Supporting Information

Direct Aminoalkylation of Allylic C(sp^3)-H Bonds via Synergistic Organo and Photoredox Catalysis

Jiaqi Jia, Rajesh Kancherla, Magnus Rueping,* Long Huang*

RWTH Aachen University, Institute of Organic Chemistry, Landoltweg 1, D-52074 Aachen, Germany
King Abdullah University of Science and Technology (KAUST), KAUST Catalysis Center (KCC), Thuwal, 23955-6900 (Saudi Arabia)

Magnus.Rueping@kaust.edu.sa
long.huang@rwth-aachen.de

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General Methods. Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents for chromatography were technical grade and distilled prior to use. Analytical thin-layer chromatography (TLC) was performed on Macherey-Nagel silica gel 60 aluminium plates with F-254 indicator, visualized by UV irradiation. Column chromatography was performed using MN silica gel (particle size 0.040-0.063 mm). ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a vnmrs-400 or vnmrs-600 spectrometer in $CDCl_3$ with residual proton signal of the deuterated solvents as the internal reference (δH = 7.26 ppm and δC = 77.16 ppm for $CDCl_3$). Data are reported in the following order: chemical shift (δ) in ppm; multiplicities of ^{1}H NMR are indicated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), tt (triplet of triplet), dt (doublet of triplet), td (triplet of doublet); coupling constants (*J*) are in Hertz (Hz). All ^{13}C NMR spectra were measured with ^{1}H decoupling. The multiplicities of ^{13}C NMR spectra mentioned [s (singlet, quarternary carbon), d (doublet, CH-group), t (triplet, CH_2-group), q (quartet, CH_3 group)] were determined by APT spectra. IR spectra were recorded on a Jasco FT/IR-420 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Mass spectra were acquired on a Finnigan SSQ7000 (EI/CI) spectrometer and high resolution mass spectra on a Finnigan MAT 95 (EI/CI) or on a ThermoFisher Scientific LTQOrbitrap XL (ESI). Melting points were recorded on a Büchi 560 Melting Point Apparatus. (*E*)-2-methyloct-3-en-2-ol was prepared according to a literature report.[1] The Blue LED strips 24 V (19.2 W/m, with emission maximum at λ_{max} = 450 nm) were purchased from Ledxon GmbH (Germany).

General procedure for synthesis of imines 1.

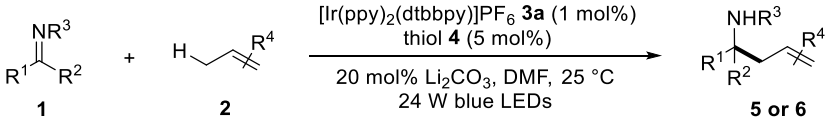
Synthesis of *N*-aryl aldimines **1a**-**o**: A flame-dried round-bottom flask was charged with the corresponding aldehyde (20 mmol, 1.0 equiv.), aniline (21 mmol, 1.05 equiv.), and 4Å molecular sieves (2.0 g) in CH_2Cl_2 (20 ml). The reaction mixture was stirred at room temperature overnight. After filtration over Celite, the solvent was evaporated under reduced pressure and the product was purified by crystallization from a mixture of Et_2O/Pentane, or by distilling off the excess of aniline *via* Kugelrohr distillation.

Synthesis of *N*-alkyl aldimines **1p**: A flame-dried round-bottom flask was charged with biphenyl-4-carboxaldehyde (2.0 mmol) and *tert*-butylamine (10.0 mmol) in dry dichloromethane (5.0 mL). The mixture was stirred for 2-3 days at room temperature until the NMR analysis showed a complete conversion of the starting material.[2]

Synthesis of *N*-aryl ketimines **1q**-**t**: A flame-dried flask purged with argon was charged with the carbonyl compound (25.0 mmol), 4Å MS (10 g), and 4-methoxyaniline (30.0 mmol) in toluene (15 ml). The mixture was stirred overnight. Then, the reaction mixture was filtered over Celite and concentrated in vacuo. The crude product was purified by recrystallization. The ^{1}H NMR spectrum of all compounds showed good agreement with the literature data.[3]

Synthesis of *N*-aryl ketimines **1u**: A mixture of benzophenone (1.0 equiv.), Et_3N (3.0 equiv.), and 4-methoxyaniline (3.0 equiv.) in CH_2Cl_2 was cooled to 0 °C under N_2, and $TiCl_4$ (1.0 equiv., 1.0 M solution in CH_2Cl_2) was added dropwise. The reaction mixture was then heated to reflux overnight. Then, the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The combined organics were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The products were purified by chromatography.

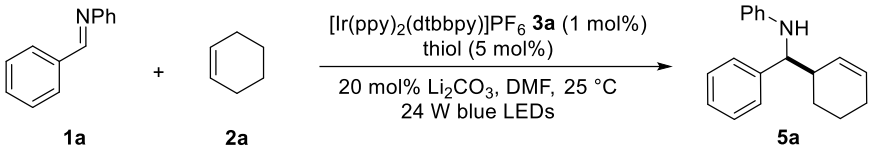
General procedure for the synthesis of homoallylic amines 5 and 6.

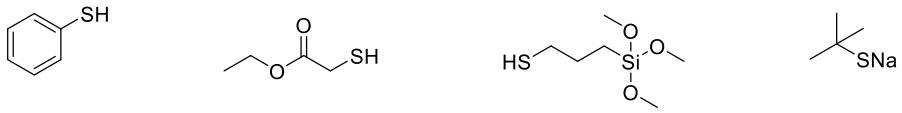


A Pyrex tube was charged with substrate **1** (0.3 mmol), catalyst **3a** (1 mol%) and Li_2CO_3 (20 mol%) under an Ar atmosphere. Then olefin substrate **2** (1.5 mmol) and triisopropylsilanethiol **4** (5 mol%) were added via microsyringe, followed by addition of DMF (1.5 mL). The resulting mixture was degassed using Freeze-Pump-Thaw methods for three cycles. The tube was subsequently placed into the 24 W Blue LEDs photoreactor (the reactor was cooled with air flow to keep the temperature around 25 °C). The reaction was stirred and irradiated for 24 h. The crude product was either purified by column chromatography on silica gel directly or diluted with ethyl acetate and washed successively with sat. $NaHCO_3$, brine, dried over $MgSO_4$, filtered and concentrated in *vacuo*, and purified by column chromatography (elution with hexane/ ethyl acetate = 200:1- 100:1).

Details about the light source: The Blue LED strips 24 V (19.2 W/m, with emission maximum at λ_{max} = 450 nm) were purchased from ledxon gmbh (Germany). Below is a picture of the photochemical setup employed in this project.

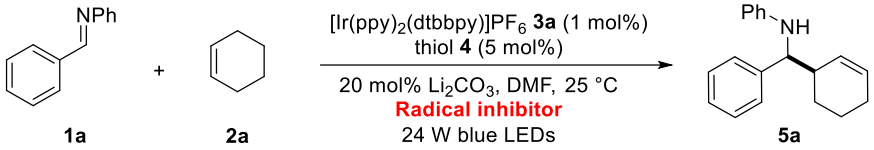
Screening of different thiol catalysts





nr 58% 12% nr

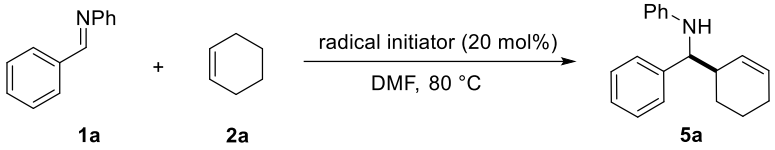
Radical inhibition experiment



Radical inhibitor	Yield of **5a**
none	81%
TEMPO (1 equiv.)	0
1,1-diphenylethylene (1 equiv.)	21%

The above results implied the involvement of radical intermediates in the photoredox process.

Reactions with radical initiators



Radical initiators	Yield of **5a**
AIBN	0
Benzoyl peroxide	0
tert-Butyl peroxide	0
BEt_3/air	0

Several experiments with radical initiators gave no products, indicating that those initiators cannot act as hydrogen atom transfer reagents.

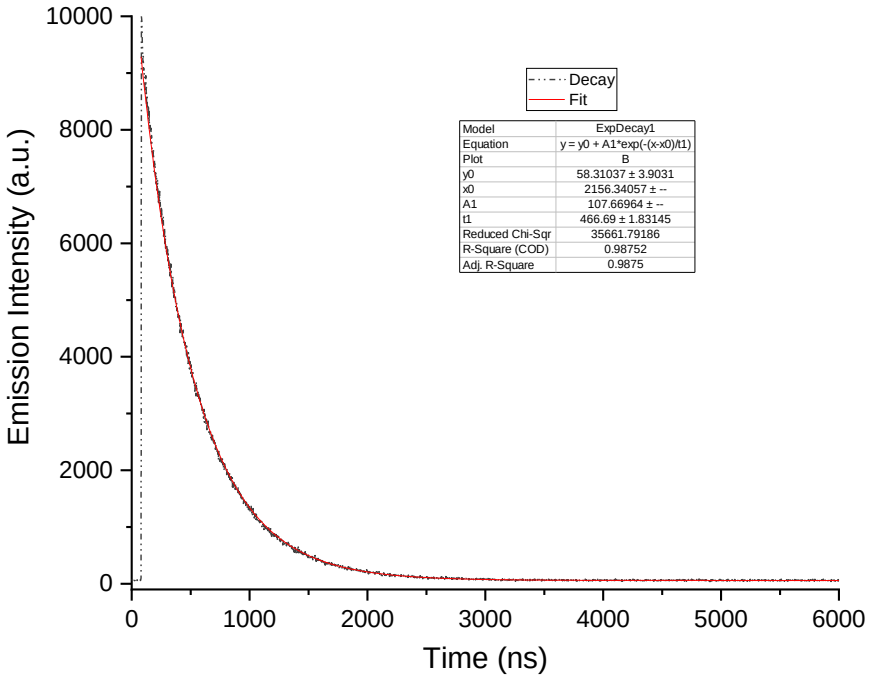


Figure S1. Life-time determination of the excited-state photocatalyst ***3a** (0.00001 M) in tetrahydrofuran solvent.

Steady-state Stern-Volmer quenching experiments:

Emission spectra were collected on fluoromax-4 spectrophotometer with excitation and emission slit widths of 5 nm. Quenching experiments were carried out using a $1x10^{-5}$ M solution of $[Ir(ppy)_2(dtbbpy)]PF_6$ **3a** in DMF and variable concentrations of quencher **4** (20, 60, 100, 200, 300, 400, 500, 600, 700, 800, 900 μM) in the presence of Li_2CO_3 (double the concentration of **4**) dispensed in DMF. Stock solution of thiol **4** and the base was prepared by stirring **4** (2.1 μL) and Li_2CO_3 (1.47 mg) in 10 mL of DMF overnight. The samples were prepared in 2 mL quartz cuvettes, equipped with PTFE stoppers, and sealed with parafilm inside nitrogen filled glove-box, removed from the glovebox and an emission spectrum was collected. Samples were excited at 400 nm and the intensity of emission was monitored at 573 nm expressed as the ratio I_0/I, where I_0 is the emission intensity of **3a** at 573 nm in the absence of a quencher and I is the observed intensity, as a function of the quencher concentration was measured (Figure S2 and S6).

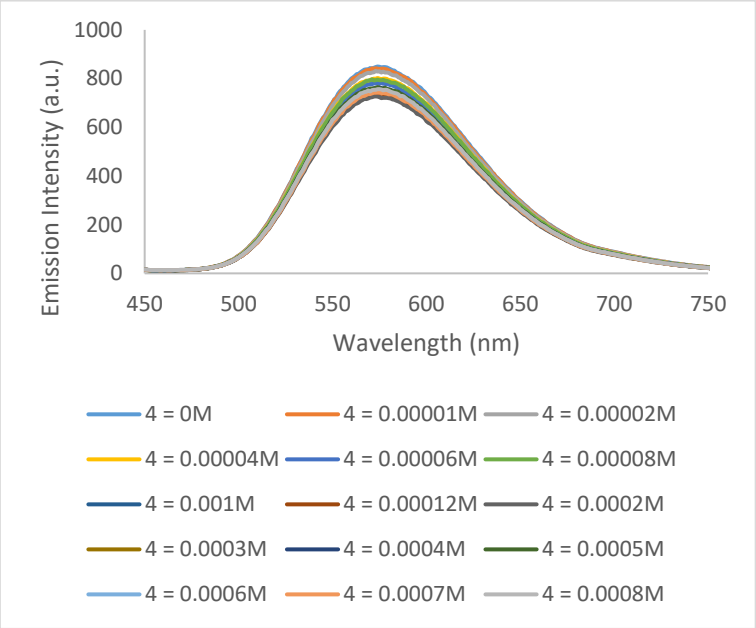


Figure S2. Fluorescence quenching experiment with **4**.

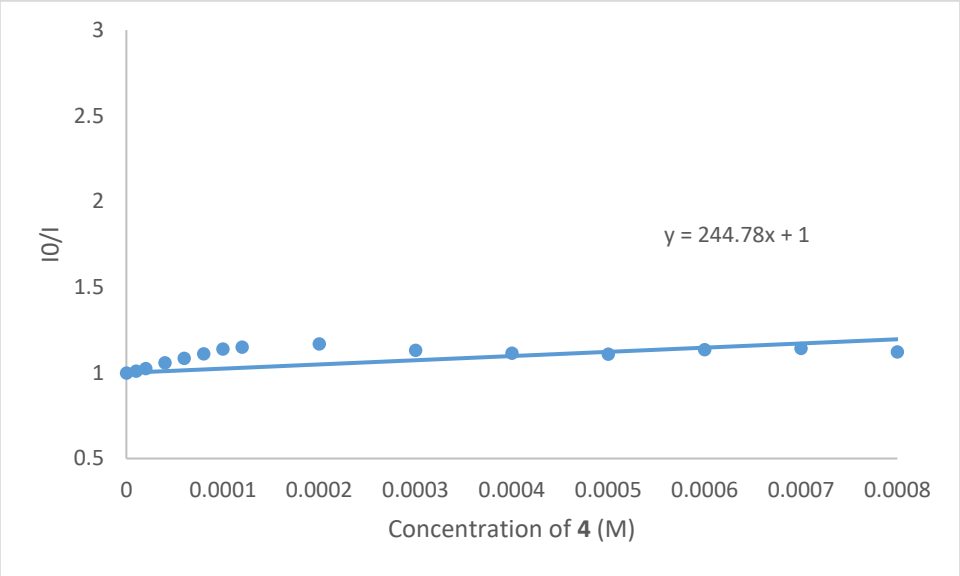


Figure S3. Steady-state Stern-Volmer quenching experiment with **4**.

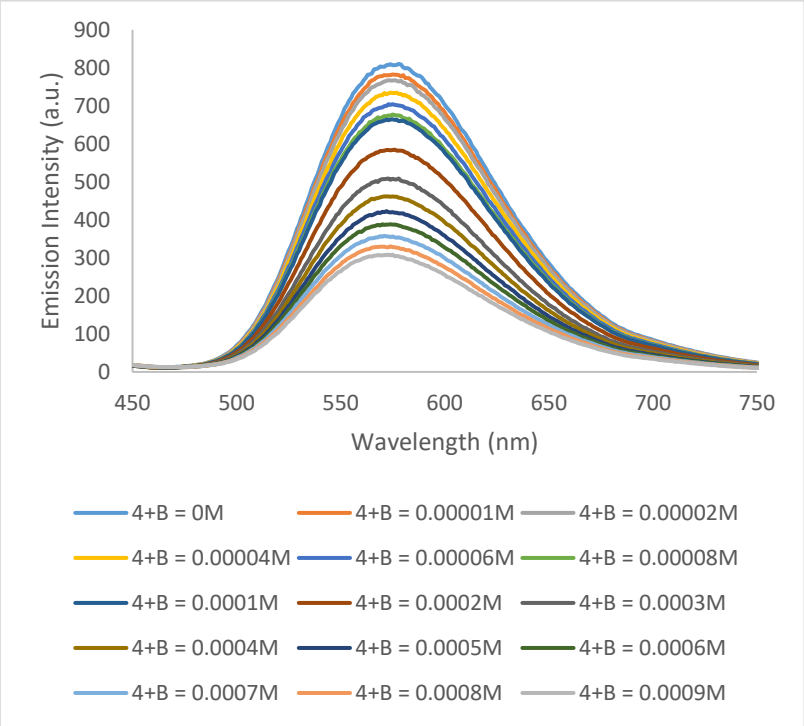


Figure S4. Fluorescence quenching experiment with the mixture of **4** and **base**.

Photoluminescence lifetime (Time resolved Stern-Volmer quenching) experiments:

Time resolved Stern-Volmer quenching experiments were carried out using $1x10^{-5}$ M solution of $[Ir(ppy)_2(dtbbpy)]PF_6$ **3a** in DMF and variable concentrations of quencher **4** (20, 60, 100, 200, 300, 400, 500, 600, 700, 800, 900 μM) in the presence of Li_2CO_3 (double the concentration of **4**) dispensed in DMF. The samples were prepared in 2 mL quartz cuvettes, equipped with screw cap PTFE stoppers, and sealed with parafilm inside the argon filled glove-box. The intensity of the emission peak at 573 nm expressed as the ratio k_{obs}/k_0, where k_0 is the decay of **3a** at 573 nm in the absence of a quencher and k_{obs} is the observed decay as a function of the quencher concentration was measured. An Ar-saturated $1x10^{-5}$ M solution in DMF were used for the determination of photoluminescence lifetimes of **3a**. Photoluminescence decay traces were acquired based on time-correlated single-photon-counting (TCSPC) technique using a fluoromax-4 spectrophotometer from Horiba Scientific. A Nano LED-370 nm pulsed diode laser light source was used as the excitation source. The photoluminescence signals were obtained using an automated motorized monochromator. Time resolved emission data were fit to a single exponential decay to extract the observed rate constant (k_{obs}). Phosphorescence emission spectra and Stern-Volmer plots for each component are given in figure S5 and S6).

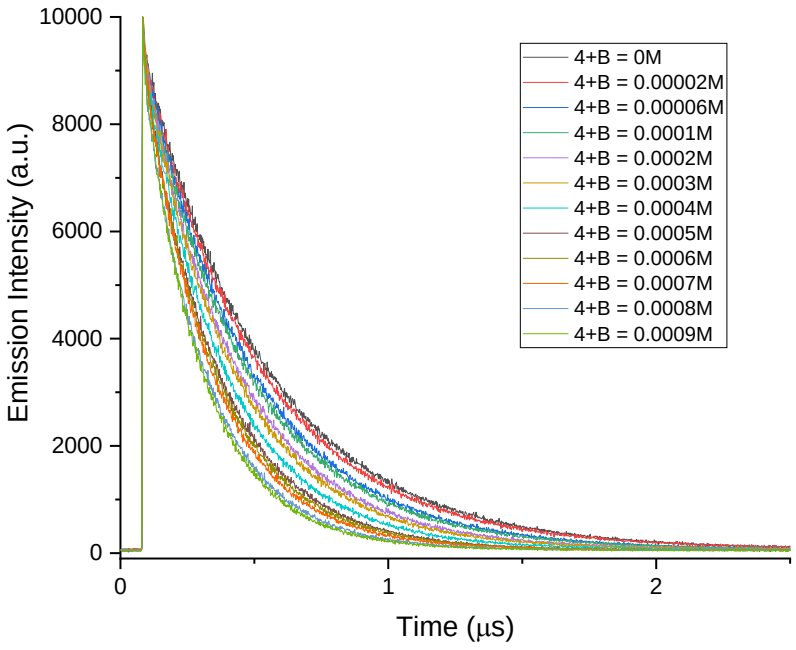


Figure S5. Phosphorescence lifetimes of excited-state photocatalyst ***3a** (0.00001 M) at different concentrations of quencher mixture of **4** and **base**. Spectroscopic experiments were performed one single time.

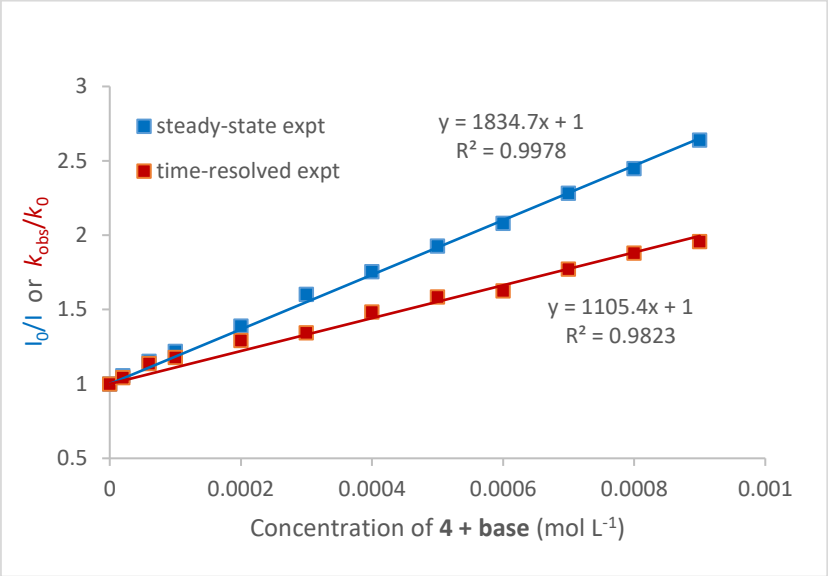


Figure S6. Steady-state and time-resolved Stern-Volmer quenching with the mixture of **4** and **base**.

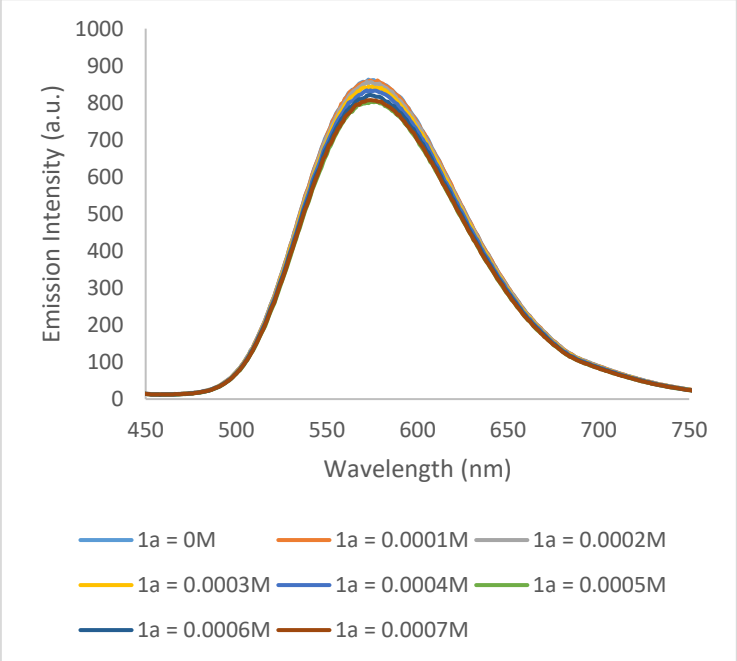


Figure S7. Fluorescence quenching experiment with **1a**.

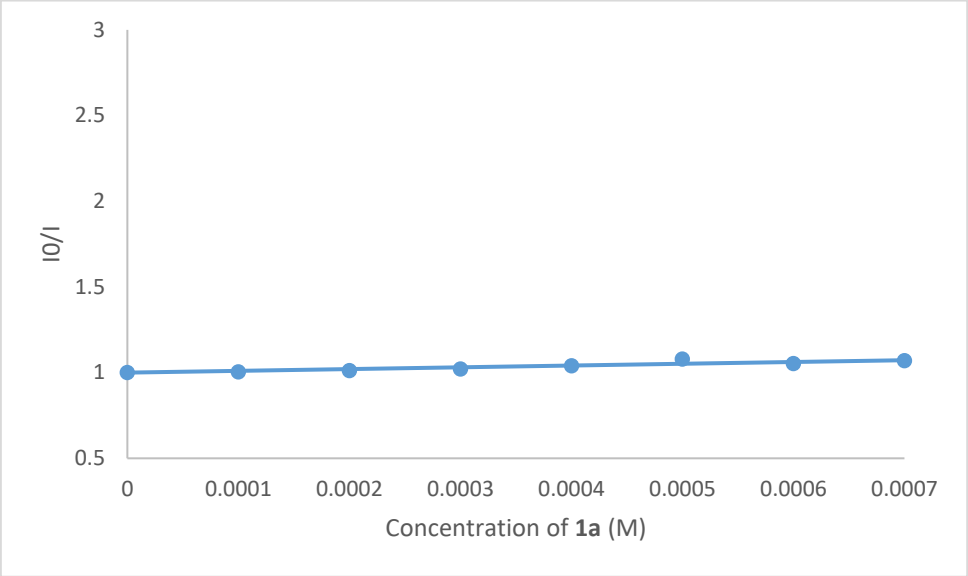


Figure S8. Steady-state Stern-Volmer quenching experiment with **1a**.

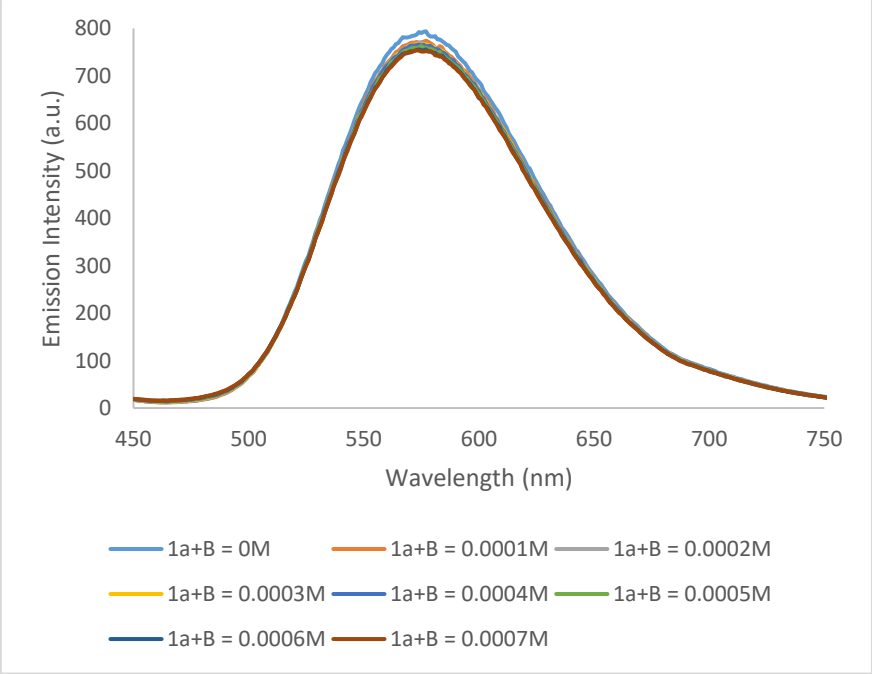


Figure S9. Fluorescence quenching experiment with the mixture of **1a** and **base**.

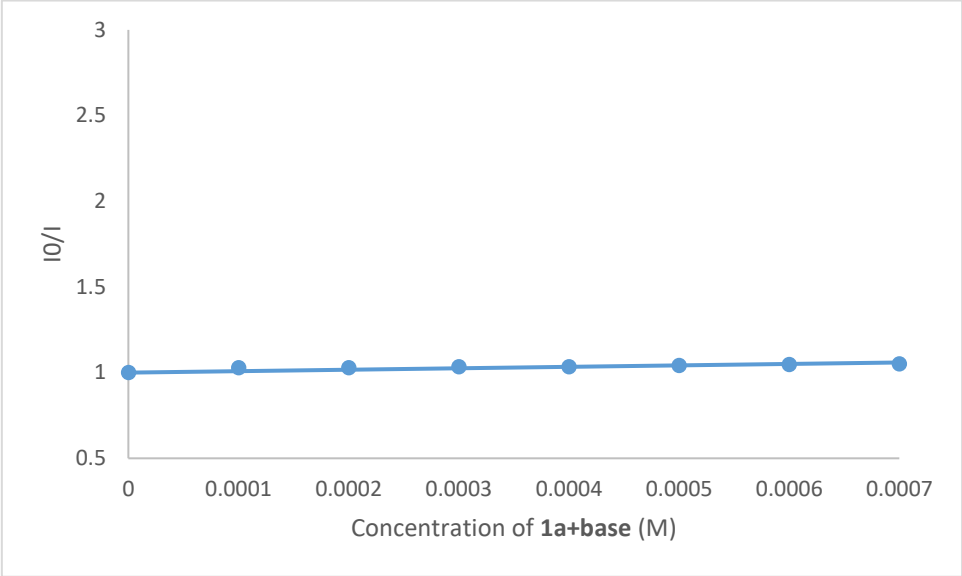


Figure S10. Steady-state Stern-Volmer quenching experiment with the mixture of **1a** and **base**.

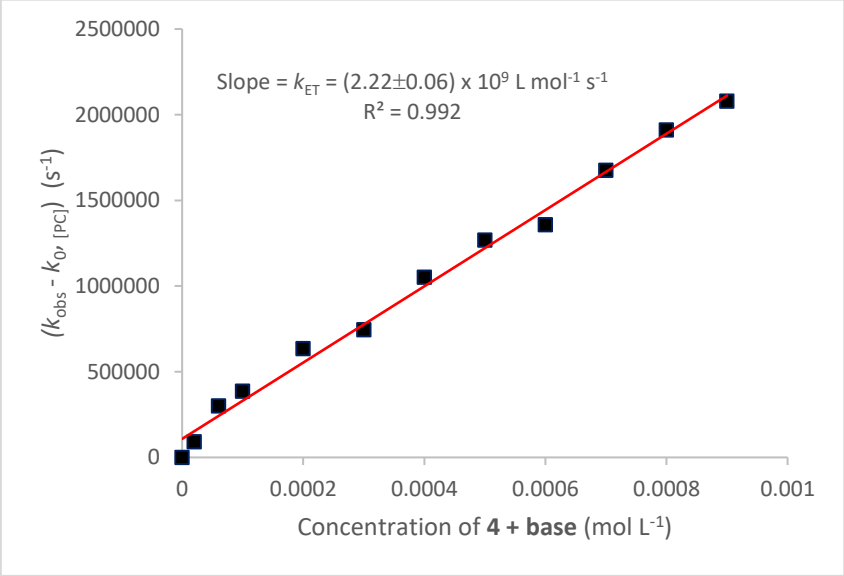
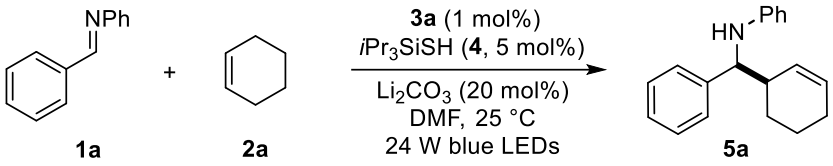


Figure S11. Rate of the electron transfer between excited-state photocatalyst ***3a** and **4** in the presence of base.



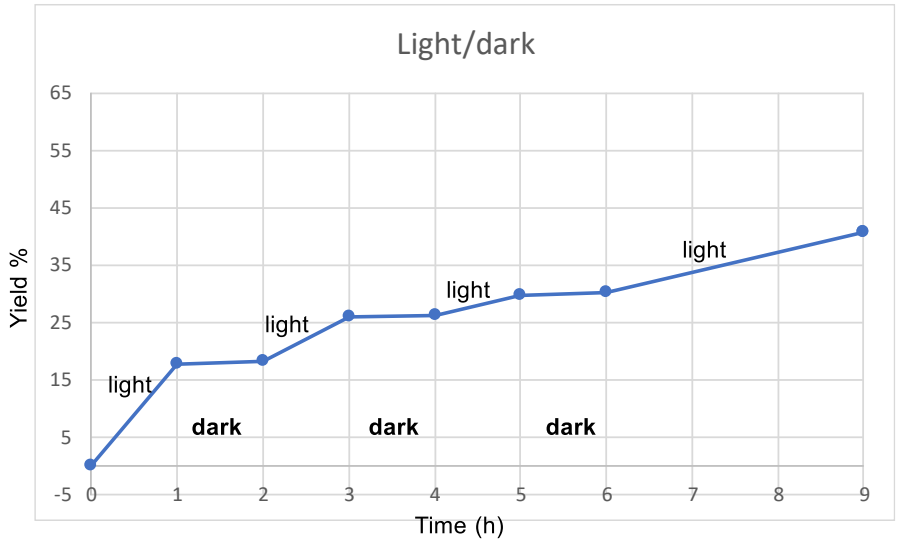
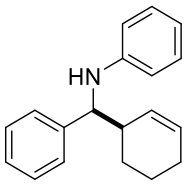


Figure S12. **Light on-off experiment.** Light on-off experiments were carried following the general procedure, using imine **1a** (0.1 mmol) and cyclohexene **2** (0.5 mmol). The light was kept off during the off-periods and the yields of the reaction products were determined by GC analysis using trimethoxy benzene as an internal standard. No reaction was observed during the light off-cycles which confirms that the reaction is not likely proceeding by radical chain propagation mechanism.

Characterization of the products

Compound 5a:



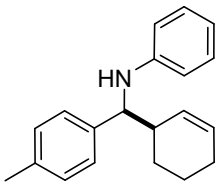
Following the general procedure with imine **1a** (0.2 mmol) and purified by flash column chromatography to afford the title compound in 81% yield as a light yellow oil with 1:1 dr.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40-7.33 (m, 8H), 7.28-7.24 (m, 2H), 7.13-7.09 (m, 4H), 6.69-6.64 (m, 2H), 6.53-6.51 (m, 4H), 5.96-5.89 (m, 2H), 5.65 (dd, *J* = 10.4, 2.4 Hz, 1H), 5.57 (dd, *J* = 10.4, 2.7 Hz, 1H), 4.36-4.33 (m, 2H), 4.15 (brs, 2H), 2.66-2.64 (m, 2H), 2.07-2.06 (m, 4H), 1.84-1.78 (m, 3H), 1.64-1.47 (m, 5H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.0 (s), 147.7 (s), 142.8 (s), 142.3 (s), 131.3 (d), 130.5 (d), 129.3 (d), 129.2 (d), 129.1 (d), 128.5 (d), 128.4 (d), 127.1 (d), 126.9 (d, 2C), 126.2 (d), 117.3 (d), 116.9 (d), 113.6 (d), 113.1 (d), 62.1 (d), 61.4 (d), 43.3 (d), 43.0 (d), 27.9 (t), 25.4 (t, 2C), 24.0 (t), 22.05 (t), 21.9 (t).

IR (ATR) ν 2970, 2676, 2347, 2106, 1743, 1371, 1216, 900 cm^{-1}. Spectroscopic and physical data are in accordance with previous report.[4]

Compound 5b:



Following the general procedure with imine **1b** (0.3 mmol) and purified by flash column chromatography to afford the title compound in 79% yield as a light yellow oil with 1:1 dr.

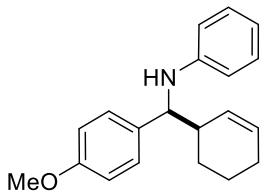
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.26-7.22 (m, 4H), 7.14-7.12 (m, 4H), 7.10-7.07 (m, 4H), 6.65-6.61 (m, 2H), 6.51-6.49 (m, 4H), 5.92-5.86 (m, 2H), 5.65-5.53 (m, 2H), 4.30-4.27 (m, 2H), 4.10 (brs, 2H), 2.60 (brs, 2H), 2.34 (s, 3H), 2.33 (s, 3H), 2.04-2.03 (m, 4H), 1.81-1.75 (m, 3H), 1.58-1.45 (m, 5H).

^{13}C NMR (151 MHz, $CDCl_3$): 148.1 (s), 147.8 (s), 139.7 (s), 139.2 (s), 136.4 (s, 2C), 131.2 (d), 130.3 (d), 129.4 (d), 129.2 (d), 129.1 (d, 2C), 127.0 (d), 126.8 (d), 126.4 (d), 117.3 (d), 116.9 (d), 113.7 (d), 113.1 (d), 61.9 (d), 61.2 (d), 43.3 (d), 43.0 (d), 27.9 (d), 25.4 (d), 25.4 (d), 24.1 (d), 22.1 (d), 22.0 (d), 21.2 (q, 2C).

IR (ATR) ν 3343, 2968, 2308, 2078, 1740, 1603, 1368, 1217, 1030 cm^{-1}.

HRMS (ESI) for $C_{20}H_{24}N^+$ $(M+H)^+$: 278.1903; Found : 278.1898.

Compound 5c:



Following the general procedure with imine **1c** (0.3 mmol) and purified by flash column chromatography to afford the title compound in 70% yield as a light yellow oil with 1:1 dr (inseparable mixture).

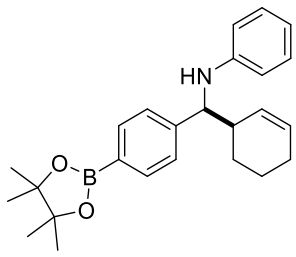
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (t, *J* = 8.7 Hz, 4H), 7.12-7.07 (m, 4H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.67-6.62 (m, 2H), 6.53-6.50 (m, 4H), 5.93-5.86 (m, 2H), 5.67-5.53 (m, 2H), 4.29-4.26 (m, 2H), 4.11 (brs, 2H), 3.80 (s, 3H), 3.79 (s, 3H), 2.61-2.56 (m, 2H), 2.06-2.04 (m, 4H), 1.81-1.77 (m, 3H), 1.61-1.45 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.5 (s, 2C), 148.1 (s), 147.8 (s), 134.7 (d), 134.3 (d), 131.1 (d), 130.3 (d), 129.3 (d), 129.2 (d), 129.1 (d), 128.0 (d), 127.9 (d), 126.4 (d), 117.3 (d), 116.9 (d), 113.8 (d, 2C), 113.7 (d), 113.2 (d), 61.5 (d), 60.9 (d), 55.3 (q), 43.3 (d), 43.1 (d), 27.7 (t), 25.4 (t, 2C), 24.1 (t), 22.0 (t), 21.9 (t).

IR (ATR) ν 3841, 3748, 3627, 3398, 2664, 2341, 2094, 1810, 1606, 1506, 1156, 831, 726 cm^{-1}.

HRMS (ESI) for $C_{20}H_{23}ONK^{+}$ $(M+K)^{+}$: 332.1411; Found : 332.1409.

Compound 5d:



Following the general procedure with imine **1d** (0.2 mmol) and purified by flash column chromatography to afford the title compound in 74% yield as a light yellow oil with 1:1 dr (inseparable mixture).

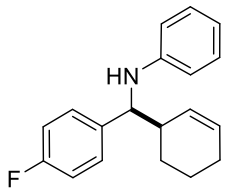
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.9 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.10 – 7.03 (m, 4H), 6.67 – 6.58 (m, 2H), 6.52 – 6.44 (m, 4H), 5.94 – 5.83 (m, 2H), 5.64 – 5.48 (m, 2H), 4.32 (t, *J* = 5.0 Hz, 2H), 4.23 – 4.05 (m, 2H), 2.70 – 2.53 (m, 2H), 2.09 – 1.98 (m, 4H), 1.83 – 1.73 (m, 3H), 1.65 – 1.45 (m, 5H), 1.40 – 1.29 (m, 24H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0, 147.6, 146.2, 145.8, 135.0, 135.0, 131.3, 130.6, 129.2, 129.2, 129.1, 126.5, 126.4, 126.1, 117.4, 117.0, 113.7, 113.2, 83.8, 62.3, 61.7, 43.2, 42.9, 27.8, 25.4, 25.3, 25.0 (2C), 23.9, 22.0, 21.9.

IR (ATR) ν 2970, 2676, 2347, 2106, 1743, 1371, 1216, 900 cm^{-1}.

GC-MS: m/z 389.3, 308.2, 208.1, 182.1, 104.0, 77.0, 43.0.

Compound 5e:



Following the general procedure with imine **1e** (0.3 mmol) and purified by flash column chromatography to afford the title compound in 69% yield as a light yellow oil with 1:1 dr (inseparable mixture).

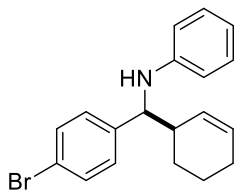
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.31 (m, 4H), 7.14-7.09 (m, 4H), 7.06-7.01 (m, 4H), 6.71-6.65 (m, 2H), 6.50 (d, J = 8.1 Hz, 4H), 5.98-5.89 (m, 2H), 5.64-5.53 (m, 2H), 4.34-4.31 (m, 2H), 4.13 (brs, 2H), 2.63-2.58 (m, 2H), 2.09-2.04 (m, 4H), 1.84-1.78 (m, 3H), 1.61-1.46 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8 (s, J_{C-F} = 244.8 Hz, 2C), 147.9 (s), 147.5 (s), 138.1 (s, J_{C-F} = 2.9 Hz, 2C), 131.5 (d), 130.7 (d), 129.2 (d), 129.1 (d), 129.0 (d), 128.5 (d, J_{C-F} = 8.2 Hz), 128.3 (d, J_{C-F} = 7.6 Hz), 125.9 (d), 117.6 (d), 117.1 (d), 115.3 (d, J_{C-F} = 20.9 Hz, 2C), 113.7 (d), 113.2 (d), 61.5 (d), 60.9 (d), 43.3 (d), 43.0 (d), 27.7 (t), 25.4 (t), 25.3 (t), 24.0 (t), 22.0 (t), 21.9 (t).

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.3, -116.4.

IR (ATR) ν 3672, 3411, 3027, 2923, 2574, 2170, 2018, 1601, 1502, 1224, 837, 737 cm^{-1}. HRMS (EI) for $C_{19}H_{20}NF^{+}$ $(M)^{+}$: 281.1574; Found : 281.1585.

Compound 5f:



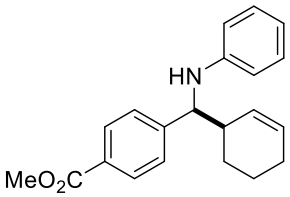
Following the general procedure with imine **1f** (0.3 mmol) and purified by flash column chromatography to afford the title compound in 61% yield as a light yellow oil with 1:1 dr (inseparable mixture).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.5, 4H), 7.25-7.21 (m, 4H), 7.11-7.06 (m, 4H), 6.69-6.62 (m, 2H), 6.47-6.45 (m, 4H), 5.94-5.87 (m, 2H), 5.56 (dd, J = 10.2, 2.4 Hz, 1H), 5.51 (dd, J = 10.2, 2.4 Hz, 1H), 4.28-4.25 (m, 2H), 4.09 (brs, 2H), 2.60-2.56 (m, 2H), 2.04-2.02 (m, 4H), 1.81-1.76 (m, 3H), 1.58-1.45 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7 (s), 147.3 (s), 141.9 (s), 141.4 (s), 131.7 (d), 131.6 (d, 2C), 130.9 (d), 129.3 (d), 129.1 (d), 128.9 (d), 128.8 (d), 128.7 (d), 125.7 (d), 120.6 (s), 117.7 (d), 117.3 (d), 113.7 (d), 113.2 (d), 61.6 (d), 61.0 (d), 43.1 (d), 42.8 (d), 27.7 (t), 25.3 (t, 2C), 23.8 (t), 21.9 (t), 21.8 (t).

IR (neat) ν 3407, 3020, 2923, 2322, 1913, 1729, 1600, 1494, 1294, 1076, 1009, 825, 723 cm^{-1}. HRMS (ESI) for $C_{19}H_{21}NBr^{+}$ $(M+H)^{+}$: 342.0852; Found : 342.0850.

Compound 5g:



Following the general procedure with imine **1g** (0.3 mmol) and purified by flash column chromatography to afford the title compound in 82% yield as a light yellow solid (mp. 102-103 ºC) with 1:1 dr (inseparable mixture).

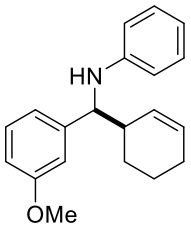
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.99 (d, *J* = 8.3 Hz, 2H), 7.42 (t, *J* = 8.6 Hz, 4H), 7.09-7.05 (m, 4H), 6.67-6.61 (m, 2H), 6.45 (d, *J* = 7.9 Hz, 4H), 5.93-5.87 (m, 2H), 5.57-5.49 (m, 2H), 4.35-4.34 (m, 2H), 4.15 (brs, 2H), 3.90 (s, 3H), 3.89 (s, 3H), 2.64-2.61 (m, 2H), 2.04-2.01 (m, 4H), 1.81-1.72 (m, 3H), 1.60-1.43 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1 (s, 2C), 148.4 (s), 148.0 (s), 147.7 (s), 147.3 (s), 131.7 (d), 130.9 (d), 129.9 (d), 129.8 (d), 129.2 (d), 129.1 (d), 129.0 (s), 128.9 (s), 128.8 (d), 127.1 (d), 127.0 (d), 125.6 (d), 117.7 (d), 117.3 (d), 113.7 (d), 113.1 (d), 62.0 (d), 61.4 (d), 52.1 (q), 43.1 (d), 42.8 (d), 27.7 (t), 25.3 (t), 25.2 (t), 23.9 (t), 21.9 (t), 21.8 (t).

IR (ATR) ν 3407, 3020, 2923, 2322, 1913, 1729, 1600, 1494, 1294, 1076, 1009, 825, 723 cm^{-1}.

HRMS (ESI) for $C_{21}H_{24}O_2N^+$ $(M+H)^+$: 322:1802; Found : 322:1797.

Compound 5h:



Following the general procedure with imine **1h** (0.3 mmol) and purified by flash column chromatography to afford the title compound in 91% yield as a light yellow oil with 1:1 dr (inseparable mixture).

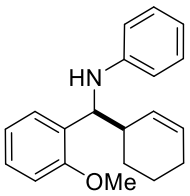
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29-7.26 (m, 2H), 7.14-7.11 (m, 4H), 7.01-6.94 (m, 4H), 6.83-6.80 (m, 2H), 6.70-6.65 (m, 2H), 6.56-6.54 (m, 4H), 5.96-5.90 (m, 2H), 5.70-5.56 (m, 2H), 4.33-4.31 (m, 2H), 3.82 (s, 6H), 4.14 (brs, 2H), 2.66-2.64 (m, 2H), 2.08-2.06 (m, 4H), 1.84-1.81 (m, 3H), 1.63-1.50 (m, 5H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 159.8 (s, 2C), 148.1 (s), 147.7 (s), 144.7 (s), 144.2 (s), 131.2 (d), 130.4 (d), 129.4 (d, 2C), 129.3 (d), 129.2 (d), 129.1 (d), 126.3 (d), 119.5 (d), 119.3 (d), 117.4 (d), 116.9 (d), 113.6 (d), 113.1 (d), 112.9 (d, 2C), 111.9 (d, 2C), 62.1 (d), 61.5 (d), 55.2 (q), 43.2 (d), 42.9 (d), 27.9 (t), 25.4 (t), 25.3 (t), 24.1 (t), 22.0 (t), 21.9 (t).

IR (ATR) ν 3405, 2920, 2337, 2089, 1922, 1740, 1595, 1478, 1267, 1047, 880, 733 cm^{-1}.

HRMS (ESI) for $C_2H_{24}ON^+$ $(M+H)^+$: 294.1852; Found : 294.1851.

Compound 5i:



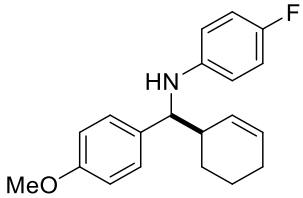
Following the general procedure with imine **1i** (0.3 mmol) and purified by flash column chromatography to afford the title compound in 92% yield as a light yellow oil with 1:1 dr (inseparable mixture).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.26-7.22 (m, 2H), 7.13-7.09 (m, 4H), 6.94-6.89 (m, 4H), 6.68-6.61 (m, 2H), 6.55-6.52 (m, 4H), 5.96-5.92 (m, 1H), 5.89-5.85 (m, 1H), 5.70 (dd, *J* = 10.5, 2.4 Hz, 1H), 5.55 (dd, *J* = 10.3, 2.4 Hz, 1H), 4.72 (t, *J* = 6.1 Hz, 2H), 4.23 (brs, 2H), 3.92 (s, 3H), 3.91 (s, 3H), 2.85-2.71 (m, 1H), 2.73-2.71 (m, 1H), 2.14-2.02 (m, 4H), 1.85-1.80 (m, 3H), 1.64-1.48 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1 (s), 156.9 (s), 148.2 (s), 147.8 (s), 130.7 (d), 130.3 (s), 130.0 (d), 129.8 (s), 129.6 (d), 129.1 (d), 129.0, 128.4 (d), 127.7 (d), 127.1 (d), 120.5 (d), 120.4 (d), 117.0 (d), 116.6 (d), 113.4 (d), 113.0 (d), 110.5 (d, 2C), 56.7 (d), 56.0 (d), 55.4 (q, 2C), 40.5 (d), 39.9 (d), 27.7 (t), 25.4 (t), 24.5 (t), 22.2 (t), 22.0 (t).

