Contra-Thermodynamic Positional Isomerization of Olefins

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Supporting Information

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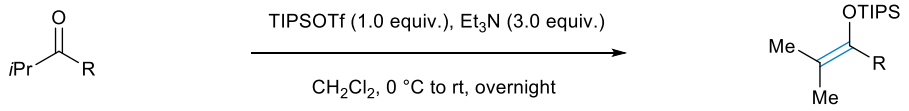
General Information

Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.[1] All solvents were purified according to the method of Grubbs.[2] Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using a water bath. Chromatographic purification of products was accomplished by flash chromatography on a Biotage Isolera One with cartridges containing Fluka 230–400 mesh silica gel. Thin-layer chromatography (TLC) was performed on Silicycle 250 μm silica gel plates. Visualization of the developed chromatogram was performed by irradiation with UV light or treatment with a solution of phosphomolybdic acid, ceric ammonium molybdate, *p*-anisaldehyde stains, potassium permanganate, and cobalt (II) thiocyanate followed by heating when necessary.[3] Yields refer to purified compounds unless otherwise noted.

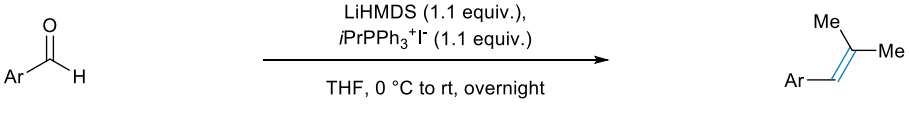
All ^{1}H, NOESY, and ^{13}C{^{1}H} NMR spectra were recorded on Bruker Avance II 500 (500 and 126 MHz for ^{1}H and ^{13}C respectively), and Bruker Avance III HD 800 (800 MHz for 1 H) instruments and were referenced to residual protio-solvent signals: $CDCl_3$ at δ 7.26 and 77.16 ppm, and DMSO-d_6 at δ 2.50 and 39.52 ppm. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), broad peak (br), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, h = hextet, m = multiplet), coupling constant (Hz) and integration; data for ^{13}C NMR are reported in terms of chemical shift and no special nomenclature is used for equivalent carbons. IR spectra were recorded on a Thermo Scientific Nicolet 6700 FT-IR spectrometer and are reported in terms of frequency of absorption (cm^{-1}). High-resolution mass spectra were obtained at Princeton University Mass Spectrometry Facility using an Agilent 6210 TOF LC/MS (Electrospray Ionization, ESI) or an Agilent 7200 Q-TOF GC/MS (Electron Ionization, EI) or at Princeton University Proteomics and Mass Spectrometry Core Facility using a Thermo Scientific LTQ Orbitrap XL Mass Spectrometer (Electrospray Ionization, ESI).

Synthesis of Starting Materials

General Procedure A



General Procedure B

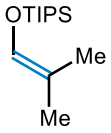


General Procedure A: Preparation of silyl enol ethers

Following a literature procedure, triethylamine (3.00 equiv.) was added dropwise to a stirring solution of the ketone substrate (1.00 equiv.) in dichloromethane (0.200 M) at 0 ºC, followed by the addition of triisopropylsilyl trifluoromethanesulfonate (1.00 equiv.). This mixture was allowed to warm to rt, stirred overnight, and then filtered through a short plug of silica with dichloromethane as eluent. The resulting filtrate was concentrated, and the desired enol ether product was purified by silica gel flash column chromatography (EtOAc in hexanes).[4]

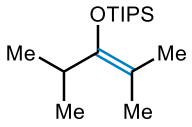
General Procedure B: Preparation of styrene derivatives using Wittig olefination

To an oven-dried round-bottom flask equipped with a stir bar, was added isopropyltriphenylphosphonium iodide (1.10 equiv.) and lithium bis(trimethylsilyl)amide (1.10 equiv.) in a glove box. The flask was then sealed with a septum, removed from the glove box, and connected to a nitrogen inlet. The flask was then cooled with an ice bath and was added tetrahydrofuran (THF, 0.100 M). The resulting red suspension was allowed to warm to rt and stirred for 1.5 h. The freshly prepared Wittig reagent was then cooled to 0 ºC and was added aryl aldehyde (1.00 equiv. in 0.2 M THF) via a syringe. The resulting reaction mixture was stirred overnight at rt. During this time, the red color disappears and furnishes a white precipitate. The suspension was subsequently concentrated to a small volume, suspended in diethyl ether, sonicated for 5 min, and then filtered through a plug of silica. The filter cake was rinsed with diethyl ether for three times. The filtrate was collected, concentrated to a small volume, and purified by silica gel flash column chromatography (EtOAc in hexanes) to afford the desired olefin product.[5]



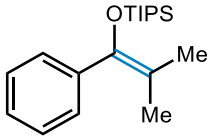
Triisopropyl((2-methylprop-1-en-1-yl)oxy)silane (1)

The title compound was synthesized following general procedure A using isobutyraldehyde. Yield and spectra are consistent with reported literature values.[4]



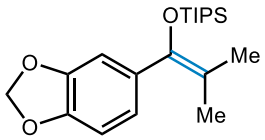
((2,4-dimethylpent-2-en-3-yl)oxy)triisopropylsilane (2)

The title compound was synthesized following general procedure A using 2,4-dimethyl-3-pentanone (1.00 g, 8.76 mmol) and purified by silica gel flash column chromatography (0% to 5% EtOAc in hexanes). The desired enol ether compound was obtained as a colorless liquid (2.01 g, 84%). Spectra are consistent with reported literature values.[6]



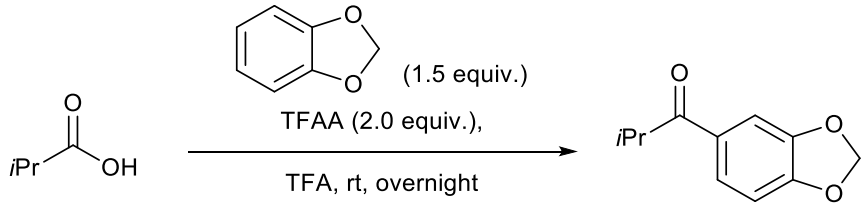
Triisopropyl((2-methyl-1-phenylprop-1-en-1-yl)oxy)silane (3)

The title compound synthesized following general procedure A using 2-methyl-1-phenylpropan-1-one (1.00 g, 6.75 mmol) and purified by silica gel flash column chromatography (0% to 25% EtOAc in hexanes). The desired enol ether compound was obtained as a colorless oil (1.80 g, 87%). Spectra are consistent with reported literature values.[7]



((1-(benzo[*d*][1,3]dioxol-5-yl)-2-methylprop-1-en-1-yl)oxy)triisopropylsilane (4)

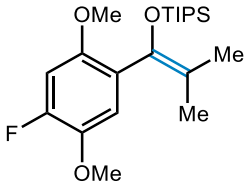
The title compound was synthesized via sequential Friedel-Crafts acylation of benzo[*d*][1,3]dioxole using isobutyric acid and the silylation of 1-(benzo[*d*][1,3]dioxol-5-yl)-2-methylpropan-1-one following general procedure A.[8]



1-(benzo[*d*][1,3]dioxol-5-yl)-2-methylpropan-1-one was prepared by following a literature procedure. Benzo[*d*][1,3]dioxole (1.00 g, 8.19 mmol, 1.50 equiv.) and isobutyric acid (481 mg, 5.46 mmol, 1.00 equiv.) were added to trifluoroacetic acid (10 mL) at rt. Then, trifluoroacetic anhydride (1.54 mL, 10.9 mmol, 2.00 equiv.) was added to the reaction mixture in one portion.

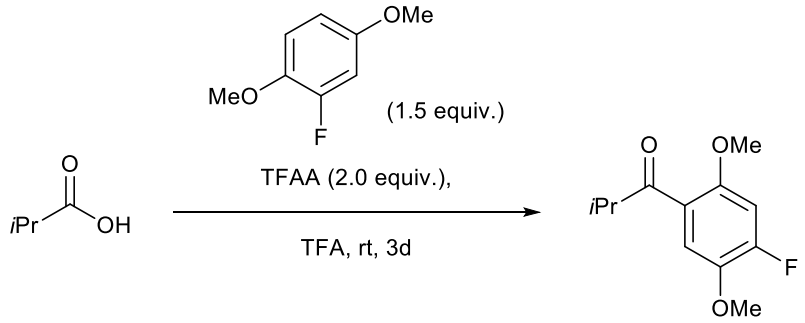
The colorless solution slowly turned purple. The resulting mixture was stirred at rt overnight and was then concentrated to a small volume, diluted with hexane (20 mL), and washed with sat. $NaHCO_3$ aq. (20 mL) for three times to fully remove the residual trifluoroacetic acid. The organic layer was collected, dried over anhydrous $MgSO_4$, filtered, and concentrated to a small volume. The crude oil was purified by column chromatography (0% to 5% EtOAc in hexanes). 1-(benzo[*d*][1,3]dioxol-5-yl)-2-methylpropan-1-one was obtained as a colorless oil (0.959 g, 91%). Spectra are consistent with reported literature values.[9]

The title compound was synthesized following general procedure A using 1-(benzo[*d*][1,3]dioxol-5-yl)-2-methylpropan-1-one (0.959 g, 4.99 mmol) and purified by silica gel flash column chromatography (0% to 10% EtOAc in hexanes). The title compound was obtained as a colorless oil (1.08 g, 62%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.81 – 6.72 (m, 3H), 5.95 (s, 2H), 1.79 (s, 3H), 1.56 (s, 3H), 0.99 – 0.94 (m, 21H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 146.95, 146.59, 143.78, 133.48, 123.17, 111.54, 110.05, 107.65, 101.00, 20.18, 18.35, 18.06, 13.27. **IR (neat)**: 2939, 2864, 1483, 1434, 1234, 1035, 933, 877, 675 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{20}H_{33}O_3Si$) requires *m/z* 349.21935, found *m/z* 349.21949.



((1-(4-fluoro-2,5-dimethoxyphenyl)-2-methylprop-1-en-1-yl)oxy)triisopropylsilane (5)

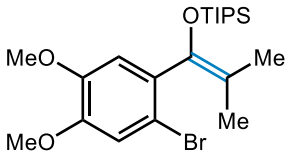
The title compound was synthesized via sequential Friedel-Crafts acylation of 2-fluoro-1,4-dimethoxybenzene using isobutyric acid and the silylation of 1-(4-fluoro-2,5-dimethoxyphenyl)-2-methylpropan-1-one following general procedure A.[8]



1-(4-fluoro-2,5-dimethoxyphenyl)-2-methylpropan-1-one was prepared by following a literature procedure. 2-fluoro-1,4-dimethoxybenzene (5.00 g, 32.0 mmol, 1.50 equiv.) and isobutyric acid (1.88 g, 21.4 mmol, 1.00 equiv.) were added to trifluoroacetic acid (30 mL) at rt. Then, trifluoroacetic anhydride (6 mL, 42.7 mmol, 2.00 equiv.) was added to the reaction mixture in one portion. The colorless solution slowly turned purple. The resulting mixture was stirred at rt for 3 days and was then concentrated to a small volume, diluted with hexane (20 mL), and washed with sat. $NaHCO_3$ aq. (20 mL) three times to fully remove the residual trifluoroacetic acid. The organic layer was collected, dried over anhydrous $MgSO_4$, filtered, and concentrated to a small volume. The crude oil was purified by column chromatography (0% to 5% EtOAc in hexanes). 1-(4-fluoro-2,5-dimethoxyphenyl)-2-methylpropan-1-one was obtained as a white solid (2.35 g, 48%). **^{1}H**

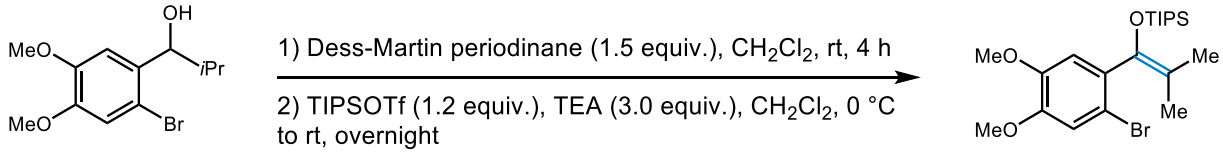
NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 9.8 Hz, 1H), 6.74 (d, *J* = 12.6 Hz, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 3.54 (hept, *J* = 6.9 Hz, 1H), 1.13 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 205.90, 155.15 (d, *J* = 253.3 Hz), 153.14 (d, *J* = 8.5 Hz), 141.67 (d, *J* = 11.0 Hz), 123.50 (d, *J* = 3.4 Hz), 115.75 (d, *J* = 4.1 Hz), 101.30 (d, J = 22.4 Hz), 56.87, 56.38, 40.09, 18.79. **IR (neat)**: 2969, 2870, 1670, 1584, 1506, 1462, 1398, 1282, 1217, 1132, 1032, 792 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{12}H_{16}FO_3$) requires *m/z* 227.10780, found *m/z* 227.10800.

The title compound was synthesized following general procedure A using 1-(4-fluoro-2,5-dimethoxyphenyl)-2-methylpropan-1-one (1.00 g, 4.42 mmol) and purified by silica gel flash column chromatography (hexanes). The title compound was obtained as a white solid (1.30 g, 76%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.87 (d, *J* = 9.8 Hz, 1H), 6.65 (d, *J* = 13.1 Hz, 1H), 3.82 (s, 3H), 3.72 (s, 3H), 1.80 (s, 3H), 1.41 (s, 3H), 1.00 – 0.90 (m, 21H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 152.36 (d, *J* = 236.7 Hz), 151.35, 140.53 (d, *J* = 11.1 Hz), 139.46, 123.67 (d, *J* = 3.8 Hz), 117.38, 113.11, 100.48 (d, *J* = 22.0 Hz), 57.22, 55.74, 19.83, 17.97, 17.84, 13.17. **IR (neat):** 2861, 2362, 1591, 1506, 1457, 1393, 1326, 1202, 1151, 1035, 873, 783, 677, 648 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{21}H_{36}O_3FSi$) requires *m/z* 383.24123, found *m/z* 383.24057.

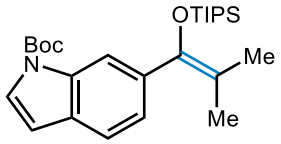


((1-(2-bromo-4,5-dimethoxyphenyl)-2-methylprop-1-en-1-yl)oxy)triisopropylsilane (6)

The title compound was synthesized via sequential oxidation of 1-(2-bromo-4,5-dimethoxyphenyl)-2-methylpropan-1-ol, which was prepared following a literature condition,[11] using Dess-Martin periodinane,[12] and the silylation of 1-(2-bromo-4,5-dimethoxyphenyl)-2-methylpropan-1-onefollowing general procedure A.

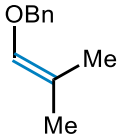


Dess-Martin periodinane (2.64 g, 6.22 mmol, 1.50 equiv.) were added to 1-(2-bromo-4,5-dimethoxyphenyl)-2-methylpropan-1-ol (1.20 g, 4.15 mmol, 1.00 equiv.) in CH_2Cl_2 (20 mL) at rt. The resulting suspension was stirred for 4 h at rt. Then, the resulting mixture was filtered through a plug of silica gel using CH_2Cl_2 as the eluent. The filtrate was collected, concentrated to a small volume, and was diluted with CH_2Cl_2 (20 mL). The resulting solution was then cooled to 0 ℃. Triethylamine (1.74 mL, 12.5 mmol, 3.00 equiv.) and triisopropylsilyl trifluoromethanesulfonate (1.67 mL, 6.22 mmol, 1.50 equiv.) were sequentially added. The mixture was allowed to warm to rt, stirred overnight, and then filtered through a plug of silica gel using hexanes as the eluent. The filtrate was collected, concentrated to a small volume, and then purified by silica gel flash column chromatography (0% to 20% EtOAc in hexanes). The desired enol ether compound was obtained as a white solid (881 mg, 47%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.99 (s, 1H), 6.81 (s, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 1.80 (s, 3H), 1.45 (s, 3H), 1.07 – 0.92 (m, 21H). **^{13}C NMR (126 MHz, $CDCl_3$, mixture of rotamers)** δ 148.94, 147.91, 142.47, 132.62, 115.17, 114.67, 114.22, 112.93, 56.23, 56.11, 19.83, 18.10, 18.03, 17.78, 13.23. **IR (neat):** 2937, 2861, 1599, 1500, 1456, 1376, 1243, 1206, 1157, 1025, 869, 820, 780, 648 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{21}H_{36}BrO_3Si$) requires *m/z* 443.16116 and 445.15911, found *m/z* 443.16134 and 445.15907.



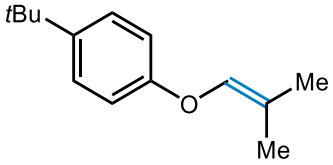
***tert*-butyl 6-(2-methyl-1-((triisopropylsilyl)oxy)prop-1-en-1-yl)-1*H*-indole-1-carboxylate (7)**

The title compound was synthesized following general procedure A using *tert*-butyl 6-isobutyryl-1*H*-indole-1-carboxylate (770 mg, 2.68 mmol, 1.00 equiv.), which was prepared using a reported procedure and purified by silica gel flash column chromatography (0% to 20% EtOAc in hexanes). The desired enol ether compound was obtained as a colorless oil (1.19 g, quant.).[10] **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.06 (s, 1H), 7.61 (d, J = 3.8 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.21 (dd, J = 8.1, 1.4 Hz, 1H), 6.55 (d, J = 3.7 Hz, 1H), 1.84 (s, 3H), 1.67 (s, 9H), 1.61 (s, 3H), 0.99 – 0.87 (m, 21H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 149.95, 144.89, 135.60, 134.54, 129.73, 126.44, 124.46, 120.04, 116.51, 111.48, 107.30, 83.78, 28.36, 20.33, 18.50, 18.11, 13.27. **IR (neat):** 2937, 2864, 1734, 1433, 1378, 1336, 1148, 882, 834, 671 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{26}H_{42}NO_3Si$) requires *m/z* 444.29285, found *m/z* 444.29333.



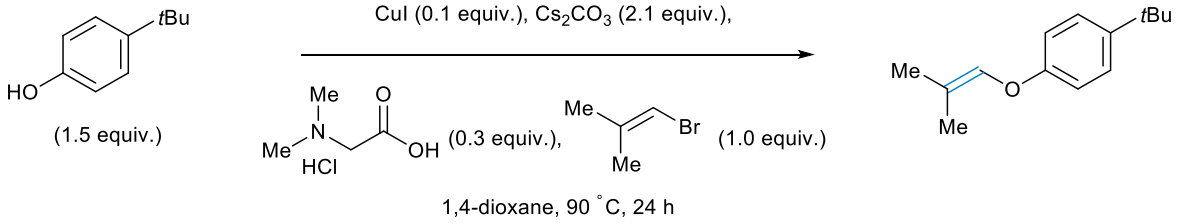
(((2-methylprop-1-en-1-yl)oxy)methyl)benzene (8)

The title compound was synthesized following a literature procedure. Spectra are consistent with reported literature values.[13]



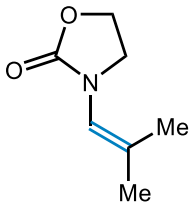
1-(*tert*-butyl)-4-((2-methylprop-1-en-1-yl)oxy)benzene (9)

The title compound was synthesized by copper-catalyzed *O*-vinylation of 4-(*tert*-butyl)phenol with 1-bromo-2-methylpropene following a literature procedure.[14]

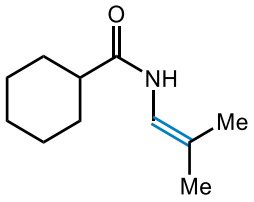


To an oven-dried 100-mL round bottom flask, charged with a stir bar, was added 4-(*tert*-butyl)phenol (676 mg, 4.50 mmol, 1.50 equiv.) and *N*,*N*-dimethylglycine hydrochloride (126 mg, 0.900 mmol, 0.300 equiv.). The flask was then transferred into a glove box and was charged with copper(I) iodide (57.1 mg, 0.300 mmol, 0.100 equiv.), cesium carbonate (2.05 g, 6.30 mmol, 2.10 equiv.), 1,4-dioxane (10 mL), and 1-bromo-2-methyl-prop-1-ene (0.307 mL, 3.00 mmol, 1.00 equiv.). The flask was then fitted with a reflux condenser equipped with a septum and removed from the glove box. The reaction mixture was heated to 90 °C for 24 h under nitrogen atmosphere and then cooled to rt. The resulting mixture was diluted with EtOAc (50 mL) and was filtered

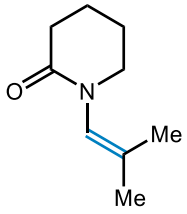
through a plug of silica. Additional EtOAc (50 mL) was used to rinse the reaction flask and filtered through the silica plug. The filtrate was collected and concentrated to a small volume. The crude oil was purified by silica gel flash column chromatography (0% to 5% EtOAc in hexanes). The desired enol ether compound was obtained as a colorless liquid (510 mg, 83% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.31 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.18 (hept, *J* = 1.5 Hz, 1H), 1.72 (d, *J* = 1.5 Hz, 3H), 1.69 (d, *J* = 1.5 Hz, 3H), 1.30 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 155.68, 144.76, 135.54, 126.41, 117.41, 115.38, 34.30, 31.65, 19.66, 15.30. **IR:** 2959, 2868, 1690, 1606, 1506, 1237, 1118, 1125, 1105, 823, 556 cm^{-1} **HRMS (EI):** exact mass calculated for $[M]^+$ ($C_{14}H_{20}O$) requires *m/z* 204.15087, found *m/z* 204.15090.



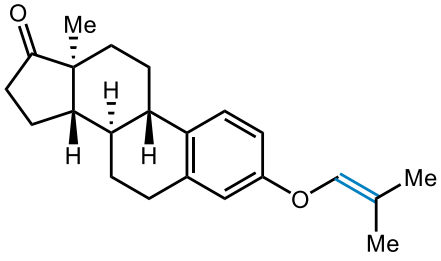
3-(2-methylprop-1-en-1-yl)oxazolidin-2-one (10)
The title compound was synthesized following a literature procedure. Spectra are consistent with reported literature values. Spectra are consistent with reported literature values.[15]



***N*-(2-methylprop-1-en-1-yl)cyclohexanecarboxamide (11)**
The title compound was synthesized following a literature procedure. Spectra are consistent with reported literature values. Spectra are consistent with reported literature values.[15]

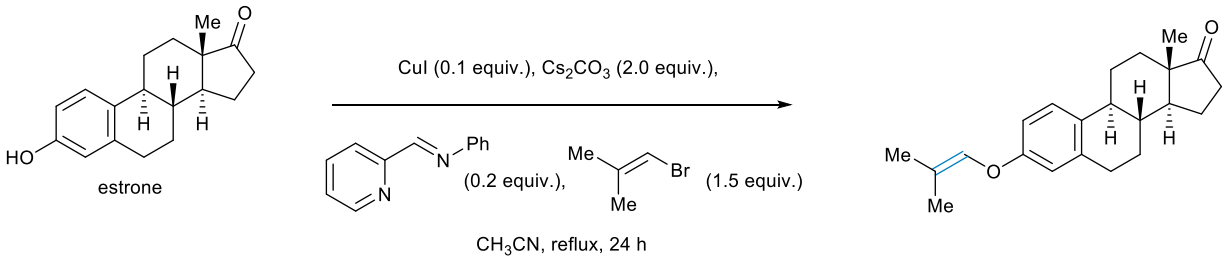


1-(2-methylprop-1-en-1-yl)piperidin-2-one (12)
The title compound was synthesized following a literature procedure. Spectra are consistent with reported literature values. Spectra are consistent with reported literature values.[15]

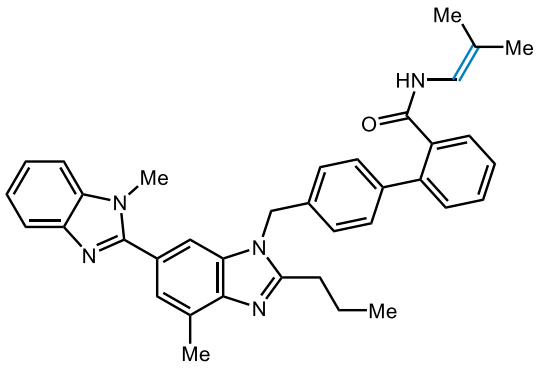


(8*R*,9*S*,13*S*,14*S*)-13-methyl-3-((2-methylprop-1-en-1-yl)oxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (13)

The title compound was synthesized by copper-catalyzed *O*-vinylation of estrone with 1-bromo-2-methyl-prop-1-ene following a literature procedure.[16]

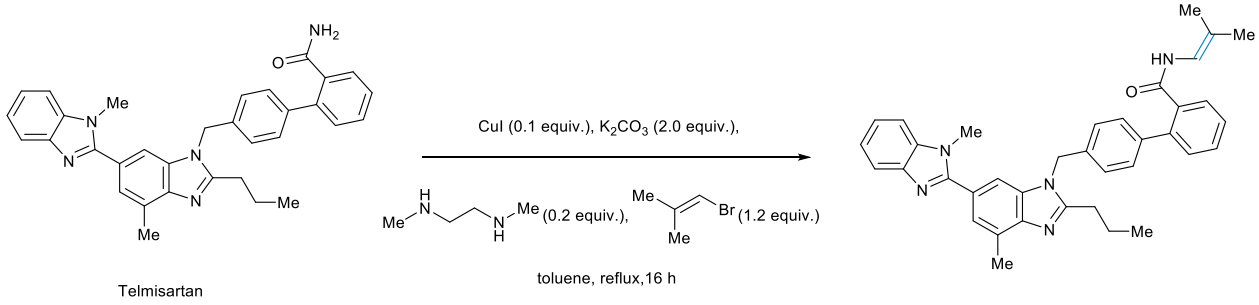


To an oven-dried 100-mL round bottom flask, charged with a stir bar, was added estrone (1.00 g, 3.70 mmol, 1.00 equiv.) and (*E*)-*N*-phenyl-1-(pyridin-2-yl)methanimine (135 mg, 0.740 mmol, 0.200 equiv.). The flask was then transferred into a glove box and was charged with copper(I) iodide (70.4 mg, 0.370 mmol, 0.100 equiv.), cesium carbonate (2.41 g, 7.40 mmol, 2.00 equiv.), MeCN (25 mL), and 1-bromo-2-methyl-prop-1-ene (0.570 mL, 5.55 mmol, 1.50 equiv.). The flask was then fitted with a reflux condenser equipped with a septum and removed from the glove box. The reaction mixture was heated to reflux for 24h under nitrogen atmosphere and then cooled to rt. The resulting mixture was diluted with EtOAc (50 mL) and was filtered through a plug of silica. Additional EtOAc (50 mL) was used to rinse the reaction flask and filtered through the silica plug. The filtrate was collected and concentrated to a small volume. The crude oil was purified by silica gel flash column chromatography (0% to 60% EtOAc in hexanes). The title compound was obtained as a white solid (350 mg, 29%).**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.21 (d, *J* = 8.6 Hz, 1H), 6.78 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.71 (d, *J* = 2.7 Hz, 1H), 6.17 (t, *J* = 1.5 Hz, 1H), 2.92 – 2.86 (m, 2H), 2.51 (dd, *J* = 19.0, 8.7 Hz, 1H), 2.44 – 2.34 (m, 1H), 2.26 (td, *J* = 10.7, 4.4 Hz, 1H), 2.14 (dd, *J* = 19.1, 9.0 Hz, 1H), 2.10 – 1.91 (m, 3H), 1.71 (s, 3H), 1.69 (s, 3H), 1.67 – 1.37 (m, 6H), 0.91 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 221.11, 155.94, 138.03, 135.40, 133.39, 126.54, 117.53, 115.87, 113.46, 50.52, 48.13, 44.15, 38.43, 36.01, 31.69, 29.72, 26.63, 26.04, 21.72, 19.66, 15.29, 13.98. **IR (neat)**: 2921, 2868,1736, 1688, 1605, 1496, 1451, 1246, 1163, 1125, 1004, 815, 786 cm^{-1}. **HRMS (ESI)**: exact mass calculated for $[M+H]^+$ ($C_{22}H_{29}O_2$) requires *m/z* 325.21621, found *m/z* 325.21619.

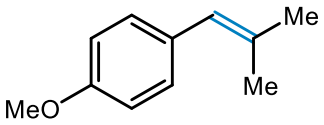


4'-((1,7'-dimethyl-2'-propyl-1*H*,3'*H*-[2,5'-bibenzo[*d*]imidazol]-3'-yl)methyl)-*N*-(2-methylprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxamide (14)

The title compound was synthesized by copper-catalyzed *N*-vinylation of Telmisartan with 1-bromo-2-methyl-prop-1-ene following a literature procedure.[15]

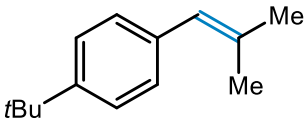


To an oven-dried 100-mL round bottom flask, charged with a stir bar, was added Telmisartan (1.93 g, 3.76 mmol, 1.00 equiv.), *N*,*N*′-dimethylethane-1,2-diamine (81.0 µL, 0.751 mmol, 0.200 equiv.), and anhydrous potassium carbonate (1.04 g, 7.51 mmol, 2.00 equiv.). The flask was then transferred into a glove box and charged with copper(I) iodide (71.6 mg, 0.375 mmol, 0.100 equiv.), toluene (25 mL), and 1-bromo-2-methyl-prop-1-ene (0.462 mL, 4.51 mmol, 1.20 equiv.). The flask was then fitted with a reflux condenser equipped with a septum and removed from the glove box. The reaction mixture was heated to reflux for 16 h under nitrogen atmosphere and then cooled to rt. The resulting mixture was diluted with EtOAc (50 mL) and was filtered through a plug of silica. Additional EtOAc (50 mL) was used to rinse the reaction flask and filtered through the same silica plug. The combined filtrate was collected and concentrated to a small volume. The crude oil was purified by silica gel flash column chromatography (80% to 100% EtOAc in hexanes). The title compound was obtained as a white solid (1.20 g, 56%). **^{1}H NMR (500 MHz, DMSO-*d6*)** δ 9.16 (d, *J* = 9.6 Hz, 1H), 7.77 (s, 1H), 7.64 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.58 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.50 – 7.39 (m, 4H), 7.37 – 7.30 (m, 3H), 7.24 (dtd, *J* = 22.0, 7.2, 1.2 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.27 (dt, *J* = 9.6, 1.5 Hz, 1H), 5.61 (s, 2H), 3.84 (s, 3H), 2.90 (dd, *J* = 8.6, 6.6 Hz, 2H), 2.63 (s, 3H), 1.82 (hept, *J* = 7.4 Hz, 2H), 1.47 (d, *J* = 1.5 Hz, 3H), 1.23 (d, *J* = 1.4 Hz, 3H), 1.00 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (126 MHz, DMSO-*d6*)** δ 166.44, 156.14, 154.04, 142.67, 142.54, 139.48, 138.93, 136.69, 136.39, 136.08, 134.75, 129.87, 129.63, 128.81, 128.24, 128.18, 127.16, 126.42, 123.35, 123.24, 122.05, 121.80, 118.72, 117.58, 116.09, 110.38, 109.22, 45.92, 31.81, 28.76, 22.41, 20.70, 16.51, 16.40, 13.88. **IR(neat)**: 2955, 2869, 1645, 1503, 1445, 1382, 1241, 1087, 840, 740 cm^{-1}. **HRMS (ESI)**: exact mass calculated for $[M+H]^+$ ($C_{37}H_{38}N_5O$) requires *m/z* 568.30709, found *m/z* 568.30721.



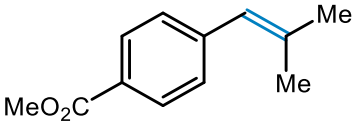
1-methoxy-4-(2-methylprop-1-en-1-yl)benzene (16)

The title compound was synthesized following a literature condition, and spectra are consistent with reported literature values.[17]



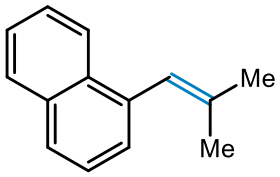
1-(*tert*-butyl)-4-(2-methylprop-1-en-1-yl)benzene (17)

The title compound was synthesized following a literature condition, and spectra are consistent with reported literature values.[17]



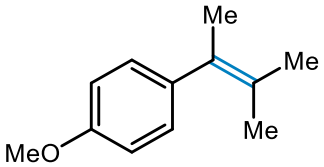
Methyl 4-(2-methylprop-1-en-1-yl)benzoate (18)

The title compound was synthesized following a literature condition, and spectra are consistent with reported literature values.[18]



1-(2-methylprop-1-en-1-yl)naphthalene (19)

The title compound was synthesized following a literature condition, and spectra are consistent with reported literature values.[19]

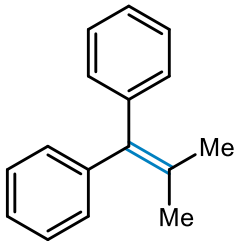


1-methoxy-4-(3-methylbut-2-en-2-yl)benzene (20)

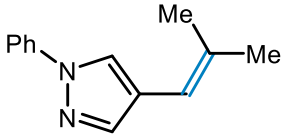
The title compound was synthesized using modified Wittig olefination with isopropyltriphenylphosphonium iodide and 1-(4-methoxyphenyl)ethan-1-one.

To an oven-dried 50-mL round bottom flask, charged with a stir bar, was added isopropyltriphenylphosphonium iodide (2.59 g, 5.99 mmol, 1.80 equiv.). The flask was then

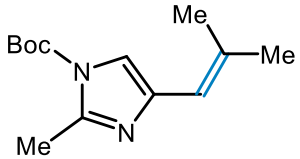
transferred into a glove box and was added potassium bis(trimethylsilyl)amide (1.20 g, 5.99 mmol, 1.80 equiv.) and toluene (20 mL). The reaction mixture was stirred at rt for 10 min and eventually turned dark red. A solution of 1-(4-methoxyphenyl)ethan-1-one (500 mg, 3.33 mmol, 1.00 equiv.) in toluene (5 mL) was added to the reaction mixture at rt. The flask was then fitted with a condenser sealed with a septum and was removed out of the glove box. After connecting to a nitrogen inlet, the reaction mixture was refluxed for 2 h and was then allowed to cool to rt and stirred overnight. The resulting reaction mixture was concentrated to a small volume under reduce pressure, diluted with ether (50 mL), and filtered through a plug of silica. The flask was rinsed with another portion of ether (50 mL), which was filtered through the plug of silica. The filtrate was collected and concentrated to a small volume under reduced pressure. The crude oil was purified by silica gel flash column chromatography (0% to 35% EtOAc in hexanes). The title compound was obtained as a colorless oil (525 mg, 89% yield). Spectra are consistent with reported literature values.[20]



(2-methylprop-1-ene-1,1-diyl)dibenzene (21)
The title compound was synthesized following a literature condition, and spectra are consistent with reported literature values.[21]



4-(2-methylprop-1-en-1-yl)-1-phenyl-1*H*-pyrazole (22)
The title compound was synthesized following general procedure B using 1-phenyl-1*H*-pyrazole-4-carbaldehyde (1.00 g, 5.81 mmol) and purified by filtrating the crude reaction mixture through a plug of silica with ether as eluent. The desired product was obtained as a white solid (525 mg, 45%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.83 (s, 1H), 7.68 (d, *J* = 7.6 Hz, 3H), 7.45 (dd, *J* = 8.5, 7.2 Hz, 2H), 7.29 – 7.26 (m, 1H), 6.08 (s, 1H), 1.92 (s, 3H), 1.91 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 141.11, 140.22, 134.75, 129.55, 126.39, 124.64, 121.99, 119.05, 114.51, 26.91, 20.17. **IR (neat):** 2970, 2914, 1594, 1543, 1496, 1384, 1217, 1001, 856, 747, 682, 655 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{13}H_{15}N_2$) requires *m/z* 199.12297, found *m/z* 199.12290.

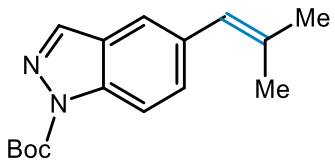


***tert*-butyl 2-methyl-4-(2-methylprop-1-en-1-yl)-1*H*-imidazole-1-carboxylate (23)**

The title compound was synthesized following general procedure B using *tert*-butyl 4-formyl-2-methyl-1*H*-imidazole-1-carboxylate, which was prepared by amine Boc protection of 2-methyl-1*H*-imidazole-4-carbaldehyde.[10]

To a solution of 2-methyl-1*H*-imidazole-4-carbaldehyde (1.00 g, 9.08 mmol, 1.00 equiv.) in CH_2Cl_2 (25 mL) was added di-*tert*-butyl dicarbonate (1.98 g, 9.08 mmol, 1.00 equiv.) and one chip of 4-dimethylaminopyridine (~5 mg). The resulting solution was stirred at rt for 3h. Then, the solvent was evaporated under reduced pressure to afford *tert*-butyl 4-formyl-2-methyl-1*H*-imidazole-1-carboxylate (1.90 g, 99%) as a pale yellow solid, which was used in the next step without further purification. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.85 (s, 1H), 7.98 (s, 1H), 2.68 (s, 3H), 1.64 (s, 9H).

The title compound was synthesized following general procedure B using *tert*-butyl 4-formyl-2-methyl-1*H*-imidazole-1-carboxylate (1.07 g, 5.10 mmol) and purified by recrystallization from hot hexane. The title compound was obtained as a colorless crystal (400 mg, 35%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.14 (s, 1H), 6.05 (s, 1H), 2.61 (s, 3H), 1.95 (s, 3H), 1.89 (s, 3H), 1.61 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$, mixture of rotamers)** δ 148.17, 146.78, 138.05, 136.79, 132.28, 132.20, 128.69, 128.59, 117.07, 114.70, 85.16, 28.09, 27.08, 20.26, 17.07. **IR (neat):** 2976, 2931, 1743, 1528, 1441, 1358, 1248, 1142, 1110, 824, 743 cm^{-1} **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{13}H_{21}N_2O_2$) requires *m/z* 237.15973, found *m/z* 237.15975.



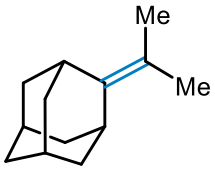
***tert*-butyl 5-(2-methylprop-1-en-1-yl)-1*H*-indazole-1-carboxylate (24)**

The title compound was synthesized following general procedure B using *tert*-butyl 5-formyl-1*H*-indazole-1-carboxylate, which was prepared by amine Boc protection of 1*H*-indazole-5-carbaldehyde.[10]

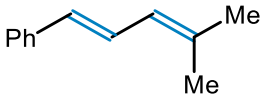
To a solution of 1*H*-indazole-5-carbaldehyde (1.00 g, 6.84 mmol, 1.00 equiv.) in CH_2Cl_2 (20 mL) was added di-*tert*-butyl dicarbonate (1.64 g, 7.53 mmol, 1.10 equiv.) and one chip of 4-dimethylaminopyridine (~5 mg). The resulting solution was stirred at rt overnight and was then filtered through a plug of silica. The filtrate was collected and concentrated under reduced pressure to afford *tert*-butyl 5-formyl-1*H*-indazole-1-carboxylate (1.31 g, 77%) as a pale yellow oil, which was used in the next step without further purification. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 10.11 (s, 1H), 8.38 – 8.24 (m, 3H), 8.08 (dd, *J* = 8.7, 1.6 Hz, 1H), 1.74 (s, 9H).

The title compound was synthesized following general procedure B using *tert*-butyl 4-formyl-2-methyl-1*H*-imidazole-1-carboxylate (0.800 g, 3.25 mmol) and purified by silica gel flash column chromatography (0% to 40% EtOAc in hexanes), the title compound was obtained as a colorless oil (522 mg, 59% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.14 (s, 1H), 8.09 (d, *J* = 8.7 Hz, 1H), 7.54 (s, 1H), 7.39 (dd, *J* = 8.7, 1.6 Hz, 1H), 6.36 (s, 1H), 1.93 (s, 3H), 1.87 (s, 3H), 1.73 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 149.39, 139.81, 138.17, 136.10, 134.65, 130.62, 126.18, 124.54, 120.48, 114.15, 84.90, 28.34, 26.92, 19.52. **IR (neat):** 2974, 2928, 1731, 1433, 1378, 1286,1245,

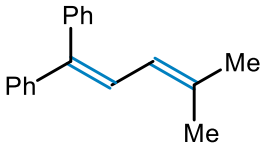
1136, 1027, 841, 763 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{16}H_{21}N_2O_2$) requires *m/z* 273.15975, found *m/z* 273.15993.



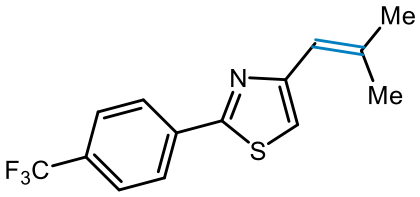
2-(propan-2-ylidene)adamantane (26)
The title compound was synthesized following a literature condition, and spectra are consistent with reported literature values.[22]



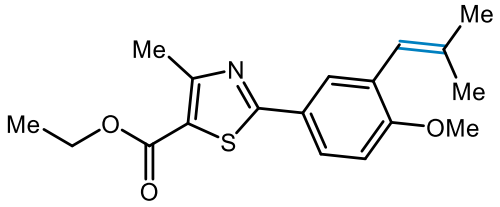
(*E*)-(4-methylpenta-1,3-dien-1-yl)benzene (28)
The title compound was synthesized following general procedure B using cinnamaldehyde (1.00 g, 7.57 mmol) and purified by silica gel flash column chromatography (0% to 20% EtOAc in hexanes), the title compound was obtained as a colorless oil (385 mg, 32% yield). Spectra are consistent with reported literature values.[23]



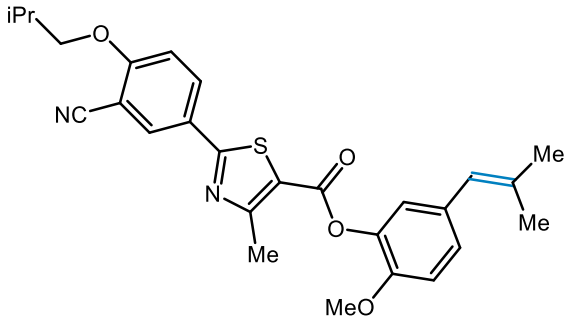
(4-methylpenta-1,3-diene-1,1-diyl)dibenzene (29)
The title compound was synthesized following general procedure B using 3,3-diphenylacrylaldehyde (0.800 g, 3.84 mmol) and purified by silica gel flash column chromatography (0% to 20% EtOAc in hexanes), the title compound was obtained as a colorless oil (600 mg, 53% yield). Spectra are consistent with reported literature values.[24]



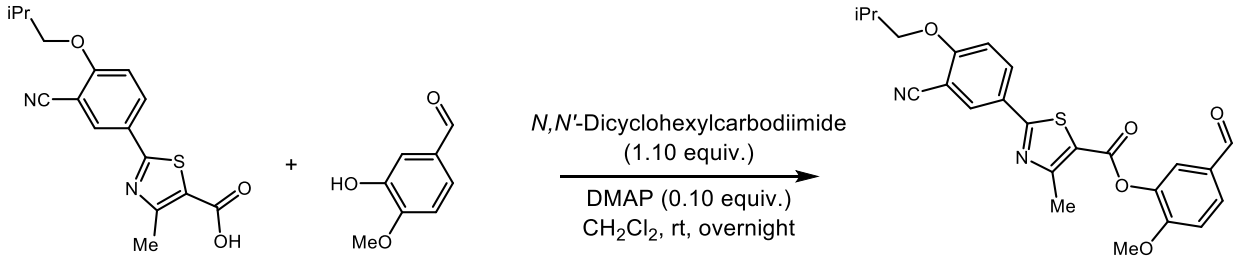
4-(2-methylprop-1-en-1-yl)-2-(4-(trifluoromethyl)phenyl)thiazole (30)
The title compound was synthesized following general procedure B using 2-(4-(trifluoromethyl)phenyl)thiazole-4-carbaldehyde (1.00 g, 3.89 mmol) and purified by silica gel flash column chromatography (0% to 40% EtOAc in hexanes). The title compound was obtained as a white solid (785 mg, 71%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.09 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.06 (s, 1H), 6.38 (p, *J* = 1.5 Hz, 1H), 2.15 (d, *J* = 1.5 Hz, 3H), 1.97 (d, *J* = 1.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.89, 155.57, 139.45, 136.88, 131.59 (q, *J* = 32.6 Hz), 126.85, 126.06 (q, *J* = 3.8 Hz), 124.08 (q, *J* = 272.1 Hz), 118.44, 115.69, 27.31, 20.32. **IR(neat):** 2939, 1611, 1480, 1459, 1325, 1165,1108, 1062, 996, 835, 730, 803 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{14}H_{13}SNF_3$) requires *m/z* 284.07153, found *m/z* 284.07182.



