

Supporting Information

A Mild Hydroaminoalkylation of Conjugated Dienes using a Unified Cobalt and Photoredox Catalytic System

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Materials and Methods:

Unless noted, all reactions were performed in oven-dried glassware and carried out under an atmosphere of argon or nitrogen with magnetic stirring. All photochemical reactions were run in dram vials fitted with Teflon caps under irradiation from a Blue H150 Kessil 35W LED lamp. All column chromatography was performed using general flash techniques on SiliCycle®SilicaFlash® P60, 40–63 μm 60 \AA .¹ For particularly difficult separations, an Teledyne Isco Combiflash using CombiFlash gold pre-packed columns. Thin layer chromatography was performed on SiliCycle® 250 μm 60 \AA plates. Visualization was accomplished with 254 nm UV light, Seebach's stain, or I₂.

¹H NMR spectra were recorded on Varian 300 or 400 MHz spectrometers OR Bruker 400 or 500 MHz spectrometers at ambient temperature. Chemical shift is reported in parts per million (ppm) from CDCl₃ (7.26 ppm) with multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, and m = multiplet) and coupling constants (Hz). ¹³C NMR was recorded on Varian 400 MHz spectrometers (100 MHz) or Bruker 500 MHz spectrometers (125 MHz) at ambient temperature. Chemical shifts are reported in ppm from CDCl₃ (77.2 ppm). Mass spectra were recorded on a Waters Acquity H uPLC-MS. Infrared spectra were collected on a Perkin Elmer Spectrum Two FT-IR Spectrometer.

All cyclic voltammetry studies were performed on a CH instruments Model 1232B potentiostat. All experiments were run using an EDAQ 1-mm disk glassy carbon working electrode in conjunction with an EDAQ Ag/AgCl reference electrode. Platinum wire from VWR served as the counter electrode. All voltammetry measurements for the cobalt complexes were run in anhydrous acetonitrile from Sigma-Aldrich at 5 mM using tetrabutylammonium hexafluorophosphate (0.1 M) as the electrolyte. Unless otherwise noted, the scan rate was set at 100 mV/s with a sensitivity of 1.0x10⁻⁵.

Unless otherwise mentioned, all starting materials were obtained from commercial sources including Sigma-Aldrich, TCI, Matrix, Alfa-Aesar, and Oakwood Scientific. Anhydrous CoBr₂, bis-1,3-diphenylphosphinopropane (dppp), anhydrous acetonitrile, and anhydrous CsOPiv were obtained from Sigma-Aldrich and stored in an argon glovebox. Photocatalysts used in this studied were either synthesized through known methods or bought from commercial sources. [Ir(dF-CF₃ppy)₂(dtbbpy)]PF₆, in particular, was synthesized according to a reported literature procedure² or purchased from Aspira Scientific.

Extended Optimization Studies

In addition to the control experiments shown in Table 1, additional optimization studies were performed as shown below. Unless shown otherwise, reactions were run on 0.1 mmol scale using 1a (2 equiv), 2a (1 equiv), Co Source (10 mol %), ligand (10 mol %), photocatalyst (0.5 mol %), and base (40 mol %) in acetonitrile (0.1 M).

Table S1: Control Studies



Entry	Co Source	Base	Ligand	Photocatalyst	Yield
1	CoBr ₂	KOAc	dppp	PC	52
2	CoBr ₂	KOAc	-	PC	trace
3	-	CsOPiv	dppp	PC	trace
4	CoBr ₂	CsOPiv	dppp	-	0
5*	CoBr ₂	CsOPiv	dppp	PC	0
6	CoBr ₂	-	dppp	PC	trace

*Reaction run in the absence of light

Table S2: Carboxylate Base effect



Entry	Co Source	Base	Yield
1	Co(dppp)Br ₂	CsOPiv	71
2	Co(dppp)Br ₂	KOAc	52
3	Co(dppp)Br ₂	imidazole	trace
4	Co(dppp)Br ₂	Cs ₂ CO ₃	trace
5	Co(dppp)Br ₂	K ₃ PO ₄	trace
6	Co(dppp)Br ₂	KOtBu	0
7	Co(dppp)Br ₂	NaOH	0
8	Co(dppp)(OPiv) ₂	CsOPiv	70
9	Co(dppp)(OPiv) ₂	KOAc	45
10	Co(dppp)(OPiv) ₂	imidazole	20
11	Co(dppp)(OPiv) ₂	Cs ₂ CO ₃	46
12	Co(dppp)(OPiv) ₂	K ₃ PO ₄	30
13	Co(dppp)(OPiv) ₂	KOtBu	0
14	Co(dppp)(OPiv) ₂	NaOH	0

Cyclic Voltammetry Studies

Cyclic Voltammetry Studies were run using a glassy carbon electrode, platinum wire counter electrode, and Ag/AgCl reference electrode. For all studies, tetrabutylammonium hexafluorophosphate was used as the electrolyte in a solution of acetonitrile while nitrogen was bubbled through the solution prior to data collection. For all listed CVs, sweeps were run negative (reductive) on first pass.

Table S3: Tabulated Maximum Reduction Potentials for Included Compounds

Entry	Compound	Additives	Co ^{II} /Co ^I (V _{red})	Co ^I /Co ^{II} (V _{ox})	Figure
1	CoBr ₂	-	-1.13	-	S1
2	Co(OPiv) ₂	-	-	-	S2
3	Co(dppp)Br ₂	-	-0.67	-0.09	S3
4	Co(dppp)OPiv ₂	-	-1.25	-1.03	S4
5	Co(dppp)Br ₂	Cs ₂ CO ₃	-0.62	-0.02	S5
6	Co(dppp)Br ₂	Butadiene	-0.75	-0.07	S6
7	Co(dppp)Br ₂	HOPIV	-0.63	-0.03	S7
8	Co(dppp)Br ₂	HOPIV, Butadiene	-0.63	-	S8
9	Co(dppp)Br ₂	TFA	-0.64	-0.07	S9
10	Co(dppp)Br ₂	TFA, Butadiene	-0.66	-	S10

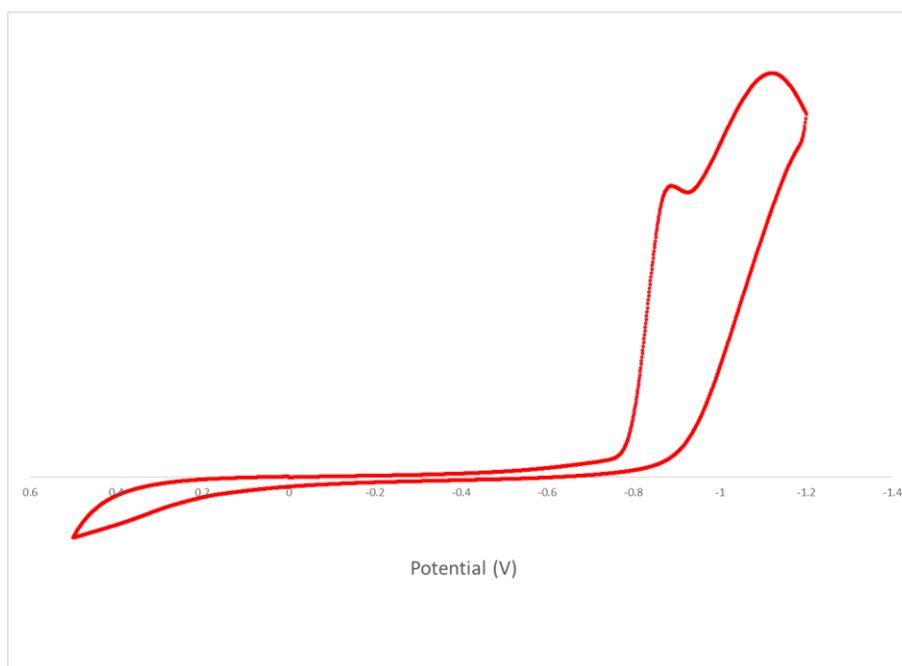
Figure S1: CoBr₂ versus Ag/AgCl

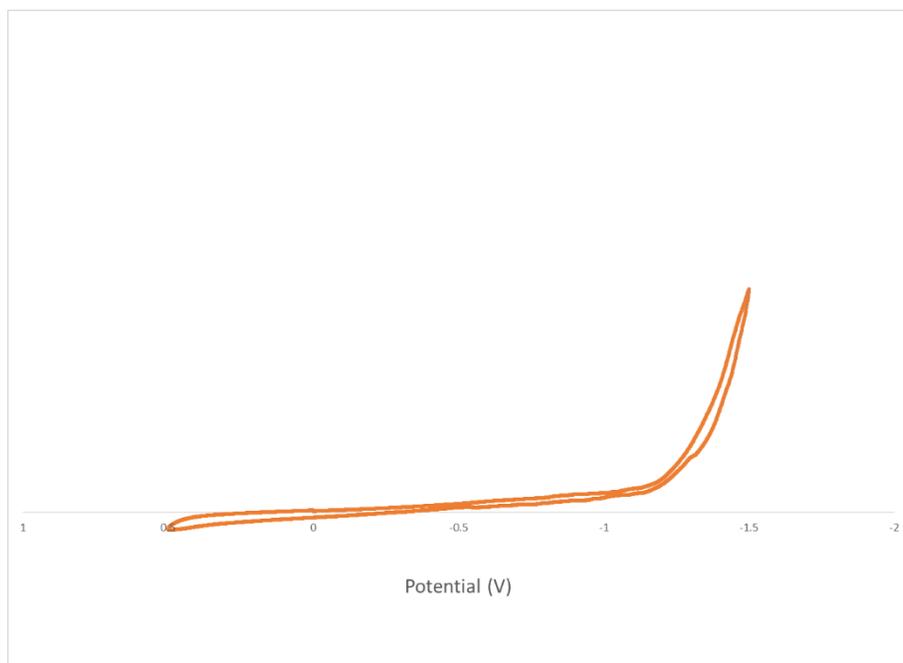
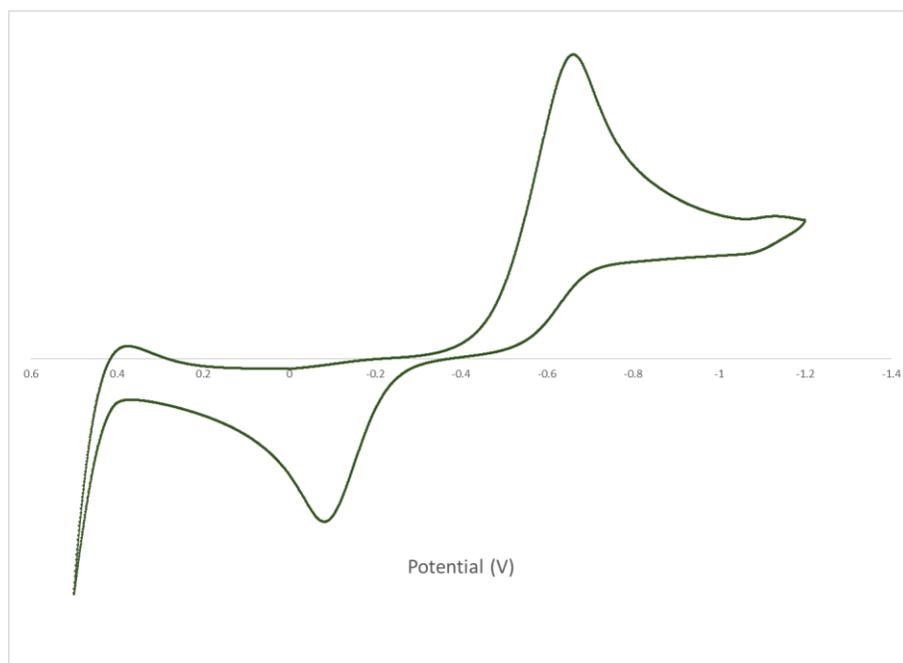
Figure S2: Co(OPiv)₂ versus Ag/AgCl**Figure S3:** Co(dppp)Br₂ versus Ag/AgCl

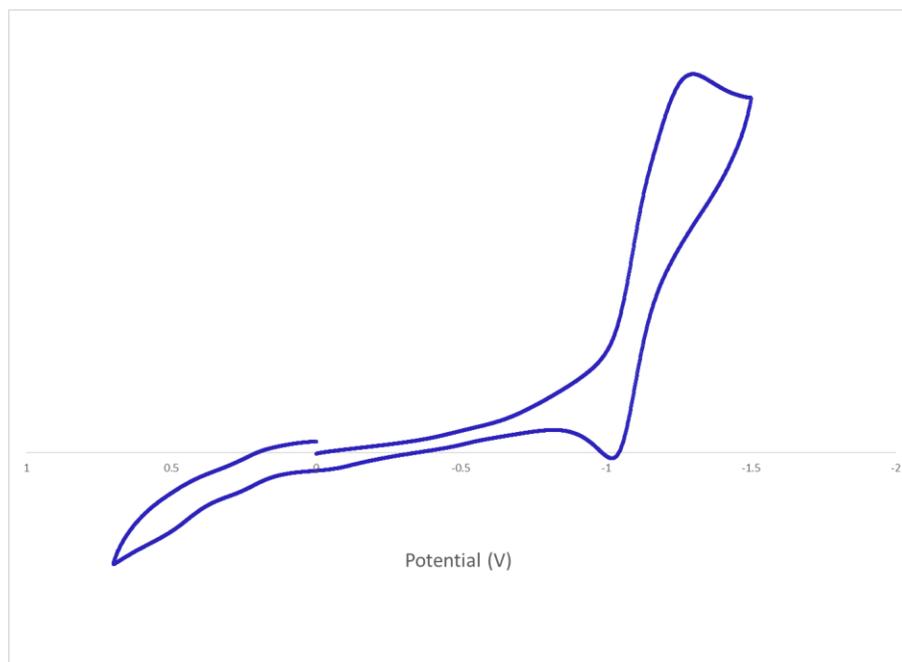
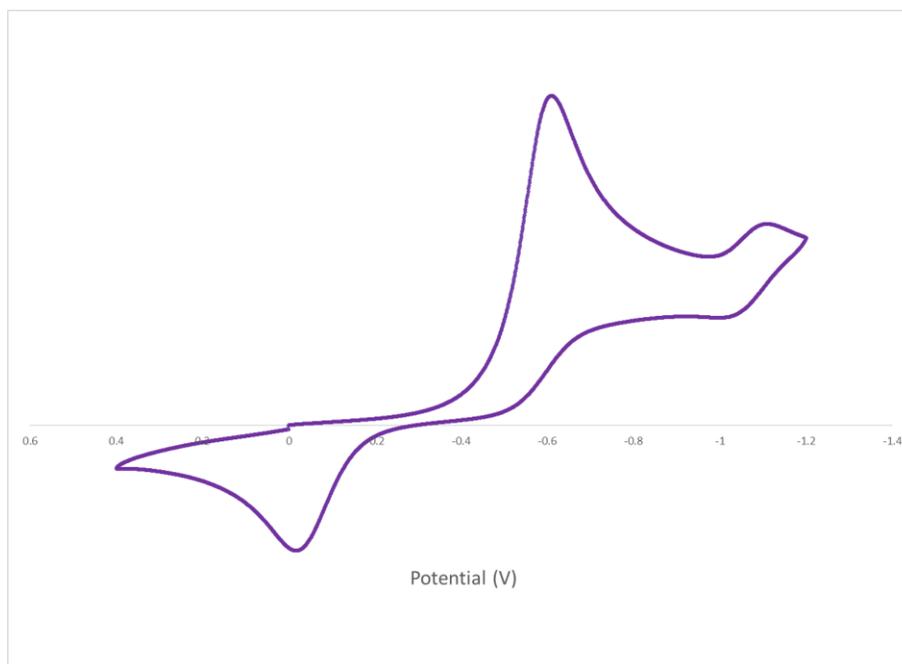
Figure S4: Co(dppp)(OPiv)₂ versus Ag/AgCl**Figure S5:** Co(dppp)Br₂ with Cs₂CO₃ (5 equiv) versus Ag/AgCl

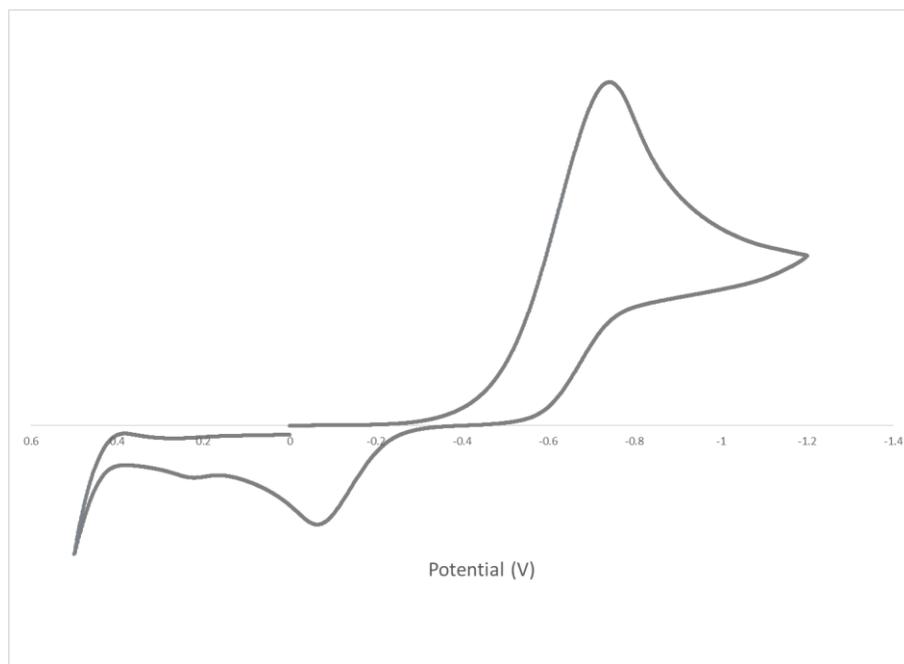
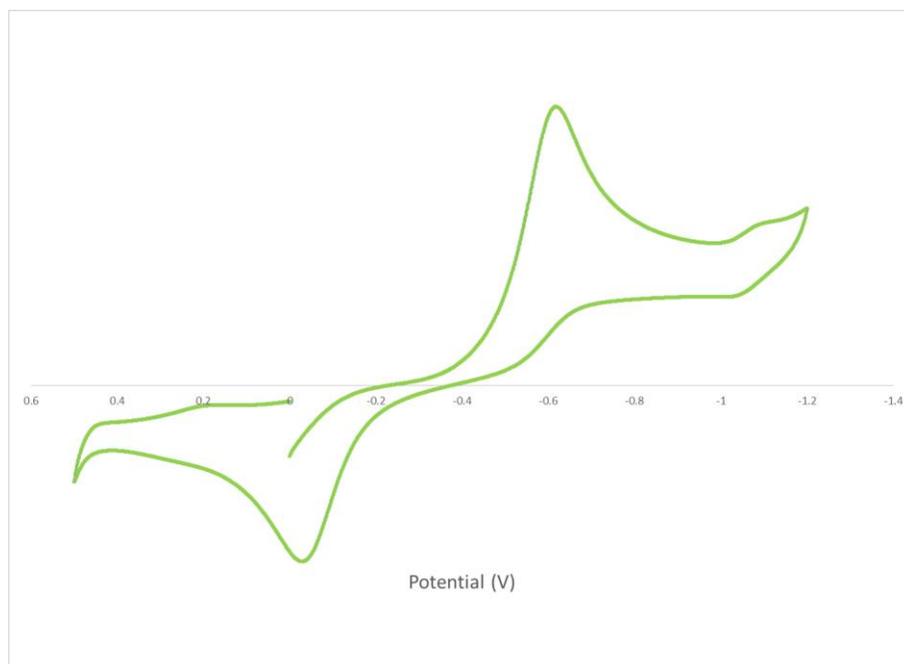
Figure S6: Co(dppp)Br₂ with butadiene (30 equiv) versus Ag/AgCl**Figure S7:** Co(dppp)Br₂ with HOPiv (5 equiv) versus Ag/AgCl

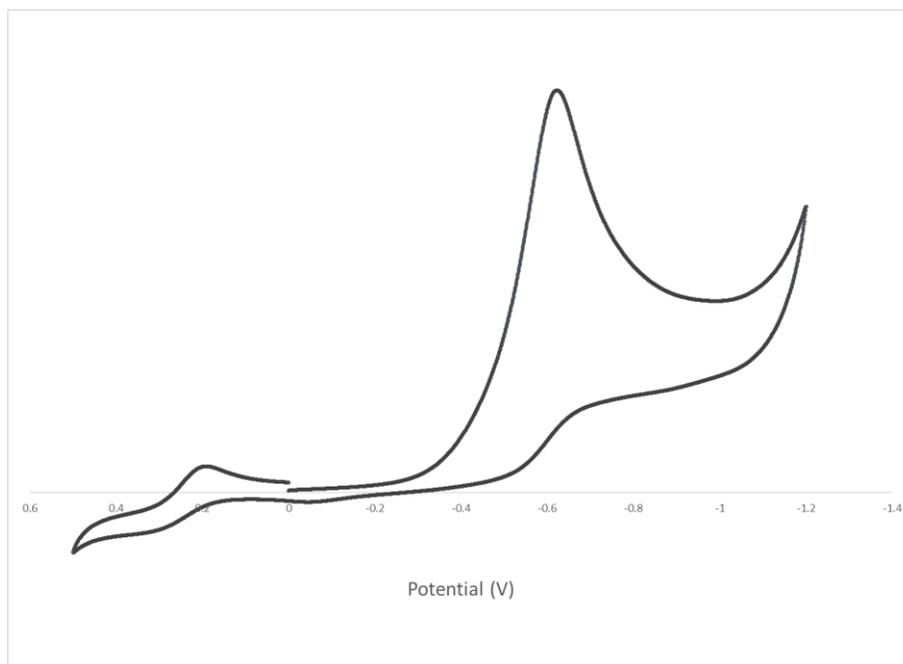
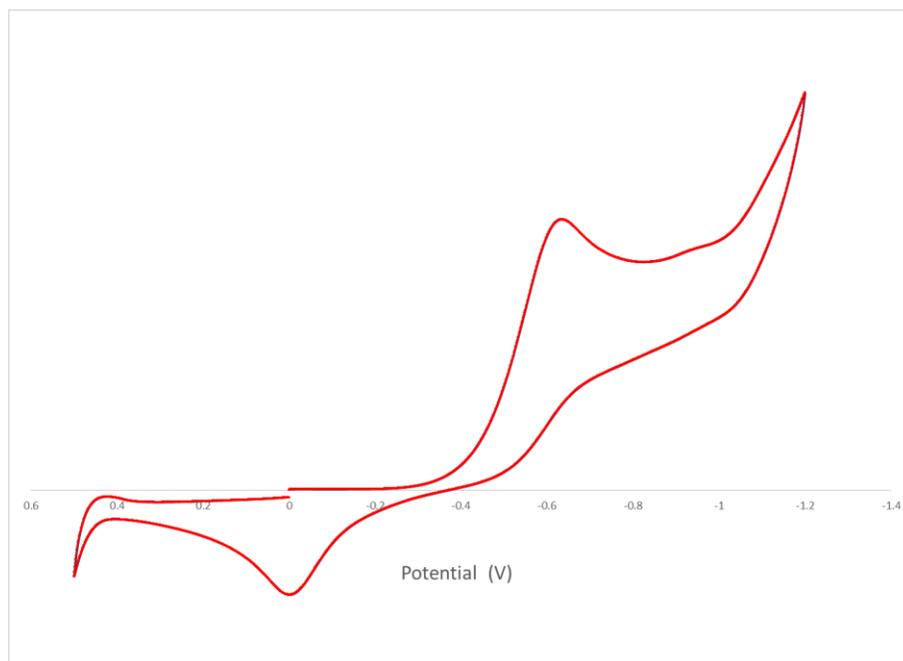
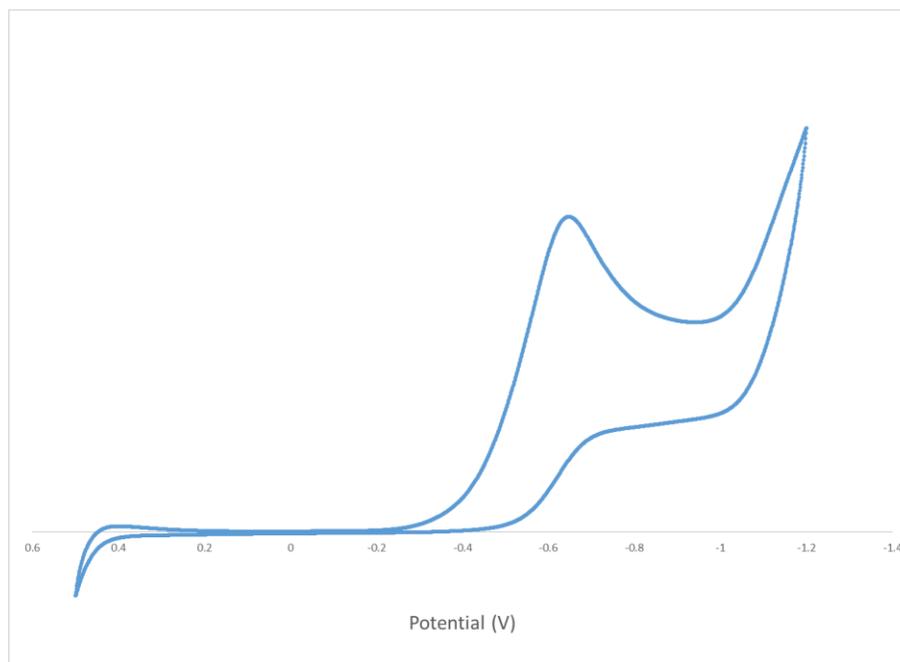
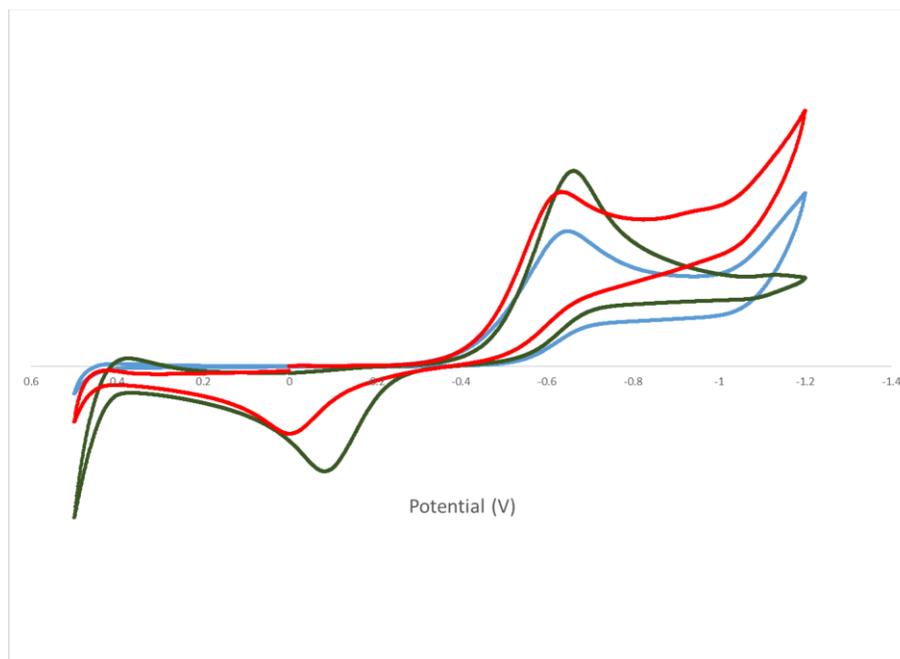
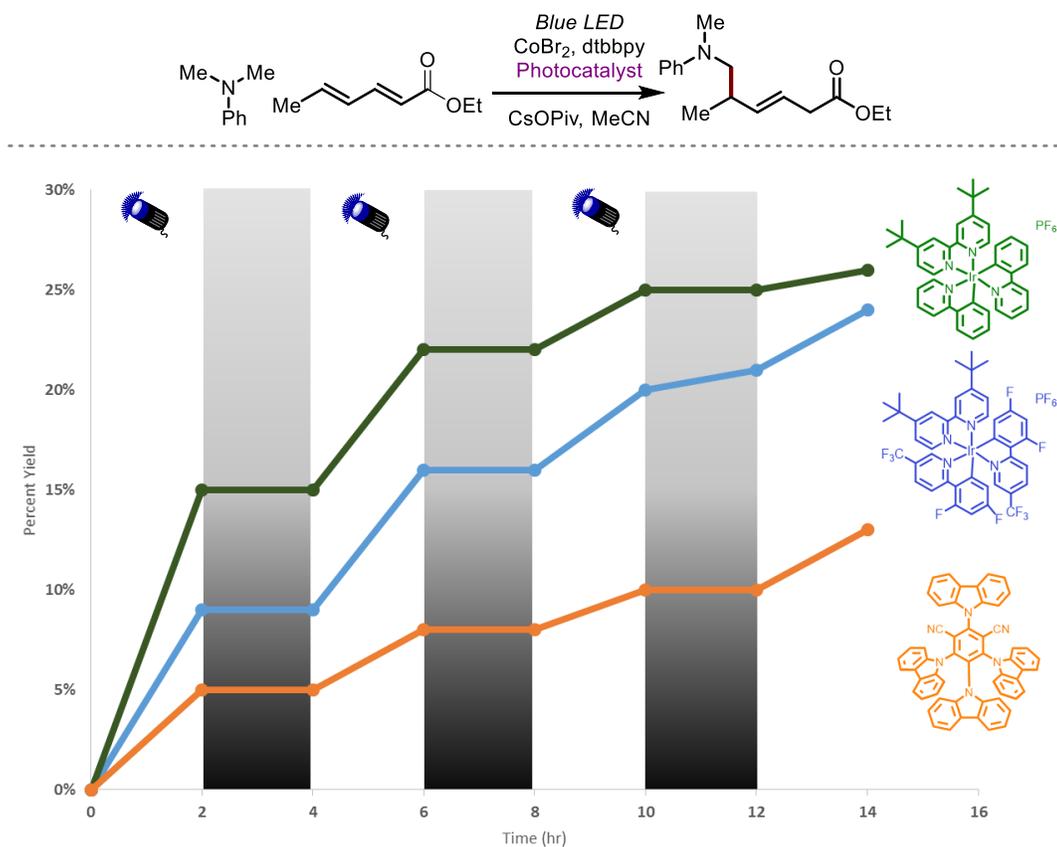
Figure S8: Co(dppp)Br₂ with HOPiv (5 equiv) and butadiene (30 equiv.) versus Ag/AgCl**Figure S9:** Co(dppp)Br₂ with TFA (5 equiv) versus Ag/AgCl

