Supporting Information

Visible-Light-Controlled Ruthenium-Catalyzed Olefin Metathesis

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General Information.

All reactions were carried out in oven-dried glassware under an argon or nitrogen atmosphere employing standard techniques in handling air-sensitive materials.

All solvents were reagent grade. Dichloromethane (anhydrous, ≥99.8%), hexane (anhydrous, 95%), pyridine (anhydrous, 99.8%) and toluene (anhydrous, 99.8%) were purchased from Sigma-Aldrich and used as supplied. Benzene (anhydrous, 99.8%) was purchased from Merck and used as supplied. Grubbs 1st and 2nd generation catalysts and SIMes were purchased from Sigma Aldrich and used as supplied. IMes was purchased from TCI Chemicals and used as supplied. All photocatalysts used were either synthesized by known methods or bought from commercial sources. 2,4,6-Triphenylpyrylium tetrafluoroborate in particular was purchased from Sigma Aldrich and used as supplied. Trichloro(5-norbornen-2-yl)silane was synthesized based on a reported procedure.[1] All other reagents were used as supplied.

All photochemical reactions were performed in 1-dram vials fitted with Teflon caps under irradiation with two blue PR160-440nm Kessil 40W LED lamps. Reactions were magnetically stirred and monitored by thin layer chromatography using SiliCycle® 250 µm 60 Å plates. Flash chromatography was performed with silica gel 60 Å (particle size 40-63 µm) supplied by SiliCycle®. Yields refer to chromatographically and spectroscopically pure compounds unless otherwise stated.

All polymer patterning experiments were performed in BRAND® petri dishes (glass, 40 mm x 12 mm or 80 mm x 15 mm) purchased from Sigma Aldrich. A UKing ZQ-J33 200 mW 532nm & 450 nm double light 5 in 1 USB laser pointer was purchased from www.laserpointerpro.com. Silicon wafers (4”, 2850 Å oxide layer, resistivity .001-.005 ohm-cm, p-type, orientation <100>) were purchased from NOVA Electronic Materials (Item #HS39626-OX). Masks were drawn in CAD software and printed by CAD/ART Services, Inc. (Brandon, OR).

Proton NMR spectra were recorded using an internal deuterium lock at ambient temperature on a Bruker 500 MHz spectrometer. Internal reference of δ_H 7.26 was used for $CDCl_3$. Data are presented as follows: chemical shift (in ppm on the δ scale relative to $\delta_{TMS} = 0$), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br. = broad, app. = apparent), coupling constant (*J*/Hz) and integration. Resonances that are either partially or fully obscured are denoted obscured (obs.). Carbon-13 NMR spectra were recorded at 125 MHz using

$CDCl_3$ (δ_C 77.16) as internal reference. Fluorine-19 NMR spectra were recorder at 470 MHz using CF_3CH_2OH (δ_F – 77.59) as external reference.

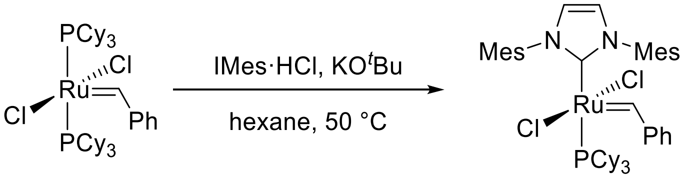
High-resolution mass spectra were obtained on a Waters XEVO G2XSQToF mass spectrometer. Infrared spectra were recorded on a Perkin Elmer Spectrum Two FT-IR Spectrometer. GPC analysis were performed on an Agilent 1260 Infinity GPC using 2x300 mm Agilent PLGel Mixed-D columns and G1362A RI or G1365D multiwavelength detectors, calibrated against polystyrene standards.

All cyclic voltammetry studies were performed on a CH instruments Model 1232B potentiostat using an EDAQ 1-mm disk glassy carbon working electrode in conjunction with an EDAQ Ag/AgCl reference electrode and a platinum wire from VWR as counter electrode. All experiments were performed in anhydrous dichloromethane ($RuCl_2(CHPh)(IMes)_2$ and $RuCl_2(CHPh)(SIMes)_2$) or tetrahydrofuran (free IMes and free SIMes) at 5 mM using tetrabutylammonium hexafluorophosphate (0.1 M) as electrolyte. The scan rate was set at 100 mV/s.

Plasma treatments were conducted using a PE-50 Compact Benchtop Plasma Cleaning System manufactured by Plasma Etch, Inc. Micrographs of the patterned silicon wafers were recorded on a Nikon Eclipse LV150N microscope. Step heights were measured by imaging 10 µm sections (0.5 Hz, 256 samples/line) on a Bruker Dimension Icon AFM using a Scanasyst-Air probe in Scanasyst mode.

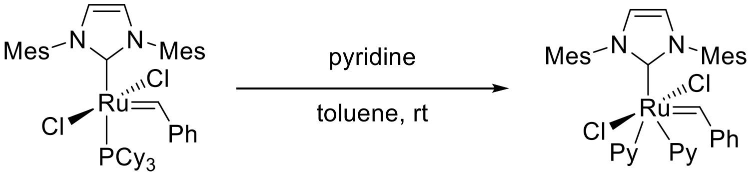
Synthesis of $RuCl_2(CHPh)(IMes)_2$

- **Synthesis of $RuCl_2(CHPh)(PCy_3)(IMes)$**



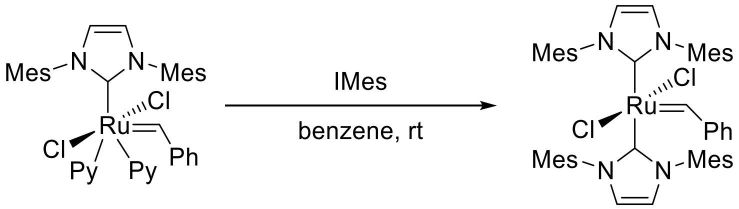
$RuCl_2(CHPh)(PCy_3)(IMes)$ was synthesized according to a procedure reported by Nolan.[2] In a glovebox, a 50 mL round bottom flask was charged with Grubbs 1st generation (1.5 g, 1.82 mmol), IMes·HCl (933 mg, 2.73 mmol), KO^{t}Bu (450 mg, 4.0 mmol) and anhydrous hexane (15 mL). The flask was sealed and removed from the glovebox before stirring at 50 °C for 5h. The resulting suspension was cooled to room temperature and filtered through a collection frit. The precipitate was finally washed with water and a minimal amount of hexane before being dried under vacuum to afford the desired $RuCl_2(CHPh)(PCy_3)(IMes)$ as a purple-brown solid (846 mg, 1.0 mmol, 67% yield). The NMR data are in agreement with the literature values.[3]

- **Synthesis of $RuCl_2(CHPh)(Py)_2(IMes)$**



$RuCl_2(CHPh)(Py)_2(IMes)$ was synthesized according to a procedure reported by Grubbs.[4] In a glovebox, $RuCl_2(CHPh)(PCy_3)(IMes)$ (846 mg, 1 mmol) was dissolved in anhydrous toluene (2.5 mL) and pyridine (6.5 mL). The reaction mixture was stirred for 30 min at room temperature. During that time, a quick change in color from red to green could be observed. The reaction mixture was then concentrated under vacuum before pentane was added. The green residue was triturated in pentane and allowed to precipitate for 30 minutes at -20 °C. The precipitate was then filtered, washed with cold pentane (-20 °C) and finally dried under vacuum to afford $RuCl_2(CHPh)(Py)_2(IMes)$ as a green solid (689 mg, 0.95 mmol, 95% yield). The NMR data are in agreement with the literature values.[5]

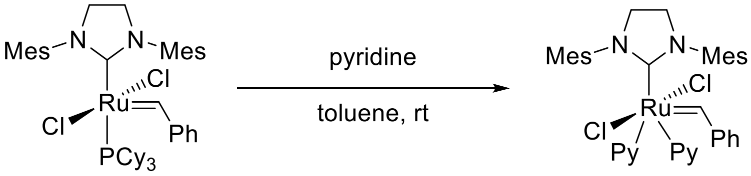
- **Synthesis of $RuCl_2(CHPh)(IMes)_2$**



$RuCl_2(CHPh)(IMes)_2$ was synthesized according to a procedure reported by Fogg.[3b] In a glovebox, a 100 mL round bottom flask was charged with $RuCl_2(CHPh)(Py)_2(IMes)$ (944 mg, 1.30 mmol), IMes (397 mg, 1.30 mmol) and anhydrous benzene (50 mL). The brown reaction mixture was stirred overnight at room temperature, filtered and concentrated under vacuum. The crude residue was then precipitated from cold pentane (-20 °C), filtered and washed with cold pentane (-20 °C). To improve its purity, the complex was extracted multiple times with boiling hexanes. The precipitate was therefore taken up in boiling hexanes and filtrated through a collection frit. This was repeated multiple times to recover most of the desired complex. The combined organic layers were finally concentrated under vacuum to afford the desired $RuCl_2(CHPh)(IMes)_2$ as a brown solid (670 mg, 0.77 mmol, 59% yield). The NMR data are in agreement with the literature values.[4b]

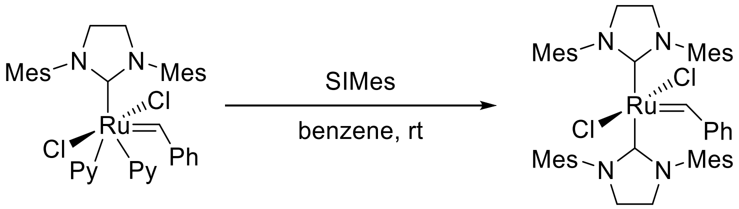
Synthesis of $RuCl_2(CHPh)(SIMes)_2$

- **Synthesis of $RuCl_2(CHPh)(Py)_2SIMes$**



$RuCl_2(CHPh)(Py)_2(SIMes)$ was synthesized according to a procedure reported by Grubbs.[4a] In a glovebox, Grubbs 2nd generation (250 mg, 294 µmol) was dissolved in anhydrous toluene (750 µL) and pyridine (1.8 mL). The reaction mixture was stirred for 30 min at room temperature. During that time, a quick change in color from red to green could be observed. The reaction mixture was then poured into cold pentane (-20 °C) inducing precipitation of a green solid. The solid was allowed to fully precipitate for 30 minutes at -20 °C before being filtered, washed with cold pentane (-20 °C) and finally dried under vacuum to afford $RuCl_2(CHPh)(Py)_2(SIMes)$ as a green solid (196 mg, 270 µmol, 92% yield). The NMR data are in agreement with the literature values.[3]

- **Synthesis of $RuCl_2(CHPh)(SIMes)_2$**

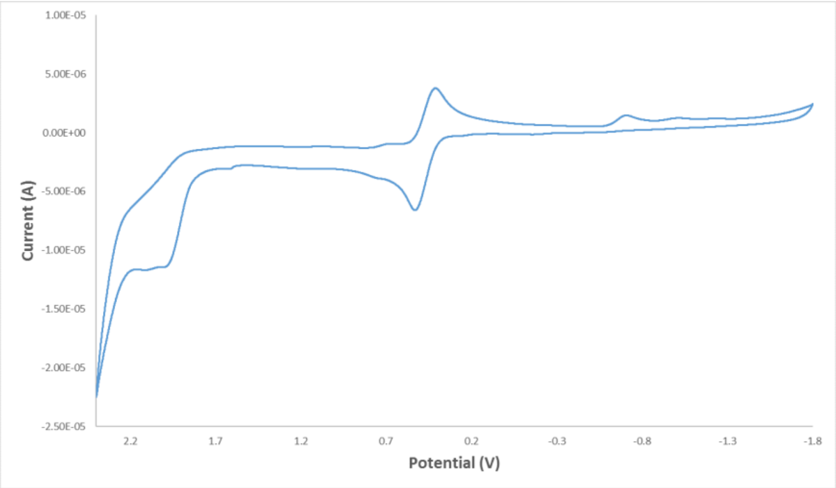


$RuCl_2(CHPh)(SIMes)_2$ has already been reported by Grubbs.[6] In a glovebox, a 25 mL round bottom flask was charged with $RuCl_2(CHPh)(Py)_2(SIMes)$ (196 mg, 270 µmol), SIMes (83 mg, 270 mmol) and benzene (9 mL). The brown reaction mixture was stirred at 45 °C for 24h before being cooled to room temperature and concentrated under vacuum. The crude residue was then precipitated from cold pentane (-20 °C), filtered and washed with cold pentane (-20 °C). To improve its purity, the complex was extracted multiple times with boiling hexanes. The precipitate was therefore taken up in boiling hexanes and filtrated through a collection frit. This was repeated multiple times to recover most of the desired complex. The combined organic layers were finally concentrated under vacuum to furnish the desired $RuCl_2(CHPh)(SIMes)_2$ as a brown solid (150 mg, 171 µmol, 63% yield). The NMR data are in agreement with the literature values.[6]

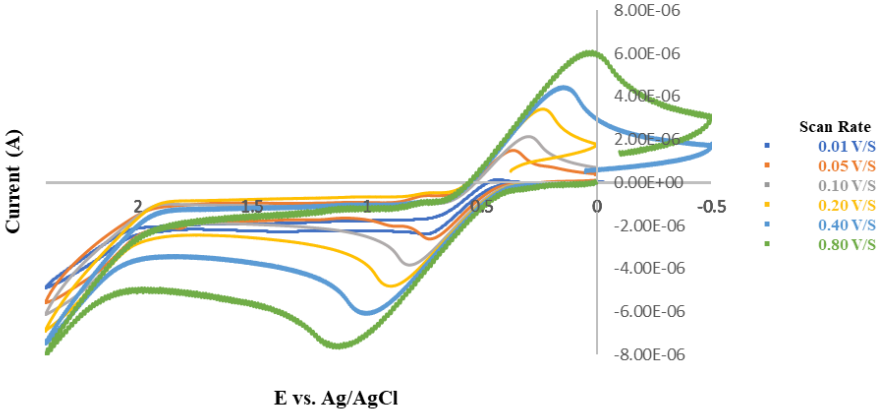
Cyclic Voltammetry Studies

Cyclic voltammetry studies were run using a glassy carbon electrode, a platinum wire counter electrode and an Ag/AgCl reference electrode. For all studies, tetrabutylammonium hexafluorophosphate was used as the electrolyte in a solution of dichloromethane ($RuCl_2(CHPh)(IMes)_2$ and $RuCl_2(CHPh)(SIMes)_2$) or tetrahydrofuran (free IMes and free SIMes) while nitrogen was bubbled through the solution prior to data collection. Sweeps were run negative (reductive) on first pass.