Ethyl 2-(4-methoxy-3-(2-methylprop-1-en-1-yl)phenyl)-4-methylthiazole-5-carboxylate (31) The title compound was synthesized following general procedure B using ethyl 2-(3-formyl-4-methoxyphenyl)-4-methylthiazole-5-carboxylate (1.00 g, 3.27 mmol) and purified by silica gel flash column chromatography (0% to 40% EtOAc in hexanes). The desired product was obtained as a white solid (788mg, 51% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.85 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.76 (d, *J* = 2.3 Hz, 1H), 6.91 (d, *J* = 8.6 Hz, 1H), 6.28 (s, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 3.89 (s, 3H), 2.76 (s, 3H), 1.95 (d, *J* = 1.5 Hz, 3H), 1.85 (d, *J* = 1.5 Hz, 3H), 1.38 (t, *J* = 7.2 Hz, 3H).**^{13}C NMR (126 MHz, $CDCl_3$)** δ 170.36, 162.60, 161.10, 159.54, 137.21, 129.27, 128.26, 126.42, 125.26, 120.85, 119.72, 110.59, 61.28, 55.83, 26.75, 19.78, 17.71, 14.52. **IR (neat):** 2965, 2911, 1687, 1595, 1428, 1369, 1322, 1254, 1095, 1048, 1016, 818, 757 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{18}H_{22}SNO_3$) requires *m/z* 332.13149, found *m/z* 332.13194.



***tert*-butyl 3-(4-methoxyphenyl)-4-(2-methylprop-1-en-1-yl)-1*H*-pyrazole-1-carboxylate (32)** The title compound was synthesized following general procedure B using 5-(2,5-dimethylphenoxy)-1-(4-methoxyphenyl)-2,2-dimethylpentan-1-one, which was synthesized following a literature condition.[25]



1.10 equiv. 1.00 equiv.

Febuxostat (2.50 g, 7.90 mmol, 1.10 equiv.), *N*,*N'*-dicyclohexylcarbodiimide (1.63 g, 7.90 mmol, 1.10 equiv.), and *N*,*N*-dimethylaminopyridine (87.8 mg, 0.718 mmol, 0.100 equiv.) were added to a stirring solution of 3-hydroxy-4-methoxybenzaldehyde (1.09 g, 7.18 mmol, 1.00 equiv.) in anhydrous dichloromethane (16 mL) under a N_2 atmosphere. The reaction mixture was stirred

overnight at room temperature. The reaction mixture was then filtered through a plug of silica gel using dichloromethane (~50 mL) as the eluent. The filtrate was concentrated and dissolved in a 1:1 solvent mixture of dichloromethane (80 mL) and hexane (80 mL) with gentle heating. Upon cooling to rt, this solution was poured into 400 mL hexane to afford a suspension. The resulting suspension was filtered, and the solid was rinsed with hexane for three times and dried by pulling air through for an additional 15 min. The desired product was obtained as a white solid (2.50 g, 77%). This compound was used in the next step without further purification. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.89 (s, 1H), 8.22 (d, *J* = 2.3 Hz, 1H), 8.13 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.82 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.71 (d, *J* = 2.1 Hz, 1H), 7.13 (d, *J* = 8.5 Hz, 1H), 7.04 (d, *J* = 8.9 Hz, 1H), 3.93 (s, 3H), 3.91 (d, *J* = 6.5 Hz, 2H), 2.82 (s, 3H), 2.20 (dh, *J* = 13.3, 6.5 Hz, 1H), 1.09 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 190.08, 168.53, 163.51, 162.82, 159.75, 156.58, 139.81, 132.84, 132.36, 130.60, 130.08, 125.91, 123.78, 120.06, 115.48, 112.81, 112.27, 103.17, 75.85, 56.50, 28.27, 19.18, 17.83.

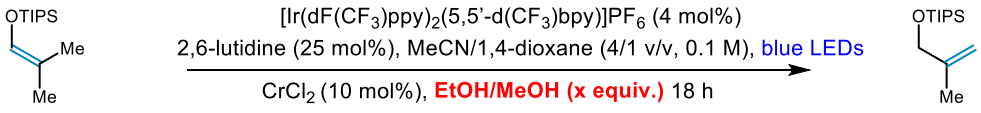
The title compound was synthesized following general procedure B using 5-(2,5-dimethylphenoxy)-1-(4-methoxyphenyl)-2,2-dimethylpentan-1-one (2.00 g, 4.44 mmol) and purified by silica gel flash column chromatography (hexanes). The title compound was obtained as a white solid (555 mg, 26%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.23 (d, *J* = 2.2 Hz, 1H), 8.13 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.10 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.05 – 7.01 (m, 2H), 6.96 (d, *J* = 8.5 Hz, 1H), 6.19 (s, 1H), 3.91 (d, *J* = 6.5 Hz, 2H), 3.84 (s, 3H), 2.82 (d, *J* = 1.2 Hz, 3H), 2.21 (dp, *J* = 13.5, 6.8 Hz, 1H), 1.87 (dd, *J* = 11.5, 1.4 Hz, 6H), 1.10 (dd, *J* = 6.8, 1.2 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 168.11, 162.95, 162.74, 160.18, 149.30, 138.84, 135.29, 132.80, 132.34, 132.00, 127.64, 126.09, 123.85, 123.26, 120.79, 115.54, 112.78, 112.24, 103.17, 75.84, 56.18, 28.30, 26.97, 19.54, 19.21, 17.80. **IR (neat):** 2958, 2226, 1707, 1605, 1508, 1435, 1334, 1294, 1262, 1219, 1116, 1012, 813, 751cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{27}H_{29}N_2O_4S$) requires *m/z* 477.18425, found *m/z* 477.18444.

Optimization Studies

General procedure for optimization studies

An oven-dried 2-dram vial equipped with a magnetic stir bar was charged with the alkene substrate (0.050 mmol, 1.00 equiv), the appropriate photocatalyst at a given amount, and/or $CrCl_3$ at a given amount (if applicable), and the appropriate Brønsted base. The vial was brought into a glove box under an atmosphere of nitrogen, where the appropriate anhydrous solvent and/or $CrCl_2$ at a given amount (if applicable) were added. The vial was then sealed with a cap outfitted with a PTFE septum, sealed with electrical tape, and removed from the glovebox. An N_2 inlet needle was added through the septum, followed by the appropriate proton co-catalyst at a given amount via a microsyringe. The vial was placed on a stir plate approximately 2 cm away from Kessil H150B LED lamps, and the reaction solution was allowed to stir under blue light irradiation (~ 450 nm) for 18 h (see **Figure S2** for the reaction setup). The average temperature of the reaction setup was 35 °C with cooling fans running constantly; variations of up to ±5 °C were observed. After 18 h, irradiation was ceased, and the crude reaction mixture was diluted with CH_2Cl_2 and filtered through a pipette silica plug containing ~2 cm of silica gel eluting with ~5 mL CH_2Cl_2. The filtrate was concentrated to a small volume, diluted with $CDCl_3$, and added *N*,*N*-dimethylformamide (0.0500 mmol, 1.0 equiv., 3.87 µL) as an internal standard. Yields were determined by ^1H NMR relative to as an internal standard.

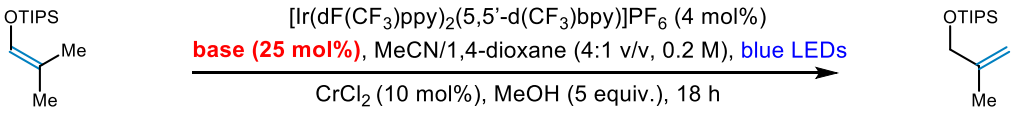
Table S1. Preliminary Proton Source Screen and Loading Screen for Enol Ether **1**



Entry	Proton Source	Recovery (%)	Pdt (%)
1	CF_3CH_2OH (50 equiv.)	trace	13
2	$CF_3CH(OH)CF_3$ (50 equiv.)	trace	trace
3	*t*-BuOH (50 equiv.)	26	13
4	EtOH (100 equiv)	trace	49
5	**EtOH (5 equiv.)**	6	**56**
6	EtOH (3 equiv.)	19	44
7	EtOH (1 equiv.)	27	25
8	EtOH (0.5 equiv.)	40	14
9	MeOH (10 equiv.)	trace	60
10	**MeOH (5 equiv.)**	**trace**	**65**

Note: adopting conditions from Glorius's prior work, we found that 5 equivalents of methanol afforded the desired deconjugation product **1a** (**Table 2** in the text) with an optimal 65% yield. Notably, this preliminary optimization was conducted at 0.1M concentration, which was later identified to be less efficient than the 0.2M condition (see **Table S2**, entry 12).

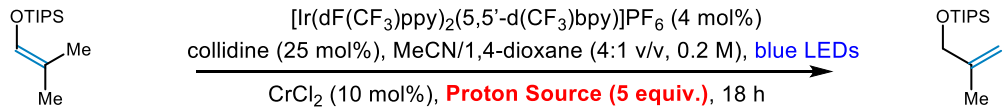
Table S2. Brønsted Base Screen for Enol Ether **1**



Entry	Base	Recovery (%)	Pdt (%)
1	**Li_2CO_3**	trace	73
2	Na_2CO_3	43	32
3	K_2CO_3	9	57
4	Cs_2CO_3	trace, complete desilyation	trace
5	$PBu_4^+(PhO)_2P(O)O^-$	40	33
6	$PBu_4^+(MeO)_2P(O)O^-$	21	60
7	$PBu_4^+(t\text{-}BuO)_2P(O)O^-$	45	26
8	$PBu_4^+(n\text{-}BuO)_2P(O)O^-$	75	trace
9	$PBu_4^+CF_3CO_2^-$	10	61
10	**2,4,6-collidine**	trace	**83**
11	2-methyl-2-oxazoline	5	54
12	**2,6-lutidine**	trace	**82**
13	$PBu_4^+PhCO_2^-$	51	23
14	CH_3CO_2K	decomposed	trace
15	K_2HPO_4	13	49

Note: from the initial optimization study, 2,4,6-collidine and 2,6-lutidine were identified as the most efficient Brønsted base co-catalyst for this system, wherein 2,4,6-collidine was slightly more effective and was used for the following optimization studies. We also found that lithium carbonate was the most efficient inorganic Brønsted base.

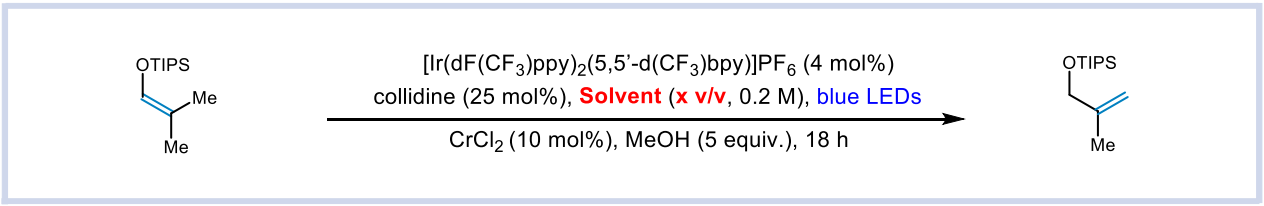
Table S3. Further Proton Source Screen for Enol Ether **1**



Entry	Proton Source	Recovery (%)	Pdt (%)
1	H_2O	23	34
2	**MeOH**	trace	**82**
3	EtOH	trace	75
4	BnOH	trace	78
5	*i*-PrOH	~14	39
6	CF_3CH_2OH	11	39
7	HFIP	13	15
8	PivOH	trace	trace

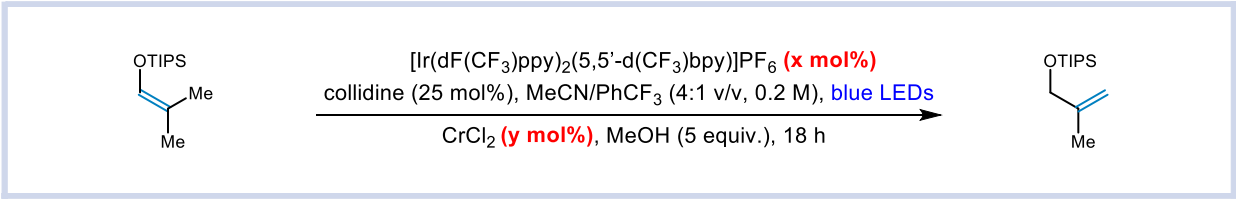
Note: we conducted further proton source screen following **Table S1** but with the optimized condition from **Table S2**. Primary aliphatic alcohols were found to be generally optimal. Methanol was chosen for its marginally better performance and its volatility that simplifies the workup procedure. Decomposition of the substrate was observed for entry 5 to 8.

Table S4. Solvent Screen for Enol Ether **1**



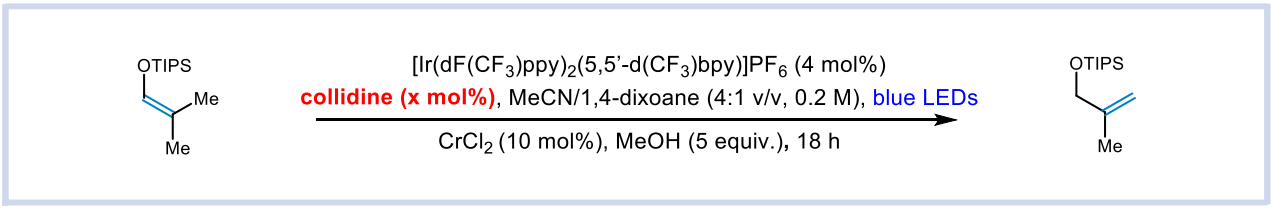
Entry	Solvent (v/v ratio)	Recovery (%)	Pdt (%)
1	1,4-dioxane/MeCN (1:4)	trace	82
2	$PhCF_3$	12	77
3	**$PhCF_3$/MeCN (1:4)**	trace	**87**
4	**$PhCF_3$/MeCN (1:1)**	trace	**86**
5	$PhCF_3$/MeCN (4:1)	4	80
6	MeCN	trace	80
7	PhMe/MeCN (1:4)	trace	75
8	$ClCH_2CH_2Cl$/MeCN (1:4)	11	55
9	*t*-BuCN (with 25 mol% lutidine instead)	39	47
10	*t*-BuCN (with 25 mol% Li_2CO_3 instead)	10	59
11	$PhCF_3$/*t*-BuCN (1:4, with 25 mol% Li_2CO_3 instead)	trace	78
12	$PhCF_3$/*t*-BuCN (1:4)	30	60

Table S5. Loading Screen of the Ir-based Photocatalyst and $CrCl_2$ for Enol Ether **1**



Entry	Photocat loading x (mol%)	$CrCl_2$ loading y (mol%)	Recovery (%)	Pdt (%)
1	1	10	50	55
2	2	10	20	56
3	4	5	trace	75
4	**4**	**10**	**trace**	**82**
5	4	20	trace	75

Table S6. Loading Screen for Brønsted Base Co-catalyst for Enol Ether **1**



Entry	Collidine loading (mol%)	Recovery (%)	Pdt (%)
1	100	14	65
2	50	4	75
3	**25**	trace	**82**
4	10	4	53
5	5	trace	39

Note: we observed the formation of a blue-colored homogeneous complex after adding pyridine-derived Brønsted base co-catalyst (**Figure S1**), which we attributed to a ligation event with Cr catalyst, and the optimal ratio of ligand to Cr was around 2:1.

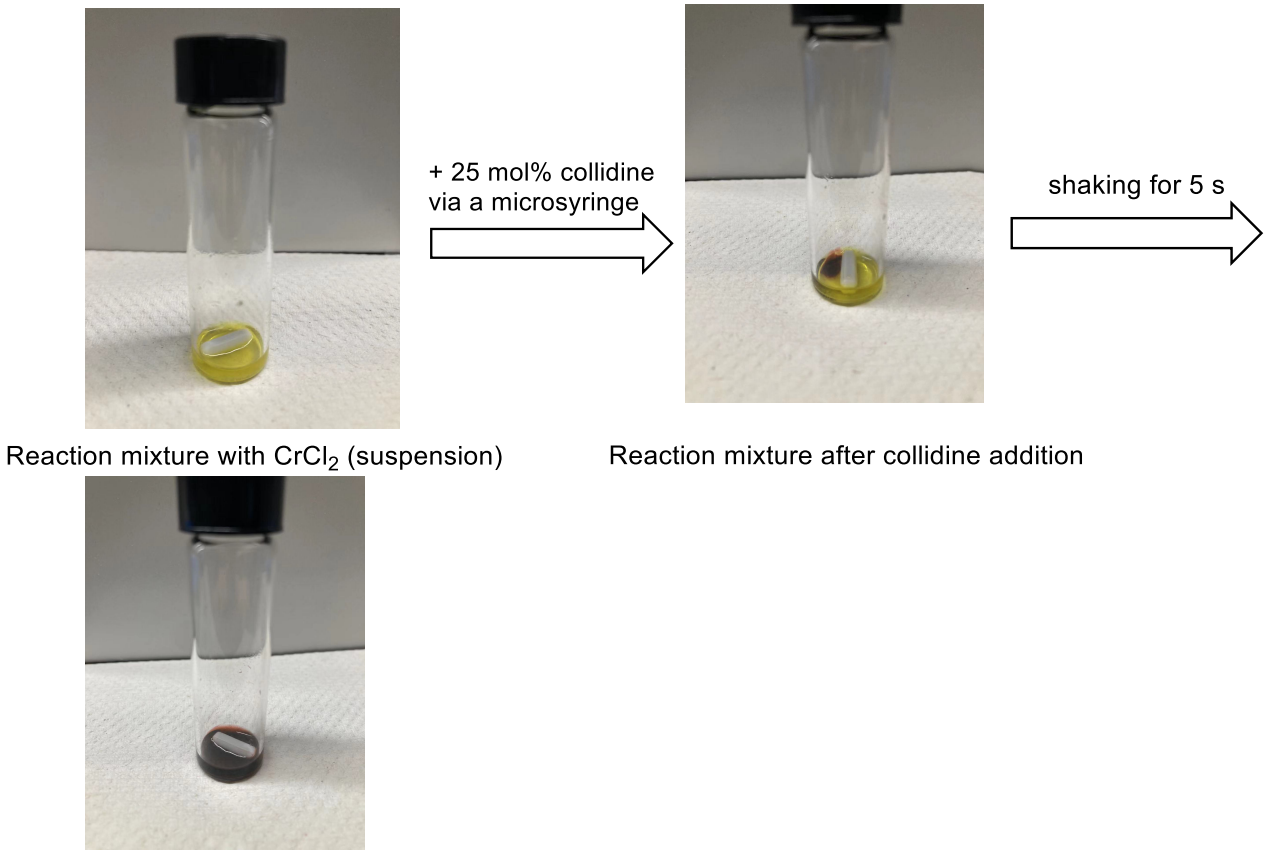
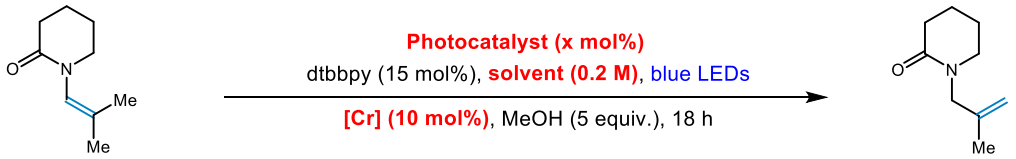


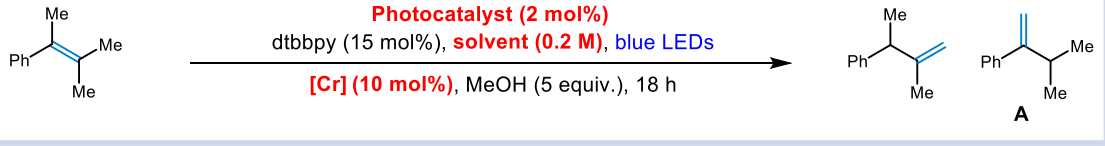
Figure S1. Color change during the addition of pyridine derived Brønsted base co-catalyst.

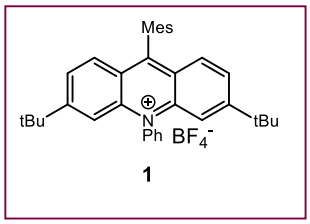
Table S7. Optimization Studies for Enamide Substrate **12**



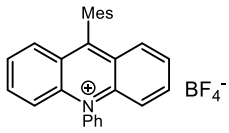
Entry	Photocat./solvent/[Cr]	Recovery (%)	Pdt (%)
1	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (2 mol%), MeCN/$PhCF_3$(4:1 v/v, 0.2M), $CrCl_2$	15	9
2	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (2 mol%), MeCN/$PhCF_3$ (4:1 v/v, 0.2M), $CrCl_3$	6	26
3	**$[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$ (2 mol%), CH_2Cl_2 (0.2M),** $CrCl_2$ or $CrCl_3$	trace 5	**80** ($CrCl_3$) 51 ($CrCl_2$)
4	$[Ir(dF(CF_3)ppy)_2(5,5'\text{-}d(CF_3)bpy)]PF_6$ (4 mol%), MeCN/$PhCF_3$ (4:1 v/v, 0.2M), $CrCl_2$ or $CrCl_3$	40-50	6-8
5	4CzIPN (2 mol%),CH_2Cl_2(0.2M), $CrCl_3$	trace	68
6	4CzIPN (2 mol%), CH_2Cl_2 (0.05M), $CrCl_3$	trace	71

Table S8. Optimization Studies for Styrene Substrate



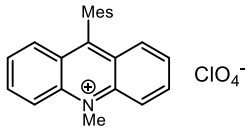


1

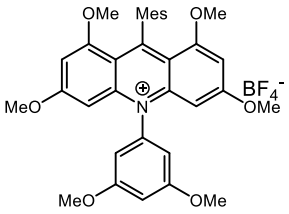


2

(E^*_{red} = 2.15 V)



3

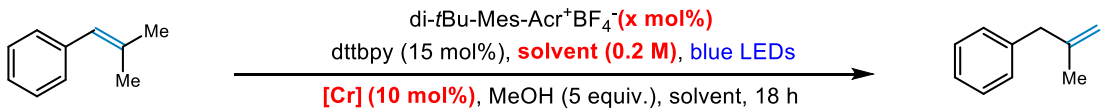


4

(E^*_{red} = 1.65 V)

Entry	Cat.	[Cr]	Solvent	Recovery (%)	Pdt (%)
1	4CzIPN	$CrCl_2$	CH_2Cl_2	53	35
2	4CzIPN	$CrCl_3$	CH_2Cl_2	12 ~10% **A**	73
3	1	$CrCl_2$	CH_2Cl_2	trace	85
4	1	**$CrCl_3$**	**CH_2Cl_2**	trace 2% to 4% **A**	**89**
5	1	$CrCl_2$	$ClCH_2CH_2Cl$	trace	79
6	1	$CrCl_3$	$ClCH_2CH_2Cl$	trace	73
7	2	$CrCl_3$	CH_2Cl_2	trace	80
8	3 (5 mol%)	$CrCl_2$	CH_2Cl_2/MeCN (3:2 v/v)	trace	66
9	4	$CrCl_2$	MeCN	67	20
10	4	$CrCl_2$	CH_2Cl_2	76	17

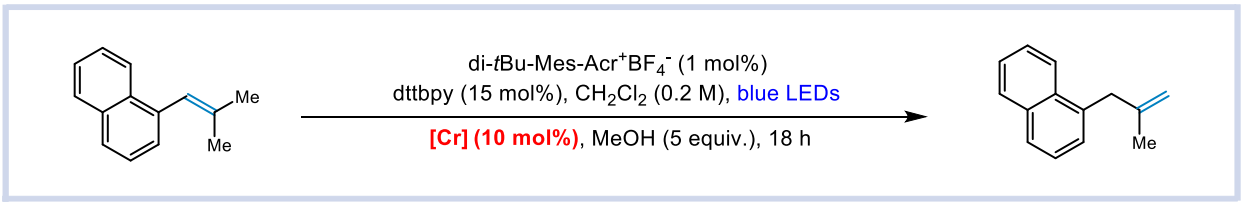
Table S9. Photocatalyst Loading/Solvent/[Cr] Screen for Styrene Substrate **15**



Entry	Solvent	Photocat. loading	[Cr]	Recovery (%)	Pdt (%)
1	CH_2Cl_2	3%	$CrCl_3$	trace	69
2	**CH_2Cl_2**	**1%**	**$CrCl_2$**	trace	**82**
3	**CH_2Cl_2**	**1%**	**$CrCl_3$**	trace	**81**
4	CH_2Cl_2	0.5%	$CrCl_3$	trace	75
5	$ClCH_2CH_2Cl$	0.5%	$CrCl_3$	trace	62
6	MeCN	0.5%	$CrCl_3$	54	16
7	MeCN	0.5%	$CrCl_2$	59	11
8	CH_2Cl_2	1%	CrF_3	44	5
9	CH_2Cl_2	1%	CrF_2	39	0

Note: even though $CrCl_2$ and $CrCl_3$ were similarly effective for styrene **15** (**Table 3** in the text), $CrCl_3$ was selected as it is bench-stable.

Table S10. [Cr] Catalyst Screen for Styrene Substrate **19**



Entry	[Cr]	Recovery (%)	Pdt (%)
1	**$CrCl_3$**	trace	**quant.**
2	$Cr_2(SO_4)_3.xH_2O$ (~ 5% loading)	60	10
3	$CrCl_3.THF_3$	trace	87
4	$Cr(acac)_3$	8	34
5	$Cr(TMHD)_3$	17	25
6	$(CH_3CO_2)_7Cr_3(OH)_2$	trace	77
7	$K_3Cr(C_2O_4)_3 \cdot 3H_2O$	28	5
8	no [Cr]	60	trace

Note: due to the volatility of phenylated substrate **15**, we instead used naphthylated substrate **19** as a model substrate for the survey of chromium catalyst. A variety of chromium(III) complexes were tested and found effective to some extent for the reaction of **19**, and $CrCl_3$, a bench-stable salt, was identified as the most effective chromium catalyst. Notably, the control experiment (entry 8) showed that no desired deconjugation product **19a** was observed in the absence of chromium catalyst, suggesting that [Cr] is essential for this reaction. This is also in line with the conclusion from the control experiments demonstrated in **Table 1** in the text.

Limitations

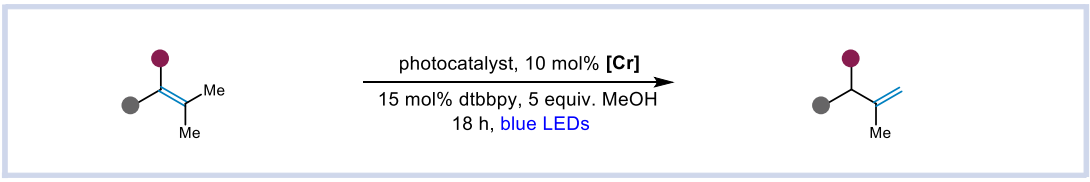
While these conditions are amendable to substrates bearing *gem*-dimethyl olefin termini, other olefin patterns are less efficient. Although Kanai and Glorius previously demonstrated that 1,2-disubstituted olefins worked well in their respective aldehyde allylation systems, we reason that the protodemetalation might be more challenging for allylchromium(III), wherein only the electron-donating *gem*-dimethyl type olefin patterns are efficient.

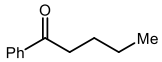
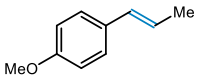
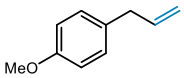
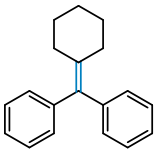
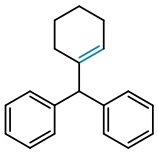
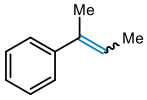
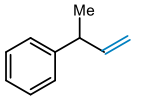
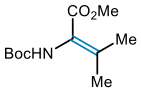
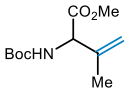
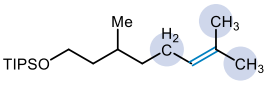
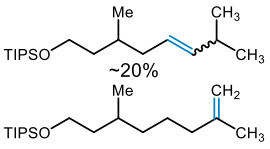
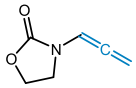
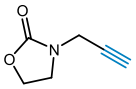
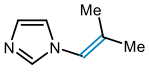
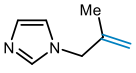
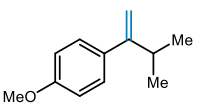
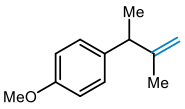
Another limitation of this method is the regioselectivity. For olefins with multiple allylic positions for potential double-bond migrations, a mixture of regioisomers is often obtained. Moreover, when the allylic radical is formed at a non-terminal position, a low yield of the desired terminal olefin is often observed along with decomposition of the substrate. We reason that this is presumably because that Cr(II) is sensitive to sterics and the radical capture step is unfavorable for non-terminal type allylic radicals.

Finally, we found that olefins with $E_{1/2} > 1.9$ V vs SCE in MeCN are not reactive, even though the electron transfer is still favorable with the acridinium photocatalyst ($E^* \sim 2.1$ V vs SCE in MeCN). Rapid back electron transfer event presumably outcompetes the deprotonation step in these substrates, resulting in lack of the desired reactivity.

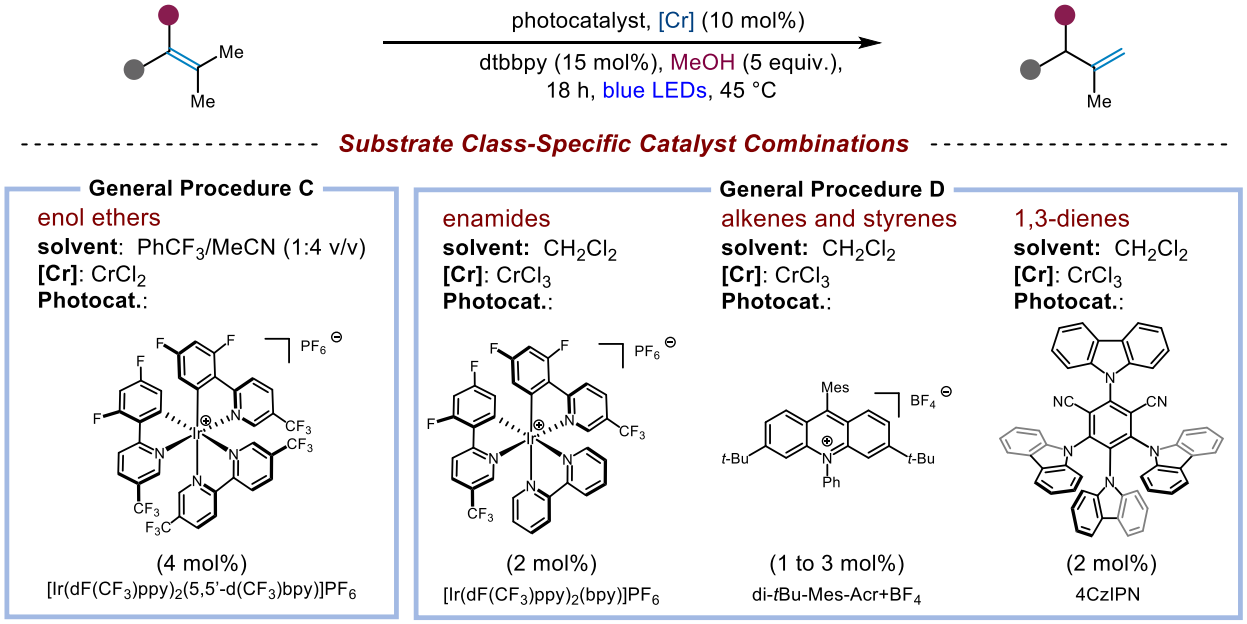
Select examples of less successful substrates are shown in **Table S11.** These reactions were set up on 0.05 mmol scale following the general procedure described in the optimization studies section.

Table S11. Currently Challenging Examples



Starting Material	Product	Preliminary conditions for best results (change from condition shown above)	Result
 ~4:1 *E*/*Z*		4 mol% $[Ir(dF(CF_3)ppy)_2(5,5'\text{-}d(CF_3)bpy)]PF_6$ MeCN/TFT (4:1 v/v, 0.2 M), $CrCl_2$	no desired product or recovered starting material, only the ketone product from desilylation was recovered
		2 mol% $Ir(dF(CF_3)ppy)_2(bpy)]PF_6$, $CrCl_3$, CH_2Cl_2 (0.2 M)	39% product, 48% recovery of starting material as *E*/*Z* isomers
		2 mol% acridinium **2**, 25 mol% Li_2CO_3 (instead of dtbbpy), $CrCl_3$, CH_2Cl_2 (0.2 M)	21% product, ~20% recovery of starting material
		2 mol% acridinium **2**, $CrCl_3$, CH_2Cl_2 (0.2 M)	20% product, ~15% recovery of starting material
		5 mol% acridinium **1**, $CrCl_3$, CH_2Cl_2 (0.2 M), 48 h	23% product, ~52% recovery of starting material
	 ~20% 19% ~6% of a unknown olefin	5 mol% acridinium **3**, 25 mol% Li_2CO_3 (instead of dtbbpy), $CrCl_3$, CH_3CN/CH_2Cl_2 (3:2, 0.2 M)	50% recovery of starting material, ~50% of all olefin isomers
		2 mol% acridinium **1**, $CrCl_3$, CH_2Cl_2 (0.2 M)	no conversion
		2 mol% acridinium **1**, $CrCl_3$, CH_2Cl_2 (0.2 M)	no conversion
		2 mol% acridinium **1**, $CrCl_3$, CH_2Cl_2 (0.2 M)	no desired product, moderate recovery of starting material

Synthesis of Products



General Procedure C:

An oven-dried screw cap 2-dram vial outfitted with a PTFE/silicone septum was charged with the relevant olefin substrate (0.500 mmol, 1.00 equiv.), $[Ir(dF(CF_3)ppy)_2(5,5'\text{-}d(CF_3)bpy)]PF_6$ (0.0200 mmol, 4.00 mol%, 23.1 mg), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.0750 mmol, 15.0 mol%, 20.1 mg). The 2-dram vial was brought into a glove box under an atmosphere of nitrogen, where the $CrCl_2$ (0.0500 mmol, 10.0 mol%, 6.15 mg) was weighed in. Then, a solvent premix (2.50 mL) consisting of $PhCF_3$ (3.00 mL), MeCN (12.0 mL) and MeOH (0.600 mL) were added in the glovebox. The 2-dram vial was then sealed with PTFE, electric tape and removed from the glovebox, and sonicated for 10 minutes. The 2-dram vial was then sealed with PTFE, electric tape and removed from the glovebox, and sonicated for 10 minutes. The vial was placed on a stir plate approximately 2 cm away from Kessil H150B LED lamps, and the reaction solution was allowed to stir under blue light irradiation (~ 450 nm) for 18 h (see **Figure S2** for the reaction setup). The average temperature of the reaction setup was 40 °C with cooling fans running constantly; variations of up to ±5 °C were observed. After 18 h, the irradiation was ceased, and the crude mixtures were concentrated and purified by flash column chromatography. All preparative-scale reactions were run in duplicates, and the reported yields are the average yields of the two runs.

General Procedure D:

An oven-dried screw cap 2-dram vial outfitted with a PTFE/silicone septum was charged with the relevant olefin substrate (0.500 mmol, 1.00 equiv.), $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$ (0.0100 mmol, 2.00 mol%, 10.1 mg) or 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (0.00500 mmol, 1.00 mol%, 2.87 mg) or 2,4,5,6-tetra(9*H*-carbazol-9-yl)isophthalonitrile (0.0100 mmol, 2.00 mol%, 7.89 mg), $CrCl_3$ (0.0500 mmol, 10.0 mol%, 7.92 mg), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.0750 mmol, 15.0 mol%, 20.1 mg). The 2-dram vial was brought into a glove box under an atmosphere of nitrogen, where a solvent premix (2.50 mL) consists of CH_2Cl_2 (15.0 mL)

and MeOH (0.600 mL) were added in the glovebox. The 2-dram vial was then sealed with PTFE, electric tape and removed from the glovebox, and sonicated for 10 minutes. The vial was placed on a stir plate approximately 2 cm away from Kessil H150B LED lamps, and the reaction solution was allowed to stir under blue light irradiation (~450 nm) for 18 h (see **Figure S2** for the reaction setup). The average temperature of the reaction setup was 40 °C with cooling fans running constantly; variations of up to ±5 °C were observed. After 18 h, the irradiation was ceased, and the crude mixtures were concentrated and purified by flash column chromatography. All preparative-scale reactions were run in duplicates, and the reported yields are the average yields of the two runs.

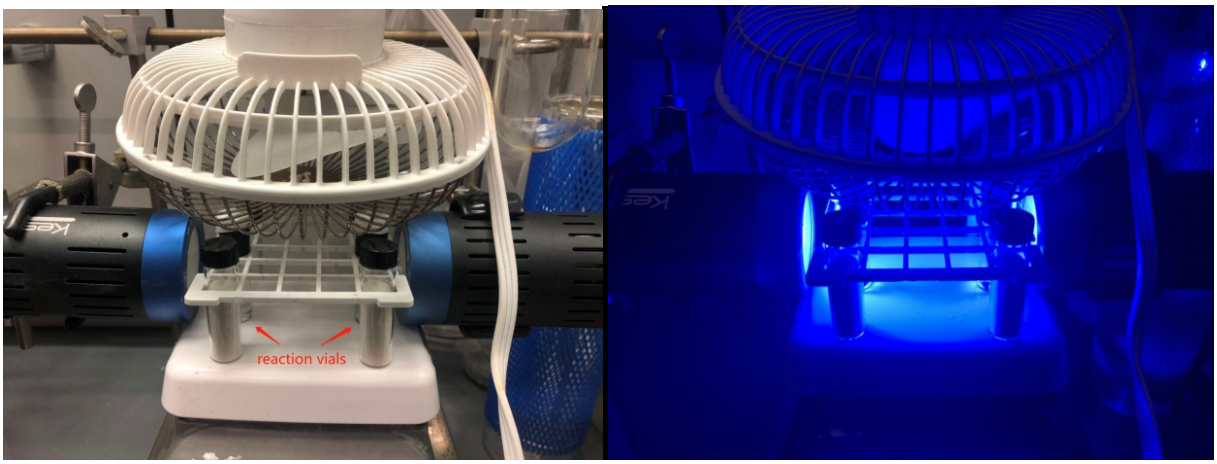
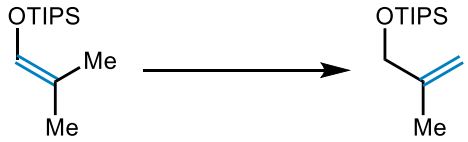
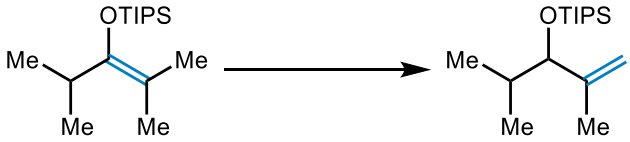


Figure S2. Lamps with one fan setup examples. A test tube rack is used to hold the reaction vials.



Triisopropyl((2-methylallyl)oxy)silane (1a)

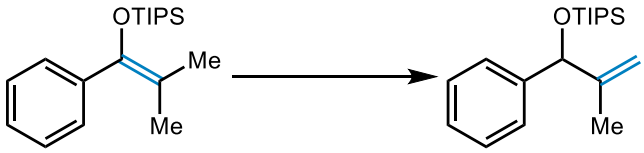
The title compound was prepared on 0.500 mmol scale following general procedure C with triisopropyl((2-methylprop-1-en-1-yl)oxy)silane (**1**). The crude material was purified by silica gel column chromatography (0% to 10% EtOAc in hexanes) to afford the title compound as a colorless liquid (102 mg, 89%). Spectra are consistent with reported literature values.[26]



((2,4-dimethylpent-1-en-3-yl)oxy)triisopropylsilane (2a)

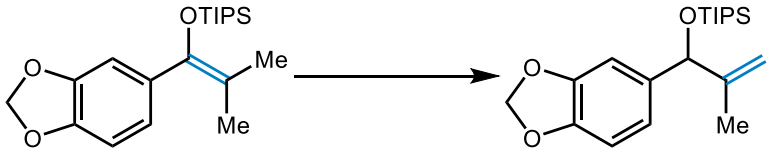
The title compound was prepared on 0.500 mmol scale following general procedure C with ((2,4-dimethylpent-2-en-3-yl)oxy)triisopropylsilane (**2**). The crude material was purified by silica gel column chromatography (0% to 5% EtOAc in hexanes) to afford the title compound as a colorless liquid (128 mg, 95%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 4.83 – 4.78 (m, 2H), 3.84 (d, *J* = 7.1 Hz, 1H), 1.71 (h, *J* = 6.8 Hz, 1H), 1.68 (s, 3H), 1.08 – 1.03 (m, 21H), 0.95 (d, J = 6.8 Hz, 3H), 0.80 (d,

J = 6.8 Hz, 3H).**^{13}C NMR (126 MHz, $CDCl_3$, mixture of rotamers)** δ 146.86, 112.39, 82.90, 32.80, 19.16, 19.10, 18.40, 18.36, 18.29, 18.12, 17.84, 12.85. **IR (neat):** 2943, 2866, 1483, 1383, 1371, 1082, 1058, 897, 881, 829, 874, 663 cm^{-1}. **HRMS (EI)**: exact mass calculated for $[M]^+$ ($C_{16}H_{34}OSi$) requires *m/z* 270.23734, found *m/z* 270.23747.



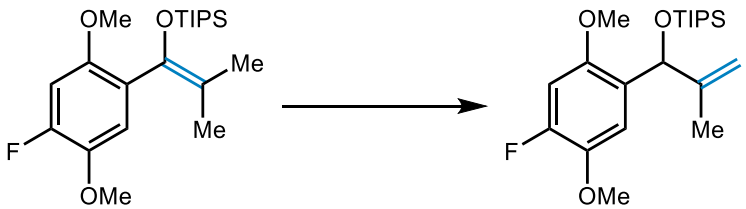
Triisopropyl((2-methyl-1-phenylallyl)oxy)silane (3a)

The title compound was prepared on 0.500 mmol scale following general procedure C with triisopropyl((2-methyl-1-phenylprop-1-en-1-yl)oxy)silane (**3**). The crude material was purified by silica gel column chromatography (0% to 5% EtOAc in hexanes) to afford the title compound as a colorless liquid (129 mg, 85%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.32 – 7.28 (m, 2H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.16 – 7.12 (m, 1H), 5.13 (s, 1H), 5.10 (t, *J* = 1.8, 1H), 4.72 (t, *J* = 1.8 Hz, 1H), 1.48 (s, 3H), 1.08 – 0.90 (m, 21H). **^{13}C NMR (126 MHz, $CDCl_3$, mixture of rotamers)** δ 148.38, 143.83, 127.95, 126.96, 126.16, 110.34, 78.88, 18.15, 18.13, 17.14, 12.40. **IR (neat):** 2942, 2891, 2865, 1463, 1387,1092, 1062, 881, 836, 679 cm^{-1}. **HRMS (EI):** exact mass calculated for $[M]^+$ ($C_{19}H_{32}OSi$) requires *m/z* 304.22224, found *m/z* 304.22149.



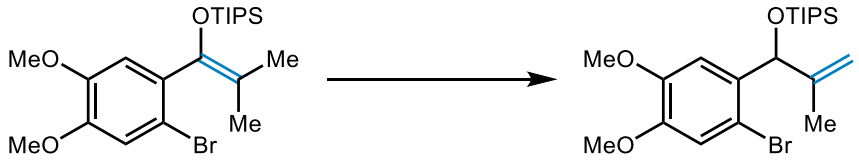
((1-(benzo[*d*][1,3]dioxol-5-yl)-2-methylallyl)oxy)triisopropylsilane (4a)

The title compound was prepared on 0.500 mmol scale following modified general procedure C with ((1-(benzo[*d*][1,3]dioxol-5-yl)-2-methylprop-1-en-1-yl)oxy)triisopropylsilane (**4**) and irradiated for 36 h instead. The crude material was purified by silica gel column chromatography (0% to 5% EtOAc in hexanes) to afford the title compound as a colorless liquid (145 mg, 83%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.89 (d, *J* = 1.7 Hz, 1H), 6.82 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 5.98 – 5.91 (m, 2H), 5.17 – 5.13 (m, 1H), 5.11 (s, 1H), 4.78 (t, *J* = 1.8 Hz, 1H), 1.55 (s, 3H), 1.16 – 1.06 (m, 3H), 1.05 – 0.99 (m, 18H). **^{13}C NMR (126 MHz, $CDCl_3$, mixture of rotamers)** δ 148.38, 147.43, 146.48, 138.11, 119.38, 110.22, 107.64, 106.76, 100.95, 78.55, 18.16, 18.14, 17.22, 12.38. **IR (neat):** 2904, 2864, 1482, 1439, 1240, 1089, 1041, 880, 852, 677 cm^{-1}. **HRMS (EI):** exact mass calculated for $[M]^+$ ($C_{20}H_{32}O_3Si$) requires *m/z* 348.21152, found *m/z* 348.21182.



