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Tethered photocatalyst-directed palladium-catalysed C–H allenylation of *N*-aryl tetrahydroisoquinolines

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Supporting Information

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List of acronyms and abbreviations

Ac	acetyl
Ar	aryl
bpy	2,2’-bipyridine
Bu	butyl
Cy	cyclohexyl
DCM	dichloromethane
dF(CF_3)ppy	2-(2,4-difluorophenyl)-5-trifluoromethylpyridine
DMF	*N,N*-dimethylformamide
dtbbpy	4,4’-di-*tert*-butyl-2,2’-bipyridine
Me	methyl
NBS	*N*-bromosuccinimide
Ph	phenyl
ppy	2-phenylpyridine
Pr	propyl
SPhos	2-dicyclohexylphosphino-2’,6’-dimethoxybiphenyl
TFA	trifluoroacetic acid

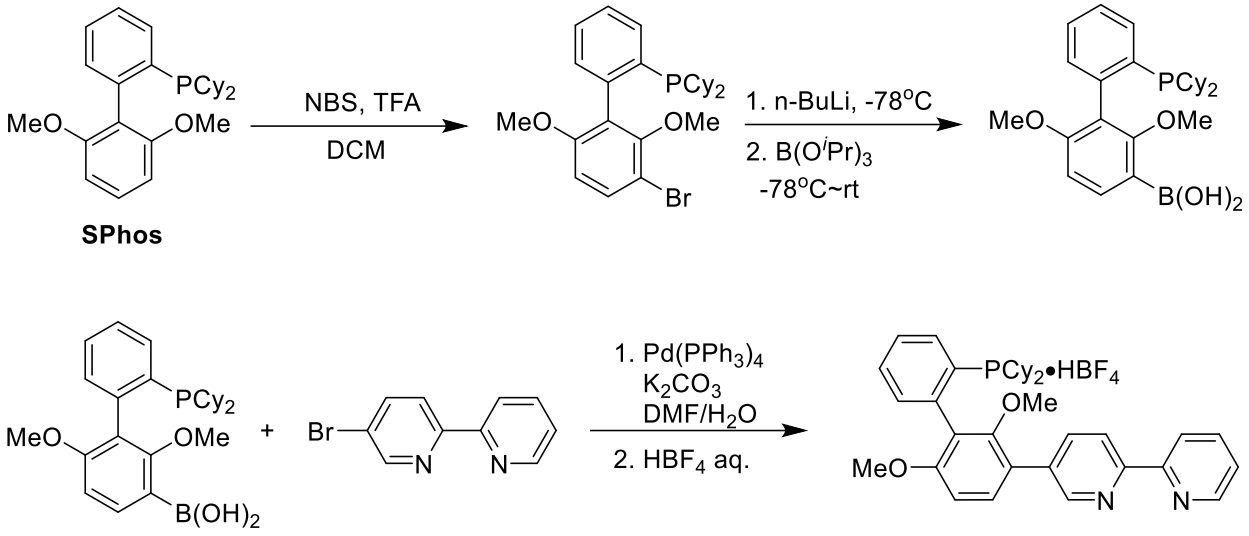
General information

Materials: Commercially available reagents and solvents were used as received. Commercial dry solvents (Aldrich Sure/Seal^{TM}) were sparged with nitrogen before used in catalytic reactions. Solvents used for column chromatography were analytical grade. Blue LED strips (2 meter, 19 W) were purchased from Inleds Lighting Pte Ltd (Singapore).

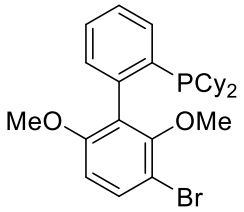
Methods: Unless otherwise noted, all experiments were set up under an atmosphere of nitrogen in a glovebox or using standard Schlenk techniques. Reactions were monitored by thin layer chromatography (TLC) or nuclear magnetic resonance (NMR) analysis. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 300-400 mesh). Yields refer to isolated yields after flash column chromatography purification.

Characterization: Products were characterized by means of nuclear magnetic resonance (NMR), mass spectrometry (MS). ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on Bruker 400 MHz and 500 MHz spectrometer with tetramethylsilane as internal standard. Chemical shifts were reported relative to tetramethylsilane (0 ppm) for ^{1}H NMR and relative to $CDCl_3$ (77.0 ppm) for ^{13}C NMR. ^{19}F spectra were calibrated from external standard ($CFCl_3$: 0 ppm). ^{31}P spectra were calibrated from external standard (85 wt% phosphoric acid: 0 ppm). NMR data are reported as: chemical shift (parts per million, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), and integration. X-ray diffraction was performed on Bruker D8 Venture single crystal X-ray diffractometer. Absorption and emission spectra were taken at ambient temperature using Edinburgh FS5 spectrofluorometer. Preparative HPLC was performed on a Shimadzu *i*-series HPLC system equipped with photodiode array (PDA) detector and Agilent Zorbax SB-C18 columns (5 μm, 9.4 x 250 mm).

Preparation of covalently tethered SPhos-PCs



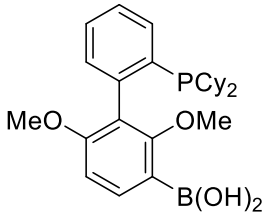
(3'-bromo-2',6'-dimethoxy-[1,1'-biphenyl]-2-yl)dicyclohexylphosphane



TFA (5.57 ml, 75 mmol) was added to a solution of SPhos (4.10 g, 10 mmol) in 20 mL DCM, then NBS (1.78 g, 10 mmol) was added over ten minutes at 0 °C. After addition, the resulting reaction mixture was stirred at this temperature for 10 min. The reaction was quenched with saturated NaOH (3.00 g, 75 mmol) aqueous to pH 9-10 and extracted with DCM three times. The combined organic phases were washed with water and brine, dried over Na_2SO_4, and concentrated under vacuum to give the desired product SPhos-Br as a white solid which was directly used in the next step without further purification (4.7 g, 96% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.56 (m, 1H), 7.50 (d, *J* = 8.9 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.23 – 7.18 (m, 1H), 6.60 (d, *J* = 8.9 Hz, 1H), 3.67 (s, 3H), 3.45 (s, 3H), 1.98 – 1.87 (m, 1H), 1.75 – 1.60 (m, 10H), 1.52 (d, *J* = 11.1 Hz, 1H), 1.30 – 1.01 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.13 (d, *J* = 1.0 Hz), 154.92, 141.91 (d, *J* = 32.3 Hz), 136.59 (d, *J* = 19.2 Hz), 132.56 (d, *J* = 3.5 Hz), 132.20, 130.93 (d, *J* = 6.2 Hz), 127.97, 127.46 (d, *J* = 7.1 Hz), 126.79, 108.24, 107.27, 60.28, 55.50, 34.98 (d, *J* = 14.3 Hz)1, 33.67 (d, *J* = 13.2 Hz), 30.21, 30.04, 29.73 (d, *J* = 2.5 Hz), 29.61, 29.46 (d, *J* = 11.1 Hz), 27.66 (d, *J* = 2.0 Hz), 27.57, 27.40 (d, *J* = 4.0 Hz), 27.30 (d, *J* = 6.8 Hz), 26.49 (d, *J* = 8.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -8.85. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{26}H_{35}BrO_2P]^+$[M+H]$^+$: 489.1553, Found: 489.1548.

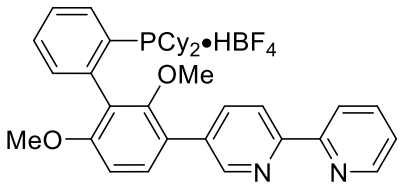
(2'-(dicyclohexylphosphaneyl)-2,6-dimethoxy-[1,1'-biphenyl]-3-yl)boronic acid



To a stirred solution of SPhos-Br (3.40 g, 6.95 mmol) in THF (35 mL) was added *n*-BuLi (2.0 M in cyclohexane, 4.20 mL, 8.40 mmol) at -78 ºC under nitrogen. After the mixture was stirred for 1 hour at -78 ºC, triisopropyl borate (2.13 mL, 9.23 mmol) was added in one portion. Then, the mixture was warmed to 25 ºC and was stirred for 20 min. Then the reaction was quenched with 1 M HCl aqueous solution and stirred for another 1 hour to hydrolyze borate completely. After that, the solution was extracted with DCM three times. The combined organic phases were neutralized with 1 M NaOH aqueous solution. The DCM layer was dried over Na_2SO_4 and evaporated to obtain the crude SPhos-$B(OH)_2$ that was purified by flash column chromatography with DCM/MeOH 60:1 to give the pure product as white solid (2.26 g, 72% yield).[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 1H), 7.63 – 7.58 (m, 1H), 7.42 – 7.34 (m, 2H), 7.32 – 7.27 (m, 1H), 6.79 (d, *J* = 8.5 Hz, 1H), 6.38 (s, 2H), 3.72 (s, 3H), 3.30 (s, 3H), 2.07 – 1.96 (m, 1H), 1.79 – 1.49 (m, 12H), 1.22 – 1.05 (m, 6H), 0.94 – 0.82 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.92 (d, *J* = 1.6 Hz), 160.63, 141.92 (d, *J* = 32.0 Hz), 136.75, 136.56 (d, *J* = 19.6 Hz), 132.75 (d, *J* = 3.6 Hz), 131.71 (d, *J* = 6.0 Hz), 127.94, 126.65, 124.27 (d, *J* = 7.2 Hz), 106.63, 103.14, 61.13, 55.43, 35.12 (d, *J* = 15.2 Hz), 32.90 (d, *J* = 13.5 Hz), 30.00 (d, *J* = 18.0 Hz), 29.76 (d, *J* = 7.2 Hz), 29.66, 29.53, 28.76 (d, *J* = 6.8 Hz), 27.72 (d, *J* = 11.8 Hz), 27.54 (d, *J* = 6.9 Hz), 27.29 (d, *J* = 9.7 Hz), 27.12, 26.48 (d, *J* = 3.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -8.85. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{26}H_{37}BO_4P]^+$[M+H]$^+$: 455.2517, Found: 455.2526.

(3'-([2,2'-bipyridin]-5-yl)-2',6'-dimethoxy-[1,1'-biphenyl]-2-yl) dicyclohexylphosphonium tetrafluoroborate

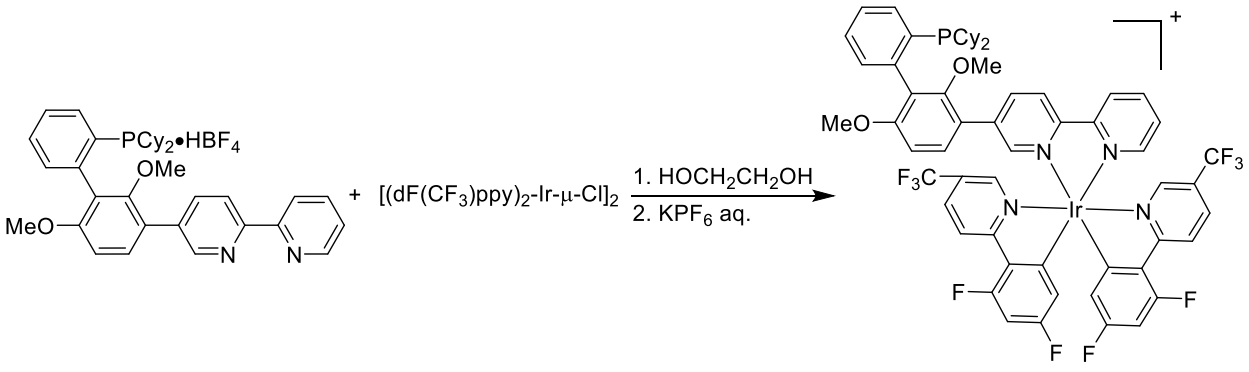


5-bromo-2,2'-bipyridine (361.3 mg, 1.53 mmol, prepared according to the literature procedure[2]), SPhos-$B(OH)_2$ (838 mg, 1.84 mmol) and $Pd(PPh_3)_4$ (60 mg, 0.05 mmol) was added into a round bottom flask in the glove box under N_2 atmosphere. Degassed DMF 15 mL and degassed 1 M K_2CO_3 aqueous solution (36.9 mL, 36.9 mmol) were added via syringe. Then the mixture was heated at 100 ºC overnight. The reaction mixture was added water and extracted with ethyl acetate for three times. The combined organic layers were dried with

Na_2SO_4 and evaporated to obtain the crude product that was purified by flash column chromatography (neutral Al_2O_3) with hexane and ethyl acetate (10:1) to give the pure product.[3] Then DCM 4 mL and tetrafluoroboric acid solution (48 wt. % in H_2O) 1 mL were added and stirred for 1 hour. The reaction mixture was added water and extracted with DCM three times. The DCM layers were dried over Na_2SO_4 and evaporated to obtain product SPhos-bpy·HBF_4 as a yellow solid which was directly used in the next step without further purification (435.1 mg, 44% yield).[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, *J* = 1.5 Hz, 1H), 8.76 (d, *J* = 4.3 Hz, 1H), 8.53 (d, *J* = 8.3 Hz, 1H), 8.43 (d, *J* = 8.0 Hz, 1H), 8.32 (dd, *J* = 8.3, 2.2 Hz, 1H), 8.06 (td, *J* = 7.8, 1.8 Hz, 1H), 7.97 – 7.88 (m, 1H), 7.80 (t, *J* = 7.5 Hz, 1H), 7.72 (t, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 8.7 Hz, 1H), 7.57 – 7.47 (m, 2H), 7.02 (d, *J* = 8.8 Hz, 1H), 6.78 (brs, 0.5H), 5.56 (brs, 0.5H), 5.03 (brs, 2H), 3.79 (s, 3H), 3.09 (s, 3H), 2.96 – 2.81 (m, 1H), 2.71 – 2.54 (m, 1H), 2.03 – 1.94 (m, 1H), 1.91 – 1.81 (m, 4H), 1.75 – 1.62 (m, 5H), 1.55 – 1.27 (m, 7H), 1.22 – 1.06 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 154.5, 150.9, 149.6, 148.0, 147.3, 140.7, 140.5, 140.4, 140.0, 135.3, 134.1, 134.1, 133.7, 133.6, 133.3, 133.2, 133.1, 129.2, 129.1, 125.5, 123.2, 122.3, 122.2, 121.1, 108.7, 60.9, 56.0, 29.7, 29.2, 28.8, 28.4, 27.1, 26.8, 26.1, 25.9, 25.8, 25.6, 25.1, 25.0. (Observed complexity due to P-C splitting; definitive assignments have not yet been made). ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.75. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{36}H_{42}N_2O_2P]^+$[M-BF4]$^+$: 565.2978, Found: 565.2979.

SPhos-PC1

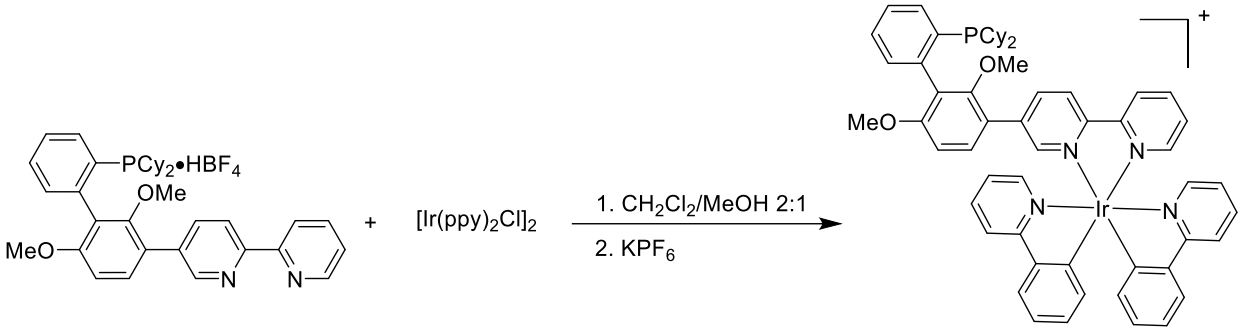


SPhos-bpy·HBF_4 (88.2 mg, 0.14 mmol) and [(dF(CF_3)ppy)$_2$-Ir-μ-Cl]$_2$ (91.5 mg, 0.06 mmol, prepared according to the literature procedure[5,6]) were dissolved in 2.4 mL ethylene glycol and reflux for 4 hours at 120 °C. The reaction

mixture was precipitated with saturated solution of KPF_6 aqueous 2.4 mL. The solution was filtered, and the residue was washed with distilled water three times, Et_2O three times to give the desired product as a yellow powder (175.0 mg, 94% yield).[7]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (d, *J* = 8.7 Hz, 1H), 8.66 – 8.59 (m, 2H), 8.49 (t, *J* = 11.1 Hz, 2H), 8.27 (td, *J* = 7.8, 1.5 Hz, 1H), 8.13 (d, *J* = 2.1 Hz, 1H), 8.10 – 8.06 (m, 2H), 7.98 (d, *J* = 5.3 Hz, 1H), 7.85 – 7.79 (m, 2H), 7.76 – 7.72 (m, 1H), 7.66 – 7.63 (m, 2H), 7.57 (s, 1H), 7.54 – 7.51 (m, 1H), 7.33 (d, *J* = 8.8 Hz, 1H), 6.95 (d, *J* = 8.9 Hz, 1H), 6.67 – 6.56 (m, 2H), 6.51 (d, *J* = 9.2 Hz, 0.5H), 5.69 (dd, *J* = 7.9, 2.3 Hz, 1H), 5.61 (dd, *J* = 7.9, 2.3 Hz, 1H), 5.53 (d, *J* = 9.5 Hz, 0.5H), 3.75 (s, 3H), 2.81 (s, 3H), 2.76 – 2.69 (m, 1H), 2.50 – 2.41 (m, 1H), 1.82 – 1.60 (m, 10H), 1.56 – 1.50 (m, 2H), 1.44 – 1.36 (m, 3H), 1.19 – 0.96 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.82, 167.78, 165.93, 165.84, 163.85, 163.75, 163.67, 163.57, 163.46, 161.57, 161.47, 161.36, 158.90, 155.66, 154.30, 154.12, 154.07, 153.89, 153.84, 152.92, 150.34, 149.55, 145.01, 144.98, 144.94, 144.90, 142.14, 141.12, 139.84, 139.80, 139.65, 136.94, 136.80, 134.41, 134.34, 134.27, 133.04, 132.96, 132.88, 129.58, 129.49, 128.91, 126.47, 126.31, 126.18, 125.75, 125.54, 124.00, 123.85, 123.71, 122.64, 121.63, 120.71, 120.67, 120.47, 114.47, 114.33, 114.07, 113.93, 113.64, 113.01, 108.90, 100.42, 100.22, 100.02, 99.82, 60.79, 56.01, 29.71, 29.58, 29.25, 28.28, 27.94, 26.64, 26.62, 26.41, 26.13, 25.94, 25.84, 25.81, 25.74, 25.69, 25.64, 24.98, 24.67. (Observed complexity due to P-C, F-C splitting; definitive assignments have not yet been made). ^{31}P NMR (202 MHz, $CDCl_3$) δ 16.24, -133.93, -137.45, -140.97, -144.50, -148.02, -151.54, -155.07. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.75, -62.85, -71.68, -73.58. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{60}H_{52}F_{16}IrN_4O_2P_2]^+[M\text{-}BF_4]^+$: 1419.2939, Found: 1419.2933; Calcd. for Chemical Formula: $[C_{60}H_{51}F_{10}IrN_4O_2P]^+[M\text{-}BF_4\text{-}HPF_6]^+$: 1273.3219, Found: 1273.3234; Calcd. for Chemical Formula: $[C_{60}H_{52}F_{10}IrN_4O_2P]^{2+}[M\text{-}BF_4\text{-}PF_6]^{2+}$: 637.1646, Found: 637.1654.

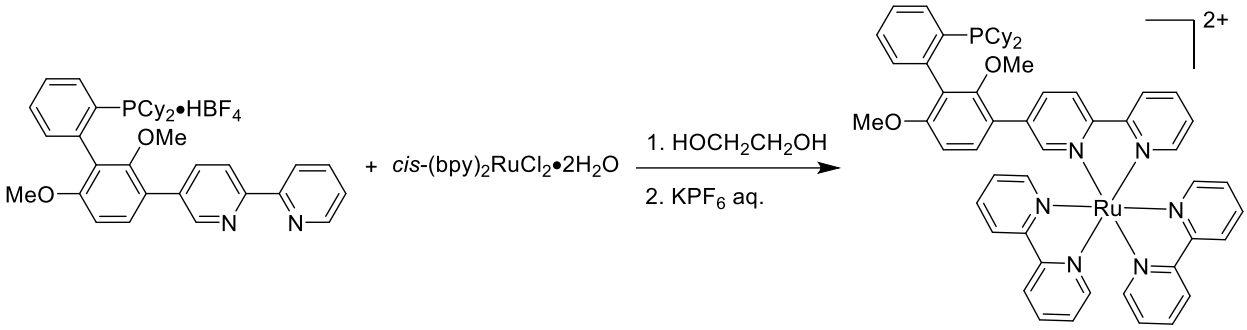
SPhos-PC2



SPhos-bpy·HBF_4 (78.3 mg, 0.12 mmol) and $[Ir(ppy)_2Cl]_2$ (53.6 mg, 0.05 mmol, prepared according to the literature procedure[8]) were dissolved in degassed 2:1 mixture of DCM/MeOH 12 mL under N_2 atmosphere in the dark. The reaction mixture was refluxed at 50 °C for 23 hours. After cooling down the solution to room temperature, KPF_6 (92.0 mg, 0.5 mmol) was added. The insoluble inorganic solid was filtered off and the filtrate was evaporated to afford crude product, which was washed with DCM 0.5 mL one time, Et_2O 5 mL three times to give the desired product as a yellow powder (112.0 mg, 86% yield).[9]

^{1}H NMR (500 MHz, Acetone-d_6) δ 8.94 – 8.82 (m, 2H), 8.53 (d, *J* = 8.4 Hz, 0.5H), 8.43 (d, *J* = 7.6 Hz, 0.5H), 8.34 (d, *J* = 7.0 Hz, 1H), 8.31 – 8.22 (m, 2H), 8.20 (d, *J* = 8.3 Hz, 0.5H), 8.19 – 8.12 (m, 1H), 8.09 (t, *J* = 6.1 Hz, 1H), 8.01 – 7.89 (m, 6H), 7.90 – 7.84 (m, 1H), 7.85 – 7.79 (m, 1.5H), 7.74 – 7.67 (m, 2H), 7.54 (d, *J* = 8.7 Hz, 0.5H), 7.31 – 7.22 (m, 1H), 7.22 – 7.14 (m, 2H), 7.15 – 7.09 (m, 1H), 7.07 – 7.00 (m, 1.5H), 6.98 – 6.83 (m, 3H), 6.41 (t, *J* = 6.8 Hz, 1H), 6.34 (dd, *J* = 7.9, 2.2 Hz, 1H), 3.84 (s, 3H), 3.06 (s, 1.5H), 2.75 (s, 1.5H), 2.01 – 1.92 (m, 2H), 1.88 – 1.69 (m, 7H), 1.67 – 1.59 (m, 3H), 1.53 – 1.43 (m, 3H), 1.40 – 1.28 (m, 5H), 1.16 – 1.07 (m, 2H). ^{13}C NMR (126 MHz, Acetone-d_6) δ 206.2, 168.7, 168.6, 168.6, 168.5, 159.8, 159.7, 156.9, 156.8, 155.8, 155.4, 155.2, 155.1, 151.5, 151.5, 151.1, 151.0, 150.8, 150.3, 150.2, 150.2, 145.2, 145.1, 144.9, 141.2, 141.2, 140.7, 140.5, 140.3, 139.7, 139.6, 139.5, 139.0, 138.5, 135.3, 135.2, 135.1, 135.0, 134.2, 134.2, 134.2, 134.1, 133.8, 133.1, 132.7, 132.4, 131.3, 131.3, 130.0, 129.9, 129.3, 125.9, 125.8, 125.8, 125.6, 125.5, 124.7, 124.5, 124.4, 123.5, 123.3, 123.0, 122.5, 120.9, 120.8, 120.6, 109.9, 109.8, 61.6, 61.3, 56.7, 29.8, 28.9, 28.7, 28.5, 28.4, 27.8, 27.7, 27.6, 27.4, 26.7, 26.5, 26.5, 26.5, 26.4, 26.4, 26.3, 26.1, 25.9, 25.8. ^{31}P NMR (202 MHz, Acetone-d_6) δ 17.46, 17.13, 16.76, -133.76, -137.25, -140.75, -144.25, -147.74, -151.24, -154.73. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{58}H_{58}F_6IrN_4O_2P_2]^+$[M-$BF_4$]$^+$: 1211.3568, Found: 1211.3573; Calcd. for Chemical Formula: $[C_{58}H_{57}IrN_4O_2P]^+$[M-$BF_4$-$HPF_6$]$^+$: 1065.3847, Found: 1065.3855; Calcd. for Chemical Formula: $[C_{58}H_{58}IrN_4O_2P]^{2+}$[M-$BF_4$-$PF_6$]$^{2+}$: 533.1960, Found: 533.1969.

SPhos-PC3



SPhos-bpy·HBF_4 (171.5 mg, 0.26 mmol) and *cis*-$(bpy)_2RuCl_2 \cdot 2H_2O$ (115.7 mg, 0.22 mmol, prepared according to the literature procedure[10]) were dissolved in 5 mL ethylene glycol and reflux for 2 hours at 120 °C. The reaction mixture was precipitated with saturated solution of KPF_6 aqueous 4 mL. The solution was filtered, and the residue was washed with distilled water three times, Et_2O three times to give the desired product as an orange powder (273.0 mg, 92% yield).[7]

^{1}H NMR (500 MHz, CD_3CN) 1:1 dr δ 8.60 – 8.51 (m, 5H), 8.43 (d, *J* = 9.4 Hz, 1H), 8.31 – 8.21 (m, 1H), 8.12 – 8.04 (m, 4H), 8.03 – 7.98 (m, 1H), 7.91 – 7.70 (m, 9H), 7.57 – 7.49 (m, 1H), 7.49 – 7.35 (m, 6H), 6.98 (dd, *J* = 16.4, 8.8 Hz, 1H), 6.50 (td, *J* = 9.0, 4.4 Hz, 0.5H), 5.53 (td, *J* = 9.1, 4.4 Hz, 0.5H), 3.75 (s, 1.5H), 3.74 (s, 1.5H), 3.06 (s, 1.5H), 2.87 – 2.76 (m, 1H), 2.65 (s, 1.5H), 2.59 – 2.49 (m, 1H), 1.90 – 1.54 (m, 10H), 1.49 – 1.23 (m, 8H), 1.16 – 1.08 (m, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 159.42, 159.32, 157.98, 157.91, 157.88, 157.85, 157.77, 156.34, 156.31, 155.63, 155.41, 152.95, 152.89, 152.79, 152.70, 152.67, 152.65, 152.61, 152.56, 151.28, 150.99, 141.10, 141.06, 139.08, 138.87, 138.76, 138.67, 138.65, 138.20, 138.01, 135.27, 134.87, 134.84, 134.80, 134.77, 134.14, 134.07, 134.01, 133.58, 133.24, 129.98, 129.94, 129.88, 129.85, 128.62, 128.51, 128.47, 128.44, 128.39, 128.36, 125.38, 125.23, 125.17, 125.13, 124.73, 124.71, 123.06, 122.82, 122.01, 121.72, 114.47, 113.84, 109.60, 109.45, 61.68, 61.11, 56.82, 56.79, 29.91, 29.57, 28.94, 28.60, 27.77, 27.46, 27.43, 27.40, 27.37, 27.32, 27.29, 26.54, 26.48, 26.42, 26.37, 26.30, 26.19, 26.08, 25.77, 25.65. (1:1 dr. observed complexity due to P-C splitting; definitive assignments have not yet been made). ^{31}P NMR (162 MHz, CD_3CN) δ 17.34, 17.23, -135.90, -140.26, -144.62, -148.98, -153.34. HRMS (m/z, ESI): Calcd. for Chemical Formula: Calcd. for Chemical Formula:

$[C_{56}H_{58}BF_{10}N_6O_2P_2Ru]^+[M\text{-}PF_6]^+$: 1211.3090, Found: 1211.0967; $[C_{56}H_{57}F_6N_6O_2P_2Ru]^+[M\text{-}HBF_4\text{-}PF_6]^+$: 1123.2976, Found: 1123.2972; Calcd. for Chemical Formula: $[C_{56}H_{57}N_6O_2PRu]^{2+}[M\text{-}HBF_4\text{-}(PF_6)_2]^{2+}$: 489.1664, Found: 489.1667.

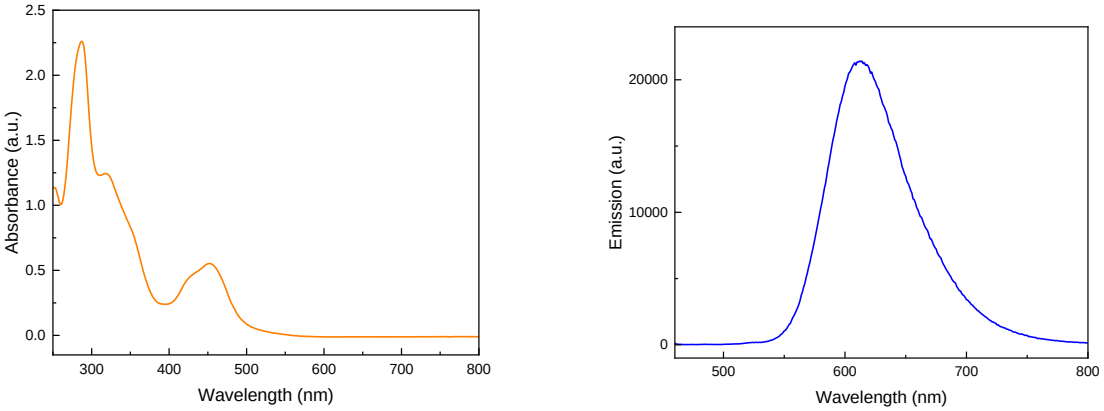


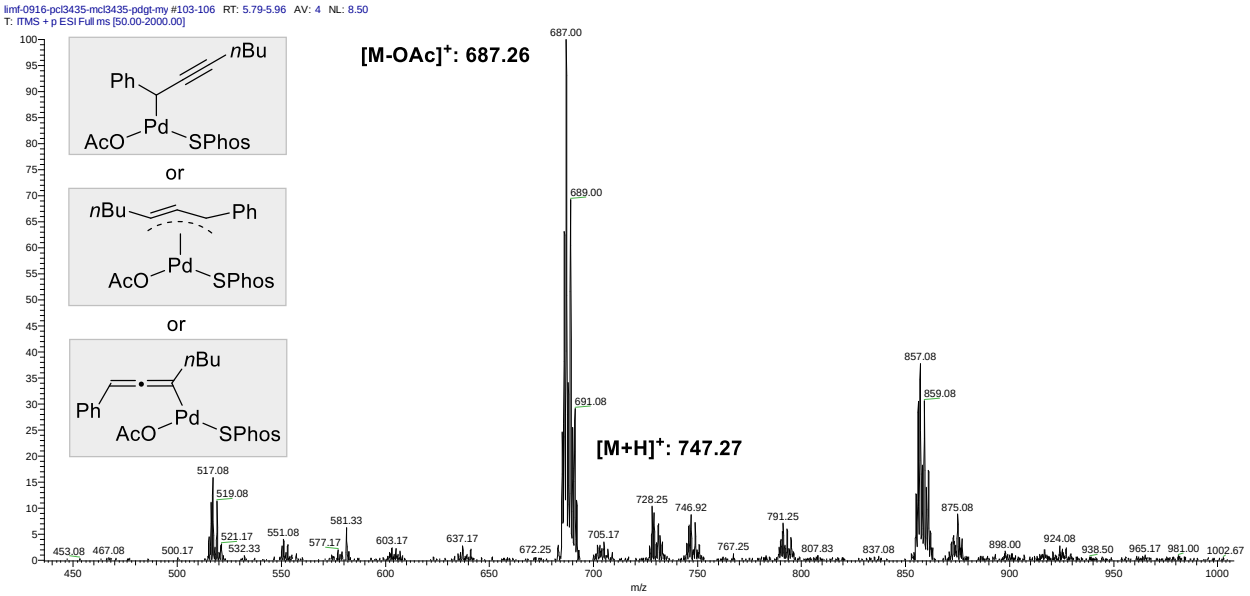
Figure S1 Absorption and emission spectra of **SPhos-PC3** (5.0 x 10^{-5} M) in acetonitrile. Emission spectra was excited at 452 nm.

Table S1. Photophysical Data of **SPhos-PC3** compared to **$[Ru(bpy)_3]^{2+}$**

compound	Absorption: λ_{max} (nm)[a]	ε ($M^{-1}cm^{-1}$)	Emission: λ_{max} (nm)
$[Ru(bpy)_3]^{2+}$ (ref. 11)	450	$1.46x10^4$	615
SPhos-PC3	452	$1.1x10^4$	612

[a]Maxima of the lowest energy MLCT absorption.

Figure S2 Detailed explanation for ESI-MS spectra of allenyl-Pd-SPhos complex



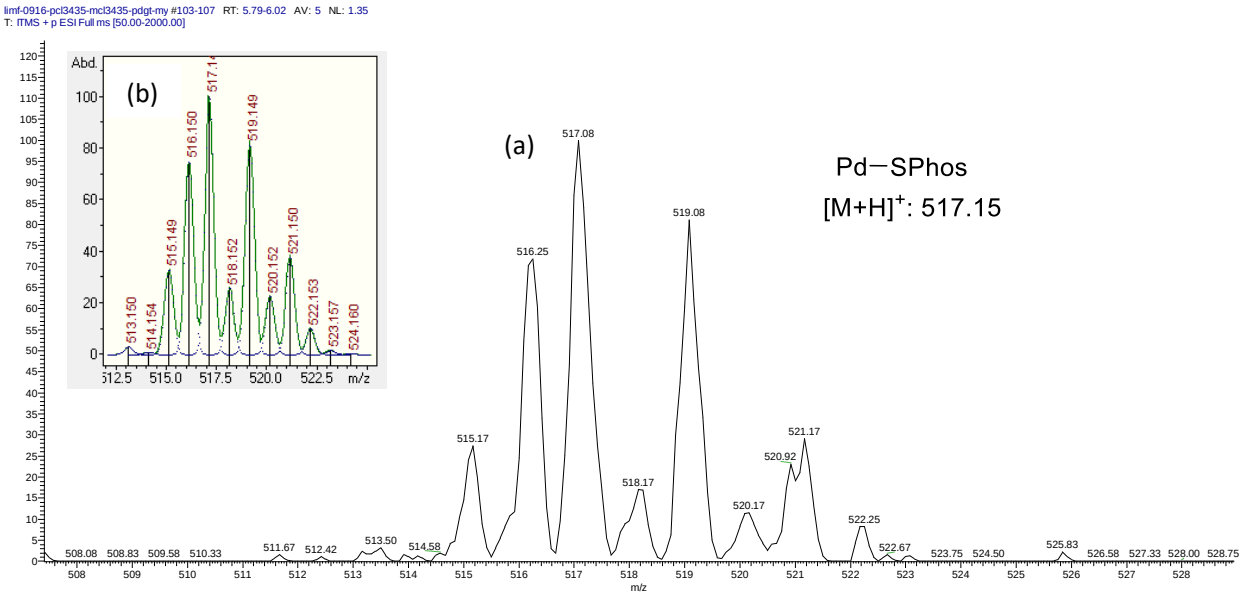


Figure S2A Isotopic distribution of Pd-SPhos complex. (a) Measured isotopic distribution for $[C_{26}H_{36}O_2PPd]^+[M+H]^+$: 517.08. (b) Simulated isotopic distribution for $[C_{26}H_{36}O_2PPd]^+[M+H]^+$: 517.15.

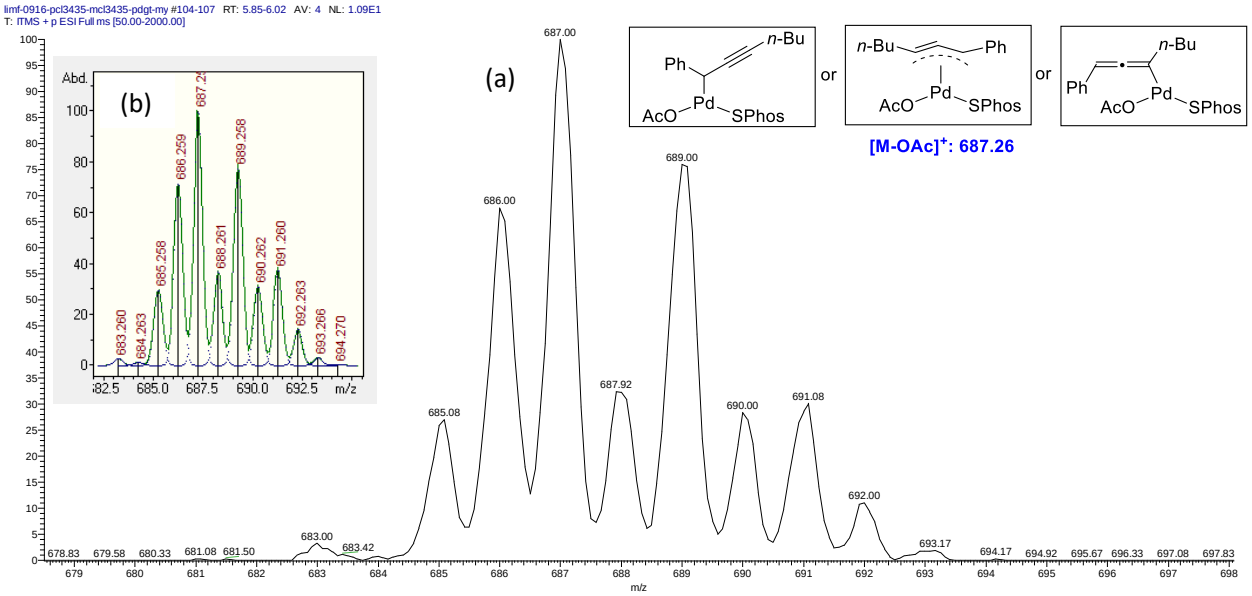


Figure S2B Isotopic distribution of allenyl/propargyl–Pd–SPhos complexes. (a) Measured isotopic distribution for $[C_{39}H_{50}O_2PPd]^+[M\text{-}OAc]^+$: 687.00. (b) Simulated isotopic distribution for $[C_{39}H_{50}O_2PPd]^+[M\text{-}OAc]^+$: 687.26.

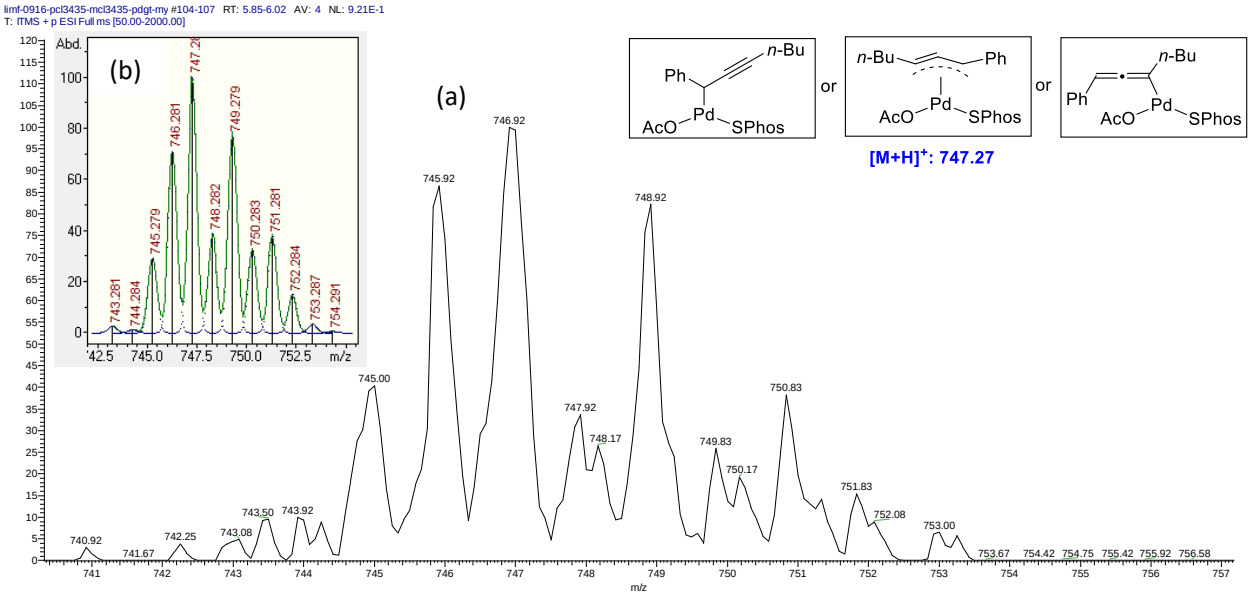


Figure S2C Isotopic distribution of allenyl/propargyl–Pd–SPhos complexes. (a) Measured isotopic distribution for $[C_{41}H_{54}O_4PPd]^+[M+H]^+$: 746.92. (b) Simulated isotopic distribution for $[C_{41}H_{54}O_4PPd]^+[M+H]^+$: 747.28.

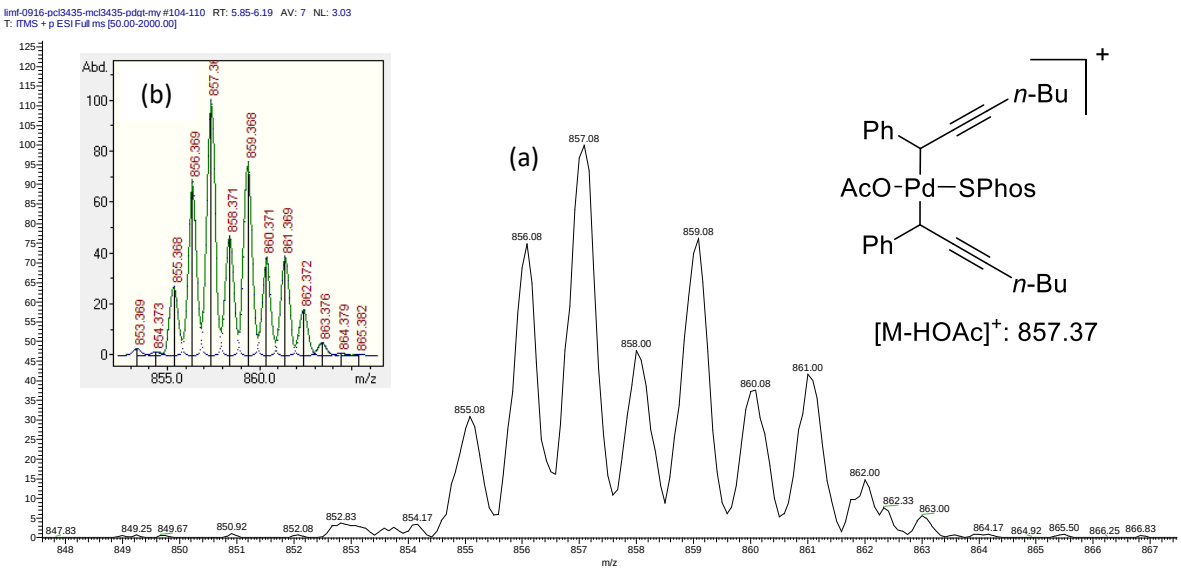


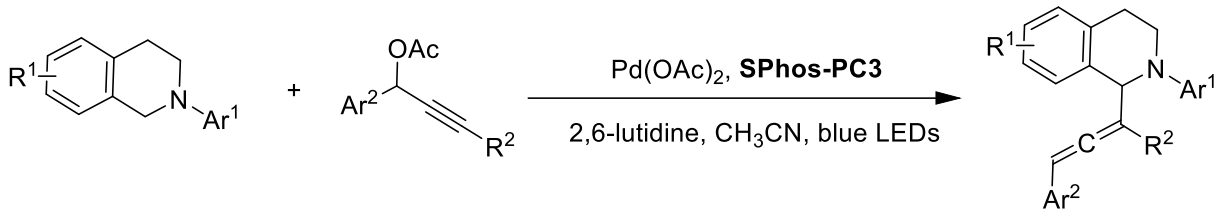
Figure S2D Isotopic distribution of di-allenyl/propargyl–Pd–SPhos complexes. (a) Measured isotopic distribution for $[C_{52}H_{64}O_2PPd]^+[M\text{-}HOAc]^+$: 857.08. (b) Simulated isotopic distribution for $[C_{52}H_{64}O_2PPd]^+[M\text{-}HOAc]^+$: 857.37.

Preparation of substrates

N-aryl-tetrahydroisoquinolines was prepared according to the literature procedure.[12]

Propargylic acetate derivatives were prepared according to the literature procedure.[13]

General procedure of C–H allenylation reaction

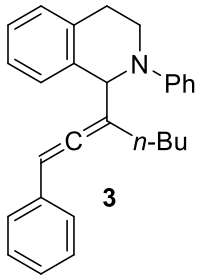


In a N_2-filled glove-box, an oven-dried culture tube (20 mL, 16 × 125 mm) with a magnetic stir bar was charged with $Pd(OAc)_2$ (1.3 mg, 0.006 mmol), **SPhos-PC3** (4.1 mg, 0.003 mmol), 2,6-lutidine (64.3 mg, 0.6 mmol) and CH_3CN (1.5 mL). The vessel was sealed with a screw cap (white silicone septum) and the mixture was stirred at room temperature for 20 min. *N*-aryl-tetrahydroisoquinolines **1** (0.3 mmol), propargylic acetates **2** (0.6 mmol), and CH_3CN (1.5 mL) were added. Then the resulting reaction mixture was irradiated with blue LEDs (2-meter strips, 19 W) for 6~15.5 hours (specified for each substrate in the next section) at 55 ^oC (Note: The 55 ^oC reaction temperature was caused by irradiation of the LEDs). Upon completion of the reaction, the reaction mixture was cooled to room temperature, and concentrated in *vacuo*. The crude mixture was then purified by silica gel chromatography to afford the desired product. Preparative HPLC was used to separate diastereomers for characterization.

Characterization data of C–H allenylation products

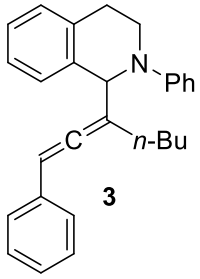
2-phenyl-1-(1-phenylhepta-1,2-dien-3-yl)-1,2,3,4-tetrahydroisoquinoline (3)

The reaction time was 7 h. White oil, 80.7 mg, 71% total yield of 1:1 diastereomers (0.3 mmol scale).



diastereomer 1

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.29 (m, 1H), 7.28 – 7.23 (m, 5H), 7.22 – 7.12 (m, 6H), 7.04 – 6.89 (m, 2H), 6.86 – 6.77 (m, 1H), 6.21 – 6.15 (m, 1H), 5.27 (d, *J* = 2.3 Hz, 1H), 3.70 – 3.60 (m, 1H), 3.59 – 3.49 (m, 1H), 3.13 – 2.97 (m, 1H), 2.96 – 2.88 (m, 1H), 2.18 – 2.02 (m, 2H), 1.44 – 1.35 (m, 2H), 1.34 – 1.26 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.0, 149.3, 136.3, 135.6, 135.0, 129.2, 128.4, 128.1, 127.6, 126.9, 126.7, 126.6, 125.9, 117.6, 114.4, 112.1, 97.3, 62.5, 43.8, 29.8, 29.2, 28.1, 22.6, 14.0. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{28}H_{30}N]^+$[M+H]$^+$: 380.2373, Found: 380.2384.

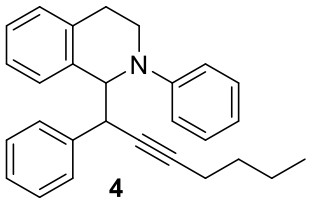


diastereomer 2

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 4H), 7.22 – 7.11 (m, 7H), 6.95 (dd, *J* = 13.4, 7.8 Hz, 2H), 6.79 (q, *J* = 7.4 Hz, 1H), 6.22 – 6.11 (m, 1H), 5.31 (d, *J* = 2.0 Hz, 0.5H, **diastereomer 2**), 5.27 (d, *J* = 2.3 Hz, 0.5H, **diastereomer 1**), 3.78 – 3.48 (m, 2H), 3.12 – 2.87 (m, 2H), 2.18 – 2.02 (m, 2H), 1.50 – 1.39 (m, 2H), 1.35 – 1.28 (m, 2H), 0.84 (td, *J* = 7.3, 2.2 Hz, 3H). **Diastereomer 2**: ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.9, 149.2, 136.4, 135.6, 135.3, 129.1, 128.3, 128.1, 127.7, 126.7, 126.6, 126.5, 125.8, 117.4, 114.3, 112.4, 97.6, 62.4, 43.5, 29.8, 29.4, 28.0, 22.6, 13.9. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{28}H_{30}N]^+$[M+H]$^+$: 380.2373, Found: 380.2374.

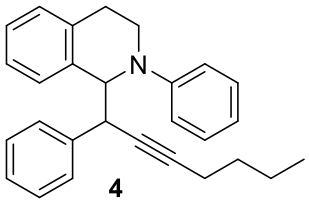
2-phenyl-1-(1-phenylhept-2-yn-1-yl)-1,2,3,4-tetrahydroisoquinoline (4)

This compound was isolated from the reaction mixture using dual catalyst system: $Pd(OAc)_2$, SPhos, and $Ru(bpy)_3(PF_6)_2$.



diastereomer 1

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.32 – 7.26 (m, 2H), 7.28 – 7.20 (m, 3H), 7.23 – 7.15 (m, 2H), 7.04 (dd, *J* = 1.7, 0.8 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 2H), 6.81 – 6.71 (m, 2H), 5.02 (d, *J* = 5.0 Hz, 1H), 4.30 (dt, *J* = 5.0, 2.3 Hz, 1H), 3.90 – 3.80 (m, 1H), 3.55 – 3.42 (m, 1H), 3.25 – 3.13 (m, 1H), 3.10 – 2.99 (m, 1H), 2.17 (td, *J* = 7.0, 2.3 Hz, 2H), 1.49 – 1.39 (m, 2H), 1.36 – 1.30 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 140.0, 135.6, 135.2, 129.1, 128.6, 128.6, 128.1, 128.1, 126.9, 126.9, 124.8, 117.8, 114.6, 86.3, 80.0, 65.7, 43.9, 42.4, 30.7, 27.7, 21.9, 18.6, 13.6. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{28}H_{30}N]^+$[M+H]$^+$: 380.2373, Found: 380.2377.

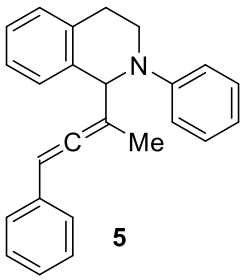


diastereomer 2

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.17 (m, 5H), 7.13 – 7.08 (m, 3H), 6.91 – 6.84 (m, 4H), 6.79 (d, *J* = 7.6 Hz, 2H), 5.01 (d, *J* = 4.5 Hz, 1H), 4.33 – 4.24 (m, 1H), 3.60 – 3.51 (m, 1H), 3.14 – 3.02 (m, 1H), 2.99 – 2.85 (m, 1H), 2.42 – 2.33 (m, 1H), 2.22 – 2.13 (m, 2H), 1.50 – 1.40 (m, 4H), 0.85 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.8, 138.9, 136.5, 134.1, 129.6, 129.3, 129.0, 127.6, 127.1, 127.0, 125.0, 116.8, 112.4, 85.5, 80.2, 64.8, 43.6, 43.5, 30.9, 27.3, 22.0, 18.7, 13.7. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{28}H_{30}N]^+$[M+H]$^+$: 380.2373, Found: 380.2378.

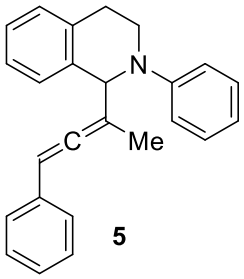
2-phenyl-1-(4-phenylbuta-2,3-dien-2-yl)-1,2,3,4-tetrahydroisoquinoline (5)

The reaction time was 8.5 h. White oil, 27.7 mg, 41% total yield of 1:1 diastereomers (0.2 mmol scale).



diastereomer 1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.27 – 7.19 (m, 5H), 7.19 – 7.10 (m, 4H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.81 (t, *J* = 7.2 Hz, 1H), 6.12 (q, *J* = 2.7 Hz, 1H), 5.28 (d, *J* = 2.0 Hz, 1H), 3.81 – 3.70 (m, 1H), 3.63 – 3.51 (m, 1H), 3.21 – 3.07 (m, 1H), 3.04 – 2.93 (m, 1H), 1.82 (d, *J* = 2.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.4, 149.1, 136.1, 135.6, 135.1, 129.1, 128.4, 128.1, 127.7, 126.9, 126.9, 126.6, 126.0, 117.5, 114.2, 106.8, 95.7, 62.9, 43.8, 28.3, 16.3. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{25}H_{24}N]^+$[M+H]$^+$: 338.1903, Found: 338.1905.



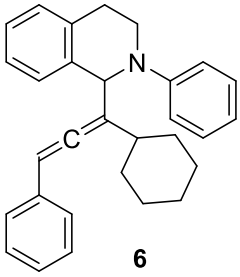
5

diastereomer 2

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.23 (m, 6H), 7.22 – 7.20 (m, 2H), 7.19 – 7.13 (m, 3H), 6.95 (d, *J* = 8.1 Hz, 2H), 6.82 (t, *J* = 7.3 Hz, 1H), 6.15 – 6.09 (m, 1H), 5.24 (d, *J* = 2.2 Hz, 1H), 3.71 – 3.60 (m, 1H), 3.59 – 3.47 (m, 1H), 3.04 (s, 1H), 2.93 (dt, *J* = 15.5, 5.4 Hz, 1H), 1.81 (d, *J* = 2.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.2, 149.4, 136.1, 135.7, 134.9, 129.2, 128.4, 128.1, 127.6, 126.9, 126.7, 126.0, 117.7, 114.5, 106.6, 95.4, 62.9, 44.0, 28.4, 16.0. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{25}H_{24}N]^+[M+H]^+$: 338.1903, Found: 338.1905.

1-(1-cyclohexyl-3-phenylpropa-1,2-dien-1-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (6)

The reaction time was 15.5 h. White oil, 42.2 mg, 52% total yield of 1:1.2 diastereomers (0.2 mmol scale).

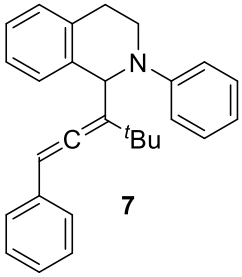


6

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 3H), 7.22 – 7.06 (m, 8H), 6.97 (d, *J* = 8.2 Hz, 0.92H), 6.93 (d, *J* = 8.1 Hz, 1.08H), 6.82 – 6.74 (m, 1H), 6.14 (t, *J* = 2.1 Hz, 0.54H), 6.12 (t, *J* = 2.0 Hz, 0.46H), 5.41 (d, *J* = 2.4 Hz, 0.46H), 5.38 (d, *J* = 2.7 Hz, 0.54H), 3.78 – 3.71 (m, 0.46H), 3.66 – 3.59 (m, 1H), 3.57 – 3.51 (m, 0.54H), 3.00 – 2.87 (m, 2H), 2.09 – 1.93 (m, 2H), 1.83 – 1.62 (m, 4H), 1.33 – 1.11 (m, 5H). **Major diastereomer**: ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.35, 149.44, 136.46, 135.67, 135.05, 129.15, 128.41, 128.10, 127.69, 126.80, 126.54, 126.49, 125.65, 117.57, 117.35, 114.19, 98.13, 61.16, 43.35, 38.94, 33.87, 33.03, 27.38, 26.64, 26.57, 26.17. **Minor diastereomer**: ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.30, 149.31, 136.51, 135.55, 135.33, 129.13, 128.35, 128.20, 127.80, 126.72, 126.56, 126.44, 125.61, 117.76, 117.49, 114.36, 98.30, 60.89, 43.00, 39.12, 33.45, 33.16, 27.15, 26.64, 26.57, 26.17. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{30}H_{32}N]^+[M+H]^+$: 406.2529, Found: 406.2537.

1-(4,4-dimethyl-1-phenylpenta-1,2-dien-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (7)

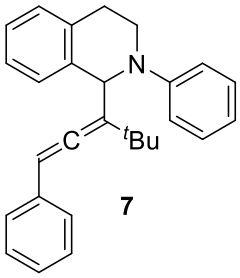
The reaction time was 14 h. White oil, 21.7 mg, 57% total yield of 1:1.1 diastereomers (0.1 mmol scale).



