Electronic Supplementary Material (ESI) for ChemComm.

Cu-catalyzed Highly Regioselective 1,2-Hydrocarboxylation of 1,3-Dienes with CO_2

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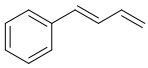
Supporting Information

1. General Considerations

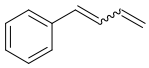
All manipulations were conducted with Schlenk tube. ^{1}H NMR spectra were recorded on a Bruker AVIII-400 spectrometers. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) or δ = 7.26 ppm in $CDCl_3$ as an internal standard. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.00 ppm). ^{19}F NMR spectra were obtained by the same NMR and CF_3COOH was employed as external standard for the ^{19}F-NMR measurement. ^{11}B NMR spectra were obtained by the same NMR and $B(OMe)_3$ was employed as external standard for the ^{11}B NMR measurement. High resolution mass spectrometry (HRMS) data were obtained on a QTOF mass analyzer with electrospray ionization (ESI) through a Bruker Daltonicmior OTOF-QII. Substrates were purchased from Aldrich, TCI, Acros, Energy, Aladdin, or synthesized according to the procedures outlined below. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

2. Synthesis of Diene Substrates

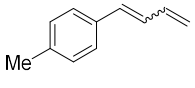
These substrates were prepared according to the corresponding literature reports. Analytical data (^{1}H NMR, ^{13}C NMR) matches with the literature.



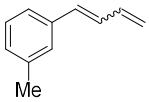
1a-trans: (*E*)-buta-1,3-dien-1-ylbenzene [1]



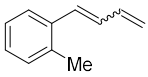
1a: (*E,Z*)-buta-1,3-dien-1-ylbenzene [1] *E:Z* = 1:1.3



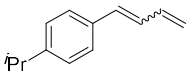
1b: (*E,Z*)-1-(buta-1,3-dien-1-yl)-4-methylbenzene [3] *E:Z* = 1:1.6



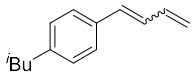
1c: (*E,Z*)-1-(buta-1,3-dien-1-yl)-3-methylbenzene [2] *E:Z* = 1:1.4



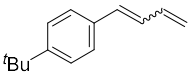
1d: (*E,Z*)-1-(buta-1,3-dien-1-yl)-2-methylbenzene [1] *E:Z* = 1:1.5



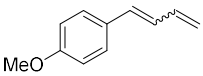
1f: (*E,Z*)-1-(buta-1,3-dien-1-yl)-4-isopropylbenzene [4] *E:Z* = 1:1.5



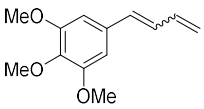
1g: (*E,Z*)-1-(buta-1,3-dien-1-yl)-4-isobutylbenzene [1] *E:Z* = 1:1.6



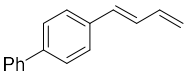
1h: (*E,Z*)-1-(buta-1,3-dien-1-yl)-4-(*tert*-butyl)benzene[5] *E:Z* = 1:1.5



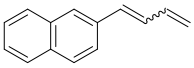
1i: (*E,Z*)-1-(buta-1,3-dien-1-yl)-4-methoxybenzene [1] *E:Z* = 1:1.6



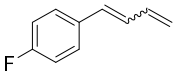
1k: (*E,Z*)-5-(buta-1,3-dien-1-yl)-1,2,3-trimethoxybenzene [4] *E:Z* = 1:2



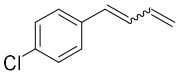
(*E*)-4-(buta-1,3-dien-1-yl)-1,1'-biphenyl [6] *E:Z* = 1:2.7



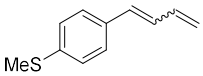
1m: (*E,Z*)-2-(buta-1,3-dien-1-yl)naphthalene [3] *E:Z* = 1:1.4



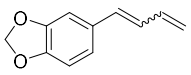
1n: (*E,Z*)-1-(buta-1,3-dien-1-yl)-4-fluorobenzene [1] *E:Z* = 1:1.5



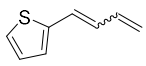
1o: (*E,Z*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene [3] *E:Z* = 1:1.2



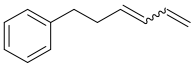
1p: (*E,Z*)-(4-(buta-1,3-dien-1-yl)phenyl)(methyl)sulfane [7] *E:Z* = 1:1.5



1s: (*E,Z*)-5-(buta-1,3-dien-1-yl)benzo[*d*][1,3]dioxole[8] *E:Z* = 1:1.4

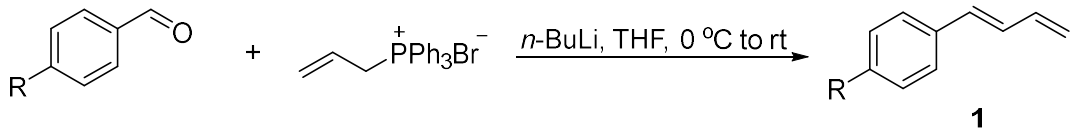


1u: (*E,Z*)-2-(buta-1,3-dien-1-yl)thiophene [6] *E:Z* = 1:1



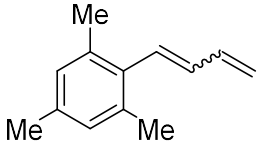
1w: (*E,Z*)-hexa-3,5-dien-1-ylbenzene [9] *E:Z* = 1.2:1

Representative procedure for preparing 1,3-dienes via Wittig olefination



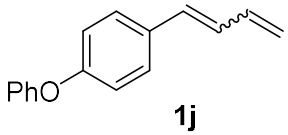
1

A suspension of allyltriphenylphosphonium bromide (3.1 g, 8.1 mmol) in dry THF (30 ml) under inert atmosphere was cooled at 0 ºC with an ice bath. Then *n*-BuLi (3.2 ml, 2.5 M in n-hexane, 8.1 mmol) was added dropwise. After stirring for 30 min, corresponding aldehyde (5.4 mmol) (dissolved in THF (20 ml)) was added dropwise and the reaction mixture was warmed to room temperature for an additional hour. Then the reaction mixture was quenched with sat. NH_4Cl aq. (20 mL) and extracted with EtOAc (20 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica-gel column chromatography to give the 1,3-dienes **1**.



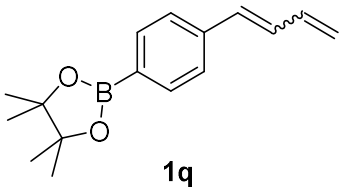
1e

(*E,Z*)-2-(buta-1,3-dien-1-yl)-1,3,5-trimethylbenzene (1e). The general procedure was followed using 2,4,6-trimethylbenzaldehyde (799 mg, 5.4 mmol), afforded product **1e** (698 mg, 75% yield) as mixture of isomers (*E:Z* = 1:1). colorless oil. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 6.89 (s, 2H), 6.62-6.51 (m, 1H), 6.39-6.26 (m, 1.52H), 6.17-6.10 (m, 0.49H), 5.31-5.24 (m, 1H), 5.16 (d, *J* = 10.4 Hz, 0.53H), 5.09 (d, *J* = 10.4 Hz, 0.50H), 2.32-2.29 (m, 6H), 2.19 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 137.7, 136.3, 136.0, 134.7, 133.9, 133.5, 133.3, 131.6, 131.0, 129.8, 128.7, 127.9, 118.0, 116.6, 21.0, 20.96, 20.92, 20.4 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{17}$ $(M + H)^+$: 173.1330, found 173.1336.



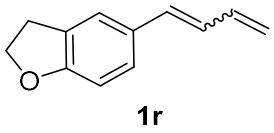
1j

(*E,Z*)-1-(buta-1,3-dien-1-yl)-4-phenoxybenzene (1j). The general procedure was followed using 4-phenoxybenzaldehyde (1.07 g, 5.4 mmol), afforded product **1j** (960 mg, 80% yield) as mixture of isomers (*E:Z* = 1:2.8). colorless oil. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.41-7.31 (m, 4H), 7.16-7.12 (m, 0.87H), 7.08-6.88 (m, 5.29H), 6.77-6.71 (m, 0.26H), 6.58-6.43 (m, 1H), 6.26 (t, *J* = 11.4 Hz, 0.7H), 5.43-5.32 (m, 1H), 5.26 (d, *J* = 10.0 Hz, 0.71H), 5.18 (d, *J* = 10.0 Hz, 0.25H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 157.0, 156.3, 137.2, 133.1, 132.4, 132.3, 132.0, 130.4, 130.2, 129.8, 129.6, 128.8, 128.1, 127.8, 123.4, 119.5, 119.0, 118.9, 118.7, 118.5, 117.2 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{16}H_{15}O$ $(M + H)^+$: 223.1123, found 223.1131.



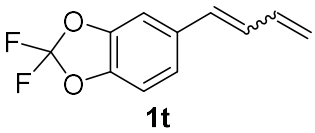
1q

(*E,Z*)-2-(4-(buta-1,3-dien-1-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1q). The general procedure was followed using 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) -benzaldehyde (1.25 g, 5.4 mmol), afforded product **1q** (954 mg, 69% yield) as mixture of isomers (*E:Z* = 1:2). light yellow oil. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.80-7.75 (m, 2H), 7.41 (d, *J* = 8.0 Hz, 0.65H), 7.33 (d, *J* = 8.0 Hz, 1.36H), 6.95-6.83 (m, 1H), 6.59-6.46 (m, 1.32H), 6.29 (t, *J* = 11.4 Hz, 0.67H), 5.42-5.34 (m, 1H), 5.24 (d, *J* = 10.4 Hz, 0.66H), 5.20 (d, *J* = 10.4 Hz, 0.33H), 1.35 (s, 12H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 140.1, 139.8, 137.1, 135.0, 134.6, 133.1, 132.8, 131.4, 130.5, 130.3, 128.3, 125.7, 120.0, 118.2, 83.76, 83.74, 24.8; ^{11}B NMR ($CDCl_3$, 128 MHz) δ: 31.03 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{16}H_{22}BO_2$ $(M + H)^+$: 257.1716, found 257.1720.



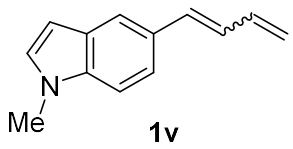
1r

(*E,Z*)-5-(buta-1,3-dien-1-yl)-2,3-dihydrobenzofuran (1r). The general procedure was followed using 2,3-dihydrobenzofuran-5-carbaldehyde (799 mg, 5.4 mmol), afforded product **1r** (707 mg, 76% yield) as mixture of isomers (*E:Z* = 1:1.8). colorless oil. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.30 (s, 0.35H), 7.19 (s, 0.61H), 7.17-7.08 (m, 1H), 6.95-6.85 (m, 0.67H)，6.78-6.62 (m, 1.41H), 6.53-6.38 (m, 1.36H), 6.17 (t, *J* = 11.2 Hz, 0.60H), 5.37-5.33 (m, 0.65H), 5.29-5.25 (m, 0.37H), 5.22-5.09 (m, 1H), 4.61-4.56 (m, 2H), 3.24-3.18 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 160.0, 159.3, 137.4, 133.4, 132.8, 130.4, 130.0, 129.2, 128.9, 127.04, 127.01, 125.5, 122.6, 118.7, 116.1, 109.3, 109.0, 71.42, 71.36, 29.6, 29.5 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_{13}O$ $(M + H)^+$: 173.0966, found 173.0977.



1t

(*E,Z*)-5-(buta-1,3-dien-1-yl)-2,2-difluorobenzo[*d*][1,3]dioxole (1t). The general procedure was followed using 2,2-difluorobenzo[*d*][1,3]dioxole-5-carbaldehyde (1.00 g, 5.4 mmol), afforded product **1t** (703 mg, 62% yield) as mixture of isomers (*E:Z* = 1:1.2). colorless oil. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.14 (d, *J* = 1.6 Hz, 0.44H), 7.07-6.98 (m, 2.52H), 6.84-6.66 (m, 1H), 6.53-6.37 (m, 1.47H), 6.27 (t, *J* = 11.2 Hz, 0.53H), 5.44-5.34 (m, 1H), 5.28 (d, *J* = 10.0 Hz, 0.53H), 5.22 (d, *J* = 10.0 Hz, 0.45H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 144.3, 143.8, 143.1, 142.6, 136.6, 133.8, 133.5, 132.4, 131.3, 130.0, 128.8, 124.5, 122.5, 120.6, 118.4, 109.9, 109.4, 109.1, 106.5 ppm; ^{19}F NMR ($CDCl_3$, 376 MHz) δ: -50.10, -50.21; **HRMS** (ESI-TOF) *m/z* calcd for $C_{11}H_9F_2O_2$ $(M + H)^+$: 211.0571, found 211.0573.

