Supplementary Information (SI) for Organic & Biomolecular Chemistry.
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Visible light-mediated decarboxylative allylic alkylation of Morita-Baylis-Hillman acetates with unactivated aliphatic acids

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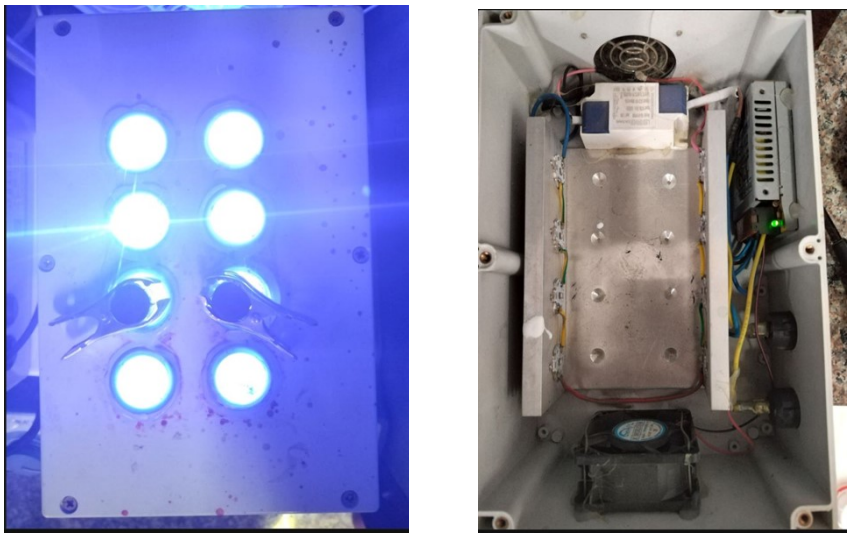
(A) General Information

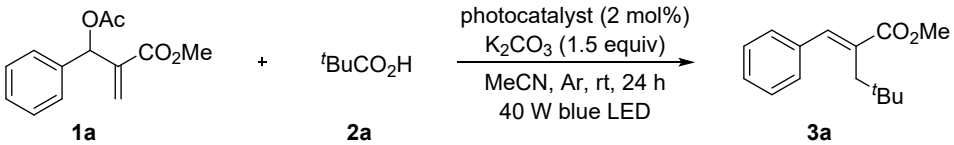
All reactions and manipulations which are sensitive to moisture or air were performed under inert atmosphere of argon. All chemicals were purchased from J&K, Acros and Aldrich, and were used as received. Anhydrous CH_2Cl_2, THF, DMSO, ethyl acetate (EA), DMF and MeCN were freshly distilled from calcium hydride. ^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 and chemical shifts are reported in δ (ppm) referenced to residual undeuterated solvent signal for ^{1}H NMR (7.26 ppm) and ^{13}C NMR (77.00 ppm). The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. HRMS spectra were recorded on a Waters Acquity UPLC/Xevo TQD-MS-MS quadrupole mass spectrometer. The light source for the photocatalytic reaction is manufactured by GeAo chemistry with a power of 40 W, a broad band source (450–465 nm). A fan was used to maintain the reaction temperature at room temperature (about 25-30 °C). The reactions were carried out in a borosilicate glass vessel and the distance from the light source to the irradiation vessel is about 1 cm. The starting materials Morita–Baylis–Hillman (MBH) acetates **1** were prepared according to the related literatures.[1]



Photoreactor (GeAo)

(B) Optimization of the reaction conditions.

Table S1. Photocatalyst screening[a]

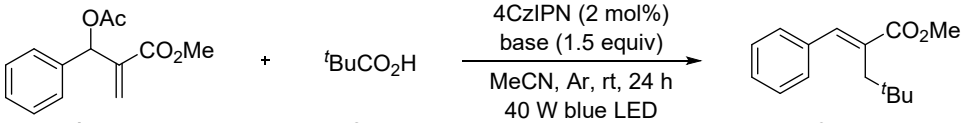


1a **2a** **3a**

Entry	photocatalyst (2 mol%)	Yield (%)[b]	*E*/*Z*-selectivity[c]
1	Rhodamine 6G	23	10:1
2	Eosin Y	trace	–
3	Rose Bengal	trace	–
4	4CzIPN	76	1.2:1
5	Ph-Acr-Mes$^+$BF$_4^-$	58	10:1

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), photocatalyst (2 mol%), K_2CO_3 (1.5 equiv), MeCN (2 mL), 40 W blue LED (450-465 nm), Ar, rt, 24 h. [b]Isolated yield. [c]*E/Z* selectivity was determined by using ^{1}H NMR.

Table S2. Base screening[a]

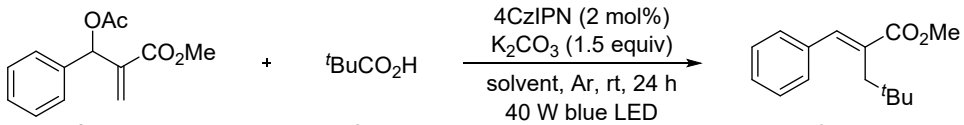


1a **2a** **3a**

Entry	Base (1.5 equiv)	Yield(%)[b]	*E/Z*-selectivity[c]
1	K_2CO_3	76	1.2:1
2	Na_2CO_3	11	1.6:1
3	Cs_2CO_3	71	1.8:1
4	K_2HPO_4	22	1.6:1
5	Et_3N	trace	–
6	DABCO	trace	–
7	DBU	17	1.7:1

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), 4CzIPN (2 mol%), base (1.5 equiv), MeCN (2 mL), 40 W blue LED (450-465 nm), Ar, rt, 24 h. [b]Isolated yield. [c]*E/Z* selectivity was determined by using ^{1}H NMR.

Table S3. Solvent screening[a]

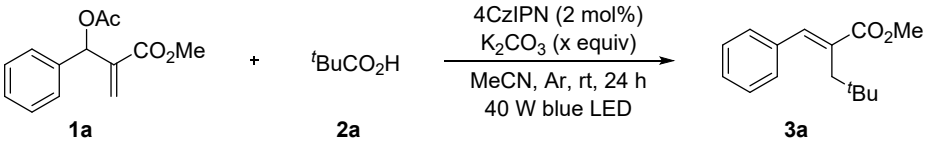


1a **2a** **3a**

Entry	Solvent	Yield (%)[b]	*E/Z*-selectivity[c]
1	CH_2Cl_2	trace	–
2	EA	trace	–
3	THF	37	1.21
4	DMF	60	1.3:1
5	DMSO	54	1.1:1
6	H_2O	0	–
7	MeCN	76	1.2:1
8	MeCN/CH_2Cl_2 (3:1)	19	1:1.7
9	MeCN/CH_2Cl_2 (1:1)	15	1:1.6
10	MeCN/CH_2Cl_2 (1:3)	13	1:1.6

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), 4CzIPN (2 mol%), K_2CO_3 (1.5 equiv), solvent (2 mL), 40 W blue LED (450-465 nm), Ar, rt, 24 h. [b]Isolated yield. [c]*E/Z* selectivity was determined by using ^{1}H NMR.

Table S4. The equivalent of base screening[a]

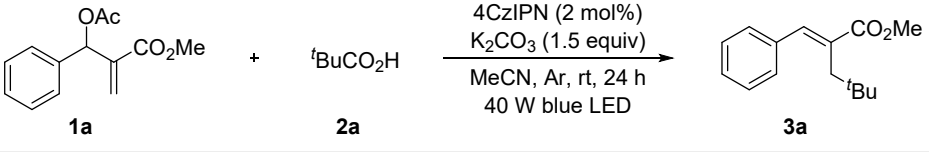


1a **2a** **3a**

entry	K_2CO_3 (x equiv)	Yield (%)[b]	*E/Z*-selectivity[c]
1	1.5 equiv	76	1.2:1
2	1.0 equiv	60	1.2
3	0.5 equiv	26	1.4:1
4	0.1 equiv	11	1.3:1
5	0 equiv	NR	–

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), 4CzIPN (2 mol%), K_2CO_3 (x equiv), MeCN (2 mL), 40 W blue LED (450-465 nm), Ar, rt, 24 h. [b]Isolated yield. [c]*E/Z* selectivity was determined by using ^{1}H NMR.

Table S5. Control experiments[a]

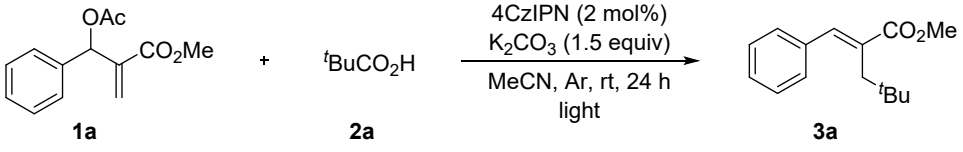


1a **2a** **3a**

Entry	Control experiments	Yield (%)[b]	*E/Z*-selectivity[c]
1	Without 4CzIPN	NR	–
2	Without K_2CO_3	NR	–
3	Without light	0	–
4	Open air	0	–

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), 4CzIPN (2 mol%), K_2CO_3 (1.5 equiv), MeCN (2 mL), 40 W blue LED (450-465 nm), Ar, rt, 24 h. [b]Isolated yield. [c]*E/Z* selectivity was determined by using ^{1}H NMR.

Table S6. Screening of light sources[a]



1a **2a** **3a**

Entry	Light source	Yield (%)[b]	*E/Z*-selectivity[c]
1	40 W purple LED (365-375 nm)	63	1.3:1
2	40 W blue LED (450-465 nm)	76	1.2:1
3	40 W green LED (510-520 nm)	trace	–

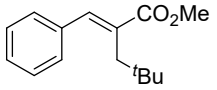
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), 4CzIPN (2 mol%), K_2CO_3 (1.5 equiv), MeCN (2 mL), light, Ar, rt, 24 h. [b]Isolated yield. [c]*E/Z* selectivity was determined by using ^{1}H NMR.

(C) General procedure for the synthesis of products 3.

To an 8 mL vial equipped with a magnetic stir bar was added **1** (0.2 mmol), carboxylic acids **2** (0.3 mmol), 4CzIPN (3.2 mg, 0.004 mmol), K_2CO_3 (41.4 mg, 0.3 mmol) and MeCN (2 mL) under argon atmosphere and sealed with PTFE cap. Then the reaction mixture was stirred upon 40

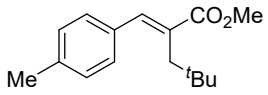
W blue LED (450–465 nm) at room temperature for 24 h. The solvent was concentrated in vacuo and the residue was purified by a column chromatography on silica gel with petroleum ether/ethyl acetate as eluent to provide the desired product **3**.

Methyl (*E*)-2-benzylidene-4,4-dimethylpentanoate (3a)[2]



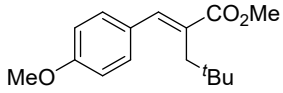
Colorless oil, 36 mg, 76% yield. *E/Z* selectivity = 1.2:1. R_f = 0.7 (petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (s, 0.45H), 7.36-7.21(m, 5H), 6.62 (s, 0.55H), 3.80 (s, 1.35H), 3.60 (s, 1.65H), 2.66 (s, 0.9H), 2.40 (s, 1.1H), 0.96 (s, 5H), 0.76 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.1, 170.3, 139.9, 136.5, 136.3, 136.2, 132.8, 132.6, 128.9, 128.3, 128.1, 127.9, 127.7, 127.6, 51.9, 51.5, 49.1, 38.2, 33.3, 32.1, 29.5, 29.1.

Methyl (*E*)-4,4-dimethyl-2-(4-methylbenzylidene)pentanoate (3b)[2]



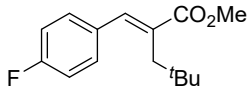
Colorless oil, 31 mg, 63% yield. *E/Z* selectivity = 1.8:1. R_f = 0.7 (petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (s, 0.35H), 7.43-7.24 (m, 5H), 6.72 (s, 0.65H), 3.94 (s, 1.1H), 3.78 (s, 1.9H), 2.82 (s, 0.7H), 2.53 (s, 1.3H), 2.50 (s, 1.1H), 2.48 (s, 1.9H), 1.09 (s, 5.8H), 0.92 (s, 3.2H), ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.2, 170.4, 139.9, 137.8, 137.5, 136.3, 133.6, 133.3, 131.9, 131.8, 129.0 (2), 128.8, 128.0, 51.8, 51.4, 49.2, 38.3, 33.4, 32.1, 29.6, 29.2, 21.2 (2).

Methyl (*E*)-2-(4-methoxybenzylidene)-4,4-dimethylpentanoate (3c)[2]



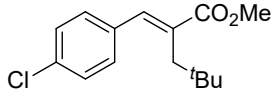
Colorless oil, 28 mg, 53% yield. *E/Z* selectivity = 1.7:1. R_f = 0.6 (petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (s, 0.35H), 7.36 (d, *J* = 8.8 Hz, 0.75H), 7.18 (d, *J* = 8.8 Hz, 1.25H), 6.89 (d, *J* = 8.8 Hz, 0.75H), 6.83 (d, *J* = 8.8 Hz, 1.25H), 6.54 (s, 0.65H), 3.82 (s, 1.1H), 3.80 (s, 1.9H), 3.79 (s, 1.1H), 3.63 (s, 1.9H), 2.68 (s, 0.75H), 2.37 (s, 1.25H), 0.94 (s, 5.7H), 0.79 (s, 3.3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.3, 170.5, 159.3, 159.2, 139.6, 136.0, 130.8, 130.7 (2), 129.5, 128.9, 128.7, 113.8, 113.5, 55.2, 51.8, 51.4, 49.2, 38.2, 33.5, 32.1, 29.6, 29.2.

Methyl (*E*)-2-(4-fluorobenzylidene)-4,4-dimethylpentanoate (3d)



Colorless oil, 33 mg, 66% yield. *E/Z* selectivity = 2:1. R_f = 0.7 (petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (s, 0.33H), 7.33 (d, *J* = 8.4, 5.6 Hz, 0.65H), 7.20 (d, *J* = 8.4, 5.2 Hz, 0.65H), 7.07-6.96 (m, 2H), 6.56 (s, 0.66H), 3.81 (s, 3H), 3.80 (s, 1H), 3.61 (s, 2H), 2.62 (s, 0.65H), 2.38 (s, 1.35H), 0.94 (s, 6H), 0.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.7, 170.1, 162.2 (*J* = 246.4 Hz), 138.7, 135.2, 132.9 (2), 132.7, 132.6, 132.5 (2), 130.7 (*J* = 8.1 Hz), 129.8 (*J* = 8.1 Hz), 115.4 (*J* = 21.2 Hz), 115.0 (*J* = 21.2 Hz), 51.9, 51.5, 49.1, 38.2, 33.4, 32.1, 29.5, 29.2. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{20}FO_2$: 251.1442; Found: 251.1434.

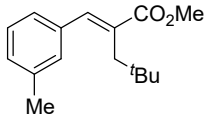
Methyl (*E*)-2-(4-chlorobenzylidene)-4,4-dimethylpentanoate (3e)



Colorless oil, 26 mg, 49% yield. *E/Z* selectivity = 2:1. R_f = 0.7 (petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (s, 0.32H), 7.35-7.14 (m, 4H), 6.55 (s, 0.7H), 3.80 (s, 1H), 3.61 (s, 2H), 2.61 (s, 0.65H), 2.38 (s, 1.35H), 0.94 (s, 6H), 0.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ:

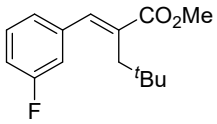
170.7, 170.0, 138.5, 135.0, 134.8, 133.6 (2), 133.4, 133.3, 130.3, 129.3, 128.6, 128.3, 52.0, 51.6, 49.1, 38.3, 33.4, 32.1, 29.5, 29.2. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{20}ClO_2$: 267.1146; Found: 267.1149.

Methyl (*E*)-4,4-dimethyl-2-(3-methylbenzylidene)pentanoate (3f)



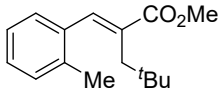
Colorless oil, 35 mg, 71% yield. *E/Z* selectivity = 1.5:1. R_f = 0.7 (petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (s, 0.4H), 7.24-7.01 (m, 4H), 6.58 (s, 0.6H), 3.80 (s, 1.2H), 3.60 (s, 1.8H), 2.65 (s, 0.8H), 2.39 (s, 1.2H), 2.36 (s, 1.2H), 2.33 (s, 1.8H), 0.95 (s, 5.4H), 0.77 (s, 3.6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.2, 170.4, 140.0, 137.9, 137.6, 136.5, 136.3, 136.2, 132.6, 132.4, 129.7, 128.7, 128.5, 128.4, 128.2, 128.0, 125.9, 125.0, 51.9, 51.4, 49.2, 38.4, 33.3, 32.1, 29.6, 29.2, 21.4, 21.3. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{23}O_2$: 247.1693; Found: 247.1688.

Methyl (*E*)-2-(3-fluorobenzylidene)-4,4-dimethylpentanoate (3g)



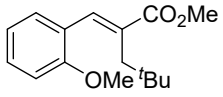
Colorless oil, 31 mg, 62% yield. *E/Z* selectivity = 1.5:1. R_f = 0.7 (petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (s, 0.4H), 7.35-6.92 (m, 4H), 6.56 (s, 0.6H), 3.80 (s, 1.2H), 3.61 (s, 1.8H), 2.62 (s, 0.8H), 2.38 (s, 1.2H), 0.94 (s, 5.4H), 0.75 (s, 3.6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.6, 170.0, 162.6 (*J* = 246.4 Hz), 162.6 (*J* = 246.4 Hz) (2), 138.7 (*J* = 7.1 Hz), 138.5 (*J* = 8.1 Hz), 138.4 (*J* = 2.0 Hz), 134.8 (*J* = 2.0 Hz), 134.1, 133.8, 129.9 (*J* = 9.1 Hz), 129.5 (*J* = 8.1 Hz), 124.7 (*J* = 3.0 Hz), 123.8 (*J* = 3.0 Hz), 115.6 (*J* = 22.2 Hz), 114.9, 114.8, 114.6 (3), 114.4, 52.0, 51.6, 49.1, 38.3, 33.4, 32.1, 29.5, 29.2. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{20}FO_2$: 251.1442; Found: 251.1438.

Methyl (*E*)-4,4-dimethyl-2-(2-methylbenzylidene)pentanoate (3h)



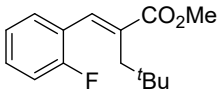
Colorless oil, 25 mg, 51% yield. *E/Z* selectivity = 1.3:1. R_f = 0.7 (petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (s, 0.57H), 7.19-7.02 (m, 4H), 6.70 (s, 0.43H), 3.81 (s, 1.8H), 3.49 (s, 1.2H), 2.51 (s, 1.2H), 2.42 (s, 0.8H), 2.30 (s, 1.2H), 2.28 (s, 1.8H), 0.96 (s, 4H), 0.70 (s, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.7, 170.1, 139.7, 136.5, 136.4 (2), 135.8, 135.4, 133.3, 132.9, 130.0, 129.6, 128.4, 127.7, 127.5, 125.5, 125.4, 51.9, 51.3, 48.5, 38.3, 32.9, 31.9, 29.4, 29.2, 20.0 (2). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{23}O_2$: 247.1693; Found: 247.1686.

Methyl (*E*)-2-(2-methoxybenzylidene)-4,4-dimethylpentanoate (3i)



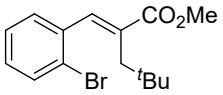
Colorless oil, 41 mg, 78% yield. *E/Z* selectivity = 1.8:1. R_f = 0.6 (petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (s, 0.33H), 7.29-7.19 (m, 1H), 6.95-6.77 (m, 3H), 6.58 (s, 0.66H), 3.81 (s, 1.1H), 3.80 (s, 1.1H), 3.79 (s, 1.9H), 3.61 (s, 1.9H), 2.65 (s, 0.7H), 2.38 (s, 1.3H), 0.95 (s, 5.8H), 0.77 (s, 3.2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.1, 170.3, 159.4, 159.3, 139.7, 137.9, 137.6, 135.8, 133.1, 132.8, 129.3, 129.1, 121.3, 120.4, 114.4, 113.5, 113.3, 113.2, 55.2, 55.1, 51.9, 51.5, 49.2, 38.4, 33.3, 32.1, 29.6, 29.2. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{22}O_3Na$: 285.1461; Found: 285.1452.

