Supporting Information for

Contrasteric Coupling of Allenes and Tetrahydroisoquinolines by Iron-Catalysed Allenic C(sp^2)–H Functionalisation

Yue Xia, Nicholas W. Wade, Philip N. Palermo, Yidong Wang* and Yi-Ming Wang*

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, United States

E-mail: yiw121@pitt.edu, ym.wang@pitt.edu

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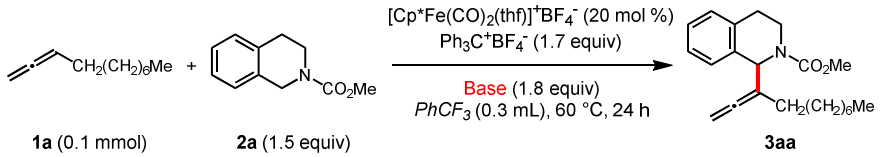
General Information

General Reagent Information: Anhydrous trifluorotoluene were purchased from Frontier Scientific (J&KSeal packaging) and was transferred into an argon-filled glovebox and used as received. Other dry solvents were obtained by distillation and storage over 4Å molecular sieves. Triphenylcarbenium tetrafluoroborate ($Ph_3C^+BF_4^-$) was purchased from Alfa Aesar and stored in an argon-filled glove box. All other reagents were purchased from Oakwood, Acros, Alfa Aesar, or Sigma Aldrich and used as received. Compounds were purified by flash column chromatography using SiliCycle SiliaFlash® F60 silica gel and preparative thin-layer chromatography (TLC) using Silicycle 1000 µm silica gel plates, unless otherwise indicated.

General Analytical Information: New compounds were characterized by ^{1}H NMR, ^{13}C NMR and HRMS. Copies of the ^{1}H NMR and ^{13}C NMR spectra can be found at the end of the Supporting Information. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 500 MHz instruments. All ^{1}H NMR data are reported in δ units, parts per million (ppm), and were measured relative to the residual proton signal in the deuterated solvent at 7.26 ppm ($CDCl_3$). All ^{13}C NMR spectra are ^{1}H decoupled and reported in ppm relative to the solvent signal at 77.16 ppm ($CDCl_3$). Thin-layer chromatography (TLC) was performed on Silicycle 250 µm (analytical) or 1000 µm (preparative) silica gel plates. Compounds were visualized by irradiation with UV light, or by staining with potassium permanganate, or cerium molybdate stain (Hanessian's stain). Yields refer to isolated compounds, unless otherwise indicated. High resolution mass spectra were recorded on a Thermo Scientific Q-Exactive mass spectrometer. NMR yield was determined by using 1,3-dinitrobenzene or 2,4-dinitrotoluene as internal standard for ^{1}H spectroscopy and using $CDCl_3$ as the reference for ^{2}H spectroscopy.

Optimization of Reaction Conditions

1. Optimization of base.

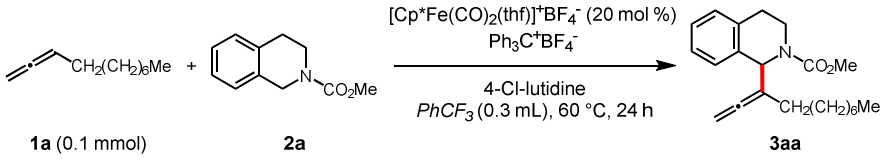


1a (0.1 mmol) **2a** (1.5 equiv) **3aa**

Entry	Base	NMR Yield (%) [a]
1	TMPH	5
2	2,4,6-collidine	17
3	2,6-lutidine	54
4	4-Br-lutidine	55
5	4-Cl-lutidine	74

[a] NMR yields were determined by ^{1}H NMR using 1,3-dinitrobenzene as internal standard.

2. Optimization of reagent ratio.

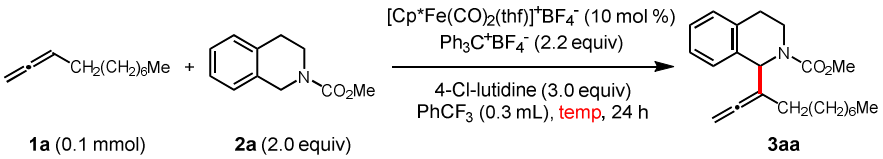


1a (0.1 mmol) **2a** **3aa**

Entry	1a: 2a: Ph_3CBF_4: 4-Cl-lutidine	NMR Yield (%) [a]
1	1.0:1.5:1.7:1.8	74
2	1.5:1.0:1.1:1.0	53
3	1.5:1.0:1.1:1.5	72
4	1.0:2.0:2.2:2.5	85
5[b]	1.0:2.0:2.2:2.5	69
6[b]	1.0:2.0:2.2:3.0	74
7	1.0:2.0:2.2:3.0	92
8[b]	1.0:2.0:2.2:4.0	58

[a] NMR yields were determined by ^{1}H NMR using 1,3-dinitrobenzene as internal standard. [b] 10 mol % catalyst used.

3. Optimization of temperature.

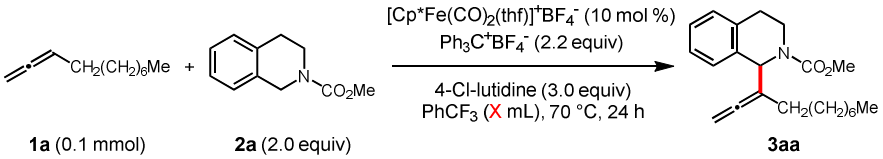


1a (0.1 mmol) **2a** (2.0 equiv) **3aa**

Entry	Temperature (°C)	NMR Yield (%) [a]
1	40	5
2	60	74
3	70	75
4 [b]	70	92 [c]
5	80	72

[a] NMR yields were determined by ^{1}H NMR using 1,3-dinitrobenzene as internal standard. [b] 20 mol % catalyst used. [c] While no significant change was observed by elevating reaction temperature from 60 °C to 70 °C using standard substrates **2a**, a significant increase in the yield from 36% (NMR yield) to 47% was seen on more challenging substrate **2d**.

4. Optimization of concentration.



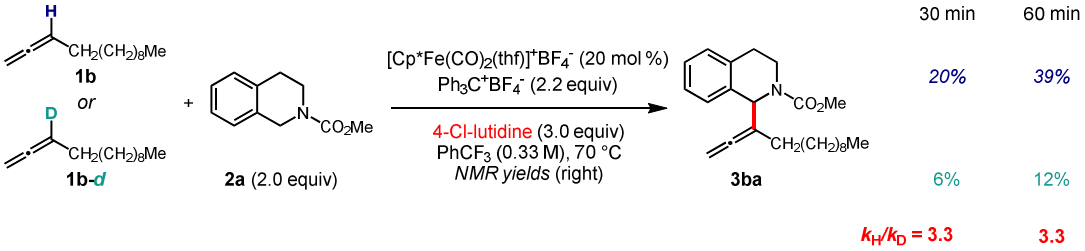
1a (0.1 mmol) **2a** (2.0 equiv) **3aa**

Entry	Solvent Volume (mL)	NMR Yield (%) [a]
1	0.5	67
2	0.3	75
3	0.2	66

[a] NMR yields were determined by ^{1}H NMR using 1,3-dinitrobenzene as internal standard.

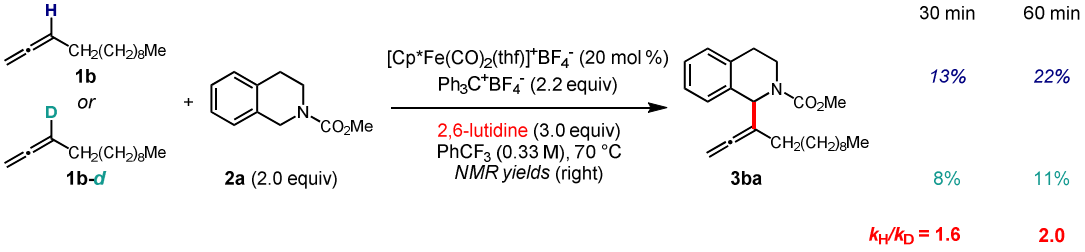
Kinetic isotope effect experiments

KIE experiment using 4-chloro-2,6-lutidine as base



A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was capped with a Teflon/silicone septum (Thermo/National part # C4015-66A) screw cap and flame dried under vacuum. The reaction tube was cooled under nitrogen and transferred into an argon-filled glovebox. In the glovebox, a suspension of carbamate **2a** (38.2 mg, 0.20 mmol, 2.0 equiv) and $Ph_3C^+BF_4^-$ (72.6 mg, 0.22 mmol, 2.2 equiv) in dry trifluorotoluene (0.2 mL) was stirred at room temperature for 3 hours to generate the iminium salt. Then $[Cp^*Fe(CO)_2(thf)]^+[BF_4]^-$ (20 mol %, 8.1 mg), allene **1b** (18.0 mg, 0.1 mmol, 1.0 equiv) or **1b-*d*** (18.1 mg, 0.1 mmol, 1.0 equiv), 4-chloro-2,6-lutidine (38.2 μL, 0.30 mmol, 3.0 equiv) and trifluorotoluene (0.1 mL) were added in rapid succession. The reaction tube was capped and removed from the glovebox. The reaction tube was placed in an oil bath preheated to 70 °C, where it was stirred for 30 minutes or 60 minutes. The NMR yields were determined by ^{1}H NMR using 1,3-dinitrobenzene as internal standard.

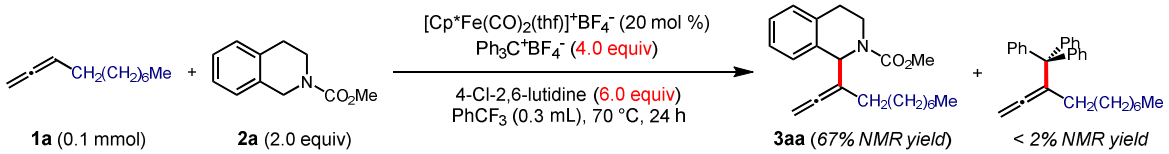
KIE experiment using 2,6-lutidine as base



A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was capped with a Teflon/silicone septum (Thermo/National part # C4015-66A) screw cap and flame dried under vacuum. The reaction tube was cooled under nitrogen and transferred into an argon-filled glovebox. In the glovebox, a suspension of carbamate **2a** (38.2 mg, 0.20 mmol, 2.0 equiv) and $Ph_3C^+BF_4^-$ (72.6 mg, 0.22 mmol, 2.2 equiv) in dry trifluorotoluene (0.2 mL) was stirred at room temperature for 3 hours to generate the iminium salt. Then $[Cp^*Fe(CO)_2(thf)]^+[BF_4]^-$ (20 mol %, 8.1 mg), allene **1b** (18.0 mg, 0.1 mmol, 1.0 equiv) or **1b-*d*** (18.1 mg, 0.1 mmol, 1.0 equiv), 2,6-lutidine (34.7 μL, 0.30 mmol, 3.0 equiv) and trifluorotoluene (0.1 mL) were added in rapid succession. The reaction tube was capped and removed from the

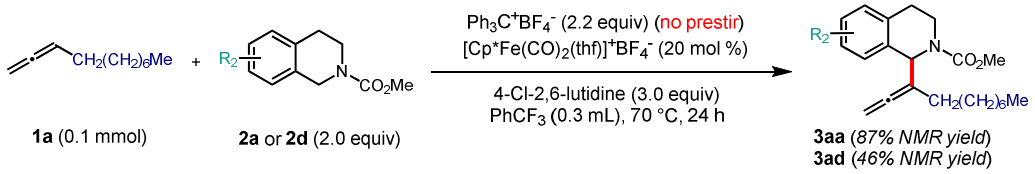
glovebox. The reaction tube was placed in an oil bath preheated to 70 °C, where it was stirred for 30 minutes or 60 minutes. The NMR yields were determined by ^{1}H NMR using 1,3-dinitrobenzene as internal standard.

Competition experiment



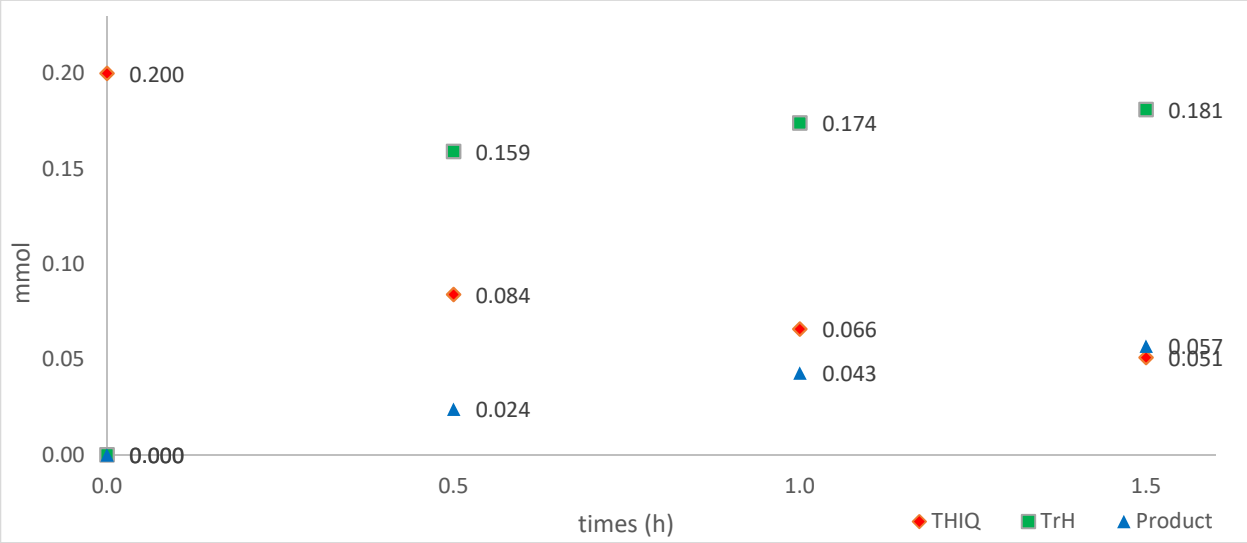
A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was capped with a Teflon/silicone septum (Thermo/National part # C4015-66A) screw cap and flame dried under vacuum. The reaction tube was cooled under nitrogen and transferred into an argon-filled glovebox. In the glovebox, a suspension of carbamate **2a** (38.2 mg, 0.20 mmol, 2.0 equiv) and $Ph_3C^+BF_4^-$ (132.1 mg, 0.40 mmol, 4.0 equiv) in dry trifluorotoluene (0.2 mL) was stirred at room temperature for 3 hours to generate the iminium salt. Then $[Cp^*Fe(CO)_2(thf)]^+[BF_4]^-$ (20 mol %, 8.1 mg), allene **1b** (18.0 mg, 0.1 mmol, 1.0 equiv), 4-chloro-2,6-dimethylpyridine (76.3 µL, 0.60 mmol, 6.0 equiv) and trifluorotoluene (0.1 mL) were added in rapid succession. The reaction tube was capped and removed from the glovebox. The reaction tube was placed in an oil bath preheated to 70 °C, where it was stirred for 24 h. The NMR yields were determined by ^{1}H NMR using 1,3-dinitrobenzene as internal standard.

One-step, one-pot protocol



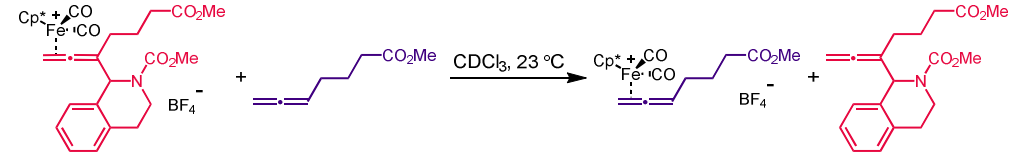
A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was capped with a Teflon/silicone septum (Thermo/National part # C4015-66A) screw cap and flame dried under vacuum. The reaction tube was cooled under nitrogen and transferred into an argon-filled glovebox. In the glovebox, a mixture of $[Cp^*Fe(CO)_2(thf)]^+[BF_4]^-$ (20 mol %, 8.1 mg) and $Ph_3C^+BF_4^-$ (72.6 mg, 0.22 mmol, 2.2 equiv) was dissolved in dry trifluorotoluene (0.2 mL), then allene **1a** (30.4 mg, 0.20 mmol, 1.0 equiv), carbamate **2a** (38.2 mg, 0.40 mmol, 2.0 equiv) or **2d** (47.2 mg, 0.40 mmol, 2.0 equiv), 4-chloro-2,6-dimethylpyridine (38.2 µL, 0.30 mmol, 3.0 equiv) and trifluorotoluene (0.1 mL) were added in rapid succession. The reaction tube was capped and removed from the glovebox. The reaction tube was placed in an oil bath preheated to 70 °C, where it was stirred for 24 h. The NMR yields were determined by ^{1}H NMR using 1,3-dinitrobenzene as internal standard.

The composition of reaction mixture for synthesis of **3aa** was monitored by ^{1}H NMR over time. The results at 0.5, 1.0, and 1.5 h suggest the rapid conversion of THIQ into dihydroisoquinolinium tetrafluoroborate salt, as indicated by consumption of THIQ and formation of triphenylmethane. The initial rate of product formation under the one-step, one-pot protocol was similar to the rate under the usual two-step procedure (see "General procedure for iron catalyzed allenic C(sp^2)-H functionalization" below).

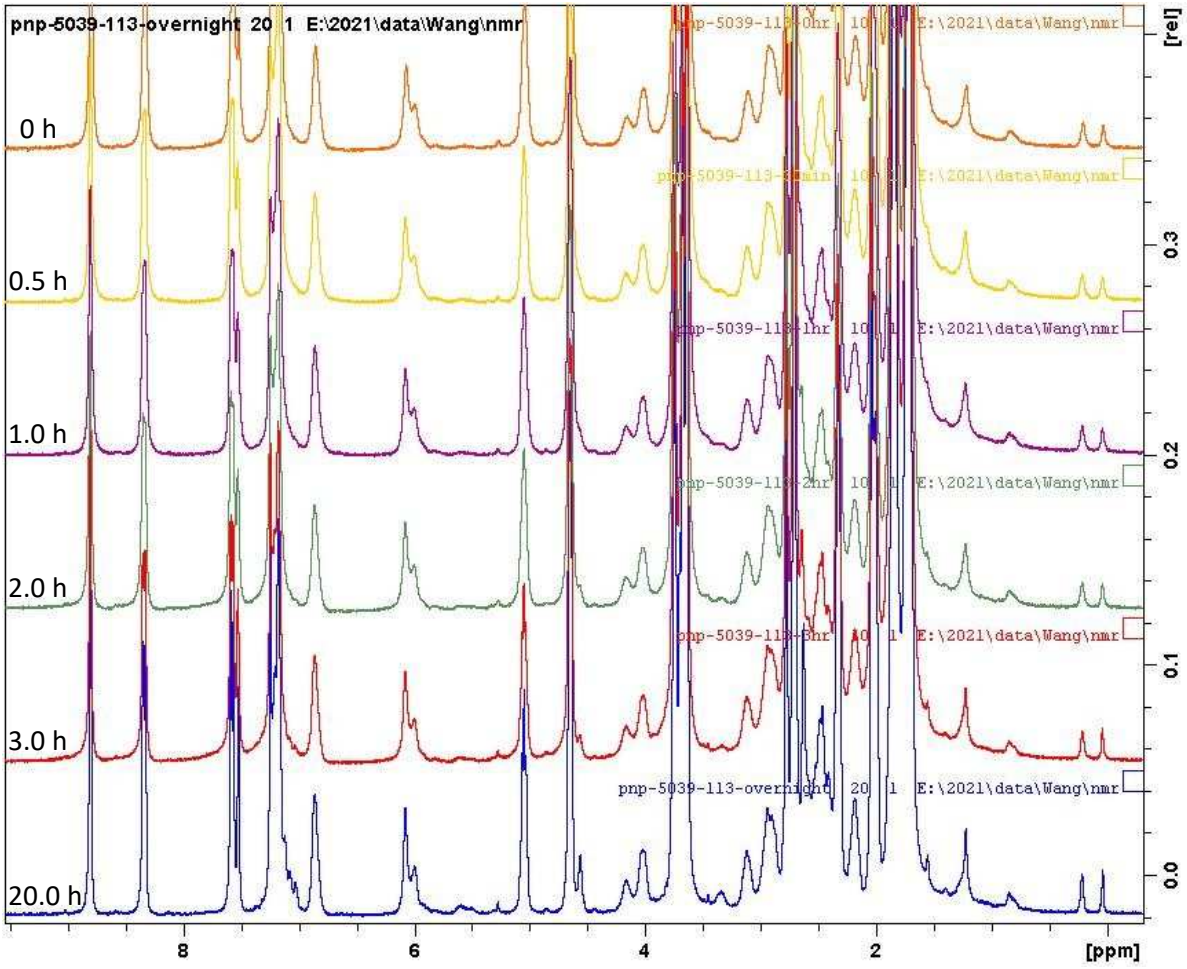


Stoichiometric experiments

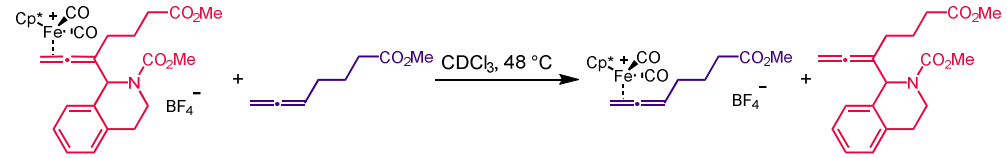
Allene exchange at 23 °C



In an argon-filled glovebox, **3fa**·$(Fp^*)^+BF_4^-$ (12.6 mg, 19 μmol, 1.0 equiv) was added to an NMR tube and dissolved in $CDCl_3$ (0.5 mL). Then allene **1f** (2.6 mg, 19 μmol, 1.0 equiv) was added to the above solution. The NMR tube was capped and removed from the glovebox and shaken by hand. Then the NMR tube was placed under dark, and the reaction was monitored by ^{1}H NMR using 2,4-dinitrotoluene as internal standard. No significant allene exchange was observed.

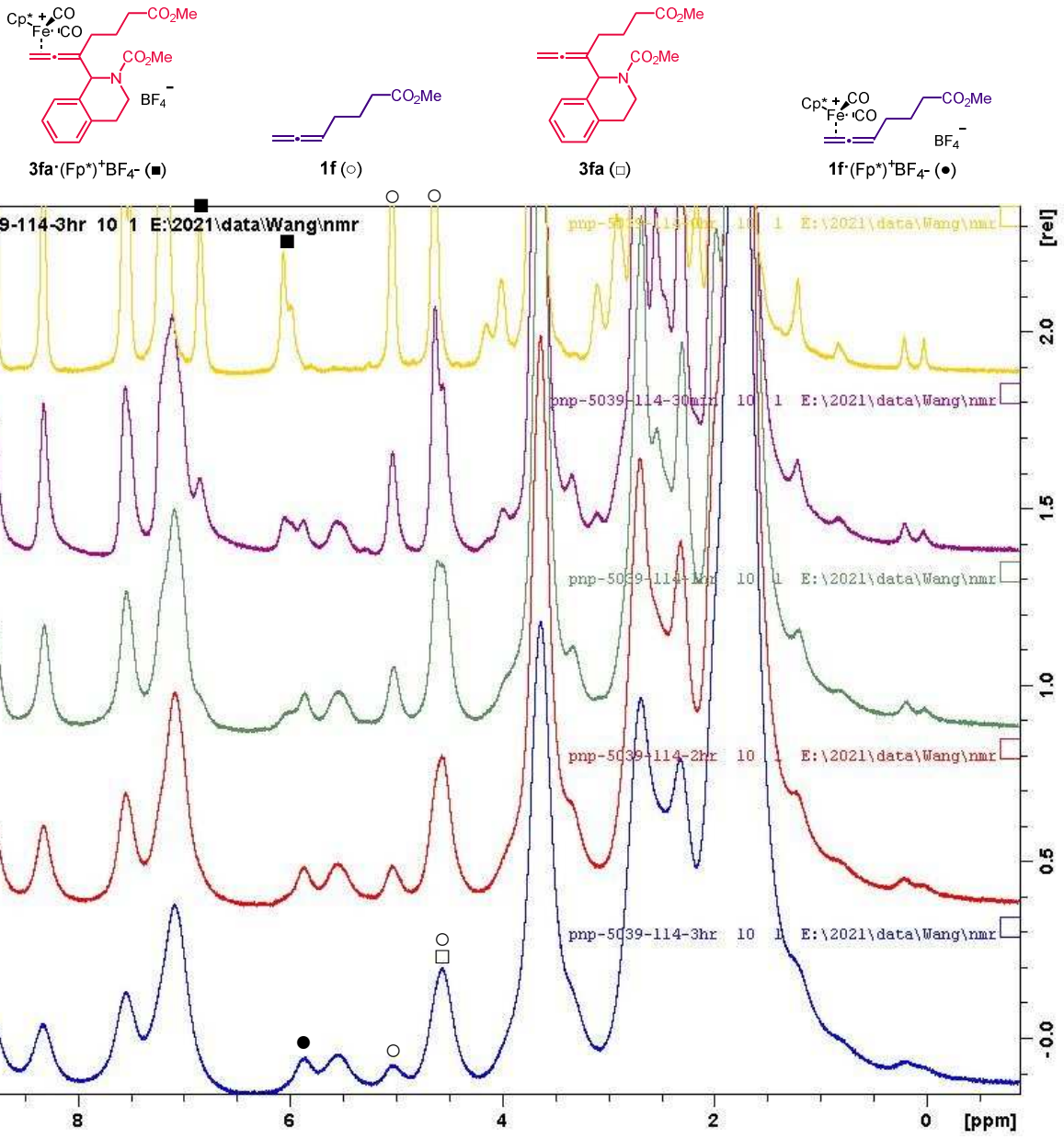


Allene exchange at 48 °C

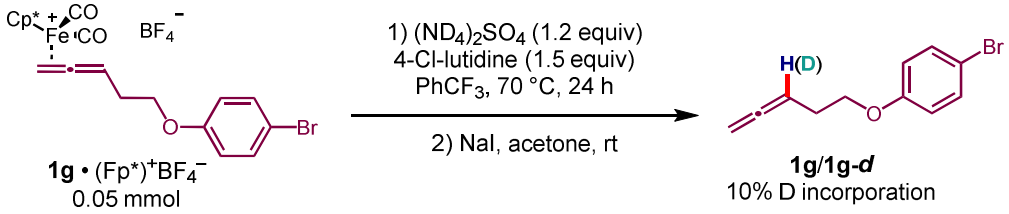


3fa·(Fp*)$^+$BF$_4^-$ (19.0 µmol) **1f**, 1.0 equiv **1f**·(Fp*)$^+$BF$_4^-$ **3fa**

In an argon-filled glovebox, **3fa**·(Fp*)$^+$BF$_4^-$ (12.6 mg, 19 µmol, 1.0 equiv) was added to an NMR tube and dissolved in $CDCl_3$ (0.5 mL). Then allene **1f** (2.6 mg, 19 µmol, 1.0 equiv) was added to the above solution. The NMR tube was capped and removed from the glovebox and shaken by hand. Then the NMR tube was placed in an oil bath under dark, preheated to 48 °C, and the reaction was monitored by ^{1}H NMR using 2,4-dinitrotoluene as internal standard. The allene exchange was found to be complete after 3 h.

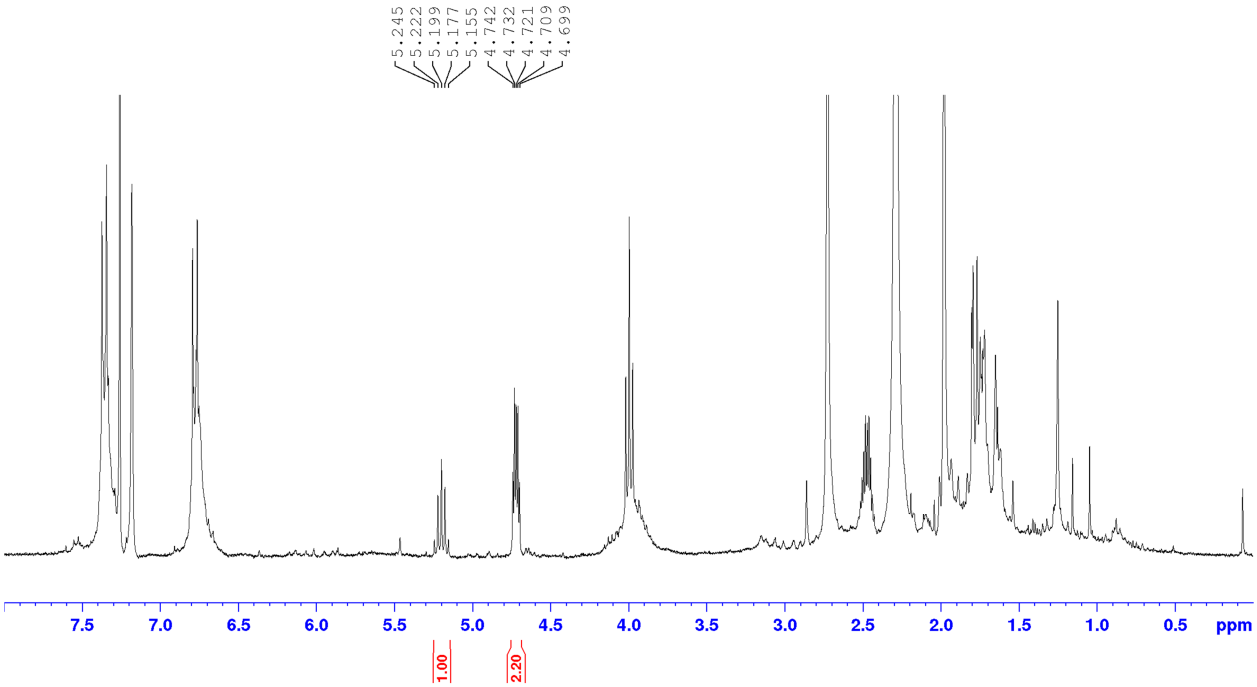


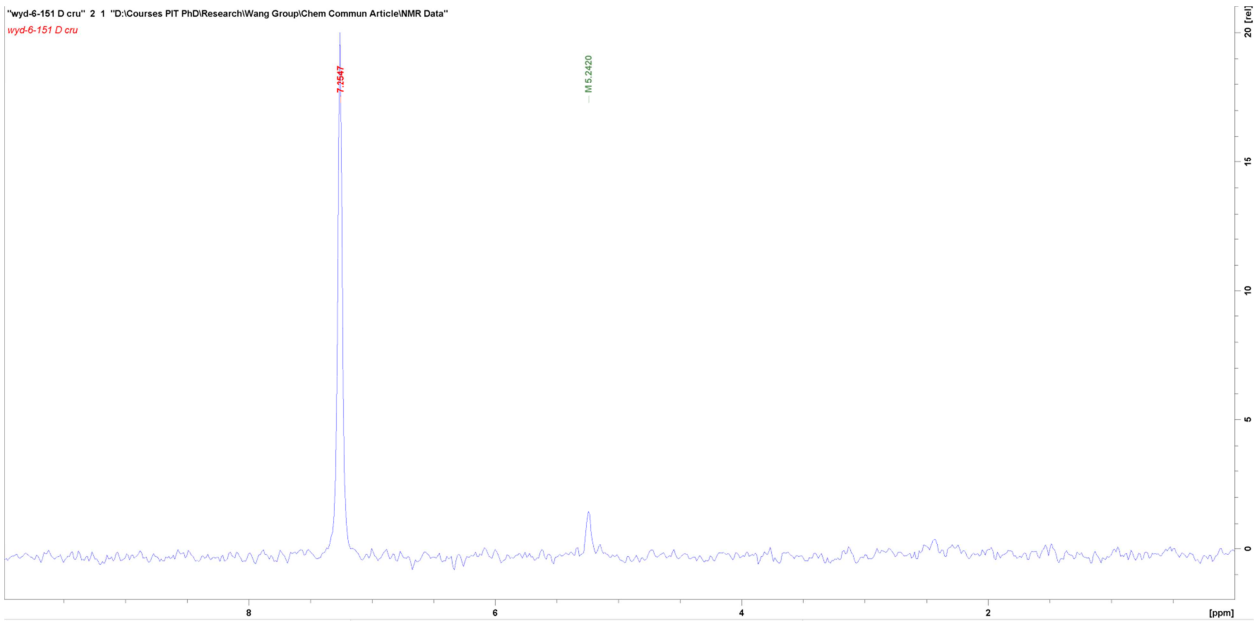
Stoichiometric reaction of [1g•Fp*]$^+$BF$_4^-$ with $(ND_4)_2SO_4$



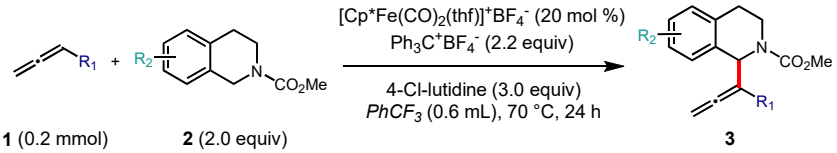
In the glovebox, $(ND_4)_2SO_4$ (8.4 mg, 0.06 mmol, 1.2 equiv), [**1g**•Fp*]$^+$BF$_4^-$ (28.6 mg, 0.05 mmol, 1.0 equiv), dry $PhCF_3$ (0.1 mL) and 4-Cl-lutidine (10 μL, 0.075 mmol, 1.5 equiv) were

added in rapid succession. The reaction tube was capped and removed from the glovebox. The reaction tube was placed in an 70 °C oil bath with vigorous stirring for 24 h. After then, the reaction mixture was cooled to room temperature. 1 mL acetone and NaI (15 mg, 0.1 mmol, 2.0 equiv) were added to the above solution. The reaction mixture was stirred at r.t. for another 30 min. The crude mixture was concentrated *in vacuo* and the crude product was then analyzed by ^{1}H and ^{2}H NMR spectroscopy. The chemical shift was referenced to $CDCl_3$ (δ 7.26 ppm) for ^{2}H spectroscopy.