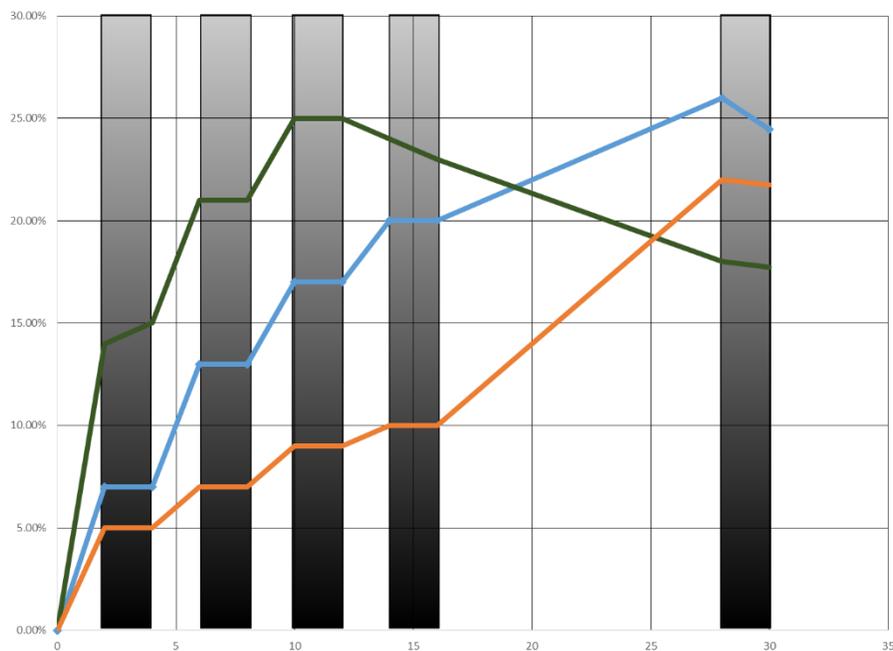
Figure S10: Co(dppp)Br₂ with TFA (5 equiv) and butadiene (30 equiv) versus Ag/AgCl**Figure S11:** Overlay of Figures S3 (Green), S9 (Red), and S10 (Blue) versus Ag/AgCl

On/Off studies and Quantum Yield Determination

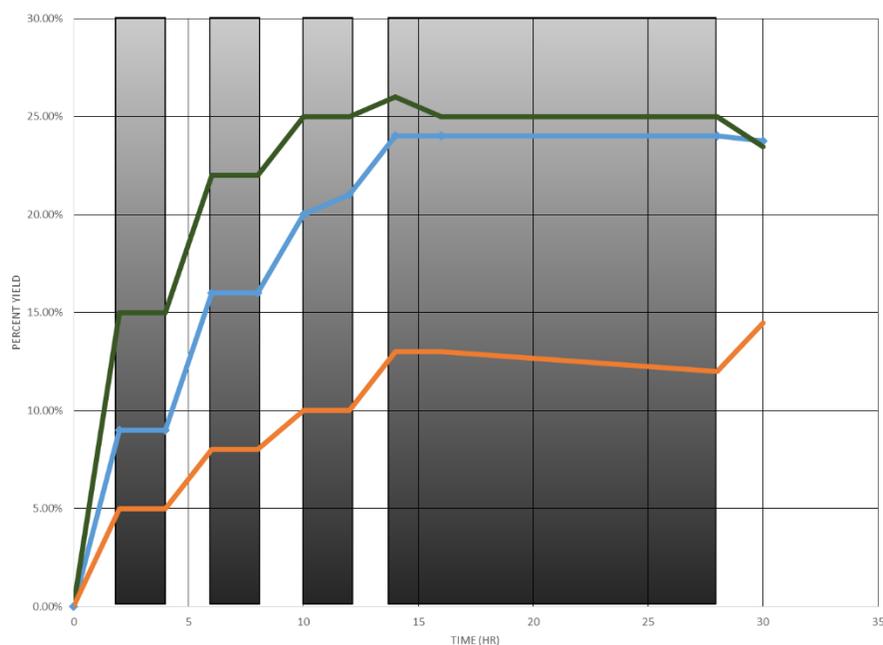
On/off studies were performed using the reaction conditions using CoBr_2 , 4,4'-di-tertbutyl 2,2'-bipyridine, and CsOPiv on dimethylaniline and ethyl sorbate using mesitylene as an internal standard. Three different photocatalysts were screened ($\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$, $\text{Ir}(\text{dF-CF}_3\text{ppy})_2(\text{dtbbpy})\text{PF}_6$, and 4Cz-IPN) over a period of time alternating cycles of irradiation and darkness. Reactions were run simultaneously and in duplicate. The reactions were performed in a dark room and set up under red light in order to avoid starting the reaction prematurely. Aliquots were taken every two hours and injected onto an HPLC with a known standard in order to determine yield. Overall, these cycles seem detrimental for the reaction, as the reaction never goes fully to completion during these cycles.



Increasing the length of the reaction overnight and thus extending the reaction time indicated, that the more strongly reducing catalyst, $\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ dies over the course of the reaction and leads to loss of yield. The cause of this is not fully understood, though this could potentially be conversion to one of the bis-products. Longer irradiation also demonstrates the superiority of the optimized catalyst.



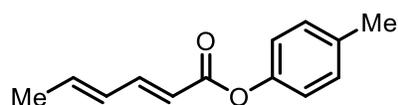
Extending the length of the darkness in comparison, showed that the reaction remains off during long periods of darkness and shows slight reinitiation (especially with 4Cbz-IPN). There are potentially some other processes that lead to degradation of product as indicated as some loss in yield over extended periods of darkness, especially in the case of Ir(ppy)₂(dtbbpy)PF₆. Overall, these cycles seem detrimental for the reaction, as the reaction never goes to completion following these on/off cycles.



A chemical actinometer, made from potassium ferrioxalate was set up based on prior examples^{3,4} in order to measure the quantum yield of the experiment. For our experiment, a NMR tube with 1.4 mg (0.005 mmol) Ir(dF-CF₃ppy)₂(dtbbpy)PF₆, 5.8 mg (0.025 mmol) CoBr₂, 3.90 mg (0.025 mmol) bipyridine, 63.38 μ L (0.5 mmol) N,N-

dimethylaniline, 36.32 μL (0.25 mmol) ethyl sorbate, and 23.40 mg (0.1 mmol) CsOPiv in 1 mL of deuterated MeCN. The reactions were monitored by ^1H NMR using mesitylene as the internal standard. After 30 hr, the quantum yield of the reaction was measured to be 10%, or 4% product per photon.

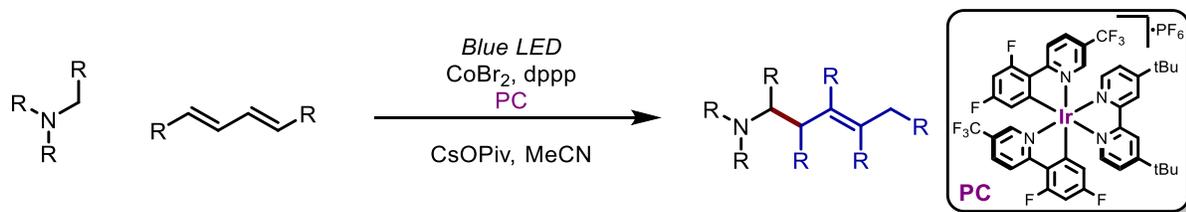
Starting Material Synthesis and Characterization Data



p-tolyl hexa-2,4-dienoate (**2c**)

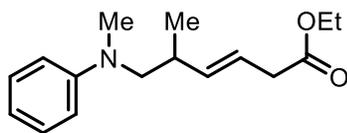
Compound was prepared using a DCC coupling between sorbic acid and *p*-cresol as described by Lam and coworkers.⁵ White Solid. 92% Yield ¹H NMR (500 MHz, CDCl₃) δ 7.45 (dd, *J* = 15.1, 10.2 Hz, 1H), 7.23 – 7.17 (m, 2H), 7.06 – 6.99 (m, 2H), 6.36 – 6.20 (m, 2H), 5.98 (dd, *J* = 15.4, 0.6 Hz, 2H), 2.37 (s, 3H), 1.92 (d, *J* = 6.0 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 165.9 – 165.7 (m), 148.5 (s), 140.5 (s), 135.4 (s), 129.9 (s), 121.3 (s), 118.2 (s), 21.0 (s), 18.7 (s). IR (ATR): 2906, 1722, 1643, 1619, 1505, 1332, 1238, 1198, 1125, 1007 R_f: 0.20 (5% EtOAc:Hexanes) LRMS (ESI+APCI) *m/z* [C₁₆H₂₄NO₂]⁺ ([M+H]⁺) calculated: 202.25, found 202.4.

Standard Reaction Conditions



Reactions were typically set-up in a glovebox under inert atmosphere but could also be performed under proper Schlenk techniques, back filling with an inert atmosphere. In an oven-dried vial, load 1.4 mg of photocatalyst (0.0012 mmol, 0.005 equiv), 5.4 mg CoBr₂ (0.025 mmol, 0.1 equiv), 10.35 mg dppp (0.025 mmol, 0.1 equiv), and 23.43 mg CsOPiv (0.1 mmol, 0.4 equiv). Add 2 mL of anhydrous acetonitrile (0.05 M) and magnetic stir-bar and stir solution until solution is a homogeneous purple color. Add 0.31 mmol (1.25 equiv) of the amine and stir briefly until homogeneous. Subsequently add 0.25 mmol (1.0 equiv) of diene and 3.36 μL (0.11 equiv) of mesitylene as an internal standard. Seal tightly and place ~2-6 inches from a Kessil lamp and irradiate and stir for 12 to 16 hr at room temperature. Upon completion by TLC, reactions were run through a short silica plug to remove cobalt species and concentrated *in vacuo*. Products were purified using flash column chromatography using EtOAc:Hexanes or Et₂O:Hexanes as an eluent.

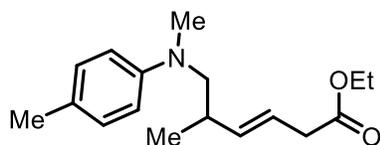
Characterization Data for Homo-Allylic Amines



ethyl 5-methyl-6-(methyl(phenyl)amino)hex-3-enoate (**3a**)

Prepared using standard reaction conditions from commercially available dimethylaniline and ethyl sorbate.

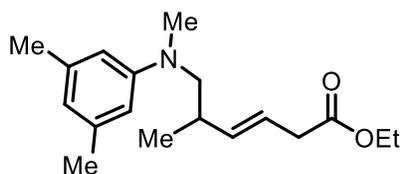
Colorless Oil. 72% Yield 20:1 dr. Complete after 12 hours. ^1H NMR (500 MHz, CDCl_3) δ 7.24 (t, 2H), 6.79 – 6.65 (m, 3H), 5.58 – 5.52 (m, 2H), 4.15 (q, $J = 7.1$ Hz, 2H), 3.24 (dd, $J = 7.4, 2.5$ Hz, 2H), 3.03 (dd, $J = 6.0, 1.0$ Hz, 2H), 2.95 (s, 3H), 2.68 (dt, $J = 13.9, 7.0$ Hz, 2H), 1.28 (t, $J = 7.1$ Hz, 3H), 1.05 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 171.9 (s), 149.4 (s), 137.7 (s), 129.1 (s), 121.5 (s), 115.7 (s), 111.8 (s), 60.7 (s), 59.0 (s), 39.5 (s), 38.3 (s), 35.8 (s), 17.6 (s), 14.1 (s). IR (ATR): 2961, 1734, 1599, 1506, 1370, 1243, 1172, 1033, 991, 747, 692. R_f : 0.30 (10% Et_2O :Hexanes) LRMS (ESI+APCI) m/z [$\text{C}_{16}\text{H}_{24}\text{NO}_2$] $^+$ ($[\text{M}+\text{H}]^+$) calculated: 262.37, found 262.2.



ethyl 5-methyl-6-(methyl(p-tolyl)amino)hex-3-enoate (**3b**)

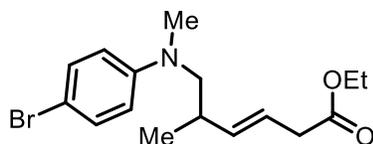
Prepared using standard reaction conditions from commercially available N,N,4-trimethylaniline and ethyl sorbate.

Colorless Oil. 66% Yield, 20:1 dr. Complete after 12 hours. 92% purity with inseparable impurity. ^1H NMR (400 MHz, cdcl_3) δ 7.03 (d, $J = 8.2$ Hz, 2H), 6.59 (d, $J = 8.5$ Hz, 2H), 5.52 (m 2H), 4.13 (q, $J = 7.1$ Hz, 2H), 3.17 (dd, $J = 7.3, 2.8$ Hz, 2H), 3.00 (d, $J = 5.7$ Hz, 2H), 2.91 (s, 3H), 2.65 (dd, $J = 13.2, 6.7$ Hz, 1H), 2.24 (s, 3H), 1.24 (t, $J = 7.1$ Hz, 3H), 1.01 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (101 MHz, cdcl_3) δ 172.0 (s), 147.0 (s), 137.8 (s), 129.8 (s), 125.0 (s), 121.6 (s), 112.1 (s), 60.5 (s), 59.3 (s), 39.5 (s), 38.2 (s), 35.6 (s), 20.1 (s), 17.61 (m), 14.2 (s). IR (ATR): 2922, 1734, 1618, 1521, 1458, 1368, 1173, 1035, 971, 801 cm^{-1} R_f : 0.40 (5% EtOAc :Hexanes) LRMS (ESI+APCI) m/z [$\text{C}_{17}\text{H}_{26}\text{NO}_2$] $^+$ ($[\text{M}+\text{H}]^+$) calculated: 276.39, found 276.4.

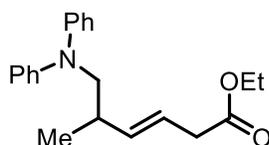


ethyl 6-((3,5-dimethylphenyl)(methyl)amino)-5-methylhex-3-enoate (**3c**)

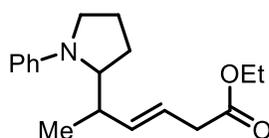
Prepared using standard reaction conditions from commercially available N,N,3,5-tetramethylaniline and ethyl sorbate. Colorless Oil. 75% Yield, 20:1 *E:Z*. Complete after 12 hours. ^1H NMR (500 MHz, CDCl_3) δ 6.37 (s, 1H), 6.33 (s, 2H), 5.60 – 5.53 (m, 2H), 4.16 (q, $J = 7.1$ Hz, 2H), 3.20 (dd, $J = 7.3, 3.0$ Hz, 2H), 3.04 (d, $J = 5.5$ Hz, 2H), 2.94 (s, 3H), 2.67 (dt, $J = 13.6, 6.7$ Hz, 1H), 2.30 (s, 3H), 1.28 (t, $J = 7.1$ Hz, 3H), 1.05 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 172.0 (s), 149.6 (s), 138.6 (s), 137.9 (s), 121.5 (s), 117.9 (s), 109.9 (s), 60.6 (s), 59.2 (s), 39.6 (s), 38.3 (s), 35.7 (s), 21.8 (s), 17.7 (s), 14.2 (s). IR (ATR): 2918, 1735, 1597, 1486, 1367, 1301, 1163, 1033, 969, 815, 691 cm^{-1} R_f : 0.40 (10% EtOAc :Hexanes) LRMS (ESI+APCI) m/z [$\text{C}_{18}\text{H}_{28}\text{NO}_2$] $^+$ ($[\text{M}+\text{H}]^+$) calculated: 290.42, found 290.2.

ethyl 6-((4-bromophenyl)(methyl)amino)-5-methylhex-3-enoate (**3d**)

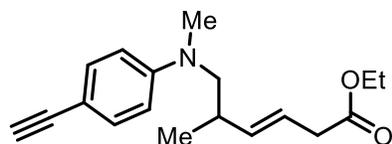
Prepared using standard reaction conditions from commercially available N,N-dimethyl-4-bromoaniline and ethyl sorbate. White Solid. 81% Yield, 20:1 *E:Z*. Complete after 12 hours. ^1H NMR (400 MHz, cdCl_3) δ 7.26 (d, $J = 6.6$, 2H), 6.55 – 6.47 (d, $J = 6.6$, 2H), 5.49 (m, 2H), 4.12 (q, $J = 7.1$ Hz, 2H), 3.18 (d, $J = 7.4$ Hz, 2H), 2.99 (d, $J = 5.4$ Hz, 2H), 2.91 (s, 3H), 2.74 – 2.56 (m, 1H), 1.25 (t, $J = 7.1$ Hz, 3H), 1.00 (d, $J = 6.7$ Hz, 2H). ^{13}C NMR (101 MHz, cdCl_3) δ 148.2 (s), 137.3 (s), 131.7 (s), 121.9 (s), 113.4 (s), 60.6 (s), 59.0 (s), 39.5 (s), 38.1 (s), 35.5 (s), 17.7 (s), 14.2 (s). IR (ATR): 2949, 1734, 1653, 1590, 1497, 1434, 1358, 1194, 1164, 969, 807 cm^{-1} R_f: 0.40 (5% EtOAc:Hexanes) LRMS (ESI+APCI) m/z $[\text{C}_{16}\text{H}_{22}\text{BrNO}_2]^+$ ($[\text{M}+\text{H}]^+$) calculated: 341.26, found 341.2.

ethyl 6-(diphenylamino)-5-methylhex-3-enoate (**3e**)

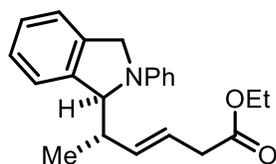
Prepared using standard reaction conditions from commercially available diphenylmethylamine and ethyl sorbate. Colorless Oil. 70% Yield 10:1 *E:Z* Complete after 12 hours. ^1H NMR (400 MHz, cdCl_3) δ 7.24 (m, 4H), 6.95 (m, 6H), 5.57 – 5.48 (m, 2H), 4.11 (q, $J = 7.1$ Hz, 2H), 3.67 – 3.58 (m, 2H), 2.99 (d, $J = 5.7$, 2H), 2.66 (m, 1H), 1.24 (t, 3H), 1.05 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (101 MHz, cdCl_3) δ 171.9 (s), 148.4 (s), 137.5 (s), 129.2 (s), 121.8 (s), 121.2 (s), 121.1 (s), 60.5 (s), 58.3 (s), 38.2 (s), 35.4 (s), 17.8 (s), 14.2 (s). IR (ATR): 2921.7, 2851.2, 1734.4, 1588.5, 1496.2, 1367.4, 1245.4, 1172.3, 1029.6, 748.8, 695.6 cm^{-1} R_f: 0.40 (2% Et₂O:Hexanes) LRMS (ESI+APCI) m/z $[\text{C}_{21}\text{H}_{26}\text{NO}_2]^+$ ($[\text{M}+\text{H}]^+$) calculated: 324.44, found: 324.2.

ethyl 5-(1-phenylpyrrolidin-2-yl)hex-3-enoate (**3f**)

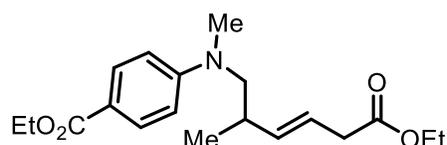
Prepared using standard reaction conditions from commercially available N-phenylpyrrolidine and ethyl sorbate. Light yellow Oil. 65% Yield 1:1 dr 20:1 *E:Z* Complete after 16 hours. ^1H NMR (400 MHz, CDCl_3) δ 7.25 (m, 4H), 6.81 – 6.60 (m, 6H), 5.68 – 5.35 (m, 4H), 4.23 – 4.05 (m, 4H), 3.82 (dd, $J = 7.6$, 3.2 Hz, 4H), 3.76 – 3.62 (m, 4H), 3.60 – 3.40 (m, 4H), 3.31 – 3.06 (m, 4H), 3.03 (dd, $J = 10.2$, 9.2 Hz, 4H), 2.89 – 2.78 (m, 2H), 2.07 – 1.77 (m, 8H), 1.77 – 1.61 (m, 4H), 1.35 – 1.14 (m, 6H), 1.07 (d, $J = 7.4$ Hz, 3H), 0.94 (d, $J = 6.3$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 172.1 (s), 171.9 (s), 147.6 (s), 147.5 (s), 137.4 (s), 135.7 (s), 129.1 (s), 122.1 (s), 121.6 (s), 115.5 (s), 112.4 (s), 112.4 (s), 63.0 (s), 62.0 (s), 60.5 (s), 49.6 (s), 49.3 (s), 41.3 (s), 38.5 (s), 38.3 (s), 37.8 (s), 37.5 (s), 27.2 (s), 26.5 (s), 26.3 (s), 24.3 (s), 24.0 (s), 23.8 (s), 18.2 (s), 16.5 (s), 14.3 (s), 14.2 (s), 13.6 (s). IR (ATR): 2963, 1731, 1597, 1503, 1366, 1159, 1032, 992, 748, 694 cm^{-1} R_f: 0.30 (5% Et₂O:Hexanes) LRMS (ESI+APCI) m/z $[\text{C}_{18}\text{H}_{26}\text{NO}_2]^+$ ($[\text{M}+\text{H}]^+$) calculated: 288.40, found 288.4.

ethyl 6-((4-ethynylphenyl)(methyl)amino)-5-methylhex-3-enoate (**3g**)

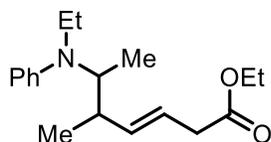
Prepared using standard reaction conditions from commercially available N,N-dimethyl-4-ethynylaniline and ethyl sorbate. Yellow Oil. 57% Yield 20:1 *E:Z* Complete after 12 hours. $^1\text{H NMR}$ (400 MHz, cdCl_3) δ 7.34 (d, 2H), 6.55 (d, 2H), 5.58 – 5.41 (m, 2H), 4.12 (q, $J = 7.1$ Hz, 2H), 3.23 (d, $J = 7.4$ Hz, 2H), 3.02 – 2.91 (m, 3H), 2.63 (m, 1H), 1.23 (t, 3H), 1.01 (d, $J = 6.8$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, cdCl_3) δ 171.8 (s), 149.2 (s), 137.2 (s), 133.2 (s), 122.0 (s), 111.2 (s), 84.9 (s), 74.6 (s), 60.6 (s), 58.7 (s), 39.5 (s), 38.2 (s), 35.6 (s), 17.7 (s), 14.2 (s). IR (ATR): 2922, 1730, 1596, 1525, 1371, 1269, 1179, 1032, 823 cm^{-1} R_f : 0.25 (10% EtOAc:Hexanes) LRMS (ESI+APCI) m/z $[\text{C}_{18}\text{H}_{24}\text{NO}_2]^+$ ($[\text{M}+\text{H}]^+$) calculated: 287.39, found 287.4.

ethyl 5-(2-phenylisoindolin-1-yl)hex-3-enoate (**3h**)