Methyl (*E*)-2-(2-fluorobenzylidene)-4,4-dimethylpentanoate (3j)[2]



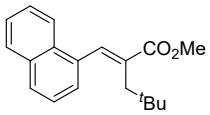
Colorless oil, 21 mg, 42% yield. *E/Z* selectivity = 1.4:1. R_f = 0.7 (petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (s, 0.4H), 7.35-7.01 (m, 4H), 6.62 (s, 0.6H), 3.81 (s, 1.3H), 3.59 (s, 1.7H), 2.54 (s, 0.8H), 2.42 (s, 1.2H), 0.95 (s, 5.2H), 0.72 (s, 3.8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.2, 169.5, 159.9 (*J* = 248.5 Hz), 159.8 (*J* = 248.5 Hz), 134.9 (2), 133.2 (*J* = 2.0 Hz), 130.0 (*J* = 3.0 Hz), 129.8, 129.7 (2), 129.6 (2), 129.3 (*J* = 8.1 Hz), 124.6, 124.5 (2), 124.3, 123.8 (*J* = 4.0 Hz), 123.6 (*J* = 3.0 Hz), 115.7 (*J* = 22.2 Hz), 120.3 (*J* = 22.2 Hz), 52.0, 51.5, 48.7, 38.8, 33.1, 32.0, 29.3, 29.1.

Methyl (*E*)-2-(2-bromobenzylidene)-4,4-dimethylpentanoate (3k)[2]



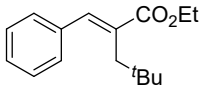
Colorless oil, 29 mg, 47% yield. *E/Z* selectivity = 1:1. R_f = 0.7 (petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (s, 0.5H), 7.57 (dd, *J* = 12.4, 8.0 Hz, 1H), 7.32-7.10 (m, 3H), 6.70 (s, 0.5H), 3.82 (s, 1.5H), 3.50 (s, 1.5H), 2.52 (s, 1H), 3.42 (s, 1H), 0.97 (s, 4.5H), 0.71 (s, 4.5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.2, 169.6, 139.3, 137.5, 137.1, 136.4, 134.3, 133.5, 132.7, 132.2, 130.0, 129.4, 129.1, 128.9, 127.1, 126.8, 124.0, 122.9, 52.1, 51.4, 48.2, 38.3, 33.1, 32.2, 29.3, 29.2.

Methyl (*E*)-4,4-dimethyl-2-(naphthalen-1-ylmethylene)pentanoate (3l)



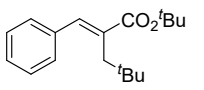
Colorless oil, 18 mg, 32% yield. *E/Z* selectivity = 1.5:1. R_f = 0.7 (petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.09 (s, 0.6H), 7.95-7.77 (m, 3H), 7.52-7.37 (m, 4H), 7.15 (s, 0.4H), 3.87 (s, 1.9H), 3.37 (s, 1.1H), 2.56 (s, 1.3H), 2.54 (s, 0.7H), 1.04 (s, 3.3H), 0.64 (s, 5.7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.7, 170.0, 138.7, 135.3, 135.1, 134.6, 134.5, 133.8, 133.4, 133.3, 131.5, 131.2, 128.4, 128.1, 127.9, 126.2 (2), 126.0 (2), 125.8, 125.4, 125.2 (2), 125.0, 124.6, 52.0, 51.3, 48.7, 38.9, 32.8, 32.1, 29.5, 29.3. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{22}O_2Na$: 305.1512; Found: 305.1512.

Ethyl (*E*)-2-benzylidene-4,4-dimethylpentanoate (3m)[2]



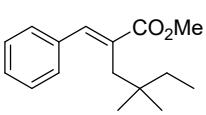
Colorless oil, 31 mg, 63% yield. *E/Z* selectivity = 1.8:1. R_f = 0.7 (petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (s, 0.33H), 7.36-7.22 (m, 5H), 6.62 (s, 0.67H), 4.26 (q, *J* = 7.2 Hz, 0.7H), 4.07 (q, *J* = 7.2 Hz, 1.3H), 2.65 (s, 0.7H), 2.39 (m, 1.3H), 1.35 (t, *J* = 7.2 Hz, 1.1H), 1.07 (q, *J* = 7.2 Hz, 1.9H), 0.96 (s, 5.7H), 0.76 (s, 3.3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.6, 169.8, 139.6, 136.7, 136.5, 136.1, 133.3, 132.9, 128.9, 128.3, 128.1, 128.0, 127.7, 127.5, 60.8, 60.5, 49.0, 38.2, 33.4, 32.1, 29.6, 29.2, 14.2, 13.6.

***tert*-Butyl (*E*)-2-benzylidene-4,4-dimethylpentanoate (3n)**[2]



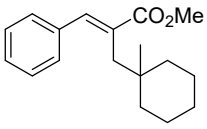
Colorless oil, 26 mg, 47% yield. *E/Z* selectivity = 2:1. R_f = 0.7 (petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (s, 0.33H), 7.34-7.21 (m, 5H), 6.57 (s, 0.7H), 2.60 (s, 0.66H), 2.34 (s, 1.34H), 1.53 (s, 3H), 1.27 (s, 6H), 0.95 (s, 6H), 0.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.1, 168.7, 138.4, 136.8, 136.7, 135.1, 134.5, 134.0, 128.6, 127.9 (2), 127.5, 127.1, 126.8, 80.5, 80.2, 48.4, 37.8, 33.1, 31.8, 29.4, 29.0, 27.7, 27.2.

Methyl (*E*)-2-benzylidene-4,4-dimethylhexanoate (3o)



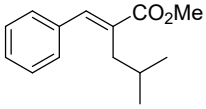
Colorless oil, 46 mg, 93% yield. *E/Z* selectivity = 1.7:1. R_f = 0.7 (petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (s, 0.34H), 7.27-7.12 (m, 5H), 6.53 (s, 0.66H), 3.72 (s, 1.1H), 3.52 (s, 1.9H), 2.56 (s, 0.75H), 2.31 (s, 1.25H), 1.25-1.19 (m, 1.3H), 1.05 (q, *J* = 7.6 Hz, 0.7H), 0.80 (m, 4.4H), 0.78-0.77 (m, 1.9H), 0.62-0.60 (m, 1.1H), 0.58 (m, 2.6H), . ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.1, 170.4, 139.8, 136.6, 136.3, 136.0, 132.8, 132.7, 128.9, 128.3, 128.1, 127.9, 127.7, 127.6, 51.9, 51.4, 47.0, 36.4, 35.9, 34.9, 34.6, 34.4, 26.0 (2), 8.4, 8.3. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{23}O_2$: 247.1693; Found: 247.1690.

Methyl (*E*)-2-((1-methylcyclohexyl)methyl)-3-phenylacrylate (3p)[2]



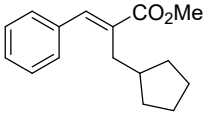
Colorless oil, 35 mg, 64% yield. *E/Z* selectivity = 13:1. R_f = 0.7 (petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (s, 1H), 7.37-7.27 (m, 5H), 3.80 (s, 3H), 2.65 (s, 2H), 1.34-1.26 (m, 5H), 1.17-1.10 (m, 5H), 0.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.5, 139.8, 136.7, 132.5, 128.9, 128.3, 127.6, 51.9, 37.7, 37.6, 35.9, 26.2, 24.0, 21.9.

Methyl (*E*)-2-benzylidene-4-methylpentanoate (3q)[2]



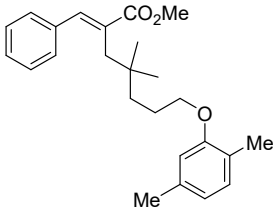
Colorless oil, 28 mg, 64% yield. *E/Z* selectivity = 3:1. R_f = 0.7 (petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (s, 0.22H), 7.27-7.11 (m, 5H), 6.49 (s, 0.7H), 3.70 (s, 0.8H), 3.53 (s, 2.2H), 2.38 (d, *J* = 7.2 Hz, 2H), 2.19 (dd, *J* = 7.2, 1.2 Hz, 2H), 1.79-1.67 (m, 1H), 0.85 (d, *J* = 6.4 Hz, 4.5H), 0.75 (d, *J* = 6.8 Hz, 1.5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.6, 169.4, 139.5, 136.2, 136.0, 134.0, 133.8, 133.1, 129.2, 128.4, 128.1 (2), 128.0, 127.6, 51.9, 51.5, 45.0, 35.6, 28.2, 27.3, 22.4, 22.2.

Methyl (*E*)-2-(cyclopentylmethyl)-3-phenylacrylate (3r)[2]



Colorless oil, 23 mg, 47% yield. *E/Z* selectivity = 4:1. R_f = 0.7 (petroleum ether/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (s, 0.2H), 7.38-7.21 (m, 5H), 6.61 (s, 0.8H), 3.81 (s, 0.6H), 3.64 (s, 2.4H), 2.60 (d, *J* = 7.6 Hz, 0.4H), 2.42 (d, *J* = 7.2 Hz, 1.6H), 2.07-1.99 (m, 1H), 1.83-1.75 (m, 2H), 1.68-1.50(m, 4H), 1.26-1.14 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.6, 138.9, 136.3, 134.6, 133.0, 129.2, 128.4, 128.1 (2), 128.0, 127.6, 51.9, 51.6, 41.9, 40.1, 38.8, 32.3 (2), 25.0, 24.7.

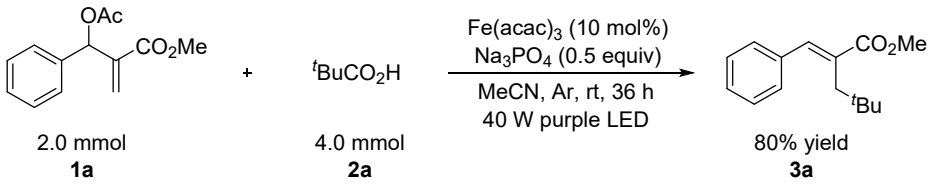
Methyl (*E*)-2-benzylidene-7-(2,5-dimethylphenoxy)-4,4-dimethylheptanoate (3s)[3]



Colorless oil, 66 mg, 87% yield. *E/Z* selectivity = 1.2:1. R_f = 0.6 (petroleum ether/ethyl acetate = 30:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (s, 0.45H), 7.34-7.20 (m, 5H), 7.01-6.98 (m, 1H), 6.67-6.63 (m, 2H), 6.57 (s, 0.5H), 3.92 (t, *J* = 6.4 Hz, 1.1H), 3.80 (s, 1.3H), 3.74 (t, *J* = 6.4 Hz, 0.9H), 3.59 (s, 1.6H), 2.70 (s, 0.9H), 2.45 (s, 1.1H), 2.31 (s, 3H), 2.18 (s, 1.8H), 2.15 (s, 1.3H), 1.83-1.77 (m, 1H), 1.64-1.56 (m, 1H), 1.45-1.41 (m, 1H), 1.26-1.22 (m, 1H), 0.96 (s, 3.4H), 0.74 (s, 2.6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.1, 170.2, 157.0, 140.0, 136.5, 136.4, 136.3, 136.2, 132.5, 132.4, 130.2 (2), 128.8, 128.4, 128.1, 127.9, 127.8, 127.6, 123.6, 123.5, 120.6, 120.5, 112.0 (2), 68.5, 51.9, 51.5, 47.4, 38.8, 38.4, 36.5, 35.6, 34.4, 26.6, 26.5, 24.3, 24.2, 21.4, 15.8, 15.7.

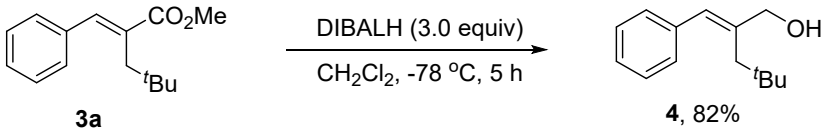
(D) Synthetic application

(1) Scale-up reaction of 3a at 2.0 mmol.



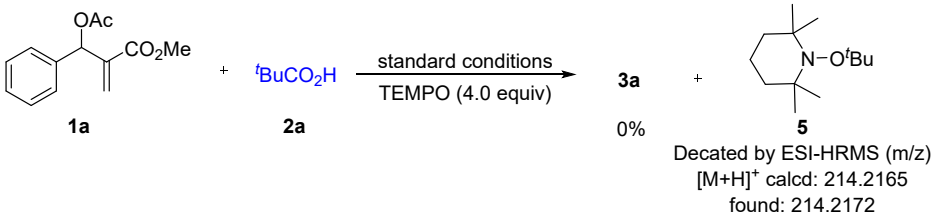
To an 50 mL vial equipped with a magnetic stir bar was added **1a** (468.0 mg, 2.0 mmol), pivalic acid **2a** (321.0 mg, 3.0 mmol), K_2CO_3 (414.0 mg, 3.0 mmol), 4CzIPN (32.0 mg, 0.02 equiv) and MeCN (20 mL) under argon atmosphere and sealed with PTFE cap. Then the reaction mixture was stirred upon 40 W blue LED (450–465 nm) at room temperature for 48 h. The solvent was concentrated in vacuo and the residue was purified by a column chromatography on silica gel with petroleum ether/ethyl acetate (100:1) as eluent to provide the desired product **3a** as a colorless oil (281 mg, 61% yield).

(2) Synthetic transformation of 3a.



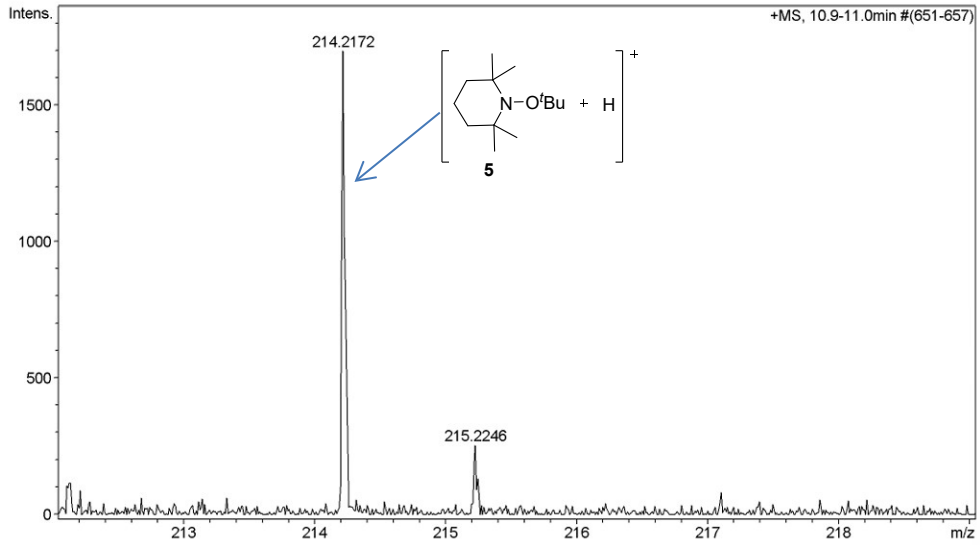
To a solution of **3a** (120 mg, 0.52 mmol) in anhydrous CH_2Cl_2 was added DIBALH (1.6 mL, 3 equiv, 1M in hexane) dropwise at -78 °C. The reaction mixture was stirred at the same temperature for another 5 h. The reaction mixture was quenched with H_2O (0.5 mL), extracted with CH_2Cl_2 (5 mL X 3), the combined extractes were washed with saturated NaCl (10 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was chromatographed on a silica gel column with petroleum ether/ethyl acetate (10:1) as eluent to afford the product **4** (82 mg, 78% yield). **Major** (48 mg, colorless oil, 46% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34-7.30 (m, 2H), 7.25-7.20 (m, 3H), 6.43 (s, 1H), 4.30 (s, 2H), 2.22 (s, 2H), 0.99 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 139.8, 137.1, 131.9, 128.8, 128.2, 126.7, 62.1, 48.0, 32.2, 29.9. **Minor** (34 mg, colorless oil, 32% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32-7.17 (m, 5H), 6.70 (s, 1H), 4.24 (s, 2H), 2.32 (s, 2H), 0.80 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 140.8, 138.5, 128.8, 128.1, 127.7, 126.2, 68.4, 40.6, 32.8, 30.4. HRMS (ESI) m/z: $[M+K]^+$ calcd for $C_{14}H_{18}O_2K$: 257.0938; Found: 257.0945.

(E) Radical trapping experiment with TEMPO



To an 8 mL vial equipped with a magnetic stir bar was added **1a** (46.8 mg, 0.2 mmol), pivalic acid **2a** (32.1 mg, 0.3 mmol), 4CzIPN (3.2 mg, 0.02 mmol), K_2CO_3 (41.4 mg, 1.5 equiv), TEMPO

(124.8 mg, 0.8 mmol) and MeCN (2 mL) under argon atmosphere and sealed with PTFE cap. Then the reaction mixture was stirred upon 40 W blue LED (450–465 nm) at room temperature for 24 h. HRMS (ESI) m/z: compound **5**, [**5**+H]$^+$ calcd for $C_{13}H_{28}ON$: 214.2165; Found: 214.2172.



(F) Stern-Volmer fluorescence quenching experiments

Stern-Volmer fluorescence quenching experiments were run with freshly prepared solutions of 1.25 μM 4CzIPN, in dry MeCN at room temperature. The solutions were irradiated at 375 nm and fluorescence was measured from 385 nm to 740 nm. Control experiments showed that the excited state photocatalyst 4CzIPN* was mainly quenched by ^{t}BuCO$_2$H + K$_2$CO$_3$.

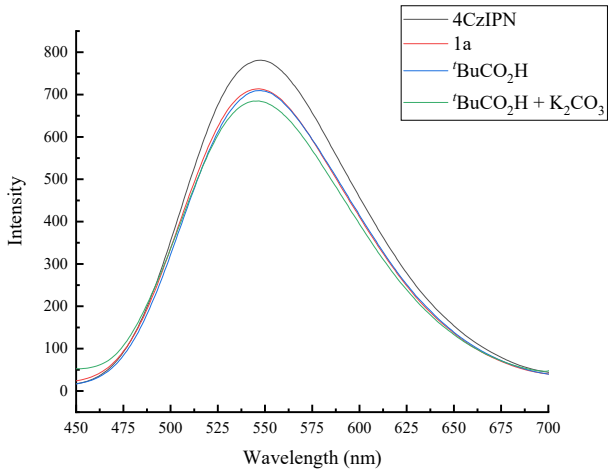


Figure S1. Fluorescence quenching of excited 4CzIPN with **1a**, ^{t}BuCO$_2$H, ^{t}BuCO$_2$H + K$_2$CO$_3$ in MeCN (excitation wavelength: 375 nm). 4CzIPN (1.25 μM) in MeCN (black line), 4CzIPN (1.25 μM) with **1a** (5.00 mM) in MeCN (blue line), 4CzIPN (1.25 μM) with ^{t}BuCO$_2$H (5.00 mM) in MeCN (red line), 4CzIPN (1.25 μM) with ^{t}BuCO$_2$H + K$_2$CO$_3$ (5.00 mM) in MeCN (green line).

