Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Catalytic tert-alkylation on enamides via C-C bond cleavage under photoredox conditions

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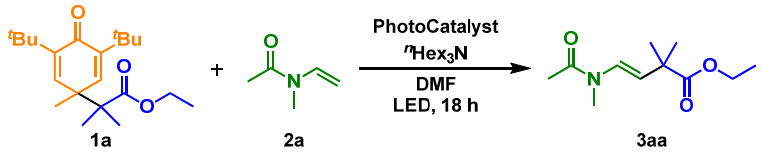
1. General Information

All reactions were carried out under nitrogen (99.95%) atmosphere. For TLC analyses precoated Kieselgel 60 F254 plates (Merck, 0.25 mm thick) were used; for column chromatography Silica *Flash*® P60 (SiliCycle, 40-63 μm) was used. Visualization was accomplished by UV light (254 nm), ^{1}H and ^{13}C NMR spectra were obtained using a JEOL 500 MHz NMR spectrometer. Chemical shifts for ^{1}H NMR were described in parts per million (chloroform as an internal standard δ = 7.26) in $CDCl_3$, unless otherwise noted. Chemical shifts for ^{13}C NMR were expressed in parts per million in $CDCl_3$ as an internal standard (δ = 77.16), unless otherwise noted. High resolution mass analyses (HRMS) were obtained using an ACQUITY UPLC/ TOF-MS for ESI. Infrared spectra were recorded on Agilent Technologies Cary 630 FTIR. Anhydrous solvents were purchased from Kanto Chemical Co., Ltd. Other chemicals (Such as PDI) were purchased from TCI, Aldrich, and Wako and directly used without further purification.

2. Screening of Reaction Conditions

Screening of photocatalysts. We started the screening of photocatalysts in the reaction of cyclohexadienone **1a** and enamide **2a** (Supporting Table 1). The reaction using Eosin Y, Rhodamine B and Rose Bengal upon 525 nm LED irradiation were not proceeded (entry 1-3). When the reaction using PTH and BDN respectively was conducted, trace product was obtained (entry 4,5). However, PDI produced the product **3aa** in 33% NMR yield (entry 6). When 4CzIPN was used upon 450 nm LED irradiation, the reaction was not proceeded (entry 7).

Supporting Table 1 Screening of photocatalysts.[a]

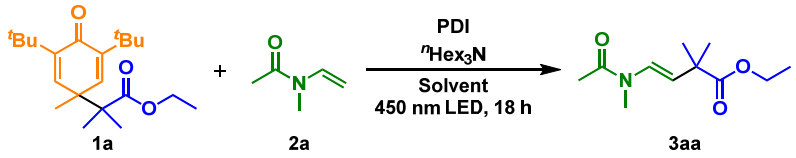


entry	photocatalyst	**3aa**[b]
1[c]	Eosin Y	0%
2[c]	Rhodamine B	0%
3[c]	Rose Bengal	0%
4[d]	PTH	6%
5[d]	BDN	Trace
6[e]	PDI	33%
7[e,f]	4CzIPN	0%

[a]A mixture of **1a** (0.50 mmol), **2a** (1.50 mmol), photocatalyst (2.50×10^{-3} mmol, 0.5 mol%), $^{n}Hex_3N$ (0.50 mmol), and DMF (1.0 mL) was irradiated for 18 h. [b]The product yields were determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. [c]525 nm LED light was used. [d]365 nm LED light was used. [e]450 nm LED light was used. [f]*n*-Bu_3N was used as base and NMP was used as solvent.

Screening of solvents. To obtain information about optimal solvents in the reaction of cyclohexadienone **1a** and enamide **2a** (Supporting Table 2). Several solvents did not afford the product **3aa** (entry 1-5). However, the reaction proceeded to give the product **3aa** in 68% NMR yield (isolated yield 58%) when NMP was used.

Supporting Table 2 Screening of solvents.[a]

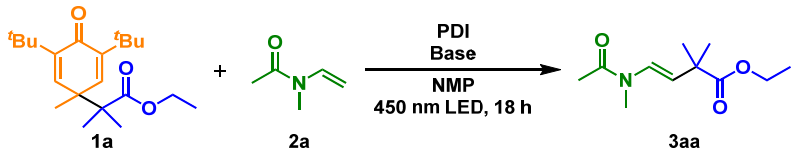


entry	solvent	**3aa**[b]
1	Toluene	0%
2	MeCN	0%
3	1,4-dioxane	0%
4	DCM	0%
5	DMSO	0%
6	DMF	33%
7[f]	NMP	68% (58%)[c]

[a]A mixture of **1a** (0.50 mmol), **2a** (1.50 mmol), PDI (2.50×10^{-3} mmol, 0.5 mol%), $^{n}Hex_3N$ (0.50 mmol), and solvent (1.0 mL) was irradiated for 18 h. [b]The product yields were determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. [c]Isolated product yields are shown in parentheses.

Screening of bases. We investigated the effects of bases (Supporting Table 3). Addition of Et_3N or $^{n}Bu_3N$ was increased the yield of **3aa** (entry 1,2). On the other hand, the product yield was decreased when DIPEA was used (entry 4). Several bases, such as $^{i}Pr_2NH$ and aniline, did not afford the product **3aa** (entry 5-9).

Supporting Table 3 Screening of bases.[a]

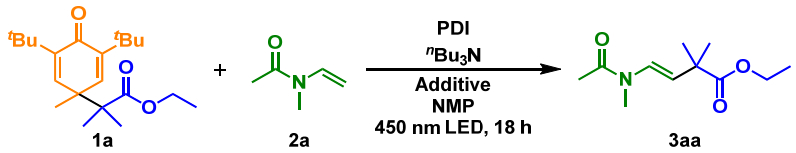


entry	base	**3aa**[b]
1	Et_3N	72% (60%)[c]
2	$^{n}Bu_3N$	78% (61%)[c]
3	$^{n}Hex_3N$	68% (58%)[c]
4	DIPEA	32% (21%)[c]
5	$^{i}Pr_2NH$	0%
6	pyrrolidine	0%
7[f]	DABCO	0%
8	DBU	0%
9	aniline	0%

[a]A mixture of **1a** (0.50 mmol), **2a** (1.50 mmol), PDI (2.50×10^{-3} mmol, 0.5 mol%), base (0.50 mmol), and NMP (1.0 mL) was irradiated for 18 h. [b]The product yields were determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. [c]Isolated product yields are shown in parentheses.

Screening of additives. To obtain information about effects of additive in the reaction of cyclohexadienone **1a** and enamide **2a** (Supporting Table 4). When the reaction using inorganic base such as Cs_2CO_3 and NaO^{t}Bu was conducted, the product **3aa** was not obtained (entry 1,2). Next, we investigated about the effects of Lewis acid. Although addition of $MgBr_2$ was decreased the product yield, the yield of **3aa** was improved when $MgCl_2$ was added (entry 3,4). When 30 mol% of $MgCl_2$ was added, the reaction proceeded to give the product **3aa** in 81% NMR yield (isolated yield: 68%) (entry 5). However, addition of $AlCl_3$ was decreased the yield of **3aa** (entry 6). Finally, we did not get a good effect when metal such as Mg and Al was added in the reaction mixture (entry 7,8).

Supporting Table 4 Screening of additives.[a]

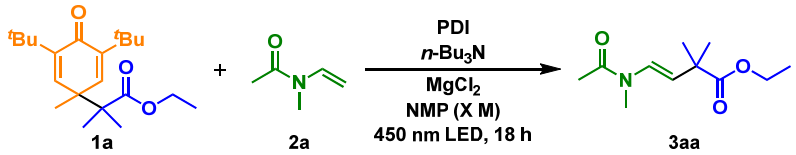


entry	additive	**3aa**[b]
1	Cs_2CO_3	0%
2	NaO^{t}Bu	0%
3	$MgBr_2$	55%
4	$MgCl_2$	83%
5[c]	$MgCl_2$	81% (68%)[d]
6	$AlCl_3$	24%
7[f]	Mg	65%
8	Al	63%

[a]A mixture of **1a** (0.50 mmol), **2a** (1.50 mmol), PDI (2.50×10^{-3} mmol, 0.5 mol%), ^{n}Bu$_3$N (0.50 mmol), additive (0.50 mmol) and NMP (1.0 mL) was irradiated for 18 h. [b]The product yields were determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. [c]30 mol% of $MgCl_2$ was used. [d]Isolated product yields are shown in parentheses.

Screening of concentration. We investigated the effects of concentration (Supporting Table 5). When the reaction was performed at a low concentration, the desired product **3aa** was obtained in 77% NMR yield (entry 2). On the other hand, the reaction at 0.6 M proceeded to give the product **3aa** in >99% NMR yield (isolated yield: 80%) (entry 3).

Supporting Table 5 Screening of concentration.[a]

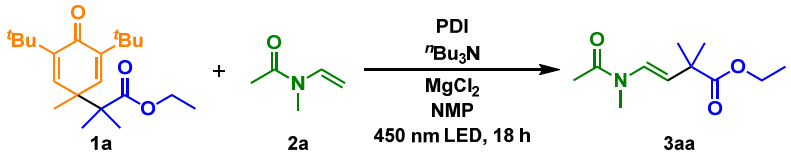


entry	concentration (X M)	**3aa**[b]
1	0.5 M	81% (68%)[c]
2	0.4 M	77%
3	0.6 M	>99% (80%)[c]

[a]A mixture of **1a** (0.30 mmol), **2a** (0.90 mmol), PDI (1.50×10^{-3} mmol, 0.5 mol%), ^{n}Bu$_3$N (0.30 mmol), $MgCl_2$ (9.0×10^{-2} mmol, 30 mol%) and NMP was irradiated for 18 h. [b]The product yields were determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. [c]Isolated product yields are shown in parentheses.

Control experiments. In the reaction of cyclohexadienone **1a** and enamide **2a**, the control experiments were carried out (Supporting Table 6). In the absence of PDI or ^{n}Bu$_3$N, the reaction did not proceed (entry 1,2). Next, the product was not afforded when the reaction was performed without LED light irradiation (entry 3). These results indicate that photocatalyst, amine reductant and visible light were all required for this transformation. We investigated the effect of LED wavelength. When 525 nm or 365 nm LED light was irradiated, the reaction did not proceed (entry 4,5). Finally, the reaction proceeded to give the product **3aa** in 75% NMR yield when 30 W 450 nm LED was irradiated (entry 6).

Supporting Table 6 Control experiments.[a]



entry	variation	3aa[b]
1	Without PDI	0%
2	Without $^{n}Bu_3N$	0%
3	In the dark	0%
4	525 nm LED irradiation	0%
5	365 nm LED irradiation	0%
6	30 W 450 nm LED irradiation	75%

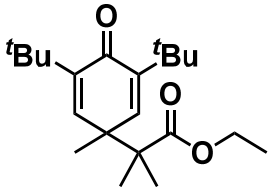
[a]A mixture of **1a** (0.30 mmol), **2a** (0.90 mmol), PDI (1.50×10^{-3} mmol, 0.5 mol%), $^{n}Bu_3N$ (0.30 mmol), $MgCl_2$ (9.0×10^{-2} mmol, 30 mol%) and NMP (0.5 mL) was irradiated for 18 h. [b]The product yields were determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard.

3. Procedures and Characterization data of alkyl transfer reaction

General procedure for synthesis of cyclohexadienone

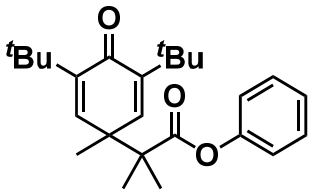
CuI (10 mol%), dtbbpy (10 mol%), and BHT (1.0 equiv.) were sequentially added under air to a dram vial equipped with a stir bar. The corresponding α-bromo carbonyl compound (1.0 equiv.) and DBU (2.0 equiv.), and dried toluene (1.0 M) were added by syringe, and the resulting mixture was vigorously stirred under nitrogen atmosphere [charged by general N_2 (99.95%) gas flow] for overnight at room temperature. After this time, the contents of the flask were filtered through a plug of silica gel and then concentrated by rotary evaporation. The residue was purified by flash chromatography, eluting with hexane/EtOAc to afford the product **1**.

ethyl 2-(3,5-di-tert-butyl-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)-2-methylpropanoate (**1a**)[1]



Following the general procedure above, using BHT (605.0 mg, 3.0 mmol), ethyl 2-bromo-2-methylpropanoate (585.2 mg, 3.0 mmol), CuI (57.2 mg, 0.30 mmol), dtbbpy (81.6 mg, 0.30 mmol), DBU (913.4 mg, 6.0 mmol) and dried toluene (3.0 mL) at room temperature for overnight, yielded the product **1a** (948.1 mg, 94%) as yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ: 6.55 (s, 2H), 4.13 (q, J = 7.2 Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H), 1.23 (s, 18H), 1.21 (s, 3H), 1.14 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 186.2, 175.4, 147.0, 143.7, 60.7, 49.0, 42.9, 34.9, 29.5, 21.9, 21.6, 14.3.

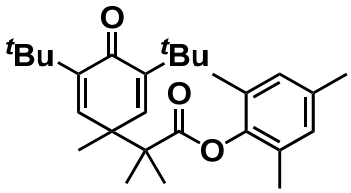
phenyl 2-(3,5-di-tert-butyl-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)-2-methylpropanoate (**1b**)



Following the general procedure above, using BHT (220.6 mg, 1.0 mmol), phenyl 2-bromo-2-methylpropanoate (247.5 mg, 1.0 mmol), CuI (19.0 mg, 0.10 mmol), dtbbpy (26.4 mg, 0.10 mmol), DBU (304.5 mg, 2.0 mmol) and dried toluene (1.0 mL) at room temperature for overnight, yielded the product **1b** (641.9 mg, 85%) as yellow oil; IR (cm^{-1}): 2951, 2867, 1744, 1656, 1628, 1591, 1482, 1454, 1363, 1249, 1185, 1160, 1100, 930, 879, 744, 689; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.39 (t, J = 8.0 Hz, 2H), 7.24 (t, J =

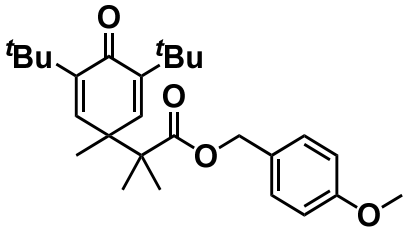
7.4 Hz, 1H), 7.05-7.02 (m, 2H), 6.68 (s, 2H), 1.34 (s, 3H), 1.31 (s, 6H), 1.23 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 186.2, 174.2, 150.7, 147.4, 143.3, 129.5, 125.9, 121.4, 49.4, 43.1, 35.1, 29.5, 22.1, 21.8; HRMS (TOF-MS) calcd. for $C_{25}H_{34}O_3Na$ ($M+Na^+$): 405.2406; found 405.2404.

mesityl 2-(3,5-di-tert-butyl-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)-2-methylpropanoate (**1c**)



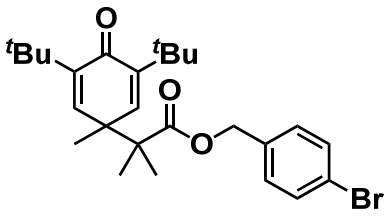
Following the general procedure above, using BHT (220.4 mg, 1.0 mmol), mesityl 2-bromo-2-methylpropanoate (301.4 mg, 1.1 mmol), CuI (19.5 mg, 0.10 mmol), dtbbpy (26.8 mg, 0.10 mmol), DBU (456.7 mg, 3.0 mmol) and dried toluene (1.0 mL) at room temperature for overnight, yielded the product **1c** (879.0 mg, 99%) as yellow oil; IR (cm^{-1}): 2952, 2868, 1734, 1639, 1464, 1248, 1192, 1125, 1101, 877, 853; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.88 (s, 2H), 6.77 (s, 2H), 2.27 (s, 3H), 2.13 (s, 6H), 1.42 (s, 3H), 1.34 (s, 6H), 1.24 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 186.3, 173.9, 147.6, 146.2, 143.6, 135.5, 129.5, 129.4, 49.7, 43.4, 35.1, 29.6, 22.8, 22.1, 20.8, 17.1; HRMS (TOF-MS) calcd. for $C_{28}H_{40}O_3Na$ ($M+Na^+$): 447.2875; found 447.2876.

4-methoxybenzyl 2-(3,5-di-tert-butyl-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)-2-methylpropanoate (**1d**)



Following the general procedure above, using BHT (221.5 mg, 1.0 mmol), 4-methoxybenzyl 2-bromo-2-methylpropanoate (284.2 mg, 0.99 mmol), CuI (19.3 mg, 0.10 mmol), dtbbpy (26.8 mg, 0.10 mmol), DBU (456.7 mg, 3.0 mmol) and dried toluene (1.0 mL) at room temperature for overnight, yielded the product **1d** (846.0 mg, 99%) as yellow oil; IR (cm^{-1}): 2953, 2867, 1720, 1657, 1637, 1514, 1457, 1364, 1245, 1132, 1035, 879, 821; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.30 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 6.48 (s, 2H), 5.06 (s, 2H), 3.80 (s, 3H), 1.18 (s, 18H), 1.16 (s, 3H), 1.13 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 186.2, 175.4, 159.7, 147.2, 143.6, 130.2, 128.0, 114.0, 66.4, 55.3, 49.1, 43.0, 34.9, 29.5, 22.0, 21.6; HRMS (TOF-MS) calcd. for $C_{27}H_{38}O_4Na$ ($M+Na^+$): 449.2668; found 449.2667.

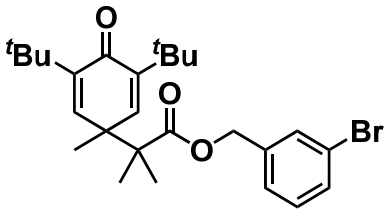
4-bromobenzyl 2-(3,5-di-tert-butyl-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)-2-methylpropanoate (**1e**)



Following the general procedure above, using BHT (440.8 mg, 2.0 mmol), 4-bromobenzyl 2-bromo-2-methylpropanoate (672.0 mg, 2.0 mmol), CuI (38.0 mg, 0.20 mmol), dtbbpy (53.6 mg, 0.20 mmol), DBU (608.9 mg, 4.0 mmol) and dried toluene (2.0 mL) at room temperature for overnight, yielded the product **1e** (760.8 mg, 80%) as yellow oil; IR (cm^{-1}): 2954, 2866, 1724, 1657, 1638, 1487, 1458, 1364, 1250, 1133, 1107, 1070, 1012, 879, 798; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.49 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 6.48 (s, 2H), 5.05 (s, 2H), 1.18 (s, 21H), 1.16 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 186.2, 175.2, 147.3, 143.3, 134.8, 131.8, 130.1, 122.4, 65.8, 49.2, 43.0, 34.9, 29.4, 22.0, 21.6; HRMS (TOF-MS) calcd.

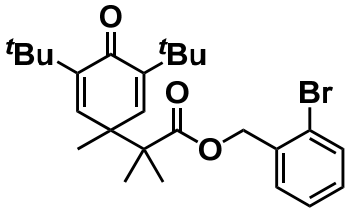
for $C_{26}H_{35}BrO_3Na$ ($M+Na^+$): 497.1667; found 497.1669.

3-bromobenzyl 2-(3,5-di-tert-butyl-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)-2-methylpropanoate (**1f**)



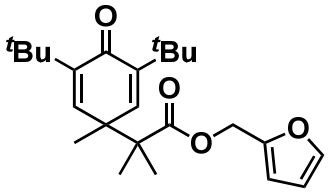
Following the general procedure above, using BHT (440.8 mg, 2.0 mmol), 3-bromobenzyl 2-bromo-2-methylpropanoate (672.0 mg, 2.0 mmol), CuI (38.0 mg, 0.20 mmol), dtbbpy (53.6 mg, 0.20 mmol), DBU (608.9 mg, 4.0 mmol) and dried toluene (2.0 mL) at room temperature for overnight, yielded the product **1f** (779.8 mg, 82%) as yellow oil; IR (cm^{-1}): 2953, 2866, 1723, 1657, 1637, 1487, 1457, 1364, 1249, 1131, 1070, 1012, 879, 799; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.52 (d, J = 8.1 Hz, 1H), 7.47 (d, J = 8.1 Hz, 1H), 7.29 (d, J = 8.1 Hz, 1H), 7.23 (d, J = 7.8 Hz, 1H), 6.49 (s, 2H), 5.07 (s, 2H), 1.19 (s, 3H), 1.19 (s, 18H), 1.17 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 186.2, 175.2, 147.3, 143.3, 138.0, 131.5, 131.3, 130.3, 126.8, 122.7, 65.7, 49.3, 43.0, 35.0, 29.5, 22.0, 21.6; HRMS (TOF-MS) calcd. for $C_{26}H_{35}BrO_3Na$ ($M+Na^+$): 497.1667; found 497.1667.

2-bromobenzyl 2-(3,5-di-tert-butyl-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)-2-methylpropanoate (**1g**)



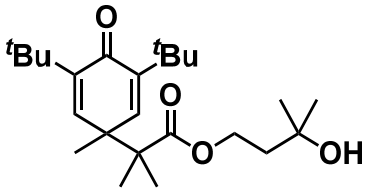
Following the general procedure above, using BHT (440.8 mg, 2.0 mmol), 2-bromobenzyl 2-bromo-2-methylpropanoate (672.0 mg, 2.0 mmol), CuI (38.0 mg, 0.20 mmol), dtbbpy (53.6 mg, 0.20 mmol), DBU (608.9 mg, 4.0 mmol) and dried toluene (2.0 mL) at room temperature for overnight, yielded the product **1g** (770.2 mg, 81%) as yellow oil; IR (cm^{-1}): 2954, 2866, 1726, 1658, 1638, 1458, 1364, 1241, 1133, 1046, 879, 750; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.59 (d, J = 7.9 Hz, 1H), 7.42 (d, J = 7.9 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.21 (t, J = 7.8 Hz, 1H), 6.52 (s, 2H), 5.19 (s, 2H), 1.23 (s, 3H), 1.18 (s, 24H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 186.3, 175.2, 147.3, 143.5, 135.1, 133.0, 130.4, 130.0, 127.6, 123.8, 66.3, 49.4, 43.0, 34.9, 29.5, 22.1, 21.7; HRMS (TOF-MS) calcd. for $C_{26}H_{35}BrO_3Na$ ($M+Na^+$): 497.1667; found 497.1669.

furan-2-ylmethyl 2-(3,5-di-tert-butyl-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)-2-methylpropanoate (**1h**)



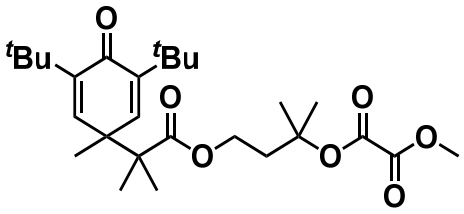
Following the general procedure above, using BHT (220.0 mg, 1.0 mmol), furan-2-ylmethyl 2-bromo-2-methylpropanoate (245.9 mg, 1.0 mmol), CuI (19.5 mg, 0.10 mmol), dtbbpy (26.6 mg, 0.10 mmol), DBU (456.7 mg, 3.0 mmol) and dried toluene (1.0 mL) at room temperature for overnight, yielded the product **1h** (637.1 mg, 82%) as yellow oil; IR (cm^{-1}): 2953, 2867, 1724, 1658, 1638, 1457, 1364, 1250, 1126, 1079, 1016, 918, 880, 814, 740; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.41 (dd, J = 0.8, 1.9 Hz, 1H), 6.49 (s, 2H), 6.42 (dd, J = 0.4, 3.5 Hz, 1H), 6.36 (dd, J = 1.8, 3.3 Hz, 1H), 5.08 (s, 2H), 1.20 (s, 18H), 1.15 (s, 3H), 1.13 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 186.2, 175.1, 149.4, 147.2, 143.5, 143.3, 110.9, 110.6, 58.2, 49.1, 43.0, 34.9, 29.5, 21.9, 21.5; HRMS (TOF-MS) calcd. for $C_{24}H_{34}O_4Na$ ($M+Na^+$): 409.2355; found 409.2357.

3-hydroxy-3-methylbutyl-2-(3,5-di-tert-butyl-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)-2-methylpropanoate (**1i**)



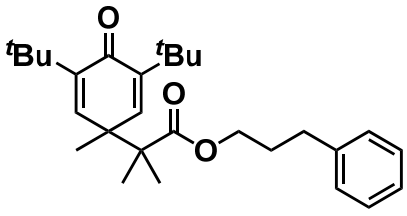
Following the general procedure above, using BHT (4406.8 mg, 20 mmol), 3-hydroxy-3-methylbutyl 2-bromo-2-methylpropanoate (5062.8 mg, 20 mmol), CuI (380.9 mg, 2.0 mmol), dtbbpy (536.8 mg, 2.0 mmol), DBU (6089.6 mg, 40 mmol) and dried toluene (40 mL) at room temperature for overnight, yielded the product **1i** (3376.2 mg, 43%) as a yellow oil; IR (cm^{-1}): 3515, 2958, 2868, 1719, 1657, 1637, 1458, 1364, 1251, 1165, 1137, 1079, 931, 879, 739; ^1H NMR (500 MHz, $CDCl_3$) δ: 6.54 (s, 2H), 4.25 (t, J = 7.1 Hz, 2H), 1.85 (t, J = 7.1 Hz, 2H), 1.27 (s, 6H), 1.23 (s, 18H), 1.21 (s, 3H), 1.14 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 186.2, 175.5, 147.2, 143.5, 69.9, 61.8, 49.0, 43.0, 41.7, 35.0, 29.7, 29.5, 21.9, 21.7; HRMS (TOF-MS) calcd. for $C_{24}H_{40}O_4Na$ ($M+Na^+$): 415.2824; found 415.2826.

4-((2-(3,5-di-tert-butyl-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)-2-methylpropanoyl)oxy)-2-methylbutan-2-yl methyl oxalate (**1j**)



Cyclohexadienone **1i** (7066.4 mg, 18 mmol) and DMAP (219.9 mg, 1.8 mmol) were added under air to a flask equipped with a stir bar and Et_3N (4.99 mL, 36 mmol) and dried DCM (55 mL) were added by syringe. Then, methyl 2-chloro-2-oxoacetate (1.82 mL, 19.8 mmol) was dropped into the mixture at 0℃. After stirring overnight at room temperature, the contents were washed with saturated aqueous $NaHCO_3$ and brine (20 mL). The combined organic layer was dried over $MgSO_4$ and evaporated. The crude residue was purified by flash chromatography, eluting hexane-EtOAc to afford the product **1j** (4135.4 mg, 48%) as yellow oil; IR (cm^{-1}): 2954, 1723, 1658, 1637, 1457, 1364, 1324, 1251, 1201, 1167, 1128, 880, 790, 739; ^1H NMR (500 MHz, $CDCl_3$) δ: 6.53 (s, 2H), 4.20 (t, J = 7.2 Hz, 2H), 3.87 (s, 3H), 2.21 (t, J = 7.2 Hz, 2H), 1.59 (s, 6H), 1.23 (s, 18H), 1.21 (s, 3H), 1.14 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 186.1, 175.3, 158.6, 156.6, 147.1, 143.4, 85.2, 60.6, 53.4, 49.1, 42.9, 39.1, 34.9, 29.5, 25.9, 21.9, 21.6; HRMS (TOF-MS) calcd. for $C_{27}H_{42}O_7Na$ ($M+Na^+$): 501.2828; found 501.2829.

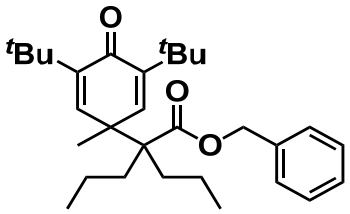
3-phenylpropyl 2-(3,5-di-tert-butyl-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)-2-methylpropanoate (**1k**)



Following the general procedure above, using BHT (220.1 mg, 1.0 mmol), 3-phenylpropyl 2-bromo-2-methylpropanoate (282.9 mg, 1.0 mmol), CuI (19.6 mg, 0.10 mmol), dtbbpy (26.7 mg, 0.10 mmol), DBU (456.7 mg, 3.0 mmol) and dried toluene (1.0 mL) at room temperature for overnight, yielded the product **1k** (424.0 mg, 99%) as yellow oil; IR (cm^{-1}): 2952, 2865, 1721, 1658, 1637, 1454, 1364, 1251, 1164, 1136, 1020, 879, 741, 698; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.31-7.28 (m, 2H), 7.22-7.16 (m, 3H), 6.55 (s, 2H), 4.11 (t, J = 6.6 Hz, 2H), 2.70 (t, J = 7.7 Hz, 2H), 2.00-1.97 (m, 2H), 1.23 (s, 18H), 1.22 (s, 3H), 1.15 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 186.2, 175.5, 147.2, 143.6, 141.0, 128.5, 128.4, 126.2, 64.2, 49.2,

43.0, 35.0, 32.3, 30.3, 29.5, 22.0, 21.7; HRMS (TOF-MS) calcd. for $C_{28}H_{40}O_3Na$ ($M+Na^+$): 447.2875; found 447.2876.

benzyl 2-(3,5-di-tert-butyl-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)-2-propylpentanoate (**1l**)

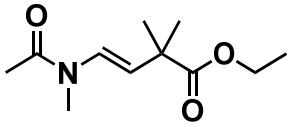


Following the general procedure above, using BHT (305.5 mg, 1.4 mmol), benzyl 2-bromo-2-propylpentanoate (438.5 mg, 1.4 mmol), CuI (27.3 mg, 0.14 mmol), dtbbpy (37.5 mg, 0.14 mmol), DBU (426.3 mg, 2.8 mmol) and dried toluene (1.4 mL) at room temperature for overnight, yielded the product **1l** (92.9 mg, 89%) as yellow oil; IR (cm^{-1}): 2958, 2871, 1720, 1656, 1637, 1455, 1363, 1211, 1140, 1044, 903, 880, 739, 696; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.38-7.33 (m, 5H), 6.56 (s, 2H), 5.15 (s, 2H), 1.73-1.66 (m, 2H), 1.54-1.49 (m, 2H), 1.23-1.21 (m, 4H), 1.18 (s, 18H), 1.14 (s, 3H), 0.83 (t, J = 7.3 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 186.1, 174.5, 145.8, 144.6, 135.7, 128.6, 128.4, 128.1, 66.5, 56.1, 43.9, 42.1, 34.9, 34.2, 29.3, 23.2, 21.0, 18.5, 14.9, 14.2; HRMS (TOF-MS) calcd. for $C_{30}H_{44}O_3Na$ ($M+Na^+$): 475.3188; found 475.3190.