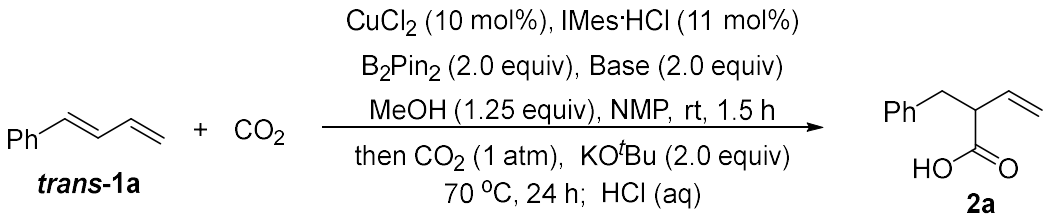


1v

(*E,Z*)-5-(buta-1,3-dien-1-yl)-1-methyl-1H-indole (1v). The general procedure was followed using 1-methyl-1H-indole-5-carbaldehyde (859mg, 5.4 mmol), afforded product **1v** (712 mg, 72% yield) as mixture of isomers (*E:Z* = 1:1.6). light yellow solid. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.62-7.60 (m, 1H), 7.37-7.20 (m, 2H), 7.05-6.96 (m, 1.59H)，6.81-6.45 (m, 2.72H)，6.25-6.19 (m, 0.59H)，5.37-5.26 (m, 1H), 5.18 (d, *J* = 10.0 Hz, 0.61H), 5.09 (d, *J* = 10.0 Hz, 0.37H)，3.78 (s, 1.81H)，3.76 (s, 1.11H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 137.7, 135.9, 134.4, 133.9, 131.8, 129.4, 129.3, 128.73, 128.69, 128.4, 126.9, 123.2, 121.4, 120.1, 119.6, 118.3, 115.6, 109.4, 108.9, 101.3, 101.2, 32.9 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{14}N$ $(M + H)^+$: 184.1126, found 184.1135.

3. The effect of different reaction conditions

Table S1. The effect of different bases[a,b]

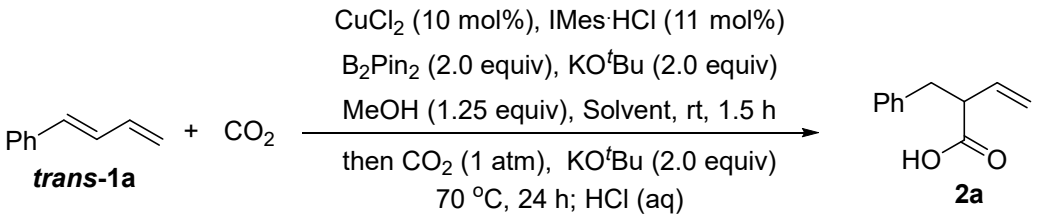


***trans*-1a** **2a**

entry	base	yield (%)[b]
1	LiO^tBu	4
2	NaO^tBu	8
3	KO^tBu	50
4	KF	15
5	K_2CO_3	10
6	Na_2CO_3	7
7	K_3PO_4	15
8	KOMe	12

[a] ***trans*-1a** (0.2 mmol), B_2pin_2 (0.4 mmol), Base (0.4 mmol), $CuCl_2$ (10 mol%), PPh_3 (11 mol%), MeOH (1.25 equiv), NMP (1.5 ml), after 1.5 h; then CO_2 (1 atm), KO^tBu (0.4 mmol) 70 °C, 24 h; then HCl (aq) was added, r.t. [b] Yields were determined by GC using 2-Methoxynaphthalene as an internal standard.

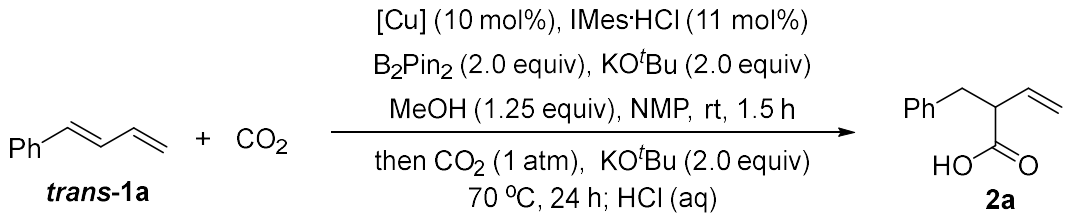
Table S2. The effect of different solvents [a,b]



entry	solvent	yield (%)[b]
1	NMP	50
2	DMA	43
3	DMF	41
4	DCE	0
5	Cyclohexne	8
6	THF	7
7	EA	6
8	toluene	9
9	DME	9
10	1,4-dioxane	11

[a] ***trans*-1a** (0.2 mmol), B_2pin_2 (0.4 mmol), KO^{t}Bu (0.4 mmol), $CuCl_2$ (10 mol%), PPh_3 (11 mol%), MeOH (1.25 equiv), Solvent (1.5 ml), after 1.5 h; then CO_2 (1 atm), KO^{t}Bu (0.4 mmol) 70 °C, 24 h; then HCl (aq) was added, r.t. [b] Yields were determined by GC using 2-Methoxynaphthalene as an internal standard.

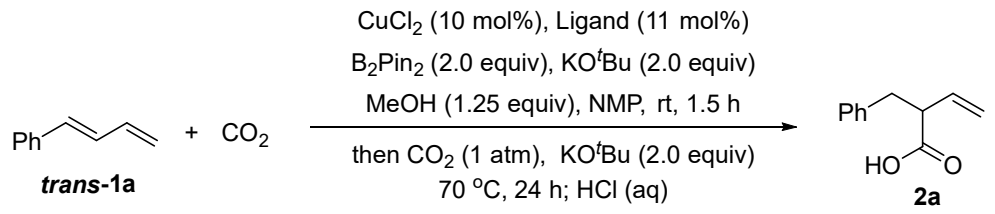
Table S3. The effect of different [Cu][a,b]

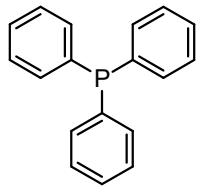


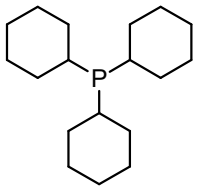
entry	[Cu]	yield (%)[b]
1	$CuCl_2$	50
2	CuCl	46
3	CuF_2	4
4	$CuBr_2$	29
5	CuI	13
6	$Cu(OTf)_2$	24
7	$Cu(OAc)_2$	15
8	$Cu(acac)_2$	17
9	CuTc	27

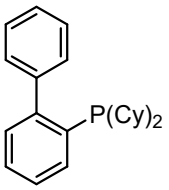
[a] ***trans*-1a** (0.2 mmol), B_2pin_2 (0.4 mmol),KO^tBu (0.4 mmol), cat (10 mol%), PPh_3 (11 mol%), MeOH (1.25 equiv), NMP (1.5 ml), after 1.5 h; then CO_2 (1 atm), KO^tBu (0.4 mmol) 70 °C, 24 h; then HCl (aq) was added, r.t. [b] Yields were determined by GC using 2-Methoxynaphthalene as an internal standard.

Table S4. The effect of different ligands [a,b]

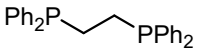


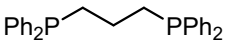

68% (63%)


24%



23%


14%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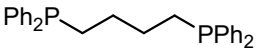
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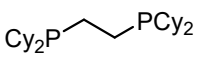
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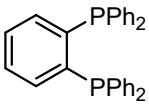
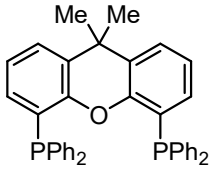

19%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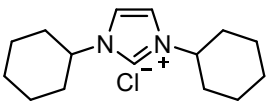
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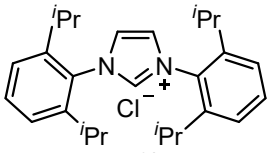
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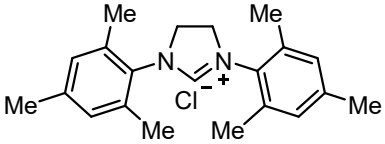
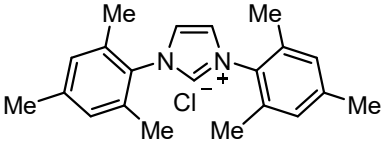

27%

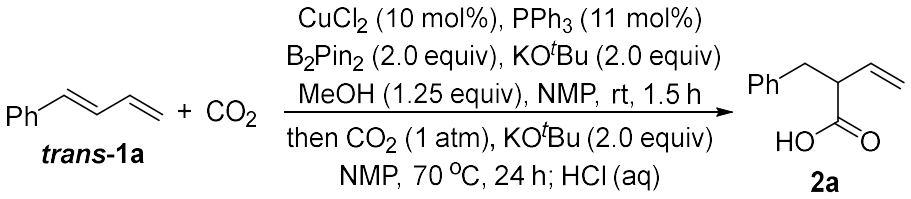

50%

[a] ***trans*-1a** (0.2 mmol), B_2pin_2 (0.4 mmol),KO^{t}-Bu (0.4 mmol), $CuCl_2$ (10 mol%), Ligand (11 mol%), MeOH (1.25 equiv), NMP (1.5 ml), after 1.5 h; then CO_2 (1 atm), KO^{t}Bu (0.4 mmol) 70 ^{o}C, 24 h; then HCl (aq) was added, r.t. [b] Yields were determined by GC using 2-Methoxynaphthalene as an internal standard.

4. General procedure for the reaction

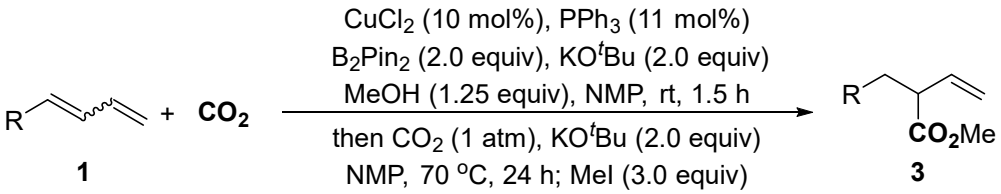
General procedure for Cu-catalyzed Highly Regioselective 1,2-Hydrocarboxylation of 1,3-Dienes with CO_2:

General procedure A



In an oven dried 25-ml Schlenk tube, which containing a stirring bar, was charged with $CuCl_2$ (2.7 mg, 0.02 mmol, 10 mol%), PPh_3 (5.8 mg, 0.022 mmol, 11 mol%), B_2Pin_2 (102 mg, 0.40 mmol, 2.0 equiv) and KO^{t}Bu (45 mg, 0.4 mmol, 2.0 equiv). The tube was then evacuated and back-filled under a N_2 flow (this sequence was repeated three times). Diene **1** (0.20 mmol, 1.0 equiv), MeOH (8 mg, 0.25 mmol), anhydrous NMP (1.5 ml) were added subsequently under N_2. The reaction mixture was stirred for 1.5 h at rt, then KO^{t}Bu (45 mg, 0.4 mmol, 2.0 equiv) (dissolved in anhydrous NMP (0.5 ml)) were added, the tube was evacuated and back-filled with CO_2 (this sequence was repeated three times). the tube was stirred at 70 ^{o}C for 24 h. After cooling to room temperature, the resulting mixture was diluted with 2 mL EtOAc and quenched by 2 mL 2N HCl. Then it was extracted with EtOAc (10 ml × 3). The organic layer was combined and dried over Na_2SO_4, filtered and concentrated by rotary evaporation. The residue was purified by silica gel column chromatography to afford the product **2a.**