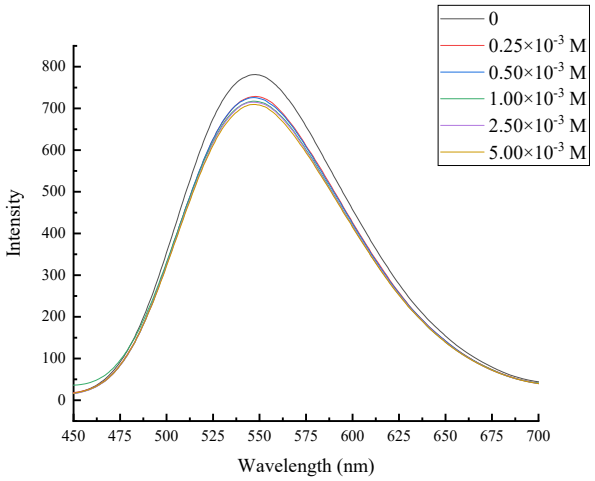


Figure S2. Luminescence quenching of 4CzIPN by $^{t}BuCO_2H$

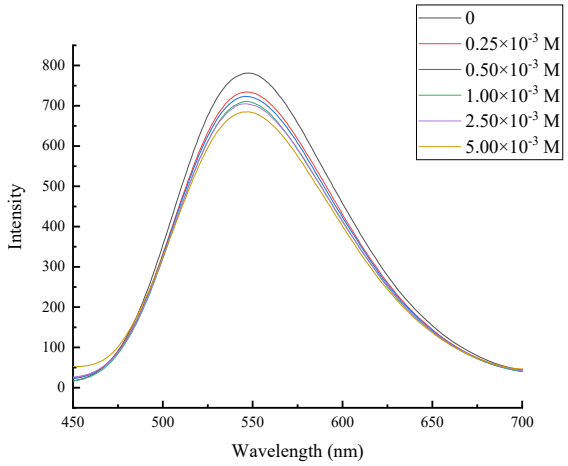


Figure S3. Luminescence quenching of 4CzIPN by $^{t}BuCO_2H + K_2CO_3$

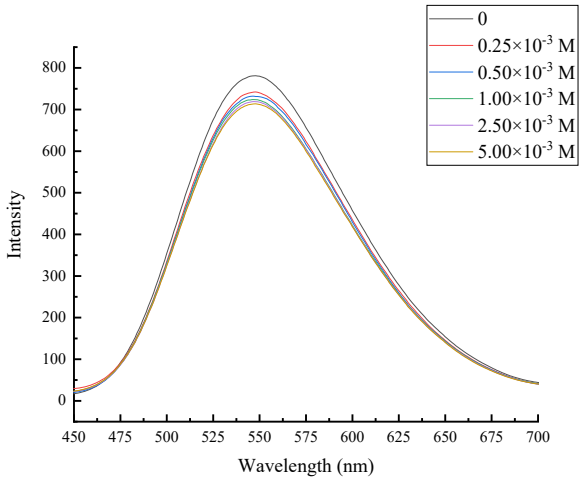


Figure S4. Luminescence quenching of 4CzIPN by **1a**

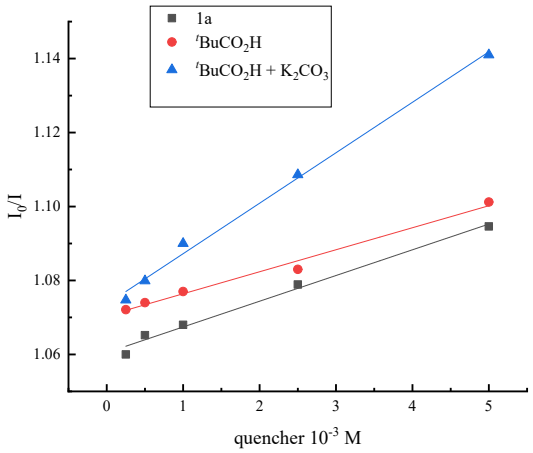


Figure S5. Stern-Volmer plots of 4CzIPN and three quenchers. I_0 and I are luminescence intensities in the absence and presence of the indicated concentrations (10^{-3} M) of the corresponding quencher.

These results suggested that the excited photocatalyst 4CzIPN* was primarily quenched by ^{t}BuCO$_2$H + K_2CO_3, while **1a** and ^{t}BuCO$_2$H showed much less effect.

(G) UV-vis absorption spectroscopy

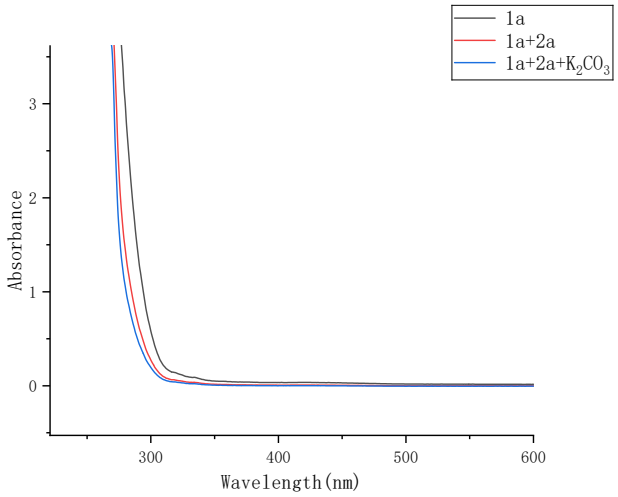
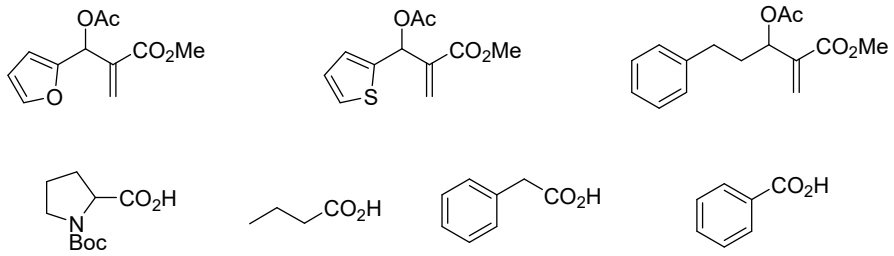


Figure S6 UV-vis absorption spectra of **1a** (0.1M), Pivalic acid **2a** (0.015 M) and K_2CO_3 (0.15M).

1a (0.1 M); the mixture of **1a** (0.1 M) and **2a** (0.015 M); the mixture of **1a** (0.1 M), **2a** (0.015 M) and K_2CO_3 (0.15M) in CH_3CN were performed on UV visible spectrophotometer, respectively. This findings suggest that there is no the formation of EDA complex between **1a** and **2a**, as well as **1a** and pivalic acid anion.

(H) Unsuccessful examples



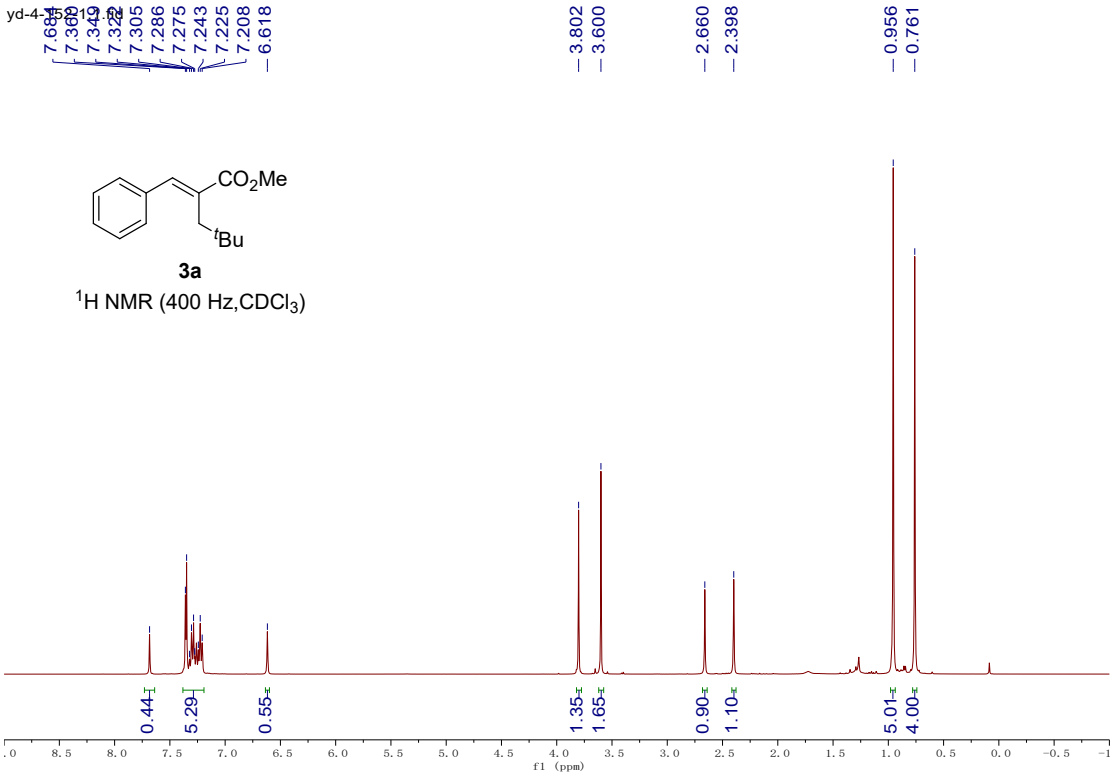
References:

[1] Suga, T.; Takada, R.; Shimazu, S.; Sakata, M.; Ukaji, Y. Highly (*E*)-Selective Trisubstituted Alkene Synthesis by Low-Valent Titanium-Mediated Homolytic Cleavage of Alcohol C-O Bond. *J. Org. Chem.* **2022**, *87*, 7487-7493.

[2] Zhang, D.-R.; Hu, L.-P.; Liu, F.-L.; Huang, X.-H.; Li, X.; Liu, B.; Huang, G.-L. Metal-Free, Visible-Light-Promoted Decarboxylative Alkylation of Baylis-Hillman Acetates with *N*-(acloxy)phthalimides. *Green Chem.* **2022**, *24*, 6840-6844.

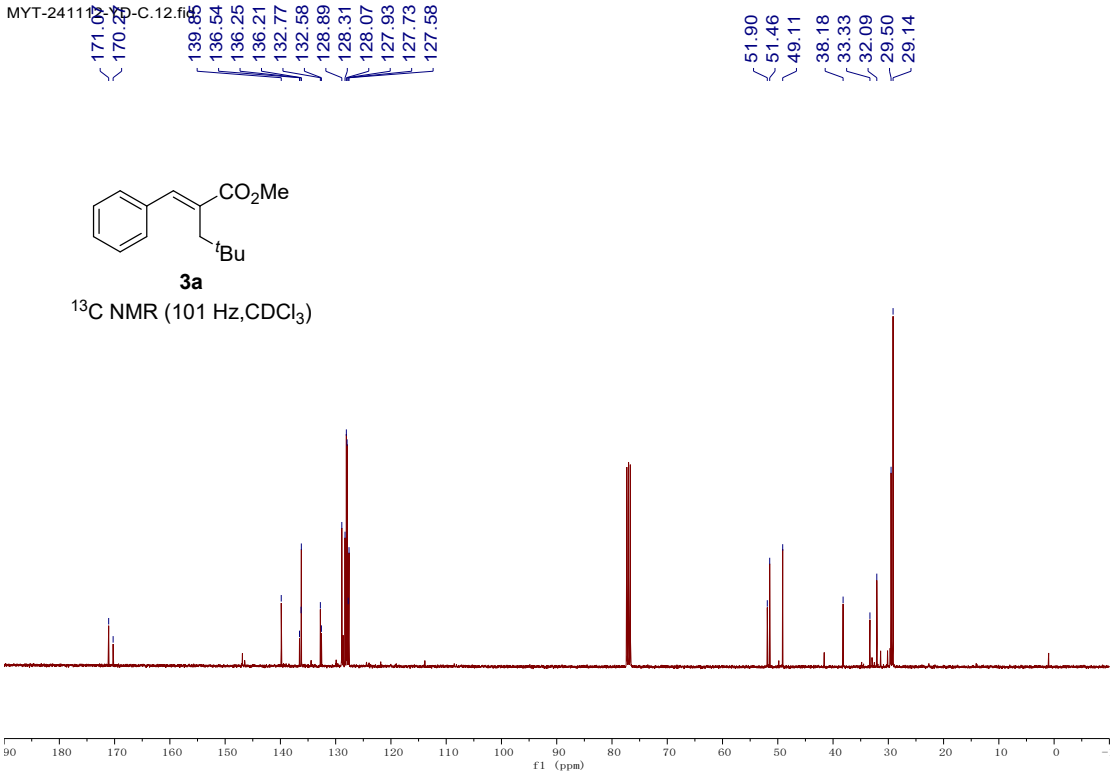
[3] Golagani, D.; Prakash, K.-K.; Thapa, S.; Naik, M.-B.-S.; Akondi, S.-M. Visible-Light-Promoted Iron(II)/Lewis Base Catalysis for the Alkylation of Morita-Baylis-Hillman Acetates Using Carboxylic Acids. *Org. Lett.* **2024**, *26*, 8583-8588.

(I) NMR Spectra of New Compounds



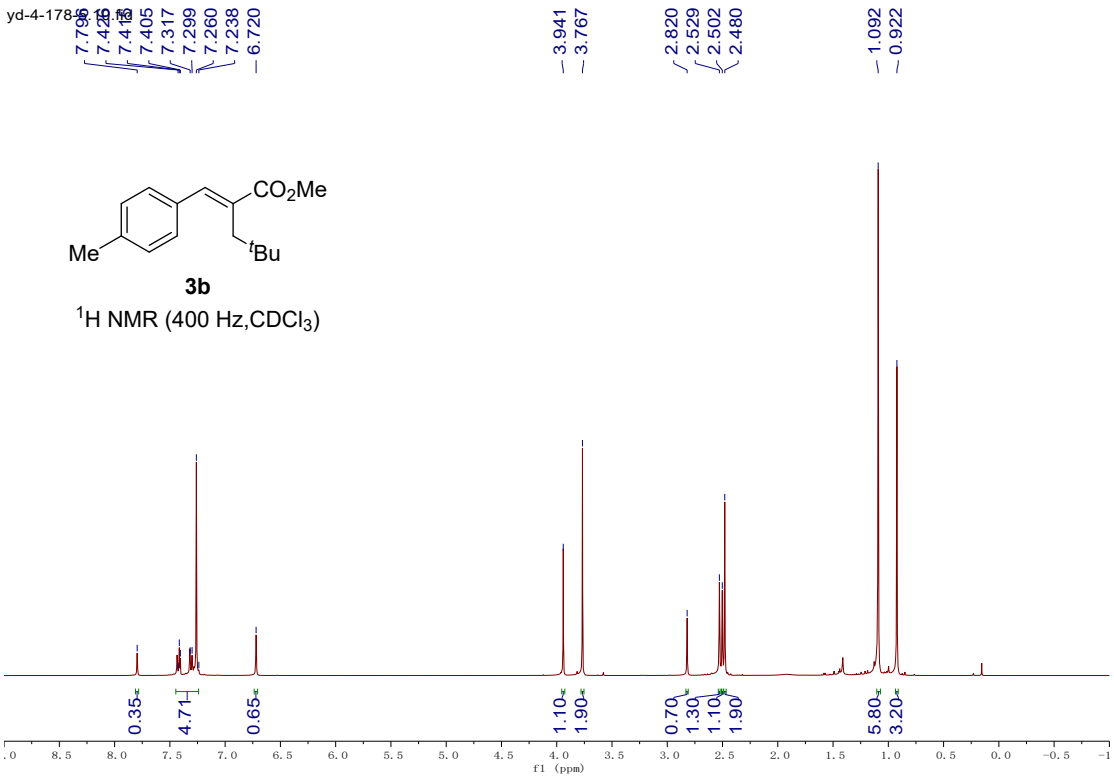
3a

^{1}H NMR (400 Hz,$CDCl_3$)



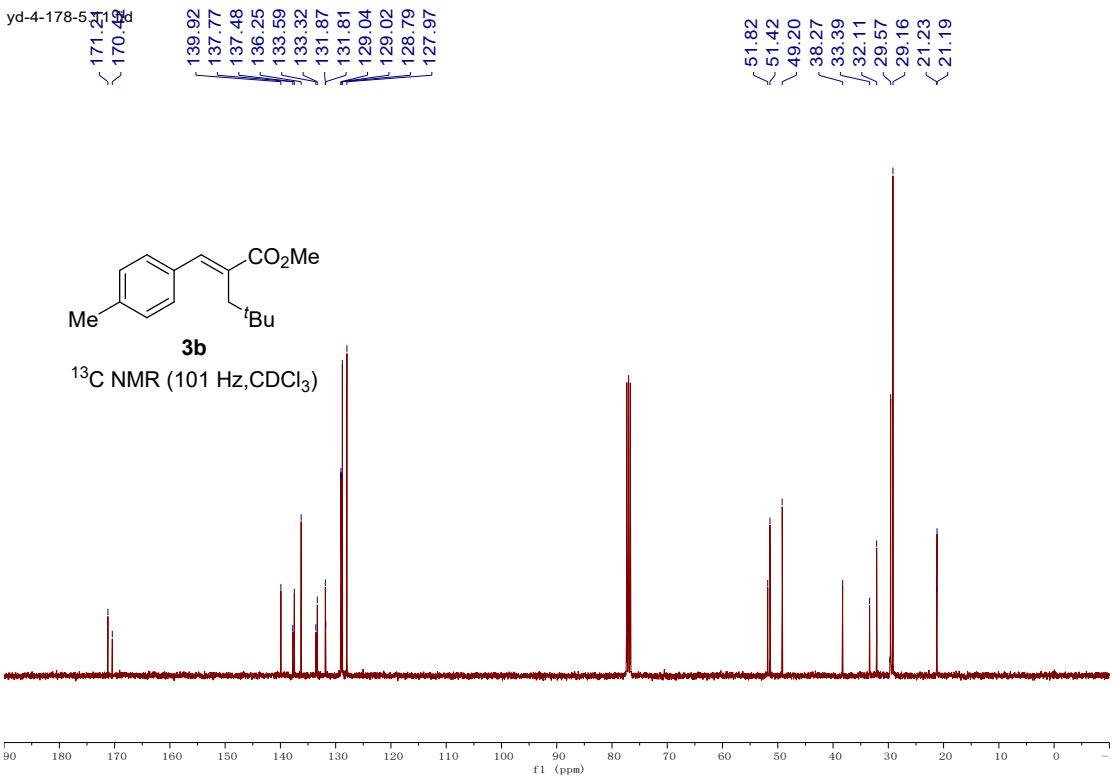
3a

^{13}C NMR (101 Hz,$CDCl_3$)



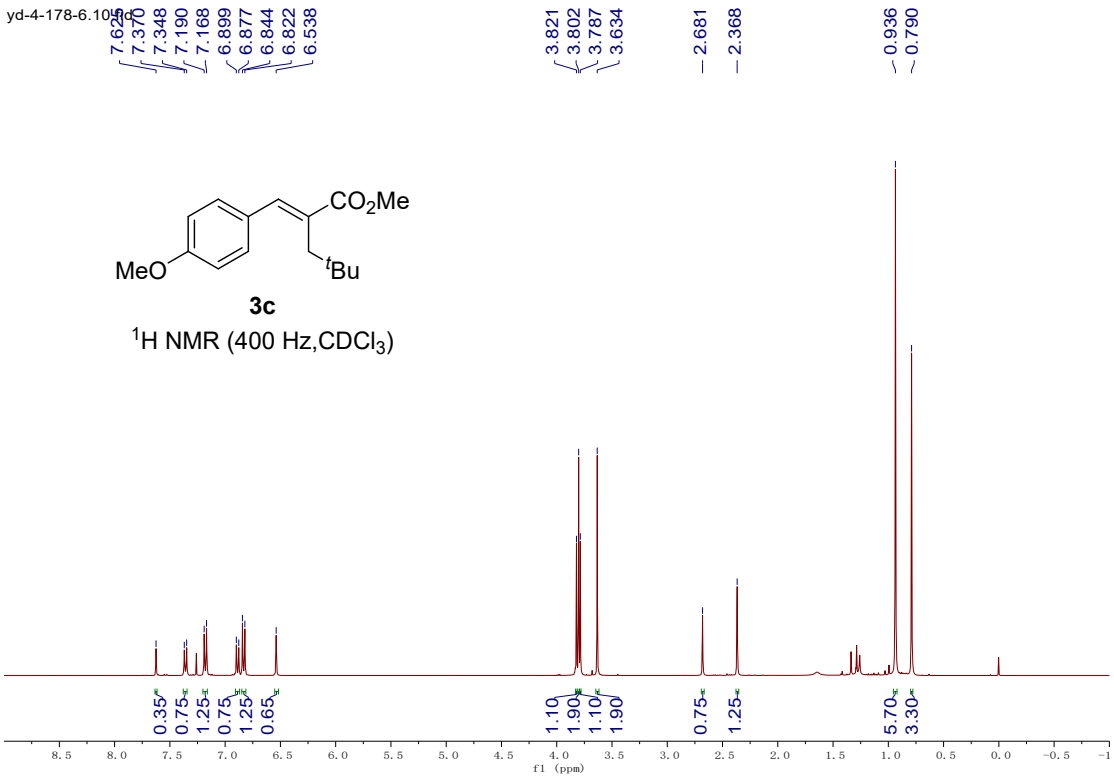
3b

^{1}H NMR (400 Hz,$CDCl_3$)