General procedure for alkyl transfer reaction

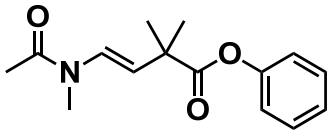
1 (0.50 mmol, 1.0 equiv), PDI (1.8 mg, 2.5×10^{-3} mmol, 0.50 mol%) were added into a 5 mL screw-vial under air. Then, $MgCl_2$ (14.2 mg, 0.15 mmol, 30 mol%), **2** (1.5 mmol, 3.0 equiv), ^{n}Bu$_3$N (0.50 mmol, 1.0 equiv) and dried NMP (0.8 mL) were added in glovebox and sealed the vial. The reaction mixture was stirred upon 450 nm LED light irradiation in the photoreactor. After 18 hours, the reaction mixture was extracted with AcOEt and dried with anhydrous $MgSO_4$. After removal of the solvent in vacuum, the residue was purified with silica gel column chromatography to give desired products **3** as rotamers.

ethyl (E)-2,2-dimethyl-4-(N-methylacetamido)but-3-enoate (**3aa**)



Following the general procedure above, using **1a** (100.3 mg, 0.30 mmol), **2a** (89.2 mg, 0.90 mmol), PDI (1.1 mg, 1.5×10^{-3} mmol), ^{n}Bu$_3$N (55.6 mg, 0.30 mmol), $MgCl_2$ (8.3 mg, 0.09 mmol) and dried NMP (0.5 mL) upon 450 nm LED light irradiation for 18 h, yielded the product **3aa** (51.2 mg, 80%) as red oil; IR (cm^{-1}): 2976, 1723, 1675, 1642, 1380, 1245, 1140, 1018, 936; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.43 and 6.68 (both d, J = 14.8 and 14.0 Hz, 1H, rotamers), 5.20 and 5.19 (both d, J = 14.8 and 14.1 Hz, 1H, rotamers), 4.14 and 4.12 (both q, J = 7.0 and 7.2 Hz, 2H, rotamers), 3.10 and 3.06 (both s, 3H, rotamers), 2.21 and 2.20 (both s, 3H, rotamers), 1.35 (s, 6H), 1.27-1.23 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 176.8 and 176.4 (rotamers), 169.3 and 169.1 (rotamers), 128.2 and 126.2 (rotamers), 116.2 and 115.9 (rotamers), 60.9 and 60.8 (rotamers), 43.0 and 42.8 (rotamers), 33.1 and 29.5 (rotamers), 25.69 and 25.66 (rotamers), 22.8 and 22.0 (rotamers), 14.24 and 14.22 (rotamers); HRMS (TOF-MS) calcd. for $C_{11}H_{20}NO_3$ ($M+H^+$): 214.1443; found 214.1445.

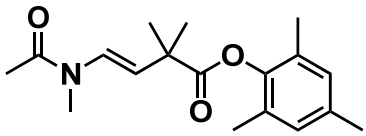
phenyl (E)-2,2-dimethyl-4-(N-methylacetamido)-but-3-enoate (**3ba**)



Following the general procedure above, using **1b** (191.3 mg, 0.50 mmol), **2a** (148.7 mg, 1.5 mmol), PDI (1.8 mg, 2.5×10^{-3} mmol), ^{n}Bu$_3$N (92.7 mg, 0.5 mmol), $MgCl_2$ (14.2 mg, 0.15 mmol) and dried NMP (0.8

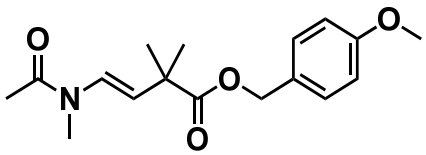
mL) upon 450 nm LED light irradiation for 18 h, yielded the product **3ba** (91.5 mg, 70%) as red oil; IR (cm^{-1}): 2974, 1745, 1675, 1642, 1472, 1380, 1191, 1101, 1018; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.57 and 6.82 (both d, J = 14.9 and 14.1 Hz, 1H, rotamers), 7.40-7.35 (m, 2H), 7.25-7.22 (m, 1H), 7.06-7.04 (m, 2H), 5.32 (d, J = 14.4 Hz, 1H), 3.14 and 3.11 (both s, 3H, rotamers), 2.25 and 2.23 (both s, 3H, rotamers), 1.51 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 175.3 and 175.0 (rotamers), 169.4 and 169.3 (rotamers), 151.1 and 151.0 (rotamers), 129.5 and 129.4 (rotamers), 128.9 and 126.9 (rotamers), 125.9 and 125.8 (rotamers), 121.5 and 121.4 (rotamers), 115.2 and 115.0 (rotamers), 43.4 and 43.1 (rotamers), 33.1, 29.5, 25.7, 22.8, 22.0; HRMS (TOF-MS) calcd. for $C_{15}H_{20}NO_3$ ($M+H^+$): 262.1443; found 262.1443.

mesityl (E)-2,2-dimethyl-4-(N-methylacetamido)-but-3-enoate (**3ca**)



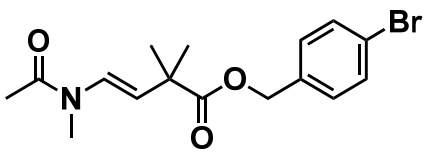
Following the general procedure above, using **1c** (212.1 mg, 0.5 mmol), **2a** (148.7 mg, 1.5 mmol), PDI (1.8 mg, 2.5×10^{-3} mmol), $^nBu_3N$ (92.7 mg, 0.5 mmol), $MgCl_2$ (16.5 mg, 0.15 mmol) and dried NMP (0.83 mL) upon 450 nm LED light irradiation for 18 h, yielded the product **3ca** (100.0 mg, 66%) as red oil; IR (cm^{-1}): 2922, 1738, 1640, 1473, 1378, 1353, 1306, 1244, 1193, 1118, 1022, 960, 868; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.57 and 6.84 (both d, J = 14.8 and 14.2 Hz, 1H, rotamers), 6.85 and 6.84 (both s, 2H, rotamers), 5.40 and 5.39 (both d, J = 14.9 and 14.1 Hz, 1H, rotamers), 3.14 and 3.11 (both s, 3H, rotamers), 2.26 and 2.25 (both s, 3H, rotamers), 2.23 (s, 3H), 2.06 (s, 6H), 1.54 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 174.4 and 174.1 (rotamers), 169.3 and 169.2 (rotamers), 145.99 and 145.91 (rotamers), 135.3 and 135.1 (rotamers), 129.68 and 129.60 (rotamers), 129.38 and 129.31 (rotamers), 128.9 and 126.8 (rotamers), 115.4 and 115.2 (rotamers), 43.5 and 43.2 (rotamers), 33.1 and 29.4 (rotamers), 25.7, 22.8 and 22.0 (rotamers), 20.8, 16.3; HRMS (TOF-MS) calcd. for $C_{18}H_{26}NO_3$ ($M+H^{+)}$: 304.1913 found 304.1914.

4-methoxybenzyl (E)-2,2-dimethyl-4-(N-methylacetamido)-but-3-enoate (**3da**)



Following the general procedure above, using **1d** (213.5 mg, 0.5 mmol), **2a** (148.7 mg, 1.5 mmol), PDI (1.7 mg, 2.5×10^{-3} mmol), $^nBu_3N$ (92.7 mg, 0.5 mmol), $MgCl_2$ (16.9 mg, 0.15 mmol) and dried NMP (0.8 mL) upon 450 nm LED light irradiation for 18 h, yielded the product **3da** (109.7 mg, 71%) as red oil; IR (cm^{-1}): 2969, 1722, 1674, 1641, 1513, 1465, 1381, 1302, 1241, 1120, 1018, 932, 821; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.43 and 6.63 (both d, J = 15.1 and 14.1 Hz, 1H, rotamers), 7.27 (m, 2H), 6.89-6.86 (m, 2H), 5.19 and 5.16 (both d, J = 14.9 and 14.1 Hz, 1H, rotamers), 5.06 and 5.04 (both s, 2H, rotamers), 3.80 (s, 3H), 3.06 and 3.02 (both s, 3H, rotamers), 2.20 and 2.13 (both s, 3H, rotamers), 1.35 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 176.6 and 176.2 (rotamers), 169.3 and 169.1 (rotamers), 159.6 and 159.5 (rotamers), 129.8 and 129.7 (rotamers), 128.4 and 128.3 (rotamers), 128.2 and 126.3 (rotamers), 116.0 and 115.6 (rotamers), 113.98 and 113.93 (rotamers), 66.4 and 66.3 (rotamers), 55.3, 43.1 and 42.9 (rotamers), 33.1 and 29.4 (rotamers), 25.7 and 25.5 (rotamers), 22.7 and 21.9 (rotamers); HRMS (TOF-MS) calcd. for $C_{17}H_{24}NO_4$ ($M+H^+$): 306.1705; found 306.1705.

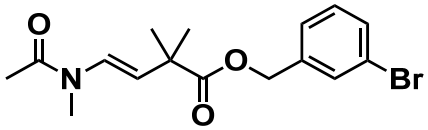
4-bromophenyl (E)-2,2-dimethyl-4-(N-methylacetamido)-but-3-enoate (**3ea**)



Following the general procedure above, using **1e** (237.8 mg, 0.5 mmol), **2a** (148.7 mg, 1.5 mmol), PDI (1.8

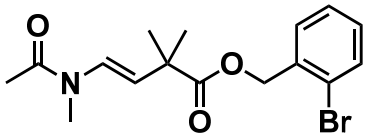
mg, 2.5×10^{-3} mmol), $^{n}Bu_3N$ (92.7 mg, 0.5 mmol), $MgCl_2$ (16.9 mg, 0.15 mmol) and dried NMP (0.83 mL) upon 450 nm LED light irradiation for 18 h, yielded the product **3ea** (106.4 mg, 60%) as red oil; IR (cm^{-1}): 2971, 1725, 1675, 1642, 1380, 1242, 1121, 1012, 936, 799; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.48 (m, 2H), 7.45 and 6.66 (both d, J = 14.6 and 14.1 Hz, 1H, rotamers), 7.21 (m, 2H), 5.17 (d, J = 13.9 Hz, 1H), 5.07 and 5.05 (both s, 2H, rotamers), 3.07 and 3.04 (both s, 3H, rotamers), 2.21 and 2.16 (both s, 3H, rotamers), 1.37 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 176.4 and 176.1 (rotamers), 169.3 and 169.2 (rotamers), 135.2 and 135.1 (rotamers), 131.8 and 131.7 (rotamers), 129.7 and 129.6 (rotamers), 128.5 and 126.6 (rotamers), 122.3 and 122.1 (rotamers), 115.6 and 115.3 (rotamers), 65.8 and 65.7 (rotamers), 43.1 and 42.9 (rotamers), 33.1 and 29.4 (rotamers), 25.69 and 25.61 (rotamers), 22.8 and 21.9 (rotamers); HRMS (TOF-MS) calcd. for $C_{16}H_{21}BrNO_3$ ($M+H^+$): 354.0705; found 354.0705.

3-bromobenzyl (E)-2,2-dimethyl-4-(N-methylacetamido)-but-3-enoate (**3fa**)



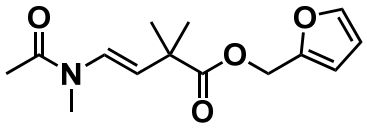
Following the general procedure above, using **1f** (237.8 mg, 0.5 mmol), **2a** (148.7 mg, 1.5 mmol), PDI (1.6 mg, 2.5×10^{-3} mmol), $^{n}Bu_3N$ (92.7 mg, 0.5 mmol), $MgCl_2$ (17.6 mg, 0.15 mmol) and dried NMP (0.83 mL) upon 450 nm LED light irradiation for 18 h, yielded the product **3fa** (99.2 mg, 56%) as red oil; IR (cm^{-1}): 2975, 1725, 1673, 1640, 1570, 1473, 1380, 1242, 1120, 1017, 780; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.48-7.42 (m, 2H), 7.24-7.20 (m, 2H), 6.68 (d, J = 14.0 Hz, 1H), 5.19 and 5.18 (both d, J = 14.9 and 14.1 Hz, 1H, rotamers), 5.09 and 5.07 (both s, 2H, rotamers), 3.09 and 3.05 (both s, 3H, rotamers), 2.21 and 2.17 (both s, 3H, rotamers), 1.39 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 176.3 and 175.9 (rotamers), 169.3 and 169.2 (rotamers), 138.6 and 138.4 (rotamers), 131.3 and 131.1 (rotamers), 130.7 and 130.6 (rotamers), 130.24 and 130.20 (rotamers), 128.7 and 126.6 (rotamers), 126.3 and 126.2 (rotamers), 122.6 and 122.5 (rotamers), 115.5 and 115.2 (rotamers), 65.5 and 65.4 (rotamers), 43.1 and 42.9 (rotamers), 33.1 and 29.4 (rotamers), 25.6 and 25.5 (rotamers), 22.8 and 21.9 (rotamers); HRMS (TOF-MS) calcd. for $C_{16}H_{21}BrNO_3$ ($M+H^+$): 354.0705; found 354.0706.

2-bromobenzyl (E)-2,2-dimethyl-4-(N-methylacetamido)-but-3-enoate (**3ga**)



Following the general procedure above, using **1g** (237.8 mg, 0.5 mmol), **2a** (148.7 mg, 1.5 mmol), PDI (1.6 mg, 2.5×10^{-3} mmol), $^{n}Bu_3N$ (92.7 mg, 0.5 mmol), $MgCl_2$ (16.6 mg, 0.15 mmol) and dried NMP (0.83 mL) upon 450 nm LED light irradiation for 18 h, yielded the product **3ga** (106.4 mg, 60%) as red oil; IR (cm^{-1}): 2972, 1726, 1675, 1642, 1471, 1381, 1241, 1119, 1017, 936, 751; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.59-7.56 (m, 2H), 7.46 and 6.68 (both d, J = 14.7 and 14.1 Hz, 1H, rotamers), 7.37 (dd, J = 1.9, 7.6 Hz, 1H), 7.31 (m, 1H), 7.22-7.17 (m, 1H), 5.24 and 5.21 (both d, J = 14.9 and 14.1 Hz, 1H), 5.19 and 5.17 (both s, 2H, rotamers), 3.09 and 3.05 (both s, 3H, rotamers), 2.20 and 2.17 (both s, 3H, rotamers), 1.40 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 176.3 and 175.9 (rotamers), 169.3 and 169.2 (rotamers), 135.5 and 135.3 (rotamers), 133.0 and 132.9 (rotamers), 130.0 and 129.9 (rotamers), 129.78 and 129.72 (rotamers), 128.6 and 126.4 (rotamers), 127.5, 123.6 and 123.4 (rotamers), 115.7 and 115.5 (rotamers), 66.4 and 66.2 (rotamers), 43.3 and 43.0 (rotamers), 33.1 and 29.4 (rotamers), 25.7 and 25.6 (rotamers), 22.8 and 22.0 (rotamers); HRMS (TOF-MS) calcd. for $C_{16}H_{21}BrNO_3$ ($M+H^+$): 354.0705; found 354.0705.

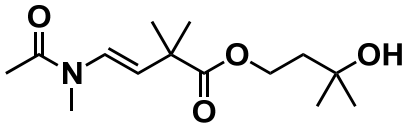
furan-2-ylmethyl (E)-2,2-dimethyl-4-(N-methylacetamido)-but-3-enoate (**3ha**)



Following the general procedure above, using **1h** (193.6 mg, 0.5 mmol), **2a** (148.7 mg, 1.5 mmol), PDI (1.7

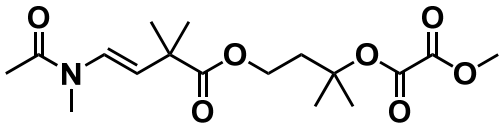
mg, 2.5×10^{-3} mmol), $^{n}Bu_3N$ (92.7 mg, 0.5 mmol), $MgCl_2$ (16.4 mg, 0.15 mmol) and dried NMP (0.8 mL) upon 450 nm LED light irradiation for 18 h, yielded the product **3ha** (85.2 mg, 64%) as red oil; IR (cm^{-1}): 2972, 1726, 1675, 1642, 1471, 1380, 1241, 1118, 1015, 920, 884, 815, 745; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.42 and 6.65 (both d, J = 15.1 and 14.1 Hz, 1H, rotamers), 7.41 (m, 1H), 6.40-6.35 (m, 2H), 5.19 and 5.15 (both d, J = 14.8 and 14.2 Hz, 1H, rotamers), 5.08 and 5.05 (both s, 2H, rotamers), 3.07 and 3.03 (both s, 3H, rotamers), 2.20 and 2.17 (both s, 3H, rotamers), 1.35 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 176.4 and 176.0 (rotamers), 169.4 and 169.2 (rotamers), 149.7 and 149.5 (rotamers), 143.3 and 143.2 (rotamers), 128.5 and 126.4 (rotamers), 115.8 and 115.5 (rotamers), 110.6, 110.5 and 110.4 (rotamers), 58.58 and 58.54 (rotamers), 43.2 and 43.0 (rotamers), 33.1 and 29.4 (rotamers), 25.7 and 25.5 (rotamers), 22.8 and 21.9 (rotamers); HRMS (TOF-MS) calcd. for $C_{14}H_{20}NO_4$ ($M+H^+$): 266.1392; found 266.1392.

3-hydroxy-3-methylbutyl (E)-2,2-dimethyl-4-(N-methylacetamido)but-3-enoate (**3ia**)



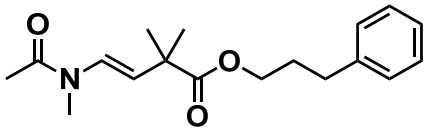
Following the general procedure above, using **1i** (196.0 mg, 0.5 mmol), **2a** (148.7 mg, 1.5 mmol), PDI (1.7 mg, 2.5×10^{-3} mmol), $^{n}Bu_3N$ (92.7 mg, 0.5 mmol), $MgCl_2$ (16.7 mg, 0.15 mmol) and dried NMP (0.83 mL) upon 450 nm LED light irradiation for 18 h, yielded the product **3ia** (92.6 mg, 68%) as red oil; IR (cm^{-1}): 3434, 2969, 1724, 1673, 1637, 1471, 1380, 1311, 1247, 1140, 1019, 937; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.43 and 6.68 (both d, J = 14.8 and 14.2 Hz, 1H, rotamers), 5.17 (d, J = 14.3 Hz, 1H), 4.28-4.23 (m, 2H), 3.09 and 3.06 (both s, 3H, rotamers), 2.21 and 2.20 (both s, 3H, rotamers), 1.85-1.82 (m, 2H), 1.35 (s, 6H), 1.26 and 1.26 (both s, 6H, rotamers); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 176.8 and 176.4 (rotamers), 169.4 and 169.3 (rotamers), 128.4 and 126.4 (rotamers), 115.8 and 115.6 (rotamers), 70.07 and 70.05 (rotamers), 62.1 and 62.0 (rotamers), 43.0 and 42.8 (rotamers), 41.5, 33.1 and 29.71 (rotamers), 29.75 and 29.4 (rotamers), 25.69 and 25.63 (rotamers), 22.8 and 22.0 (rotamers); HRMS (TOF-MS) calcd. for $C_{14}H_{26}NO_4$ ($M+H^+$): 272.1862; found 272.1862.

(E)-4-((2,2-dimethyl-4-(N-methylacetamido)but-3-enoyl)oxy)-2-methylbutan-2-yl methyl oxalate (**3ja**)



Following the general procedure above, using **1j** (239.5 mg, 0.5 mmol), **2a** (148.7 mg, 1.5 mmol), PDI (1.7 mg, 2.5×10^{-3} mmol), $^{n}Bu_3N$ (92.7 mg, 0.5 mmol), $MgCl_2$ (16.9 mg, 0.15 mmol) and dried NMP (0.83 mL) upon 450 nm LED light irradiation for 18 h, yielded the product **3ja** (155.5 mg, 87%) as orange oil; IR (cm^{-1}): 2976, 2342, 2103, 1900, 1725, 1643, 1472, 1381, 1322, 1245, 1203, 1122, 1019, 962, 790; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.43 and 6.68 (both d, J = 14.9 and 14.0 Hz, 1H, rotamers), 5.17 (d, J = 14.7 Hz, 1H), 4.22-4.18 (m, 2H), 3.87 (s, 3H), 3.09 and 3.06 (both s, 3H, rotamers), 2.23-2.19 (m, 2H), 2.21 (both s, 3H, rotamers), 1.59 and 1.58 (both s, 6H, rotamers), 1.35 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 176.7 and 176.3 (rotamers), 169.3 and 169.2 (rotamers), 158.77 and 158.73 (rotamers), 156.6, 128.4 and 126.4 (rotamers), 115.7 and 115.4 (rotamers), 85.5 and 85.4 (rotamers), 60.9 and 60.7 (rotamers), 53.4, 43.0 and 42.8 (rotamers), 39.0 and 38.9 (rotamers), 33.0 and 29.4 (rotamers), 26.08 and 26.06 (rotamers), 25.6, 22.7 and 21.9 (rotamers); HRMS (TOF-MS) calcd. for $C_{17}H_{28}NO_7$ ($M+H^+$): 358.1866; found 358.1866.

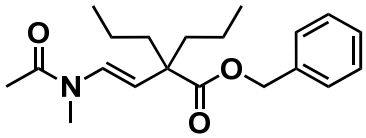
3-phenylpropyl (E)-2,2-dimethyl-4-(N-methylacetamido)but-3-enoate (**3ka**)



Following the general procedure above, using **1k** (211.8 mg, 0.50 mmol), **2a** (148.7 mg, 1.5 mmol), PDI (1.9 mg, 2.6×10^{-3} mmol), $^{n}Bu_3N$ (92.7 mg, 0.50 mmol), $MgCl_2$ (14.0 mg, 0.15 mmol) and dried NMP (0.8 mL) upon 450 nm LED light irradiation for 18 h, yielded the product **3ka** (112.4 mg, 74%) as red oil; IR

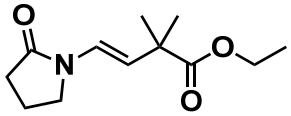
(cm^{-1}): 2966, 1722, 1675, 1642, 1380, 1245, 1140, 1017, 935, 745, 699; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.46 and 6.69 (both d, J = 14.9 and 14.3 Hz, 1H, rotamers), 7.29 (t, J = 7.3 Hz, 2H), 7.21 (d, J = 7.4 Hz, 1H), 7.17 (d, J = 8.2 Hz, 2H), 5.22 and 5.21 (both d, J = 14.9 and 14.1 Hz, 1H, rotamers), 4.12-4.07 (m, 2H), 3.10 and 3.07 (both s, 3H, rotamers), 2.70-2.66 (m, 2H), 2.21 and 2.20 (both s, 3H, rotamers), 2.00-1.93 (m, 2H), 1.37 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 176.7 and 176.3 (rotamers), 169.3 and 169.1 (rotamers), 141.2 and 141.1 (rotamers), 128.56 and 128.52 (rotamers), 128.48 and 126.3 (rotamers), 128.44 and 128.3 (rotamers), 126.1 and 126.0 (rotamers), 116.1 and 115.7 (rotamers), 64.2 and 64.0 (rotamers), 43.1 and 42.9 (rotamers), 33.0 and 32.1 (rotamers), 30.28, 30.27 and 29.4 (rotamers), 25.7, 22.7 and 21.9 (rotamers); HRMS (TOF-MS) calcd. for $C_{18}H_{25}NO_3Na$ ($M+Na^+$): 326.1732; found 326.1734.

benzyl (E)-2-(2-(N-methylacetamido)-vinyl)-2-propylpentanoate (**3la**)



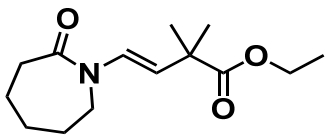
Following the general procedure above, using **1l** (226.3 mg, 0.5 mmol), **2a** (148.7 mg, 1.5 mmol), PDI (1.6 mg, 2.5×10^{-3} mmol), $^nBu_3N$ (92.7 mg, 0.5 mmol), $MgCl_2$ (16.5 mg, 0.15 mmol) and dried NMP (0.8 mL) upon 450 nm LED light irradiation for 18 h, yielded the product **3la** (61.3 mg, 37%) as red oil; IR (cm^{-1}): 2956, 2871, 1724, 1674, 1640, 1387, 1296, 1206, 1126, 1010; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.39 and 6.66 (both d, J = 14.7 and 14.4 Hz, 1H, rotamers), 7.36-7.30 (m, 5H), 5.22 and 5.07 (both d, J = 15.3 and 14.3 Hz, 1H, rotamers), 5.13 and 5.12 (both s, 2H, rotamers), 3.09 and 3.05 (both s, 3H, rotamers), 2.20 and 2.11 (both s, 3H, rotamers), 1.75-1.62 (m, 4H), 1.25-1.09 (m, 4H), 0.88 (t, J = 7.3 Hz, 3H), 0.85 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 175.9 and 175.4 (rotamers), 169.3 and 169.0 (rotamers), 136.3 and 136.1 (rotamers), 129.5 and 128.3 (rotamers), 128.6 and 128.5 (rotamers), 128.2 and 128.16 (rotamers), 128.10 and 127.1 (rotamers), 113.7 and 112.9 (rotamers), 66.5 and 66.4 (rotamers), 50.9 and 50.6 (rotamers), 39.7 and 39.5 (rotamers), 33.1 and 29.5 (rotamers), 22.8 and 22.0 (rotamers), 17.86 and 17.83 (rotamers), 14.6 and 14.5 (rotamers); HRMS (TOF-MS) calcd. for $C_{20}H_{30}NO_3$ ($M+H^+$): 332.2226; found 332.2228.

ethyl (E)-2,2-dimethyl-4-(2-oxopyrrolidin-1-yl)-but-3-enoate (**3ab**)[2]



Following the general procedure above, using **1a** (167.3 mg, 0.5 mmol), **2b** (166.7 mg, 1.5 mmol), PDI (1.8 mg, 2.5×10^{-3} mmol), $^nBu_3N$ (92.7 mg, 0.5 mmol), $MgCl_2$ (16.7 mg, 0.15 mmol) and dried NMP (0.83 mL) upon 450 nm LED light irradiation for 18 h, yielded the product **3ab** (169.0 mg, 75%) as red oil; ^1H NMR (500 MHz, $CDCl_3$) δ: 6.98 (d, J = 14.8 Hz, 1H), 5.17 (d, J = 14.7 Hz, 1H), 4.12 (q, J = 7.2 Hz, 2H), 3.52 (t, J = 7.3 Hz, 2H), 2.51-2.48 (m, 2H), 2.13-2.07 (m, 2H), 1.35 (s, 6H), 1.25 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 176.5, 173.3, 122.9, 116.8, 60.8, 45.2, 42.9, 31.3, 25.5, 17.4, 14.1. HRMS (TOF-MS) calcd. for $C_{12}H_{20}NO_3$ ($M+H^+$): 226.1443; found 226.1443.

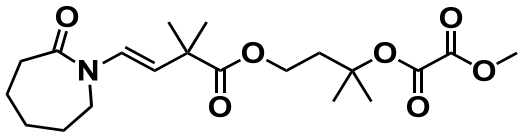
ethyl (E)-2,2-dimethyl-4-(2-oxoazepan-1-yl)-but-3-enoate (**3ac**)[2]



Following the general procedure above, using **1a** (167.6 mg, 0.5 mmol), **2c** (208.6 mg, 1.5 mmol), PDI (1.8 mg, 2.5×10^{-3} mmol), $^nBu_3N$ (92.7 mg, 0.5 mmol), $MgCl_2$ (16.5 mg, 0.15 mmol) and dried NMP (0.83 mL) upon 450 nm LED light irradiation for 18 h, yielded the product **3ac** (120.3 mg, 95%) as red oil; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.25 (d, J = 14.8 Hz, 1H), 5.25 (d, J = 15.0 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.58 (t, J = 4.9 Hz, 2H), 2.63-2.61 (m, 2H), 1.76-1.63 (m, 6H), 1.35 (s, 6H), 1.24 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 176.9, 174.4, 125.9, 115.4, 60.8, 45.3, 43.0, 37.3, 29.5, 27.3, 25.6, 23.5, 14.2. HRMS (TOF-MS) calcd. for $C_{14}H_{24}NO_3$ ($M+H^+$): 254.1756; found 254.1757.

Application

(E)-4-((2,2-dimethyl-4-(2-oxoazepan-1-yl)but-3-enoyl)oxy)-2-methylbutan-2-yl methyl oxalate (**4**)

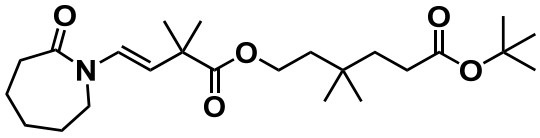


Following the general procedure above, using **1j** (256.7 mg, 0.54 mmol), **2c** (208.7 mg, 1.5 mmol), PDI (1.8 mg, 2.5×10^{-3} mmol), $^{n}Bu_3N$ (92.7 mg, 0.5 mmol), $MgCl_2$ (16.7 mg, 0.15 mmol) and dried NMP (0.83 mL) upon 450 nm LED light irradiation for 18 h, yielded the product **4** (83.4 mg, 39%) as red solid; IR (cm^{-1}): 2974, 2927, 2858, 1753, 1726, 1638, 1439, 1319, 1206, 1120, 1077, 991, 967, 817; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.25 (d, J = 15.0 Hz, 1H), 5.21 (d, J = 15.0 Hz, 1H), 4.20 (t, J = 6.7 Hz, 2H), 3.87 (s, 3H), 3.58-3.56 (m, 2H), 2.63-2.61 (m, 2H), 2.20 (t, J = 6.7 Hz, 2H), 1.77-1.63 (m, 6H), 1.58 (s, 6H), 1.34 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 176.7, 174.3, 158.7, 156.6, 126.2, 114.8, 85.5, 60.7, 53.4, 45.3, 43.0, 39.0, 37.2, 29.5, 27.3, 26.0, 25.5, 23.4; HRMS (TOF-MS) calcd. for $C_{20}H_{31}NO_7Na$ ($M+Na^+$): 420.1998; found 420.2000.

General procedure for synthesis of **5**

4 (0.50 mmol, 1.0 equiv.), $NiCl_2(Py)_2$ (5.0×10^{-2} mmol, 10 mol%), PBI (1.5 mmol, 3.0 equiv.), $MgCl_2$ (1.0 mmol, 2.0 equiv.) and Zn (2.5 mmol, 5.0 equiv.) were added into a 5 mL screw-vial under air. Then, *tert*-butyl acrylate (0.50 mmol, 1.0 equiv.) and dried DMA (0.5 M) were added by syringe, and the resulting mixture was vigorously stirred under nitrogen atmosphere [charged by general N_2 (99.95%) gas flow] for 24 h at 50°C. After 24 hours, the reaction mixture was extracted with AcOEt and dried with anhydrous $MgSO_4$. After removal of the solvent in vacuum, the residue was purified with silica gel column chromatography to give desired products **5**.

