Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Chelation-assisted iridium-catalysed hydroalkenylation and hydroarylation/cyclization with conjugated trienes

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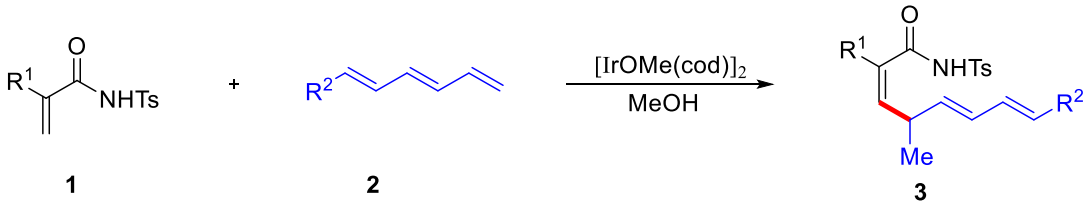
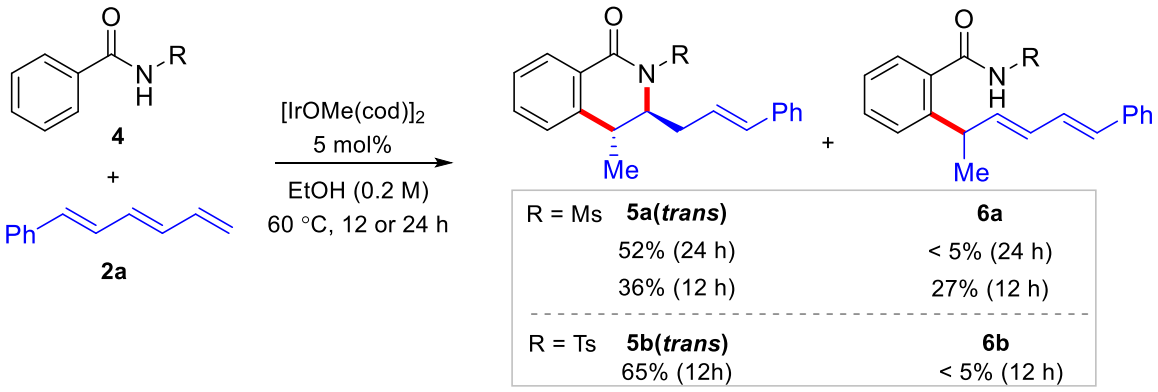
General Methods

Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate. Flash colum chromatography was performed using Merck aluminium oxide 90 active neutral with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on Bruker AMX 400 spectrophotometer ($CDCl_3$ as solvent), and Bruker AMX 500 spectrophotometer ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 7.26, singlet). Multiplicities were given as: s (singlet), d (doublet), t (triplet), dd (doublets of doublet) or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million(ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 77.0, triplet). Mass spectrometry was performed by Waters Q-Tof Premier Micromass instrument, using Electro Spray Ionization (ESI) mode. IR spectra were recorded as thin films on KBr plates on a Bio-Rad FTS 165 FTIR spectrometer and are reported in frequency of absorption (cm^{-1}). $[IrOMe(cod)]_2$ was purchased from TCI and used directly. Other reagents, unless otherwise noted below, are commercially available from TCI, Energy Chemical, Alfa Aesar (China) Chemical Co. Ltd. and used without further purification.

General Procedure for the Cross-Coupling between Acrylmides and Trienes

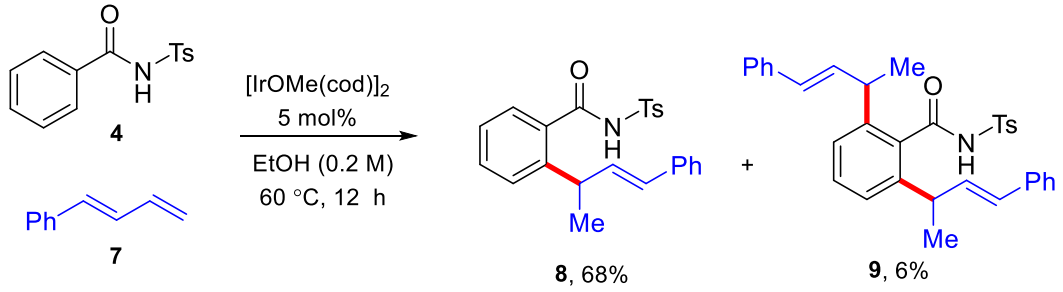


A dry screw-cap vial was charged with $[IrOMe(cod)]_2$ (5 mol%,0.01mmol) and methanol (1.0 mL). Then, acrylamide **1** (1.0 equiv, 0.2 mmol) and triene **2** (1.2 equiv, 0.24 mmol) were added into the solution in sequence. The vial was sealed under argon and heated in an oil bath to 60 ℃ with stirring for 24 h. After cooling down, the mixture was directly applied to a flash column chromatography for separation (ethyl acetate/petroleum ether mixtures) to provide 1,4,6-triene product **3**.



R = Ms	**5a(*trans*)**	**6a**
	52% (24 h)	< 5% (24 h)
	36% (12 h)	27% (12 h)
R = Ts	**5b(*trans*)**	**6b**
	65% (12h)	< 5% (12 h)

A dry screw-cap vial was charged with $[IrOMe(cod)]_2$ (5 mol%,0.01mmol) and ethanol (1.0 mL). Then, benzamide **4** (1.0 equiv, 0.2 mmol) and triene **2a** (1.2 equiv, 0.24 mmol) were added into the solution in sequence. The vial was sealed under argon and heated in an oil bath to 60 ℃ with stirring for 24 h. After cooling down, the mixture was directly applied to a flash column chromatography for separation (ethyl acetate/petroleum ether mixtures) to provide products **5a-6b**.

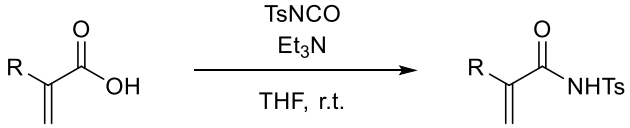


8, 68%

9, 6%

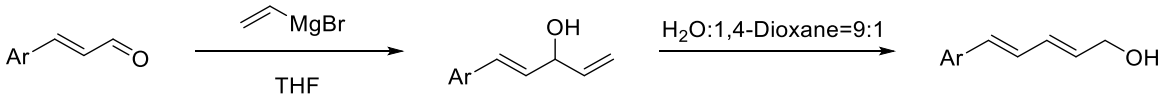
A dry screw-cap vial was charged with $[IrOMe(cod)]_2$ (5 mol%,0.01mmol) and ethanol (1.0 mL). Then, benzamide **4** (1.0 equiv, 0.2 mmol) and diene **7** (1.2 equiv, 0.24 mmol) were added into the solution in sequence. The vial was sealed under argon and heated in an oil bath to 60 ℃ with stirring for 12 h. After cooling down, the mixture was directly applied to a flash column chromatography for separation (ethyl acetate/ petroleum ether mixtures) to provide product **8** and **9**. Product **8** was obtained as a yellow oil, 55.1 mg, yield = 68%.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.41 (td, *J* = 7.9, 1.2 Hz, 1H), 7.36 – 7.34 (m, 2H), 7.29 (dd, *J* = 10.1, 5.1 Hz, 2H), 7.28 – 7.23 (m, 4H), 7.23 – 7.14 (m, 2H), 6.35 – 6.15 (m, 2H), 4.03 – 3.95 (m, 1H), 2.41 (d, *J* = 9.9 Hz, 3H), 1.43 – 1.25 (m, 3H). Product **9** was obtained as a yellow oil, 6.1 mg, yield = 6%.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 – 7.95 (m, 2H), 7.46 – 7.26 (m, 11H), 7.23 – 7.10 (m, 4H), 6.34 – 6.11 (m, 4H), 3.43 (s, 2H), 2.46 (s, 3H), 1.39 – 1.31 (m, 6H).

Substrate Synthesis



1

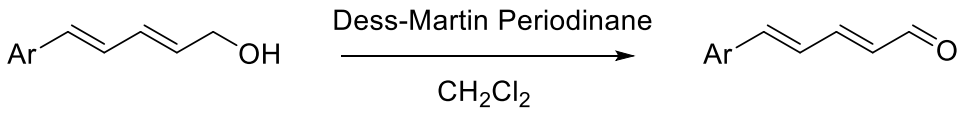
To a solution of α-substituted acrylic acid (3.0 mmol, 1.0 equiv) in dry THF (6 mL, 0.5 M) was added *p*-tosyl isocyanate (3.0 mmol, 1.0 equiv). After stirring the resulting clear solution at r.t. for 10 min, triethyl amine (3.0 mmol, 1.0 equiv) was added in dropwise, with release of gas. The progress of the reaction was monitored using TLC. Once the acrylic acids disappeared, the mixture was diluted with EtOAc and washed with 2 M HCl. The organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was subjected to column chromatography on silica-gel to deliver acrylamide **1**. [1]



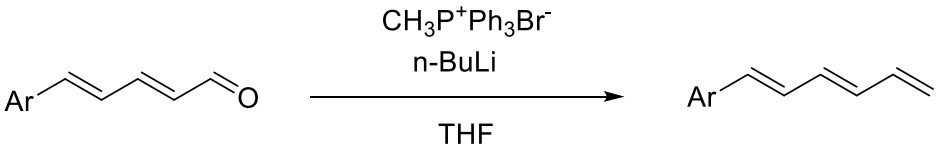
To a solution of cinnamic aldehyde (8.0 mmol) in THF (25 mL) was added vinylmagnesium bromide (1.0 M in THF, 9.6 mL, 9.6 mmol) dropwise at 0 °C. The reaction mixture was stirred at

0 °C for 30 min. Then the reaction mixture was allowed to warm to room temperature and further stirred at room temperature for 2 h. Diluted aqueous NH_4Cl solution was added to quench the reaction, and the reaction mixture was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography to afford the desired alcohol.

To a 100 mL round-bottom flask containing the alcohol(3.0 mmol) was added 1,4-dioxane (5 mL), and then to the solution was added H_2O (45 mL). The flask was fitted with a condenser and stirred vigorously for 1 h at the indicated temperature under Ar atmosphere. The resulting solution was cooled to room temperature. The mixture was extracted with EtOAc (3 × 50 mL), washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was purified by silica-gel column chromatography to afford the desired alcohol.



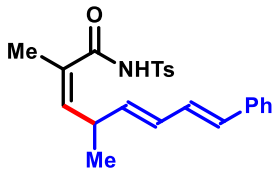
To a solution of the alcohol (1.8 mmol) in CH_2Cl_2 (20 mL) was added Dess-Martin Periodinane (2.2 mmol). The reaction mixture was stirred for 2 h before being filtered through a pad of celite to remove inorganic compound.The filtrate was concentrated, and the residue was purified by silica-gel column chromatography to give the aldehyde.



To a suspension of methyltriphenylphosphonium bromide (6.0 mmol) in dry THF (30 mL) was added *n*-BuLi (2.3 mL: 2.6 M in n-hexane, 3.6 mmol) at 0 ℃ under argon. After stirring for 40 min, (2*E*, 4*E*)-5-amino-2,4-dialdehyde derivatives (6.0 mmol) was added. The reaction mixture was warmed to room temperature and the progress of the reaction was monitored by TLC. After the reaction was completed, the reaction mixture was quenched with Sat. NH_4Cl (aqueous, 10 mL) and extracted with EtOAc (10 mL × 2). The combined organic layers were dried over $MgSO_4$, and

concentrated in vacuo. The residue was purified by silica-gel column chromatography to give the corresponding 1-aryl-1,3,5-hexatriene derivative.[2]

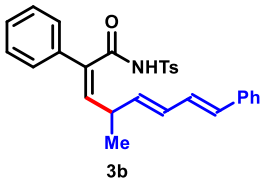
Characterization Data



3a

(2*Z*,5*E*,7*E*)-2,4-dimethyl-8-phenyl-N-tosylocta-2,5,7-trienamide(3a)

Following the general procedure, **3a** was obtained as a yellow liquid (78%, 61.7 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.31 (s, 1H), 7.99 (d, *J* = 8.5 Hz, 2H), 7.37 – 7.33 (m, 4H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.21(t, *J* = 7.25 Hz, 1H), 6.69 (dd, *J* = 10.5, 15.5 Hz, 1H), 6.50 (d, *J* = 16.0 Hz, 1H), 6.18 (dd, *J* = 10.5, 15.5 Hz, 1H), 5.67 (dd, *J* = 7.0, 15.5 Hz, 1H), 5.60 (d, *J* = 10.0 Hz, 1H), 3.49 – 3.42 (m, 1H), 3.42 (s, 3H), 1.87 (s, 3H), 1.08 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (125 Hz, $CDCl_3$): δ = 164.9, 144.2, 141.5, 136.3, 135.9, 134.6, 131.0, 128.6, 128.6, 127.6, 127.5, 126.8, 126.4, 125.3, 35.8, 28.7, 20.7, 19.8, 19.3. **HR-MS** (ESI): m/z calculated for $C_{23}H_{25}NO_3S$: $[M+H]^+$: 396.1628, found:396.1633. **FTIR** (KBr, cm^{-1}): 3854.21, 3739.25, 3444.93, 2959.81, 2934.58, 2829.82, 2715.89, 1602.46, 1364.10, 1126.17, 1078.50, 774.84.

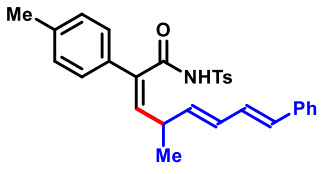


3b

(2*Z*,5*E*,7*E*)-4-methyl-2,8-diphenyl-N-tosylocta-2,5,7-trienamide (3b)

Following the general procedure, **3b** was obtained as a yellow oil (68%, 62.1 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.07 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.37 – 7.36 (m, 4H), 7.31 – 7.28 (m, 5H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.15 – 7.13 (m, 2H), 6.70 (dd, *J* = 10.0, 15.5 Hz, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 6.17 (dd, *J* = 10.0, 15.0 Hz, 1H), 5.95 (d, *J* = 10.0 Hz, 1H), 5.71 (dd, *J* = 6.5, 15.0 Hz, 1H), 3.58 – 3.52 (m,1H), 2.46 (s, 3H), 1.17 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (125 Hz, $CDCl_3$): δ = 164.1,

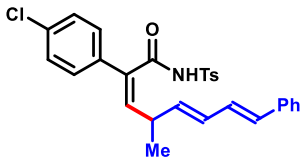
144.2, 141.9, 136.3, 135.6, 134.7,134.5, 132.7, 130.8, 129.1, 128.6, 128.0,127.7, 127.7, 127.6, 127.5, 126.4, 126.2, 125.2, 35.9, 20.7, 19.4. **HR-MS** (ESI): m/z calculated for $C_{28}H_{27}NO_3S$: $[M+Na]^+$: 480.1604, found: 480.1594. **FTIR** (KBr, cm^{-1}): 3854.21, 3450.08, 2957.00, 2830.14, 2721.50, 1602.01, 1363.69, 1120.56, 1068.83, 774.51.



3c

(2*Z*,5*E*,7*E*)-4-methyl-8-phenyl-2-(p-tolyl)-N-tosylocta-2,5,7-trienamide (3c)

Following the general procedure, **3c** was obtained as a white solid (76%, 71.5 mg), m.p.:52.0 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.06 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 7.5 Hz, 4H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.21 – 7.19 (m, 1H), 7.11 – 7.10 (m, 2H), 7.03 – 7.01 (m, 2H), 6.69 (dd, *J* = 10.0, 15.5 Hz, 1H), 6.47 (d, *J* = 15.5 Hz, 1H), 6.16 (dd, *J* = 10.5, 15.5 Hz, 1H), 5.90 (d, *J* = 10.5 Hz, 1H), 5.71 (dd, *J* = 7.0, 15.5 Hz, 1H), 3.57 – 3.53 (m,1H), 2.46 (s, 3H), 2.34 (s, 3H), 1.16 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (125 Hz, $CDCl_3$): δ = 164.2, 144.1, 137.7, 136.3, 135.8, 134.5, 132.6, 131.9, 130.7, 129.0, 128.7, 128.6, 127.7, 127.5, 126.4, 126.1, 125.2, 35.8, 20.7, 20.1, 19.4. **HR-MS** (ESI): m/z calculated for $C_{29}H_{29}NO_3S$: $[M+Na]^+$: 494.1760, found: 494.1764. **FTIR** (KBr, cm^{-1}): 3854.21, 3444.91, 2951.40, 2830.03, 2724.30, 1601.80, 1363.66, 1120.64, 1068.78, 774.53.

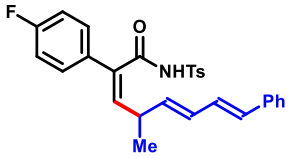


3d

(2*Z*,5*E*,7*E*)-2-(4-chlorophenyl)-4-methyl-8-phenyl-N-tosylocta-2,5,7-trienamide (3d)

Following the general procedure, **3d** was obtained as a yellow oil (73%, 71.7 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.07 (s, 1H), 7.87 (d, *J* = 8.5 Hz, 2H), 7.31 – 7.29 (m, 4H), 7.25 – 7.21 (m, 2H), 7.20 – 7.17 (m, 2H), 7.14 (t, *J* = 7.0 Hz, 1H),7.01 – 6.99 (m, 2H), 6.62 (dd, *J* = 10.0, 15.5 Hz, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 6.08 (dd, *J* = 10.5, 15.0 Hz, 1H), 5.86 (d, *J* = 10.5 Hz, 1H), 5.62 (dd, *J* = 7.0, 15.0 Hz, 1H), 3.42 – 3.34 (m,1H), 2.40 (s, 3H), 1.10 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (125 Hz,

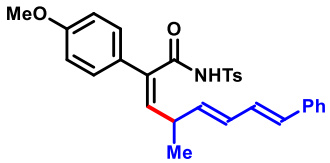
$CDCl_3$): δ = 163.9, 144.4, 141.3, 136.2, 135.2, 134.3, 133.7, 131.9, 131.1, 129.3, 128.6, 128.1, 127.6, 127.5, 127.5, 127.3, 126.5, 125.3, 36.1, 28.7, 20.7, 19.4. **HR-MS** (ESI): m/z calculated for $C_{28}H_{26}ClNO_3S$: $[M+Na]^+$: 514.1214, found:514.1207. **FTIR** (KBr, cm^{-1}): 3848.60, 3747.66, 3444.88, 2959.81, 2830.02, 2715.89, 1602.10, 1363.52, 1114.23, 1072.90, 774.59.



3e

(2*Z*,5*E*,7*E*)-2-(4-fluorophenyl)-4-methyl-8-phenyl-N-tosylocta-2,5,7-trienamide (3e)

Following the general procedure, **3e** was obtained as a white solid (57%,54.5 mg), m.p.: 52.1 °C.**^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.12 (s, 1H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.29 – 7.27 (m, 4H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.05 – 7.03 (m, 2H),6.91 – 6.88 (m, 2H), 6.61 (dd, *J* = 10.5, 15.5 Hz, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 6.07 (dd, *J* = 10.5, 15.5 Hz, 1H), 5.80 (d, *J* = 10.0 Hz, 1H), 5.61 (dd, *J* = 7.0, 15.5 Hz, 1H), 3.41 – 3.34 (m,1H), 2.39 (s, 3H), 1.08 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (125 Hz, $CDCl_3$): δ = 164.1, 163.4 (d, J_{C-F} = 247.75 Hz), 144.3, 141.1, 136.2, 135.4, 134.4, 131.9, 130.9, 130.8 (d, J_{C-F} = 3.75 Hz), 129.2, 128.6, 172.9 (d, J_{C-F} = 8.25 Hz), 127.6, 127.4, 126.4, 125.3, 115.0 (d, J_{C-F} = 21.25 Hz), 36.0, 20.7, 19.4. ^{19}F NMR (471 Hz, $CDCl_3$): δ = -112.40. **HR-MS** (ESI): m/z calculated for $C_{28}H_{26}FNO_3S$: $[M+ Na]^+$: 498.1510, found: 498.1499. **FTIR** (KBr, cm^{-1}): 3854.33, 3747.79, 3445.18, 2959.95, 2829.06, 2716.02, 1605.75, 1365.95, 1120.71, 1073.05, 774.36.

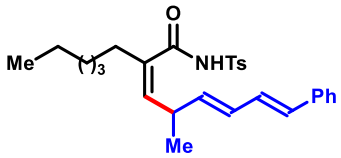


3f

(2*Z*,5*E*,7*E*)-2-(4-methoxyphenyl)-4-methyl-8-phenyl-N-tosylocta-2,5,7-trienamide(3f)

Following the general procedure, **3f** was obtained as a yellow oil (20%, 19.4 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 8.5 Hz, 2H), 7.39 – 7.36 (m, 4H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.21 – 7.19 (m, 1H), 7.09 – 7.06 (m, 2H), 6.85 – 6.82 (m, 2H), 6.70 (dd, *J* = 10.5, 15.5 Hz, 1H), 6.48 (d, *J*

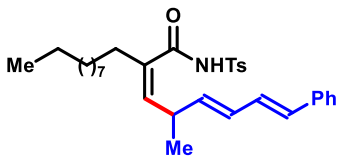
= 15.5 Hz, 1H), 6.16 (dd, *J* = 10.5, 15.5 Hz, 1H), 5.87 (d, *J* = 10.0 Hz, 1H), 5.71 (dd, *J* = 7.0, 15.5 Hz, 1H), 3.81 (s, 3H), 3.58 – 3.51 (m,1H), 2.47 (s, 3H), 1.12 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (125 Hz, $CDCl_3$): δ = 164.2, 159.0, 144.2, 141.0, 136.3, 135.9, 134.6, 132.2, 130.7, 129.0, 128.6, 127.8, 127.6, 127.6, 127.5, 127.2, 126.4, 125.2, 113.4, 54.4, 35.8, 20.7, 19.5. **HR-MS** (ESI): m/z calculated for$C_{29}H_{29}NO_4S$: $[M+Na]^+$: 510.1710, found: 510.1702. **FTIR** (KBr, cm^{-1}): 3854.21, 3750.47, 3450.76, 2965.42, 2829.27, 2721.50, 1605.94, 1365.20, 1126.17, 1068.59, 774.41.



3g

(2*Z*,5*E*,7*E*)-2-hexyl-4-methyl-8-phenyl-N-tosylocta-2,5,7-trienamide (3g)

Following the general procedure, **3g** was obtained as a yellow oil (66%,61.8 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.33 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.38 – 7.33 (m, 4H), 7.30 (t, *J* = 11.5 Hz, 2H), 7.21(t, *J* = 7.5 Hz, 1H), 6.69 (dd, *J* = 10.5, 15.5 Hz, 1H), 6.50 (d, *J* = 16.0 Hz, 1H), 6.16 (dd, *J* = 10.5, 15.5 Hz, 1H), 5.68 (dd, *J* = 7.0, 15.0 Hz, 1H), 5.47 (d, *J* = 10.0 Hz, 1H), 3.28 – 3.21 (m,1H), 2.43 (s, 3H), 2.22 – 2.08 (m, 2H), 1.26 – 1.15 (m, 8H), 1.09 (d, *J* = 6.5 Hz, 3H), 0.85 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (125 Hz, $CDCl_3$): δ = 165.6, 144.1, 137.7, 136.2, 136.1, 134.6, 133.1, 131.0, 128.9, 128.6, 127.6, 127.5, 126.5, 125.3, 36.0, 33.3, 30.4, 27.6, 27.1, 21.5, 20.7, 20.0, 13.0. **HR-MS** (ESI): m/z calculated for $C_{28}H_{35}NO_3S$: $[M+Na]^+$: 488.2230, found: 488.2222. **FTIR** (KBr, cm^{-1}): 3851.40, 3739.25, 3445.01, 2957.01, 2928.97, 2830.40, 2721.50, 1601.76, 1363.43, 1123.36, 1068.64, 774.81.

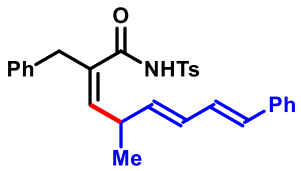


3h

(2*Z*,5*E*,7*E*)-2-butyl-4-methyl-8-phenyl-N-tosylocta-2,5,7-trienamide (3h)

Following the general procedure, **3h** was obtained as a colorless oil (71%, 55.5 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.17 (s, 1H), 7.98 (d, *J* = 7.0 Hz, 2H), 7.39 – 7.32 (m, 4H), 7.31 (t, *J* = 7.5 Hz,

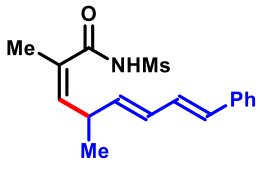
2H), 7.22 (t, *J* = 7.5 Hz, 1H), 6.71 (dd, *J* = 10.5, 16.0 Hz, 1H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.17 (dd, *J* = 10.5, 15.5 Hz, 1H), 5.68 (dd, *J* = 7.0, 15.5 Hz, 1H), 5.48 (d, *J* = 10.5 Hz, 1H), 3.28 – 3.21 (m, 1H), 2.44 (s, 3H), 2.22 – 2.07 (m, 2H), 1.31 – 1.19 (m, 16H), 1.09 (d, *J* = 6.5 Hz, 3H), 0.87 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (125 Hz, $CDCl_3$): δ = 165.5, 144.1, 137.7, 136.2, 136.0, 134.6, 133.1, 131.1, 129.0, 128.6, 127.6, 127.4, 126.5, 125.3, 36.0, 33.3, 30.9, 28.6, 28.5, 28.3, 28.3, 28.0, 27.1, 21.7, 20.7, 20.1, 13.1. **HR-MS** (ESI): m/z calculated for $C_{32}H_{43}NO_3S$: $[M+Na]^+$: 544.2856, found: 544.2854. **FTIR** (KBr, cm^{-1}): 3851.40, 3445.90, 2962.62, 2931.78, 2829.53, 2715.89, 1602.64, 1365.32, 1201.87, 1120.56, 1068.71, 774.42.



3i

(2*Z*,5*E*,7*E*)-2-benzyl-4-methyl-8-phenyl-N-tosylocta-2,5,7-trienamide (3i)

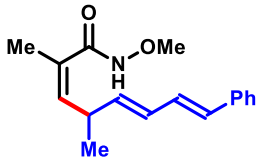
Following the general procedure, **3i** was obtained as a yellow oil (93%, 87.7 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.13 (s, 1H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.38 – 7.36 (m, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.25 (m, 2H), 7.22 – 7.19 (m, 4H), 7.04 – 7.00 (m, 2H), 6.70 (dd, *J* = 10.0, 16.0 Hz, 1H), 6.49 (d, *J* = 15.5 Hz, 1H), 6.19 (dd, *J* = 10.0, 15.0 Hz, 1H), 5.69 (dd, *J* = 7.0, 15.0 Hz, 1H), 5.59 (d, *J* = 10.0 Hz, 1H), 3.53 – 3.41 (m, 3H), 2.42 (s, 3H), 1.12 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (125 Hz, $CDCl_3$): δ = 164.8, 143.8, 140.5, 136.3, 136.2, 125.7, 134.3, 131.5, 131.0, 129.1, 128.5, 127.9, 127.6, 127.5, 127.3, 126.4, 125.9, 125.3, 39.4, 35.9, 20.7, 19.8. **HR-MS** (ESI): m/z calculated for $C_{29}H_{29}NO_3S$: $[M+Na]^+$: 494.1760, found: 494.1755. **FTIR** (KBr, cm^{-1}): 3859.81, 3742.06, 3445.02, 2956.12, 2829.07, 2724.30, 1605.40, 1365.56, 1123.36, 1068.61, 774.29.