3b

^{13}C NMR (101 Hz,$CDCl_3$)



3c

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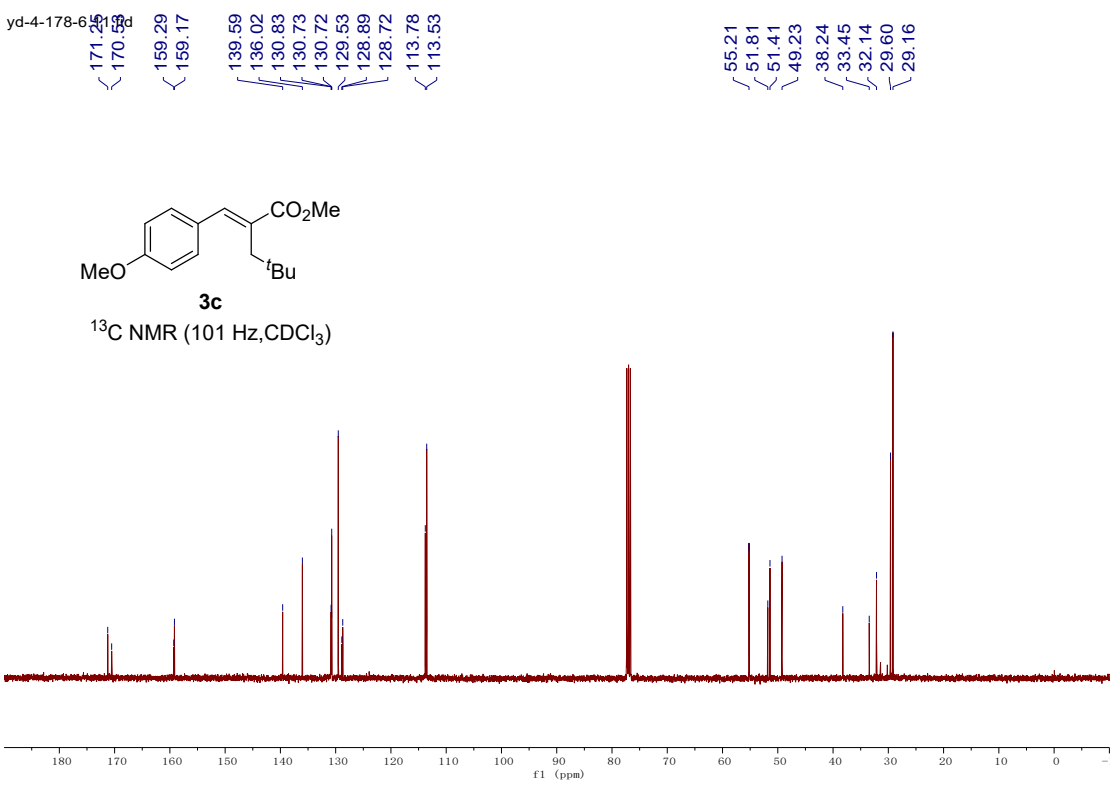

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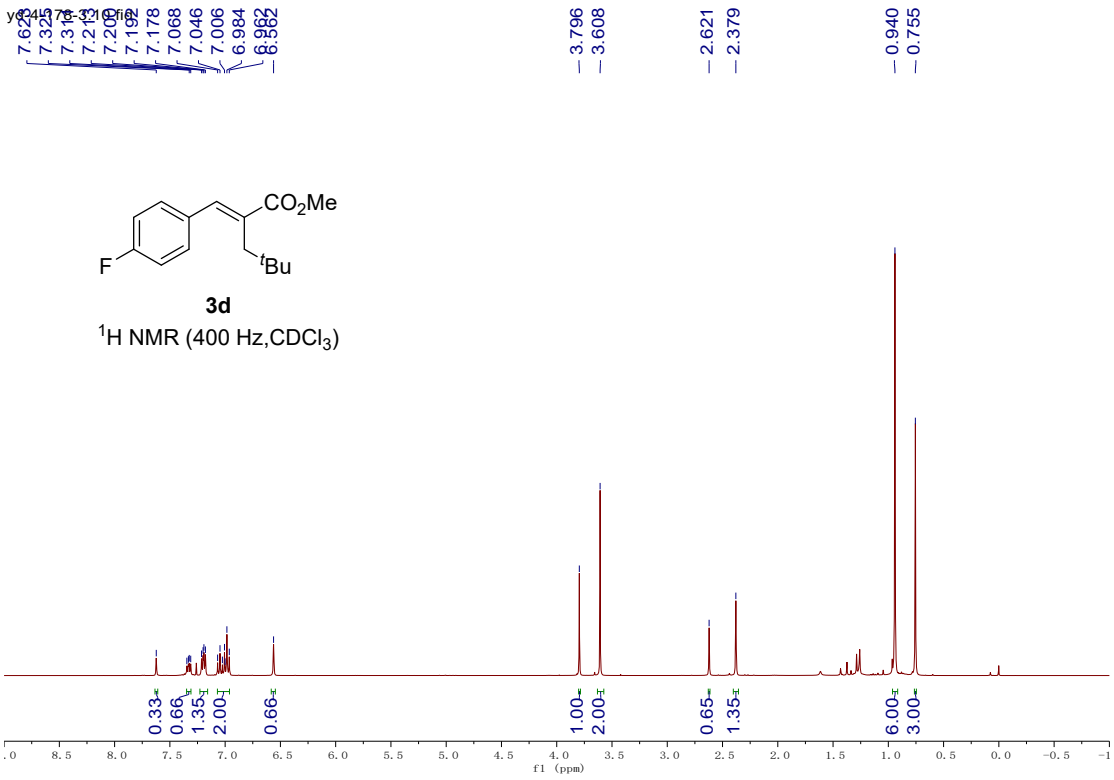
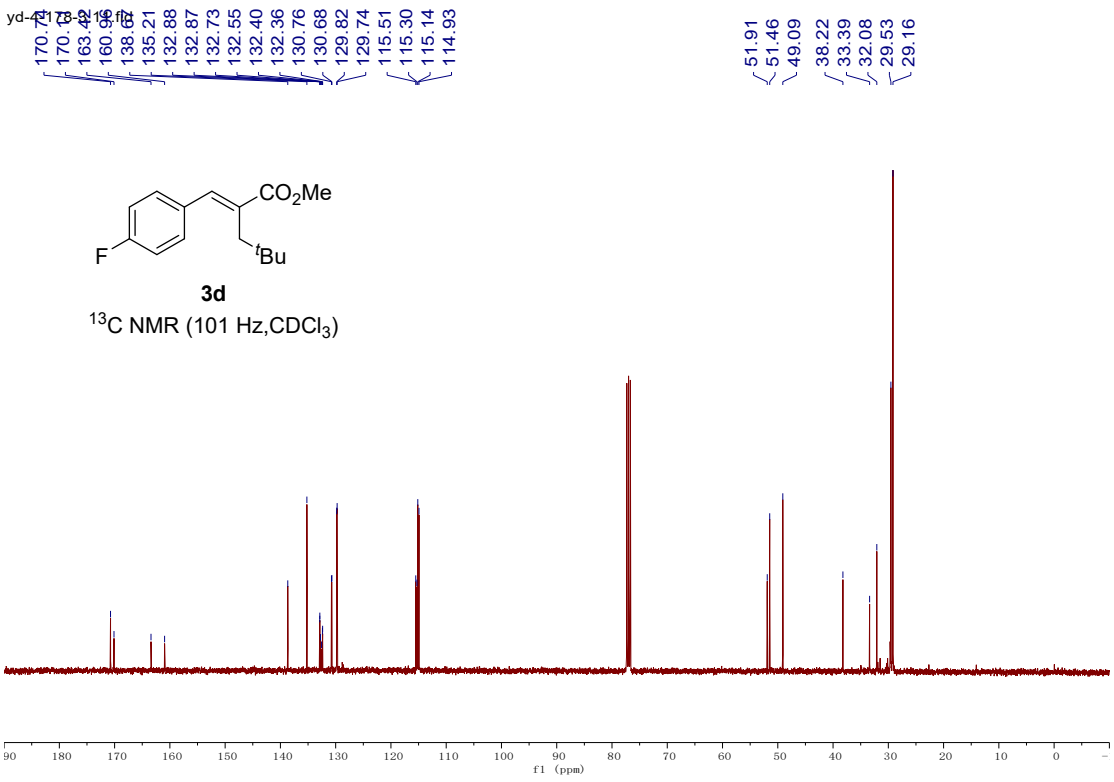


3d

^{1}H NMR (400 Hz,$CDCl_3$)



3d

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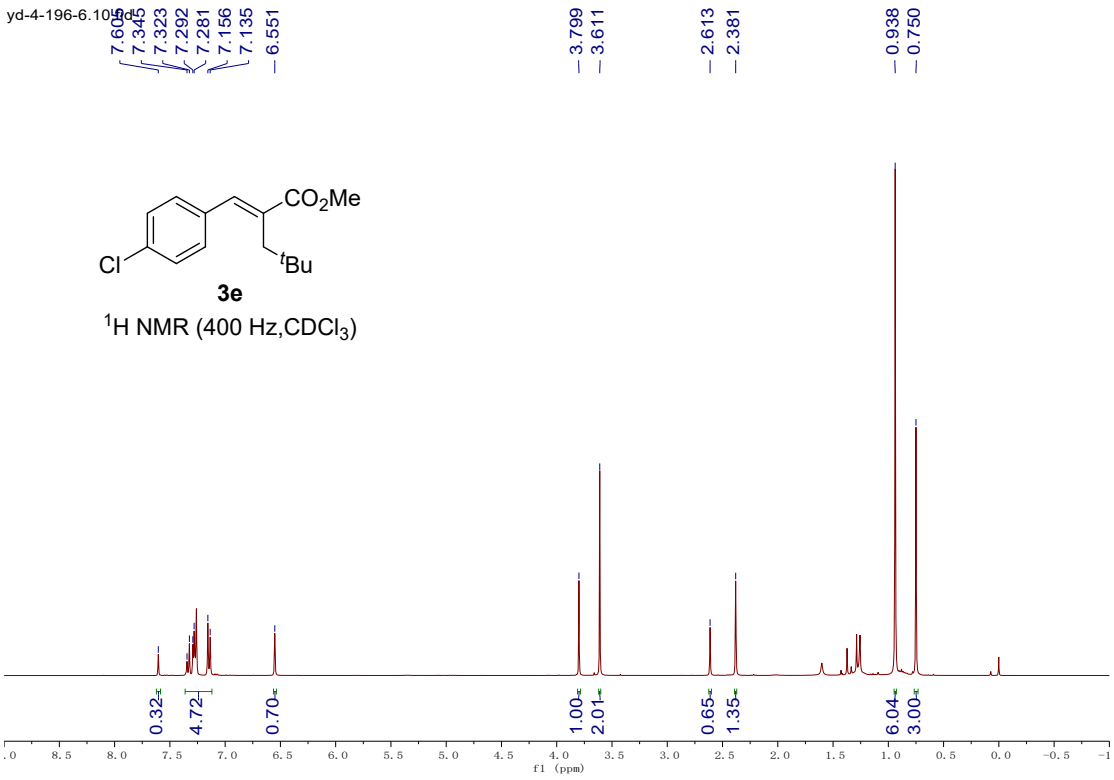

3e

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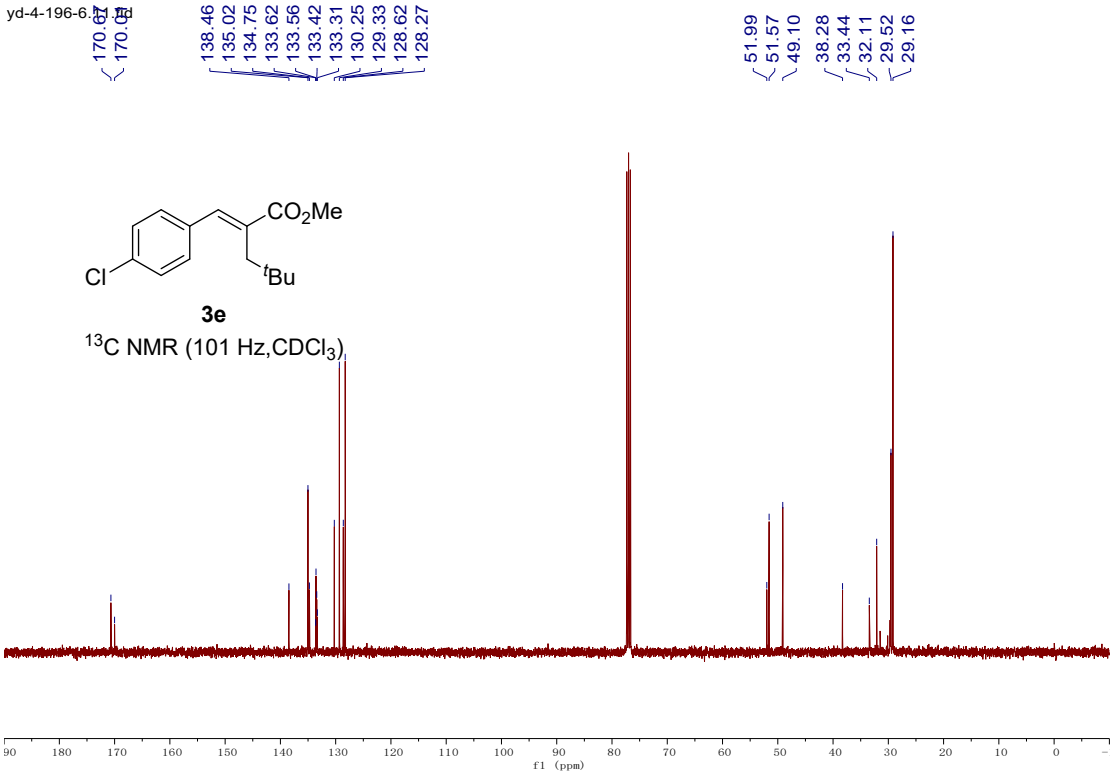

3e

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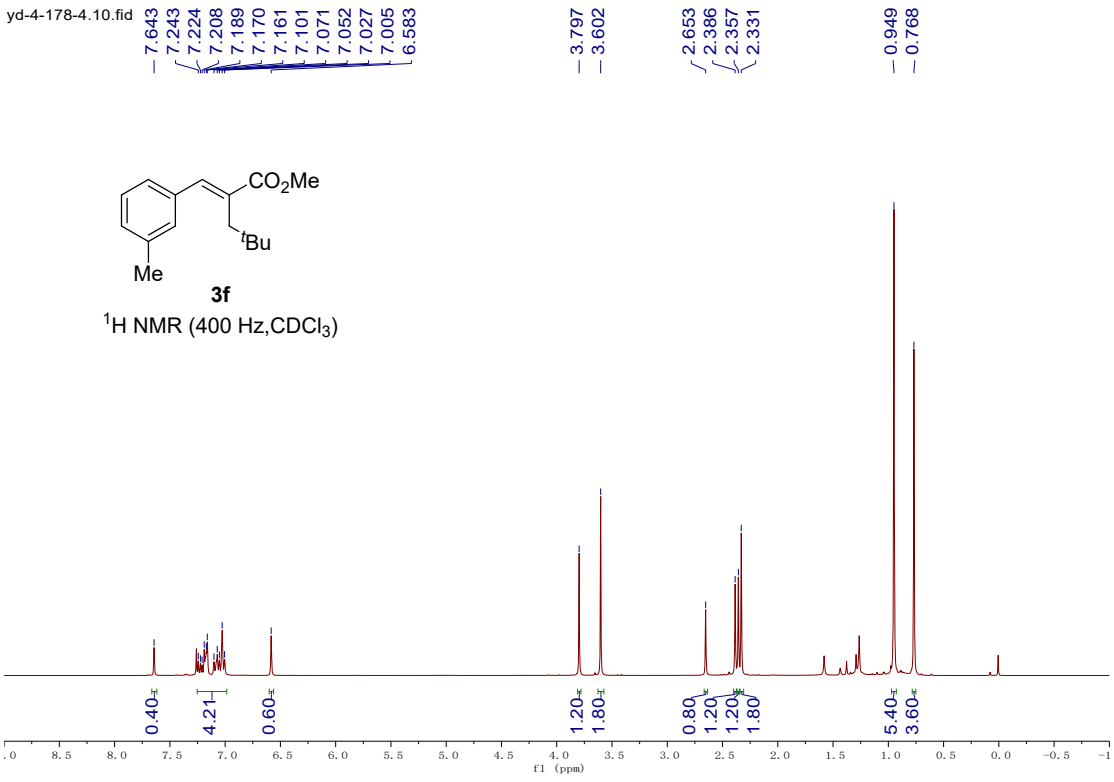
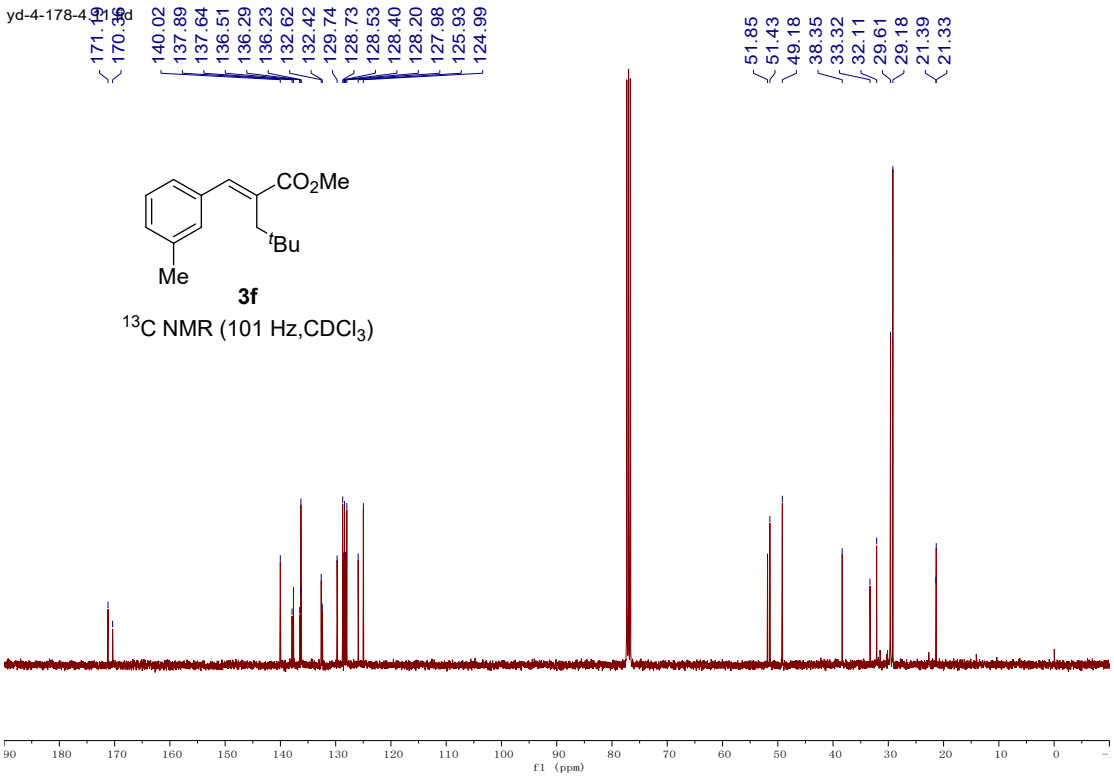


