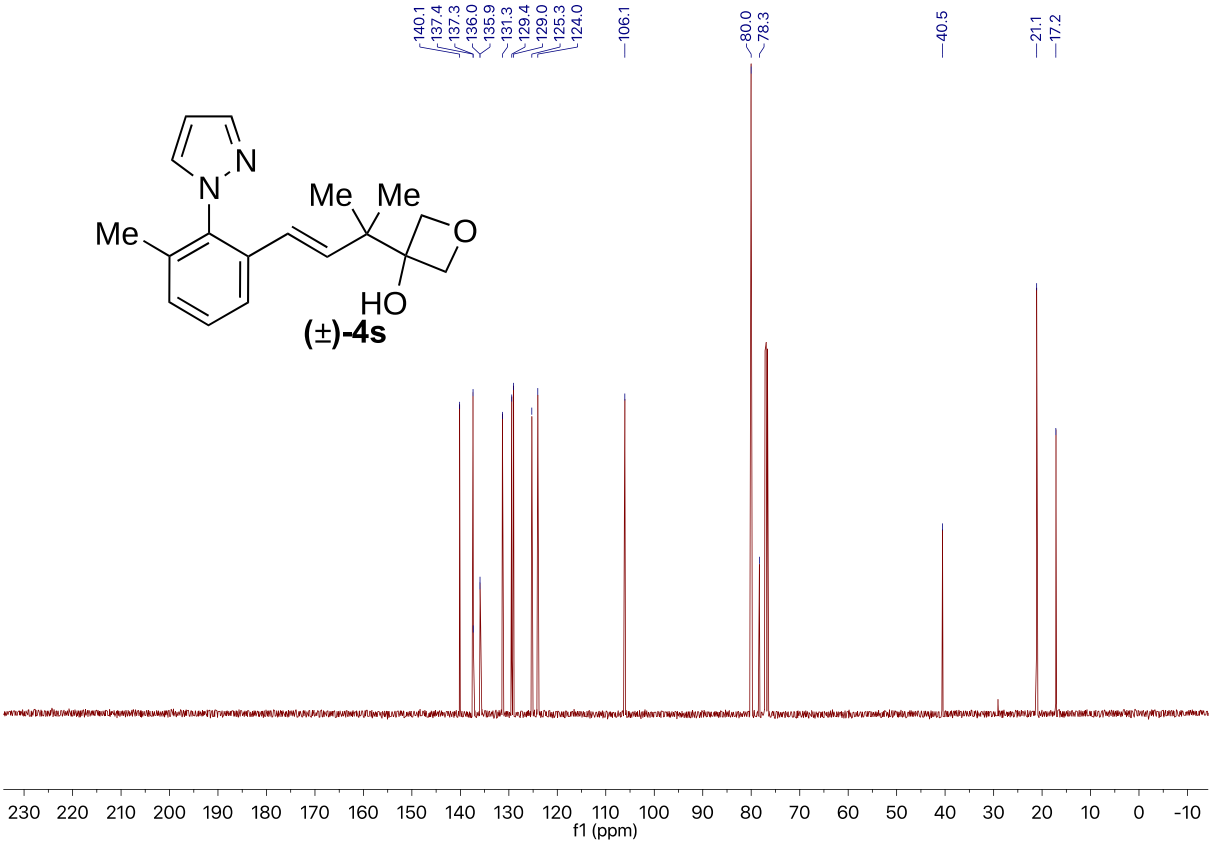
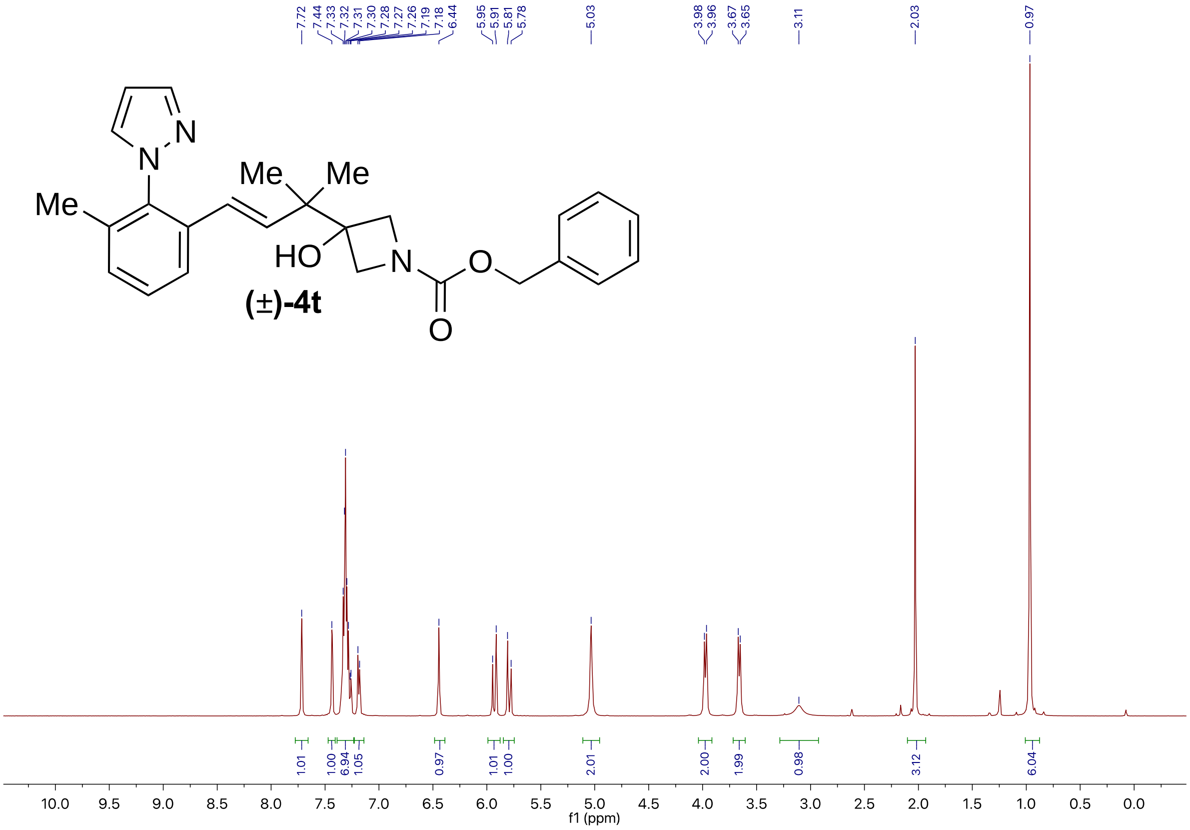
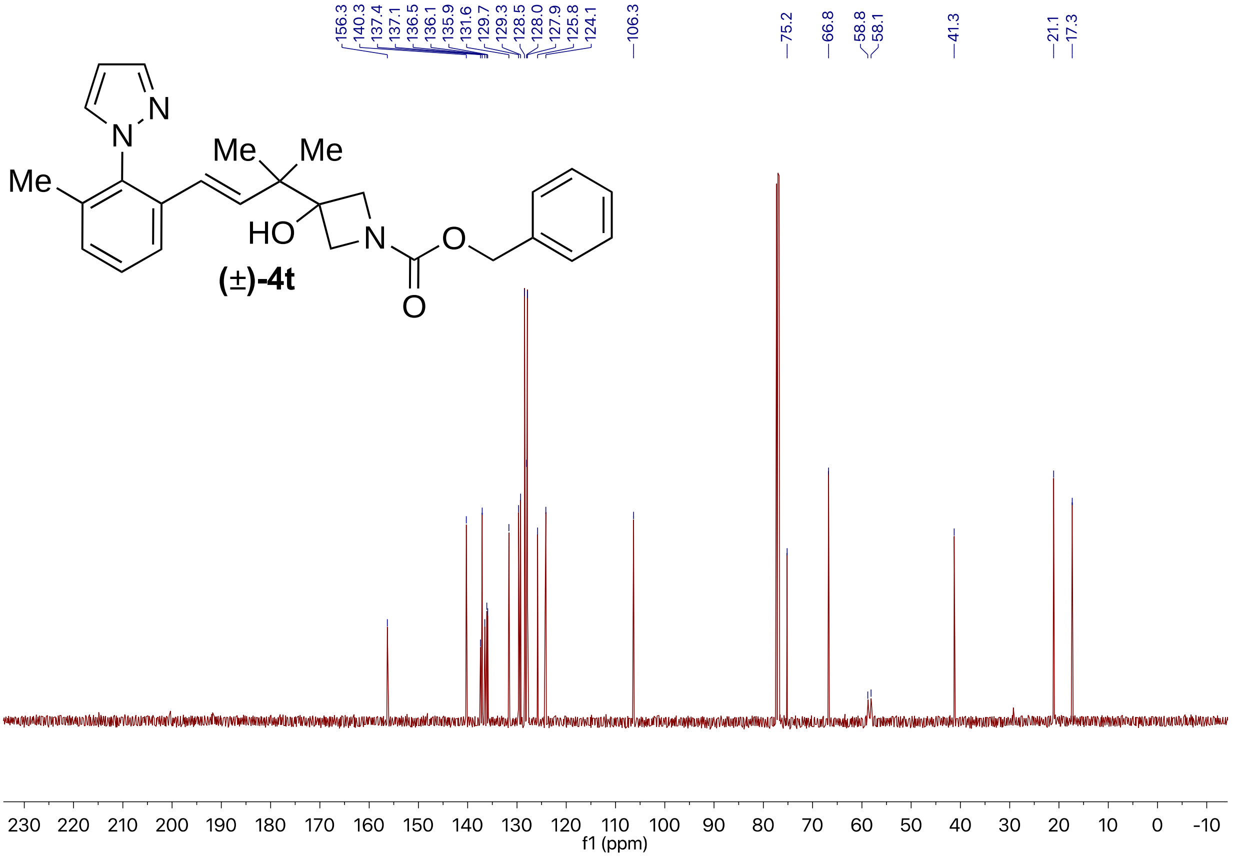
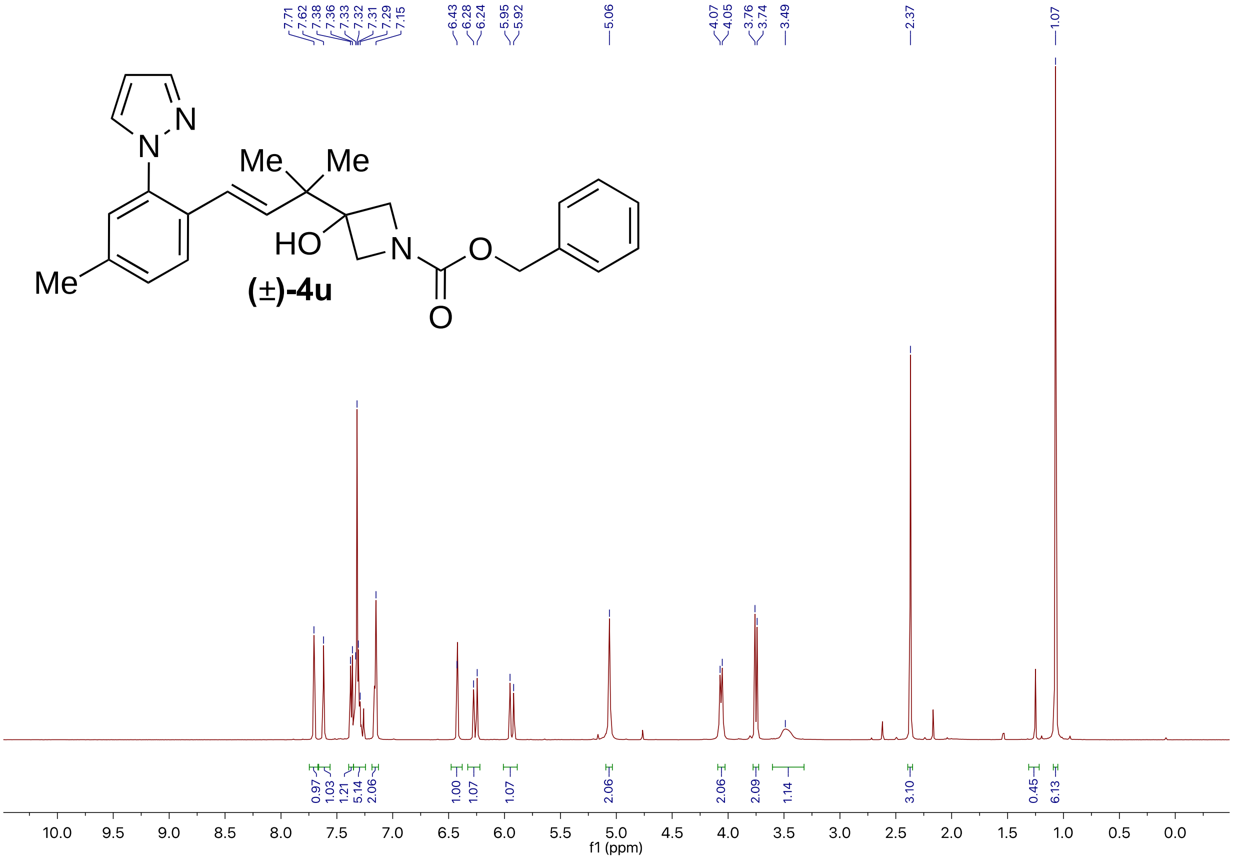
140.4
137.8
136.5
136.3
136.0
135.4
131.7
129.7
129.3
127.0
126.7
125.8
124.0
122.3
108.7
106.2
80.3
43.4
26.3
22.2
20.4
17.5
N
N
Me
Me
Me
Cl
HO
O
N
Me
(±)-4r
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.59
7.31
7.22
7.20
7.16
7.14
7.13
7.04
7.03
6.31
5.85
5.81
5.66
5.63
4.40
4.38
4.26
4.24
2.76
1.88
0.88
Me
N
N
Me
Me
O
HO
(±)-4s
0.93
0.94
0.98
1.11
0.99
0.94
1.00
1.00
2.05
2.07
0.93
3.08
6.05
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
f1 (ppm)


140.1
137.4
137.3
136.0
135.9
131.3
129.4
129.0
125.3
124.0
106.1
80.0
78.3
40.5
21.1
17.2
Me
N
N
Me
Me
O
HO
(±)-4s
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


(±)-4t
N
N
Me
Me
Me
HO
N
O
O
7.72
7.44
7.33
7.32
7.31
7.30
7.28
7.27
7.26
7.19
7.18
6.44
5.95
5.91
5.81
5.78
5.03
3.98
3.96
3.67
3.65
3.11
2.03
0.97
1.01
1.00
6.94
1.05
0.97
1.01
1.00
2.01
2.00
1.99
0.98
3.12
6.04
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
f1 (ppm)


(±)-4t
N
N
Me
Me
Me
HO
N
O
O
156.3
140.3
137.4
137.1
136.5
136.1
135.9
131.6
129.7
129.3
128.5
128.0
127.9
125.8
124.1
106.3
75.2
66.8
58.8
58.1
41.3
21.1
17.3
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



(±)-4u

7.71
7.62
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7.31
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7.15
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6.24
5.95
5.92
5.06
4.07
4.05
3.76
3.74
3.49
2.37
1.07
Me
Me
Me
HO
N
N
N
O
O
0.97
1.03
1.21
5.14
2.06
1.00
1.07
1.07
2.06
2.06
2.09
1.14
3.10
0.45
6.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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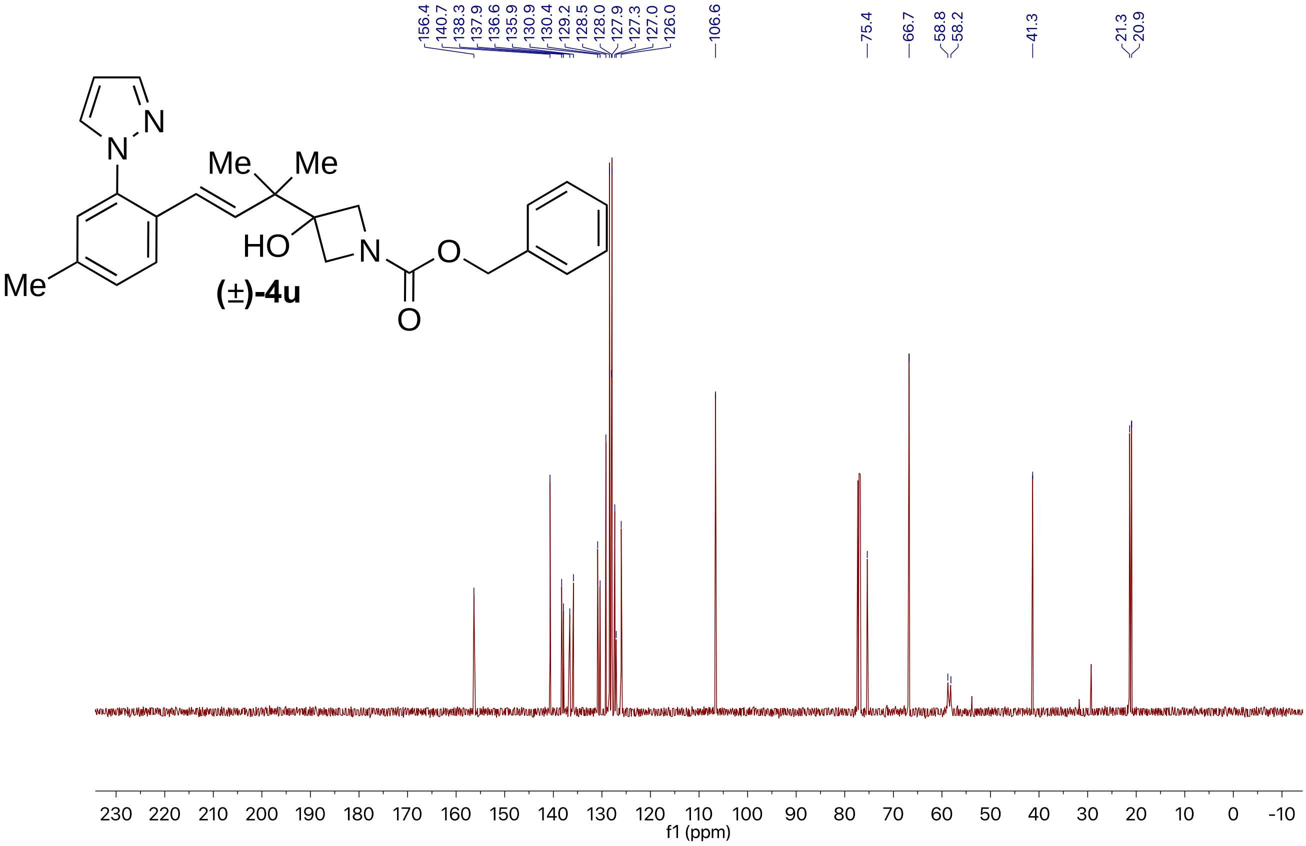
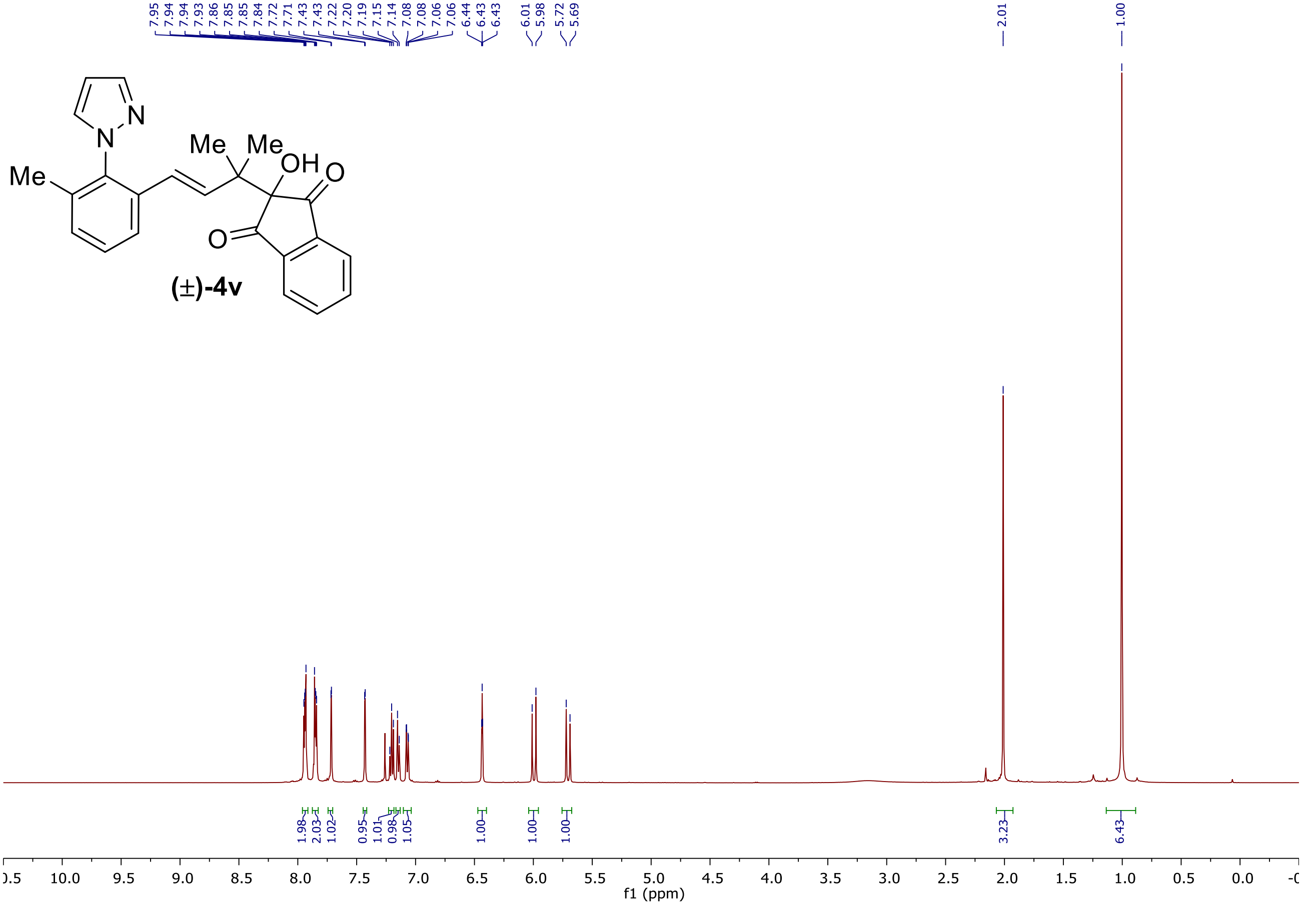
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