3j

(2*Z*,5*E*,7*E*)-2,4-dimethyl-N-(methylsulfonyl)-8-phenylocta-2,5,7-trienamide (3j)

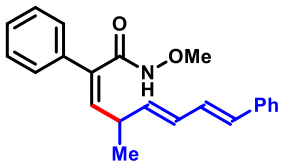
Following the general procedure, **3j** was obtained as a white oil (53%,39.5 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.27 (s, 1H), 7.38 – 7.32 (m, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.5 Hz, 1H), 6.72 (dd, *J* = 10.0, 15.5 Hz, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.27 (dd, *J* = 10.0, 15.0 Hz, 1H), 5.76 – 5.71 (m, 2H), 3.70 – 3.66 (m, 1H), 3.35 (s, 3H), 1.95 (d, *J* = 15.0 Hz, 3H), 1.17 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (125 Hz, $CDCl_3$): δ = 166.0, 143.3, 136.2, 135.8, 131.1, 129.2, 127.6, 127.5, 126.5, 126.2, 125.3, 40.7, 35.9, 19.8, 19.3. **HR-MS** (ESI): m/z calculated for $C_{17}H_{21}NO_3S$: $[M+Na]^+$: 342.1134, found: 342.1127. **FTIR** (KBr, cm^{-1}): 3851.40, 3744.86, 3444.33, 2968.22, 2829.67, 2724.30, 1601.51, 1364.59, 1114.95, 1072.90, 774.64.



3k

(2*Z*,5*E*,7*E*)-N-methoxy-2,4-dimethyl-8-phenylocta-2,5,7-trienamide (3k)

Following the general procedure, **3k** was obtained as a yellow oil (42%,11.4 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.35 (s, 1H), 7.38 – 7.36 (m, 2H), 7.31 – 7.29 (m, 2H), 7.23 – 7.20 (m, 1H), 6.73 (dd, *J* = 10.0, 15.5 Hz, 1H), 6.50 (d, *J* = 15.5 Hz, 1H), 6.20 (dd, *J* = 10.5, 15.5 Hz, 1H), 5.76 (dd, *J* = 7.0, 15.5 Hz, 1H), 5.47 (d, *J* = 10.0 Hz, 1H), 3.82 (s, 3H), 3.40 (s, 1H), 1.93 (s, 3H), 1.15 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (125 Hz, $CDCl_3$): δ = 166.8, 137.2, 136.3, 130.7, 128.4, 127.7, 127.6, 126.4, 125.2, 63.6, 36.1, 28.7, 20.1, 19.6. **HR-MS** (ESI): m/z calculated for $C_{17}H_{21}NO_2$: $[M+Na]^+$: 294.1465, found: 294.1455. **FTIR** (KBr, cm^{-1}): 3857.01, 3747.66, 3445.18, 2957.01, 2829.92, 2715.89, 1604.04, 1363.81, 1123.36, 1064.49, 774.66.

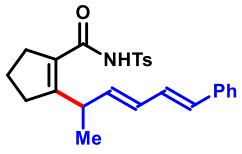


3l

(2*Z*,5*E*,7*E*)-N-methoxy-4-methyl-2,8-diphenylocta-2,5,7-trienamide (3l)

Following the general procedure, **3l** was obtained as a yellow oil (62%, 41.5 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.26 (s, 1H), 7.41 – 7.28 (m, 9H), 7.22 – 7.19 (m, 1H), 6.75 (dd, *J*= 10.5, 15.5

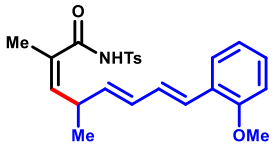
Hz, 1H), 6.51 (d, *J* = 15.5 Hz, 1H), 6.27 (dd, *J* = 10.5, 15.5 Hz, 1H), 5.98 (d, *J* = 10.0 Hz, 1H), 5.82 (dd, *J* = 7.0, 15.5 Hz, 1H), 3.86 (s, 3H), 3.58 – 3.56 (m, 1H), 1.26 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (125 Hz, $CDCl_3$): δ = 165.3, 137.5, 136.5, 136.3, 135.4, 132.4, 130.7, 128.8, 127.7, 127.6, 127.2, 126.4, 125.4, 125.2, 63.6, 36.5, 19.8. **HR-MS** (ESI): m/z calculated for $C_{22}H_{23}NO_2$: $[M+Na]^+$: 356.1621, found: 356.1613. **FTIR** (KBr, cm^{-1}): 3854.33, 3750.59, 3421.92, 2962.75, 2829.67, 2718.83, 2570.23, 2186.12, 1603.79, 1365.22, 1070.24, 774.60.



3m

2-((3*E*,5*E*)-6-phenylhexa-3,5-dien-2-yl)-N-tosylcyclopent-1-ene-1-carboxamide (3m)

Following the general procedure, **3m** was obtained as a yellow oil (21%, 17.7 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.22 (s, 1H), 8.01 – 7.99 (m, 2H), 7.36 – 7.34 (m, 4H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.22 – 7.18 (m, 1H), 6.69 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.46 (d, *J* = 15.7 Hz, 1H), 6.24 – 6.17 (m, 1H), 5.74 (dd, *J* = 15.2, 7.1 Hz, 1H), 4.31 – 4.24 (m, 1H), 2.57 – 2.46 (m, 4H), 2.43 (s, 3H), 1.87 – 1.79 (m, 2H), 1.13 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (125 Hz, $CDCl_3$): δ = 163.6, 161.6, 143.8, 136.3, 135.2, 134.9, 130.5 129.3 128.5, 127.8, 127.5, 127.5 126.3, 125.2 125.1, 35.1, 32.8, 32.3, 20.6, 17.3. **HR-MS** (ESI): m/z calculated for $C_{25}H_{27}NO_3S$: $[M+Na]^+$: 444.1604, found: 444.1615. **FTIR** (KBr, cm^{-1}): 3857.01, 3744.86, 3444.05, 2959.81, 2833.64, 2713.08, 2357.01, 1601.38, 1365.13, 1075.70, 775.40.

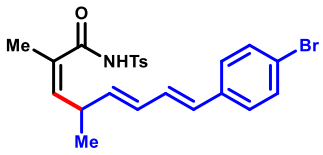


3n

(2*Z*,5*E*,7*E*)-8-(2-methoxyphenyl)-2,4-dimethyl-N-tosylocta-2,5,7-trienamide (3n)

Following the general procedure, **3n** was obtained as a yellow oil (44%, 37.7 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.25 (s, 1H), 8.00 (d, *J* = 8.5 Hz, 2H), 7.44 – 7.42 (m, 1H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.23 – 7.19 (m, 1H), 6.92 (t, *J* = 7.5 Hz, 1H),6.88 – 6.83 (m, 2H),6.75 – 6.70 (m, 1H), 6.99

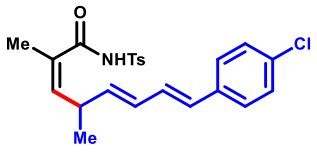
(dd, *J* = 10.0, 15.5 Hz, 1H), 5.68 – 5.60 (m, 2H), 3.86 (s, 3H), 3.46 – 3.39 (m, 1H), 2.45 (s, 3H), 1.87 (d, *J* = 1.5 Hz, 3H),1.09 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (125 Hz, $CDCl_3$): δ = 164.9, 155.7, 144.1, 141.5 135.2, 134.6, 129.8 128.6 128.1, 127.5, 127.5 125.9, 119.6, 109.9 54.5, 35.8 20.7 19.8, 19.3. **HR-MS** (ESI): m/z calculated for $C_{24}H_{27}NO_4S$: $[M+Na]^+$: 448.1553, found: 448.1544. **FTIR** (KBr, cm^{-1}): 3851.11, 3742.36, 3453.79, 2957.44, 2829.68, 2716.39, 1604.18, 1365.14, 1120.64, 1068.62, 774.76.



3o

(2*Z*,5*E*,7*E*)-8-(4-bromophenyl)-2,4-dimethyl-N-tosylocta-2,5,7-trienamide (3o)

Following the general procedure, **3o** was obtained as a yellow oil (61%, 57.5 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.32 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.42 – 7.40 (m, 2H), 7.35 – 7.34 (m, 2H), 7.23 – 7.21 (m,2 H), 6.67 (dd, *J* = 10.0, 15.5 Hz, 1H), 6.42 (d, *J* = 15.5 Hz, 1H), 6.16 (dd, *J* = 10.5, 15.5 Hz, 1H), 5.70 (dd, *J* = 7.0, 15.0 Hz, 1H), 5.59 (dd, *J* = 1.5, 10.0 Hz, 1H), 3.47 – 3.43 (m, 1H), 2.44 (s, 3H), 1.87 (d, *J* = 1.0 Hz, 3H), 1.09 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (125 Hz, $CDCl_3$): δ = 164.9 144.1, 141.4, 136.7 135.2, 134.6, 130.7, 129.6 128.7, 128.6 128.2, 127.5 126.9, 126.7, 120.1, 35.8, 20.7, 19.7, 19.3. **HR-MS** (ESI): m/z calculated for $C_{23}H_{24}BrNO_3S$: $[M+Na]^+$: 496.0552, found: 496.0552. **FTIR** (KBr, cm^{-1}): 3849.47, 3740.57, 3441.06, 2962.62, 2829.58, 2724.30, 1602.03, 1364.08, 1117.44, 1072.90, 774.56.

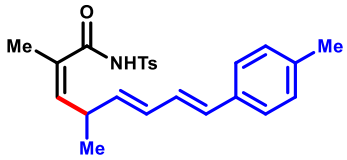


3p

(2*Z*,5*E*,7*E*)-8-(4-chlorophenyl)-2,4-dimethyl-N-tosylocta-2,5,7-trienamide (3p)

Following the general procedure, **3p** was obtained as a yellow oil (64%, 55.3 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.33 (s, 1H), 7.98 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.25 (m, 4H), 6.66 (dd, *J* = 10.5, 15.5 Hz, 1H), 6.44 (d, *J* = 15.5 Hz, 1H), 6.16 (dd, *J* = 10.5, 15.5 Hz, 1H),

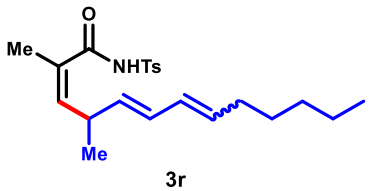
5.69 (dd, *J* = 7.0, 15.0 Hz, 1H), 5.59 (dd, *J* = 1.5, 10.0 Hz, 1H), 3.50 – 3.43 (m, 1H), 2.43 (s, 3H), 1.87 (d, *J* = 1.5 Hz, 3H), 1.09 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (125 Hz, $CDCl_3$): δ = 164.9, 144.1, 141.4, 136.6, 134.8, 134.6, 131.9, 129.6, 128.7, 128.6, 128.1, 127.7, 127.5, 126.9, 126.4, 35.8, 28.7, 20.7, 19.7, 19.3. **HR-MS** (ESI): m/z calculated for $C_{23}H_{24}ClNO_3S$: $[M+Na]^+$: 452.1058, found: 452.1055. **FTIR** (KBr, cm^{-1}): 3849.47, 3740.57, 3444.49, 2959.81, 2829.34, 2718.69, 1602.52, 1363.46, 1120.64, 1072.90, 774.51.



3q

(2*Z*,5*E*,7*E*)-2,4-dimethyl-8-(p-tolyl)-N-tosylocta-2,5,7-trienamide (3q)

Following the general procedure, **3q** was obtained as a yellow oil (49%, 40.1 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.18 (s, 1H), 7.99 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.28 – 7.26 (m, 2H), 7.12 – 7.11 (m, 2H), 6.65 (dd, *J* = 10.5, 16.0 Hz, 1H), 6.48 (d, *J* = 15.5 Hz, 1H), 6.17 (dd, *J* = 10.0, 15.0 Hz, 1H), 5.67 – 5.60 (m, 2H), 3.48 – 3.41 (m, 1H), 2.44 (s, 3H), 2.33 (s, 3H), 1.86 (d, *J* = 1.5 Hz, 3H), 1.09 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (125 Hz, $CDCl_3$): δ = 164.8, 144.1, 141.5, 136.4, 135.2, 134.6, 133.4, 131.1, 129.2, 128.6, 128.3, 127.5, 126.9, 126.5, 125.2, 35.9, 20.7, 20.2, 19.9, 19.3. **HR-MS** (ESI): m/z calculated for $C_{24}H_{27}NO_3S$: $[M+ Na]^+$: 432.1604, found: 432.1609. **FTIR** (KBr, cm^{-1}): 3849.47, 3737.37, 3445.05, 2951.53, 2829.30, 2716.02, 1605.24, 1363.94, 1114.23, 1073.05, 774.38.

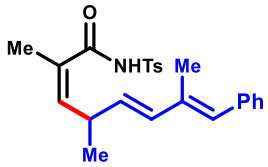


3r

(2*Z*)-2,4-dimethyl-N-tosyltrideca-2,5,7-trienamide (3r)

Following the general procedure, **3r** was obtained as a yellow oil as a mixture of isomers (47%, 37.3 mg, (5*E*,7*E*):(5*E*,7*Z*)=80:20). Data for major(5*E*,7*E*) isomer: **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.15 (s, 1H), 7.98 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.02 – 5.89 (m, 2H), 5.71 – 5.64

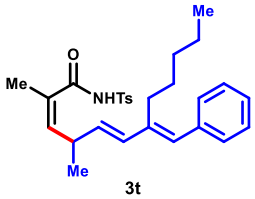
(m, 1H), 5.58 (dd, *J* = 1.5, 10.5 Hz, 1H), 5.43 (dd, *J* = 7.0, 14.5 Hz, 1H), 3.36 – 3.28 (m, 1H), 2.45(s, 3H), 2.06 (q, *J* = 7.0 Hz, 2H), 1.84 (d, *J* = 1.5 Hz, 3H), 1.41 – 1.26 (m, 6H), 1.07 – 1.04 (m, 3H), 0.89 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (125 Hz, $CDCl_3$): δ = 165.0, 144.1, 141.4, 134.7, 134.1, 132.6, 129.2, 128.6, 128.4, 127.5, 126.9, 35.7, 31.6, 30.4, 17.9, 21.5, 20.7, 20.0, 19.3, 13.0. **HR-MS** (ESI): m/z calculated for $C_{22}H_{31}NO_3S$: $[M+Na]^+$: 412.1917, found: 412.1910. **FTIR** (KBr, cm^{-1}): 3848.60, 3744.86, 3460.36, 2959.81, 2829.25, 2715.89, 1604.62, 1364.67, 1120.64, 1070.09, 774.50.



3s

(2*Z*,5*E*,7*E*)-2,4,7-trimethyl-8-phenyl-N-tosylocta-2,5,7-trienamide (3s)

Following the general procedure, **3s** was obtained as a yellow oil (50%, 41.2 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.26 (s, 1H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.20 (m, 4H), 7.28 – 7.27 (m, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 6.49 (s, 1H), 6.22 (d, *J* = 15.5 Hz, 1H), 5.65 – 5.60 (m, 2H), 3.50 –3.43 (m, 1H), 2.43 (s, 3H), 1.96 (s, 3H), 1.87 (d, *J* = 1.0 Hz, 3H), 1.11 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (125 Hz, $CDCl_3$): δ = 164.5, 144.1, 141.7, 136.8, 134.6, 134.1, 133.8, 130.9, 130.2, 128.6, 128.2, 127.5, 127.1, 126.8, 125.5, 36.0, 20.7, 20.2, 19.3, 12.9. **HR-MS** (ESI): m/z calculated for $C_{24}H_{27}NO_3S$: $[M+Na]^+$: 432.1604, found: 432.1599. **FTIR** (KBr, cm^{-1}): 3851.40, 3744.86, 3442.05, 2962.62, 2829.71, 2718.69, 1602.15, 1363.61, 1120.64, 1067.29, 774.51.

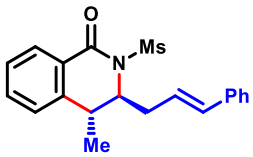


3t

(2*Z*,5*E*)-7-((*E*)-benzylidene)-2,4-dimethyl-N-tosyldodeca-2,5-dienamide (3t)

Following the general procedure, **3t** was obtained as a white oil (51%, 47.6 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.19 (s, 1H), 7.99 (d, *J* = 8.5 Hz, 2H), 7.36 – 7.32 (m, 4H), 7.27 – 7.26 (m, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 6.44 (s, 1H), 6.10 (d, *J* = 16.0 Hz, 1H), 5.66 – 5.61 (m, 2H), 3.49 – 3.42 (m, 1H), 2.44 (s, 3H), 2.41 – 2.36 (m, 2H), 1.88 (d, *J* = 1.0 Hz, 3H), 1.56 – 1.49 (m, 2H), 1.35 –

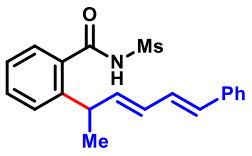
1.31 (m, 4H), 1.11 (d, *J* = 6.5 Hz, 3H), 0.91 – 0.88 (m, 3H). **^{13}C NMR** (125 Hz, $CDCl_3$): δ = 164.9, 144.1, 141.6, 139.1, 136.7, 134.7, 132.8, 130.6, 129.7, 128.6, 127.7, 127.2, 127.0, 125.6, 36.1, 31.1, 27.8, 26.4, 21.4, 20.7, 20.3, 19.3, 13.0. **HR-MS** (ESI): m/z calculated for $C_{28}H_{35}NO_3S$: $[M+Na]^+$: 488.2230, found: 488.2223. **FTIR** (KBr, cm^{-1}): 3857.01, 3740.57, 3450.53, 2956.68, 2829.41, 2716.68, 1603.11, 1363.38, 1120.64, 1068.56, 774.39.



5a(*trans*)

***N*-Methylsulfonyl-*trans*-3-cinnamyl-4-methyltetrahydroisoquinolinone (5a)**

Following the general procedure, 5**a** was obtained as a yellow oil (52%, 36.7 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.8 Hz, 1H), 7.59 – 7.56 (m, 1H), 7.43 – 7.40 (m, 1H), 7.31 – 7.27 (m, 4H), 7.24 – 7.20 (m, 1H), 6.27 (d, *J* = 15.7 Hz, 1H), 6.16 – 6.10 (m, 1H), 4.68 (td, *J* = 7.3, 1.7 Hz, 1H), 3.44 (s, 3H), 3.15 (q, *J* = 6.9 Hz, 1H), 2.56 – 2.50 (m, *J* = 14.4, 7.3, 1.2 Hz, 1H), 2.43 – 2.33 (m, 1H), 1.37 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (125 Hz, $CDCl_3$): δ = 163.7, 143.2, 136.6, 134.4, 133.8, 129.3, 128.7, 128.5, 128.20, 128.0, 127.7, 127.6, 126.5, 126.2, 125.0, 60.7, 43.0, 38.6, 36.9, 22.1. **HR-MS** (ESI): m/z calculated for $C_{20}H_{21}NO_3S$: $[M+Na]^+$: 378.1134, found: 378.1125. **FTIR** (KBr, cm^{-1}): 3447.66, 2830.84, 2715.89, 1600.00, 1358.88, 1070.09, 775.70.

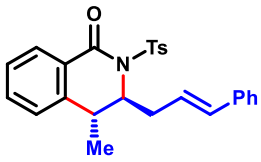


6a

(N-(methylsulfonyl)-2-((3*E*,5*E*)-6-phenylhexa-3,5-dien-2-yl)benzamide (6a)

Following the general procedure, **6a** was obtained as a yellow oil (27%, 19.2 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.32 (s, 1H), 7.53 – 7.46 (m, 2H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.32 – 7.27 (m, 3H), 7.22 – 7.19 (m, 1H), 6.74 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.49 (d, *J* = 15.7 Hz, 1H), 6.32 – 6.15 (m, 1H), 5.95 (dd, *J* = 15.3, 6.8 Hz, 1H),4.20 – 4.14 (m, 1H), 3.40 (s, 3H), 1.45 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (125 Hz, $CDCl_3$): δ = 167.6, 144.9, 138.7, 137.2, 132.3, 132.0, 131.9,

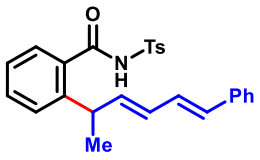
130.2, 128.6, 128.6, 128.3, 127.5, 127.5, 126.6, 126.3, 41.7, 38.0, 21.1. **HR-MS** (ESI): m/z calculated for $C_{20}H_{21}NO_3S$: $[M+Na]^+$: 378.1134, found: 378.1134. **FTIR** (KBr, cm^{-1}): 3444.86, 2833.64, 2721.50, 1600.00, 1364.49, 1070.09, 775.70.



5b(*trans*)

***N*-Tosyl-*trans*-3-cinnamyl-4-methyltetrahydroisoquinolinone (5b)**

Following the general procedure, **5b** was obtained as a yellow oil (65%, 56.1 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 8.4 Hz, 2H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.51 – 7.48 (m, 1H), 7.33 – 7.26 (m, 7H), 7.24 – 7.21 (m, 1H), 7.17 (dd, *J* = 7.6, 1.1 Hz, 1H), 6.25 (d, *J* = 15.8 Hz, 1H), 6.14 – 6.08 (m, 1H), 4.80 (ddd, *J* = 9.4, 5.1, 1.7 Hz, 1H), 3.19 (qd, *J* = 6.9, 1.7 Hz, 1H), 2.74 – 2.69 (m, 1H), 2.42 – 2.37 (m, 4H), 1.29 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (125 Hz, $CDCl_3$): δ = 162.4, 144.8, 142.8, 136.9, 136.4, 134.0, 133.8, 129.3, 129.2, 129.2, 129.1, 129.1, 128.6, 128.3, 127.7, 127.6, 127.5, 127.0, 126.2, 124.8, 61.5, 38.7, 36.3, 22.5, 21.7. **HR-MS** (ESI): m/z calculated for $C_{26}H_{25}NO_3S$: $[M+Na]^+$: 454.1447, found: 454.1444. **FTIR** (KBr, cm^{-1}): 3439.25, 2957.01, 2828.04, 2721.50, 1605.61, 1364.49, 1070.09, 770.09.



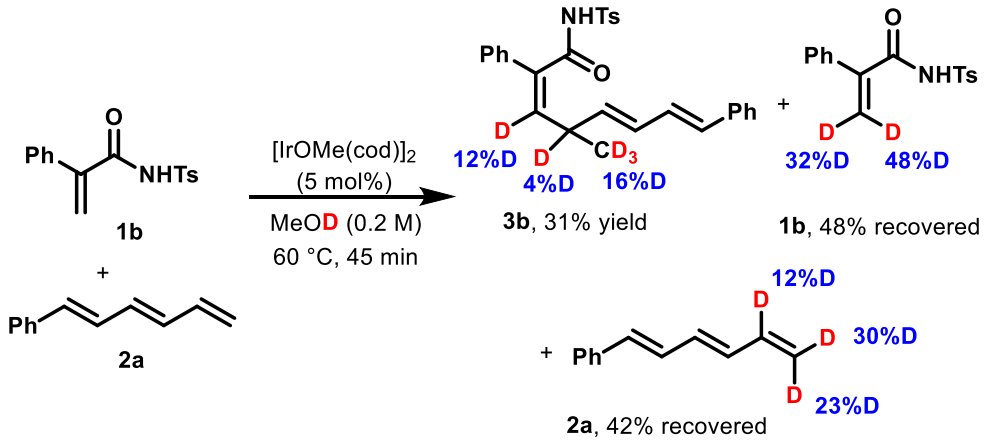
6b

2-((3*E*,5*E*)-6-phenylhexa-3,5-dien-2-yl)-N-tosylbenzamid (6b)

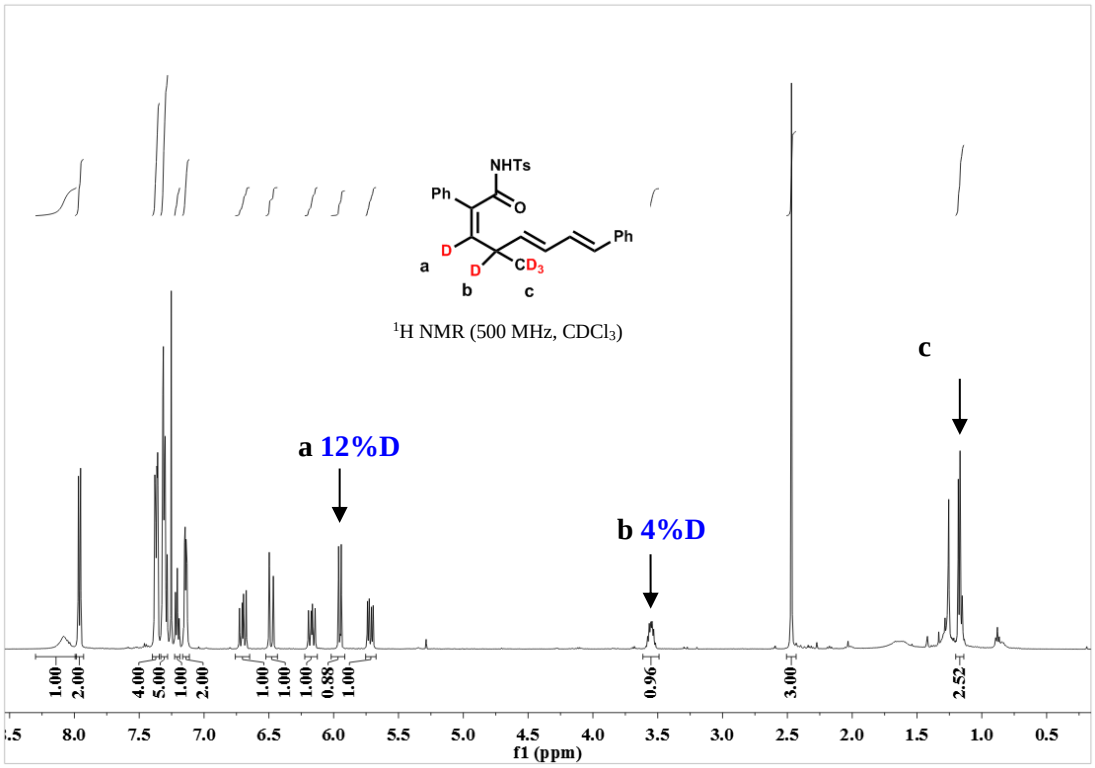
Following the general procedure, **6b** was obtained as a yellow oil (19%, 16.4 mg). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.53 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.43 (td, *J* = 7.6, 1.4 Hz, 1H), 7.36 – 7.33 (m, 6H), 7.31 – 7.28 (m, 2H), 7.24 – 7.17 (m, 2H), 6.66 (dd, *J* = 15.6, 10.3 Hz, 1H), 6.43 (d, *J* = 15.7 Hz, 1H), 6.05 (dd, *J* = 15.3, 10.2 Hz, 1H), 5.86 (dd, *J* = 15.3, 6.6 Hz, 1H), 3.95 – 3.90 (m, 1H), 2.45 (s, 2H), 1.31 (d, *J* = 7.0 Hz, 2H). **^{13}C NMR** (125 Hz, $CDCl_3$): δ = 166.5, 145.2, 144.7, 138.8, 137.3, 135.5, 132.4, 131.9, 131.6, 129.9, 129.7, 128.7, 128.6, 128.1, 127.4, 127.2, 126.4, 126.3,

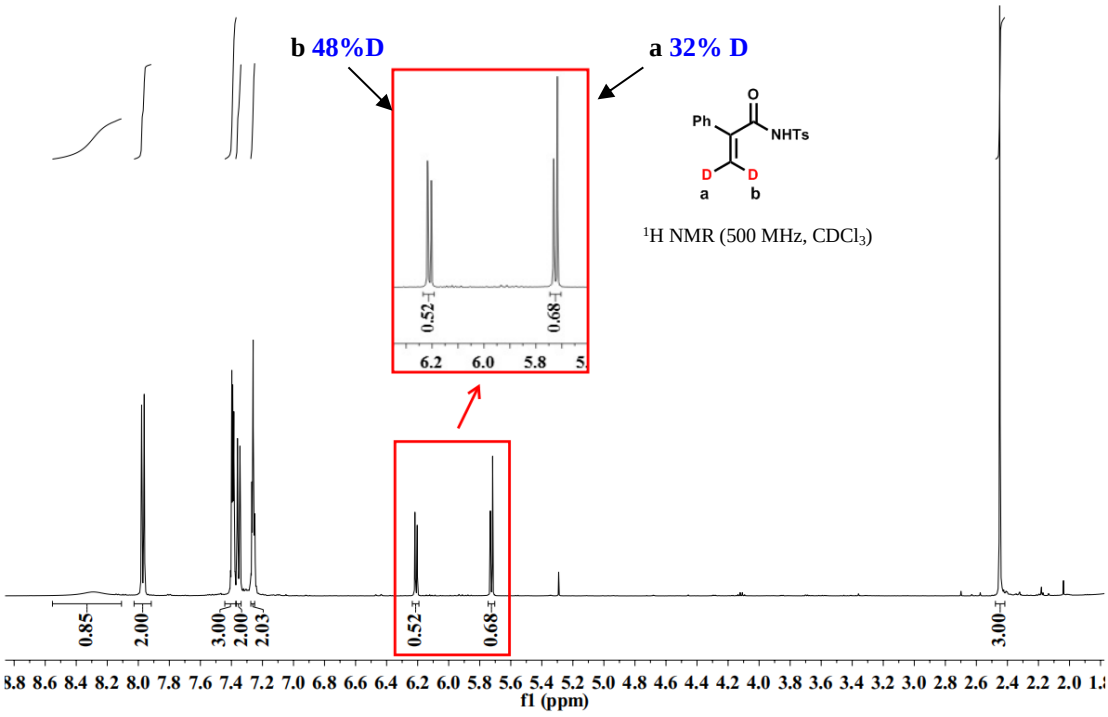
37.7, 21.8, 21.1. **HR-MS** (ESI): m/z calculated for $C_{26}H_{25}NO_3S$: $[M+Na]^+$: 454.1447, found: 454.1444. **FTIR** (KBr, cm^{-1}): 3444.99, 2828.17, 2718.83, 1611.36, 1364.49, 1070.09, 775.70.