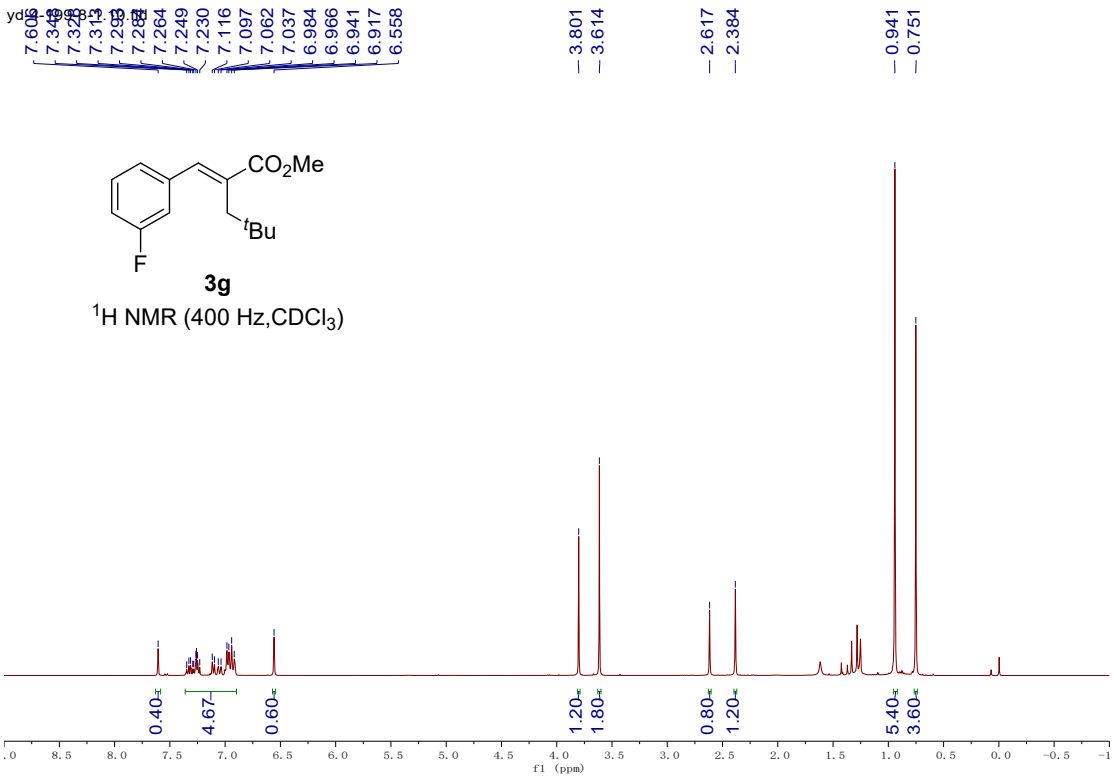
3f

^{1}H NMR (400 Hz,$CDCl_3$)



3f

^{13}C NMR (101 Hz,$CDCl_3$)



3g

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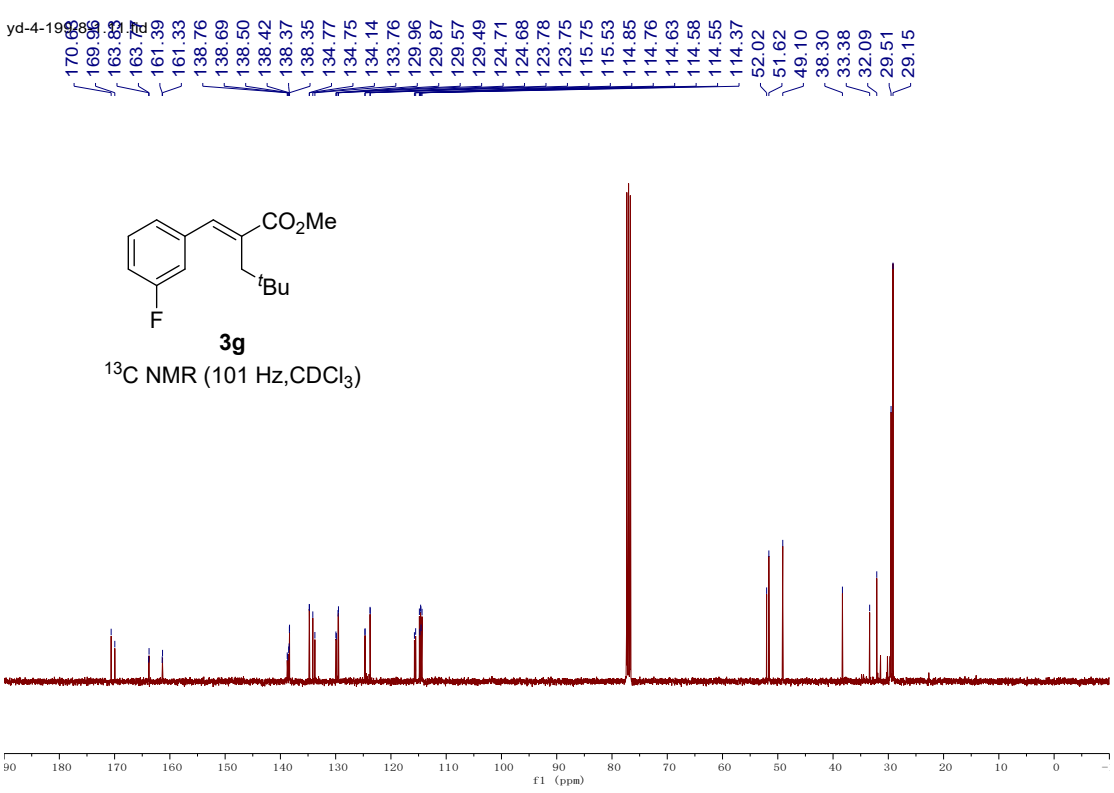
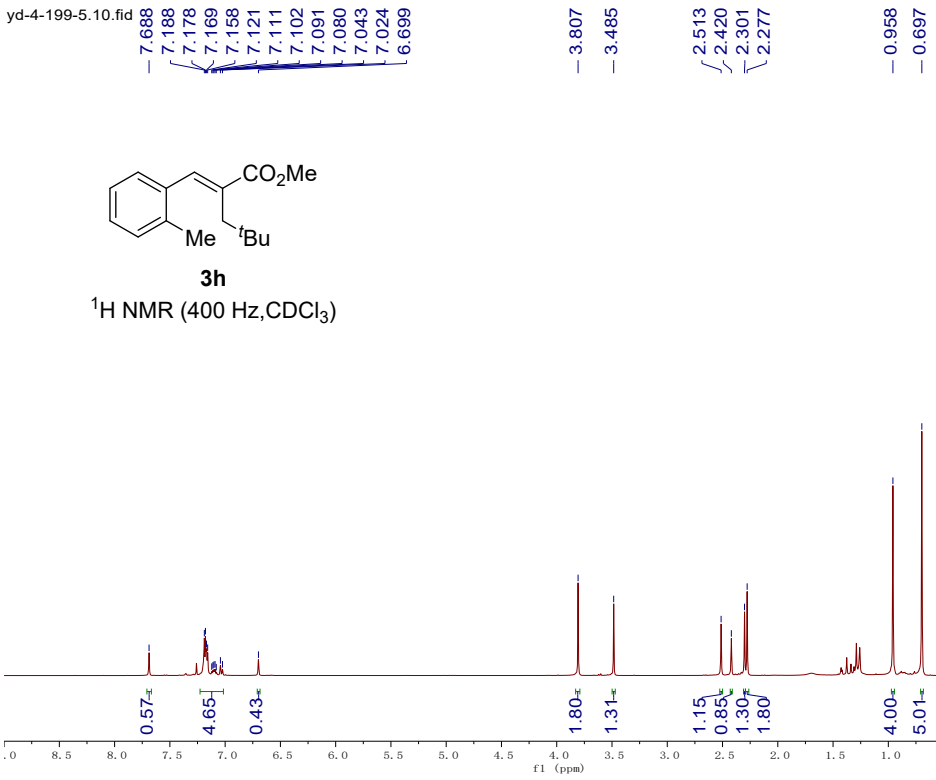


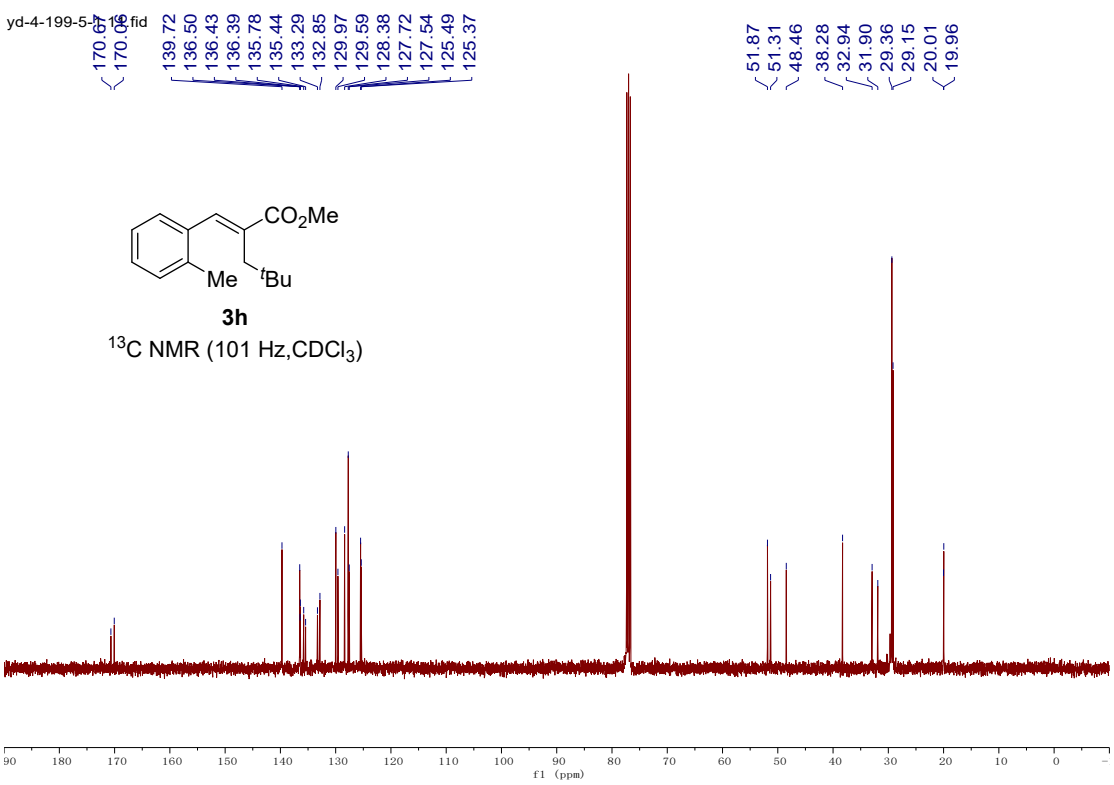
3g

^{13}C NMR (101 Hz,$CDCl_3$)



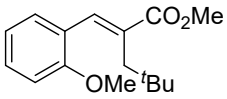
3h

^{1}H NMR (400 Hz,$CDCl_3$)



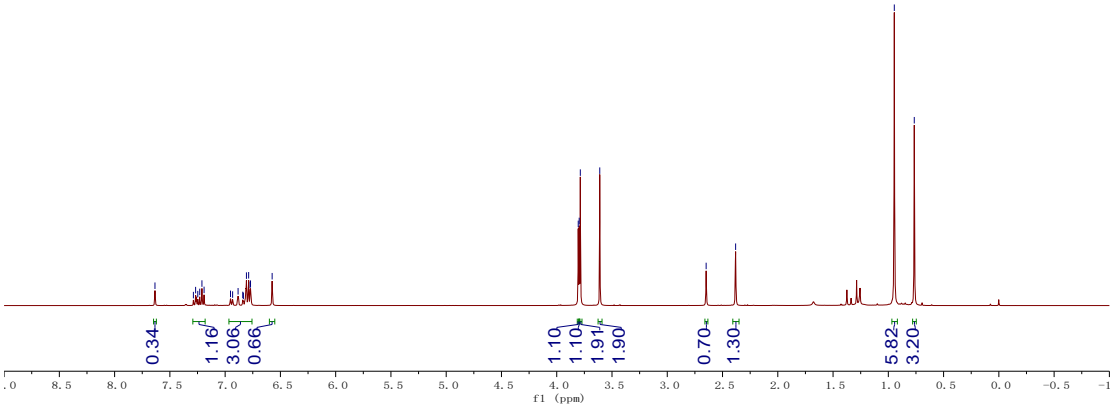
3h

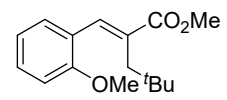
^{13}C NMR (101 Hz,$CDCl_3$)



3i

^{1}H NMR (400 Hz,$CDCl_3$)





3i

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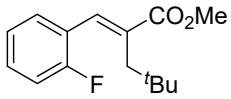

3j

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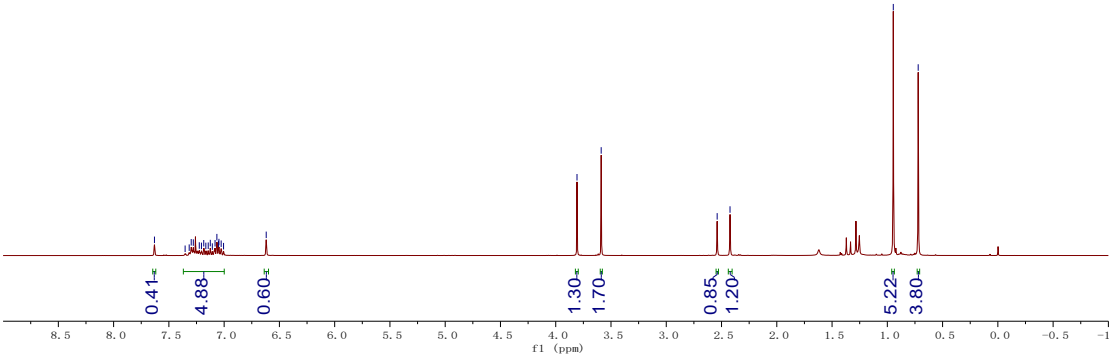

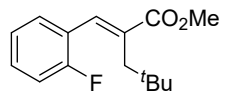

3j

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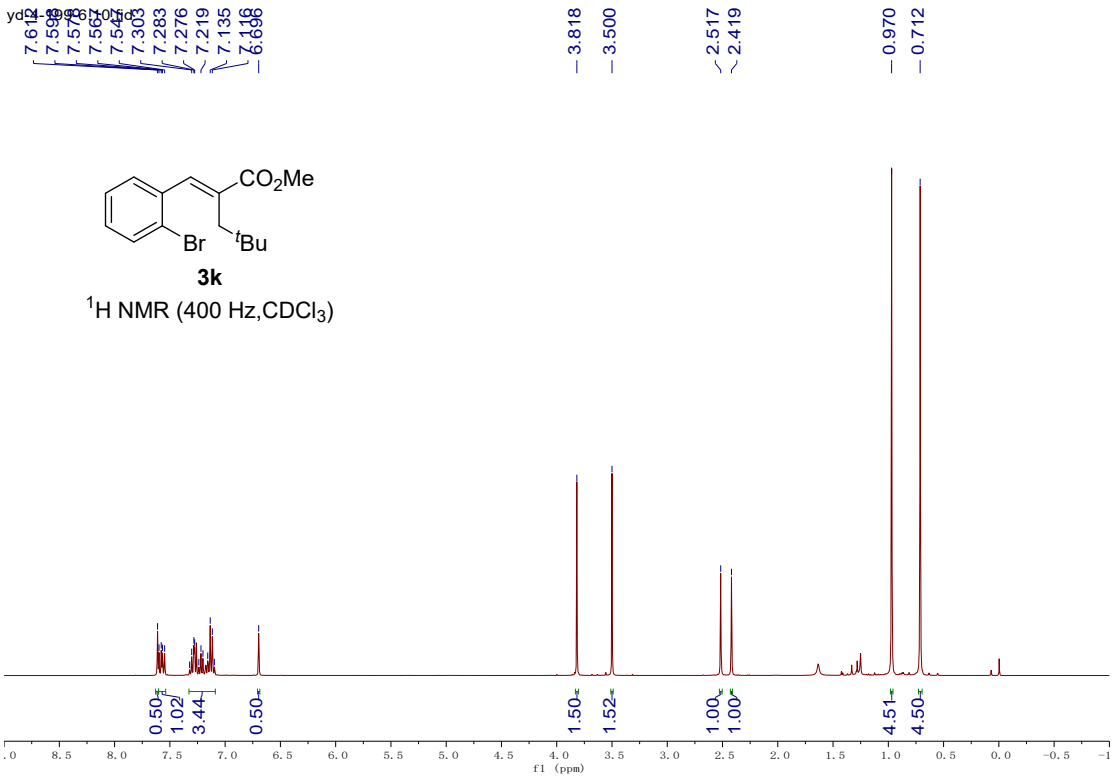
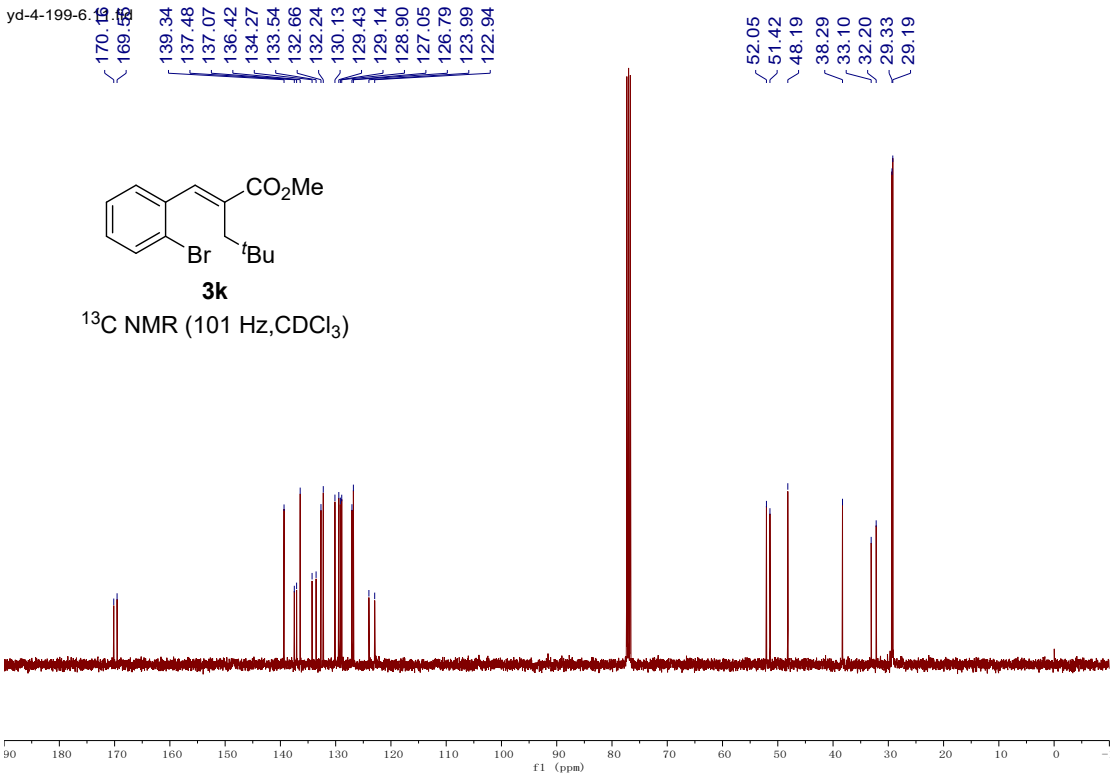