(±)-4u

156.4
140.7
138.3
137.9
136.6
135.9
130.9
130.4
129.2
128.5
128.0
127.9
127.3
127.0
126.0
106.6
75.4
66.7
58.8
58.2
41.3
21.3
20.9
Me
Me
Me
HO
N
N
N
O
O
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.71
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7.43
7.22
7.20
7.19
7.15
7.14
7.08
7.08
7.06
6.44
6.43
6.43
6.01
5.98
5.72
5.69
2.01
1.00
Me
N
N
Me
Me
OH
O
O
(±)-4v
1.98
2.03
1.02
0.95
1.01
0.98
1.05
1.00
1.00
1.00
3.23
6.43
10.5
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
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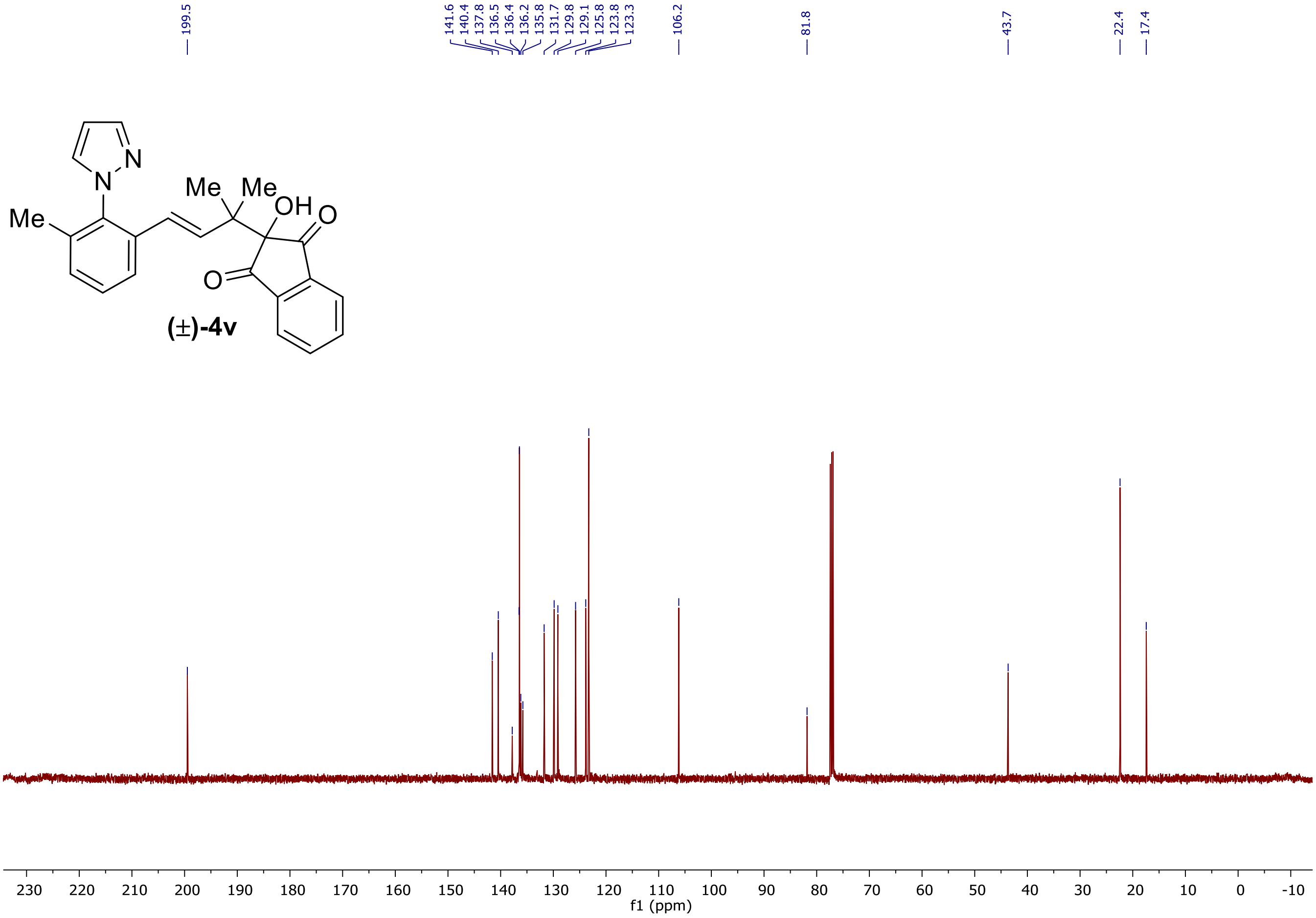
-0
f1 (ppm)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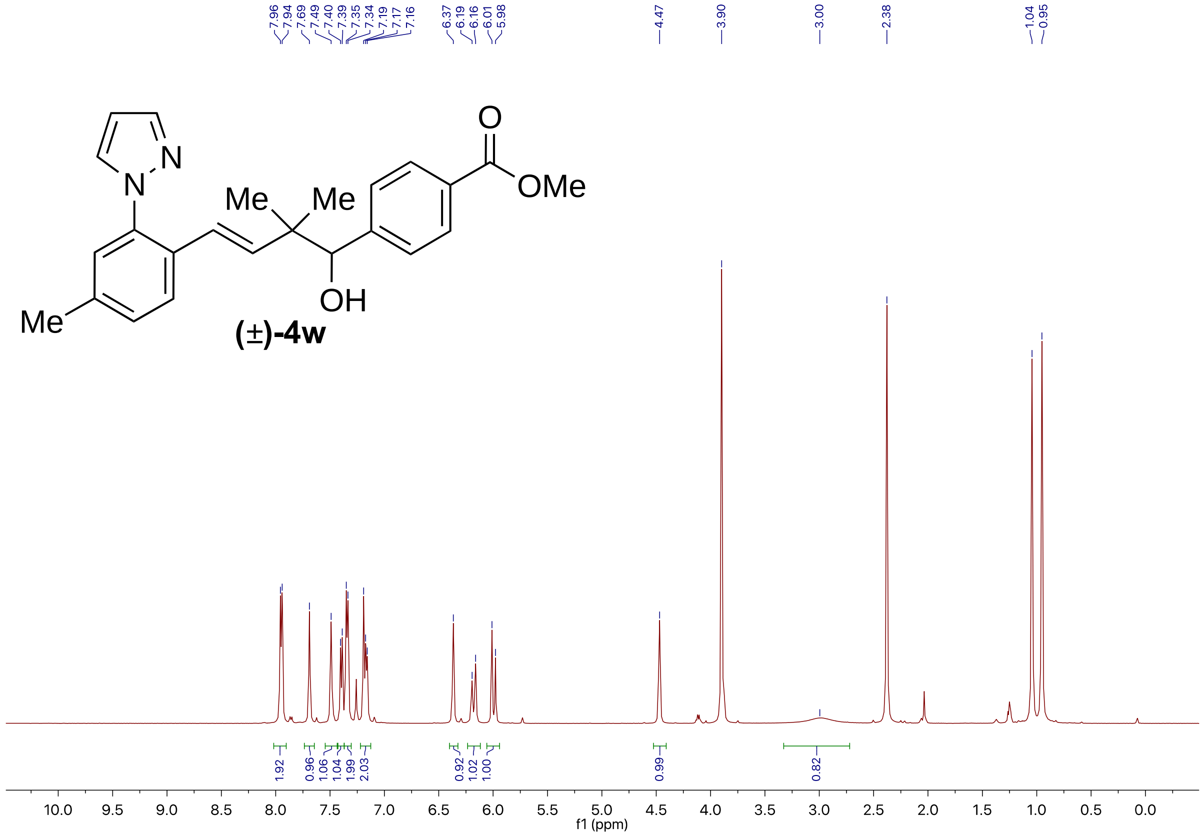
136.4
136.2
135.8
131.7
129.8
129.1
125.8
123.8
123.3
106.2
81.8
43.7
22.4
17.4
Me
N
N
Me
Me
OH
O
O
(±)-4v
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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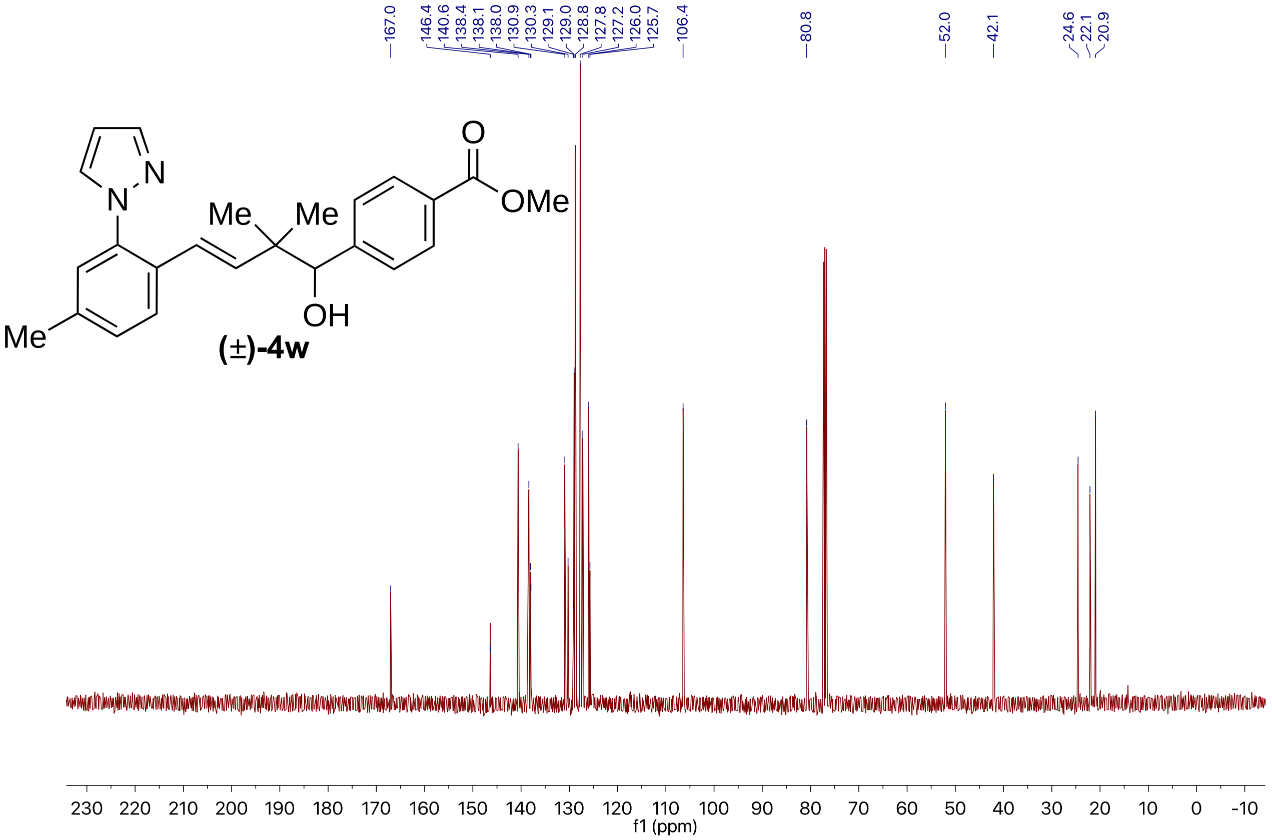
7.17
7.16
6.37
6.19
6.16
6.01
5.98
4.47
3.90
3.00
2.38
1.04
0.95
N
N
Me
Me
O
OMe
OH
Me
(±)-4w
1.92
0.96
1.06
1.04
1.99
2.03
0.92
1.02
1.00
0.99
0.82
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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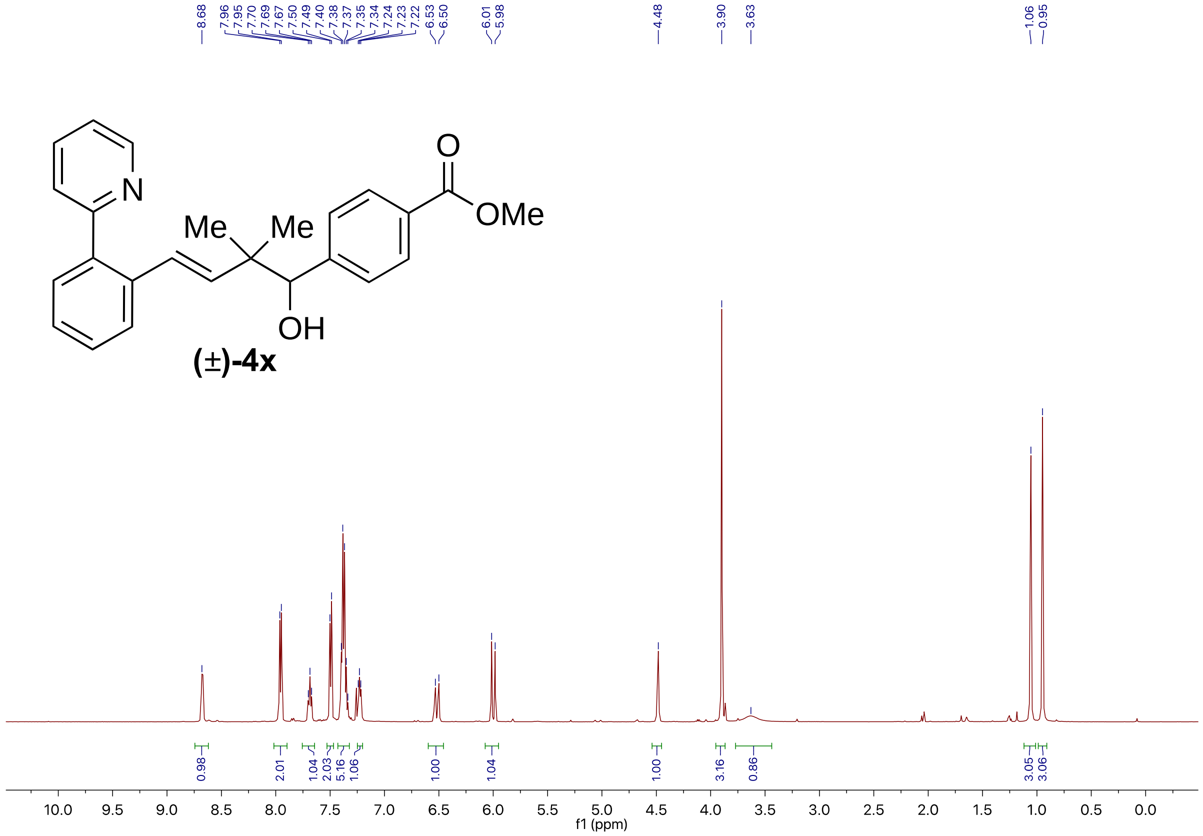
146.4
140.6
138.4
138.1
138.0
130.9
130.3
129.1
129.0
128.8
127.8
127.2
126.0
125.7
106.4
80.8
52.0
42.1
24.6
22.1
20.9
N
N
Me
Me
O
OMe
OH
Me
(±)-4w
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.95
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7.69
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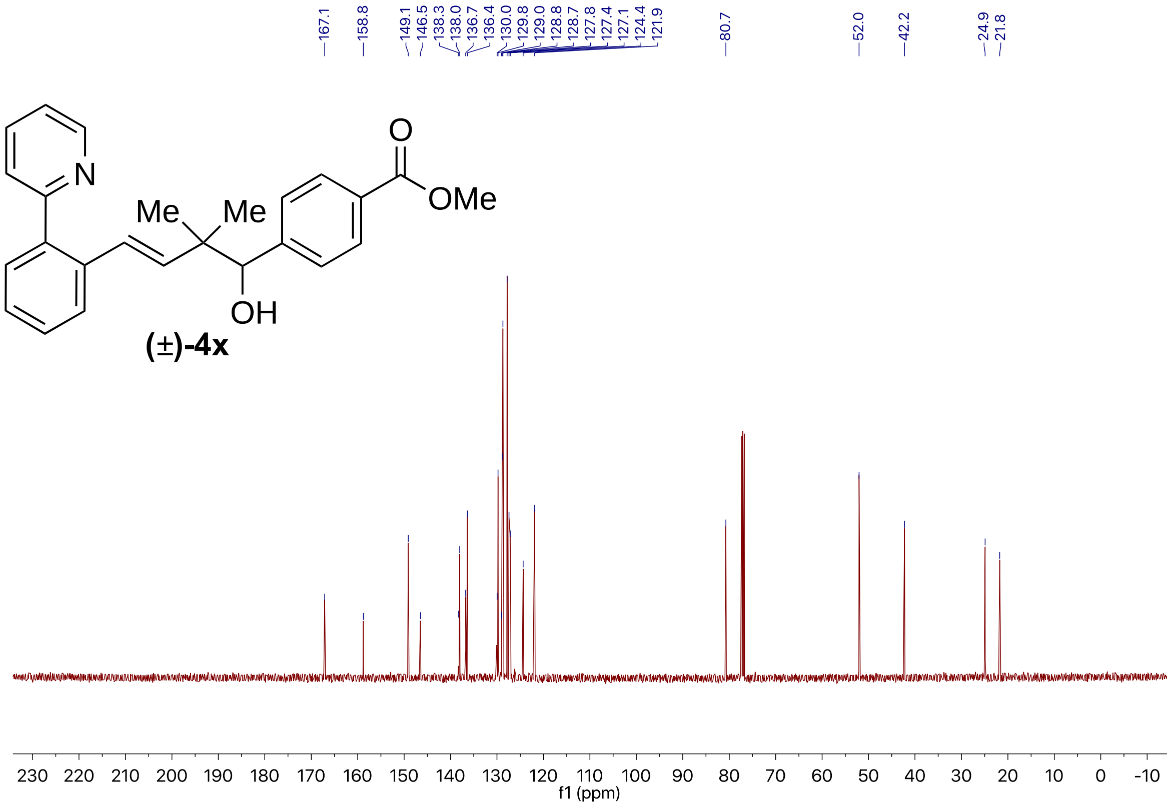
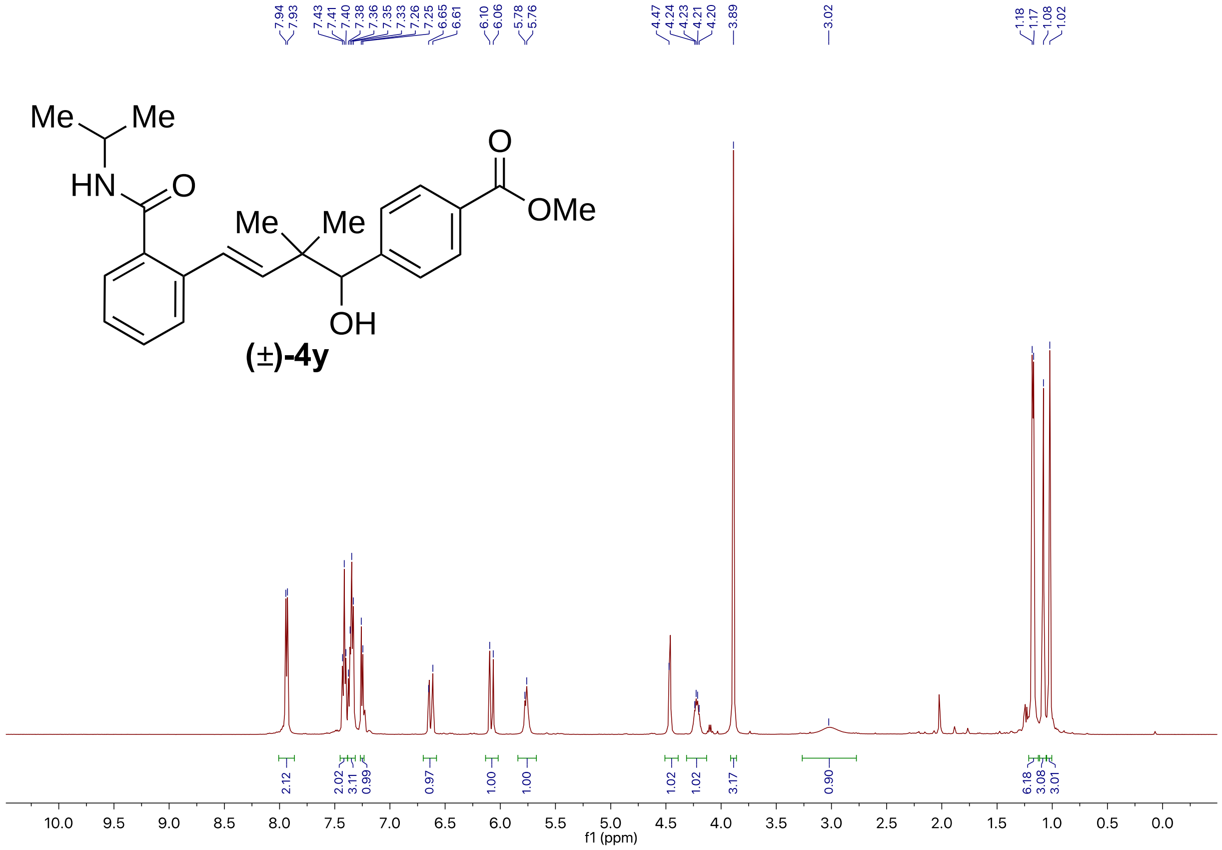
7.49
7.40
7.38
7.37
7.35
7.34
7.24
7.23
7.22
6.53
6.50
6.01
5.98
4.48
3.90
3.63
1.06
0.95
N
Me
Me
O
OMe
OH
(±)-4x
0.98
2.01
1.04
2.03
5.16
1.06
1.00
1.04
1.00
3.16
0.86
3.05
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