IR (ATR) ν 3854, 3393, 2927, 2341, 2084, 1862, 1748, 1608, 1501, 1238, 1035, 817 cm^{-1}. HRMS (ESI) for $C_{20}H_{24}ON^{+}$ $(M+H)^{+}$: 294.1852; Found : 294.1847.

Compound 5j:



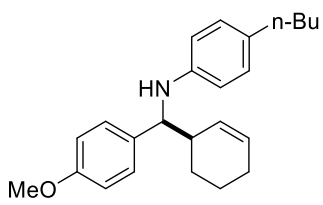
Following the general procedure with imine **1j** (0.3 mmol) and purified by flash column chromatography to afford the title compound in 72% yield as a light yellow oil with 1:1 dr (inseparable mixture).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.77 (t, *J* = 8.8 Hz, 2H), 6.76 (t, *J* = 8.8 Hz, 2H), 6.42-6.37 (m, 4H), 5.91-5.83 (m, 2H), 5.64-5.49 (m, 2H), 4.18-4.16 (m, 2H), 3.97 (brs, 2H), 3.78 (s, 3H), 3.77 (s, 3H), 2.57-2.51 (m, 2H), 2.04-2.00 (m, 4H), 1.79-1.71 (m, 3H), 1.58-1.41 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6 (s, 2C), 155.7 (s, J_{C-F} = 235.5 Hz), 155.6 (s, J_{C-F} = 234.5 Hz), 144.5 (s), 144.1 (s), 134.5 (s), 134.0 (s), 131.1 (d), 130.5 (d), 129.2 (d), 128.0 (d), 127.9 (d), 126.4 (d), 115.6 (d, d: J_{C-F} = 22.2 Hz), 115.5 (d, d: J_{C-F} = 22.2 Hz), 114.4 (d, d: J_{C-F} = 7.3 Hz), 113.9 (d, 2C), 113.8 (d), 62.2 (d), 61.6 (d), 55.3 (q), 43.3 (d), 43.1 (d), 27.7 (t), 25.4 (t, 2C), 24.1 (t), 22.0 (t), 21.9 (t).

^{19}F NMR (376 MHz, $CDCl_3$) δ -128.45 to -128.49 (m, 1F), -128.98 to -129.01 (m, 1F).

IR (ATR) ν 3836, 3433, 2937, 2671, 2338, 2091, 1750, 1484, 1378, 1217, 1029, 812 cm^{-1}. HRMS (EI) for $C_{20}H_{22}ONF_2^{+}$ $(M)^{+}$: 311.1680; Found : 311.1678.

Compound 5k:



Following the general procedure with imine **1k** (0.2 mmol) and purified by flash column chromatography to afford the title compound in 79% yield as a light yellow oil with 1:1 dr (inseparable mixture).

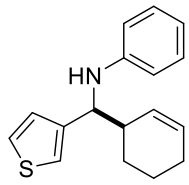
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 4H), 6.95 – 6.85 (m, 8H), 6.46 (d, *J* = 8.5 Hz, 2H), 6.45 (d, *J* = 8.4 Hz, 2H), 5.95 – 5.84 (m, 2H), 5.69 – 5.52 (m, 2H), 4.26 (t, *J* = 5.1 Hz, 2H), 4.01 (brs, 2H), 3.81 (s, 3H), 3.80 (s, 3H), 2.58 (brs, 2H), 2.47 (t, *J* = 7.7 Hz, 4H), 2.05 (d, *J* = 3.9 Hz, 4H), 1.86 – 1.71 (m, 4H), 1.59 – 1.47 (m, 8H), 1.40 – 1.30 (m, 4H), 0.93 (t, *J* = 7.3 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 158.4, 146.1, 145.7, 135.0, 134.6, 131.6, 131.2, 130.9, 130.3, 129.4, 129.0, 128.9, 128.1, 127.9, 126.6, 113.8 (2C), 113.6, 113.1, 61.8, 61.2, 55.3, 43.4, 43.1, 34.8, 34.1 (2C), 27.7, 25.4 (2C), 24.1, 22.5, 22.0 (2C), 14.1.

IR (ATR) ν 2970, 2676, 2347, 2106, 1743, 1371, 1216, 900 cm^{-1}.

GC-MS: m/z 349.3, 268.1, 238.1, 225.1, 201.1, 160.1, 121.1, 81.1.

Compound 5l:



Following the general procedure with imine **1l** (0.3 mmol) and purified by flash column chromatography to afford the title compound in 46% yield as a brown oil with 1:1 dr (inseparable mixture).

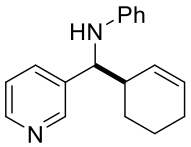
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18-7.11 (m, 6H), 6.98-6.95 (m, 4H), 6.72-6.67 (m, 2H), 6.60 (dd, *J* = 8.2, 3.8 Hz, 4H), 5.97-5.92 (m, 1H), 5.90-5.85 (m, 1H), 5.71 (dd, *J* = 10.3, 2.4 Hz, 1H), 5.57 (dd, *J* = 10.2, 2.4 Hz, 1H), 4.62-4.59 (m, 2H), 4.10 (brs, 2H), 2.73-2.67 (m, 2H), 2.06-2.03 (m, 4H), 1.84-1.76 (m, 3H), 1.59-1.51 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 148.3 (s), 147.8 (s), 147.7 (s), 147.6 (s), 131.7 (d), 130.6 (d), 129.3 (d), 129.2 (d), 128.5 (d), 126.9 (d), 126.8 (d), 126.2 (d), 124.1 (d), 124.0 (d), 123.8 (d), 123.7 (d), 117.9 (d), 117.6 (d), 113.8 (d), 113.3 (d), 58.5 (d), 58.0 (d), 43.7 (d), 43.3 (d), 27.2 (t), 25.4 (t), 25.3 (t), 24.7 (t), 21.9 (t), 21.8 (t).

IR (ATR) ν 3395, 2915, 2307, 2088, 1739, 1491, 1234, 1036, 930, 806 cm^{-1}.

HRMS (ESI) for $C_{17}H_{19}NNaS^+$ $(M+Na)^+$: 292.1130; Found : 292.1131.

Compound 5m:



Following the general procedure with imine **1m** (0.3 mmol) and purified by flash column chromatography to afford the title compound in 63% yield as a white solid (melting point = 121-122 ºC) with 1:1 dr (inseparable mixture).

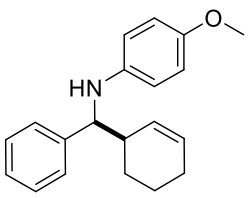
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64-8.62 (m, 2H), 8.49 (t, *J* = 4.9, 2H), 7.65-7.62 (m, 2H), 7.24-7.20 (m, 2H), 7.08 (t, *J* = 7.9, 4H), 6.68-6.63 (m, 2H), 6.47 (d, *J* = 8.1 Hz, 4H), 5.95-5.88 (m, 2H), 5.58 (dd, *J* = 10.2, 2.4 Hz, 1H), 5.51 (dd, *J* = 10.2, 2.4 Hz, 1H), 4.38-4.34 (m, 2H), 4.19-4.10 (m, 2H), 2.64-2.61 (m, 2H), 2.05-2.02 (m, 4H), 1.81-1.75 (m, 3H), 1.58-1.46 (m, 5H).

^{13}C NMR (101 MHz, c) δ 149.2 (d, 2C), 148.5 (d), 148.4 (d), 147.4 (s), 147.1 (s), 138.0 (s), 137.6 (s), 134.7 (d), 134.4 (d), 131.9 (d), 131.1 (d), 129.3 (d), 129.2 (d), 128.3 (d), 125.3 (d), 123.4 (d), 117.8 (d), 117.4 (d), 113.7 (d), 113.1 (d), 59.9 (d), 59.4 (d), 43.0 (d), 42.7 (d), 27.5 (t), 25.2 (t), 25.2 (t), 23.9 (t), 21.8 (t), 21.7 (t).

IR (ATR) ν 3841, 3740, 3406, 3242, 3023, 2925, 2647, 2180, 2025, 1741, 1594, 1500, 1230, 836, 711 cm^{-1}.

HRMS (EI) for $C_{18}H_{21}N_2^+$ $(M+H)^+$: 265.1699; Found : 265.1693.

Compound 5n:



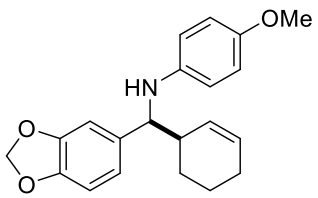
Following the general procedure with imine **1n** (0.3 mmol) and purified by flash column chromatography to afford the title compound in 81% yield as a light yellow oil with 1:1 dr (inseparable mixture).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39-7.33 (m, 8H), 7.27-7.23 (m, 2H), 6.72 (d, *J* = 8.4 Hz, 2H), 6.71 (d, *J* = 8.4 Hz, 2H), 6.47 (brs, 4H), 5.93-5.89 (m, 2H), 5.68 (d, *J* = 10.2 Hz, 1H), 5.57 (d, *J* = 10.3 Hz, 1H), 4.26 (brs, 2H), 3.93-3.91 (m, 2H), 3.71 (s, 6H), 2.62 (brs, 2H), 2.06-2.05 (m, 4H), 1.82-1.78 (m, 3H), 1.60-1.49 (m, 5H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.0 (s), 151.6 (s), 143.0 (s), 142.6 (s), 142.3 (s), 142.0 (s), 130.9 (d), 130.5 (d), 129.4 (d), 128.4 (d, 2C), 127.1 (d), 127.0 (d), 126.8 (d, 2C), 126.5 (d), 114.9 (d), 114.7 (d), 114.1 (d), 62.9 (d), 62.3 (d), 55.8 (q, 2C), 43.3 (d), 43.1 (d), 27.8 (t), 25.4 (t), 25.3 (t), 23.9 (t), 22.0 (t), 21.9 (t).

Spectroscopic and physical data are in accordance with previous report.[4]

Compound 5o:



Following the general procedure with imine **1o** (0.3 mmol) and purified by flash column chromatography to afford the title compound in 78% yield as a light yellow oil with 1:1 dr (inseparable mixture).

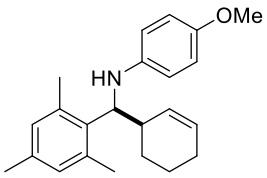
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.87-6.86 (m, 1H), 6.84-6.74 (m, 5H), 6.71-6.68 (m, 4H), 6.45 (brs, 4H), 5.94-5.85 (m, 6H), 5.66 (d, *J* = 10.3 Hz, 1H), 5.51 (dd, *J* = 10.2, 2.5 Hz, 1H), 4.13 (brs, 2H), 3.84 (s, 2H), 3.70 (s, 6H), 2.53-2.50 (m, 2H), 2.04-2.02 (m, 4H), 1.80-1.71 (m, 3H), 1.60-1.43 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 151.9 (s), 151.6 (s), 147.7 (s, 2C), 146.2 (s), 142.1 (s), 141.8 (s), 137.1 (s), 136.6 (s), 130.8 (d), 130.3 (d), 129.1 (d), 126.4 (d), 120.1 (d), 119.9 (d), 114.8 (d), 114.6 (d), 114.0 (d), 108.0 (d), 107.4 (d), 107.1 (d), 100.8 (t, 2C), 62.6 (d), 62.1 (d), 55.7 (q), 43.3 (d), 43.1 (d), 27.5 (t), 25.3 (t), 25.2 (t), 23.9 (t), 21.9 (t), 21.8 (t).

IR (ATR) ν 3398, 2913, 2317, 2095, 1738, 1613, 1487, 1232, 1036, 925, 806 cm^{-1}.

HRMS (ESI) for $C_{21}H_{23}O_3NNa^+$ $(M+Na)^+$: 360.1570; Found : 360.1571.

Compound 5p:



Following the general procedure with imine **1p** (0.3 mmol) and purified by flash column chromatography to afford the title compound in 74% yield as a light yellow oil with 1:1 dr (inseparable mixture).

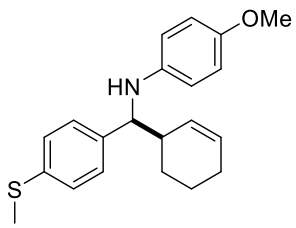
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.77-6.66 (m, 8H), 6.42 (brs, 4H), 5.95 (d, *J* = 10.5 Hz, 1H), 5.86 (dt, *J* = 10.2, 3.1 Hz, 1H), 5.69 (dt, *J* = 10.0, 3.4 Hz, 1H), 5.18 (dd, *J* = 10.3, 2.7 Hz, 1H), 4.50 (brs, 2H), 3.68 (brs, 8H), 2.68 (s, 2H), 2.42 (s, 12H), 2.22 (s, 6H), 2.07-1.98 (m, 5H), 1.85- 1.45 (m, 7H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 151.7, 142.6, 136.6, 136.1, 135.8 (2C), 131.7, 129.5, 129.3, 129.1, 129.0, 128.4, 115.0, 113.7, 59.8, 55.9, 41.1, 39.9, 27.2, 26.9, 25.4 (2C), 22.3, 21.7, 21.2, 20.8 (2C).

IR (ATR) ν 3393, 2932, 2324, 2077, 1855, 1617, 1495, 1235, 1035, 912, 728 cm^{-1}.

HRMS (ESI) for $C_{23}H_{29}ONNa^+$ $(M+Na)^+$: 358.2141; Found : 358.2140.

Compound 5q:



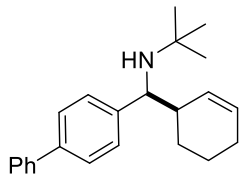
Following the general procedure with imine **1q** (0.3 mmol) and purified by flash column chromatography to afford the title compound in 83% yield as a light yellow oil with 1:1 dr (inseparable mixture).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.18 (m, 8H), 6.68-6.65 (m, 4H), 6.43-6.40 (m, 4H), 5.89-5.83 (m, 2H), 5.61 (dd, *J* = 10.3, 2.4 Hz, 1H), 5.51 (dd, *J* = 10.2, 2.4 Hz, 1H), 4.19-4.16 (m, 2H), 3.85 (brs, 2H), 3.68 (s, 6H), 2.56-2.52 (m, 2H), 2.46 (s, 3H), 2.45 (s, 3H), 2.02-2.00 (m, 4H), 1.79-1.72 (m, 3H), 1.55-1.42 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 152.0 (s), 151.7 (s), 142.2 (s), 141.9 (s), 140.1 (s), 139.6 (s), 136.4 (s), 131.0 (d), 130.6 (d), 129.2 (d), 127.7 (d), 127.5 (d), 126.8 (d), 126.7 (d), 126.4 (d), 114.9 (d), 114.8 (d), 114.2 (d), 62.5 (d), 61.9 (d), 55.9 (q), 55.8 (q), 43.3 (d), 43.0 (d), 27.7 (t), 25.4 (t), 25.3 (t), 23.9 (t), 22.0 (t), 21.9 (t), 16.1 (q, 2C).

IR (ATR) ν 3842, 3386, 2923, 2332, 2090, 1745, 1508, 1371, 1232, 1036, 817, 728 cm^{-1}. HRMS (ESI) for $C_{21}H_{25}ONNaS^+$ $(M+Na)^+$: 362.1549; Found : 362.1550.

Compound 5r:



Following the general procedure with imine **1r** (0.3 mmol) and purified by flash column chromatography to afford the title compound in 58% yield as a light yellow oil with 1:1 dr (inseparable mixture).

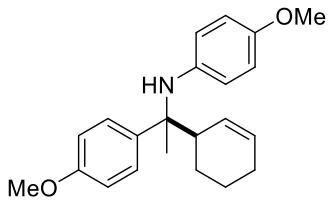
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 7.9 Hz, 4H), 7.53 (d, *J* = 8.3, 2H), 7.52 (d, *J* = 8.3, 2H), 7.45-7.40 (m, 8H), 7.31 (t, *J* = 7.4 Hz, 2H), 5.89-5.85 (m, 1H), 5.81-5.75 (m, 2H), 5.47-5.43 (m, 1H), 3.79 (d, *J* = 6.1 Hz, 1H), 3.63 (d, *J* = 6.7 Hz, 1H), 2.37-2.35 (m, 2H), 1.99-1.96 (m, 4H), 1.76-1.40 (m, 8H), 1.00 (s, 9H), 0.99 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 146.6 (s), 146.1 (s), 141.3 (s), 141.2 (s), 139.0 (s, 2C), 130.2 (d), 129.6 (d), 128.9 (d), 128.8 (d), 128.7 (d), 128.4 (d), 128.0 (d), 127.1 (d), 127.0 (d, 2C), 126.6 (d), 126.4 (d), 61.1 (d), 60.7 (d), 51.2 (s), 43.9 (d), 30.4 (q), 30.3 (q), 27.8 (t), 25.5 (t), 25.5 (t), 24.5 (t), 22.2 (t), 22.0 (t).

IR (ATR) ν 2971, 2667, 2338, 2100, 1741, 1368, 1216, 896, 746 cm^{-1}.

HRMS (ESI) for $C_{23}H_{30}N^+$ $(M+H)^+$: 320.2373; Found : 320.2371.

Compound 5s:



Following the general procedure with imine **1s** (0.3 mmol) and purified by flash column chromatography to afford the title compound in 51% yield as a light yellow oil with 1:1 dr (inseparable mixture).

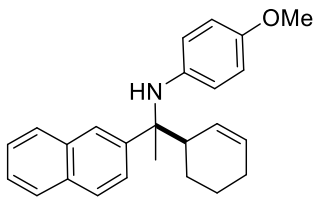
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 6.89-6.86 (m, 4H), 6.65-6.62 (m, 4H), 6.38-6.34 (m, 4H), 5.97-5.93 (m, 1H), 5.88-5.85 (m, 1H), 5.78 (dd, *J* = 10.4, 2.2 Hz, 1H), 5.65 (d, *J* = 10.4 Hz, 1H), 3.82-3.70 (m, 14H), 2.42-2.40 (m, 2H), 2.01-1.98 (m, 4H), 1.80-1.63 (m, 9H), 1.50-1.35 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.0 (s), 151.9 (s), 151.8 (s), 140.6 (s), 140.3 (s), 138.2 (s), 137.8 (s), 131.8 (d), 130.5 (d), 128.4 (d), 128.2 (d), 127.2 (d), 127.0 (d), 117.1 (d), 114.4 (d), 114.3 (d), 113.4 (d), 113.3 (d), 60.5 (s), 55.7 (q), 55.3 (q), 49.8 (d), 49.7 (d), 25.4 (t), 25.3 (t), 24.6 (t, 2C), 22.8 (q), 22.5 (t, 2C), 21.6 (q).

IR (ATR) ν 3397, 2929, 2051, 1863, 1608, 1497, 1237, 1033, 814 cm^{-1}.

HRMS (ESI) for $C_{22}H_{27}O_2NK^+$ $(M+K)^+$: 376.1673; Found : 376.1673.

Compound 5t:



Following the general procedure with imine **1t** (0.3 mmol) and purified by flash column chromatography to afford the title compound in 74% yield as a light yellow oil with 1:1 dr (inseparable mixture).

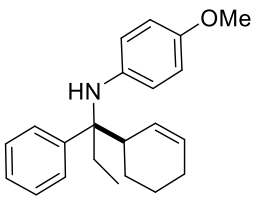
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93-7.83 (m, 8H), 7.72-7.65 (m, 2H), 7.51-7.49 (m, 4H), 6.65-6.62 (m, 4H), 6.42 (t, *J* = 8.0 Hz, 4H), 6.02-5.88 (m, 2H), 5.86-5.72 (m, 2H), 3.98 (s, 2H), 3.70 (s, 6H), 2.62 -2.59 (m, 2H), 2.03-2.01 (m, 4H), 1.86 (s, 3H), 1.81-1.65 (m, 6H), 1.53-1.39 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$): 152.0 (s), 144.1 (s), 143.8 (s), 140.6 (s), 140.2 (s), 133.4 (s), 133.3 (s), 132.3 (s), 132.1 (d), 130.7 (d), 128.3 (d), 127.8, (d) 127.6 (d), 127.5 (d), 127.1 (d), 126.8 (d), 126.1 (d), 125.9 (d), 125.8 (d), 125.7 (d), 125.6 (d), 117.3 (d, 2C), 114.4 (d, 2C), 61.2 (s), 61.1 (s), 55.7 (d), 49.7 (d), 49.3 (d), 25.4 (t), 25.3 (t), 24.6 (t), 22.9 (q), 22.5 (t), 22.4 (t), 21.4 (q).

IR (ATR) ν 3399, 2932, 2320, 2086, 1740, 1497, 1372, 1229, 1037, 812 cm^{-1}.

HRMS (ESI) for $C_{25}H_{28}ON^+$ $(M+H)^+$: 358.2165; Found : 358.2154.

Compound 5u:



Following the general procedure with imine **1u** (0.3 mmol) and purified by flash column chromatography to afford the title compound in 87% yield as a light yellow oil with 1:1 dr (inseparable mixture).

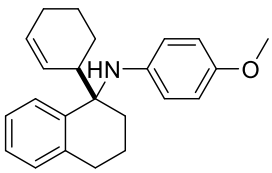
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H) 7.32-7.29 (m, 4H), 7.26-7.22 (m, 2H), 6.63 (d, *J* = 9.0 Hz, 2H), 6.61 (d, *J* = 9.0 Hz, 2H), 6.35 (d, *J* = 8.9 Hz, 2H), 6.28 (d, *J* = 8.9 Hz, 2H), 6.10 (dt, *J* = 10.4, 2.1 Hz, 1H), 5.78-5.76 (m, 1H), 5.74-5.71 (m, 1H), 5.68-5.65 (m, 1H), 3.78 (brs, 2H), 3.70 (s, 3H), 3.68 (s, 3H), 2.58-2.56 (m, 2H), 2.36-2.24 (m, 4H), 1.89-1.84 (m, 3H), 1.80-1.66 (m, 5H), 1.52 -1.44 (m, 1H), 1.43-1.39 (m, 2H), 1.13-1.07 (m, 1H), 0.88 (t, *J* = 7.3 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 151.8 (s), 151.7 (s), 143.6 (s), 143.0 (s), 140.3 (s), 130.2 (d), 129.3 (d), 128.1 (d), 128.0 (d), 127.6 (d, 2C), 127.3 (d), 126.8 (d), 126.4 (d), 126.3 (d), 116.9 (d), 116.8 (d), 114.4 (d), 114.3 (d), 64.1 (s), 63.8 (s), 55.7 (q, 2C), 44.5 (d), 44.4 (d), 25.3 (t), 25.2 (t), 25.1 (t), 24.4 (t), 24.2 (t), 23.9 (t), 22.5 (t), 21.9 (t), 8.1 (q), 7.9 (q).

IR (ATR) ν 3416, 2923, 2084, 1848, 1609, 1498, 1238, 1040, 814 cm^{-1}.

HRMS (ESI) for $C_{22}H_{27}ONNa^+$ $(M+Na)^+$: 344.1985; Found : 344.1978.

Compound 5v:



Following the general procedure with imine **1v** (0.3 mmol) and purified by flash column chromatography to afford the title compound in 66% yield as a light yellow oil with 1:1 dr (inseparable mixture).

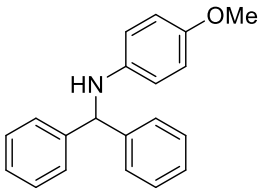
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.4 Hz, 1H), 7.43 (d, *J* = 7.4 Hz, 1H), 7.17-7.10 (m, 6H), 6.62-6.57 (m, 4H), 6.33-6.26 (m, 4H), 5.95-5.89 (m, 3H), 5.63 (d, *J* = 10.5 Hz, 1H), 3.79 (brs, 2H), 3.68 (s, 6H), 2.87-2.76 (m, 4H), 2.65 (brs, 2H), 2.31-2.24 (m, 2H), 2.07-1.71 (m, 12H), 1.65-1.40 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 152.3 (s), 152.1 (s), 140.6 (s), 140.2 (s), 140.0 (s), 139.6 (s), 137.5 (s), 137.4 (s), 131.4 (d), 130.4 (d), 129.1 (d), 128.9 (d), 128.2 (d), 127.1 (d), 127.0 (d), 126.3 (d), 126.2 (d), 125.3 (d, 2C), 118.5 (d), 117.7 (d), 114.2 (d), 114.1 (d), 59.7 (s), 59.2 (s), 55.6 (q), 55.5 (q), 46.0 (d), 45.5 (d), 29.1 (t), 29.0 (t, 2C), 25.4 (t), 25.3 (t), 24.4 (t, 2C), 22.6 (t, 2C), 19.9 (t, 2C).

IR (ATR) ν 3404, 3021, 2930, 2667, 2289, 2070, 1846, 1736, 1608, 1504, 1236, 1178, 1124, 1037, 942, 896, 819, 752 cm^{-1}.

HRMS (ESI) for $C_{23}H_{27}ONNa^+$ $(M+Na)^+$: 356.1985; Found : 356.1983.

Compound 5w:



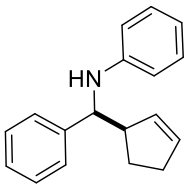
Following the general procedure with imine **1w** (0.3 mmol) and purified by flash column chromatography to afford the title compound in 96% yield as a colorless oil .

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 7.1 Hz, 4H), 7.36 (t, *J* = 7.5 Hz, 4H), 7.29 (t, *J* = 7.2 Hz, 2H), 6.76 (d, *J* = 8.9 Hz, 2H), 6.55 (d, *J* = 8.8 Hz, 2H), 5.47 (s, 1H), 4.05 (s, 1H), 3.74 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 152.2 (s), 143.3 (s), 141.7 (s), 128.8 (d), 127.5 (d), 127.3 (d), 114.8 (d), 114.7 (d), 63.9 (d), 55.7 (q).

Spectroscopic and physical data are in accordance with previous report.[5]

Compound 6a:



Following the general procedure with imine **1a** (0.2 mmol), cyclopentene (1.0 mmol) and purified by flash column chromatography to afford the title compound in 85% yield as a light yellow oil with 1:1 dr (inseparable mixture).

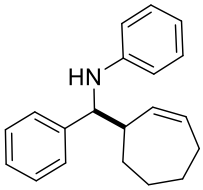
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40-7.33 (m, 8H), 7.27-7.25 (m, 2H), 7.12-7.09 (m, 4H), 6.68-6.64 (m, 2H), 6.53-6.51 (m, 4H), 6.00-5.91 (m, 2H), 5.64-5.51 (m, 2H), 4.42-4.27 (m, 2H), 4.17 (brs, 2H), 3.27-3.16 (m, 2H), 2.46-2.35 (m, 4H), 2.12-2.08 (m, 1H), 1.97-1.92 (m, 1H), 1.89-1.83 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 147.8 (s), 147.6 (s), 143.3 (s), 143.2 (s), 134.6 (d), 133.3 (d), 132.1 (d), 129.8 (d), 129.2 (d), 129.1 (d), 128.5 (d), 127.0 (d), 126.9 (d), 126.8 (d), 126.7 (d), 117.3 (d), 116.9 (d), 113.6 (d), 113.2 (d), 62.0 (d), 60.9 (d), 53.7 (d), 53.6 (d), 32.7 (t), 32.2 (t), 27.3 (t), 25.9 (t).

IR (ATR) ν 3830, 3404, 3037, 2920, 2340, 2093, 1896, 1744, 1599, 1495, 1304, 1027, 865, 718 cm^{-1}.

HRMS (ESI) for $C_{18}H_{20}N^+$ $(M+H)^+$: 250.1590; Found : 250.1588.

Compound 6b:



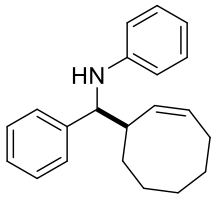
Following the general procedure with imine **1a** (0.2 mmol), cycloheptene (1.0 mmol) and purified by flash column chromatography to afford the title compound in 90% yield as a light yellow oil with 1:1 dr(inseparable mixture).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.30 (m, 8H), 7.25-7.23 (m, 2H), 7.09 (t, *J* = 7.6 Hz, 4H), 6.67-6.62 (m, 2H), 6.50 (d, *J* = 8.5 Hz, 4H), 5.93-5.85 (m, 2H), 5.78-5.71 (m, 2H), 4.44 (d, *J* = 4.7 Hz, 1H), 4.31 (d, *J* = 5.9 Hz, 1H), 4.15 (brs, 2H), 2.77-2.69 (m, 2H), 2.25-2.08 (m, 4H), 2.00-1.93 (m, 2H), 1.78-1.67 (m, 4H), 1.56-1.25 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8 (s, 2C), 142.9 (s), 142.1 (s), 134.7 (d), 133.9 (d), 133.1 (d), 132.4 (d), 129.2 (d), 128.5 (d), 128.4 (d), 127.3 (d), 127.2 (d), 127.0 (d), 126.9 (d), 117.3 (d), 117.1 (d), 113.4 (d), 113.2 (d), 63.1 (d), 62.5 (d), 47.3 (d), 46.9 (d), 31.9 (t), 30.6 (t), 30.4 (t), 28.8 (t), 28.7 (t), 27.9 (t), 26.8 (t), 26.6 (t).

IR (ATR) ν 3834, 3413, 2903, 2344, 2091, 1750, 1604, 1483, 1294, 1062, 869, 715 cm^{-1}. HRMS (ESI) for $C_{20}H_{24}N^+$ $(M+H)^+$: 278.1903; Found : 278.1902.

Compound 6c:



Following the general procedure with imine **1a** (0.2 mmol), cyclooctene (1.0 mmol), Li_2CO_3 (20 mol%), triisopropylsilanethiol **4** (10 mol%), $[Ir(ppy)_2(dtbbpy)]PF_6$ **3a** (1 mol%) in DMF (1.0 mL) and purified by flash column chromatography to afford the title compound in 62% yield as a light yellow oil with 1:1 dr (inseparable mixture).

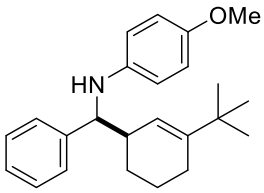
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.37 (m, 2H), 7.33-7.19 (m, 8H), 7.07-7.01 (m, 4H), 6.60 (t, *J* = 7.3 Hz, 2H), 6.50-6.47 (m, 4H), 5.91-5.84 (m, 1H), 5.76-5.69 (m, 1H), 5.47-5.38 (m, 2H), 4.37 (d, *J* = 5.2 Hz, 1H), 4.24 (brs, 2H), 3.99 (d, *J* = 9.2 Hz, 1H), 3.06-2.99 (m, 1H), 2.81-2.72 (m, 1H), 2.29-2.20 (m, 2H), 2.16-2.05 (m, 2H), 1.80-1.58 (m, 5H), 1.52-1.37 (m, 5H), 1.32-1.16 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.9 (s), 147.4 (s), 143.5 (s), 141.6 (s), 132.6 (d), 131.9 (d), 131.6 (d), 129.9 (d), 129.2 (d), 129.1 (d), 128.5 (d), 128.3 (d), 127.8 (d), 127.6 (d), 127.1 (d), 127.0 (d), 117.3 (d), 117.1 (d), 113.5 (d), 113.3 (d), 64.0 (d), 61.6 (d), 43.9 (d), 42.6 (d), 32.9 (t), 32.4 (t), 29.6 (t, 2C), 27.3 (t), 27.1 (t), 26.7 (t), 25.7 (t), 25.6 (t).

IR (ATR) ν 3832, 3415, 2923, 2672, 2332, 2093, 1897, 1741, 1600, 1468, 1364, 1216, 1076, 884, 721 cm^{-1}.

HRMS (ESI) for $C_{21}H_{26}N^+$ $(M+H)^+$: 292.2060; Found : 292.2060.

Compound 6d:



Following the general procedure with imine **1a** (0.2 mmol), 1-*tert*-butyl-1-cyclohexene (1.0 mmol) and purified by flash column chromatography to afford the title compound in 91% yield as a light yellow oil with 1:1 dr (inseparable mixture).

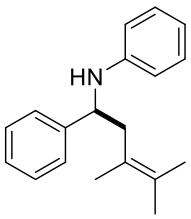
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39-7.32 (m, 8H), 7.26-7.23 (m, 2H), 6.71-6.69 (m, 4H), 6.45 (d, *J* = 8.9 Hz, 2H), 6.44 (d, *J* = 8.9 Hz, 2H), 5.46-5.45 (m, 1H), 5.35-5.34 (m, 1H), 4.27 (d, *J* = 4.9 Hz, 1H), 4.23 (d, *J* = 4.9 Hz, 1H), 3.88 (brs, 2H), 3.71 (s, 6H), 2.64-2.60 (m, 2H), 2.13-2.07 (m, 2H), 2.04-1.97 (m, 2H), 1.84-1.74 (m, 3H), 1.48-1.37 (m, 5H), 1.06 (s, 18H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 152.0 (s), 151.6 (s), 150.0 (s), 149.8 (s), 143.2 (s), 142.8 (s), 142.2 (s), 128.4 (d), 128.3 (d), 127.1 (d), 127.0 (d), 126.8 (d), 126.7 (d), 120.1 (d), 116.8 (d), 114.9 (d), 114.8 (d, 2C), 114.2 (d), 63.7 (d), 62.8 (d), 55.9 (q, 2C), 43.6 (d), 43.5 (d), 35.9 (s), 35.7 (s), 29.3 (q), 29.2 (q), 27.6 (t), 24.9 (t), 24.8 (t), 23.8 (t), 22.9 (t), 22.8 (t).

IR (ATR) ν 3865, 3392, 2934, 2337, 2094, 1854, 1639, 1498, 1238, 1038, 815, 734 cm^{-1}. HRMS (ESI) for $C_{24}H_{32}ON^+$ $(M+H)^+$: 350.2478; Found : 350.2478.

Compound 6e/6e':

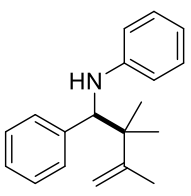
Following the general procedure with imine **1a** (0.2 mmol), 2,3-dimethyl-2-butene (1.0 mmol) and purified by flash column chromatography to afford the title compounds **6e** (50% yield, light yellow oil) and **6e'** (12% yield, light yellow oil).



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.06 (t, *J* = 7.8 Hz, 2H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.46 (d, *J* = 8.0 Hz, 2H), 4.36 (dd, *J* = 9.1, 5.8 Hz, 1H), 4.11 (s, 1H), 2.65 (dd, *J* = 13.6, 9.1 Hz, 1H), 2.35 (dd, *J* = 13.6, 5.8 Hz, 1H), 1.69 (s, 3H), 1.66 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9 (s), 144.7 (s), 129.1 (d), 128.6 (d), 128.5 (s), 126.9 (d), 126.3 (d), 124.2 (s), 117.4 (d), 113.8 (d), 57.0 (d), 44.4 (t), 21.0 (q), 20.7 (q), 18.4 (q).

IR (ATR) ν 3836, 3376, 2916, 2344, 2089, 1745, 1602, 1469, 1367, 1215, 1039, 878, 724 cm^{-1}. HRMS (ESI) for $C_{19}H_{24}N^+$ $(M+H)^+$: 266.1903; Found : 266.1902.



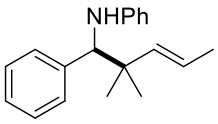
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 7.4 Hz, 2H), 7.33-7.20 (m, 3H), 7.00 (t, *J* = 7.7 Hz, 2H), 6.58 (t, *J* = 7.3 Hz, 1H), 6.37 (d, *J* = 8.0 Hz, 2H), 4.99 (s, 2H), 4.14 (s, 1H), 4.12 (brs, 1H), 1.75 (s, 3H), 1.03 (s, 3H), 0.99 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.6 (s), 148.1 (s), 140.4 (s), 129.1 (d), 129.0

(d), 127.9 (d), 127.1 (d), 117.3 (d), 113.4 (d), 112.4 (s), 63.4 (d), 43.8 (s), 26.1 (q), 20.8 (q), 19.3 (q). IR (ATR) ν 3837, 3461, 2970, 2673, 2334, 2092, 1742, 1368, 1216, 1074, 898, 739 cm^{-1}. HRMS (ESI) for $C_{19}H_{24}N^+$ $(M+H)^+$: 266.1903; Found : 266.1904.

Compound 6f/6f':

Following the general procedure with imine **1a** (0.2 mmol), trans-4-methyl-2-pentene (1.0 mmol) and purified by flash column chromatography to afford the title compounds **6f** (35% yield, light yellow oil) and **6f'** (55% yield, light yellow oil, 1:1 dr).

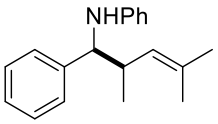


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.17 (m, 5H), 7.02 (dd, *J* = 8.6, 7.1 Hz, 2H), 6.57 (t, *J* = 7.3 Hz, 1H), 6.42 (dd, *J* = 8.3, 1.3 Hz, 2H), 5.57 (dq, *J* = 15.6, 6.1 Hz, 1H), 5.46 (dq, *J* = 15.6, 1.5 Hz, 1H), 4.23 (s, 1H), 4.00 (s, 1H), 1.75 (dd, *J* = 6.1, 1.4 Hz, 3H), 1.10 (s, 3H), 0.94 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9 (s), 140.8 (s), 137.8 (d), 129.1 (d), 128.8 (d), 127.8 (d), 127.0 (d), 124.4 (d), 117.0 (d), 113.5 (d), 66.4 (d), 40.7 (s), 26.6 (q), 23.8 (q), 18.4 (q).

IR (ATR) ν 2972, 2678, 2339, 2094, 1741, 1370, 1215 cm^{-1}.

HRMS (ESI) for $C_{19}H_{24}N^+$ $(M+H)^+$: 266.1903; Found : 266.1903.



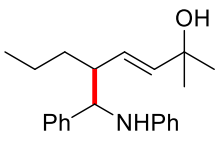
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.2 Hz, 2H), 7.34-7.22 (m, 8H), 7.10-7.04 (m, 4H), 6.65-6.60 (m, 2H), 6.51-6.48 (m, 4H), 5.08 (dt, *J* = 9.9, 1.5 Hz, 1H), 5.00 (dt, *J* = 9.9, 1.5 Hz, 1H), 4.32 (d, *J* = 5.1 Hz, 1H), 4.29 (brs, 2H), 3.91 (d, *J* = 8.1 Hz, 1H), 2.96-2.87 (m, 1H), 2.70-2.60 (m, 1H), 1.77 (d, *J* = 1.4 Hz, 3H), 1.73 (d, *J* = 1.4 Hz, 3H), 1.65 (s, 6H), 0.98 (d, *J* = 6.9 Hz, 3H), 0.89 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1 (s), 147.4 (s), 143.4 (s), 141.3 (s), 134.0 (s), 133.3 (s), 129.1 (d, 2C), 128.4 (d), 128.0 (d), 127.8 (d), 127.6 (d), 127.0 (d), 126.8 (d), 126.2 (d), 117.3 (d), 117.0 (d), 113.7 (d), 113.4 (d), 64.3 (d), 62.2 (d), 40.5 (d), 38.5 (d), 26.1 (q, 2C), 18.4 (q), 18.3 (q), 17.6 (q).

IR (ATR) ν 3830, 3405, 2946, 2340, 2093, 1743, 1600, 1491, 1313, 1068, 855, 705 cm^{-1}.

HRMS (ESI) for $C_{19}H_{24}N^+$ $(M+H)^+$: 266.1903; Found : 266.1899.

Compound 6g:



Following the general procedure with imine **1a** (0.2 mmol), (*E*)-2-methyloct-3-en-2-ol (1.0 mmol) and purified by flash column chromatography to afford the title compound in 51% yield as a light yellow oil with 1:1 dr (inseparable mixture).

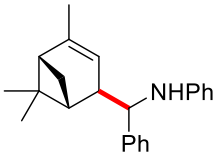
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.18 (m, 10H), 7.07-7.02 (m, 4H), 6.63-6.58 (m, 2H), 6.49-6.45 (m, 4H), 5.65 (dd, *J* = 15.7, 9.2 Hz, 2H), 5.43 (dd, *J* = 15.6, 9.1 Hz, 1H), 5.29 (dd, *J* = 15.6, 9.7 Hz, 1H), 4.34 (d, *J* = 5.1 Hz, 1H), 4.26 (brs, 2H), 4.09 (d, *J* = 7.4 Hz, 1H), 2.41 (tt, *J* = 9.3, 4.3 Hz, 1H), 2.33-2.25 (m, 1H), 1.56-1.12 (m, 20H), 0.86 (t, *J* = 7.1 Hz, 3H), 0.80 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.8 (s), 147.2 (s), 143.1 (s), 141.8 (d), 141.3 (d), 129.2 (d, 2C), 128.4 (d), 128.2 (d), 127.8 (d), 127.5 (d, 2C), 127.1 (d), 127.0 (d), 117.3 (d), 117.2 (d), 113.5 (d), 113.4 (d), 70.9 (s), 70.8 (s), 61.8 (d), 61.2 (d), 50.0 (d), 48.8 (d), 33.8 (t), 33.6 (t), 30.2 (q), 30.1 (q), 30.0 (q), 29.9 (q), 20.8 (t), 20.7 (t), 14.2 (q), 14.1 (q).

IR (ATR) ν 3397, 2946, 1925, 1736, 1601, 1495, 1346, 983, 707 cm^{-1}.

HRMS (ESI) for $C_{22}H_{29}ONNa^+$ $(M+Na)^+$: 346.2141; Found : 346.2142.

Compound 6h:



Following the general procedure with imine **1a** (0.2 mmol), (-)-alpha-pinene (1.0 mmol) and purified by flash column chromatography to afford the title compound in 65% yield (combined yields of all isomers, dr **6h-1**:**6h-2**:**6h-3**:**6h-4** = 1.2:1:1:1:1) as a light yellow oil.

Diastereomers 6h-1+6h-2: Inseparable mixture of two diastereomers with ratio 1:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.18 (m, 10H), 7.08-7.03 (m, 4H), 6.62-6.58 (m, 2H), 6.53-6.49 (m, 4H), 5.50-5.49 (m, 1H), 4.65-4.64 (m, 1H), 4.27-4.16 (m, 4H), 2.51-2.47 (m, 2H), 2.39-2.36 (m, 1H), 2.29-2.17 (m, 2H), 2.02-1.97 (m, 2H), 1.72 (t, *J* = 1.9 Hz, 3H), 1.70-1.68 (m, 1H), 1.62 (t, *J* = 1.9 Hz, 3H), 1.36 (d, *J* = 8.9 Hz, 1H), 1.32 (s, 3H), 1.30 (d, *J* = 8.9 Hz, 1H), 1.20 (s, 3H), 0.86 (s, 3H), 0.82 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.8 (s), 147.3 (s), 146.7 (s), 143.3 (s), 143.2 (s), 129.2 (d), 128.5 (d, 2C), 127.4 (d), 127.0 (d), 126.9 (d), 117.1 (d), 117.0 (d, 2C), 116.8 (d), 113.3 (d, 2C), 61.5 (d), 60.8 (d), 47.9 (d), 47.6 (d), 47.4 (d), 47.3 (d), 43.9 (d), 43.3 (d), 41.4 (s), 41.3 (s), 28.6 (t), 28.0 (t), 26.8 (q), 26.5 (q), 23.4 (q), 23.3 (q), 20.7 (q), 20.5 (q).

Diastereomers 6h-3+6h-4: Inseparable mixture of two diastereomers with ratio 1.6:1.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33-7.26 (m, 6.3H$_{major+minor}$), 7.24-7.19 (m, 1.7H$_{major+minor}$), 7.08-7.04 (m, 3.1H$_{major+minor}$), 6.53-6.51 (m, 4.7H$_{major+minor}$), 5.68 (s, 0.7H $_{minor}$), 4.65-4.64 (m, 1H$_{major}$), 4.48-4.46 (d, *J* = 10.7 Hz, 1.8H$_{major+minor}$), 4.15 (brs, 1.6H$_{major+minor}$), 2.66-2.64 (m, 2.7H$_{major+minor}$), 2.56-2.53 (m, 1H$_{major}$), 2.36-2.32 (m, 0.7H$_{minor}$), 1.98-1.94 (m, 1.6H$_{major+minor}$),

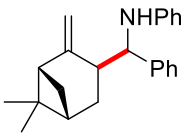
1.74 (t, *J* = 1.9 Hz, 1.8H$_{minor}$), 1.68-1.66 (m, 0.7H$_{minor}$), 1.61 (t, *J* = 1.9 Hz, 3H$_{major}$), 1.36 (d, *J* = 8.9 Hz, 1H), 1.32 (s, 3H$_{major}$), 1.28 (d, *J* = 8.6 Hz, 1H$_{major}$), 1.22-1.19 (m, 4.3H$_{minor}$), 1.14 (s, 3H$_{major}$).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.8 (s), 147.7 (s), 146.1 (s), 145.1 (s), 143.8 (s), 143.5 (s), 129.2 (d), 129.2 (d), 128.6 (d), 128.5 (d), 127.4 (d), 127.3 (d), 127.0 (d, 2C), 117.1 (d), 117.0 (d, 2C), 116.9 (d), 113.4 (d), 59.3 (d), 59.0 (d), 52.0 (d), 47.5 (d), 43.4 (d, 2C), 38.3 (s), 38.2 (s), 34.4 (t), 34.3 (t), 27.2 (q), 27.1 (q), 24.1 (q), 23.4 (q), 23.3 (q), 23.1 (q).

IR (ATR) ν 3411, 2929, 2075, 1922, 1743, 1600, 1489, 1304, 1082, 854, 714 cm^{-1}.

HRMS (ESI) for $C_{23}H_{28}N^+$ $(M+H)^+$: 318.2216; Found : 318.2210.

Compound 6i:



Following the general procedure with imine **1a** (0.2 mmol), (-)-beta-pinene (1.0 mmol) and purified by flash column chromatography to afford the title compound in 69% yield (combined yields of all isomers, dr 3:3:1:1) as a light yellow oil (inseparable mixture).

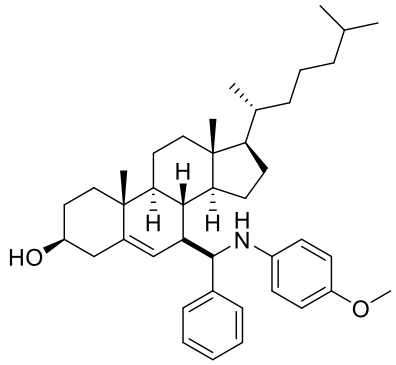
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.21 (m, 14.1H$_{major+minor}$), 7.11-7.04 (m, 5.6H$_{major+minor}$), 6.68-6.45 (m, 8.7H$_{major+minor}$), 5.48 (s, 1H$_{major}$), 5.42 (s, 1H$_{major}$), 4.75 (s, 0.6H$_{major}$), 4.67 (d, *J* = 5.8 Hz, 0.6H$_{major}$), 4.60 (s, 0.6H$_{major}$), 4.55 (d, *J* = 5.7 Hz, 0.6H$_{major}$), 4.31-4.18 (m, 4.7H$_{major+minor}$), 3.16-3.10 (m, 1H$_{major}$), 2.53-2.24 (m, 12H$_{major+minor}$), 2.16-2.02 (m, 5.9H$_{major+minor}$), 1.95-1.91 (m, 1.8H$_{major+minor}$), 1.78-1.71 (m, 1H$_{major}$), 1.29 (s, 3H$_{major}$), 1.28 (s, 1.3H$_{minor}$), 1.24 (s, 3H$_{major}$), 1.23 (s, 1.3H$_{minor}$), 1.19 (d, *J* = 8.6 Hz, 1H$_{major}$), 1.07 (d, *J* = 8.7 Hz, 1H$_{major}$), 0.88 (s, 3H$_{major}$), 0.81 (s, 1.2H$_{minor}$), 0.78 (s, 1.2H$_{minor}$), 0.74 (s, 3H$_{major}$).

^{13}C NMR (101 MHz, $CDCl_3$): δ 151.7, 151.2, 148.1, 148.0, 147.6, 145.7, 145.3, 144.9, 144.7, 142.7, 142.4, 129.2, 129.1, 129.1, 129.0, 128.7, 128.7, 128.3, 128.2, 127.5, 126.9, 126.9, 126.3, 126.2, 120.8, 120.4, 117.6, 117.4, 117.3, 117.3, 114.0, 113.7, 113.7, 63.3, 62.4, 55.9, 55.7, 52.9, 52.7, 47.7, 47.3, 45.7, 44.9, 41.8, 41.7, 41.0, 40.8, 40.8, 40.6, 38.2, 38.0, 32.1, 31.8, 31.6, 31.6, 30.1, 27.4, 27.3, 26.6, 26.4, 26.3, 26.3, 26.0, 22.0, 21.8, 21.5, 21.2.

IR (ATR) ν 3398, 2917, 2346, 2089, 1891, 1594, 1482, 1302, 1068, 886, 718 cm^{-1}.