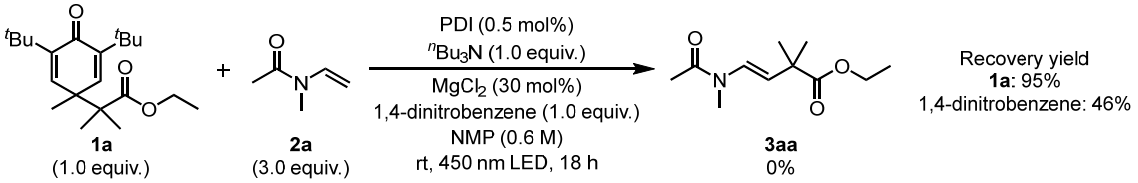
tert-butyl (E)-6-((2,2-dimethyl-4-(2-oxoazepan-1-yl)but-3-enoyl)oxy)-4,4-dimethylhexanoate (**5**)



Following the general procedure above, using **4** (203.8 mg, 0.51 mmol), *tert*-butyl acrylate (65.4 mg, 0.51 mmol), $NiCl_2(Py)_2$ (22.3 mg, 5.0×10^{-2} mmol), PBI (292.8 mg, 1.5 mmol), $MgCl_2$ (95.2 mg, 1.0 mmol), Zn (163.5 mg, 2.5 mmol) and dried DMA (1.0 mL) at 50°C for 24 h, yielded the product **5** (125.4 mg, 58%) as a red oil; IR (cm^{-1}): 3072, 2974, 2875, 1737, 1696, 1651, 1458, 1399, 1295, 1203, 1125, 965, 808; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.25 (d, J = 15.8 Hz, 1H), 5.24 (d, J = 15.0 Hz, 1H), 4.11 (t, J = 7.3 Hz, 2H), 3.59-3.57 (m, 2H), 2.63-2.61 (m, 2H), 2.21-2.18 (m, 2H), 1.75-1.65 (m, 6H), 1.54 (m, 4H), 1.44 (s, 9H), 1.34 (s, 6H), 0.91 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 176.9, 174.3, 173.5, 126.0, 115.2, 80.2, 62.1, 45.3, 43.0, 39.5, 37.3, 37.0, 32.0, 30.8, 29.5, 28.1, 27.3, 27.0, 25.6, 23.5; HRMS (TOF-MS) calcd. for $C_{24}H_{42}NO_5$ ($M+H^+$): 424.3063; found 424.3063.

4. Control experiments and analysis results

Inhibition of single-electron-transfer

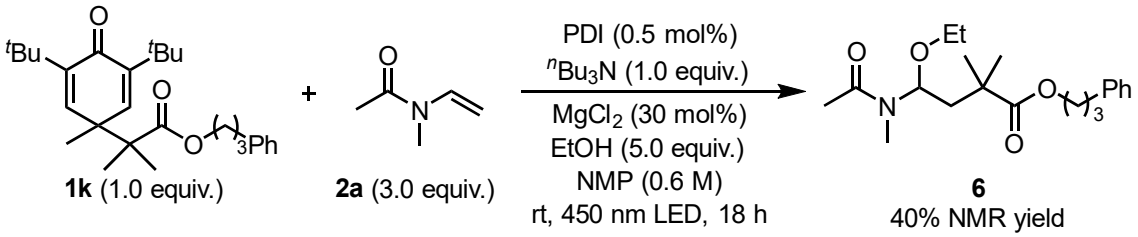


General procedure for inhibition of single-electron-transfer

1a (0.50 mmol, 1.0 equiv.), PDI (1.8 mg, 2.5×10^{-3} mmol, 0.50 mol%) and 1,4-dinitrobenzene (84.1 mg, 0.50 mmol) were added into a 5 mL screw-vial under air. Then, $MgCl_2$ (14.2 mg, 0.15 mmol, 30 mol%), **2a** (1.5 mmol, 3.0 equiv.), $^{n}Bu_3N$ (0.50 mmol, 1.0 equiv.) and dried NMP (0.8 mL) were added in glovebox and sealed the vial. The reaction mixture was stirred upon 450 nm LED light irradiation in the photoreactor.

After 18 hours, the reaction mixture was extracted with AcOEt and dried with anhydrous $MgSO_4$. After removal of the solvent in vacuum, the residue was purified with silica gel column chromatography. As a result, the product **3aa** was not obtained, cyclohexadienone **1a** (95% isolated yield) and 1,4-dinitrobenzene (46% NMR yield) were recovered. This result suggested that single-electron-transfer from PDI as photoredox catalyst to cyclohexadienone **1a** was occurred in this reaction and 1,4-dinitrobenzene inhibited single-electron-transfer process.

Study for trapping of cation intermediate B



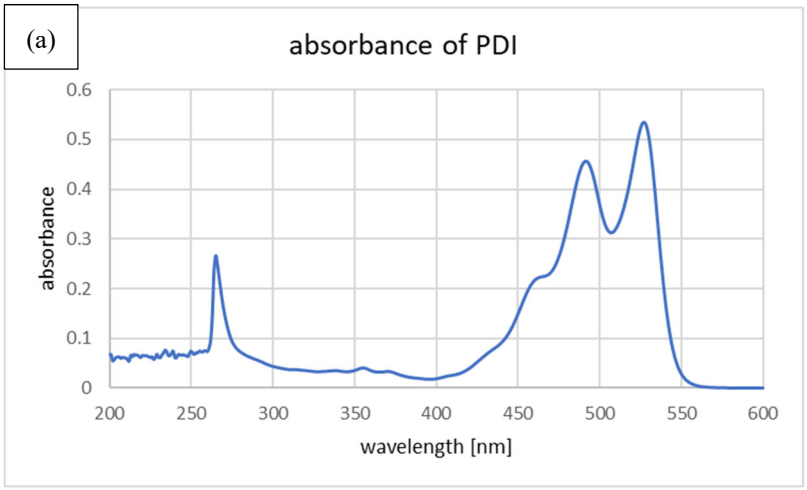
1k (1.0 equiv.) + **2a** (3.0 equiv.) → **6**, 40% NMR yield

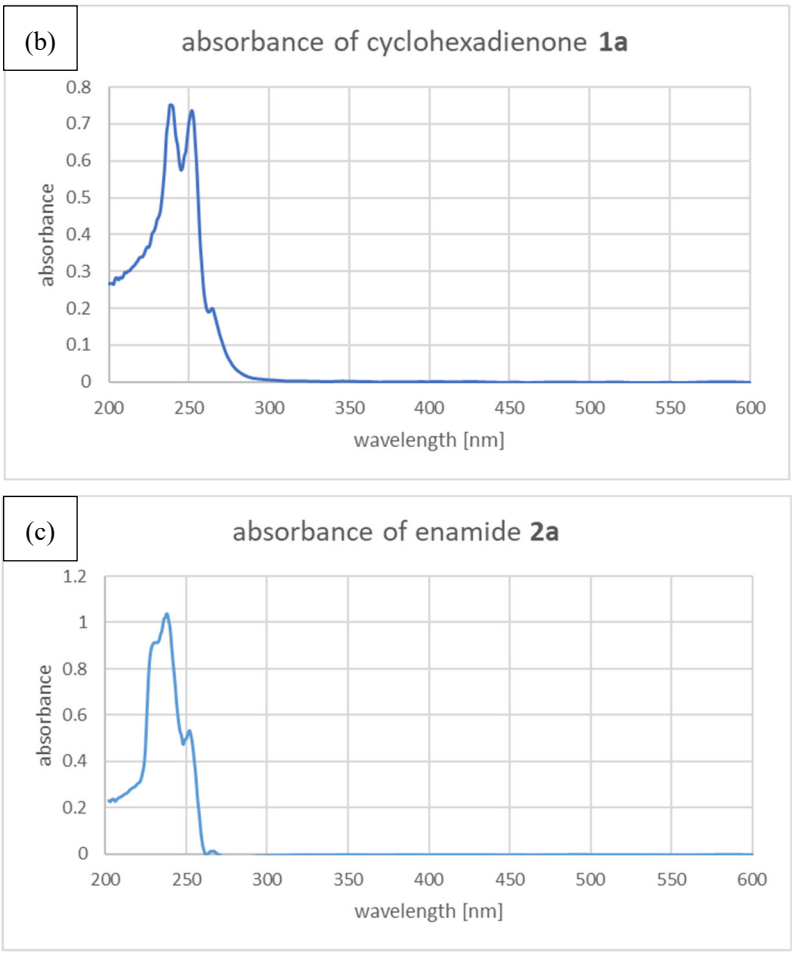
General procedure for trapping of cation intermediate **B**

1k (0.50 mmol, 1.0 equiv.) and PDI (1.8 mg, 2.5×10^{-3} mmol, 0.50 mol%) were added into a 5 mL screw-vial under air. Then, $MgCl_2$ (14.2 mg, 0.15 mmol, 30 mol%), **2a** (1.5 mmol, 3.0 equiv.), ^{n}Bu$_3$N (0.50 mmol, 1.0 equiv.), EtOH (0.15 mL, 2.5 mmol) and dried NMP (0.8 mL) were added in glovebox and sealed the vial. The reaction mixture was stirred upon 450 nm LED light irradiation in the photoreactor. After 18 hours, the reaction mixture was extracted with AcOEt and dried with anhydrous $MgSO_4$. After removal of the solvent in vacuum, the ^{1}H NMR was taken to determine the yield of **6**.[3] As a result, the product **6** was obtained in 40% NMR yield. This result suggested that enamide-Heck type reaction proceeded via cation intermediate **B**.

Absorbance measurement

Absorbance measurement was performed to obtain absorbance information about PDI as a photoredox catalyst [4], cyclohexadienone **1a** and enamide **2a** (Supporting Figure 1). As a result, PDI has absorption between 420 nm and 550 nm, but cyclohexadienone **1a** and enamide **2a** have no absorption around 450 nm.

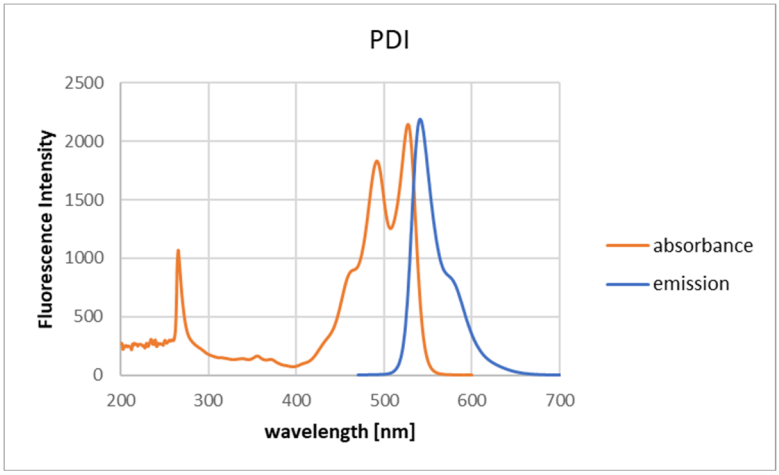


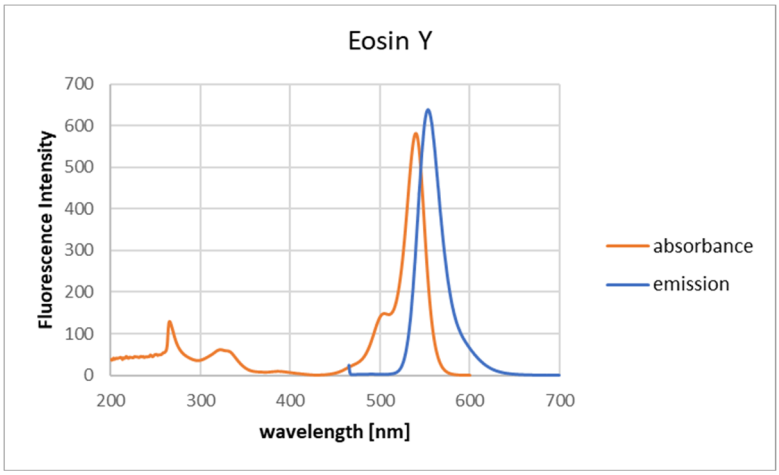


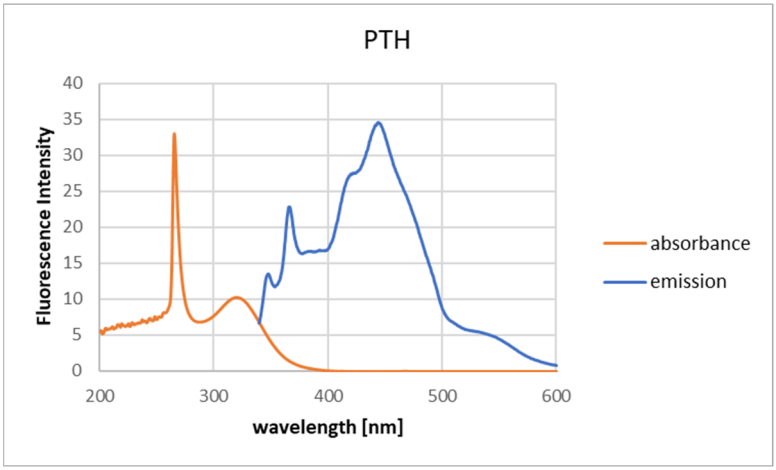
Supporting Figure 1 Absorbance of (a)PDI, (b)cyclohexadienone **1a**, (c)enamide **2a**.

Absorbance and emission spectrum

Fluorescence spectra were collected on Agilent Fluorescence Spectrophotometer JASCO FP-8250 for all experiments. PDI solution was excited at 460 nm, Eosin Y solution was excited at 450 nm, and PTH solution was excited at 330 nm. In PDI and Eosin Y experiments, the emission spectrum of 5×10^{-6} M solution of in DMF was collected. In PTH experiment, the emission spectrum of 2.5×10^{-5} M solution of in DMF was collected.

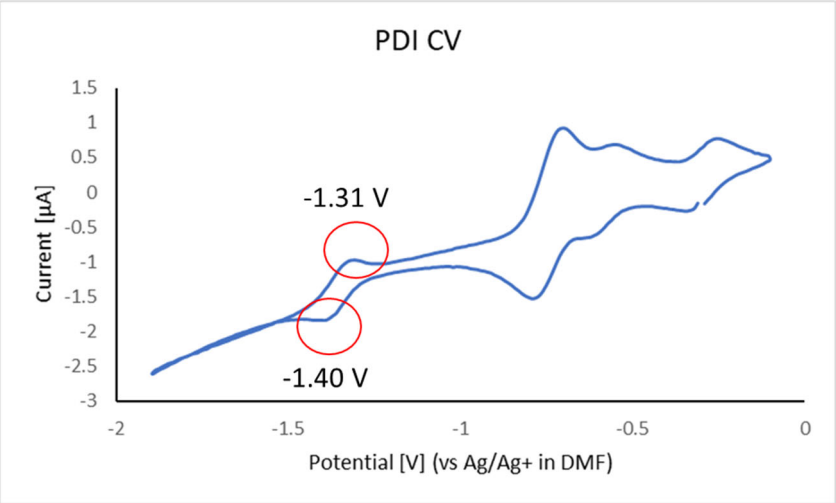




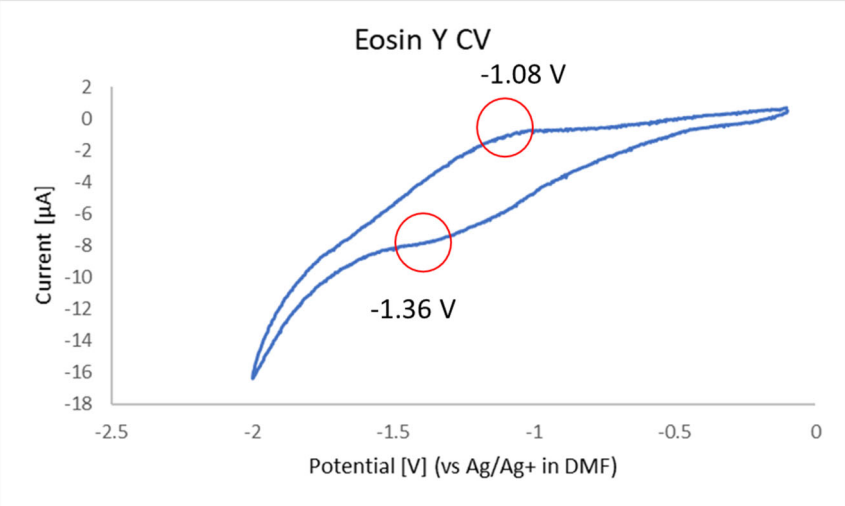


Cyclic voltammetry

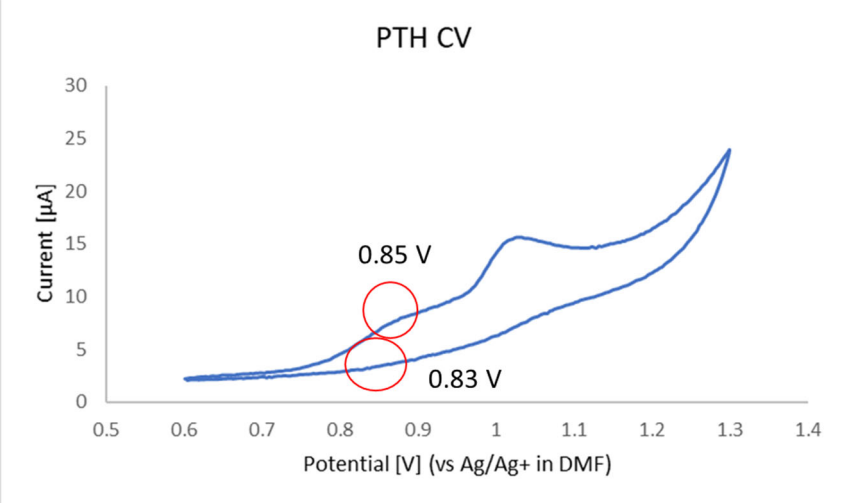
Cyclic voltammetry of photoredox catalysts (PDI, Eosin Y and PTH) were measured (Supporting Figure 2,3 and 4). First, the redox potential of PDI was $E_{1/2}[PDI^{-\cdot}/PDI^{*}]$ = -0.87 V to -0.90 V (vs Fc in DMF). PDI was reported by König group[4]. Next, the redox potential of Eosin Y was $E_{1/2}[EY^{-\cdot}/EY^{*}]$ = -0.96 V to -0.99 V (vs Fc in DMF). Then, the redox potential of PTH was $E_{1/2}[PTH^{+\cdot}/PTH^{*}]$ = -1.99 V to -2.87 V (vs Fc in DMF). Finally, cyclic voltammetry of cyclohexadienone **1a** was measured (Supporting Figure 5). The redox potential of cyclohexadienone **1a** was $E_{1/2}[\mathbf{1a}^{-\cdot}/\mathbf{1a}]$ = -0.80 V (vs Fc in DMF).
Therefore, we proposed the catalytic cycle of PDI. Excited PDI^{*} is reductively quenched by $^{n}Bu_3N$ to give $PDI^{-\cdot}$ and the radical cation of *n*-butylamine ($^{n}Bu_3N^{\bullet+}$). Upon the second excitation, $PDI^{-\cdot *}$ reduces the cyclohexadienone **1** yielding the anion radical of cyclohexadienone **1** ($\mathbf{1}^{-\cdot}$) and regenerating the neutral PDI.



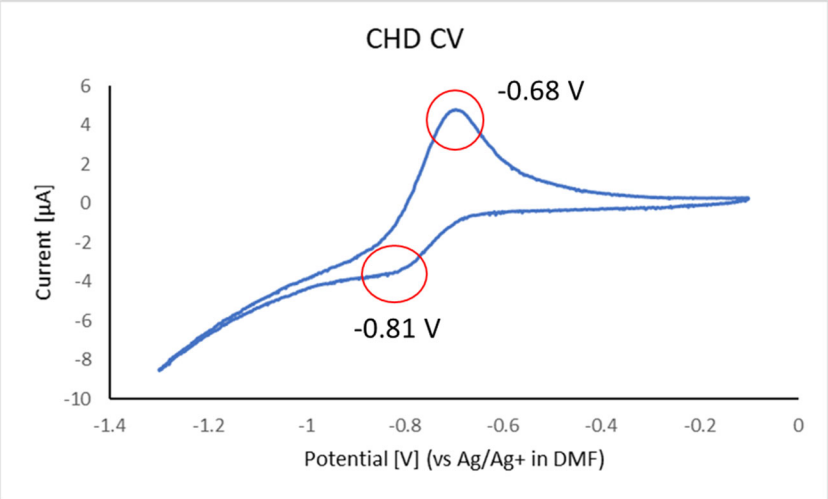
Supporting Figure 2 Cyclic voltammetry of PDI as photoredox catalyst.



Supporting Figure 3 Cyclic voltammetry of Eosin Y as photoredox catalyst.

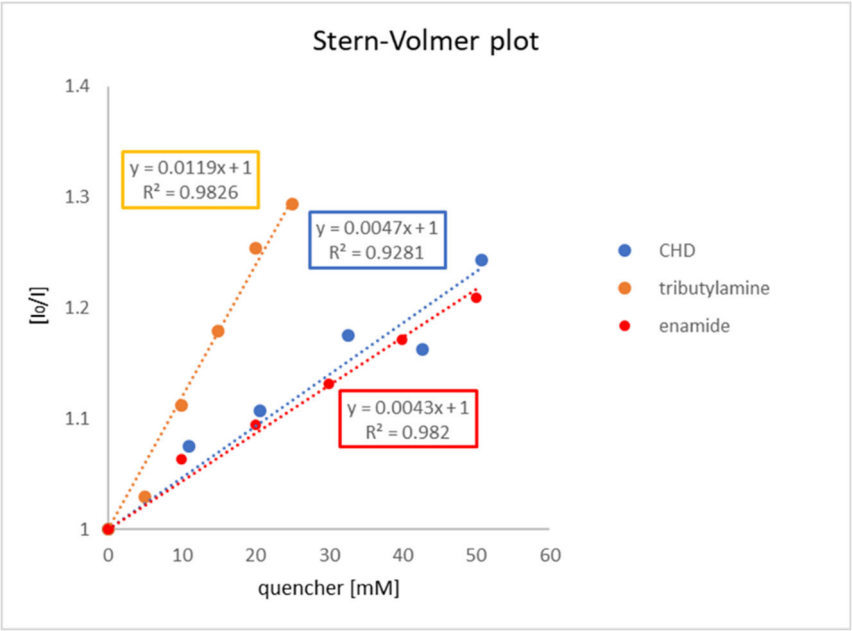


Supporting Figure 4 Cyclic voltammetry of PTH as photoredox catalyst.



Supporting Figure 5 Cyclic voltammetry of cyclohexadienone **1a**.

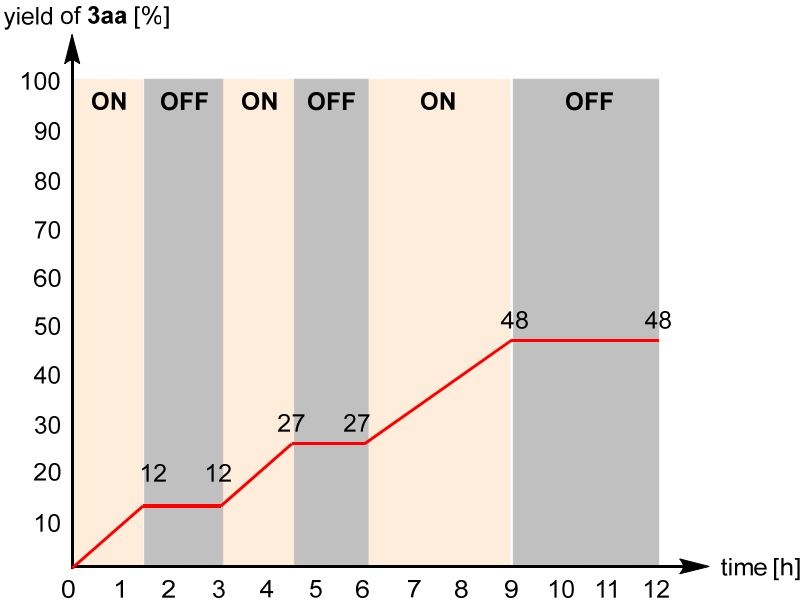
Stern-Volmer quenching studies. Emission intensities were recorded using Agilent Technologies of Cary Eclipse Fluorescence spectrophotometer. All PDI solutions were excited at 450 nm and the emission intensity was collected at 460-700 nm. In a typical experiment, to a 10×10^{-3} M solution of PDI in NMP (1-methyl-2-pyrrolidone) was added the appropriate amount of quencher in a screw-top 1.0 cm quartz cuvette. the emission of the sample was collected. The Stern-Volmer quenching studies suggested that tributylamine ($^{n}Bu_3N$) rather than cyclohexadienone **1a** or enamide **2a** quenches the luminescence of the excited state of the photocatalyst.



Supporting Figure 6 Stern-Volmer plot.

Light ON/OFF experiment. The reactions were set up in an N_2 filled glovebox. An oven-dried vial equipped with a stir-bar were added cyclohexadienone **1a** (166.9 mg, 0.5 mmol), PDI (2.1 mg, 2.5×10^{-3} mmol), $MgCl_2$ (14.8 mg, 0.15 mmol, 30 mol%) and triphenylmethane (121.8 mg, 0.5 mmol as internal standard). Next, enamide **2a** (0.15 mL, 1.5 mmol), $^{n}Bu_3N$ (0.12 mL, 0.5 mmol) and NMP (0.6 M) were added via a syringe. Then irradiated with a 450 nm LED lamp with cooling from a fan for corresponding

time. Afterwards, the ^{1}H NMR was taken to determine the yield of **3a**. The grey boxes represent the periods in which the reaction vessels were covered (dark period). The results shown that when the light was switched off, the reaction hardly carried out. These results demonstrated that the reaction might not undergo a radical-chain process.



Supporting Figure 7 Light ON/OFF experiment.

5. References

1. N. Tsuchiya, T. Nishikata, *Chem. Lett.* 2019, **48**, 718.

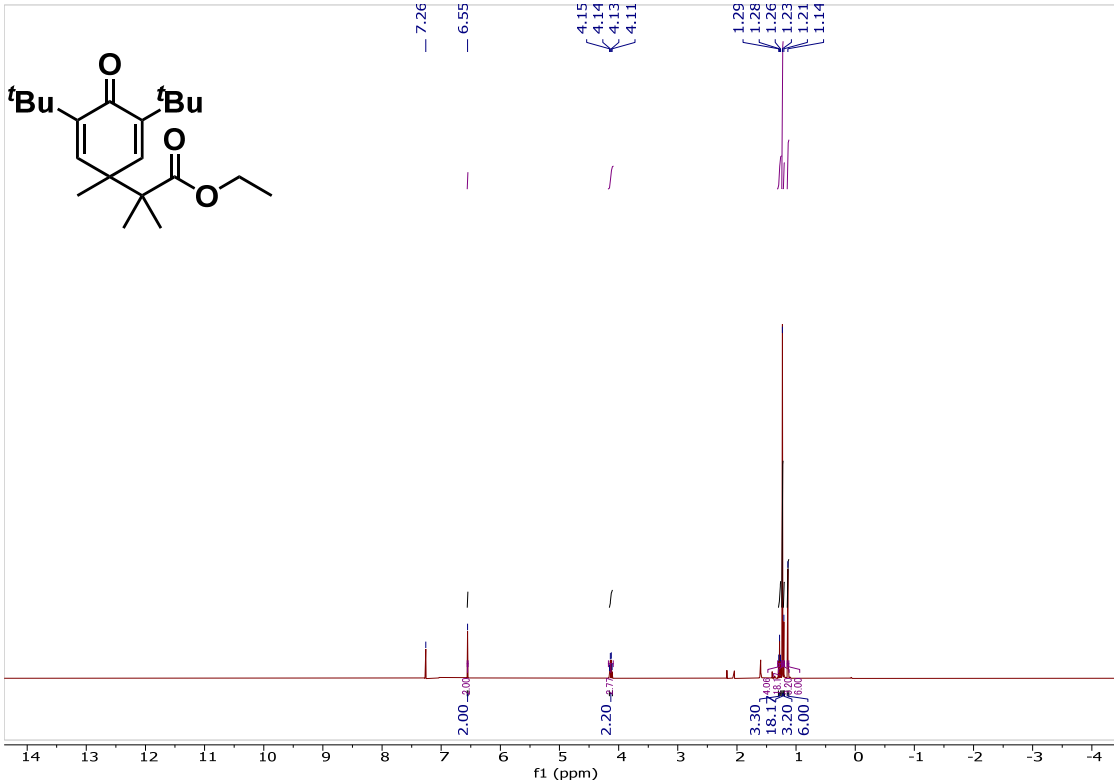
2. S. Bertho, R. Maazaoui, D. Torun, I. Dondasse, R. Abderrahim, C. Nicolas, I. Gillaizeau, *New J. Chem.* 2021, **45**, 17475.

3. Y. Murata, T. Nishikata, *Chem. Eur. J.* 2018, **24**, 6354.

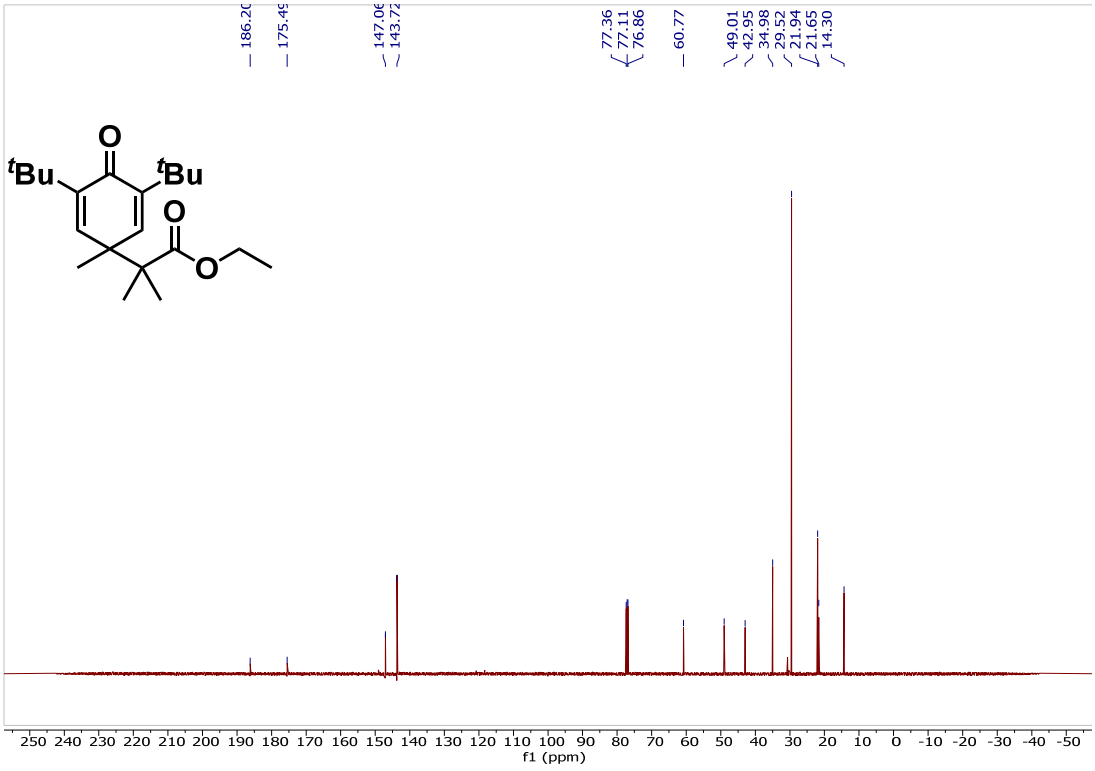
4. I. Ghosh, T. Ghosh, J. I. Bardagi, B. König, *Science*, 2014, **346**, 725.

