

Visible-light photoredox catalyzed dehydrogenative synthesis of allylic carboxylates from styrenes

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General Methods.

¹H-NMR spectra were recorded on Varian 400 (400 MHz) spectrometers. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (deuteriochloroform: 7.24 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet doublet, t = triplet, td = triple doublet, dt = double triplet, q = quartet, sext = sextet, sept = septet, p = pseudo, b = broad, m = multiplet), coupling constants (Hz). ¹³C-NMR spectra were recorded on a Varian 400 (100 MHz) spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard (deuteriochloroform: 77.0 ppm).

GC-MS spectra were taken by EI ionization at 70 eV on a Hewlett-Packard 5971 with GC injection. They are reported as: *m/z* (rel. intense). LC-electrospray ionization mass spectra were obtained with Agilent Technologies MSD1100 single-quadrupole mass spectrometer.

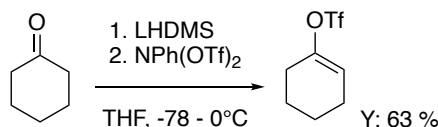
Chromatographic purification was done with 240-400 mesh silica gel. Other anhydrous solvents were supplied by Sigma Aldrich in Sureseal® bottles and used without any further purification. Reactions requiring temperatures higher than r.t. were carried out in an oil bath on a heated stirring plate. Commercially available chemicals were purchased from Sigma Aldrich, Stream and TCI and used without any further purification. Melting points were determined with Bibby Stuart Scientific Melting Point Apparatus SMP 3 and are not corrected. Agilent Technologies LC/MSD Trap 1100 series (nebulizer: 15.0 PSI, dry Gas: 5.0 L/min, dry Temperature: 325 °C, capillary voltage positive scan: 4000 mA, capillary voltage negative scan: 3500 mA). Compounds **1a**, **2a** – **2m** are commercially available.

UV-vis absorption spectra were recorded at room temperature by means of Perkin-Elmer Lambda 45 spectrophotometer. Quartz cuvettes (Hellma) with optical path length of 1 cm were used. The fluorescence spectra were recorded with an Edinburgh FLS920 equipped photomultiplier Hamamatsu R928P. The same instrument connected to a PCS900 PC card was used for the Time Correlates Single Photon Counting (TCSPC) experiments. Luminescence quantum yields (uncertainty, ± 15%) were determined using rhodamine 101 solution in ethanol as a reference ($\Phi = 1.0$). Fluorescence intensities were corrected for inner filter effects according to standard methods.¹

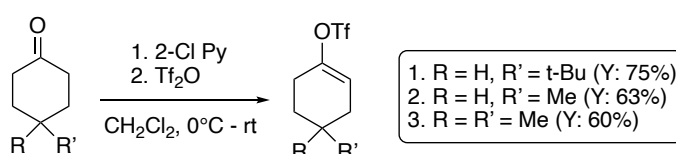
Synthesis of olefins for intermolecular reactions

Substrates of enol triflates

The enol triflate of the cyclohexanone was obtained in 63% following the procedure described in the literature.²

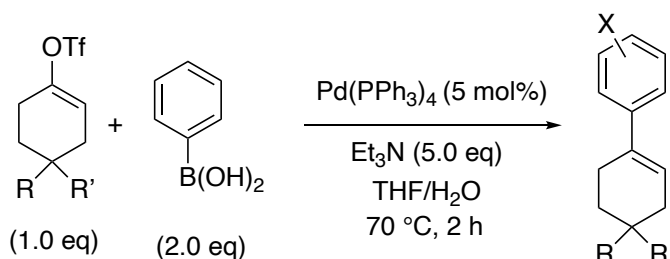


The enol triflate deriving from 4-substituted cyclohexanones were obtained following the procedure described in the literature.²



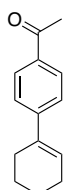
The enol triflates were subsequently converted into the corresponding phenylcyclohexenes **1b-d** by using the following procedure.

Synthesis of the 1-phenylcyclohexenes **1b-h/l-n**

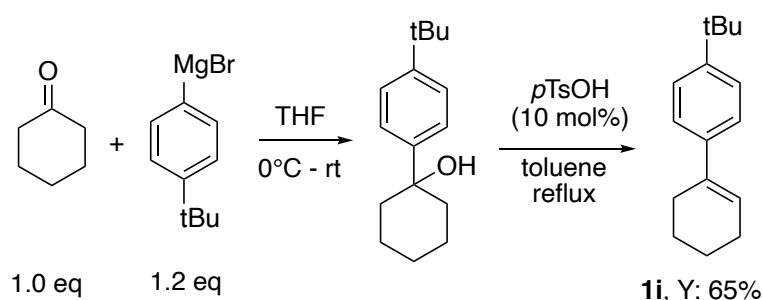


- | | |
|---|--|
| 1b (R = t-Bu, R' = H, X = H), Y: 77% | 1g (R = R' = H, X = 3,5-Me ₂), Y: 65% |
| 1c (R = Me, R' = X = H), Y: 72% | 1h (R = R' = H, X = 4-Me), Y: 72% |
| 1d (R = R' = Me, X = H), Y: 73% | 1l (R = R' = H, X = 2-Me), Y: 75% |
| 1e (R = R' = H, X = 3-Me), Y: 73% | 1m (R = R' = H, X = 4-CO ₂ Me), Y: 70% |
| 1f (R = R' = H, X = 3-F), Y: 72% | 1n (R = R' = H, X = 4-COMe), Y: 75% |

Under N₂, a dry Schlenk tube was charged with THF (5 ml), deionized H₂O (1 mL) and Et₃N (5.0 mmol). Then phenylboronic acid (2.0 mmol) and the triflate (1.0 mmol) were added. The reaction was stirred at 70 °C for 2 hours or until completion (TLC). Then H₂O (5 mL) was added and the resulting mixture was extracted with EtOAc (2 x 15 mL), then the organic phase was dried over Na₂SO₄ and concentrated under vacuum. The residue was purified with gel flash chromatography. The NMR spectra of compounds **1b-d** and **1e-h/l,m** were in agreement with those reported in the literature.^{3,4}


1n. White solid. M.p. = 73.9 – 75.1 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 6.27 – 6.24 (m, 1H), 2.57 (s, 3H), 2.43 – 2.38 (m, 2H), 2.25 – 2.20 (m, 2H), 1.81 – 1.75 (m, 2H), 1.69 – 1.63 (m, 2H). **¹³C NMR** (100 MHz, CDCl₃) δ 179.69, 147.23, 135.80, 135.18, 128.39, 127.41, 124.83, 27.11, 26.51, 25.97, 22.84, 21.92. **GC-MS**: 185 (100), 200 (75), 129 (48), 157 (45); **Anal. Calc.** for (C₁₄H₁₆O: 200.12): C, 83.96; H, 8.05; O, 7.99; found: C, 84.24; H, 8.19; O, 8.23.

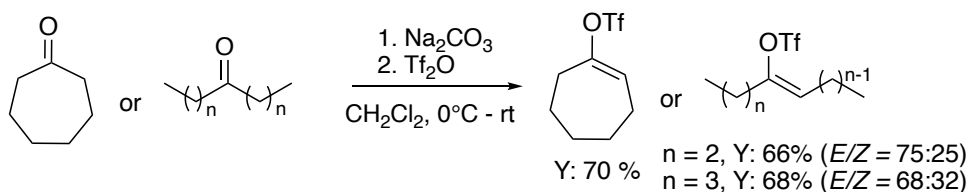
Synthesis of the 1-phenylcyclohexene **1i**



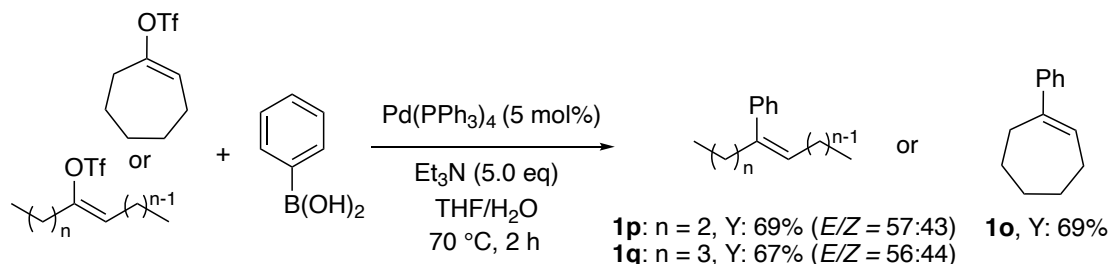
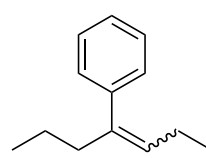
In a dry three-necked flask equipped with condenser the cyclohexanone (3 mmol) was dissolved in 1 ml of THF and added dropwise at 0 °C to a solution of freshly prepared 4-tert-butylphenylmagnesium bromide (3.6 mmol, ca. 0.5 mM). The reaction was stirred at rt for 2 h when the TLC showed the reaction completed. Then, a saturated aqueous solution of NH₄Cl was added (5 mL) at 0 °C and the resulting mixture was extracted with AcOEt (3 x 5 mL). The organic phase was dried over Na₂SO₄ and concentrated under vacuum. The reaction crude was used directly in the next step without further purification. A Schlenk tube was charged with 5 mL of reagent grade toluene, the tertiary alcohols (crude product, ca. 3 mmol) and *p*TsOH (10 mol%). The reaction was stirred at reflux until completion (TLC). Then H₂O (5 mL) was added, and the resulting mixture was extracted with EtOAc (2 x 15 mL), then the organic phase was dried over Na₂SO₄ and concentrated under vacuum. The residue was purified with flash chromatography (*n*Hex 100%) to give **1i** as a colorless oil (380 mg, 65%). The NMR spectra of **1i** is in agreement with that reported in literature.⁸

Synthesis of substrates **1o-q**

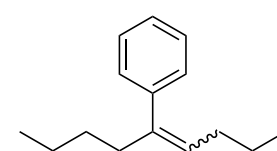
The first step for the synthesis of the compounds **1o-q** involves the formation of enol triflates. Enol triflate precursors were obtained through the following procedure.⁵ The spectra of the enol triflates are in agreement with those reported in literature.^{6,7}



The enol triflate was subsequently used in the Suzuki-cross coupling as previously described for substates **1b-n**. The spectra of olefin **1o** is in agreement with that reported in literature.⁸

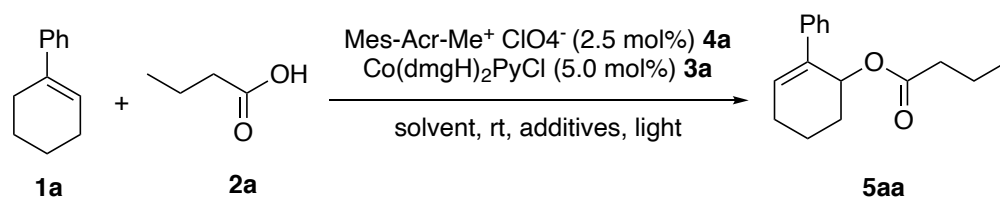



1p. Colorless oil. ¹H NMR (400 MHz, CDCl₃) Signal of isomer **Z-1p** δ 7.34 – 7.18 (m, 4H), 7.13 – 7.11 (m, 1H), 5.41 (t, *J* = 7.3 Hz, 1H), 2.28 (td, *J* = 7.5 Hz, *J* = 0.8 Hz, 2H), 1.92 (p, *J* = 7.4 Hz, 2H), 1.40 – 1.25 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H), 0.89 – 0.83 (m, 3H). Signal of isomer **E-1p** δ 7.34 – 7.18 (m, 4H), 7.13 – 7.11 (m, 1H), 5.64 (t, *J* = 7.2 Hz, 1H), 2.48 – 2.44 (m, 2H), 2.20 (p, *J* = 7.5 Hz, 2H), 1.40 – 1.25 (m, 2H), 1.04 (t, *J* = 7.5 Hz, 3H), 0.89 – 0.83 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 143.40, 141.47, 140.16, 130.87, 129.02, 128.37, 128.06, 127.86, 126.32, 126.20, 41.27, 31.60, 22.19, 21.84, 21.82, 21.18, 14.72, 14.41, 13.91, 13.57. **GC-MS**: 174 (6), 145 (22), 131 (100), 117 (32); The signals of the two stereoisomers were assigned by the 1D-NOESY experiment.



1q. Colorless oil. ¹H NMR (400 MHz, CDCl₃) Sum of the signals of the two isomers δ 7.33 – 7.13 (m, 8H), 7.12 - 7.09 (m, 2H), 5.62 (t, *J* = 7.2 Hz, 1H), 5.41 (t, *J* = 7.3 Hz, 1H), 2.49 - 2.45 (m, 2H), 2.31 – 2.29 (m, 2H), 2.18 – 2.13 (m, 2H), 1.90 – 1.85 (m, 2H), 1.50 – 1.41 (m, 2H), 1.35 - 1.24 (m, 10H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.87 – 0.80 (m, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 143.51, 141.63, 141.05, 140.20, 128.88, 128.42, 128.05, 127.84, 127.02, 126.30, 126.28, 126.13, 39.01, 30.91, 30.87, 30.60, 30.35, 29.45, 23.24, 23.04, 22.66, 22.22, 13.94, 13.93, 13.90, 13.74. **GC-MS**: 202 (14), 173 (13), 145 (60), 118 (100);

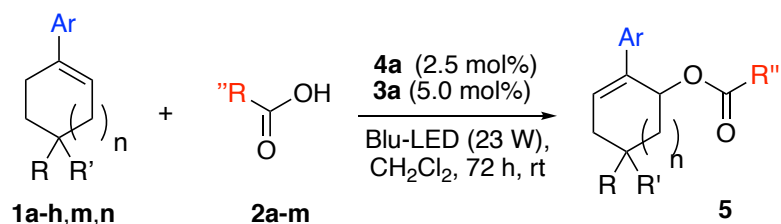
Table S1. Optimization of the intermolecular reaction conditions.



Entry	Reaction conditions	Yield (%) ^a
1	Toluene	17
2	DMSO	Traces
3	CH ₃ CN	46
4	CH ₂ Cl ₂ /CH ₃ CN (20:1)	54
5	CH ₂ Cl ₂ /CH ₃ CN (10:1)	46
6	CH ₂ Cl ₂ /HFIP (1:1)	0
7	chlorobenzene	19
8	AcOEt	Traces
9	cHex/CH ₂ Cl ₂ (5:1)	Traces
10	3a:4a (1:1, 5 mol%)	59
11	3a:4a (1:2, 1.25/2.5 mol%)	25
12	0.5 M in CH ₂ Cl ₂	48
13	0.2 M in CH ₂ Cl ₂	44
14	0.025 M in CH ₂ Cl ₂	17
15	ZnF ₂ (1 eq.) as an additive	42
16	BLUE LED 23 W (20 h)	< 10
17	BLUE LED 40 W (20 h)	38

^a Isolated yields after flash chromatography.

Optimized general procedure for the intermolecular process with PC 4a.

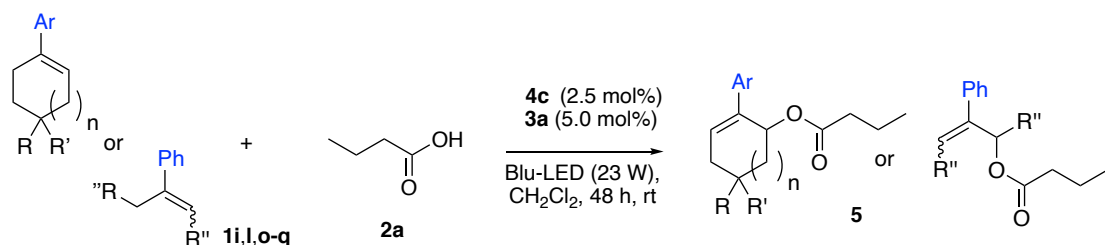


A 5 mL dry vial equipped with a stirring bar was charged with: acridinium **4a** (1 mg, 2.5 mol%), [Co(dmgH)₂(Py)(Cl)] (2.0 mg, 5 mol%), dry DCM (1 mL), styryl derivative **1** (0.1 mmol) and the desired carboxylic acid (1.0 mmol). The solution was degassed with N₂ then stirred under 23 W blue LED irradiation (465 nm) for 72 h. Then, the solvent was removed under vacuum and the residue purified via flash chromatography.

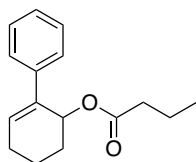
1-mmol Procedure:

A 20 mL dry schlenk tube, equipped with a stirring bar was charged with: acridinium **4a** (10 mg, 2.5 mol%), [Co(dmgH)₂(Py)(Cl)] (20.0 mg, 5 mol%), dry DCM (10 mL), 1 phenylcyclohexene **1a** (158.0 mg, 1.0 mmol) and butyric acid (880.0 mg, 10.0 mmol). The solution was degassed with N₂ then stirred under 23 W blue LED irradiation (465 nm) for 72 h. Then, the solvent was removed under vacuum and the residue purified via flash chromatography to obtain **5aa** in 40% yield (97.6 mg).

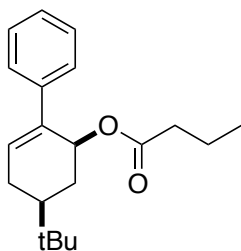
Optimized general procedure for the intermolecular process with PC 4c.



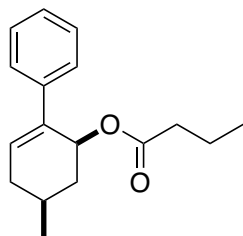
A 5 mL dry vial equipped with a stirring bar was charged with: acridinium **4c** (1.4 mg, 2.5 mol%), [Co(dmgH)₂(Py)(Cl)] (2.0 mg, 5 mol%), dry DCM (1 mL), styryl derivative **1** (0.1 mmol) and the desired carboxylic acid (1.0 mmol). The solution was degassed with N₂ then stirred under 23 W blue LED irradiation (465 nm) for 48 h. Then, the solvent was removed under vacuum and the residue purified via flash chromatography.



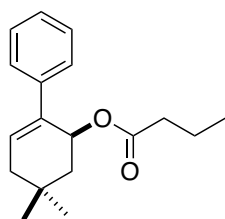
5aa. Viscous oil. cHex:EtOAc: 100:1. Yield = 63% (15.2 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.32 – 7.25 (m, 4H), 7.22 – 7.18 (m, 1H), 6.31 (dd, *J* = 4.6 Hz, *J* = 3.4 Hz, 1H), 5.94 (t, *J* = 3.9 Hz, 1H), 2.35 – 2.27 (m, 1H), 2.23 – 2.19 (m, 1H), 2.17 – 2.12 (m, 2H), 2.00 – 1.94 (m, 1H), 1.90 – 1.82 (m, 1H), 1.76 – 1.67 (m, 2H), 1.49 (sext, *J* = 7.4 Hz, 2H), 0.79 (t, *J* = 7.4 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 173.32, 139.61, 135.70, 130.78, 128.25, 126.98, 125.58, 67.16, 36.52, 29.08, 25.85, 18.50, 17.63, 13.41; **GC-MS**: 156 (100), 141 (18), 128 (19), 115 (21), 91 (23); **Anal. Calc.** for (C₁₆H₂₀O₂: 244.15): C, 78.65; H, 8.25; found: C, 78.76; H, 8.37.



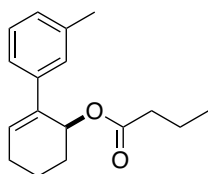
5ba. *dr* = 60:40. Viscous oil. cHex:EtOAc: 100:1. Yield = 71% (21.3 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.35 - 7.34 (m, 1H), 7.30 - 7.14 (m, 4H), 6.40 (dd, *J* = 5.7 Hz, *J* = 2.4 Hz, 1H), 6.00 (m, 1H), 2.38 – 2.31 (m, 1H), 2.29 – 2.21 (m, 1H), 2.20 – 2.16 (m, 2H), 2.12 – 1.97 (m, 1H), 1.61-1.34 (m, 4H), 0.89 (s, 9H), 0.83 (t, *J* = 7.4 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 173.44, 173.36, 139.42, 139.14, 138.05, 134.47, 131.31, 129.95, 128.35, 128.04, 127.07, 126.68, 125.94, 125.43, 70.94, 68.05, 42.81, 38.00, 36.63, 36.41, 32.20, 31.64, 30.85, 30.48, 27.76, 27.10, 27.03, 18.69, 18.28, 13.47. **GC-MS**: 155 (100), 212 (17), 115 (14), 128 (11), 91 (11); **Anal. Calc.** for (C₂₀H₂₈O₂: 300.44): C, 79.96; H, 9.39; found: C, 80.15; H, 9.56. Diagnostic signal of the minor diastereoisomer: **¹H NMR** (401 MHz, CDCl₃) δ 6.09 – 6.07 (m, 2H), 0.90 (s, 9H) 0.73 (t, *J* = 7.4 Hz, 3H).



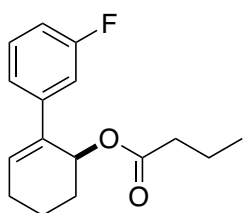
5ca. *dr* = 68:32. Viscous oil. cHex:EtOAc: 100:1. Yield = 51% (13.2 mg); **¹H NMR** (400 MHz, CDCl₃) δ 7.34 – 7.32 (m, 1H), 7.29 – 7.19 (m, 4H), 6.34 (dd, *J* = 5.5 Hz, *J* = 2.4 Hz, 1H), 5.97 – 5.94 (m, 1H), 2.41 – 2.34 (m, 1H), 2.30 – 2.21 (m, 1H), 2.19 – 2.15 (m, 2H), 2.06 – 1.78 (m, 1H), 1.63 - 1.37 (m, 4H), 1.02 (d, *J* = 4.3 Hz, 3H), 0.79 (t, *J* = 7.4 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 173.32, 139.48, 139.30, 137.65, 134.85, 130.70, 129.50, 128.31, 128.05, 127.06, 126.74, 125.94, 125.53, 69.57, 67.67, 37.43, 37.38, 36.55, 36.40, 34.65, 34.18, 27.78, 23.39, 21.51, 21.34, 18.54, 18.32, 13.45, 13.37; **GC-MS**: 170 (100), 155 (74), 91 (5), 115 (21); **Anal. Calc.** for (C₁₇H₂₂O₂: 258.16): C, 79.03; H, 8.58; found: C, 79.26; H, 8.67. Diagnostic signal of the minor diastereoisomer: **¹H NMR** (401 MHz, CDCl₃) δ 6.09 – 6.05 (m, 2H), 1.07(d, *J* = 4.3 Hz, 3H), 0.74 (t, *J* = 7.4 Hz, 3H).



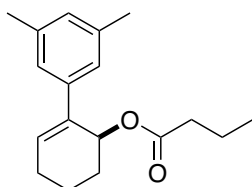
5da. Viscous oil. cHex:EtOAc: 100:1. Yield = 41% (11.2 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.27 – 7.26 (m, 4H), 7.23 – 7.17 (m, 1H), 6.12 (dd, *J* = 5.8 Hz, *J* = 2.4 Hz, 1H), 6.05 – 6.02 (t, *J* = 5.6 Hz, 1H), 2.11 – 2.03 (m, 4H), 1.93 (dd, *J* = 13.4 Hz, *J* = 6.0 Hz, 1H), 1.62 (dd, *J* = 13.4 Hz, *J* = 6.7 Hz, 1H), 1.43 (sext, *J* = 7.4 Hz, 2H), 1.04 (s, 3H), 1.02 (s, 3H), 0.75 (t, *J* = 7.4 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 173.42, 139.31, 135.58, 128.98, 128.16, 126.86, 125.84, 68.04, 41.70, 39.81, 36.46, 29.95, 29.45, 27.69, 18.36, 13.46; **GC-MS**: 184 (100), 154 (65), 91 (14); **Anal. Calc.** for (C₁₈H₂₄O₂: 272.18): C, 79.37; H, 8.88; found: C, 79.51; H, 9.17.



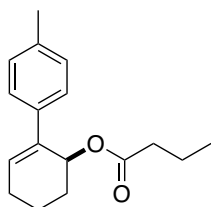
5ea. Viscous oil. cHex:EtOAc: 100:1. Yield = 43% (11.1 mg). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.18 – 7.09 (m, 3H), 7.02 (d, $J = 7.3$ Hz, 1H), 6.31 – 6.29 (dd, $J = 4.7$ Hz, $J = 3.5$ Hz, 1H), 5.92 – 5.90 (t, $J = 3.9$ Hz, 1H), 2.31 (s, 3H), 2.29 – 2.26 (m, 1H), 2.22 – 2.18 (m, 1H), 2.17 – 2.13 (m, 2H), 2.00 – 1.94 (m, 1H), 1.89 – 1.81 (m, 1H), 1.75 – 1.66 (m, 2H), 1.50 (sext, $J = 7.4$ Hz, 2H), 0.80 (t, $J = 7.4$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 173.34, 139.60, 137.72, 135.71, 130.62, 128.14, 127.74, 126.83, 122.66, 67.27, 36.53, 29.06, 25.84, 21.45, 18.52, 17.62, 13.42; **GC-MS:** 170 (100), 155 (36), 105 (23); **Anal. Calc.** for ($\text{C}_{17}\text{H}_{22}\text{O}_2$: 258.16): C, 79.03; H, 8.58; found: C, 79.27; H, 8.73.



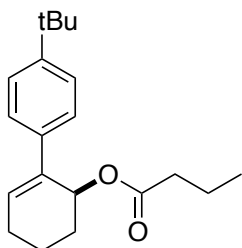
5fa. Yellow viscous oil. cHex:EtOAc: 100:1. Yield = 42% (11.0 mg). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.25 – 7.20 (m, 1H), 7.08 – 7.06 (m, 1H), 7.02 – 7.00 (m, 1H), 6.92 – 6.87 (m, 1H), 6.33 (dd, $J = 4.7$ Hz, $J = 3.3$ Hz, 1H), 5.87 (t, $J = 4.0$ Hz, 1H), 2.35 – 2.27 (m, 1H), 2.23 – 2.19 (m, 1H), 2.18 – 2.14 (m, 2H), 2.00 – 1.94 (m, 1H), 1.89 – 1.81 (m, 1H), 1.74 – 1.67 (m, 2H), 1.49 (sext, $J = 7.4$ Hz, 2H), 0.80 (t, $J = 7.4$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 173.26, 162.89 (d, $J = 245$ Hz, 1C), 142.03 (d, $J = 7.7$ Hz, 1C), 134.86 (d, $J = 2.0$ Hz, 1C), 131.91, 129.65 (d, $J = 8.4$ Hz, 1C), 121.15 (d, $J = 2.7$ Hz, 1C), 113.78 (d, $J = 21.1$ Hz, 1C), 112.62 (d, $J = 22.1$ Hz, 1C), 67.00, 36.49, 28.97, 25.82, 18.50, 17.51, 13.40; $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -113.58 – 113.65 (m, 1F); **GC-MS:** 174 (100), 146 (18), 109 (23); **Anal. Calc.** for ($\text{C}_{16}\text{H}_{19}\text{FO}_2$: 262.14): C, 73.26; H, 7.30; found: C, 73.44; H, 7.48.



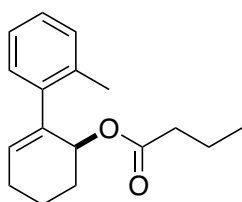
5ga. Viscous oil. cHex:EtOAc: 100:1. Yield = 69% (18.8 mg). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.93 (m, 2H), 6.86 (m, 1H), 6.28 (dd, $J = 4.6$ Hz, $J = 3.4$ Hz, 1H), 5.89 (t, $J = 4.0$ Hz, 1H), 2.34 – 2.29 (m, 1H), 2.27 (s, 6H), 2.22 – 2.19 (m, 1H), 2.18 – 2.13 (m, 2H), 2.00 – 1.94 (m, 1H), 1.88 – 1.80 (m, 1H), 1.73 – 1.65 (m, 2H), 1.51 (sext, $J = 7.2$ Hz, 2H), 0.80 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 173.37, 139.62, 137.60, 135.74, 130.49, 128.66, 123.50, 67.40, 36.55, 29.05, 25.84, 21.33, 18.56, 17.63, 13.43; **GC-MS:** 184 (100), 169 (39), 119 (18); **Anal. Calc.** for ($\text{C}_{18}\text{H}_{24}\text{O}_2$: 272.18): C, 79.37; H, 8.88; found: C, 80.21; H, 9.17.



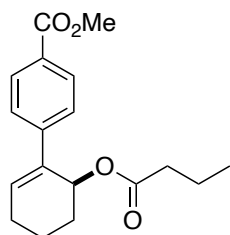
5ha. Viscous oil. cHex:EtOAc: 100:1. Yield = 49% (12.6 mg). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.20 (d, $J = 8.0$ Hz, 2H), 7.08 (d, $J = 8.0$ Hz, 2H), 6.28 (dd, $J = 4.7$ Hz, $J = 3.5$ Hz, 1H), 5.91 (m, 1H), 2.30 (s, 3H), 2.32 – 2.25 (m, 1H), 2.22 – 2.19 (m, 1H), 2.17 – 2.13 (m, 2H), 2.00 – 1.94 (m, 1H), 1.88 – 1.79 (m, 1H), 1.74 – 1.67 (m, 2H), 1.51 (sext, $J = 7.4$ Hz, 2H), 0.80 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 173.35, 136.69, 136.64, 135.35, 129.97, 128.96, 125.37, 67.14, 36.53, 29.08, 25.83, 20.99, 18.51, 17.56, 13.43; **GC-MS:** 170 (100), 155 (34), 105 (21); **Anal. Calc.** for ($\text{C}_{17}\text{H}_{22}\text{O}_2$: 258.16): C, 79.03; H, 8.58; found: C, 79.23; H, 8.75.



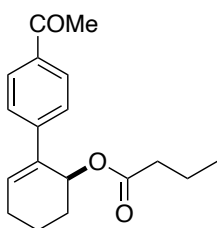
5ia. Viscous oil. cHex:EtOAc: 100:1. Yield = 41% (12.3 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.30 – 7.28 (m, 2H), 7.25 – 7.23 (m, 2H), 6.30 (dd, *J* = 4.7 Hz, *J* = 3.3 Hz, 1H), 5.92 (t, *J* = 3.7 Hz, 1H), 2.34 – 2.26 (m, 1H), 2.22 – 2.14 (m, 3H), 2.02 – 1.94 (m, 1H), 1.76 – 1.68 (m, 1H), 1.49 (sext, *J* = 7.4 Hz, 2H), 1.28 (s, 9H), 0.77 (t, *J* = 7.4 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 173.37, 149.90, 136.64, 135.29, 129.98, 125.16, 125.15, 67.19, 36.58, 34.38, 31.25, 29.08, 25.83, 18.53, 17.57, 13.38; **GC-MS**: 212 (97), 197 (100), 155 (48); **Anal. Calc.** for (C₂₀H₂₈O₂: 300.21): C, 79.96; H, 9.39; found: C, 80.45; H, 9.77.



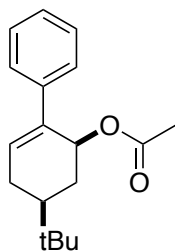
5la Viscous oil. cHex:EtOAc: 100:1. Yield = 39% (10.1 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.12 - 7.10 (m, 2H), 7.09 – 7.05 (m, 1H), 7.05 – 7.04 (m, 1H), 5.79 (t, *J* = 3.8 Hz, 1H), 5.77 (t, *J* = 4.5 Hz, 1H), 2.25 – 2.21 (m, 1H), 2.26 (s, 3H), 2.19 – 2.12 (m, 1H), 2.11 – 2.02 (m, 2H), 1.94 – 1.88 (m, 2H), 1.80 – 1.70 (m, 2H), 1.46 – 1.37 (m, 2H), 0.71 (t, *J* = 7.4 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 173.00, 140.68, 137.02, 135.76, 131.54, 129.76, 129.06, 126.84, 125.15, 69.46, 36.46, 29.01, 25.30, 19.85, 18.35, 18.19, 13.37; **GC-MS**: 187 (8), 170 (100), 155 (40), 142 (78); **Anal. Calc.** for (C₁₇H₂₂O₂: 258.16): C, 79.03; H, 8.58; found: C, 79.23; H, 8.94.



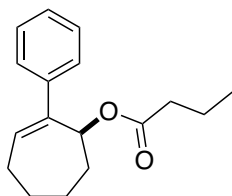
5ma. Yellow viscous oil. cHex:EtOAc: 80:1. Yield = 46% (13.9 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.94 (m, 2H), 7.39 (m, 2H), 6.42 (dd, *J* = 4.6 Hz, *J* = 3.5 Hz, 1H), 5.95 (t, *J* = 4.1 Hz, 1H), 3.88 (s, 3H), 2.38 – 2.29 (m, 1H), 2.26 – 2.20 (m, 1H), 2.16 – 2.11 (m, 2H), 2.00 – 1.94 (m, 1H), 1.91 - 1.84 (m, 1H), 1.75 – 1.68 (m, 2H), 1.49 (sext, *J* = 7.4 Hz, 2H), 0.79 (t, *J* = 7.4 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 173.25, 166.93, 144.12, 135.15, 132.92, 129.64, 128.62, 125.46, 66.82, 51.98, 36.44, 28.97, 25.96, 18.47, 17.55, 13.44; **GC-MS**: 214 (100), 155 (44), 115 (13); **Anal. Calc.** for (C₁₈H₂₂O₄: 302.15): C, 71.50; H, 7.33; found: C, 71.76; H, 7.48.



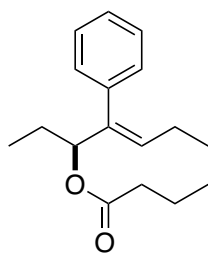
5na. Yellow viscous oil. cHex:EtOAc: 80:1. Yield = 35% (10.0 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.87 (m, 2H), 7.41 (m, 2H), 6.44 (dd, *J* = 4.7 Hz, *J* = 3.4 Hz, 1H), 5.96 (t, *J* = 4.0 Hz, 1H), 2.57 (s, 3H), 2.39 – 2.30 (m, 1H), 2.27 – 2.19 (m, 1H), 2.16 - 2.12 (m, 2H), 2.00 – 1.95 (m, 1H), 1.92 - 1.84 (m, 1H), 1.78 – 1.69 (m, 2H), 1.50 (sext, *J* = 7.4 Hz, 2H), 0.81 (t, *J* = 7.4 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 197.83, 173.44, 144.49, 135.88, 135.28, 133.33, 128.66, 125.83, 66.95, 36.63, 29.16, 26.72, 26.18, 18.66, 17.70, 13.63; **GC-MS**: 198 (100), 183 (48), 155 (34), 115 (15); **Anal. Calc.** for (C₁₈H₂₂O₃: 286.16): C, 75.50; H, 7.74; found: C, 75.65; H, 7.92.



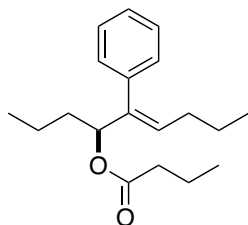
5bb. *dr* = 65:35. Viscous oil. *c*Hex:EtOAc: 100:1. Yield = 68% (18.5 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.35 – 7.34 (m, 1H), 7.31 – 7.20 (m, 4H), 6.40 (dd, *J* = 5.6 Hz, *J* = 2.3 Hz, 1H), 5.98 (m, 1H), 2.38 – 2.23 (m, 2H), 2.15 – 1.94 (m, 1H), 1.96 (s, 3H), 1.64 – 1.36 (m, 2H), 0.89 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃) δ 170.93, 170.74, 139.33, 139.13, 137.81, 134.36, 131.55, 130.10, 128.40, 128.08, 127.11, 127.71, 125.83, 125.40, 71.26, 68.38, 42.78, 37.95, 32.20, 31.62, 30.82, 30.37, 27.75, 27.09, 27.02, 26.68, 21.31, 21.09; **GC-MS**: 155 (100), 212 (14), 115 (12), 128 (9), 91 (10); **Anal. Calc.** for (C₁₈H₂₄O₂: 272.18): C, 79.37; H, 8.88; found: C, 79.52; H, 9.07. Diagnostic signal of the minor diastereoisomer: **¹H NMR** (401 MHz, CDCl₃) δ 6.10 – 6.04 (m, 2H), 1.82 (s, 3H), 0.90 (s, 9H)



5oa. Viscous oil. *c*Hex:EtOAc: 100:1. Yield = 43% (11.1 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.28 – 7.25 (m, 4H), 7.21 – 7.17 (m, 1H), 6.12 (t, *J* = 6.7 Hz, 1H), 5.84 (d, *J* = 7.8 Hz, 1H), 2.52 – 2.44 (m, 1H), 2.30 – 2.24 (m, 1H), 2.23 – 2.17 (m, 2H), 2.15 – 2.07 (m, 1H), 1.96 – 1.91 (m, 1H), 1.84 – 1.77 (m, 2H), 1.74 – 1.67 (m, 1H), 1.64 – 1.59 (m, 1H), 1.58 – 1.50 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 172.79, 143.18, 142.34, 134.03, 127.98, 126.65, 126.55, 74.33, 36.43, 30.77, 27.50, 26.55, 25.47, 18.41, 13.58. **GC-MS**: 170 (91), 155 (50), 142 (100), 129 (38); **Anal. Calc.** for (C₁₇H₂₂O₂: 258.16): C, 79.03; H, 8.58; found: C, 79.48; H, 8.79.

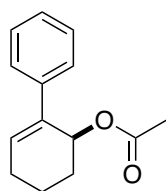


5pa. Viscous oil. *c*Hex:EtOAc: 100:1. *E:Z* = 53:47. Yield = 42% (10.9 mg). **¹H NMR** (400 MHz, CDCl₃) diagnostic signal for *Z*-**5pa** δ 5.77 (t, *J* = 7.2 Hz, 1H); diagnostic signal isomer *E*-**5pa** δ 5.33 (t, *J* = 6.6 Hz, 1H); sum of the other signals of the two isomers δ 7.37 – 7.25 (m, 8H), 7.17 – 7.15 (m, 2H), 5.67 (t, *J* = 6.9 Hz, 1H), 5.64 (t, *J* = 7.2 Hz, 1H), 2.43 – 2.26 (m, 6H), 1.92 – 1.85 (m, 2H), 1.71 – 1.60 (m, 4H), 1.60 – 1.50 (m, 4H), 1.04 (t, *J* = 8.4 Hz, 3H), 0.96 – 0.80 (m, 15H); **¹³C NMR** (100 MHz, CDCl₃) δ 172.99, 172.93, 141.26, 138.94, 138.19, 138.10, 136.56, 131.99, 129.20, 128.20, 127.94, 127.83, 126.85, 126.72, 78.99, 73.90, 36.61, 36.52, 26.36, 26.24, 21.86, 21.52, 18.50, 18.43, 14.28, 14.24, 13.67, 13.63, 10.07, 9.82; **GC-MS**: 190 (23), 172 (70), 157 (100), 143 (74); **Anal. Calc.** for (C₁₇H₂₄O₂: 260.18): C, 78.42; H, 9.29; found: C, 79.56; H, 9.41. The signals of the two isomers were assigned by the 1D-NOESY experiment.

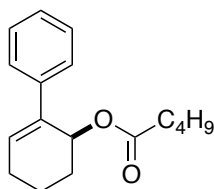


5qa. Viscous oil. *c*Hex:EtOAc: 100:1. *E:Z* = 50:50. Yield = 52% (15.0 mg). **¹H NMR** (400 MHz, CDCl₃) diagnostic signal isomer *Z*-**5qa** δ 5.87 (dd, *J* = 8.1 Hz, *J* = 6.5 Hz, 1H); diagnostic signal isomer *E*-**5qa** δ 5.40 (t, *J* = 6.7 Hz, 1H); sum of the other signals of the two isomers δ 7.37 – 7.22 (m, 8H), 7.17 – 7.15 (m, 2H), 5.67 (t, *J* = 7.5 Hz, 1H), 5.62 (t, *J* = 7.5 Hz, 1H), 2.36 – 2.26 (m, 6H), 1.88 – 1.82 (m, 2H), 1.69 – 1.62 (m, 4H), 1.53 – 1.43 (m, 4H), 1.40 – 1.19 (m, 8H), 0.97 – 0.90 (m, 9H), 0.85 – 0.77 (m, 9H); **¹³C NMR** (100 MHz, CDCl₃) δ 172.98, 172.91, 141.40, 140.03, 139.07, 138.26, 134.65, 130.20, 129.29, 128.19, 127.92, 127.83, 126.81, 126.71, 77.74, 72.35, 36.62, 36.52, 35.50, 35.50, 30.41, 30.15, 22.92, 22.75, 18.94, 18.81, 18.49, 18.43, 13.84, 13.74, 13.69, 13.64, 13.63. **GC-**

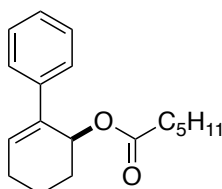
MS: 218 (18), 200 (51), 171 (100), 129 (68); **Anal. Calc.** for (C₁₉H₂₈O₂: 288.21): C, 79.12; H, 9.79; found: C, 79.43; H, 10.07. The signals of the two isomers were assigned by the 1D-NOESY experiment.



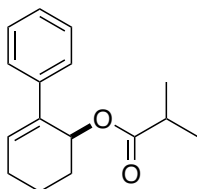
5ab. Viscous oil. cHex:EtOAc: 100:1. Yield = 58% (12.5 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.33 – 7.26 (m, 4H), 7.24 – 7.19 (m, 1H), 6.32 (dd, *J* = 4.8 Hz, *J* = 3.3 Hz, 1H), 5.93 – 5.91 (t, *J* = 4.0 Hz, 1H), 2.35 – 2.27 (m, 1H), 2.24 – 2.19 (m, 1H), 2.03 – 1.96 (m, 1H), 1.93 (s, 3H), 1.89 – 1.81 (m, 1H), 1.79 – 1.66 (m, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 170.76, 139.55, 135.45, 131.04, 128.32, 127.03, 125.50, 67.03, 28.97, 25.86, 21.28, 17.52; **GC-MS:** 156 (100), 141 (19), 128 (22), 115 (24), 91 (19); **Anal. Calc.** for (C₁₄H₁₆O₂: 216.12): C, 77.75; H, 7.46; found: C, 77.90; H, 7.62.



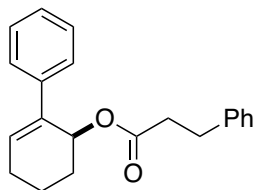
5ac. Viscous oil. cHex:EtOAc: 100:1. Yield = 70% (18.1 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.32 – 7.29 (m, 2H), 7.29 – 7.24 (m, 2H), 7.23 – 7.18 (m, 1H), 6.31 (dd, *J* = 4.7 Hz, *J* = 3.4 Hz, 1H), 5.94 (t, *J* = 3.9 Hz, 1H), 2.35 – 2.27 (m, 1H), 2.23 – 2.20 (m, 1H), 2.19 – 2.14 (m, 2H), 2.00 – 1.94 (m, 1H), 1.90 – 1.82 (m, 1H), 1.78 – 1.67 (m, 2H), 1.44 (p, *J* = 7.5 Hz, 2H), 1.21 – 1.12 (m, 2H), 0.78 (t, *J* = 7.3 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) 173.52, 139.61, 135.70, 130.80, 128.26, 126.99, 125.99, 67.15, 34.37, 29.06, 27.08, 25.85, 22.03, 17.63, 13.61; **GC-MS:** 156 (100), 141 (19), 128 (23), 115 (27), 91 (29); **Anal. Calc.** for (C₁₇H₂₂O₂: 258.16): C, 79.03; H, 8.58; found: C, 79.24; H, 8.67.



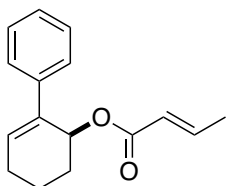
5ad. Viscous oil. cHex:EtOAc: 100:1. Yield = 55% (15.0 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.32 – 7.25 (m, 4H), 7.22 – 7.19 (m, 1H), 6.31 (dd, *J* = 4.4 Hz, *J* = 3.7 Hz, 1H), 5.94 (t, *J* = 3. Hz, 1H), 2.35 – 2.27 (m, 1H), 2.22 – 2.19 (m, 1H), 2.18 – 2.13 (m, 2H), 2.00 – 1.94 (m, 1H), 1.90 – 1.82 (m, 1H), 1.76 – 1.68 (m, 2H), 1.50 – 1.42 (m, 2H), 1.22 – 1.08 (m, 4H), 0.80 (t, *J* = 7.1 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 173.53, 139.60, 135.69, 130.80, 128.26, 126.99, 125.58, 67.13, 34.62, 31.07, 29.06, 25.85, 24.72, 22.21, 17.62, 13.80; **GC-MS:** 156 (100), 141 (19), 128 (21), 115 (26), 91 (27). **Anal. Calc.** for (C₁₈H₂₄O₂: 272.39): C, 79.37; H, 8.88; found: C, 79.54; H, 9.02.



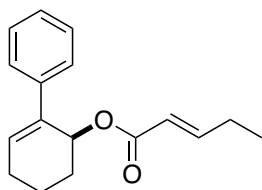
5ae. Viscous oil. cHex:EtOAc: 100:1. Yield = 45% (11.0 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.31 – 7.25 (m, 4H), 7.22 – 7.18 (m, 1H), 6.30 (dd, *J* = 4.5 Hz, *J* = 3.5 Hz, 1H), 5.92 (t, *J* = 4.2 Hz, 1H), 2.39 (sept, *J* = 6.8 Hz, 1H), 2.33 – 2.26 (m, 1H), 2.23 – 2.17 (m, 1H), 1.98 – 1.91 (m, 1H), 1.91 – 1.83 (m, 1H), 1.74 – 1.68 (m, 2H), 1.02 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 176.78, 139.62, 135.88, 130.55, 128.21, 126.96, 125.61, 67.13, 34.08, 29.03, 25.83, 18.79, 18.75, 17.78; **GC-MS:** 156 (100), 141 (19), 128 (25), 115 (36), 91 (34); **Anal. Calc.** for (C₁₆H₂₀O₂: 244.33): C, 78.65; H, 8.25; found: C, 78.79; H, 8.37.



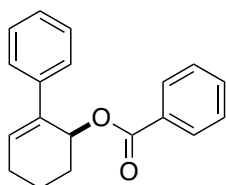
5af. Viscous oil. cHex:EtOAc: 100:1. Yield = 58% (17.8 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.31 – 7.25 (m, 4H), 7.24 – 7.13 (m, 4H), 7.08 (d, *J* = 7.6 Hz, 2H), 6.32 (m, 1H), 5.94 (m, 1H), 2.81 (t, *J* = 7.8 Hz, 2H), 2.50 (t, *J* = 7.8 Hz, 2H), 2.35 – 2.26 (m, 1H), 2.22 – 2.14 (m, 1H), 1.96 – 1.89 (m, 1H), 1.79 – 1.87 (m, 1H), 1.69 – 1.63 (m, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 172.57, 140.39, 139.58, 135.52, 130.99, 128.36, 128.32, 128.16, 127.03, 126.09, 125.56, 67.55, 36.03, 30.91, 28.99, 25.84, 17.53; **GC-MS**: 156 (100), 141 (16), 128 (18), 115 (22), 91 (57); **Anal. Calc.** for (C₂₁H₂₂O₂: 306.16): C, 82.32; H, 7.24; found: C, 82.49; H, 7.38.



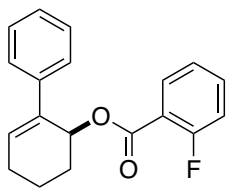
5ag. Viscous oil. cHex:EtOAc: 100:1. Yield = 43% (10.4 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.34 – 7.31 (m, 2H), 7.29 – 7.25 (m, 2H), 7.22 – 7.18 (m, 1H), 6.87 (dq, *J* = 15.5 Hz, *J* = 6.9 Hz, 1H), 6.34 (dd, *J* = 4.8 Hz, *J* = 3.2 Hz, 1H), 5.96 (t, *J* = 3.8 Hz, 1H), 5.74 (dq, *J* = 15.5 Hz, *J* = 1.7 Hz, 1H), 2.36 – 2.28 (m, 1H), 2.24 – 2.14 (m, 1H), 2.05 – 1.99 (m, 1H), 1.90 – 1.82 (m, 1H), 1.79 (dd, *J* = 6.9 Hz, *J* = 1.7 Hz, 3H), 1.77 – 1.66 (m, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 166.18, 144.54, 139.63, 135.45, 130.94, 128.30, 126.96, 125.46, 122.94, 67.12, 29.02, 25.91, 17.88, 17.50; **GC-MS**: 156 (100), 141 (20), 128 (27), 115 (31), 91 (29); **Anal. Calc.** for (C₁₆H₁₈O₂: 242.13): C, 79.31; H, 7.49; 13.20 found: C, 79.58; H, 7.74.



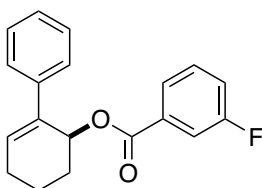
5ah. Viscous oil. cHex:EtOAc: 100:1. Yield = 43% (11.0 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.34 – 7.25 (m, 4H), 7.22 – 7.18 (m, 1H), 6.93 (dt, *J* = 15.7 Hz, *J* = 6.3 Hz, 1H), 6.35 (dd, *J* = 4.4 Hz, *J* = 3.6 Hz, 1H), 5.97 (t, *J* = 3.6 Hz, 1H), 5.71 (d, *J* = 15.7 Hz, 1H), 2.37 – 2.29 (m, 1H), 2.24 – 2.20 (m, 1H), 2.18 – 2.11 (m, 2H), 2.07 – 2.00 (m, 1H), 1.90 – 1.82 (m, 1H), 1.77 – 1.66 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 166.48, 150.77, 139.63, 135.44, 130.95, 128.30, 126.96, 125.46, 120.48, 67.13, 29.01, 25.92, 25.20, 17.50, 11.97; **GC-MS**: 156 (100), 141 (19), 128 (25), 115 (30), 91 (28); **Anal. Calc.** for (C₁₇H₂₀O₂: 256.35): C, 79.65; H, 7.86; found: C, 79.89; H, 8.02.



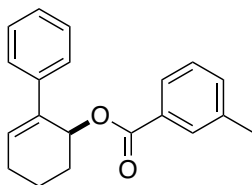
5ai. Viscous oil. cHex:EtOAc: 100:1. Yield = 45% (12.5 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.92 (d, *J* = 7.2 Hz, 2H), 7.51 – 7.46 (m, 1H), 7.39 – 7.33 (m, 4H), 7.27 – 7.24 (m, 2H), 7.20 – 7.16 (m, 1H), 6.40 (dd, *J* = 4.7 Hz, *J* = 3.3 Hz, 1H), 6.14 (t, *J* = 3.6 Hz, 1H), 2.42 – 2.34 (m, 1H), 2.29 – 2.20 (m, 1H), 2.17 – 2.11 (m, 1H), 2.00 – 1.91 (m, 1H), 1.88 – 1.79 (m, 1H), 1.79 – 1.70 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ 166.22, 139.76, 135.51, 132.70, 131.15, 130.61, 129.57, 128.34, 128.19, 127.0, 125.54, 68.26, 29.09, 25.95, 17.61; **GC-MS**: 156 (100), 141 (19), 128 (22), 115 (24), 91 (22), 77 (53). **Anal. Calc.** for (C₁₉H₁₈O₂: 278.13): C, 81.99; H, 6.52; found: C, 82.12; H, 6.67.



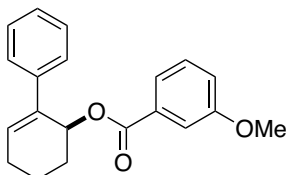
5aj. Viscous oil. cHex:EtOAc: 100:1. Yield = 71% (21.0 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.70 (td, *J* = 7.6 Hz, *J* = 1.8 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.39 – 7.37 (m, 2H), 7.29 – 7.25 (m, 2H), 7.21 – 7.18 (m, 1H), 7.10 – 7.02 (m, 2H), 6.38 (dd, *J* = 4.8 Hz, *J* = 3.3 Hz, 1H), 6.17 (t, *J* = 3.7 Hz, 1H), 2.41 – 2.33 (m, 1H), 2.29 – 2.24 (m, 1H), 2.21 – 2.13 (m, 1H), 2.00 – 1.92 (m, 1H), 1.89 – 1.80 (m, 1H), 1.80 – 1.71 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ 163.91, 161.87 (d, *J* = 260 Hz, 1C), 139.70, 135.37, 134.08 (d, *J* = 9.0 Hz, 1C), 131.83 (d, *J* = 1.0 Hz, 1C), 131.33, 128.33, 127.02, 125.61, 123.72 (d, *J* = 4.0 Hz, 1C), 119.25 (d, *J* = 10.0 Hz, 1C), 116.80 (d, *J* = 22.2 Hz, 1C), 68.62, 29.07, 25.92, 17.56; **¹⁹F NMR** (376 MHz, CDCl₃) δ -109.95 - 110.01 (m, 1F); **GC-MS**: 156 (100), 141 (20), 123 (42), 91 (27); **Anal. Calc.** for (C₁₉H₁₇FO₂: 296.34): C, 77.01; H, 5.78; found: C, 77.35; H, 5.84.



5ak. Viscous oil. cHex:EtOAc: 100:1. Yield = 41% (12.1 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.71 – 7.69 (m, 1H), 7.59 – 7.56 (m, 1H), 7.36 – 7.25 (m, 5H), 7.20 – 7.15 (m, 2H), 6.39 (dd, *J* = 4.8 Hz, *J* = 3.3 Hz, 1H), 6.13 (t, *J* = 3.8 Hz, 1H), 2.42 – 2.34 (m, 1H), 2.29 – 2.20 (m, 1H), 2.16 – 2.10 (m, 1H), 2.00 – 1.92 (m, 1H), 1.83 – 1.70 (m, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 165.10, 163.19 (d, *J* = 247 Hz, 1C), 139.64, 135.34, 132.76 (d, *J* = 7.4 Hz, 1C), 131.36, 129.79 (d, *J* = 7.8 Hz, 1C), 128.36, 127.07, 125.54, 125.28 (d, *J* = 3.0 Hz, 1C), 119.76 (d, *J* = 21.3 Hz, 1C), 116.43 (d, *J* = 22.9 Hz, 1C), 68.76, 29.04, 25.90, 17.59; **¹⁹F NMR** (376 MHz, CDCl₃) δ -112.62 – 112.69 (m, 1F); **GC-MS**: 156 (100), 141 (21), 91 (26); **Anal. Calc.** for (C₁₉H₁₇FO₂: 296.12): C, 77.01; H, 5.78; found: C, 77.34; H, 5.86.