HRMS (ESI) for $C_{23}H_{27}NNa^+$ $(M+Na)^+$: 340.2036; Found : 340.2030.

Compound 6j:



Following the general procedure with imine **1b** (0.2 mmol), cholesterol (0.6 mmol), Li_2CO_3 (20 mol%), triisopropylsilanethiol **4** (10 mol%), $[Ir(ppy)_2(dtbbpy)]PF_6$ **3a** (1 mol%) in DMF (2.0 mL) and purified by flash column chromatography to afford the title compound in 75% yield (red oil, dr **6j-1**:**6j-2**:**6j-3**:**6j-4** = 1.6:1.6:1:1).

Diastereomers 6j-1 and 6j-2: Inseparable mixture of two diastereomers with ratio 1:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.16 (m, 10H), 6.66 (d, *J* = 8.6 Hz, 4H), 6.35 (d, *J* = 8.9 Hz, 2H), 6.31 (d, *J* = 8.9 Hz, 2H), 5.13 (d, *J* = 4.7 Hz, 1H), 4.96-4.95 (m, 1H), 4.67 (brs, 2H), 3.95 (brs, 2H), 3.67 (s, 6H), 3.47-3.40 (m, 2H), 2.41-2.31 (m, 6H), 2.10-1.68 (m, 16H), 1.61-1.43 (m, 9H), 1.40-1.22 (m, 13H), 1.19-0.95 (m, 20H), 0.92-0.85 (m, 16H), 0.70 (s, 3H), 0.61 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 151.4, 151.3, 146.1, 146.0, 144.2, 143.3, 142.1, 140.7, 128.3 (2C), 126.8, 126.7, 126.6, 126.5, 120.3, 120.2, 115.0, 113.8, 113.7, 72.8, 71.3, 58.2, 58.0, 55.9 (2C), 55.6, 55.5, 54.5, 51.2, 50.8, 49.2, 44.3 (2C), 43.8, 43.0, 42.9, 42.4, 40.3, 39.6 (2C), 39.0, 38.0, 37.5, 37.2, 36.3 (2C), 36.1, 35.9 (2C), 35.8, 34.6, 31.9, 31.7, 28.7, 28.3, 28.2, 27.2, 25.4, 24.1, 23.9, 23.0 (2C), 22.7, 21.9, 21.5, 19.7, 19.6, 19.0, 18.9, 12.5, 12.1.

Diastereomers 6j-3 and 6j-4: Inseparable mixture of two diastereomers with ratio 1:1. Diastereoisomers **6j-3 and 6j-4** are not stable in $CDCl_3$ and decomposition was observed during the NMR analysis.

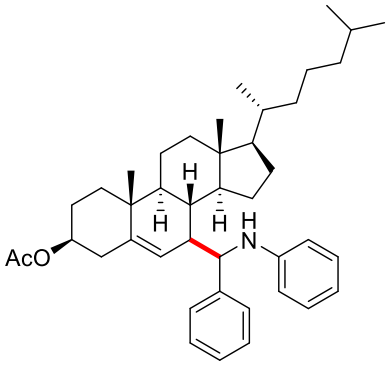
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.11 (m, 10H), 6.67-6.64 (m, 4H), 6.52 (d, *J* = 9.0 Hz, 2H), 6.48 (d, *J* = 9.0 Hz, 2H), 5.64 (d, *J* = 3.9 Hz, 1H), 5.54 (t, *J* = 2.5 Hz, 1H), 4.96-4.95 (m, 1H), 3.66 (s, 6H), 3.50-3.44 (m, 2H), 2.59-2.57 (m, 1H), 2.45-2.24 (m, 6H), 2.07-0.80 (m, not assigned due to the complexity), 0.75 (s, 3H), 0.69-0.67 (m, 1H), 0.63 (s, 3H), 0.52-0.45 (m, 2H), 0.25-0.18 (m, 2H), 0.01 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 152.2, 152.1, 144.1, 143.5, 142.7, 142.0, 141.6, 140.8, 131.2, 129.8, 129.1, 128.9, 128.7, 127.6, 127.4, 127.0 (2C), 122.3, 122.0, 121.2, 115.4, 115.2, 114.8, 114.5, 71.4, 71.1, 61.7, 59.8, 58.1, 56.1, 55.8, 55.7, 55.6, 50.9, 50.4, 47.3, 43.8, 43.5, 43.1, 42.9, 42.1, 41.5, 40.3, 39.6 (2C), 39.2, 37.1, 36.9, 36.4, 36.3, 36.2, 36.0 (2C), 35.4, 33.7, 31.8, 31.6, 28.6, 28.4, 28.2, 28.1, 26.8, 25.4, 24.1, 24.0, 23.0 (2C), 22.7 (2C), 21.8, 20.8, 19.2, 19.0, 18.9, 17.5, 12.5, 11.4.

IR (ATR) ν 3852, 2934, 2679, 2341, 2095, 1741, 1511, 1371, 1218, 1040, 818, 691 cm^{-1}.

HRMS (ESI) for $C_{41}H_{59}O_2NNa^+$ $(M+Na)^+$: 620.4438; Found : 620.4437.

Compound 6k:



Following the general procedure with imine **1a** (0.2 mmol), cholesteryl acetate (0.6 mmol), Li_2CO_3 (20 mol%), triisopropylsilanethiol **4** (10 mol%), $[Ir(ppy)_2(dtbbpy)]PF_6$ **3a** (1 mol%) in DMF (2.0 mL) and purified by flash column chromatography to afford the title compound in 82% yield (red oil, dr **6k-1**:**6k-2**:**6k-3**:**6k-4** = 1.2:1:1:1:1).

Diastereomers 6k-1 and 6k-2: Inseparable mixture of two diastereomers with ratio 1.2:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.24 (m, 8H), 7.20-7.16 (m, 2H), 7.09-7.04 (m, 4H), 6.61-6.57 (m, 4H), 6.40 (d, *J* = 8.6 Hz, 2H), 5.16 (d, *J* = 3.3 Hz, 1H), 5.00 (brs, 1H), 4.80-4.73 (m, 3H), 4.55-4.49 (m, 1H), 3.95 (brs, 2H), 4.17 (d, *J* = 8.7 Hz, 1H), 4.06 (d, *J* = 7.8 Hz, 1H), 2.48-2.37 (m, 6H), 2.15-0.85 (m, not assigned due to the complexity), 0.70 (s, 3H), 0.61 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.7, 170.6, 147.6, 146.2, 145.3, 145.2, 143.8, 142.8, 129.3, 128.4 (2C), 126.7 (2C), 126.6, 126.5, 121.2, 120.9, 116. (2C), 113.2, 112.9, 74.3, 73.5, 58.0, 57.5, 55.5 (2C), 53.9, 51.1, 50.7, 49.1, 44.4, 44.2, 43.8, 43.0, 40.2, 39.7, 38.9, 38.5, 38.3, 37.6, 37.4, 37.2, 36.3 (2C), 36.0 (2C), 35.9 (3C), 34.6, 28.7, 28.3, 28.2, 28.0, 27.8, 27.1, 25.5, 24.1, 23.9, 23.0 (2C), 22.7, 21.9, 21.6, 21.5, 21.4, 19.5 (2C), 19.0, 18.9, 12.5, 12.1.

IR (ATR) ν 3410, 2936,2323, 1735, 1601, 1471, 1363, 1236, 1028, 901, 715 cm^{-1}.

HRMS (ESI) for $C_{42}H_{59}O_2NNa^+$ $(M+Na)^+$: 632.4438; Ffound : 632.4444.

Loh107-2

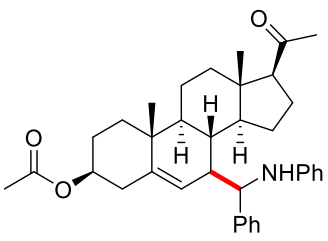
Diastereomers 6k-3 and 6k-4: Inseprable mixtures of two diastereomers (1:1 ratio) together with minor uncharacterized isomers.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.32 (m, 2H), 7.29-7.12 (m, 8H), 7.08-7.02 (m, 4H); 6.62-6.55 (m, 4H), 6.49 (d, *J* = 8.7 Hz, 2H), 5.68 (dd, *J* = 5.2, 1.5 Hz, 1H), 5.56 (t, *J* = 2.4 Hz, 1H), 4.68 (d, *J* = 3.4 Hz, 1H), 4.60-4.53 (m, 3H), 4.19 (brs, 2H), 2.62-2.60 (m, 1H), 2.47-2.32 (m, 5H), 2.05-0.84 (m, not assigned due to the complexity), 0.77 (s, 3H), 0.65-0.60 (m, 5H), 0.55-0.48 (m, 2H), 0.31-0.23 (m, 2H), 0.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.7, 170.6, 147.7, 147.3, 143.1, 142.8, 142.3, 140.6, 129.8, 129.2, 129.1, 129.0, 127.8, 127.5, 127.2, 127.0, 122.9, 122.0, 117.4, 117.4, 113.7 (2C), 73.5 (2C), 60.7, 58.6, 58.0, 56.1, 55.7, 50.8, 50.4, 47.3, 43.8, 43.3, 42.9, 41.5, 40.3, 39.7, 39.6, 39.2, 39.0, 38.0, 37.2, 36.6, 36.4, 36.3, 36.0 (2C), 35.9, 35.5, 33.7, 28.6, 28.4, 28.2 (2C), 27.8, 27.7, 26.8, 25.5, 24.1, 24.0, 23.0 (2C), 22.7 (2C), 21.7, 21.6, 21.5, 20.8, 19.2, 19.0 (2C), 18.9, 17.5, 12.5, 11.5.

IR (ATR) ν 3401, 2933, 1730, 1602, 1468, 1363, 1243, 1028, 711 cm^{-1}.

HRMS (ESI) for $C_{42}H_{59}O_2NNa^+$ $(M+Na)^+$: 632.4438; Found : 632.4439.

Compound 6l:



Following the general procedure with imine **1a** (0.2 mmol), pregnenolone acetate (0.6 mmol), Li_2CO_3 (20 mol%), triisopropylsilanethiol **4** (10 mol%), $[Ir(ppy)_2(dtbbpy)]PF_6$ **3a** (1 mol%) in DMF (2.0 mL) and purified by flash column chromatography to afford the title compounds in 79% yield (yellow oil, dr **6l-1**:**6l-2**:**6l-3** = 1:1.9:1.9). The high regioselectivity of the reaction could be confirmed using 2D NMR techniques such as COSY, HSQC and HMBC.

Diastereomer 6l-1: Isolated as a single diastereomer.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.06 (m, 5H), 7.08 (t, *J* = 7.7 Hz, 2H), 6.60 (t, *J* = 7.3 Hz, 1H), 6.40 (d, *J* = 8.2 Hz, 2H), 5.14 (d, *J* = 3.9 Hz, 1H), 4.80-4.72 (m, 2H), 4.15 (brs, 1H), 2.51 (t, *J* = 9.2 Hz, 1H), 2.48-2.47 (m, 1H), 2.44-2.38 (m, 2H), 2.29-2.16 (m, 2H), 2.12-1.89 (m, 9H),1.80-1.41 (m, 8H), 1.35-1.20 (m, 2H), 1.03 (s, 3H), 0.64 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 209.5, 170.7, 146.2, 145.3, 143.4, 129.4, 128.5, 126.7, 126.5, 120.6, 117.0, 113.2, 74.2, 63.1, 54.2, 51.1, 44.5, 44.2 (2C), 38.5, 38.1, 37.6, 37.3, 35.9, 31.8, 27.7, 25.6, 23.0, 21.6, 21.4, 19.5, 13.4; IR (ATR) ν 3394, 2936, 1911, 1715, 1600, 1490, 1355, 1239, 1028, 907, 725 cm^{-1}.

HRMS (ESI) for $C_{36}H_{46}O_3N^+$ $(M+H)^+$: 540.3472; Found : 540.3472.

Loh108-2

Diastereomers 6l-2 and 6l-3: Isolated as a mixture of two diastereomers with ratio 1:1 (However, one diastereomer could be seperated by another flash column chromatography for the determination of regioselectivity).

^{1}H $NMR_{mixture}$ (400 MHz, $CDCl_3$): δ 7.33-7.17 (m, 10H), 7.09-7.03 (m, 4H), 6.63-6.55 (m, 4H), 6.39 (d, *J* = 8.2 Hz, 2H), 5.62 (dd, *J* = 5.2, 1.5 Hz, 1H), 5.01 (d, *J* = 1.6 Hz, 1H), 4.72 (dd, *J* = 8.1, 2.3 Hz, 1H), 4.63 (d, *J* = 3.8 Hz, 1H), 4.64-4.49 (m, 2H), 4.15 (brs, 1H), 4.02 (d, *J* = 8.1 Hz, 1H), 2.64-1.58 (m, 39H), 1.51-1.26 (m, 11H), 1.14 (s, 3H), 0.90 (s, 3H), 0.59 (s, 3H), 0.56 (s, 3H).

^{1}H $NMR_{single\ diastereomer}$ (600 MHz, $CDCl_3$): δ 7.29-7.27 (m, 4H), 7.22-7.19 (m, 1H), 7.07 (dd, *J* = 8.6, 7.3 Hz, 2H), 6.60 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.40 (d, *J* = 7.6 Hz, 2H), 5.02 (dd, *J* = 2.7, 1.4 Hz, 1H), 4.73 (s, 1H), 4.56-4.51 (m, 1H), 4.03 (d, *J* = 5.4 Hz, 1H), 2.55 (t, *J* = 9.3 Hz, 1H), 2.46 (d, *J* = 7.7 Hz, 1H), 2.43 (d, *J* = 8.4 Hz, 2H), 2.30-2.25 (m, 1H), 2.24-2.18 (m, 1H), 2.13 (s, 3H),

2.07-2.02 (m, 4H), 1.94-1.89 (m, 2H), 1.82-1.76 (m, 2H), 1.71-1.60 (m, 3H), 1.51-1.46 (m, 2H), 1.44-1.37 (m, 1H), 1.15-1.10 (m, 4H), 1.09-1.04 (m, 1H), 0.57 (s, 3H).

^{13}C NMR$_{mixture}$ (101 MHz, $CDCl_3$): δ 209.4 (2C), 170.6 (2C), 147.5, 147.1, 145.3, 142.5 (2C), 142.1, 129.5, 129.4, 129.2, 128.5, 127.9, 127.4, 126.8, 126.6, 122.9, 120.9, 117.5, 116.9, 113.7, 112.9, 73.4, 73.3, 63.5, 63.1, 58.7, 57.9, 57.4, 50.9, 50.5, 48.9, 45.2, 44.5, 43.1, 41.6, 39.3, 38.9, 38.3, 38.2, 37.3, 37.2, 36.0, 35.8, 34.7, 31.8, 31.7, 28.0, 27.7, 27.3, 25.7, 23.5, 23.1, 21.8, 21.6, 21.5, 20.8, 19.5, 19.2, 13.9, 12.7.

^{13}C NMR *single diastereomer* (151 MHz, $CDCl_3$) δ 209.4 (s), 170.7 (s), 147.5 (s), 145.3 (s), 142.5 (s), 129.4 (d), 128.5 (d), 126.8 (d), 126.6 (d), 120.9 (d), 116.9 (d), 112.9 (d), 73.3 (d), 63.1 (d), 58.0 (d), 57.5 (d), 51.0 (d), 48.9 (d), 45.3 (s), 39.4 (t), 38.3 (t), 37.2 (t), 36.0 (s), 34.7 (d), 31.8 (q), 28.0 (t), 27.3 (t), 23.5 (t), 21.8 (t), 21.5 (q), 19.5 (q), 13.9 (q).

IR (ATR) ν 3392, 2927, 1922, 1712, 1474, 1237, 1026, 721 cm^{-1}.

HRMS (ESI) for $C_{36}H_{46}O_3N^+$ $(M+H)^+$: 540.3472; Found : 540.3473.

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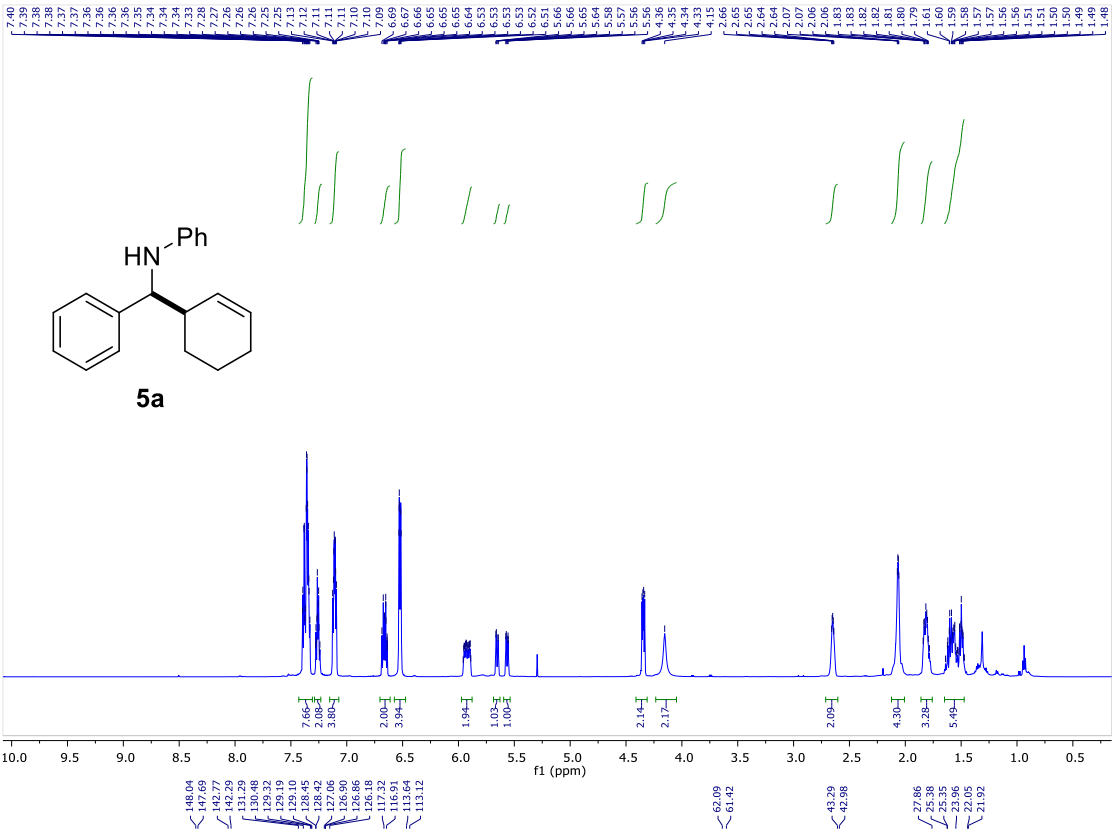
[4] I. L. Lysenko, H. G. Lee, J. K. Cha, *Org. Lett.* **2009**, *11*, 3132-3134.