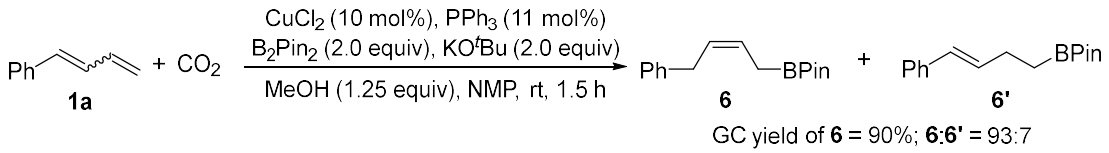
General procedure B:



In an oven dried 25-ml Schlenk tube, which containing a stirring bar, was charged with $CuCl_2$ (2.7 mg, 0.02 mmol, 10 mol%), PPh_3 (5.8 mg, 0.022 mmol, 11 mol%), B_2Pin_2 (102 mg, 0.40 mmol, 2.0 equiv) and KO^{t}Bu (45 mg, 0.4 mmol, 2.0 equiv). The tube was then evacuated and back-filled under a N_2 flow (this sequence was repeated three times). Diene **1** (0.20 mmol, 1.0 equiv), MeOH (8 mg, 0.25 mmol), anhydrous NMP (1.5 ml) were added subsequently under N_2. The reaction mixture was stirred for 1.5 h at rt, then KO^{t}Bu (45 mg, 0.4 mmol, 2.0 equiv) (dissolved in anhydrous NMP (0.5 ml)) was added, the tube was evacuated and back-filled with CO_2 (this sequence was repeated three times). The reaction was stirred at 70 ^{o}C for 24 h. After cooling to room temperature, MeI (85 mg, 3.0 equiv) was added via syringe and the reaction tube was sealed. The resulting mixture was further stirred for 3 h at 60 °C. After cooling to room temperature, the resulting mixture was diluted with 2 mL EtOAc and quenched by 2 mL H_2O. Then it was extracted with EtOAc (10 mL × 3). The organic layer was combined and dried over Na_2SO_4, filtered and concentrated by rotary evaporation. The residue was purified by silica gel column chromatography to afford the product **3.**

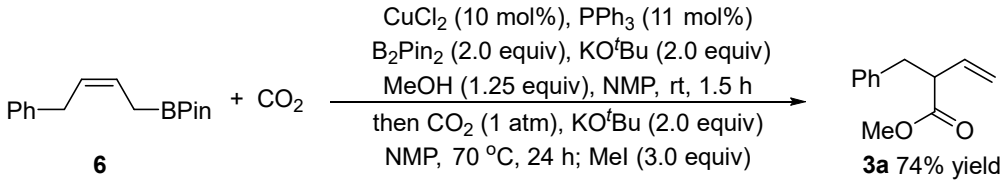
5. Control experiments

5-1. The reaction without **CO_2**



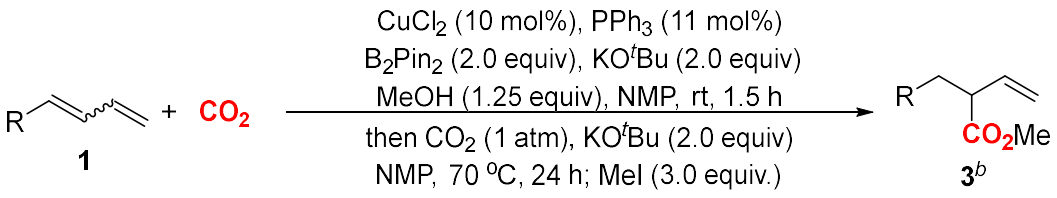
In an oven dried 25-ml Schlenk tube, which containing a stirring bar, was charged with $CuCl_2$ (2.7 mg, 0.02 mmol, 10 mol%), PPh_3 (5.8 mg, 0.022 mmol, 11 mol%), B_2Pin_2 (102 mg, 0.40 mmol, 2.0 equiv) and KO^{t}Bu (45 mg, 0.4 mmol, 2.0 equiv). The tube was then evacuated and back-filled under a N_2 flow (this sequence was repeated three times). Diene **1a** (0.20 mmol, 1.0 equiv), MeOH (8 mg, 0.25 mmol), anhydrous NMP (1.5 ml) were added subsequently under N_2. The reaction mixture was stirred for 1.5 h at r.t., the resulting mixture was diluted with 10 mL EtOAc and quenched by 10 mL H_2O, and then it was extracted with EtOAc (10 ml × 3). The organic layer was combined and dried over Na_2SO_4, filtered and concentrated by rotary evaporation. The residue was purified by silica gel column chromatography to afford the product **8** with 90% of GC yield (isolated 27mg, isolated yield was 52%). Spectral data matches that of the literature.[12] ^{1}H NMR ($CDCl_3$, 400 MHz) d: 7.28-7.14 (m, 5H), 5.68-5.54 (m, 2H), 3.39 (d, J = 6.8 Hz, 2H), 1.79 (d, J = 7.6 Hz, 2H), 1.24 (s, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz) d: 141.2, 128.4, 128.2, 128.0, 125.6, 125.2, 83.2, 33.2, 24.7 ppm; ^{11}B NMR ($CDCl_3$, 128 MHz) δ 33.00; HRMS (ESI-TOF) m/zcalcd for $C_{16}H_{23}BO_2Na$ (M + Na)+: 281.1689, found 281.1693.

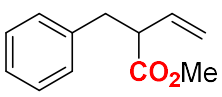
5-2. The reaction of **6** with **CO_2**



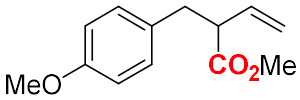
In an oven dried 25-ml Schlenk tube, which containing a stirring bar, was charged with $CuCl_2$ (2.7 mg, 0.02 mmol, 10 mol%), PPh_3 (5.8 mg, 0.022 mmol, 11 mol%), B_2Pin_2 (102 mg, 0.40 mmol, 2.0 equiv) and KO^{t}Bu (45 mg, 0.4 mmol, 2.0 equiv). The tube was then evacuated and back-filled under a N_2 flow (this sequence was repeated three times). **6** (52 mg, 0.20 mmol, 1.0 equiv), MeOH (10.0 μL, 1.25 equiv), anhydrous NMP (1.5 ml) were added subsequently under N_2. The reaction mixture was stirred for 1.5 h at rt, then KO^{t}Bu (45 mg, 0.4 mmol, 2.0 equiv) (dissolved in anhydrous NMP (0.5 ml)) were added, the tube was evacuated and back-filled with CO_2 (this sequence was repeated three times). The tube was stirred at 70 °C for 24 h. After cooling to room temperature, MeI (85 mg, 3.0 equiv) was added via syringe and the reaction tube was sealed. The resulting mixture was further stirred for 3 h at 60 °C. After cooling to room temperature, the resulting mixture was diluted with 2 mL EtOAc and quenched by 2 mL H_2O. Then it was extracted with EtOAc (10 mL × 3). The organic layer was combined and dried over Na_2SO_4, filtered and concentrated by rotary evaporation. The residue was purified by silica gel column chromatography to afford the product **3a** (28 mg, 74%).

5-3: The effect of the substrate configuration (trans-and cis) on the reaction

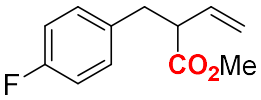




3a
trans-1a: 63%
1a: 59%



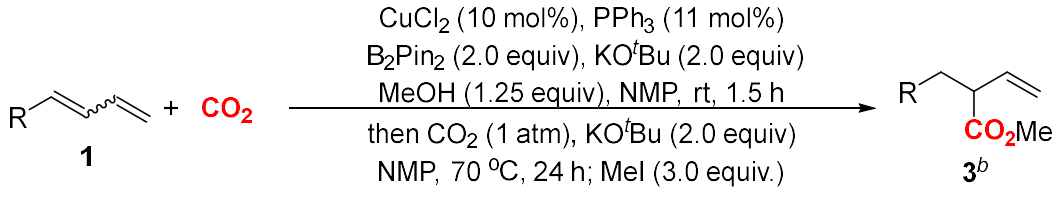
3i
trans-1i: 64%
1n: 59%

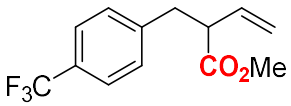


3n
trans-1n: 54%
1n: 51%

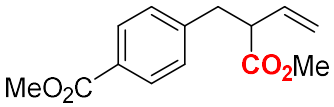
[a] **1** (0.2 mmol), B_2Pin_2 (0.4 mmol), KO^{t}Bu (0.4 mmol), [Cat] (10 mol%), PPh_3 (11 mol%), MeOH (0.25 mmol), NMP (1.5 ml), after 1.5 h; CO2 (1 atm), KO^{t}Bu (0.4 mmol) 70 °C, 24 h, then MeI (0.6 mmol) was added, r.t., 3 h. [b] Isolated yield.

5-4: Some failed examples.

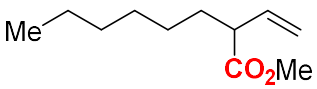




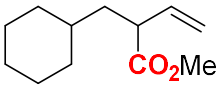
3x: 46%[c]



3y: yield < 10%



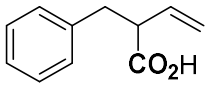
3z; yield < 10%



3aa; yield < 10%

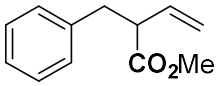
[a] **1** (0.2 mmol), B_2Pin_2 (0.4 mmol), KO^{t}Bu (0.4 mmol), [Cat] (10 mol%), PPh_3 (11 mol%), MeOH (0.25 mmol), NMP (1.5 ml), after 1.5 h; CO2 (1 atm), KO^{t}Bu (0.4 mmol) 70 °C, 24 h, then MeI (0.6 mmol) was added, r.t., 3 h. [b] NMR yield. [c] this product can not be separated with an unknown byproduct by silica gel column .

6. Analytical data for compounds



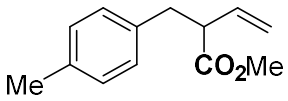
2a

2-benzylbut-3-enoic acid (**2a**): The general procedure A was followed using (*E*)-buta-1,3-dien-1-ylbenzene (**trans-1a**, 26 mg, 0.20 mmol). Purification of this material by chromatography on silica gel (EtOAc: petroleum ether = 1:1) afforded product **2a** as a colorless oil (22 mg, 63% yield): R_f = 0.4 (EtOAc: petroleum ether = 1:1); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 11.28 (brs, 1H), 7.29-7.26 (m, 2H), 7.22-7.16 (m, 3H), 5.89-5.81 (m, 1H), 5.16-5.09 (m, 2H), 3.37-3.32 (m, 1H), 3.15-3.09 (m, 1H), 2.88-2.83(m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 179.6, 138.2, 134.6, 129.0, 128.4, 126.5, 118.4, 51.7, 38.0 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{11}H_{13}O_2$ $(M + H)^+$: 177.0916, found 177.0924.



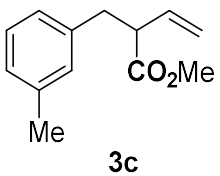
3a

methyl 2-benzylbut-3-enoate (**3a**): The general procedure B was followed using (*E,Z*)-buta-1,3-dien-1-ylbenzene (**1a**, 26 mg, 0.20 mmol, *E:Z* = 1:1.3). Purification of this material by chromatography on silica gel (EtOAc: petroleum ether = 1:20) afforded product **3a** as a colorless oil (22 mg, 59% yield): R_f = 0.6 ((EtOAc: petroleum ether = 1:10); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.29-7.25 (m, 2H), 7.22-7.15 (m, 3H), 5.90-5.81 (m, 1H), 5.13-5.06 (m, 2H), 3.64 (s, 3H), 3.37-3.31 (m, 1H), 3.12-3.07 (m, 1H), 2.87-2.82 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 173.8, 138.6, 135.3, 129.0, 128.3, 126.4, 117.7, 52.0, 51.8, 38.4 ppm; **HRMS** (ESI-TOF) *m/z*calcd for $C_{12}H_{15}O_2$ $(M + H)^+$: 191.1072, found 191.1073.