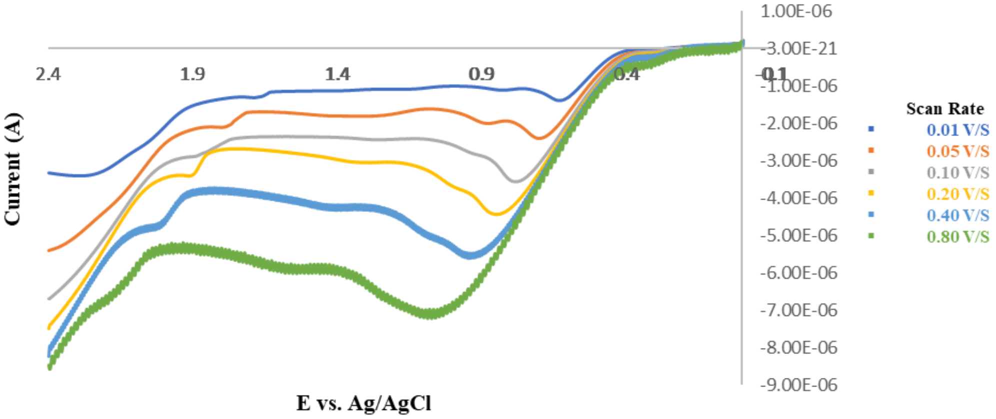
- $RuCl_2(CHPh)(IMes)_2$ versus Ag/AgCl



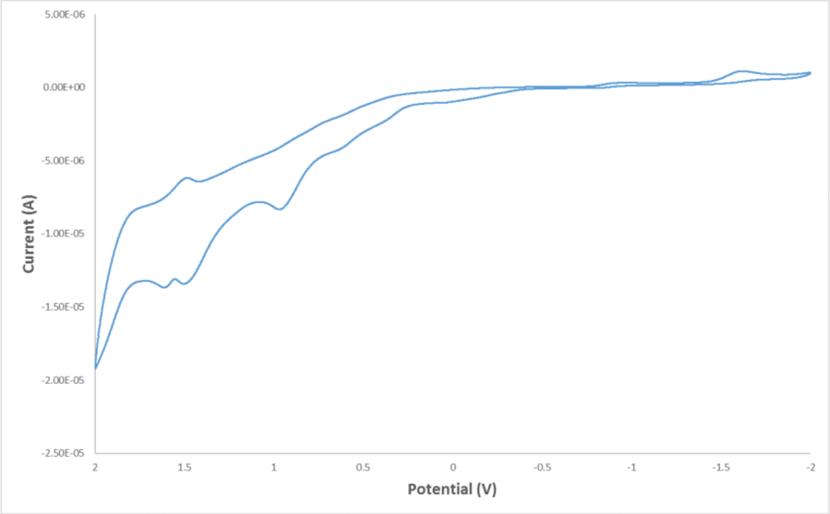
- RuCl$_2$(CHPh)(IMes)$_2$ versus Ag/AgCl (Differential Scan Rates – Cyclic Voltammetry)



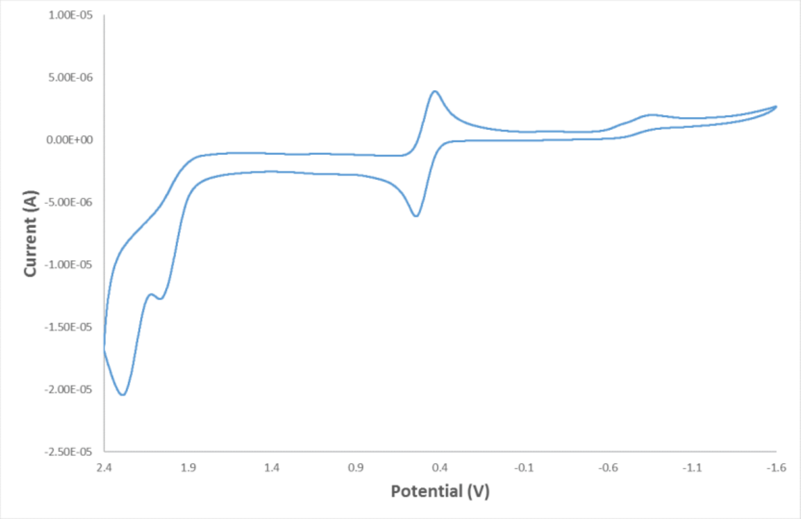
- RuCl$_2$(CHPh)(IMes)$_2$ versus Ag/AgCl (Differential Scan Rates – Linear Voltammetry)



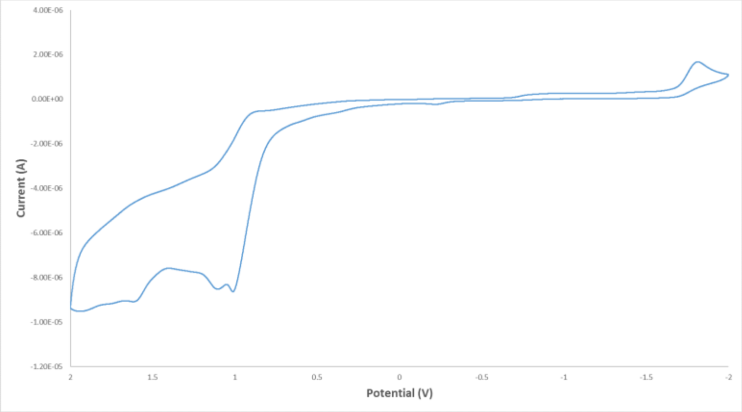
- IMes versus Ag/AgCl



- $RuCl_2(CHPh)(SIMes)_2$ versus Ag/AgCl



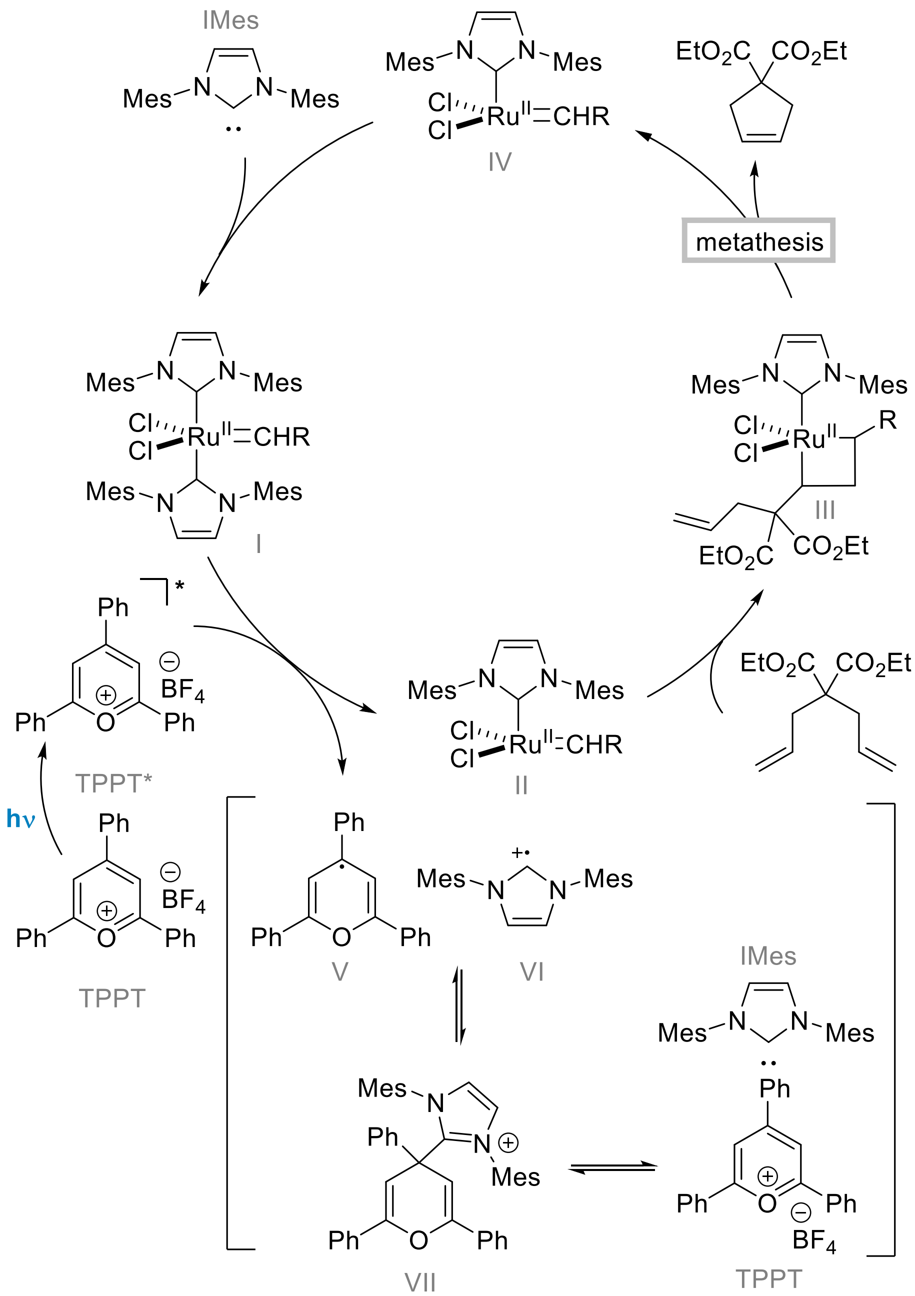
- SIMes versus Ag/AgCl



The cyclic voltammograms of ruthenium complexes $RuCl_2(CHPh)(IMes)_2$ and $RuCl_2(CHPh)(SIMes)_2$ both display a pseudo-reversible oxidation at 0.47 V (0.44 V vs SCE) and 0.49 V (0.43 V vs SCE), respectively, which are most probably related to the Ru(II)/Ru(III) couple. In addition, oxidation events at high potentials (> 1.8 V) are also observed on both cyclic voltammograms and are probably related to the oxidation of the carbene ligands. [7] These oxidation events do not appear to be reversible. While the first oxidation process should be accessible by most Ru- and Ir-based photocatalysts, the events at high potentials are only accessible by much oxidizing photocatalysts such as acridinium and pyrylium derivatives. As described on the next page, only those highly oxidizing photocatalysts display some reactivity.

Mechanistic Discussion

- Proposed mechanistic cycle

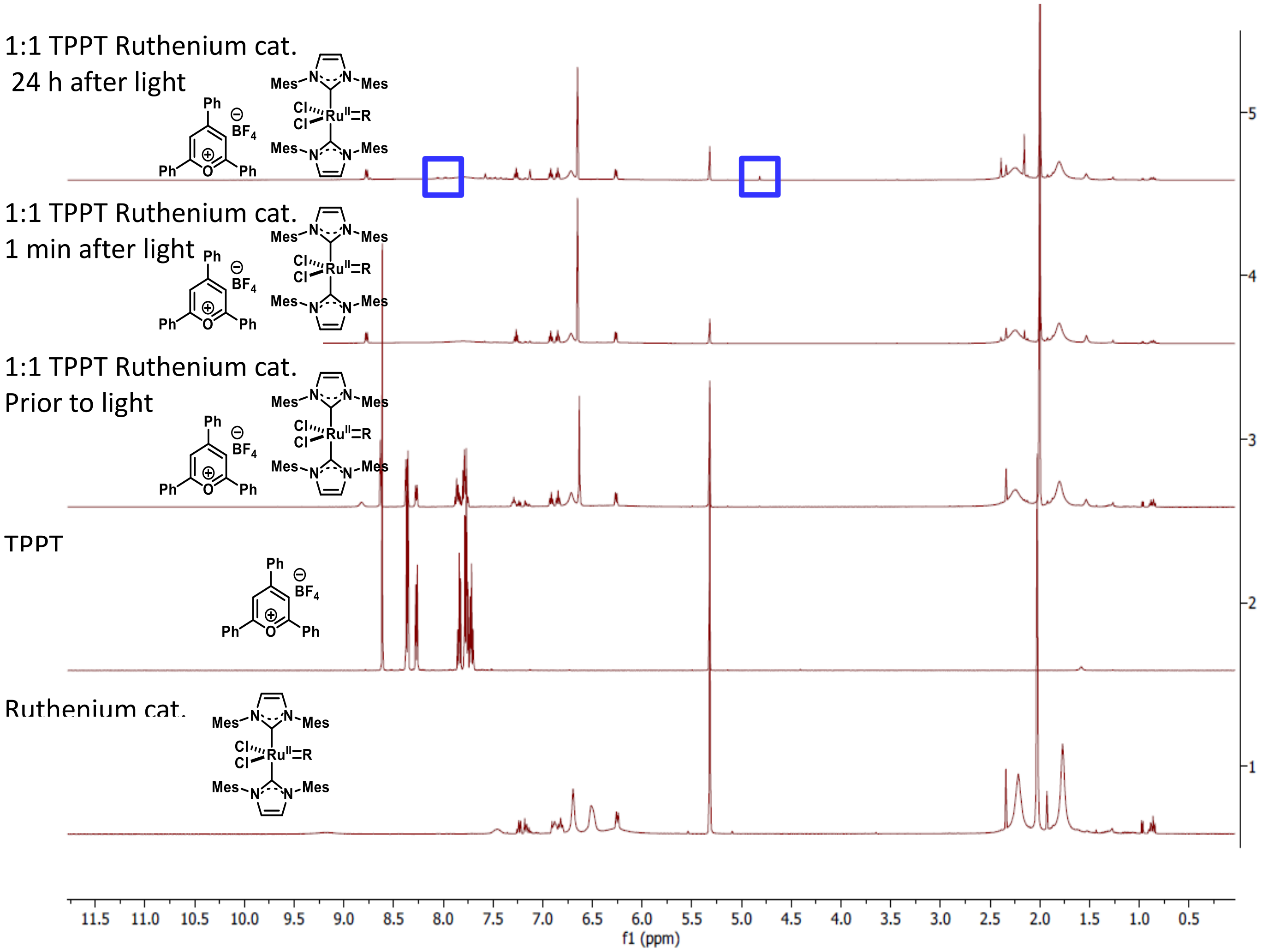


Evaluation of the optimized conditions and cyclic voltammetry support the above mechanisms. Given the high oxidation potential of the Ru catalyst and the necessity of a highly oxidizing photocatalyst we propose oxidation of the IMes ligand to liberate the active Ru(II) catalyst . Literature precedent of analogous redox couples with TPPT[8] invoke formation of intermediate VII.