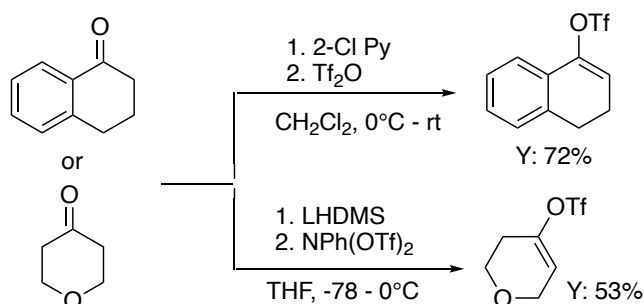
5al. Viscous oil. cHex:EtOAc: 100:1. Yield = 55% (16.1 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.71 (d, *J* = 7.3 Hz, 2H), 7.38 – 7.35 (m, 2H), 7.30 – 7.22 (m, 4H), 7.21 – 7.15 (m, 1H), 6.40 (dd, *J* = 4.8 Hz, *J* = 3.3 Hz, 1H), 6.13 (t, *J* = 3.7 Hz, 1H), 2.42 – 2.34 (m, 1H), 2.33 (s, 3H), 2.29 – 2.19 (m, 1H), 2.18 – 2.10 (m, 1H), 1.98 – 1.90 (m, 1H), 1.88 – 1.60 (m, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 166.40, 139.77, 137.97, 135.52, 133.46, 131.09, 130.54, 130.07, 128.32, 128.08, 126.97, 126.71, 125.52, 68.17, 29.10, 25.96, 21.18, 17.62; **GC-MS**: 156 (100), 141 (19), 128 (20), 115 (25), 91 (59); **Anal. Calc.** for (C₂₀H₂₀O₂: 292.15): C, 82.16; H, 6.90; found: C, 82.32; H, 7.21.



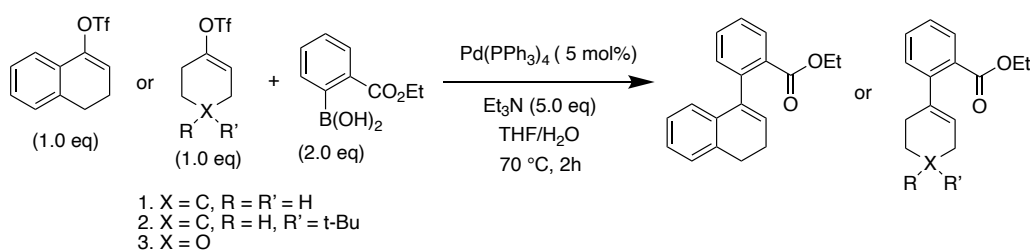
5am. Viscous oil. cHex:EtOAc: 80:1. Yield = 45% (13.9 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.50 (dd, *J* = 7.6 Hz, *J* = 1.0 Hz, 1H), 7.42 – 7.41 (m, 1H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 3H), 7.24 – 7.23 (m, 1H), 7.03 – 7.00 (m, 1H), 6.38 – 6.36 (m, 1H), 6.12 – 6.10 (m, 1H), 3.77 (s, 3H), 2.41 – 2.33 (m, 1H), 2.28 – 2.18 (m, 1H), 2.15 – 2.09 (m, 1H), 2.00 – 1.92 (m, 1H), 1.87 – 1.70 (m, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 166.11, 159.40, 139.81, 135.58, 131.94, 131.13, 129.20, 128.32, 126.98, 125.58, 121.97, 119.18, 114.05, 68.49, 55.34, 29.08, 25.93, 17.68; **GC-MS**: 156 (100), 141 (20), 128 (20), 115 (23), 91 (24); **Anal. Calc.** for (C₂₀H₂₀O₃: 308.38): C, 77.90; H, 6.54; found: C, 78.13; H, 6.73.

Synthesis of substrates 6a-d

Synthesis of the enol triflates through the procedures reported in the literatures.²

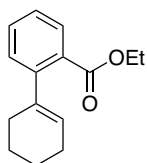


The enol triflates were subsequently converted into the corresponding acids **6** using the following procedure.

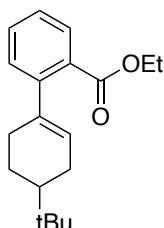


Under N₂, a dry Schlenk tube was charged with reagent grade THF (5 mL), deionized H₂O (1 mL) and Et₃N (5.0 eq). Then (2-(ethoxycarbonyl) phenylboronic acid (2.0 eq, 2.0 mmol, 386 mg) and triflate (1 mmol, 1.0 eq) was added. The reaction was stirred at 70 °C for 2 hours or until completion (TLC). Then H₂O was added, and the resulting mixture was extracted with EtOAc (2 x 15 mL). The organic phase was dried over Na₂SO₄ and concentrated under vacuum. The residue was purified with gel chromatography.

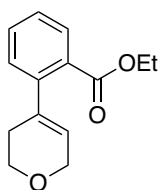
Viscous oil. cHex:EtOAc: 40:1. Yield = 95% (264 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.91 (dd, dd, *J* = 7.2 Hz, *J* = 1.2 Hz, 1H), 7.52 (td, *J* = 7.5 Hz, *J* = 1.4 Hz, 1H), 7.41 (td, *J* = 7.8 Hz, *J* = 1.3 Hz, 1H), 7.34 (dd, *J* = 7.6 Hz, *J* = 1.0 Hz, 1H), 7.18 (dd, *J* = 7.3 Hz, *J* = 0.8 Hz, 1H), 7.12 (td, *J* = 7.4 Hz, *J* = 1.3 Hz, 1H), 7.04 (td, *J* = 7.5 Hz, *J* = 1.4 Hz, 1H), 6.68 (d, *J* = 7.5 Hz, 1H), 3.99 (bs, 3H), 2.94 - 2.88 (m, 2H), 2.44 (d, *J* = 5.2 Hz, 2H), 0.99 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.93, 141.17, 139.98, 135.85, 135.64, 131.78, 131.41, 131.25, 129.94, 127.40, 127.31, 126.79, 126.69, 126.32, 124.31, 60.78, 28.16, 23.54, 13.72. **GC-MS**: 231 (100), 202 (44), 215 (15), 278 (13).



Viscous oil. cHex:EtOAc: 40:1. Yield = 78% (179 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.71 (dd, *J* = 7.7 Hz, *J* = 1.1 Hz, 1H), 7.39 (td, *J* = 7.5 Hz, *J* = 1.4 Hz, 1H), 7.25 (td, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.18 (dd, *J* = 7.7 Hz, *J* = 0.9 Hz, 1H), 5.55 – 5.52 (m, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.27 - 2.22 (m, 2H), 2.15 - 2.10 (m, 2H), 1.78 - 1.72 (m, 2H), 1.69 - 1.63 (m, 2H), 1.34 (t, *J* = 7.2 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 168.74, 145.32, 139.08, 131.01, 130.45, 129.44, 129.27, 126.33, 125.01, 60.84, 30.05, 25.47, 23.04, 21.97, 14.27; **GC-MS**: 184 (100), 165 (51), 128 (37), 115 (35), 230 (33).

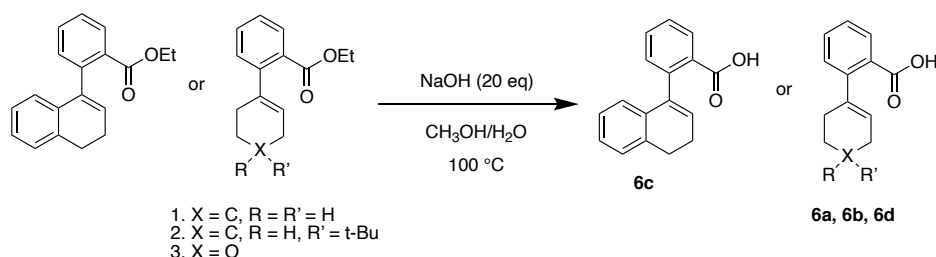


Viscous oil. cHex:EtOAc: 40:1. Yield = 72% (206 mg). δ **¹H NMR** (400 MHz, CDCl₃) δ 7.71 (dd, *J* = 7.7 Hz, *J* = 0.8 Hz, 1H), 7.38 (td, *J* = 7.5 Hz, *J* = 1.4 Hz, 1H), 7.27-7.23 (m, 1H), 7.18 (dd, *J* = 7.6 Hz, *J* = 0.7 Hz, 1H), 7.18 (dd, *J* = 7.3 Hz, *J* = 0.8 Hz, 1H), 5.56 - 5.54 (m, 1H), 4.33 - 4.25 (m, 2H), 2.36 – 2.29 (m, 2H), 2.19 – 2.14 (m, 1H), 1.94 - 1.86 (m, 2H), 1.42 – 1.36 (m, 1H), 1.34 (t, *J* = 7.1 Hz, 3H), 0.90 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃) δ 168.65, 145.07, 138.89, 131.04, 130.40, 129.46, 129.34, 126.34, 125.32, 60.83, 43.62, 32.22, 31.56, 27.20, 27.18, 24.44, 14.26; **GC-MS**: 165 (100), 183 (72), 57 (57), 286 (31).

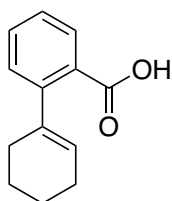


Viscous oil. cHex:EtOAc: 10:1 Yield = 65% (151 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.79 (dd, *J* = 7.8 Hz, *J* = 1.2 Hz, 1H), 7.43 (td, *J* = 7.5 Hz, *J* = 1.3 Hz, 1H), 7.31 (td, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.20 (dd, *J* = 7.8 Hz, *J* = 0.9 Hz, 1H), 5.56 – 5.55 (m, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 4.25 (q, *J* = 2.6 Hz, 2H), 2.37 - 2.34 (m, 2H) 1.35 (t, *J* = 7.1 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 167.95, 144.48, 137.07, 131.49, 129.95, 129.87, 129.37, 127.02, 123.03, 65.55, 64.48, 61.01, 30.02, 14.25; **GC-MS**: 157 (100), 129 (89), 186 (87), 232 (4).

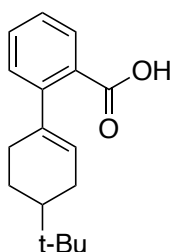
Hydrolysis of the ethyl esters



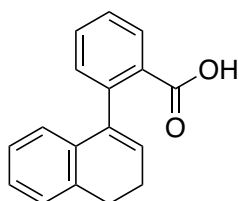
A one-necked flask was charged with MeOH (9 mL), H₂O (1 mL), the substrates obtained in the previous step and finally with NaOH (20 eq) finely powdered. The reaction was refluxed for 1 hours or until completion (TLC). The solution obtained was extracted with CH₂Cl₂ (2 x 15 mL). The aqueous layer was collected and HCl (6 M) was added to acidify the solution. Then EtOAc (2 x 15 mL) was used to extract the product. The organic layers were combined, dried over Na₂SO₄ and concentrated under vacuum.



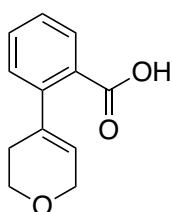
6a. White solid. Yield = 70% (125 mg). M.p. = 76 - 80 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.93 – 7.91 (m, 1H), 7.49 – 7.45 (m, 1H), 7.33 – 7.22 (m, 2H), 5.58 (m, 1H), 2.26 (m, 2H), 2.15 (m, 2H), 1.76 (m, 2H), 1.68 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 172.91, 146.68, 139.90, 132.30, 130.55, 129.87, 128.34, 126.54, 125.16, 30.34, 25.50, 23.04, 21.91. **GC-MS:** 184 (100), 128 (57), 115 (57), 202 (56), 91 (27). **Anal. Calc.** for ($\text{C}_{13}\text{H}_{14}\text{O}_2$: 202.25): C, 77.20; H, 6.98; found: C, 77.42; H, 7.14.



6b. Pale grey solid. Yield = 62% (128 mg). M.p. = 134 – 136 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.92 (dd, $J = 7.8$ Hz, $J = 1.1$ Hz, 1H), 7.46 (td, $J = 7.5$ Hz, $J = 1.4$ Hz, 1H), 7.30 (td, $J = 7.7$ Hz, $J = 1.3$ Hz, 1H), 7.20 (dd, $J = 7.6$ Hz, $J = 1.0$ Hz, 1H), 5.56 (m, 1H), 2.36 – 2.30 (m, 2H), 2.24 – 2.14 (m, 1H), 1.97 – 1.87 (m, 2H), 1.43 – 1.29 (m, 2H), 0.90 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 172.52, 144.26, 139.31, 132.28, 130.59, 129.44, 128.34, 126.56, 125.66, 43.57, 33.23, 31.81, 27.21, 24.45. **GC-MS:** 165 (100), 184 (94), 202 (58), 258 (42); **Anal. Calc.** for ($\text{C}_{17}\text{H}_{22}\text{O}_2$: 258.36): C, 79.03; H, 8.58; found: C, 79.31; H, 8.80.



6c. White solid. Yield = 80% (211 mg). M.p. = 137 – 139 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.56 (bs, 1H), 7.94 (dd, $J = 7.8$ Hz, $J = 1.2$ Hz, 1H), 7.54 (td, $J = 7.5$ Hz, $J = 1.3$ Hz, 1H), 7.39 (td, $J = 7.6$ Hz, $J = 1.1$ Hz, 1H), 7.30 (dd, $J = 7.6$ Hz, $J = 1.0$ Hz, 1H), 7.13 (d, $J = 7.2$ Hz, 1H), 7.07 (td, $J = 7.4$ Hz, $J = 1.1$ Hz, 1H), 7.01 – 6.95 (m, 1H), 6.56 (d, $J = 7.5$ Hz, 1H), 5.88 (t, $J = 4.6$ Hz, 1H), 2.86 – 2.80 (m, 2H), 2.39 – 2.35 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 172.20, 142.32, 139.56, 135.87, 132.46, 131.42, 130.68, 129.87, 128.34, 127.28, 127.25, 126.70, 126.53, 126.18, 124.09, 27.99, 23.43. **GC-MS:** 178 (100), 231 (88), 250 (78); **Anal. Calc.** for ($\text{C}_{17}\text{H}_{14}\text{O}_2$: 250.10): C, 81.58; H, 5.64; found: C, 81.72; H, 5.82.

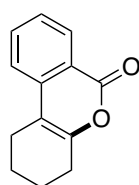


6d. Viscous oil. Yield = 59% (89.1 mg). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.97 (dd, $J = 7.8$ Hz, $J = 1.2$ Hz, 1H), 7.50 (td, $J = 7.5$ Hz, $J = 1.4$ Hz, 1H), 7.35 (td, $J = 7.6$ Hz, $J = 1.3$ Hz, 1H), 7.23 (dd, $J = 7.6$ Hz, $J = 1.2$ Hz, 1H), 5.58 (m, 1H), 4.30 – 4.28 (m, 2H), 3.92 (t, $J = 5.3$ Hz, 2H), 2.40 – 2.37 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 172.28, 144.66, 137.33, 132.64, 130.91, 129.90, 128.19, 127.19, 122.81, 65.54, 64.51, 30.12. **GC-MS:** 157 (100), 129 (80), 146 (62), 105 (53) 202 (31). **Anal. Calc.** for ($\text{C}_{12}\text{H}_{12}\text{O}_3$: 204.08): C, 70.58; H, 5.92; found: C, 70.74; H, 6.25.

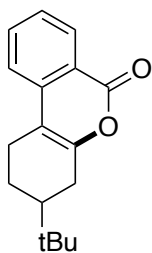
General procedure for intramolecular process.



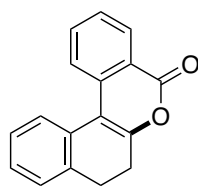
A 5 ml dry vial equipped with a stirring bar was charged with: $\text{Mes-Acr-Me}^+\text{ClO}_4^-$ (1.0 mg, 2.5 mol%), $[\text{Co(dmgH)}_2(\text{Py})(\text{Cl})]$ (2.0 mg, 5 mol%), dry DCM (1 ml) and acid (0.1 mmol). The solution was degassed with N_2 then stirred under 23 W blue LED irradiation (465 nm) for 72 h. The solvent was removed under vacuum and the residue purified by flash chromatography.



7a. White solid. *c*Hex:EtOAc: 20:1. Yield = 47% (9.4 mg). M.p. = 106 – 109 °C. **¹H NMR** (400 MHz, CDCl_3) δ 8.28 (dd, $J = 8.3$ Hz, $J = 1.5$ Hz, 1H), 7.72 (ddd, $J = 8.3$ Hz, $J = 7.2$ Hz, $J = 1.5$ Hz, 1H), 7.46 – 7.42 (m, 2H), 2.61 – 2.55 (m, 4H), 1.91 – 1.78 (m, 4H). **¹³C NMR** (100 MHz, CDCl_3) δ 162.7, 152.42, 138.03, 134.54, 129.73, 127.11, 121.33, 120.55, 109.30, 27.36, 22.65, 22.03. **GC-MS:** 144 (100), 200 (95), 115 (56), 102 (31). **Anal. Calc.** for $(\text{C}_{13}\text{H}_{12}\text{O}_2)$: 200.08; C, 77.98; H, 6.04; found: C, 78.18; H, 6.28. Diagnostic signal of the minor isomer: **¹H NMR** (400 MHz, CDCl_3) δ 7.87 – 7.85 (m, 1H), 7.65– 7.61 (m, 1H), 7.51 – 7.47 (m, 1H), 7.37 – 7.35 (m, 1H), 6.21 – 6.16 (m, 1H), 5.46 – 5.44 (m, 1H).

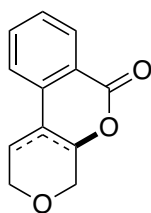


7b. Pale grey solid. *c*Hex:EtOAc: 50:1. Yield = 43% (11.0 mg). M.p. = 150 – 153 °C. **¹H NMR** (400 MHz, CDCl_3) δ 8.28 (dd, $J = 7.8$ Hz, $J = 1.4$ Hz, 1H), 7.70 (td, $J = 7.7$ Hz, $J = 1.4$ Hz, 1H), 7.46 – 7.42 (m, 2H), 2.79 – 2.74 (m, 1H), 2.59 – 2.52 (m, 1H), 2.52 – 2.44 (m, 1H), 2.44 – 2.34 (m, 1H), 2.11 – 2.05 (m, 1H), 1.58 – 1.51 (m, 1H), 1.38 – 1.29 (m, 1H), 0.94 (s, 9H). **¹³C NMR** (100 MHz, CDCl_3) δ 162.84, 152.72, 137.85, 134.53, 129.74, 127.07, 121.47, 120.43, 109.10, 44.09, 32.20, 29.17, 27.07, 23.53, 23.46. **GC-MS:** 256 (100), 200 (42), 144 (19), 115 (24). **Anal. Calc.** for $(\text{C}_{17}\text{H}_{20}\text{O}_2)$: 256.35; C, 79.65; H, 7.86; found: C, 79.83; H, 7.99.



7c. White solid. *c*Hex:EtOAc: 20:1. Yield = 82% (20.3 mg). M.p. = 158 – 159 °C. **¹H NMR** (400 MHz, CDCl_3) δ 8.38 – 8.36 (m, 1H), 8.10 (d, $J = 8.2$ Hz, 1H), 7.77 – 7.71 (m, 2H), 7.53 – 7.49 (m, 1H), 7.32 – 7.29 (m, 2H), 7.24 – 7.20 (m, 1H), 2.93 (t, $J = 7.4$ Hz, 2H), 2.76 (t, $J = 7.6$ Hz, 2H). **¹³C NMR** (100 MHz, CDCl_3) δ 161.96, 155.69, 135.76, 135.28, 134.45, 130.96, 130.39, 128.10, 127.39, 126.78, 126.43, 125.63, 123.67, 121.59, 110.98, 28.37, 27.34. **GC-MS:** 248 (100), 219 (48), 189 (38), 165 (22). **Anal. Calc.** for $(\text{C}_{17}\text{H}_{12}\text{O}_2)$: 248.08; C, 82.24; H, 4.87; found: C, 82.42; H, 5.02.

Diagnostic signal of minor the isomer: **¹H NMR** (401 MHz, CDCl₃) δ 8.77 (d, *J* = 8.7 Hz, 1H), 8.65 (d, *J* = 8.2 Hz, 1H), 8.49 (dd, *J* = 7.9 Hz, *J* = 1.1 Hz, 1H), 7.95 – 7.93 (m, 1H), 7.90 – 7.96 (m, 1H), 7.68 – 7.66 (m, 1H), 7.64 - 7.60 (m, 1H), 7.56 – 7.54 (m, 1H).

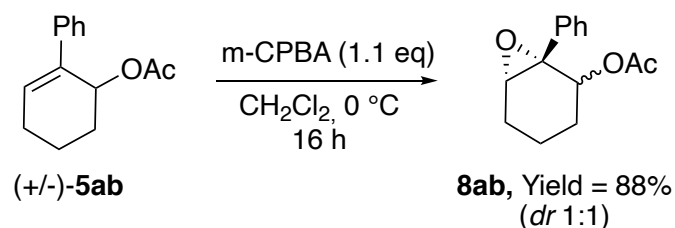


7d. Viscous oil. cHex:EtOAc: 20:1. Yield = 40% (8.1 mg), as a 57:43 regioisomeric mixture. **¹H NMR** (400 MHz, CDCl₃) δ 8.30 (dd, *J* = 7.9 Hz, *J* = 1.0 Hz, 1H), 7.75 (m, 1H), 7.49 (m, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 4.43 (t, *J* = 2.0 Hz, 2H), 4.01 (t, *J* = 5.5 Hz, 2H), 2.72 – 2.68 (m, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 149.75, 134.88, 134.24, 130.12, 129.37, 127.81, 125.68, 121.57, 121.10, 100.21, 64.69, 64.08, 63.12, 35.55, 22.61; **GC-MS**: 155 (100), 202 (88), 145 (42), 102 (34); **Anal. Calc.** for (C₁₂H₁₀O₃: 202.06): C, 71.28; H, 4.98; found: C, 71.43; H, 5.24. Diagnostic signal of the minor isomer: **¹H NMR** (401 MHz, CDCl₃) δ 7.87 (dd, *J* = 7.6 Hz, *J* = 1.0 Hz, 1H), 7.66 (td, *J* = 7.5 Hz, *J* = 1.1 Hz, 1H), 7.53 (m, 1H), 7.38 (m, 1H), 6.75 (d, *J* = 6.1 Hz, 1H), 4.68 (dd, *J* = 6.1 Hz, *J* = 2.1 Hz, 1H), 4.35 - 4.31 (m, 1H), 4.22 - 4.29 (m, 1H), 2.40 - 2.32 (m, 1H), 2.06 – 2.00 (m, 1H); **GC-MS**: 157 (100), 202 (24), 129 (81), 146 (58).

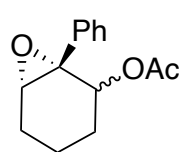
Functionalization of 5ab

Epoxidation reaction

The epoxidation reaction of (+/-)-**5ab** was performed using the following procedure.⁹



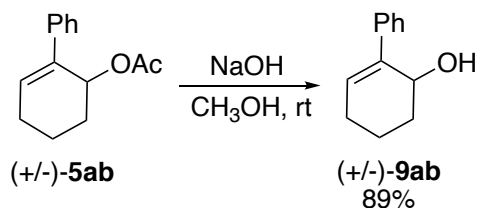
A dry two-necked flask was charged with DCM (1 mL) and (+/-)-**5ab** (94 μmol , 21.8 mg). The solution was cooled to 0 $^\circ\text{C}$ and *m*CPBA (17.2 mg, 0.1 mmol) was added. The reaction mixture was stirred 16 h at rt or until completion (TLC). Then H₂O was added and the resulting mixture was extracted with DCM (3 x 5 mL), then the organic phase was dried over Na₂SO₄ and concentrated under vacuum. The residue was purified with gel chromatography (cHex/AcOEt = 40/1) to give **8ab** as a viscous oil (19.2 mg, 88%). The two diastereomers were effectively separated by flash chromatography.



8ab: ¹H NMR (400 MHz, CDCl₃) δ 7.39-7.37 (m, 1H), 7.36- 7.35 (m, 1H), 7.31 – 7.29 (m, 1H), 7.29 – 7.25 (m, 2H), 5.41 (t, *J* = 4.1 Hz, 1H), 3.36 - 3.35 (m, 1H), 2.07 - 2.03 (m, 2H), 1.93 - 1.86 (m, 1H), 1.81 (s, 3H), 1.64 - 1.55 (m, 2H), 1.49 – 1.41 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 169.66, 138.18, 127.90, 127.87, 127.49, 70.18, 61.49, 59.48, 25.70, 23.33, 20.85, 14.67. **GC-MS**: 133 (100), 105 (96), 77 (51). **Anal. Calc.** for (C₁₄H₁₆O₃: 232.28): C, 72.39; H, 6.94; found: C, 72.58; H, 7.21.

8ab': ¹H NMR (400 MHz, CDCl₃) δ 7.36-7.35 (m, 1H), 7.33- 7.30 (m, 3H), 7.30 – 7.25 (m, 1H), 5.74 (dd, *J* = 9.4 Hz, *J* = 5.5 Hz, 1H), 3.13 (d, *J* = 4.3 Hz, 1H), 2.04 - 1.92 (m, 2H), 1.90 (s, 3H), 1.88 - 1.81 (m, 1H), 1.70 - 1.61 (m, 2H), 1.51 – 1.43 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 138.21, 128.33, 127.59, 125.48, 71.49, 64.55, 61.36, 25.49, 23.35, 20.90, 19.77. **GC-MS**: 133 (100), 105 (89), 77 (44). **Anal. Calc.** for (C₁₄H₁₆O₃: 232.28): C, 72.39; H, 6.94; found: C, 72.57; H, 7.24.

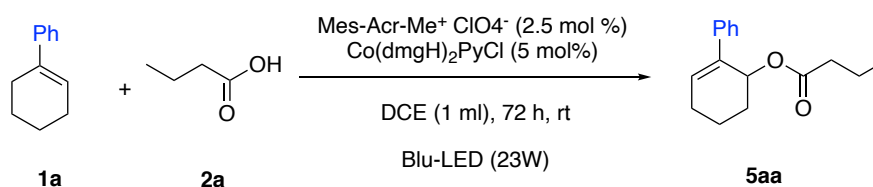
Hydrolysis



A flask was charged with MeOH (1 mL) and (+/-)-**5ab** (0.12 mmol, 26 mg). Then a solution of NaOH (3 mL, 1 M) was added. The reaction was checked over time until the SM disappeared. Then H₂O was added, and the resulting mixture was extracted with AcOEt (3 x 5 mL), then the organic phase was dried over Na₂SO₄ and concentrated under vacuum. The residue was purified with gel chromatography (cHex/AcOEt = 15/1) to give (+/-)-**9ab** as a viscous oil (18.5 mg, 89%).

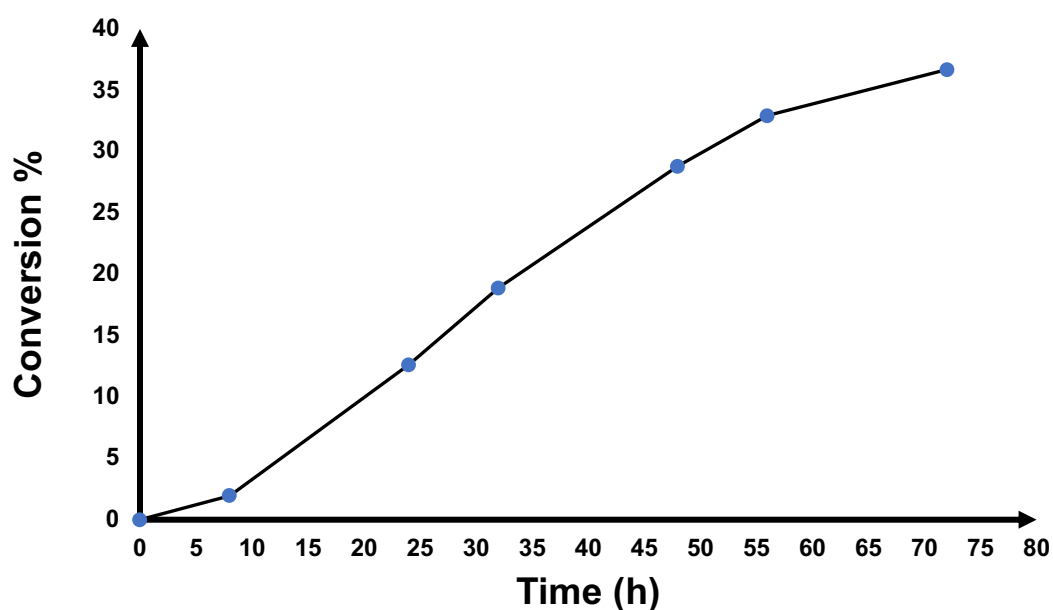
(+/-)-**9ab**. ¹H NMR (400 MHz, CDCl₃) δ 7.47-7.44 (m, 2H), 7.34- 7.30 (m, 2H), 7.26 – 7.22 (m, 1H), 6.15 (dd, *J* = 4.6 Hz, *J* = 3.5 Hz, 1H), 4.71 (m, 1H), 2.30 - 2.22 (m, 1H), 2.20 - 2.17 (m, 1H), 1.99 – 1.92 (m, 1H), 1.89 - 1.82 (m, 1H), 1.81 – 1.73 (m, 1H), 1.71 - 1.63 (m, 1H), 1.61 (bs, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 140.14, 139.07, 128.65, 128.49, 127.06, 125.96, 65.44, 31.53, 26.03, 17.32. **GC-MS**: 174 (100), 115 (99), 91 (92), 156 (52). **Anal. Calc.** for (C₁₂H₁₄O): 174.10; C, 82.72; H, 8.10; found: C, 82.97; H, 8.23.

Monitoring of the reaction conversion.

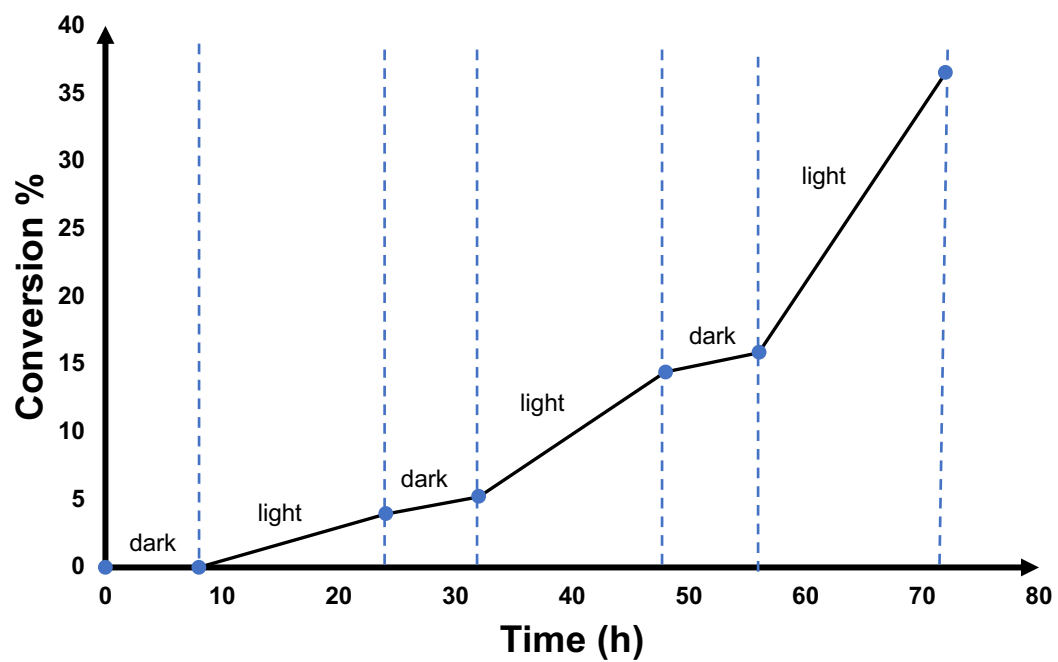


Two different dry vials equipped with a stirring bar were charged with: Mes-Acr-Me⁺ClO₄⁻ (1.0 mg, 2.5 mol%), [Co(dmgh)₂(Py)(Cl)] (2.0 mg, 5 mol%), dry DCE (1 ml), **1a** (0.1 mmol) and **2a** (1.0 mmol). The solutions were degassed with N₂ then stirred under 23 W blue LED irradiation. Samples injected into HPLC were prepared by taking 50 μL from the vial reaction and subsequently diluted. In the case of the first graph (**Scheme S1**) showed below, one of the two catalysis was monitored by taking samples during 72 h. In the second graph (**Scheme S2**) the second catalysis was always monitored over 72 h but exposing the reaction alternatively to the dark and to irradiation.

Scheme S1. Experiment with continuous irradiation.

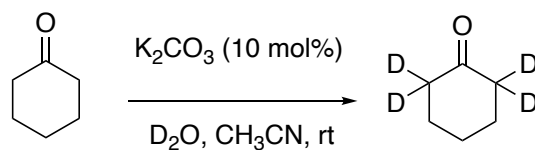


Scheme S2. On-off experiment

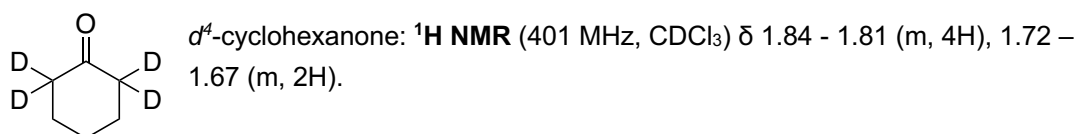


Kinetic isotope effect

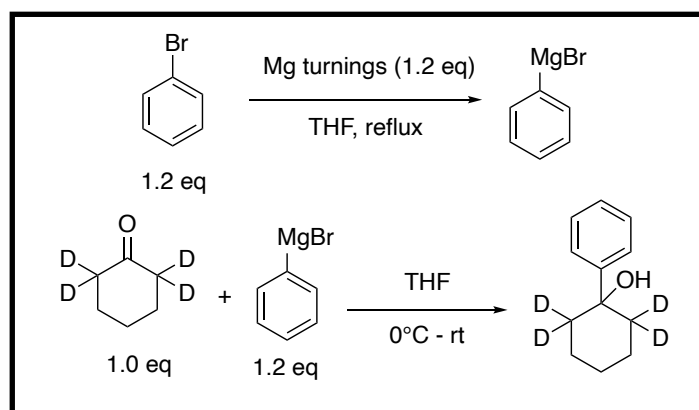
Synthesis of d^3 -1a.¹⁰

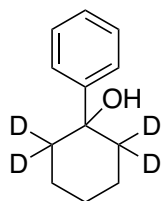


A dry two-necked flask was charged with D₂O (9 ml), CH₃CN (0.3 ml), cyclohexanone (309 μl, 3.0 mmol) and potassium carbonate (41 mg, 10 mol%). The reaction mixture was stirred at room temperature and controlled by ¹H NMR analysis until an almost total conversion of cyclohexanone into the corresponding d^4 analogous was observed. Then the mixture was extracted with DCM (3 x 5 mL) and the organic phase was dried over Na₂SO₄. Upon removal of the solvent under reduced pressure, a reaction crude was obtained and used directly in the next step.



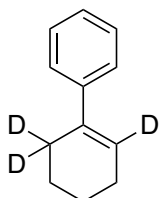
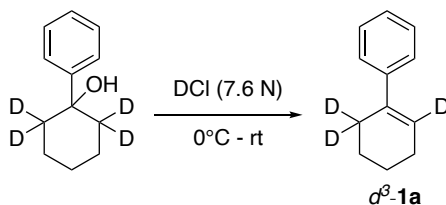
In the second step in a dry three-necked flask equipped with condenser the d^4 -cyclohexanone (ca. 3 mmol) was dissolved in 2 ml of THF was added dropwise at 0 °C to a solution of freshly prepared PhMgBr (3.6 mmol ca. 0.5 M). The reaction was stirred at rt for 7 h when the TLC showed the reaction completed. Then, a sat. NH₄Cl solution was added (5 mL) at 0 °C and the resulting mixture was extracted with AcOEt (3 x 5 mL). The organic phase was dried over Na₂SO₄ and concentrated under vacuum. The reaction crude was used directly in the next step.





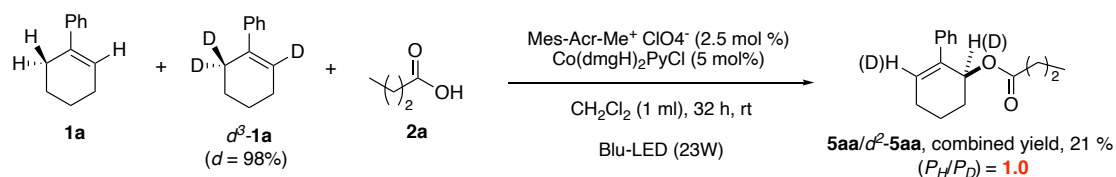
*d*⁴-1-Phenylcyclohexan-1-ol: **¹H NMR** (401 MHz, CDCl₃) δ 7.51 – 7.41 (m, 2H), 7.37 – 7.33 (m, 2H), 7.26 – 7.24 (m, 1H), 1.77 - 1.74 (m, 2H), 1.77 - 1.74 (m, 2H), 1.73 – 1.70 (m, 2H), 1.64 – 1.62 (m, 2H). **GC-MS**: 134 (100), 105 (59), 77 (39), 180 (37), 56 (29)

In the final step a dry two-necked flask a solution of deuterated hydrochloric acid (DCI) 7.6 N (12.0 mmol, 1.6 ml) was added drop wise at 0 °C to the reaction crude of the previous step dissolved in 2 ml of THF. The reaction was stirred at rt until the SM disappeared. Then, the resulting mixture was extracted with Et₂O (3 x 5 mL). The organic phase was dried over Na₂SO₄ and concentrated under vacuum. The residue was purified with gel chromatography (*n*Hex = 100%) to give *d*³-**1a** as a colorless oil (106 mg, 22%, unoptimized).

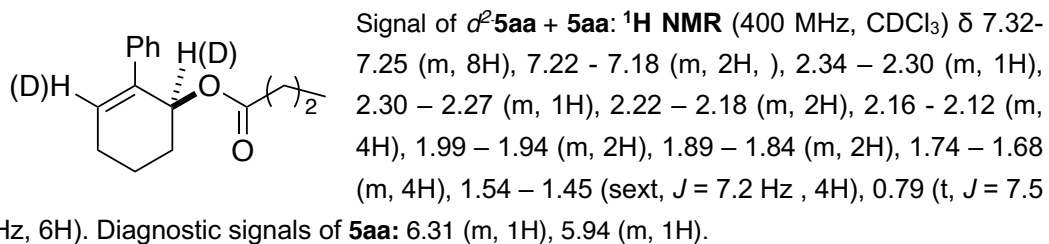


*d*³-**1a**: **¹H NMR** (400 MHz, CDCl₃) δ 7.38-7.35 (m, 2H), 7.31- 7.27 (m, 2H), 7.21 – 7.17 (m, 1H), 2.19 (t, *J* = 6.1 Hz, 2H), 1.77 – 1.74 (m, 2H), 1.68 – 1.62 (m, 2H). **¹³C NMR** (100 MHz, CDCl₃) δ 142.61, 136.64, 128.13, 126.43, 124.86, 124.45 (C-D, t, *J* = 18.0 Hz, 1C), 26.54 (C-D₂, quintet, *J* = 20.5 Hz, 1C), 25.71, 22.83, 22.07. **GC-MS**: 181 (100), 131 (80), 145 (46), 116 (39). **Anal. Calc.** for (C₁₂H₁₁D₃: 161.13): C, 89.38; H, 10.62; found: C, 89.53; H, 10.83

KIE investigation from intermolecular competition

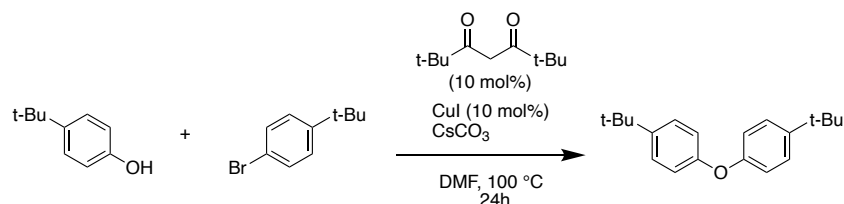


For this type of experiment a 5 mL dry vial equipped with a stirring bar was charged with: Mes-Acr-Me⁺ClO₄⁻ (1.0 mg, 2.5 mol%), [Co(dmgh)₂(Py)(Cl)] (2.0 mg, 5 mol%), dry DCM (1 mL), **1a** (50 μmol), **d³-1a** (50 μmol) and **2a** (1.0 mmol). The solution was degassed with N₂ then stirred under 23 W blue LED irradiation (465 nm) for 32 h. Then, the solvent was removed under vacuum and the residue purified via flash chromatography (cHex/AcOEt = 100/1, Yield: 21%). The KIE value was given after ¹H NMR analysis.

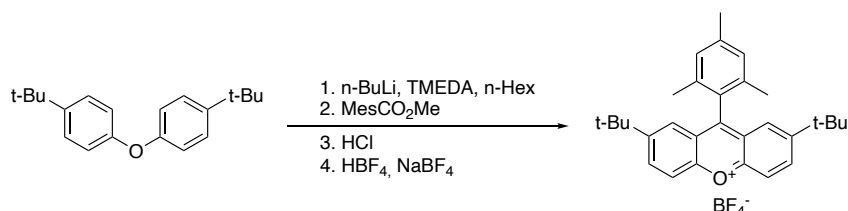


Synthesis of the photocatalyst **4c**

The photocatalyst **4c** was synthesized following the procedure described in the literature with slight modification.¹¹



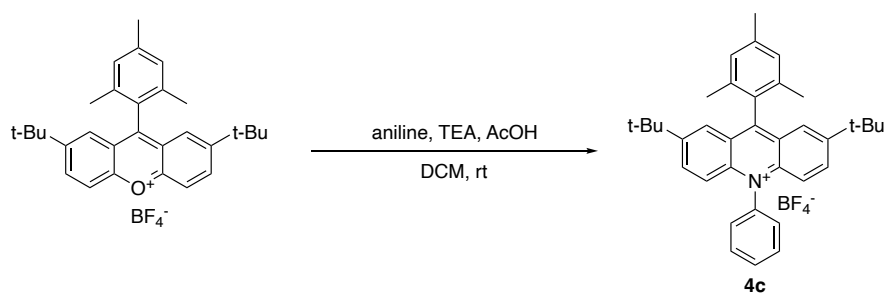
In the first step a Schlenk tube was charged with 1-bromo-4-(tert-butyl)benzene (1.06 g, 5.0 mmol), 4-(tert-butyl)phenol (1.13 mg, 7.5 mmol), Cs₂CO₃ (3.25 g, 10 mmol), CuI (95 mg, 10 mol%), 2,2,6,6-tetramethylheptane-3,5-dione (92 mg, 10 mol%) and anhydrous DMF (1.5 ml). The reaction was stirred at 100 °C for 24 h, then cooled at room temperature and the DMF removed under vacuum. Et₂O was added and the reaction crude was filtered through celite until the washing layers became colorless. The filtrate was washed with water (2 x 10 ml) followed by brine (1 x 10 ml). The organic phase was dried over Na₂SO₄ and concentrated under vacuum. The residue was purified with gel chromatography (cHex/AcOEt = 98/2) to give 4,4'-oxybis(tert-butylbenzene) as a viscous oil (630 mg, 45%).



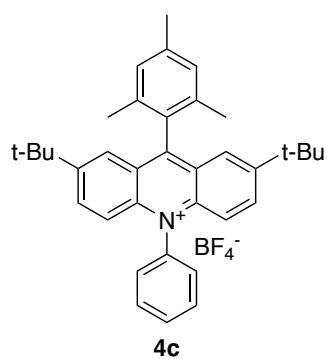
In the second step a flame-dried 3-necked 50 mL round bottom flask was charged under nitrogen with 4,4'-oxybis(tert-butylbenzene) (630 mg, 2.23 mmol), TMEDA (680 μ l, 4.57 mmol) and anhydrous *n*Hex (3 mL). The resulting solution was cooled to -78 °C and *n*-butyllithium (2.5 M in *n*Hex, 1.83 ml, 4.57 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred at room temperature for 4 h.

The reaction was cooled to -78 °C and a solution of methyl 2,4,6-trimethylbenzoate (401 mg, 2.25 mmol) in anhydrous *n*-hexane (3 ml) was added dropwise. After the addition, the reaction was allowed to slowly warm to room temperature and stirred overnight. The reaction was quenched with water and the biphasic mixture was stirred vigorously for 30 min. The mixture was diluted with Et₂O and the layers were separated. The organic layer was washed with water and brine. The organic layer was transferred to a 50 mL round bottom flask equipped with a stir bar. To the vigorously stirred solution was added conc. HCl (1 mL) resulting in a bright yellow precipitate that slowly turned brown over the course of addition. The brown suspension was stirred vigorously for 30 min then diluted with water. The layers were separated, and the organic

layer was extracted with water until the washings become colorless. To the combined aqueous layers was added solid NaBF₄ (736 mg, 6.69 mmol) resulting in a bright yellow precipitate. The resulting suspension was extracted with dichloromethane until the washings become colorless. To the combined organic layers was added HBF₄ (48 wt% in water, 0.29 mL, 2.23 mmol). Water was added, the phases were separated, and the organic layer was washed once with water and then once with aq. NaBF₄ (1 M, 7.85 ml). The organic layer was dried over solid NaBF₄, filtered, and concentrated to dryness. The residue was purified by trituration with n-hexane and filtered. The solid was rinsed with n-pentane and dried in vacuo to give 2,7-di-tert-butyl-9-mesitylxanthylum tetrafluoroborate (264 mg, 0.53 mmol, 24% yield, unoptimized) as a yellow-orange solid.



To an oven-dried Schlenk tube under nitrogen were added 2,7-di-tert-butyl-9-mesitylxanthylum tetrafluoroborate (263 mg, 0.53 mmol) and dry, degassed dichloromethane (1.5 mL). To the resulting solution were added acetic acid (0.091 mL, 95 mg, 1.59 mmol) followed by NEt₃ (0.11 mL, 80 mg, 0.795 mmol). Aniline (0.059 mL, 60 mg, 0.64 mmol) was then added dropwise. The flask was covered with aluminum foil and stirred at room temperature for 12 h. The reaction was transferred to a separatory funnel and washed with water followed by sat. aq. NaHCO₃. To the organic layer was added HBF₄ (48 wt% in water, 0.096 mL, 0.53 mmol). Water was added, the phases were separated and the organic layer was washed once with water and then once with aq. NaBF₄ (1M, 1.85 mL). The organic layer was dried over solid NaBF₄, filtered, and concentrated to dryness. The residue was purified by trituration with 1:2 Et₂O/hexanes and filtered. The solid was rinsed with n-pentane and dried in vacuo to give 2,7-di-tert-butyl-9-mesityl-10-phenylacridin-10-ium tetrafluoroborate **4c** (237 mg, 0.41 mmol, 78% yield) as a bright yellow solid.



4c. Bright yellow solid. M.p. = decomposition; ¹H NMR (400 MHz, CDCl₃) δ 8.16 (dd, *J* = 9.5 Hz, *J* = 2.1 Hz, 2H), 7.92 – 7.89 (m, 2H), 7.87 – 7.83 (m, 1H), 7.70 (d, *J* = 1.9 Hz, 2H), 7.68 – 7.66 (m, 2H), 7.54 (d, *J* = 9.4 Hz, 2H), 7.17 (s, 2H), 2.50 (s, 3H), 1.82 (s, 6H), 1.28 (s, 18H). ¹³C NMR (100 MHz, CDCl₃) δ 162.70, 162.65, 151.94, 151.90, 140.24, 140.20, 140.06, 140.03, 137.90, 137.86, 136.73, 136.70, 135.89, 135.79, 131.92, 131.89, 131.62, 131.60, 129.18, 129.15, 129.00, 128.98, 127.87, 127.84, 125.84, 125.83, 122.69, 119.87, 119.86, 35.25, 30.57, 21.36, 20.15. All aromatic

carbons except one (122.69 ppm) appear splitted into two slightly broad signals. **¹⁹F NMR** (377 MHz, CDCl₃) δ -154.31 (s, 1 F) -154.36 (s, 4 F). Two signals in 4:1 intensity ratio are observed due to the natural abundance of ¹⁰B (20%) and ¹¹B (80%) **HRMS**: 486.31608 [M-BF₄]

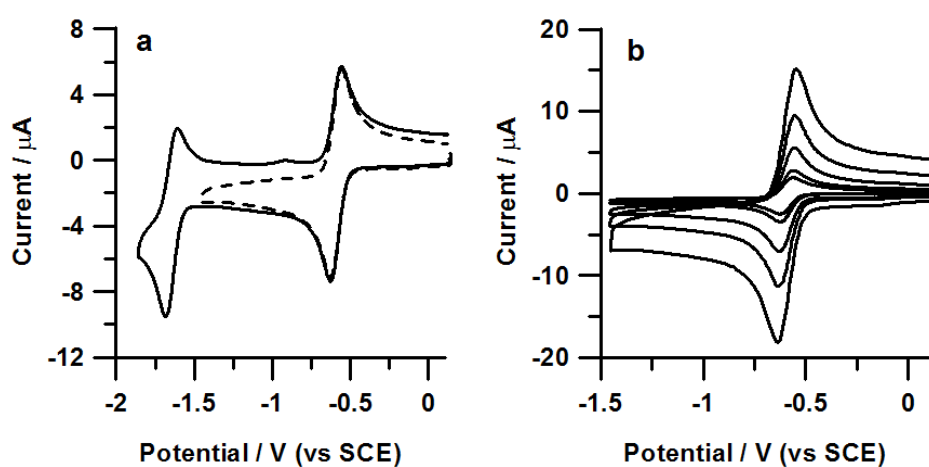
Stern-Volmer experiments

Quenching of the excited state of **4a** and **4c** was investigated by measuring the excited state lifetime (by TCSPC) in the presence of increasing amount of quencher Q (**1a**). The data were analyzed according to the Stern-Volmer equation in order to determine the quenching constant k_q :

$$\frac{\tau_0}{\tau} = 1 + \tau_0 k_q [Q]$$

In order to elucidate the reaction mechanism and to rule out the possible reaction of the excited **4c** with butyric acid the lifetime of **4c** in the presence of butyric acid up to 80 mM concentration was measured. No effect of the carboxylic acid on **4c** excited state lifetime was detected.

Figure S1: Cyclic Voltammetry curves



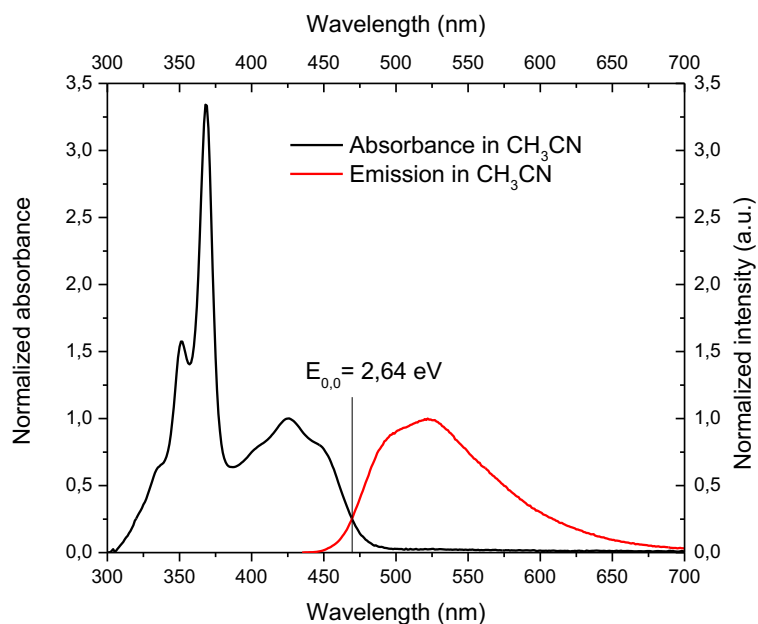
Experimental details: 1 mM solution of **4c** in a 0.07 M TBAH/CH₃CN electrolyte working electrode, Glassy carbon disk, 1mm diameter at a) 1Vs⁻¹ and b) 0.1, 0.2, 1, 2 and 5 Vs⁻¹

Table S2. Half-wave (E_{1/2}) redox potentials (vs. SCE)

Species	E _{1/2} / V (ΔE/mV) ^[a]	
4c	-0.59	-1.65
	(69)	(75)

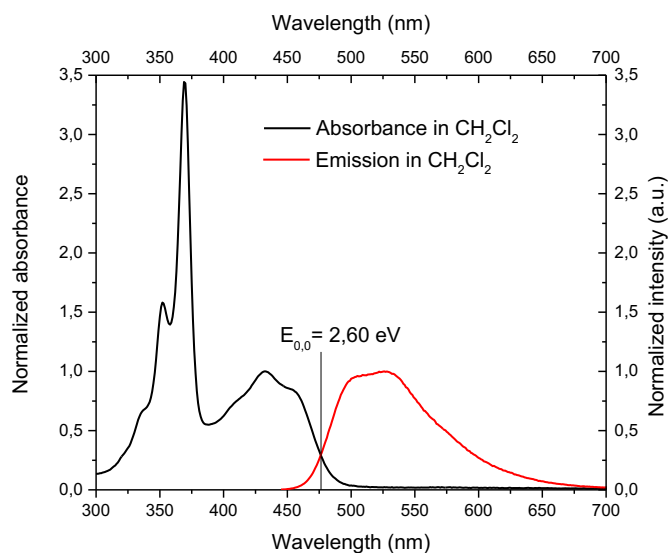
[a] Reduction potentials measured in CH₃CN solution.

Figure S2: Absorption and fluorescence spectra in CH₃CN

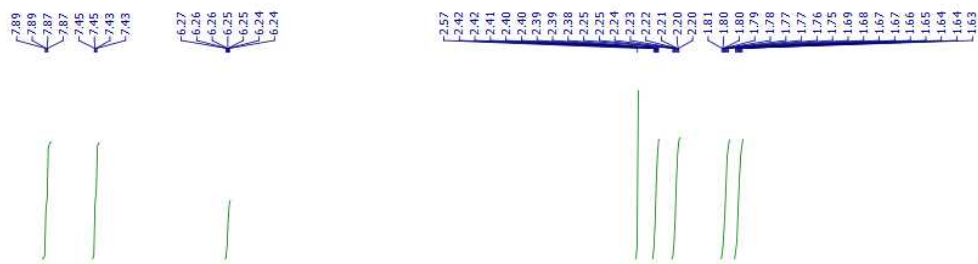
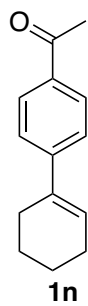


Experimental details: $\lambda_{\text{exc}} = 420 \text{ nm}$, **4c** $5 \times 10^{-5} \text{ M}$ in CH₃CN at room temperature. Fluorescence quantum yields and excited state lifetimes were 29% ($\tau = 10.9 \text{ ns}$) and 38% ($\tau = 13.7 \text{ ns}$) in aerated and de-aerated conditions respectively.