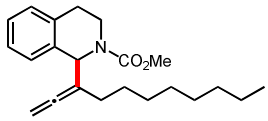
General procedure for iron catalyzed allenic C(sp^2)-H functionalization



1 (0.2 mmol) **2** (2.0 equiv) **3**

A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was capped with a Teflon/silicone septum (Thermo/National part # C4015-66A) screw cap and flame dried under vacuum. The reaction tube was cooled under nitrogen and transferred into an argon-filled glovebox. In the glovebox, a suspension of carbamate **2** (0.40 mmol, 2.0 equiv) and $Ph_3C^+BF_4^-$ (145.3 mg, 0.44 mmol, 2.2 equiv) in dry trifluorotoluene (0.4 mL) was stirred at room temperature for 3 hours to generate the iminium salt. Then $[Cp^*Fe(CO)_2(thf)]^+[BF_4]^-$ (20 mol %, 16.2 mg), allene **1** (0.20 mmol, 1.0 equiv), 4-chloro-2,6-dimethylpyridine (76.3 µL, 0.60 mmol, 3.0 equiv) and trifluorotoluene (0.2 mL) were added in rapid succession. The reaction tube was capped and removed from the glovebox. The reaction tube was placed in an oil bath, preheated to 70 °C, where it was stirred for 24 h. After completion of the reaction, the reaction mixture was cooled to room temperature. The crude mixture was concentrated *in vacuo* and purified by flash column chromatography to provide the desired product **3**.

Characterization Data for Product 3



3aa

Methyl 1-(undeca-1,2-dien-3-yl)-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (3aa): Prepared following general procedure, using undeca-1,2-diene (**1a**, 30.4 mg, 0.20 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1*H*)-carboxylate (**2a**, 76.5 mg, 0.40 mmol, 2.0 equiv). The crude mixture was purified via column chromatography on silica gel (gradient from 2% acetone in hexanes to 5% acetone in hexanes, followed by a gradient from 5% EtOAc in hexanes to 10% EtOAc in hexanes) to afford the product **3aa** as a pale-yellow oil (56.7 mg, 83% yield).

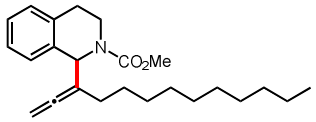
^{1}H NMR (500 MHz, $CDCl_3$, rotamers observed) δ 7.17-7.06 (m, 4H), 5.67 (br, 0.5H), 5.54 (br, 0.5H), 4.58-4.51 (m, 2H), 4.07 (br, 0.5H), 3.90 (br, 0.5H), 3.74 (s, 3H), 3.39 (br, 1H), 2.89 (br, 1H), 2.78 (dt, *J* = 16.1, 4.5 Hz, 1H), 1.99 (br, 2H), 1.49-1.43 (m, 2H), 1.36-1.21 (m, 10H), 0.88 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, rotamers observed) δ 207.3, 156.3, 135.4, 134.8, 128.5, 128.2, 126.9, 125.6, 106.6, 77.8, 57.2, 52.8, 39.0, 32.0, 29.6, 29.5, 29.4, 28.2, 27.7, 22.8, 14.2.

HRMS (ESI) calcd for $C_{22}H_{32}NO_2$ $[M+H]^+$: 342.2433, found: 342.2426.

One-step, one-pot protocol at 1 mmol scale:

A reaction tube (20 mm × 125 mm, Fisherbrand, part # 14-959-37A) equipped with a magnetic stir bar was capped with a Teflon/silicone septum (Thermo/National part # B7995-18) screw cap and flame dried under vacuum. The reaction tube was cooled under nitrogen and transferred into an argon-filled glovebox. In the glovebox, a mixture of $[Cp^*Fe(CO)_2(thf)]^+[BF_4]^-$ (20 mol %, 81.2 mg) and $Ph_3C^+BF_4^-$ (726.3 mg, 2.20 mmol, 2.2 equiv) in dry trifluorotoluene (3.0 mL) was added allene **1a** (152.6 mg, 1.00 mmol, 1.0 equiv), 4-chloro-2,6-dimethylpyridine (381.7 µL, 3.00 mmol, 3.0 equiv) and carbamate **2a** (382.5 mg, 2.00 mmol, 2.0 equiv) in rapid succession. The reaction tube was quickly capped and removed from the glovebox. The reaction tube was placed in an oil bath, preheated to 70 °C, where it was stirred for 24 h. After completion of the reaction, the reaction mixture was cooled to room temperature. The crude mixture was concentrated in vacuo and purified by flash column chromatography on silica gel (gradient from 2% acetone in hexanes to 5% acetone in hexanes, followed by a gradient from 5% EtOAc in hexanes to 10% EtOAc in hexanes) to provide the desired product **3aa** as a yellow oil (267.7 mg, 78%).



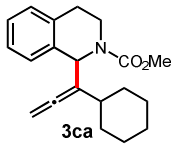
3ba

Methyl 1-(trideca-1,2-dien-3-yl)-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (3ba): Prepared following general procedure, using trideca-1,2-diene (**1b**, 36.1 mg, 0.20 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1*H*)-carboxylate (**2a**, 76.5 mg, 0.40 mmol, 2.0 equiv). The crude mixture was purified via column chromatography on silica gel (gradient from 2% acetone in hexanes to 5% acetone in hexanes, followed by a gradient from 5% EtOAc in hexanes to 10% EtOAc in hexanes) to afford the product **3ba** as a pale-yellow oil (60.3 mg, 82% yield).

^{1}H NMR (500 MHz, $CDCl_3$, rotamers observed) δ 7.15-7.06 (m, 4H), 5.67 (br, 0.5H), 5.54 (br, 0.5H), 4.58-4.51 (m, 2H), 4.06 (br, 0.5H), 3.89 (br, 0.5H), 3.74 (s, 3H), 3.39 (br, 1H), 2.89 (br, 1H), 2.78 (dt, *J* = 16.1, 4.5 Hz, 1H), 1.99 (br, 2H), 1.49-1.43 (m, 2H), 1.36-1.21 (m, 14H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, rotamers observed) δ 207.3, 156.3, 135.5, 134.7, 128.5, 128.3, 126.9, 125.6, 106.6, 77.8, 57.2, 52.8, 39.0, 32.1, 29.8, 29.8, 29.6, 29.5, 29.5, 29.4, 28.2, 27.7, 22.8, 14.3.

HRMS (ESI) calcd for $C_{24}H_{36}NO_2$ $[M+H]^+$: 370.2746, found: 370.2748.



3ca

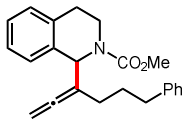
Methyl 1-(1-cyclohexylpropa-1,2-dien-1-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (3ca): Prepared following general procedure, using propa-1,2-dien-1-ylcyclohexane (**1c**, 24.4 mg, 0.20 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1H)-carboxylate (**2a**, 76.5 mg, 0.40 mmol, 2.0 equiv). The crude mixture was purified via column chromatography on silica gel (gradient from 2% acetone in hexanes to 5% acetone in hexanes, followed by gradient from 10%

Et_2O in hexanes to 20% Et_2O in hexanes) to afford the product **3ca** as a pale-yellow oil (40.2 mg, 65% yield).

^{1}H NMR (500 MHz, $CDCl_3$, rotamers observed) δ 7.14-7.00 (m, 4H), 5.80 (s, 0.5H), 5.65 (s, 0.5H), 4.51 (s, 2H), 4.08 (br, 0.5H), 3.88 (br, 0.5H), 3.74 (s, 3H), 3.41-3.33 (m, 1H), 2.93-2.87 (m, 1H), 2.74 (dt, *J* = 16.1, 4.0 Hz, 1H), 2.00 (d, *J* = 11.9 Hz, 1H), 1.88-1.65 (m, 5H), 1.36-1.09 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$, rotamers observed) δ 207.4, 156.4, 156.1, 135.9, 135.5, 134.9, 134.6, 128.7, 128.4, 128.3, 128.1, 126.8, 125.6, 112.4, 112.2, 78.6, 55.9, 52.8, 38.7, 38.2, 37.5, 33.0, 32.6, 28.2, 28.0, 26.8, 26.7, 26.6, 26.4.

HRMS (ESI) calcd for $C_{20}H_{26}NO_2$ $[M+H]^+$: 312.1964, found: 312.1954.



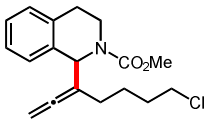
3da

Methyl 1-(6-phenylhexa-1,2-dien-3-yl)-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (3da): Prepared following general procedure, using 6-phenylhexa-1,2-diene (**1d**, 31.6 mg, 0.20 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1*H*)-carboxylate (**2a**, 76.5 mg, 0.40 mmol, 2.0 equiv). The crude mixture was purified via column chromatography on silica gel (gradient from 2% acetone in hexanes to 5% acetone in hexanes) to afford the product **3da** as a pale-yellow oil (54.3 mg, 78% yield).

^{1}H NMR (500 MHz, $CDCl_3$, rotamers observed) δ 7.30-7.26 (m, 2H), 7.19-7.04 (m, 7H), 5.69 (br, 0.5H), 5.55 (br, 0.5H), 4.63-4.57 (m, 2H), 4.07 (br, 0.5H), 3.89 (br, 0.5H), 3.73 (s, 3H), 3.41 (br, 1H), 2.90 (br, 1H), 2.79 (dt, *J* = 16.1, 4.1 Hz, 1H), 2.69-2.60 (m, 2H), 2.07 (br, 2H), 1.86-1.78 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$, rotamers observed) δ 207.2, 156.3, 142.5, 135.2, 134.8, 128.6, 128.5, 128.4, 128.2, 127.0, 125.8, 125.7, 106.2, 78.2, 57.2, 52.8, 39.1, 38.8, 35.6, 29.6, 29.0, 28.2.

HRMS (ESI) calcd for $C_{23}H_{26}NO_2$ $[M+H]^+$: 348.1964, found: 348.1959.

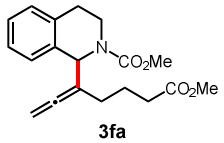


3ea

Methyl 1-(7-chlorohepta-1,2-dien-3-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (3ea): Prepared following general procedure, using 7-chlorohepta-1,2-diene (**1e**, 26.1 mg, 0.20 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1H)-carboxylate (**2a**, 76.5 mg, 0.40 mmol, 2.0 equiv). The crude mixture was purified via column chromatography on silica gel (gradient from 2% acetone in hexanes to 5% acetone in hexanes, followed by gradient from 10% Et_2O in hexanes to 20% Et_2O in hexanes) to afford the product **3ea** as a pale-yellow oil (42.1 mg, 66% yield).

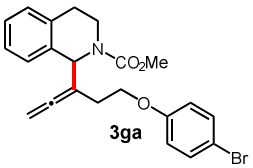
^{1}H NMR (500 MHz, $CDCl_3$, rotamers observed) δ 7.15-7.05 (m, 4H), 5.66 (br, 0.5H), 5.55 (br, 0.5H), 4.62-4.55 (m, 2H), 4.05 (br, 0.5H), 3.90 (br, 0.5H), 3.74 (s, 3H), 3.53 (t, *J* = 6.7 Hz, 2H), 3.38 (br, 1H), 2.89 (br, 1H), 2.78 (dt, *J* = 16.1, 4.5 Hz, 1H), 2.03 (br, 2H), 1.84-1.78 (m, 2H), 1.66-1.59 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$, rotamers observed) δ 207.2, 156.3, 135.2, 134.8, 128.6, 128.2, 127.0, 125.7, 106.0, 78.3, 57.1, 52.9, 45.1, 39.0, 32.3, 28.7, 28.2, 25.0.
HRMS (ESI) calcd for $C_{18}H_{23}ClNO_2$ $[M+H]^+$: 320.1417, found: 320.1414.



3fa

Methyl 1-(7-methoxy-7-oxohepta-1,2-dien-3-yl)-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (3fa): Prepared following general procedure, using methyl hepta-5,6-dienoate (**1f**, 28.0 mg, 0.20 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1*H*)-carboxylate (**2a**, 76.5 mg, 0.40 mmol, 2.0 equiv). The crude mixture was purified via column chromatography on silica gel (gradient from 10% EtOAc in hexanes to 20% EtOAc in hexanes) to afford the product **3fa** as a pale-yellow oil (52.6 mg, 80% yield).
^{1}H NMR (500 MHz, $CDCl_3$, rotamers observed) δ 7.15-7.04 (m, 4H), 5.65 (br, 0.5H), 5.54 (br, 0.5H), 4.62-4.55 (m, 2H), 4.04 (br, 0.5H), 3.90 (br, 0.5H), 3.73 (s, 3H), 3.66 (s, 3H) 3.37 (br, 1H), 2.88 (br, 1H), 2.77 (dt, *J* = 16.1, 4.6 Hz, 1H), 2.35 (t, *J* = 7.6 Hz, 2H), 2.04 (br, 2H), 1.87-1.76 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$, rotamers observed) δ 207.1, 174.1, 156.3, 135.1, 134.7, 128.6, 128.2, 127.0, 125.7, 105.7, 78.5, 57.1, 52.9, 51.6, 39.0, 33.6, 28.8, 28.2, 23.0.
HRMS (ESI) calcd for $C_{19}H_{24}NO_4$ $[M+H]^+$: 330.1705, found: 330.1700.
Scale-up to 5 mmol:
In an argon-filled glovebox, a suspension of carbamate (**2a**, 1912.3 mg, 10.00 mmol, 2.0 equiv) and $Ph_3C^+BF_4^-$ (3631.4 mg, 11.00 mmol, 2.2 equiv) in dry trifluorotoluene (10.0 mL) was stirred in a 50 mL flame-dried round-bottom flask at room temperature for 3 hours to generate the iminium salt. Then $[Cp^*Fe(CO)_2(thf)]^+[BF_4]^-$ (15 mol %, 304.5 mg), allene (**1f**, 700.9 mg, 5.00 mmol, 1.0 equiv), 4-chloro-2,6-dimethylpyridine (1.9 mL, 15.00 mmol, 3.0 equiv) and trifluorotoluene (5.0 mL) were added in rapid succession. The reaction tube was capped and removed from the glovebox. The reaction tube was placed in an oil bath, preheated to 70 °C, where it was stirred for 24 h. After completion of the reaction, the reaction mixture was cooled to room temperature. The crude mixture was concentrated in vacuo and purified by flash column chromatography on silica gel (gradient from 10% EtOAc in hexanes to 20% EtOAc in hexanes) to provide the desired product **3fa** as a yellow oil (1244.7 mg, 76%).



3ga

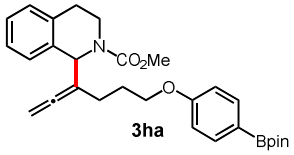
Methyl 1-(5-(4-bromophenoxy)penta-1,2-dien-3-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (3ga): Prepared following general procedure, using 1-bromo-4-(penta-3,4-dien-1-yloxy)benzene (**1g**, 47.8 mg, 0.20 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1*H*)-carboxylate (**2a**, 76.5 mg, 0.40 mmol, 2.0 equiv). The crude mixture was purified via column

chromatography on silica gel (gradient from 10% acetone in hexanes to 20% acetone in hexanes) to afford the product **3ga** as a yellow oil (62.6 mg, 73% yield) [1].

^{1}H NMR (500 MHz, $CDCl_3$, rotamers observed) δ 7.35 (d, *J* = 8.9 Hz, 2H), 7.16-7.09 (m, 4H), 6.77 (d, *J* = 9.0 Hz, 2H), 5.74 (br, 0.6H), 5.66 (br, 0.4H), 4.64-4.57 (m, 2H), 4.05 (t, *J* = 6.1 Hz, 2H), 4.05 (br, 0.4H), 3.95 (br, 0.6H), 3.74 (s, 3H), 3.40 (br, 1H), 2.91 (br, 1H), 2.78 (dt, *J* = 16.1, 4.4 Hz, 1H), 2.51 (br, 2H).

^{13}C NMR (125 MHz, $CDCl_3$, rotamers observed) δ 207.2, 158.2, 156.3, 134.8, 134.8, 132.3, 128.7, 128.3, 127.2, 125.8, 116.5, 102.9, 78.7, 66.6, 57.2, 53.0, 38.9, 29.2, 28.2.

HRMS (ESI) calcd for $C_{22}H_{23}BrNO_3$ $[M+H]^+$: 428.0861, found: 428.0841.



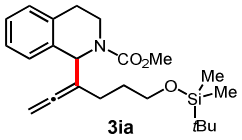
3ha

Methyl 1-(6-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)hexa-1,2-dien-3-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (3ha): Prepared following general procedure, using 2-(4-(hexa-4,5-dien-1-yloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1h**, 60.0 mg, 0.20 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1*H*)-carboxylate (**2a**, 76.5 mg, 0.40 mmol, 2.0 equiv). The crude mixture was purified via column chromatography on silica gel (gradient from 10% acetone in hexanes to 20% acetone in hexanes) to afford the product **3ha** as a yellow oil (66.7 mg, 68% yield).

^{1}H NMR (500 MHz, $CDCl_3$, rotamers observed) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.18-7.06 (m, 4H), 6.88 (d, *J* = 8.4 Hz, 2H), 5.69 (br, 0.5H), 5.58 (br, 0.5H), 4.63-4.57 (m, 2H), 4.01 (t, *J* = 6.3 Hz, 2H), 4.01 (br, 0.5H), 3.88 (br, 0.5H), 3.73 (s, 3H), 3.40 (br, 1H), 2.89 (br, 1H), 2.78 (dt, *J* = 16.0, 4.5 Hz, 1H), 2.19 (br, 2H), 2.01-1.93 (m, 2H), 1.34 (s, 12H).

^{13}C NMR (125 MHz, $CDCl_3$, rotamers observed) δ 207.0, 161.8, 156.3, 136.6, 135.1, 134.8, 128.6, 128.2, 127.0, 125.7, 114.0, 105.9, 83.6, 78.6, 67.2, 57.3, 52.9, 39.1, 28.2, 27.4, 25.9, 25.0.

HRMS (ESI) calcd for $C_{29}H_{36}BNO_5$ $[M+H]^+$: 490.2765, found: 490.2751.

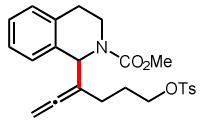


3ia

Methyl 1-(6-((*tert*-butyldimethylsilyl)oxy)hexa-1,2-dien-3-yl)-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (3ia): Prepared following general procedure, using *tert*-butyl(hexa-4,5-dien-1-yloxy)dimethylsilane (**1i**, 42.5 mg, 0.20 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1*H*)-carboxylate (**2a**, 76.5 mg, 0.40 mmol, 2.0 equiv). The crude mixture was purified via column chromatography on silica gel (gradient from 50% DCM in hexanes to 100% DCM) to afford the product **3ia** as a pale-yellow oil (72.9 mg, 91% yield).

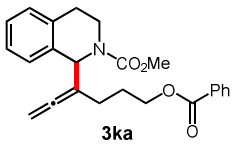
^{1}H NMR (500 MHz, $CDCl_3$, rotamers observed) δ 7.14-7.05 (m, 4H), 5.67 (br, 0.5H), 5.54 (br, 0.5H), 4.61-4.54 (m, 2H), 4.05 (br, 0.5H), 3.89 (br, 0.5H), 3.73 (s, 3H), 3.63 (t, *J* = 6.4 Hz, 2H) 3.39 (br, 1H), 2.89 (br, 1H), 2.78 (dt, *J* = 16.1, 4.5 Hz, 1H), 2.04 (br, 2H), 1.73-1.64 (m, 2H), 0.89 (s, 9H), 0.04 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$, rotamers observed) δ 207.0, 156.2, 135.2, 134.8, 128.6, 128.2, 127.0, 125.7, 106.3, 78.3, 62.8, 57.3, 52.8, 39.1, 30.9, 28.2, 26.1, 25.7, 18.5, -5.2.
HRMS (ESI) calcd for $C_{23}H_{36}NO_3Si$ $[M+H]^+$: 402.2464, found: 402.2460.



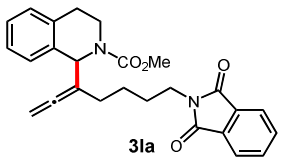
3ja

Methyl 1-(6-(tosyloxy)hexa-1,2-dien-3-yl)-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (3ja): Prepared following general procedure, using hexa-4,5-dien-1-yl-4-methylbenzenesulfonate (**1j**, 50.5 mg, 0.20 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1*H*)-carboxylate (**2a**, 76.5 mg, 0.40 mmol, 2.0 equiv). The crude mixture was purified via column chromatography on silica gel (gradient from 5% acetone in hexanes to 15% acetone in hexanes) to afford the product **3ja** as a pale-yellow oil (65.2 mg, 74% yield).
^{1}H NMR (500 MHz, $CDCl_3$, rotamers observed) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.16-7.08 (m, 3H), 6.98 (d, *J* = 7.0 Hz, 1H), 5.59 (br, 0.5H), 5.49 (br, 0.5H), 4.58-4.51 (m, 2H), 4.05 (t, *J* = 6.2 Hz, 2H), 4.01 (br, 0.5H), 3.88 (br, 0.5H), 3.72 (s, 3H), 3.32 (br, 1H), 2.87 (br, 1H), 2.75 (dt, *J* = 16.1, 4.5 Hz, 1H), 2.45 (s, 3H), 2.03 (br, 2H), 1.85-1.79 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$, rotamers observed) δ 206.7, 156.3, 144.8, 135.0, 134.7, 133.3, 130.0, 128.6, 128.2, 128.0, 127.1, 125.8, 105.3, 78.9, 70.1, 57.1, 52.9, 39.0, 28.2, 27.0, 25.2, 21.8.
HRMS (ESI) calcd for $C_{24}H_{28}NO_5S$ $[M+H]^+$: 442.1688, found: 442.1678.



3ka

Methyl 1-(6-(benzoyloxy)hexa-1,2-dien-3-yl)-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (3ka): Prepared following general procedure, using hexa-4,5-dien-1-yl benzoate (**1k**, 40.4 mg, 0.20 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1*H*)-carboxylate (**2a**, 76.5 mg, 0.40 mmol, 2.0 equiv). The crude mixture was purified via column chromatography on silica gel (gradient from 5% acetone in hexanes to 10% acetone in hexanes) to afford the product **3ka** as a pale-yellow oil (64.3 mg, 82% yield).
^{1}H NMR (500 MHz, $CDCl_3$, rotamers observed) δ 8.03 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.17-7.06 (m, 4H), 5.70 (br, 0.5H), 5.57 (br, 0.5H), 4.65-4.58 (m, 2H), 4.38-4.31 (m, 2H), 4.06 (br, 0.5H), 3.90 (br, 0.5H), 3.71 (s, 3H), 3.40 (br, 1H), 2.89 (br, 1H), 2.78 (dt, *J* = 16.1, 4.5 Hz, 1H), 2.19 (br, 2H), 2.00-1.91 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$, rotamers observed) δ 207.0, 166.8, 156.4, 135.1, 134.7, 133.0, 130.6, 129.7, 128.6, 128.5, 128.2, 127.1, 125.8, 105.7, 78.7, 64.5, 57.2, 52.9, 39.0, 28.2, 26.9, 25.9.
HRMS (ESI) calcd for $C_{24}H_{26}NO_4$ $[M+H]^+$: 392.1862, found: 392.1854.

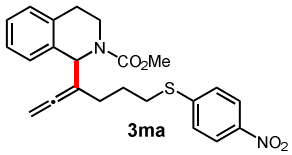


Methyl 1-(7-(1,3-dioxoisoindolin-2-yl)hepta-1,2-dien-3-yl)-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (3la): Prepared following general procedure, using 2-(hepta-5,6-dien-1-yl)isoindoline-1,3-dione (**1l**, 48.3 mg, 0.20 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1*H*)-carboxylate (**2a**, 76.5 mg, 0.40 mmol, 2.0 equiv). The crude mixture was purified via column chromatography on silica gel (gradient from 5% acetone in hexanes to 15% acetone in hexanes) to afford the product **3la** as a pale-yellow oil (70.2 mg, 82% yield).

^{1}H NMR (500 MHz, $CDCl_3$, rotamers observed) δ 7.83 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.13-7.04 (m, 4H), 5.64 (br, 0.5H), 5.51 (br, 0.5H), 4.57-4.50 (m, 2H), 4.02 (br, 0.5H), 3.88 (br, 0.5H), 3.71 (s, 3H), 3.67 (t, *J* = 7.2 Hz, 2H), 3.36 (br, 1H), 2.87 (br, 1H), 2.76 (dt, *J* = 16.1, 4.5 Hz, 1H), 2.03 (br, 2H), 1.75-1.66 (m, 2H), 1.56-1.47 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$, rotamers observed) δ 207.1, 168.5, 156.2, 135.3, 134.7, 134.0, 132.3, 128.5, 128.2, 126.9, 125.7, 123.3, 105.9, 78.3, 57.1, 52.8, 38.9, 38.0, 28.8, 28.2, 28.1, 24.8.

HRMS (ESI) calcd for $C_{26}H_{27}N_2O_4$ $[M+H]^+$: 431.1971, found: 431.1963.

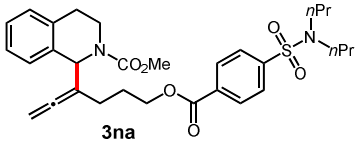


Methyl 1-(6-((4-nitrophenyl)thio)hexa-1,2-dien-3-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (3ma): Prepared following general procedure, using hexa-4,5-dien-1-yl(4-nitrophenyl)sulfane (**1m**, 47.1 mg, 0.20 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1*H*)-carboxylate (**2a**, 76.5 mg, 0.40 mmol, 2.0 equiv). The crude mixture was purified via column chromatography on silica gel (gradient from 5% acetone in hexanes to 15% acetone in hexanes) to afford the product **3ma** as a yellow oil (30.1 mg, 35% yield).

^{1}H NMR (500 MHz, $CDCl_3$, rotamers observed) δ 8.11 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.18-7.04 (m, 4H), 5.65 (br, 0.6H), 5.57 (br, 0.4H), 4.66-4.59 (m, 2H), 4.05 (br, 0.4H), 3.88 (br, 0.6H), 3.74 (s, 3H), 3.39 (br, 1H), 3.04 (t, *J* = 7.1 Hz, 2H), 2.89 (br, 1H), 2.79 (dt, *J* = 16.0, 4.5 Hz, 1H), 2.18 (br, 2H), 1.92-1.87 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$, rotamers observed) δ 206.9, 156.3, 147.9, 145.0, 134.9, 134.8, 128.6, 128.1, 127.2, 126.2, 125.8, 124.1, 105.5, 78.9, 57.2, 52.9, 39.2, 31.5, 28.5, 28.2, 26.7.

HRMS (ESI) calcd for $C_{23}H_{25}N_2O_4S$ $[M+H]^+$: 425.1535, found: 425.1521.



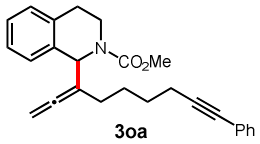
Methyl 1-(6-((4-(*N*,*N*-dipropylsulfamoyl)benzoyl)oxy)hexa-1,2-dien-3-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (3na): Prepared following general procedure, using hexa-4,5-dien-1-yl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (**1n**, 73.1 mg, 0.20 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1*H*)-carboxylate (**2a**, 76.5 mg, 0.40 mmol, 2.0 equiv). The

crude mixture was purified via column chromatography on silica gel (gradient from 5% acetone in hexanes to 15% acetone in hexanes) to afford the product **3na** as a pale-yellow oil (80.9 mg, 73% yield).