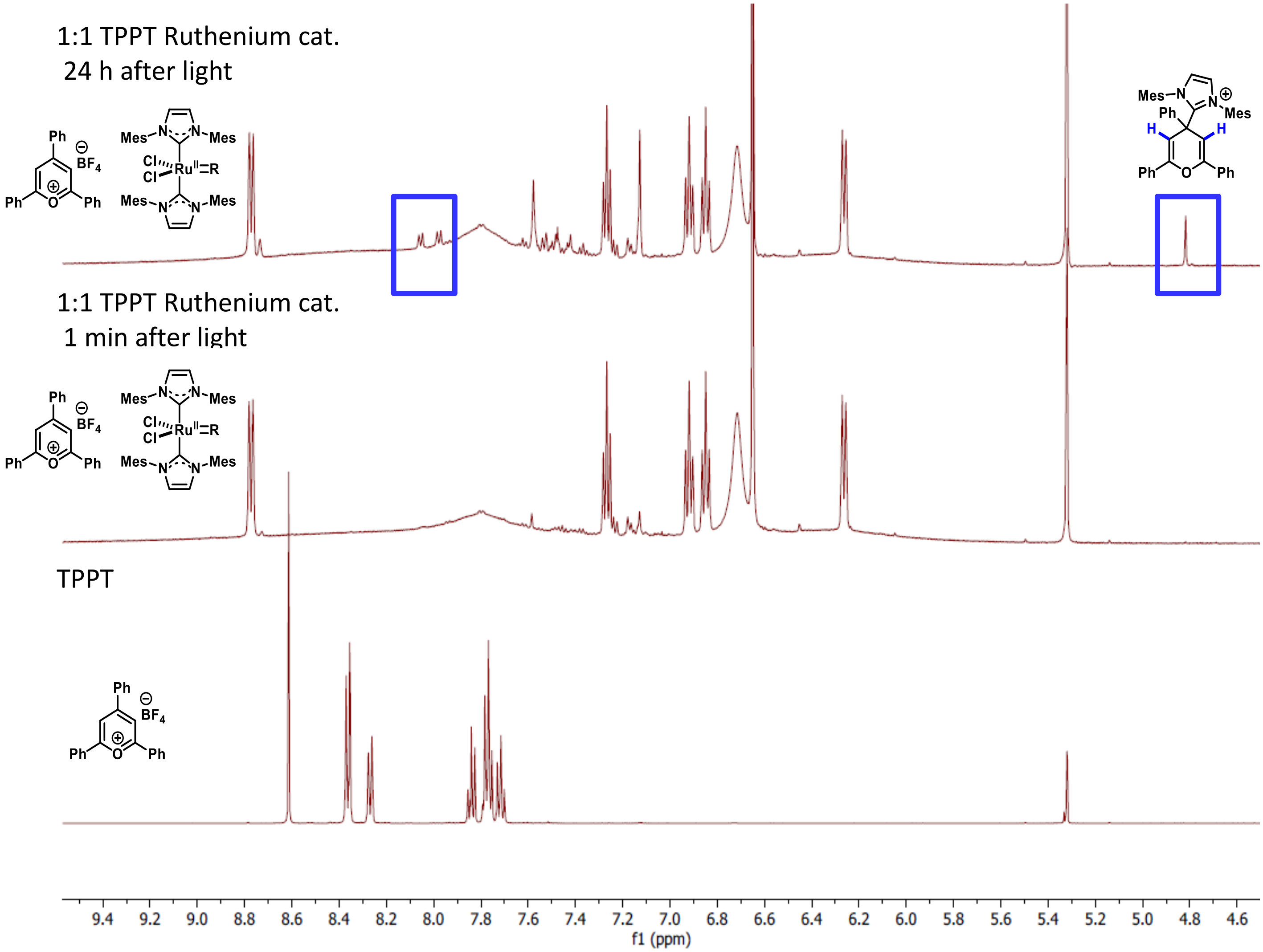
Upon decomplexation, the ground state of TPPT is regenerated and the IMes can coordinate to IV. This complex formation between the reduced TPPT and oxidized IMes rationalizes the imperfect temporal control (0-3% increase during dark periods). TPPT is the optimal catalyst because it is highly oxidizing and lewis acidic, which is accounted for in the proposed mechanism.

NMR experiments probe the nature of the Ru catalysts/TPPT before and after light. A 1:1 solution of the TPPT/Ruthenium catalyst was evaluated over a 36h period with ^{1}H NMRs recorded every 10 min. Upon irradiation with blue light (5 min) NMR experiments were performed. Diagnostic TPPT peaks have diminished/broadened in the aromatic range. Over the course of the kinetic study new peaks appear to form ~4.8 ppm and ~8.0-8.1 ppm as TPPT appears to disappear after light irradiation. We believe this could be due to complexation between the TPPT and the IMes ligand to form intermediate **VII**. Further mechanistic studies are currently underway that model the reaction conditions more closely.

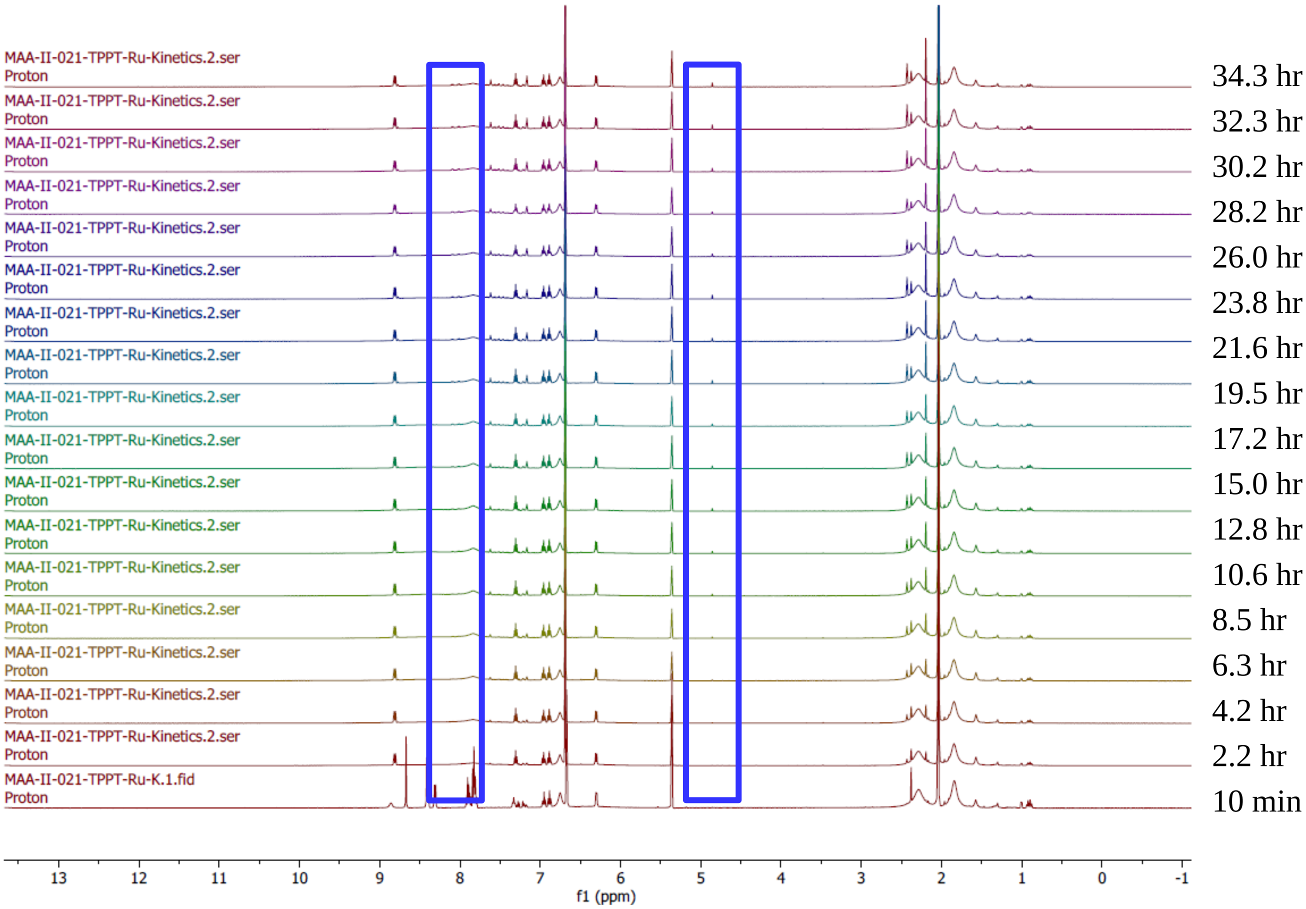
Comparison of Ruthenium and TPPT catalysts prior and after blue light irradiation.

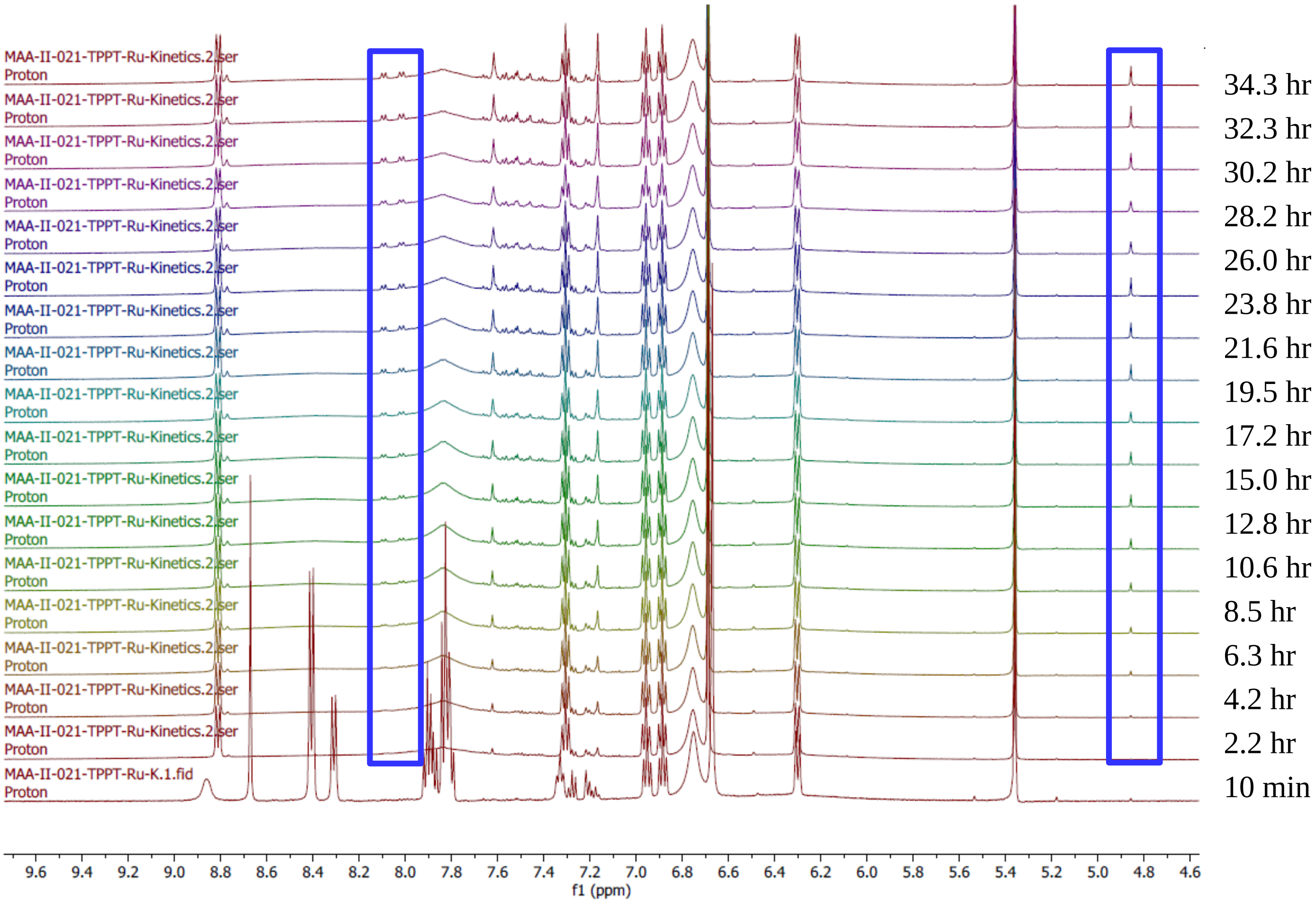


Diagnostic peaks suggesting complexation of TPPT to potentially form intermediate **VII**.



Kinetic NMR Spectroscopy of a 1:1 solution of TPPT and $RuCl_2(CHPh)(IMes)_2$ in d-DCM.




MAA-II-021-TPPT-Ru-Kinetics.2.ser
Proton
MAA-II-021-TPPT-Ru-Kinetics.2.ser
Proton
MAA-II-021-TPPT-Ru-Kinetics.2.ser
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MAA-II-021-TPPT-Ru-Kinetics.2.ser
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30.2 hr
28.2 hr
26.0 hr
23.8 hr
21.6 hr
19.5 hr
17.2 hr
15.0 hr
12.8 hr
10.6 hr
8.5 hr
6.3 hr
4.2 hr
2.2 hr
10 min
9.6
9.4
9.2
9.0
8.8
8.6
8.4
8.2
8.0
7.8
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7.4
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6.4
6.2
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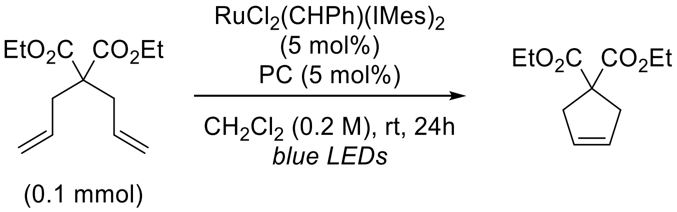
5.8
5.6
5.4
5.2
5.0
4.8
4.6
f1 (ppm)

Extended Optimization Studies:

Screening of Photocatalysts

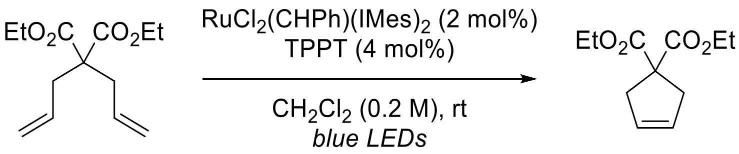


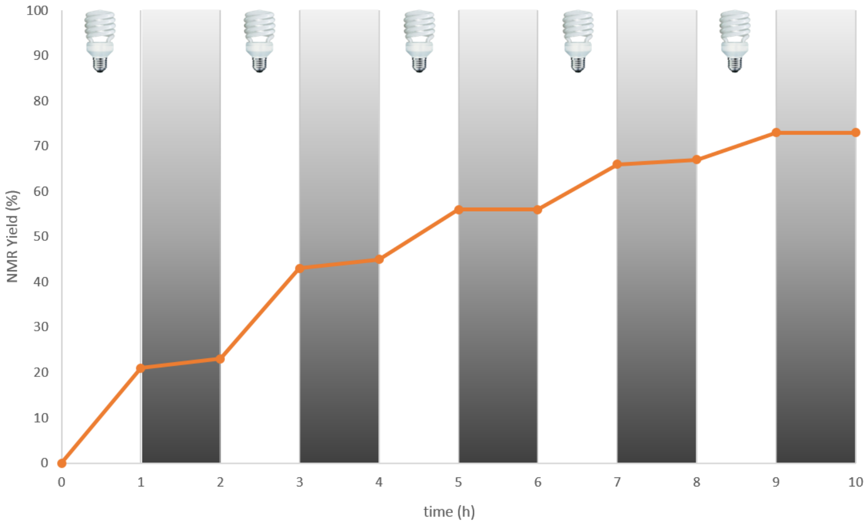
Photocatalyst	Excited state oxidation potential (V vs SCE)	Excited state energy (kcal/mol)	Yield (%)
$Ir(ppy)_3$	0.31	55.20	0
$[Ir(ppy)_2(dtbbpy)]PF_6$	0.66	49.21	0
$Ru(bpy)_3Cl_2$	0.77	46.49	0
Fluorescein	0.77	44.74	0
Rose Bengal	0.81	41.51	0
Eosin Y	0.83	44.05	0
Rhodamine B	0.84	41.51	0
Rhodamine 6G	0.95	48.20	0
$[Ir(dF\text{-}CF_3ppy)_2(dtbbpy)]PF_6$	1.21	60.10	0
4CzIPN	1.35	n/a	0
$Ru(bpz)_3Cl_2$	1.45	48.38	0
TAPT	1.84	S_1: 53.96; T_1: 50.96	0
$MesAcrPhBF_4$	2.12	n/a	33
$MesAcrMeClO_4$	2.18	S_1: 61.57; T_1: 44.74	8
$MesAcrMe\ BF_4$	2.18	S_1:61.57; T_1: 44.74	16
TPPT	2.55	S_1:65.26; T_1: 53.04	84

Some known triplet sensitizers such as benzophenone, 4,4’-dimethoxybenzophenone, 4,4’-bis(dimethylamino)benzophenone (or Michler’s ketone) and 9-fluorenone have also been investigated to promote the ring closing metathesis of diallyl diethylmalonate. As for most photocatalysts displayed in the above chart, no reaction was observed.