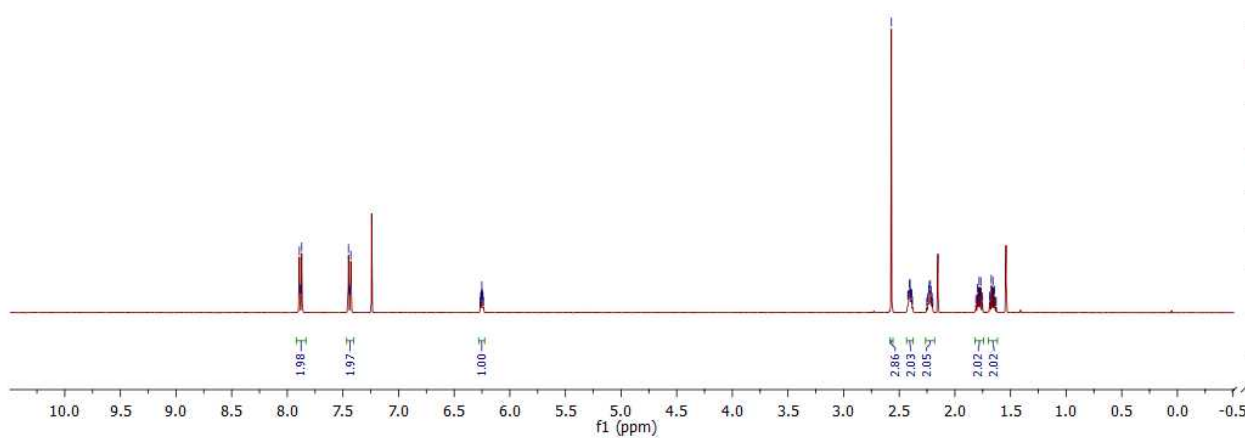
Figure S3: Absorption and fluorescence spectra in CH₂Cl₂

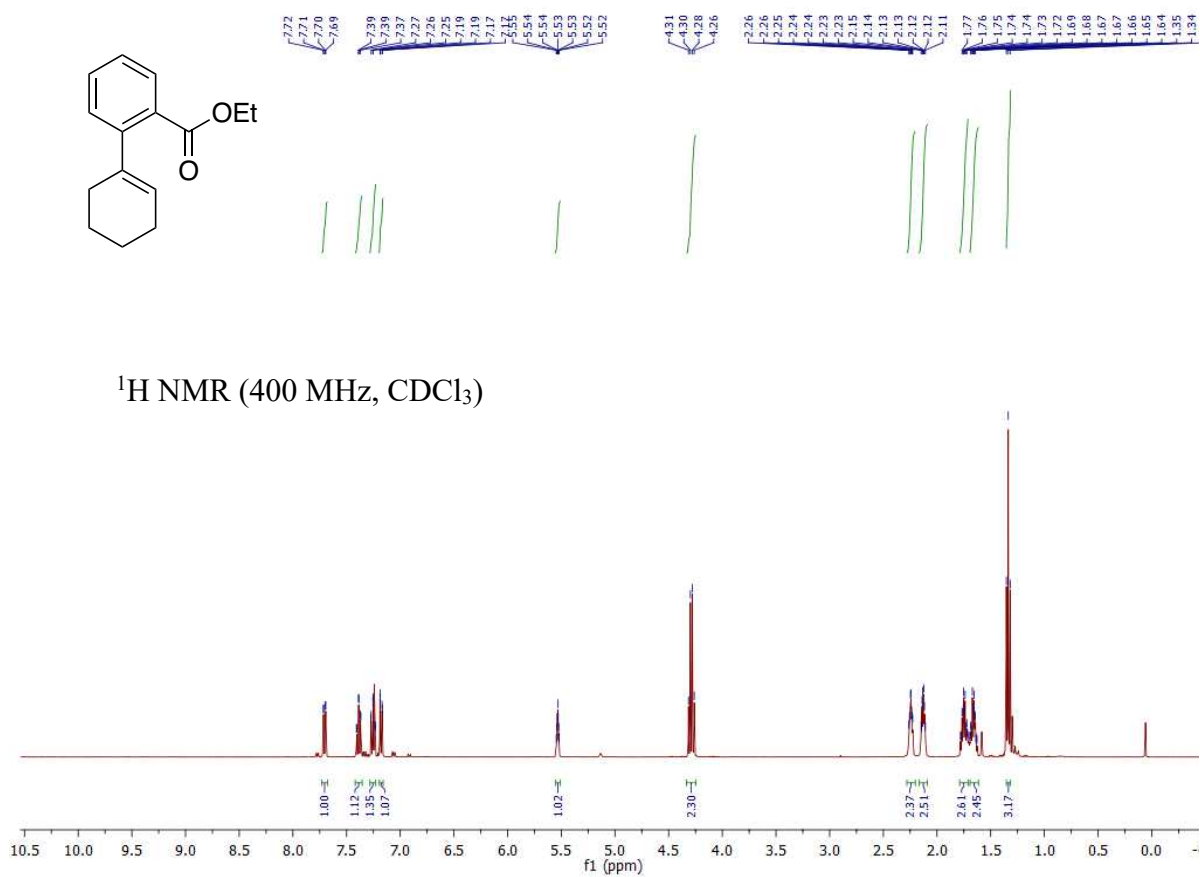
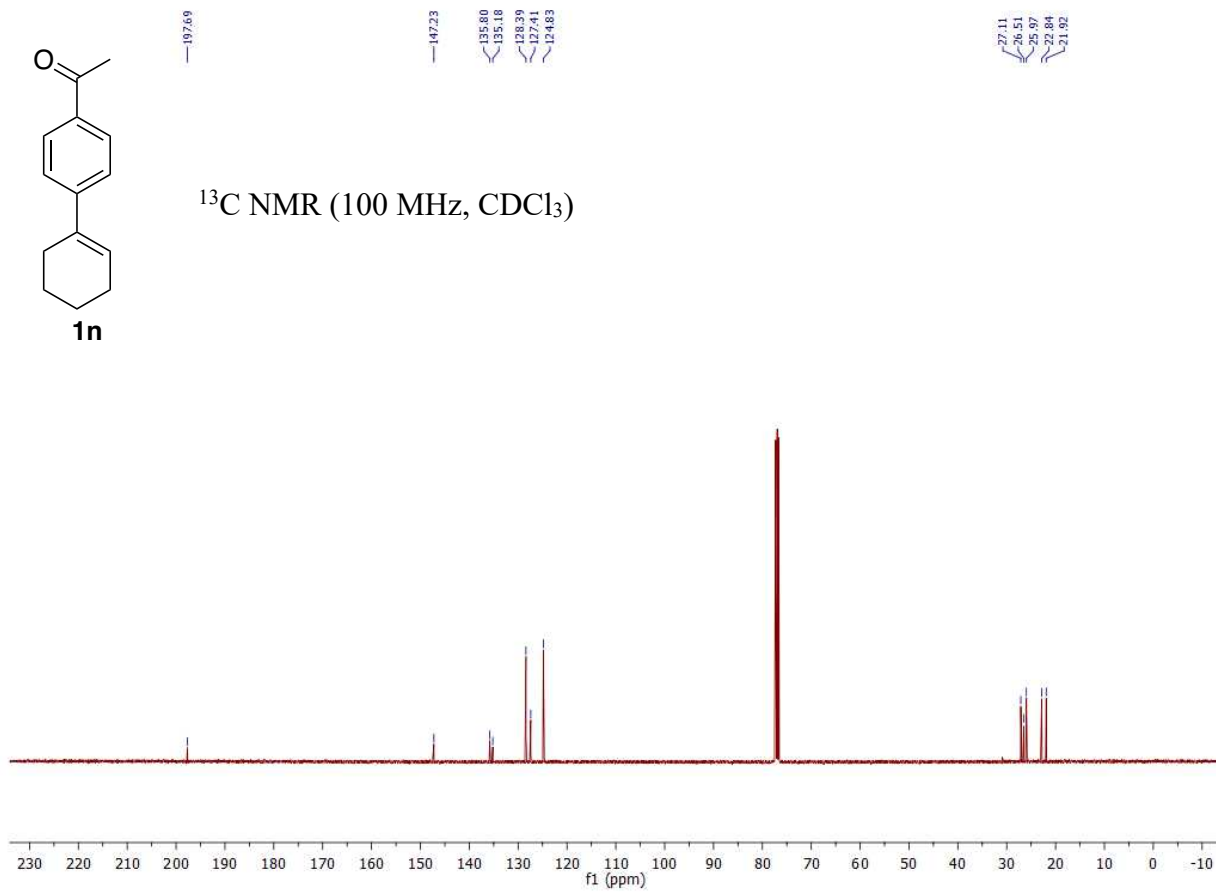


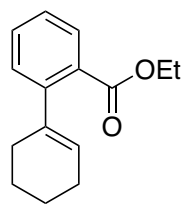
Experimental details: ($\lambda_{\text{exc}} = 420 \text{ nm}$), **4c** $5 \times 10^{-5} \text{ M}$ in CH₂Cl₂ at room temperature. Fluorescence quantum yields and excited state lifetimes were 84% ($\tau = 17.0 \text{ ns}$) and 90% ($\tau = 17.6 \text{ ns}$) in aerated and de-aerated conditions respectively.



^1H NMR (400 MHz, CDCl_3)





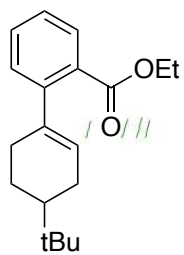
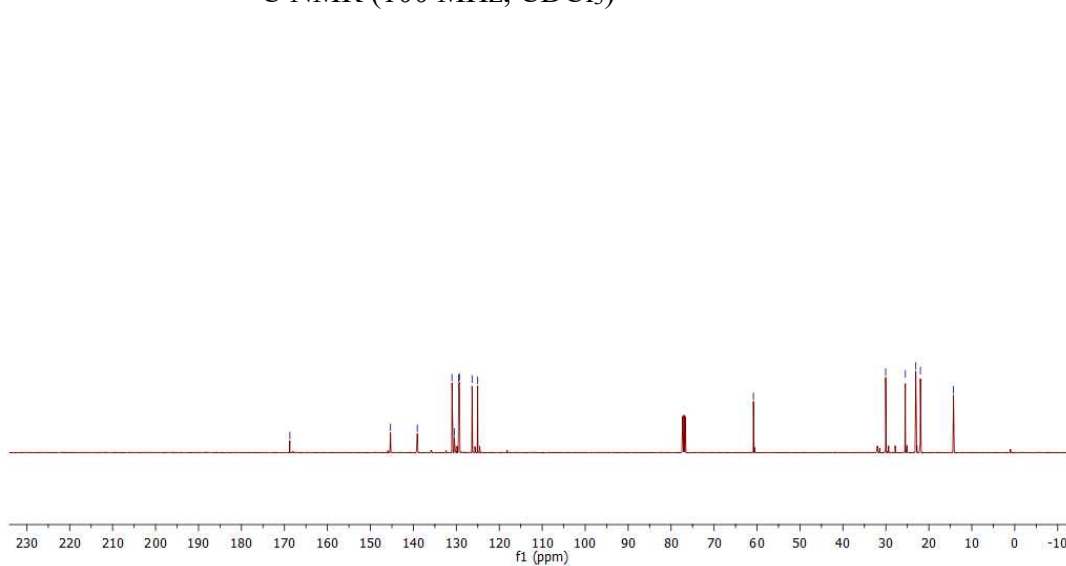


168.74
145.32
139.08
136.45
131.01
129.44
126.33
125.01

60.84

30.05
25.47
23.04
21.97
14.27

¹³C NMR (100 MHz, CDCl₃)

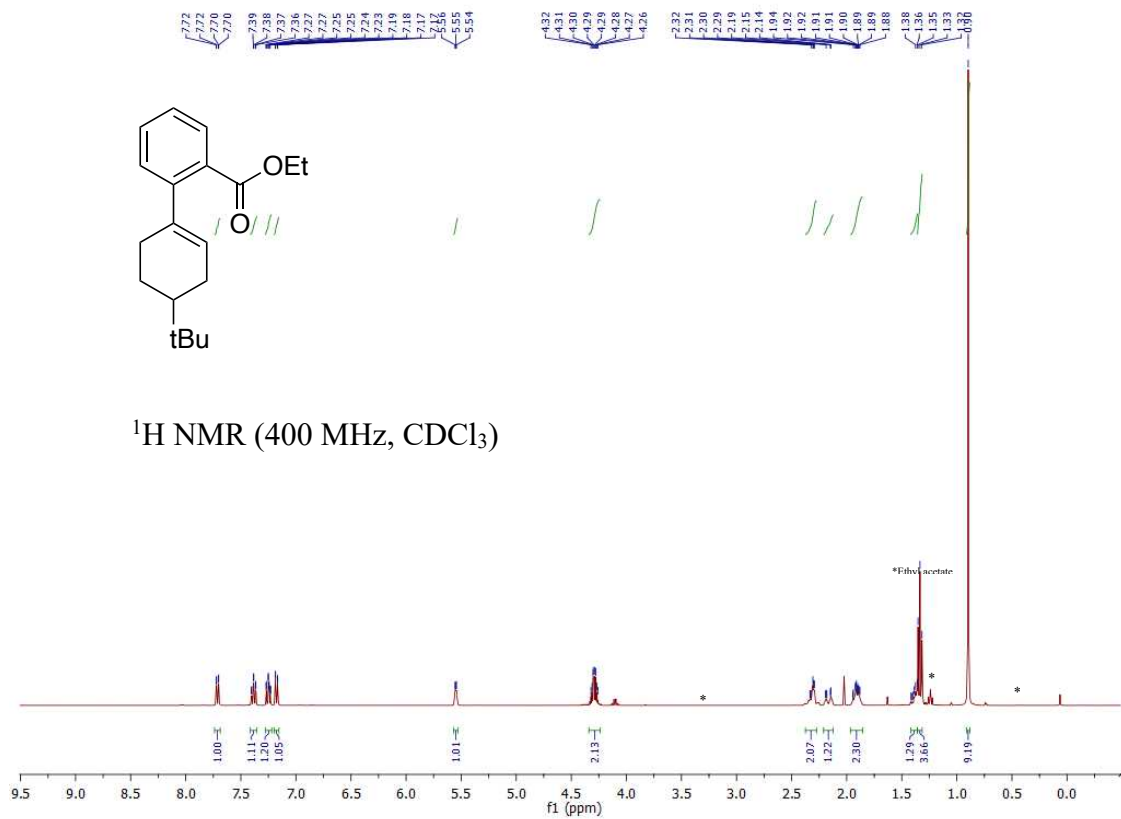


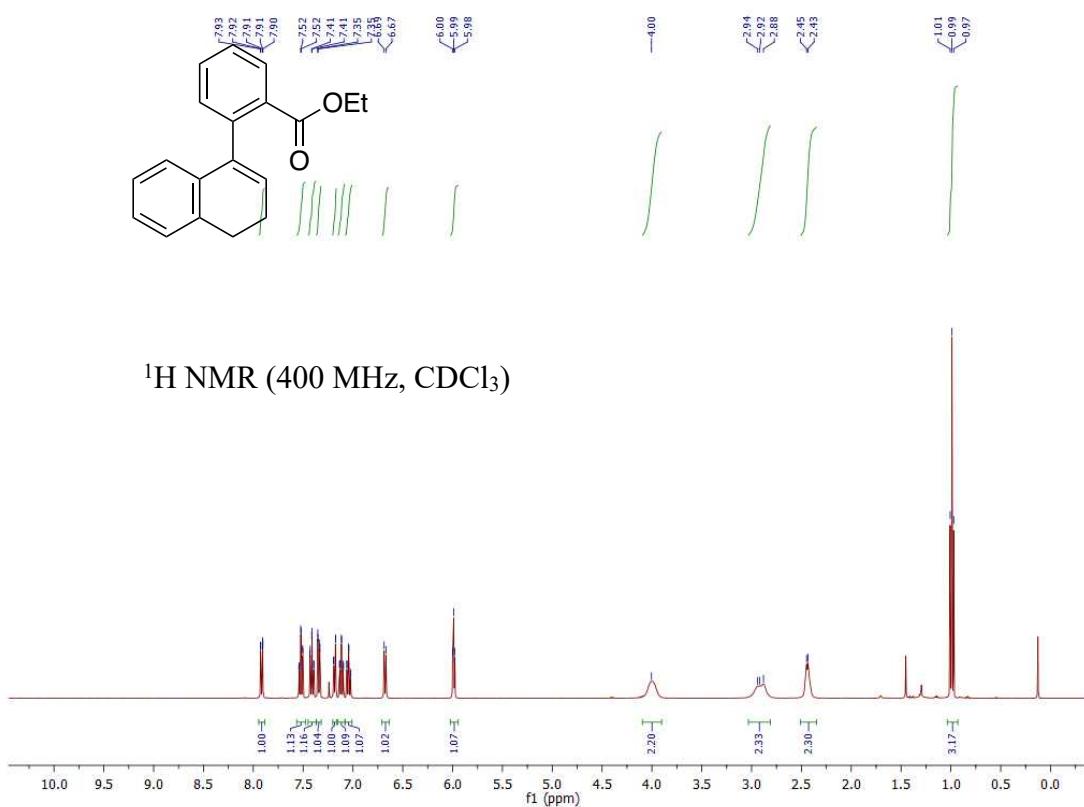
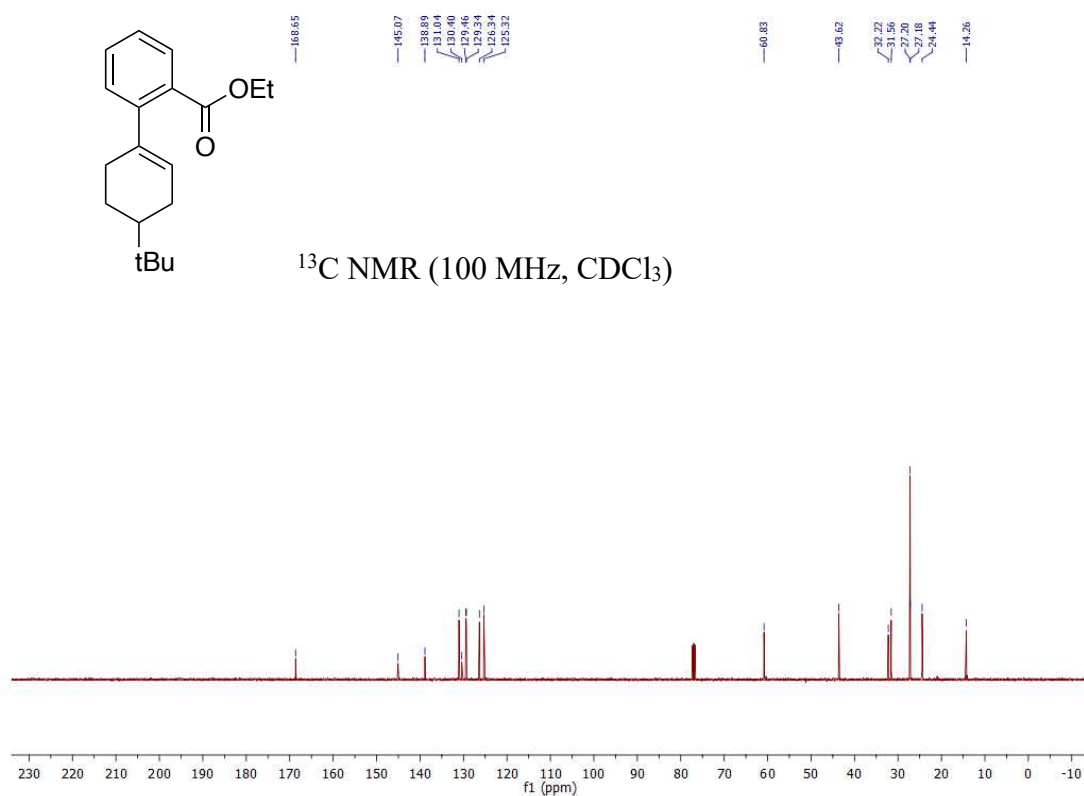
7.772
7.772
7.700
7.39
7.38
7.37
7.36
7.27
7.25
7.25
7.24
7.23
7.19
7.18
7.17
5.55
5.54

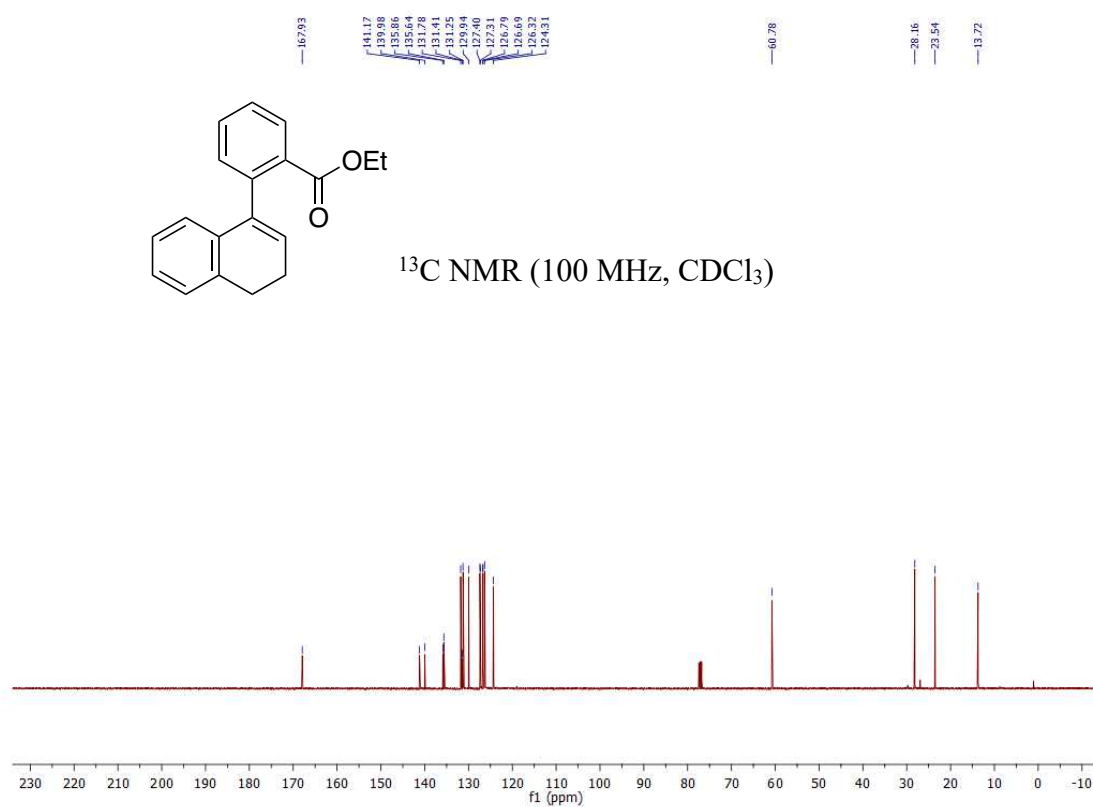
4.32
4.31
4.30
4.29
4.29
4.28
4.27
4.26

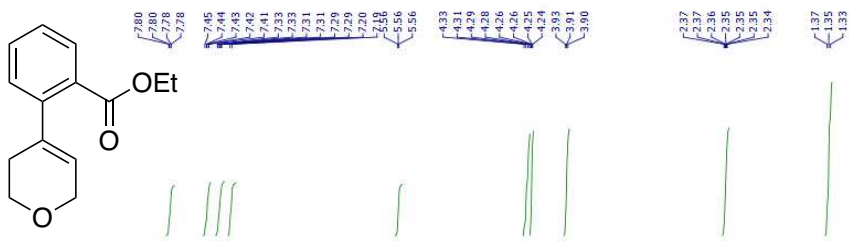
2.32
2.31
2.30
2.29
2.19
2.15
2.14
1.94
1.92
1.91
1.91
1.90
1.89
1.88
1.38
1.36
1.35
1.33
0.97

¹H NMR (400 MHz, CDCl₃)

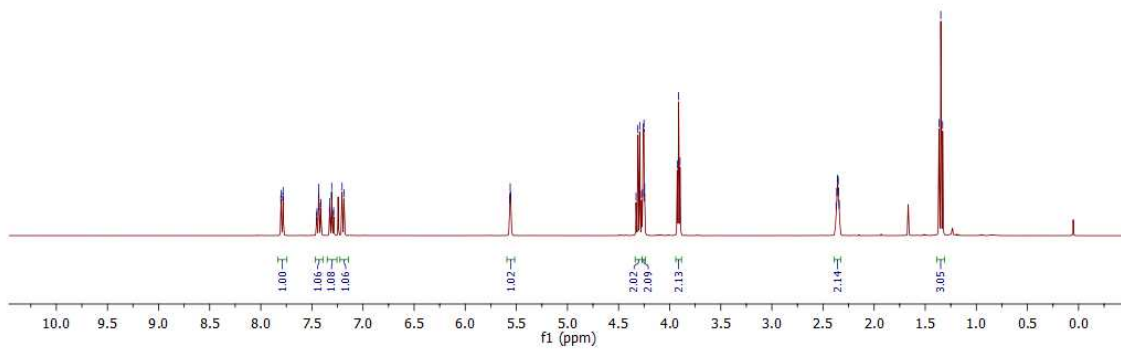


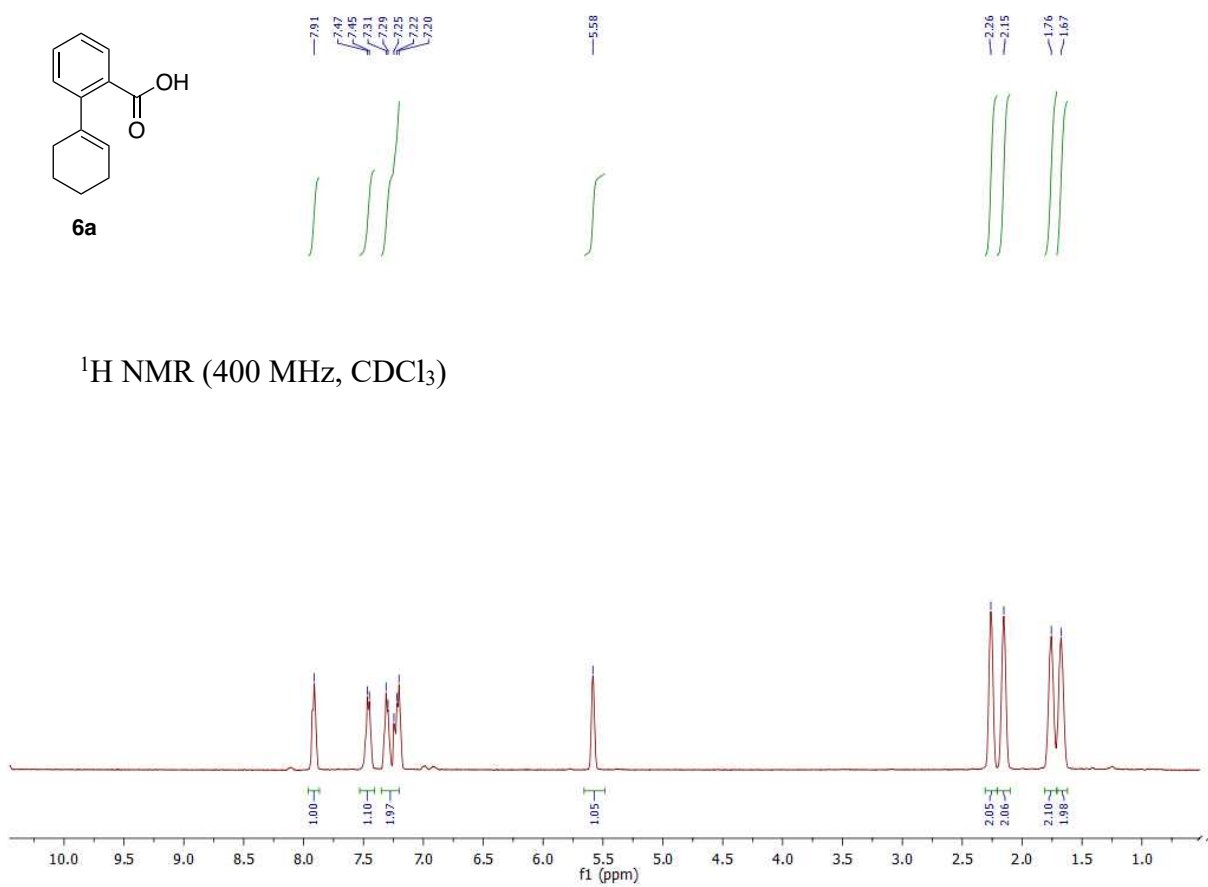
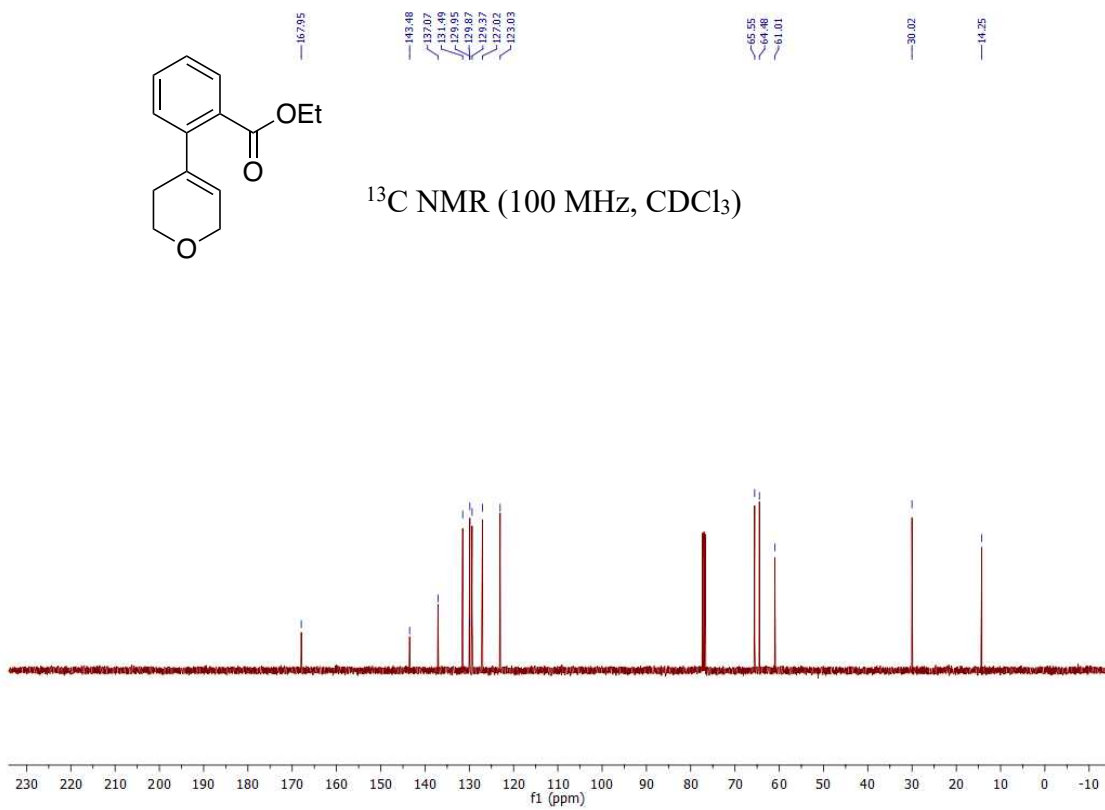


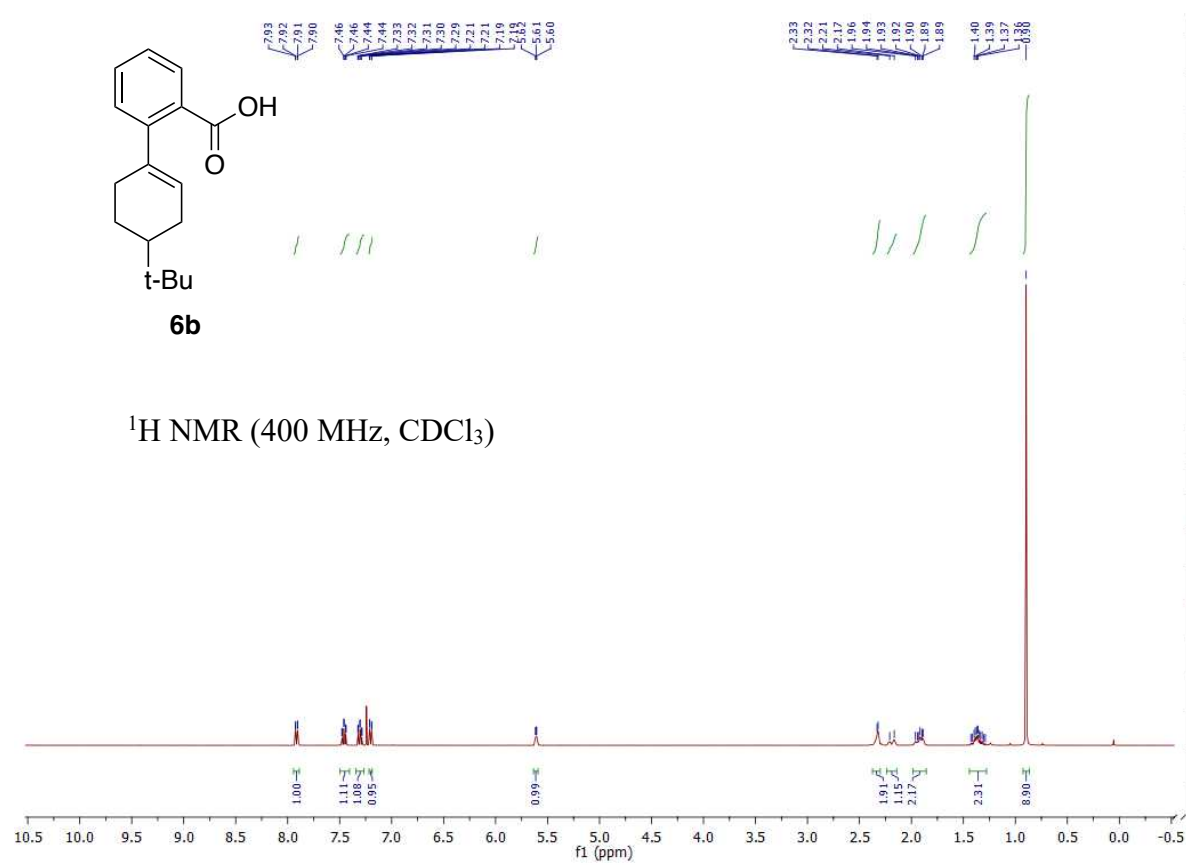
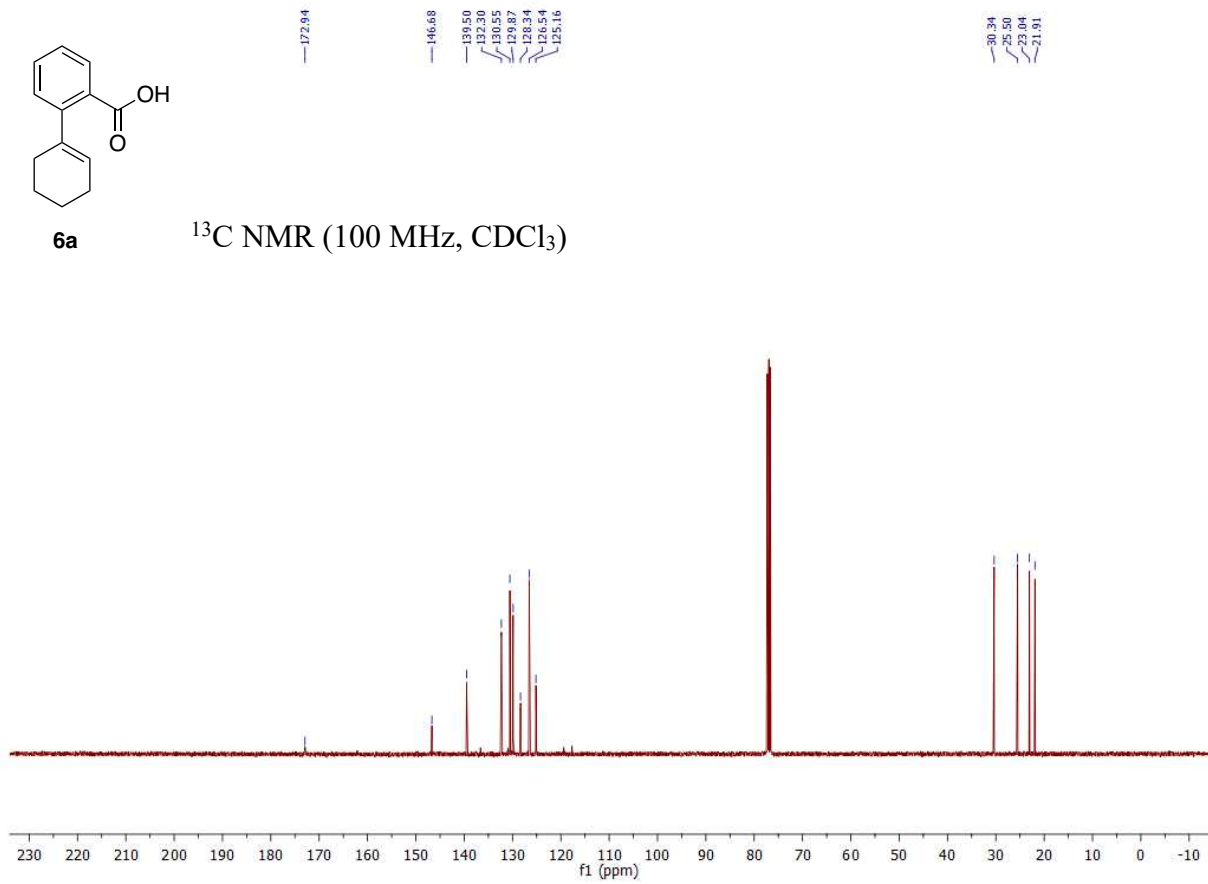


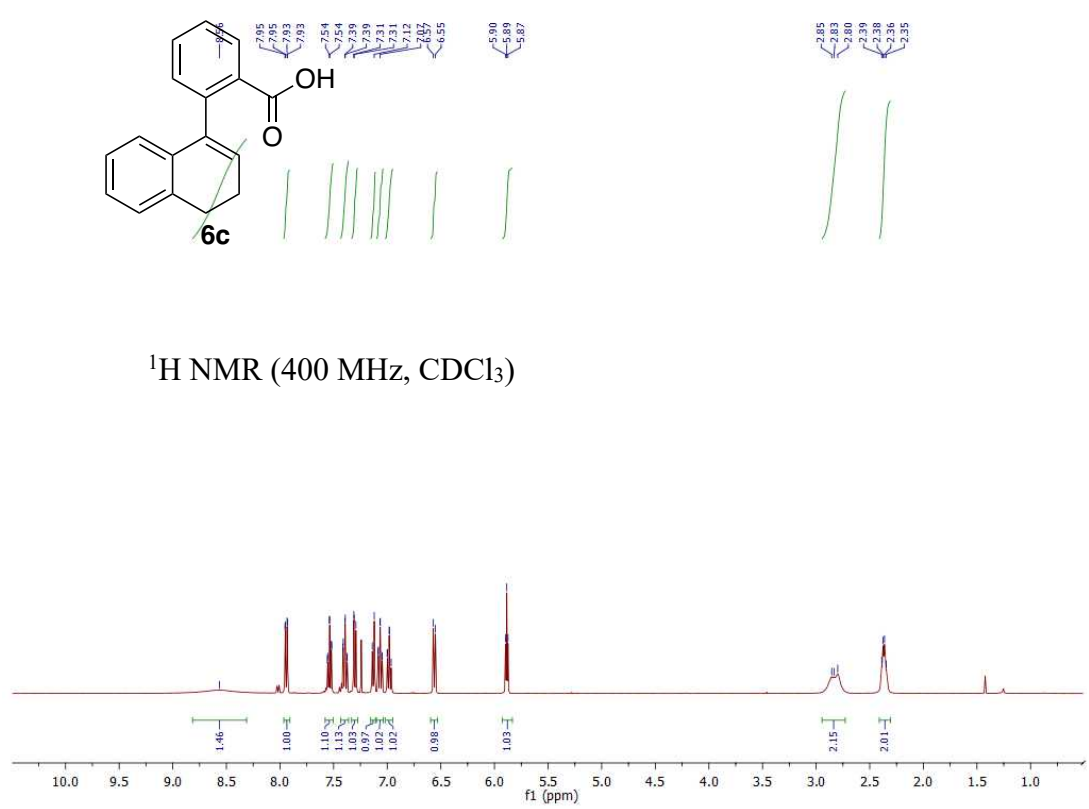
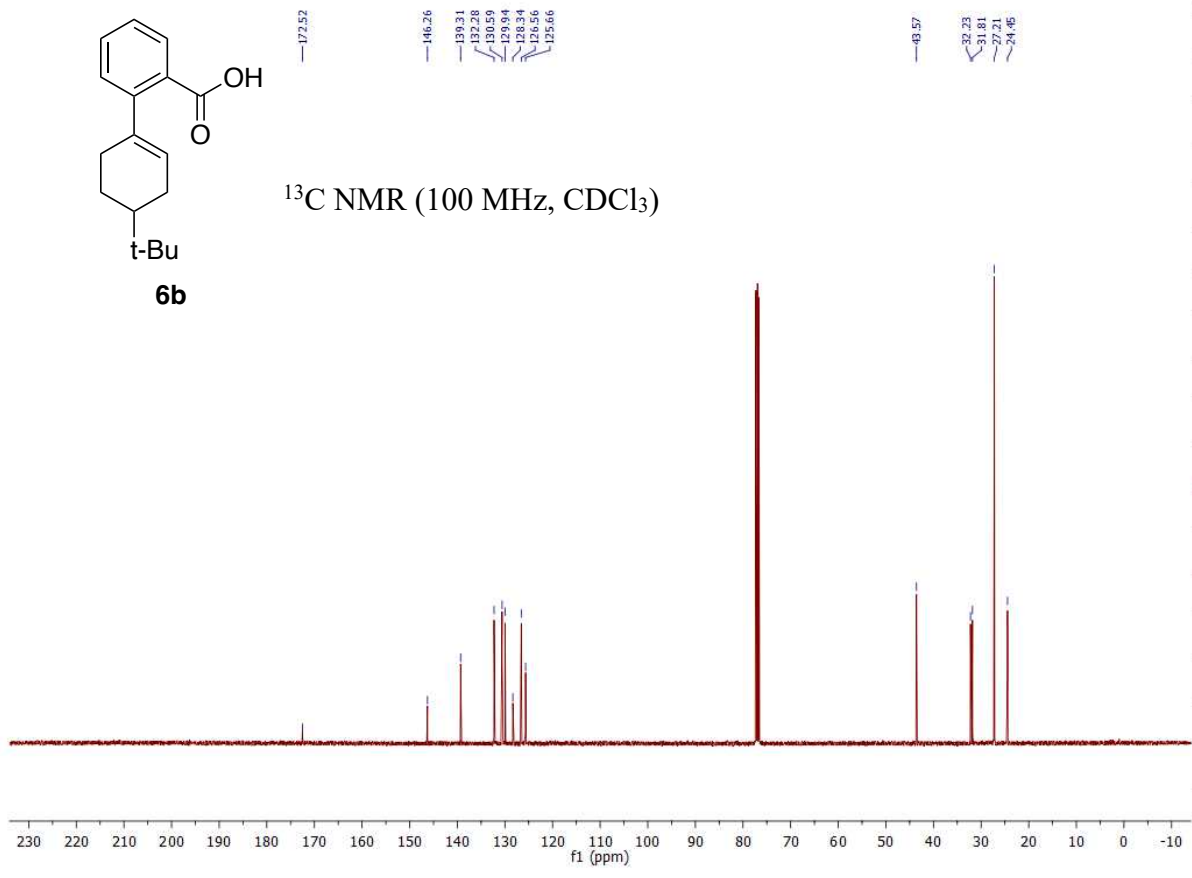


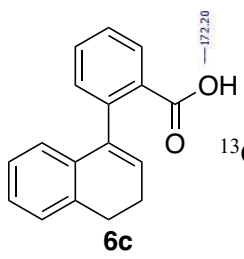
^1H NMR (400 MHz, CDCl_3)







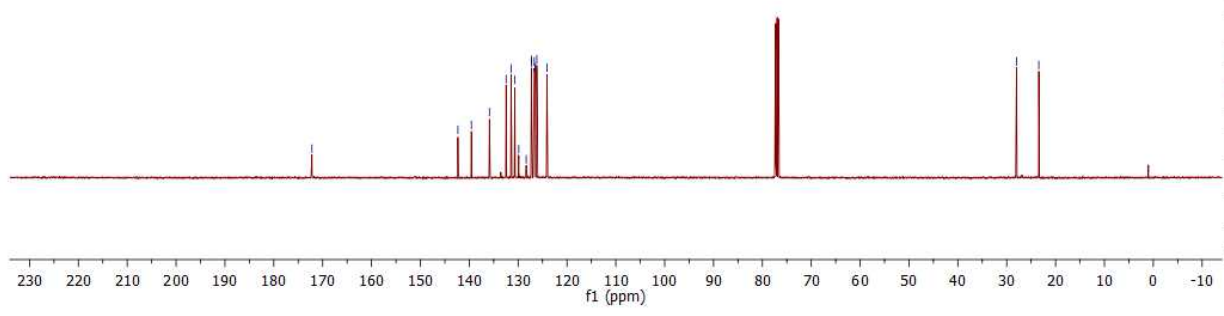


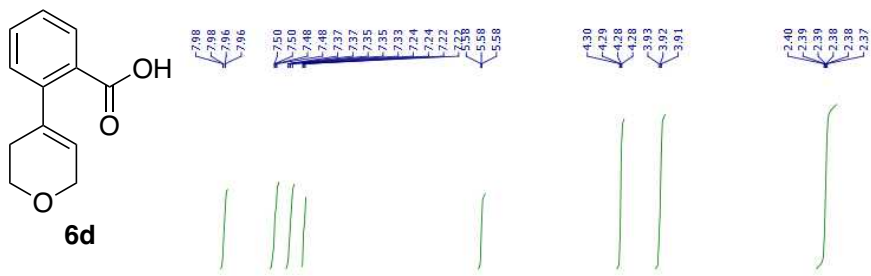


¹³C NMR (100 MHz, CDCl₃)

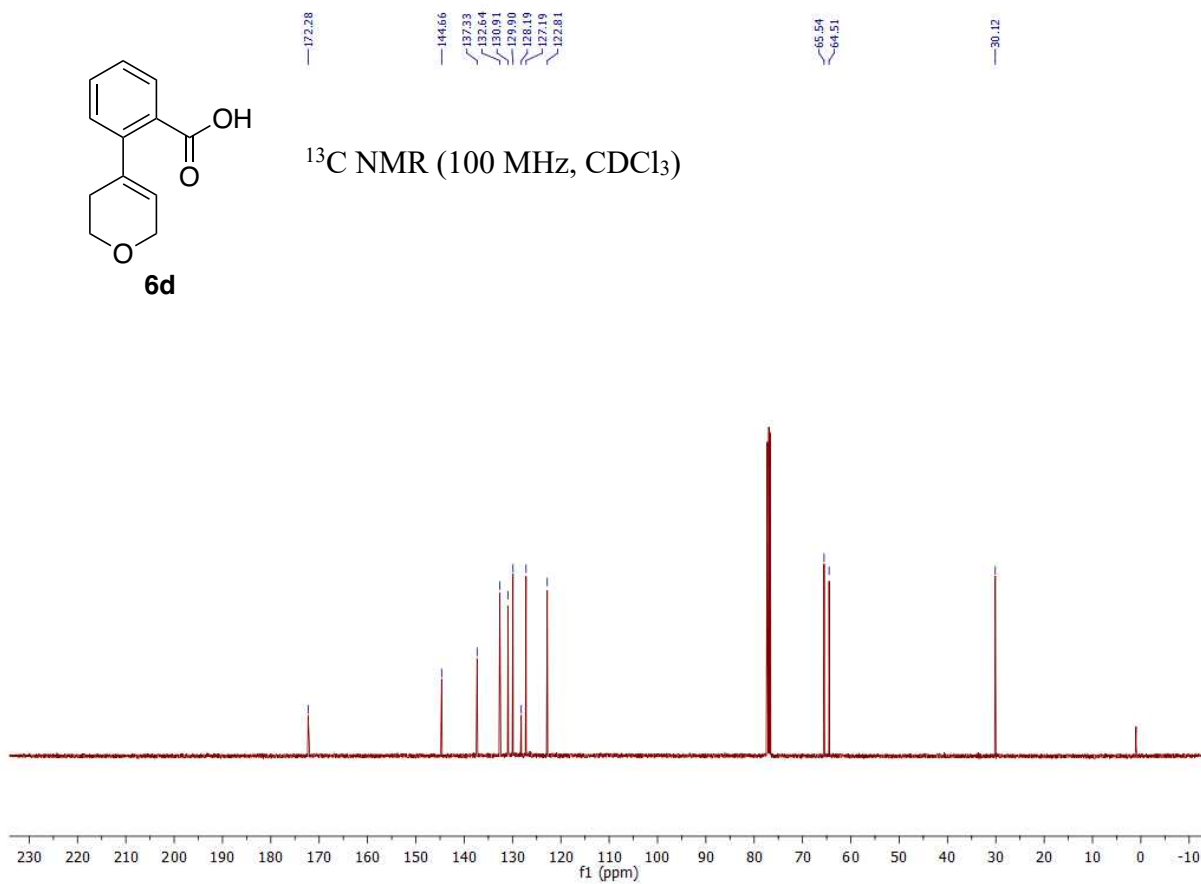
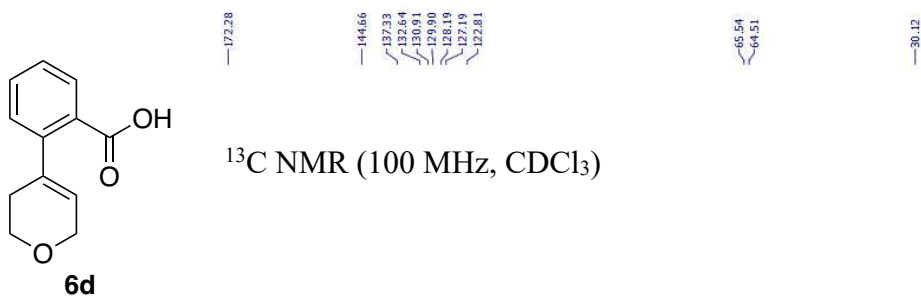
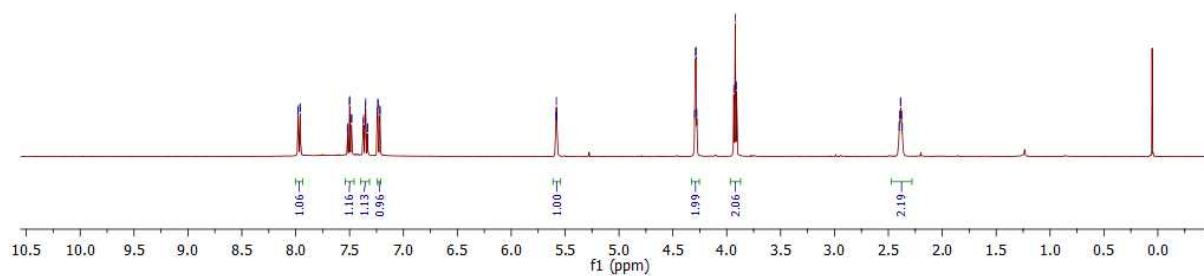
- 142.32
- 139.56
- 135.87
- 132.46
- 131.42
- 130.68
- 129.87
- 128.34
- 127.28
- 127.25
- 126.70
- 126.53
- 126.18
- 124.09