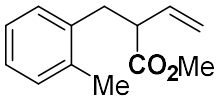
3b

methyl 2-(4-methylbenzyl)but-3-enoate (**3b**): The general procedure B was followed using (*E,Z*)-1-(buta-1,3-dien-1-yl)-4-methylbenzene (**1b**, 29 mg, 0.20 mmol, *E:Z* = 1:1.6). Purification of this material by chromatography on silica gel (EtOAc: petroleum ether = 1:20) afforded product **3b** as a colorless oil (24 mg, 59% yield): R_f = 0.6 (EtOAc: petroleum ether = 1:10); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.09-7.03 (m, 4H), 5.89-5.81 (m, 1H), 5.12-5.06 (m, 2H), 3.64 (s, 3H), 3.32-3.28 (m, 1H), 3.08-3.03 (m, 1H), 2.83-2.78 (m, 1H) 2.31 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 173.8, 135.9, 135.5, 135.4, 129.0, 128.8, 117.6, 52.0, 51.8, 38.0, 21.0 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{17}O_2$ $(M + H)^+$: 205.1228, found 205.1239.



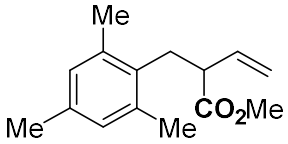
3c

methyl 2-(3-methylbenzyl)but-3-enoate (**3c**): The general procedure B was followed using (*E,Z*)-1-(buta-1,3-dien-1-yl)-3-methylbenzene (**1c**, 29 mg, 0.20 mmol, *E:Z* = 1:1.4). Purification of this material by chromatography on silica gel (EtOAc: petroleum ether = 1:20) afforded product **3c** as a colorless oil (27 mg, 65% yield): R_f = 0.6 (EtOAc: petroleum ether = 1:10); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.16 (t, 1H), 7.03-6.95 (m, 3H), 5.91-5.82 (m, 1H), 5.13-5.07 (m, 2H), 3.64 (s, 3H), 3.36-3.30 (m, 1H), 3.09-3.04 (m, 1H), 2.83-2.78 (m, 1H), 2,32 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 173.8, 138.5, 137.8, 135.4, 129.8, 128.2, 127.1, 126.0, 117.6, 51.9, 51.8, 38.3, 21.4 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{17}O_2$ $(M + H)^+$: 205.1228, found 205.1223.



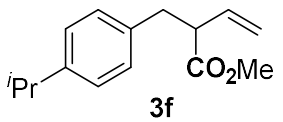
3d

methyl 2-(2-methylbenzyl)but-3-enoate (**3d**): The general procedure B was followed using (*E,Z*)-1-(buta-1,3-dien-1-yl)-2-methylbenzene (**1d**, 29 mg, 0.20 mmol, *E:Z* = 1:1.5). Purification of this material by chromatography on silica gel (EtOAc: petroleum ether = 1:20) afforded product **3d** as a colorless oil (29 mg, 70% yield): R_f = 0.6 (EtOAc: petroleum ether = 1:10); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.15-7.08 (m, 4H), 5.94-5.85 (m, 1H), 5.13-5.04 (m, 2H), 3.64 (s, 3H), 3.37-3.31 (m, 1H), 3.14-3.09 (m, 1H), 2.88-2.82 (m, 1H), 2.33 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 173.9, 136.8, 136.2, 135.4, 130.3, 129.6, 126.5, 125.8, 117.5, 51.8, 50.7, 35.6, 19.4 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{17}O_2$ $(M + H)^+$: 205.1228, found 205.1228.



3e

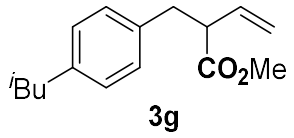
methyl 2-(2,4,6-trimethylbenzyl)but-3-enoate (**3e**): The general procedure B was followed using (*E,Z*)-2-(buta-1,3-dien-1-yl)-1,3,5-trimethylbenzene (**1e**, 34 mg, 0.20 mmol, *E:Z* = 1:1). Purification of this material by chromatography on silica gel (EtOAc: petroleum ether = 1:20) afforded product **3e** as a colorless oil (27 mg, 57% yield): R_f = 0.6 (EtOAc: petroleum ether = 1:10); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 6.81 (s, 2H), 5.97-5.88 (m, 1H), 5.04-4.91 (m, 2H), 3.66 (s, 3H), 3.28-3.22 (m, 1H), 3.11-3.06 (m, 1H), 2.91-2.86 (m, 1H), 2.27 (s, 6H), 2.23 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 174.4, 136.6, 135.6, 135.3, 132.3, 129.0, 117.2, 51.8, 50.4, 32.0, 20.8, 20.2 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{15}H_{21}O_2$ $(M + H)^+$: 233.1542, found 233.1543.



3f

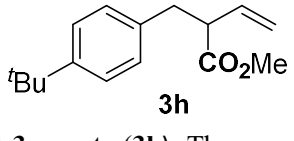
methyl 2-(4-isopropylbenzyl)but-3-enoate (**3f**): The general procedure B was followed using (*E,Z*)-1-(buta-1,3-dien-1-yl)-4-isopropylbenzene (**1f**, 34 mg, 0.20 mmol, *E:Z* = 1:1.5). Purification of this material by chromatography on silica gel (EtOAc: petroleum ether = 1:20) afforded product **3f** as a colorless oil (28 mg, 59% yield): R_f = 0.6 (EtOAc: petroleum ether = 1:10); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.14-7.07 (m, 4H), 5.90-5.81 (m, 1H), 5.13-5.07 (m, 2H), 3.64 (s, 3H),

3.37-3.30 (m, 1H), 3.09-3.04 (m, 1H), 2.90-2.79 (m, 2H), 1.23 (s, 3H), 1.22 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 173.9, 146.9, 135.9, 135.5, 128.9, 126.4, 117.5, 51.9, 51.8, 38.0, 33.7, 24.0 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{15}H_{21}O_2$ $(M + H)^+$: 233.1542, found 233.1548.



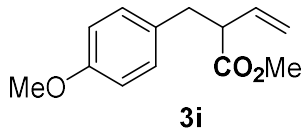
3g

methyl 2-(4-isobutylbenzyl)but-3-enoate (**3g**): The general procedure B was followed using (*E,Z*)-1-(buta-1,3-dien-1-yl)-4-isobutylbenzene (**1g**, 37 mg, 0.20 mmol, *E:Z* = 1:1.6). Purification of this material by chromatography on silica gel (EtOAc: petroleum ether = 1:20) afforded product **3f** as a colorless oil (33 mg, 68% yield): R_f = 0.6 (EtOAc: petroleum ether = 1:10); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.07-7.03 (m, 4H), 5.90-5.81 (m, 1H), 5.12-5.05 (m, 2H), 3.63 (s, 3H), 3.35-3.29 (m, 1H), 3.09-3.03 (m, 1H), 2.84-2.79 (m, 1H), 2.43 (d, *J* = 7.2 Hz, 2H), 1.89-1.80 (m, 1H), 0.89 (s, 3H), 0.87 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 173.9, 139.7, 135.8, 135.4, 129.0, 128.7, 117.5, 52.0, 51.8, 45.0, 38.1, 30.2, 22.34, 22.33 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{16}H_{21}O_2$ $(M - H)^-$: 245.1542, found 245.1557.



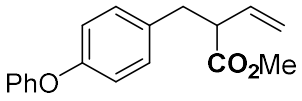
3h

methyl 2-(4-(tert-butyl)benzyl)but-3-enoate (**3h**): The general procedure B was followed using (*E,Z*)-1-(buta-1,3-dien-1-yl)-4-(tert-butyl)benzene (**1h**, 37 mg, 0.20 mmol, *E:Z* = 1:1.5). Purification of this material by chromatography on silica gel (EtOAc: petroleum ether = 1:20) afforded product **3h** as a colorless oil (35 mg, 70% yield): R_f = 0.6 (EtOAc: petroleum ether = 1:10); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ:7.30-7.27 (m, 2H), 7.10-7.08 (m, 2H), 5.91-5.82 (m, 1H), 5.13-5.08 (m, 2H), 3.64 (s, 3H), 3.37-3.31 (m, 1H), 3.09-3.04 (m, 1H), 2.84-2.79 (m, 1H), 1.30 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 173.9, 149.2, 135.5, 128.6, 125.2, 117.5, 51.82, 51.81, 37.8, 34.4, 31.3 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{16}H_{23}O_2$ $(M + H)^+$: 247.1698, found 247.1700.



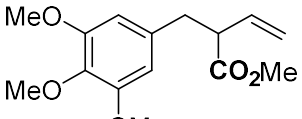
3i

methyl 2-(4-methoxybenzyl)but-3-enoate (**3i**): The general procedure B was followed using (*E,Z*)-1-(buta-1,3-dien-1-yl)-4-methoxybenzene (**1i**, 32 mg, 0.20 mmol, *E:Z* = 1:1.6). Purification of this material by chromatography on silica gel (EtOAc: petroleum ether = 1:20) afforded product **3i** as a colorless oil (29 mg, 59% yield): R_f = 0.5 (EtOAc: petroleum ether = 1:10); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.09-7.06 (m, 2H), 6.83-6.80 (m, 2H), 5.89-5.80 (m, 1H), 5.12-5.05 (m, 2H), 3.78 (s, 3H), 3.63 (s, 3H), 3.32-3.26 (m, 1H), 3.06-3.00 (m, 1H), 2.81-2.76 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 173.8, 158.1, 135.4, 130.6, 130.0, 117.6, 113.7, 55.2, 52.2, 51.8, 37.6 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{17}O_3$ $(M + H)^+$: 221.1178, found 221.1173.



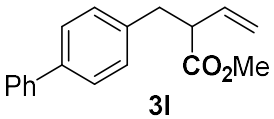
3j

methyl 2-(4-phenoxybenzyl)but-3-enoate (**3j**): The general procedure B was followed using (*E,Z*)-1-(buta-1,3-dien-1-yl)-4-phenoxybenzene (**1j**, 45 mg, 0.20 mmol, *E:Z* = 1:2.8). Purification of this material by chromatography on silica gel (EtOAc: petroleum ether = 1:20) afforded product **3j** as a colorless oil (30 mg, 53% yield): R_f = 0.4 (EtOAc: petroleum ether = 1:10); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ:7.34-7.30 (m, 2H), 7.13-7.07 (m, 3H), 6.99-6.97 (m, 2H), 6.93-6.91 (m, 2H), 5.91-5.82 (m, 1H), 5.12-5.08 (m, 2H), 3.65 (s, 3H), 3.35-3.29 (m, 1H), 3.10-3.05 (m, 1H), 2.85-2.80 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 173.7, 157.4, 155.7, 135.2, 133.5, 130.3, 129.7, 123.1, 118.8, 118.7, 117.7, 52.1, 51.9, 37.7 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{18}H_{17}O_3$ $(M - H)^-$: 281.1178, found 281.1183.



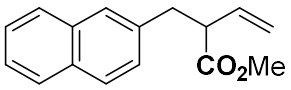
3k

methyl 2-(3,4,5-trimethoxybenzyl)but-3-enoate (**3k**): The general procedure B was followed using (*E,Z*)-5-(buta-1,3-dien-1-yl)-1,2,3-trimethoxybenzene (**1k**, 44 mg, 0.20 mmol, *E:Z* = 1:1.8). Purification of this material by chromatography on silica gel (EtOAc: petroleum ether = 1:20) afforded product **3k** as a colorless oil (36 mg, 64% yiel): R_f = 0.1 (EtOAc: petroleum ether = 1:10); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 6.37 (s, 2H), 5.90-5.81 (m, 1H), 5.15-5.09 (m, 2H), 3.83 (s, 6H), 3.81 (s, 3H) 3.65 (s, 3H), 3.35-3.29 (m, 1H), 3.06-3.01 (m, 1H), 2.80-2.75 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 173.7, 153.0, 136.5, 135.3, 134.3, 117.7, 105.8, 60.8, 56.0, 52.0, 51.9, 38.7 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{15}H_{19}O_5$ $(M - H)^-$: 279.1233, found 279.1225.



