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Supporting Information

Visible-Light-Promoted Iron-Catalyzed C(sp^2)–C(sp^3) Kumada Cross-Coupling in Flow

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Contents

1: General information

Unless otherwise specified, reagents were obtained from commercial sources and used without further purification.

Thin layer chromatography (TLC) was carried out on silica gel 60 F254 plates (Merck) using reagent grade solvents. Purification of the crude products was conducted by automatic column chromatography using a Biotage® Isolera Four, with Biotage® SNAP KP-Sil 10 or 25 g flash chromatography cartridges.

GC-MS measurements were performed using a 6890 Series Gas Chromatograph (Agilent Technologies) system comprising a 7683 Series injector and auto sampler, J&W HP-5MS column (20 m x 0.18 mm ID, 0.18 μm film thickness) from Agilent Technologies coupled to a 5973N MSD Mass Selective Detector (single quadrupole, Agilent Technologies). The MS detector was configured with an electronic impact ionization /chemical ionization source (EI/CI). EI low-resolution mass spectra were acquired by scanning from 50 to 550 at a rate of 14.29 scan/s. The source temperature was maintained at 230°C. Helium was used as the nebulizer gas.

GC-FID measurements were performed sing a Shimadzu GC-2010 Plus Gas Chromatograph, equipped with a Restek Rtx-1 column (30 m x0.32 mm ID, 0.25 μm film thickness), and coupled with a Shimadzu AOC-20s auto-sampler and AOC-20i auto-injector.

NMR spectra were recorded on Bruker DPX-400 or Bruker AV-500 spectrometers with standard pulse sequences, operating at 400 MHz and 500 MHz respectively. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS), which was used as an internal standard. Spectra were calibrated relative to solvent's residual proton and carbon chemical shift: $CDCl_3$ (δ = 7.27 ppm for ^{1}H NMR and δ = 77.0 ppm for ^{13}C NMR). NMR spectra uses the following abbreviations to describe the multiplicity; s = singlet, brs = broad singlet, d = doublet, t = triplet, m = multiplet, dd = double doublet, td = triple doublet, dt = double triplet, ddd = doublet of doublet of doublets, tt = triplet of triplets.

The reactions were carried out in a Vapourtec photoreactor UV-150 fixed on an E-series Vapourtec equipment with Gen 1 type blue LED with the wavelength of 450 nm, radiant power of 24 W. The reactor used was 2 mL reactor cartridge from Vapourtec.

All microfluidic fittings were purchased from IDEX Health and Science. The syringes were connected to the capillary using 1/16 flat-bottom flangeless fittings. The peristaltic pumps of the Vapourtec system were used to feed liquid reagents through a high purity perfluoroalkoxyalkane (PFA) capillary tubing (ID = 0.8 mm) to a Tefzel® tee mixer (ID = 500 µm).

High resolution mass spectra were recorded on a Finnigan MAT 4200S, a Bruker Daltonics Micro Tof, a Waters-Micromass Quatro LCZ (ESI); peaks are given in m/z.

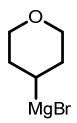
In-line UV-Vis spectra were recorded using Avantes spectrometer AvaSpec 2048 Fiber-optic and AvaLight-DH-S-BAL light source (deuterium lamp). The software employed was the one included with the spectrometer (AvaSoft 8.5). The micro flow Z-cell type is: Micro flow Z-cell-10. The optical path length is 10 mm. A 3D-printed peristaltic pump was employed to pump the reaction mixture through the UV flow cell.

Figure S1: Peristaltic pump developed and produced in-house. Left: rendering of the pump design in Autodesk Inventor; Centre: internal structure of the pump also showing the IDEX tubing adapters, Right: assembled pump showing the NEMA17 motor in the back

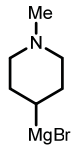
2: General procedure for the synthesis of Grignard reagents in flow (GP1)

The preparation of the Grignard reagent in flow followed the procedure of the previous literature.[1]

Preparation of Mg column: a SolventPlusTM column (bore: 10 mm, length: 100 mm, AF; Omnifit, cat. no. 006EZS-10-10-AF) is filled with 4 g of magnesium (20-230 mesh, Sigma Aldrich Cat. NO.: 254126) weight in a beaker using a filter funnel. General flow procedure for magnesium activation and organomagnesium synthesis: 5 mL of DIBALH 1M in THF was passed through a 10 mm internal diameter Omni-fit column containing Mg (4 g) at 1 mL/min at room temperature. After that, a solution of TMSCl 2.0 M and 1-bromo-2-chloroethane 0.24 M in 10 mL THF was passed through the column at 1 mL/min at room temperature. After the activation, a solution of aliphatic bromide in THF was passed through the column at 0.5 mL/min and at 40 °C. The solution was collected in a sealed vial under nitrogen.



(tetrahydro-2H-pyran-4-yl)magnesium bromide: Prepared according to GP1 starting from 1.21 mL (10.8 mmol) of 4-bromotetrahydro-2H-pyran in 12 mL THF (0.83 M). Titration: An accurately weighed sample of benzoic acid and some crystal of 4-(phenylazo)diphenylamina are dissolved in 1 mL THF and stirred at rt under nitrogen while the Grignard reagent was added slowly. A yellow color formed initially, the end point being indicated by a change of this color to dark red. Concentration = 0.6 M.



(1-methylpiperidin-4-yl)magnesium bromide: Prepared according to GP1 starting from 1.25 g (7 mmol) of 4-bromo-1-methylpiperidine in 8 mL THF (0.88 M). Titration: An accurately weighed sample of benzoic acid and some crystal of 4-(phenylazo)diphenylamina are dissolved in 1 mL THF and stirred at rt under nitrogen while the Grignard reagent was added slowly. A yellow color formed initially, the end point being indicated by a change of this color to dark red. Concentration = 0.7 M.

3: General procedure for the iron-catalyzed Kumada cross-coupling

3.1: General procedure for the Kumada cross-coupling reactions in flow (GP2)

SIPr-HCl (34.2 mg, 4 mol%), dry THF (2 mL), and 3 mL of Grignard reagent (1.5 equiv.) were charged into vial 1 under N_2. The solution was stirred for 10 minutes at rt. $Fe(acac)_3$ (14.1 mg, 2 mol%), chloroarene (2 mmol, 1 equiv), and dry THF (5 mL) were charged into vial 2 under N_2. The two solution were transferred into syringes (5 mL) and loaded onto a syringe pump. The reaction temperature was maintained at 25 °C by the gas flowing through a jar filling with dry ice with the control of the Vapourtec machine. After the reaction was completed (residence time = 5 min), the reaction mixture was collected, quenched with 20 mL 1.0 M HCl solution (for NH-containing substrates, basic NH_4/NH_3 aqueous solution was used to ensure efficient extraction), and extracted with pentane or DCM (3x20 mL), the organic fraction was washed with brine and evaporated. The crude residue was purified by silica gel column chromatography on Biotage with pentane/EtOAc to afford the pure product.

For reactions under irradiation Gen 1 type blue LED (450 nm, 24 W) were used; reactions without light were performed following the same procedure, and analyzed via GC or LC.

3.2: General procedure for the Kumada cross-coupling reactions in flow with *i*PrMgCl as additive (GP3)

SIPr-HCl (128.1 mg, 15 mol%), dry THF, and 0.3 mL isopropylmagnesium chloride (1.0 M in THF, 0.3 equiv.) were charged into vial 1 under N_2. The mixture was stirred until complete dissolution of the solid, then the Grignard reagent (1.5 or 2.5 equiv) was added. The solution was stirred for 10 minutes at rt. $Fe(acac)_3$ (35.3 mg, 5 mol%), chloroarene (2 mmol, 1 equiv), and dry THF (5 mL) were charged into vial 2 under N_2. The two solutions were transferred into syringes (5 mL) and loaded onto a syringe pump. The reaction temperature was maintained at 25 °C by the gas flowing through a jar filling with dry ice with the control of the Vapourtec machine. After the reaction was completed (residence time = 20 min), the reaction mixture was collected, quenched with 20 mL 1.0 M HCl solution (for NH-containing substrates, basic NH_4/NH_3 aqueous solution was used to ensure efficient extraction), and extracted with pentane

(3x20 mL), the organic fraction was washed with brine and evaporated. The crude residue was purified by silica gel column chromatography on Biotage with pentane/EtOAc to afford the pure product.

For reactions under irradiation Gen 1 type blue LED (450 nm, 24 W) were used; reactions without light were performed following the same procedure, and analyzed via LC.

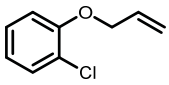
3.3: General procedure for the Kumada cross-coupling reactions in batch (GP4)

SIPr-HCl (128.1 mg, 30 mol%), dry THF (2.5 mL), and 2.5 mL (trimethylsilyl)methylmagnesium chloride (1.0 M in diethyl ether, 2.5 equiv.) were charged into vial 1 under N_2. After stirring for several minutes, a lot of white solid was formed. $Fe(acac)_3$ (35.3 mg, 10 mol%), 1-chloro-4-methoxybenzene or 5-chloro-1H-indole (2 mmol, 1 equiv), and 5 mL THF were charged into vial 2 under N_2. As the mixture in vial 1 gave a lot of white solid upon stirring, flow experiments were not possible in these cases. The solution in vial 2 was therefore added into vial 1, which was placed in front of two 34 W blue LED. After 4 h irradiation, the reaction mixture was quenched with 20 mL 1.0 M HCl solution (for 1-chloro-4-methoxybenzene) or basic $NH_4Cl/NH_3.H_2O$ aqueous solution (for 5-chloro-1H-indole), and extracted with pentane (3x20 mL), the organic fraction was washed with brine and evaporated. The crude residue was purified by silica gel column chromatography on Biotage with pentane/EtOAc to afford the pure product.

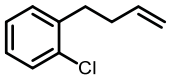
For reactions under irradiation blue LED (450 nm, 34 W) were used; reactions without light were performed following the same procedure, and analyzed via GC or LC.

4: Preparation of the starting materials for radical clock experiments

The substrates for the radical clock reactions, 1-(allyloxy)-2-chlorobenzene and 1-(but-3-en-1-yl)-2-chlorobenzene, were prepared according to the literature. [2,3]

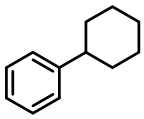


1-(allyloxy)-2-chlorobenzene. The title compound was prepared according to the literature.[2] Purification: column chromatography (pentane). Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.22 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.03 (ddd, *J* = 8.3, 7.4, 1.6 Hz, 1H), 6.78 – 6.68 (m, 2H), 5.91 (ddd, *J* = 12.2, 10.5, 5.3 Hz, 1H), 5.41 – 5.26 (m, 1H), 5.15 (dq, *J* = 10.5, 1.5 Hz, 1H), 4.43 (dt, *J* = 5.1, 1.7 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ: 153.91, 132.52, 130.12, 127.48, 122.79, 121.32, 117.54, 113.58, 69.38.

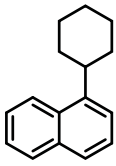


1-(but-3-en-1-yl)-2-chlorobenzene. The title compound was prepared according to the literature.[3] Purification: column chromatography (pentane). Colorless oil. **^{1} H NMR** (400 MHz, $CDCl_3$): δ 7.28 (dd, J = 7.7, 1.4 Hz, 1H), 7.20 – 7.00 (m, 3H), 5.87-5.77 (m, 1H), 5.01 (dd, J = 17.1, 1.7 Hz, 1H), 4.95 (dd, J = 10.1, 1.6 Hz, 1H), 2.77 (dd, J = 9.0, 6.7 Hz, 2H), 2.47 – 1.99 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 139.32, 137.68, 133.91, 130.37, 129.42, 127.28, 126.63, 115.12, 33.68, 33.07.

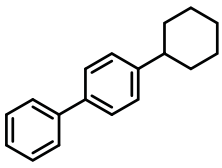
5: Characterization of the compounds



Cyclohexylbenzene (3ab)[4]: The title compound was prepared according to general procedure **GP2**. Solution 1: chlorobenzene (225.1 mg, 2.0 mmol, 1.0 equiv), $Fe(acac)_3$ (14.2 mg, 2 mol%) in dry THF (5.0 mL); Solution 2: SIPr-HCl (34.2 mg, 4 mol%), cyclohexylmagnesium chloride (3.0 mL, 1.5 equiv.) in dry THF (2.0 mL) at 25 °C with 5 minutes residence time. Purification via chromatography (pentane, 100%) gave the desired product **3ab** as colorless oil in 91% yield (291.7 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = δ 7.35-7.31(m, 2H), 7.26-7.21(m, 3H), 2.57-2.51(m, 1H), 1.95-1.85(m, 4H), 1.82-1.77(m, 1H), 1.54-1.28(m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ148.06, 128.24, 126.79, 125.73, 44.59, 34.36, 26.92, 26.17.

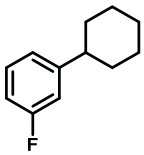


1-Cyclohexylnaphthalene (3bb)[5]: The title compound was prepared according to general procedure **GP2.** Solution 1: 1-chloronaphthalene (324.0 mg, 2.0 mmol, 1.0 equiv), $Fe(acac)_3$ (14.2 mg, 2 mol%) in dry THF (5.0 mL); Solution 2: SIPr-HCl (34.2 mg, 4 mol%), cyclohexylmagnesium chloride (3.0 mL, 1.5 equiv.) in dry THF (2.0 mL) at 25 °C with 5 minutes residence time. Purification via chromatography (pentane, 100%) gave the desired product **3bb** as colorless oil in 83% yield (348.8 mg). **^{1} H NMR** (400 MHz, $CDCl_3$): δ 8.19(d, *J* = 4.0 Hz, 1H), 7.91(d, *J* = 8.0 Hz, 1H), 7.76-7.74(m, 1H), 7.58-7.44 (m, 4H), 3.40-3.39(m, 1H), 2.12-2.09 (m, 2H), 2.01-1.97 (m, 2H), 1.93-1.89 (m, 1H), 1.63 (dd, *J* = 11.4, 8.4 Hz, 4H), 1.41 (tdt, *J* = 12.8, 9.2, 3.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ143.78, 133.92, 131.34, 128.91, 128.89, 126.19, 125.63, 125.55, 123.18, 122.24, 39.28, 34.22, 27.29, 26.55.

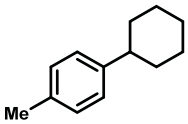


4-Cyclohexyl-1,1'-biphenyl (3cb)[6]: The title compound was prepared according to general procedure **GP2.** Solution 1: 4-chloro-1,1'-biphenyl (376.1 mg, 2.0 mmol, 1.0 equiv), $Fe(acac)_3$ (14.2 mg, 2 mol%) in dry THF (5.0 mL); Solution 2: SIPr-HCl (34.2 mg, 4 mol%), cyclohexylmagnesium chloride (3.0 mL, 1.5 equiv.) in dry THF (2.0 mL) at 25 °C with 5 minutes residence time. Purification via chromatography (pentane, 100%) gave the desired product **3cb** as white solid in 90% yield (425.1 mg). Melting point: 75.3 °C. **^{1} H NMR** (400 MHz, $CDCl_3$): δ 7.61-7.58 (m,

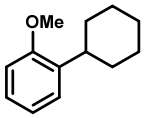
2H), 7.55-7.53(m, 2H), 7.46-7.42(m, 2H), 7.35-7.31(m, 1H), 7.30-7.29(m, 2H), 2.59-2.53(m, 1H), 1.96-1.86(m, 4H), 1.81-1.76(m, 1H), 1.53-1.25 (m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ147.22, 141.18, 138.71, 128.66, 127.21, 127.02, 127.00, 126.91, 44.24, 34.47, 26.92, 26.17.



1-Cyclohexyl-3-fluorobenzene (3db)[7]: The title compound was prepared according to general procedure **GP2.** Solution 1: 1-chloro-3-fluorobenzene (260.0 mg, 2.0 mmol, 1.0 equiv), $Fe(acac)_3$ (14.2 mg, 2 mol%) in dry THF (5.0 mL); Solution 2: SIPr-HCl (34.2 mg, 4 mol%), cyclohexylmagnesium chloride (3.0 mL, 1.5 equiv.) in dry THF (2.0 mL) at 25 °C with 5 minutes residence time. Purification via chromatography (pentane, 100%) gave the desired product **3db** as colorless oil in 88% yield (313.5 mg). **^{1} H NMR** (400 MHz, $CDCl_3$): δ 7.32-7.29 (m, 1H), 7.04 (d, *J* = 4.0 Hz, 1H), 6.99-6.90 (m, 2H), 2.61-2.53 (m, 1H), 1.98-1.92 (m, 4H), 1.85- 1.78 (m, 1H), 1.49-1.27(m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ162.97 (d, *J* = 244.6 Hz), 150.74 (d, *J* = 6.7 Hz), 129.56 (d, *J* = 8.3 Hz), 122.48 (d, *J* = 2.6 Hz), 113.57 (d, *J* = 20.9 Hz), 112.49 (d, *J* = 21.0 Hz), 44.34 (d, *J* = 1.7 Hz), 34.29, 26.77, 26.07. **^{19}F NMR** (126 MHz, $CDCl_3$): -113.91.

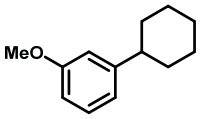


1-Cyclohexyl-4-methylbenzene (3eb)[8]: The title compound was prepared according to general procedure **GP2.** Solution 1: 1-chloro-4-methylbenzene (252.0 mg, 2.0 mmol, 1.0 equiv), $Fe(acac)_3$ (14.2 mg, 2 mol%) in dry THF (5.0 mL); Solution 2: SIPr-HCl (34.2 mg, 4 mol%), cyclohexylmagnesium chloride (3.0 mL, 1.5 equiv.) in dry THF (2.0 mL) at 25 °C with 5 minutes residence time. Purification via chromatography (pentane, 100%) gave the desired product **3eb** as colorless oil in 99% yield (344.8 mg). **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K): δ 7.14 (s, 4H), 2.53 – 2.46 (m, 1H), 2.35(s, 3H), 1.94 – 1.84 (m, 4H), 1.79 – 1.75 (m, 1H), 1.54 – 0.89 (m, 5H). **^{13}C NMR** (101 MHz, CDCl3): δ 145.13, 135.14, 128.94, 126.66, 44.16, 34.58, 26.95, 26.19, 20.96.

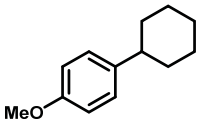


1-Cyclohexyl-2-methoxybenzene (3fb)[9]: The title compound was prepared according to general procedure **GP2.** Solution 1: 1-chloro-2-methoxybenzene (285.2 mg, 2.0 mmol, 1.0 equiv), $Fe(acac)_3$ (14.2 mg, 2 mol%) in dry THF (5.0 mL); Solution 2: SIPr-HCl (34.2 mg, 4 mol%), cyclohexylmagnesium chloride (3.0 mL, 1.5 equiv.) in dry THF (2.0 mL) at 25 °C with 5 minutes residence time. Purification via

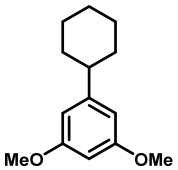
chromatography (pentane, 100%) gave the desired product **3fb** as colorless oil in 89% yield (338.4 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.22-7.15 (m, 2H), 6.94(t, *J* = 8.0 Hz, 1H), 6.87(d, *J* = 8.0 Hz, 1H), 3.84(s, 3H), 3.01-2.95(m, 1H), 1.86-1.75(m, 5H), 1.47-1.25(m, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.70, 136.25, 126.51, 126.42, 120.53, 110.35, 100.36, 55.37, 36.76, 33.22, 27.11, 26.45.



1-Cyclohexyl-3-methoxybenzene (3gb)[10]: The title compound was prepared according to general procedure **GP2.** Solution 1: 1-chloro-3-methoxybenzene (285.2 mg, 2.0 mmol, 1.0 equiv), $Fe(acac)_3$ (14.2 mg, 2 mol%) in dry THF (5.0 mL); Solution 2: SIPr-HCl (34.2 mg, 4 mol%), cyclohexylmagnesium chloride (3.0 mL, 1.5 equiv.) in dry THF (2.0 mL) at 25 °C with 5 minutes residence time. Purification via chromatography (pentane, 100%) gave the desired product **3gb** as colorless oil in 85% yield (323.2 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.22 (t, *J* = 8.0 Hz, 1H), 6.84 – 6.73 (m, 3H), 3.82 (s, 3H), 2.53 – 2.46 (m, 1H), 1.92 – 1.83 (m, 4H), 1.78 – 1.74 (m, 1H), 1.45 – 1.24 (m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ159.58, 149.84, 129.16, 129.29, 112.79, 110.82, 55.11, 44.67, 34.41, 26.89, 26.17.

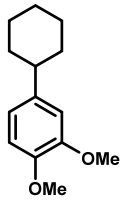


1-Cyclohexyl-4-methoxybenzene (3hb)[5]: The title compound was prepared according to general procedure **GP2.** Solution 1: 1-chloro-4-methoxybenzene (285.2 mg, 2.0 mmol, 1.0 equiv), $Fe(acac)_3$ (14.2 mg, 2 mol%) in dry THF (5.0 mL); Solution 2: SIPr-HCl (34.2 mg, 4 mol%), cyclohexylmagnesium chloride (3.0 mL, 1.5 equiv.) in dry THF (2.0 mL) at 25 °C with 5 minutes residence time. Purification via chromatography (pentane, 100%) gave the desired product **3hb** as white solid in 93% yield (353.7 mg). Melting point: 58.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.14 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 3.80 (s, 3H), 2.50 – 2.42 (m, 1H), 1.89 – 1.83 (m, 4H), 1.78 – 1.72 (m, 1H), 1.46 – 1.22 (m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ157.63, 140.37, 127.60, 113.64, 103.38, 55.23, 43.68, 34.72, 26.96, 26.18.

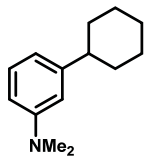


1-Cyclohexyl-3,5-dimethoxybenzene (3ib): The title compound was prepared according to general procedure **GP2.** Solution 1: 1-chloro-3,5-dimethoxybenzene (344.0 mg, 2.0 mmol, 1.0 equiv), $Fe(acac)_3$ (35.3 mg, 5

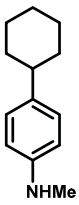
mol%) in dry THF (5.0 mL); Solution 2: SIPr-HCl (85.4 mg, 10 mol%), cyclohexylmagnesium chloride (3.0 mL, 1.5 equiv.) in dry THF (2.0 mL) at 25 °C with 20 minutes residence time. Purification via chromatography (pentane, 100%) gave the desired product **3ib** as colorless oil in 71% yield (312.2 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.44 (d, *J* = 2.3 Hz, 2H), 6.35 (d, *J* = 2.3 Hz, 1H), 3.82 (s, 6H), 2.49(m, 1H), 1.95-1.87(m, 4H), 1.82-1.76(m, 1H), 1.51-1.27 (m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 160.63, 150.57, 104.94, 97.57, 55.08, 44.93, 34.30, 26.82, 26.11. **HRMS** (ESI) (m/z): $[M+Na]^+$ calcd. for $C_{14}H_{20}NaO_2$: 243.1361, found: 243.1365**.**



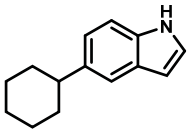
4-Cyclohexyl-1,2-dimethoxybenzene(3jb)[11]: The title compound was prepared according to general procedure **GP2.** Solution 1: 4-chloro-1,2-dimethoxybenzene (344.0 mg, 2.0 mmol, 1.0 equiv), $Fe(acac)_3$ (35.3 mg, 5 mol%) in dry THF (5.0 mL); Solution 2: SIPr-HCl (85.4 mg, 10 mol%), cyclohexylmagnesium chloride (3.0 mL, 1.5 equiv.) in dry THF (2.0 mL) at 25 °C with 20 minutes residence time. Purification via chromatography (pentane, 100%) gave the desired product **3jb** as colorless oil in 61% yield (268.5 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.83-6.81 (m, 1H), 6.77-6.76 (m, 2H), 3.90 (s, 3H), 3.87 (s, 3H), 2.50-2.43(m, 1H), 1.91-1.84 (m, 4H), 1.79-1.74(m, 1H), 1.47-1.25 (m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 148.56, 146.90, 140.77, 118.17, 111.03, 110.22, 55.70, 55.59, 44.02, 34.56, 26.78, 26.01.



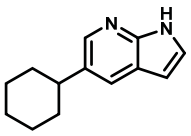
3-Cyclohexyl-N,N-dimethylaniline (3kb): The title compound was prepared according to general procedure **GP2.** Solution 1: 3-chloro-N,N-dimethylaniline (310.1 mg, 2.0 mmol, 1.0 equiv), $Fe(acac)_3$ (14.2 mg, 2 mol%) in dry THF (5.0 mL); Solution 2: SIPr-HCl (34.2 mg, 4 mol%), cyclohexylmagnesium chloride (3.0 mL, 1.5 equiv.) in dry THF (2.0 mL) at 25 °C with 5 minutes residence time. Purification via chromatography (pentane/EtOAc 2-5%) gave the desired product **3kb** as colorless oil in 96% yield (390.1 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.22 (t, *J* = 7.9 Hz, 1H), 6.67 – 6.62 (m, 3H), 2.99 (s, 6H), 2.54 – 2.47 (m, 1H), 1.97 – 1.92 (m, 4H), 1.82 – 1.77 (m, 1H), 1.55 – 1.38 (m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ150.71, 149.02, 128.89, 115.33, 111.50, 110.38, 45.19, 40.72, 34.53, 29.02, 27.01, 26.25.



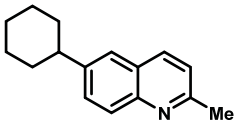
4-Cyclohexyl-N-methylaniline (3lb)[12]: The title compound was prepared according to general procedure **GP2.** Solution 1: 4-chloro-N-methylaniline (282.1 mg, 2.0 mmol, 1.0 equiv), $Fe(acac)_3$ (35.3 mg, 5 mol%) in dry THF (5.0 mL); Solution 2: SIPr-HCl (85.4 mg, 10 mol%), cyclohexylmagnesium chloride (5.0 mL, 2.5 equiv.) at 25 °C with 20 minutes residence time. Purification via chromatography (pentane, 100%) gave the desired product **3lb** as colorless oil in 82% yield (310.1 mg). **^{1} H NMR** (400 MHz, $CDCl_3$): δ 7.08 (d, *J* = 8.0 Hz, 2H), 6.60 (d, *J* = 8.0 Hz, 2H), 3.60 (brs, 1H), 2.85(s, 3H), 2.46 – 2.39 (m, 1H), 1.90 – 1.83 (m, 4H), 1.78 – 1.73 (m, 1H), 1.46 – 1.24 (m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ147.39, 137.16, 127.39, 112.45, 43.60, 34.76, 30.98, 27.01, 26.22.



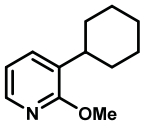
5-Cyclohexyl-1H-indole (3mb)[13]: The title compound was prepared according to general procedure **GP2.** Solution 1: 5-chloro-1H-indole (302.0 mg, 2.0 mmol, 1.0 equiv), $Fe(acac)_3$ (7.1 mg, 2 mol%) in dry THF (5.0 mL); Solution 2: SIPr-HCl (17.1 mg, 4 mol%), cyclohexylmagnesium chloride (5.0 mL, 2.5 equiv.) at 25 °C with 5 minutes residence time. Purification via chromatography (pentane/EtOAc, 90%) gave the desired product **3mb** as white solid with 91% yield (362.4mg). Melting point: 91.1 °C. **^{1} H NMR** (400 MHz, $CDCl_3$): δ 8.05(brs, 1H), 7.50-7.49(m, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.19-7.18(m, 1H), 7.10(dd, *J* = 8.0, 4.0 Hz, 1H), 6.53-6.51(m, 1H), 2.65-2.57(m, 1H), 1.98-1.84(m, 4H), 1.81-1.75(m, 1H), 1.56-1.25(m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 139.81, 134.37, 127.96, 124.17, 121.73, 117.97, 110.64, 102.41, 44.69, 35.19, 27.15, 26.32.



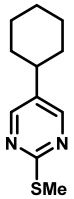
5-Cyclohexyl-1H-pyrrolo[2,3-b]pyridine (3nb)[14]: The title compound was prepared according to general procedure **GP2.** Solution 1: 5-chloro-1H-pyrrolo[2,3-b]pyridine (304.0 mg, 2.0 mmol, 1.0 equiv), $Fe(acac)_3$ (14.2 mg, 2 mol%) in dry THF (5.0 mL); Solution 2: SIPr-HCl (34.2 mg, 4 mol%), cyclohexylmagnesium chloride (5.0 mL, 2.5 equiv.) at 25 °C with 5 minutes residence time. Purification via chromatography (pentane/EtOAc, 90%) gave the desired product **3nb** as white solid in 91% yield (362.4mg). **^{1} H NMR** (400 MHz, $CDCl_3$): δ 11.81(s, 1H), 8.28-8.27(m, 1H), 7.84(s, 1H), 7.41(s, 1H), 6.49(s, 1H), 2.71-2.64(m, 1H), 2.00-1.89(m, 4H), 1.84-1.79(m, 1H), 1.60-1.31(m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ147.83, 142.10, 135.09, 126.58, 125.41, 120.35, 100.03, 42.25, 35.07, 26.98, 26.11.



6-Cyclohexyl-2-methylquinoline (3ob)[15]: The title compound was prepared according to general procedure **GP2** with solution 1: 6-chloro-2-methylquinoline (354.0 mg, 2.0 mmol, 1.0 equiv), $Fe(acac)_3$ (14.2 mg, 2 mol%) in dry THF (5.0 mL); Solution 2: SIPr-HCl (34.2 mg, 4 mol%), cyclohexylmagnesium chloride (3.0 mL, 1.5 equiv.) in 2.0 mL THF at 25 °C with 5 minutes residence time. Purification via chromatography (pentane/EtOAc, 90%) gave the desired product **3ob** as colorless oil in 68% yield (306.2 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95 (dd, *J* = 8.4, 3.9 Hz, 2H), 7.58 - 7.50 (m, 2H), 7.21 (d, *J* = 8.4 Hz, 1 H), 2.71(s, 3H), 2.66 - 2.61(m, 1H), 1.97 - 1.84(m, 4H), 1.79 - 1.75(m, 1H), 1.54 - 1.25(m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ157.88, 146.64, 145.32, 135.79, 129.58, 128.22, 126.41, 123.91, 121.72, 44.28, 34.31, 26.78, 25.12.

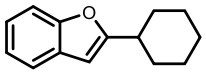


3-Cyclohexyl-2-methoxypyridine (3pb): The title compound was prepared according to general procedure **GP2.** Solution 1: 3-chloro-2-methoxypyridine(286.0 mg, 2.0 mmol, 1.0 equiv), $Fe(acac)_3$ (7.1 mg, 2 mol%) in dry THF (5.0 mL); Solution 2: SIPr-HCl (17.1 mg, 4 mol%), cyclohexylmagnesium chloride (3.0 mL, 1.5 equiv.) in 2.0 mL THF at 25 °C with 15 minutes residence time. Purification via chromatography (pentane/EtOAc, 90%) gave the desired product **3pb** as colorless oil in 45% yield (172.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.99 (dd, *J* = 5.0, 1.9 Hz, 1H), 7.41 (dd, *J* = 7.3, 1.9 Hz, 1H), 6.83 (dd, *J* = 7.3, 5.0 Hz, 1H), 3.95 (s, 3H), 2.81(tt, *J* = 11.6, 3.1 Hz, 1H), 1.89 - 1.81 (m, 4H), 1.79 - 1.73 (m, 1H), 1.49-1.20(m, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.47, 143.52, 134.49, 130.15, 116.76, 53.16, 36.92, 32.57, 26.85, 26.29. **HRMS** (ESI) (m/z): $[M+H]^+$ calcd. for $C_{12}H_{18}NO$: 192.1388, found: 192.1393**.**

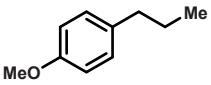


5-Cyclohexyl-2-(methylthio)pyrimidine (3qb): The title compound was prepared according to general procedure **GP2.** Solution 1: 5-chloro-2-(methylthio)pyrimidine (320.0 mg, 2.0 mmol, 1.0 equiv), $Fe(acac)_3$ (7.1 mg, 2 mol%) in dry THF (5.0 mL); Solution 2: SIPr-HCl (17.1 mg, 4 mol%), cyclohexylmagnesium chloride (3.0 mL, 1.5 equiv.) in 2.0 mL THF at 25 °C with 1 minutes residence time. Purification via chromatography (pentane/EtOAc, 90%) gave the desired product **3qb** as colorless oil in 84% yield (349.6 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.38(s, 2H), 2.55(s, 3H), 2.49-2.41(m, 1H), 1.89-1.82(m, 4H),

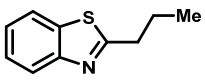
1.79-1.73(m, 1H), 1.45-1.22(m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ169.85, 155.96, 134.91, 39.27, 33.76, 26.46, 25.67, 14.03. **HRMS** (ESI) (m/z): $[M+Na]^+$ calcd. for $C_{11}H_{16}N_2NaS$: 231.0932, found: 231.0940**.**



2-Cyclohexylbenzofuran (3rb)[16]: The title compound was prepared according to general procedure **GP2.** Solution 1: 2-chlorobenzofuran (152.0 mg, 1.0 mmol, 1.0 equiv), $Fe(acac)_3$ (17.7 mg, 5 mol%) in dry THF (2.5 mL); Solution 2: cyclohexylmagnesium chloride (1.5 mL, 1.5 equiv.), SIPr-HCl (42.7mg, 10 mol%), in dry THF (1.0 mL) at 25 °C with the residence time of 20 minutes. Purification via chromatography (pentane, 100%) gave the desired product **3rb** as colorless oil in 75% yield (150.0 mg). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ δ 7.51-7.42(m, 2H), 7.20(td, J = 6.8, 1.6 Hz), 6.36(s, 1H), 2.78 (tt, *J* = 11.2, 3.6 Hz, 1H), 2.17 – 2.07 (m, 2H), 1.86 (dt, *J* = 12.3, 3.5 Hz, 2H), 1.79-1.73(m, 1H), 1.56 – 1.33 (m, 4H), 1.32 (ddt, *J* = 15.6, 12.1, 5.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 164.05, 154.37, 128.87, 122.96, 122.26, 120.24, 110.70, 99.75, 37.58, 31.32, 26.08, 25.92.

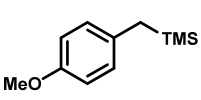


1-Methoxy-4-propylbenzene (3ha)[17]: The title compound was prepared according to general procedure **GP2.** Solution 1: 1-chloro-4-methoxybenzene (285.2 mg, 2.0 mmol, 1.0 equiv), $Fe(acac)_3$ (14.2 mg, 2 mol%) in dry THF (5.0 mL); Solution 2: SIPr-HCl (34.2 mg, 4 mol%), propylmagnesium bromide (2.0 M in Et_2O solution), (1.5 mL, 1.5 equiv.) in 3.5 mL THF at 25 °C with 20 minutes residence time. Purification via chromatography (pentane, 100%) gave the desired product **3ha** as colorless oil in 95% yield (285.0 mg). **^{1} H NMR** (400 MHz, $CDCl_3$): δ 7.12 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 3.81 (s, 3H), 2.56 (t, *J* = 8.0 Hz, 2H), 1.67-1.58 (m, 2H), 0.98-0.90 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ157.63, 134.79, 129.28, 113.61, 55.21, 37.14, 24.78, 13.76.

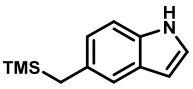


2-Propylbenzo[d]thiazole (3ra)[18]: The title compound was prepared according to general procedure **GP2.** Solution 1: 2-chlorobenzo[d]thiazole (378.0 mg, 2.0 mmol, 1.0 equiv), $Fe(acac)_3$ (35.3 mg, 5 mol%) in dry THF (5.0 mL); Solution 2: SIPr-HCl (128.1 mg, 15 mol%), propylmagnesium bromide (2.0 M in Et_2O solution) (1.5 mL, 1.5 equiv.) in 3.5 mL THF at 25 °C with 20 minutes residence time. Purification via chromatography (pentane/EtOAc, 90%) gave the desired product **3ra** as colorless oil in 55%

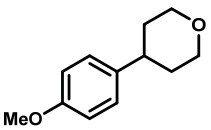
yield (194.8mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.0, Hz, 1H), 7.46 (ddd, *J* = 8.2, 7.2, 1.3 Hz, 1H), 7.35 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 3.11 (dd, *J* = 8.0, 7.2 Hz, 2H), 1.93 (h, *J* = 7.4 Hz, 2H), 1.07 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ172.16, 153.25, 135.14, 125.83, 124.59, 122.49, 121.45, 36.24, 23.08, 13.70.