7

diastereomer 1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 2H), 7.25 – 7.06 (m, 8H), 6.98 (d, *J* = 7.9 Hz, 2H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.78 (t, *J* = 7.3 Hz, 1H), 5.84 (d, *J* = 2.0 Hz, 1H), 5.46 (d, *J* = 2.0 Hz, 1H), 3.84 – 3.72 (m, 2H), 2.82 – 2.72 (m, 1H), 2.36 – 2.26 (m, 1H), 1.23 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.0, 149.1, 136.8, 135.3, 134.8, 129.3, 128.8, 128.7, 128.5, 127.9, 127.6, 126.9, 126.6, 126.3, 125.5, 117.6, 97.4, 58.4, 43.0, 35.2, 30.2, 24.4. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{28}H_{30}N]^+$[M+H]$^+$: 380.2373, Found: 380.2371.



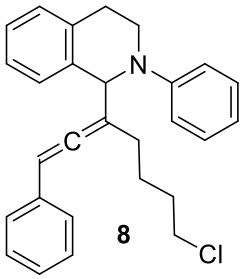
7

diastereomer 2

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.17 (m, 4H), 7.16 (d, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 7.3 Hz, 1H), 7.03 – 6.96 (m, 4H), 6.95 – 6.87 (m, 3H), 6.80 (t, *J* = 7.2 Hz, 1H), 5.97 (d, *J* = 2.0 Hz, 1H), 5.54 (s, 1H), 3.92 – 3.83 (m, 1H), 3.76 (dd, *J* = 13.9, 5.6 Hz, 1H), 2.92 – 2.80 (m, 1H), 2.62 – 2.51 (m, 1H), 1.26 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.0, 149.2, 137.0, 135.0, 134.5, 129.2, 128.5, 128.1, 127.9, 126.4, 126.3, 126.2, 125.3, 121.0, 118.8, 116.9, 97.3, 57.8, 42.3, 35.3, 30.3, 24.8. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{28}H_{30}N]^+$[M+H]$^+$: 380.2373, Found: 380.2373.

1-(7-chloro-1-phenylhepta-1,2-dien-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (8)

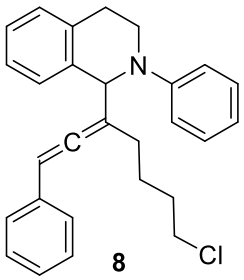
The reaction time was 6 h. White oil, 53.8 mg, 65% total yield of 1:1.2 diastereomers (0.2 mmol scale).



8

diastereomer 1

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 3H), 7.25 – 7.23 (m, 1H), 7.23 – 7.19 (m, 3H), 7.18 – 7.11 (m, 4H), 6.98 (d, *J* = 8.2 Hz, 2H), 6.80 (t, *J* = 7.2 Hz, 1H), 6.20 (td, *J* = 3.4, 2.0 Hz, 1H), 5.32 (d, *J* = 2.0 Hz, 1H), 3.74 (t, *J* = 11.7 Hz, 1H), 3.63 – 3.55 (m, 1H), 3.43 (t, *J* = 6.7 Hz, 2H), 3.11 – 3.03 (m, 1H), 3.03 – 2.94 (m, 1H), 2.22 – 2.09 (m, 2H), 1.80 – 1.71 (m, 2H), 1.66 – 1.52 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.8, 149.2, 136.2, 135.5, 135.0, 129.1, 128.4, 128.2, 127.7, 126.9, 126.7, 126.7, 125.9, 117.7, 114.4, 111.8, 98.0, 62.5, 44.8, 43.6, 32.3, 28.8, 28.0, 24.8. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{28}H_{29}ClN]^+$[M+H]$^+$: 414.1983, Found: 414.1989.



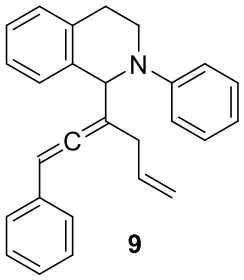
8

diastereomer 2

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 5H), 7.22 – 7.11 (m, 6H), 7.02 – 6.91 (m, 2H), 6.83 (t, *J* = 7.3 Hz, 1H), 6.22 (q, *J* = 3.1 Hz, 1H), 5.29 (d, *J* = 2.1 Hz, 1H), 3.70 – 3.61 (m, 1H), 3.59 – 3.51 (m, 1H), 3.44 (t, *J* = 6.7 Hz, 2H), 3.11 – 2.98 (m, 1H), 2.94 (dt, *J* = 15.6, 5.7 Hz, 1H), 2.26 – 2.15 (m, 1H), 2.15 – 2.04 (m, 1H), 1.83 – 1.70 (m, 2H), 1.68 – 1.48 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.8, 149.3, 136.1, 135.5, 134.7, 129.2, 128.5, 128.2, 127.6, 126.9, 126.8, 126.8, 125.9, 117.9, 114.8, 111.5, 97.7, 62.4, 44.8, 44.0, 32.3, 28.5, 28.1, 24.8. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{28}H_{29}ClN]^+$[M+H]$^+$: 414.1983, Found: 414.1990.

2-phenyl-1-(1-phenylhexa-1,2,5-trien-3-yl)-1,2,3,4-tetrahydroisoquinoline (9)

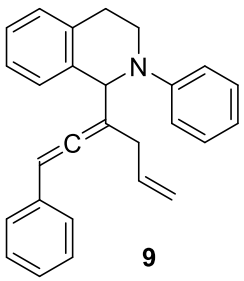
The reaction time was 15.5 h. White oil, 14.2 mg, 39% total yield of 1:1 diastereomers (0.1 mmol scale).



9

diastereomer 1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.21 (m, 3H), 7.21 – 7.16 (m, 4H), 7.15 – 7.07 (m, 4H), 6.96 (d, *J* = 8.1 Hz, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.13 (q, *J* = 2.8 Hz, 1H), 5.91 – 5.73 (m, 1H), 5.32 (d, *J* = 2.2 Hz, 1H), 5.15 – 4.95 (m, 2H), 3.76 – 3.67 (m, 1H), 3.63 – 3.53 (m, 1H), 3.07 – 2.93 (m, 2H), 2.92 – 2.81 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.5, 149.1, 136.0, 135.5, 135.5, 134.9, 129.1, 128.4, 128.2, 127.8, 126.9, 126.8, 126.7, 125.9, 117.8, 116.5, 114.5, 110.6, 97.5, 61.9, 43.5, 34.7, 27.7. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{27}H_{26}N]^+$[M+H]$^+$: 364.2060, Found: 364.2060.



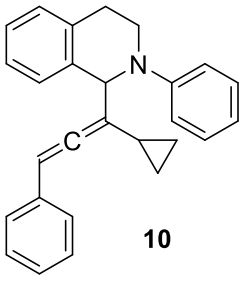
9

diastereomer 2

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 5H), 7.22 – 7.18 (m, 2H), 7.17 – 7.11 (m, 4H), 6.96 (d, *J* = 8.1 Hz, 2H), 6.81 (t, *J* = 7.2 Hz, 1H), 6.17 (q, *J* = 2.9 Hz, 1H), 5.84 (ddt, *J* = 17.0, 10.1, 6.9 Hz, 1H), 5.32 (d, *J* = 2.4 Hz, 1H), 5.10 (dq, *J* = 17.0, 1.6 Hz, 1H), 5.03 (dq, *J* = 10.1, 1.4 Hz, 1H), 3.69 – 3.61 (m, 1H), 3.59 – 3.52 (m, 1H), 3.03 – 2.91 (m, 3H), 2.90 – 2.82 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.6, 149.3, 136.0, 135.6, 135.5, 134.6, 129.2, 128.4, 128.2, 127.7, 126.9, 126.8, 125.9, 117.8, 116.5, 114.7, 110.5, 97.3, 61.8, 43.8, 34.4, 27.8. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{27}H_{26}N]^+$[M+H]$^+$: 364.2060, Found: 364.2064.

1-(1-cyclopropyl-3-phenylpropa-1,2-dien-1-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (10)

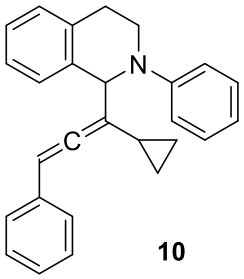
The reaction time was 6 h. White oil, 42.2 mg, 58% total yield of 1:1.2 diastereomers (0.2 mmol scale).



10

diastereomer 1

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 1H), 7.28 – 7.27 (m, 1H), 7.26 – 7.12 (m, 7H), 7.11 – 7.06 (m, 2H), 7.05 – 6.94 (m, 2H), 6.83 – 6.75 (m, 1H), 6.21 – 6.11 (m, 1H), 5.50 (d, *J* = 2.0 Hz, 1H), 3.83 – 3.75 (m, 1H), 3.67 – 3.59 (m, 1H), 3.19 – 3.08 (m, 1H), 3.02 (dt, *J* = 15.6, 5.9 Hz, 1H), 1.34 – 1.26 (m, 1H), 0.73 – 0.62 (m, 2H), 0.47 – 0.41 (m, 1H), 0.37 – 0.31 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.6, 149.2, 136.5, 135.6, 134.9, 129.0, 128.4, 128.2, 128.0, 127.8, 126.8, 126.7, 125.9, 117.3, 115.4, 114.0, 98.3, 62.7, 43.2, 28.2, 10.6, 7.5, 7.3. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{27}H_{26}N]^+$[M+H]$^+$: 364.2060, Found: 364.2067.



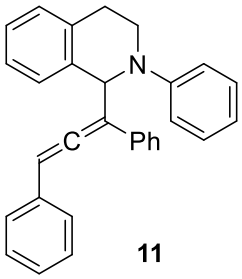
10

diastereomer 2

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.5 Hz, 1H), 7.26 – 7.20 (m, 4H), 7.20 – 7.11 (m, 4H), 7.03 (d, *J* = 7.5 Hz, 2H), 6.93 (d, *J* = 8.1 Hz, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.17 (t, *J* = 2.2 Hz, 1H), 5.44 (d, *J* = 2.1 Hz, 1H), 3.74 – 3.65 (m, 1H), 3.62 – 3.52 (m, 1H), 3.08 – 2.89 (m, 2H), 1.29 – 1.22 (m, 1H), 0.74 – 0.59 (m, 2H), 0.51 – 0.40 (m, 1H), 0.35 – 0.27 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.5, 149.4, 136.4, 135.6, 134.6, 129.2, 128.4, 128.1, 127.8, 126.9, 126.8, 126.7, 125.8, 117.4, 115.1, 114.2, 98.0, 62.6, 43.3, 28.3, 10.5, 8.2, 6.6. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{27}H_{26}N]^+$[M+H]$^+$: 364.2060, Found: 364.2067.

1-(1,3-diphenylpropa-1,2-dien-1-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (11)

The reaction time was 14 h. White oil, 24.0 mg, 60% total yield of 1:1.1 diastereomers (0.1 mmol scale).

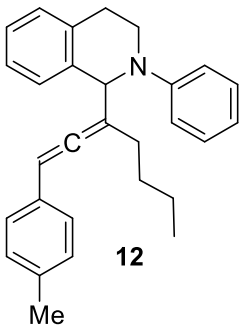


11

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 3H), 7.32 – 7.29 (m, 2H), 7.28 – 7.25 (m, 3H), 7.22 (d, *J* = 7.2 Hz, 3H), 7.18 – 7.14 (m, 3H), 7.13 – 7.10 (m, 1H), 7.05 (t, *J* = 7.2 Hz, 3H), 6.88 – 6.83 (m, 1H), 6.40 (d, *J* = 2.1 Hz, 0.66H), 6.33 (d, *J* = 2.1 Hz, 0.34H), 5.89 (d, *J* = 2.1 Hz, 0.34H), 5.85 (d, *J* = 2.1 Hz, 0.66H), 3.84 – 3.56 (m, 2H), 2.95 – 2.68 (m, 2H). **Major diastereomer**: ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.11, 149.47, 136.09, 135.42, 133.73, 129.25, 128.54, 128.43, 128.32, 127.75, 127.51, 127.40, 127.13, 126.98, 126.87, 126.83, 125.80, 118.51, 115.8, 114.06, 98.14, 60.90, 43.74, 27.09. **Minor diastereomer**: ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.82, 149.23, 135.76, 135.56, 134.12, 129.20, 128.54, 128.43, 128.32, 127.94, 127.45, 127.33, 127.13, 127.02, 126.87, 126.78, 125.74, 118.43, 115.71, 113.92, 98.41, 60.65, 43.42, 26.72. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{30}H_{26}N]^+$[M+H]$^+$: 400.2060, Found: 400.2062.

2-phenyl-1-(1-(p-tolyl)hepta-1,2-dien-3-yl)-1,2,3,4-tetrahydroisoquinoline (12)

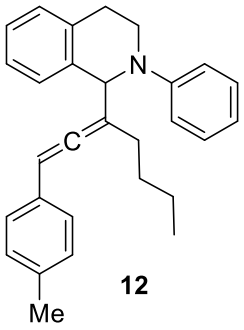
The reaction time was 6 h. White oil, 49.7 mg, 63% total yield of 1:1 diastereomers (0.2 mmol scale).



12

diastereomer 1

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.25 – 7.22 (m, 1H), 7.21 – 7.17 (m, 2H), 7.15 – 7.12 (m, 1H), 7.03 (s, 4H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.79 (t, *J* = 7.2 Hz, 1H), 6.15 (q, *J* = 3.1 Hz, 1H), 5.29 (d, *J* = 2.0 Hz, 1H), 3.79 – 3.69 (m, 1H), 3.62 – 3.52 (m, 1H), 3.15 – 3.03 (m, 1H), 2.97 (dt, *J* = 15.5, 5.7 Hz, 1H), 2.32 (s, 3H), 2.16 – 2.06 (m, 2H), 1.50 – 1.39 (m, 2H), 1.38 – 1.25 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.6, 149.3, 136.5, 136.2, 135.6, 132.3, 129.1, 129.1, 128.1, 127.7, 126.8, 126.6, 125.8, 117.4, 114.1, 112.2, 97.4, 62.6, 43.5, 29.8, 29.5, 28.0, 22.6, 21.1, 14.0. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{29}H_{32}N]^+$[M+H]$^+$: 394.2529, Found: 394.2535.



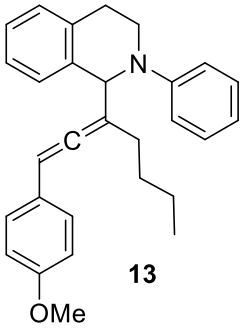
12

diastereomer 2

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.28 (m, 1H), 7.28 – 7.24 (m, 2H), 7.22 – 7.14 (m, 3H), 7.11 – 7.01 (m, 4H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.81 (t, *J* = 7.3 Hz, 1H), 6.15 (td, *J* = 3.4, 2.2 Hz, 1H), 5.25 (d, *J* = 2.3 Hz, 1H), 3.69 – 3.60 (m, 1H), 3.57 – 3.48 (m, 1H), 3.10 – 2.98 (m, 1H), 2.92 (dt, *J* = 15.6, 5.6 Hz, 1H), 2.36 (s, 3H), 2.18 – 2.03 (m, 2H), 1.50 – 1.37 (m, 2H), 1.36 – 1.27 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.5, 149.4, 136.5, 136.3, 135.7, 132.1, 129.2, 129.1, 128.0, 127.6, 126.8, 126.6, 125.8, 117.4, 114.3, 112.0, 97.2, 62.4, 43.8, 29.8, 29.2, 28.1, 22.6, 21.2, 14.0. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{29}H_{32}N]^+$[M+H]$^+$: 394.2529, Found: 394.2533.

1-(1-(4-methoxyphenyl)hepta-1,2-dien-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (13)

The reaction time was 6 h. White oil, 49.2 mg, 60% total yield of 1:1.1 diastereomers (0.2 mmol scale).

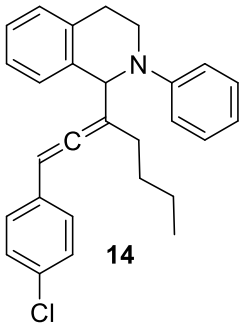


13

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.12 (m, 3H), 7.13 – 7.01 (m, 3H), 7.01 – 6.90 (m, 2H), 6.89 – 6.79 (m, 2H), 6.76 – 6.62 (m, 3H), 6.07 – 5.98 (m, 1H), 5.18 (d, *J* = 2.0 Hz, 0.47H), 5.15 (d, *J* = 2.2 Hz, 0.53H), 3.72 (s, 1.59H), 3.69 (s, 1.41H), 3.66 – 3.39 (m, 2H), 3.06 – 2.76 (m, 2H), 2.08 – 1.90 (m, 2H), 1.35 – 1.27 (m, 2H), 1.26 – 1.15 (m, 2H), 0.73 (td, *J* = 7.3, 1.2 Hz, 3H). **Major diastereomer**: ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.17, 158.52, 149.44, 136.54, 135.64, 129.12, 128.04, 127.78, 127.63, 127.61, 126.78, 125.82, 117.38, 114.32, 113.94, 111.93, 96.70, 62.48, 55.31, 43.80, 29.82, 29.20, 28.13, 22.60, 13.96. **Minor diastereomer**: ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.21, 158.42, 149.21, 136.57, 135.59, 129.06, 128.04, 127.78, 127.72, 127.46, 126.78, 125.82, 117.30, 114.02, 113.88, 112.16, 97.03, 62.63, 55.28, 43.53, 29.80, 29.52, 28.02, 22.58, 13.96. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{29}H_{32}NO]^+$[M+H]$^+$: 410.2478, Found: 410.2483.

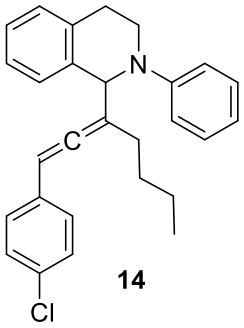
1-(1-(4-chlorophenyl)hepta-1,2-dien-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (14)

The reaction time was 6 h. White oil, 49.7 mg, 58% total yield of 1:1 diastereomers (0.2 mmol scale).



diastereomer 1

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.26 (m, 1H), 7.26 – 7.23 (m, 1H), 7.19 – 7.10 (m, 6H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.1 Hz, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.08 (q, *J* = 3.0 Hz, 1H), 5.25 (d, *J* = 2.1 Hz, 1H), 3.74 – 3.61 (m, 1H), 3.57 – 3.48 (m, 1H), 3.14 – 3.01 (m, 1H), 2.99 – 2.90 (m, 1H), 2.17 – 2.04 (m, 2H), 1.43 – 1.34 (m, 2H), 1.33 – 1.23 (m, 2H), 0.81 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.9, 149.0, 136.3, 135.6, 133.8, 132.0, 129.1, 128.5, 128.1, 127.9, 127.6, 127.0, 125.9, 117.4, 113.8, 112.9, 96.9, 62.4, 43.6, 29.7, 29.5, 28.0, 22.5, 13.9. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{28}H_{29}ClN]^+$[M+H]$^+$: 414.1983, Found: 414.1992.

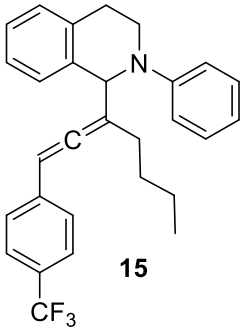


diastereomer 2

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.28 (m, 1H), 7.27 (d, *J* = 1.5 Hz, 1H), 7.26 – 7.21 (m, 3H), 7.20 – 7.12 (m, 3H), 7.04 (d, *J* = 8.2 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.83 (t, *J* = 7.2 Hz, 1H), 6.13 (q, *J* = 3.4 Hz, 1H), 5.27 (d, *J* = 2.1 Hz, 1H), 3.68 – 3.59 (m, 1H), 3.58 – 3.50 (m, 1H), 3.05 – 2.87 (m, 2H), 2.21 – 2.00 (m, 2H), 1.50 – 1.36 (m, 2H), 1.35 – 1.24 (m, 2H), 0.84 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.1, 149.3, 136.2, 135.5, 133.6, 132.1, 129.2, 128.6, 128.2, 127.8, 127.5, 126.9, 125.9, 117.9, 114.7, 112.6, 96.4, 62.5, 43.9, 29.8, 29.1, 28.0, 22.6, 13.9. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{28}H_{29}ClN]^+$[M+H]$^+$: 414.1983, Found: 414.1989.

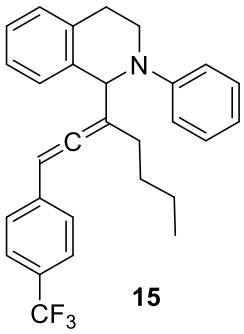
2-phenyl-1-(1-(4-(trifluoromethyl)phenyl)hepta-1,2-dien-3-yl)-1,2,3,4-tetrahydroisoquinoline (15)

The reaction time was 6 h. Yellow oil, 50.2 mg, 56% total yield of 1:1 diastereomers (0.2 mmol scale).



diastereomer 1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.24 (m, 3H), 7.23 – 7.21 (m, 1H), 7.20 – 7.19 (m, 1H), 7.16 (d, *J* = 8.1 Hz, 3H), 6.93 (d, *J* = 7.8 Hz, 2H), 6.79 (t, *J* = 7.2 Hz, 1H), 6.18 (q, *J* = 3.1 Hz, 1H), 5.30 (d, *J* = 2.2 Hz, 1H), 3.76 – 3.68 (m, 1H), 3.60 – 3.52 (m, 1H), 3.14 – 3.05 (m, 1H), 2.98 (dt, *J* = 15.6, 5.5 Hz, 1H), 2.21 – 2.08 (m, 2H), 1.47 – 1.38 (m, 2H), 1.36 – 1.26 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.8, 148.9, 139.1, 136.1, 135.6, 129.1, 128.1, 127.6, 127.1, 126.7, 125.9, 125.25 (q, *J* = 3.9 Hz), 122.12 (q, *J* = 272.8 Hz), 117.5, 113.8, 113.2, 97.0, 62.3, 43.6, 29.7, 29.5, 28.0, 22.5, 13.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.37. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{29}H_{29}F_3N]^+$[M+H]$^+$: 448.2247, Found: 448.2250.

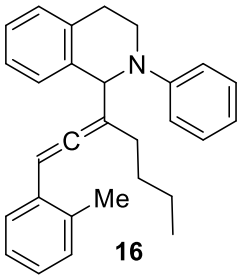


diastereomer 2

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.1 Hz, 2H), 7.26 – 7.22 (m, 1H), 7.25 – 7.09 (m, 7H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.81 (t, *J* = 7.3 Hz, 1H), 6.16 (q, *J* = 3.1 Hz, 1H), 5.27 (d, *J* = 2.2 Hz, 1H), 3.64 – 3.57 (m, 1H), 3.56 – 3.49 (m, 1H), 2.99 – 2.87 (m, 2H), 2.19 – 2.02 (m, 2H), 1.46 – 1.34 (m, 2H), 1.32 – 1.24 (m, 2H), 0.82 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.0, 149.3, 139.0, 136.0, 135.5, 129.2, 128.27 (q, *J* = 32.0 Hz), 128.2, 127.83 (q, *J* = 23.7 Hz), 127.5, 127.0, 126.7, 125.9, 125.35 (q, *J* = 3.9 Hz), 122.15 (d, *J* = 272.1 Hz), 118.0, 114.8, 112.9, 96.4, 62.4, 43.8, 29.8, 29.2, 28.0, 22.6, 13.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.32. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{29}H_{29}F_3N]^+$[M+H]$^+$: 448.2247, Found: 448.2248.

2-phenyl-1-(1-(o-tolyl)hepta-1,2-dien-3-yl)-1,2,3,4-tetrahydroisoquinoline (16)

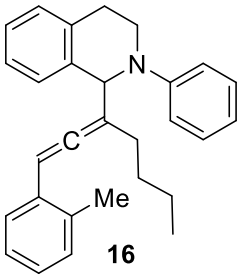
The reaction time was 6 h. White oil, 53.6 mg, 68% total yield of 1:1 diastereomers (0.2 mmol scale).



16

diastereomer 1

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.28 (m, 1H), 7.28 – 7.26 (m, 1H), 7.22 – 7.16 (m, 3H), 7.14 – 7.09 (m, 2H), 7.09 – 6.95 (m, 5H), 6.79 (t, *J* = 7.0 Hz, 1H), 6.34 – 6.26 (m, 1H), 5.31 (d, *J* = 2.1 Hz, 1H), 3.76 – 3.67 (m, 1H), 3.63 – 3.55 (m, 1H), 3.05 – 2.92 (m, 2H), 2.25 (s, 3H), 2.17 – 2.06 (m, 2H), 1.49 – 1.40 (m, 2H), 1.36 – 1.26 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.6, 149.2, 136.4, 135.5, 134.5, 133.6, 130.1, 129.1, 128.1, 127.8, 127.3, 126.8, 126.5, 125.9, 125.8, 117.6, 114.4, 111.3, 94.8, 62.5, 43.3, 29.9, 29.4, 27.7, 22.6, 19.7, 14.0. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{29}H_{32}N]^+$[M+H]$^+$: 394.2529, Found: 394.2533.



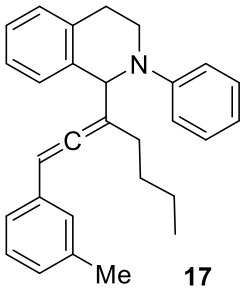
16

diastereomer 2

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 3H), 7.21 – 7.13 (m, 4H), 7.13 – 7.07 (m, 3H), 7.02 – 6.90 (m, 2H), 6.85 – 6.76 (m, 1H), 6.33 (q, *J* = 3.1 Hz, 1H), 5.27 (d, *J* = 2.2 Hz, 1H), 3.68 – 3.59 (m, 1H), 3.57 – 3.50 (m, 1H), 3.06 – 2.95 (m, 1H), 2.94 – 2.86 (m, 1H), 2.24 (s, 3H), 2.18 – 2.02 (m, 2H), 1.51 – 1.40 (m, 2H), 1.38 – 1.27 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.6, 149.4, 136.4, 135.6, 134.6, 133.2, 130.3, 129.1, 128.1, 127.6, 127.1, 126.8, 126.5, 125.9, 125.8, 117.5, 114.4, 111.1, 94.6, 62.3, 43.8, 29.8, 29.2, 28.0, 22.6, 19.7, 14.0. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{29}H_{32}N]^+$[M+H]$^+$: 394.2529, Found: 394.2535.

2-phenyl-1-(1-(m-tolyl)hepta-1,2-dien-3-yl)-1,2,3,4-tetrahydroisoquinoline (17)

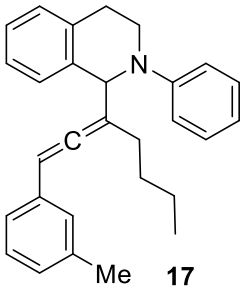
The reaction time was 6 h. White oil, 52.8 mg, 67% total yield of 1:1 diastereomers (0.2 mmol scale).



17

diastereomer 1

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 1H), 7.25 – 7.23 (m, 1H), 7.22 – 7.19 (m, 1H), 7.19 – 7.15 (m, 2H), 7.14 – 7.11 (m, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.99 – 6.86 (m, 5H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.12 (q, *J* = 3.0 Hz, 1H), 5.25 (d, *J* = 2.1 Hz, 1H), 3.76 – 3.67 (m, 1H), 3.58 – 3.48 (m, 1H), 3.17 – 3.05 (m, 1H), 2.94 (dt, *J* = 15.6, 5.4 Hz, 1H), 2.21 (s, 3H), 2.15 – 2.04 (m, 2H), 1.43 – 1.36 (m, 2H), 1.32 – 1.24 (m, 2H), 0.81 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.8, 149.1, 138.0, 136.5, 135.7, 135.2, 129.1, 128.2, 128.0, 127.7, 127.5, 127.4, 126.9, 125.9, 123.9, 117.3, 113.9, 112.3, 97.7, 62.6, 43.6, 29.7, 29.5, 28.1, 22.6, 21.3, 13.9. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{29}H_{32}N]^+$[M+H]$^+$: 394.2529, Found: 394.2535.



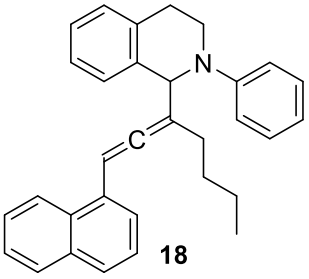
17

diastereomer 2

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 3H), 7.22 – 7.14 (m, 4H), 7.02 (d, *J* = 7.5 Hz, 1H), 7.00 – 6.97 (m, 2H), 6.94 (d, *J* = 8.2 Hz, 2H), 6.80 (t, *J* = 7.3 Hz, 1H), 6.16 (td, *J* = 3.4, 2.1 Hz, 1H), 5.28 (d, *J* = 2.2 Hz, 1H), 3.68 – 3.61 (m, 1H), 3.58 – 3.51 (m, 1H), 3.08 – 2.99 (m, 1H), 2.93 (dt, *J* = 15.6, 5.6 Hz, 1H), 2.33 (s, 3H), 2.19 – 2.11 (m, 1H), 2.11 – 2.02 (m, 1H), 1.50 – 1.38 (m, 2H), 1.35 – 1.26 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.8, 149.4, 138.0, 136.5, 135.7, 135.0, 129.1, 128.3, 128.1, 127.6, 127.5, 127.4, 126.8, 125.8, 123.9, 117.4, 114.3, 112.0, 97.3, 62.4, 43.8, 29.8, 29.1, 28.2, 22.6, 21.4, 14.0. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{29}H_{32}N]^+$[M+H]$^+$: 394.2529, Found: 394.2534.

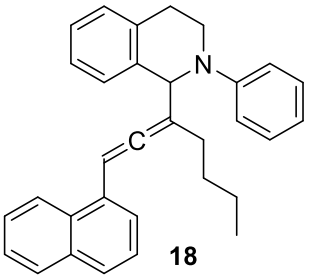
1-(1-(naphthalen-1-yl)hepta-1,2-dien-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (18)

The reaction time was 7 h. White oil, 23.7 mg, 55% total yield of 1:1 diastereomers (0.1 mmol scale).



diastereomer 1

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.5 Hz, 1H), 7.82 (d, *J* = 7.5 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.41 (m, 2H), 7.31 – 7.27 (m, 3H), 7.26 – 7.16 (m, 4H), 7.14 – 7.10 (m, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.80 (s, 2H), 5.35 (d, *J* = 2.2 Hz, 1H), 3.79 – 3.67 (m, 1H), 3.64 – 3.54 (m, 1H), 3.00 (d, *J* = 6.9 Hz, 2H), 2.29 – 2.10 (m, 2H), 1.55 – 1.45 (m, 2H), 1.39 – 1.27 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.4, 149.2, 136.3, 135.5, 133.8, 131.5, 130.7, 129.1, 128.5, 128.2, 127.8, 127.0, 126.9, 125.8, 125.7, 125.6, 125.5, 125.3, 123.7, 117.6, 114.4, 111.1, 94.1, 62.5, 43.4, 29.9, 29.6, 27.7, 22.6, 14.0. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{32}H_{32}N]^+$[M+H]$^+$: 430.2529, Found: 430.2534.

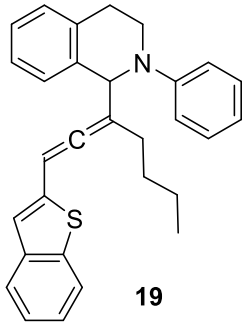


diastereomer 2

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.2 Hz, 1H), 7.88 – 7.83 (m, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.52 – 7.42 (m, 2H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.34 (s, 1H), 7.29 – 7.21 (m, 3H), 7.22 – 7.11 (m, 3H), 6.98 – 6.90 (m, 2H), 6.87 (q, *J* = 3.2 Hz, 1H), 6.80 (t, *J* = 7.3 Hz, 1H), 5.30 (d, *J* = 2.3 Hz, 1H), 3.68 – 3.57 (m, 1H), 3.53 – 3.43 (m, 1H), 3.06 – 2.90 (m, 1H), 2.88 – 2.76 (m, 1H), 2.28 – 2.07 (m, 2H), 1.56 – 1.45 (m, 2H), 1.36 (t, *J* = 14.5 Hz, 2H), 0.87 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.3, 149.2, 136.3, 135.6, 133.8, 131.2, 130.7, 129.1, 128.5, 128.1, 127.6, 127.1, 126.9, 125.9, 125.8, 125.6, 125.1, 123.6, 117.5, 114.3, 110.8, 93.9, 62.4, 44.0, 29.9, 29.2, 27.9, 22.6, 14.0. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{32}H_{32}N]^+$[M+H]$^+$: 430.2529, Found: 430.2535.

1-(1-(benzo[b]thiophen-2-yl)hepta-1,2-dien-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (19)

The reaction time was 11.5 h. Yellow oil, 43.6 mg, 50% total yield of 1:1 diastereomers (0.2 mmol scale).

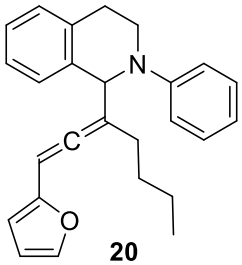


19

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.72 (m, 1H), 7.68 – 7.60 (m, 1H), 7.34 – 7.26 (m, 5H), 7.23 – 7.09 (m, 3H), 7.04 (d, *J* = 8.2 Hz, 1H), 6.98 (d, *J* = 10.6 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.82 (q, *J* = 7.0 Hz, 1H), 6.59 – 6.36 (m, 1H), 5.38 (d, *J* = 2.2 Hz, 0.5H), 5.30 (d, *J* = 2.8 Hz, 0.5H), 3.92 – 3.82 (m, 0.5H), 3.77 – 3.64 (m, 1H), 3.60 – 3.52 (m, 0.5H), 3.20 – 2.93 (m, 2H), 2.24 – 2.12 (m, 2H), 1.56 – 1.45 (m, 2H), 1.42 – 1.32 (m, 2H), 0.92 – 0.84 (m, 3H). **Diastereomer 1**: ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.49, 149.29, 140.50, 140.34, 139.42, 136.01, 135.77, 129.17, 128.07, 127.90, 127.04, 125.83, 124.18, 124.00, 122.94, 122.10, 120.82, 117.34, 113.85, 113.47, 92.77, 62.17, 43.46, 29.85, 29.74, 27.72, 22.56, 14.00. **Diastereomer 2**: ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.93, 149.49, 140.74, 140.39, 139.42, 135.87, 135.37, 129.22, 128.43, 127.98, 126.82, 125.70, 124.22, 124.02, 122.99, 122.13, 120.90, 118.03, 115.12, 113.34, 92.34, 62.58, 43.08, 29.82, 29.67, 27.38, 22.61, 13.98. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{30}H_{30}NS]^+$[M+H]$^+$: 436.2093, Found: 436.2099.

1-(1-(furan-2-yl)hepta-1,2-dien-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (20)

The reaction time was 14 h. White oil, 15.5 mg, 42% total yield of 1:1 diastereomers (0.1 mmol scale).



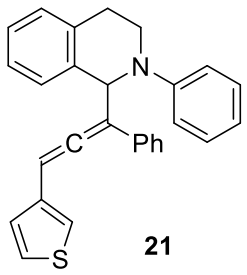
20

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 1H), 7.26 – 7.22 (m, 2H), 7.21 – 7.04 (m, 4H), 7.01 – 6.93 (m, 1H), 6.88 (d, *J* = 8.1 Hz, 1H), 6.80 – 6.72 (m, 1H), 6.37 – 6.32 (m, 0.5H), 6.32 – 6.28 (m, 0.5H), 6.14 – 6.04 (m, 1.5H), 5.99 (d, *J* = 3.3 Hz, 0.5H), 5.28 (d, *J* = 2.0 Hz, 0.5H), 5.20 (d, *J* = 2.7 Hz, 0.5H), 3.81 – 3.74 (m, 0.5H), 3.66 – 3.56 (m, 1H), 3.52 – 3.44 (m, 0.5H), 3.19 – 3.12 (m, 0.5H), 3.01 – 2.87 (m, 1.5H), 2.11 – 2.01 (m, 2H), 1.46 – 1.36 (m, 2H), 1.34 – 1.24 (m, 2H), 0.86 – 0.78 (m, 3H). **Diastereomer 1**: ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.89, 149.24, 141.64, 136.01, 129.07, 129.03, 128.18, 127.90, 127.82, 127.73, 126.97, 126.75, 125.75, 113.58, 111.29, 106.64, 88.11, 62.30,

43.86, 29.69, 29.25, 27.74, 22.46, 13.94. **Diastereomer 2**: ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.63, 149.24, 141.53, 136.14, 129.07, 129.03, 128.18, 127.90, 127.82, 127.73, 126.97, 126.75, 125.79, 114.95, 111.29, 106.57, 87.71, 62.66, 43.29, 29.69, 29.33, 27.75, 22.39, 13.92. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{26}H_{28}NO]^+$[M+H]$^+$: 370.2165, Found: 370.2165.

2-phenyl-1-(1-phenyl-3-(thiophen-3-yl)propa-1,2-dien-1-yl)-1,2,3,4-tetrahydroisoquinoline (21)

The reaction time was 6.5 h. White oil, 43.9 mg, 54% total yield of 1:1.3 diastereomers (0.2 mmol scale).



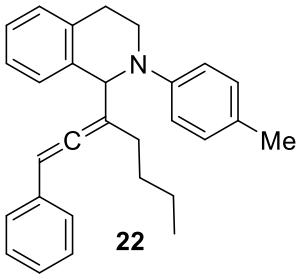
21

56:44 mixture of diastereomers

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.30 – 7.27 (m, 2H), 7.25 – 7.20 (m, 3H), 7.19 – 7.14 (m, 2H), 7.13 – 7.09 (m, 2H), 7.05 – 7.00 (m, 3H), 6.98 – 6.96 (m, 0.56H), 6.94 – 6.92 (m, 0.44H), 6.89 – 6.86 (m, 1H), 6.85 – 6.79 (m, 1H), 6.45 (d, *J* = 2.1 Hz, 0.56H), 6.38 (d, *J* = 2.1 Hz, 0.44H), 5.84 (d, *J* = 2.1 Hz, 0.44H), 5.80 (d, *J* = 2.1 Hz, 0.56H), 3.79 – 3.73 (m, 0.44H), 3.71 – 3.62 (m, 1H), 3.61 – 3.55 (m, 0.56H), 2.91 – 2.71 (m, 2H). **Major diastereomer**: ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.12, 149.45, 136.11, 135.44, 134.93, 129.25, 128.42, 128.31, 127.89, 127.73, 127.56, 127.35, 126.83, 126.34, 125.81, 125.75, 121.23, 118.43, 115.65, 113.18, 92.64, 60.88, 43.71, 27.11. **Minor diastereomer**: ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.78, 149.19, 135.88, 135.65, 135.18, 129.25, 129.22, 128.31, 127.89, 127.73, 127.52, 127.30, 126.80, 126.45, 125.81, 125.71, 121.27, 118.34, 115.48, 113.03, 92.79, 60.63, 43.44, 26.86. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{28}H_{24}NS]^+$[M+H]$^+$: 406.1624, Found: 406.1627.

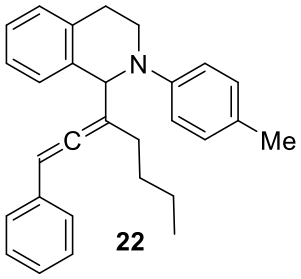
1-(1-phenylhepta-1,2-dien-3-yl)-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (22)

The reaction time was 6 h. White oil, 80.4 mg, 68% total yield of 1.2:1 diastereomers (0.3 mmol scale).



diastereomer 1

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.21 (m, 3H), 7.21 – 7.13 (m, 5H), 7.13 – 7.06 (m, 3H), 6.96 – 6.87 (m, 2H), 6.20 – 6.07 (m, 1H), 5.28 (d, *J* = 1.9 Hz, 1H), 3.78 – 3.66 (m, 1H), 3.63 – 3.52 (m, 1H), 3.06 – 2.89 (m, 2H), 2.30 (s, 3H), 2.15 – 2.06 (m, 2H), 1.45 – 1.37 (m, 2H), 1.34 – 1.25 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.1, 147.3, 136.4, 135.4, 129.6, 128.4, 128.2, 127.8, 126.7, 126.5, 125.7, 115.1, 112.4, 97.2, 62.8, 43.8, 29.8, 29.4, 27.8, 22.6, 20.4, 13.9. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{29}H_{32}N]^+$[M+H]$^+$: 394.2529, Found: 394.2533.

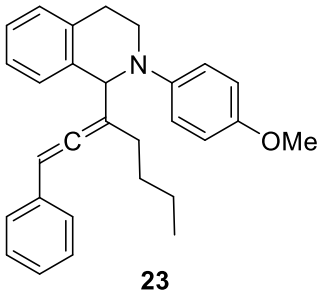


diastereomer 2

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 2H), 7.20 – 7.11 (m, 1H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.88 (d, *J* = 8.1 Hz, 1H), 6.17 (q, *J* = 3.0 Hz, 0H), 5.24 (d, *J* = 2.1 Hz, 0H), 3.66 – 3.59 (m, 0H), 3.55 – 3.48 (m, 1H), 3.01 – 2.88 (m, 0H), 2.31 (s, 1H), 2.19 – 2.11 (m, 0H), 2.08 – 2.00 (m, 0H), 1.46 – 1.37 (m, 0H), 1.34 – 1.26 (m, 0H), 0.83 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.1, 147.5, 136.5, 135.6, 135.1, 129.7, 128.3, 128.1, 127.6, 126.7, 126.7, 126.5, 125.7, 115.4, 112.3, 97.0, 62.7, 44.3, 29.8, 29.1, 28.1, 22.6, 20.4, 14.0. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{29}H_{32}N]^+$[M+H]$^+$: 394.2529, Found: 394.2535.

2-(4-methoxyphenyl)-1-(1-phenylhepta-1,2-dien-3-yl)-1,2,3,4-tetrahydroisoquinoline (23)

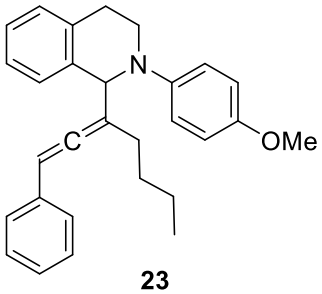
The reaction time was 10 h. White oil, 59.9 mg, 73% total yield of 1.2:1 diastereomers (0.2 mmol scale).



23

diastereomer 1

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.27 (m, 1H), 7.26 – 7.23 (m, 2H), 7.22 – 7.15 (m, 5H), 7.11 (d, *J* = 7.2 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.13 – 6.05 (m, 1H), 5.20 (s, 1H), 3.81 (s, 3H), 3.71 – 3.64 (m, 1H), 3.53 – 3.46 (m, 1H), 3.00 – 2.89 (m, 2H), 2.11 – 2.02 (m, 2H), 1.45 – 1.35 (m, 2H), 1.32 – 1.23 (m, 2H), 0.82 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.3, 152.8, 144.2, 136.4, 135.5, 135.4, 128.4, 128.3, 127.8, 126.7, 126.6, 126.5, 125.7, 117.8, 114.5, 112.2, 96.9, 63.7, 55.7, 45.0, 29.8, 29.3, 28.0, 22.6, 13.9. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{29}H_{32}NO]^+$[M+H]$^+$: 410.2478, Found: 410.2480.



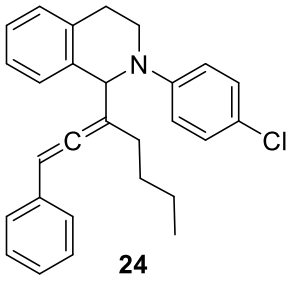
23

diastereomer 2

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 6.8 Hz, 1H), 7.24 (t, *J* = 7.3 Hz, 2H), 7.19 – 7.12 (m, 4H), 7.03 (d, *J* = 7.0 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 6.21 – 6.15 (m, 1H), 5.18 (s, 1H), 3.81 (s, 3H), 3.60 – 3.54 (m, 1H), 3.47 – 3.40 (m, 1H), 3.04 – 2.96 (m, 1H), 2.89 (dt, *J* = 15.9, 5.7 Hz, 1H), 2.18 – 2.10 (m, 1H), 1.98 – 1.90 (m, 1H), 1.42 – 1.34 (m, 2H), 1.30 – 1.21 (m, 2H), 0.81 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.6, 153.3, 144.5, 136.6, 135.5, 135.1, 128.3, 127.6, 126.7, 126.5, 126.5, 125.8, 119.0, 114.6, 111.9, 96.6, 63.9, 55.6, 46.1, 29.8, 28.7, 28.6, 22.6, 13.9. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{29}H_{32}NO]^+$[M+H]$^+$: 410.2478, Found: 410.2482.

2-(4-chlorophenyl)-1-(1-phenylhepta-1,2-dien-3-yl)-1,2,3,4-tetrahydroisoquinoline (24)

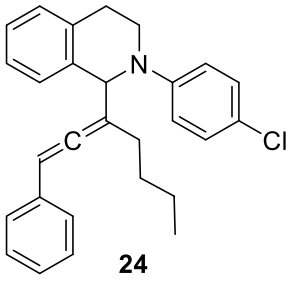
The reaction time was 6 h. White oil, 67.1 mg, 54% total yield of 1:1 diastereomers (0.3 mmol scale).



24

diastereomer 1

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 6H), 7.19 – 7.12 (m, 3H), 7.13 – 7.07 (m, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 6.18 (q, *J* = 3.2, 2.7 Hz, 1H), 5.23 (d, *J* = 2.1 Hz, 1H), 3.74 – 3.65 (m, 1H), 3.55 – 3.46 (m, 1H), 3.17 – 3.08 (m, 1H), 2.96 (dt, *J* = 15.5, 5.4 Hz, 1H), 2.13 – 2.03 (m, 2H), 1.44 – 1.39 (m, 2H), 1.33 – 1.27 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.8, 147.7, 136.1, 135.4, 135.0, 128.8, 128.4, 128.1, 127.7, 127.1, 126.7, 126.6, 126.0, 122.0, 115.0, 111.9, 97.9, 62.5, 43.9, 29.7, 29.4, 28.1, 22.6, 13.9. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{28}H_{29}ClN]^+$[M+H]$^+$: 414.1983, Found: 414.1986.



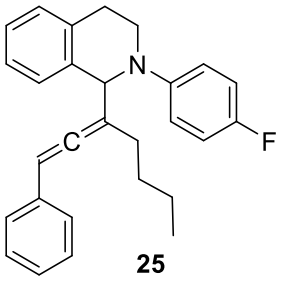
24

diastereomer 2

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.29 (m, 1H), 7.28 – 7.24 (m, 2H), 7.24 – 7.16 (m, 6H), 7.15 – 7.11 (m, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.18 (q, *J* = 3.3 Hz, 1H), 5.19 (d, *J* = 2.3 Hz, 1H), 3.62 – 3.55 (m, 1H), 3.50 – 3.43 (m, 1H), 3.08 – 2.99 (m, 1H), 2.90 (dt, *J* = 15.5, 5.4 Hz, 1H), 2.14 – 1.99 (m, 2H), 1.49 – 1.37 (m, 2H), 1.35 – 1.27 (m, 2H), 0.84 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.7, 147.9, 136.0, 135.4, 134.9, 128.9, 128.5, 128.1, 127.6, 127.0, 126.8, 126.7, 126.0, 122.2, 115.4, 111.5, 97.5, 62.5, 44.2, 29.7, 29.0, 28.1, 22.6, 13.9. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{28}H_{29}ClN]^+$[M+H]$^+$: 414.1983, Found: 414.1984.

2-(4-fluorophenyl)-1-(1-phenylhepta-1,2-dien-3-yl)-1,2,3,4-tetrahydroisoquinoline (25)

The reaction time was 12 h. White oil, 81.2 mg, 68% total yield of 1:1.2 diastereomers (0.3 mmol scale).

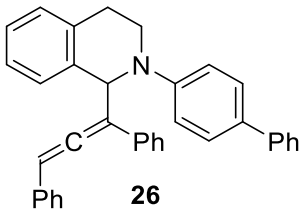


25

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.10 (m, 8H), 7.10 – 7.03 (m, 1H), 7.01 – 6.90 (m, 2H), 6.92 – 6.84 (m, 2H), 6.16 (td, *J* = 3.4, 1.9 Hz, 0.45H), 6.12 (td, *J* = 3.4, 1.9 Hz, 0.55H), 5.19 (d, *J* = 1.9 Hz, 0.55H), 5.17 (d, *J* = 1.9 Hz, 0.45H), 3.70 – 3.63 (m, 0.55H), 3.63 – 3.53 (m, 0.45H), 3.53 – 3.38 (m, 1H), 3.08 – 2.82 (m, 2H), 2.12 – 1.93 (m, 2H), 1.45 – 1.34 (m, 2H), 1.30 – 1.24 (m, 2H), 0.86 – 0.77 (m, 3H). **Major diastereomer**: ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.08, 156.13 (d, *J* = 236.5 Hz), 146.38, 146.06, 136.21, 135.40, 135.22, 128.40, 128.17, 127.73, 126.85, 126.68, 126.59, 125.91, 116.18 (d, *J* = 7.4 Hz), 115.36 (d, *J* = 22.0 Hz), 112.04, 97.42, 63.29, 44.63, 29.77, 29.34, 28.09, 22.57, 13.92. **Minor diastereomer**: ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.20, 156.40 (d, *J* = 236.9 Hz), 146.40, 146.07, 136.25, 135.40, 134.95, 128.40, 128.20, 127.60, 126.80, 126.70, 126.59, 125.90, 117.05 (d, *J* = 7.4 Hz), 115.53 (d, *J* = 22.0 Hz), 111.79, 97.04, 63.29, 45.23, 29.77, 28.88, 28.36, 22.57, 13.92. **Major diastereomer**: ^{19}F NMR (377 MHz, $CDCl_3$) δ -127.40. **Minor diastereomer**: ^{19}F NMR (377 MHz, $CDCl_3$) δ -126.64. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{28}H_{29}FN]^+$[M+H]$^+$: 398.2279, Found: 398.2280.

2-([1,1'-biphenyl]-4-yl)-1-(1,3-diphenylpropa-1,2-dien-1-yl)-1,2,3,4-tetrahydroisoquinoline (26)

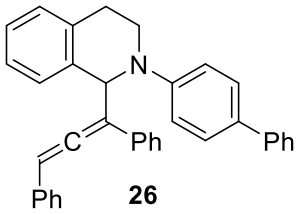
The reaction time was 6.5 h. White solid, 61.9 mg, 65% total yield of 1:1.1 diastereomers (0.2 mmol scale).



26

diastereomer 1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 2H), 7.57 – 7.53 (m, 2H), 7.47 – 7.42 (m, 4H), 7.35 – 7.29 (m, 3H), 7.28 – 7.16 (m, 7H), 7.16 – 7.09 (m, 4H), 7.08 – 7.03 (m, 1H), 6.44 (d, *J* = 2.1 Hz, 1H), 5.91 (d, *J* = 2.1 Hz, 1H), 3.74 (ddd, *J* = 12.7, 7.8, 5.1 Hz, 1H), 3.66 (dt, *J* = 12.0, 5.7 Hz, 1H), 3.02 – 2.90 (m, 1H), 2.86 (dt, *J* = 10.5, 5.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.0, 148.7, 141.0, 136.0, 135.7, 135.4, 133.7, 131.0, 128.7, 128.6, 128.5, 128.3, 127.8, 127.8, 127.6, 127.5, 127.2, 126.9, 126.9, 126.4, 126.2, 125.9, 115.6, 114.0, 98.2, 60.9, 43.6, 27.2. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{36}H_{30}N]^+$[M+H]$^+$: 476.2373, Found: 476.2382.



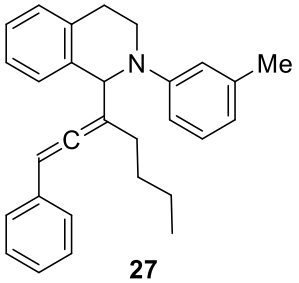
26

diastereomer 2

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.7 Hz, 2H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.38 – 7.29 (m, 4H), 7.28 – 7.16 (m, 4H), 7.16 – 6.99 (m, 10H), 6.99 – 6.95 (m, 1H), 6.25 (d, *J* = 2.1 Hz, 1H), 5.85 (d, *J* = 2.1 Hz, 1H), 3.79 – 3.68 (m, 1H), 3.67 – 3.58 (m, 1H), 2.94 – 2.79 (m, 1H), 2.69 (dt, *J* = 16.1, 5.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.8, 148.4, 141.1, 135.9, 135.5, 135.3, 134.0, 131.0, 128.7, 128.5, 128.5, 128.4, 127.9, 127.8, 127.5, 127.4, 127.1, 127.0, 126.9, 126.4, 126.2, 125.8, 115.6, 113.8, 98.5, 60.7, 43.4, 26.9. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{36}H_{30}N]^+$[M+H]$^+$: 476.2373, Found: 476.2374.

1-(1-phenylhepta-1,2-dien-3-yl)-2-(m-tolyl)-1,2,3,4-tetrahydroisoquinoline (27)

The reaction time was 6 h. White oil, 81.6 mg, 69% total yield of 1:1.4 diastereomers (0.3 mmol scale).

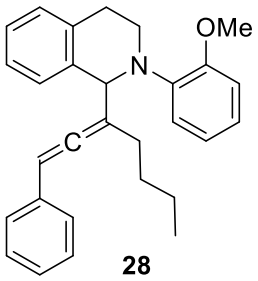


27

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.08 (m, 4H), 7.07 – 7.00 (m, 6H), 6.66 (d, *J* = 11.7 Hz, 2H), 6.51 (t, *J* = 7.1 Hz, 1H), 6.13 – 6.00 (m, 1H), 5.20 (d, *J* = 2.0 Hz, 0.58H), 5.17 (d, *J* = 2.2 Hz, 0.42H), 3.66 – 3.39 (m, 2H), 2.98 – 2.77 (m, 2H), 2.25 (s, 1.74H), 2.17 (s, 1.26H), 2.07 – 1.93 (m, 2H), 1.37 – 1.28 (m, 2H), 1.23 – 1.17 (m, 2H), 0.76 – 0.69 (m, 3H). **Major diastereomer**: ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.05, 149.38, 138.63, 136.51, 135.65, 135.40, 128.94, 128.39, 128.12, 127.79, 126.80, 126.76, 126.51, 125.83, 118.40, 115.10, 112.44, 111.43, 97.54, 62.61, 43.54, 29.85, 29.47, 28.05, 22.62, 22.04, 13.98. **Minor diastereomer**: ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.95, 149.61, 138.81, 136.55, 135.69, 135.16, 129.03, 128.46, 128.12, 127.65, 126.79, 126.74, 126.59, 125.83, 118.58, 115.27, 112.29, 111.69, 97.23, 62.46, 43.80, 29.85, 29.16, 28.17, 22.64, 21.95, 14.00. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{29}H_{32}N]^+$[M+H]$^+$: 394.2529, Found: 394.2533.

2-(2-methoxyphenyl)-1-(1-phenylhepta-1,2-dien-3-yl)-1,2,3,4-tetrahydroisoquinoline (28)

The reaction time was 6 h. White oil, 56.6 mg, 69% total yield of 1:1.3 diastereomers (0.2 mmol scale).

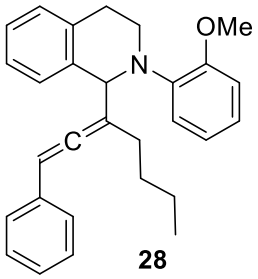


28

diastereomer 1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 3.5 Hz, 1H), 7.18 – 7.04 (m, 8H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.87 – 6.80 (m, 3H), 6.12 (t, *J* = 3.5 Hz, 1H), 5.46 (s, 1H), 3.73 (s, 3H), 3.64 – 3.55 (m, 1H), 3.45 – 3.37 (m, 1H), 3.00 – 2.84 (m, 2H), 2.12 – 2.01 (m, 1H), 1.83 – 1.74 (m, 1H), 1.29 – 1.21 (m, 2H), 1.20 – 1.11 (m, 2H), 0.73 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.3, 154.1, 140.1, 137.0, 135.4, 135.2, 128.6, 128.2, 127.6, 126.6, 126.2, 126.1, 125.5, 123.5, 123.2, 121.0, 112.2, 111.7, 95.7, 62.8, 55.4, 46.1, 29.7, 29.3, 28.7, 22.5, 13.9.

HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{29}H_{32}NO]^+$[M+H]$^+$: 410.2478, Found: 410.2483.