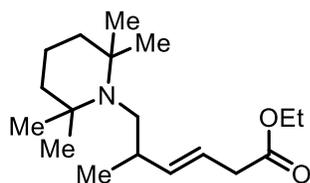
Prepared using standard reaction conditions from commercially available ethyl sorbate and prepared phenyl isoindoline.⁶ Colorless Oil. 61% Yield Complete after 12 hr. 8:1 dr. Major diastereomer tentatively assigned as the drawn structure based on structures reported by Singh and coworkers.⁷ Oxidation of the isoindoline product observed as one of the byproducts. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.37 – 7.29 (m, 5H), 7.28 – 7.21 (m, 1H), 6.79 – 6.70 (m, 3H), 5.89 (dt, $J = 16.0, 3.8$ Hz, 1H), 5.71 (dtd, $J = 16.0, 7.0, 1.2$ Hz, 1H), 5.22 (t, $J = 3.0$ Hz, 1H), 4.79 (dd, $J = 13.3, 3.1$ Hz, 1H), 4.57 (d, $J = 13.3$ Hz, 1H), 4.23 (q, $J = 7.1$ Hz, 2H), 3.20 (dt, $J = 7.0, 1.2$ Hz, 2H), 1.33 (t, $J = 7.1$ Hz, 3H), 0.61 (d, $J = 6.7$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.9 (s), 146.0 (s), 138.0 (s), 138.4 (s), 136.7 (s), 129.4 (s), 126.5 (s), 123.4 (s), 122.4 (s), 122.2 (s), 116.0 (s), 112.0 (s), 67.2 (s), 60.7 (s), 54.8 (s), 38.5 (s), 37.8 (s), 14.3 (s), 12.3 (s). IR (ATR): 2979, 2918, 1734, 1599, 1496, 1178, 1120, 1058, 933, 752, 691 cm^{-1} R_f : 0.3 (10% EtOAc:Hexanes) LRMS (ESI+APCI) m/z $[\text{C}_{22}\text{H}_{26}\text{NO}_2]^+$ ($[\text{M}+\text{H}]^+$) calculated: 336.45, found 336.2.

ethyl 4-((6-ethoxy-2-methyl-6-oxohex-3-en-1-yl)(methyl)amino)benzoate (**3i**)

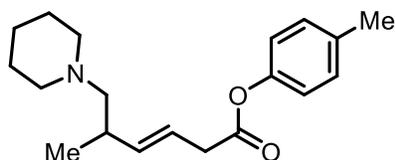
Prepared using standard reaction conditions from commercially available ethyl 4-dimethylaminobenzoate and ethyl sorbate. Off white solid. 72% Yield 20:1 *E:Z* Complete after 12 hours. $^1\text{H NMR}$ (400 MHz, cdCl_3) δ 7.92 (d, $J = 8.9$ Hz, 2H), 6.73 (d, $J = 8.9$ Hz, 2H), 5.57 – 5.42 (m, 2H), 4.32 (q, $J = 7.2$ Hz, 2H), 4.12 (q, $J = 7.1$ Hz, 2H), 3.30 (dd, $J = 7.4, 3.1$ Hz, 2H), 3.05 – 2.91 (m, 5H), 2.64 (m, 1H), 1.35 (t, $J = 7.2$ Hz, 3H), 1.24 (t, $J = 7.1$ Hz, 3H), 1.03 (d, $J = 6.8$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, cdCl_3) δ 171.7 (s), 136.7 (s), 131.3 (s), 122.5 (s), 111.6 (s), 77.3 (s), 60.6 (s), 60.2 (s), 38.0 (s), 35.5 (s), 17.8 (s), 14.4 (s), 14.2 (s). IR (ATR): 2920, 1734, 1697, 1603, 1523, 1463, 1366, 1276, 1182.2, 1104, 1023, 973, 770 cm^{-1} R_f : 0.40 (5% EtOAc:Hexanes) LRMS (ESI+APCI) m/z $[\text{C}_{19}\text{H}_{28}\text{NO}_4]^+$ ($[\text{M}+\text{H}]^+$) calculated: 334.43, found 334.4.

ethyl 6-(ethyl(phenyl)amino)-5-methylhept-3-enoate (**3j**)

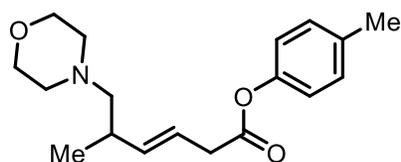
Prepared using standard reaction conditions from commercially available *N,N*-diethylaniline and ethyl sorbate. Colorless Oil. 45% Yield 1:1 dr Complete after 20 hours. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.22 (dd, $J = 14.7, 8.5$ Hz, 6H), 6.77 (d, $J = 11.2$ Hz, 3H), 6.68 (dd, $J = 21.6, 15.4$ Hz, 3H), 5.67 – 5.37 (m, 4H), 4.22 – 4.15 (m, 2H), 4.15 – 4.06 (m, 2H), 3.66 (ddd, $J = 13.5, 7.8, 4.2$ Hz, 2H), 3.39 – 3.02 (m, 6H), 2.94 (d, $J = 5.7$ Hz, 2H), 2.60 – 2.38 (m, 1H), 1.33 – 0.97 (m, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 172.2 (s), 157.4 (s), 148.8 (s), 138.3 (s), 137.9 (s), 129.1 (s), 129.0 (s), 122.1 (s), 121.0 (s), 115.8 (s), 113.7 (s), 113.4 (s), 60.6 (s), 60.5 (s), 59.3 (s), 58.5 (s), 42.2 (s), 41.1 (s), 38.2 (s), 38.1 (s), 18.6 (s), 17.8 (s), 16.4 (s), 16.0 (s), 14.2 (s), 14.2 (s), 13.9 (s), 13.8 (s). IR (ATR): 2966, 2924, 2852, 1735, 1596, 1501, 1453, 1368, 1263, 1174, 746, 692 cm^{-1} R_f: 0.40 (10% EtOAc:Hexanes) LRMS (ESI+APCI) m/z [$\text{C}_{18}\text{H}_{28}\text{NO}_2$]⁺ ($[\text{M}+\text{H}]^+$) calculated: 290.42, found 290.2.

ethyl 5-methyl-6-(2,2,6,6-tetramethylpiperidin-1-yl)hex-3-enoate (**3k**)

Prepared using standard reaction conditions from commercially available 1,2,2,6,6-pentamethylpiperidine and ethyl sorbate. Difficulties were had in removing ethyl sorbate dimerization products (trace peaks in NMR). Colorless Oil. 65% Yield 20:1 *E:Z* Complete after 16 hours. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 5.51 (dd, $J = 10.8, 6.8$ Hz, 19H), 5.38 – 5.32 (m, 20H), 4.20 – 4.07 (m, 48H), 2.90 – 2.83 (m, 16H), 2.55 (ddd, $J = 10.3, 9.2, 3.9$ Hz, 40H), 2.30 (t, $J = 7.4$ Hz, 32H), 1.82 (d, $J = 1.3$ Hz, 6H), 1.68 – 1.61 (m, 56H), 1.28 (t, 152H), 1.04 (d, 3H), 0.99 (t, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 127.6 (s), 125.6 (s), 77.3 (s), 77.0 (s), 76.8 (s), 59.9 (s), 54.5 (s), 50.7 (s), 47.8 (s), 41.3 (s), 28.8 (s), 17.8 (s), 14.3 (s), 12.8 (s). IR (ATR): 2965, 2926, 1730, 1464, 1367, 1257, 1160, 1026, 704 cm^{-1} R_f: 0.20 (10% EtOAc:Hexanes) LRMS (ESI+APCI) m/z [$\text{C}_{18}\text{H}_{34}\text{NO}_2$]⁺ ($[\text{M}+\text{H}]^+$) calculated: 296.47, found 296.4.

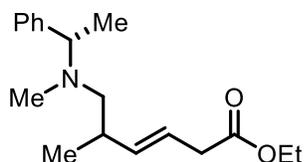
*p*-tolyl-5-methyl-6-(piperidin-1-yl)hex-3-enoate (**3l**)

Prepared using standard reaction conditions from commercially available *N*-methyl piperine and previously prepared *p*-tolyl sorbate, **2c**. Colorless Oil. 62% Yield 2.5:1 rr Final Product 84% pure of minor diastereomer. Complete after 16 hours. $^1\text{H NMR}$ (500 MHz, CDCl_3) 7.19 (d, $J = 8.4$ Hz, 2H), 6.97 (m, 3H), 5.66 (dd, $J = 4.7, 3.1$ Hz, 2H), 3.29 (d, $J = 4.9$ Hz, 2H), 2.48-2.45 (m, 1H), 2.22 (s, 3H), 2.26 – 2.15 (m, 4H), 1.57 (m, $J = 81.0$ Hz, 4H), 1.44 (m, 2H), 1.04 (d). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 170.8 (s), 148.5 (s), 139.8 (s), 135.4 (s), 129.9 (s), 121.2 (s), 119.7 (s), 65.6 (s), 54.9 (s), 38.2 (s), 34.2 (s), 26.0 (s), 24.6 (s), 20.9 (s), 18.6 (s). IR (ATR): 2930, 2853, 1755, 1507, 1452, 1196, 1165, 1122, 970 cm^{-1} R_f: 0.20 (50% EtOAc:Hexanes) Visualized using Seebach's stain or using EDCI on CombiFlash. LRMS (ESI+APCI) m/z [$\text{C}_{19}\text{H}_{28}\text{NO}_2$]⁺ ($[\text{M}+\text{H}]^+$) calculated 302.43, found 302.2.



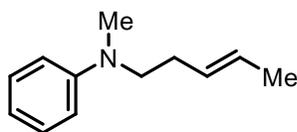
p-tolyl 5-methyl-6-morpholinohex-3-enoate (**3m**)

Prepared using standard reaction conditions from commercially available N-methyl morpholine and and previously prepared *p*-tolyl sorbate, **2c**. Colorless Oil. 51% Yield 6:1 *rr* 20:1 *E:Z* Product 85% pure of minor anisole impurity (singlet at 3.85). Complete after 16 hours. ¹H NMR (500 MHz, CDCl₃) δ 7.56 (d, *J* = 9.0 Hz, 3H), 7.29 (m, 16H), 7.19 (dt, *J* = 12.1, 3.1 Hz, 12H), 7.01 – 6.95 (d, 2H), 5.69 – 5.63 (m, 2H), 3.71 (t, 2H), 3.30 (dd, *J* = 3.6, 1.9 Hz, 2H), 2.50 – 2.37 (m, 2H), 2.36 (s, 3H), 2.21 (dd, *J* = 12.1, 7.5 Hz, 2H), 1.05 (d, *J* = 6.7 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 170.7 (s) 148.5 (s), 139.3 (s), 129.9 (s), 121.2 (s), 67.0 (s), 54.0 (s), 38.2 (s), 33.8 (s), 20.9 (s). IR (ATR): 2925, 1729, 1507, 1378, 1295, 1119, 1165, 1199, 1026, 969 cm⁻¹ R_f: 0.2 (50% EtOAc:Hexanes) Visualized using EDCI on CombiFlash or Seebach's stain. LRMS (ESI+APCI) *m/z* [C₁₈H₂₆NO₃]⁺ ([M+H]⁺) calculated: 304.40, found 304.4.



ethyl 5-methyl-6-(methyl(1-phenylethyl)amino)hex-3-enoate (**3n**)

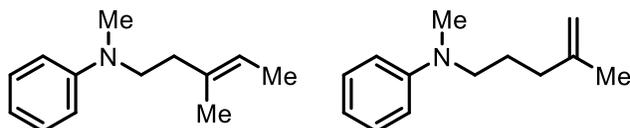
Prepared using standard reaction conditions from commercially available N,N-dimethyl-1-phenylethylamine and ethyl sorbate. Due to co-elution with dimeric ethyl sorbate products, after running the crude product through a silica plug, reaction mixture was washed with 3x 5 mL 2M HCl. Aqueous fractions were basified using a saturated NaHCO₃ solution and extracted 3x with 5 mL of EtOAc. Organic fractions were combined, dried over Mg₂SO₄ and concentrated *in vacuo* to afford mixture of product, bis-addition products, and starting amine. Product was purified using a CombiFlash Gold column, equipped with EDCI. Colorless Oil. 61% Yield 2:1 *dr*, 20:1 *E:Z* Product 91% pure from an inseparable impurity. Complete after 16 hours. ¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, *J* = 2.3 Hz, 3H), 7.24 (dd, *J* = 10.2, 3.8 Hz, 2H), 5.61 – 5.36 (m, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.66 – 3.52 (m, 1H), 3.03 (d, *J* = 6.5 Hz, 2H), 2.45 – 2.11 (m, 1H), 2.25 – 2.12 (m, 5H), 2.25 – 2.11 (m, 2H), 1.38 – 1.23 (m, 6H), 0.99 (d, *J* = 6.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.2 (s), 144.23 (s), 127.9 (s), 126.7 (s), 120.4 (s), 63.3 (s), 60.5 (s), 38.3 (s), 34.8 (s), 17.5 (s), 14.1 (s). IR (ATR): 2958, 2924, 1720, 1648, 1451, 1368, 1223, 1264, 1175, 1033, 701 cm⁻¹ R_f: 0.20 (25% EtOAc:Hexanes) Visualized though EDCI on Combiflash or using K₃MnO₄. LRMS (ESI+APCI) *m/z* [C₁₈H₂₈NO₂]⁺ ([M+H]⁺) calculated 290.42, found 290.2.



N-methyl-N-(pent-3-en-1-yl)aniline (**4b**)

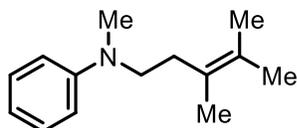
Prepared using standard reaction conditions from commercially available N,N-dimethylaniline and 20% weight butadiene in toluene. 2:1 mixture of inseparable *E* and *Z* isomers. Some regioisomer is also present. Colorless Oil.

50% Yield 2:1 rr, 2:1 *E:Z*. Complete after 12 hours. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.26 (m, 2H), 6.80 – 6.61 (m, 3H), 5.86 (dd, $J = 17.0, 10.3$ Hz, 2H), 5.61 – 5.24 (m, 2H), 5.14 – 4.97 (m, 2H), 3.41 – 3.27 (m, 2H), 2.96 (s, 2H), 2.49 – 2.04 (m, 4H), 1.80 – 1.58 (m, 9H), 1.67 (d, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 149.1 (s), 138.2 (s), 129.2 (s), 128.3 (s), 127.2 (s), 127.0 (s), 116.0 (s), 115.0 (s), 112.1 (s), 52.9 (s), 52.4 (s), 52.2 (s), 38.3 (s), 31.2 (s), 29.8 (s), 25.8 (s), 24.8 (s), 18.1 (s). IR (ATR): 2916, 1598, 1504, 1356, 1192, 990, 966, 746, 691 cm^{-1} . R_f : 0.20 (2% $\text{Et}_2\text{O}:\text{Hexanes}$) LRMS (ESI+APCI) m/z [$\text{C}_{12}\text{H}_{18}\text{N}$] $^+$ ($[\text{M}+\text{H}]^+$) calculated 176.28, found 176.2.



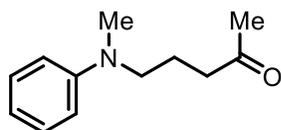
N-methyl-N-(3-methylpent-3-en-1-yl)aniline (**4a**)

Prepared using standard reaction conditions from commercially available *N,N*-dimethylaniline and isoprene. Mixture of inseparable regio- and *E* and *Z* isomers. Colorless Oil. 71% Yield 2:1 rr, 2:1 *E:Z* Complete after 12 hours. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.31 – 7.19 (m, 2H), 6.72 (dd, $J = 16.2, 7.8$ Hz, 3H), 5.75 (t, $J = 11.2$ Hz, 1H), 5.37 – 5.17 (m, 1H), 5.17 (s, 1H), 5.01 (d, $J = 5.0$ Hz, 1H), 4.75 (d, $J = 16.9$ Hz, 2H), 3.46 – 3.38 (m, 2H), 3.38 – 3.30 (m, 2H), 3.00 – 2.92 (m, 3H), 2.35 – 2.20 (m, 2H), 2.08 (t, $J = 7.6$ Hz, 2H), 1.84 – 1.67 (m, 6H), 1.67 – 1.56 (m, 6H), 1.07 (d, $J = 6.8$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 149.4 (s), 149.1 (s), 145.3 (s), 129.2 (s), 120.3 (s), 115.9 (s), 115.9 (s), 112.1 (s), 112.1 (s), 110.1 (s), 52.4 (s), 51.9 (s), 38.3 (s), 38.2 (s), 36.2 (s), 35.2 (s), 24.5 (s), 22.5 (s), 16.0 (s), 13.5 (s). IR (ATR): 2922, 1598, 1505, 1448, 1371, 990, 887, 746, 691 cm^{-1} . R_f : 0.20 (2% $\text{Et}_2\text{O}:\text{Hexanes}$) LRMS (ESI+APCI) m/z [$\text{C}_{13}\text{H}_{20}\text{N}$] $^+$ ($[\text{M}+\text{H}]^+$) calculated 190.30, found 190.2.



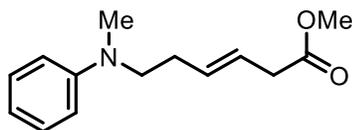
N-(3,4-dimethylpent-3-en-1-yl)-N-methylaniline (**4c**)

Prepared using standard reaction conditions from commercially available *N,N*-dimethylaniline and 2,3 dimethyl butadiene. Iseperable from terminal alkene regioisomer using CombiFlash Gold columns on Isco CombiFlash. Colorless Oil. 58% Yield 2:1 rr Complete after 12 hours. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.31 – 7.21 (m, 2H), 6.80 – 6.66 (m, 3H), 4.77 (m, 1H), 3.36 (dd, $J = 8.6, 7.1$ Hz, 2H), 3.29 (t, 2H), 2.96 (s, 3H), 2.35 – 2.27 (m, 1H), 2.07 (d, $J = 3.5$ Hz, 1H), 1.77 – 1.63 (m, 9H), 1.08 (dd, $J = 6.9, 2.5$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 149.0 (s), 129.1 (s), 126.0 (s), 124.7 (s), 115.8 (s), 112.5 (s), 112.1 (s), 110.1 (s), 51.0 (s), 39.2 (s), 38.1 (s), 31.8 (s), 30.9 (s), 21.8 (s), 20.6 (s), 20.2 (s), 20.0 (s), 19.0 (s), 18.9 (s). IR (ATR): 2920, 2859, 1598, 1505, 1448, 1370, 1199, 1115, 1034, 990, 889, 746, 690 cm^{-1} . R_f : 0.20 (2% $\text{Et}_2\text{O}:\text{Hexanes}$) LRMS (ESI+APCI) m/z [$\text{C}_{14}\text{H}_{21}\text{N}$] $^+$ ($[\text{M}+\text{H}]^+$) calculated 204.33, found 204.3.



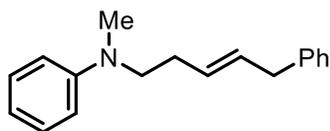
5-(methyl(phenyl)amino)pentan-2-one (**4d**)

Prepared using standard reaction conditions from commercially available *N,N*-dimethylaniline and 2-(trimethylsiloxy)-1,3-butadiene. Colorless Oil. 66% Yield Complete after 12 hours. ^1H NMR (500 MHz, CDCl_3) δ 7.25 (t, $J = 7.9$ Hz, 2H), 6.73 (m, 3H), 3.34 (t, 2H), 2.93 (s, 3H), 2.49 (t, $J = 7.0$ Hz, 2H), 2.14 (s, 3H), 1.93 – 1.85 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 208.3 (s), 129.2 (s), 116.3 (s), 112.3 (s), 51.8 (s), 40.7 (s), 38.1 (s), 30.0 (s), 21.1 (s). IR (ATR): 2922, 1713, 1598, 1505, 1363, 1164, 990, 748, 693 cm^{-1} R_f : 0.20 (10% EtOAc:Hexanes) LRMS (ESI+APCI) m/z $[\text{C}_{12}\text{H}_{18}\text{NO}]^+$ ($[\text{M}+\text{H}]^+$) calculated 192.27, found 192.2.



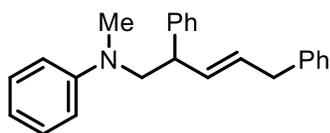
methyl 6-(methyl(phenyl)amino)hex-3-enoate (**4e**)

Prepared using standard reaction conditions from commercially available *N,N*-dimethylaniline and methyl 2,4-penadienoate. Colorless Oil. 60% Yield 20:1 *E:Z* Complete after 12 hours. ^1H NMR (400 MHz, cdcl_3) δ 7.24 (m, 2H), 6.70 (d, $J = 7.8$ Hz, 3H), 5.64 – 5.48 (m, 2H), 3.68 (s, 3H), 3.38 (t, 2H), 3.04 (d, $J = 5.5$ Hz, 2H), 2.93 (s, 3H), 2.32 (dd, $J = 13.9, 6.2$ Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 208.3 (s), 129.2 (s), 116.3 (s), 112.3 (s), 51.8 (s), 40.7 (s), 38.1 (s), 30.0 (s), 21.1 (s). IR (ATR): 2915, 1709, 1598, 1506, 1448, 1355, 1193, 1033, 992, 748, 693 cm^{-1} R_f : 0.30 (5% EtOAc:Hexanes) LRMS (ESI+APCI) m/z $[\text{C}_{14}\text{H}_{19}\text{NO}_2]^+$ ($[\text{M}+\text{H}]^+$) calculated 233.31, found 233.2.



N-methyl-*N*-(5-phenylpent-3-en-1-yl)aniline (**4f**)

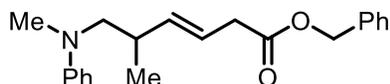
Prepared using standard reaction conditions from commercially available *N,N*-dimethylaniline and 1-phenyl-1,3-butadiene. Inseparable mixture of diastereomers using CombiFlash Gold columns on Isco CombiFlash. Colorless Oil. 90% Yield 2:1 *E:Z* Complete after 12 hours. ^1H NMR (500 MHz, CDCl_3) δ 7.41 – 7.28 (m, 98H), 7.28 – 7.18 (m, 101H), 6.78 – 6.56 (m, 55H), 6.44 (d, $J = 17.3$ Hz, 5H), 6.27 (s, 6H), 5.70 (dd, $J = 16.1, 5.4$ Hz, 21H), 5.54 (dd, $J = 20.6, 12.2$ Hz, 20H), 3.46 – 3.32 (m, 82H), 2.95 (d, $J = 18.6$ Hz, 35H), 2.52 – 2.46 (m, 18H), 2.46 – 2.26 (m, 33H), 1.80 (t, $J = 11.3$ Hz, 8H). ^{13}C NMR (126 MHz, CDCl_3) δ 140.7 (s), 131.0 (s), 130.1 (s), 129.1 (s), 128.5 (s), 128.5 (s), 128.4 (s), 128.3 (s), 127.4 (s), 125.9 (s), 116.2 (s), 116.0 (s), 112.4 (s), 39.26 – 39.10 (m), 29.87 – 29.71 (m), 24.72 (s). IR (ATR): 3024, 2921, 1598, 1504, 1452, 1358, 990, 965, 745, 693 cm^{-1} R_f : 0.30 (1% Et_2O :Hexanes) LRMS (ESI+APCI) m/z $[\text{C}_{18}\text{H}_{22}\text{N}]^+$ ($[\text{M}+\text{H}]^+$) calculated 252.37, found 252.2.



N-(2,5-diphenylpent-3-en-1-yl)-*N*-methylaniline (**4g**)

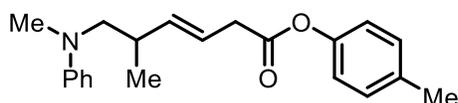
Prepared using standard reaction conditions from commercially available *N,N*-dimethylaniline and 1,4-diphenyl 1,3-butadiene. Off White Solid. 77% Yield 5:1 *E:Z* Complete after 16 hours. ^1H NMR (500 MHz, CDCl_3) δ 7.39 – 7.14 (m, 10H), 7.13 (d, 2H), 6.77 – 6.63 (m, 3H), 5.80 (dd, $J = 12.0, 5.8$ Hz, 1H), 5.67 (dd, $J = 14.5, 7.5$ Hz, 1H), 4.82 – 3.66 (m, 2H), 3.55 (dd, $J = 14.5, 7.0$ Hz, 1H), 3.37 (d, $J = 6.7$ Hz, 2H), 2.73 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ

143.4 (s), 132.3 (s), 131.0 (s), 129.1 (s), 128.6 (s), 127.8 (s), 126.6 (s), 125.9 (s), 115.7 (s), 112.0 (s), 59.3 (s), 47.3 (s), 39.6 (s), 39.1 (s). IR (ATR): 3025, 2922, 1598, 1505, 1452, 1343, 1193, 967, 991, 746, 699 cm^{-1} R_f: 0.30 (1% Et₂O:Hexanes) LRMS (ESI+APCI) m/z [C₂₄H₂₆N]⁺ ([M+H]⁺) calculated 328.47, found 328.2.



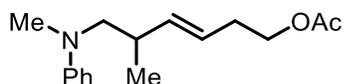
benzyl 5-methyl-6-(methyl(phenyl)amino)hex-3-enoate (**4h**)

Prepared using standard reaction conditions from commercially available N,N-dimethylaniline and previously reported **2d** (benzyl sorbate), which was made through a similar DCC coupling as **2c**. Colorless Oil. 52% Yield 20:1 *E:Z* Complete after 12 hours. ¹H NMR (500 MHz, CDCl₃) δ 7.34 (m, 5H), 7.23 (d, *J* = 8.8 Hz, 2H), 6.77 – 6.64 (m, 2H), 5.64 – 5.48 (m, 2H), 5.14 (s, 2H), 3.22 (d, *J* = 10.2 Hz, 2H), 3.09 (d, *J* = 5.4 Hz, 2H), 2.94 (s, 3H), 2.68 (dt, *J* = 14.0, 7.0 Hz, 1H), 1.04 (d, *J* = 6.7 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 171.7 (s), 149.3 (s), 138.0 (s), 135.9 (s), 129.1 (s), 128.6 (s), 128.2 (s), 121.4 (s), 115.8 (s), 112.1 (s), 66.4 (s), 59.1 (s), 39.5 (s), 38.2 (s), 35.7 (s), 17.7 (s). IR (ATR): 2920, 1735, 1598, 1506, 1455, 1239, 1159, 992, 970, 747, 694 cm^{-1} R_f: 0.40 (5% EtOAc:Hexanes) LRMS (ESI+APCI) m/z [C₂₁H₂₅NO₂]⁺ ([M+H]⁺) calculated 324.44, found 324.2.