(4-Methoxybenzyl)trimethylsilane (3hc)[6]: The title compound was prepared according to general procedure **GP4.** 1-Chloro-4-methoxybenzene (142.6 mg, 1.0 mmol, 1.0 equiv), (Trimethylsilyl)methylmagnesium chloride solution (1.0 M in diethyl ether)(1.5 mL, 1.5 equiv.), SIPr-HCl (128.1mg, 30 mol%), $Fe(acac)_3$ (35.3mg, 10 mol%) in dry THF (5 mL) at the irradiation of blue LED in batch for 4 hours. Purification via chromatography (pentane, 100%) gave the desired product **3hc** as colorless oil in 73% yield (142.0 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.93 (d, *J* = 4.0 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 3.79 (s, 3H), 2.02(s, 2H), 0.01 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ156.49, 132.33, 128.78, 113.64, 55.23, 25.49, -1.94.

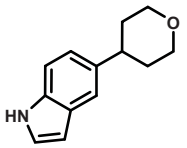


5-((Trimethylsilyl)methyl)-1H-indole (3nc)[19]: The title compound was prepared according to general procedure **GP4.** 5-Chloro-1H-indole (151.0 mg, 1.0 mmol, 1.0 equiv), (trimethylsilyl)methylmagnesium chloride solution (1.0 M in diethyl ether) (2.5 mL, 2.5 equiv.), SIPr-HCl (128.1mg, 30 mol%), $Fe(acac)_3$ (35.3mg, 10 mol%) in dry THF (2.5 mL) at the irradiation of blue LED in batch for 4 hours. Purification via chromatography (pentane/EtOAc, 90%) gave the desired product **3nc** as colorless oil in 75% yield (152.3 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.88 (brs, 1H), 7.26-7.23 (m, 1H), 7.20 (d, J = 8.0 Hz, 1H), 7.08 (s, 1H), 6.87-6.84 (m, 1H), 6.44-6.42 (m, 1H), 2.16 (d, J = 4.0 Hz, 2H), 0.00 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 133.43, 131.41, 128. 17, 123.96, 123.93, 123.19, 119.01, 110.50, 110.47, 101.88, 26.54, -1.81.

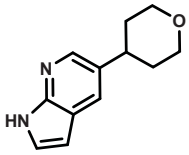


4-(4-Methoxyphenyl)tetrahydro-2H-pyran (3hd)[20]: The title compound was prepared according to general procedure **GP2.** Solution 1: 1-chloro-4-methoxybenzene (284.0 mg, 2.0 mmol, 1.0 equiv), $Fe(acac)_3$ (35.3 mg, 5 mol%) in dry THF (5.0 mL); Solution 2: (tetrahydro-2H-pyran-4-yl)magnesium bromide (5.0 mL, 1.5 equiv.), SIPr-HCl (128.1 mg, 15 mol%) at 25 °C at the residence time of 20 minutes.

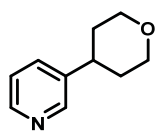
Purification via chromatography (pentane, 100%) gave the desired product **3hd** as colorless oil in 70% yield (268.9 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.18-7.14 (m, 2H), 6.90-6.86(m, 2H), 4.11-4.06 (m, 2H), 3.09 (s, 3H), 3.57-3.50 (m, 2H), 2.72 (tt, *J* = 10.9, 4.9 Hz, 1H), 1.83–1.74 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ158.00, 138.07, 127.54, 113.84, 68.40, 55.21, 40.66, 34.17.



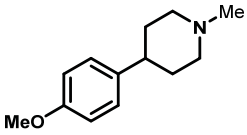
5-(Tetrahydro-2H-pyran-4-yl)-1H-indole (3nd): The title compound was prepared according to general procedure **GP2.** Solution 1: 5-chloro-1H-indole (151.0 mg, 1.0 mmol, 1.0 equiv), $Fe(acac)_3$ (17.7 mg, 5 mol%) in dry THF (3.4 mL); Solution 2: (tetrahydro-2H-pyran-4-yl)magnesium bromide (3.4 mL, 2.0 equiv.), SIPr-HCl (64.0 mg, 15 mol%), at 40 °C at the residence time of 20 minutes. Purification via chromatography (pentane/EtOAc, 90%) gave the desired product **3nd** as white solid in 70% yield (141.0 mg). Melting point: 122.0 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.17 (brs, 1H), 7.52 (d, *J* = 1.6 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.21 (t, *J* = 2.8 Hz, 1H), 7.11 (dd, *J* = 8.4, 1.7 Hz, 1H), 6.56 – 6.50 (m, 1H), 4.18 – 4.09 (m, 2H), 3.59 (td, *J* = 11.6, 2.4 Hz, 2H), 2.92 – 2.76 (m, 1H), 2.06 – 1.76 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ137.52, 134.58, 128.03, 124.47, 121.37, 118.07, 110.94, 102.40, 68.63, 41.68, 34.68.



5-(Tetrahydro-2H-pyran-4-yl)-1H-indole (4od)[21]: The title compound was prepared according to general procedure **GP3.** Solution 1: 5-chloro-1H-pyrrolo[2,3-b]pyridine (152.0 mg, 1.0 mmol, 1.0 equiv), $Fe(acac)_3$ (17.7 mg, 5 mol%) in dry THF (4.2 mL); Solution 2: (tetrahydro-2H-pyran-4-yl)magnesium bromide(4.2 mL, 2.5 equiv.), isopropylmagnesium chloride (1.0 M in THF) (0.3 mL, 0.3 equiv.), SIPr-HCl (128.1 mg, 15 mol%), at 25 °C at the residence time of 20 minutes. Purification via chromatography (pentane/EtOAc, 90%) gave the desired product **4od** as colorless oil in 78% yield (315.3 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.93 (s, 1H), 8.26 (d, *J* = 2.1 Hz, 1H), 7.83 (d, *J* = 2.0 Hz, 1H), 7.38 (dd, *J* = 3.6, 1.4 Hz, 1H), 6.49 (dd, *J* = 3.5, 0.9 Hz, 1H), 4.13 (dd, *J* = 11.6, 4.4, Hz, 2H), 3.59 (td, *J* = 11.8, 2.2 Hz, 2H), 2.91 (tt, *J* = 12.0, 4.0 Hz, 1H), 1.97-1.91 (m, 2H), 1.86 – 1.82 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.90, 142.22, 133.21, 126.57, 125.52, 120.29, 100.40, 68.44, 39.36, 34.53, 34.51.



3-(Tetrahydro-2H-pyran-4-yl)pyridine (3sd)[22]: The title compound was prepared according to general procedure **GP3.** Solution 1: 5-chloro-1H-pyrrolo[2,3-b]pyridine (226.0 mg, 2.0 mmol, 1.0 equiv), $Fe(acac)_3$ (35.3 mg, 5 mol%) in dry THF (5.0 mL); Solution 2: (tetrahydro-2H-pyran-4-yl)magnesium bromide (0.6 M in THF) (5.0 mL, 1.5 equiv.), SIPr-HCl (128.1 mg, 15 mol%) at 25 °C at the residence time of 20 minutes. Purification via chromatography (DCM) gave the desired product **3sd** as colorless oil in 95% yield (309.9 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 2.3 Hz, 1H), 8.48 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.54 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.27 – 7.19 (m, 1H), 4.14 – 4.07 (m, 2H), 3.55 (td, *J* = 11.5, 2.8 Hz, 2H), 2.85 – 2.74 (m, 1H), 1.97 – 1.72 (m, 4H) .**^{13}C NMR** (101 MHz, $CDCl_3$): δ148.87, 147.90, 133.98, 123.47, 68.15, 39.12, 33.54.

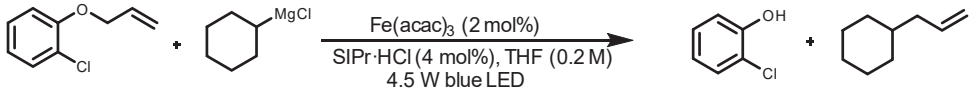


4-(4-Methoxyphenyl)-1-methylpiperidine (3he)[23]: The title compound was prepared according to general procedure **GP3.** Solution 1: 1-chloro-4methoxybenzene (284.0 mg, 2.0 mmol, 1.0 equiv), $Fe(acac)_3$ (35.3 mg, 5 mol%) in dry THF (5.0 mL); Solution 2: (1-methylpiperidin-4-yl)magnesium bromide (4.3 mL, 1.5 equiv.), isopropylmagnesium chloride (1.0 M in THF) (0.3 mL, 0.3 equiv.), SIPr-HCl (128.1 mg, 15 mol%), in dry THF (0.7 mL) at 25 °C with the residence time of 20 minutes. Purification via chromatography (pentane/EtOAc, 90%) gave the desired product **3he** as colorless oil in 85% yield (348.8 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 7.1 Hz, 2H), 6.85(d, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 2.99-2.96 (m, 2H), 2.46-2.39 (m, 1H), 2.33 (d, *J* = 1.9 Hz, 3H), 2.05 (td, *J* = 12.2, 3.1 Hz, 2H), 1.84–1.76 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ157.87, 138.44, 127.65, 113.76, 56.39, 55.20, 46.44, 41.13, 33.69.

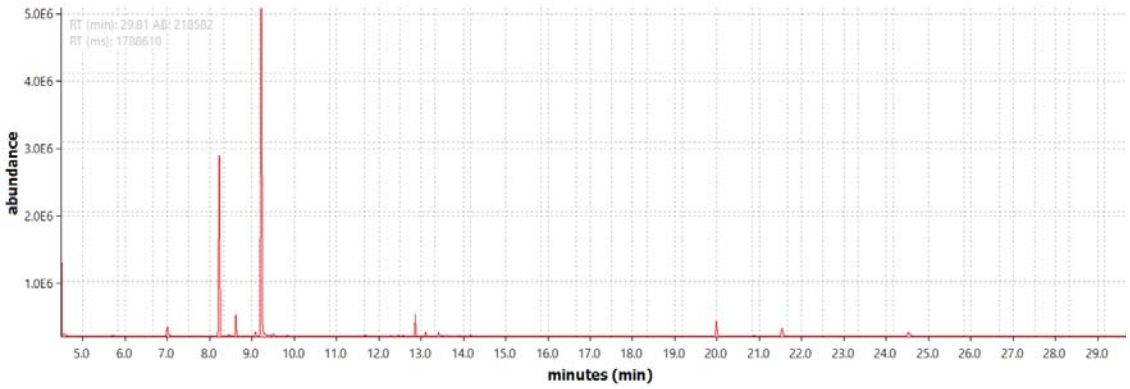
6: Mechanistic studies

6.1: Radical clock experiments

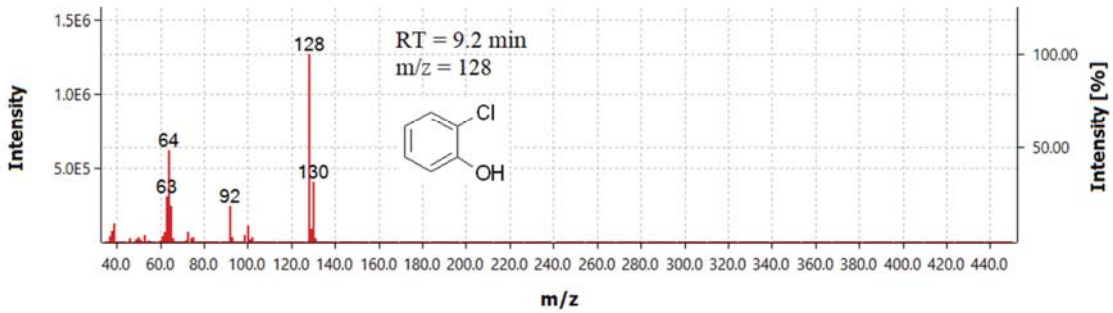
Radical clock experiments were performed on 1-(allyloxy)-2-chlorobenzene and *o*-butenylchlorobenzene.

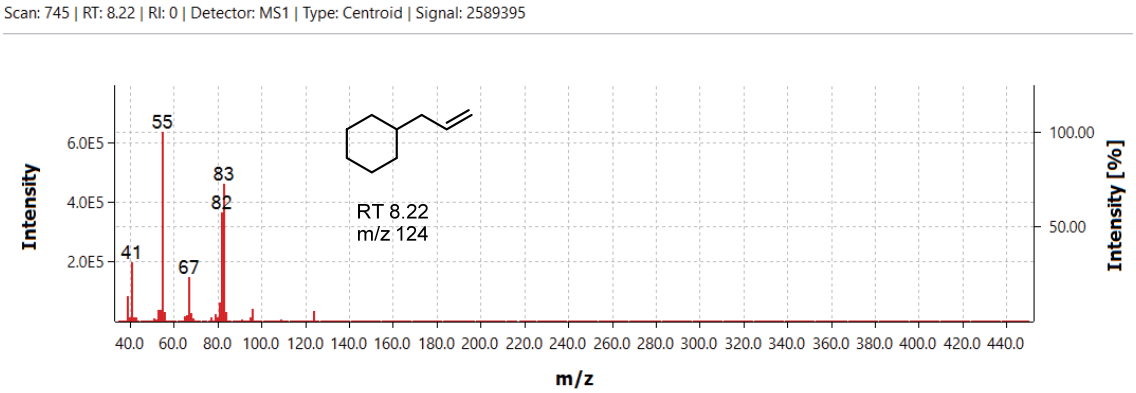


1-(Allyloxy)-2-chlorobenzene was subjected to the standard reaction conditions. After 15 minutes irradiation, the reaction crude was analyzed via GC-MS. Two main peaks were observed, identified as *o*-hydroxychlorobenzene (from C-O cleavage) and propenylcyclohexane. These might result from the nucleophilic attack of the cyclohexyl to the alkene, with consequent release of the hydroxychlorobenzene.

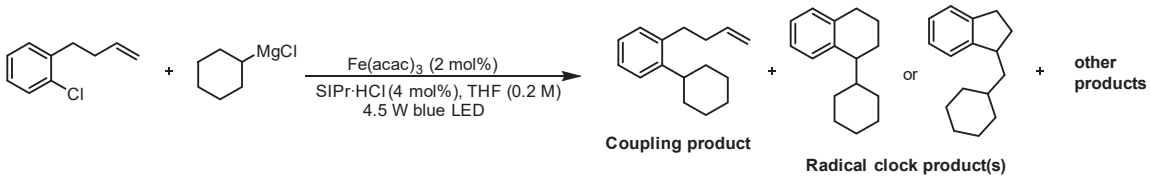


Scan: 944 | RT: 9.215 | RI: 0 | Detector: MS1 | Type: Centroid | Signal: 4417384



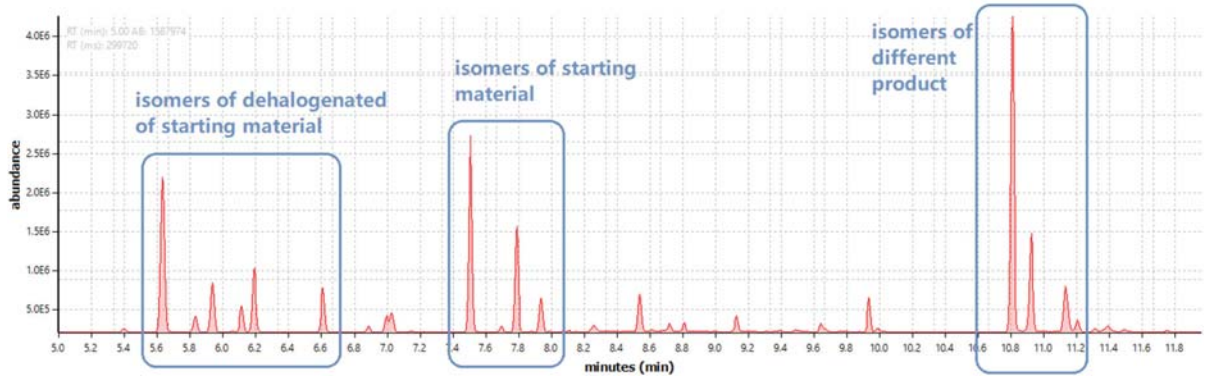


The reaction between *o*-butenylchlorobenzene and cyclohexylmagnesium chloride mainly resulted in the formation of the expected coupling product, but a broad array of side products was observed, including some possibly deriving from a radical pathways. GC-MS data for the identified compounds are shown below.

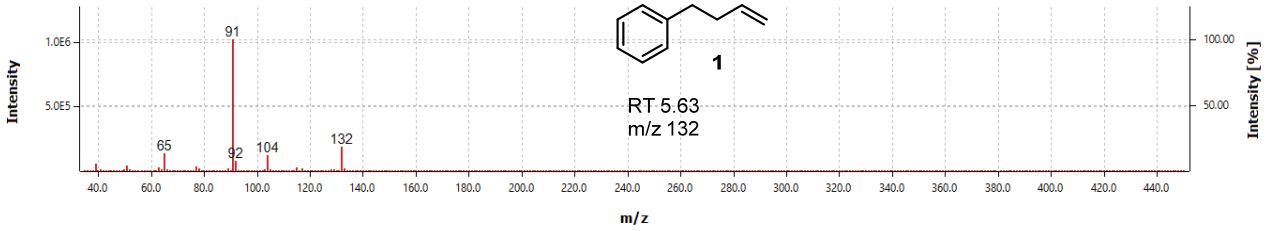


Apart from dehalogenation of the aryl chloride, isomerization (loss of -CH_3 fragments in some of the peaks, only possible from isomerized alkenyl chains) and hydrogenation of the alkenyl chain (both in the aryl chloride and the dehalogenated derivative) was observed. Reductive dehalogenation and hydrogenation might come from a Fe hydride intermediate formed upon β-hydrogen elimination of the Fe-alkyl species [2]. The formation of bi(cyclohexane) from homocoupling of the Grignard reagent was also observed here, as in other examples in the scope. Besides the formation of the expected coupling product (RT 10.81min), other products are observed with the same m/z values (RT 10.93, 11.20), but considerably different fragmentation patterns. The expected coupling product is recognizable by the loss of a $–CH_2CH=CH_2$ fragment (m/z 173, M-41, similar fragmentation in the starting aryl chloride), and a cyclohexyl (m/z 131). These peaks are not observed in the other products, which instead show the peak at m/z 117 (M-43, $-CH_2CH_2CH_3$). This suggests that the butenyl chain in no longer present in the product and the fragmentation might be due to the (fused) alkylic residue (radical clock products). As

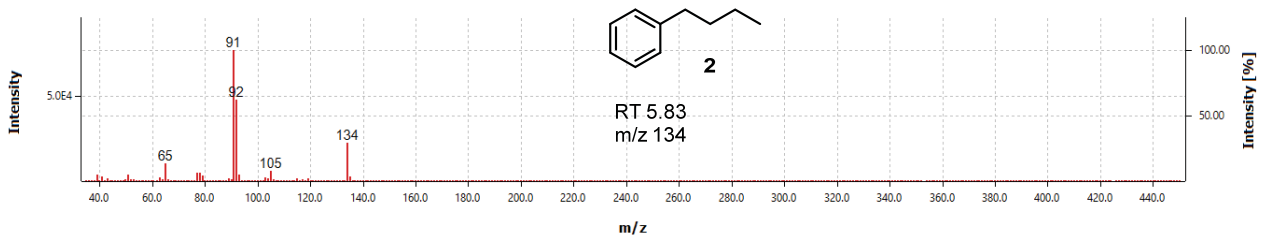
these are minor compounds, we do not believe a free radical mechanism to be predominant under the reaction conditions.



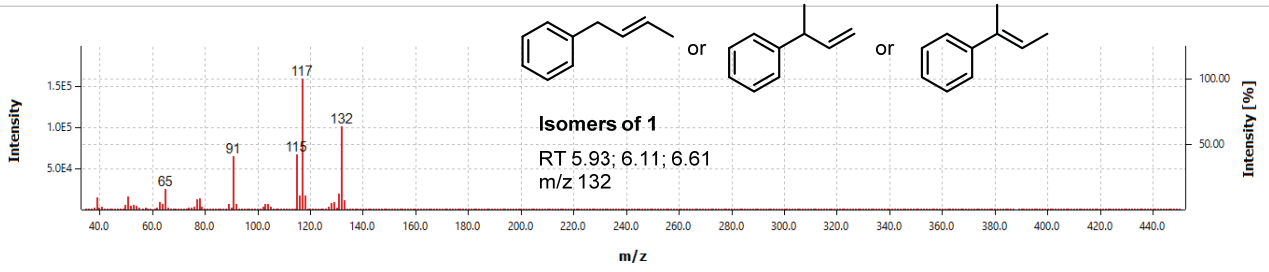
Scan: 227 | RT: 5.63 | RI: 0 | Detector: MS1 | Type: Centroid | Signal: 2219629



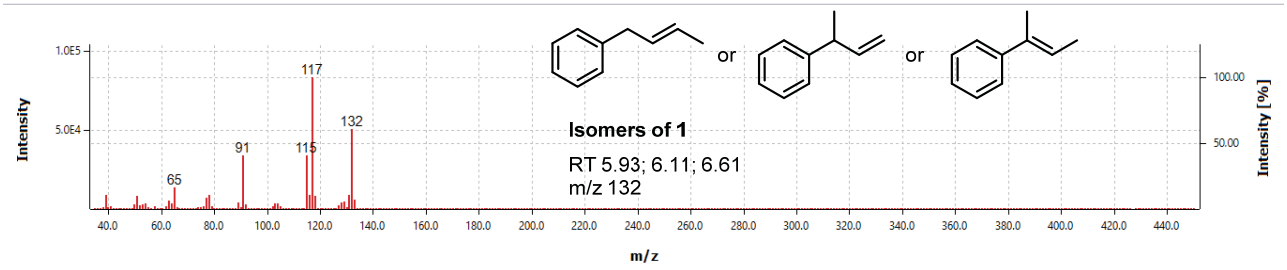
Scan: 267 | RT: 5.83 | RI: 0 | Detector: MS1 | Type: Centroid | Signal: 416593



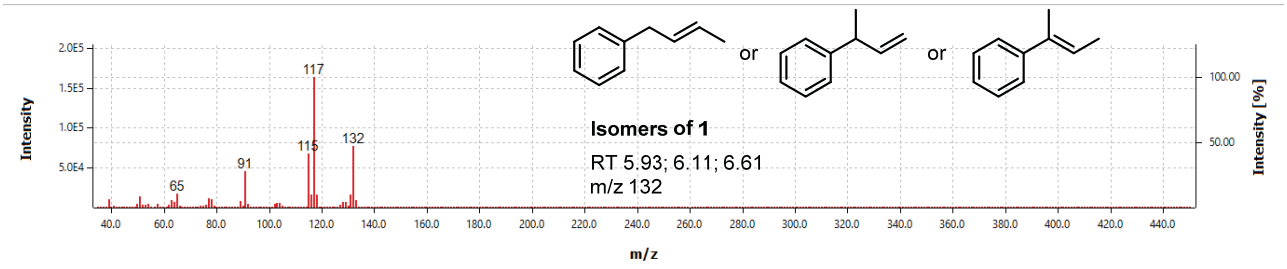
Scan: 288 | RT: 5.935 | RI: 0 | Detector: MS1 | Type: Centroid | Signal: 851960



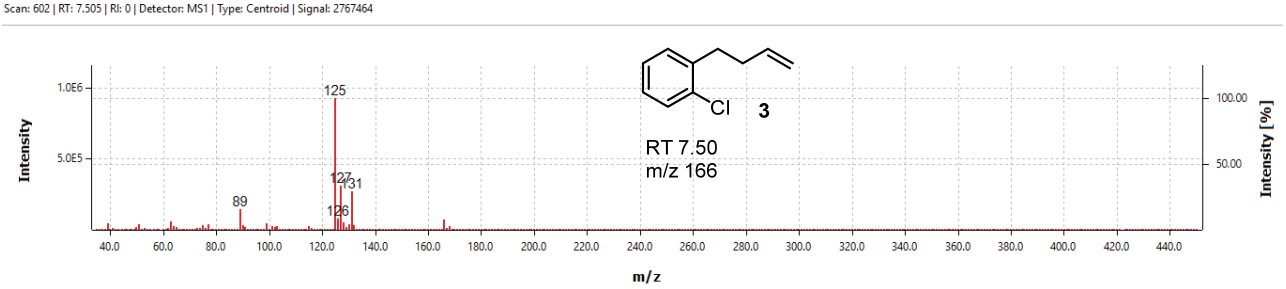
Scan: 324 | RT: 6.115 | RI: 0 | Detector: MS1 | Type: Centroid | Signal: 546881



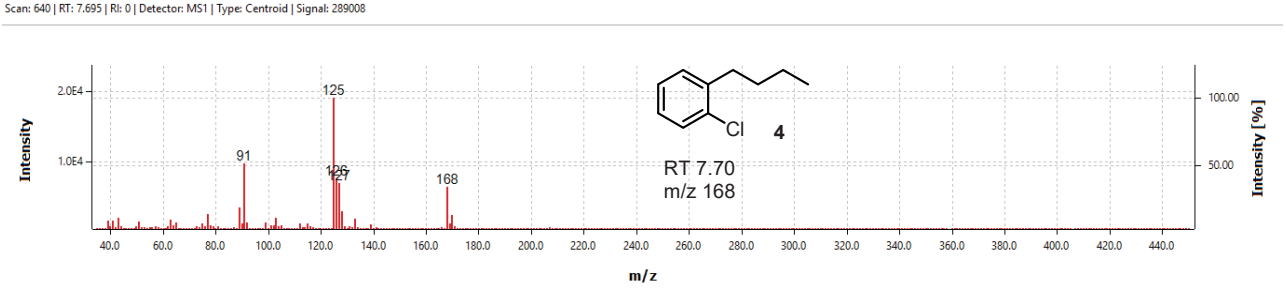
Scan: 423 | RT: 6.61 | RI: 0 | Detector: MS1 | Type: Centroid | Signal: 785193



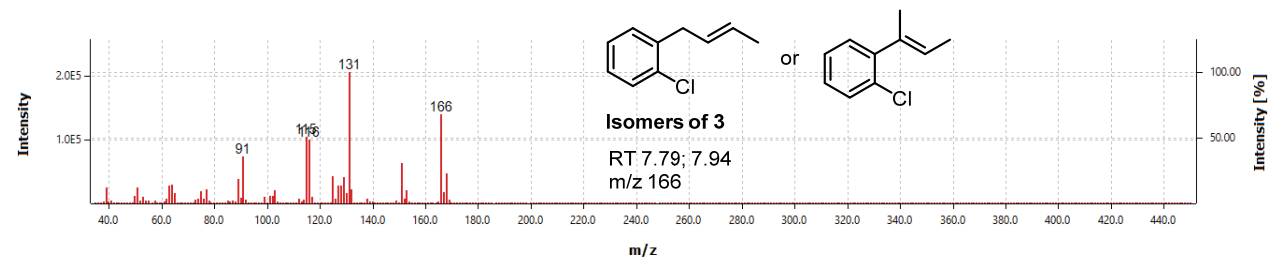
Scan: 602 | RT: 7.505 | RI: 0 | Detector: MS1 | Type: Centroid | Signal: 2767464

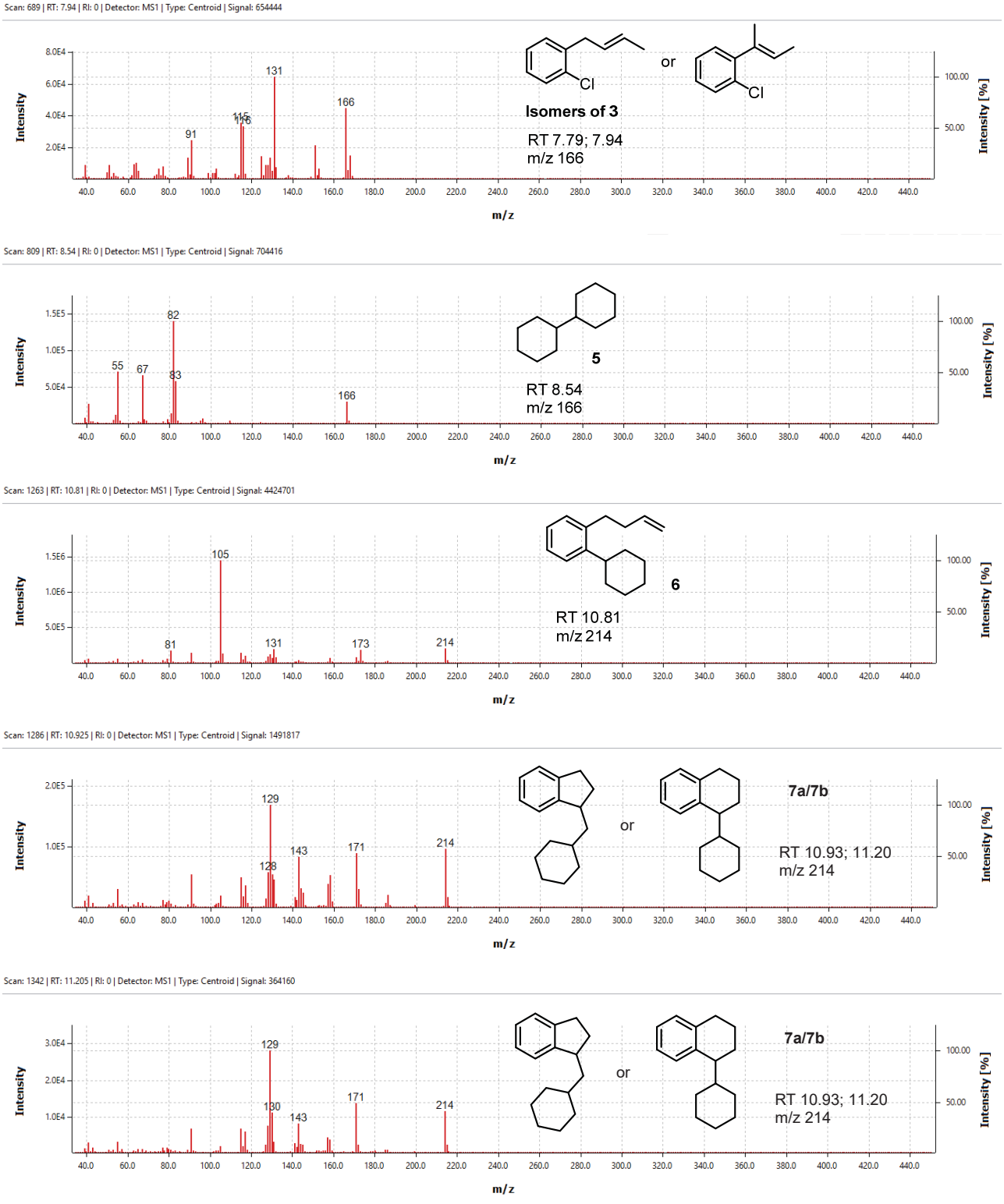


Scan: 640 | RT: 7.695 | RI: 0 | Detector: MS1 | Type: Centroid | Signal: 289008



Scan: 659 | RT: 7.79 | RI: 0 | Detector: MS1 | Type: Centroid | Signal: 1577139




Scan: 689 | RT: 7.94 | RI: 0 | Detector: MS1 | Type: Centroid | Signal: 654444
Intensity
m/z
Intensity [%]
131
166
115
116
91
or
Cl
Cl
Isomers of 3
RT 7.79; 7.94
m/z 166
Scan: 809 | RT: 8.54 | RI: 0 | Detector: MS1 | Type: Centroid | Signal: 704416
82
55
67
83
166
5
RT 8.54
m/z 166
Scan: 1263 | RT: 10.81 | RI: 0 | Detector: MS1 | Type: Centroid | Signal: 4424701
105
81
131
173
214
6
RT 10.81
m/z 214
Scan: 1286 | RT: 10.925 | RI: 0 | Detector: MS1 | Type: Centroid | Signal: 1491817
129
128
143
171
214
or
7a/7b
RT 10.93; 11.20
m/z 214
Scan: 1342 | RT: 11.205 | RI: 0 | Detector: MS1 | Type: Centroid | Signal: 364160
129
130
143
171
214
or
7a/7b
RT 10.93; 11.20
m/z 214

6.2: Kinetic measurements, general procedure

Measurements of reaction profiles were performed in batch in 7 ml vials under irradiation of blue LED light (4.5 W), using the setup shown in Figure S2. Reactions with or without light were performed at the same time to ensure reproducibility. One of the vial was exposed to light during the reaction, while the second was covered with aluminum foil for the whole time.

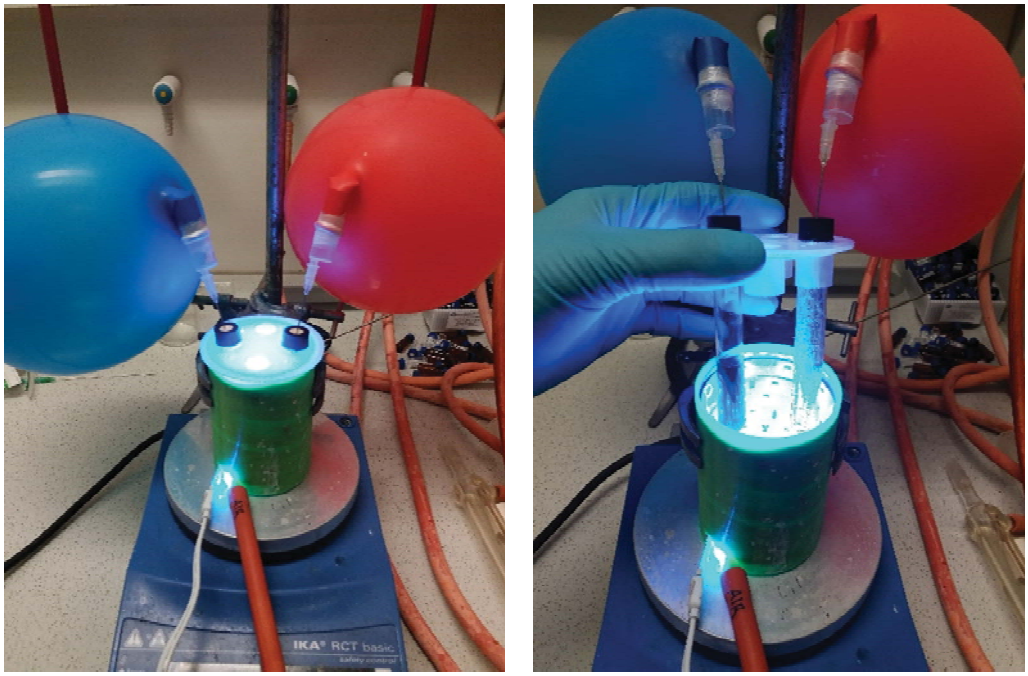
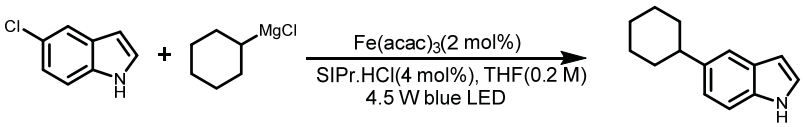


Figure S2: Batch setup used for kinetic measurements

SIPr·HCl (17 mg, 0.04 mmol) was charged into each of the two vials, the vials were flushed with Ar, and closed with a screw-cap with an Ar balloon attached. A stock solution of $Fe(acac)_3$ (14 mg, 0.04 mmol), aryl chloride (2.0 mmol), and decane (internal standard, 80 µL, 0.4 mmol) in 6 mL dry THF was prepared, and half of this was added, under Ar, into each of the vials. Cyclohexylmagnesium chloride (1.5 mL of a 1.0 M solution in 2-MeTHF, 1.5 mmol) was then added into each vial, and the vials were placed into the reactor and stirred (1000 rpm) at room temperature. Samples of 0.2 mL were then taken at different times from each vial and transferred into a 1.5 mL GC vial, the excess Grignard reagent was quenched with acetone, and the solid formed was filtered over celite before injecting the samples into GC-FID.

6.3: Light on/off reaction



SIPr·HCl (17 mg, 0.04 mmol) was charged into three vials, the vials were flushed with Ar, and closed with a screw-cap with an Ar balloon. Cyclohexyl magnesium chloride (2.5 mL of a 1.0 M solution in 2-MeTHF, 2.5 mmol) was then added into each vial, and the vials were placed into the reactor and stirred at room temperature for 10 minutes. A stock solution of $Fe(acac)_3$ (21.2 mg, 0.06 mmol), 5-chloroindole (3.0 mmol), and decane (internal standard, 256 mg) in 7.5 mL THF was prepared. 2.5 mL of the stock solution was added under Ar into each of the three vials. Samples of 0.1 mL were taken at different times from each vial and transferred into a 1.5 mL GC vial, the excess Grignard reagent was quenched with acetone, and the solid formed was filtered over celite before injecting the samples into GC-FID.