167.1
158.8
149.1
146.5
138.3
138.0
136.7
136.4
130.0
129.8
129.0
128.8
128.7
127.8
127.4
127.1
124.4
121.9
80.7
52.0
42.2
24.9
21.8
N
Me
Me
O
OMe
OH
(±)-4x
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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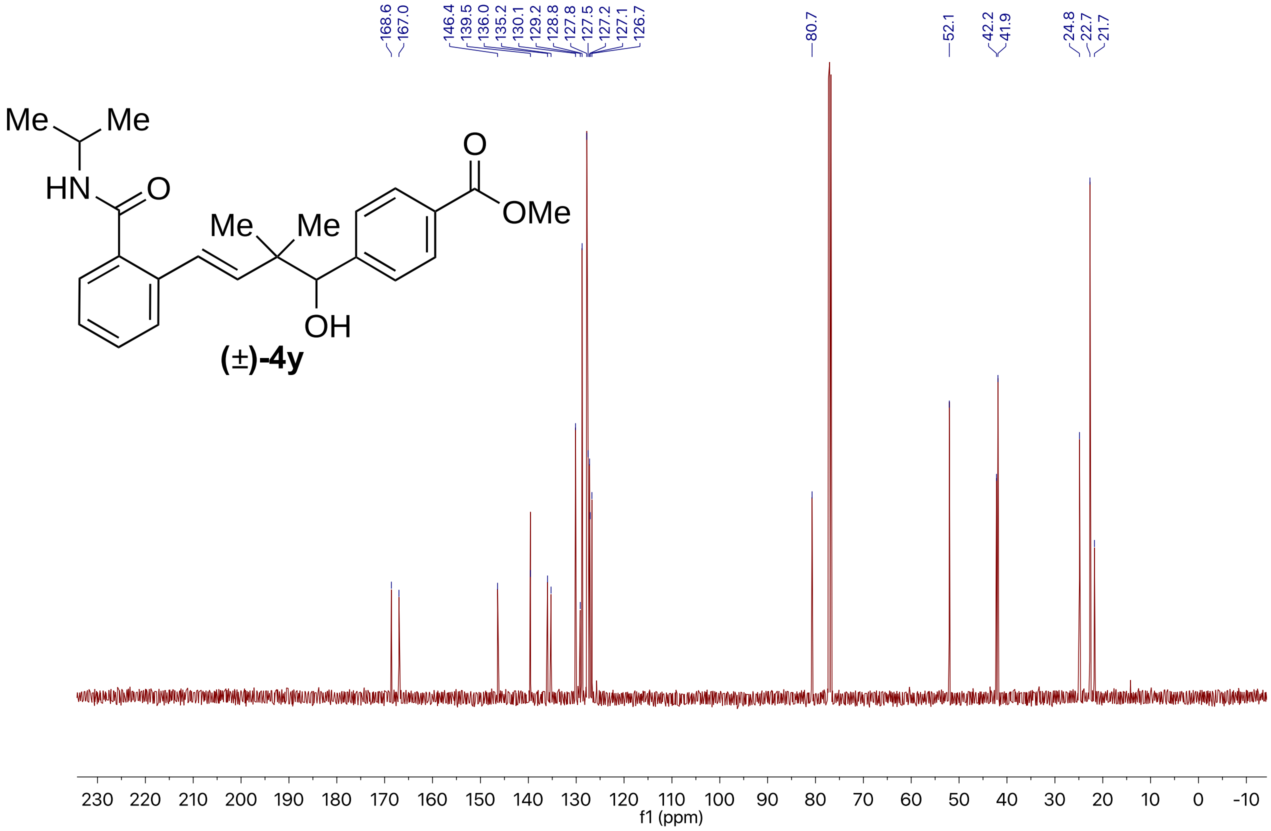
7.93
7.43
7.41
7.40
7.38
7.36
7.35
7.33
7.26
7.25
6.65
6.61
6.10
6.06
5.78
5.76
4.47
4.24
4.23
4.21
4.20
3.89
3.02
1.18
1.17
1.08
1.02
Me
Me
HN
O
Me
Me
O
OMe
OH
(±)-4y
2.12
2.02
3.11
0.99
0.97
1.00
1.00
1.02
1.02
3.17
0.90
6.18
3.08
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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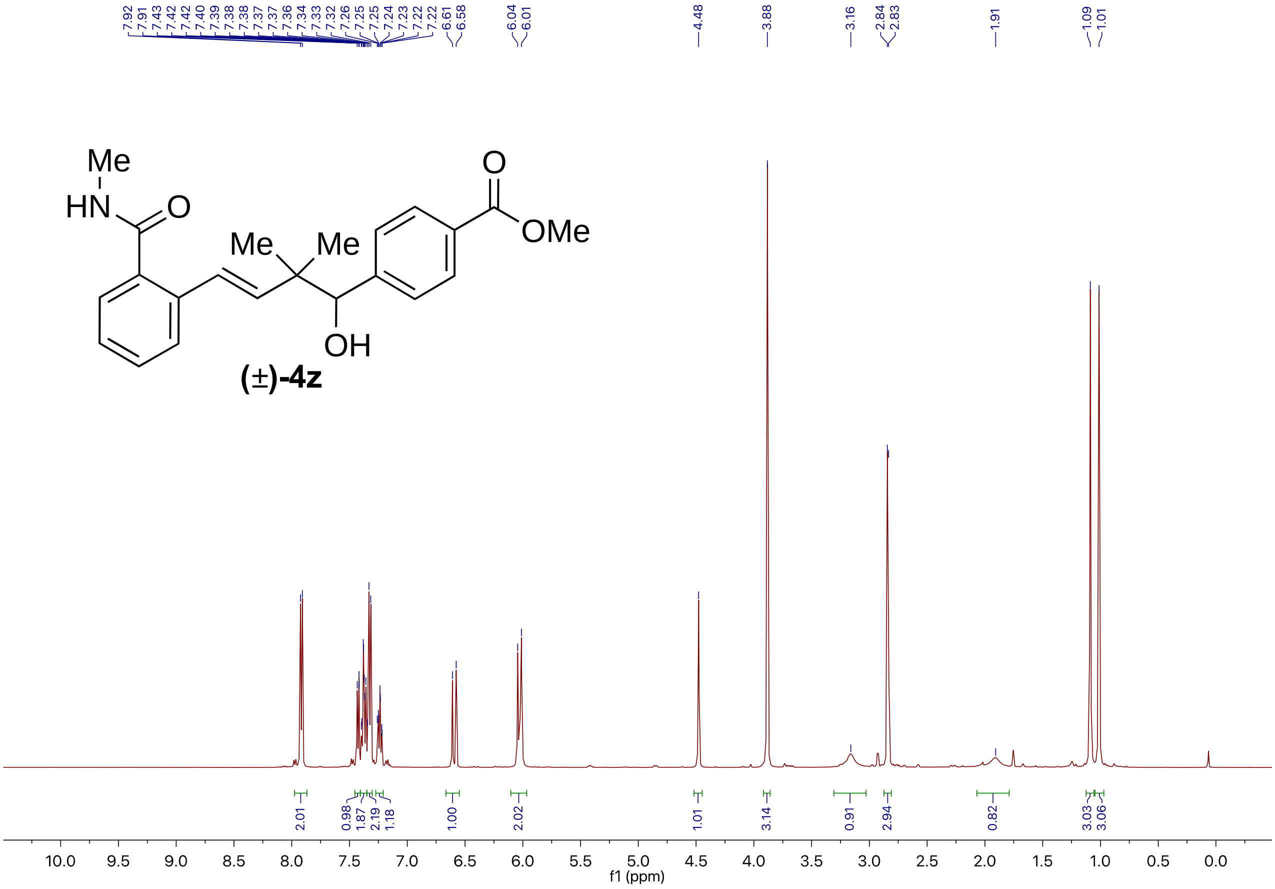
136.0
135.2
130.1
129.2
128.8
127.8
127.5
127.2
127.1
126.7
80.7
52.1
42.2
41.9
24.8
22.7
21.7
Me
Me
HN
O
Me
Me
O
OMe
OH
(±)-4y
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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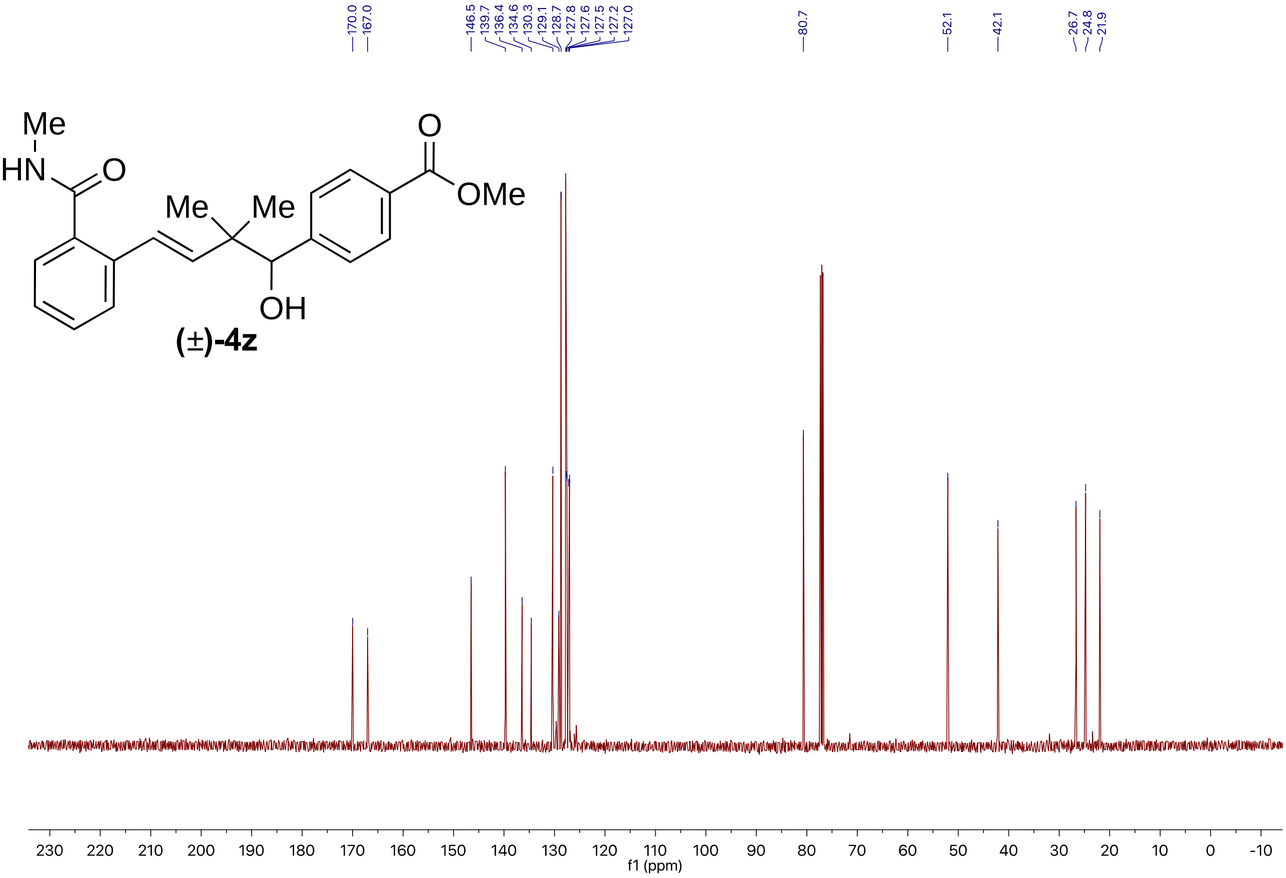
7.39
7.38
7.38
7.37
7.36
7.34
7.33
7.32
7.26
7.25
7.25
7.24
7.23
7.22
7.22
6.61
6.58
6.04
6.01
4.48
3.88
3.16
2.84
2.83
1.91
1.09
1.01
Me
HN
O
Me
Me
O
OMe
OH
(±)-4z
2.01
0.98
1.87
2.19
1.18
1.00
2.02
1.01
3.14
0.91
2.94
0.82
3.03
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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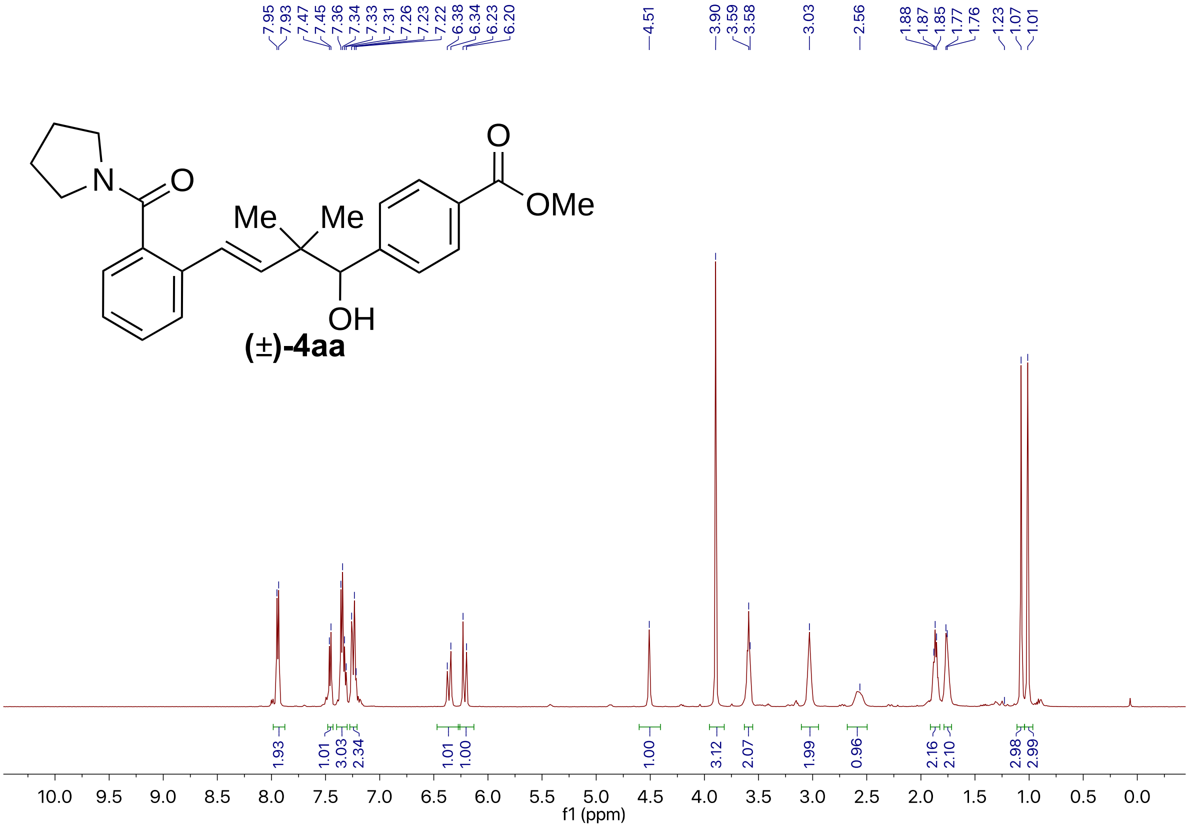
139.7
136.4
134.6
130.3
129.1
128.7
127.8
127.6
127.5
127.2
127.0
80.7
52.1
42.1
26.7
24.8
21.9
Me
HN
O
Me
Me
O
OMe
OH
(±)-4z
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.47
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7.36
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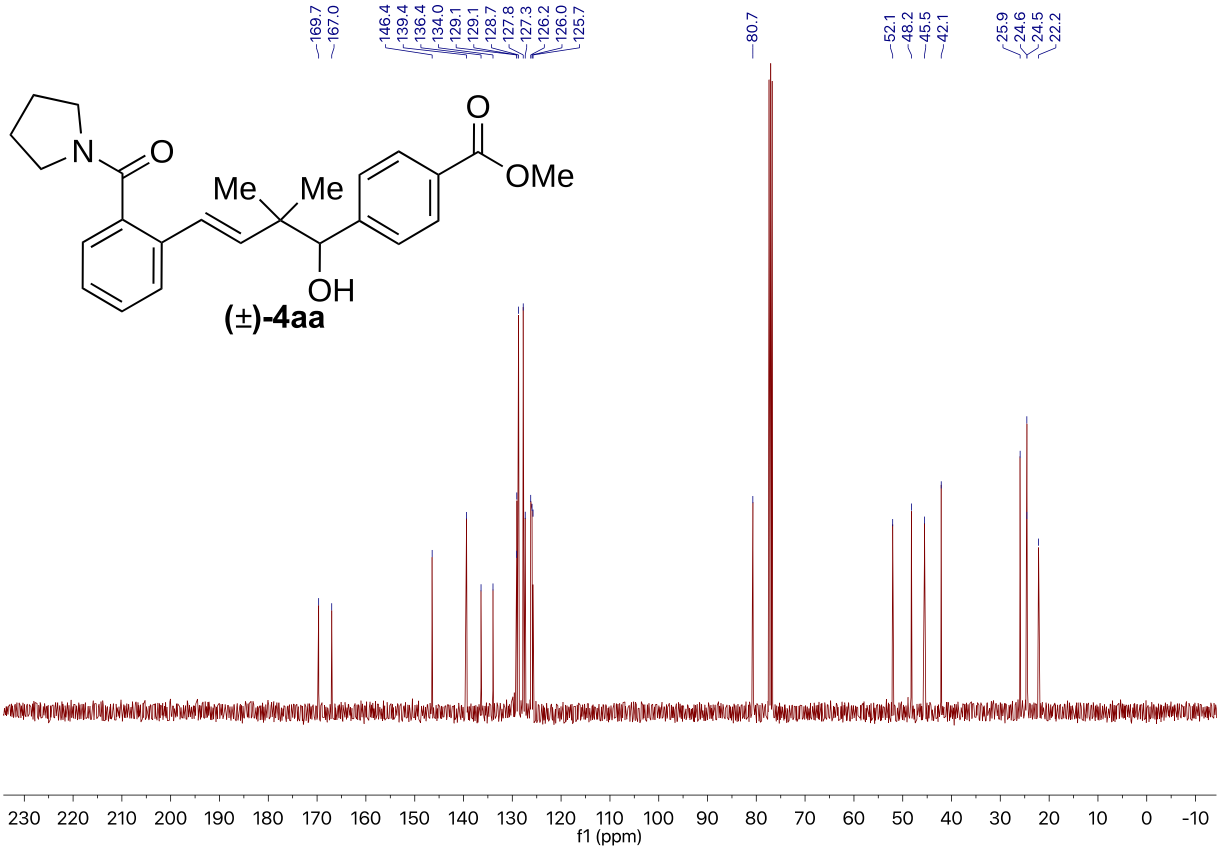
7.23
7.22
6.38
6.34
6.23
6.20
4.51
3.90
3.59
3.58
3.03
2.56
1.88
1.87
1.85
1.77
1.76
1.23
1.07
1.01
O
N
O
Me
Me
OMe
OH
(±)-4aa
1.93
1.01
3.03
2.34
1.01
1.00
1.00
3.12
2.07
1.99
0.96
2.16
2.10
2.98
2.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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139.4
136.4
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129.1
129.1
128.7
127.8
127.3
126.2
126.0
125.7
80.7
52.1
48.2
45.5
42.1
25.9
24.6
24.5
22.2
O
N
O
Me
Me
OMe
OH
(±)-4aa
230
220
210
200
190
180
170
160
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120
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100
90
80
70
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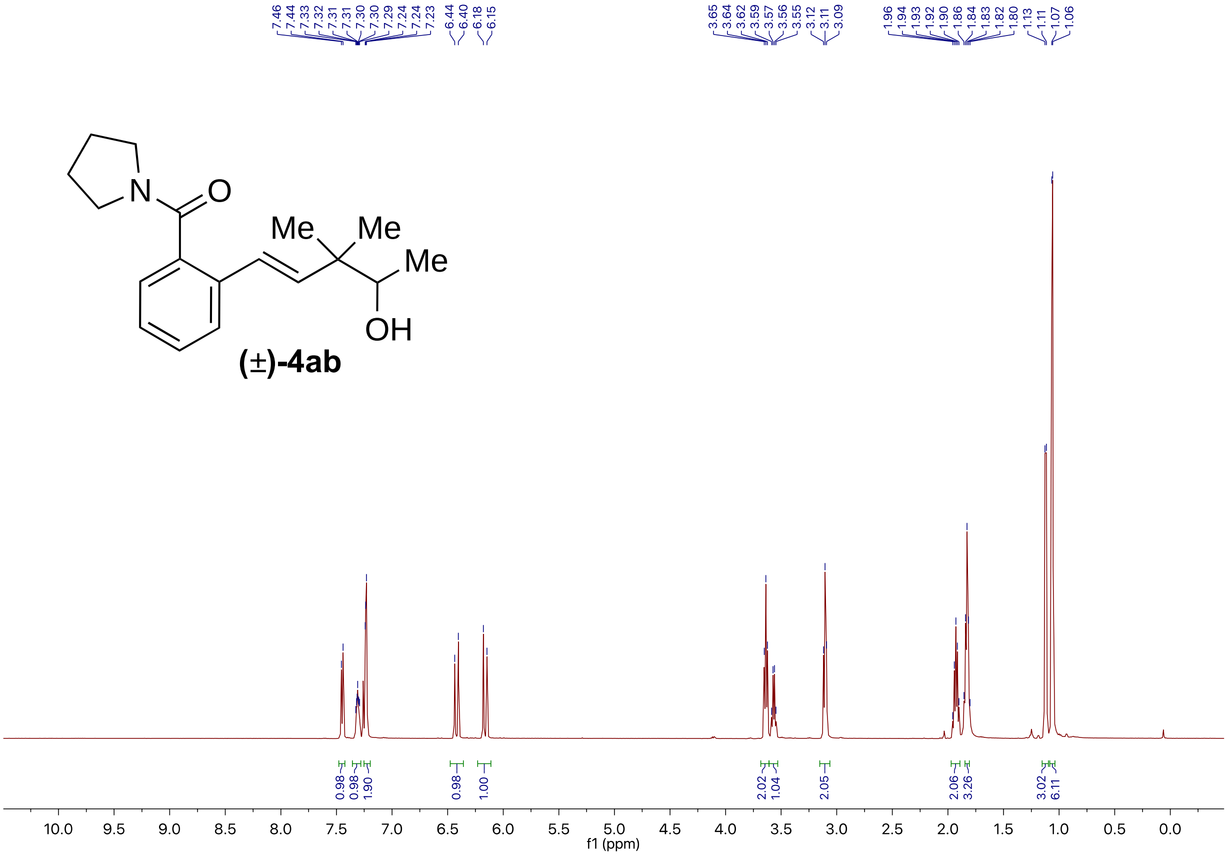
50
40
30
20
10
0
-10
f1 (ppm)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7.23
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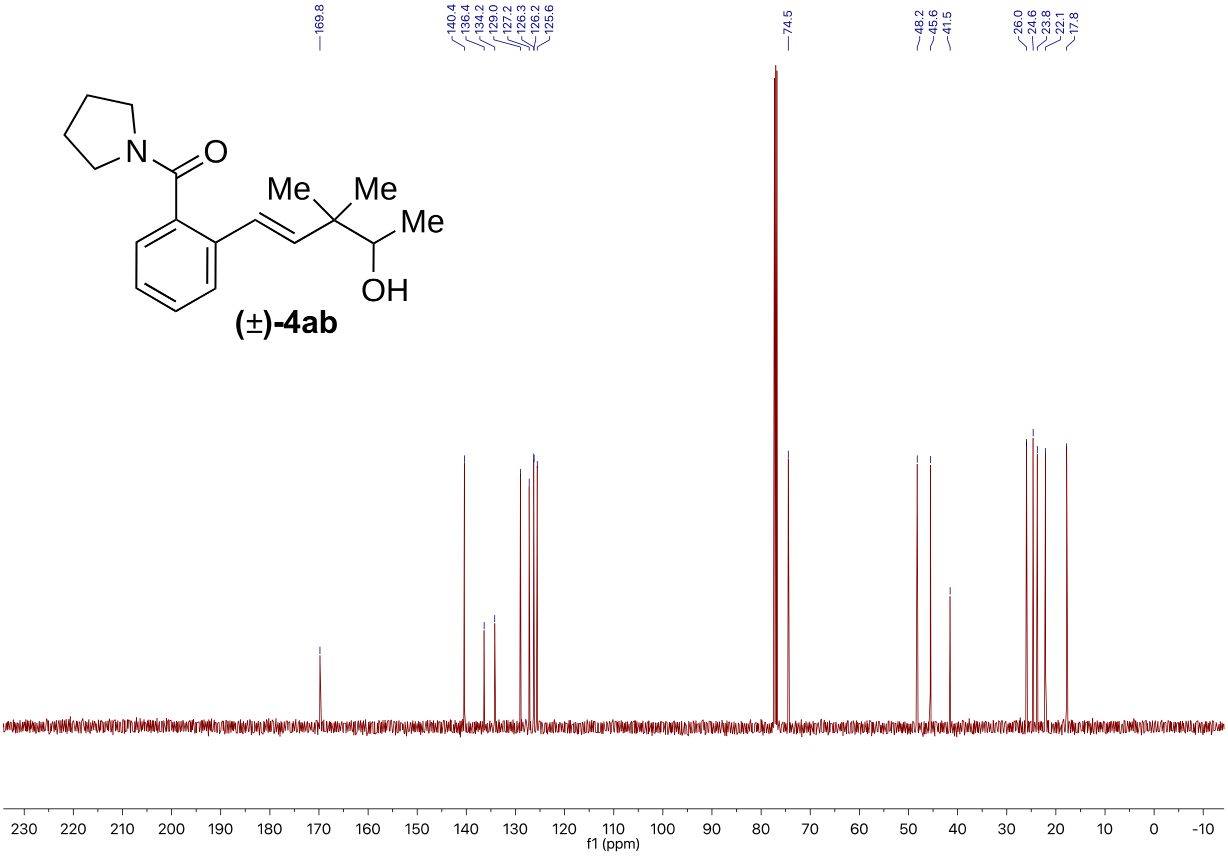
6.18
6.15
3.65
3.64
3.62
3.59
3.57
3.56
3.55
3.12
3.11
3.09
1.96
1.94
1.93
1.92
1.90
1.86
1.84
1.83
1.82
1.80
1.13
1.11
1.07
1.06
N
O
Me
Me
Me
OH
(±)-4ab
0.98
0.98
1.90
0.98
1.00
2.02
1.04
2.05
2.06
3.26
3.02
6.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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74.5
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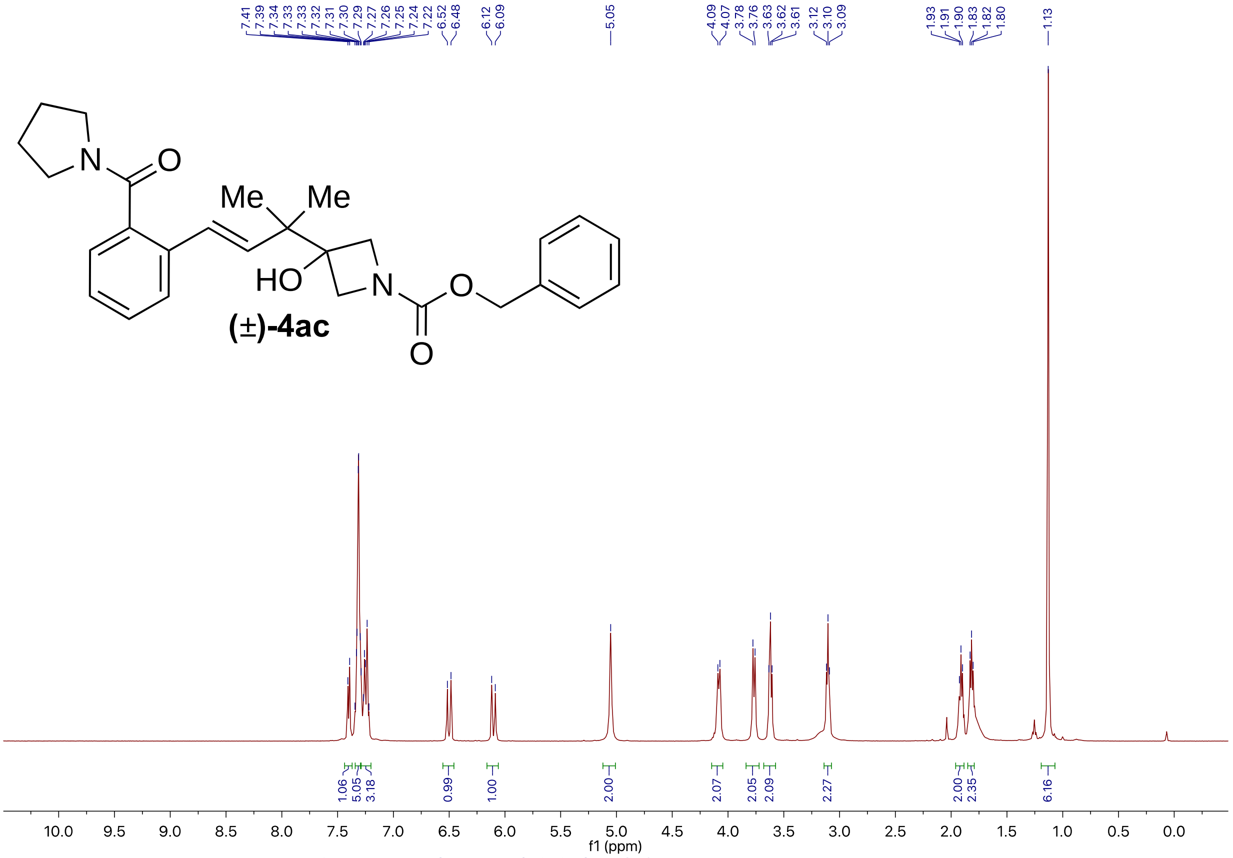
45.6
41.5
26.0
24.6
23.8
22.1
17.8
N
O
Me
Me
Me
OH
(±)-4ab
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.24
7.22
6.52
6.48
6.12
6.09
5.05
4.09
4.07
3.78
3.76
3.63
3.62
3.61
3.12
3.10
3.09
1.93
1.91
1.90
1.83
1.82
1.80
1.13
Me
Me
N
O
HO
N
O
O
(±)-4ac
1.06
5.05
3.18
0.99
1.00
2.00
2.07
2.05
2.09
2.27
2.00
2.35
6.16
10.0
9.5
9.0
8.5
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7.5
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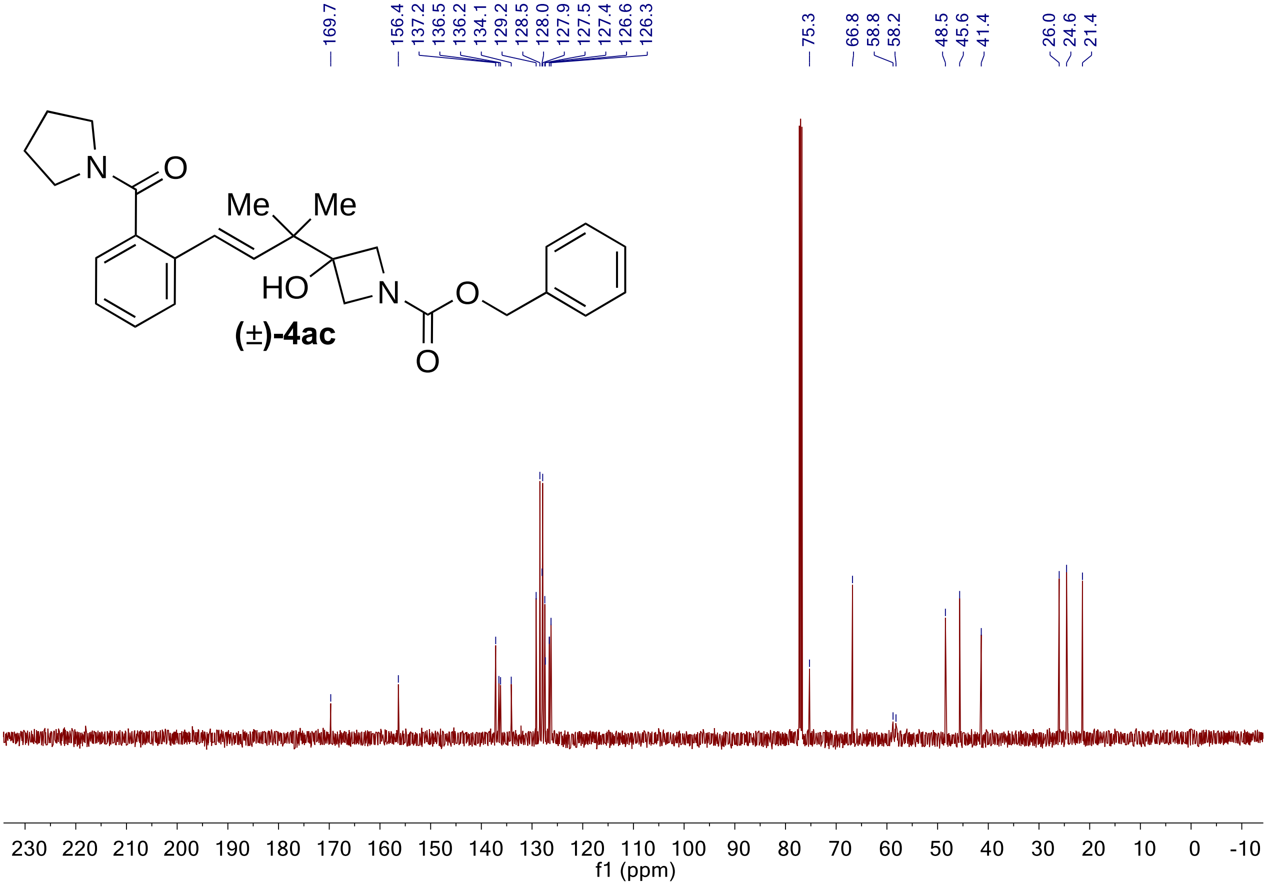
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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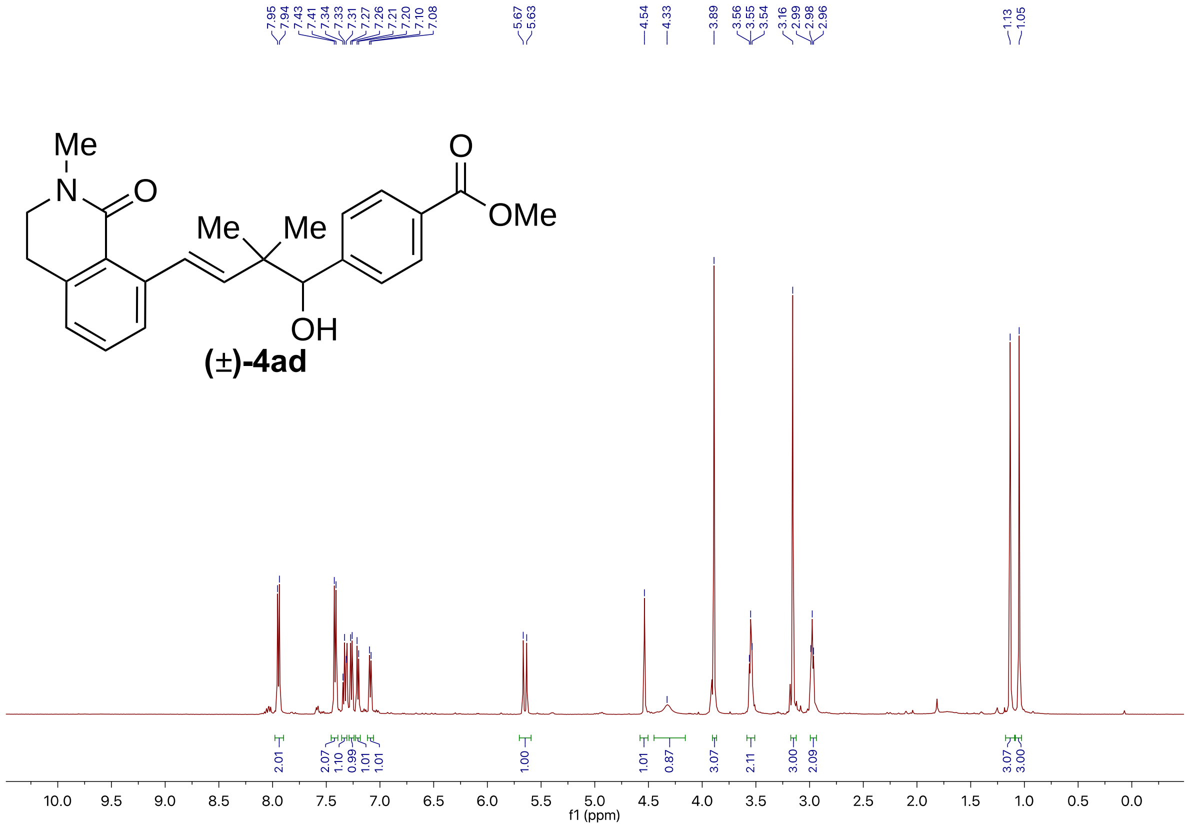
136.5
136.2
134.1
129.2
128.5
128.0
127.9
127.5
127.4
126.6
126.3
75.3
66.8
58.8
58.2
48.5
45.6
41.4
26.0
24.6
21.4
Me
Me
N
O
HO
N
O
O
(±)-4ac
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.27
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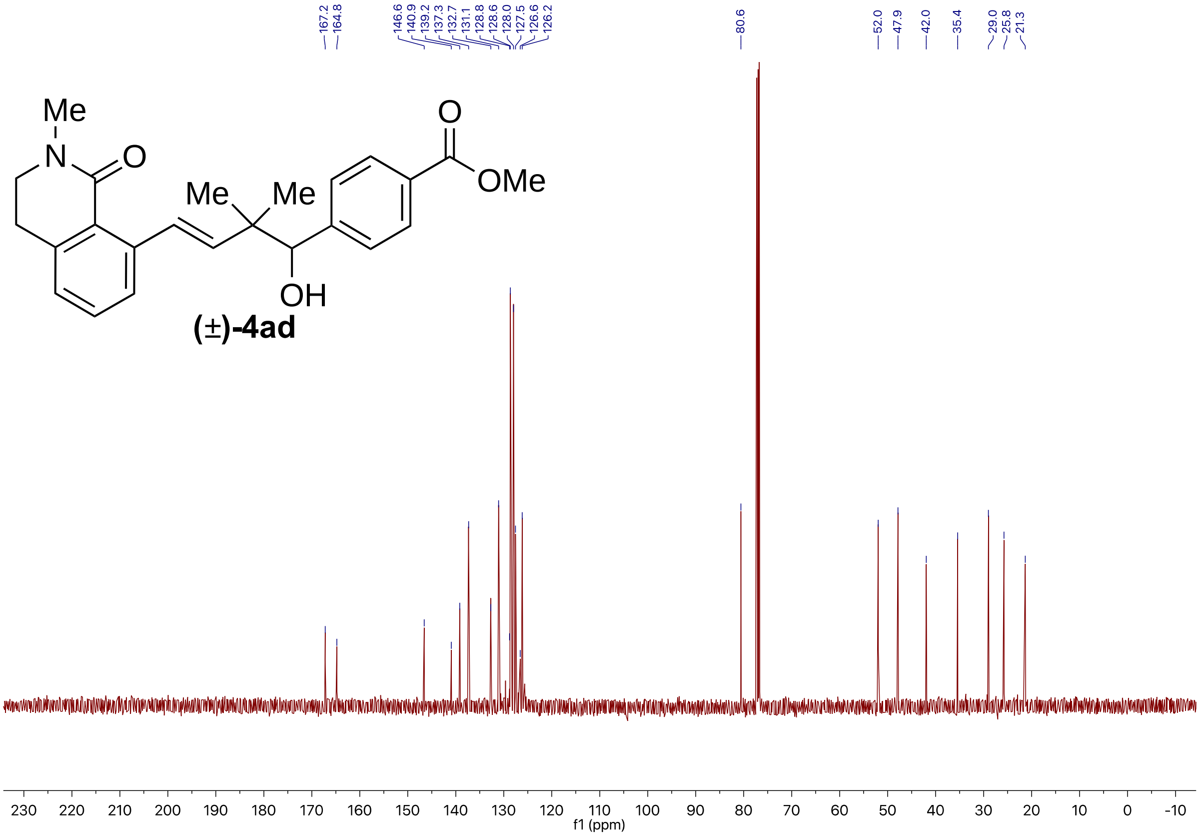
7.10
7.08
5.67
5.63
4.54
4.33
3.89
3.56
3.55
3.54
3.16
2.99
2.98
2.96
1.13
1.05
Me
N
O
Me
Me
O
OMe
OH
2.01
2.07
1.10
0.99
1.01
1.01
1.00
1.01
0.87
3.07
2.11
3.00
2.09
3.07
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

(±)-4ad


167.2
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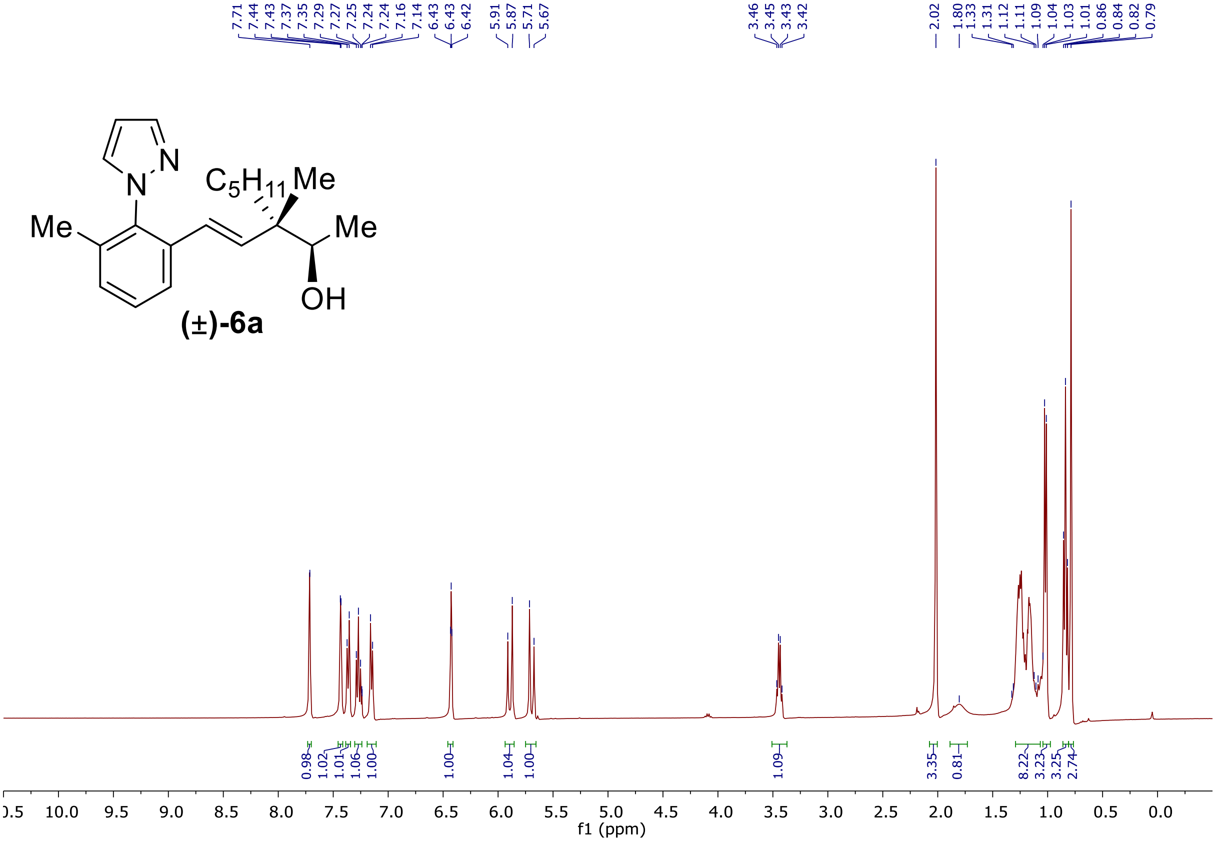
140.9
139.2
137.3
132.7
131.1
128.8
128.6
128.0
127.5
126.6
126.2
80.6
52.0
47.9
42.0
35.4
29.0
25.8
21.3
Me
N
O
Me
Me
O
OMe
OH
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