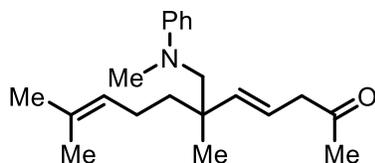
p-tolyl 5-methyl-6-(methyl(phenyl)amino)hex-3-enoate (**4i**)

Prepared using standard reaction conditions from commercially available N,N-dimethylaniline and previously synthesized **2c**. White Solid. 60% Yield 20:1 *E:Z* Complete after 12 hours. 87% purity due to inseparable anisole impurity. ¹H NMR (500 MHz, CDCl₃) δ 7.31 – 7.05 (m, 3H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.70 (d, *J* = 9.4 Hz, 2H), 5.71 – 5.62 (m, 2H), 3.27 (d, *J* = 7.2 Hz, 2H), 2.96 (s, 3H), 2.72 (dd, *J* = 17.6, 15.5 Hz, 1H), 2.37 (s, 3H), 1.08 (d, *J* = 6.7 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 170.5 (s), 149.4 (s), 148.5 (s), 138.5 (s), 135.4 (s), 129.6 (s), 121.1 (s), 115.8 (s), 111.9 (s), 59.2 (s), 39.5 (s), 38.2 (s), 35.8 (s), 20.85 (s), 17.77 (s). IR (ATR): 2917, 2849, 1755, 1598, 1506, 1452, 1371, 1343, 1196, 1165, 1128, 970, 748, 692 cm^{-1} R_f: 0.30 (10% EtOAc:Hexanes) LRMS (ESI+APCI) m/z [C₂₁H₂₅NO₂]⁺ ([M+H]⁺) calculated 324.44, found 324.2.

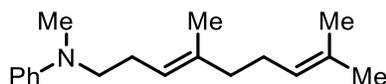


4-methyl-5-(methyl(phenyl)amino)pent-2-en-1-yl acetate (**4j**)

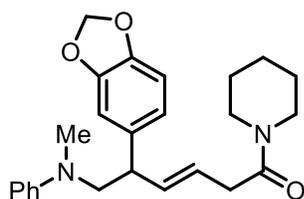
Prepared using standard reaction conditions from commercially available N,N-dimethylaniline and 2,4-hexadienyl-1-acetate. Reaction produces ~10% of the allylation product as well ([M+H]⁺ = 202.3). Colorless Oil. 50% Yield 2:1 *rr*. Complete after 16 hours. ¹H NMR (500 MHz, CDCl₃) δ 7.33 – 7.17 (m, 2H), 6.72 (d, *J* = 9.4 Hz, 3H), 5.75 – 5.65 (m, 1H), 5.75 – 5.39 (m, 1H), 4.10 – 4.05 (m, 2H), 3.28 (d, 2H), 2.97 (s, 3H), 2.09 (s, 64H), 1.61 (s, 30H). ¹³C NMR (126 MHz, CDCl₃) δ 171.4 (s), 129.1 (s), 127.4 (s), 126.3 (s), 116.2 (s), 112.2 (s), 65.0 (s), 54.4 (s), 39.6 (s), 36.8 (s), 26.7 (s), 21.0 (s), 12.9 (s). IR (ATR): 2920, 2851, 1742, 1596, 1507, 1463, 1051, 1033 R_f: 0.20 (30% EtOAc:Hexanes) LRMS (ESI+APCI) m/z [C₁₆H₂₄NO₂]⁺ ([M+H]⁺) calculated 262.37, found 262.2.

6,10-dimethyl-6-((methyl(phenyl)amino)methyl)undeca-4,9-dien-2-one (**4k**)

Prepared using standard reaction conditions from commercially available *N,N*-dimethylaniline and pseudoionone. Colorless Oil. 61% Yield 20:1 *E:Z* Complete after 16 hours. ^1H NMR (500 MHz, CDCl_3) δ 7.29 – 7.20 (m, 2H), 6.78 – 6.67 (m, 3H), 5.07 (d, $J = 8.1$ Hz, 2H), 4.95 (d, $J = 7.2$ Hz, 1H), 3.35 (dd, $J = 18.1, 6.0$ Hz, 2H), 3.11 (d, $J = 18.5$ Hz, 2H), 2.91 (s, 3H), 2.50 (d, $J = 15.5$ Hz, 2H), 2.36 (dd, $J = 14.8, 10.7$ Hz, 2H), 2.09 (s, 3H), 2.08–1.93 (m, 2H), 1.69 (s, 3H), 1.61 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 149.4 (s), 137.7 (s), 131.5 (s), 129.0 (s), 124.1 (s), 112.0 (s), 39.3 (s), 30.0 (s), 26.44 (s), 25.7 (s), 18.0 (s). IR (ATR): 2921, 2851, 1713, 1599, 1507, 1449, 1375, 1033, 746, 692 cm^{-1} R_f: 0.20 (20% EtOAc:Hexanes) LRMS (ESI+APCI) m/z [$\text{C}_{21}\text{H}_{32}\text{NO}$]⁺ ([M+H]⁺) calculated 314.49, found 314.2.

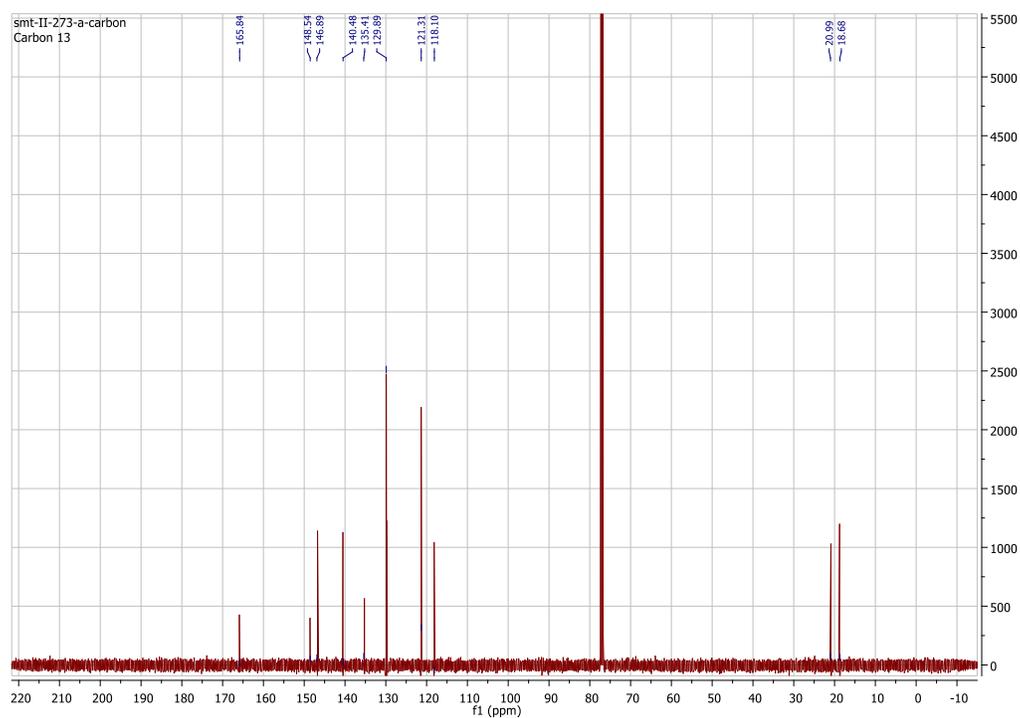
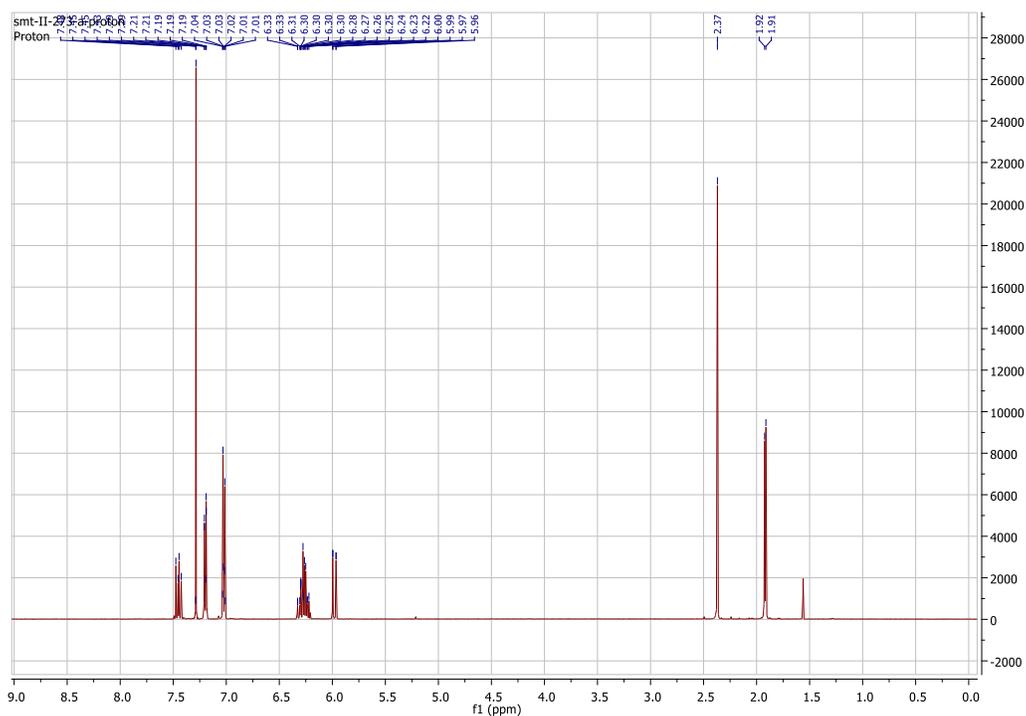
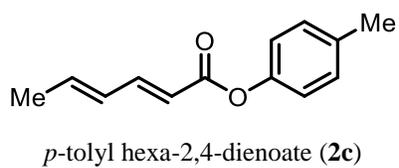
N-(4,8-dimethylnona-3,7-dien-1-yl)-N-methylaniline (**4l**)

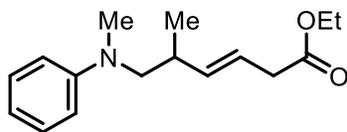
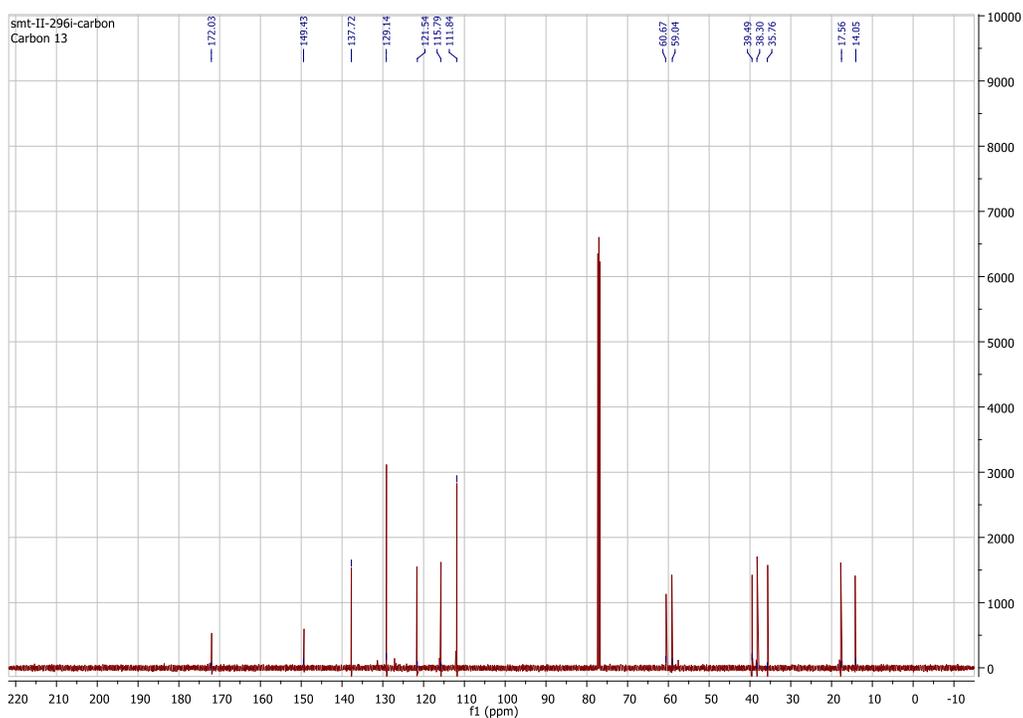
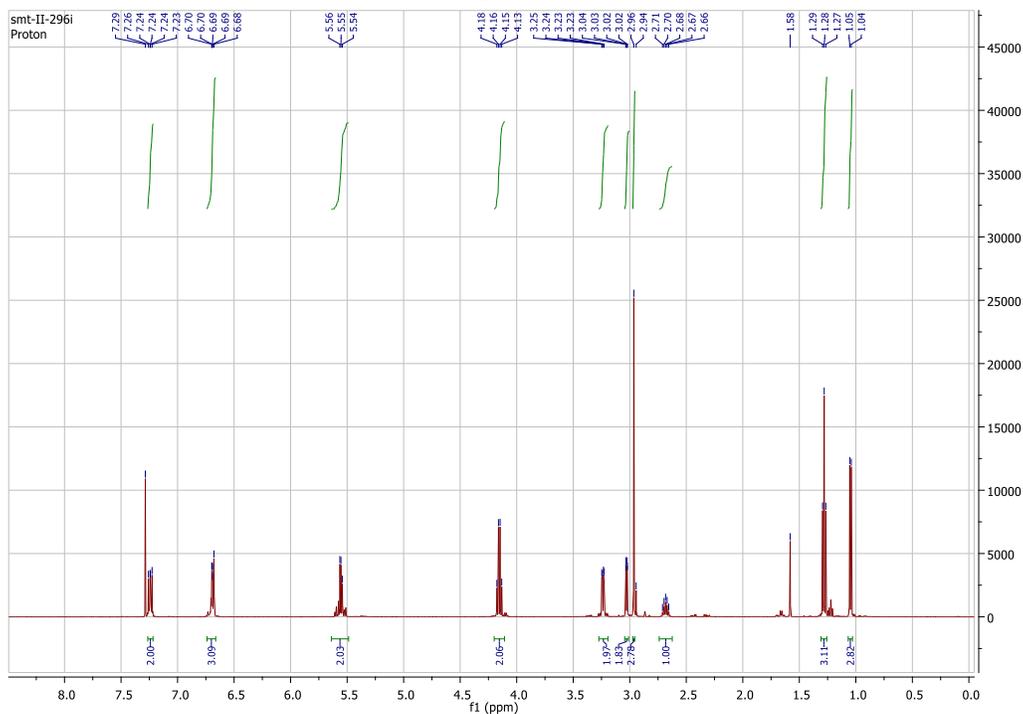
Prepared using standard reaction conditions from commercially available *N,N*-dimethylaniline and myrcene. Colorless Oil. 39% Yield 1:1 rr 20:1 *E:Z* Complete after 12 hours. ^1H NMR (500 MHz, CDCl_3) δ 7.31 – 7.16 (m, 2H), 6.72 (dt, $J = 14.7, 7.6$ Hz, 3H), 5.31 (m, 1H), 5.17 (m, 1H), 3.45 – 3.23 (m, 2H), 2.96 (s, 3H), 2.93 (s, 3H), 2.36 – 2.25 (m, 2H), 2.25 – 1.91 (m, 2H), 1.73 (s, 3H), 1.63 (s, 3H), 1.57 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 148.8 (s), 137.7 (s), 137.2 (s), 132.1 (s), 129.2 (s), 124.2 (s), 120.7 (s), 120.3 (s), 116.0 (s), 115.9 (s), 112.1 (s), 52.3 (s), 51.3 (s), 38.1 (s), 37.5 (s), 33.3 (s), 27.0 (s), 26.9 (s), 25.7 (s), 17.7 (s), 13.3 (s). IR (ATR): 2920, 2854, 1599, 1505, 1448, 1374, 1191, 990, 746, 690 cm^{-1} R_f: 0.30 (2% Et₂O:Hexanes) LRMS (ESI+APCI) m/z [$\text{C}_{18}\text{H}_{28}\text{N}$]⁺ ([M+H]⁺) calculated 258.42, found 258.3.

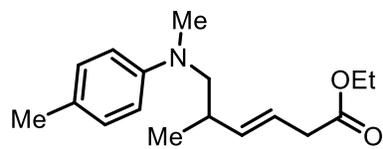
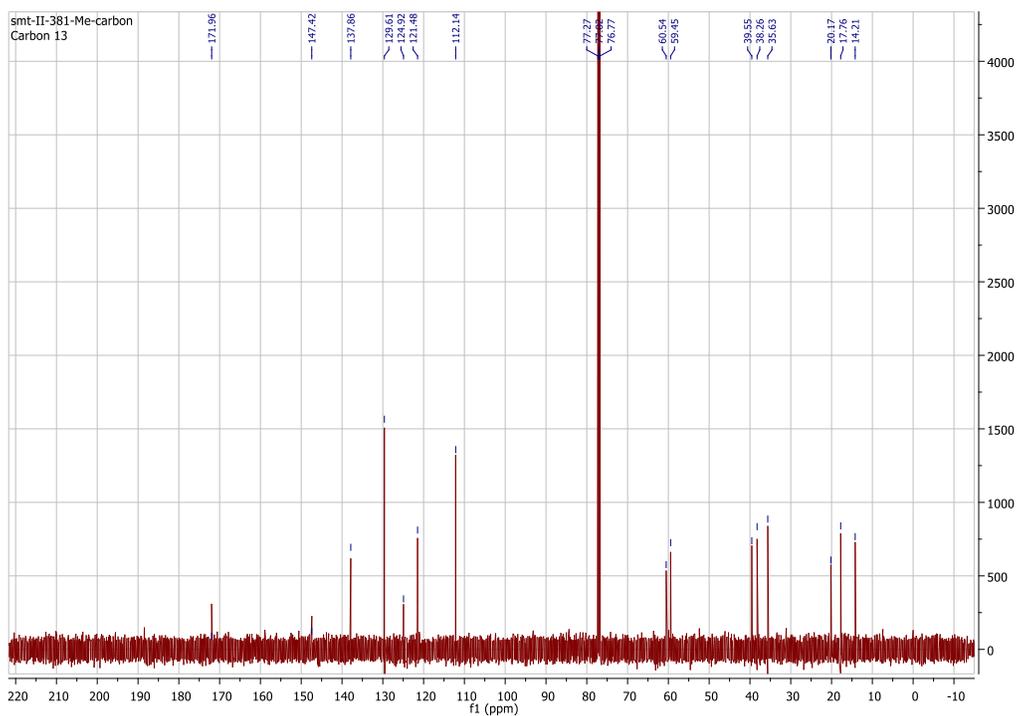
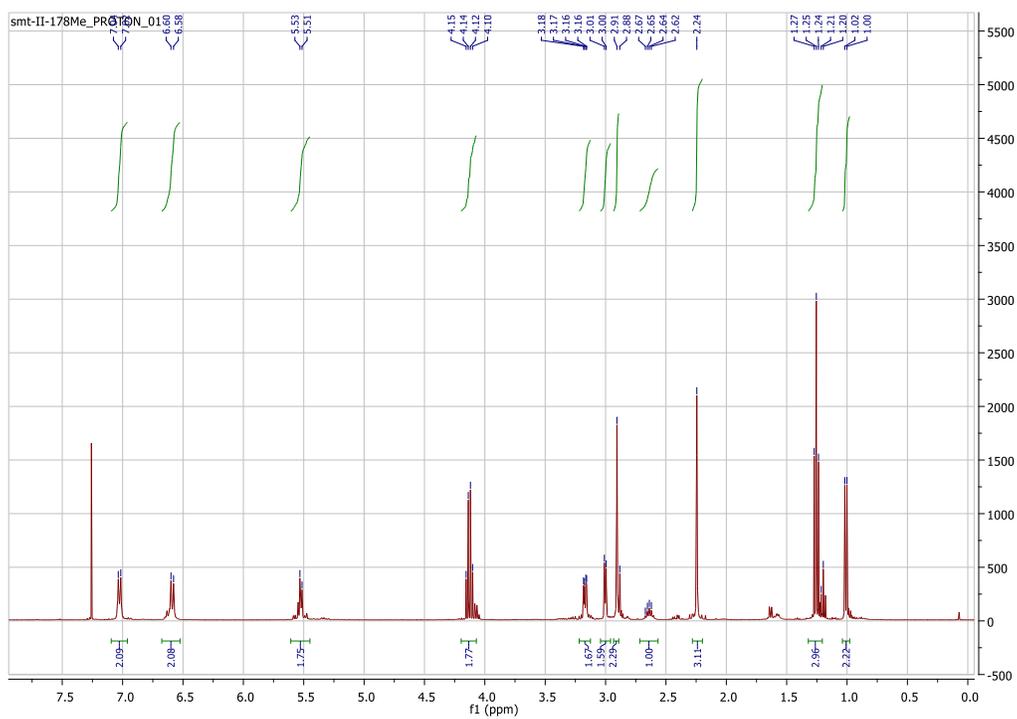
5-(benzo[d][1,3]dioxol-5-yl)-6-(methyl(phenyl)amino)-1-(piperidin-1-yl)hex-3-en-1-one (**4m**)

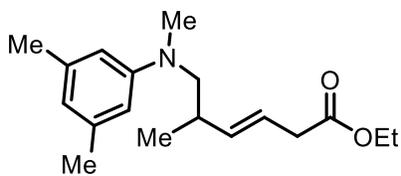
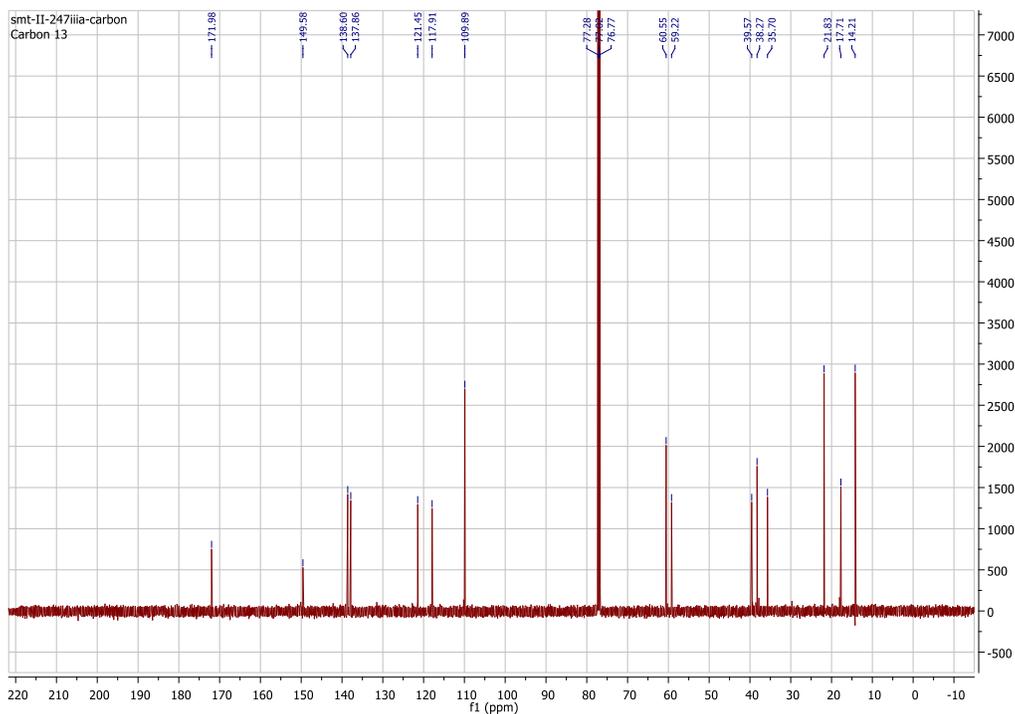
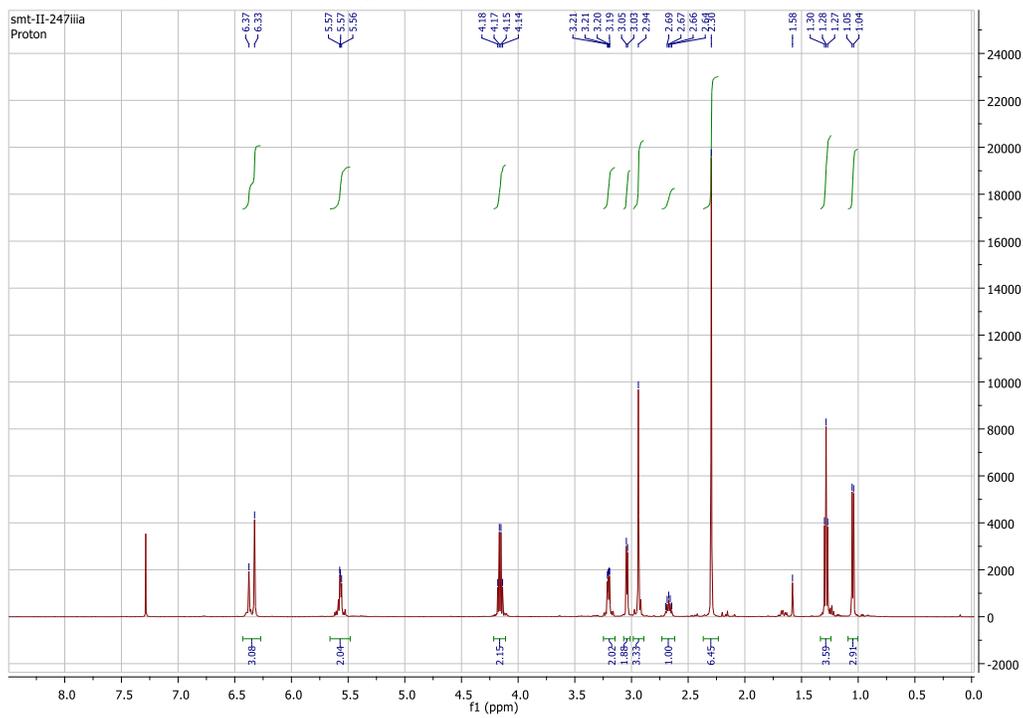
Prepared using standard reaction conditions from commercially available *N,N*-dimethylaniline and piperine. Colorless Oil. 34% Yield Complete after 16 hours. ^1H NMR (500 MHz, CDCl_3) δ 7.31 – 7.19 (m, 2H), 6.80 – 6.57 (m, 5H), 5.95 (s, 2H), 5.73 – 5.56 (m, 2H), 3.80 (m, 2H), 3.62 – 3.54 (m, 2H), 3.54 – 3.22 (m, 28H), 2.97 (s, 3H), 1.61 – 1.49 (m, 4H), 1.34 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 170.8 (s), 148.8 (s), 147.6 (s), 145.8 (s), 133.8 (s), 132.5 (s), 129.3 (s), 128.5 (s), 116.0 (s), 111.9 (s), 109.3 (s), 107.8 (s), 100.9 (s), 56.1 (s), 43.3 (s), 39.8 (s), 26.4 (s), 25.7 (s), 24.5 (s). IR (ATR): 2912, 2852, 1630, 1503, 1489, 1443, 1245, 1163, 1120, 1033, 1010, 927, 696. R_f: 0.10 (40% EtOAc:Hexanes) LRMS (ESI+APCI) m/z [$\text{C}_{25}\text{H}_{31}\text{N}_2\text{O}_3$]⁺ ([M+H]⁺) calculated 407.53, found 407.3.