28

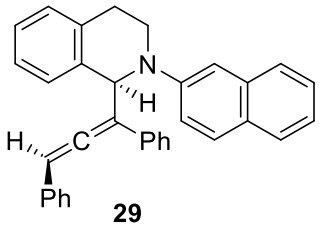
diastereomer 2

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.26 – 7.21 (m, 3H), 7.20 – 7.10 (m, 3H), 7.09 – 6.96 (m, 3H), 6.90 (t, *J* = 7.9 Hz, 2H), 5.84 (s, 1H), 5.40 (s, 1H), 3.86 (s, 3H), 3.65 – 3.54 (m, 1H), 3.48 – 3.36 (m, 1H), 2.93 – 2.84 (m, 1H), 2.83 – 2.70 (m, 1H), 2.00 – 1.80 (m, 2H), 1.32 – 1.23 (m, 2H), 1.21 – 1.12 (m, 2H), 0.74 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.1, 153.4, 140.1, 136.7, 135.9, 135.2, 128.6, 128.5, 127.8, 126.6, 126.4, 126.1, 125.4, 123.1, 122.2, 120.8, 111.8, 111.3, 95.6, 62.8, 55.6, 45.0, 29.8, 28.5, 22.4, 13.9.

HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{29}H_{32}NO]^+$[M+H]$^+$: 410.2478, Found: 410.2480.

1-(1,3-diphenylpropa-1,2-dien-1-yl)-2-(naphthalen-2-yl)-1,2,3,4-tetrahydroisoquinoline (29)

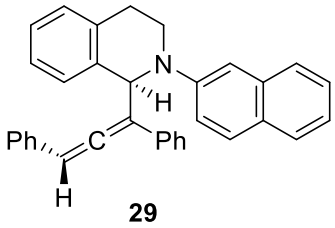
The reaction time was 8 h. White solid, 27.0 mg, 60% total yield of 1:1.1 diastereomers (0.1 mmol scale).



29

diastereomer 1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (t, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 1H), 7.36 – 7.25 (m, 4H), 7.21 – 7.19 (m, 1H), 7.18 – 7.00 (m, 11H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.24 (d, *J* = 2.1 Hz, 1H), 5.94 (d, *J* = 2.1 Hz, 1H), 3.86 – 3.69 (m, 2H), 2.90 – 2.76 (m, 1H), 2.61 (dt, *J* = 16.2, 4.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.0, 147.1, 135.9, 135.6, 135.3, 134.8, 134.1, 128.9, 128.5, 128.5, 128.1, 127.9, 127.4, 127.4, 127.2, 127.1, 126.9, 126.8, 126.6, 126.1, 125.8, 122.8, 118.9, 113.8, 110.6, 98.6, 60.5, 43.6, 26.8. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{34}H_{28}N]^+$[M+H]$^+$: 450.2216, Found: 450.2219.



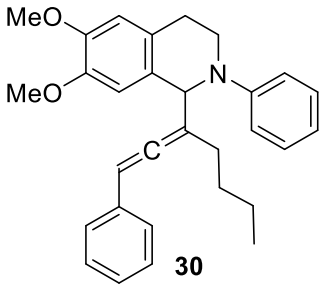
29

diastereomer 2

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.7 Hz, 2H), 7.63 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.45 – 7.35 (m, 4H), 7.33 – 7.29 (m, 2H), 7.28 – 7.18 (m, 6H), 7.15 – 7.04 (m, 5H), 6.41 (d, *J* = 2.1 Hz, 1H), 6.01 (d, *J* = 2.0 Hz, 1H), 3.87 – 3.72 (m, 2H), 3.03 – 2.90 (m, 1H), 2.90 – 2.78 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.4, 147.3, 135.9, 135.7, 135.3, 134.8, 133.6, 128.9, 128.5, 128.4, 128.4, 128.1, 128.0, 127.9, 127.5, 127.4, 127.1, 126.9, 126.9, 126.6, 126.1, 125.9, 122.9, 118.9, 113.9, 110.7, 98.2, 60.8, 44.0, 27.1. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{34}H_{28}N]^+$[M+H]$^+$: 450.2216, Found: 450.2221.

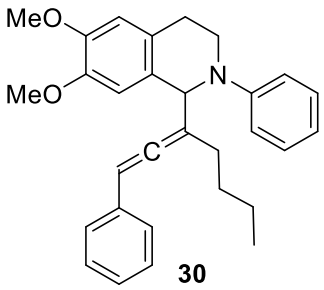
6,7-dimethoxy-2-phenyl-1-(1-phenylhepta-1,2-dien-3-yl)-1,2,3,4-tetrahydroisoquinoline (30)

The reaction time was 8.5 h. White oil, 48.4 mg, 55% total yield of 1:1.3 diastereomers (0.2 mmol scale).



diastereomer 1

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.27 – 7.20 (m, 4H), 7.19 – 7.14 (m, 1H), 7.03 (s, 2H), 6.84 (d, *J* = 17.3 Hz, 1H), 6.75 (s, 1H), 6.62 (s, 1H), 6.19 (s, 1H), 5.28 (d, *J* = 1.7 Hz, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 3.77 – 3.68 (m, 1H), 3.66 – 3.58 (m, 1H), 2.92 (s, 2H), 2.09 (s, 2H), 1.40 (d, *J* = 7.3 Hz, 2H), 1.35 – 1.25 (m, 2H), 0.82 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.1, 149.4, 147.8, 147.3, 135.4, 129.1, 128.5, 128.1, 127.4, 126.7, 126.6, 117.9, 114.9, 110.9, 110.7, 97.1, 62.5, 56.0, 55.9, 43.6, 29.8, 28.9, 27.5, 22.6, 13.9. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{30}H_{34}NO_2]^+$[M+H]$^+$: 440.2584, Found: 440.2592.



diastereomer 2

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 4H), 7.22 – 7.14 (m, 3H), 7.04 – 6.93 (m, 2H), 6.86 – 6.77 (m, 1H), 6.66 (s, 1H), 6.61 (s, 1H), 6.12 (q, *J* = 3.0 Hz, 1H), 5.27 (d, *J* = 2.3 Hz, 1H), 3.85 (s, 3H), 3.69 – 3.63 (m, 2H), 3.62 (s, 3H), 2.96 – 2.86 (m, 1H), 2.84 – 2.71 (m, 1H), 2.26 – 2.08 (m, 2H), 1.52 – 1.41 (m, 2H), 1.40 – 1.27 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.4, 149.5, 147.8, 146.8, 135.0, 129.2, 128.5, 128.0, 127.2, 126.7, 117.9, 115.1, 112.4, 111.0, 110.9, 97.1, 61.7, 55.8, 55.7, 43.0, 29.9, 29.3, 26.8, 22.7, 14.0. HRMS (m/z, ESI): Calcd. for Chemical Formula: $[C_{30}H_{34}NO_2]^+$[M+H]$^+$: 440.2584, Found: 440.2591.

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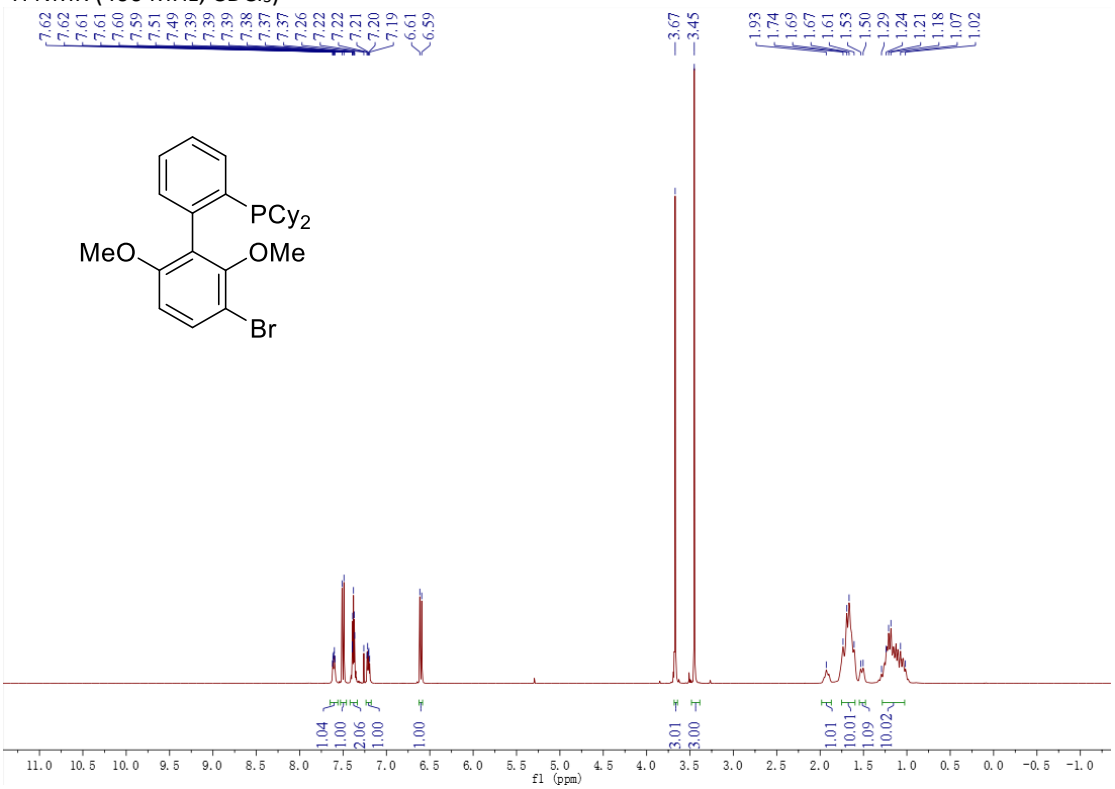
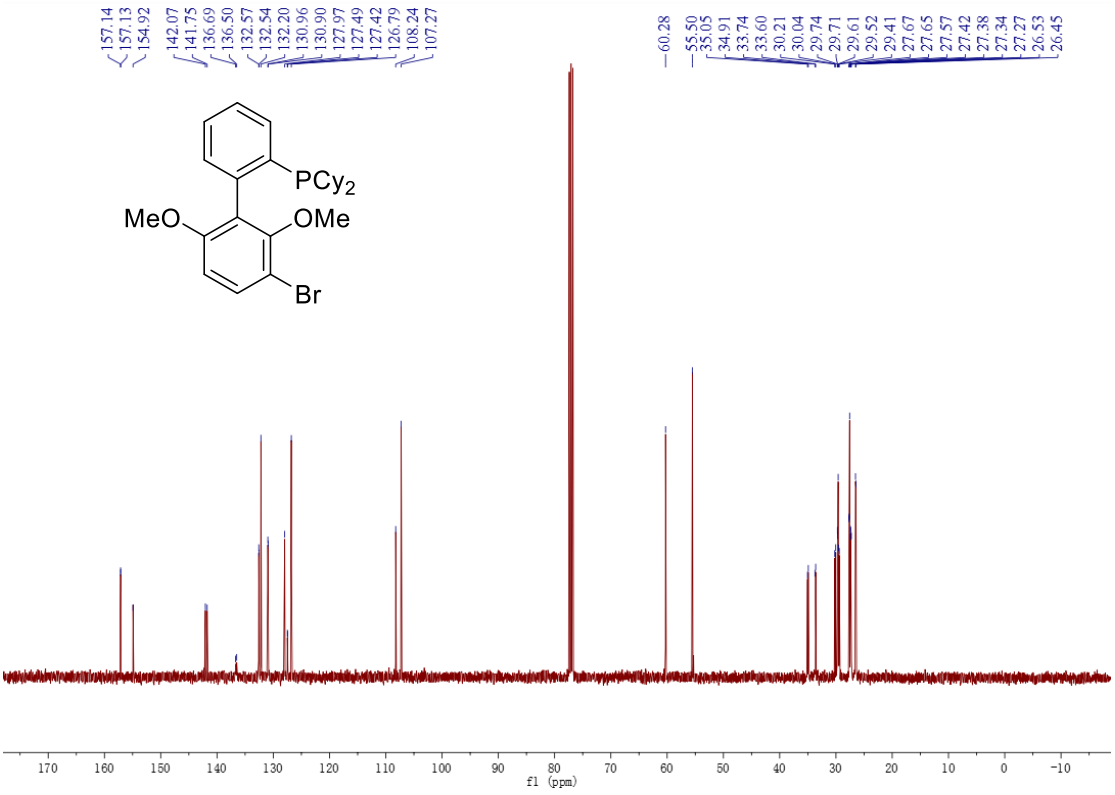
NMR spectra

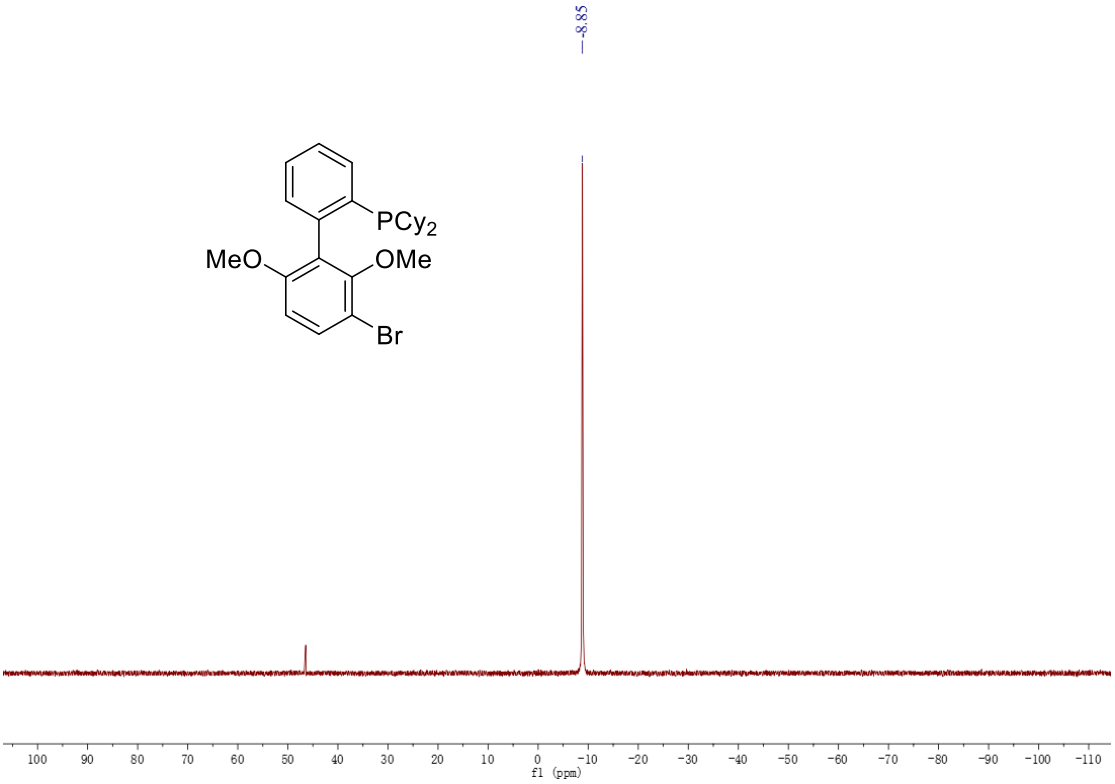
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



^{31}P NMR (162 MHz, $CDCl_3$)



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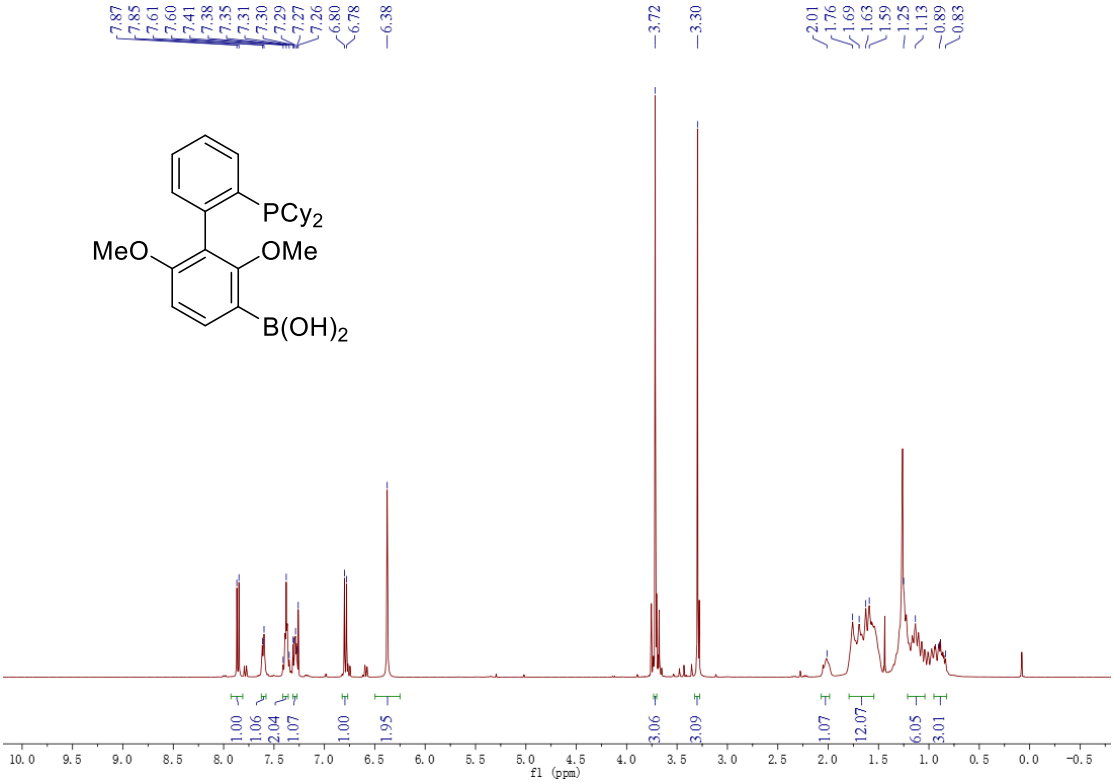

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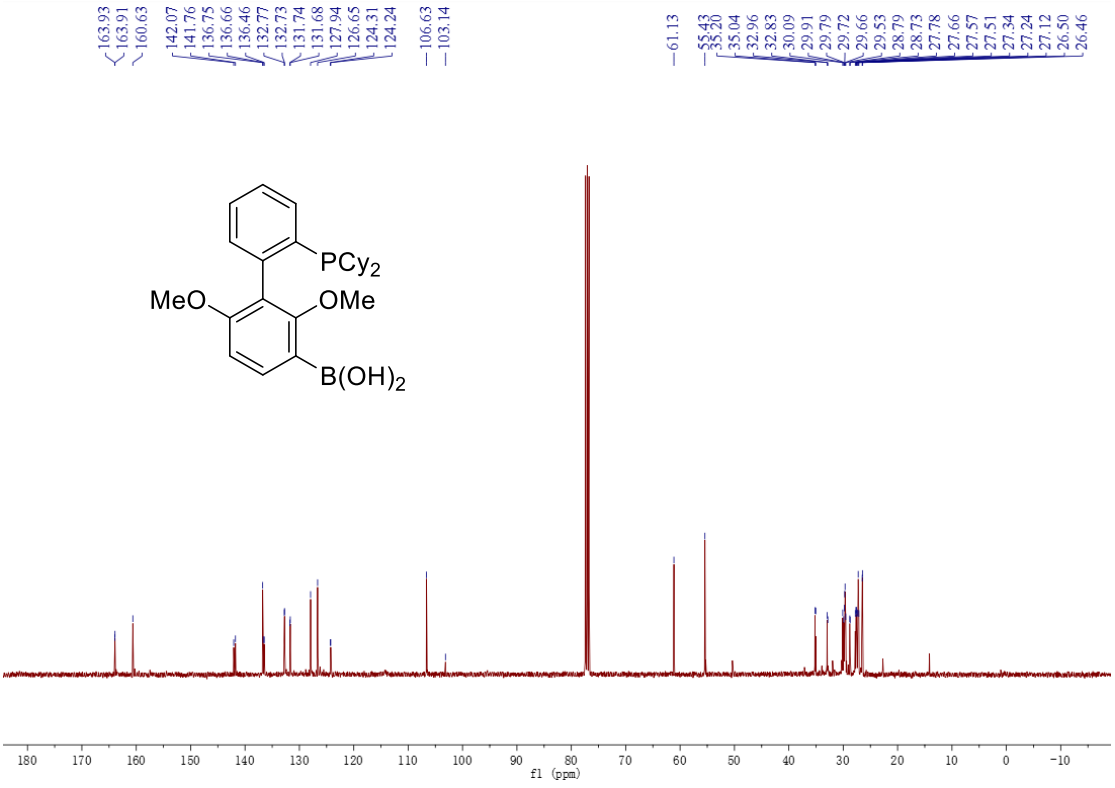

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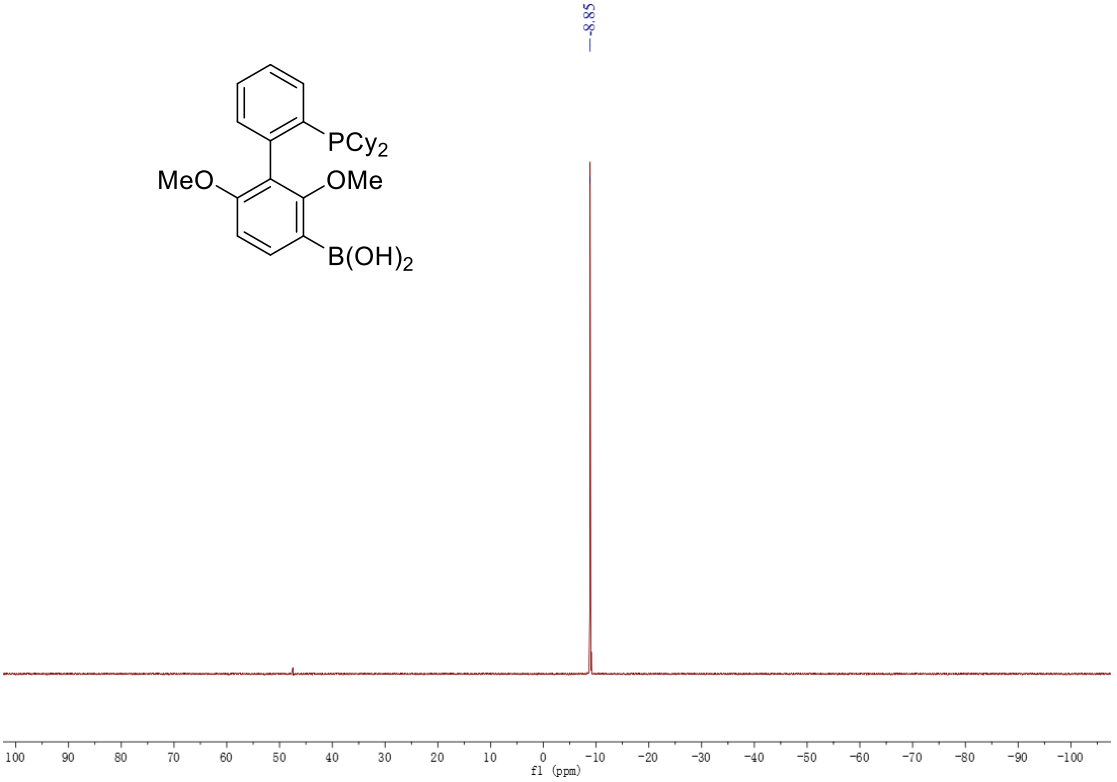

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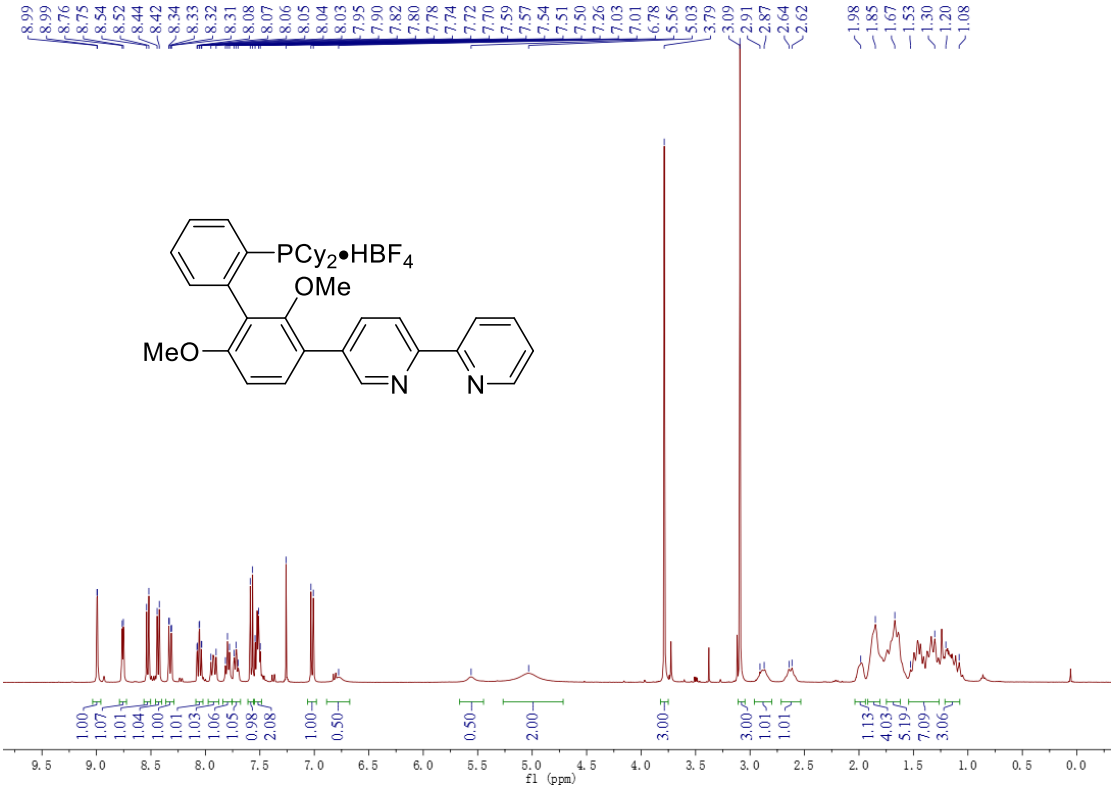
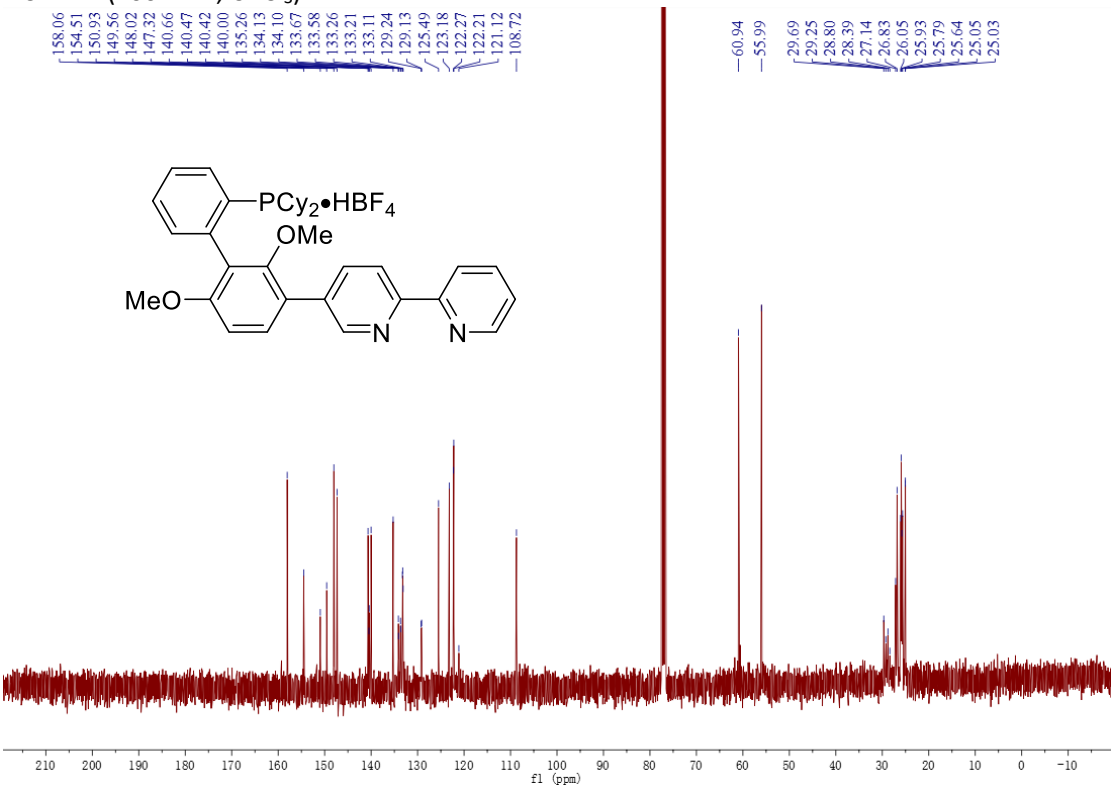
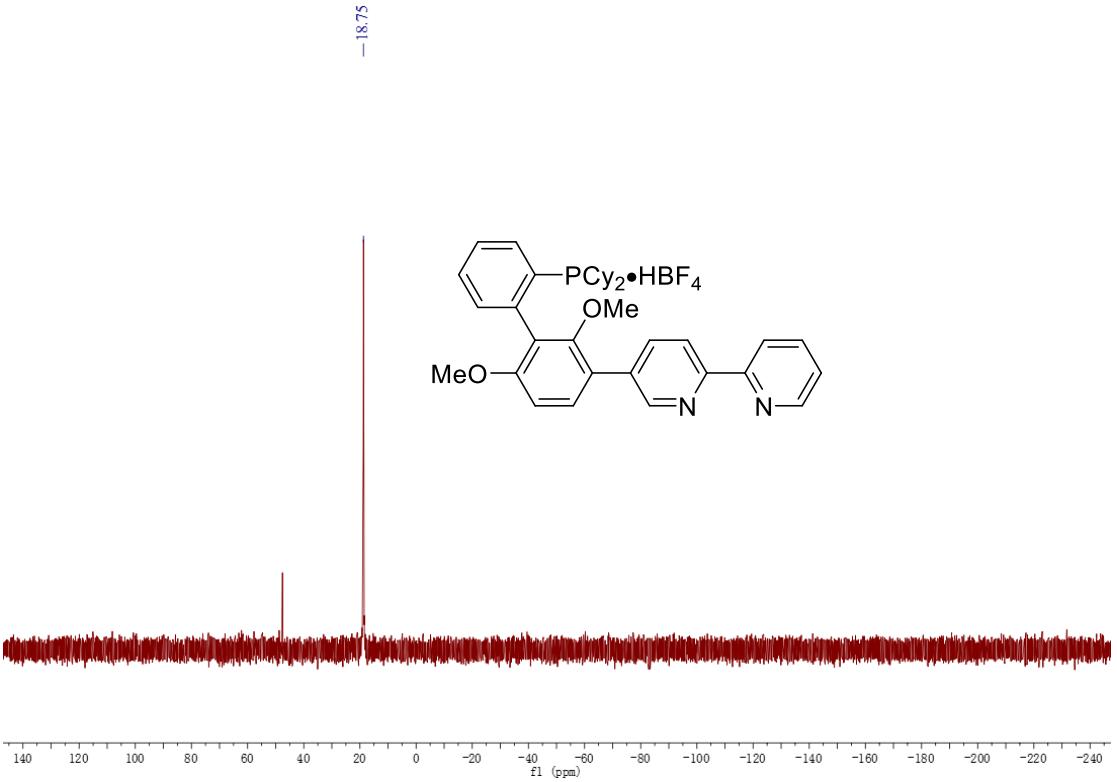


^{13}C NMR (100 MHz, $CDCl_3$)



^{31}P NMR (162 MHz, $CDCl_3$)



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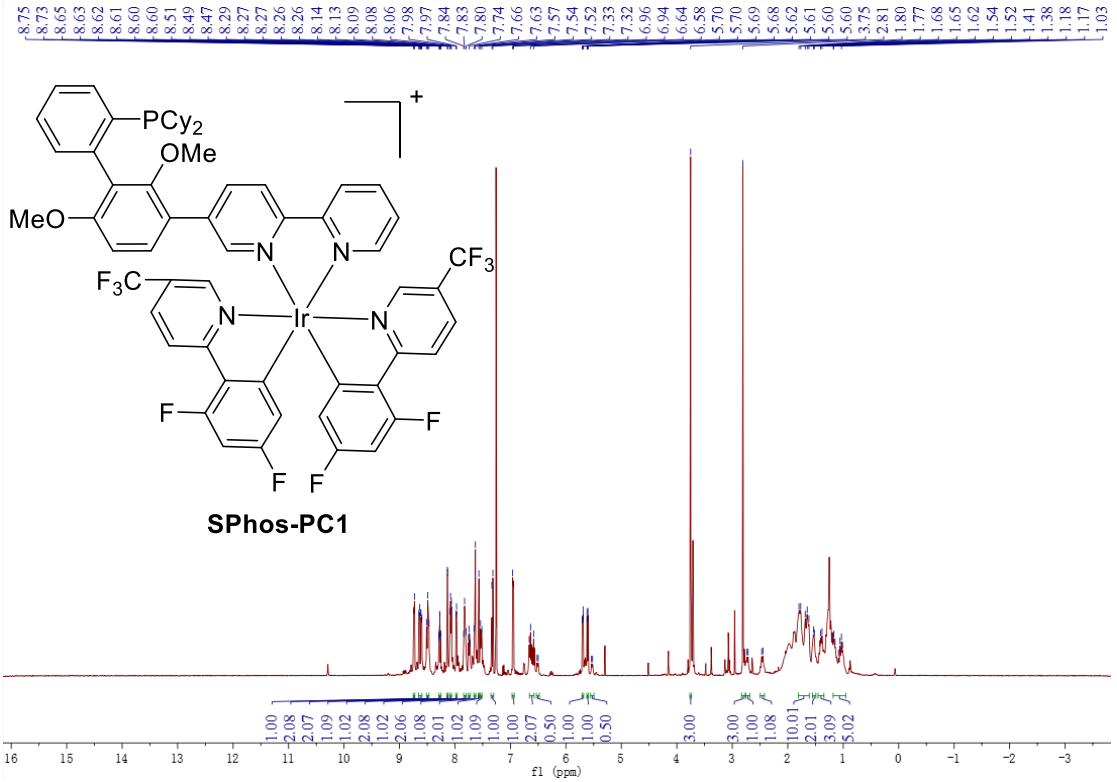
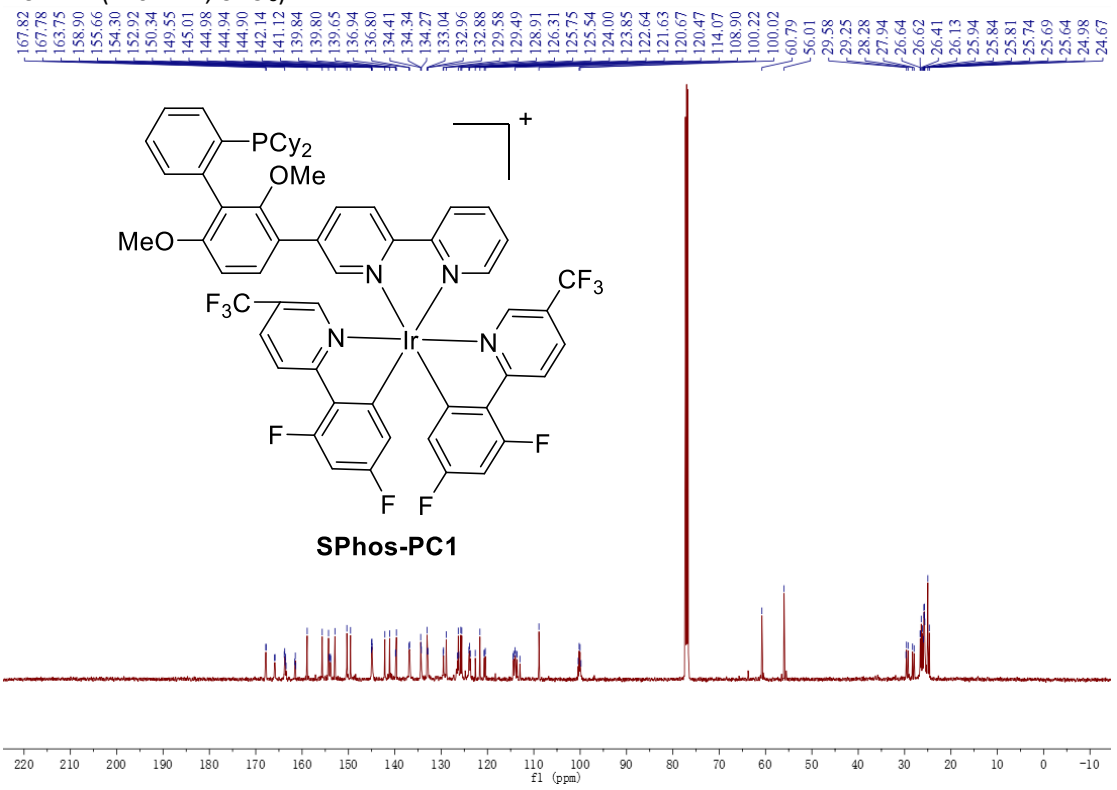


^{13}C NMR (126 MHz, $CDCl_3$)



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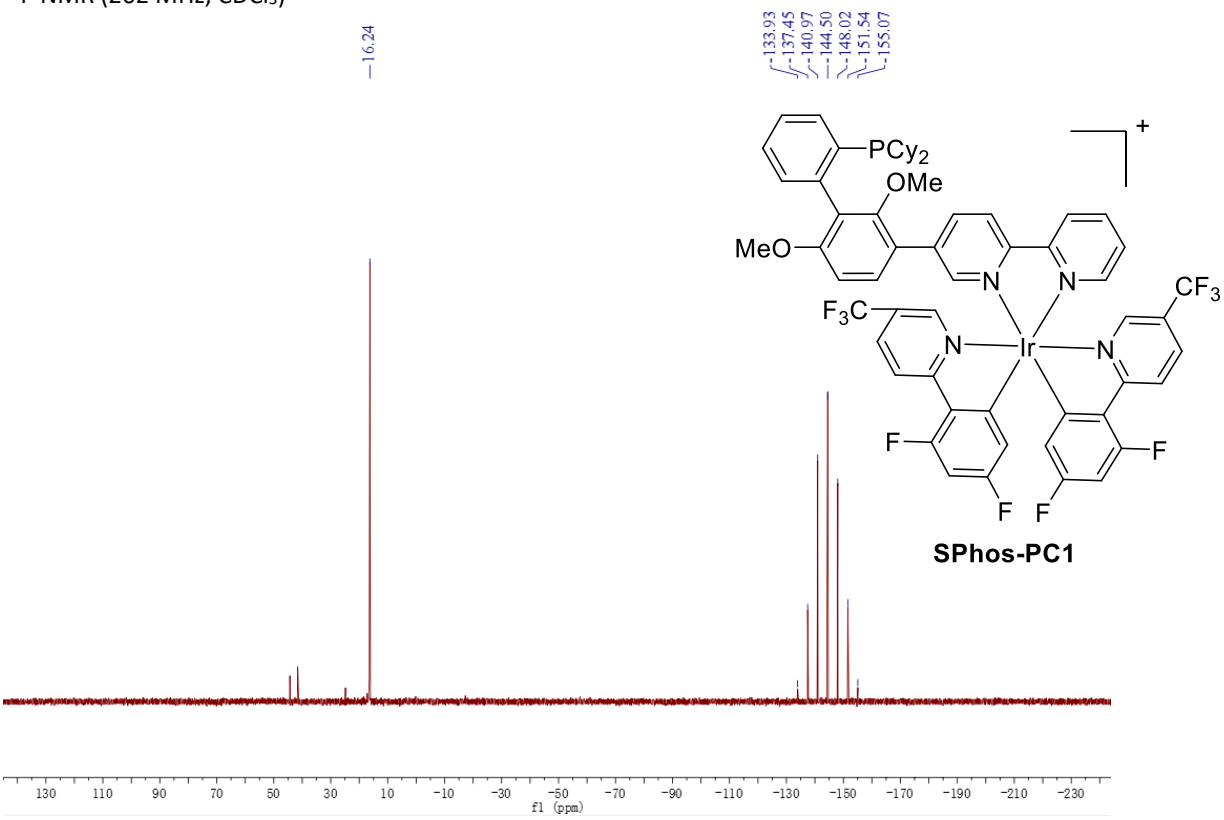

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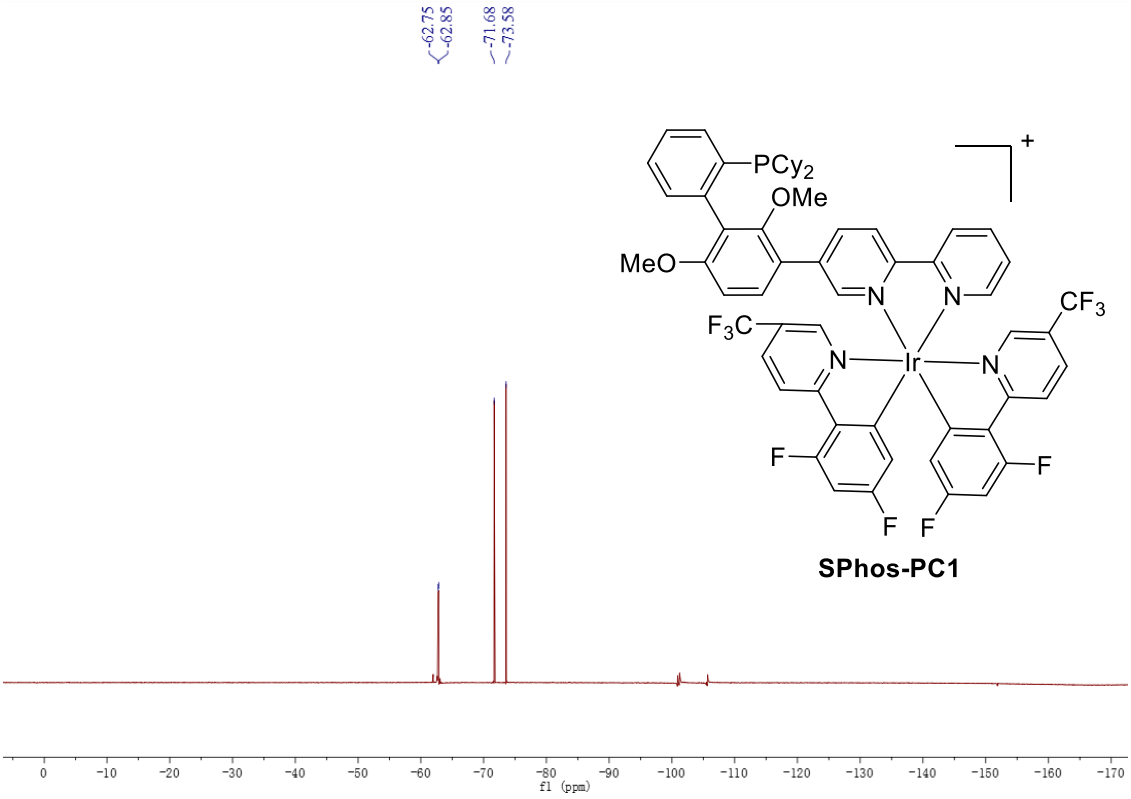

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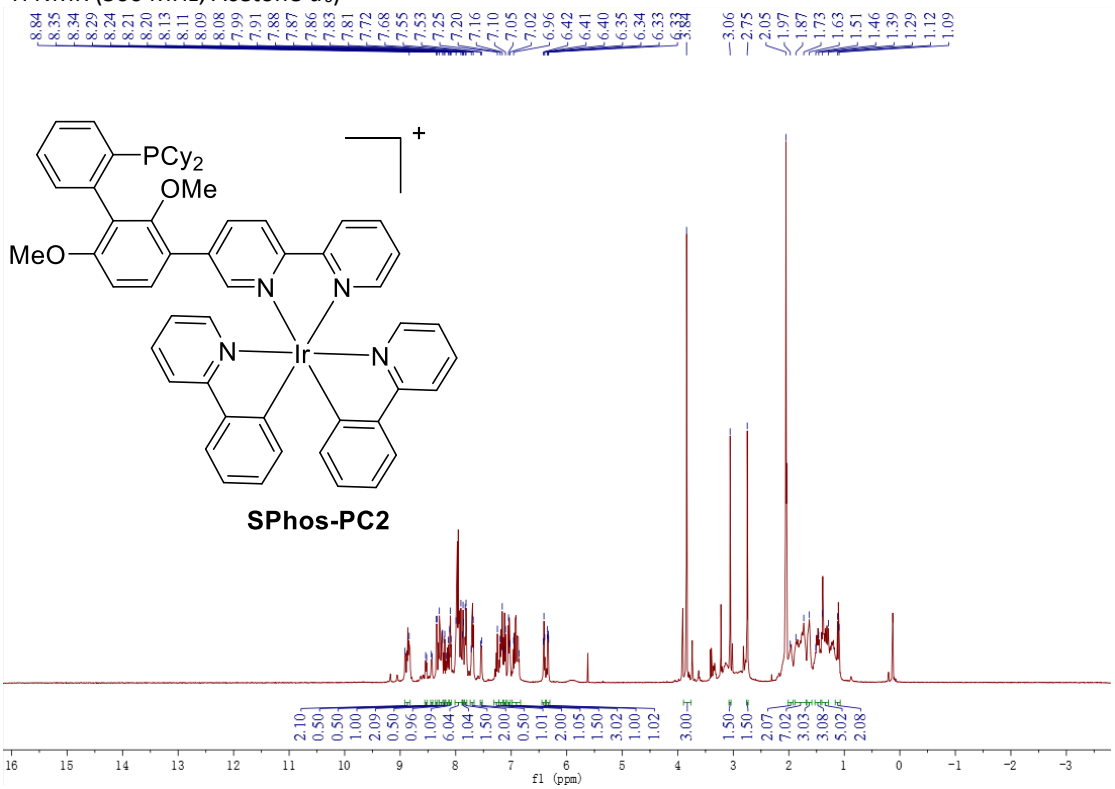
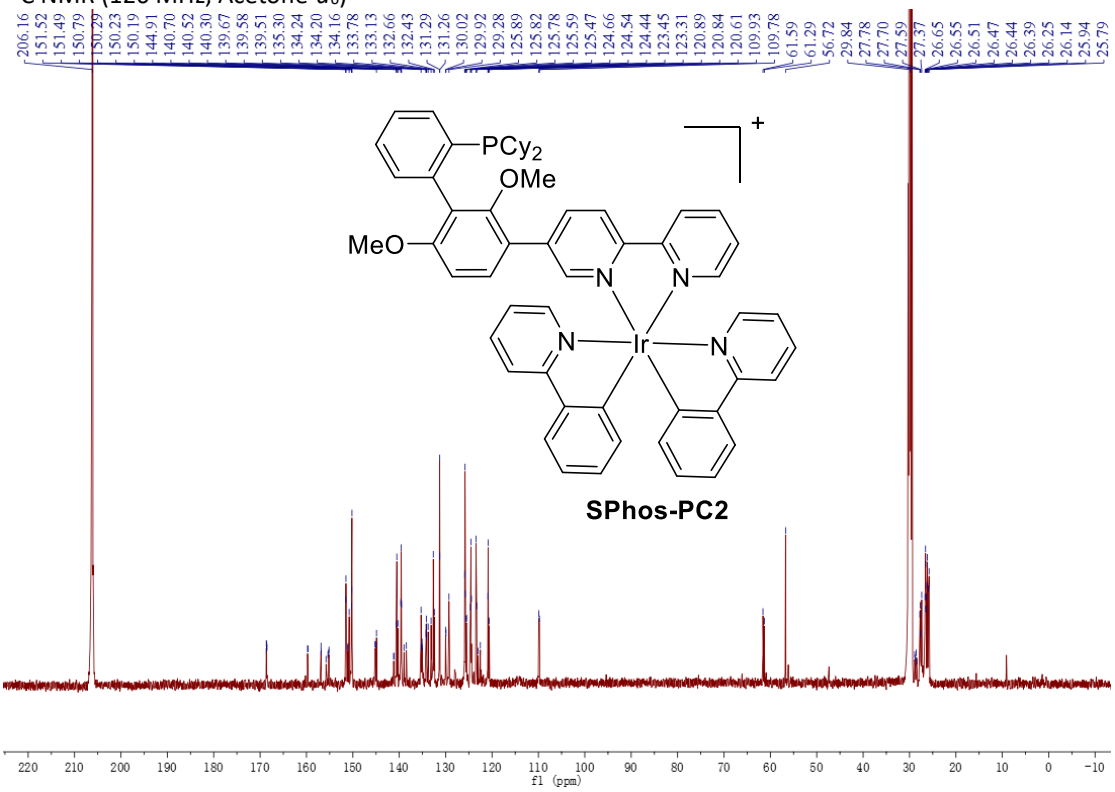
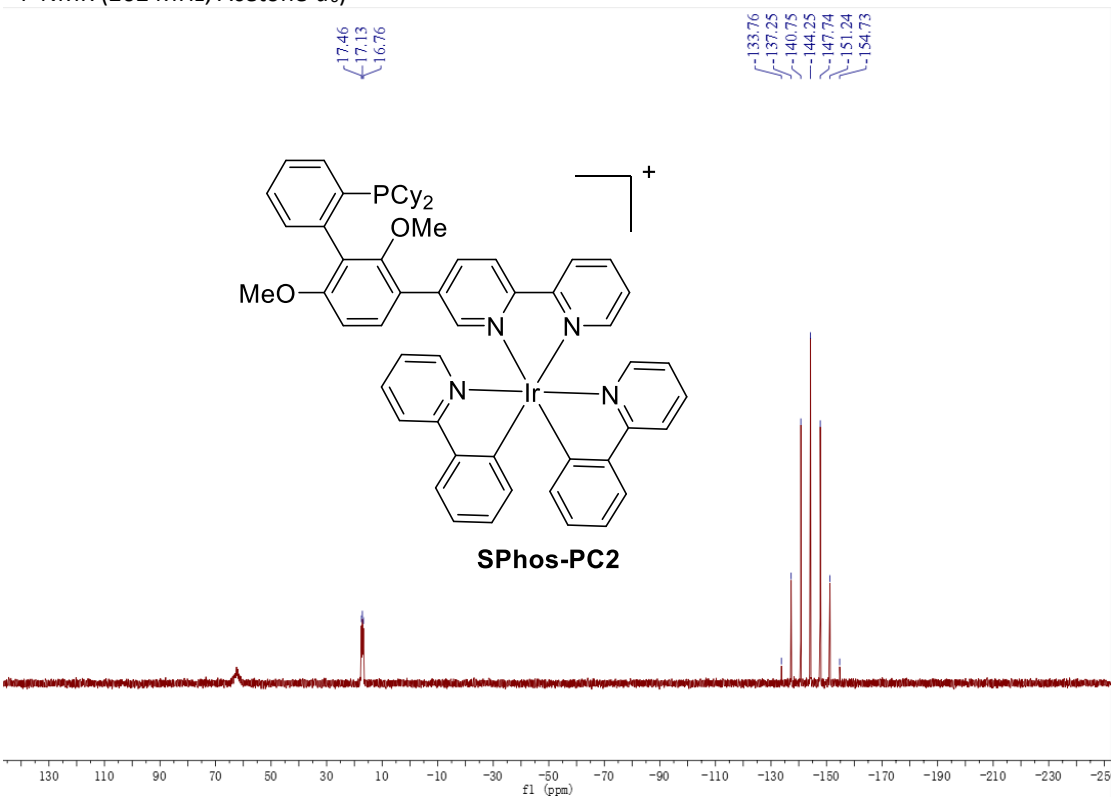


^{13}C NMR (126 MHz, Acetone-d_6)



^{31}P NMR (202 MHz, Acetone-d_6)



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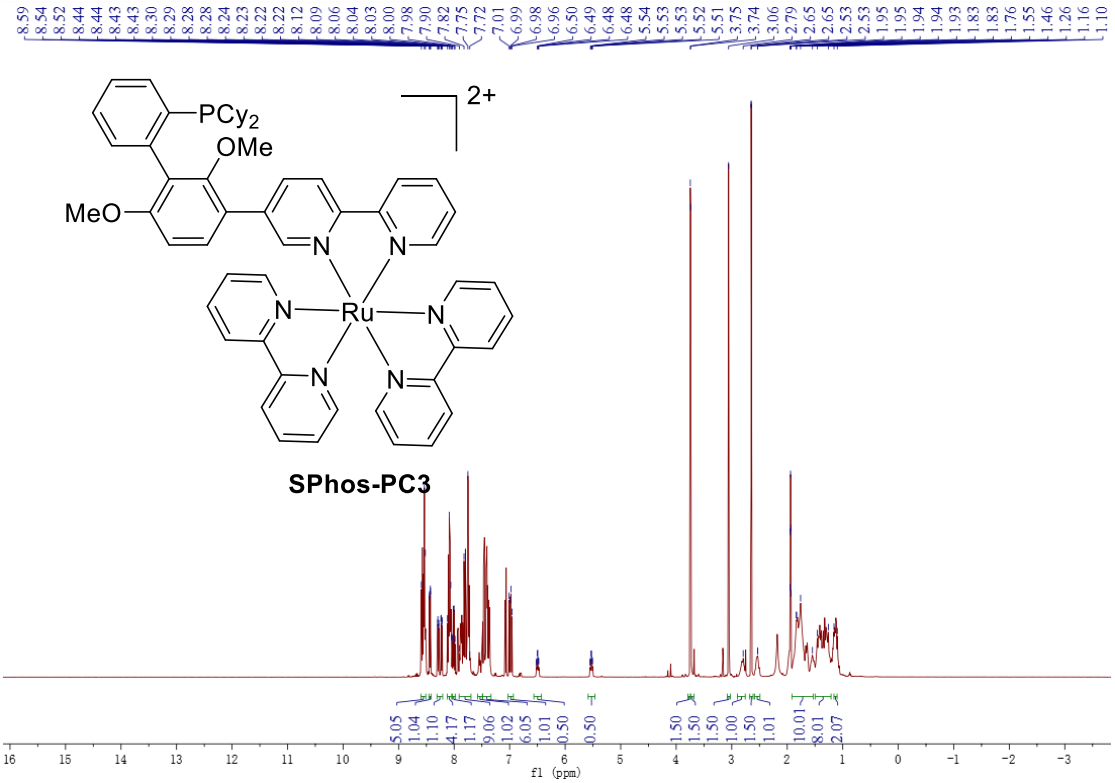