(±)-4ad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7.44
7.43
7.37
7.35
7.29
7.27
7.25
7.24
7.24
7.16
7.14
6.43
6.43
6.42
5.91
5.87
5.71
5.67
3.46
3.45
3.43
3.42
2.02
1.80
1.33
1.31
1.12
1.11
1.09
1.04
1.03
1.01
0.86
0.84
0.82
0.79
N
N
C_5H_{11}
Me
Me
Me
OH
(±)-6a
0.98
1.02
1.01
1.06
1.00
1.00
1.04
1.00
1.09
3.35
0.81
8.22
3.23
3.25
2.74
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
2.5
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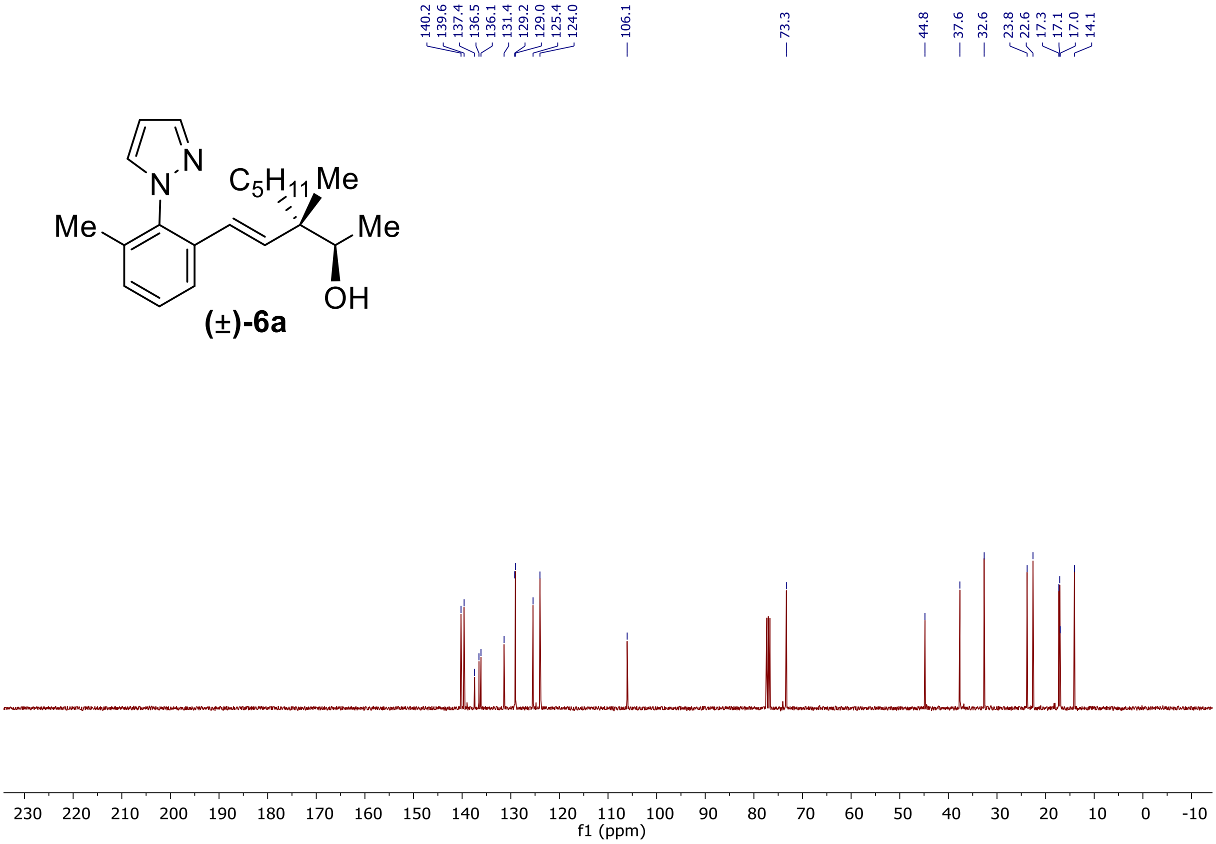
1.0
0.5
0.0
f1 (ppm)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131.4
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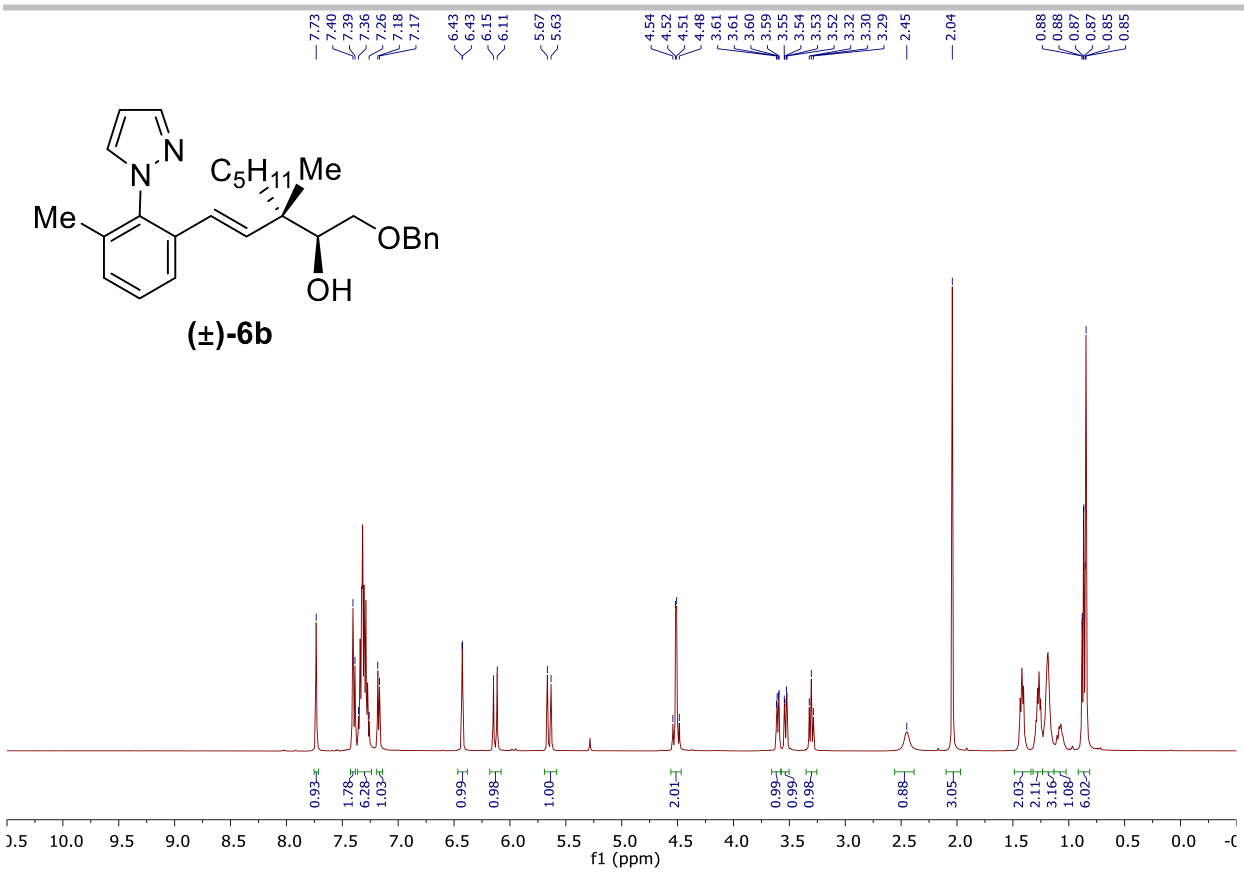
129.0
125.4
124.0
106.1
73.3
44.8
37.6
32.6
23.8
22.6
17.3
17.1
17.0
14.1
N
N
C_5H_{11}
Me
Me
Me
OH
(±)-6a
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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6.11
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5.63
4.54
4.52
4.51
4.48
3.61
3.61
3.60
3.59
3.55
3.54
3.53
3.52
3.32
3.30
3.29
2.45
2.04
0.88
0.88
0.87
0.87
0.85
0.85
N
N
Me
C_5H_{11}
Me
OBn
OH
(±)-6b
0.93
1.78
6.28
1.03
0.99
0.98
1.00
2.01
0.99
0.99
0.98
0.88
3.05
2.03
2.11
3.16
1.08
6.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
2.5
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1.0
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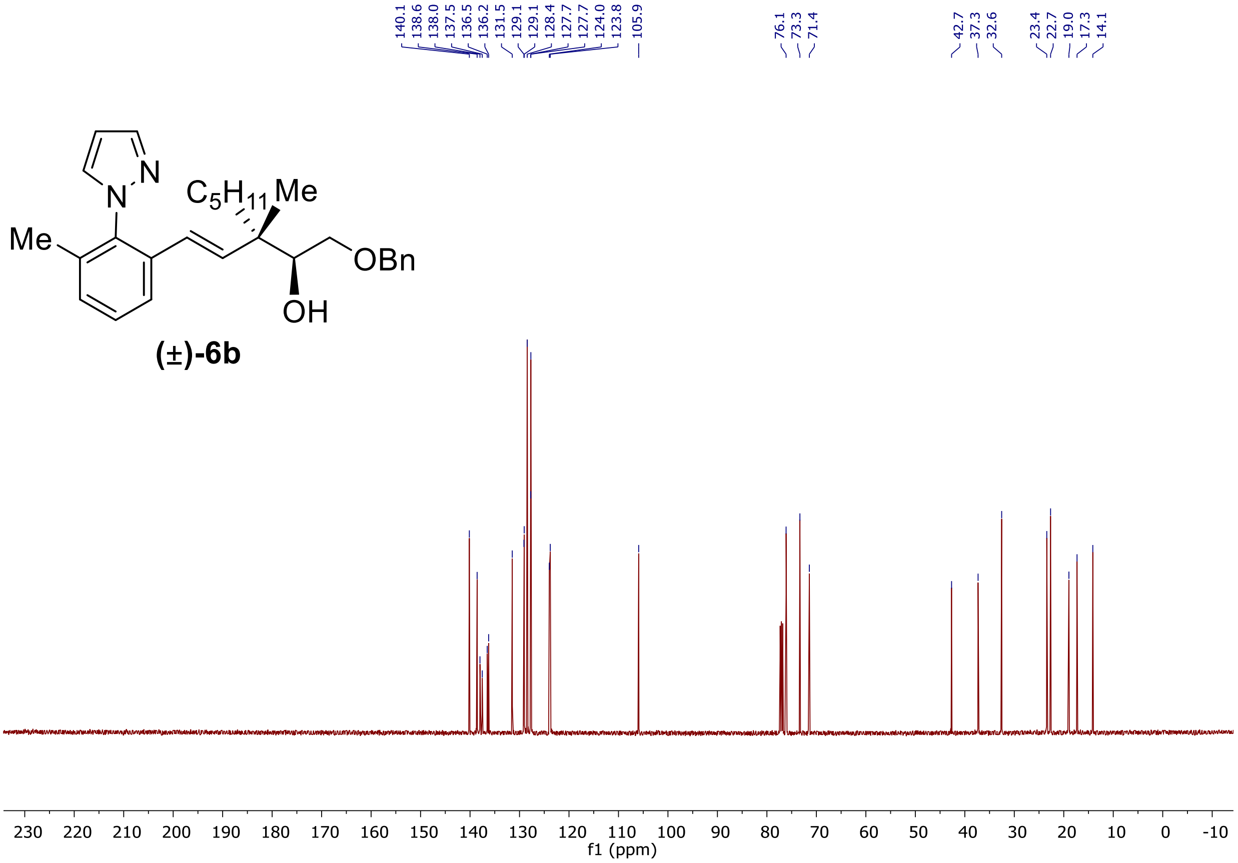
0.0
f1 (ppm)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128.4
127.7
127.7
124.0
123.8
105.9
76.1
73.3
71.4
42.7
37.3
32.6
23.4
22.7
19.0
17.3
14.1
N
N
Me
C_5H_{11}
Me
OBn
OH
(±)-6b
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
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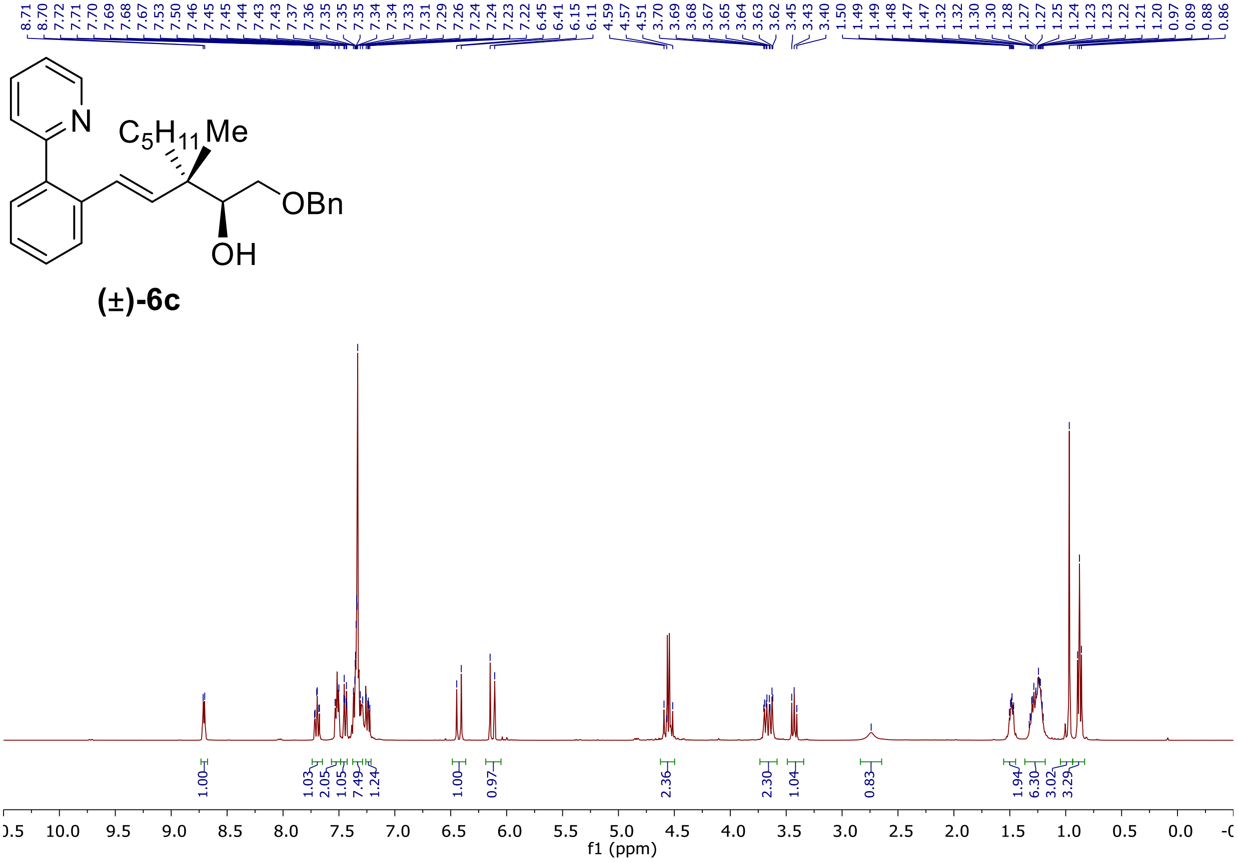
0
-10
f1 (ppm)



(±)-6c

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7.68
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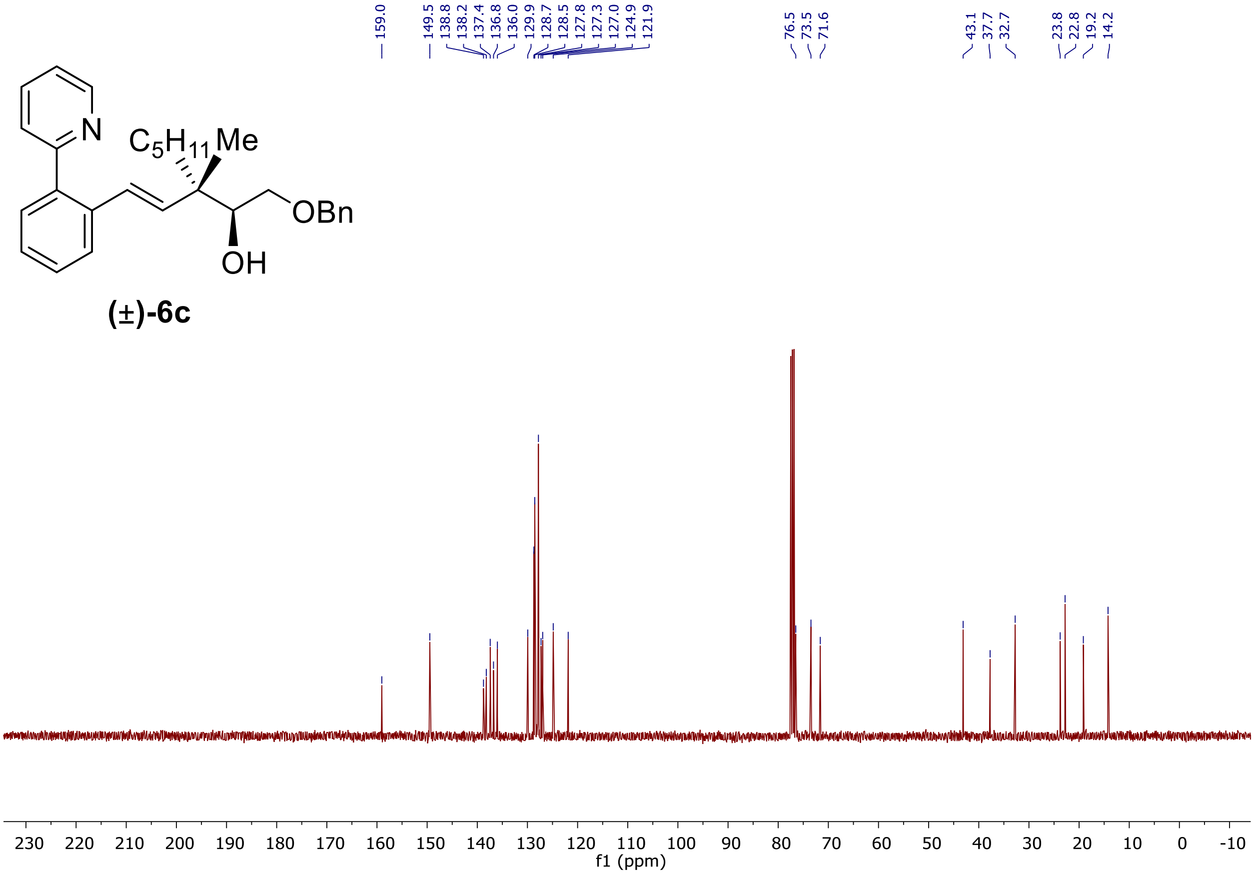
7.45
7.45
7.44
7.43
7.43
7.37
7.36
7.35
7.35
7.35
7.34
7.34
7.33
7.31
7.29
7.26
7.24
7.24
7.23
7.22
6.45
6.41
6.15
6.11
4.59
4.57
4.51
3.70
3.69
3.68
3.67
3.65
3.64
3.63
3.62
3.45
3.43
3.40
1.50
1.49
1.48
1.47
1.32
1.32
1.30
1.30
1.28
1.27
1.27
1.25
1.24
1.23
1.23
1.22
1.21
1.20
0.97
0.89
0.88
0.86
N
C_5H_{11}
Me
OBn
OH
1.00
1.03
2.05
1.05
7.49
1.24
1.00
0.97
2.36
2.30
1.04
0.83
1.94
6.30
3.02
3.29
10.5
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
-0
f1 (ppm)



(±)-6c

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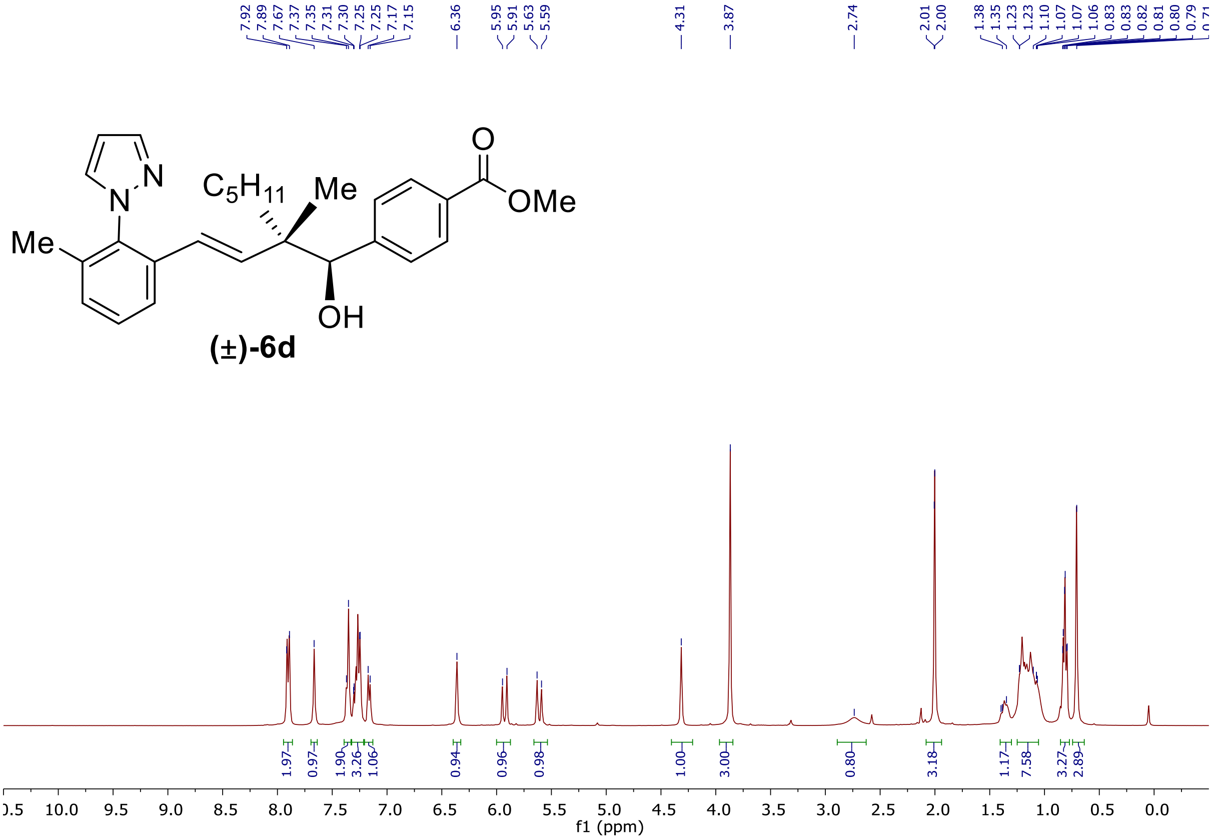
149.5
138.8
138.2
137.4
136.8
136.0
129.9
128.7
128.5
127.8
127.3
127.0
124.9
121.9
76.5
73.5
71.6
43.1
37.7
32.7
23.8
22.8
19.2
14.2
N
C_5H_{11}
Me
OBn
OH
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.31
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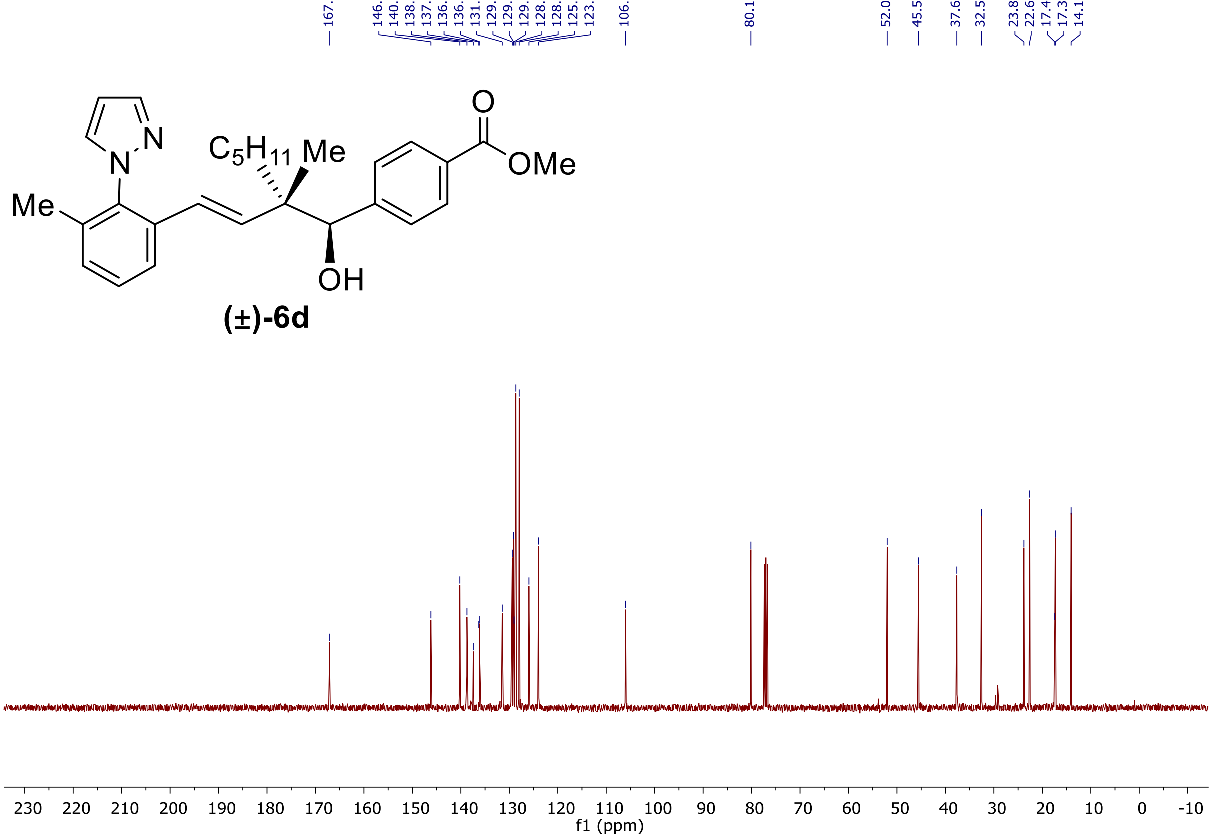
7.25
7.25
7.17
7.15
6.36
5.95
5.91
5.63
5.59
4.31
3.87
2.74
2.01
2.00
1.38
1.35
1.23
1.23
1.10
1.07
1.07
1.06
0.83
0.83
0.82
0.81
0.80
0.79
N
N
Me
C5H11
Me
O
OMe
OH
(±)-6d
1.97
0.97
1.90
3.26
1.06
0.94
0.96
0.98
1.00
3.00
0.80
3.18
1.17
7.58
3.27
2.89
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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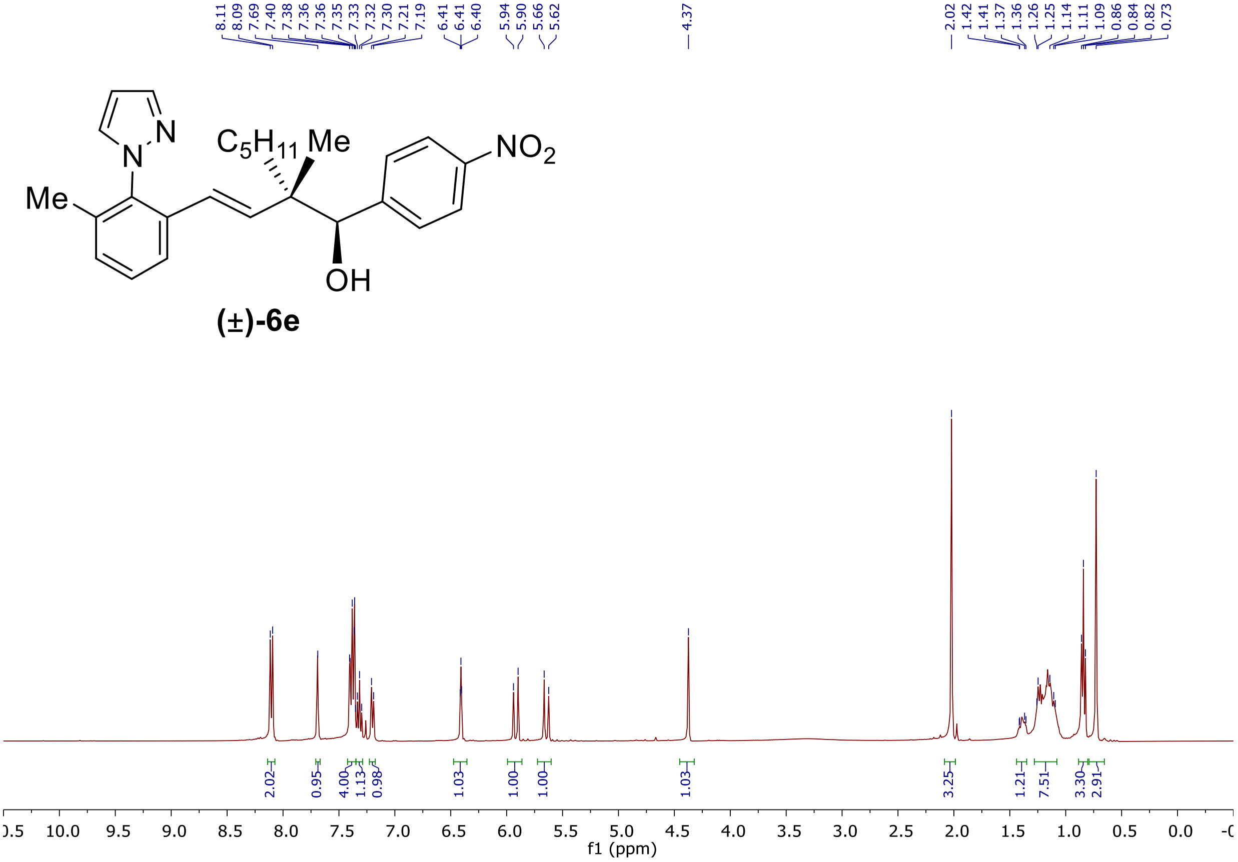
136.3
136.1
131.5
129.4
129.1
129.0
128.6
128.0
125.9
123.9
106.0
80.1
52.0
45.5
37.6
32.5
23.8
22.6
17.4
17.3
14.1
N
N
Me
C5H11
Me
O
OMe
OH
(±)-6d
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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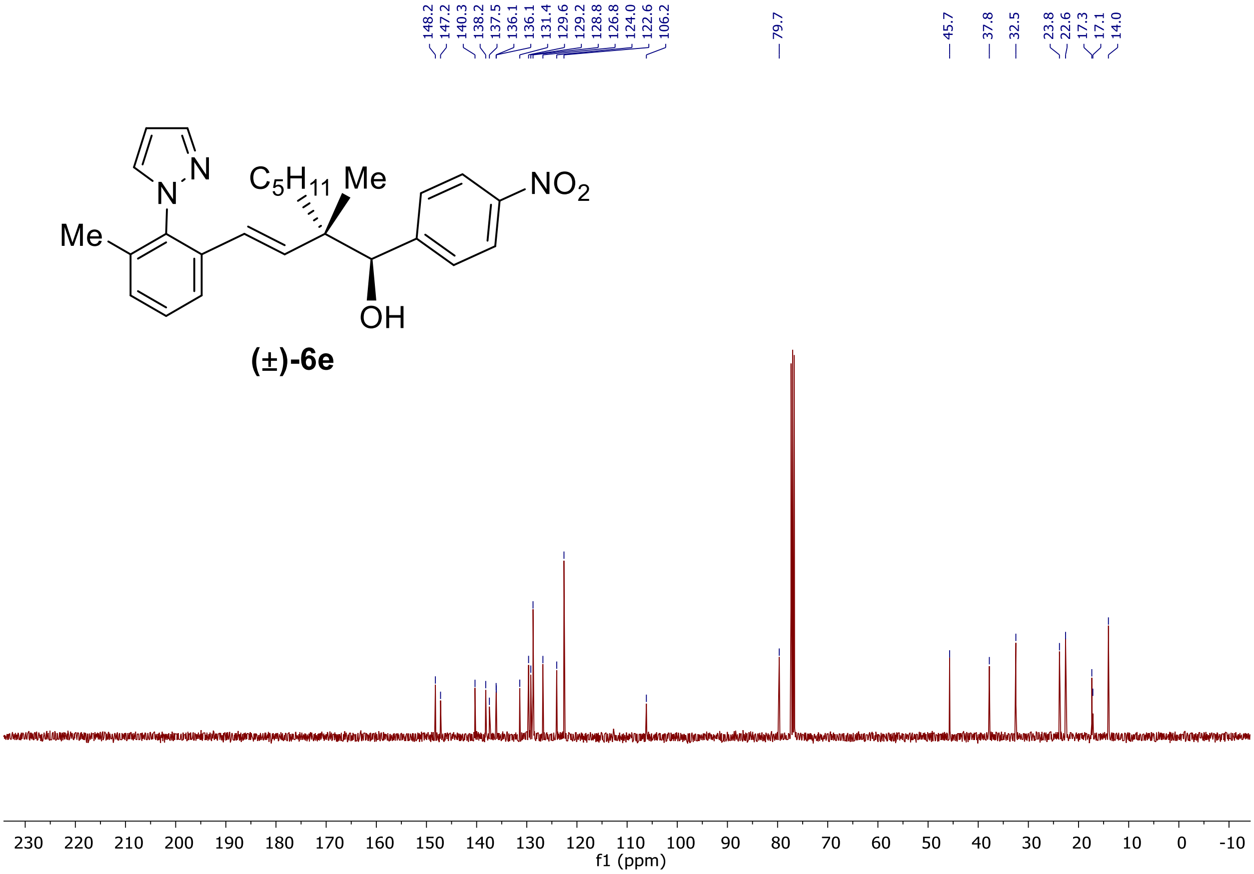
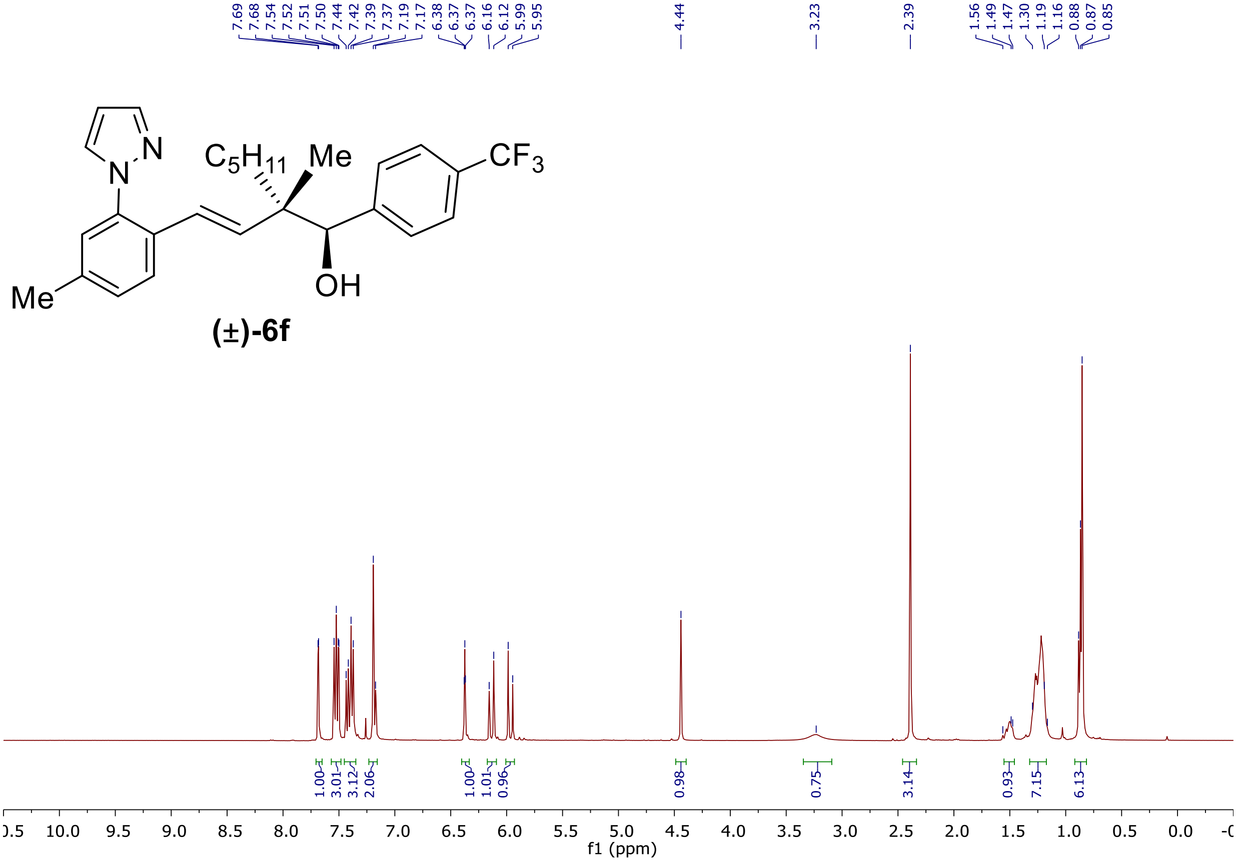
7.32
7.30
7.21
7.19
6.41
6.41
6.40
5.94
5.90
5.66
5.62
4.37
2.02
1.42
1.41
1.37
1.36
1.26
1.25
1.14
1.11
1.09
0.86
0.84
0.82
0.73
N
N
C5H11
Me
NO2
Me
OH
(±)-6e
2.02
0.95
4.00
1.13
0.98
1.03
1.00
1.00
1.03
3.25
1.21
7.51
3.30
2.91
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