6. Spectroscopic data

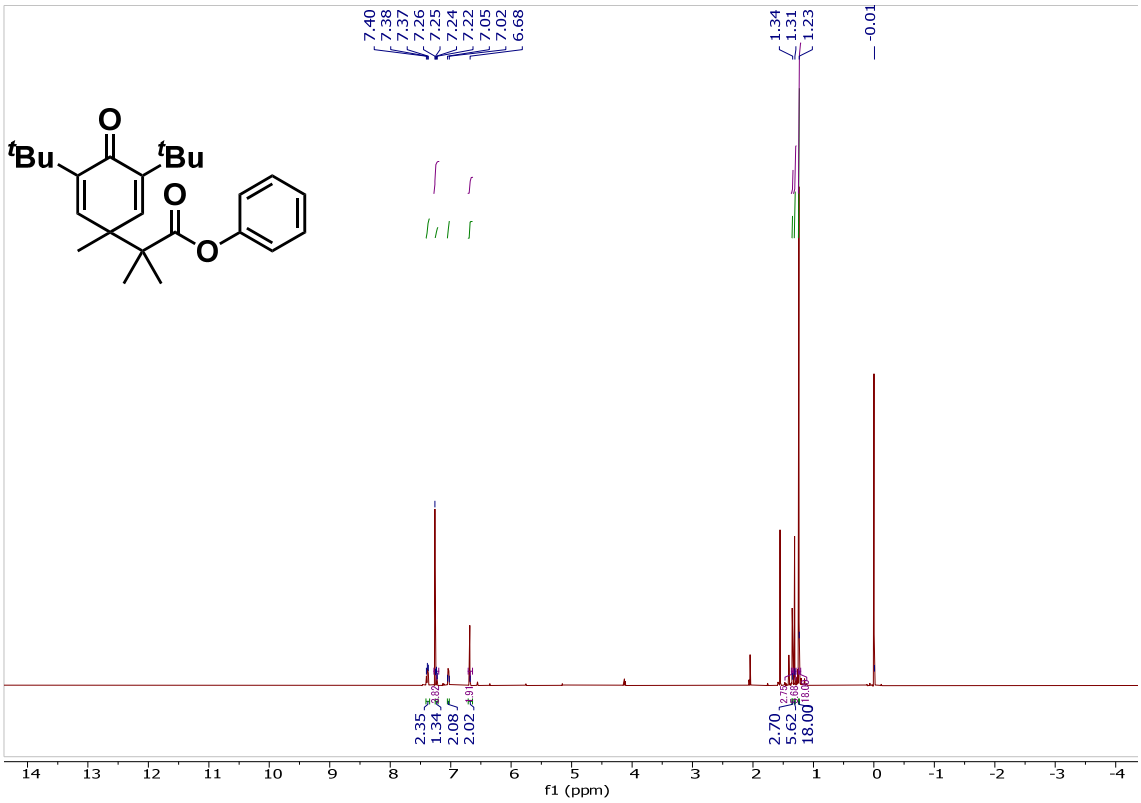
^{1}H NMR (**1a**)



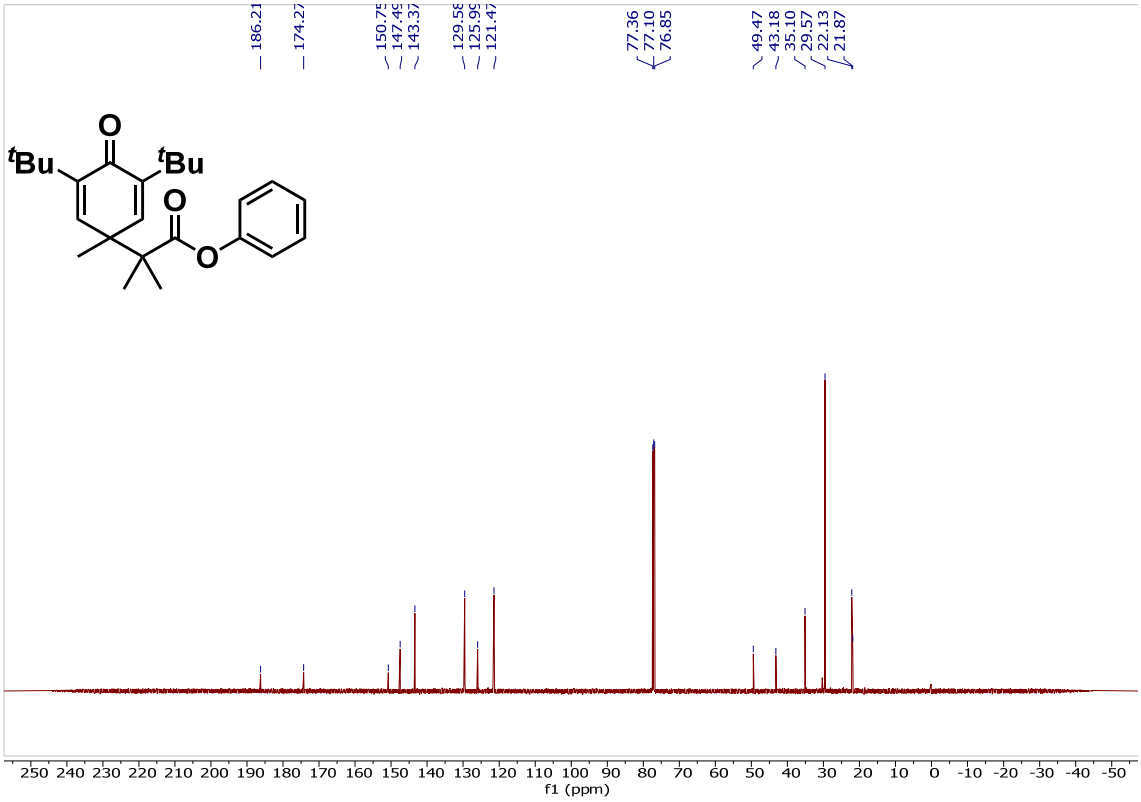
^{13}C NMR (**1a**)



^{1}H NMR (**1b**)



^{13}C NMR (**1b**)



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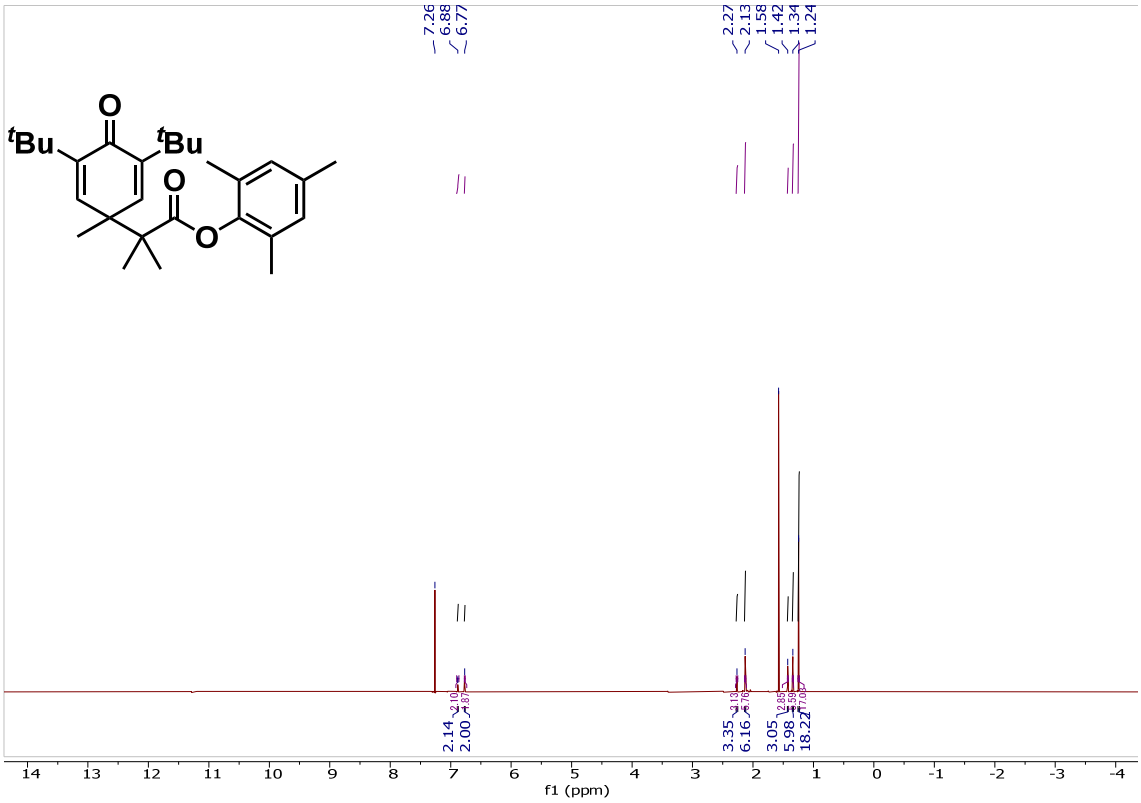

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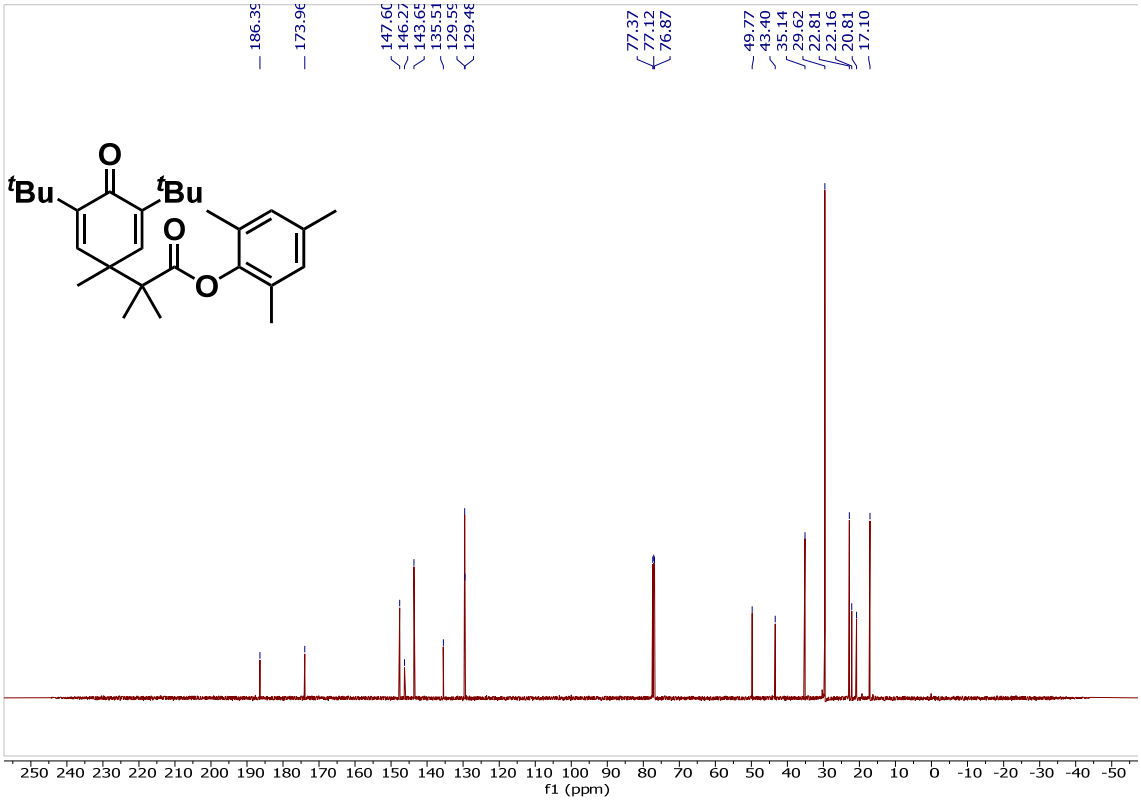
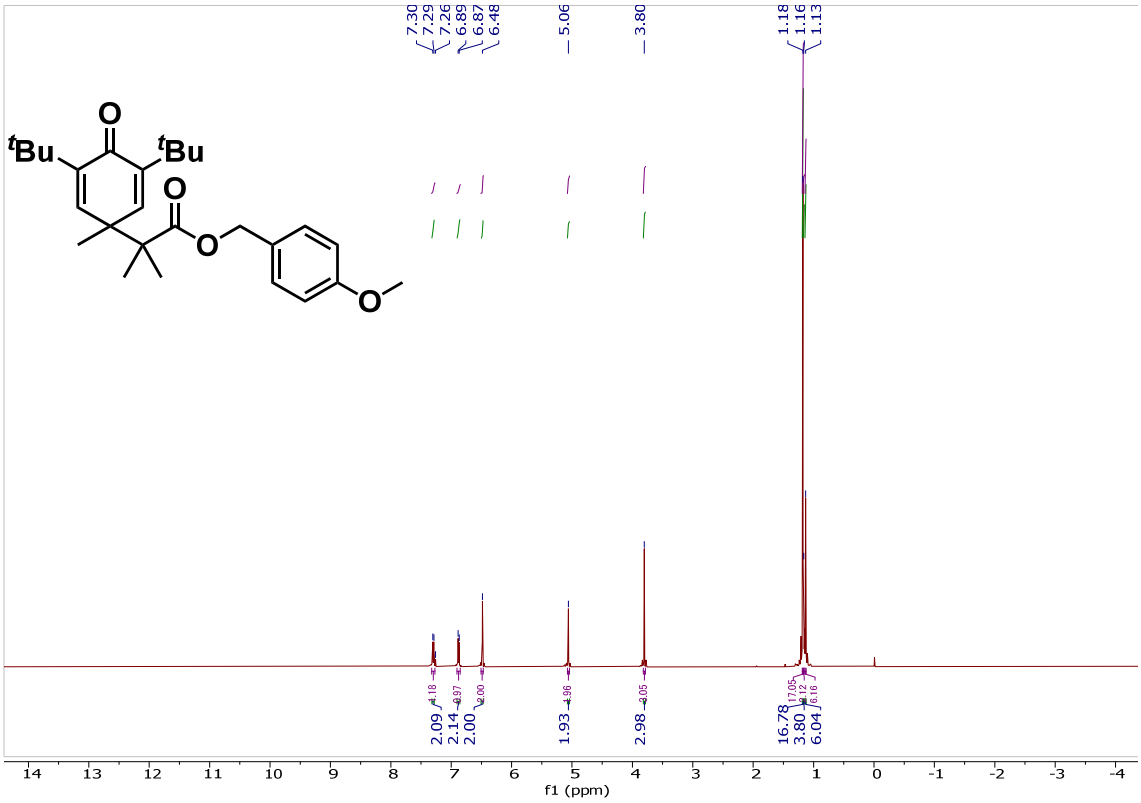


^{1}H NMR (**1d**)



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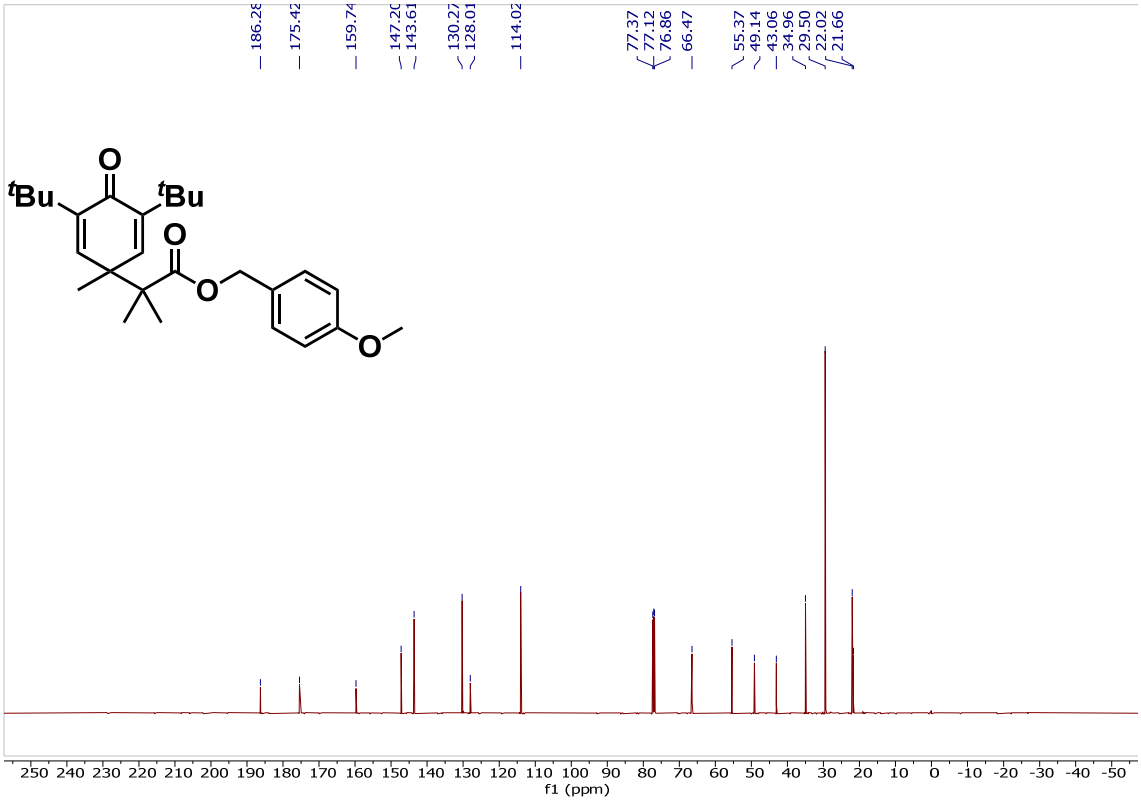

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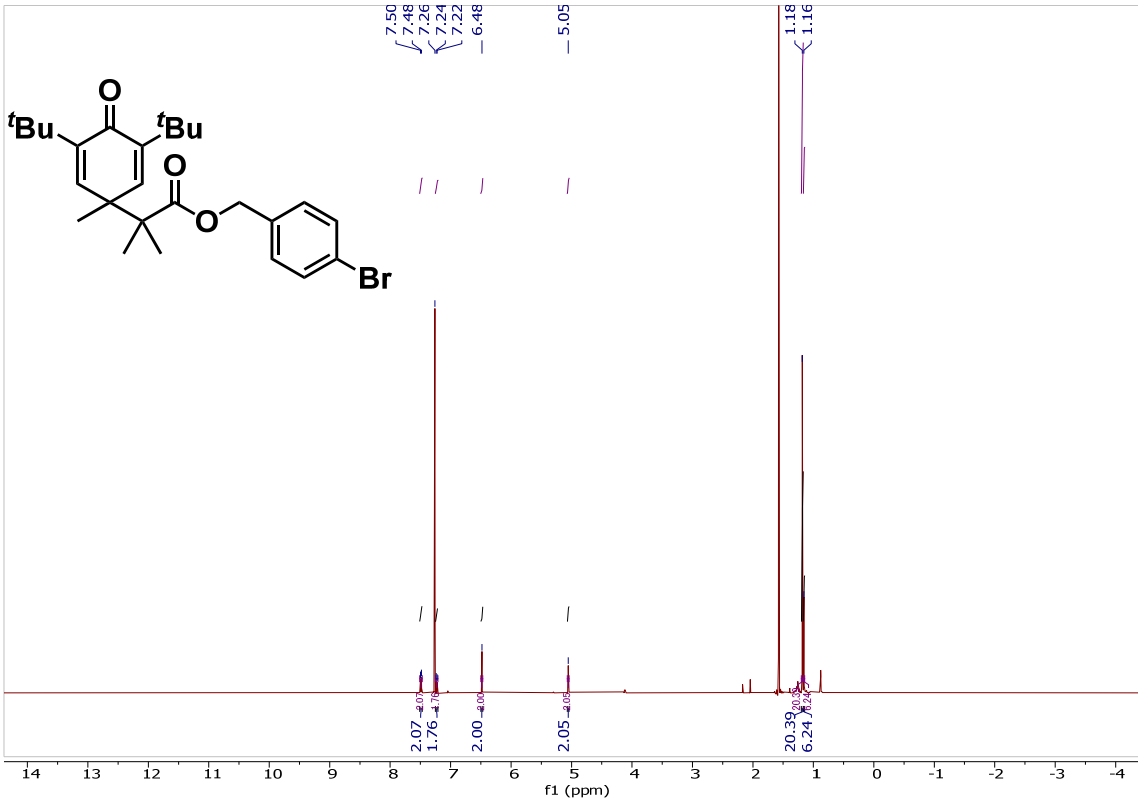
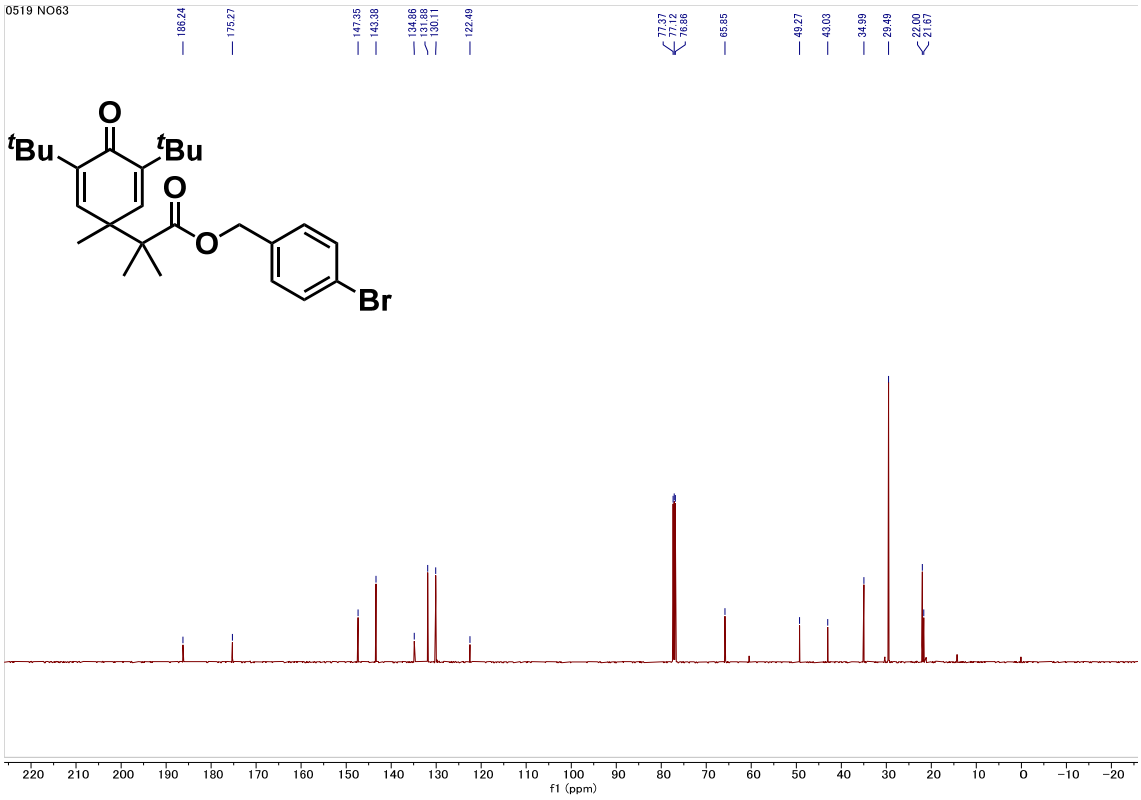


^{13}C NMR (**1e**)



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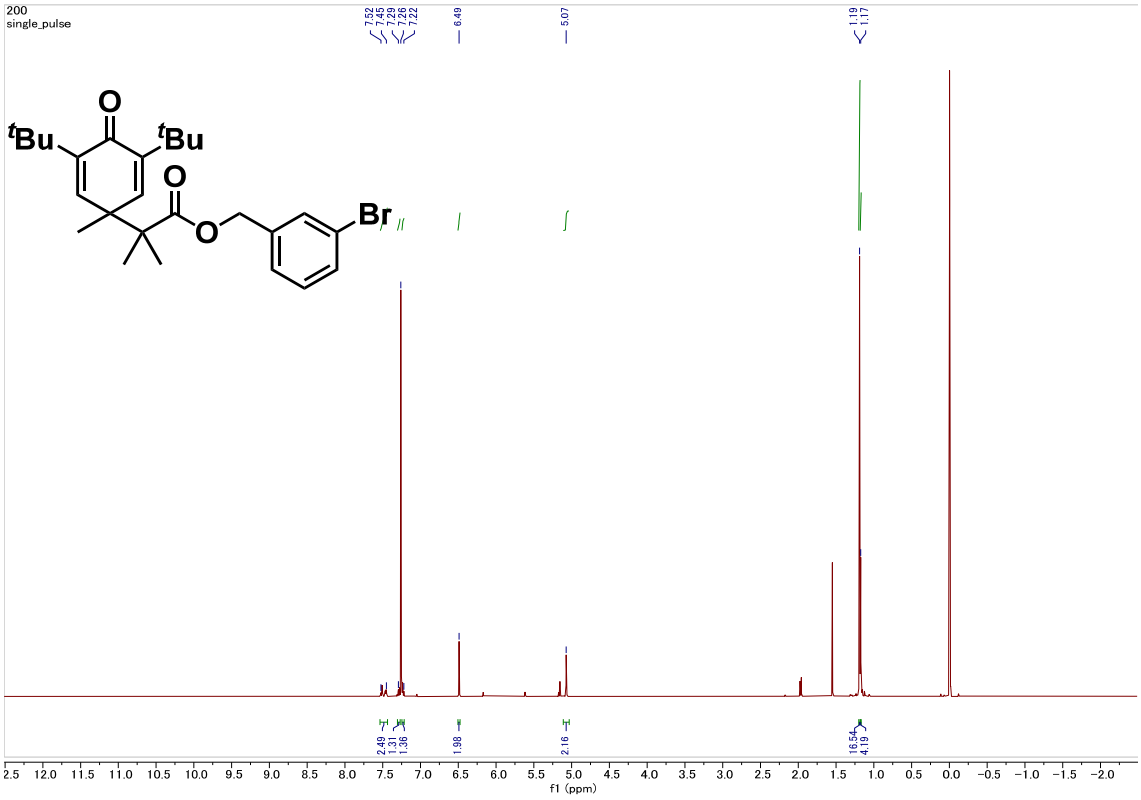
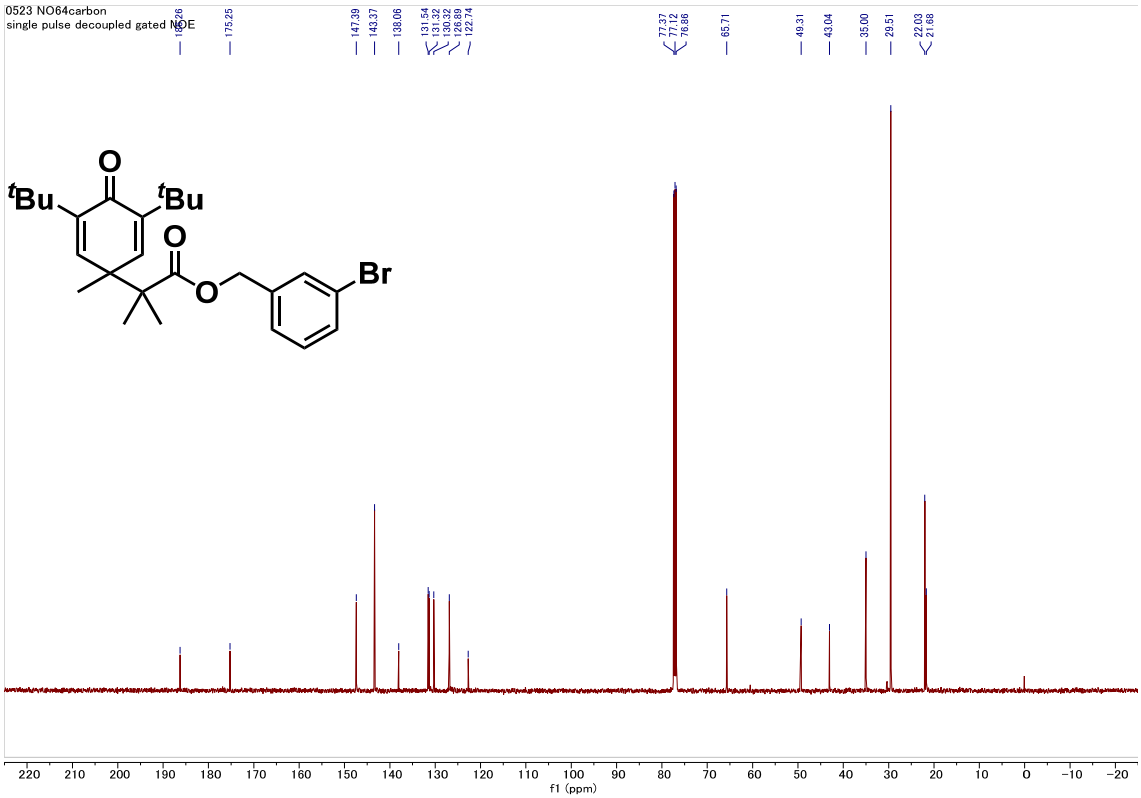


^{13}C NMR (**1f**)