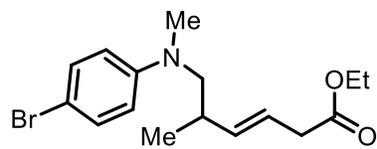
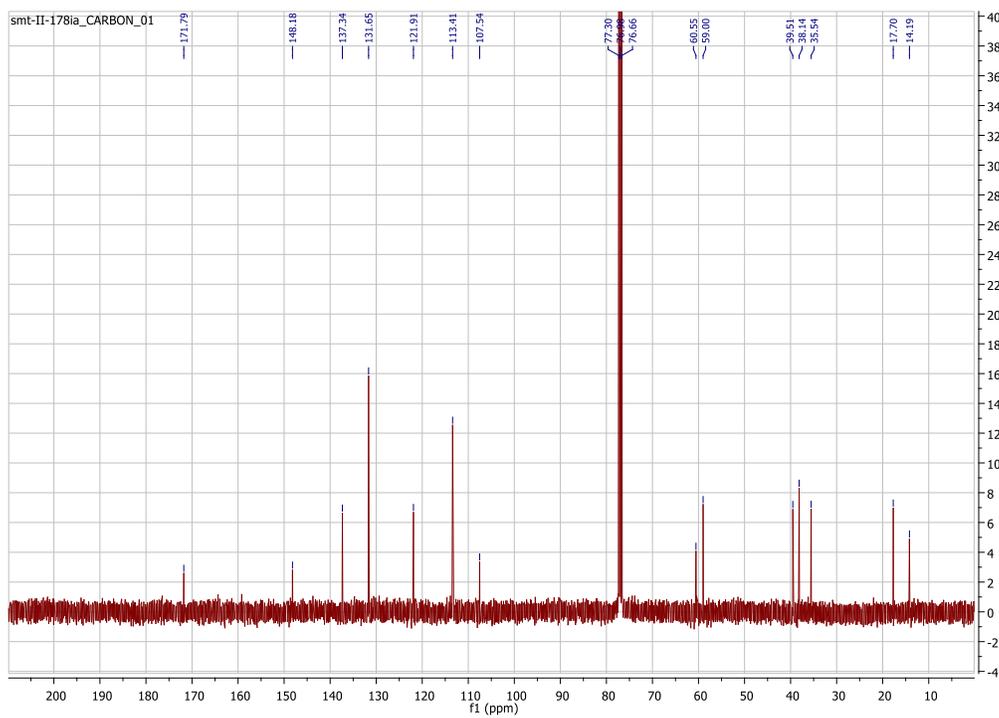
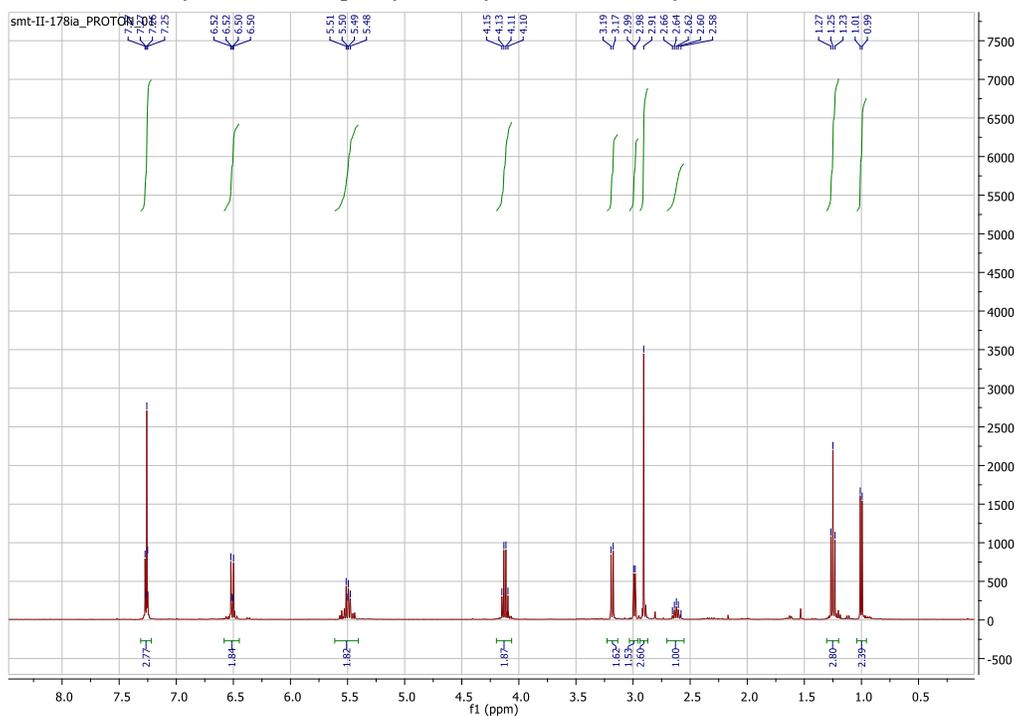
NMR Spectra

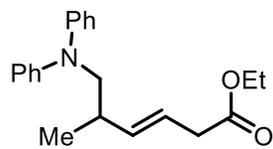
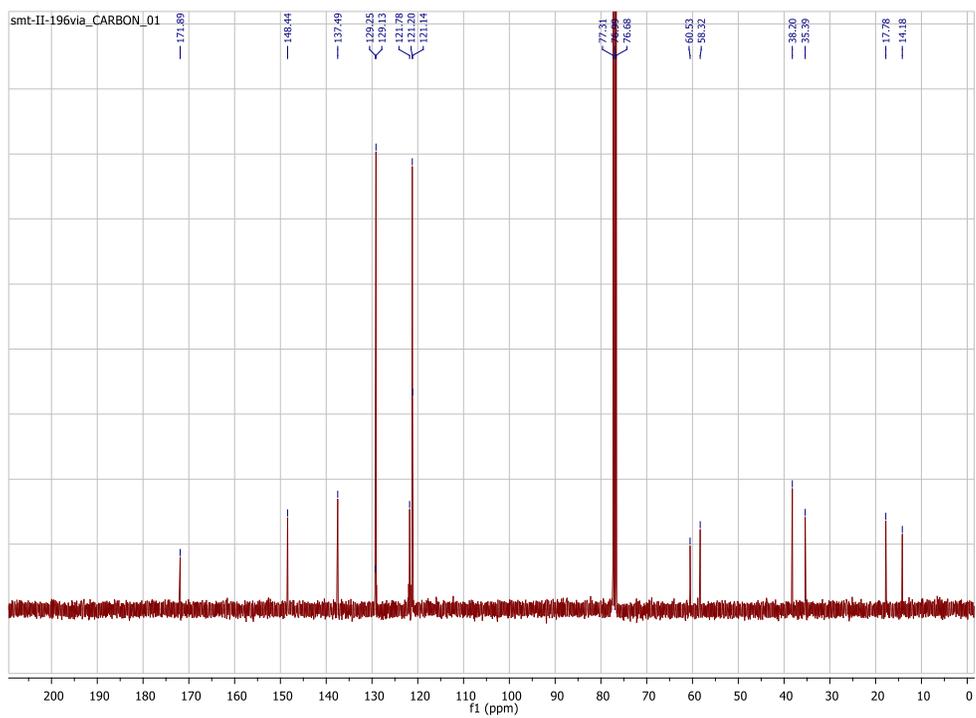
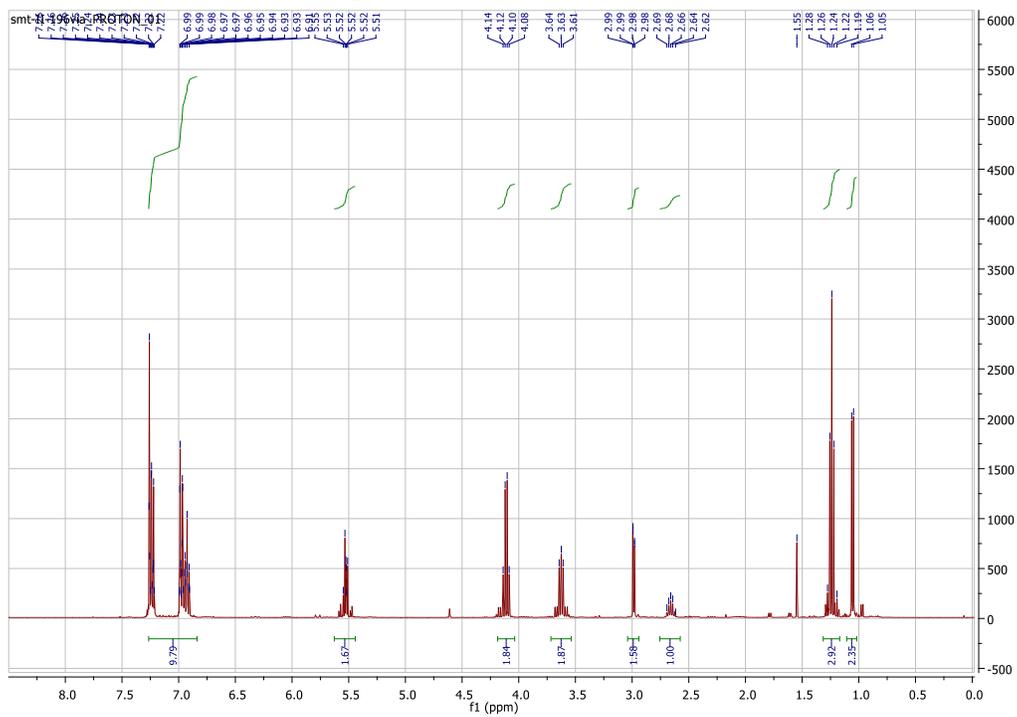


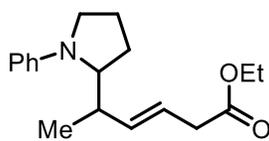
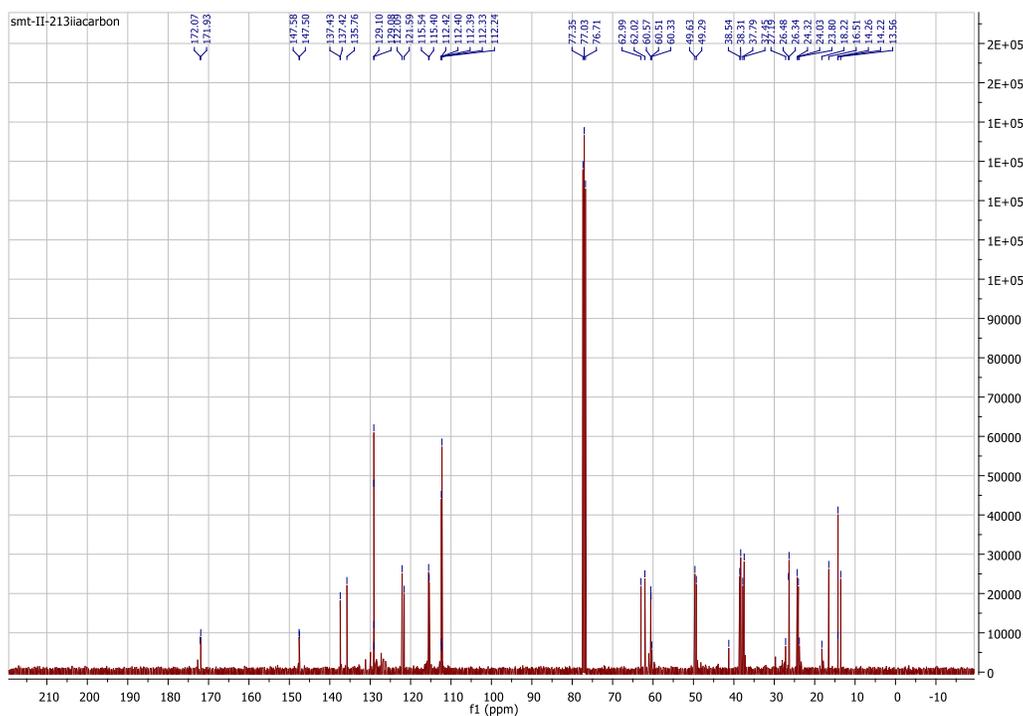
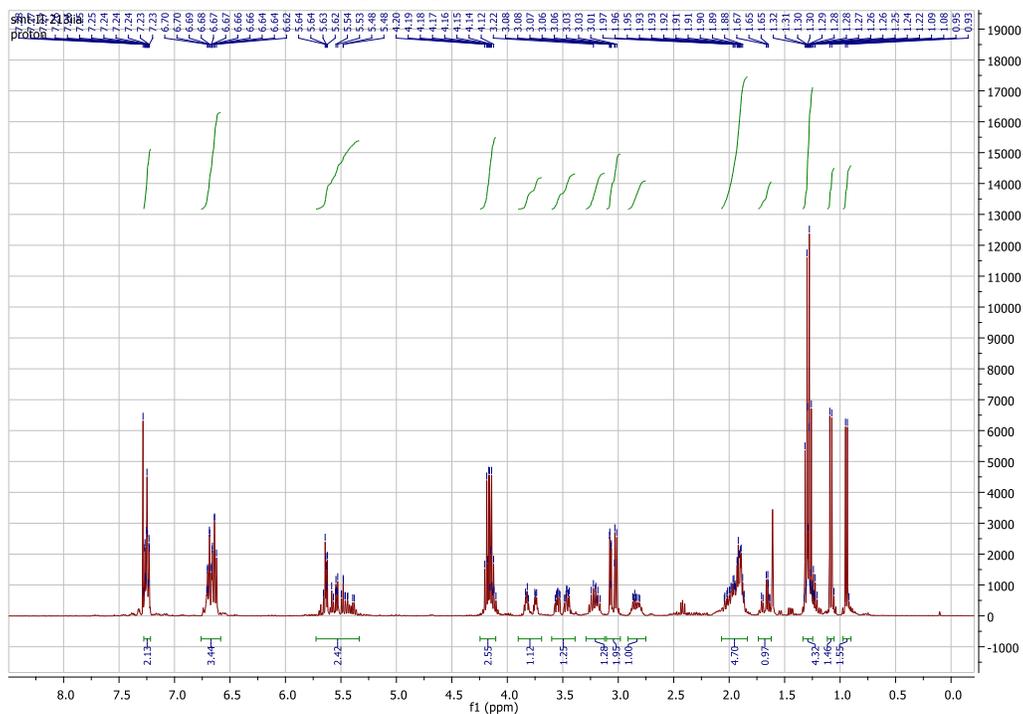
ethyl 5-methyl-6-(methyl(phenyl)amino)hex-3-enoate (**3a**)

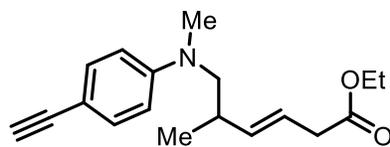
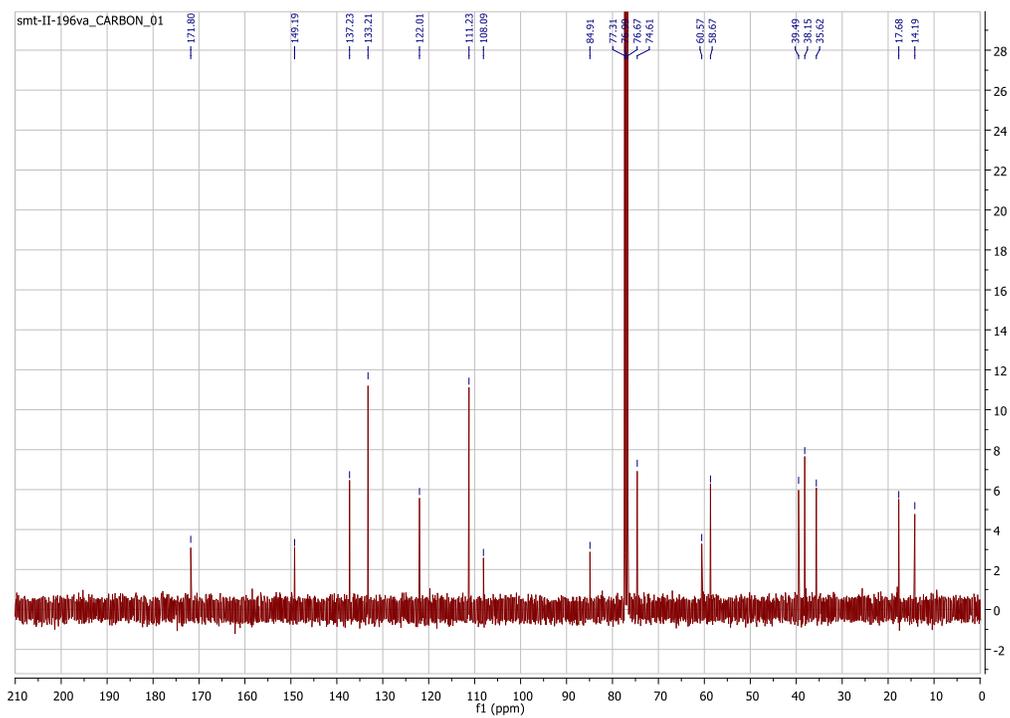
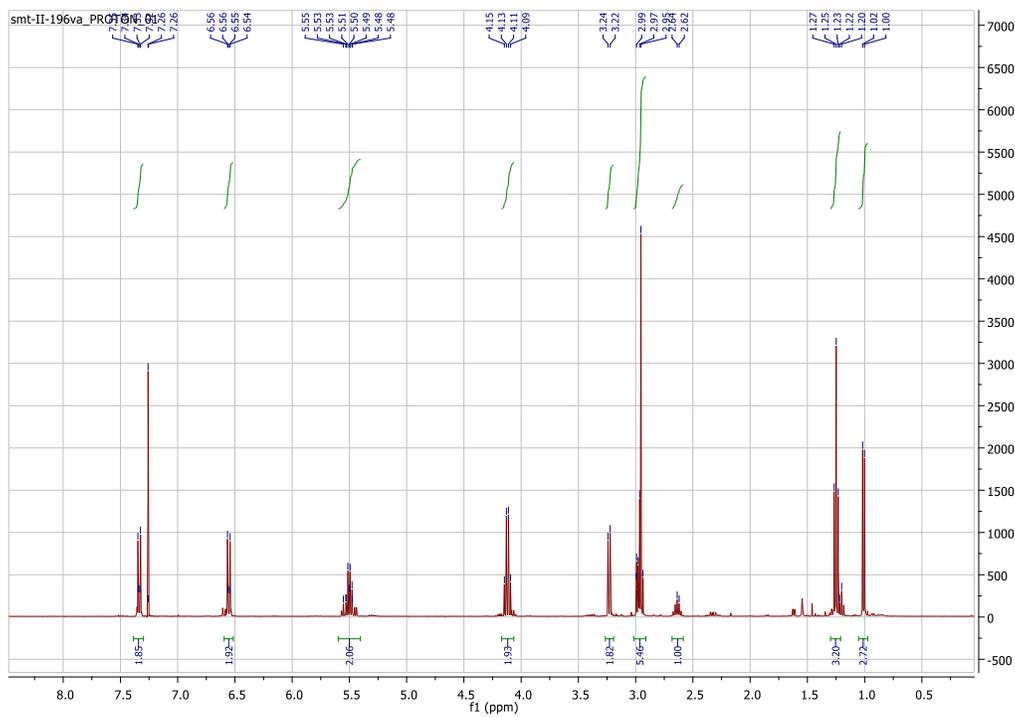
ethyl 5-methyl-6-(methyl(p-tolyl)amino)hex-3-enoate (**3b**)

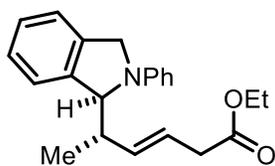
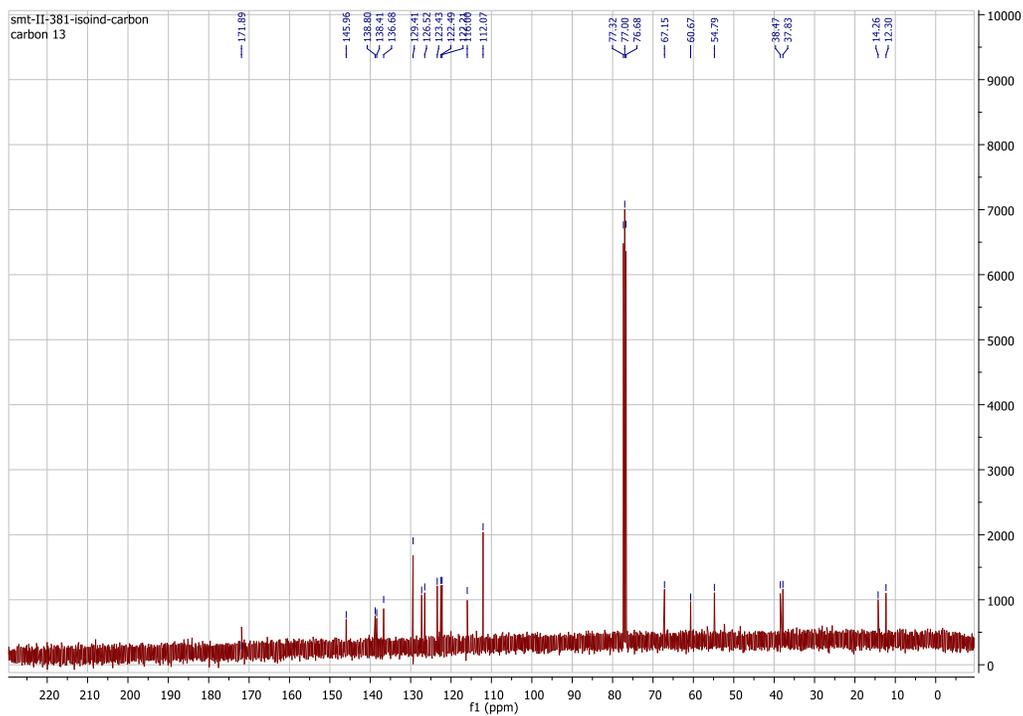
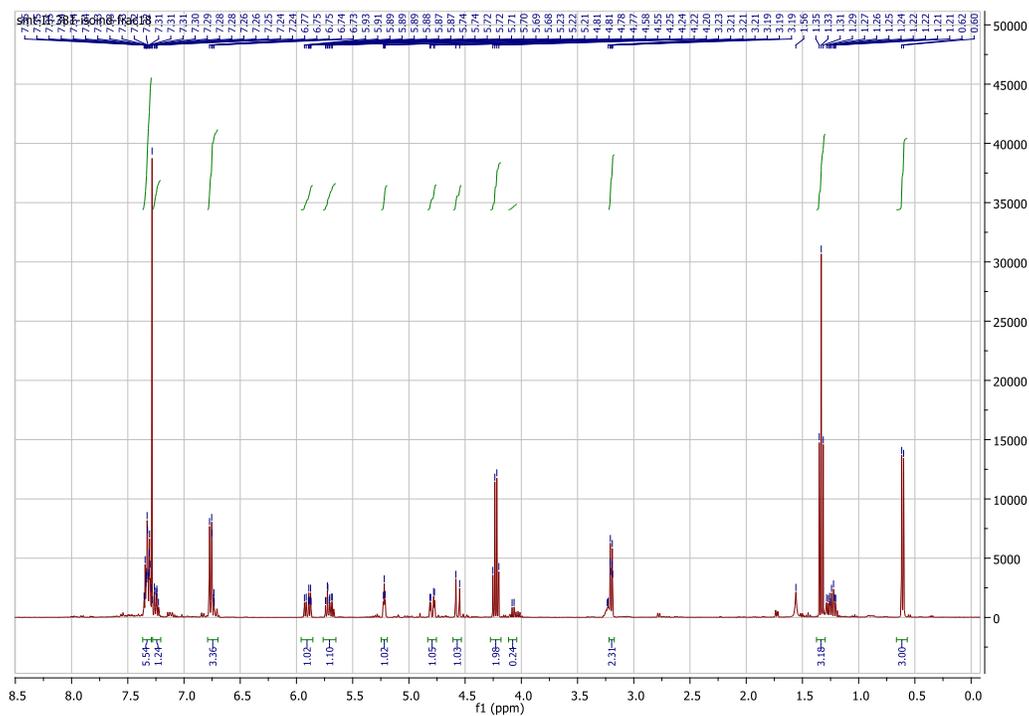
ethyl 6-((3,5-dimethylphenyl)(methyl)amino)-5-methylhex-3-enoate (**3c**)

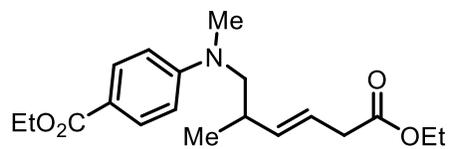
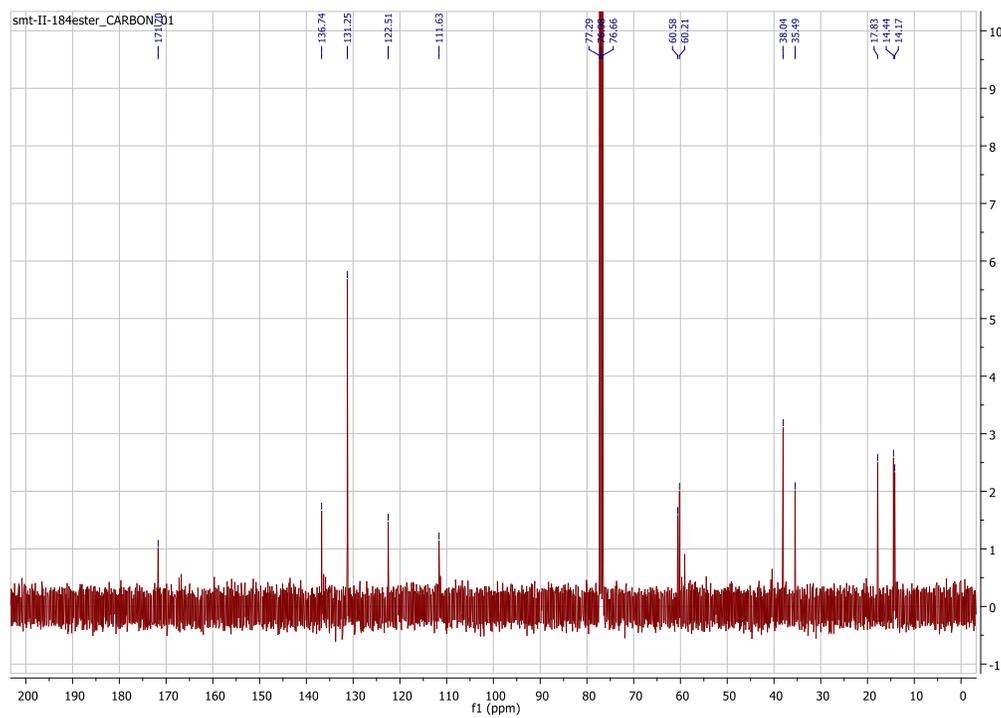
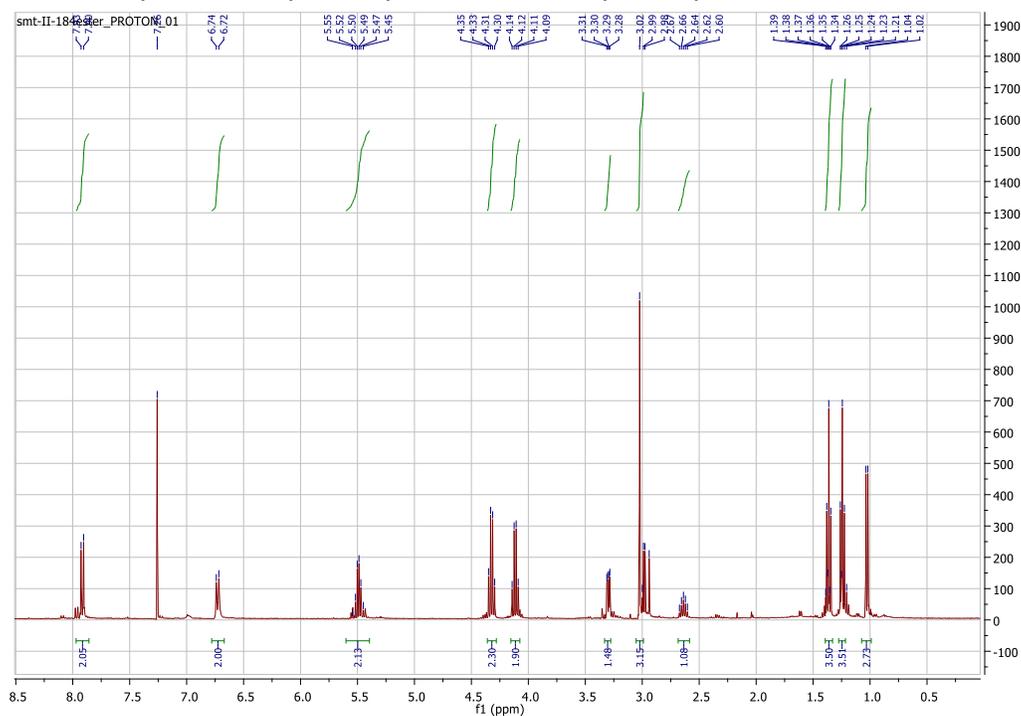
ethyl 6-((4-bromophenyl)(methyl)amino)-5-methylhex-3-enoate (**3d**)