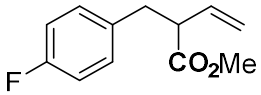
3l

methyl 2-([1,1'-biphenyl]-4-ylmethyl)but-3-enoate (**3l**): The general procedure B was followed using (*E,Z*)-4-(buta-1,3-dien-1-yl)-1,1'-biphenyl (**1l**, 41 mg, 0.20 mmol, *E:Z* = 1:2.7). Purification of this material by chromatography on silica gel (EtOAc: petroleum ether = 1:20) afforded product **3l** as a colorless oil (22 mg, 40% yield): R_f = 0.5 (EtOAc: petroleum ether = 1:10); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.60-7.58 (m, 2H), 7.53-7.51 (m, 2H), 7.45-7.41 (m, 2H), 7.35-7.32 (m, 1H), 7.25-7.23 (m, 2H), 5.94-5.85 (m, 1H), 5.17-5.11 (m, 2H), 3.66 (s, 3H), 3.42-3.36 (m, 1H), 3.18-3.12 (m, 1H), 2.92-2.87 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 173.7, 140.8, 139.3, 137.7, 135.3, 129.4, 128.7, 127.1, 127.0, 126.95, 117.8, 51.9, 38.0 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{18}H_{19}O_2$ $(M + H)^+$: 267.1385, found 267.1400.



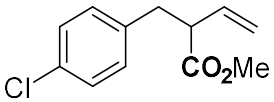
3m

methyl 2-(naphthalen-2-ylmethyl)but-3-enoate (**3m**): The general procedure B was followed using (*E,Z*)-2-(buta-1,3-dien-1-yl)naphthalene (**1m**, 36 mg, 0.20 mmol, *E:Z* = 1:1.4). Purification of this material by chromatography on silica gel (EtOAc: petroleum ether = 1:20) afforded product **3m** as a colorless oil (16 mg, 34% yield):R_f = 0.6 (EtOAc: petroleum ether = 1:10); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.81-7.75 (m, 3H), 7.61 (s, 1H), 7.47-7.40 (m, 2H), 7.31-7.29 (m, 1H), 5.95-5.86 (m, 1H), 5.13-5.08 (m, 2H), 3.63 (s, 3H), 3.47-3.41 (m, 1H), 3.29-3.24 (m, 1H), 3.03-2.98 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 173.8, 136.1, 135.3, 133.5, 132.2, 127.9, 127.59, 127.56, 127.5, 127.4, 125.9, 125.4, 117.8, 51.91, 51.88, 38.5 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{16}H_{17}O_2$ $(M + H)^+$: 241.1228, found 241.1229.



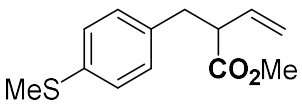
3n

methyl 2-(4-fluorobenzyl)but-3-enoate (**3n**): The general procedure B was followed using (*E,Z*)-1-(buta-1,3-dien-1-yl)-4-fluorobenzene (**1n**, 30 mg, 0.20 mmol, *E:Z* = 1:1.5). Purification of this material by chromatography on silica gel (EtOAc: petroleum ether = 1:20) afforded product **3n** as a colorless oil (21 mg, 51% yield): R_f = 0.6 (EtOAc: petroleum ether = 1:10); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.13-7.09 (m, 2H), 6.98-6.93 (m, 2H), 5.88-5.79 (m, 1H), 5.14-5.06 (m, 2H), 3.64 (s, 3H), 3.32-3.26 (m, 1H), 3.09-3.03 (m, 1H), 2.84-2.79 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 173.6, 161.6 (d, *J* = 240.0 Hz), 135.1, 134.25, 134.22, 130.5, 130.4, 117.9, 115.2, 115.0, 52.1, 51.9, 37.6 ppm; ^{19}F NMR ($CDCl_3$, 376 MHz) δ: -116.69, -116.70, -116.71, -116.72, -116.74, -116.75, -116.76; **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_{14}FO_2$ $(M + H)^+$: 209.0978, found 209.0978.



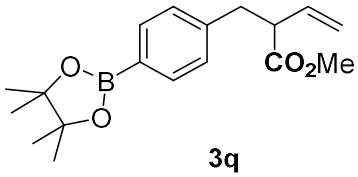
3o

methyl 2-(4-chlorobenzyl)but-3-enoate (**3o**): The general procedure B was followed using (*E,Z*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (**1o**, 33 mg, 0.20 mmol, *E:Z* = 1:1.2). Purification of this material by chromatography on silica gel (EtOAc: petroleum ether = 1:20) afforded product **3o** as a colorless oil (18 mg, 39% yield): R_f = 0.6 (EtOAc: petroleum ether = 1:10); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.25-7.23 (m, 2H), 7.10-7.08 (m, 2H), 5.87-5.79 (m, 1H), 5.14-5.06 (m, 2H), 3.64 (s, 3H), 3.32-3.26 (m, 1H), 3.09-3.03 (m, 1H), 2.84-2.78 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 173.5, 137.0, 135.0, 132.2, 130.4, 128.5, 118.0, 51.9, 51.8, 37.6 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_{14}O_2Cl$ $(M + H)^+$: 225.0682, found 225.0688.



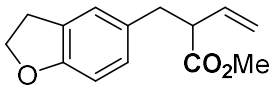
3p

methyl 2-(4-(methylthio)benzyl)but-3-enoate (**3p**): The general procedure B was followed using (*E,Z*)-(4-(buta-1,3-dien-1-yl)phenyl)(methyl)sulfane (**1p**, 35 mg, 0.20 mmol, *E:Z* = 1:1.5). Purification of this material by chromatography on silica gel (EtOAc: petroleum ether = 1:20) afforded product **3p** as a colorless oil (25 mg, 53% yield): R_f = 0.6 (EtOAc: petroleum ether = 1:10); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.18-7.16 (m, 2H), 7.09-7.07 (m, 2H), 5.88-5.80 (m, 1H), 5.13-5.06 (m, 2H), 3.64 (s, 3H), 3.33-3.27 (m, 1H), 3.08-3.02 (m, 1H), 2.83-2.77 (m, 1H), 2.46 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 173.7, 136.1, 135.5, 135.2, 129.5, 126.7, 117.8, 51.90, 51.85, 37.8, 16.0 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{17}O_2S$ $(M + H)^+$: 237.0949, found 237.0936.



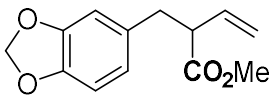
3q

methyl 2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)but-3-enoate (**3q**): The general procedure B was followed using (*E,Z*)-2-(4-(buta-1,3-dien-1-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1q**, 51 mg, 0.20 mmol, *E:Z* = 1:2). Purification of this material by chromatography on silica gel (EtOAc: petroleum ether = 1:10) afforded product **3q** as a colorless oil (26 mg, 41% yield): R_f = 0.4 (EtOAc: petroleum ether = 1:5); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.89-5.80 (m, 1H), 5.11-5.05 (m, 2H), 3.63 (s, 3H), 3.37-3.31 (m, 1H), 3.13-3.08 (m, 1H), 2.88-2.82 (m, 1H), 1.33 (s, 12H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 173.7, 141.9, 135.2, 134.8, 128.4, 127.6, 117.7, 83.7, 51.83, 51.77, 38.5, 24.85, 24.82 ppm; ^{11}B NMR ($CDCl_3$, 128 MHz) δ: 31.38; **HRMS** (ESI-TOF) *m/z* calcd for $C_{18}H_{26}BO_4$ $(M + H)^+$: 316.1960, found 316.1964.



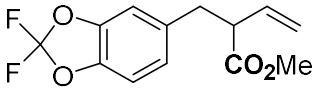
3r

methyl 2-((2,3-dihydrobenzofuran-5-yl)methyl)but-3-enoate (**3r**): The general procedure B was followed using (*E,Z*)-5-(buta-1,3-dien-1-yl)-2,3-dihydrobenzofuran (**1r**, 34 mg, 0.20 mmol, *E:Z* = 1:1.8). Purification of this material by chromatography on silica gel (EtOAc: petroleum ether = 1:10) afforded product **3r** as a colorless oil (20 mg, 44% yieldr): R_f = 0.4 (EtOAc: petroleum ether = 1:10); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 6.99 (s, *J* = 8.4 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.68 (d, 1H), 5.89-5.80 (m, 1H), 5.13-5.06 (m, 2H), 4.54 (t, *J* = 8.8 Hz, 2H), 3.64 (s, 3H), 3.31-3.25 (m, 1H), 3.17 (t, *J* = 8.8 Hz, 2H), 3.04-2.99 (m, 1H), 2.79-2.74 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 173.9, 158.7, 135.5, 130.5, 128.5, 127.0, 125.5, 117.5, 108.9, 71.1, 52.4, 51.8, 37.9, 29.7 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{14}H_{15}O_3$ $(M - H)^-$: 231.1021, found 231.1026.



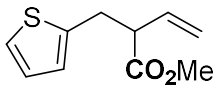
3s

methyl 2-(benzo[*d*][1,3]dioxol-5-ylmethyl)but-3-enoate (**3s**): The general procedure B was followed using (*E,Z*)-5-(buta-1,3-dien-1-yl)benzo[d][1,3]dioxole (**1s**, 35 mg, 0.20 mmol, *E:Z* = 1:1.4). Purification of this material by chromatography on silica gel (EtOAc: petroleum ether = 1:10) afforded product **3s** as a colorless oil (31 mg, 66% yield): R_f = 0.4 (EtOAc: petroleum ether = 1:10); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ:6.72-6.59 (m, 3H), 5.92 (s, 2H), 5.85-5.79 (m, 1H), 5.13-5.07 (m, 2H), 3.65 (s, 3H), 3.30-3.24 (m, 1H), 3.03-2.98 (m, 1H), 2.79-2.73 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 173.7, 147.5, 146.0, 135.2, 132.3, 122.0, 117.7, 109.4, 108.1, 100.8, 52.2, 51.8, 38.2 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{13}O_4$ $(M - H)^-$: 233.0814, found 233.0807.



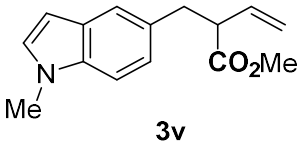
3t

methyl 2-((2,2-difluorobenzo[*d*][1,3]dioxol-5-yl)methyl)but-3-enoate (**3t**): The general procedure B was followed using (*E,Z*)-5-(buta-1,3-dien-1-yl)-2,2-difluorobenzo[*d*][1,3]dioxole (**1t**, 42 mg, 0.20 mmol, *E:Z* = 1:1.2). Purification of this material by chromatography on silica gel (EtOAc: petroleum ether = 1:10) afforded product **3t** as a colorless oil (27 mg, 50% yield): R_f = 0.4 (EtOAc: petroleum ether = 1:10); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 6.96-6.84 (m, 3H), 5.87-5.78 (m, 1H), 5.16-5.08 (m, 2H), 3.65 (s, 3H), 3.31-3.26 (m, 1H), 3.11-3.05 (m, 1H), 2.85-2.80 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 173.3, 143.7, 142.4, 134.8, 134.7, 131.6, 124.0, 118.2, 110.2, 109.1, 52.03, 51.98, 38.0 ppm; ^{19}F NMR ($CDCl_3$, 376 MHz) δ: -49.97; **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{11}F_2O_4$ $(M - H)^-$: 269.0625, found 269.0644.



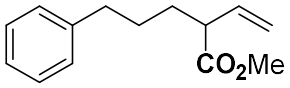
3u

methyl 2-(thiophen-2-ylmethyl)but-3-enoate (**3u**): The general procedure B was followed using (*E,Z*)-2-(buta-1,3-dien-1-yl)thiophene (**1u**, 27 mg, 0.20 mmol, *E:Z* = 1:1). Purification of this material by chromatography on silica gel (EtOAc: petroleum ether = 1:20) afforded product **3u** as a colorless oil (21 mg, 52% yield): R_f = 0.6 (EtOAc: petroleum ether = 1:10); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.14-7.12 (m, 1H), 6.92-6.89 (m, 1H), 6.81-6.80 (m, 1H), 5.88-5.81 (m, 1H), 5.19-5.15 (m, 2H), 3.68 (s, 3H), 3.39-3.29 (m, 2H), 3.12-3.05 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 173.4, 140.9, 134.8, 126.7, 125.7, 123.9, 118.2, 52.1, 52.0, 32.3 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{10}H_{11}O_2S$ $(M - H)^-$: 195.0480, found 195.0486.