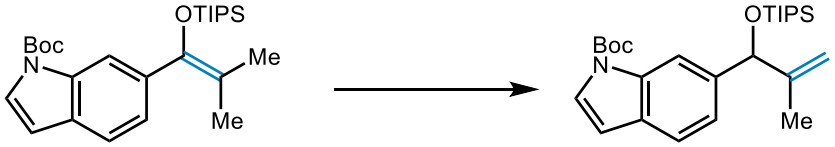
((1-(4-fluoro-2,5-dimethoxyphenyl)-2-methylallyl)oxy)triisopropylsilane (5a)

The title compound was prepared on 0.500 mmol scale following general procedure C with ((1-(4-fluoro-2,5-dimethoxyphenyl)-2-methylprop-1-en-1-yl)oxy)triisopropylsilane (**5**). The crude material was purified by silica gel column chromatography (0% to 5% EtOAc in hexanes) to afford the title compound as a white solid (173 mg, 93%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.13 (s, 1H), 6.92 (s, 1H), 5.49 (s, 1H), 5.28 (dt, *J* = 2.1, 1.0 Hz, 1H), 4.84 (t, *J* = 1.9 Hz, 1H), 3.84 (s, 3H), 3.75 (s, 3H), 1.62 (s, 3H), 1.15 – 1.07 (m, 3H), 1.05 – 1.00 (m, 9H), 1.00 – 0.94 (m, 9H). **^{13}C NMR (126 MHz, $CDCl_3$, mixture of rotamers)** δ 151.60 (d, *J* = 244.1 Hz), 149.81 (d, *J* = 8.0 Hz), 147.17, 141.22 (d, *J* = 10.8 Hz), 128.00 (d, *J* = 3.7 Hz), 113.27, 110.13, 100.25 (d, *J* = 22.2 Hz), 70.89, 57.02, 56.16, 18.09, 18.02, 17.33, 12.29. **IR (neat):** 2942, 2865, 1504, 1463, 1404, 1322, 1208, 1115, 1062, 1041 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{21}H_{36}O_3FSi$) requires *m/z* 383.24123, found *m/z* 383.24122.



((1-(2-bromo-4,5-dimethoxyphenyl)-2-methylallyl)oxy)triisopropylsilane (6a)

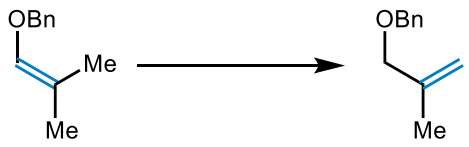
The title compound was prepared on 0.500 mmol scale following general procedure C with ((1-(2-bromo-4,5-dimethoxyphenyl)-2-methylprop-1-en-1-yl)oxy)triisopropylsilane (**6**). The crude material was purified by silica gel column chromatography (0% to 20% EtOAc in hexanes) to afford the title compound as a colorless liquid (187 mg, 84%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.13 (s, 1H), 6.92 (s, 1H), 5.49 (s, 1H), 5.28 (dt, *J* = 2.1, 1.1 Hz, 1H), 4.84 (t, *J* = 2.1 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 1.62 (s, 3H), 1.18 – 1.07 (m, 3H), 1.04 – 0.95 (m, 18H). **^{13}C NMR (126 MHz, $CDCl_3$, mixture of rotamers)** δ 148.59, 148.47, 146.39, 134.95, 114.64, 112.04, 111.22, 111.08, 76.18, 56.19, 55.97, 18.11, 18.05, 18.01, 17.63, 12.31. **IR (neat):** 2941, 2863, 1499, 1459, 1377, 1251, 1204, 1153, 1086, 1066, 879, 678 cm^{-1}. **HRMS (EI):** exact mass calculated for $[M]^+$ ($C_{21}H_{35}BrO_3Si$) requires *m/z* 442.15334 and 444.15129, found *m/z* 442.15362 and 444.15177.



***tert*-butyl 6-(2-methyl-1-((triisopropylsilyl)oxy)allyl)-1*H*-indole-1-carboxylate (7a)**

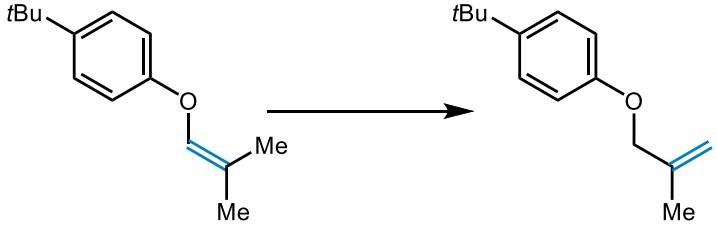
The title compound was prepared on 0.500 mmol scale following general procedure C with *tert*-butyl 6-(2-methyl-1-((triisopropylsilyl)oxy)prop-1-en-1-yl)-1*H*-indole-1-carboxylate (**7**). The crude material was purified by silica gel column chromatography (0% to 20% EtOAc in hexanes) to afford the title compound as a colorless liquid (183 mg, 82%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.14 (s, 1H), 7.59 (d, *J* = 3.7 Hz, 1H), 7.49 (d, *J* = 8.1 Hz, 1H), 7.35 – 7.31 (m, 1H), 6.55 (d, *J* = 3.7 Hz, 1H), 5.33 (s, 1H), 5.26 (s, 1H), 4.81 (s, 1H), 1.69 (s, 9H), 1.61 (s, 3H), 1.12 – 1.00 (m, 21H). **^{13}C NMR (126 MHz, $CDCl_3$, mixture of rotamers)** δ 150.18, 148.77, 140.47, 135.11, 129.80, 126.03, 121.25, 120.30, 113.22, 109.95, 107.28, 83.63, 79.36, 28.36, 18.18, 18.16, 17.48, 13.54, 13.27, 12.42. **IR (neat):** 2939, 2864, 1733, 1436, 1335, 1250, 1143, 1123, 1072, 882, 840,

724, 676 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{26}H_{42}NO_3Si$) requires *m/z* 444.29285, found *m/z* 444.29287.



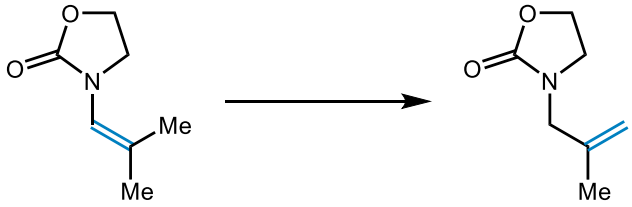
(((2-methylallyl)oxy)methyl)benzene (8a)

The title compound was prepared on 0.500 mmol scale following general procedure C with (((2-methylprop-1-en-1-yl)oxy)methyl)benzene (**8**). The crude material was purified by silica gel column chromatography (0% to 10% EtOAc in hexanes) to afford the title compound a colorless liquid (70.2 mg, 86%). Spectra are consistent with reported literature values.[27]



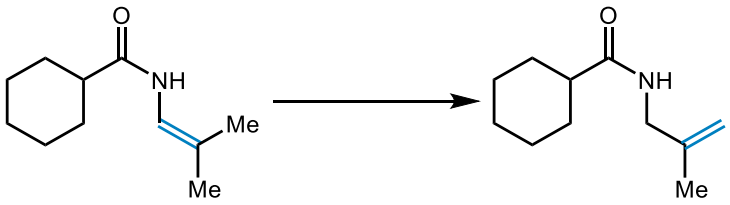
1-(*tert*-butyl)-4-((2-methylallyl)oxy)benzene (9a)

The title compound was prepared on 0.500 mmol scale following general procedure C with 1-(tert-butyl)-4-((2-methylprop-1-en-1-yl)oxy)benzene (**9**). The crude material was purified by silica gel column chromatography (0% to 5% EtOAc in hexanes) to afford the title compound as a pale-yellow solid (88.3 mg, 86%). Spectra are consistent with reported literature values.[28]



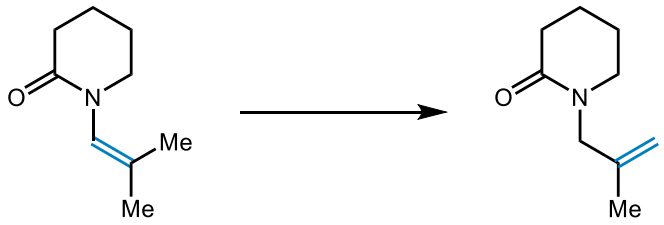
3-(2-methylallyl)oxazolidin-2-one (10a)

The title compound was prepared on 0.500 mmol scale following general procedure D using $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$ as the photocatalyst and 3-(2-methylprop-1-en-1-yl)oxazolidin-2-one (**10**). The crude material was purified by silica gel column chromatography (20% to 80% EtOAc in hexanes) to afford the title compound as a colorless liquid (70.6 mg, quant.). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 4.92 (s, 1H), 4.87 (s, 1H), 4.33 (dd, *J* = 8.9, 7.0 Hz, 2H), 3.78 (s, 2H), 3.47 (dd, *J* = 8.8, 6.8 Hz, 2H), 1.71 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 158.67, 139.93, 113.73, 61.86, 50.68, 44.33, 19.96. **IR (neat):** 2915, 1732, 1423, 1256, 1197, 1084, 1042, 901, 761, 651 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_7H_{12}O_2N$) requires *m/z* 142.08626, found *m/z* 142.08654.



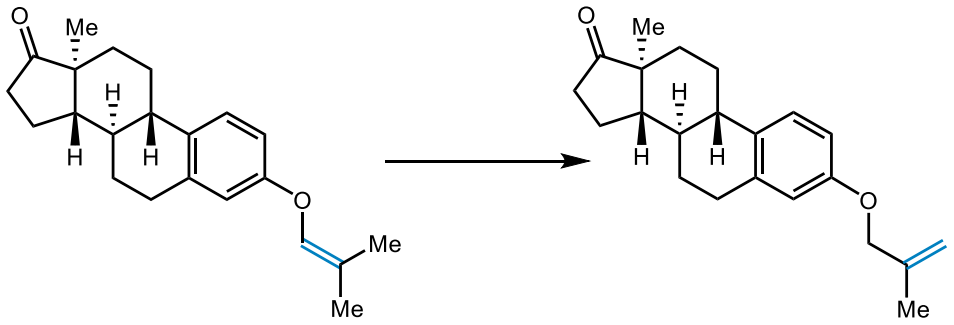
_N_-(2-methylallyl)cyclohexanecarboxamide (11a)

The title compound was prepared on 0.500 mmol scale following general procedure D using $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$ as the photocatalyst and *N*-(2-methylprop-1-en-1-yl)cyclohexanecarboxamide (**11**). The crude material was purified by silica gel column chromatography (0% to 80% EtOAc in hexanes) and then recrystallized from hot hexane to afford the title compound as a colorless crystal (77.0 mg, 85%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 5.50 (br, 1H), 4.85 – 4.79 (m, 2H), 3.81 (d, *J* = 5.9 Hz, 2H), 2.11 (tt, *J* = 11.8, 3.5 Hz, 1H), 1.89 (ddt, *J* = 12.0, 3.6, 1.8 Hz, 2H), 1.80 (dq, *J* = 12.9, 3.5 Hz, 2H), 1.73 (s, 3H), 1.71 – 1.60 (m, 1H), 1.45 (qd, *J* = 12.3, 3.5 Hz, 2H), 1.35 – 1.16 (m, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 176.02, 142.48, 110.78, 45.82, 44.83, 29.94, 25.90, 25.89, 20.49. **IR (neat):** 3267, 2926, 2852, 1636, 1551, 1444, 1421, 1256, 1216, 885 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{11}H_{20}ON$) requires *m/z* 182.15394, found *m/z* 182.15407.



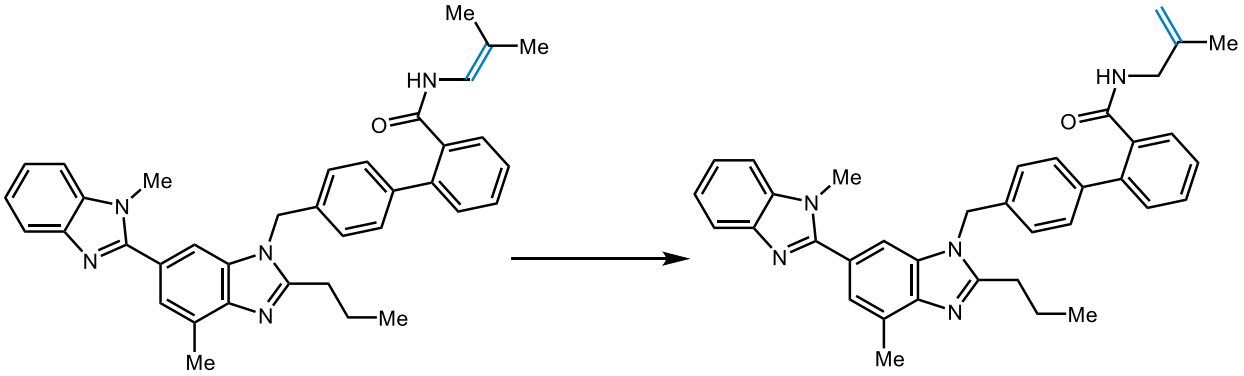
1-(2-methylallyl)piperidin-2-one (12a)

The title compound was prepared on 0.500 mmol scale following general procedure D using $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$ as the photocatalyst and 1-(2-methylprop-1-en-1-yl)piperidin-2-one (**12**). The crude material was purified by silica gel column chromatography (20% to 100% EtOAc in hexanes) to afford the title compound as a colorless oil (60.4 mg, 79%). Spectra are consistent with reported literature values.[29]



(8*R*,9*S*,13*S*,14*S*)-13-methyl-3-((2-methylallyl)oxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (13a)

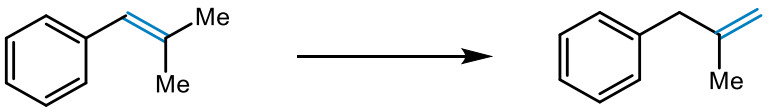
The title compound was prepared on 0.500 mmol scale following modified general procedure C with (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-((2-methylprop-1-en-1-yl)oxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (**13**) and irradiated for 48 h instead. The crude material was purified by silica gel column chromatography (0% to 60% EtOAc in hexanes) to afford the title compound as a white solid (143 mg, 88%). Spectra are consistent with reported literature values.[30]



4'-((1,7'-dimethyl-2'-propyl-1*H*,3'*H*-[2,5'-bibenzo[*d*]imidazol]-3'-yl)methyl)-*N*-(2-methylallyl)-[1,1'-biphenyl]-2-carboxamide (14a)

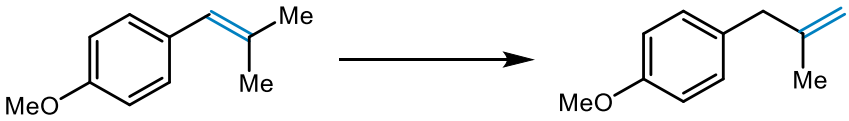
The title compound was prepared on 0.500 mmol scale following general procedure D using $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$ as the photocatalyst and 4'-((1,7'-dimethyl-2'-propyl-1*H*,3'*H*-[2,5'-bibenzo[*d*]imidazol]-3'-yl)methyl)-*N*-(2-methylprop-1-en-1-yl)-[1,1'-biphenyl]-2-carboxamide (**14**). The crude material was purified by silica gel column chromatography (10% to 100% EtOAc in hexanes) to afford the title compound as a white solid (220 mg, 77%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.81 – 7.76 (m, 1H), 7.62 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.54 (s, 1H), 7.45 (td, *J* = 7.6, 1.6 Hz, 1H), 7.43 – 7.36 (m, 5H), 7.33 – 7.28 (m, 3H), 7.10 (s, 1H), 7.09 (s, 1H), 5.44 (s, 2H), 5.38 (t, *J* = 5.9 Hz, 1H), 4.54 (s, 1H), 4.39 (s, 1H), 3.85 (s, 3H), 3.67 (d, *J* = 5.9 Hz, 2H), 2.95 – 2.88 (m, 2H), 2.78 (s, 3H), 1.88 (dt, *J* = 16.6, 7.5 Hz, 2H), 1.44 (s, 3H), 1.06 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 169.61, 156.54, 154.79, 143.30, 142.97, 141.43, 140.12, 138.68, 136.78, 135.99, 135.49, 135.23, 130.39, 130.27, 129.60, 129.51, 128.65, 127.92, 126.47, 124.11, 123.92, 122.69, 122.50, 119.67, 111.05, 109.67, 109.04, 47.01, 45.52, 32.01, 29.99, 22.01, 20.37, 17.08, 14.27. **IR (neat):** 2947, 2868, 1644, 1517, 1448,1278, 1085, 1060, 882, 840, 741 cm^{-1}. **HRMS**

(ESI): exact mass calculated for $[M+H]^+$ ($C_{37}H_{38}N_5O$) requires *m/z* 568.30709, found *m/z* 568.30723.



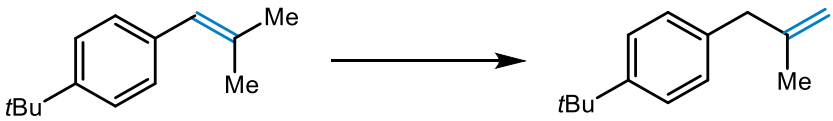
(2-methylallyl)benzene (15a)

The title compound was prepared on 0.500 mmol scale following general procedure D using 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate as the photocatalyst and (2-methylprop-1-en-1-yl)benzene (**15**). The crude material was purified by silica gel column chromatography (0% to 2% EtOAc in hexanes) to afford the title compound as a colorless oil (55.3 mg, 85%). Spectra are consistent with reported literature values.[31]



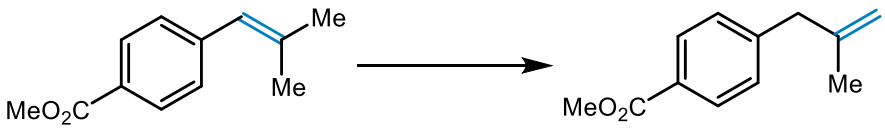
1-methoxy-4-(2-methylallyl)benzene (16a)

The title compound was prepared on 0.500 mmol scale following general procedure D using 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate as the photocatalyst and 1-methoxy-4-(2-methylprop-1-en-1-yl)benzene (**16**). The crude material was purified by silica gel column chromatography (0% to 10% EtOAc in hexanes) to afford the title compound as a colorless liquid (80.3 mg, 99%). Spectra are consistent with reported literature values.[32]

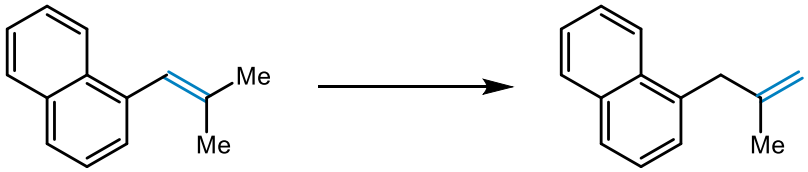


1-(*tert*-butyl)-4-(2-methylallyl)benzene (17a)

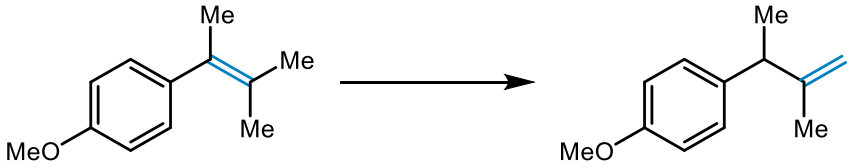
The title compound was prepared on 0.500 mmol scale following general procedure D using 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate as the photocatalyst and 1-(*tert*-butyl)-4-(2-methylprop-1-en-1-yl)benzene (**17**). The crude material was purified by silica gel column chromatography (0% to 5% EtOAc in hexanes) to afford the title compound as a colorless liquid (91.8 mg, 97%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.31 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 4.80 (s, 1H), 4.74 (s, 1H), 3.30 (s, 2H), 1.69 (s, 3H), 1.32 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 148.98, 145.49, 136.81, 128.64, 125.30, 111.84, 44.26, 34.51, 31.56, 31.53, 22.27. **IR (neat):** 2960, 2906, 1650, 1511, 1446, 1366, 1269,1110, 1021,888, 844, 800, 572 cm^{-1}. **HRMS (EI)**: exact mass calculated for $[M]^+$ ($C_{14}H_{20}$) requires *m/z* 188.15595, found *m/z* 188.15576.



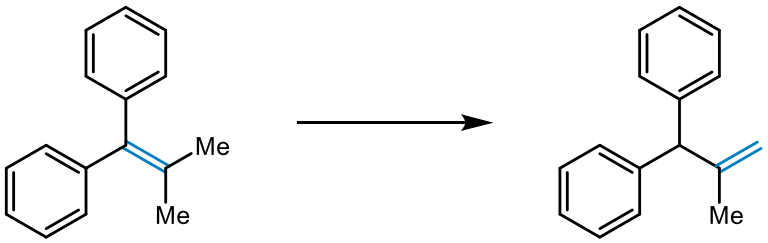
methyl 4-(2-methylallyl)benzoate (18a)
The title compound was prepared on 0.500 mmol scale following modified general procedure D using 3 mol% 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (0.0150 mmol, 8.60 mg) as the photocatalyst and methyl 4-(2-methylprop-1-en-1-yl)benzoate (**18**) and irradiated for 36h instead. Methanol was not added for this reaction. The crude material was purified by silica gel column chromatography (0% to 20% EtOAc in hexanes) to afford the title compound as a colorless oil (91.3 mg, 96%). Spectra are consistent with reported literature values.[33]



1-(2-methylallyl)naphthalene (19a)
The title compound was prepared on 0.500 mmol scale following general procedure D using 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate as the photocatalyst and 1-(2-methylprop-1-en-1-yl)naphthalene (**19**). The crude material was purified by silica gel column chromatography (0% to 5% EtOAc in hexanes) to afford the title compound as a colorless liquid solid (92.5 mg, quant.). Spectra are consistent with reported literature values.[34]

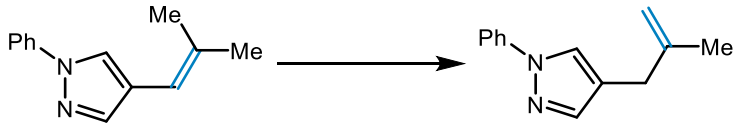


1-methoxy-4-(3-methylbut-3-en-2-yl)benzene (20a)
The title compound was prepared on 0.500 mmol scale following general procedure D using 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate as the photocatalyst and 1-methoxy-4-(3-methylbut-2-en-2-yl)benzene (**20**). The crude material was purified by silica gel column chromatography (0% to 10% EtOAc in hexanes) to afford the title compound as a colorless liquid (86.4 mg, 98%). Spectra are consistent with reported literature values.[35]



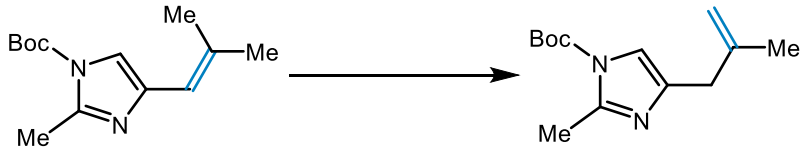
(2-methylprop-2-ene-1,1-diyl)dibenzene (21a)

The title compound was prepared on 0.500 mmol scale following general procedure D using 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate as the photocatalyst and (2-methylprop-1-ene-1,1-diyl)dibenzene (**21**). The crude material was purified by silica gel column chromatography (0% to 15% EtOAc in hexanes) to afford the title compound as a white solid (104 mg, 99%). Spectra are consistent with reported literature values.[36]



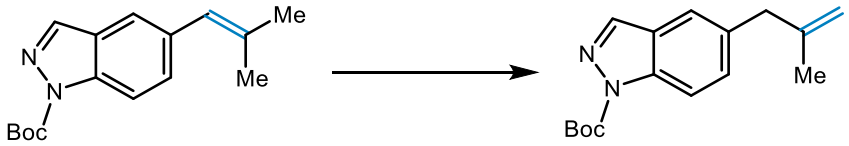
4-(2-methylallyl)-1-phenyl-1*H*-pyrazole (22a)

The title compound was prepared on 0.500 mmol scale following general procedure D using 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate as the photocatalyst and 4-(2-methylprop-1-en-1-yl)-1-phenyl-1*H*-pyrazole (**22**). The crude material was purified by silica gel column chromatography (0% to 10% EtOAc in hexanes) to afford the title compound as a colorless liquid (100 mg, quant.). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.74 (s, 1H), 7.69 – 7.62 (m, 2H), 7.55 (s, 1H), 7.44 (dd, *J* = 8.6, 7.3 Hz, 2H), 7.30 – 7.23 (m, 1H), 4.81 (s, 1H), 4.80 – 4.78 (m, 1H), 3.24 (s, 2H), 1.76 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 144.77, 141.61, 140.34, 129.51, 126.22, 125.61, 121.37, 118.87, 111.56, 33.14, 22.29. **IR (neat):** 3073, 2909, 2361, 1597, 1394, 1213, 1014, 951, 890, 752, 637, 651 cm^{-1}. **HRMS (ESI)**: exact mass calculated for $[M+H]^+$ ($C_{13}H_{15}N_2$) requires *m/z* 199.12297, found *m/z* 199.12322.



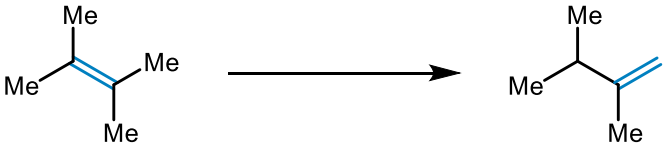
***tert*-butyl 2-methyl-4-(2-methylallyl)-1*H*-imidazole-1-carboxylate (23a)**

The title compound was prepared on 0.500 mmol scale following general procedure D using 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate as the photocatalyst and *tert*-butyl 2-methyl-4-(2-methylprop-1-en-1-yl)-1*H*-imidazole-1-carboxylate (**23**). The crude material was purified by silica gel column chromatography (7% to 60% EtOAc in hexanes) to afford the title compound as a colorless oil (85.6 mg, 72%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.04 (s, 1H), 4.84 (s, 1H), 4.80 (s, 1H), 3.20 (s, 2H), 2.59 (s, 3H), 1.75 (t, *J* = 1.1 Hz, 3H), 1.60 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 148.17, 147.49, 143.43, 138.64, 114.88, 112.35, 84.94, 36.82, 28.08, 22.36, 17.15. **IR (neat):** 2978, 2935, 1746, 1534, 1365, 1250, 1143, 1104, 1007, 888, 769, 749 cm^{-1}. **HRMS (ESI)**: exact mass calculated for $[M+H]^+$ ($C_{13}H_{21}N_2O_2$) requires *m/z* 237.15975, found *m/z* 237.15973.



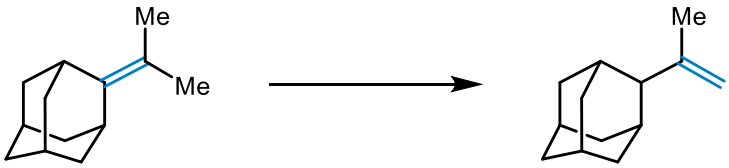
***tert*-butyl 5-(2-methylallyl)-1*H*-indazole-1-carboxylate (24a)**

The title compound was prepared on 0.500 mmol scale following general procedure D using 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate as the photocatalyst and *tert*-butyl 5-(2-methylprop-1-en-1-yl)-1*H*-indazole-1-carboxylate (**24**). The crude material was purified by silica gel column chromatography (0% to 40% EtOAc in hexanes) to afford the title compound as a colorless oil (103 mg, 75%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.11 (s, 1H), 8.09 (d, *J* = 8.7 Hz, 1H), 7.53 (d, *J* = 1.6 Hz, 1H), 7.39 – 7.36 (m, 1H), 4.84 (s, 1H), 4.74 (s, 1H), 3.44 (s, 2H), 1.72 (s, 9H), 1.68 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 149.39, 145.12, 139.54, 138.71, 135.49, 130.55, 126.31, 120.73, 114.44, 112.42, 84.88, 44.42, 28.32, 22.16. **IR (neat):** 2976, 2930, 1732, 1512, 1433, 1379, 1244, 1027, 890. 763, 599 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{16}H_{21}N_2O_2$) requires *m/z* 273.15975, found *m/z* 273.15950.



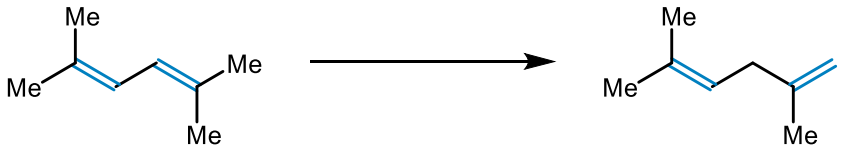
2,3-dimethylbut-1-ene (25a)

The title compound was prepared on 0.500 mmol scale following general procedure D using 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate as the photocatalyst and 2,3-dimethylbut-2-ene (**25**). Due to volatility of the product, yield was determined by GC (99% yield) against a commercial sample of the titled compound.



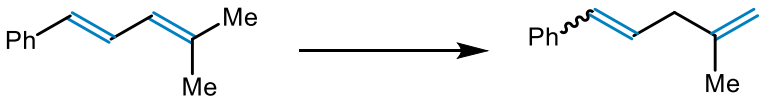
2-(prop-1-en-2-yl)adamantane (26a)

The title compound was prepared on 0.500 mmol scale following general procedure D using 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate as the photocatalyst and 2-(propan-2-ylidene)adamantane (**26**). The crude material was purified by silica gel column chromatography (0% to 5% EtOAc in hexanes) to afford the title compound as a colorless liquid (82.8 mg, 94%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 4.92 (h, *J* = 1.6 Hz, 1H), 4.77 (t, *J* = 2.1 Hz, 1H), 2.21 (br, 1H), 2.14 (br, 2H), 1.92 – 1.84 (m, 5H), 1.80 – 1.74 (m, 3H), 1.74 – 1.69 (m, 5H), 1.50 (br, 1H), 1.48 (br, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 147.38, 110.00, 49.72, 39.28, 38.10, 32.26, 29.79, 28.18, 28.11, 22.50. **IR (neat):** 2899, 2847.0, 1638, 1448, 1099, 887 cm^{-1}. **HRMS (EI):** exact mass calculated for $[M]^+$ ($C_{13}H_{20}$) requires *m/z* 176.15595, found *m/z* 176.15600.



2,5-dimethylhexa-1,4-diene (27a)

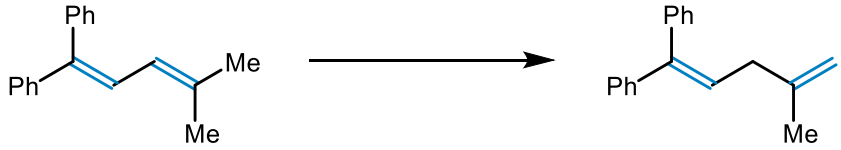
The title compound was prepared on 0.500 mmol scale following general procedure D using 2,4,5,6-tetra(9*H*-carbazol-9-yl)isophthalonitrile as the photocatalyst and 2,5-dimethylhexa-2,4-diene (**27**). The crude reaction mixture was diluted with $CDCl_3$ (10 mL) and filtrated through a plug of silica gel. The filtrate was collected and added *N*,*N*-dimethylformamide (0.500 mmol, 38.7 µL) as an internal standard. Yield averaged from two experiments was determined by ^{1}H NMR to be 92% relative to the internal standard. The spectrum is consistent with literature values.[37]



E/*Z* = 10:1

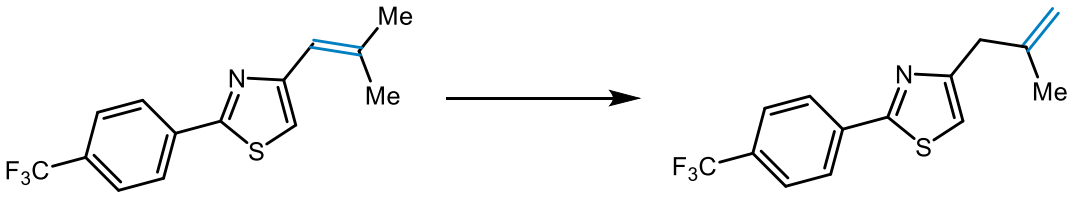
(4-methylpenta-1,4-dien-1-yl)benzene (28a)

The title compound was prepared on 0.500 mmol scale following modified general procedure D using 2,4,5,6-tetra(9*H*-carbazol-9-yl)isophthalonitrile as the photocatalyst and (*E*)-(4-methylpenta-1,3-dien-1-yl)benzene (**28**) and irradiated for 36h in *N*,*N*-dimethylformamide (2.50 mL) instead. Methanol was not added in this reaction. The crude material was purified by silica gel column chromatography (0% to 5% EtOAc in hexanes) to afford the title compound as a pale-yellow oil (71.3 mg, *E*/*Z* = 10:1, 90%). Spectra of both isomers are consistent with reported literature values.[38]



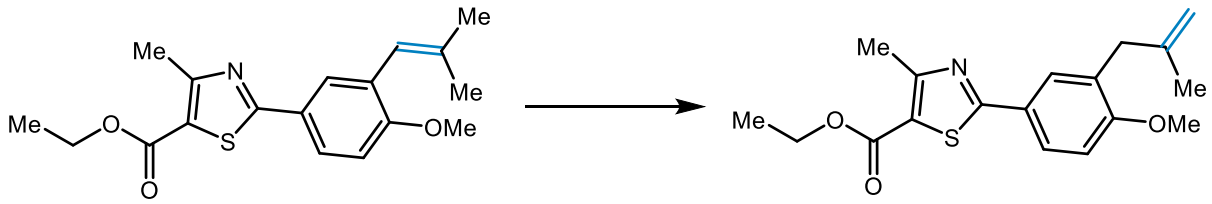
(4-methylpenta-1,4-diene-1,1-diyl)dibenzene (29a)

The title compound was prepared on 0.500 mmol scale following modified general procedure D using 2,4,5,6-tetra(9*H*-carbazol-9-yl)isophthalonitrile as the photocatalyst and (4-methylpenta-1,3-diene-1,1-diyl)dibenzene (**29**) and irradiated for 36 h in *N*,*N*-dimethylformamide (2.50 mL) instead. Methanol was not added in this reaction. The crude material was purified by silica gel column chromatography (0% to 5% EtOAc in hexanes) to afford the title compound as a colorless oil (114 mg, 95%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.39 – 7.34 (m, 2H), 7.33 – 7.22 (m, 6H), 7.22 – 7.18 (m, 2H), 6.15 (t, *J* = 7.7 Hz, 1H), 4.78 (q, *J* = 1.3 Hz, 2H), 2.80 (d, *J* = 7.7 Hz, 2H), 1.73 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 145.27, 142.95, 142.83, 140.02, 129.97, 128.28, 128.23, 127.48, 127.14, 127.13, 127.11, 110.65, 38.14, 23.15. **IR (neat):** 3024, 2968, 2918, 1491, 1441, 887, 760, 694, 625 cm^{-1}. **HRMS (EI):** exact mass calculated for $[M]^+$ ($C_{18}H_{18}$) requires *m/z* 234.14030, found *m/z* 234.14029.



4-(2-methylallyl)-2-(4-(trifluoromethyl)phenyl)thiazole (30a)

The title compound was prepared on 0.500 mmol scale following general procedure D using 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate as the photocatalyst and 4-(2-methylprop-1-en-1-yl)-2-(4-(trifluoromethyl)phenyl)thiazole (**30**). The crude material was purified by silica gel column chromatography (0% to 30% EtOAc in hexanes) to afford the title compound as a pale-yellow oil (127 mg, 89%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.06 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.03 (s, 1H), 4.91 (s, 1H), 4.82 (s, 1H), 3.57 (s, 2H), 1.81 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.88, 156.87, 143.26, 136.97, 131.54 (q, *J* = 32.5 Hz), 126.86, 126.03 (q, *J* = 3.8 Hz), 124.07 (q, *J* = 272.2 Hz), 115.55, 112.99, 40.17, 22.55. **IR (neat):** 3078, 2909, 1652, 1504, 1318, 1116, 1003, 841, 735, 670 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{14}H_{13}SNF_3$) requires *m/z* 284.07153, found *m/z* 284.07152.



Ethyl 2-(4-methoxy-3-(2-methylallyl)phenyl)-4-methylthiazole-5-carboxylate (31a)

The title compound was prepared on 0.500 mmol scale following general procedure D using 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate as the photocatalyst and ethyl 2-(4-methoxy-3-(2-methylprop-1-en-1-yl)phenyl)-4-methylthiazole-5-carboxylate (**31**). The crude material was purified by silica gel column chromatography (0% to 20% EtOAc in hexanes) to afford the title compound as a white solid (162 mg, 97%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.81 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.73 (d, *J* = 2.4 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 1H), 4.80 (s, 1H), 4.64 (s, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 3.85 (s, 3H), 3.35 (s, 2H), 2.75 (s, 3H), 1.74 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 170.23, 162.52, 161.06, 160.13, 144.20, 129.13, 129.11, 126.52, 125.57, 120.72, 111.80, 110.65, 61.17, 55.70, 37.72, 22.64, 17.65, 14.45. **IR (neat):** 2964, 2924, 2837, 1689, 1603, 1510, 1426, 1314, 1254, 1194, 1092, 1041, 820, 760 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{18}H_{22}SO_3N$) requires *m/z* 332.13149, found *m/z* 332.13171.

Crystal data of 30a (Figure S3): Compound **31a** was recrystallized from *n*-hexanes by slow evaporation. Formula $C_{18}H_{21}NO_3S$, colorless, crystal dimensions 0.426 × 0.091 × 0.078 mm^3, triclinic, space group *P* 1, *a* = 5.0349(3) Å, *b* = 10.8470(6) Å, *c* = 15.6709(10) Å, α = 94.425(2)°, β = 95.218(2)°, γ = 92.736(2)°, *V* = 848.46(9)Å^3, *Z* = 2, ρ_{calc} = 1.297 g cm^{-3}, F(000) = 352, μ(Mo Kα) = 0.205 mm^{-1}, *T* = 100 K. 53293 reflections collected, 10075 independent reflections with $I > 2\sigma(I)$ ($2\theta_{max}$ = 39.39), and 212 parameters were used for the solution of the structure. The non-hydrogen atoms were refined anisotropically. R_1 = 0.0393 and wR_2 = 0.1126. GOF = 1.034. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no.

CCDC-2104994. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Web page: http://www.ccdc.cam.ac.uk/]. Notably, one of the allylic methyl groups adopted two rotational conformers with nearly equal possibility in the crystal structure of **31a**. This resulted in a distortion of this particular methyl group in the X-ray diffraction structure of **31a**.

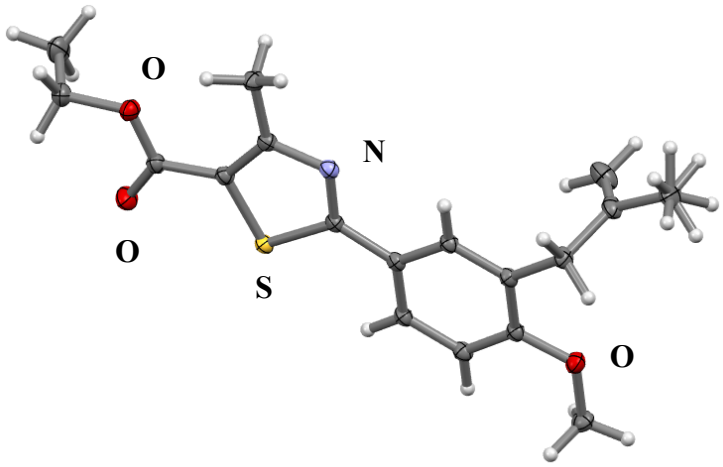
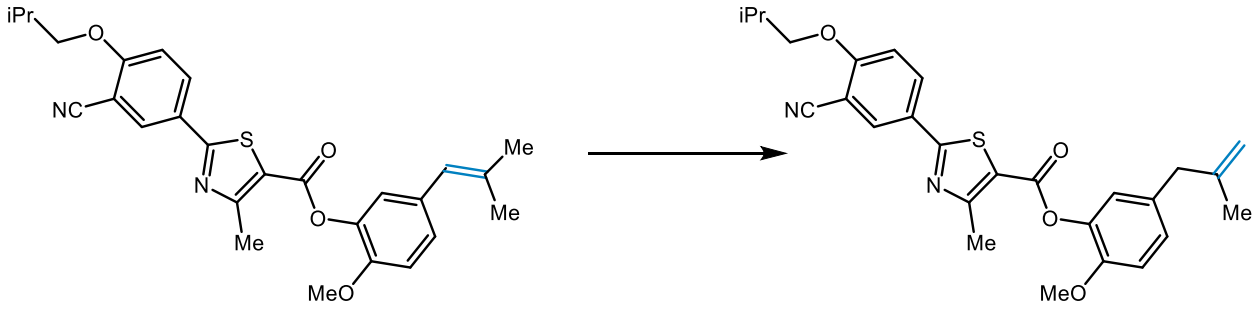


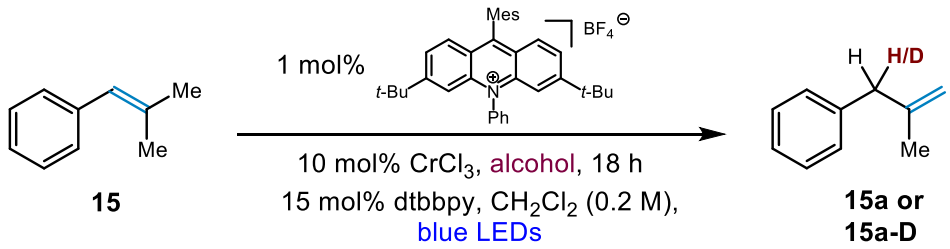
Figure S3. ORTEP drawing of 31a (with the distortion of a methyl)



2-methoxy-5-(2-methylallyl)phenyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (32a)

The title compound was prepared on 0.500 mmol scale following general procedure D using 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate as the photocatalyst and 2-methoxy-5-(2-methylprop-1-en-1-yl)phenyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (**32**). The crude material was purified by silica gel column chromatography (0% to 60 % EtOAc in hexanes) to afford the title compound as a white solid (205 mg, 86%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.22 (d, *J* = 2.3 Hz, 1H), 8.12 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.08 – 7.01 (m, 2H), 6.99 (s, 1H), 6.94 (d, J = 8.3 Hz, 1H), 4.82 (s, 1H), 4.74 (s, 1H), 3.91 (d, *J* = 6.5 Hz, 2H), 3.82 (s, 3H), 3.28 (s, 2H), 2.82 (s, 3H), 2.21 (dp, *J* = 13.3, 6.6 Hz, 1H), 1.68 (s, 3H), 1.10 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 168.11, 162.95, 162.74, 160.18, 149.66, 145.04, 139.13, 132.80, 132.62, 132.33, 127.59, 126.08, 123.39, 120.76, 115.54, 112.78, 112.46, 112.29, 103.16, 75.84, 56.20, 43.77, 28.29, 22.15, 19.21, 17.79. **IR (neat):** 2961, 2228, 1726, 1604, 1506, 1431, 1372, 1250, 1213, 1117, 1049, 1011, 809, 745 cm^{-1}. **HRMS (ESI):** exact mass calculated for $[M+H]^+$ ($C_{27}H_{29}N_2O_4S$) requires *m/z* 477.18425, found *m/z* 477.18452.

Isotope labeling and competition KIE experiments



15 **15a or 15a-D**

Following general procedure D using 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate as the photocatalyst and **15** (66.1 mg, 0.500 mmol, 1.00 equiv), CD_3OD (101 µL, 2.50 mmol, 5.00 equiv.) or 1:1 mixture of CH_3OH and CD_3OD (202 µL CH_3OH + 202 µL CD_3OD, 5 mmol each, 10 equiv. each) was added instead. After 18 h irradiation, the reaction mixture was filtered through a plug of silica gel with CH_2Cl_2 as the eluent. The filtrate was collected, concentrated to a small volume, and diluted with $CDCl_3$. Dimethylformamide (38.7 µL, 0.500 mmol) was added as the internal standard for NMR studies. This reaction mixture was then examined using an 800 MHz NMR instrument. The ratio between **15a** and **15a-D** could be determined by the respective benzylic signals at 3.32 ppm (**15a**, 2H, s) and 3.30 ppm (**15a-D**, 1H, d, J = 0.8 Hz) on ^{1}H NMR spectrum.