6.4: GC-FID calibration curves

Calibration curves for cyclohexylbenzene (**3ab**), 1-cyclohexyl-4-methoxybenzene (**3hb**), and 5-cyclohexyl-1H-indole (**3mb**) with decane as internal standard are reported in Figures S3, S4 and S5.

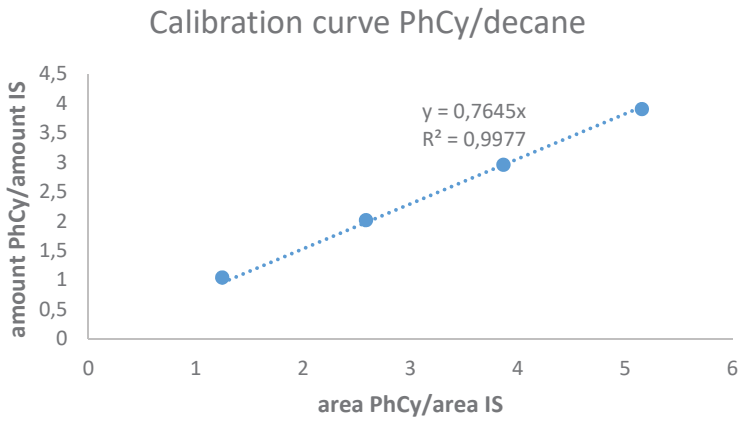


Figure S3: Calibration curve for cyclohexylbenzene 3ab (PhCy)

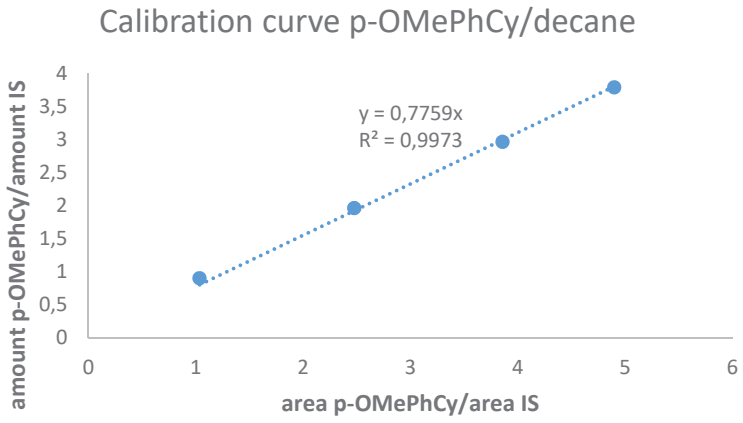


Figure S4: Calibration curve for 1-cyclohexyl-4-methoxybenzene 3hb (*p*-OMePhCy)

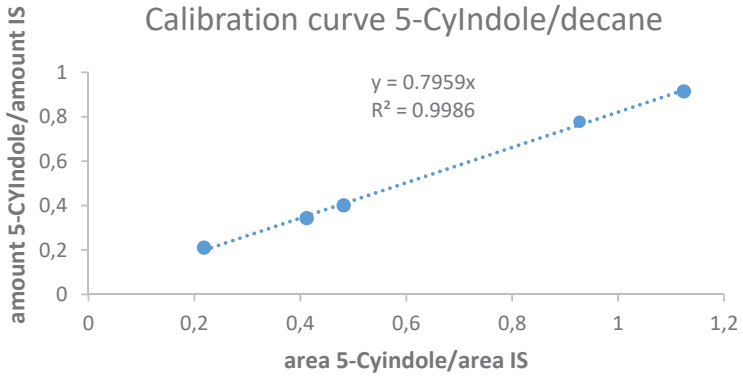


Figure S5: Calibration curve for 5-cyclohexyl-1H-indole 3mb (5-CyIndole)

6.5: In-line UV-Vis measurements

UV-Vis spectra for the reaction components are shown in Figure S6:

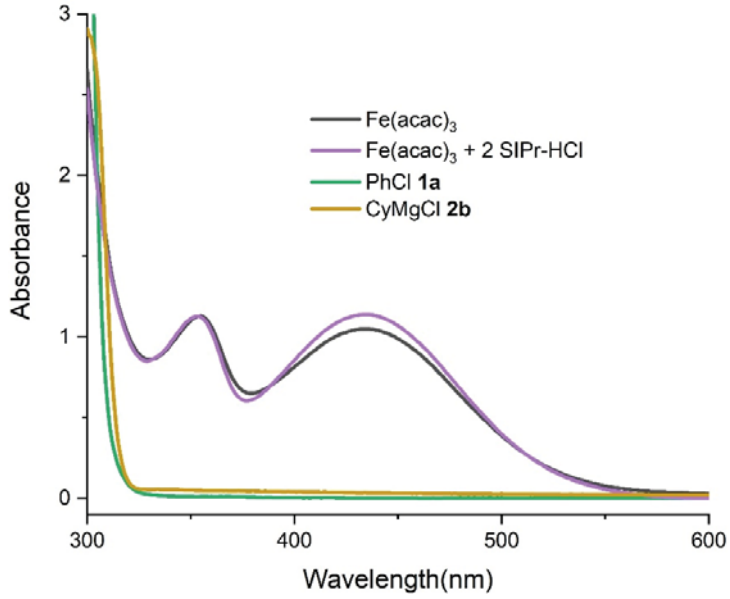


Figure S6: UV-Vis spectra for the reaction components in THF

General procedure of in-line UV-Vis analysis to test the importance of ligand: A solution of $Fe(acac)_3$ (5 mg, 0.014 mmol) [and SIPr-HCl (12 mg, 0.028 mmol)] in dry THF (20 mL) was charged into a round-bottom flask and stirred under Ar. The solution was continuously analyzed by in-line UV-Vis spectrophotometry (300-600 nm range) using the apparatus shown in Figures S7-S8, collecting one measurement per second. After approximately 2 minutes, slow additions of chlorobenzene (PhCl, **1a**) (250 µL of a 1.0 M solution in THF, 0.25 mmol) and/or cyclohexylmagnesium chloride (CyMgCl, **2b**) (250 µL of a 1.0 M solution in 2-MeTHF, 0.25 mmol) were performed via a syringe pump (20 µL/min for **2b** and 28 µL/min for **1a**).
These experiments were performed in the absence of blue light irradiation.

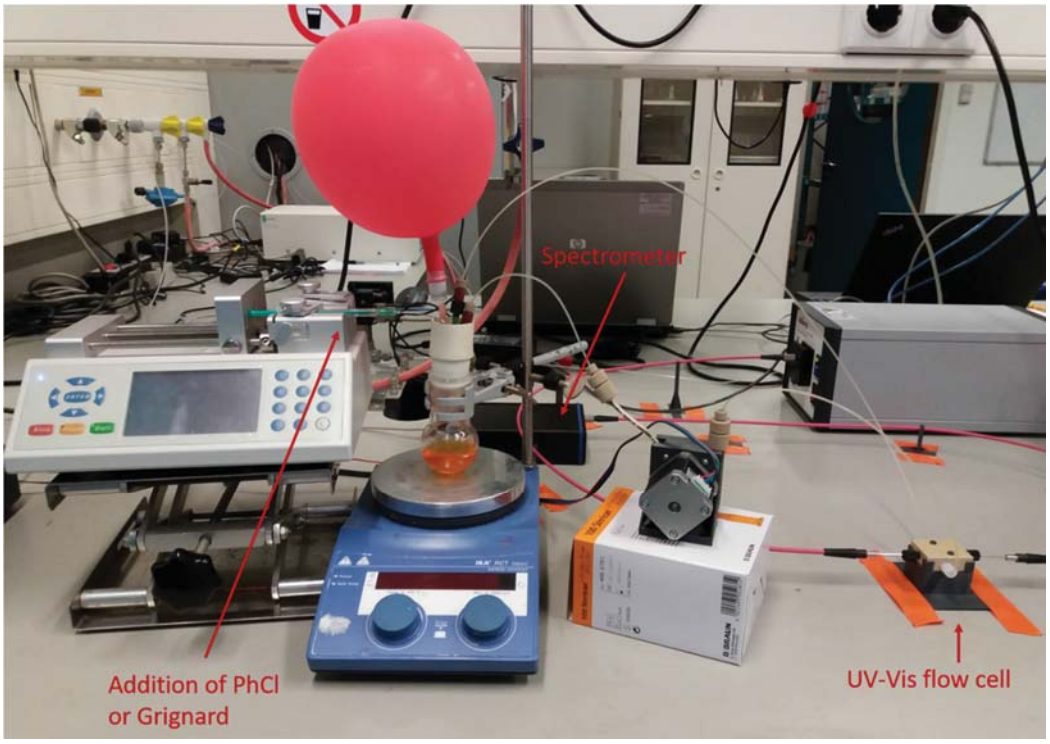


Figure S7: In-line UV-Vis setup

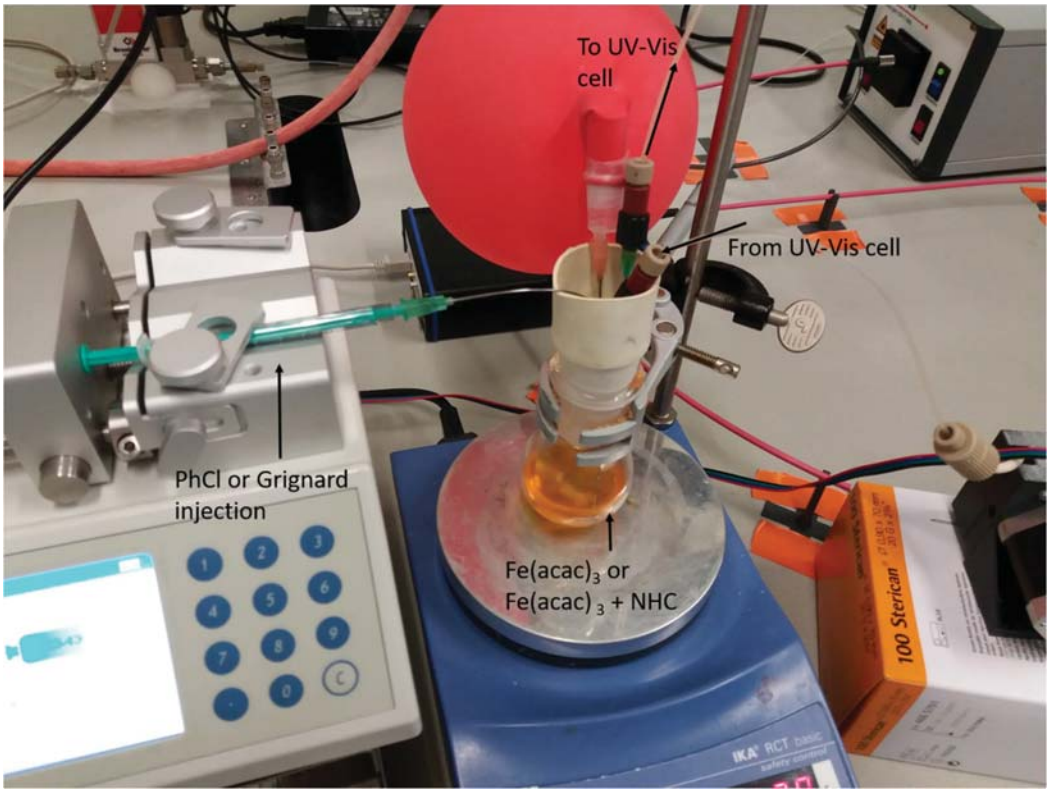


Figure S8: In-line UV-Vis setup, detail

Results: THF solutions of either $Fe(acac)_3$ or $Fe(acac)_3$/SIPr-HCl show absorption maxima at around 350 and 445 nm.

In the absence of the NHC ligand the absorption in the area between 400 and 500 nm decreases upon addition of Grignard reagent (Figure S9). In contrast, in the presence of the ligand, the addition of Grignard results only in a slight initial decrease in absorption in this area, which increases again upon further addition of Grignard (Figure S10). The slight decrease observed might be related to the role of the initial aliquots of Grignard as a base for the NHC precursor.

The difference between the two cases suggests that the NHC-coordinated reduced iron species [Fe^{red}] formed upon reaction with Grignard is more strongly absorbing in the blue light region than the non-coordinated one. This might explain the crucial role of the ligand in the reaction.

A similar behavior is observed when PhCl is added to the solution before the Grignard reagent (Figures S11-S12). The addition of the aryl chloride has no effect on the absorption spectra, suggesting that no interaction between the Fe(III) catalyst and the aryl chloride takes place. Subsequent addition of Grignard reagent induces the same effects as described above for Figures S9-S10.

This behavior suggests that Fe(III) species alone cannot interact with the aryl chloride in the absence of Grignard. The Grignard then has a role in generating the active species [Fe^{red}] before the catalytic cycle begins.

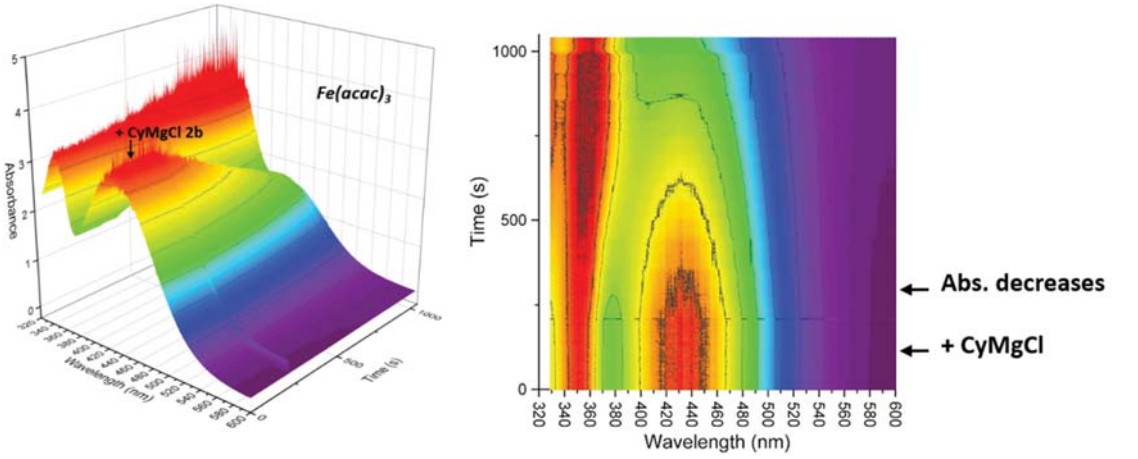


Figure S9: In-line UV-Vis measurements for the addition of cyclohexylmagnesium chloride 2b to $Fe(acac)_3$

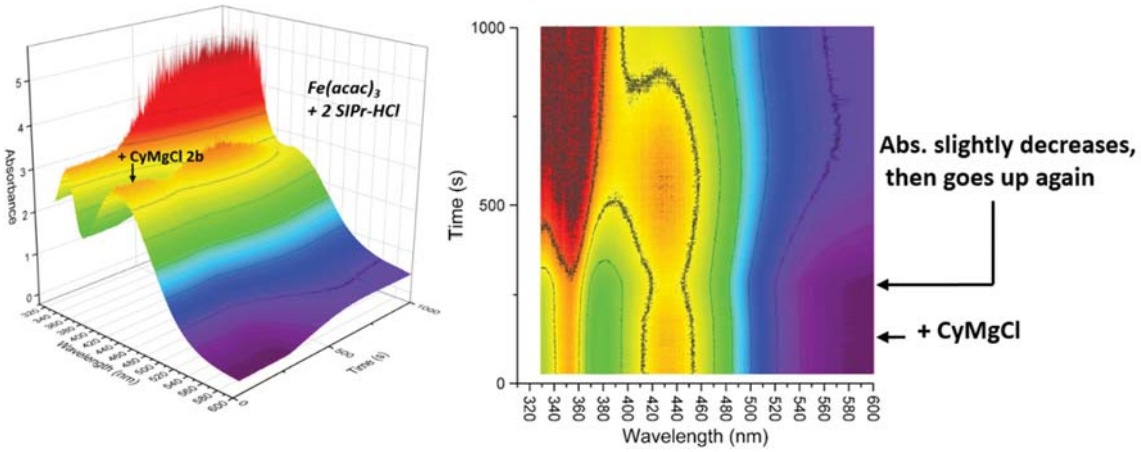


Figure S10: In-line UV-Vis measurements for the addition of cyclohexylmagnesium chloride 2b to $Fe(acac)_3$/SIPr·HCl

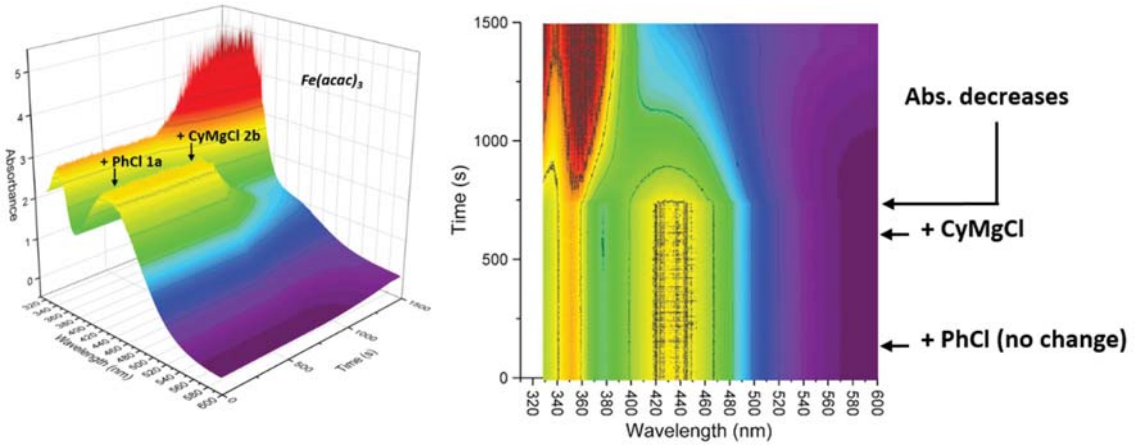


Figure S11: In-line UV-Vis measurements for the addition of chlorobenzene 1a and cyclohexylmagnesium chloride 2b to $Fe(acac)_3$

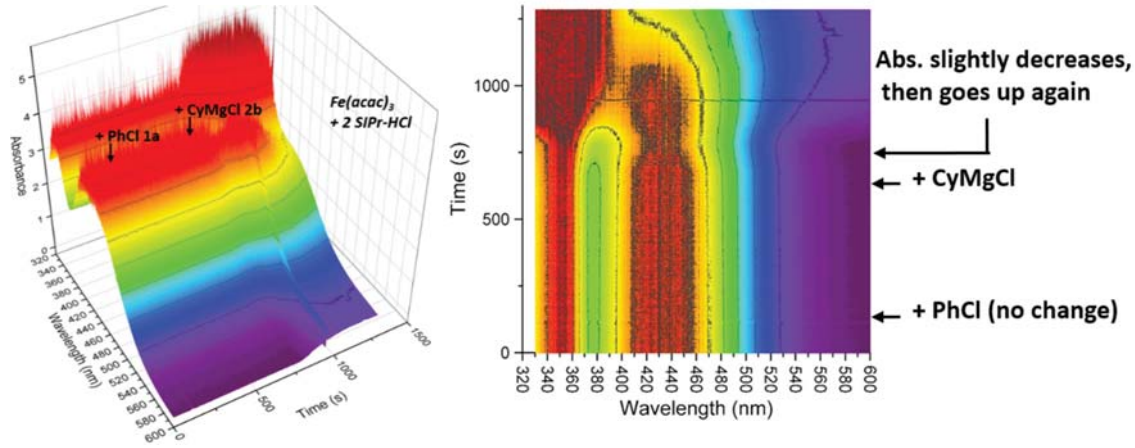


Figure S12: In-line UV-Vis measurements for the addition of chlorobenzene 1a and cyclohexylmagnesium chloride 2b to $Fe(acac)_3$/SIPr·HCl

General procedure for the inline UV analysis to test the first step of the reaction:

These experiments were performed to try to elucidate the role of light in the reaction. Due to its almost complete inertness in the absence of light (see manuscript), 5-chlorindole **1m** was used as reactant for these experiments. It is important to note that the concentration used for these experiments is much lower than the one used for the substrate scope or the kinetic profiles.

A solution of $Fe(acac)_3$ (3.5 mg, 0.01 mmol) and SIPr·HCl (8.5 mg, 0.02 mmol) in dry THF (20 mL) was charged into a reaction tube and stirred under Ar. The solution was continuously analyzed by in-line UV-Vis spectrophotometry (300-600 nm range), collecting one

measurement per second. After about 5 minutes, cyclohexylmagnesium chloride **2b** (0.5 mL of 1.0 M solution in 2-MeTHF, 0.5 mmol) was added by syringe. After other 5 minutes, 5-chloroindole **1m** (30.4 mg, 0.2 mmol in 0.5 mL THF) was added by syringe. This process was carried out in the preseance and in the absence of irradiation (18W blue LED) for comparison.

Results:

THF solutions of $Fe(acac)_3$/SIPr·HCl show absorption maxima at around 350 and 450 nm. The absorption in the area between 400 and 500 nm decreases upon addition of cyclohexylmagnesium chloride and chloroindole. The decrease in absorbance in this range is almost instantaneous upon addition of the Grignard, and a little slower upon addition of the chloroindole. After a certain time (around 40 min) under stirring and irradiation, a broad band between 450 and 600 nm appears, and remains almost unaltered for the next 100 min. After this time, this band start disappearing.

During this whole time, no conversion was observed in GC-FID. We assume the excessive dilution of the reaction to be responsible for this. Based on this observation, we propose this absorption band to be related to an intermediate necessary before the catalytic cycle begins. DFT calculations (see 4.6) suggest this band might be related to a Fe(I) intermediate, formed upon reduction of Fe(III) by the Grignard reagent.

The process under irradiation (Figure S13) or in the dark (Figure S14) show only small differences (different timings for the appearance and disappearance of the broad band at 450-600 nm). The similarity of the two is clearly observed in the graphs reported in Figures S13-S14, and suggests that the effect of light is not strong at this point of the reaction.

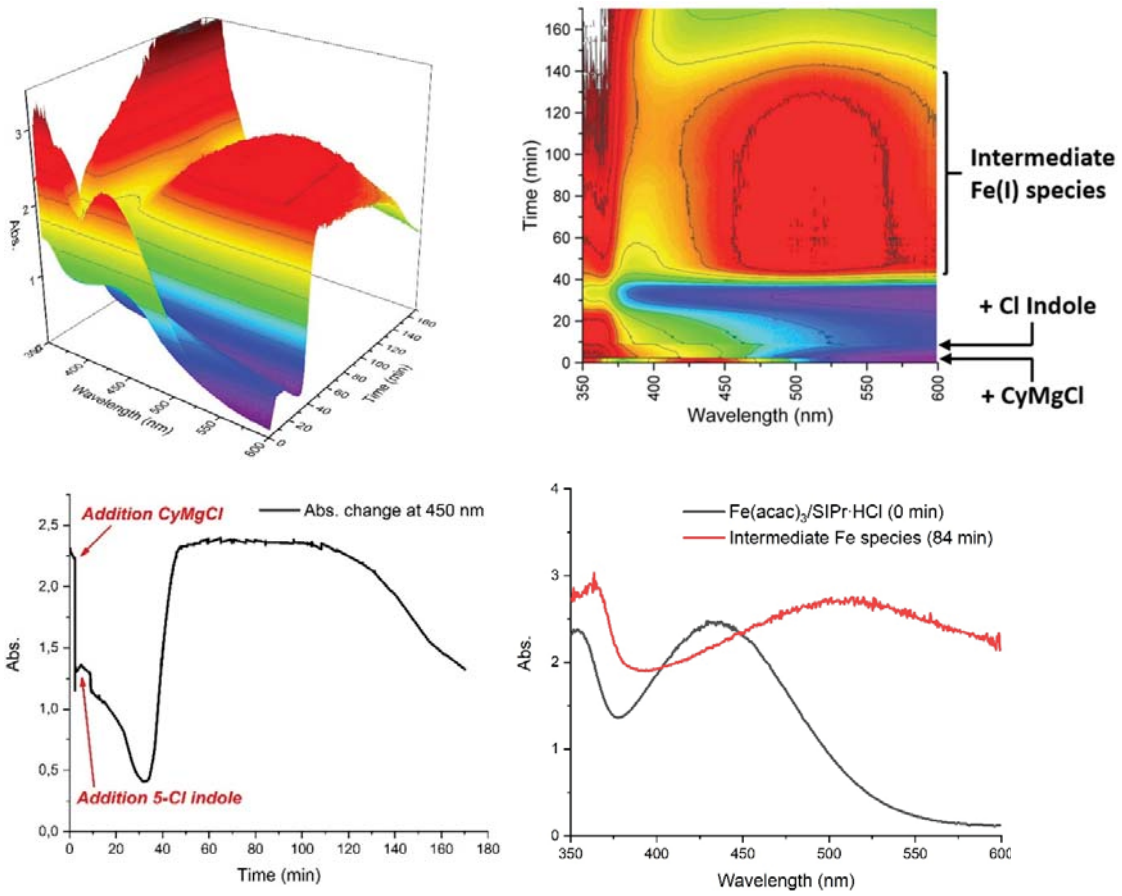


Figure S13: In-line UV-Vis with blue LED irradiation of the mixture

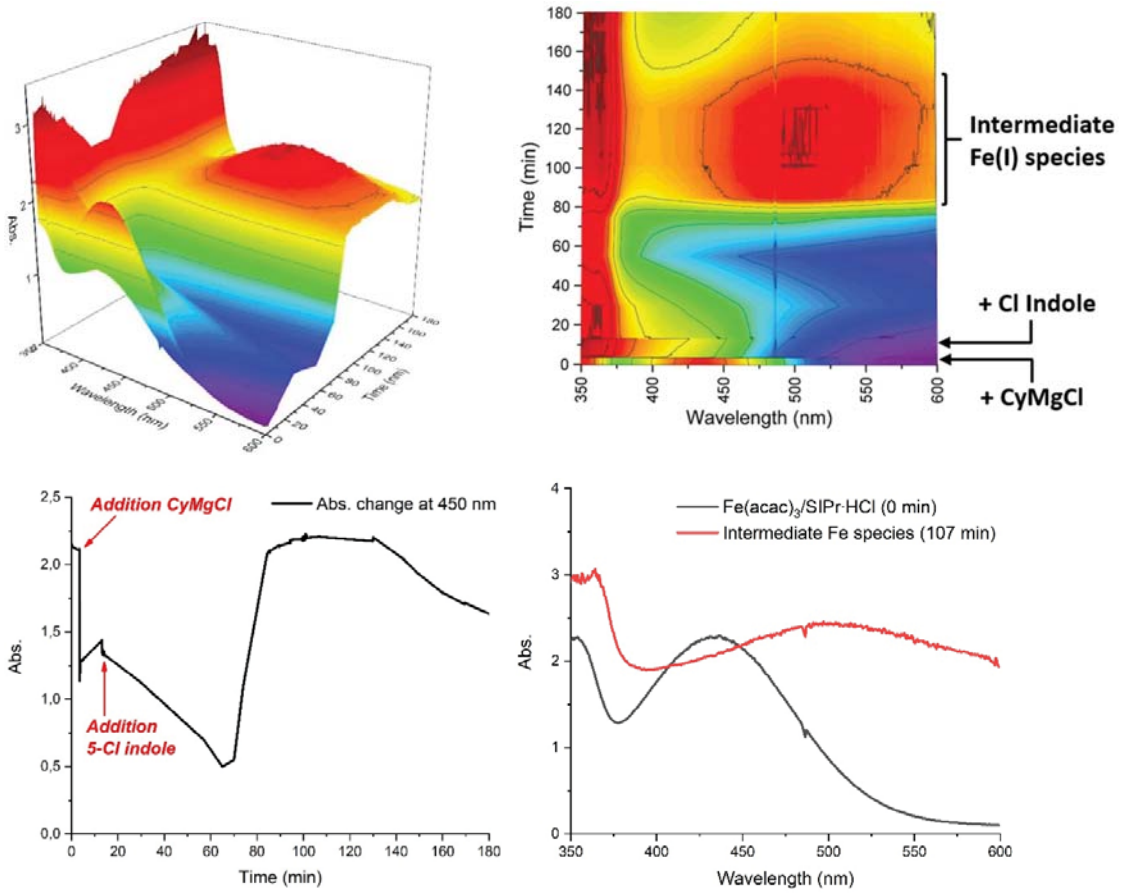


Figure S14: In-line UV-Vis without blue LED irradiation of the mixture

General procedure for the inline UV analysis with higher concentration:

UV-Vis analysis for more concentrated solutions were performed to gain insights under more realistic conditions.

SIPr·HCl (34.2 mg, 0.08 mmol, 4 mol%), cyclohexylmagnesium chloride **2b** (1.0 M in 2-MeTHF, 5.0 mL, 2.5 equiv.) and 10.0 mL dry THF were charged into a vial and stirred for 10 minutes under Ar. This solution was then added into a solution of $Fe(acac)_3$ (14.0 mg, 0.04 mmol, 2 mol%) and 5-chloroindole **1m** (303.8 mg, 2.0 mmol, 1 equiv) in 10.0 mL dry THF.

A modified flow sutup was designed to dilute the solution before analysis (Figure S15). The reaction mixture was pumped at 0.5 mL/min and diluted with dry THF (2.0 mL/min) via a T-mixer before UV-Vis flow cell.

For the first 15 minutes, the reaction was performed without light irradiation, then the light was turned on.

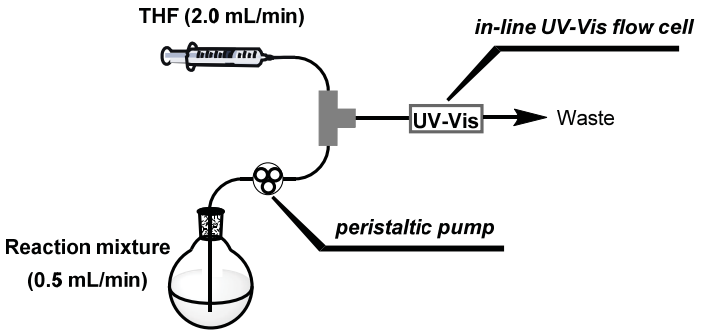


Figure S15: Modified flow setup for the analysis of concentrated reaction mixtures

Results:

Upon addition of the Grignard/NHC solution, the absorption band of $Fe(acac)_3$ at around 450 nm disappears quickly, and the concomitant appearance of the band at 450-600 nm is observed. This is similar with what we observed from the diluted solution. Under these concentrated conditions, however, this broad band disappears after about 2 minutes, after which almost no absorption in the range 350-600 is observed. At 7.5-8 minutes of reaction, a shoulder peak at 430-450 nm suddenly appears for a very short time. When the light was turned on at 15 minutes, the same peak, but much more intense, appeared and disappear immediately again (Figure S16). GC-FID measurements show almost complete conversion shortly after this point.

Based on DFT calculations and the fact that the UV absorption of the iron containing species is mainly influenced by the oxidative state of iron (see section 6.6), we suggest the sudden shoulder peak appearing at 430-450 nm to be an Fe(III) species. The sudden formation and disappearance of this shoulder might be related to the formation of an Fe(III) species formed by oxidative addition of the aryl chloride. As the intensity of the peak was much higher under irradiation, we propose that irradiation strongly promotes the formation of this species. The acceleration of an oxidative addition step is in agreement with the strong effect of light on the coupling with electron-rich substrates, as demonstrated in the manuscript.

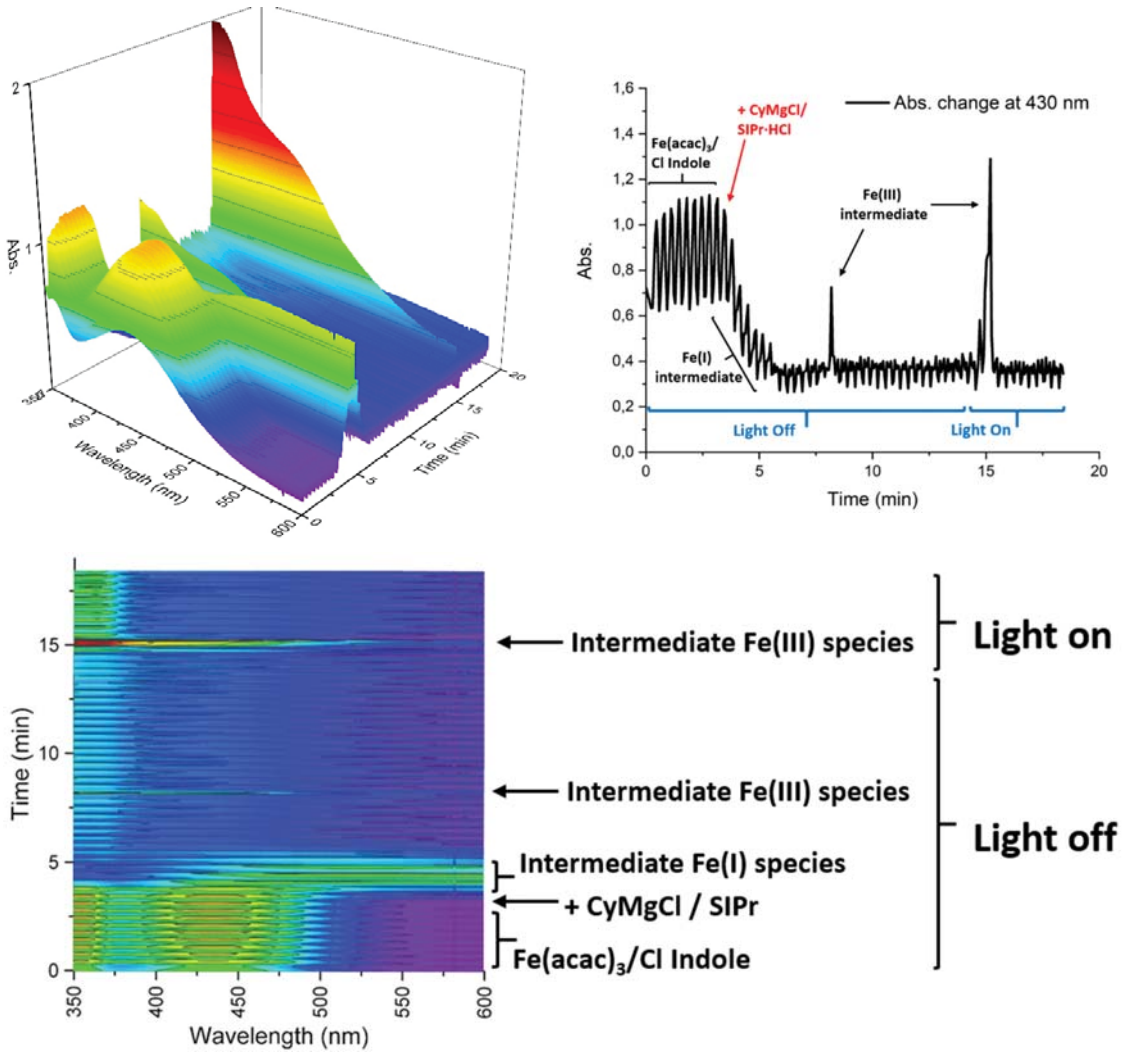


Figure S16: In-line UV-Vis at high concentration

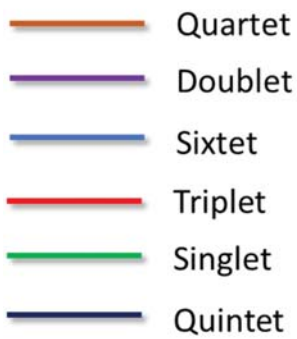
6.6: Computational details

All calculations were performed with the Gaussian09, revision D.01 suite[24] employing the DFT method, the Becke three-parameter hybrid functional[25], and Lee-Yang-Parr's gradient-corrected correlation functional (B3LYP[26]) used in conjunction with Grimme's dispersion correction with Becke-Johnson damping[27]. The ground-state geometries of the complexes were first optimized in the gas-phase. Frequency calculations were performed to ensure that the optimized structures were true minima on the potential energy surface (PES). Singlet ground state geometry optimizations for $Fe(0)(acac)_3$ and $Fe(II)(acac)_3$ were carried out at the restricted spin condition, while the triplet and quintet ground state geometry optimizations for $Fe(0)(acac)_3$ and $Fe(II)(acac)_3$ and the doublet, quartet and sextet ground state geometry optimizations for $Fe(I)(acac)_3$ and $Fe(III)(acac)_3$ were carried out at the unrestricted spin condition. All elements except Iron were assigned the 6-311G(d, p) basis set[28]. The double-ζ quality SBKJC VDZ[29] ECP basis set with an effective core potential was employed for the Iron metal ion.