[5] W. Muramatsu, K. Nakano, C.-J. Li, *Org. Lett.* **2013**, *15*, 3650-3653.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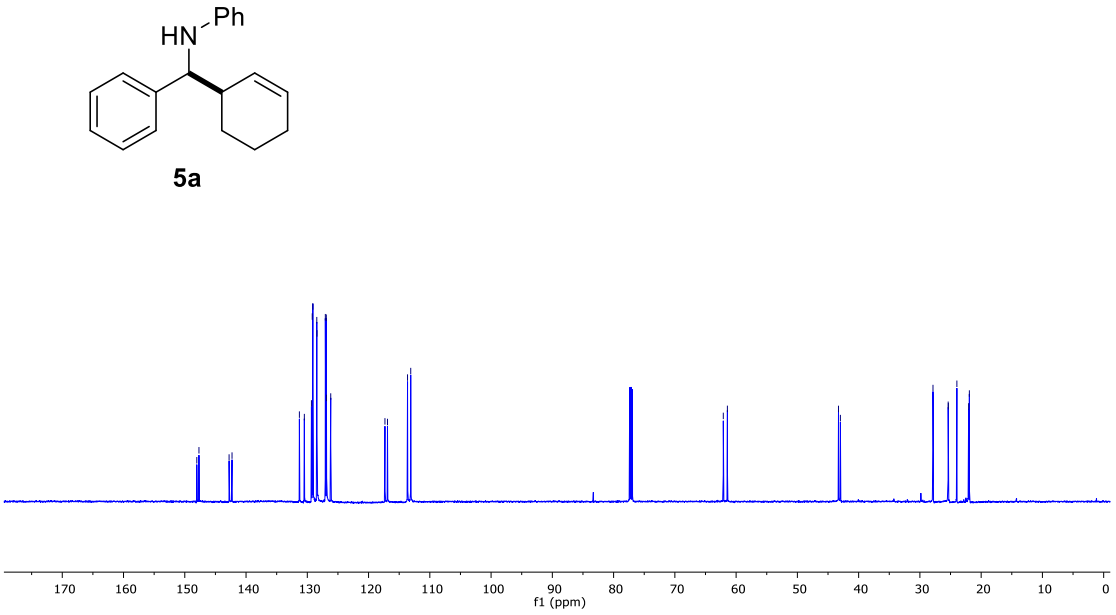
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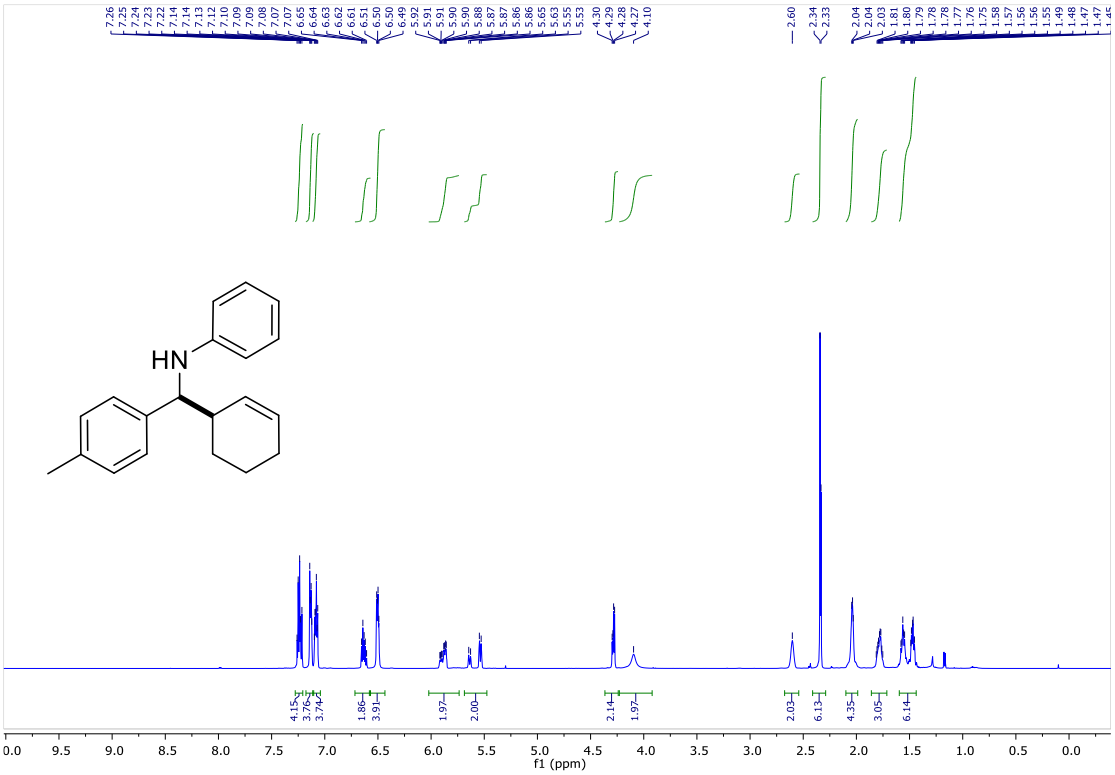
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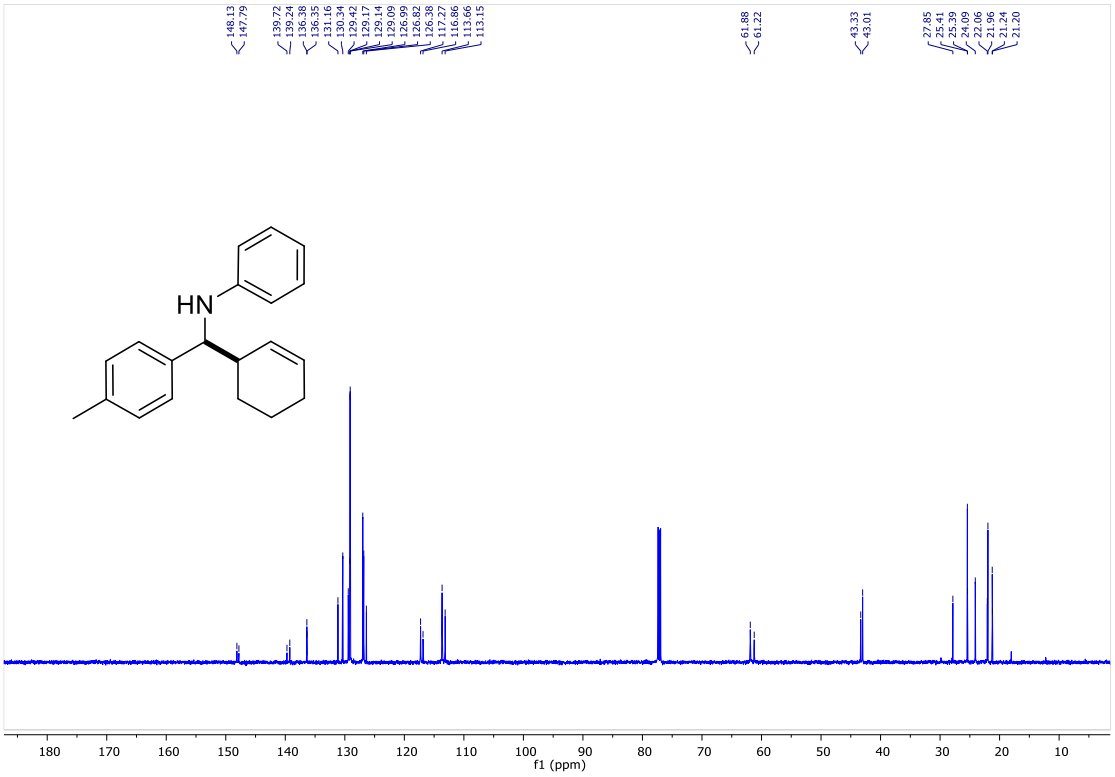
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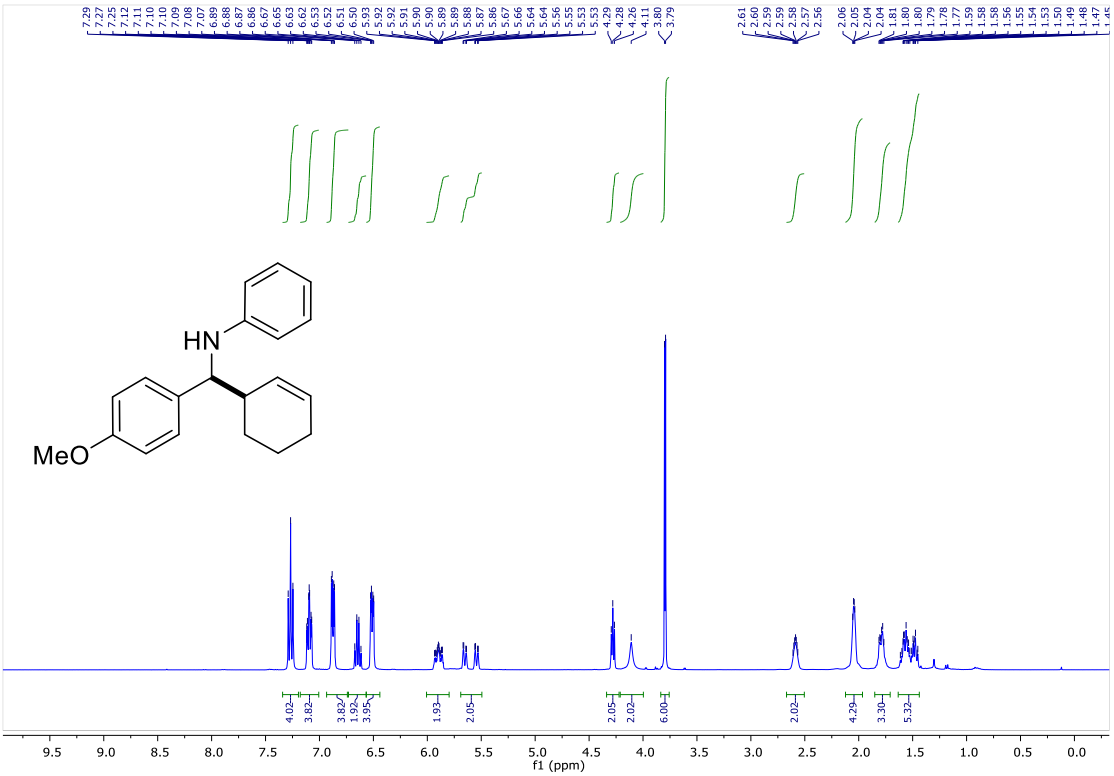
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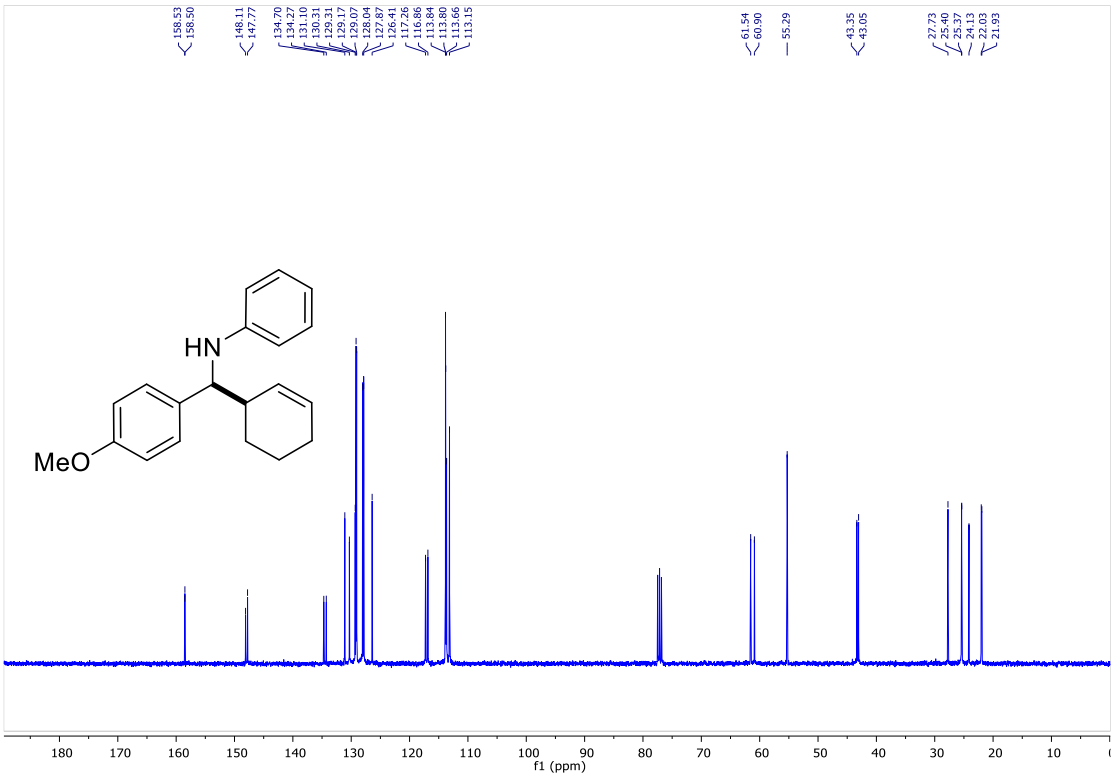
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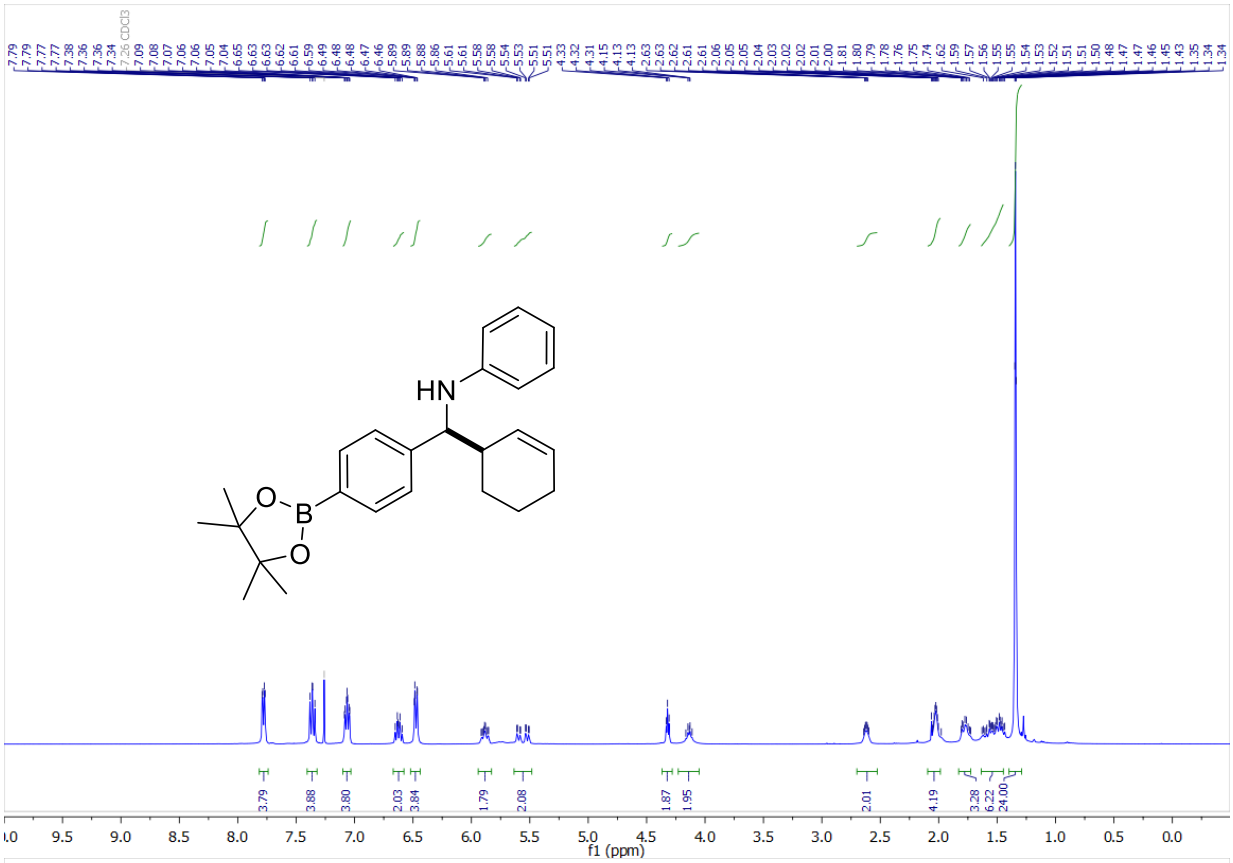
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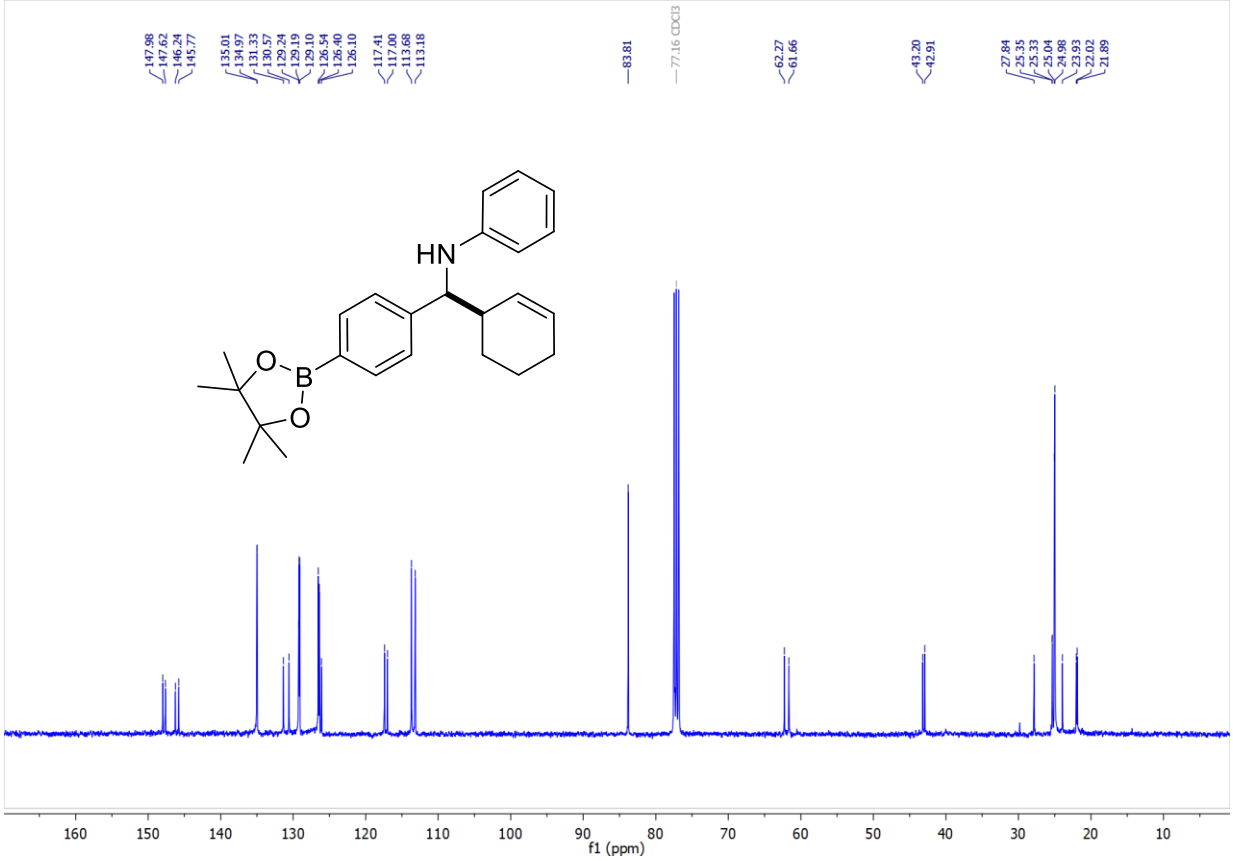
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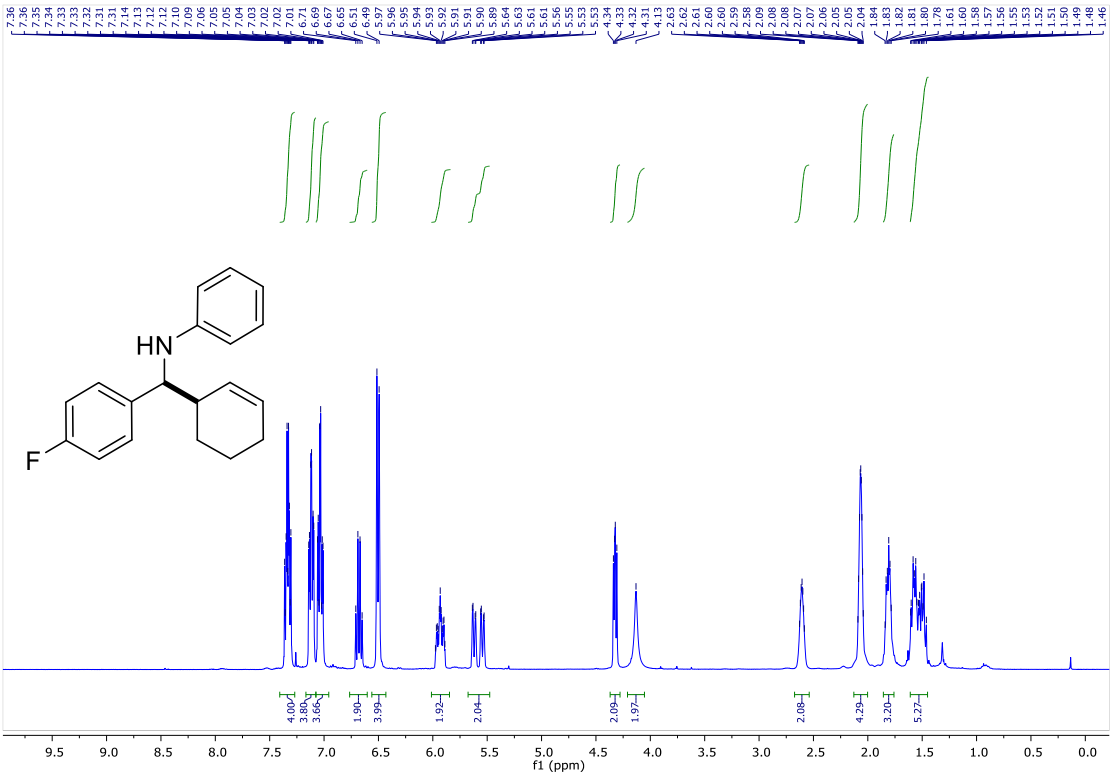
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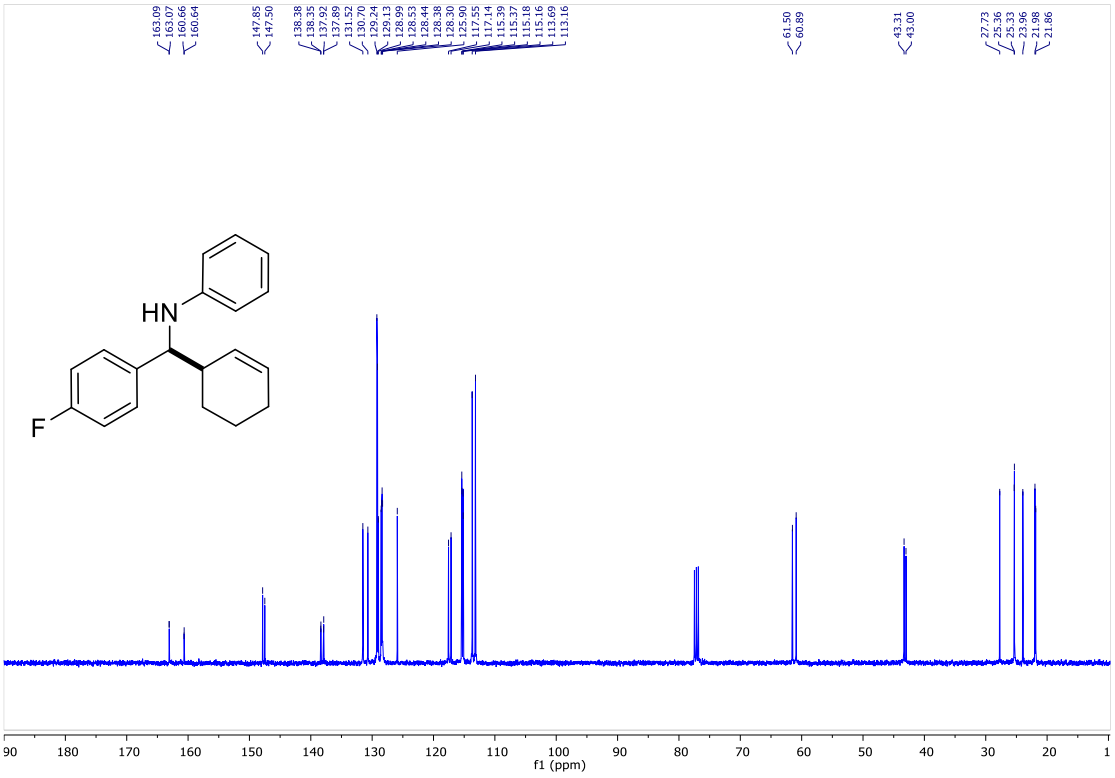
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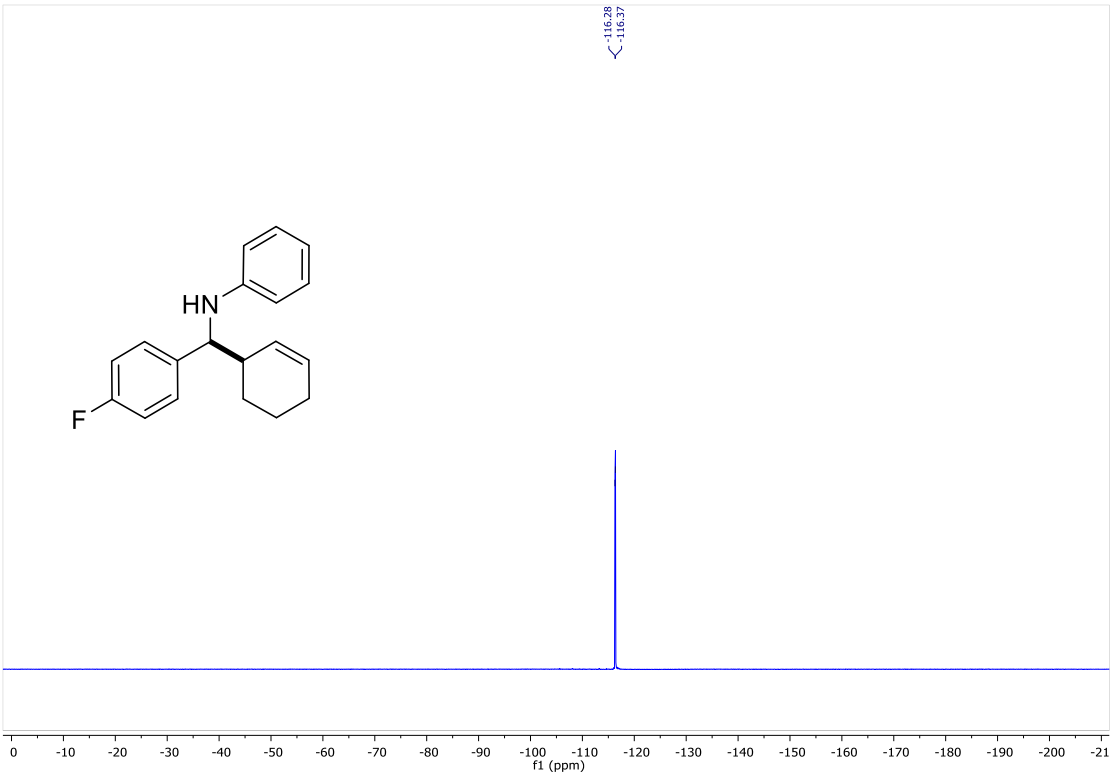
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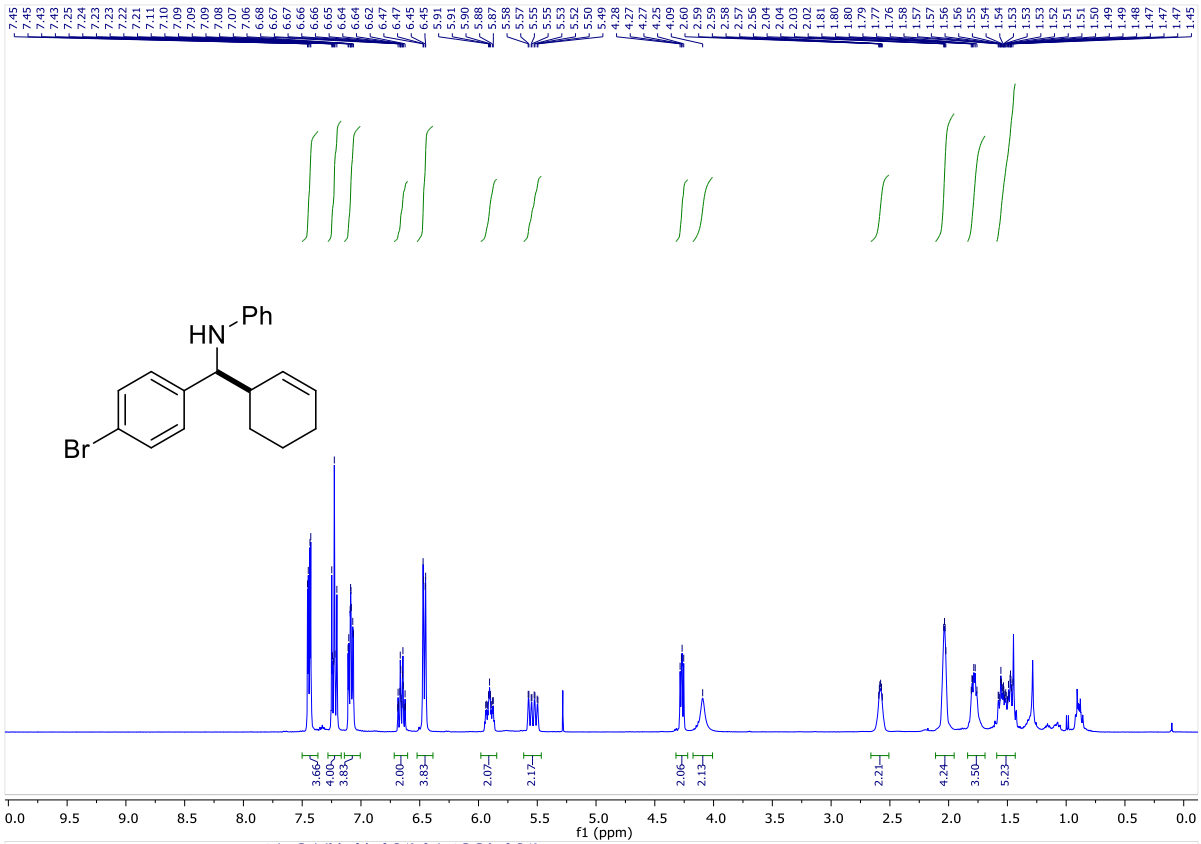
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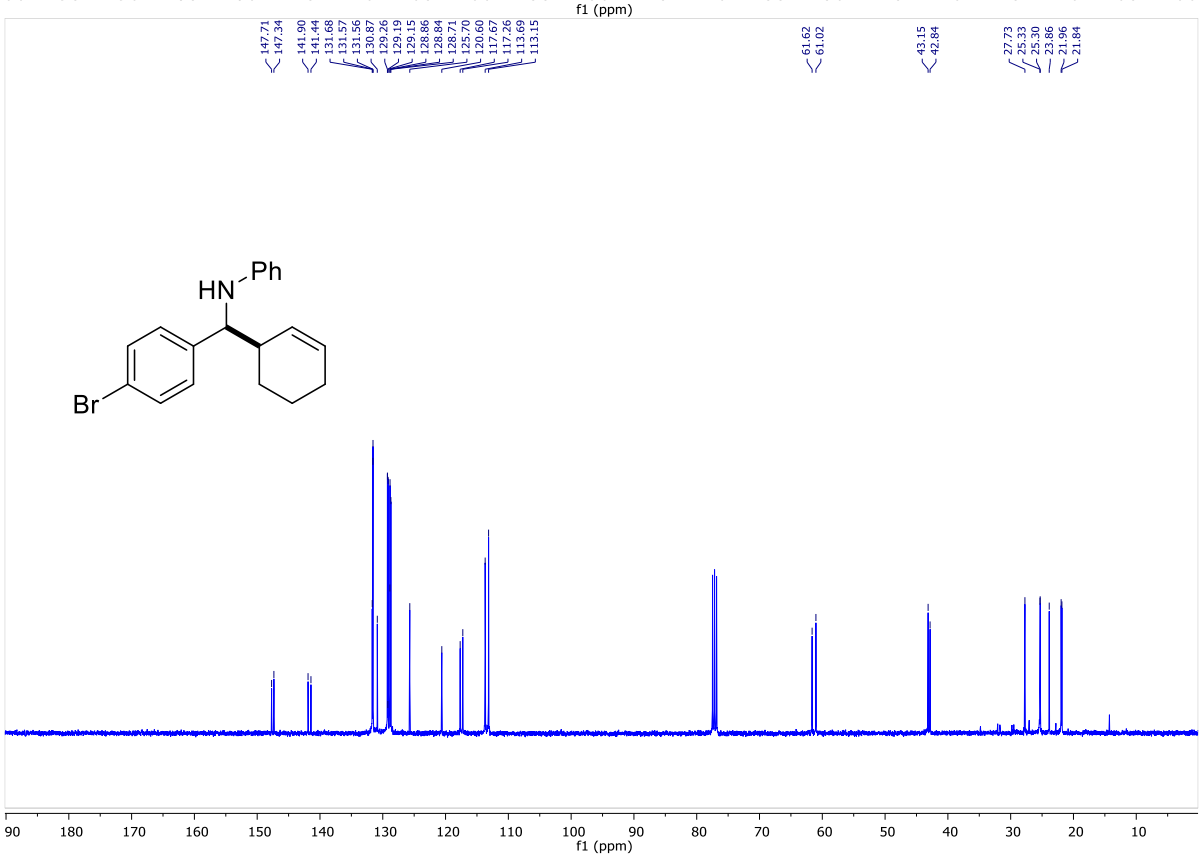
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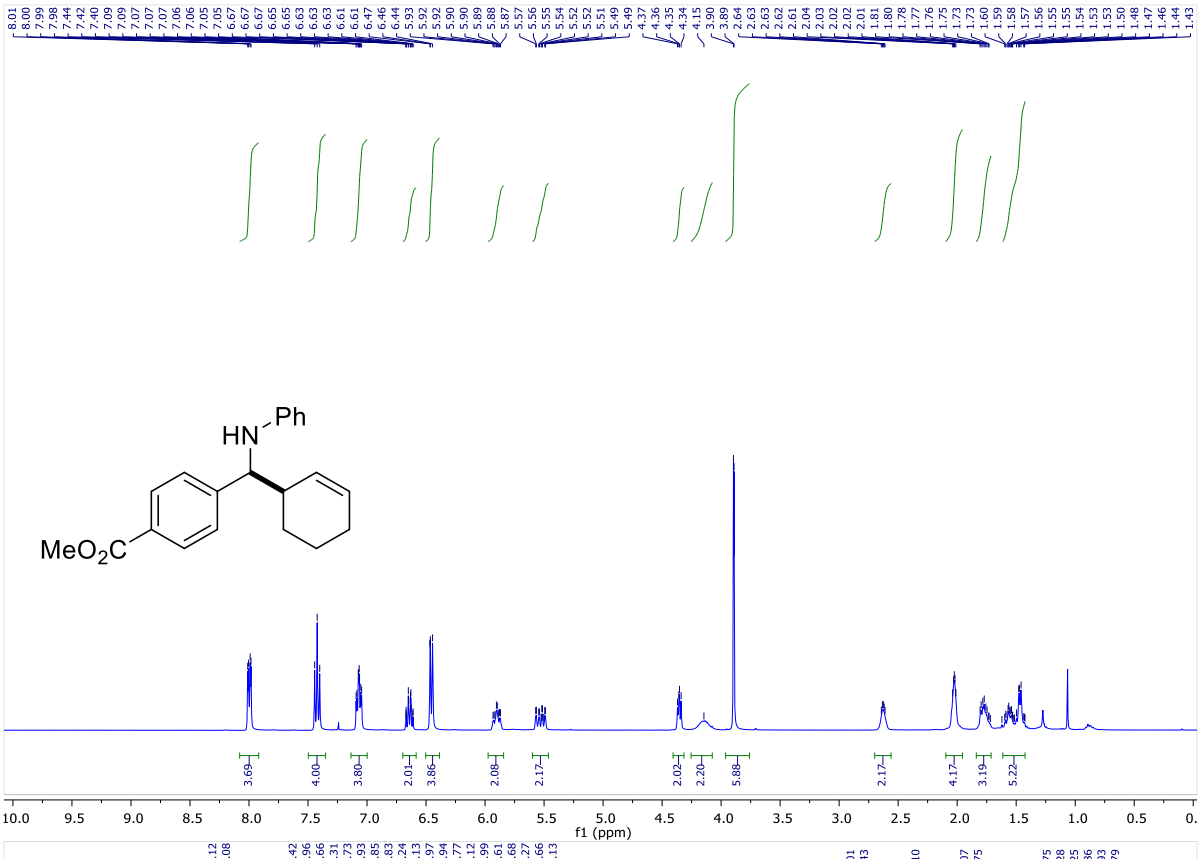
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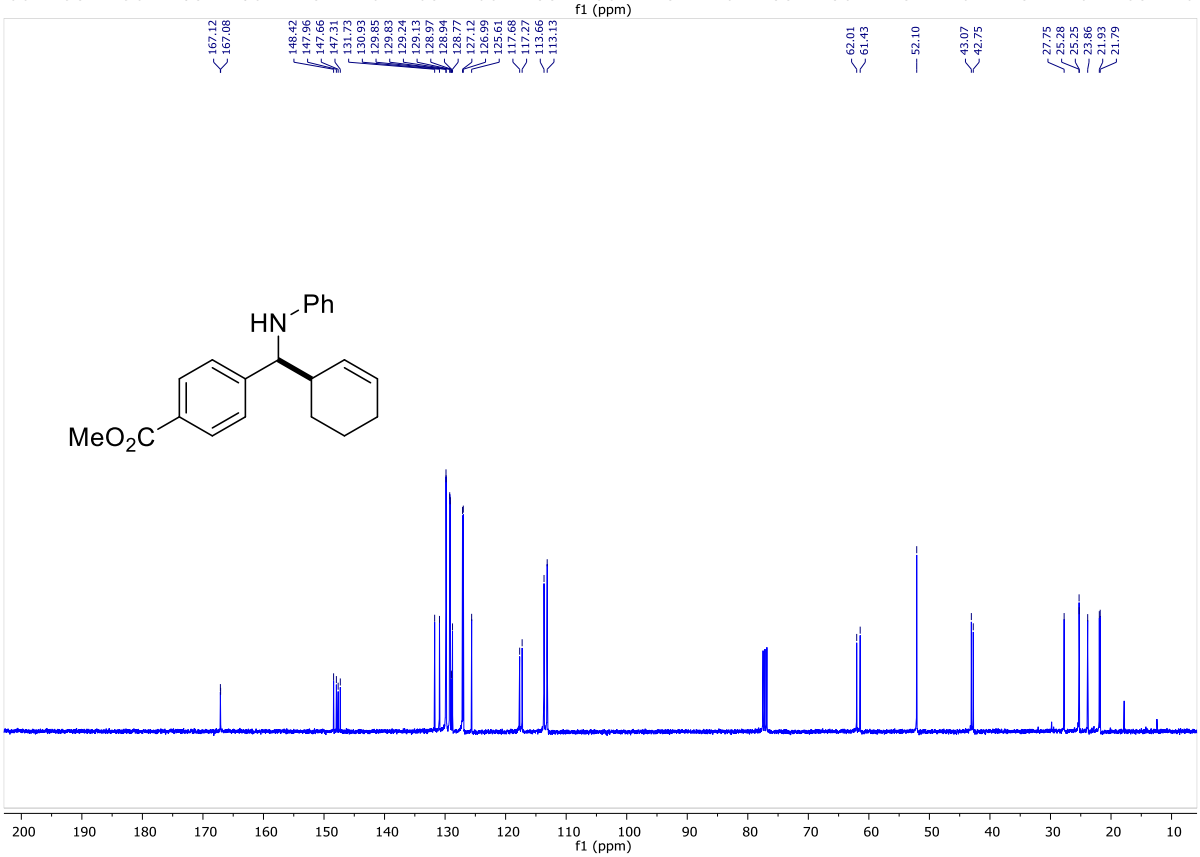
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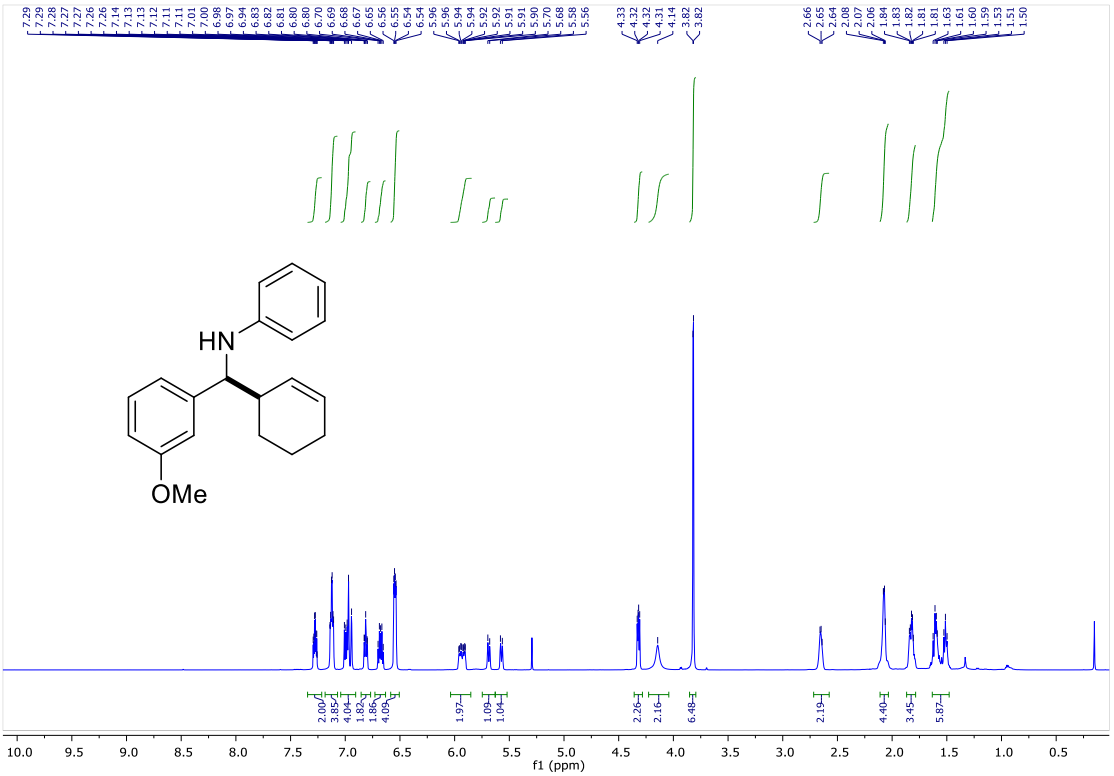
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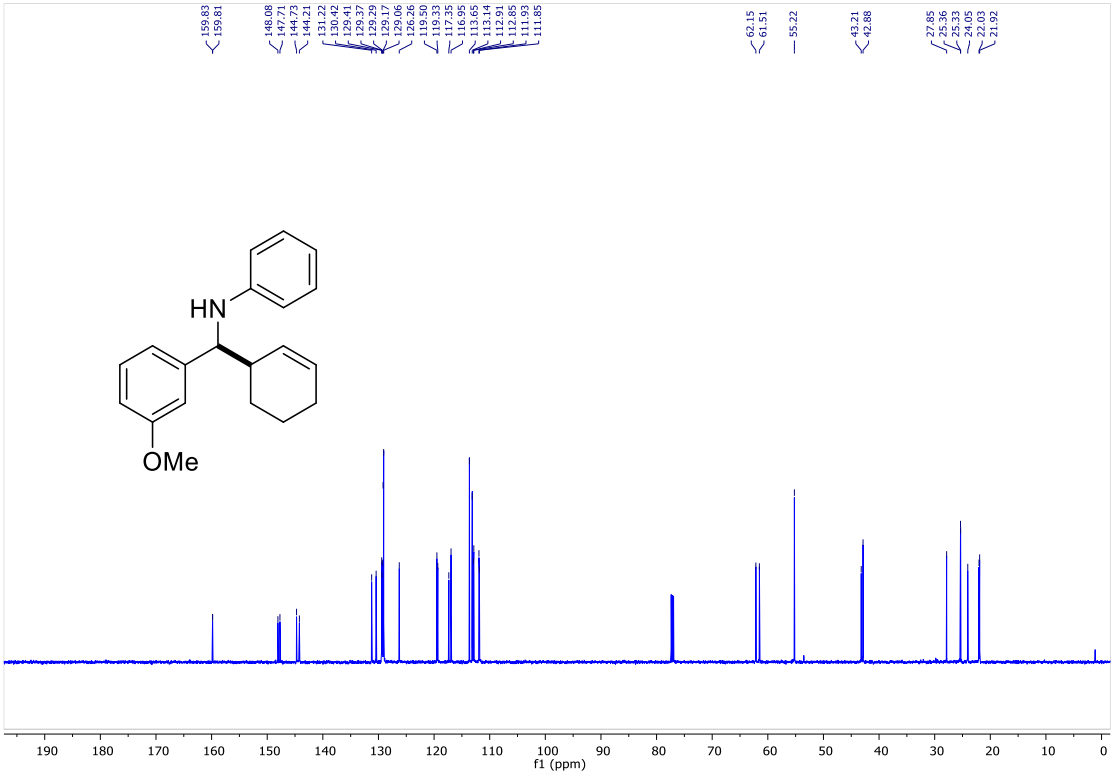
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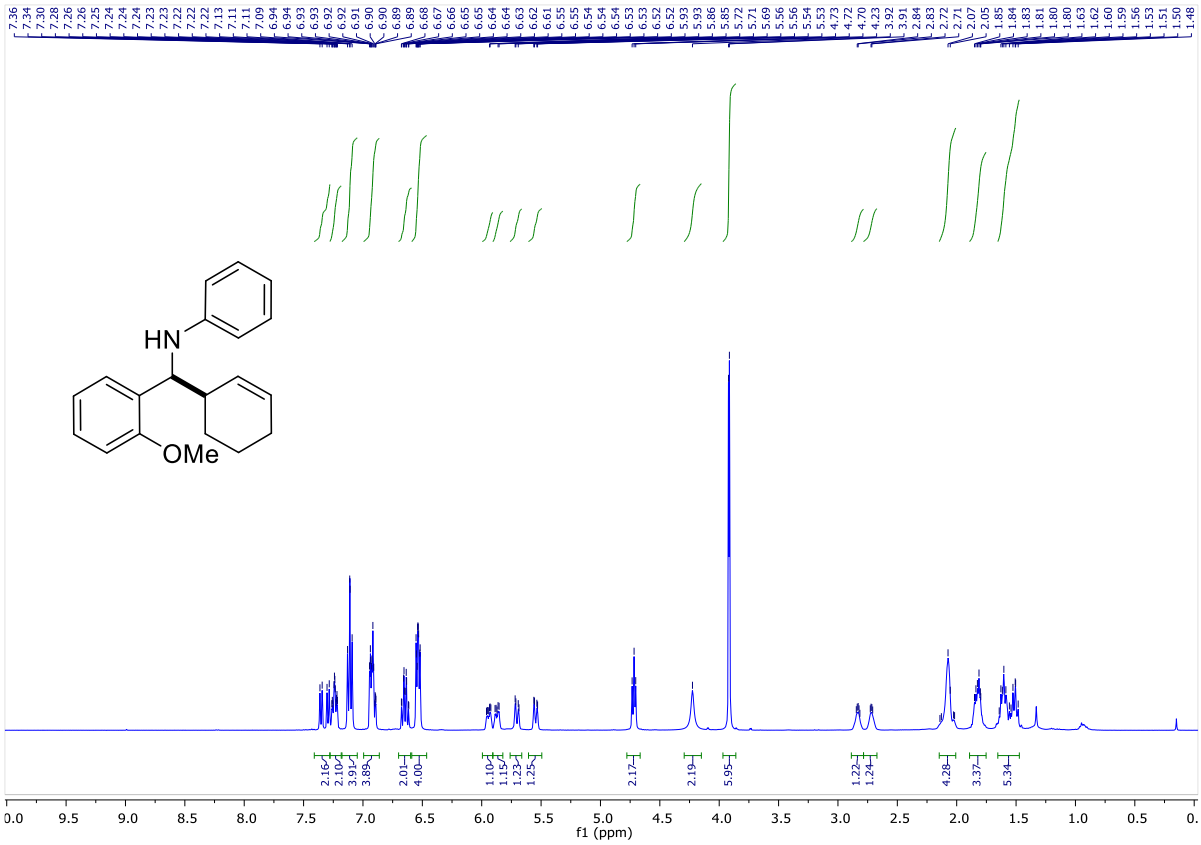
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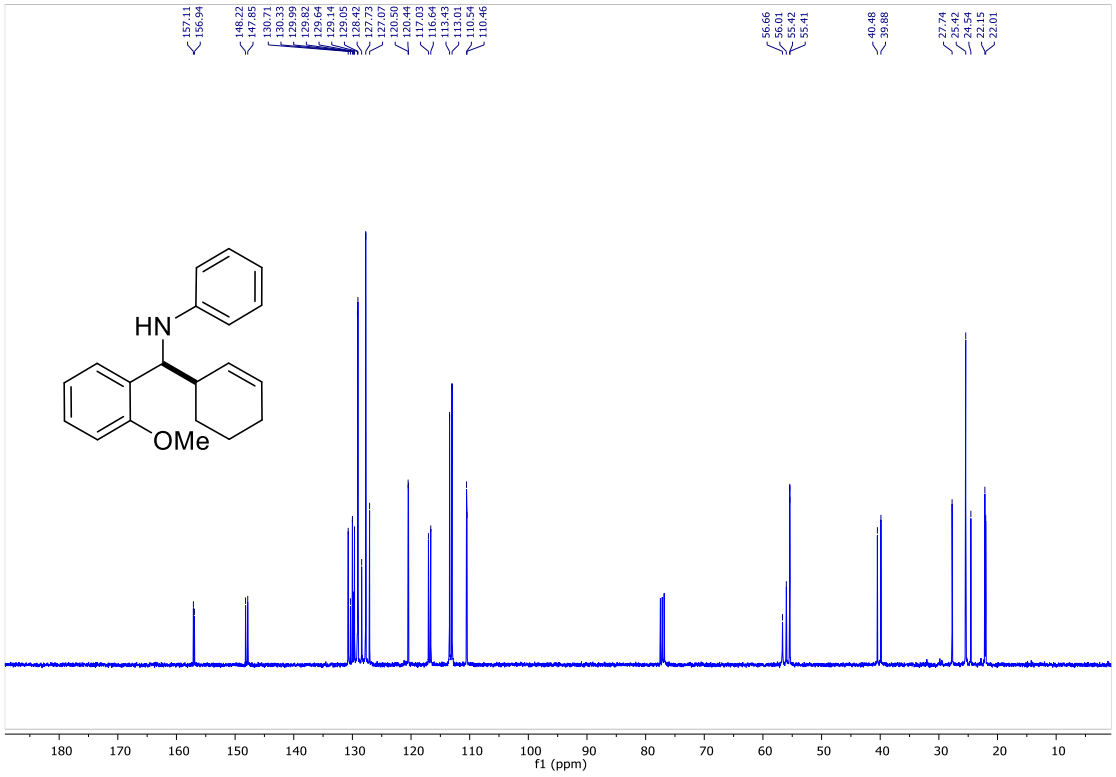
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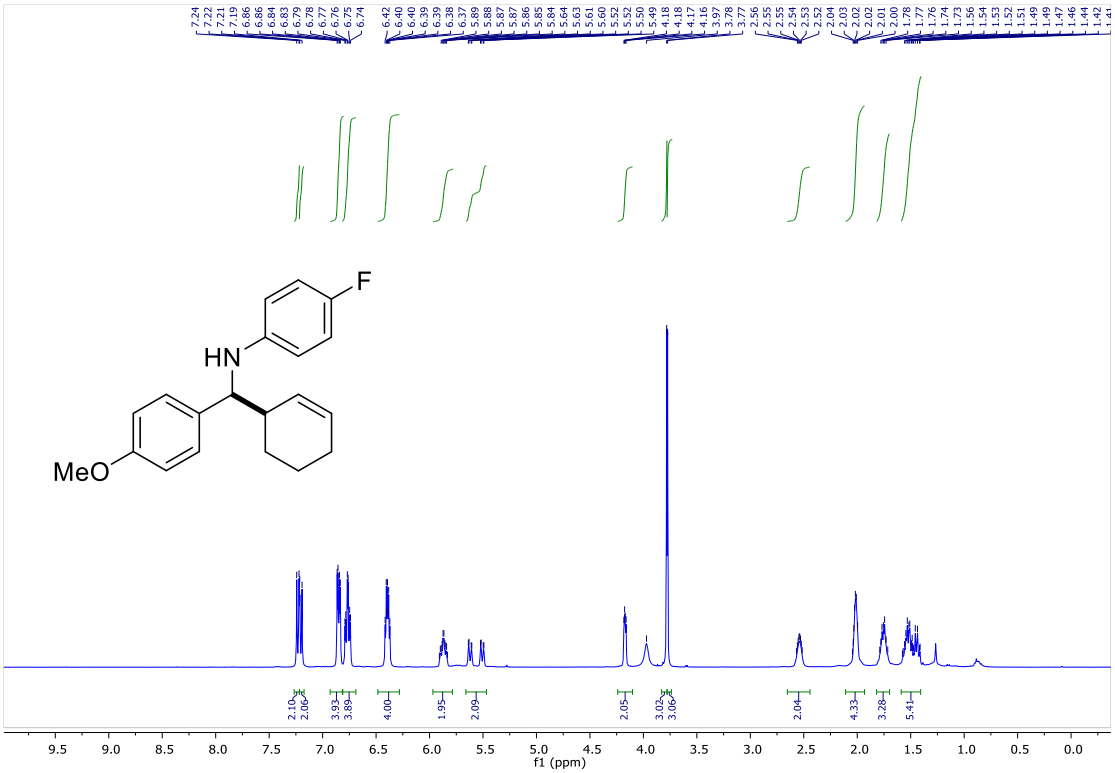
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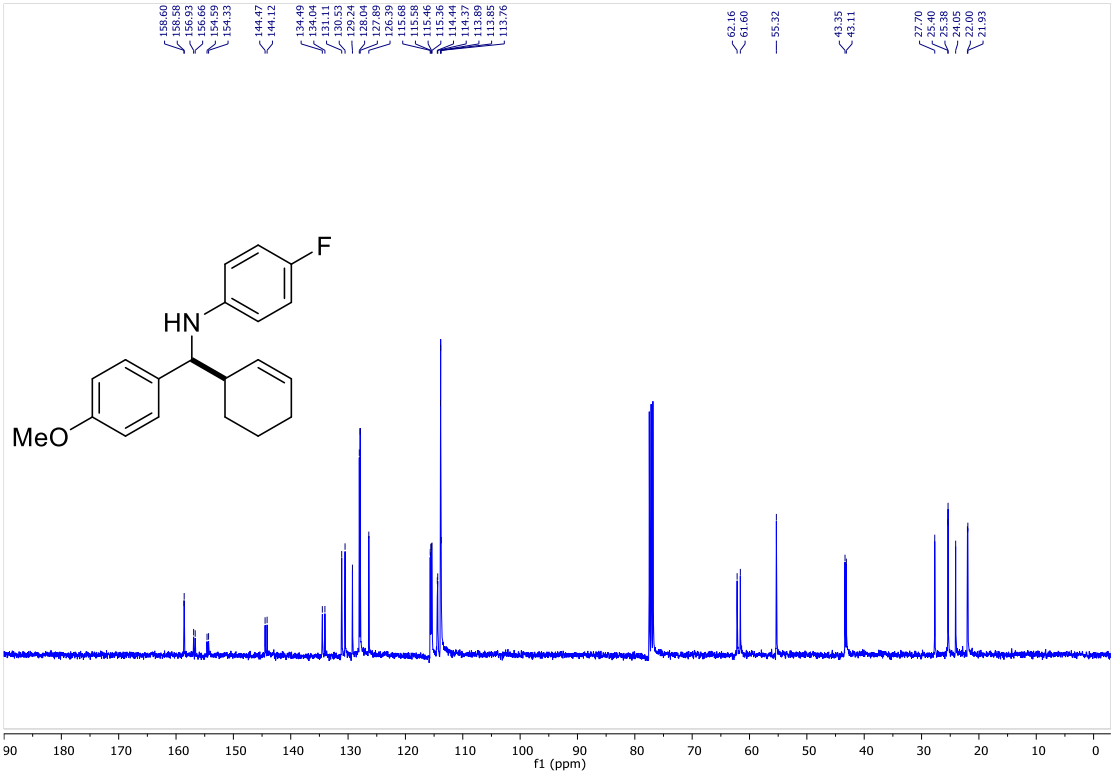
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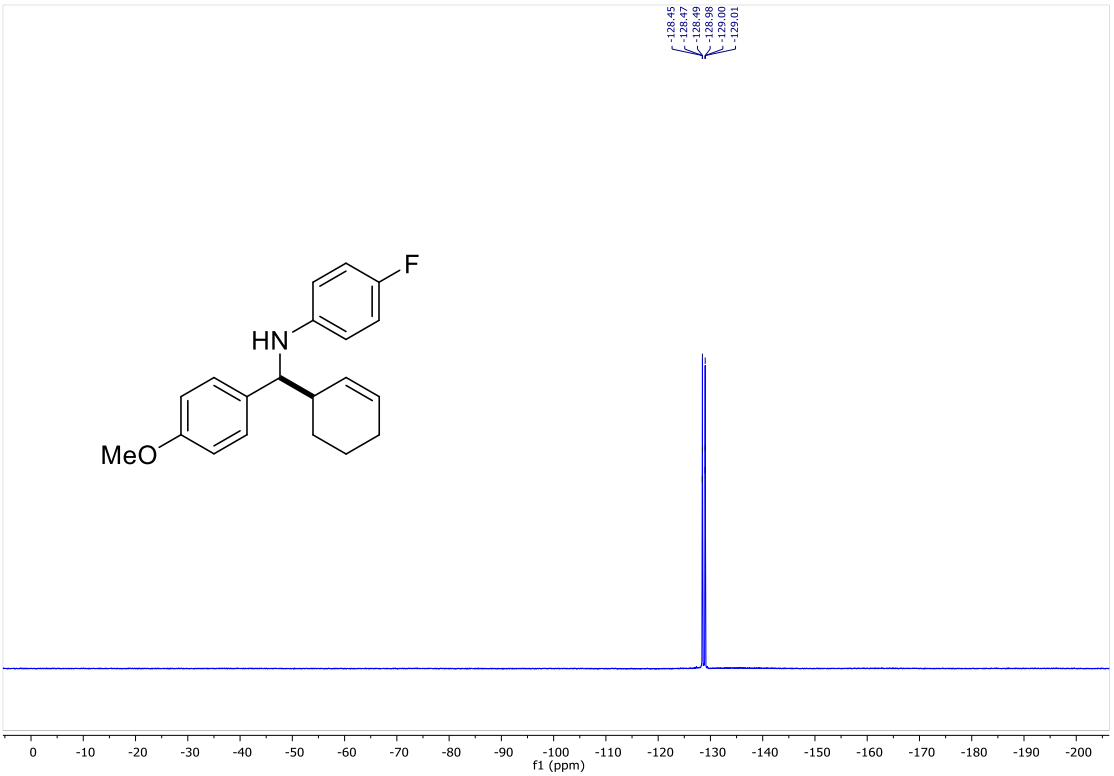
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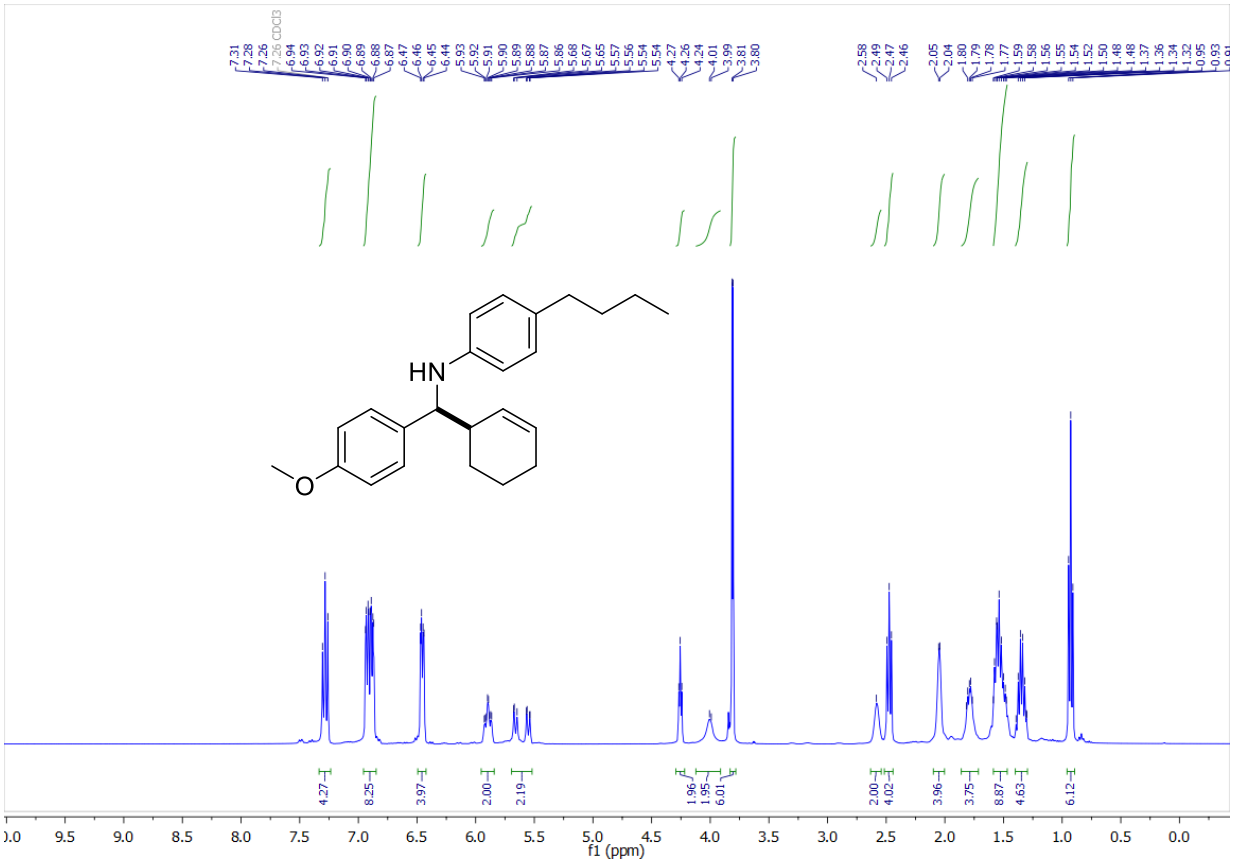
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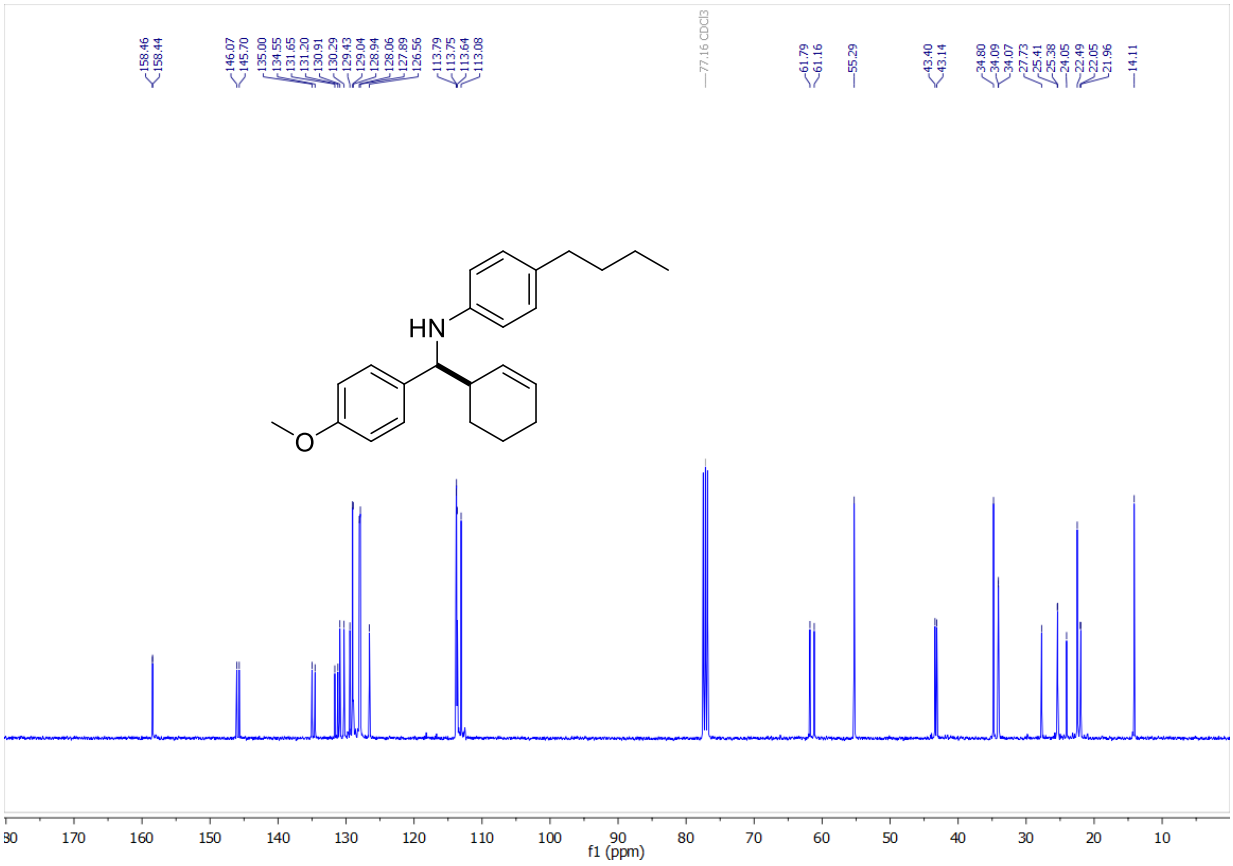
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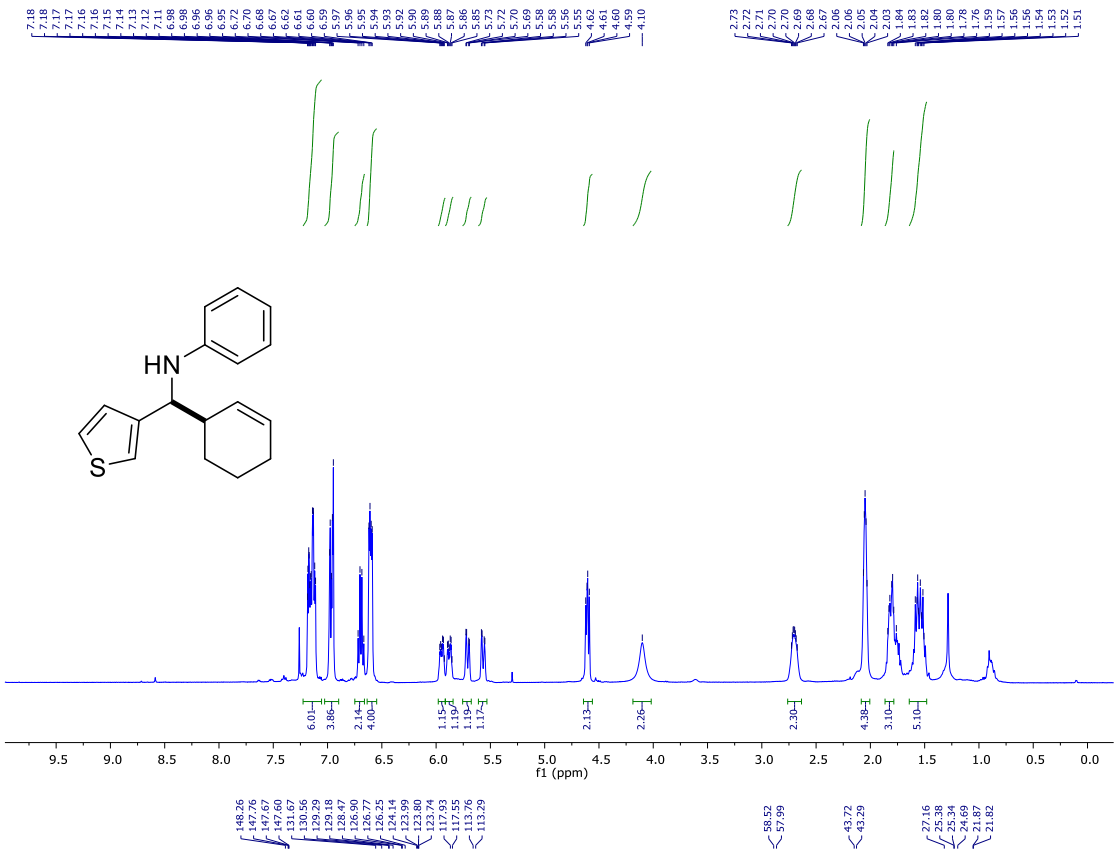
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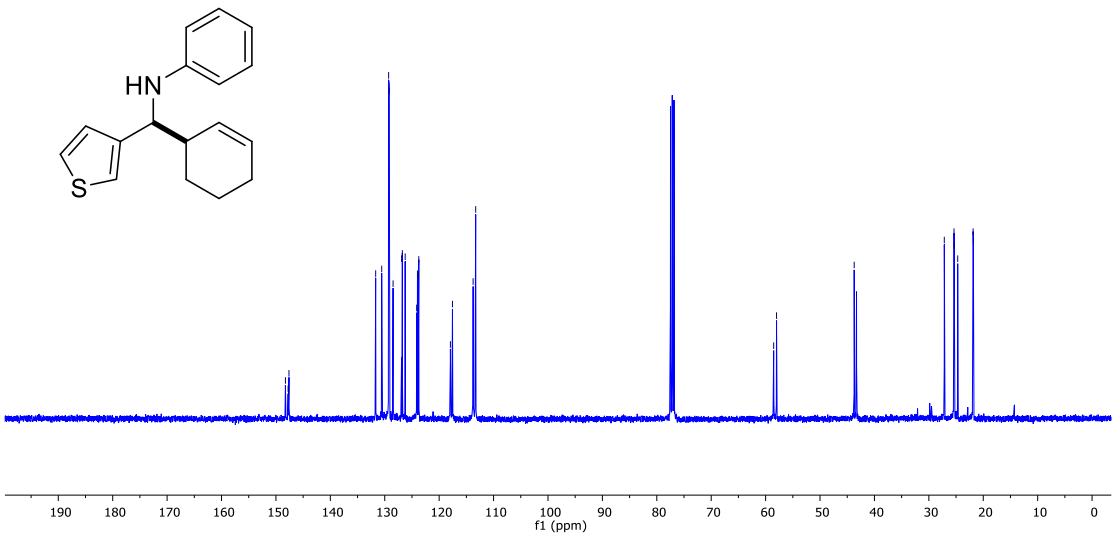
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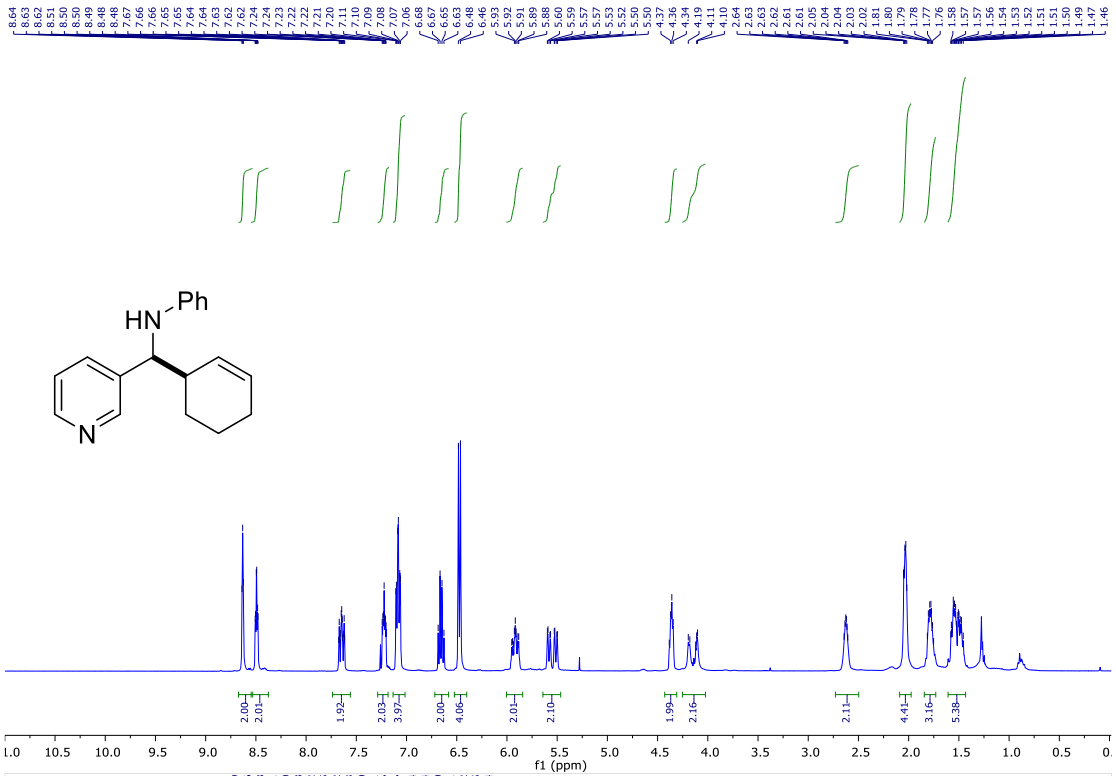
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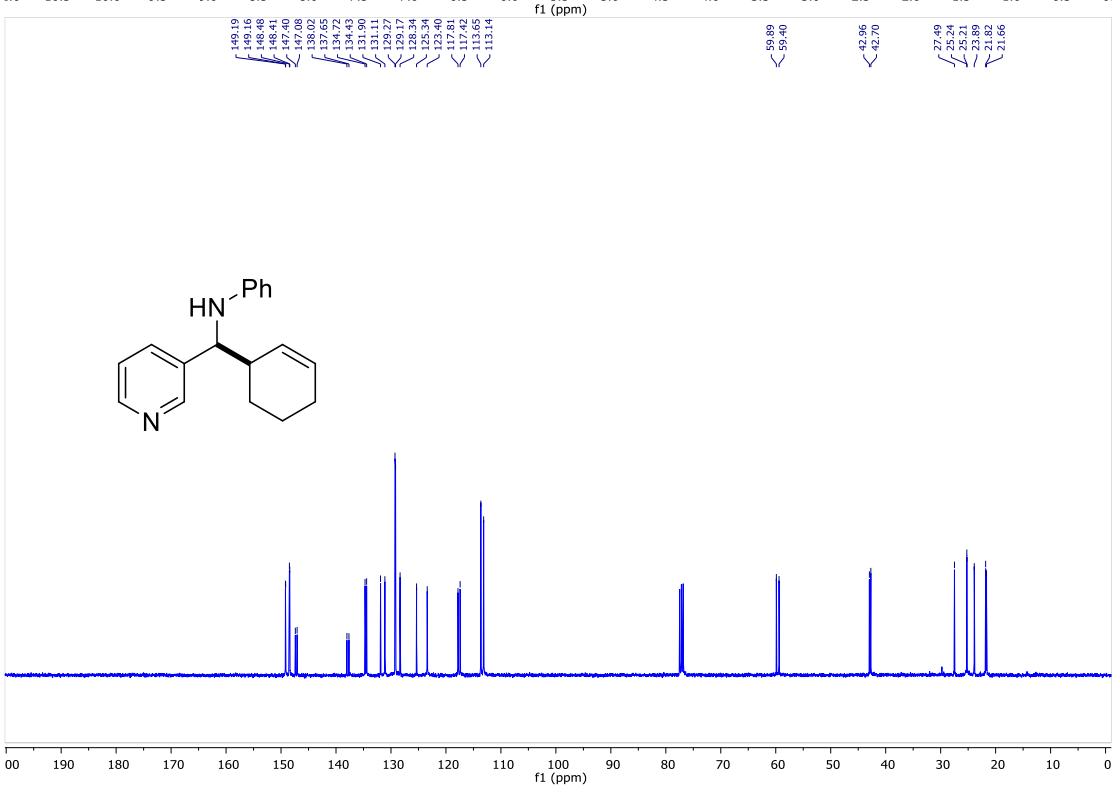
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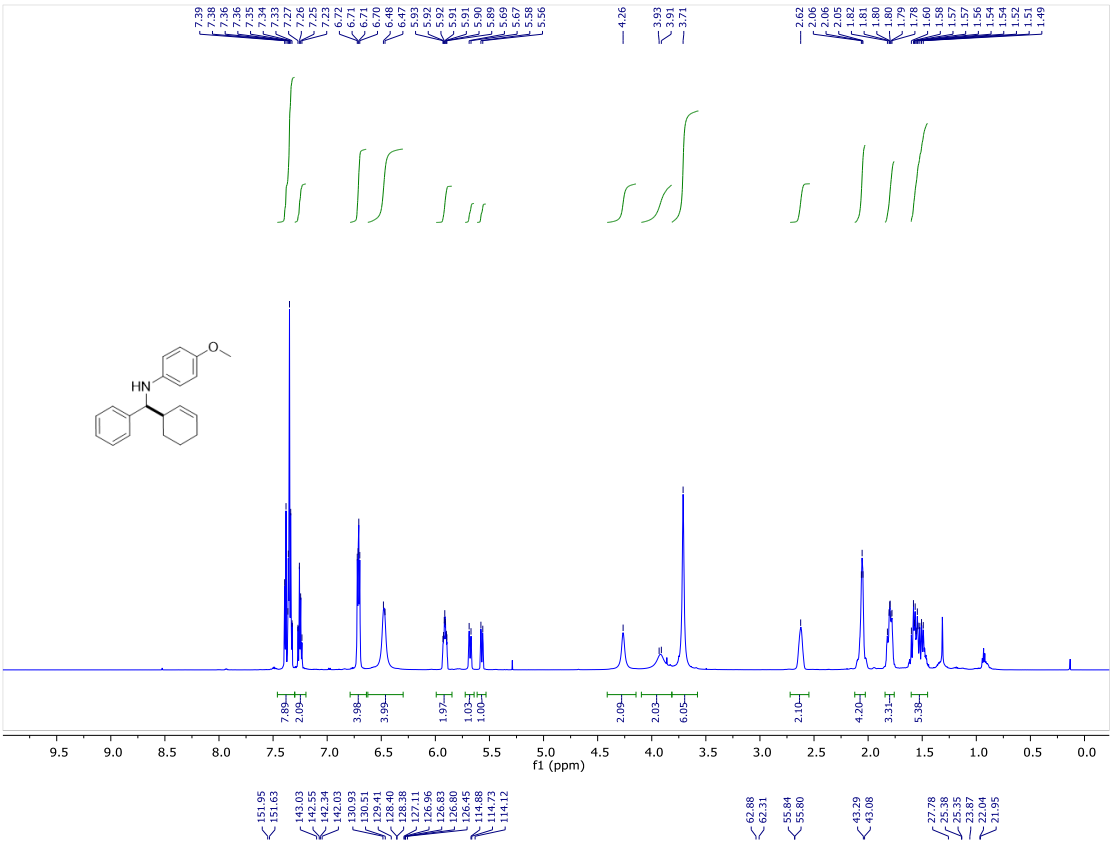
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3.71
2.62
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2.06
2.05
1.82
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1.57
1.57
1.56
1.54
1.54
1.52
1.51
1.49
HN
O
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2.09
3.98
3.99
1.97
1.03
1.00
2.09
2.03
6.05
2.10
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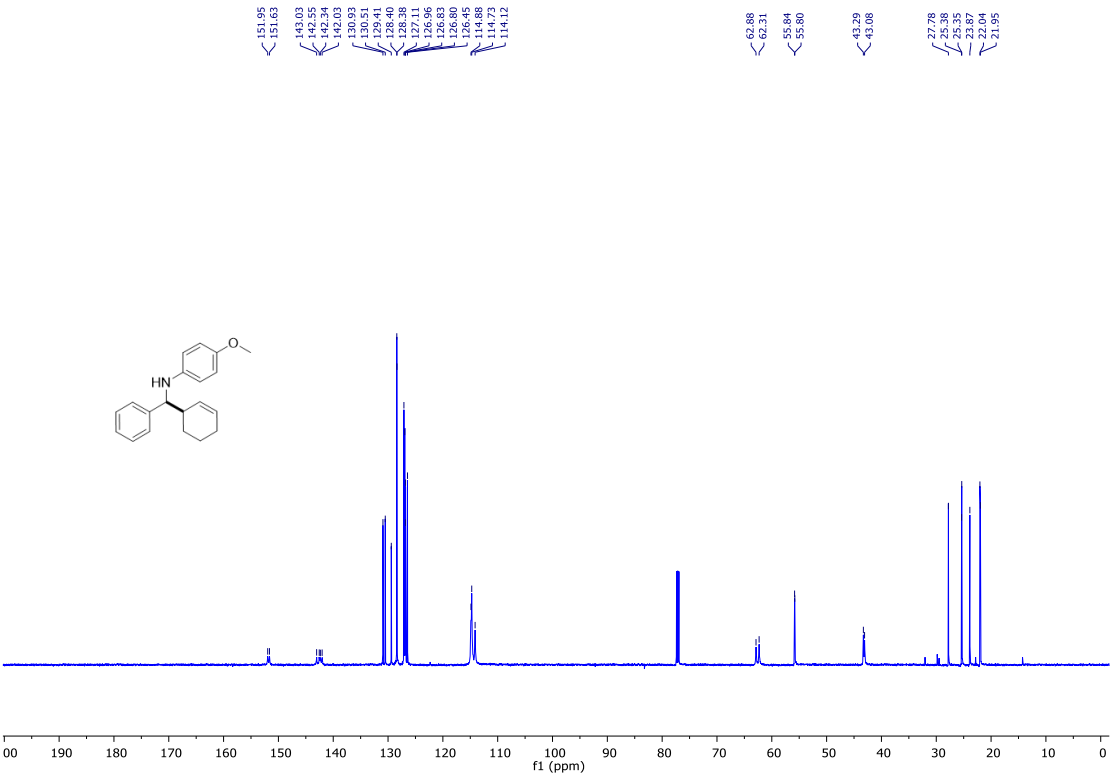
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114.88
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114.12
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62.31
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25.35
23.87
21.04
21.95
HN
O
00
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180
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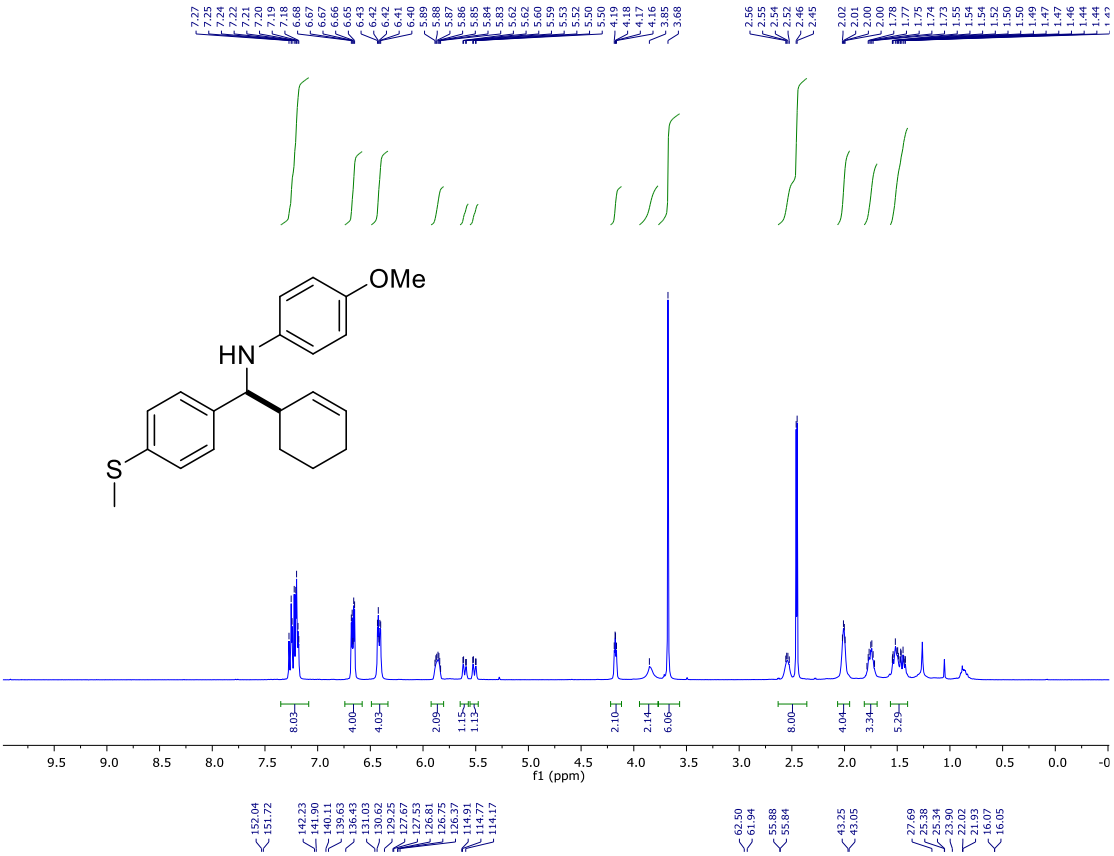
f1 (ppm)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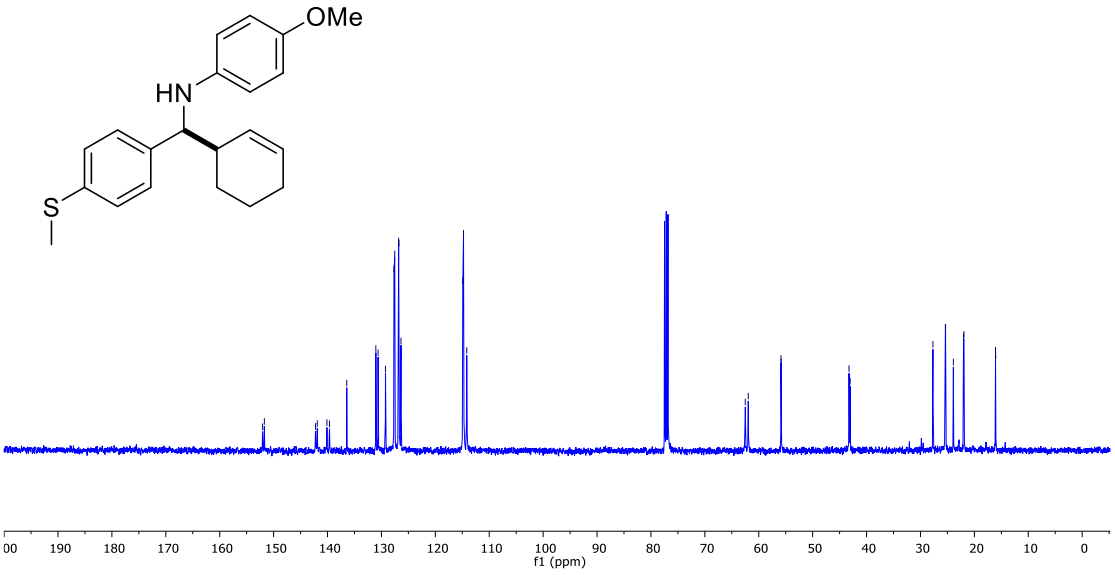
f1 (ppm)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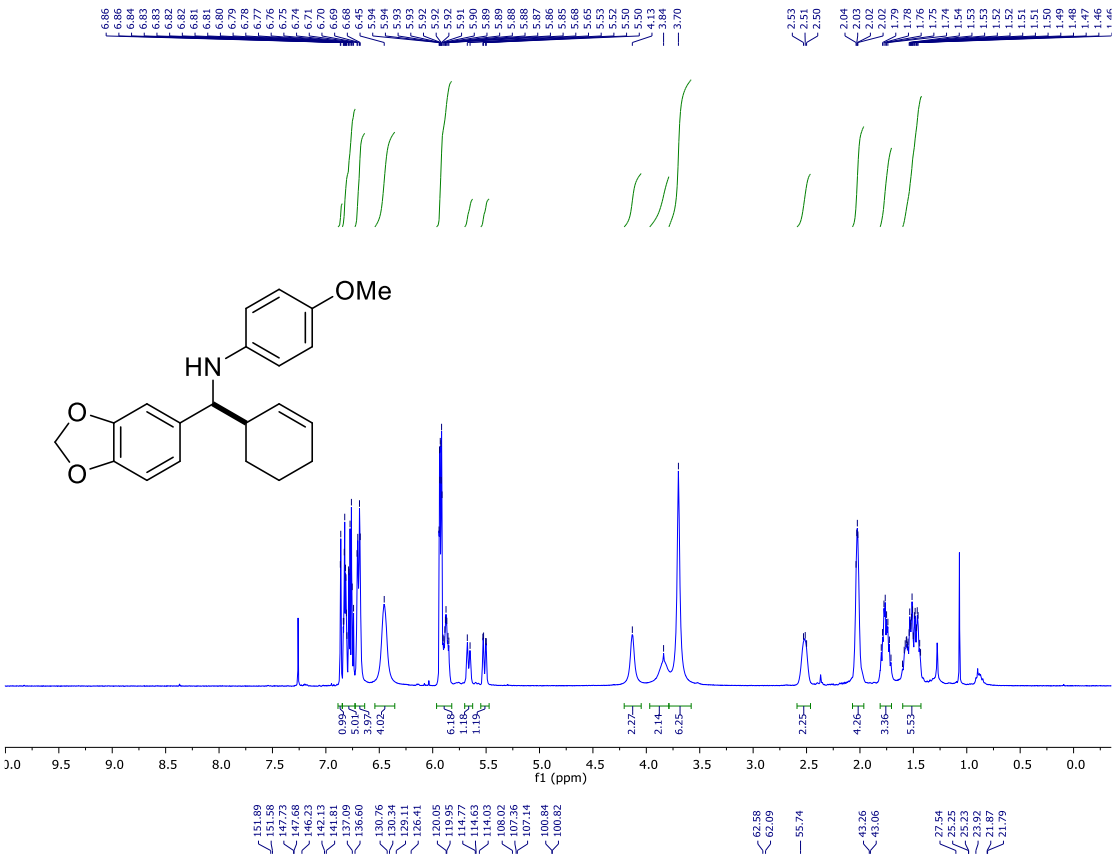
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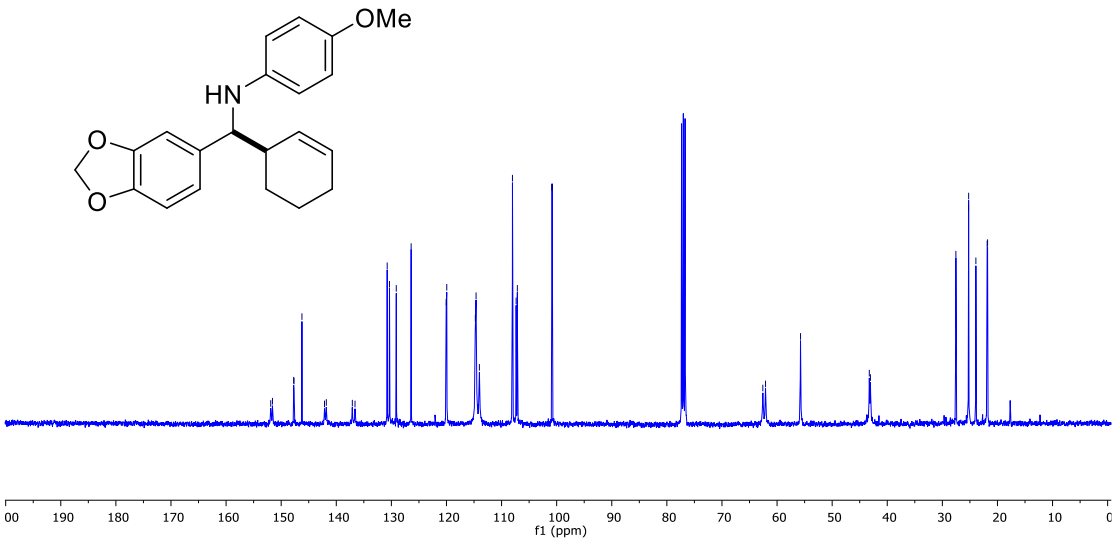
f1 (ppm)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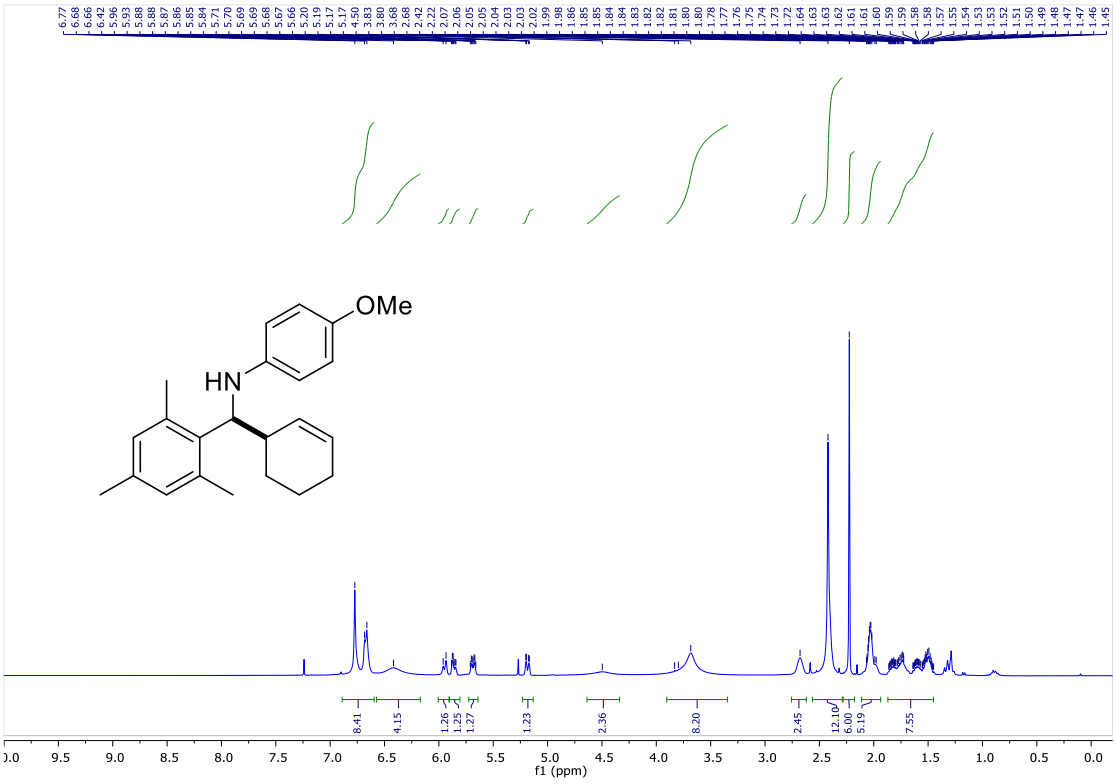
f1 (ppm)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HN
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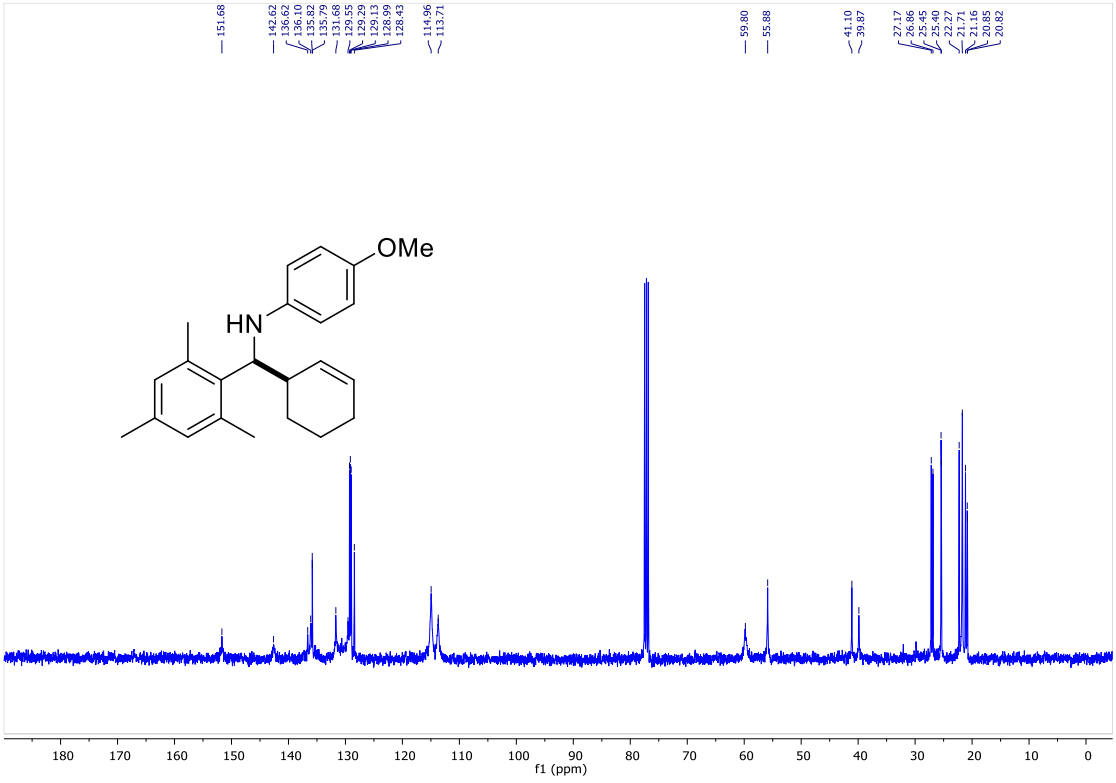
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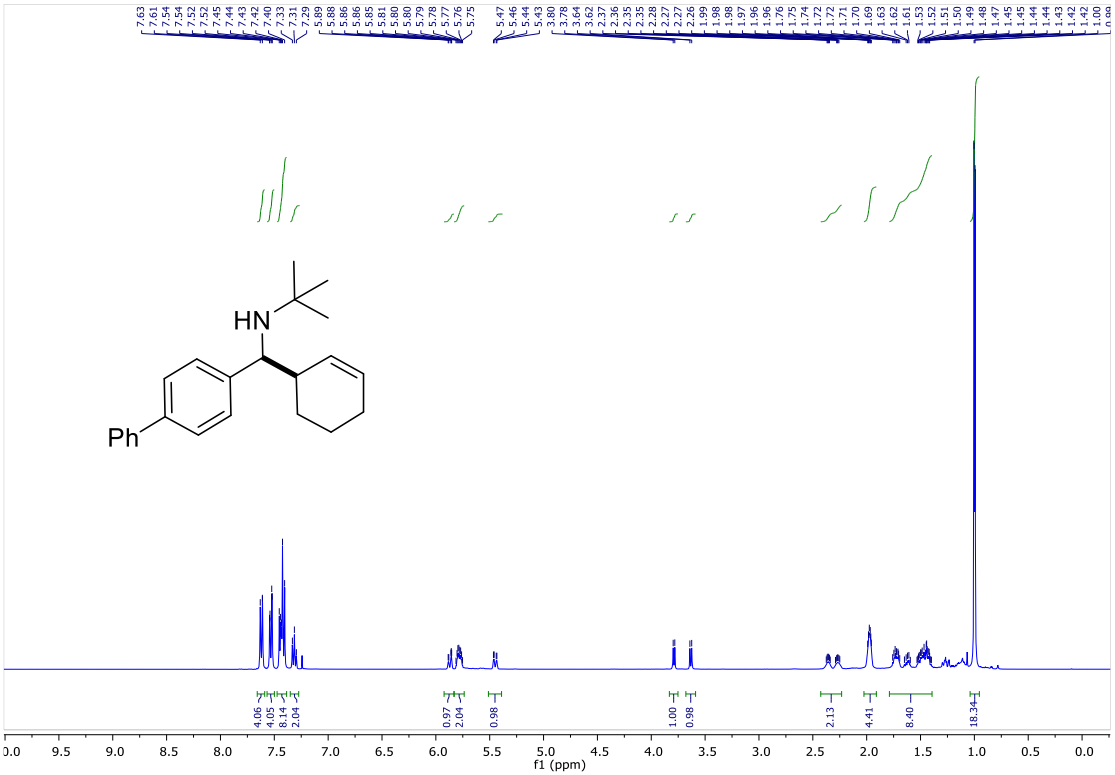
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Ph
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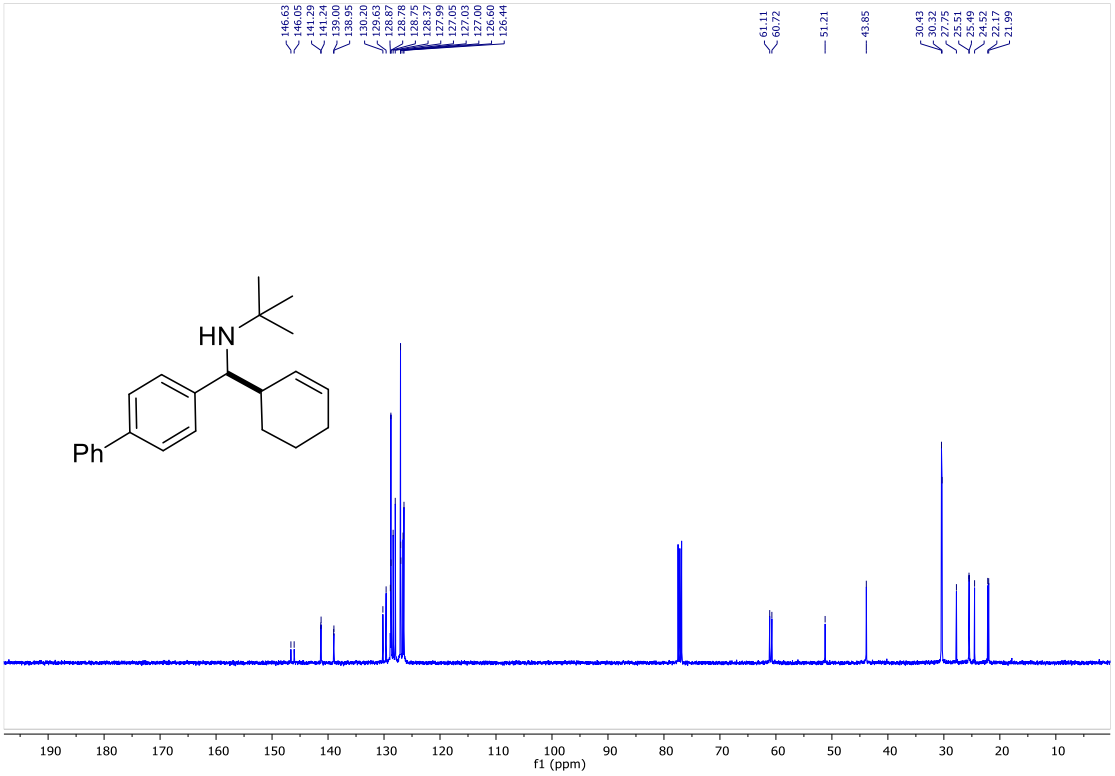
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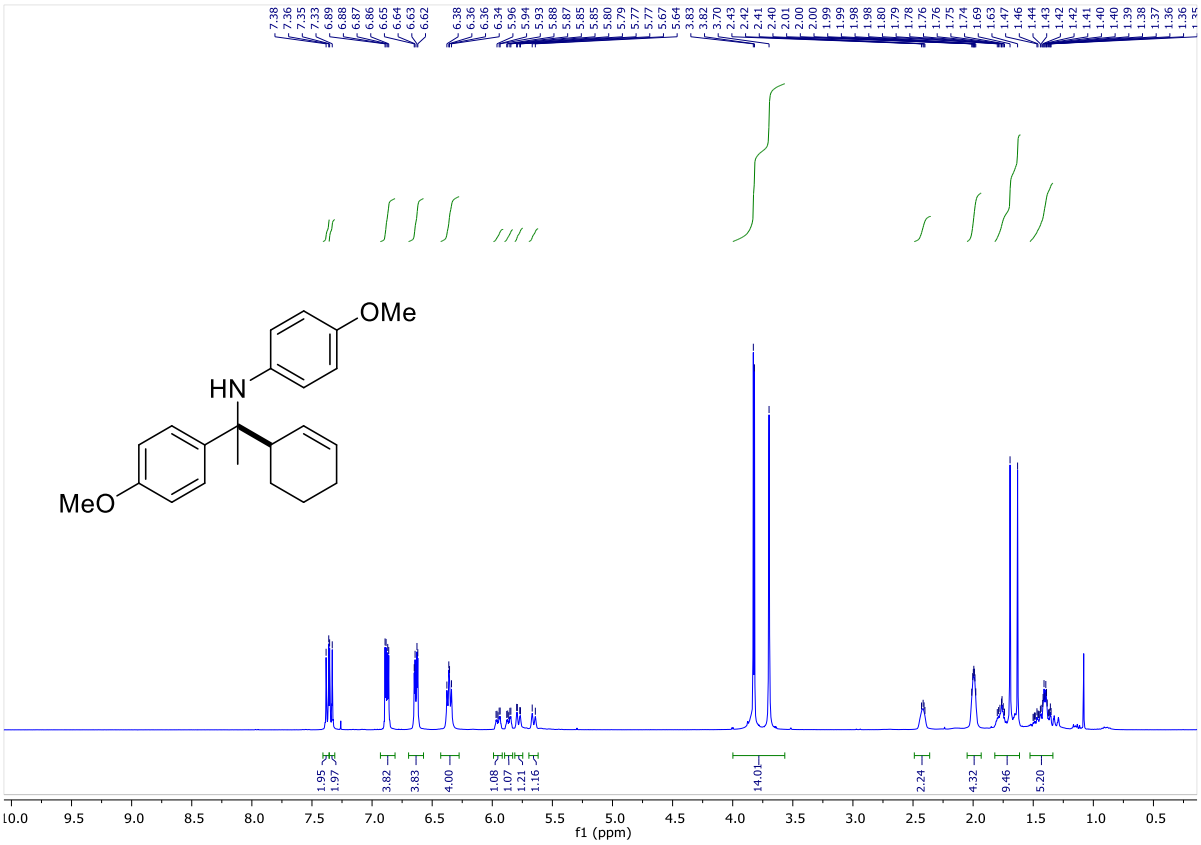
Ph
f1 (ppm)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HN
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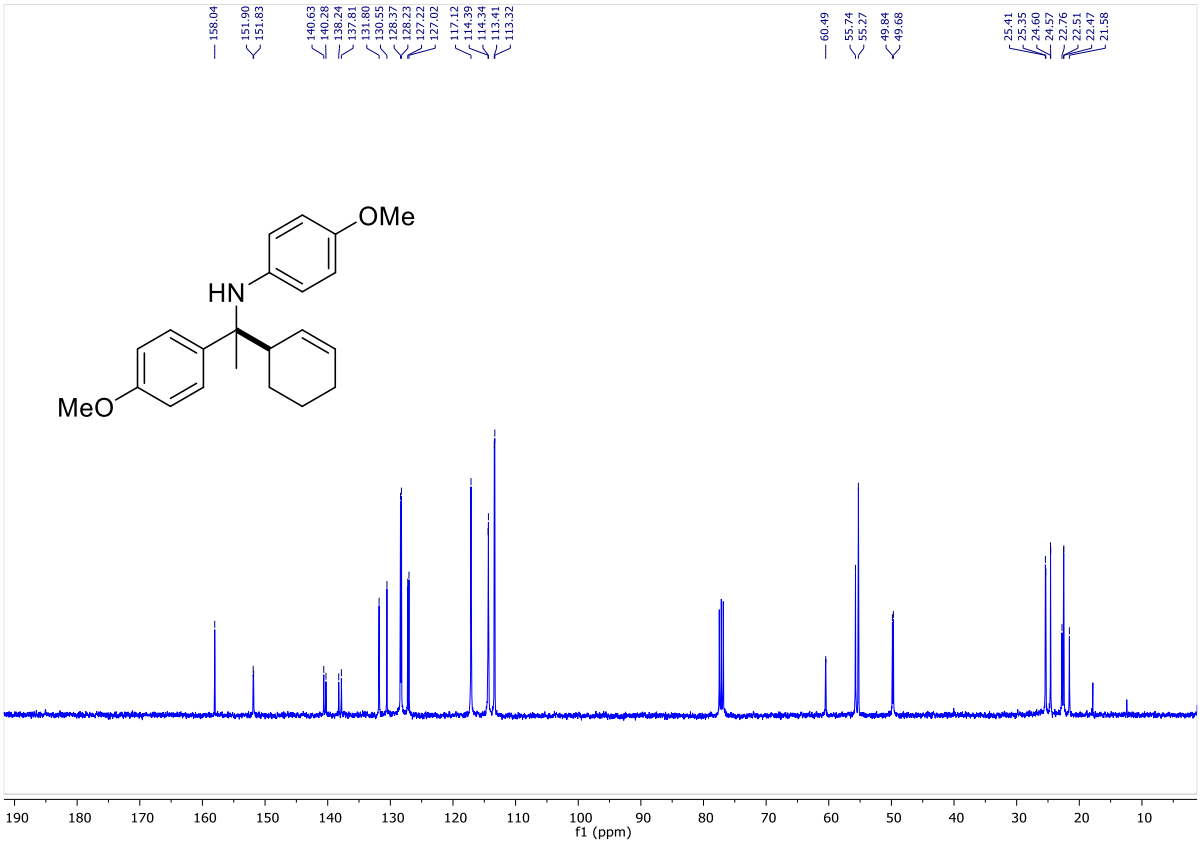
f1 (ppm)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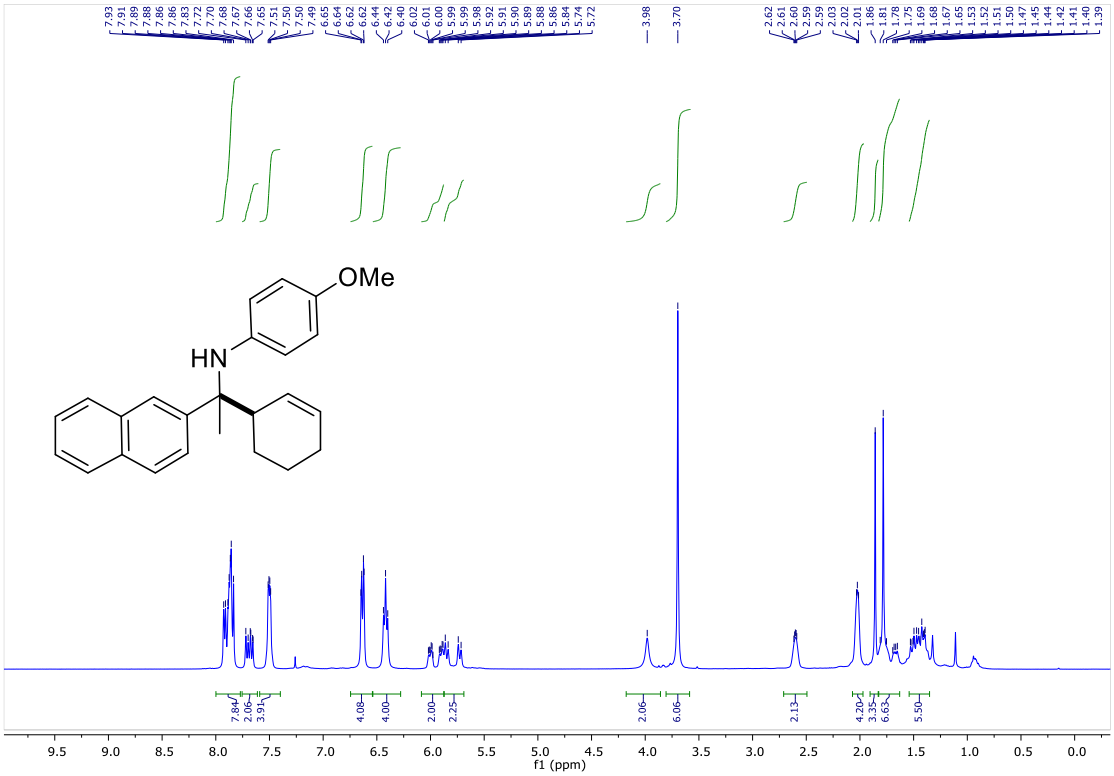
f1 (ppm)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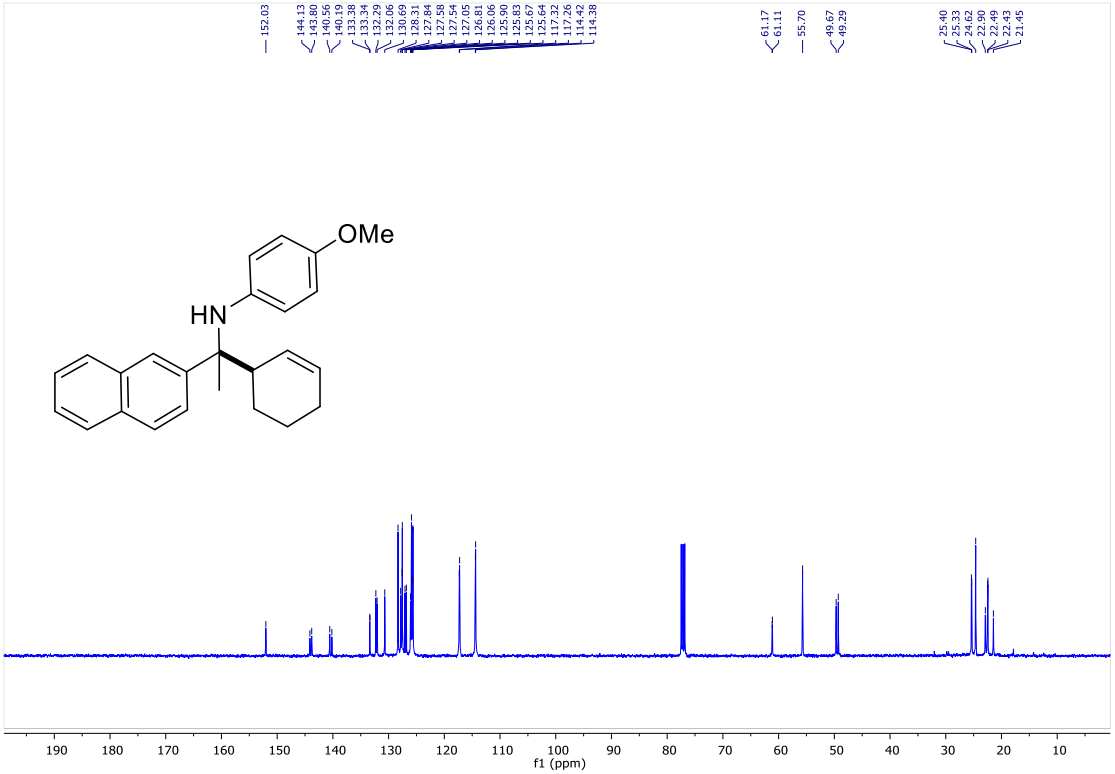
f1 (ppm)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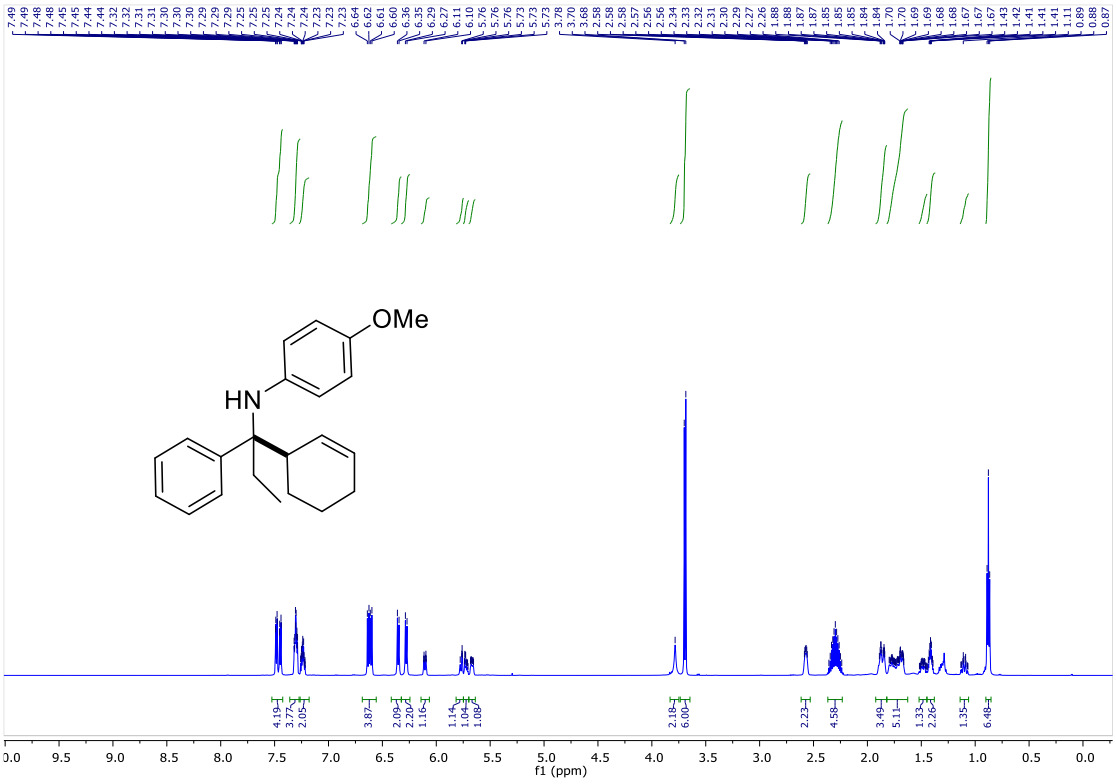
HN
f1 (ppm)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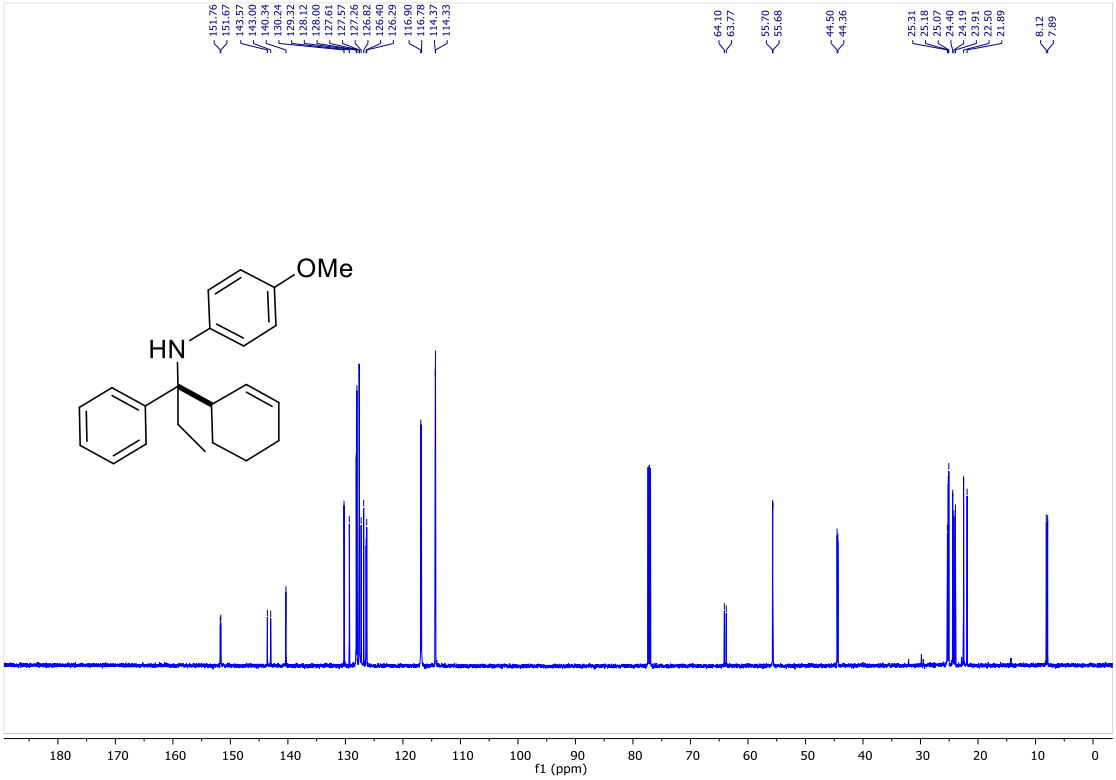
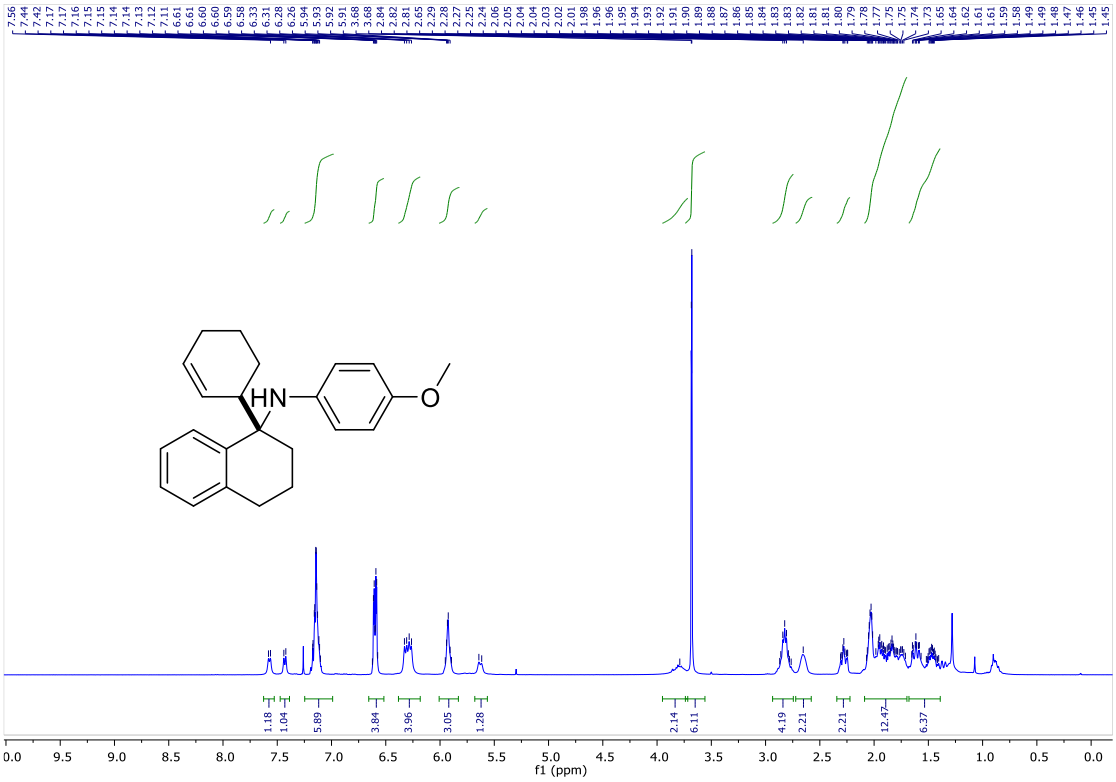