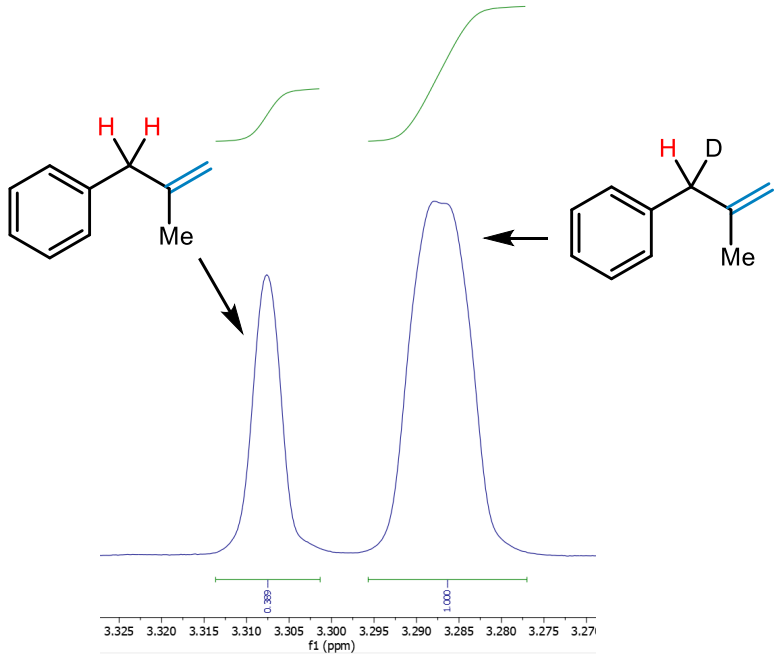


Figure S3. Crude ^{1}H NMR for isotope labeling experiment under catalytic condition with CD_3OD

Deuterium incorporation% or ratio (D/H) = 1/(0.389/2+1) × 100% = 84% or 84:16

Notably, even though high quality CD_3OD (>99% D) was used in this experiment and the reaction was set up with oven-dried glassware in a glovebox, only an 84% deuteration rate was observed. A plausible pathway, as shown in **Figure S4**, may lead to this phenomenon. CD_3O^-, a byproduct from the protodemetalation step, may re-enter the catalytic cycle as a base that deprotonates the

radical cation of **15** to forms CD_3OH *in situ*, which then participates in protodemetalation step that generates **15a-H**.

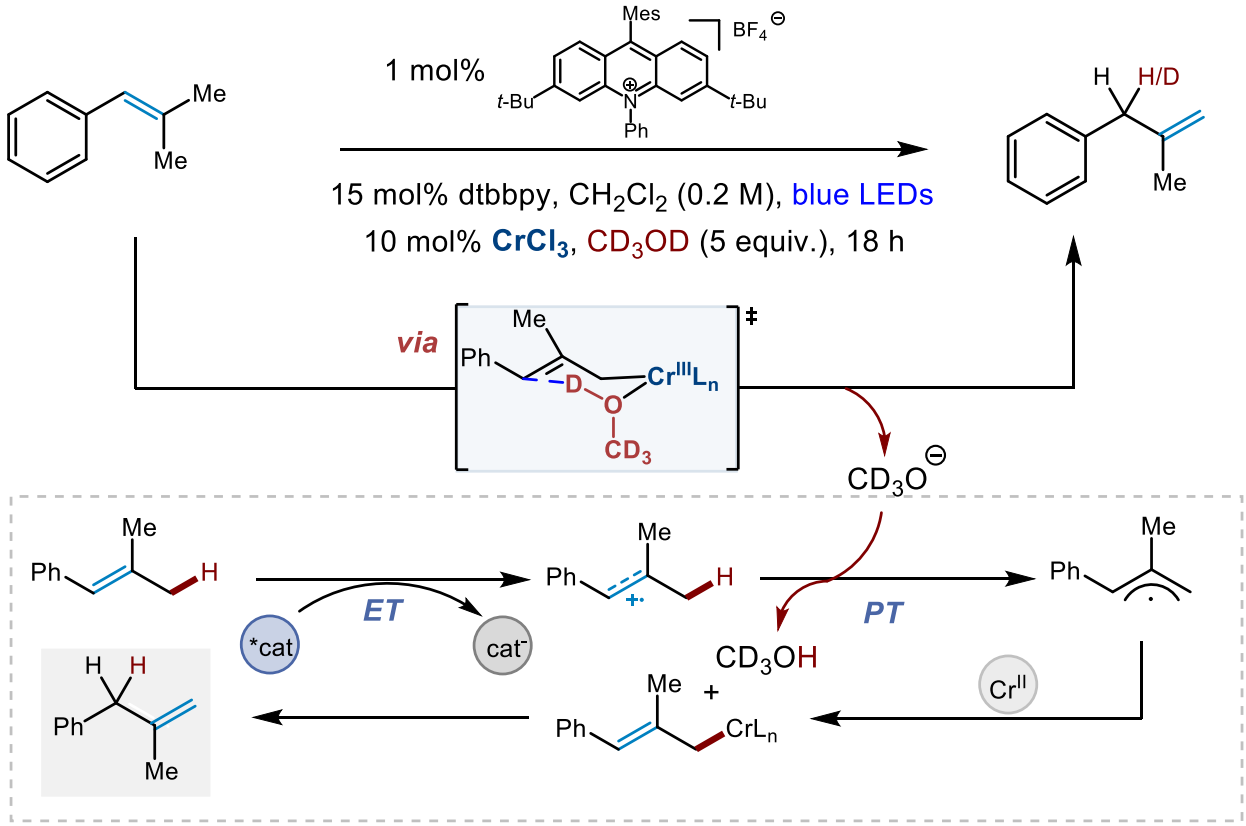


Figure S4. Mechanistic pathway that results in a lower deuteration rate in the labeling experiment under the catalytic condition.

For this reason, in order to obtain a more reliable data from the competition KIE experiment, we decided to use a large excess of alcohol to minimize this proton exchange issue. In this case, we found that a 1:1 mixture of 10 equiv. CH_3OH and 10 equiv. CD_3OD (a total of 20 equiv. alcohol) produced a consistent result under our catalytic condition. In addition, for consistency reason, we used this recipe for the stoichiometric experiment with **33** even though such a large excess of alcohol is not necessary in this case.

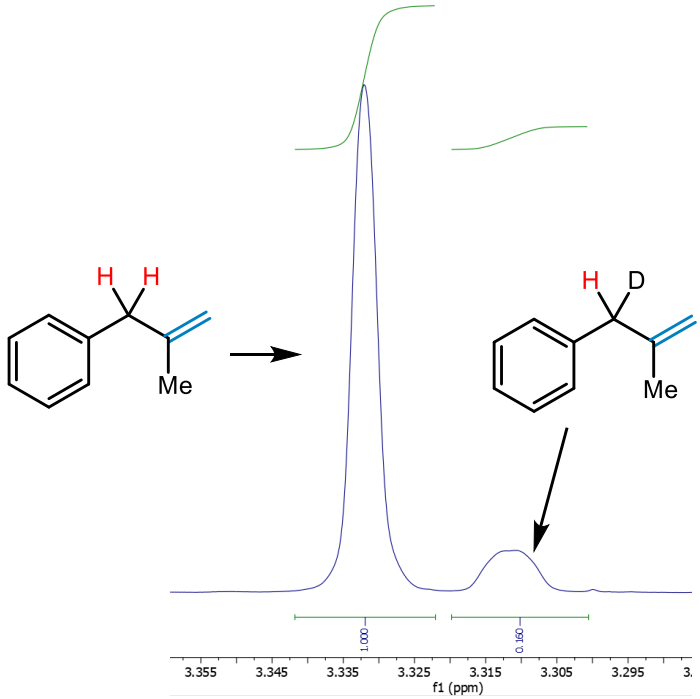
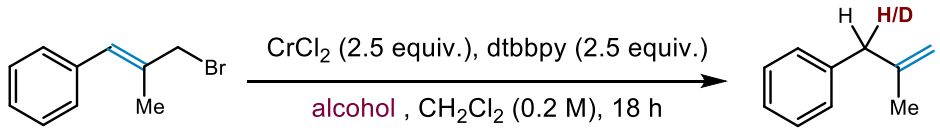


Figure S5. Crude ^{1}H NMR for competition KIE study under catalytic condition with 1:1 CH_3OH and CD_3OD

KIE (H/D) = 0.500 / 0.160 = <u>3.1</u> or <u>76:24</u>.



33 **15a or 15a-D**

Following a modified condition from Kato, under nitrogen atmosphere, $CrCl_2$ (123 mg, 1.25 mmol, 2.50 equiv.) and dtbbpy (335 mg, 1.25 mmol, 2.50 equiv.) were added to CH_2Cl_2 (2.50 mL) in a 10 mL round-bottomed flask charged with a stir bar. CD_3OD (101 µL, 2.50 mmol, 5.00 equiv.) or 1:1 mixture of CH_3OH and CD_3OD (202 µL CH_3OH + 202 µL CD_3OD, 5 mmol each, 10 equiv. each) was then added. The mixture was stirred for another 20 min until most of $CrCl_2$ dissolved to obtain a dark blue solution. To this solution was slowly added neat (*E*)-(3-bromo-2-methylprop-1-en-1-yl)benzene (106 mg, 0.500 mmol, 1.00 equiv.).[39] After the addition, a green color solution was obtained and was stirred at rt for 18h. The resulting reaction mixture was filtered through a plug of silica gel with CH_2Cl_2 as the eluent. The filtrate was collected, concentrated to a small volume, and diluted in $CDCl_3$. Dimethylformamide (38.7 µL, 0.500 mmol) was added as the internal standard for NMR studies. This reaction mixture was then examined by an 800 MHz NMR instrument. The ratio between **15a** and **15a-D** could be determined by the respective benzylic signals at 3.32 ppm (**15a**, 2H, s) and 3.30 ppm (**15a-D**, 1H, d, J = 0.8 Hz).

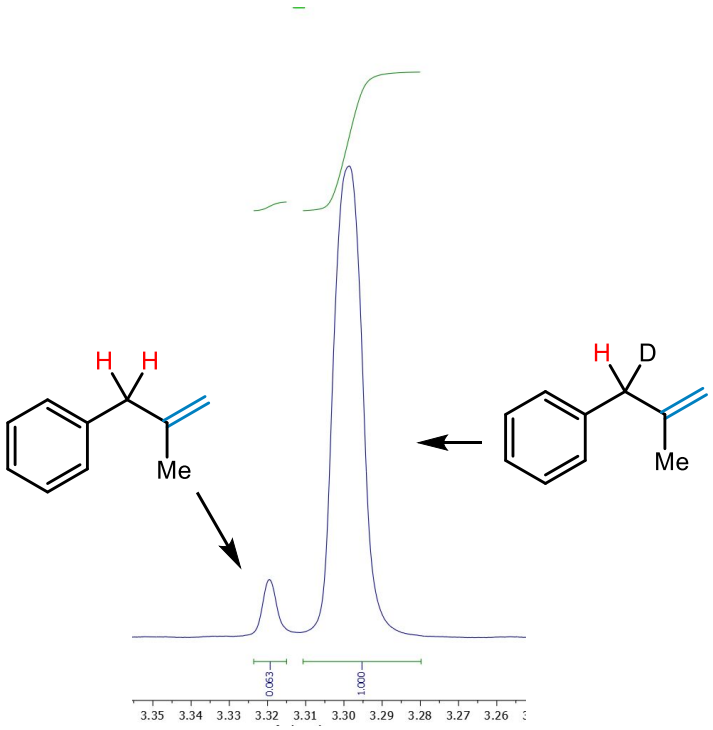


Figure S6. Crude ^{1}H NMR for isotope labeling experiment under stoichiometric condition with CD_3OD

Deuterium incorporation% or ratio (D/H) = 1/(0.063/2+1) × 100% = <u>97%</u> or <u>97:3</u>

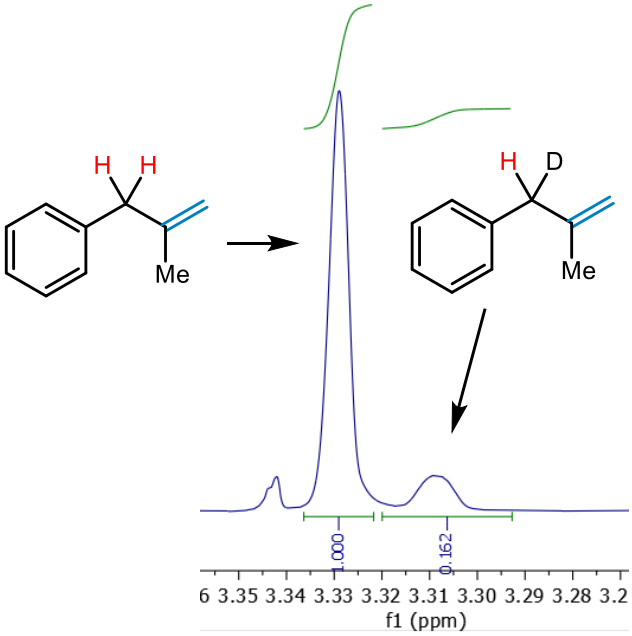
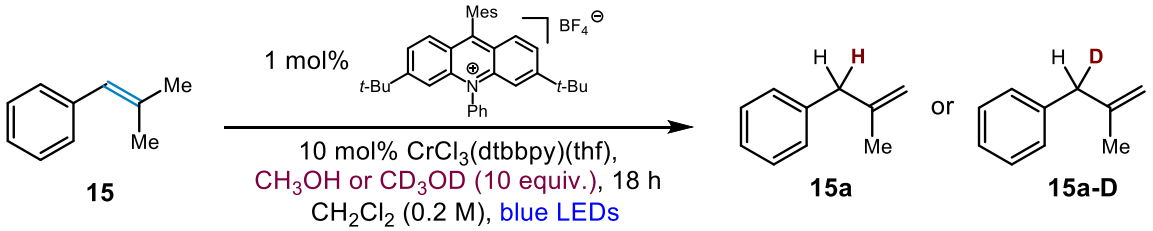


Figure S7. Crude ^{1}H NMR for competition KIE study under stoichiometric condition with 1:1 CH_3OH and CD_3OD

KIE (H/D) = 0.500 : 0.162 = <u>3.1</u> or <u>76:24</u>

Timepoint studies: determination of KIE from parallel experiments of 15 with CH_3OH and CD_3OD



Parallel experiments were conducted using reaction premix for consistency purpose, which was prepared on 2-mmol scale by mixing 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (9.73 mg, 0.0200 mmol, 1.00 mol%), **15** (264 mg, 2.00 mmol, 1.00 equiv.), CD_3OD (812 µL, 20.00 mmol, 10.0 equiv.) or CH_3OH (810 µL, 20.00 mmol, 10.0 equiv.), dibenzyl ether (397 mg, 2.00 mmol, 1.00 equiv., internal standard for GC analysis), and $CrCl_3$(dtbbpy)(thf) (99.8 mg, 0.200 mmol, 0.100 equiv.) in CH_2Cl_2 (10.0 mL) in a glovebox under nitrogen atmosphere. Notably, soluble $CrCl_3$(dtbbpy)(thf) precatalyst[40] was used in lieu of the previous $CrCl_3$ and dtbbpy combination as the kinetics of a homogeneous reaction is more consistent. In addition, in order to achieve precise control over reaction temperature, light intensity, stir rate, and irradiation time for parallel timepoint studies, Integrated Photoreactor with a 450 nm LED module was used for these timepoint experiments, in lieu of traditional Kessil LED lamps.[41]

In a glovebox under nitrogen atmosphere, 2.00 mL of the reaction premix (with CH_3OH or CD_3OD) was added into a 2-dram vial fitted with a magnetic stir bar. The vial was then sealed with a cap outfitted with a PTFE septum, sealed with electrical tape, and removed from the glovebox. A 10µL microsyringe was used to take ~5 µL aliquot from each of the mixtures through the PTFE septum. The cap of the vial was then re-sealed with PTFE tape. The aliquots were each diluted with 1.5 mL CH_2Cl_2 and were analyzed with gas chromatography (GC). This procedure was repeated at each take of the subsequent timepoints. As demonstrated in **Figure S8**, reaction vials (with CH_3OH and CD_3OD) were fitted onto a vial holder side-by-side and were irradiated in an Integrated Photoreactor with following settings: 100% light intensity, 6800 fan rpm, 1000 stir rpm, and the appropriated amount of reaction time for timepoint study.

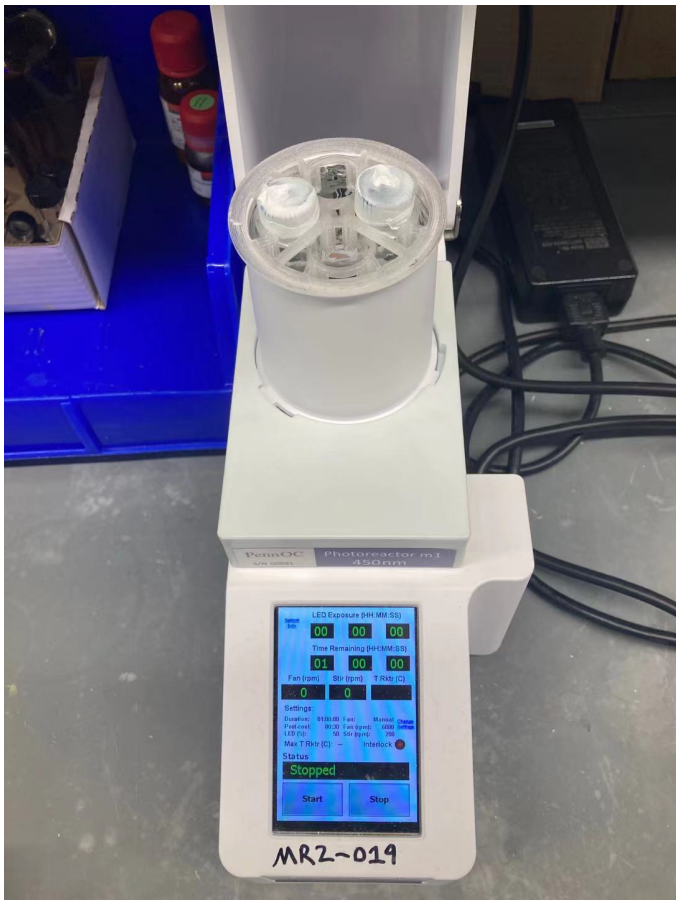


Figure S8. Reaction setup with the Integrated Photoreactor

Table S12. Timepoint studies of **15** with CH_3OH and CD_3OD

Time(h)	GC Yield for **15** w/ CH_3OH (%)	GC Yield for **15a** (%)	GC Yield for **15** w/ CD_3OD (%)	GC Yield for **15a-D** (%)
0	106	0	111	0
0.25	98.3	4.8	97.62	2.82
0.5	93.9	7.7	95.5	6.2
1	87	12.7	89.54	10.3
1.5	81.3	16.5	84	13.4
2	78.23	19.33	81.3	16.36
3	70.13	24.14	75.8	20
5	60.54	31.13	68.15	26.14
7	54	36.5	61.3	31.4
11	43.1	48.7	50.4	40.1
13	38.1	51.2	44.2	43.56
15	32.8	54.3	40.47	47.58
19	24.4	62.2	32.9	52.5
23	16.72	66.8	25.13	57.63
27	10	69.8	18.4	62.6
31	5.89	70	13.3	65

From the above timepoint studies, we discovered that the reaction was roughly first order in **15**. We then processed the data (**Table S12**) with the first order kinetics model while omitting initial 30 min as well as the last few data points wherein the reactions were not stable. We were able to obtain decent linear regression lines (**Figure S9**). The slopes of these lines, which represent the approximate rate constants for reactions of **15** with CH_3OH (gray line) and CD_3OD (blue line), could be determined. A KIE of 1.24 could then be obtained.

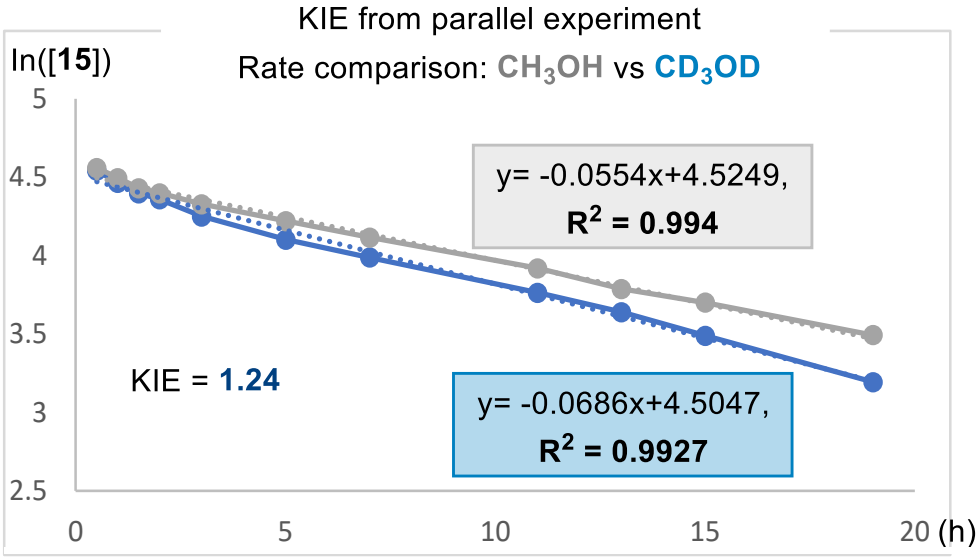
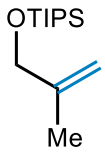
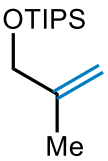


Figure S9. Determination of KIE from the parallel experiments

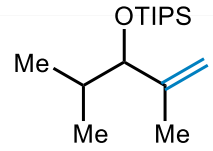
^{1}H and ^{13}C NMR Spectra of Products



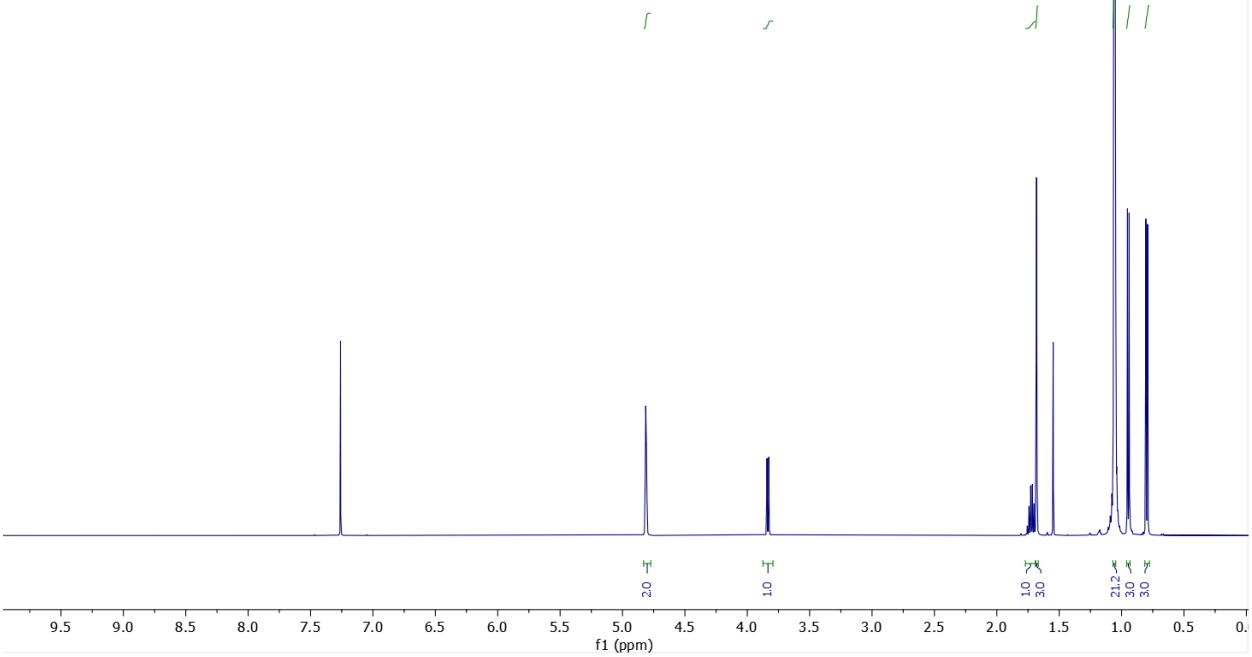
1a



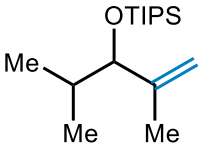
1a


OTIPS
Me
Me
Me

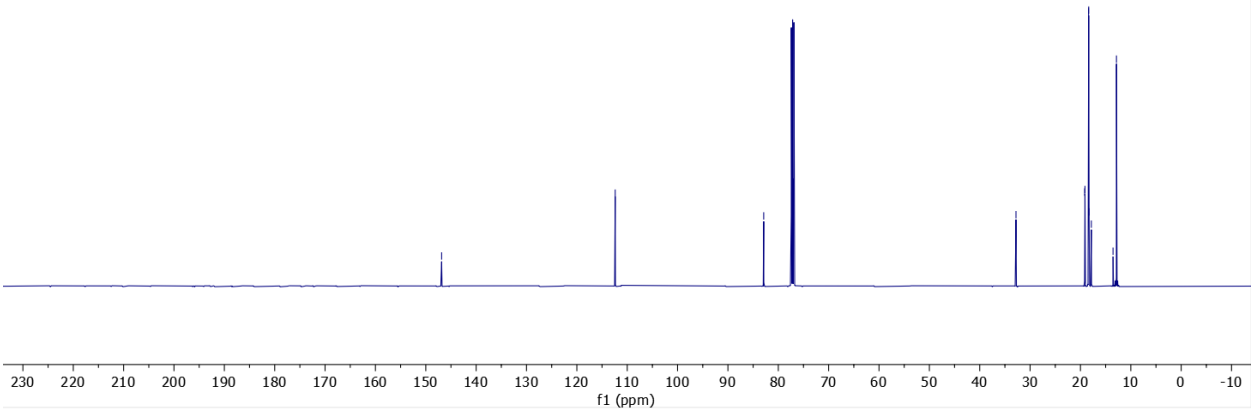
2a

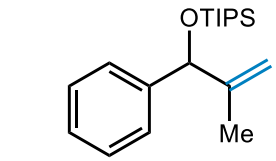

2.0
1.0
1.0
3.0
21.2
3.0
3.0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


146.86
112.39
82.90
32.80
19.16
19.10
18.39
18.36
18.28
17.84
13.53
12.85


OTIPS
Me
Me
Me

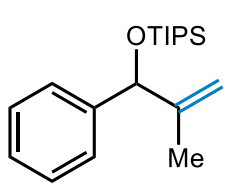
2a


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


OTIPS
Me

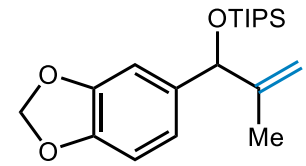
3a

2.0
2.0
1.0
1.0
1.0
1.0
3.0
21.3
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


OTIPS
Me

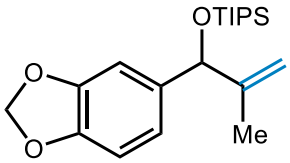
3a

148.38
143.83
127.95
126.96
126.16
110.34
78.88
18.15
18.13
17.14
12.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OTIPS
O
O
Me

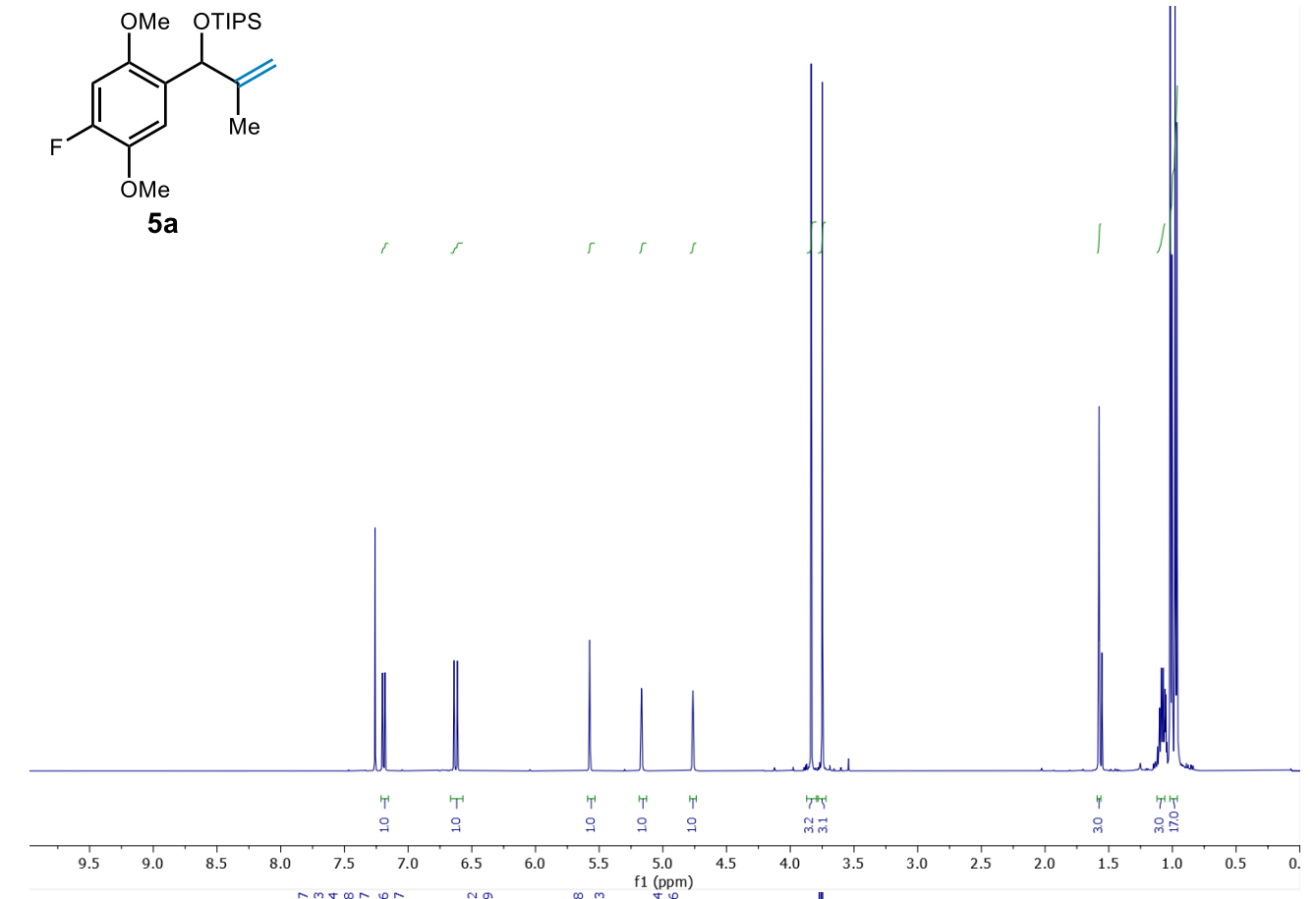
4a

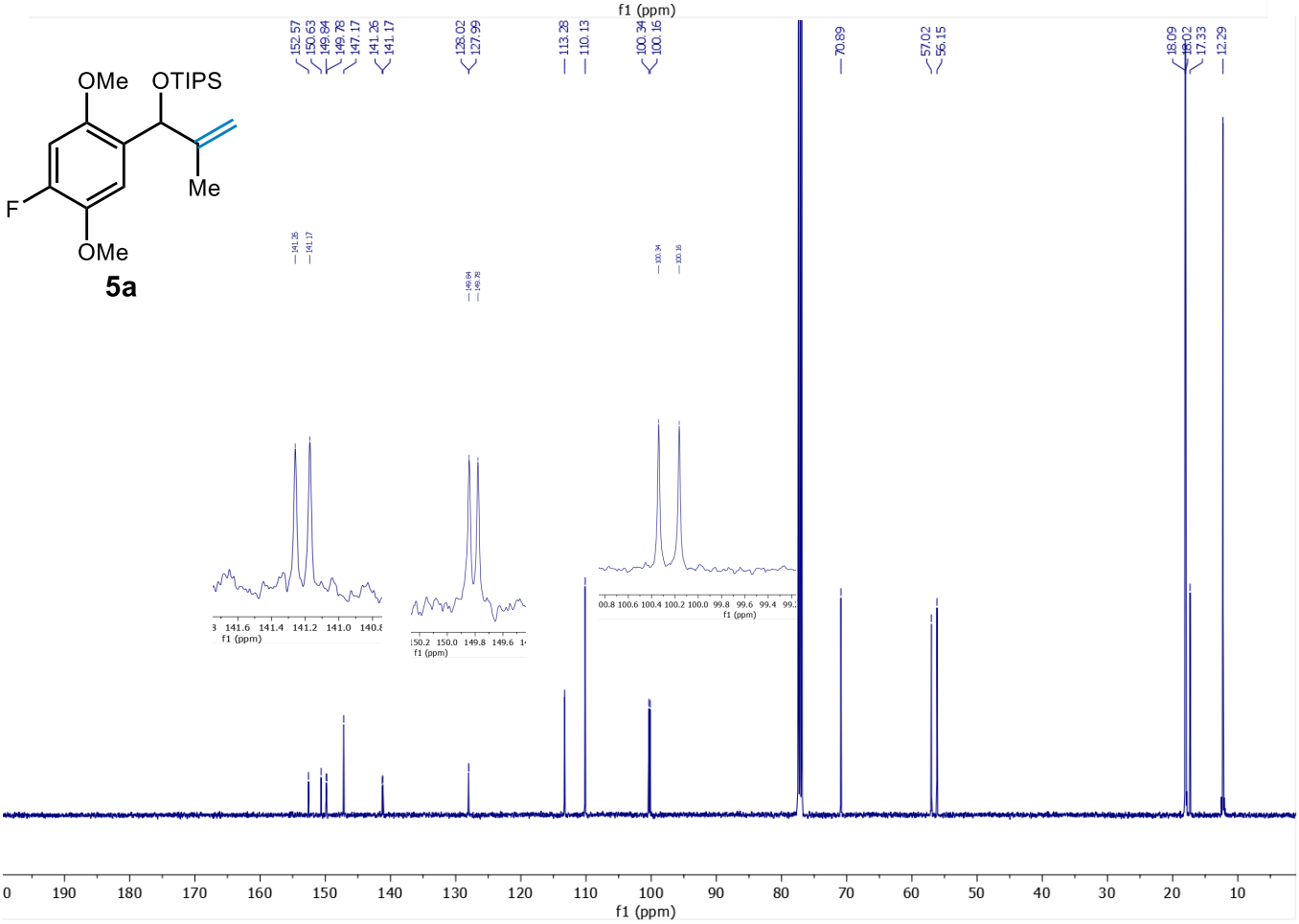
1.0
1.0
1.0
2.0
1.0
1.0
1.0
3.0
3.0
17.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

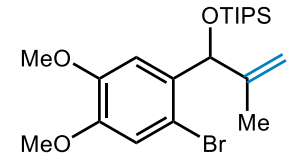

OTIPS
O
O
Me

4a

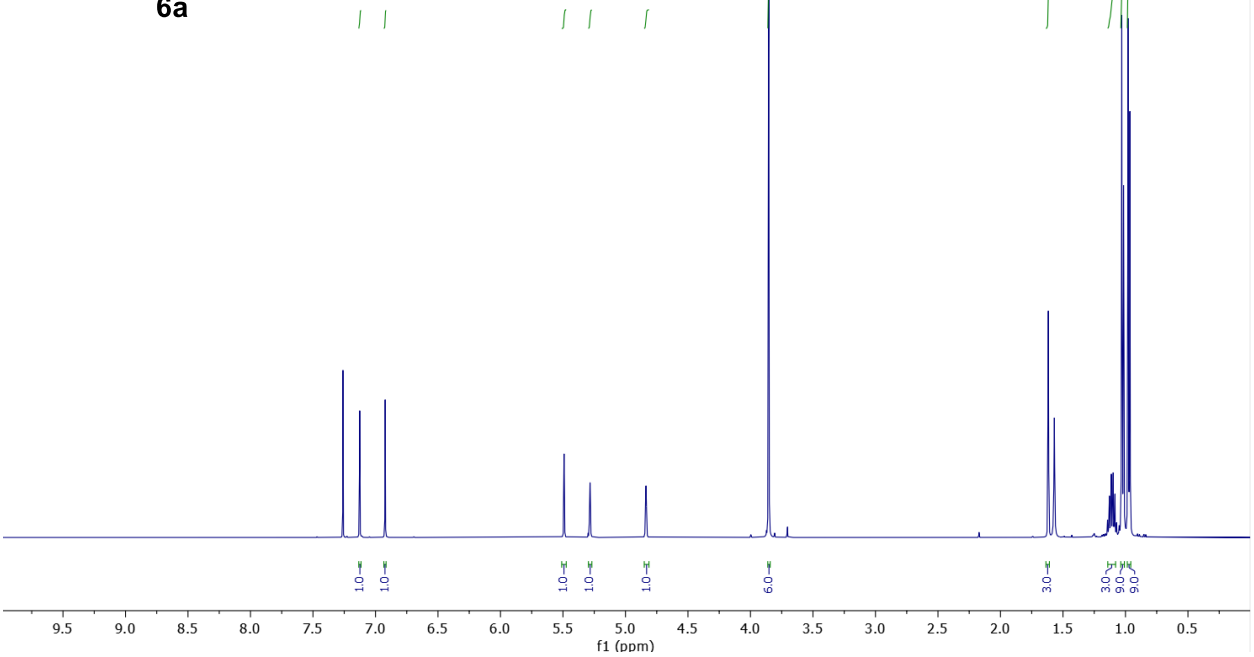
148.38
147.43
146.48
138.11
119.38
110.22
107.64
106.76
100.95
78.55
18.16
18.14
17.22
12.38
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

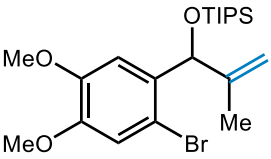

OMe
OTIPS
Me
F
OMe
5a
1.0
1.0
1.0
1.0
1.0
3.2
3.1
3.0
3.0
17.0
f1 (ppm)


OMe
OTIPS
Me
F
OMe
5a
152.57
150.63
149.84
149.78
147.17
141.26
141.17
128.02
127.99
113.28
110.13
100.34
100.16
70.89
57.02
56.15
18.09
18.02
17.33
12.29
f1 (ppm)


OTIPS
MeO
MeO
Me
Br

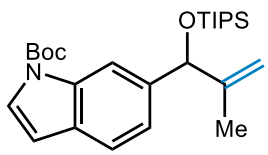
6a


1.0
1.0
1.0
1.0
1.0
6.0
3.0
3.0
9.0
9.0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


OTIPS
MeO
MeO
Me
Br

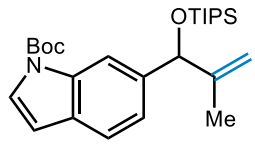
6a

148.62
148.50
146.40
134.97
114.67
112.05
111.22
111.12
76.20
56.20
55.98
18.12
18.01
17.63
12.33
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OTIPS
Boc
N
Me

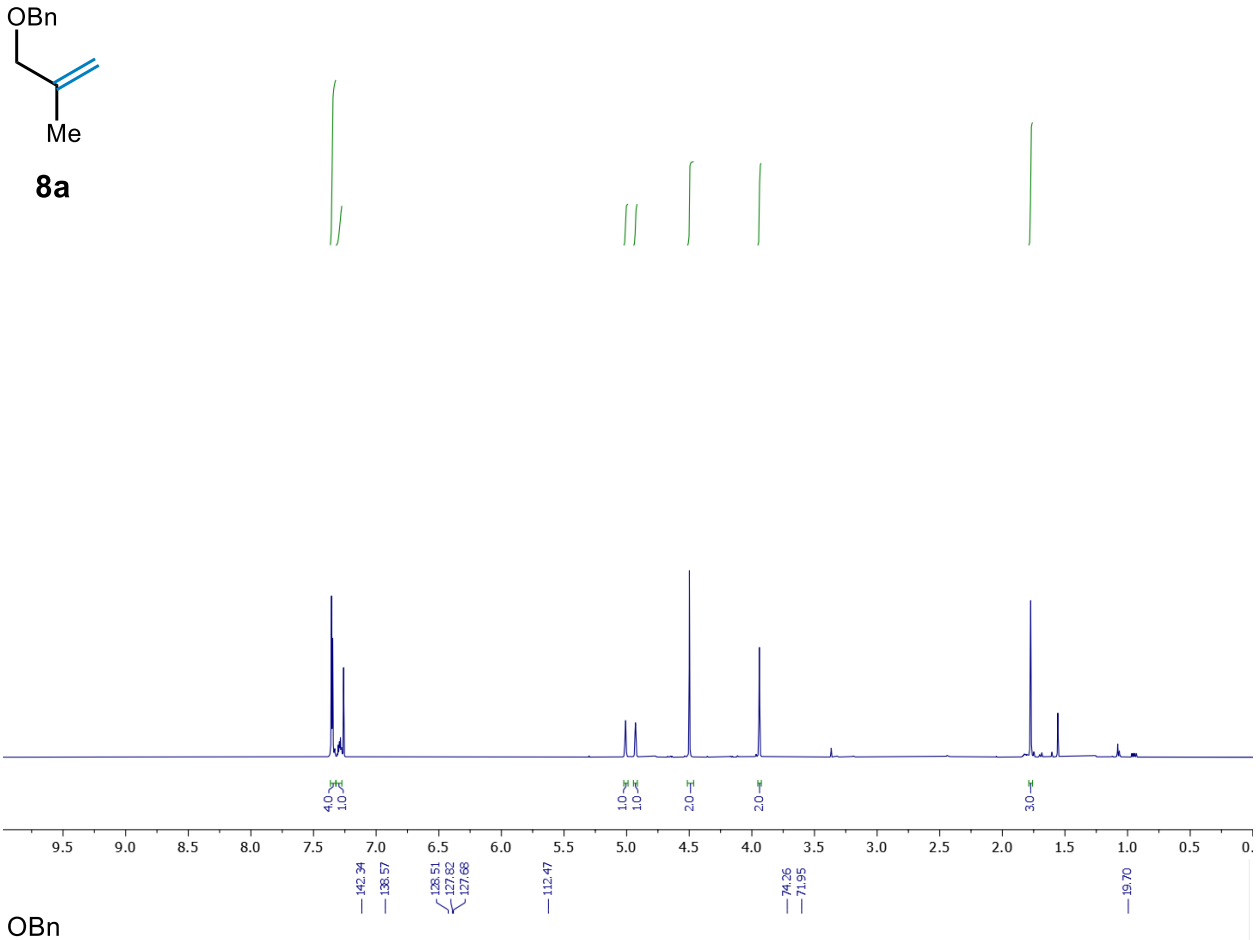
7a

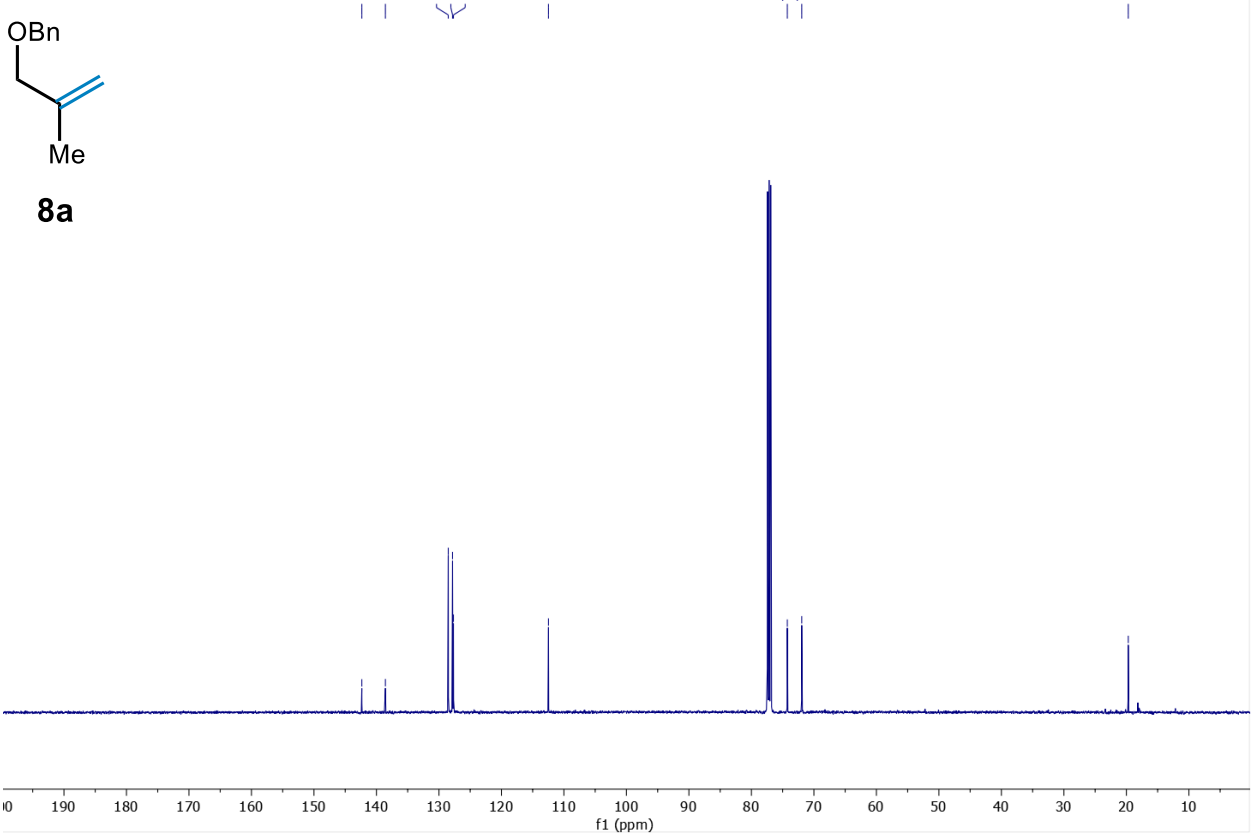
1.0
1.0
1.0
1.0
1.0
1.0
1.0
1.0
9.0
3.0
3.0
17.1
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