- 27.99
- 23.43



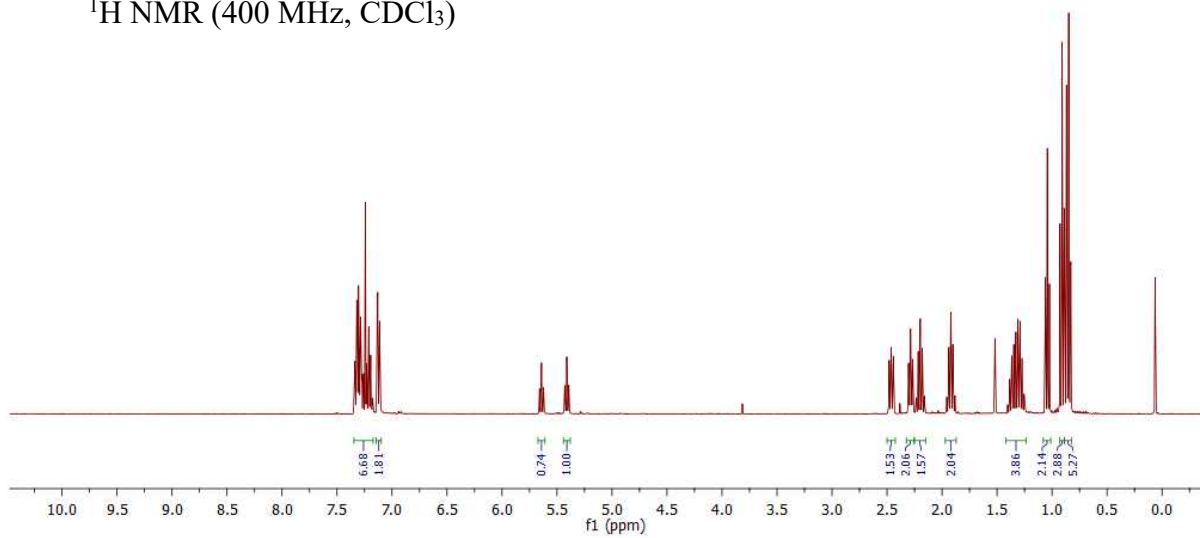


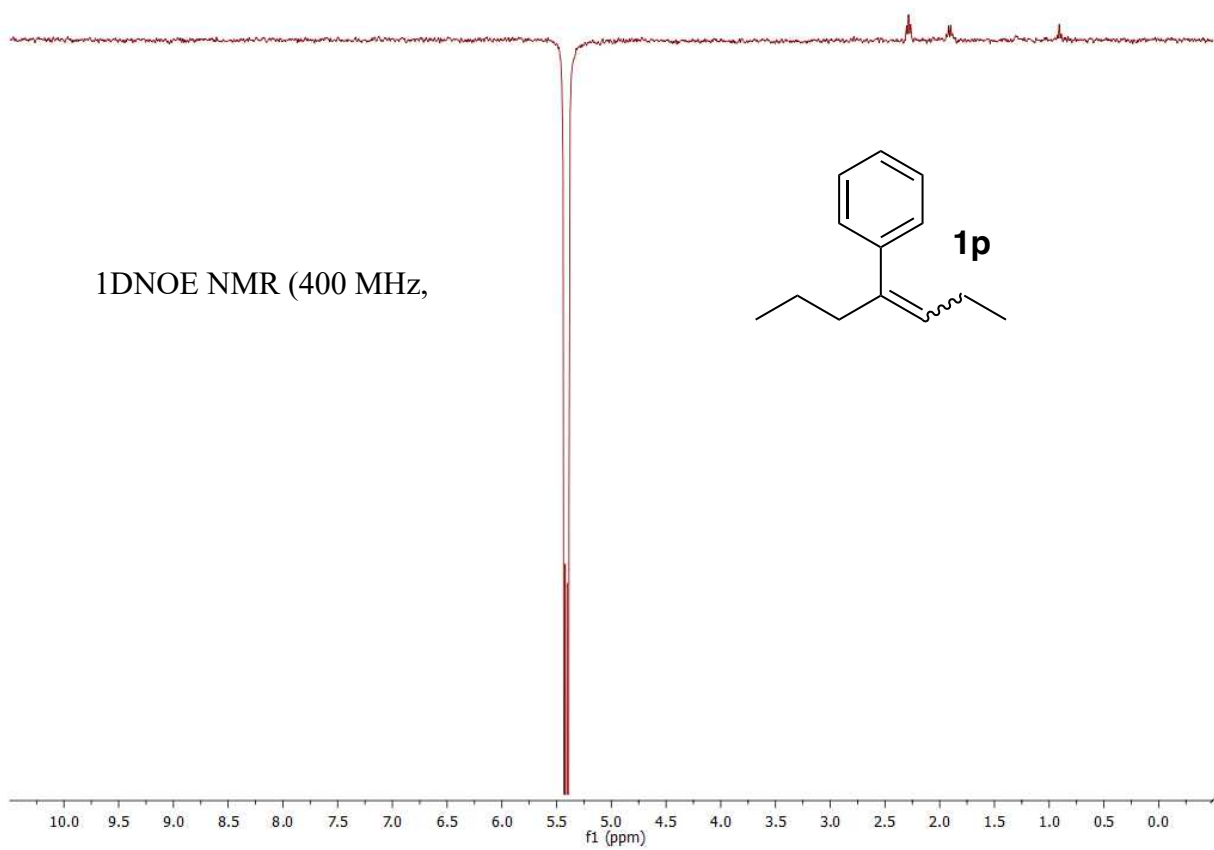
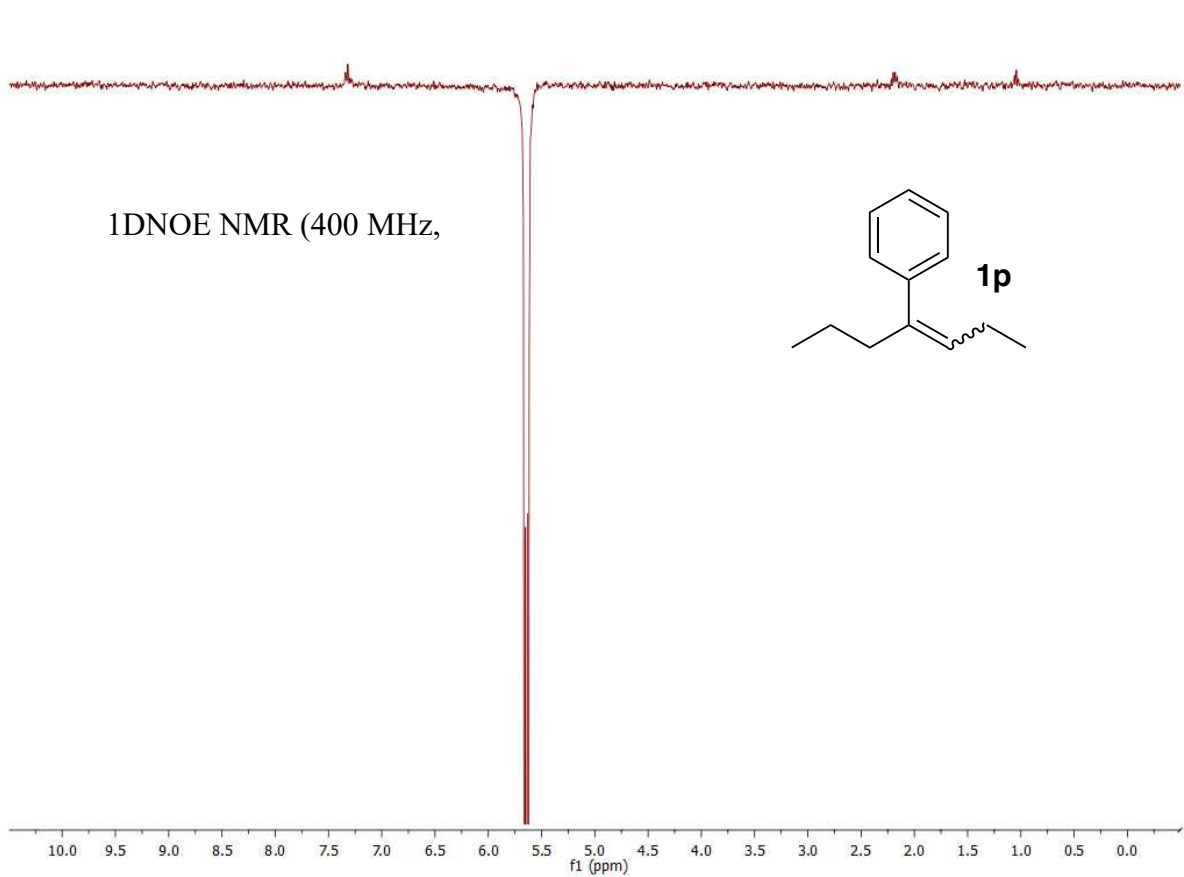
¹H NMR (400 MHz, CDCl₃)

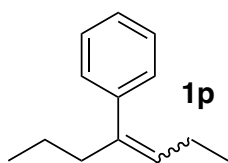




^1H NMR (400 MHz, CDCl_3)



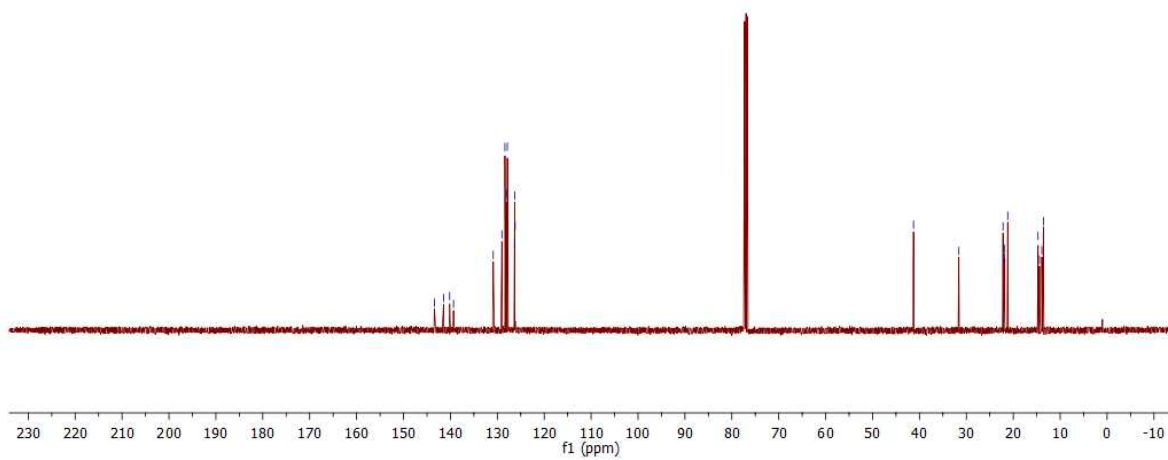


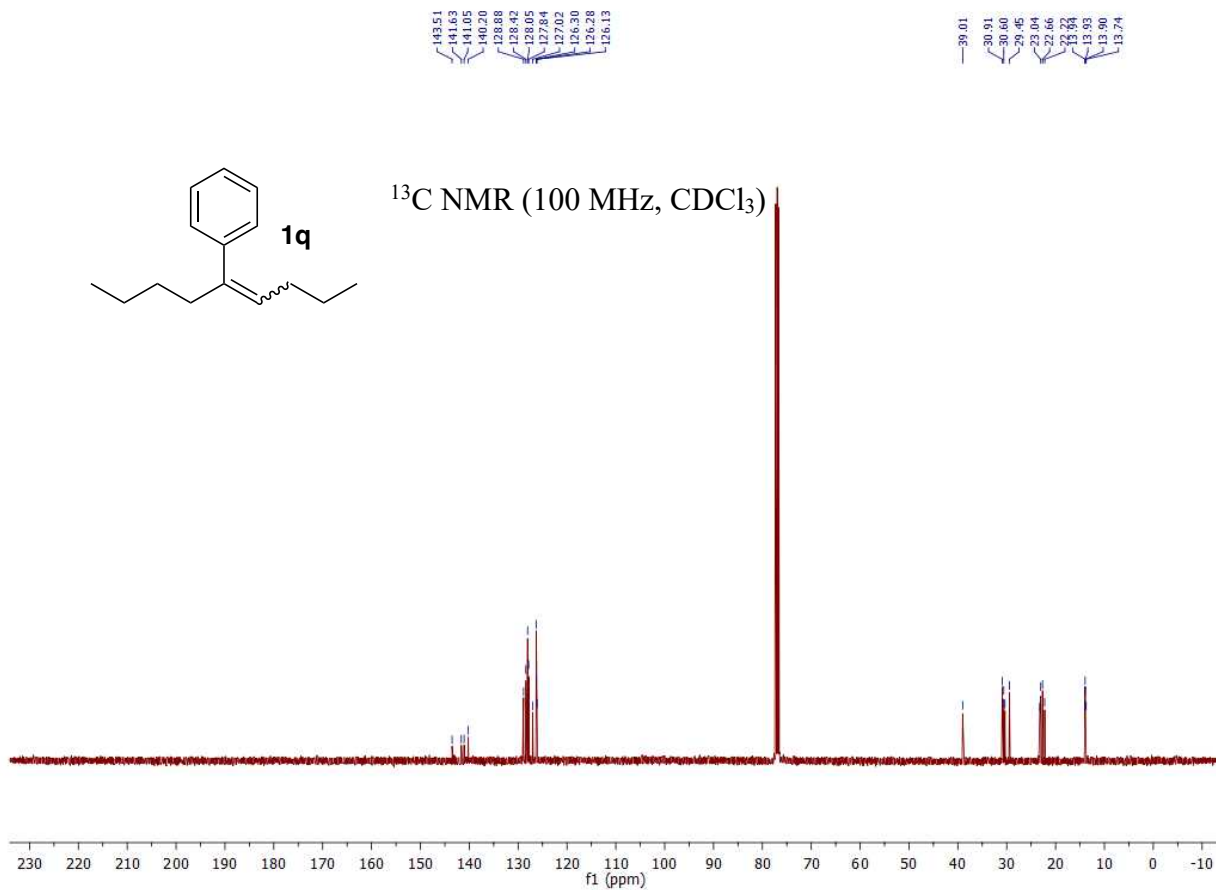
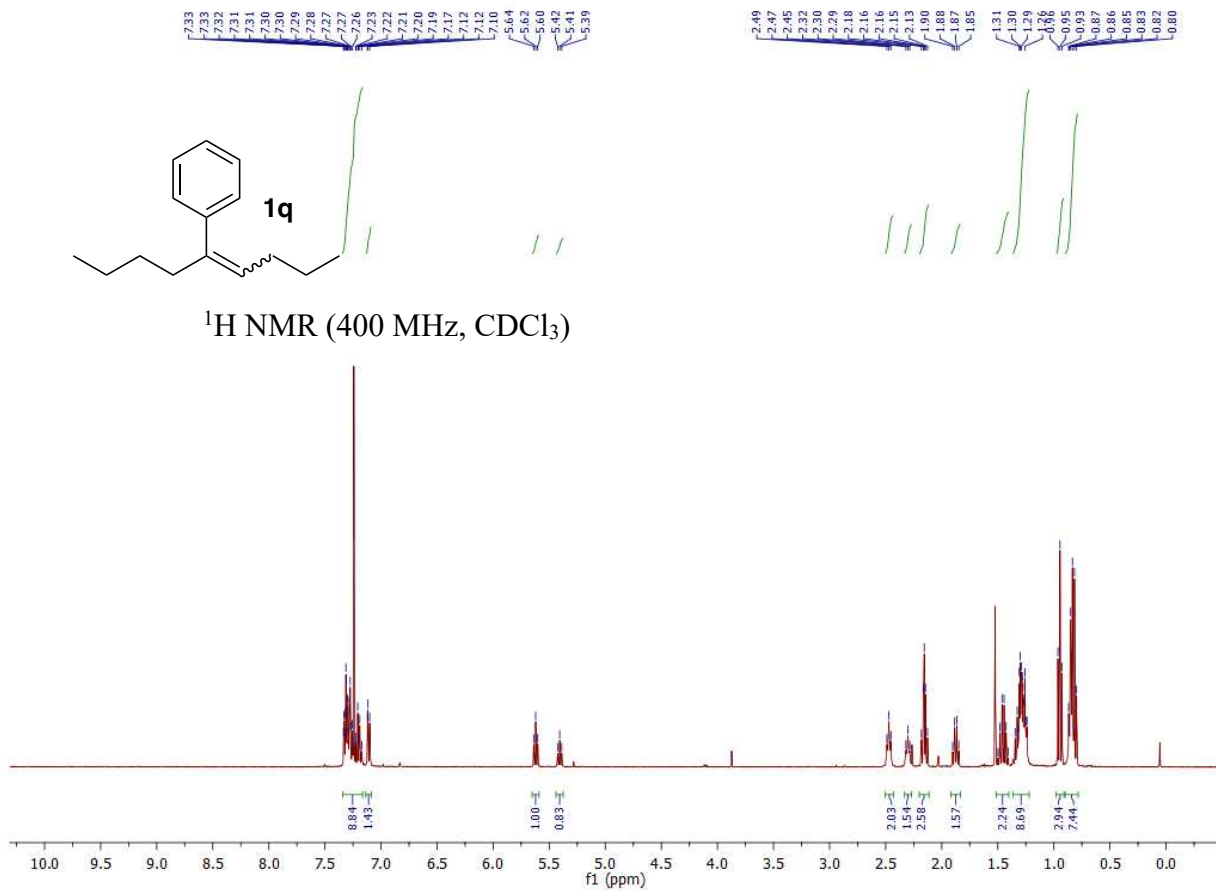


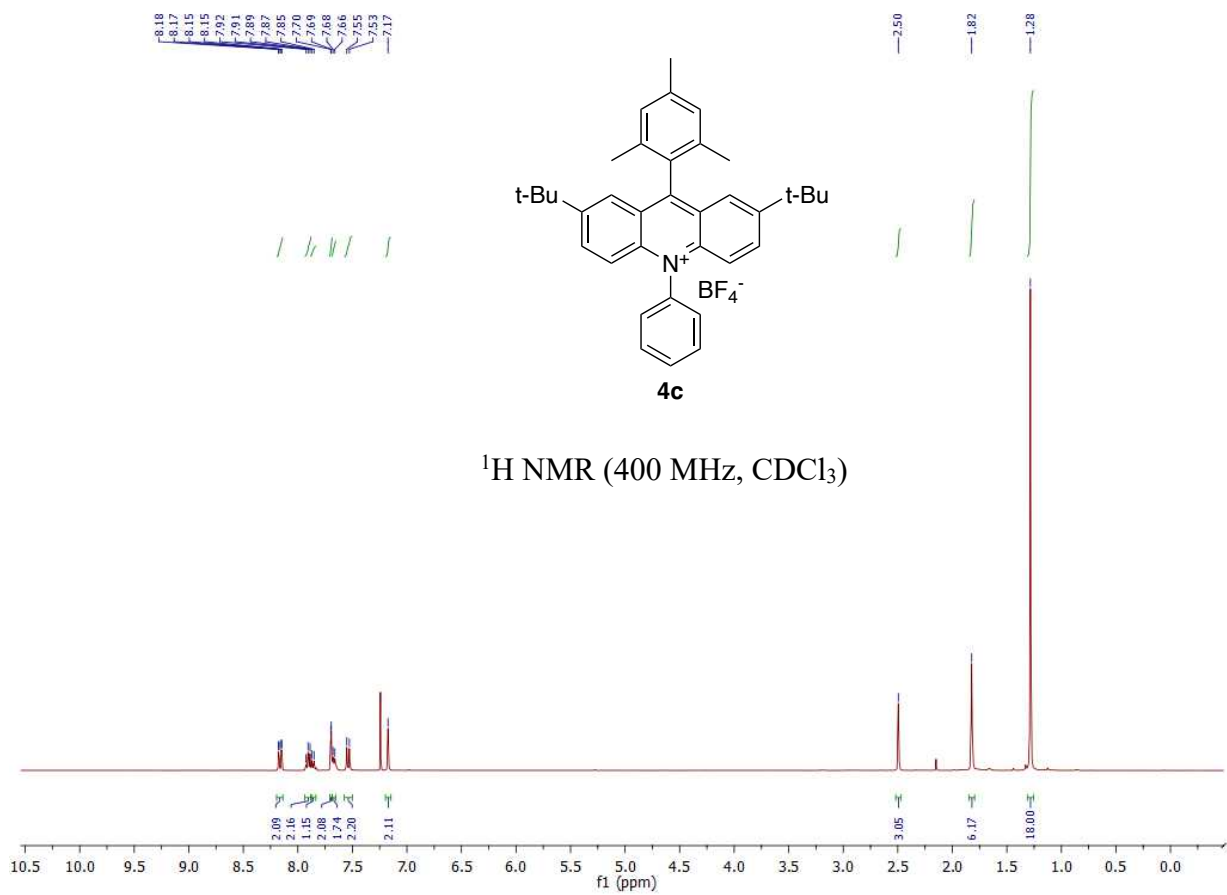
143.40
141.47
140.16
139.34
130.87
129.02
128.37
128.06
127.86
126.32
126.30
126.20

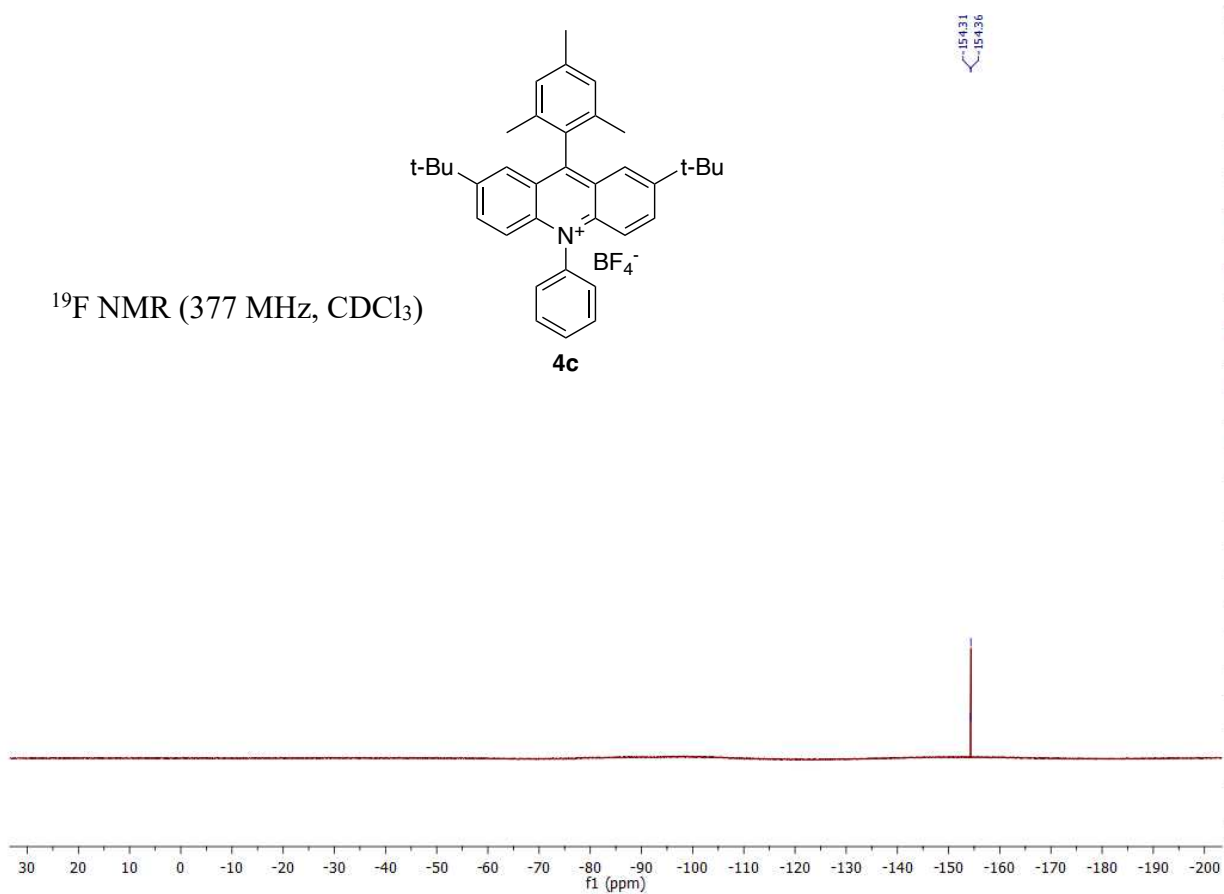
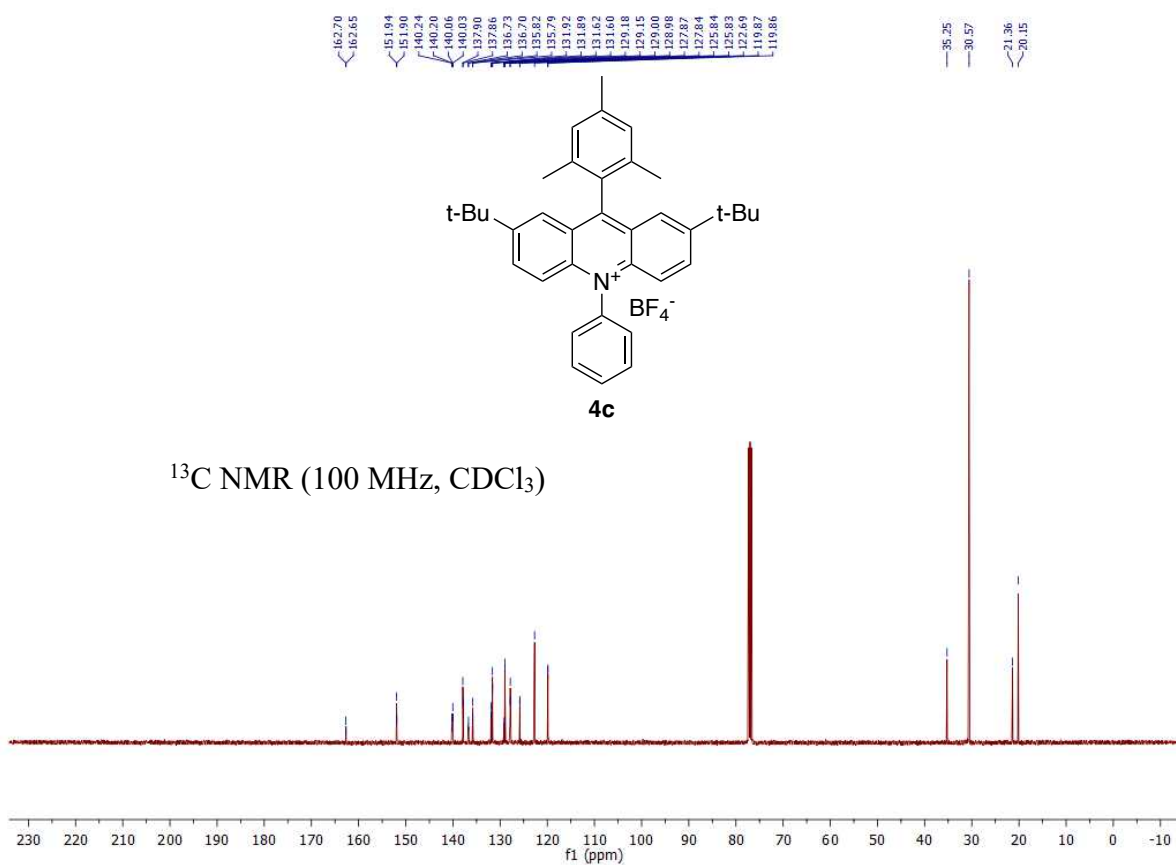
41.27
31.60
22.18
21.81
21.72
19.41
13.91
13.57

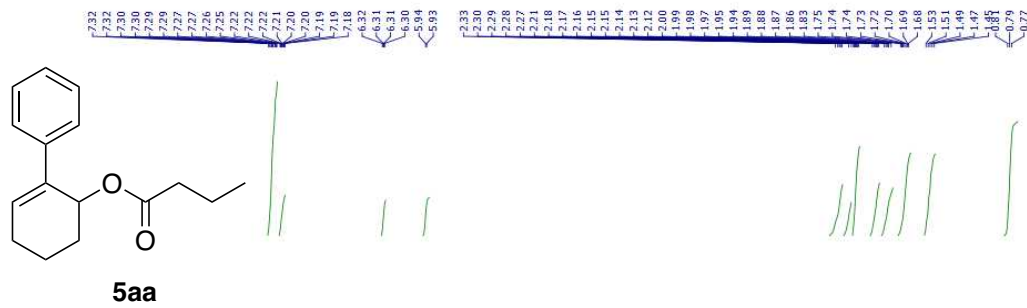
^{13}C NMR (100 MHz, CDCl_3)



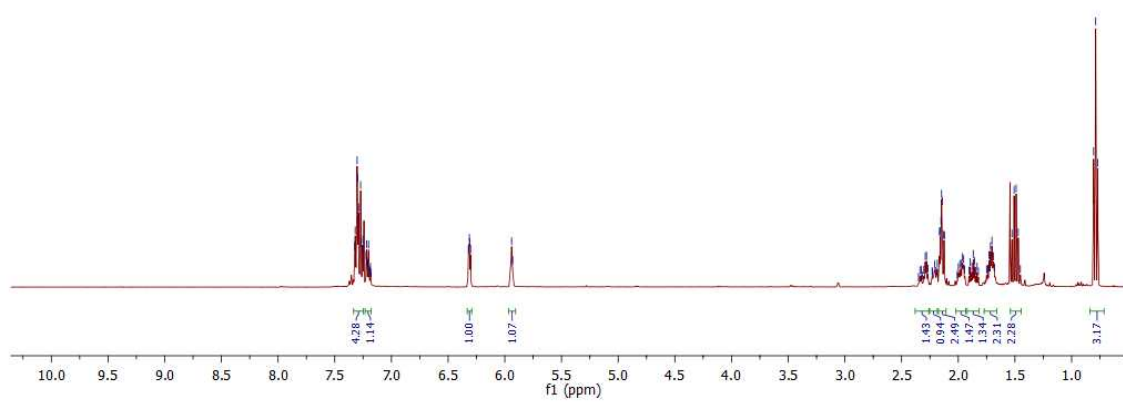


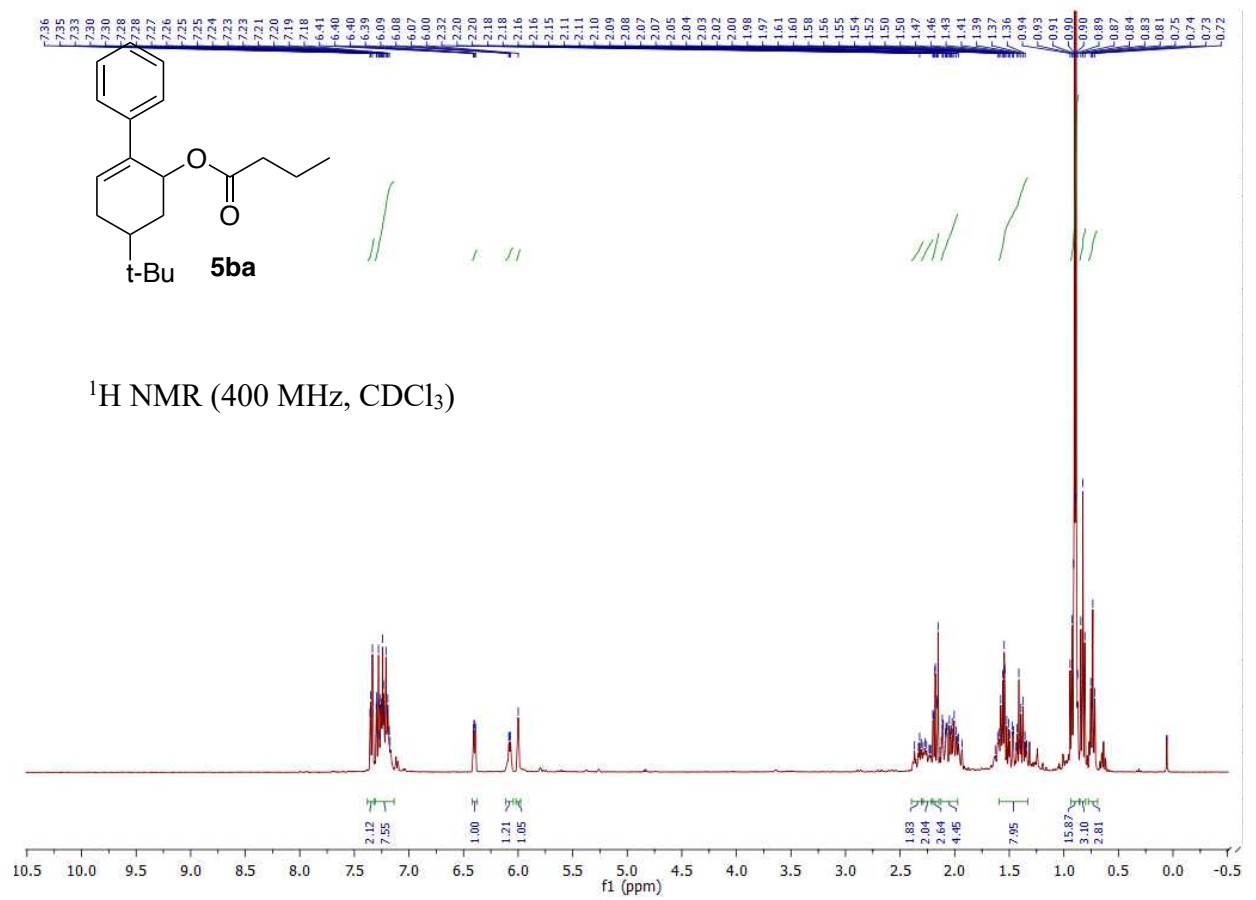
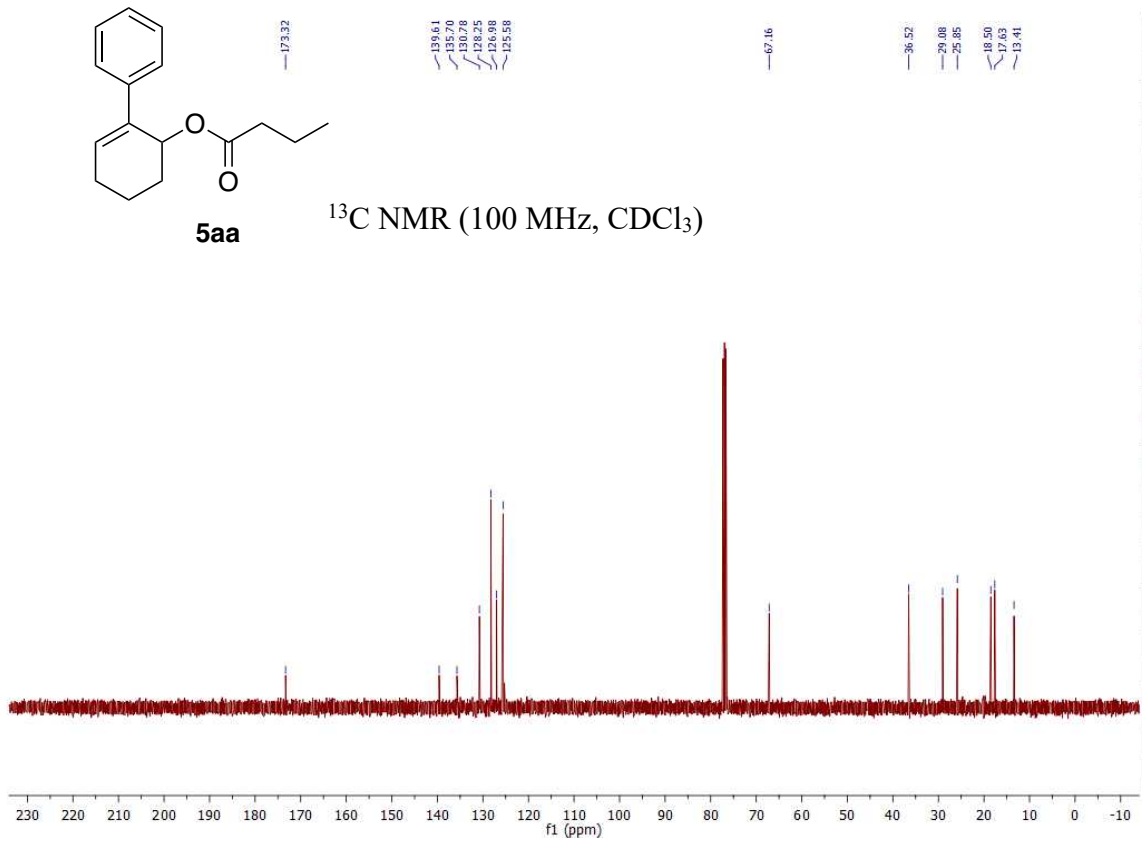


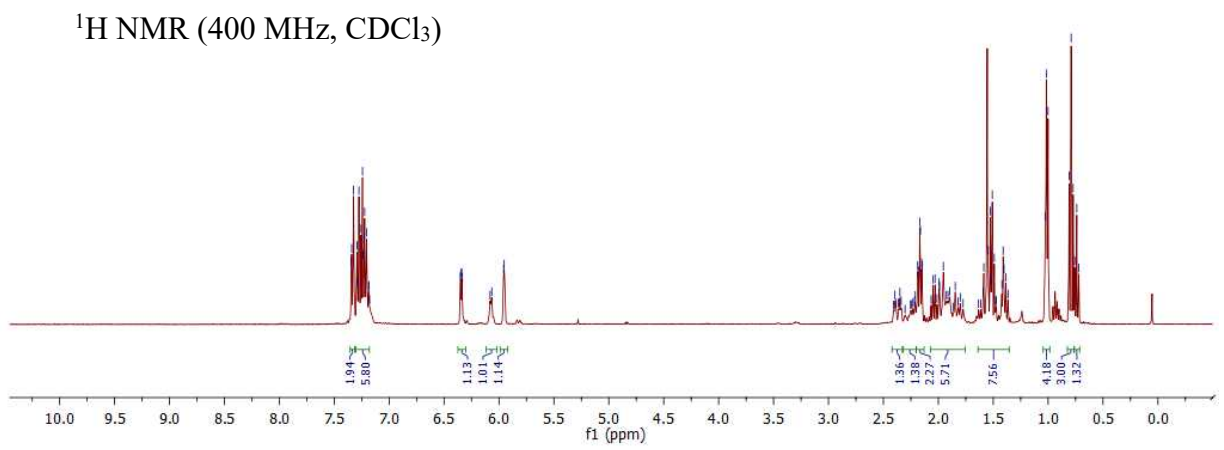
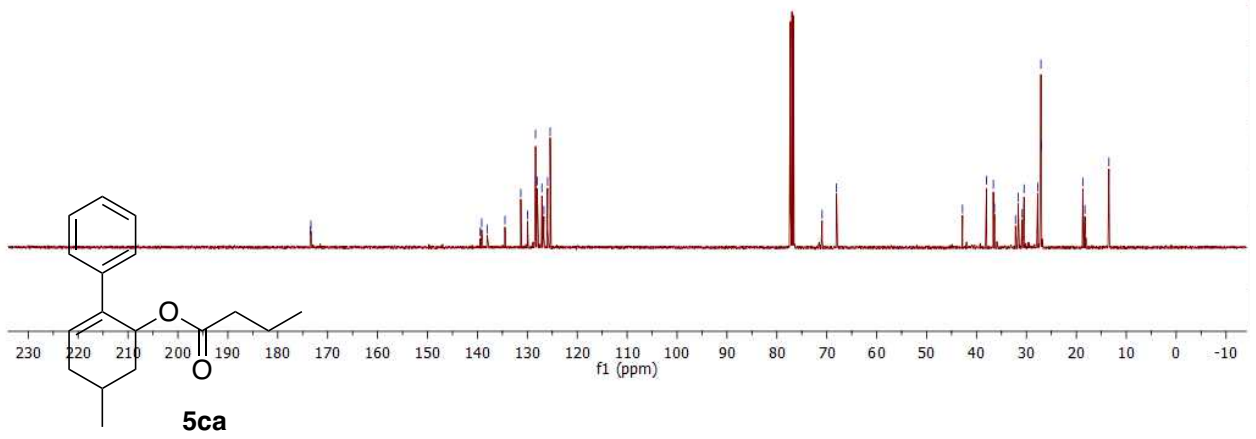
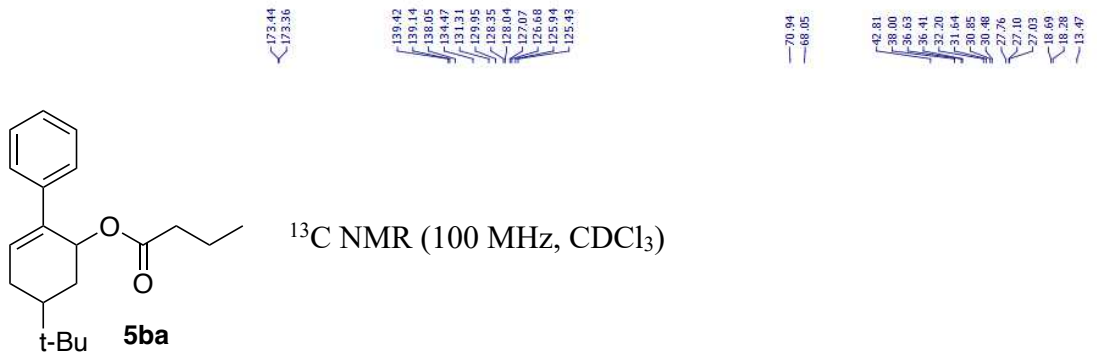


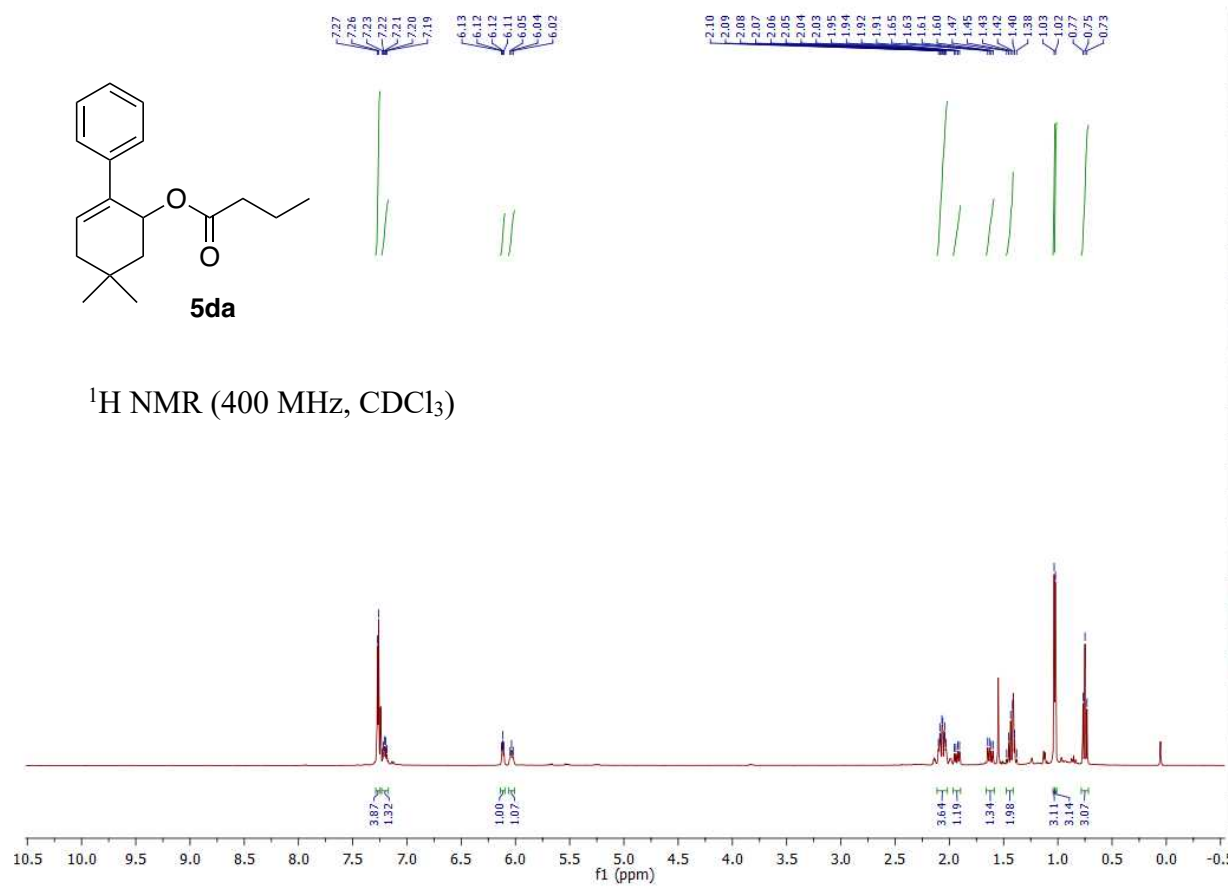
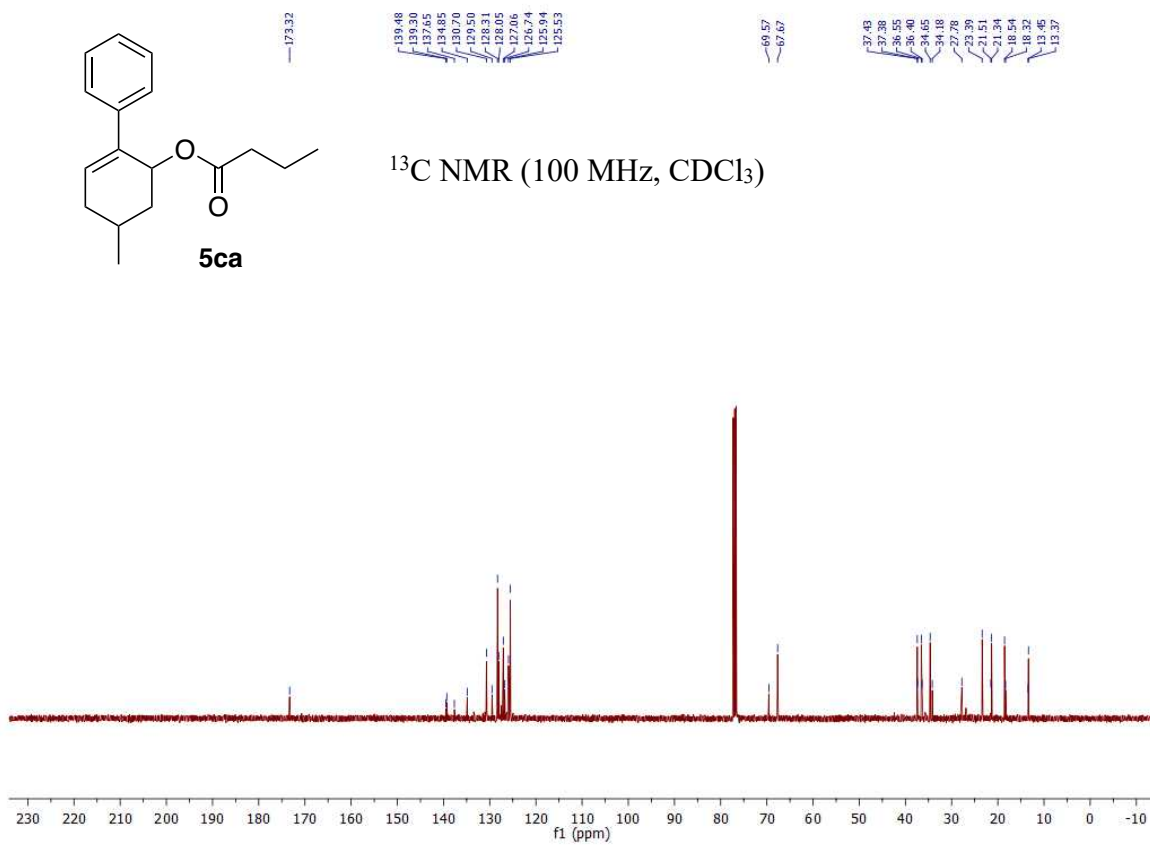


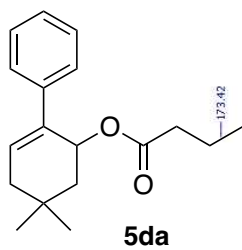
^1H NMR (400 MHz, CDCl_3)



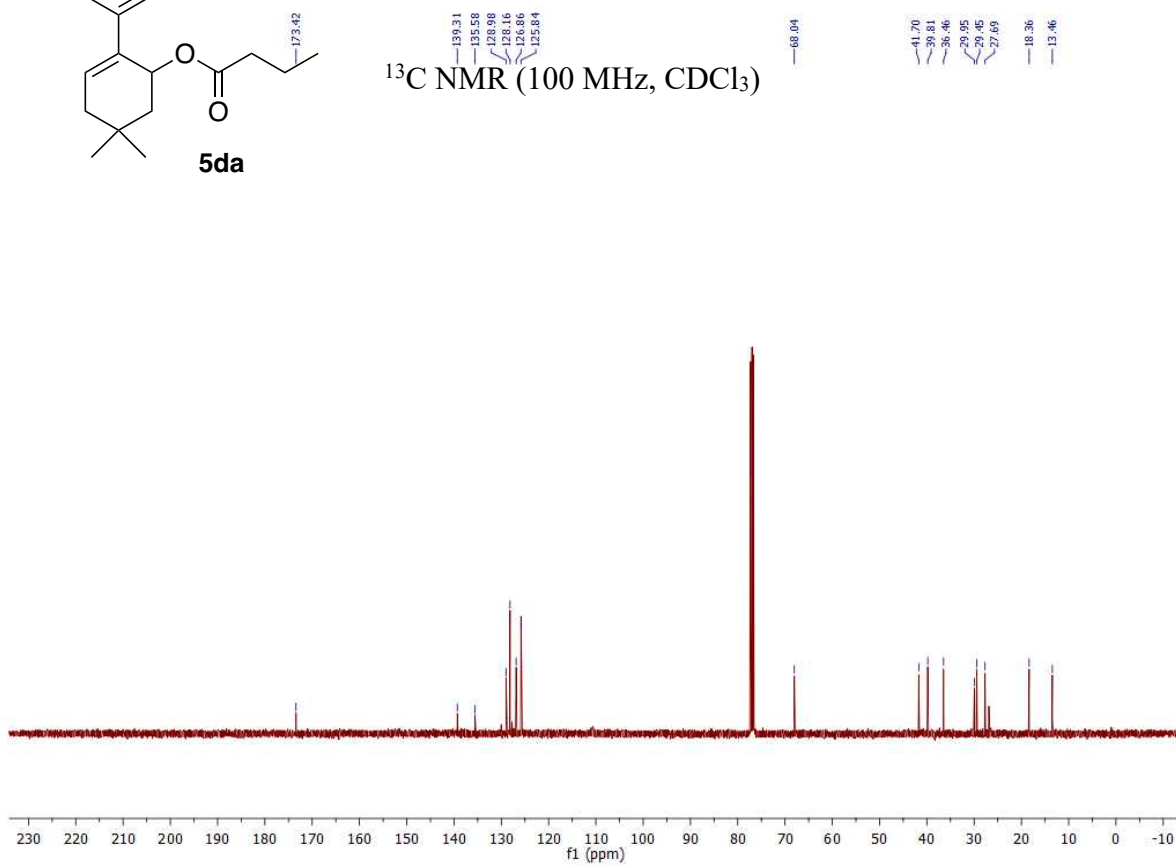


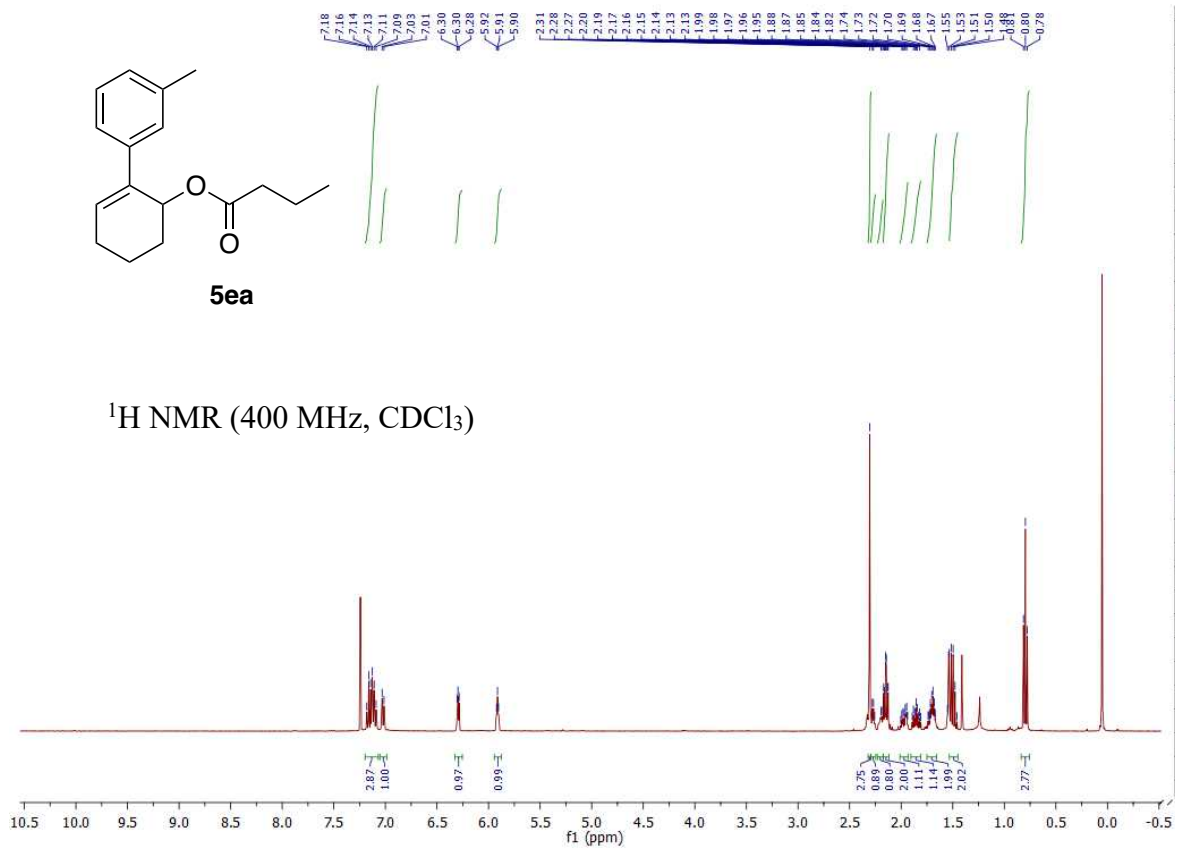


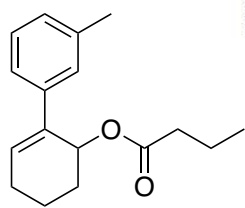




^{13}C NMR (100 MHz, CDCl_3)

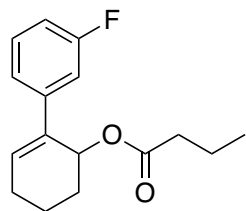
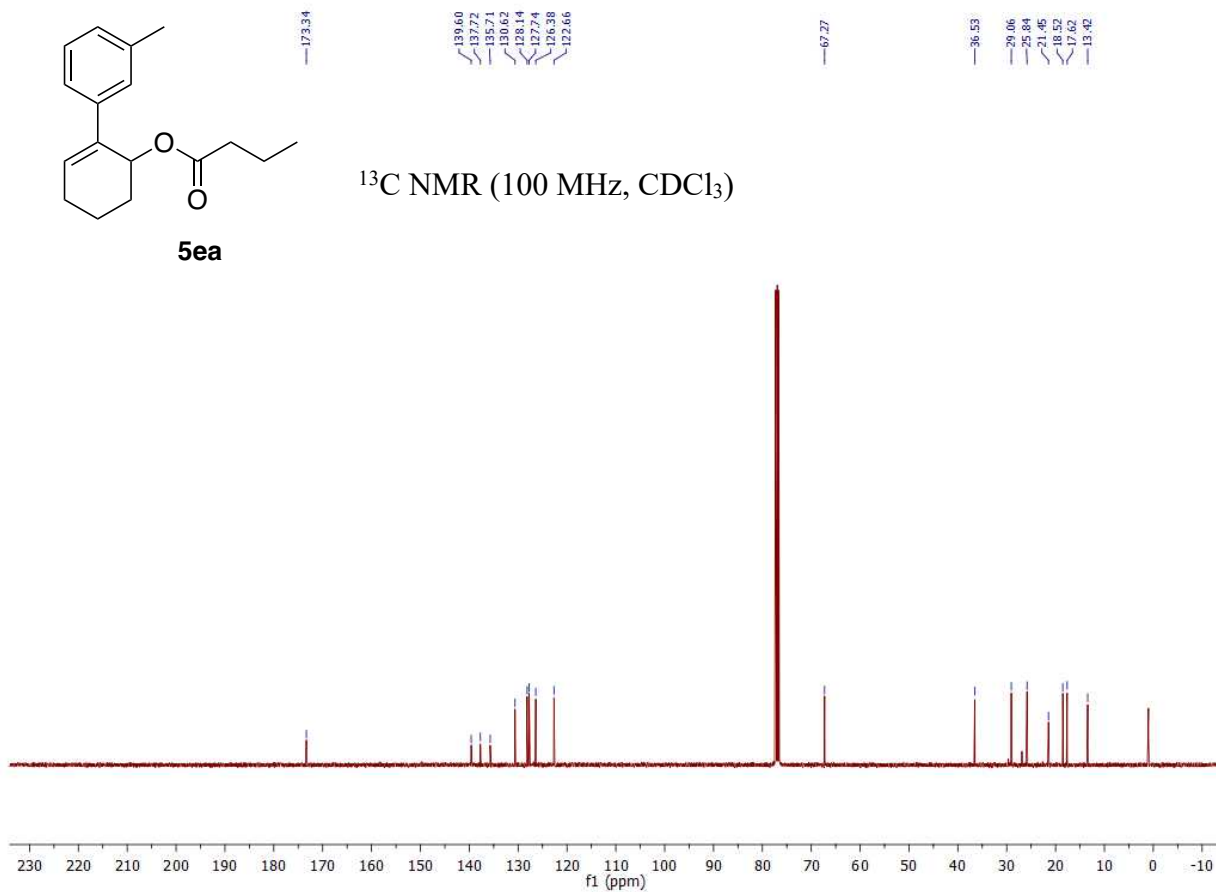