OMe
HN
f1 (ppm)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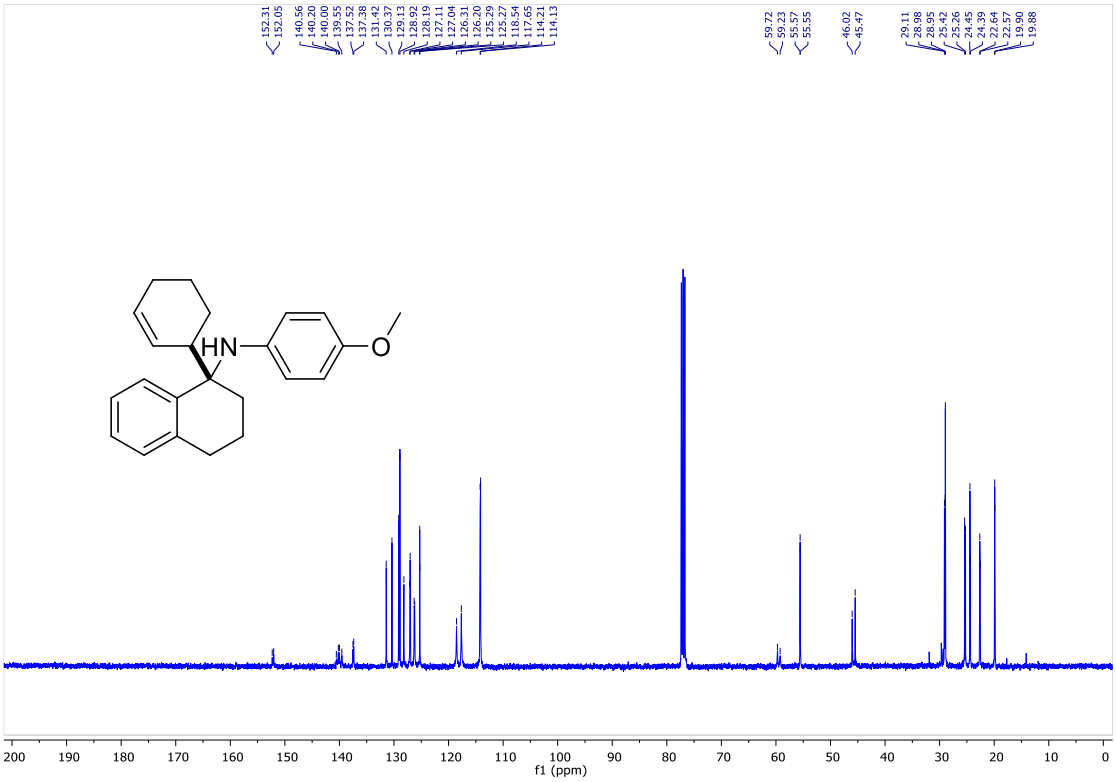
f1 (ppm)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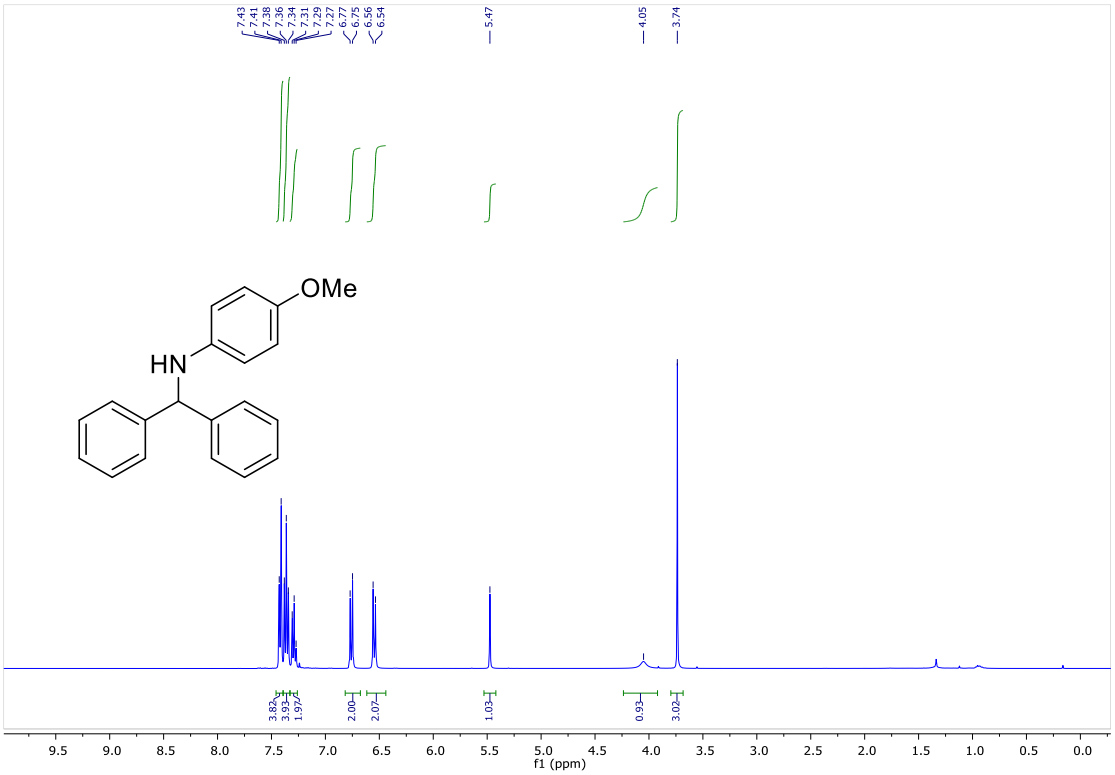
O
f1 (ppm)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6.56
6.54
5.47
4.05
3.74
OMe
HN
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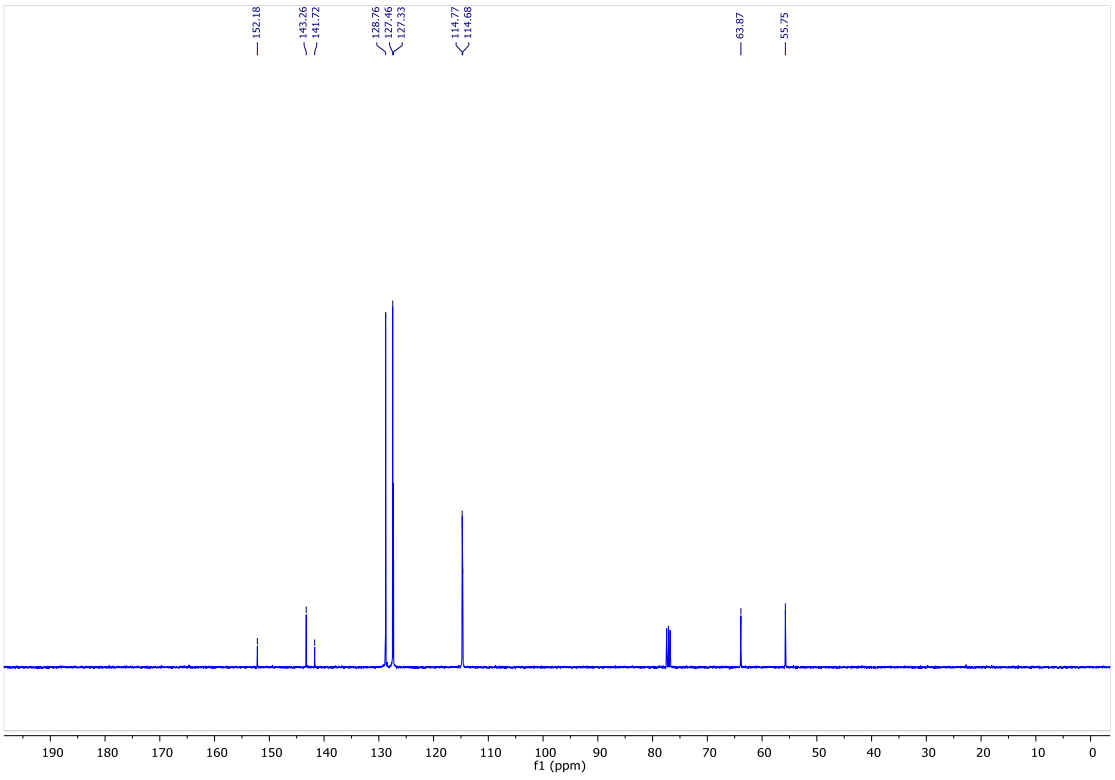
3.93
1.97
2.00
2.07
1.03
0.93
3.02
f1 (ppm)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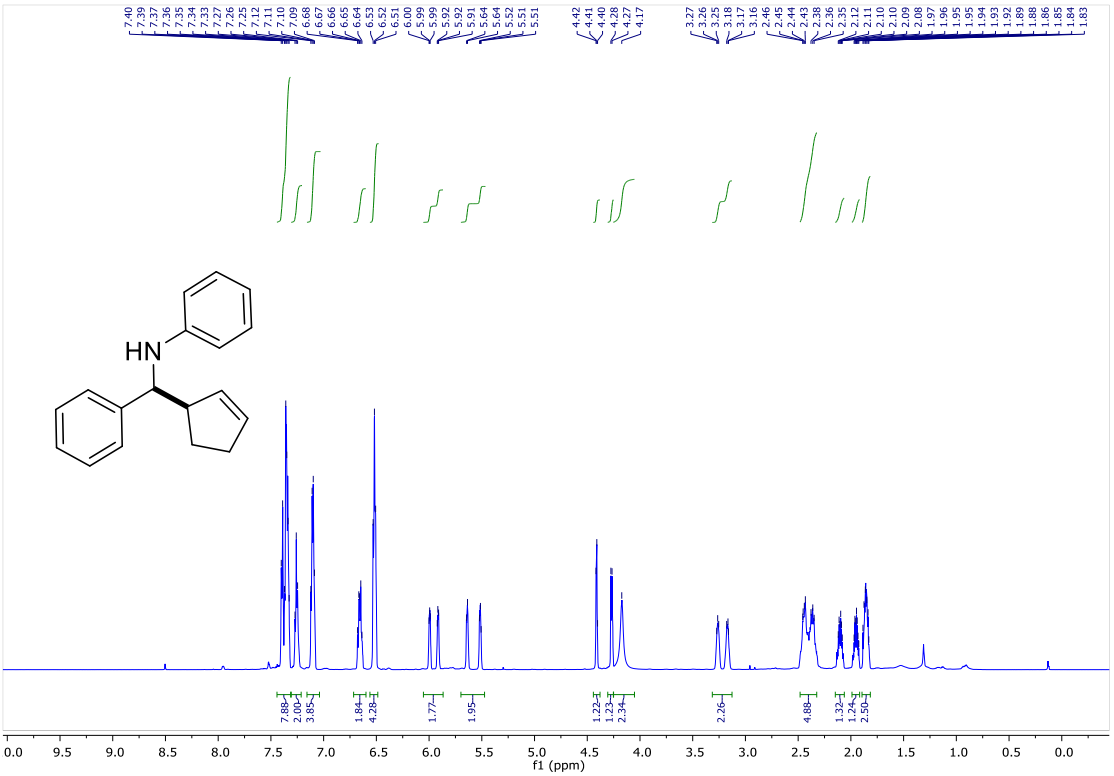
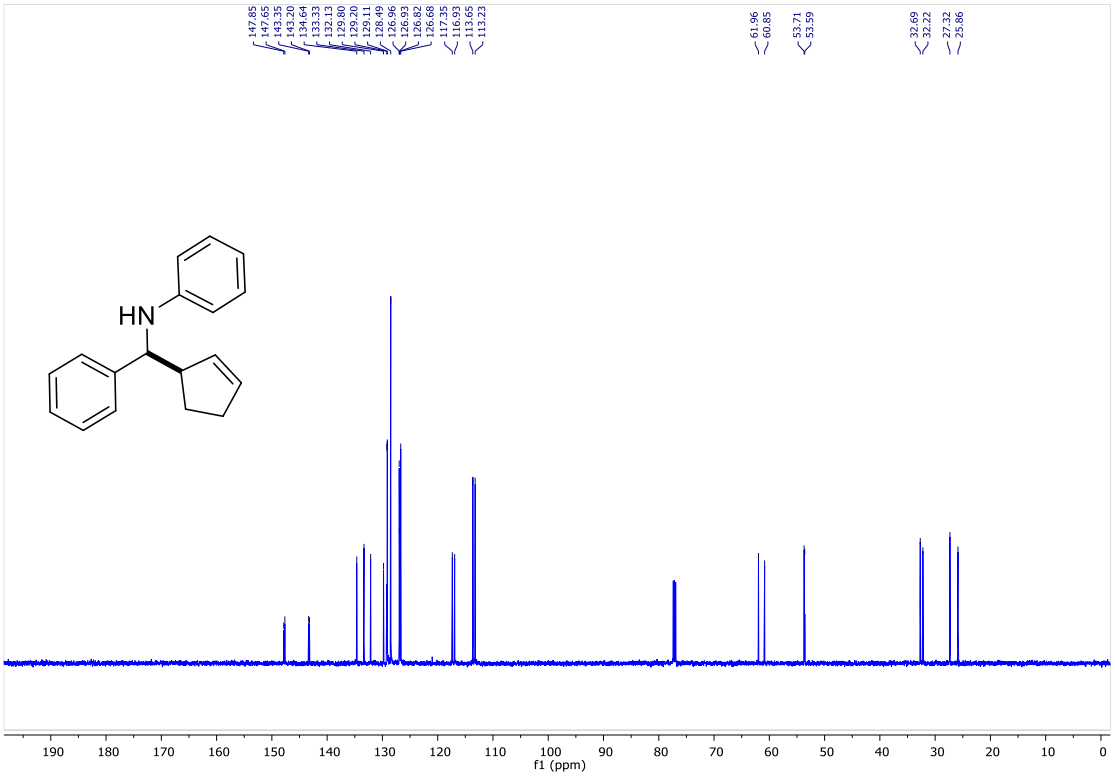
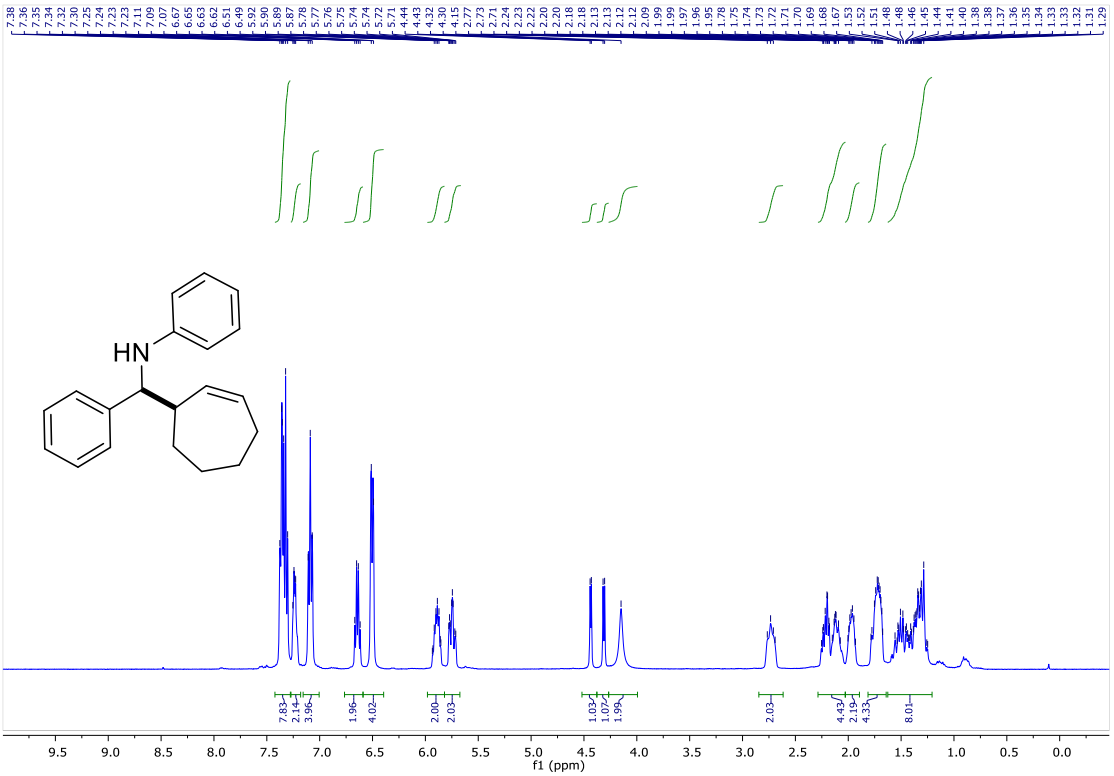
127.33
114.77
114.68
63.87
55.75
f1 (ppm)