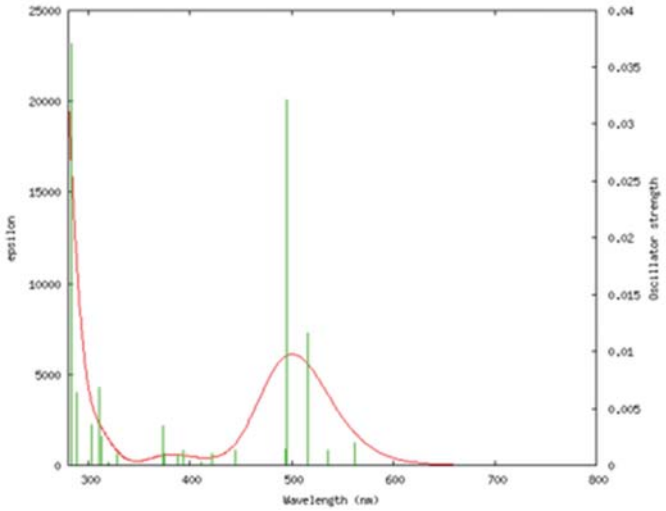
Vertical electronic excitations based on optimized geometries were computed for the lowest energy spin state of the 4 complexes using the TD-DFT[30] formalism in THF using the polarizable continuum model (PCM)[31]. *Gausssum 2.2*[32] was employed to visualize the absorption spectra (simulated with Gaussian distribution with a full-width at half maximum (fwhm) set to 3000 cm^{-1}.

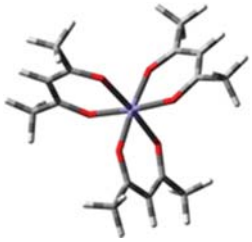
The calculated results were shown below:

Method: Ub3lyp-GD3BJ
Basis set: CHO 6-311G(d,p) Fe SBKJC VDZ ECP
Solvation: PCM=THF



Fe(III)(acac)$_3$



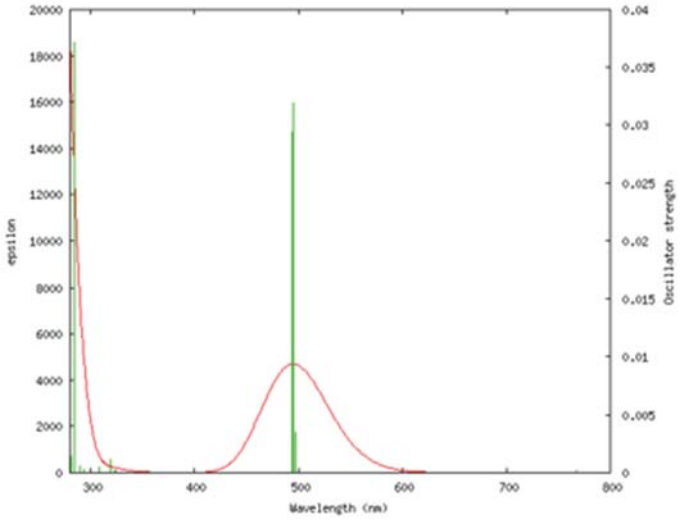


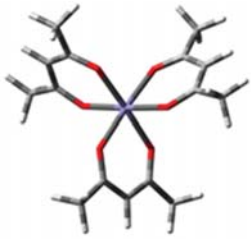
16.3 kcal/mol

13.5 kcal/mol

0 kcal/mol

Fe(II)(acac)$_3$



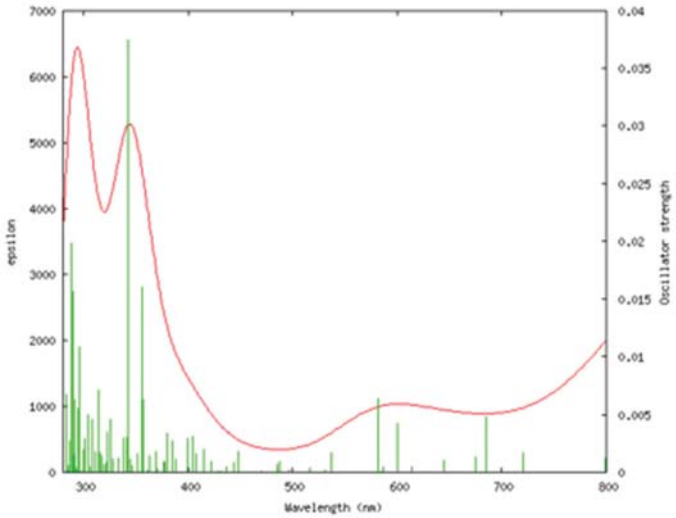


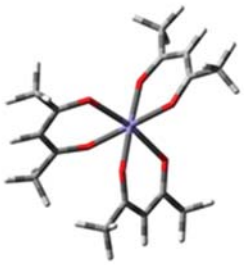
-20.8 kcal/mol

-25.2 kcal/mol

-44.8 kcal/mol

Fe(I)(acac)$_3$





51.1 kcal/mol

28.7 kcal/mol

28.4 kcal/mol

Fe(0)(acac)$_3$

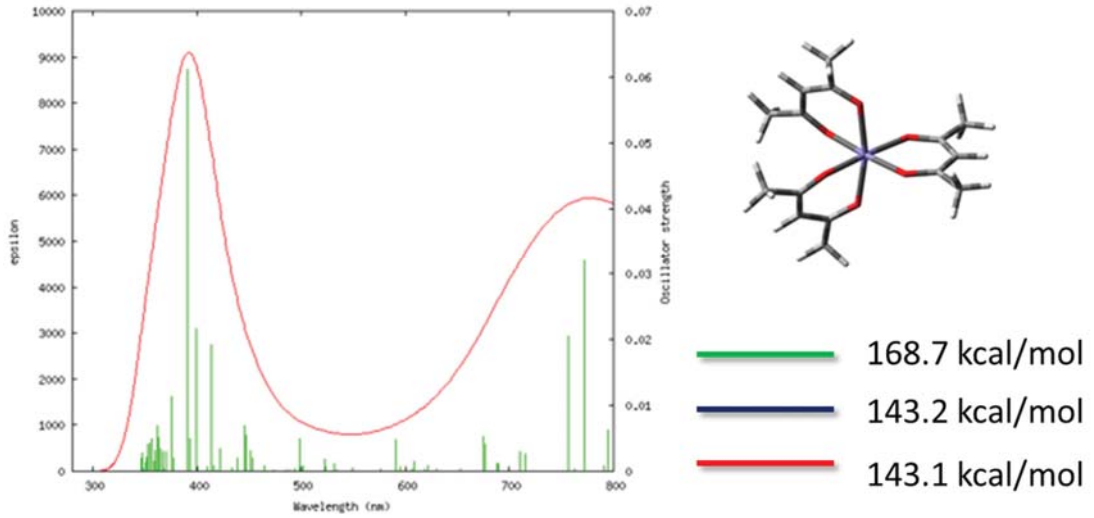


Figure S17: Predicted UV-Vis spectra of iron with different iron oxidative state, Oscillator strength and the molecular molecule images of selected electronic transitions

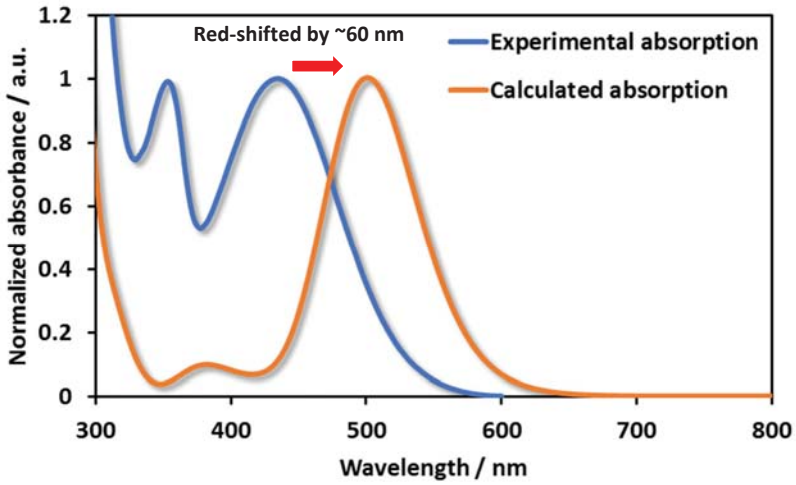


Figure S18: The calculated UV-Vis spectra and the experimental spectra

Table 1: Selected Transitions from TD-DFT calculations of $Fe(acac)_3$ in the Ground State (b3lyp/SBKJC-VDZ[Fe]6-311G**[C,H,O], PCM (THF)).

Oxidation state	Spin	State	λ/nm	f	Major transition(s)	Character
III	6	7	494.7	0.0321	H-2(B)->L+2(B) (37%) H-1(B)->L+1(B) (51%)	LMCT/LLCT
		21	373.7	0.0035	H-2(A)->L+2(A) (17%) H-1(A)->L+1(A) (14%) H(A)->L(A) (19%)	LMCT/LLCT
II	5	6	495.0	0.0319	H (B)->L (B) (81%) H (B)->L+4(B) (16%)	LMCT
		7	494.3	0.0294	H (B)->L+1(B) (65%) H (B)->L+2(B) (19%)	LMCT
I	4	16	685.3	0.0048	H (B)->L+8(B) (86%)	MC/LLCT
		23	581.1	0.0064	H (B)->L+14(B) (93%)	MLCT
0	3	28	771.6	0.0321	H-1(B)->L+9(B) (14%) H-1(B)->L+13(B) (18%) H (B)->L+17(B) (13%)	MLCT/LC
		73	413.1	0.0193	H-2(B)->L+10(B) (16%) H (B)->L+28(B) (46%) H (B)->L+29(B) (15%)	MLCT

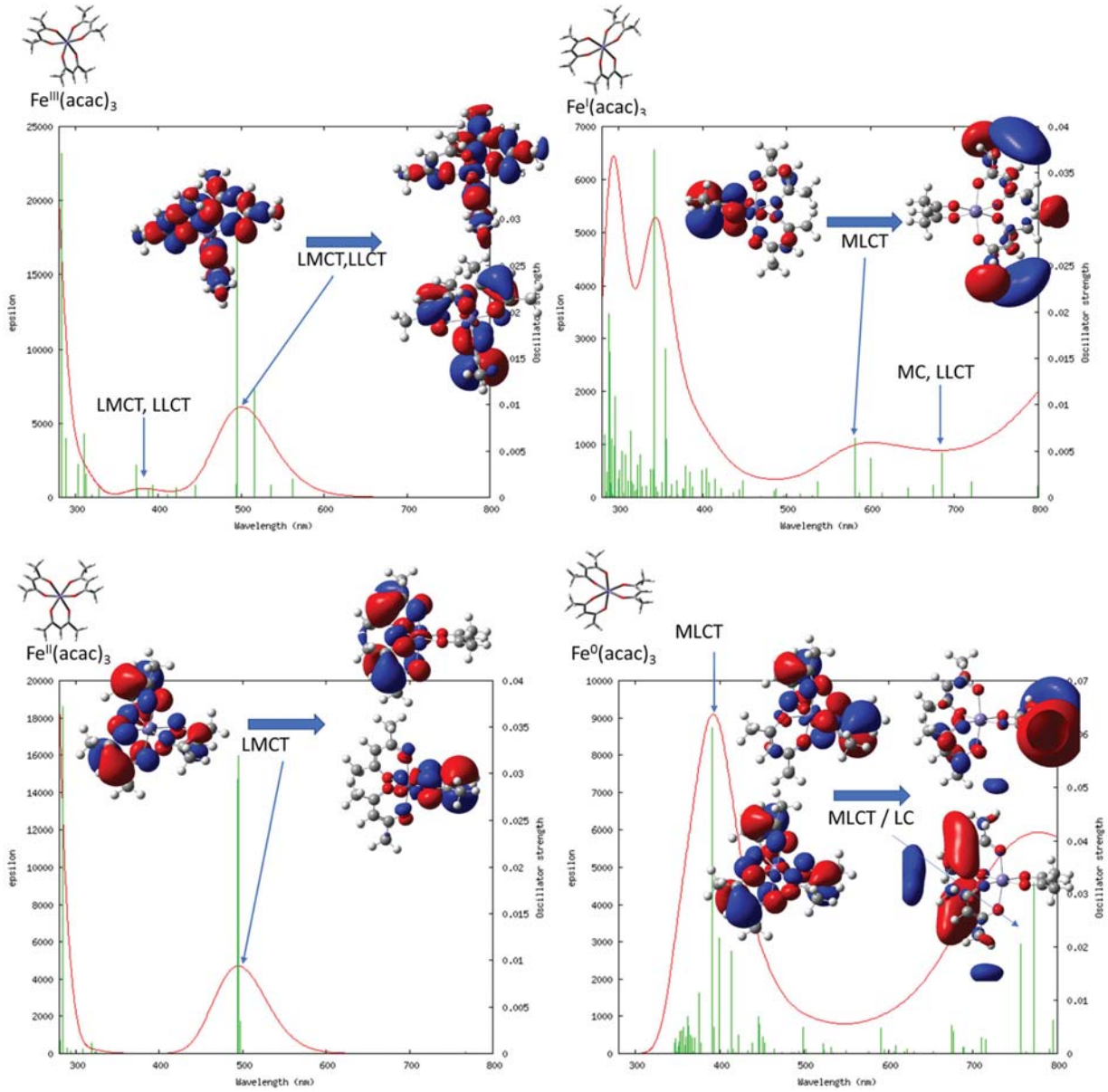


Figure S19: MOs related to the major electronic transitions of the related absorption bands.

Under the optimal reaction conditions, there are several possibilities of the combination of the intermediate $Fe(X)^{red}L_n$, (X = 0, I or II), L could be SIPr, acac, R and MgCl. Since many of the bands which gave the absorption at the visible region of iron centred complex are d-d transition, using an electronically similar ligand will gave the similar absorption when the number of electrons within d orbital is the same.[33] That means the UV-Vis absorption of the iron containing compound is mainly determined by the oxidative state of iron.

Figure S18 shows the comparison between the TD-DFT calculated UV-Vis spectra and the experimental one. The shape of the experimental spectra is similar with the calculated one but with a red shift of around 60 nm which is due to the error of TD-DFT calculations. Figure S17 shows the TD-DFT predicted UV-Vis spectra of the Fe(0)$(acac)_3$, Fe(I)$(acac)_3$, Fe(II)$(acac)_3$, Fe(III)$(acac)_3$, the major transitions of related absorption bands is compiled in Table 1.

Both Fe(III)$(acac)_3$ and Fe(II)$(acac)_3$ show an similar intense charge transfer band at ~ 500 nm, which is assigned primarily to ligand-to-metal charge transfer (LMCT) and ligand-to-ligand charge transfer (LLCT), while the Fe(III)$(acac)_3$ has an absorption at ~ 370 nm also due to the LMCT/LLCT. The low energy CT bands of Fe(I)$(acac)_3$ and Fe(0)$(acac)_3$ red-shifted by ~80 and ~200 nm compared to Fe(III)$(acac)_3$, respectively, and the nature of the charge transfer excited states are metal-to-ligand charge transfer (MLCT), this is due to the electron richer low valent iron metal ion.

As shown in Figure S13, after the activation stage of the reaction, the 430 nm LMCT band of Fe(III) species disappeared and a broad absorption band (red-shifted by ~90 nm) showed increasing intensity. This is proposed to be the MLCT band of Fe(I) species.

Table 2: DFT optimized atomic coordinates of Fe(III)$(acac)_3$

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	0.000003976	-0.000001021	0.000003496
2	6	-0.000003224	-0.000000242	-0.000010716
3	6	0.000002078	-0.000001796	-0.000002993
4	6	-0.000004354	0.000005470	0.000010828
5	8	-0.000001851	-0.000003277	-0.000009861
6	6	0.000002240	0.000000144	-0.000007810
7	8	0.000002525	0.000004558	0.000003059
8	6	-0.000002217	-0.000005821	-0.000000190
9	6	0.000002325	0.000002164	0.000009872
10	6	-0.000003077	-0.000001578	0.000002042
11	6	0.000009115	0.000001488	0.000000567
12	8	-0.000003786	0.000000490	0.000004579
13	6	-0.000003557	0.000002605	0.000006685

14	8	-0.000003195	-0.000000928	0.000004233
15	6	-0.000007603	0.000000368	-0.000002145
16	6	-0.000000595	-0.000008010	0.000004914
17	6	-0.000000222	0.000002812	0.000000724
18	6	0.000002542	-0.000000281	-0.000008369
19	8	-0.000011048	-0.000003893	0.000004004
20	6	0.000007804	0.000005264	-0.000002064
21	8	0.000003487	0.000004979	-0.000003193
22	26	0.000010689	-0.000002876	-0.000004661
23	1	0.000002231	0.000001516	-0.000002552
24	1	0.000002741	0.000001974	-0.000000926
25	1	0.000001728	0.000001235	-0.000001368
26	1	0.000000563	-0.000000213	-0.000003378
27	1	-0.000001501	-0.000001590	-0.000003999
28	1	-0.000002256	-0.000002772	-0.000004379
29	1	-0.000003338	-0.000001625	-0.000003782
30	1	-0.000003197	-0.000001890	0.000002984
31	1	-0.000001407	-0.000001169	0.000003717
32	1	-0.000002186	-0.000001158	0.000005486
33	1	-0.000000745	-0.000000386	0.000004502
34	1	0.000001537	0.000001010	0.000004783
35	1	0.000001589	0.000002128	0.000003906
36	1	0.000003423	0.000001881	0.000003573
37	1	-0.000001814	-0.000000935	-0.000000253
38	1	-0.000002282	-0.000001998	-0.000000644
39	1	-0.000002293	-0.000002189	0.000001223
40	1	-0.000000316	0.000000714	-0.000002197
41	1	0.000001650	0.000002259	-0.000002199
42	1	0.000002319	0.000000783	-0.000003667
43	1	0.000001500	0.000001806	-0.000003831

Table 3: DFT optimized atomic coordinates of Fe(II)(acac)$_3$

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	-0.000000745	-0.000000635	0.000000793
2	6	-0.000000154	0.000000142	-0.000003847
3	6	0.000002043	-0.000000121	-0.000000957
4	6	-0.000002398	0.000001621	0.000004532
5	8	-0.000004281	-0.000006246	-0.000005781
6	6	-0.000000662	0.000000694	-0.000000761
7	8	-0.000007276	0.000002657	0.000007756
8	6	-0.000000427	0.000001894	-0.000001056
9	6	-0.000007161	-0.000007441	-0.000000867
10	6	0.000001049	0.000000252	0.000005639
11	6	0.000013274	-0.000002712	0.000002861
12	8	-0.000005990	0.000002121	-0.000015026
13	6	-0.000002483	-0.000000652	0.000000167
14	8	0.000007666	0.000006177	0.000000867
15	6	0.000000594	0.000001775	0.000002747
16	6	0.000000626	-0.000001915	-0.000012176
17	6	0.000002875	-0.000000220	-0.000003068
18	6	-0.000003976	0.000012450	0.000003394
19	8	0.000005727	-0.000009777	-0.000000760
20	6	-0.000000736	-0.000004450	0.000000015
21	8	-0.000000250	-0.000002047	0.000014662
22	26	0.000004417	0.000003103	-0.000000031
23	1	0.000000075	0.000000121	0.000000267
24	1	0.000000406	0.000000280	0.000000020
25	1	-0.000000284	0.000000194	-0.000000313
26	1	-0.000000080	0.000000127	-0.000000002
27	1	0.000000016	0.000000180	-0.000000267
28	1	-0.000000056	0.000000351	-0.000000276
29	1	0.000000077	0.000000497	0.000000103
30	1	0.000000767	0.000000250	-0.000000642
31	1	0.000000287	-0.000000049	0.000000433
32	1	-0.000000939	0.000000865	-0.000001221
33	1	-0.000000402	-0.000000097	0.000000511
34	1	-0.000001623	-0.000000245	-0.000000336
35	1	0.000000406	0.000000421	0.000001410
36	1	0.000000013	0.000000089	-0.000000388
37	1	-0.000000784	-0.000000657	0.000000288
38	1	-0.000000143	0.000000467	-0.000000788
39	1	-0.000000667	-0.000000545	0.000001661

40	1	0.000000494	0.000000385	-0.000000343
41	1	-0.000000105	0.000000089	0.000000336
42	1	-0.000000058	0.000000310	-0.000000051
43	1	0.000000872	0.000000301	0.000000495

Table 4: DFT optimized atomic coordinates of Fe(I)(acac)$_3$

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	0.000001521	0.000001563	-0.000001009
2	6	-0.000007289	0.000000762	0.000006616
3	6	-0.000001402	0.000002219	0.000001969
4	6	0.000001386	0.000000214	-0.000005318
5	8	-0.000002585	-0.000004706	0.000007731
6	6	0.000000141	0.000000423	0.000001763
7	8	0.000007678	-0.000002453	-0.000011605
8	6	0.000002898	0.000000018	-0.000004440
9	6	-0.000001727	-0.000004570	-0.000002665
10	6	-0.000001650	-0.000000271	0.000004224
11	6	0.000005025	0.000006500	-0.000006930
12	8	-0.000004762	-0.000003123	0.000006544
13	6	0.000000316	-0.000000479	-0.000002904
14	8	0.000005523	0.000001729	-0.000005567
15	6	0.000001859	-0.000001092	0.000000660
16	6	-0.000005266	0.000001219	0.000003984
17	6	0.000000216	-0.000002397	-0.000000080
18	6	-0.000004176	-0.000001288	0.000005593
19	8	0.000009162	0.000002602	-0.000005821
20	6	-0.000000621	-0.000000541	0.000003553
21	8	0.000008901	-0.000001631	-0.000003740
22	26	-0.000013022	0.000004749	0.000009013
23	1	-0.000000010	0.000002500	0.000000014
24	1	-0.000000249	0.000003576	0.000000119
25	1	-0.000000613	0.000002675	-0.000000782
26	1	-0.000000093	0.000000826	0.000000166
27	1	-0.000000152	-0.000000900	0.000001255
28	1	0.000000178	-0.000002052	0.000000503
29	1	-0.000000579	-0.000001718	0.000002073
30	1	-0.000000309	-0.000002460	-0.000001579
31	1	0.000000180	0.000000023	-0.000002813
32	1	0.000001065	-0.000000260	-0.000002295

33	1	0.000000495	0.000001017	-0.000002302
34	1	-0.000000005	0.000000031	-0.000001202
35	1	0.000000437	0.000001618	-0.000001387
36	1	0.000000005	-0.000002024	0.000000680
37	1	0.000000719	-0.000003497	-0.000000285
38	1	-0.000000801	-0.000002011	-0.000000615
39	1	-0.000000145	-0.000000483	0.000001648
40	1	-0.000000602	0.000002377	0.000002201
41	1	-0.000001003	0.000001610	0.000003231
42	1	-0.000000631	0.000000953	0.000002732
43	1	-0.000000011	-0.000001247	-0.000002934

Table 5: DFT optimized atomic coordinates of Fe(0)(acac)$_3$

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	6	0.000001254	-0.000000455	-0.000001402
2	6	0.000001688	-0.000002726	0.000004795
3	6	0.000000053	0.000001549	-0.000002791
4	6	-0.000003386	0.000002284	0.000007280
5	8	0.000005183	0.000001335	-0.000005545
6	6	-0.000001388	0.000000186	0.000000394
7	8	0.000005041	0.000006651	-0.000000523
8	6	0.000001464	-0.000000488	-0.000002284
9	6	0.000002541	-0.000005162	-0.000001258
10	6	-0.000001144	0.000003260	-0.000000519
11	6	0.000001975	-0.000005940	0.000004245
12	8	0.000001414	0.000004621	-0.000002831
13	6	-0.000001682	0.000000655	-0.000000767
14	8	-0.000001957	0.000000442	0.000002236
15	6	-0.000003807	-0.000003432	-0.000000600
16	6	-0.000000566	0.000005413	-0.000005273
17	6	-0.000002560	-0.000002647	0.000004311
18	6	0.000004164	0.000003501	-0.000006527
19	8	-0.000004612	-0.000001274	0.000002899
20	6	-0.000000672	-0.000001897	0.000001942
21	8	0.000002788	-0.000003107	0.000002155
22	26	-0.000007570	-0.000004066	-0.000000966
23	1	0.000001014	0.000001300	0.000001630
24	1	0.000000881	0.000000900	0.000001465
25	1	0.000000591	0.000000930	0.000001857

26	1	0.000000197	0.000000973	0.000001413
27	1	-0.000000588	0.000000905	0.000001271
28	1	-0.000000414	0.000000745	0.000001437
29	1	-0.000001407	0.000000581	0.000001144
30	1	-0.000000900	-0.000000319	0.000000510
31	1	0.000000643	0.000001351	0.000000557
32	1	0.000000298	-0.000000270	-0.000000824
33	1	0.000001145	-0.000001169	-0.000000963
34	1	0.000001205	-0.000001112	-0.000001517
35	1	0.000001423	-0.000001583	-0.000001038
36	1	-0.000000564	-0.000000210	-0.000001253
37	1	-0.000000391	0.000000528	-0.000000724
38	1	0.000000584	-0.000000476	-0.000000598
39	1	-0.000000901	-0.000000581	-0.000000989
40	1	-0.000000529	-0.000000254	-0.000000570
41	1	-0.000000606	-0.000000190	-0.000000917
42	1	-0.000000354	-0.000000792	-0.000000662
43	1	0.000000447	0.000000037	-0.000000199

7: References

[1] L. Huck, A. de la Hoz, A. Díaz-Ortiz, J. Alcázar, *Org. Lett*. **2017**, 19, 3747-3750.

[2] Y-L, Lin, J-Y, Cheng, Y-H, Chu, *Tetrahedron,* **2007**, 63, 10949–10957.

[3] P. Nareddy, L. Mantilli, L. Guénée, C. Mazet, *Angew. Chem. Int. Ed*. **2012**, 51, 3826-3831.

[4] R. Agata, H. Takaya, H. Matsuda, N. Nakatani, K. Takeuchi, T. Iwamoto, T. Hatakeyama, M. Nakamura, *Bull. Chem. Soc. Jpn.* **2019**, 92, 381–390.

[5] S. K. Ghorai, M. Jin, T. Hatakeyama, M. Nakamura, *Org. Lett.* **2012**, 14, 1066-1069.

[6] R. Agata, T. Iwamoto, N. Nakagawa, K. Isozaki, T. Hatakeyama, H. Takaya, M. Nakamura, *Synthesis*, **2015**, 47, 1733-1740.

[7] A. Dahadhaa and W. Imhof, *ARKIVOC* **2013**, 200-216.

[8] M. Nakamura, K. Matsuo, S. Ito, E. Nakamura, *J. Am. Chem. Soc.* **2004**, 126, 3686-3687.

[9] S. D. Dreher, P. G. Dormer, D. L. Sandrock, G. A. Molander, *J. Am. Chem. Soc.* **2008**, 130, 9257-9259.

[10] X. Qian, L. N. Dawe, C. M. Kozak, *Dalton Trans*., **2011**, 40, 933-943.

[11] J. Tateiwa, E. Hayama, T. Nishimura, S. Uemura *J. Chem. Soc., Perkin Trans. 1*, **1997**, 1923-1928.

[12] H. Inami, J. Shishikura, T. Yasunaga, K. Ohno, H. Yamashita, K. Kato, S. Sakamoto, *Bioorg. Med. Chem.* **2015**, 23, 1788–1799.

[13] X. Zhang, I. Lee, X. Zhou, A. J. Berdis, *J. Am. Chem. Soc.* **2006**, 128, 143-149.

[14] P. P. Graczyk, P. Dimopoulos, A. Khan, G. S. Bhatia, C. N. Farthing, PCT Int. Appl., Patent No.:US008178552B2

[15] M. J. O'Neill, T. Riesebeck, J. Cornella, *Angew. Chem. Int. Ed.* **2018**, 57, 9103–9107.

[16] Y. Zhu, Y. Wei, *Chem. Sci*., 2014, **5**, 2379-2382

[17] M. C. Perry, A. N. Gillett, T. C. Law, *Tetrahedron Lett.* **2012**, *53*, 4436-4439.

[18] L. Pan, L. Yu, Z. Wu, Z. Li, H. Xiang, X. Zhou, *RSC Advances*, **2014**, 27775-27779.

[19] M. Tobisu, T. Takahira, N. Chatani, *Org. Lett.* **2015**, 17, 4352-4355.

[20] V. R. Bhonde, B. T. O'Neill, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2016**, 55, 1849–1853.

[21] G. A. Molander, K. M. Traister, B. T. O'Neill, *J. Org. Chem.* **2014**, 79, 5771-5780.

[22] P. Zhang, C. Le, D. W. C. MacMillan *J. Am. Chem. Soc.* **2016**, 138, 8084-8087.

[23] X. Liu, M-L. Go, *Bioorg. Med. Chem.* **2006,** 14, 153–163.

[24] M. J. Frisch, *et al*. Gaussian 09, Revision D.01 (Gaussian Inc., Wallingford, CT, 2013).

[25] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652.

[26] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785-789.

[27] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comp. Chem* **2011**, *32*, 1456-1465.

[28] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650-654.

[29] W. J. Stevens, M. Krauss, H. Basch, P. G. Jasien, *Can. J. Chem.* **1992**, *70*, 612-630.

[30] [a]M. E. Casida, C. Jamorski, K. C. Casida, D. R. Salahub, *J. Chem. Phys.* **1998**, *108*, 4439-4449; [b]R. E. Stratmann, G. E. Scuseria, M. J. Frisch, *J. Chem. Phys.* **1998**, *109*, 8218-8224.

[31] [a]M. Cossi, V. Barone, *J. Chem. Phys.* **2001**, *115*, 4708-4717; [b]V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995-2001; [c]J. Tomasi, B. Mennucci, R. Cammi, *Chem, Rev.* **2005**, *105*, 2999-3094.

[32] N. M. O'boyle, A. L. Tenderholt, K. M. Langner, *J. Comp. Chem* **2008**, *29*, 839-845.

[33] S. L. Reddy, T. Endo, G. S. Reddy, Advanced Aspects of Spectroscopy, Chapter 1, **2012** http://dx.doi.org/10.5772/50128

8: Copies of NMR Spectra

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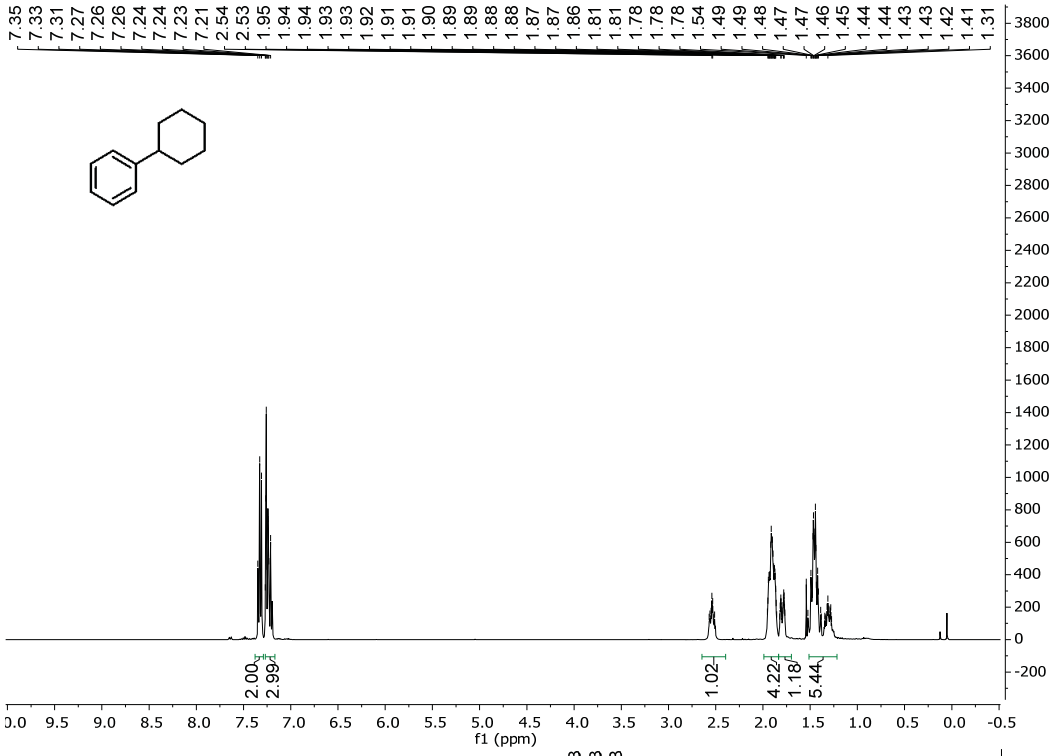