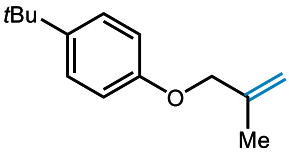

OTIPS
Boc
N
Me

7a

150.20
148.77
140.47
135.11
129.80
126.03
121.25
120.30
113.22
109.95
107.28
83.63
79.36
28.36
18.28
18.18
18.16
18.10
17.48
13.54
13.27
12.42
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

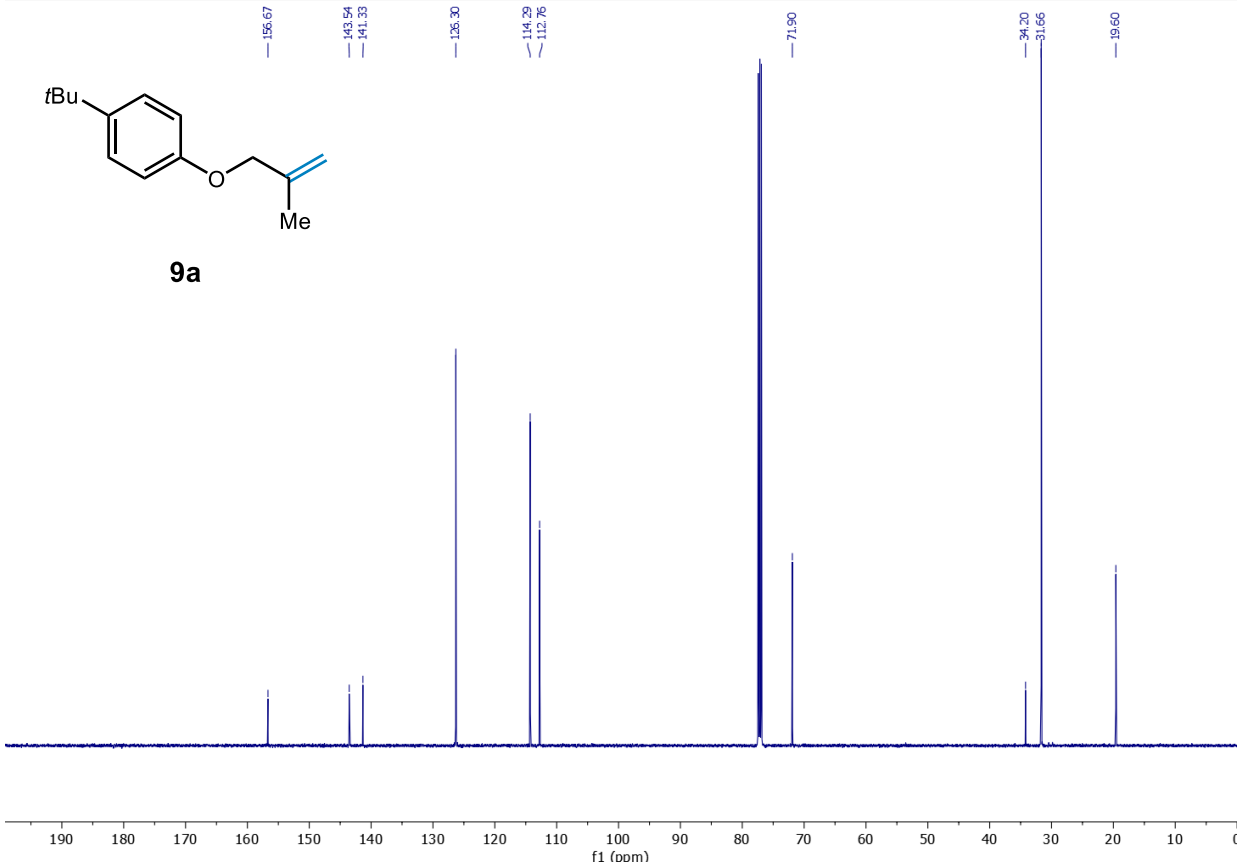

OBn
Me
8a
4.0
1.0
1.0
1.0
2.0
2.0
3.0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
142.34
138.57
128.51
127.82
127.68
112.47
74.26
71.95
19.70


OBn
Me
8a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


tBu
O
Me

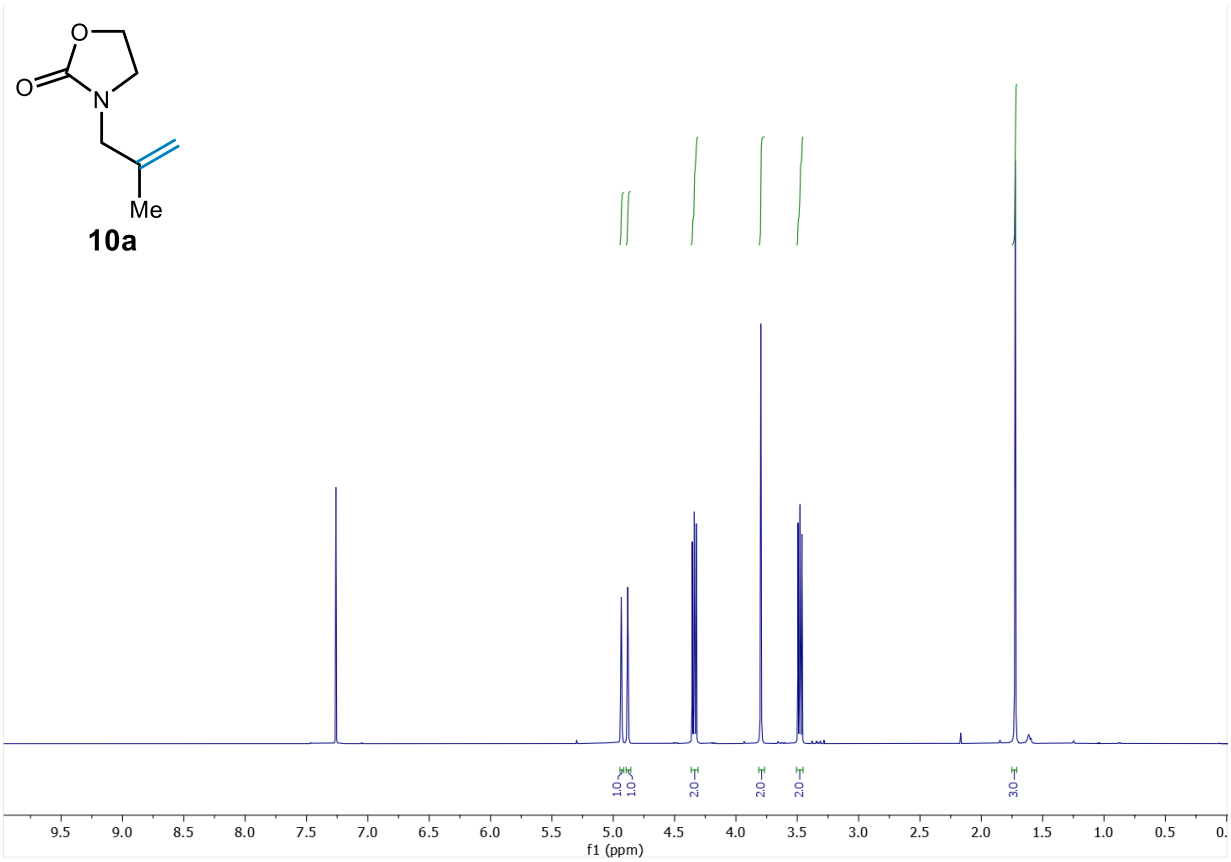
9a

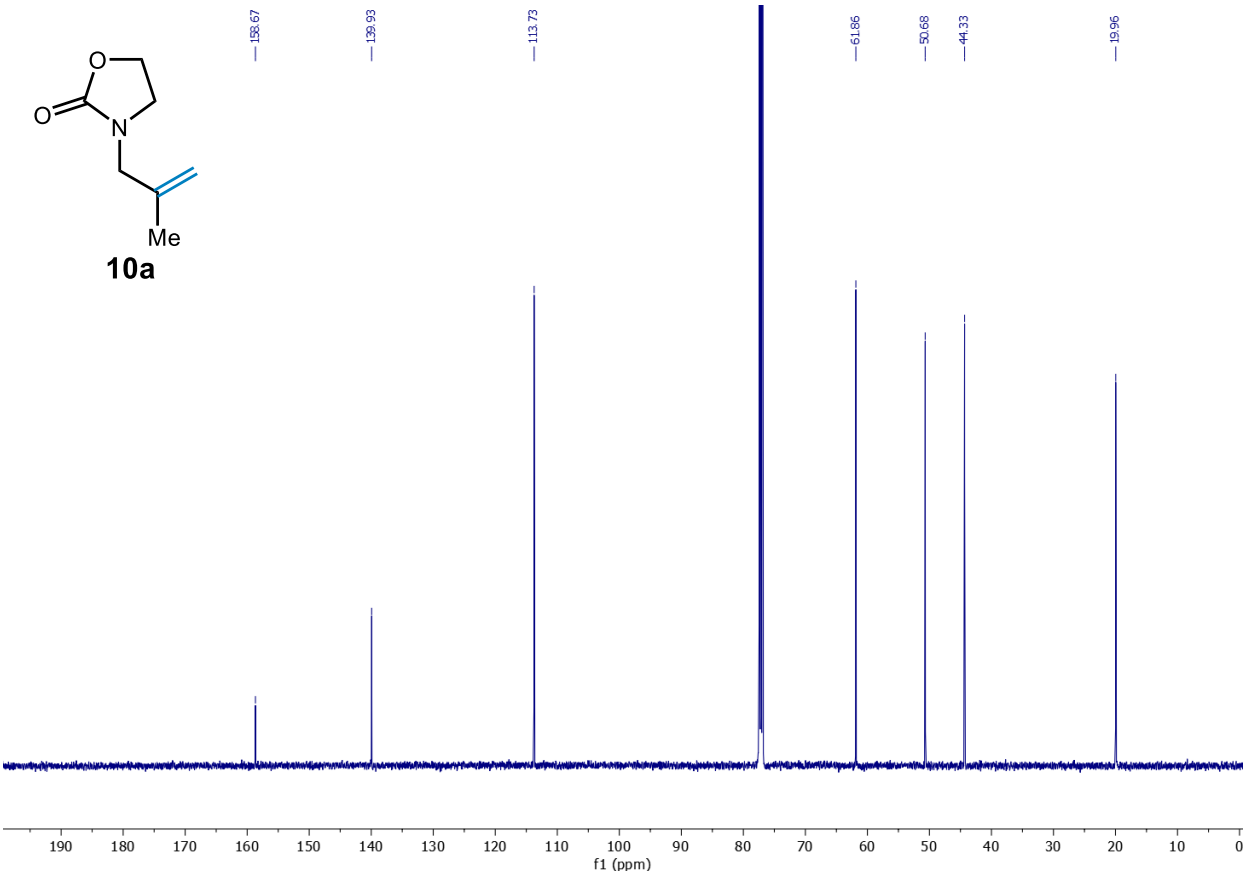
2.0
2.0
1.0
1.0
2.0
3.0
9.0
f1 (ppm)

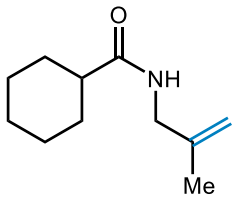

156.67
143.54
141.33
126.30
114.29
112.76
71.90
34.20
31.66
19.60
f1 (ppm)

tBu
O
Me

9a

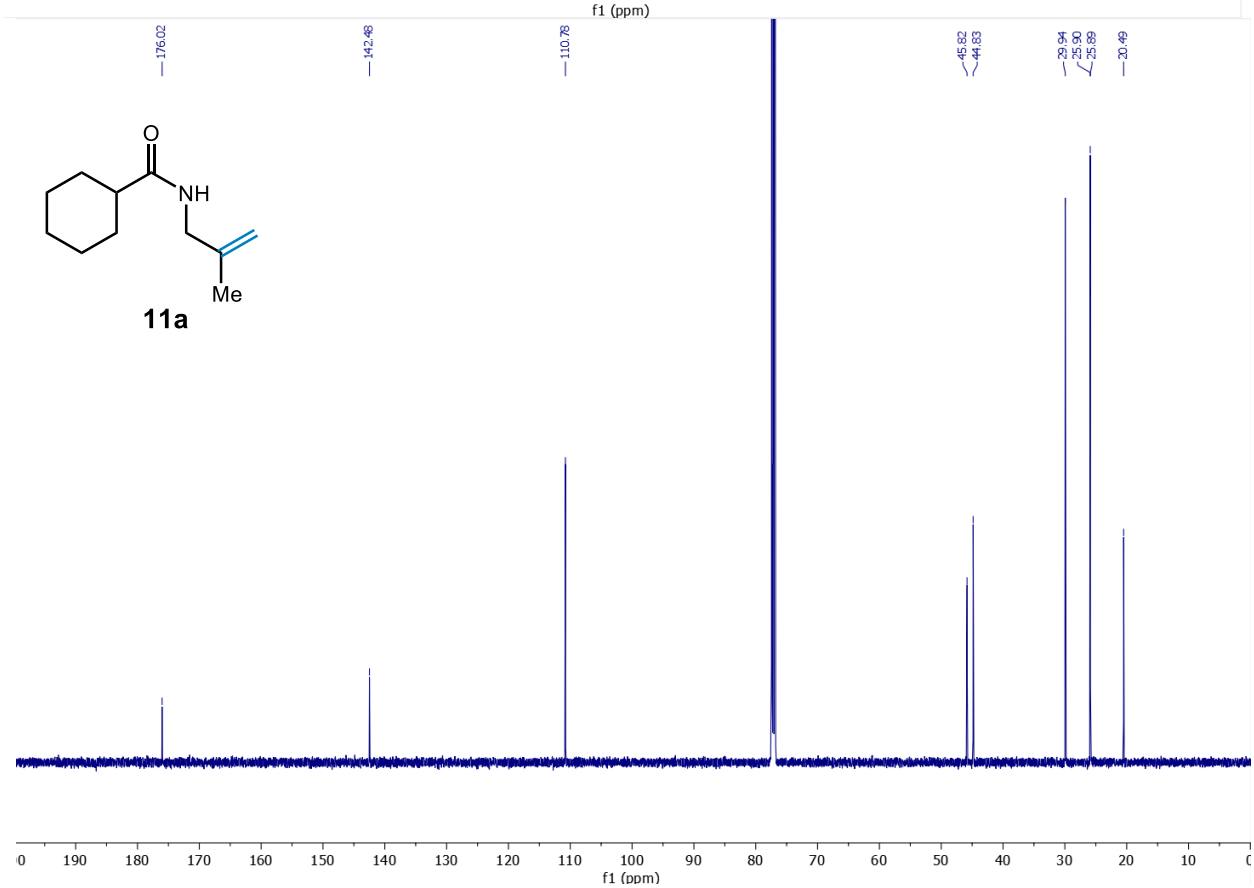

O
O
N
Me
10a
1.0
1.0
2.0
2.0
2.0
3.0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


158.67
139.93
113.73
61.86
50.68
44.33
19.96
O
O
N
Me
10a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

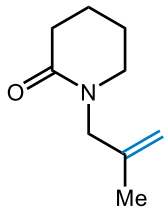

O
NH
Me

11a

0.9
2.0
2.0
1.0
2.0
2.0
1.0
2.0
3.0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

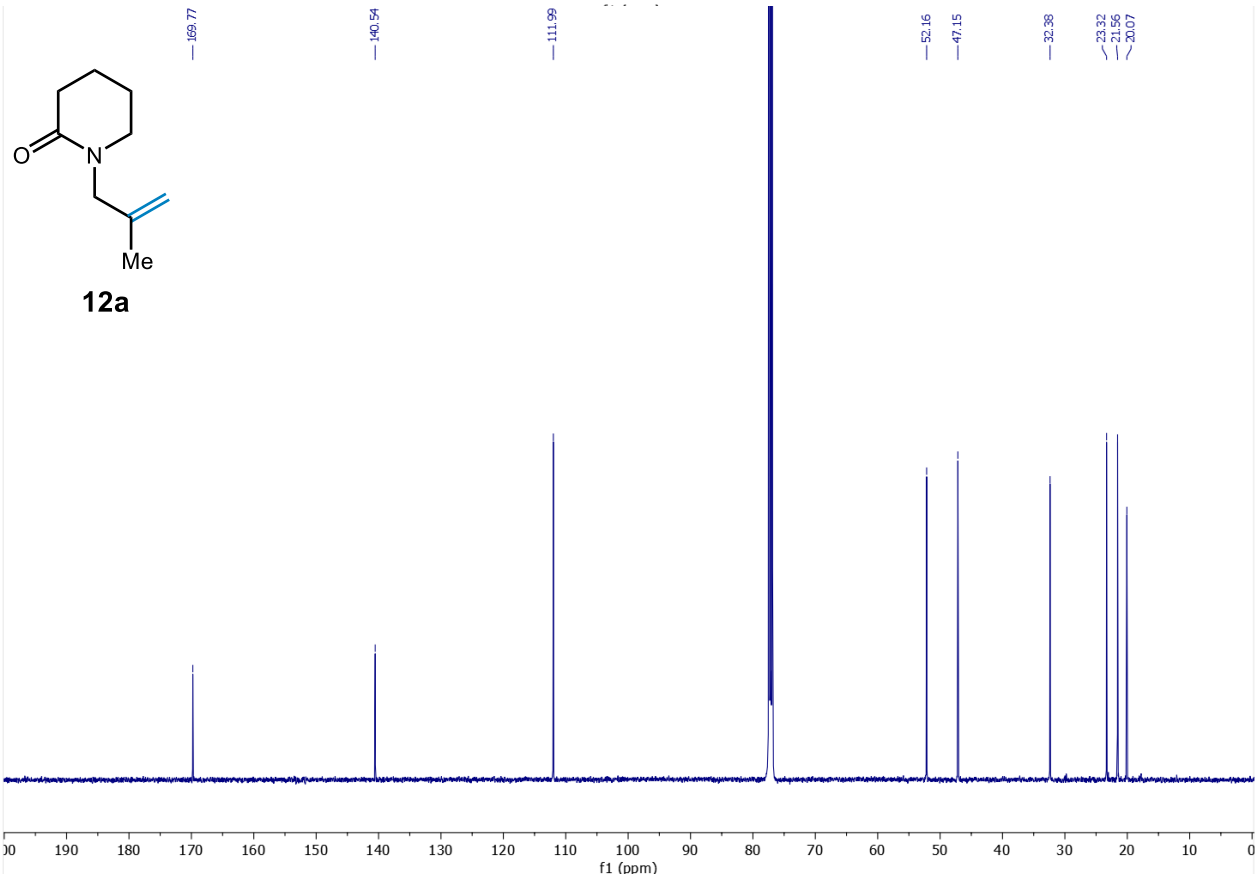

176.02
142.48
110.78
45.62
44.63
29.94
25.90
25.89
20.49
O
NH
Me
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

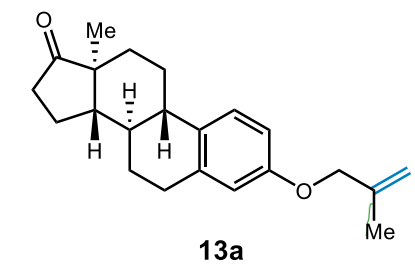
11a


O
N
Me

12a

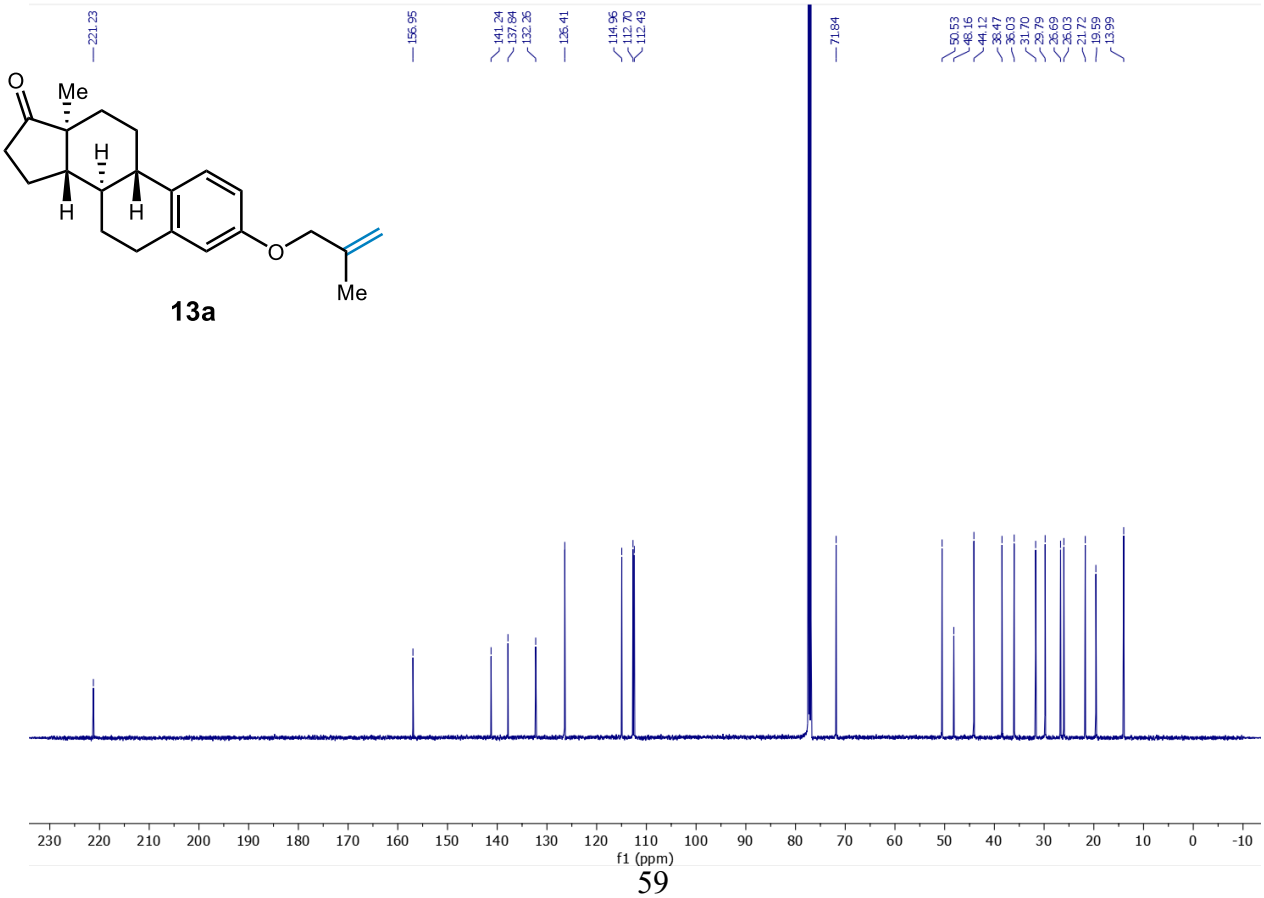
1.0
1.0
2.0
2.0
2.0
4.0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5


169.77
140.54
111.99
52.16
47.15
32.38
23.32
21.56
20.07
O
N
Me
12a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


O
Me
H
H
H
O
Me

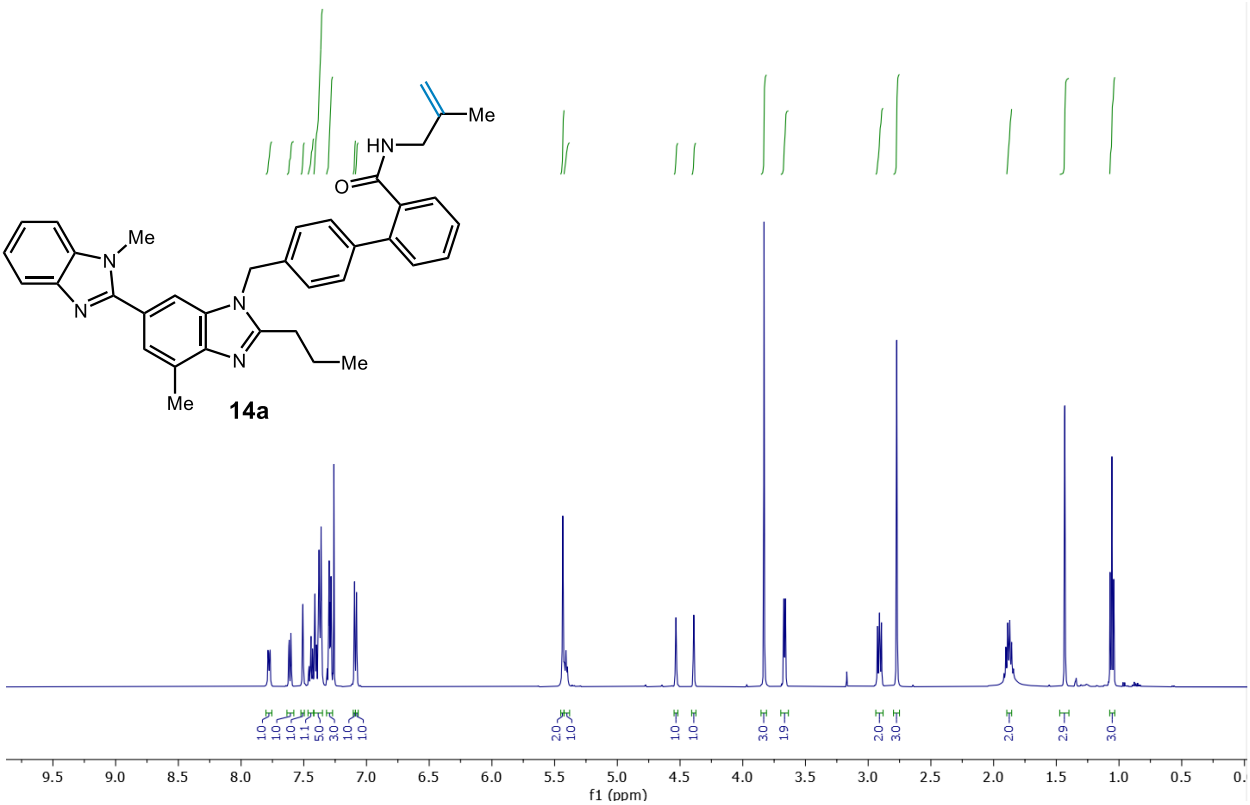
13a

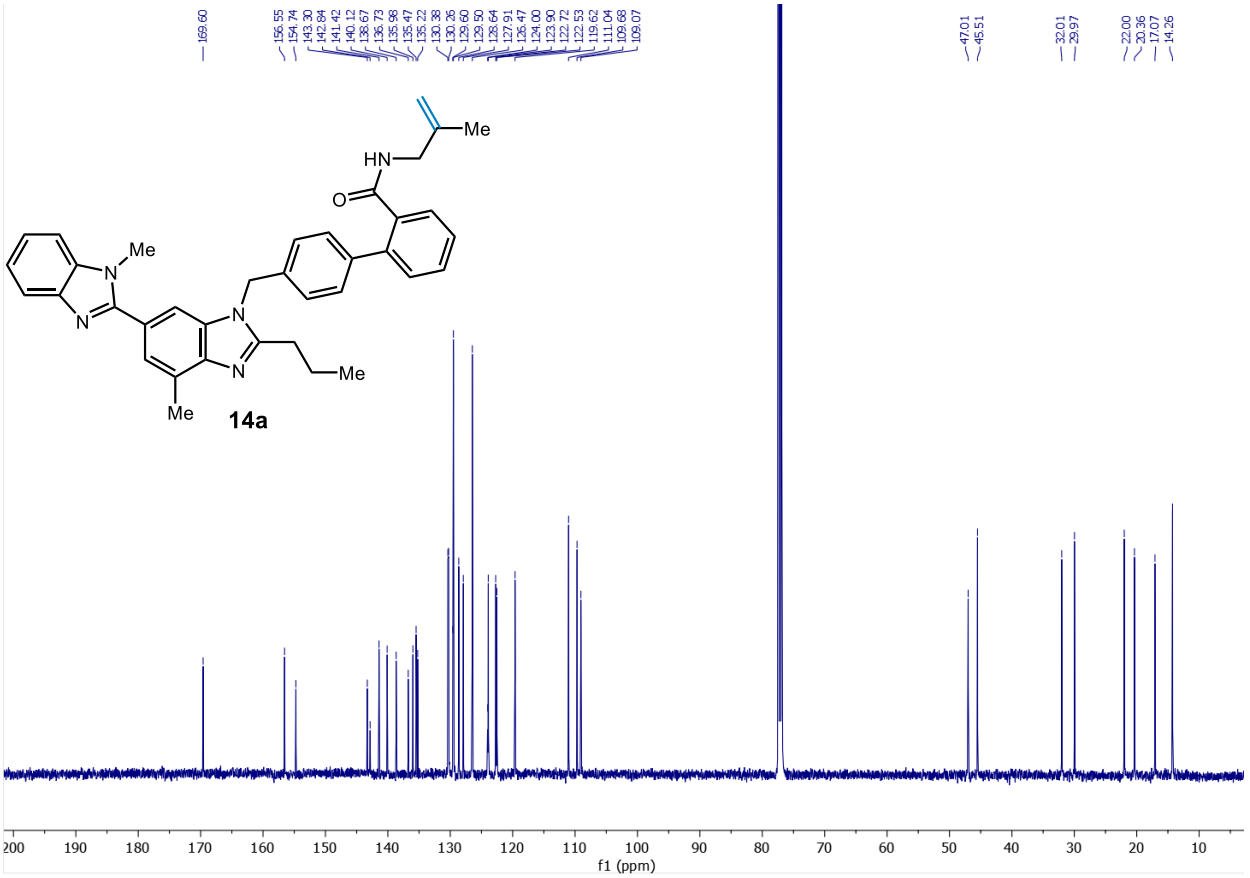
1.0
1.0
1.0
1.0
2.0
2.0
1.0
1.0
1.0
2.0
3.0
1.0
5.0
3.0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

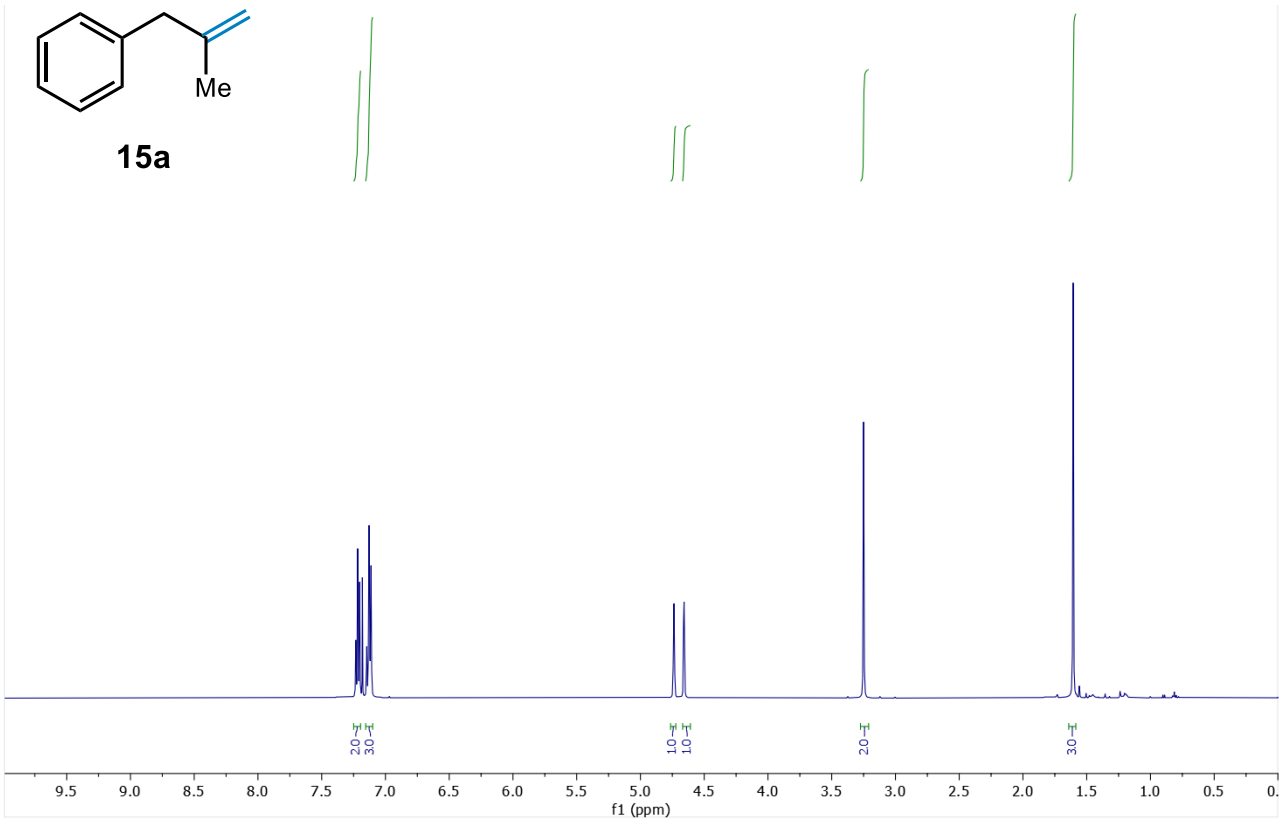

221.23
156.95
141.24
137.64
132.26
126.41
114.96
112.70
112.43
71.84
50.53
48.16
44.12
38.47
36.03
31.70
29.79
26.69
26.03
21.72
19.59
13.99
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

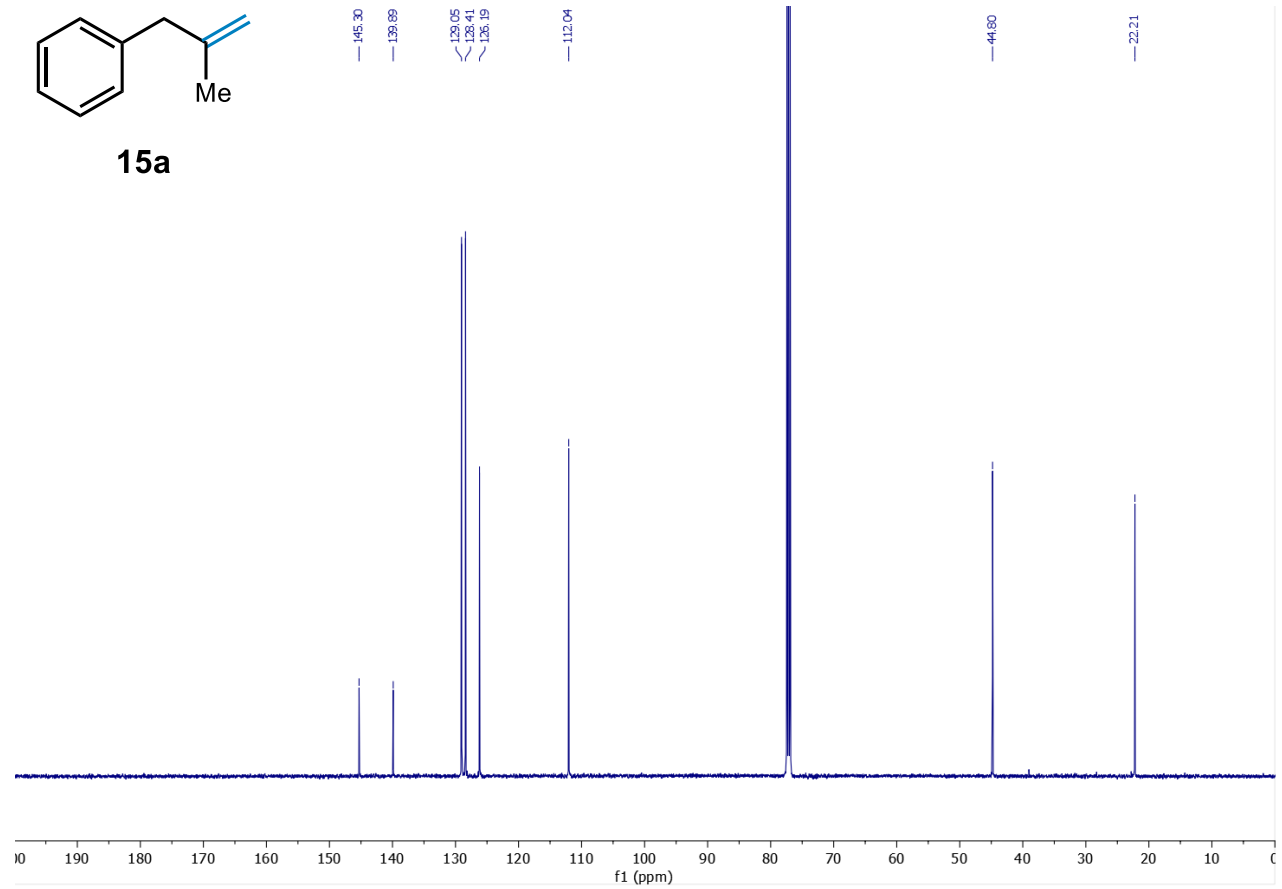
O
Me
H
H
H
O
Me

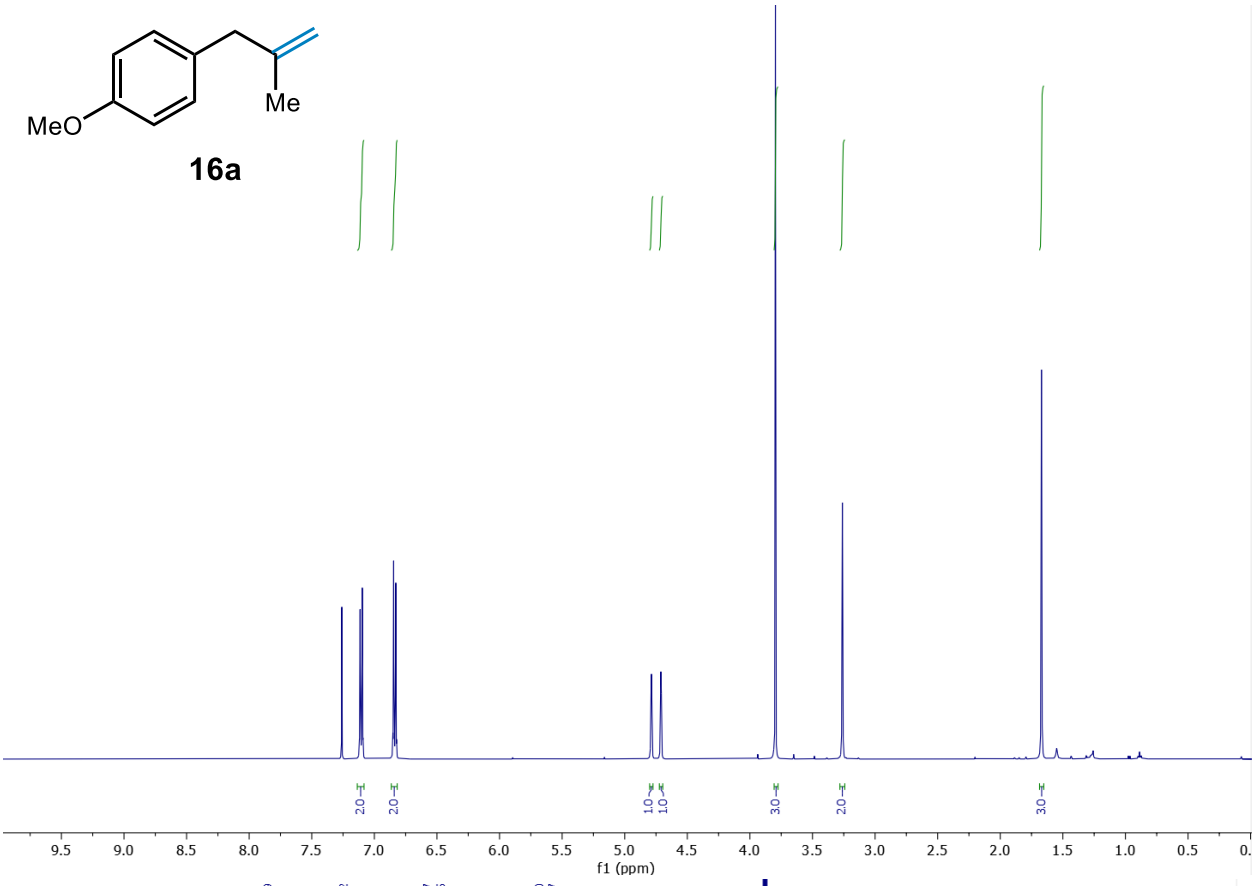
13a

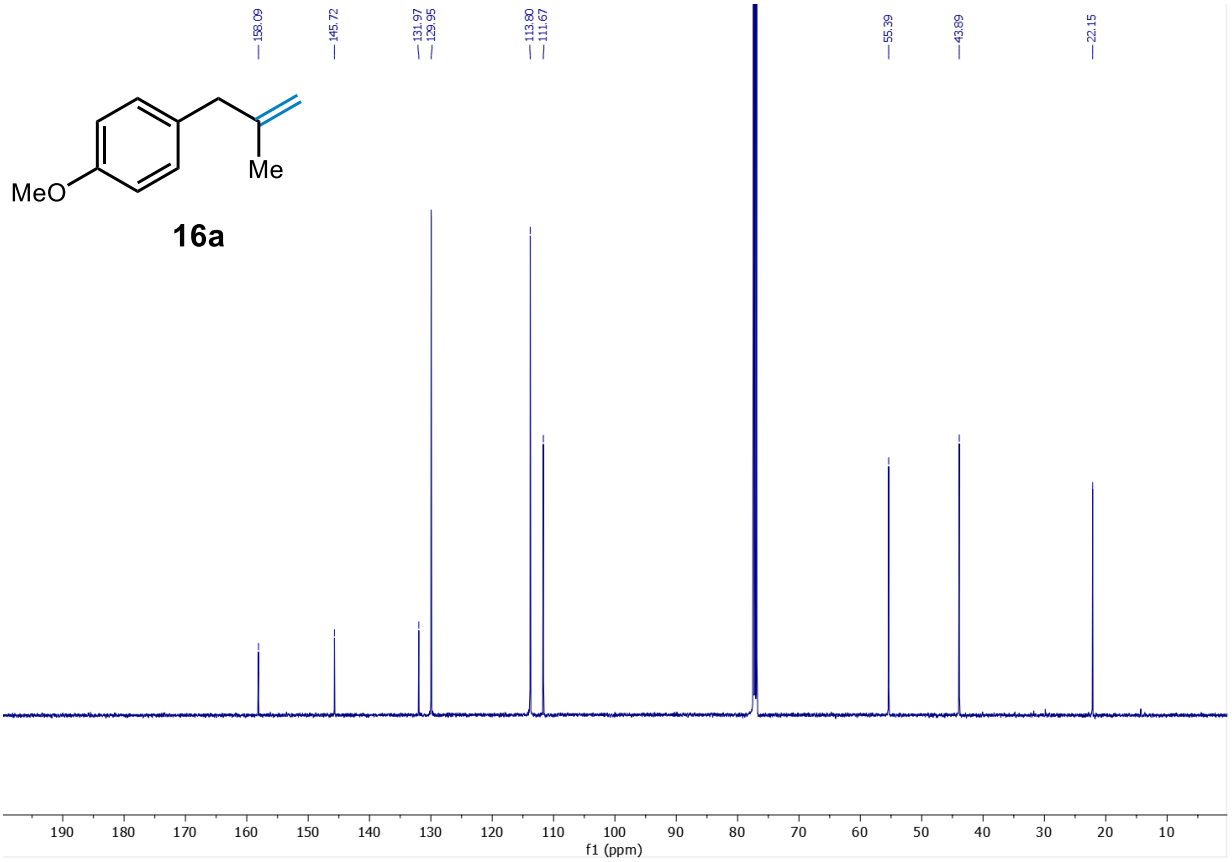

Me
HN
O
Me
N
N
N
Me
Me
14a
1.0
1.0
1.0
1.1
5.0
3.0
1.0
1.0
2.0
1.0
1.0
1.0
3.0
1.9
2.0
3.0
2.0
2.9
3.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