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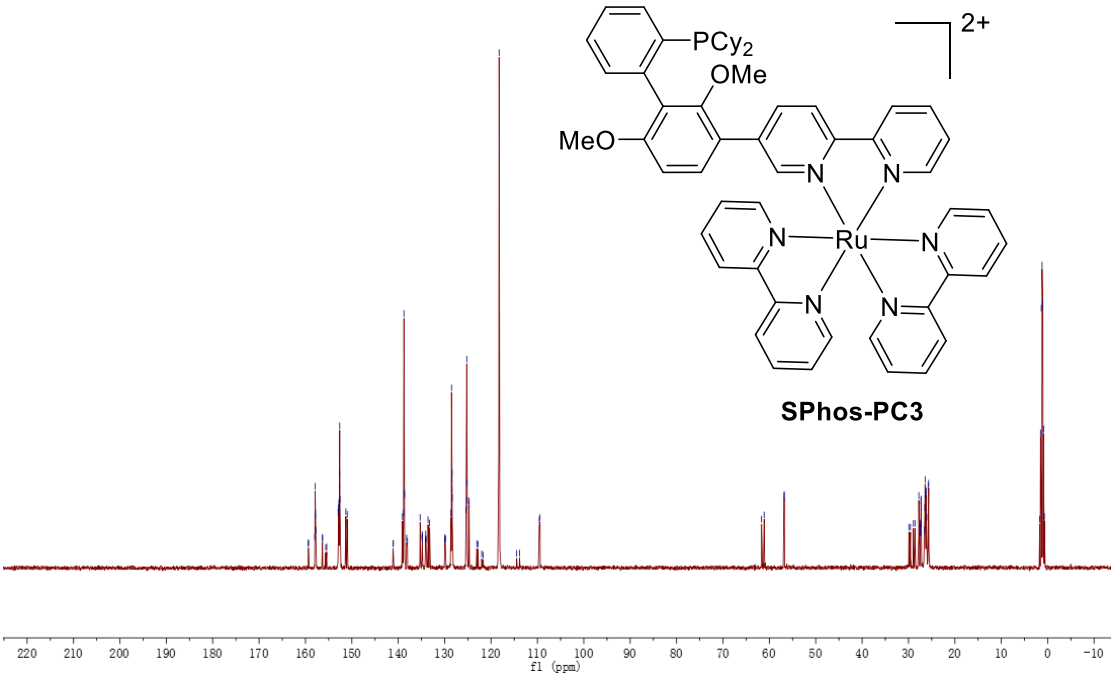
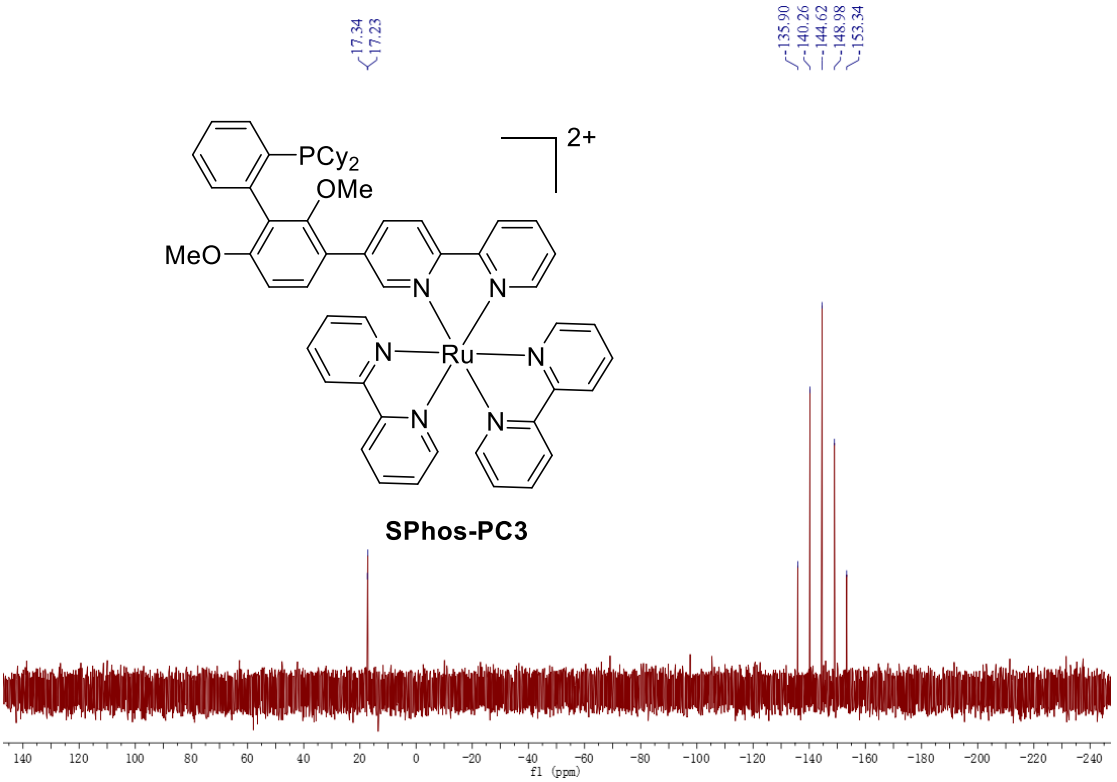


^{31}P NMR (162 MHz, CD_3CN)



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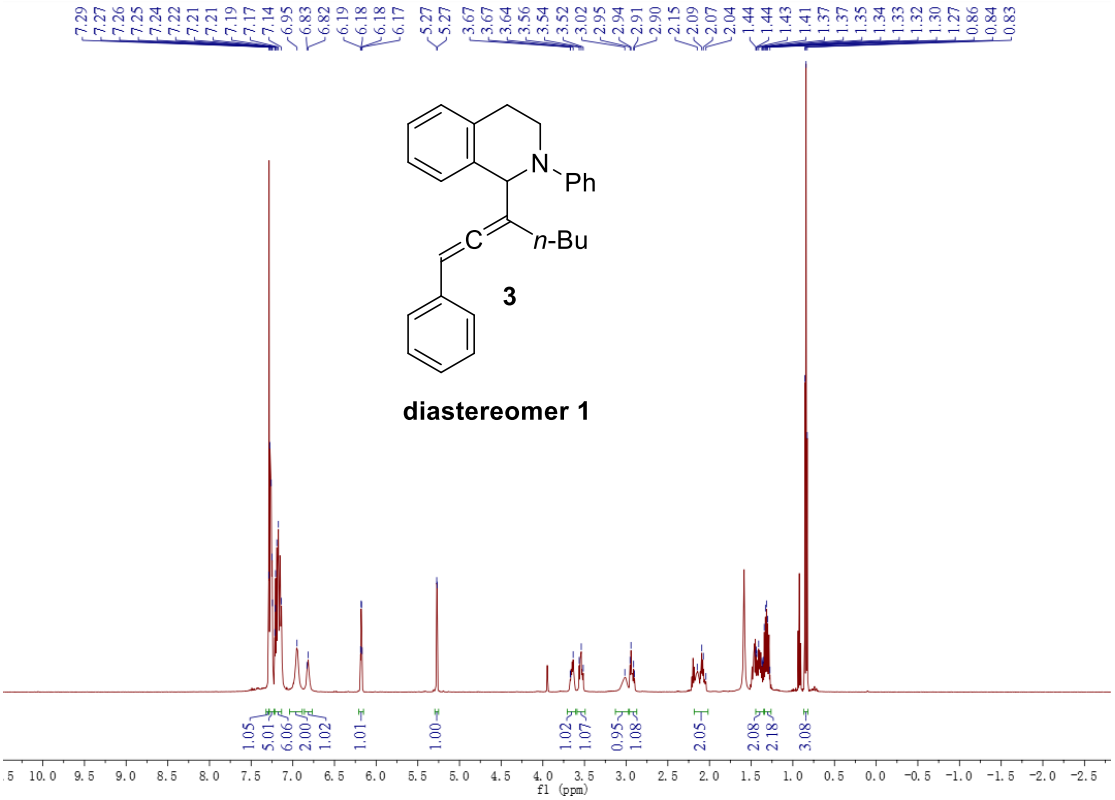

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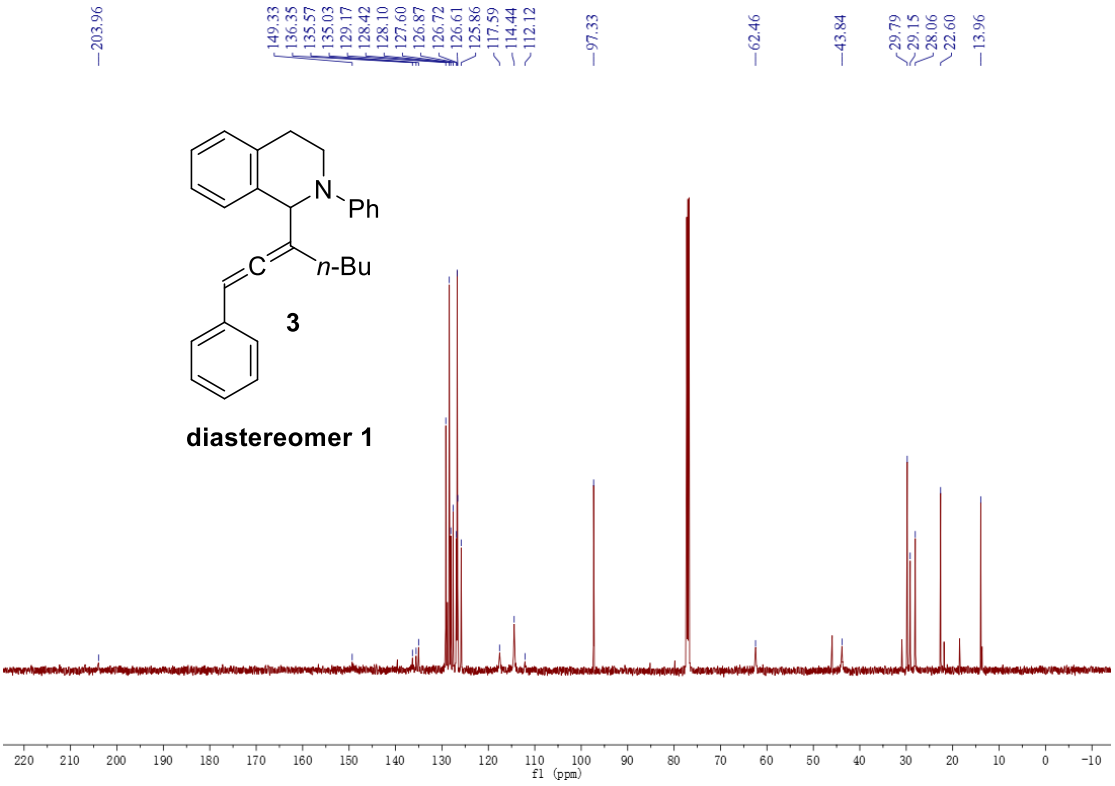

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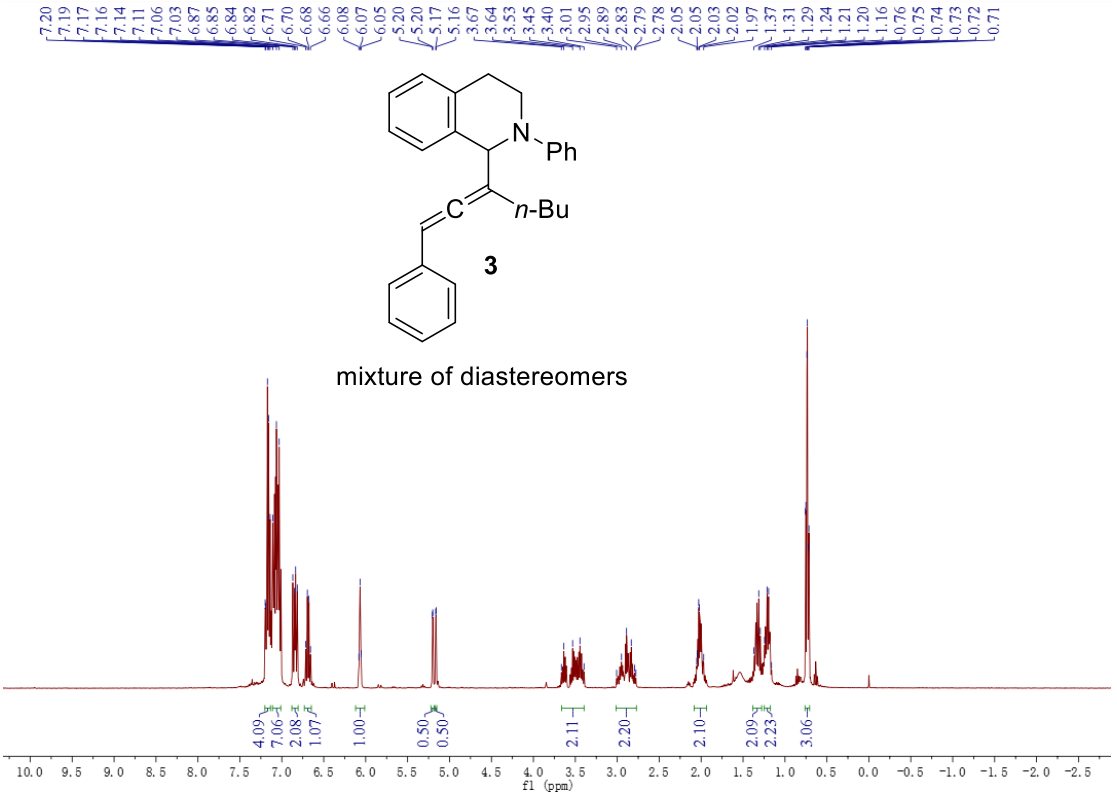

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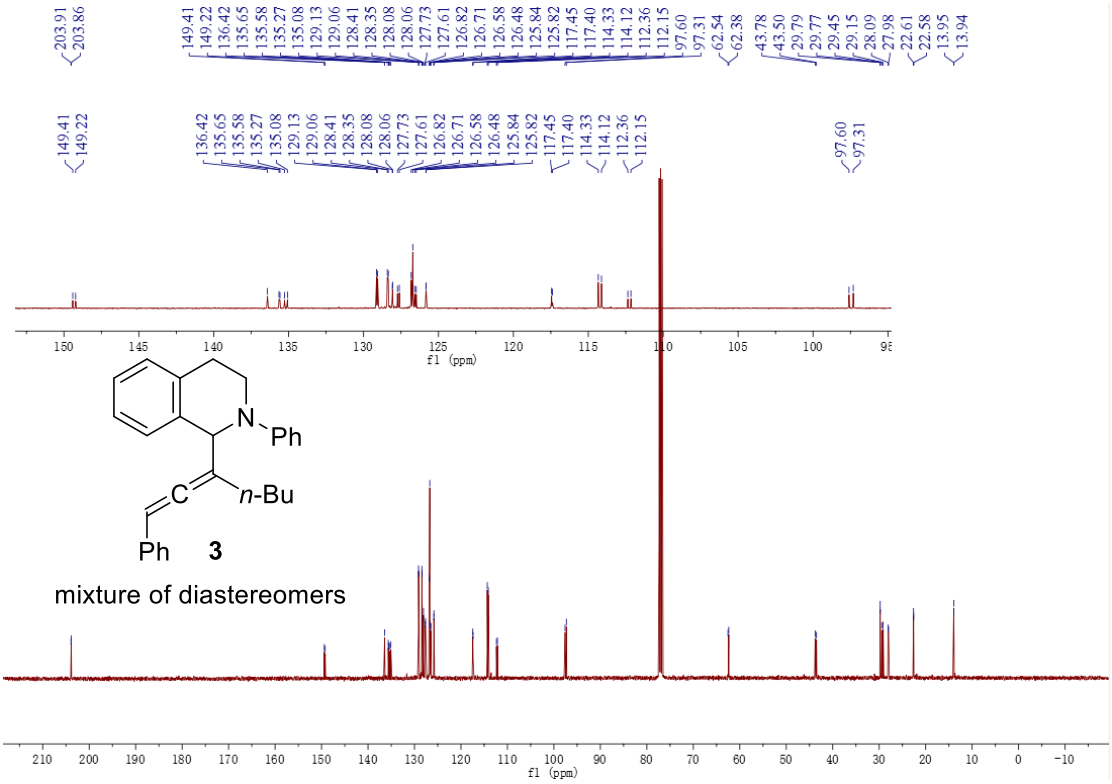

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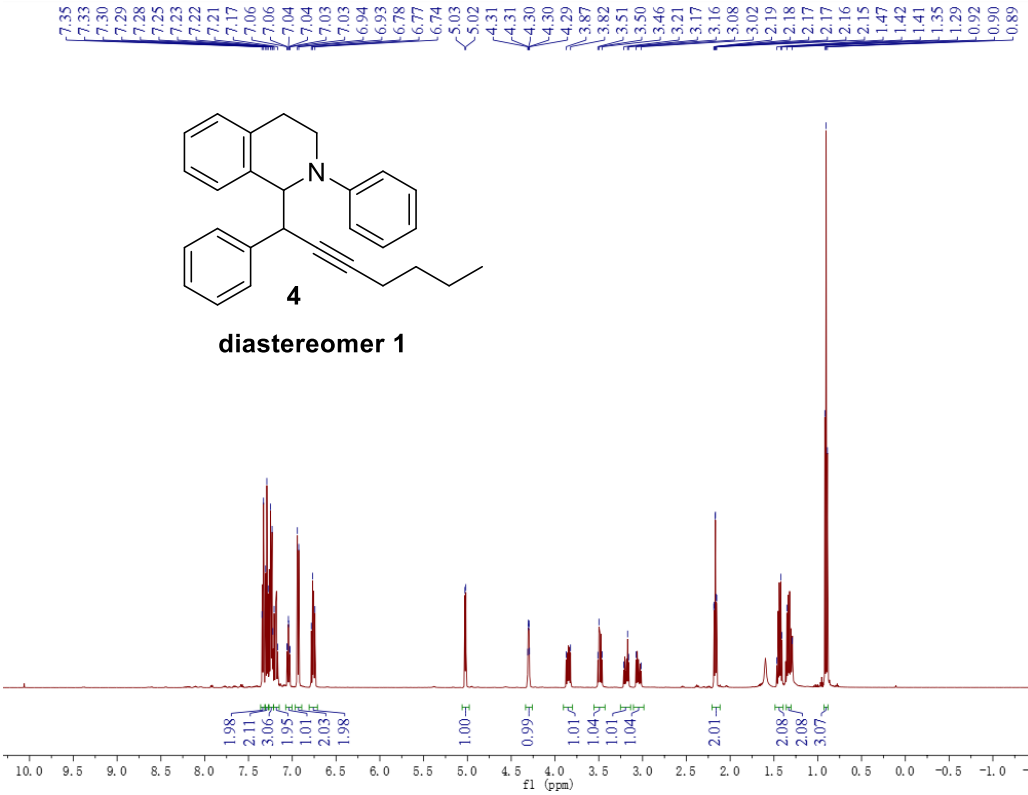

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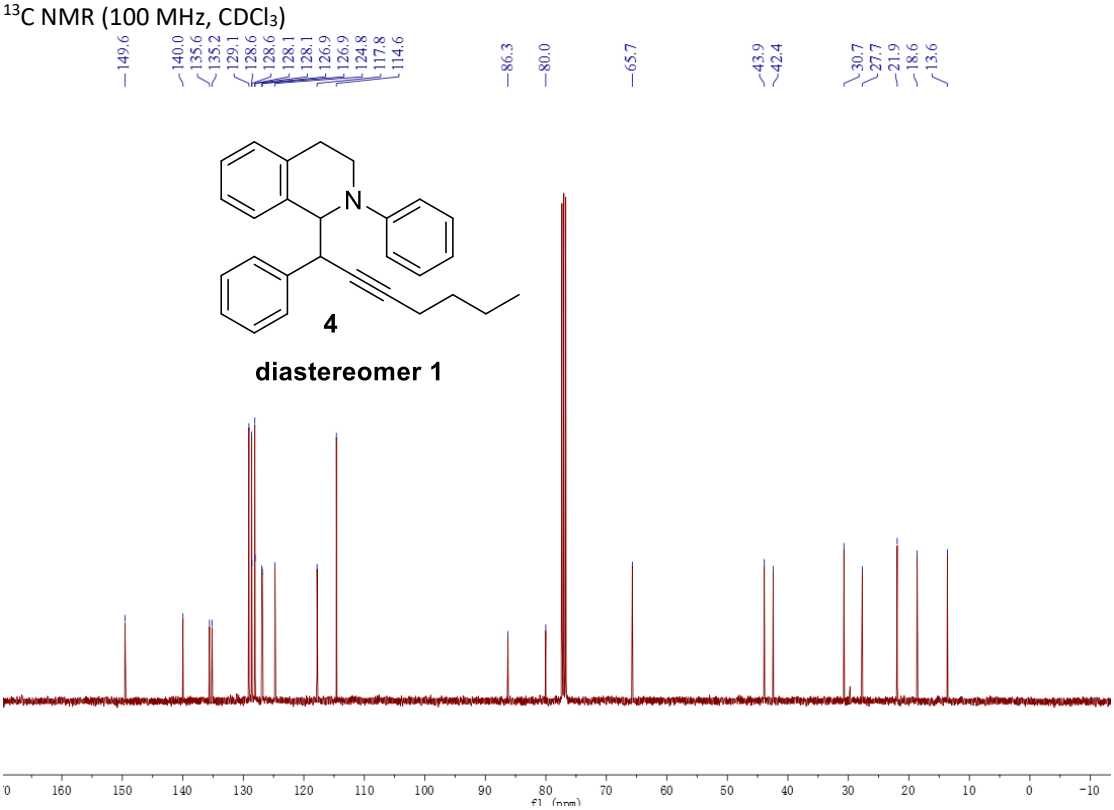

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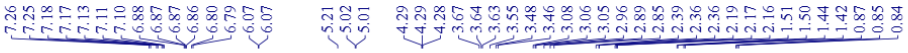
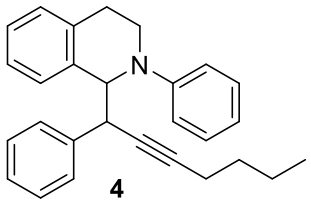
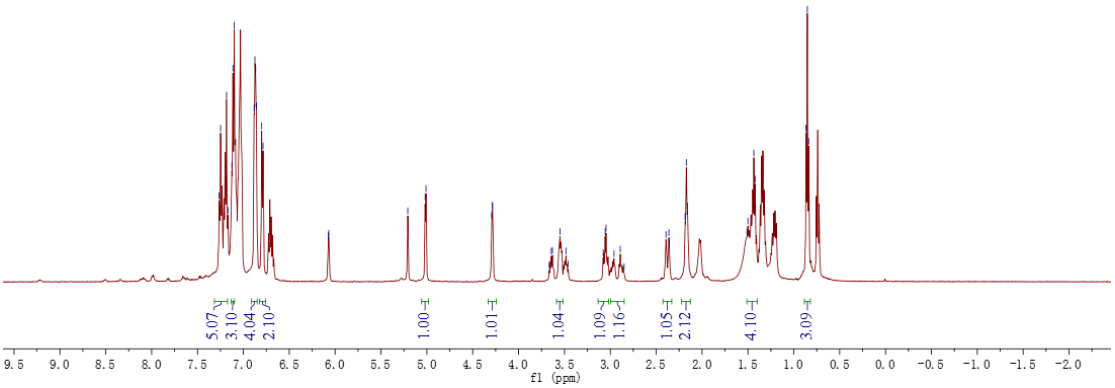


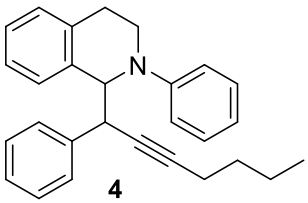


4

diastereomer 2
(mixed with **diastereomer 2** of **3**)

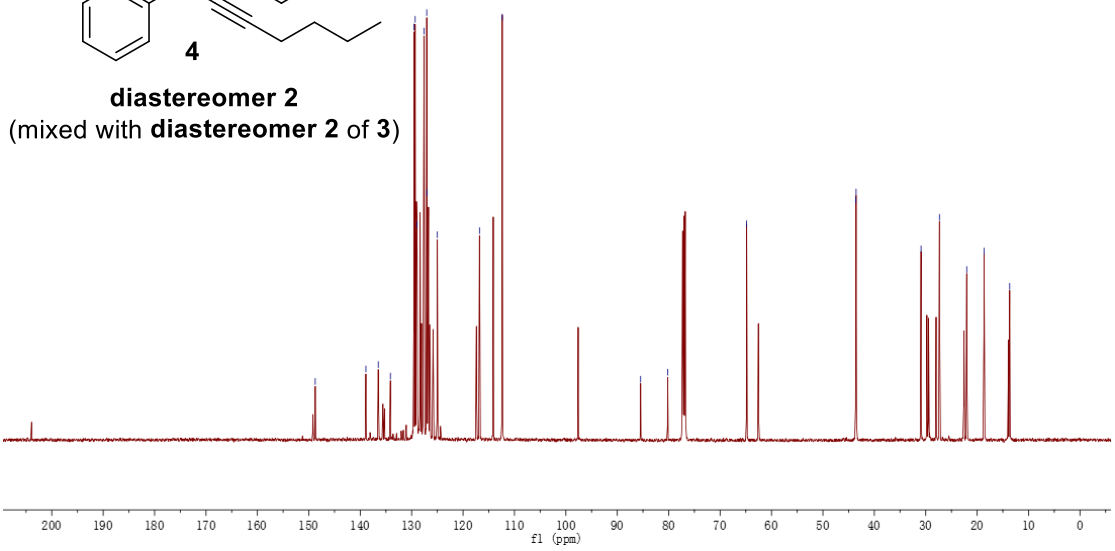


^{13}C NMR (126 MHz, $CDCl_3$)

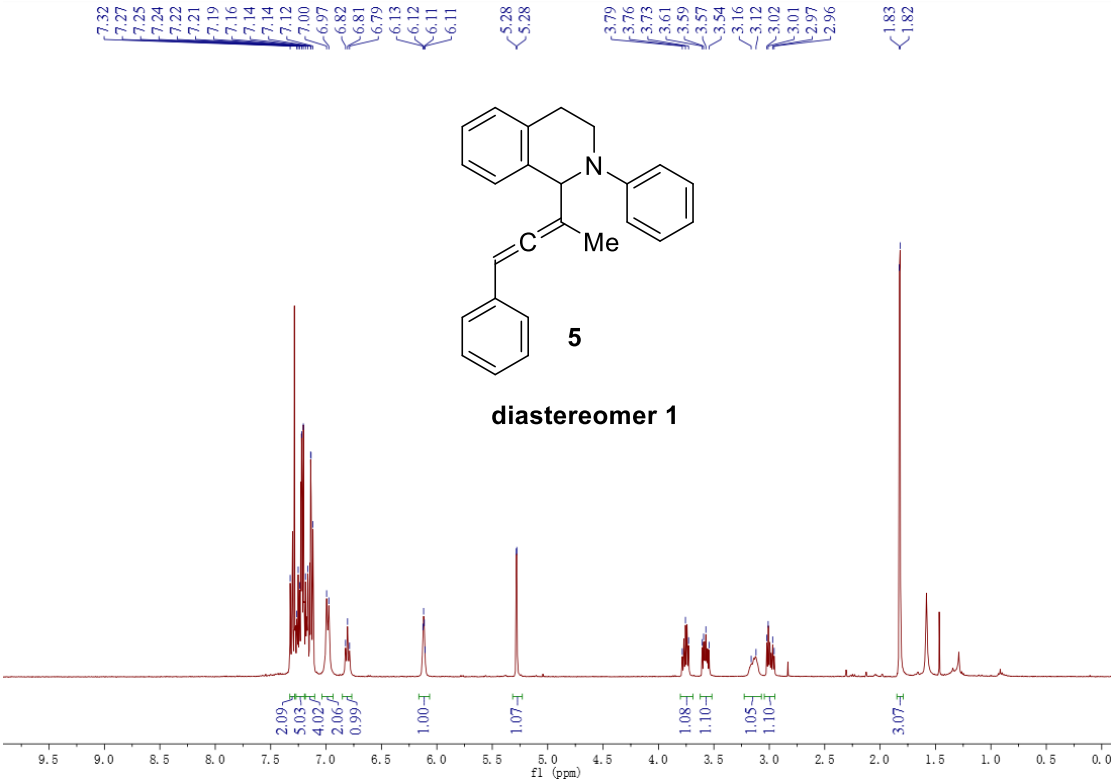


4

diastereomer 2
(mixed with **diastereomer 2** of **3**)



^{1}H NMR (400 MHz, $CDCl_3$)



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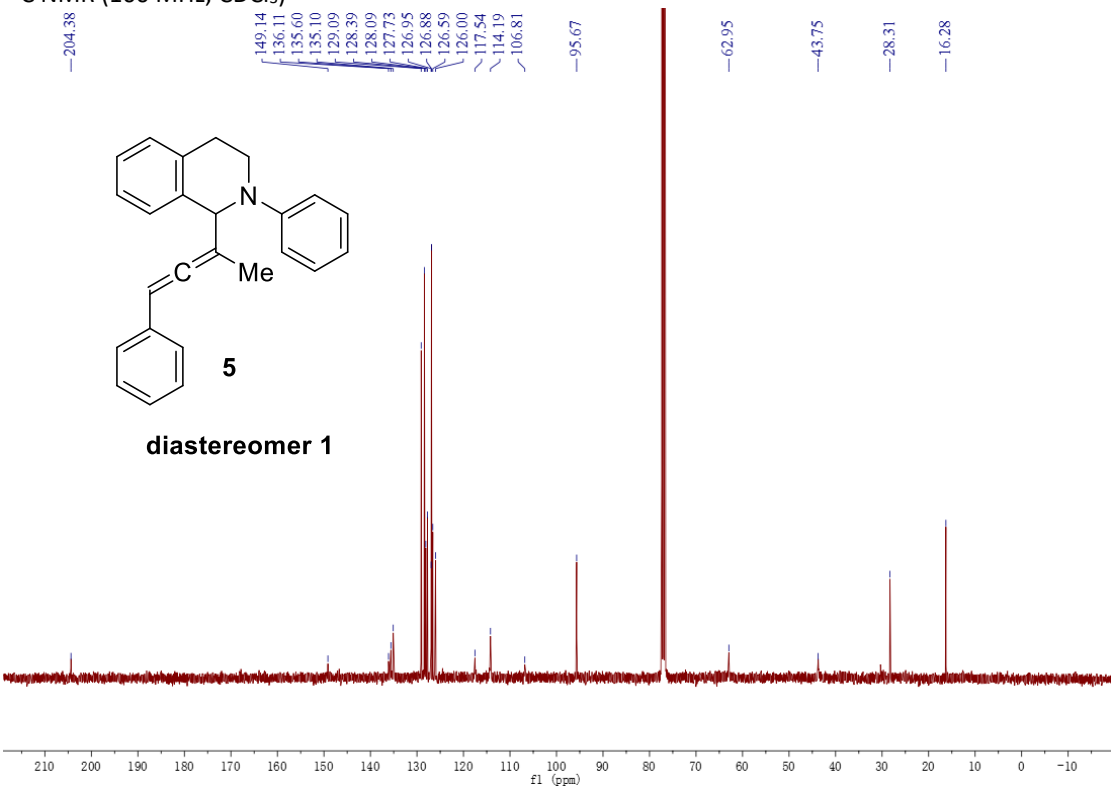

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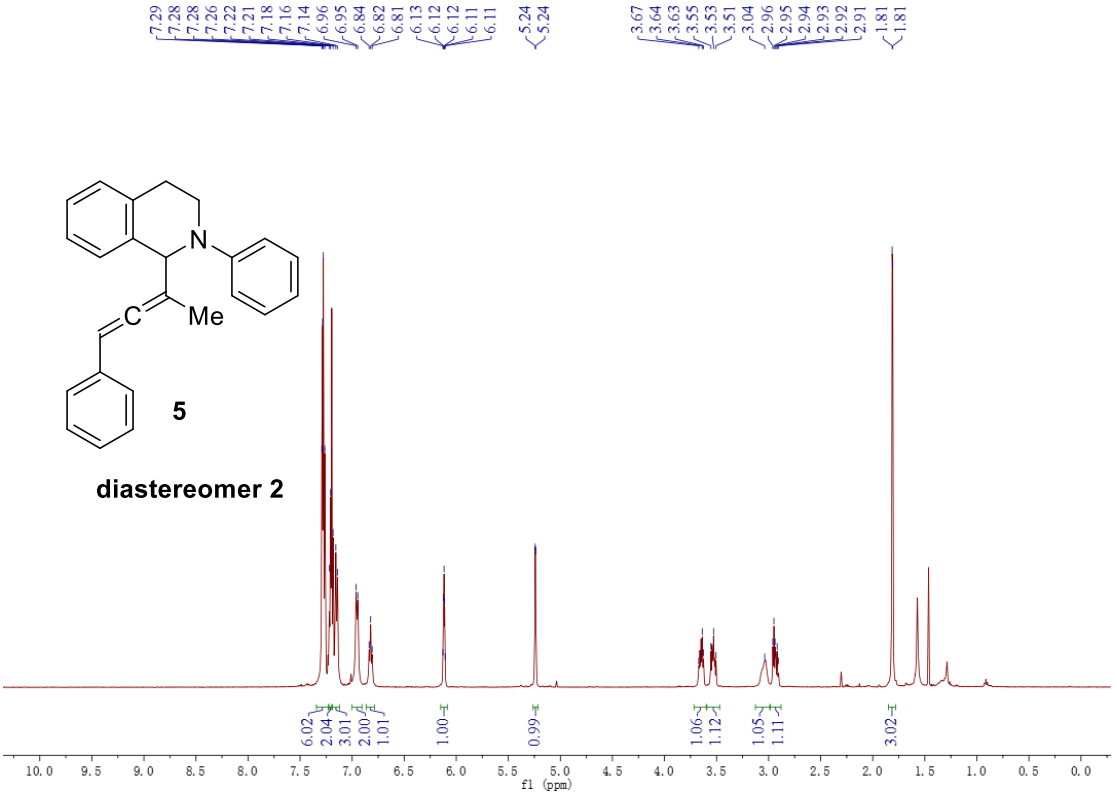

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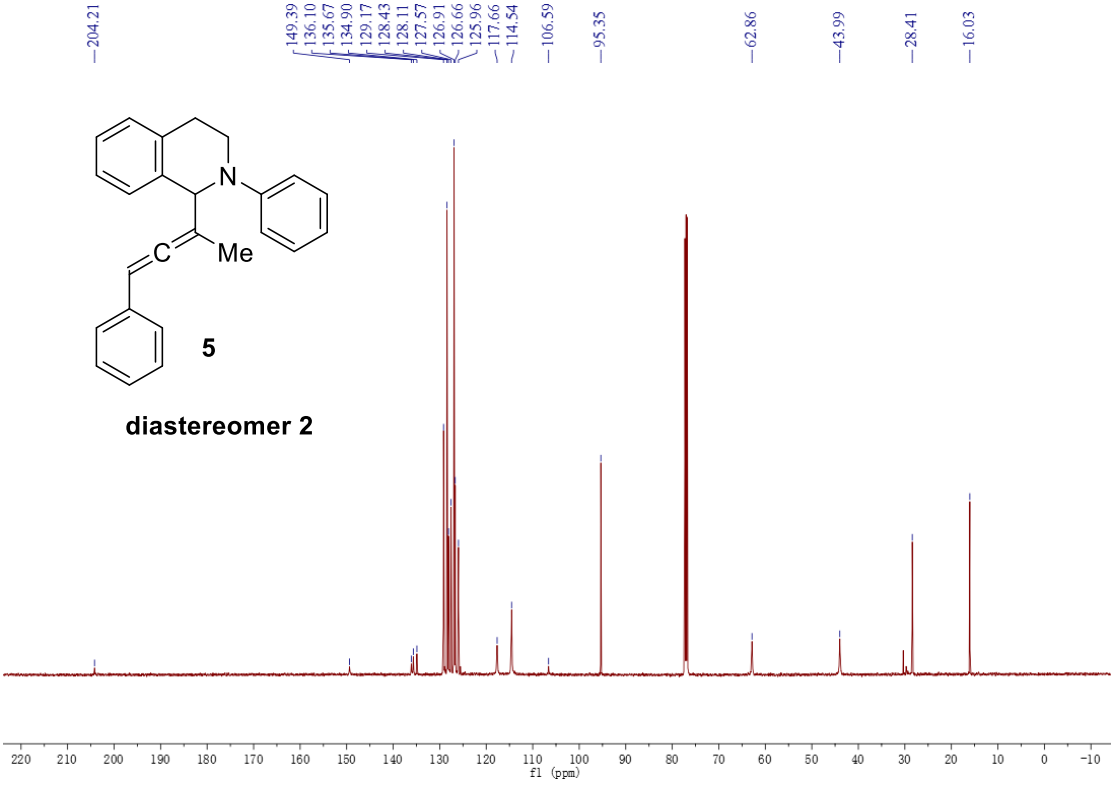

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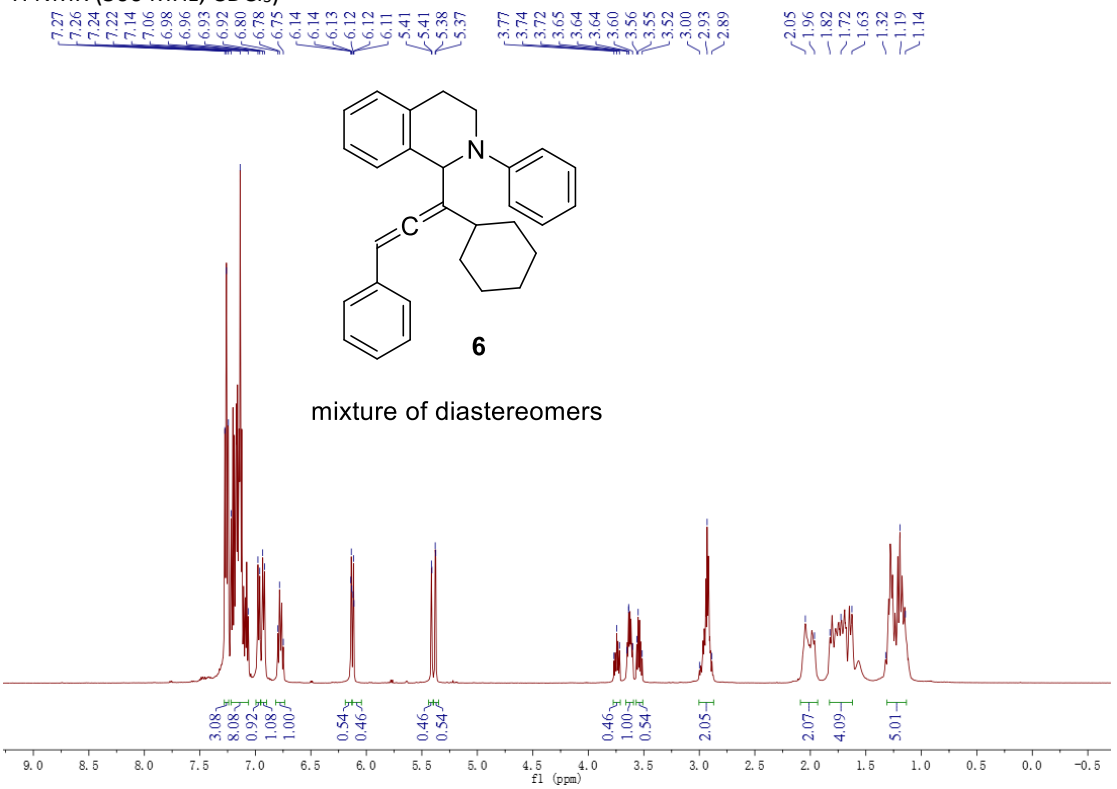

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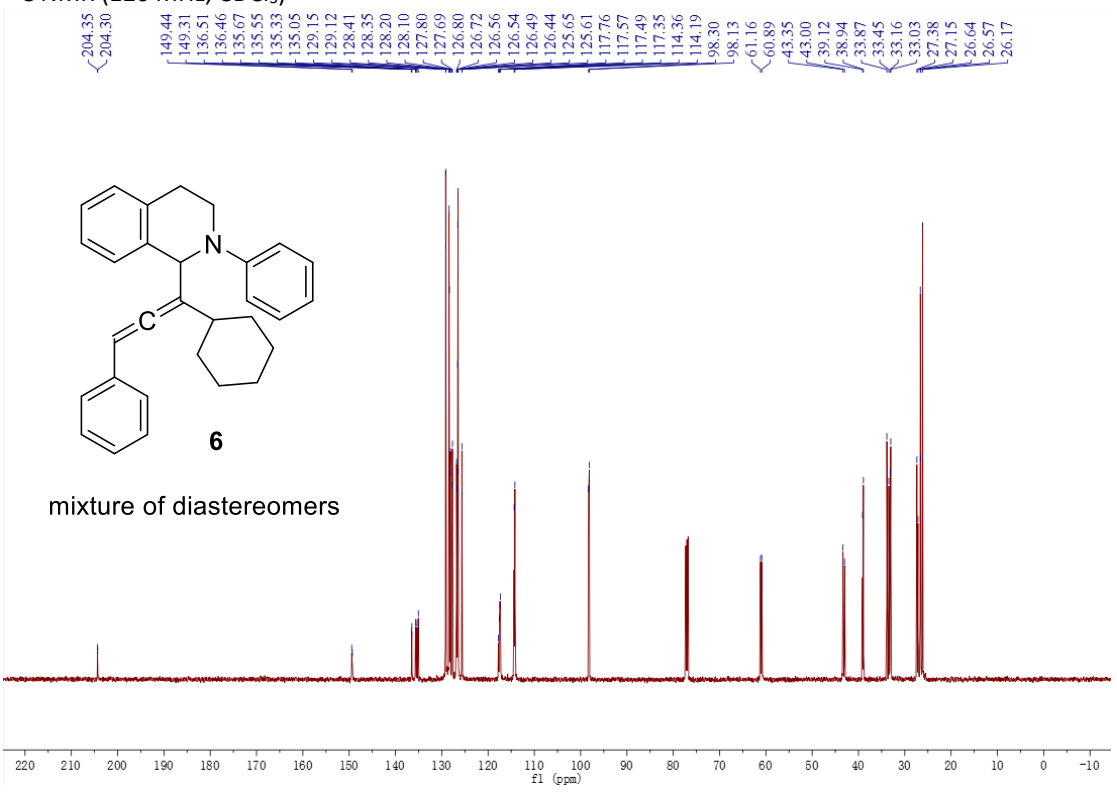

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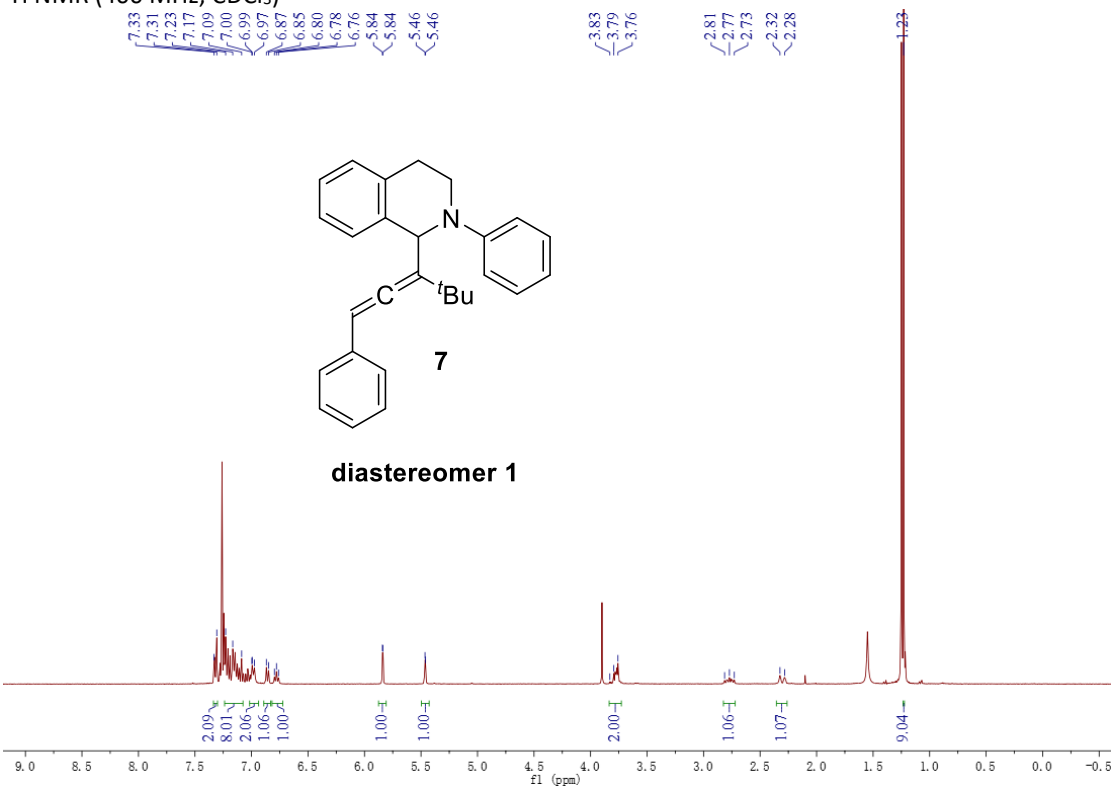

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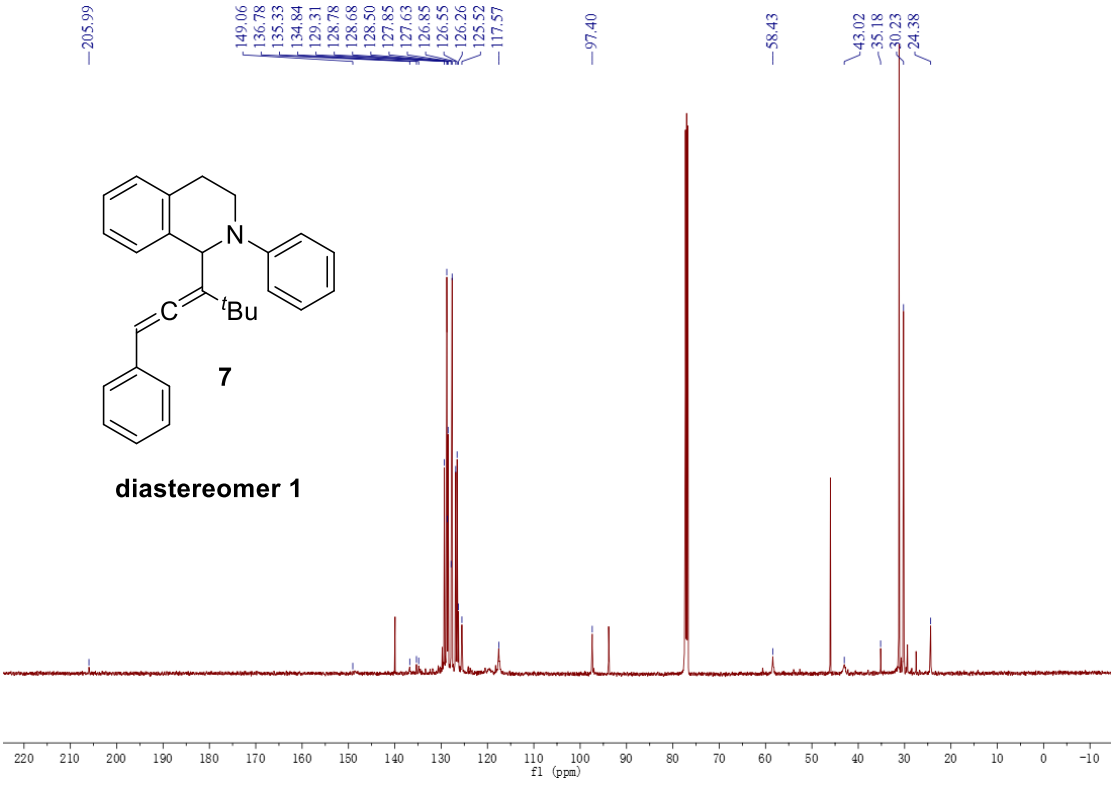

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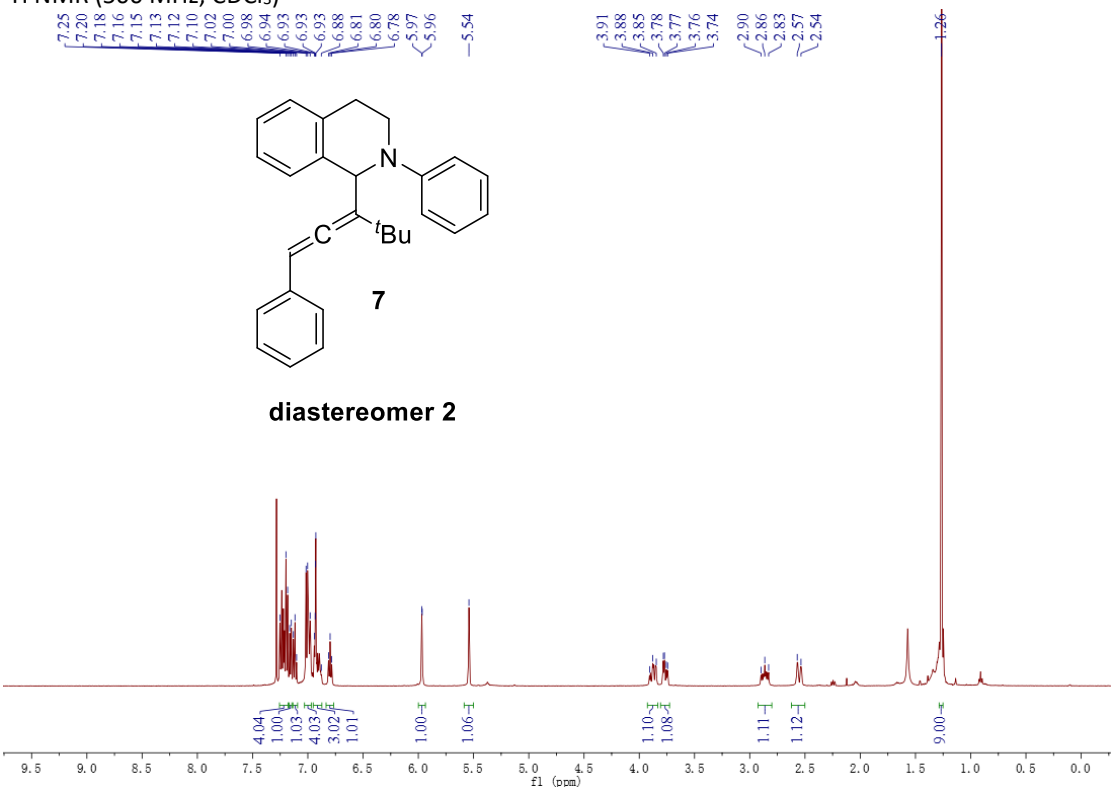

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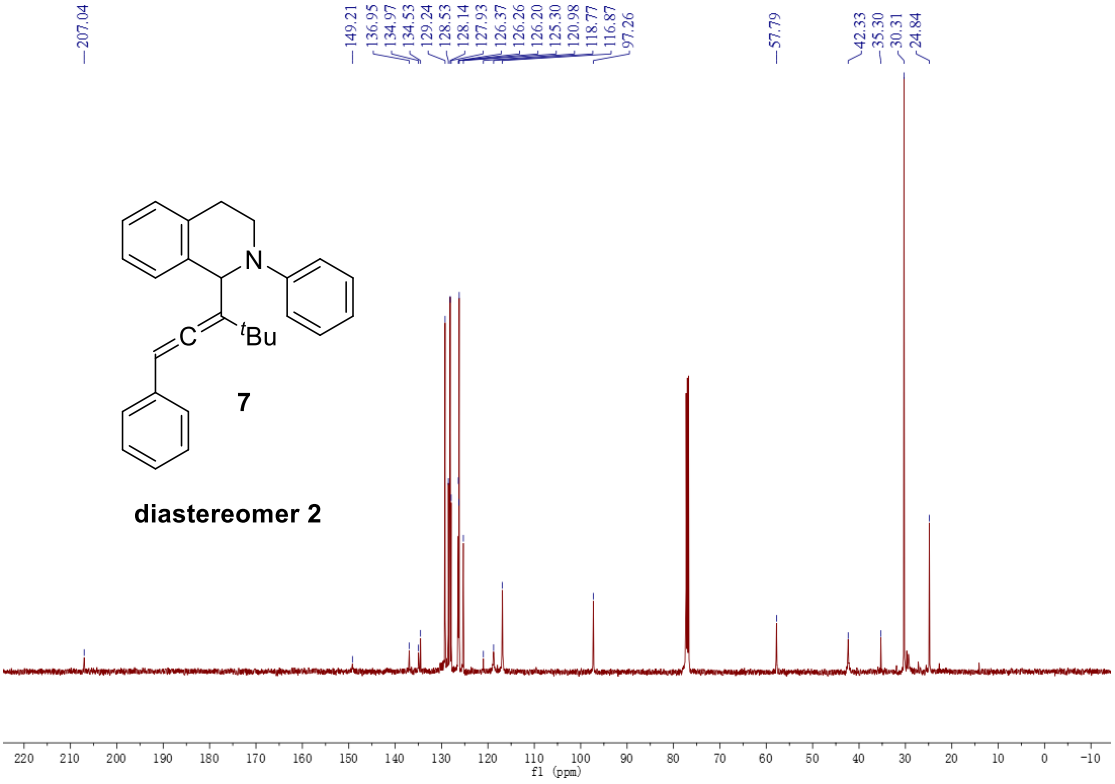

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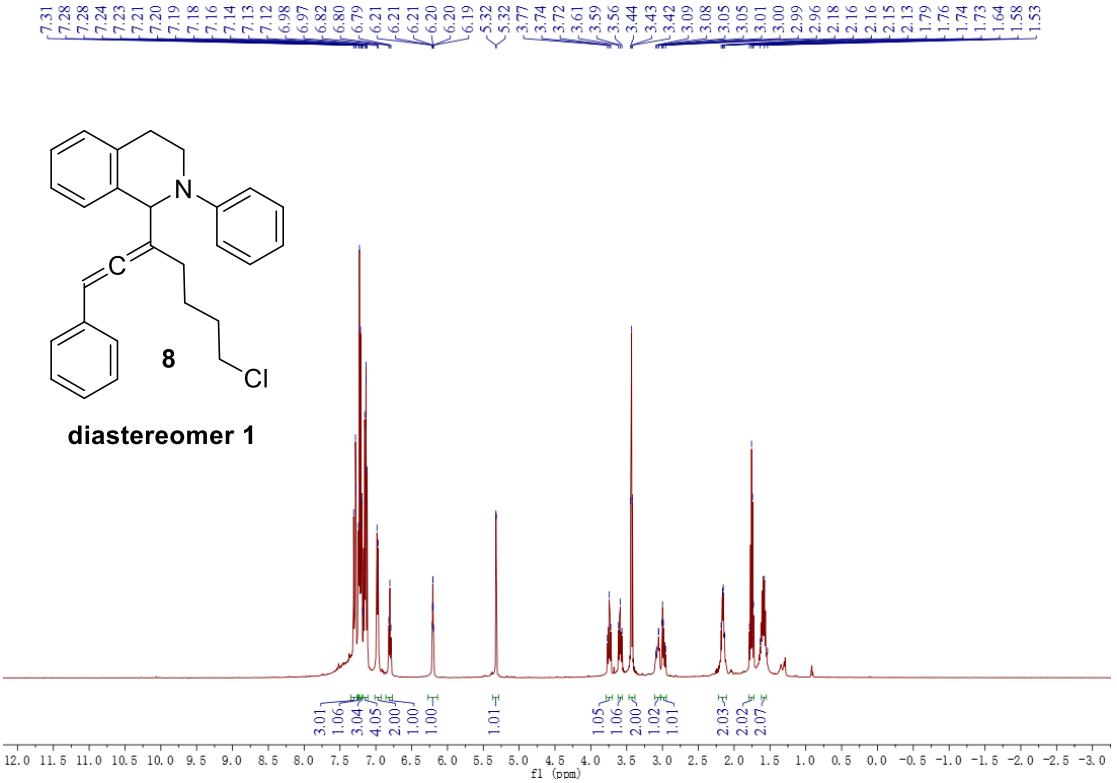

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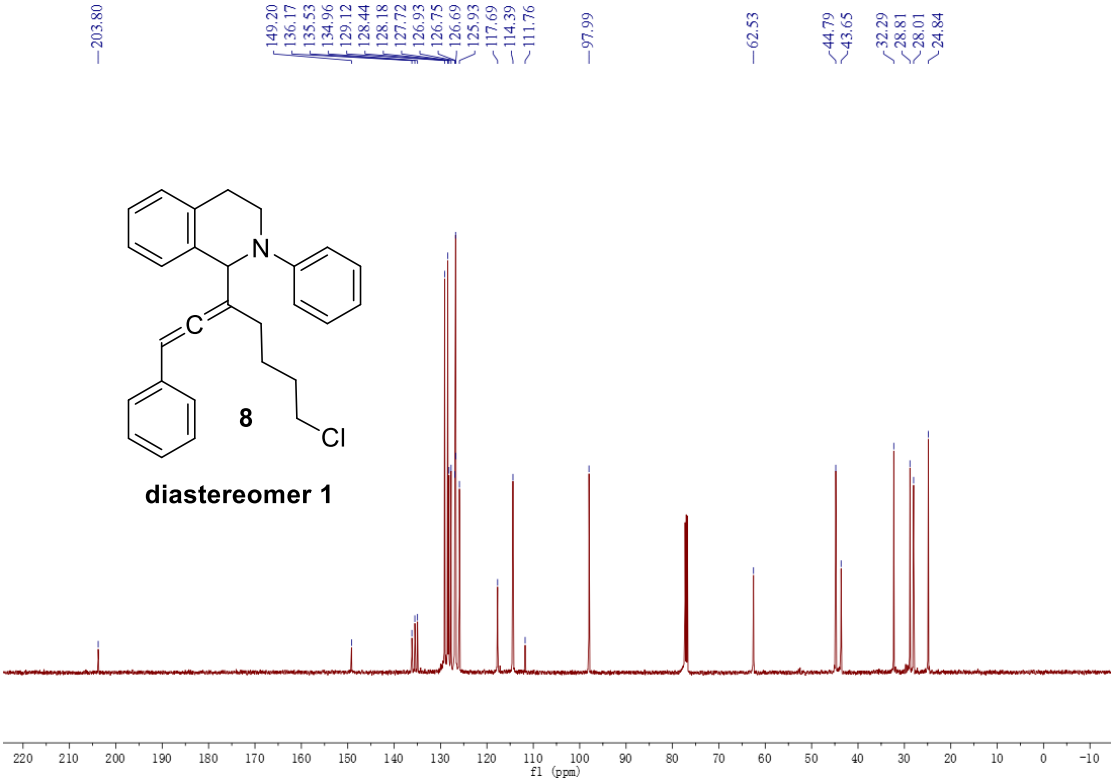