HN
f1 (ppm)


HN
f1 (ppm)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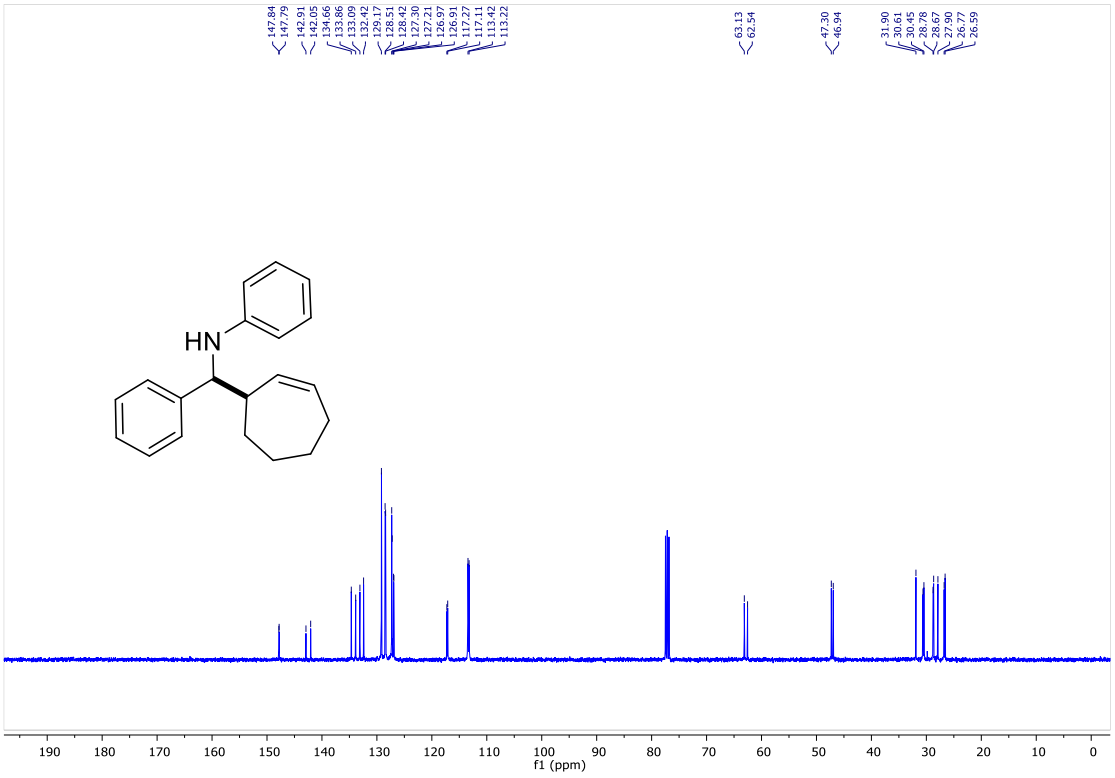
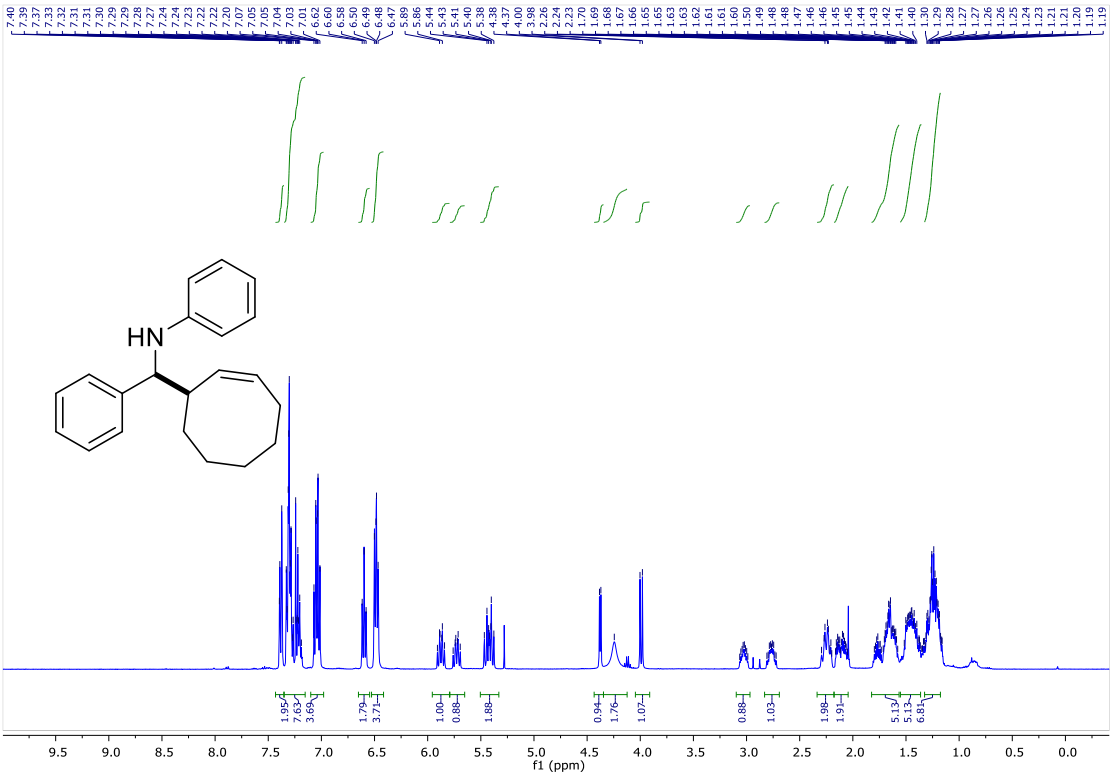
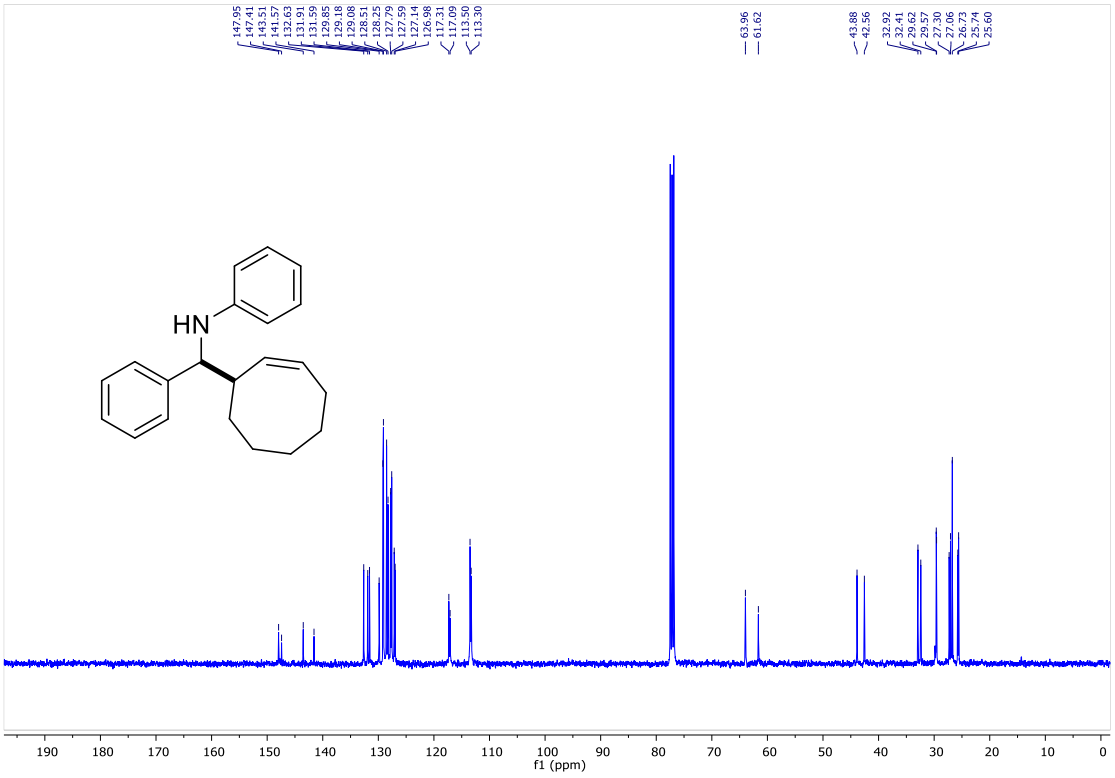
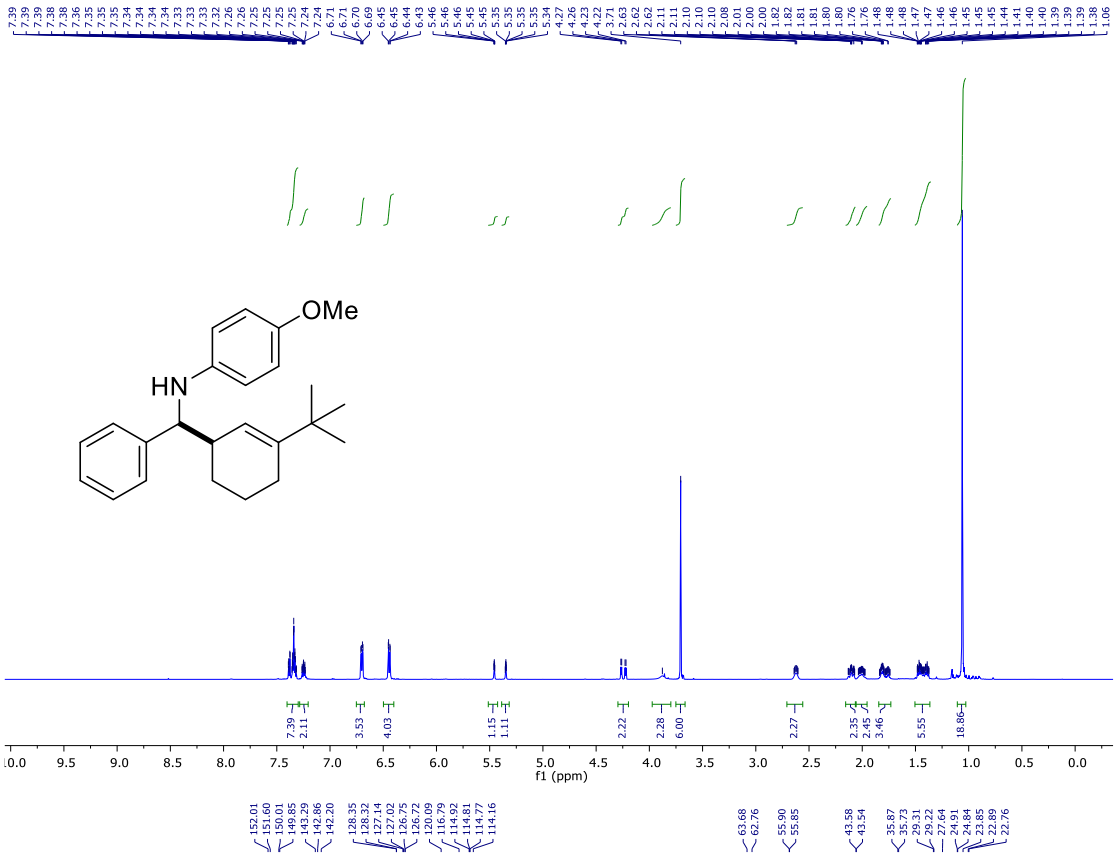
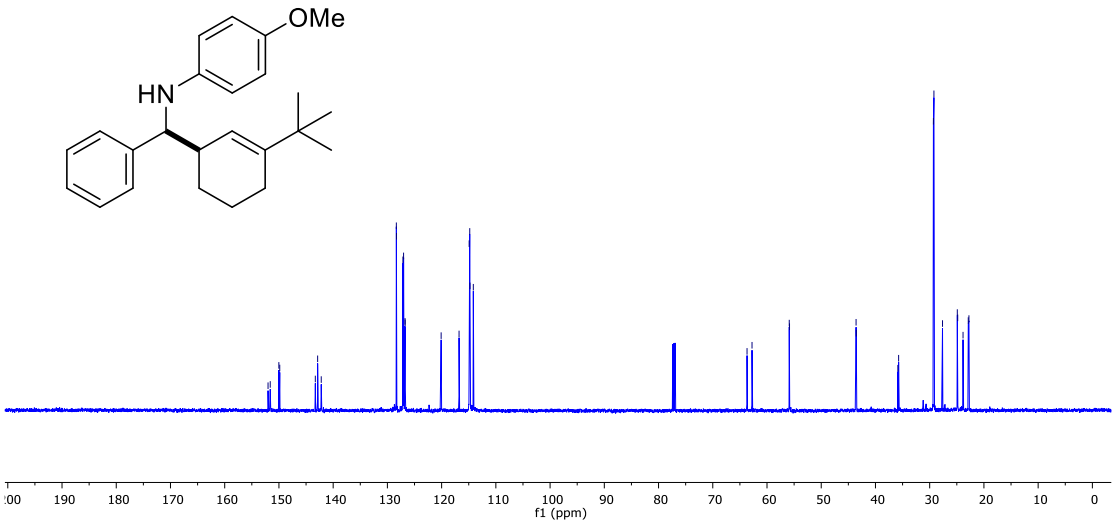
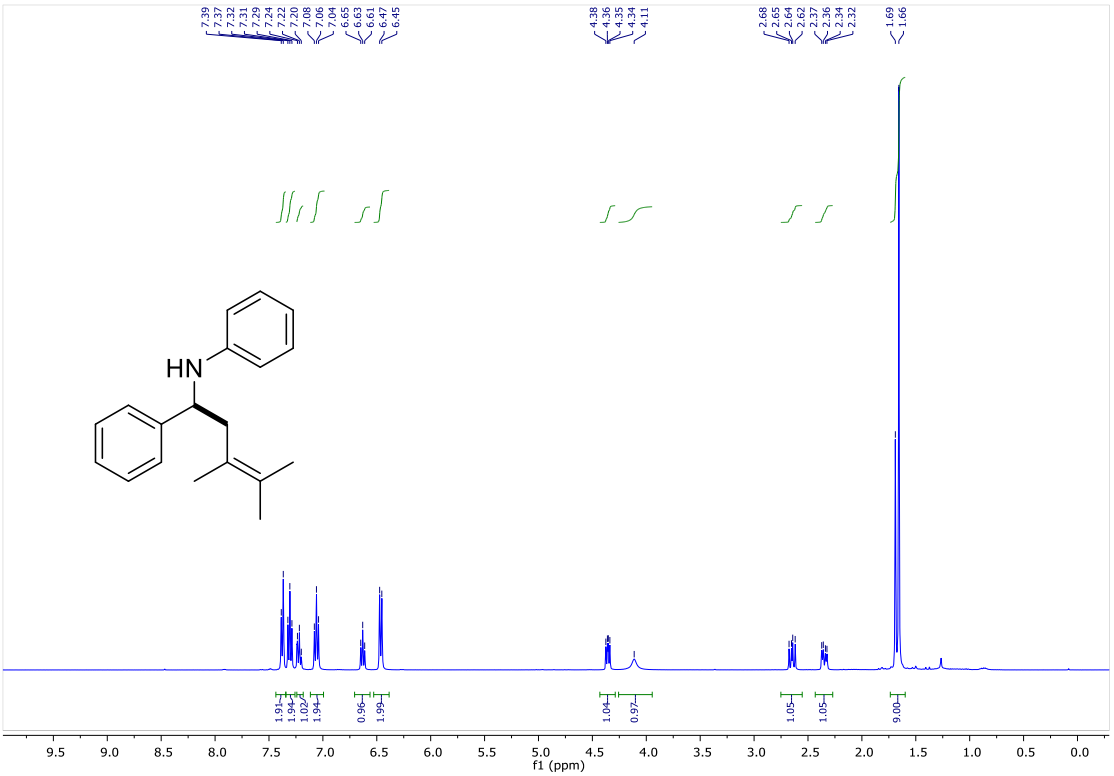

HN
f1 (ppm)


HN
f1 (ppm)


HN
f1 (ppm)


OMe
HN
f1 (ppm)


OMe
HN
f1 (ppm)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7.04
6.65
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6.61
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6.45
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4.35
4.34
4.11
2.68
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2.64
2.62
2.37
2.36
2.34
2.32
1.69
1.66
HN
1.91
1.94
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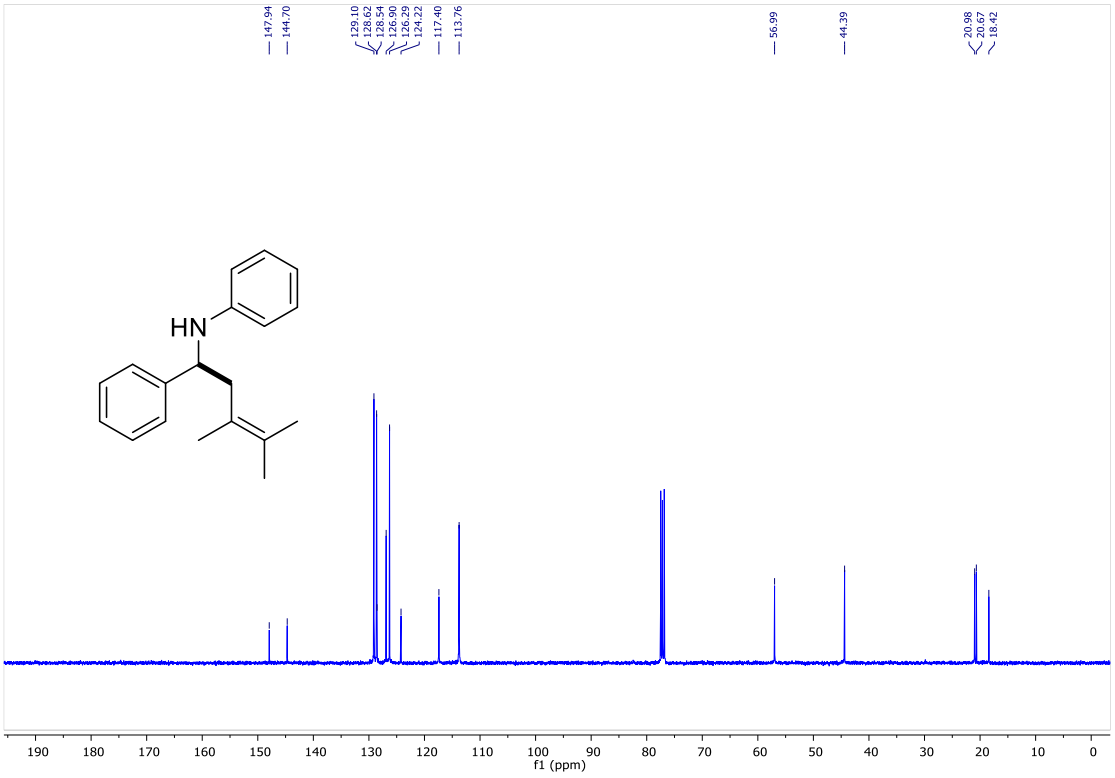
1.94
0.96
1.99
1.04
0.97
1.05
1.05
9.00
f1 (ppm)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124.22
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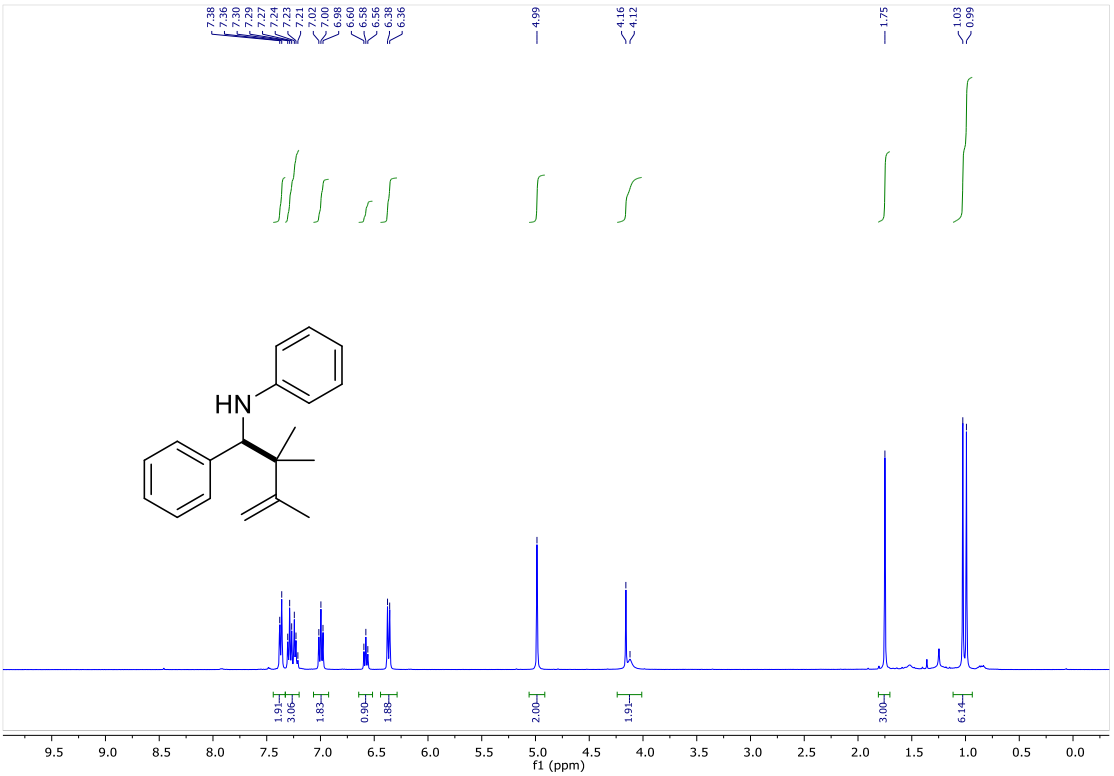
56.99
44.39
20.98
20.67
18.42
HN
f1 (ppm)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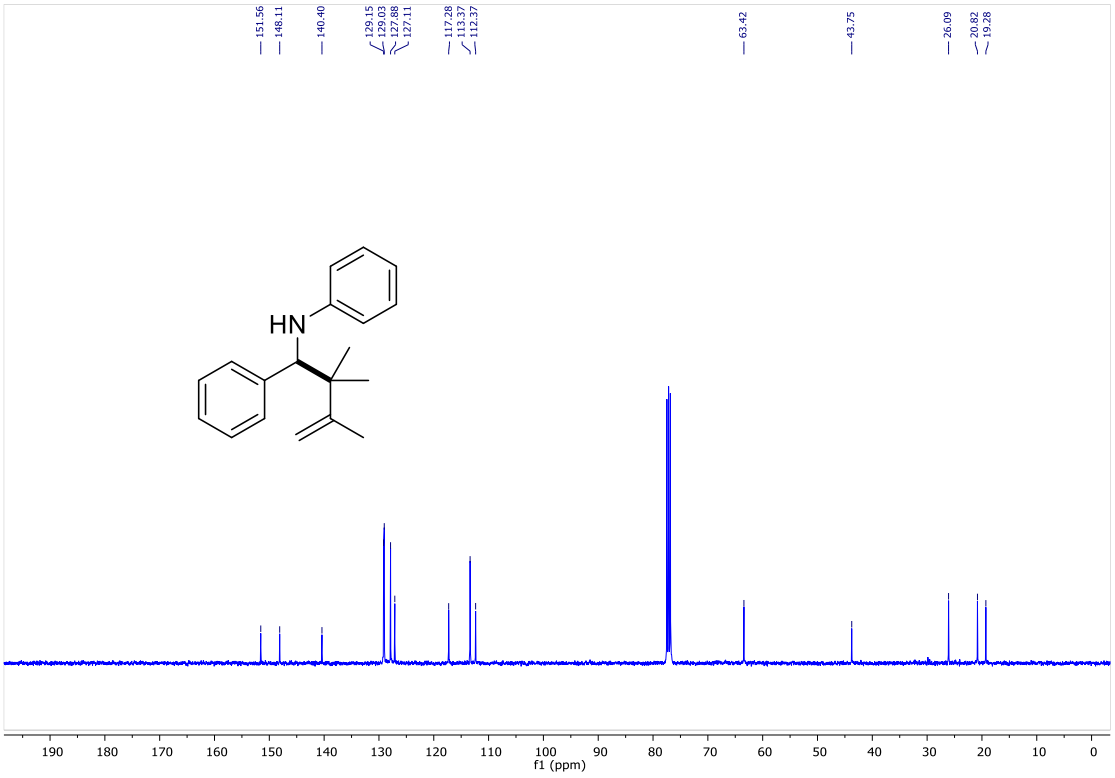
7.27
7.24
7.23
7.21
7.02
7.00
6.98
6.60
6.58
6.56
6.38
6.36
4.99
4.16
4.12
1.75
1.03
0.99
HN
1.91
3.06
1.83
0.90
1.88
2.00
1.91
3.00
6.14
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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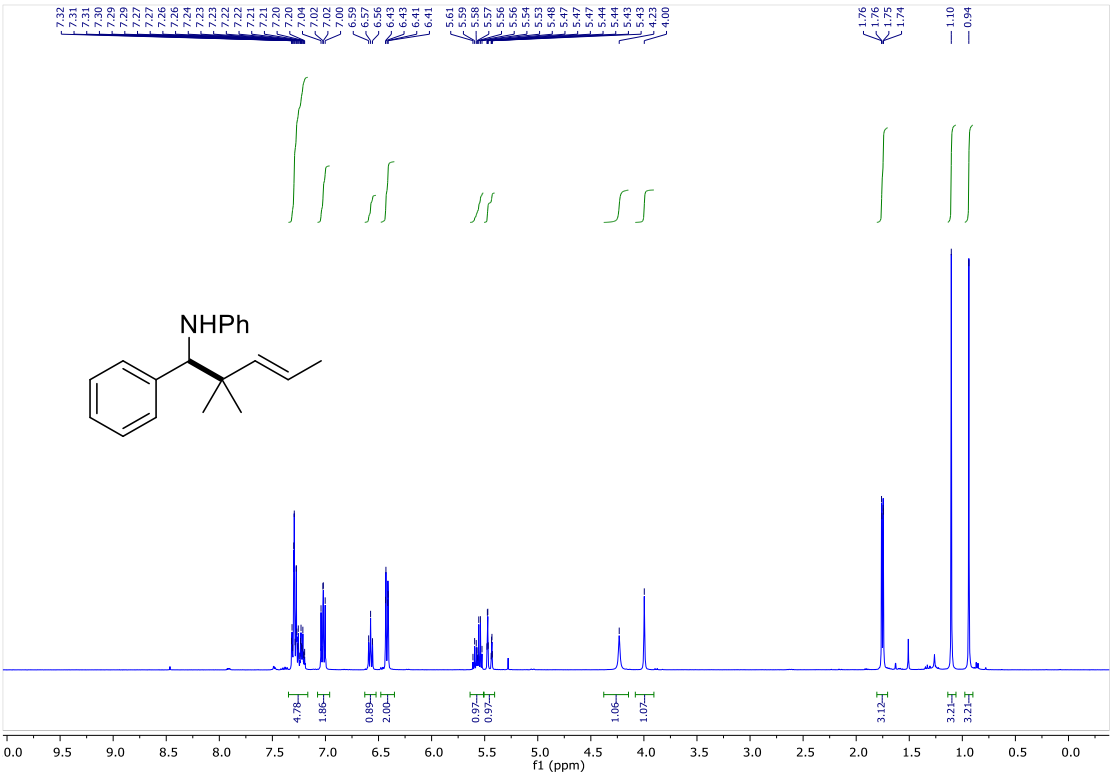
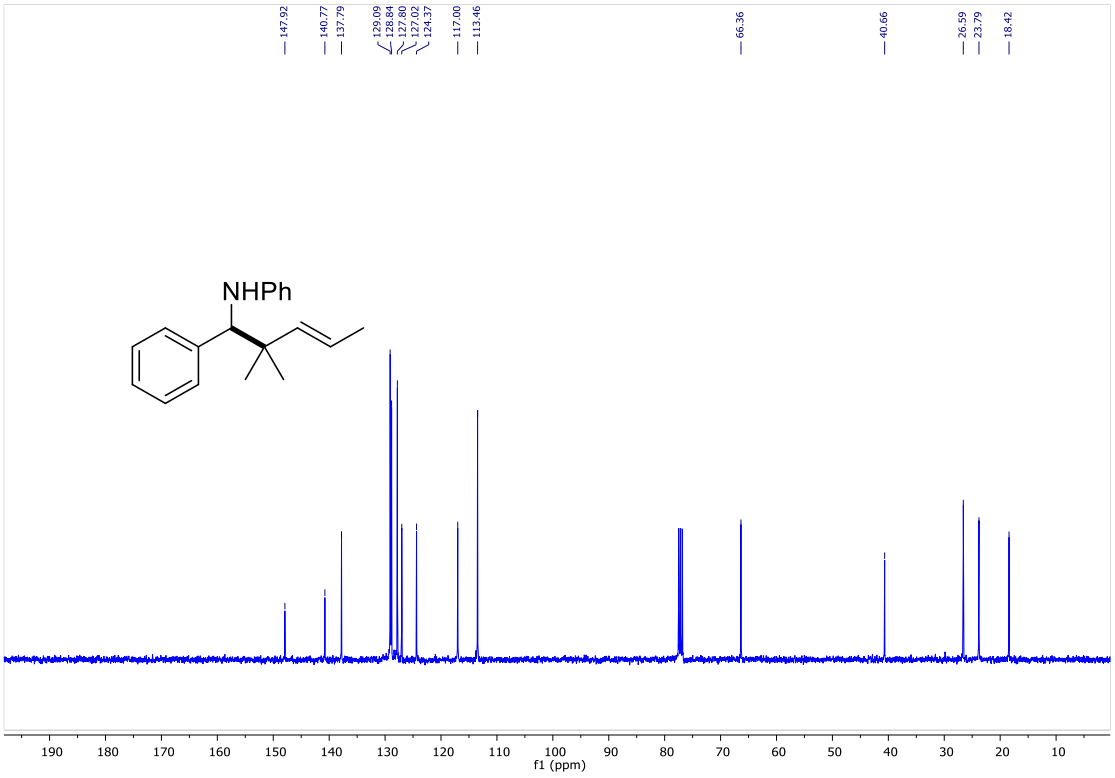
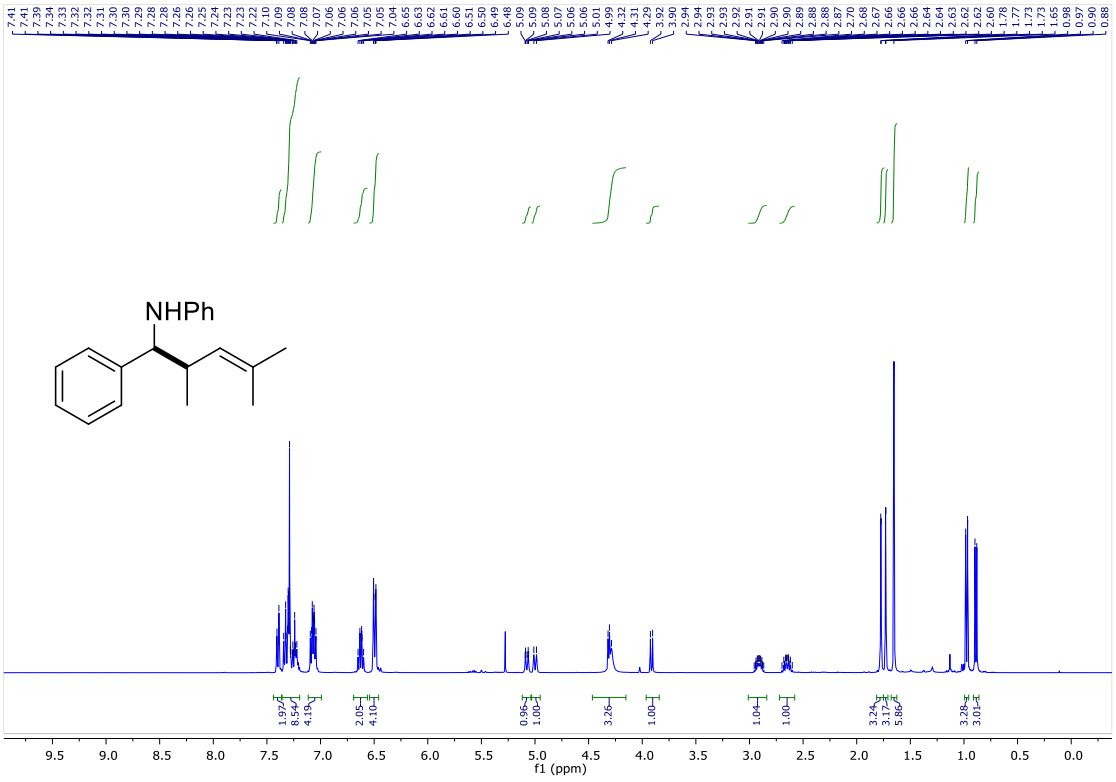
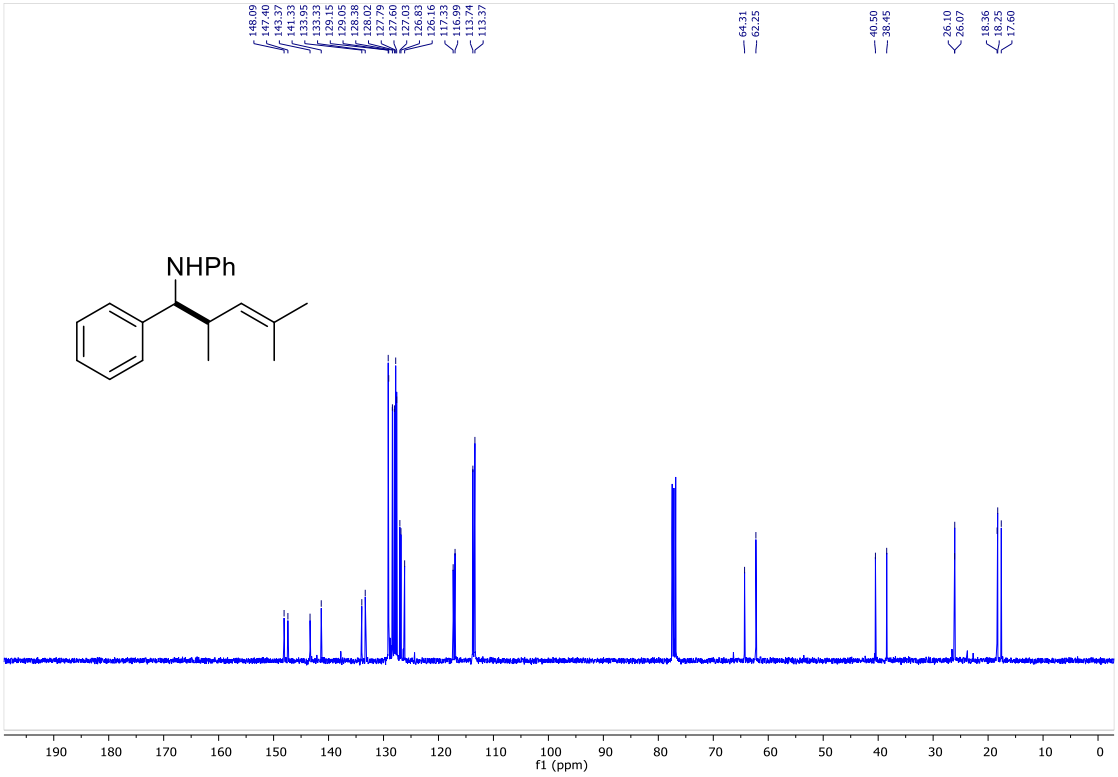
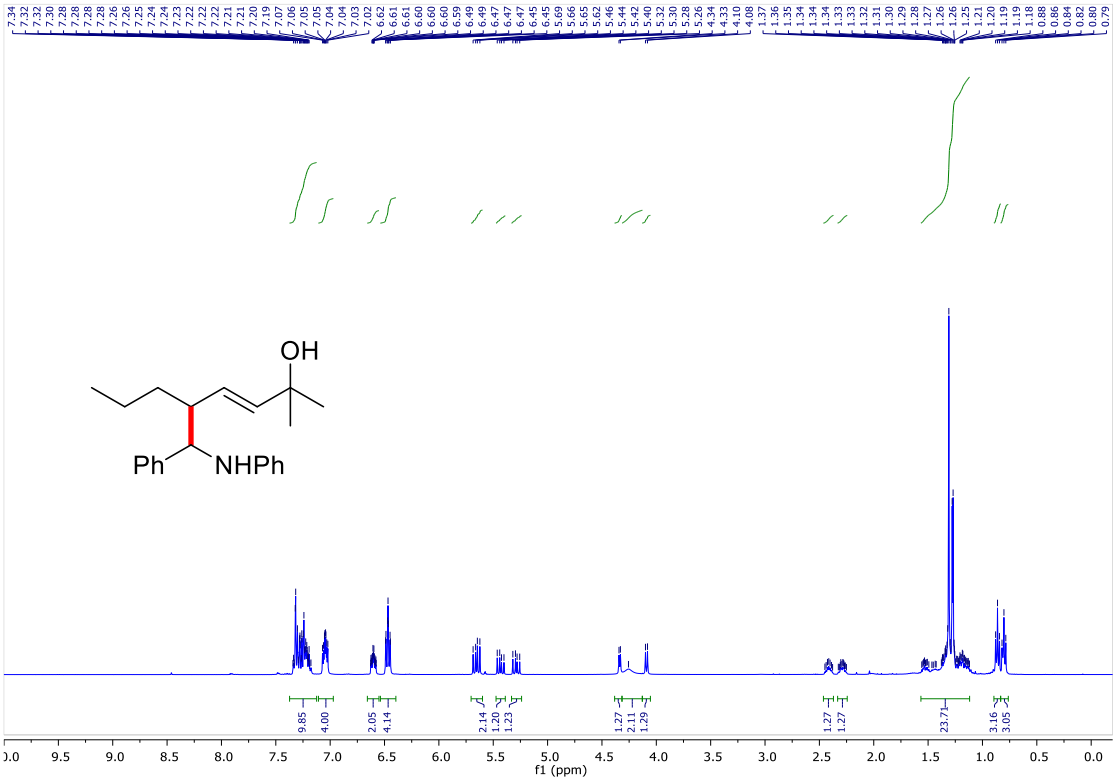
140.40
129.15
129.03
127.88
127.11
117.28
113.37
112.37
63.42
43.75
26.09
20.82
19.28
HN
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