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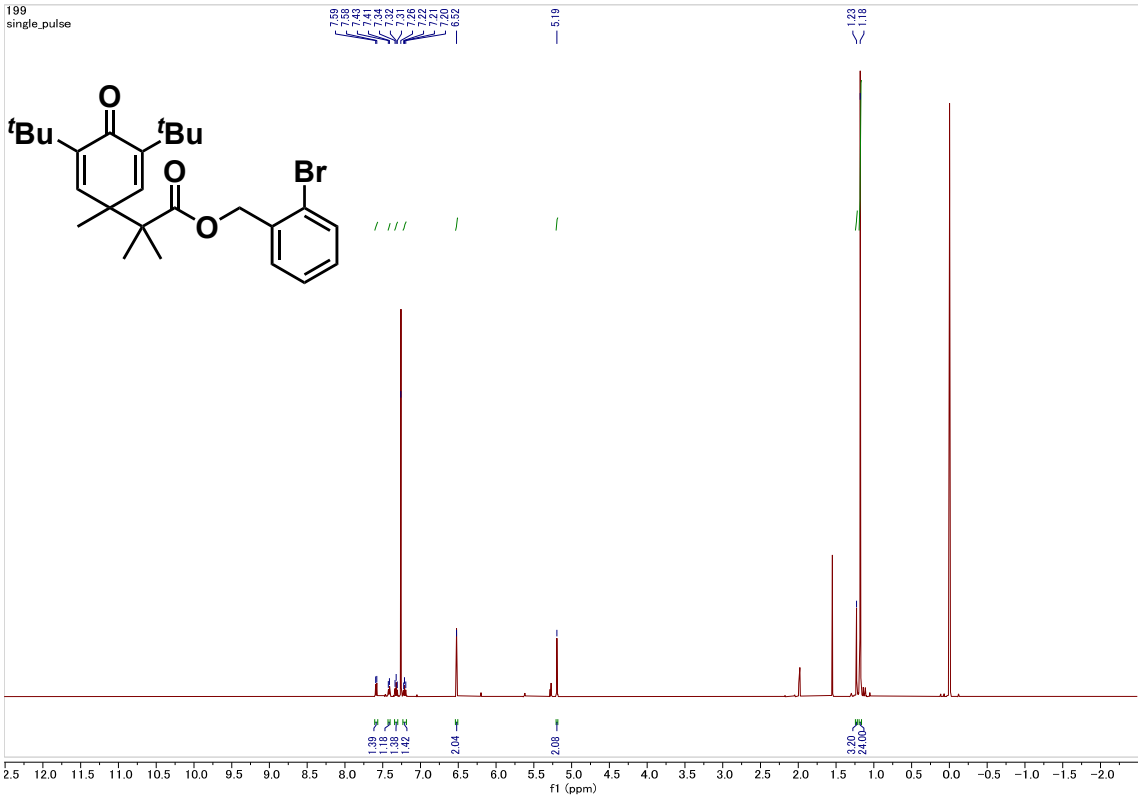

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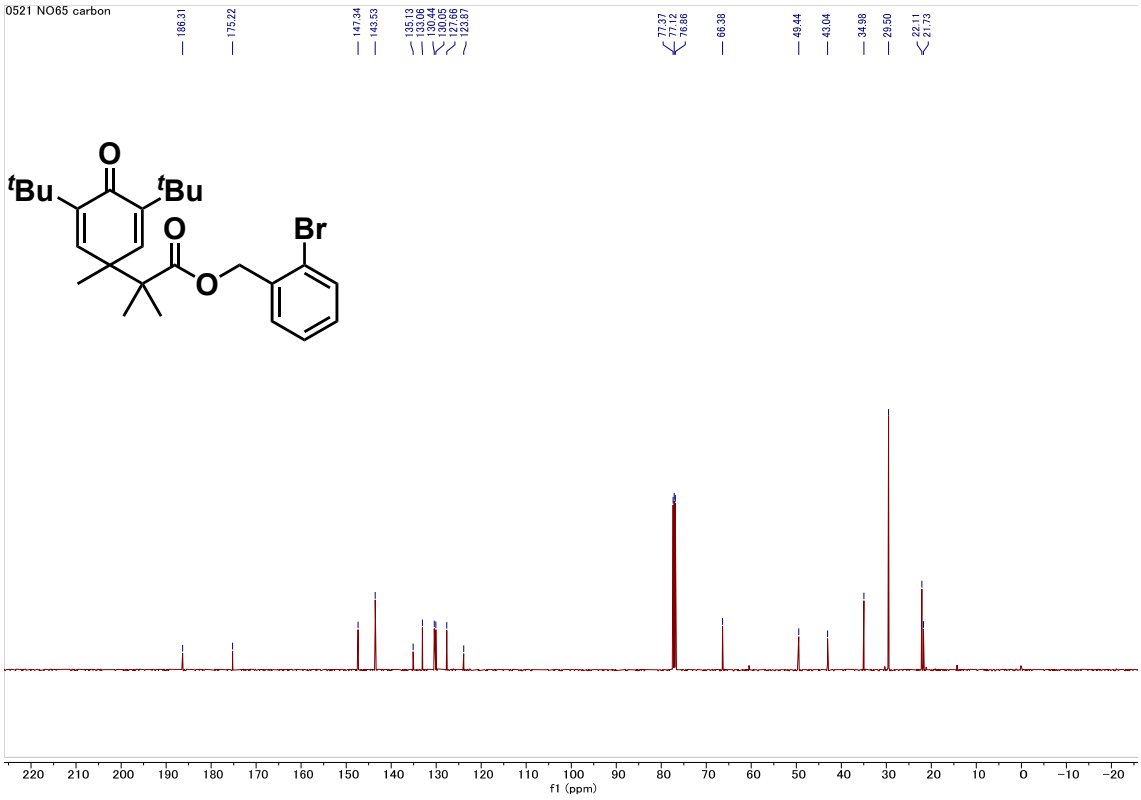

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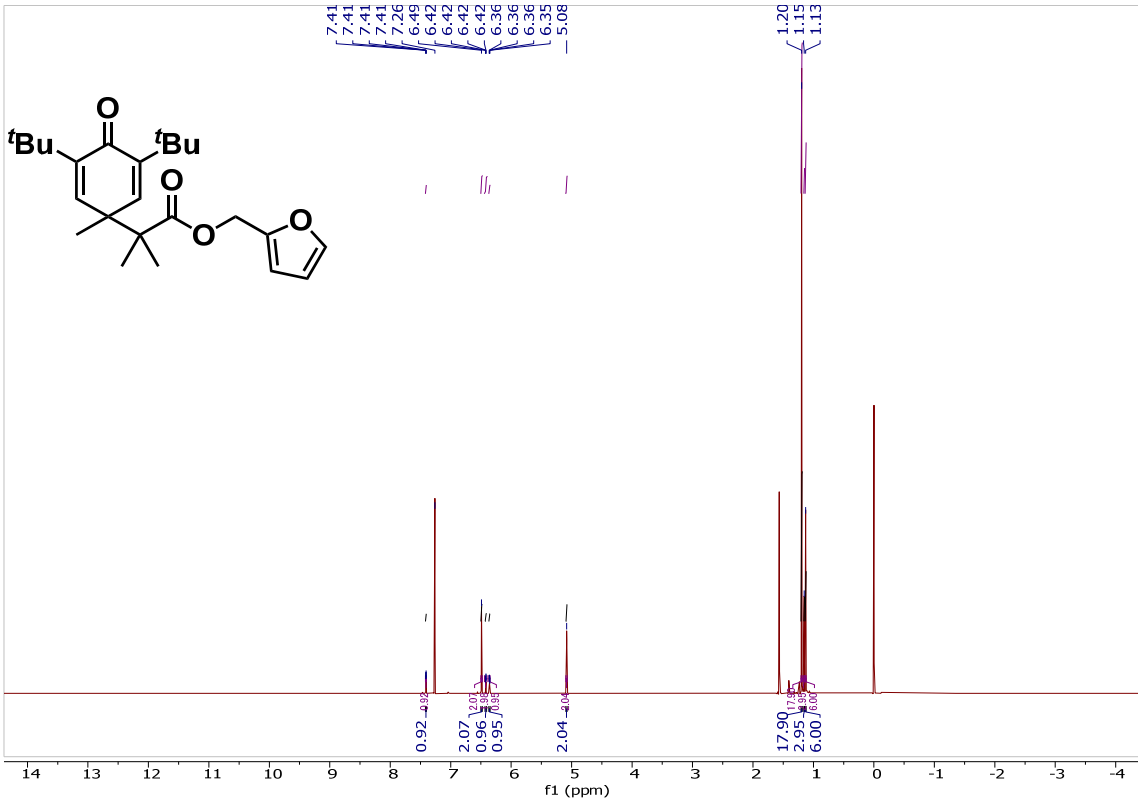

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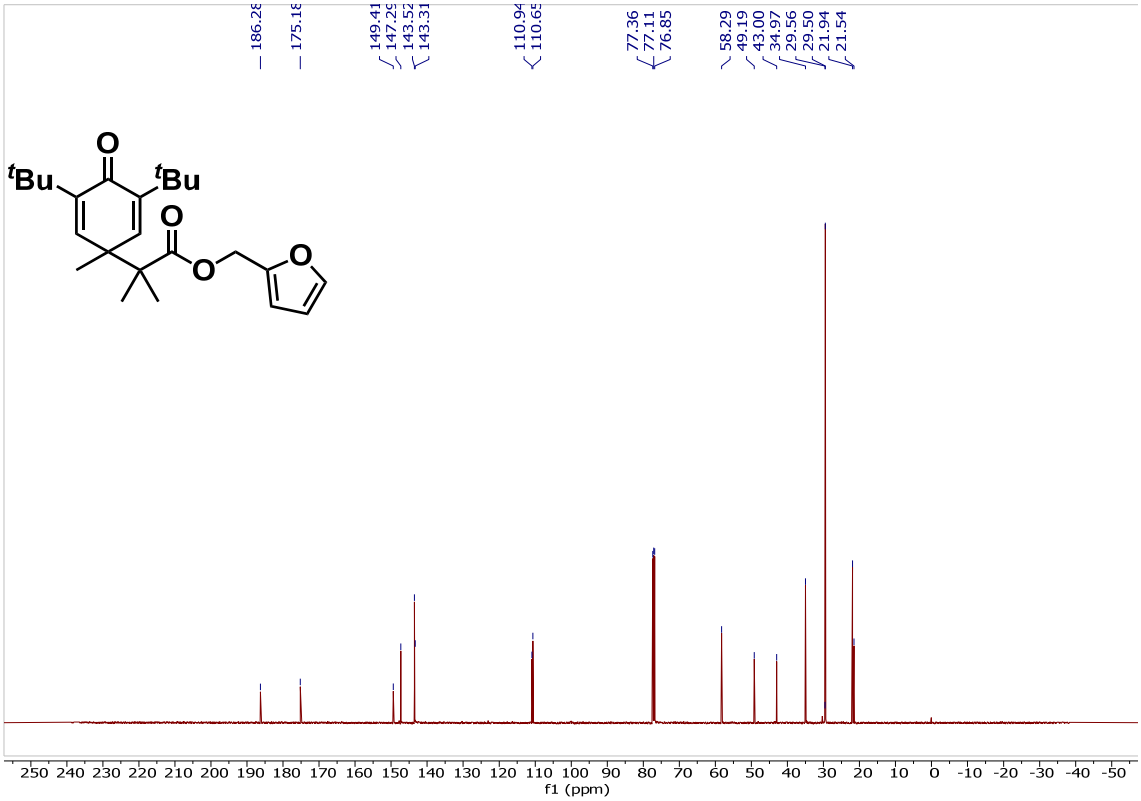
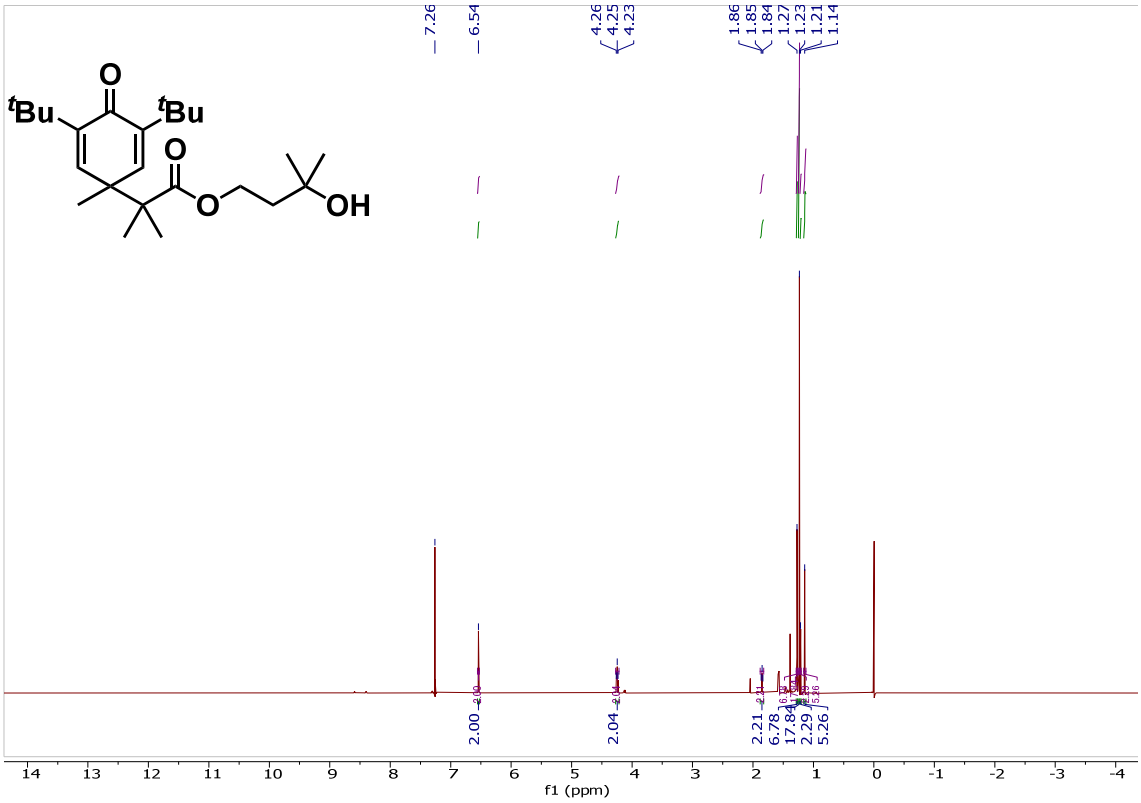


^{1}H NMR (**1i**)



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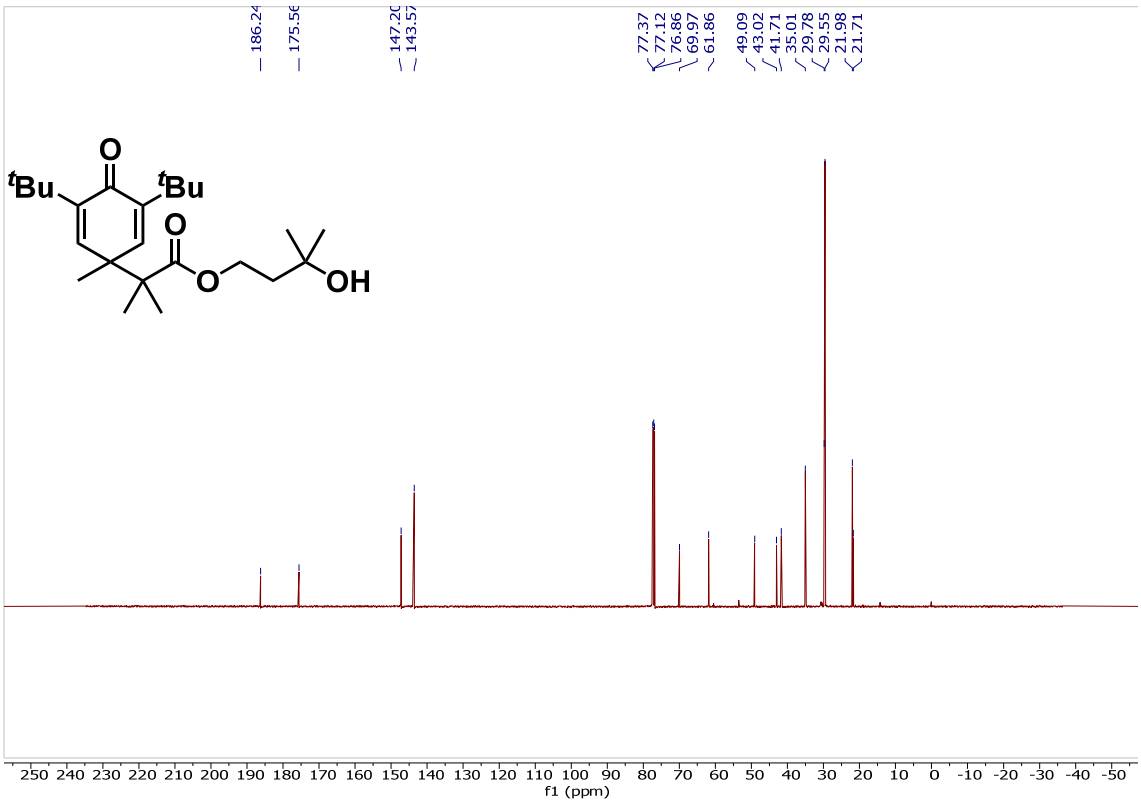

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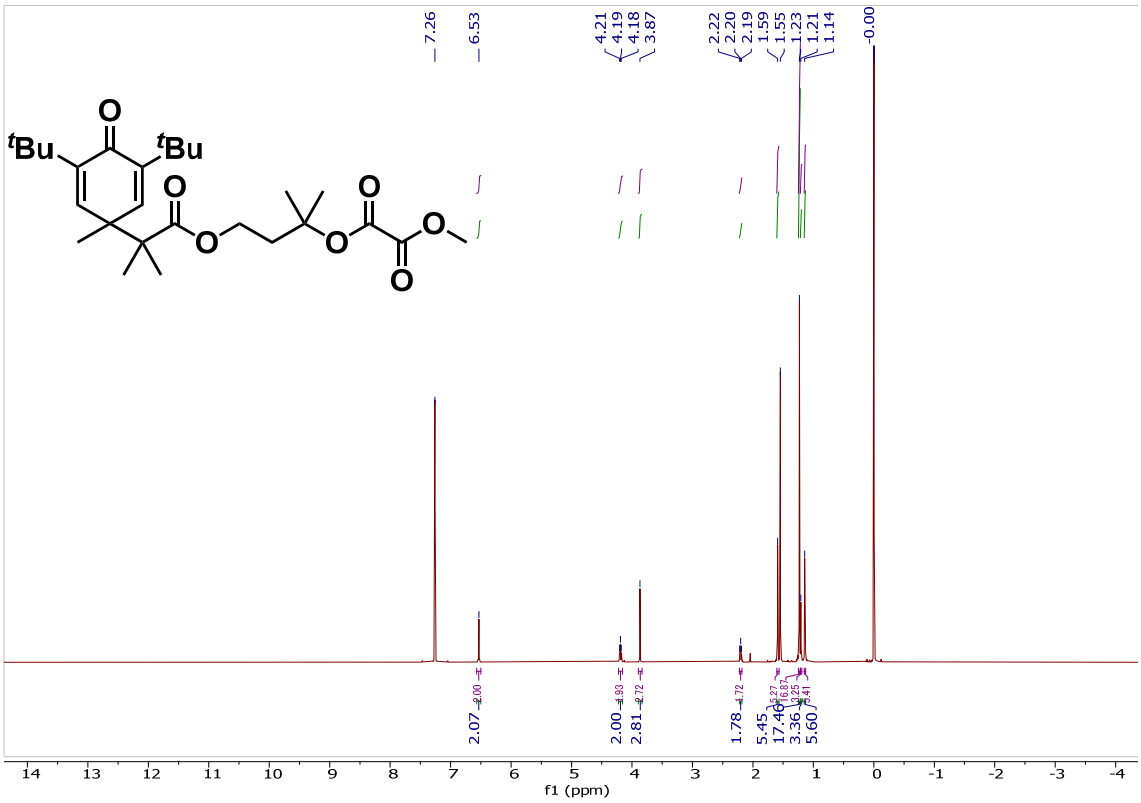
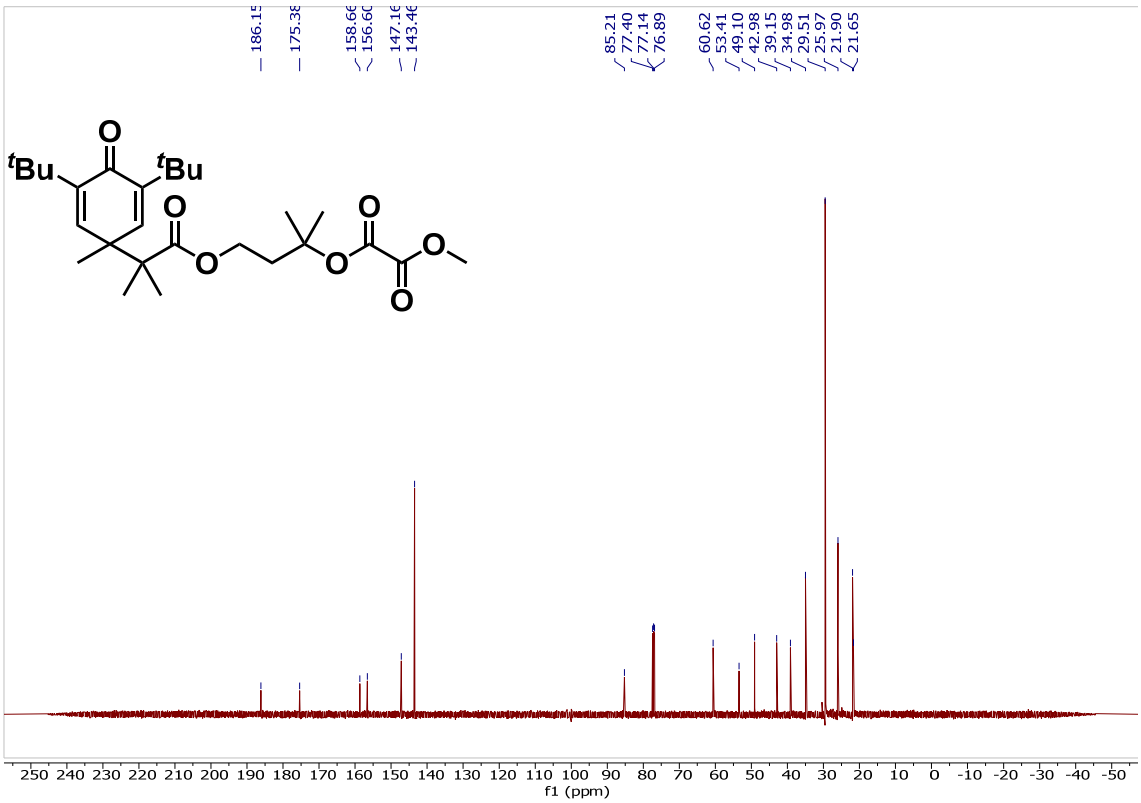


^{13}C NMR (**1j**)



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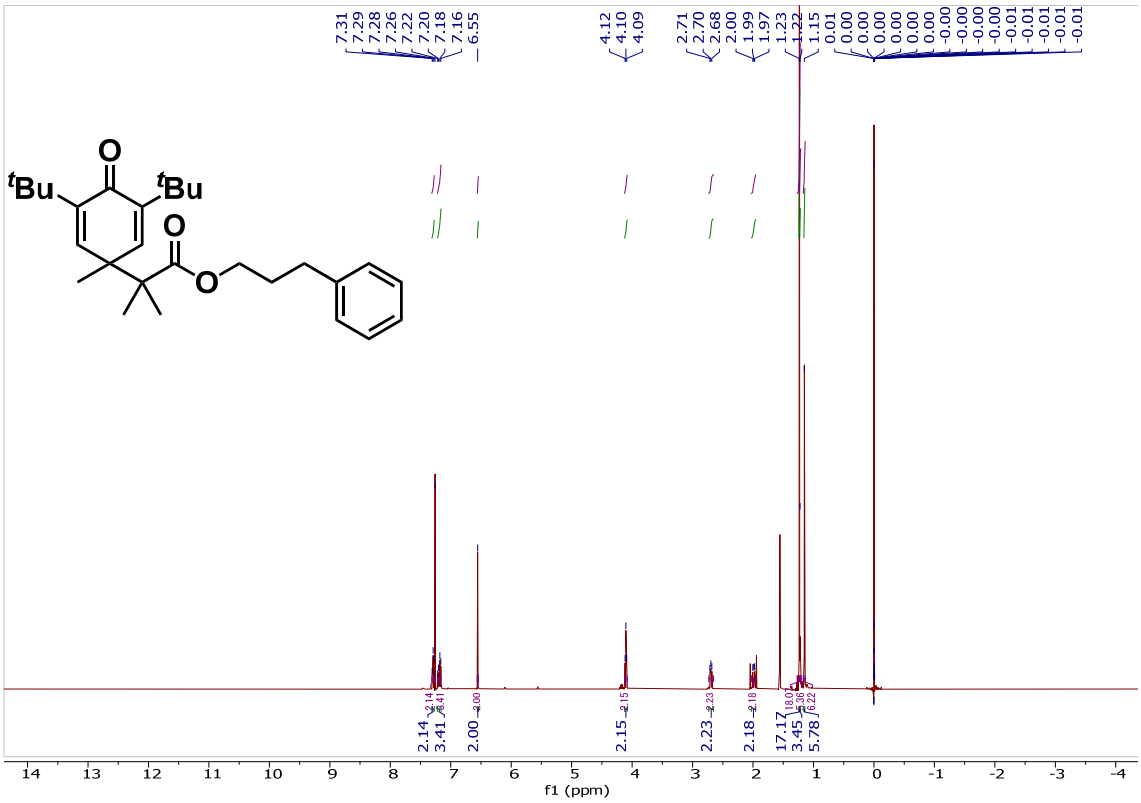

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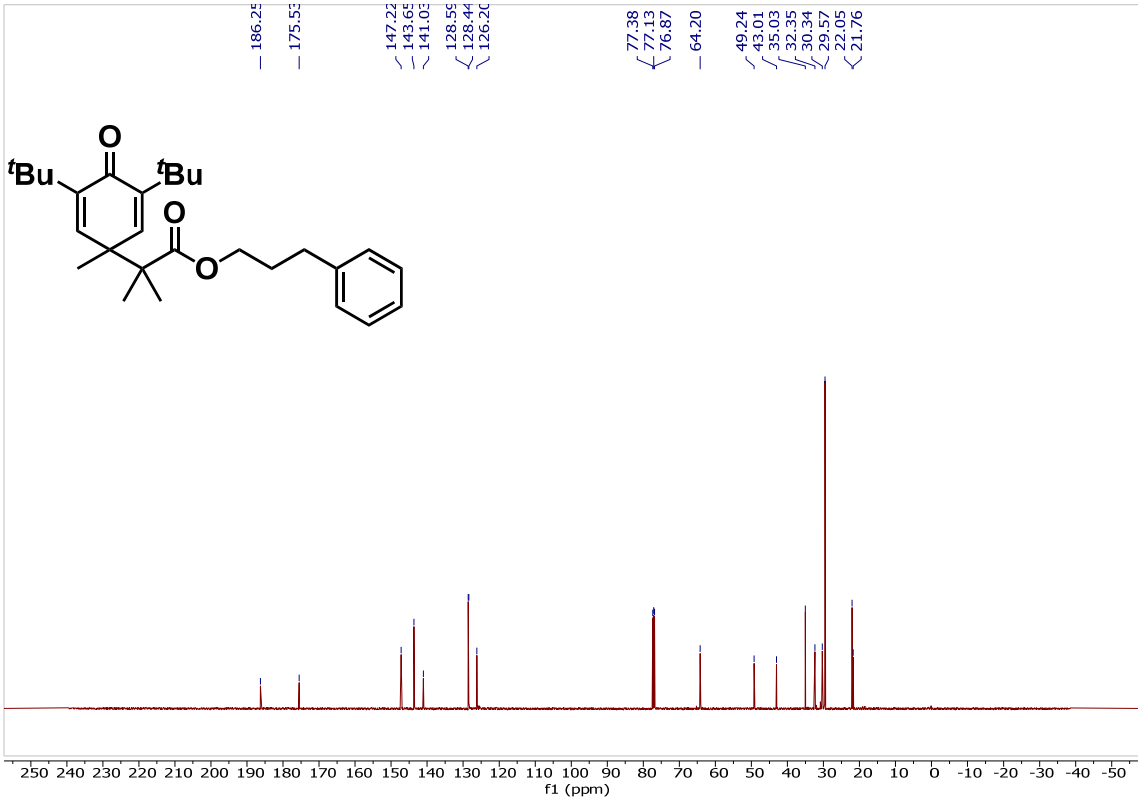
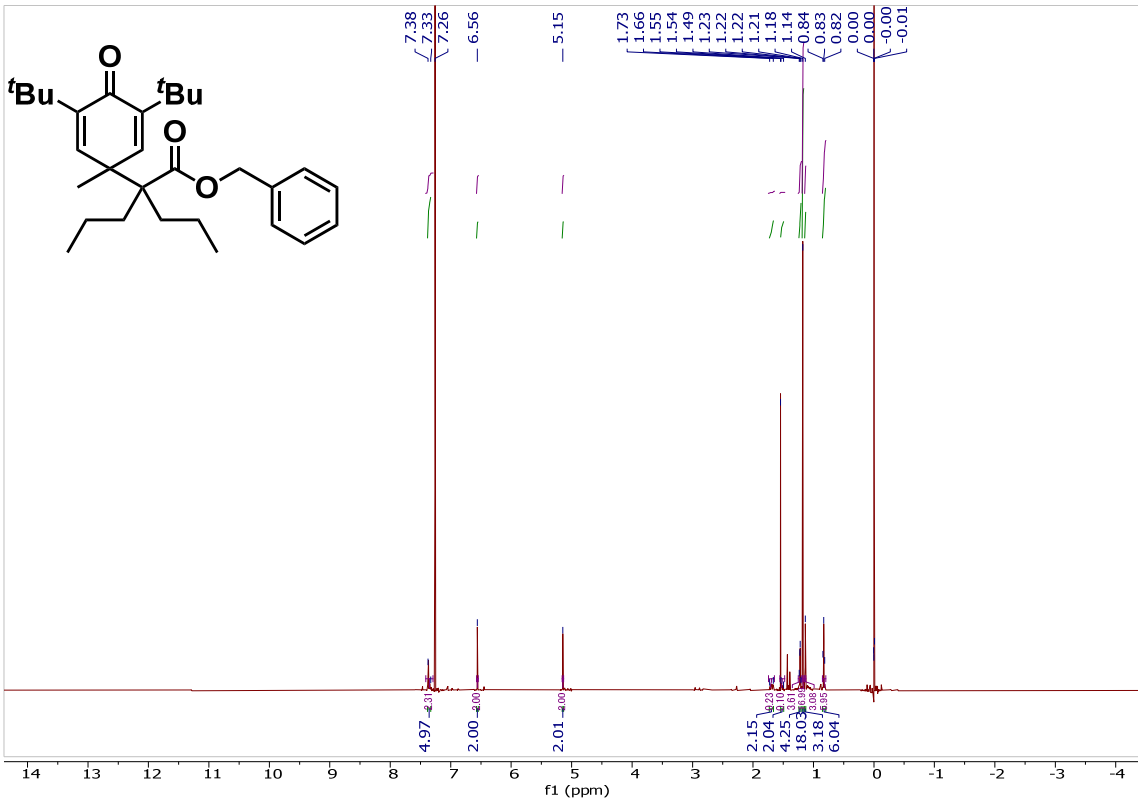


^{1}H NMR (**1l**)