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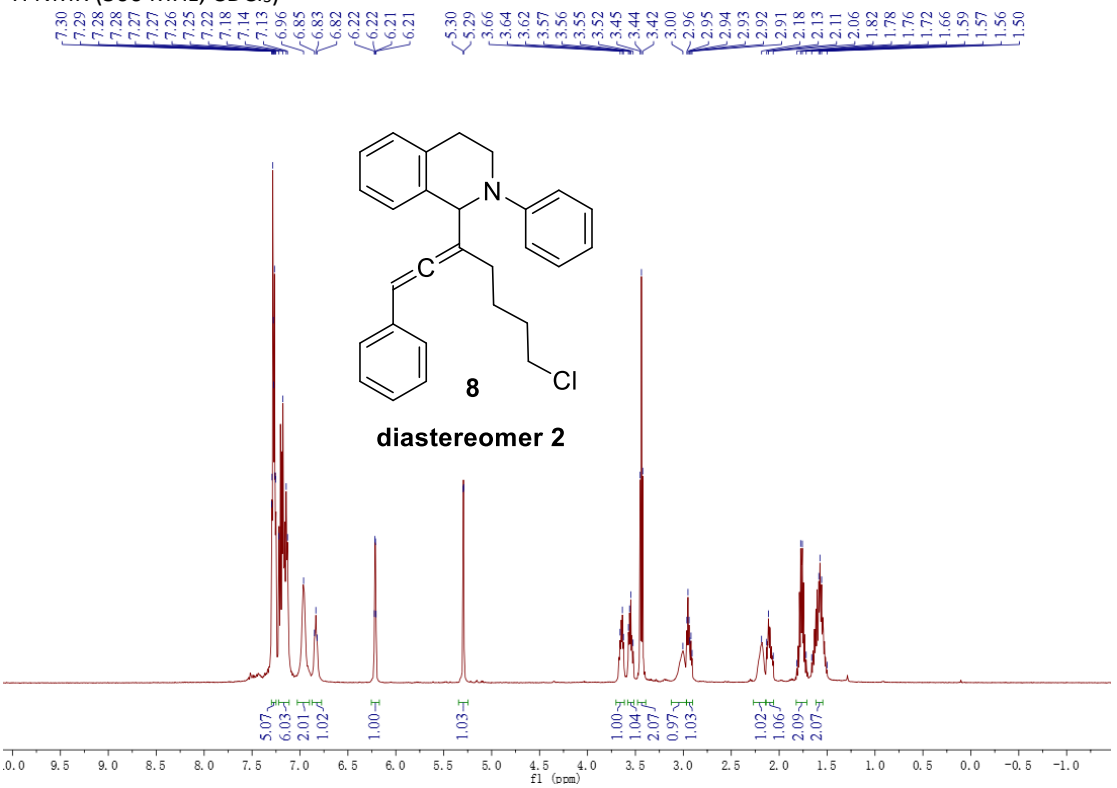

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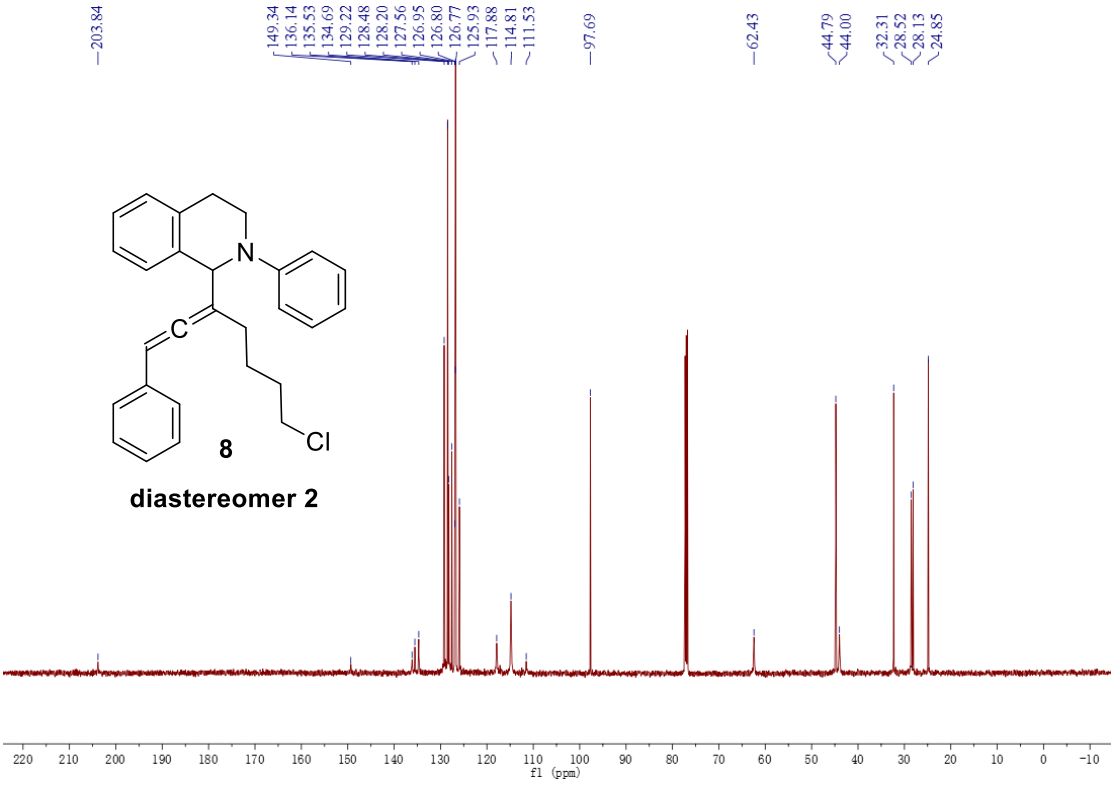

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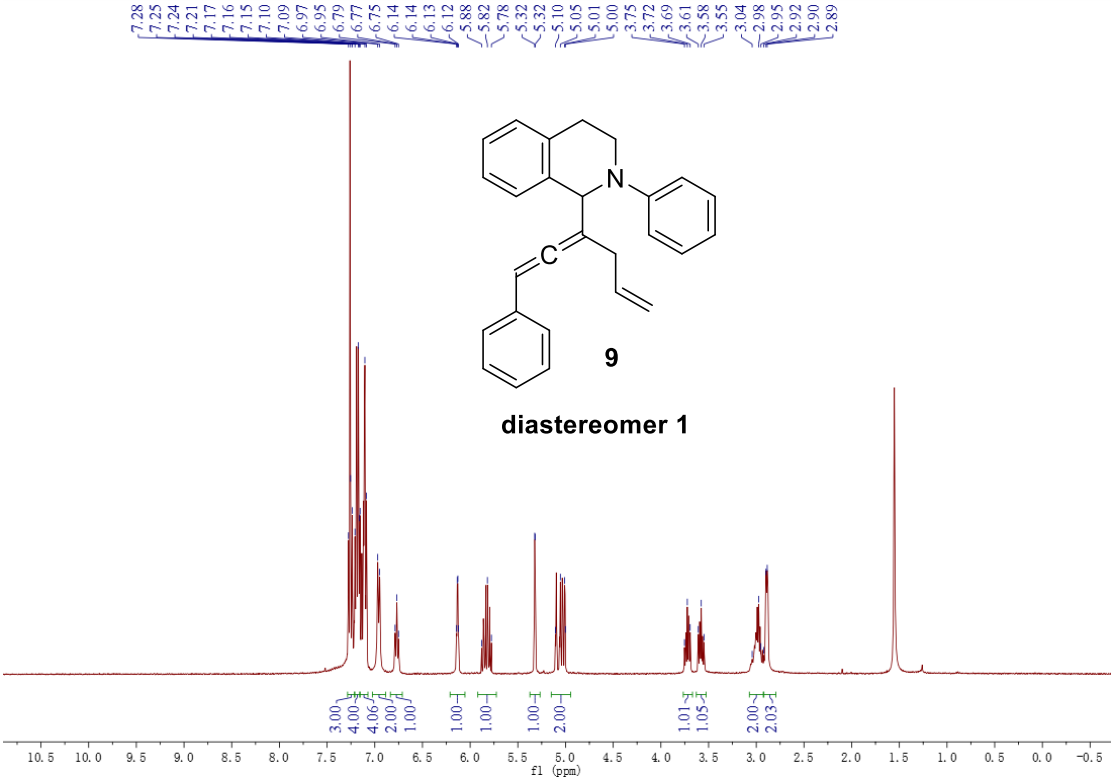

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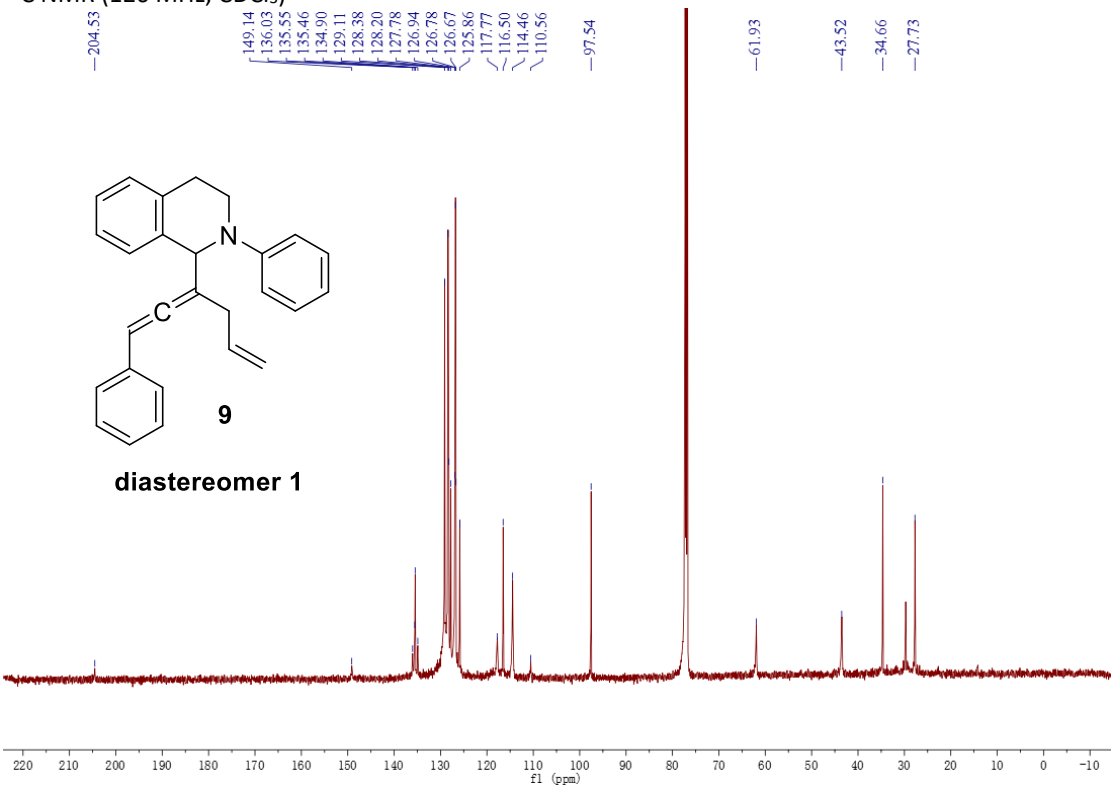

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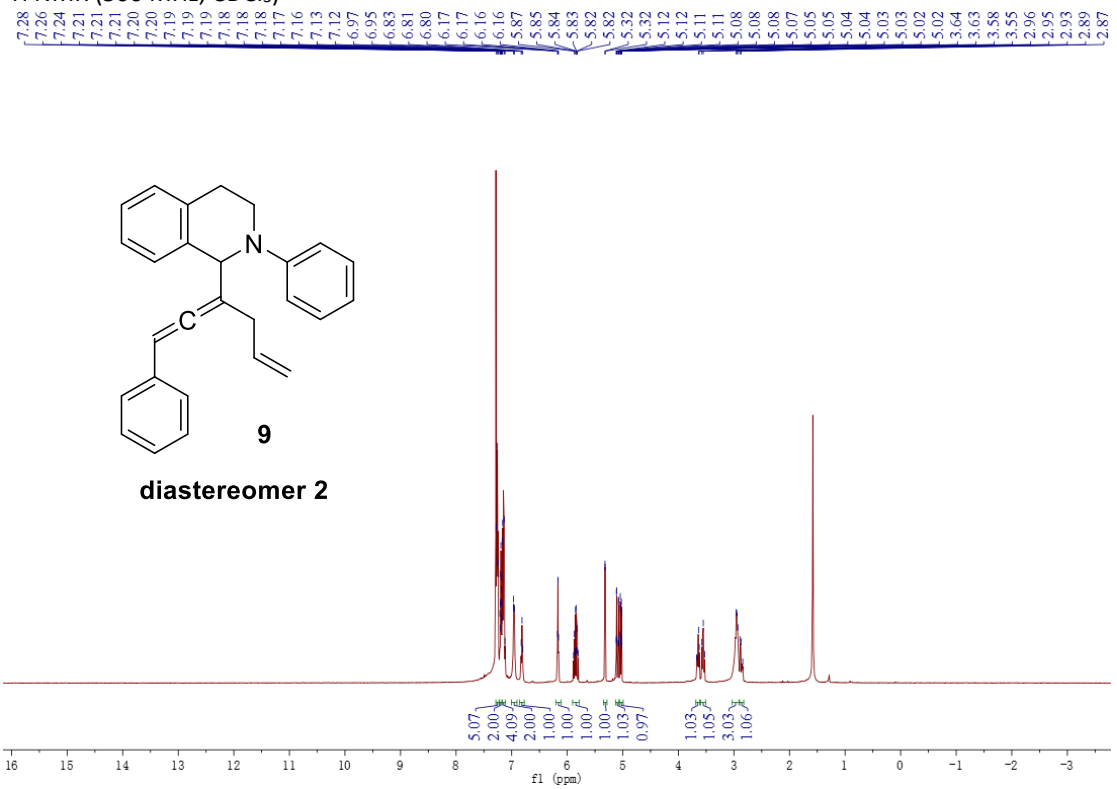

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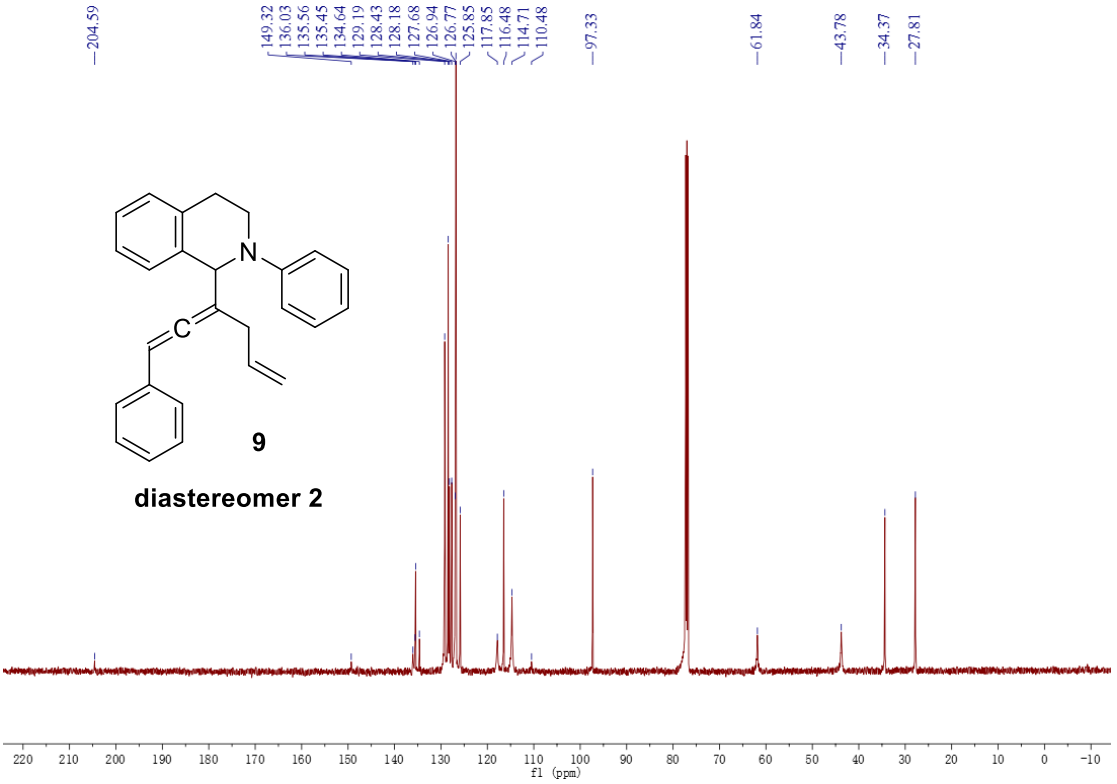

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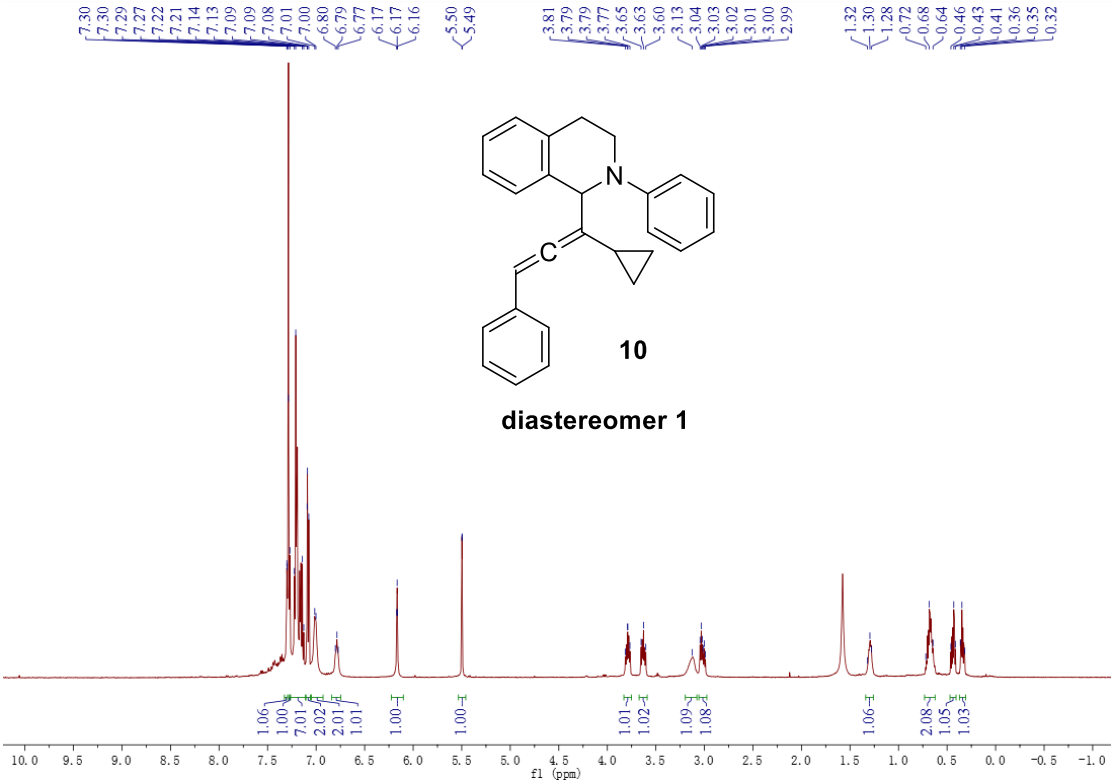
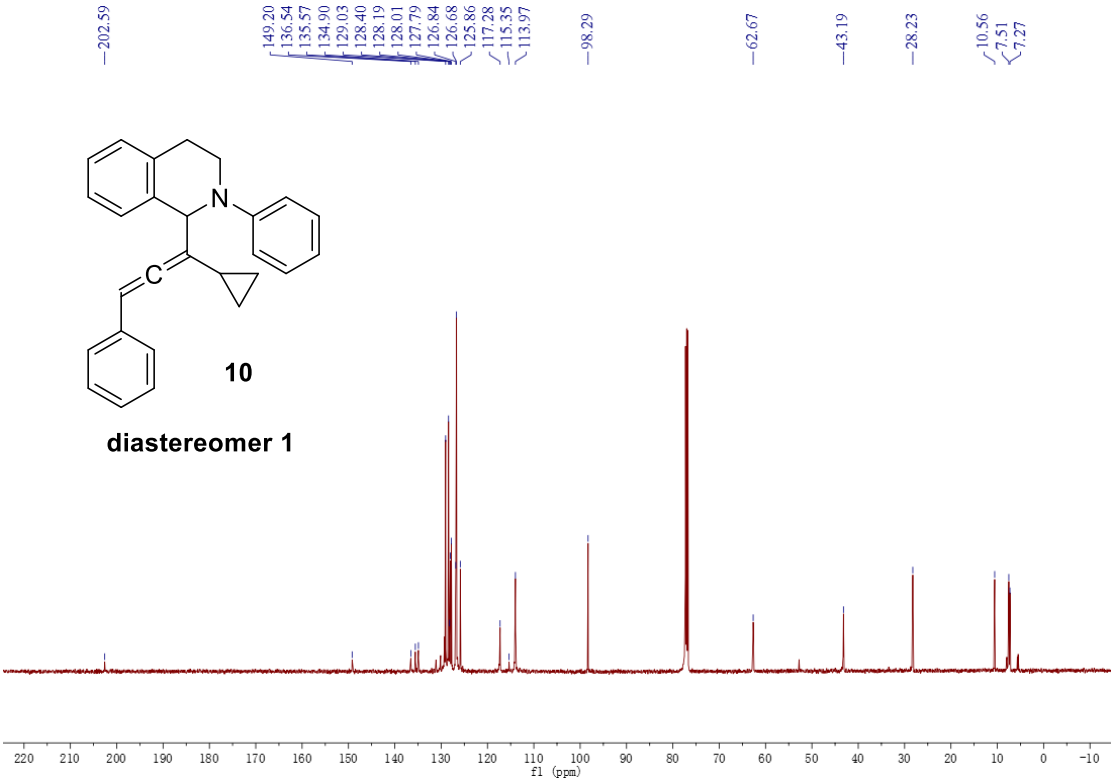
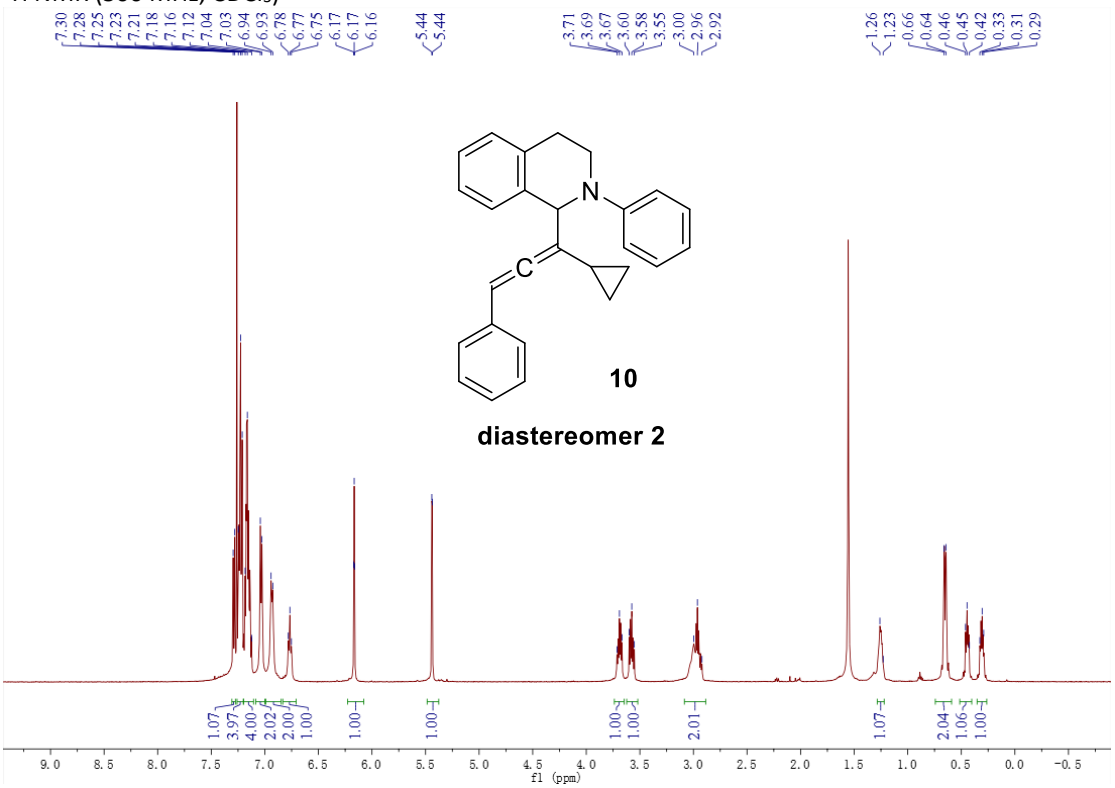


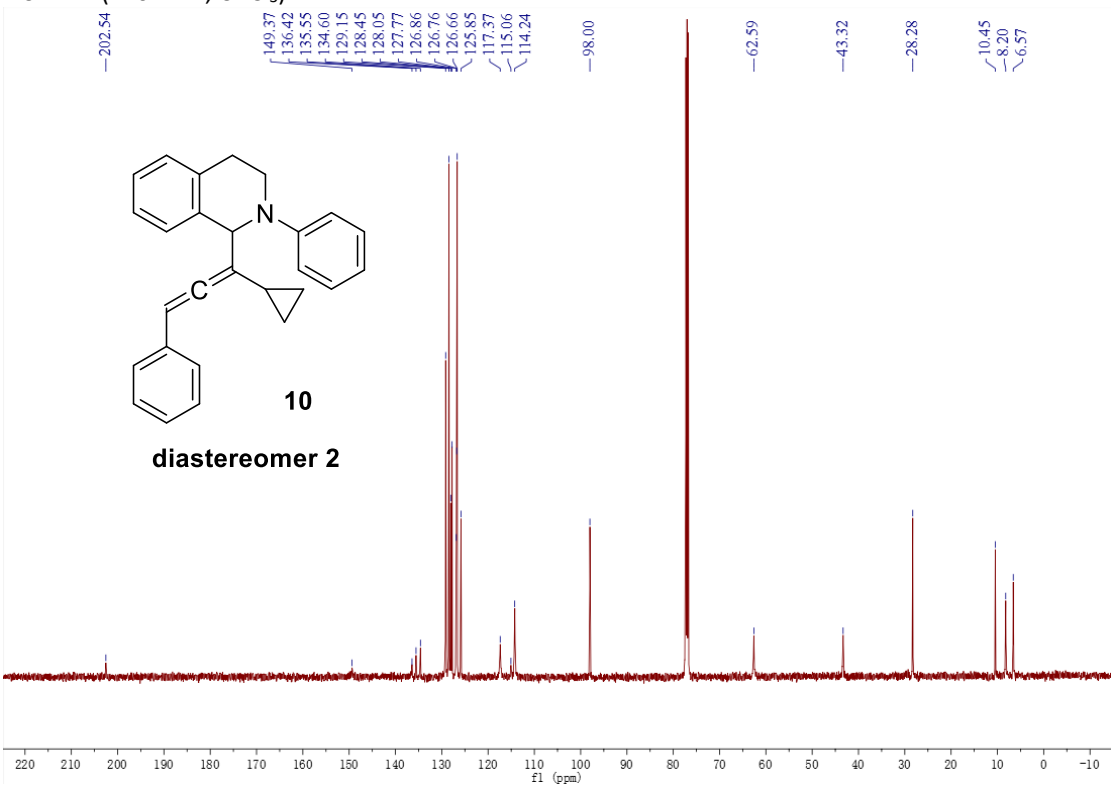
^{13}C NMR (126 MHz, $CDCl_3$)



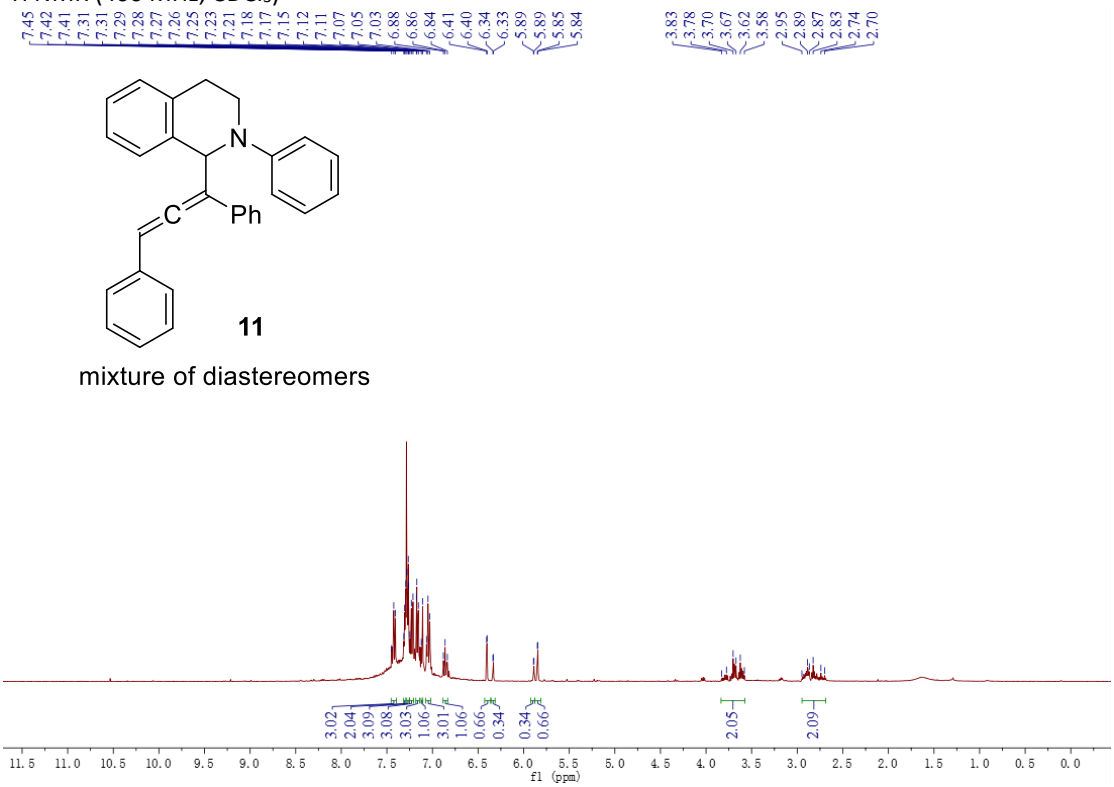
^{1}H NMR (500 MHz, $CDCl_3$)



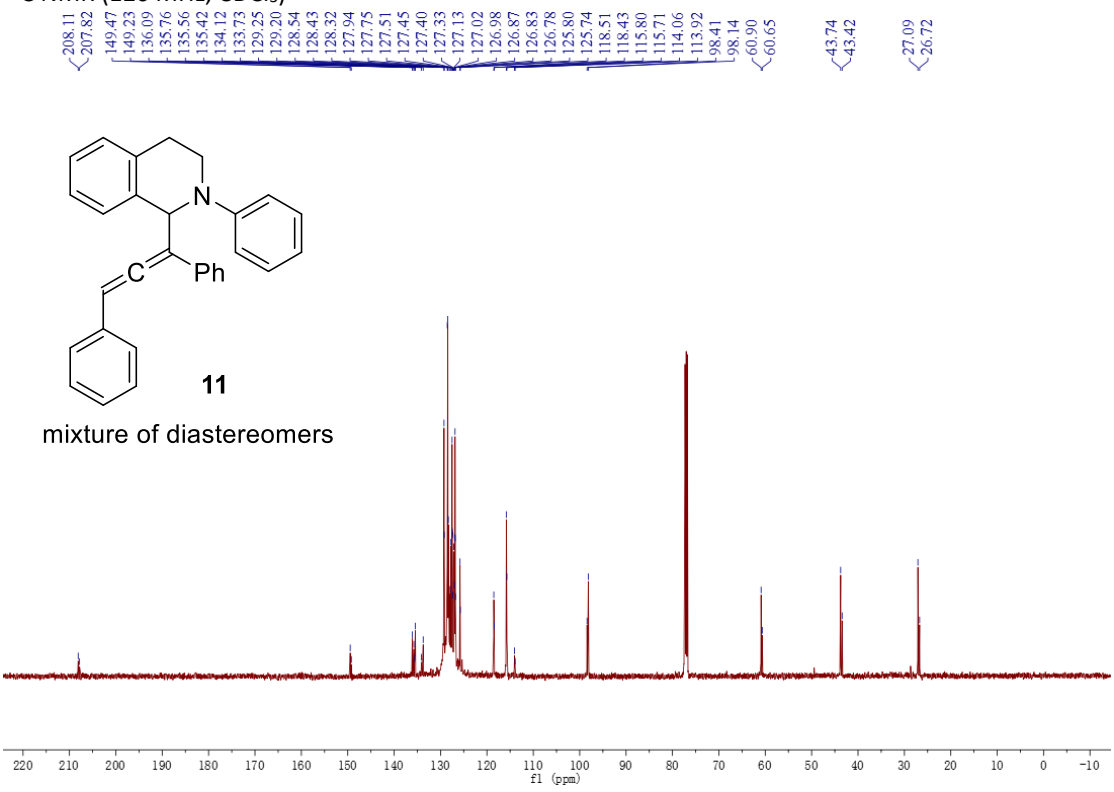
^{13}C NMR (126 MHz, $CDCl_3$)



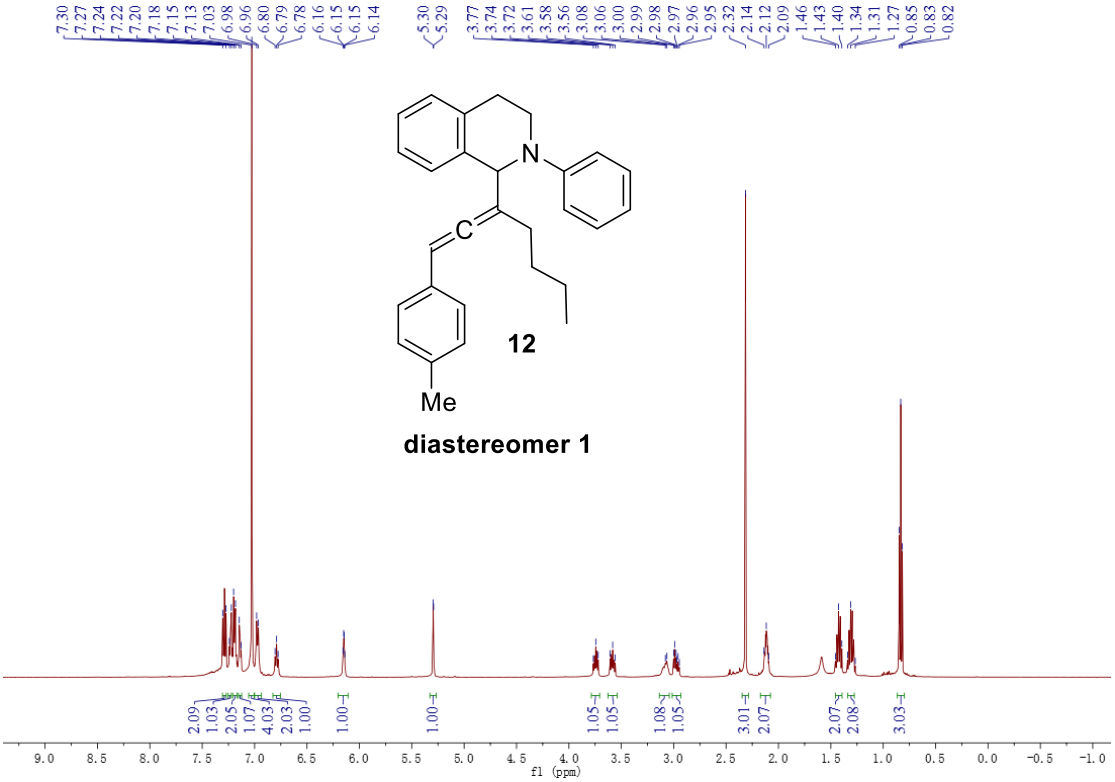
^{1}H NMR (400 MHz, $CDCl_3$)



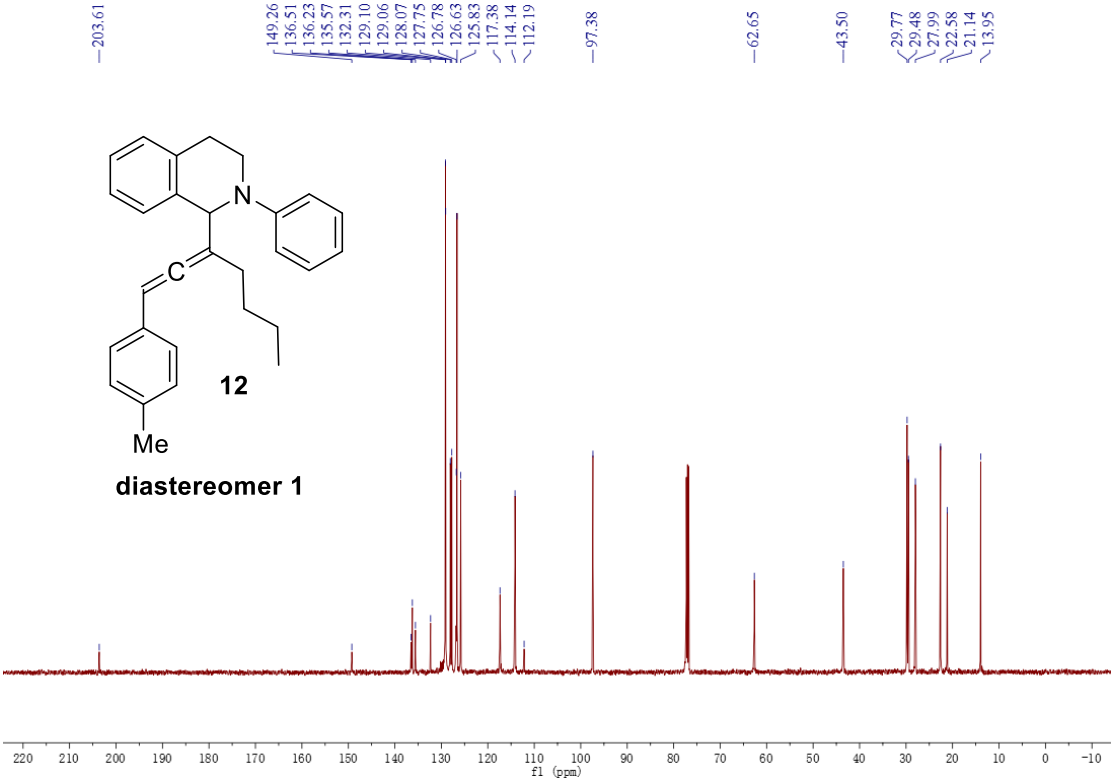
^{13}C NMR (126 MHz, $CDCl_3$)



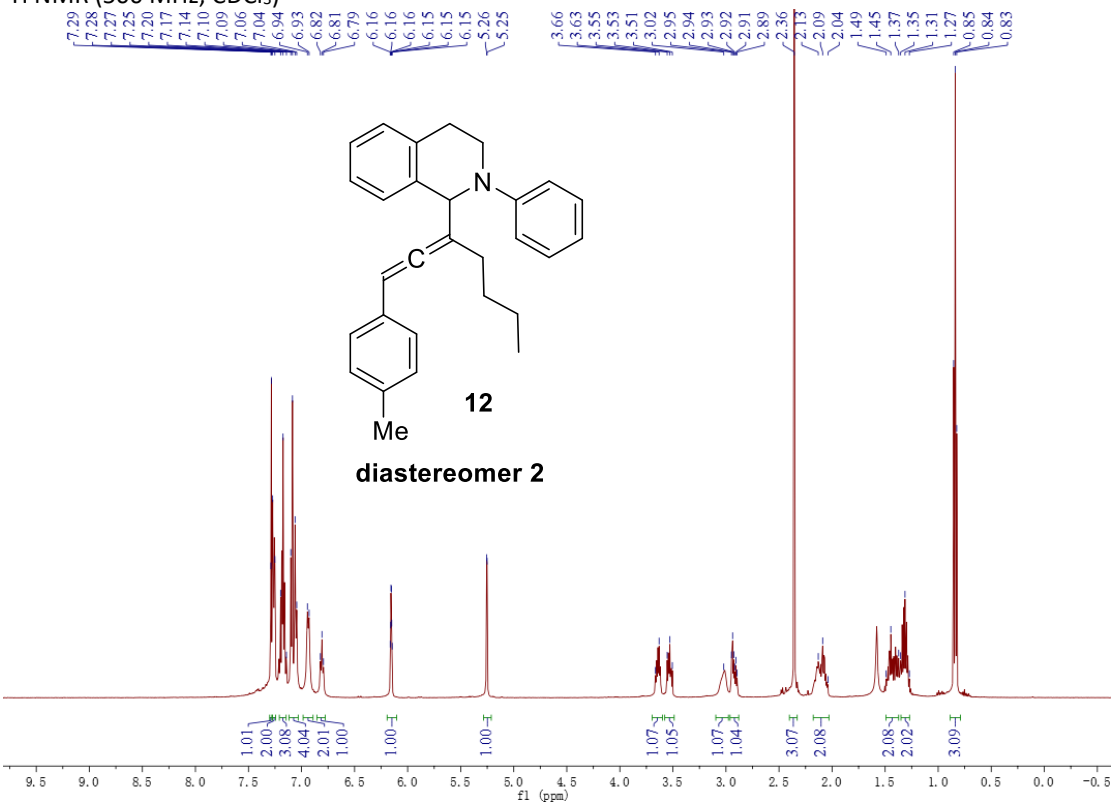
^{1}H NMR (500 MHz, $CDCl_3$)



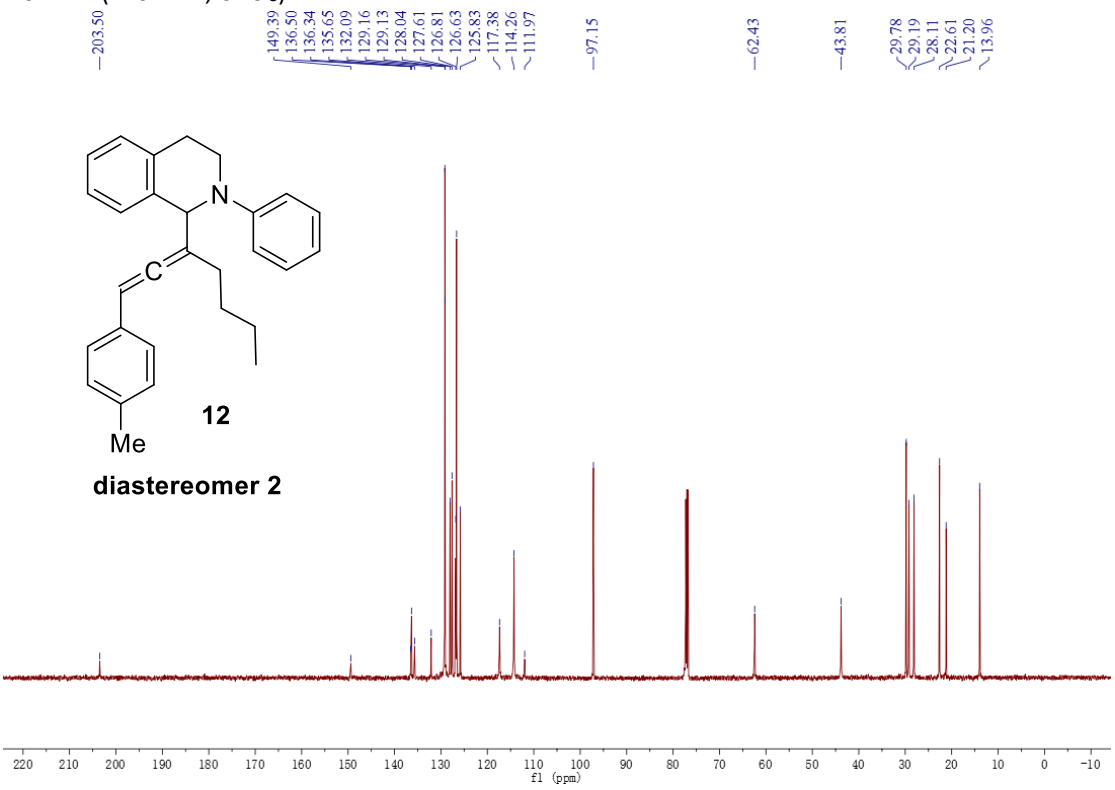
^{13}C NMR (126 MHz, $CDCl_3$)



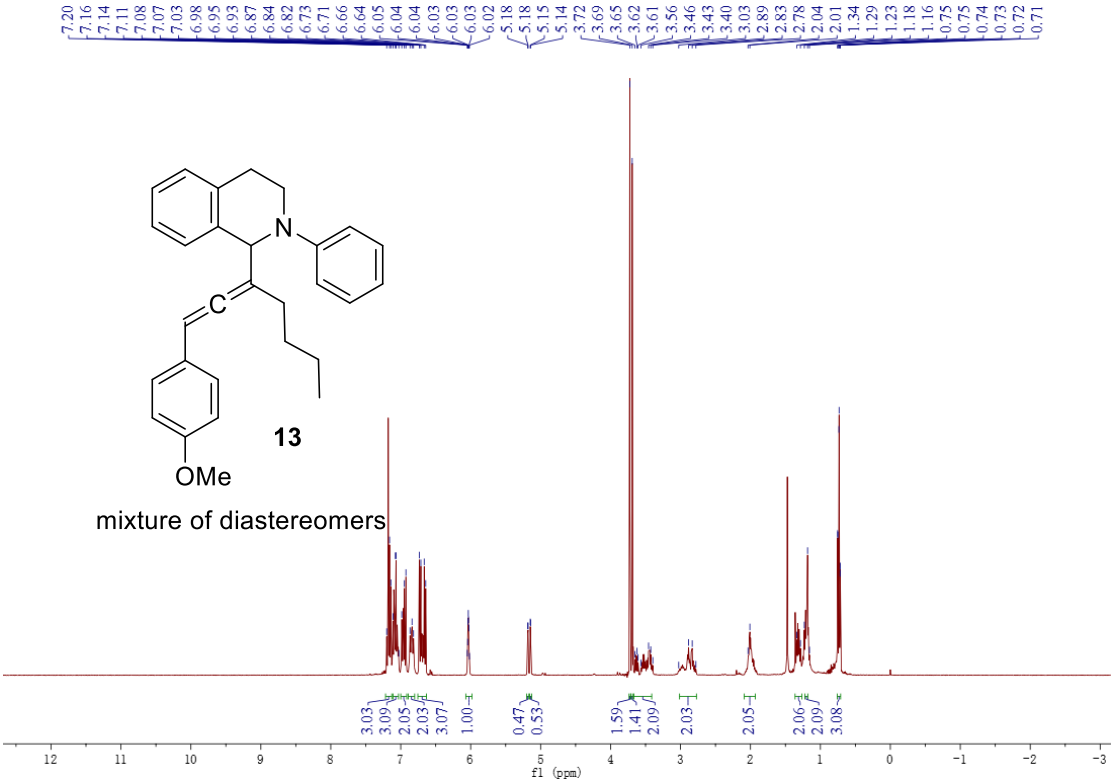
^{1}H NMR (500 MHz, $CDCl_3$)



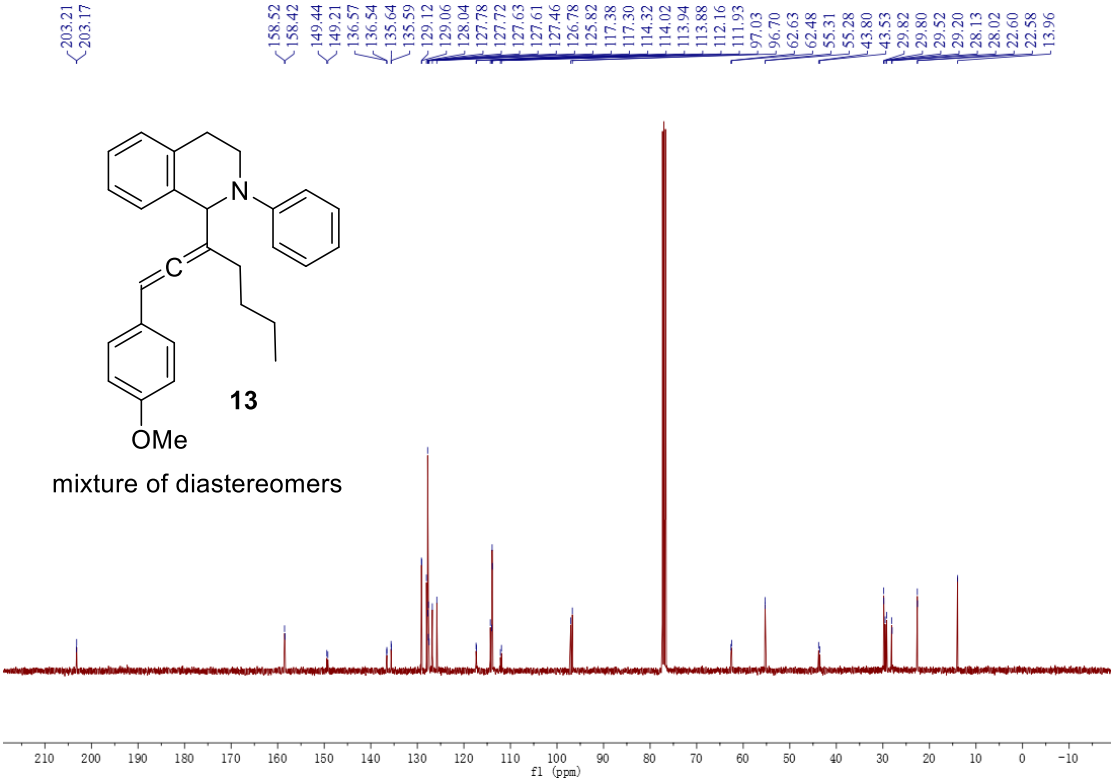
^{13}C NMR (126 MHz, $CDCl_3$)



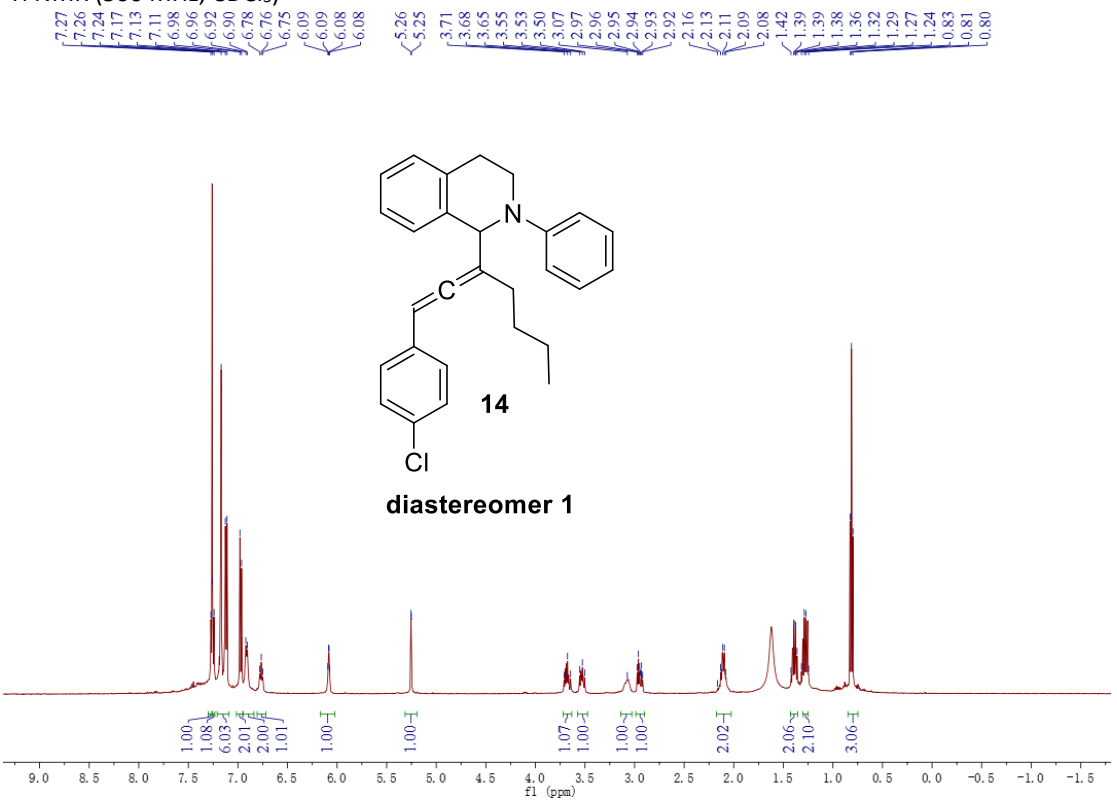
^{1}H NMR (400 MHz, $CDCl_3$)



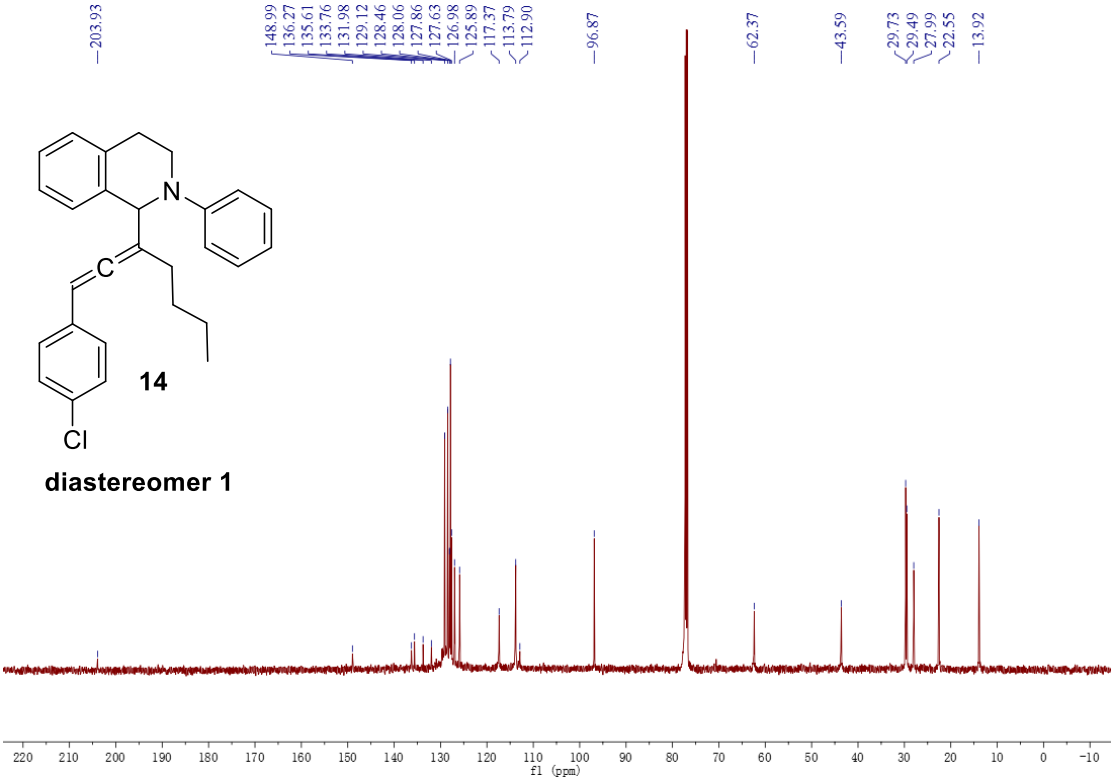
^{13}C NMR (100 MHz, $CDCl_3$)