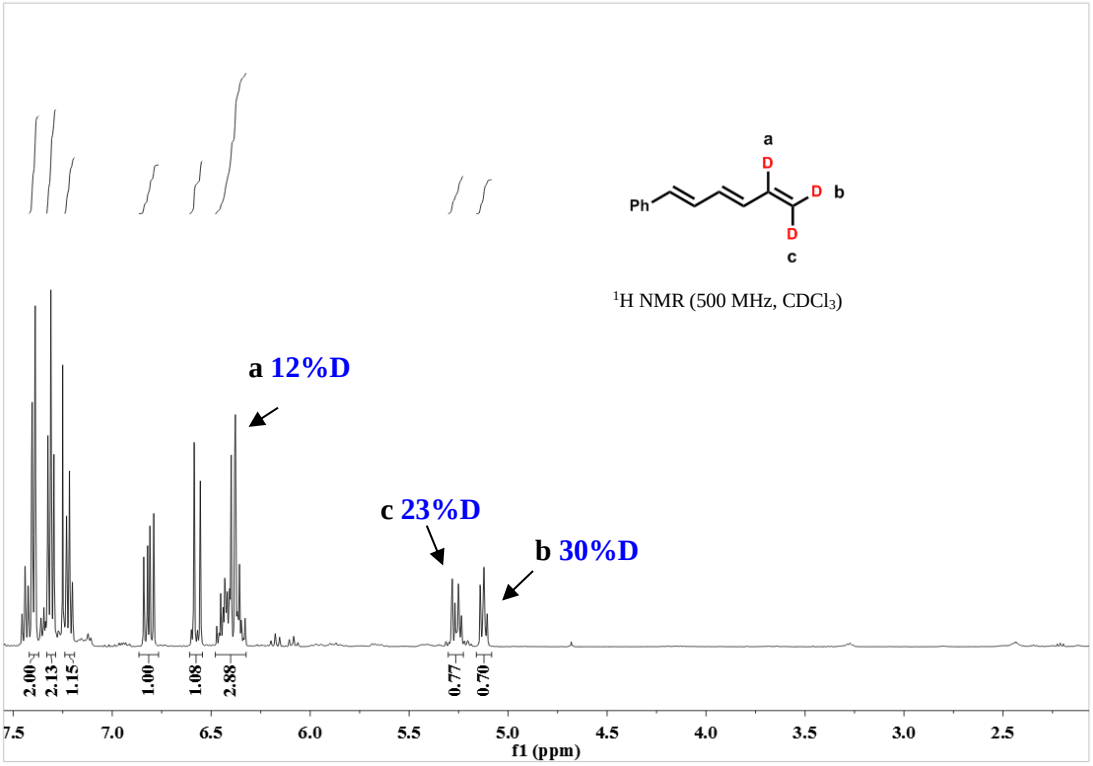
Deuterium-labelled experiment of alkenyl C-H allylation

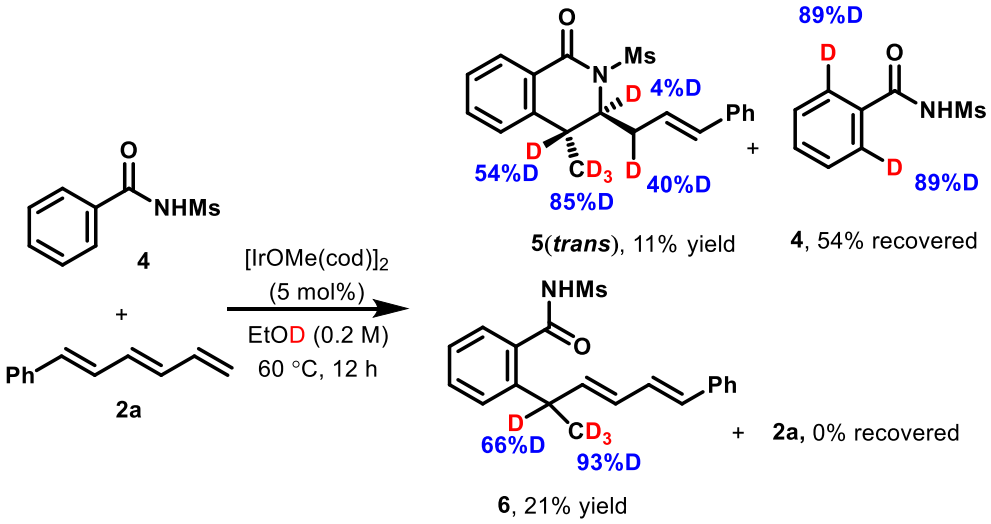


A screw-cap vial was charged with $[IrOMe(cod)]_2$ (5 mol%) and CH_3OD (1.0 mL). Then, **1b** (1.0 equiv, 0.2 mmol), **2a** (1.2 equiv, 0.24 mmol) was added into the solution in sequence. The vial was sealed under argon and heated in an oil bath to 60 °C with stirring for 45 min. After cooling down, the mixture was directly applied to a flash column chromatography (ethyl acetate/petroleum ether mixtures) for separation. The D% of product **3b**, the starting materials **1b** and **2a** were estimated by ^1H NMR.

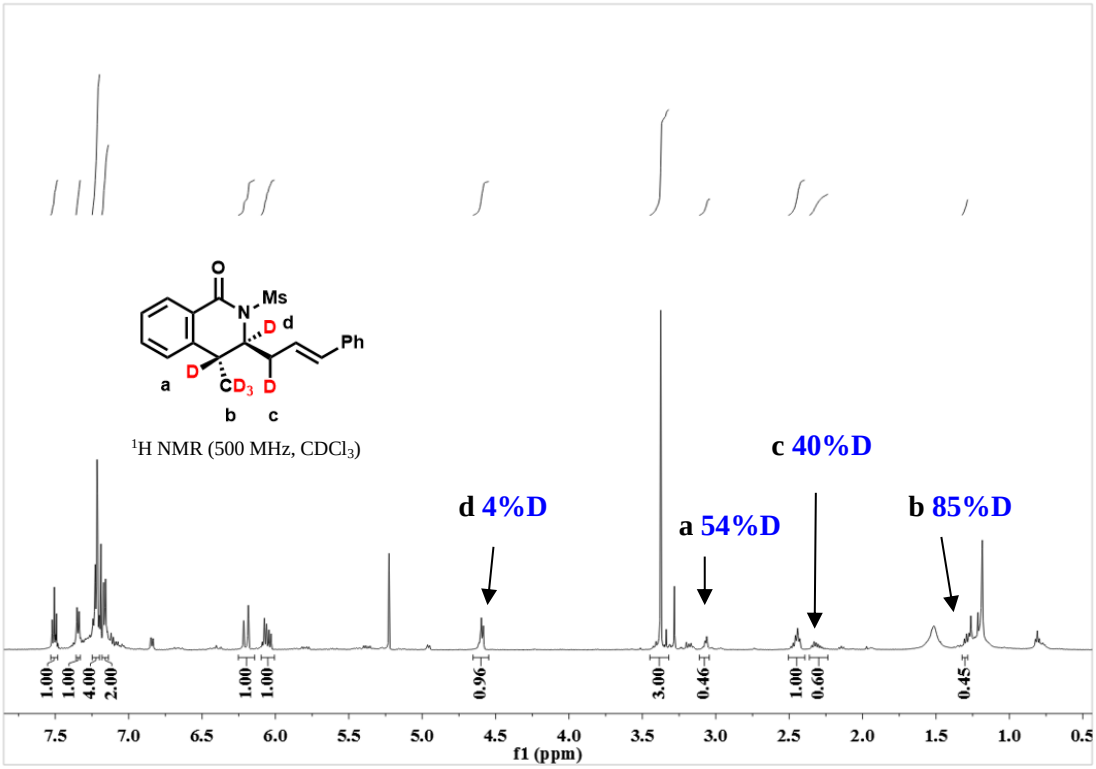

NHTs
Ph
O
D
D
CD3
Ph
a
b
c
1H NMR (500 MHz, CDCl3)
a 12%D
b 4%D
c
1.00
2.00
4.00
5.00
1.00
2.00
1.00
1.00
1.00
0.88
1.00
0.96
3.00
2.52
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

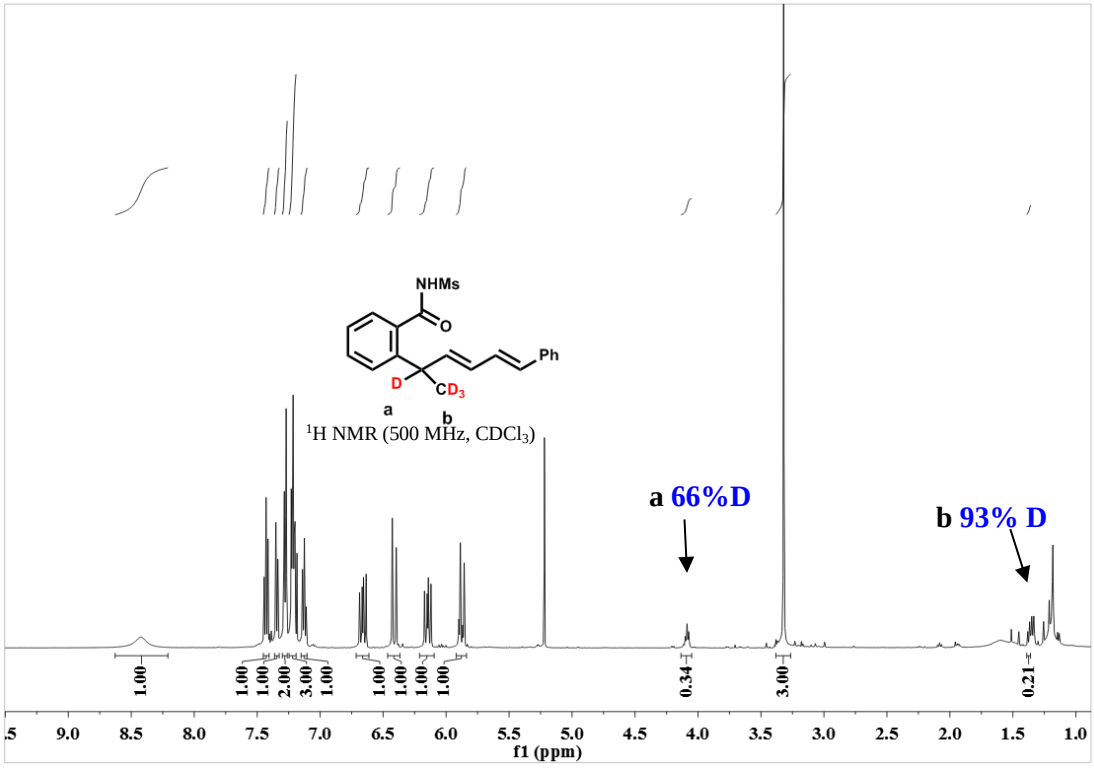

b 48%D
a 32% D
O
Ph
NHTs
D
D
a
b
1H NMR (500 MHz, CDCl3)
0.52
0.68
6.2
6.0
5.8
0.85
2.00
3.00
2.00
2.03
0.52
0.68
3.00
f1 (ppm)

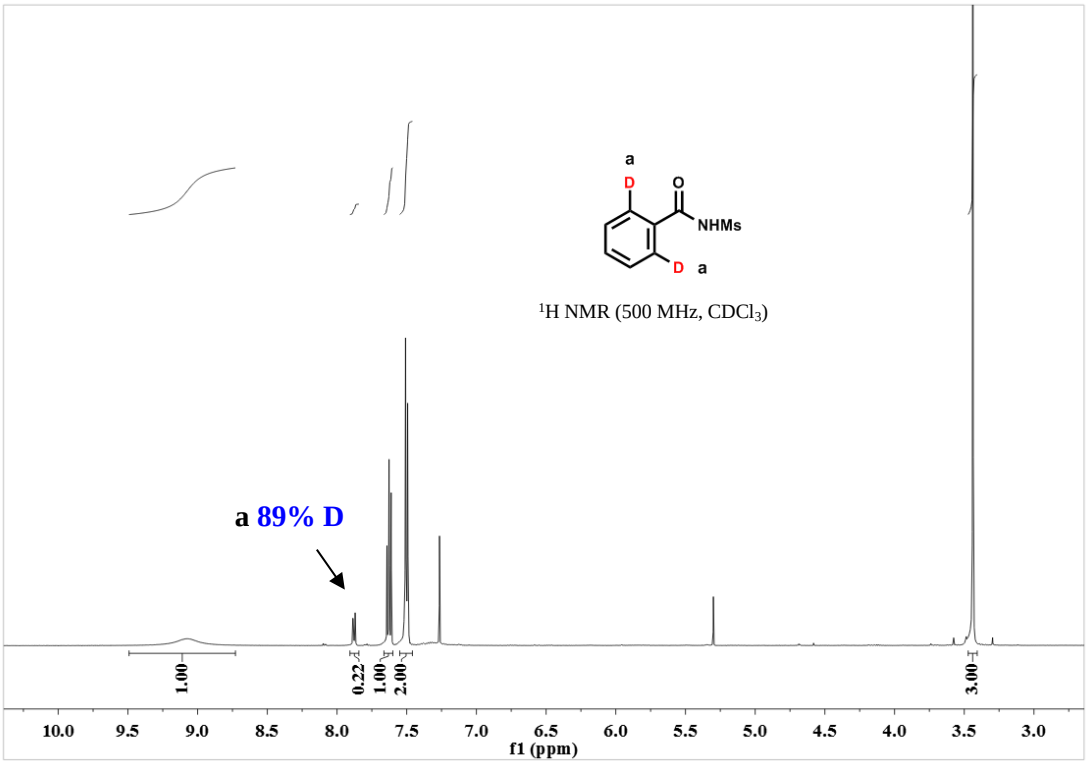




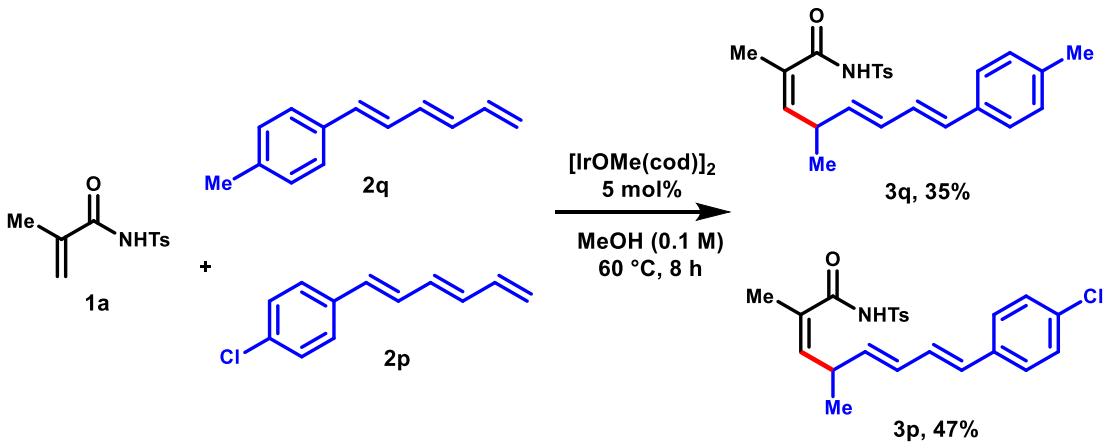
A screw-cap vial was charged with [IrOMe(cod)]$_2$ (5 mol%) and EtOD (1.0 mL). Then, **1b** (1.0 equiv, 0.2 mmol), **2a** (1.2 equiv, 0.24 mmol) was added into the solution in sequence. The vial was sealed under argon and heated in an oil bath to 60 °C with stirring for 12 h. After cooling down, the mixture was directly applied to a flash column chromatography (ethyl acetate/petroleum ether mixtures) for separation. The D% of product **5** and **6**, the starting materials **4** and **2a** were estimated by ^{1}H NMR.


Ms
N
O
D
d
Ph
D
CD3
D
a
b
c
1H NMR (500 MHz, CDCl3)
d 4%D
a 54%D
c 40%D
b 85%D
1.00
1.00
4.00
2.00
1.00
1.00
0.96
3.00
0.46
1.00
0.60
0.45
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

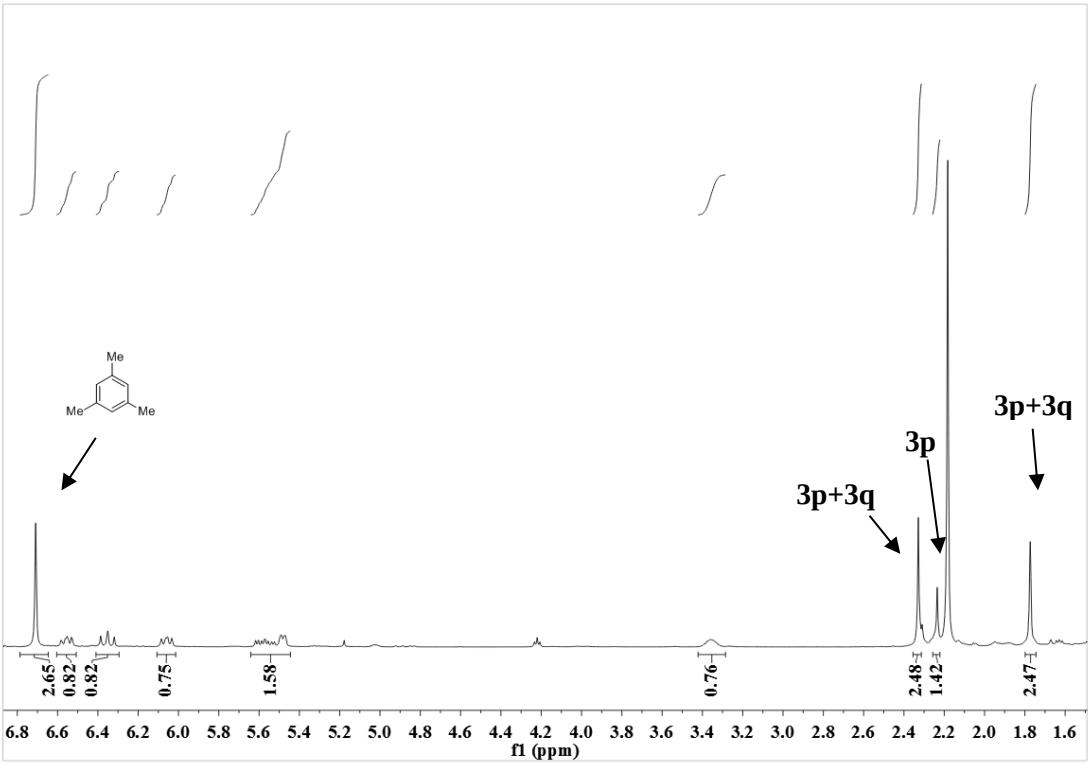

NHMs
O
Ph
D
CD3
a
b
1H NMR (500 MHz, CDCl3)
a 66%D
b 93% D
1.00
1.00
1.00
2.00
3.00
1.00
1.00
1.00
1.00
1.00
0.34
3.00
0.21
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

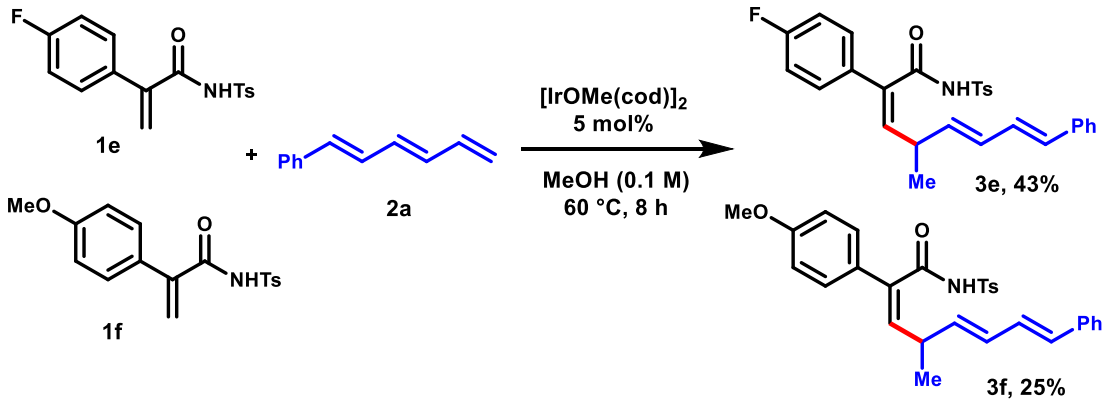

a
D
O
NHMs
D a
^{1}H NMR (500 MHz, CDCl$_3$)
a 89% D
1.00
0.22
1.00
2.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
f1 (ppm)

Competition Experiments

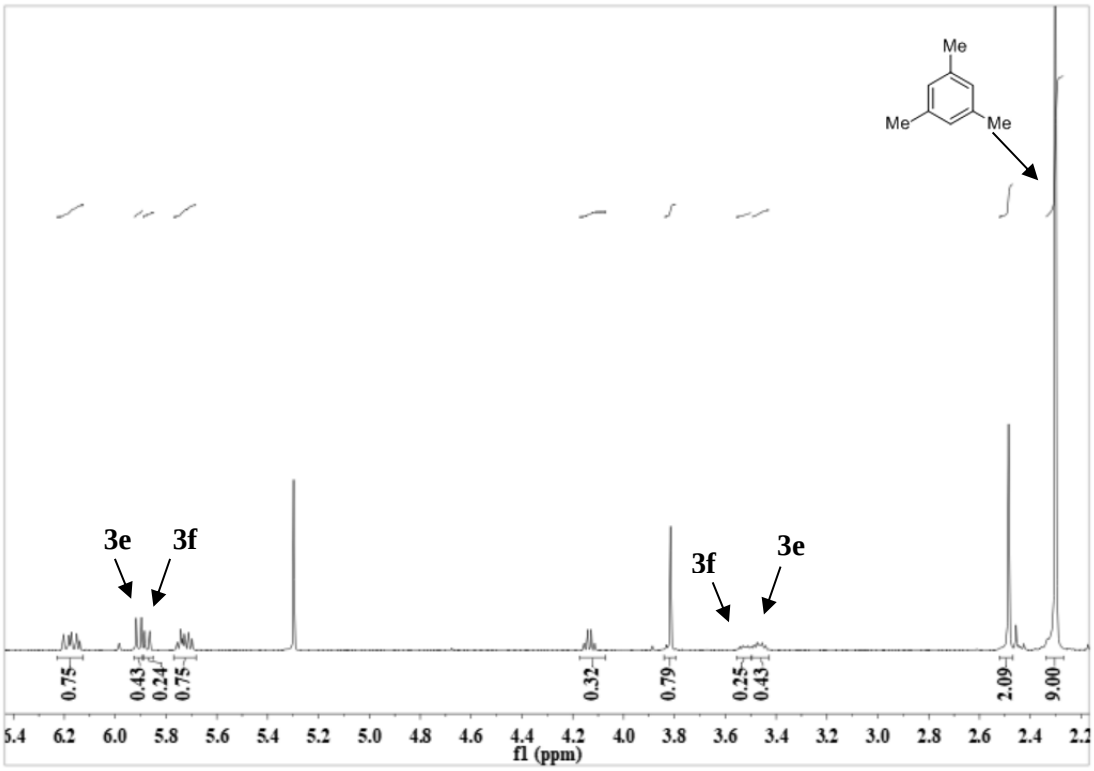


An screw-cap vial was charged with $[IrOMe(cod)]_2$ (5 mol %, 0.01 mmol) and methanol (1 mL). Then, **1a** (1.0 equiv, 0.1 mmol), **2p** (1.0 equiv, 0.1 mmol) and **2q** (1.0 equiv, 0.1 mmol) were added into the solution in sequence. The vial was sealed under argon and heated in an oil bath to 60 °C with stirring for 8 h. After cooling down, the mixture was directly applied to a flash column chromatography (ethyl acetate/petroleum ether mixtures). The product yields were estimated by ^1H NMR.

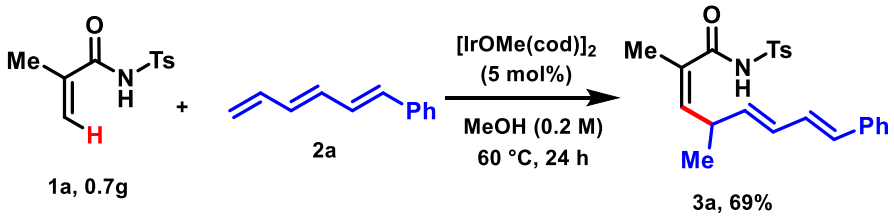




An screw-cap vial was charged with $[IrOMe(cod)]_2$ (5 mol %, 0.01 mmol) and methanol (1 mL). Then,**1e** (1.0 equiv, 0.1 mmol), **1f** (1.0 equiv, 0.1 mmol) and **2a** (1.0 equiv, 0.1 mmol) were added into the solution in sequence. The vial was sealed under argon and heated in an oil bath to 60 °C with stirring for 8 h. After cooling down, the mixture was directly applied to a flash column chromatography (ethyl acetate/petroleum ether mixtures). The product yields were estimated by ^1H NMR.

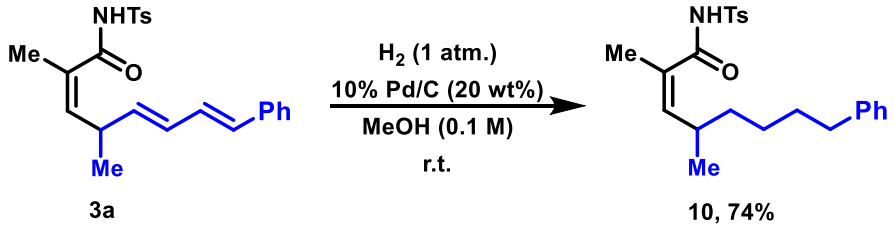


Gram-Scaled Synthesis



A dry screw-cap vial was charged with $[IrOMe(cod)]_2$ (5 mol%, 0.15 mmol, 97.7 mg) and methanol (14.0 mL). Then, acrylamide **1** (1.0 equiv, 2.93 mmol, 0.7 g) and triene **2** (1.2 equiv, 3.52 mmol, 549.3 mg) were added into the solution in sequence. The vial was sealed under argon and heated in an oil bath to 60 °C with stirring for 24 h. After cooling down, the mixture was directly applied to a flash column chromatography for separation (ethyl acetate/petroleum ether mixtures) to provide 1,4,6-triene product **3a**. The desires product **3a** was obtained as a yellow liquid (799.6 mg, 69%).