On/Off Experiments

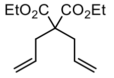
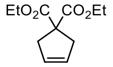
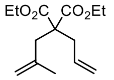
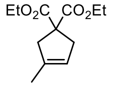
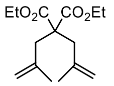
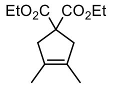
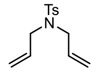
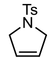
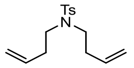
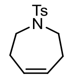
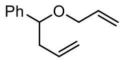
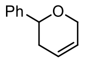
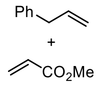
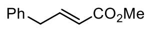
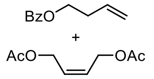
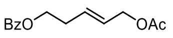
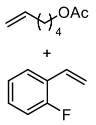
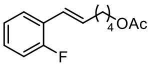
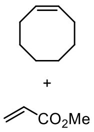
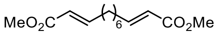
On/off experiments were performed for the ring closing metathesis of diethyl diallylmalonate using 2 mol% of $RuCl_2(CHPh)(IMes)_2$ and 4 mol% of 2,4,6-triphenylpyrylium tetrafluoroborate (TPPT) in CH_2Cl_2 (0.2M) at room temperature over a period of time alternating cycles of irradiation and darkness. The reaction was conducted in the presence of mesitylene, used as internal standard. Aliquots were taken every hour and yields were determined by ^1H NMR.



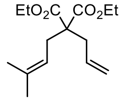
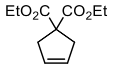
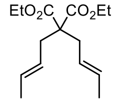
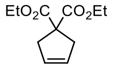
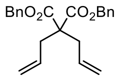
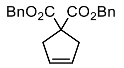
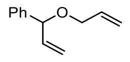
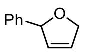
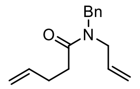
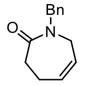
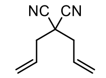
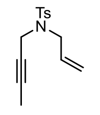
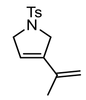
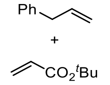
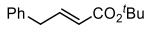
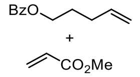
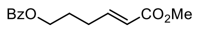
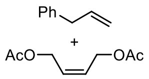
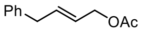
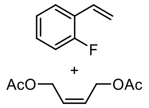
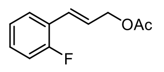
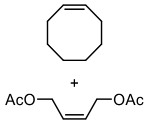
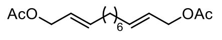
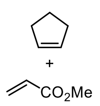
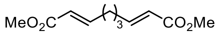


Extended Substrate Scope

These two tables display the entire scope for the synthesis of small molecules that has been studied under the conditions reported in this manuscript. The left table is reproduced below from the manuscript; additional examples may be found in the right table.

entry	substrate	product	Yield[b] (%)
1			86
2			84
3			trace
4			90
5[c]			89
6			72
7[c,d]			60
8[c,d]			70
9[c,d]			46
10[c,e]			51

[a] Conditions: substrate (0.2 mmol), $RuCl_2(CHPh)(IMes)_2$ (2 mol%), TPPT (3 mol%), CH_2Cl_2 (0.2 M), rt, blue LEDs, 4h. [b] Isolated yields. [c] 4 mol% of TPPT. [d] Top substrate (0.2 mmol), bottom substrate (0.4 mmol). [e] Top substrate (0.2 mmol), bottom substrate (0.6 mmol).

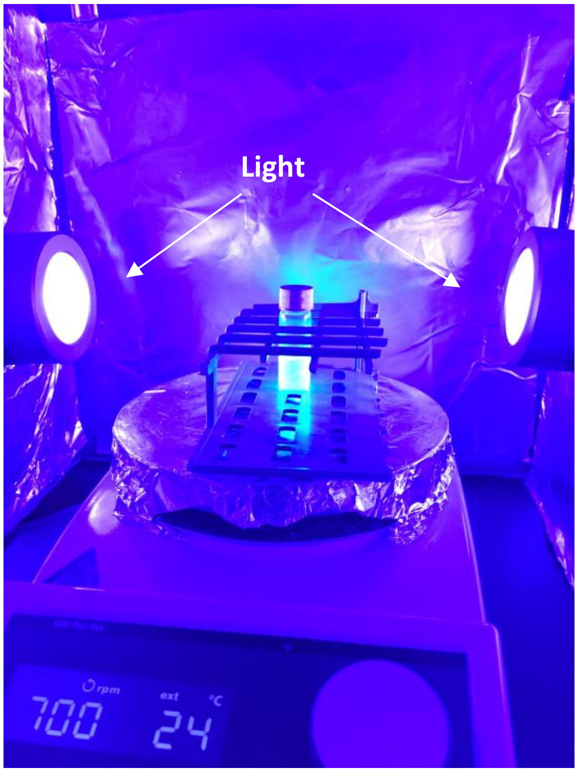
entry	substrate	product	Yield[b] (%)
1			80
2			85
3			79
4			71
5[c]			-
6			-
7[c]			40
8[c,d]			50
9[c,d]			52
10[c,d]			60
10[c,d]			51
11[c,e]			53
12[c,e]			58

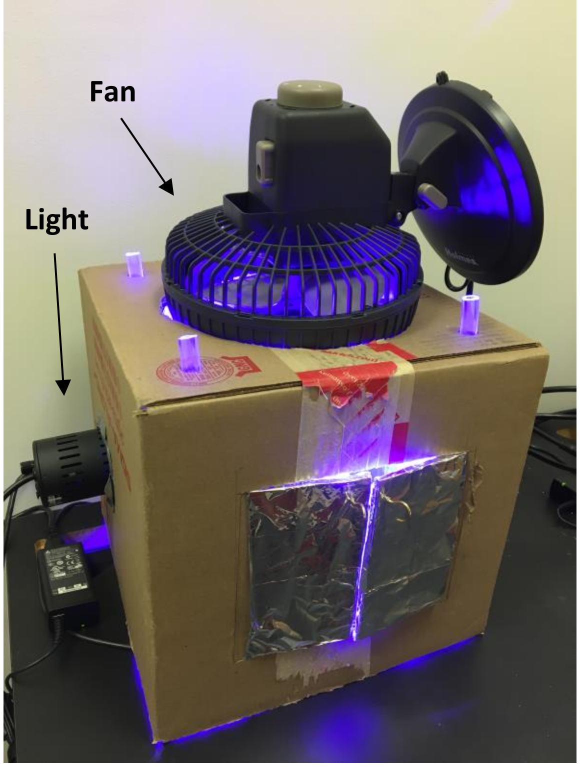
[a] Conditions: substrate (0.2 mmol), $RuCl_2(CHPh)(IMes)_2$ (2 mol%), TPPT (3 mol%), CH_2Cl_2 (0.2 M), rt, blue LEDs, 4h. [b] Isolated yields. [c] 4 mol% of TPPT. [d] Top substrate (0.2 mmol), bottom substrate (0.4 mmol). [e] Top substrate (0.2 mmol), bottom substrate (0.6 mmol).

Experimental Setups

Experimental setup 1: visible-light-controlled olefin metathesis

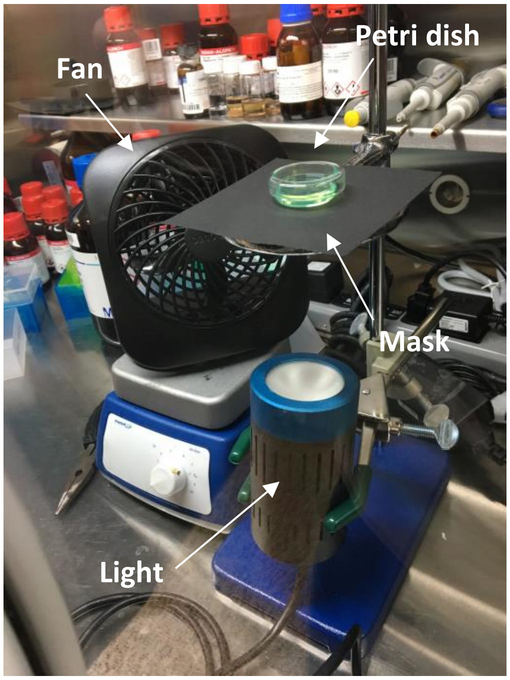
The experimental setup includes a magnetic stirrer placed in a cardboard box, two blue Kessil LED lamps (440 nm) as light sources and a fan to maintain the reaction mixture at room temperature. The Kessil lamps are placed at a distance of 5-10 cm from the vial.

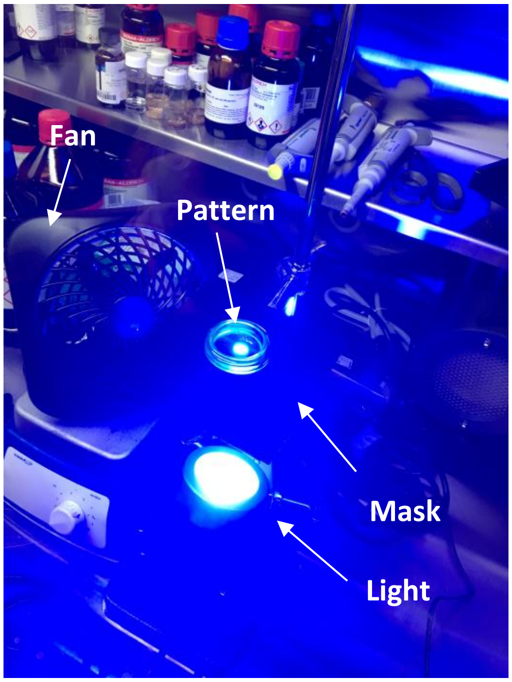




Experimental setup 2: polymer patterning using macroscopic photomasks

The polymer patterning experiments using macroscopic photomasks are conducted in a glovebox. The experimental setup includes: a BRAND® petri dish (glass) in which the polymerization is performed, a blue Kessil LED lamp (440 nm) as the light source, a black paper photomask with the appropriate pattern and a fan to maintain the reaction mixture at room temperature. The Kessil lamp is placed at a distance of 5-10 cm from the petri dish.

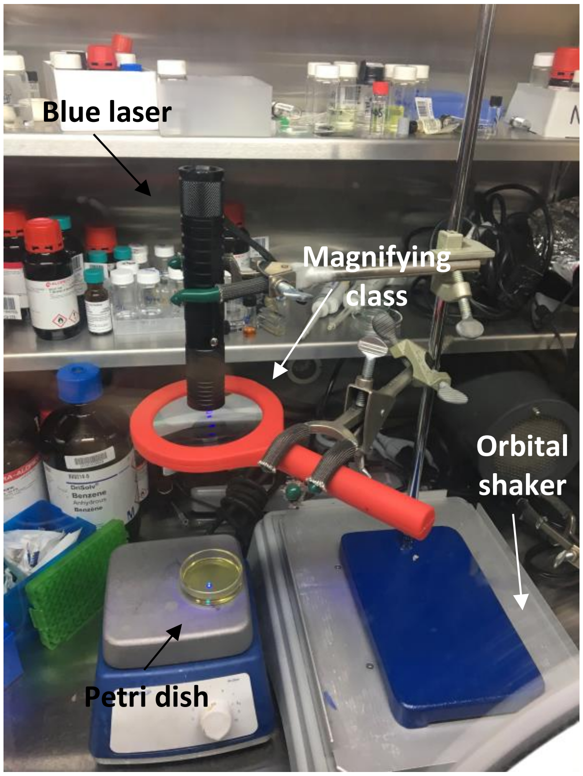




Examples of photomasks

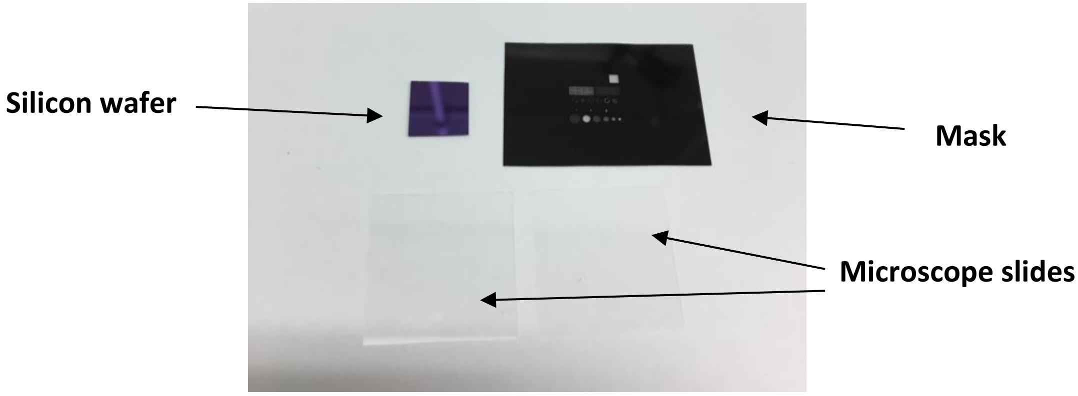
Experimental setup 3: polymer patterning using blue laser

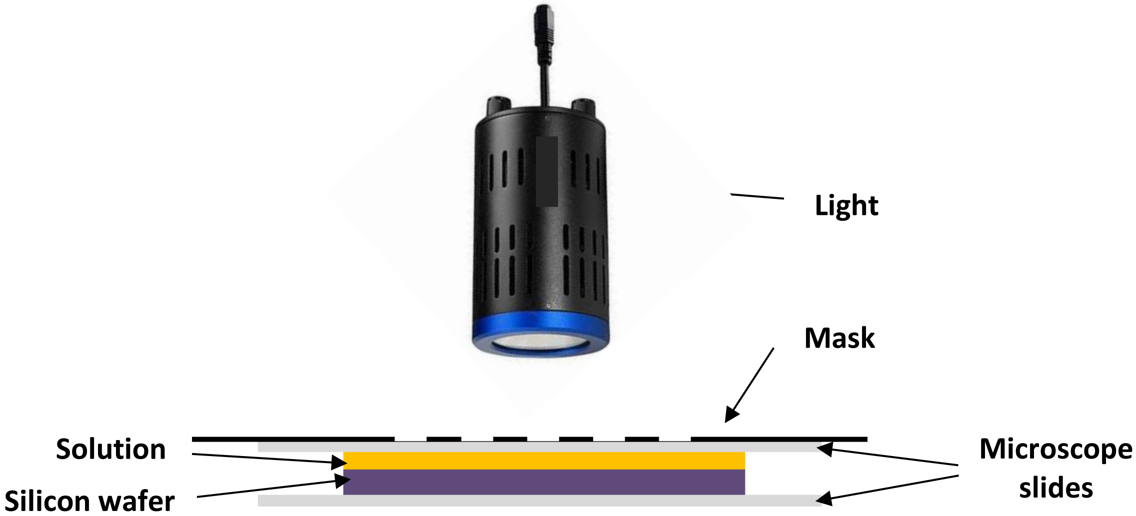
The polymer patterning experiments using blue lasers are conducted in a glovebox. The experimental setup includes: a BRAND® petri dish (glass) in which the polymerization is performed, a blue laser pointer (450 nm, 200 mW) as the light source and a magnifying glass to focus the laser beam. The support stand is moved either manually or with an orbital shaker to induce patterning. The blue laser is placed at a distance of 5-10 cm from the petri dish.