148.2
147.2
140.3
138.2
137.5
136.1
136.1
131.4
129.6
129.2
128.8
126.8
124.0
122.6
106.2
79.7
45.7
37.8
32.5
23.8
22.6
17.3
17.1
14.0
N
N
C5H11
Me
NO2
Me
OH
(±)-6e
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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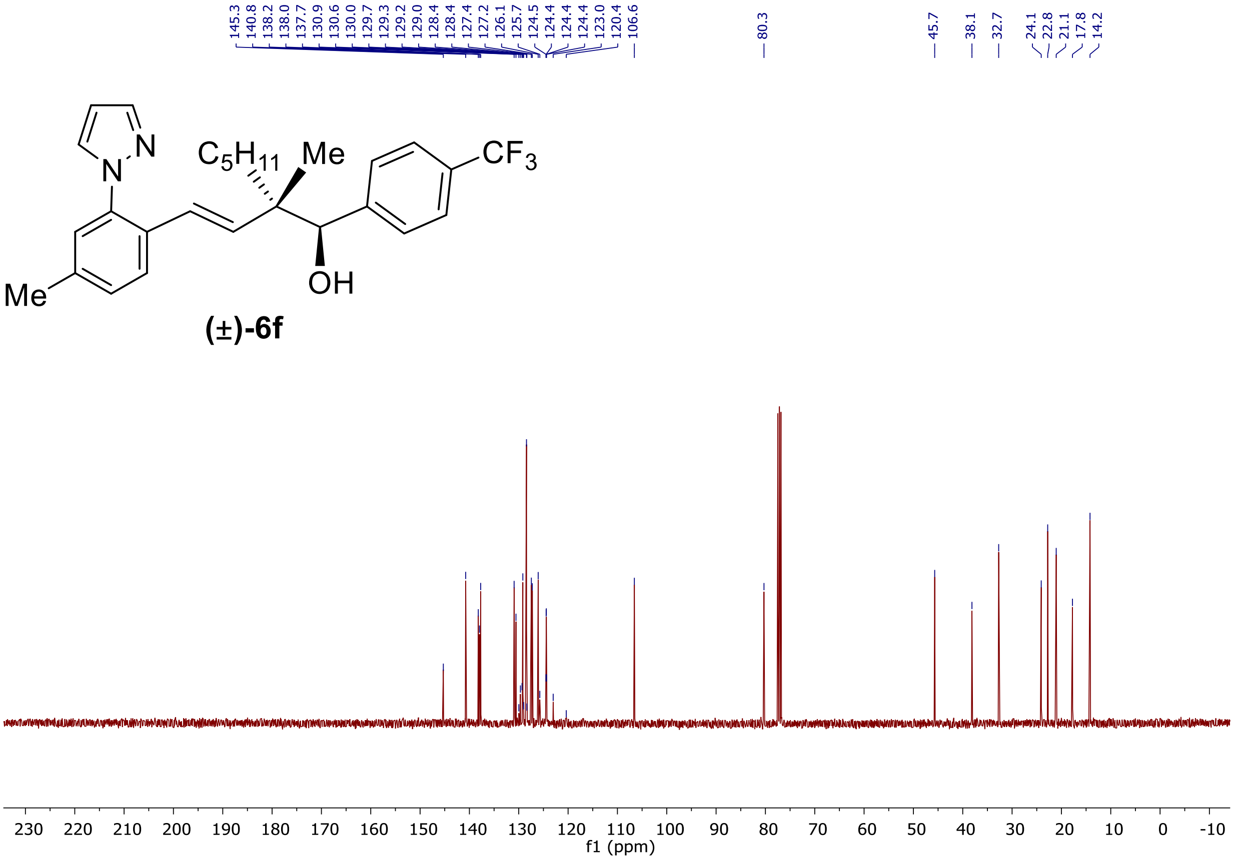
7.42
7.39
7.37
7.19
7.17
6.38
6.37
6.37
6.16
6.12
5.99
5.95
4.44
3.23
2.39
1.56
1.49
1.47
1.30
1.19
1.16
0.88
0.87
0.85
N
N
C5H11
Me
CF3
Me
OH
(±)-6f
1.00
3.01
3.12
2.06
1.00
1.01
0.96
0.98
0.75
3.14
0.93
7.15
6.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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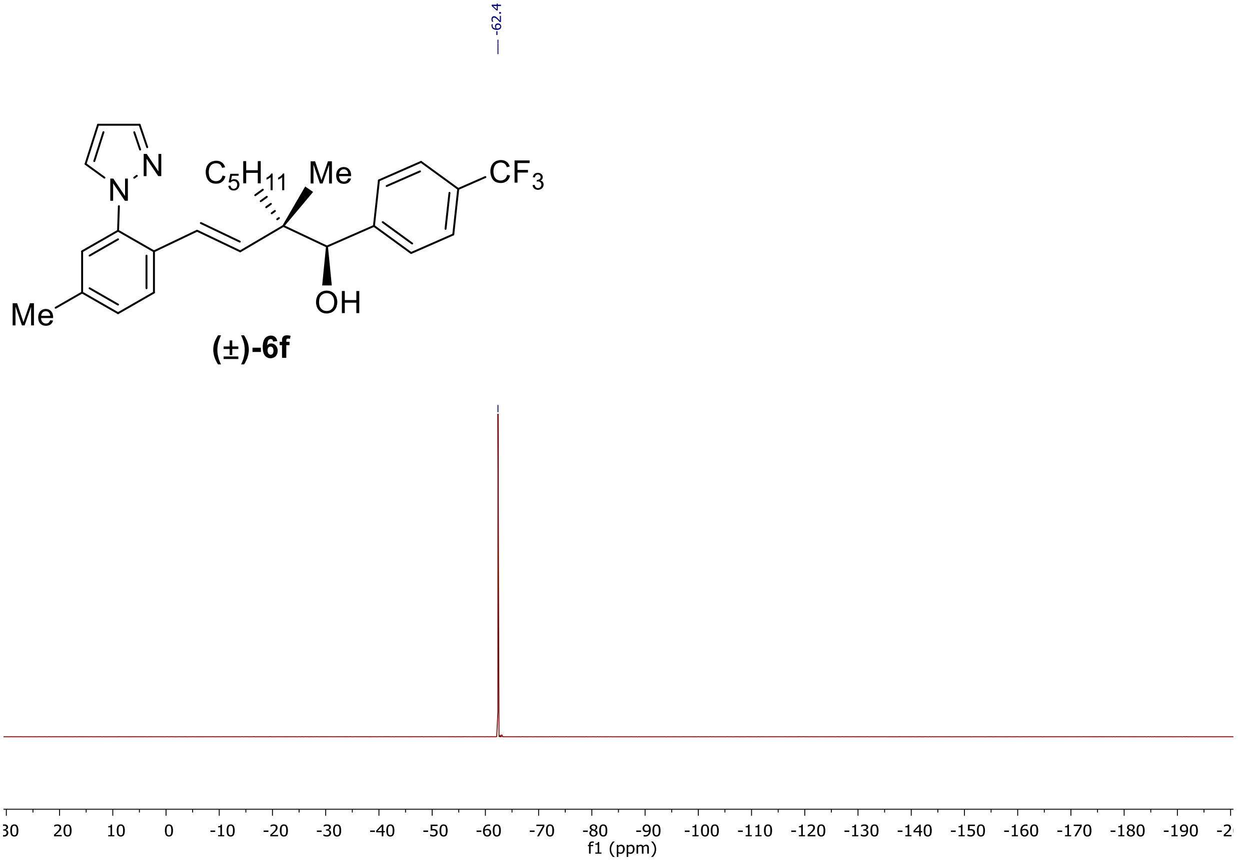
130.0
129.7
129.3
129.2
129.0
128.4
128.4
127.4
127.2
126.1
125.7
124.5
124.4
124.4
124.4
123.0
120.4
106.6
80.3
45.7
38.1
32.7
24.1
22.8
21.1
17.8
14.2
N
N
C5H11
Me
CF3
Me
OH
(±)-6f
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


(±)-6f
-62.4
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N
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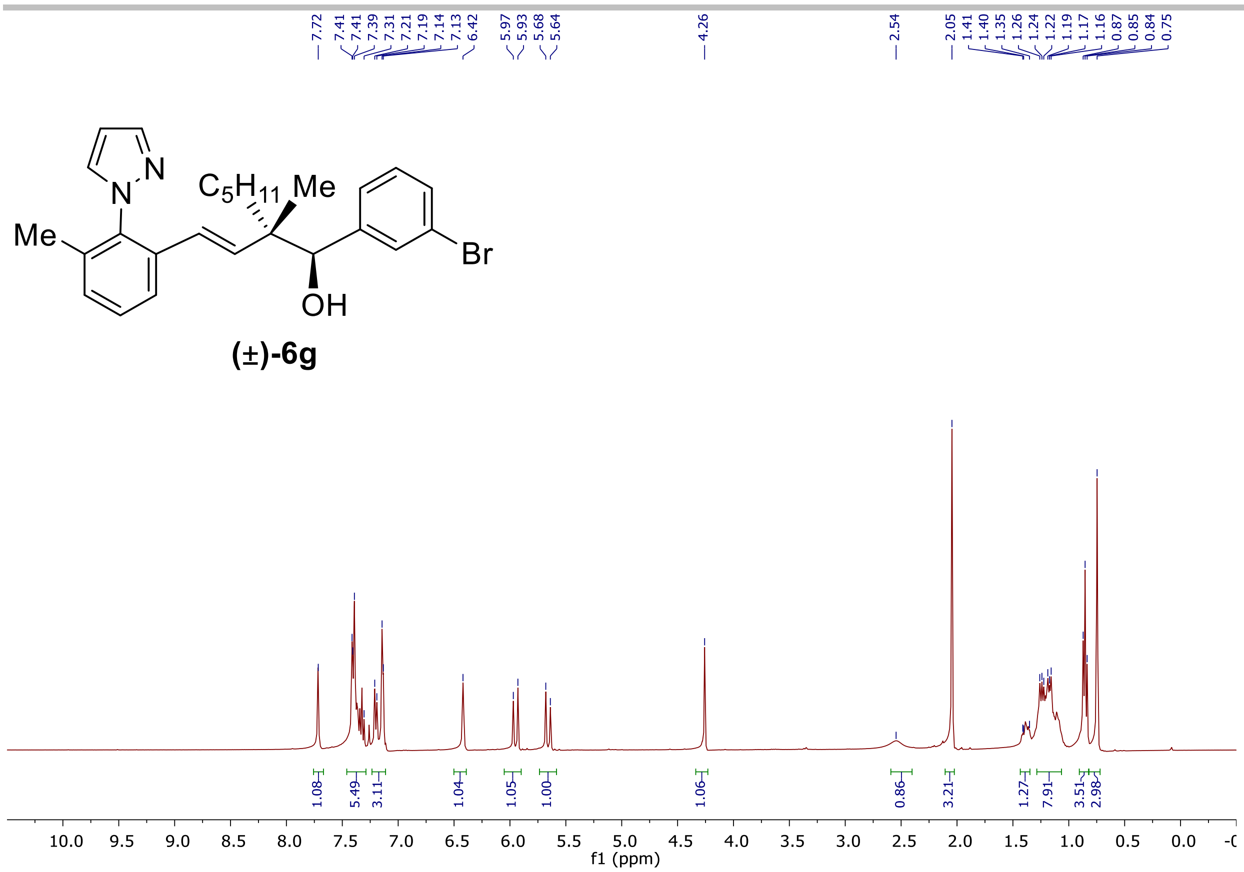
Me
CF3
Me
OH
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)


7.72
7.41
7.41
7.39
7.31
7.21
7.19
7.14
7.13
6.42
5.97
5.93
5.68
5.64
4.26
2.54
2.05
1.41
1.40
1.35
1.26
1.24
1.22
1.19
1.17
1.16
0.87
0.85
0.84
0.75
N
N
Me
C_5H_{11}
Me
Br
OH
1.08
5.49
3.11
1.04
1.05
1.00
1.06
0.86
3.21
1.27
7.91
3.51
2.98
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
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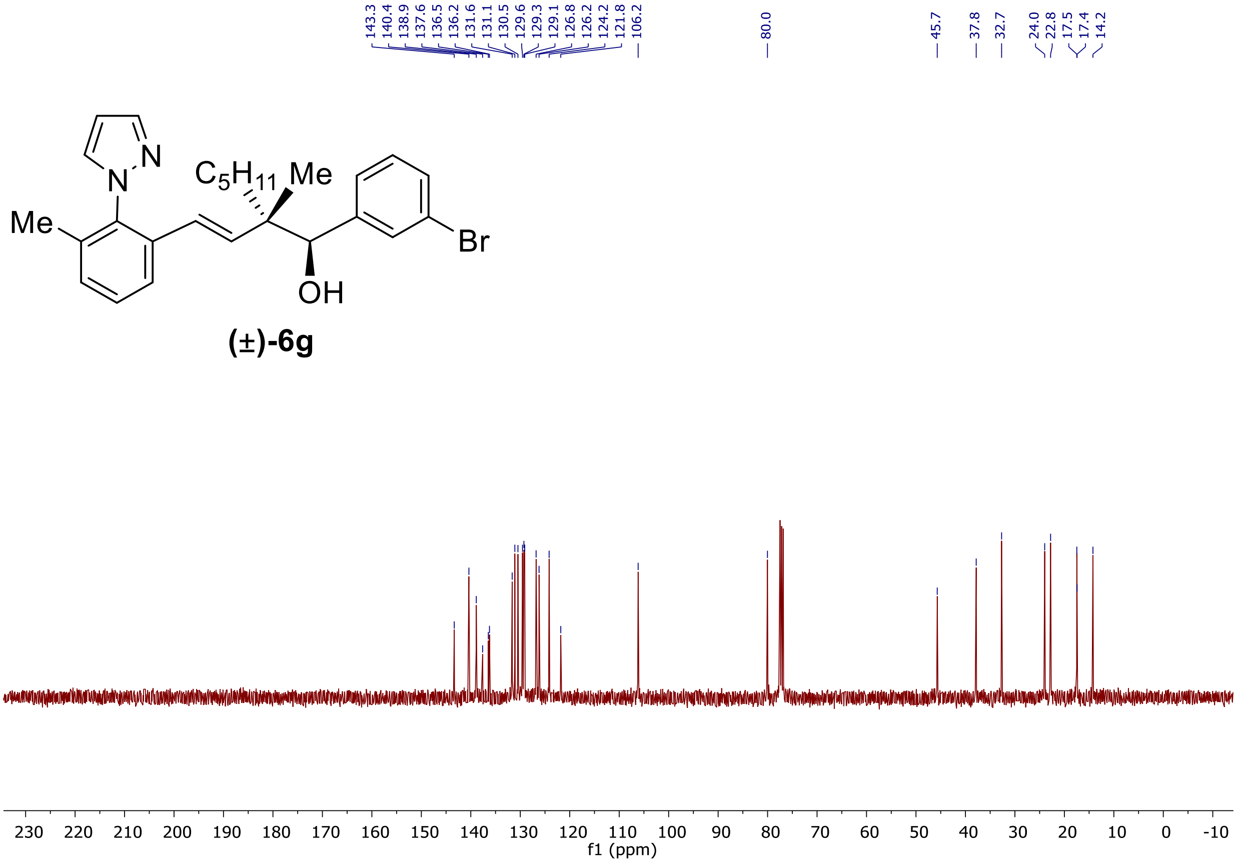
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

(±)-6g


143.3
140.4
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136.5
136.2
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131.1
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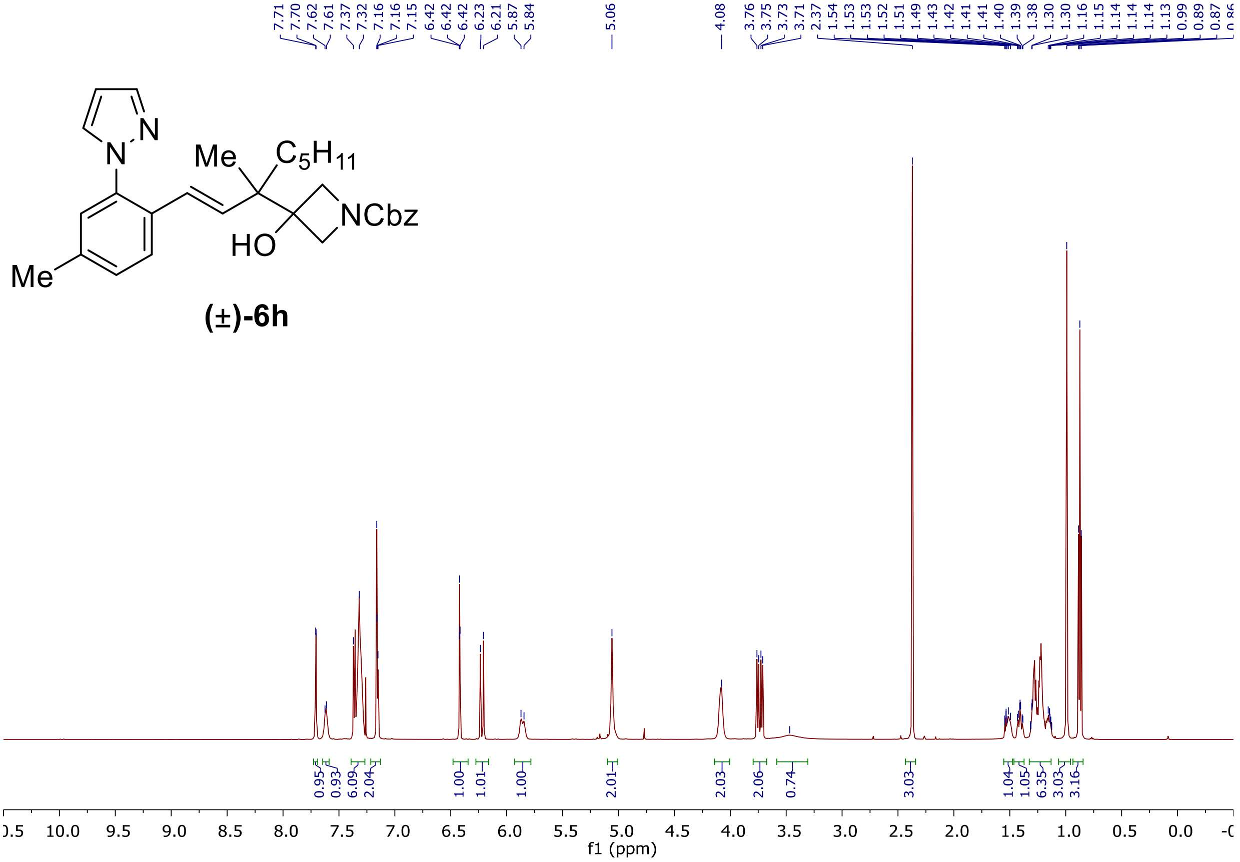
129.6
129.3
129.1
126.8
126.2
124.2
121.8
106.2
80.0
45.7
37.8
32.7
24.0
22.8
17.5
17.4
14.2
N
N
Me
C_5H_{11}
Me
Br
OH
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

(±)-6g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7.16
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6.42
6.42
6.42
6.23
6.21
5.87
5.84
5.06
4.08
3.76
3.75
3.73
3.71
2.37
1.54
1.53
1.53
1.52
1.51
1.49
1.43
1.42
1.41
1.41
1.40
1.39
1.38
1.30
1.30
1.16
1.15
1.14
1.14
1.14
1.13
0.99
0.89
0.87
N
N
Me
C5H11
NCbz
HO
Me
0.95
0.93
6.09
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1.00
1.01
1.00
2.01
2.03
2.06
0.74
3.03
1.04
1.05
6.35
3.03
3.16
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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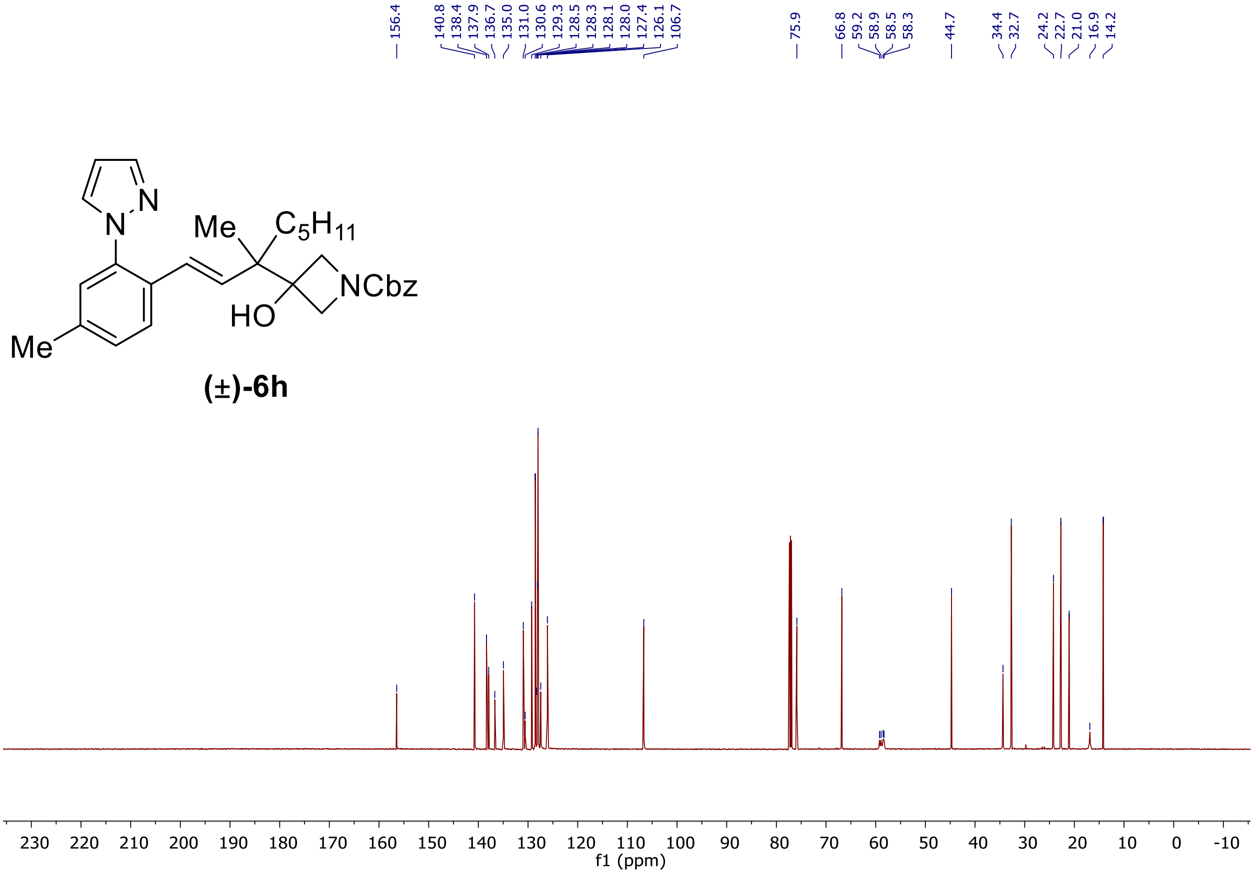
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

(±)-6h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130.6
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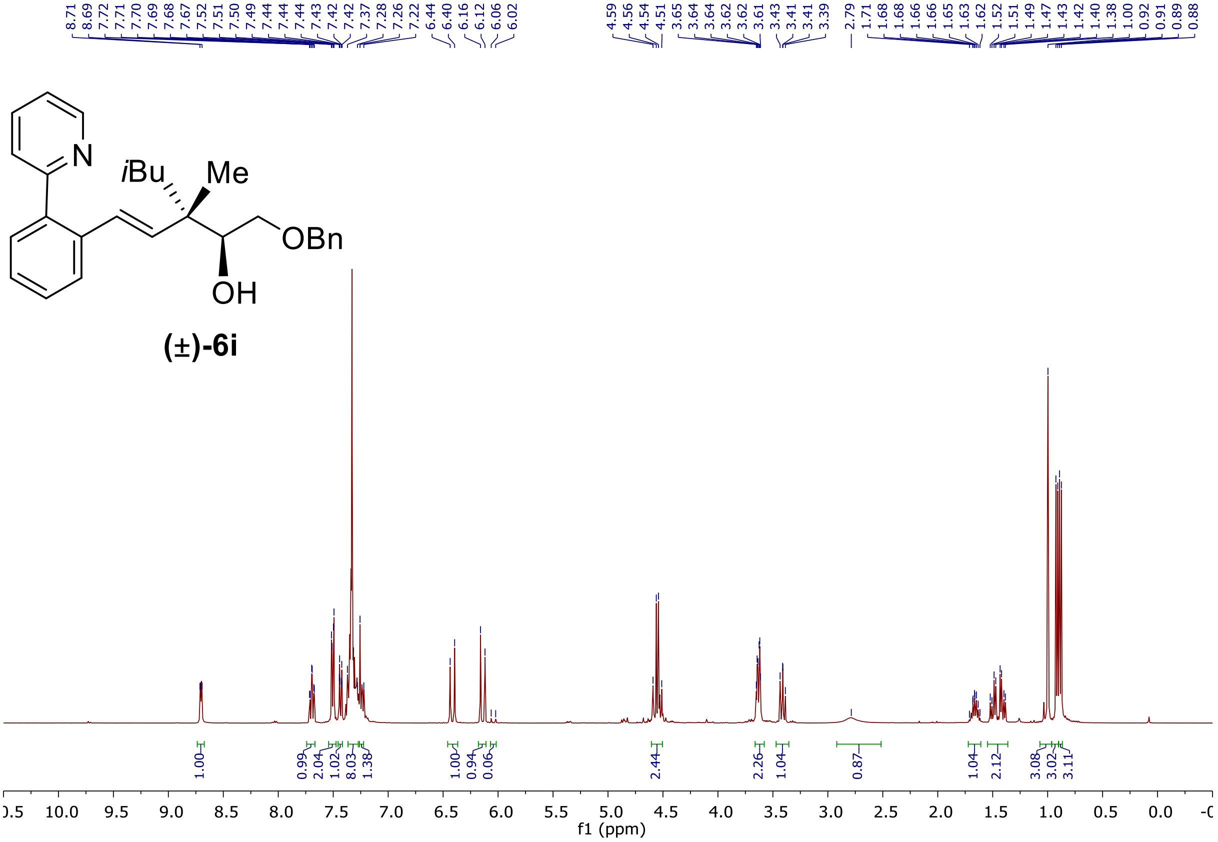
128.5
128.3
128.1
128.0
127.4
126.1
106.7
75.9
66.8
59.2
58.9
58.5
58.3
44.7
34.4
32.7
24.2
22.7
21.0
16.9
14.2
N
N
Me
C5H11
NCbz
HO
Me
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