Hydrogenation



Amide **3a** was dissolved in MeOH (1.0 mL),and Pd/C (20 mol%) was added.Under H_2,The mixture was stirred at room temperature overnight. The reaction mixture was concentrated in vacuo and applied to a flash column chromatography for separation (ethyl acetate/petroleum ether mixtures) to provide product **10**. **10** was obtained as a white oil, yield = 74%. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 8.49 (s, 1H), 8.00 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.27 – 7.24 (m, 2H), 7.18 – 7.12 (m, 3H), 6.20 (dd, *J* = 9.8, 1.1 Hz, 1H), 2.55 (td, *J* = 7.5, 4.2 Hz, 3H), 2.43 – 2.42 (s, 4H), 1.75 (d, *J* = 1.2 Hz, 4H), 1.57 – 1.51 (m, 3H), 1.40 – 1.33 (m, 2H), 0.94 (d, *J* = 6.6 Hz, 3H), 0.90 – 0.87 (m, 1H). **^{13}C NMR** (125 Hz, $CDCl_3$): δ = 165.9, 147.1, 145.0, 142.5, 135.6, 129.5, 128.6, 128.4, 128.3, 128.0, 125.7, 36.5 35.8, 33.5, 31.5, 27.0, 21.7, 19.8, 12.4. **HR-MS** (ESI): m/z

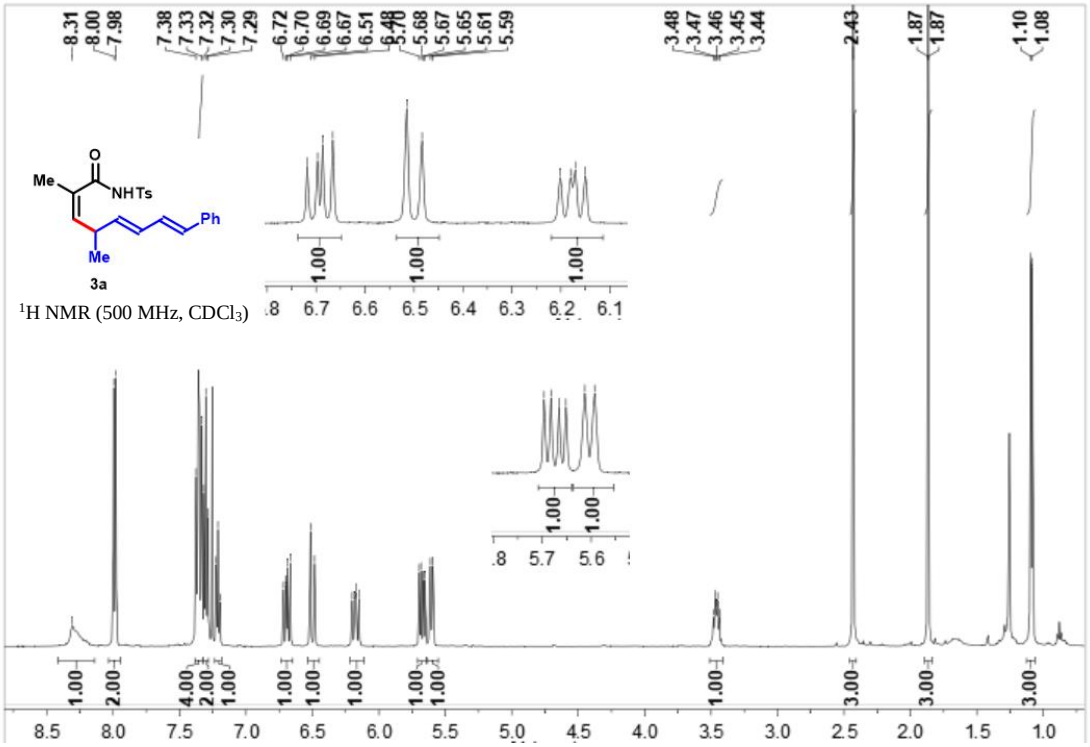
calculated for $C_{23}H_{29}NO_3S$: $[M+Na]^+$: 422.1760, found: 422.1770. **FTIR** (KBr, cm^{-1}): 3854.21, 3744.86, 3444.75, 2962.62, 2830.44, 2713.08, 2357.01, 2323.36, 1600.31, 1364.92, 1067.29, 775.62.

References

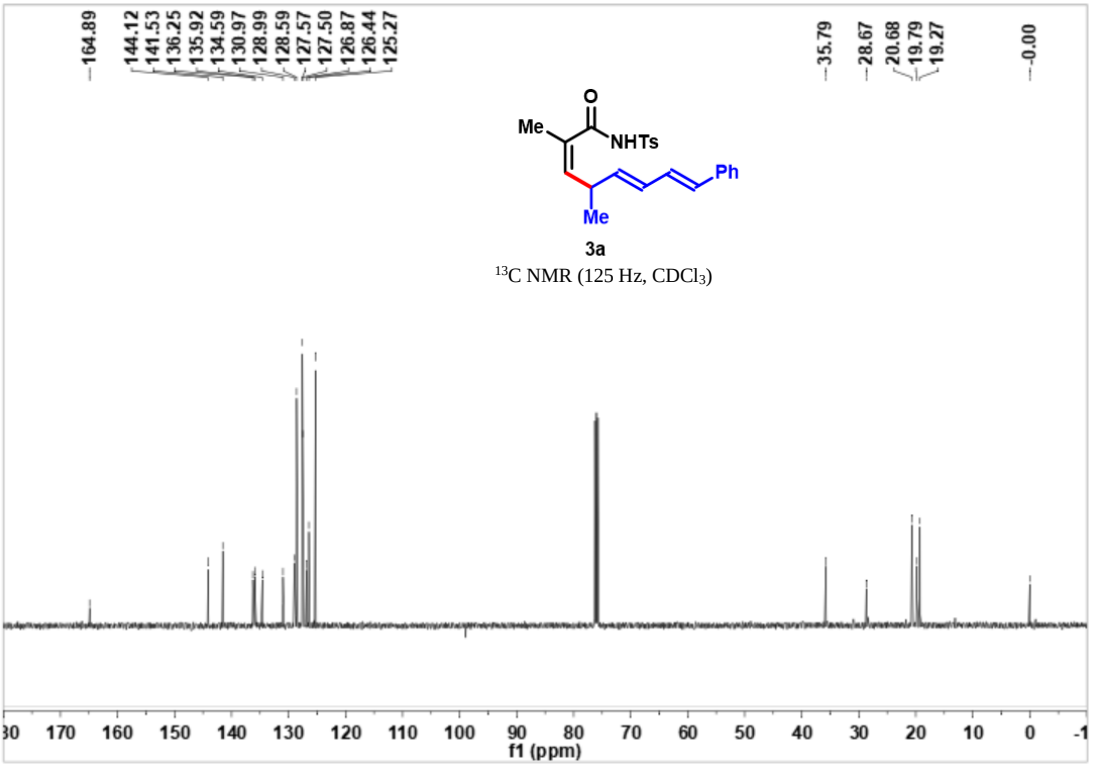
1. Xu, L.; Meng, K.; Zhang, J.; Sun, Y.; Lu, X.; Li, T.; Jiang Y.; Zhong, G. *Chem. Commun.* **2019**, *55*, 9757–9760.

2. Li, P-F.; Wang, H.-L.; Qu, J. *J. Org. Chem.* **2014**, *79*, 3955−3962.

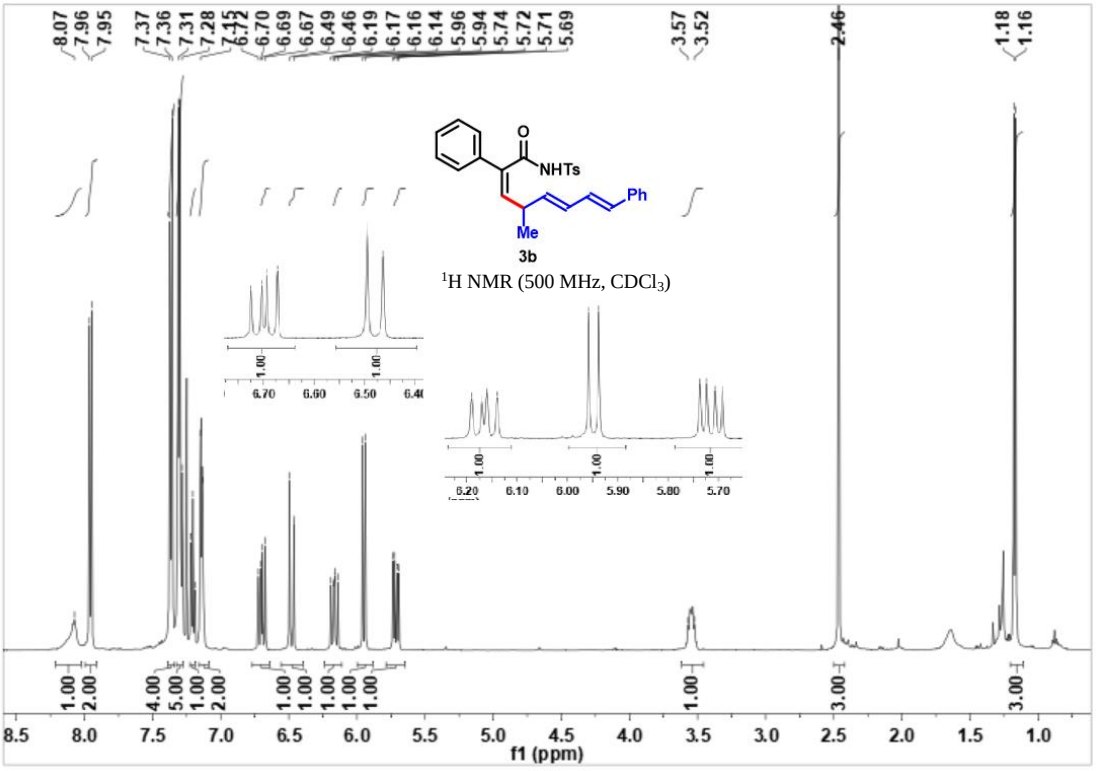
NMR Spectra



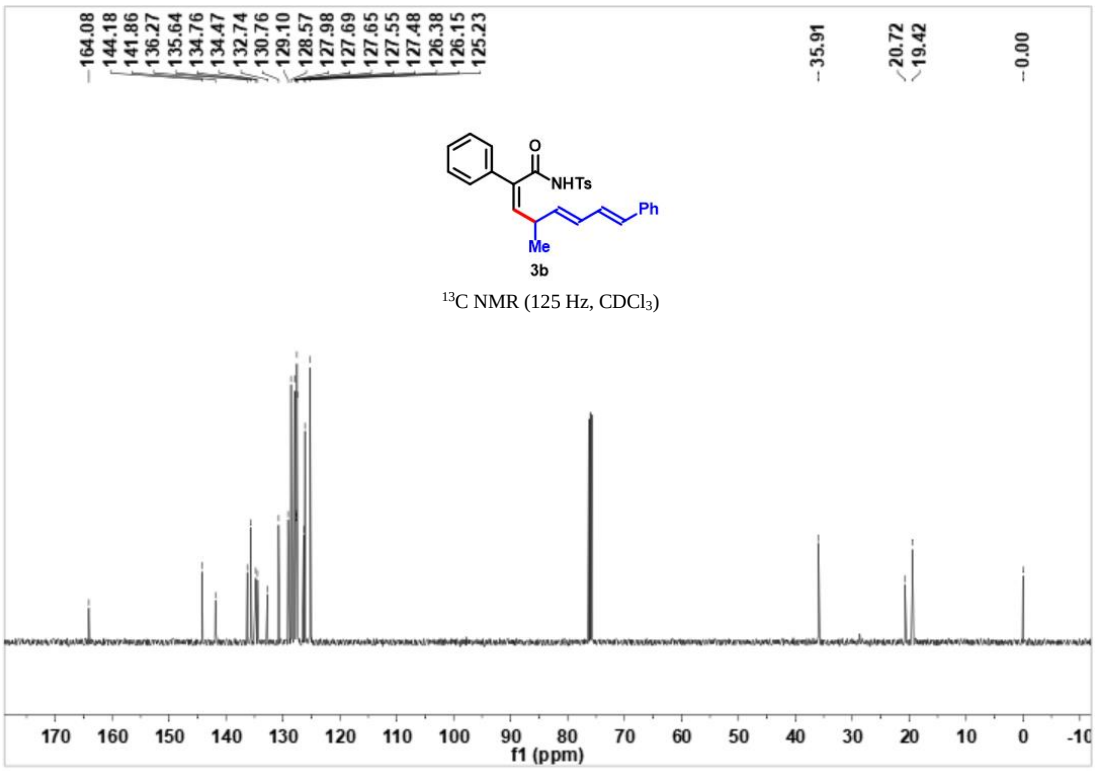
^{1}H NMR (500 MHz, $CDCl_3$)



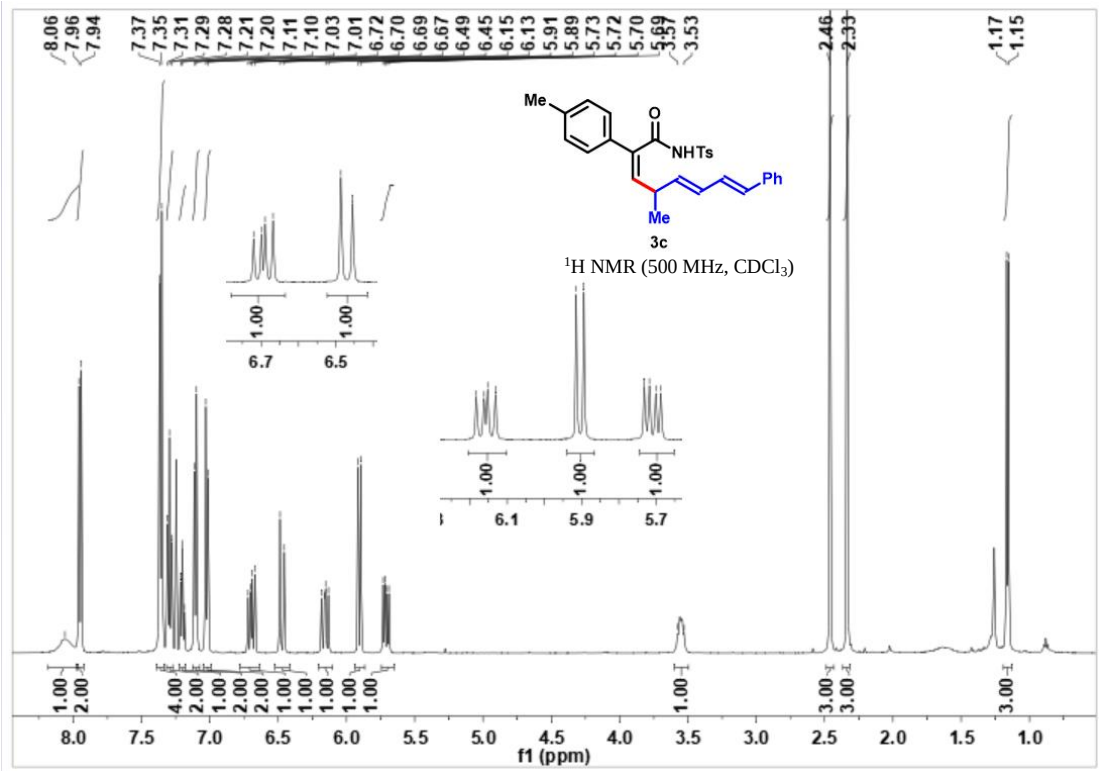
^{13}C NMR (125 Hz, $CDCl_3$)



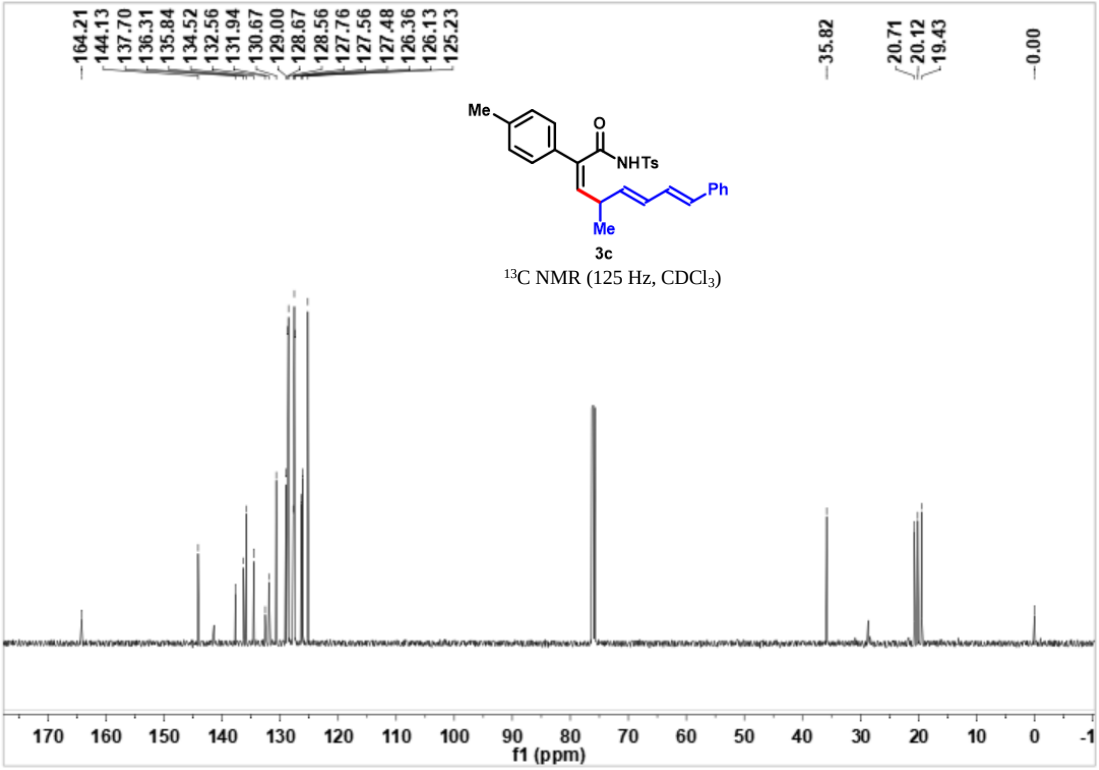
^{1}H NMR (500 MHz, $CDCl_3$)



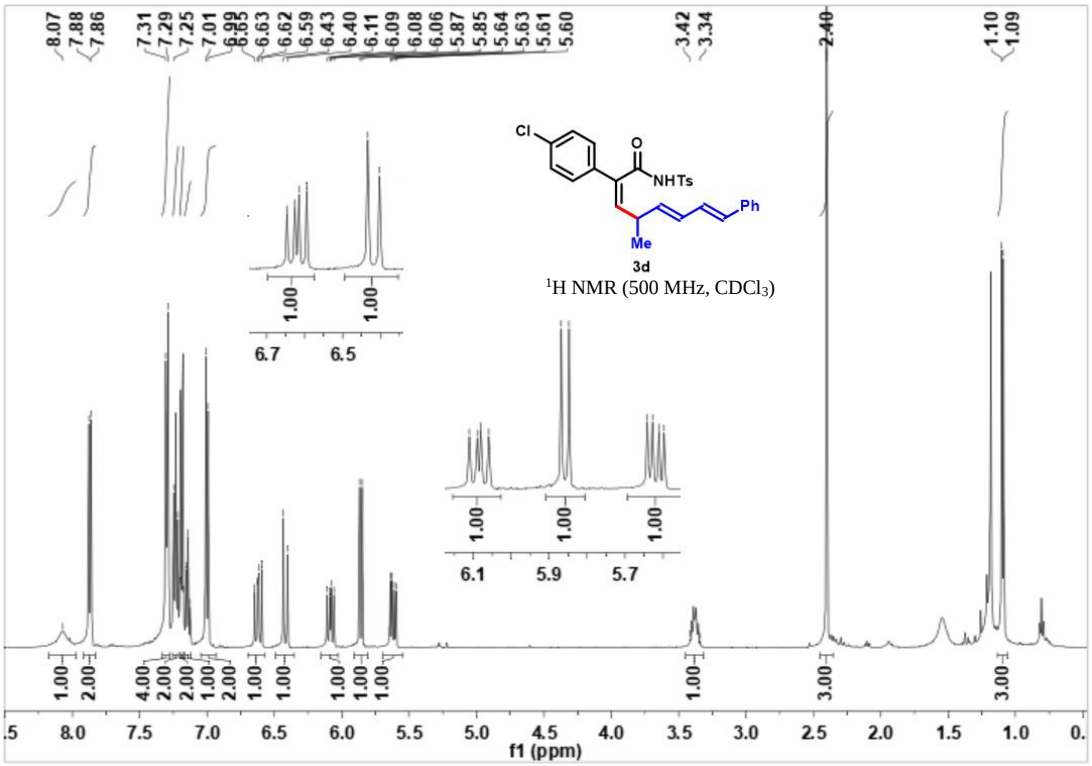
^{13}C NMR (125 Hz, $CDCl_3$)



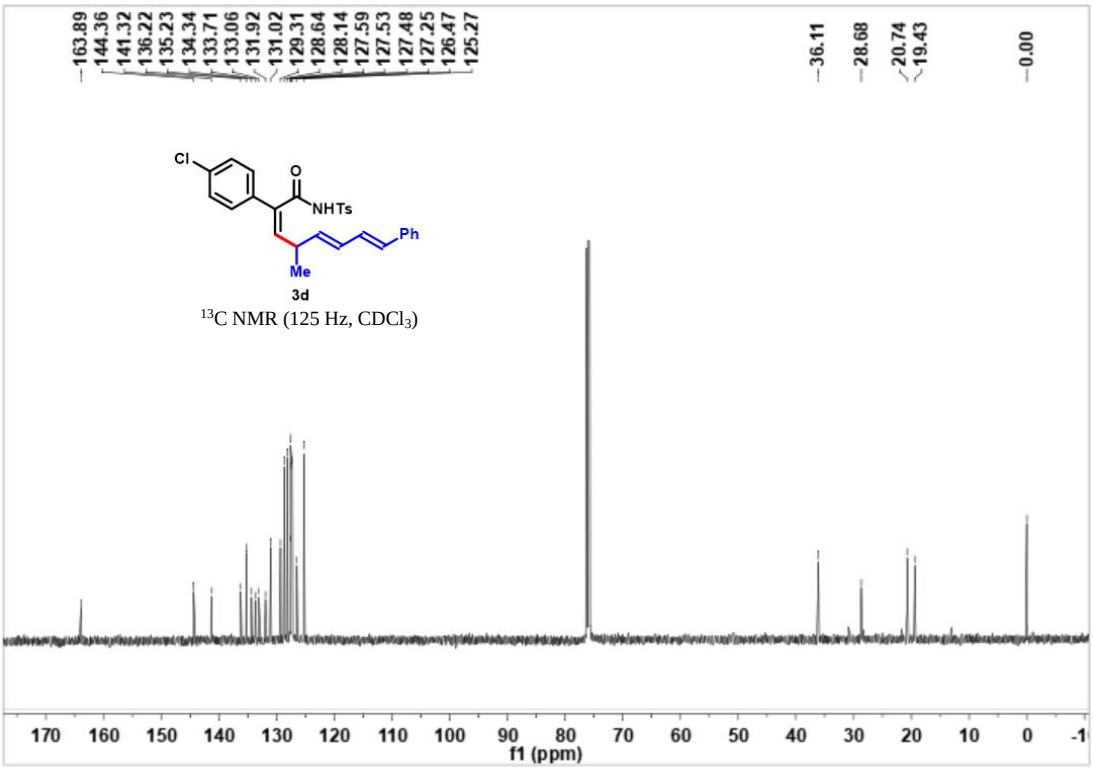
^{1}H NMR (500 MHz, $CDCl_3$)



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

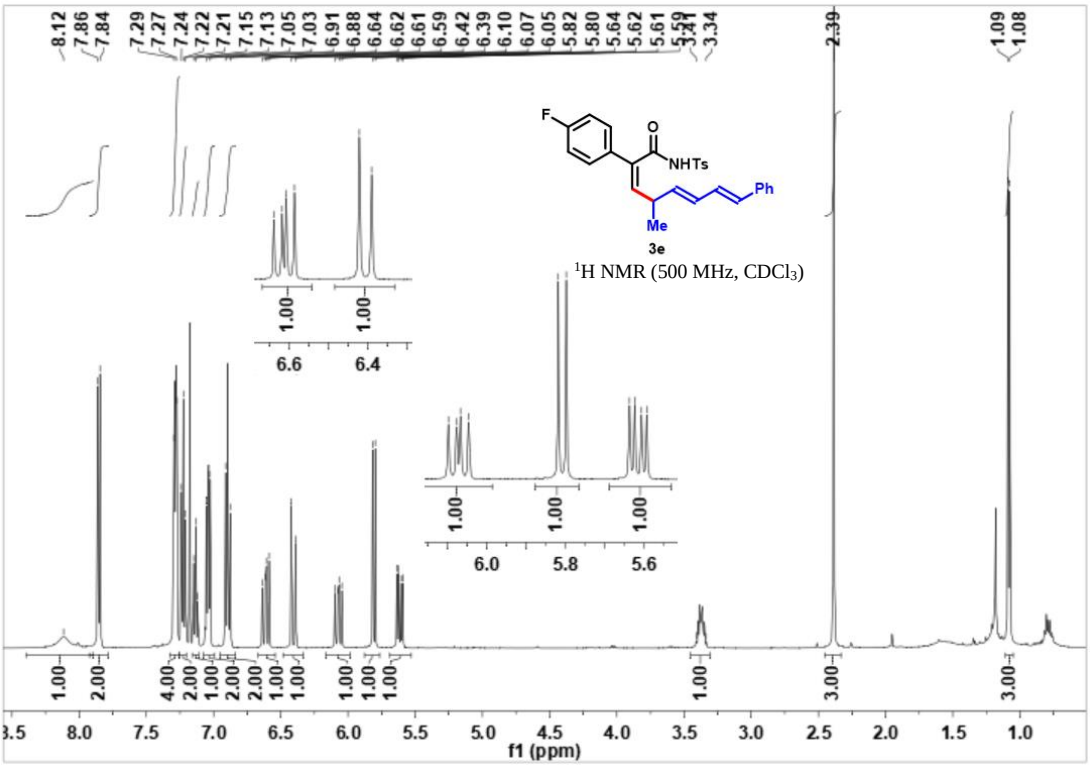


^{1}H NMR (500 MHz, $CDCl_3$)

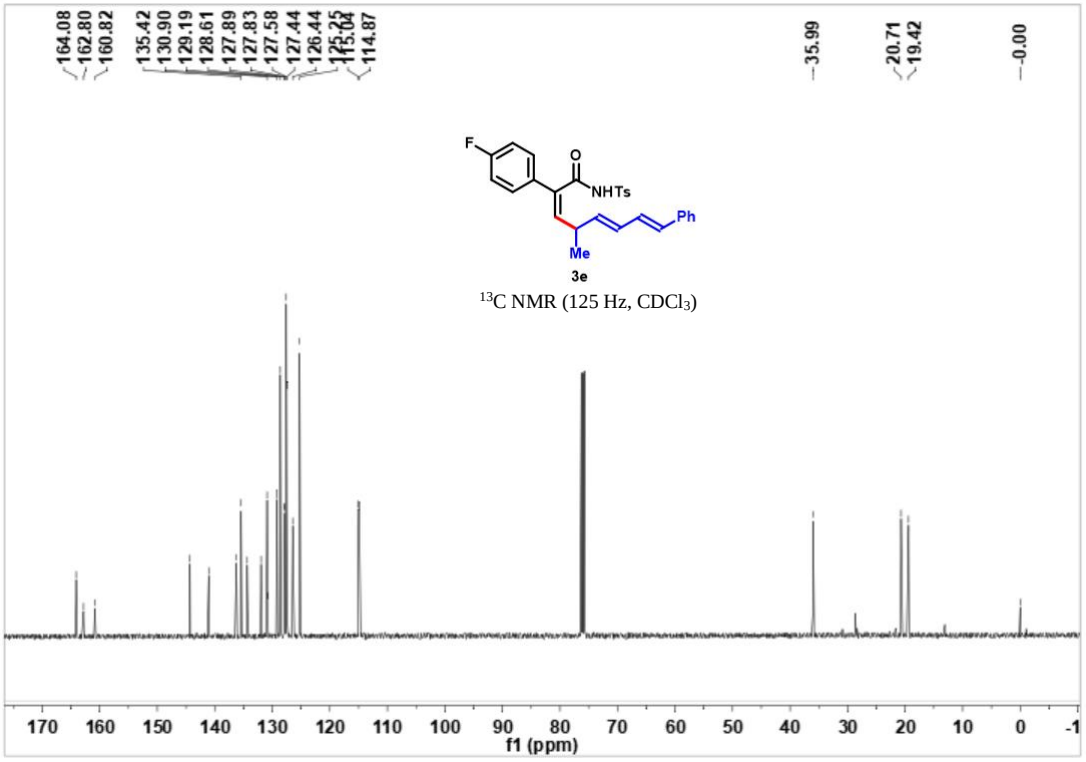


^{13}C NMR (125 Hz, $CDCl_3$)