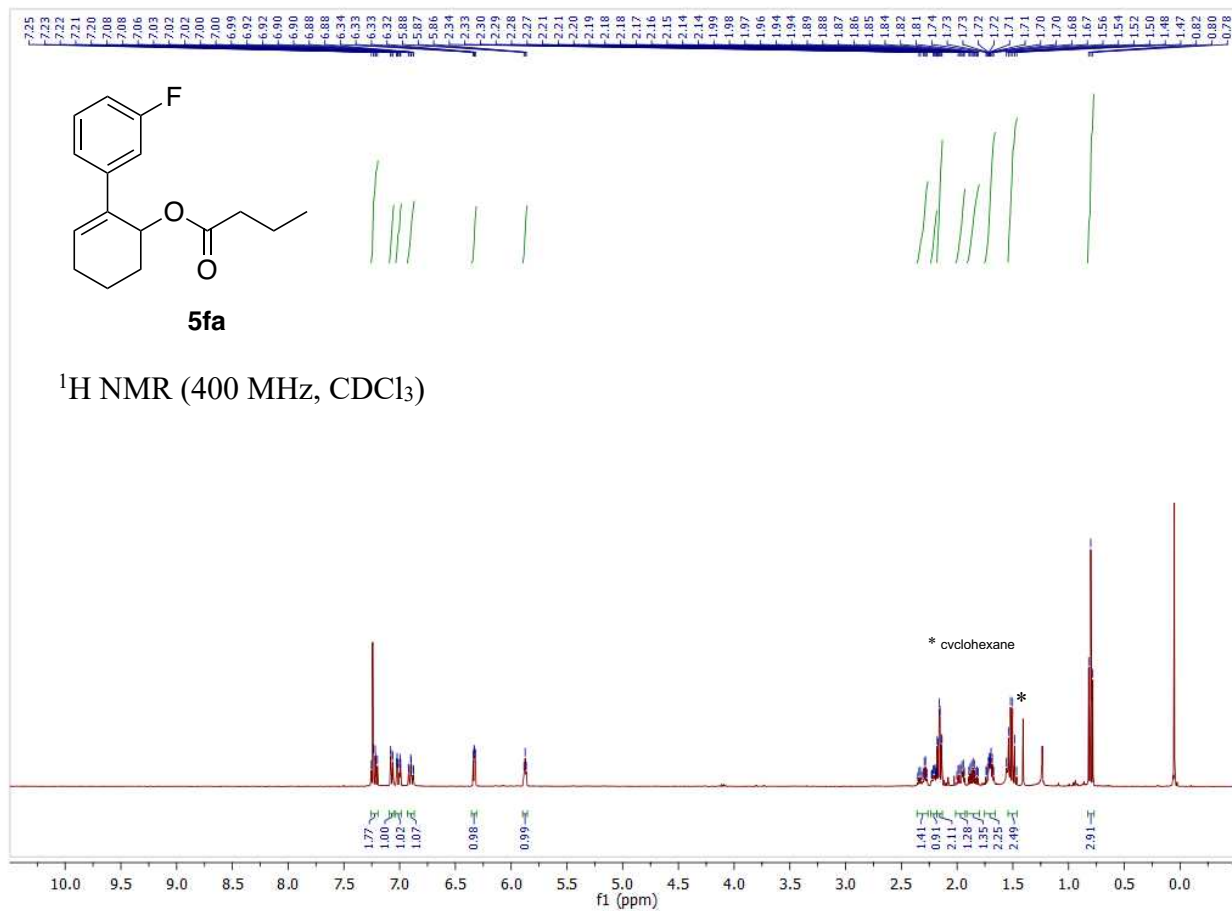
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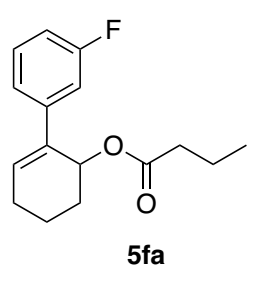
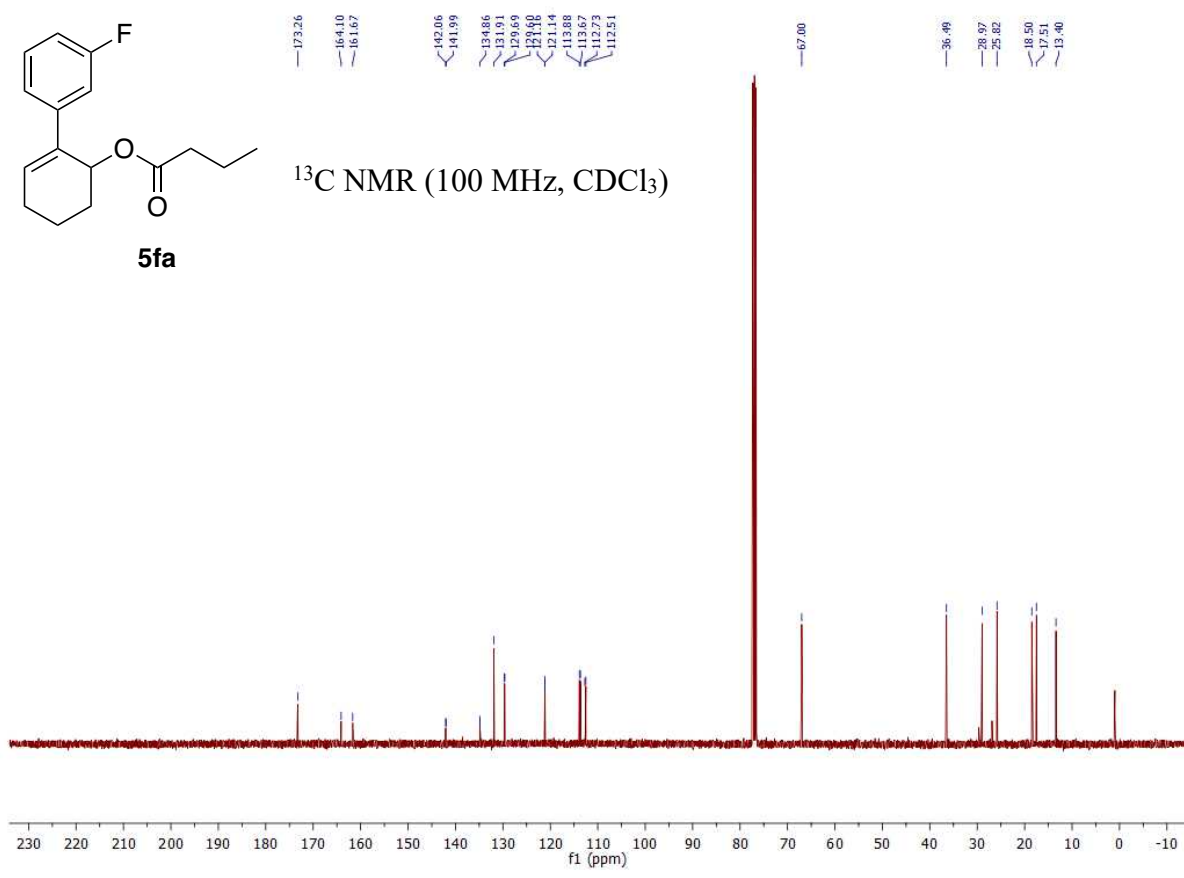
^{13}C NMR (100 MHz, CDCl_3)



5fa

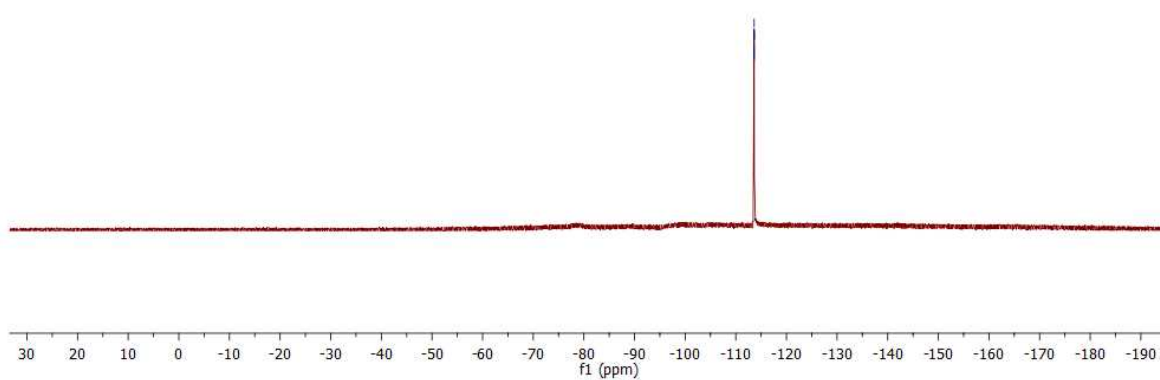
^1H NMR (400 MHz, CDCl_3)

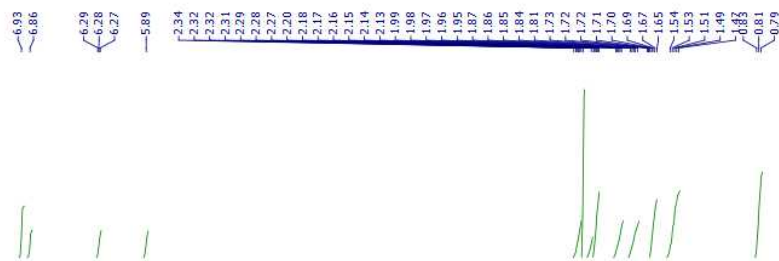
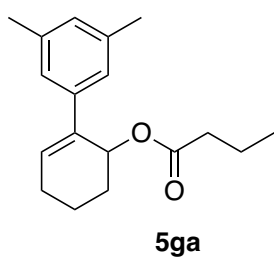




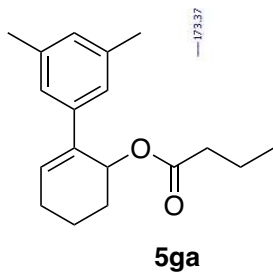
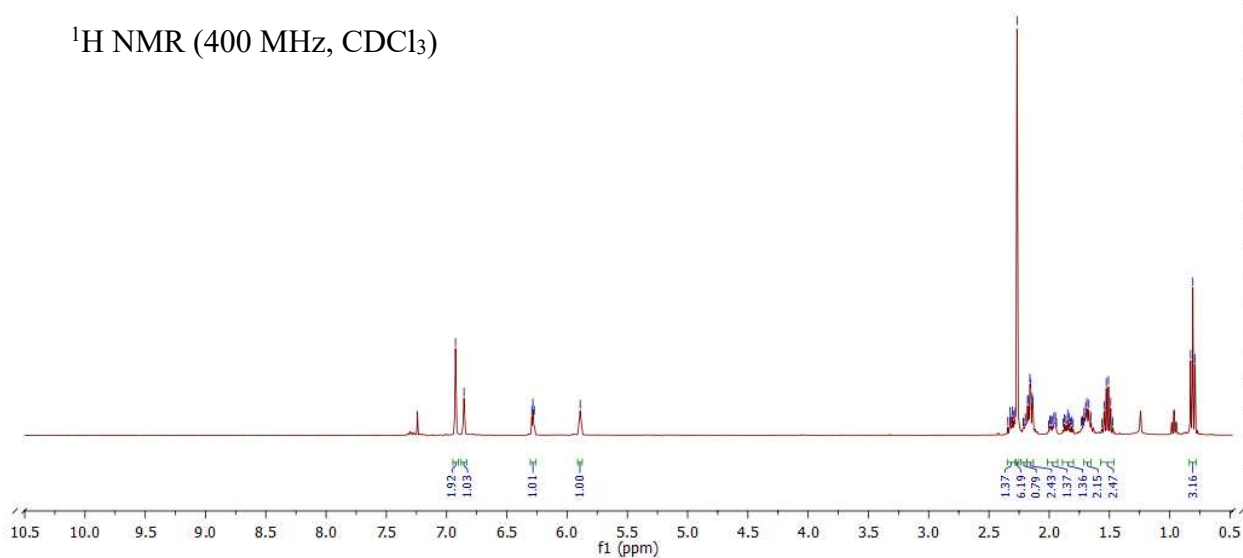
113.58
113.60
113.61
113.61
113.62
113.63
113.64
113.65

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

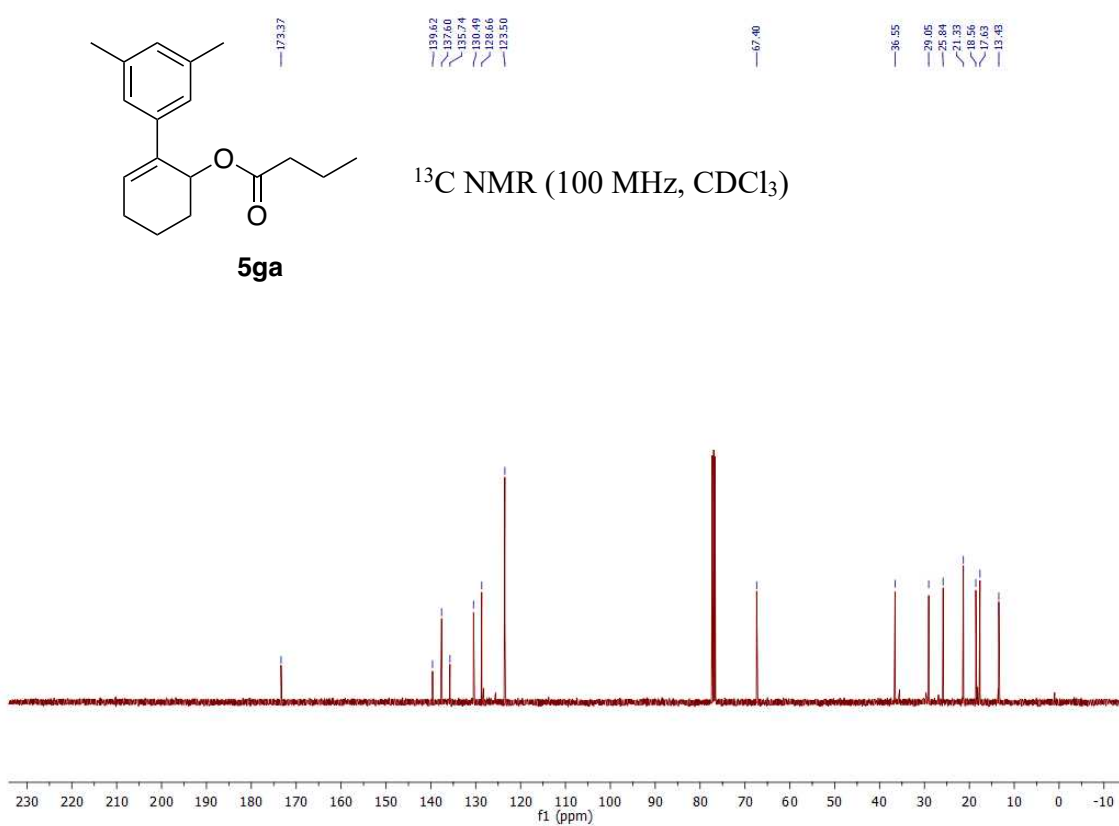


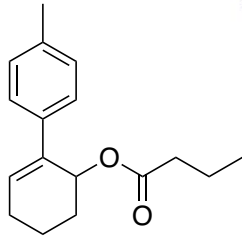


$^1\text{H NMR}$ (400 MHz, CDCl_3)

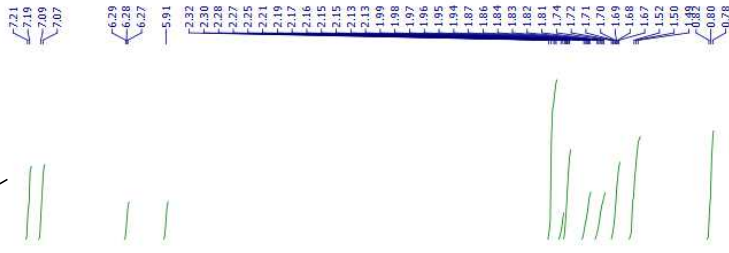


$^{13}\text{C NMR}$ (100 MHz, CDCl_3)

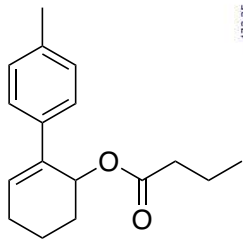
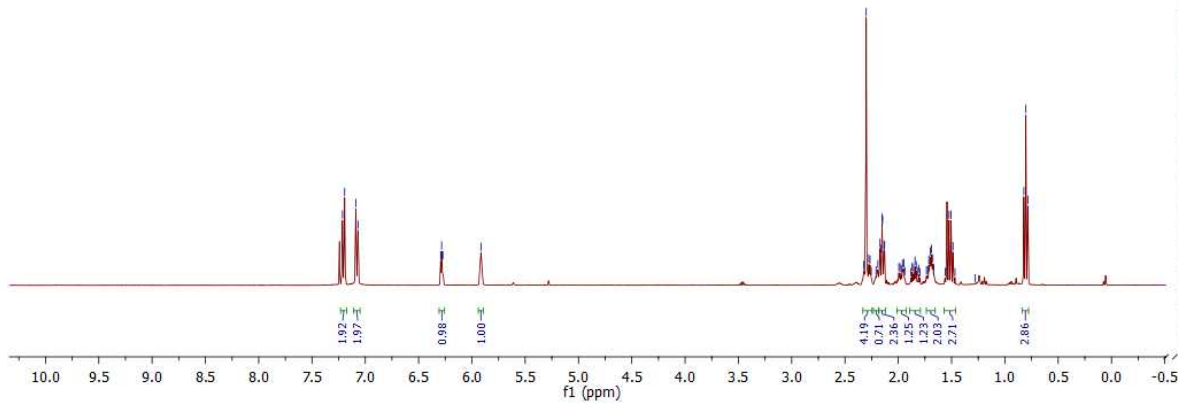




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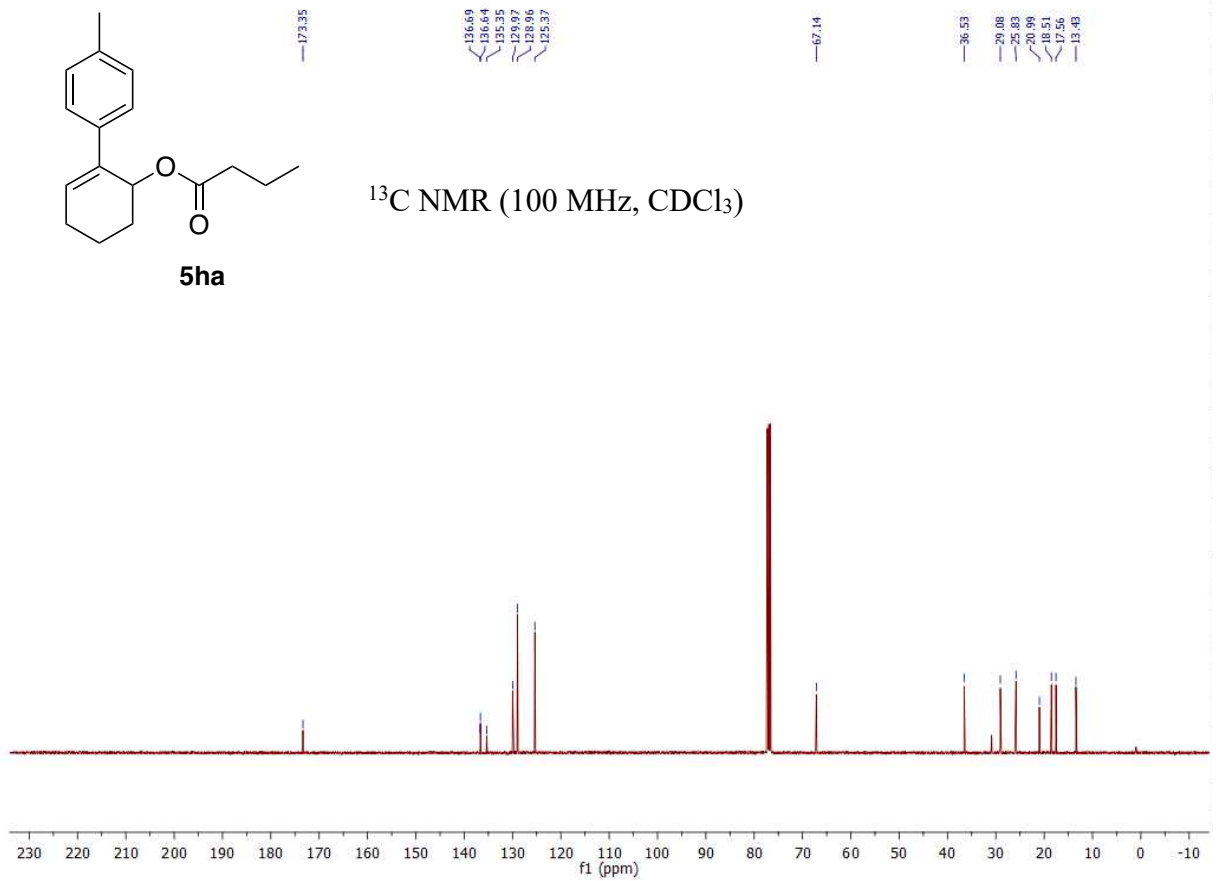


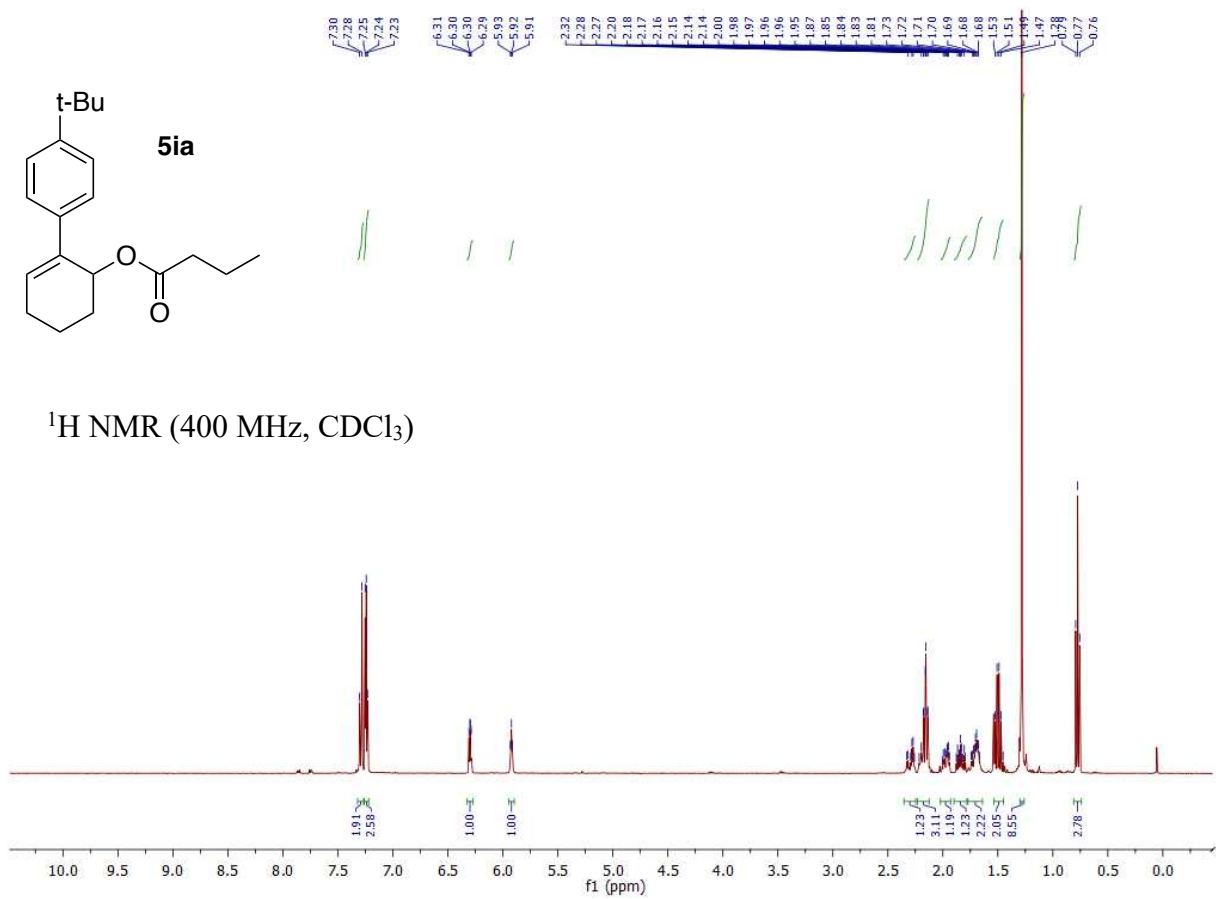
^1H NMR (400 MHz, CDCl_3)

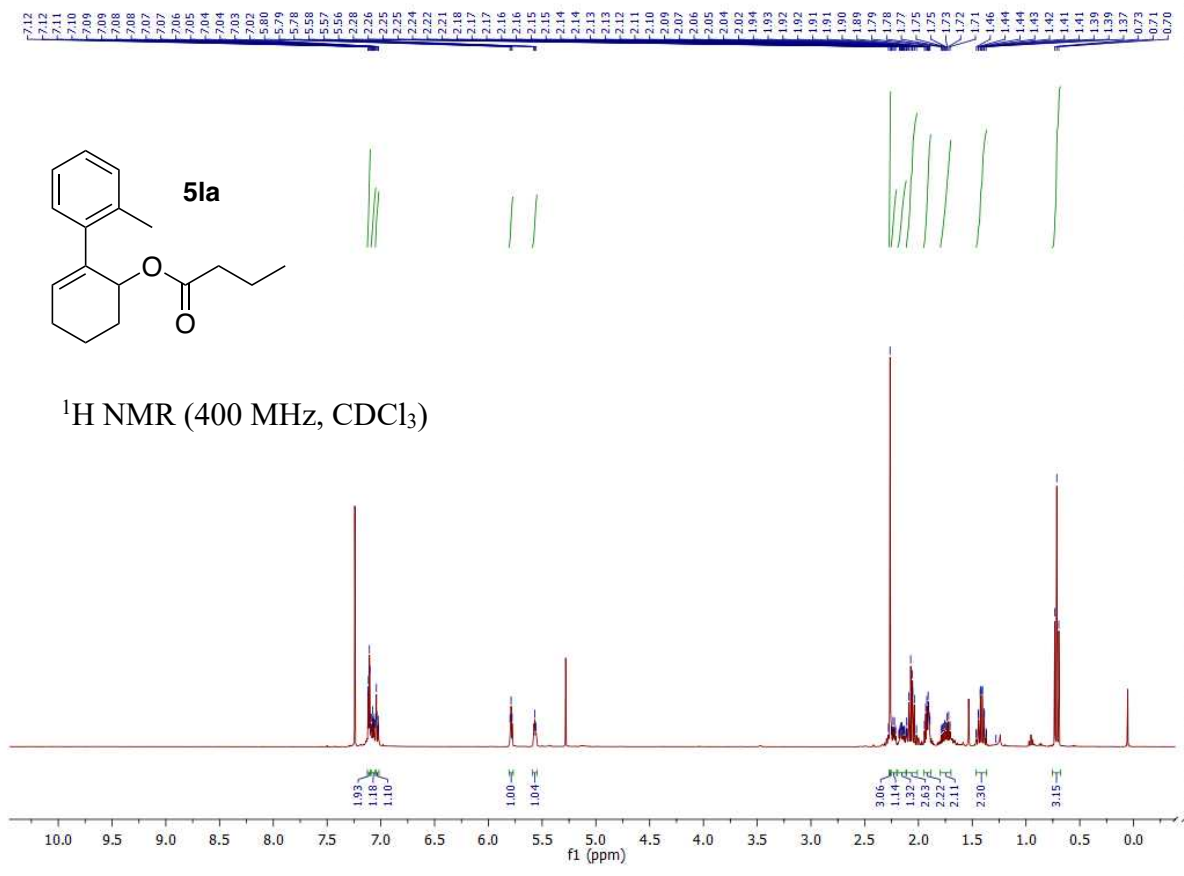
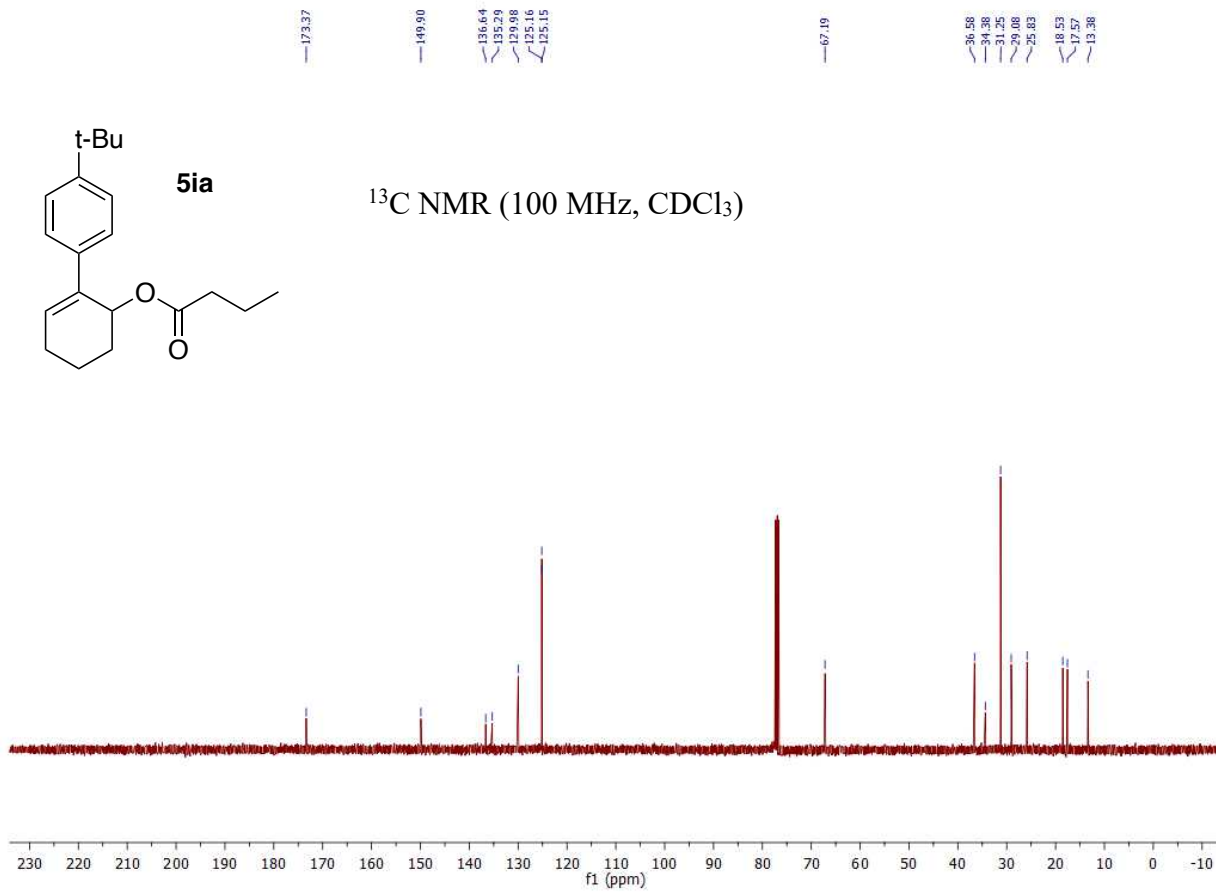


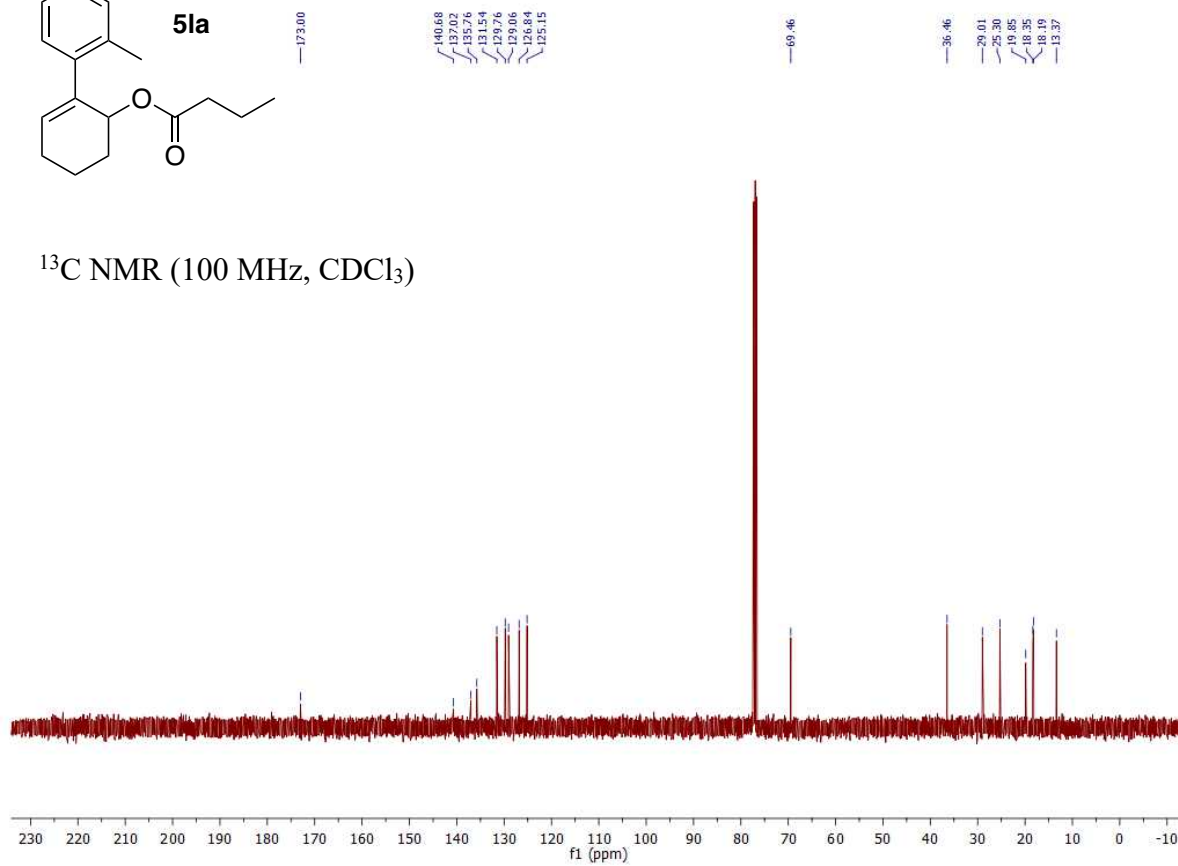
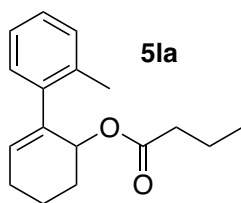
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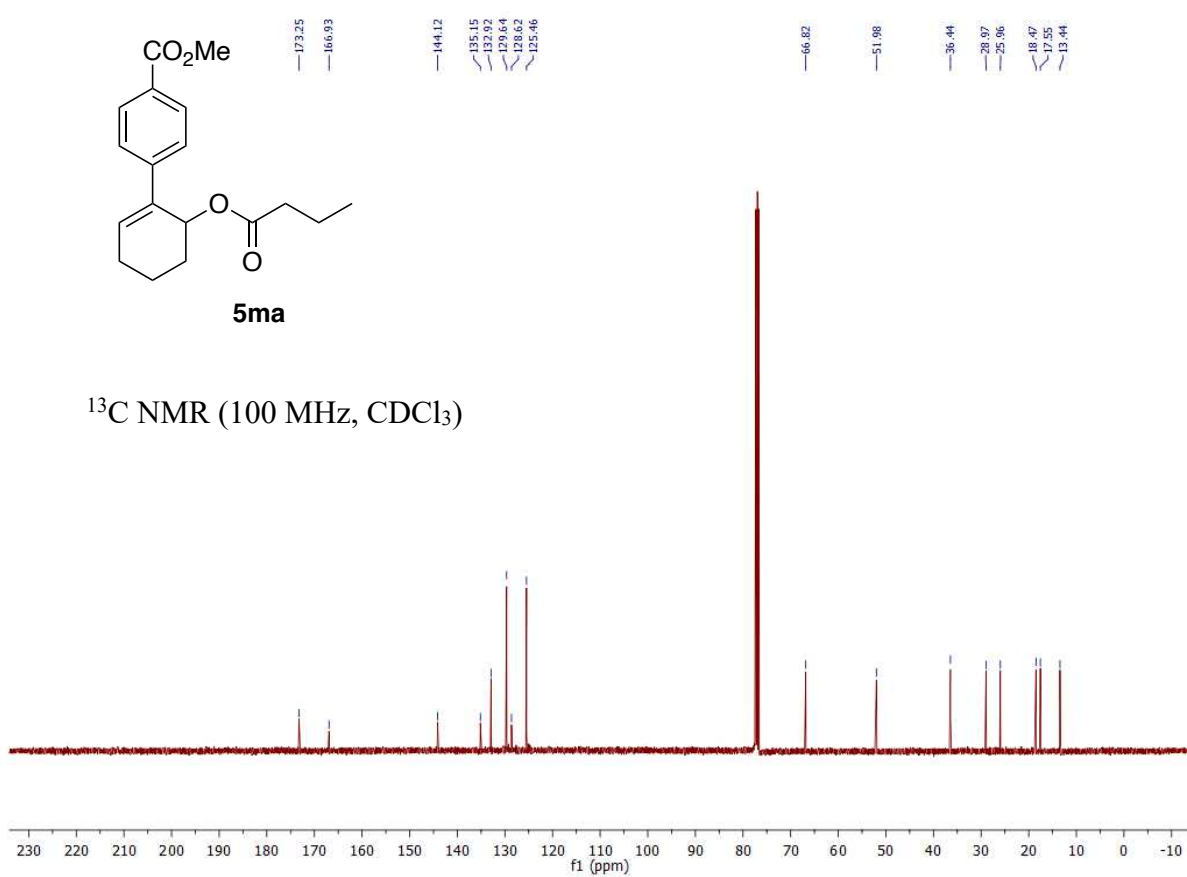
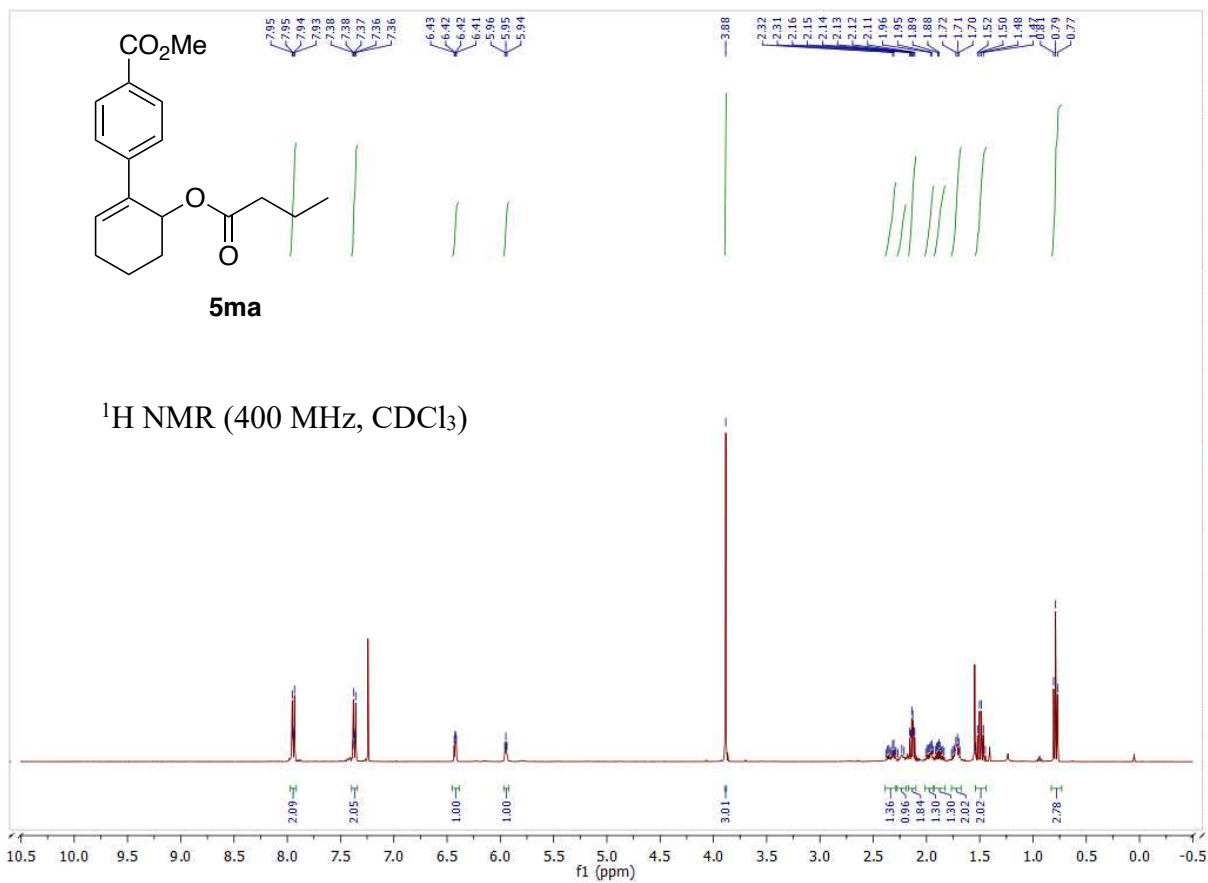
^{13}C NMR (100 MHz, CDCl_3)

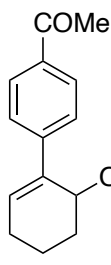






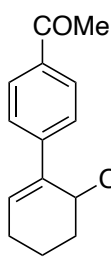
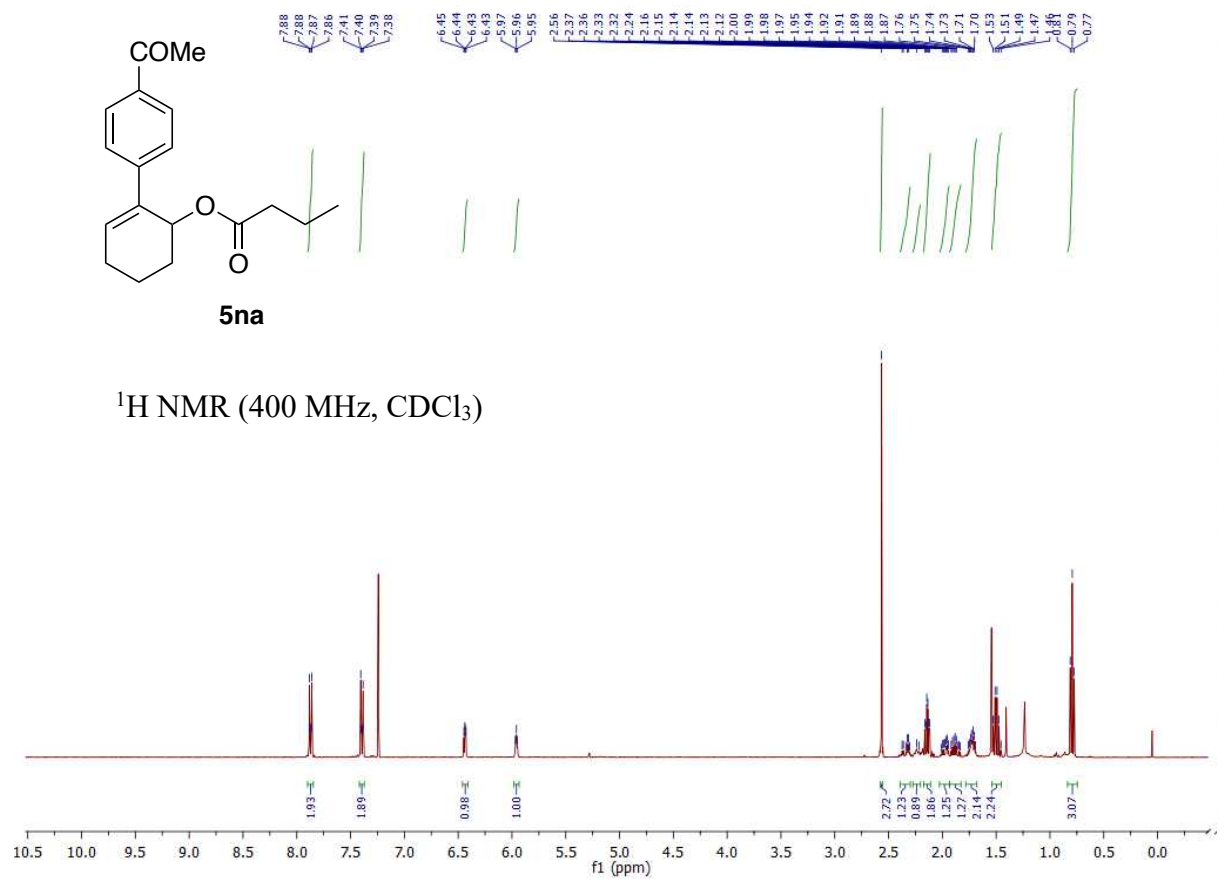






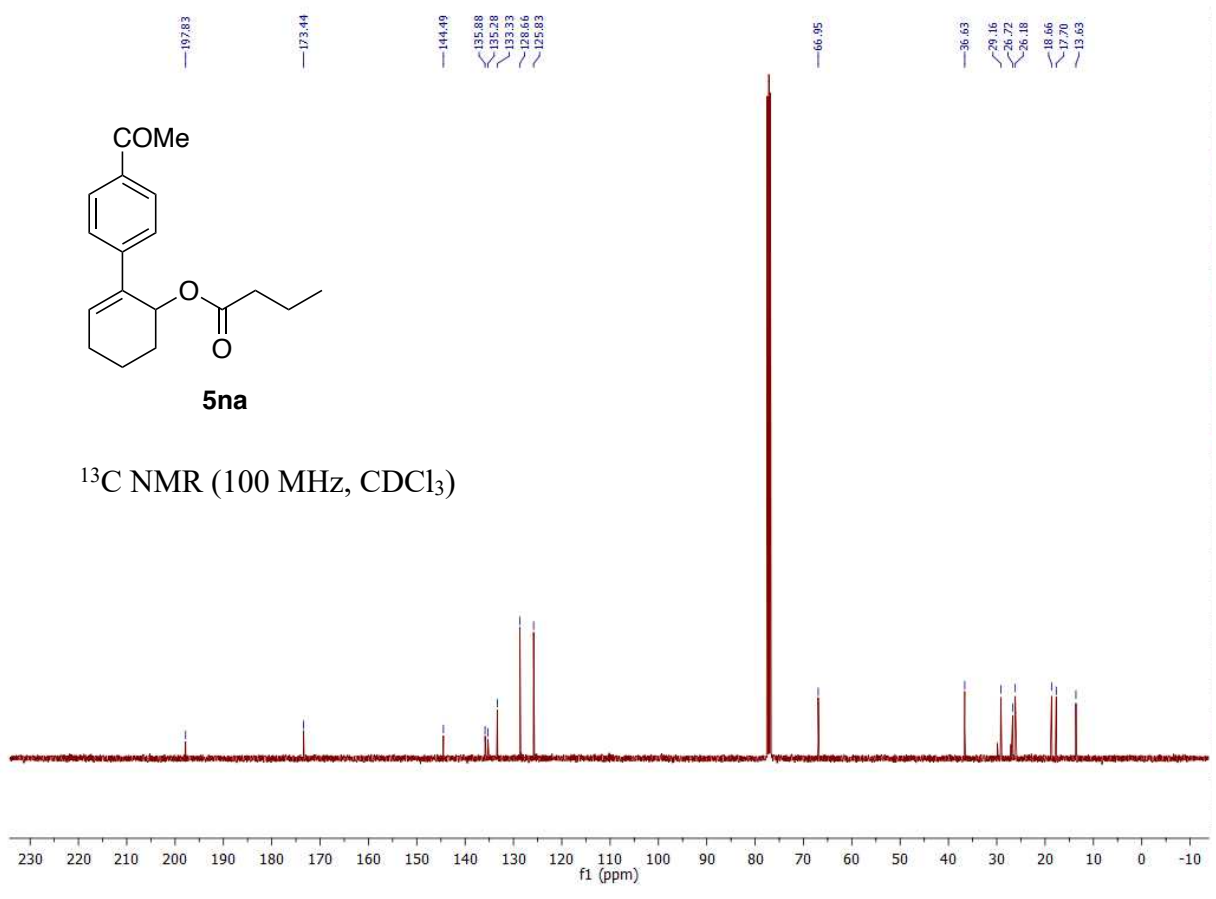
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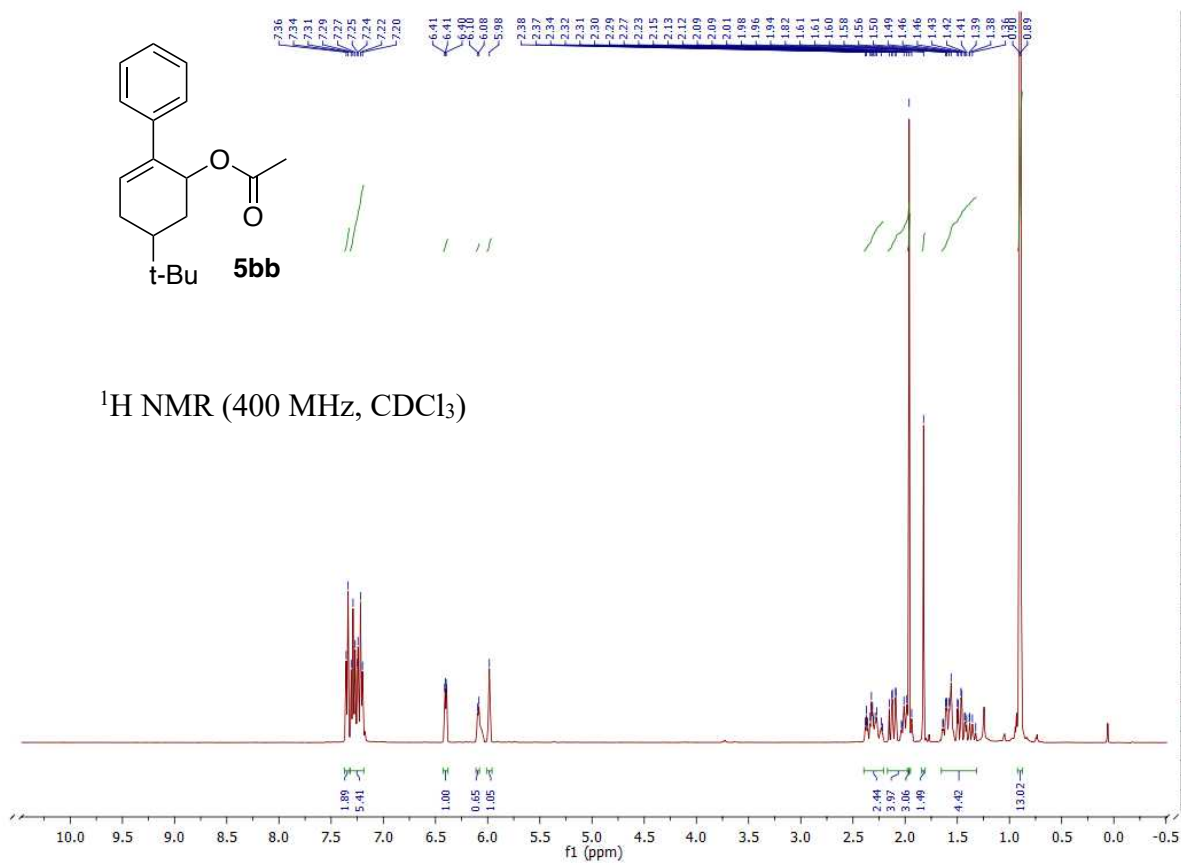
¹H NMR (400 MHz, CDCl₃)