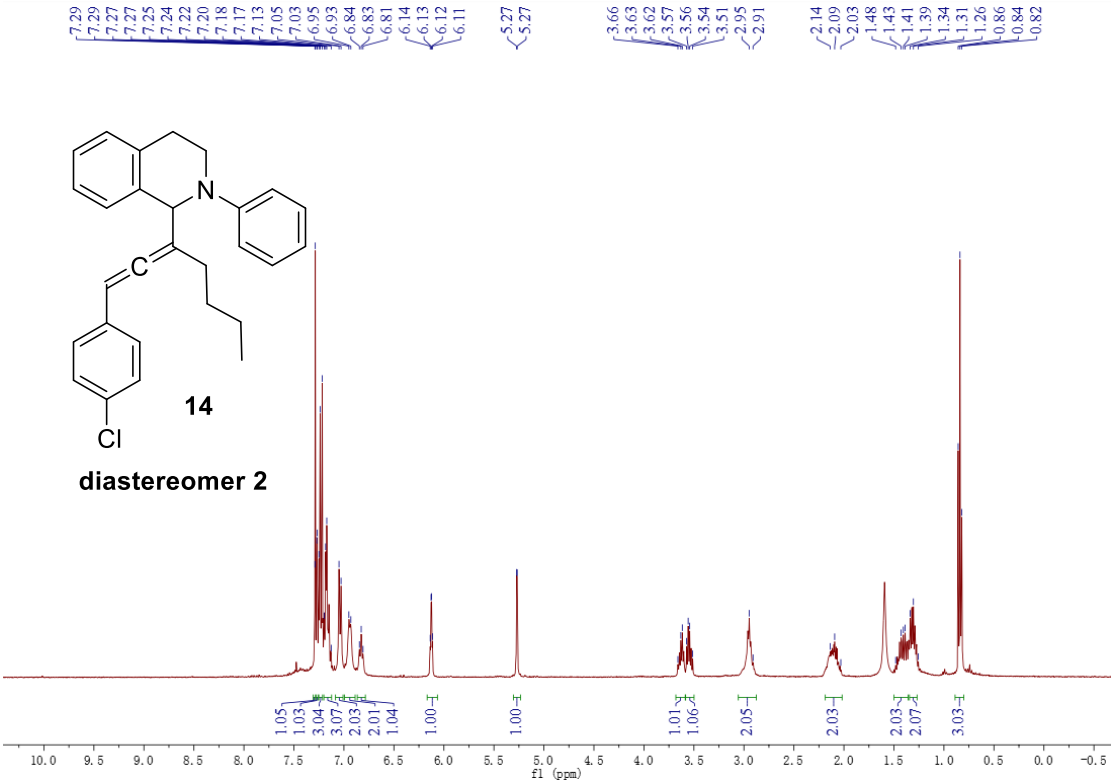
^{1}H NMR (500 MHz, $CDCl_3$)



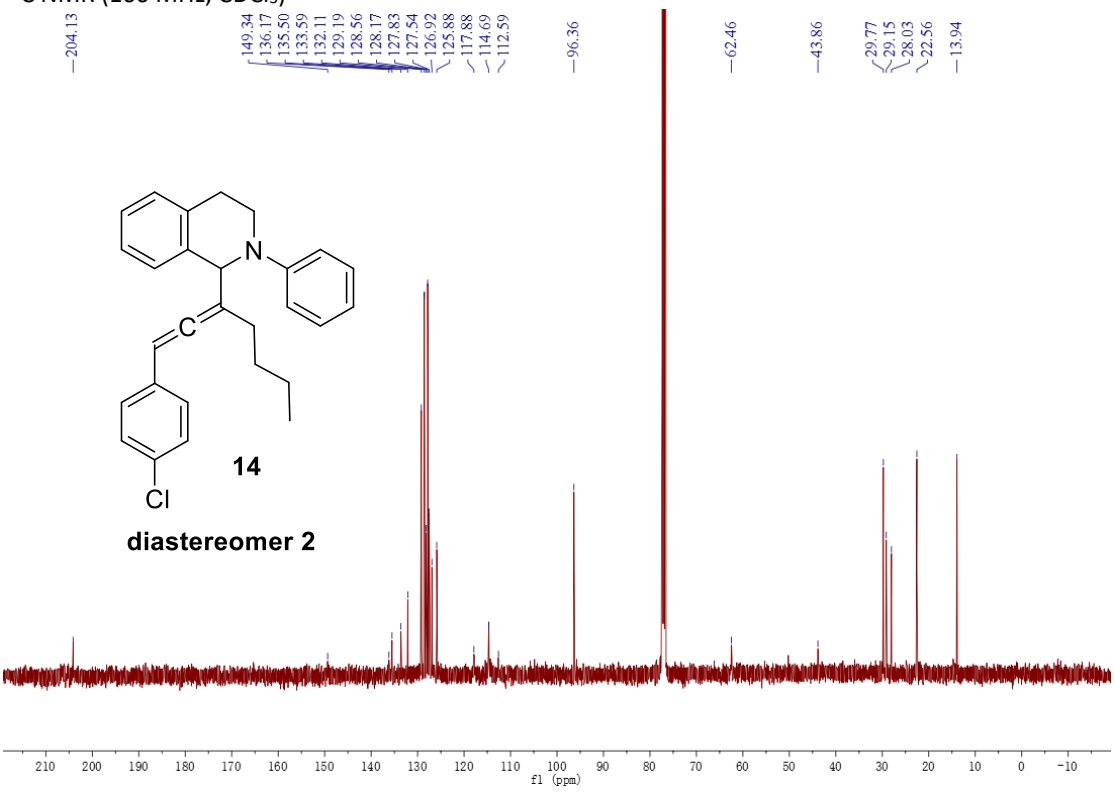
^{13}C NMR (126 MHz, $CDCl_3$)



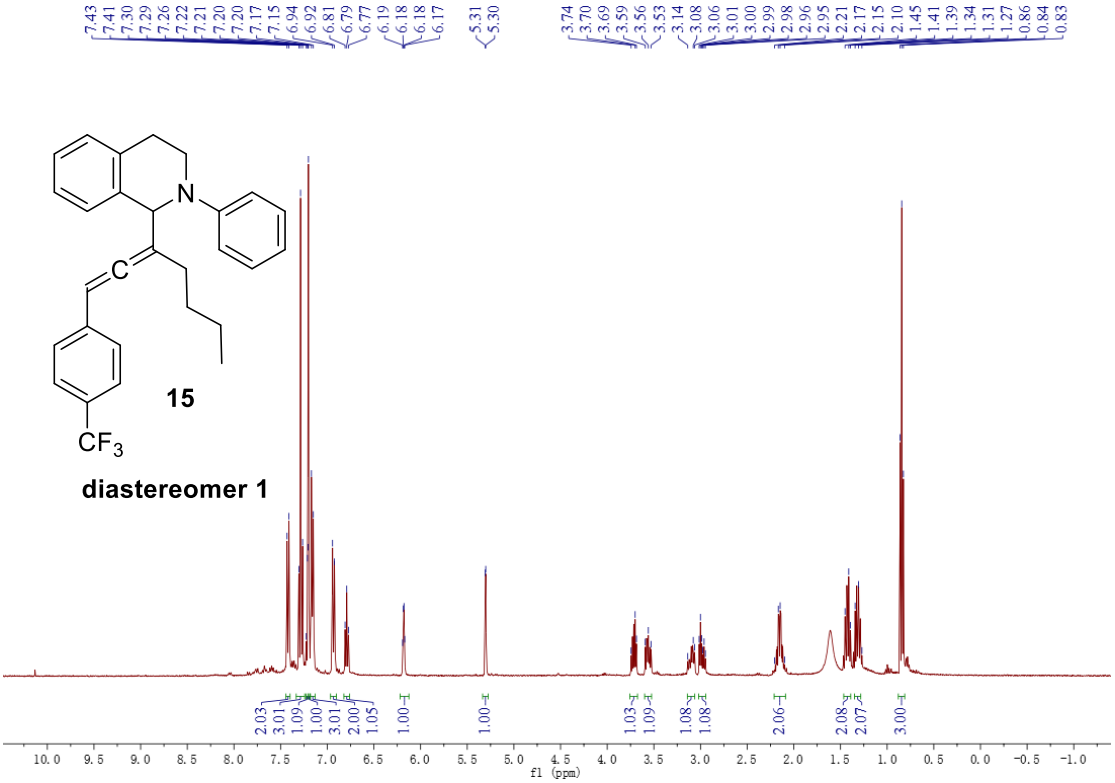
^{1}H NMR (400 MHz, $CDCl_3$)



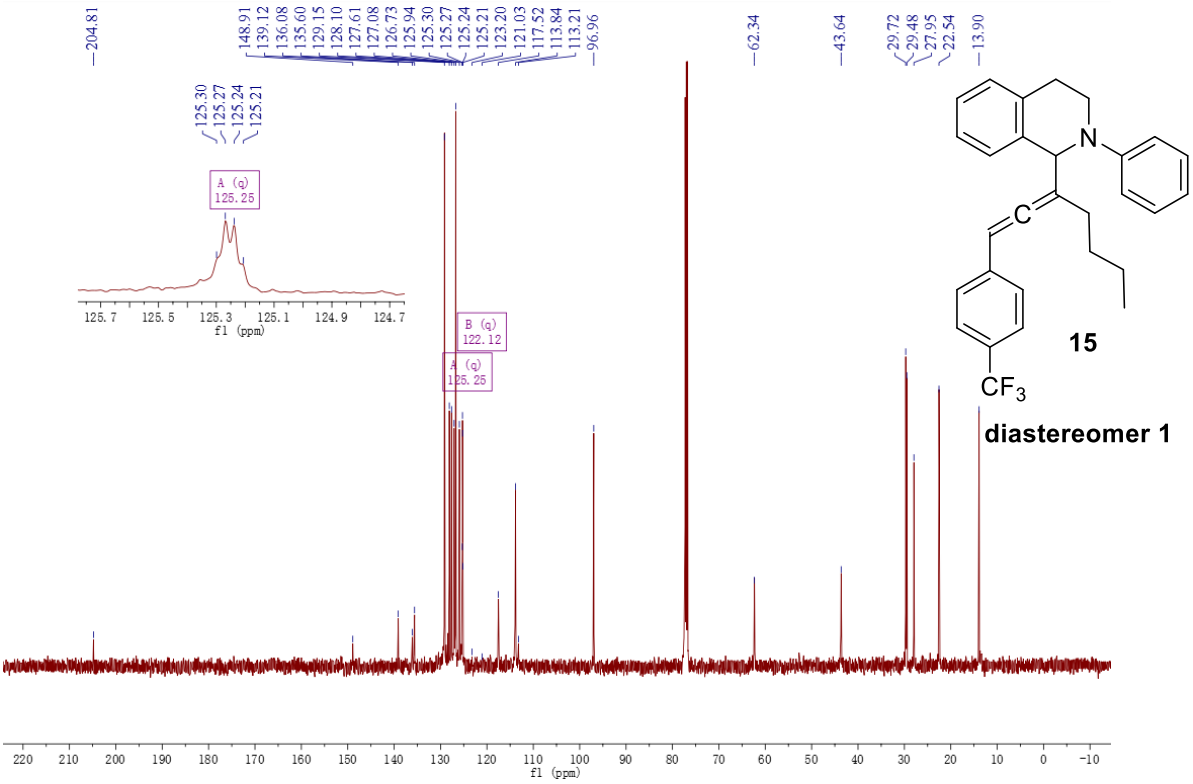
^{13}C NMR (100 MHz, $CDCl_3$)



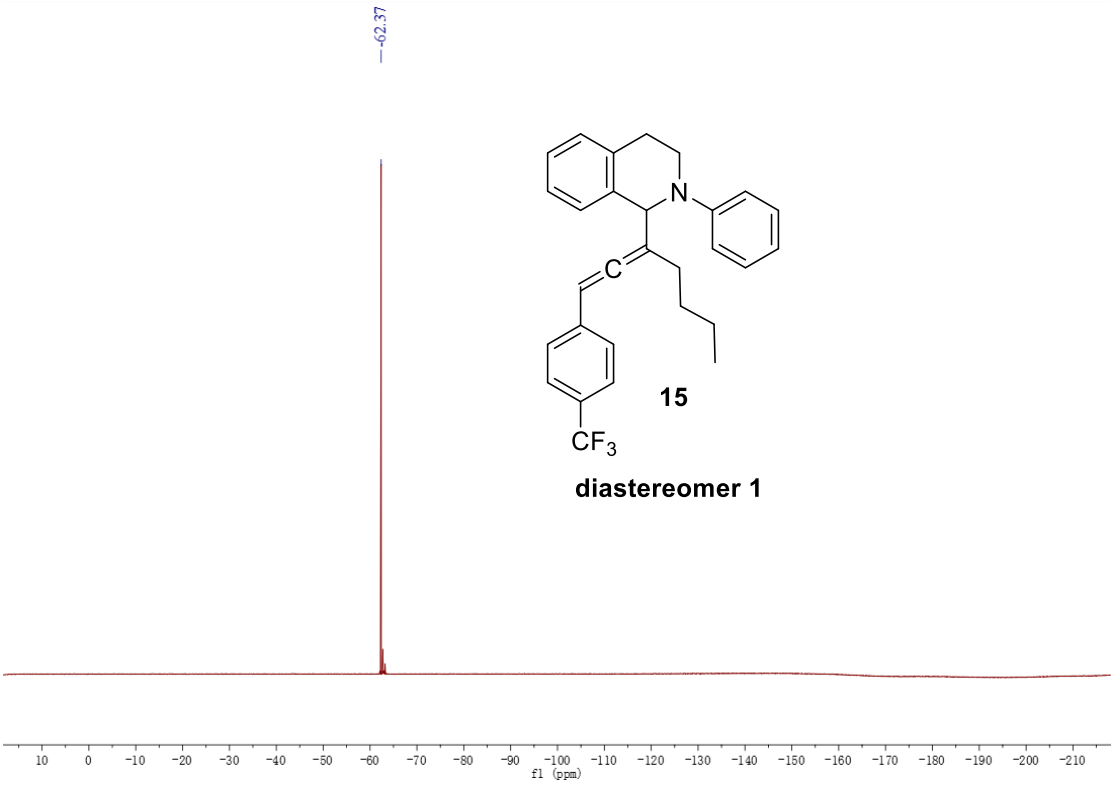
^{1}H NMR (400 MHz, $CDCl_3$)



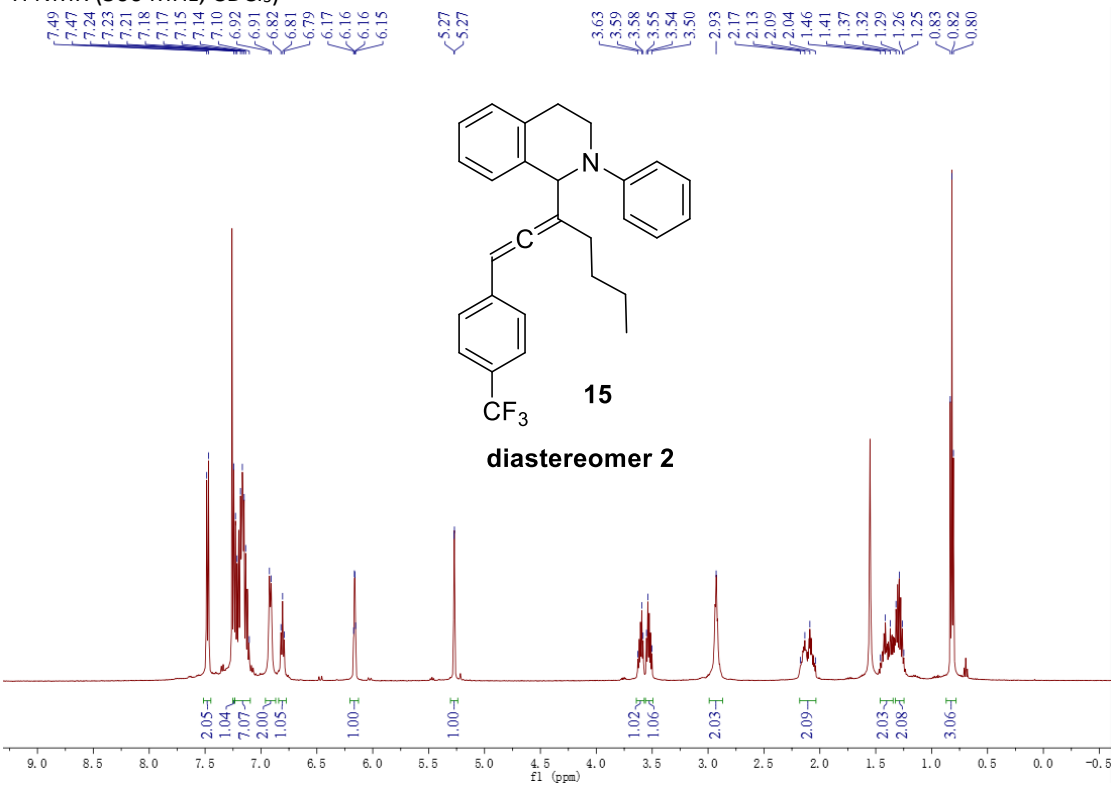
^{13}C NMR (126 MHz, $CDCl_3$)



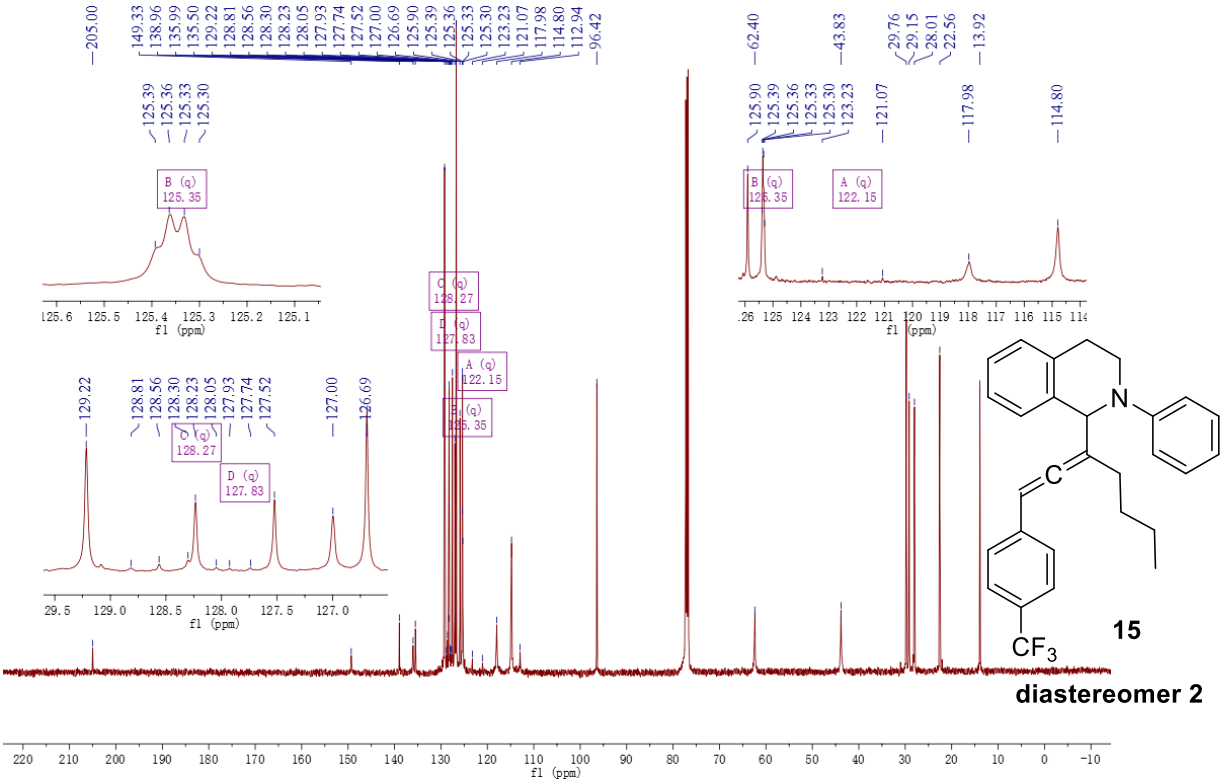
^{19}F NMR (377 MHz, $CDCl_3$)



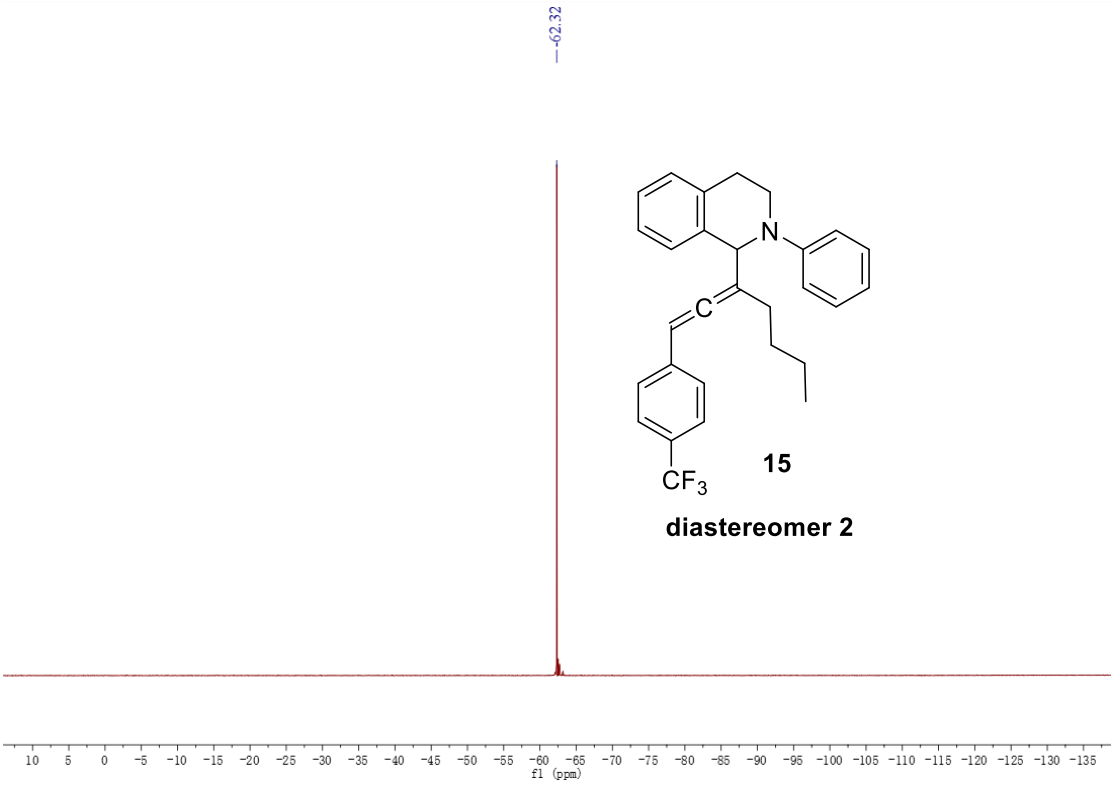
^{1}H NMR (500 MHz, $CDCl_3$)



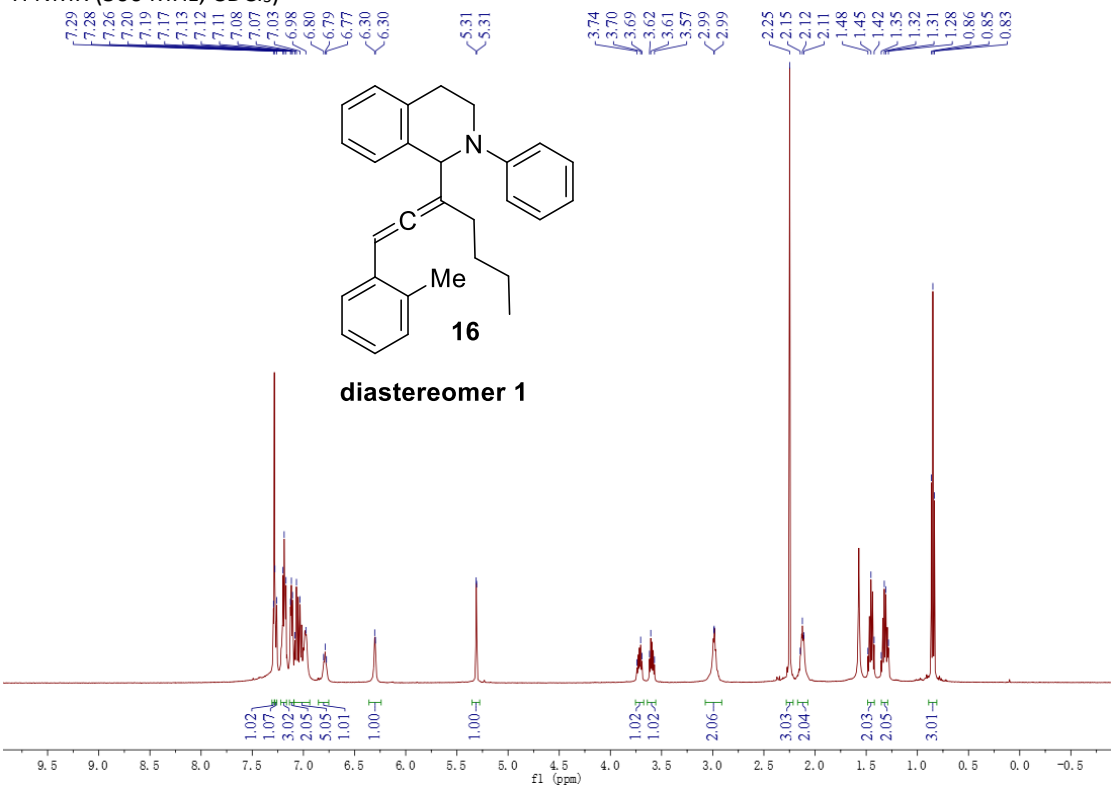
^{13}C NMR (126 MHz, $CDCl_3$)



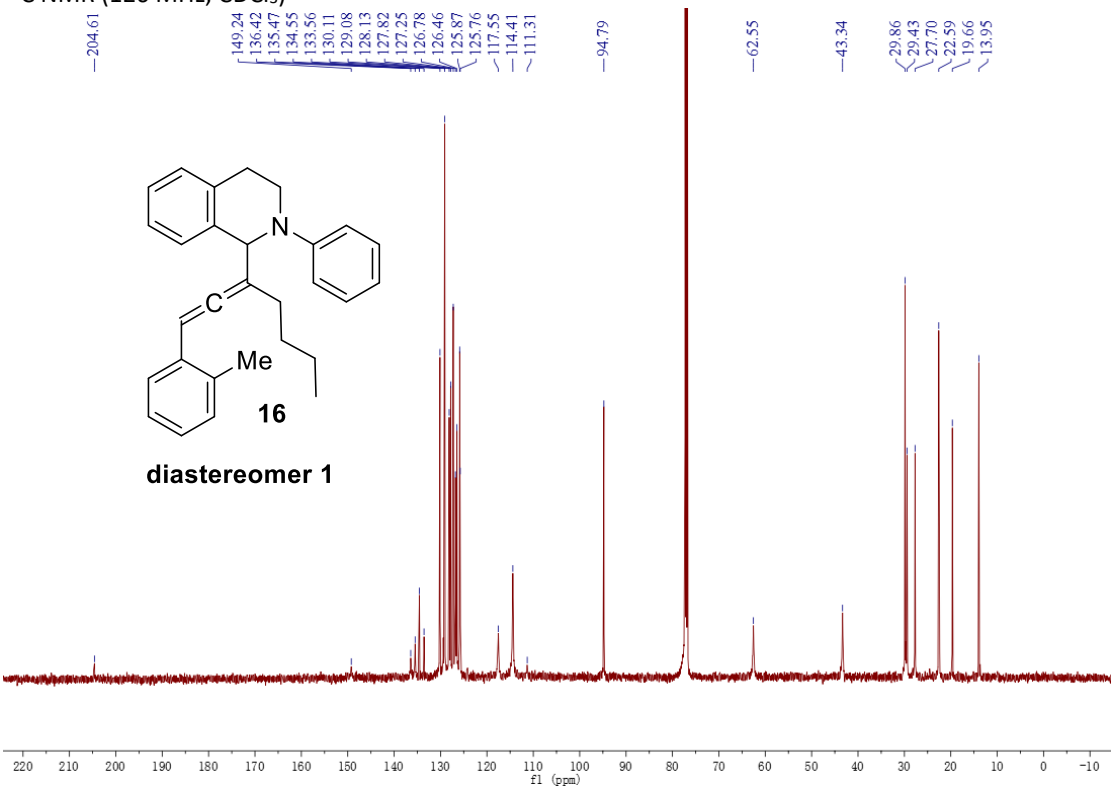
^{19}F NMR (377 MHz, $CDCl_3$)



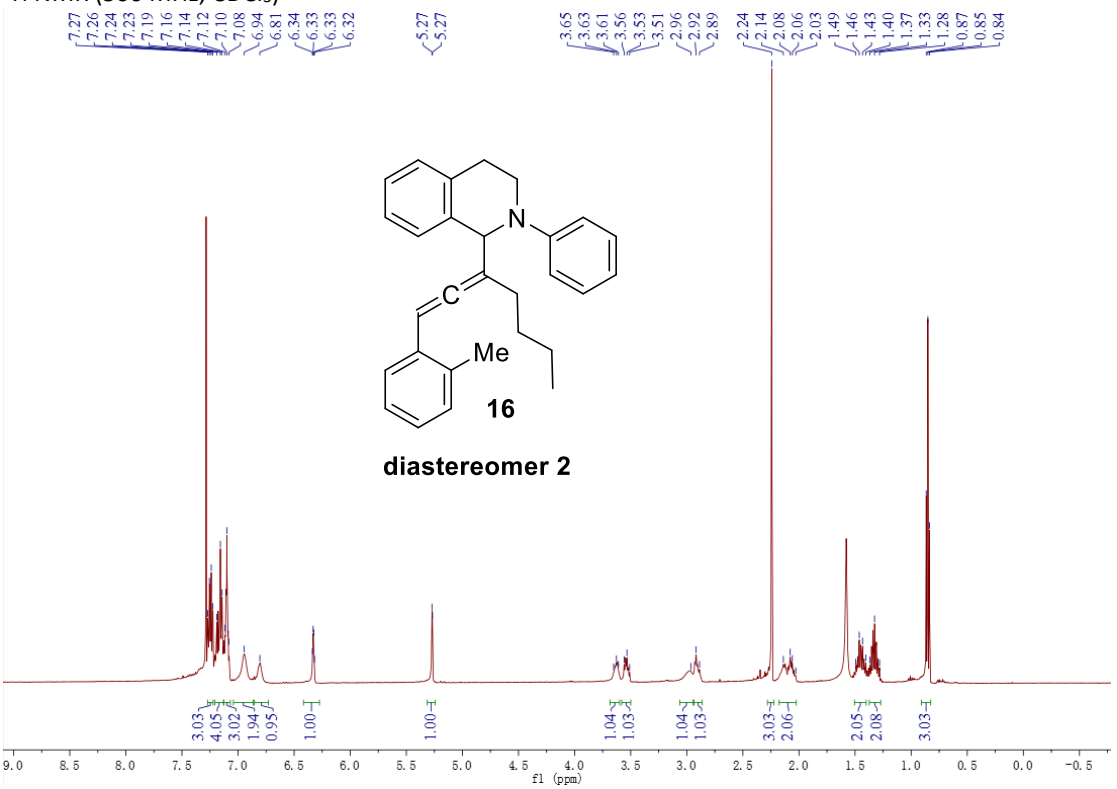
^{1}H NMR (500 MHz, $CDCl_3$)



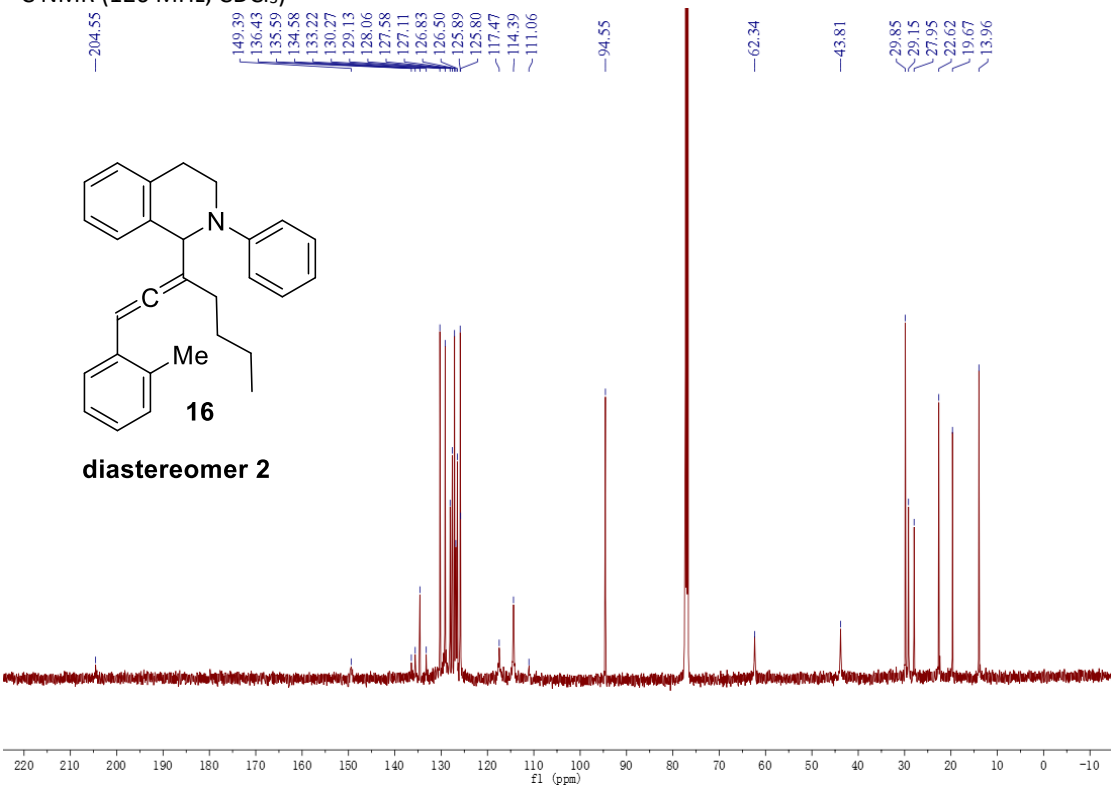
^{13}C NMR (126 MHz, $CDCl_3$)



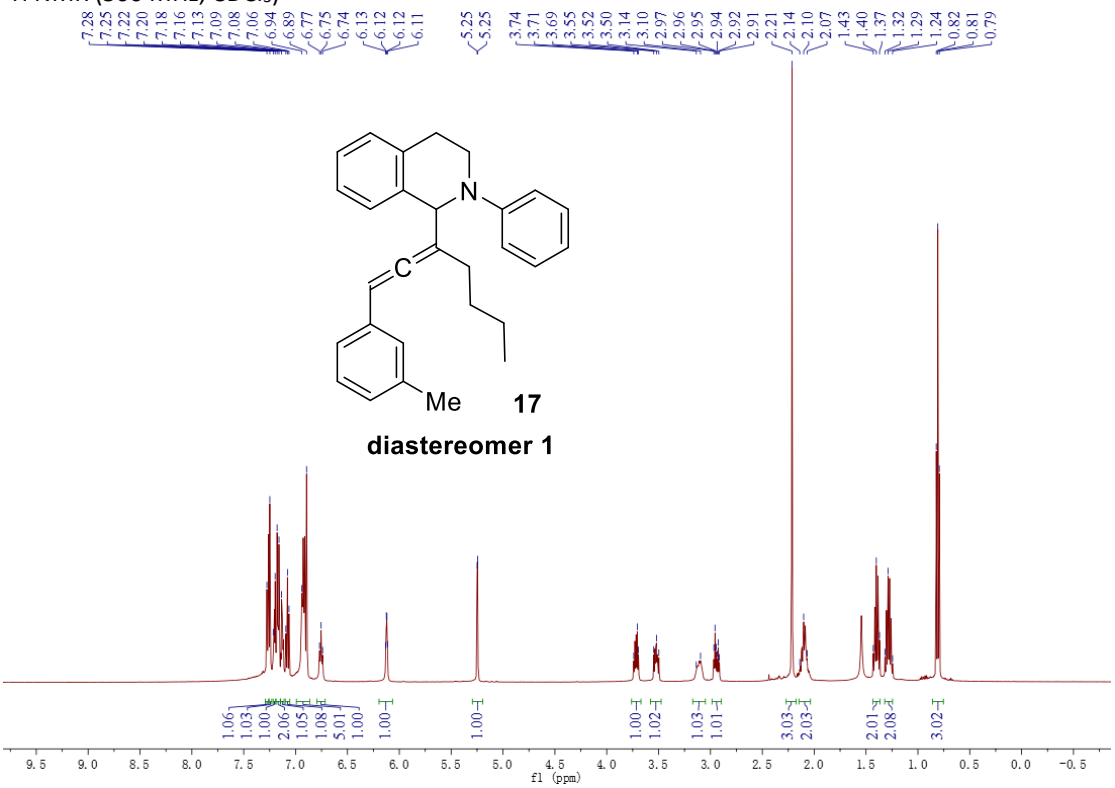
^{1}H NMR (500 MHz, $CDCl_3$)



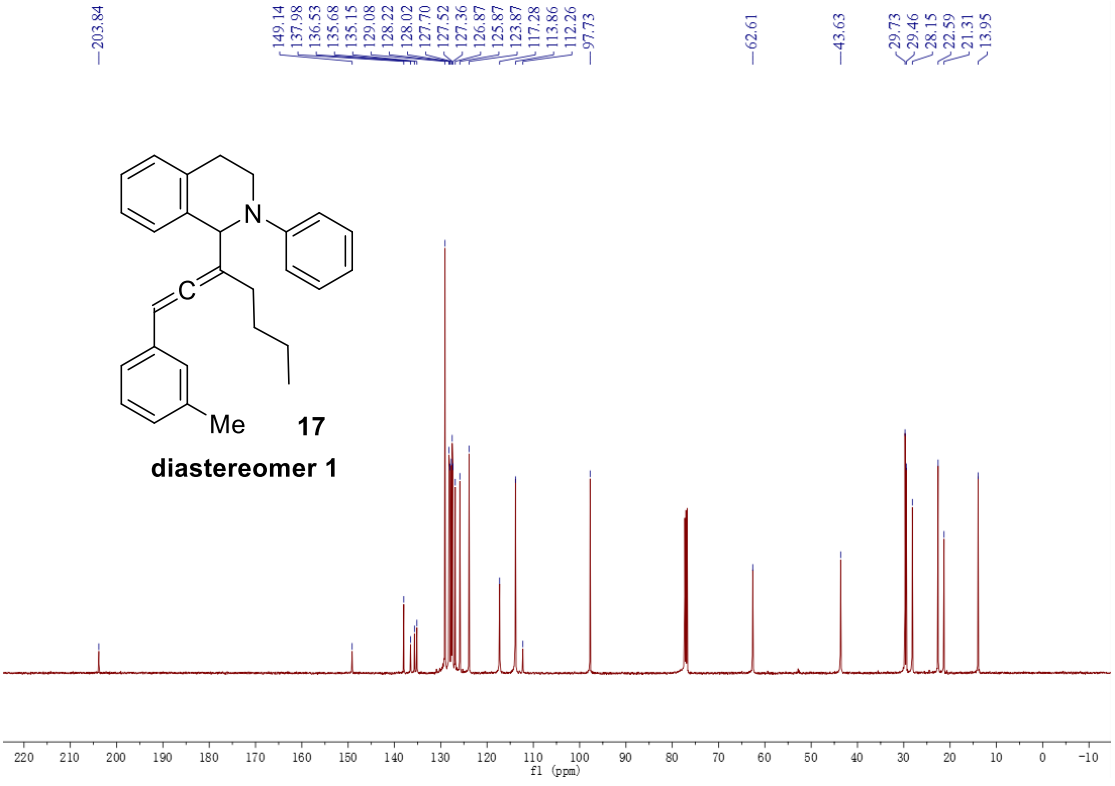
^{13}C NMR (126 MHz, $CDCl_3$)



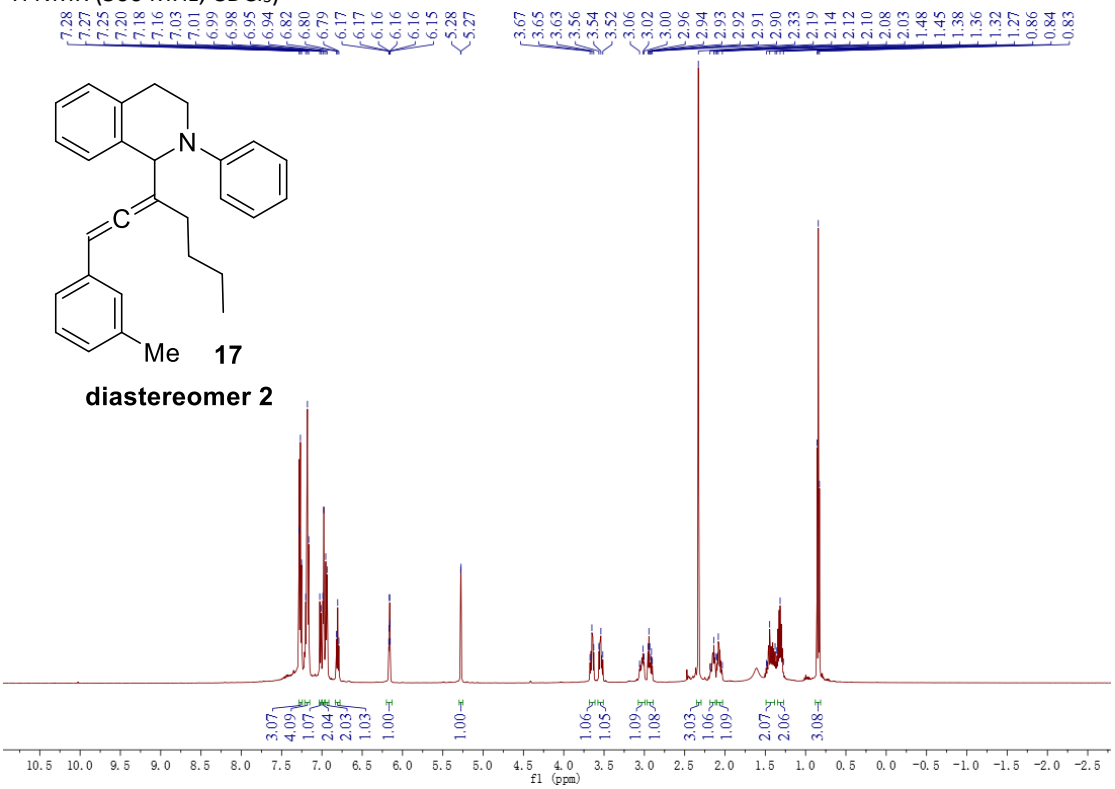
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)



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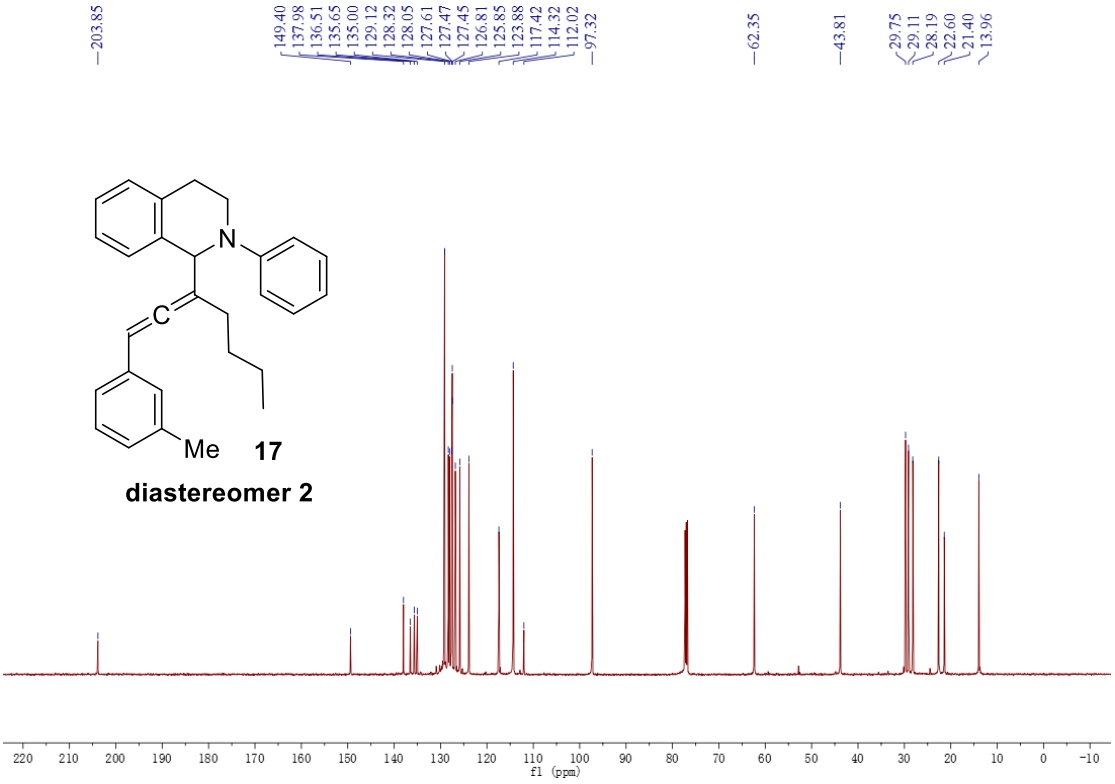
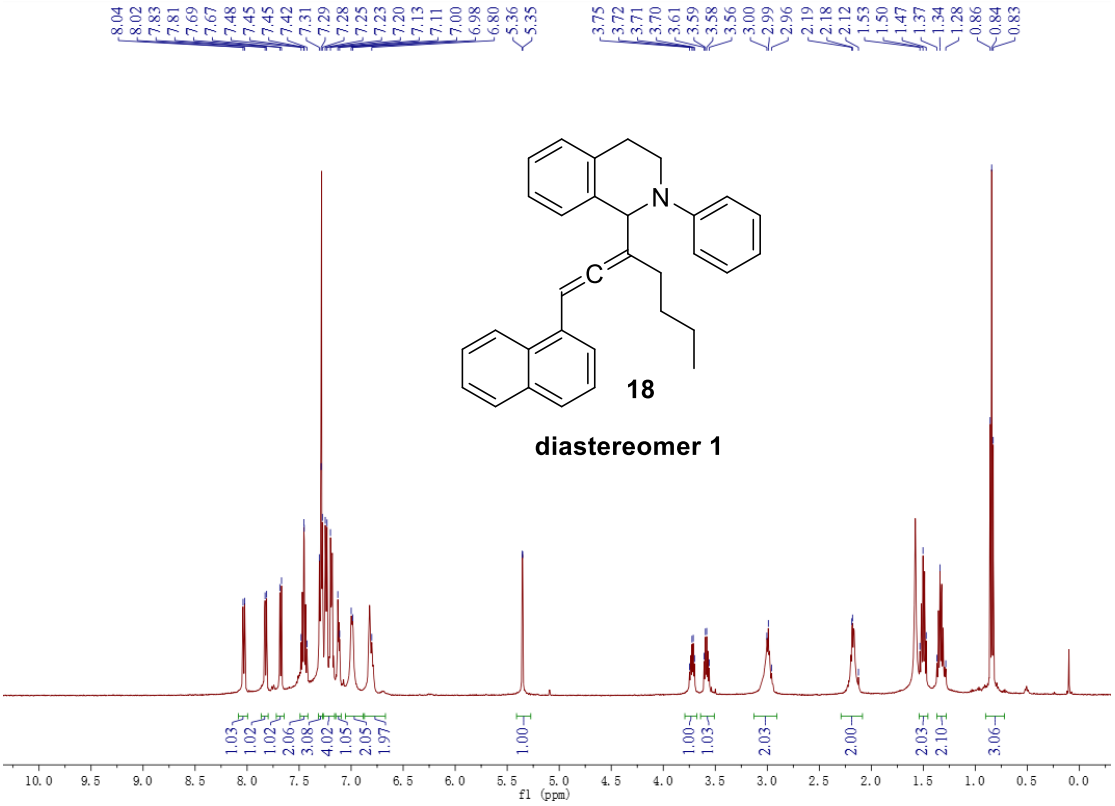


^{1}H NMR (500 MHz, $CDCl_3$)



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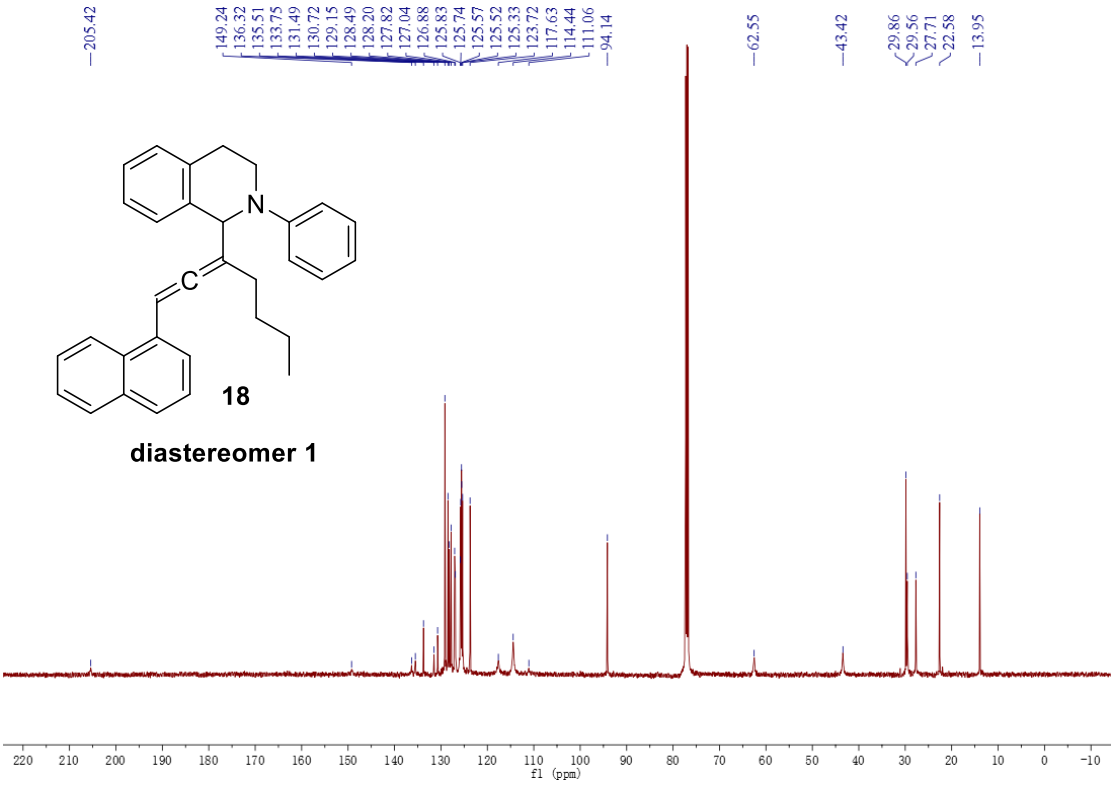
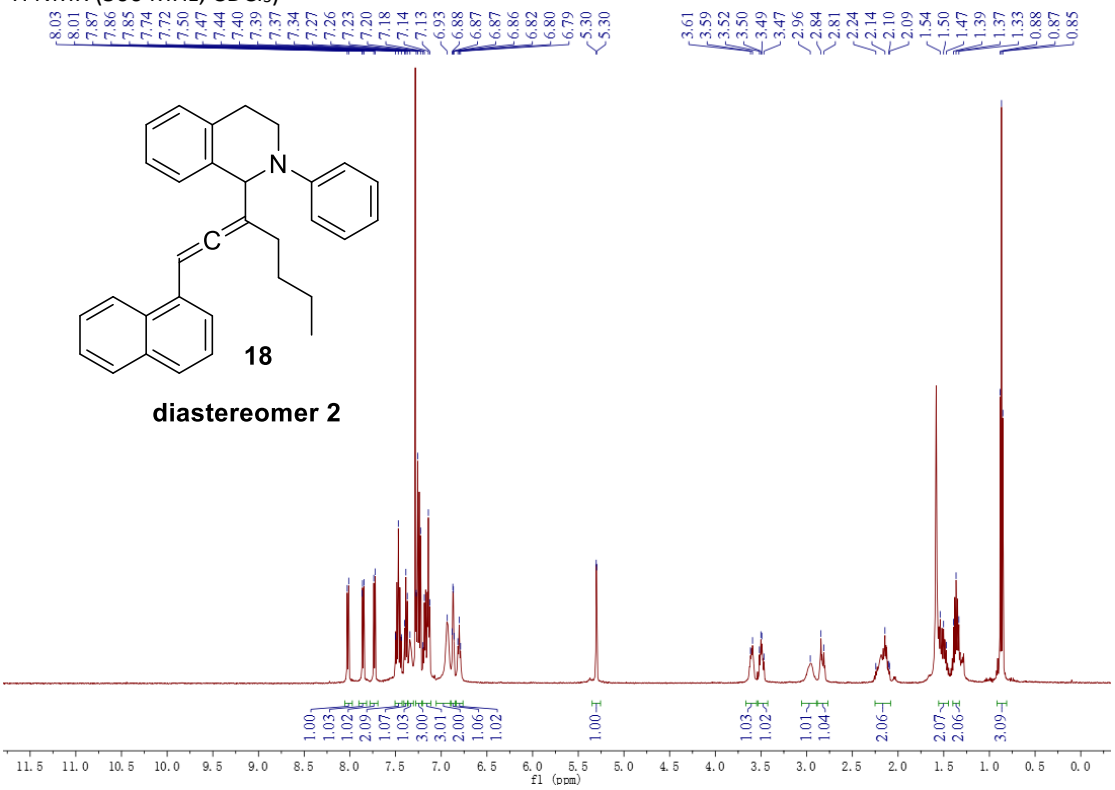
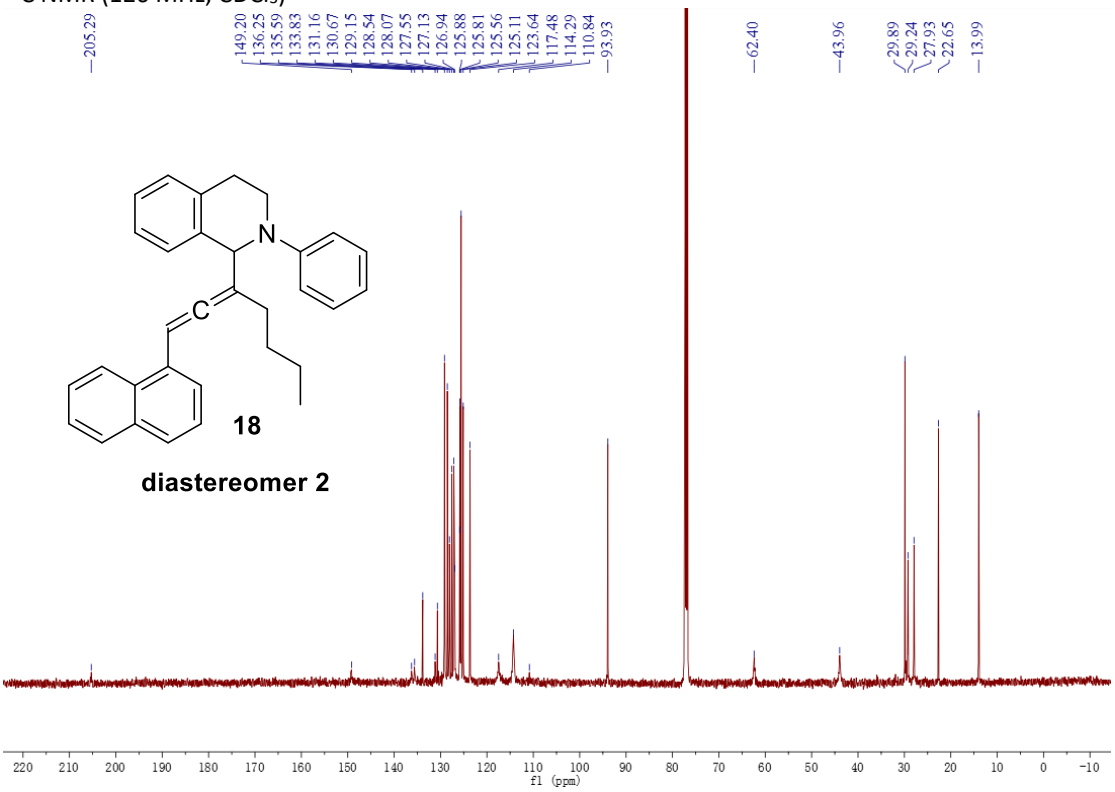