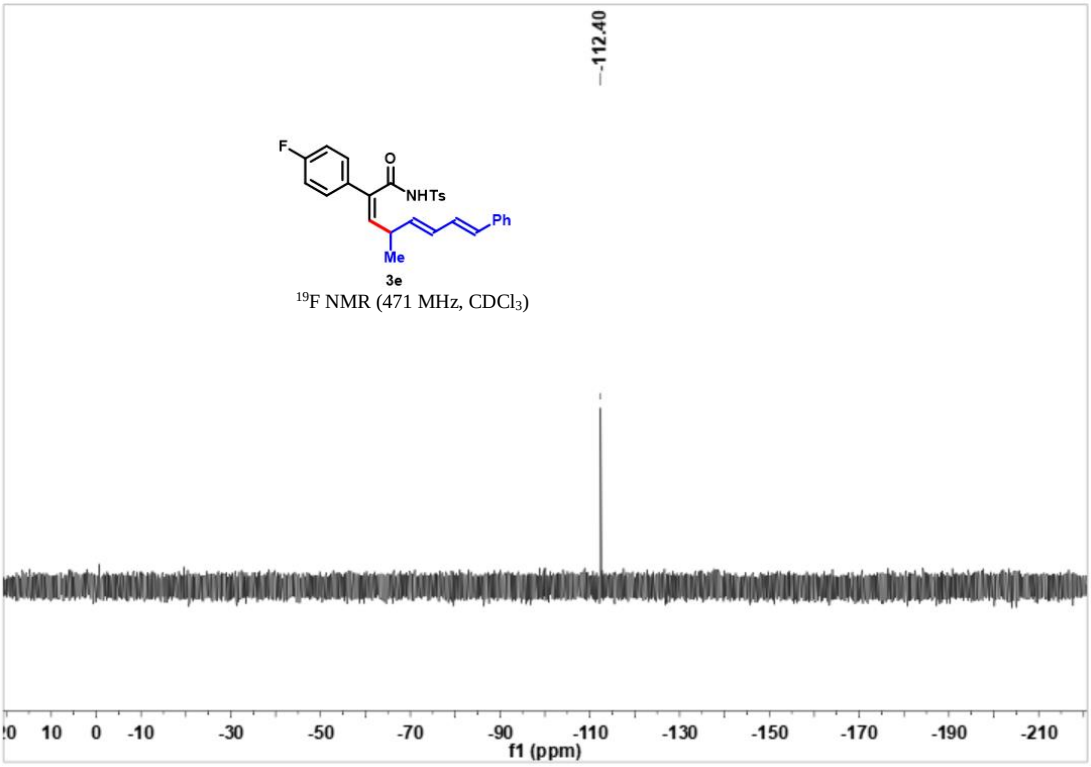
3d



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

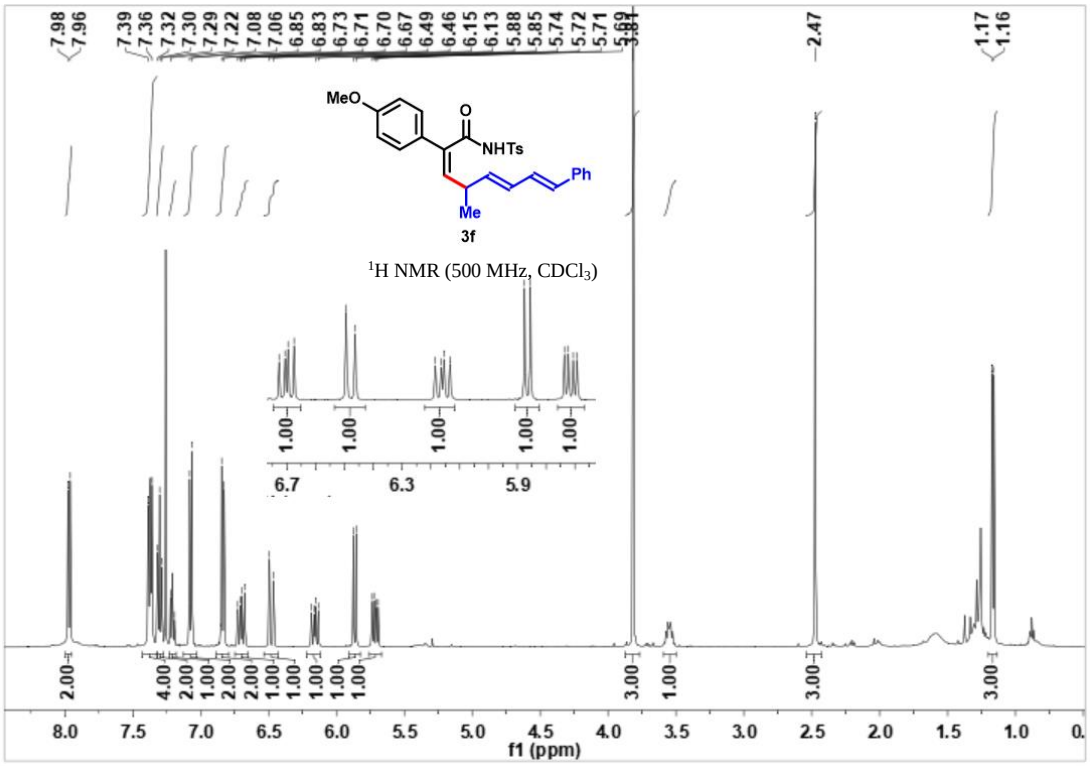


^{13}C NMR (125 Hz, $CDCl_3$)

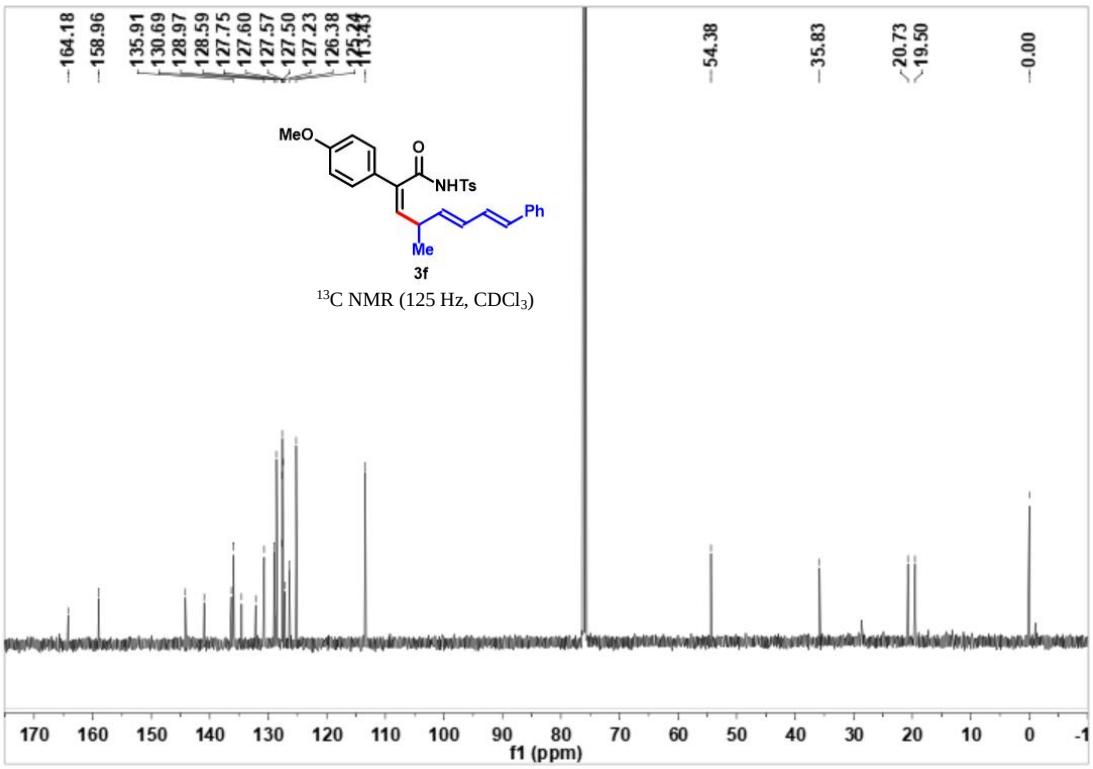


3e

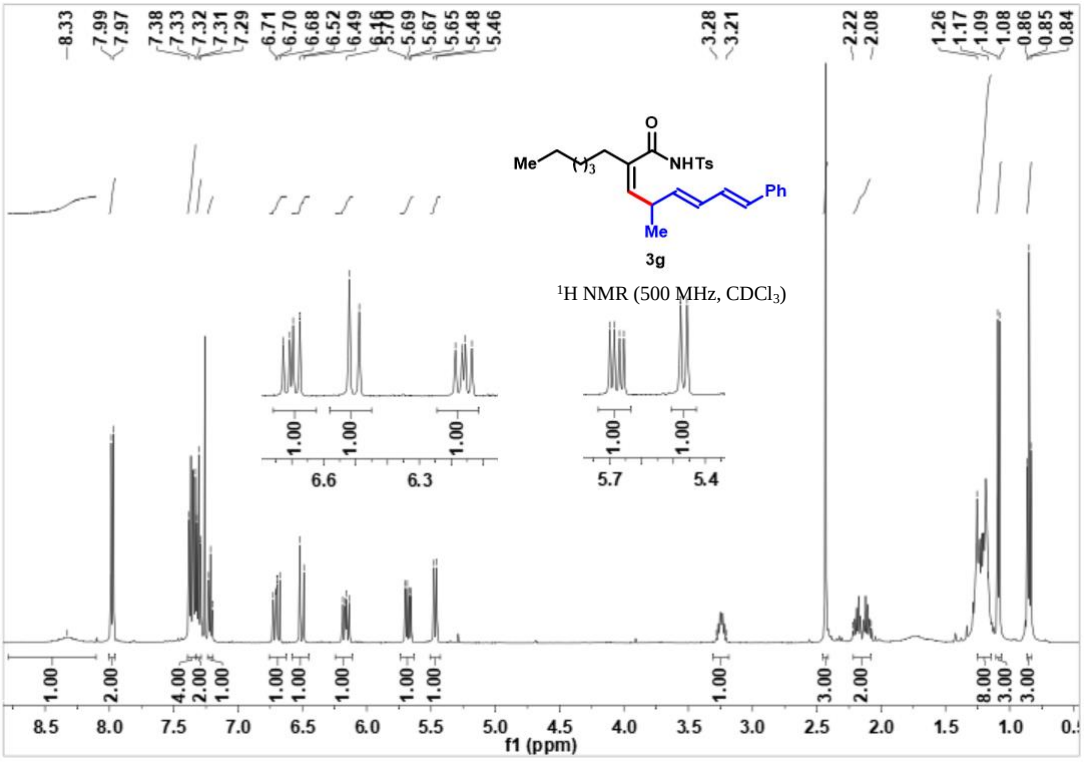
^{19}F NMR (471 MHz, $CDCl_3$)



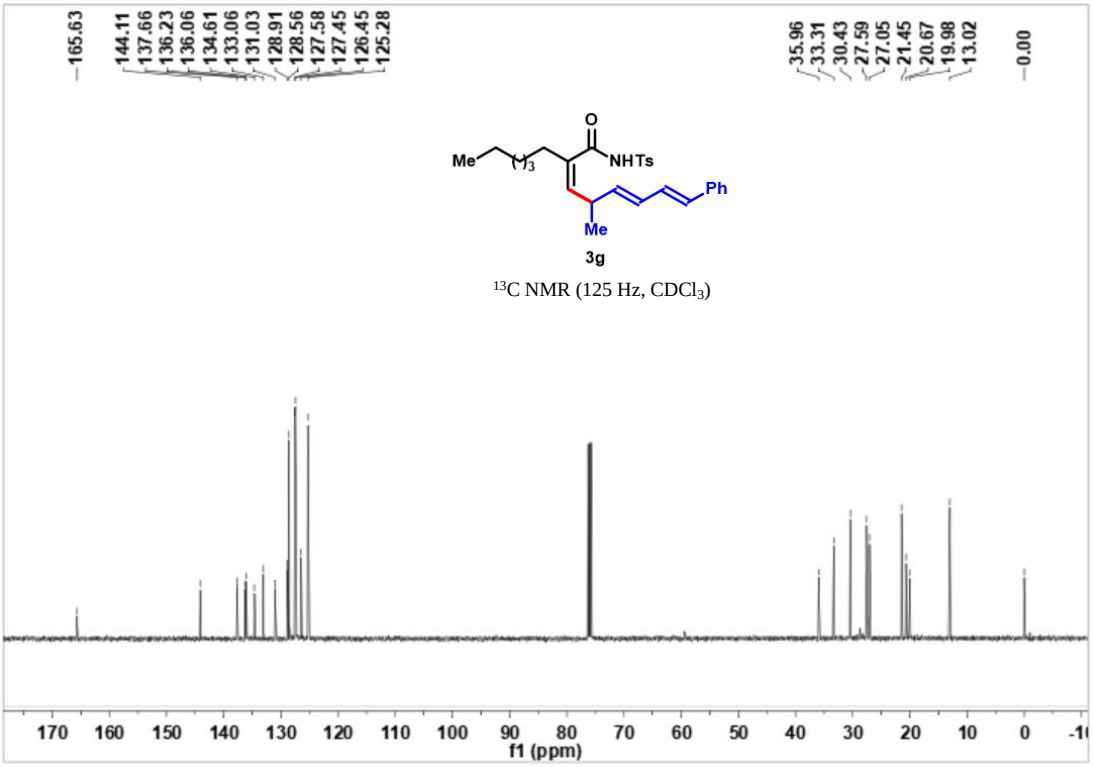
^{1}H NMR (500 MHz, $CDCl_3$)



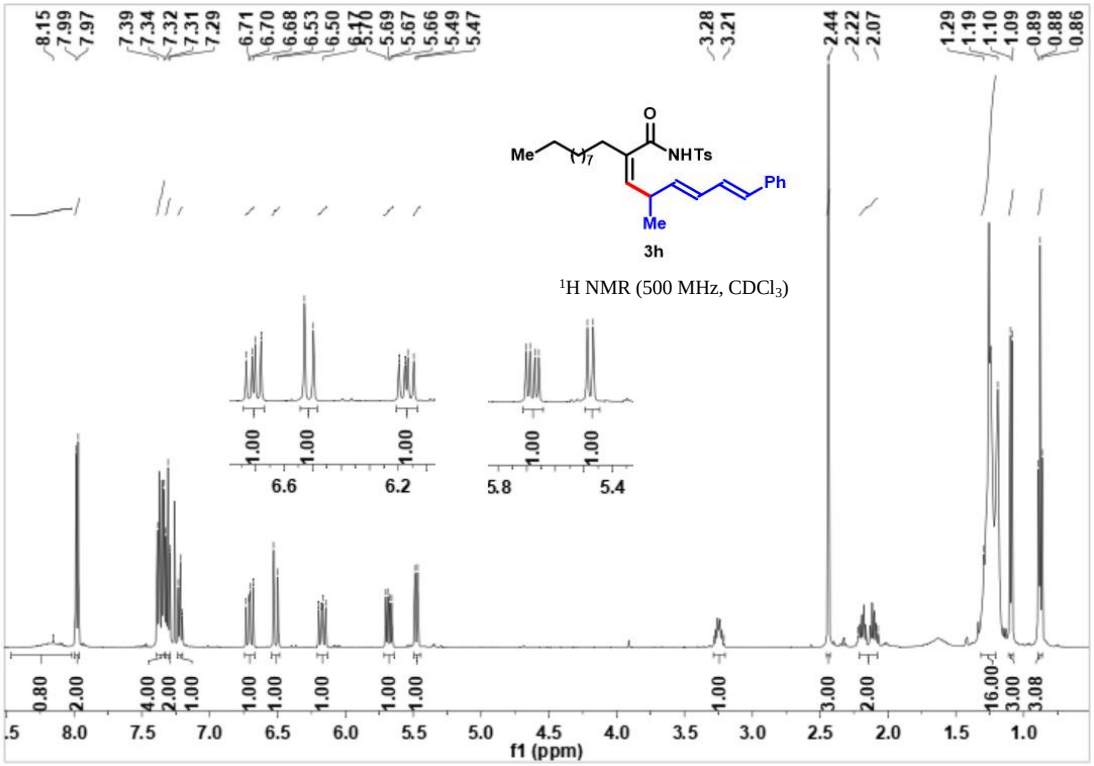
^{13}C NMR (125 Hz, $CDCl_3$)



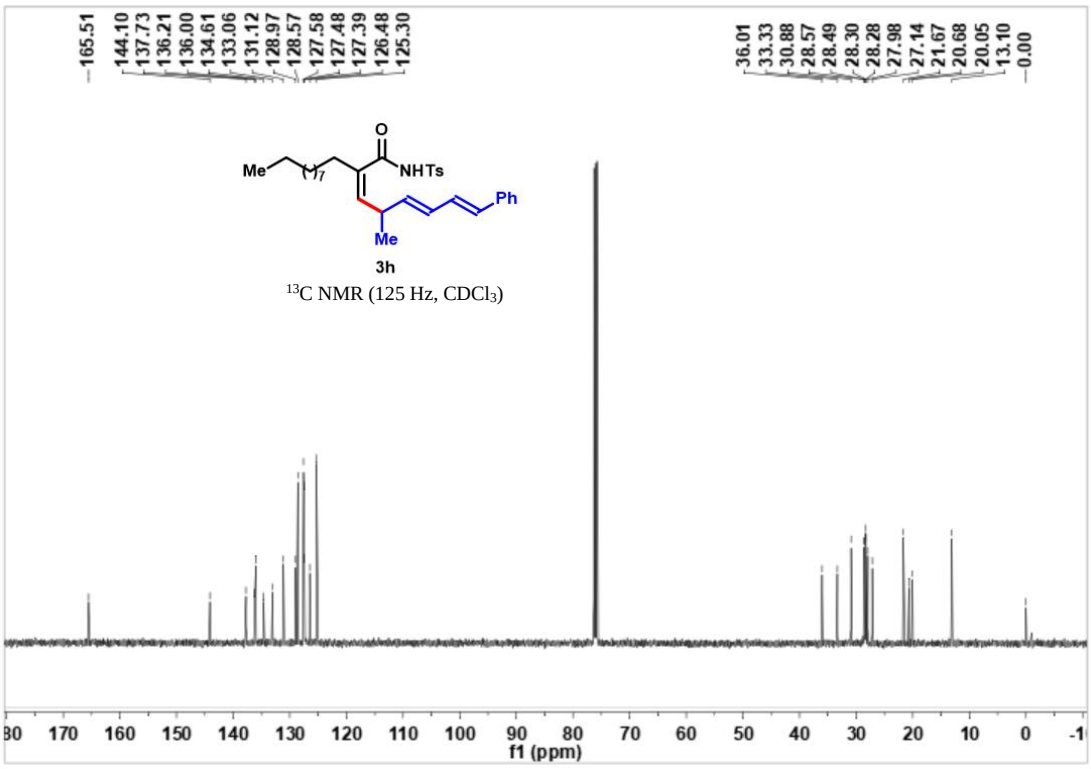
^{1}H NMR (500 MHz, $CDCl_3$)



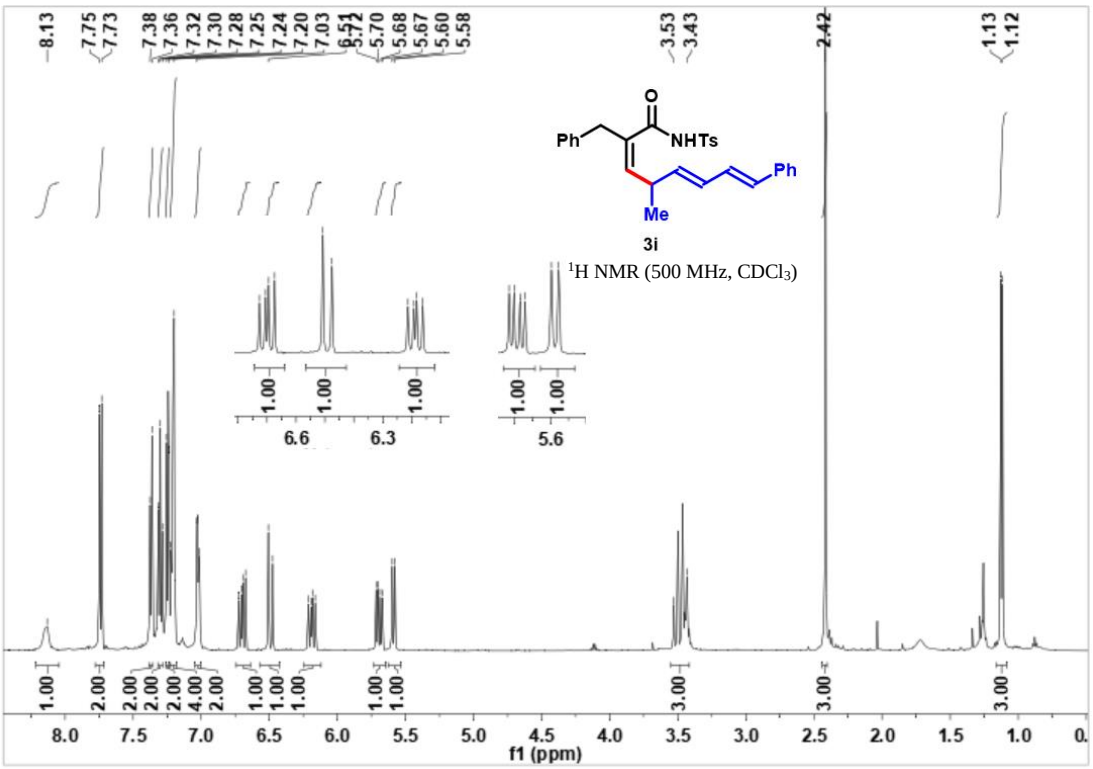
^{13}C NMR (125 Hz, $CDCl_3$)



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

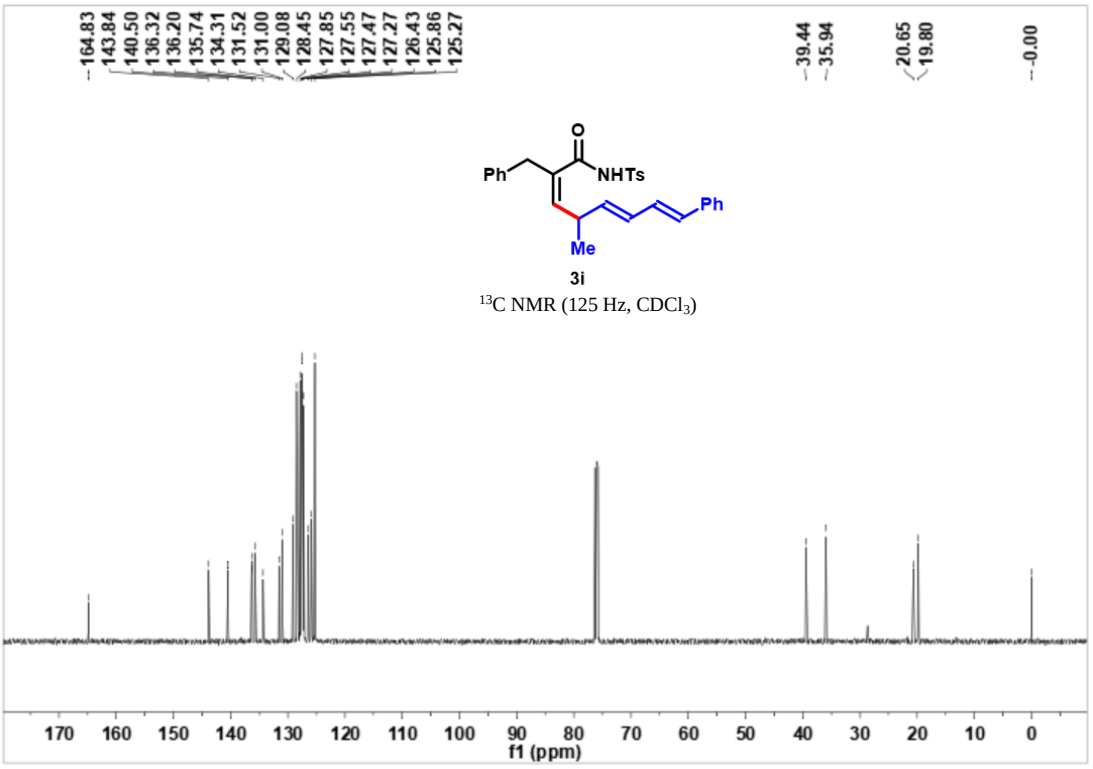


^{13}C NMR (125 Hz, $CDCl_3$)