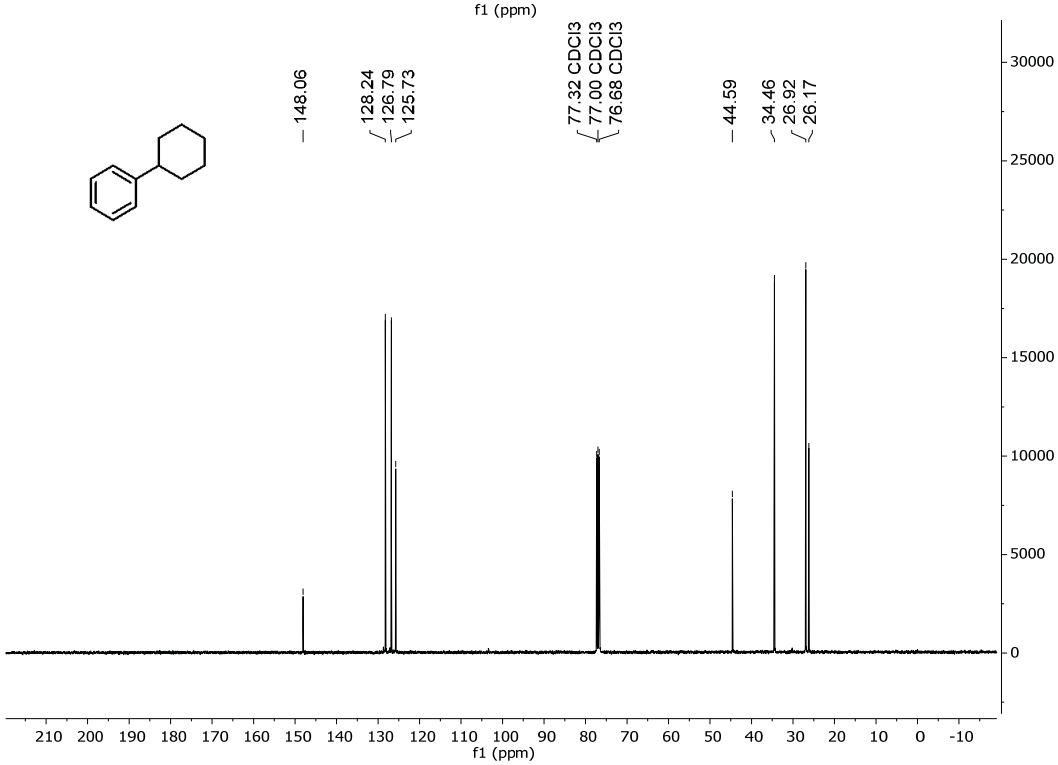

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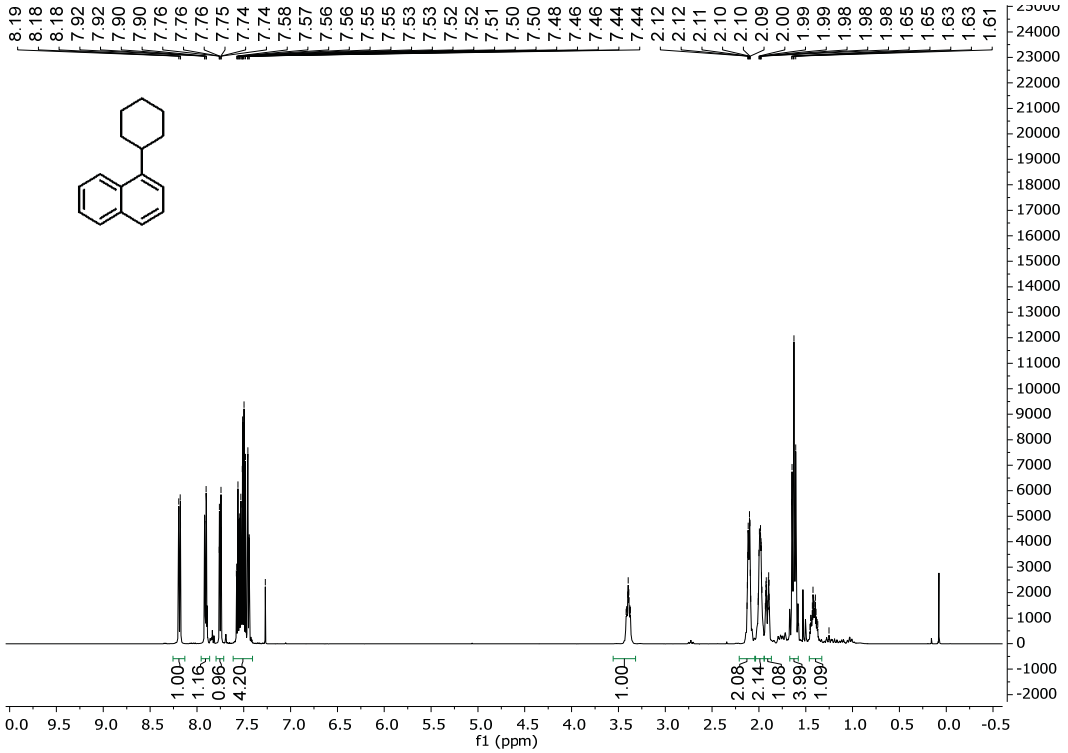
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2.12 2.12 2.11 2.10 2.10 2.09 2.00 1.99 1.99 1.98 1.98 1.98 1.65 1.65 1.63 1.63 1.61
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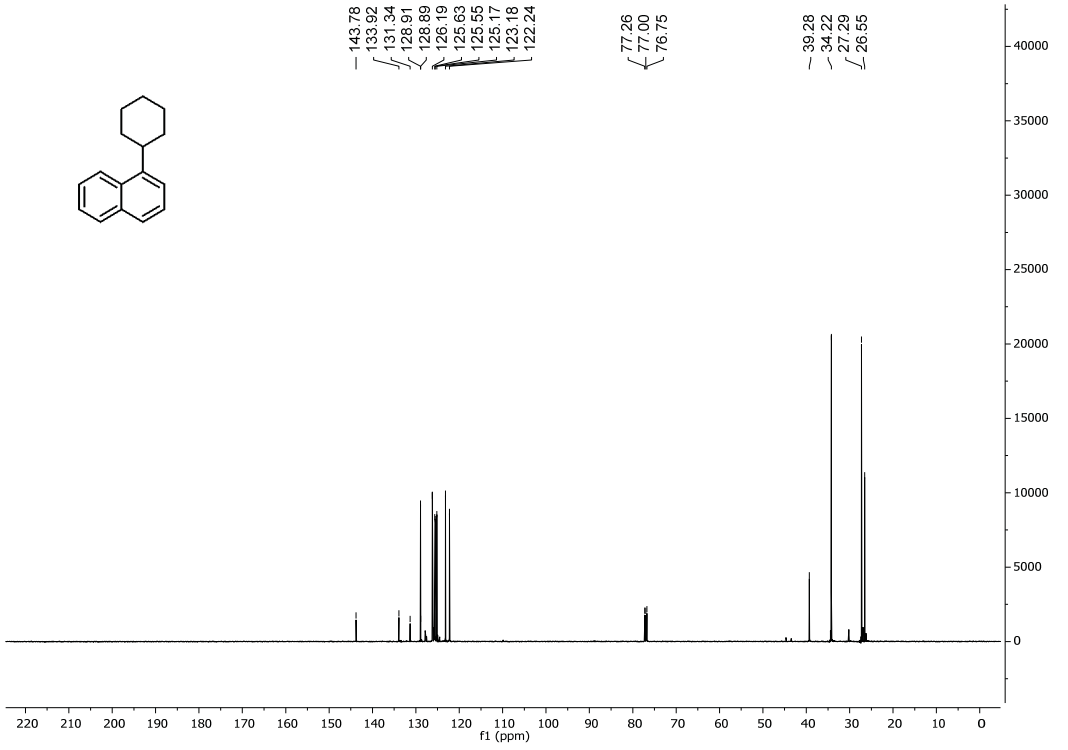
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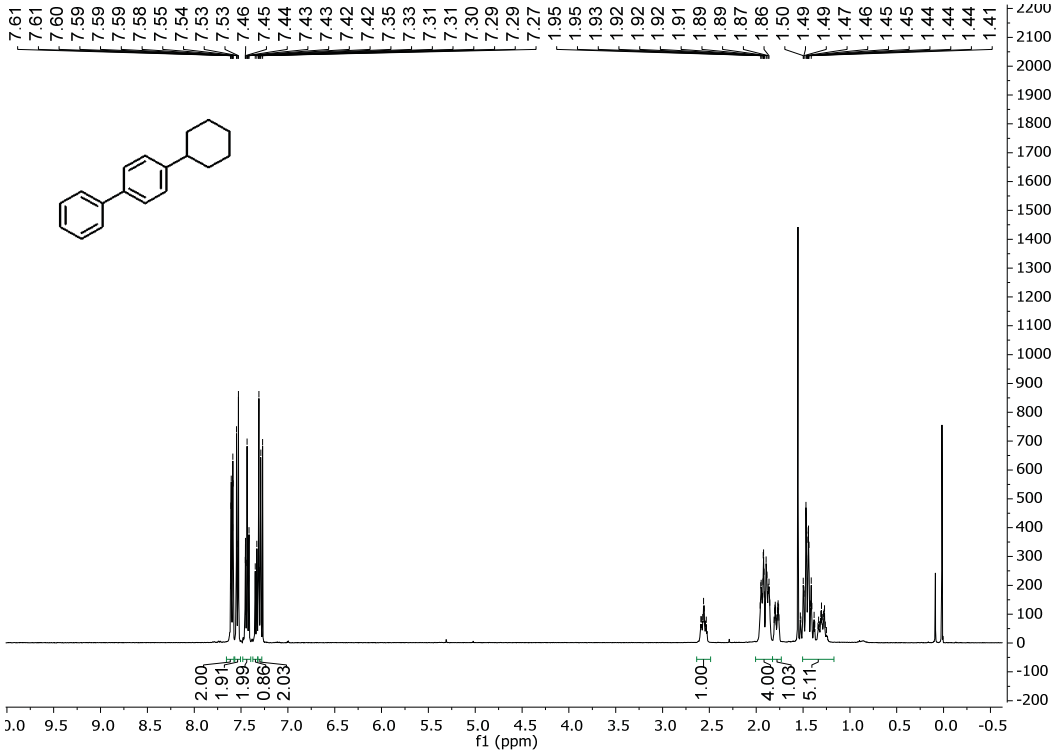
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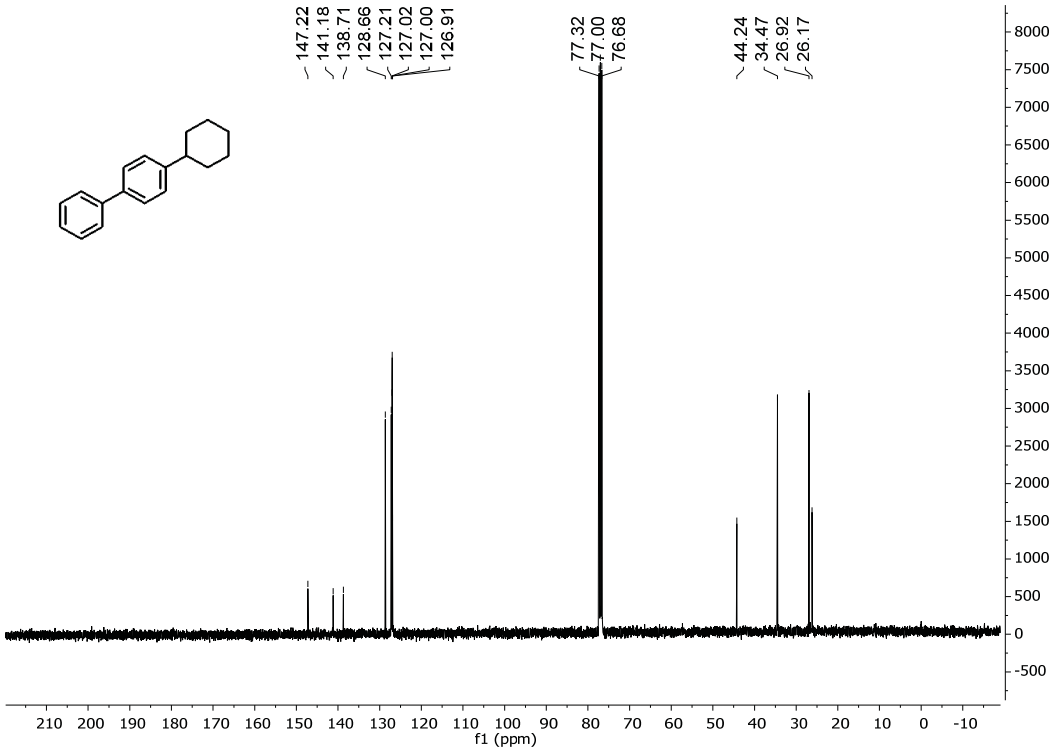
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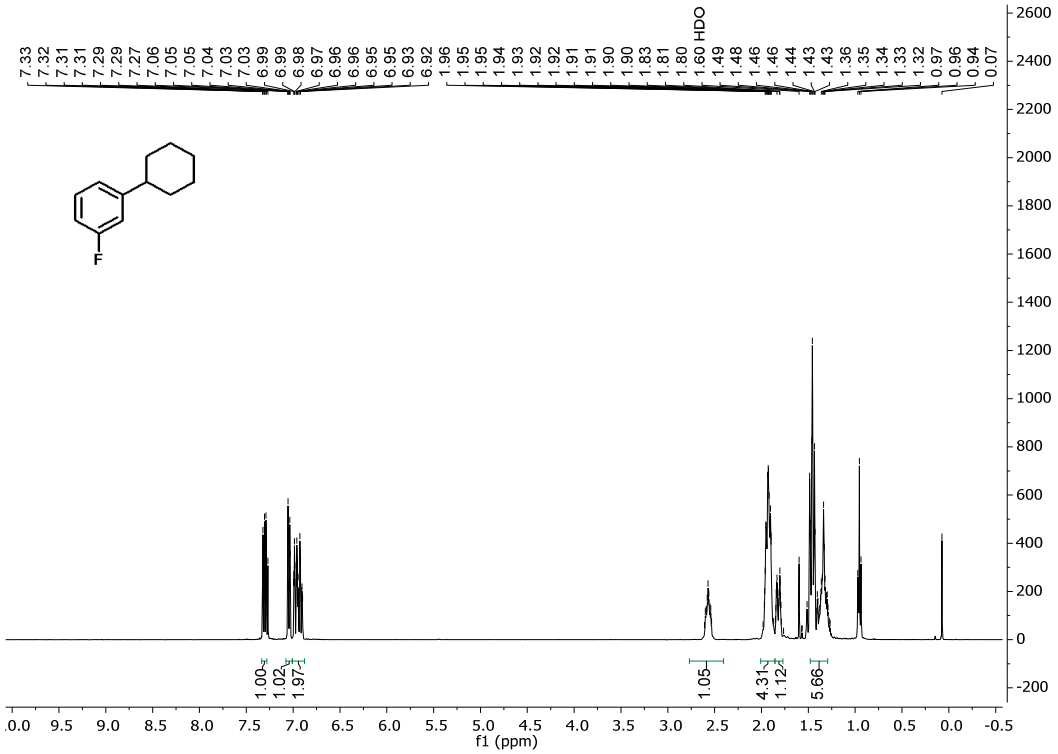
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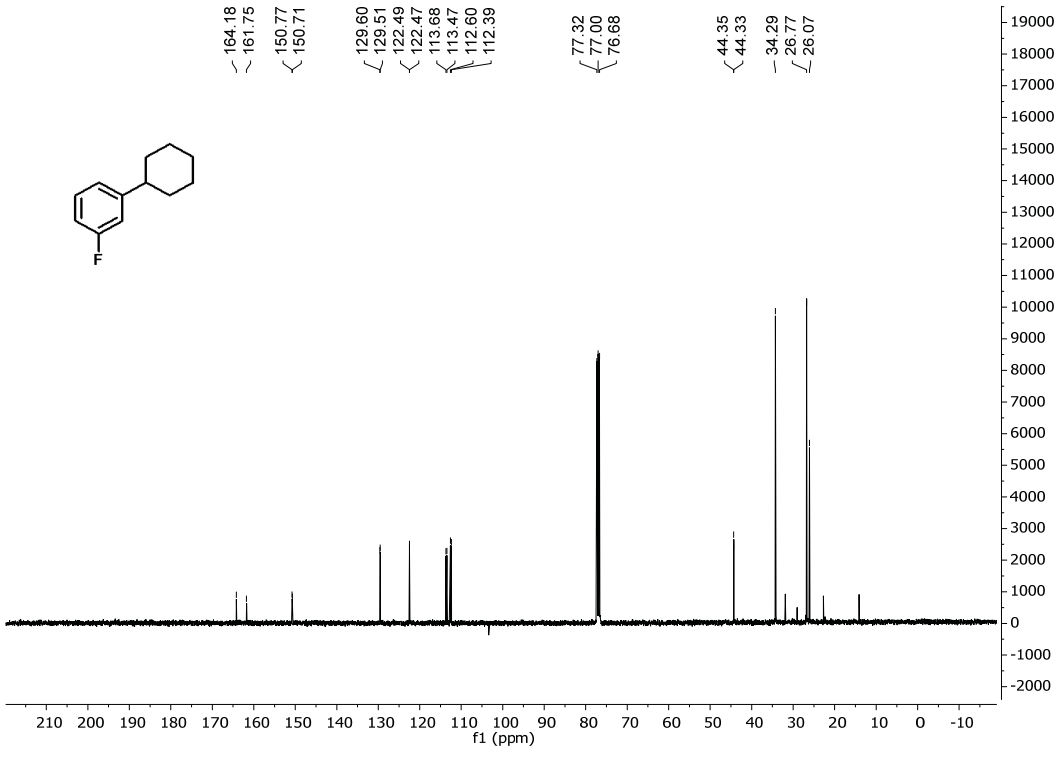
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26.77
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F
f1 (ppm)

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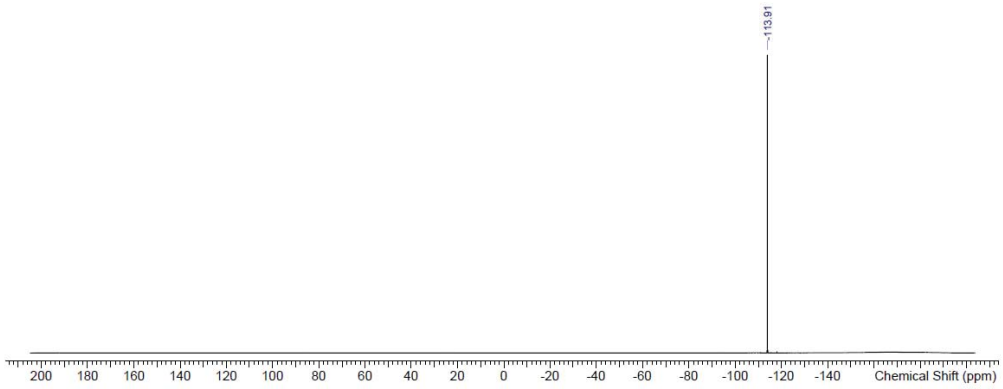
Page: 1



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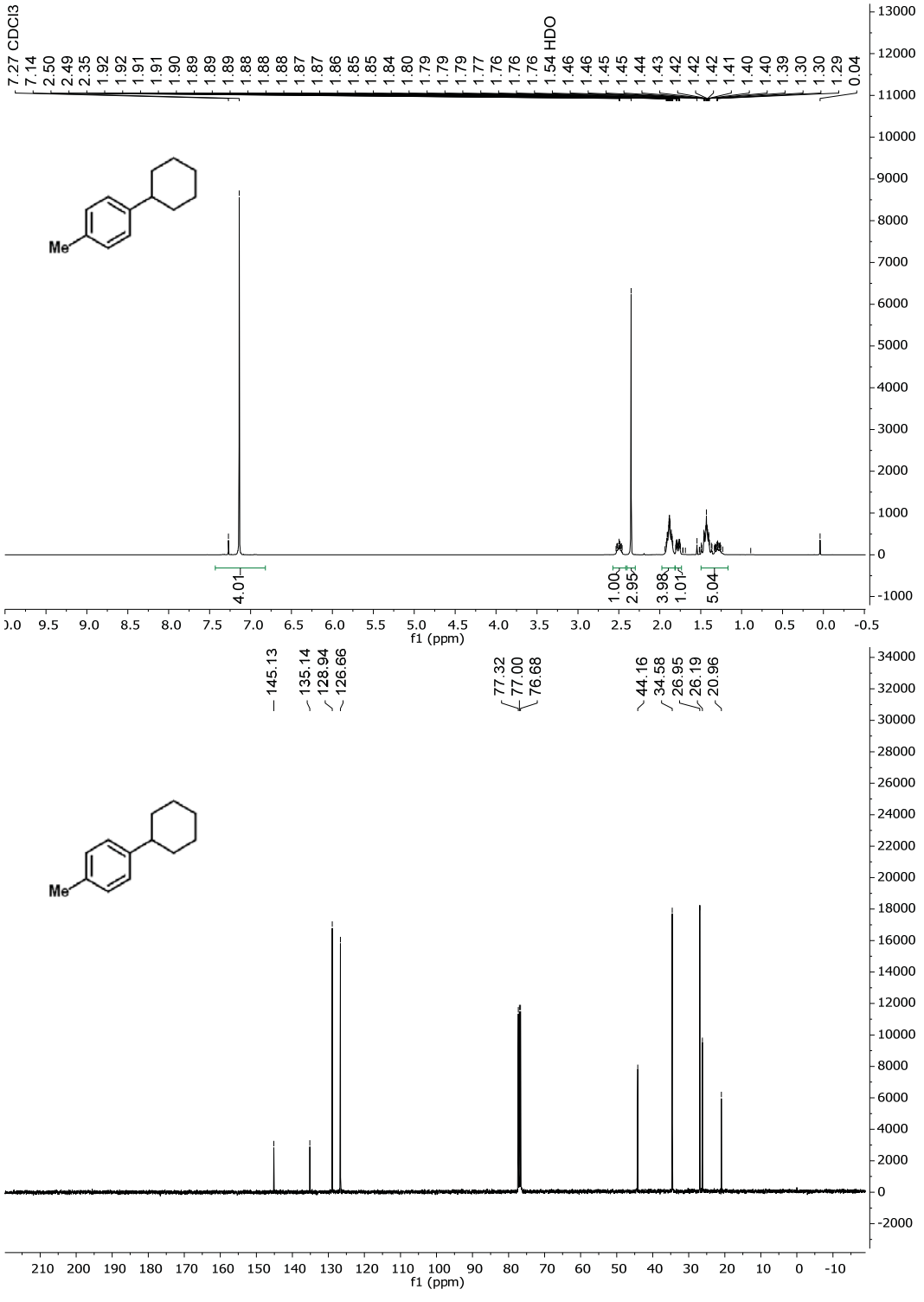
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f1 (ppm)

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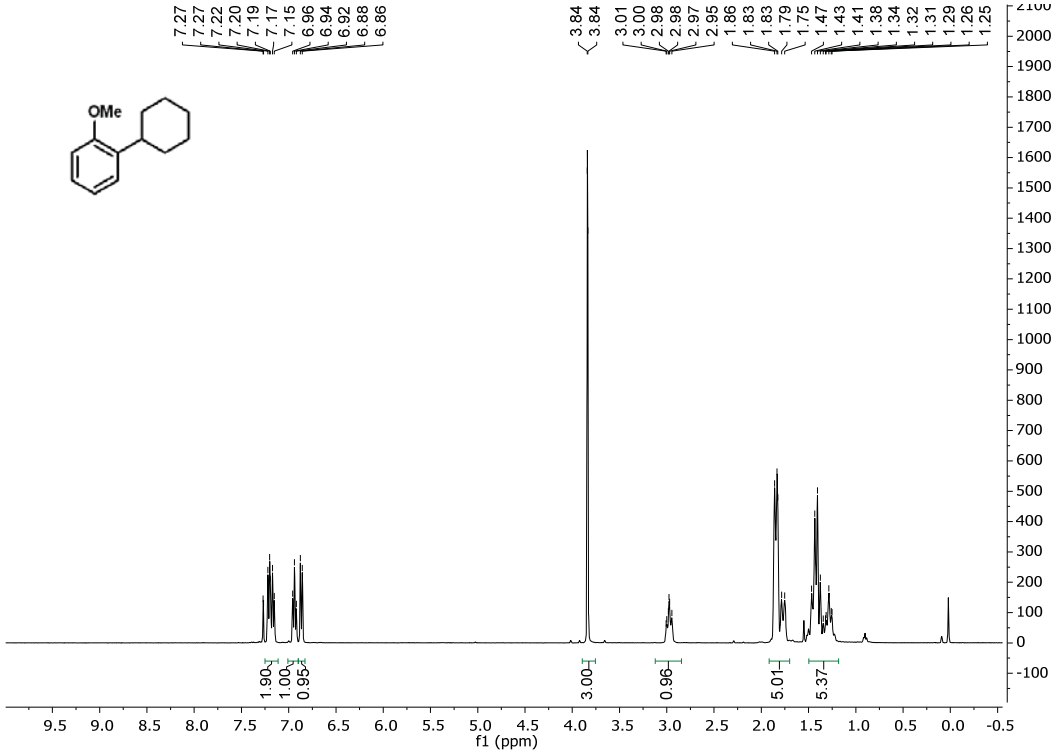
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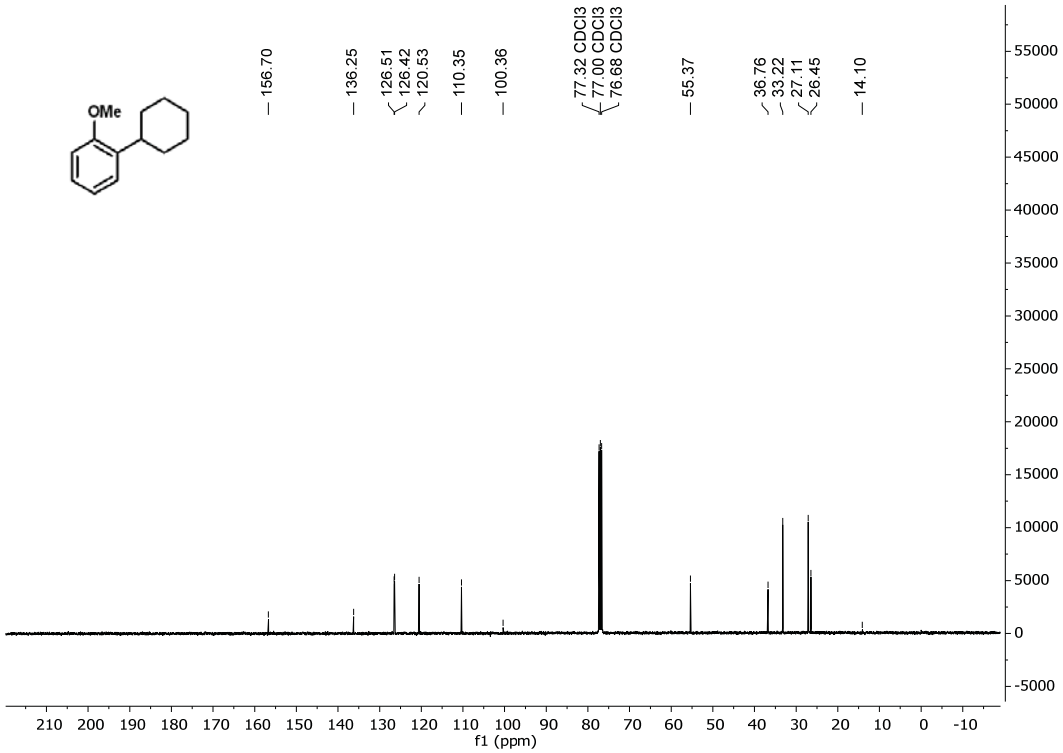
5.37
f1 (ppm)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14.10
OMe
f1 (ppm)

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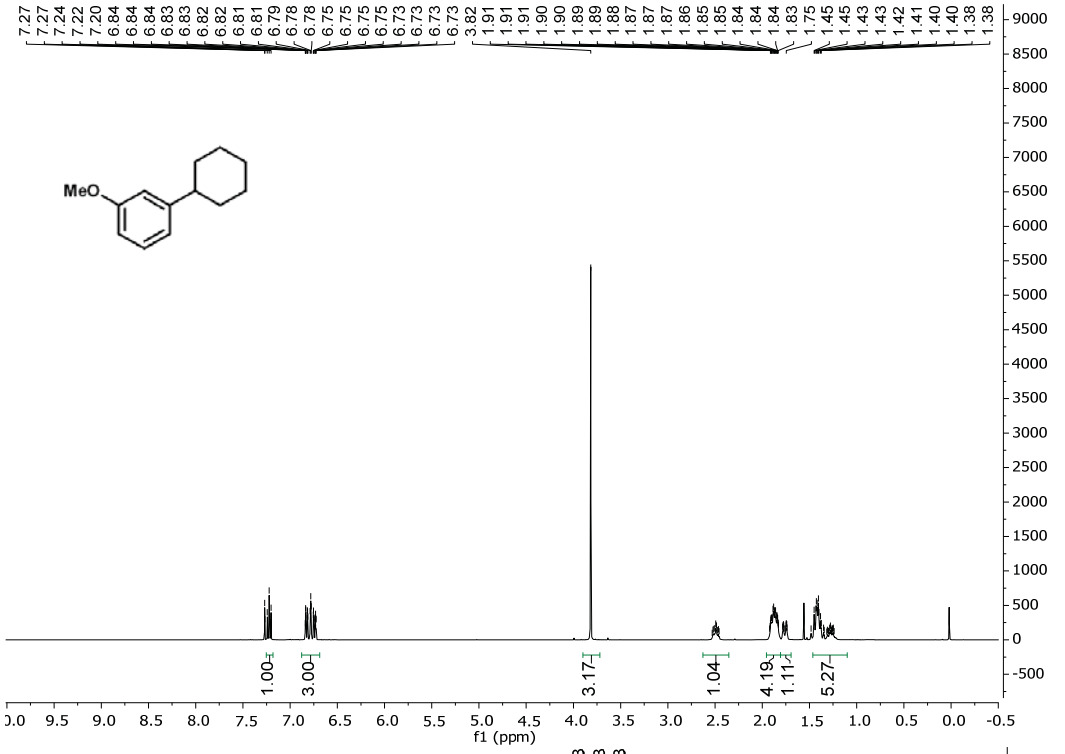
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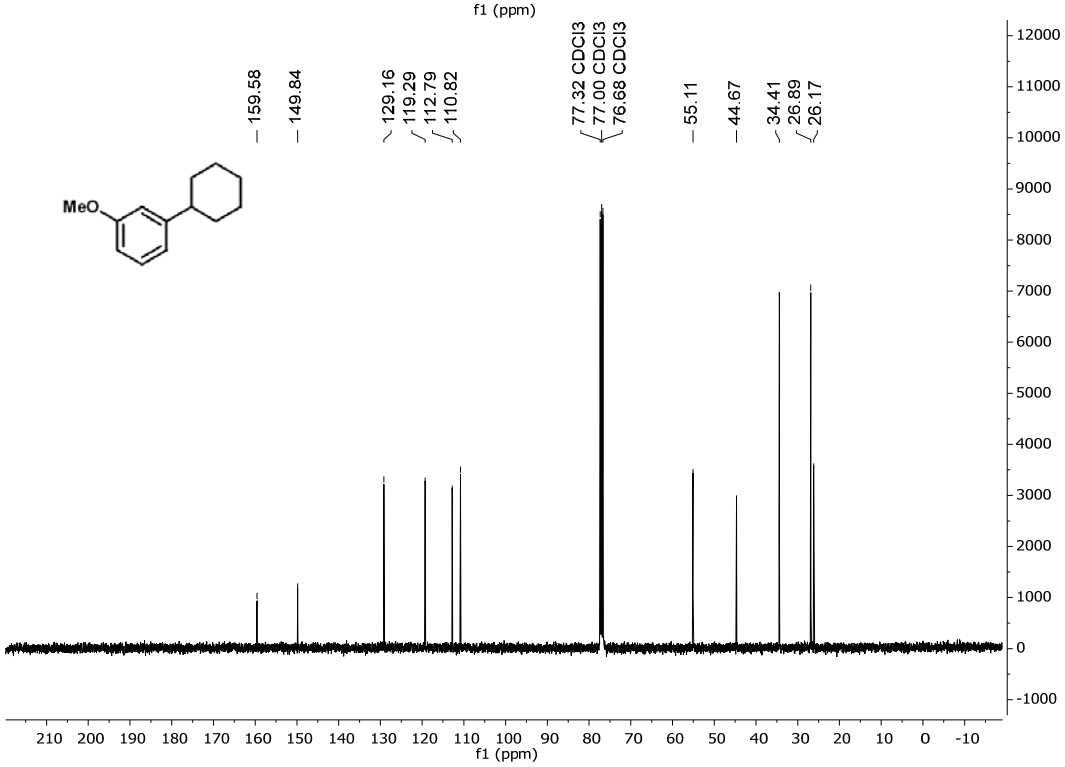
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f1 (ppm)

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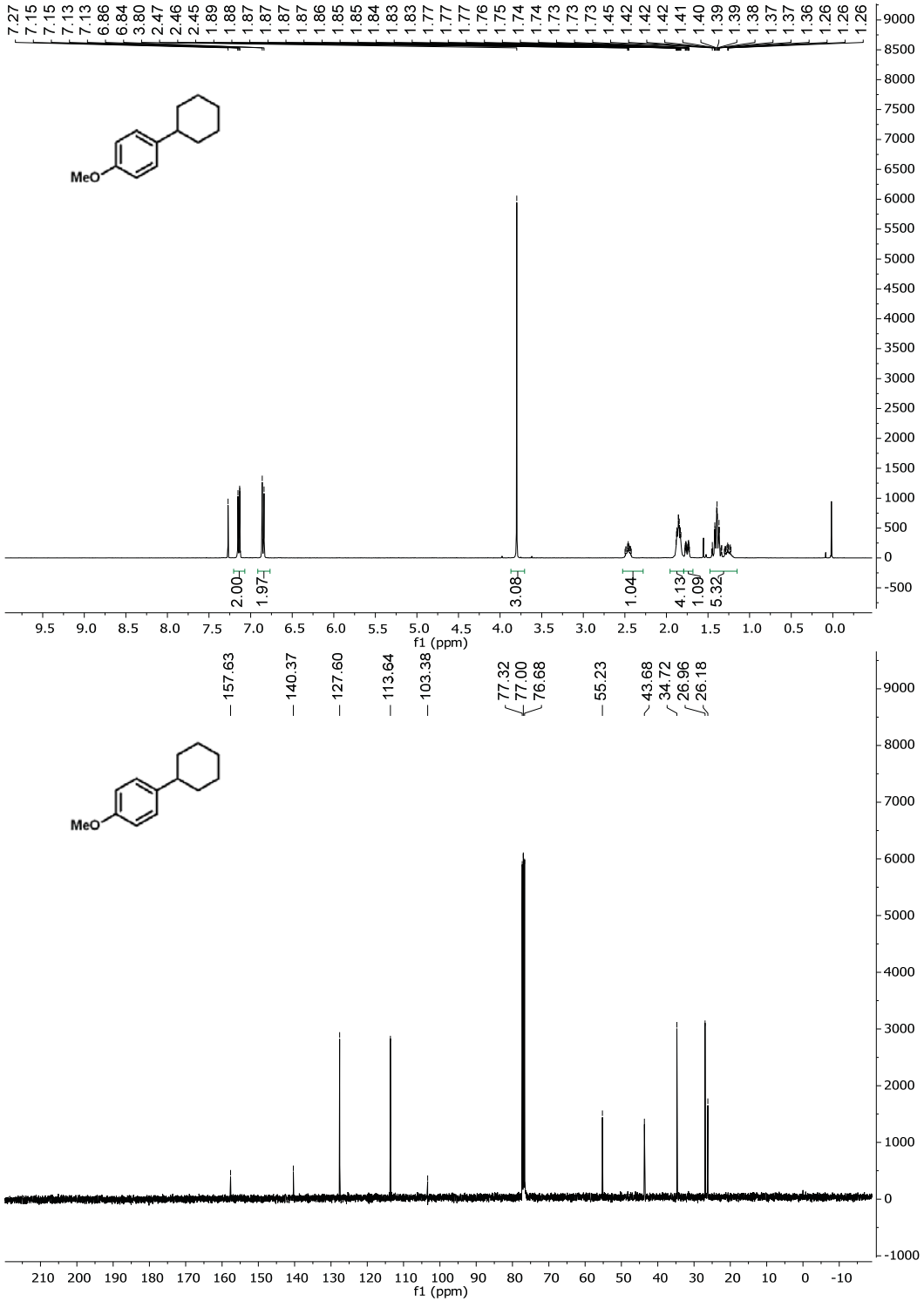
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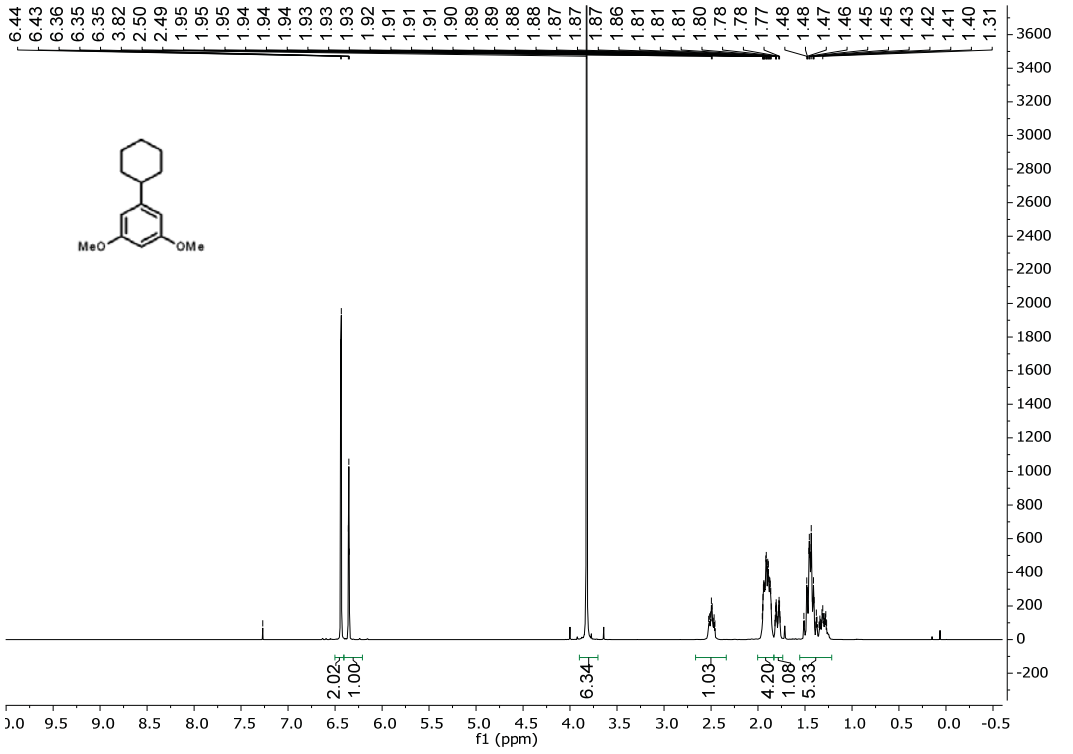
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OMe
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4.20
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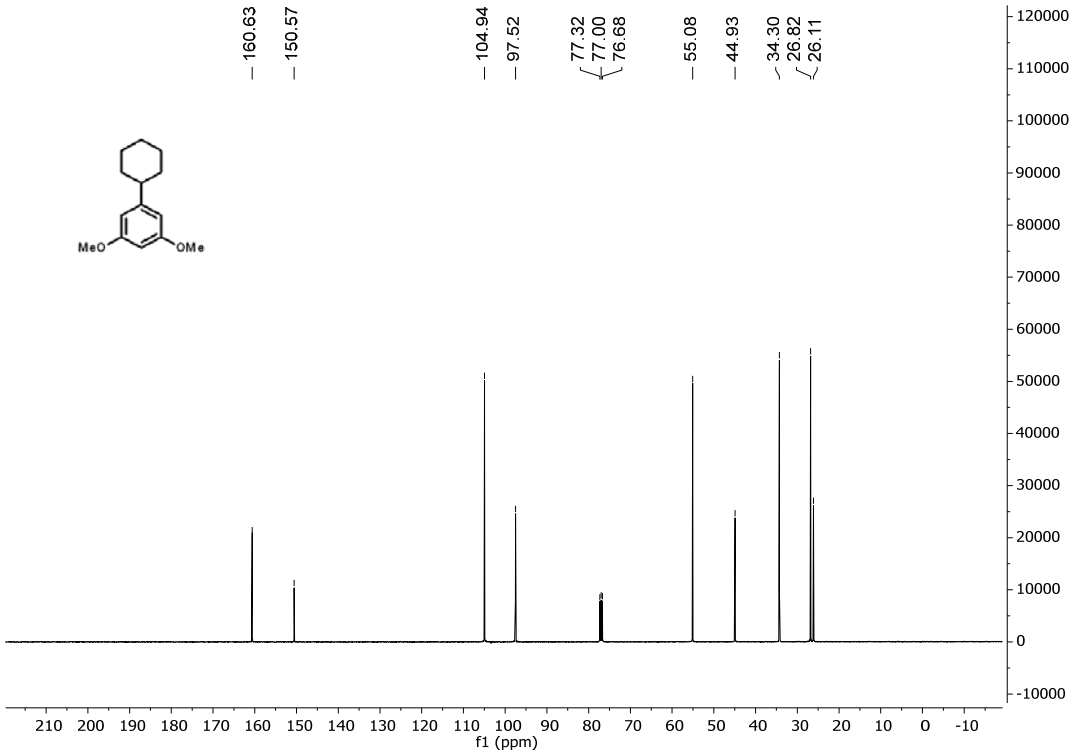
5.33
f1 (ppm)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f1 (ppm)