Experimental setup 4: photolithography on silicon wafers

The photolithographic experiments on silicon wafers are conducted in a glovebox. The experimental setup includes: a norbornene-pre-functionalized silicon wafer, two microscope slides (22 mm x 22 mm, thickness of 0.13-0.17 mm), a blue Kessil LED lamp (440 nm) as the light source, a high resolution photomask and a fan to maintain the system at room temperature. The Kessil lamp is placed at a distance of 5-10 cm from the silicon wafer.





Experimental Procedures and Characterization Data:
Metathesis for the Synthesis of Small Molecules

General Procedure A: ring closing and enyne metathesis

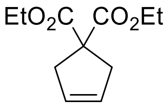
In a glovebox, an oven-dried 1-dram vial was charged with the substrate (0.2 mmol), 2,4,6-triphenylpyrylium tetrafluoroborate TPPT (2.4 mg, 6 µmol unless otherwise noted), CH_2Cl_2 (1 mL) and $RuCl_2(CHPh)(IMes)_2$ (3.5 mg, 4 µmol). The vial was tightly sealed and removed from the glovebox before stirring at room temperature under blue LEDs irradiation for 4h (experimental setup 1). The reaction mixture was then concentrated under vacuum and purified by flash column chromatography over silica gel.

General Procedure B: cross-metathesis

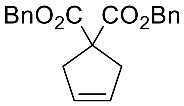
In a glovebox, an oven-dried 1-dram vial was charged with the limiting olefin (0.2 mmol), 2,4,6-triphenylpyrylium tetrafluoroborate TPPT (3.2 mg, 8 µmol), CH_2Cl_2 (1 mL), the excess olefin (0.4 mmol) and $RuCl_2(CHPh)(IMes)_2$ (3.5 mg, 4 µmol). The vial was tightly sealed and removed from the glovebox before stirring at room temperature under blue LEDs irradiation for 4h (experimental setup 1). The reaction mixture was then concentrated under vacuum and purified by flash column chromatography over silica gel.

General Procedure C: ring opening – cross-metathesis

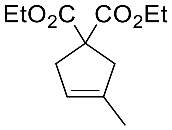
In a glovebox, an oven-dried 1-dram vial was charged with the cyclic olefin (0.2 mmol), 2,4,6-triphenylpyrylium tetrafluoroborate TPPT (3.2 mg, 8 µmol), CH_2Cl_2 (1 mL), the terminal olefin (0.6 mmol) and $RuCl_2(CHPh)(IMes)_2$ (3.5 mg, 4 µmol). The vial was tightly sealed and removed from the glovebox before stirring at room temperature under blue LEDs irradiation for 4h (experimental setup 1). The reaction mixture was then concentrated under vacuum and purified by flash column chromatography over silica gel.



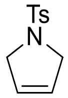
Diethyl cyclopent-3-ene-1,1-dicarboxylate. Prepared according to General Procedure A. Yield: 86% (36.7 mg, 173 μmol) from diethyl diallylmalonate, 80% (34.1 mg, 161 μmol) from diethyl 2-allyl-2-(3-methylbut-2-en-1-yl)malonate and 85% (36.2 mg, 170 μmol) from diethyl 2,2-bis-(but-2-enyl)malonate. Solvent system for flash column chromatography: hexanes/EtOAc: 95/5; Pale yellow oil. This compound has been previously reported.[9]



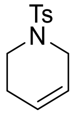
Dibenzyl cyclopent-3-ene-1,1-dicarboxylate. Prepared according to General Procedure A. Yield: 79% (53.4 mg, 159 μmol). Solvent system for flash column chromatography: hexanes/EtOAc: 95/5; Colorless oil. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.36-7.24 (m, 10H), 5.62 (s, 2H), 5.14 (s, 4H), 3.07 (s, 4H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 171.9, 135.6, 128.6, 128.3, 128.1, 127.9, 67.3, 59.0, 41.0; IR (ATR): ν_{max} 3063, 2926, 1756, 1724, 1459, 1246, 1163, 1062, 975, 731, 694, 453 cm^{-1}; ESIHRMS *m/z* calcd for $C_{21}H_{21}O_4$ [M+H]$^+$ 337.1434, found 337.1440.



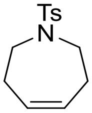
Diethyl 3-methylcyclopent-3-ene-1,1-dicarboxylate. Prepared according to General Procedure A. Yield: 84% (38.2 mg, 169 μmol). Solvent system for flash column chromatography: hexanes/EtOAc: 95/5; Colorless oil. This compound has been previously reported.[10]



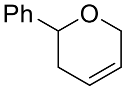
1-Tosyl-2,5-dihydro-1*H*-pyrrole. Prepared according to General Procedure A. Yield: 90% (40.2 mg, 180 µmol). Solvent system for flash column chromatography: hexanes/EtOAc: 90/10; White solid. This compound has been previously reported.[11]



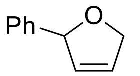
1-Tosyl-1,2,3,6-tetrahydropyridine. Prepared according to General Procedure A using 2 µmol of $RuCl_2(CHPh)(IMes)_2$ and 4 µmol of TPPT. Yield: 74% (35.3 mg, 149 µmol). Solvent system for flash column chromatography: hexanes/EtOAc: 90/10; White solid. This compound has been previously reported.[12]



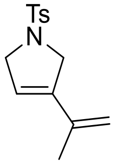
1-Tosyl-2,3,6,7-tetrahydro-1*H*-azepine. Prepared according to General Procedure A using 2 µmol of $RuCl_2(CHPh)(IMes)_2$ and 4 µmol of TPPT. Yield: 89% (45.0 mg, 179 µmol). Solvent system for flash column chromatography: hexanes/EtOAc: 95/5; White solid. This compound has been previously reported.[13]



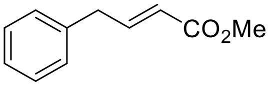
2-Phenyl-3,6-dihydro-2*H*-pyran. Prepared according to General Procedure A. Yield: 72% (23.0 mg, 143 µmol). Solvent system for flash column chromatography: hexanes/EtOAc: 97/3; Colorless oil. This compound has been previously reported.[14]



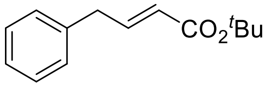
2-Phenyl-2,5-dihydrofuran. Prepared according to General Procedure A. Yield: 71% (20.8 mg, 142 µmol). Solvent system for flash column chromatography: hexanes/EtOAc: 97/3; Colorless oil. This compound has been previously reported.[15]



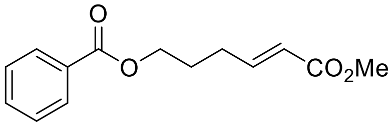
3-(Prop-1-en-2-yl)-1-tosyl-2,5-dihydro-1*H*-pyrrole. Prepared according to General Procedure A using 2 µmol of $RuCl_2(CHPh)(IMes)_2$ and 4 µmol of TPPT. Yield: 40% (21.1 mg, 80 µmol). Solvent system for flash column chromatography: hexanes/EtOAc: 97/3; White solid. This compound has been previously reported.[16]



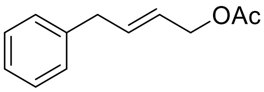
Methyl (*E*)-4-phenylbut-2-enoate. Prepared according to General Procedure B using allyl benzene (0.2 mmol) and methyl acrylate (0.4 mmol). Yield: 60% (21.3 mg, 121 µmol). Solvent system for flash column chromatography: hexanes/EtOAc: 95/5; Pale yellow oil. This compound has been previously reported.[17]



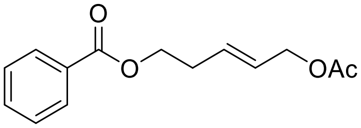
***tert*-Butyl (*E*)-4-phenylbut-2-enoate.** Prepared according to General Procedure B using allyl benzene (0.2 mmol) and *tert*-butyl acrylate (0.4 mmol). Yield: 50% (22.0 mg, 101 µmol). Solvent system for flash column chromatography: hexanes/EtOAc: 95/5; Pale yellow oil. This compound has been previously reported.[18]



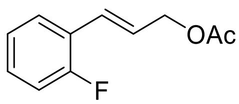
(*E*)-6-(*tert*-Butoxy)-6-oxohex-4-en-1-yl benzoate. Prepared according to General Procedure B using pent-4-en-1-yl benzoate (0.2 mmol) and methyl acrylate (0.4 mmol). Yield: 52% (25.8 mg, 104 µmol). Solvent system for flash column chromatography: hexanes/EtOAc: 90/10; Yellow oil. This compound has been previously reported.[19]



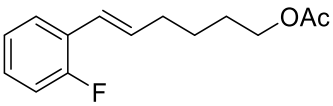
(*E*)-4-Phenylbut-2-en-1-yl acetate. Prepared according to General Procedure B using allyl benzene (0.2 mmol) and cis-1,4-diacetoxy-2-butene (0.4 mmol). Yield: 60% (*E*/*Z*: 9/1, 23.0 mg, 121 µmol). Solvent system for flash column chromatography: hexanes/EtOAc: 95/5; Colorless oil. This compound has been previously reported.[20]



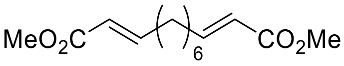
(*E*)-5-Acetoxypent-3-en-1-yl benzoate. Prepared according to General Procedure B using but-3-en-1-yl benzoate (0.2 mmol) and cis-1,4-diacetoxy-2-butene (0.4 mmol). Yield: 70% (*E*/*Z* : 9/1, 34.9 mg, 703 µmol). Solvent system for flash column chromatography: hexanes/EtOAc: 85/15; Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): *E* isomer δ 8.05 (app. d, *J* = 8.3 Hz, 2H), 7.58 (app. tt, *J* = 7.4 and 1.3 Hz, 1H), 7.46 (t, *J* = 8.1 Hz, 2H), 5.85 (dtt, *J* = 15.5, 6.6 and 1.2 Hz, 1H), 5.75 (dtt, *J* =15.5, 6.3 and 1.3 Hz, 1H), 4.55 (dd, *J* = 6.3 and 0.9 Hz, 2H), 4.39 (t, *J* = 6.5 Hz, 2H), 2.56 (qd, *J* = 6.7 and 1.1 Hz, 2H), 2.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.9, 166.6, 133.2, 131.1, 130.4, 129.7, 128.4, 127.0, 64.9, 63.8, 31.9, 21.1; IR (ATR): ν_{max} 2939, 1717, 1451, 1379, 1271, 1229, 1111, 1026, 968, 712 cm^{-1}; ESIHRMS *m/z* calcd for $C_{14}H_{16}O_4Na$ $[M+Na]^+$ 271.0941, found 271.0946.



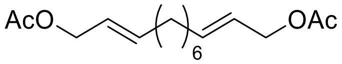
(*E*)-3-(2-Fluorophenyl)allyl acetate. Prepared according to General Procedure B using 2-fluorostyrene (0.2 mmol) and cis-1,4-diacetoxy-2-butene (0.4 mmol). Yield: 51% (20.1 mg, 103 µmol). Solvent system for flash column chromatography: hexanes/EtOAc: 90/10; Colorless oil. This compound has been previously reported.[21]



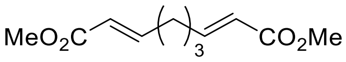
(*E*)-6-(2-Fluorophenyl)hex-5-en-1-yl acetate. Prepared according to General Procedure B using 2-fluorostyrene (0.2 mmol) and hex-5-en-1-yl acetate (0.4 mmol). Yield: 46% (21.7 mg, 92 µmol). Solvent system for flash column chromatography: hexanes/EtOAc: 96/4; Colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.42 (td, *J* = 7.7 and 1.7 Hz, 1H), 7.19-7.13 (m, 1H), 7.06 (td, *J* = 7.4 and 1.0 Hz, 1H), 7.00 (ddd, *J* = 10.9 , 8.1 and 1.1 Hz, 1H), 6.55 (d, *J* = 15.8 Hz, 1H), 6.28 (dt, *J* = 15.9 and 7.1 Hz, 1H), 4.09 (t, *J* = 6.6 Hz, 2H), 2.27 (qd, *J* = 7.4 and 1.2 Hz, 2H), 2.05 (s, 3H), 1.73-1.66 (m, 2H), 1.59-1.52 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 171.3, 160.0 (d, *J* = 246.6 Hz), 133.0 (d, *J* = 4.3 Hz), 128.2 (d, *J* = 8.3 Hz), 127.1 (d, *J* = 3.8 Hz), 125.5 (d, *J* = 12.3 Hz), 124.1 (d, *J* = 3.5 Hz), 122.8 (d, *J* = 3.6 Hz), 115.7 (d, *J* = 22.1 Hz), 64.4, 33.0, 28.2, 25.7, 21.1; ^{19}F NMR (470 MHz, CDCl$_3$): δ -119.4 (m); IR (ATR): ν_{max} 2934, 1736, 1486, 1365, 1233, 1037, 969, 754, 606 cm^{-1}; ESIHRMS *m/z* calcd for $C_{14}H_{17}FO_2Na$ $[M+Na]^+$ 259.1105, found 259.1110.



Dimethyl (2*E*,10*E*)-dodeca-2,10-dienedioate. Prepared according to General Procedure C using cis-cyclooctene (0.2 mmol) and methyl acrylate (0.6 mmol). Yield: 51% (26.0 mg, 102 µmol). Solvent system for flash column chromatography: hexanes/EtOAc: 90/10; Pale yellow oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.95 (dt, *J* = 15.5 and 6.9 Hz, 2H), 5.81 (dt, *J* = 15.6 and 1.5 Hz, 2H), 3.72 (s, 6H), 2.19 (qd, *J* = 7.2 and 1.5 Hz, 4H), 1.49-1.40 (m, 4H), 1.36-1.27 (m, 4H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 167.3, 149.7, 121.1, 51.5, 32.2, 29.0, 28.0; IR (ATR): ν_{max} 2927, 2854, 1721, 1656, 1435, 1269, 1195, 1178, 1038, 980, 716 cm^{-1}; ESIHRMS *m/z* calcd for $C_{14}H_{23}O_4$ [M+H]$^+$ 255.1591, found 255.1596.