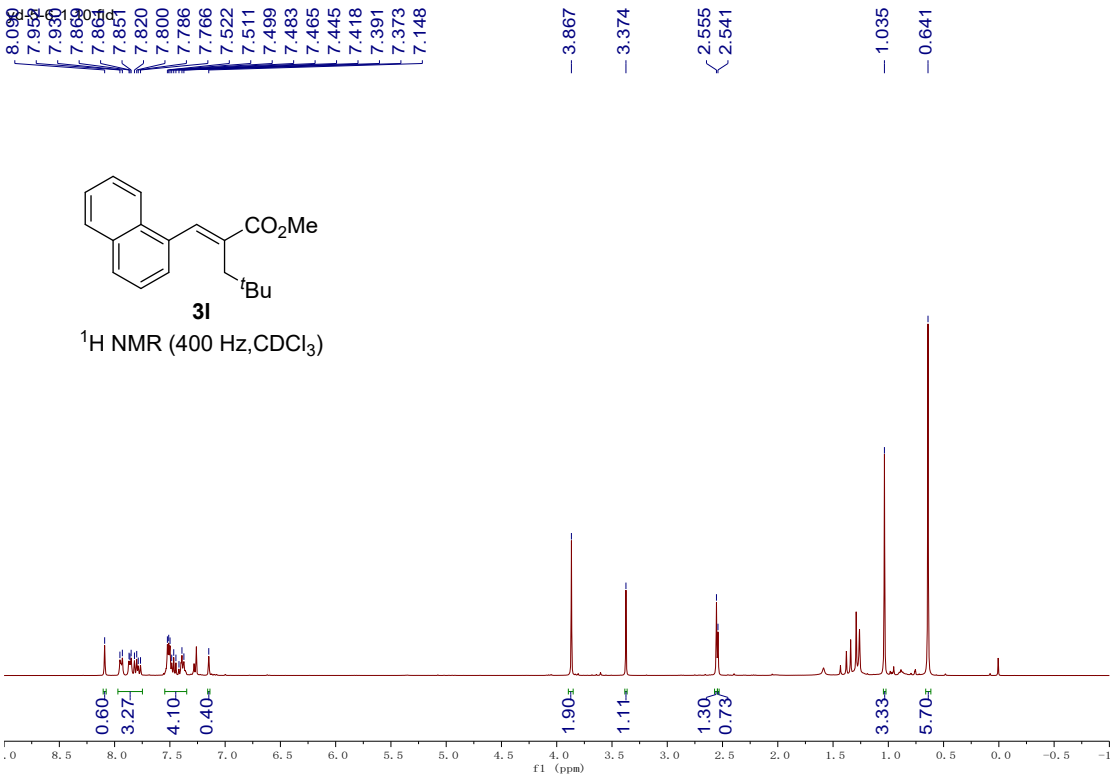
3k

^{1}H NMR (400 Hz,$CDCl_3$)



3k

^{13}C NMR (101 Hz,$CDCl_3$)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7.931
7.869
7.863
7.851
7.820
7.800
7.786
7.766
7.522
7.511
7.499
7.483
7.465
7.445
7.418
7.391
7.373
7.148
3.867
3.374
2.555
2.541
1.035
0.641
CO2Me
tBu
3I
1H NMR (400 Hz,CDCl3)
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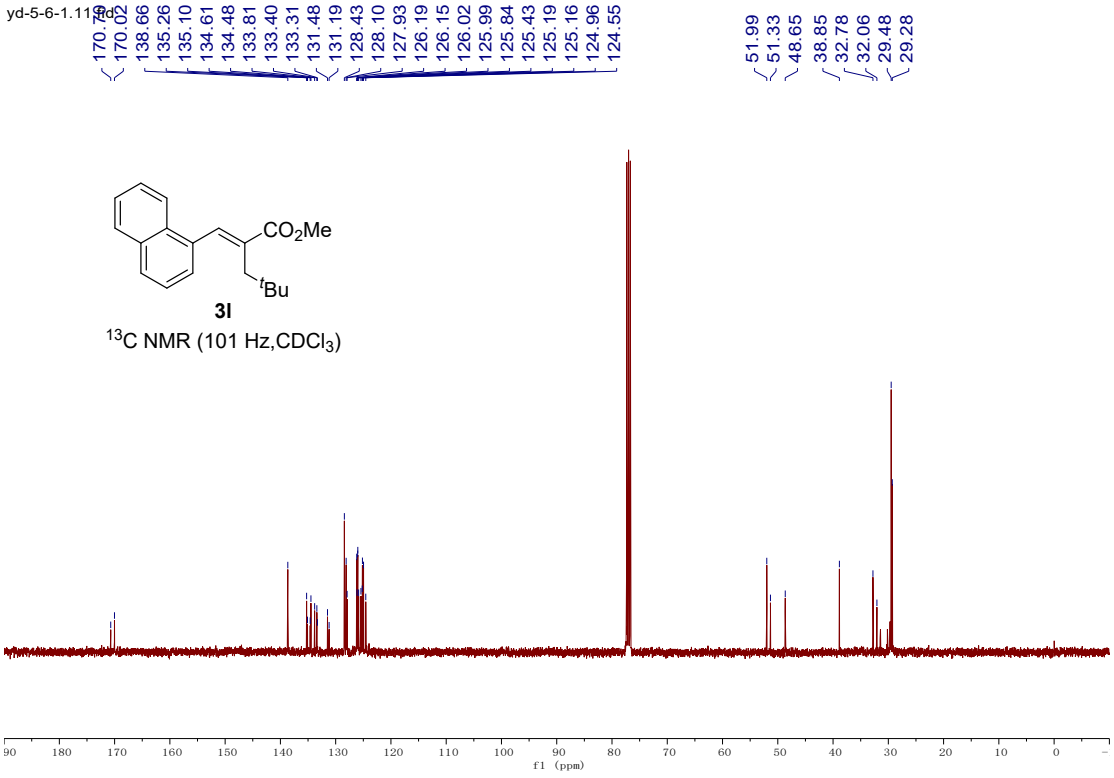
3.27
4.10
0.40
1.90
1.11
1.30
0.73
3.33
5.70
f1 (ppm)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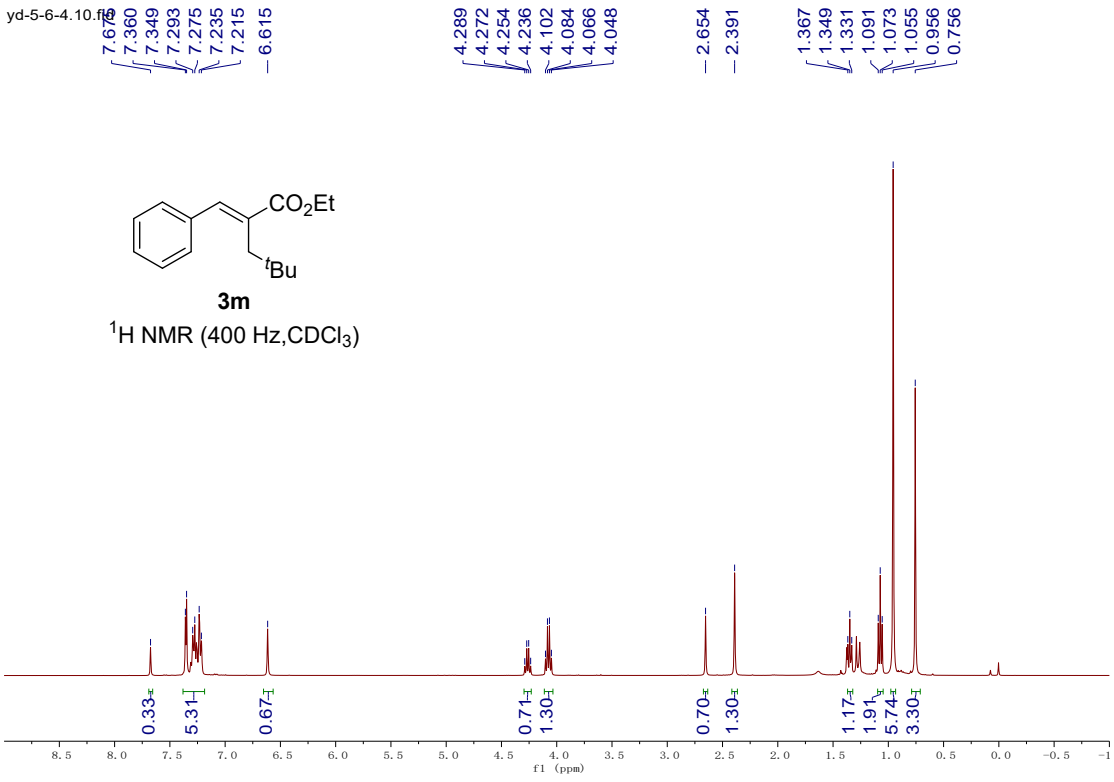
170.02
138.66
135.26
135.10
134.61
134.48
133.81
133.40
133.31
131.48
131.19
128.43
128.10
127.93
126.19
126.15
126.02
125.99
125.84
125.43
125.19
125.16
124.96
124.55
51.99
51.33
48.65
38.85
32.78
32.06
29.48
29.28
CO2Me
tBu
3I
13C NMR (101 Hz,CDCl3)
f1 (ppm)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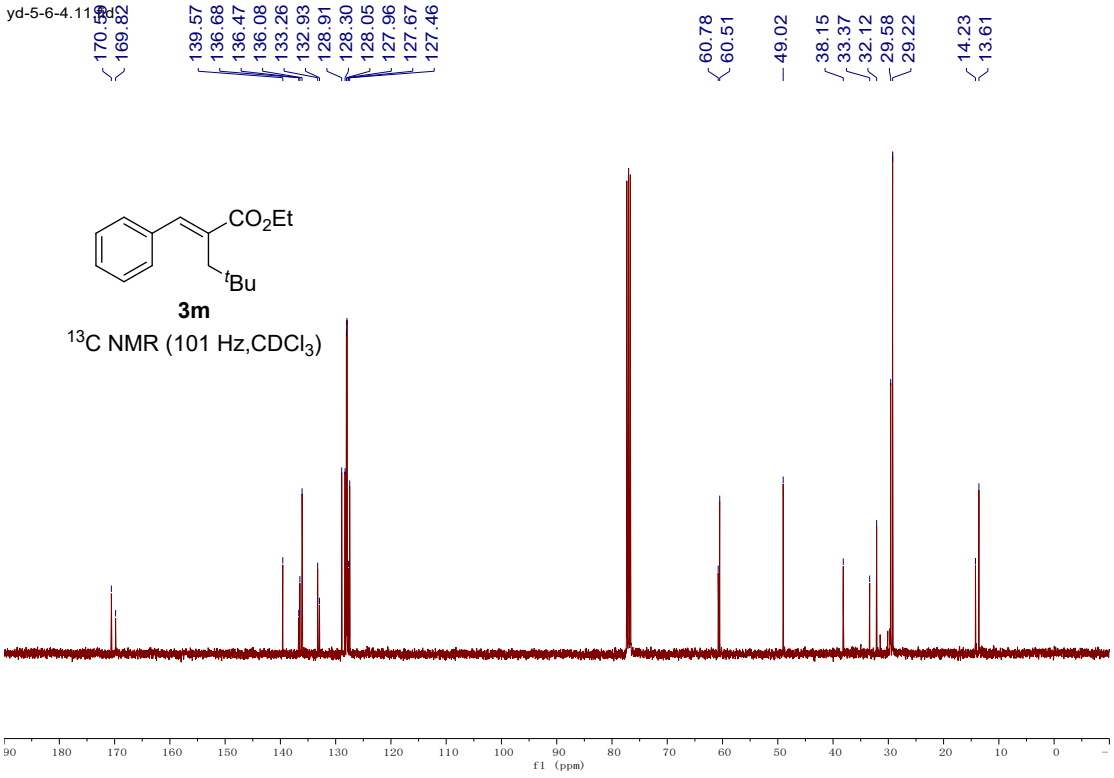
7.360
7.349
7.293
7.275
7.235
7.215
6.615
4.289
4.272
4.254
4.236
4.102
4.084
4.066
4.048
2.654
2.391
1.367
1.349
1.331
1.091
1.073
1.055
0.956
0.756
CO2Et
tBu
3m
1H NMR (400 Hz,CDCl3)
0.33
5.31
0.67
0.71
1.30
0.70
1.30
1.17
1.91
5.74
3.30
f1 (ppm)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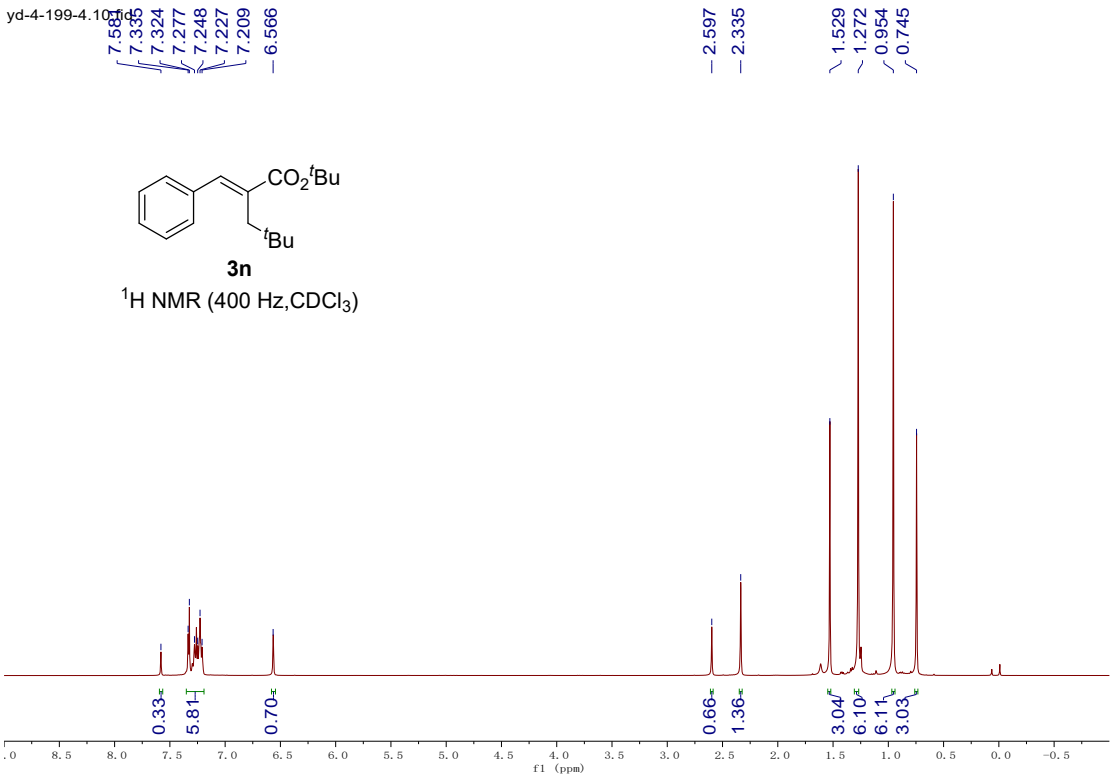
169.82
139.57
136.68
136.47
136.08
133.26
132.93
128.91
128.30
128.05
127.96
127.67
127.46
60.78
60.51
49.02
38.15
33.37
32.12
29.58
29.22
14.23
13.61
CO2Et
tBu
3m
13C NMR (101 Hz,CDCl3)
f1 (ppm)

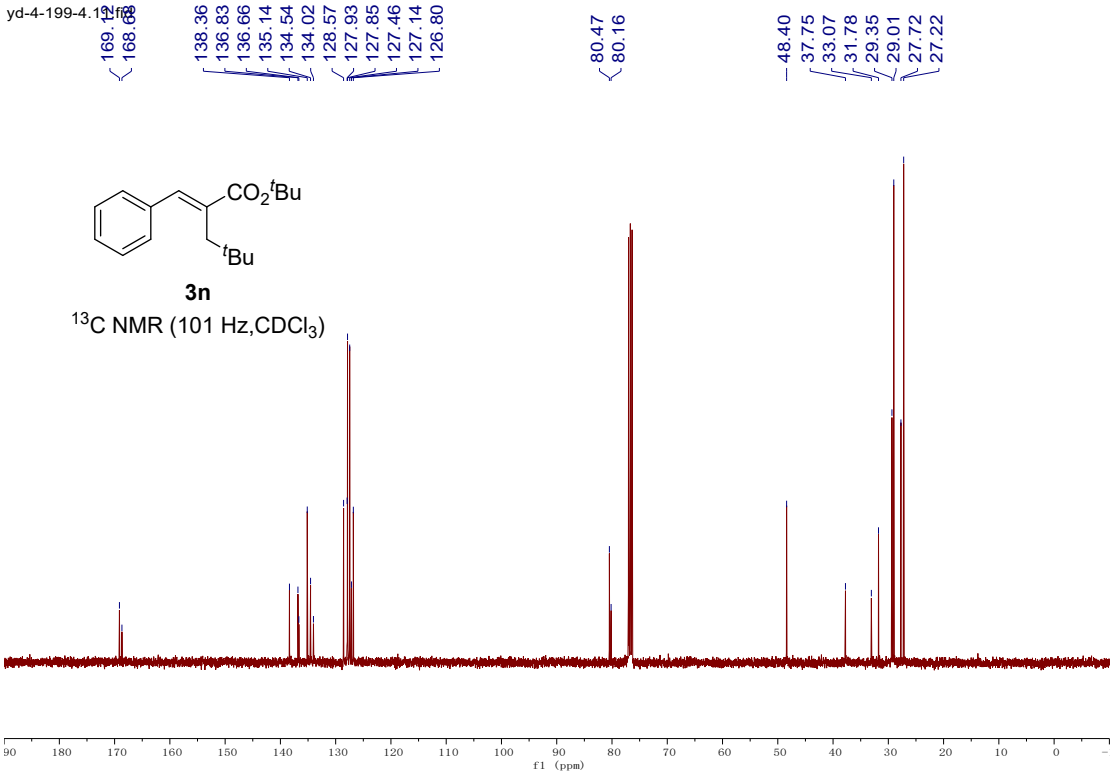


$CO_2{}^tBu$

^tBu

3n

^1H NMR (400 Hz,$CDCl_3$)