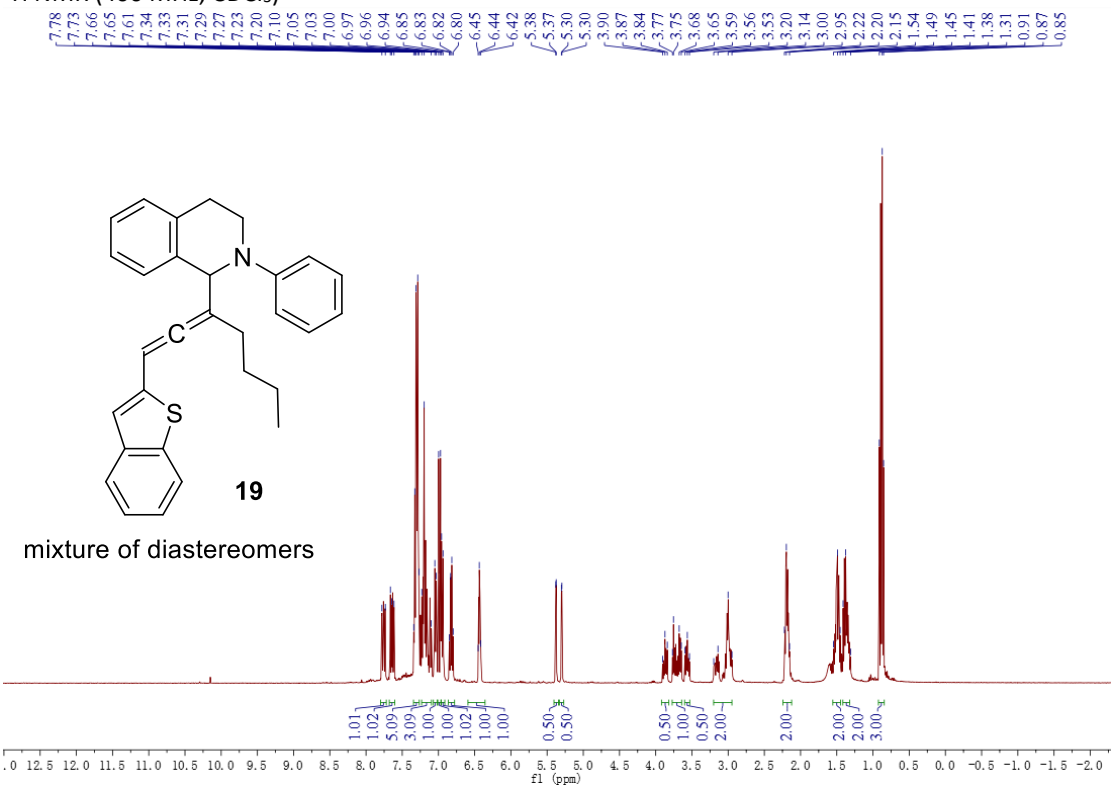
^{1}H NMR (500 MHz, $CDCl_3$)



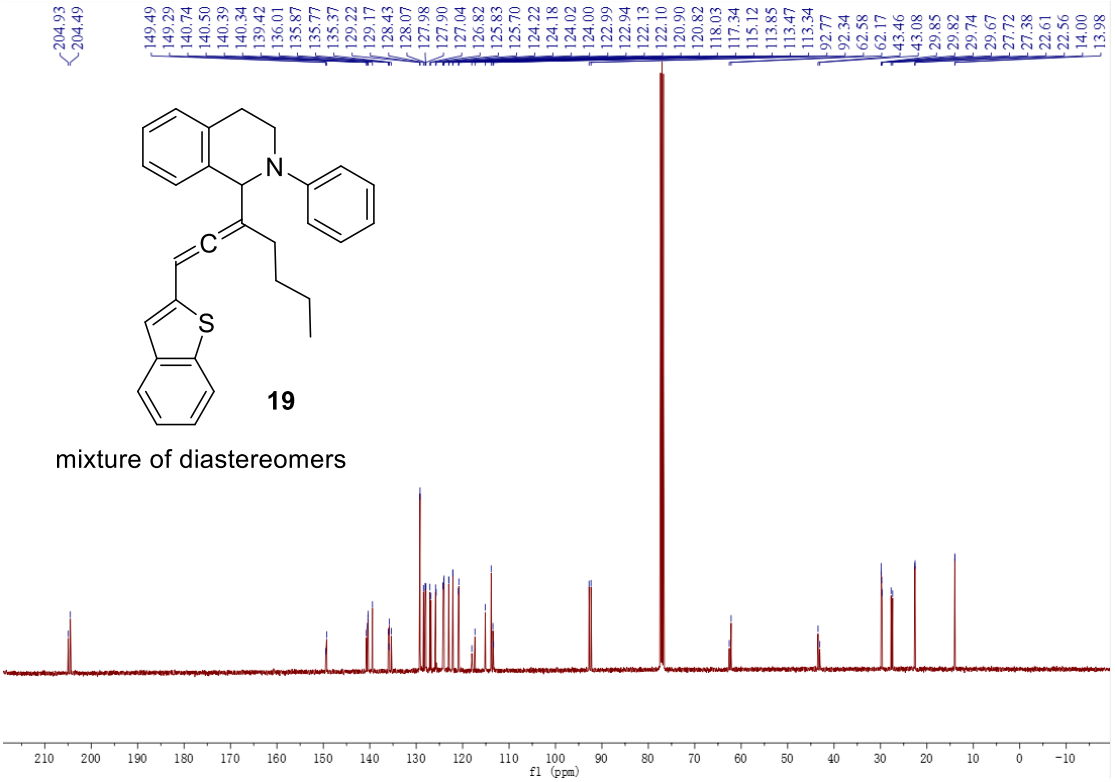
^{13}C NMR (126 MHz, $CDCl_3$)



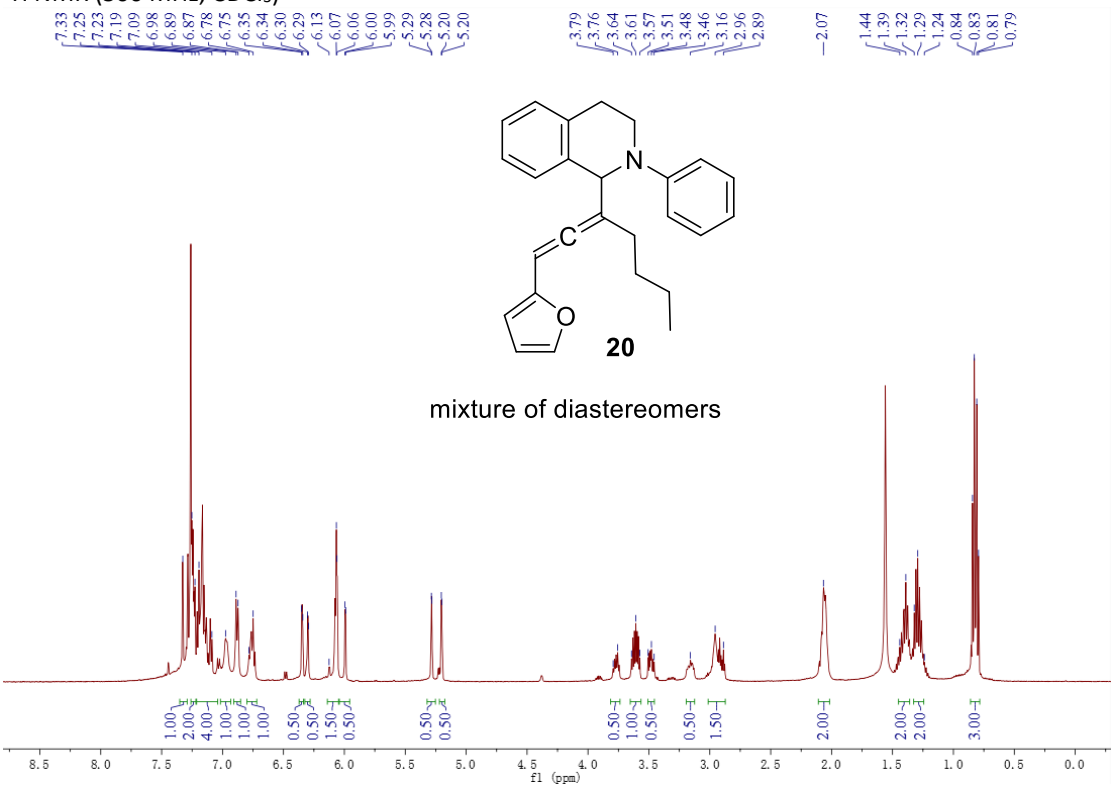
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)



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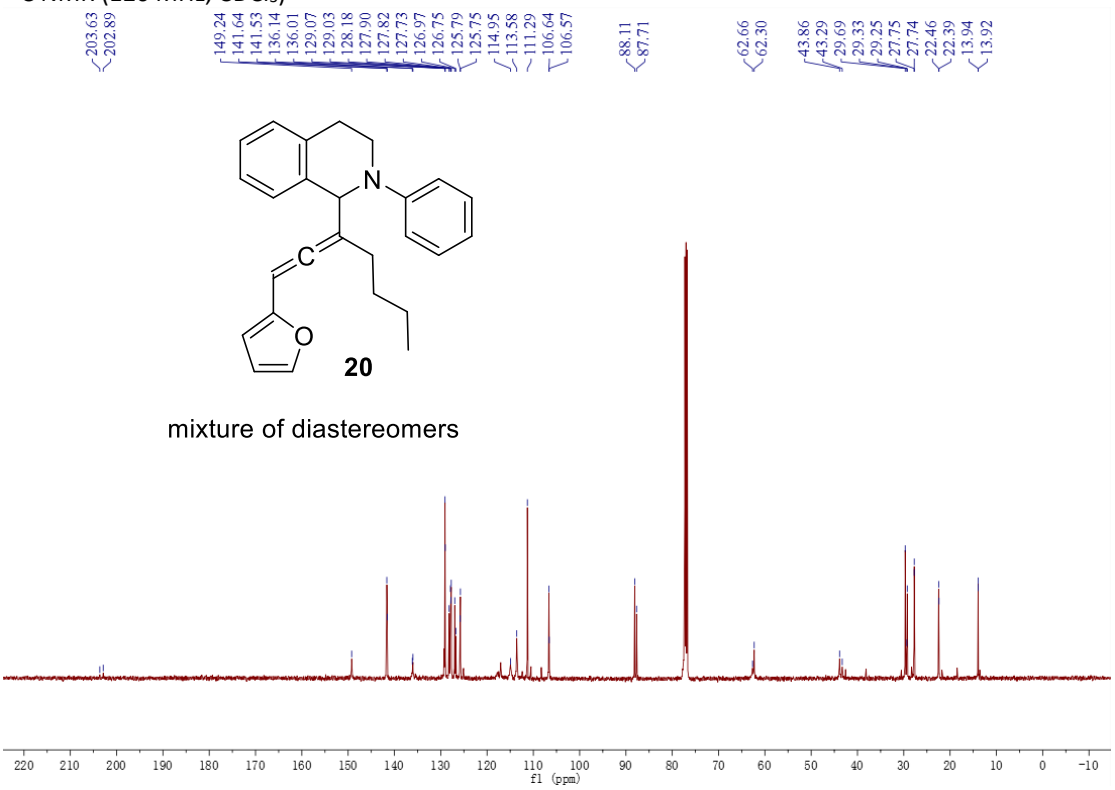

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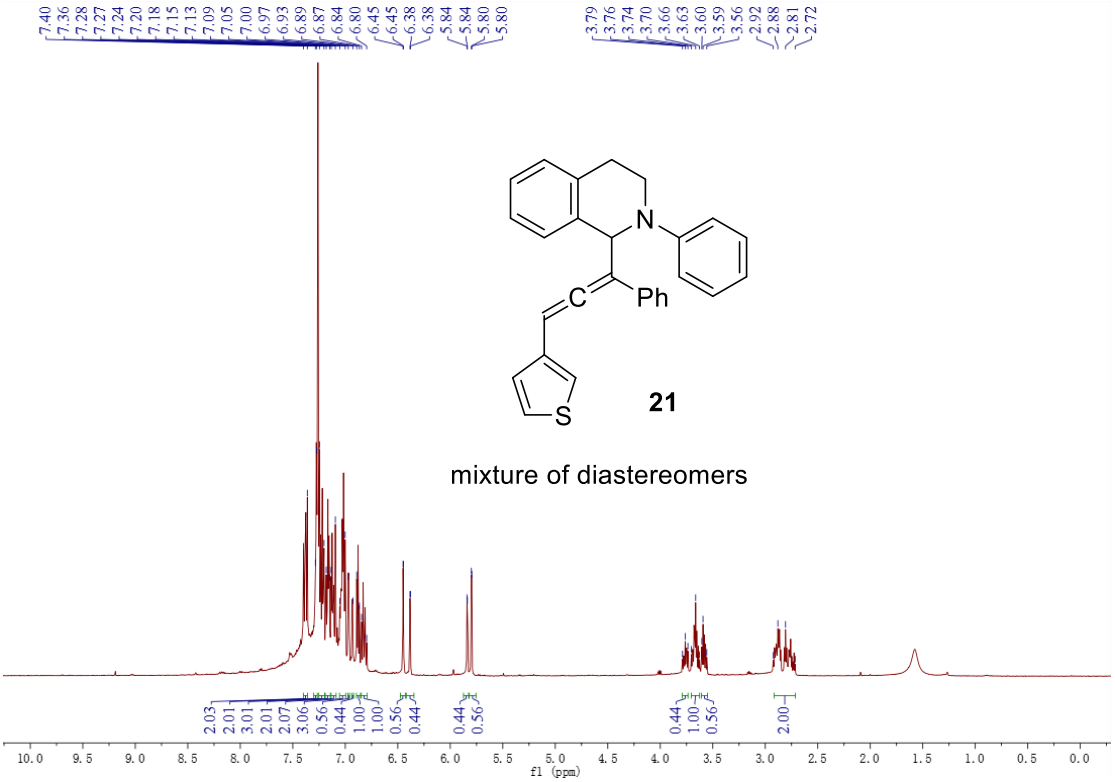
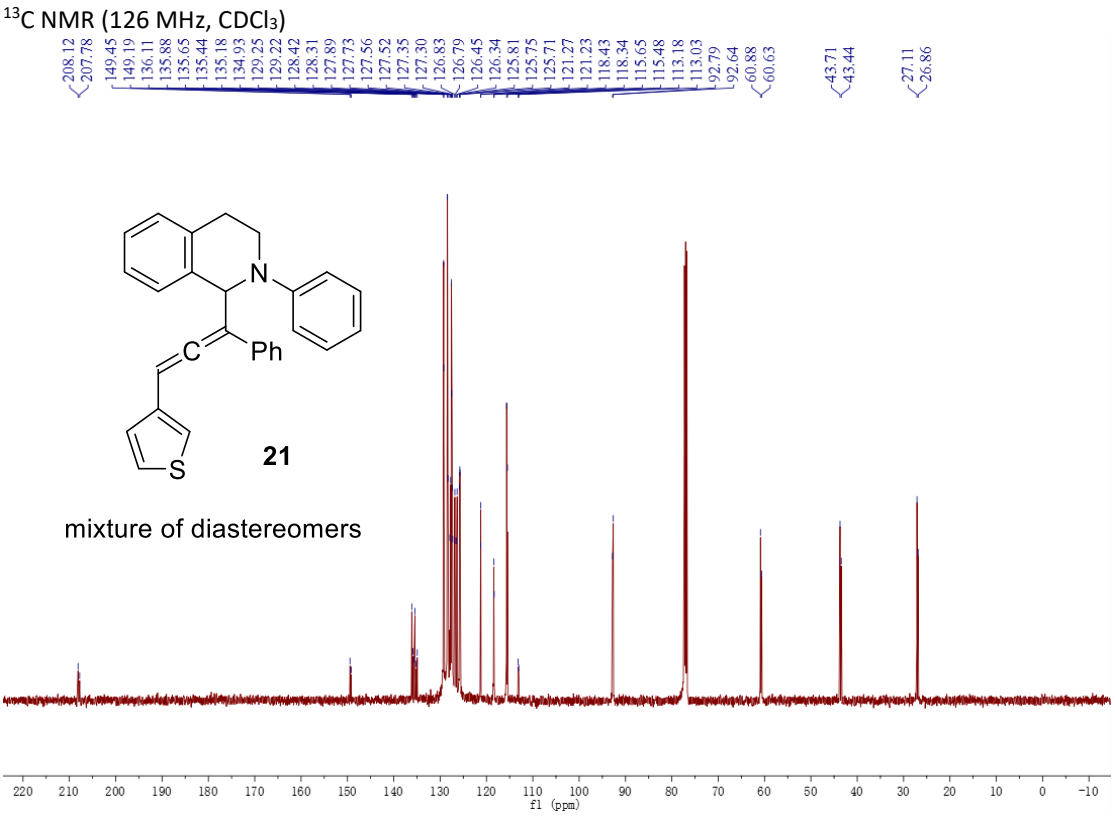
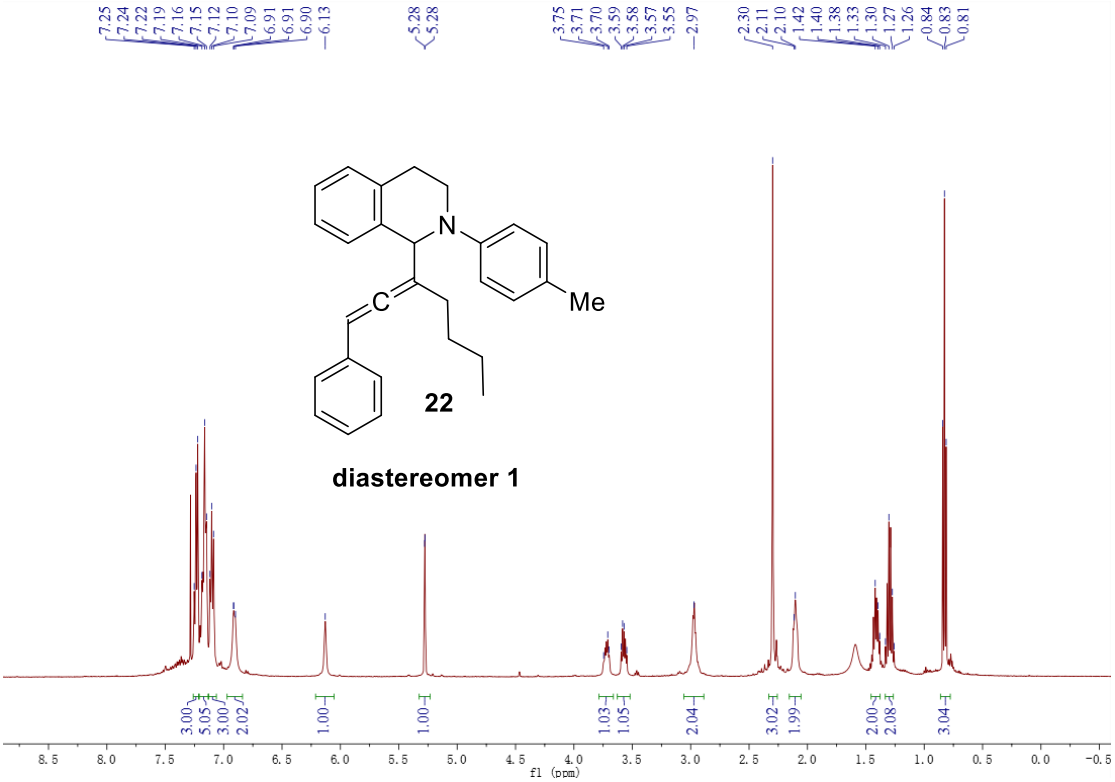


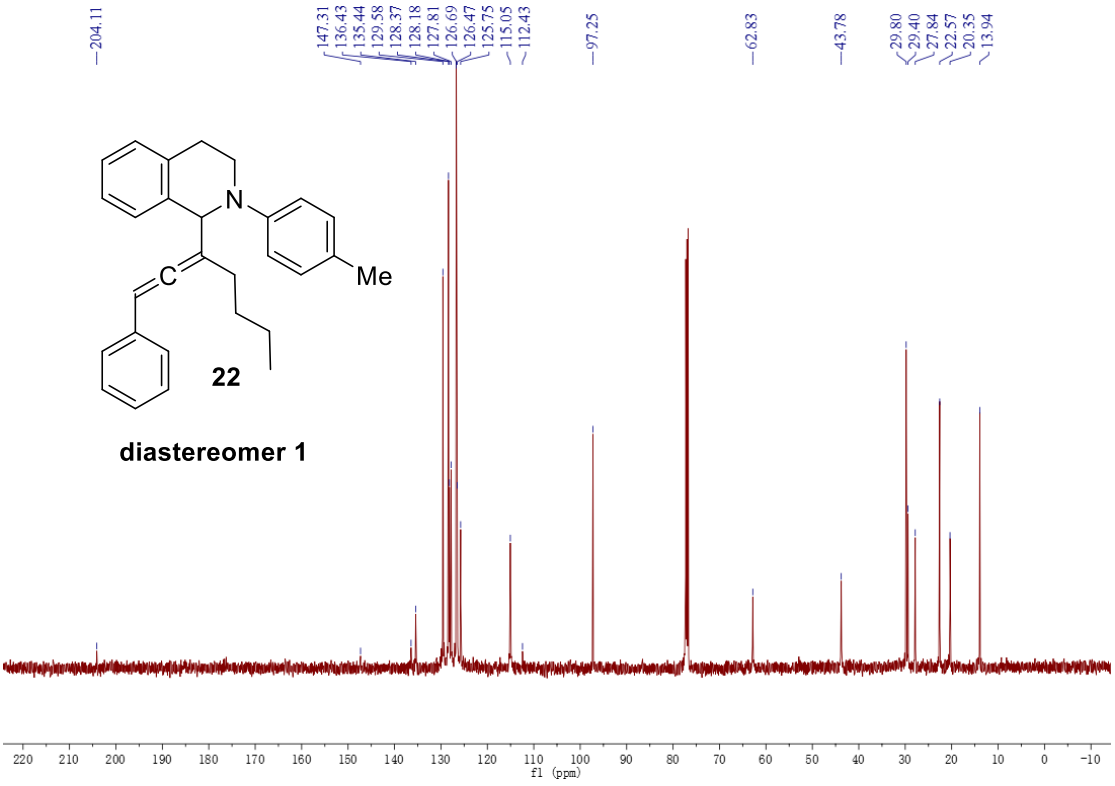
^{13}C NMR (126 MHz, $CDCl_3$)



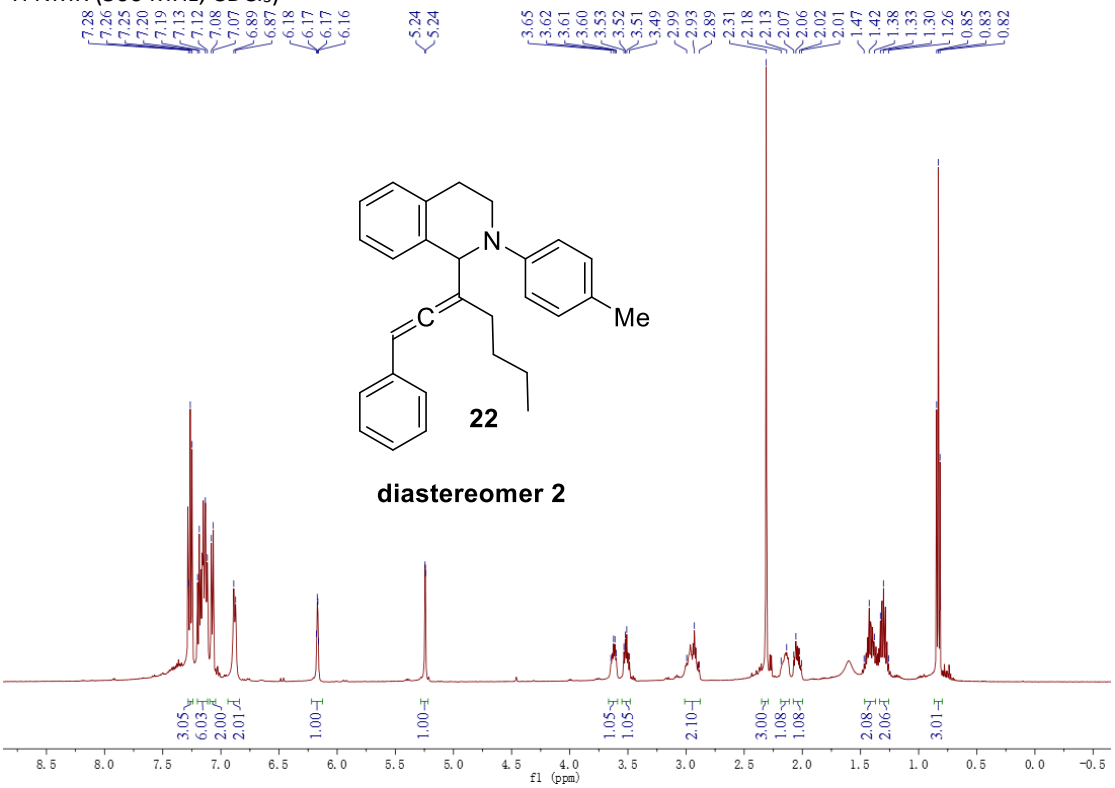
^{1}H NMR (500 MHz, $CDCl_3$)



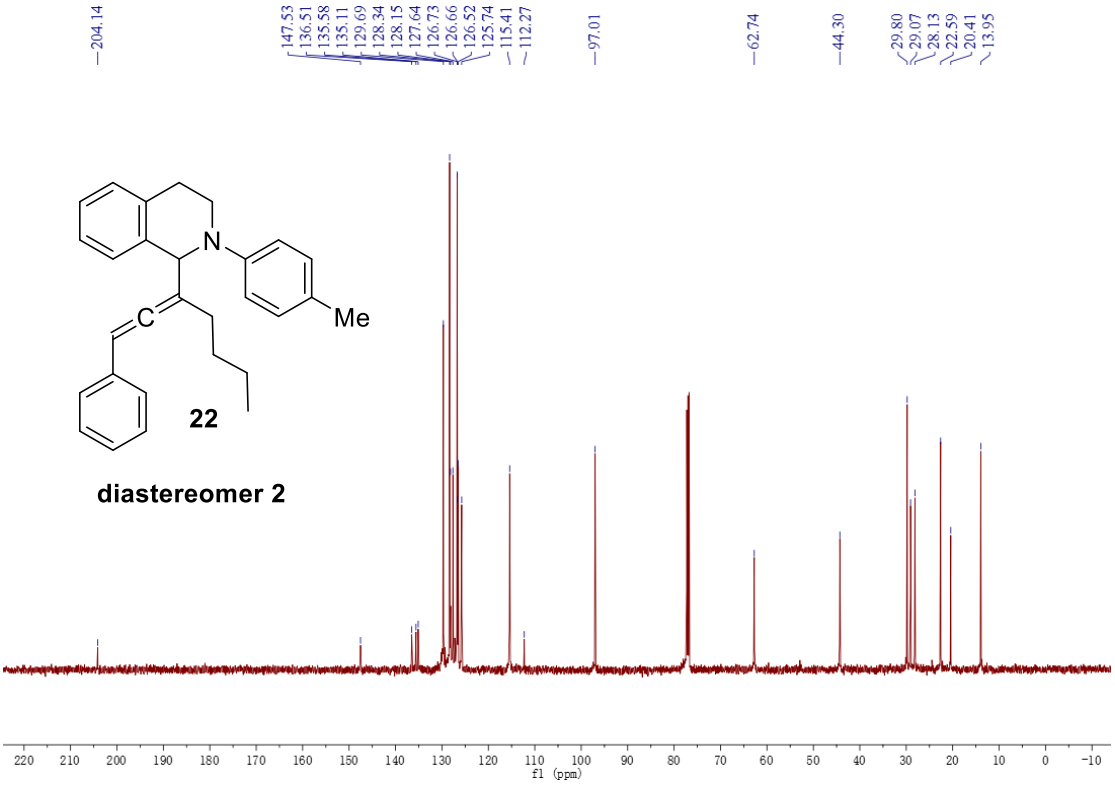
^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



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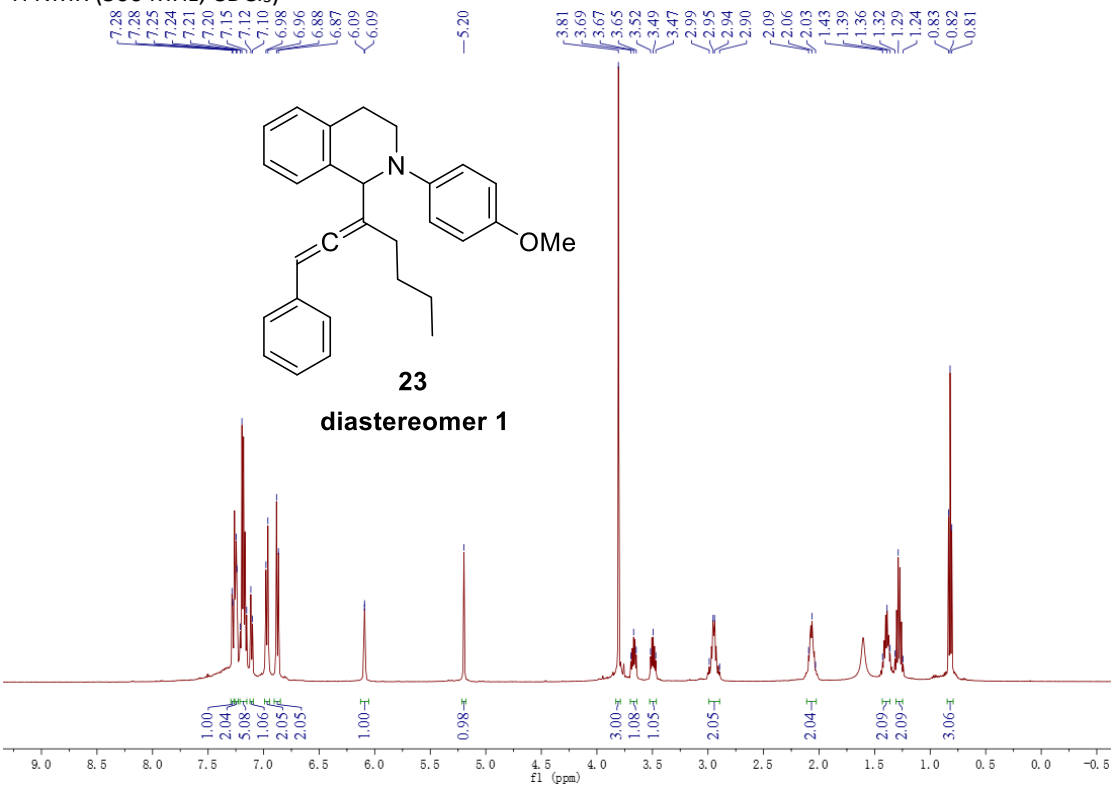

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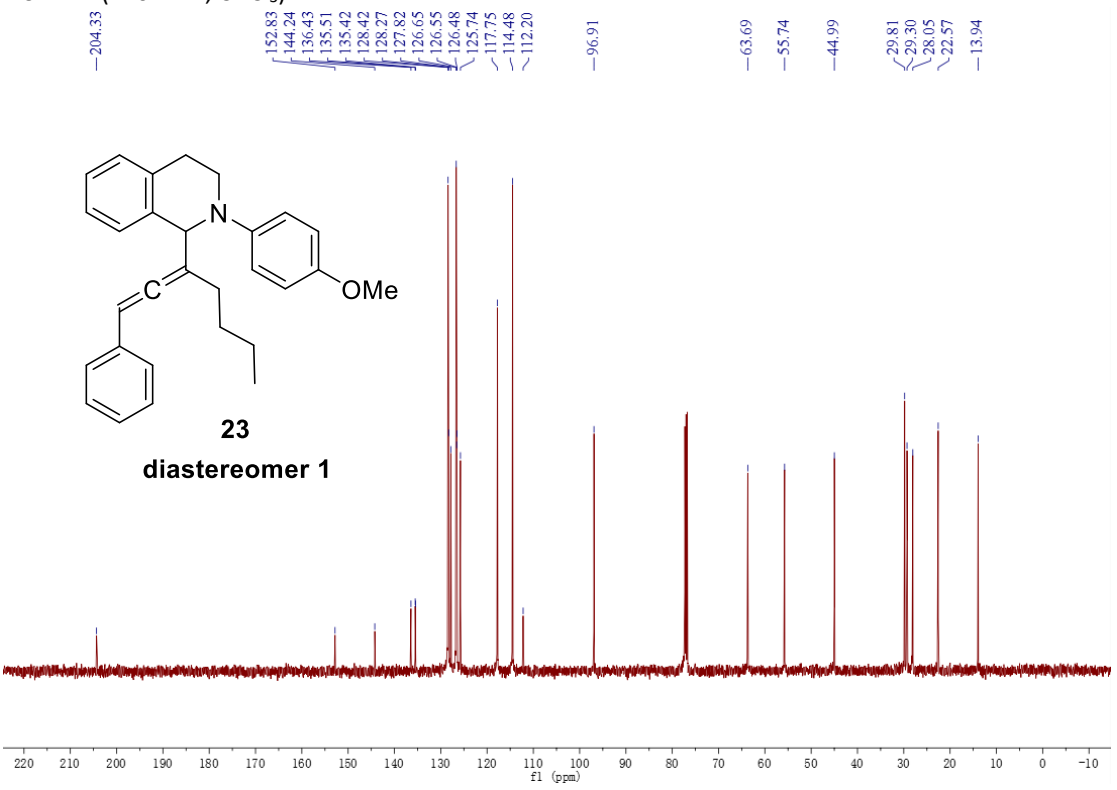
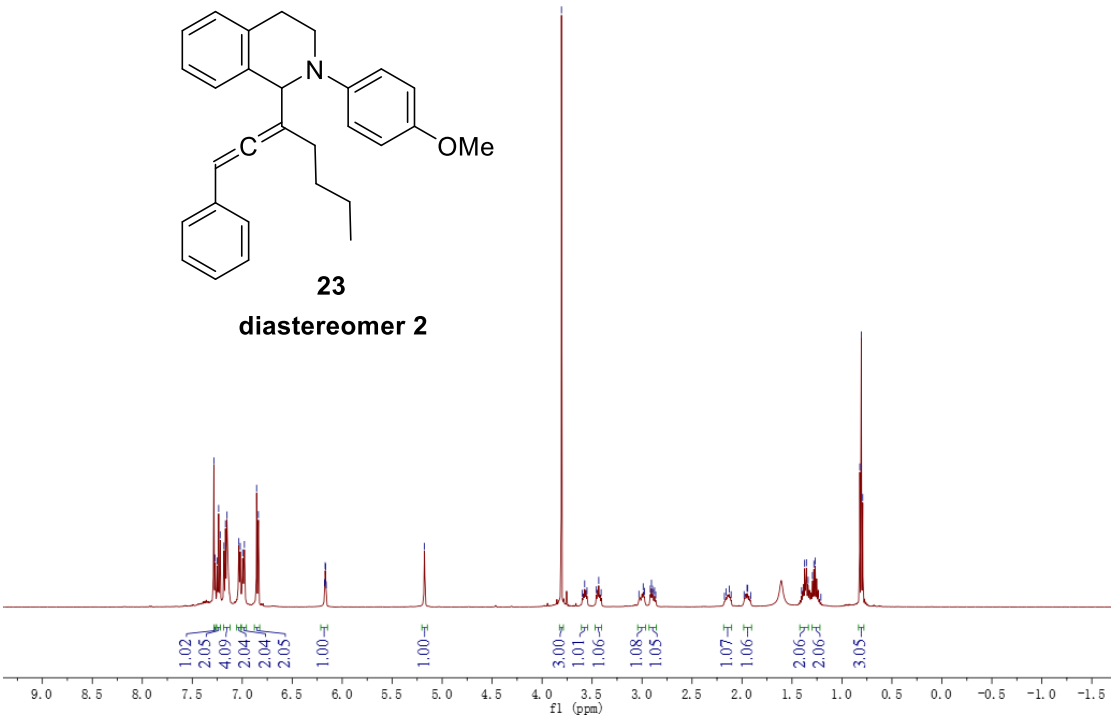
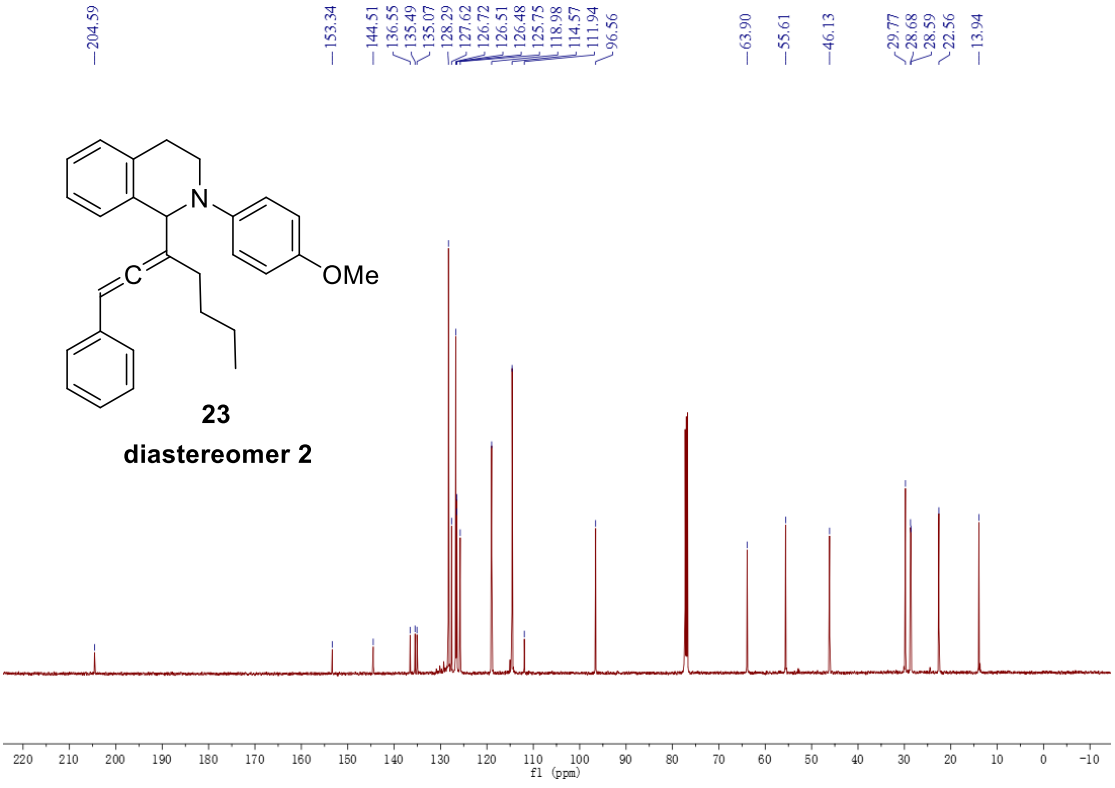


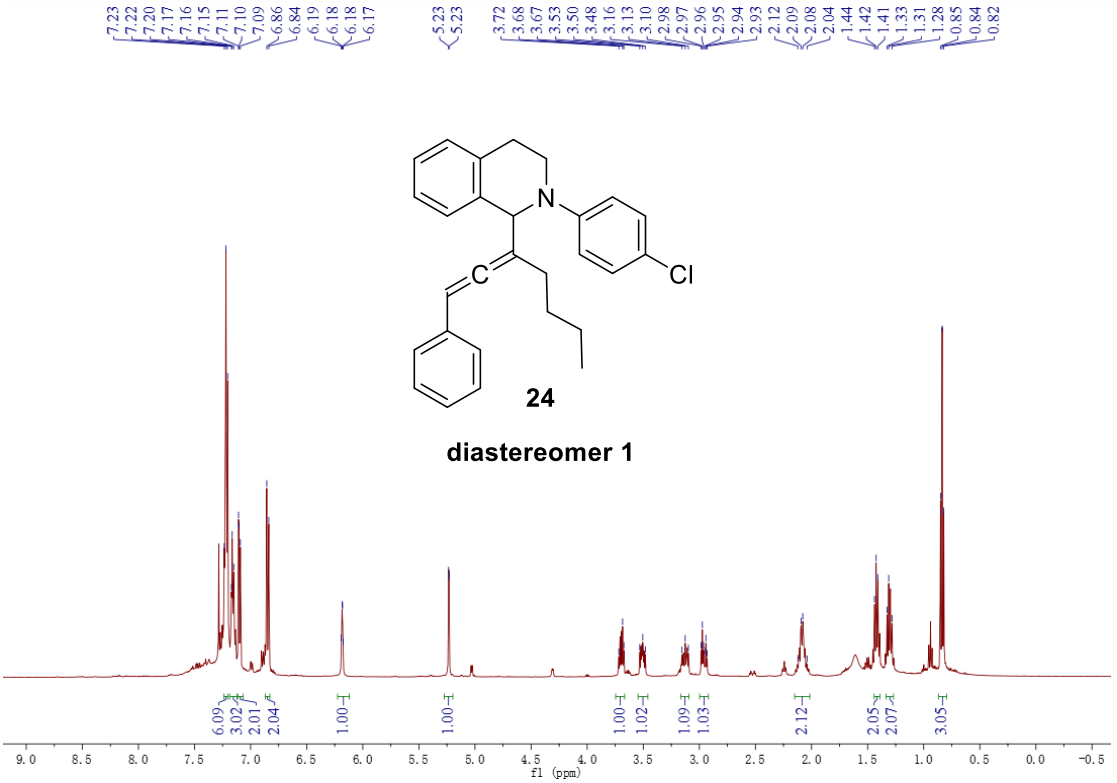
^{1}H NMR (500 MHz, $CDCl_3$)



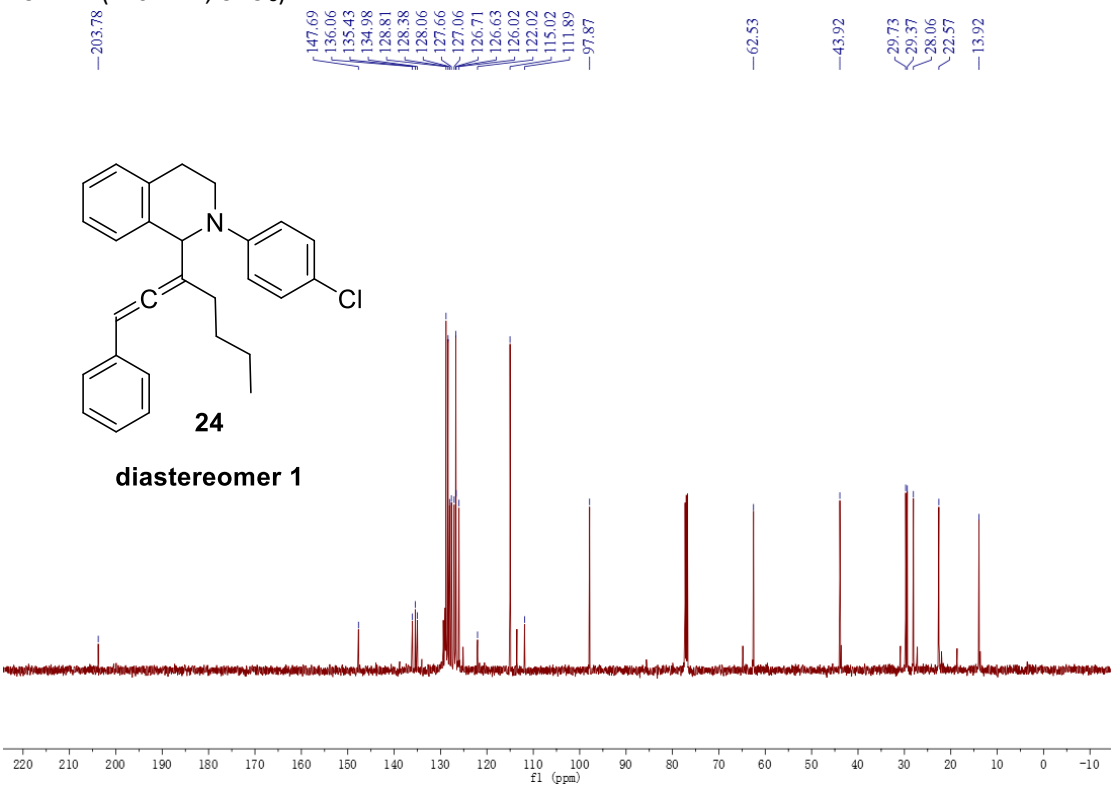
^{13}C NMR (126 MHz, $CDCl_3$)



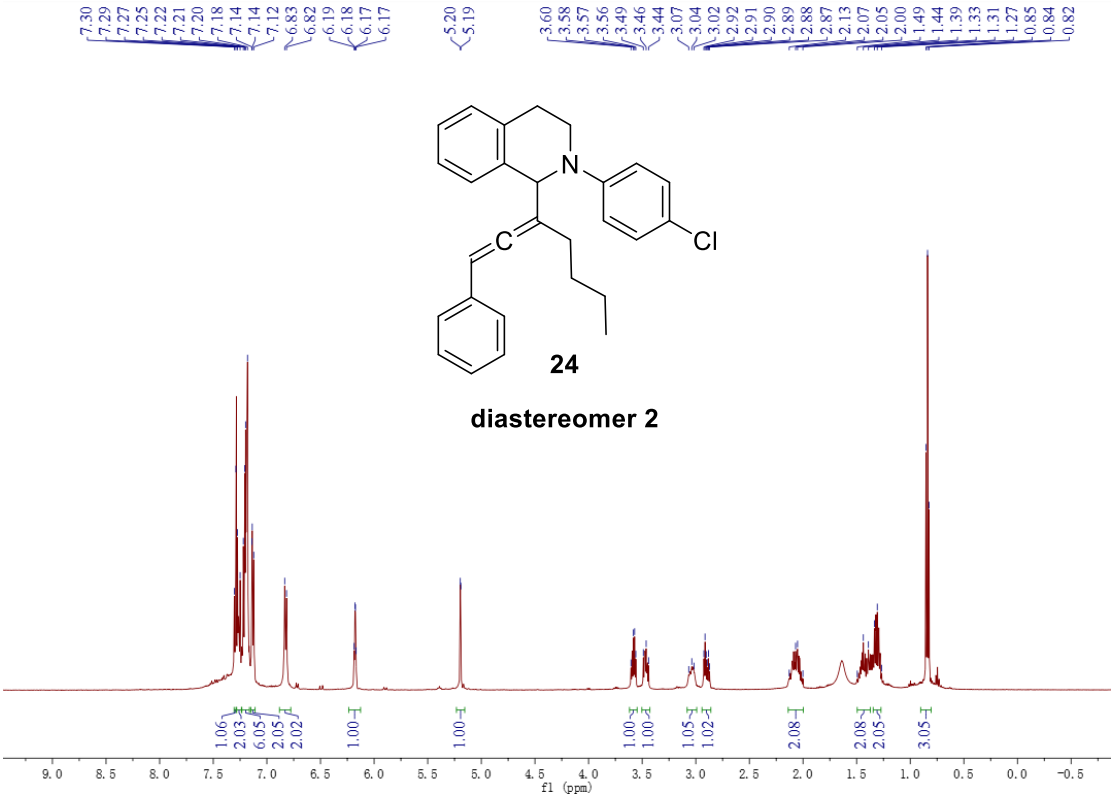
^{1}H NMR (500 MHz, $CDCl_3$)



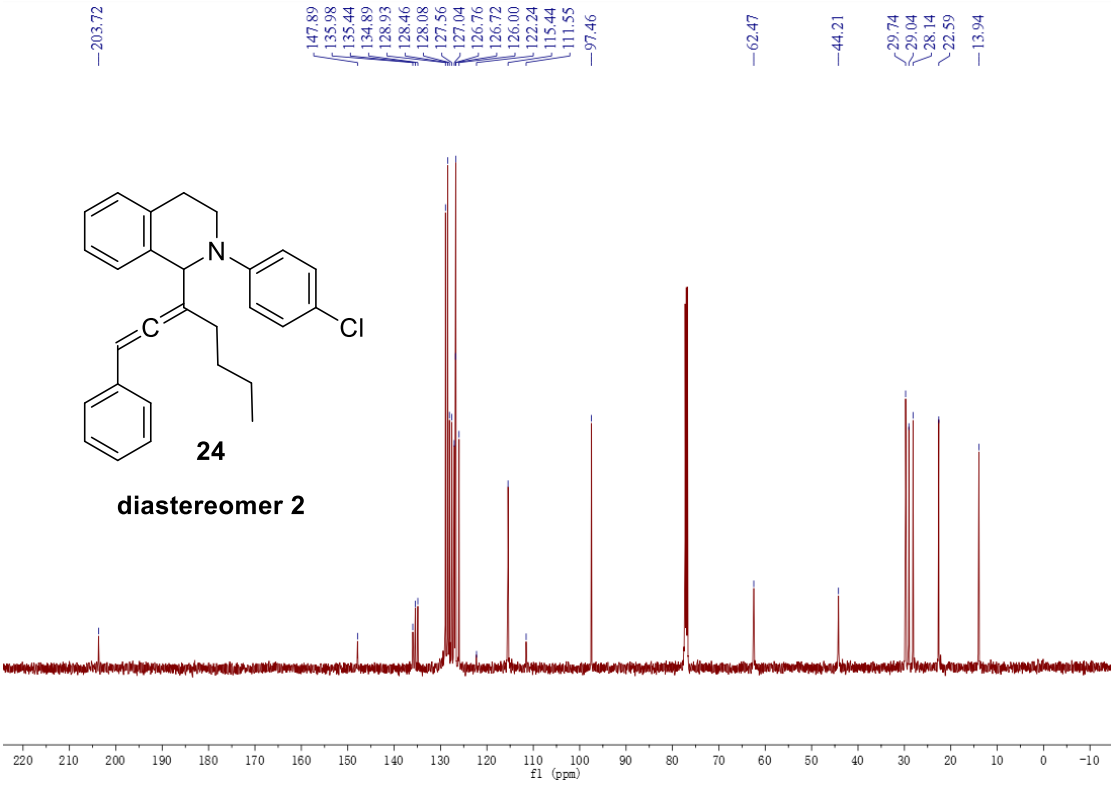
^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



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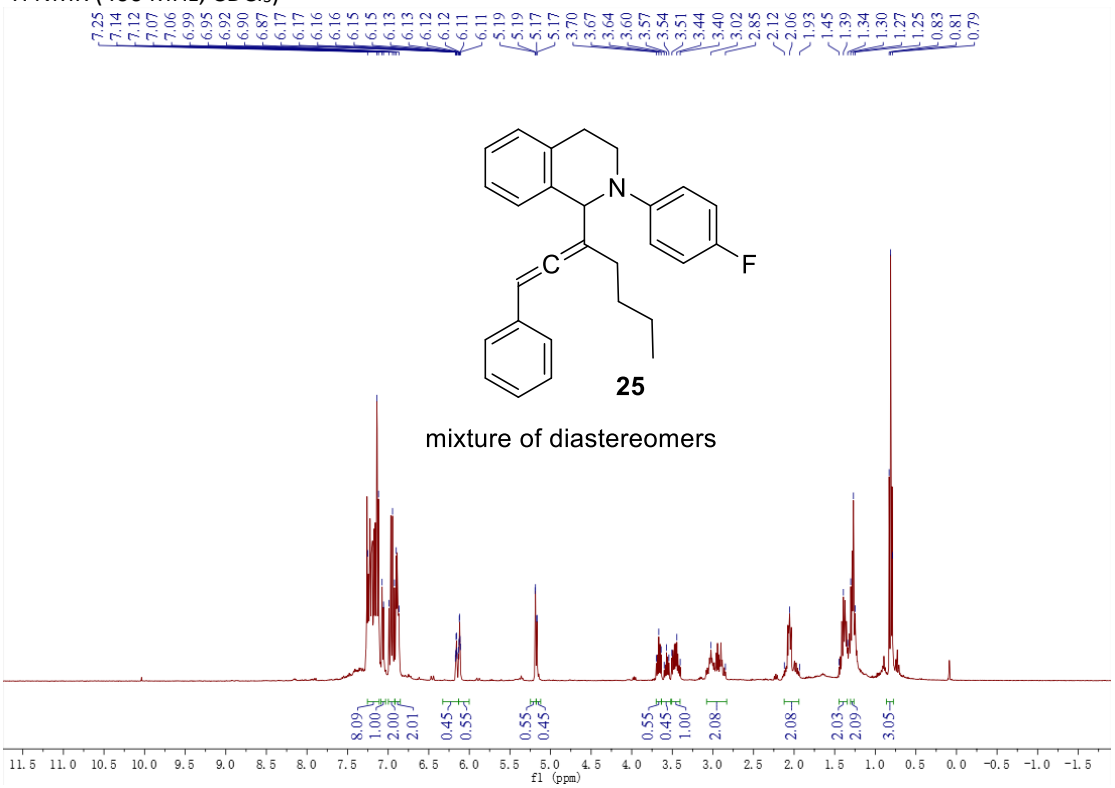
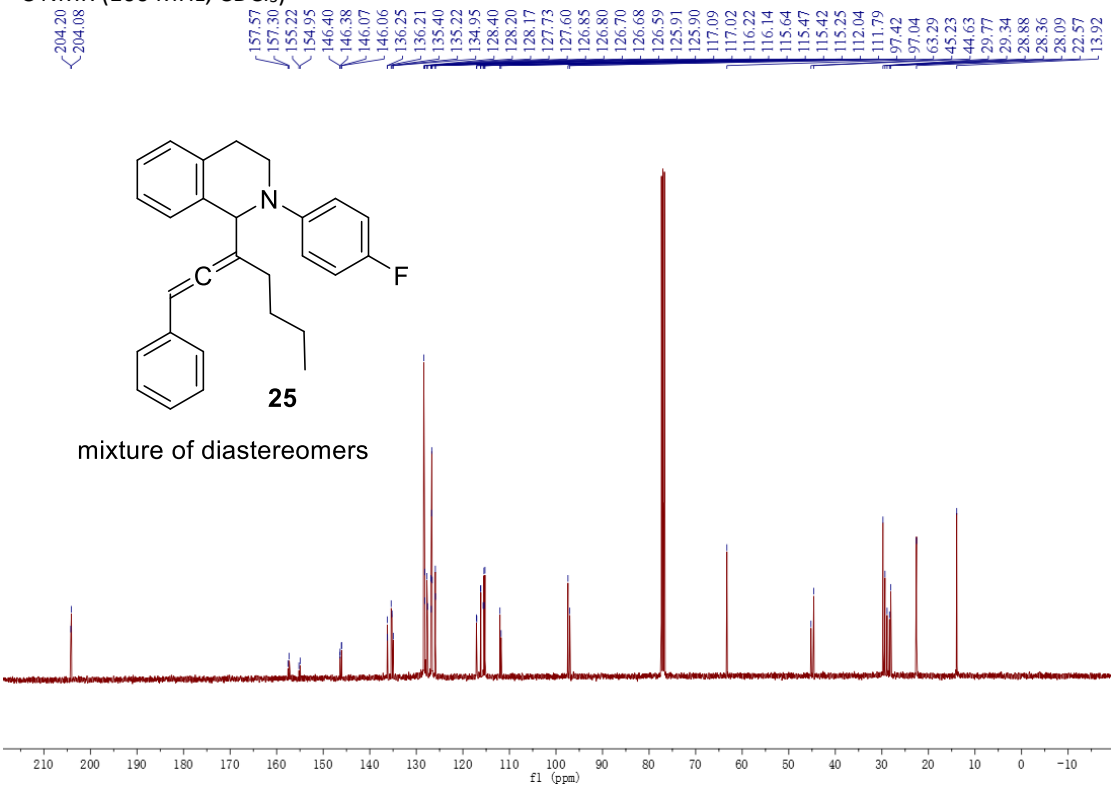
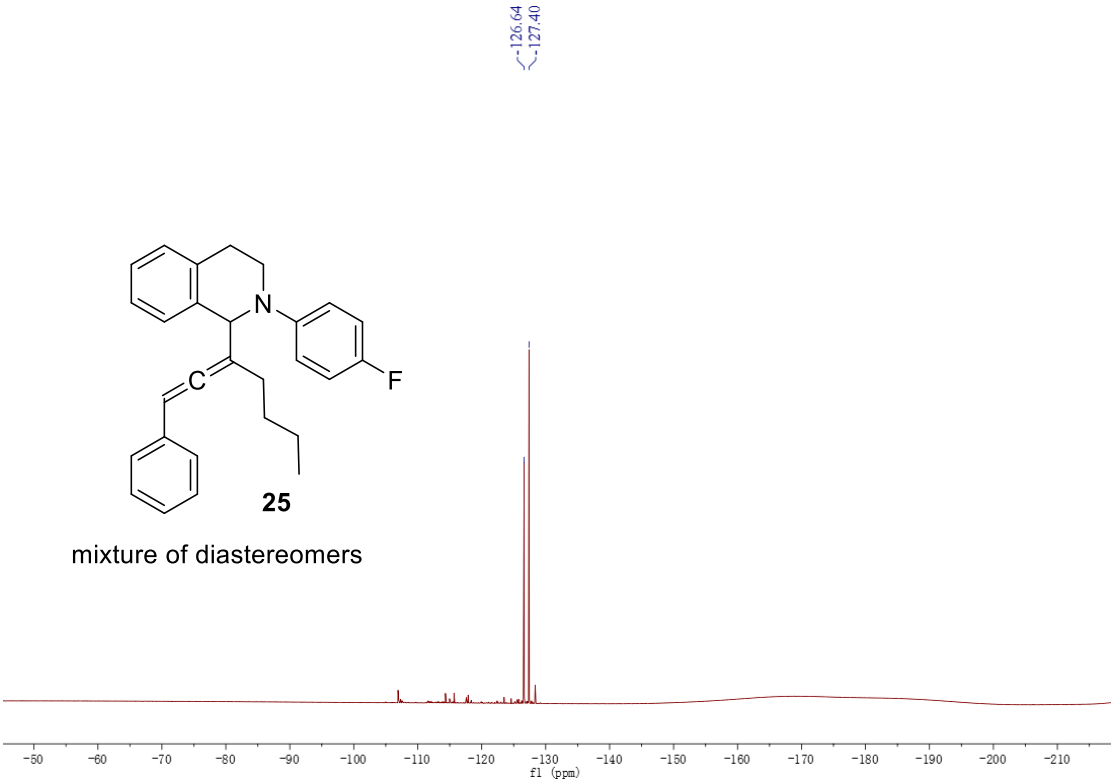