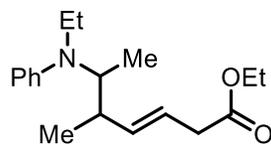
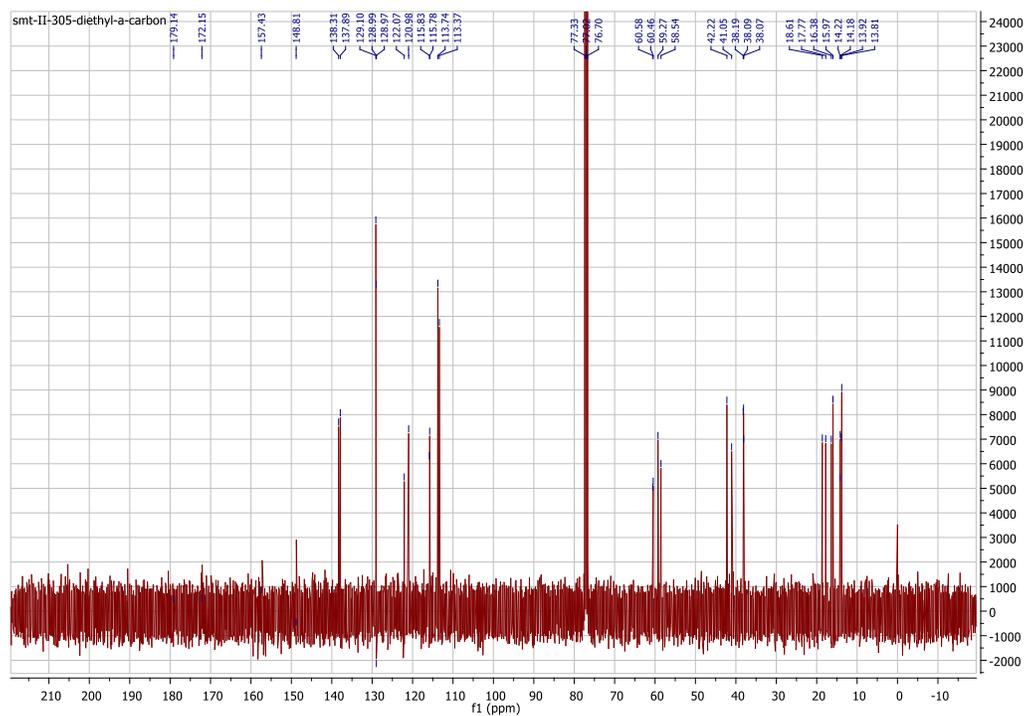
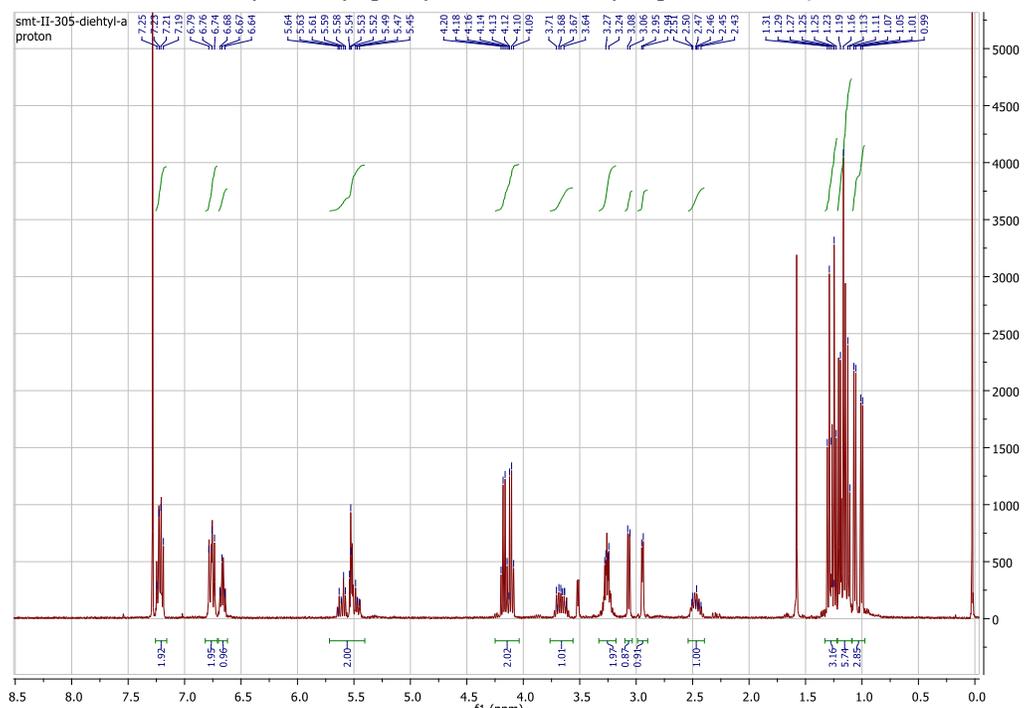
ethyl 6-(diphenylamino)-5-methylhex-3-enoate (**3e**)

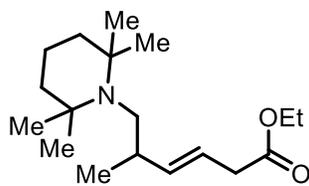
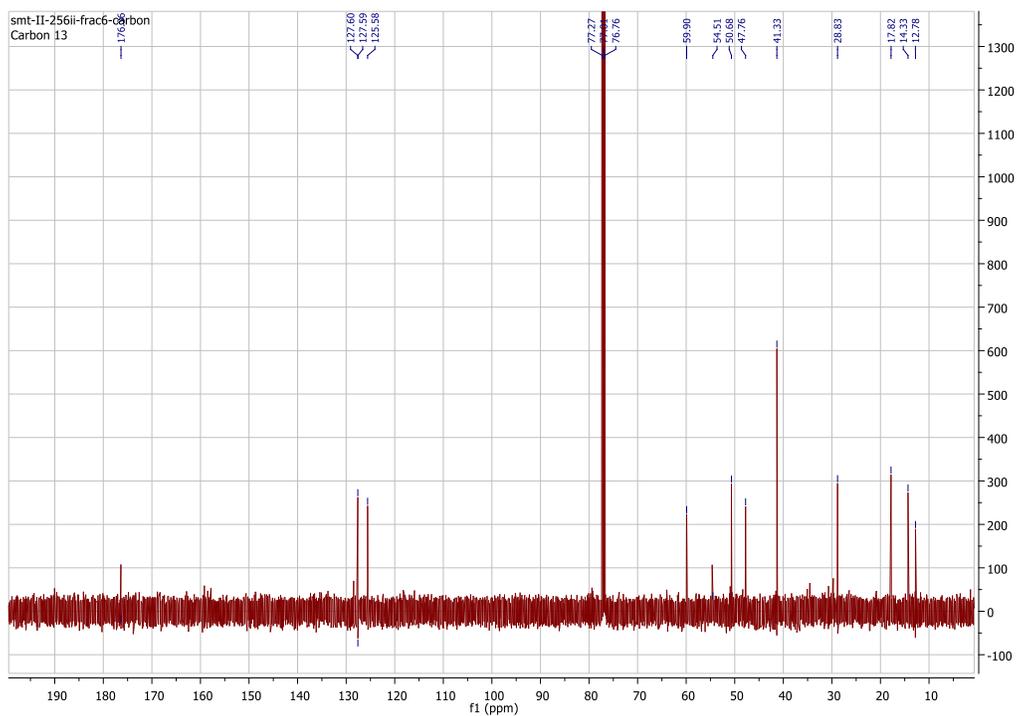
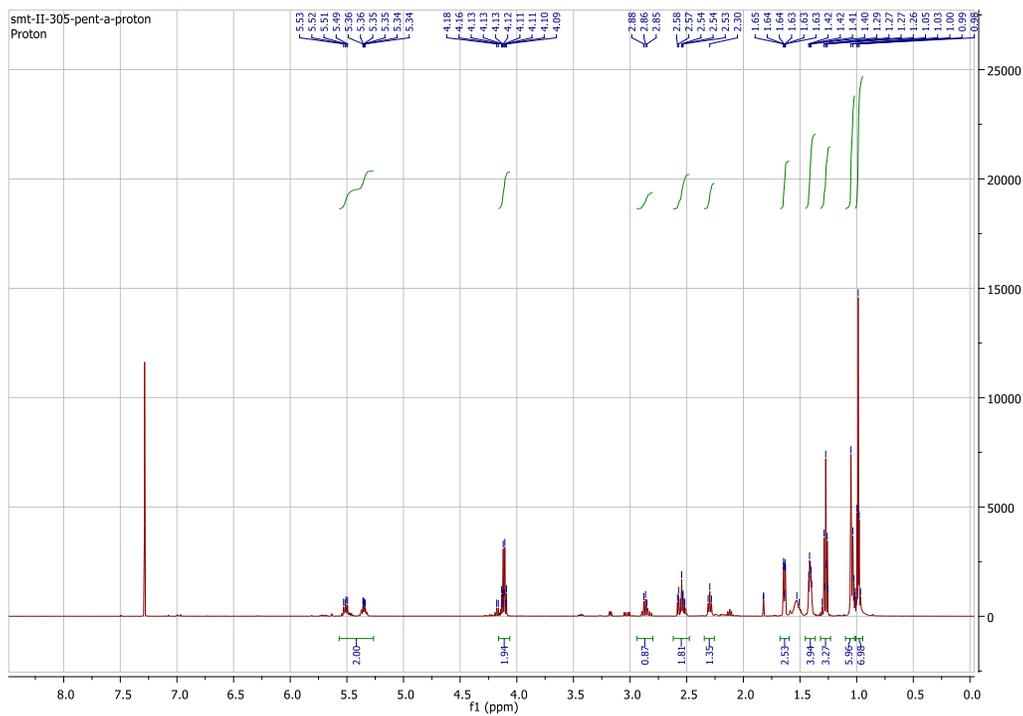
ethyl 5-(1-phenylpyrrolidin-2-yl)hex-3-enoate (**3f**)

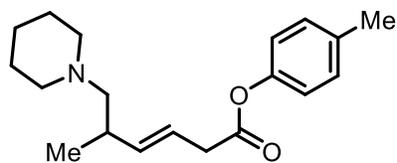
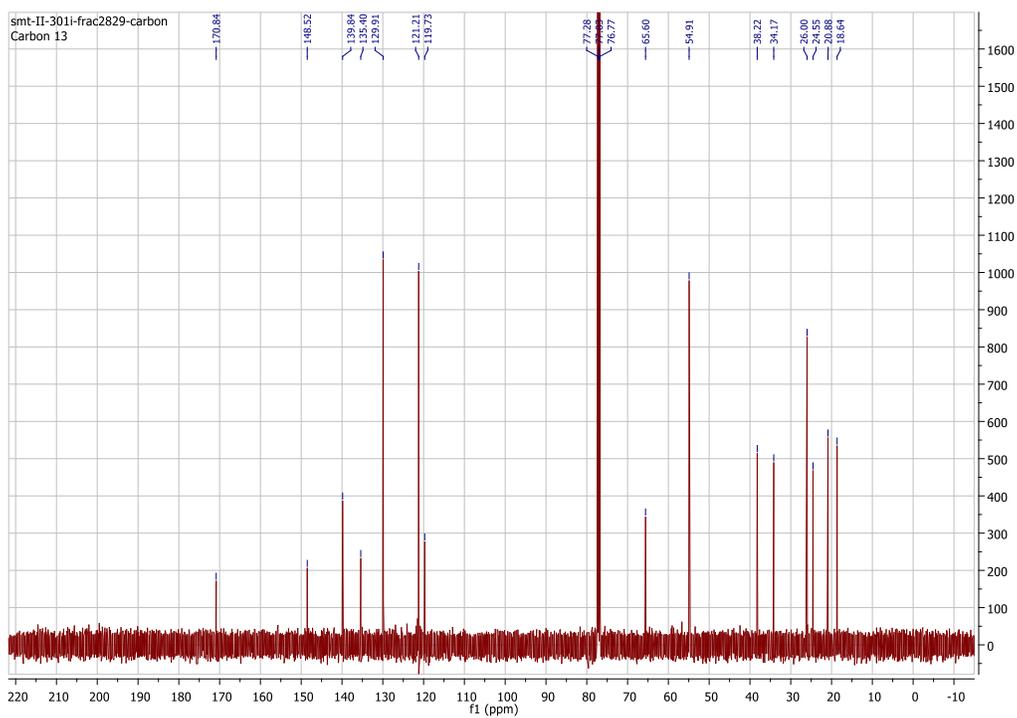
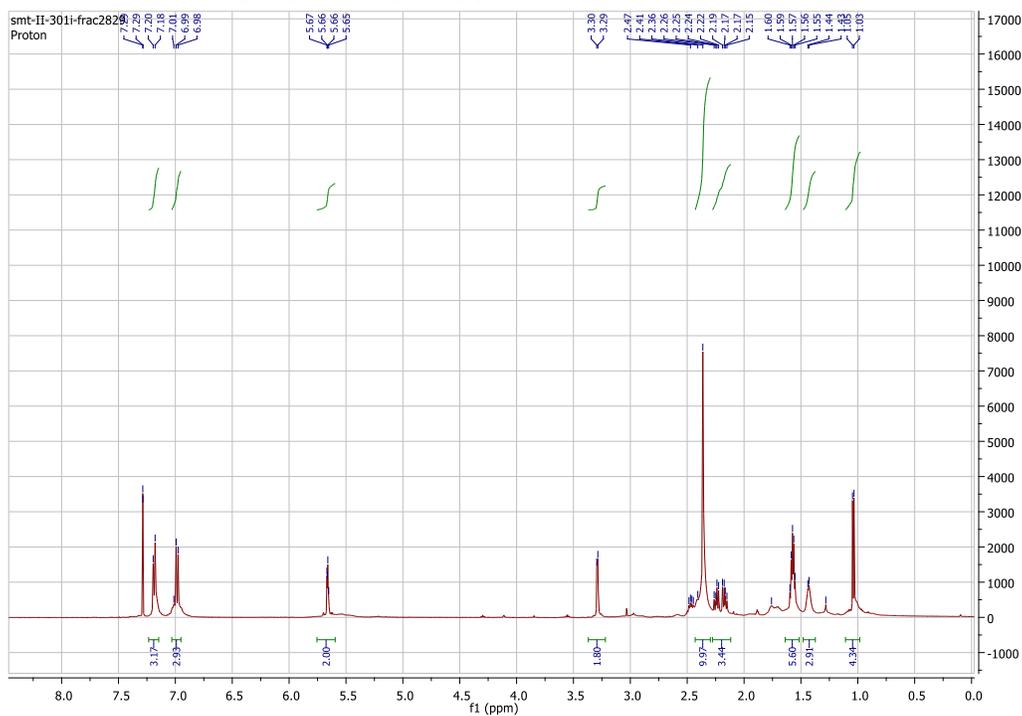
ethyl 6-((4-ethynylphenyl)(methyl)amino)-5-methylhex-3-enoate (**3g**)

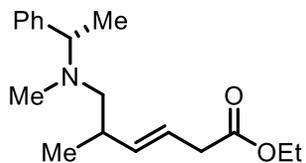
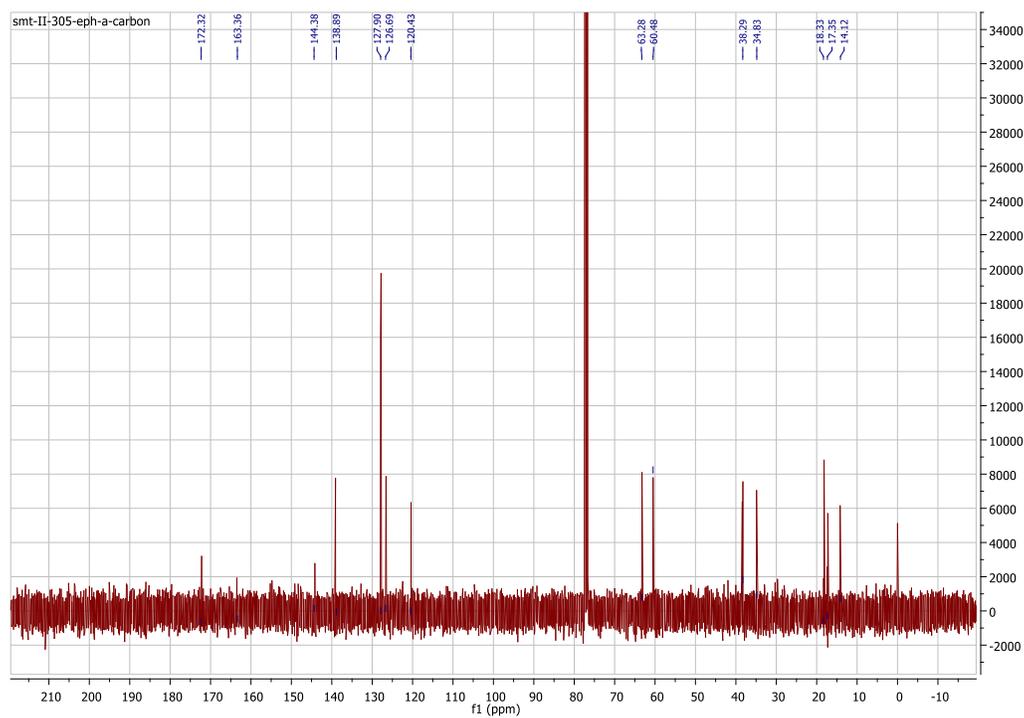
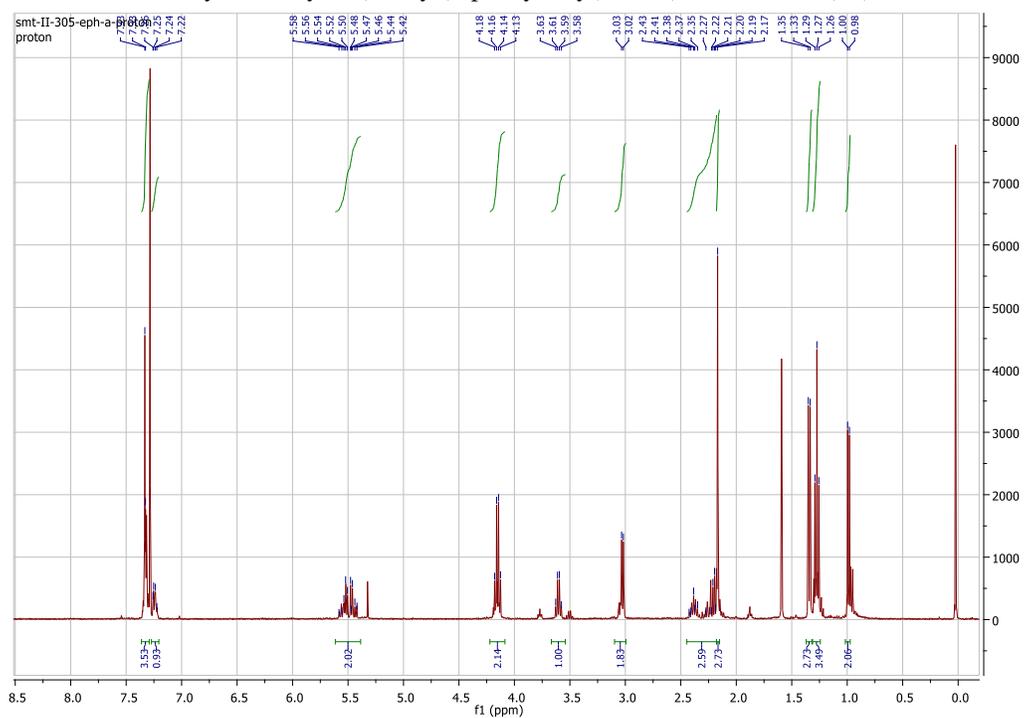
ethyl 5-(2-phenylisoindolin-1-yl)hex-3-enoate (**3h**)

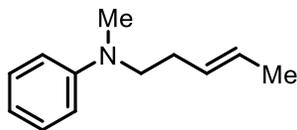
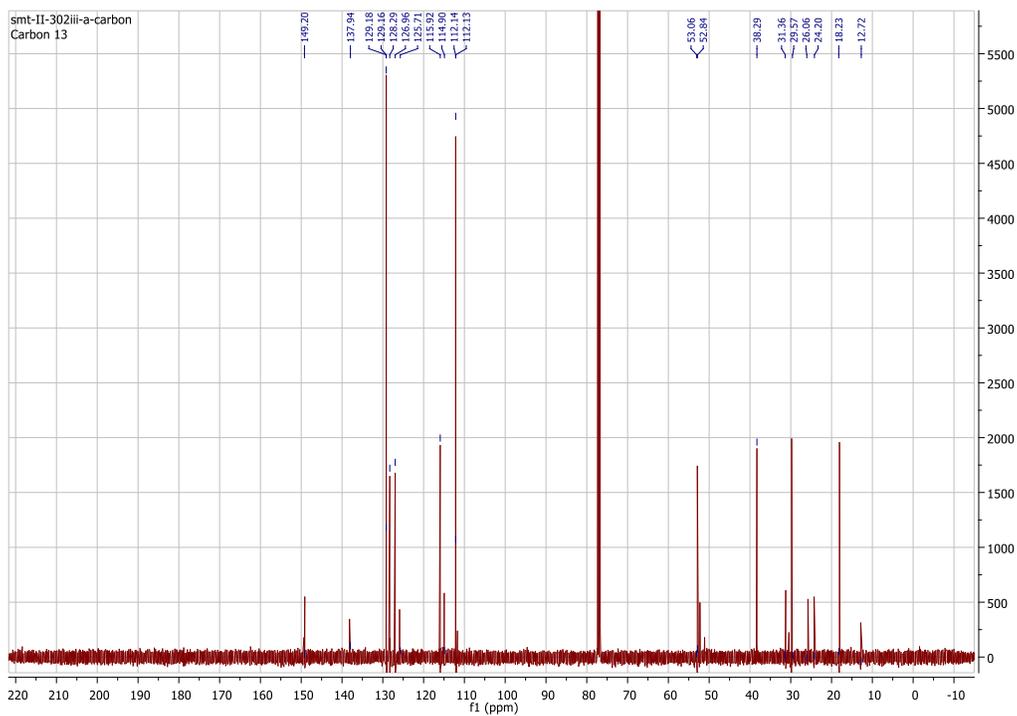
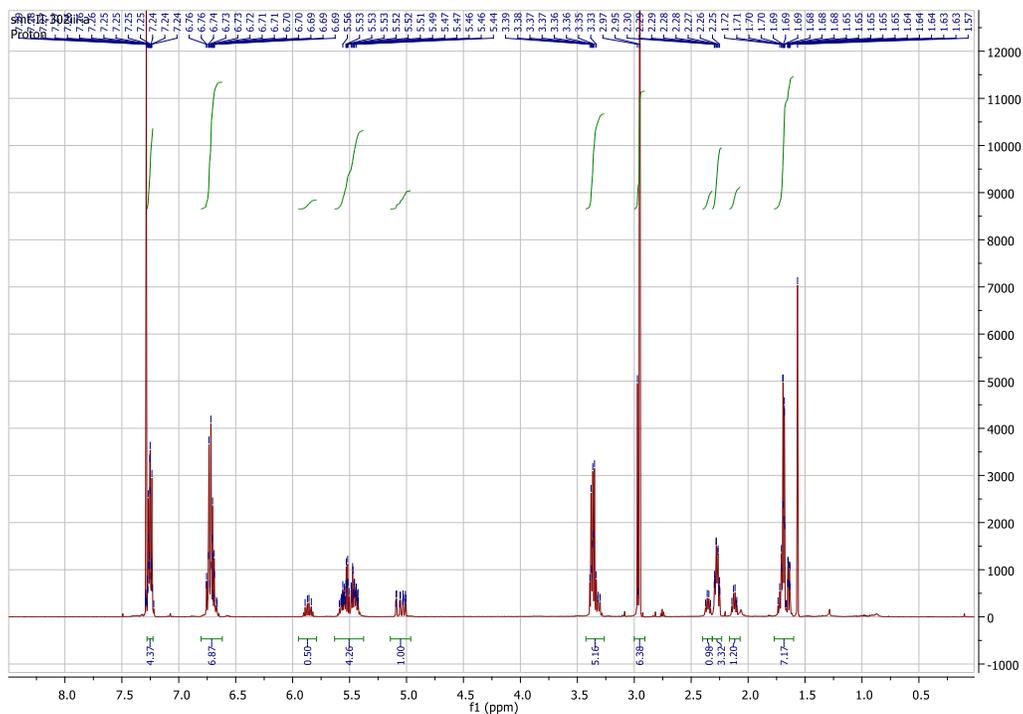
ethyl 4-((6-ethoxy-2-methyl-6-oxohex-3-en-1-yl)(methyl)amino)benzoate (**3i**)