(2*E*,10*E*)-Dodeca-2,10-diene-1,12-diyl diacetate. Prepared according to General Procedure C using cis-cyclooctene (0.2 mmol) and cis-1,4-diacetoxy-2-butene (0.6 mmol). Yield: 53% (E,E/E,Z: 9/1, 30.0 mg, 106 µmol). Solvent system for flash column chromatography: hexanes/EtOAc: 95/5; Colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$): *E*/*E* isomer δ 5.76 (app. dt, *J* = 15.3 and 6.8 Hz, 2H), 5.55 (dtt, *J* = 15.3, 6.5 and 1.3 Hz, 2H), 4.50 (dd, *J* = 6.5 and 0.7 Hz, 4H), 2.07-2.01 (m, 4H), 2.06 (obs. s, 6H), 1.42-1.33 (m, 4H), 1.32-1.25 (m, 4H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 171.0, 136.7, 123.9, 65.5, 32.3, 29.1, 28.9, 21.2; IR (ATR): ν_{max} 2926, 2854, 1737, 1446, 1363, 1228, 1023, 965, 698, 607 cm^{-1}; ESIHRMS *m/z* calcd for $C_{16}H_{26}O_4Na$ [M+Na]$^+$ 305.1723, found 305.1729.



Dimethyl (2*E*,7*E*)-nona-2,7-dienedioate. Prepared according to General Procedure C using cyclopentene (0.2 mmol) and methyl acrylate (0.6 mmol). Yield: 58% (24.5 mg, 115 µmol). Solvent system for flash column chromatography: hexanes/EtOAc: 90/10; Pale yellow oil. This compound has been previously reported.[22]

Experimental Procedure and Characterization Data:
Ring Opening Metathesis Polymerization

General Procedure

In a glovebox, an oven-dried 1-dram vial was charged with the monomer (0.2 mmol), 2,4,6-triphenylpyrylium tetrafluoroborate TPPT (0.79 mg, 2 µmol), CD_2Cl_2 (1 mL) and $RuCl_2(CHPh)(IMes)_2$ (0.87 mg, 1 µmol). Mesitylene (27.8 µL, 0.2 mmol) was added and used as internal standard to monitor conversion. The vial was tightly sealed and removed from the glovebox before stirring at room temperature under blue LEDs irradiation for 1h (experimental setup 1). The reaction mixture was then poured into methanol and the desired polymer was finally isolated by filtration, washed thoroughly with methanol and pentane and dried under vacuum.

Dicyclopentadiene was polymerized using 0.1 µmol *of* $RuCl_2(CHPh)(IMes)_2$ *and 0.5* µmol *of TPPT during 15 minutes.*

Poly[bicyclo[2.2.1]hept-2-ene] 1. Conversion: >95%. ^{1}H NMR (500 MHz, $CDCl_3$): δ5.34 (br. s, 1H), 5.21 (br. s, 1H), 2.79 (br. s, 1H), 2.43 (br. s, 1H), 1.96-1.68 (m, 3H), 1.35 (br. s, 2H), 1.12-0.93 (m, 1H).

Poly[*exo*,*exo*-dibenzyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate] 2. Conversion: >95%. ^{1}H NMR (500 MHz, $CDCl_3$): δ7.30-7.15 (m, 10H), 5.39-5.10 (m, 2H), 5.00-4.70 (m, 4H), 3.56-3.28 (m, 1H), 3.07-2.68 (m, 3H), 2.30-1.80 (m, 1H), 1.28-0.99 (m, 1H).

Poly[*exo*,*exo*-7-oxabicyclo[2.2.1]hept-5-ene-2,3-diylbis(methylene) diacetate] 3. Conversion: >95%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.79-5.52 (m, 2H), 4.49 (br. s, 1H), 4.24-4.07 (m, 5H), 2.06-2.01 (m, 6H).

Poly[(bicyclo[2.2.1]hept-5-en-2-yloxy)(*tert*-butyl)dimethylsilane] 4. Conversion: >95%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.47-5.09 (m, 2H), 3.63-3.31 (m, 2H), 3.02-2.32 (m, 2H), 2.21-1.65 (m, 3H), 1.52-1.04 (m, 2H), 0.89 (br. s, 9H), 0.02 (br. s, 6H).

Estimation of the k_{rel} light/dark for the polymerization of dicyclopentadiene 12

Following the general procedure described above, polymerization of dicyclopentadiene was performed under blue LED irradiation, stopped after 90 seconds and immediately quenched by addition of excess ethyl vinyl ether. Analysis of the crude reaction mixture by ^{1}H NMR showed 16% polymerization, which corresponds to 10.666% polymerization per minute (Experiment 1). Additionally, polymerization of dicyclopentadiene has also been performed with the reaction mixtures being maintained in the dark (wrapped with thin foil). The reaction mixtures were stirred in the dark for 24h (less than 5% polymerization observed), 3 days (5% polymerization observed) or 7 days (9% polymerization observed). From the last experiments (9% polymerization observed after 7 days), we can estimate the rate of polymerization in the dark to be $9\text{x}10^{-4}$ % polymerization per minute. The ratio between Experiment 2 and 4 ($10.6666/9\text{x}10^{-4}$) gives a k_{rel} light/dark of 12,000.

Experimental Procedures and Results:

Polymer Patterning using Masks

All patterning experiments were run in a glovebox to exclude oxygen and ensure good reproducibility. Importantly, performing the reaction outside the glovebox with no other precautions than flushing the reaction mixture with an argon flow gave identical results.

General Procedures

- Dicyclopentadiene **12** as monomer

In a glovebox, an oven-dried 20 mL scintillation vial was charged with 2,4,6-triphenylpyrylium tetrafluoroborate TPPT (2.0 mg, 5 µmol), CH_2Cl_2 (3 mL) and $RuCl_2(CHPh)(IMes)_2$ (0.87 mg, 1 µmol). Dicyclopentadiene (1.32 g, 10 mmol) was then added and the solution was transferred into a BRAND® petri dish (glass, 40 mm x 12 mm). The petri dish was placed on the mask and light was shined through the mask for 15 minutes (experimental setup 2). The petri dish was finally removed from the glovebox and the unreacted monomer was thoroughly washed away with dichloromethane to afford the desired patterned poly(dicyclopentadiene).

When the patterning experiments were performed on a bigger scale, the amounts of dicyclopentadiene, catalysts, dichloromethane and the size of the petri dish were adjusted as followed: dicyclopentadiene (7.93 g, 60 mmol), $RuCl_2(CHPh)(IMes)_2$ (5.2 mg, 6 µmol), 2,4,6-triphenylpyrylium tetrafluoroborate TPPT (11.9 mg, 30 µmol) and CH_2Cl_2 (26 mL) in a BRAND® petri dish (glass, 80 mm x 15 mm). Light was shined for 30 minutes.

- Norbornadiene **9** as monomer

In a glovebox, an oven-dried 20 mL scintillation vial was charged with 2,4,6-triphenylpyrylium tetrafluoroborate TPPT (5.9 mg, 15 µmol), CH_2Cl_2 (2.5 mL) and $RuCl_2(CHPh)(IMes)_2$ (6.5 mg, 7.5 µmol). Norbornadiene (1.52 mL, 15 mmol) was then added and the solution was transferred into a BRAND® petri dish (glass, 40 mm x 12 mm). The petri dish was placed on the mask and light was shined through the mask for 1h (experimental setup 2). The petri dish was finally removed from the glovebox and the unreacted monomer was thoroughly washed away with dichloromethane to afford the desired patterned poly(norbornadiene).

- 1,5-Cyclooctadiene **10** as monomer

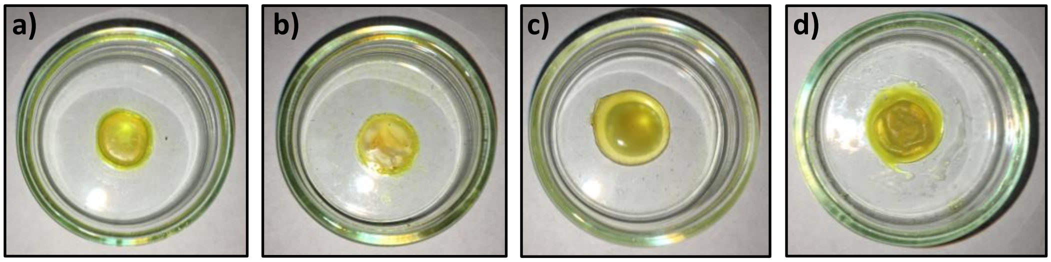
In a glovebox, an oven-dried 20 mL scintillation vial was charged with 2,4,6-triphenylpyrylium tetrafluoroborate TPPT (5.0 mg, 12.5 µmol), CH_2Cl_2 (2.5 mL) and $RuCl_2(CHPh)(IMes)_2$ (5.4 mg, 6.25 µmol). 1,5-Cyclooctadiene (1.53 mL, 12.5 mmol) was then added and the solution was transferred into a BRAND® petri dish (glass, 40 mm x 12 mm). The petri dish was placed on the mask and light was shined through the mask for 15 minutes (experimental setup 2). The petri dish was finally removed from the glovebox and the unreacted monomer was thoroughly washed away with dichloromethane to afford the desired patterned poly(1,5-cyclooctadiene).

- 5-Ethylidene-2-norbornene **11** as monomer

In a glovebox, an oven-dried 20 mL scintillation vial was charged with 2,4,6-triphenylpyrylium tetrafluoroborate TPPT (4.0 mg, 10 µmol), CH_2Cl_2 (2.5 mL) and $RuCl_2(CHPh)(IMes)_2$ (4.3 mg, 5 µmol). 5-Ethylidene-2-norbornene (1.34 mL, 10 mmol) was then added and the solution was transferred into a BRAND® petri dish (glass, 40 mm x 12 mm). The petri dish was placed on the mask and light was shined through the mask for 15 minutes (experimental setup 2). The petri dish was finally removed from the glovebox and the unreacted monomer was thoroughly washed away with dichloromethane to afford the desired patterned poly(5-ethylidene-2-norbornene).

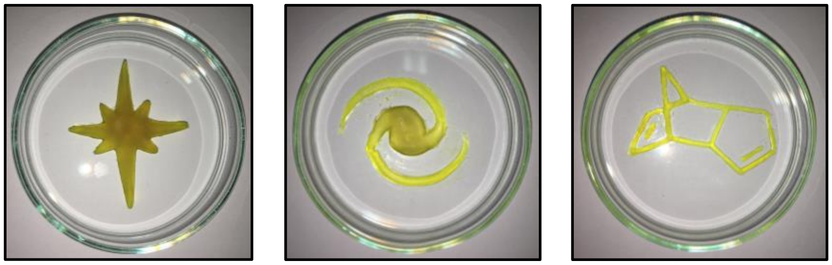
Results

- Pictures of patterned poly(**12**, **9**, **10** and **11**)



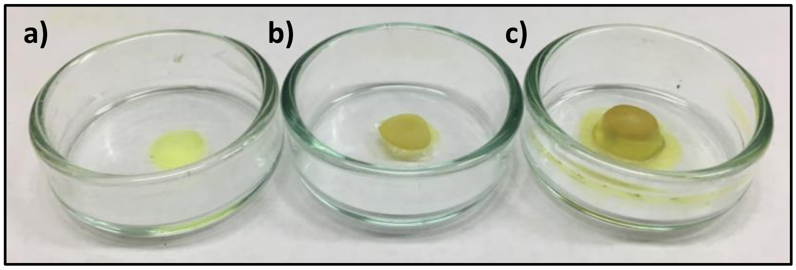
*Pictures of (a) poly(dicyclopentadiene **12**), (b) poly(norbornadiene **9**), (c) poly(1,5-cyclooctadiene **10**), (d) poly(5-ethylidene-2-norbornene **11**) in 40 mm x 12 mm petri dishes.*

- Pictures of more sophisticated patterns of poly(**12**)



*Pictures of more sophisticated patterns made of poly(dicyclopentadiene **12**) in 80 mm x 15 mm petri dishes.*

- Thickness as a function of irradiation time



*Picture of poly(dicyclopentadiene **12**) obtained after 5 minutes (a), 15 minutes (b) and 60 minutes (c) of irradiation under visible-light in 40 mm x 12 mm petri dishes.*

The thickness of the patterned polymers can be easily modulated by tuning the time of irradiation, as can be seen on the above picture displaying poly(dicyclopentadiene) patterns obtained after 5 minutes (0.2 mm), 15 minutes (1.6 – 2.0 mm) and 60 minutes (3.8 mm) of irradiation. All measures were made using an electronic digital micrometer).

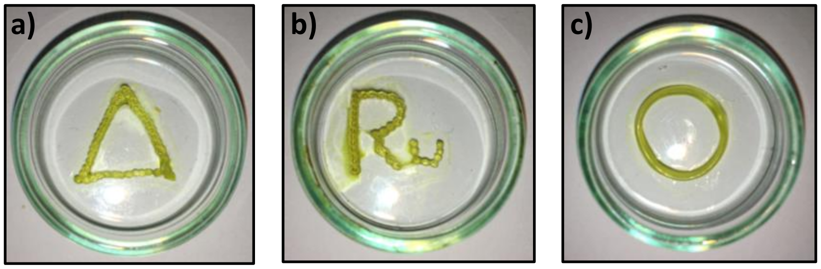
Experimental Procedure and Results:

Polymer Patterning using Blue Laser

General Procedure

In a glovebox, an oven-dried 20 mL scintillation vial was charged with 2,4,6-triphenylpyrylium tetrafluoroborate TPPT (2.0 mg, 5 µmol), CH_2Cl_2 (3 mL) and $RuCl_2(CHPh)(IMes)_2$ (0.87 mg, 1 µmol). Dicyclopentadiene (1.32 g, 10 mmol) was then added and the solution was transferred into a BRAND® petri dish (glass, 40 mm x 12 mm). Irradiation was carried out with a blue laser pointer (450 nm, 200 mW) through a magnifying glass. The support stand holding the laser was then moved either manually over 30-40 minutes or with an orbital shaker for 10 minutes (experimental setup 3). The petri dish was finally removed from the glovebox and unreacted monomer was thoroughly washed away with dichloromethane to afford the desired patterned poly(dicyclopentadiene).

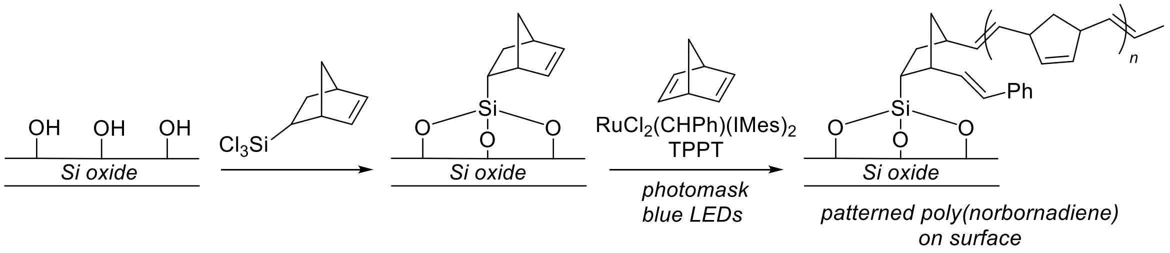
Results



(a,b) Pictures of poly(dicyclopentadiene ***12****) obtained after irradiation with a blue laser which was moved manually in 40 mm x 12 mm petri dishes. All dots required irradiation of around 20-25 seconds. The overall time of irradiation was around 30-40 minutes. (c) Picture of poly(dicyclopentadiene* ***12****) obtained after irradiation for 10 minutes with a blue laser which was moved with an orbital shaker in a 40 mm x 12 mm petri dish.*

Experimental Procedures and Results:
Photolithographic Applications on Silicon Wafers

The strategy exploited for the photolithographic ring-opening metathesis polymerization of norbornadiene onto silicon wafers is similar to the strategy previously reported by Fourkas and coworkers.[23] First, the functionalization of the silicon oxide layer of the silicon wafers with trichloro(5-norbornen-2-yl)silane was performed in order to attach a norbornene unit at the surface of the wafers. Our standard visible-light-promoted ring opening metathesis polymerization of norbornadiene was then performed on the silicon wafers which covalently bound to the growing polymer thanks to the norbornene unit present at the surface. Removal of the unreacted monomer finally afforded the desired patterned poly(norbornadiene) at the surface of the silicon wafers.