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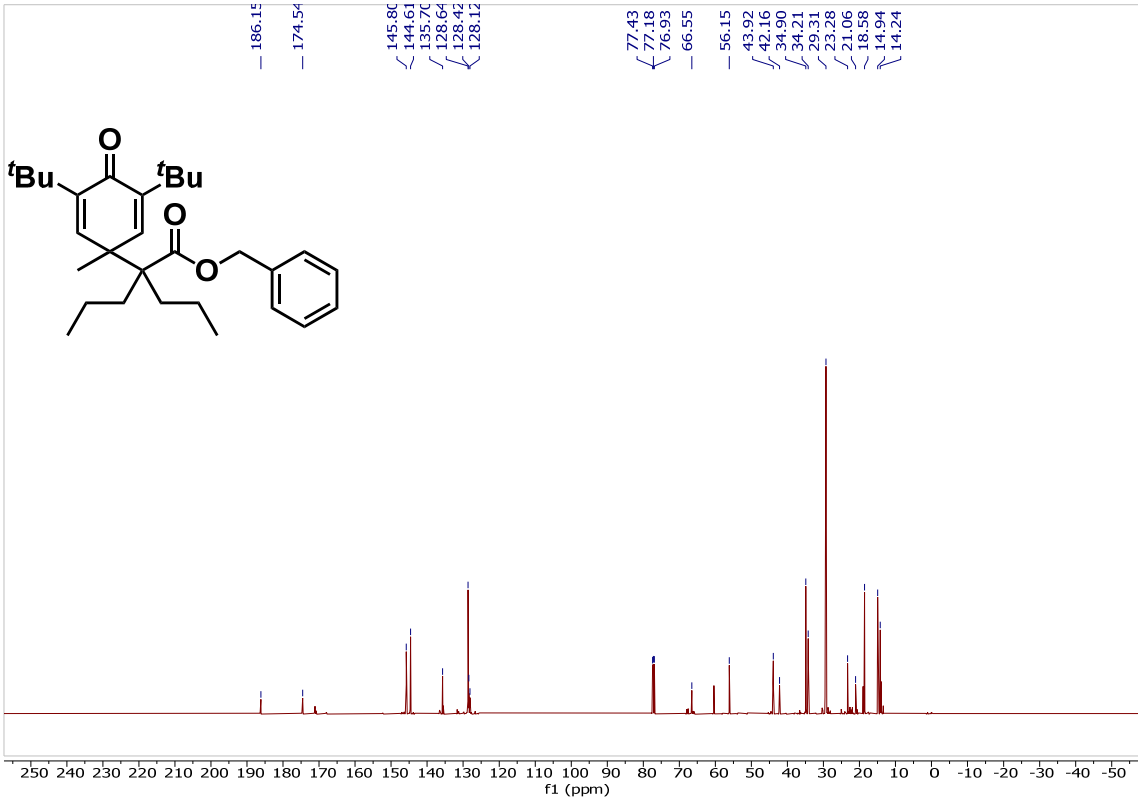

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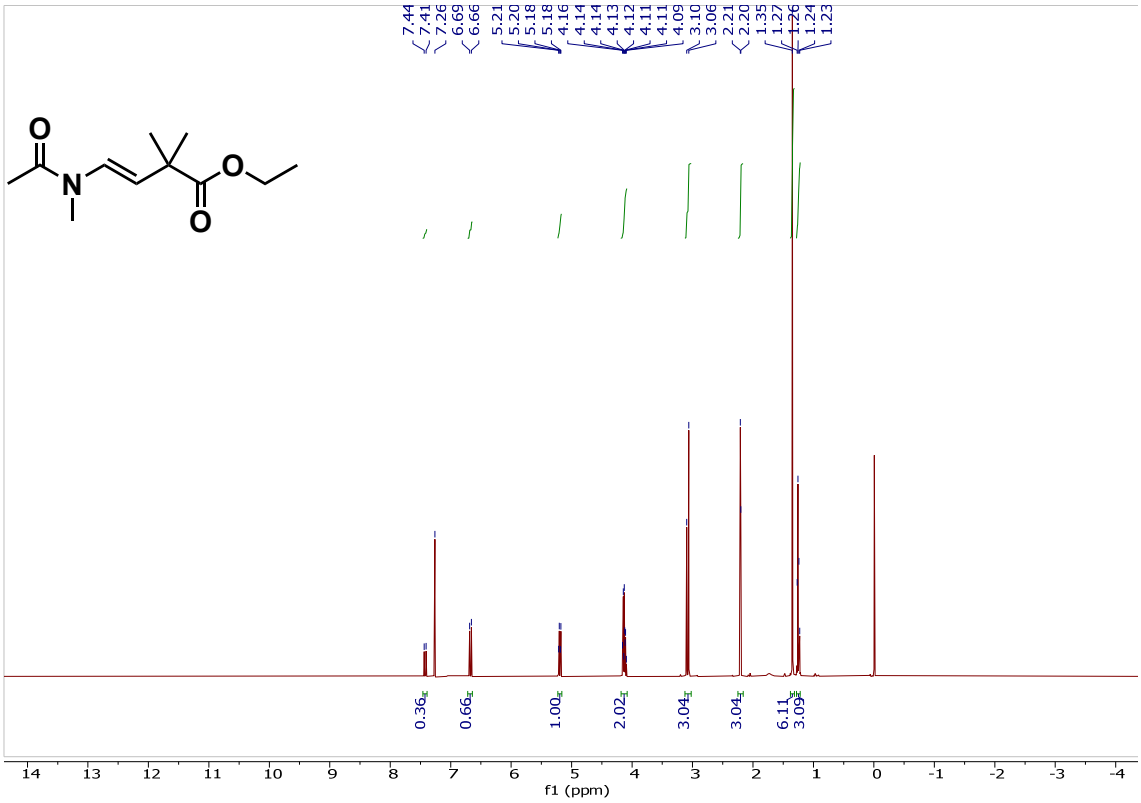

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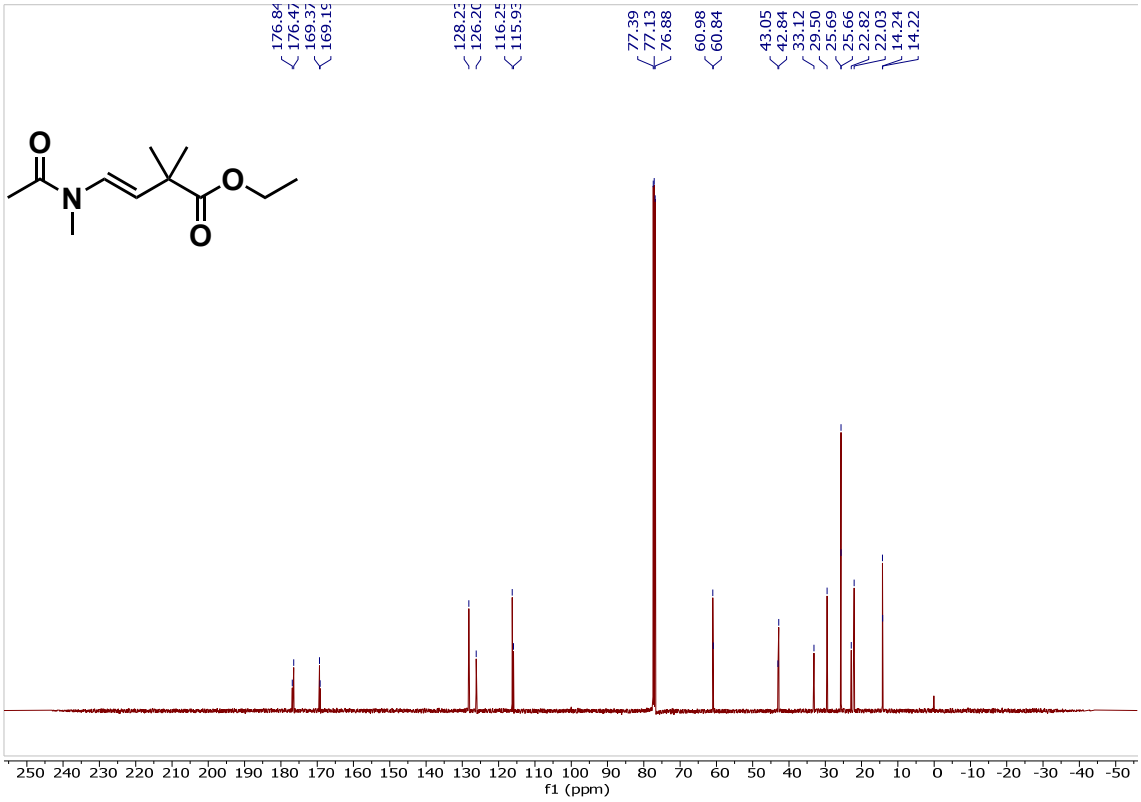

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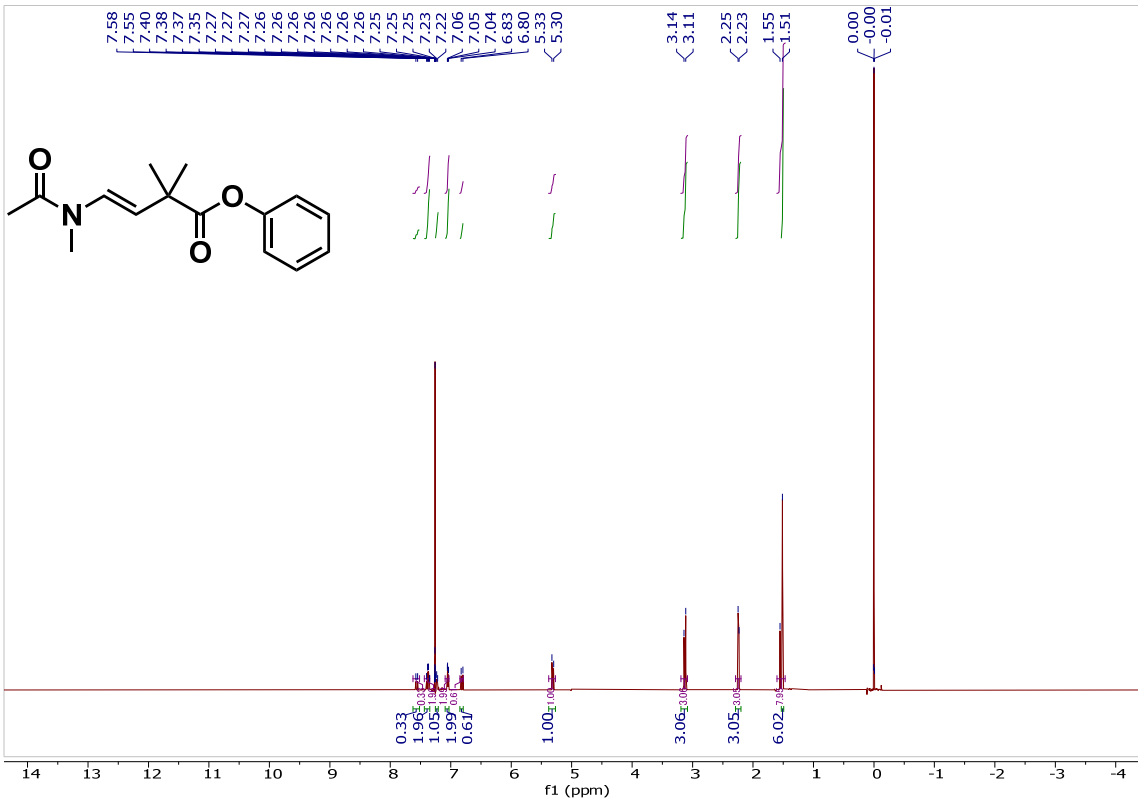

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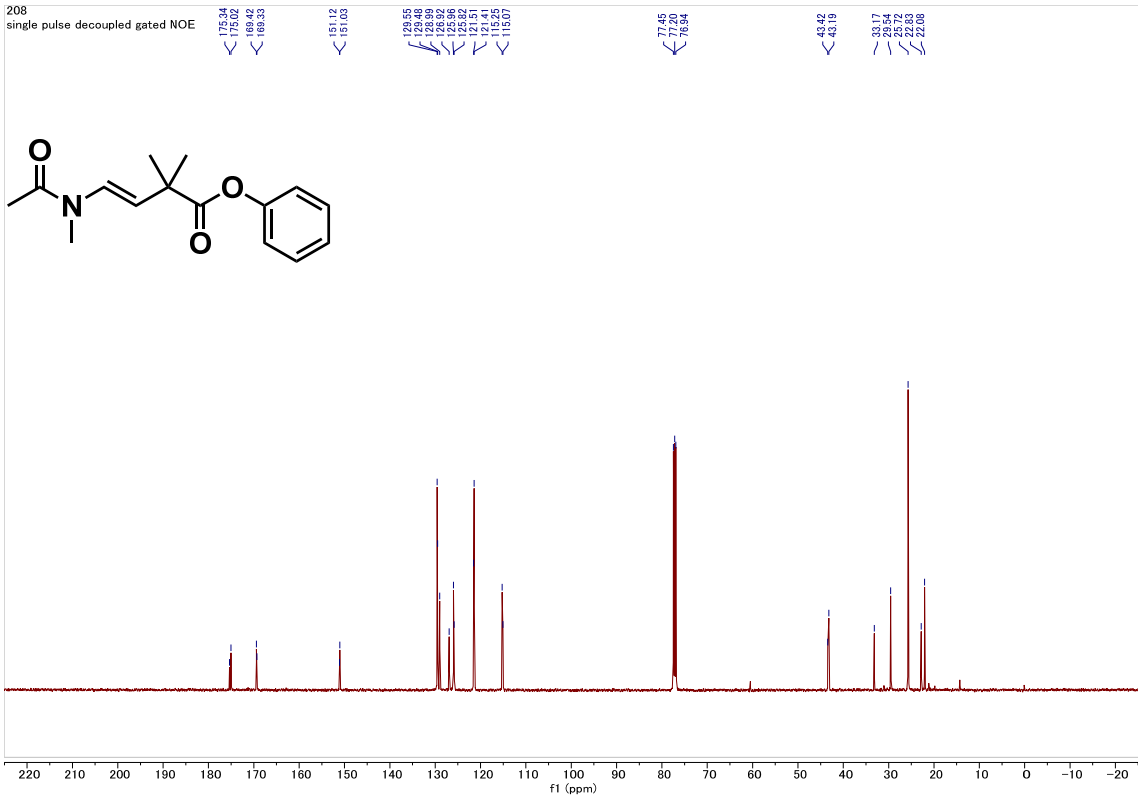

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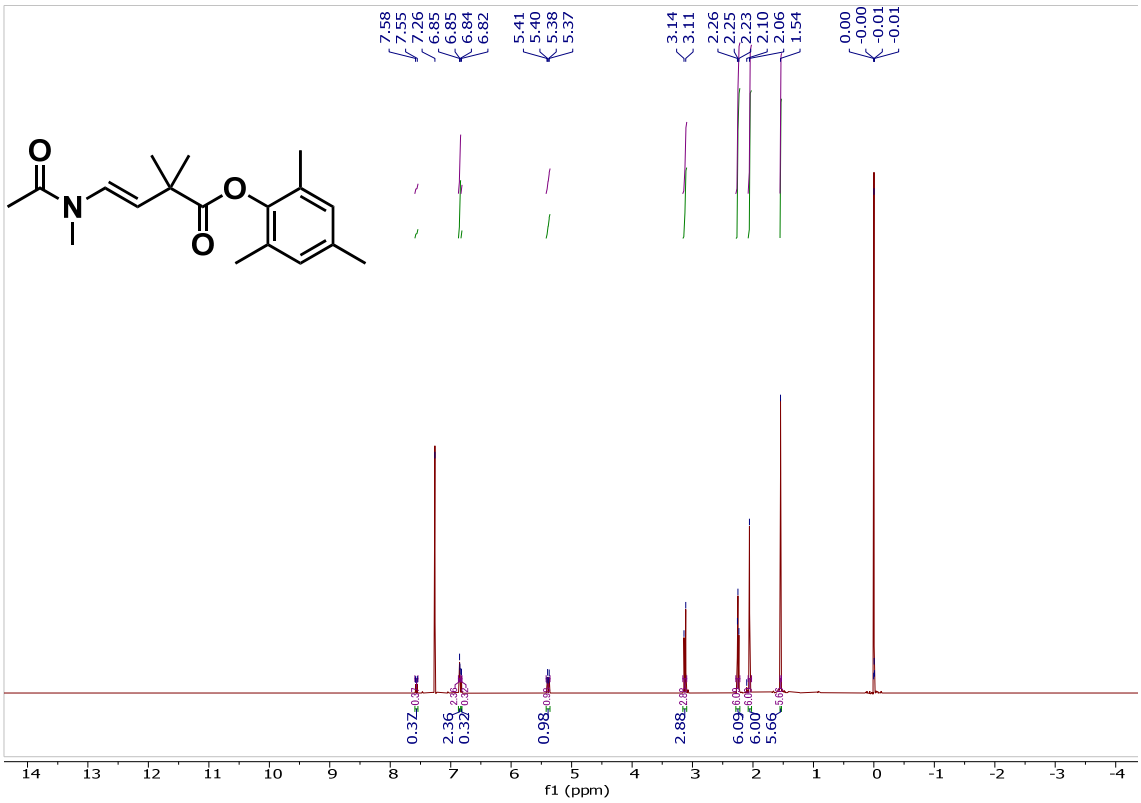

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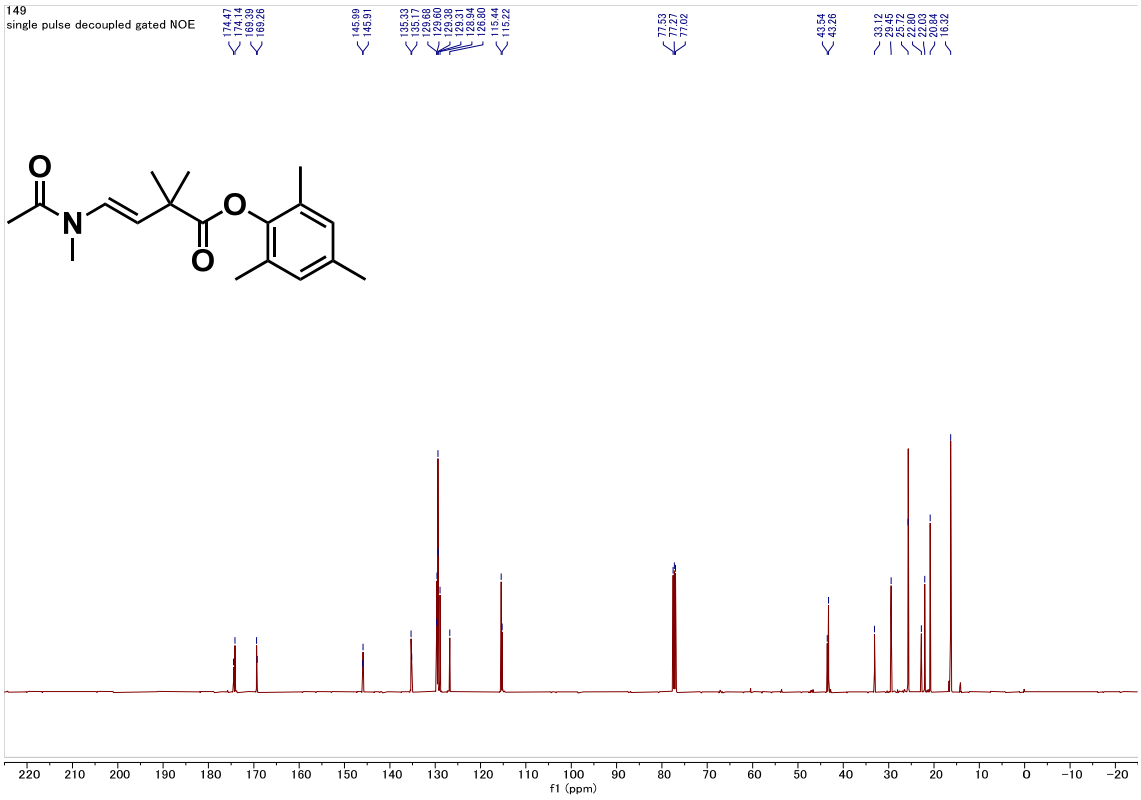

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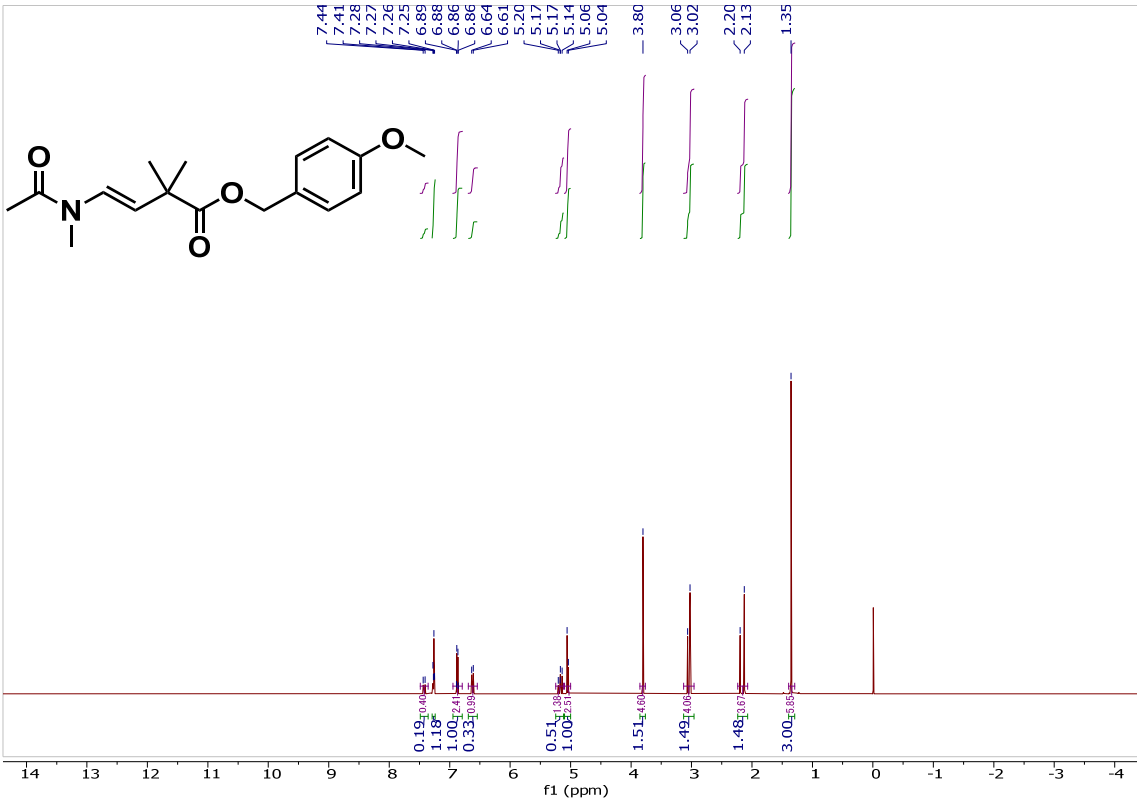

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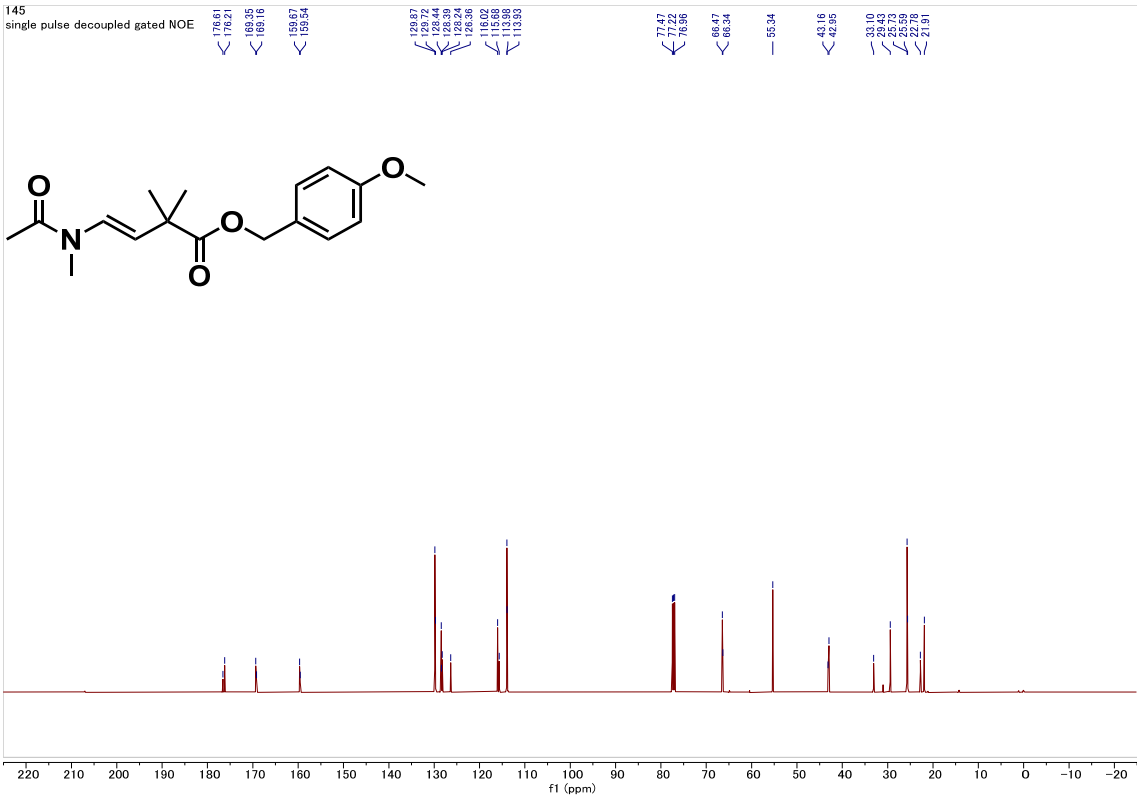

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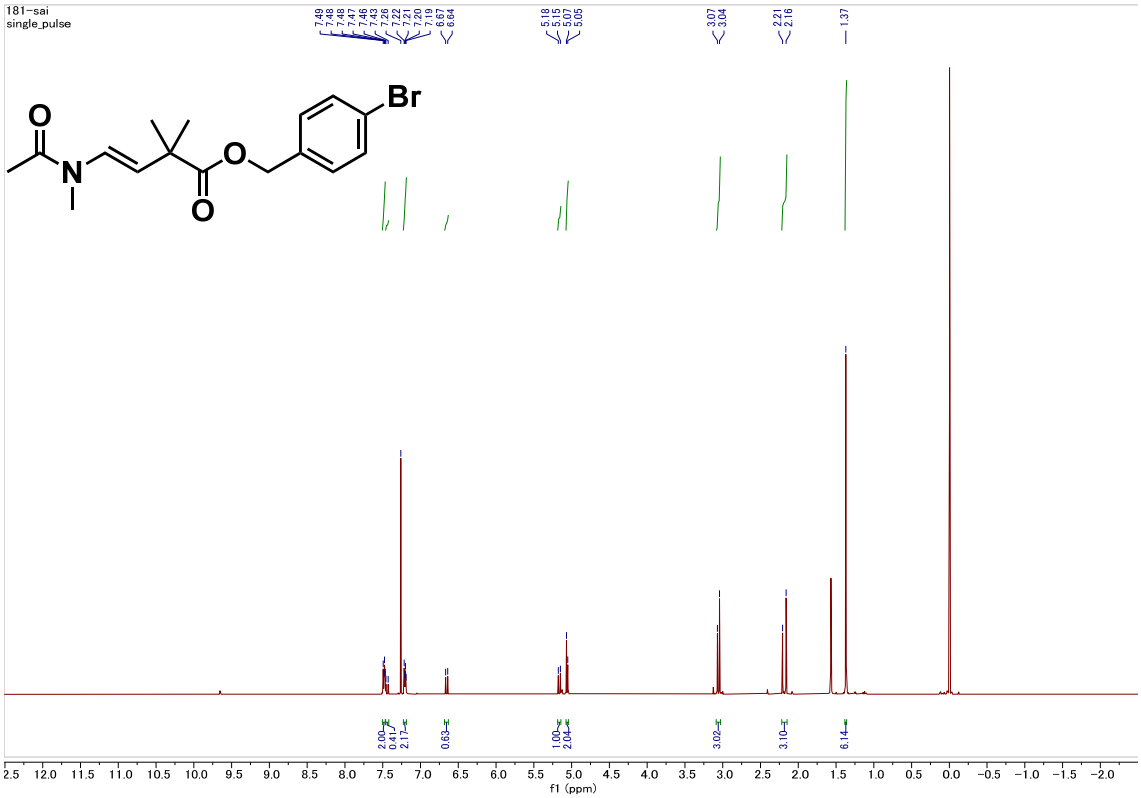

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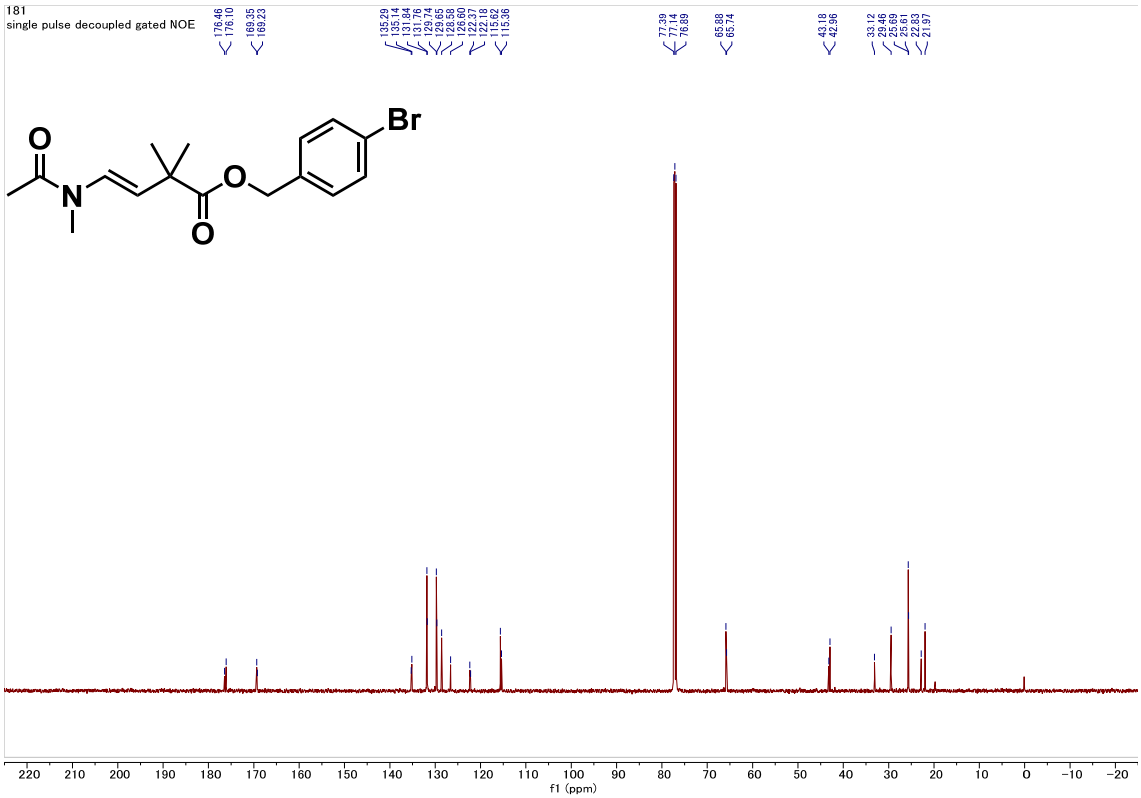