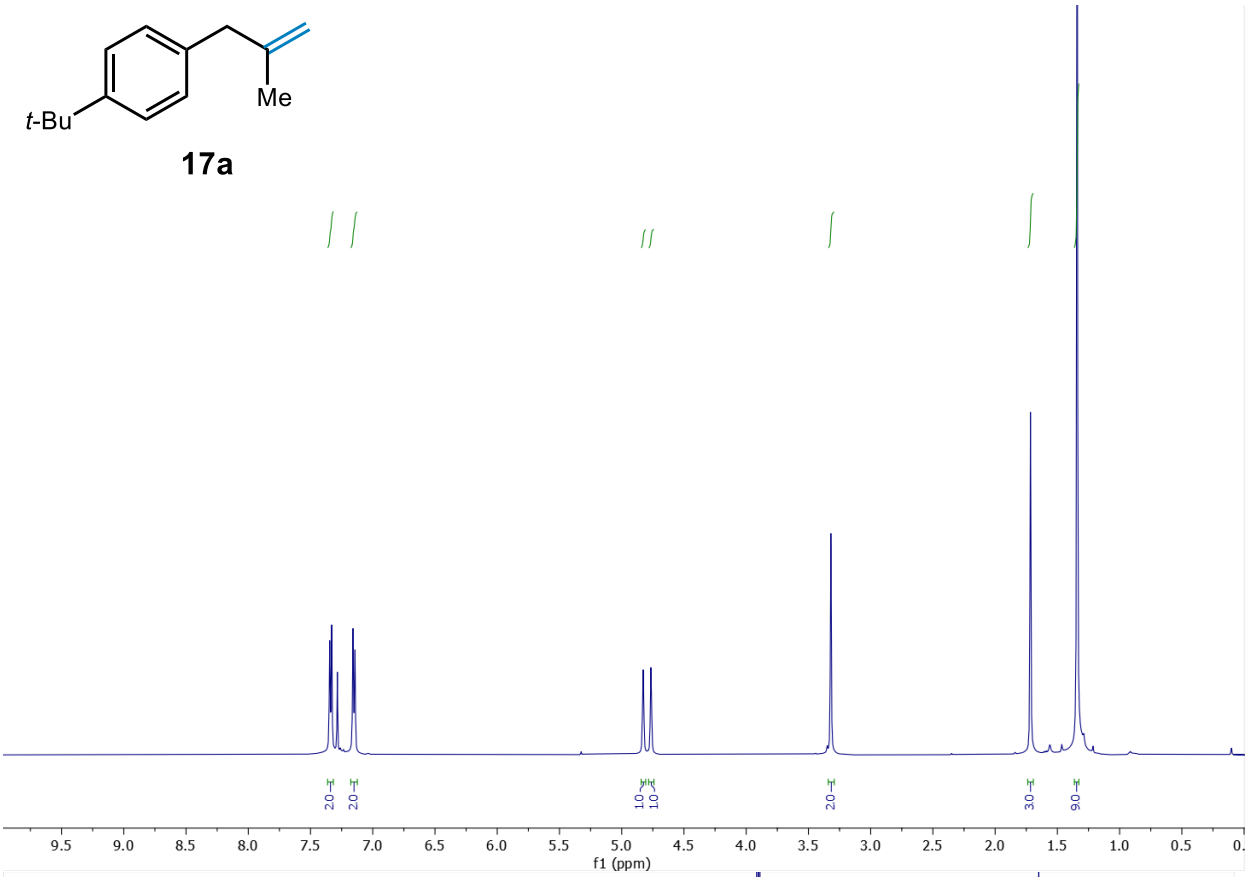

169.60
156.55
154.74
143.30
142.84
141.42
140.12
138.67
136.73
135.98
135.47
135.22
130.38
130.26
129.60
129.50
128.64
127.91
126.47
124.00
123.90
122.72
122.53
119.62
111.04
109.68
109.07
47.01
45.51
32.01
29.97
22.00
20.36
17.07
14.26
Me
HN
O
Me
N
N
N
Me
Me
14a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

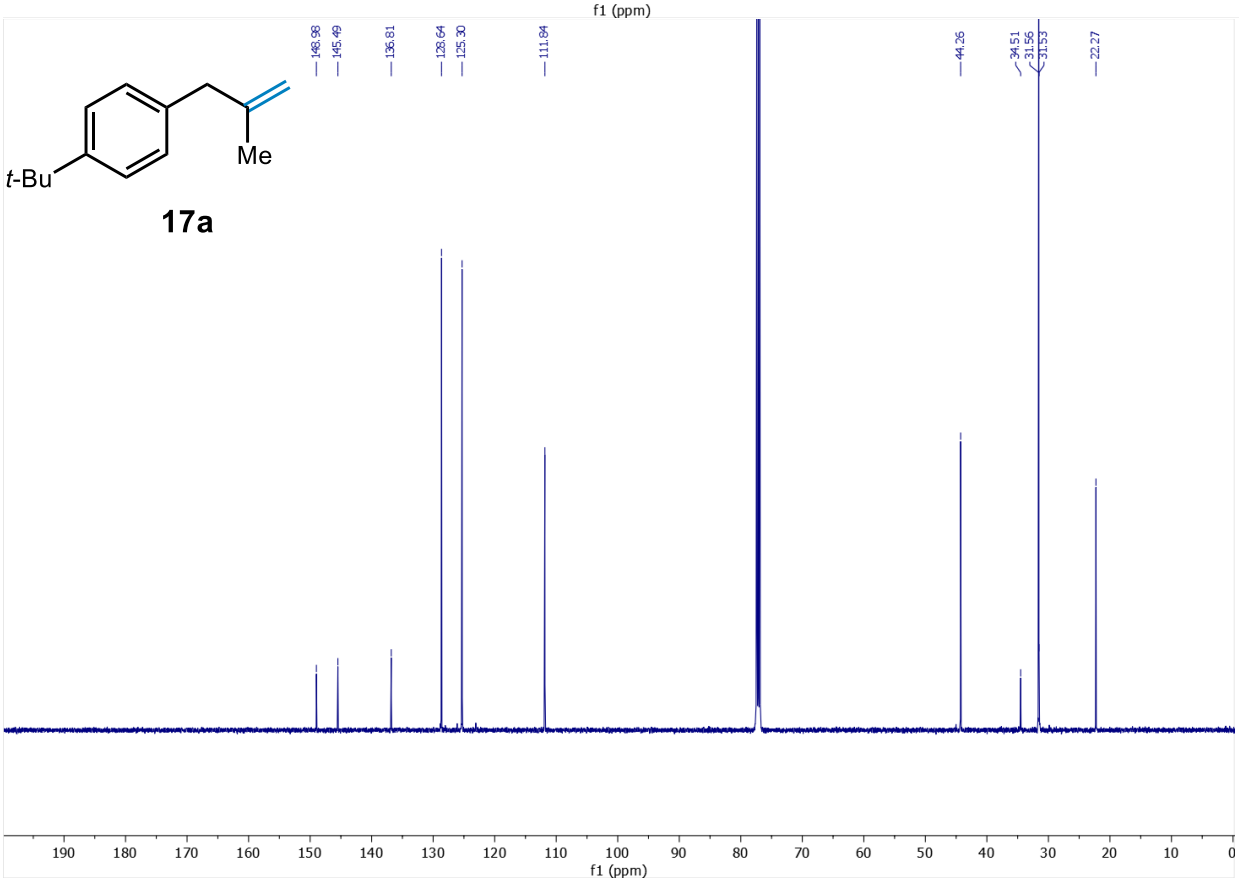

Me
15a
2.0
3.0
1.0
1.0
2.0
3.0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

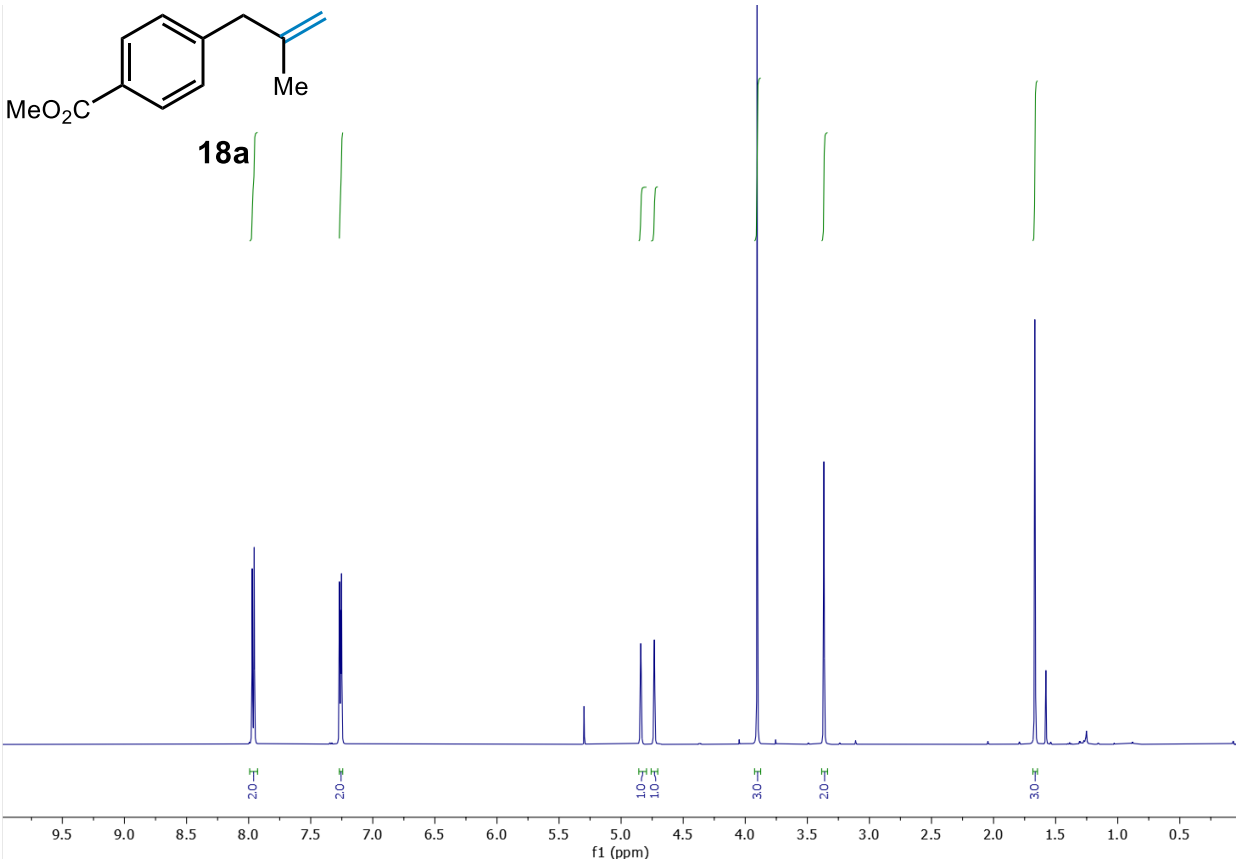

Me
15a
145.30
139.89
129.05
128.41
126.19
112.04
44.80
22.21
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

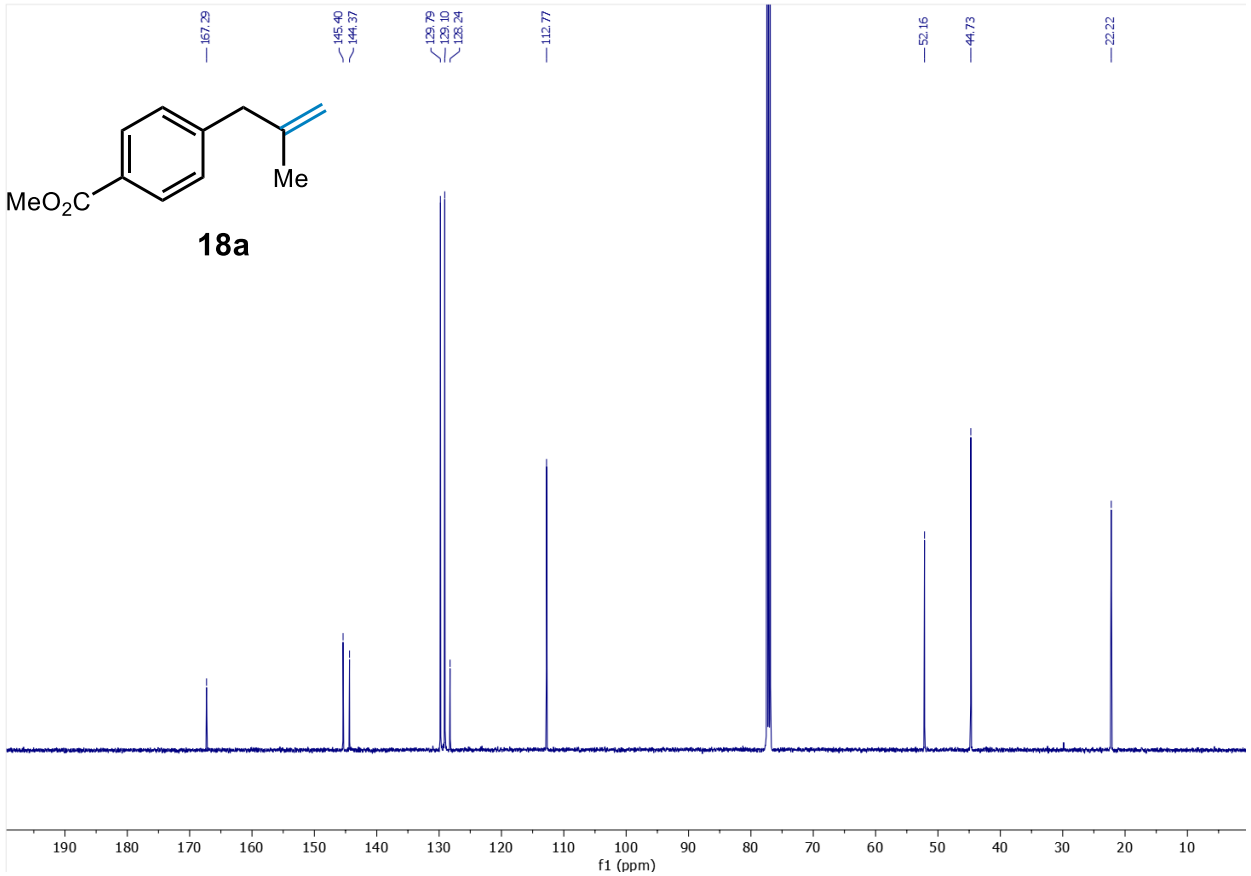

MeO
Me
16a
2.0
2.0
1.0
1.0
3.0
2.0
3.0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

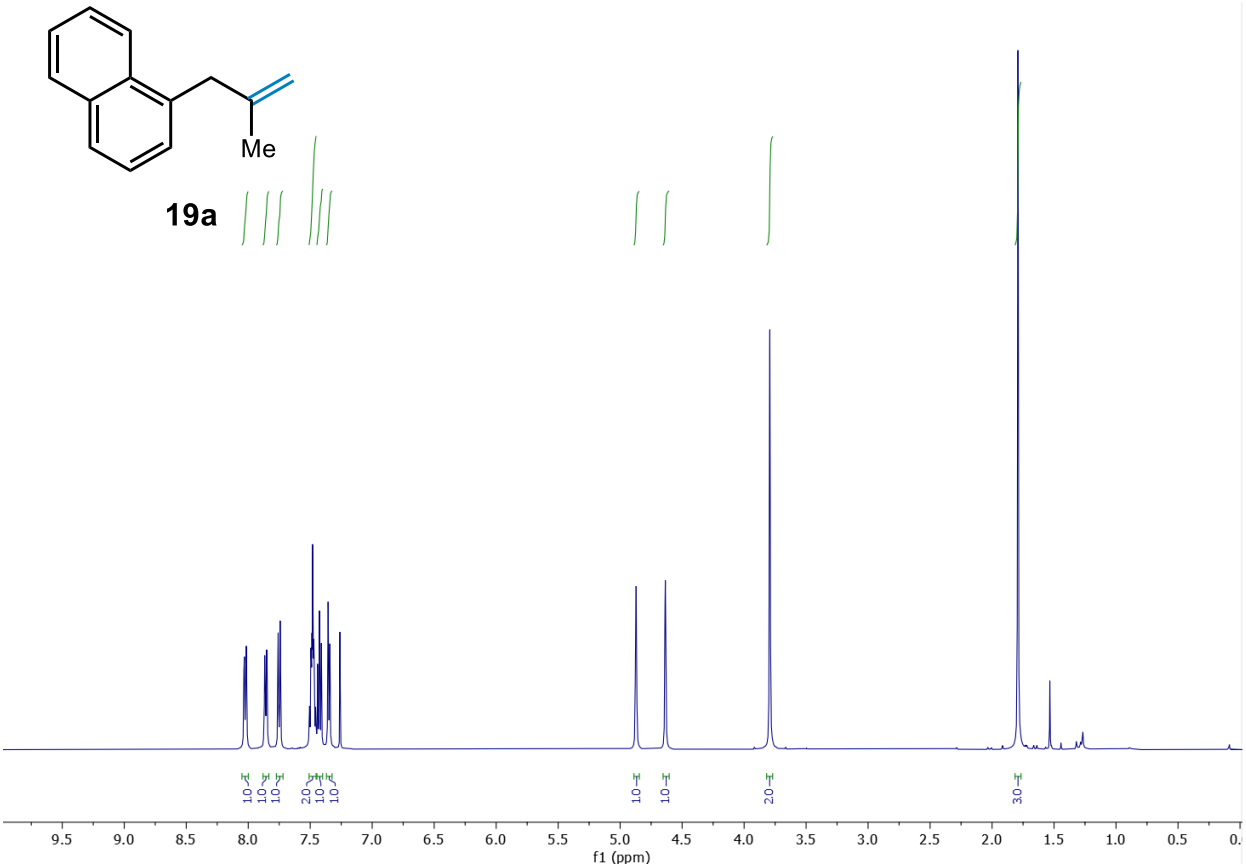

158.09
145.72
131.97
129.95
113.80
111.67
55.39
43.89
22.15
MeO
Me
16a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

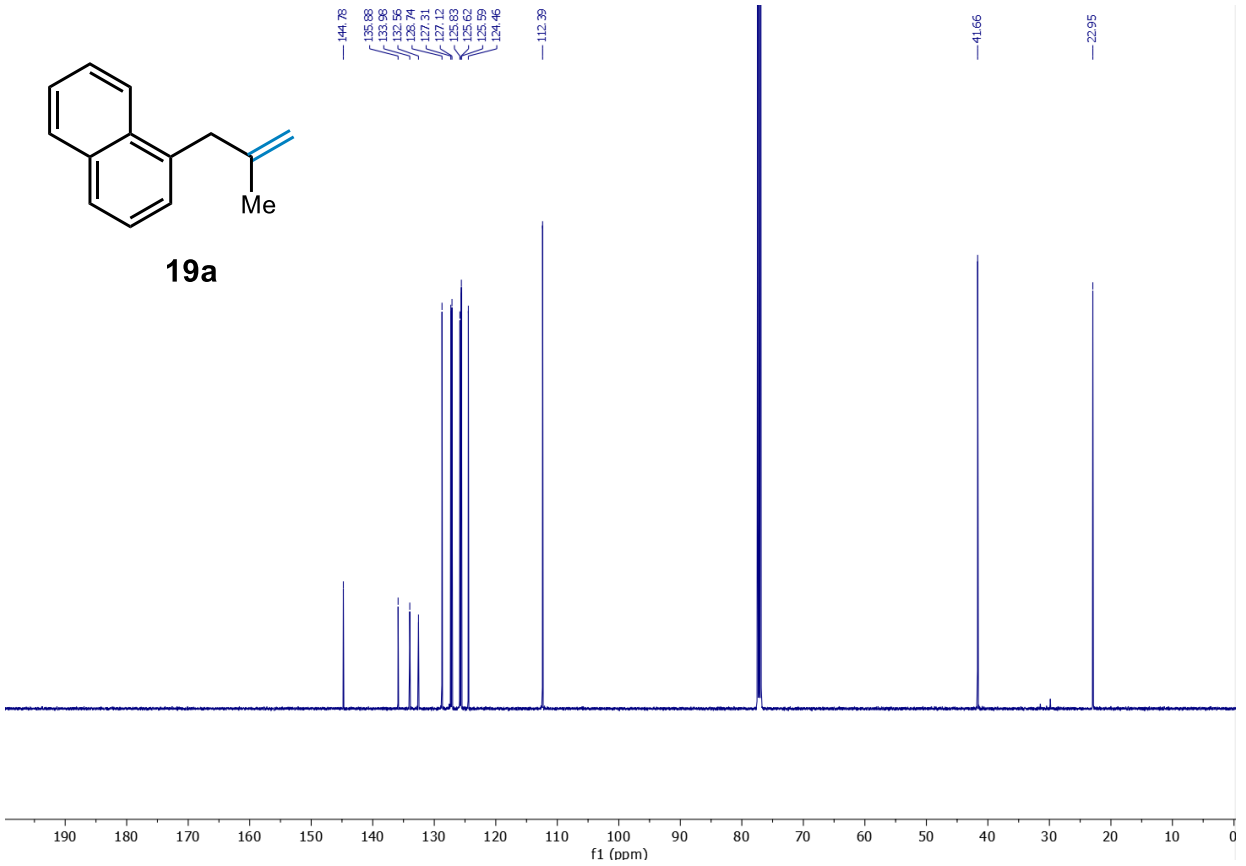

t-Bu
Me
17a
2.0
2.0
1.0
1.0
2.0
3.0
9.0
f1 (ppm)

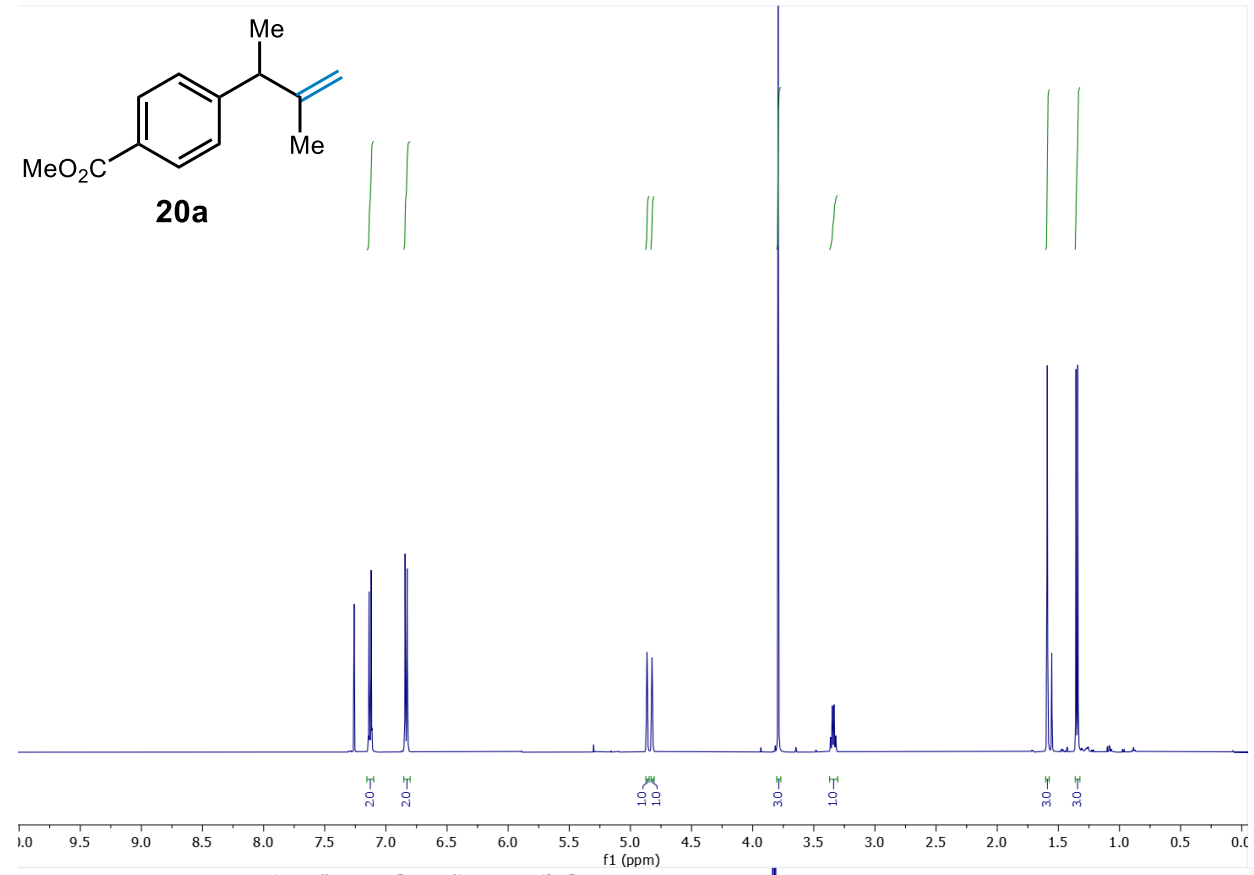

t-Bu
Me
17a
148.98
145.49
136.81
128.64
125.30
111.64
44.26
34.51
31.56
31.53
22.27
f1 (ppm)

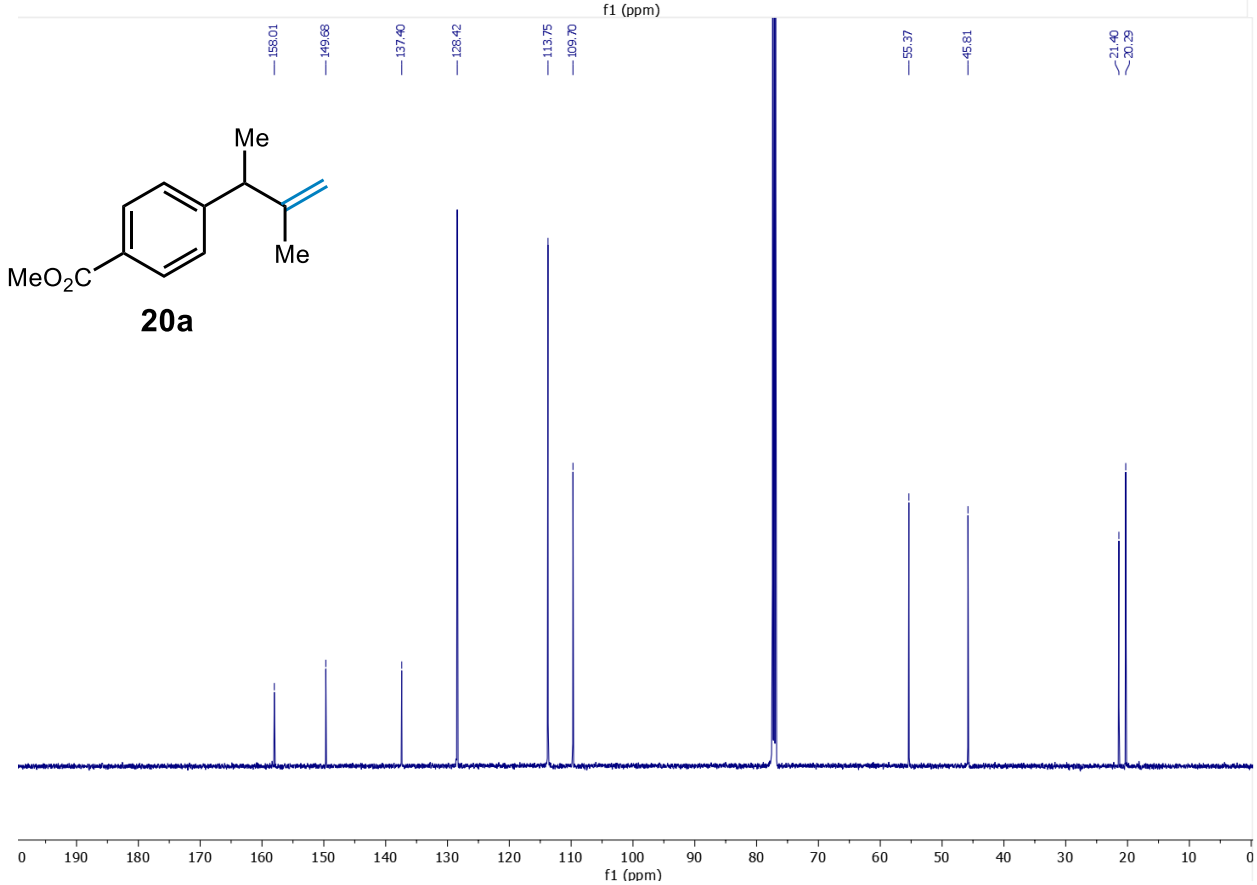

MeO2C
Me
18a
2.0
2.0
1.0
1.0
3.0
2.0
3.0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

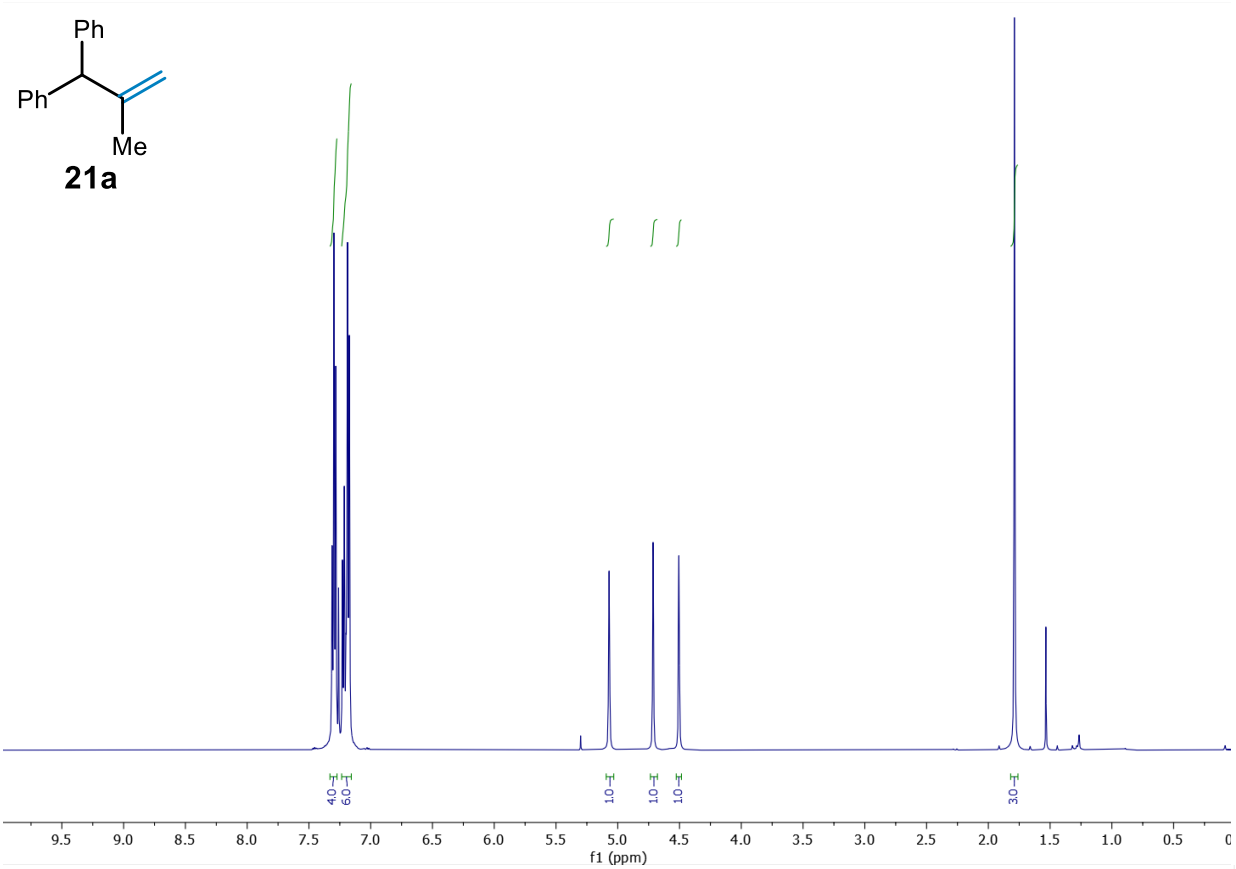

167.29
145.40
144.37
129.79
129.10
128.24
112.77
52.16
44.73
22.22
MeO2C
Me
18a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

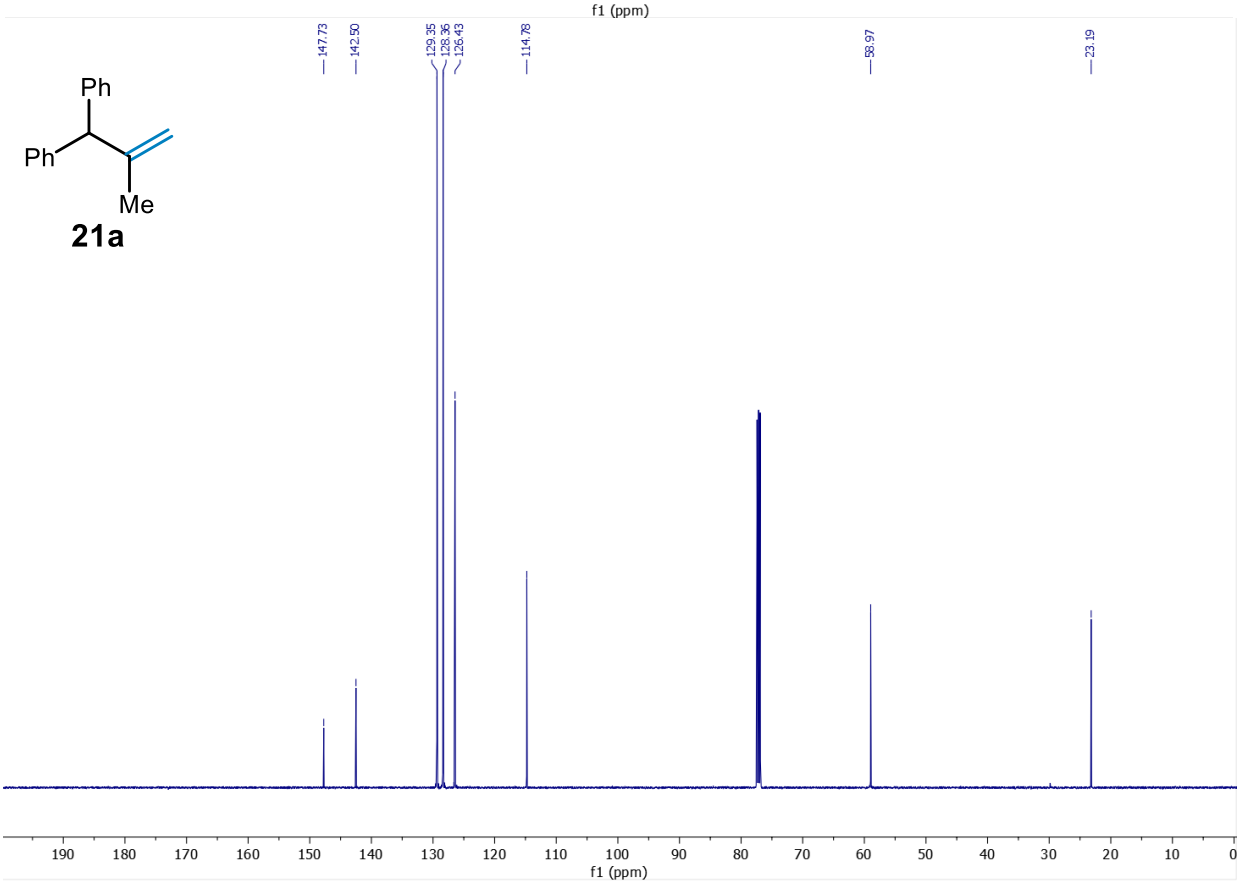

Me
19a
1.0
1.0
1.0
2.0
1.0
1.0
1.0
1.0
2.0
3.0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

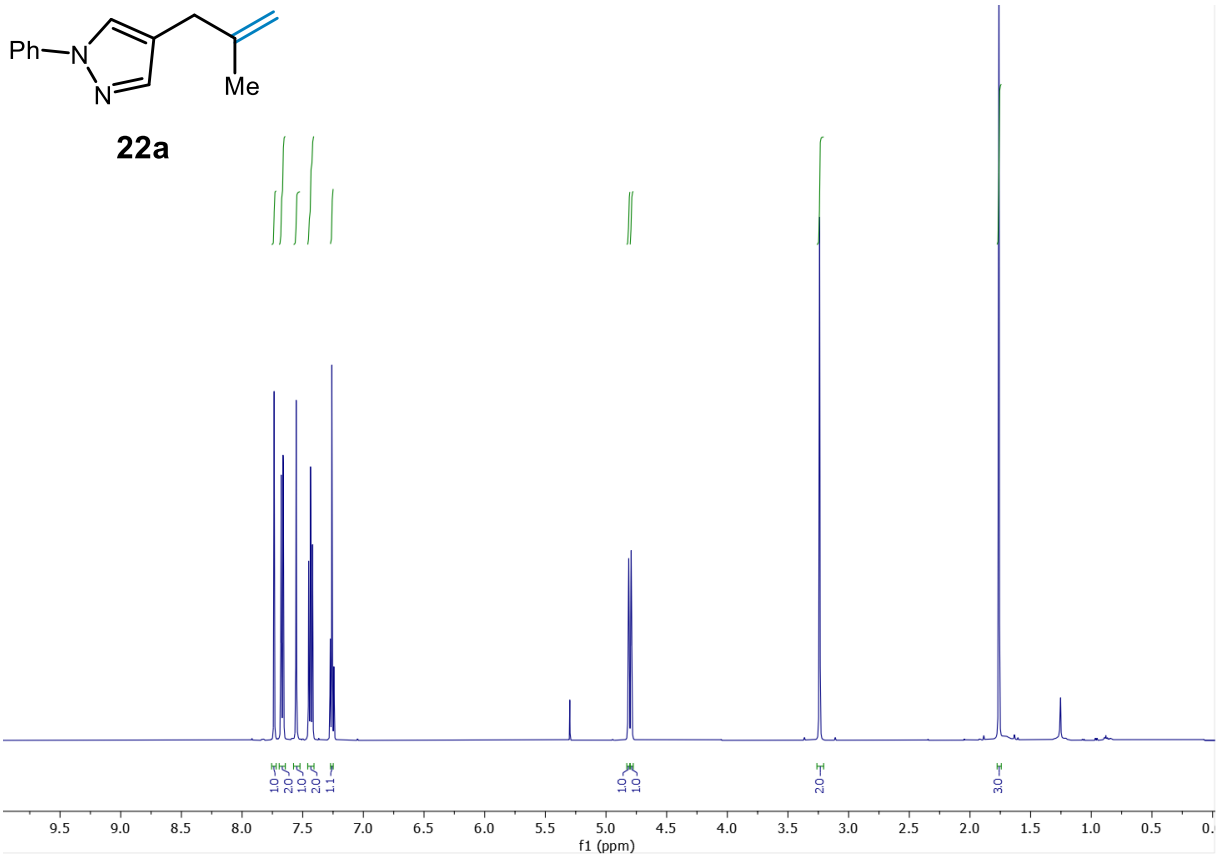

144.76
135.88
133.98
132.56
128.74
127.31
127.12
125.83
125.62
125.59
124.46
112.39
41.66
22.95
Me
19a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

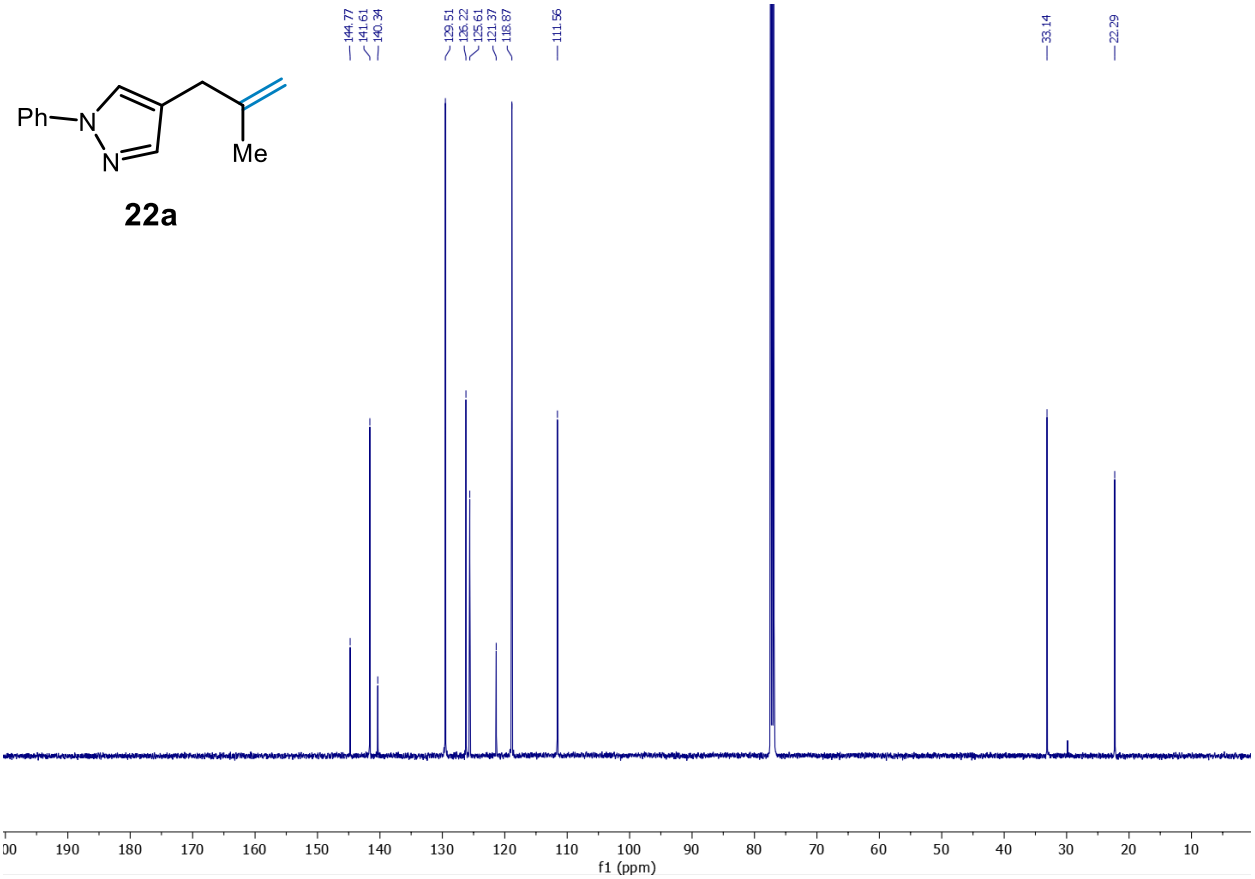

Me
Me
MeO2C
20a
2.0
2.0
1.0
1.0
3.0
1.0
3.0
3.0
f1 (ppm)

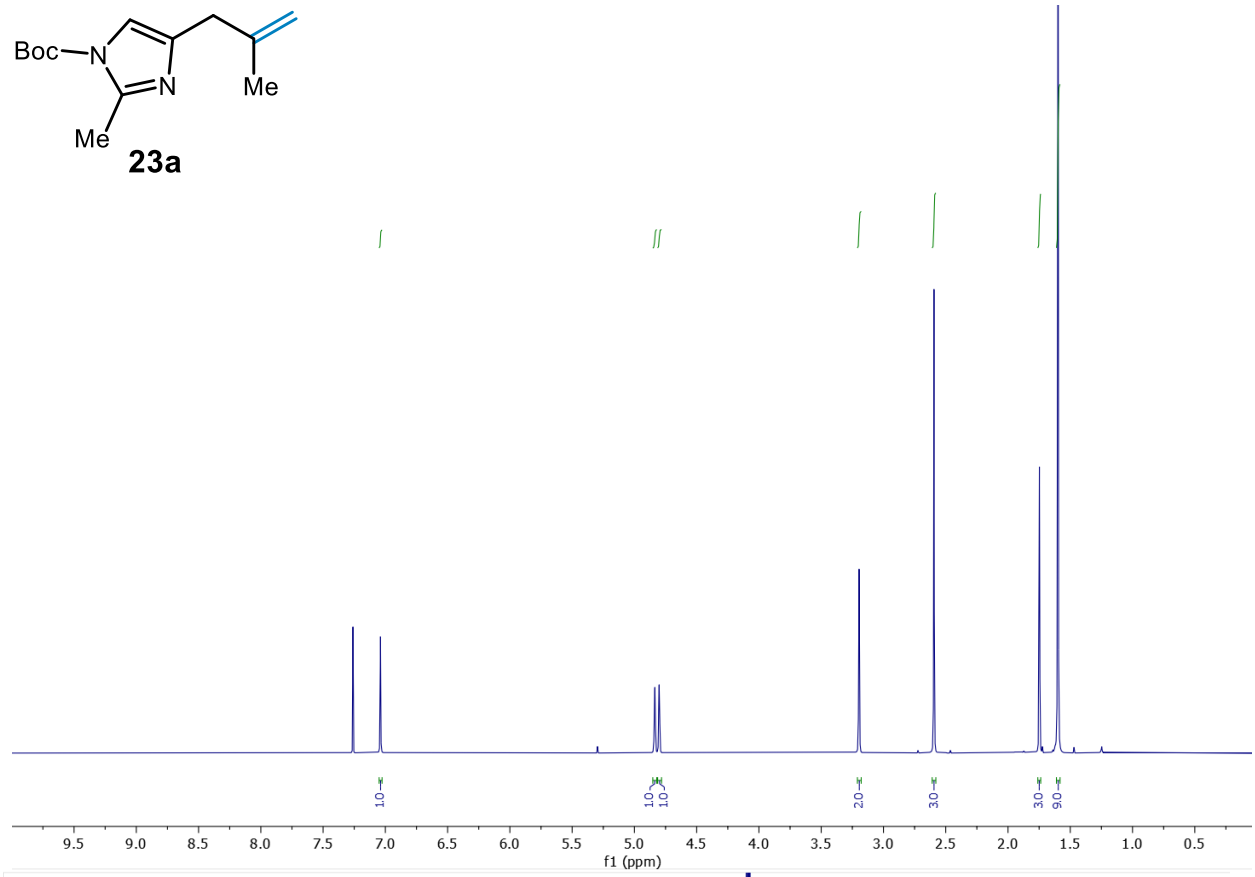

158.01
149.68
137.40
128.42
113.75
109.70
55.37
45.81
21.40
20.29
Me
Me
MeO2C
20a
f1 (ppm)