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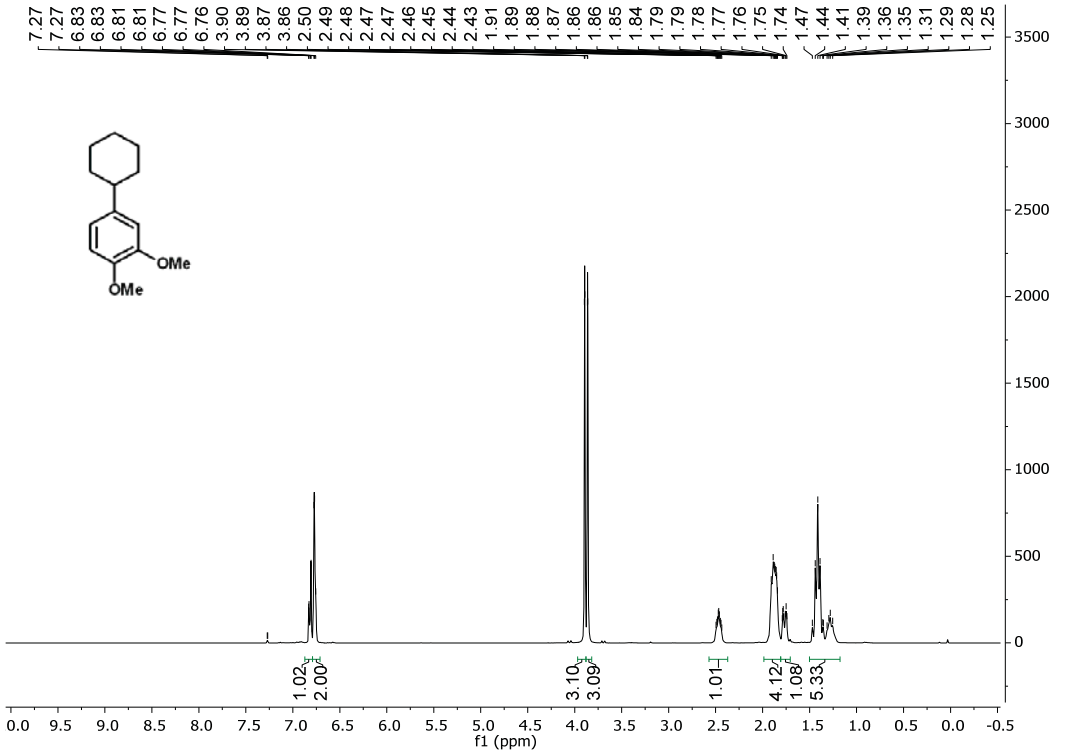
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1.74
1.47
1.44
1.41
1.39
1.36
1.35
1.31
1.29
1.28
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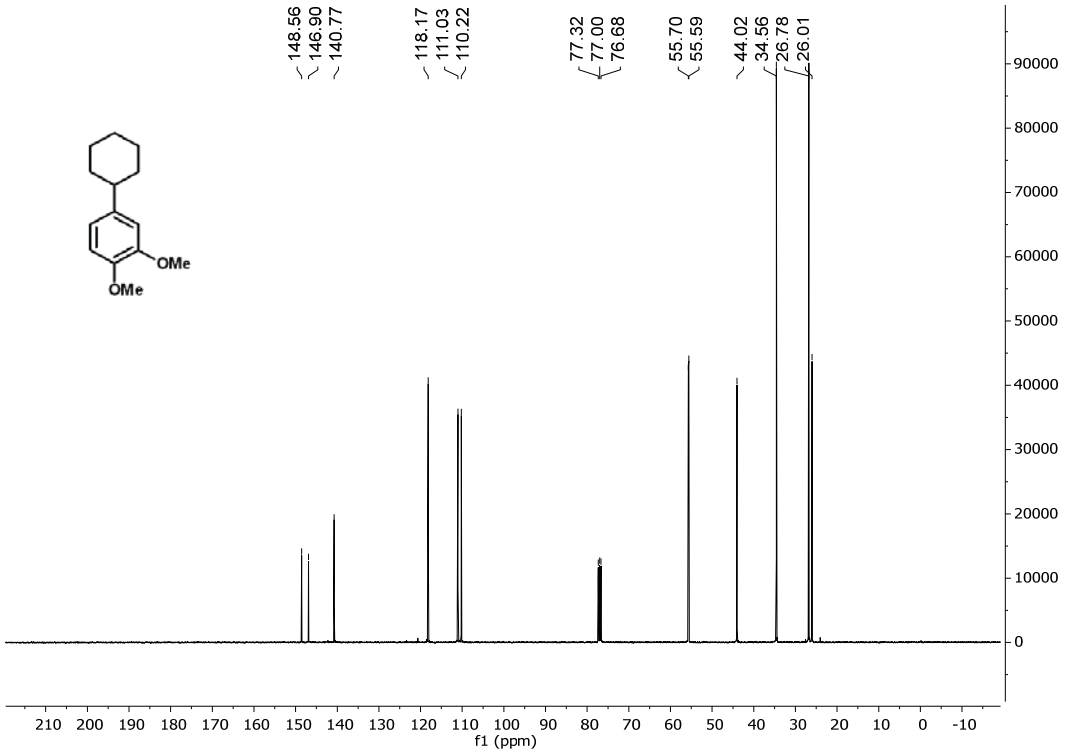
OMe
1.02
2.00
3.10
3.09
1.01
4.12
1.08
5.33
f1 (ppm)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55.59
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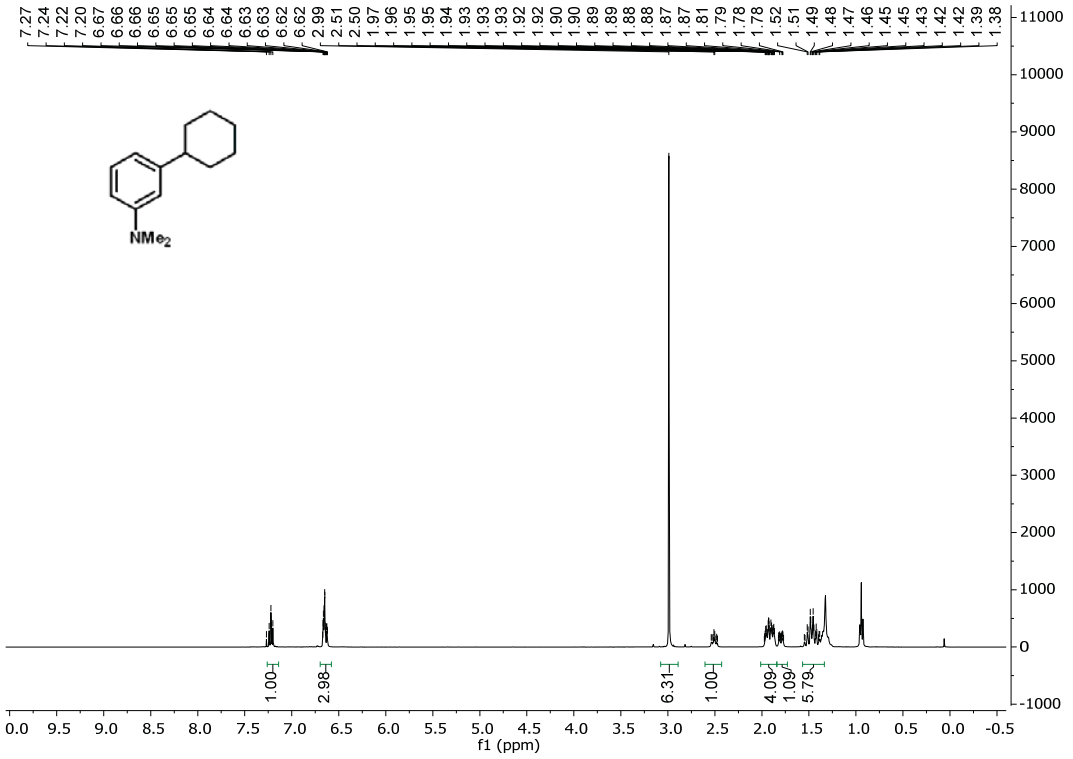
34.56
26.78
26.01
OMe
OMe
f1 (ppm)

3kb: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1.52
1.51
1.49
1.48
1.47
1.46
1.45
1.45
1.43
1.42
1.42
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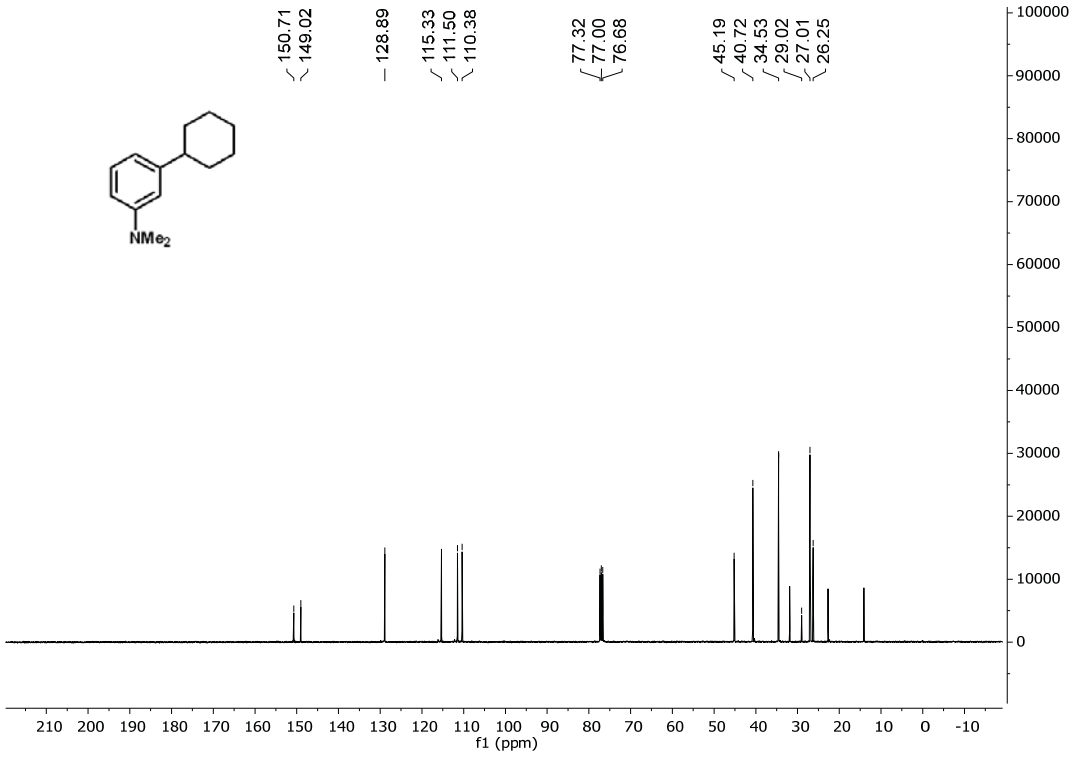
2.98
6.31
1.00
4.09
1.09
5.79
f1 (ppm)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149.02
128.89
115.33
111.50
110.38
77.32
77.00
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40.72
34.53
29.02
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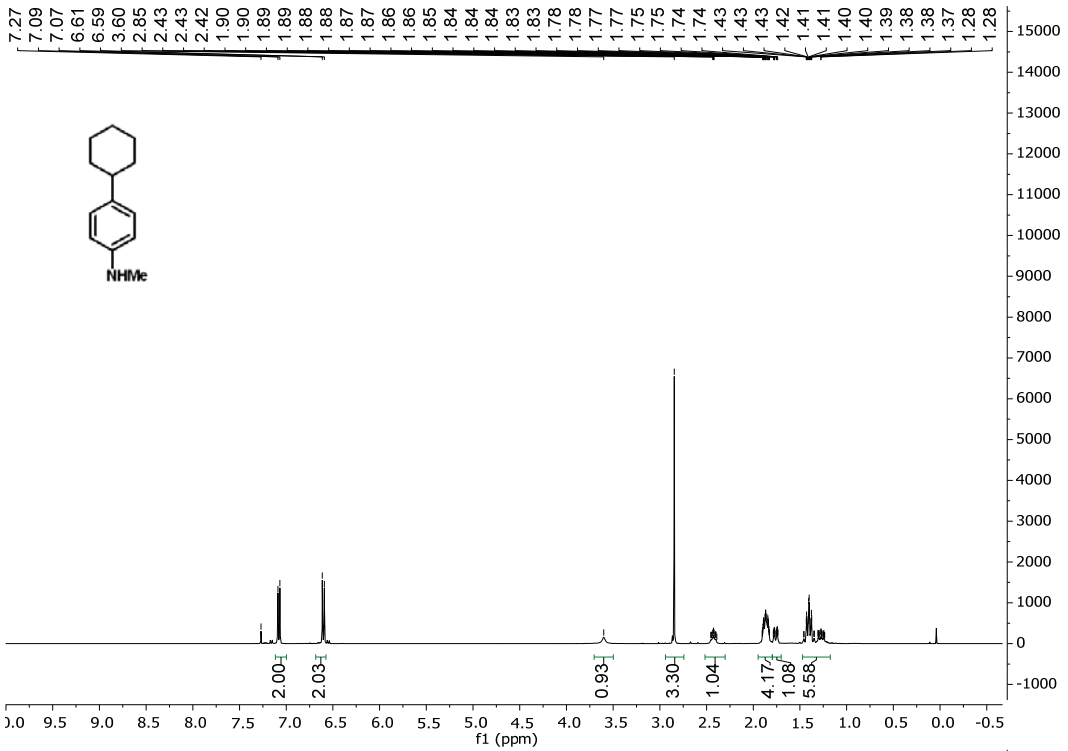
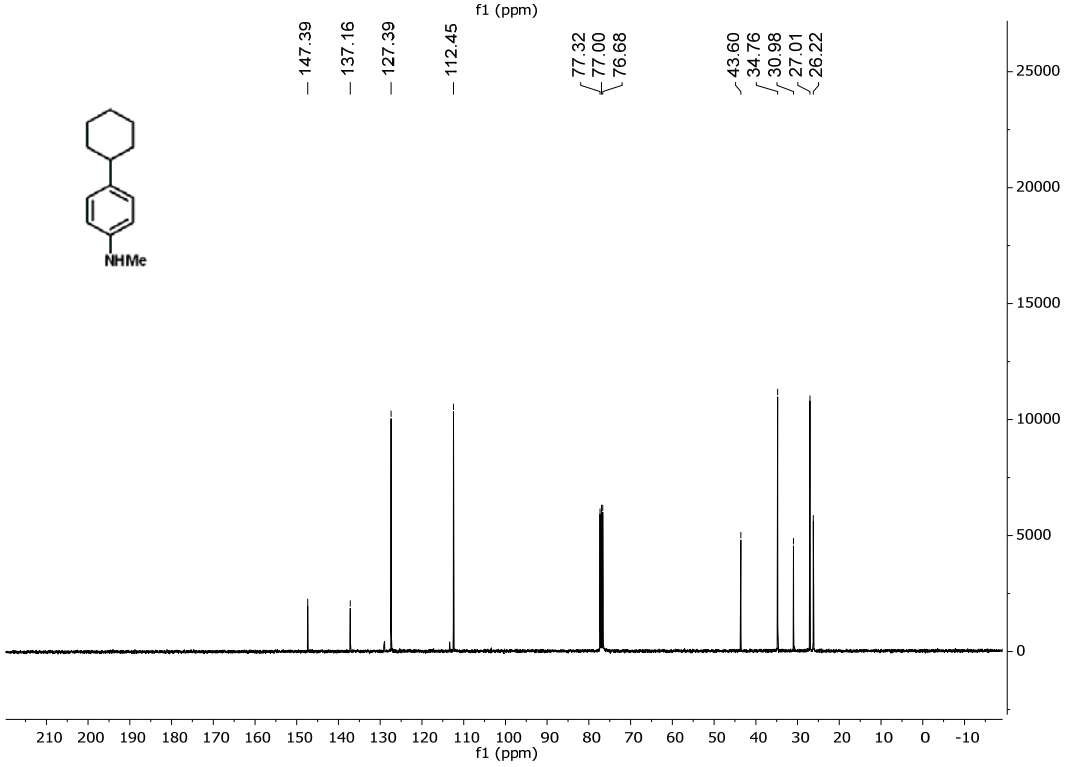
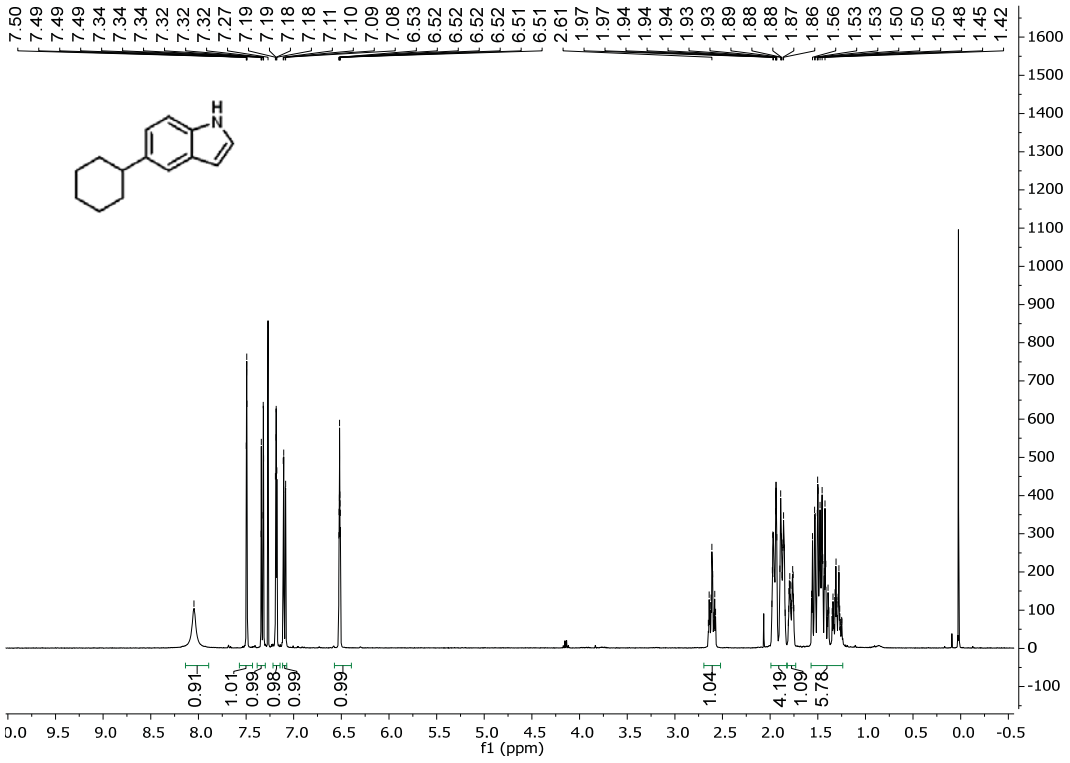
26.25
NMe2
f1 (ppm)

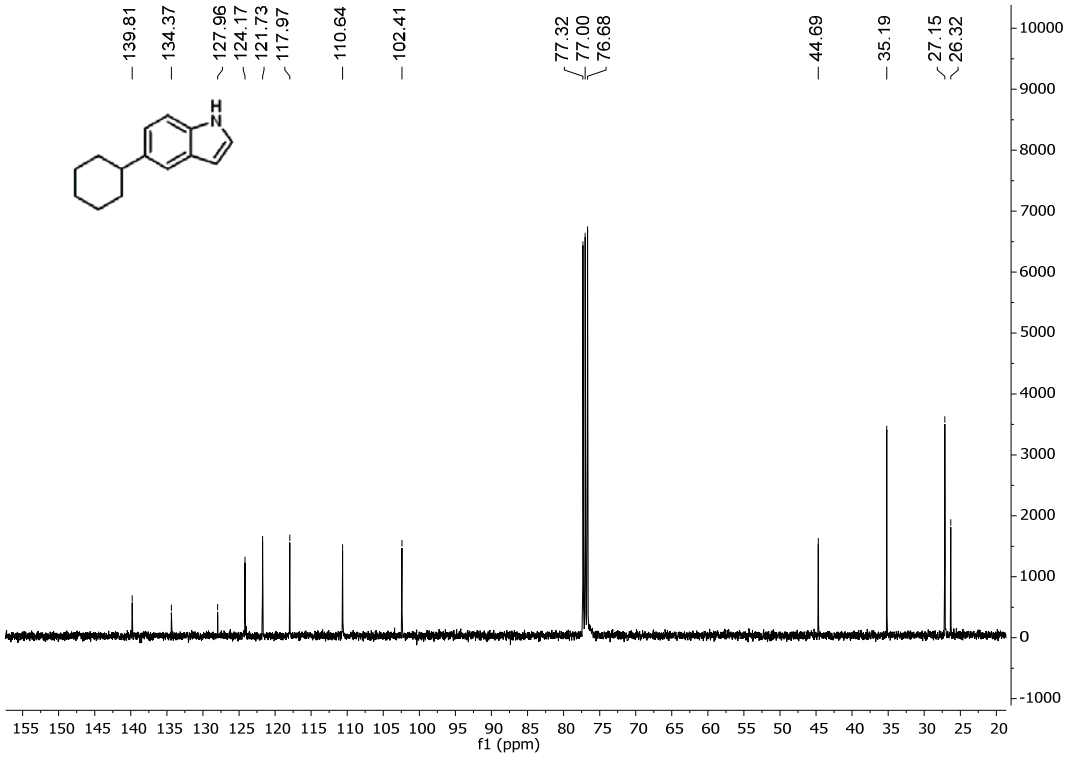
3lb:


7.27 7.09 7.07 6.61 6.59 3.60 2.85 2.43 2.43 2.42 1.90 1.90 1.89 1.89 1.89 1.88 1.88 1.87 1.87 1.86 1.86 1.85 1.84 1.84 1.84 1.83 1.83 1.78 1.78 1.77 1.77 1.75 1.75 1.74 1.74 1.43 1.43 1.43 1.42 1.41 1.41 1.40 1.40 1.39 1.38 1.38 1.37 1.28 1.28
NHMe
2.00 2.03 0.93 3.30 1.04 4.17 1.08 5.58
f1 (ppm)

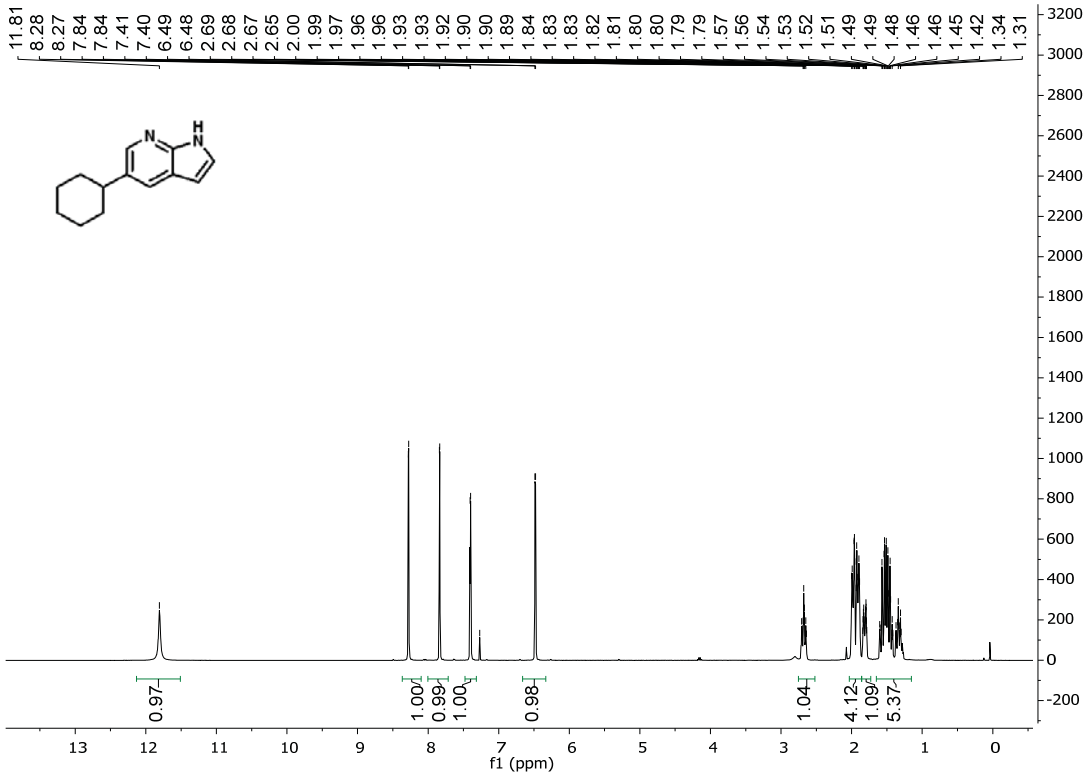

147.39 137.16 127.39 112.45 77.32 77.00 76.68 43.60 34.76 30.98 27.01 26.22
NHMe
f1 (ppm)

3mb:


7.50 7.49 7.49 7.49 7.34 7.34 7.34 7.32 7.32 7.27 7.19 7.19 7.18 7.18 7.11 7.10 7.09 7.08 6.53 6.52 6.52 6.52 6.52 6.51 6.51 2.61 1.97 1.97 1.94 1.94 1.94 1.93 1.93 1.89 1.88 1.88 1.87 1.86 1.56 1.53 1.53 1.50 1.50 1.50 1.48 1.45 1.42
0.91 1.01 0.99 0.98 0.99 0.99 1.04 4.19 1.09 5.78
f1 (ppm)


139.81 134.37 127.96 124.17 121.73 117.97 110.64 102.41 77.32 77.00 76.68 44.69 35.19 27.15 26.32
f1 (ppm)

3nb: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7.41
7.40
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6.48
2.69
2.68
2.67
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2.00
1.99
1.97
1.96
1.96
1.93
1.93
1.92
1.90
1.90
1.89
1.84
1.83
1.83
1.82
1.81
1.80
1.80
1.79
1.79
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1.56
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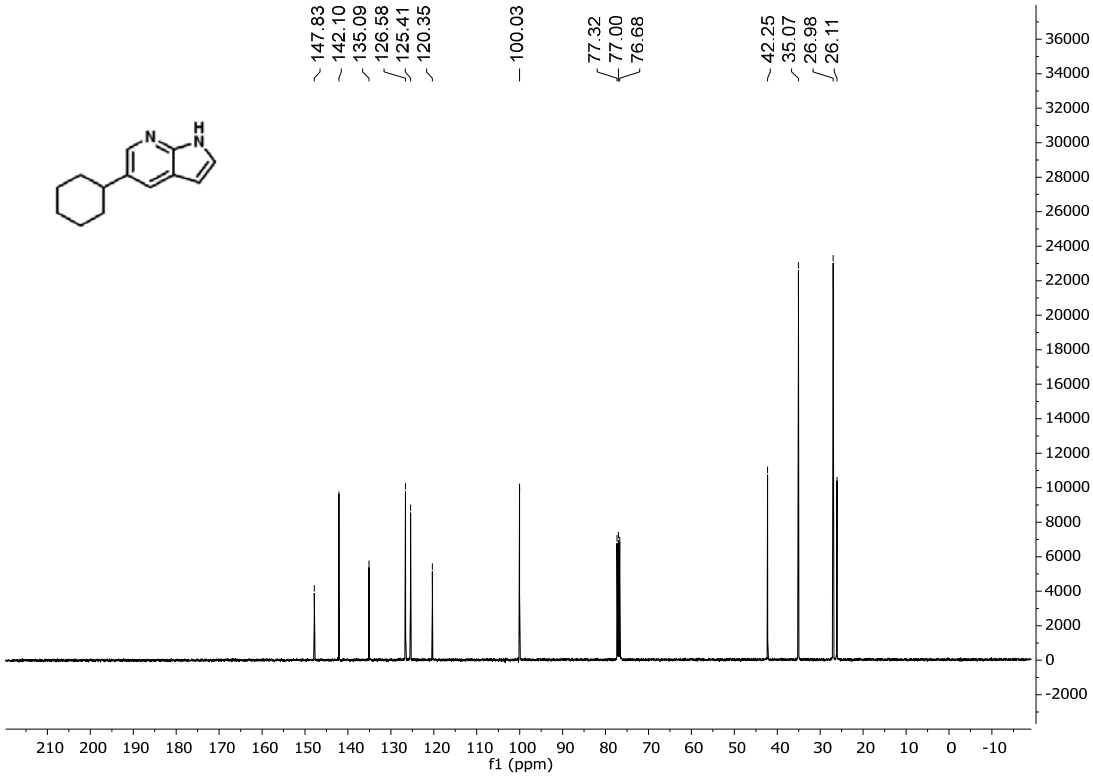
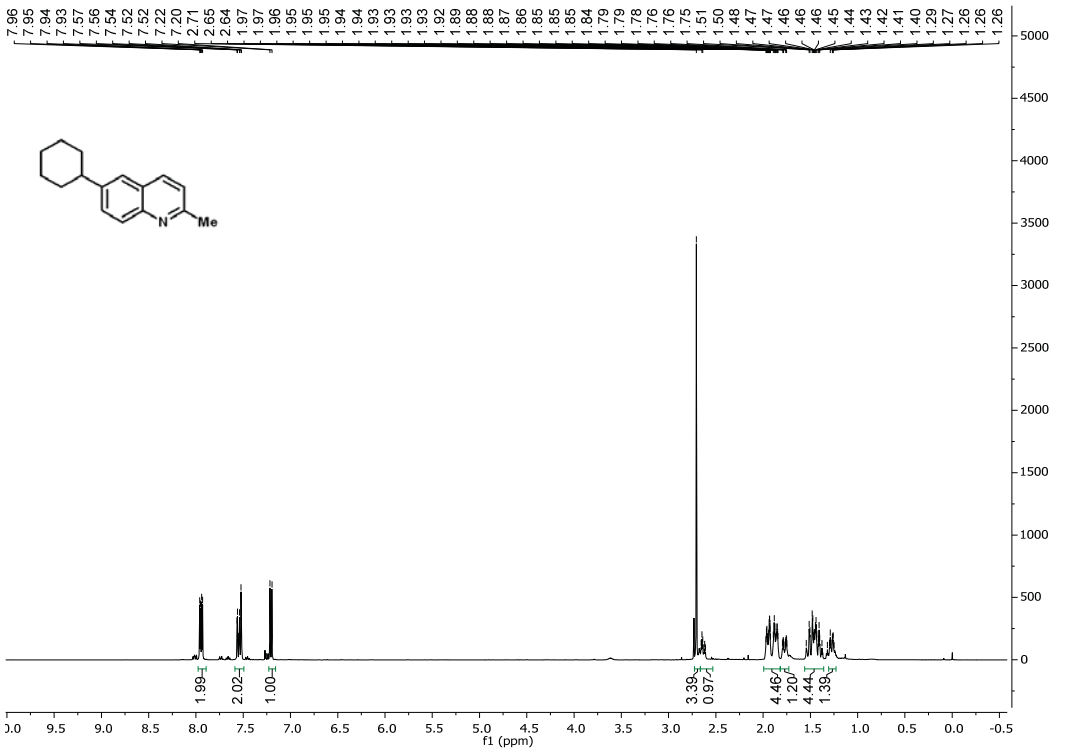
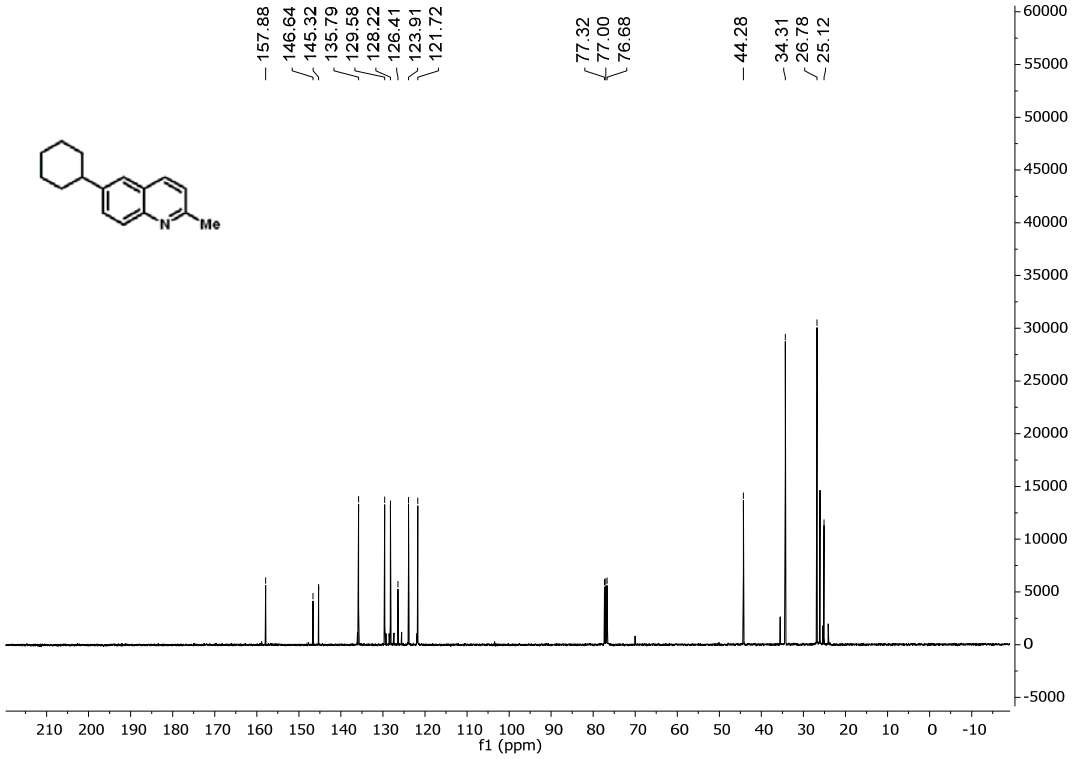
1.52
1.51
1.49
1.49
1.48
1.46
1.46
1.45
1.42
1.34
1.31
0.97
1.00
0.99
1.00
0.98
1.04
4.12
1.09
5.37
f1 (ppm)

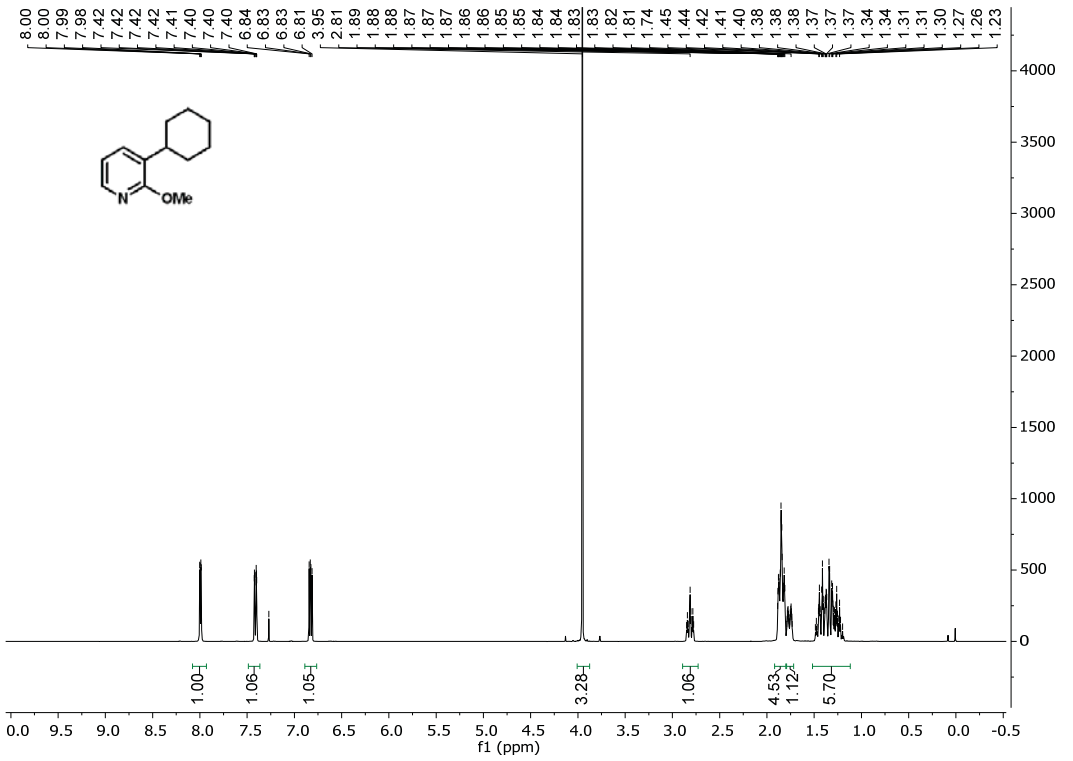

147.83
142.10
135.09
126.58
125.41
120.35
100.03
77.32
77.00
76.68
42.25
35.07
26.98
26.11
f1 (ppm)