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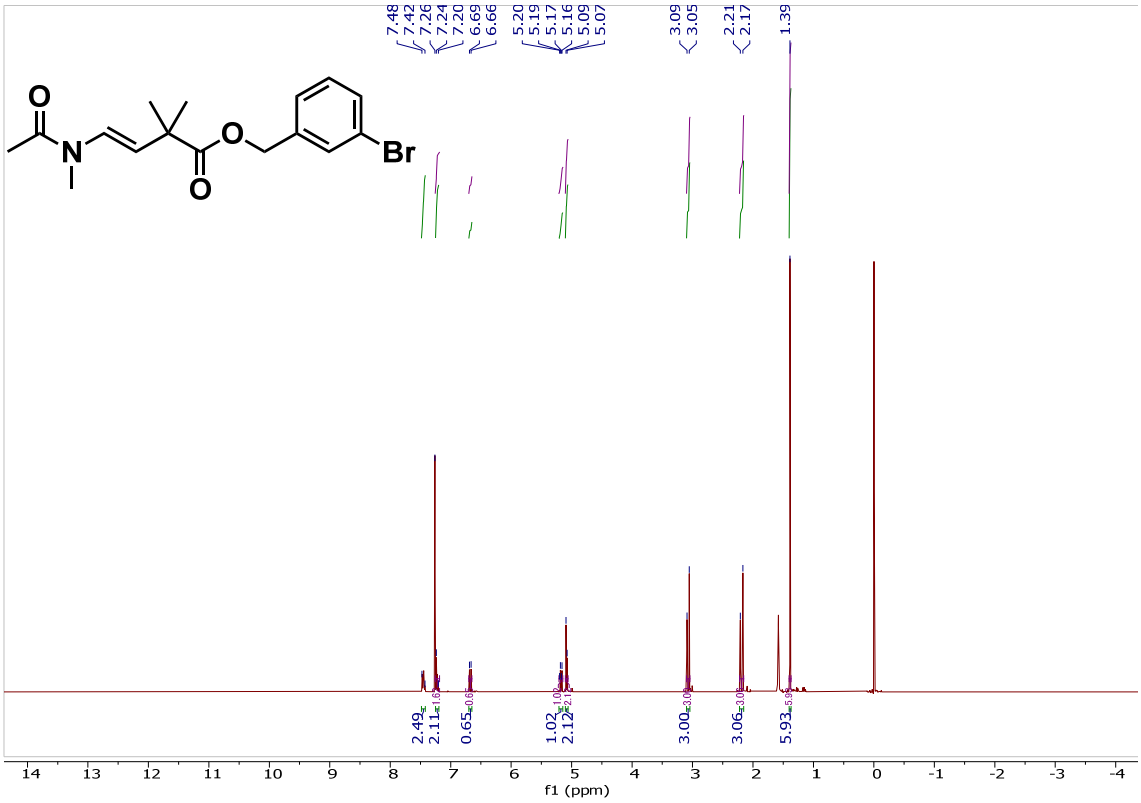

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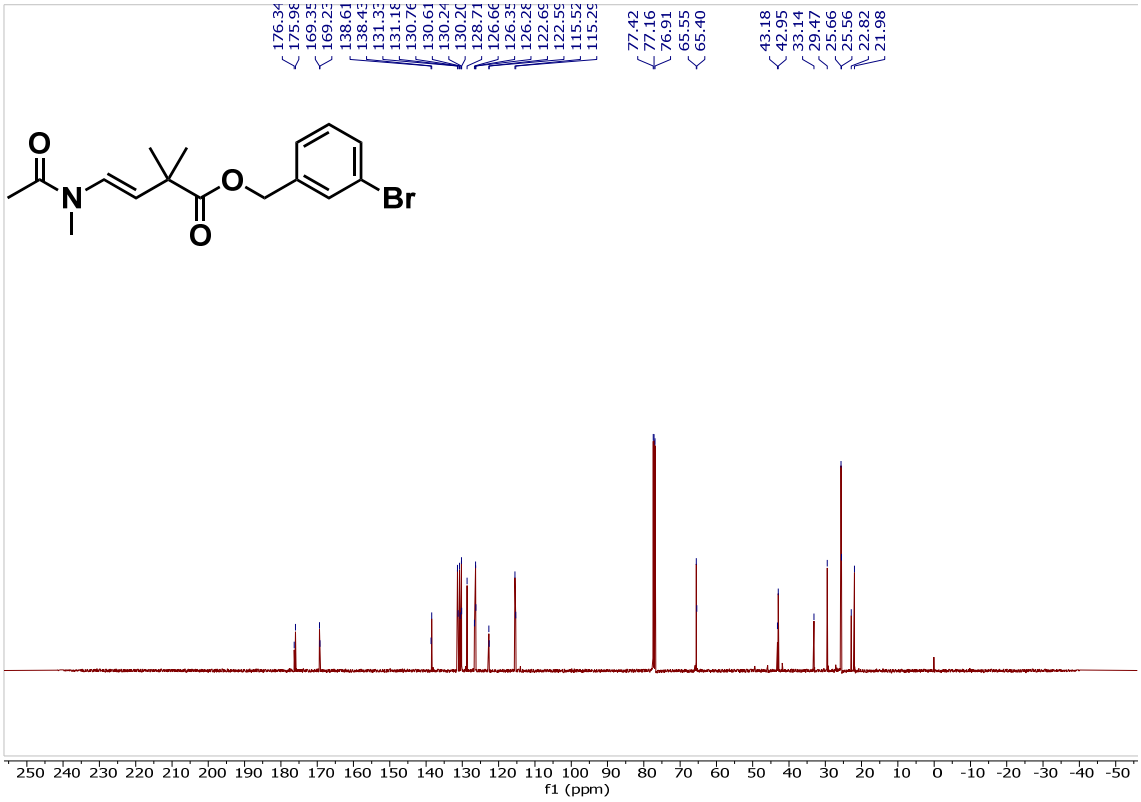

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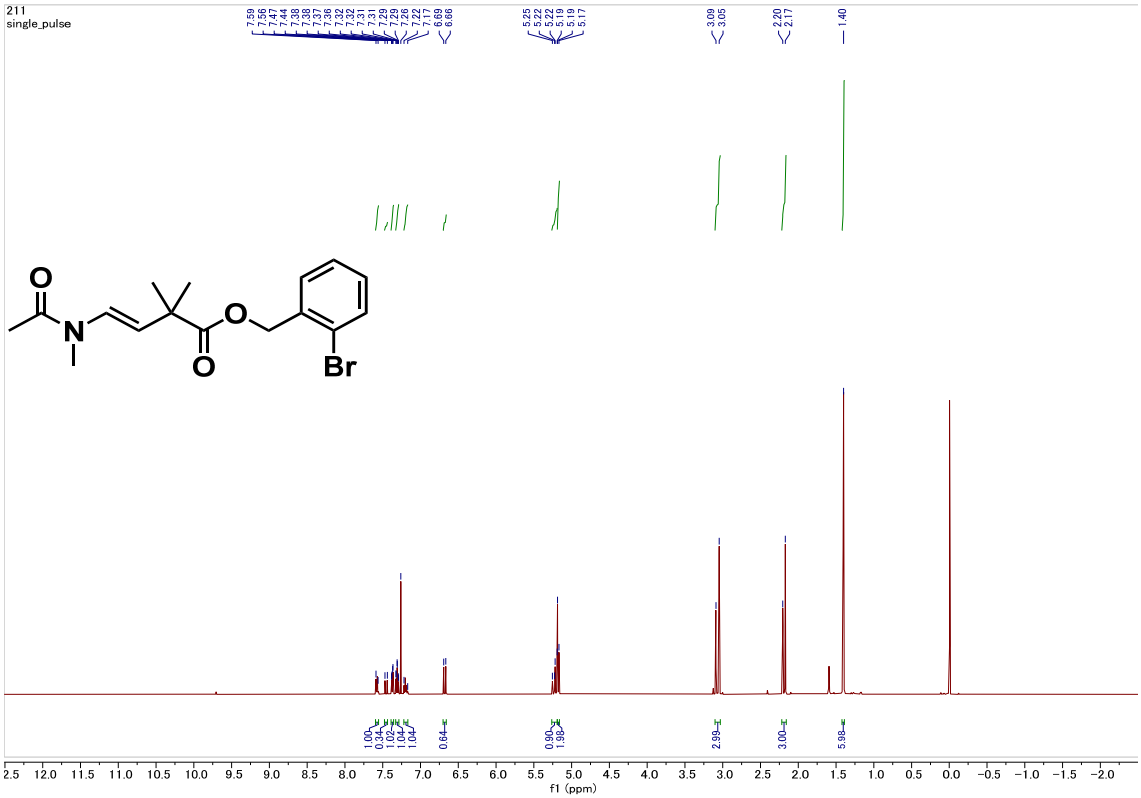

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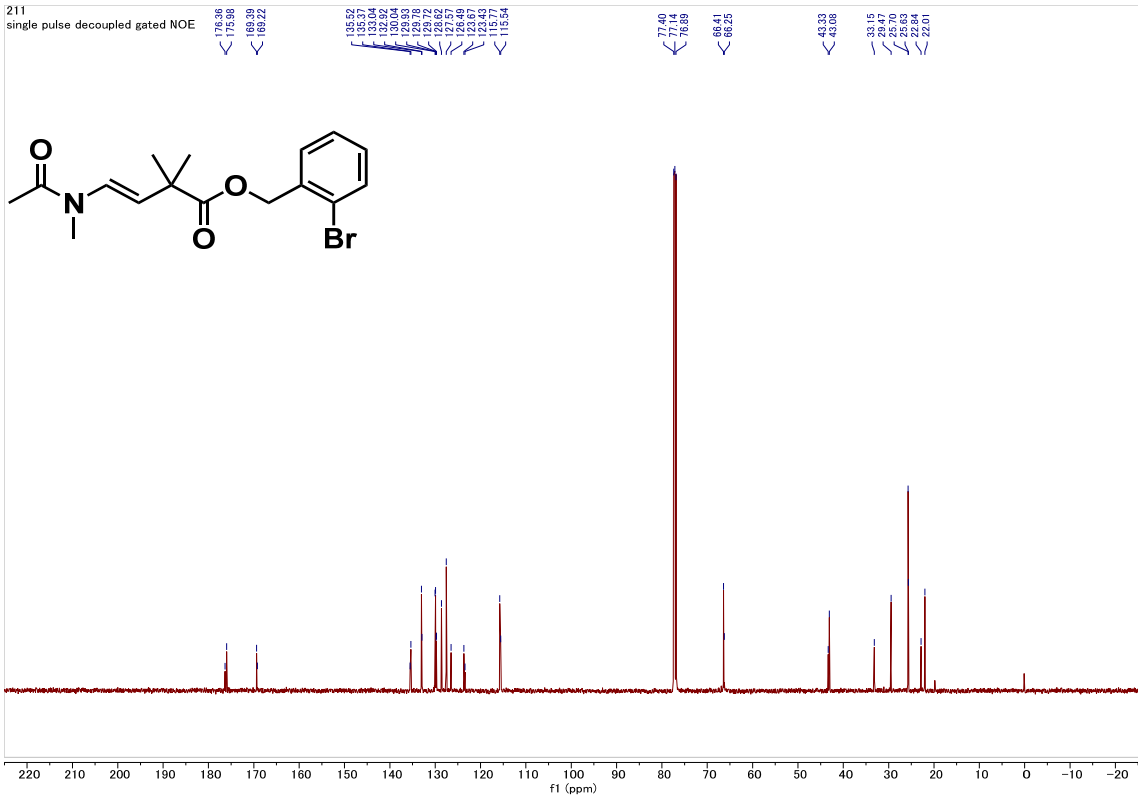

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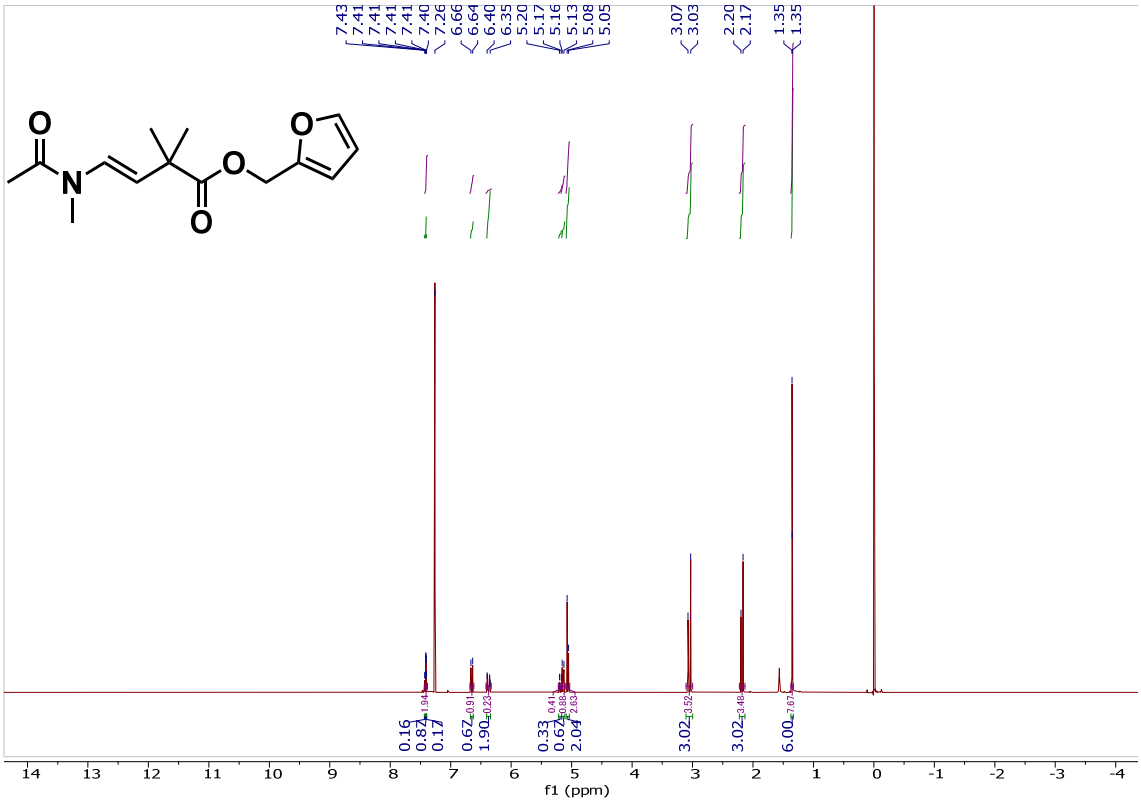

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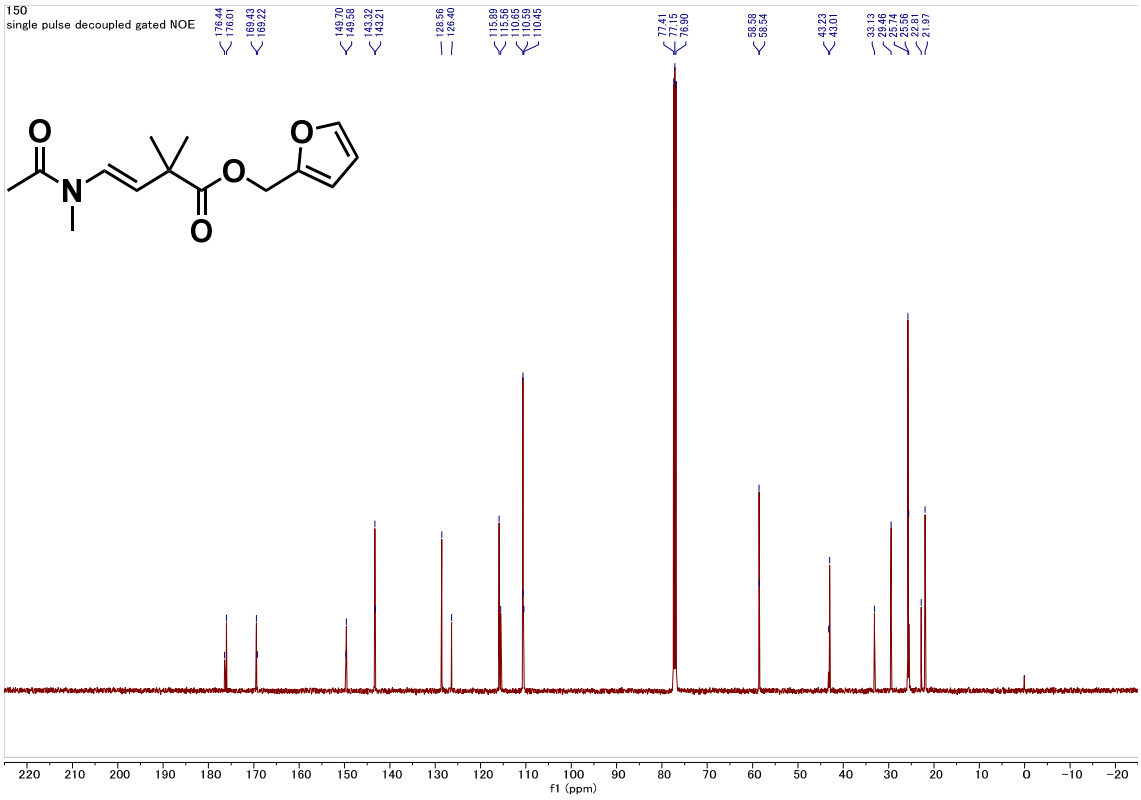
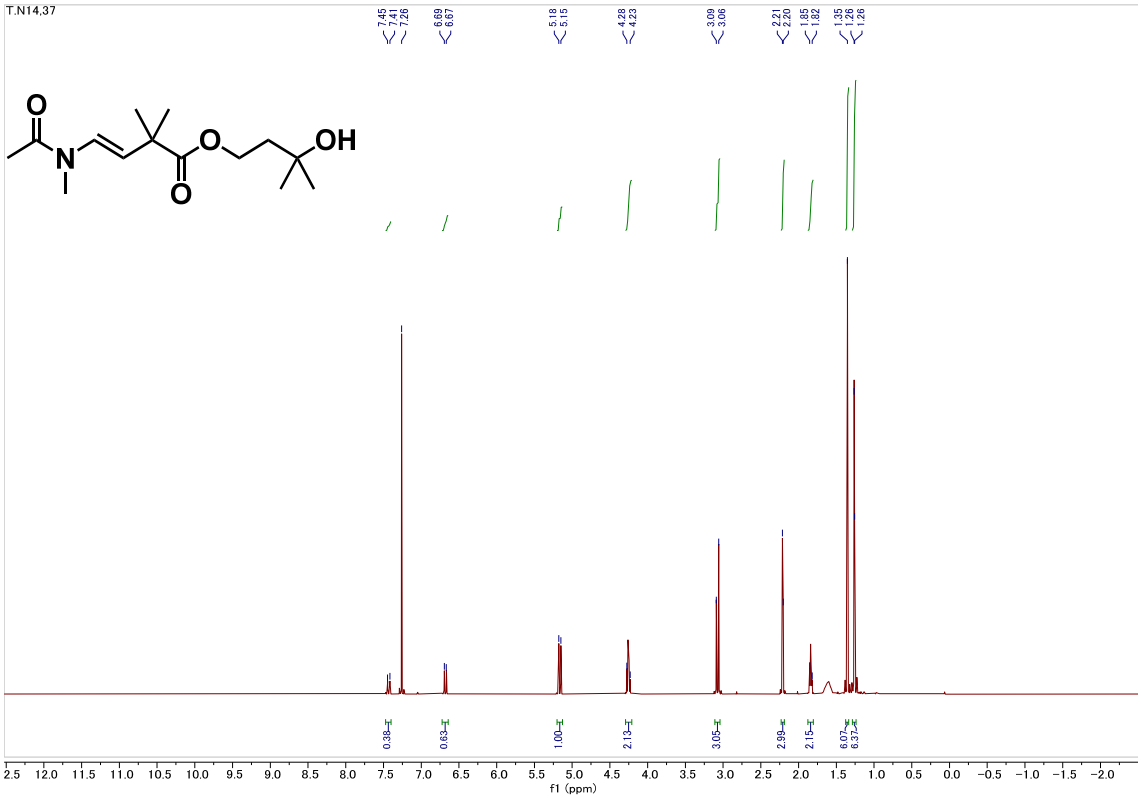
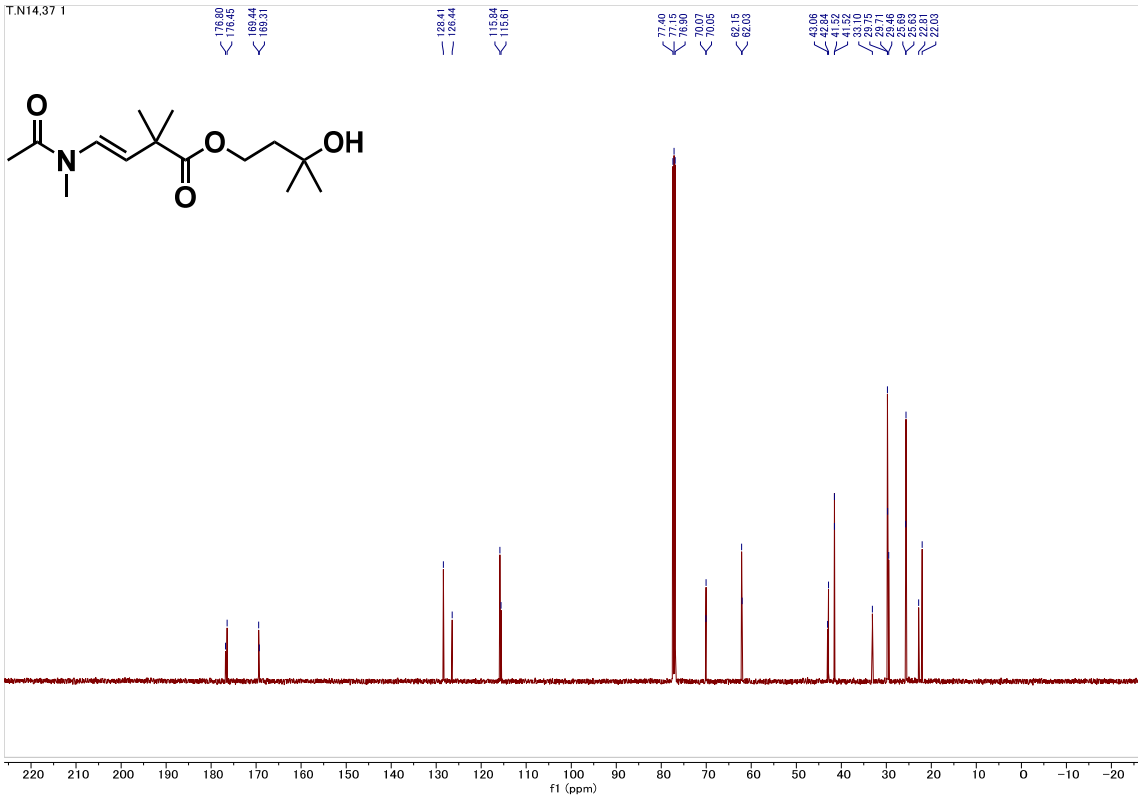


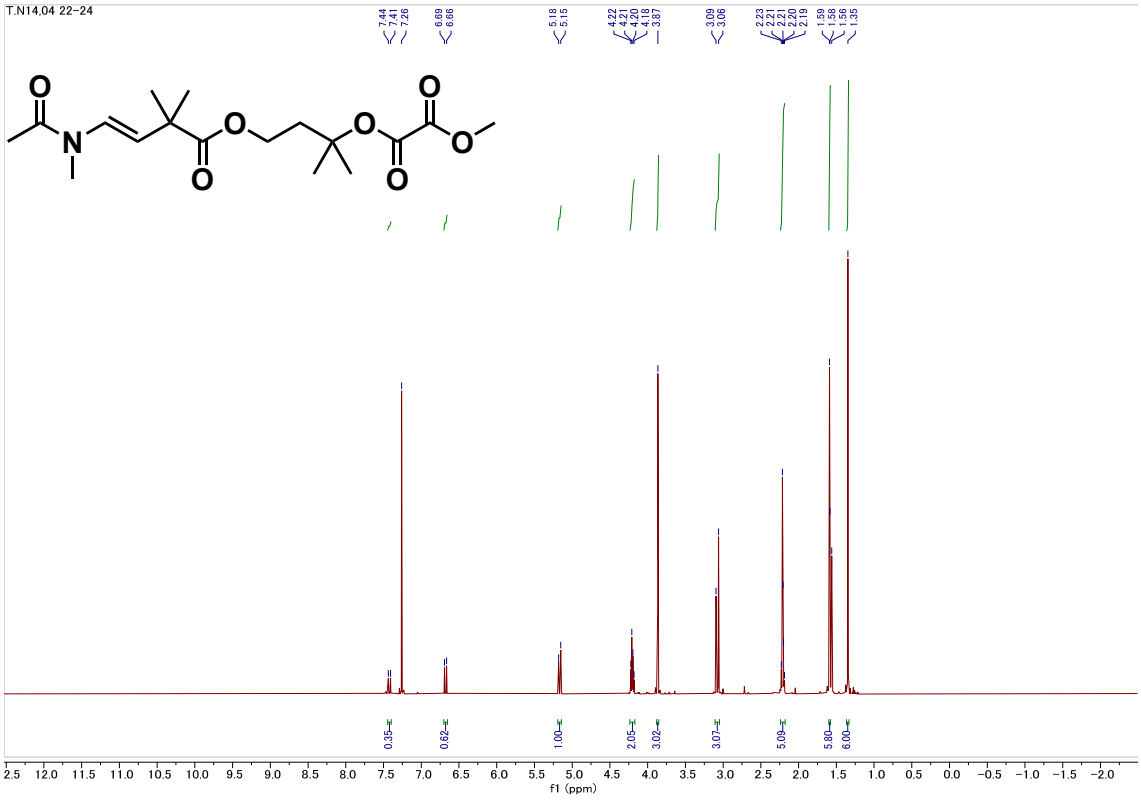
^{1}H NMR (**3ia**)



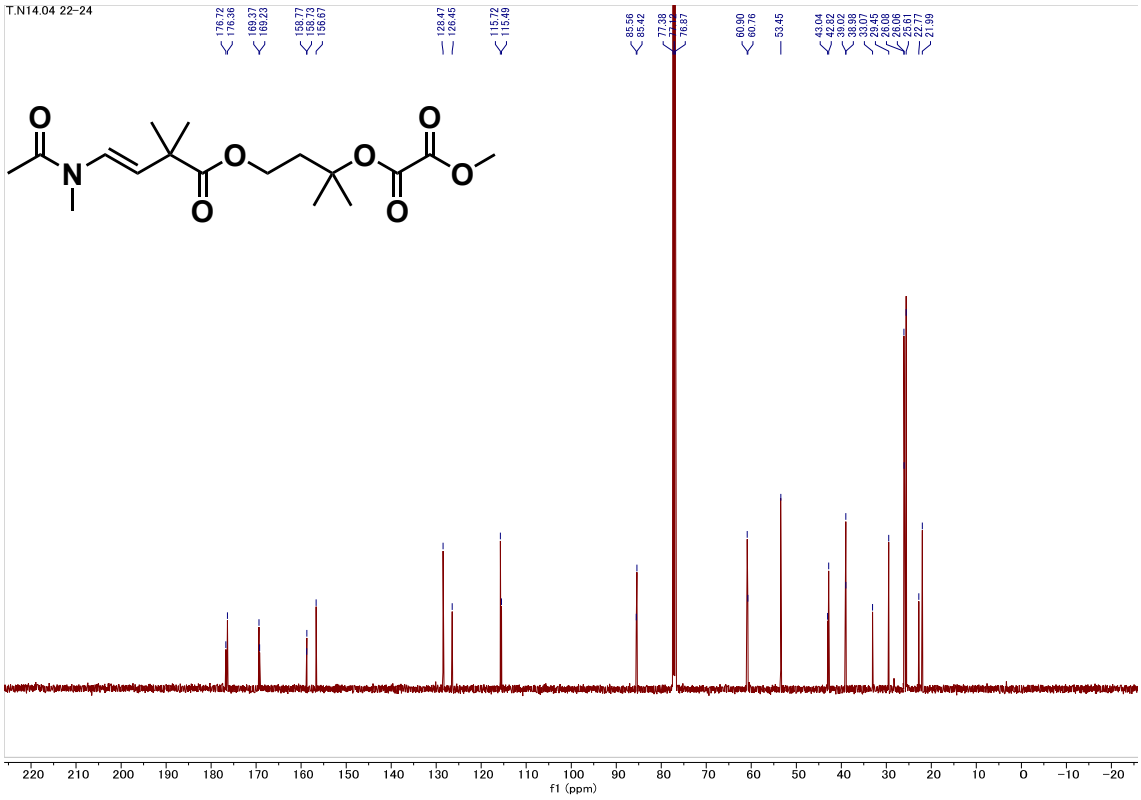
^{13}C NMR (**3ia**)