3v

methyl 2-((1-methyl-1H-indol-5-yl)methyl)but-3-enoate (**3v**): The general procedure B was followed using (*E,Z*)-5-(buta-1,3-dien-1-yl)-1-methyl-1H-indole (**1v**, 37 mg, 0.20 mmol, *E:Z* = 1:1.6). Purification of this material by chromatography on silica gel (EtOAc: petroleum ether = 1:10) afforded product **3v** as a colorless oil (24 mg, 48% yield): R_f = 0.3 (EtOAc: petroleum ether = 1:10); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ:7.41 (d, *J* = 0.8 Hz,1H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.04-7.01 (m, 2H), 6.42-6.41 (m, 1H), 5.92-5.85 (m, 1H), 5.11-5.06 (m, 2H), 3.77 (s, 3H), 3.63 (s, 3H), 3.42-3.36 (m, 1H), 3.23-3.17 (m, 1H), 2.97-2.92 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 174.1, 135.7, 135.6, 129.3, 128.9, 128.5, 122.8, 120.9, 117.3, 109.0, 100.6, 52.8, 51.8, 38.7, 32.8 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{15}H_{16}NO_2$ $(M - H)^-$: 242.1181, found 242.1184.

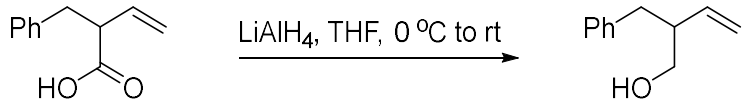


3w

methyl 5-phenyl-2-vinylpentanoate (**3w**): The general procedure B was followed using (*E,Z*)-hexa-3,5-dien-1-ylbenzene (**1w**, 32 mg, 0.20 mmol, *E:Z* = 1.2:1). Purification of this material by chromatography on silica gel (EtOAc: petroleum ether = 1:20) afforded product **3w** as a colorless oil (9 mg, 20% yield): R_f = 0.6 (EtOAc: petroleum ether = 1:10); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ: 7.29-7.26 (m, 2H), 7.20-7.15 (m, 3H), 5.84-5.75 (m, 1H), 5.15-5.10 (m, 2H), 3.68 (s, 3H), 3.06-3.00 (m, 1H), 2,63-2.60 (m, 2H), 1.86-1.73 (m, 1H), 1.67-1.56 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 174.4, 142.0, 135.9, 128.4, 128.3, 125.8, 117.3, 51.8, 50.1, 35.6, 31.7, 28.9 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{14}H_{17}O_2$ $(M - H)^-$: 217.1228, found 217.1229.

7. Further transformations for the product

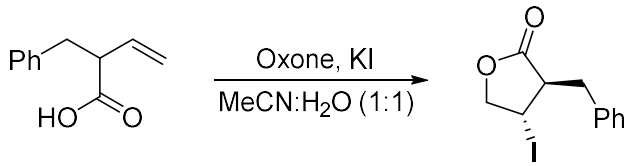
7-1 Procedure for synthesis of **4**[10]



2a **4**, 88% yield

In an oven dried 10 mL Schlenk tube, to a suspension of $LiAlH_4$ (46mg, 1.2 mmol, 3 equiv) in 2.0 mL dry THF was added dropwise to a solution of **2a** (0.40mmol, 70 mg, 1.0 equiv) in dry THF (2.0 mL) at 0 °C, The reaction mixture was stirred at room temperature under N_2 for 12 h, H_2O (2.0 mL) was added, followed by 1 N NaOH (1.0 mL) The resulting mixture was filtered through celite and washed with EtOAc. The filtrate was extracted with EtOAc (3 × 10 ml). The organic layer was separated and dried with Na_2SO_4, and solvent was removed under reduced pressure. The product was purified by silica gel column chromatography (EtOAc: petroleum ether = 1:4) to afford the product**4** as a colourless liquid (57 mg, 88% yield): R_f = 0.3 (EtOAc: petroleum ether = 1:4); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.28-7.24 (m, 2H), 7.19-7.14 (m, 3H), 5.73-5.64 (m, 1H), 5.12-5.03 (m, 2H), 3.59-3.55 (m, 1H), 3.48-3.43 (m, 1H), 2.76-2.71 (m, 1H), 2.66-2.60 (m, 1H), 2.57-2.50 (m, 1H), 1.84 (brs, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 139.6, 139.1, 129.0, 128.2, 125.9, 117.1, 64.7, 47.9, 37.2 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{11}H_{15}O$ $(M + H)^+$: 163.1123, found 163.1119.

7-2 Procedure for synthesis of **5**[11]



2a **5**, 71% yield

In an 10 mL round-bottomed flask, to the acid **2a** (0.32mmol, 56 mg, 1.0 equiv) in CH_3CN:H_2O = 1:1 (4.0 mL) was added Oxone (196 mg, 0.64 mmol) and KI (106.4 mg, 0.64 mmol). The mixture was then stirred at room temperature for 2 h. H_2O (2.0 mL) was added, followed by $Na_2S_2O_3$ (2.0 mL), The mixture was extracted with EtOAc (3 × 10 ml). The organic layer was separated and dried with Na_2SO_4, and solvent was removed under reduced pressure. The product was purified by silica gel column chromatography (EtOAc: petroleum ether = 1:8) to afford the product **6** a yellow solid (68 mg, 71% yield): R_f = 0.6 (EtOAc: petroleum ether = 1:4); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.36-7.32 (m, 2H), 7.29-7.22 (m, 3H), 4.36-4.35 (m, 1H), 3.65-3.64 (m, 1H), 3.45-3.41 (m, 1H),3.26 (t, *J* = 9.6 Hz, 1H), 3.19-3.09 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ: 168.7, 136.2, 129.0, 128.9, 127.3, 74.1, 59.0, 33.3, 3.5 ppm; **HRMS** (ESI-TOF) *m/z* calcd for $C_{11}H_{12}IO_2$ $(M + H)^+$: 302.9882, found 302.9893.

8. References

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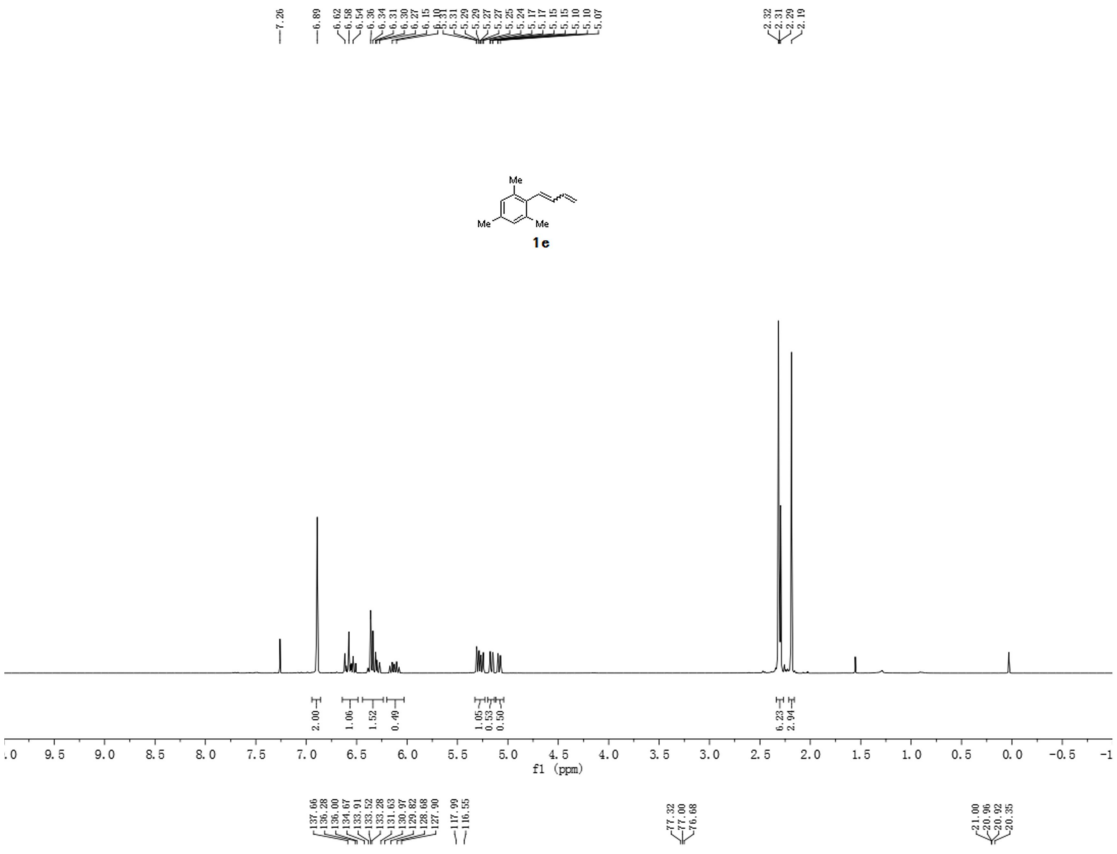
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5.10
5.07
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2.31
2.29
2.19
Me
Me
Me
1e
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1.05
0.53
0.50
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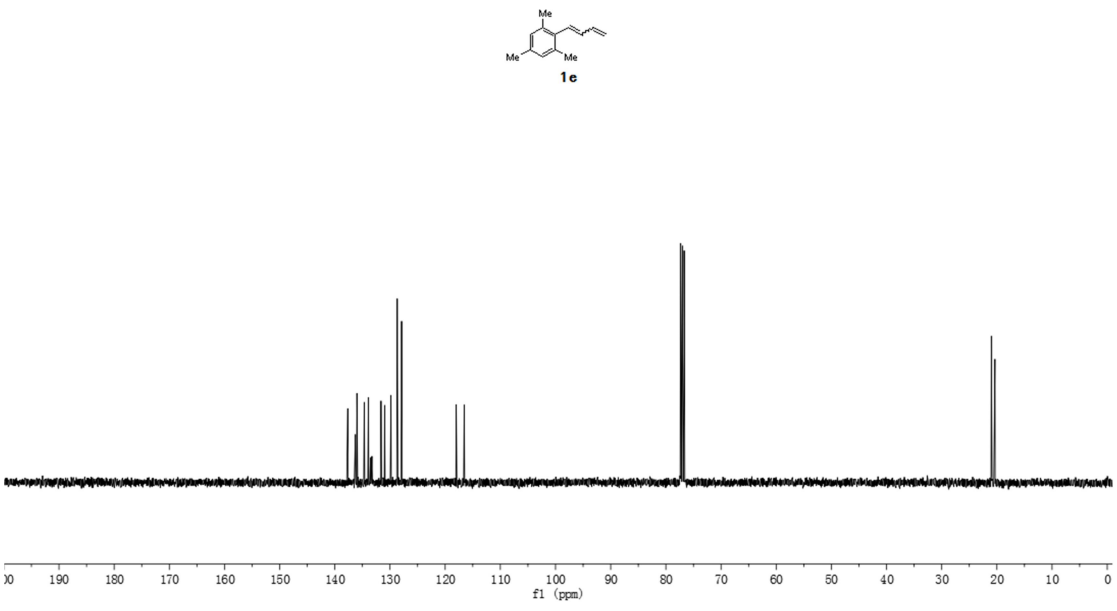
2.94
f1 (ppm)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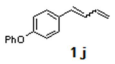
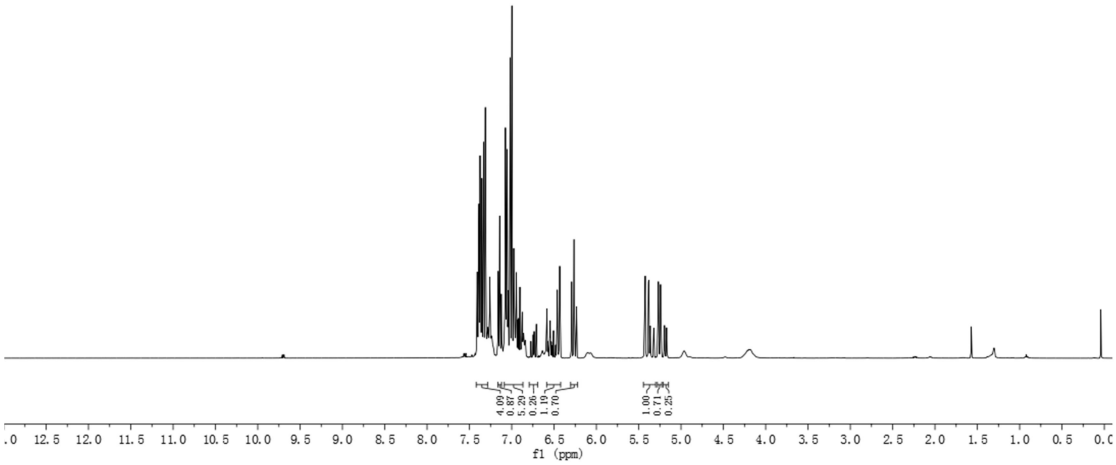
20.92
20.35
Me
Me
Me
1e
f1 (ppm)