Functionalization of silicon wafers with trichloro(5-norbornen-2-yl)silane

Silicon wafers were cleaned by sonication in acetone (2 x 15 minutes) and isopropanol (2 x 15 minutes), rinsed with isopropanol, dried under a stream of N_2 and finally placed in an O_2 plasma chamber under vacuum (100 mTorr) using a power of 50 watts for 2 minutes. The silicon wafers were immediately functionalized with trichloro(5-norbornen-2-yl)silane.

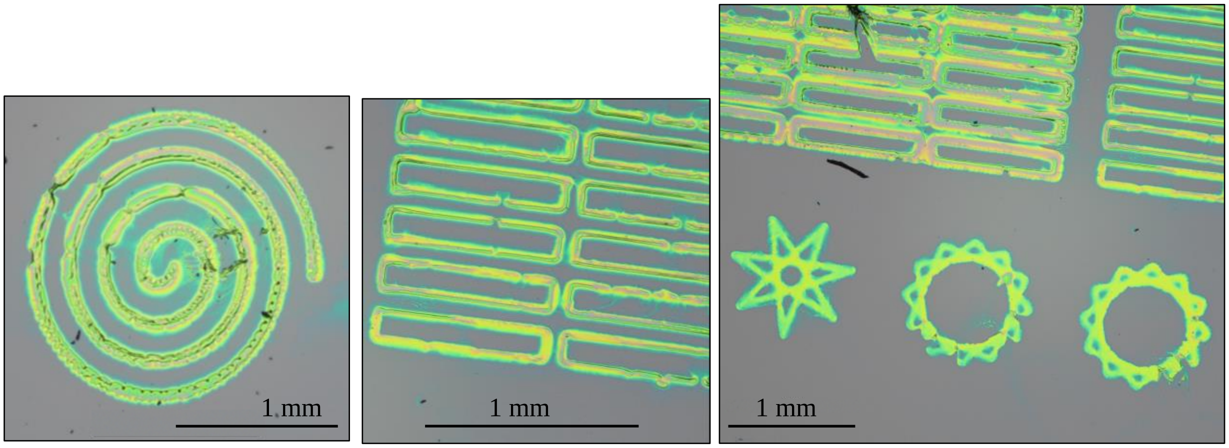
In a glovebox, a 60 mL screw-cap jar was charged with 20 mL of a solution of trichloro(5-norbornen-2-yl)silane (0.2 mL) in anhydrous toluene (20 mL). Four to five 1 cm x 1 cm silicon wafers with a native silicon oxide layer were added to the solution which was agitated overnight on an orbital shaker at room temperature. The silicon wafers were then thoroughly rinsed with anhydrous toluene, dried under a stream of N_2 and stored in a glovebox prior to use.

Angle contact measurements with a water drop were indicative of the successful grafting of the norbornene unit at the silicon wafer surface (34 ° for a non-functionalized silicon wafer, 85 ° for a norbornene-functionalized silicon wafer).

Procedure for the photolithographic patterning of norbornene-functionalized silicon wafers

In a glovebox, a norbornene-functionalized silicon wafer was placed on a microscope slide (22 mm x 22 mm, thickness of 0.13-0.17 mm). Four to five drops of a solution of norbornadiene (305 µL, 3 mmol), $RuCl_2(CHPh)(IMes)_2$ (1.3 mg, 1.5 µmol) and 2,4,6-triphenylpyrylium tetrafluoroborate (1.2 mg, 3 µmol) in CH_2Cl_2 (1 mL) were then added to cover the silicon wafer. A second microscope slide (22 mm x 22 mm, thickness of 0.13-0.17 mm) was then quickly placed on top of the silicon wafer/solution. The mask was then placed on top of the second microscope slide and light was shined through the mask for 10 minutes. The silicon wafer was developed by pouring it twice into DCM for 1 minute before letting it dry under a steam of N_2 to finally afford the desired patterned poly(norbornadiene) film.

Results

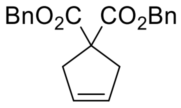


*Micrographs of poly(norbornadiene **9**) printed on norbornene-pre-functionalized silicon wafers. The width is 30 – 40 microns. The height of the poly(norbornadiene) films was evaluated to 200-300 nm by AFM measurements.*

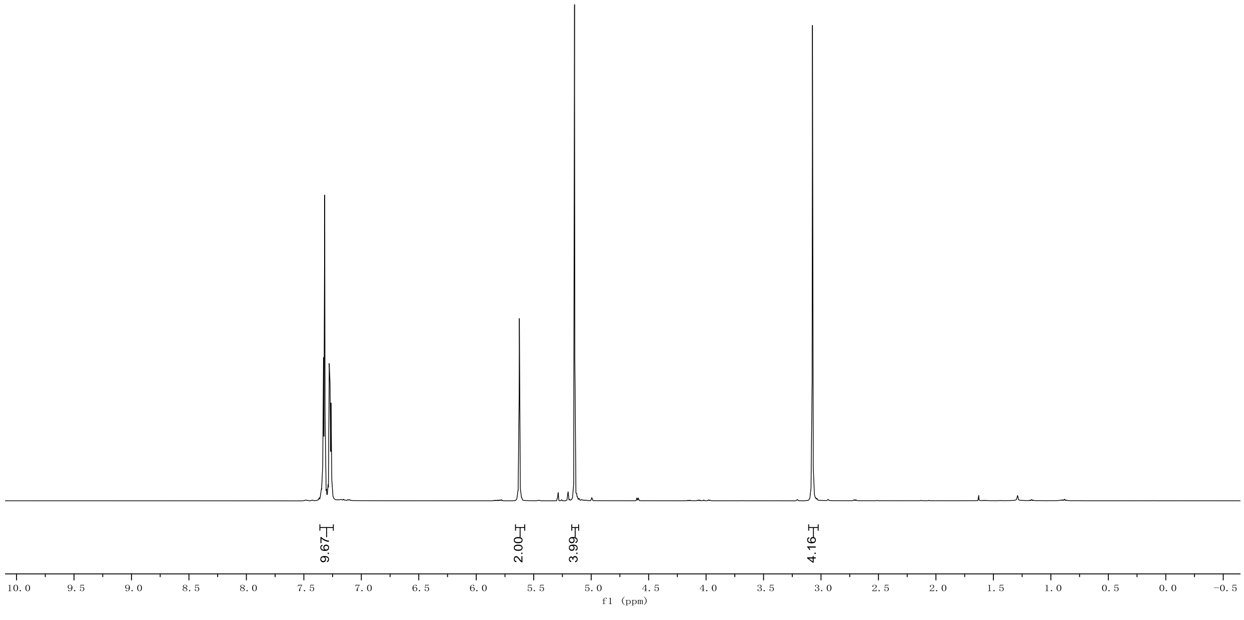
Supporting Information

^{1}H and ^{13}C NMR spectra:

Previously Unreported Compounds


BnO$_2$C
CO$_2$Bn

XX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9.5
9.0
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6.0
5.5
5.0
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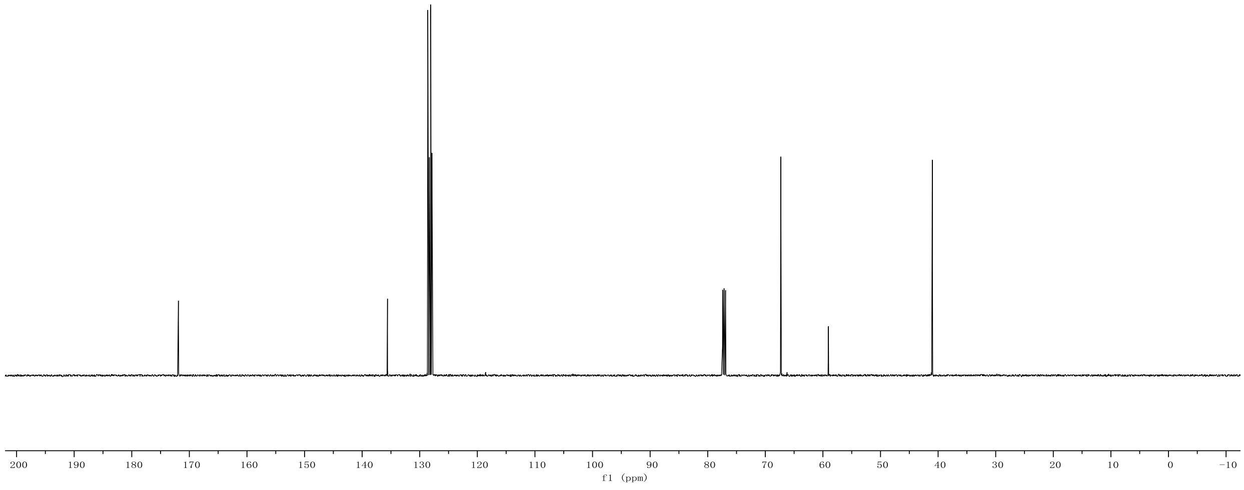
0.5
0.0
−0.5
f1 (ppm)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70
60
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30
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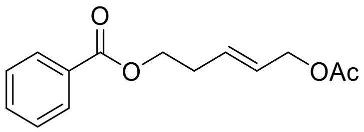
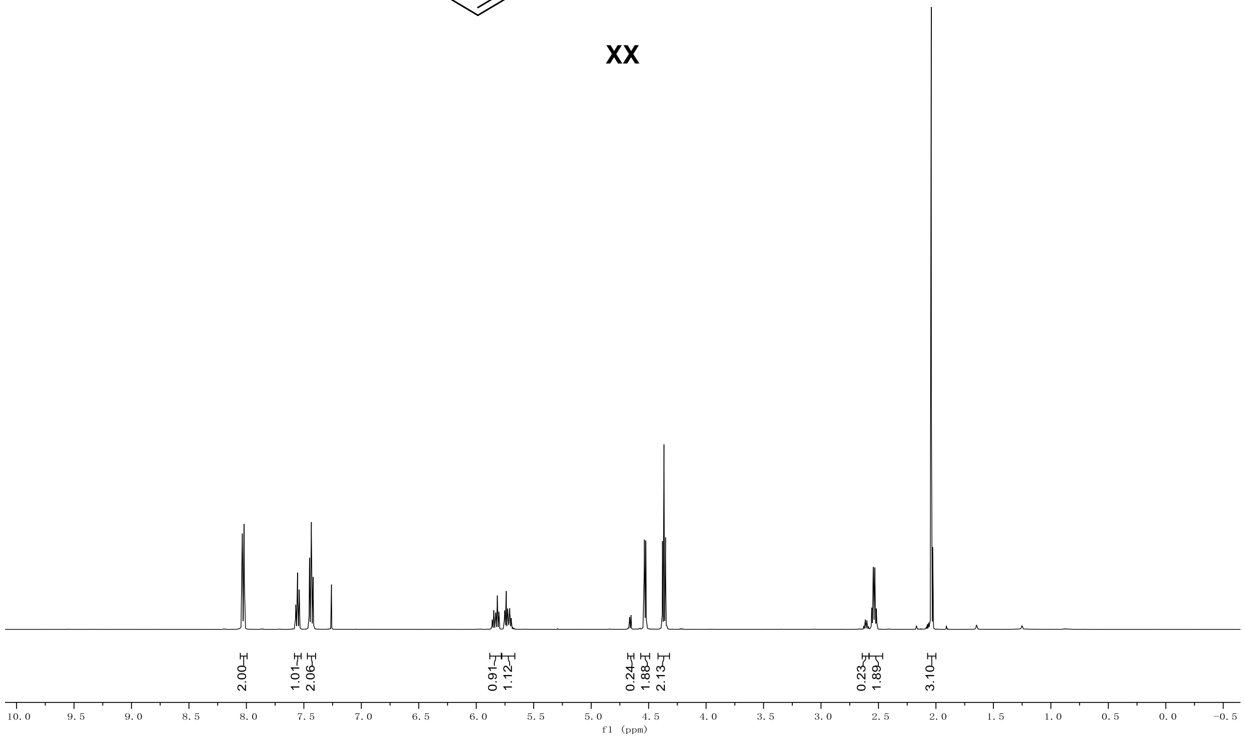
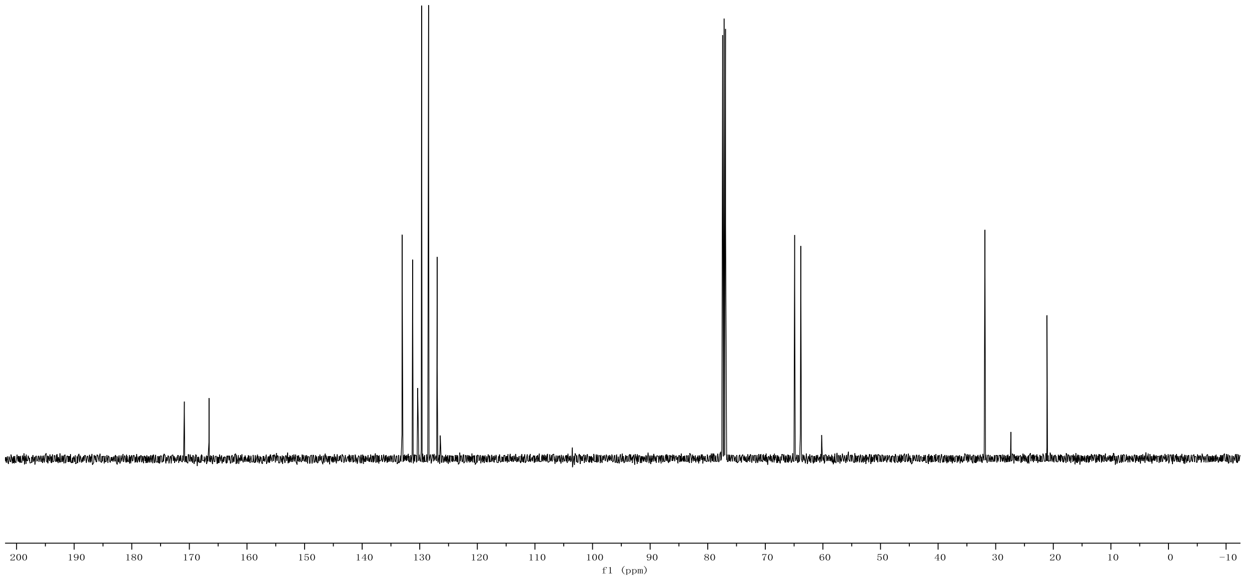
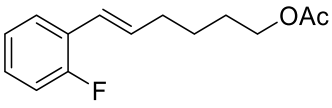
10
0
−10
f1 (ppm)