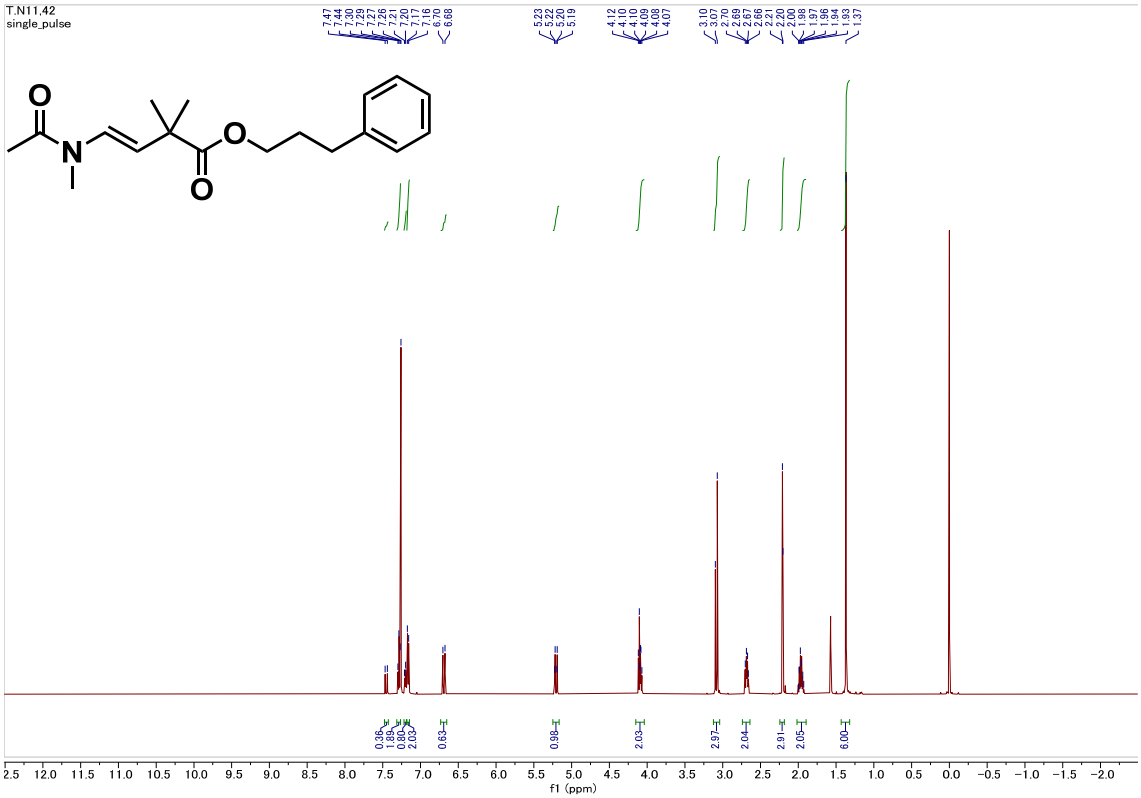
^{1}H NMR (**3ja**)



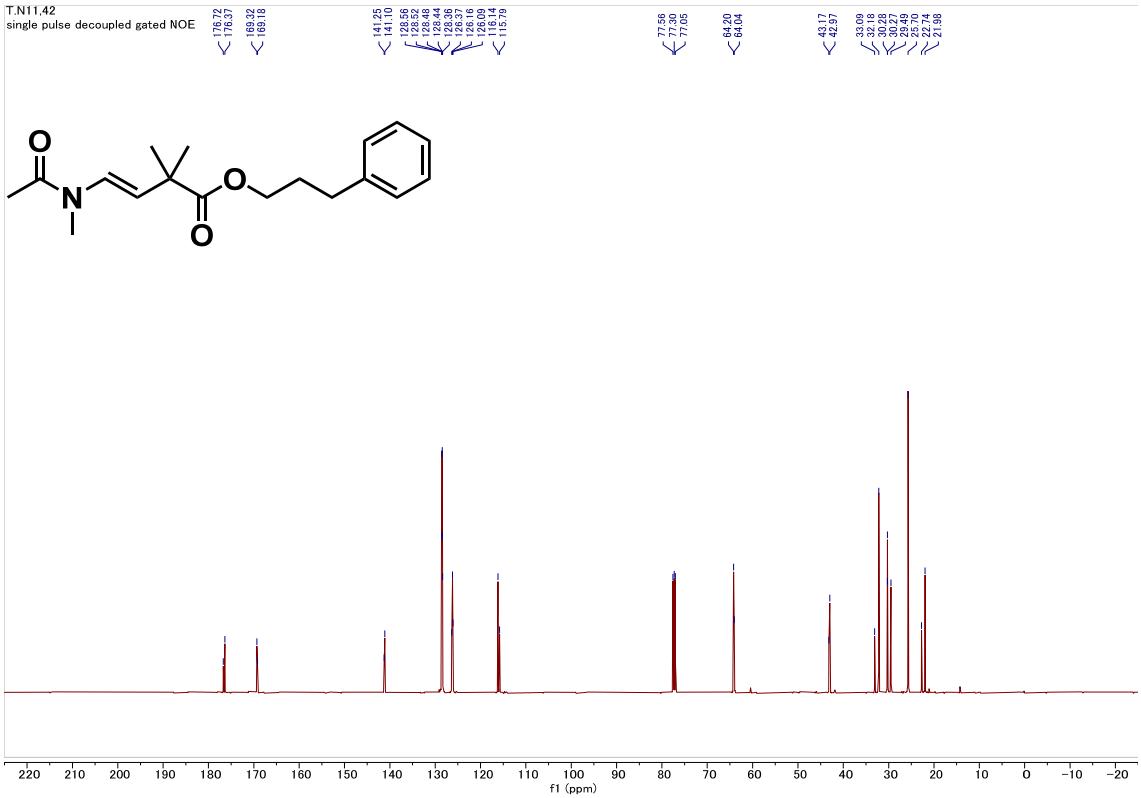
^{13}C NMR (**3ja**)



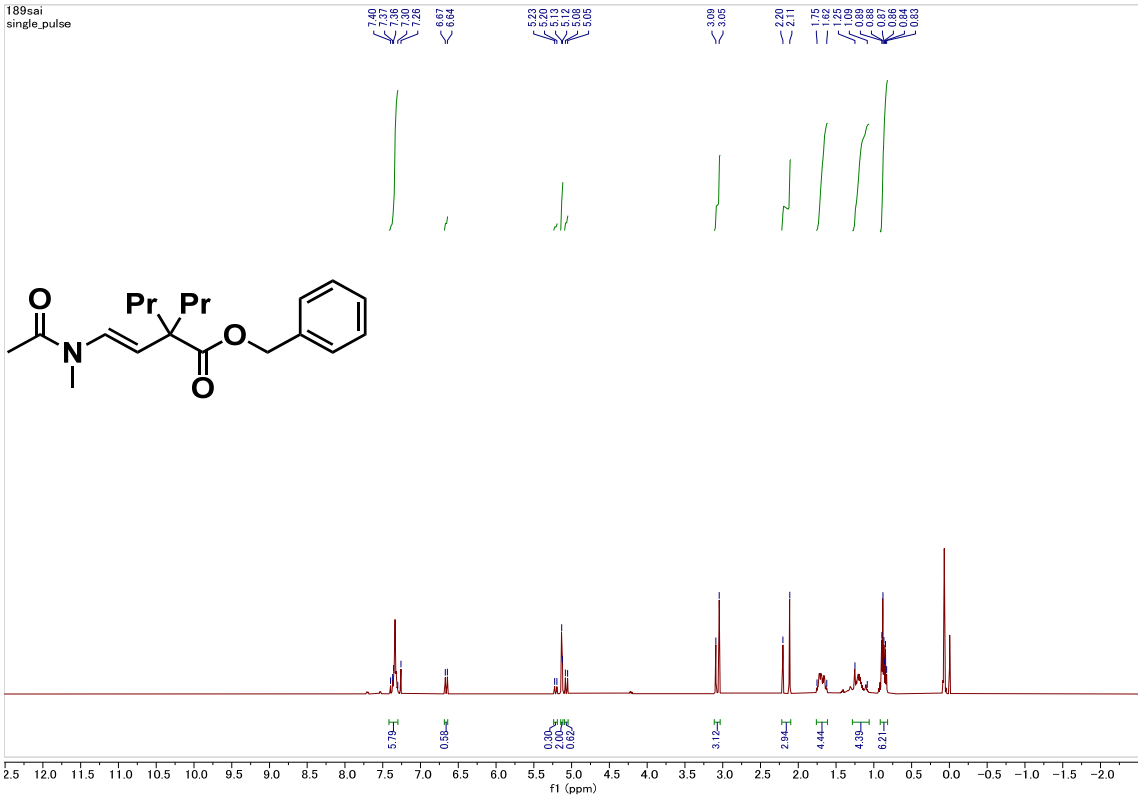
^{1}H NMR (**3ka**)



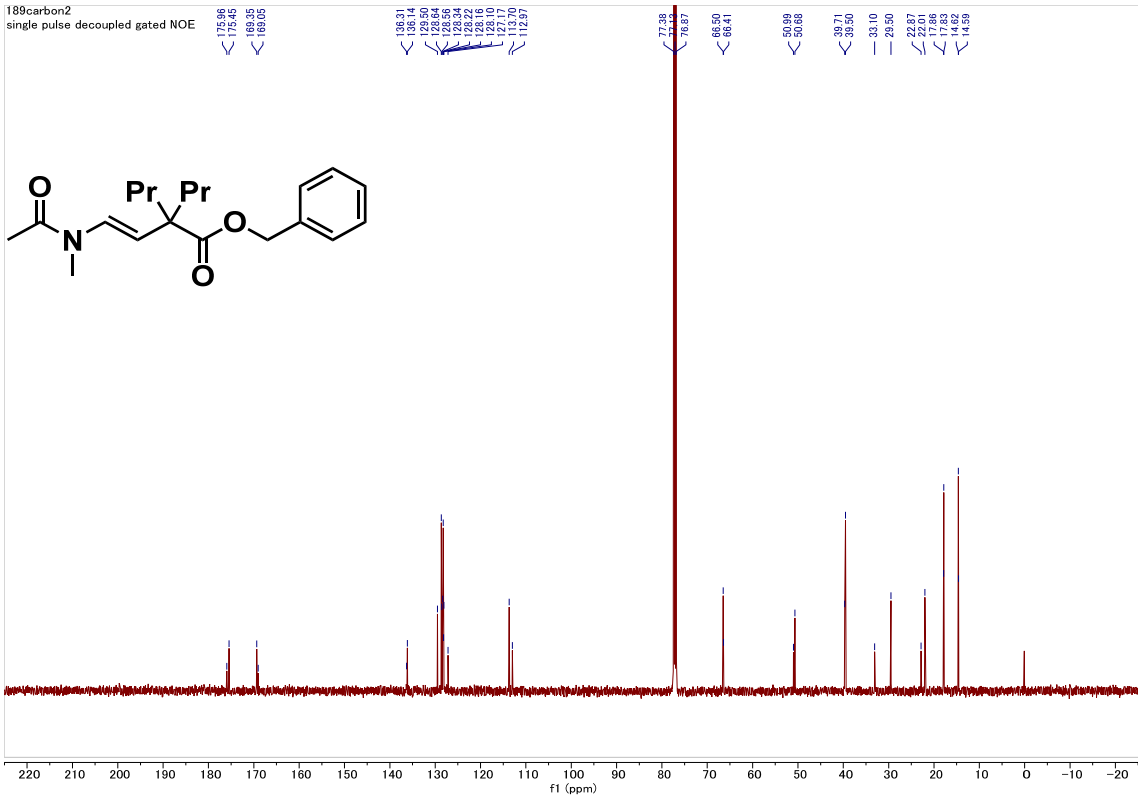
^{13}C NMR (**3ka**)



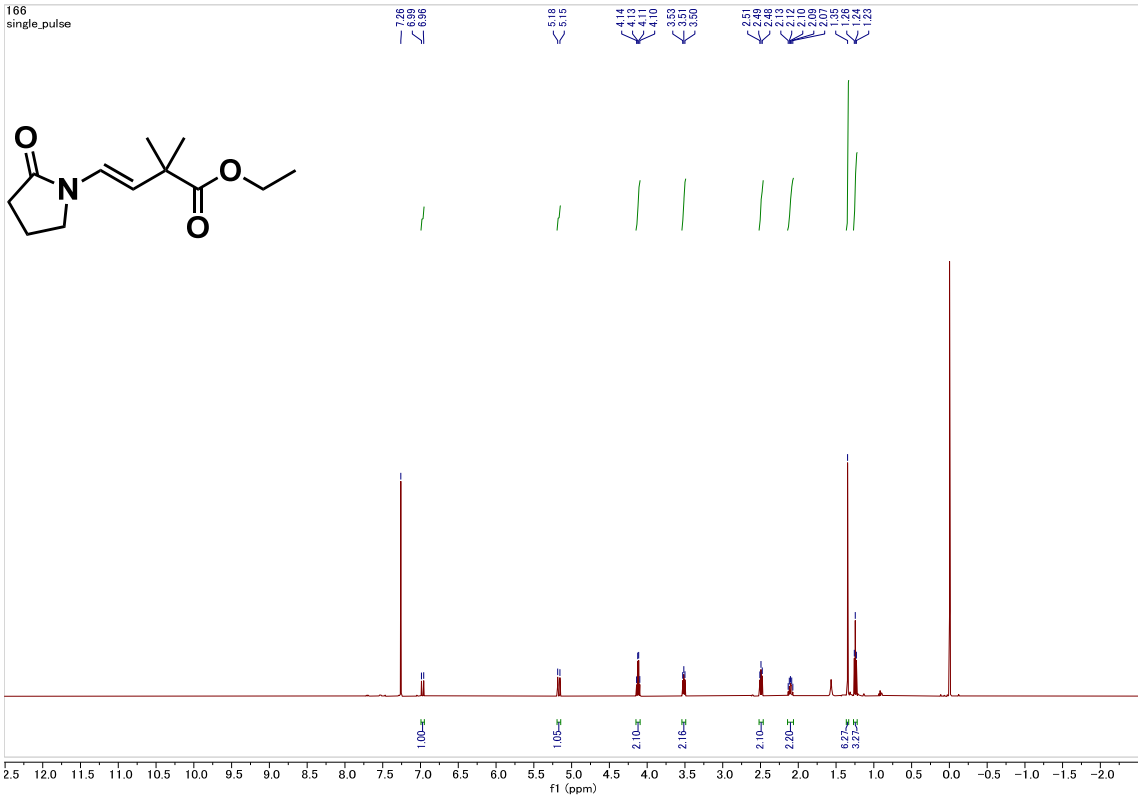
^{1}H NMR (**3la**)



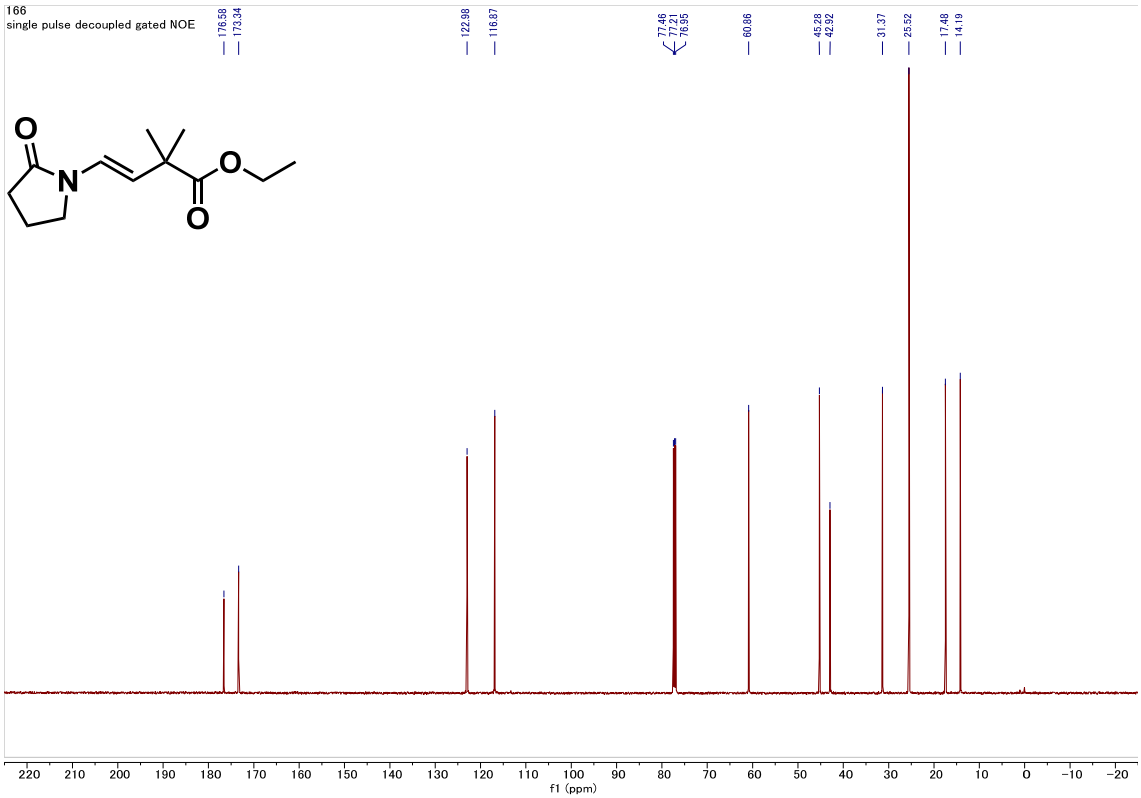
^{13}C NMR (**3la**)



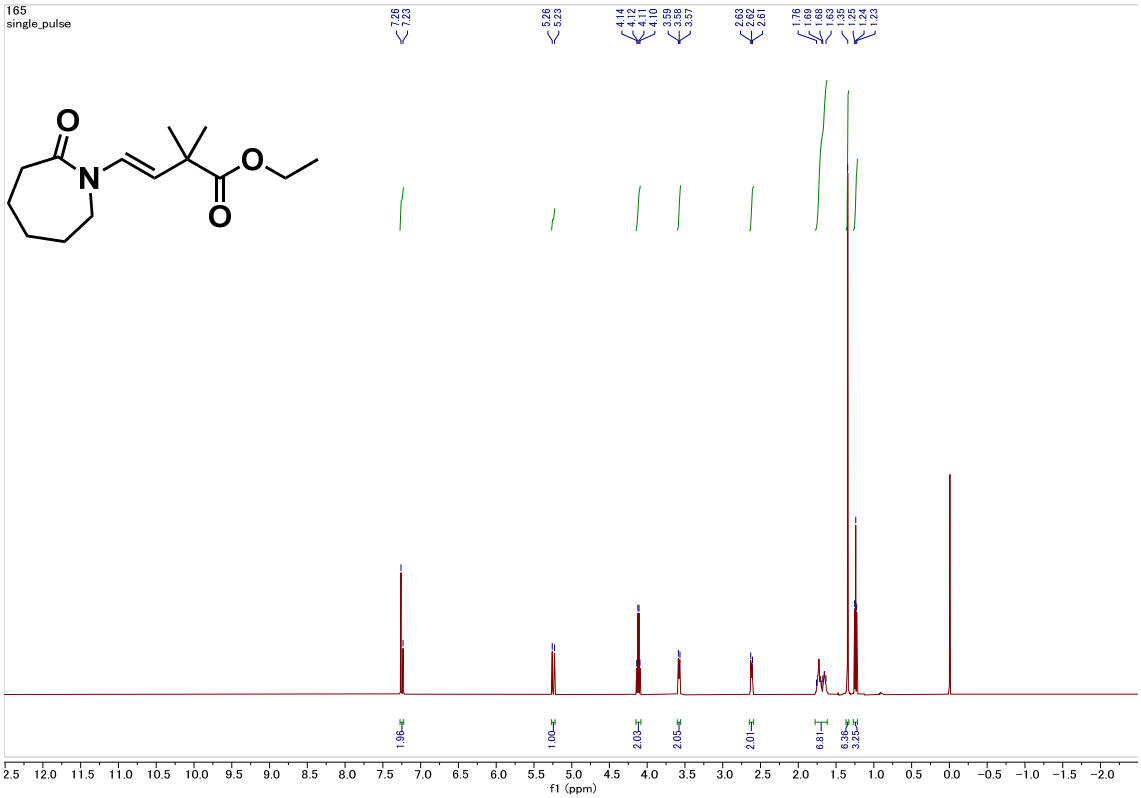
^{1}H NMR (**3ab**)



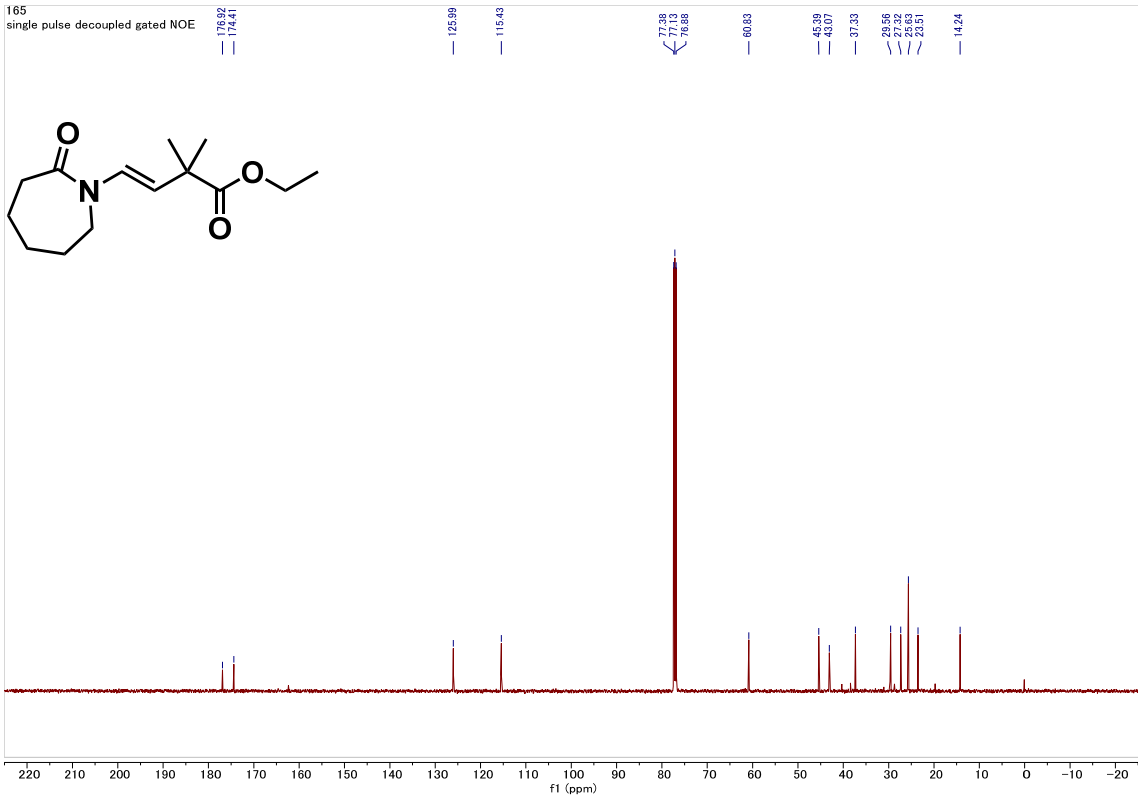
^{13}C NMR (**3ab**)



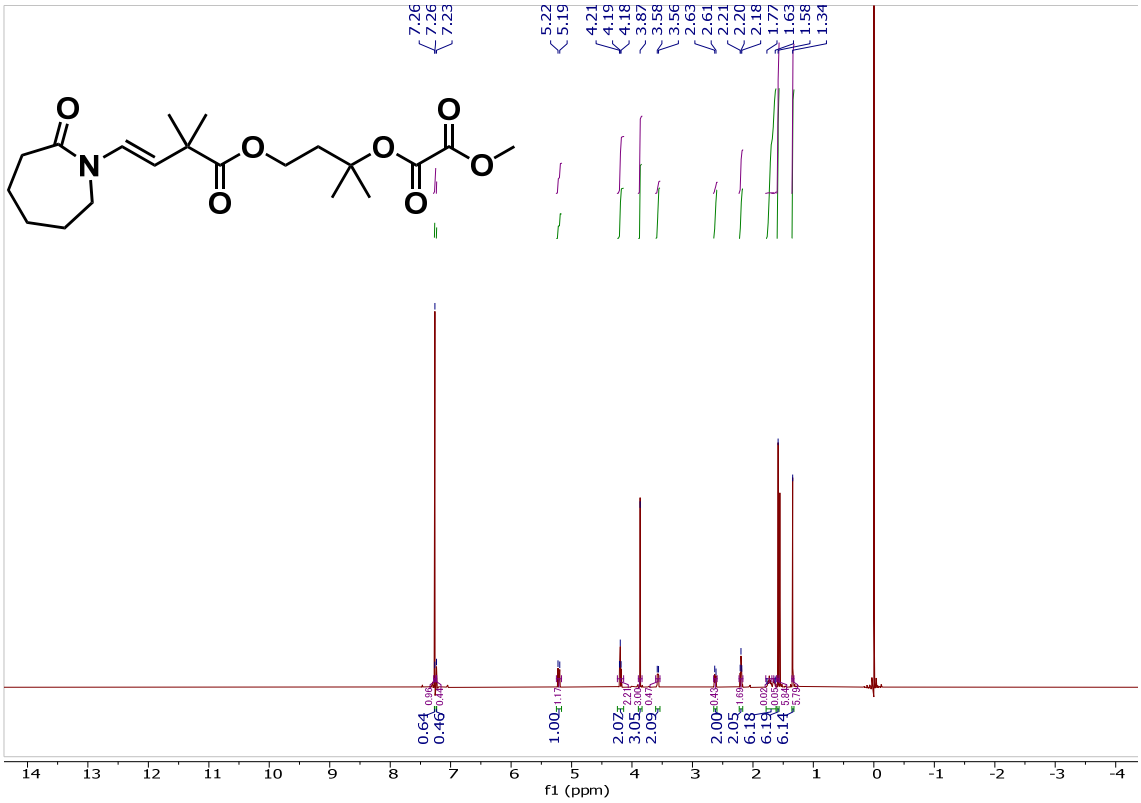
^{1}H NMR (**3ac**)



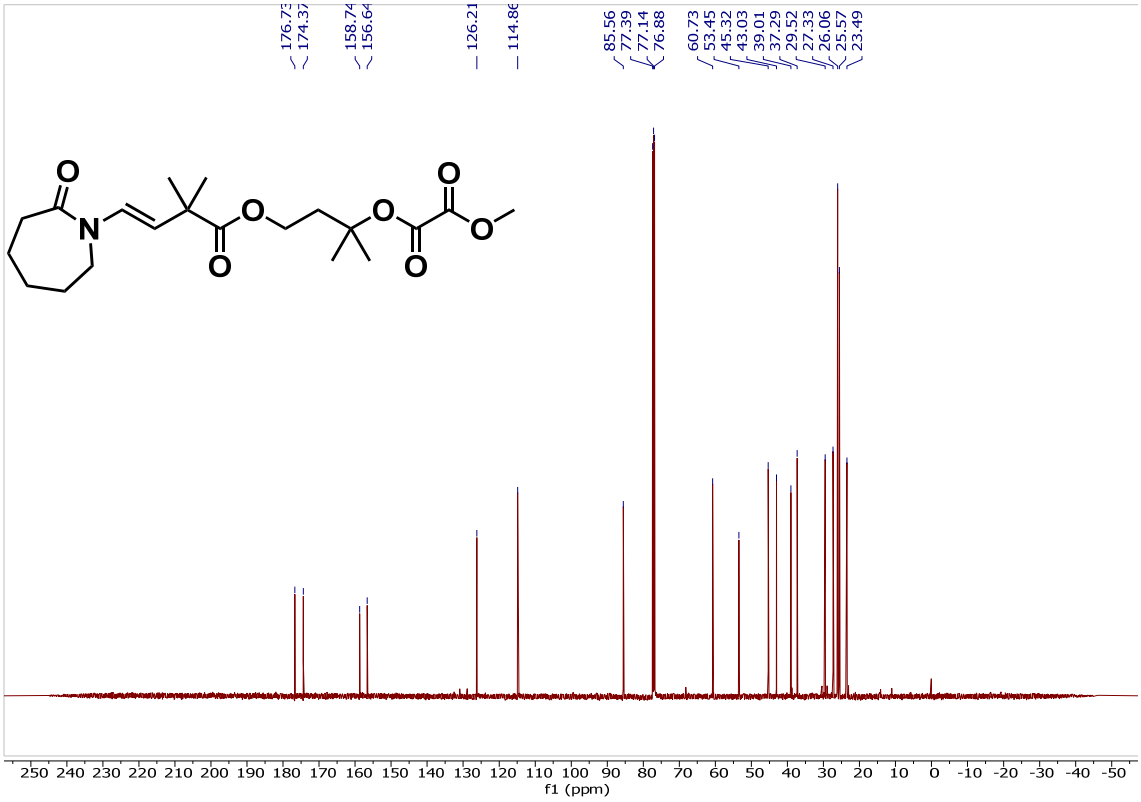
^{13}C NMR (**3ac**)



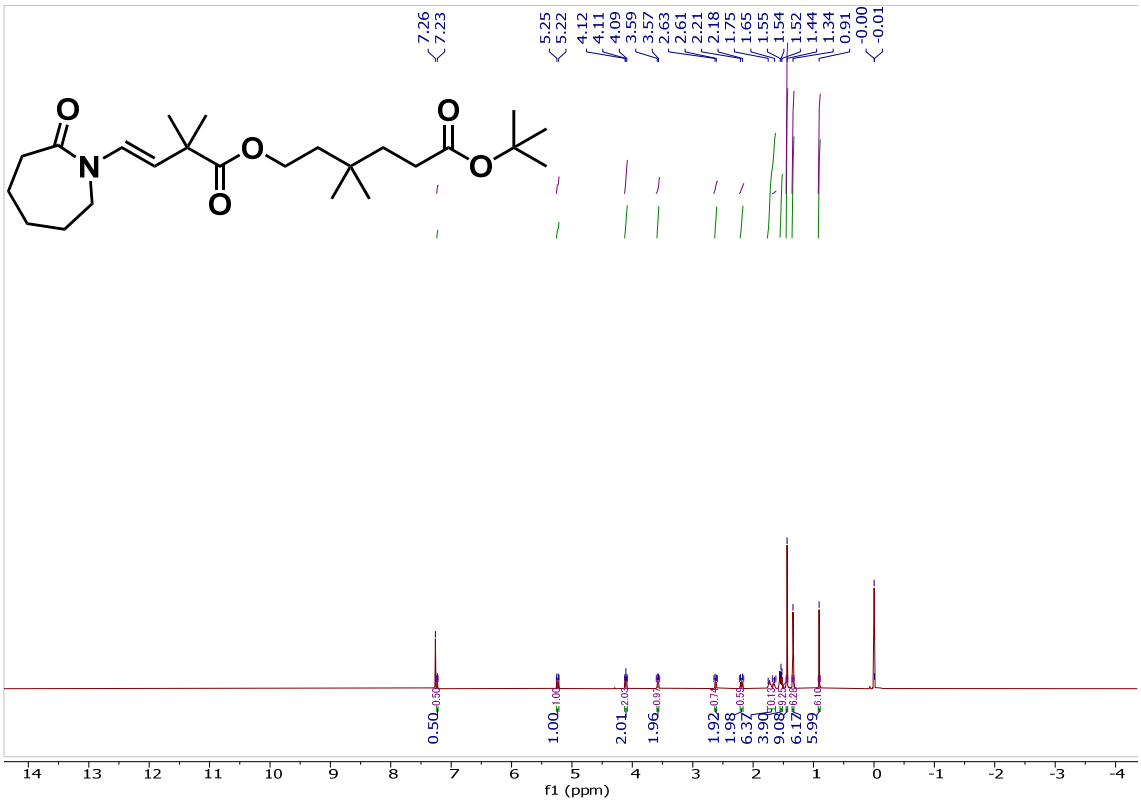
^{1}H NMR (**4**)



^{13}C NMR (**4**)



^{1}H NMR (**5**)



^{13}C NMR (**5**)