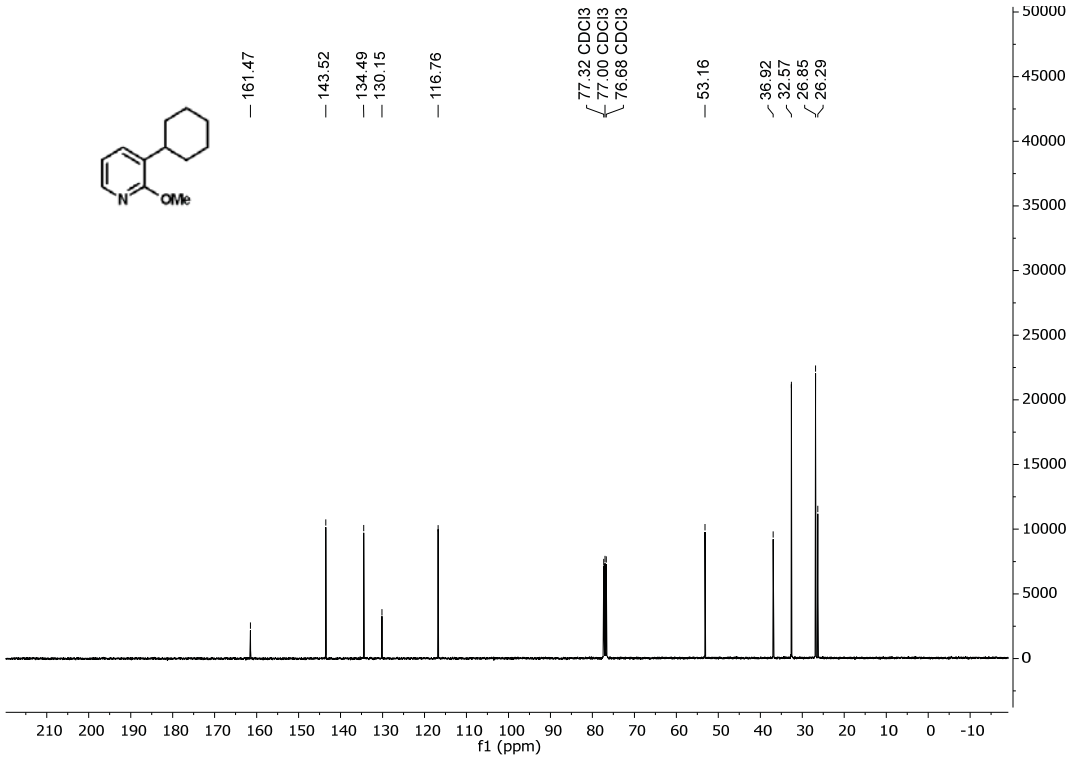
3ob:


7.96 7.95 7.94 7.93 7.57 7.56 7.54 7.52 7.52 7.22 7.20 2.71 2.65 2.64 1.97 1.97 1.96 1.95 1.95 1.95 1.94 1.94 1.93 1.93 1.93 1.92 1.89 1.88 1.88 1.87 1.86 1.85 1.85 1.85 1.84 1.79 1.79 1.78 1.76 1.76 1.75 1.51 1.50 1.48 1.47 1.47 1.46 1.46 1.46 1.45 1.44 1.43 1.42 1.41 1.40 1.29 1.27 1.26 1.26 1.26
N
Me
1.99
2.02
1.00
3.39
0.97
4.46
1.20
4.44
1.39
f1 (ppm)

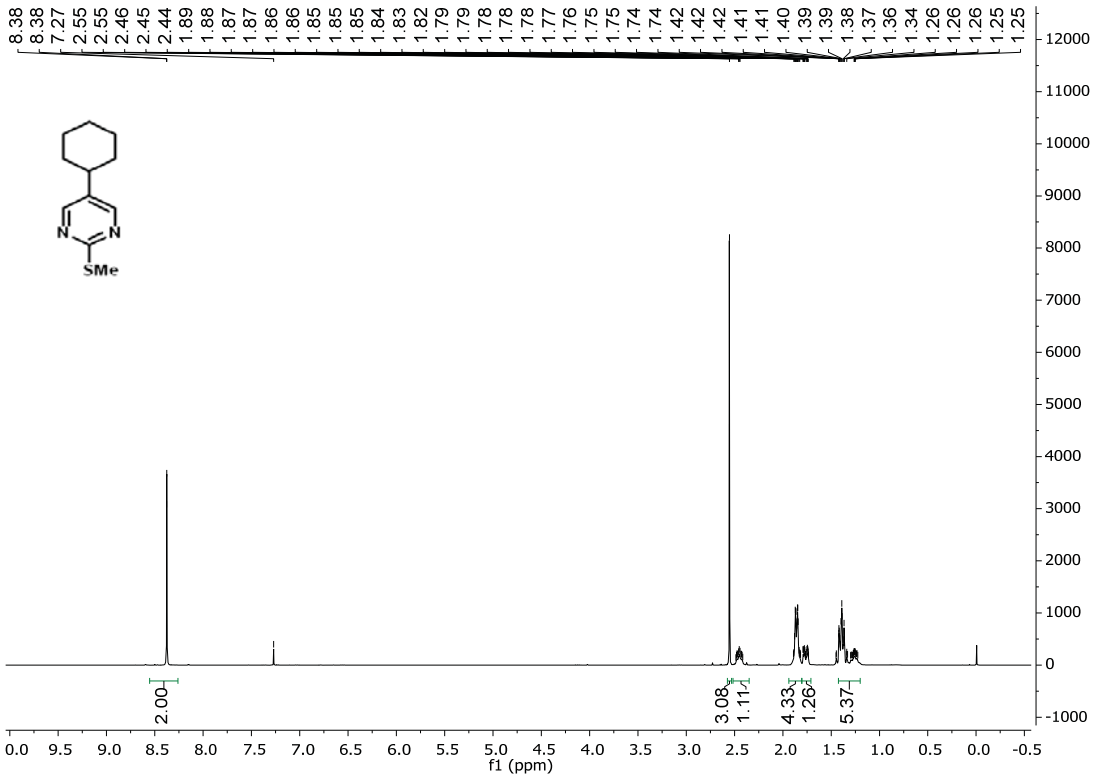

157.88 146.64 145.32 135.79 129.58 128.22 126.41 123.91 121.72
77.32 77.00 76.68
44.28
34.31 26.78 25.12
N
Me
f1 (ppm)

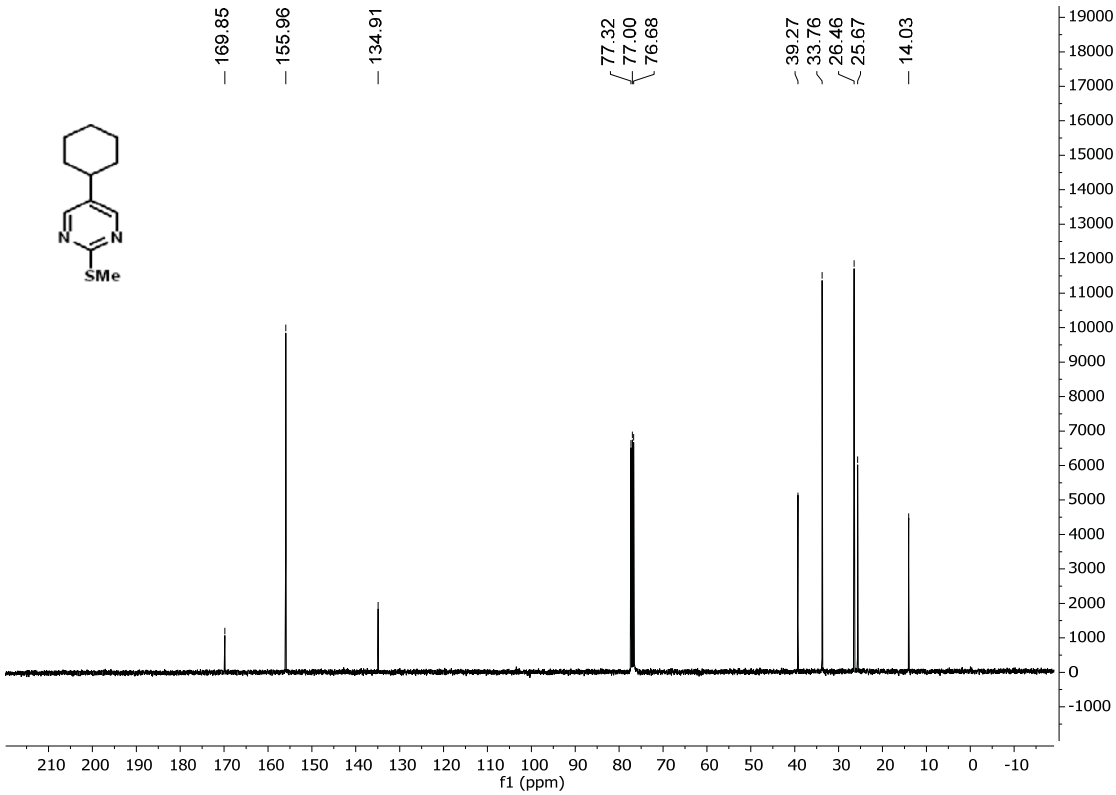
3pb:


8.00 8.00 7.99 7.98 7.42 7.42 7.42 7.42 7.41 7.40 7.40 7.40 6.84 6.83 6.83 6.81 3.95 2.81 1.89 1.88 1.88 1.87 1.87 1.87 1.86 1.86 1.85 1.85 1.84 1.84 1.84 1.83 1.83 1.82 1.81 1.74 1.45 1.44 1.42 1.41 1.40 1.38 1.38 1.38 1.37 1.37 1.37 1.34 1.34 1.31 1.31 1.30 1.27 1.26 1.23
OMe
1.00 1.06 1.05 3.28 1.06 4.53 1.12 5.70
f1 (ppm)

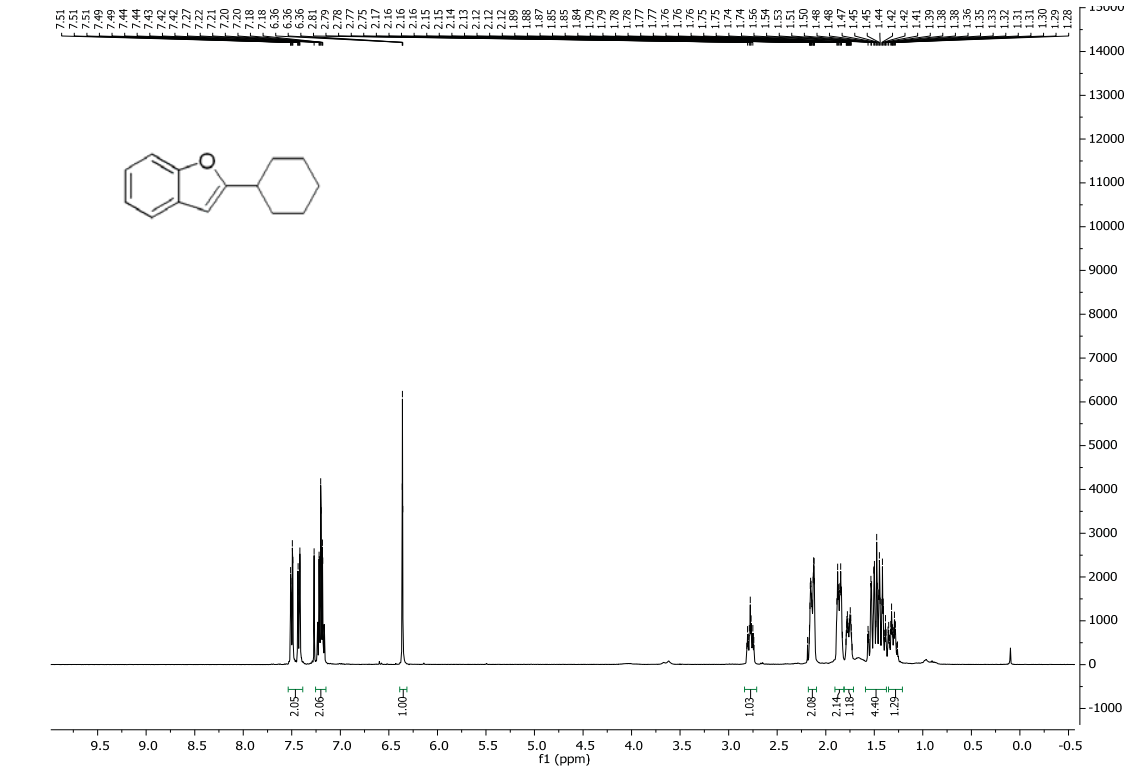

161.47 143.52 134.49 130.15 116.76 77.32 CDCl3 77.00 CDCl3 76.68 CDCl3 53.16 36.92 32.57 26.85 26.29
OMe
f1 (ppm)

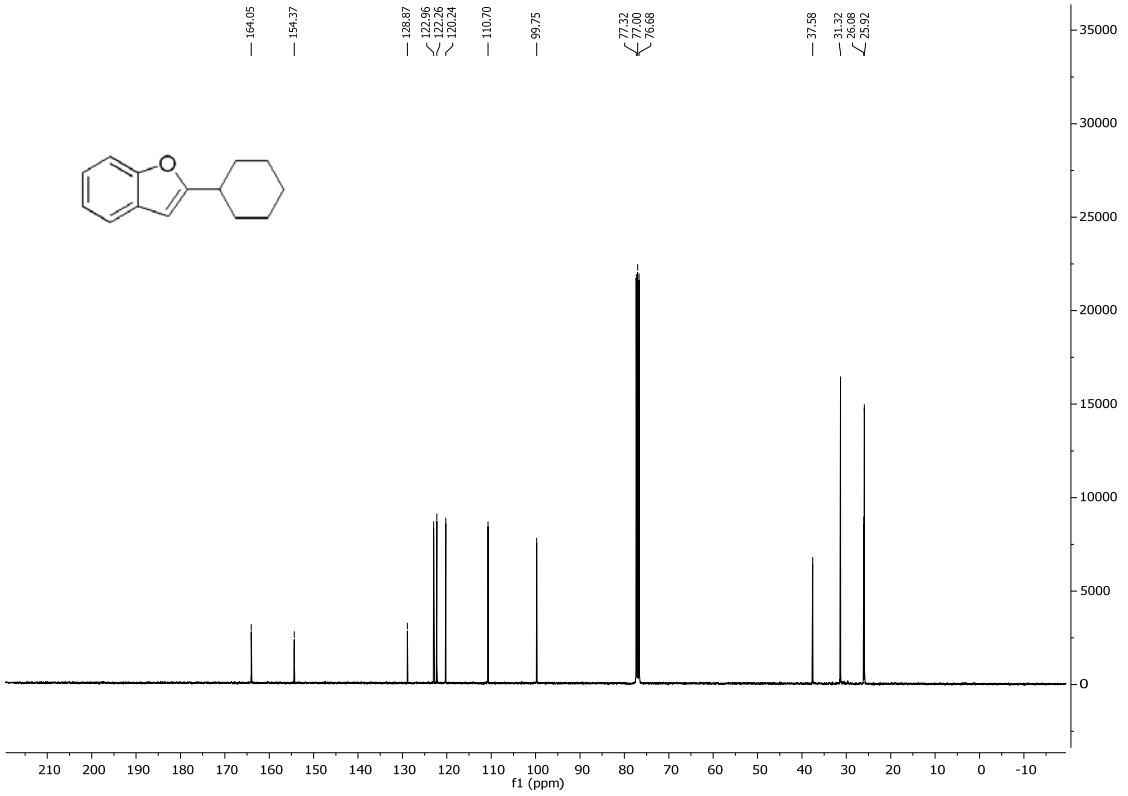
3qb:


8.38 8.38 7.27 2.55 2.46 2.45 2.44 1.89 1.88 1.87 1.87 1.86 1.86 1.85 1.85 1.85 1.84 1.83 1.82 1.79 1.79 1.78 1.78 1.78 1.77 1.76 1.75 1.75 1.74 1.74 1.42 1.42 1.41 1.41 1.40 1.39 1.39 1.38 1.37 1.36 1.34 1.26 1.26 1.26 1.25 1.25
SMe
2.00
3.08
1.11
4.33
1.26
5.37
f1 (ppm)


169.85
155.96
134.91
77.32
77.00
76.68
39.27
33.76
26.46
25.67
14.03
SMe
f1 (ppm)

3rb:


f1 (ppm)


164.05
154.37
128.87
122.96
122.26
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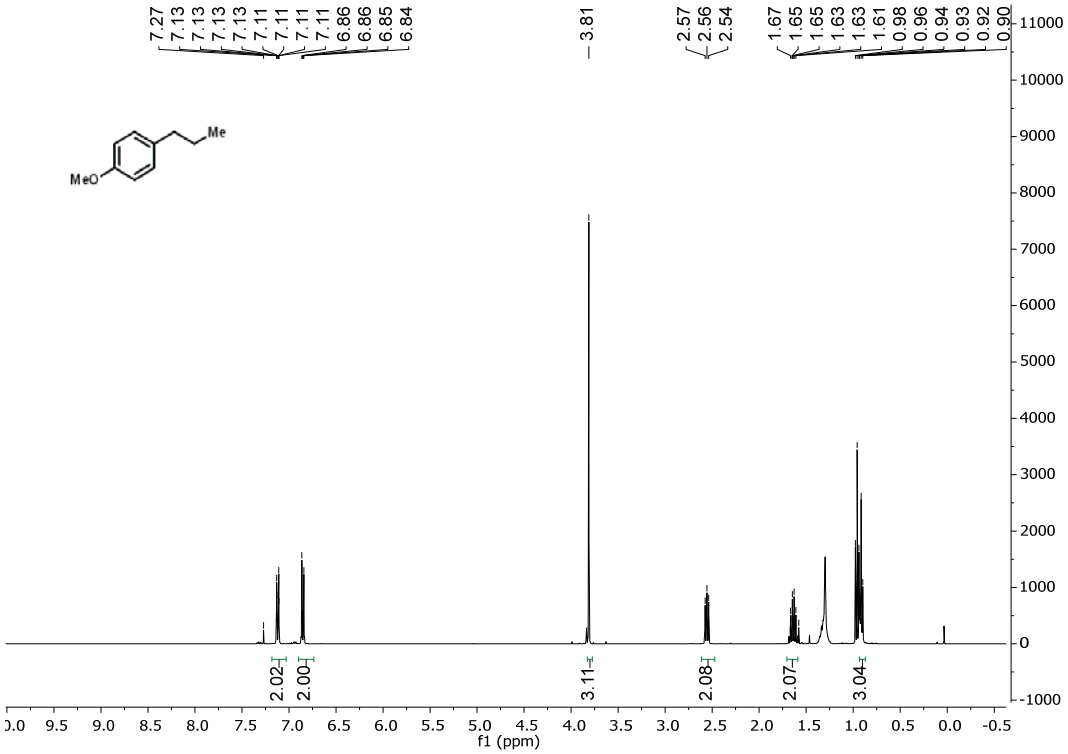
99.75
77.32
77.00
76.68
37.58
31.32
26.08
25.92
f1 (ppm)

3ha: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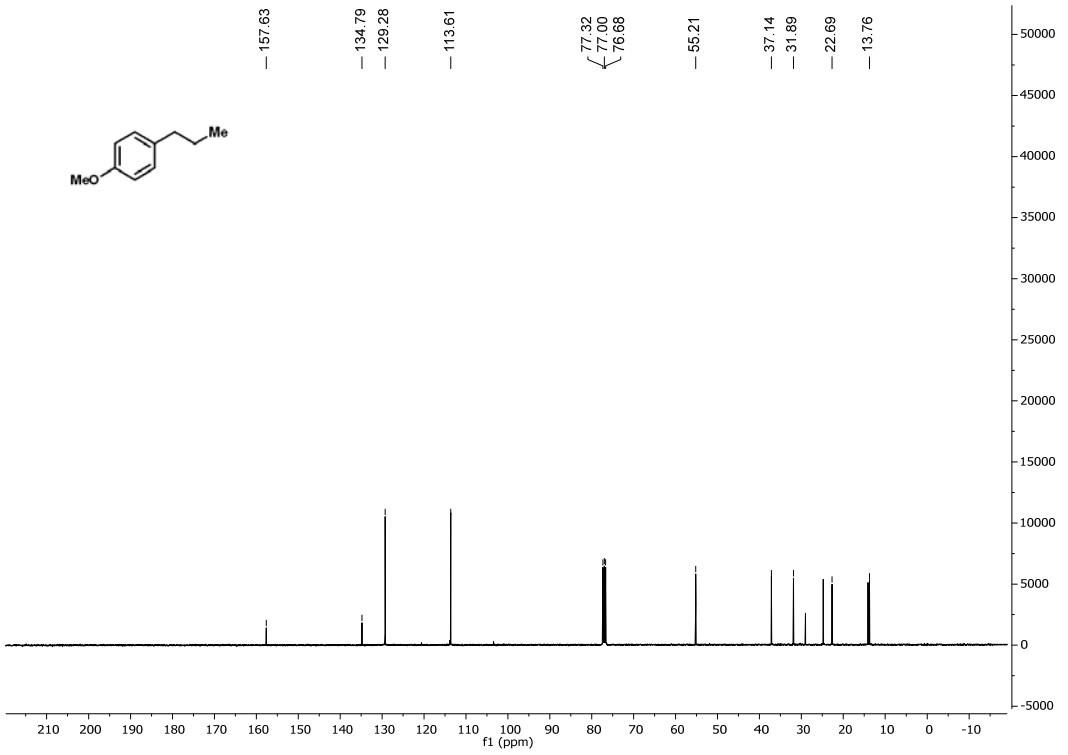
7.13
7.13
7.13
7.11
7.11
7.11
7.11
6.86
6.86
6.85
6.84
3.81
2.57
2.56
2.54
1.67
1.65
1.65
1.63
1.63
1.61
0.98
0.96
0.94
0.93
0.92
0.90
Me
MeO
2.02
2.00
3.11
2.08
2.07
3.04
f1 (ppm)


157.63
134.79
129.28
113.61
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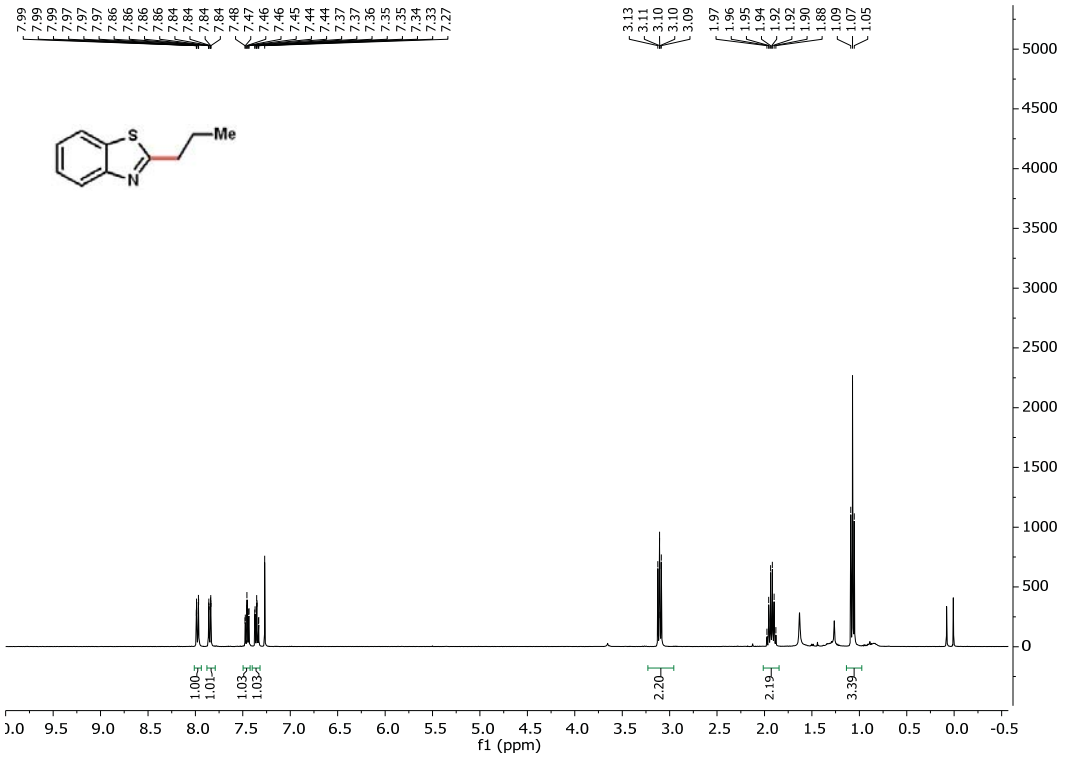
76.68
55.21
37.14
31.89
22.69
13.76
Me
MeO
f1 (ppm)

3ra: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7.86
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7.84
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7.46
7.45
7.44
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7.37
7.37
7.36
7.35
7.35
7.34
7.33
7.27
3.13
3.11
3.10
3.10
3.09
1.97
1.96
1.95
1.94
1.92
1.92
1.90
1.88
1.09
1.07
1.05
Me
S
N
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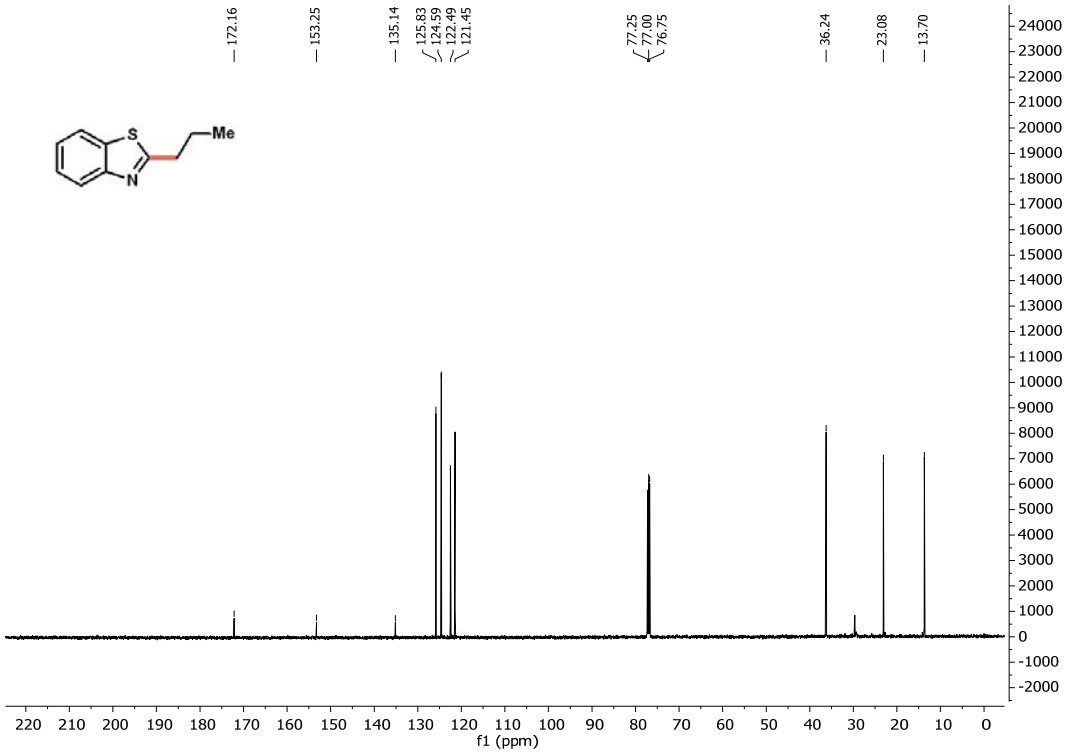
1.01
1.03
1.03
2.20
2.19
3.39
f1 (ppm)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153.25
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125.83
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121.45
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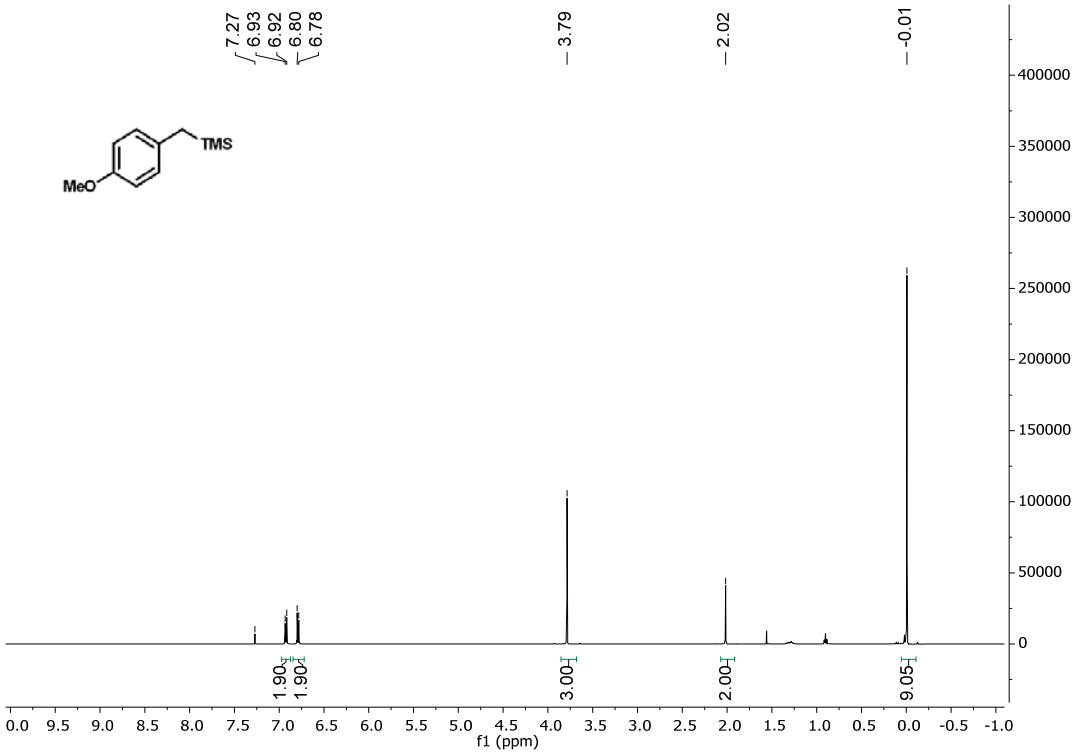
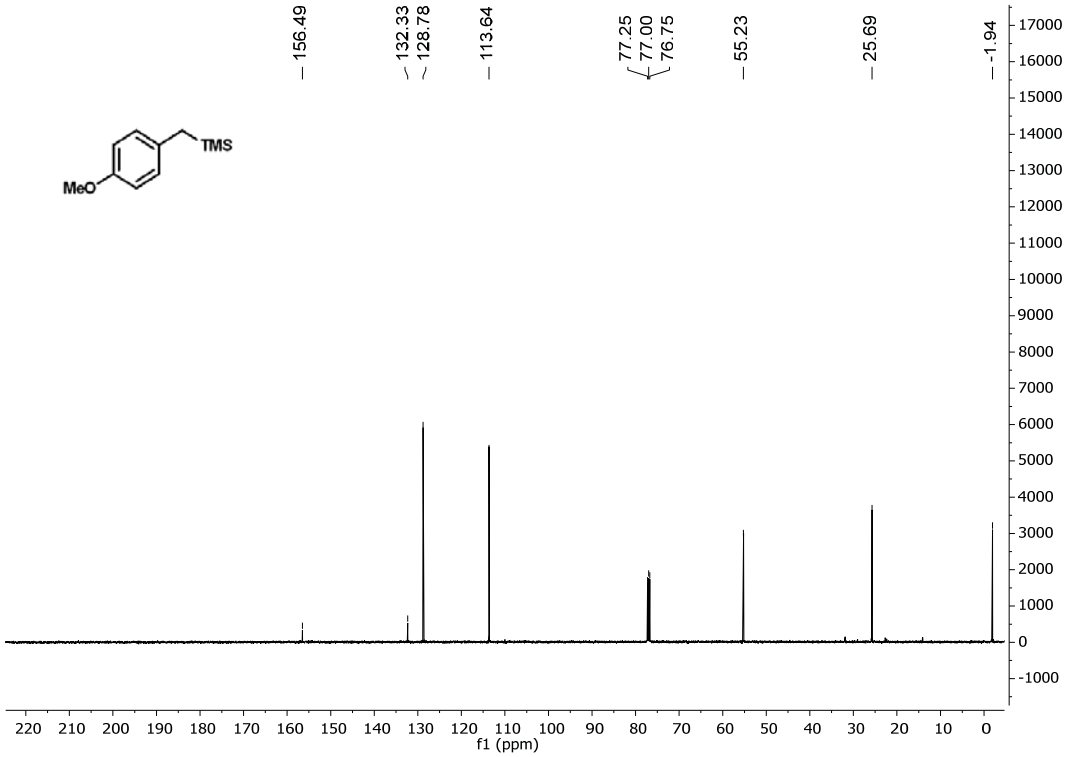
77.00
76.75
36.24
23.08
13.70
Me
S
N
f1 (ppm)

3hc:


7.27
6.93
6.92
6.80
6.78
3.79
2.02
-0.01
TMS
MeO
1.90
1.90
3.00
2.00
9.05
f1 (ppm)


156.49
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128.78
113.64
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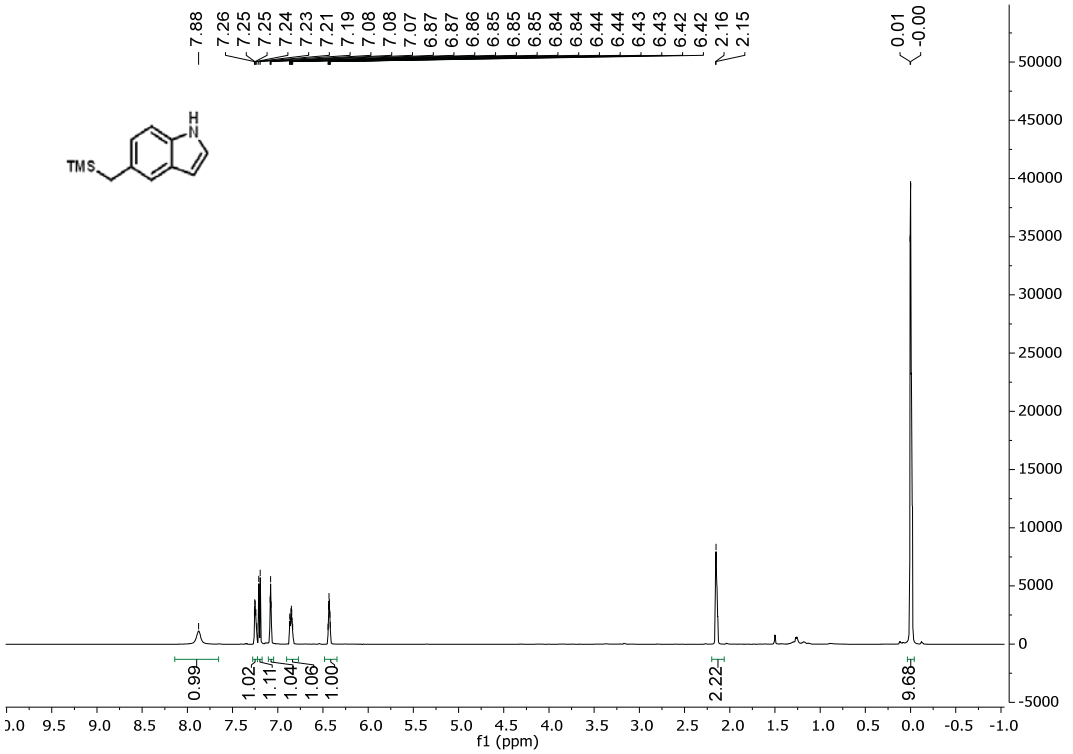
77.00
76.75
55.23
25.69
-1.94
TMS
MeO
f1 (ppm)