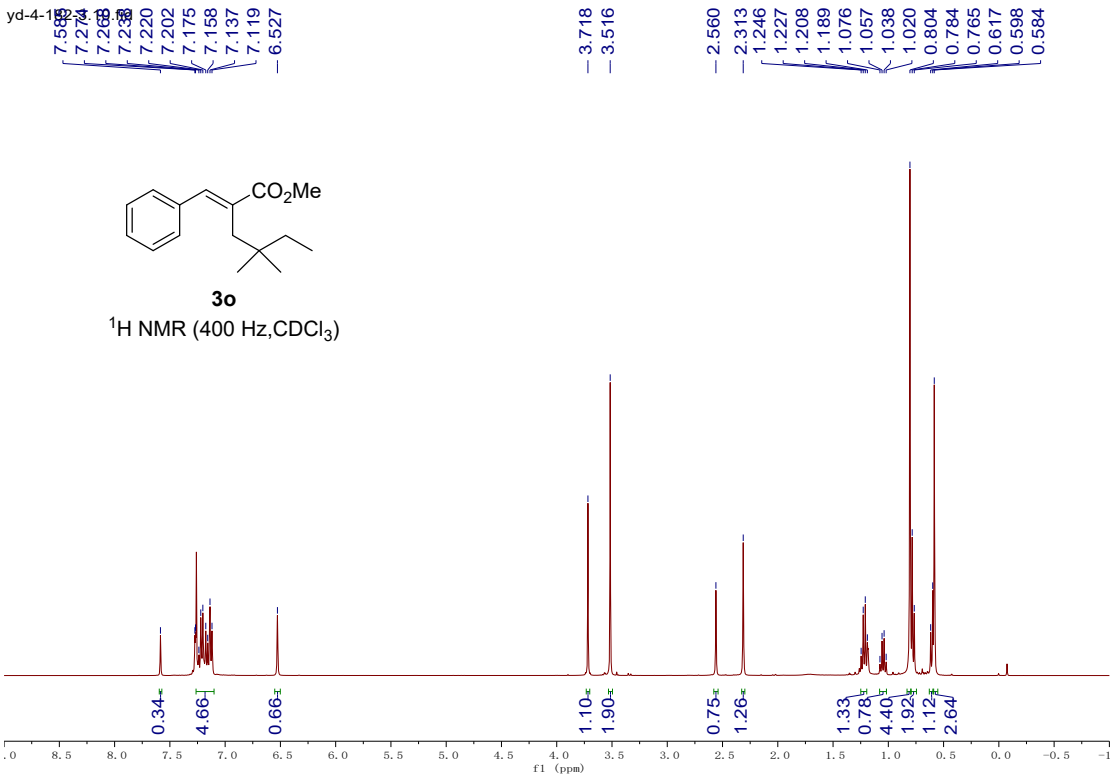


$CO_2{}^tBu$

^tBu

3n

^{13}C NMR (101 Hz,$CDCl_3$)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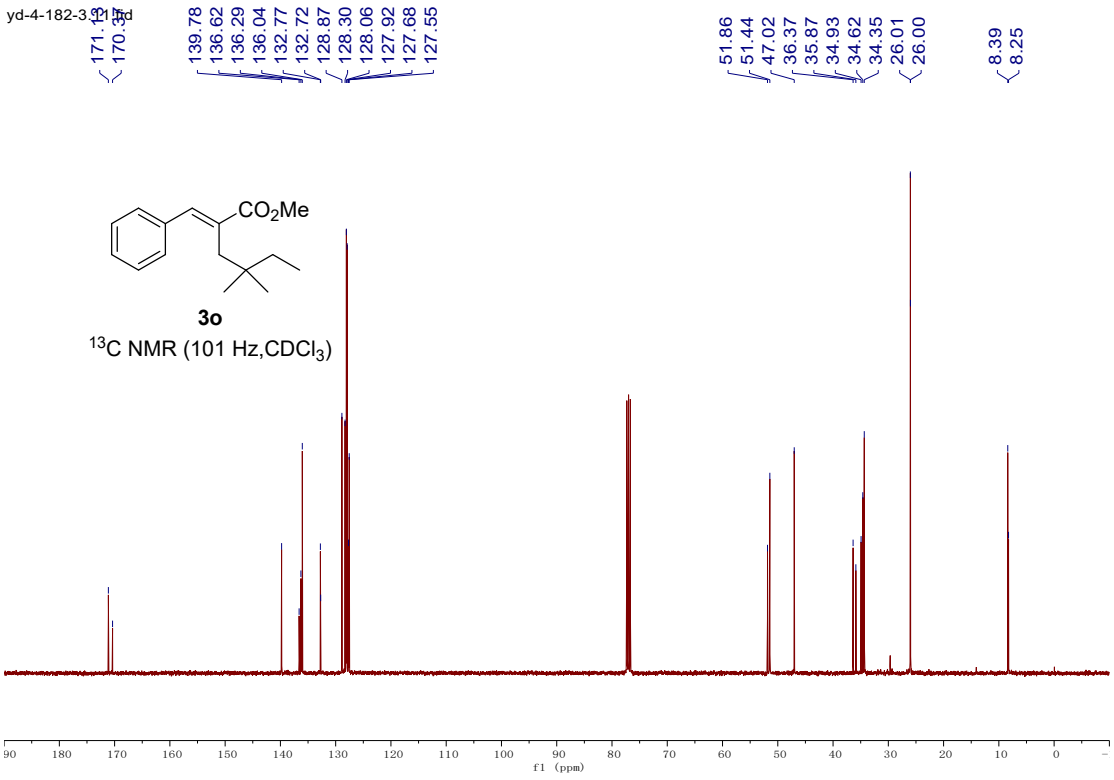
7.266
7.238
7.220
7.202
7.175
7.158
7.137
7.119
6.527
3.718
3.516
2.560
2.313
1.246
1.227
1.208
1.189
1.076
1.057
1.038
1.020
0.804
0.784
0.765
0.617
0.598
0.584
CO2Me
3o
1H NMR (400 Hz,CDCl3)
0.34
4.66
0.66
1.10
1.90
0.75
1.26
1.33
0.78
4.40
1.92
1.12
2.64
f1 (ppm)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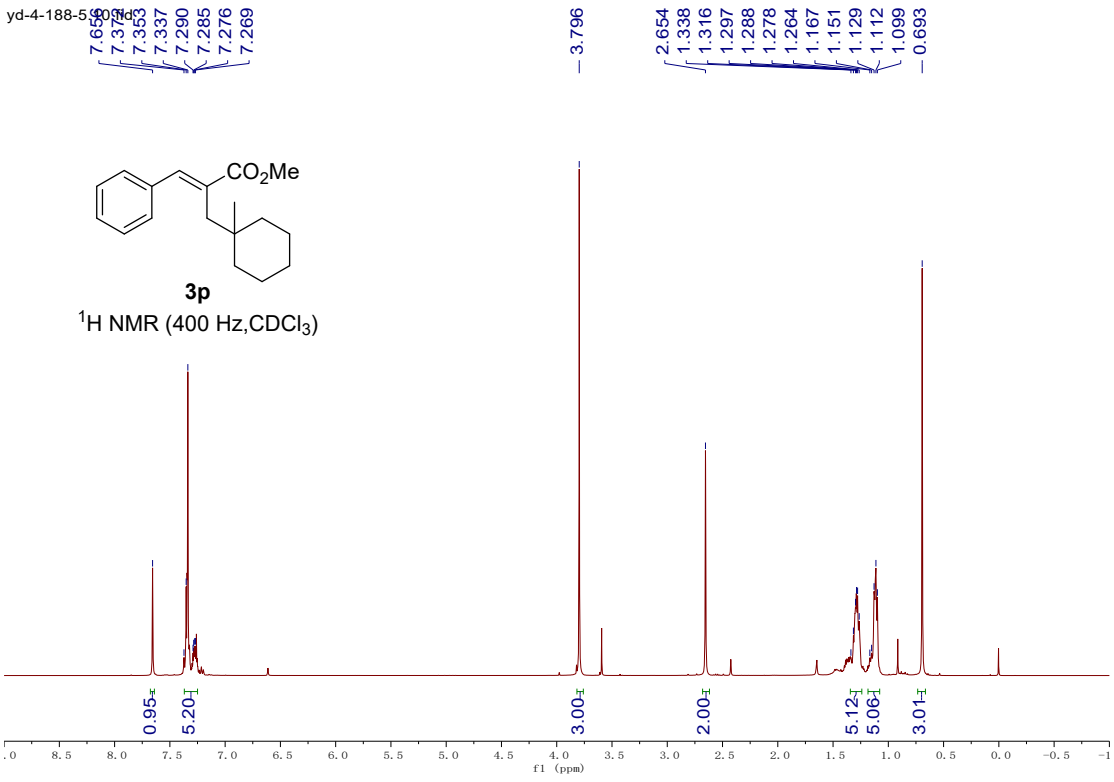
139.78
136.62
136.29
136.04
132.77
132.72
128.87
128.30
128.06
127.92
127.68
127.55
51.86
51.44
47.02
36.37
35.87
34.93
34.62
34.35
26.01
26.00
8.39
8.25
CO2Me
3o
13C NMR (101 Hz,CDCl3)
f1 (ppm)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7.374
7.353
7.337
7.290
7.285
7.276
7.269
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2.654
1.338
1.316
1.297
1.288
1.278
1.264
1.167
1.151
1.129
1.112
1.099
0.693
CO2Me
3p
1H NMR (400 Hz,CDCl3)
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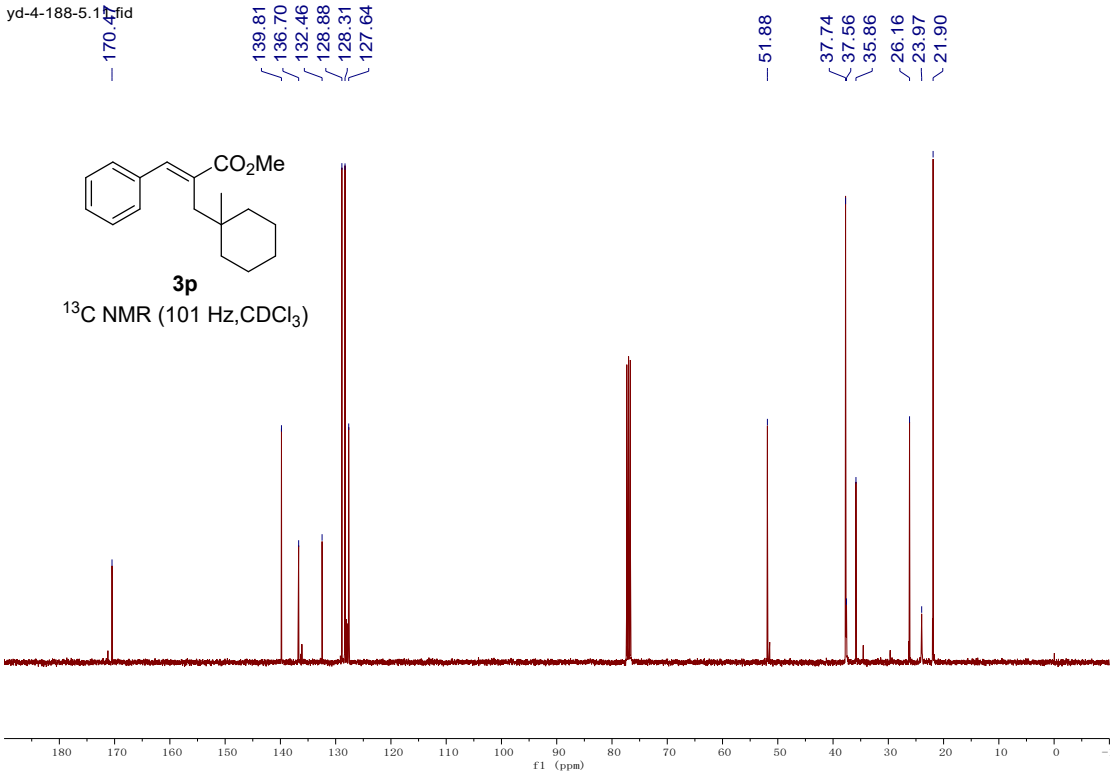
5.20
3.00
2.00
5.12
5.06
3.01
f1 (ppm)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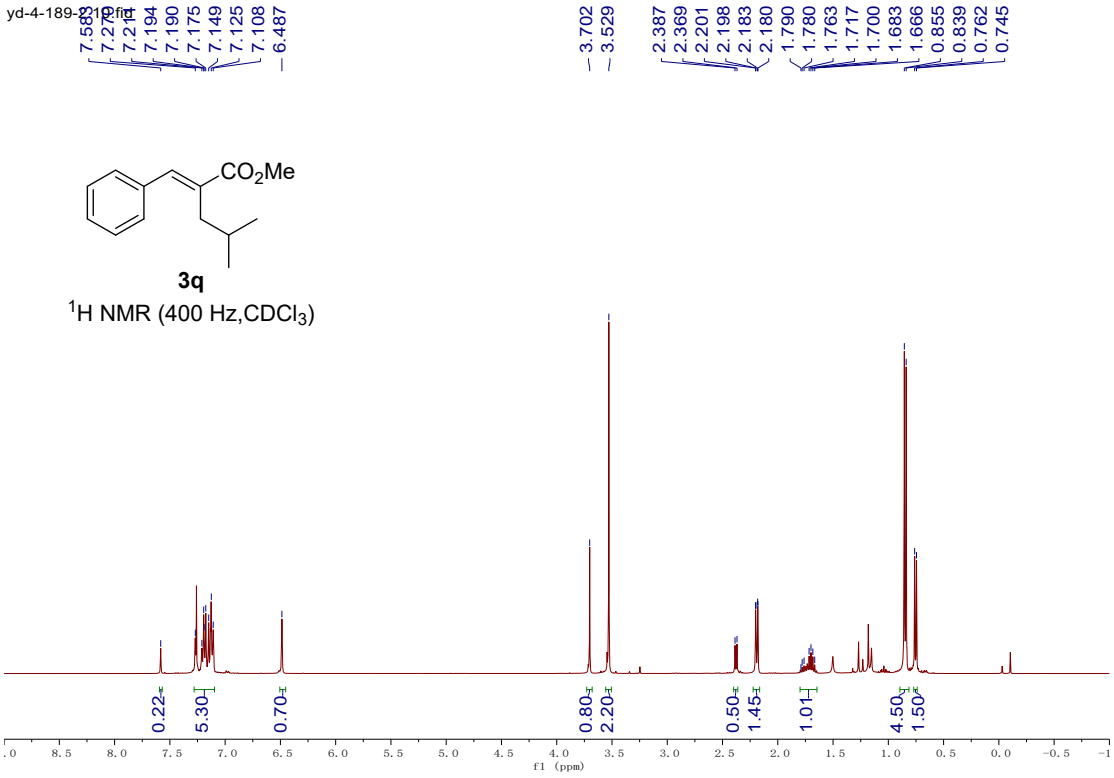
139.81
136.70
132.46
128.88
128.31
127.64
51.88
37.74
37.56
35.86
26.16
23.97
21.90
CO2Me
3p
13C NMR (101 Hz,CDCl3)
f1 (ppm)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7.175
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7.125
7.108
6.487
3.702
3.529
2.387
2.369
2.201
2.198
2.183
2.180
1.790
1.780
1.763
1.717
1.700
1.683
1.666
0.855
0.839
0.762
0.745
CO2Me
3q
1H NMR (400 Hz,CDCl3)
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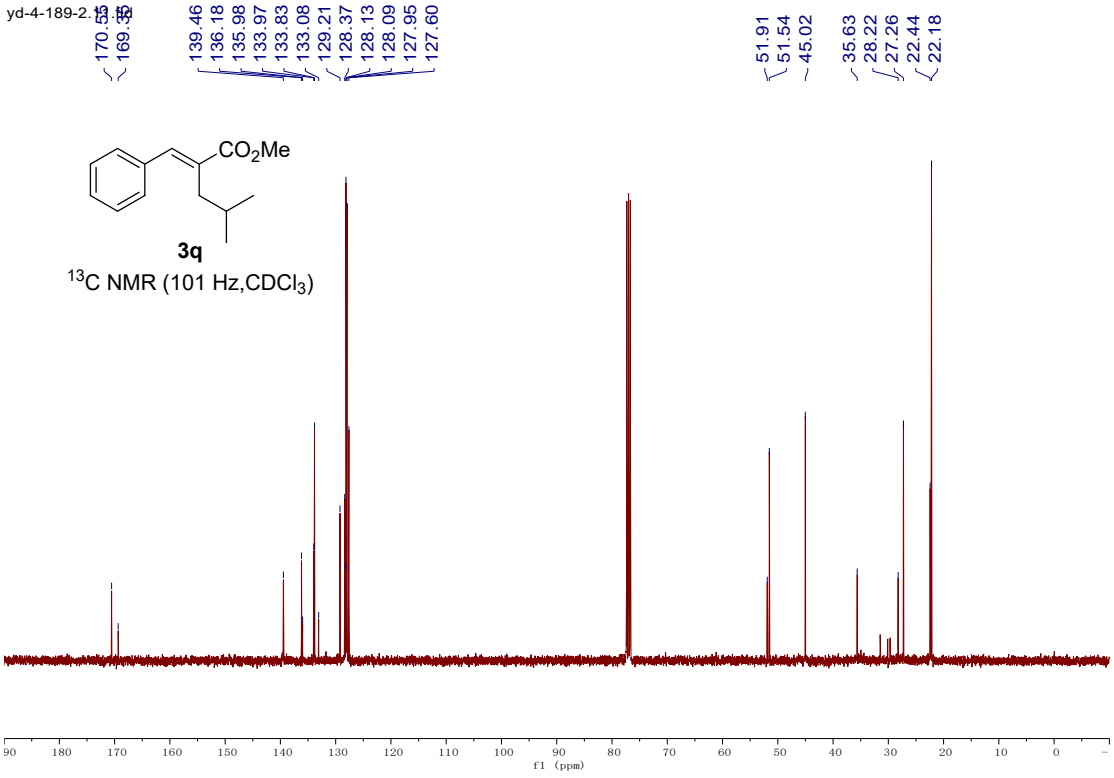
5.30
0.70
0.80
2.20
0.50
1.45
1.01
4.50
1.50
f1 (ppm)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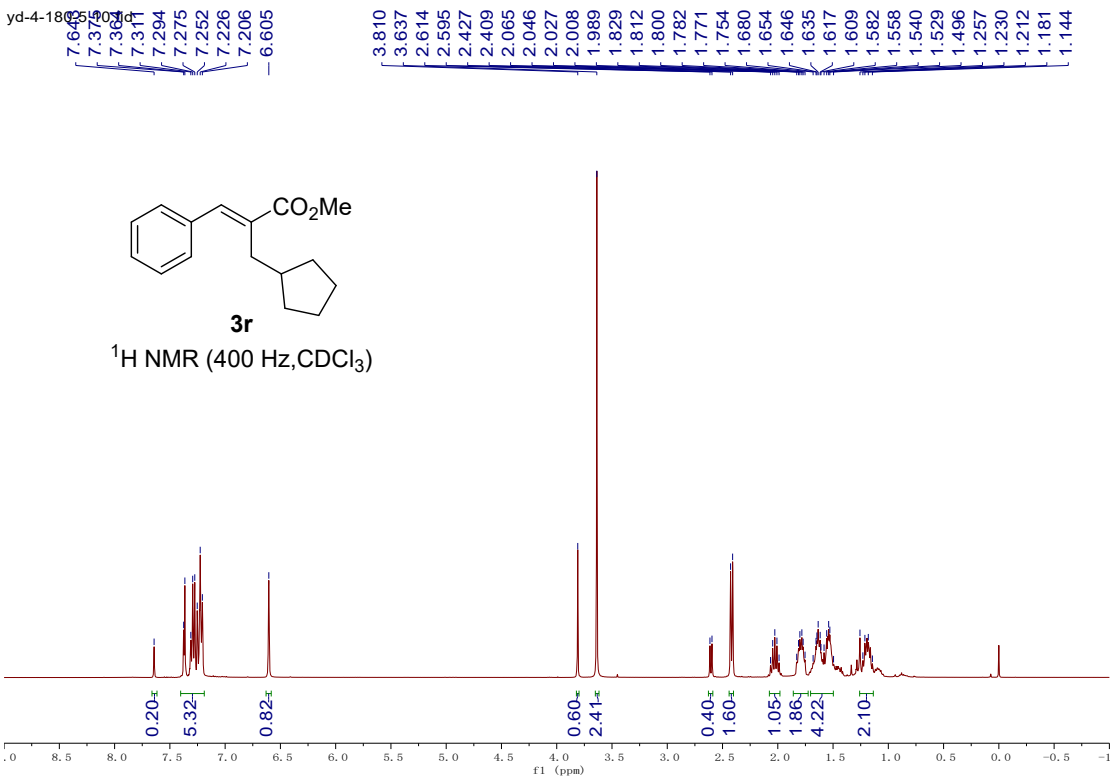
135.98
133.97
133.83
133.08
129.21
128.37
128.13
128.09
127.95
127.60
51.91
51.54
45.02
35.63
28.22
27.26
22.44
22.18
CO2Me
3q
13C NMR (101 Hz,CDCl3)
f1 (ppm)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7.364
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7.294
7.275
7.252
7.226
7.206
6.605
3.810
3.637
2.614
2.595
2.427
2.409
2.065
2.046
2.027
2.008
1.989
1.829
1.812
1.800
1.782
1.771
1.754
1.680
1.654
1.646
1.635
1.617
1.609
1.582
1.558
1.540
1.529
1.496
1.257
1.230
1.212
1.181
1.144
CO2Me
3r
1H NMR (400 Hz,CDCl3)
0.20
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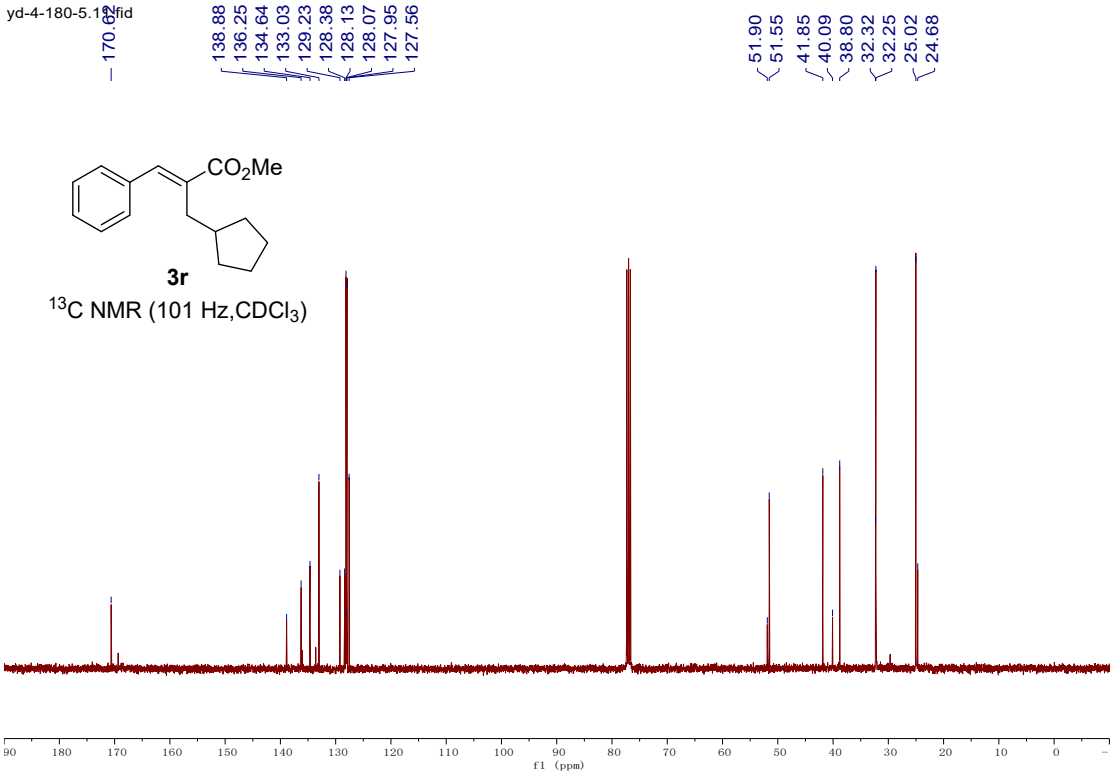
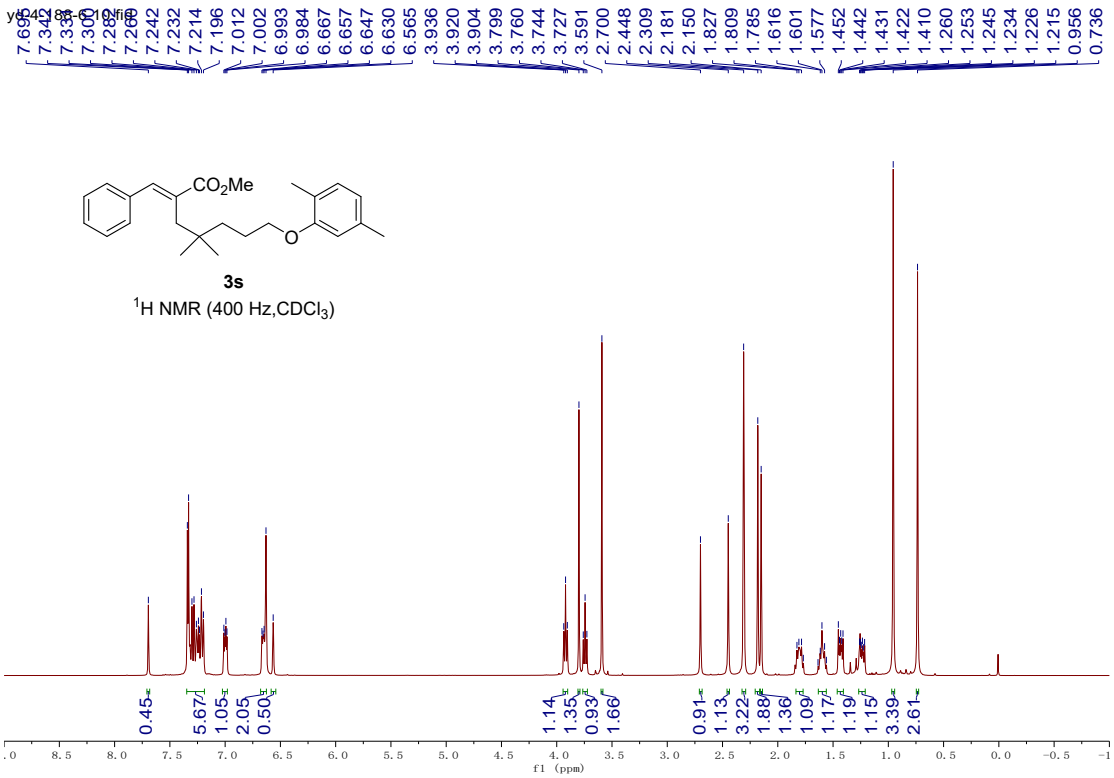
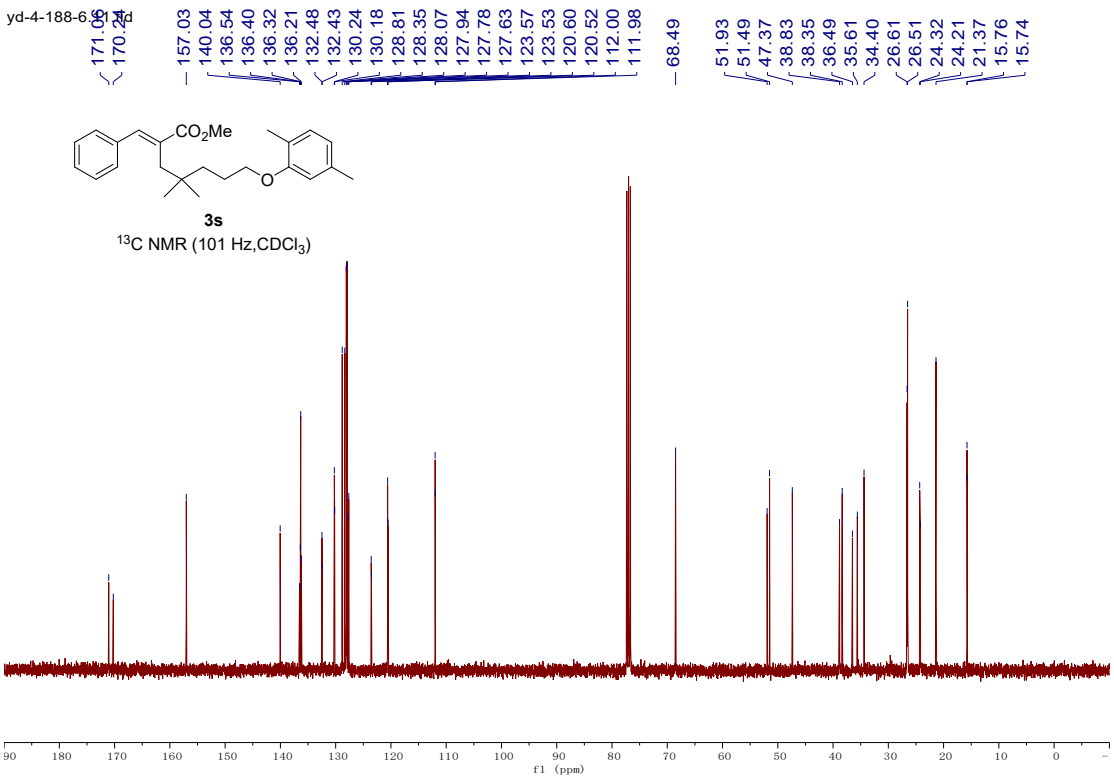
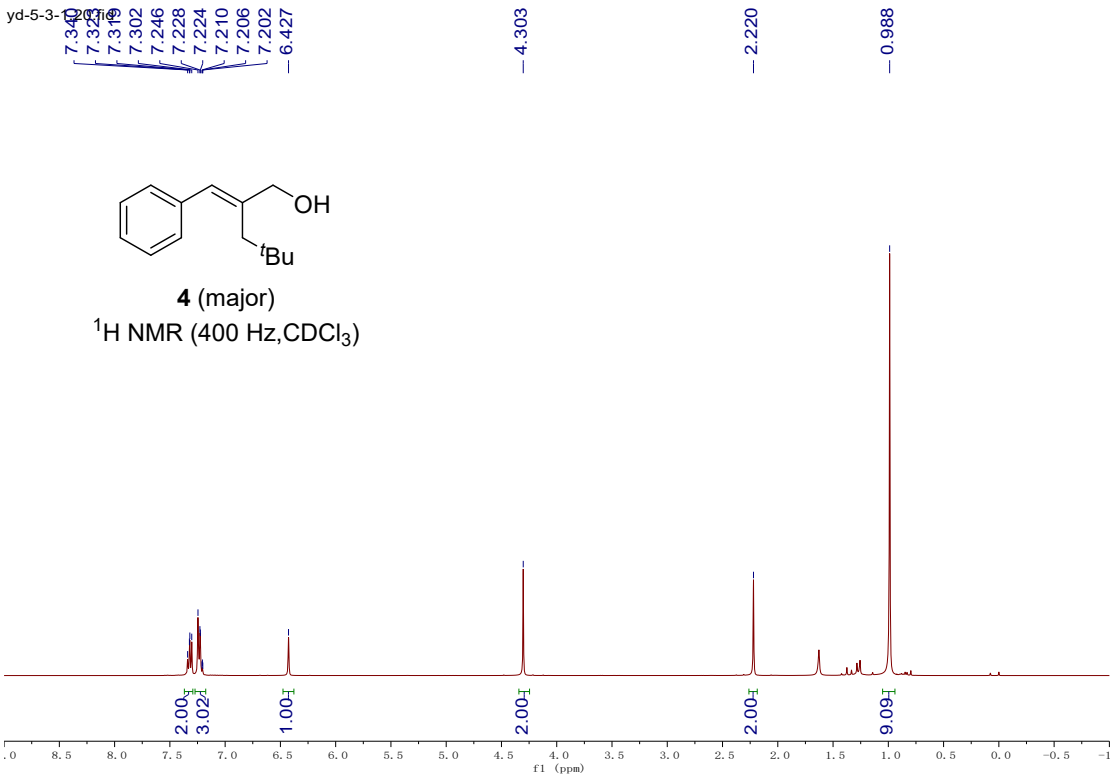
0.82
0.60
2.41
0.40
1.60
1.05
1.86
4.22
2.10
f1 (ppm)