^{1}H NMR (500 MHz, $CDCl_3$, rotamers observed) δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.5 Hz, 2H), 7.17-7.05 (m, 4H), 5.68 (br, 0.6H), 5.57 (br, 0.4H), 4.66-4.58 (m, 2H), 4.41-4.33 (m, 2H), 4.05 (br, 0.4H), 3.89 (br, 0.6H), 3.71 (s, 3H), 3.38 (br, 1H), 3.10 (t, *J* = 7.6 Hz, 4H), 2.88 (br, 1H), 2.78 (dt, *J* = 16.1, 4.5 Hz, 1H), 2.18 (br, 2H), 2.01-1.93 (m, 2H), 1.55 (sextet, *J* = 7.5 Hz, 4H) 0.87 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$, rotamers observed) δ 207.0, 165.4, 156.3, 144.3, 135.0, 134.7, 133.8, 130.3, 128.6, 128.2, 127.1, 125.8, 105.5, 78.8, 65.1, 57.2, 52.9, 50.1, 39.0, 28.2, 26.7, 25.8, 22.1, 11.3.

HRMS (ESI) calcd for $C_{30}H_{39}N_2O_6S$ $[M+H]^+$: 555.2529, found: 555.2523.



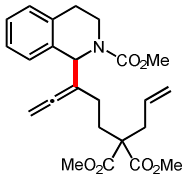
3oa

Methyl 1-(9-phenylnona-1,2-dien-8-yn-3-yl)-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (3oa): Prepared following general procedure, using nona-7,8-dien-1-yn-1-ylbenzene (**1o**, 39.3 mg, 0.20 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1*H*)-carboxylate (**2a**, 76.5 mg, 0.40 mmol, 2.0 equiv). The crude mixture was purified via column chromatography on silica gel (gradient from 2% acetone in hexanes to 5% acetone in hexanes) and preparative TLC (15% Et_2O in hexanes) to afford the product **3oa** as a pale-yellow oil (52.2 mg, 68% yield).

^{1}H NMR (500 MHz, $CDCl_3$, rotamers observed) δ 7.39-7.37 (m, 2H), 7.29-7.23 (m, 3H), 7.17-7.06 (m, 4H), 5.68 (br, 0.5H), 5.56 (br, 0.5H), 4.61-4.54 (m, 2H), 4.06 (br, 0.5H), 3.89 (br, 0.5H), 3.73 (s, 3H), 3.39 (br, 1H), 2.89 (br, 1H), 2.78 (dt, *J* = 16.1, 4.6 Hz, 1H), 2.42-2.38 (m, 2H), 2.05 (br, 2H), 1.68-1.60 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$, rotamers observed) δ 207.2, 156.3, 135.4, 134.8, 131.7, 128.5, 128.3, 128.2, 127.6, 127.0, 125.7, 124.2, 106.3, 90.4, 80.8, 78.2, 57.2, 52.9, 39.0, 29.0, 28.5, 28.2, 27.0, 19.4.

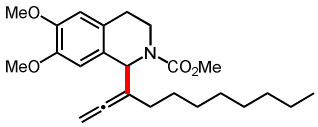
HRMS (ESI) calcd for $C_{26}H_{28}NO_2$ $[M+H]^+$: 386.2120, found: 386.2113.



3pa

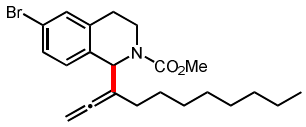
Dimethyl 2-allyl-2-(3-(2-(methoxycarbonyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)penta-3,4-dien-1-yl)malonate (3pa): Prepared following general procedure, using dimethyl 2-allyl-2-(penta-3,4-dien-1-yl)malonate (**1p**, 47.7 mg, 0.20 mmol, 1.0 equiv) and methyl 3,4-dihydroisoquinoline-2(1*H*)-carboxylate (**2a**, 76.5 mg, 0.40 mmol, 2.0 equiv). The crude mixture was purified via column chromatography on silica gel (gradient from 5% acetone in hexanes to 15% acetone in hexanes) to afford the product **3pa** as a pale-yellow oil (80.7 mg, 94% yield).

^{1}H NMR (500 MHz, $CDCl_3$, rotamers observed) δ 7.15-7.04 (m, 4H), 5.67-5.59 (m, 1.5H), 5.53 (br, 0.5H), 5.07 (s, 1H), 5.05 (d, *J* = 5.1 Hz, 1H), 4.63-4.57 (m, 2H), 4.03 (br, 0.5H), 3.87 (br, 0.5H), 3.72 (s, 3H), 3.70 (d, *J* = 1.4 Hz, 6H), 3.35 (br, 1H), 2.88 (br, 1H), 2.76 (dt, *J* = 16.1, 4.4 Hz, 1H), 2.64 (d, *J* = 7.5 Hz, 2H), 2.10-1.96 (m, 2H), 1.91-1.88 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$, rotamers observed) δ 207.0, 171.7, 171.6, 156.2, 135.1, 134.8, 132.4, 128.6, 128.2, 127.1, 125.7, 119.2, 105.9, 78.9, 57.5, 57.2, 52.8, 52.5, 38.9, 37.4, 31.1, 28.1, 24.1.
HRMS (ESI) calcd for $C_{24}H_{30}NO_6$ $[M+H]^+$: 428.2073, found: 428.2066.



3ab

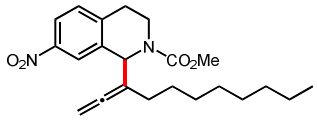
Methyl 6,7-dimethoxy-1-(undeca-1,2-dien-3-yl)-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (3ab): Prepared following general procedure, using undeca-1,2-diene (**1a**, 30.4 mg, 0.20 mmol, 1.0 equiv) and methyl 6,7-dimethoxy-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (**2b**, 100.5 mg, 0.40 mmol, 2.0 equiv). The crude mixture was purified via column chromatography on silica gel (gradient from 5% acetone in hexanes to 15% acetone in hexanes, followed by a gradient from 10% EtOAc in hexanes to 20% EtOAc in hexanes) to afford the product **3ab** as a pale-yellow oil (45.3 mg, 56% yield).
^{1}H NMR (500 MHz, $CDCl_3$, rotamers observed) δ 6.56 (s, 1H), 6.53 (s, 1H), 5.60 (br, 0.5H), 5.48 (br, 0.5H), 4.58-4.50 (m, 2H), 4.11 (br, 0.5H), 3.94 (br, 0.5H), 3.84 (s, 3H), 3.83 (s, 3H), 3.73 (s, 3H), 3.29 (br, 1H), 2.84 (br, 1H), 2.63 (dt, *J* = 15.9, 3.9 Hz, 1H), 1.98 (br, 2H), 1.64-1.43 (m, 2H), 1.35-1.24 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, rotamers observed) δ 207.4, 156.2, 147.9, 147.1, 127.2, 126.5, 111.3, 111.1, 106.5, 77.8, 56.8, 56.2, 55.9, 52.8, 38.5, 32.0, 29.6, 29.5, 29.5, 27.8, 27.8, 22.8, 14.3.
HRMS (ESI) calcd for $C_{24}H_{36}NO_4$ $[M+H]^+$: 402.2644, found: 402.2634.



3ac

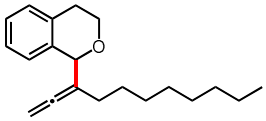
Methyl 6-bromo-1-(undeca-1,2-dien-3-yl)-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (3ac): Prepared following general procedure, using undeca-1,2-diene (**1a**, 30.4 mg, 0.20 mmol, 1.0 equiv) and methyl 6-bromo-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (**2c**, 108.1 mg, 0.40 mmol, 2.0 equiv). The crude mixture was purified via column chromatography on silica gel (gradient from 2% acetone in hexanes to 5% acetone in hexanes, followed by a gradient from 5% EtOAc in hexanes to 10% EtOAc in hexanes) to afford the product **3ac** as a pale-yellow oil (61.2 mg, 73% yield).
^{1}H NMR (500 MHz, $CDCl_3$, rotamers observed) δ 7.27 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 7.5 Hz, 1H), 5.65 (br, 0.5H), 5.51 (br, 0.5H), 4.59-4.51 (m, 2H), 4.10 (br, 0.5H), 3.94 (br, 0.5H), 3.75 (s, 3H), 3.33 (br, 1H), 2.88 (br, 1H), 2.73 (dt, *J* = 16.3, 4.0 Hz, 1H), 1.99 (br, 2H), 1.51-1.40 (m, 2H), 1.35-1.20 (m, 10H), 0.87 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, rotamers observed) δ 207.3, 156.2, 137.0, 134.6, 131.4, 130.0, 128.8, 120.5, 106.3, 78.1, 56.7, 52.9, 38.2, 32.0, 29.6, 29.5, 29.4, 28.0, 27.7, 22.8, 14.3.
HRMS (ESI) calcd for $C_{22}H_{31}BrNO_2$ $[M+H]^+$: 420.1538, found: 420.1527.



3ad

Methyl 7-nitro-1-(undeca-1,2-dien-3-yl)-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (3ad): Prepared following general procedure, using undeca-1,2-diene (**1a**, 30.4 mg, 0.20 mmol, 1.0 equiv) and methyl 7-nitro-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (**2d**, 94.5 mg, 0.40 mmol, 2.0 equiv). The crude mixture was purified via column chromatography on silica gel (from 5% EtOAc in hexanes to 15% EtOAc in hexanes) to afford the product **3ad** as a pale-yellow oil (36.0 mg, 47% yield).
^{1}H NMR (500 MHz, $CDCl_3$, rotamers observed) δ 8.00 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.93 (s, 1H), 7.24 (d, *J* = 8.3 Hz, 1H), 5.82 (br, 0.5H), 5.67 (br, 0.5H), 4.56-4.44 (m, 2H), 4.21 (br, 0.5H), 4.06 (br, 0.5H), 3.75 (s, 3H), 3.29 (br, 1H), 2.98 (br, 1H), 2.82 (dt, *J* = 16.5, 3.4 Hz, 1H), 2.03 (br, 2H), 1.54-1.41 (m, 2H), 1.35-1.24 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, rotamers observed) δ 207.7, 156.0, 146.0, 142.5, 137.1, 129.8, 123.5, 121.8, 106.2, 78.5, 56.8, 53.1, 37.4, 32.0, 29.6, 29.5, 29.4, 28.6, 27.7, 22.8, 14.3.
HRMS (ESI) calcd for $C_{22}H_{31}N_2O_4$ $[M+H]^+$: 387.2284, found: 387.2273.

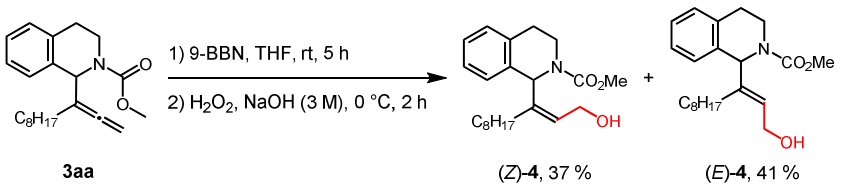


3ae

1-(undeca-1,2-dien-3-yl)isochromane (3ae): Prepared following general procedure, using undeca-1,2-diene (**1a**, 30.4 mg, 0.20 mmol, 1.0 equiv) and isochroman (**2e**, 53.7 mg, 0.40 mmol, 2.0 equiv). The crude mixture was purified via column chromatography on silica gel (gradient from 10% toluene in hexanes to 30% toluene in hexanes) to afford the product **3ae** as a pale-yellow oil (19.7 mg, 35% yield).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17-7.05 (m, 4H), 5.28 (s, 1H), 4.77-4.70 (m, 2H), 4.14 (dt, *J* = 11.3, 5.0 Hz, 1H), 3.84 (ddd, *J* = 12.5, 8.3, 4.3 Hz, 1H), 2.93 (ddd, *J* = 16.2, 8.2, 5.2 Hz, 1H), 2.76 (dt, *J* = 16.3, 4.6 Hz, 1H), 2.06-1.98 (m, 1H), 1.88-1.80 (m, 1H), 1.49-1.38 (m, 2H), 1.34-1.24 (m, 10H), 0.87 (t, *J* = 6.9 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 208.3, 136.2, 134.2, 128.7, 126.7, 126.4, 125.9, 105.2, 78.8, 76.8, 63.0, 32.0, 29.6, 29.5, 29.4, 28.8, 27.7, 27.5, 22.8, 14.3.
HRMS (ESI) calcd for $C_{20}H_{29}O$ $[M+H]^+$: 285.2218, found: 285.2202.

Synthetic Applications of Products

Synthesis of allyl alcohol 4[2]



3aa (*Z*)-**4**, 37 % (*E*)-**4**, 41 %

A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was capped with a Teflon/silicone septum (Thermo/National part # C4015-66A) screw cap and flame dried under vacuum. The tube was charged with **3aa** (34.1 mg, 0.1 mmol) and anhydrous THF (0.5 mL). 9-Borabicyclo[3.3.1]nonane (0.4 mL, 0.2 mmol, 2.0 equiv, 0.5 M in THF) was added dropwise by syringe at room temperature. The reaction mixture was stirred for 5 h. Then 1.0 mL NaOH (3 M) aqueous solution and 1.0 mL of H_2O_2 (30%) were added sequentially at 0 °C, and the reaction mixture was stirred for another 2 h at 0 °C. Subsequently, the reaction mixture was treated with water (3 mL), extracted with ethyl acetate (5 × 5 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified via column chromatography on silica gel (gradient from 10% EtOAc in hexanes to 20% EtOAc in hexanes) to afford the product (*Z*)-**4** (13.3 mg, 37% yield) as a clear oil and (*E*)-**4** (14.9 mg, 41% yield) as a clear oil.

(*Z*)-**4**:

^{1}H NMR (500 MHz, $CDCl_3$, rotamers observed) δ 7.20-7.13 (m, 3H), 7.07-7.04 (m, 1H), 6.01 (br, 1H), 5.87 (br, 1H), 4.63 (br, 1H), 4.34 (br, 1H), 4.03 (br, 1H), 3.74 (s, 3H), 3.28 (t, *J* = 11.0 Hz, 1H), 2.89 (ddd, *J* = 15.8, 11.6, 5.0 Hz, 1H), 2.79 (dt, *J* = 15.8, 3.1 Hz, 1H), 1.91 (ddd, *J* = 15.8, 9.1, 5.4 Hz, 1H), 1.75 (ddd, *J* = 15.6, 10.1, 5.6 Hz, 1H), 1.39-1.32 (m, 1H), 1.29-1.12 (m, 12H), 0.85 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, rotamers observed) δ 156.1, 142.9, 134.8, 134.1, 128.8, 126.8, 126.7, 126.3, 57.9, 54.1, 53.1, 40.9, 32.0, 31.5, 29.9, 29.6, 29.5, 29.3, 28.0, 22.8, 14.2.

HRMS (ESI) calcd for $C_{22}H_{34}NO_3$ $[M+H]^+$: 360.2539, found: 360.2529.

(*E*)-**4**:

^{1}H NMR (500 MHz, $CDCl_3$, rotamers observed) δ 7.18-7.12 (m, 3H), 7.01 (br, 1H), 5.76 (br, 0.5H), 5.61 (br, 0.5H), 5.07 (br, 1H), 4.17 (qd, *J* = 12.8, 6.7 Hz, 2H), 4.07 (br, 0.5H), 3.88 (br, 0.5H), 3.72 (s, 3H), 3.35 (br, 0.5H), 3.27 (br, 0.5H), 2.90 (br, 1H), 2.74 (dt, *J* = 16.3, 4.0 Hz, 1H), 2.16 (m, 1H), 2.05 (br, 1H), 1.51-1.24 (m, 13H), 0.89 (t, *J* = 6.8 Hz, 3H).

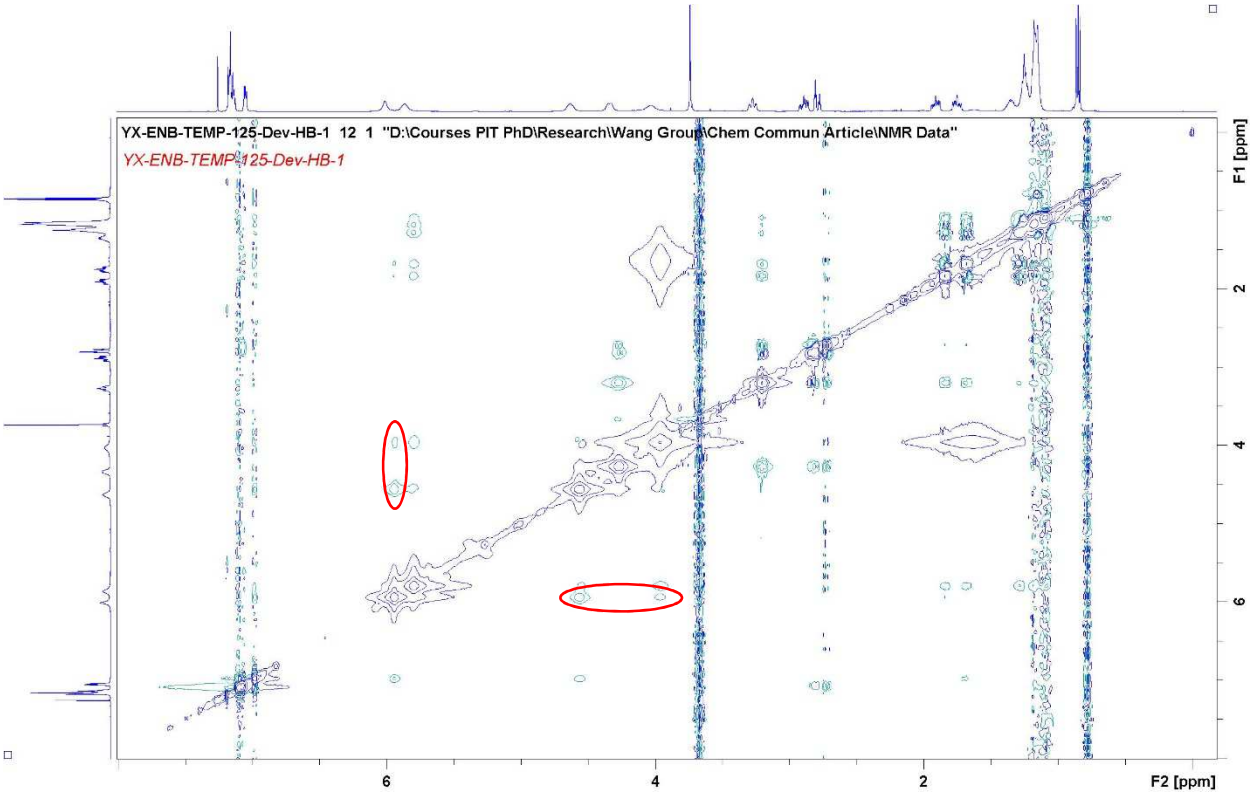
^{13}C NMR (125 MHz, $CDCl_3$, rotamers observed) δ 156.3, 143.6, 135.2, 134.9, 129.4, 128.8, 127.1, 125.9, 59.5, 58.7, 52.9, 38.5, 38.0, 32.0, 29.9, 29.5, 29.4, 29.3, 28.2, 28.0, 22.8, 14.3.

HRMS (ESI) calcd for $C_{22}H_{34}NO_3$ $[M+H]^+$: 360.2539, found: 360.2531.

The double bond geometry of (*Z*)-**4** and (*E*)-**4** were assigned via the 2D NOESY correlations illustrated below:

(*Z*)-**4** (*E*)-**4**

(*Z*)-**4**: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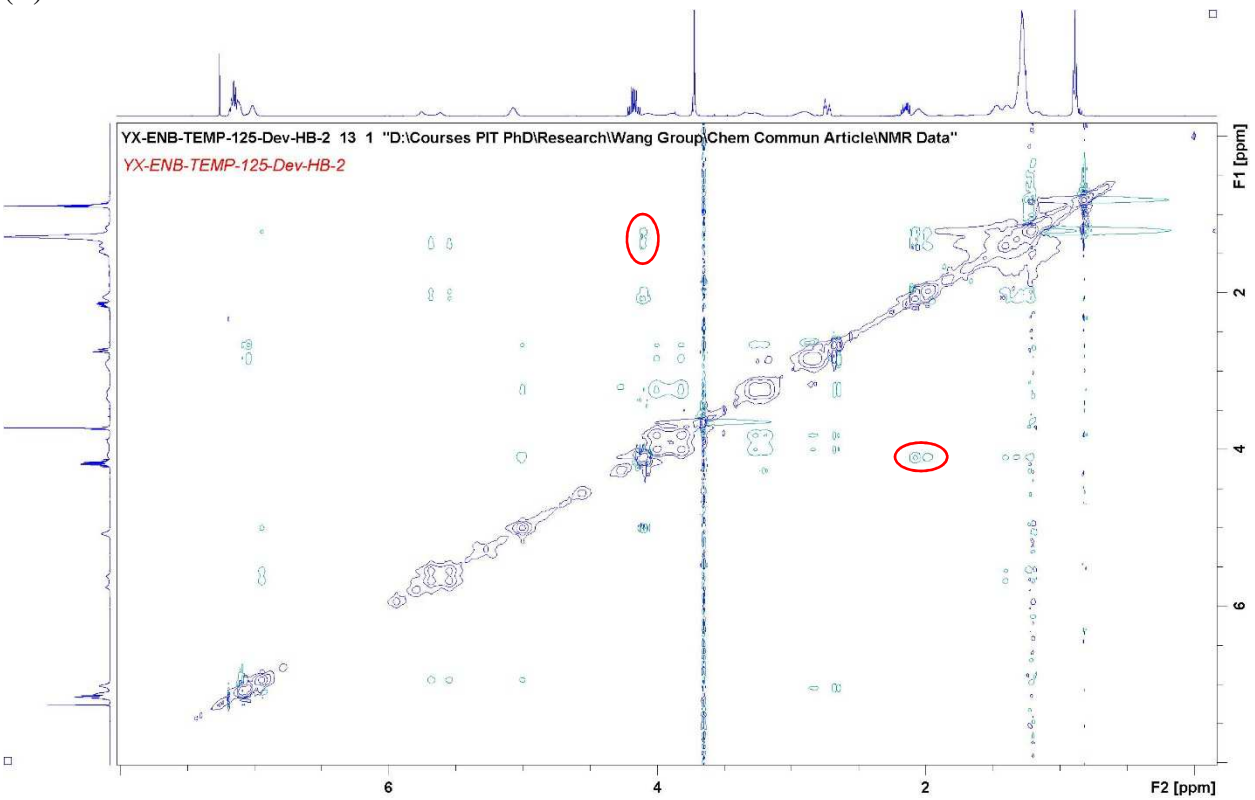
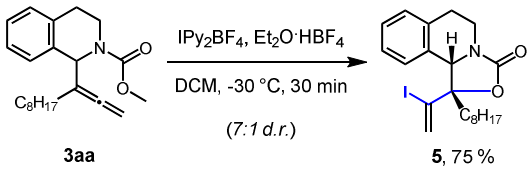
YX-ENB-TEMP-125-Dev-HB-1
F1 [ppm]
F2 [ppm]
6
4
2

(*E*)-**4**:


YX-ENB-TEMP-125-Dev-HB-2 13 1 "D:\Courses PIT PhD\Research\Wang Group\Chem Commun Article\NMR Data"
YX-ENB-TEMP-125-Dev-HB-2
F1 [ppm]
F2 [ppm]
6
4
2

Synthesis of vinyl iodide 5



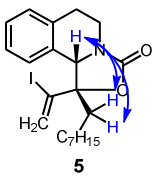
A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was capped with a Teflon/silicone septum (Thermo/National part # C4015-66A) screw cap and flame dried under vacuum. In the reaction tube, a solution of IPy_2BF_4 (111.6 mg, 0.3 mmol, 3.0 equiv) and $Et_2O{\cdot}HBF_4$ (41.2 uL, 48.6 mg, 0.3 mmol, 3.0 equiv) was stirred for 15 min at -30 °C, then a solution of **3aa** (34.1 mg, 0.1 mmol) in 0.2 mL of anhydrous dichloromethane was added by syringe. The reaction mixture was stirred for 30 min at –30 °C. Subsequently, saturated aqueous $Na_2S_2O_3$ (2 mL) was added, and extraction was performed with dichloromethane (3 × 5 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. The crude mixture was concentrated *in vacuo* and purified via column chromatography on silica gel (gradient from 5% EtOAc in hexanes to 10% EtOAc in hexanes) to afford the product **5** (34.2 mg, 75% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (td, *J* = 7.2, 1.1 Hz, 1H), 7.21 (td, *J* = 7.5, 1.3 Hz, 1H), 7.14 (d, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 7.4 Hz, 1H), 6.43 (d, *J* = 2.5 Hz, 1H), 6.01 (d, *J* = 2.5 Hz, 1H), 4.95 (s, 1H), 4.21-4.15 (m, 1H), 3.10-3.01 (m, 2H), 2.71-2.65 (m, 1H), 2.43 (ddd, *J* = 14.1, 11.4, 4.8 Hz, 1H), 2.12 (ddd, *J* = 14.2, 11.3, 4.9 Hz, 1H), 1.63-1.50 (m, 2H), 1.42-1.23 (m, 10H), 0.89 (t, *J* = 6.9 Hz, 1H).

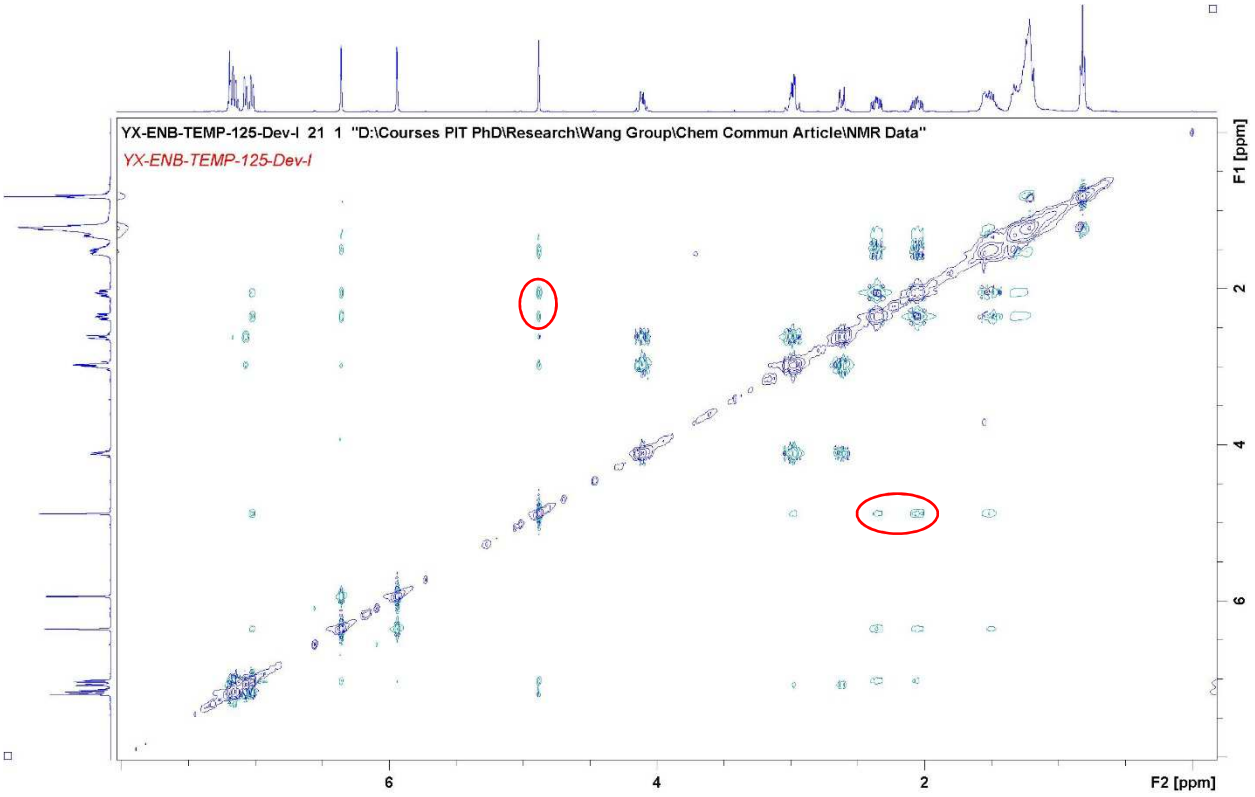
^{13}C NMR (125 MHz, $CDCl_3$) δ 156.4, 135.8, 130.4, 129.7, 129.6, 128.3, 127.9, 126.4, 108.5, 87.6, 64.0, 39.5, 39.3, 32.0, 29.9, 29.5, 29.4, 29.3, 23.5, 22.8, 14.3.

HRMS (ESI) calcd for $C_{21}H_{29}INO_2$ $[M+H]^+$: 454.1243, found: 454.1226.

The relative configuration of **5** were assigned via the 2D NOESY correlation illustrated below:



5



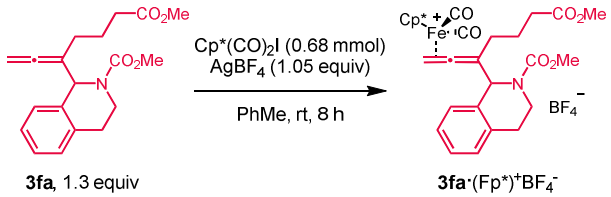
Preparation of substrates

Allene substrates 1: the identity of these substrates was confirmed by ^{1}H NMR spectra. Substrates **1a**-**1p** and **1b**-*d* were prepared using literature methods and the spectra obtained were in accord with the literature.[3]

Heterocycle substrates 2: the identity of these substrates was confirmed by ^{1}H spectra. Substrates **2a**-**2d** were prepared using literature methods and the spectra obtained were in accord with the literature. Substrate **2e** was purchased from Acros.[4]

Synthesis and characterization data of iron complex

Synthesis of iron complex 3fa·(Fp*)$^{+}$BF$_4^{-}$



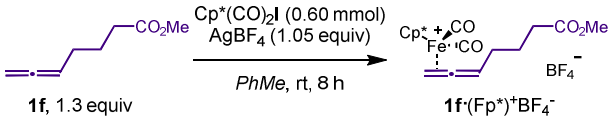
A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was capped with a Teflon/silicone septum (Thermo/National part # C4015-66A) screw cap and flame dried under vacuum. The reaction tube was cooled under nitrogen and transferred into an argon-filled glovebox. In the glovebox, a mixture of $Cp^*Fe(CO)_2I$ (254.3 mg, 0.68 mmol, 1.0 equiv) and $AgBF_4$ (134.3 mg 0.69 mmol, 1.05 equiv) in dry toluene (1.5 mL) was added **3fa** (299.5 mg, 0.91 mmol, 1.3 equiv). The reaction tube was capped and removed from the glovebox. The reaction tube was placed in the dark, where it was stirred at rt for 8 h. Upon completion, the reaction mixture was diluted with hexanes and filtered through a pad of Celite. The filter cake was rinsed with hexanes and dichloromethane until the filtrate turned colorless. The filtrate was concentrated *in vacuo* to afford **3fa**·$(Fp^*)^+BF_4^-$ as an orange solid (210.0 mg, ca. 2:1 mixture of desired iron complex and $[Cp^*Fe(CO)_2(OH_2)]^+BF_4^-$).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52. (s, 1H), 7.28-7.17 (m, 2H), 6.88 (br, 1H), 6.18-5.98 (m, 1H), 4.31-3.98 (m, 1H), 3.77 (br, 3H), 3.71 (s, 3H), 3.23-2.86 (m, 2H), 2.86-2.13 (complex, 9H), 1.87 (s, 15H).