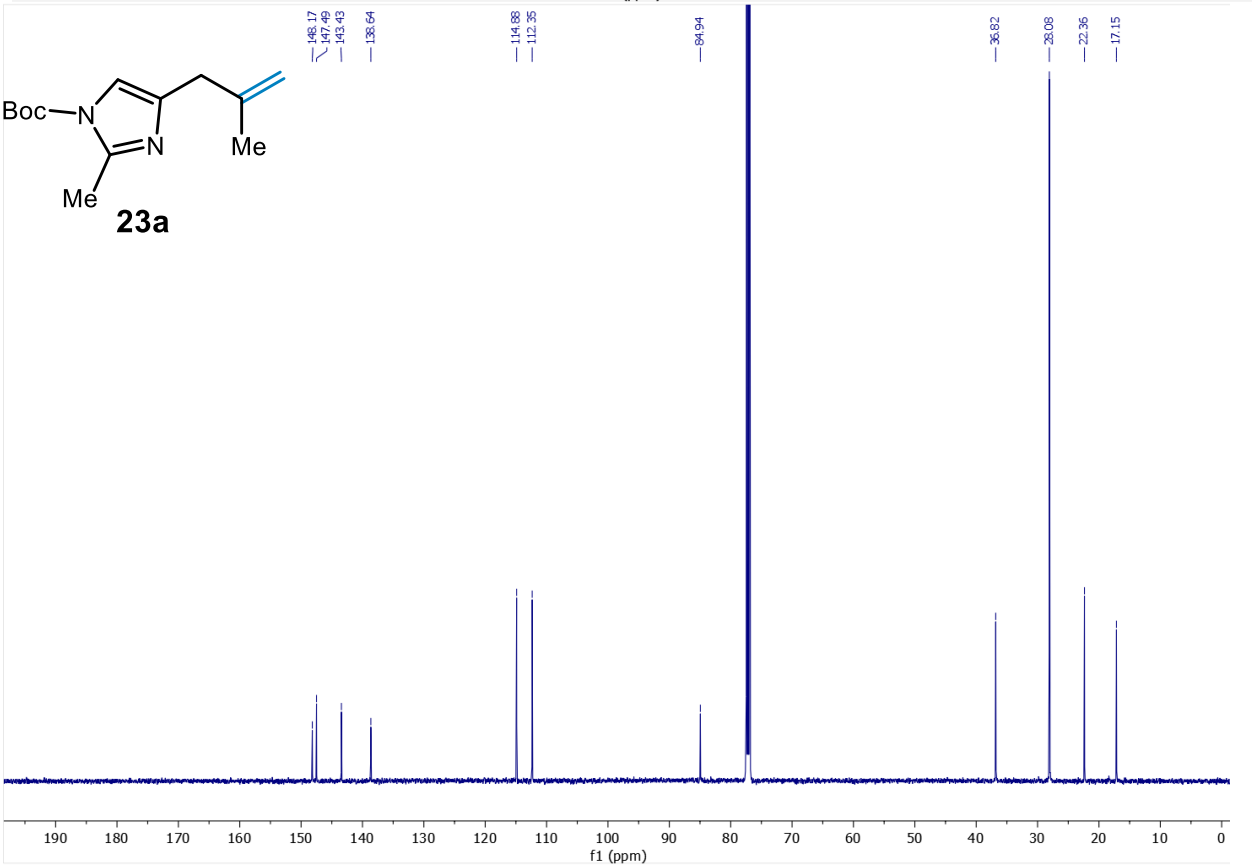

Ph
Ph
Me
21a
4.0
6.0
1.0
1.0
1.0
3.0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

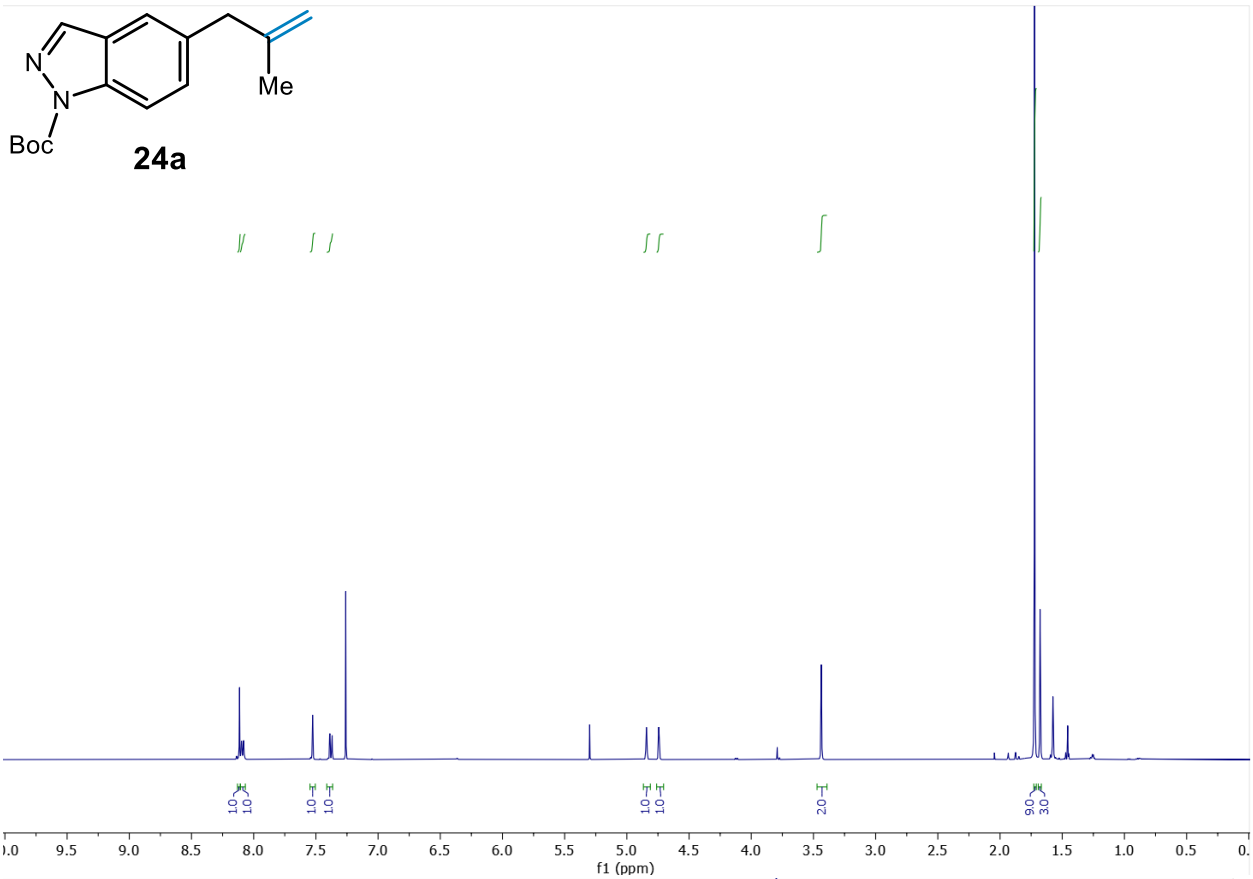

147.73
142.50
129.35
128.36
126.43
114.78
68.97
23.19
Ph
Ph
Me
21a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

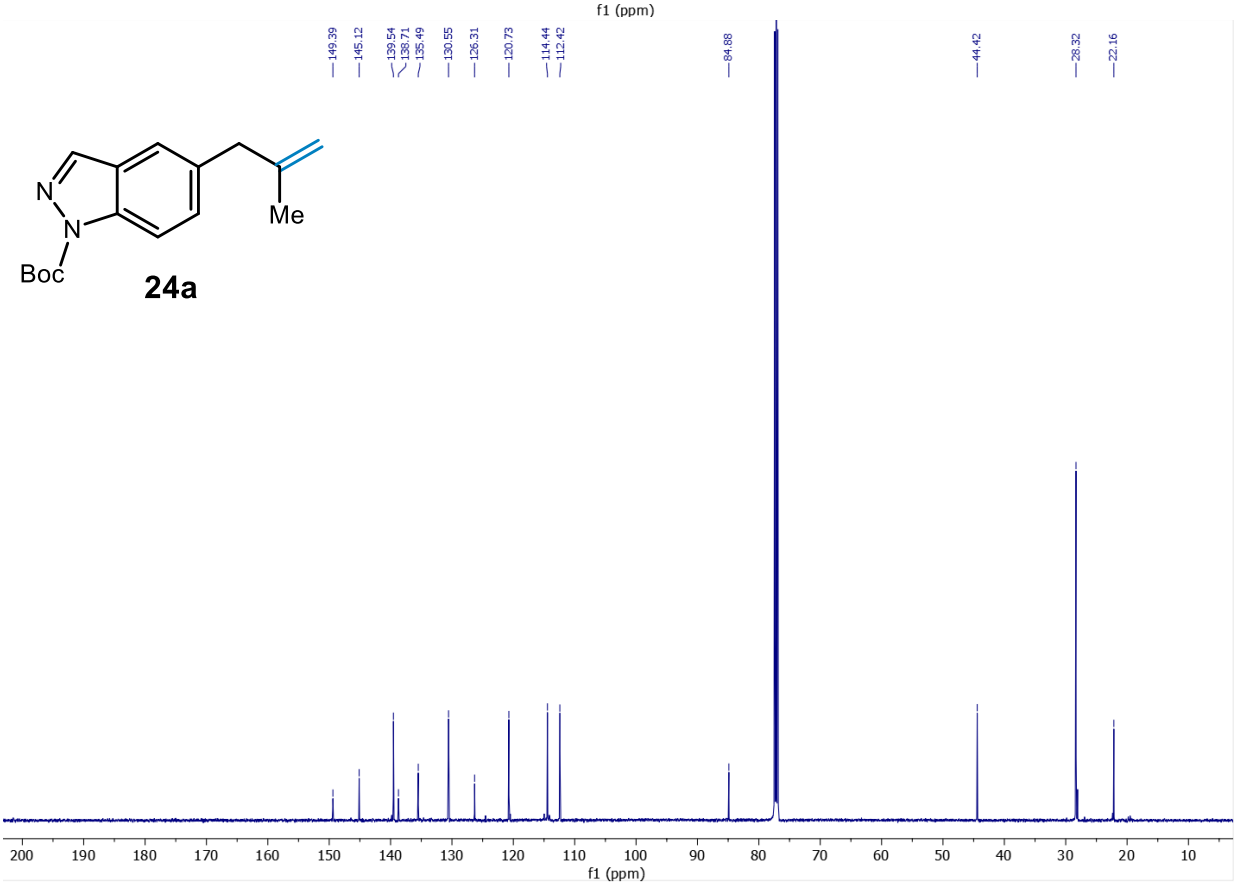

Ph
N
N
Me
22a
1.0
2.0
1.0
2.0
1.1
1.0
1.0
2.0
3.0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

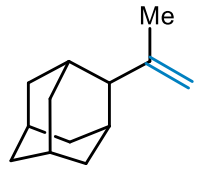

144.77
141.61
140.34
129.51
126.22
125.61
121.37
118.87
111.56
33.14
22.29
Ph
N
N
Me
22a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Boc
N
N
Me
Me
23a
1.0
1.0
1.0
2.0
3.0
3.0
9.0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


148.17
147.49
143.43
138.64
114.88
112.35
84.94
36.82
28.08
22.36
17.15
Boc
N
N
Me
Me
23a
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

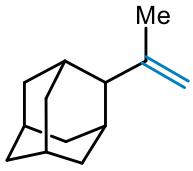

N
N
Boc
Me
24a
1.0
1.0
1.0
1.0
1.0
1.0
2.0
9.0
3.0
f1 (ppm)


149.39
145.12
139.54
138.71
135.49
130.55
126.31
120.73
114.44
112.42
84.88
44.42
28.32
22.16
N
N
Boc
Me
24a
f1 (ppm)


Me

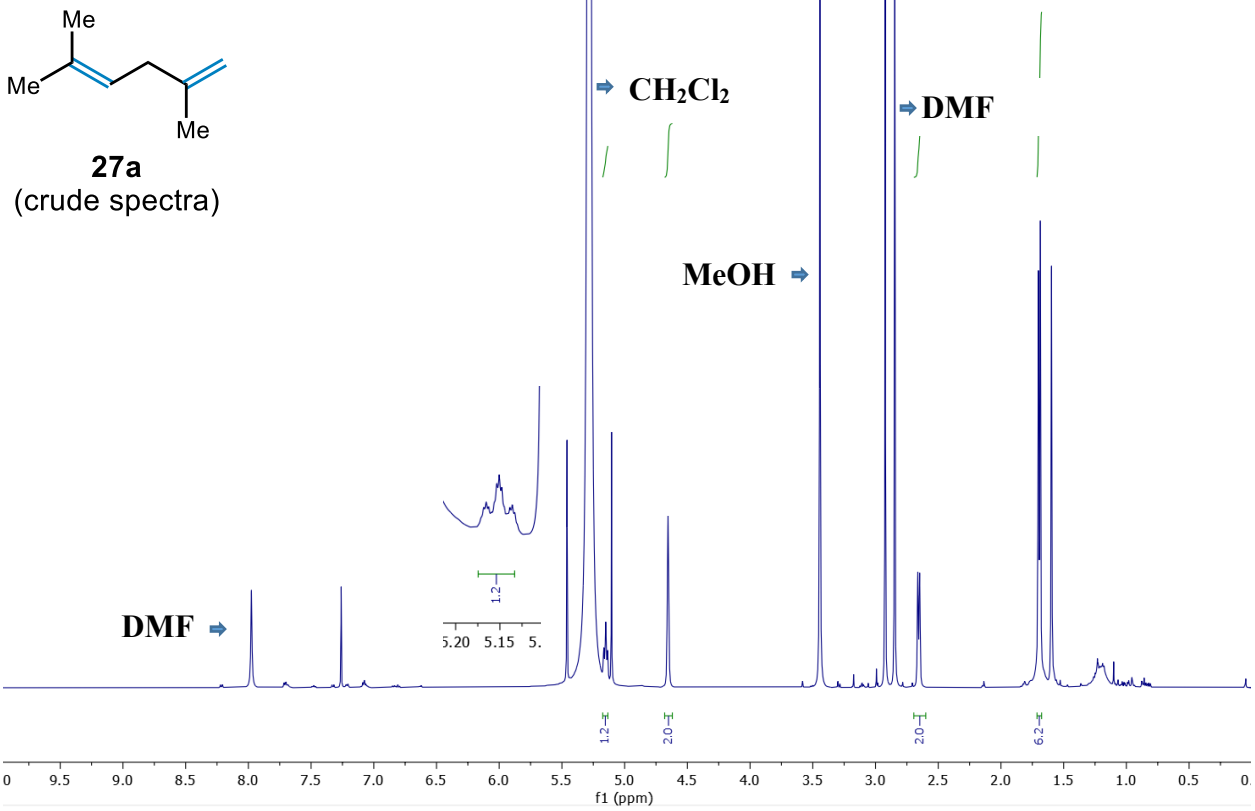
26a

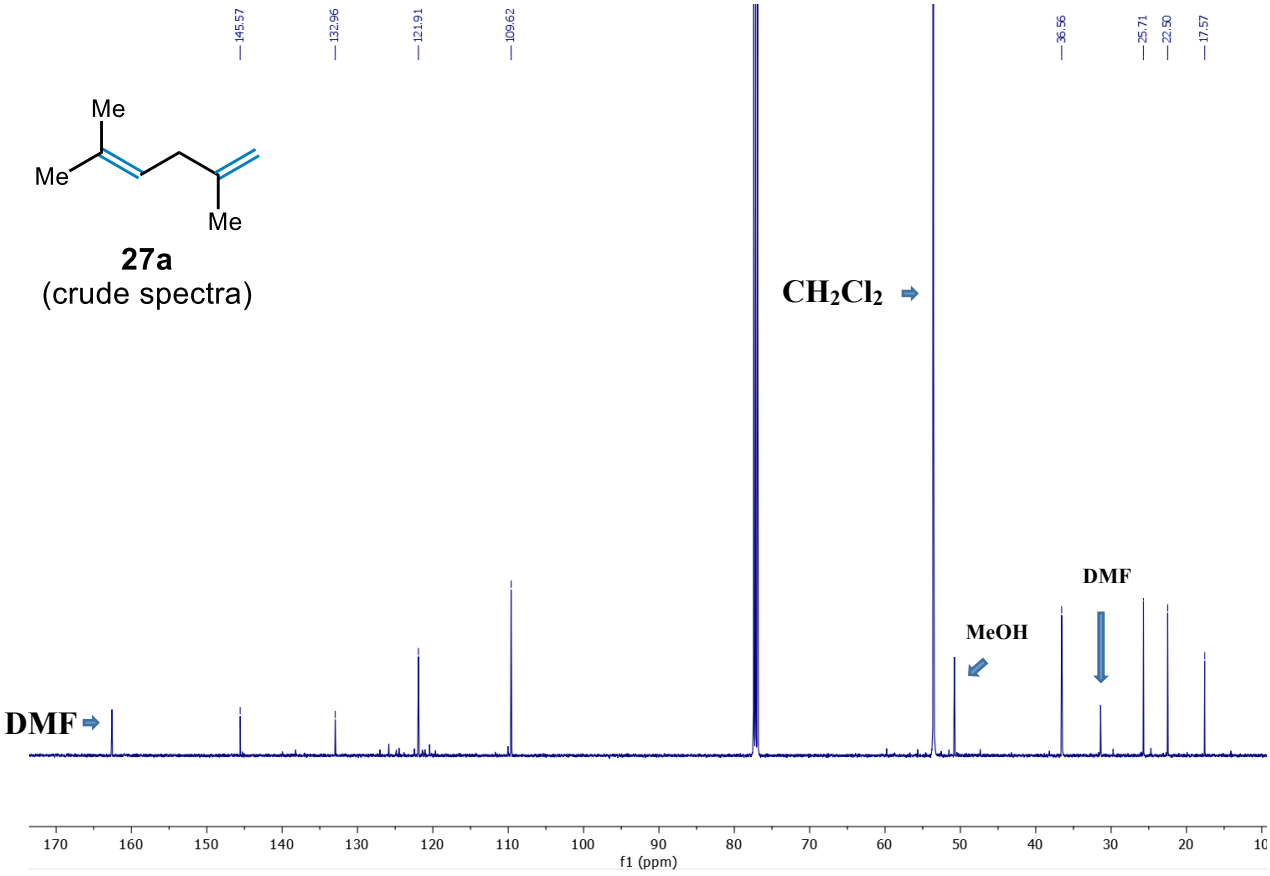
1.0
1.0
1.0
2.0
5.0
3.0
5.0
1.0
1.0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

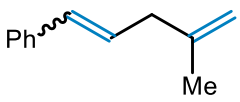

Me

26a

147.38
110.00
49.72
39.28
38.10
32.26
29.79
28.18
28.11
22.50
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

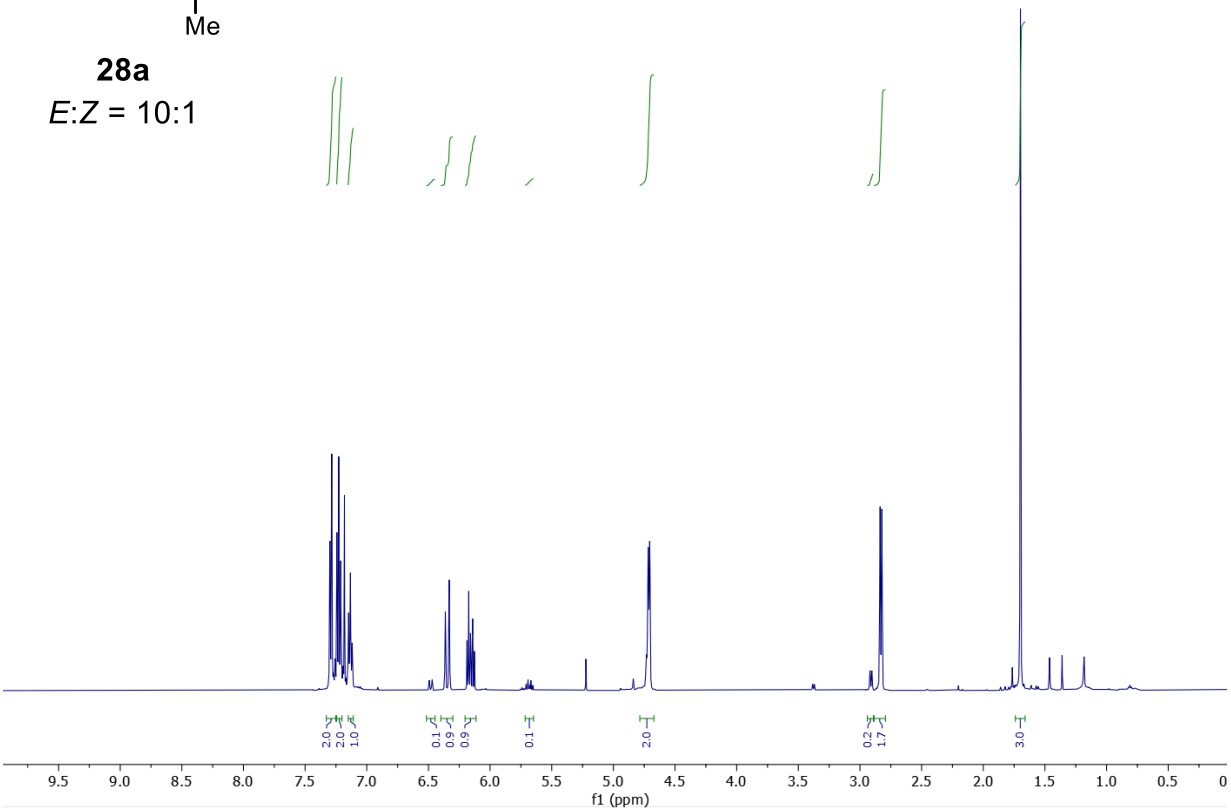

Me
Me
Me
27a
(crude spectra)
CH2Cl2
DMF
MeOH
DMF
1.2
2.0
2.0
6.2
f1 (ppm)

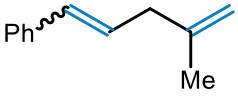

145.57
132.96
121.91
109.62
36.56
25.71
22.50
17.57
Me
Me
Me
27a
(crude spectra)
CH2Cl2
DMF
MeOH
DMF
f1 (ppm)



28a

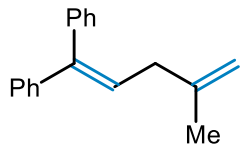
E:*Z* = 10:1





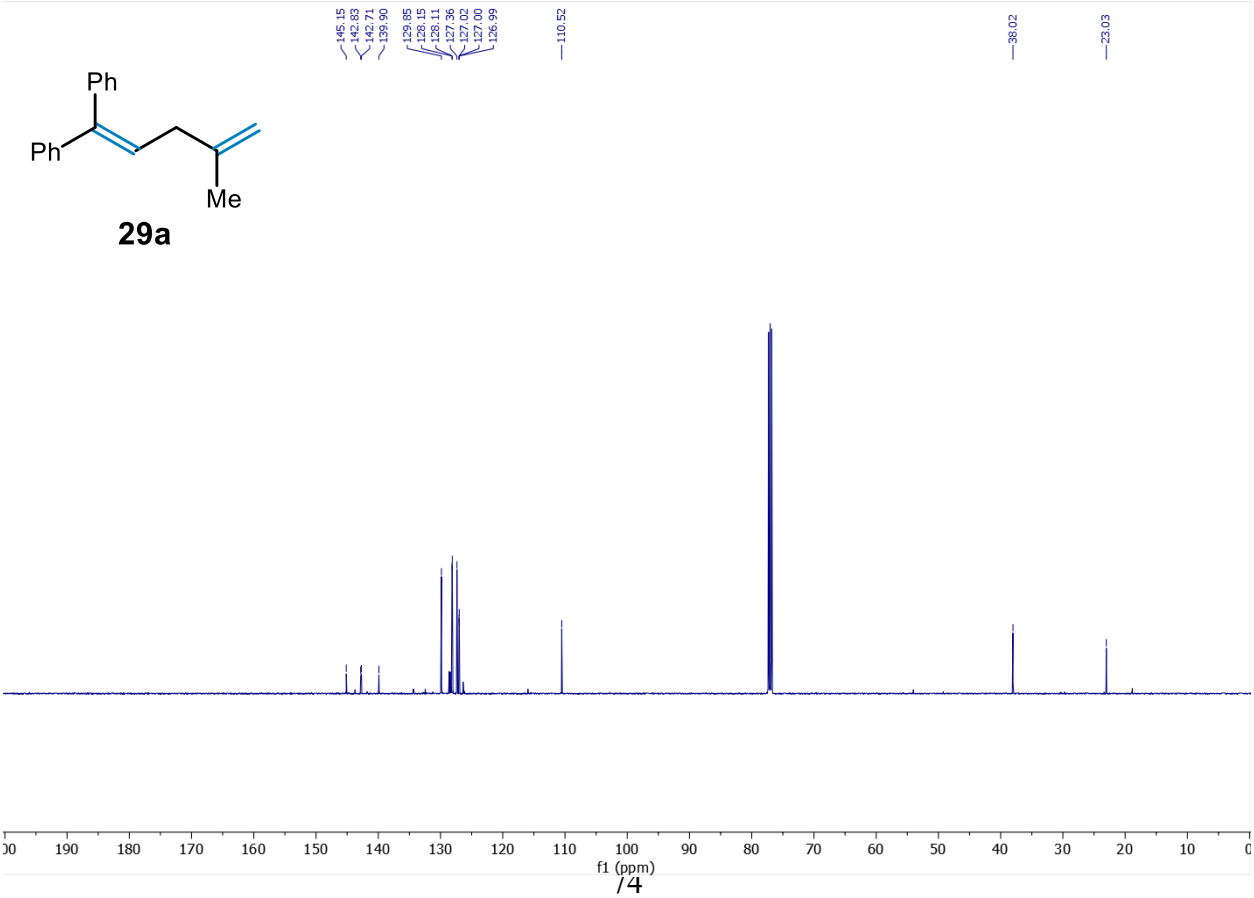
28a

E:*Z* = 10:1

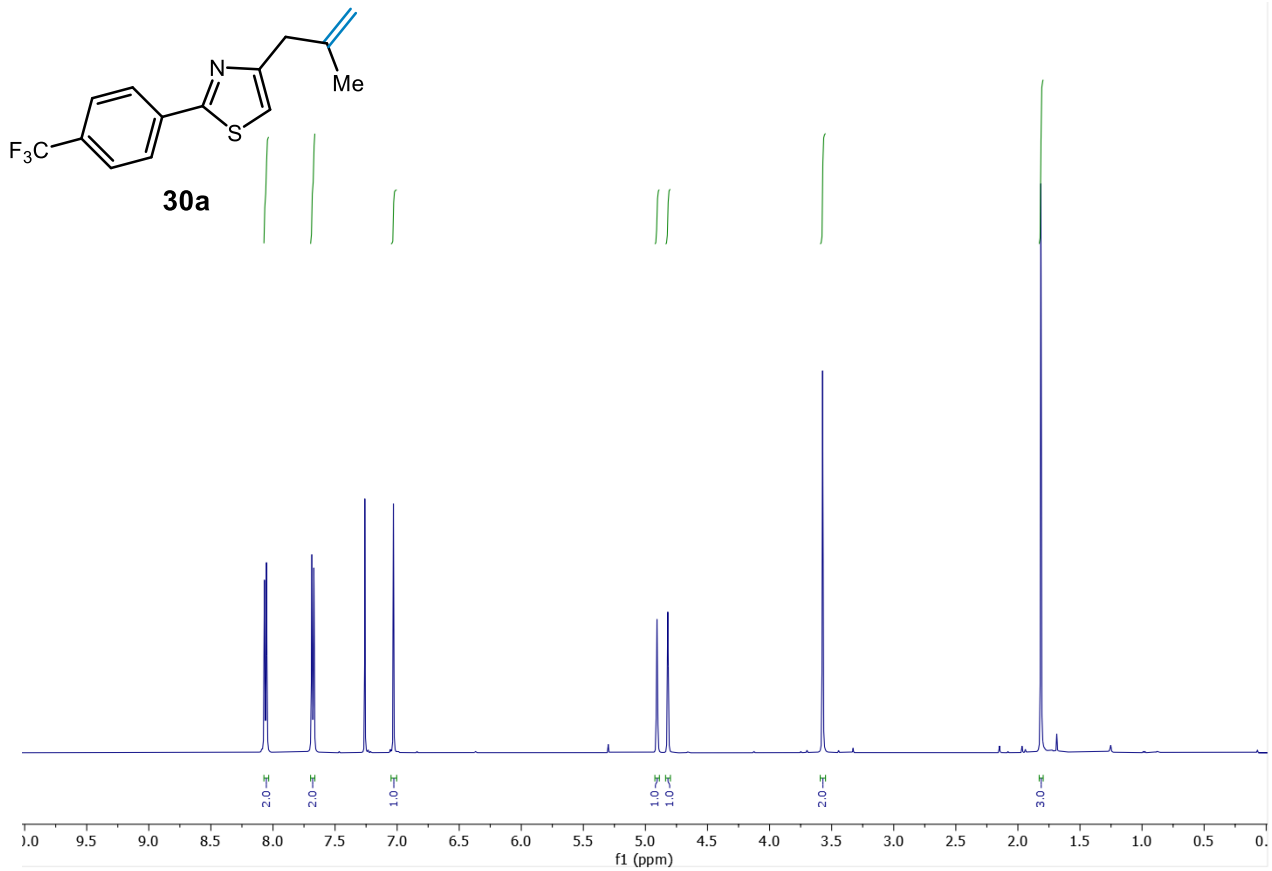

Ph
Ph
Me

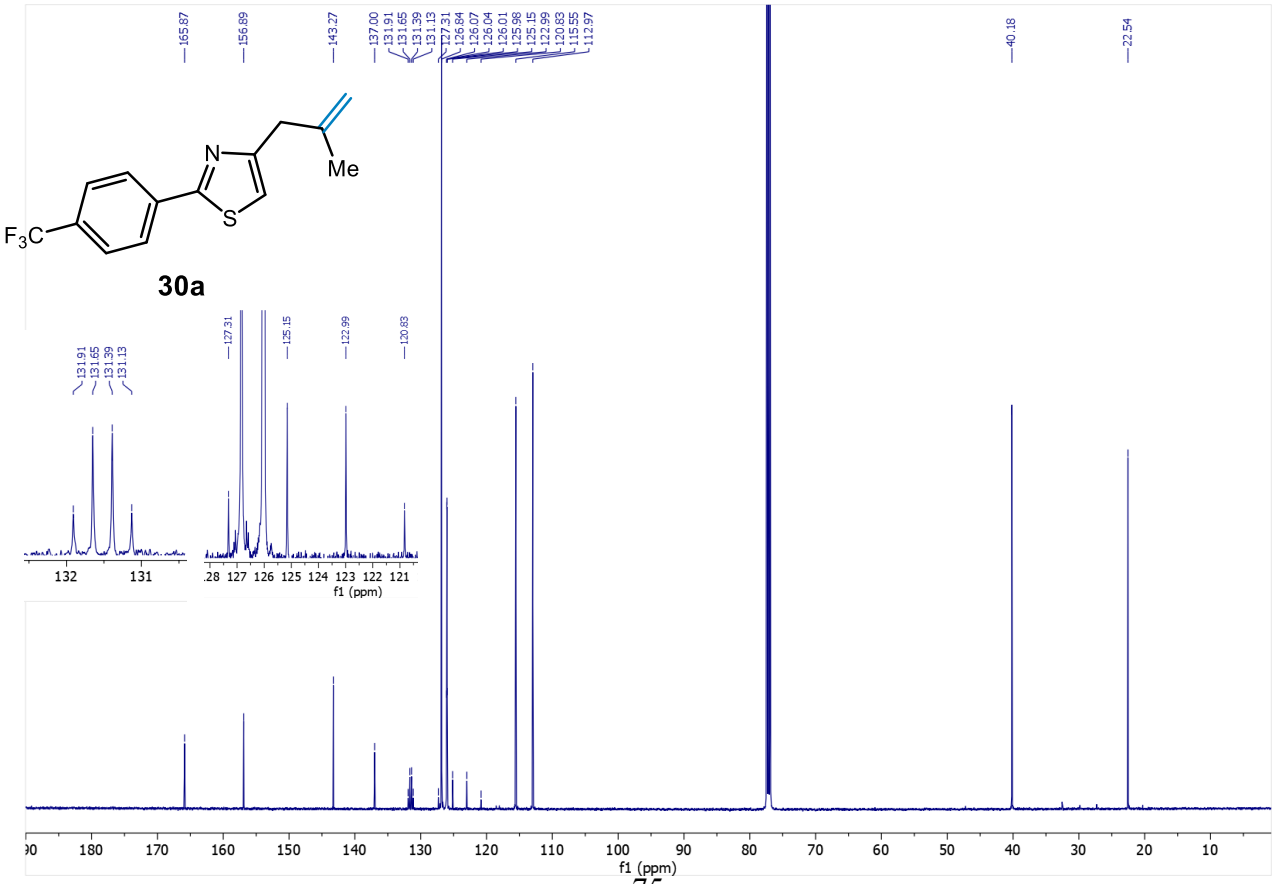
29a

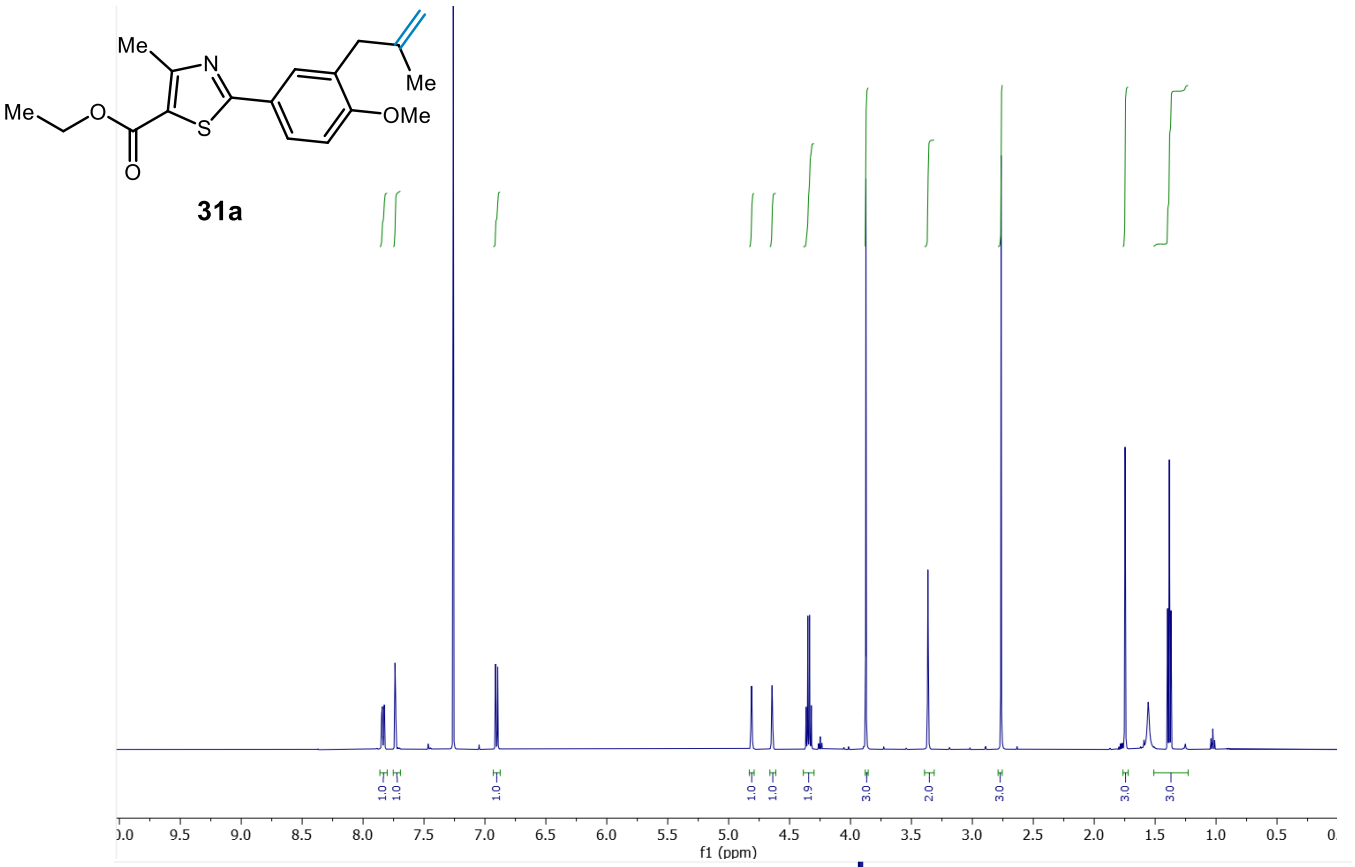
2.0
2.0
4.1
2.1
1.0
2.0
2.0
3.0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

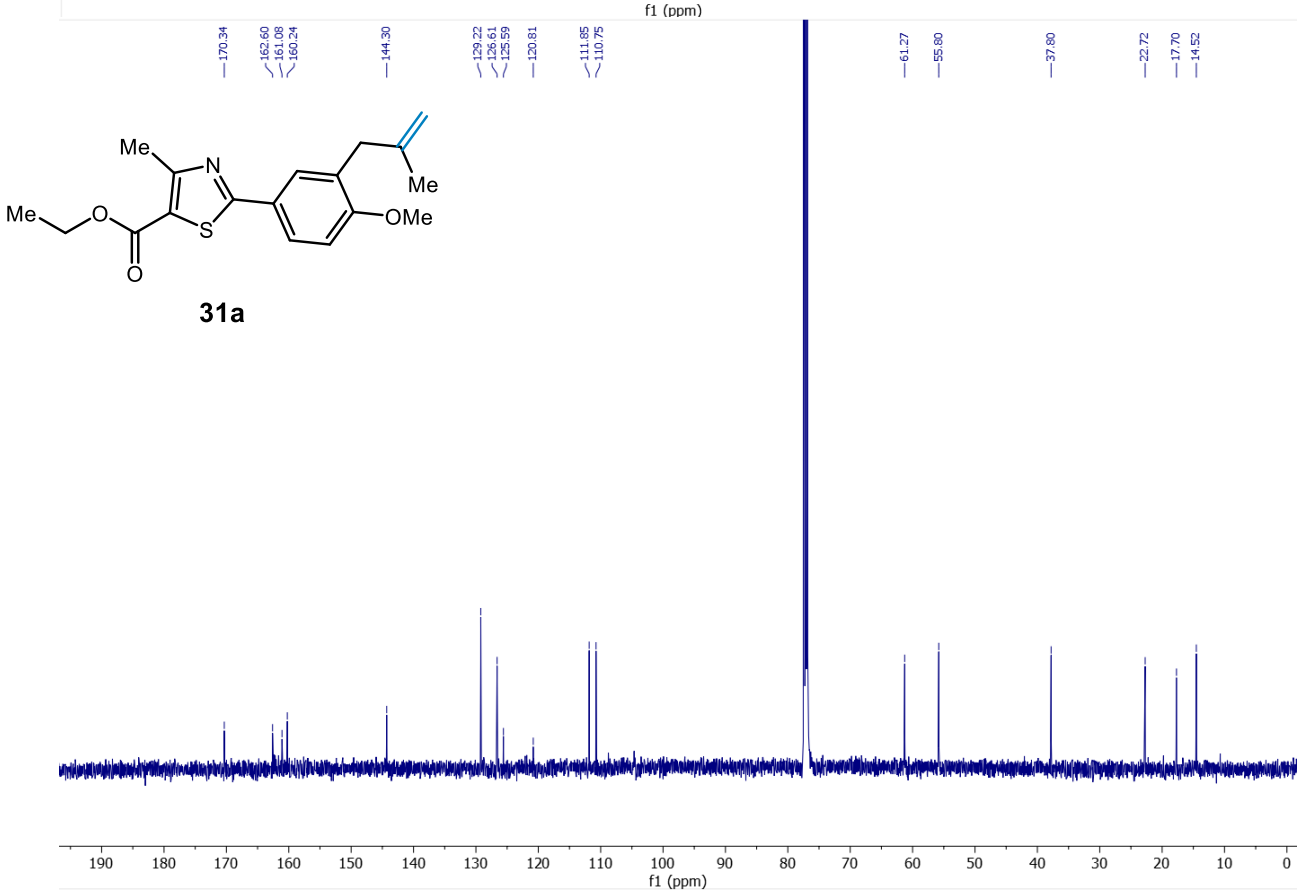

145.15
142.83
142.71
139.90
129.85
128.15
128.11
127.36
127.02
127.00
126.99
110.52
38.02
23.03
Ph
Ph
Me
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