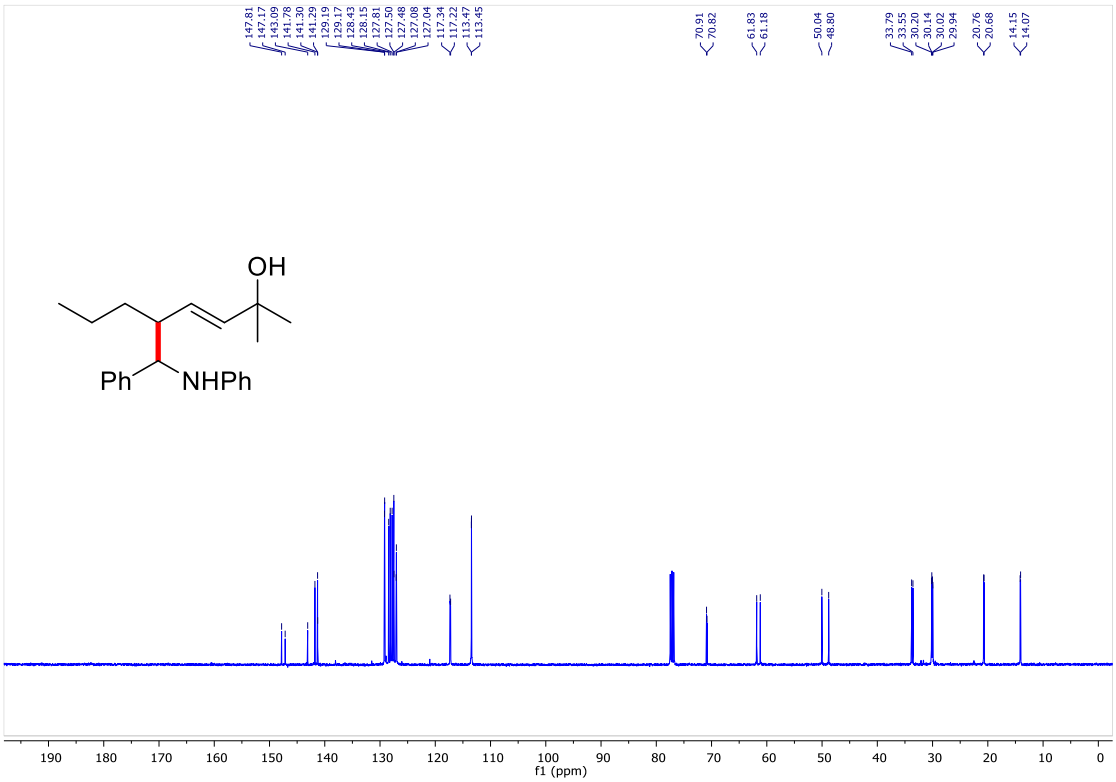

NHPh
f1 (ppm)

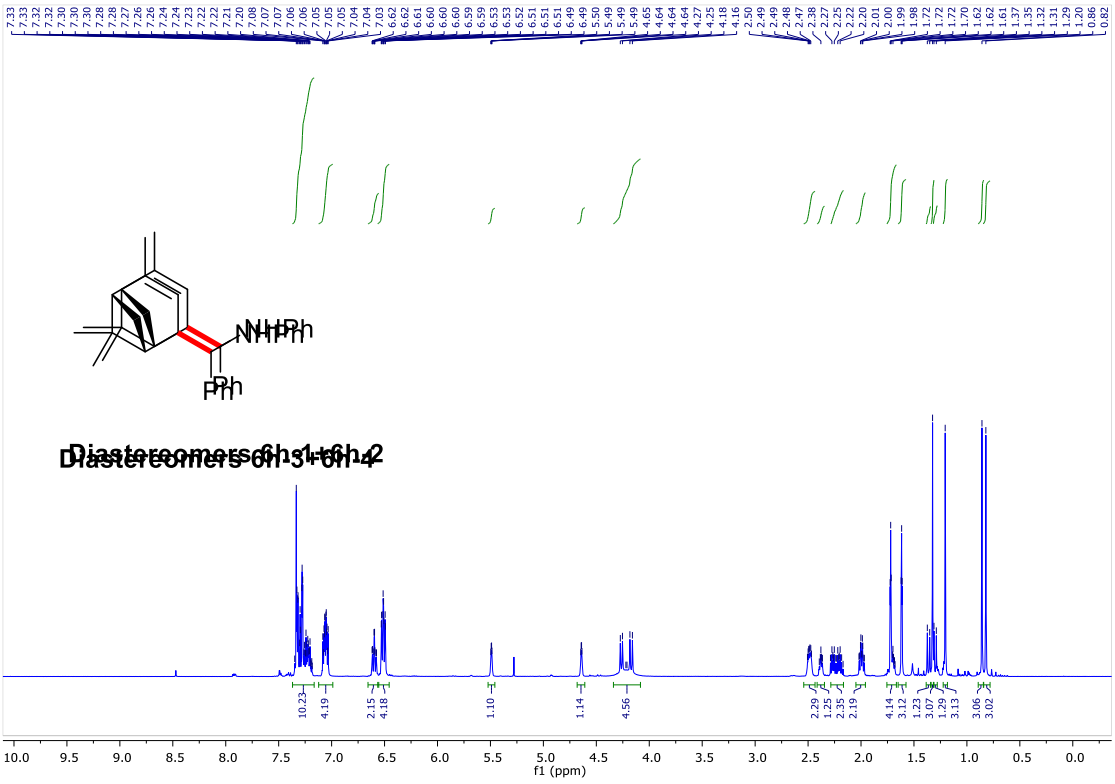

NHPh
f1 (ppm)

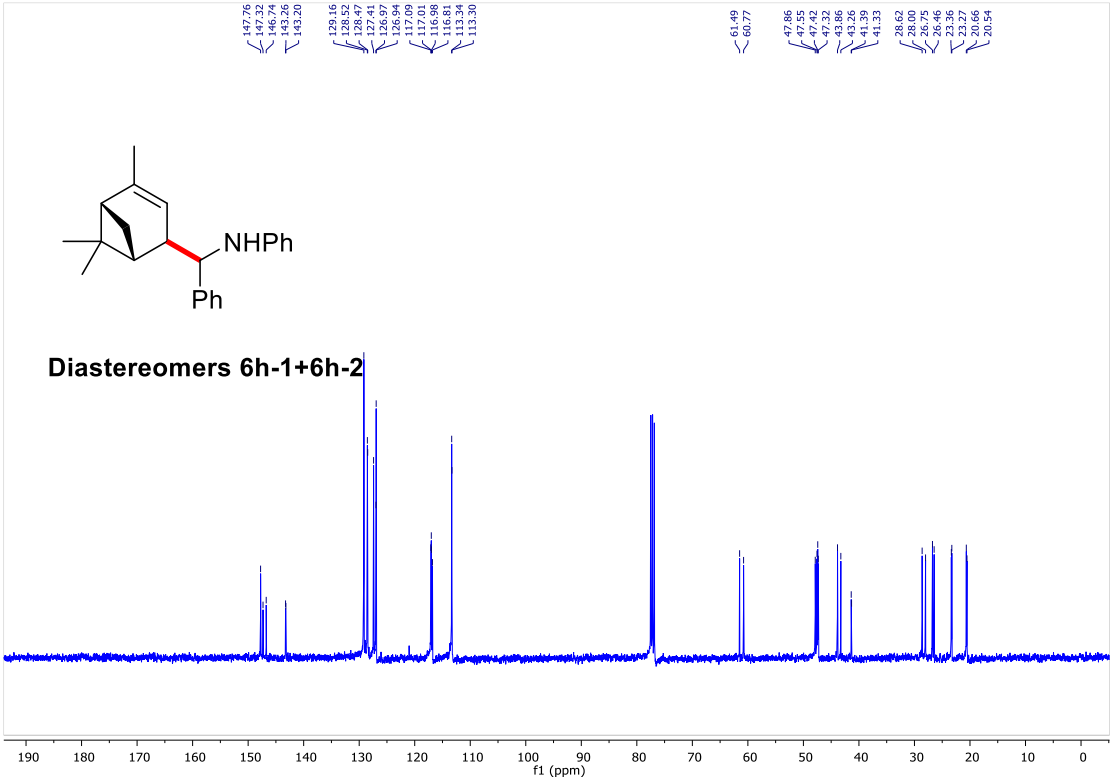

NHPh
f1 (ppm)

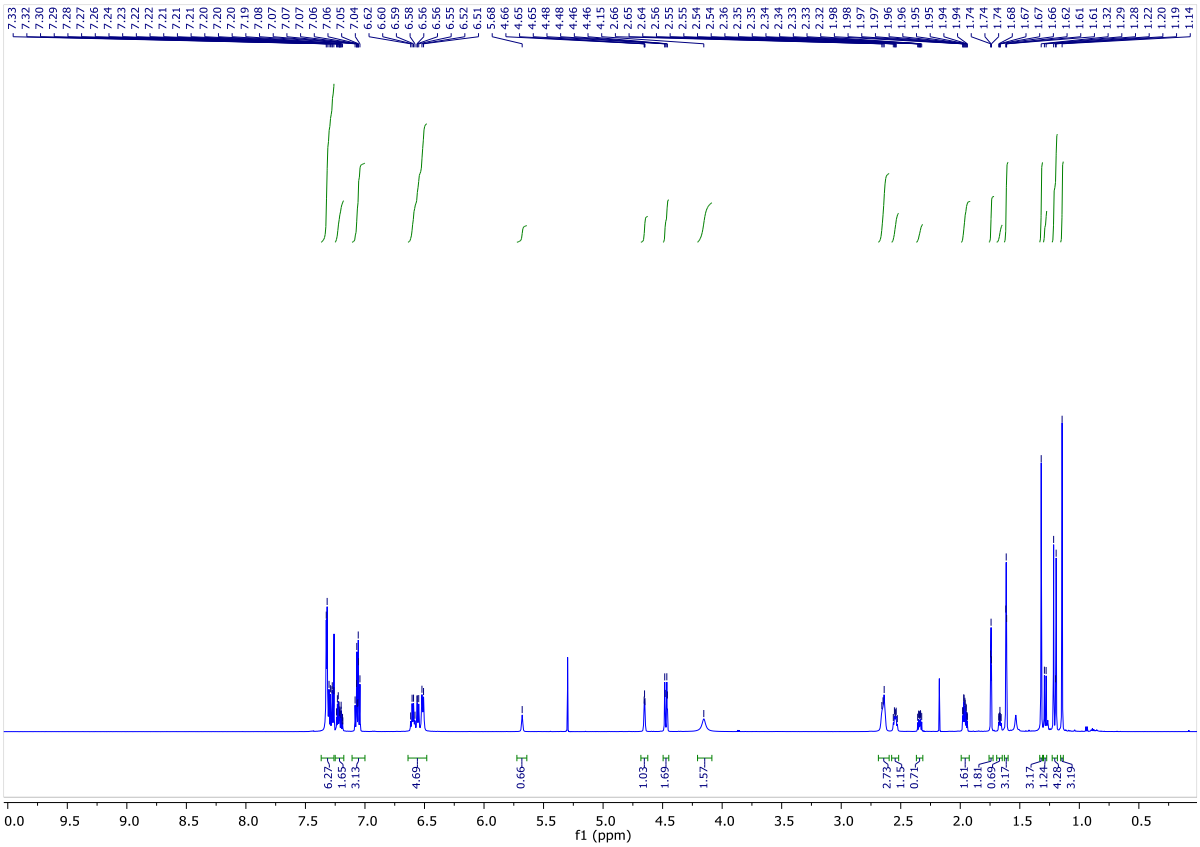

NHPh
f1 (ppm)


OH
Ph
NHPh
f1 (ppm)


OH
Ph
NHPh
f1 (ppm)


NHPh
Ph
Diastereomers 6h-1+6h-2
f1 (ppm)


NHPh
Ph
Diastereomers 6h-1+6h-2
f1 (ppm)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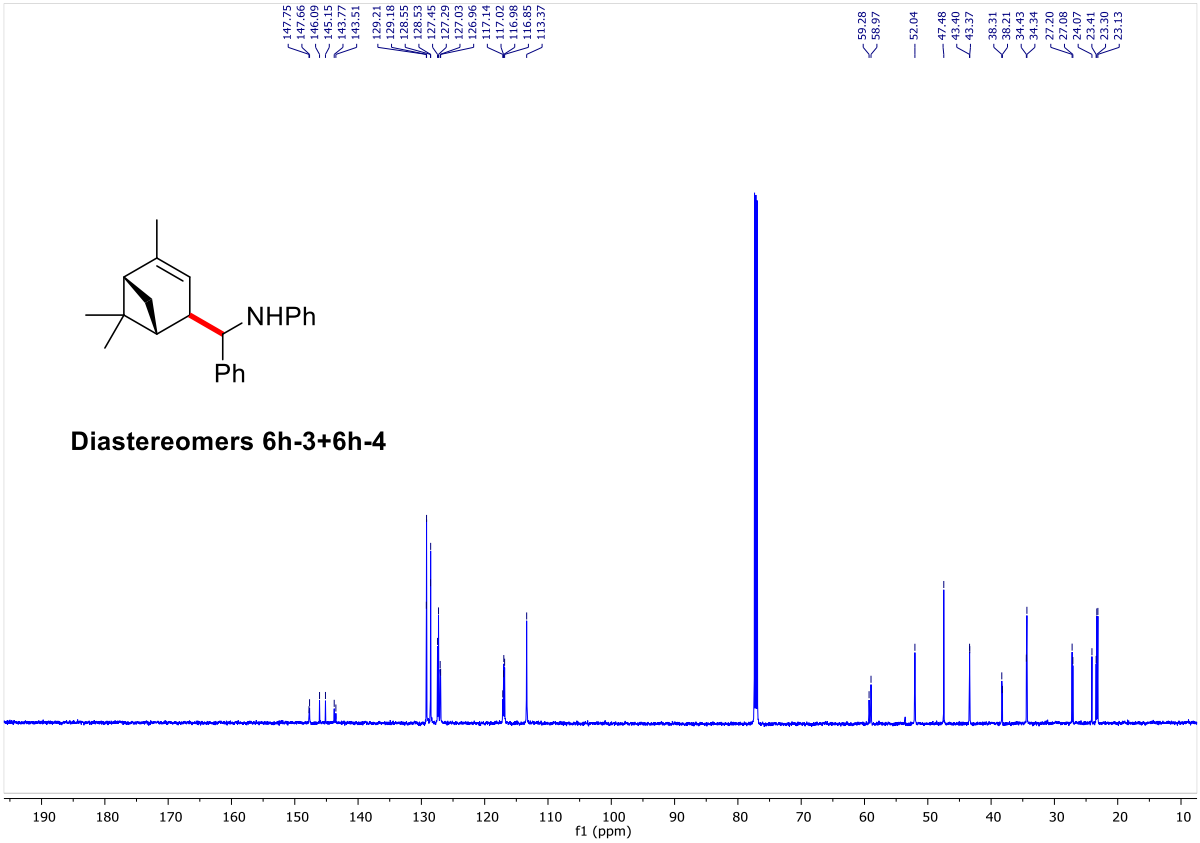
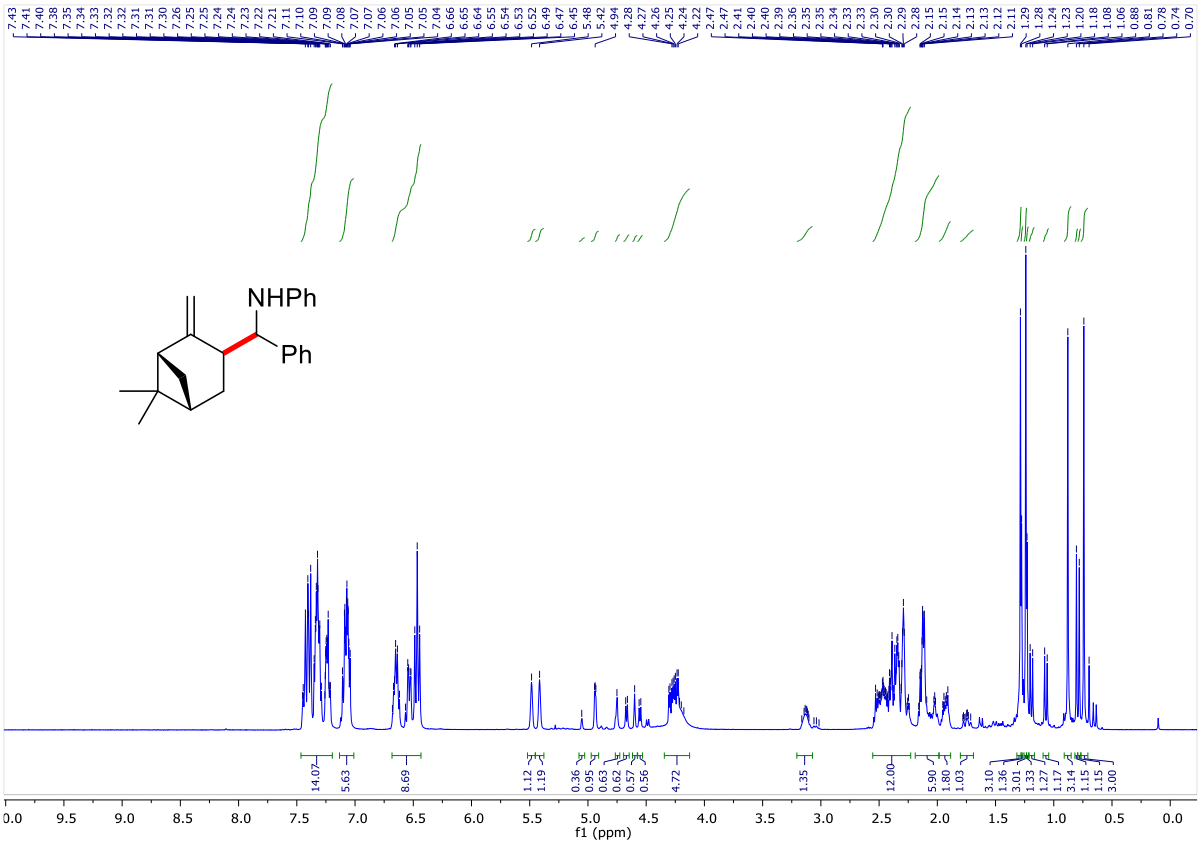
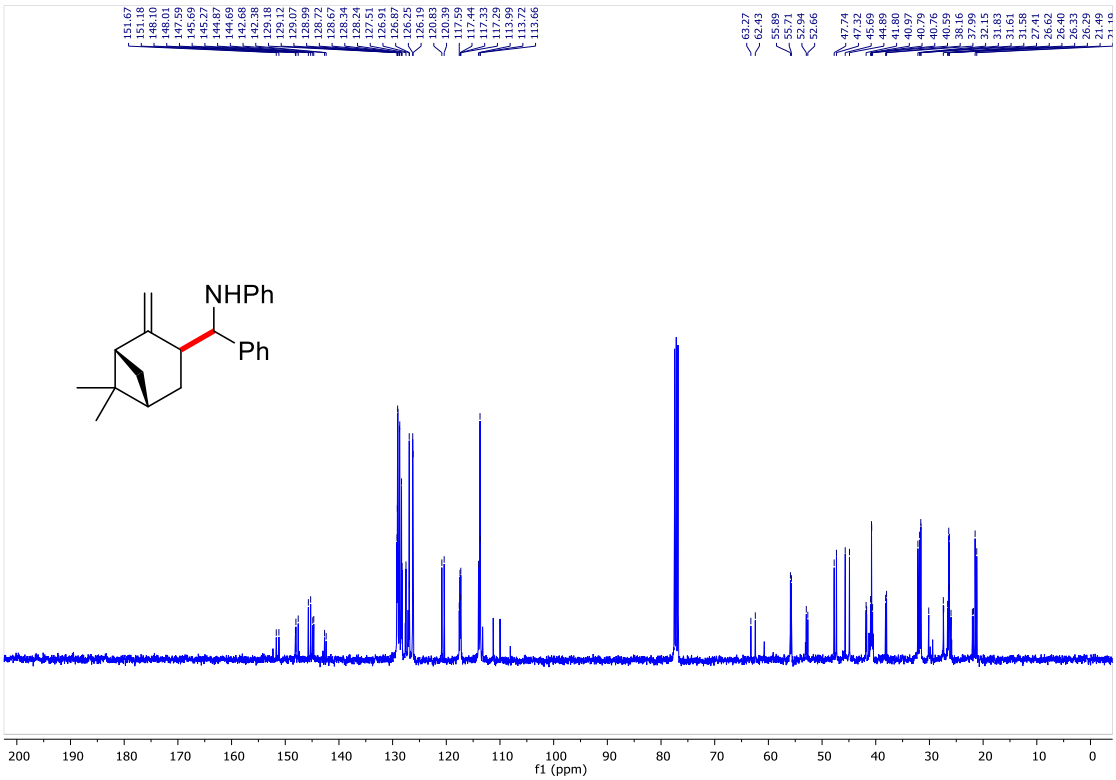
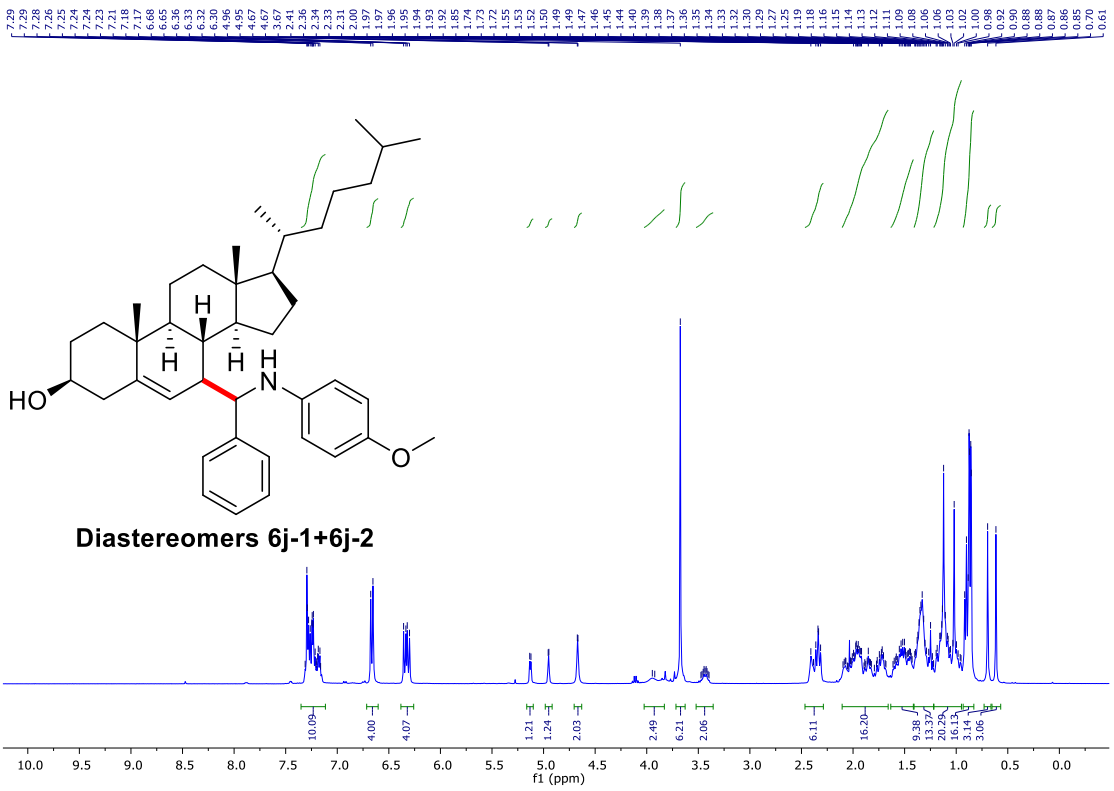
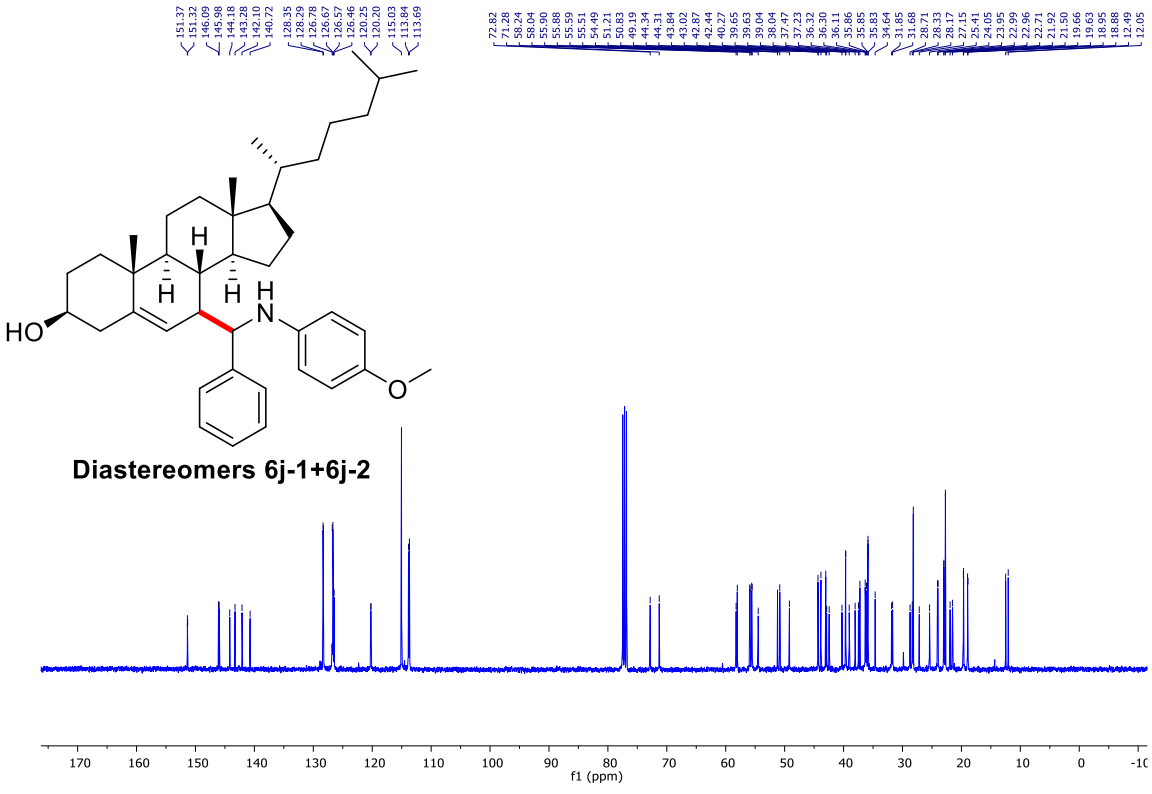
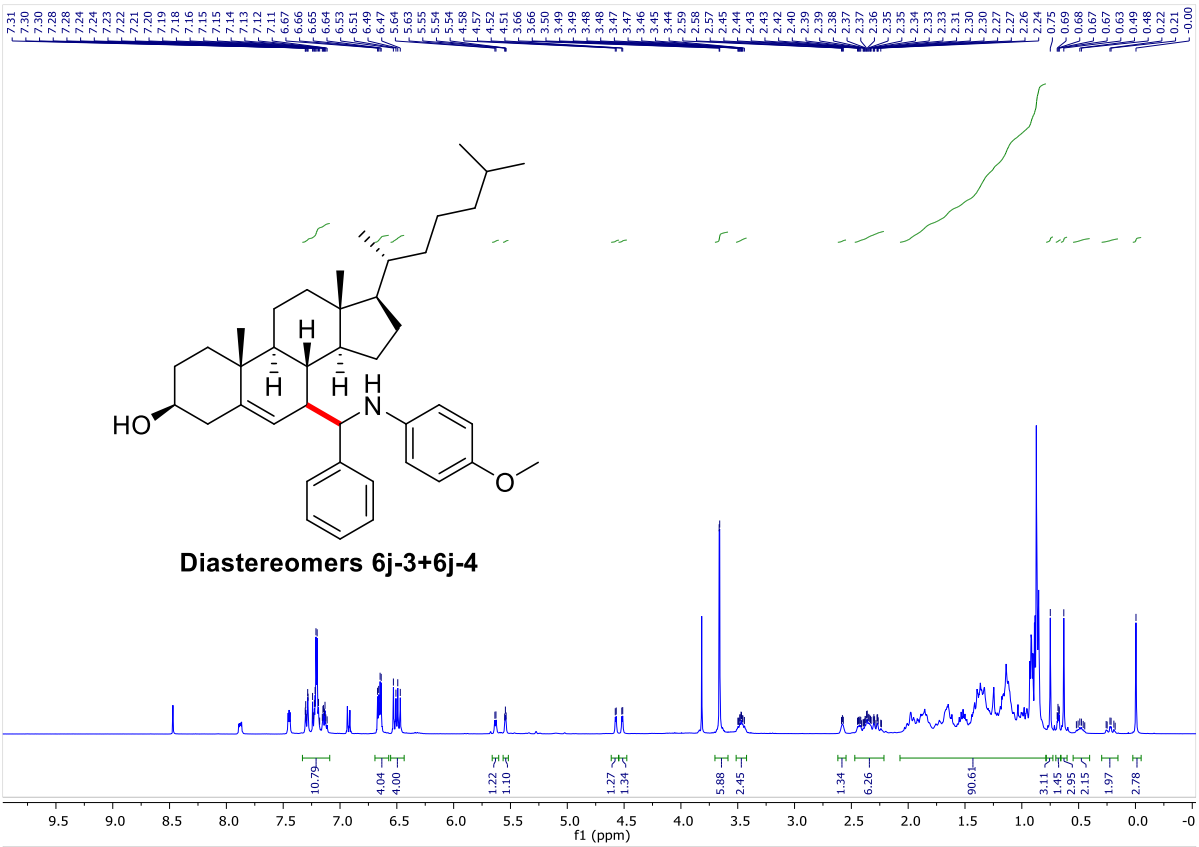

NHPh
Ph
Diastereomers 6h-3+6h-4
f1 (ppm)

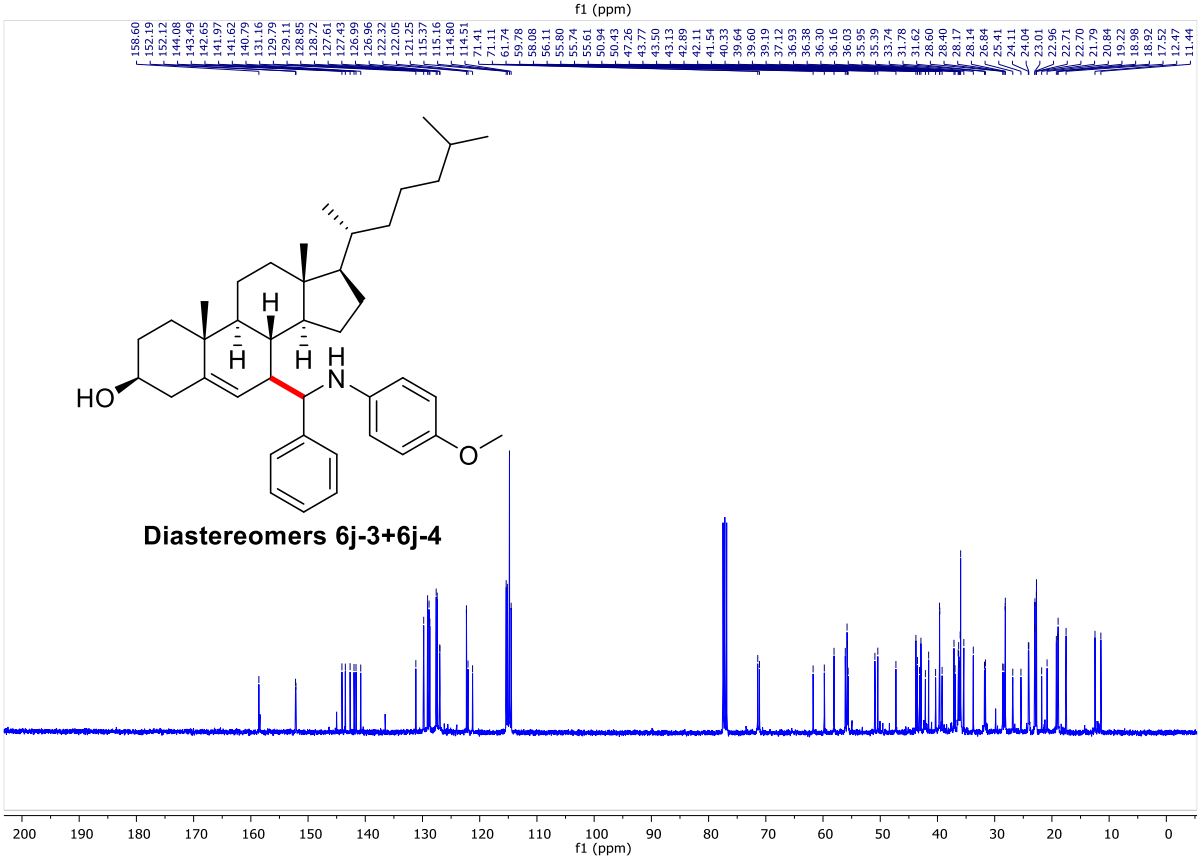

NHPh
Ph
f1 (ppm)

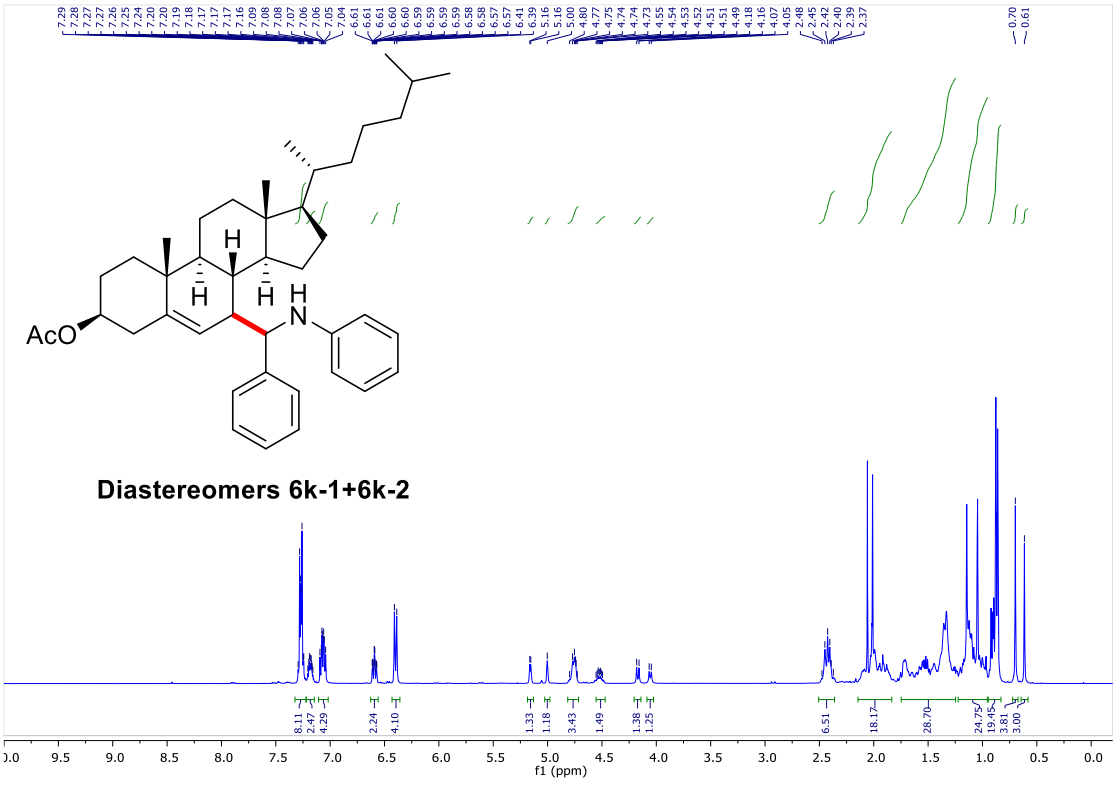

NHPh
Ph
f1 (ppm)

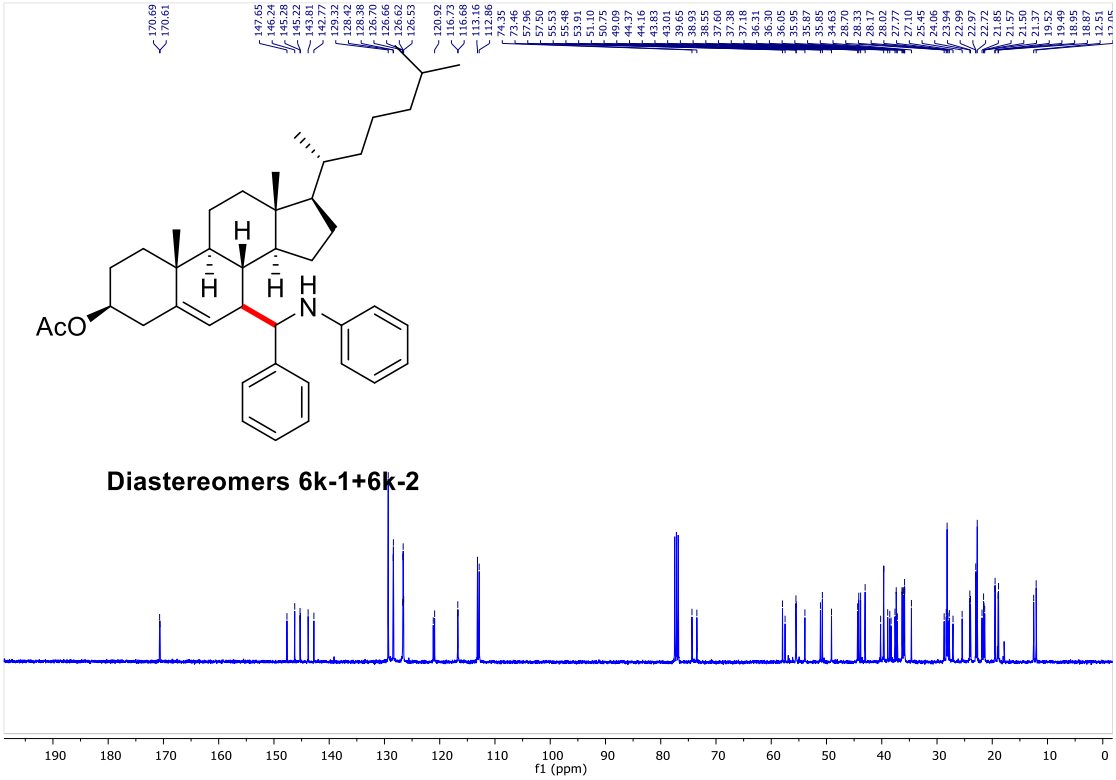

HO
H
H
H H
N
O
Diastereomers 6j-1+6j-2
f1 (ppm)

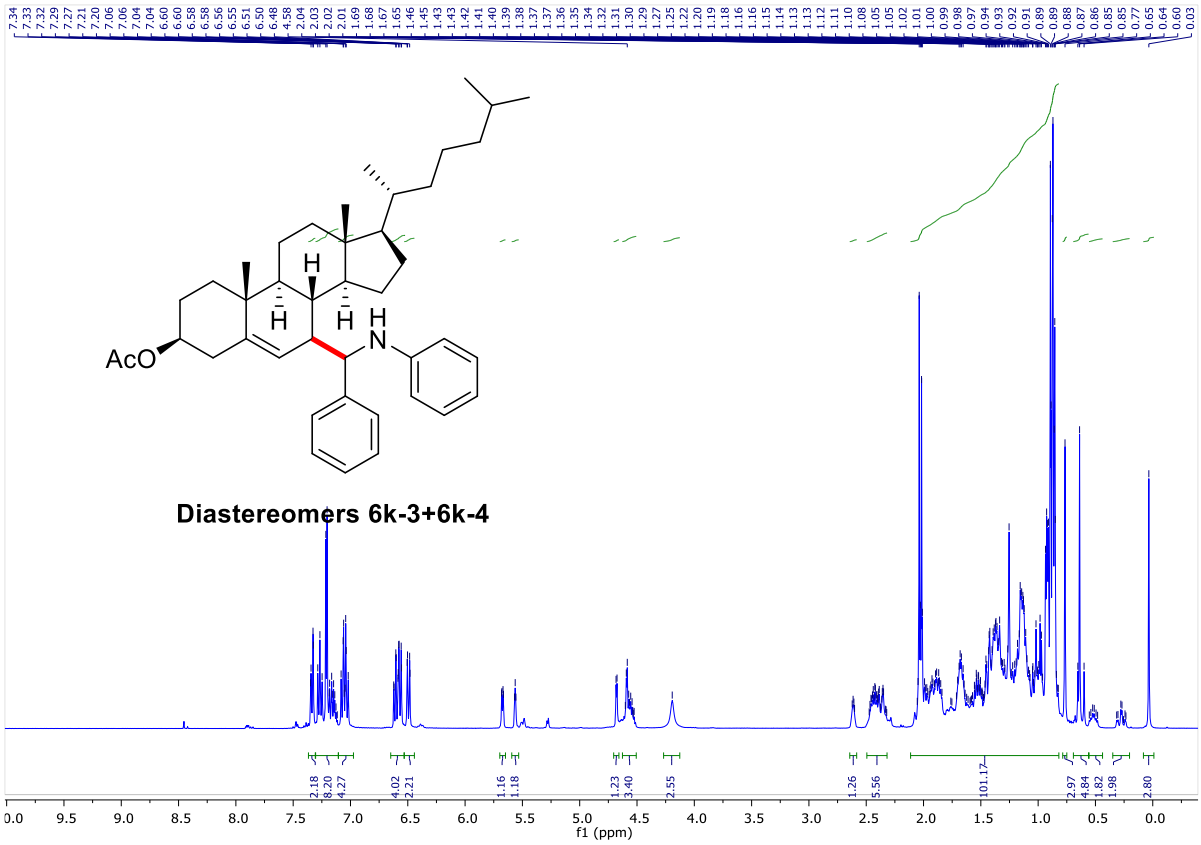

HO
H
H
H H
N
O
Diastereomers 6j-1+6j-2
f1 (ppm)

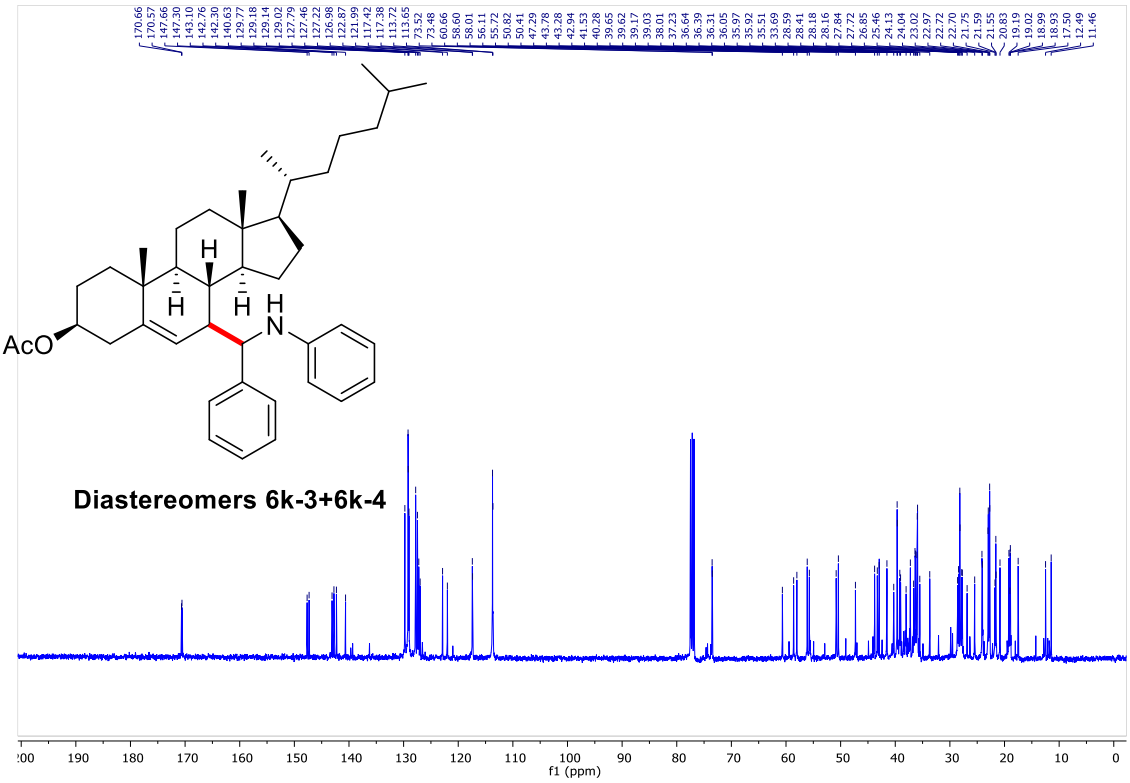

HO
H
H
H
H
N
O
Diastereomers 6j-3+6j-4
f1 (ppm)