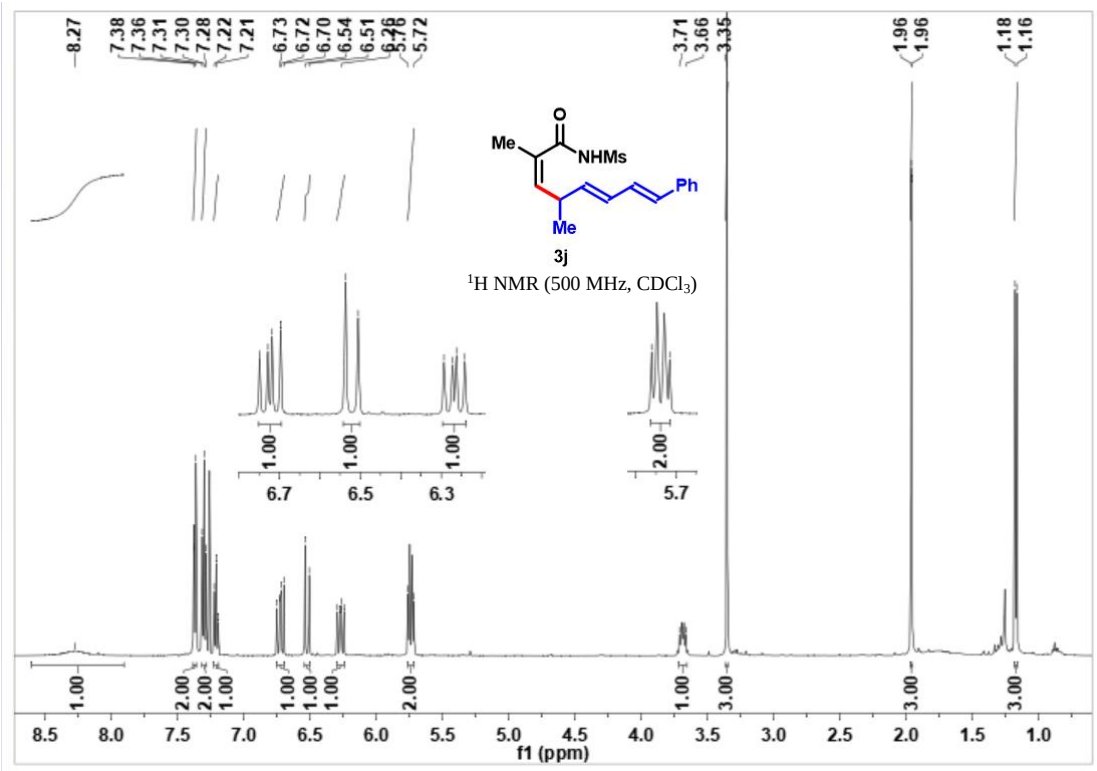
3i

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



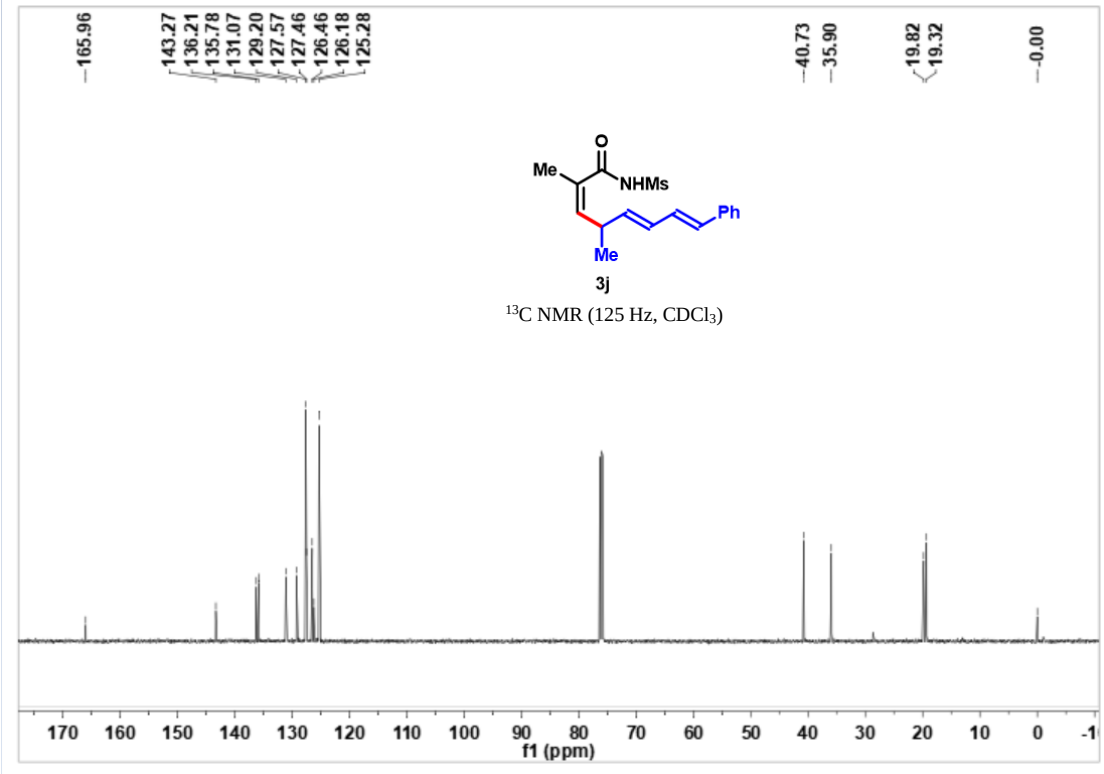
3i

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



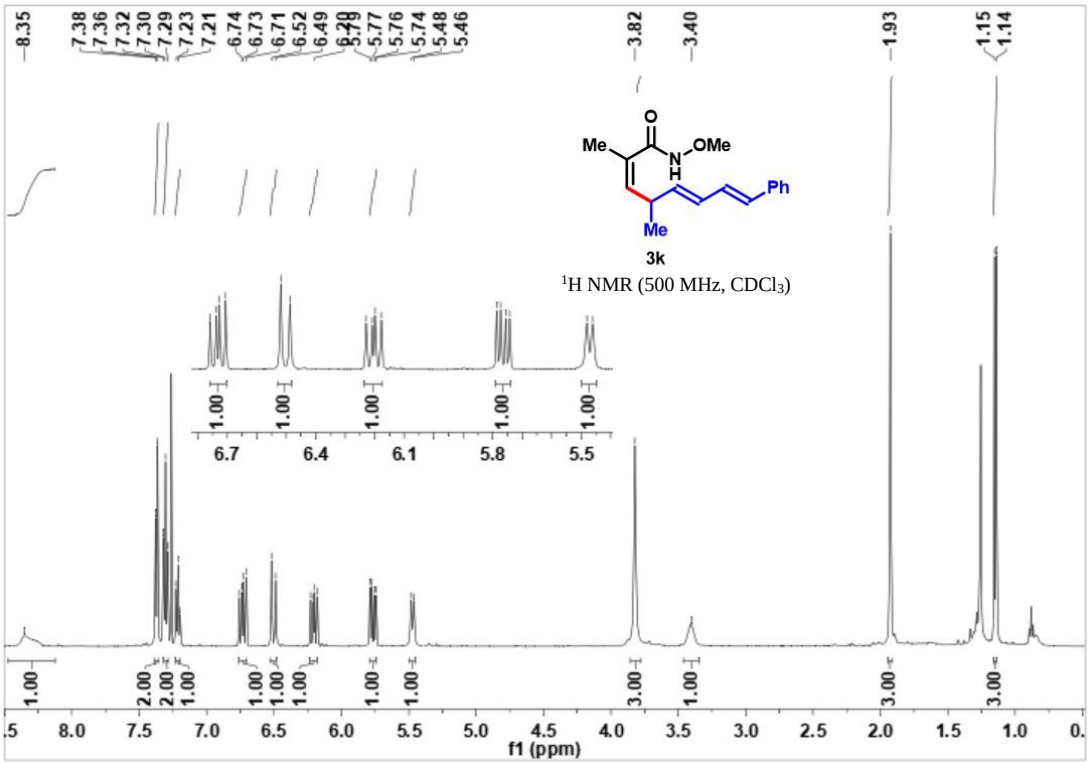
3j

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

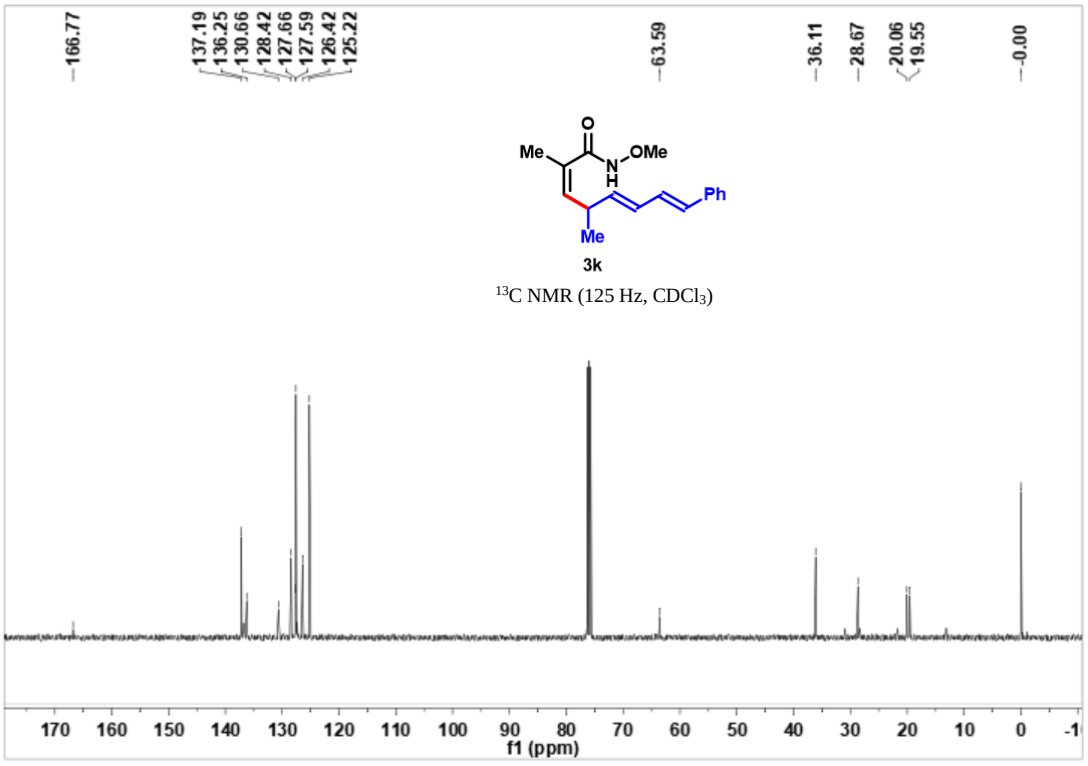


3j

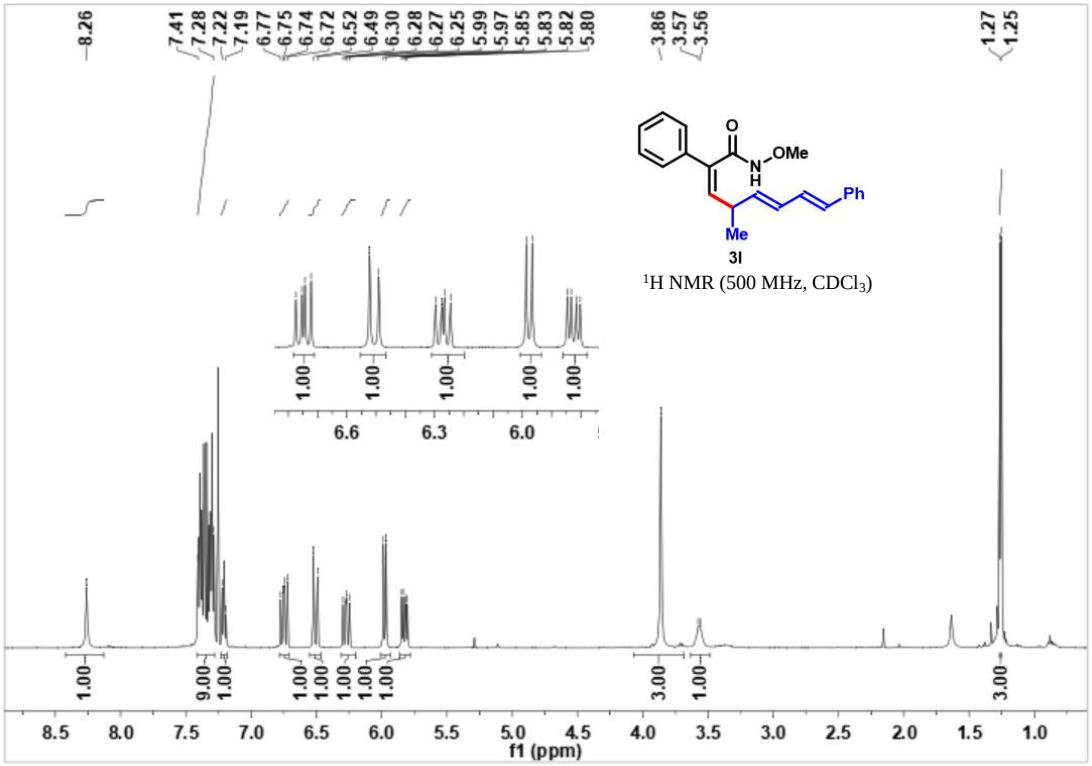
^{13}C NMR (125 Hz, $CDCl_3$)



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

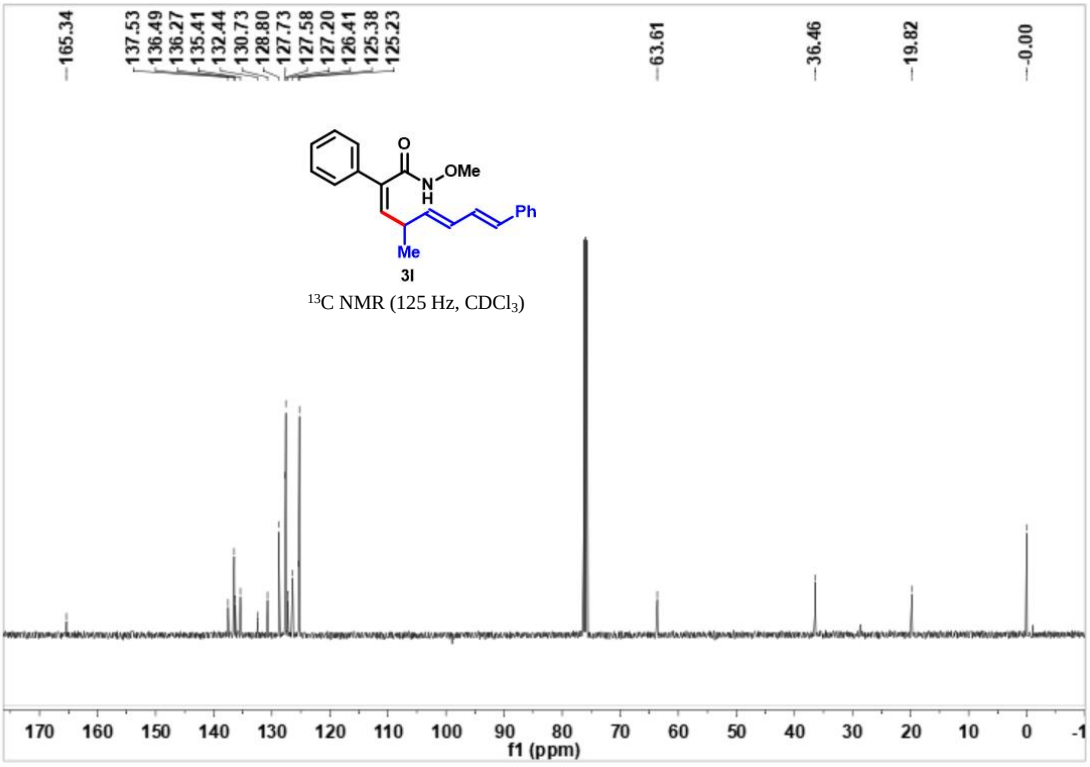


^{13}C NMR (125 Hz, $CDCl_3$)



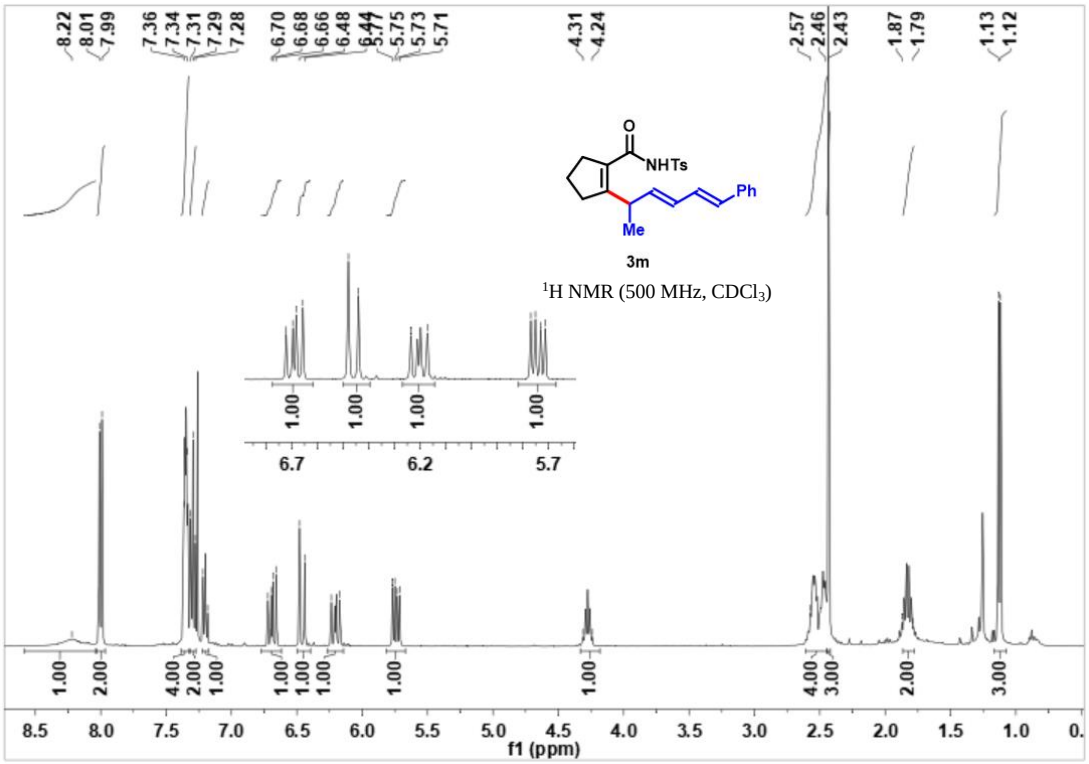
3l

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



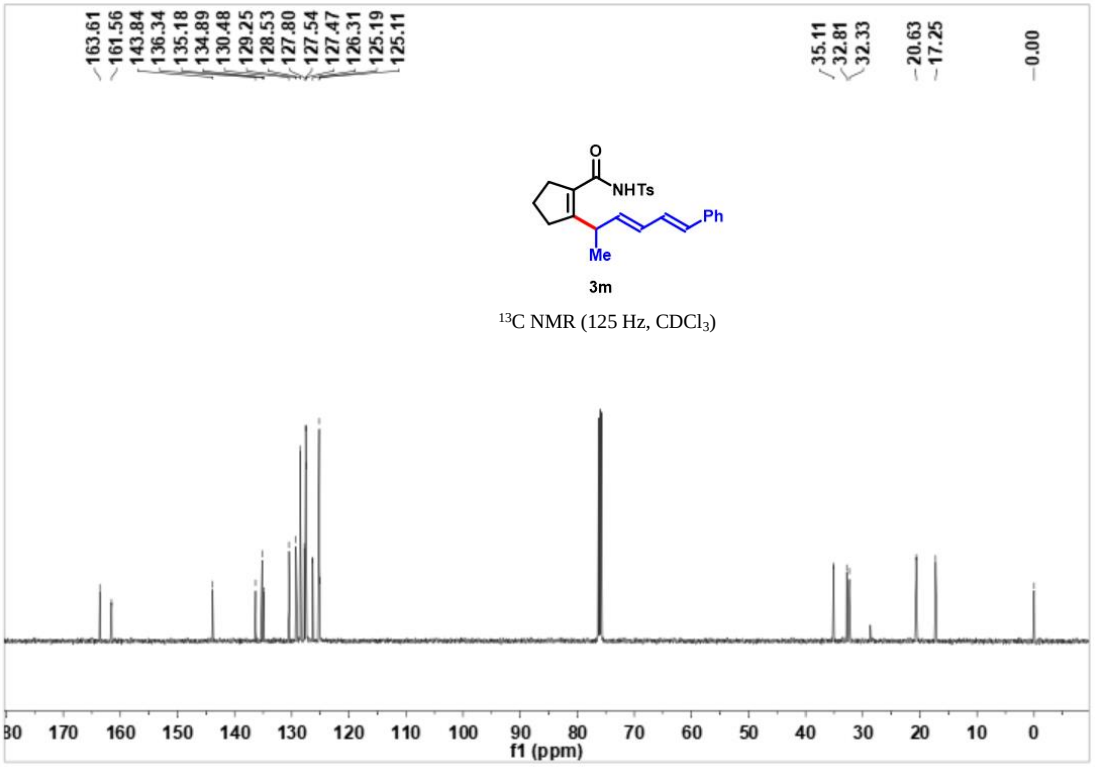
3l

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



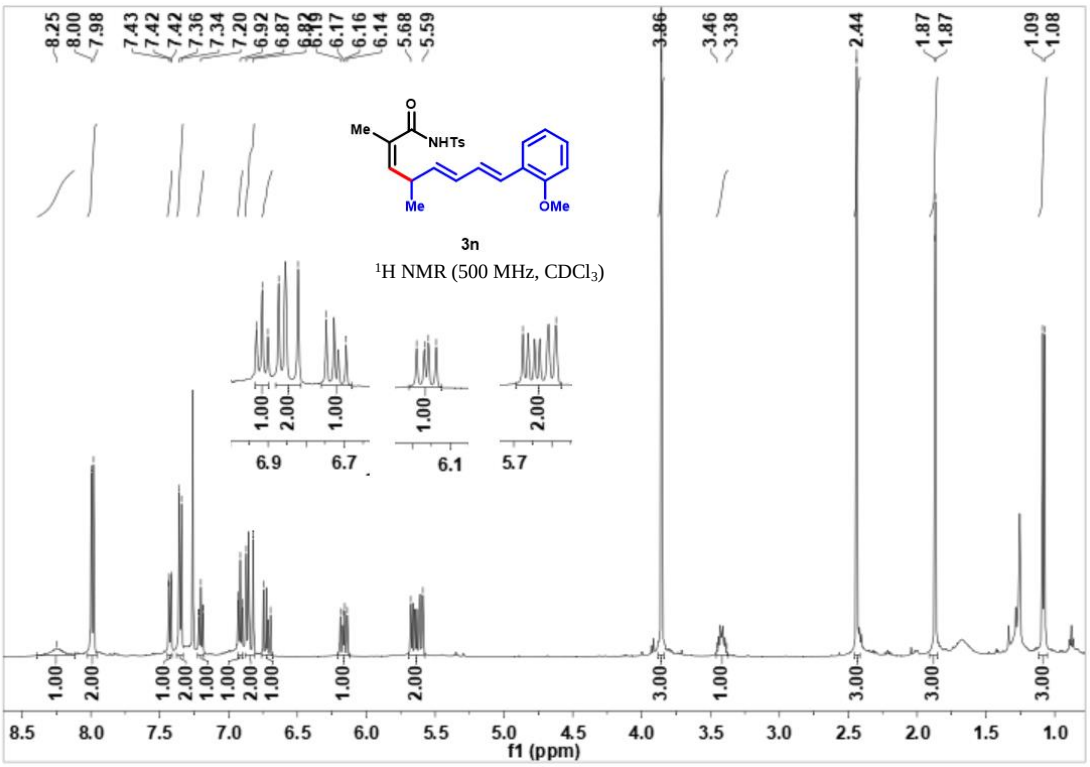
3m

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



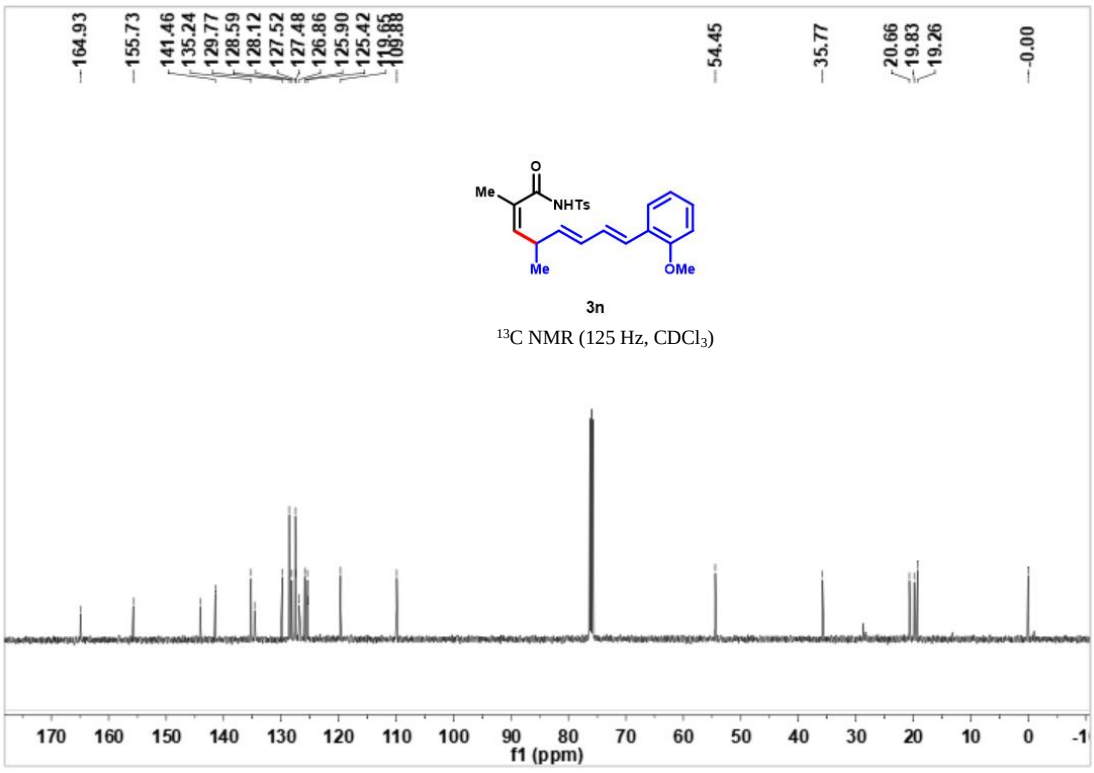
3m

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



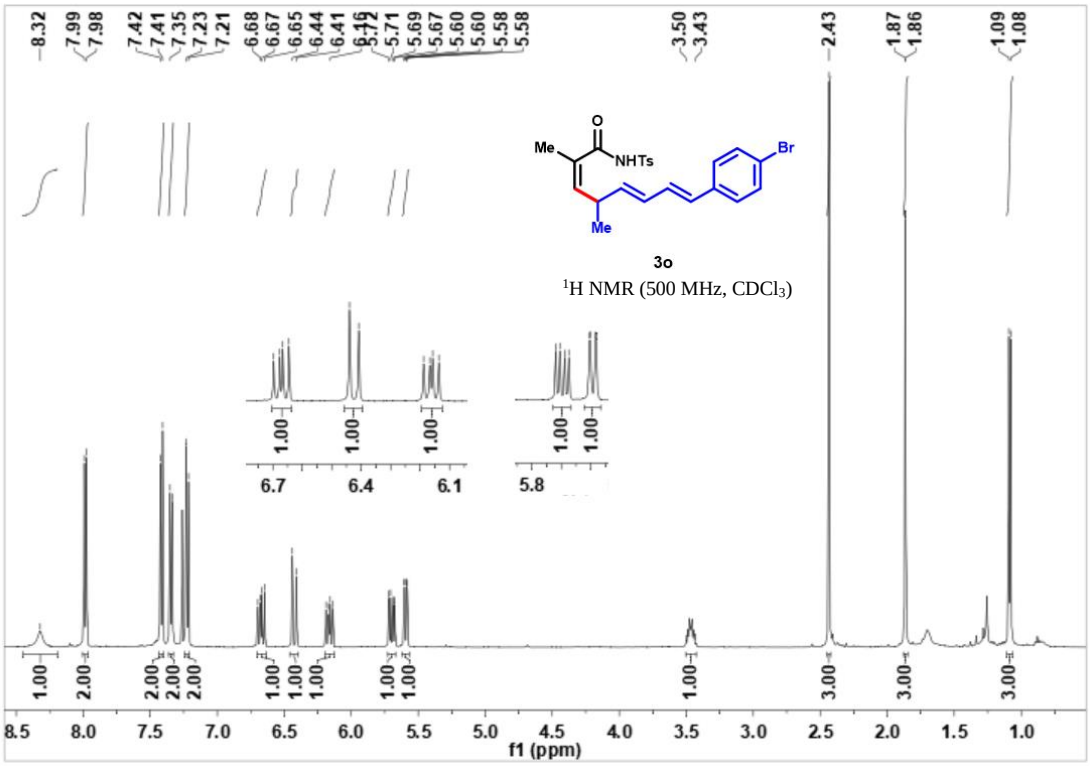
3n

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

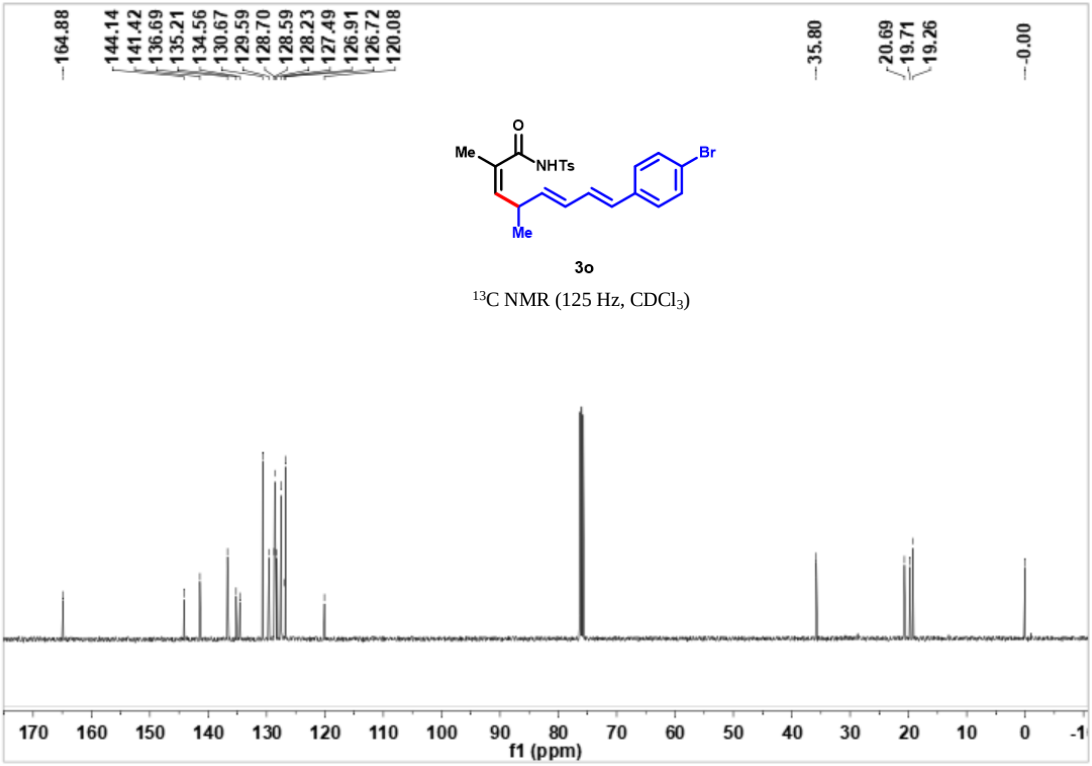


3n

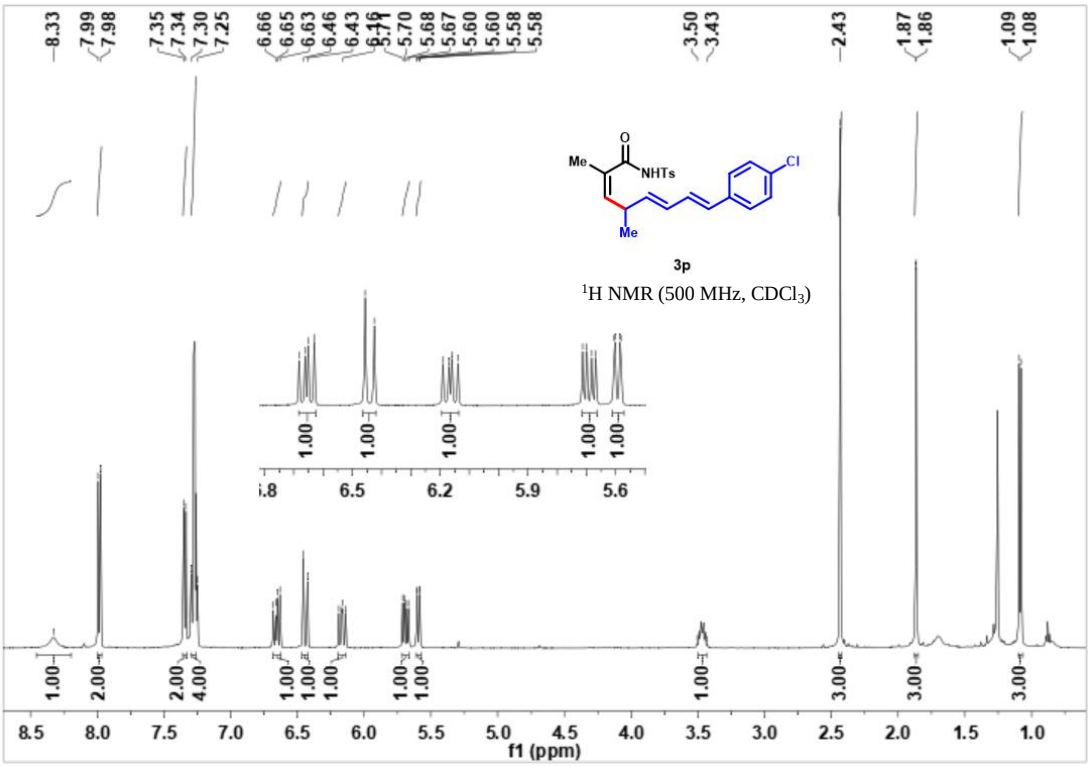
^{13}C NMR (125 Hz, $CDCl_3$)