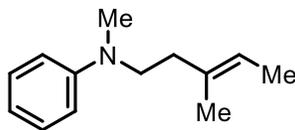
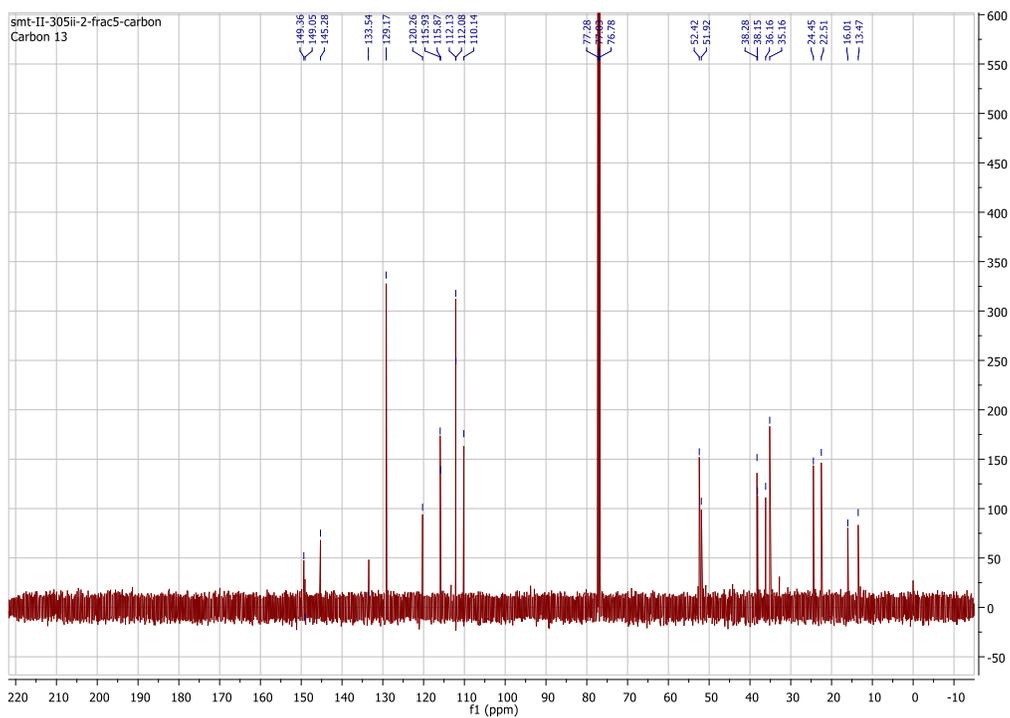
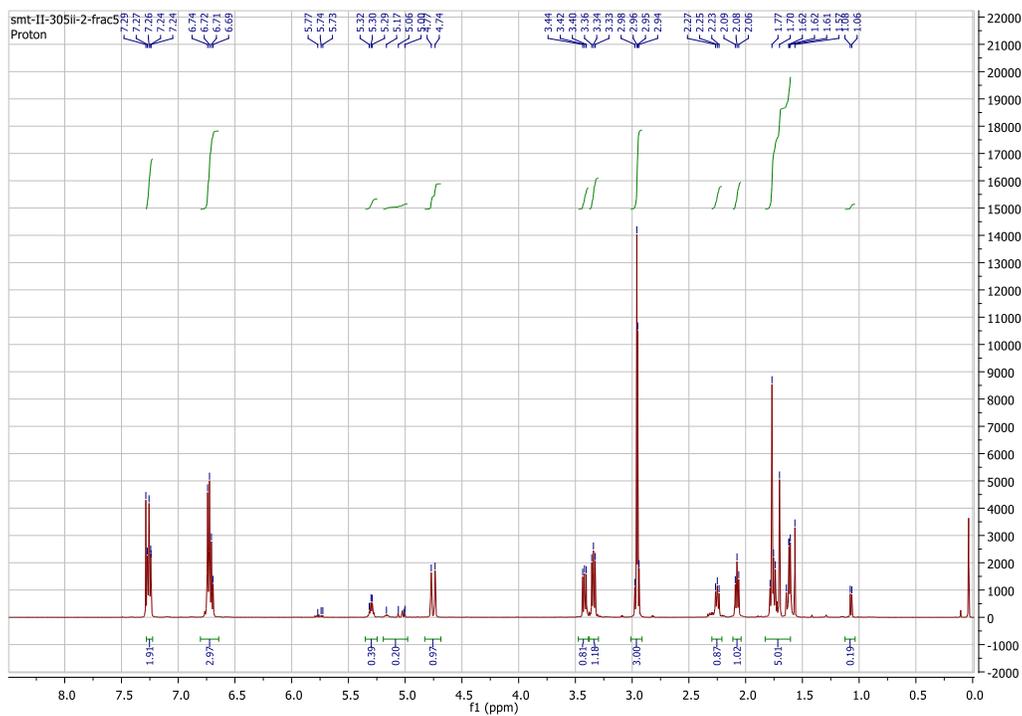
ethyl 6-(ethyl(phenyl)amino)-5-methylhept-3-enoate (**3j**)

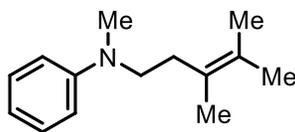
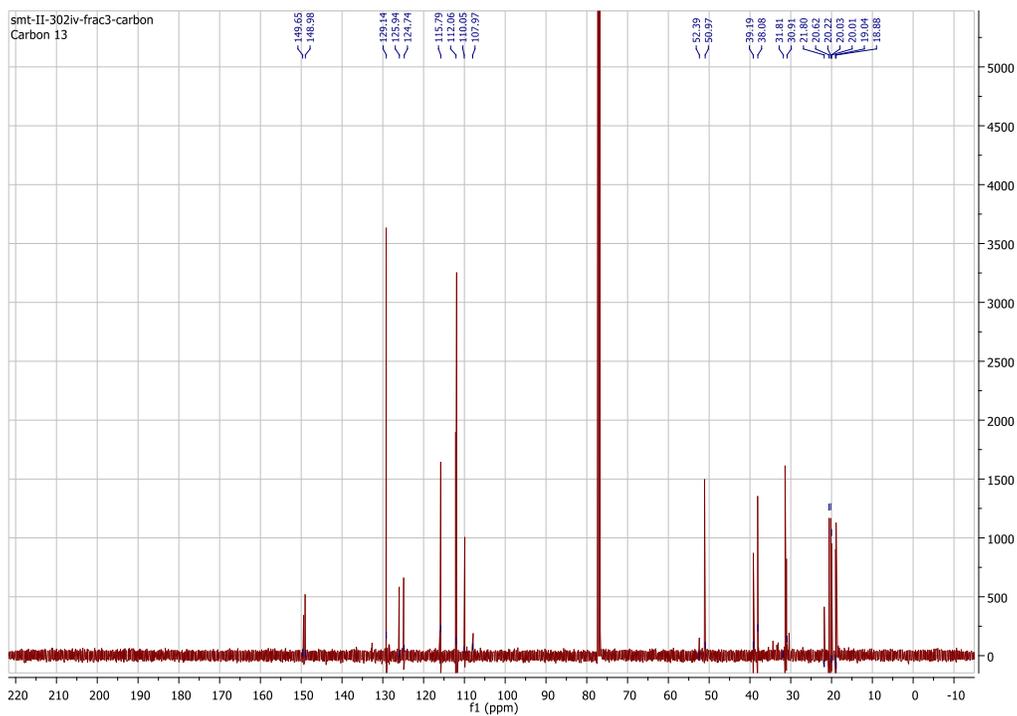
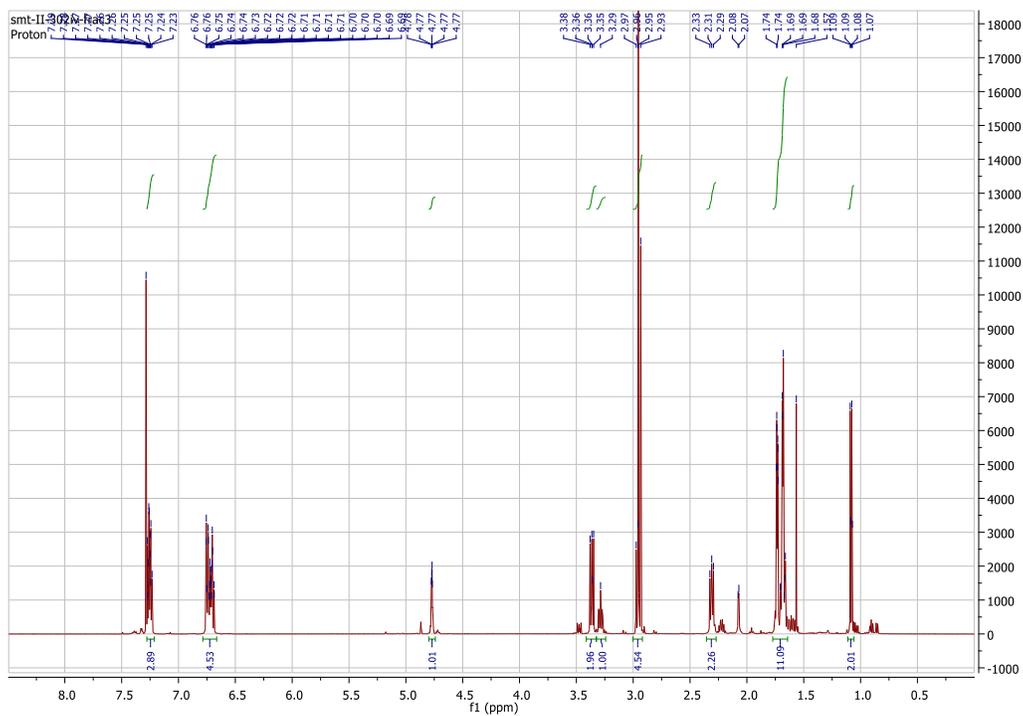
ethyl 5-methyl-6-(2,2,6,6-tetramethylpiperidin-1-yl)hex-3-enoate (**3k**)

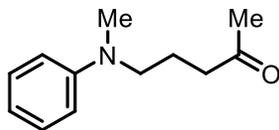
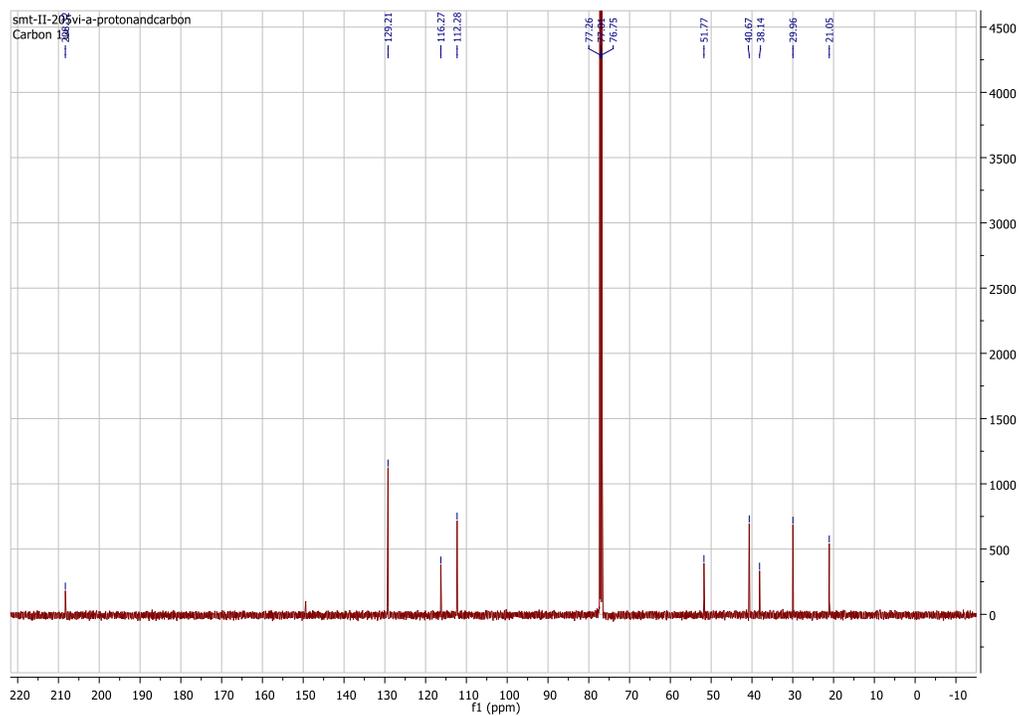
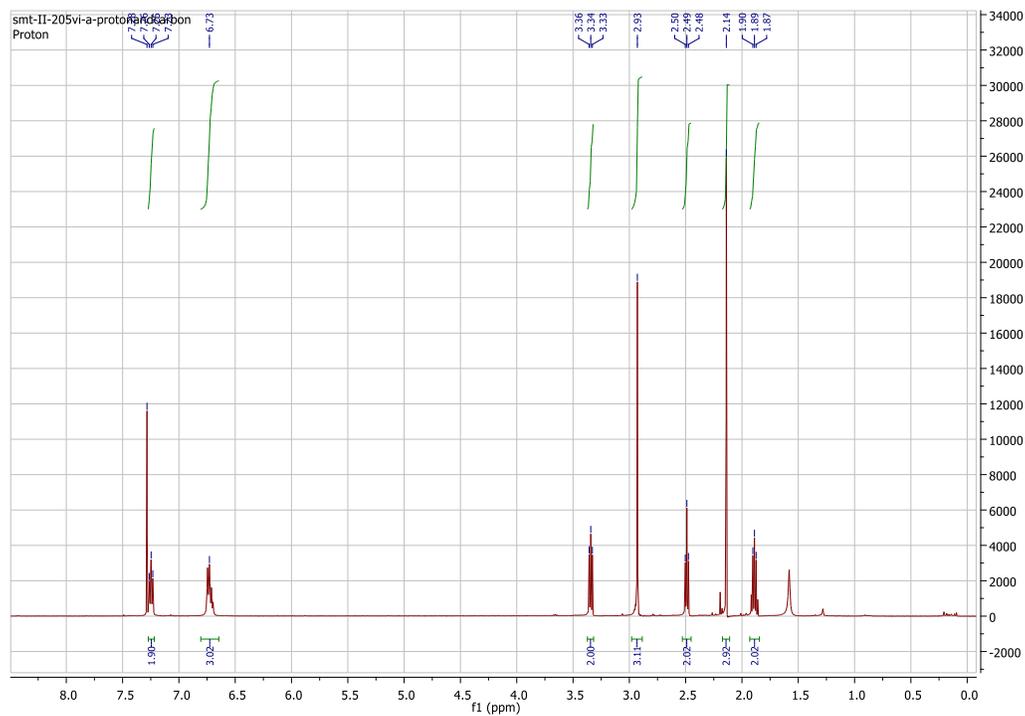
p-tolyl-5-methyl-6-(piperidin-1-yl)hex-3-enoate (**31**)

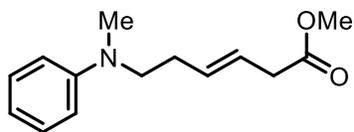
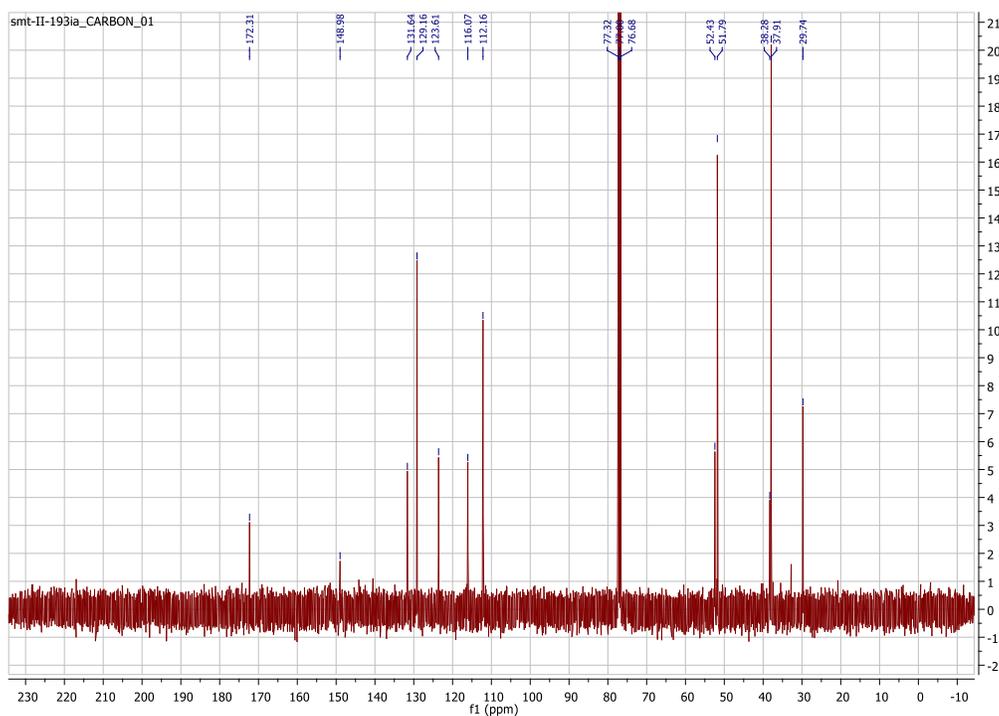
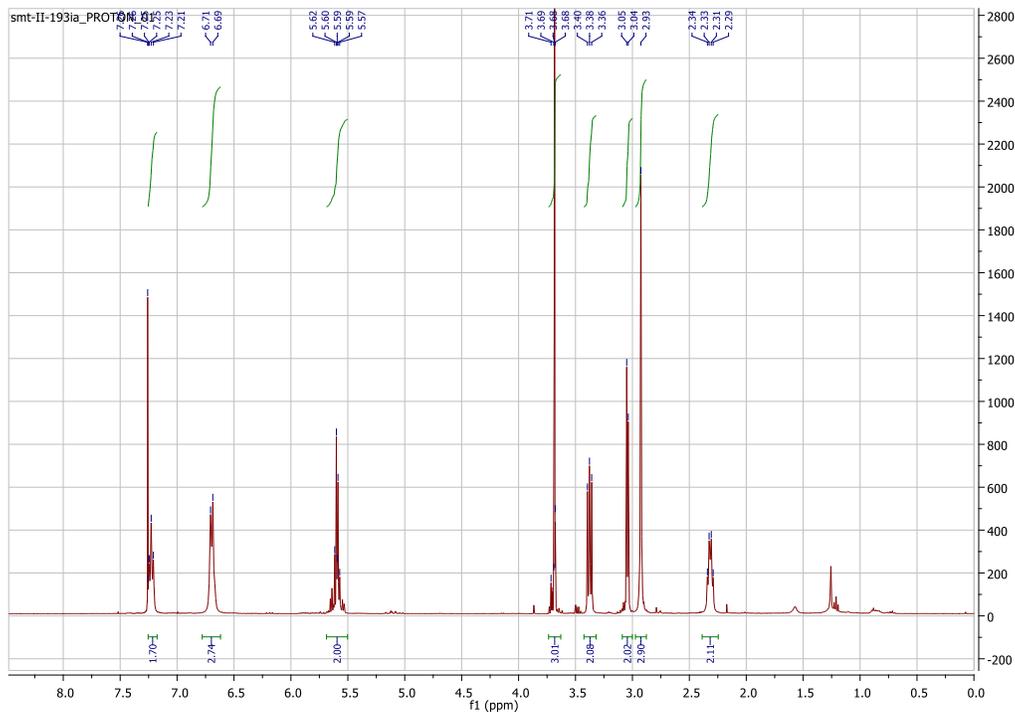
ethyl 5-methyl-6-(methyl(1-phenylethyl)amino)hex-3-enoate (**3n**)

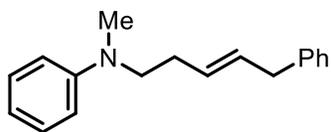
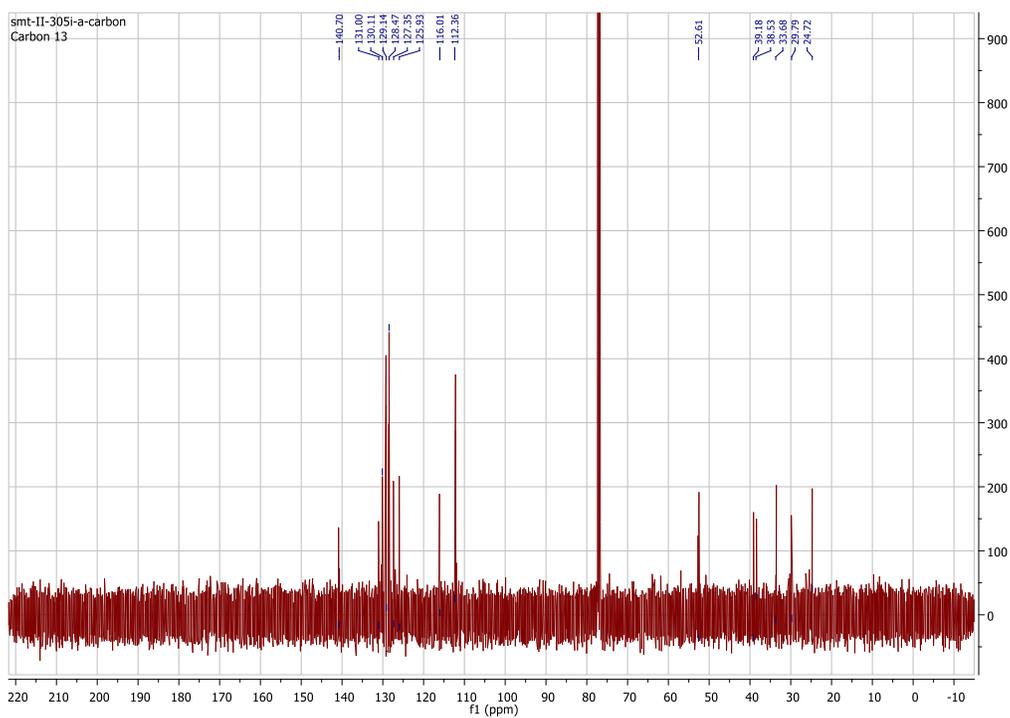
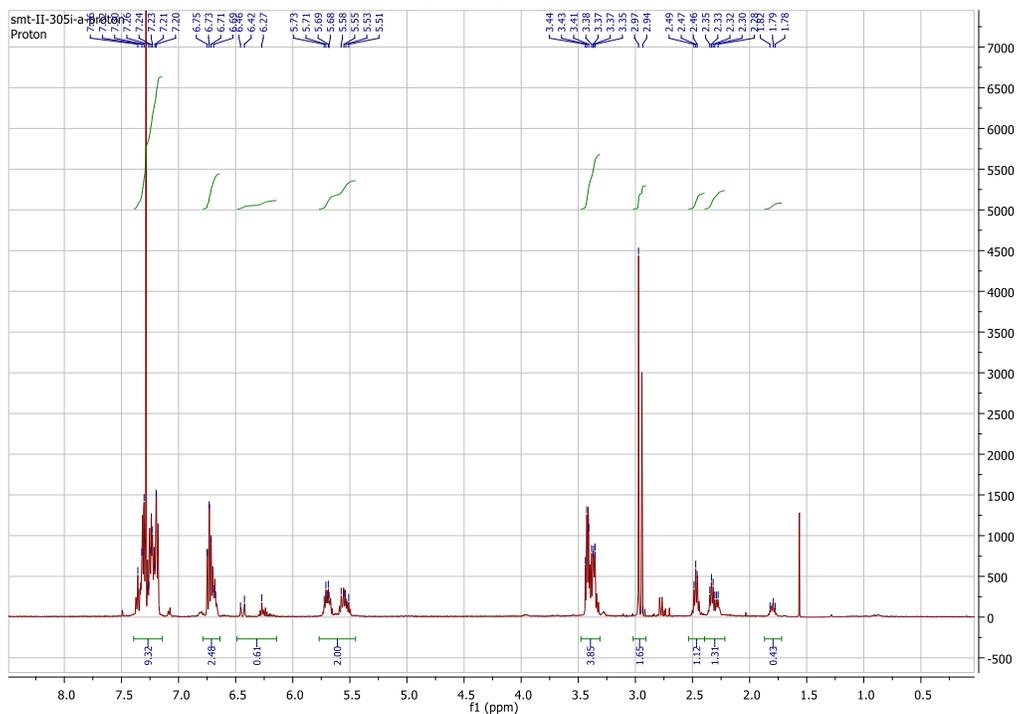
N-methyl-N-(pent-3-en-1-yl)aniline (**4b**)

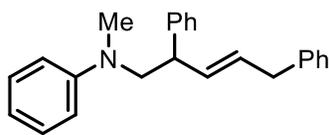
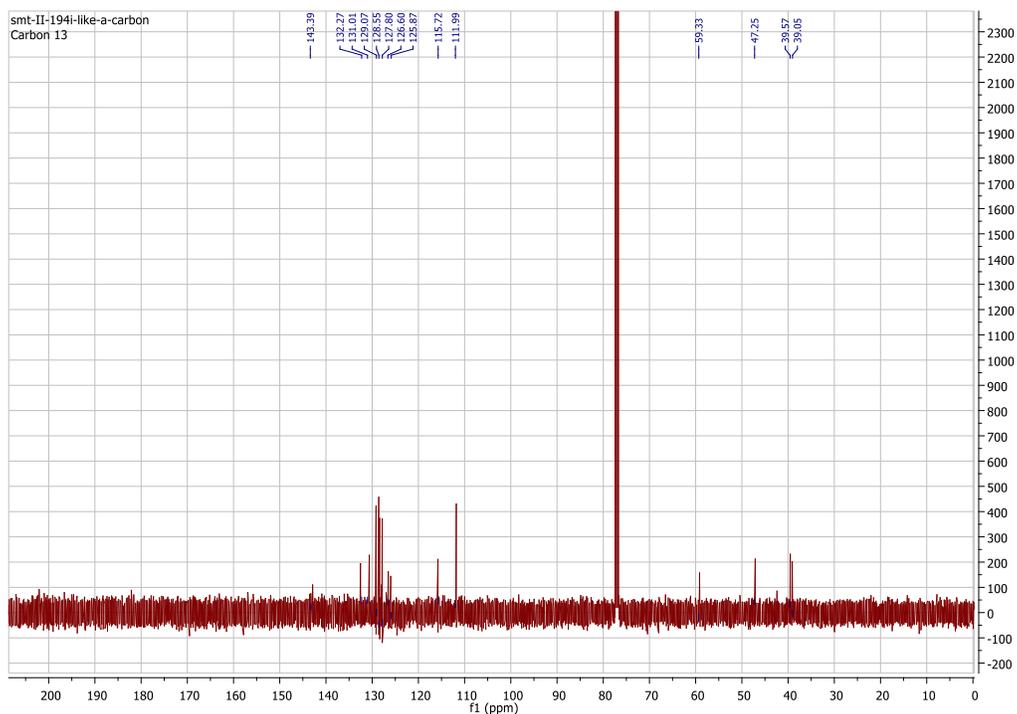
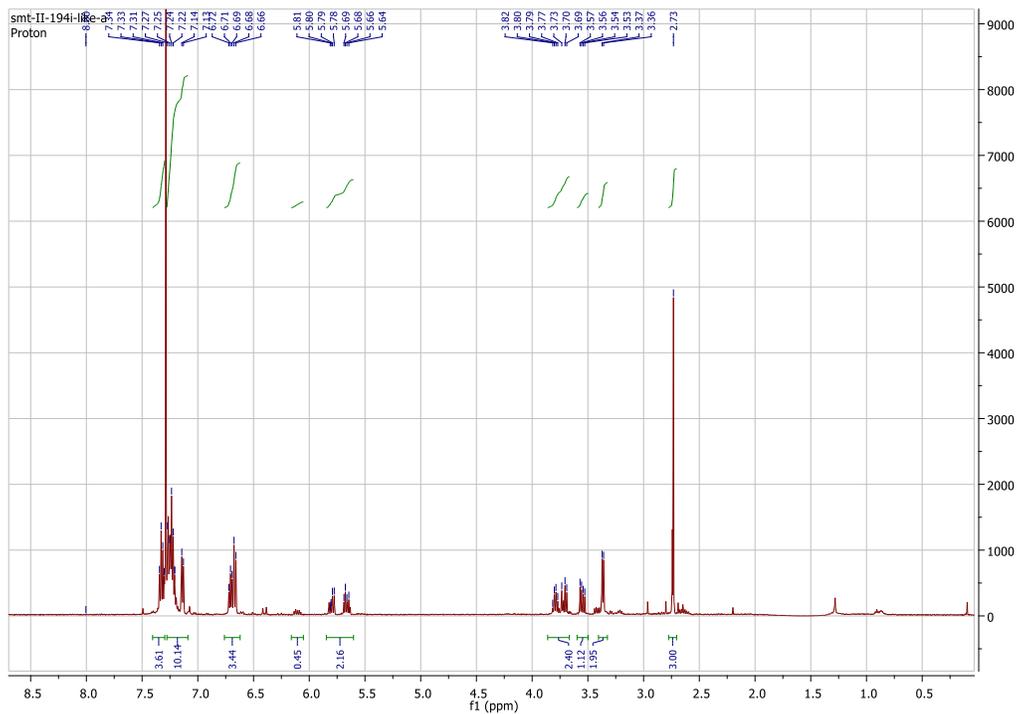
N-methyl-N-(3-methylpent-3-en-1-yl)aniline (**4a**)