(±)-6h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7.44
7.44
7.44
7.43
7.42
7.42
7.37
7.28
7.26
7.22
6.44
6.40
6.16
6.12
6.06
6.02
4.59
4.56
4.54
4.51
3.65
3.64
3.64
3.62
3.62
3.61
3.43
3.41
3.41
3.39
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1.68
1.68
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1.66
1.65
1.63
1.62
1.52
1.51
1.49
1.47
1.43
1.42
1.40
1.38
1.00
0.92
0.91
0.89
0.88
N
iBu
Me
OBn
OH
(±)-6i
1.00
0.99
2.04
1.02
8.03
1.38
1.00
0.94
0.06
2.44
2.26
1.04
0.87
1.04
2.12
3.08
3.02
3.11
.5
10.0
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
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3.0
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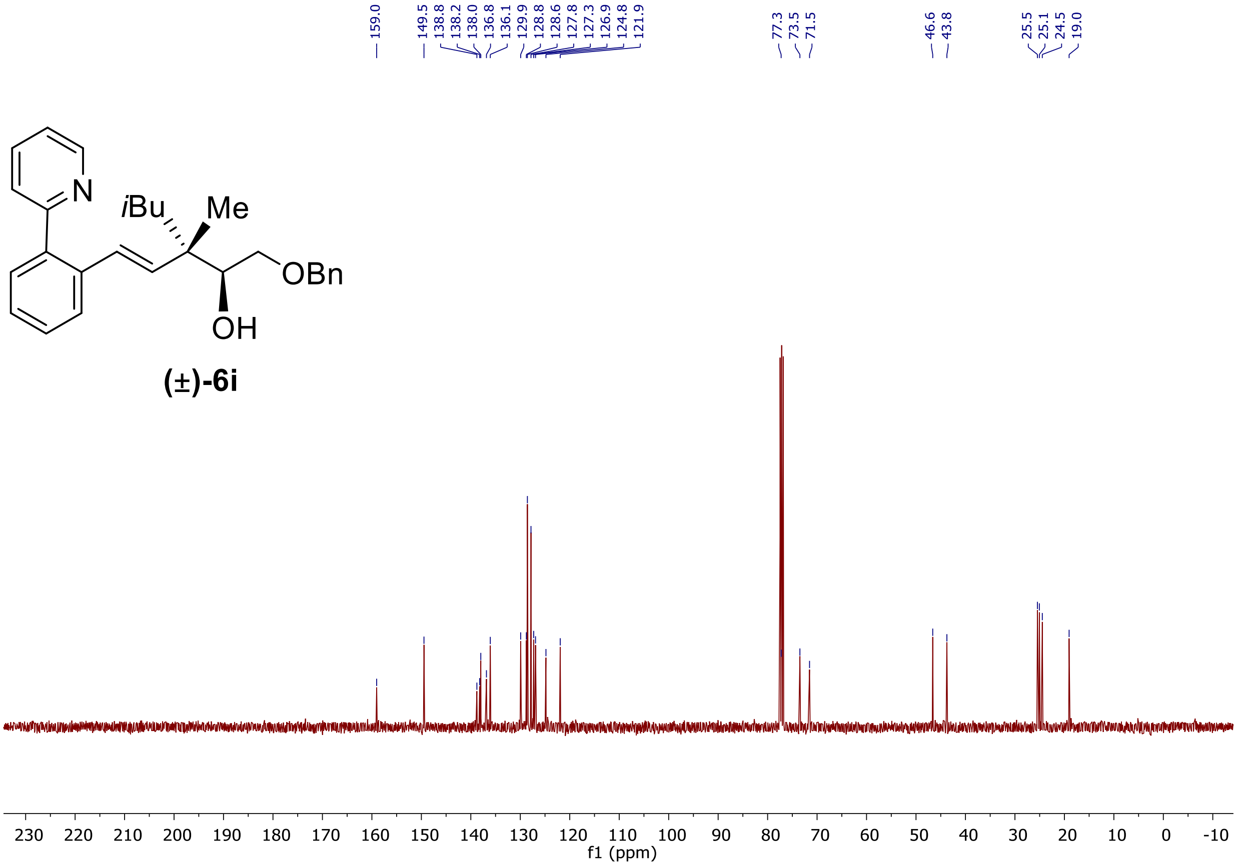
2.0
1.5
1.0
0.5
0.0
-
f1 (ppm)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128.6
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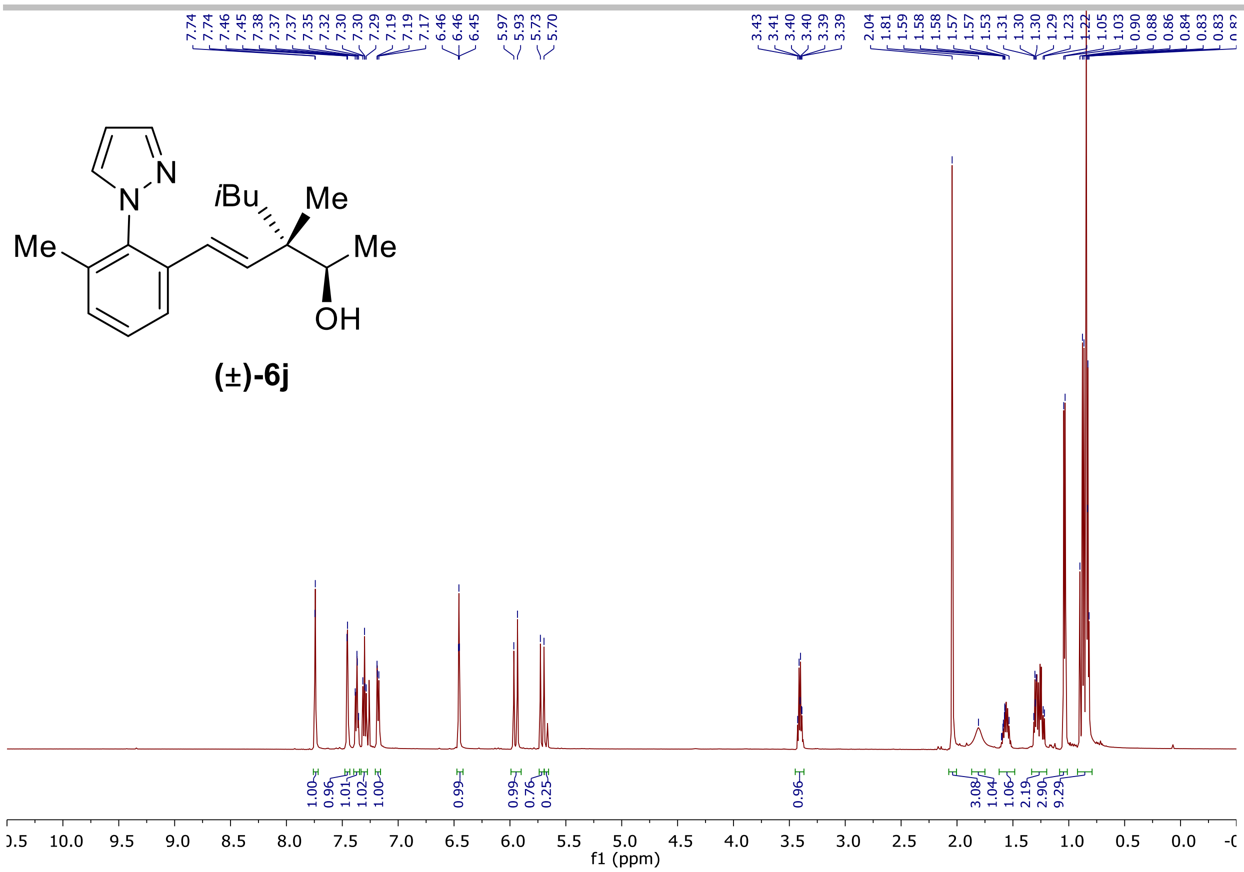
127.3
126.9
124.8
121.9
77.3
73.5
71.5
46.6
43.8
25.5
25.1
24.5
19.0
N
iBu
Me
OBn
OH
(±)-6i
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.19
7.19
7.17
6.46
6.46
6.45
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5.93
5.73
5.70
3.43
3.41
3.40
3.40
3.39
3.39
2.04
1.81
1.59
1.58
1.58
1.57
1.57
1.53
1.31
1.30
1.30
1.29
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1.22
1.05
1.03
0.90
0.88
0.86
0.84
0.83
0.83
N
N
iBu
Me
Me
Me
OH
1.00
0.96
1.01
1.02
1.00
0.99
0.99
0.76
0.25
0.96
3.08
1.04
1.06
2.19
2.90
9.29
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
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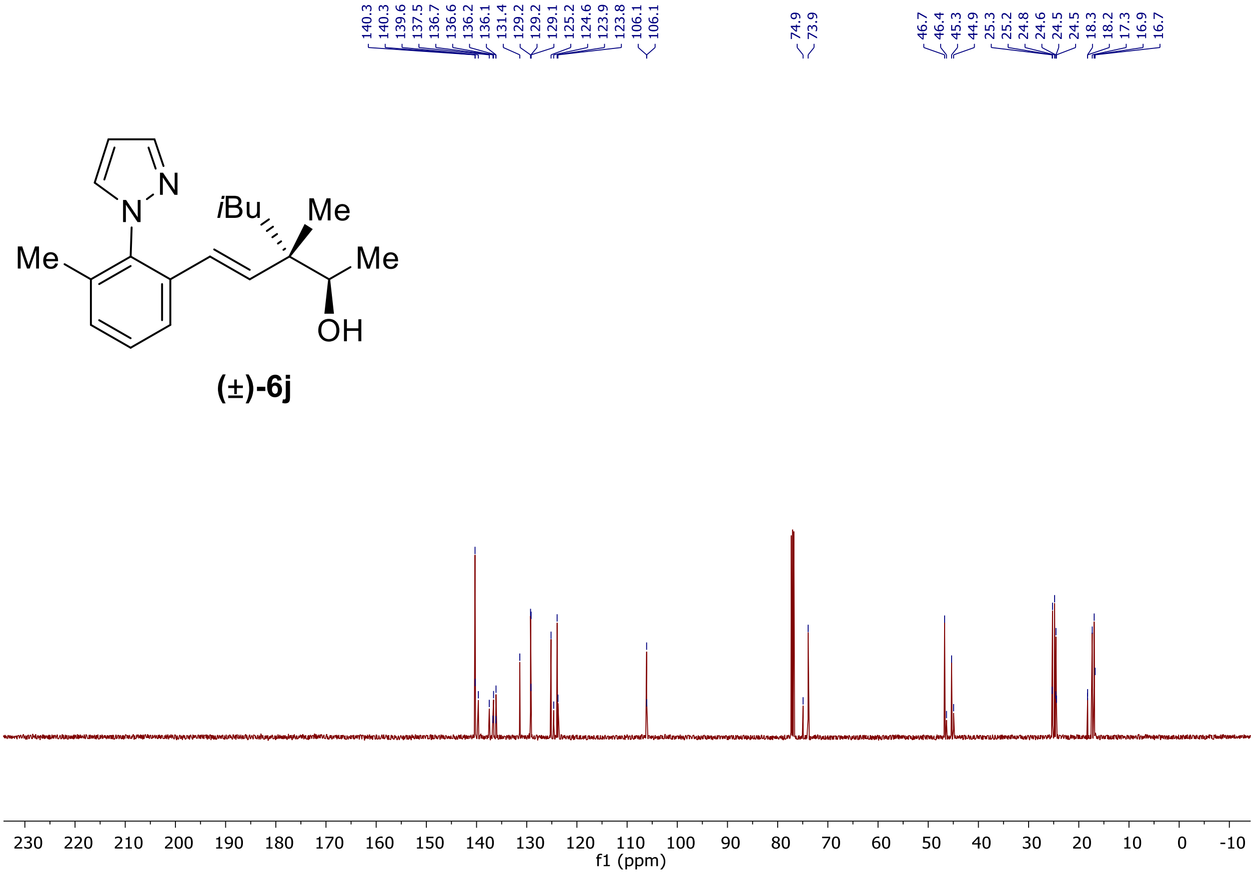
0.5
0.0
f1 (ppm)

(±)-6j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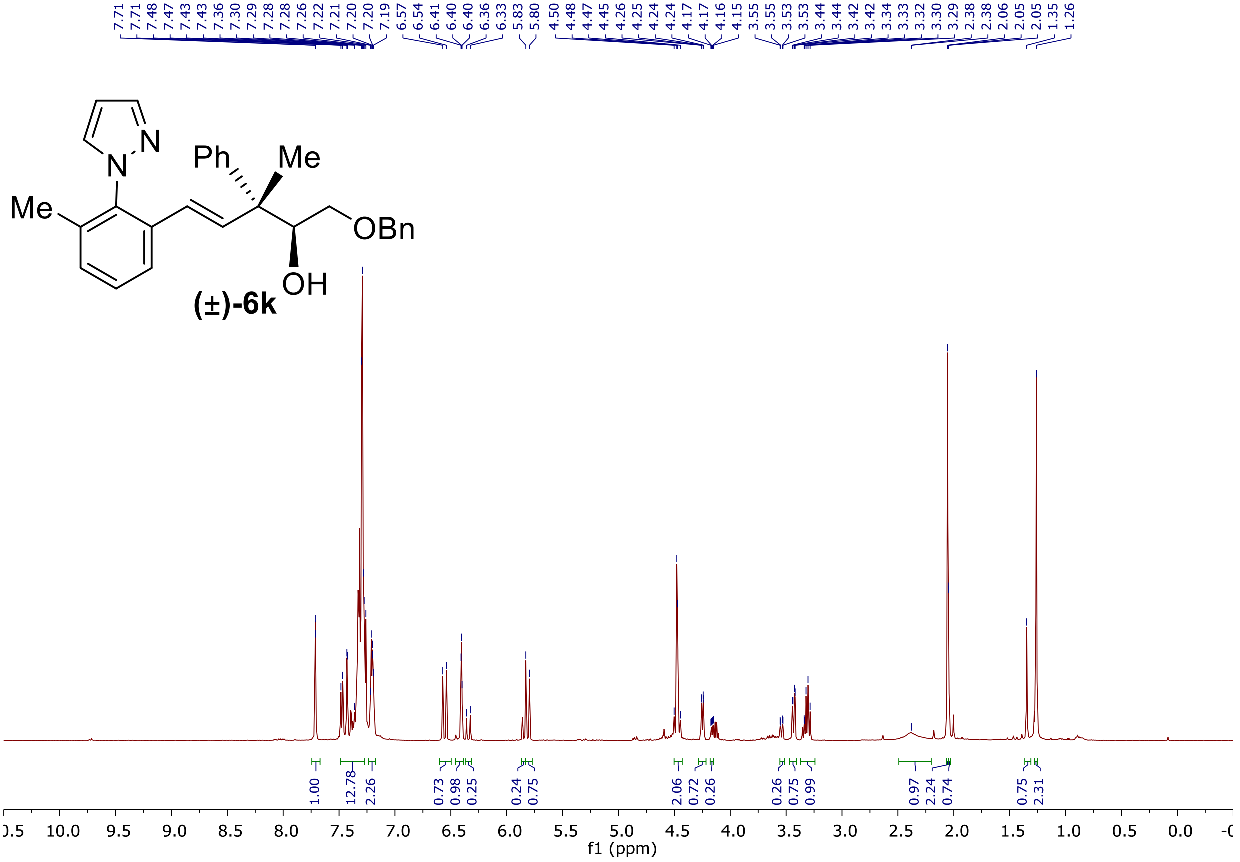
136.2
136.1
131.4
129.2
129.2
129.1
125.2
124.6
123.9
123.8
106.1
106.1
74.9
73.9
46.7
46.4
45.3
44.9
25.3
25.2
24.6
24.5
24.5
18.3
18.2
17.3
16.9
16.7
N
N
iBu
Me
Me
Me
OH
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