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

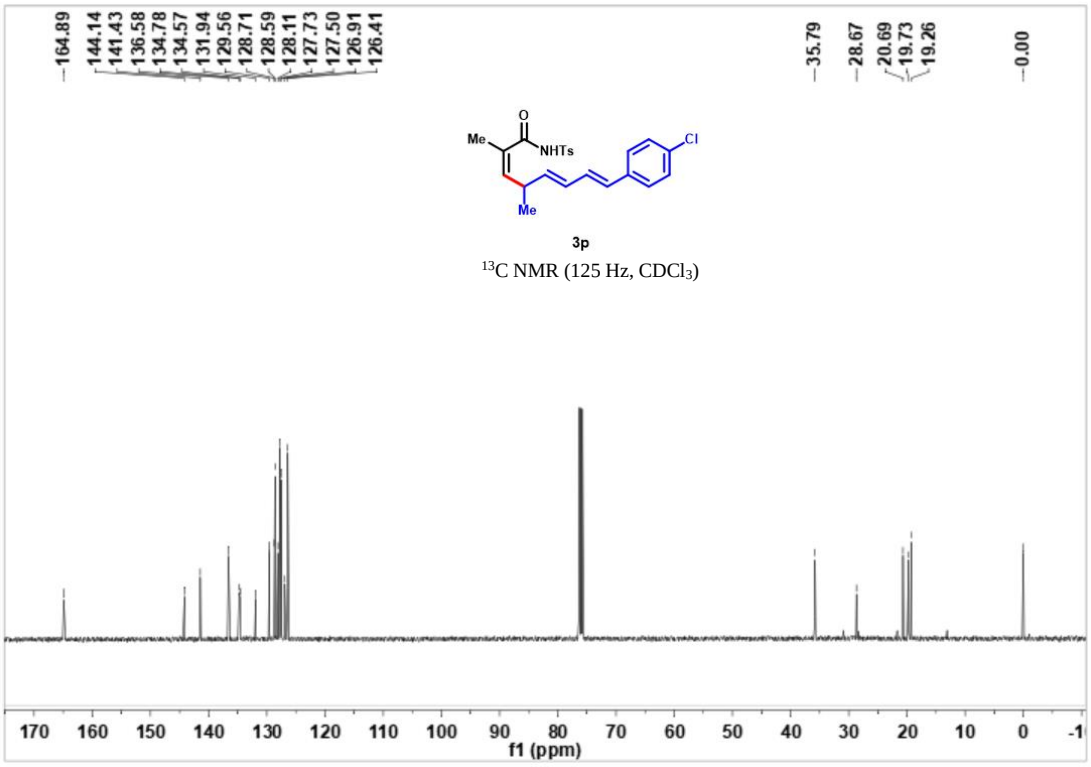


^{13}C NMR (125 Hz, $CDCl_3$)



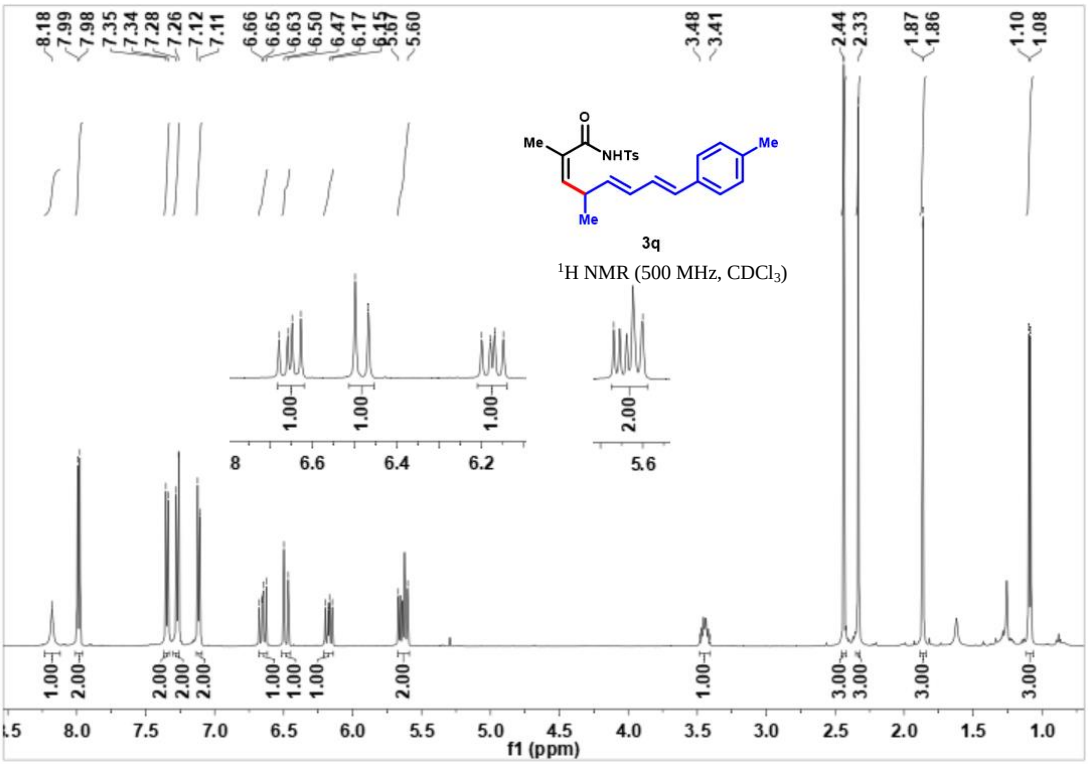
3p

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

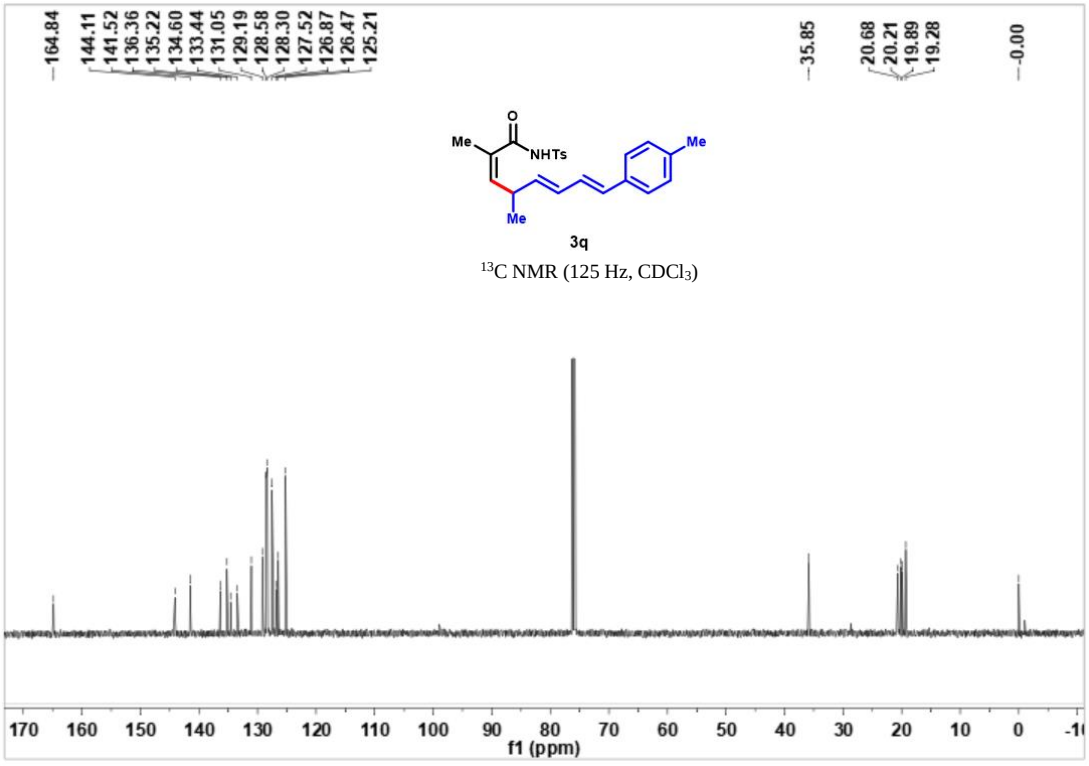


3p

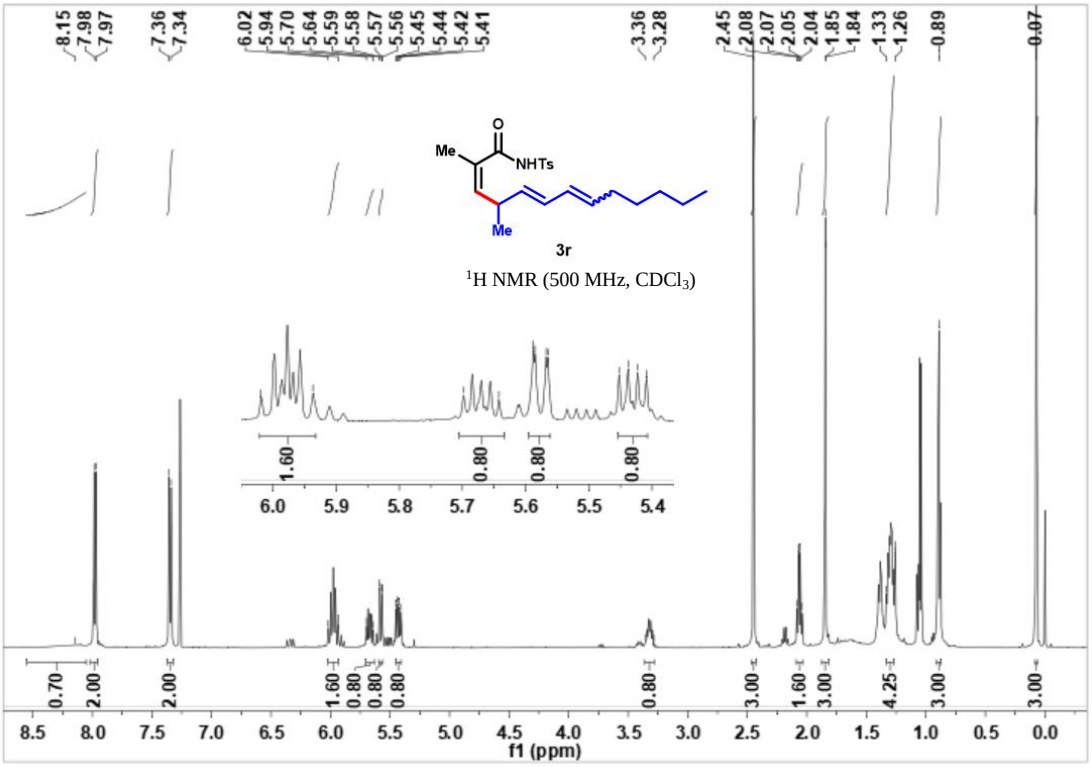
^{13}C NMR (125 Hz, $CDCl_3$)



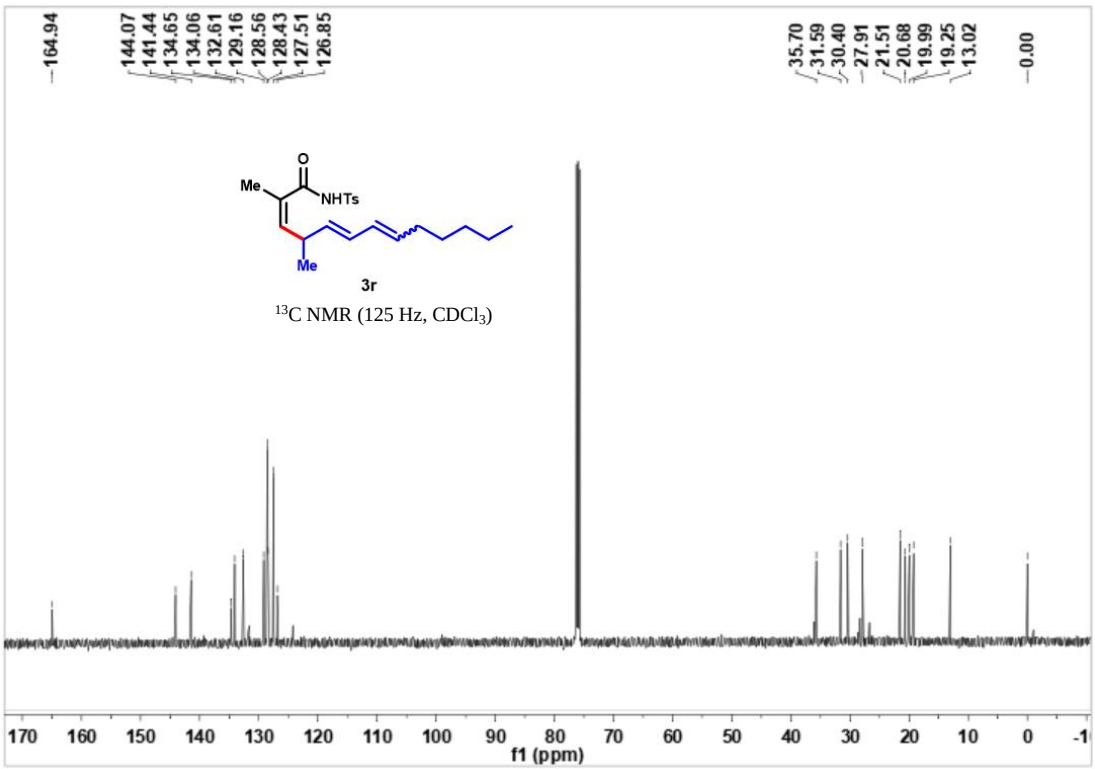
^{1}H NMR (500 MHz, $CDCl_3$)



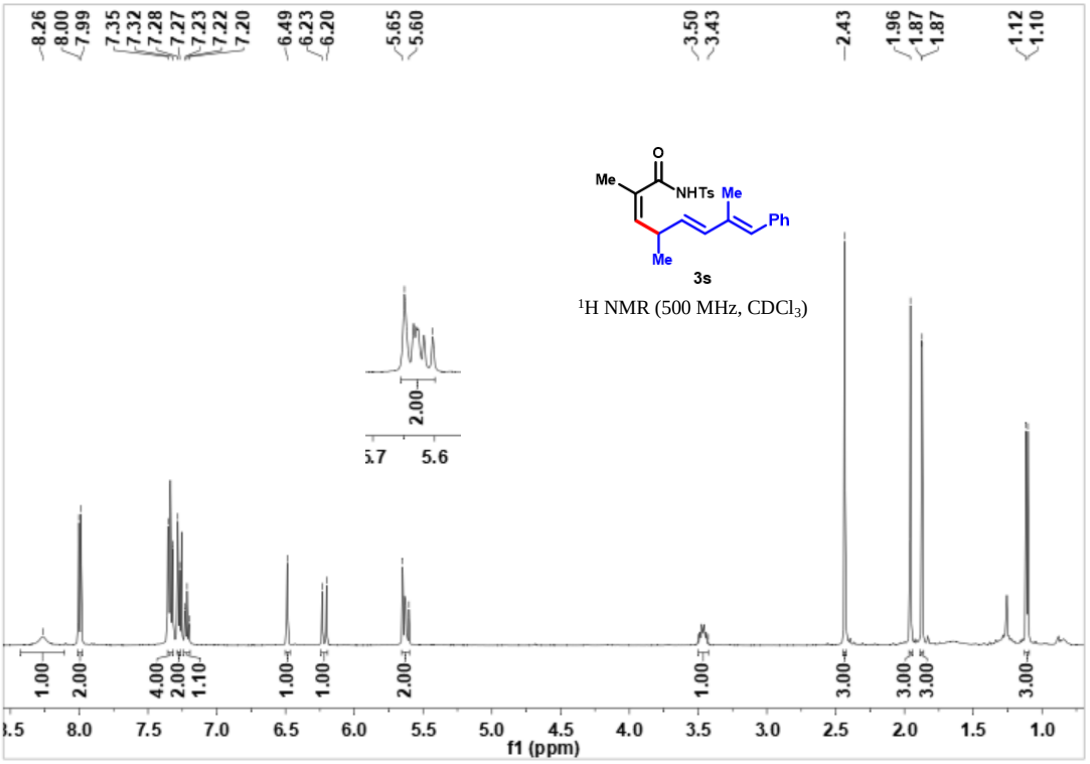
^{13}C NMR (125 Hz, $CDCl_3$)



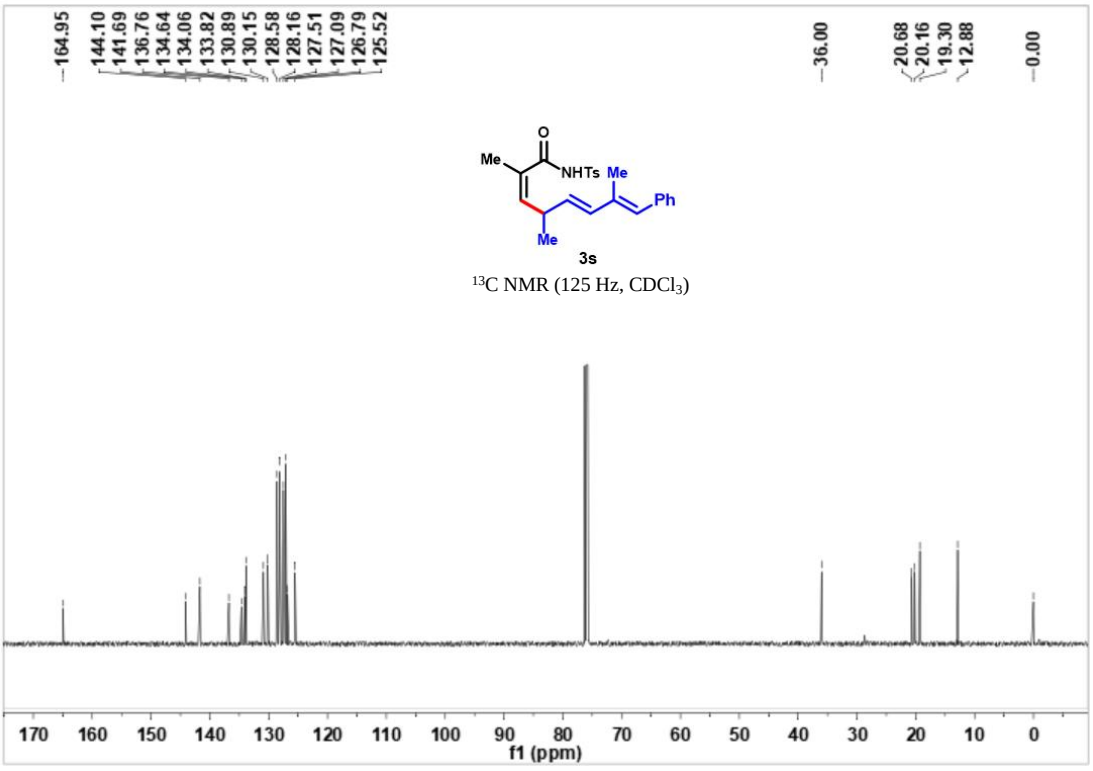
^{1}H NMR (500 MHz, $CDCl_3$)



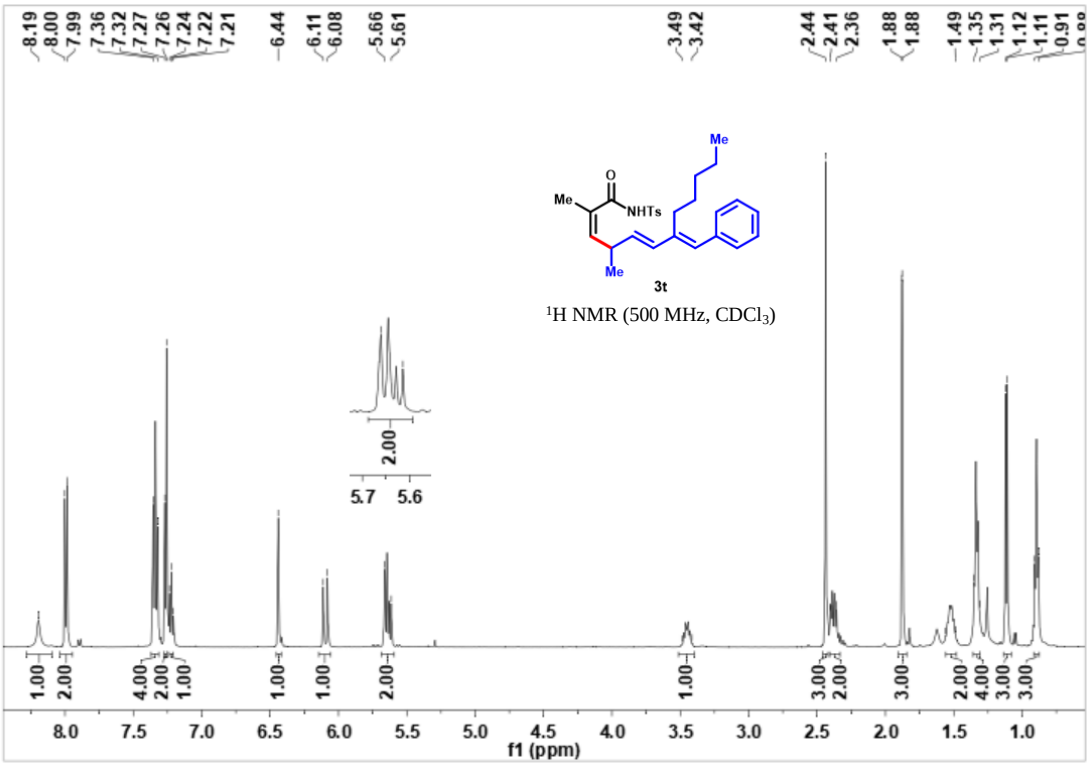
^{13}C NMR (125 Hz, $CDCl_3$)



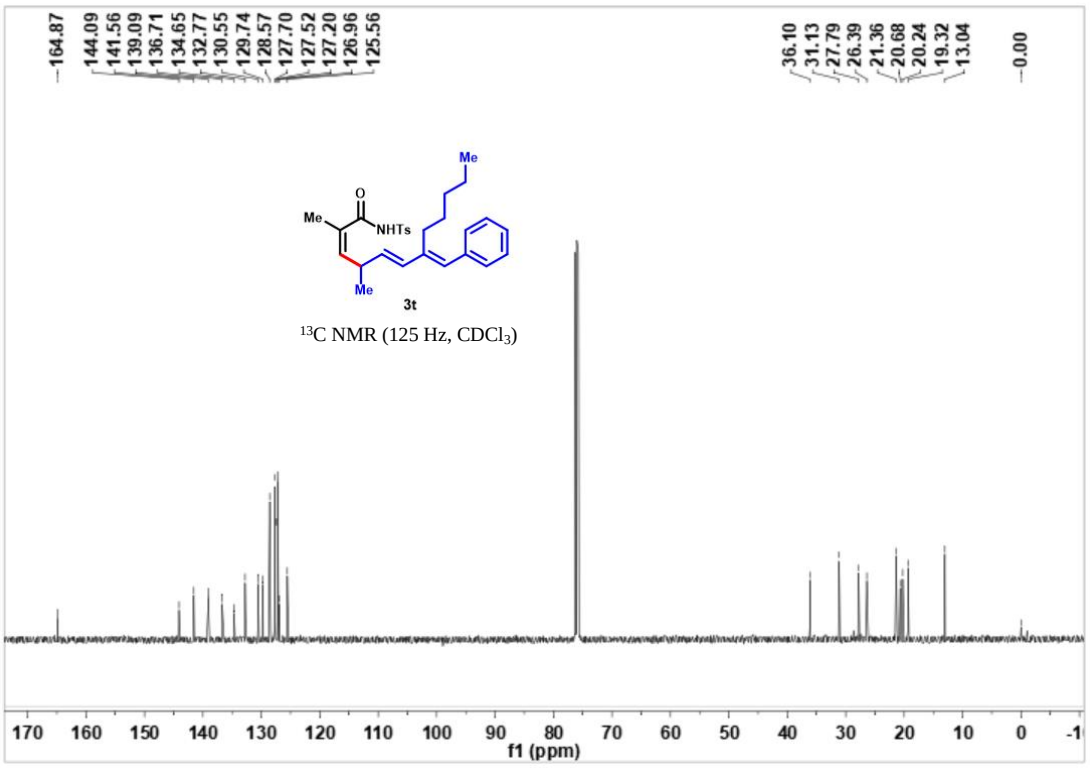
^{1}H NMR (500 MHz, $CDCl_3$)