^{13}C NMR not collected due to product instability.

HRMS (ESI) calcd for $C_{31}H_{38}FeNO_6$ $[M–BF_4]^+$: 576.2030, found: 576.2038.

Synthesis of iron complex 1f·$(Fp^*)^+BF_4^-$



A reaction tube (13 mm × 100 mm, Fisherbrand, part # 14-959-35C) equipped with a magnetic stir bar was capped with a Teflon/silicone septum (Thermo/National part # C4015-66A) screw cap and flame dried under vacuum. The reaction tube was cooled under nitrogen and transferred into an argon-filled glovebox. In the glovebox, a mixture of $Cp^*Fe(CO)_2I$ (224.4 mg, 0.60 mmol, 1.0 equiv) and $AgBF_4$ (122.6 mg 0.63 mmol, 1.05 equiv) in dry toluene (1.5 mL) was added **1f** (112.1 mg, 0.80 mmol, 1.3 equiv). The reaction tube was capped and removed from the glovebox. The reaction tube was placed in the dark, where it was stirred at rt for 8 h. Upon completion, the reaction mixture was diluted with hexanes and filtered through a pad of Celite. The filter cake was rinsed with hexanes and dichloromethane until the filtrate turned colorless. The filtrate was concentrated *in vacuo* to afford **1f**·$(Fp^*)^+BF_4^-$ as a red oil (145.0 mg, ca. 3:1 mixture of desired iron complex and $[Cp^*Fe(CO)_2(OH_2)]^+BF_4^-$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.92-5.88 (m, 1H), 3.68 (s, 3H), 2.58-2.56 (m, 2H), 2.52-2.47 (m, 2H), 2.38 (t, J = 7.2 Hz, 2H), 1.90 (s+m, 17H).

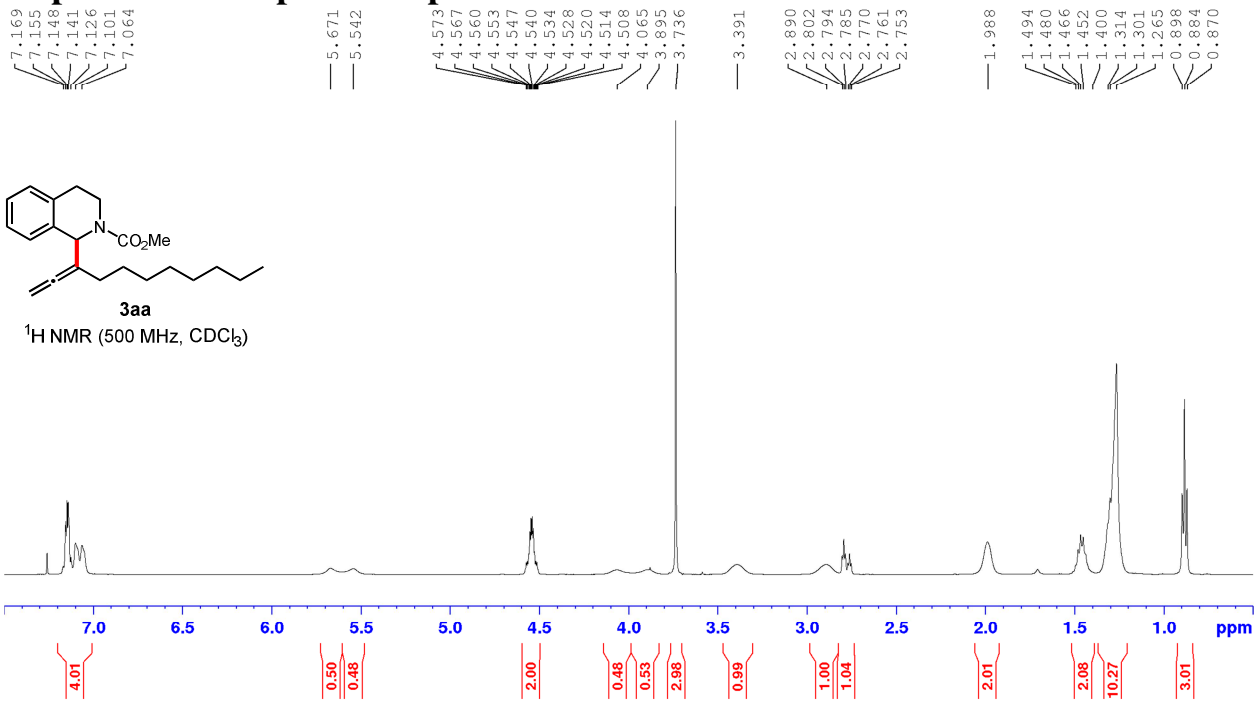
^{13}C NMR (125 MHz, $CDCl_3$) δ 211.0, 173.8, 157.7, 118.7, 104.3, 51.9, 35.5, 33.3, 24.3, 21.8, 9.3.

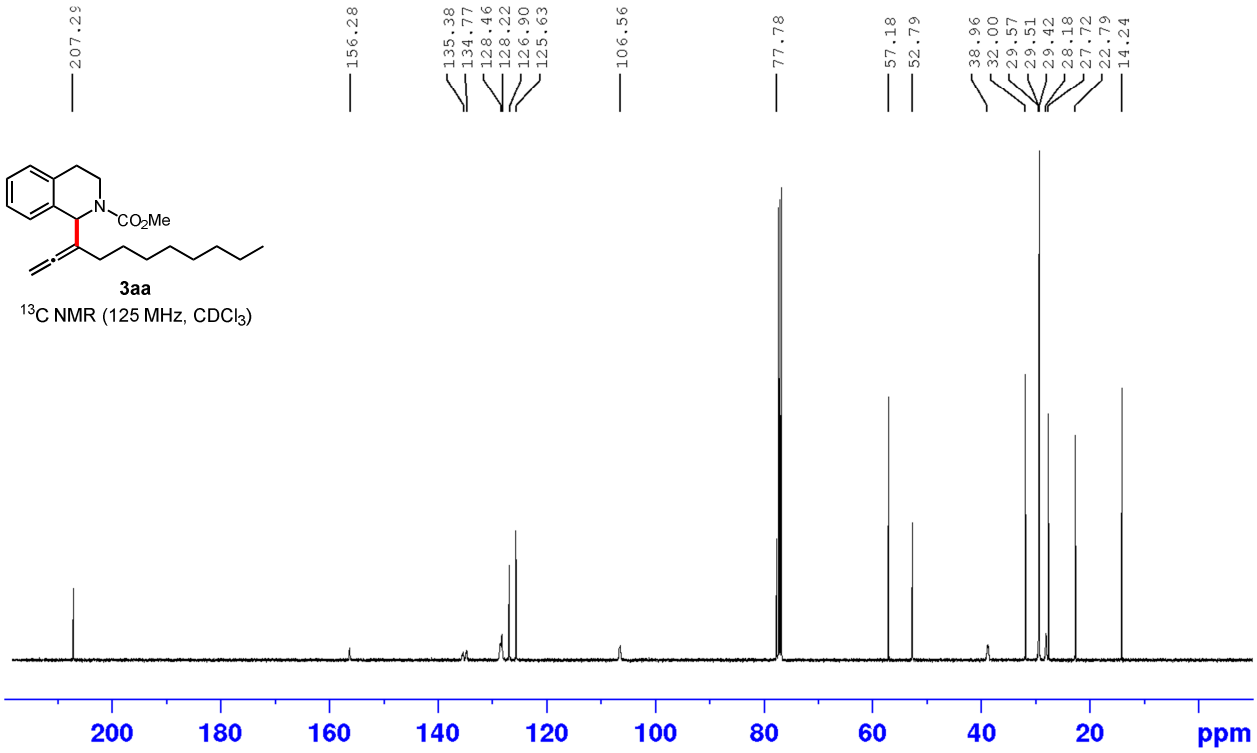
HRMS (ESI) calcd for $C_{20}H_{27}FeO_4$ $[M–BF_4]^+$: 387.1259, found: 387.1245.

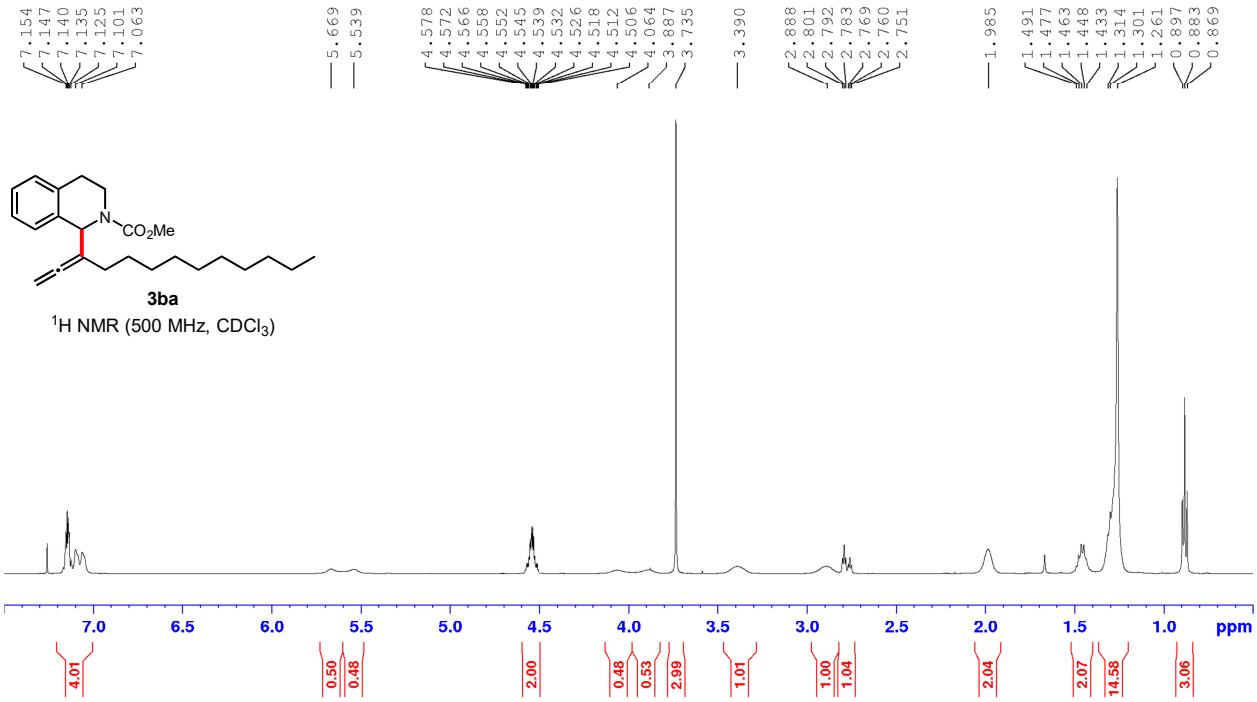
Notes and references

1. The product was isolated with corresponding iodide (detected by LC-MS; *m/z* = 476) as a 5% impurity. The allene material **3ga** (containing an aryl bromide) was contaminated with aryl iodide as a result of its synthesis via the Crabbé reaction.
2. Y. Nagashima, K. Sasaki, T. Suto, T. Sato and N. Chida, *Chem. - Asian J.,* 2018, **13**, 1024.
3. Y. Wang, S. G. Scrivener, X.-D. Zuo, R. Wang, P. N. Palermo, E. Murphy, A. C. Durham and Y.-M. Wang, *J. Am. Chem. Soc.,* 2021, **143**, 14998.
4. Y. Wang, J. Zhu, R. Guo, H. Lindberg and Y.-M. Wang, *Chem. Sci.,* 2020, **11**, 12316.

Copies of NMR spectra of products

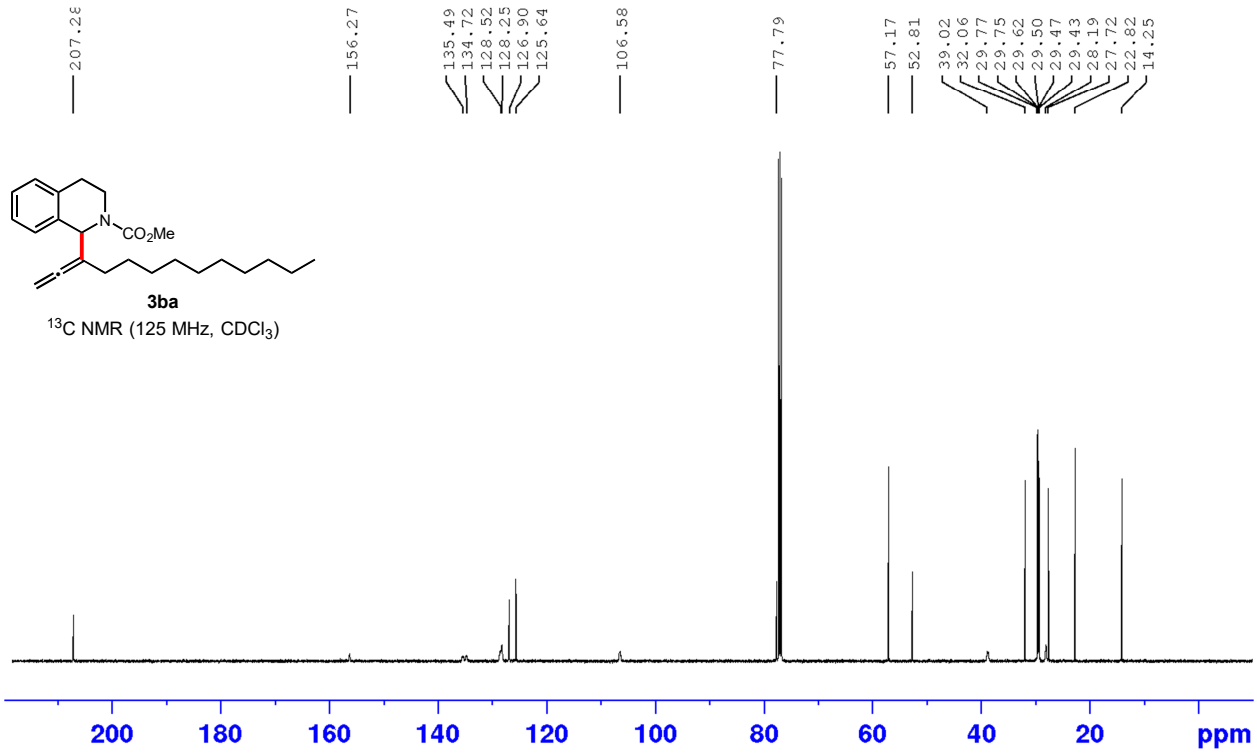






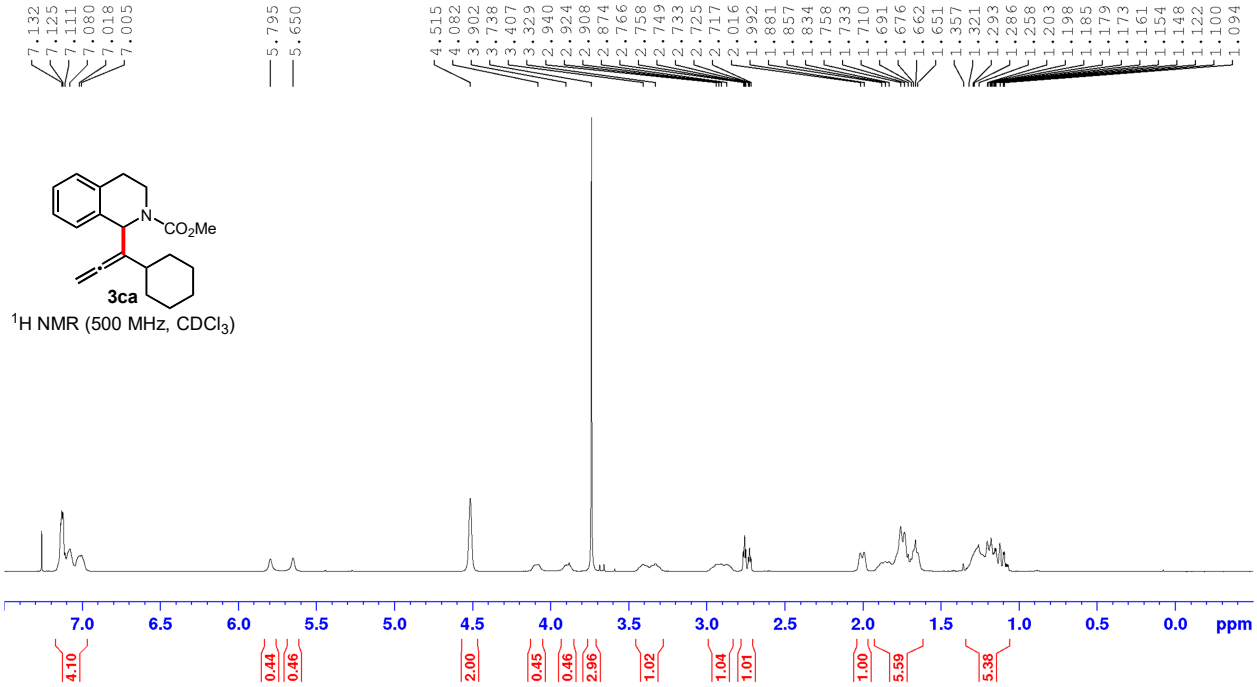
3ba

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



3ba

^{13}C NMR (125 MHz, $CDCl_3$)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5.650
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3.407
3.329
2.940
2.924
2.908
2.874
2.766
2.758
2.749
2.733
2.725
2.717
2.016
1.992
1.881
1.857
1.834
1.758
1.733
1.710
1.691
1.676
1.662
1.651
1.357
1.321
1.293
1.286
1.258
1.203
1.198
1.185
1.179
1.173
1.161
1.154
1.148
1.122
1.100
1.094
N
CO2Me
3ca
1H NMR (500 MHz, CDCl3)
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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0.46
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1.04
1.01
1.00
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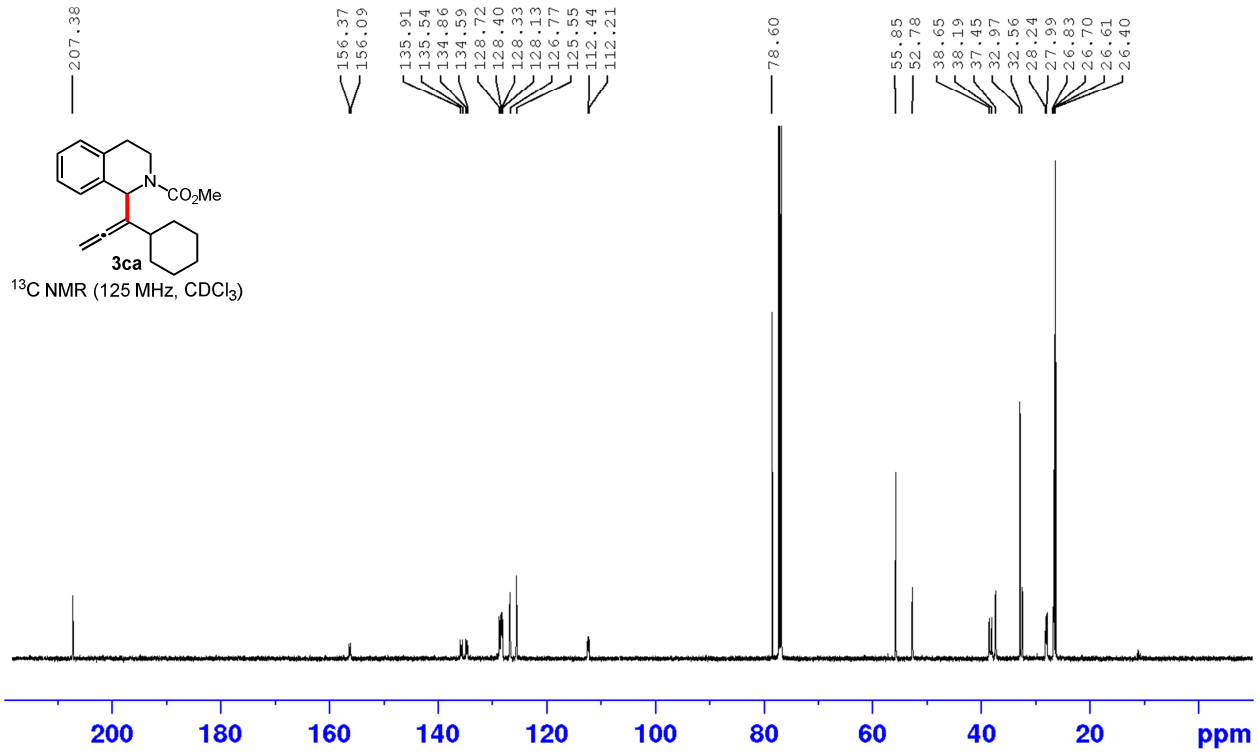
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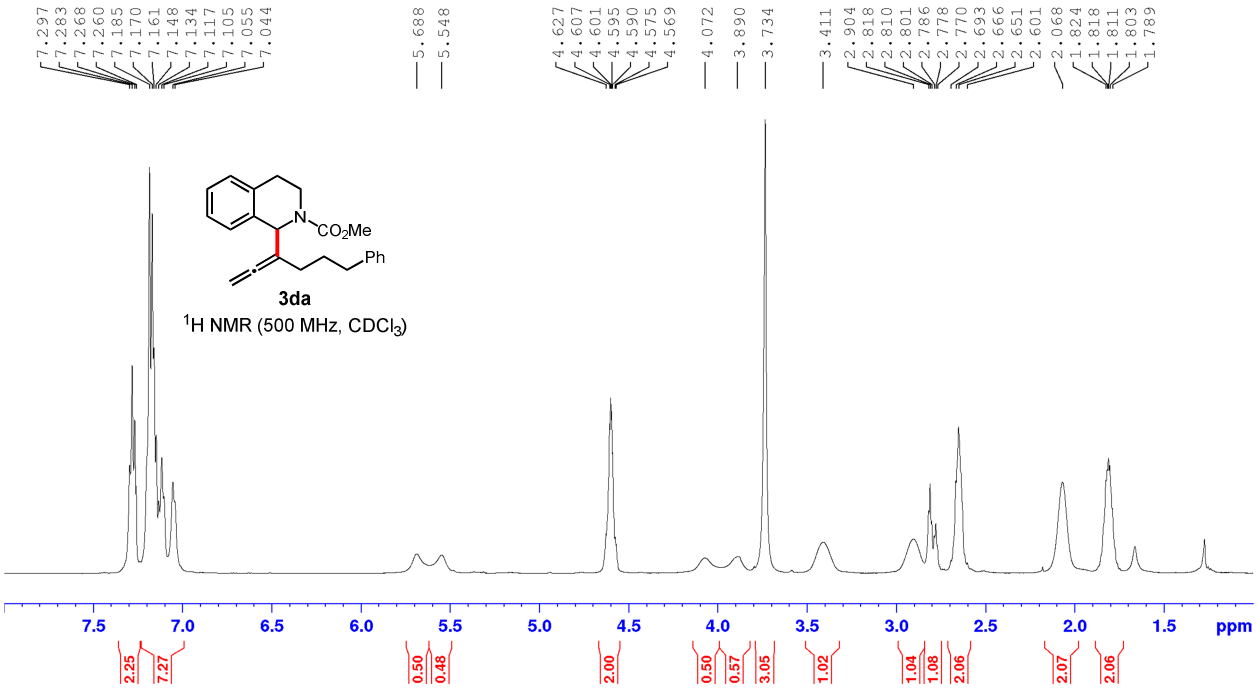
128.13
126.77
125.55
112.44
112.21
78.60
55.85
52.78
38.65
38.19
37.45
32.97
32.56
28.24
27.99
26.83
26.70
26.61
26.40
N
CO2Me
3ca
13C NMR (125 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
ppm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5.548
4.627
4.607
4.601
4.595
4.590
4.575
4.569
4.072
3.890
3.734
3.411
2.904
2.818
2.810
2.801
2.786
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2.770
2.693
2.666
2.651
2.601
2.068
1.824
1.818
1.811
1.803
1.789
N
CO2Me
Ph
3da
1H NMR (500 MHz, CDCl3)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
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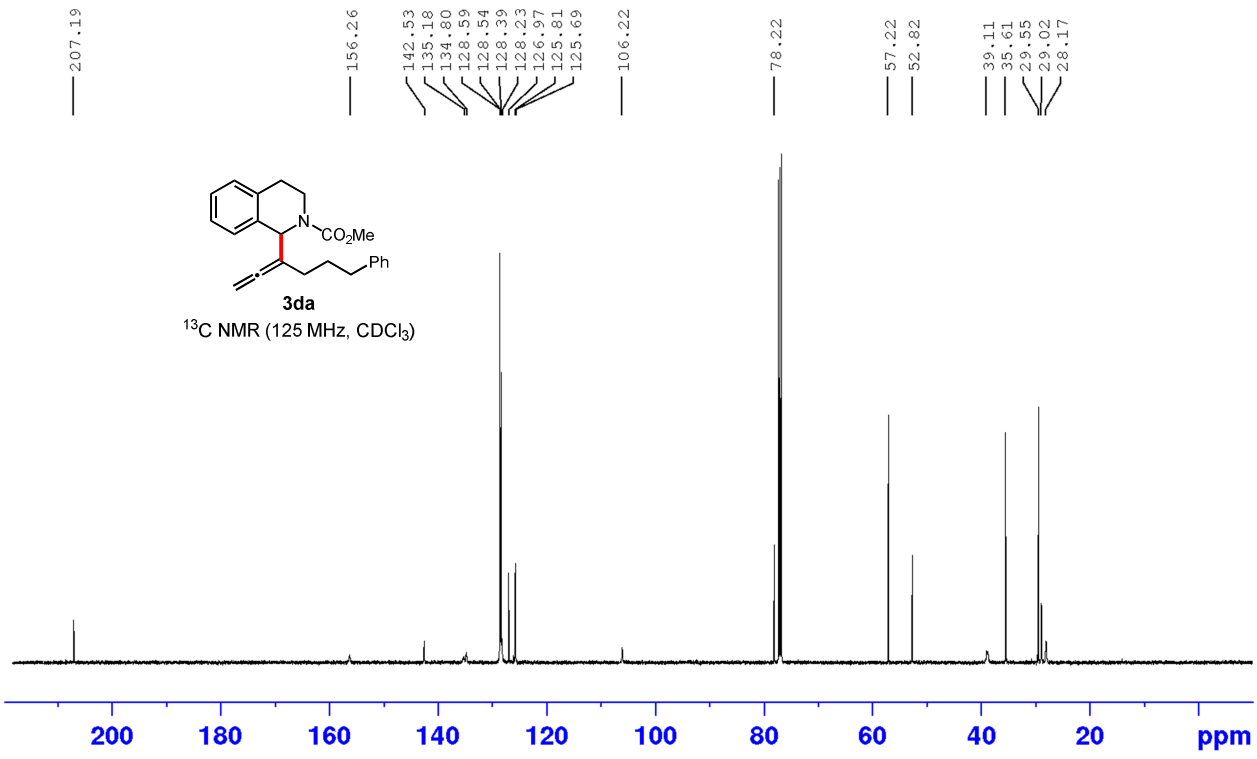
1.04
1.08
2.06
2.07
2.06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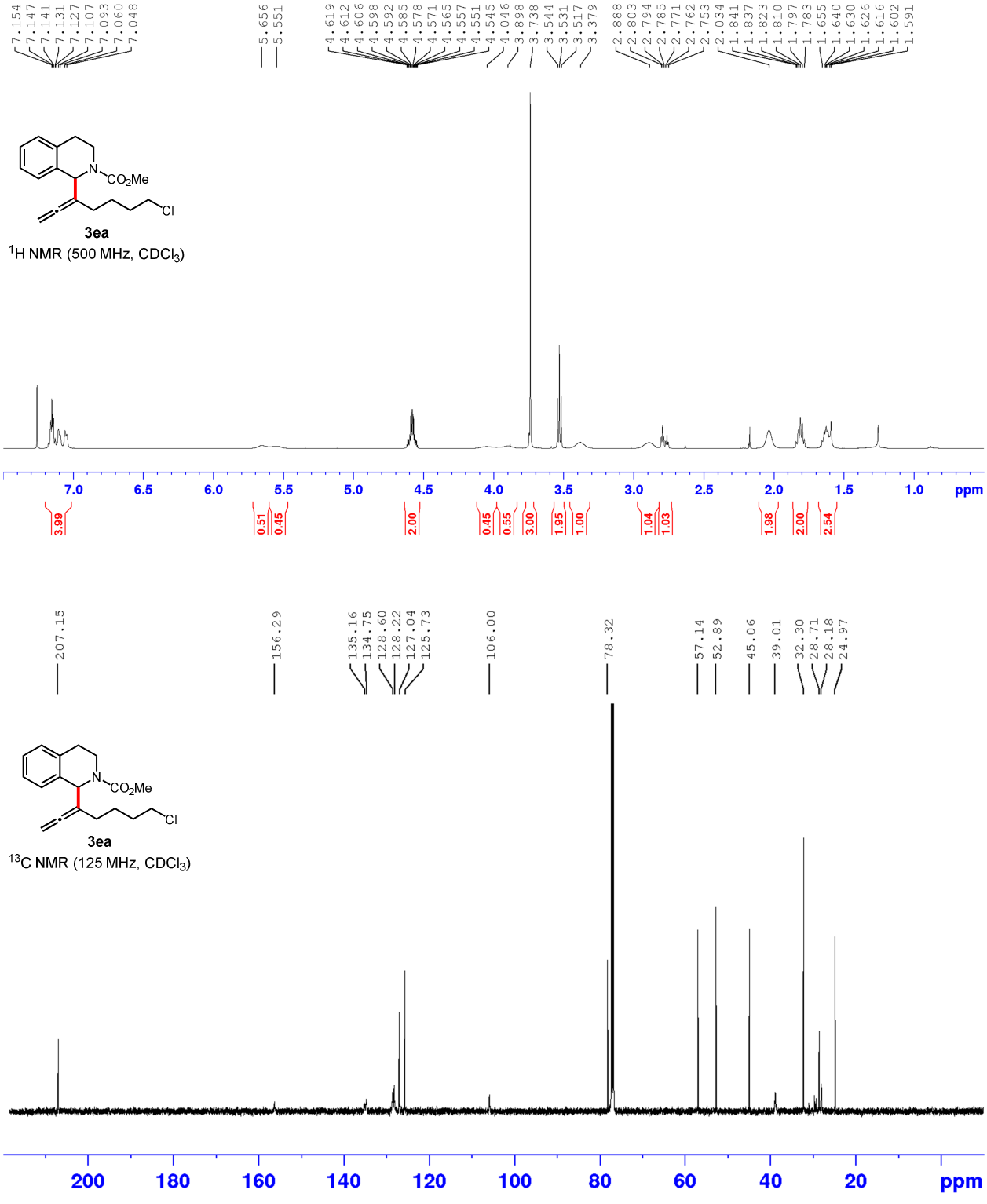
106.22
78.22
57.22
52.82
39.11
35.61
29.55
29.02
28.17
N
CO2Me
Ph
3da
13C NMR (125 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
ppm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4.606
4.598
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4.585
4.578
4.571
4.565
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4.545
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3.898
3.738
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3.531
3.517
3.379
2.888
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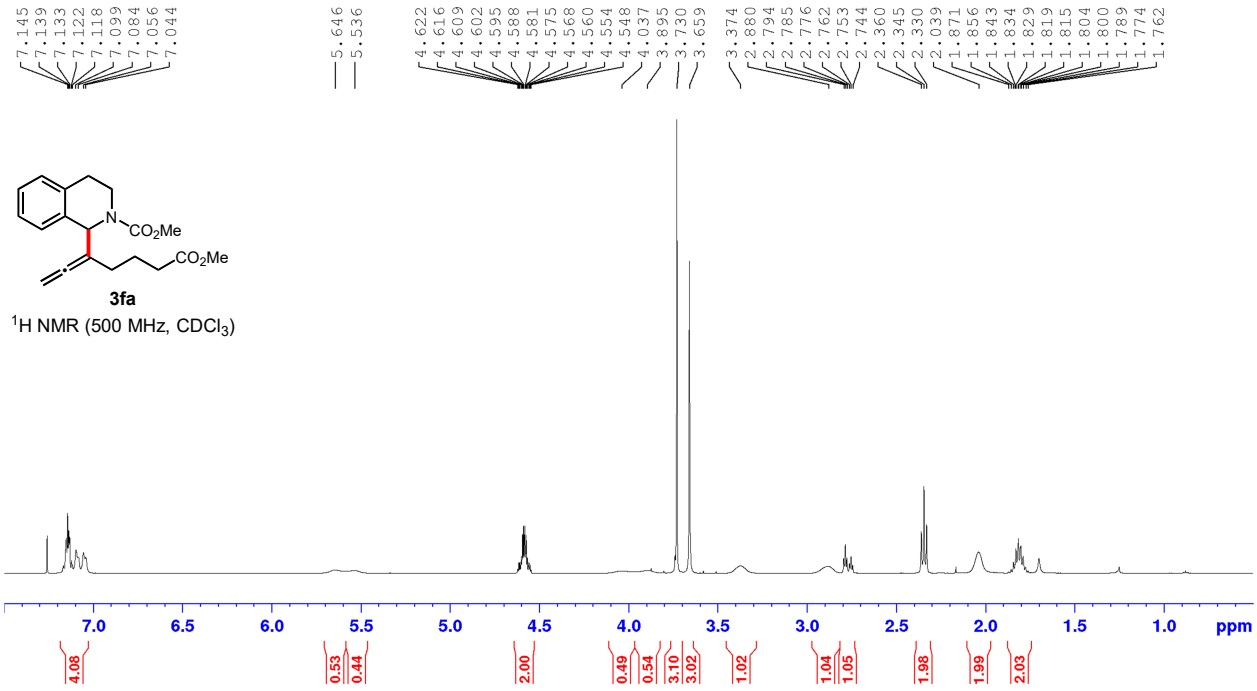
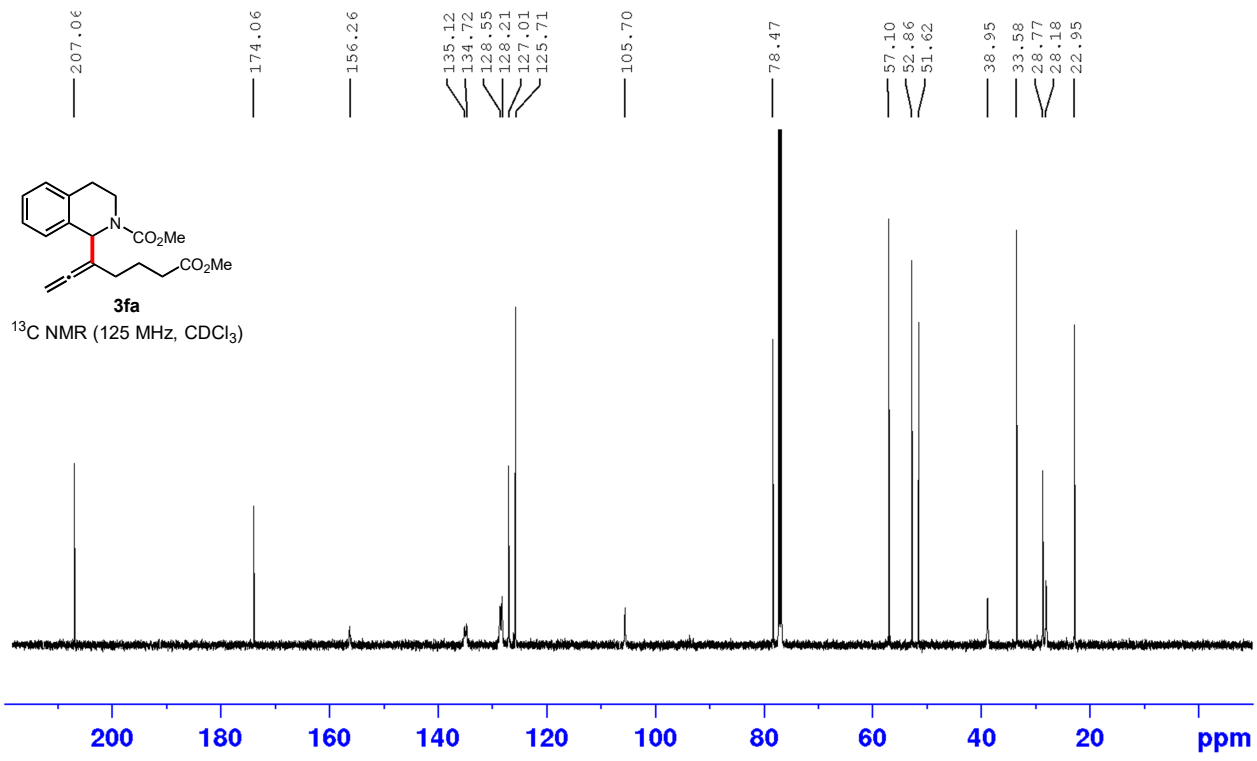
1.640
1.630
1.626
1.616
1.602
1.591
N
CO2Me
Cl
3ea
1H NMR (500 MHz, CDCl3)
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
3.99
0.51
0.45
2.00
0.45
0.55
3.00
1.95
1.00
1.04
1.03
1.98
2.00
2.54
207.15
156.29
135.16
134.75
128.60
128.22
127.04
125.73
106.00
78.32
57.14
52.89
45.06
39.01
32.30
28.71
28.18
24.97
N
CO2Me
Cl
3ea
13C NMR (125 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
ppm