(±)-6j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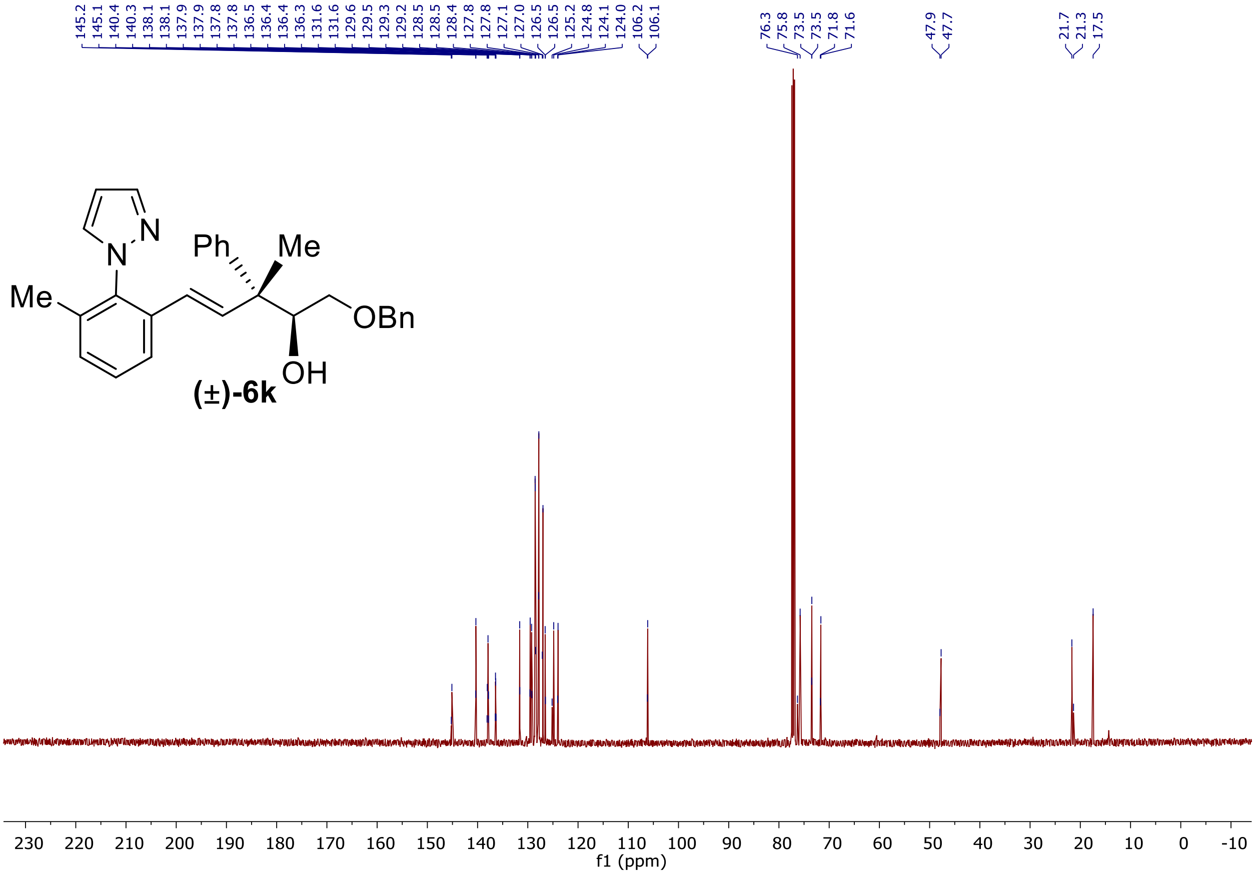
Ph
Me
N
N
Me
OBn
OH
(±)-6k
1.00
12.78
2.26
0.73
0.98
0.25
0.24
0.75
2.06
0.72
0.26
0.26
0.75
0.99
0.97
2.24
0.74
0.75
2.31
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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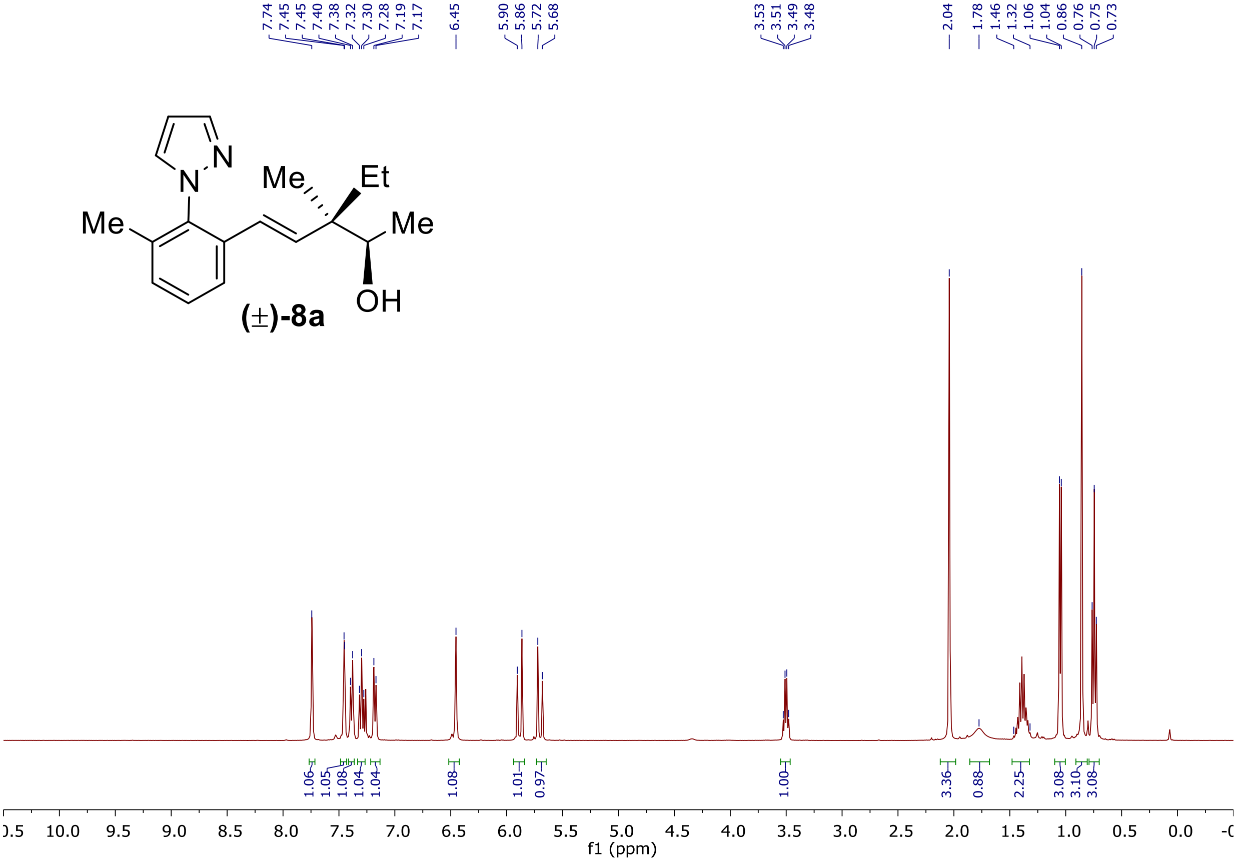
76.3 75.8 73.5 73.5 71.8 71.6
47.9 47.7
21.7 21.3 17.5
Ph
Me
N
N
Me
OBn
OH
(±)-6k
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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3.53
3.51
3.49
3.48
2.04
1.78
1.46
1.32
1.06
1.04
0.86
0.76
0.75
0.73
N
N
Me
Et
Me
Me
OH
(±)-8a
1.06
1.05
1.08
1.04
1.04
1.08
1.01
0.97
1.00
3.36
0.88
2.25
3.08
3.10
3.08
10.5
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
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3.0
2.5
2.0
1.5
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0.5
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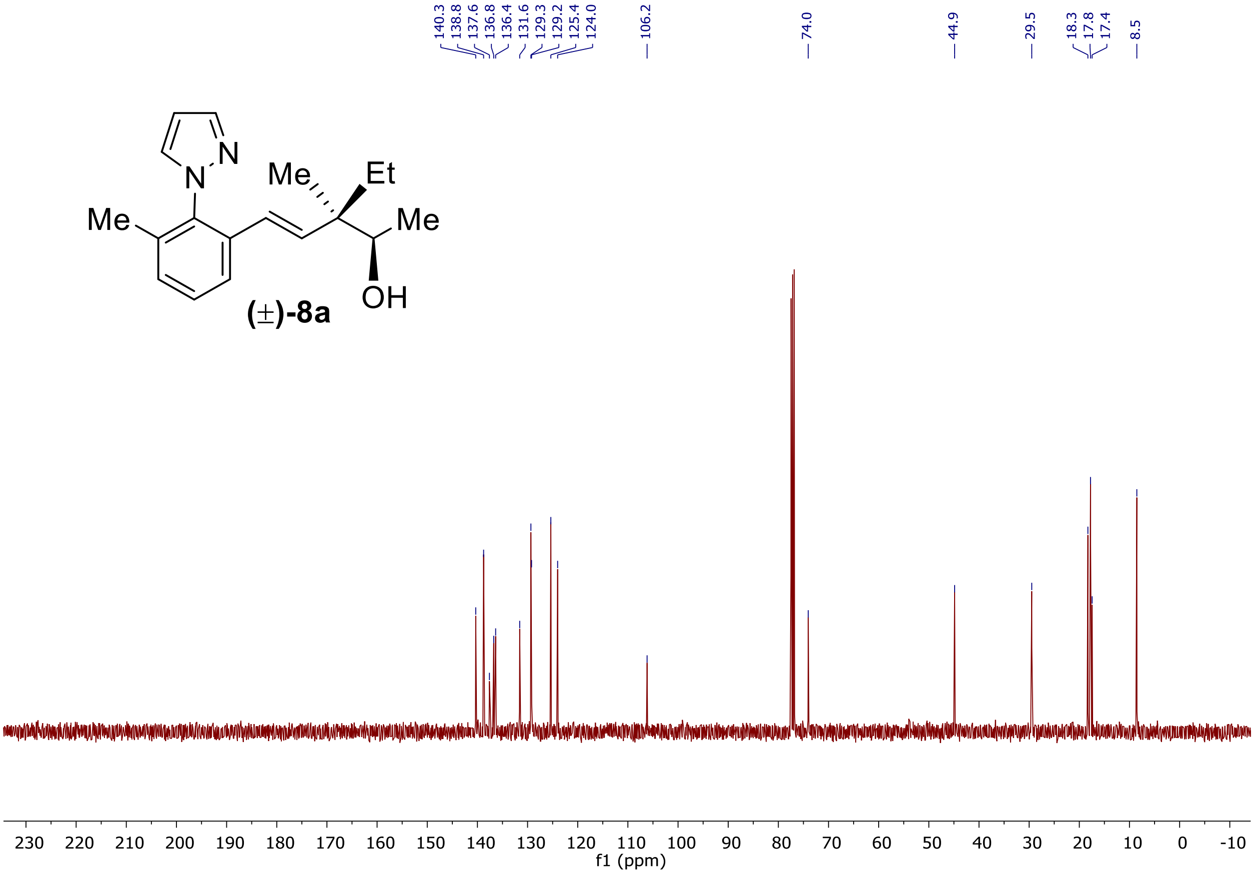
-0
f1 (ppm)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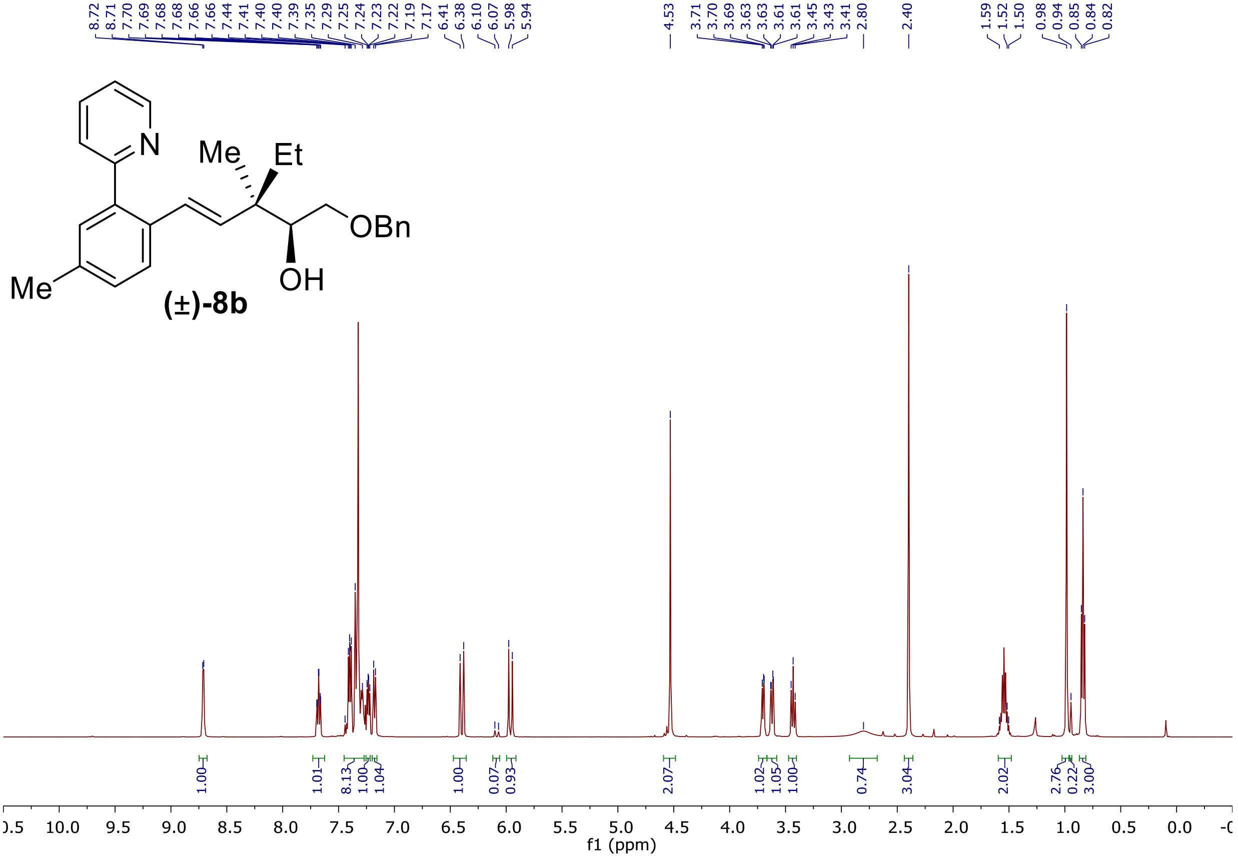
125.4
124.0
106.2
74.0
44.9
29.5
18.3
17.8
17.4
8.5
N
N
Me
Et
Me
Me
OH
(±)-8a
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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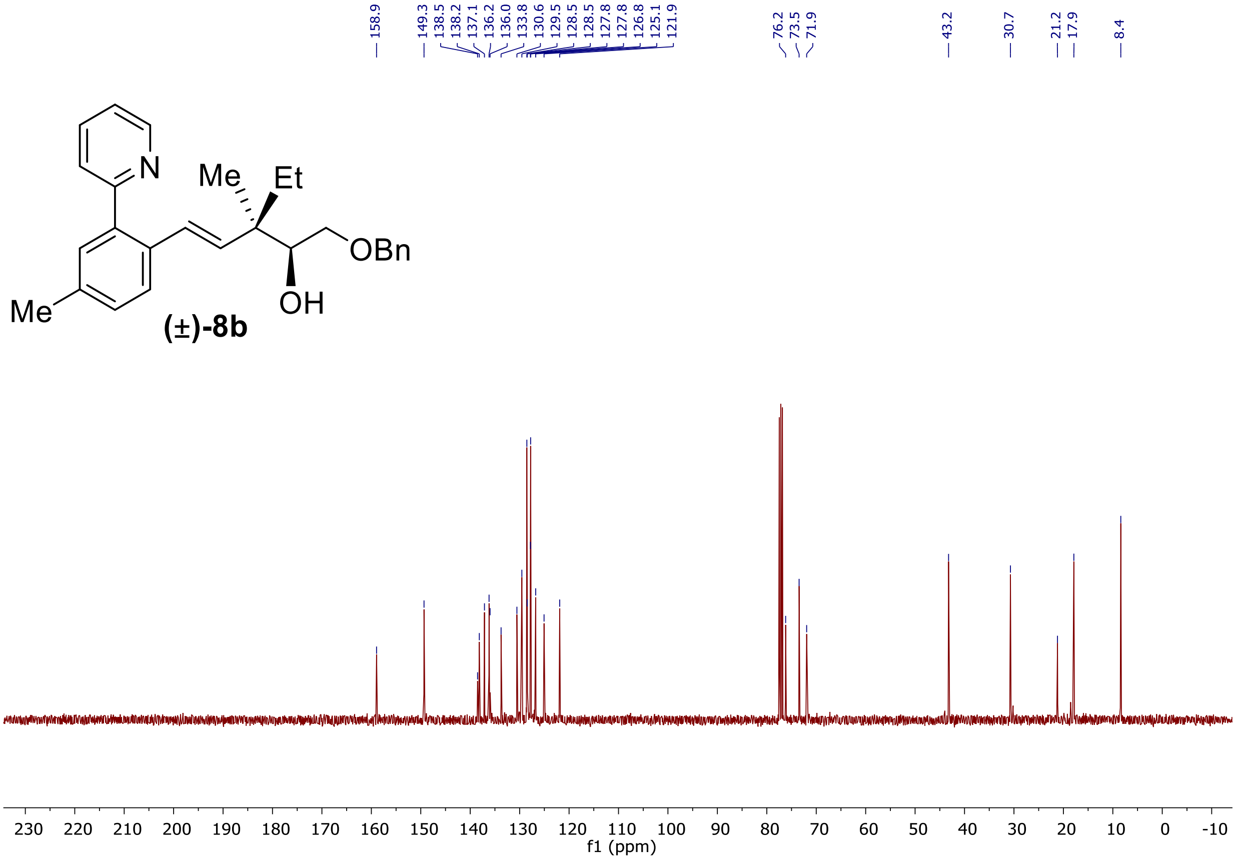
7.39
7.35
7.29
7.25
7.24
7.23
7.22
7.19
7.17
6.41
6.38
6.10
6.07
5.98
5.94
4.53
3.71
3.70
3.69
3.63
3.63
3.61
3.61
3.45
3.43
3.41
2.80
2.40
1.59
1.52
1.50
0.98
0.94
0.85
0.84
0.82
N
Me
Et
OBn
OH
Me
(±)-8b
1.00
1.01
8.13
1.00
1.04
1.00
0.07
0.93
2.07
1.02
1.05
1.00
0.74
3.04
2.02
2.76
0.22
3.00
10.5
10.0
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
-0
f1 (ppm)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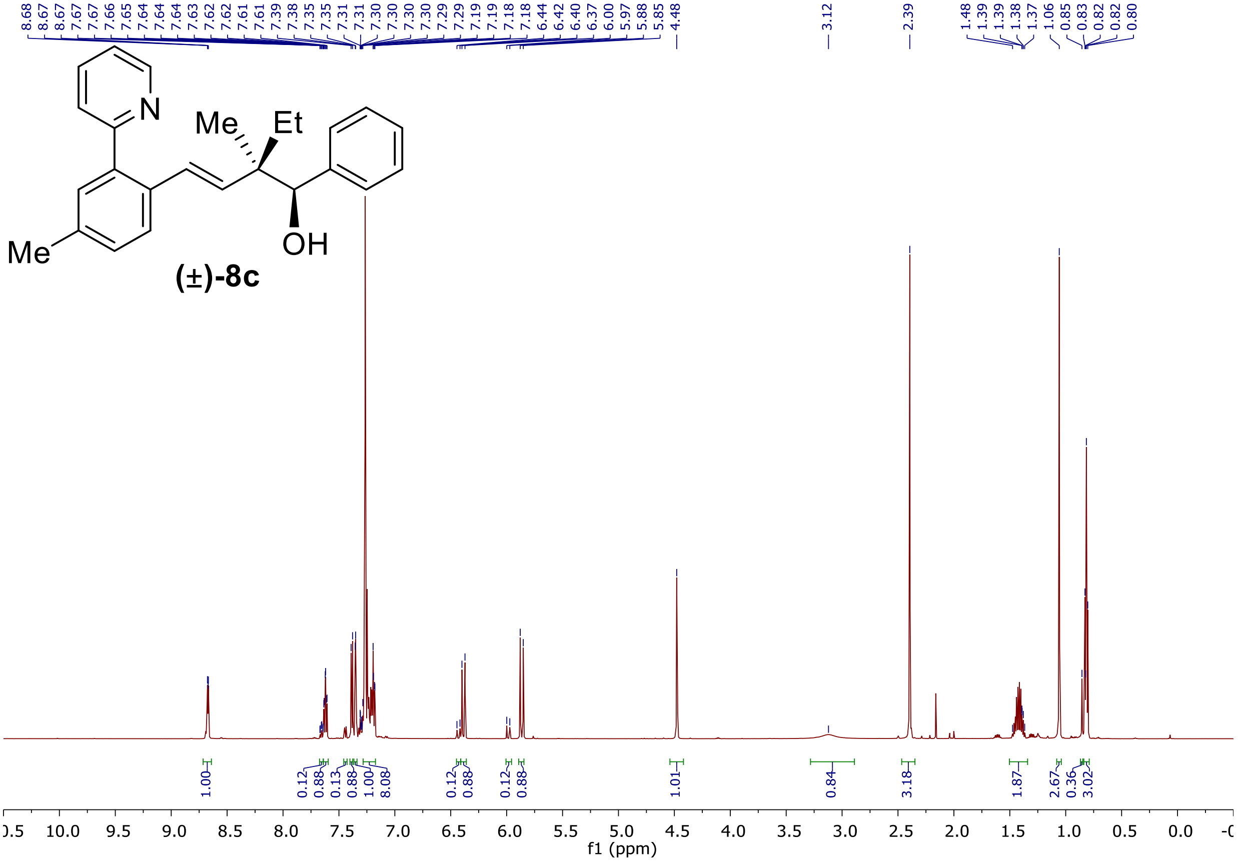
128.5
128.5
127.8
127.8
126.8
125.1
121.9
76.2
73.5
71.9
43.2
30.7
21.2
17.9
8.4
N
Me
Et
OBn
OH
Me
(±)-8b
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.63
7.62
7.62
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6.40
6.37
6.00
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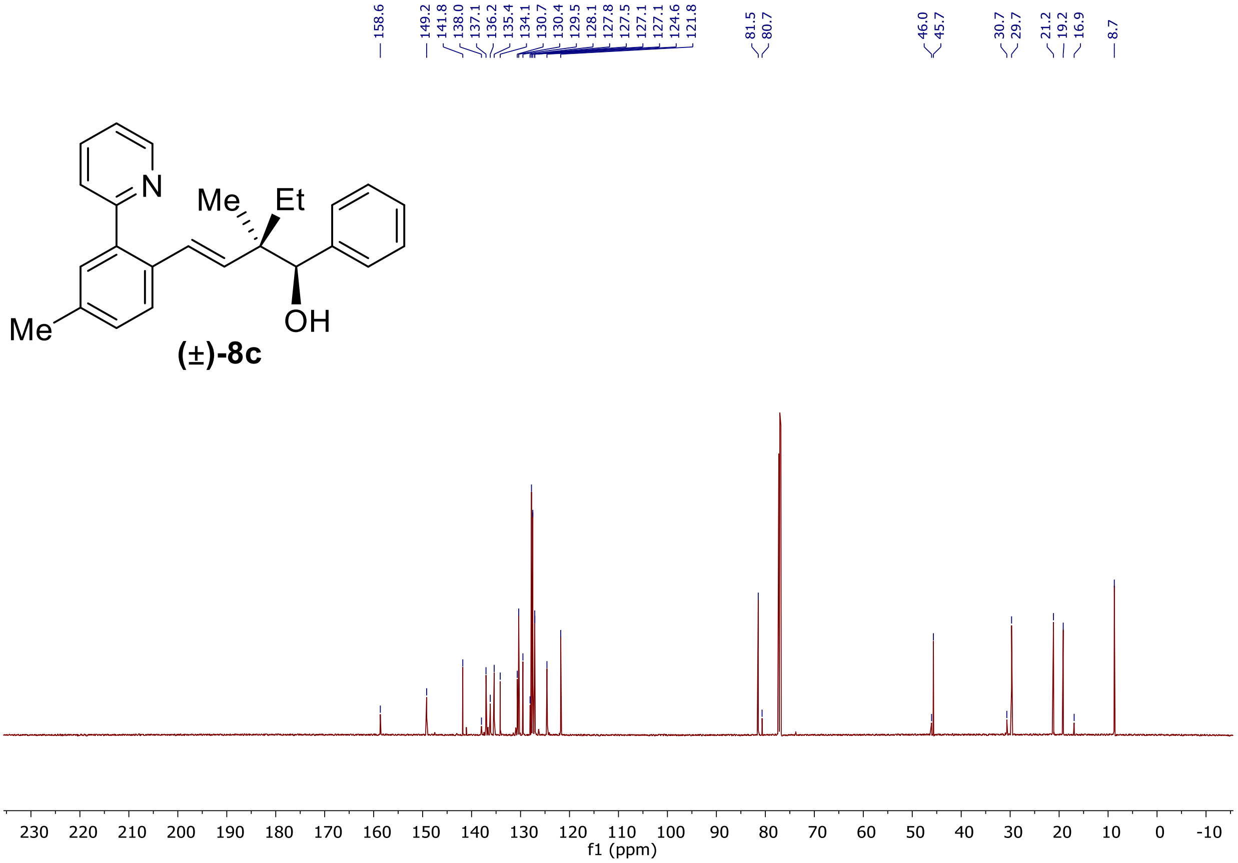
3.12
2.39
1.48
1.39
1.39
1.38
1.37
1.06
0.85
0.83
0.82
0.82
0.80
N
Me
Et
Me
OH
(±)-8c
1.00
0.12
0.88
0.13
0.88
1.00
8.08
0.12
0.88
0.12
0.88
1.01
0.84
3.18
1.87
2.67
0.36
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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136.2
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134.1
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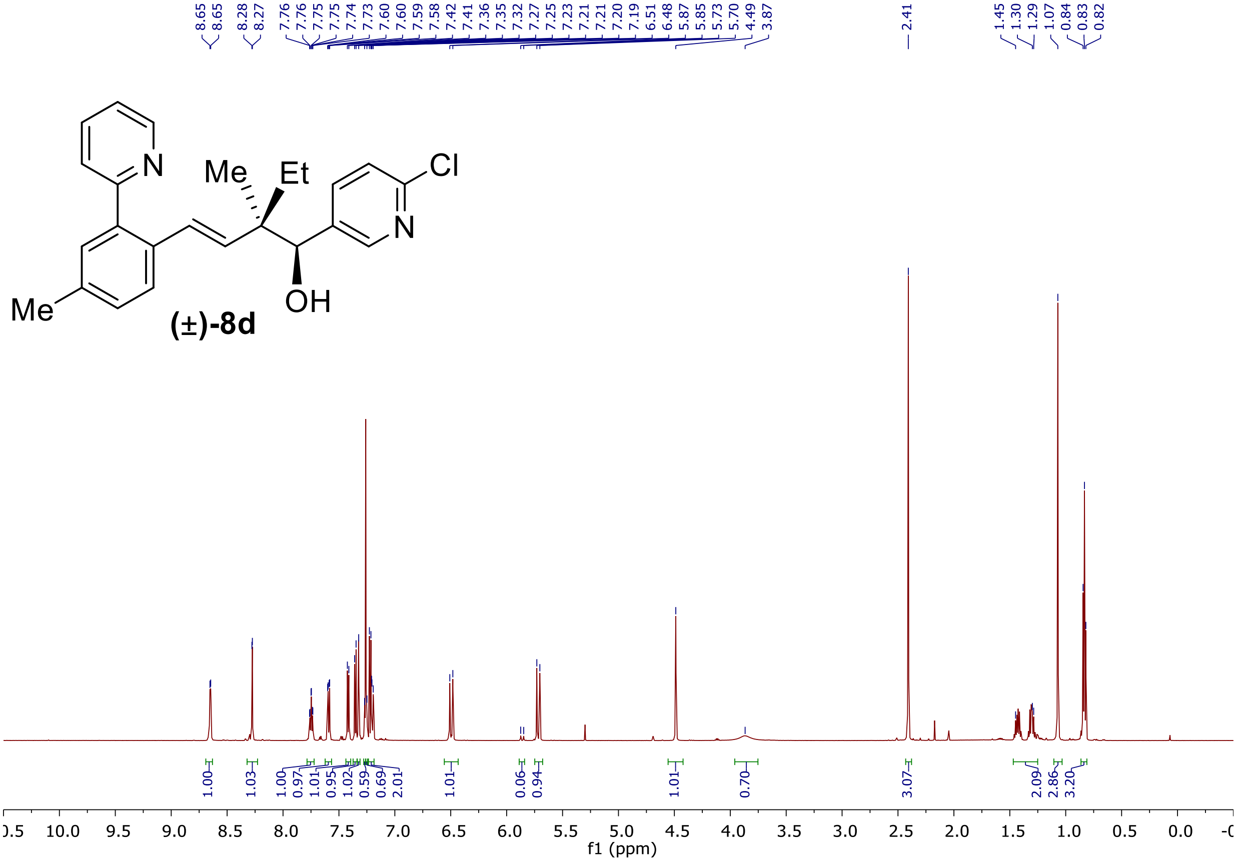
130.4
129.5
128.1
127.8
127.5
127.1
127.1
124.6
121.8
81.5
80.7
46.0
45.7
30.7
29.7
21.2
19.2
16.9
8.7
N
Me
Et
Me
OH
(±)-8c
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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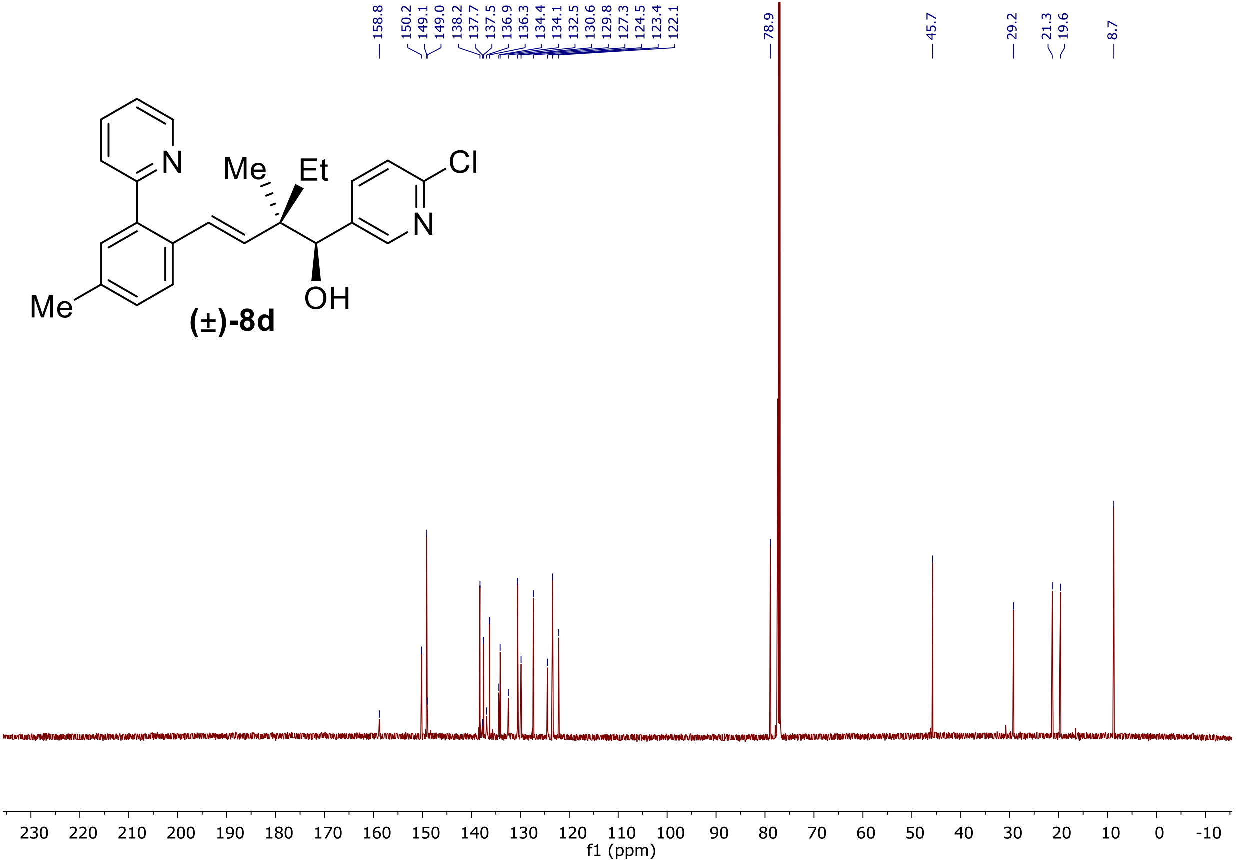
7.75
7.74
7.73
7.60
7.59
7.58
7.42
7.41
7.36
7.35
7.32
7.27
7.25
7.23
7.21
7.21
7.20
7.19
6.51
6.48
5.87
5.85
5.73
5.70
4.49
3.87
2.41
1.45
1.30
1.29
1.07
0.84
0.83
0.82
N
Me
Et
Cl
N
Me
OH
(±)-8d
1.00
1.03
1.00
0.97
1.01
0.95
1.02
0.59
0.69
2.01
1.01
0.06
0.94
1.01
0.70
3.07
2.09
2.86
3.20
10.5 10.0 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
f1 (ppm)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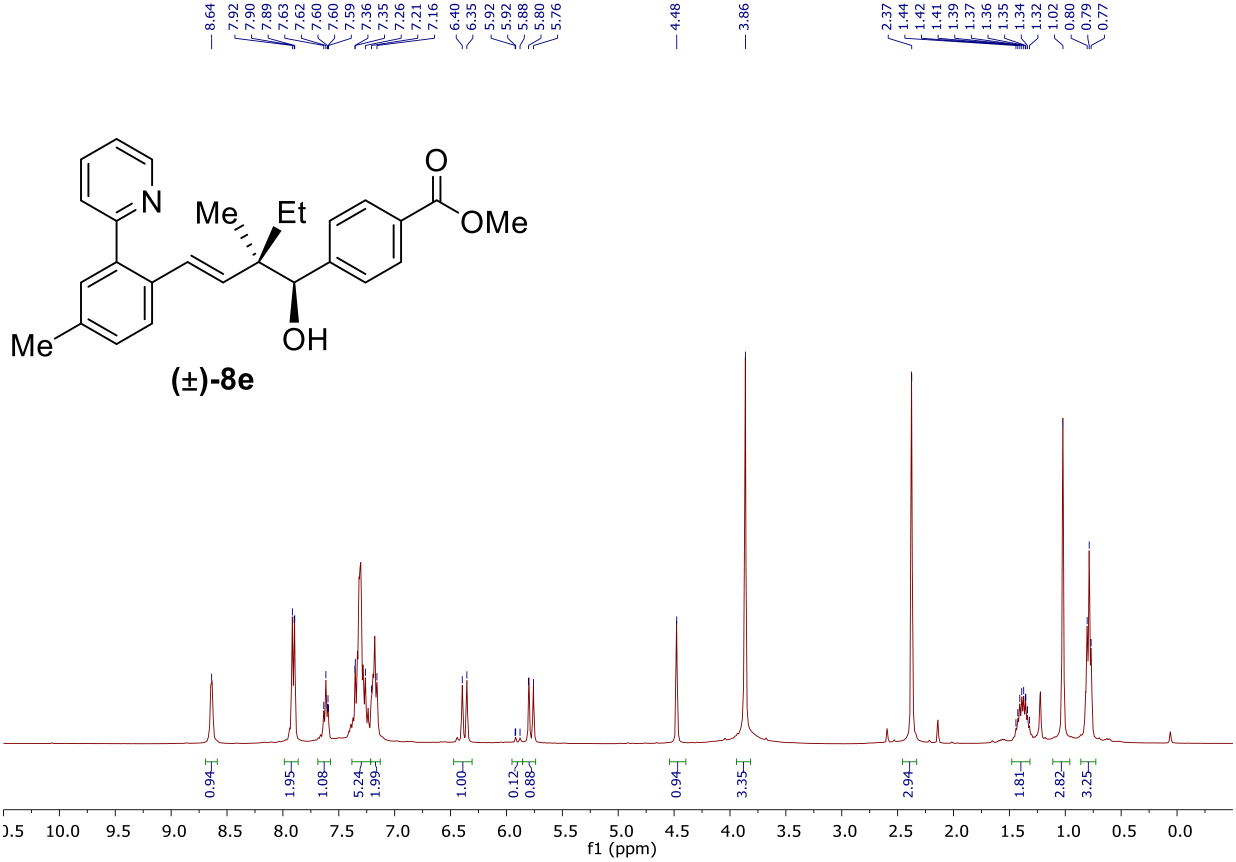
138.2
137.7
137.5
136.9
136.3
134.4
134.1
132.5
130.6
129.8
127.3
124.5
123.4
122.1
78.9
45.7
29.2
21.3
19.6
8.7
N
Me
Et
Cl
N
Me
OH
(±)-8d
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.60
7.59
7.36
7.35
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7.21
7.16
6.40
6.35
5.92
5.92
5.88
5.80
5.76
4.48
3.86
2.37
1.44
1.42
1.41
1.39
1.37
1.36
1.35
1.34
1.32
1.02
0.80
0.79
0.77
N
Me
Et
O
OMe
OH
Me
(±)-8e
0.94
1.95
1.08
5.24
1.99
1.00
0.12
0.88
0.94
3.35
2.94
1.81
2.82
3.25
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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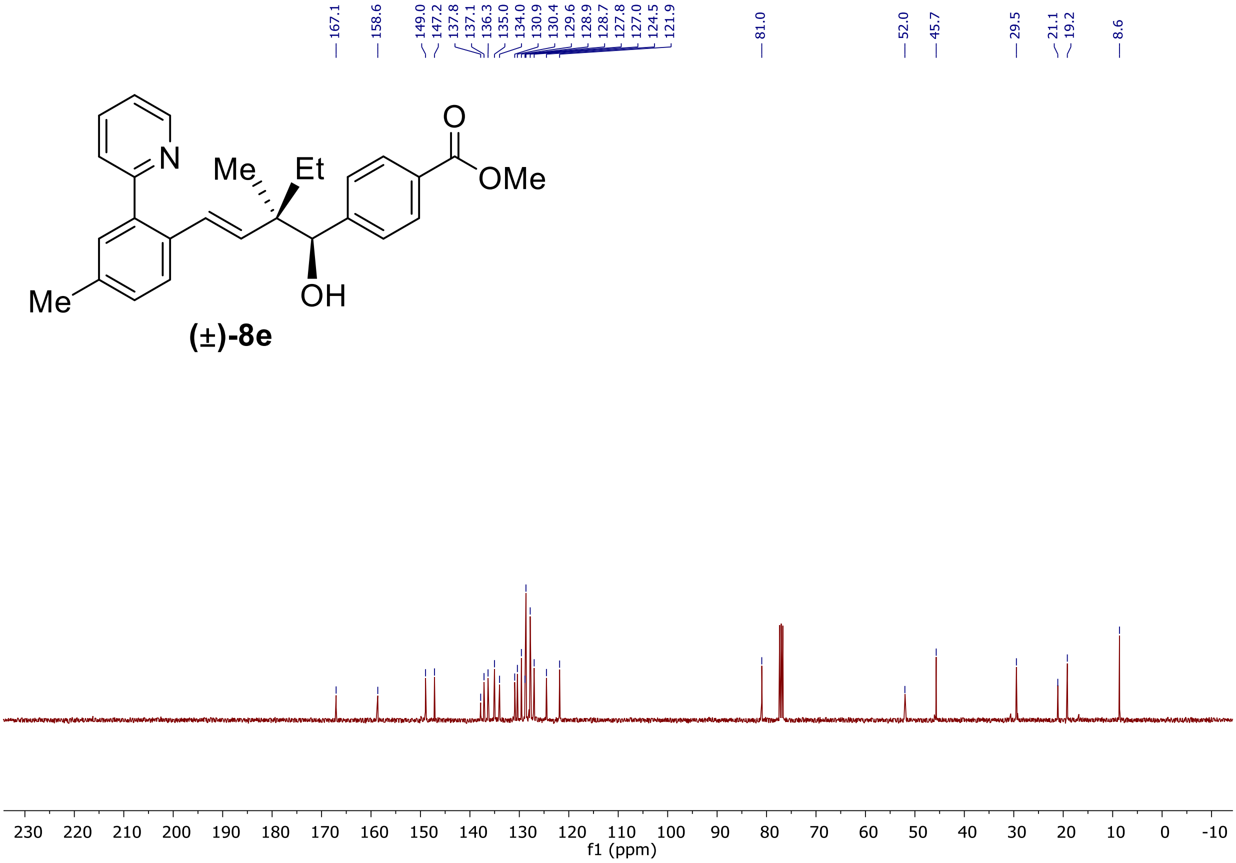
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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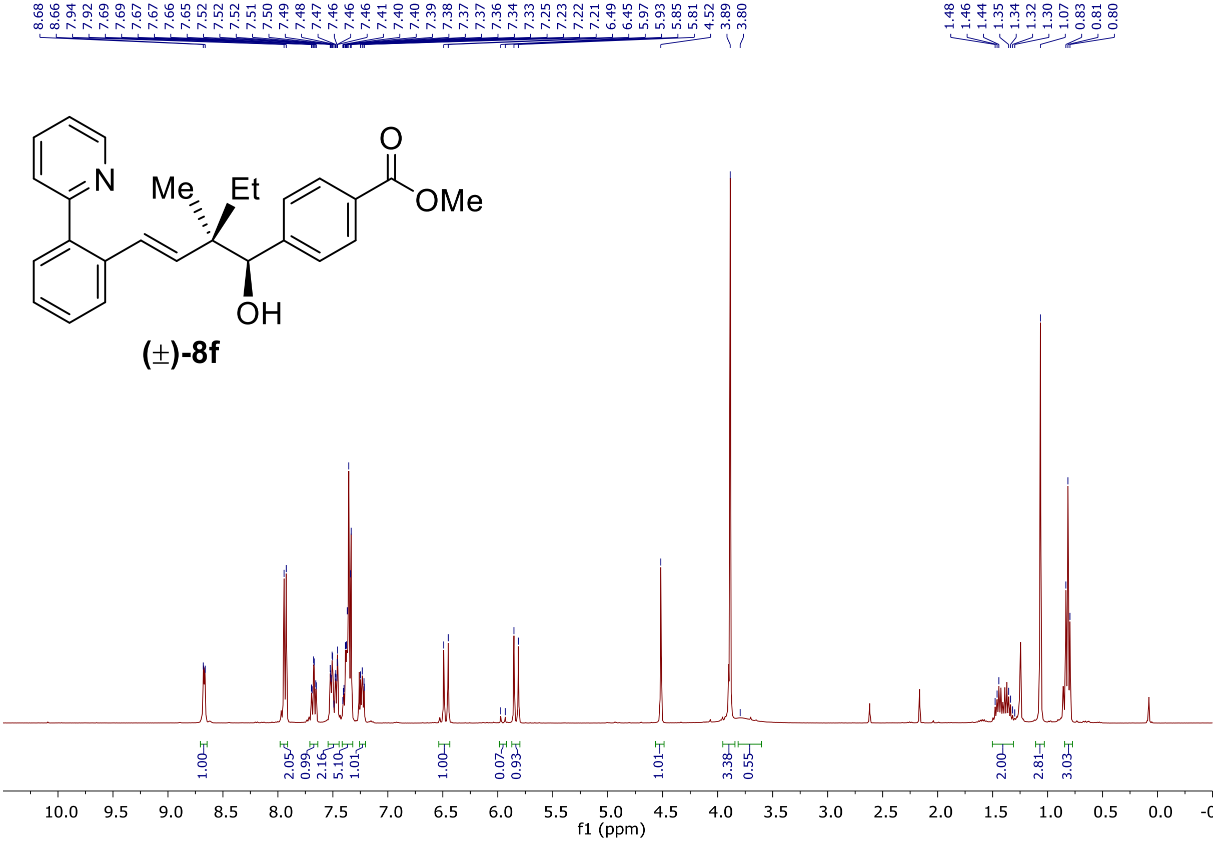
134.0
130.9
130.4
129.6
128.9
128.7
127.8
127.0
124.5
121.9
81.0
52.0
45.7
29.5
21.1
19.2
8.6
N
Me
Et
O
OMe
OH
Me
(±)-8e
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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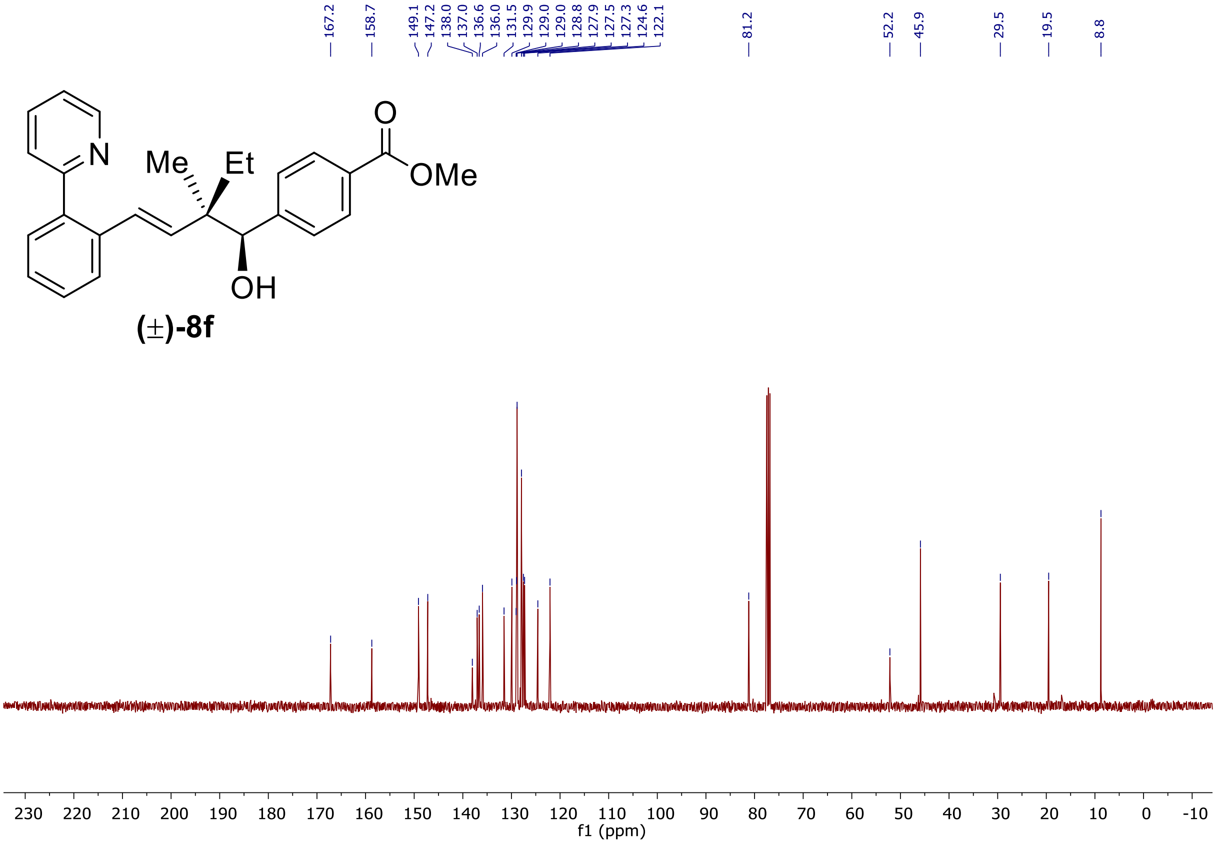
7.52
7.51
7.50
7.49
7.48
7.47
7.46
7.46
7.46
7.41
7.40
7.40
7.39
7.38
7.37
7.37
7.36
7.34
7.33
7.25
7.23
7.22
7.21
6.49
6.45
5.97
5.93
5.85
5.81
4.52
3.89
3.80
1.48
1.46
1.44
1.35
1.34
1.32
1.30
1.07
0.83
0.81
0.80
N
Me
Et
O
OMe
OH
(±)-8f
1.00
2.05
0.99
2.16
5.10
1.01
1.00
0.07
0.93
1.01
3.38
0.55
2.00
2.81
3.03
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
f1 (ppm)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129.0
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127.9
127.5
127.3
124.6
122.1
81.2
52.2
45.9
29.5
19.5
8.8
N
Me
Et
O
OMe
OH
(±)-8f
230
220
210
200
190
180
170
160
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140
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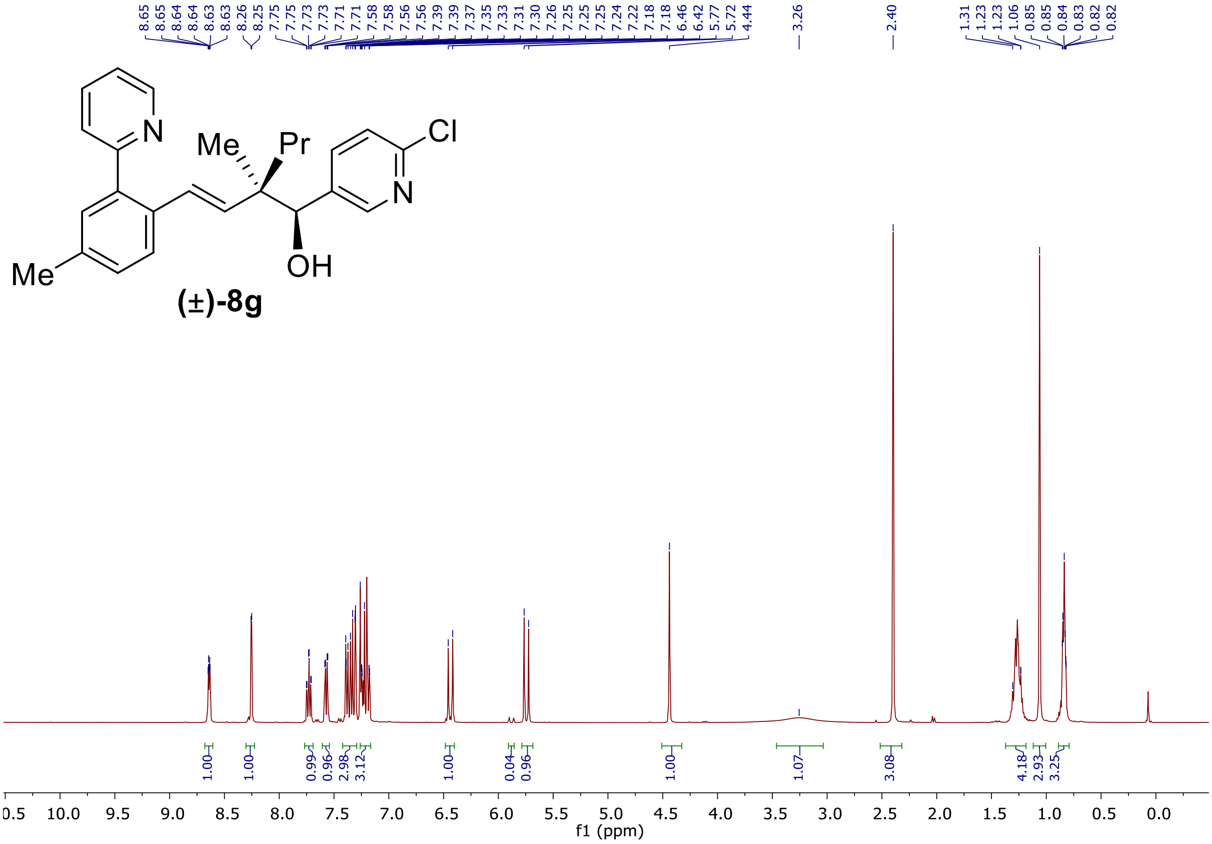
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.58
7.56
7.56
7.39
7.39
7.37
7.35
7.33
7.31
7.30
7.26
7.25
7.25
7.25
7.24
7.22
7.18
7.18
6.46
6.42
5.77
5.72
4.44
3.26
2.40
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1.23
1.23
1.06
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0.85
0.84
0.83
0.82
0.82
N
Me
Pr
Cl
N
Me
OH
(±)-8g
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1.00
0.99
0.96
2.98
3.12
1.00
0.04
0.96
1.00
1.07
3.08
4.18
2.93
3.25
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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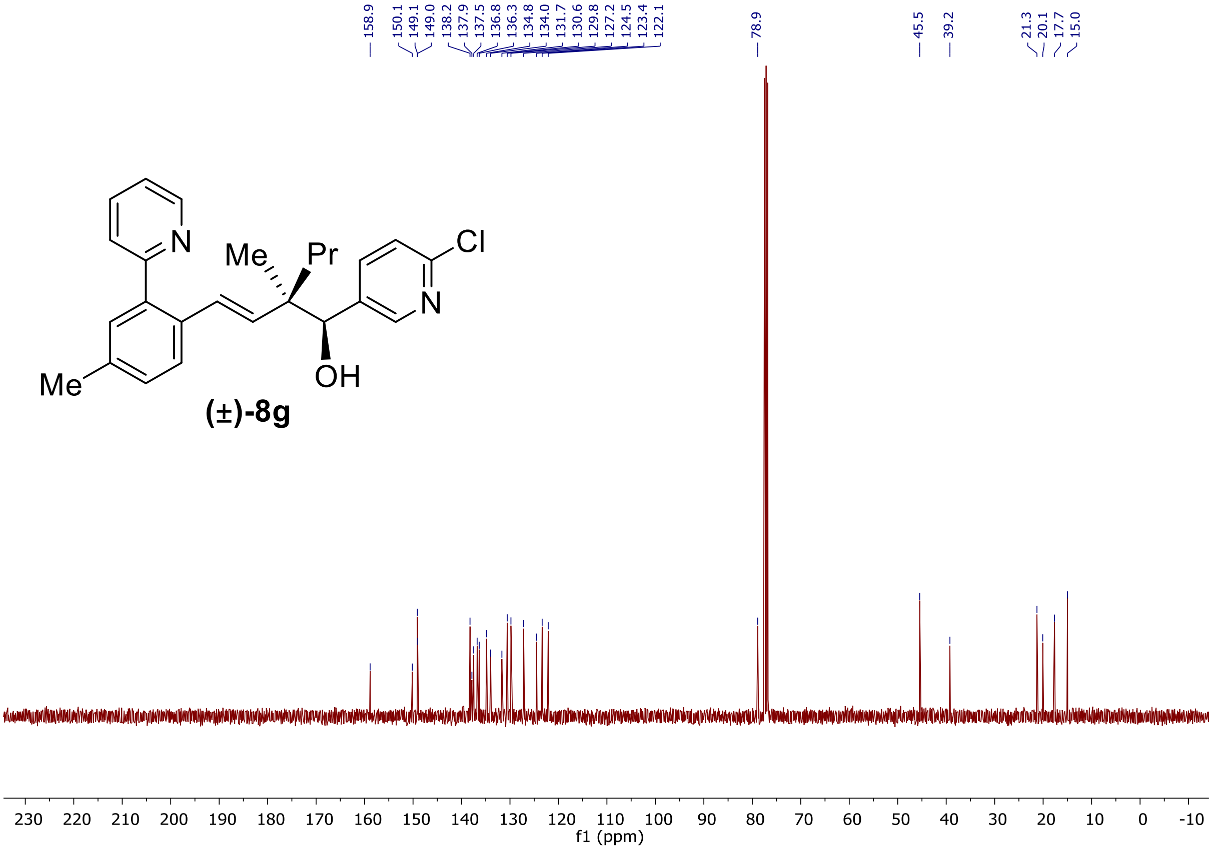
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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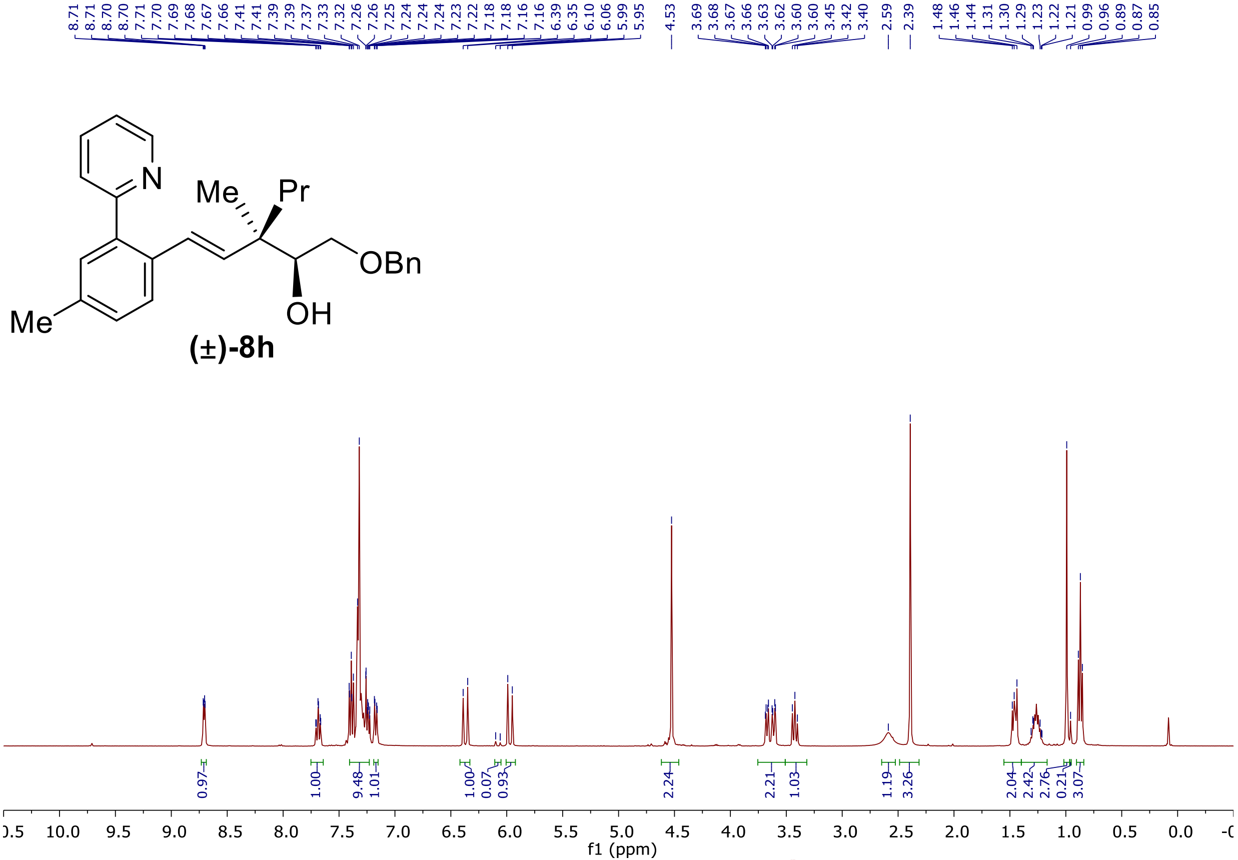
130.6
129.8
127.2
124.5
123.4
122.1
78.9
45.5
39.2
21.3
20.1
17.7
15.0
N
Me
Pr
Cl
N
Me
OH
(±)-8g
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.39
7.37
7.33
7.32
7.26
7.26
7.25
7.24
7.24
7.24
7.23
7.22
7.18
7.18
7.16
7.16
6.39
6.35
6.10
6.06
5.99
5.95
4.53
3.69
3.68
3.67
3.66
3.63
3.62
3.60
3.60
3.45
3.42
3.40
2.59
2.39
1.48
1.46
1.44
1.31
1.30
1.29
1.23
1.22
1.21
0.99
0.96
0.89
0.87
0.85
N
Me
Pr
OBn
OH
Me
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1.01
1.00
0.07
0.93
2.24
2.21
1.03
1.19
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2.04
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8.5
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7.0
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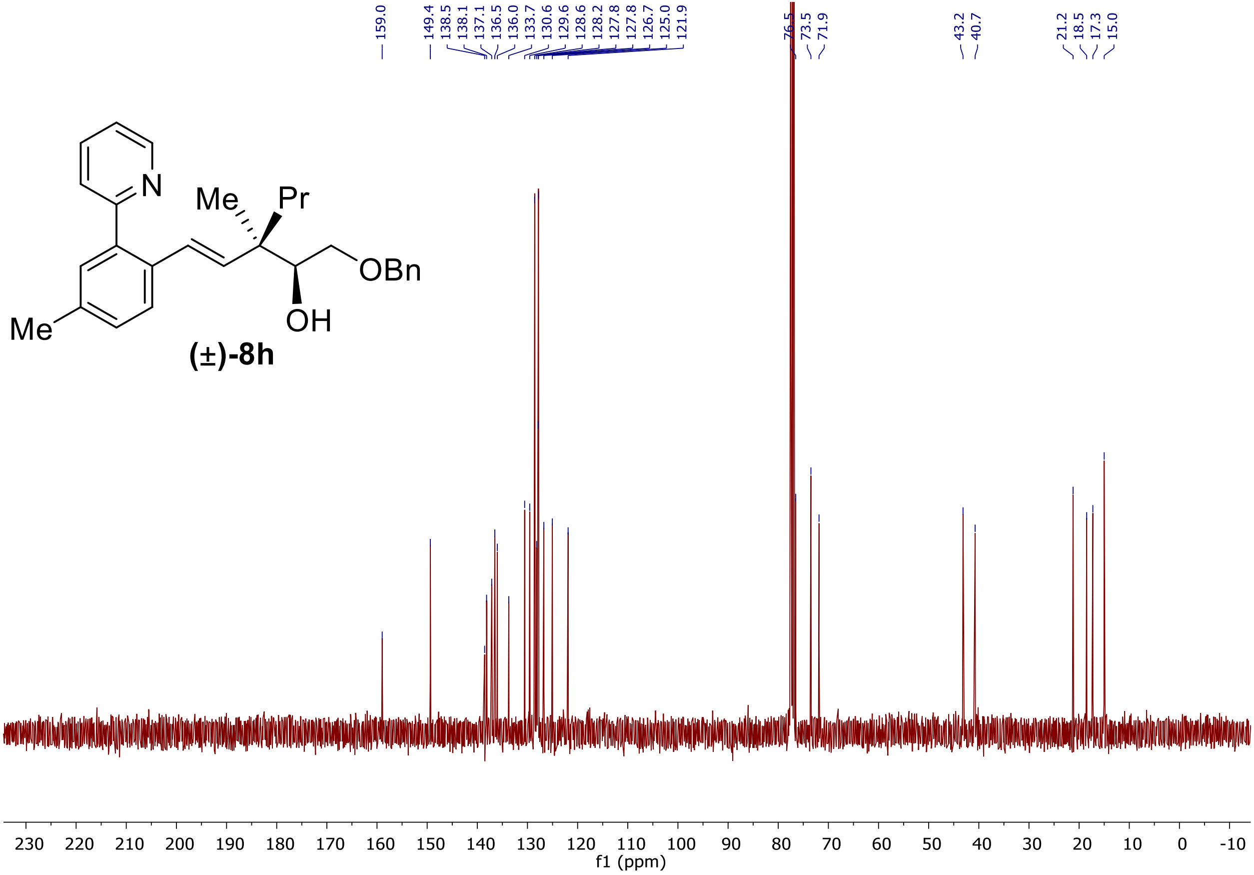
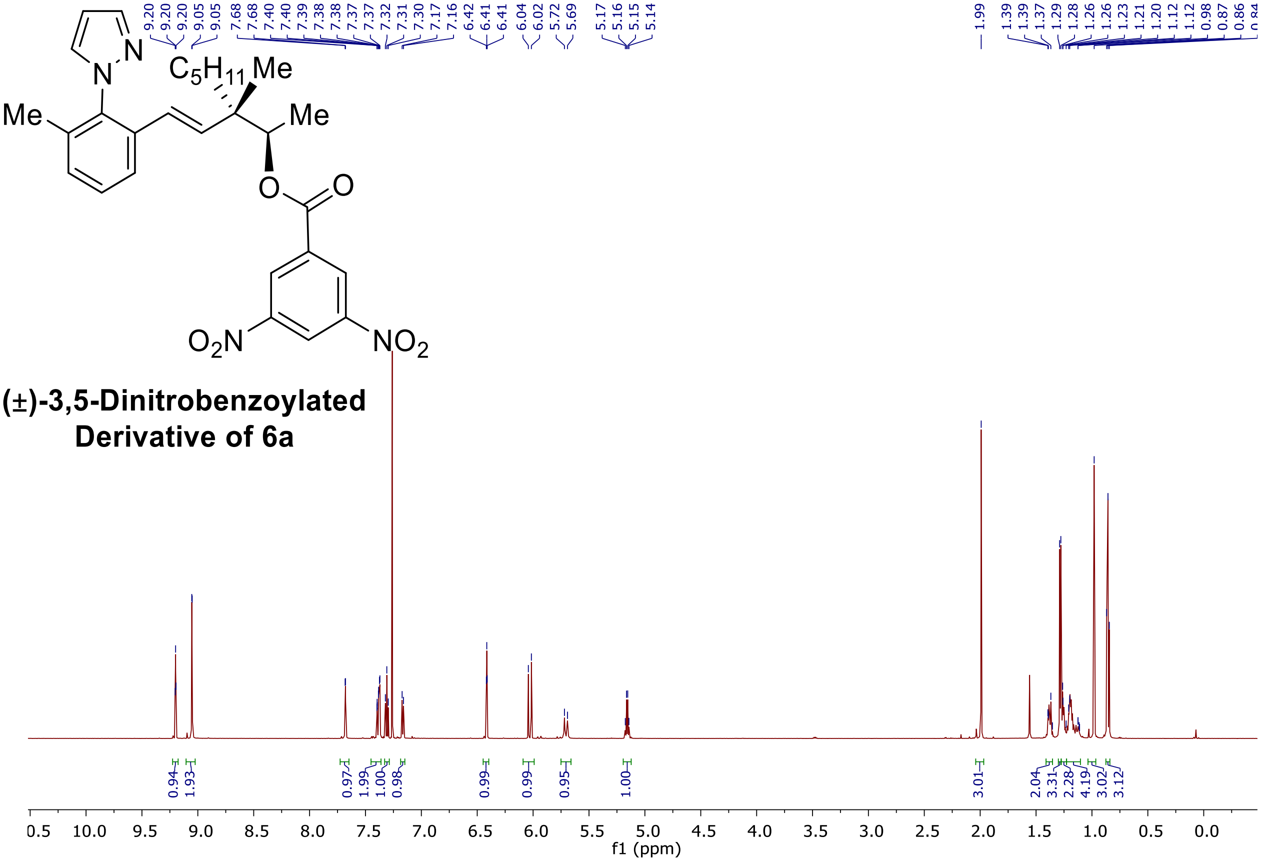
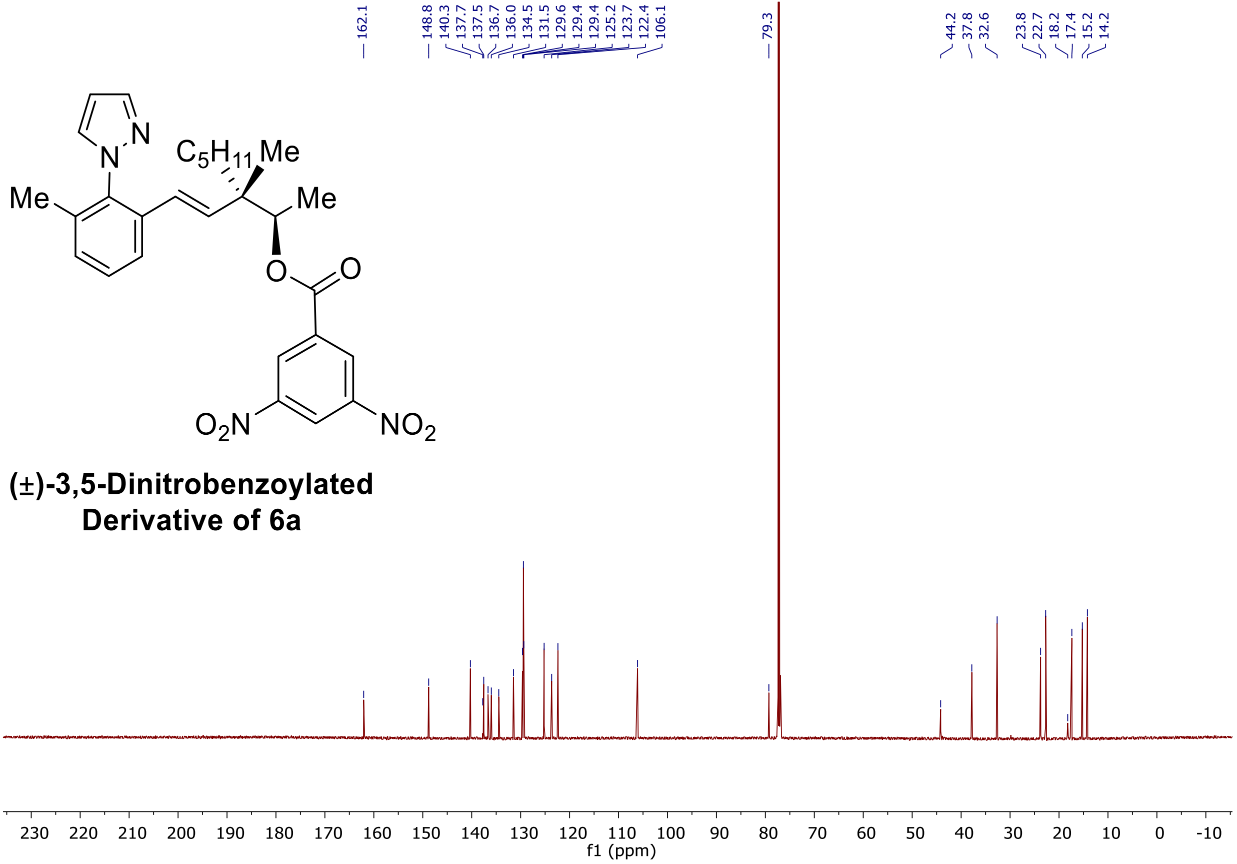
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