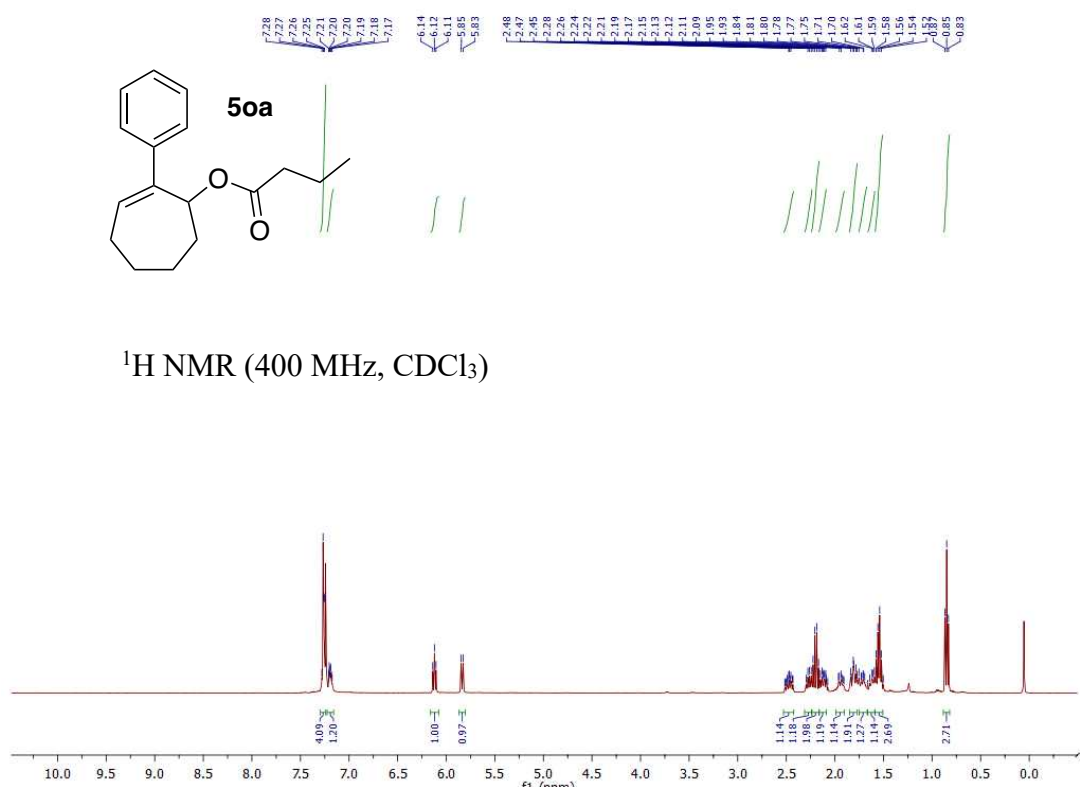
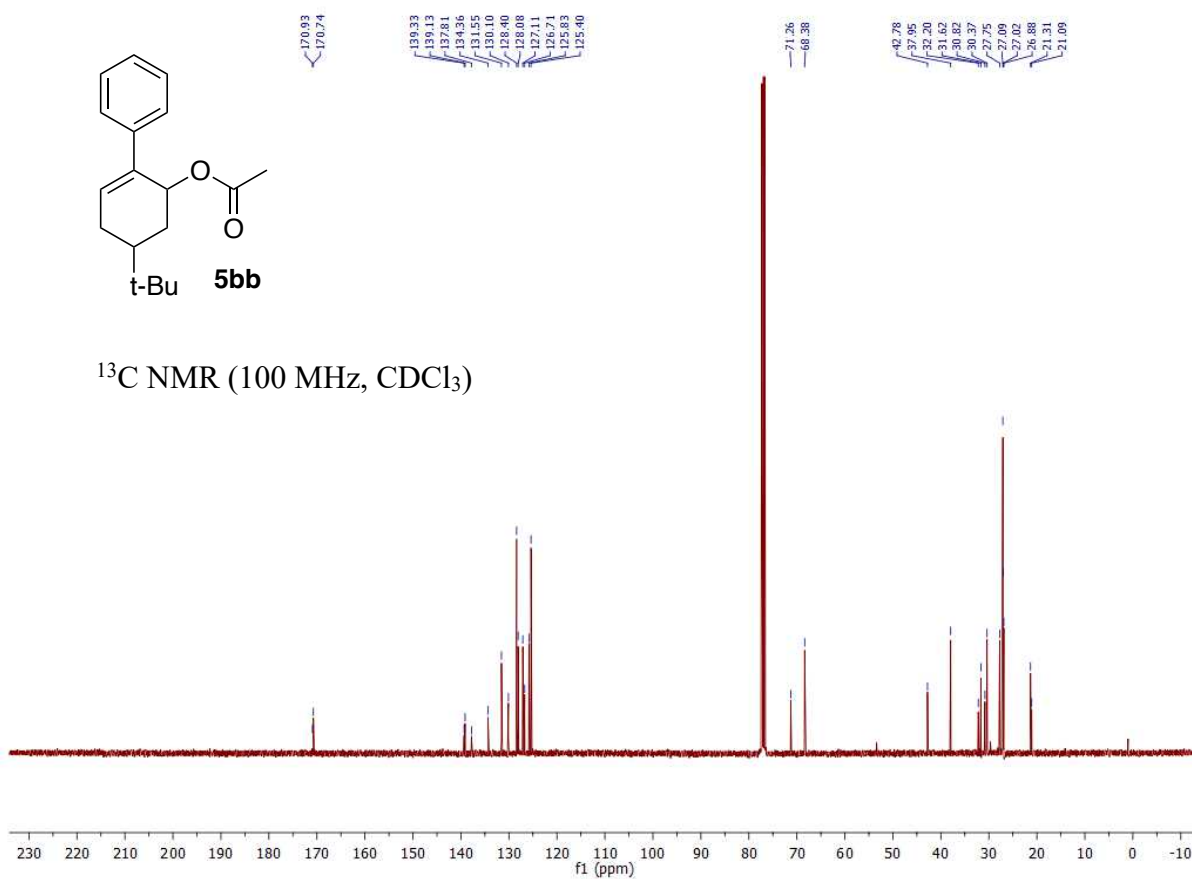


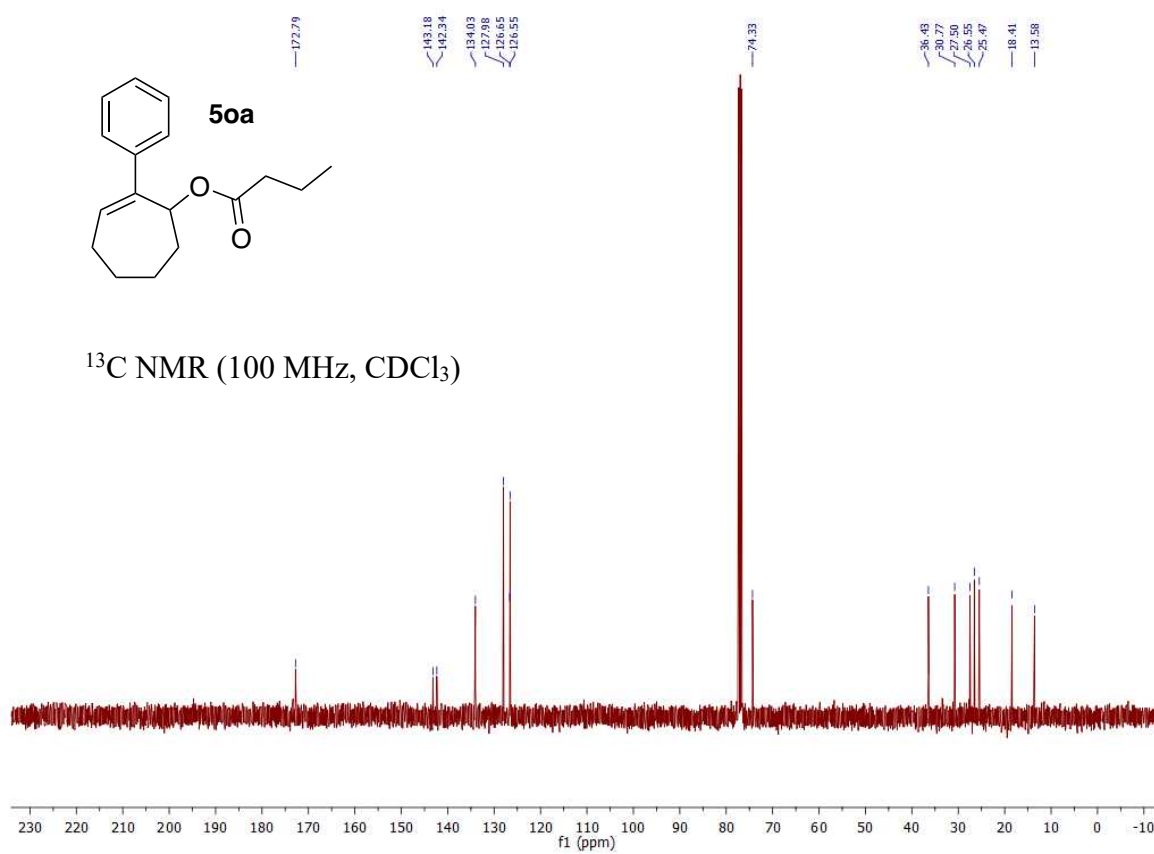
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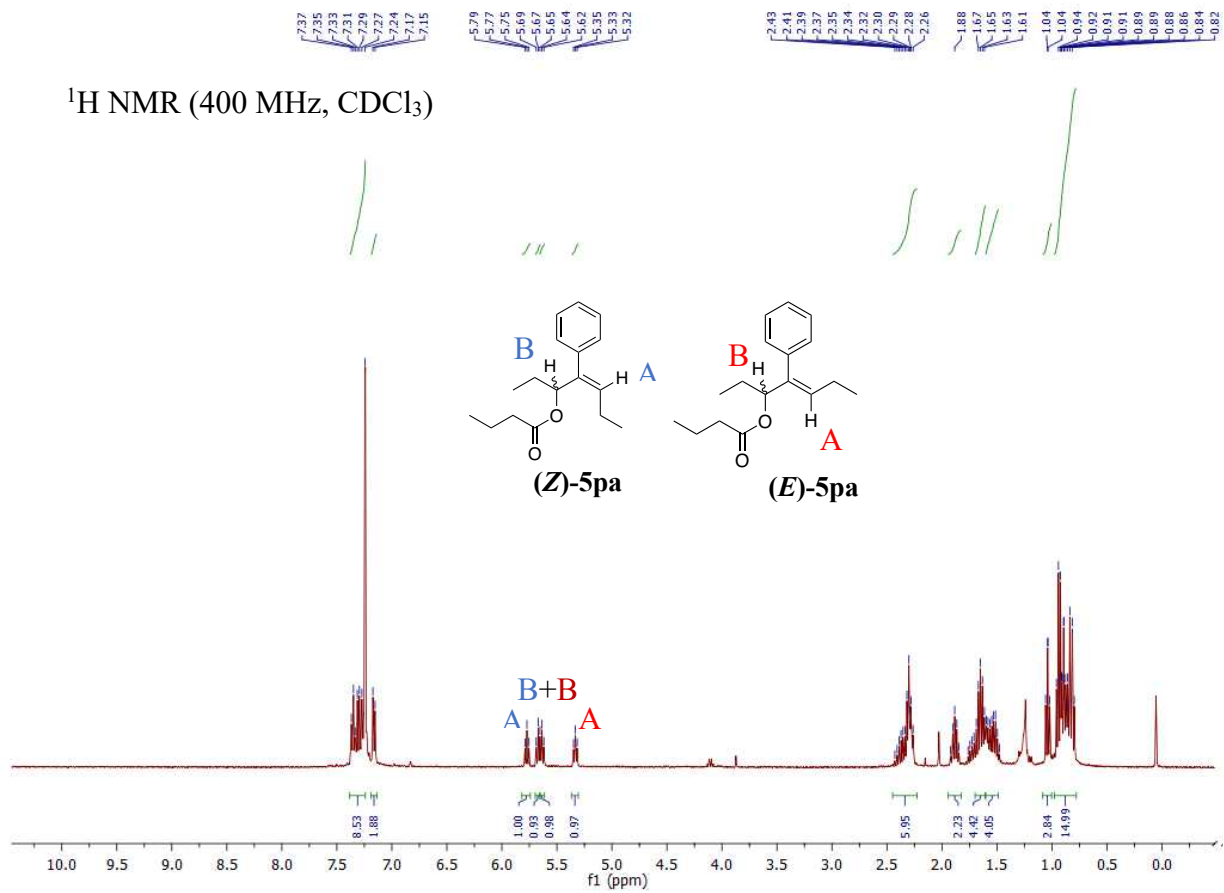
¹³C NMR (100 MHz, CDCl₃)

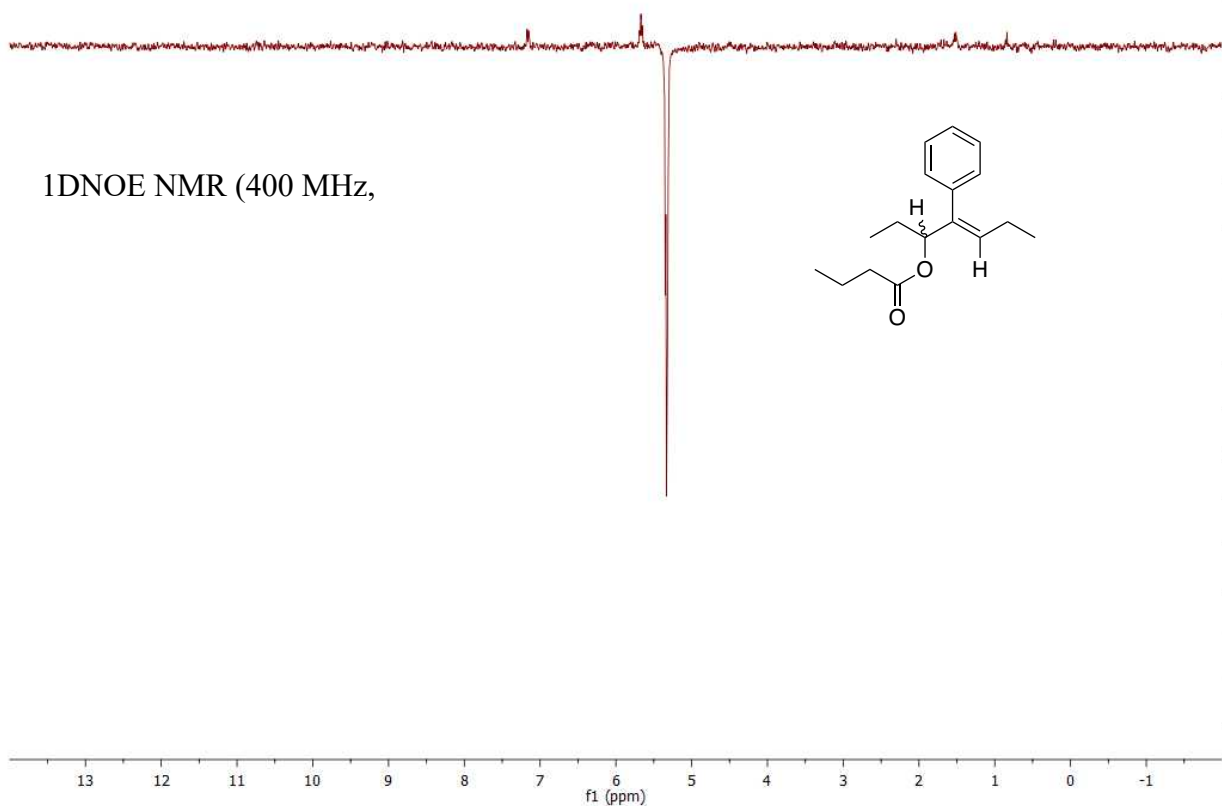
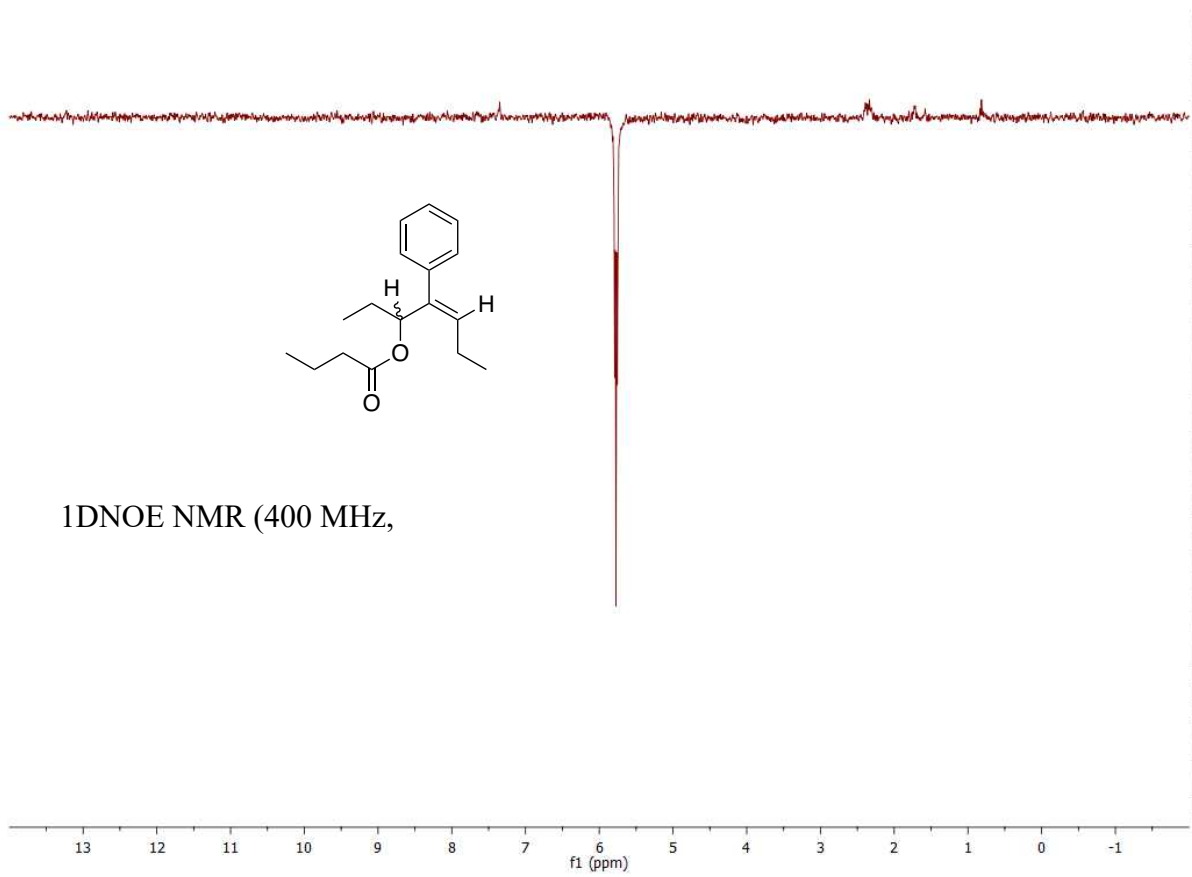


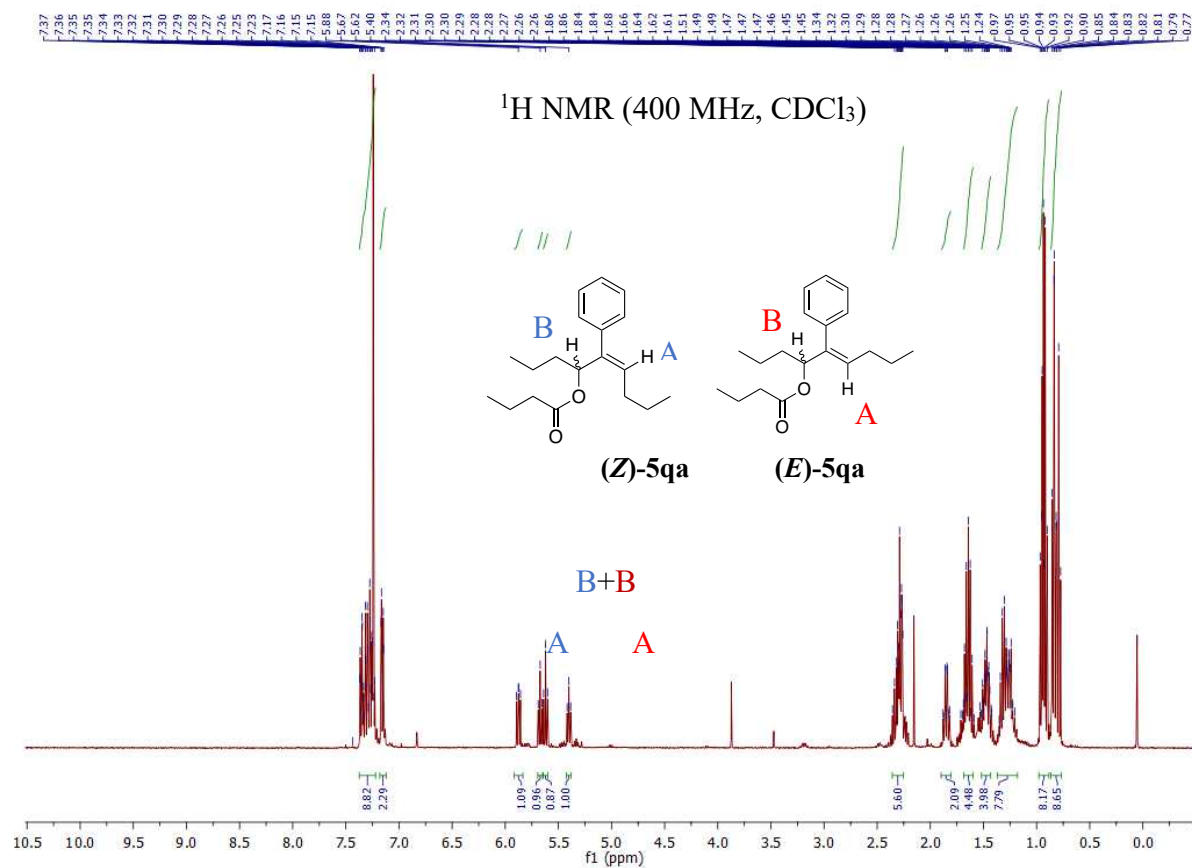
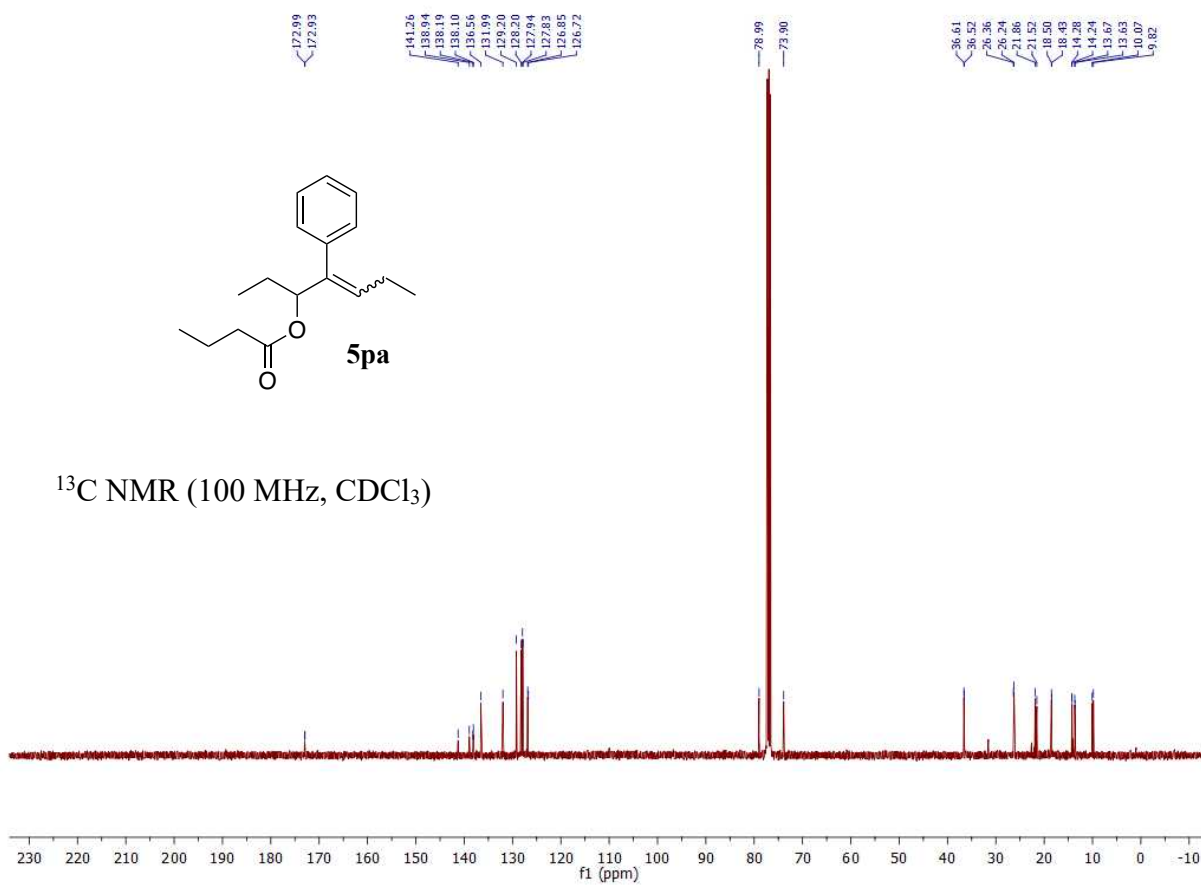


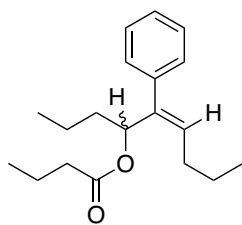
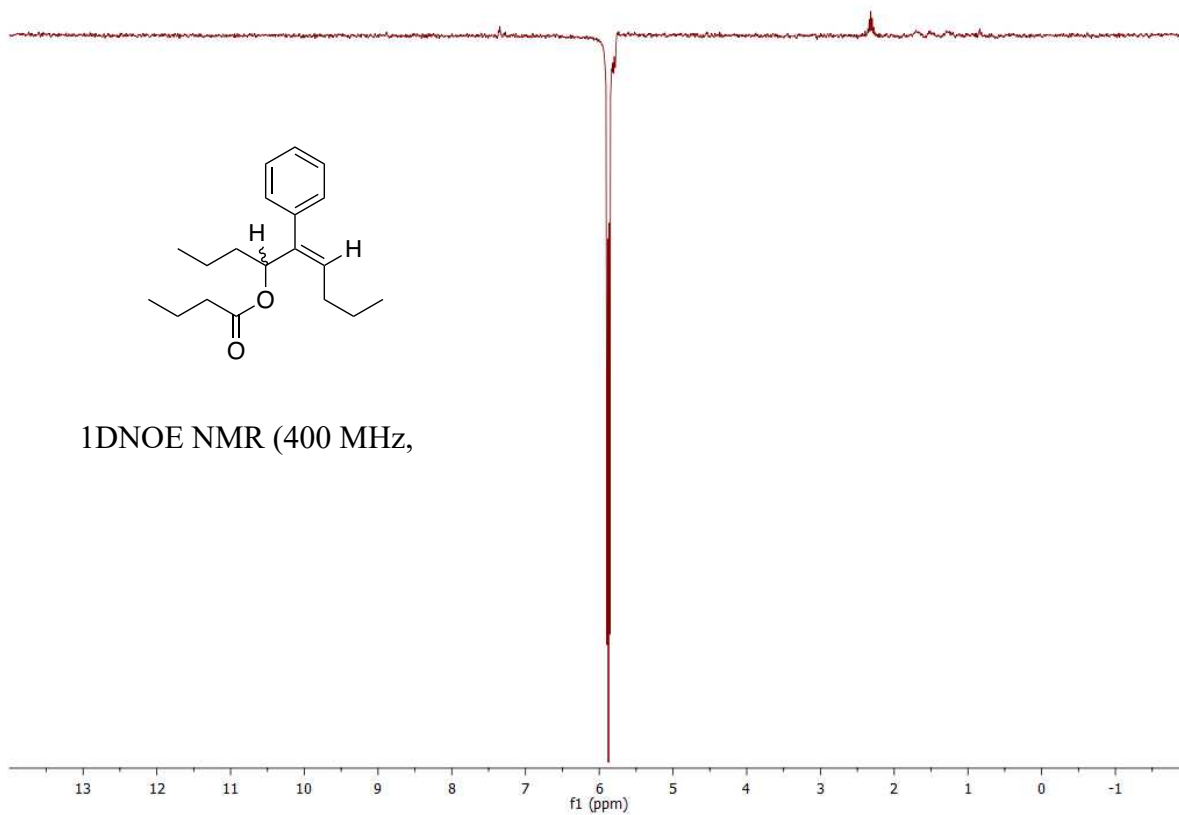


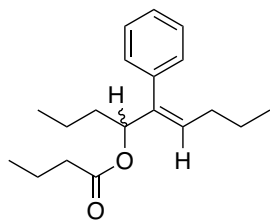




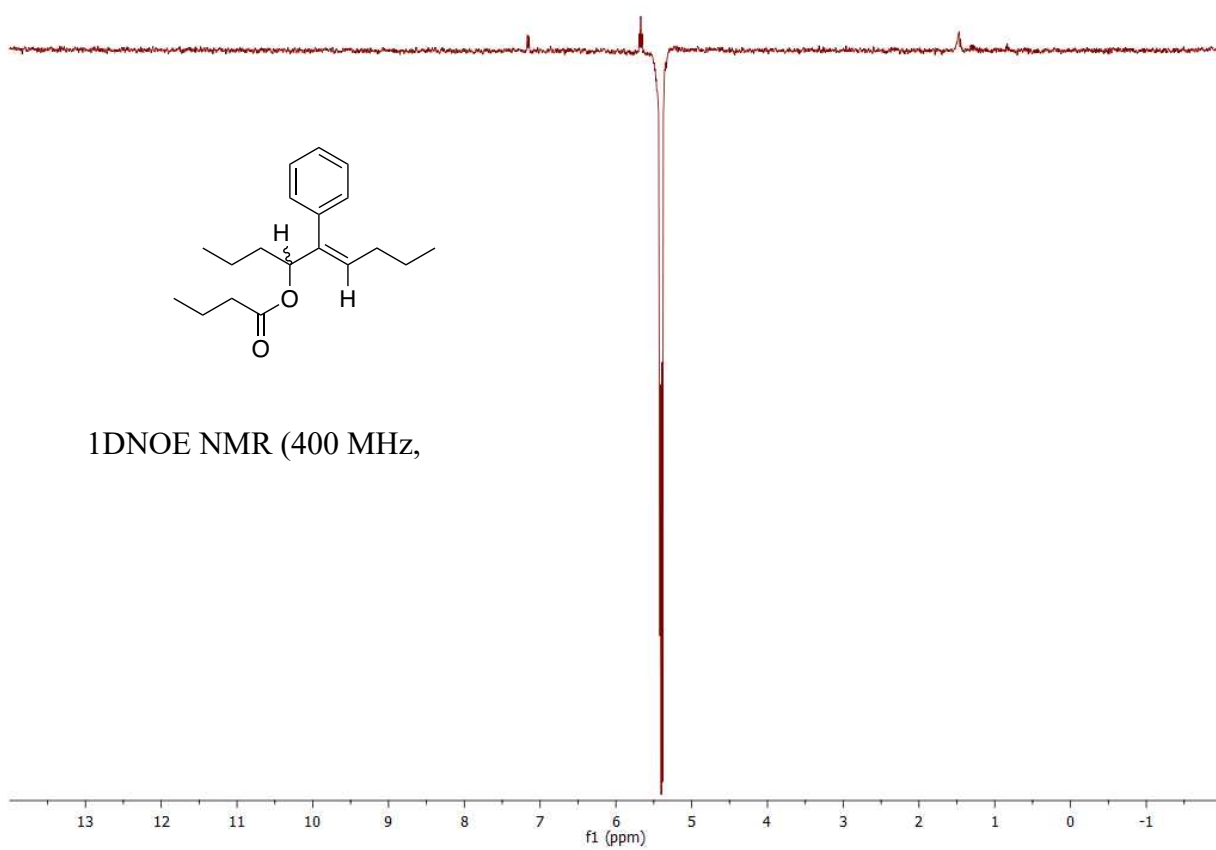


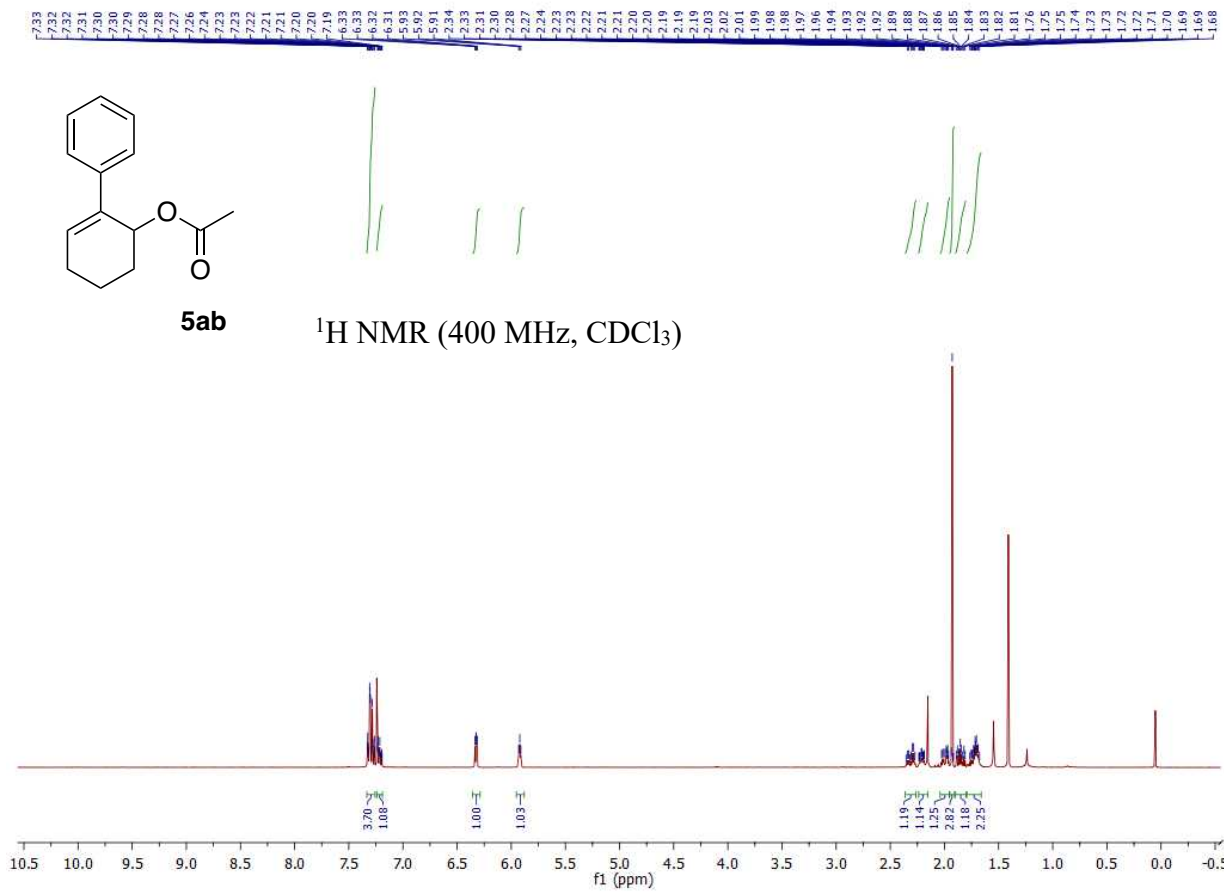
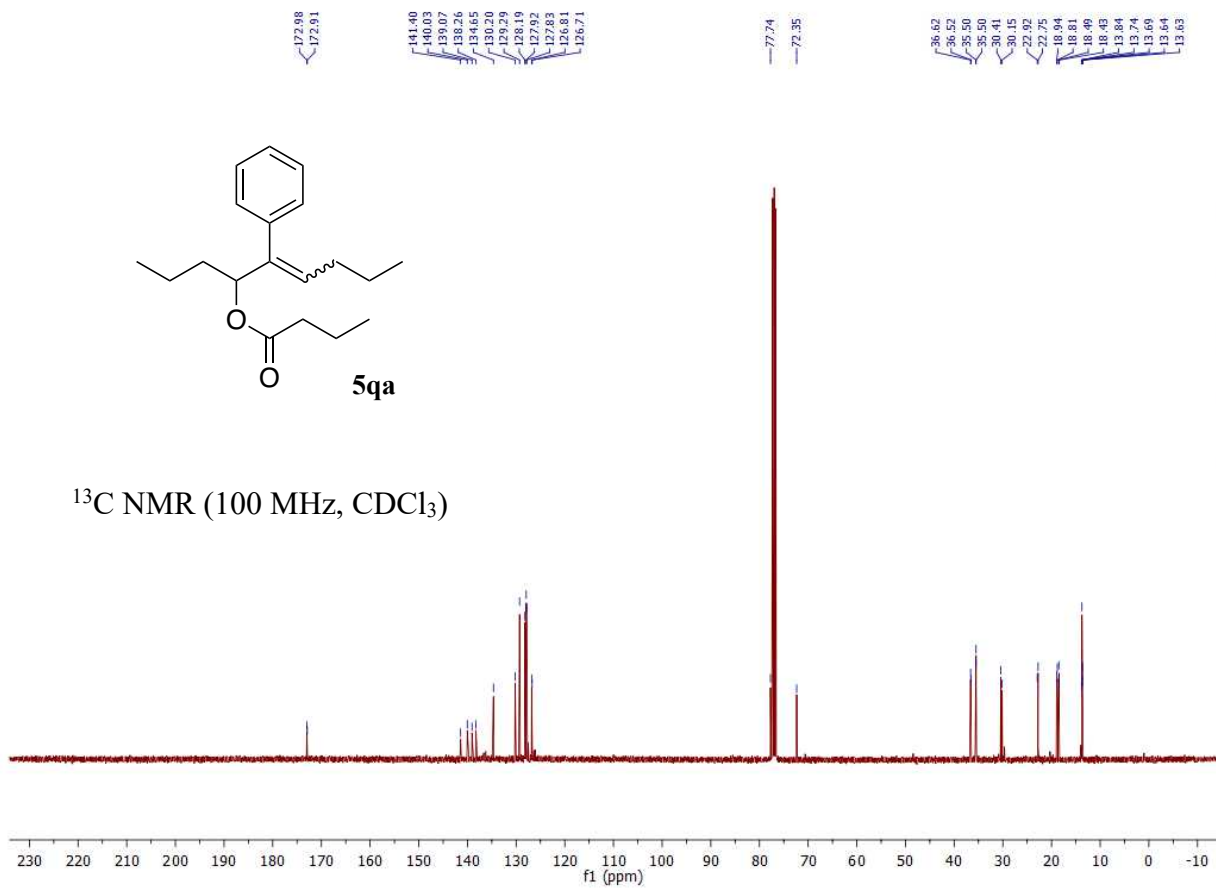


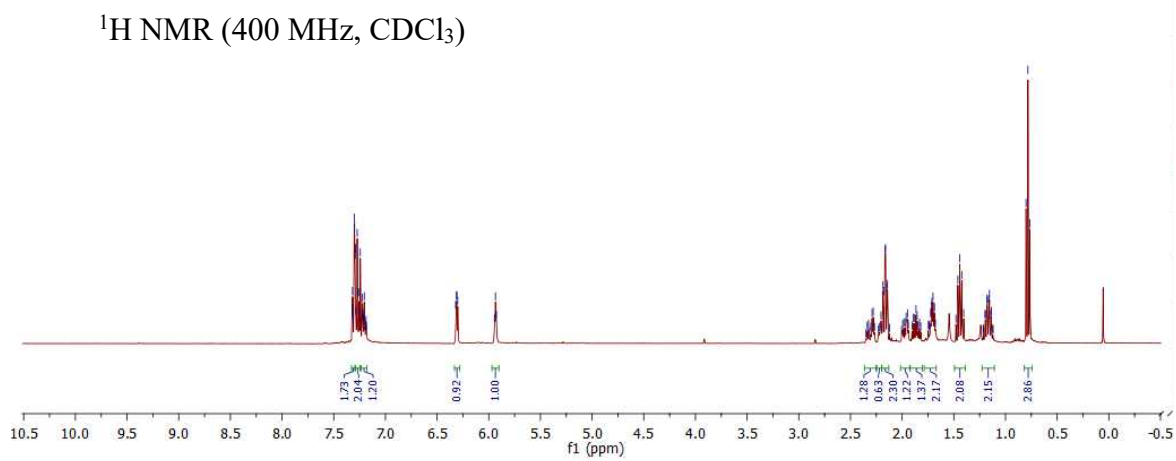
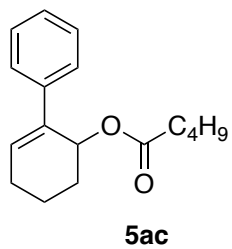
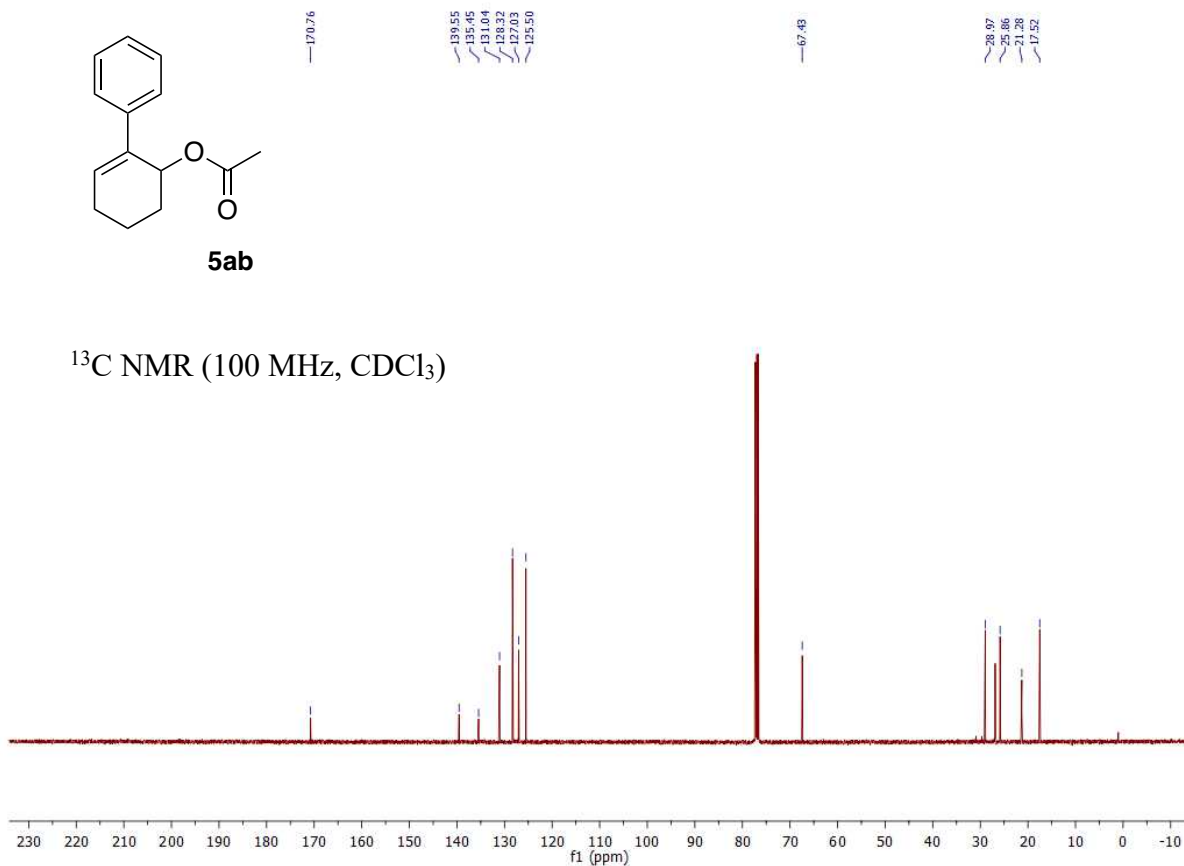
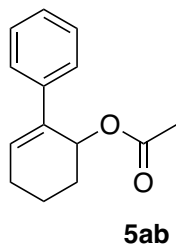


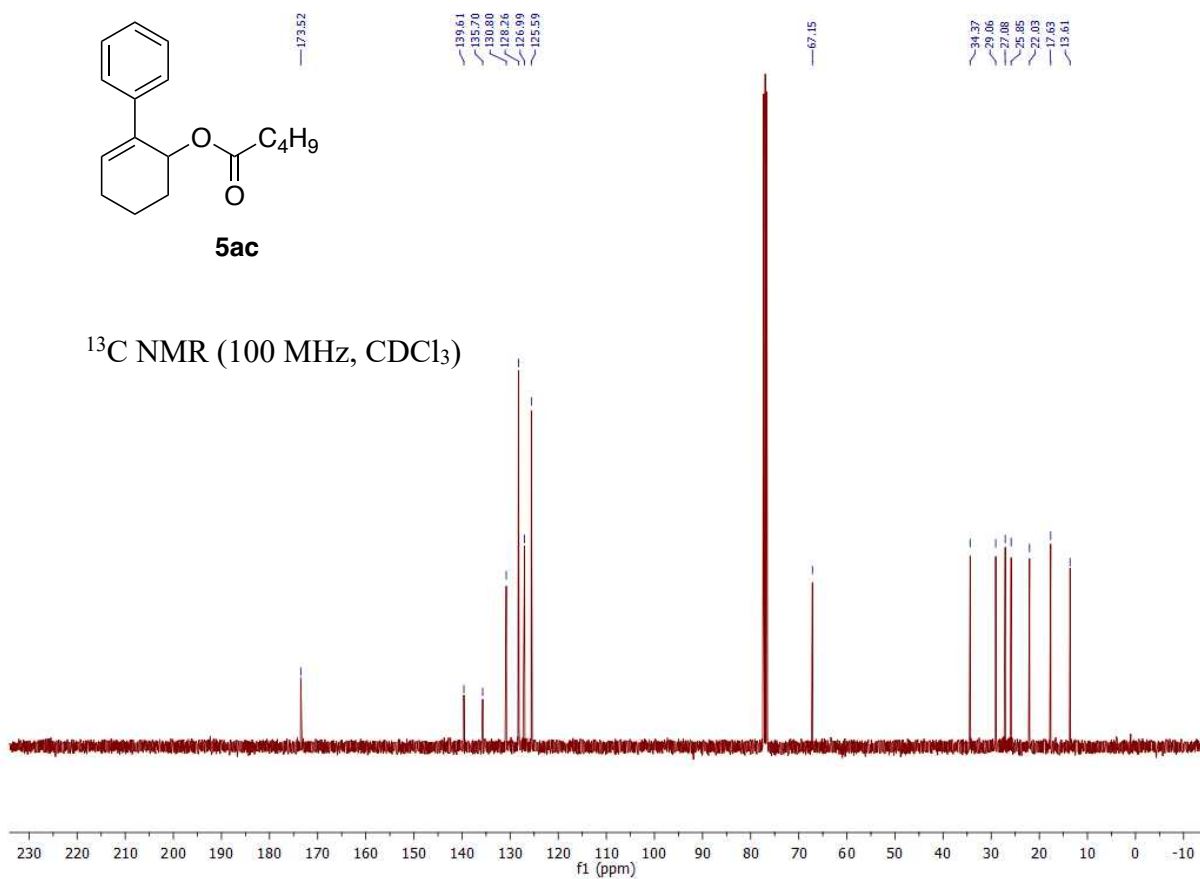
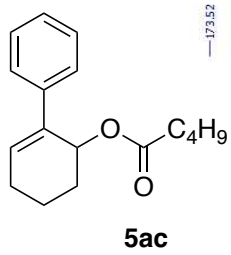


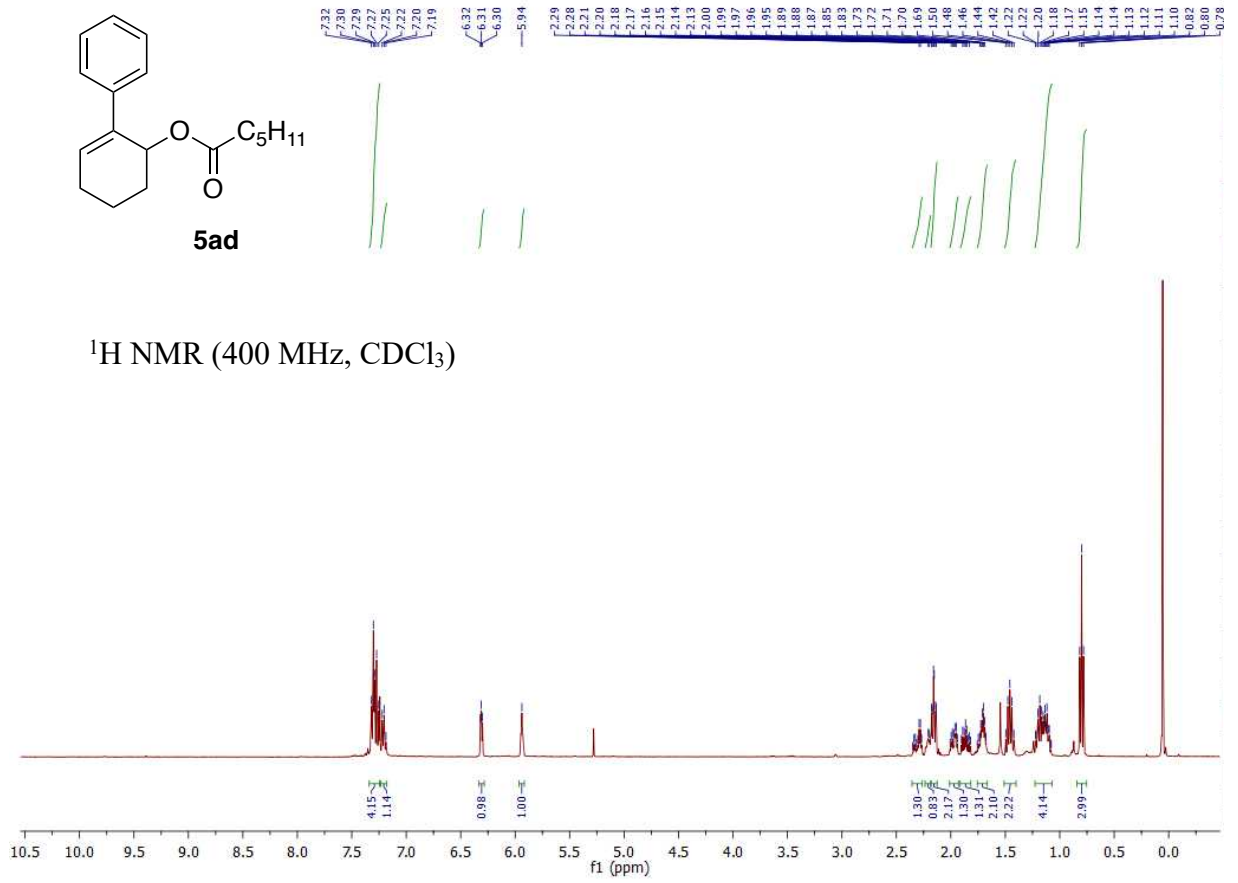
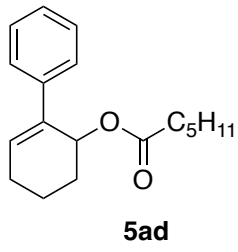
1DNOE NMR (400 MHz,

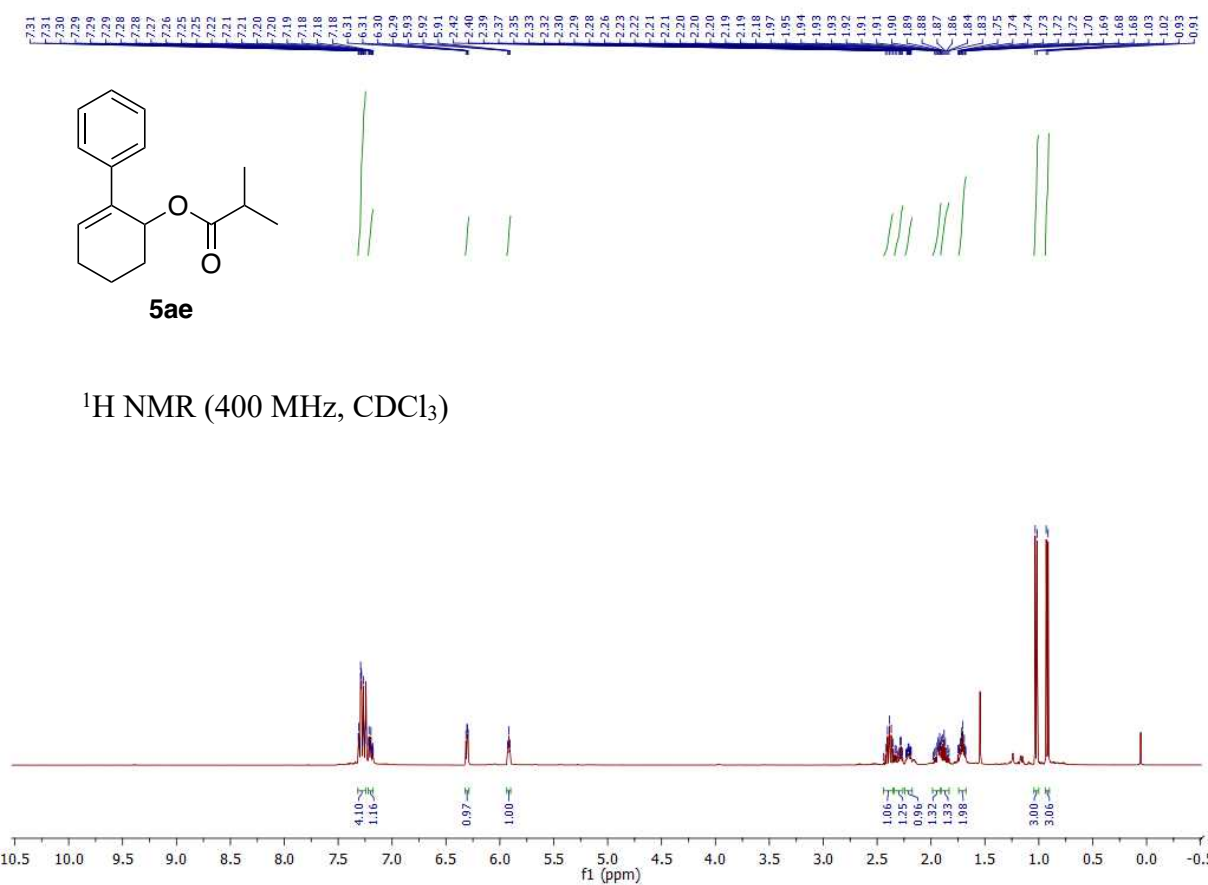
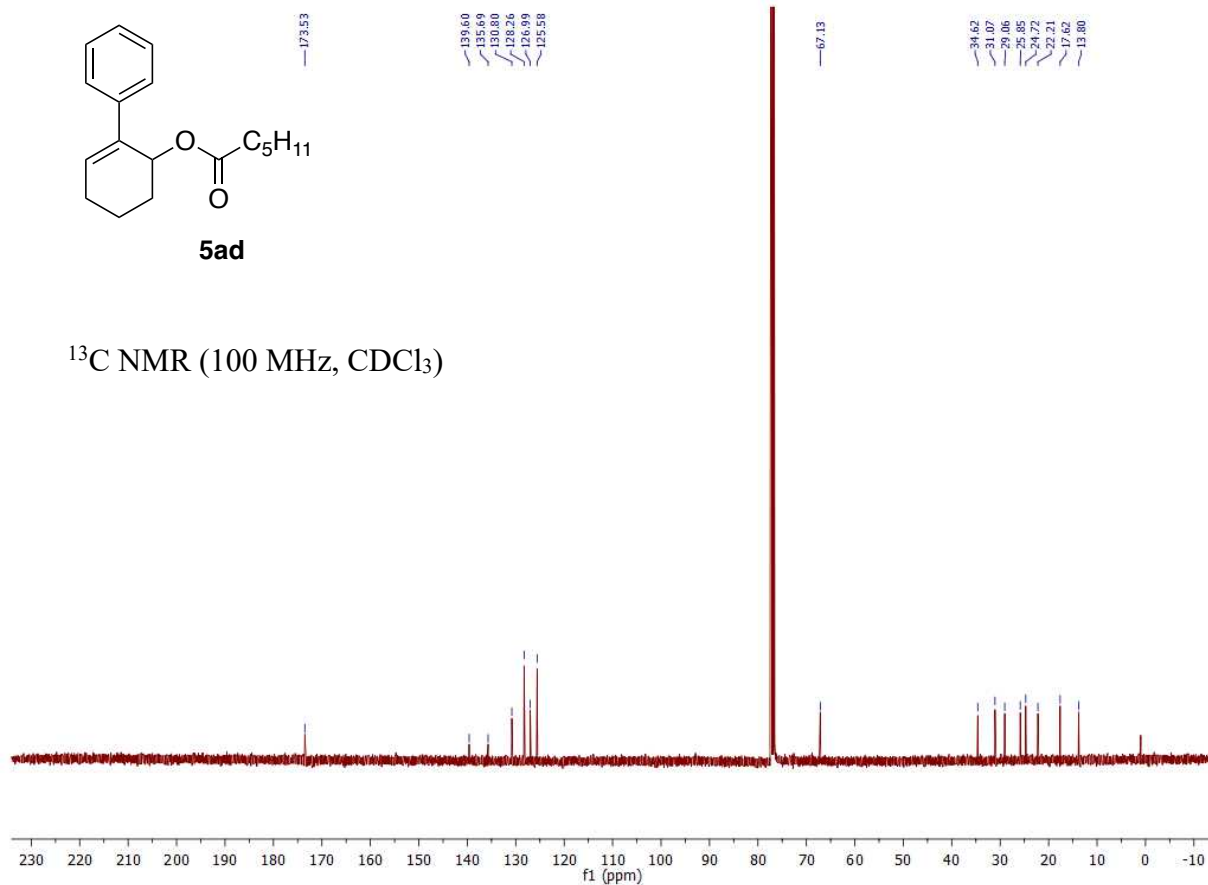