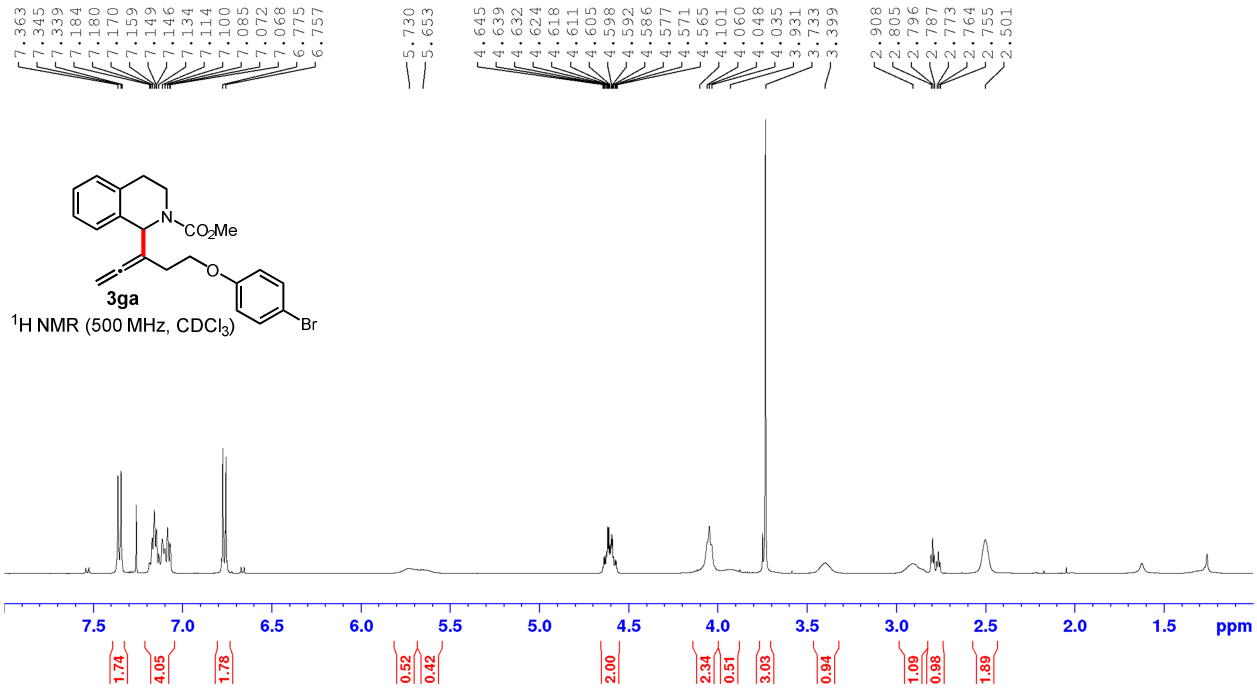
3fa

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



3fa

^{13}C NMR (125 MHz, $CDCl_3$)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7.068
6.775
6.757
5.730
5.653
4.645
4.639
4.632
4.624
4.618
4.611
4.605
4.598
4.592
4.586
4.577
4.571
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4.101
4.060
4.048
4.035
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2.787
2.773
2.764
2.755
2.501
N
CO2Me
O
Br
3ga
1H NMR (500 MHz, CDCl3)
7.5
7.0
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4.5
4.0
3.5
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ppm
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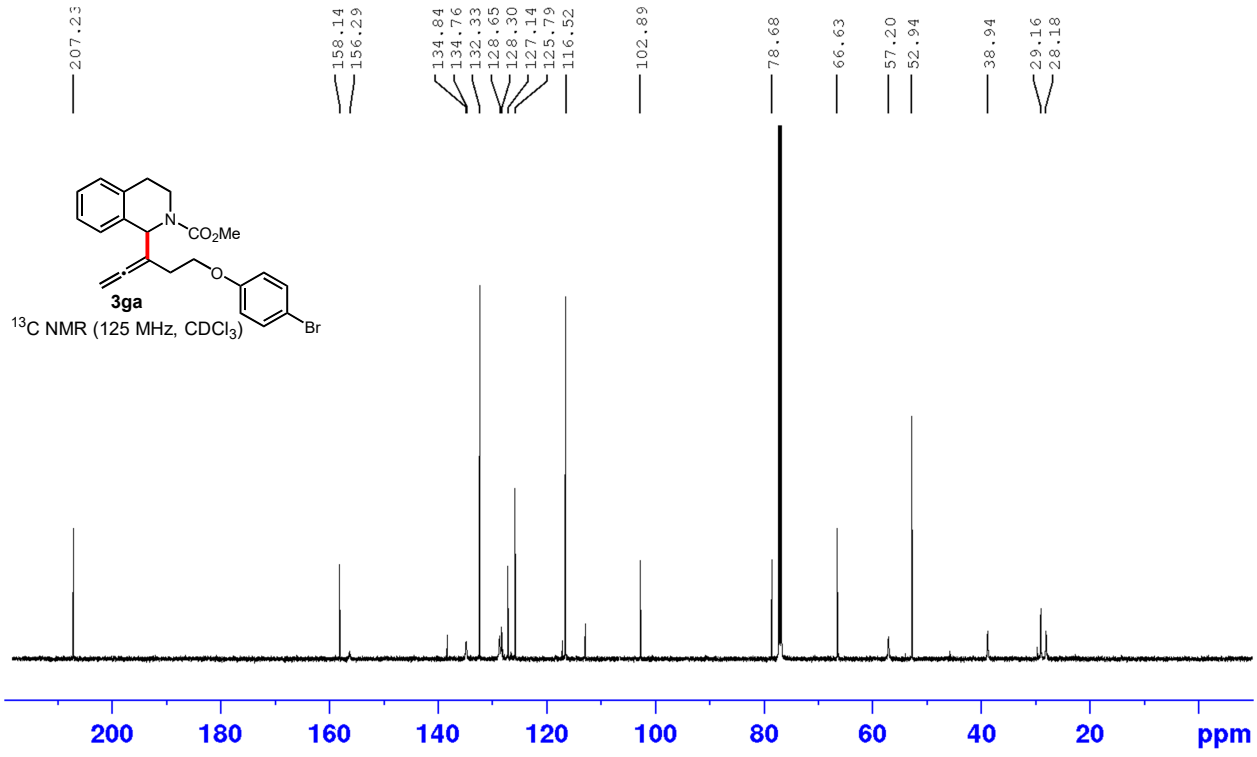
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66.63
57.20
52.94
38.94
29.16
28.18
N
CO2Me
O
Br
3ga
13C NMR (125 MHz, CDCl3)
200
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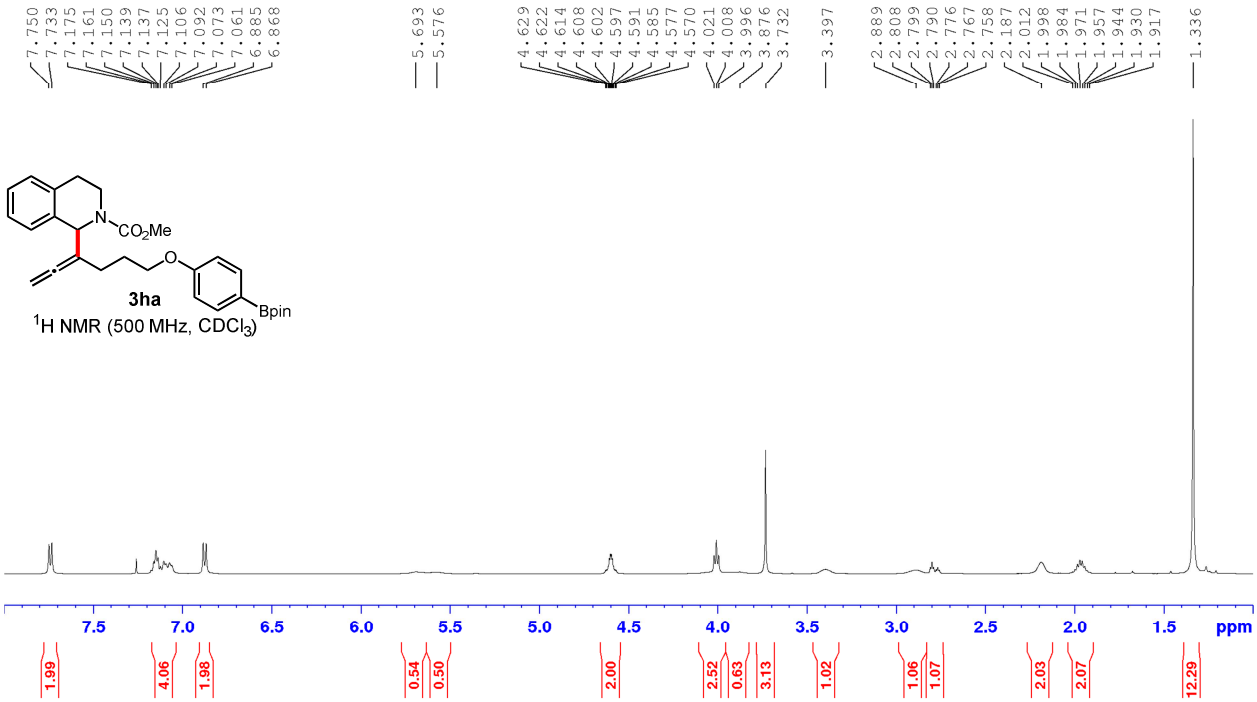
140
120
100
80
60
40
20
ppm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6.868
5.693
5.576
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4.614
4.608
4.602
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4.591
4.585
4.577
4.570
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4.008
3.996
3.876
3.732
3.397
2.889
2.808
2.799
2.790
2.776
2.767
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2.187
2.012
1.998
1.984
1.971
1.957
1.944
1.930
1.917
1.336
CO2Me
O
3ha
Bpin
1H NMR (500 MHz, CDCl3)
7.5
7.0
6.5
6.0
5.5
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4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
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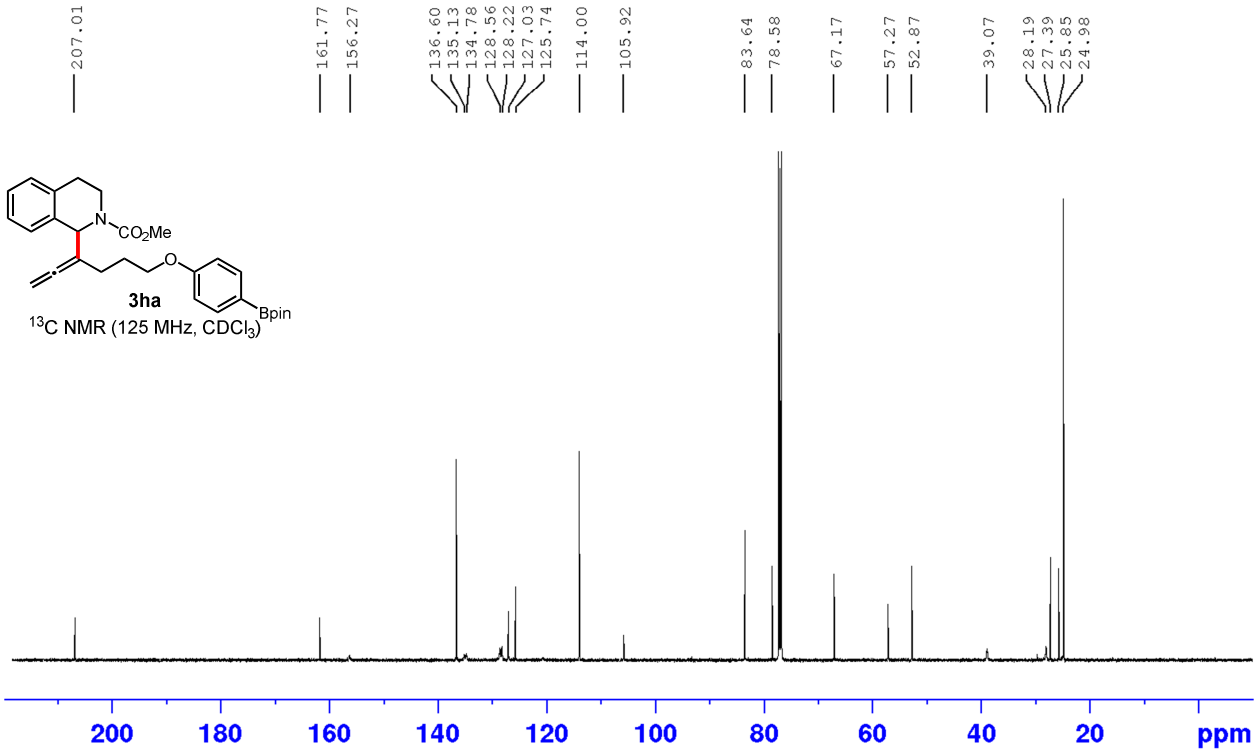
2.03
2.07
12.29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78.58
67.17
57.27
52.87
39.07
28.19
27.39
25.85
24.98
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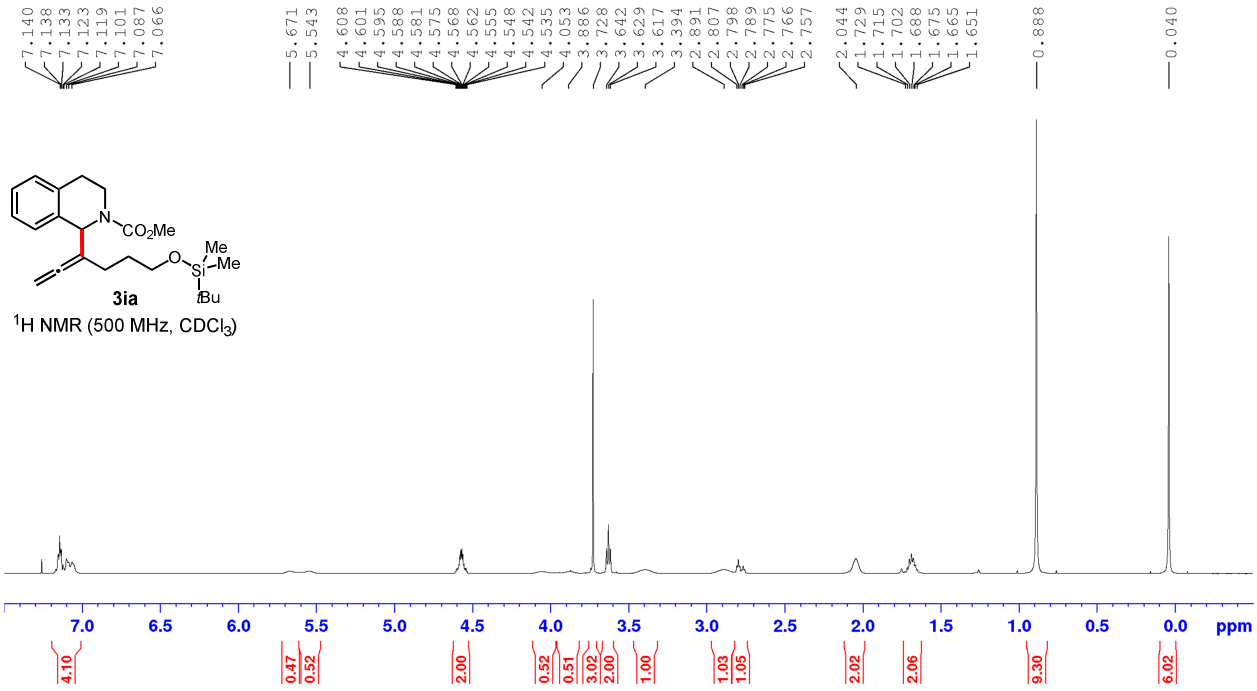
80
60
40
20
ppm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1.729
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1.675
1.665
1.651
0.888
0.040
N
CO2Me
O
Si
Me
Me
tBu
3ia
1H NMR (500 MHz, CDCl3)
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
4.10
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1.03
1.05
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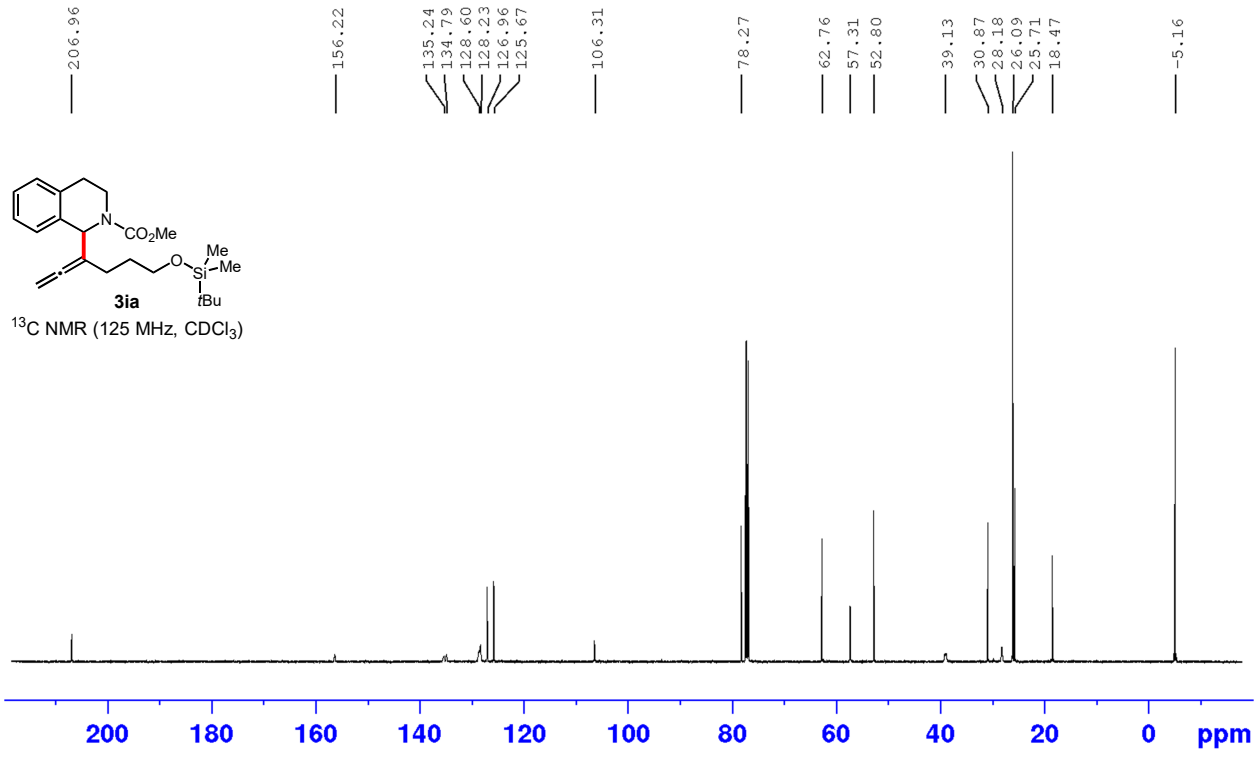
9.30
6.02


206.96
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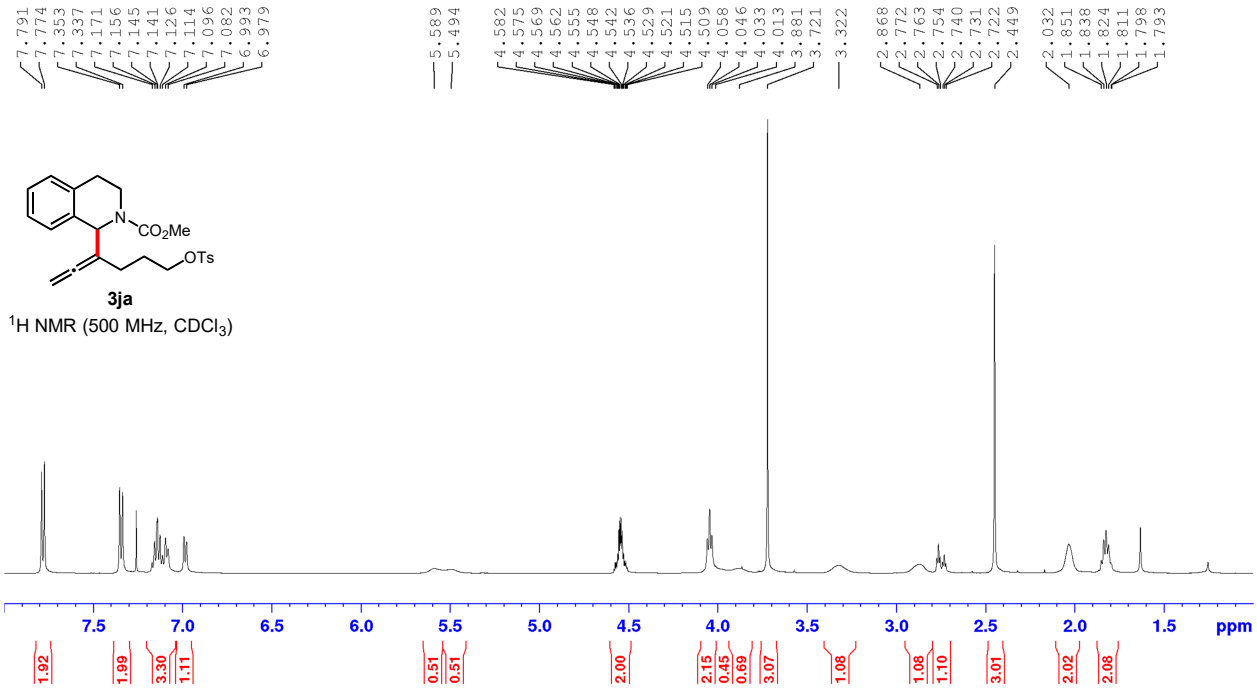
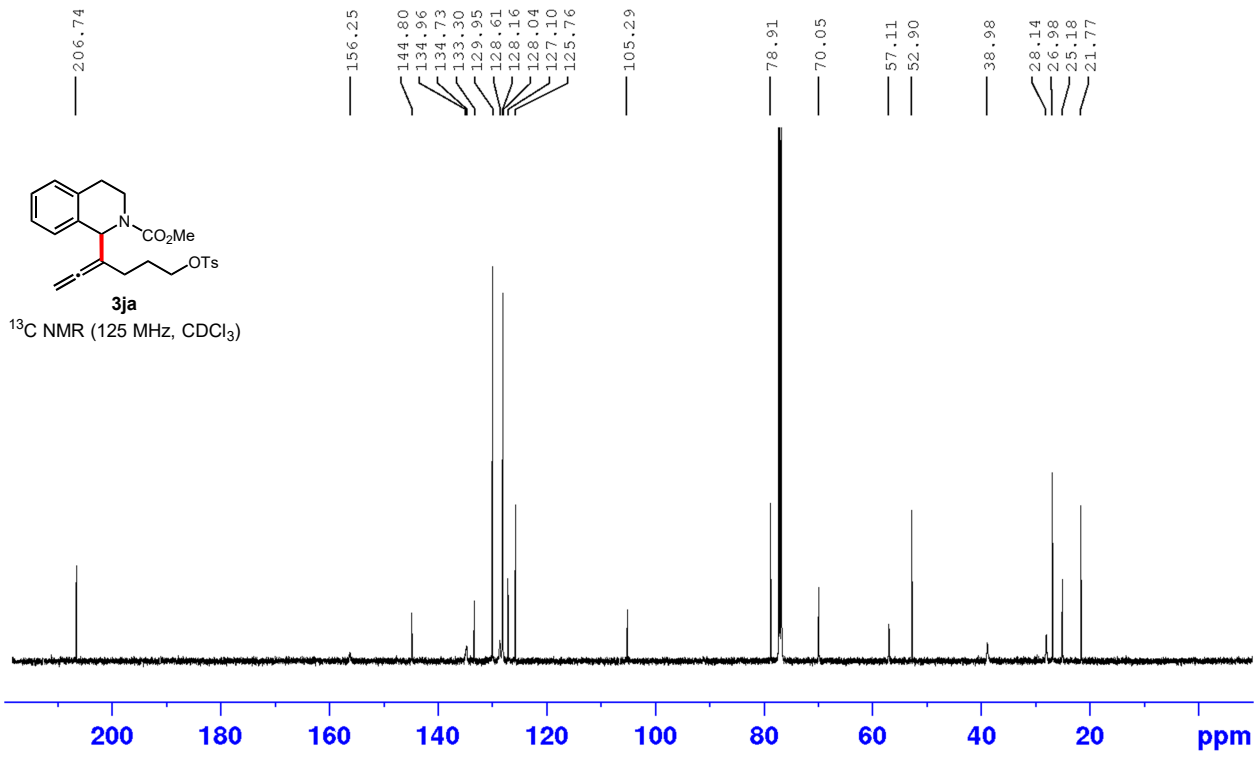
128.23
126.96
125.67
106.31
78.27
62.76
57.31
52.80
39.13
30.87
28.18
26.09
25.71
18.47
-5.16
N
CO2Me
O
Si
Me
Me
tBu
3ia
13C NMR (125 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0
ppm