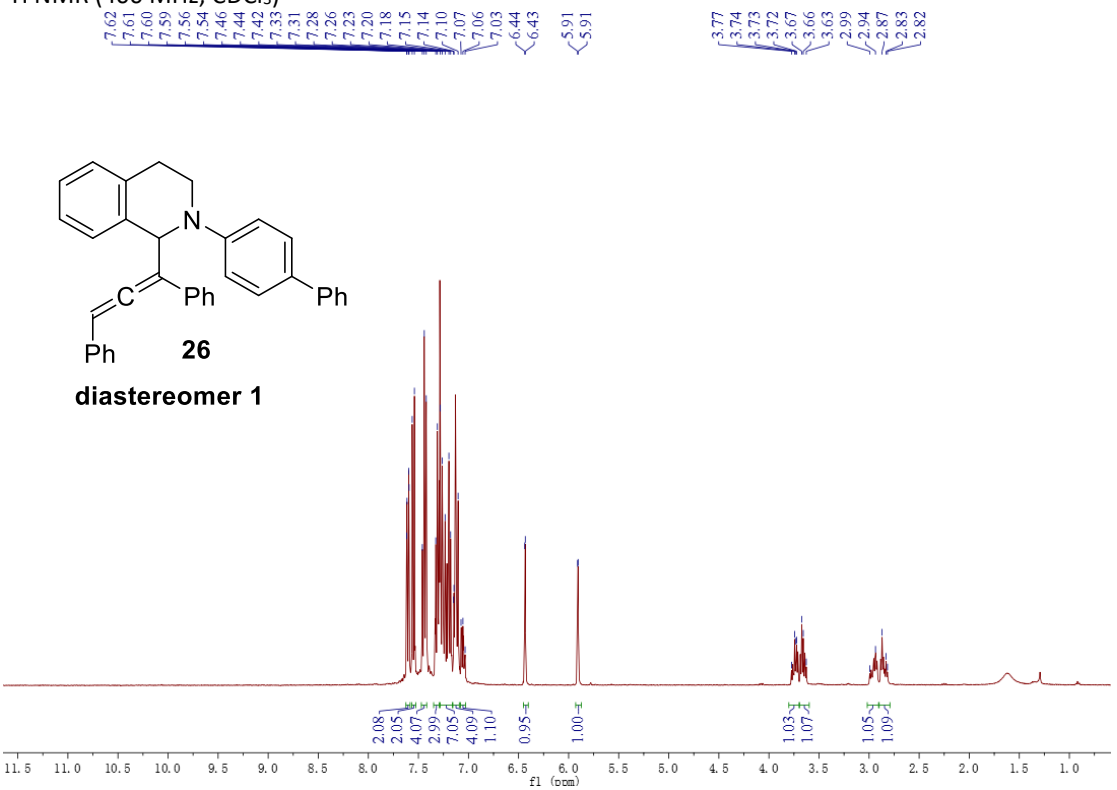
^{13}C NMR (100 MHz, $CDCl_3$)



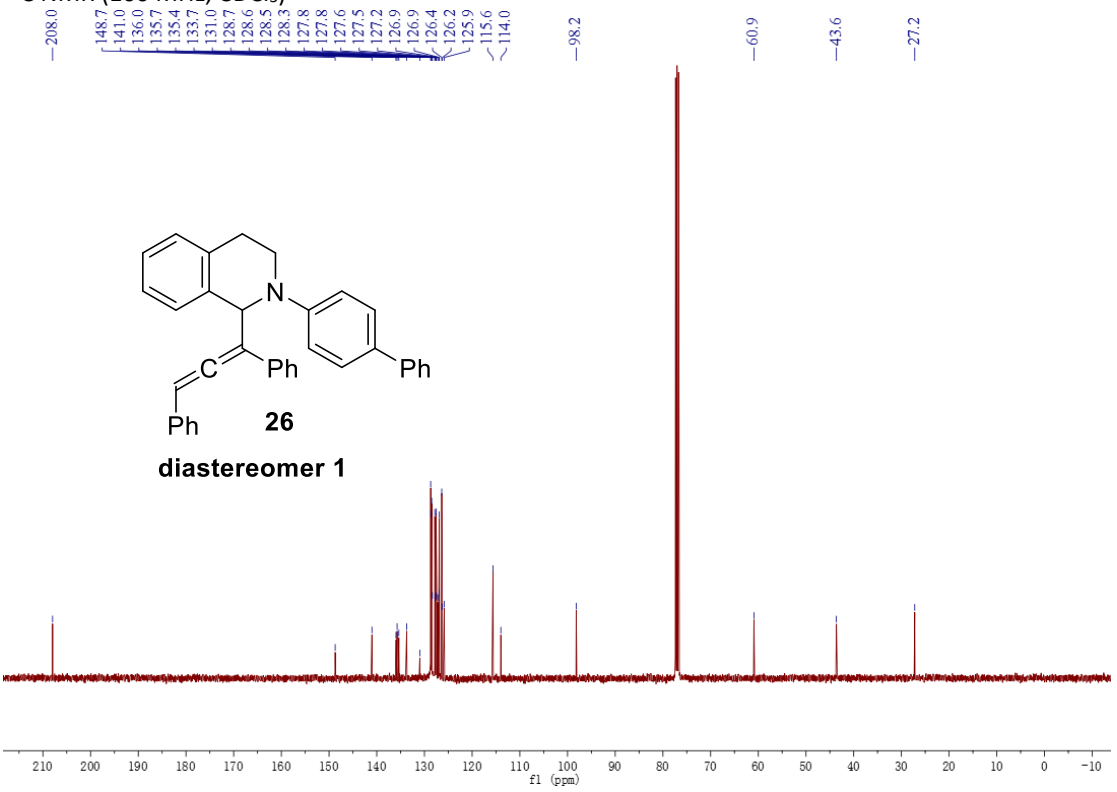
^{19}F NMR (377 MHz, $CDCl_3$)



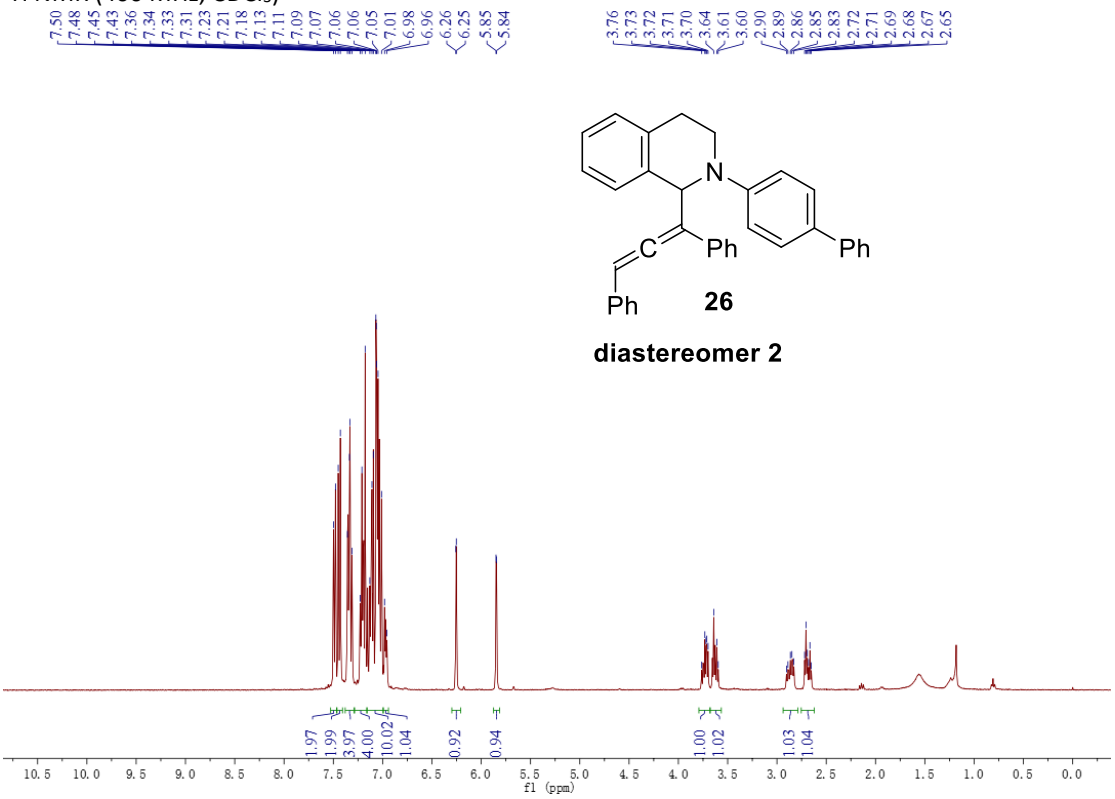
^{1}H NMR (400 MHz, $CDCl_3$)



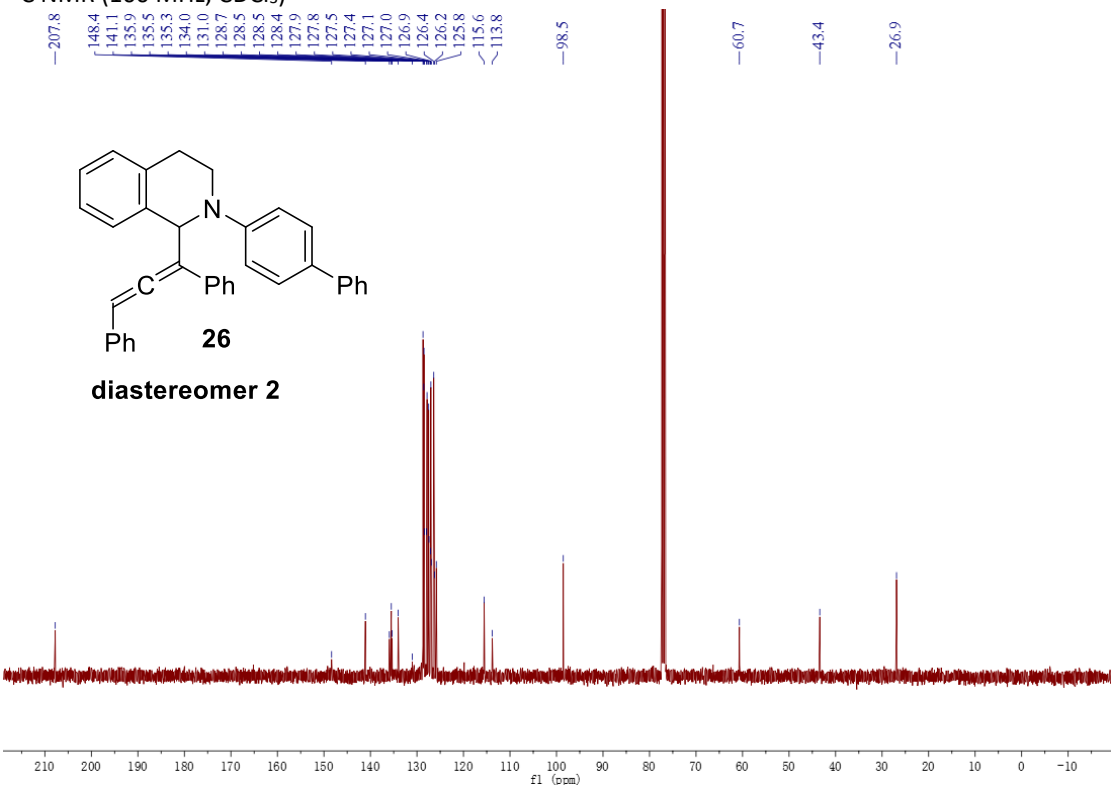
^{13}C NMR (100 MHz, $CDCl_3$)



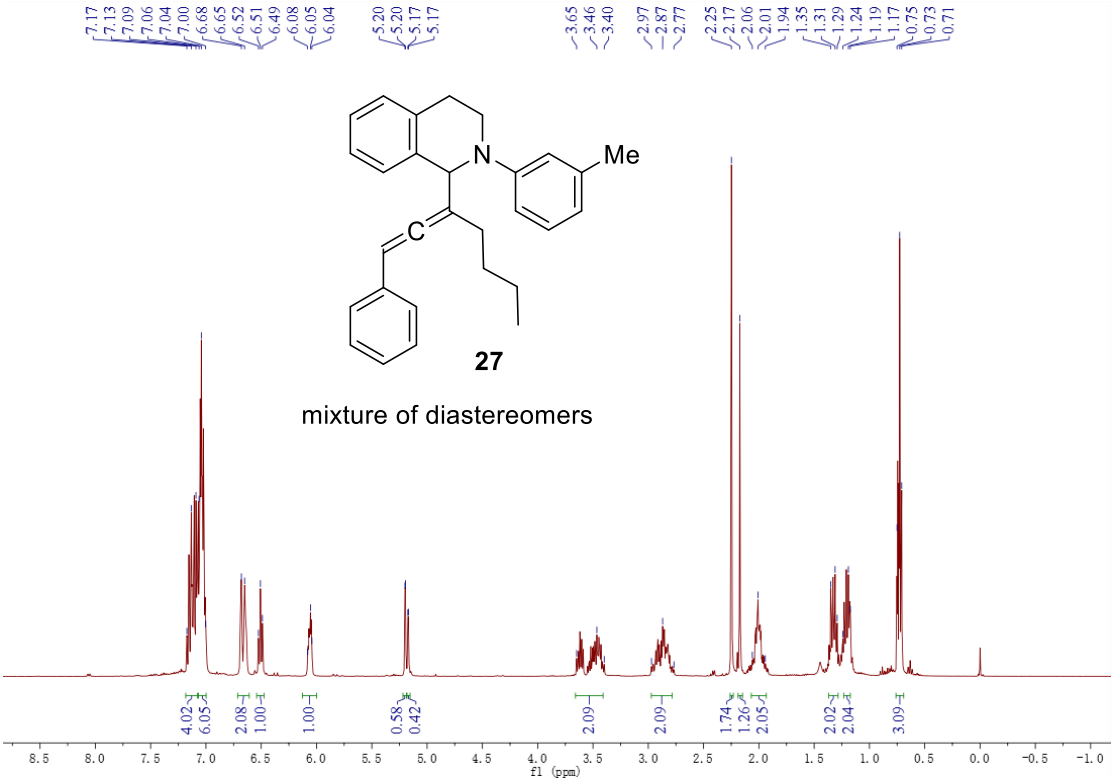
^{1}H NMR (400 MHz, $CDCl_3$)



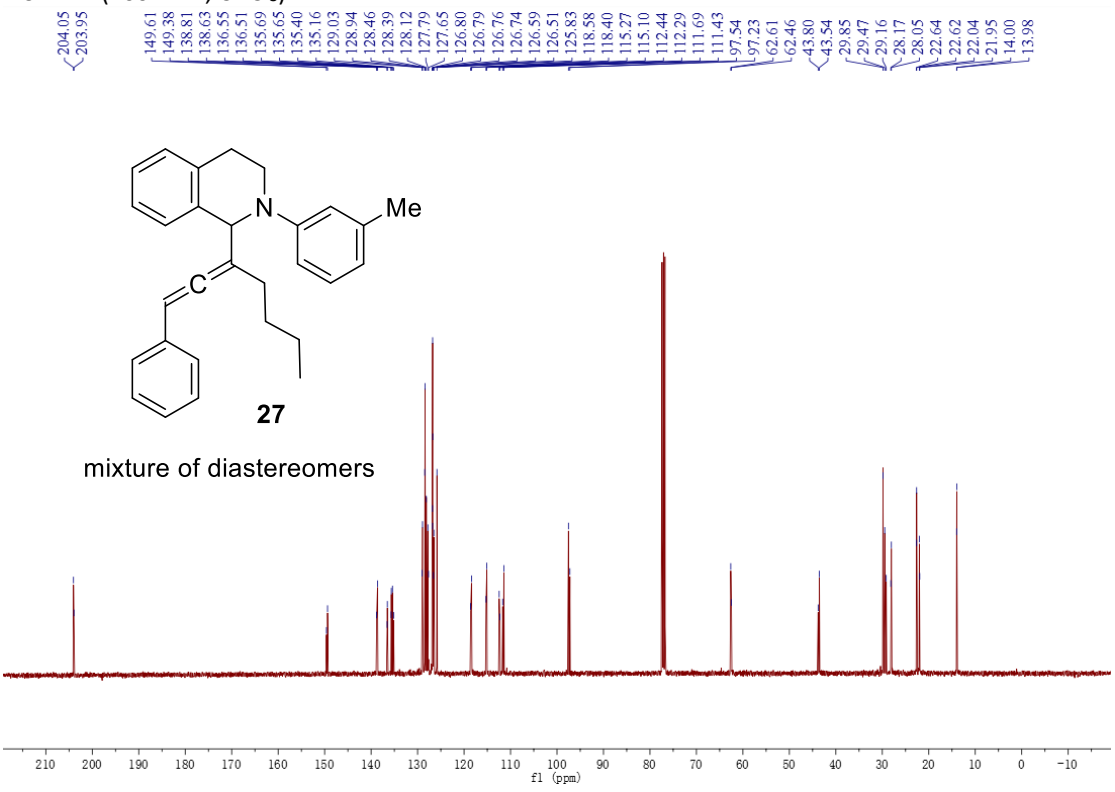
^{13}C NMR (100 MHz, $CDCl_3$)



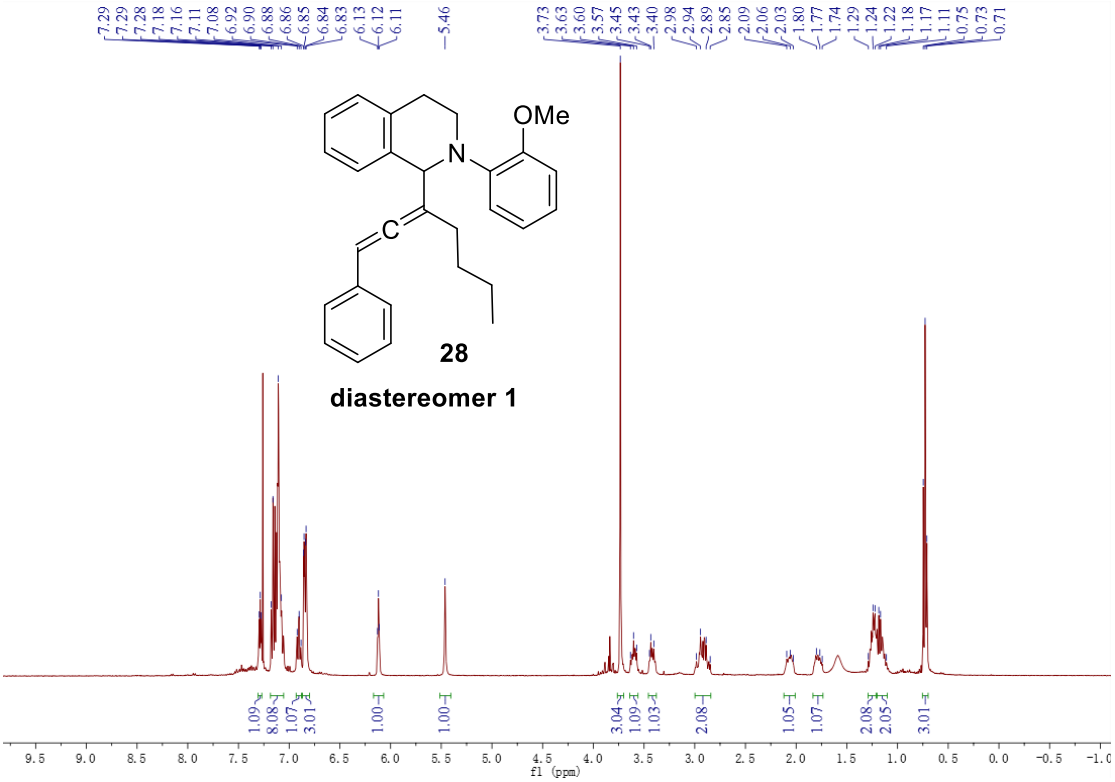
^{1}H NMR (400 MHz, $CDCl_3$)



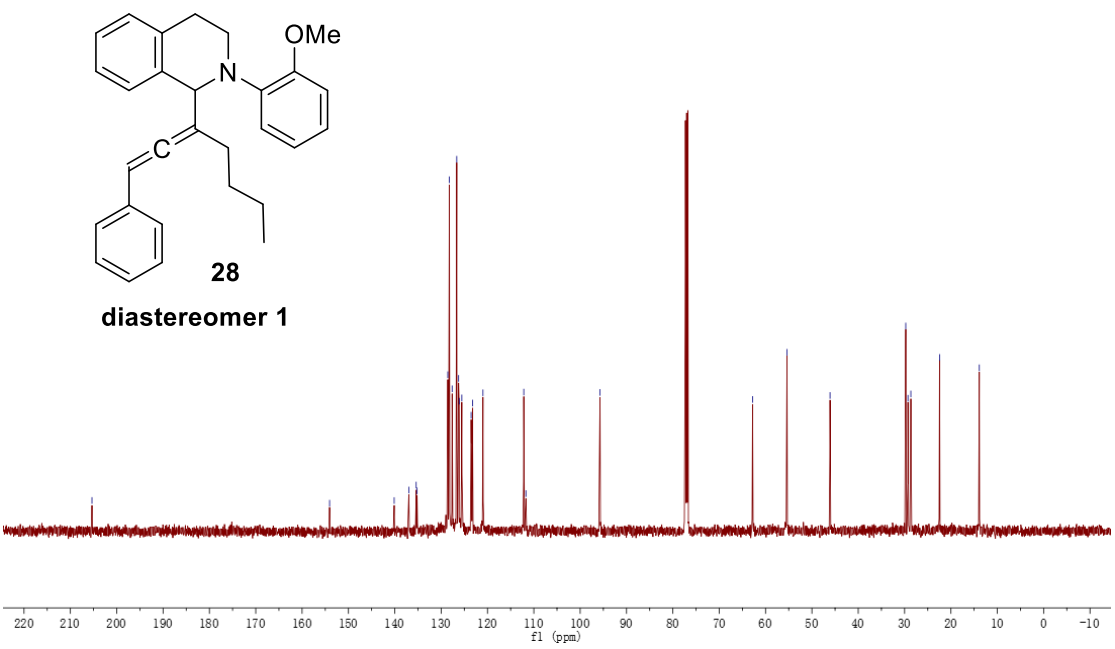
^{13}C NMR (100 MHz, $CDCl_3$)



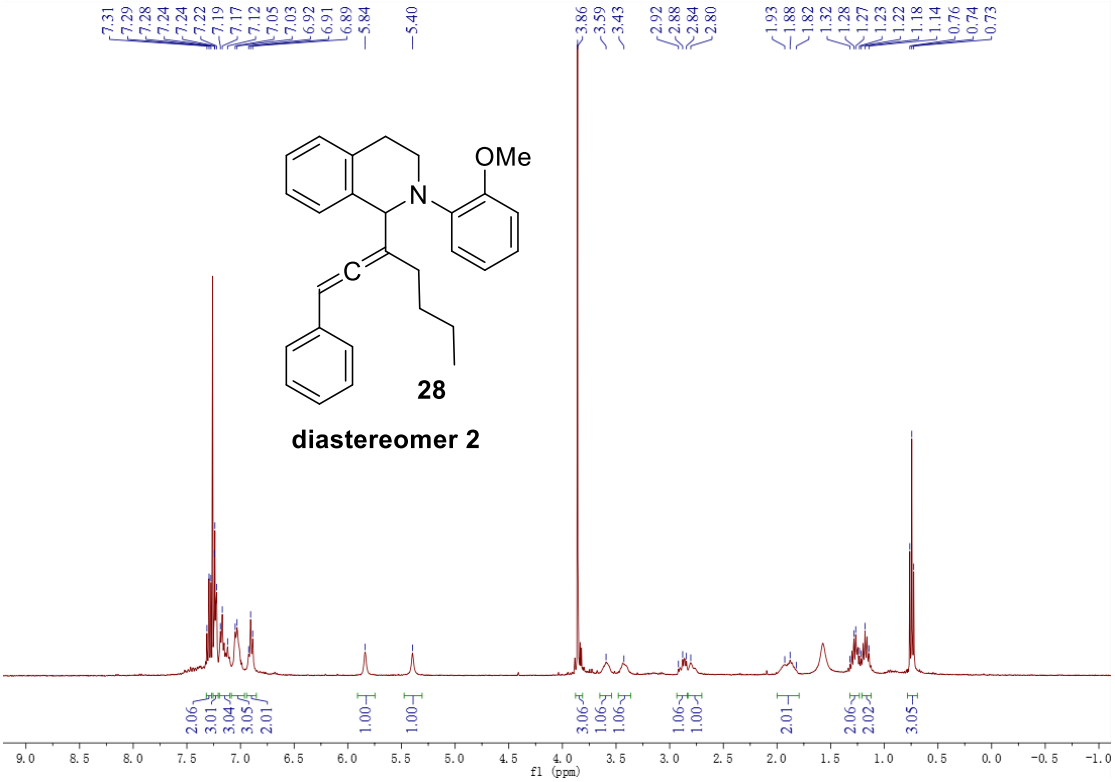
^{1}H NMR (400 MHz, $CDCl_3$)



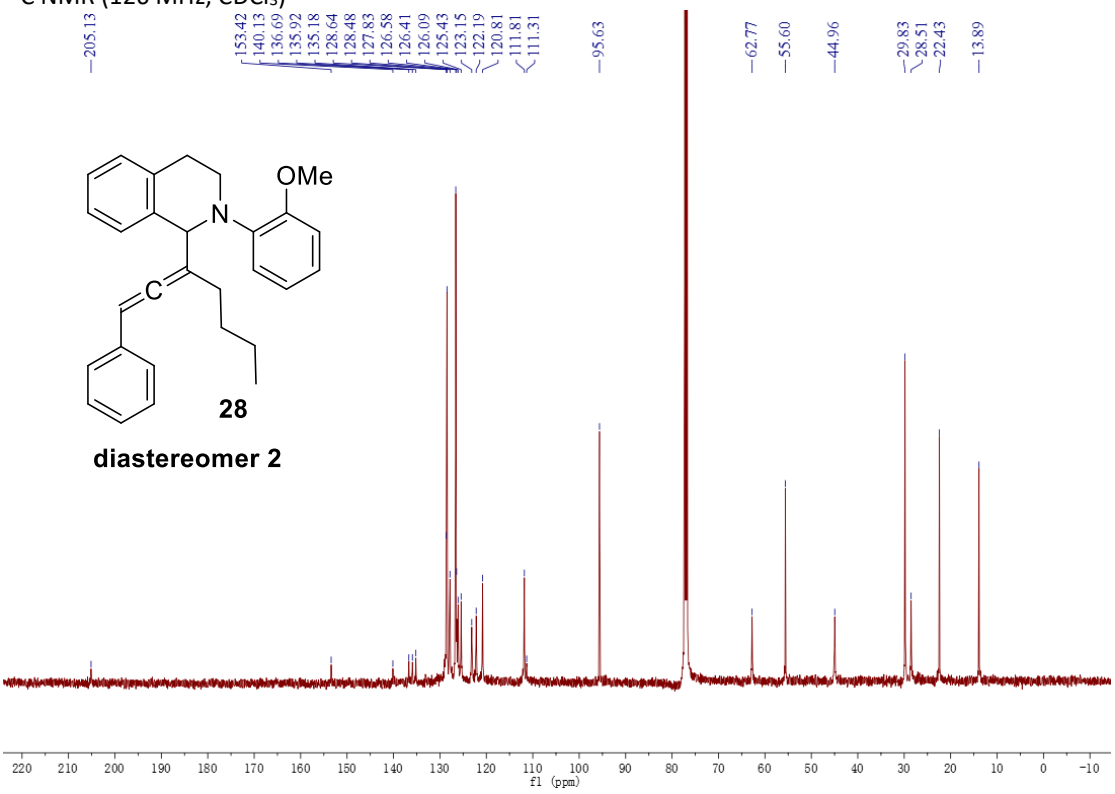
^{13}C NMR (126 MHz, $CDCl_3$)



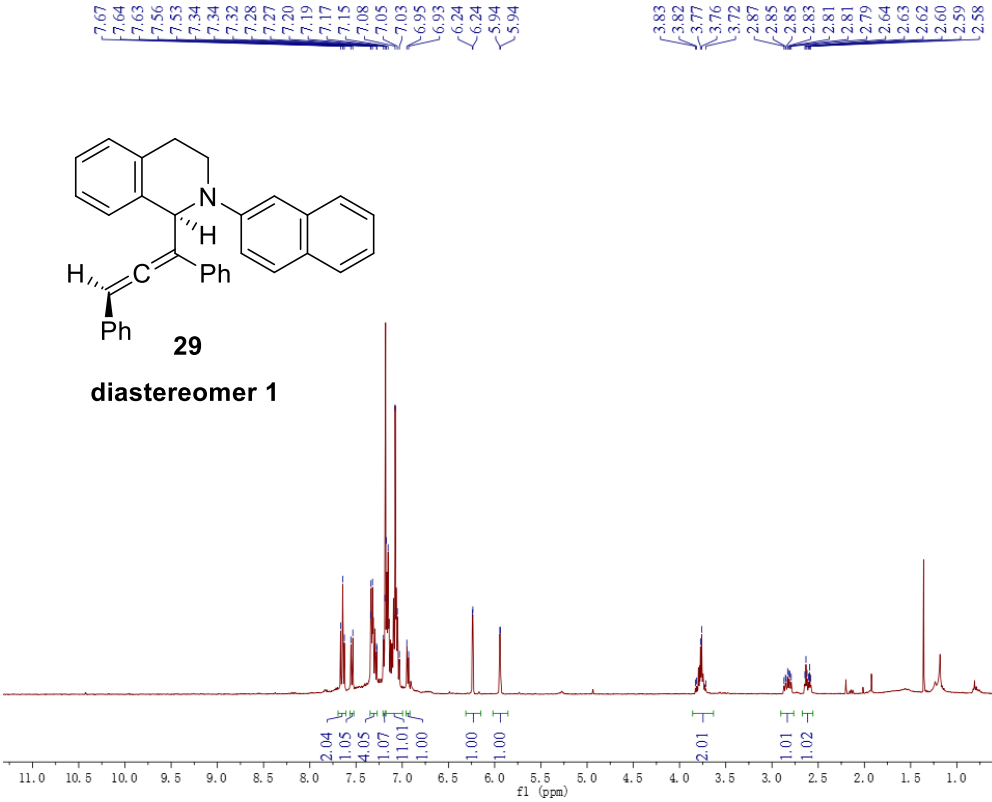
^{1}H NMR (400 MHz, $CDCl_3$)



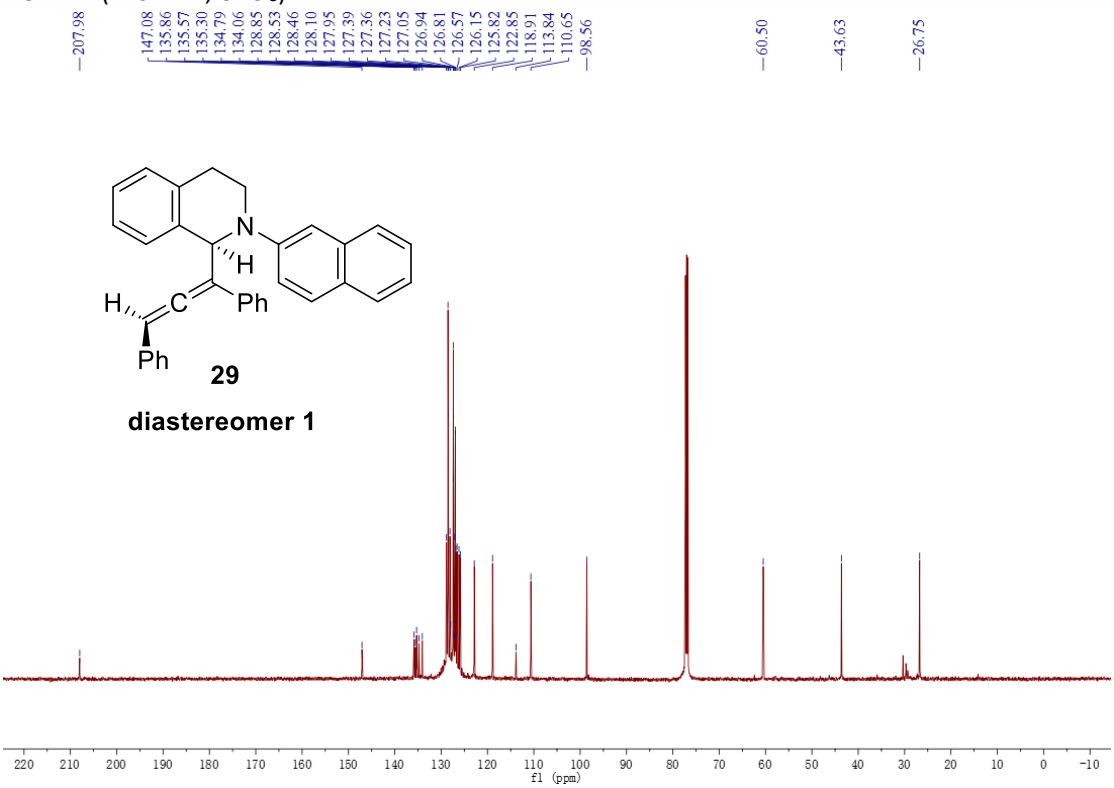
^{13}C NMR (126 MHz, $CDCl_3$)



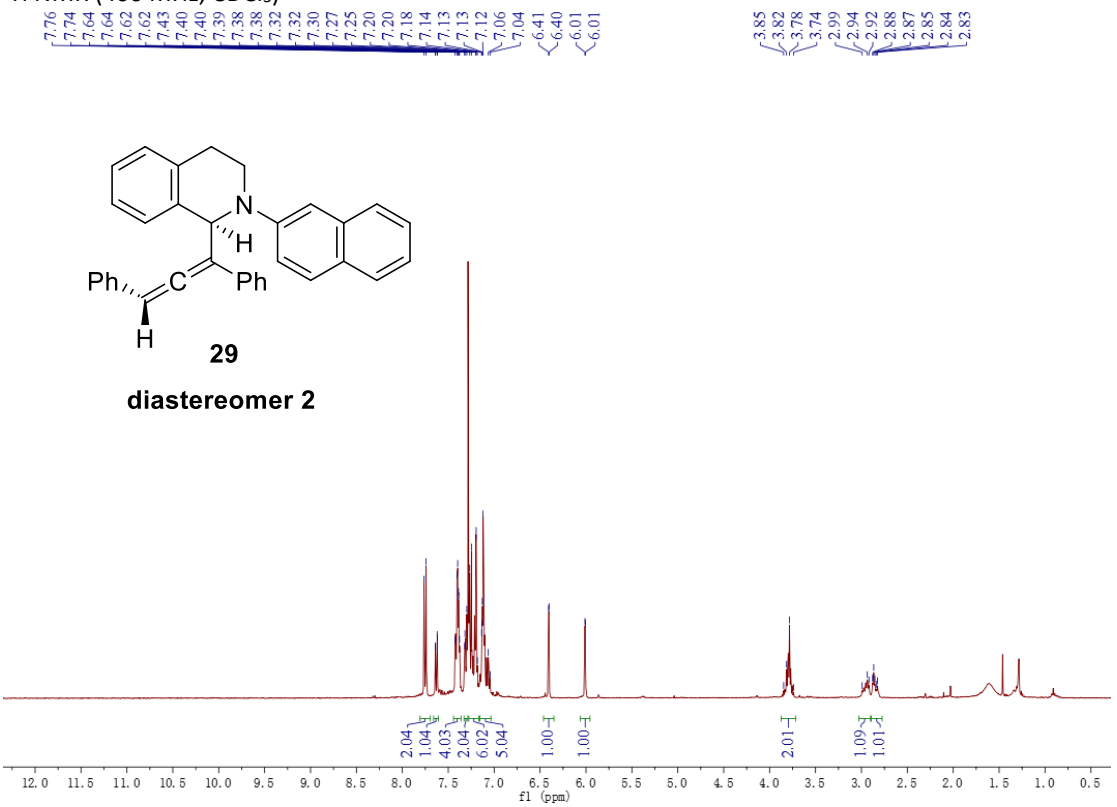
^{1}H NMR (400 MHz, $CDCl_3$)



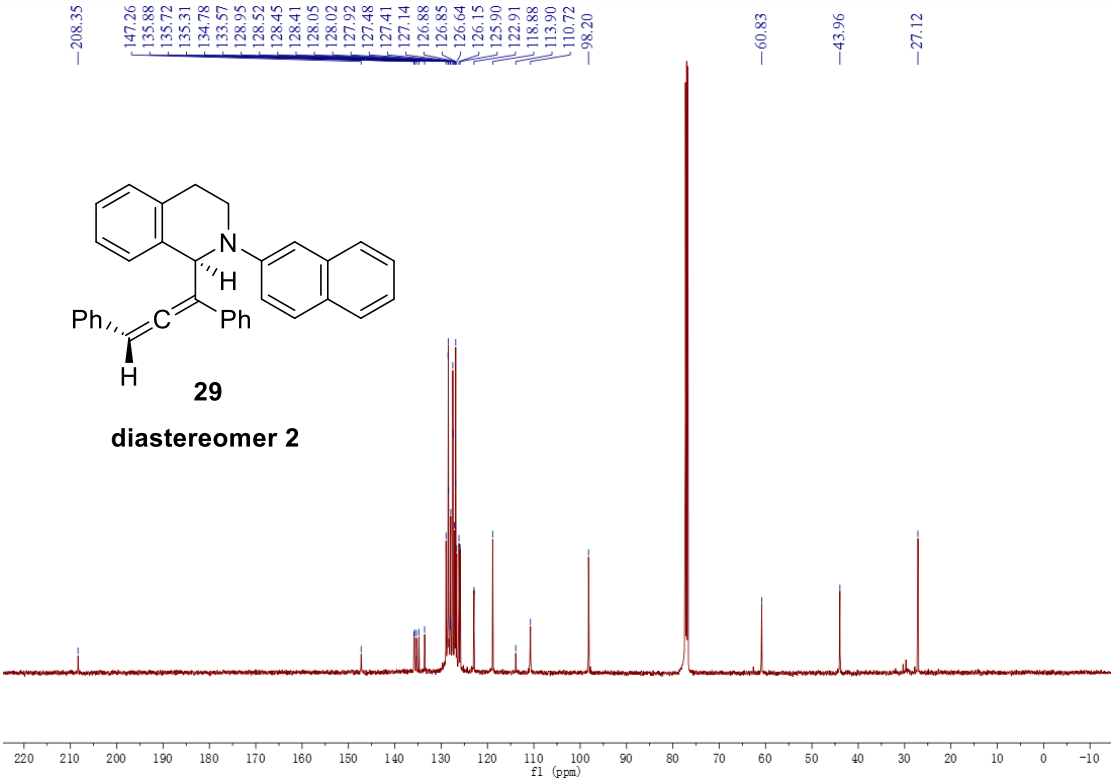
^{13}C NMR (126 MHz, $CDCl_3$)



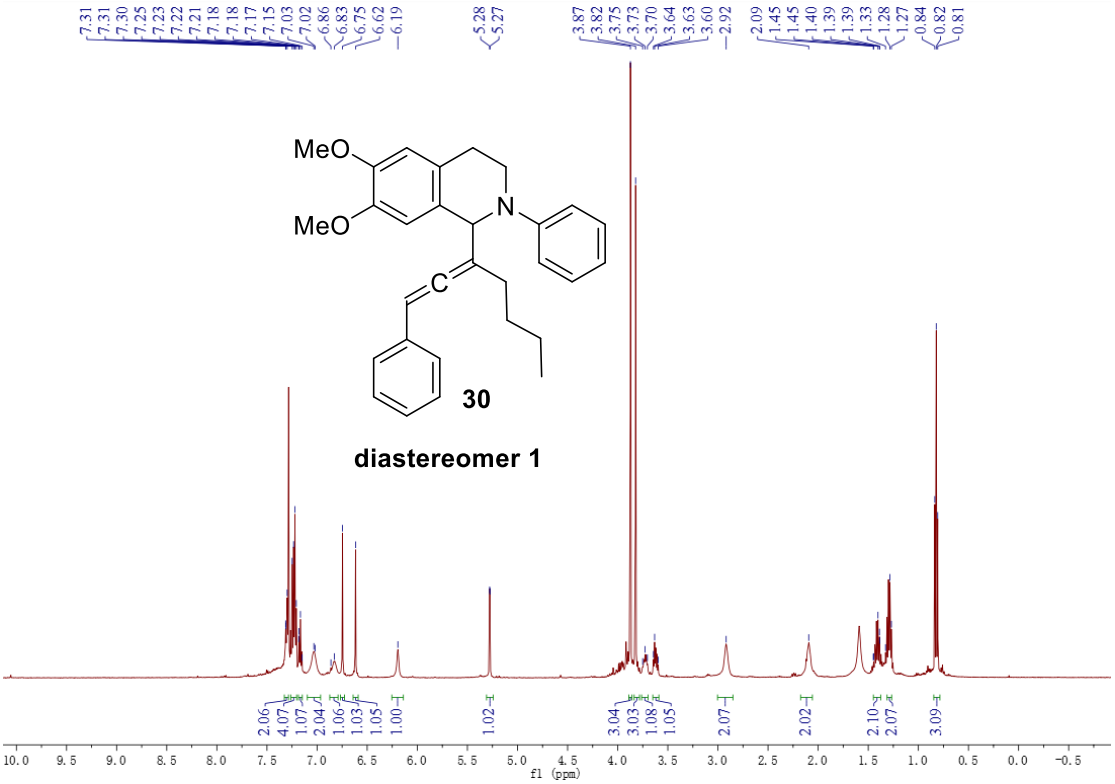
^{1}H NMR (400 MHz, $CDCl_3$)



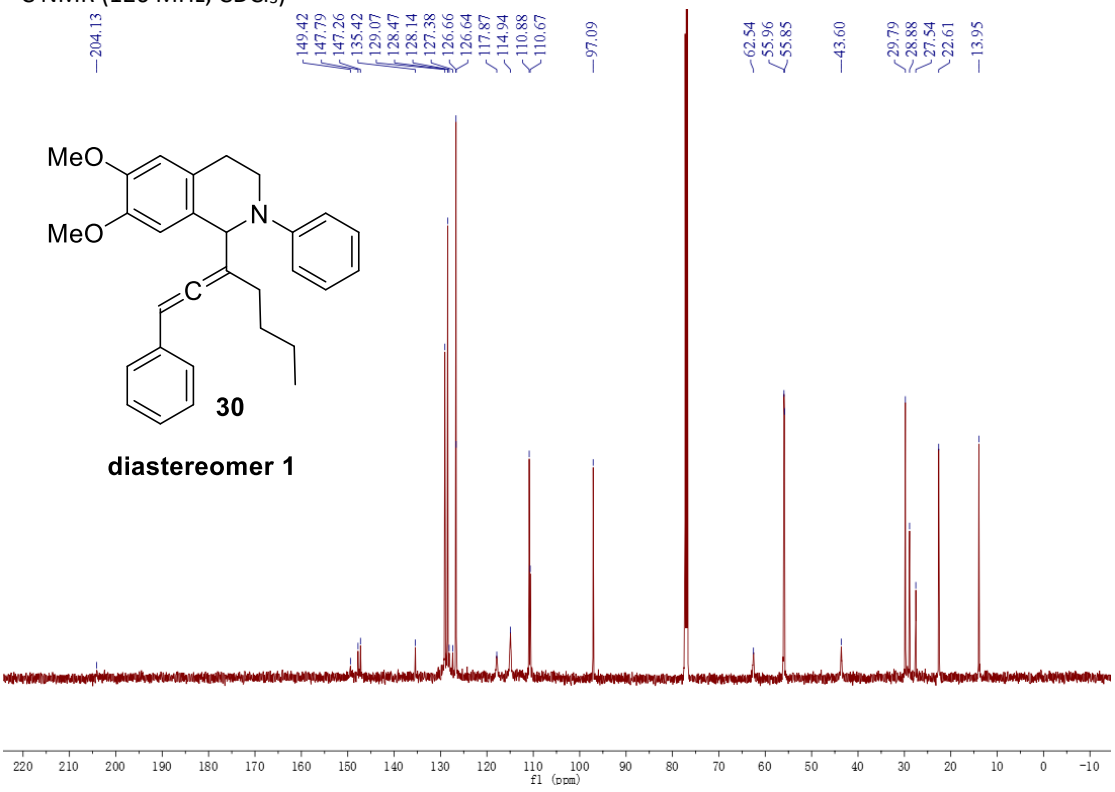
^{13}C NMR (126 MHz, $CDCl_3$)



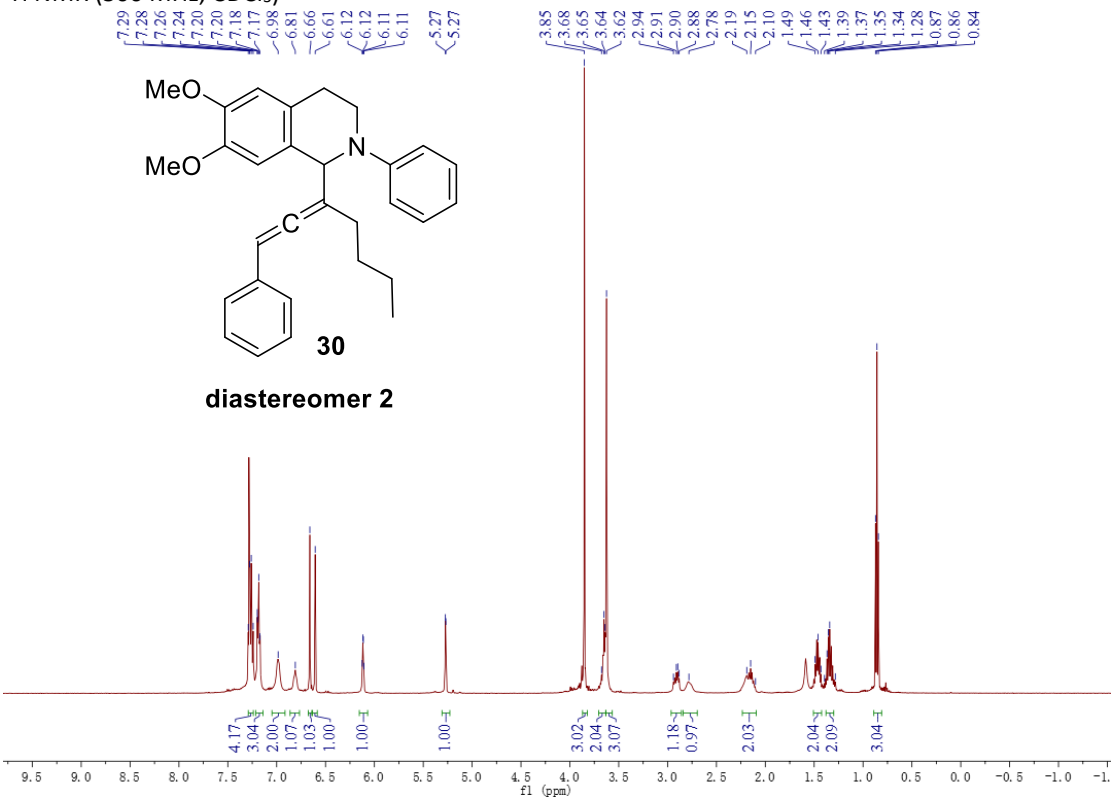
^{1}H NMR (500 MHz, $CDCl_3$)



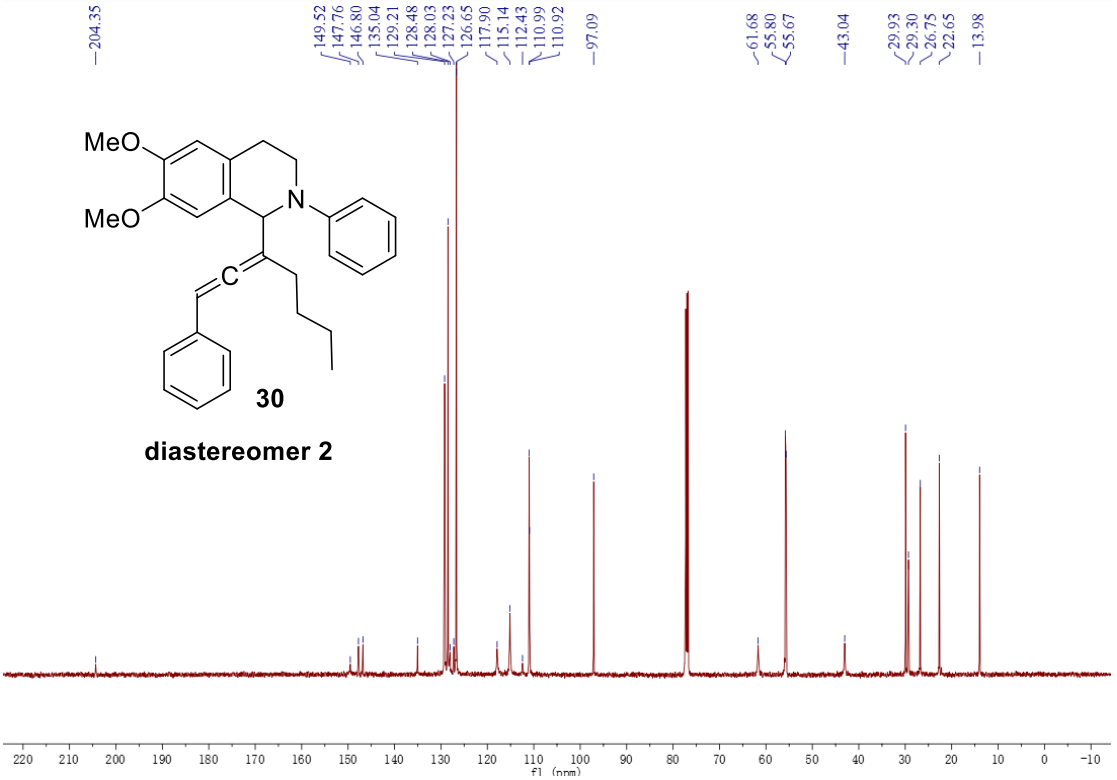
^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)



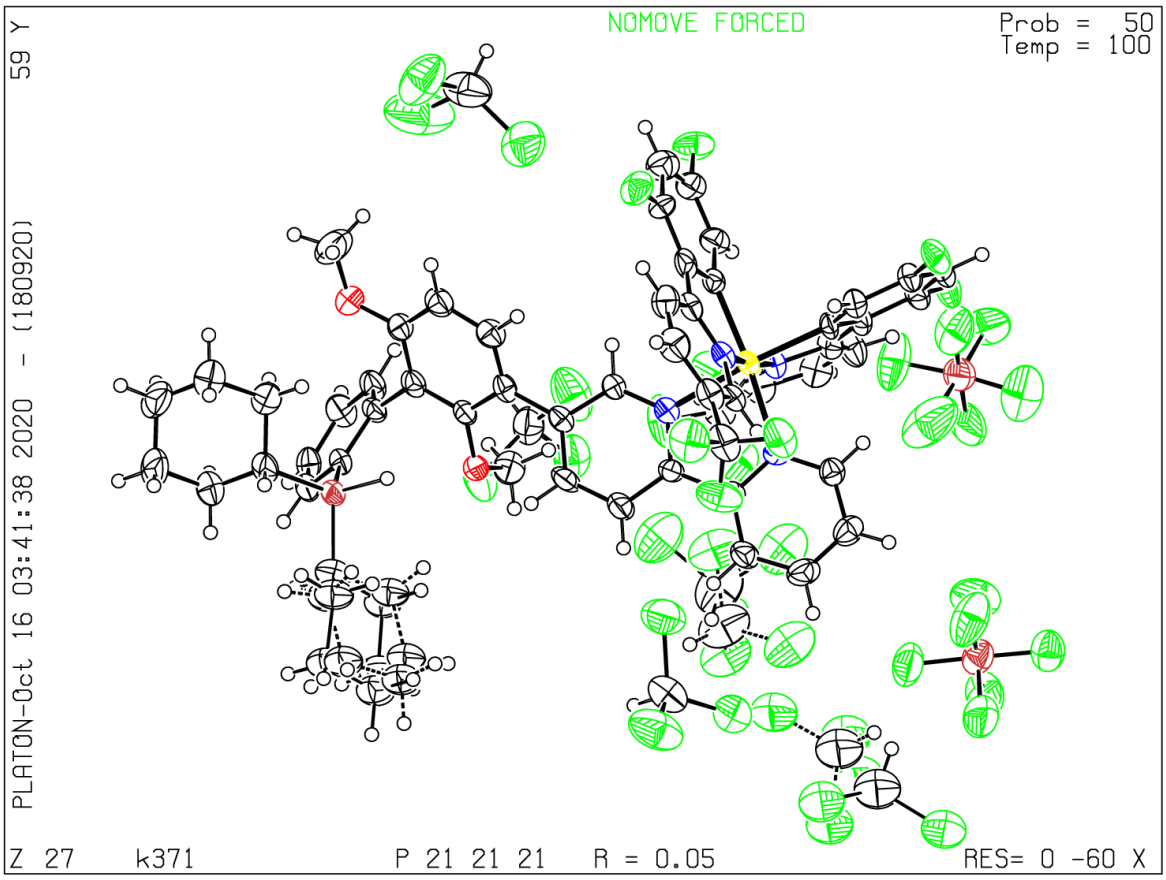
^{13}C NMR (126 MHz, $CDCl_3$)



X-ray crystallography data

Compound **SPhos-PC3**

The .cif data file is attached as a separate document. CCDC Deposition Number **2114578.**



Diastereomer 2 of Compound **29**

The .cif data file is attached as a separate document. CCDC Deposition Number **2114579.**