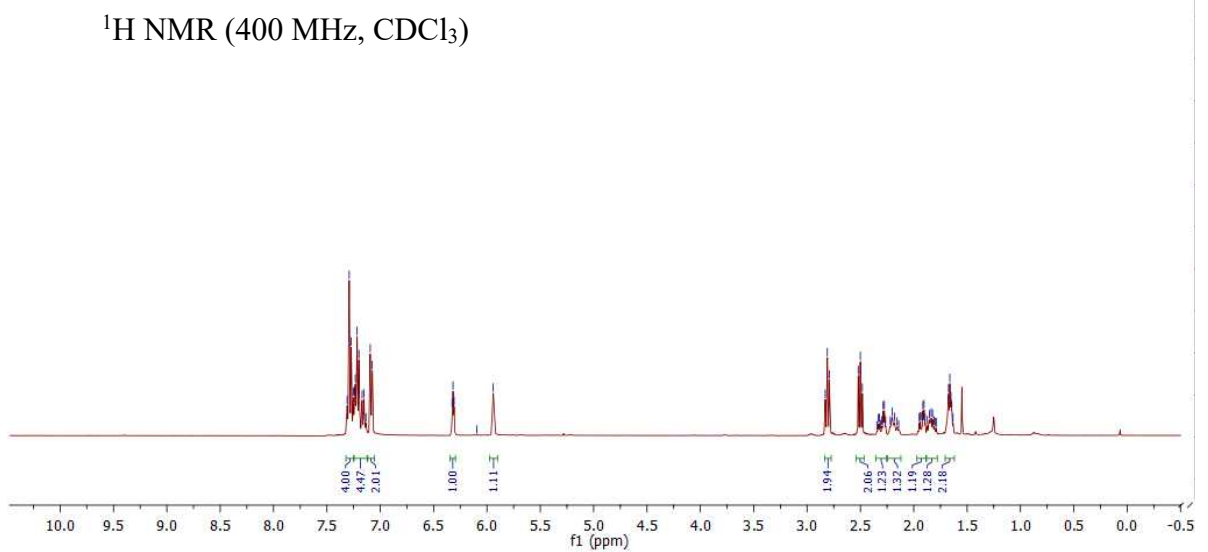
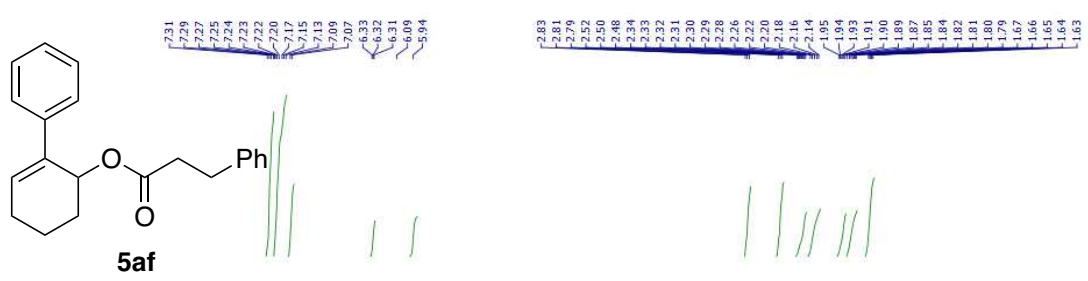
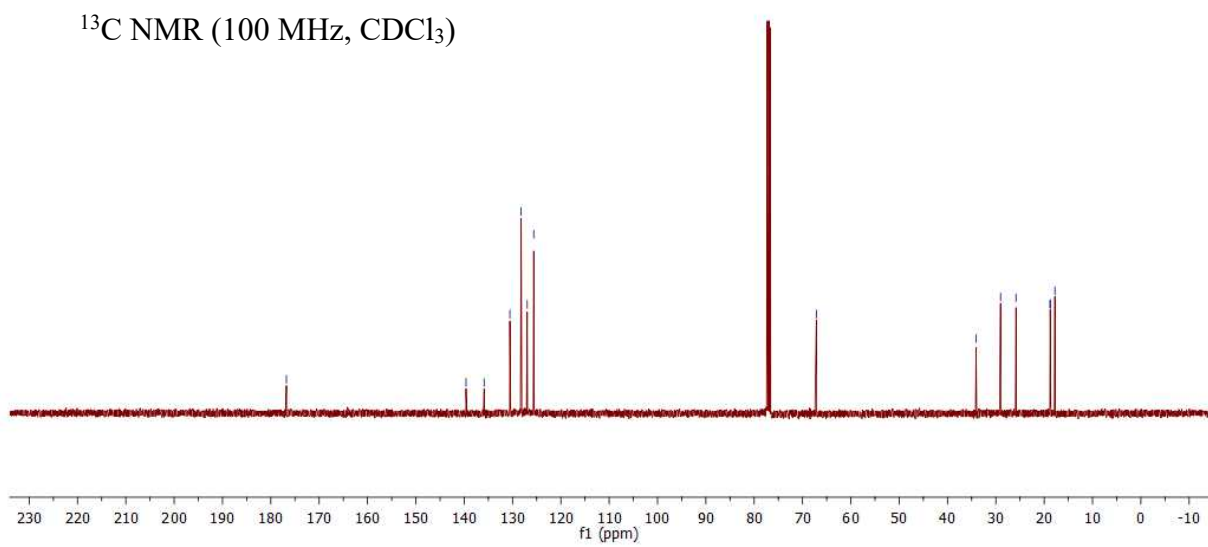
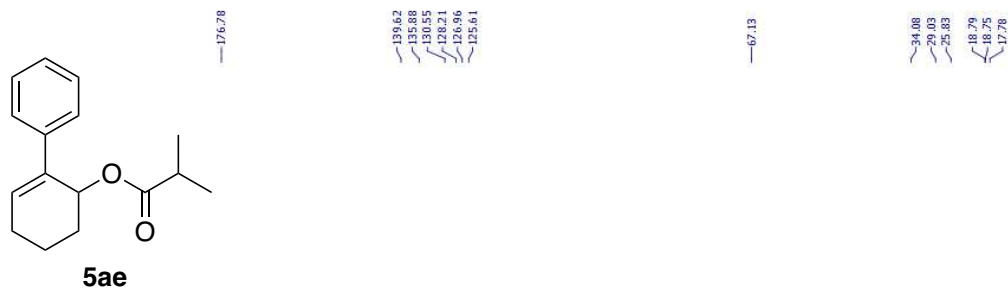


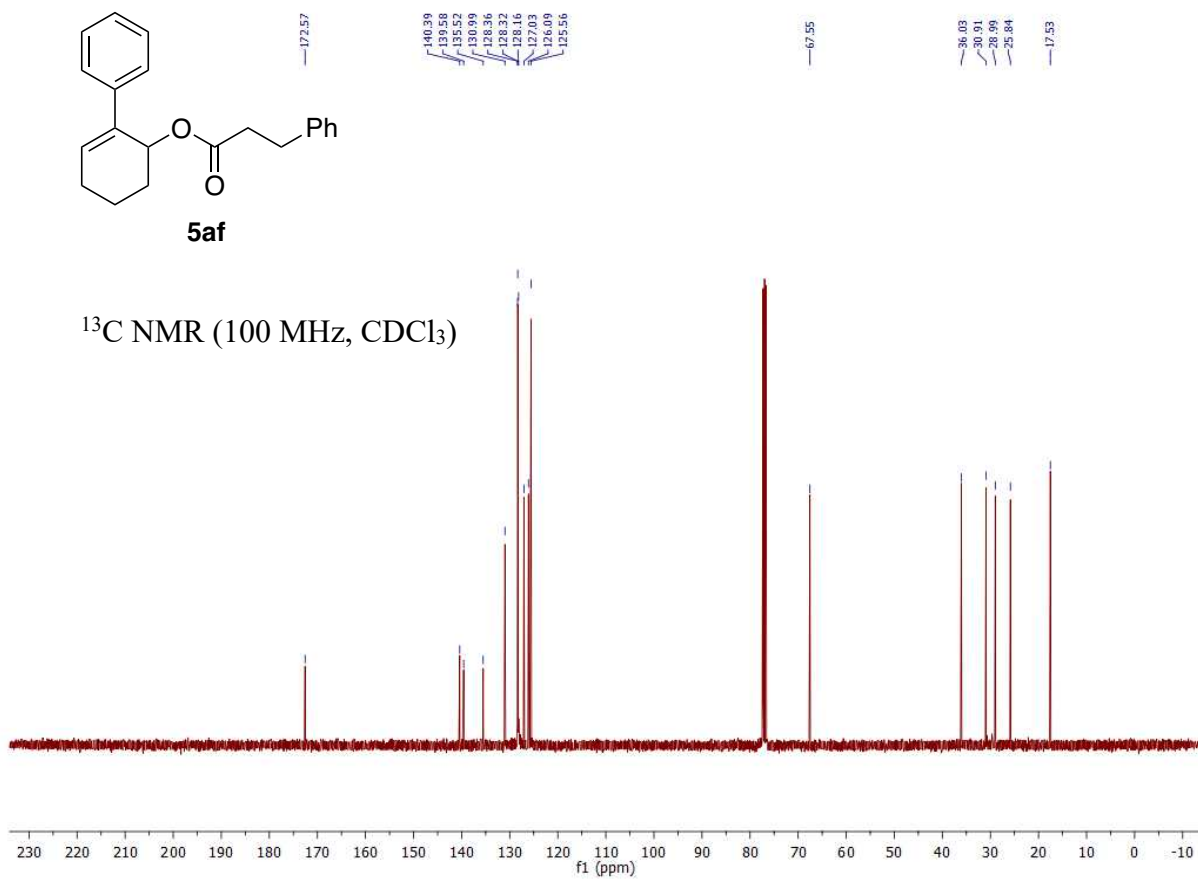
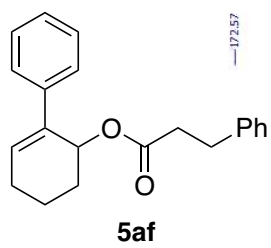


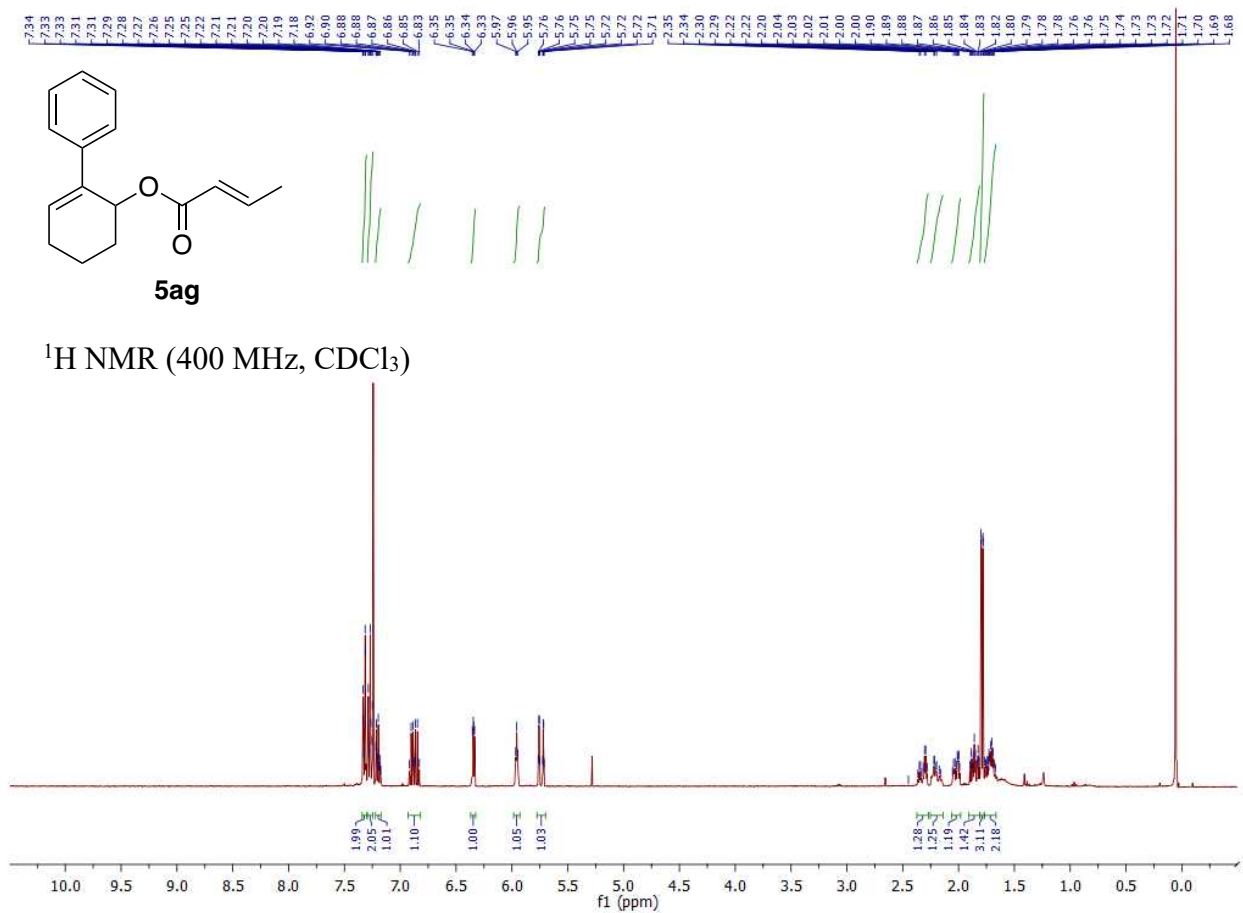


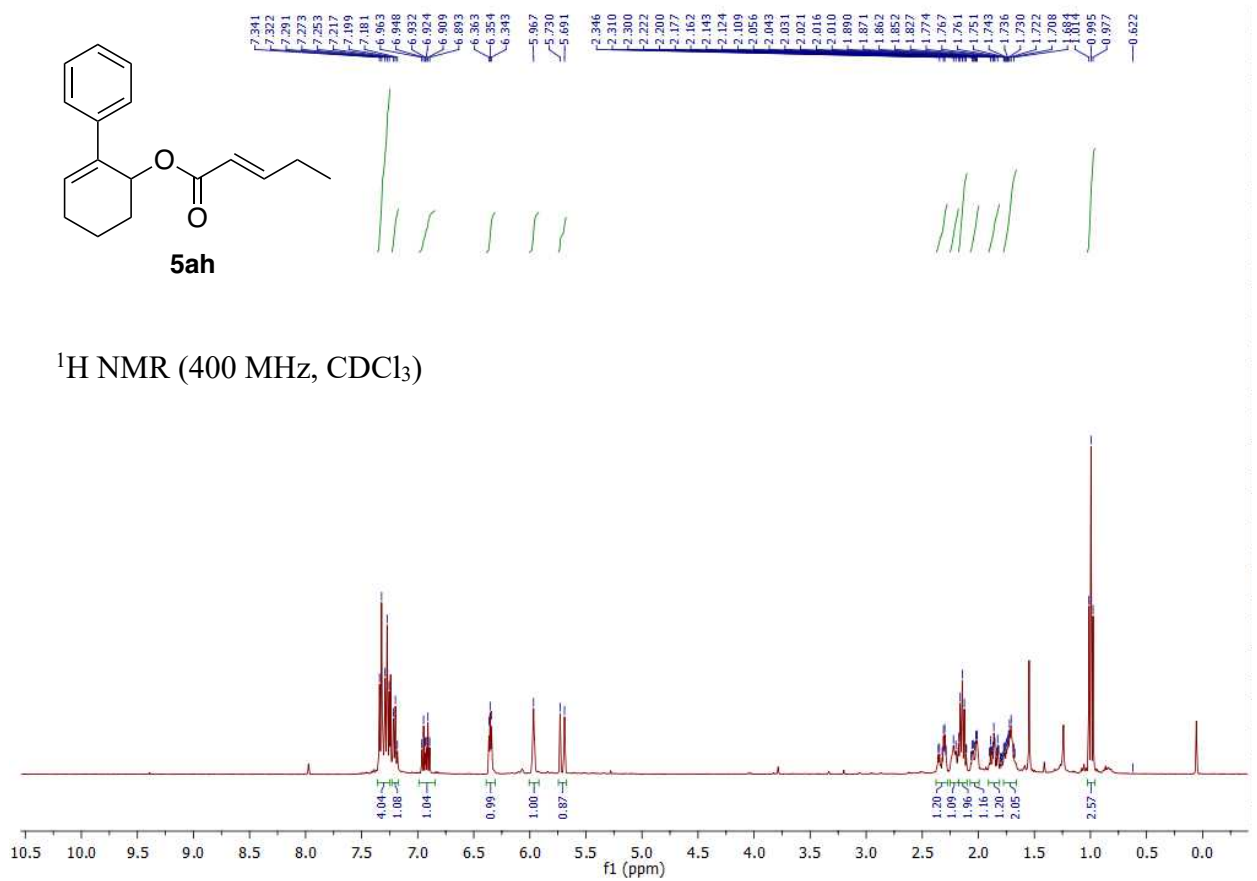
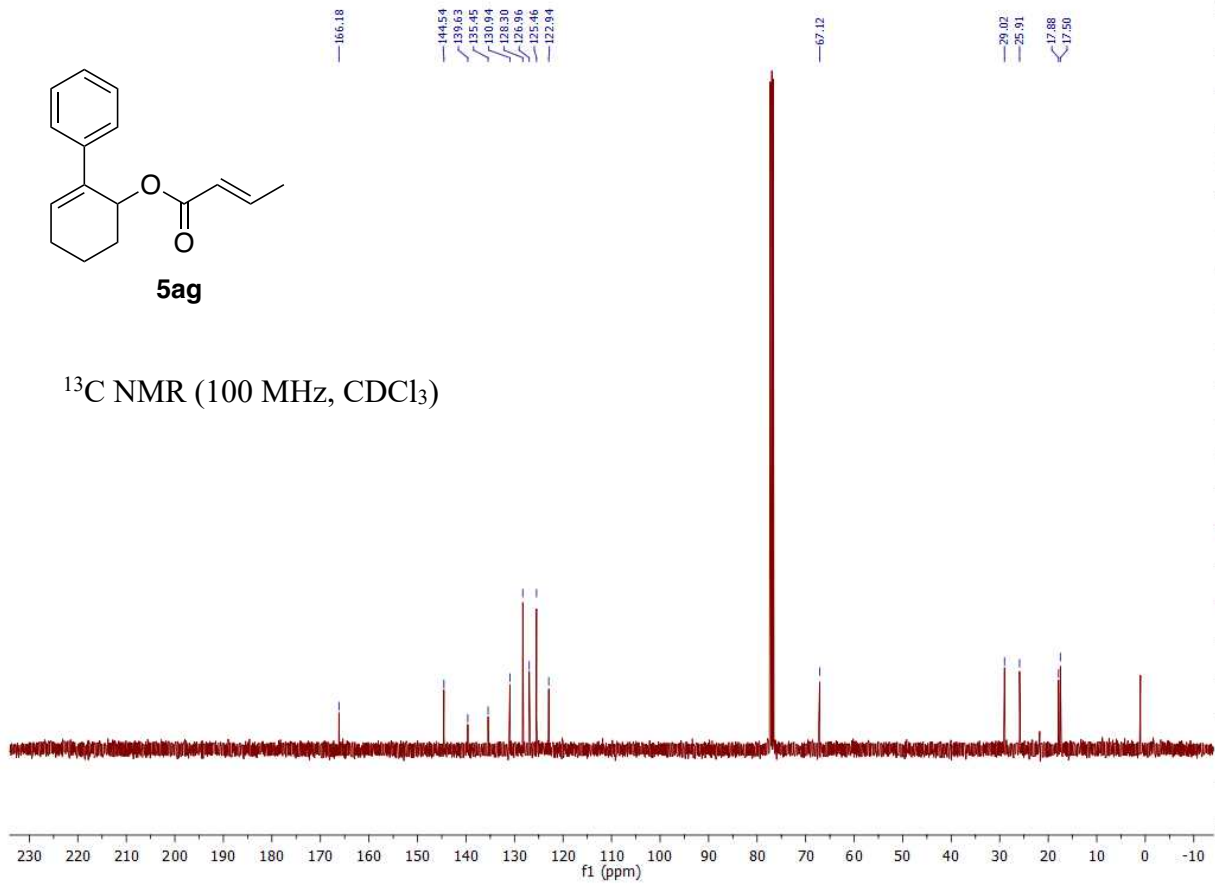


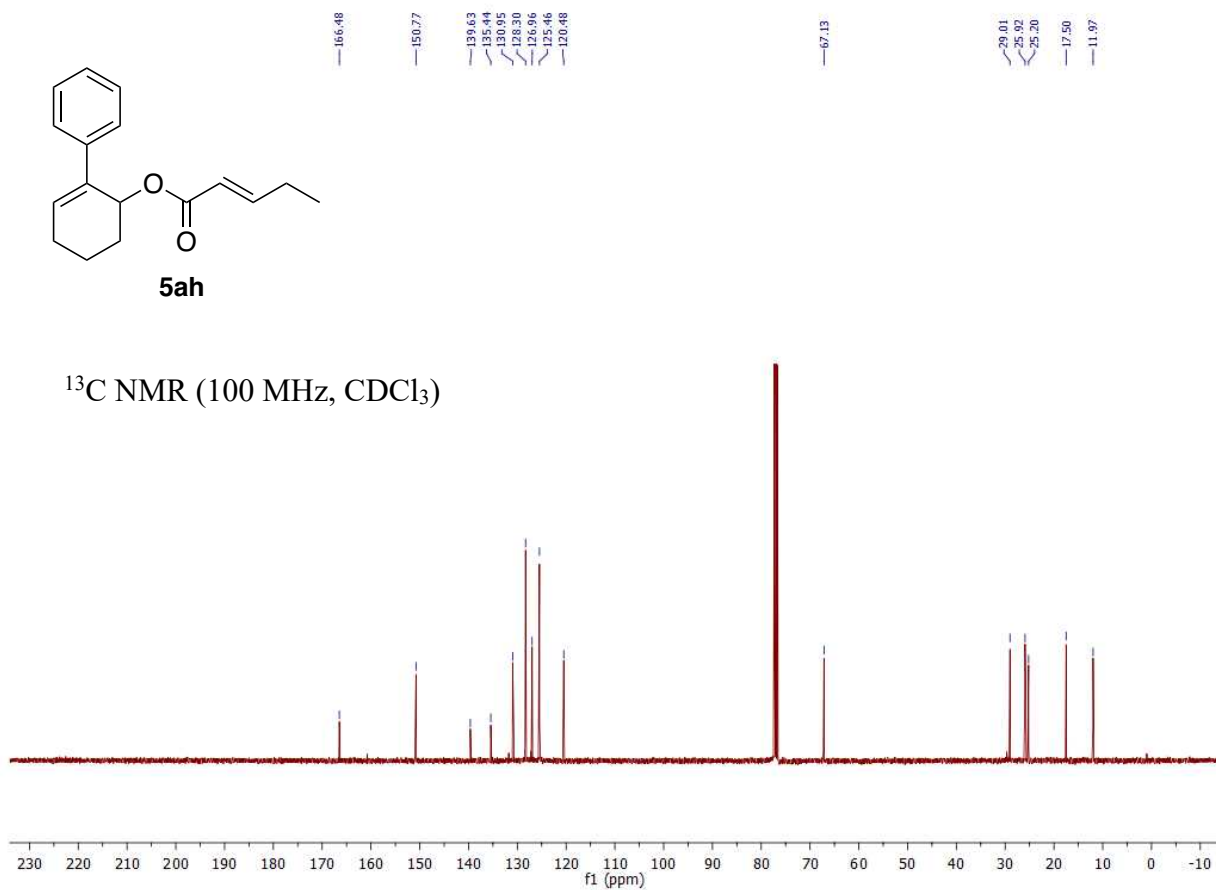
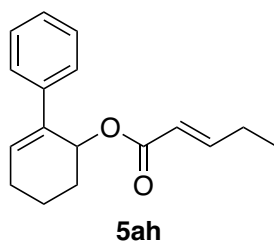




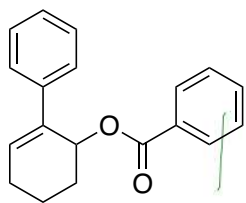






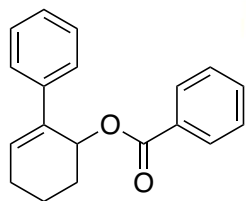
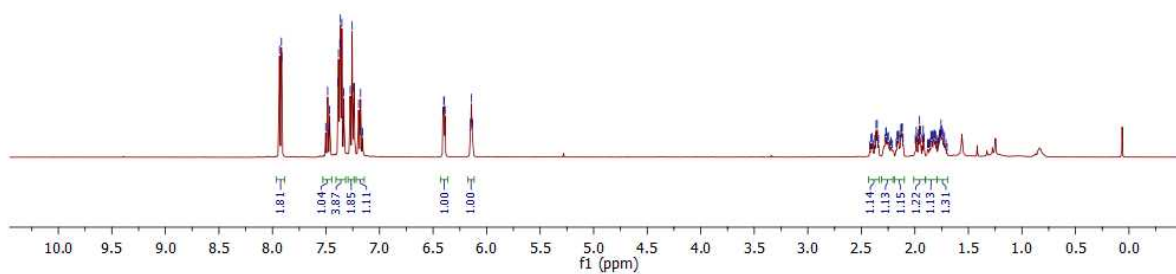


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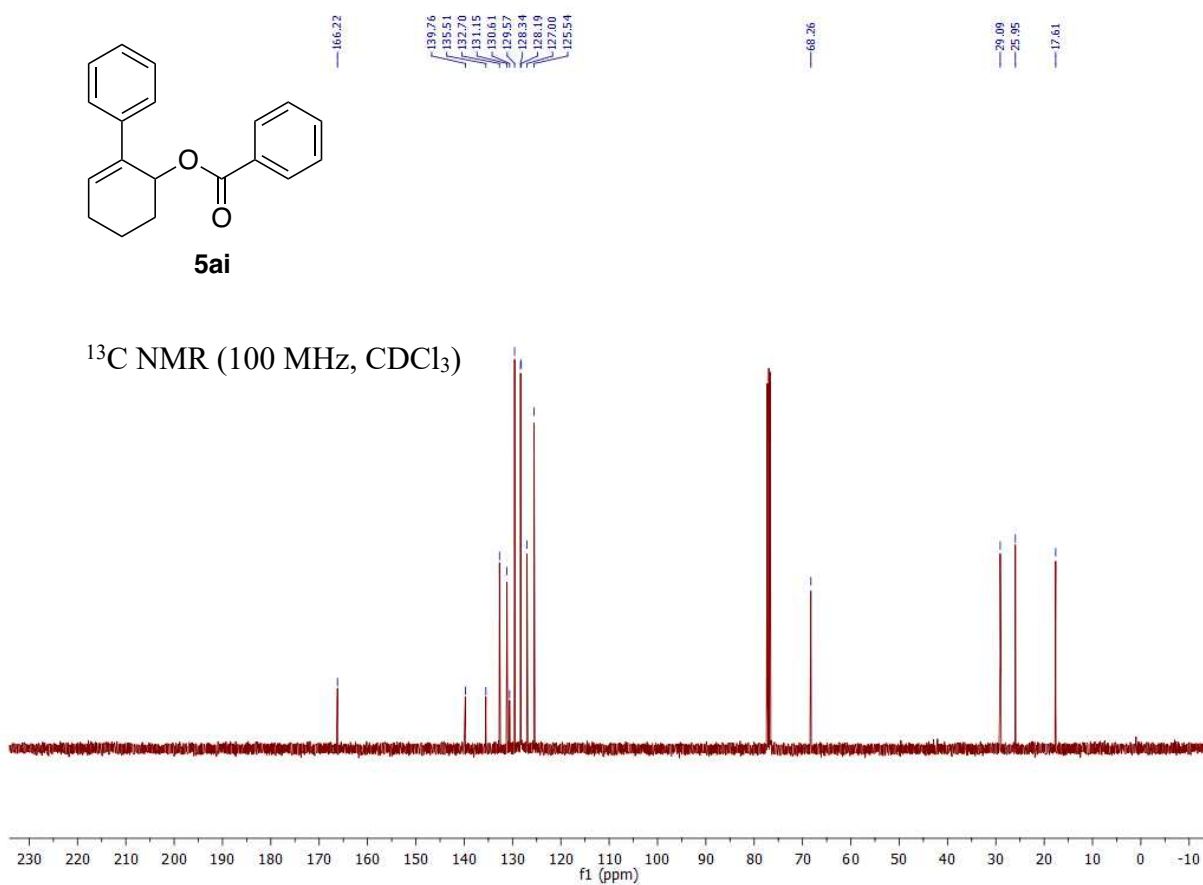
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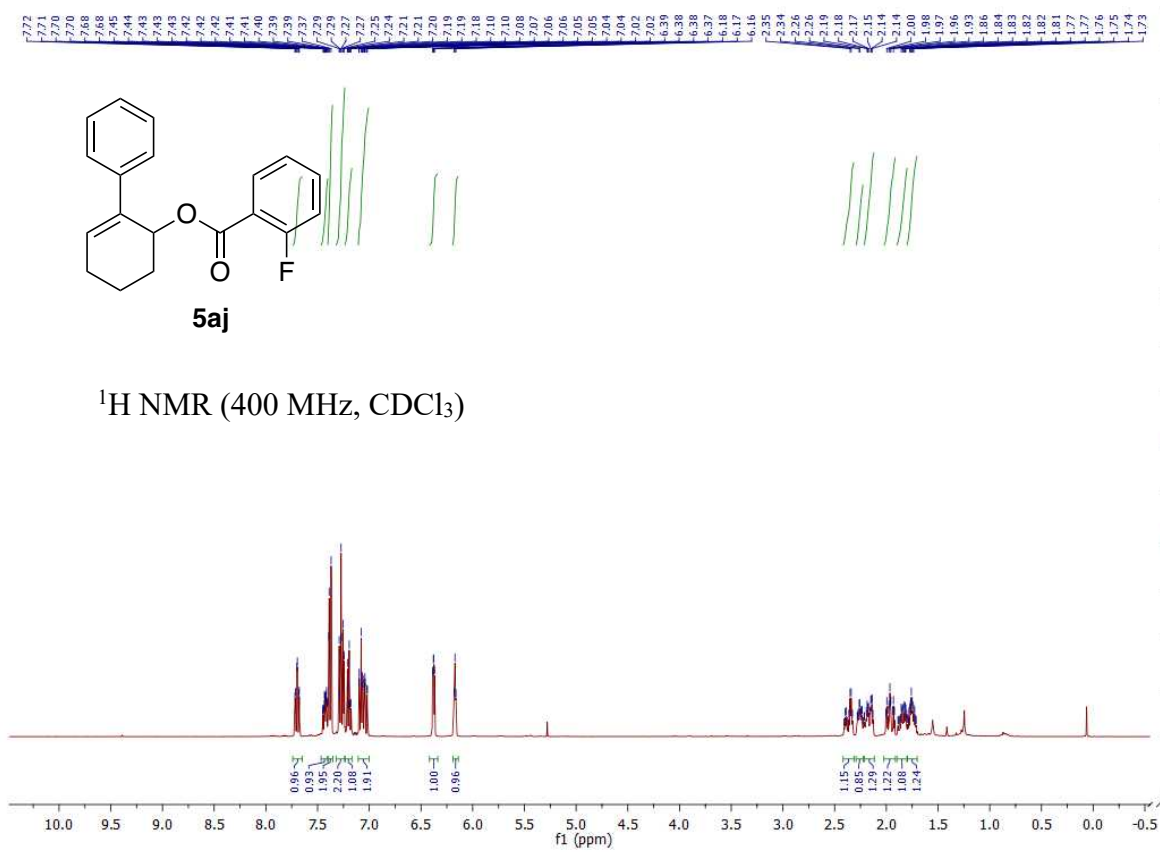
$^1\text{H NMR}$ (400 MHz, CDCl_3)

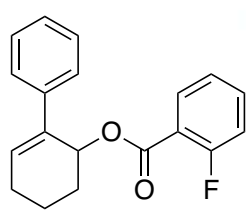


5ai

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



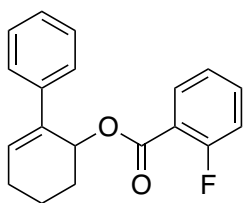
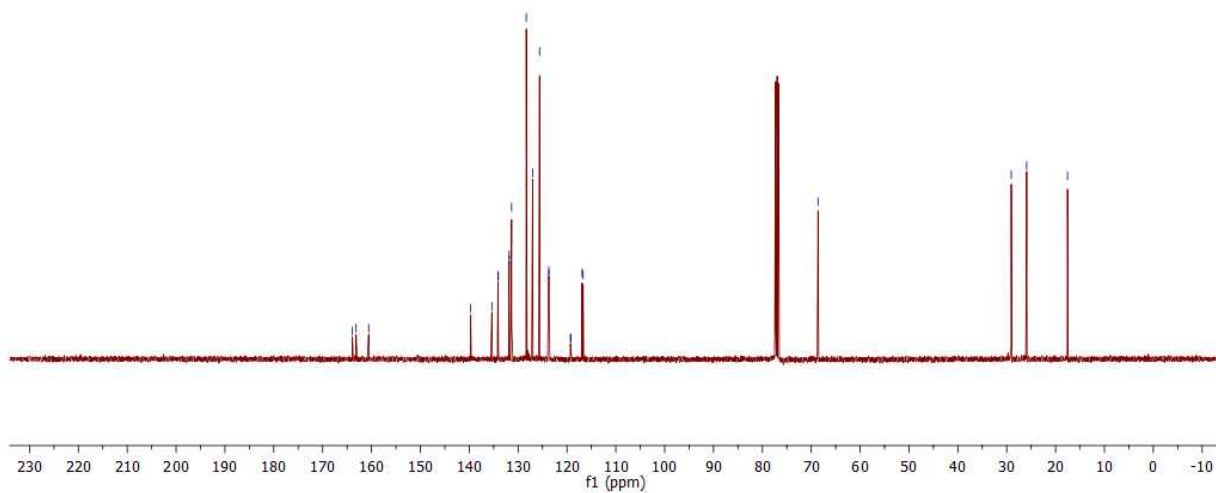




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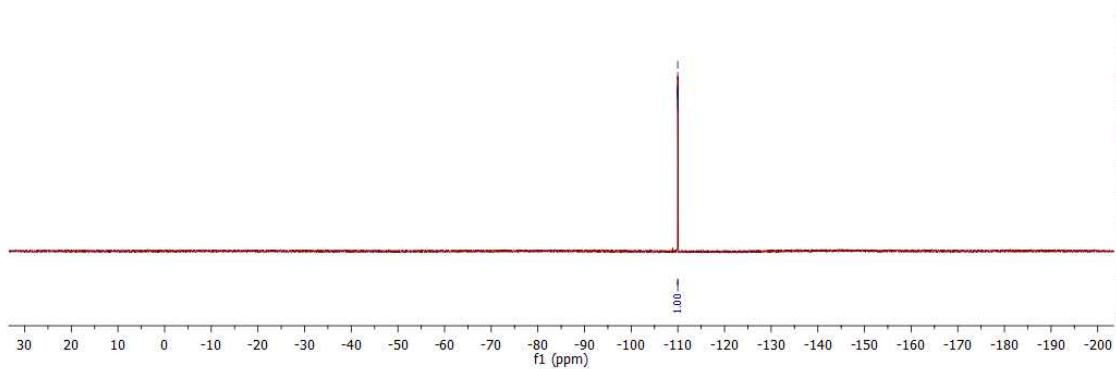
^{13}C NMR (100 MHz, CDCl_3)

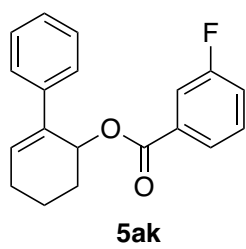
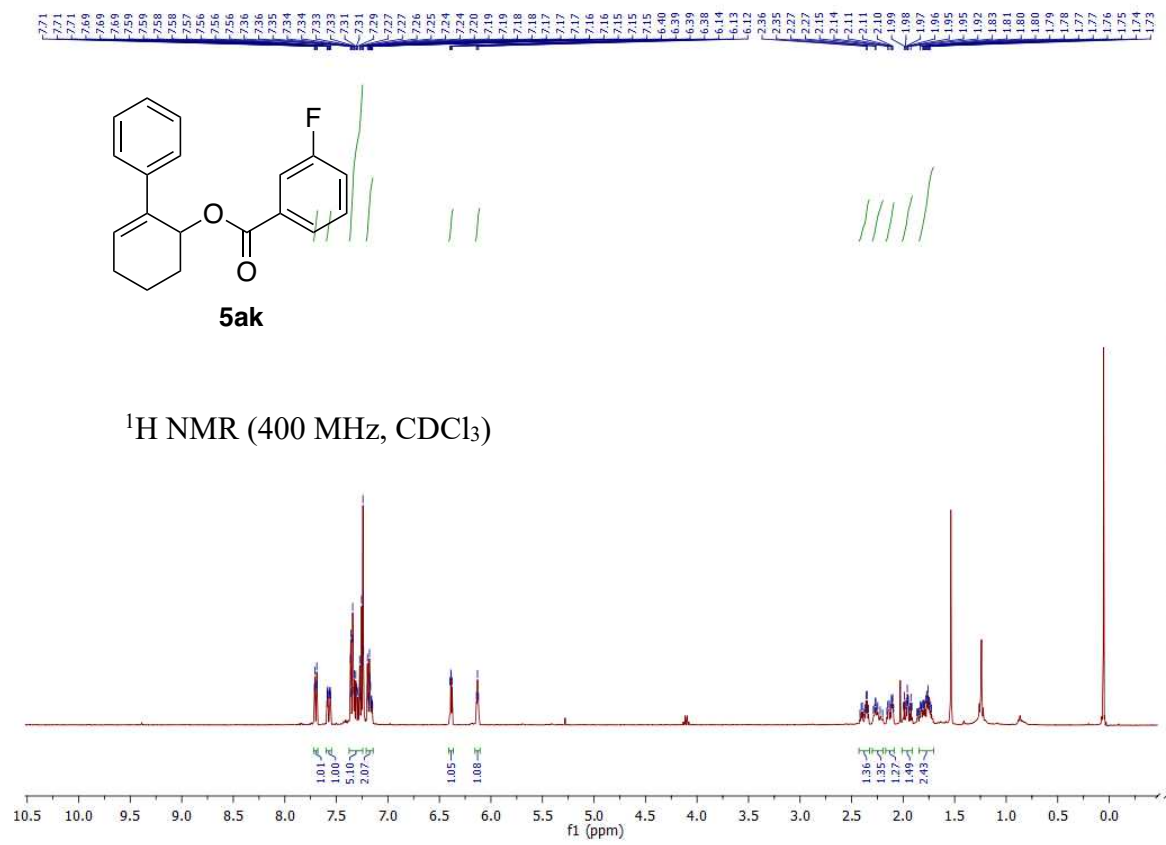


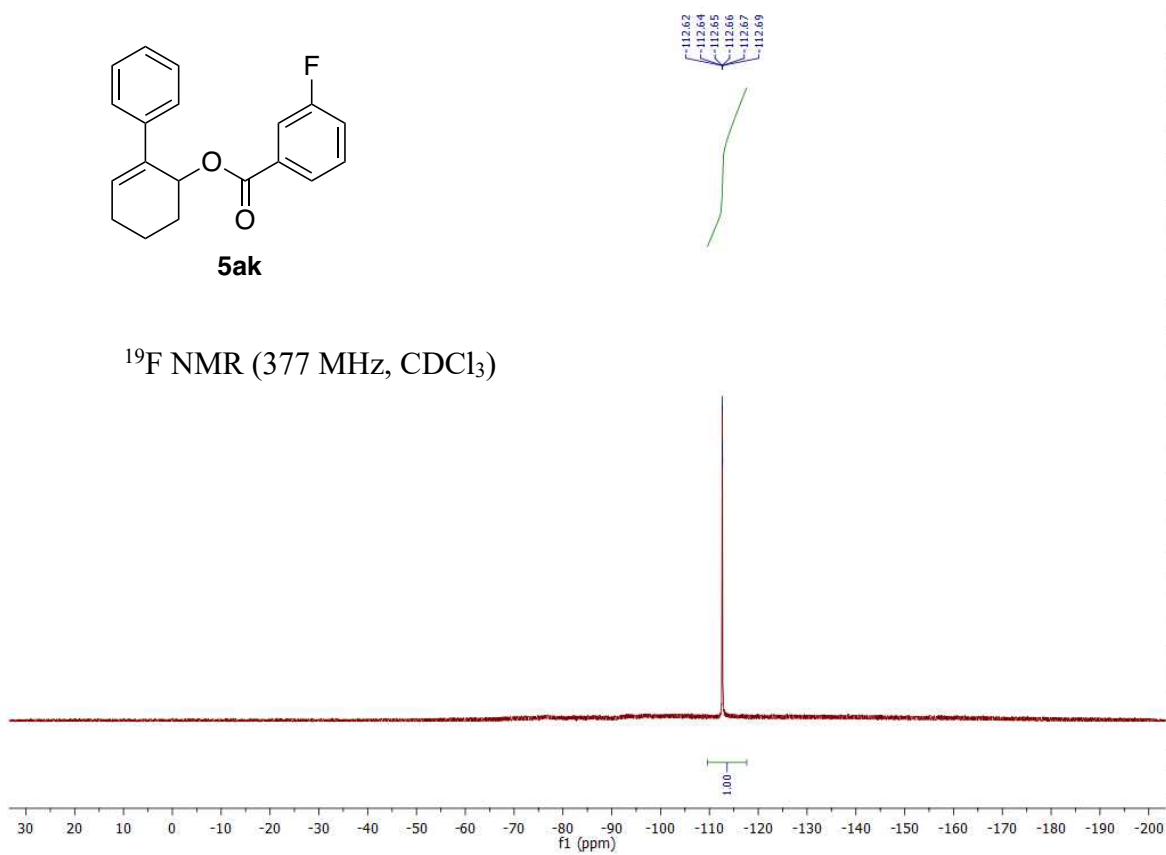
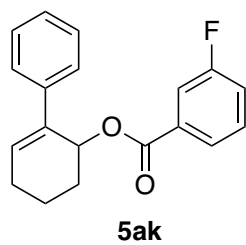
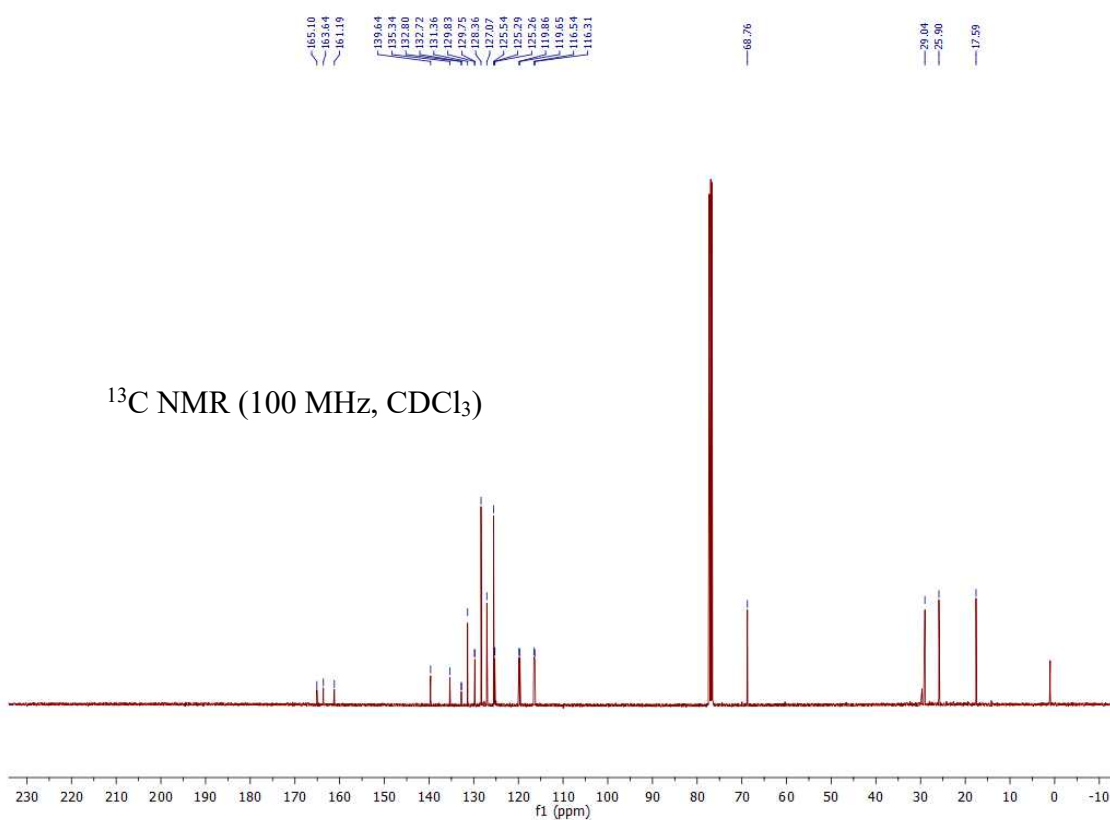
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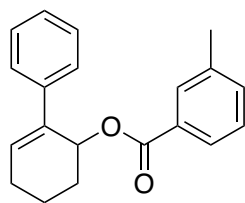


^{19}F NMR (377 MHz, CDCl_3)

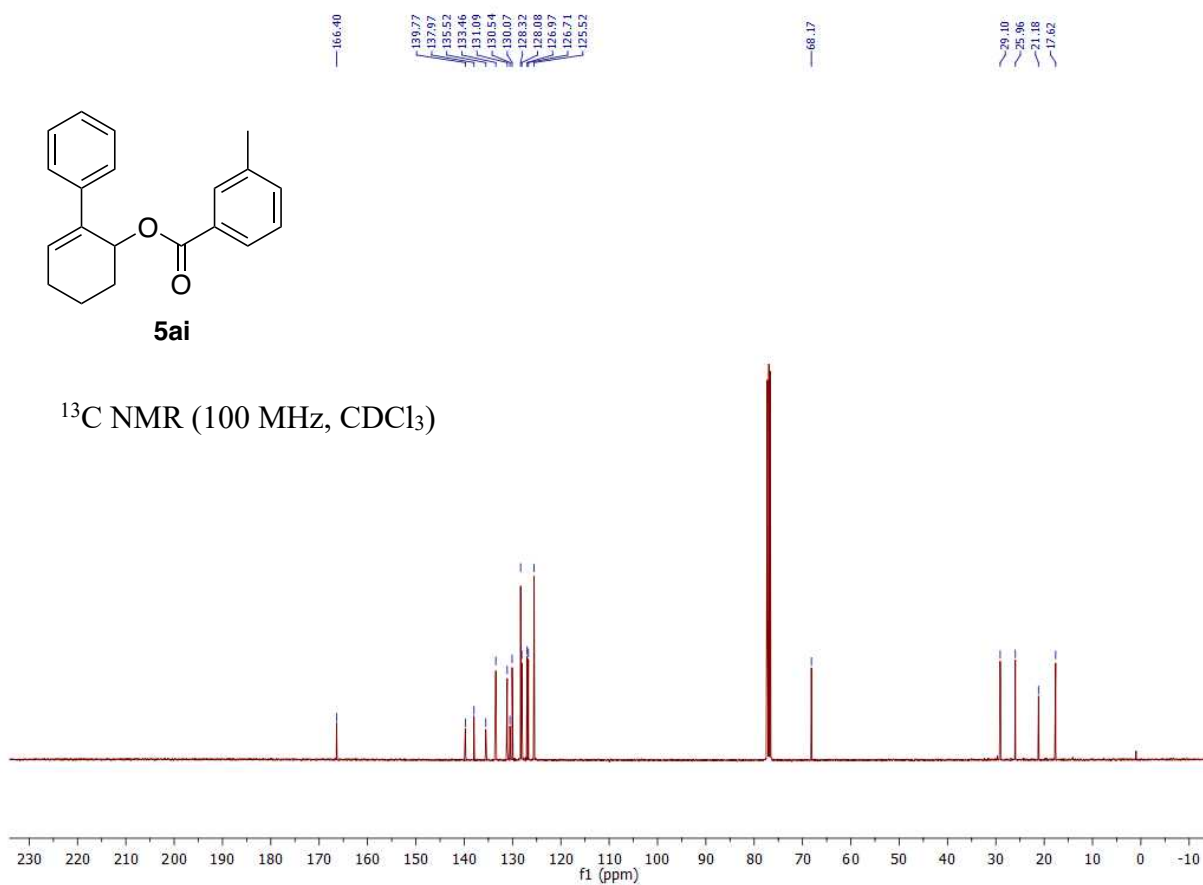


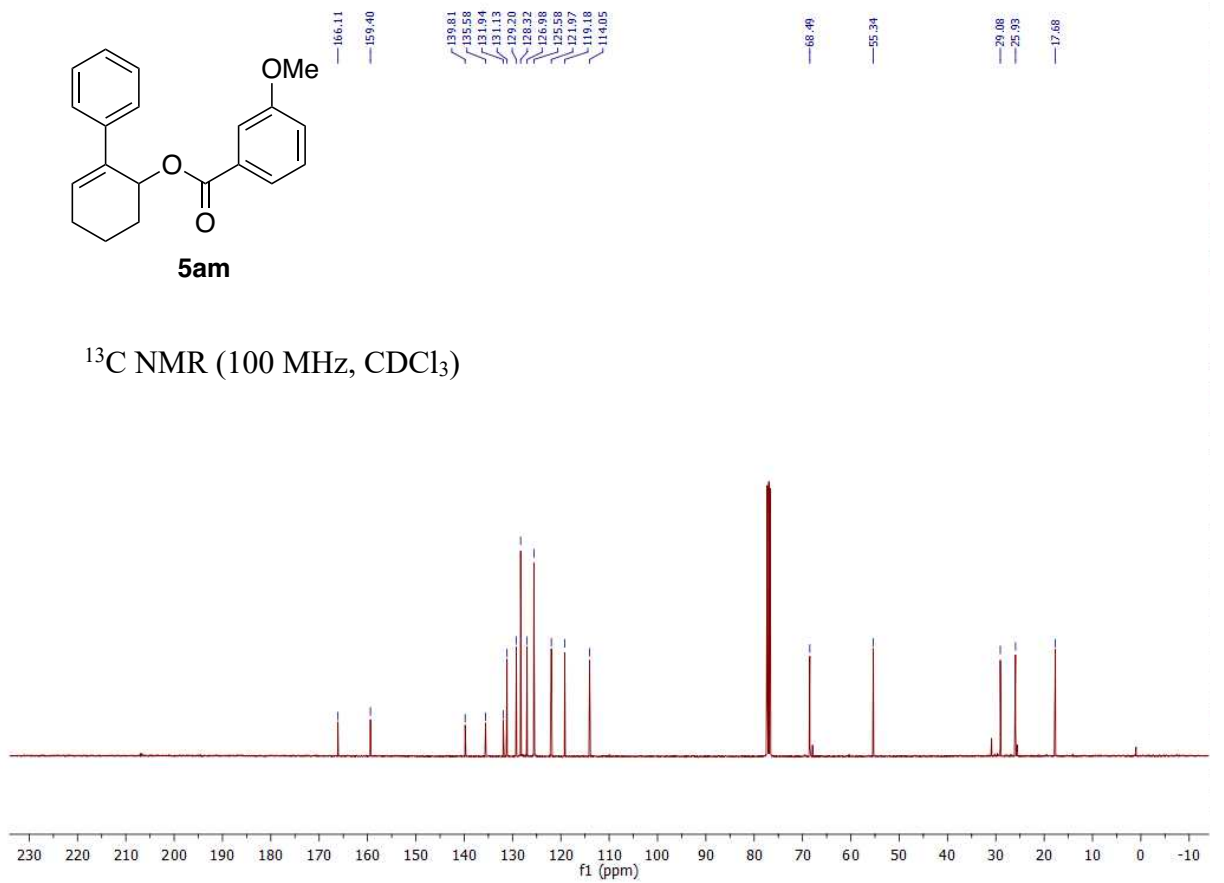
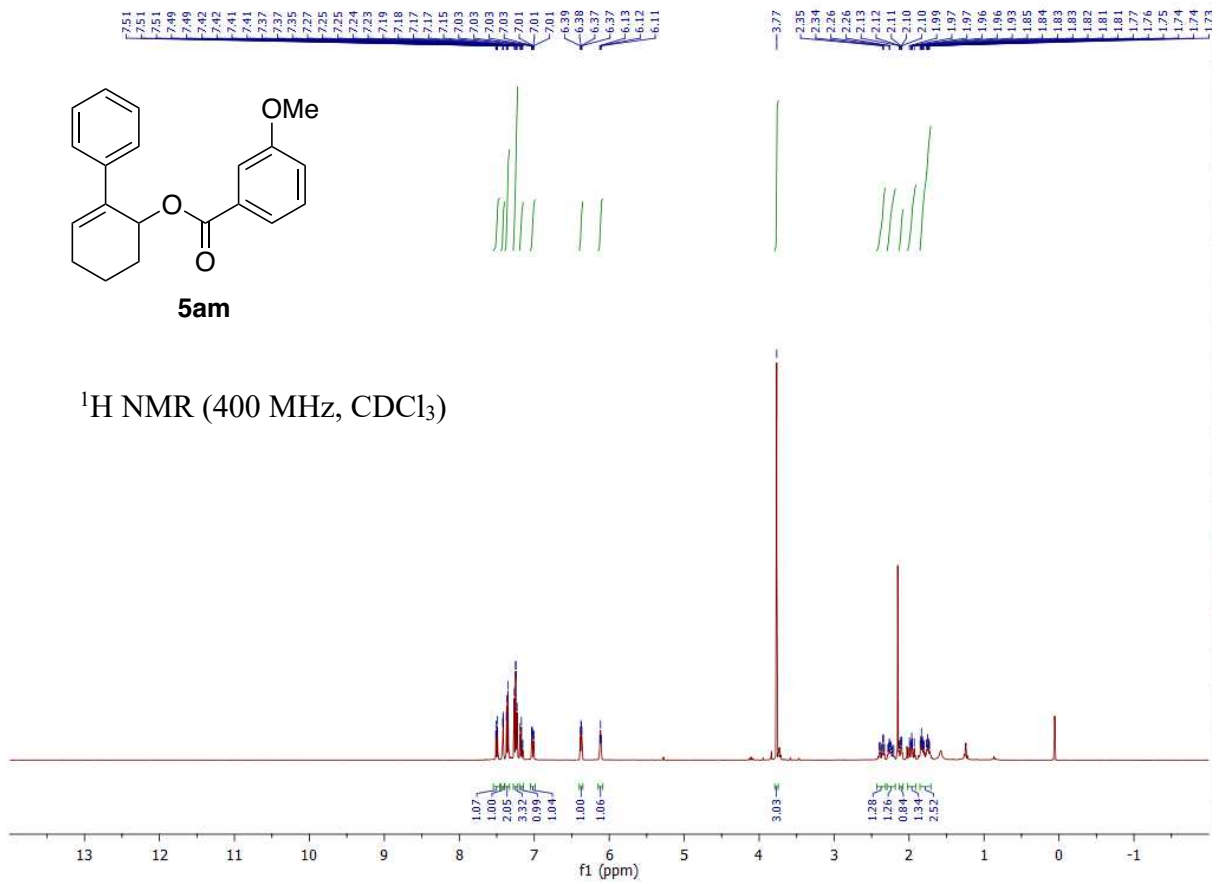