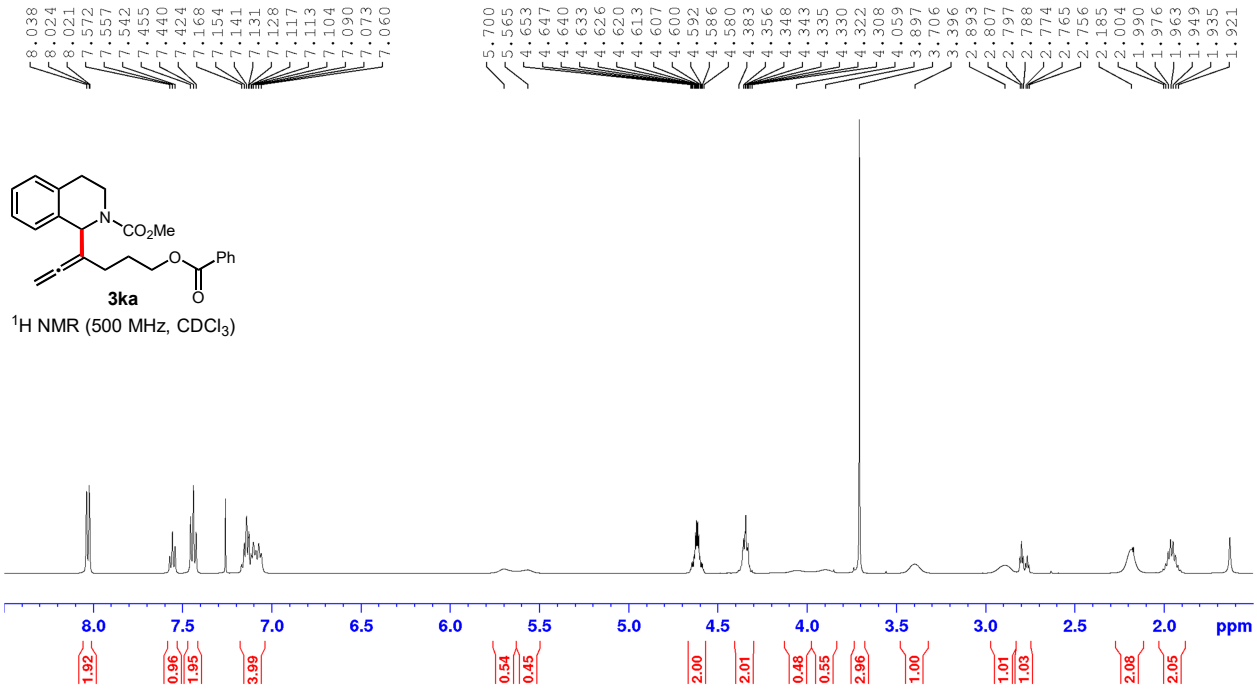
3ja

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

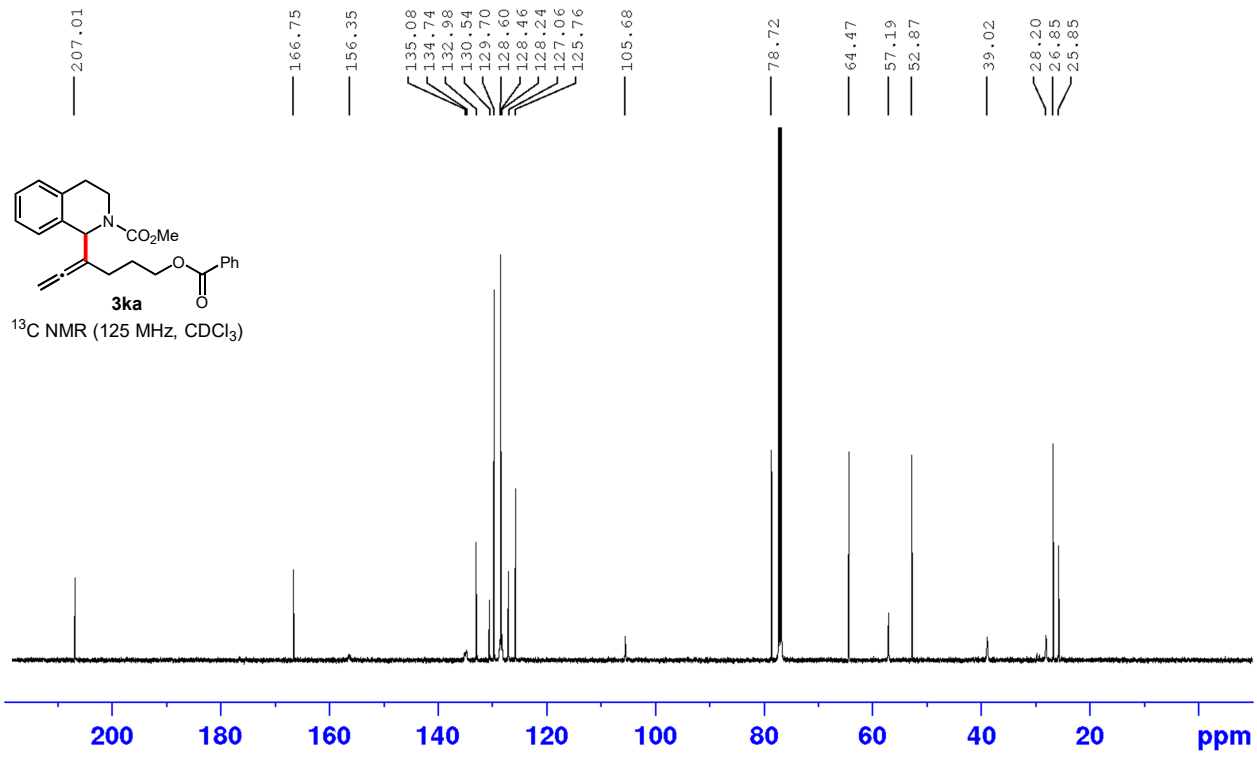


3ja

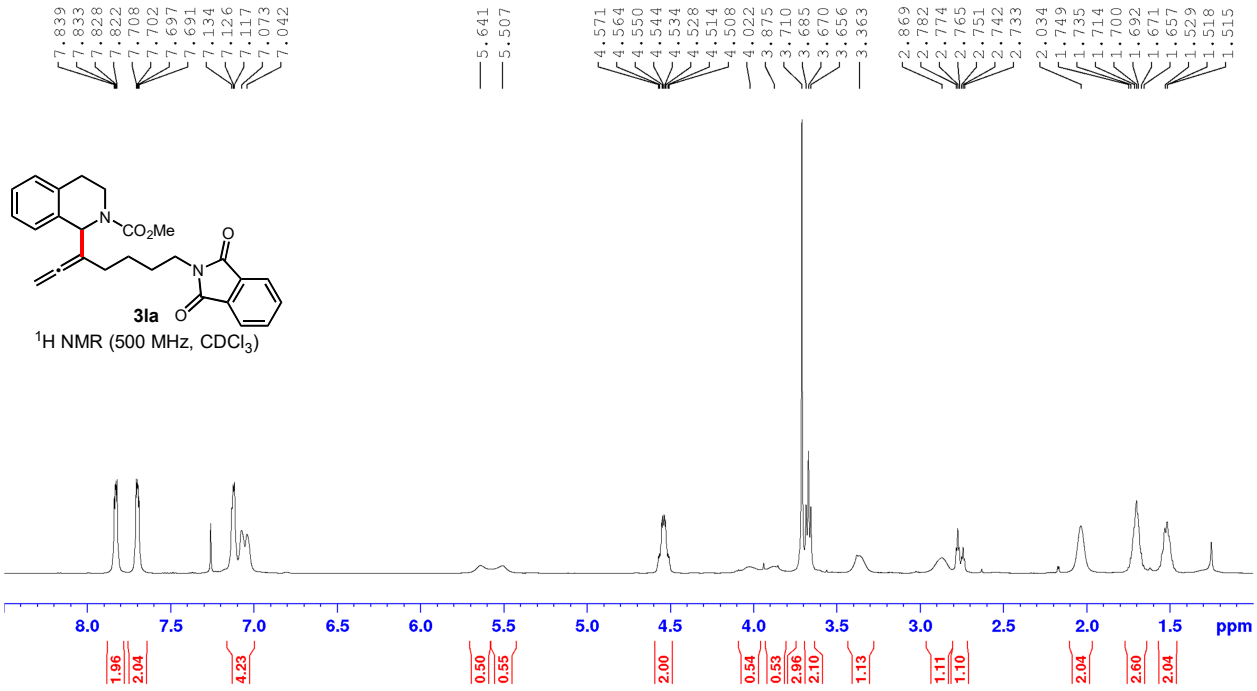
^{13}C NMR (125 MHz, $CDCl_3$)



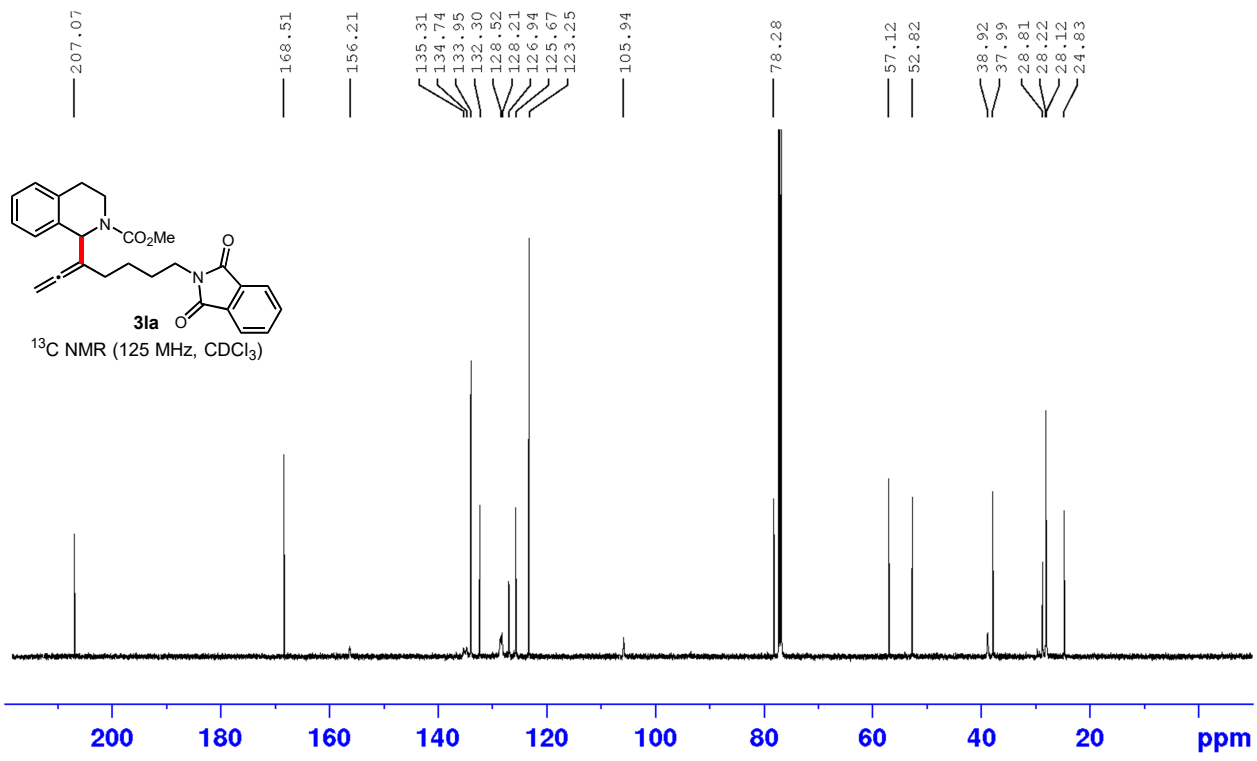
^{1}H NMR (500 MHz, $CDCl_3$)



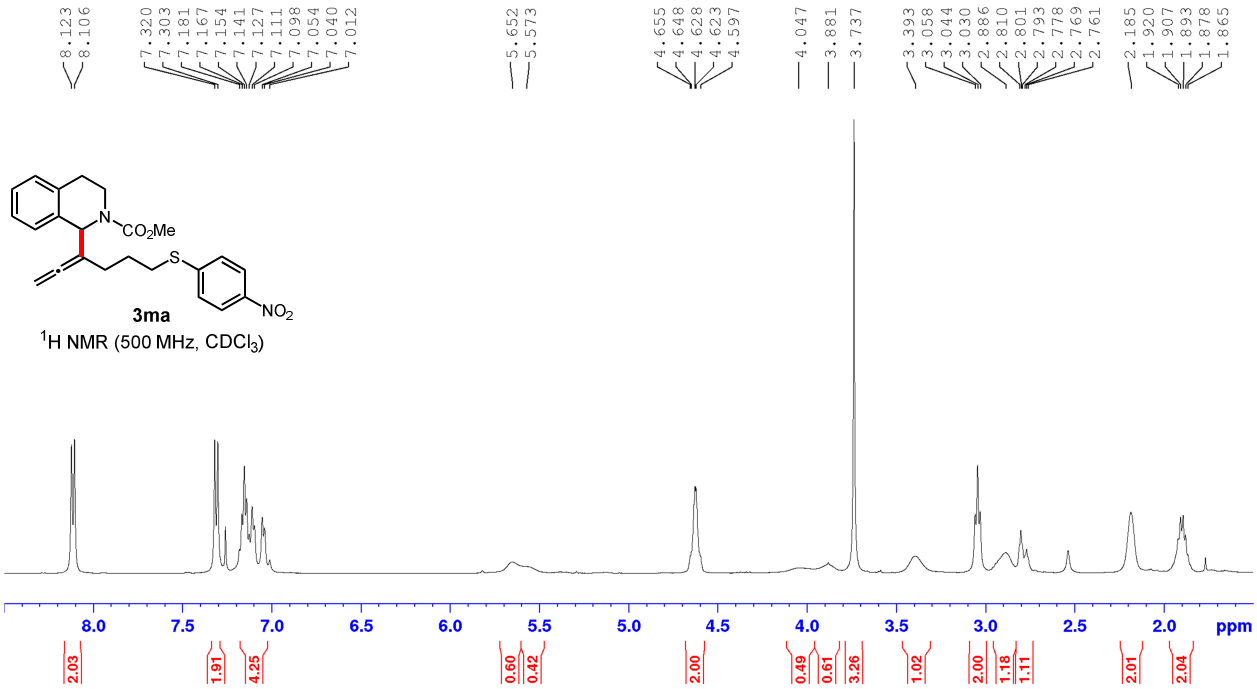
^{13}C NMR (125 MHz, $CDCl_3$)

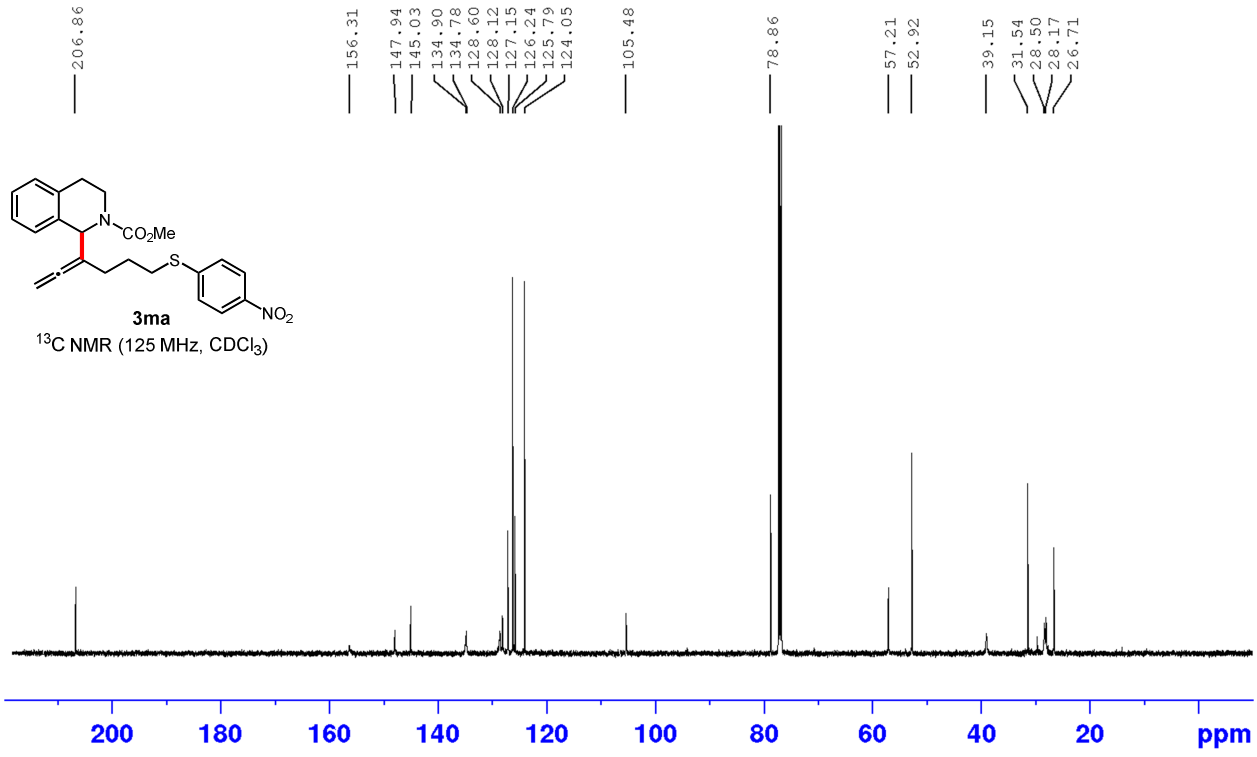


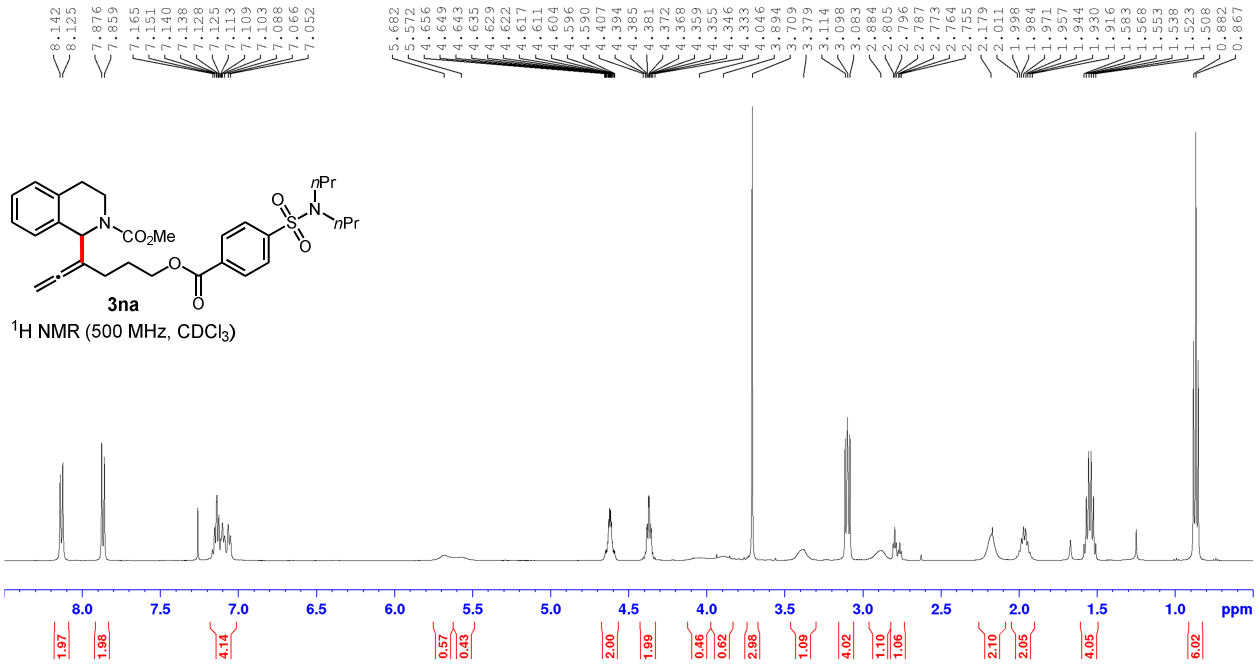
^{1}H NMR (500 MHz, $CDCl_3$)



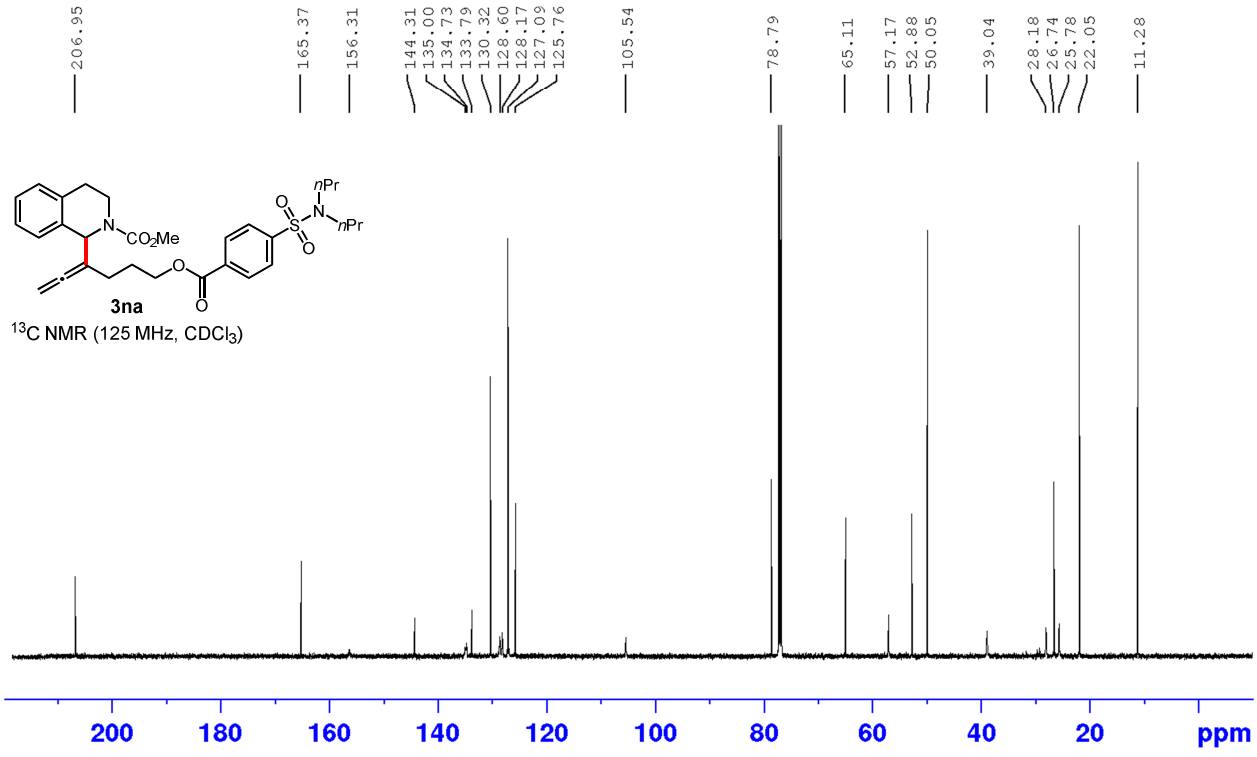
^{13}C NMR (125 MHz, $CDCl_3$)


8.123
8.106
7.320
7.303
7.181
7.167
7.154
7.141
7.127
7.111
7.098
7.054
7.040
7.012
5.652
5.573
4.655
4.648
4.628
4.623
4.597
4.047
3.881
3.737
3.393
3.058
3.044
3.030
2.886
2.810
2.801
2.793
2.778
2.769
2.761
2.185
1.920
1.907
1.893
1.878
1.865
CO2Me
S
NO2
3ma
1H NMR (500 MHz, CDCl3)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
2.03
1.91
4.25
0.60
0.42
2.00
0.49
0.61
3.26
1.02
2.00
1.18
1.11
2.01
2.04

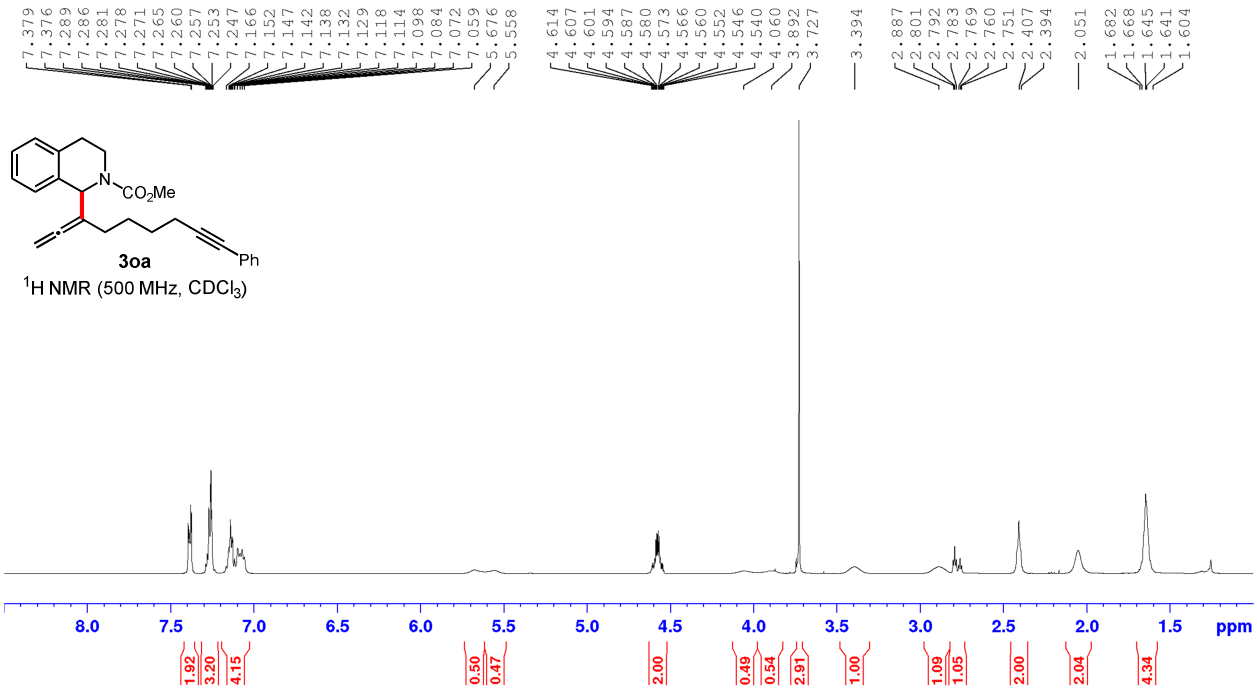

206.86
156.31
147.94
145.03
134.90
134.78
128.60
128.12
127.15
126.24
125.79
124.05
105.48
78.86
57.21
52.92
39.15
31.54
28.50
28.17
26.71
CO2Me
S
NO2
3ma
13C NMR (125 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
ppm

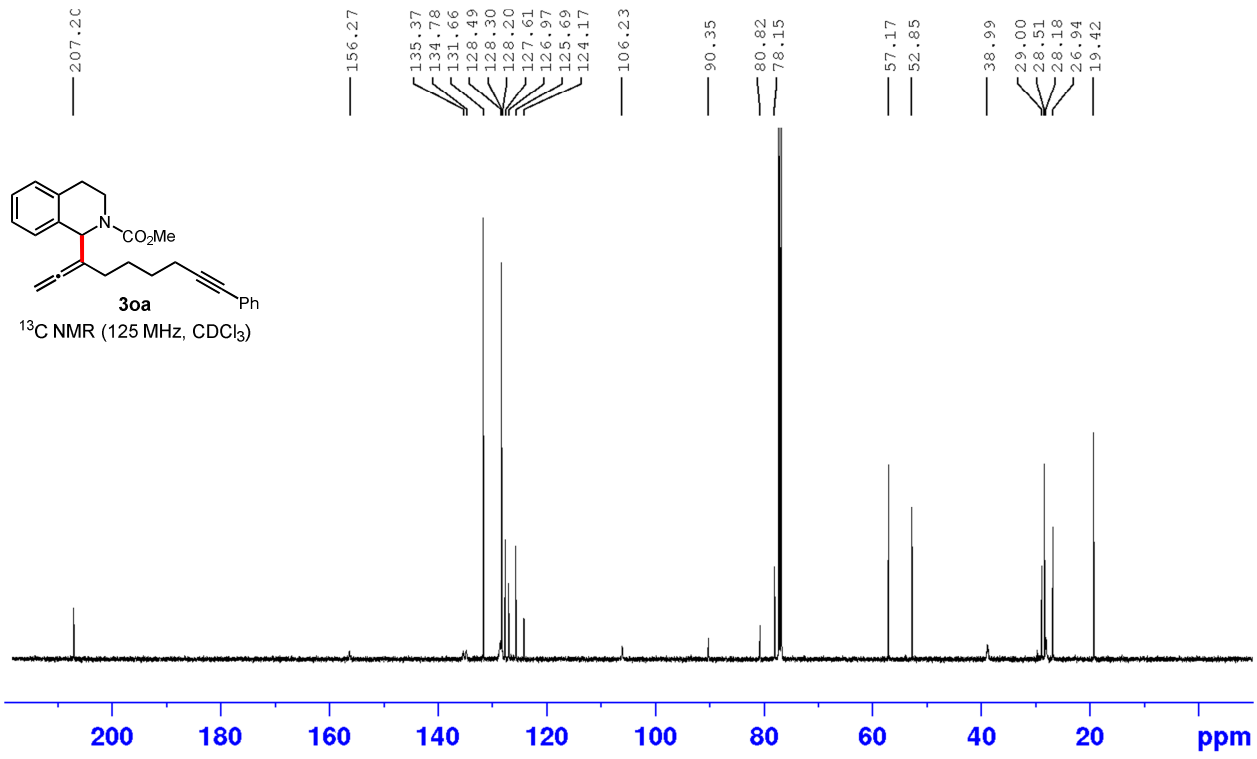


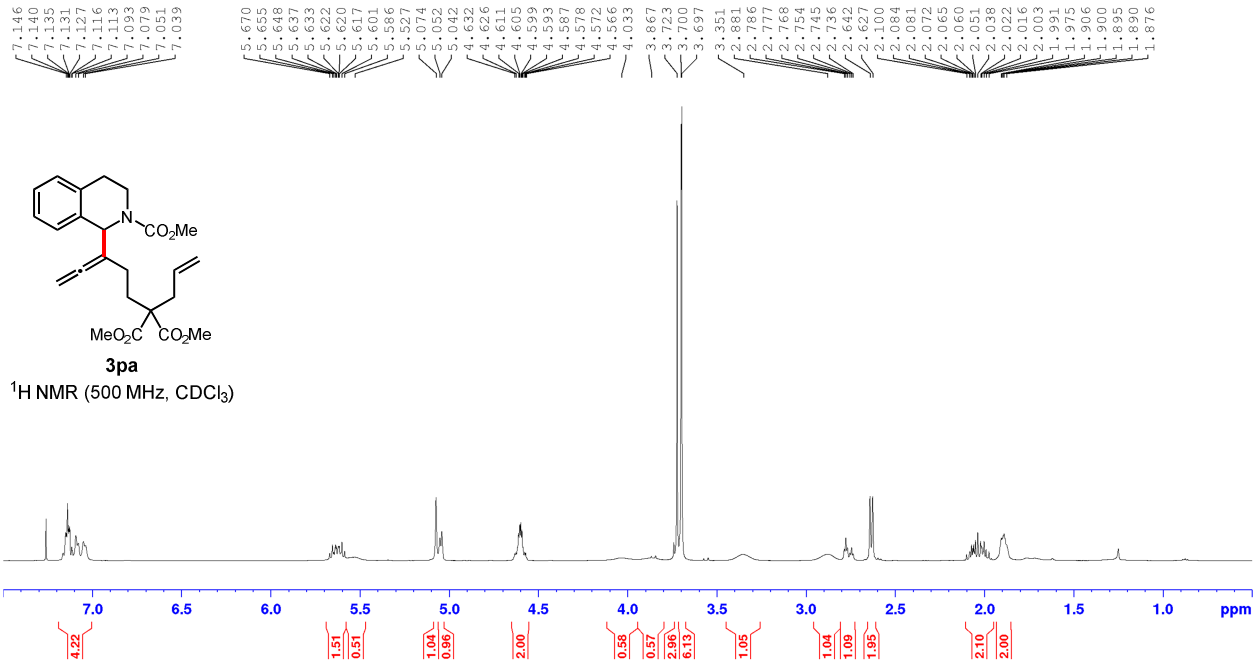
^{1}H NMR (500 MHz, $CDCl_3$)