PhO

1 j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1.00
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0.25
f1 (ppm)


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133.08
130.41
130.17
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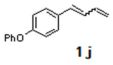
PhO

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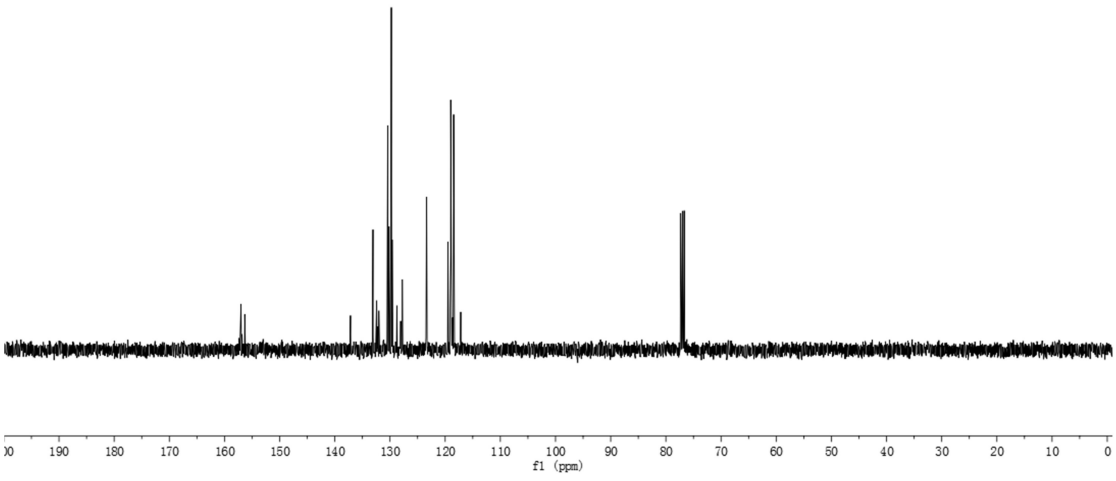
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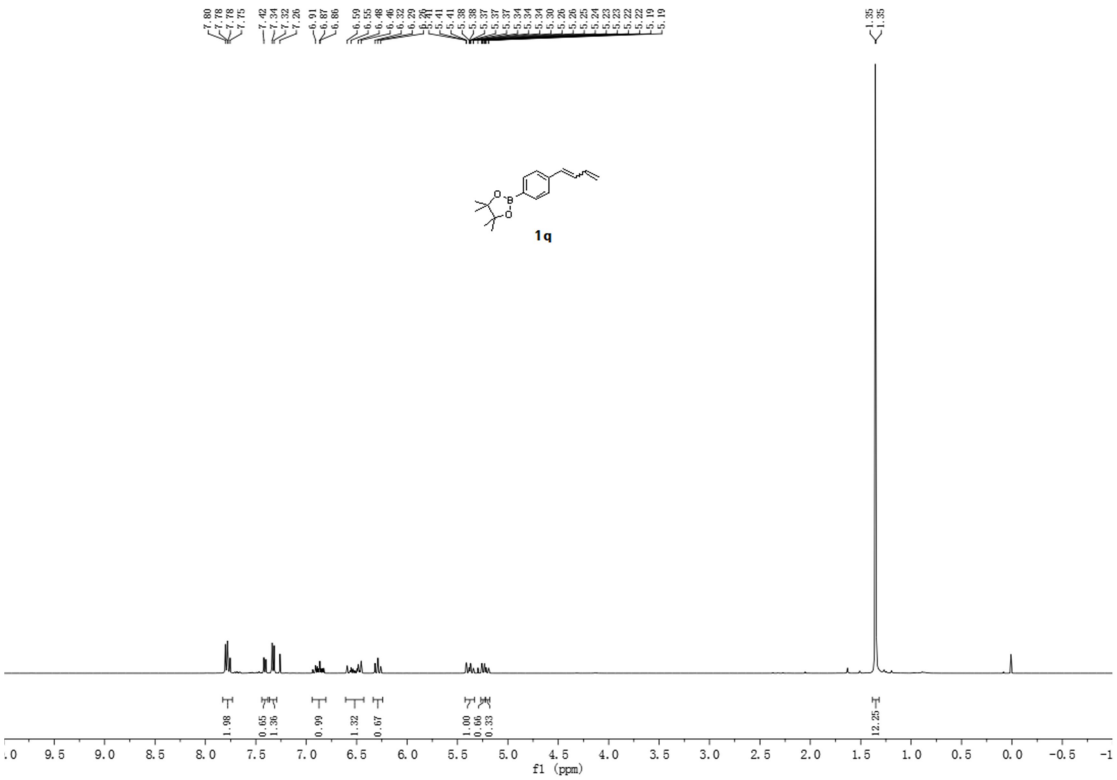
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5.22
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5.19
1.35
1.35
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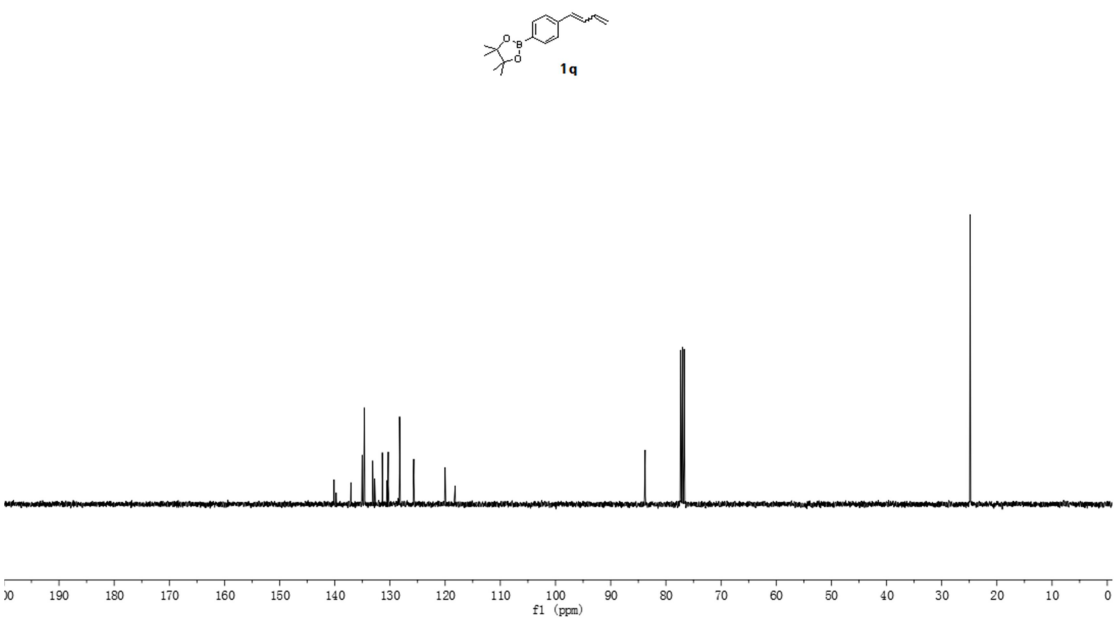
f1 (ppm)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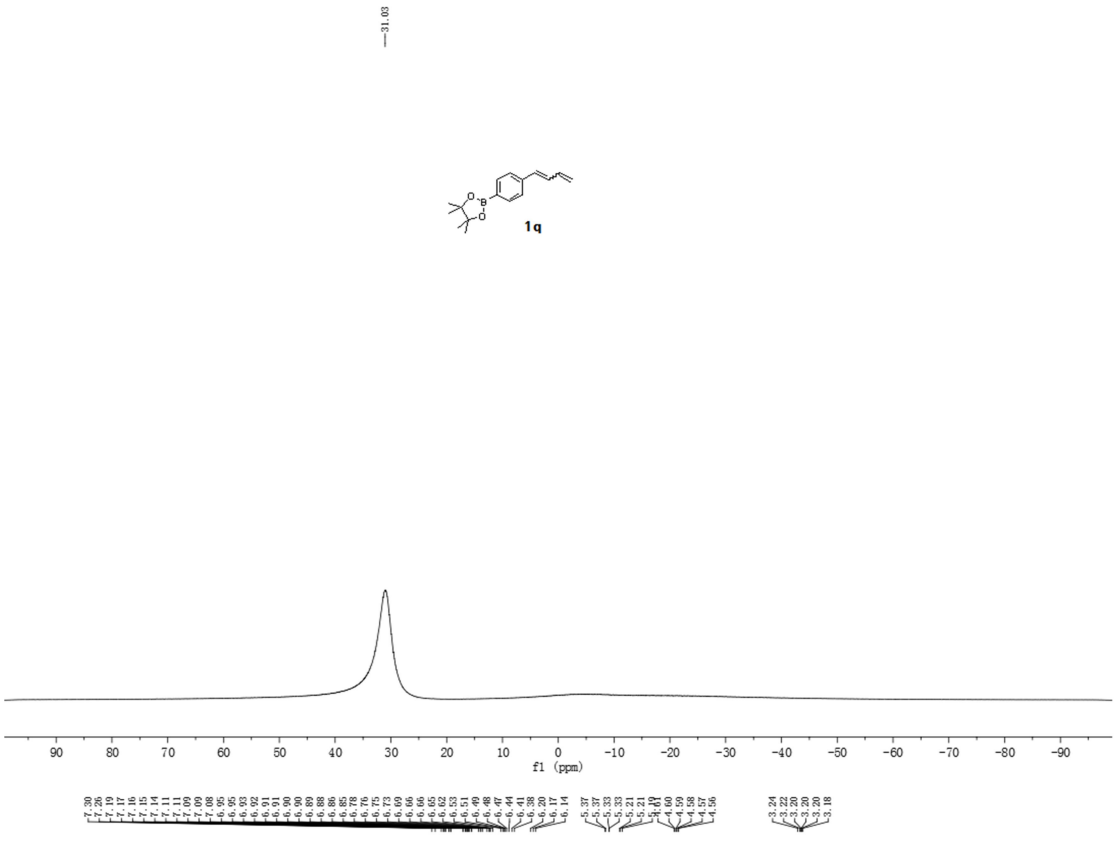
1q
f1 (ppm)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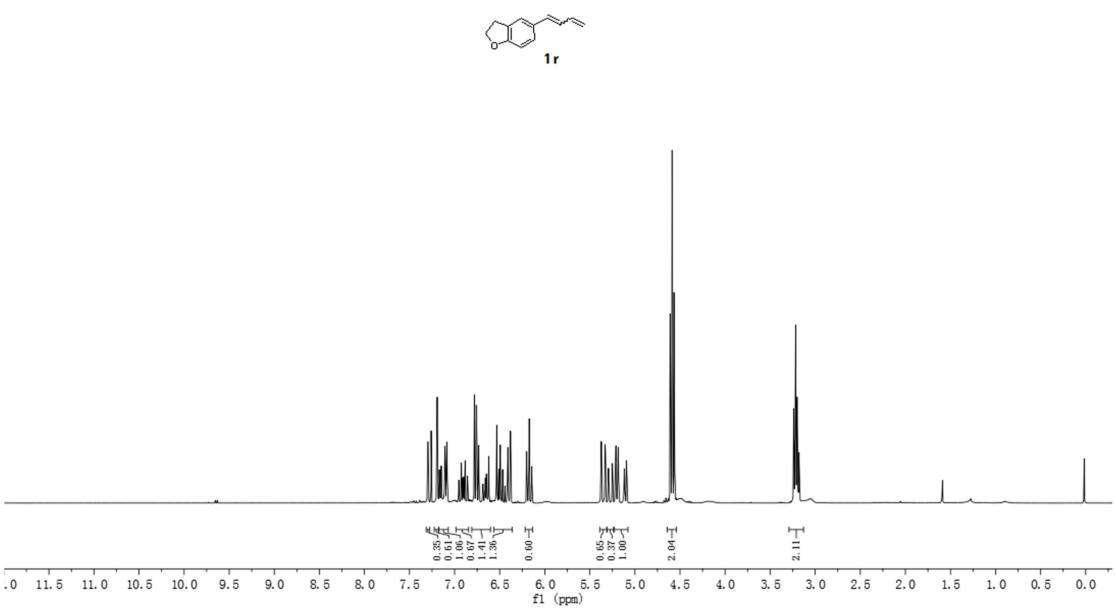
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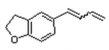
f1 (ppm)