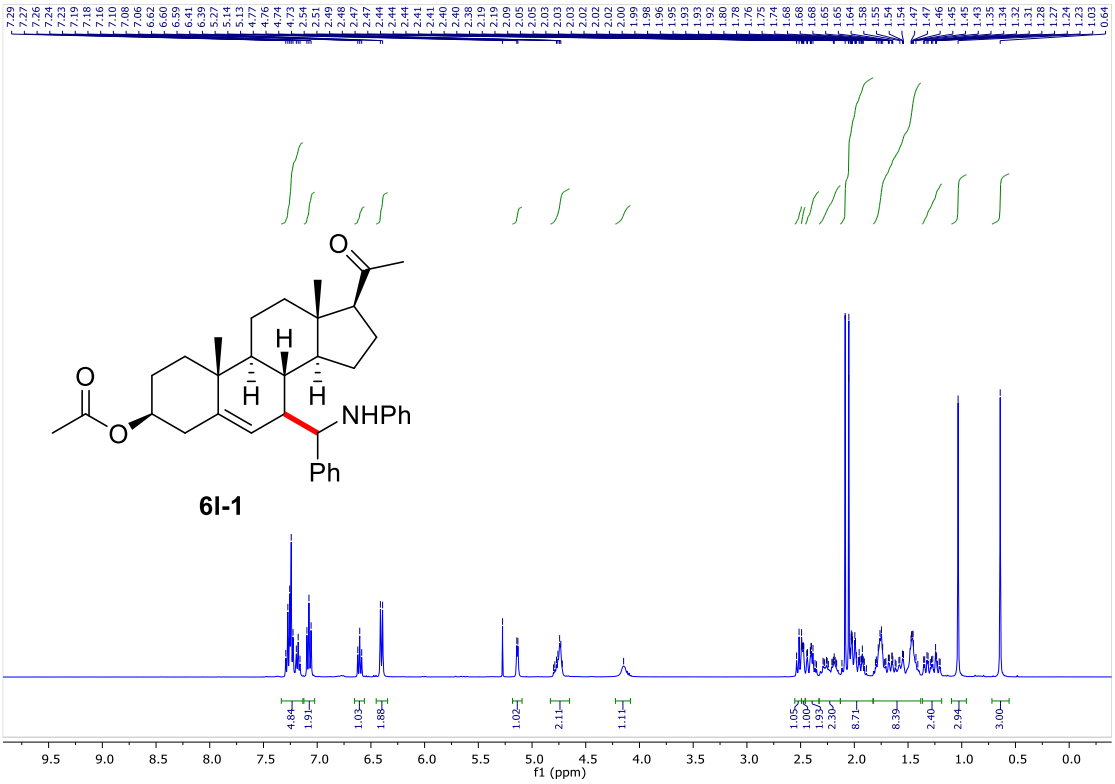

HO
H
H
H
H
N
O
Diastereomers 6j-3+6j-4
f1 (ppm)

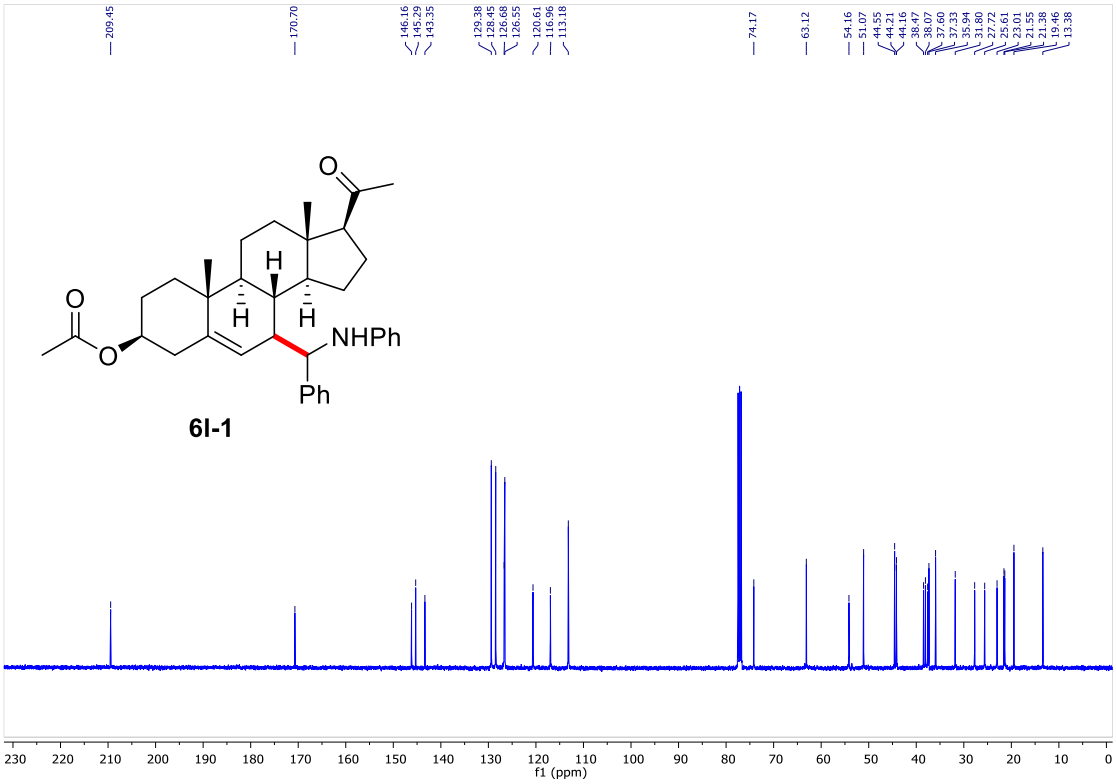

AcO
H
H
H
H
N
Diastereomers 6k-1+6k-2
f1 (ppm)


AcO
H
H
H
H
N
Diastereomers 6k-1+6k-2
f1 (ppm)

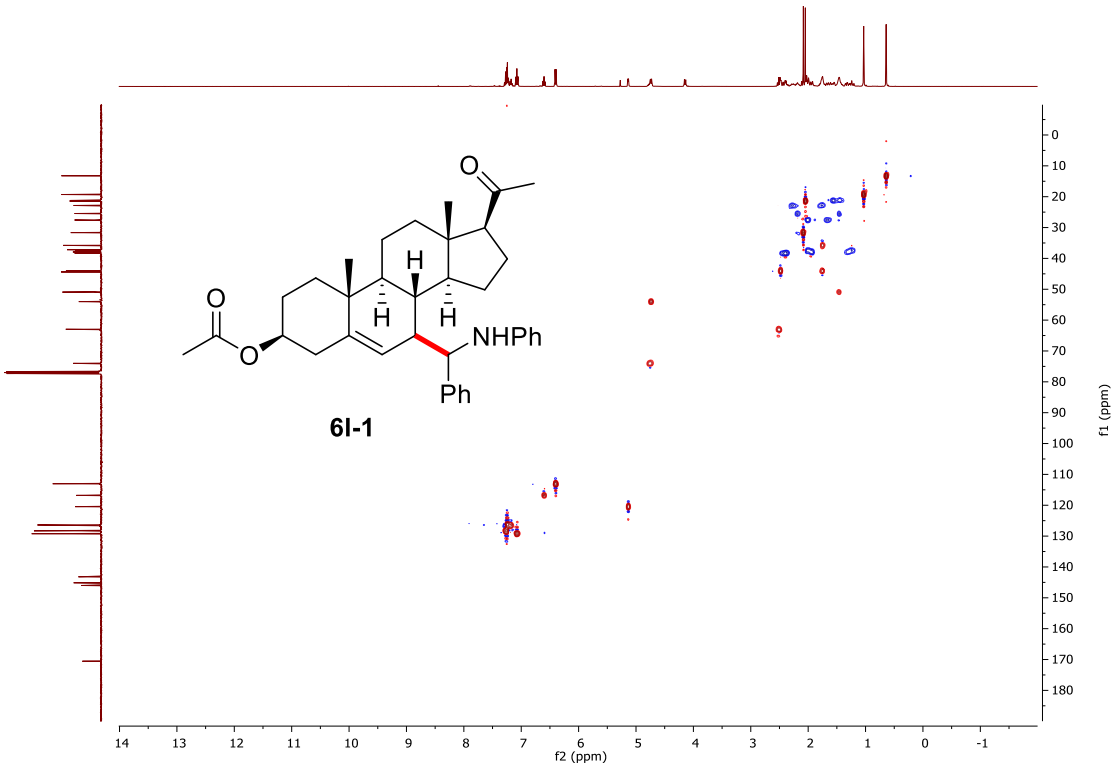

AcO
H
H
H
H
N
Diastereomers 6k-3+6k-4
f1 (ppm)

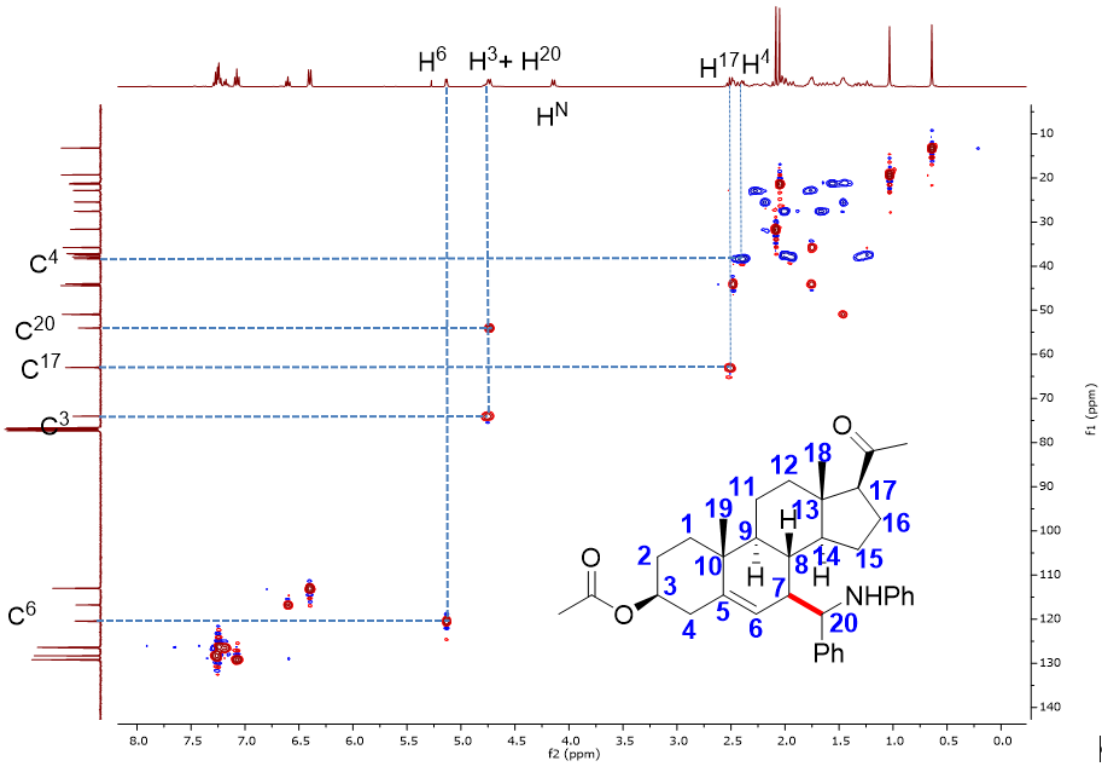

AcO
H
H
H
H
N
Diastereomers 6k-3+6k-4
f1 (ppm)


O
H
H
H
O
O
NHPh
Ph
6l-1
f1 (ppm)

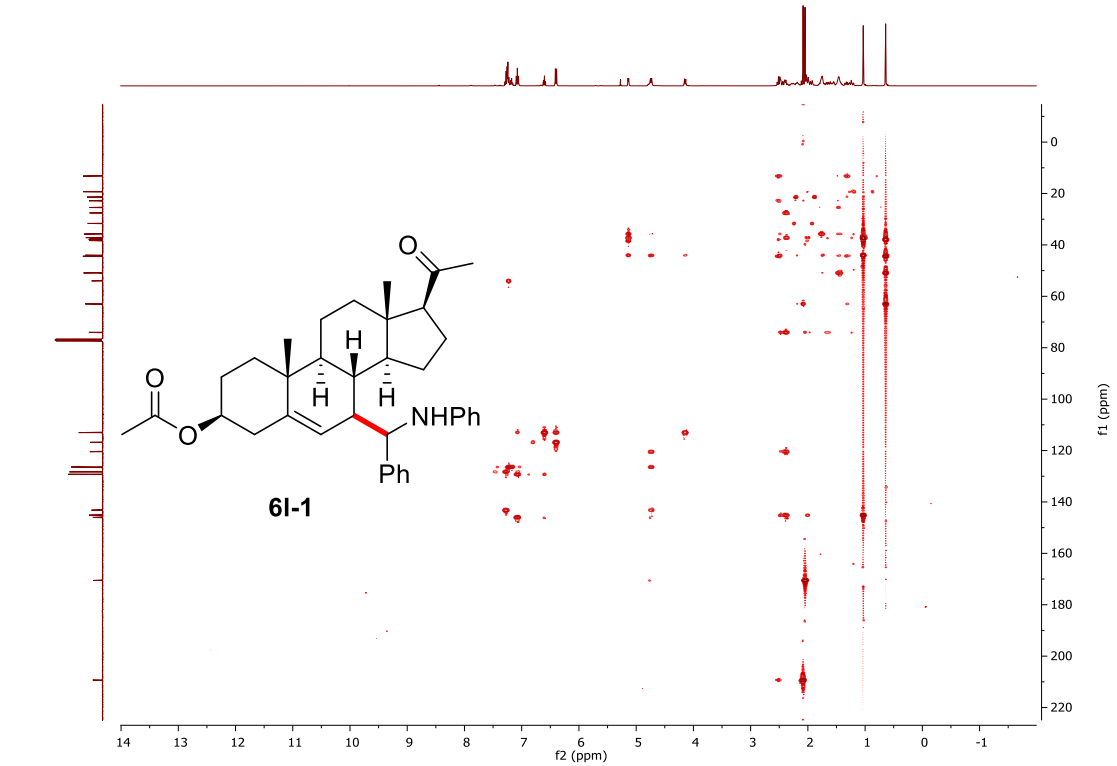

O
H
H
H
O
O
NHPh
Ph
6l-1
f1 (ppm)

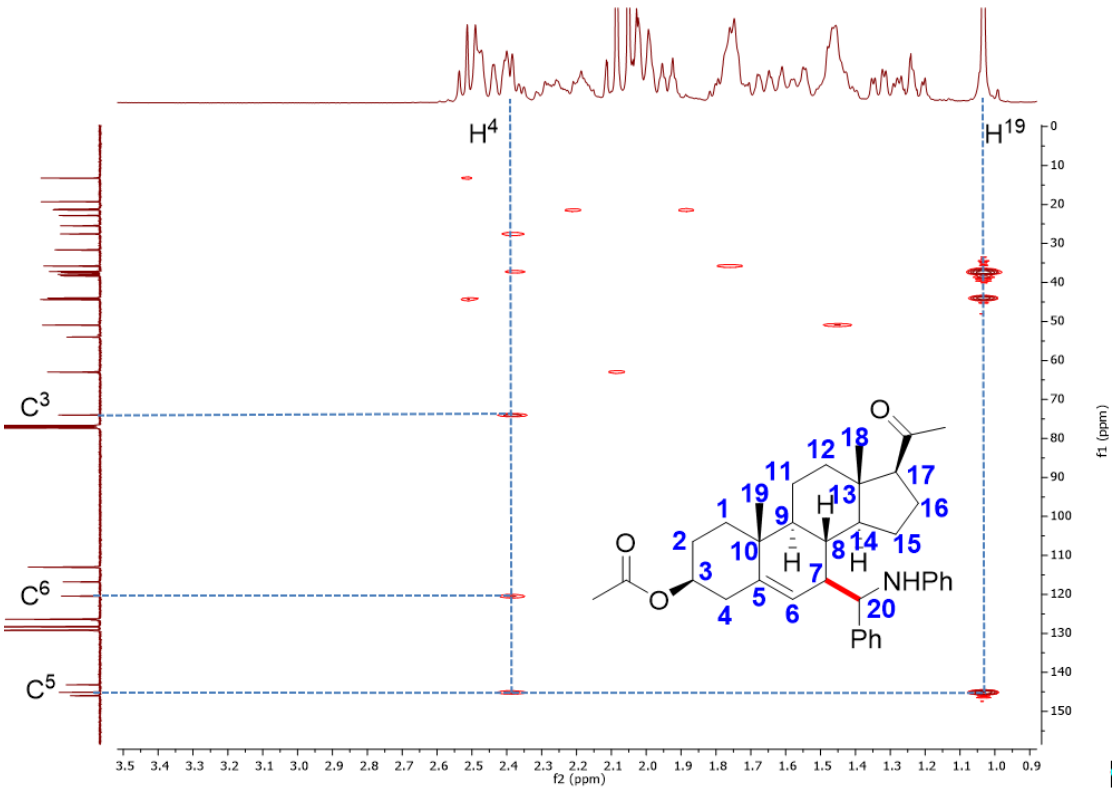
^{1}H-^{13}C HSQC

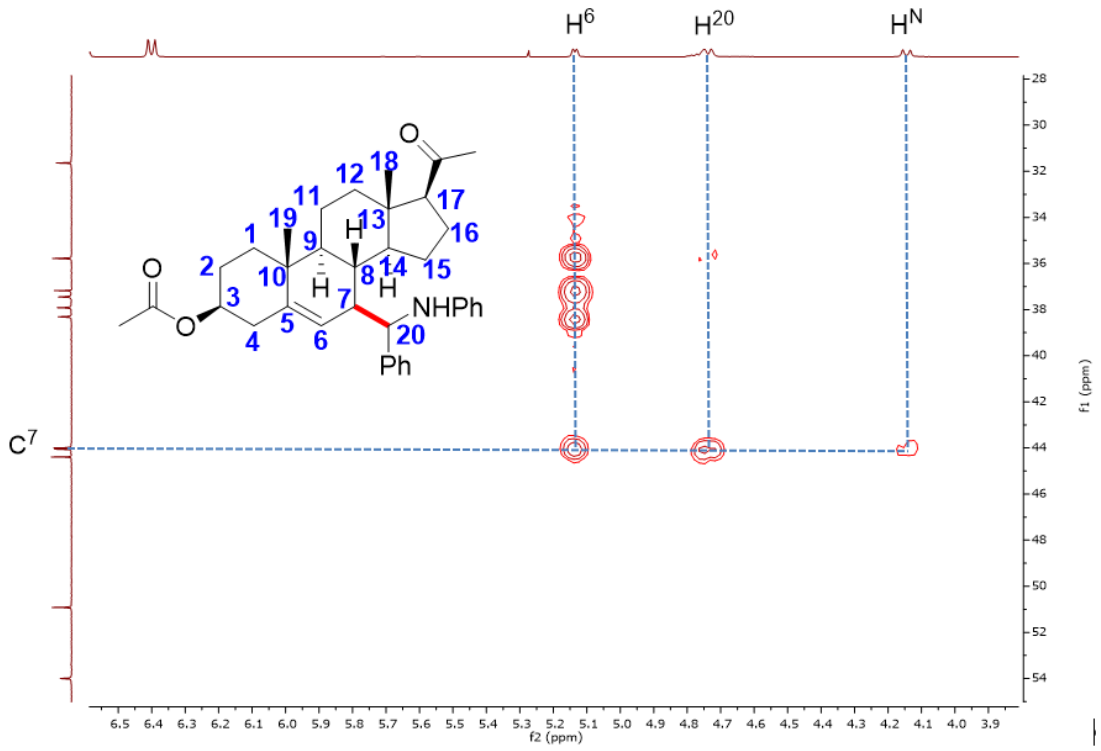

O
O
H
H
H
NHPh
Ph
6l-1
f2 (ppm)
f1 (ppm)

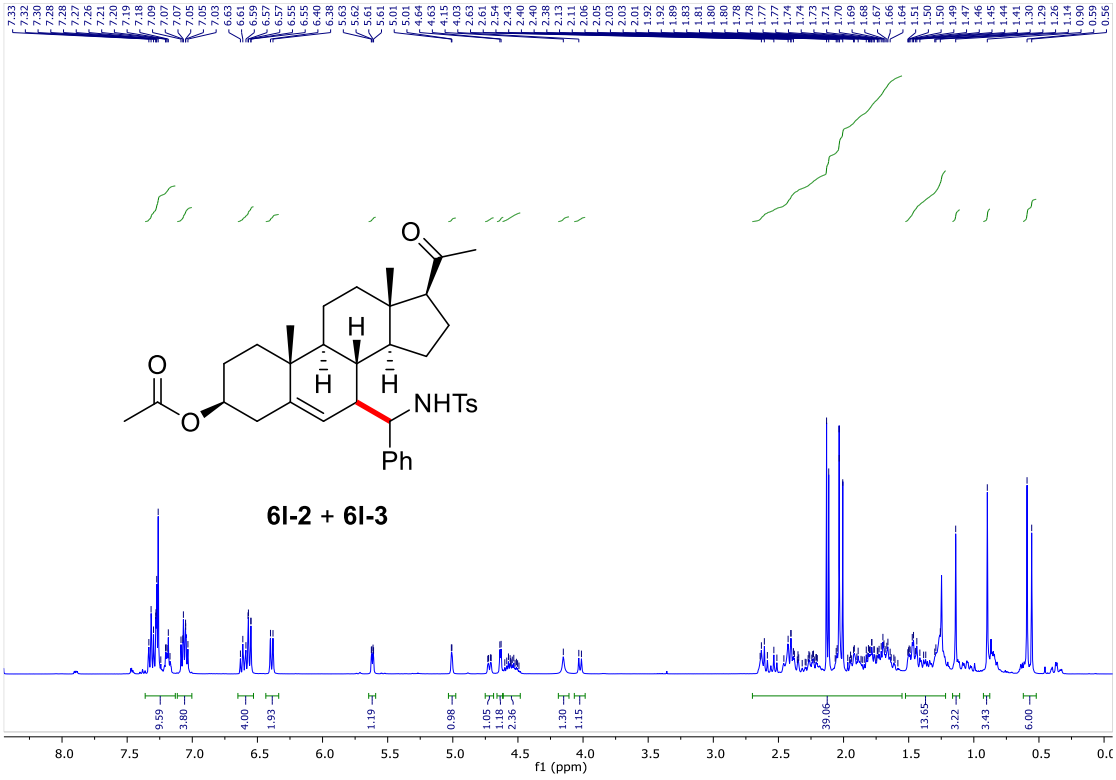

H6
H3+ H20
H17H1
HN
C4
C20
C17
C3
C6
O
H
NHPh
Ph
f2 (ppm)
f1 (ppm)

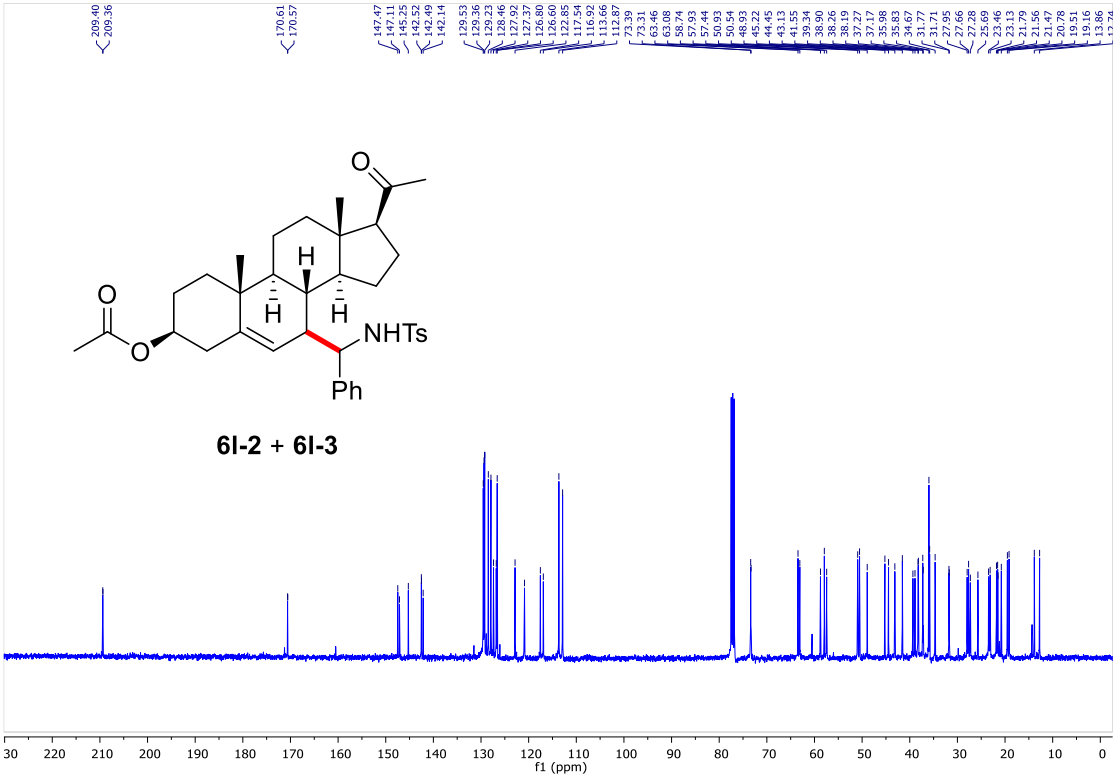
^{1}H-^{13}C HMBC

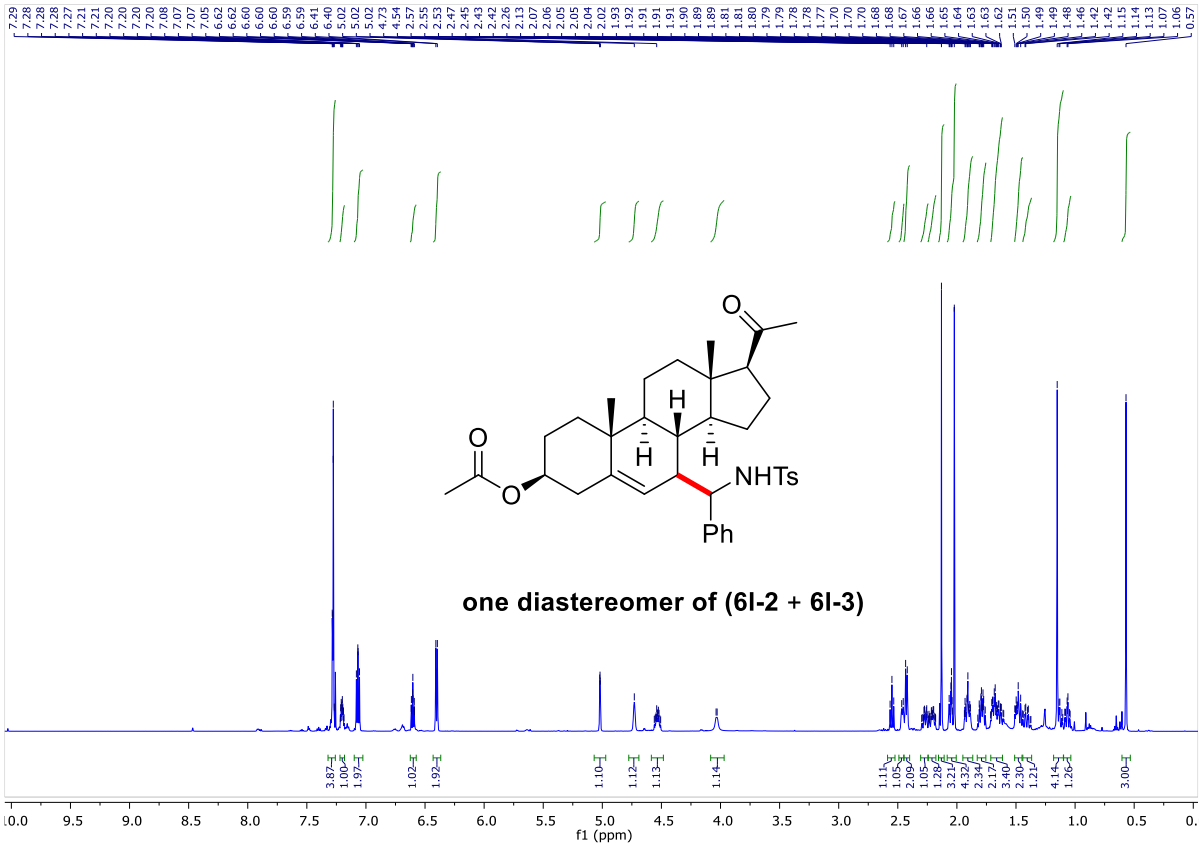

O
H
H
H
O
O
NHPh
Ph
6l-1
f2 (ppm)
f1 (ppm)


H4
H19
C3
C6
C5
O
H
H
H
NHPh
Ph
f2 (ppm)
f1 (ppm)

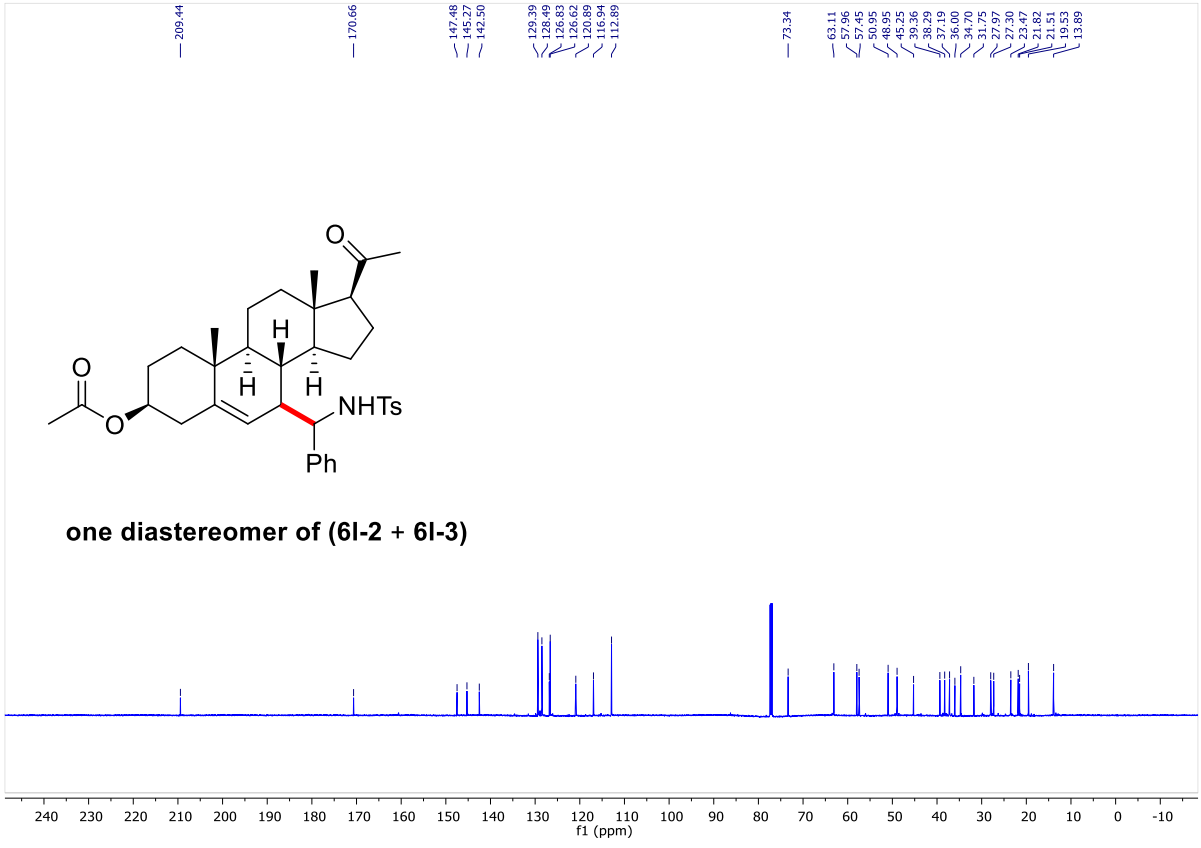

H6
H20
HN
C7
O
O
NHPh
Ph
f2 (ppm)
f1 (ppm)


O
H
O
O
H
H
NHTs
Ph
6l-2 + 6l-3
9.59
3.80
4.00
1.93
1.19
0.98
1.05
1.18
2.36
1.30
1.15
39.06
13.65
3.22
3.43
6.00
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
f1 (ppm)


O
H
O
O
H
H
NHTs
Ph
6l-2 + 6l-3
f1 (ppm)

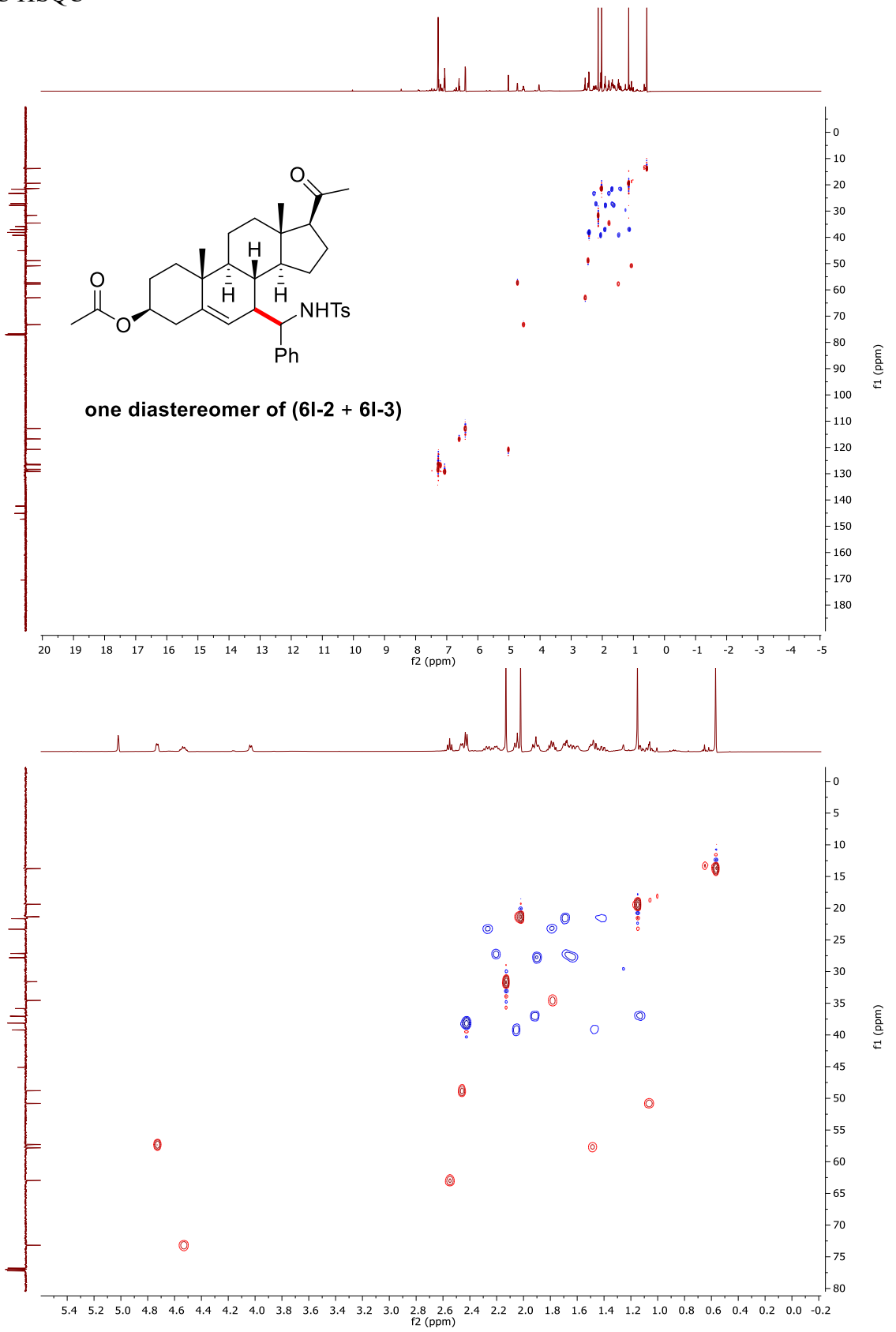


one diastereomer of (6l-2 + 6l-3)

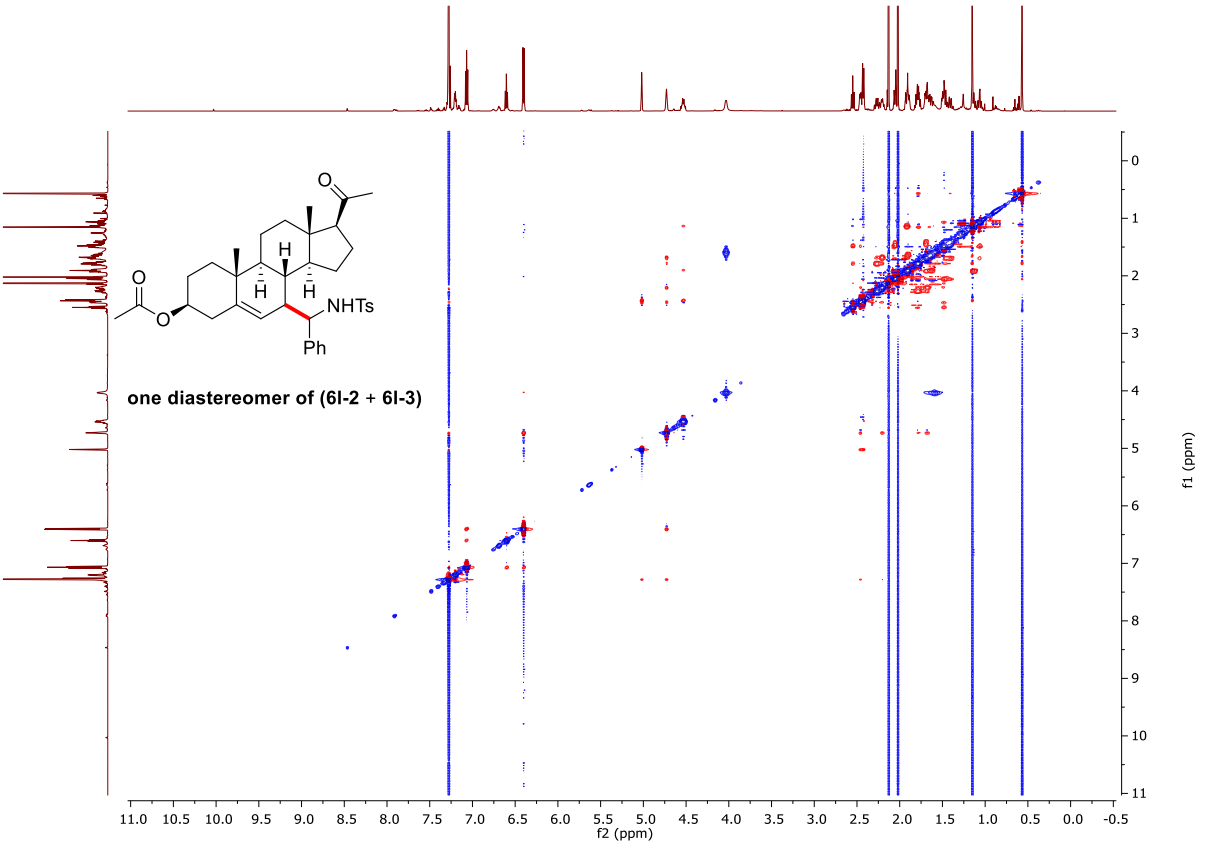


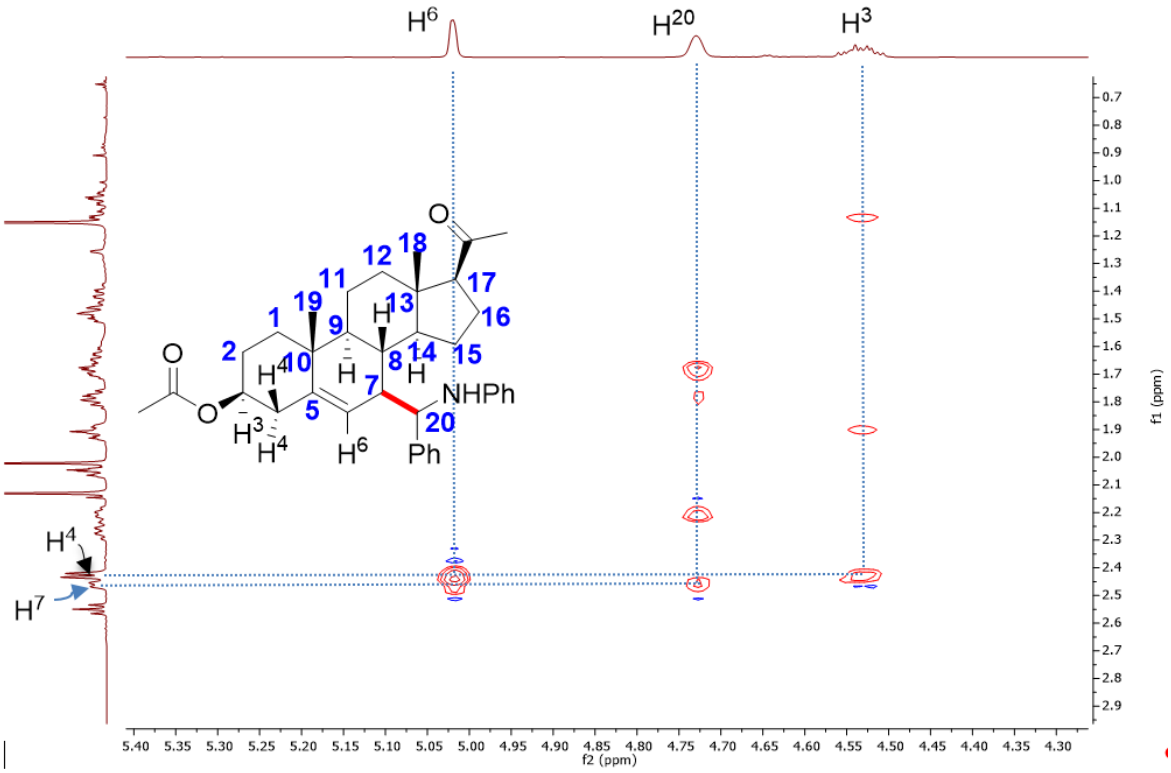
one diastereomer of (6l-2 + 6l-3)

^{1}H-^{13}C HSQC

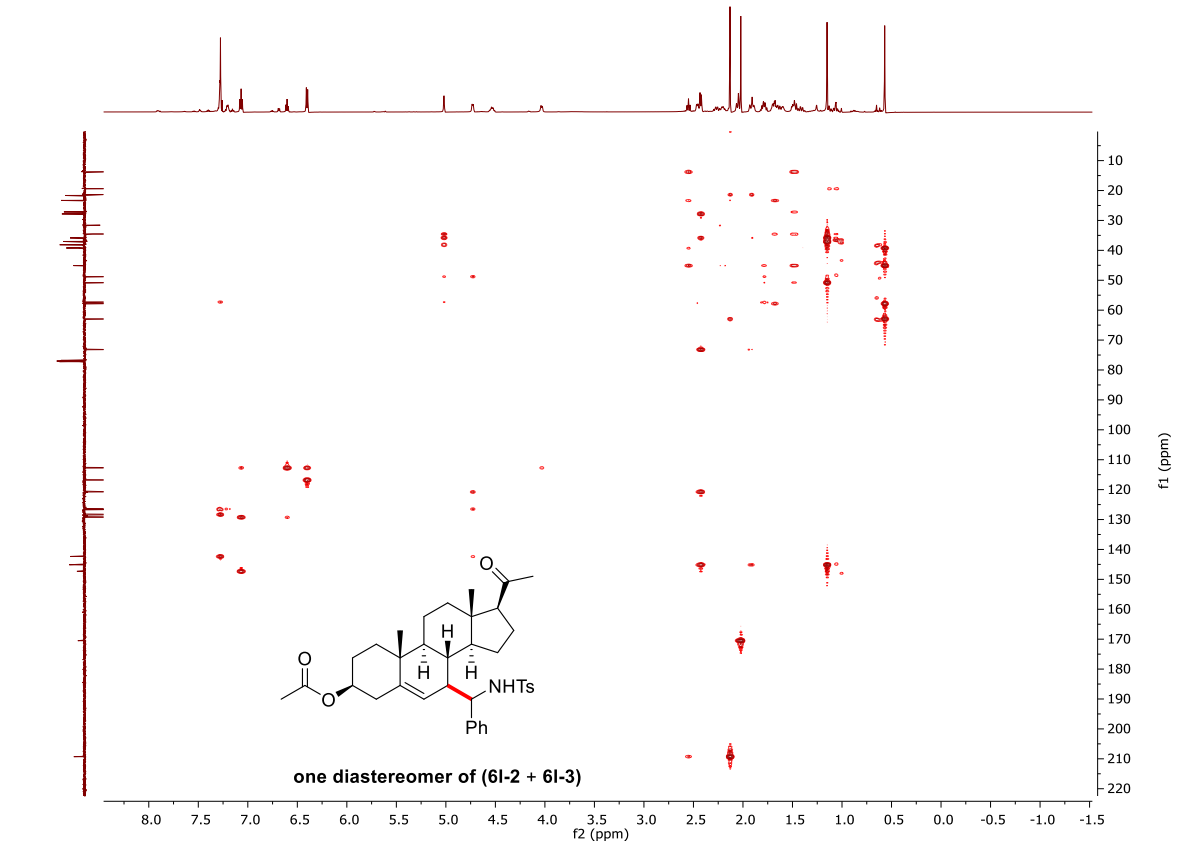


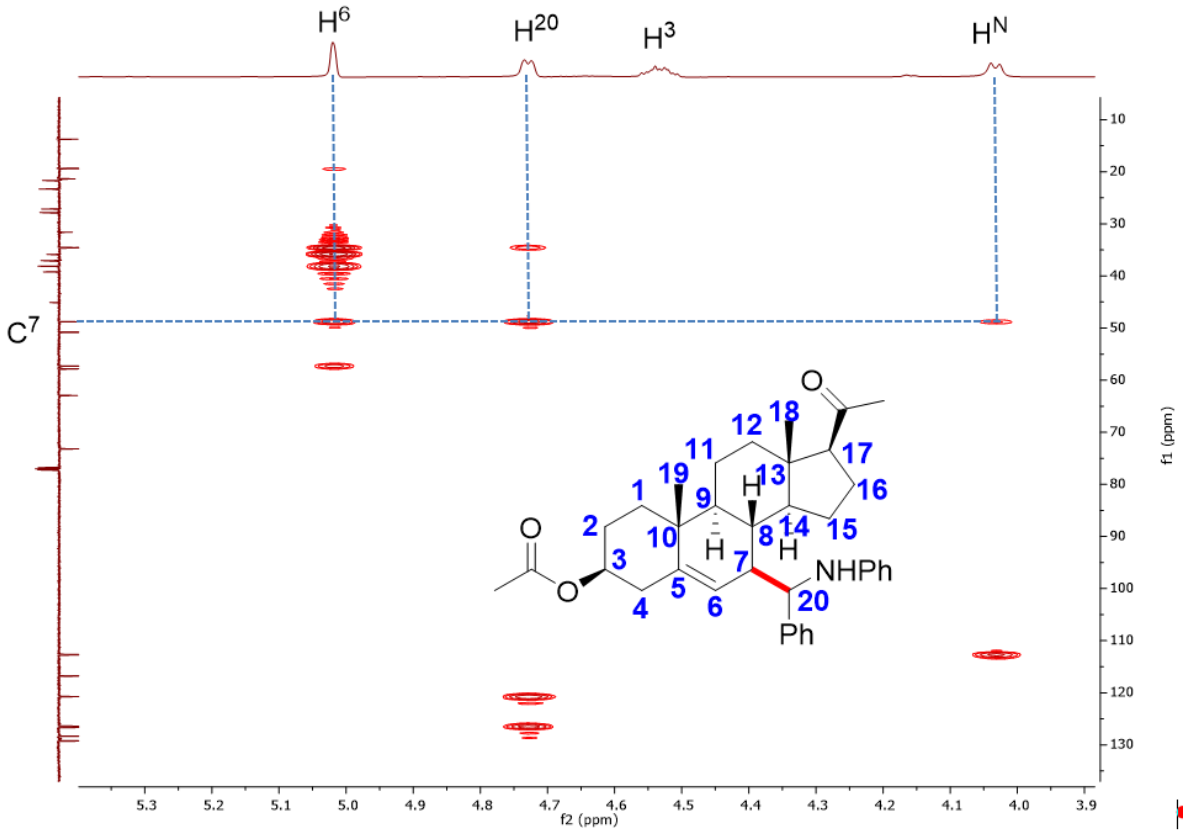
NOESY


one diastereomer of (6l-2 + 6l-3)
f2 (ppm)
f1 (ppm)


H6
H20
H3
H4
H7
f2 (ppm)
f1 (ppm)

^{1}H-^{13}C HMBC


f2 (ppm)
f1 (ppm)
one diastereomer of (6l-2 + 6l-3)
NHTs
Ph


H6
H20
H3
HN
C7
f2 (ppm)
f1 (ppm)
NHPh
Ph