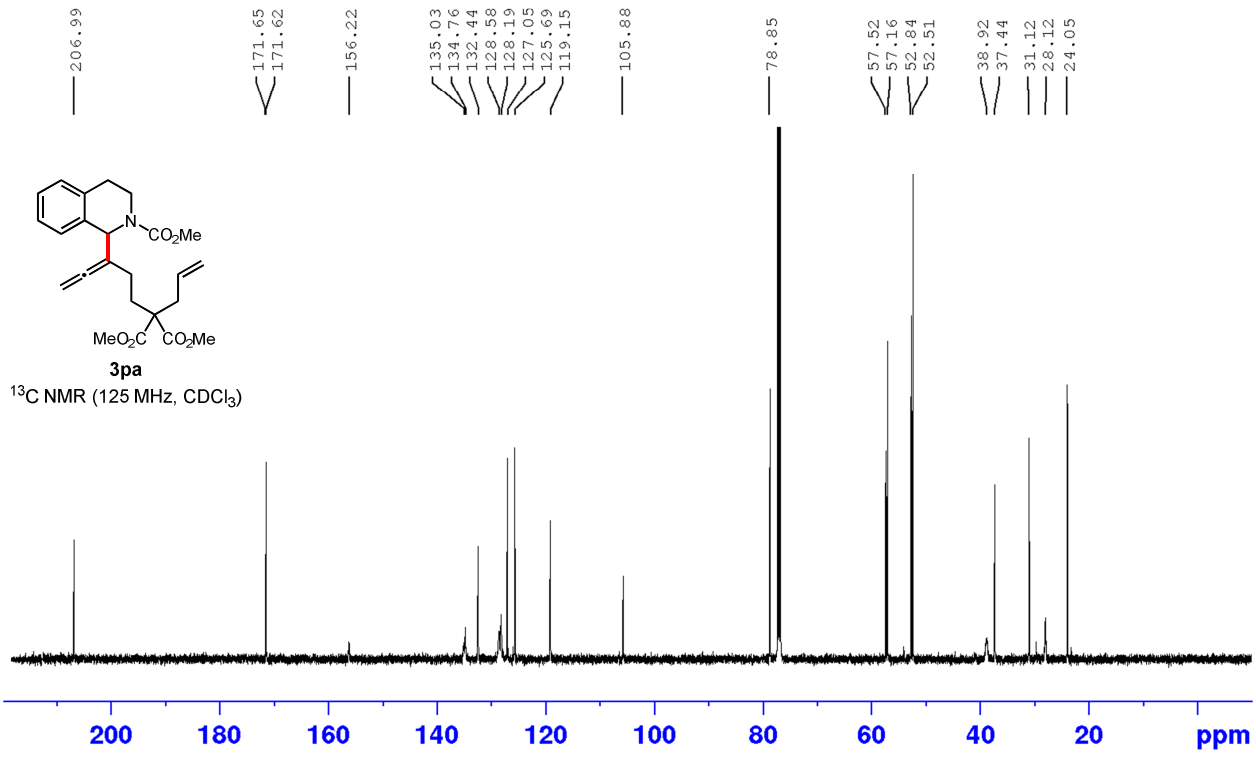


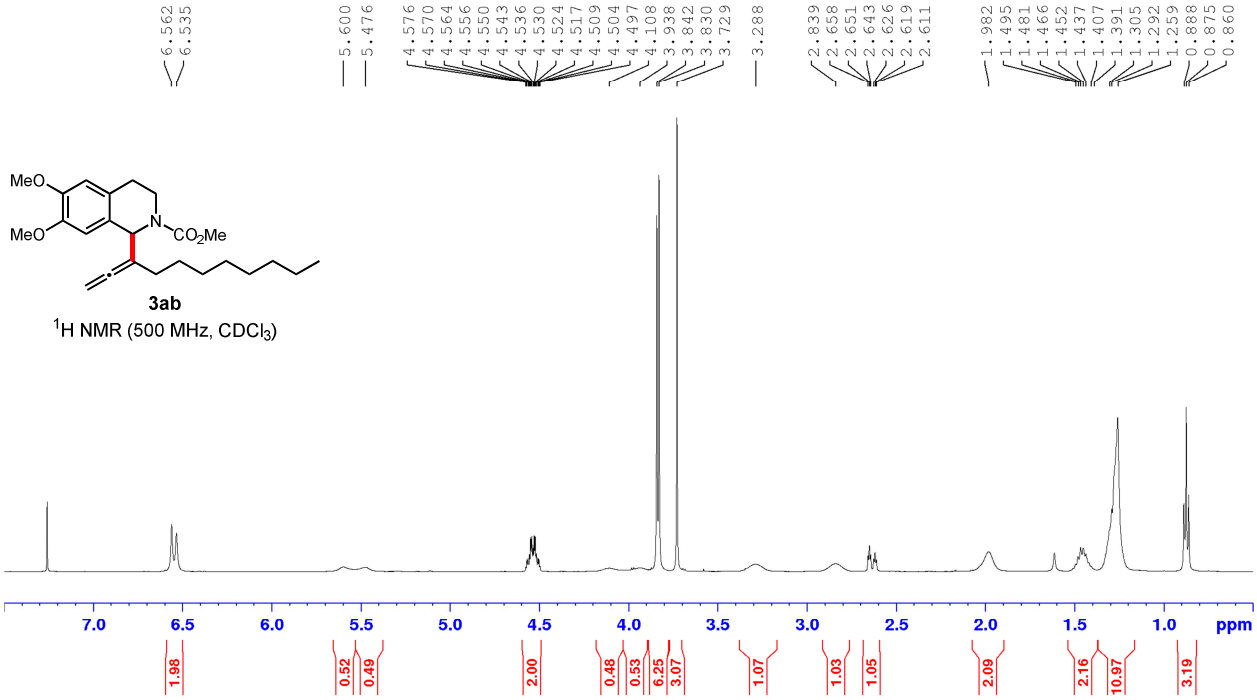
^{13}C NMR (125 MHz, $CDCl_3$)


7.379
7.376
7.289
7.286
7.281
7.278
7.271
7.265
7.260
7.257
7.253
7.247
7.166
7.152
7.147
7.142
7.138
7.132
7.129
7.118
7.114
7.098
7.084
7.072
7.059
5.676
5.558
4.614
4.607
4.601
4.594
4.587
4.580
4.573
4.566
4.560
4.552
4.546
4.540
4.060
3.892
3.727
3.394
2.887
2.801
2.792
2.783
2.769
2.760
2.751
2.407
2.394
2.051
1.682
1.668
1.645
1.641
1.604
N
CO2Me
Ph
3oa
1H NMR (500 MHz, CDCl3)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
1.92
3.20
4.15
0.50
0.47
2.00
0.49
0.54
2.91
1.00
1.09
1.05
2.00
2.04
4.34


207.20
156.27
135.37
134.78
131.66
128.49
128.30
128.20
127.61
126.97
125.69
124.17
106.23
90.35
80.82
78.15
57.17
52.85
38.99
29.00
28.51
28.18
26.94
19.42
N
CO2Me
Ph
3oa
13C NMR (125 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
ppm

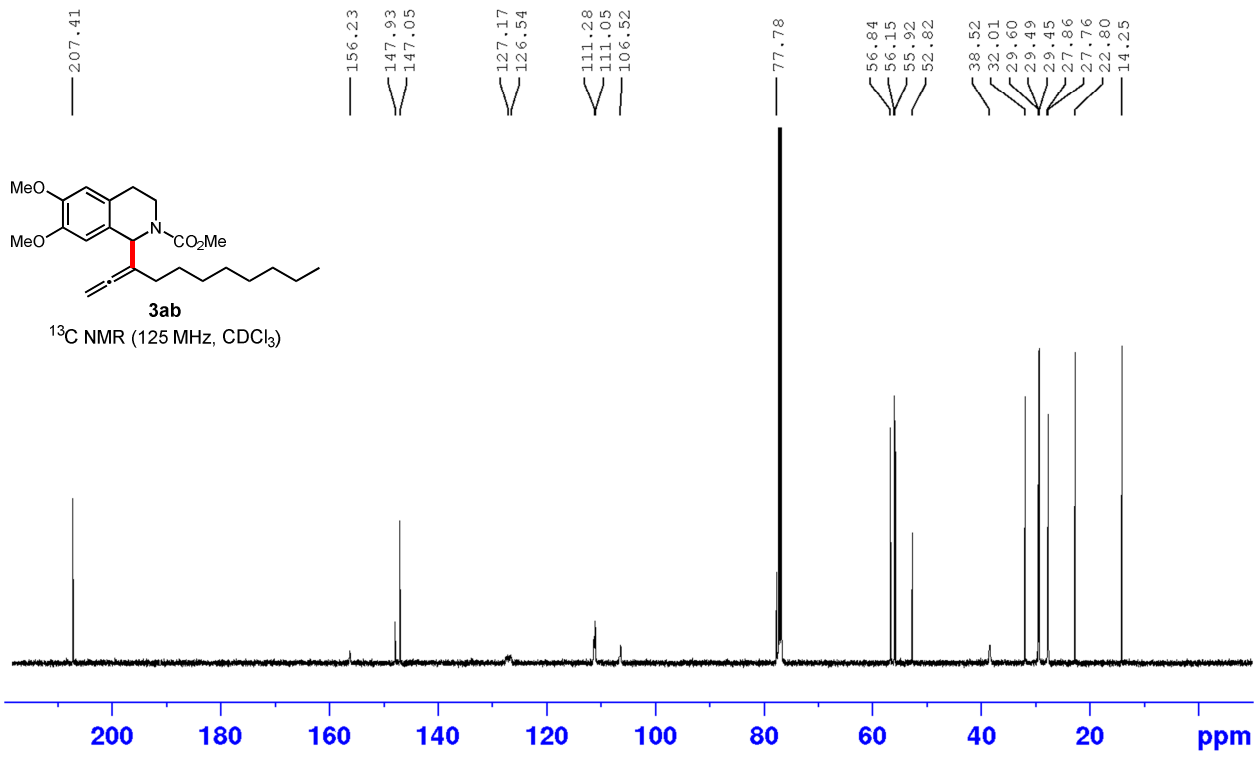

7.146
7.140
7.135
7.131
7.127
7.116
7.113
7.093
7.079
7.051
7.039
5.670
5.655
5.648
5.637
5.633
5.622
5.620
5.617
5.601
5.586
5.527
5.074
5.052
5.042
4.632
4.626
4.611
4.605
4.599
4.593
4.587
4.578
4.572
4.566
4.033
3.867
3.723
3.700
3.697
3.351
2.881
2.786
2.777
2.768
2.754
2.745
2.736
2.642
2.627
2.100
2.084
2.081
2.072
2.065
2.060
2.051
2.038
2.022
2.016
2.003
1.991
1.975
1.906
1.900
1.895
1.890
1.876
N
CO2Me
MeO2C
CO2Me
3pa
1H NMR (500 MHz, CDCl3)
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
4.22
1.51
0.51
1.04
0.96
2.00
0.58
0.57
2.96
6.13
1.05
1.04
1.09
1.95
2.10
2.00


206.99
171.65
171.62
156.22
135.03
134.76
132.44
128.58
128.19
127.05
125.69
119.15
105.88
78.85
57.52
57.16
52.84
52.51
38.92
37.44
31.12
28.12
24.05
N
CO2Me
MeO2C
CO2Me
3pa
13C NMR (125 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
ppm



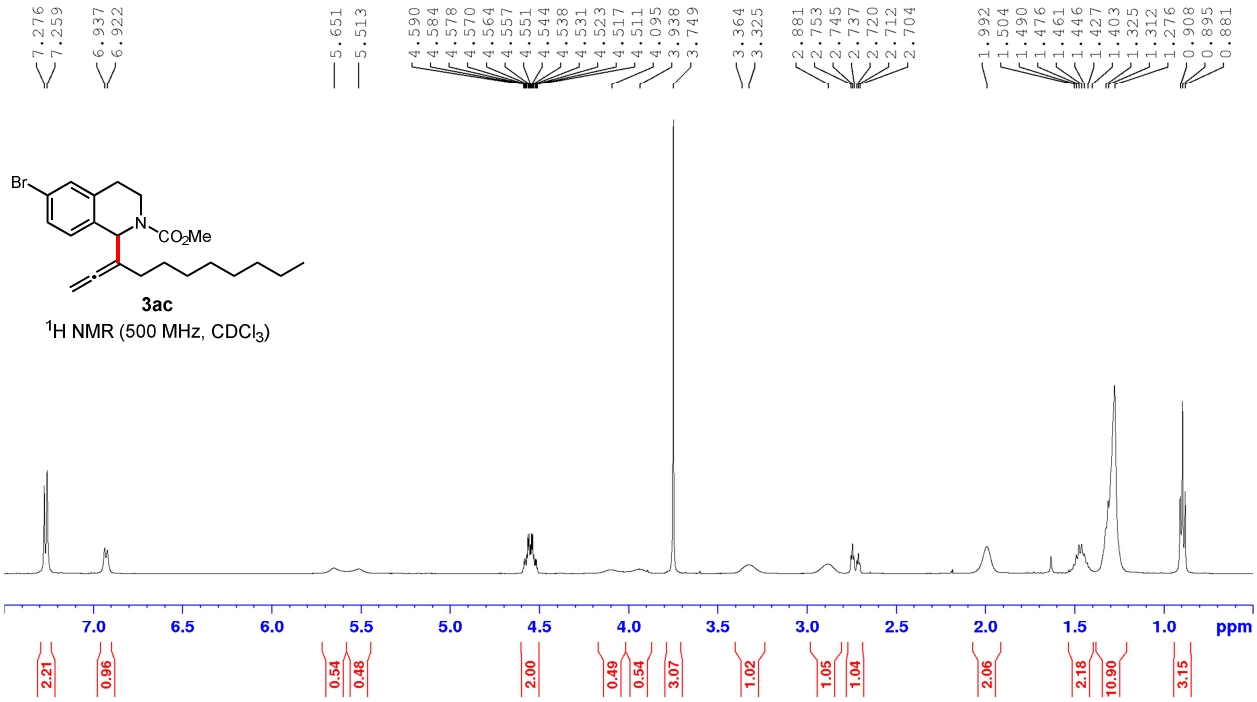
3ab

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



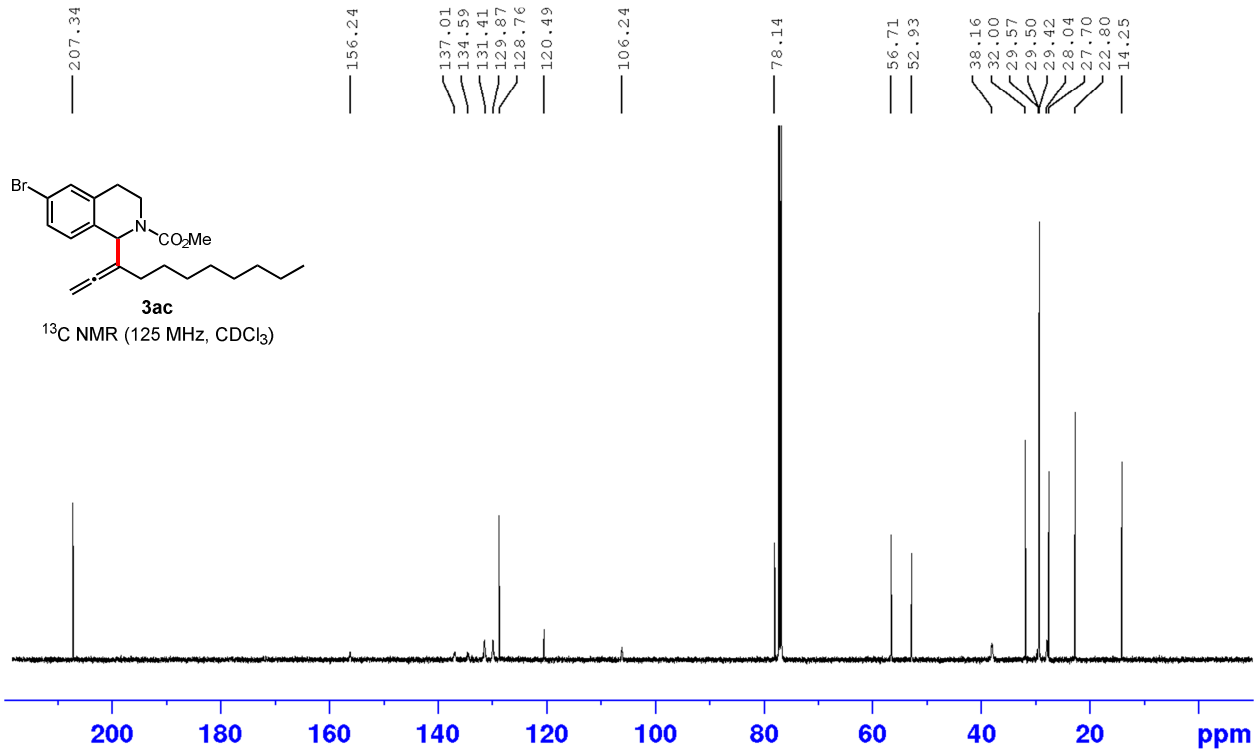
3ab

^{13}C NMR (125 MHz, $CDCl_3$)



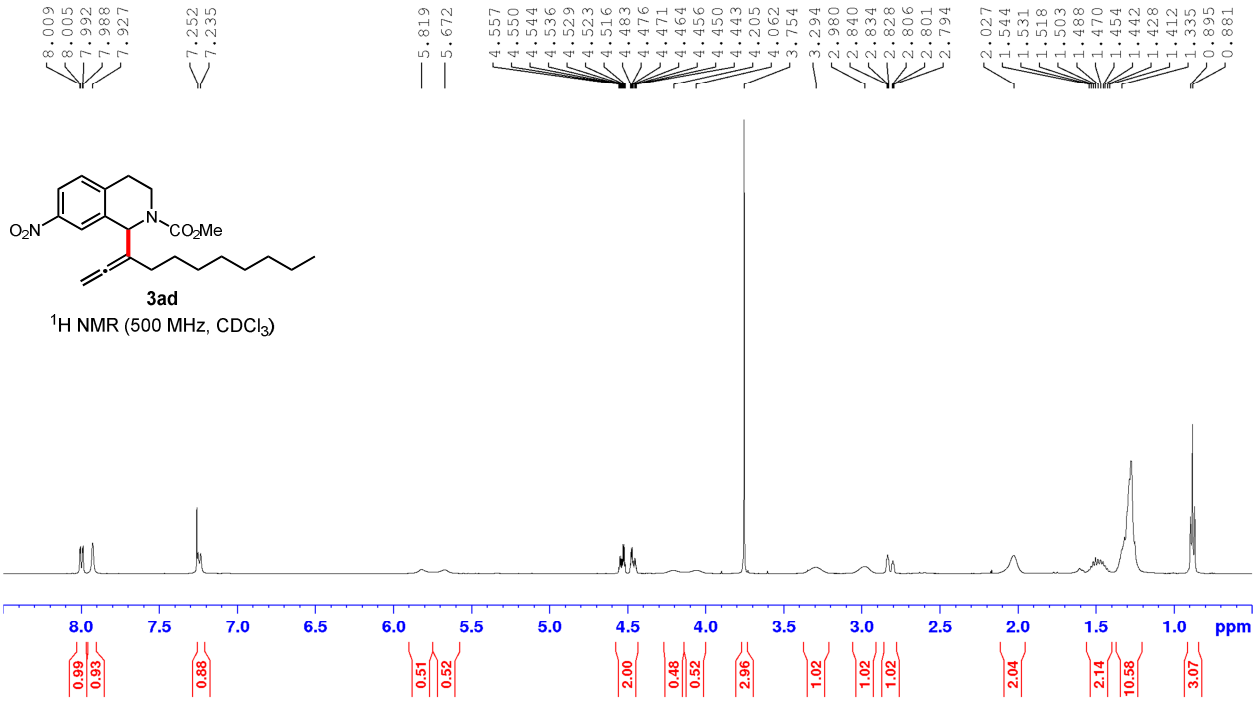
3ac

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



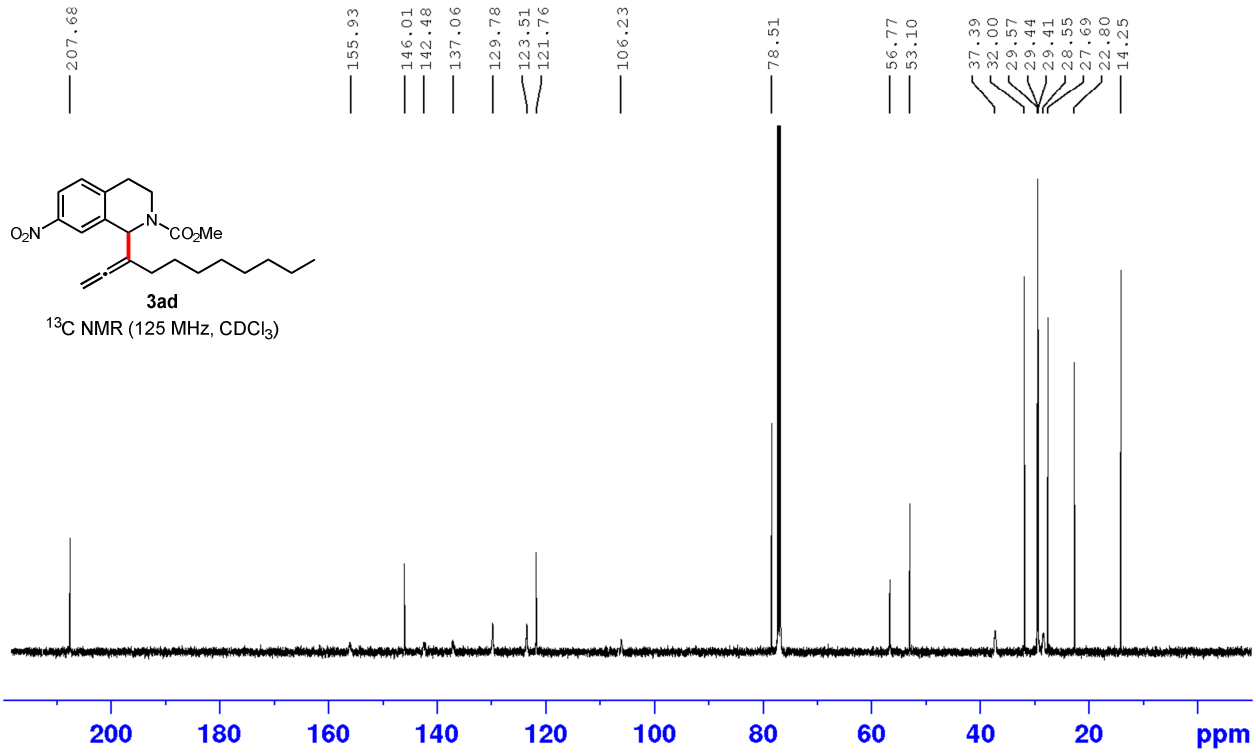
3ac

^{13}C NMR (125 MHz, $CDCl_3$)



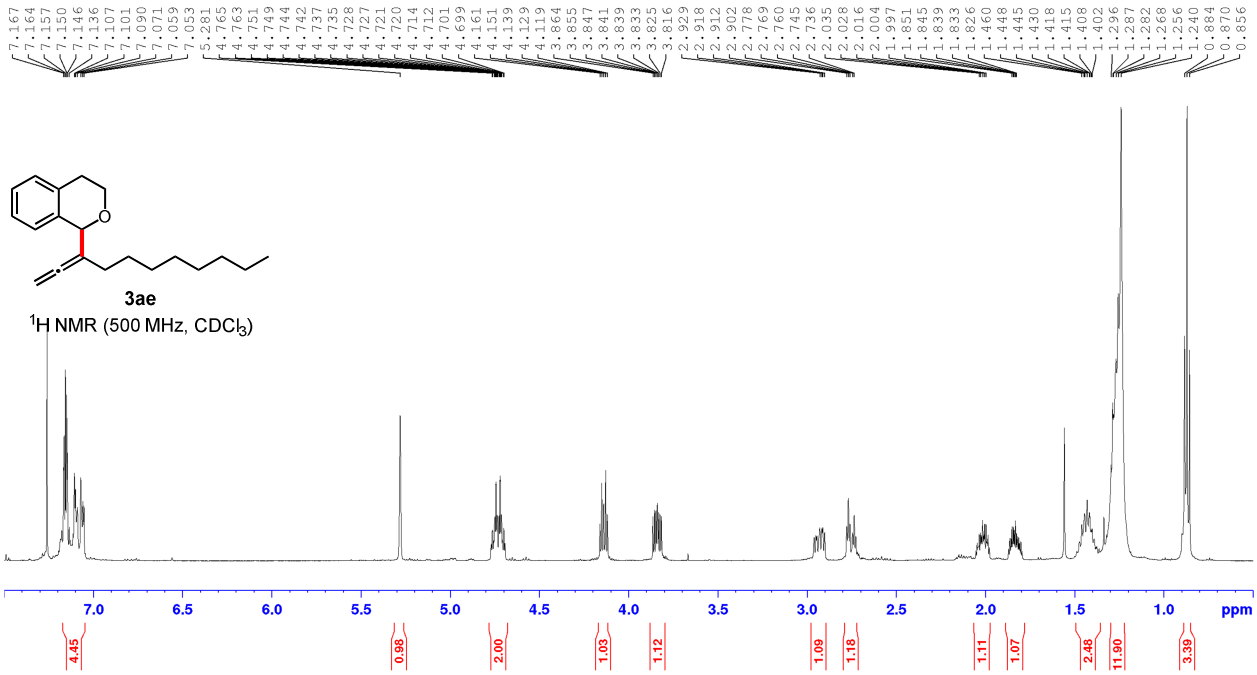
3ad

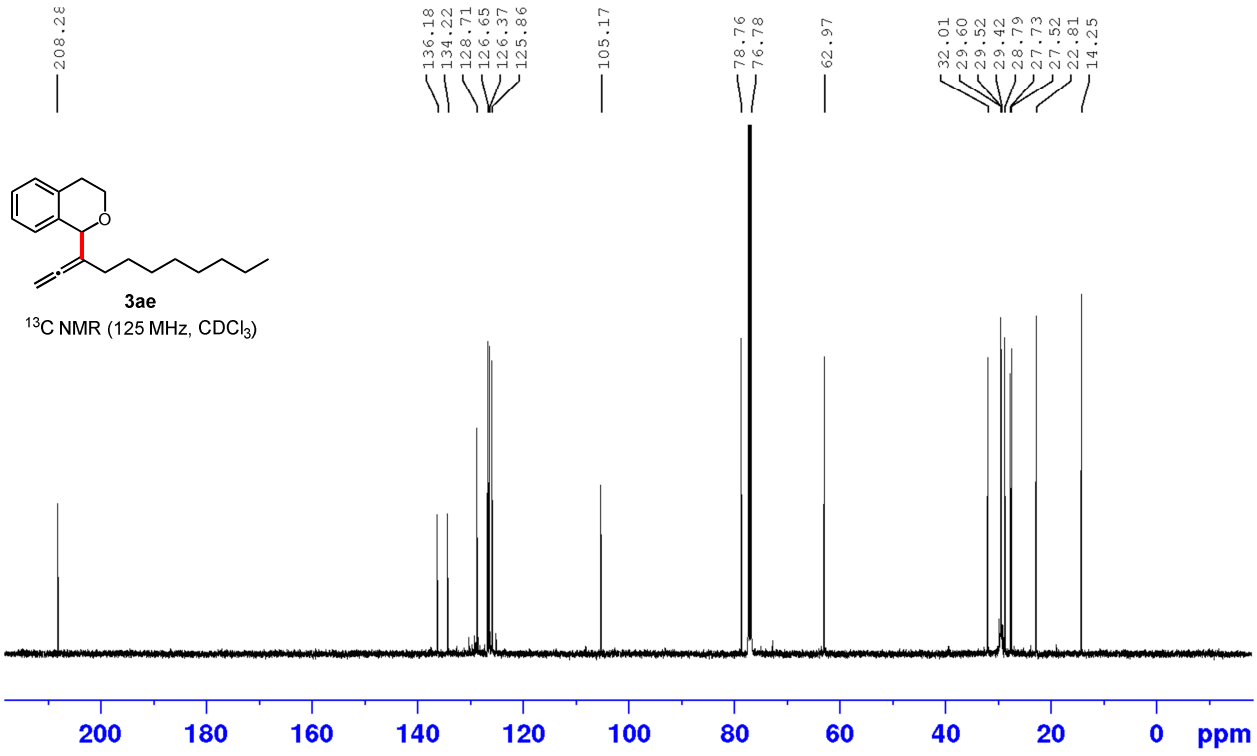
^{1}H NMR (500 MHz, $CDCl_3$)