3nc: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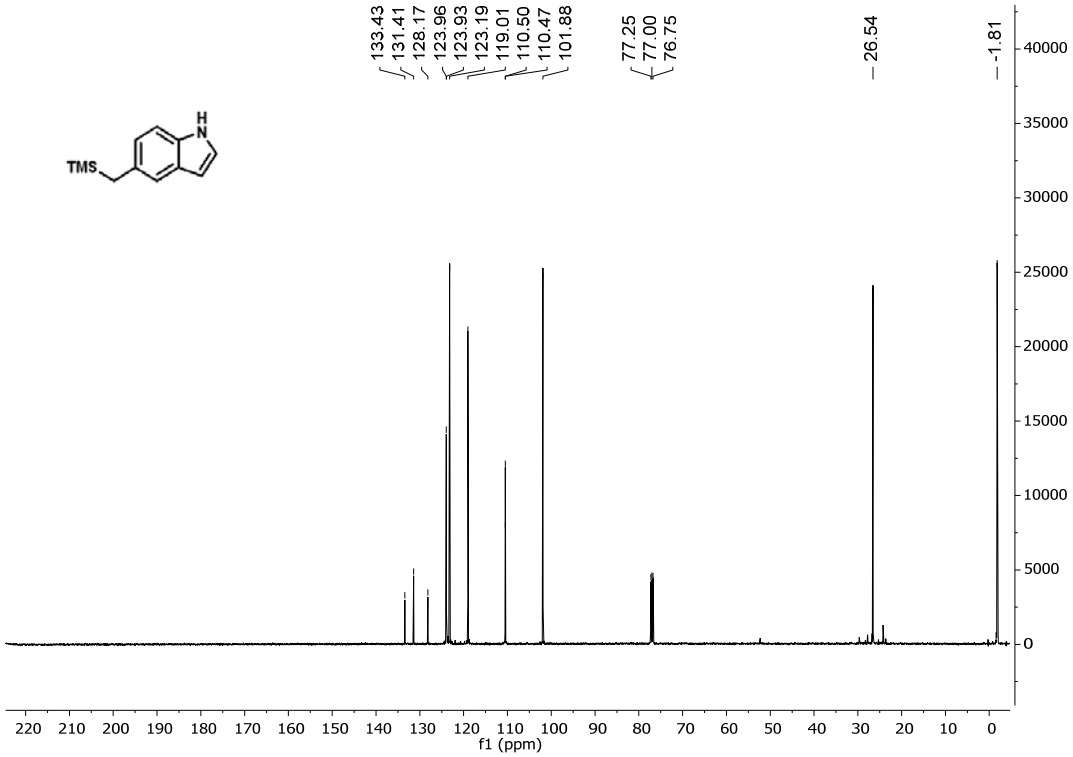
7.25
7.25
7.24
7.23
7.21
7.19
7.08
7.08
7.07
6.87
6.87
6.86
6.85
6.85
6.85
6.84
6.84
6.44
6.44
6.43
6.43
6.42
6.42
2.16
2.15
0.01
-0.00
TMS
H
N
0.99
1.02
1.11
1.04
1.06
1.00
2.22
9.68
f1 (ppm)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123.93
123.19
119.01
110.50
110.47
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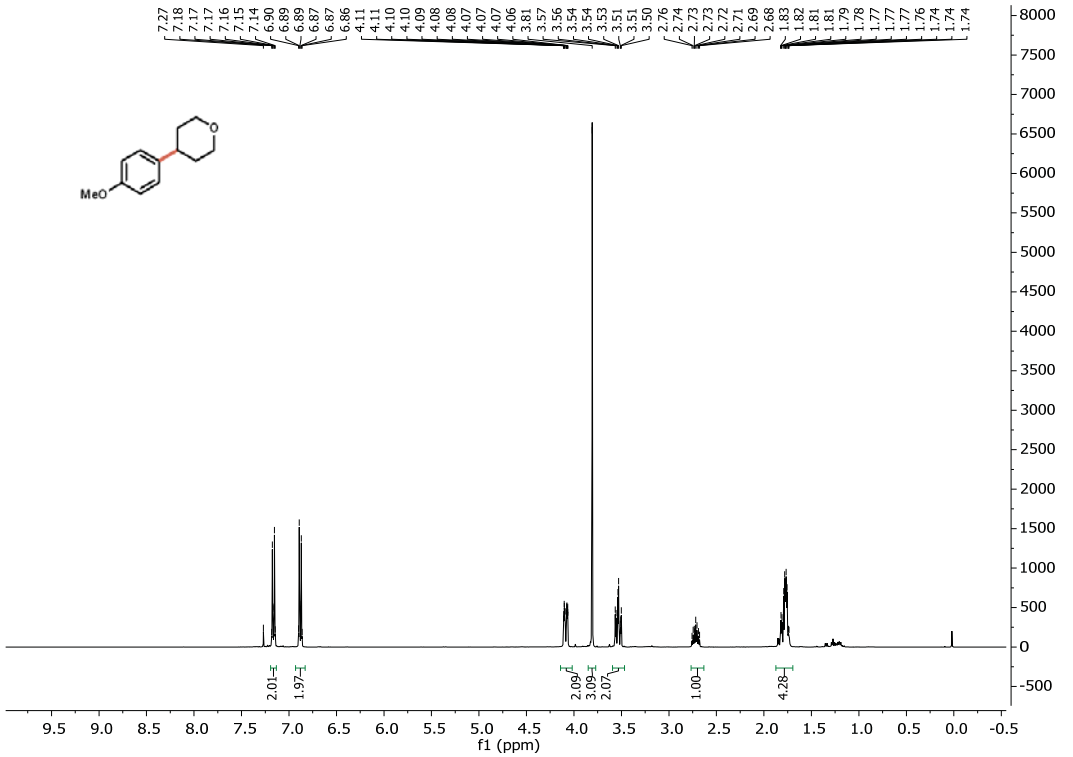
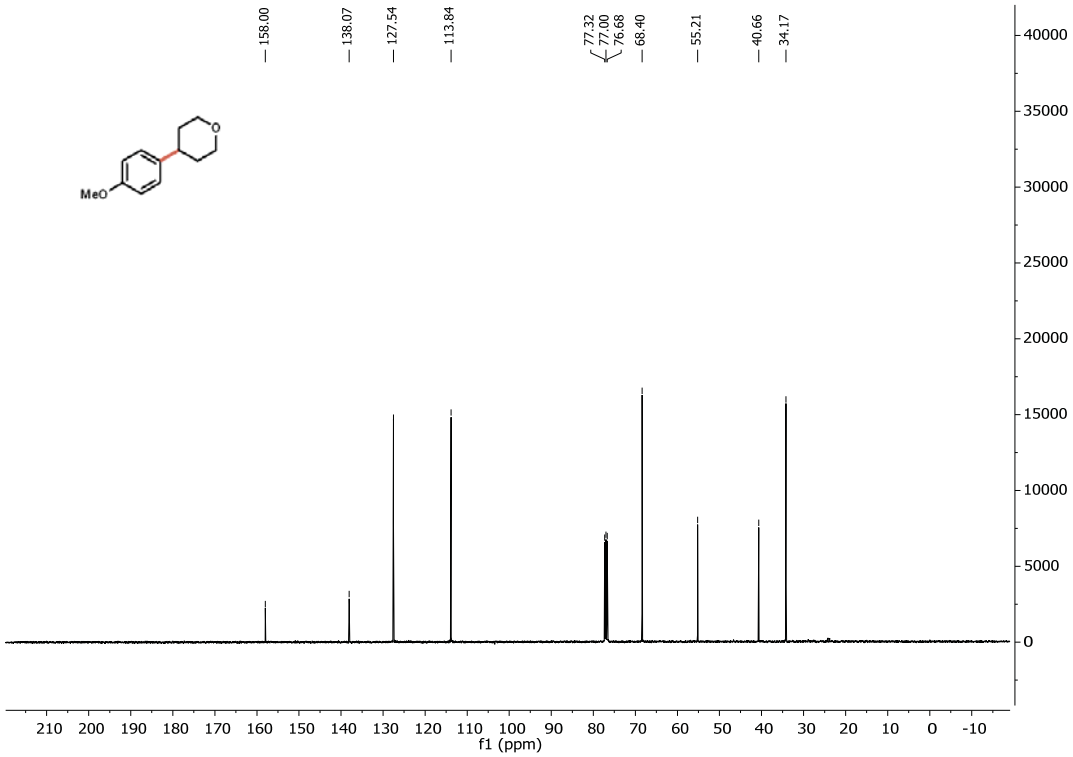
77.25
77.00
76.75
26.54
-1.81
TMS
H
N
f1 (ppm)

3hd:





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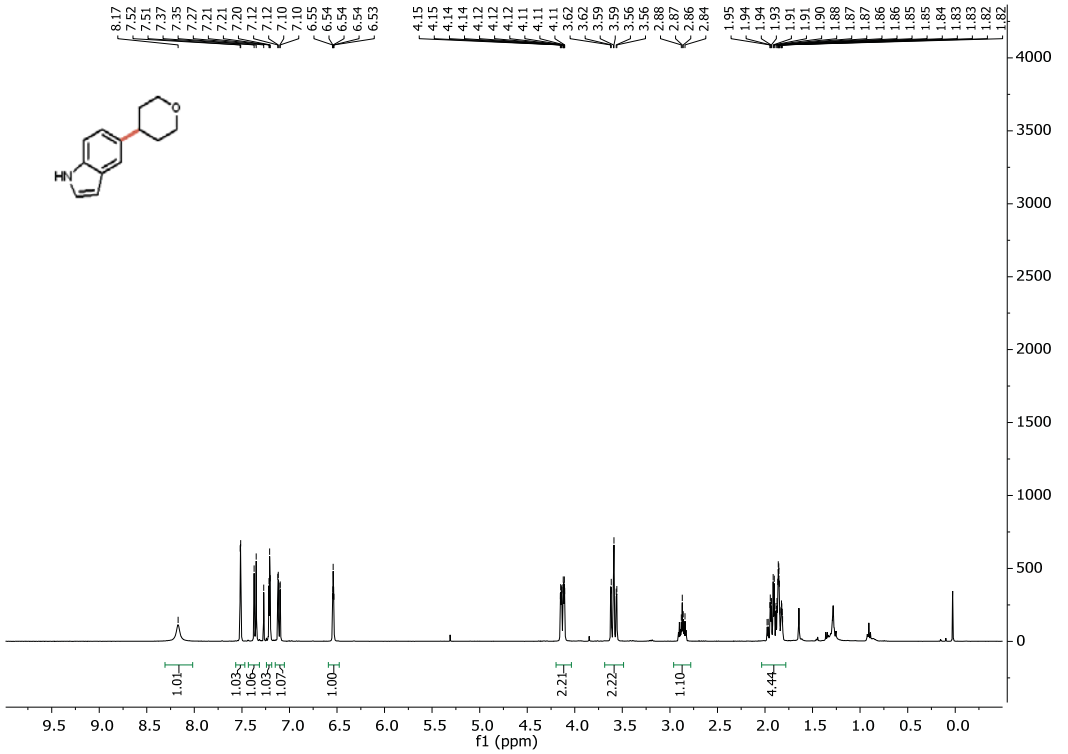
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6.54
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4.15
4.14
4.14
4.12
4.12
4.12
4.11
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4.11
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3.62
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3.59
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1.91
1.90
1.88
1.87
1.87
1.86
1.86
1.85
1.85
1.84
1.83
1.82
1.82
HN
O
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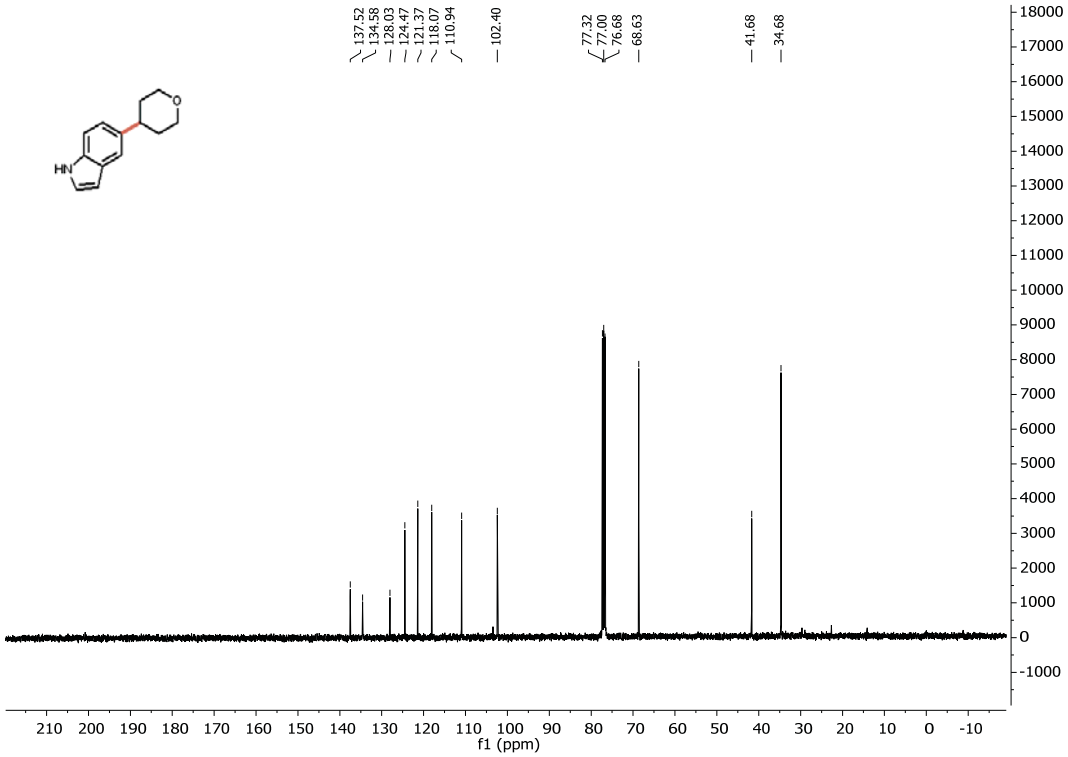
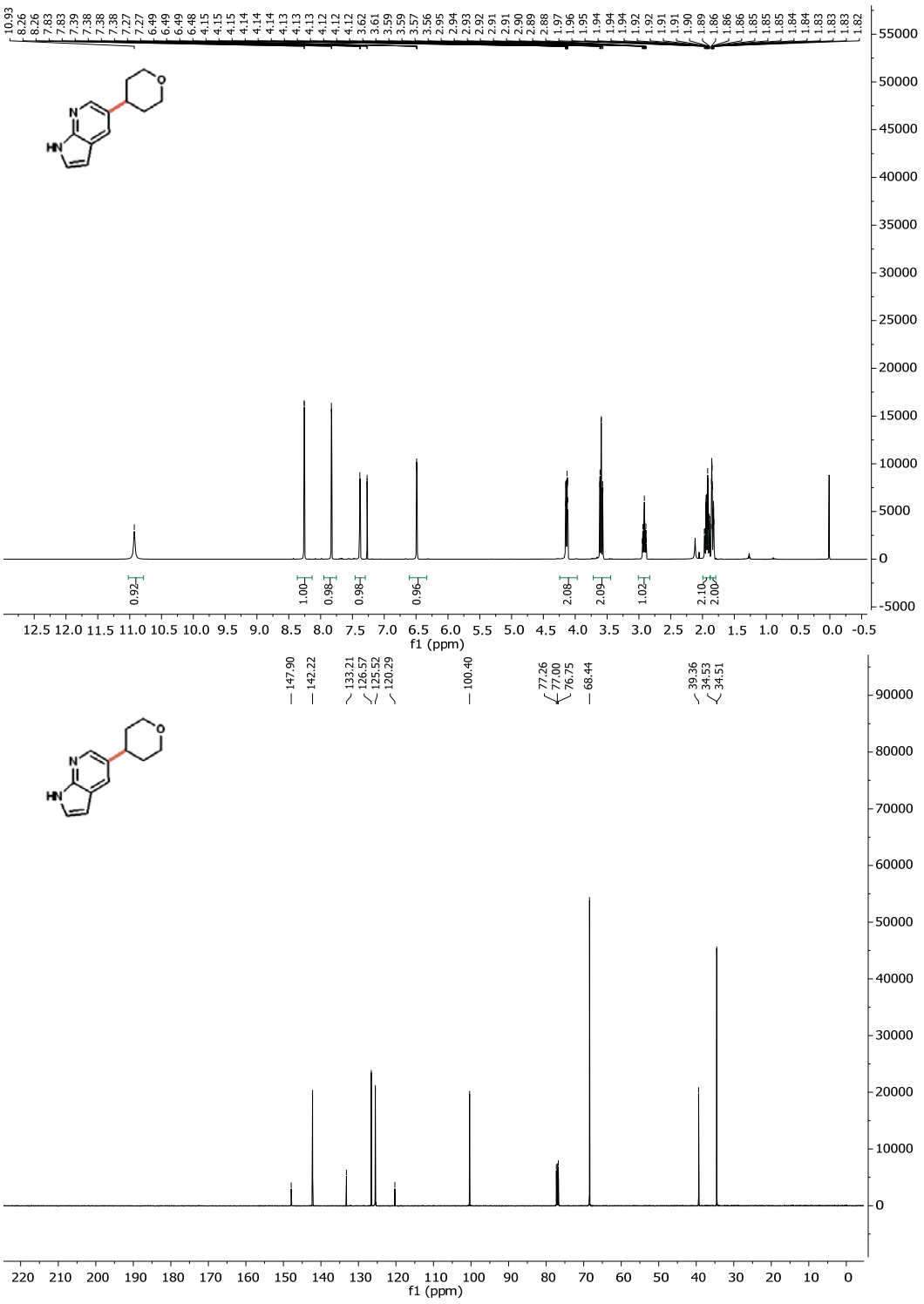
1.03
1.06
1.03
1.07
1.00
2.21
2.22
1.10
4.44
f1 (ppm)


137.52
134.58
128.03
124.47
121.37
118.07
110.94
102.40
77.32
77.00
76.68
68.63
41.68
34.68
HN
O
f1 (ppm)

3od: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7.38
7.27
7.27
6.49
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6.49
6.48
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4.15
4.15
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4.14
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4.13
4.13
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1.85
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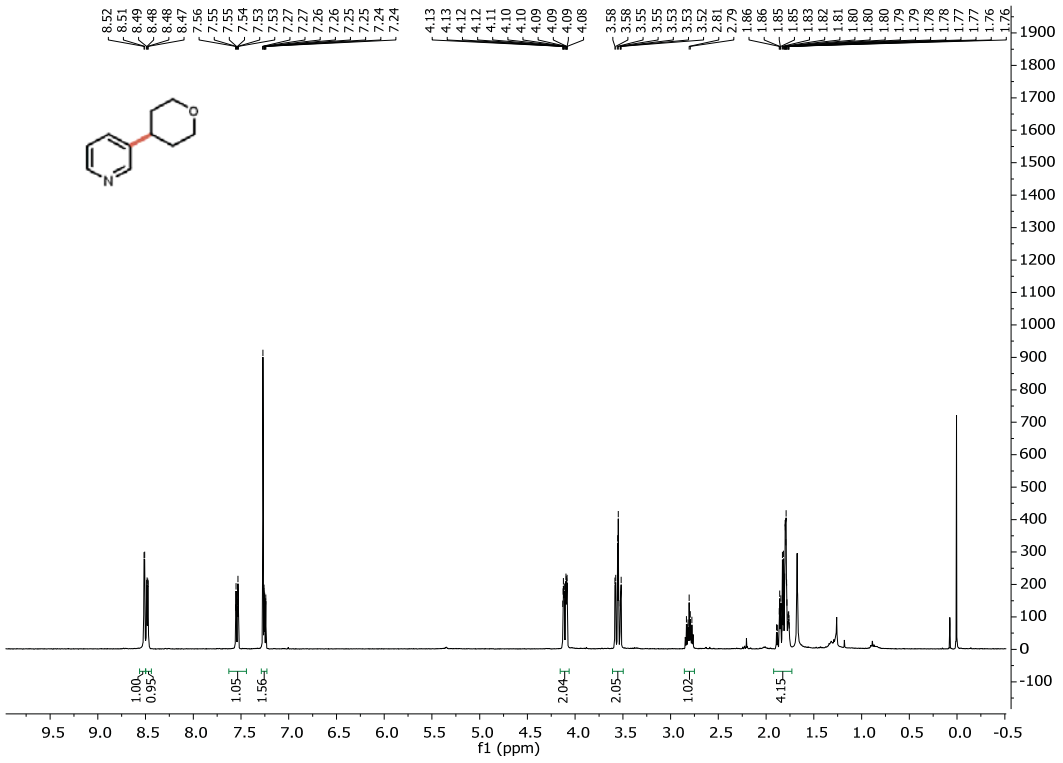
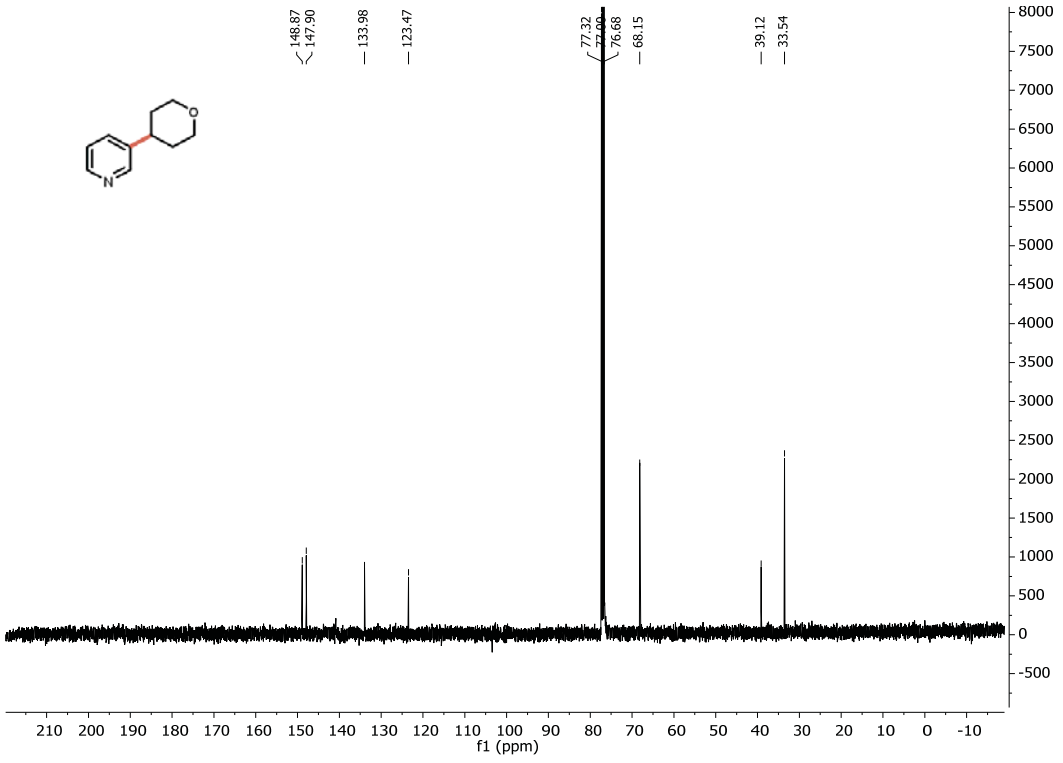
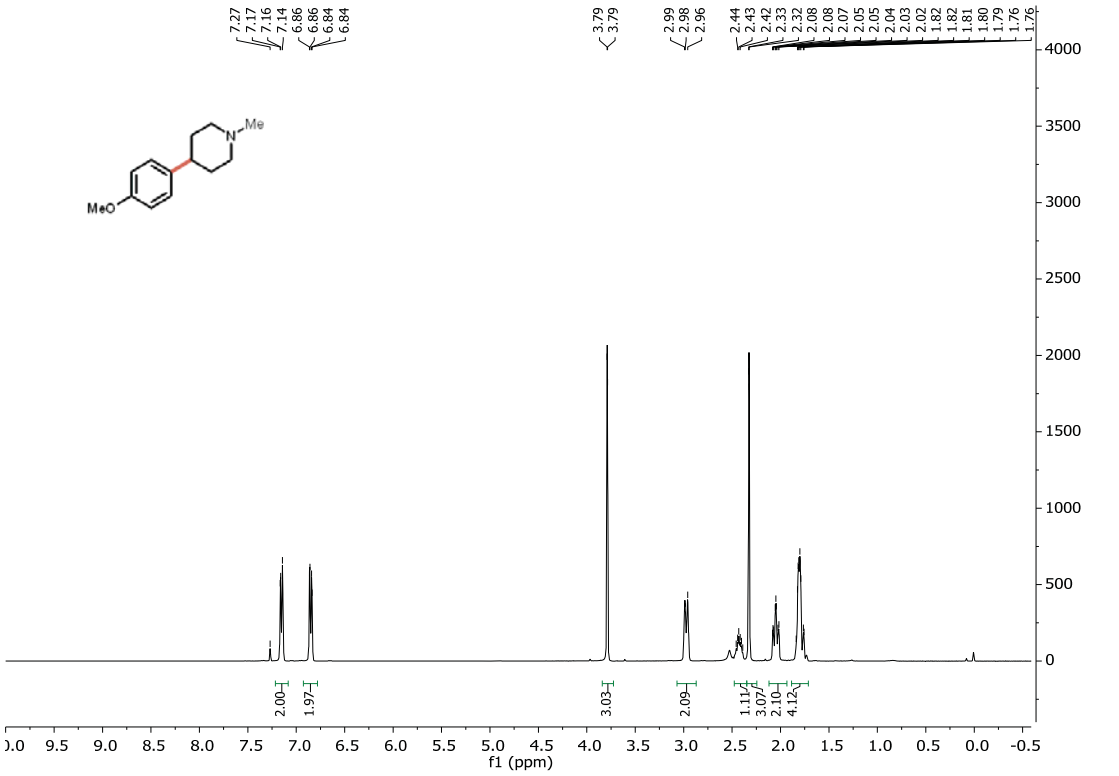
1.83
1.83
1.83
1.82
N
HN
O
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
0.92
1.00
0.98
0.98
0.96
2.08
2.09
1.02
2.10
2.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
147.90
142.22
133.21
126.57
125.52
120.29
100.40
77.26
77.00
76.75
68.44
39.36
34.53
34.51
N
HN
O
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

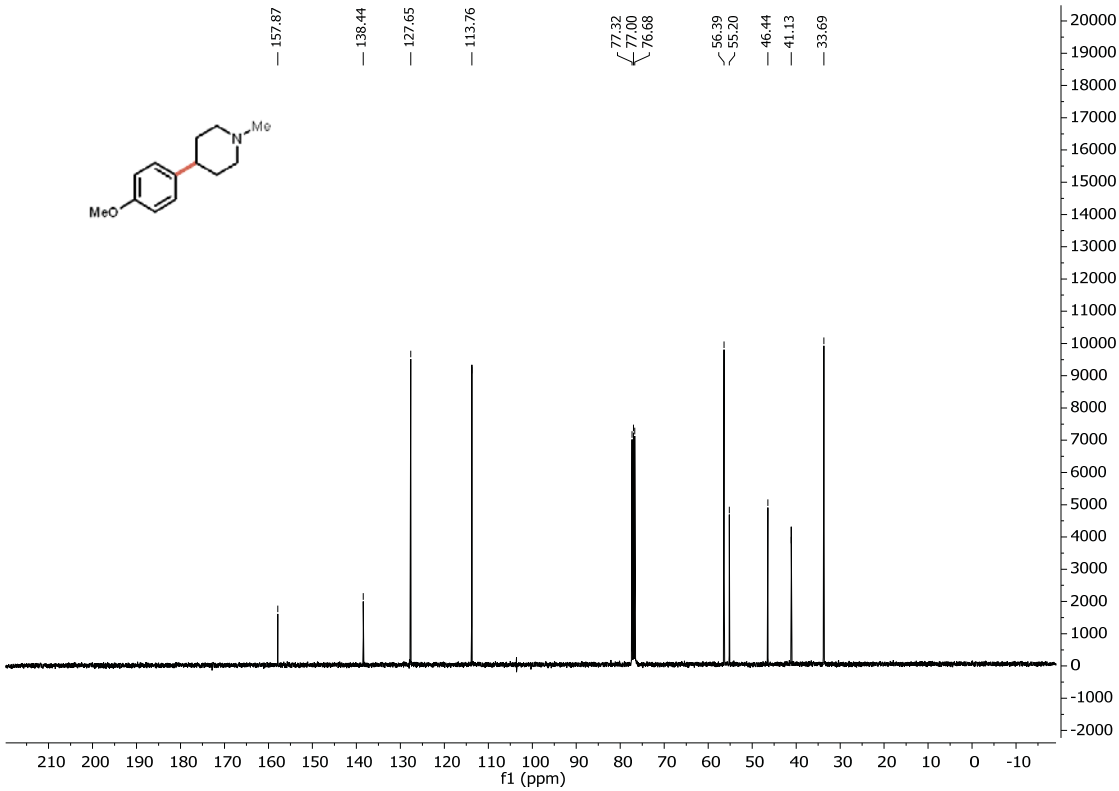
3sd:


8.52
8.51
8.49
8.48
8.48
8.47
7.56
7.55
7.55
7.54
7.53
7.53
7.27
7.27
7.26
7.26
7.25
7.25
7.24
7.24
4.13
4.13
4.12
4.12
4.11
4.10
4.10
4.09
4.09
4.09
4.08
3.58
3.58
3.55
3.55
3.53
3.53
3.52
2.81
2.79
1.86
1.86
1.85
1.85
1.83
1.82
1.81
1.80
1.80
1.79
1.79
1.78
1.78
1.77
1.77
1.76
1.76
1.00
0.95
1.05
1.56
2.04
2.05
1.02
4.15
f1 (ppm)

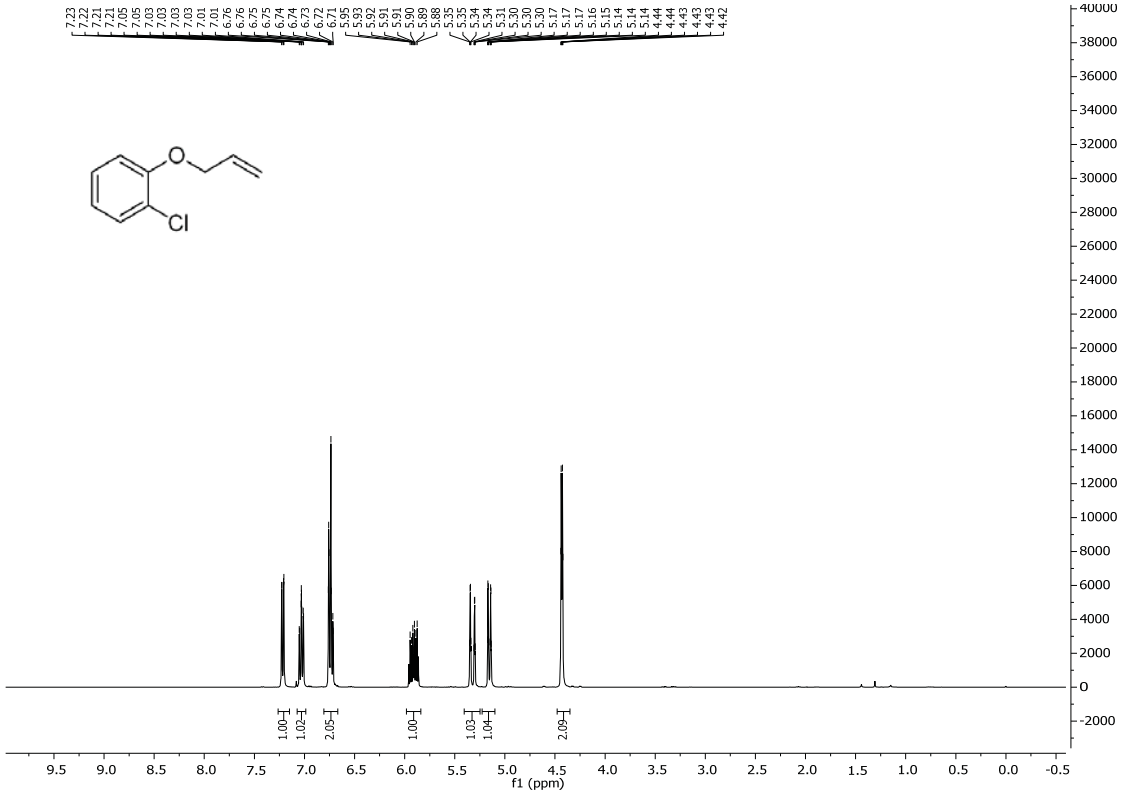

148.87
147.90
133.98
123.47
77.32
77.00
76.68
68.15
39.12
33.54
f1 (ppm)

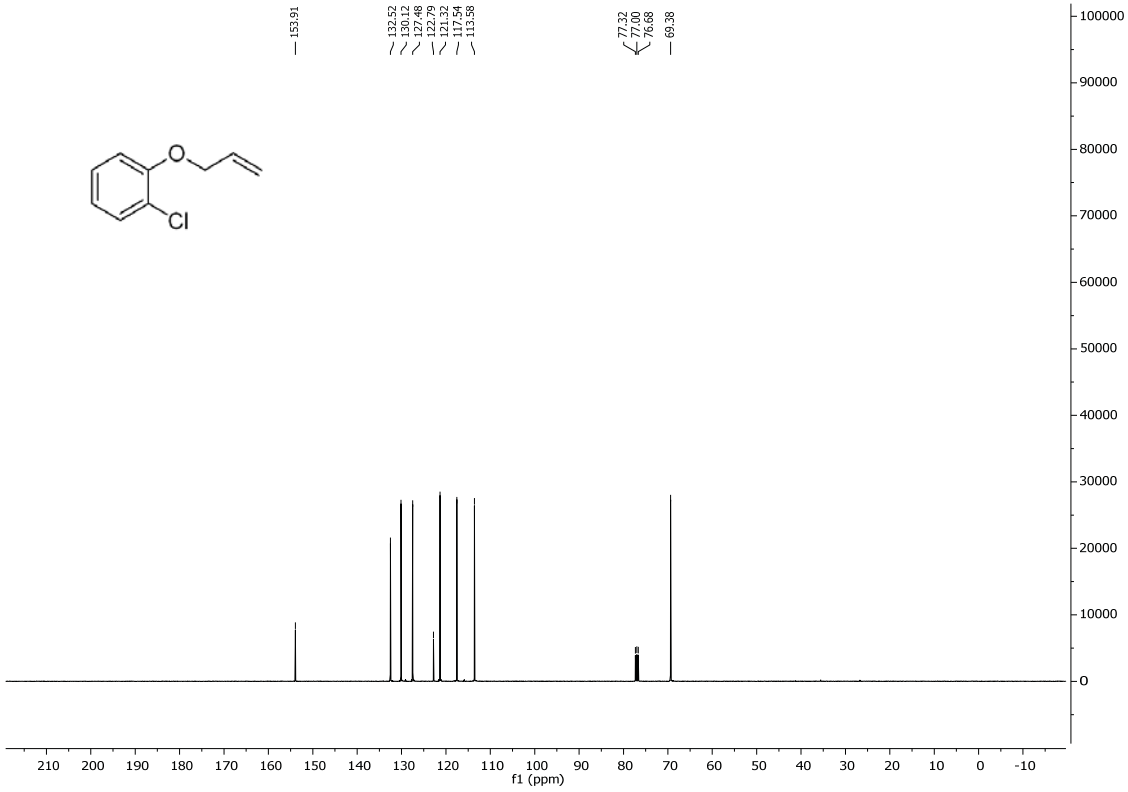
3he:


7.27
7.17
7.16
7.14
6.86
6.86
6.84
6.84
3.79
3.79
2.99
2.98
2.96
2.44
2.43
2.42
2.33
2.32
2.08
2.08
2.07
2.05
2.05
2.04
2.03
2.02
1.82
1.82
1.81
1.80
1.79
1.76
1.76
Me
N
MeO
2.00
1.97
3.03
2.09
1.11
3.07
2.10
4.12
f1 (ppm)


157.87
138.44
127.65
113.76
77.32
77.00
76.68
56.39
55.20
46.44
41.13
33.69
Me
N
MeO
f1 (ppm)

1-(allyloxy)-2-chlorobenzene





1-(but-3-en-1-yl)-2-chlorobenzene