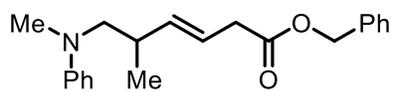
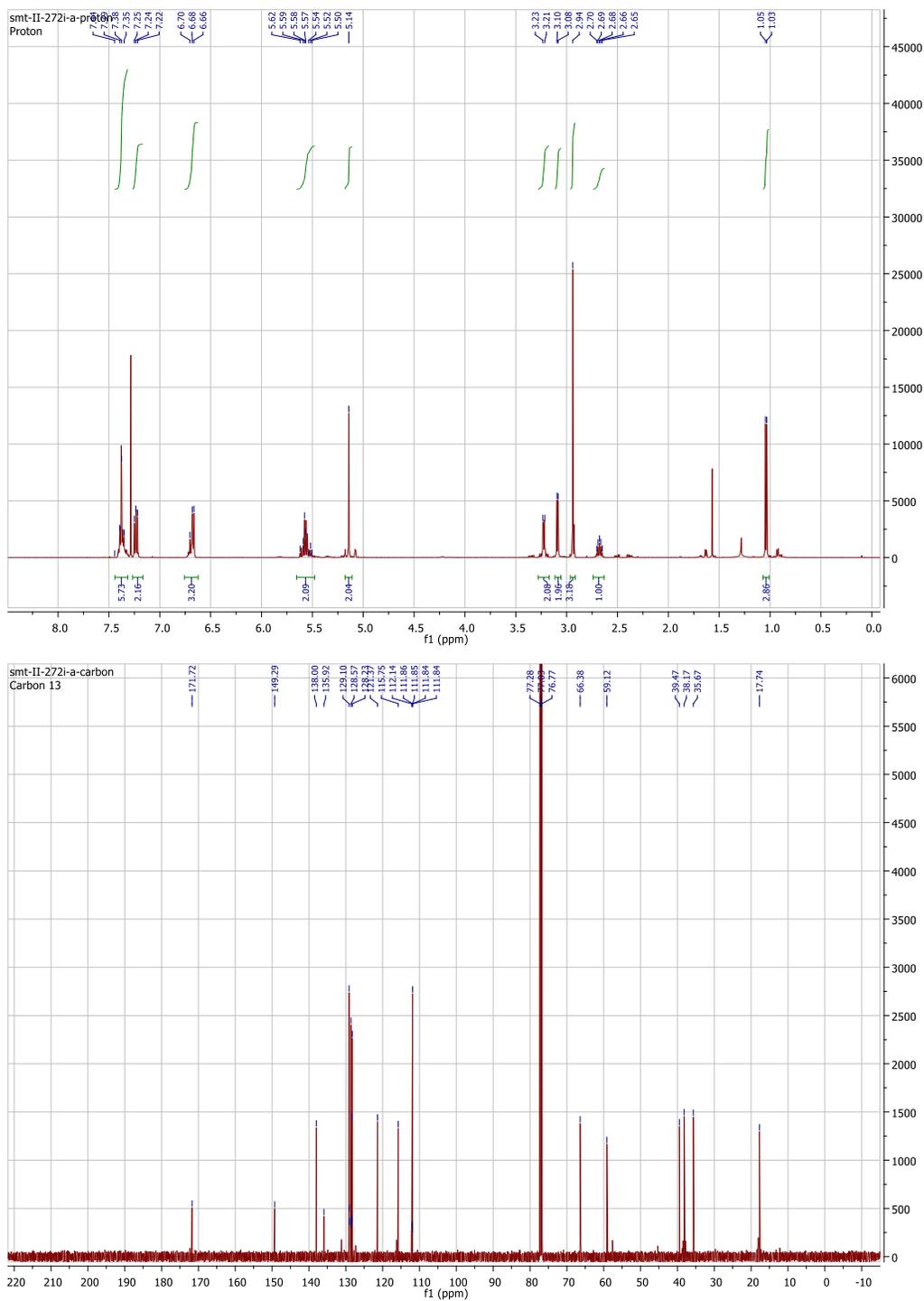
N-(3,4-dimethylpent-3-en-1-yl)-N-methylaniline (**4c**)

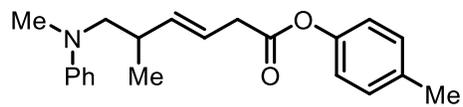
5-(methyl(phenyl)amino)pentan-2-one (**4d**)

methyl 6-(methyl(phenyl)amino)hex-3-enoate (**4e**)

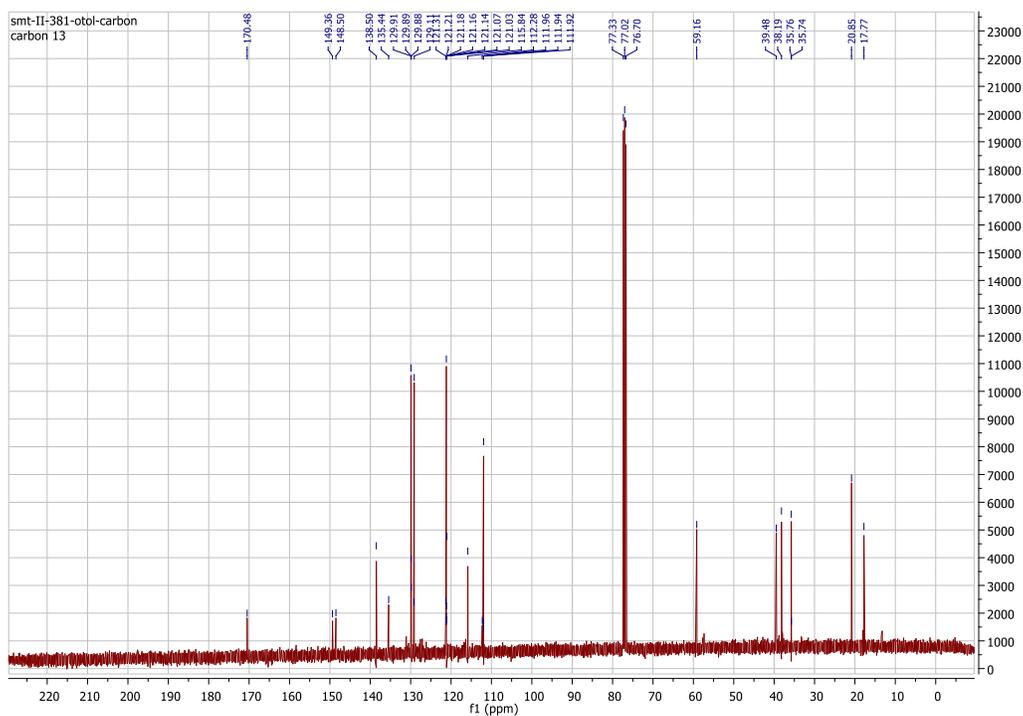
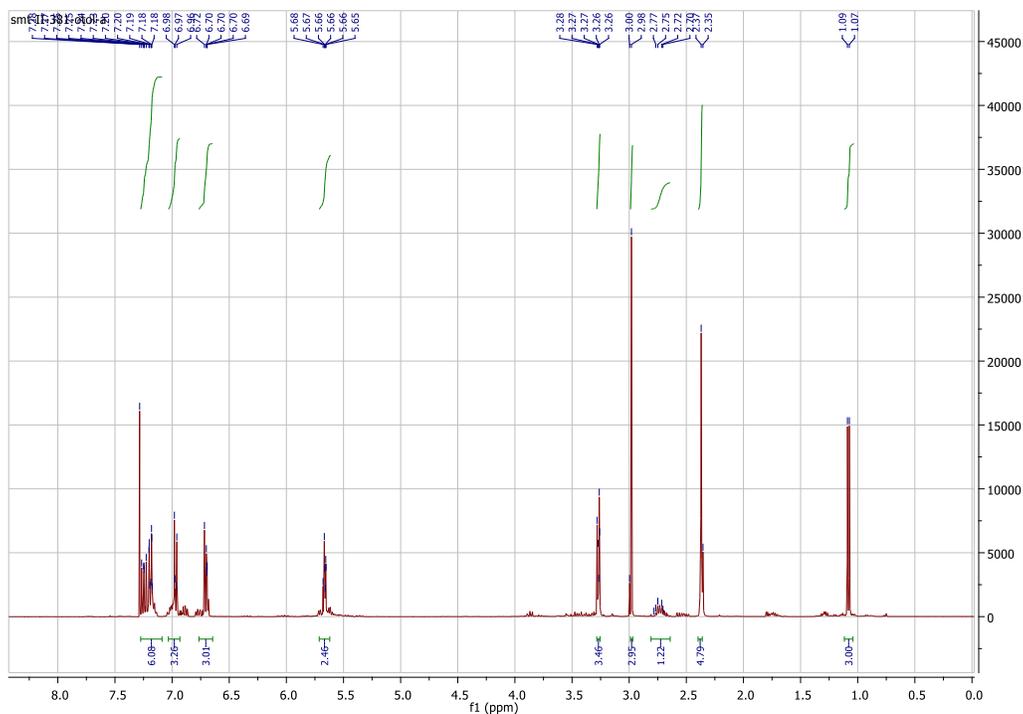
N-methyl-N-(5-phenylpent-3-en-1-yl)aniline (**4f**)

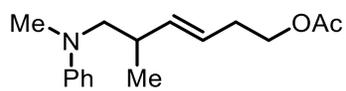
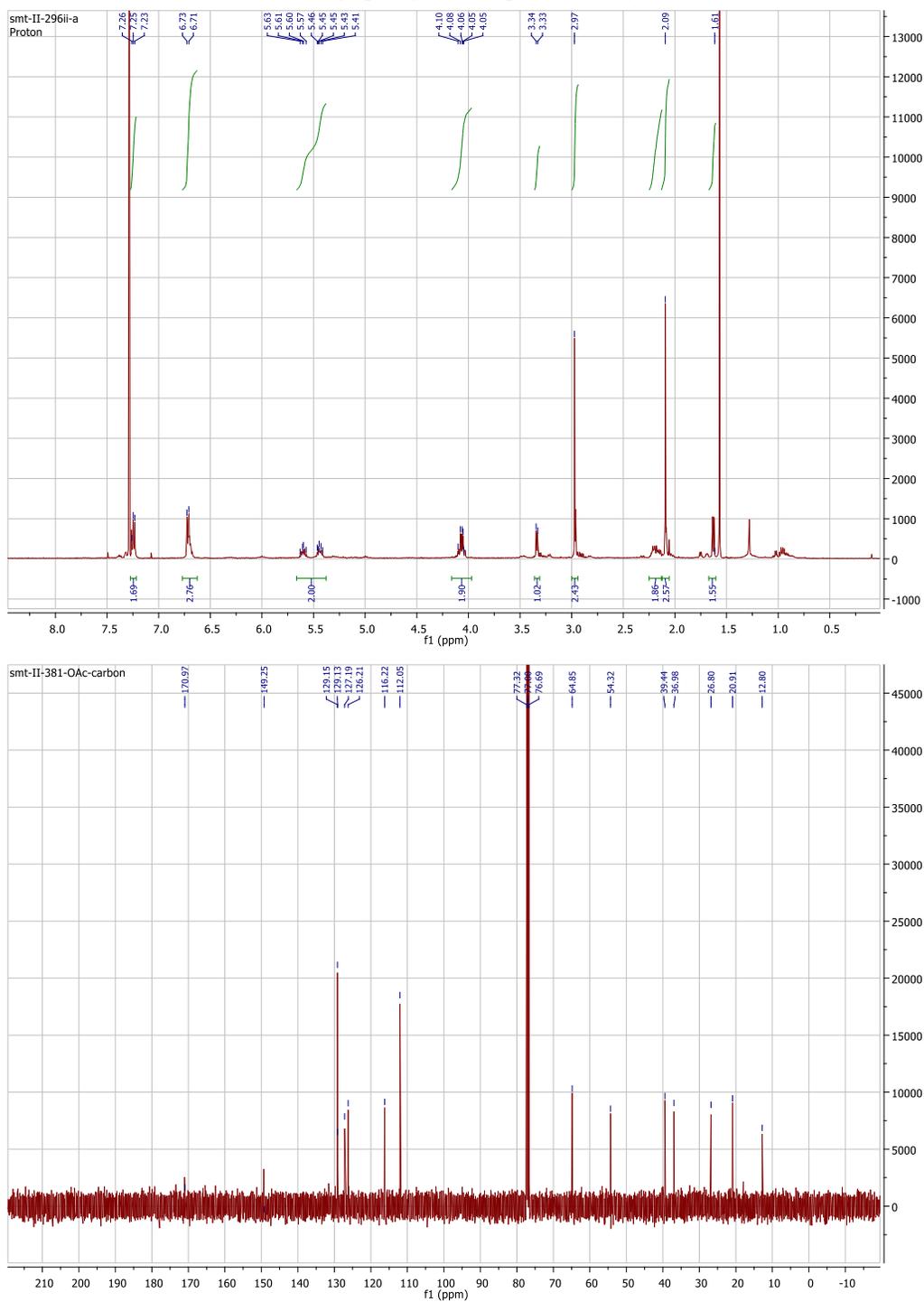
N-(2,5-diphenylpent-3-en-1-yl)-N-methylaniline (**4g**)

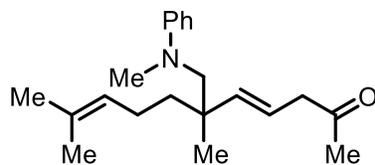
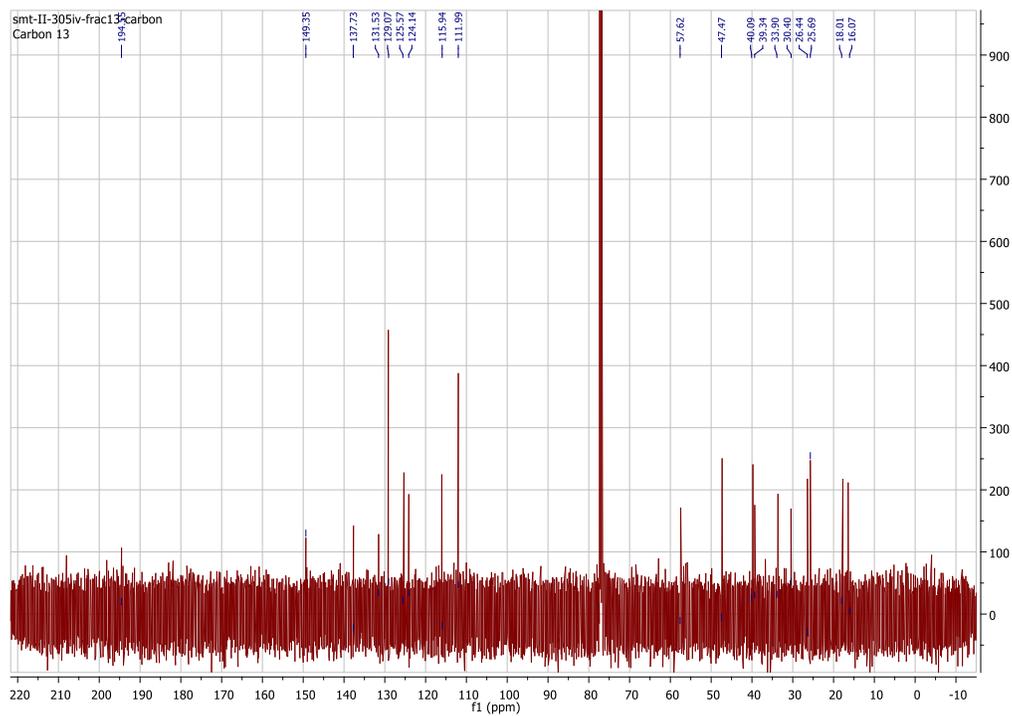
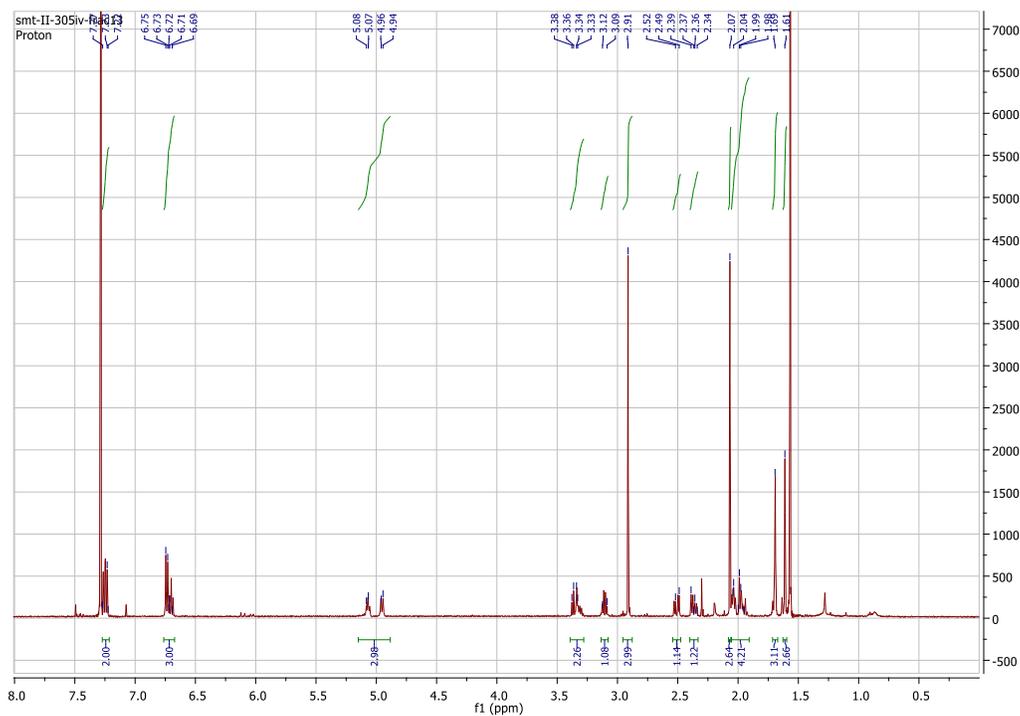
benzyl 5-methyl-6-(methyl(phenyl)amino)hex-3-enoate (**4h**)

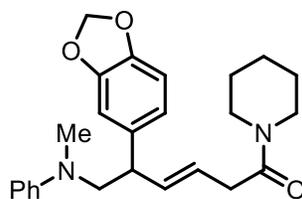
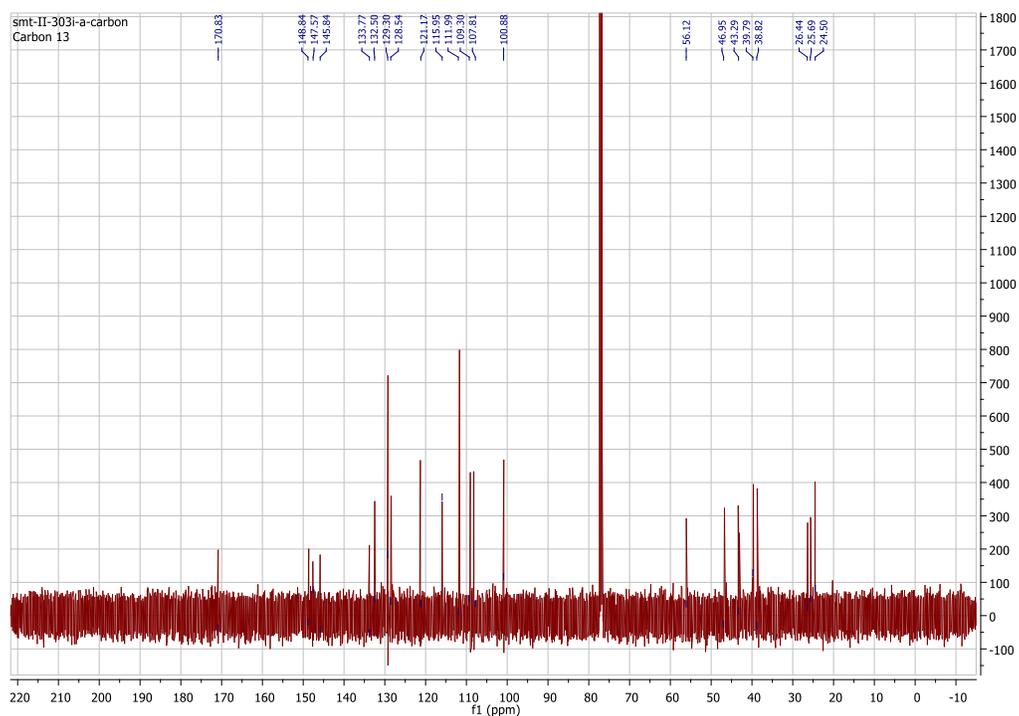
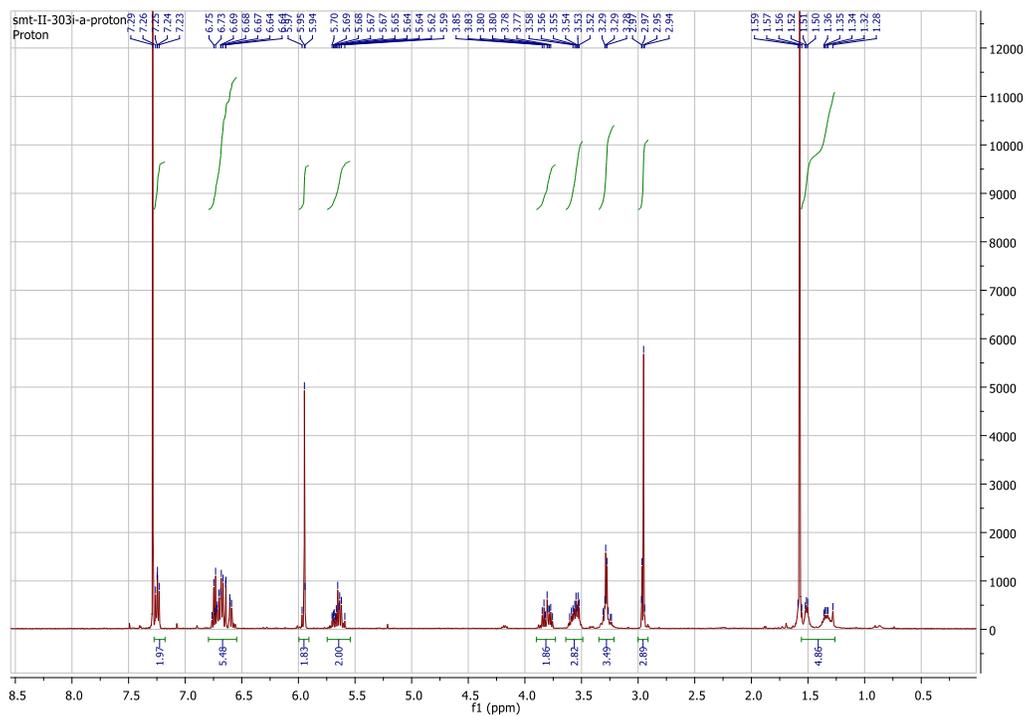


p-tolyl 5-methyl-6-(methyl(phenyl)amino)hex-3-enoate (**4i**)



4-methyl-5-(methyl(phenyl)amino)pent-2-en-1-yl acetate (**4j**)

6,10-dimethyl-6-((methyl(phenyl)amino)methyl)undeca-4,9-dien-2-one (**4k**)

5-(benzo[d][1,3]dioxol-5-yl)-6-(methyl(phenyl)amino)-1-(piperidin-1-yl)hex-3-en-1-one (**4m**)

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- ³ (a) Montaliti, M.; Credi, A.; Prodi, L.; Gandolfi, T. M. Chemical Actinometry. In *Handbook of Photochemistry*, 3rd ed.; CRC Press: Boca Raton, FL, **2006**, 601-616. (b) Cismesia, M. A.; Yoon, T. P. *Chem. Sci.* **2015**, *6*, 5426.
- ⁴ Higgins, R. F.; Fatur, S. M.; Shepard, S. G.; Stevenson, S. M.; Boston, D. J.; Ferreira, E. M. Damrauer, N. H.; Rappe, A. K.; Shores, M. P. *J. Am. Chem. Soc.* **2016**, *138*, 5451–5464.
- ⁵ Luo, Y.; Roy, I. D.; Madec, A. G. E.; Lam, H. W. *Angew. Chem. Int. Ed.* **2014**, *53*, 4186-4190.
- ⁶ Lin, C.; Zhen, L.; Cheng, Y.; Du, H.-J.; Zhao, H.; Wen, X.; Kong, L.-Y., Xu, Q.-L.; Sun, H. *Org. Lett.* **2015**, *17*, 2684-2687.
- ⁷ Karmakar, R. Suneja, A.; Bisai, V.; Singh, V.K. *Org. Lett.* **2015**, *17*, 5650-5653.