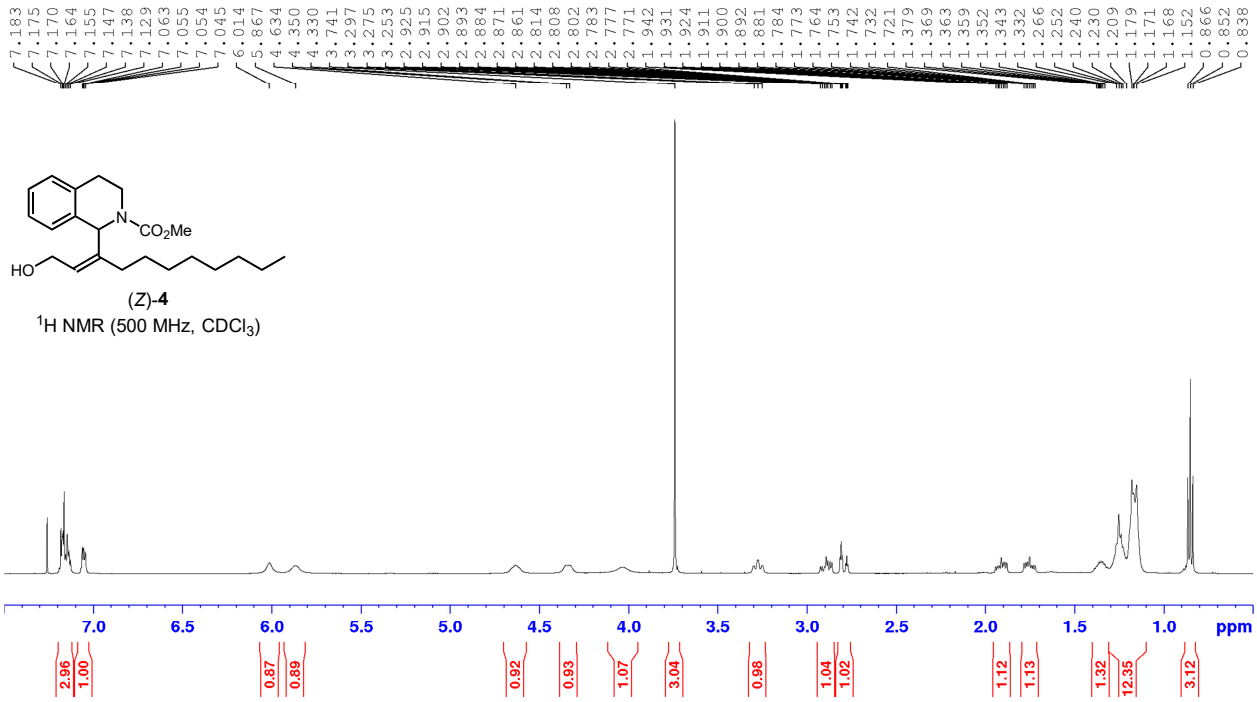


3ad

^{13}C NMR (125 MHz, $CDCl_3$)

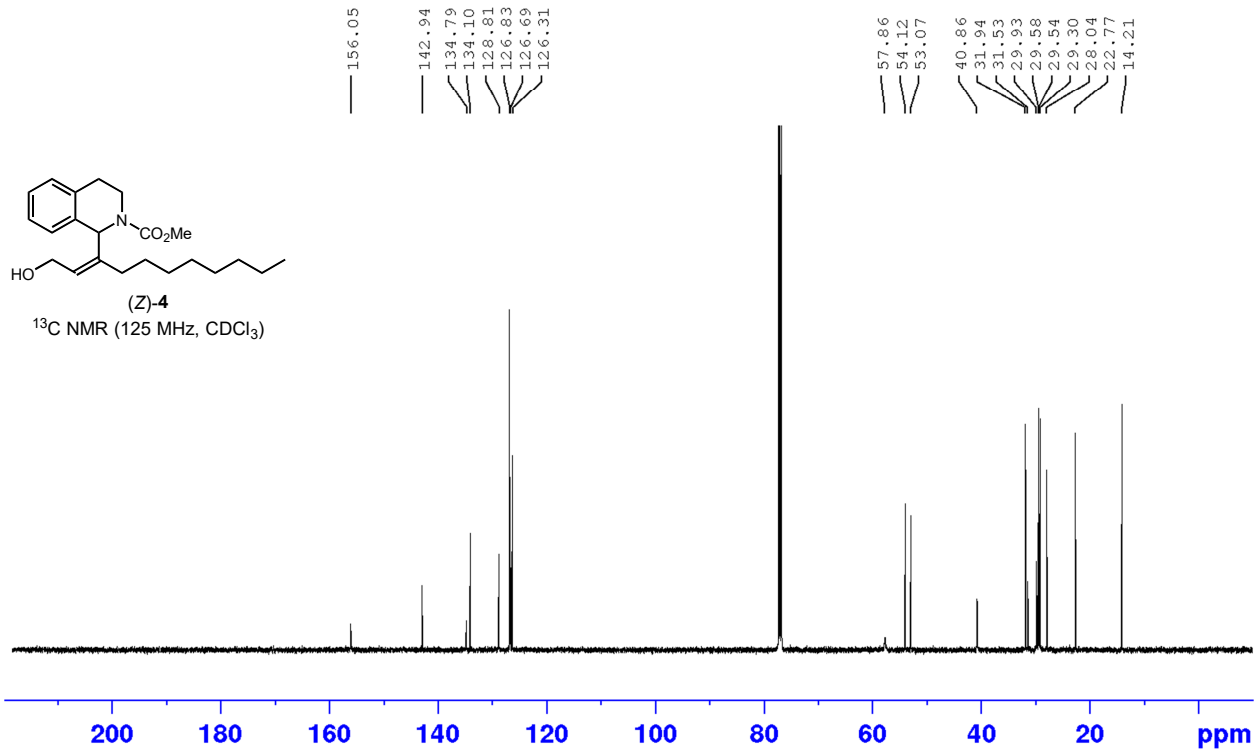

3ae
1H NMR (500 MHz, CDCl3)
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
4.45
0.98
2.00
1.03
1.12
1.09
1.18
1.11
1.07
2.48
11.90
3.39


3ae
13C NMR (125 MHz, CDCl3)
208.28
136.18
134.22
128.71
126.65
126.37
125.86
105.17
78.76
76.78
62.97
32.01
29.60
29.52
29.42
28.79
27.73
27.52
22.81
14.25
200
180
160
140
120
100
80
60
40
20
0
ppm



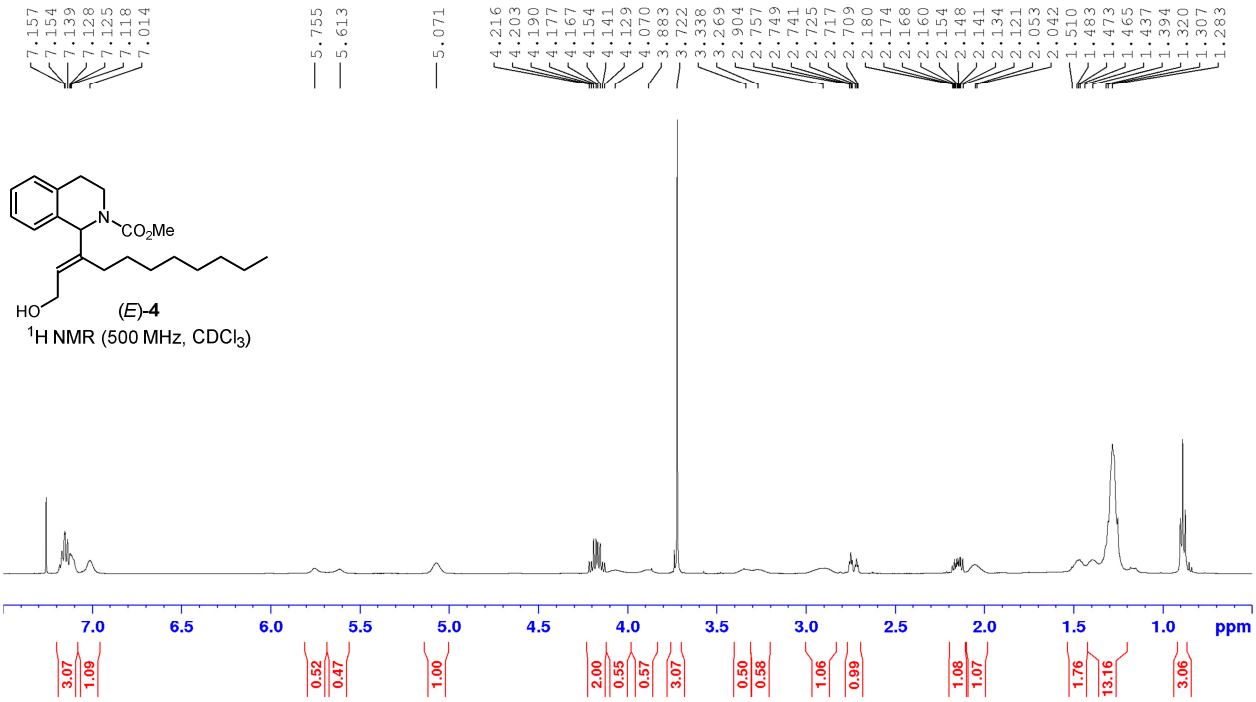
(*Z*)-**4**

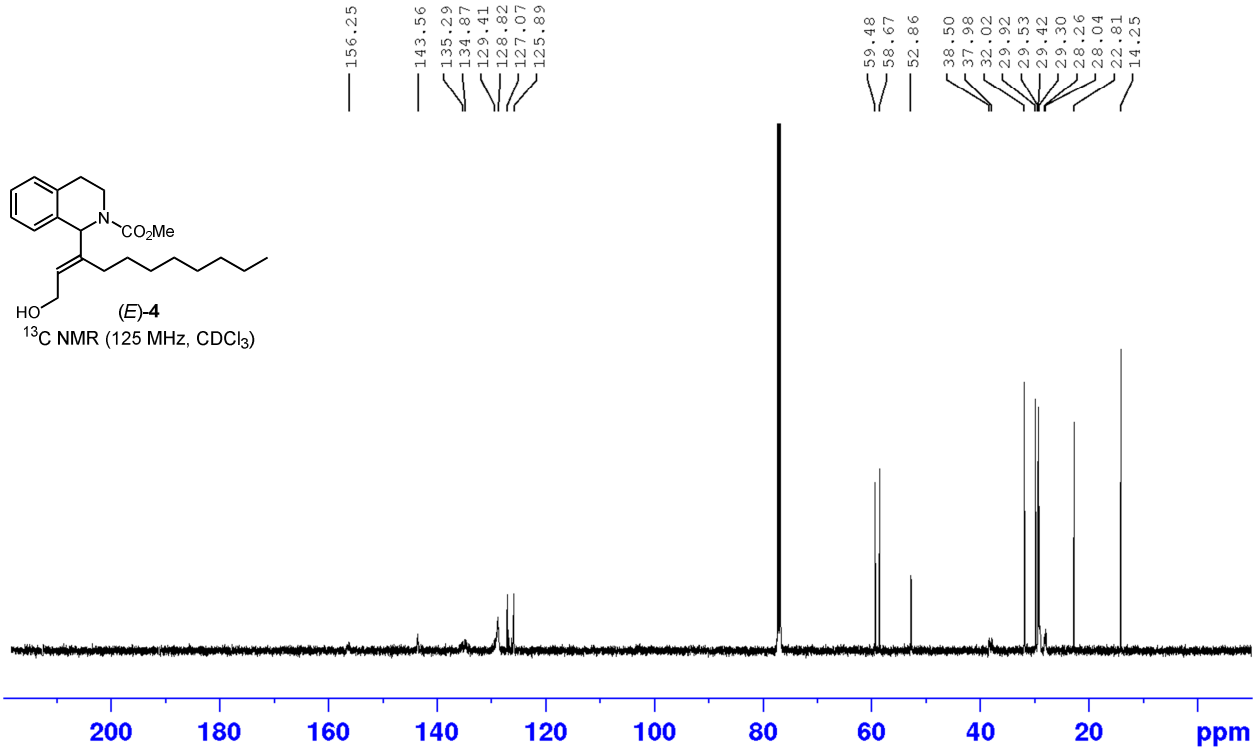
^{1}H NMR (500 MHz, $CDCl_3$)

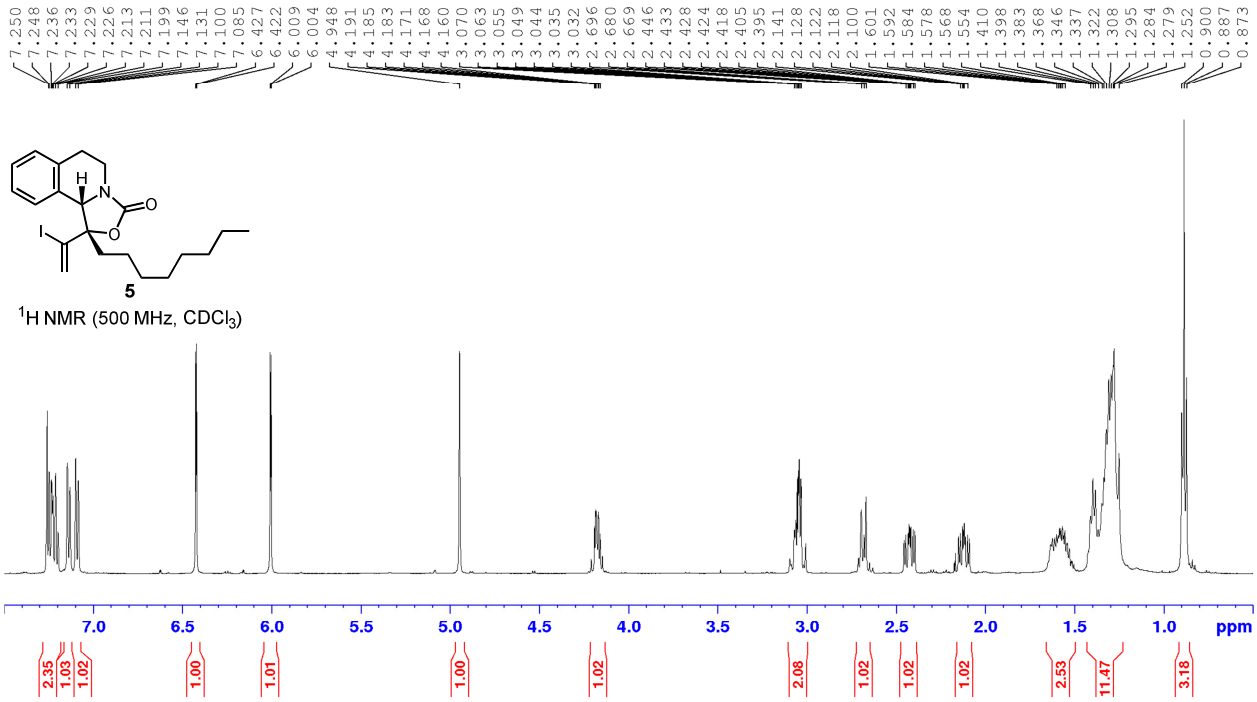


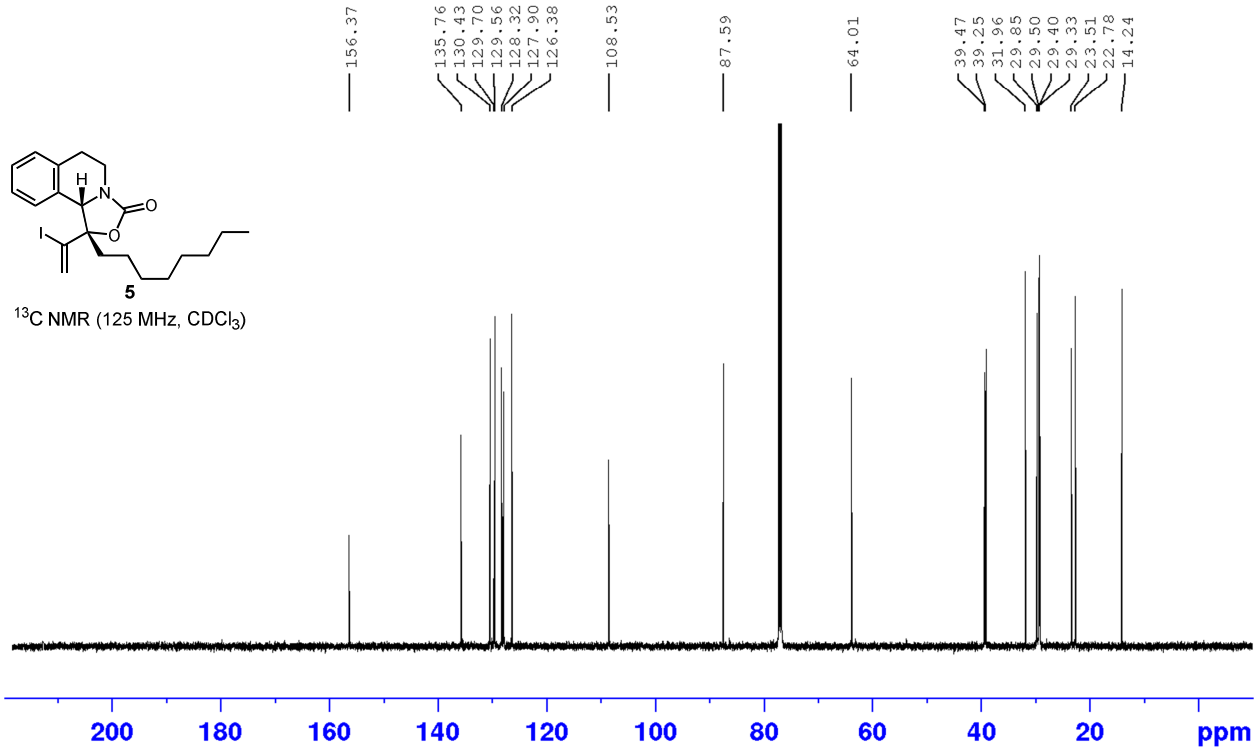
(*Z*)-**4**

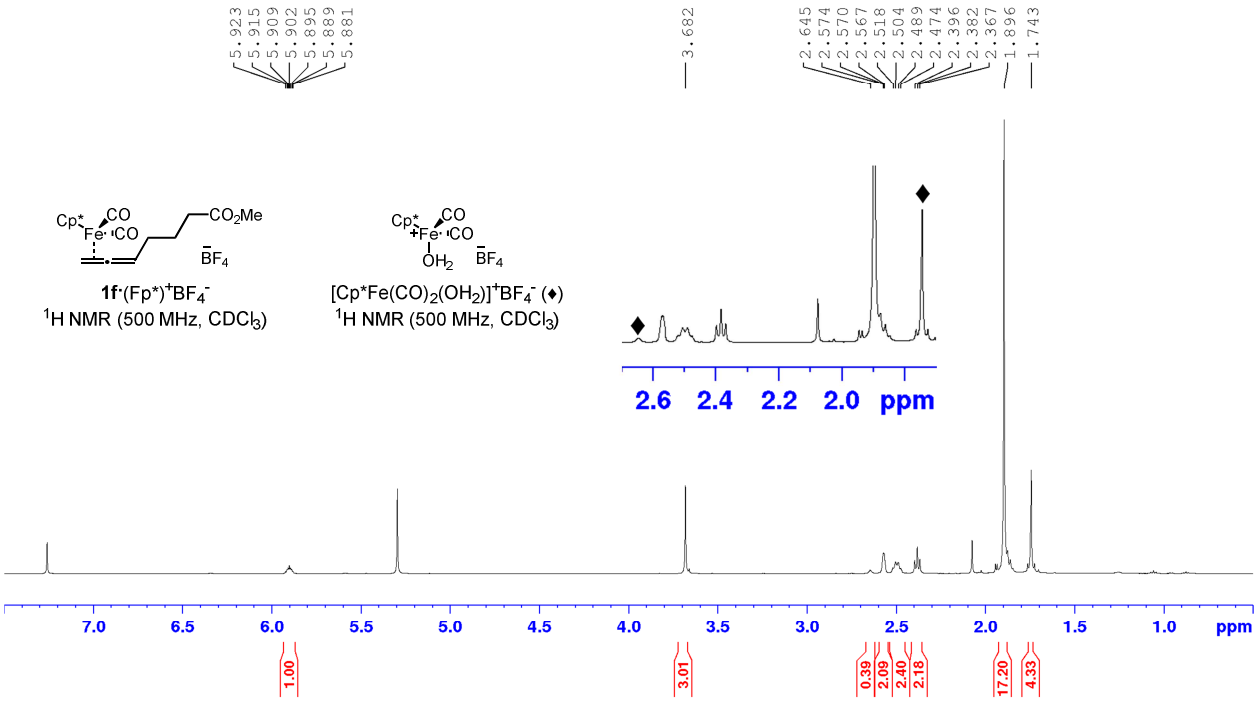
^{13}C NMR (125 MHz, $CDCl_3$)

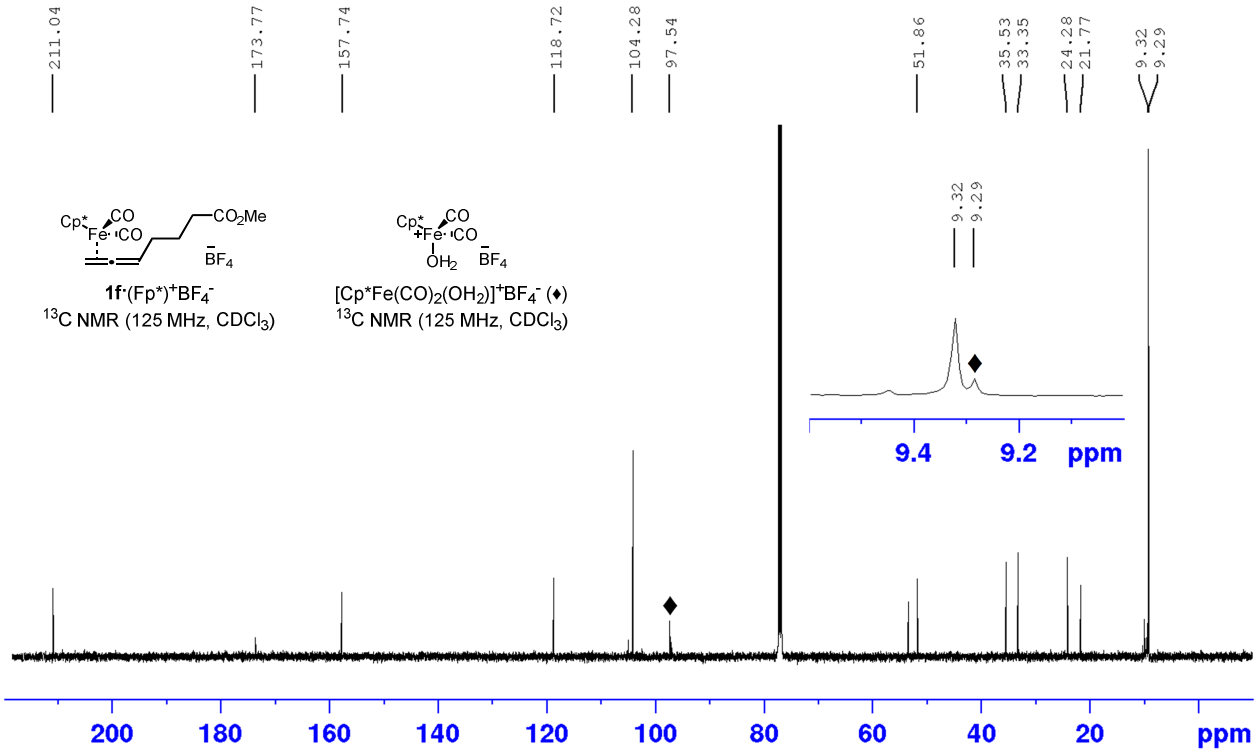

7.157
7.154
7.139
7.128
7.125
7.118
7.014
5.755
5.613
5.071
4.216
4.203
4.190
4.177
4.167
4.154
4.141
4.129
4.070
3.883
3.722
3.338
3.269
2.904
2.757
2.749
2.741
2.725
2.717
2.709
2.180
2.174
2.168
2.160
2.154
2.148
2.141
2.134
2.121
2.053
2.042
1.510
1.483
1.473
1.465
1.437
1.394
1.320
1.307
1.283
N
CO2Me
HO
(E)-4
1H NMR (500 MHz, CDCl3)
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
3.07
1.09
0.52
0.47
1.00
2.00
0.55
0.57
3.07
0.50
0.58
1.06
0.99
1.08
1.07
1.76
13.16
3.06

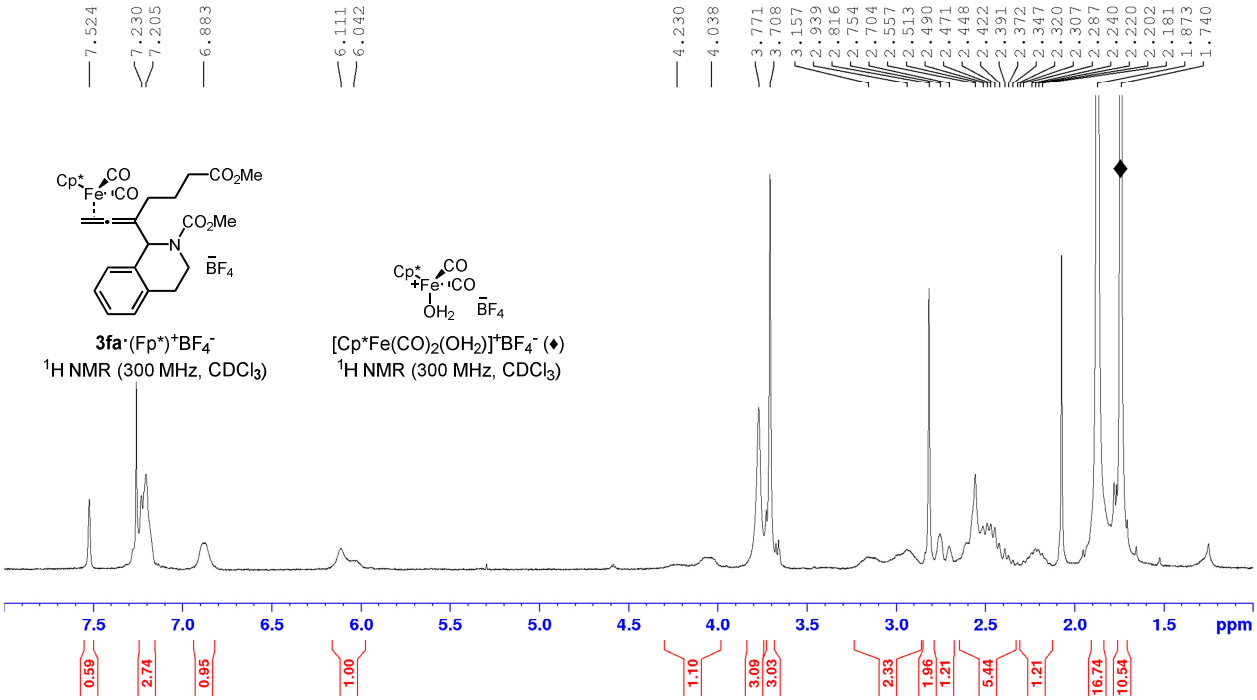

156.25
143.56
135.29
134.87
129.41
128.82
127.07
125.89
59.48
58.67
52.86
38.50
37.98
32.02
29.92
29.53
29.42
29.30
28.26
28.04
22.81
14.25
N
CO2Me
HO
(E)-4
13C NMR (125 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
ppm


7.250
7.248
7.236
7.233
7.229
7.226
7.213
7.211
7.199
7.146
7.131
7.100
7.085
6.427
6.422
6.009
6.004
4.948
4.191
4.185
4.183
4.171
4.168
4.160
3.070
3.063
3.055
3.049
3.044
3.035
3.032
2.696
2.680
2.669
2.446
2.433
2.428
2.424
2.418
2.405
2.395
2.141
2.128
2.122
2.118
2.100
1.601
1.592
1.584
1.578
1.568
1.554
1.410
1.398
1.383
1.368
1.346
1.337
1.322
1.308
1.295
1.284
1.279
1.252
0.900
0.887
0.873
H
N
O
O
I
5
1H NMR (500 MHz, CDCl3)
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.35
1.03
1.02
1.00
1.01
1.00
1.02
2.08
1.02
1.02
1.02
2.53
11.47
3.18


156.37
135.76
130.43
129.70
129.56
128.32
127.90
126.38
108.53
87.59
64.01
39.47
39.25
31.96
29.85
29.50
29.40
29.33
23.51
22.78
14.24
H
N
O
O
I
5
13C NMR (125 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
ppm


5.923
5.915
5.909
5.902
5.895
5.889
5.881
3.682
2.645
2.574
2.570
2.567
2.518
2.504
2.489
2.474
2.396
2.382
2.367
1.896
1.743
1f·(Fp*)+BF4-
1H NMR (500 MHz, CDCl3)
[Cp*Fe(CO)2(OH2)]+BF4- (♦)
1H NMR (500 MHz, CDCl3)
2.6 2.4 2.2 2.0 ppm
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
3.01
0.39
2.09
2.40
2.18
17.20
4.33


211.04
173.77
157.74
118.72
104.28
97.54
51.86
35.53
33.35
24.28
21.77
9.32
9.29
1f·(Fp*)+BF4-
13C NMR (125 MHz, CDCl3)
[Cp*Fe(CO)2(OH2)]+BF4- (♦)
13C NMR (125 MHz, CDCl3)
9.4 9.2 ppm
200 180 160 140 120 100 80 60 40 20 ppm


7.524
7.230
7.205
6.883
6.111
6.042
4.230
4.038
3.771
3.708
3.157
2.939
2.816
2.754
2.704
2.557
2.513
2.490
2.471
2.448
2.422
2.391
2.372
2.347
2.320
2.307
2.287
2.240
2.220
2.202
2.181
1.873
1.740
Cp*
Fe
CO
CO
CO2Me
CO2Me
N
BF4
3fa·(Fp*)+BF4-
1H NMR (300 MHz, CDCl3)
OH2
[Cp*Fe(CO)2(OH2)]+BF4- (♦)
1H NMR (300 MHz, CDCl3)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
0.59
2.74
0.95
1.00
1.10
3.09
3.03
2.33
1.96
1.21
5.44
1.21
16.74
10.54