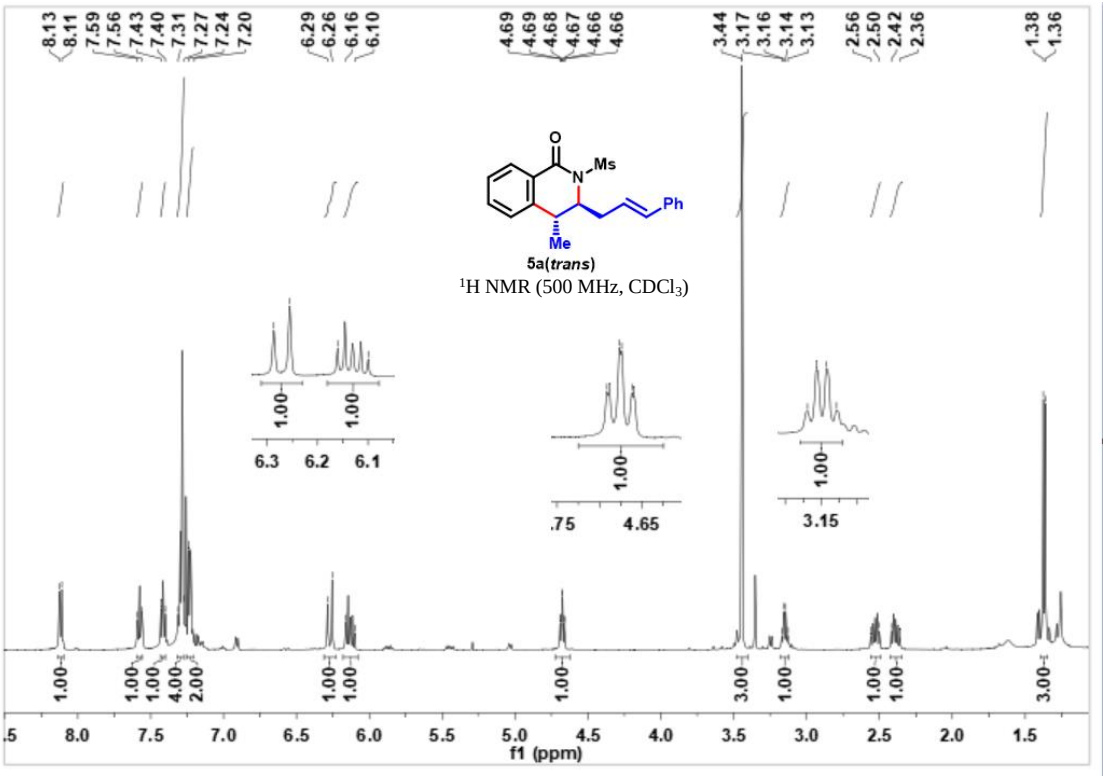
^{13}C NMR (125 Hz, $CDCl_3$)



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

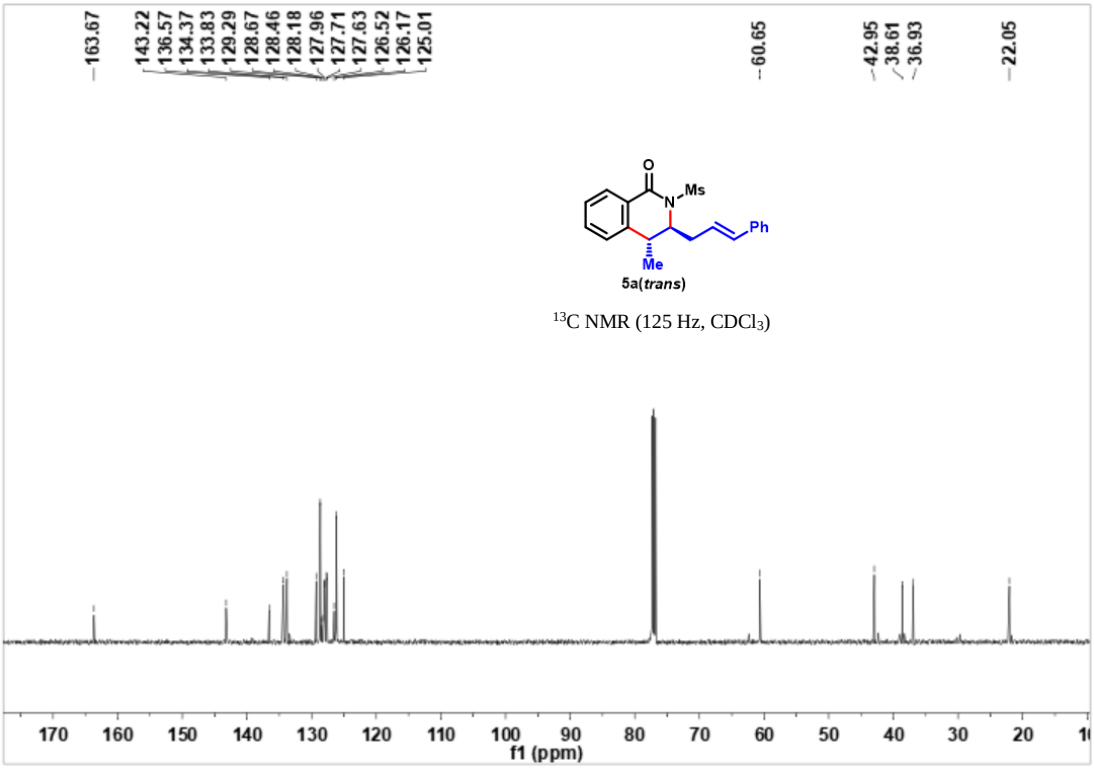


^{13}C NMR (125 Hz, $CDCl_3$)



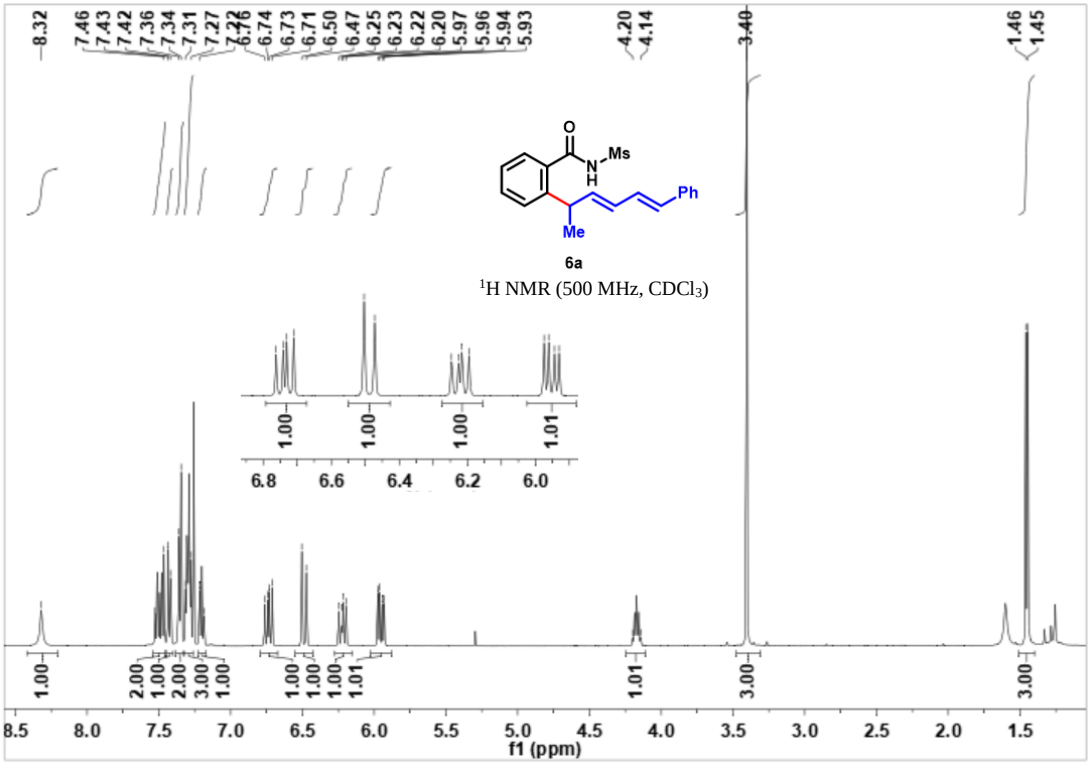
5a(*trans*)

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



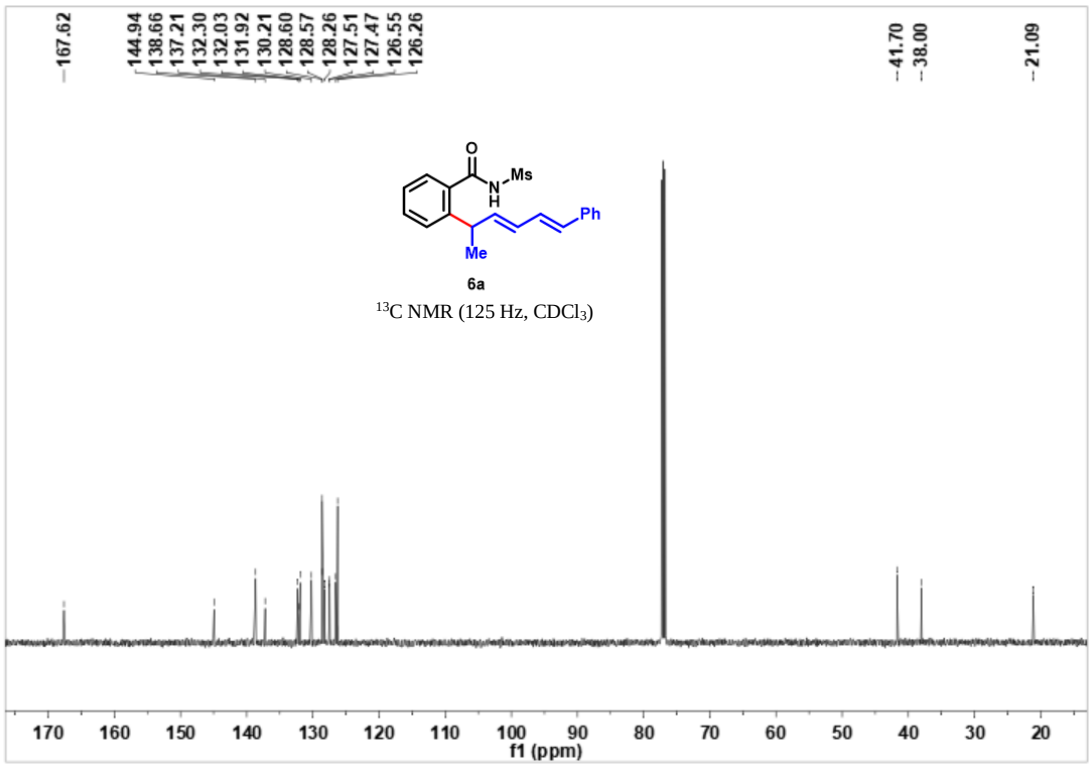
5a(*trans*)

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



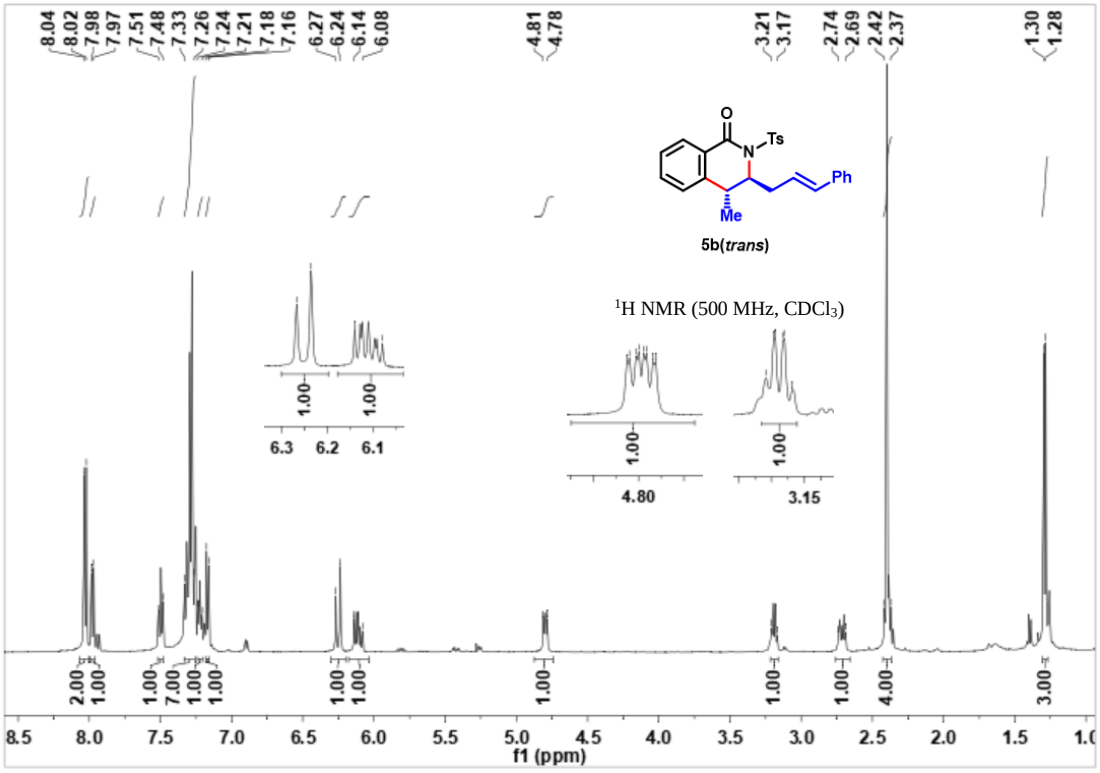
6a

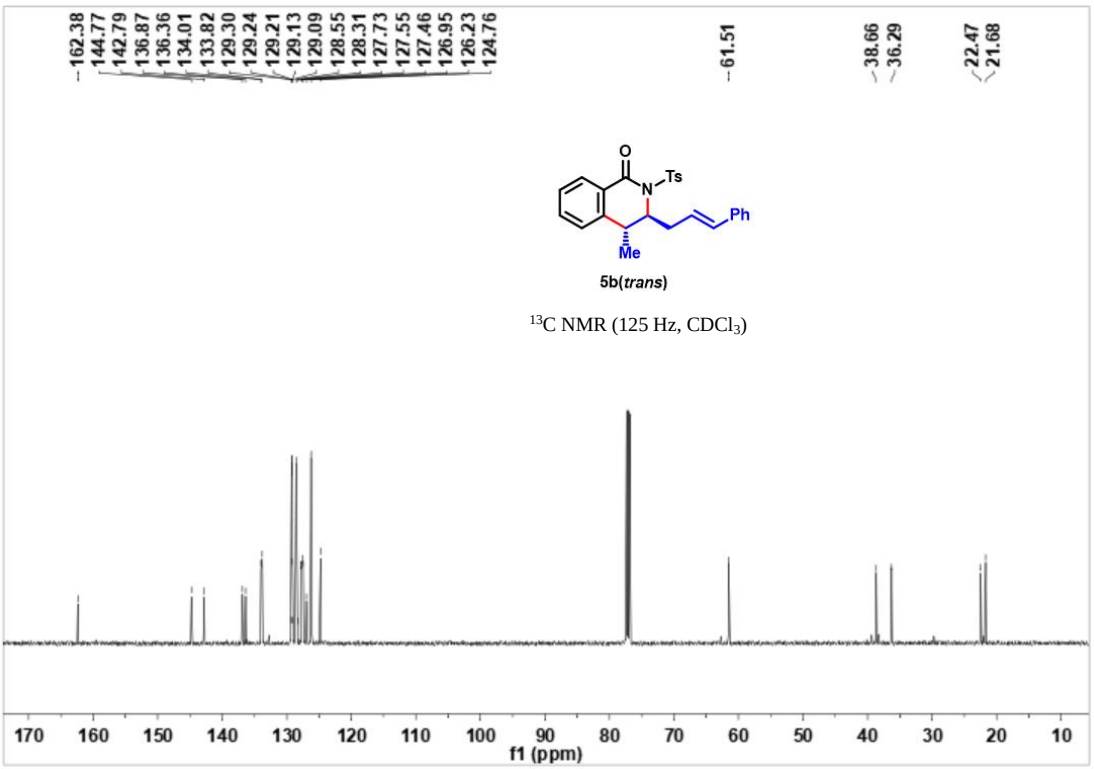
^{1}H NMR (500 MHz, $CDCl_3$)

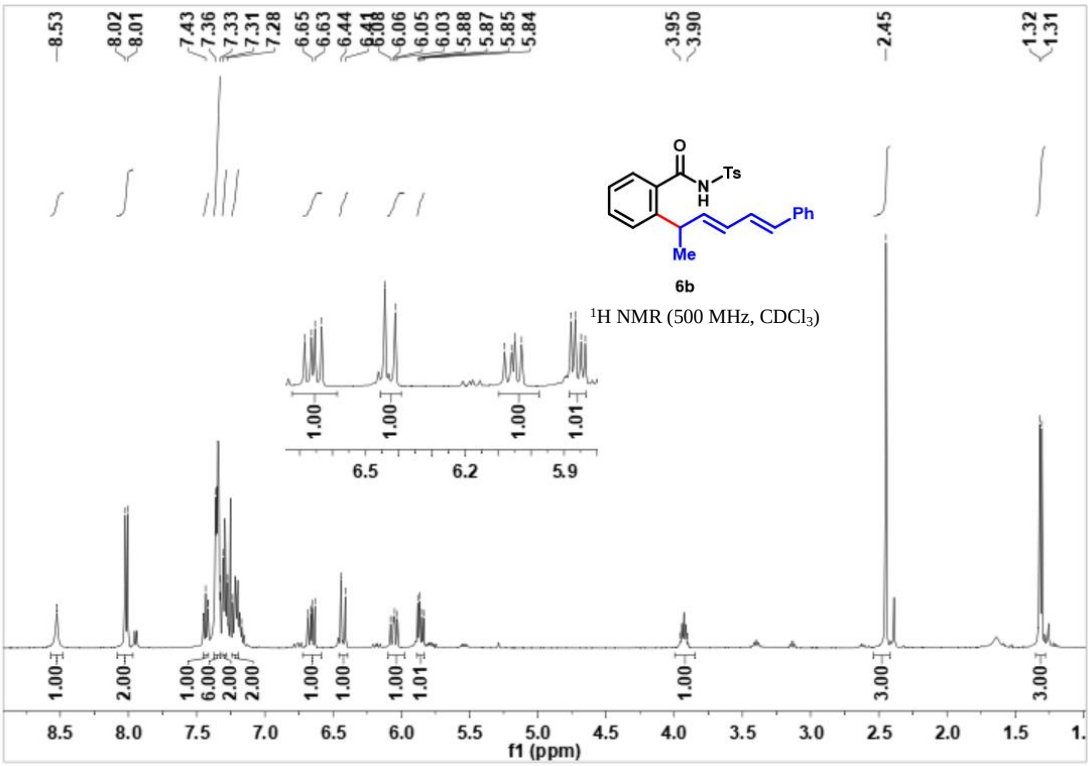


6a

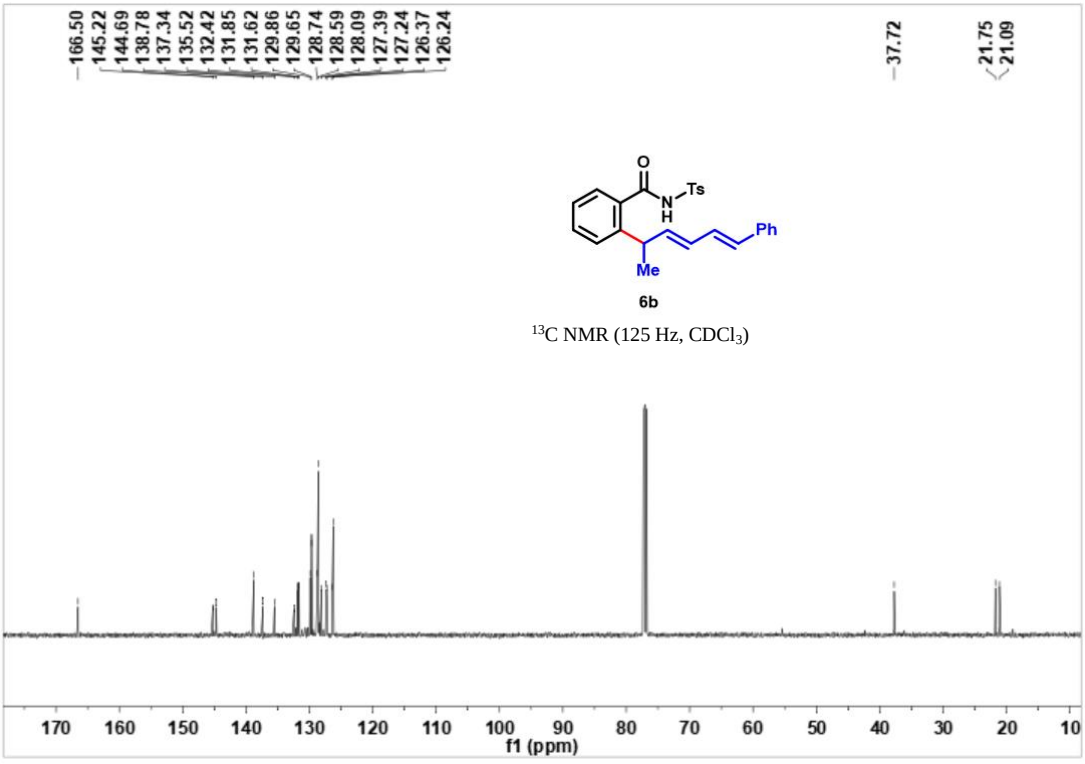
^{13}C NMR (125 Hz, $CDCl_3$)


8.04
8.02
7.98
7.97
7.51
7.48
7.33
7.26
7.24
7.21
7.18
7.16
6.27
6.24
6.14
6.08
4.81
4.78
3.21
3.17
2.74
2.69
2.42
2.37
1.30
1.28
O
N
Ts
Ph
Me
5b(trans)
1H NMR (500 MHz, CDCl3)
1.00
1.00
6.3
6.2
6.1
1.00
4.80
1.00
3.15
2.00
1.00
1.00
7.00
1.00
1.00
1.00
1.00
1.00
1.00
4.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

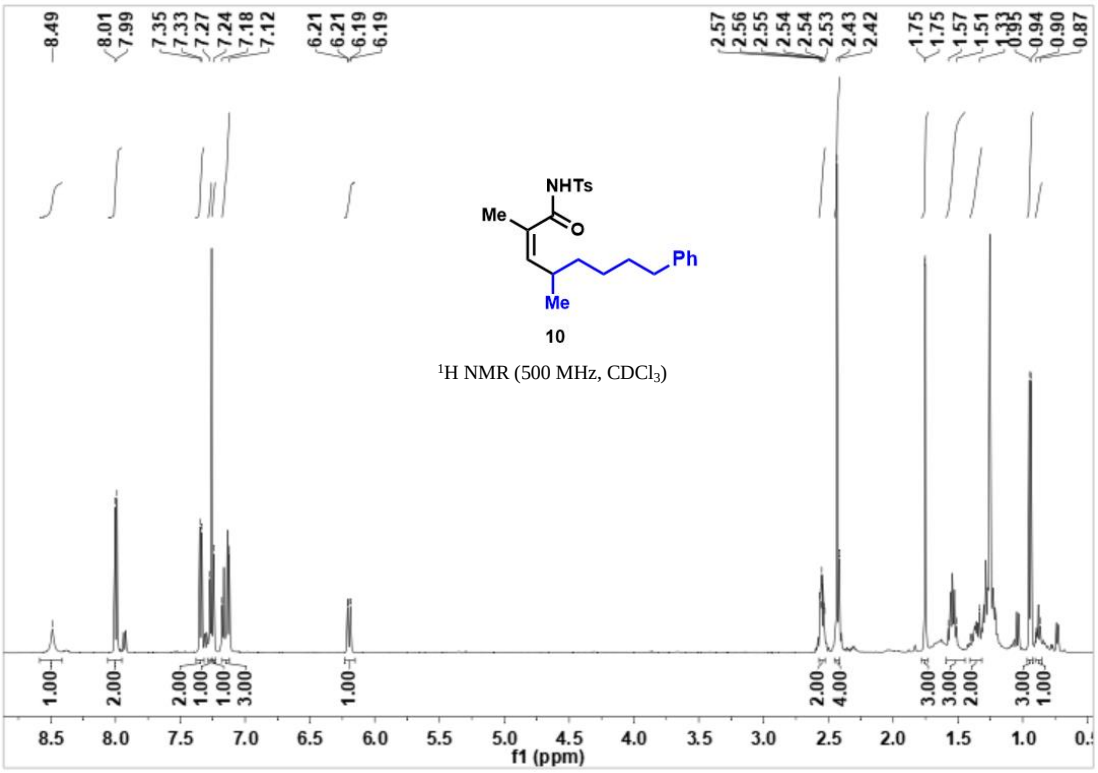

162.38
144.77
142.79
136.87
136.36
134.01
133.82
129.30
129.24
129.21
129.13
129.09
128.55
128.31
127.73
127.55
127.46
126.95
126.23
124.76
61.51
38.66
36.29
22.47
21.68
O
N
Ts
Ph
Me
5b(trans)
13C NMR (125 Hz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



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

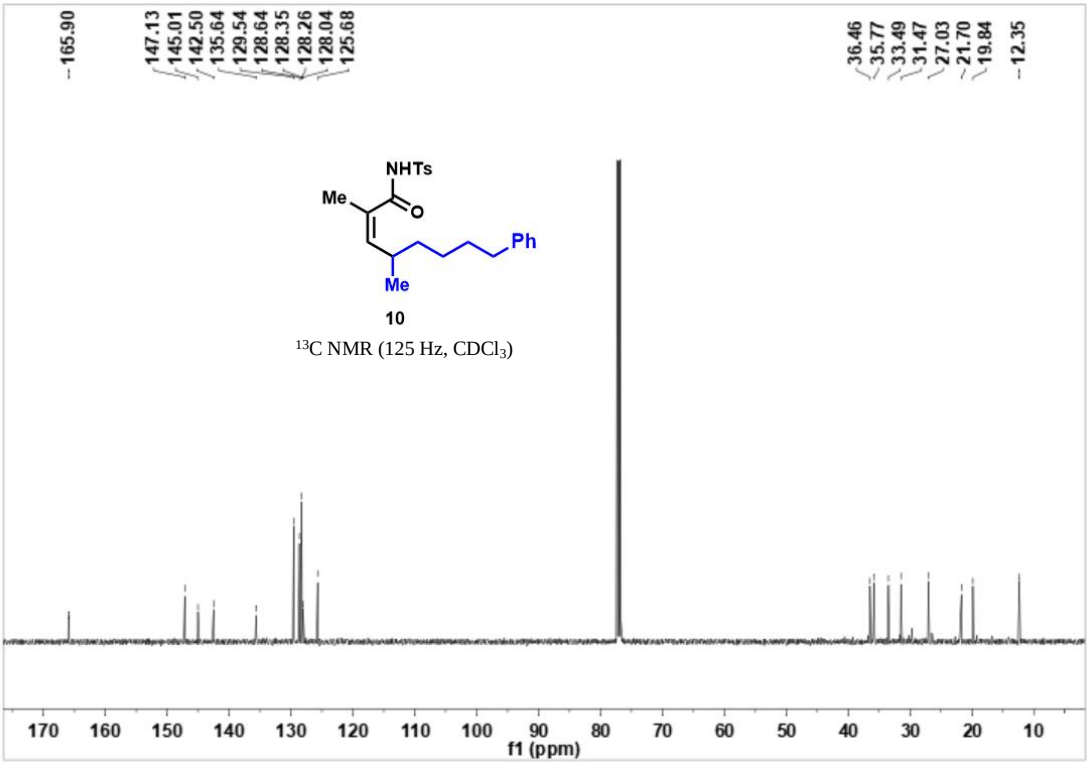


^{13}C NMR (125 Hz, $CDCl_3$)



10

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



10

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