yd-4-180-5.12.fid
170.62
138.88
136.25
134.64
133.03
129.23
128.38
128.13
128.07
127.95
127.56
51.90
51.55
41.85
40.09
38.80
32.32
32.25
25.02
24.68
CO2Me
3r
13C NMR (101 Hz,CDCl3)
f1 (ppm)

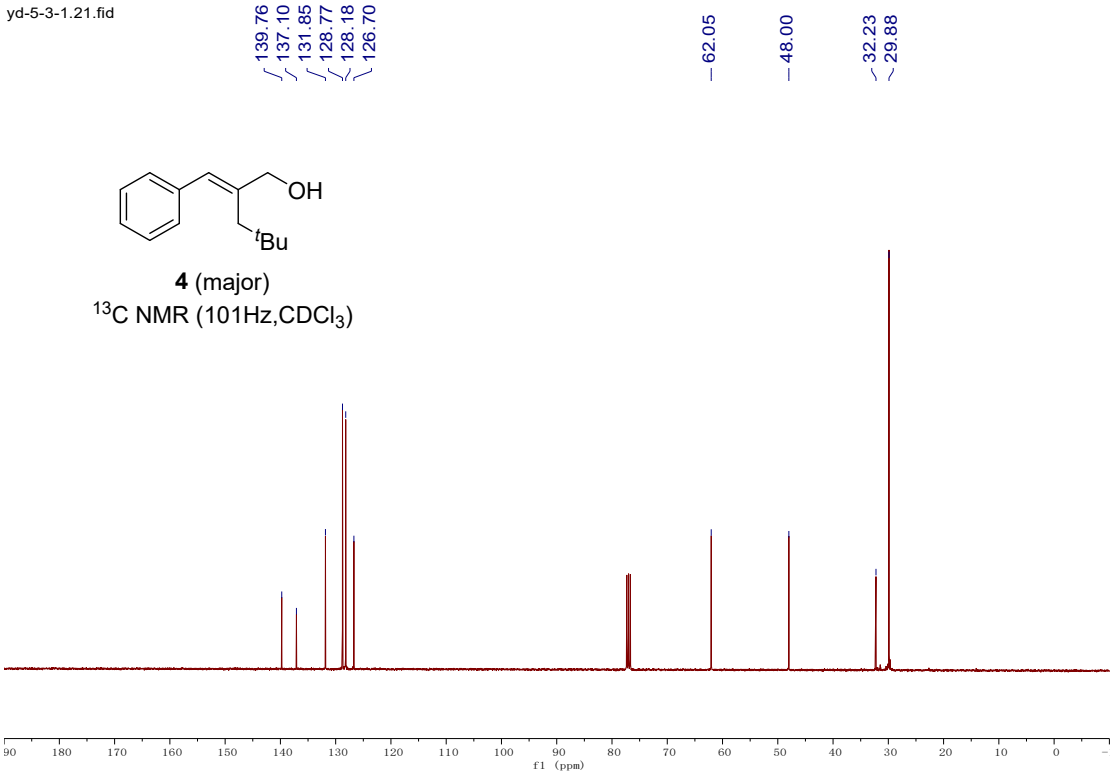

yd-4-188-6-1.10.fid
7.695
7.348
7.338
7.301
7.288
7.268
7.242
7.232
7.214
7.196
7.012
7.002
6.993
6.984
6.667
6.657
6.647
6.630
6.565
3.936
3.920
3.904
3.799
3.760
3.744
3.727
3.591
2.700
2.448
2.309
2.181
2.150
1.827
1.809
1.785
1.616
1.601
1.577
1.452
1.442
1.431
1.422
1.410
1.260
1.253
1.245
1.234
1.226
1.215
0.956
0.736
CO2Me
O
3s
1H NMR (400 Hz,CDCl3)
0.45
5.67
1.05
2.05
0.50
1.14
1.35
0.93
1.66
0.91
1.13
3.22
1.88
1.36
1.09
1.17
1.19
1.15
3.39
2.61
f1 (ppm)


yd-4-188-6-2.1.fid
171.06
170.24
157.03
140.04
136.54
136.40
136.32
136.21
132.48
132.43
130.24
130.18
128.81
128.35
128.07
127.94
127.78
127.63
123.57
123.53
120.60
120.52
112.00
111.98
68.49
51.93
51.49
47.37
38.83
38.35
36.49
35.61
34.40
26.61
26.51
24.32
24.21
21.37
15.76
15.74
CO2Me
O
3s
13C NMR (101 Hz,CDCl3)
f1 (ppm)



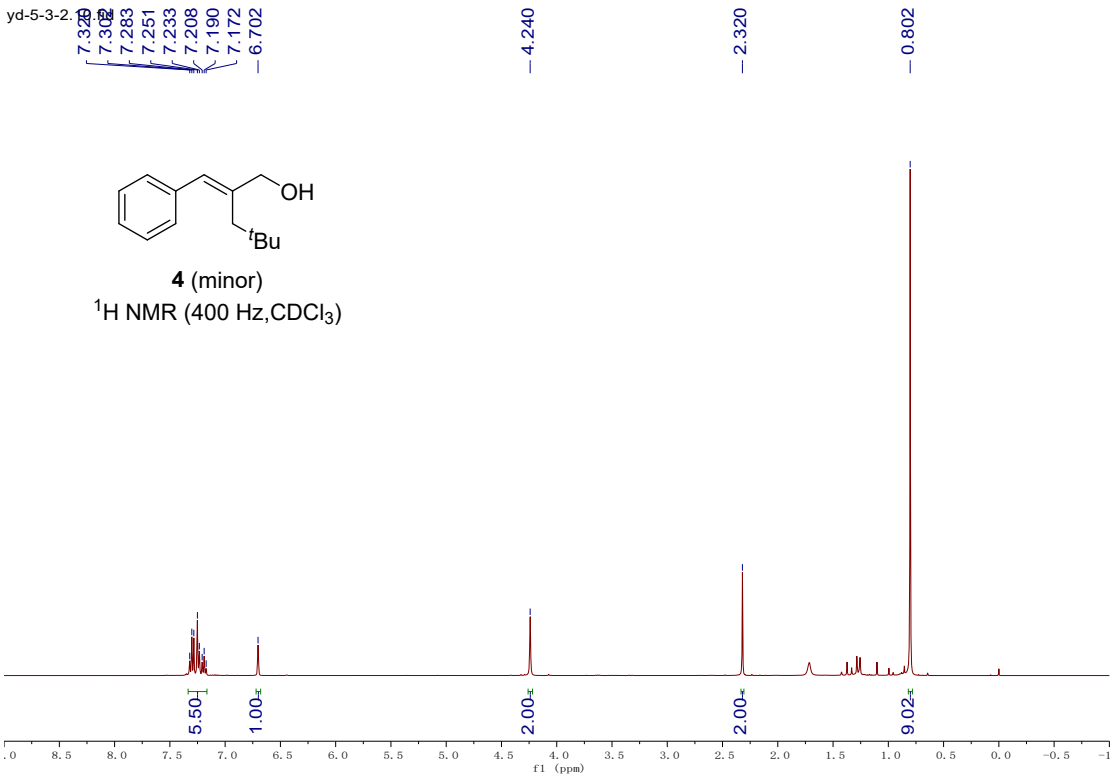
4 (major)

^{1}H NMR (400 Hz,$CDCl_3$)



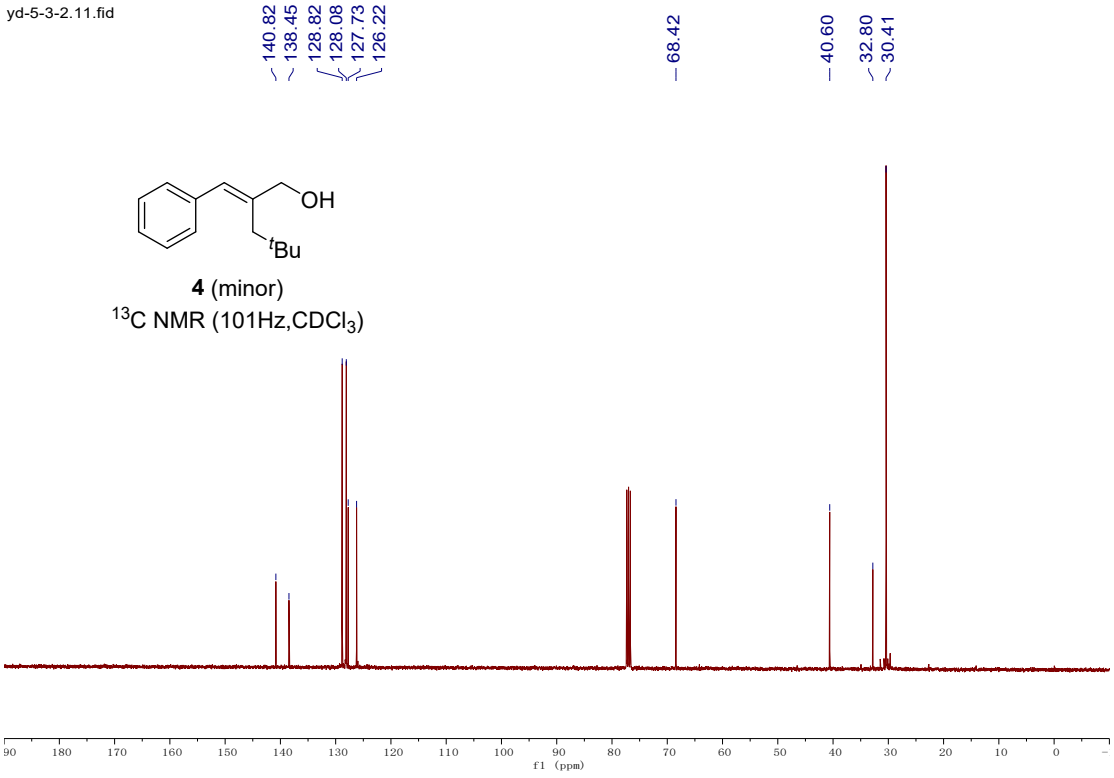
4 (major)

^{13}C NMR (101Hz,$CDCl_3$)



4 (minor)

^{1}H NMR (400 Hz,$CDCl_3$)



4 (minor)

^{13}C NMR (101Hz,$CDCl_3$)