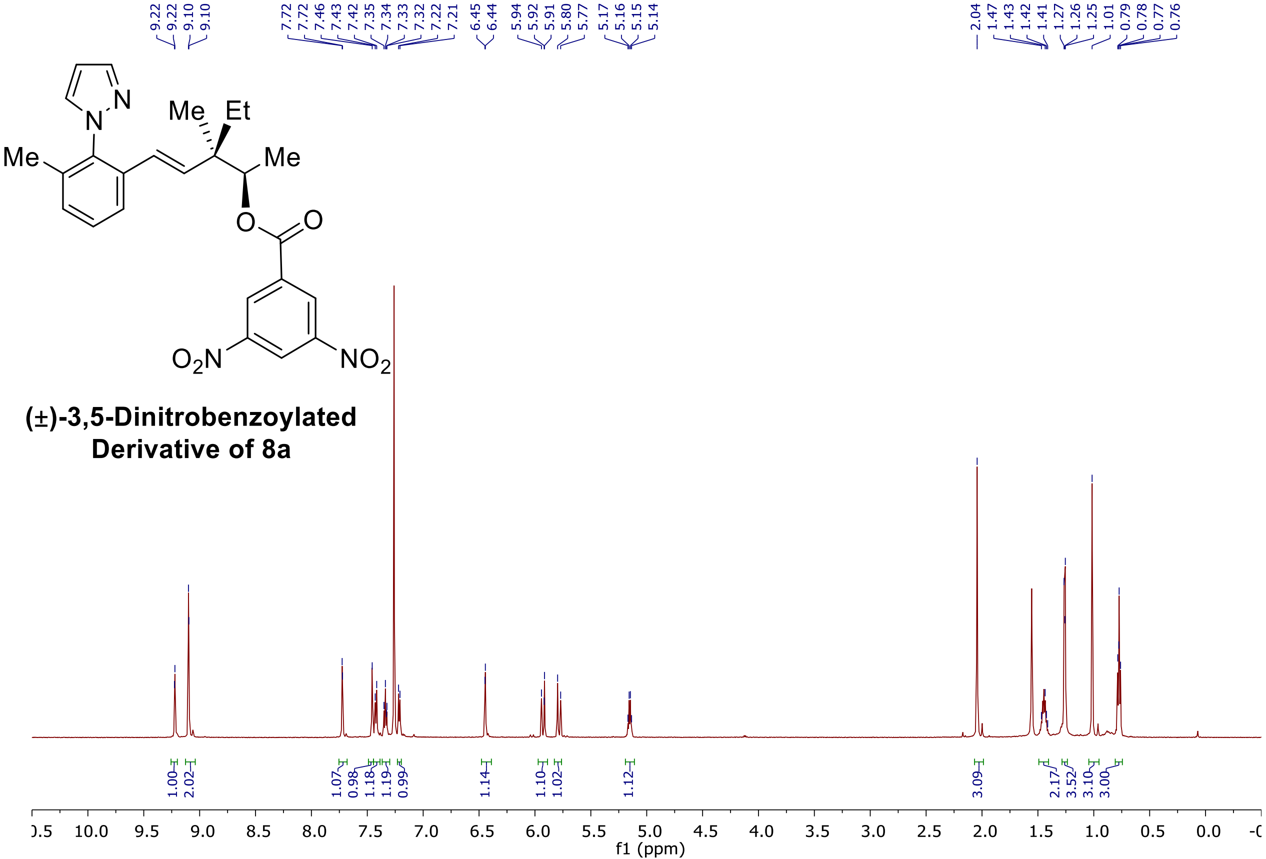
(±)-8h


159.0
149.4
138.5
138.1
137.1
136.5
136.0
133.7
130.6
129.6
128.6
128.2
127.8
127.8
126.7
125.0
121.9
76.5
73.5
71.9
43.2
40.7
21.2
18.5
17.3
15.0
N
Me
Pr
OBn
OH
Me
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

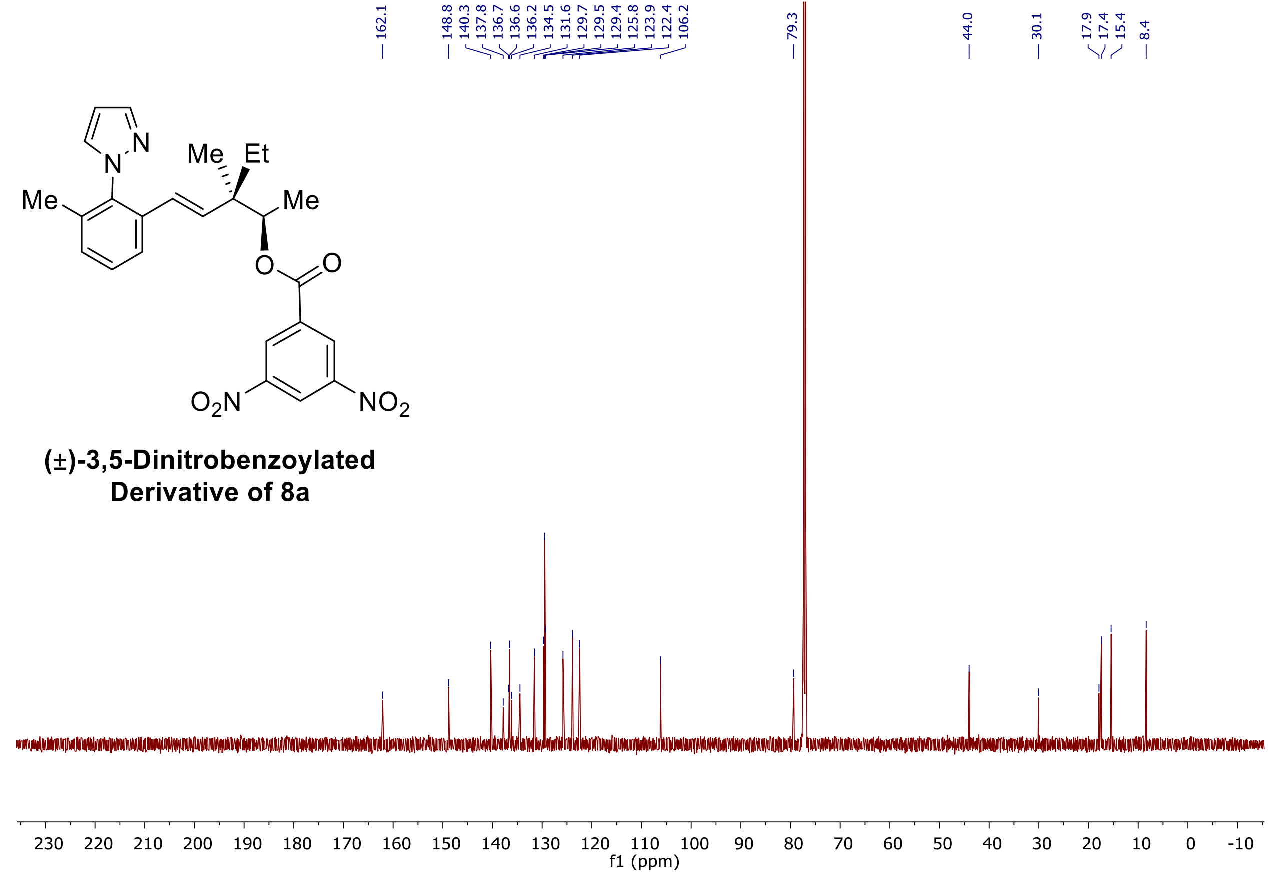
(±)-8h


9.20
9.20
9.20
9.05
9.05
7.68
7.68
7.40
7.40
7.39
7.38
7.38
7.37
7.37
7.32
7.31
7.30
7.17
7.16
6.42
6.41
6.41
6.04
6.02
5.72
5.69
5.17
5.16
5.15
5.14
1.99
1.39
1.39
1.37
1.29
1.28
1.26
1.26
1.23
1.21
1.20
1.12
1.12
0.98
0.87
0.86
0.84
N
N
Me
C_5H_{11}
Me
Me
O
O
O_2N
NO_2
(±)-3,5-Dinitrobenzoylated Derivative of 6a
0.94
1.93
0.97
1.99
1.00
0.98
0.99
0.99
0.95
1.00
3.01
2.04
3.31
2.28
4.19
3.02
3.12
0.5
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
f1 (ppm)


162.1
148.8
140.3
137.7
137.5
136.7
136.0
134.5
131.5
129.6
129.4
129.4
125.2
123.7
122.4
106.1
79.3
44.2
37.8
32.6
23.8
22.7
18.2
17.4
15.2
14.2
N
N
Me
C_5H_{11}
Me
Me
O
O
O_2N
NO_2
(±)-3,5-Dinitrobenzoylated Derivative of 6a
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



(±)-3,5-Dinitrobenzoylated Derivative of 8a



(±)-3,5-Dinitrobenzoylated Derivative of 8a