O
O
OAc

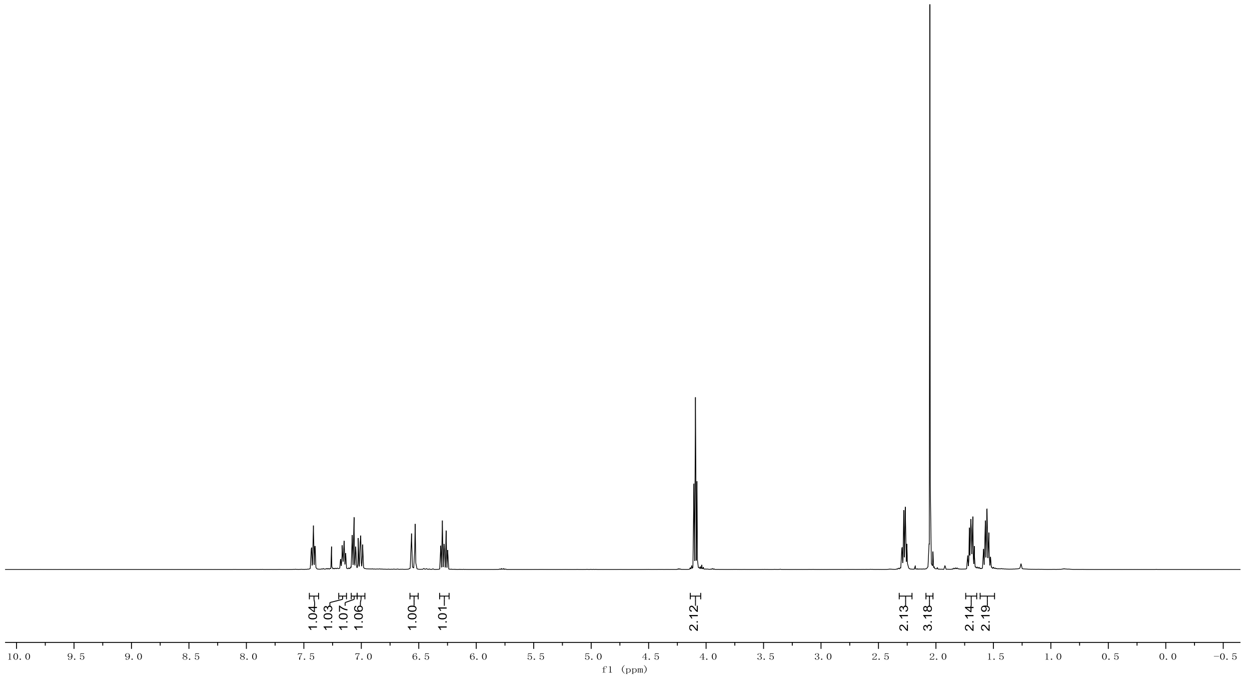
XX

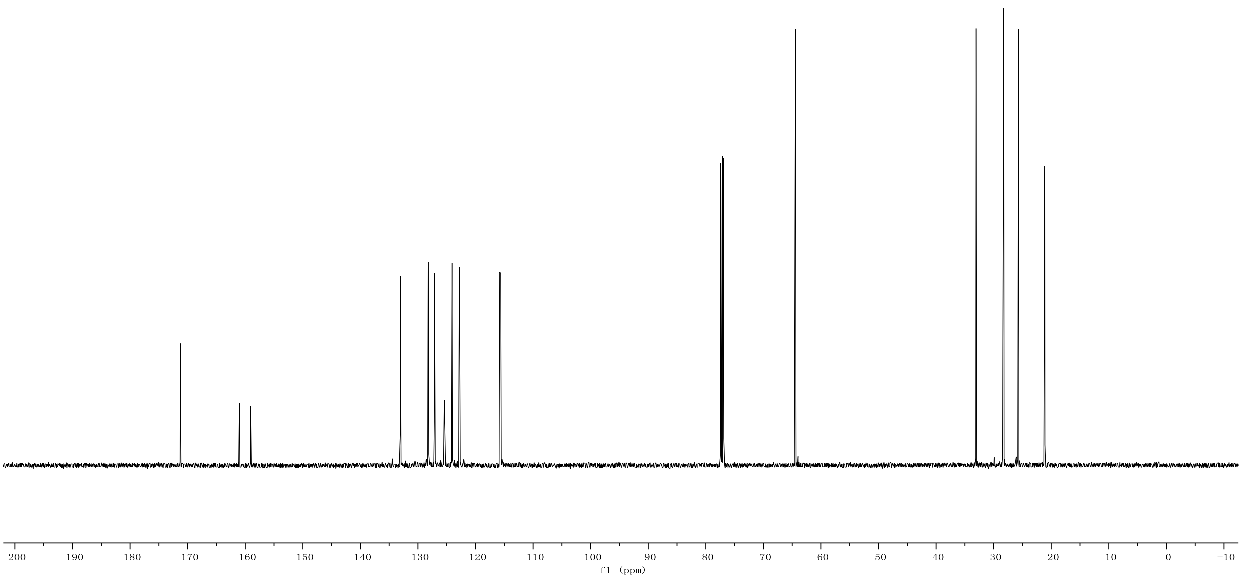

2.00
1.01
2.06
0.91
1.12
0.24
1.88
2.13
0.23
1.89
3.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

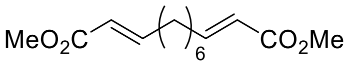

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OAc
F

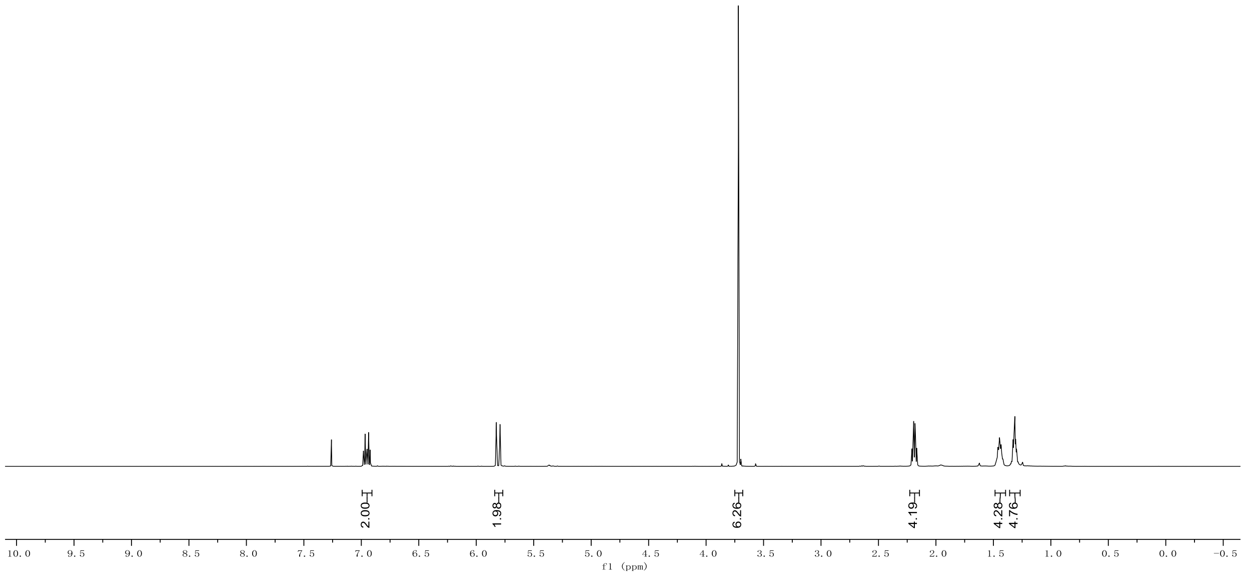
XX

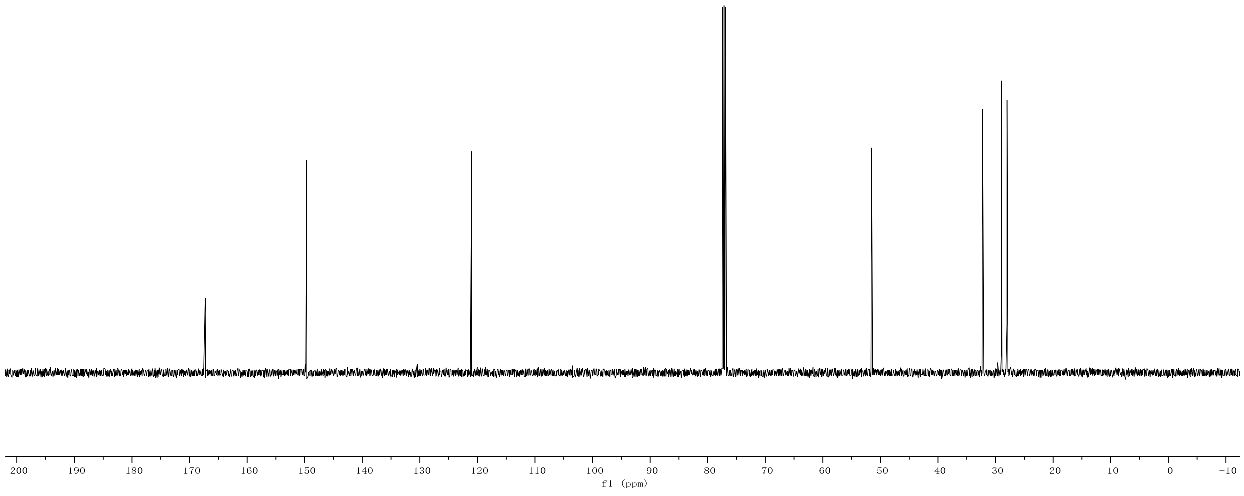

1.04
1.03
1.07
1.06
1.00
1.01
2.12
2.13
3.18
2.14
2.19
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

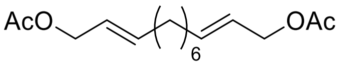

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


MeO$_2$C
6
CO$_2$Me

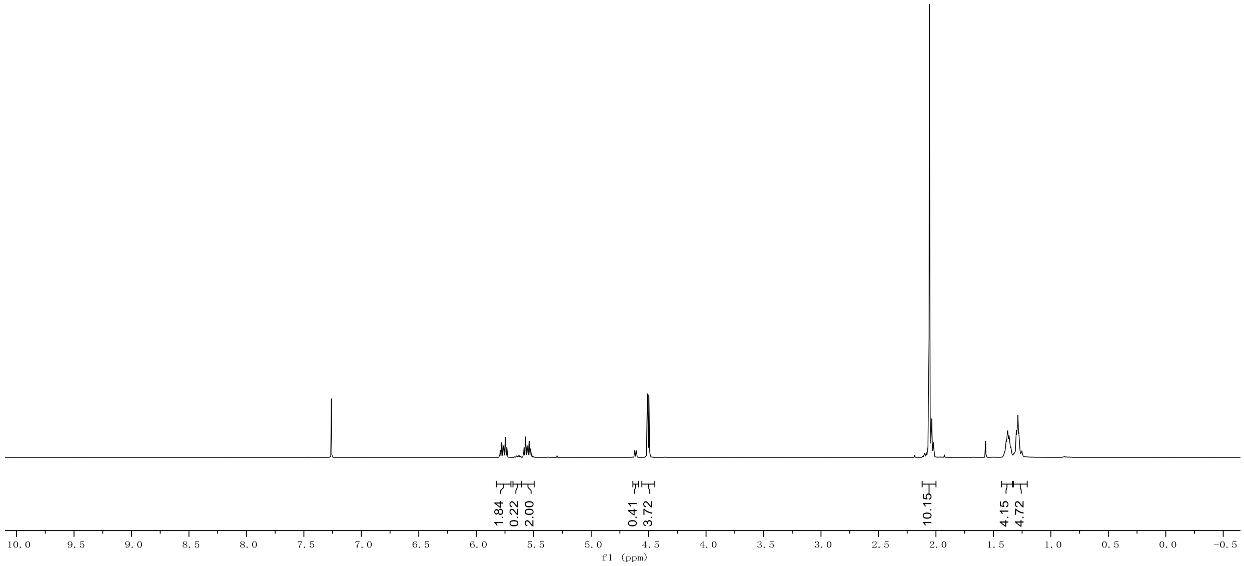
XX

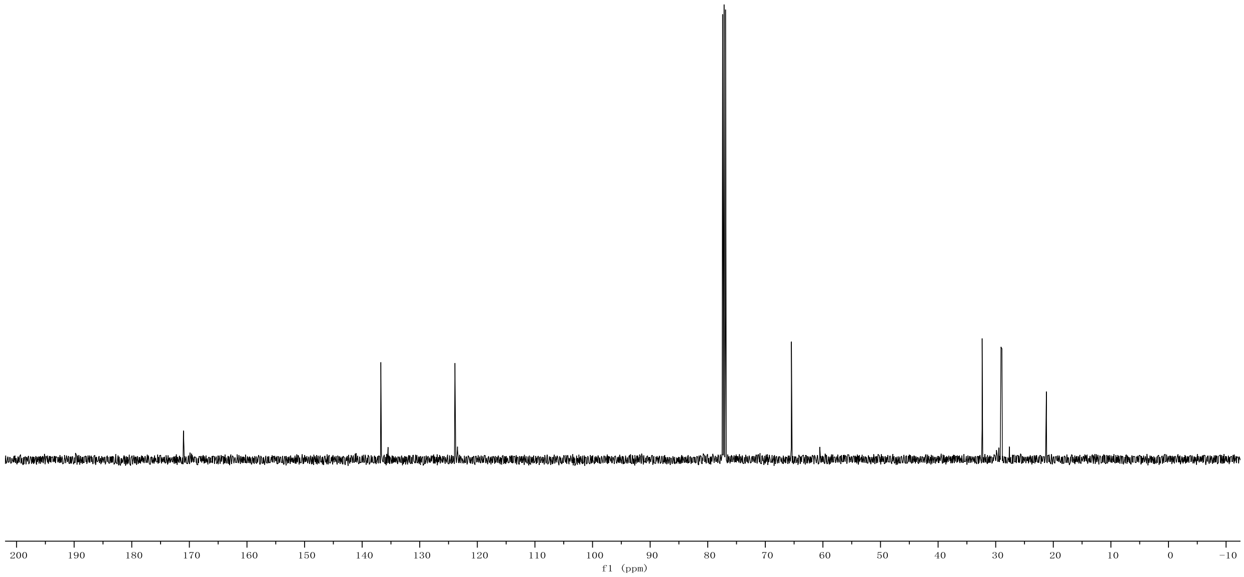

2.00
1.98
6.26
4.19
4.28
4.76
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


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


AcO
6
OAc

XX


1.84
0.22
2.00
0.41
3.72
10.15
4.15
4.72
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


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

References

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