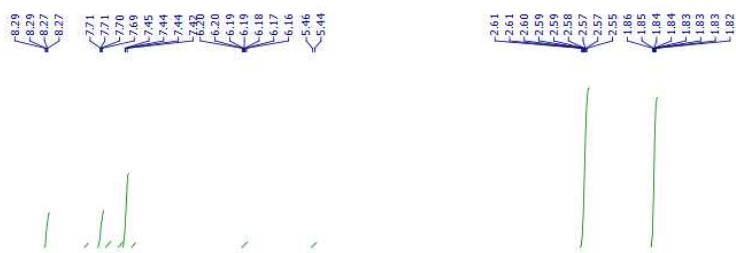
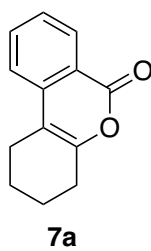




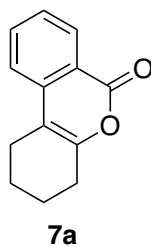
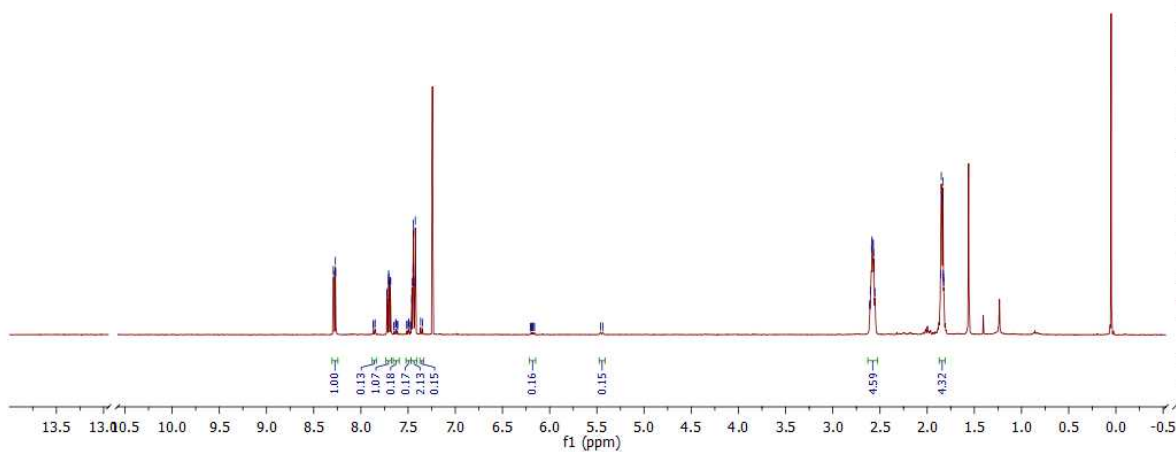
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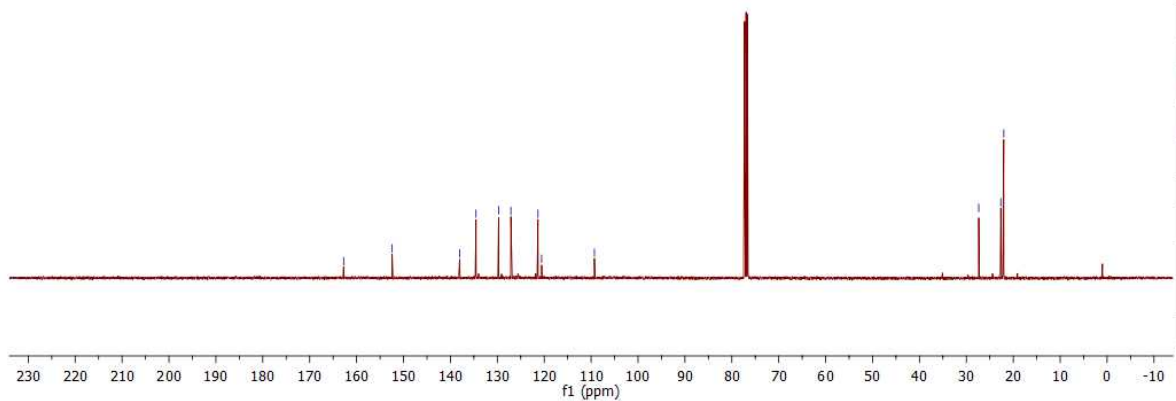


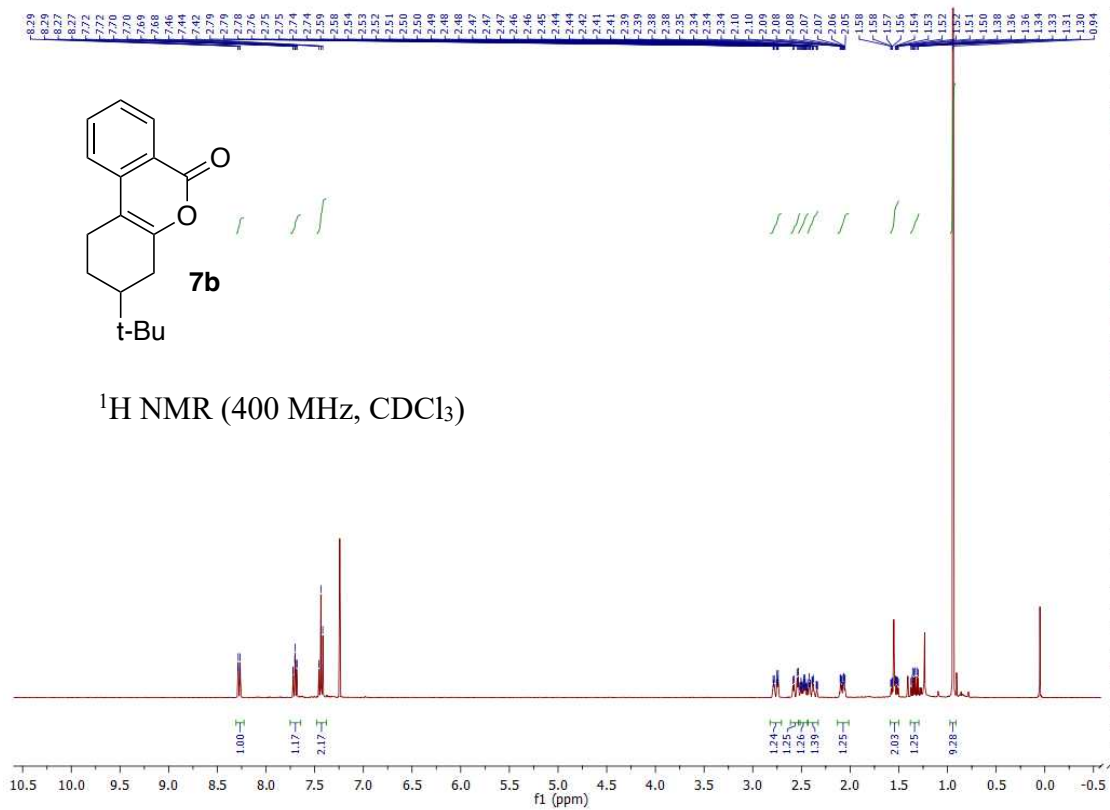


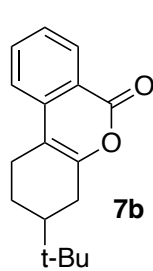
^1H NMR (400 MHz, CDCl_3)



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

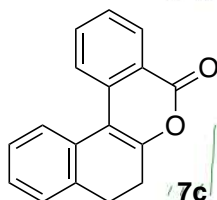
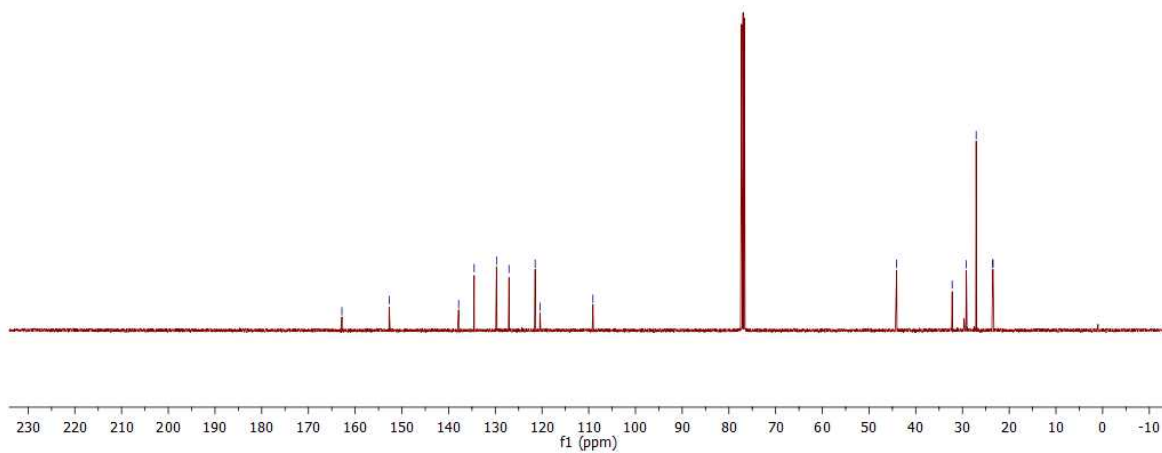






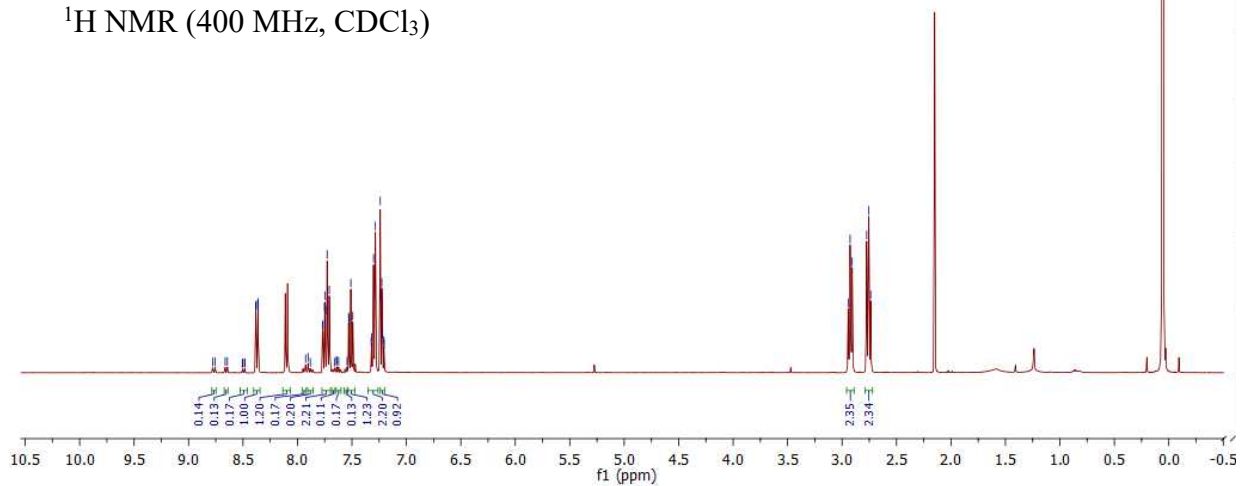
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 23.46

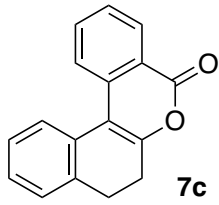
^{13}C NMR (100 MHz, CDCl_3)



8.78
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^1H NMR (400 MHz, CDCl_3)

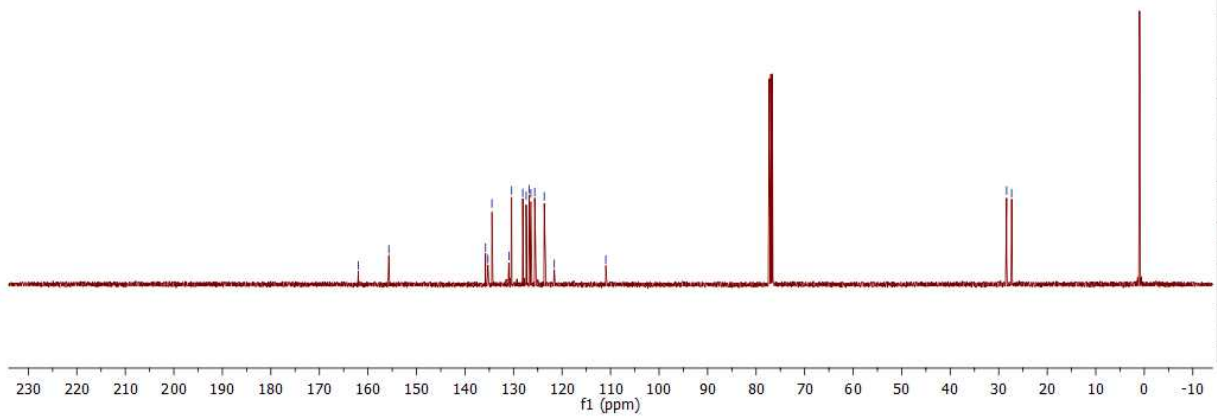




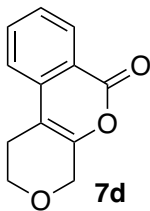
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110.98

28.37
27.34

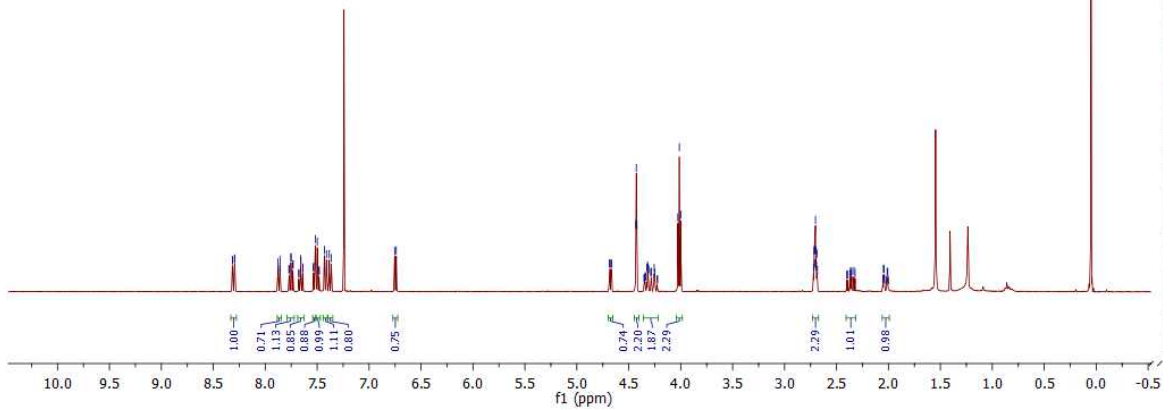
^{13}C NMR (100 MHz, CDCl_3)

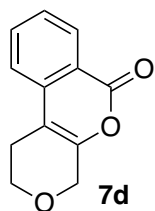


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7.66
7.64
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7.52
7.50
7.49
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7.38
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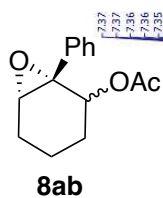
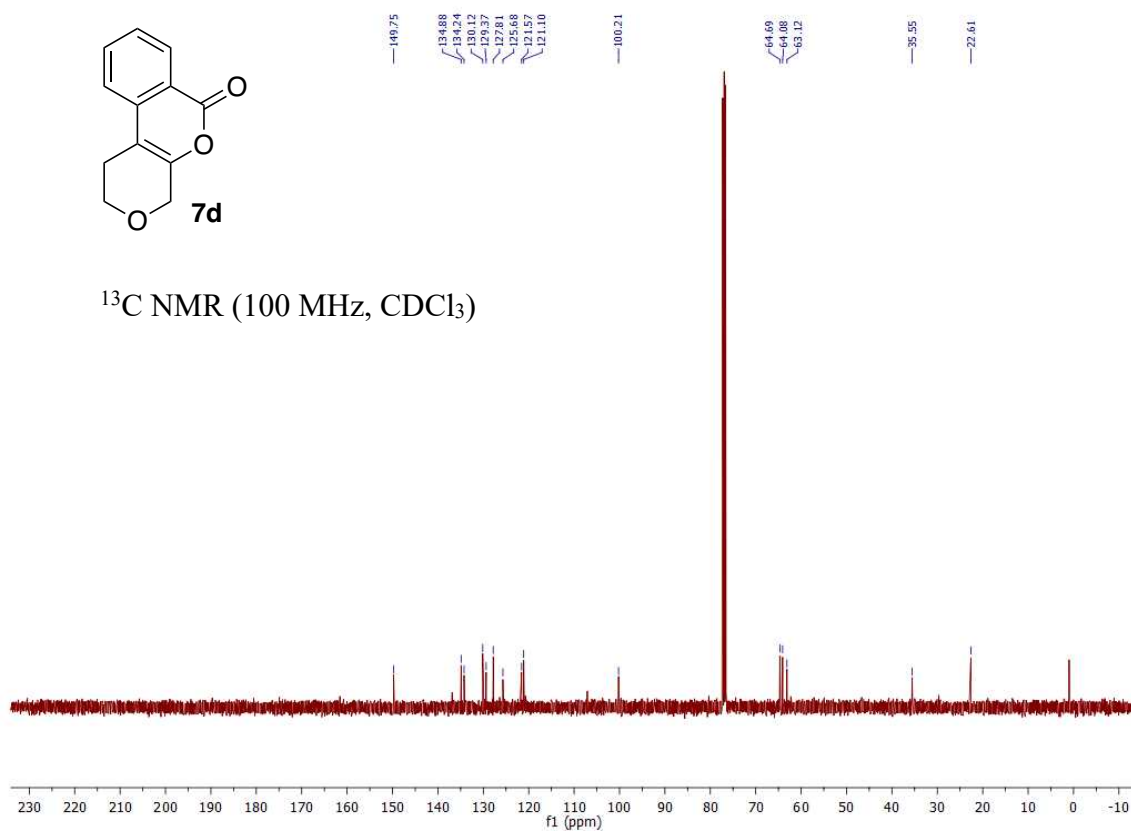


^1H NMR (400 MHz, CDCl_3)

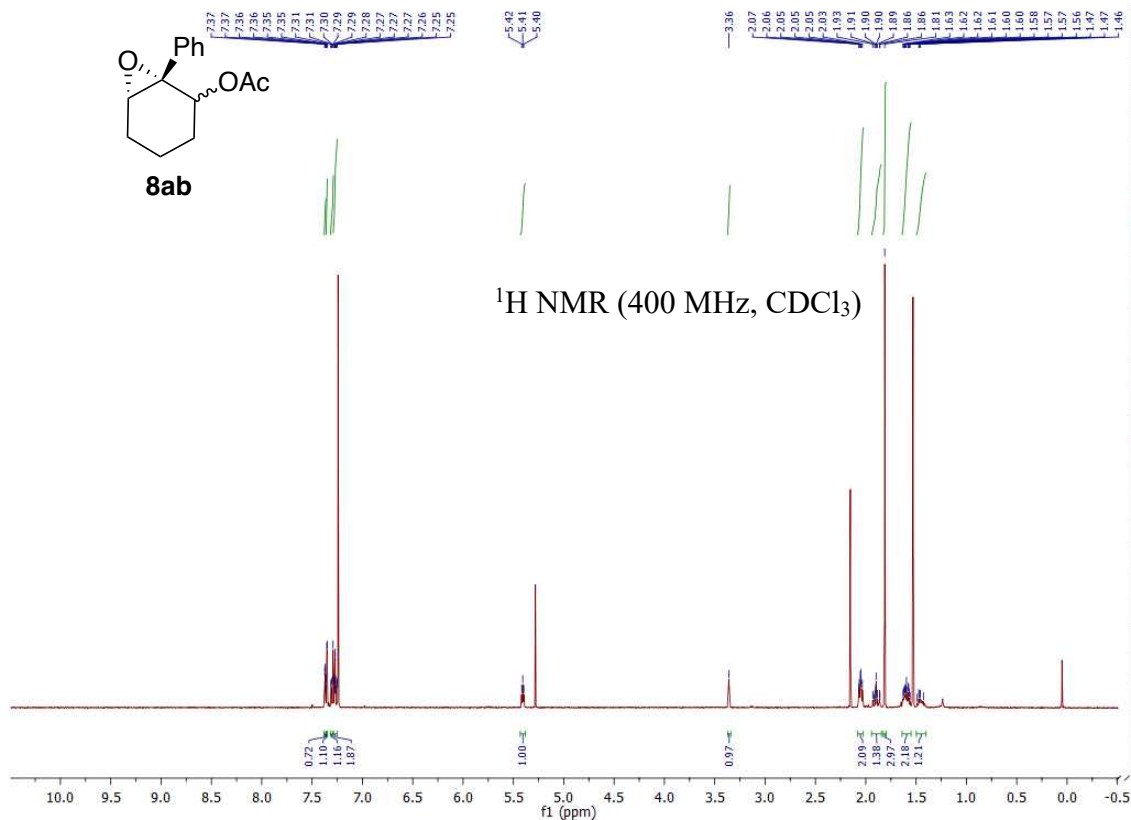


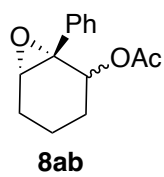


^{13}C NMR (100 MHz, CDCl_3)

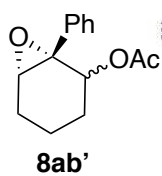
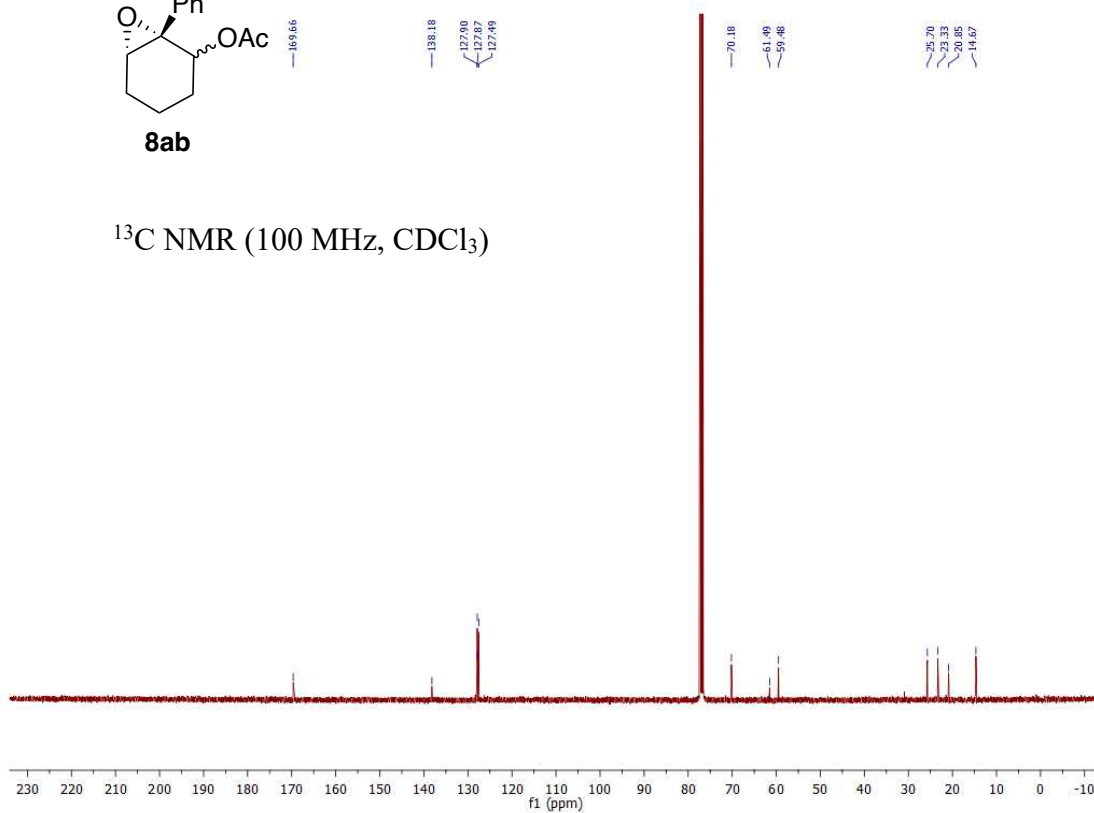


^1H NMR (400 MHz, CDCl_3)

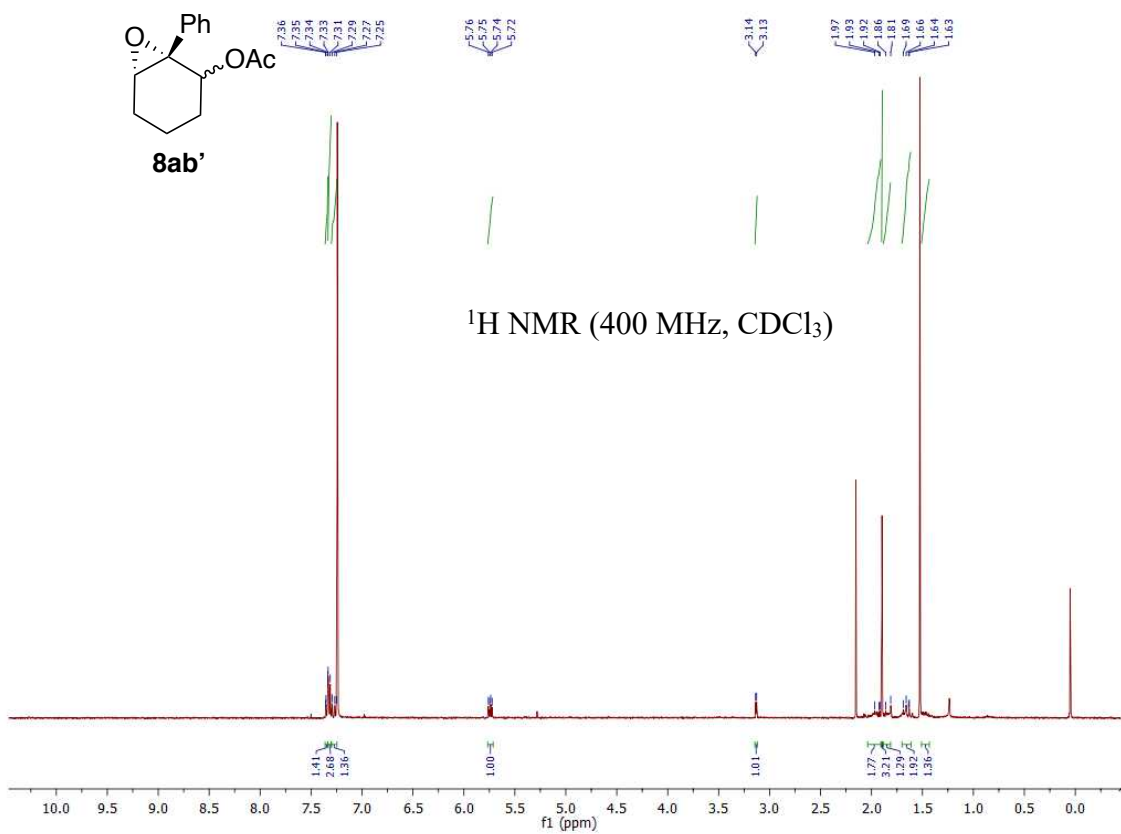


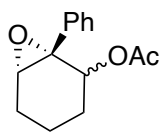


^{13}C NMR (100 MHz, CDCl_3)



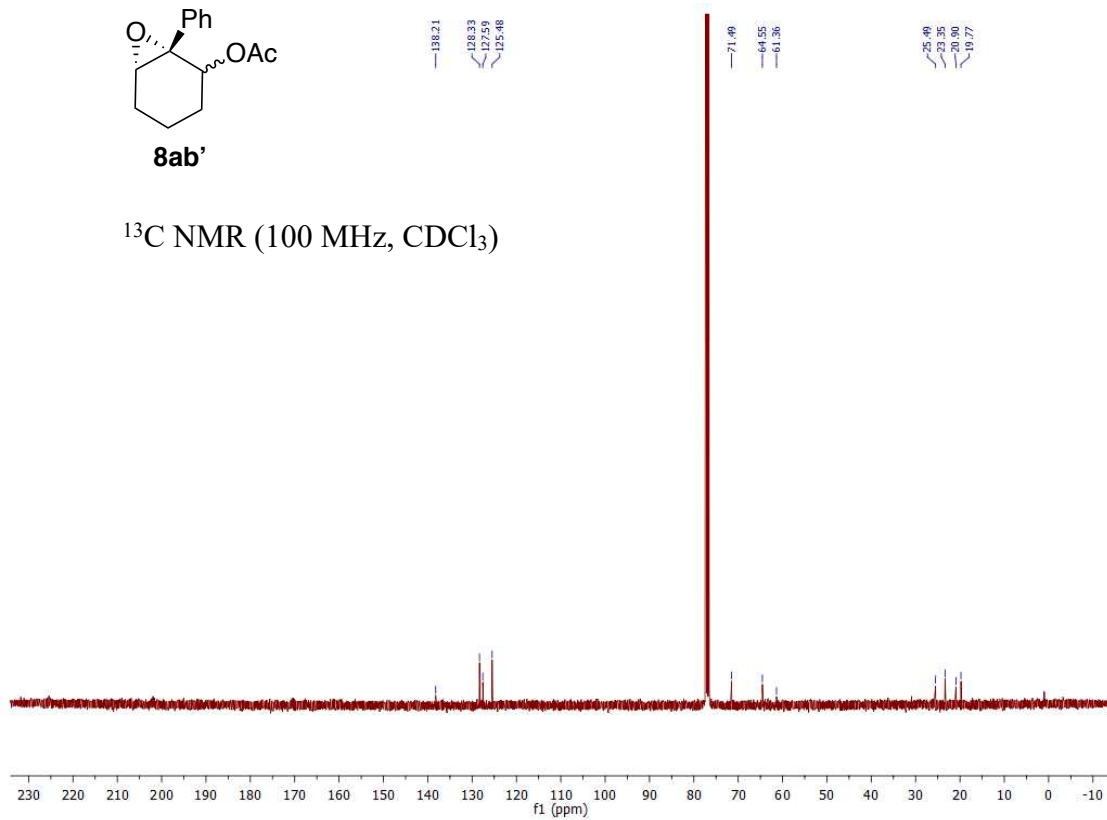
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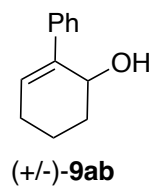
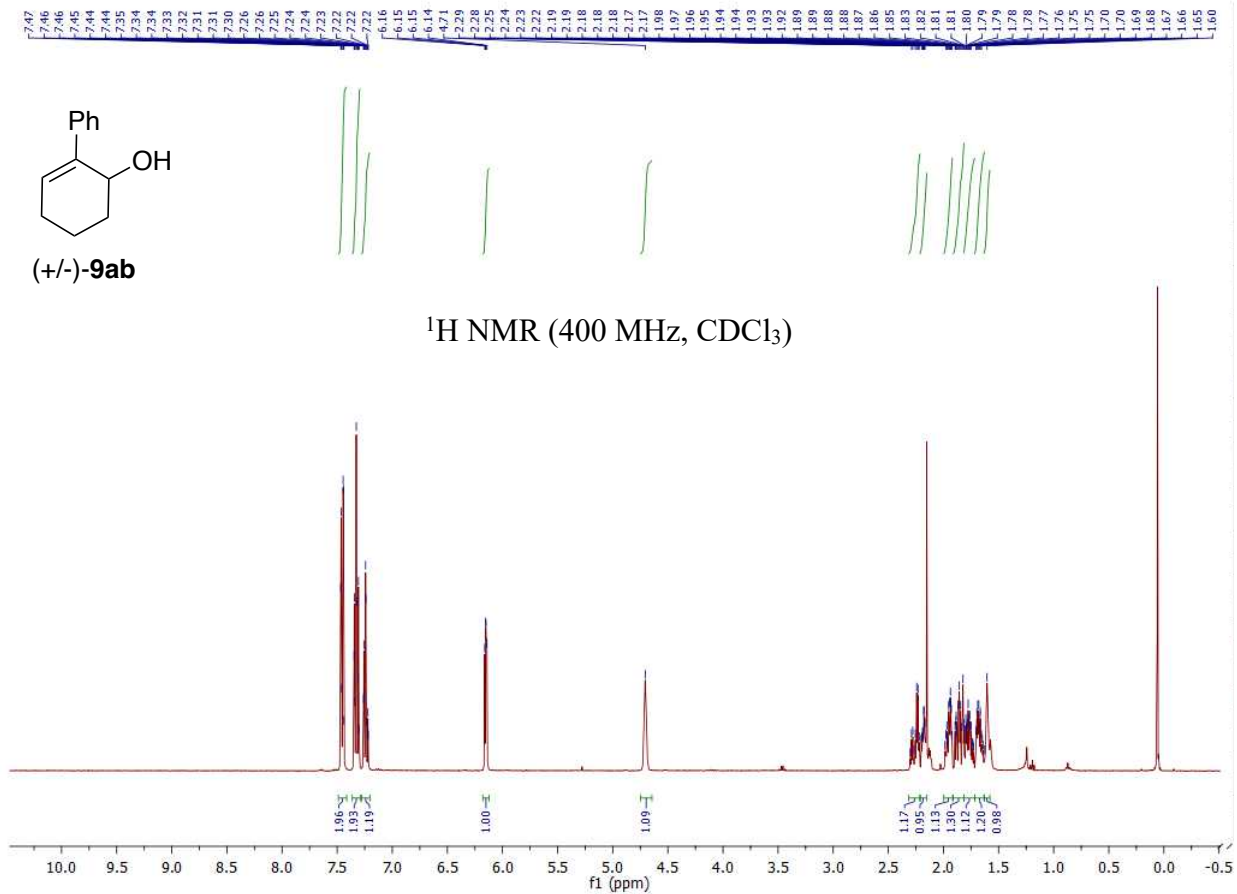


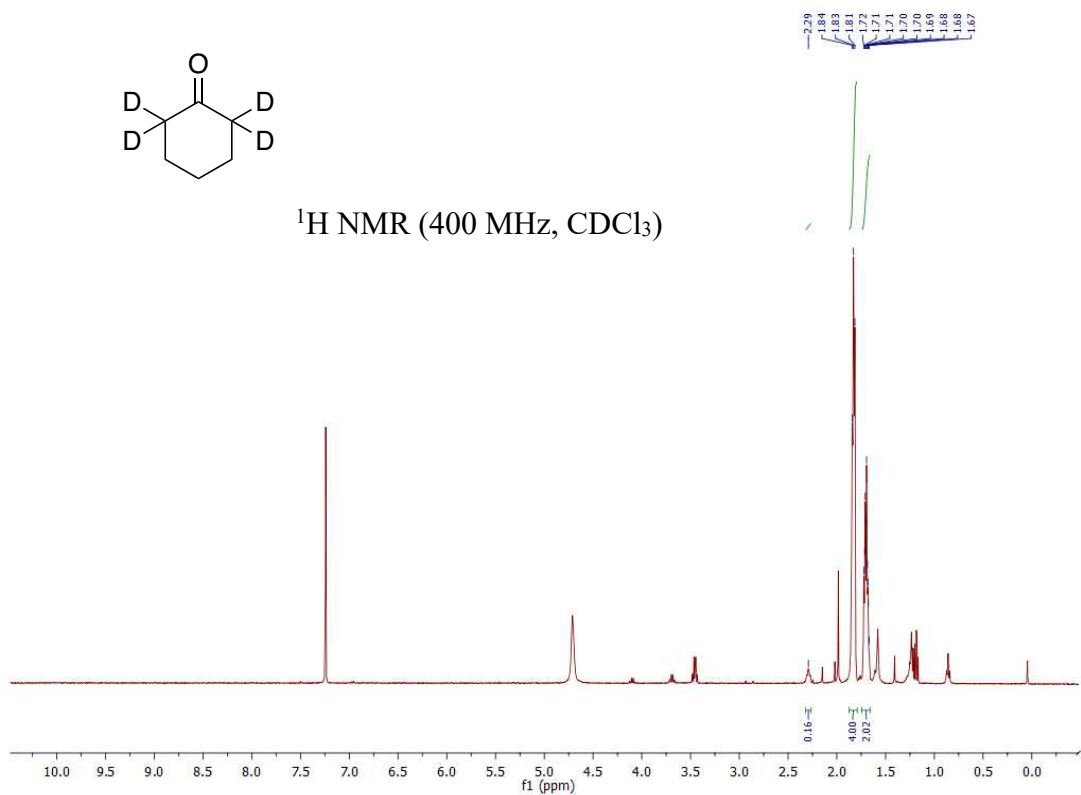
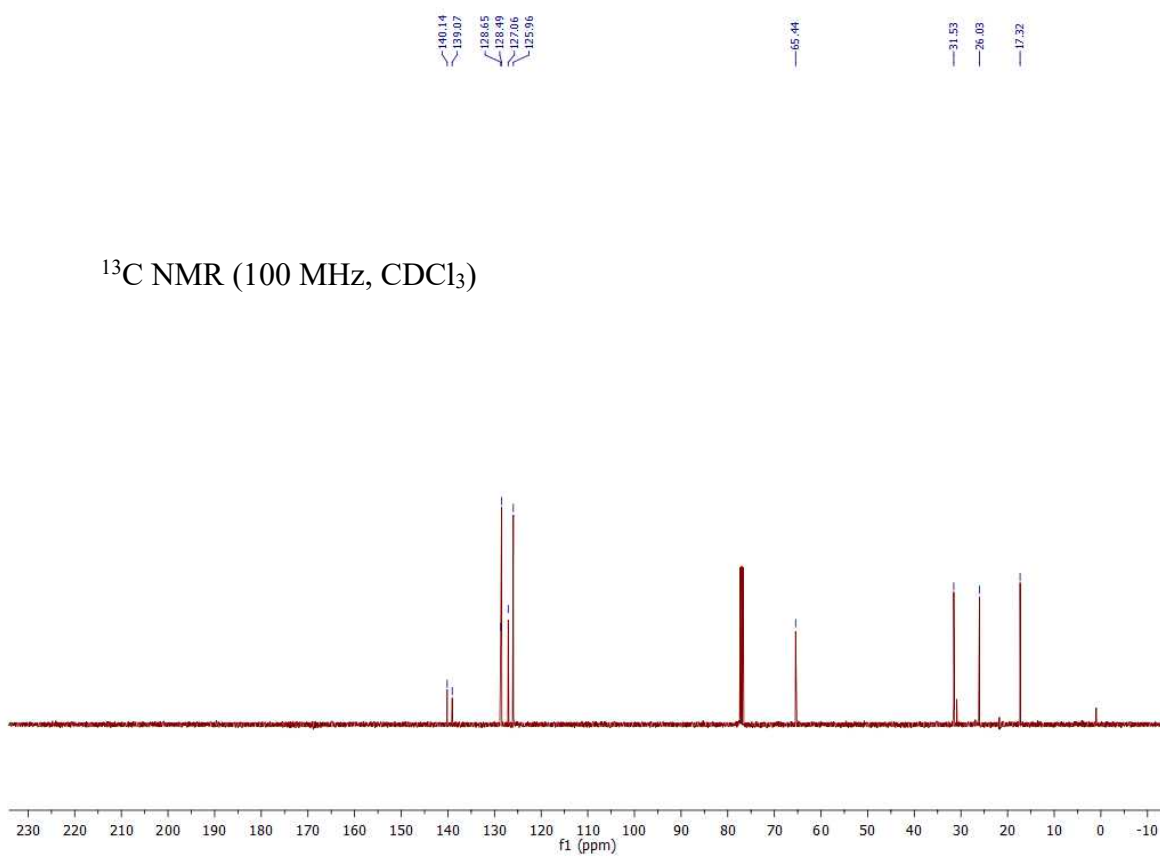


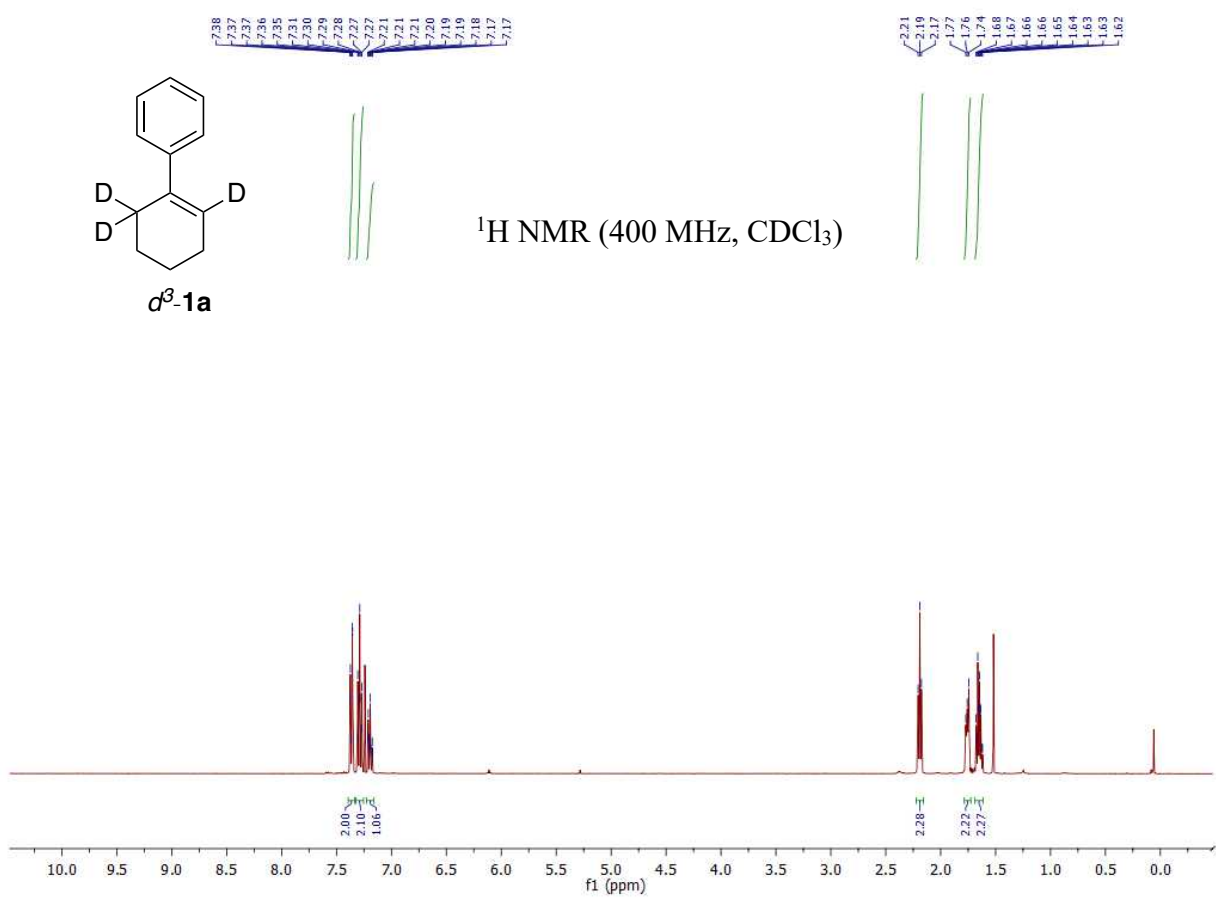
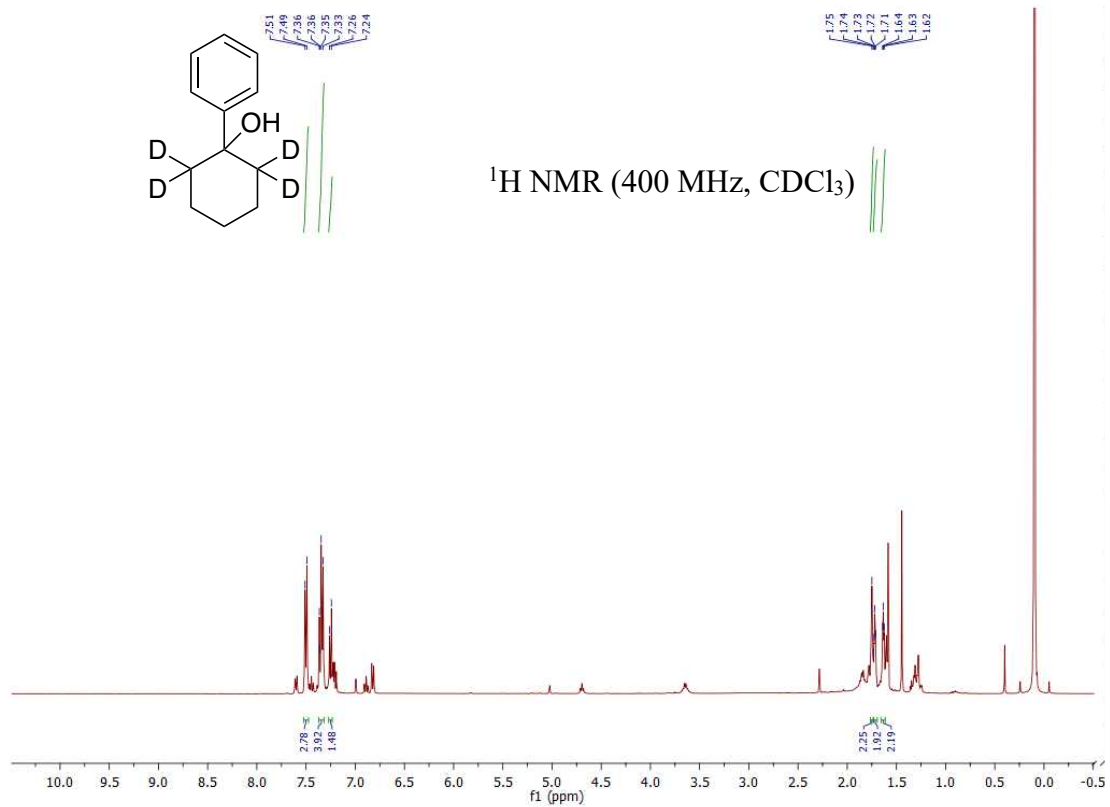
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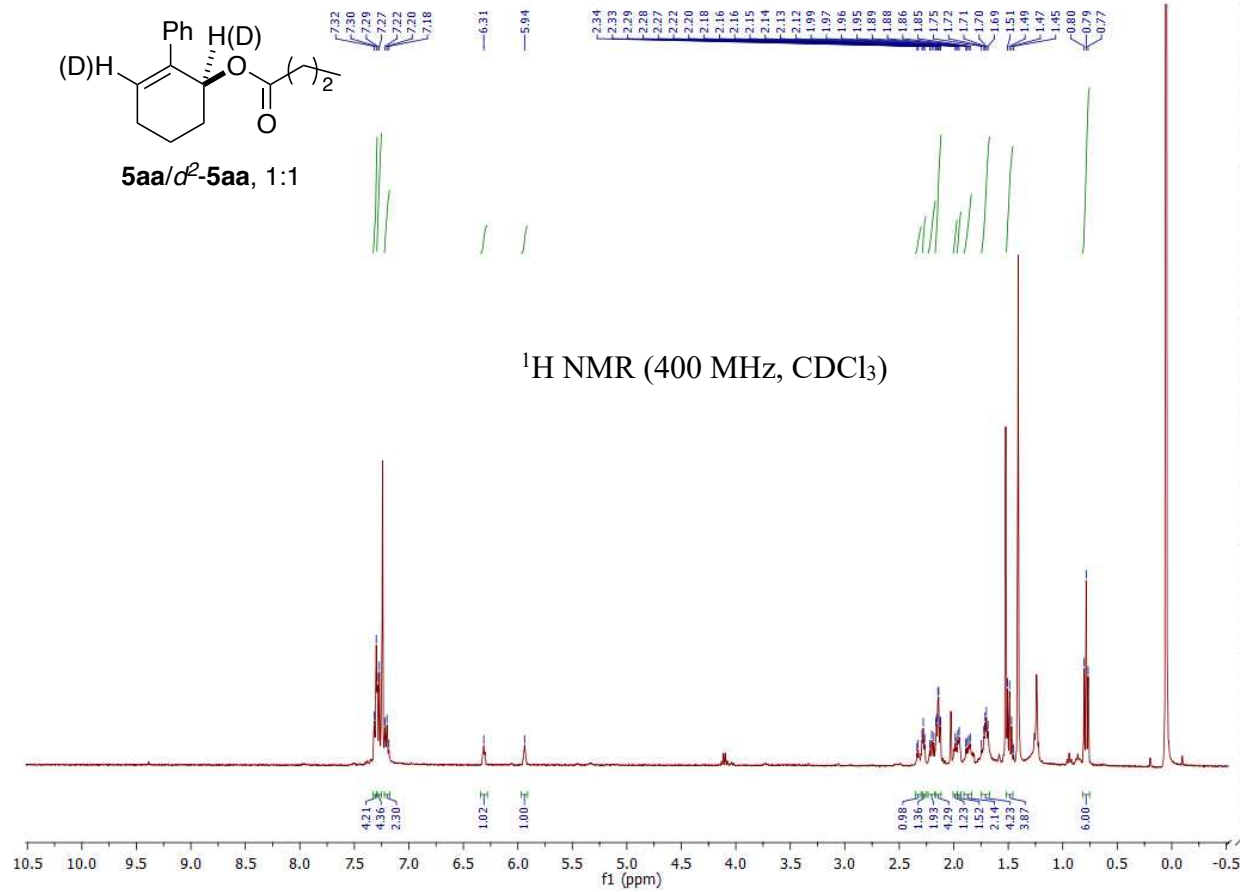
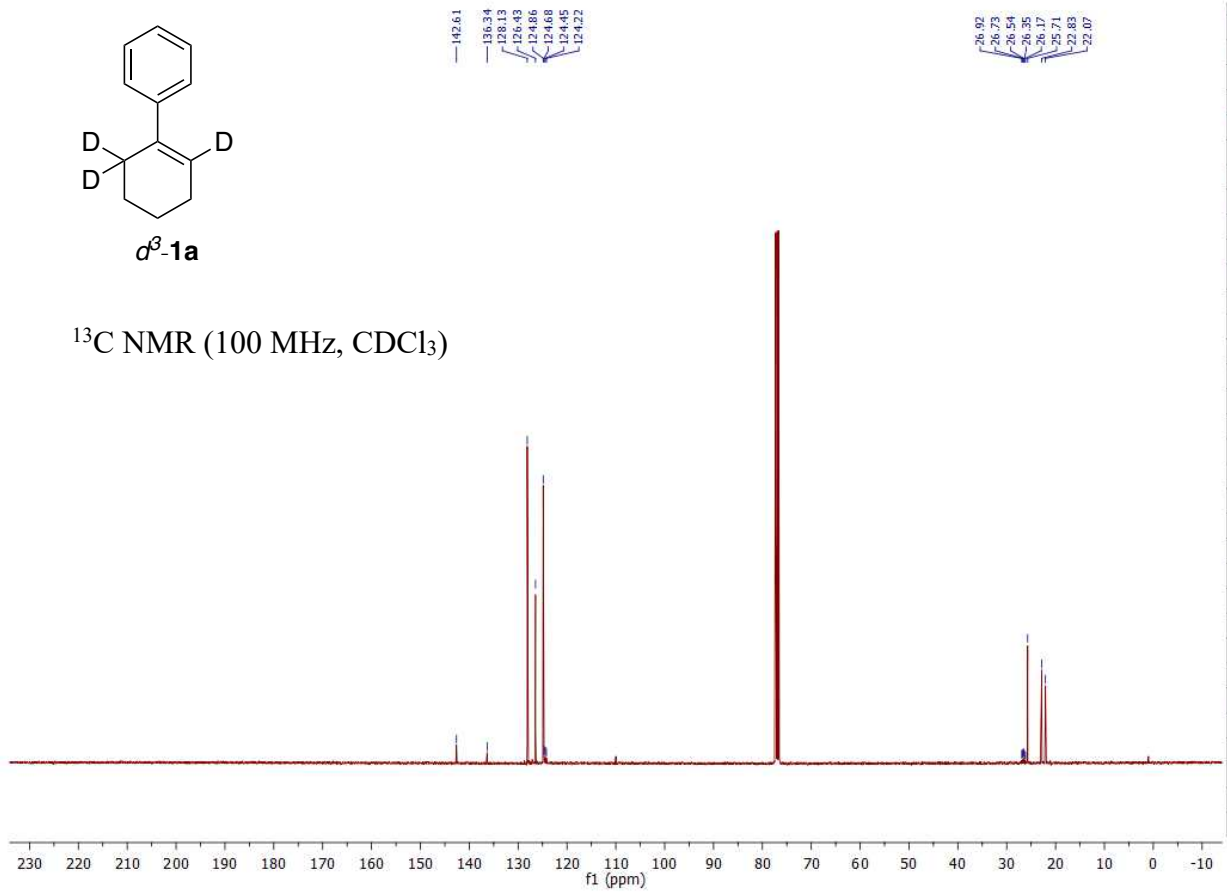
^{13}C NMR (100 MHz, CDCl_3)











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