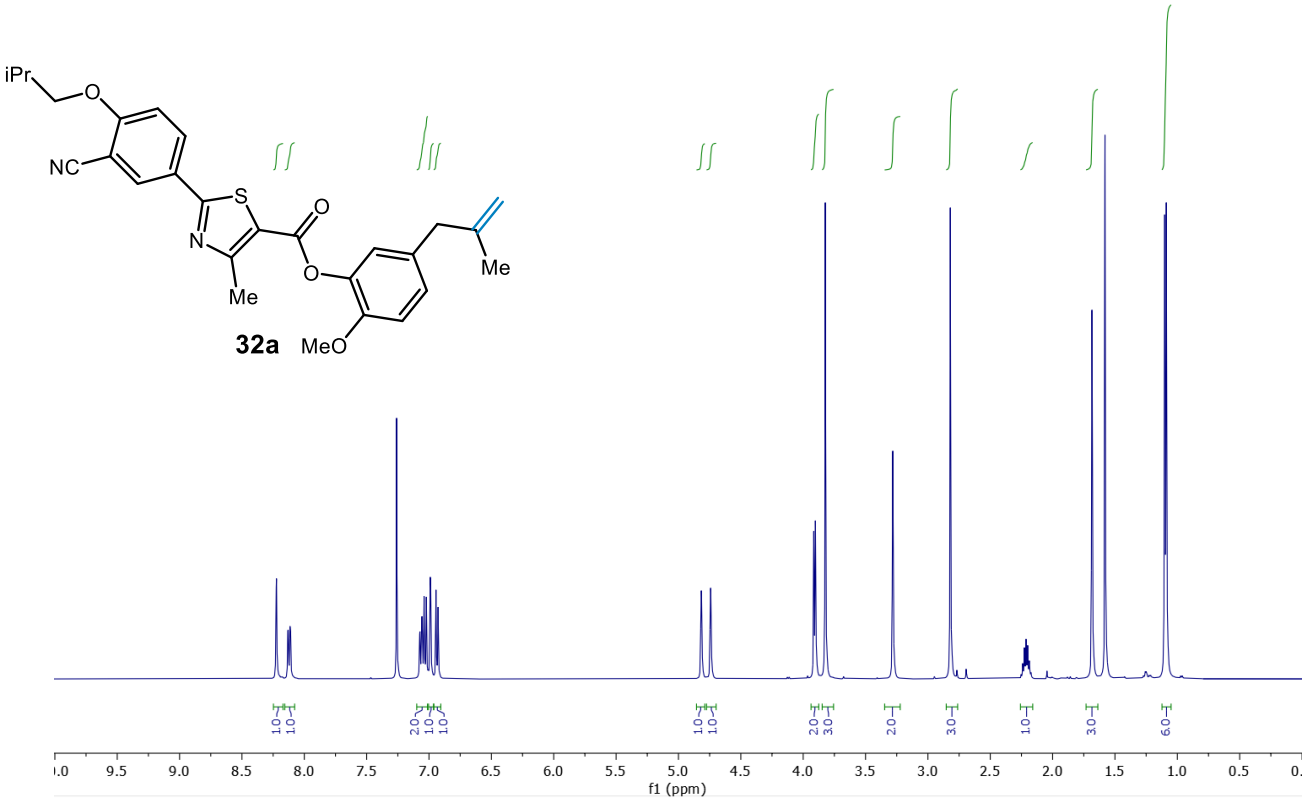
29a

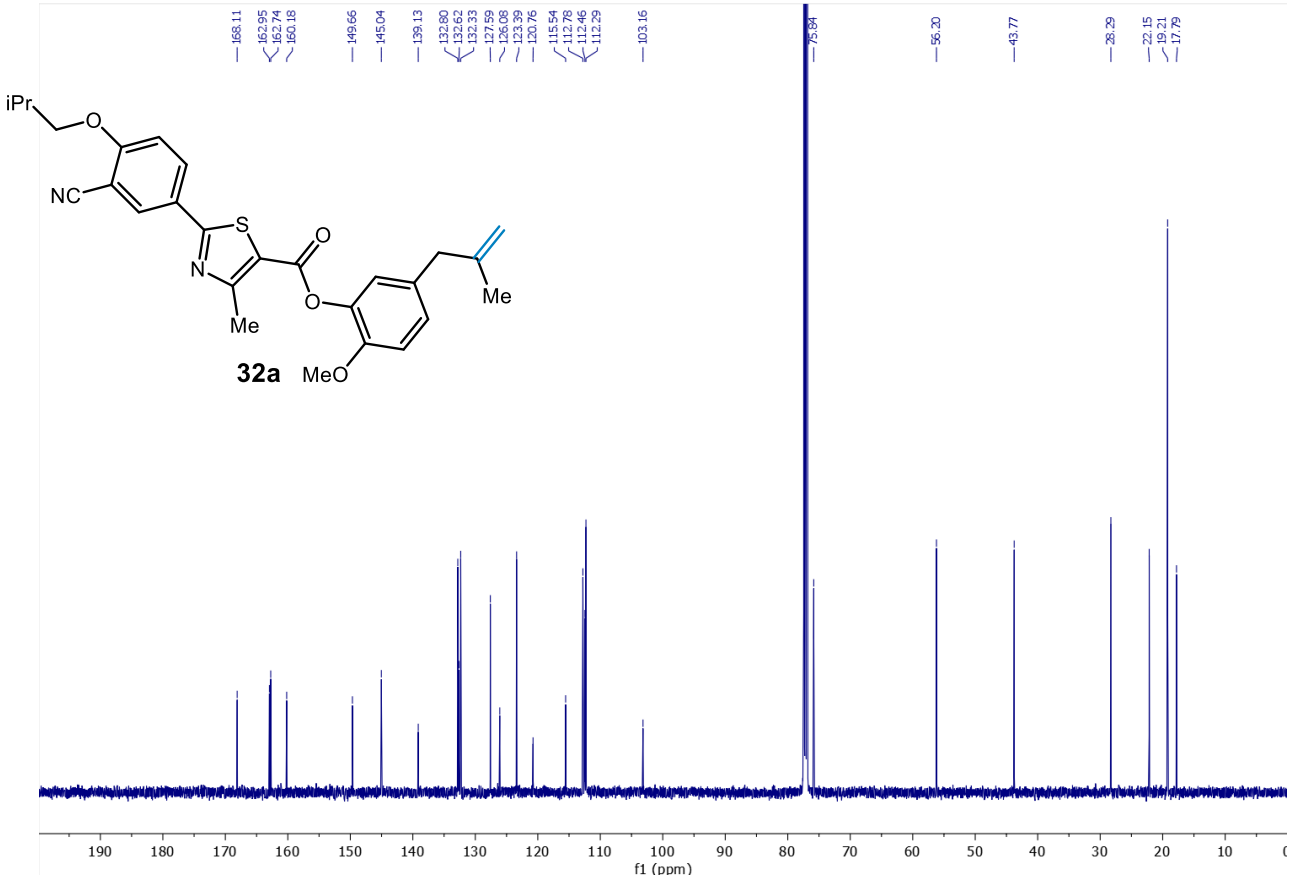

N
Me
S
F3C
30a
2.0
2.0
1.0
1.0
1.0
2.0
3.0
f1 (ppm)


165.87
156.89
143.27
137.00
131.91
131.65
131.39
131.13
127.31
126.84
126.07
126.04
126.01
125.98
125.15
122.99
120.83
115.55
112.97
40.18
22.54
N
Me
S
F3C
30a
f1 (ppm)


Me
N
Me
Me
O
S
OMe
O
31a
1.0
1.0
1.0
1.0
1.0
1.9
3.0
2.0
3.0
3.0
3.0
f1 (ppm)


170.34
162.60
161.08
160.24
144.30
129.22
126.61
125.59
120.81
111.85
110.75
61.27
55.80
37.80
22.72
17.70
14.52
Me
N
Me
Me
O
S
OMe
O
31a
f1 (ppm)


iPr
O
NC
S
N
O
O
Me
Me
32a
MeO
f1 (ppm)

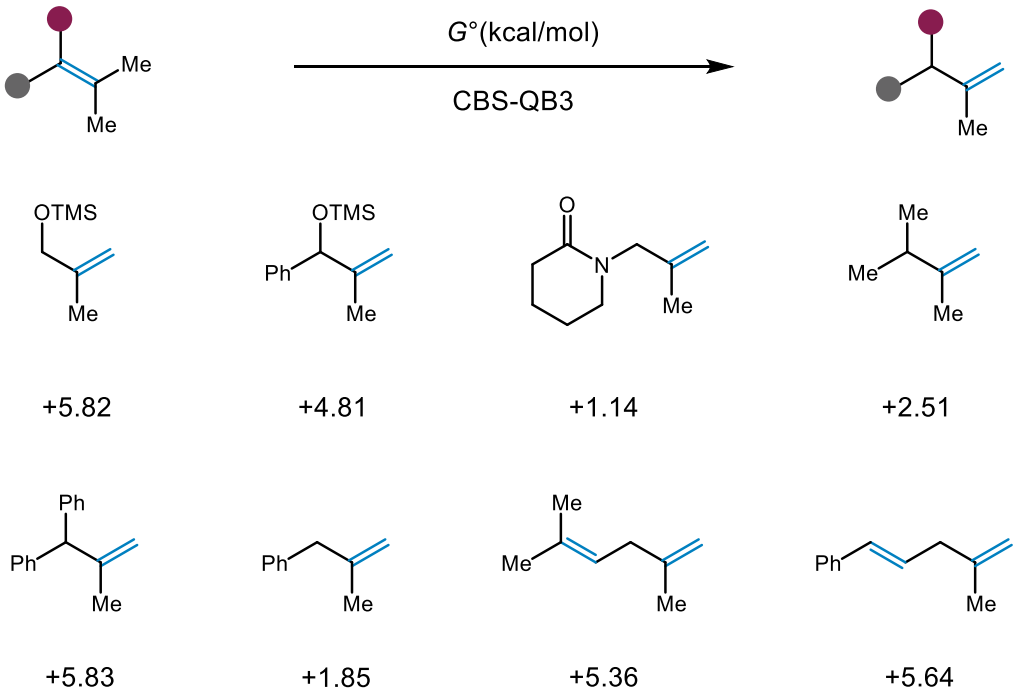

168.11
162.95
162.74
160.18
149.66
145.04
139.13
132.80
132.62
132.33
127.59
126.08
123.39
120.76
115.54
112.78
112.46
112.29
103.16
75.84
56.20
43.77
28.29
22.15
19.21
17.79
iPr
O
NC
S
N
O
O
Me
Me
32a
MeO
f1 (ppm)

CBS-QB3 Computations

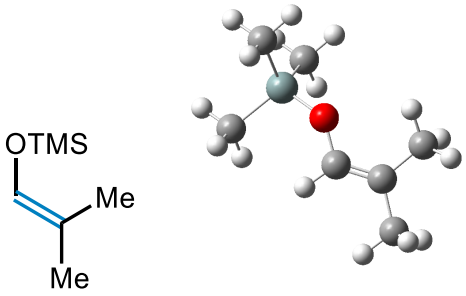
All calculations were performed in the Gaussian 16 series of computer programs.[42] All stationary points were initially optimized using the Hartree-Fock method with 3-21G basis set.[43] The preoptimized geometries were then subjected to optimization at the CBS-QB3 level of theory.[44] Harmonic vibrations were also computed at the CBS-QB3 level in order to derive thermal corrections at 298 K to the total electronic energy. Geometries and energies were calculated in the gas phase.

Calculation of isomerization energy difference: The free energy differences between the conjugated and the deconjugated olefin were determined by comparing the free energies of the two compounds *in silico*. **Table S13** (**Figure 3b** in main text) was derived as such.

Table S13. Computational Assessment of Thermochemistry of Selected Examples

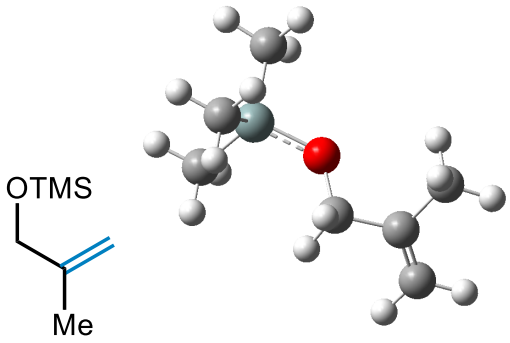


Optimized geometries:
Optimized geometries in Cartesian coordinates (Å) and energies (hartrees) for stationary points.



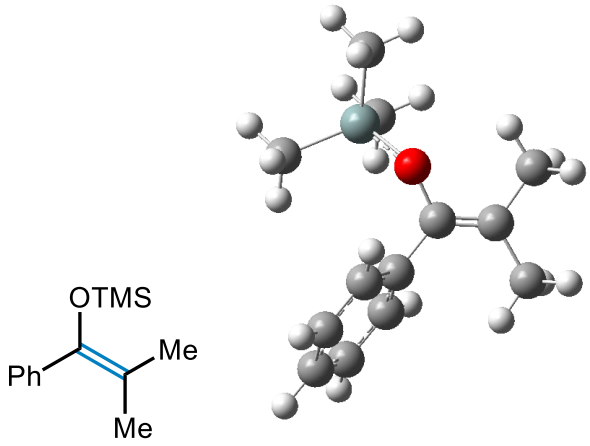
CBS-QB3 (0 K)= -640.041500
CBS-QB3 Energy= -640.027169
CBS-QB3 Enthalpy= -640.026225
CBS-QB3 Free Energy= -640.083381

Charge = 0 Multiplicity = 1
C 2.40124800 0.00358100 -0.00119000
C 1.13792800 0.43574400 -0.00418600
H 0.91324500 1.50114600 -0.00497300
C 2.75293200 -1.45815500 -0.00049700
H 1.85969300 -2.08173400 -0.00279900
H 3.35787700 -1.71491400 -0.87865600
H 3.35359100 -1.71516900 0.88052800
C 3.54135000 0.98630900 0.00142000
H 4.18037500 0.84913400 0.88230900
H 4.18425400 0.84938600 -0.87668300
H 3.18985700 2.02115000 0.00078700
O 0.05775300 -0.40601700 -0.00745800
Si -1.56512000 0.00649400 0.00028600
C -1.95796300 0.99578000 1.54590100
H -1.39626900 1.93425100 1.58043500
H -3.02239800 1.24874100 1.58658100
H -1.71353300 0.42798700 2.44829000
C -1.96749700 1.01462500 -1.53064600
H -1.40478000 1.95271200 -1.55825800
H -1.73077500 0.45725100 -2.44152800
H -3.03181000 1.26972000 -1.56032500
C -2.46369900 -1.63097700 -0.00673700
H -2.20256000 -2.22392000 0.87412700
H -3.54831800 -1.48452100 -0.00473100
H -2.20458900 -2.21543500 -0.89383400



CBS-QB3 (0 K)= -640.032845
CBS-QB3 Energy= -640.018818
CBS-QB3 Enthalpy= -640.017874
CBS-QB3 Free Energy= -640.074105

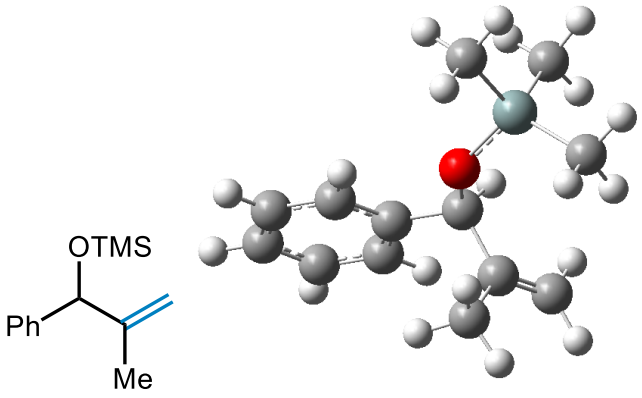
Charge = 0 Multiplicity = 1
C -3.41043300 1.01604100 -0.32008200
C -2.51993600 0.09298000 0.04055200
H -3.17085600 2.07424200 -0.30532600
H -4.41130100 0.74662500 -0.64032200
C -1.15105000 0.49214600 0.53615900
H -1.02374200 1.57659600 0.43673500
H -1.06881800 0.24112800 1.60506500
C -2.80415200 -1.38378200 0.01040700
H -2.09148300 -1.89084600 -0.64497100
H -2.68647700 -1.82515600 1.00716400
H -3.81673900 -1.58922500 -0.34107100
O -0.14498800 -0.20582000 -0.19307400
Si 1.50199300 -0.01229400 -0.05171700
C 2.23314500 -1.21885000 -1.27866600
H 3.32677000 -1.17448100 -1.27214200
H 1.93699400 -2.24477900 -1.04270600
H 1.89307700 -0.99695900 -2.29398100
C 1.98956200 1.75270800 -0.47571600
H 1.55503000 2.47732400 0.21992100
H 3.07696700 1.87365700 -0.43291400
H 1.66409300 2.02018400 -1.48532200
C 2.06137700 -0.41354000 1.69775100
H 3.14991900 -0.33135300 1.78293900
H 1.62539400 0.26879200 2.43410400
H 1.78210900 -1.43328800 1.97902700



CBS-QB3 (0 K)= -870.666877
CBS-QB3 Energy= -870.648030
CBS-QB3 Enthalpy= -870.647086
CBS-QB3 Free Energy= -870.714518

Charge = 0 Multiplicity = 1
C 0.10390900 2.26973600 -0.20370000
C -0.01528000 0.93555300 -0.32848300
C 1.42602500 2.96762200 -0.38826500
H 1.35875200 3.70660100 -1.19564500
H 1.70303100 3.52115500 0.51763700
H 2.22692800 2.27231800 -0.63027400
C -1.06098400 3.18808900 0.06613100
H -0.96524300 3.67406400 1.04518600
H -1.07779400 3.99368600 -0.67760000
H -2.02396500 2.68125300 0.03307400
O 1.07361100 0.17349000 -0.71749400
Si 1.95880800 -0.96354900 0.14170700
C 3.51926300 -1.17951300 -0.86789000
H 4.08205600 -0.24443000 -0.93535800
H 4.17330700 -1.93517400 -0.42142100
H 3.28223200 -1.50164800 -1.88588300
C 2.33369400 -0.30137000 1.85701600
H 2.88523700 0.64190500 1.81244000
H 1.41539600 -0.12601600 2.42507500
H 2.93959500 -1.01776900 2.42120400
C 1.04173700 -2.59390300 0.27482000
H 0.78942100 -2.98983200 -0.71287600
H 1.66572200 -3.33691300 0.78331400
H 0.11182600 -2.49296400 0.84003500
C -1.27638300 0.15584700 -0.18067000
C -1.68384300 -0.70545800 -1.21016200
C -2.05991100 0.22644300 0.97810500

C -2.85003900 -1.45364700 -1.09272000
H -1.07798400 -0.77729300 -2.10579700
C -3.22614800 -0.52746500 1.09844500
H -1.74548500 0.86697300 1.79401600
C -3.62682700 -1.36736300 0.06271800
H -3.15528300 -2.10552400 -1.90392400
H -3.81719400 -0.46228600 2.00537800
H -4.53403200 -1.95377200 0.15538900

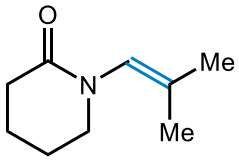


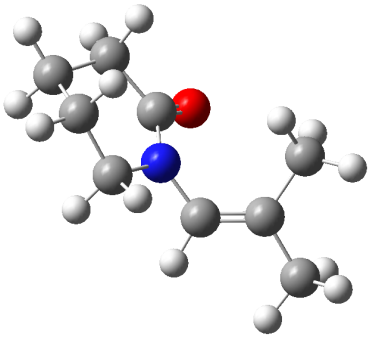
CBS-QB3 (0 K)= -870.658094
CBS-QB3 Energy= -870.639550
CBS-QB3 Enthalpy= -870.638605
CBS-QB3 Free Energy= -870.706186

Charge = 0 Multiplicity = 1
C 0.17734500 2.96086400 0.56855700
C -0.05979900 1.92246500 -0.23413100
H 0.32718800 2.83327600 1.63592800
H 0.22574400 3.97559200 0.18759600
C -0.14102600 0.51114600 0.33794500
H 0.08475900 0.57112400 1.41032100
C -0.26319200 2.06029900 -1.71824500
H 0.45356900 1.43972400 -2.26251700
H -1.26179700 1.71771100 -2.00692400
H -0.14535600 3.09665700 -2.03903600
O 0.80122600 -0.34247200 -0.30272800
Si 2.39156000 -0.63770700 0.10970400
C 2.80767300 -2.24876300 -0.74686800
H 3.85588800 -2.52044600 -0.58696200
H 2.18609700 -3.06718100 -0.37319700
H 2.64474500 -2.16923700 -1.82558000
C 3.51033200 0.73667600 -0.50840200
H 3.24379000 1.69963800 -0.06425000
H 4.55613000 0.52881200 -0.25859900
H 3.44269200 0.83999000 -1.59549300
C 2.55856100 -0.80512800 1.97430700
H 3.57802400 -1.10954900 2.23305600
H 2.36094700 0.13591400 2.49607500
H 1.87616500 -1.56229600 2.37173700
C -1.54388200 -0.07821900 0.19756500
C -2.61095700 0.51821700 0.87799200
C -1.78932700 -1.20240200 -0.59077300
C -3.89775500 -0.00046700 0.77328600
H -2.43313500 1.39745200 1.48867200

C -3.07989900 -1.72084100 -0.69811900
H -0.96223000 -1.66613400 -1.11141900
C -4.13720600 -1.12381300 -0.01775400
H -4.71397400 0.47104300 1.30961500
H -3.25660300 -2.59547800 -1.31483100
H -5.13949800 -1.52913600 -0.10037500

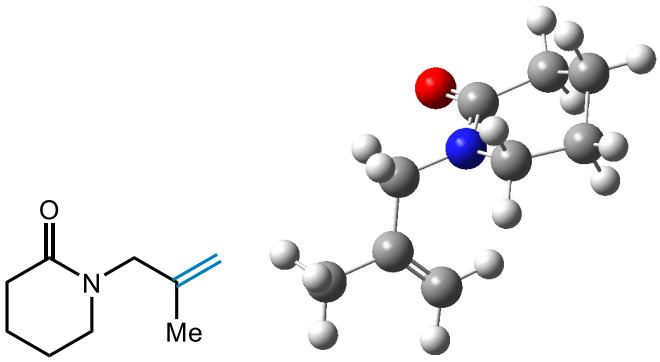
As a note, a racemic mixture was obtained from the actual reaction while the calculation here only accounted for a single enantiomer. Thus, a correction on the entropy term (-0.42kcal/mol at 298 K) was applied to the final calculation of isomerization free energy difference.





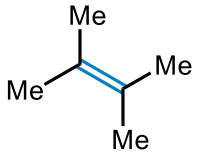
CBS-QB3 (0 K)= -481.075599
CBS-QB3 Energy= -481.063928
CBS-QB3 Enthalpy= -481.062984
CBS-QB3 Free Energy= -481.112986

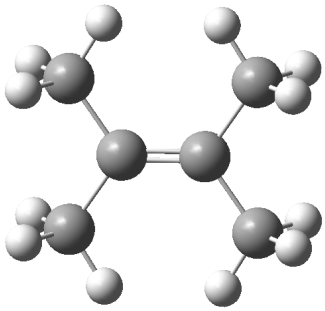
Charge = 0 Multiplicity = 1
C -2.10840800 1.20915500 -0.00449700
C -1.08626800 -1.53295400 -0.01855300
C -2.44011500 -1.18543300 0.58815200
C -3.04879200 0.01097300 -0.13859700
H -2.14026500 1.59394900 1.02240100
H -2.39652300 2.03888000 -0.65171200
H -1.23131900 -1.98219900 -1.01275900
H -0.57509700 -2.27774300 0.59625200
H -3.08748100 -2.06506100 0.52577400
H -2.31788900 -0.94858200 1.65121600
H -3.19061300 -0.23748900 -1.19714600
H -4.03631200 0.25634600 0.26243700
C -0.63649100 0.93284500 -0.30626300
O 0.10394500 1.84675800 -0.62087900
N -0.18645700 -0.36979900 -0.14124000
C 1.15456500 -0.70944800 -0.48386500
C 2.25643100 -0.21978000 0.09079500
H 1.23472000 -1.43782400 -1.28926400
C 2.22994200 0.76445800 1.22537000
H 1.29630400 0.70310500 1.78695100
H 3.06497600 0.58844200 1.91035200
H 2.30896900 1.78653000 0.84210700
C 3.61459500 -0.61597300 -0.42432800
H 4.15604400 0.26161900 -0.79611200
H 4.22629000 -1.04868600 0.37539500
H 3.54908600 -1.33982100 -1.23946600



CBS-QB3 (0 K)= -481.073570
CBS-QB3 Energy= -481.062178
CBS-QB3 Enthalpy= -481.061234
CBS-QB3 Free Energy= -481.111166

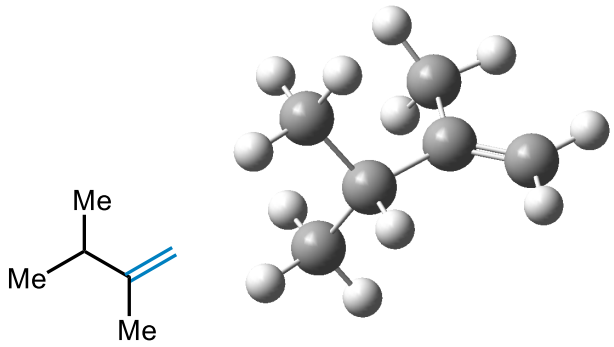
Charge = 0 Multiplicity = 1
C -2.37909000 0.82129600 0.41622100
C -0.62161700 -1.29581400 -0.59665400
C -1.92913300 -1.61321500 0.11915400
C -2.94184000 -0.49537600 -0.12179000
H -2.40248200 0.81871100 1.51269100
H -2.96709300 1.68464500 0.10052600
H -0.75662400 -1.41782000 -1.68223900
H 0.15855700 -1.99719700 -0.28971300
H -2.30253300 -2.57614400 -0.24108600
H -1.74600100 -1.71995200 1.19452000
H -3.13790200 -0.40703100 -1.19705400
H -3.89994400 -0.72102400 0.35492800
C -0.93440800 1.12566300 0.02859600
O -0.51288900 2.27049000 0.08354400
N -0.13285600 0.06244100 -0.32412300
C 3.71053700 -0.08783900 -0.37761100
H 3.95034700 0.93598400 -0.68687000
H 4.46104900 -0.40893100 0.34617400
H 3.80403000 -0.71628600 -1.27104600
C 2.31984500 -0.16348500 0.19697400
C 2.07299700 -0.60152000 1.42974700
H 1.06623000 -0.62892200 1.82922100
H 2.87470800 -0.92912700 2.08204400
C 1.23674300 0.33711600 -0.73975600
H 1.32908700 1.42086800 -0.84493400
H 1.39747600 -0.09973300 -1.73593500





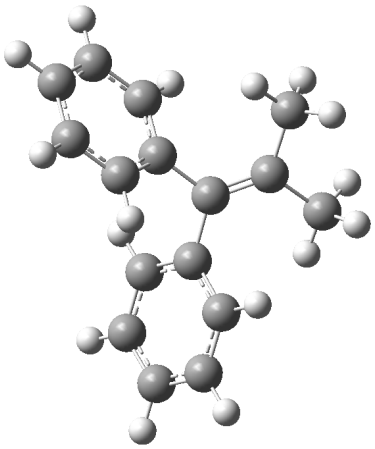
CBS-QB3 (0 K)= -235.332142
CBS-QB3 Energy= -235.323344
CBS-QB3 Enthalpy= -235.322400
CBS-QB3 Free Energy= -235.365746

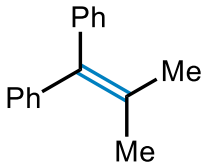
Charge = 0 Multiplicity = 1
C -0.67279900 -0.00011700 -0.00000700
C 0.67279900 -0.00011700 0.00000000
C -1.52527100 1.24932800 -0.00002000
H -2.18321500 1.26126200 0.87742000
H -0.95902800 2.17808400 -0.00011800
H -2.18333100 1.26115400 -0.87737500
C -1.52575100 -1.24928200 0.00000100
H -2.18382400 -1.26084700 0.87735000
H -2.18372900 -1.26093500 -0.87741800
H -0.95997000 -2.17829200 0.00008400
C 1.52527200 1.24932800 0.00002400
H 0.95903000 2.17808400 0.00011500
H 2.18332000 1.26115300 0.87738800
H 2.18322700 1.26126100 -0.87740700
C 1.52575100 -1.24928200 -0.00000300
H 2.18388000 -1.26081200 -0.87731000
H 2.18367200 -1.26097000 0.87745900
H 0.95996900 -2.17829300 -0.00015800



CBS-QB3 (0 K)= -235.330045
CBS-QB3 Energy= -235.322061
CBS-QB3 Enthalpy= -235.321117
CBS-QB3 Free Energy= -235.361745

Charge = 0 Multiplicity = 1
C 0.81616900 -0.12073000 -0.00007200
C 1.74386700 -1.07938500 -0.00066500
H 2.80403300 -0.84780800 -0.00050900
H 1.47439600 -2.13061000 -0.00132900
C 1.20040200 1.33941100 0.00082800
H 2.28519300 1.45885300 0.00095400
H 0.80463100 1.85948800 -0.87761200
H 0.80454300 1.85843700 0.87985000
C -0.66597400 -0.46962400 -0.00030600
H -0.72948800 -1.56346600 -0.00102400
C -1.38225000 0.03369400 -1.26755800
H -2.41725000 -0.31997700 -1.28625100
H -1.40932700 1.12653300 -1.30886600
H -0.88496800 -0.32704100 -2.17169100
C -1.38225000 0.03202600 1.26760900
H -2.41725200 -0.32166600 1.28583600
H -0.88496800 -0.32990100 2.17126500
H -1.40932400 1.12480900 1.31035600

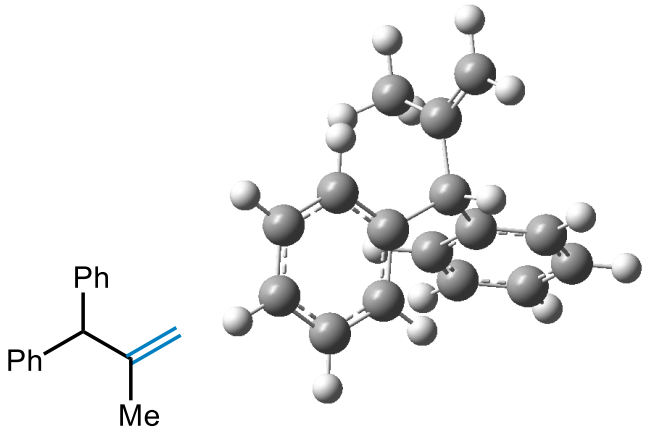




CBS-QB3 (0 K)= -618.121268
CBS-QB3 Energy= -618.106832
CBS-QB3 Enthalpy= -618.105887
CBS-QB3 Free Energy= -618.163334

Charge = 0 Multiplicity = 1
C 0.00000200 0.76119900 -0.00001600
C 0.00003800 2.11246900 -0.00002600
C -1.25750900 -0.04871800 0.05825700
C -2.27614900 0.10968200 -0.89148200
C -1.42670500 -1.02544200 1.05082800
C -3.43304600 -0.66533100 -0.83980200
H -2.15189800 0.83974800 -1.68327900
C -2.58496200 -1.79388500 1.10964300
H -0.64160600 -1.17804600 1.78293500
C -3.59421600 -1.61677400 0.16411100
H -4.20580900 -0.52819000 -1.58839400
H -2.69896000 -2.53537200 1.89287000
H -4.49405300 -2.22018200 0.20593300
C 1.25748600 -0.04875900 -0.05826400
C 2.27616500 0.10970400 0.89142200
C 1.42663000 -1.02555700 -1.05077000
C 3.43304600 -0.66533600 0.83976200
H 2.15196000 0.83984200 1.68316000
C 2.58486900 -1.79402900 -1.10956400
H 0.64150400 -1.17820100 -1.78283900
C 3.59416000 -1.61686400 -0.16407900
H 4.20584000 -0.52814700 1.58831300
H 2.69882700 -2.53557800 -1.89273800
H 4.49398500 -2.22029100 -0.20588600
C -1.24370100 2.94717600 0.19294000
H -2.10825400 2.36309700 0.50234700
H -1.05560900 3.71296500 0.95468500
H -1.50458000 3.48647800 -0.72578200

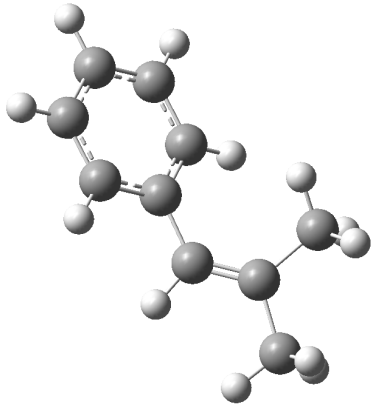
C 1.24384400 2.94708200 -0.19296300
H 1.05583400 3.71287500 -0.95472400
H 1.50473700 3.48637500 0.72576000
H 2.10836100 2.36292900 -0.50233400

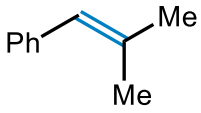


CBS-QB3 (0 K)= -618.112155
CBS-QB3 Energy= -618.098087
CBS-QB3 Enthalpy= -618.097143
CBS-QB3 Free Energy= -618.154042

Charge = 0 Multiplicity = 1
C -0.01696300 2.10269100 0.02238000
C 0.07126600 3.18201800 -0.75677200
H 0.17101000 3.10161500 -1.83411800
H 0.04579400 4.18451500 -0.34253300
C 0.01385200 0.70276100 -0.59675100
H 0.00071300 0.85712700 -1.68161100
C -0.16945700 2.21897000 1.51826000
H -1.14377100 1.84220100 1.84246500
H 0.58884200 1.63222900 2.04588800
H -0.08198800 3.25879300 1.83824000
C 1.30589100 -0.07651300 -0.30556300
C 1.37472600 -1.45141300 -0.56808000
C 2.46940600 0.56780600 0.12632400
C 2.56075500 -2.15818300 -0.39189900
H 0.49074700 -1.97473000 -0.91353400
C 3.65763700 -0.13883500 0.30911500
H 2.45362100 1.63583500 0.30775200
C 3.70873300 -1.50548400 0.05349300
H 2.58736900 -3.22151800 -0.60396000
H 4.54464500 0.38479000 0.64880800
H 4.63201500 -2.05599400 0.19501600
C -1.26979400 -0.06099000 -0.26169700
C -2.36063400 0.01957700 -1.13294000
C -1.41706500 -0.80395700 0.91555900
C -3.56323500 -0.62093500 -0.84301900
H -2.26667200 0.59422100 -2.04892100
C -2.61885200 -1.44338700 1.21097100

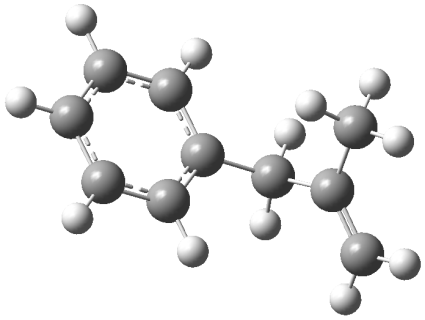
H -0.58187400 -0.89569900 1.60016300
C -3.69716500 -1.35476200 0.33295400
H -4.39329600 -0.54805500 -1.53710400
H -2.71093300 -2.01523600 2.12790700
H -4.63082800 -1.85626800 0.56152400

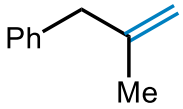




CBS-QB3 (0 K)= -387.498243
CBS-QB3 Energy= -387.488524
CBS-QB3 Enthalpy= -387.487580
CBS-QB3 Free Energy= -387.533319

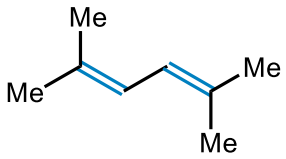
Charge = 0 Multiplicity = 1
C 1.06686700 -0.72757800 -0.30323900
C 2.17226300 -0.03534100 0.01921400
H 1.21599700 -1.73317900 -0.69262600
C -0.35028000 -0.34035500 -0.16732800
C -0.82812600 0.94990500 -0.44774300
C -1.28754900 -1.31611300 0.21235900
C -2.18008500 1.25796400 -0.31937000
H -0.14136900 1.70930700 -0.80018400
C -2.63702700 -1.00883700 0.34456000
H -0.94396600 -2.32546800 0.41468100
C -3.09007200 0.28360500 0.08382400
H -2.52466600 2.26083800 -0.54720700
H -3.33737600 -1.77931300 0.64806500
H -4.14247300 0.52479600 0.18185400
C 3.53818200 -0.62511700 -0.22762100
H 3.48044300 -1.60680000 -0.70127800
H 4.13386000 0.03011800 -0.87472500
H 4.09693200 -0.72652900 0.71038500
C 2.18510900 1.32678600 0.66502000
H 2.48956800 2.10189700 -0.04915900
H 1.21612100 1.60737100 1.07618300
H 2.92123600 1.34745200 1.47595100

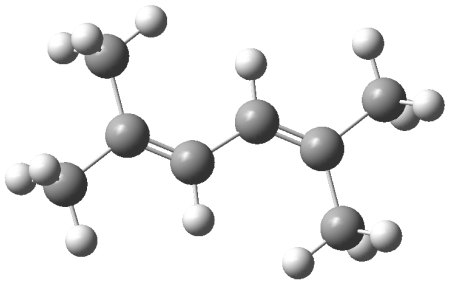




CBS-QB3 (0 K)= -387.494555
CBS-QB3 Energy= -387.484969
CBS-QB3 Enthalpy= -387.484024
CBS-QB3 Free Energy= -387.530360

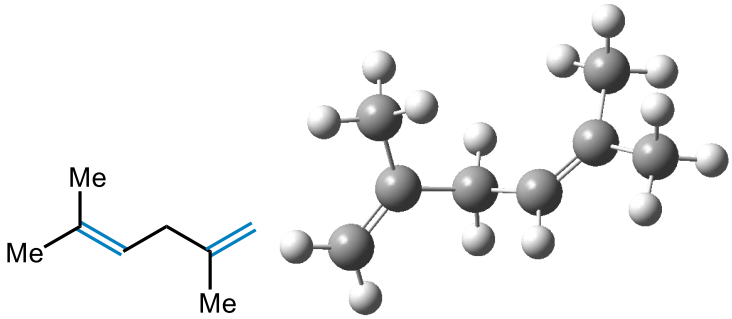
Charge = 0 Multiplicity = 1
C -3.09952300 0.92160700 -0.22314700
C -2.20834500 -0.04448100 0.00304800
H -3.87757300 1.15676700 0.49548200
H -3.08493600 1.50618500 -1.13703200
C -2.22005800 -0.87344700 1.26114900
H -2.35016400 -1.93600100 1.02418100
H -1.27044400 -0.78538400 1.79828000
H -3.02569400 -0.57195100 1.93273500
C -1.12686100 -0.37617500 -1.00797600
H -1.22151000 -1.42889900 -1.29974100
H -1.29165400 0.21629900 -1.91350400
C 0.28850900 -0.14068600 -0.50237700
C 1.21794100 -1.18206400 -0.44285000
C 0.69329700 1.13644500 -0.09654400
C 2.51898800 -0.95794600 0.00631600
H 0.92174000 -2.17895700 -0.75401900
C 1.99080300 1.36485000 0.35161400
H -0.01919300 1.95421800 -0.12793600
C 2.90976900 0.31713300 0.40469800
H 3.22513000 -1.78023500 0.04408800
H 2.28650900 2.36180400 0.65981400
H 3.92066900 0.49473300 0.75406300





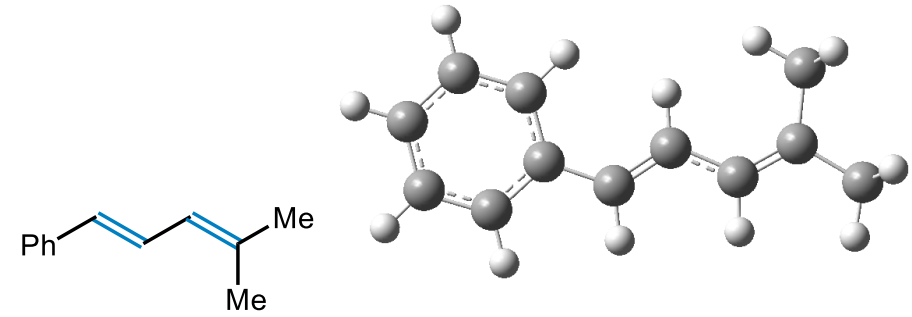
CBS-QB3 (0 K)= -312.587221
CBS-QB3 Energy= -312.576527
CBS-QB3 Enthalpy= -312.575583
CBS-QB3 Free Energy= -312.623062

Charge = 0 Multiplicity = 1
C 1.86052129 0.02089964 0.00002181
C 0.59654541 0.42546146 0.00013440
H 0.42327803 1.48461810 0.00027720
C -0.59654611 -0.42546280 0.00012912
C -1.86052149 -0.02090000 0.00000258
H -0.42327942 -1.48461947 0.00027637
C 2.32885347 -1.41937089 -0.00014394
H 2.94473452 -1.60660854 0.87541135
H 1.51856926 -2.13239392 -0.00004080
H 2.94441201 -1.60650334 -0.87594953
C 2.99985547 1.02099698 0.00006259
H 3.62759452 0.88046836 0.87605406
H 3.62734585 0.88077506 -0.87615926
H 2.63675257 2.04114235 0.00028999
C -2.99985690 -1.02099608 0.00003418
H -3.62760502 -0.88046443 0.87601867
H -3.62733791 -0.88077577 -0.87619462
H -2.63675524 -2.04114189 0.00026810
C -2.32885142 1.41937111 -0.00017131
H -2.94439929 1.60650292 -0.87598456
H -2.94474246 1.60661136 0.87537640
H -1.51856579 2.13239268 -0.00005991



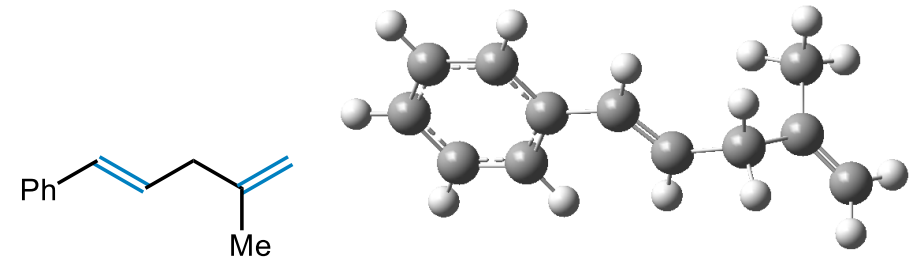
CBS-QB3 (0 K)= -312.578562
CBS-QB3 Energy= -312.568166
CBS-QB3 Enthalpy= -312.567222
CBS-QB3 Free Energy= -312.614525

Charge = 0 Multiplicity = 1
C 1.69503100 -0.14411600 -0.02439000
C 0.48601700 -0.70673100 -0.13886500
H 0.31676500 -1.64342800 0.39042100
C -0.71389600 -0.22129700 -0.91652800
H -0.47974800 0.70233500 -1.45520100
H -0.97265800 -0.96992800 -1.67403600
C -1.92853600 0.01330900 -0.03366800
C -3.01391900 -0.75594500 -0.12083600
H -3.87942900 -0.59341100 0.51300300
H -3.07514100 -1.57375500 -0.83136800
C -1.82796300 1.15713300 0.94199100
H -0.96495800 1.03141800 1.60358800
H -1.68246900 2.10655700 0.41298200
H -2.72625200 1.24305100 1.55596200
C 2.11541100 1.14737200 -0.67974800
H 1.32256900 1.61631400 -1.26153400
H 2.45129900 1.86845200 0.07459100
H 2.96784900 0.97810500 -1.34809400
C 2.77481800 -0.80149500 0.80110200
H 3.65424700 -1.02942800 0.18698600
H 3.11793200 -0.13491600 1.60133500
H 2.42820700 -1.73074400 1.25701800



CBS-QB3 (0 K)= -464.752292
CBS-QB3 Energy= -464.740111
CBS-QB3 Enthalpy= -464.739167
CBS-QB3 Free Energy= -464.791929

Charge = 0 Multiplicity = 1
C -0.13432600 -0.80117100 -0.00012900
C 0.99023700 -0.05625800 -0.00001700
H 0.90711000 1.02573100 0.00013600
C 2.31980400 -0.62735000 -0.00007900
C 3.49971600 0.02685600 0.00003900
H 2.35431300 -1.71553900 -0.00024800
C 4.79937200 -0.73378700 -0.00008800
H 5.40454200 -0.47718900 -0.87834000
H 5.40461200 -0.47736400 0.87816400
H 4.64022700 -1.81360400 -0.00019300
C 3.64880400 1.52486600 0.00026000
H 4.21777400 1.85285000 0.87838100
H 4.21785300 1.85311100 -0.87771300
H 2.69836500 2.05685100 0.00029700
H -0.02109600 -1.88387000 -0.00024900
C -1.51972100 -0.32989400 -0.00007600
C -2.55858200 -1.27687600 0.00012500
C -1.87856600 1.03099600 -0.00021600
C -3.89414800 -0.88812700 0.00020300
H -2.30703900 -2.33259600 0.00023300
C -3.21136000 1.41950500 -0.00014000
H -1.10843800 1.79342500 -0.00040400
C -4.22870100 0.46352800 0.00007200
H -4.67395300 -1.64174100 0.00036300
H -3.46135500 2.47488700 -0.00025900
H -5.26808900 0.77132600 0.00012600



CBS-QB3 (0 K)= -464.742702
CBS-QB3 Energy= -464.730740
CBS-QB3 Enthalpy= -464.729796
CBS-QB3 Free Energy= -464.782938

Charge = 0 Multiplicity = 1
C 0.00074600 0.62522600 0.51793400
C 1.07116700 -0.16710400 0.64500600
H 0.97464000 -1.24289100 0.51604400
C 2.46333100 0.31468400 0.96274800
H 2.44454700 1.40169800 1.10810400
H 2.79287900 -0.13089100 1.90839800
C 3.47429900 -0.03640900 -0.11718200
C 4.44602400 -0.92232600 0.10234100
H 5.16556200 -1.17997500 -0.66768300
H 4.55765000 -1.41794100 1.06111400
C 3.30720800 0.66946200 -1.43761000
H 2.31451100 0.48428600 -1.86005200
H 3.39524800 1.75494800 -1.31028100
H 4.05754400 0.34878700 -2.16230400
C -1.38333400 0.22788700 0.21780300
C -1.77416600 -1.10251900 -0.01165500
C -2.37334000 1.22065600 0.15377800
C -3.09695100 -1.42017700 -0.29092300
H -1.03786100 -1.89669100 0.02713100
C -3.69952400 0.90382300 -0.12590900
H -2.09406200 2.25500600 0.32716300
C -4.06832700 -0.41954100 -0.34973500
H -3.37434400 -2.45412400 -0.46467100
H -4.44379700 1.69130400 -0.16880500
H -5.09977700 -0.67163200 -0.56814000
H 0.14445600 1.69614100 0.65441300

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