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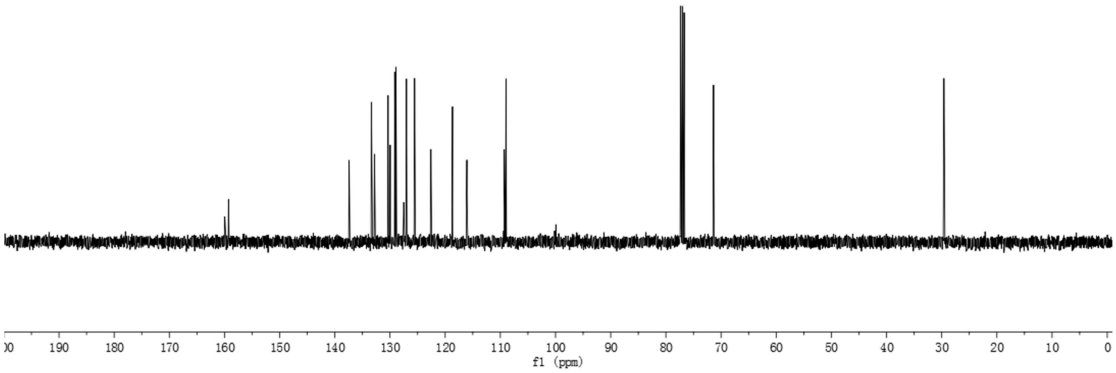

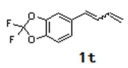

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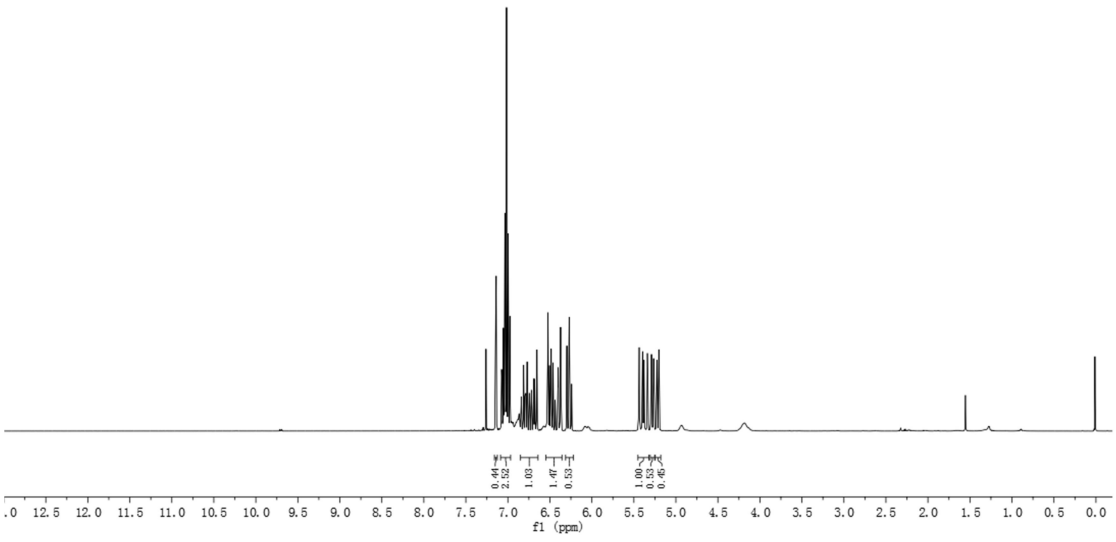


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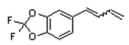

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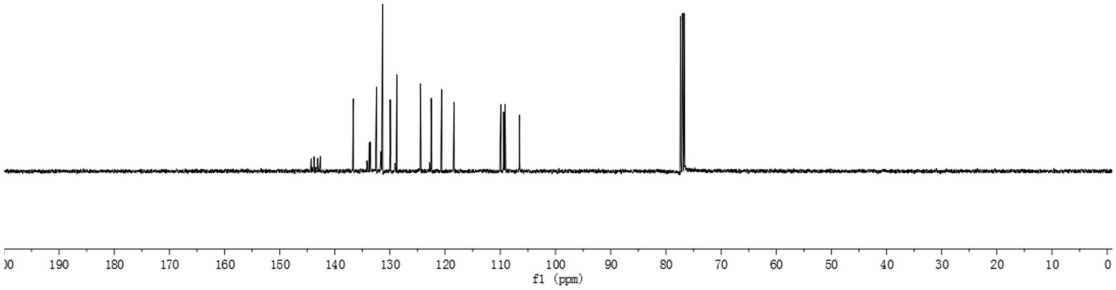
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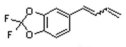
50.21



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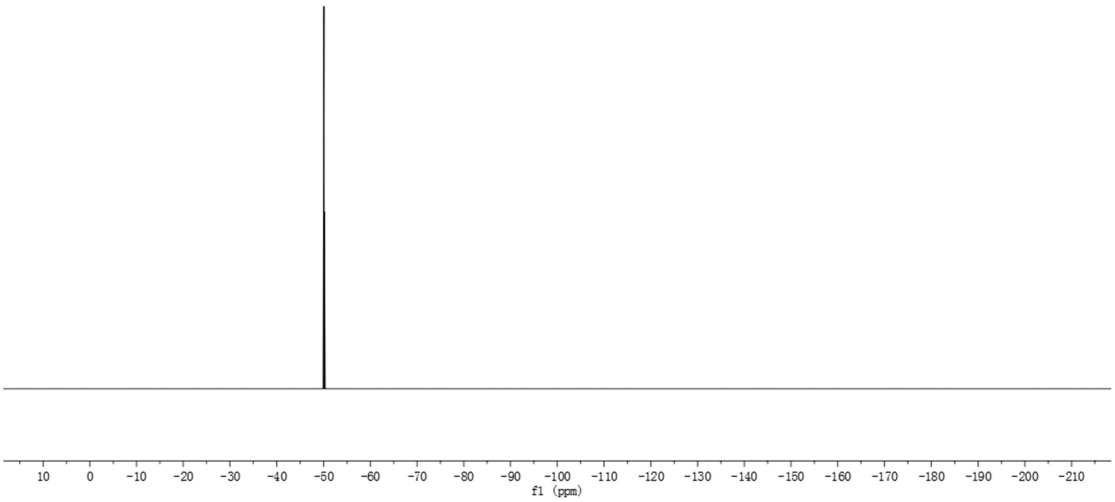
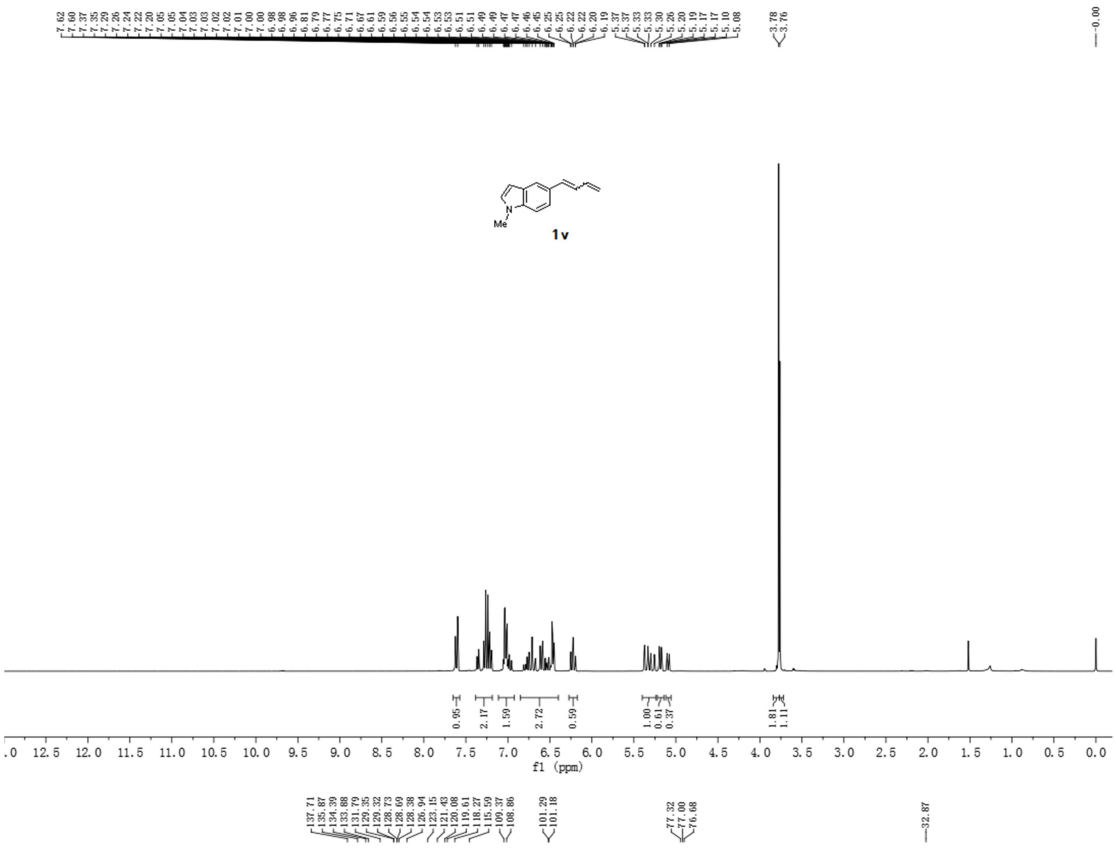
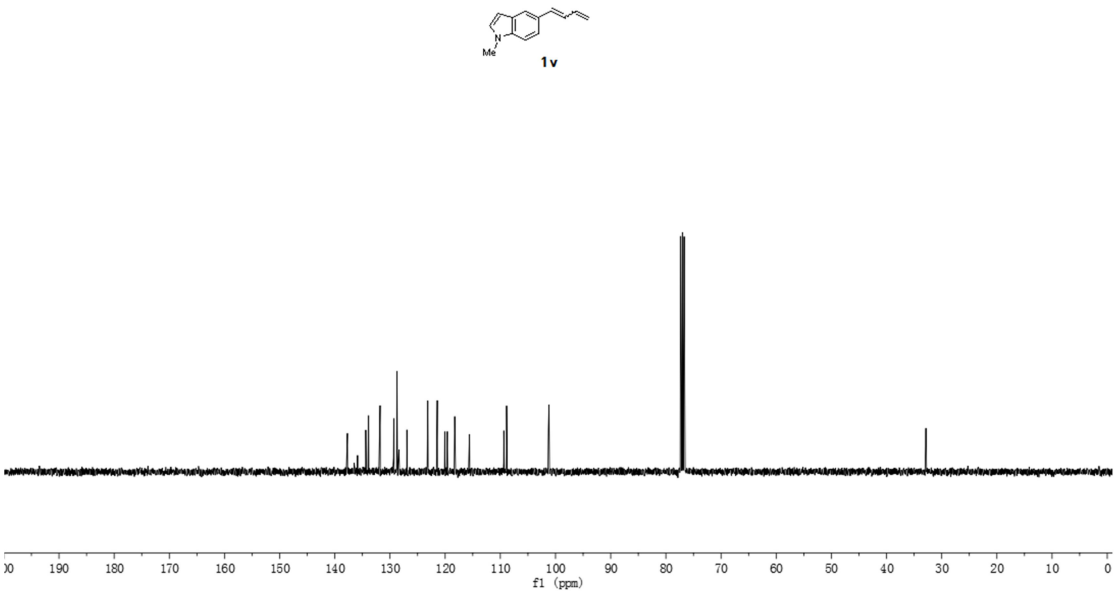

f1 (ppm)


1v
f1 (ppm)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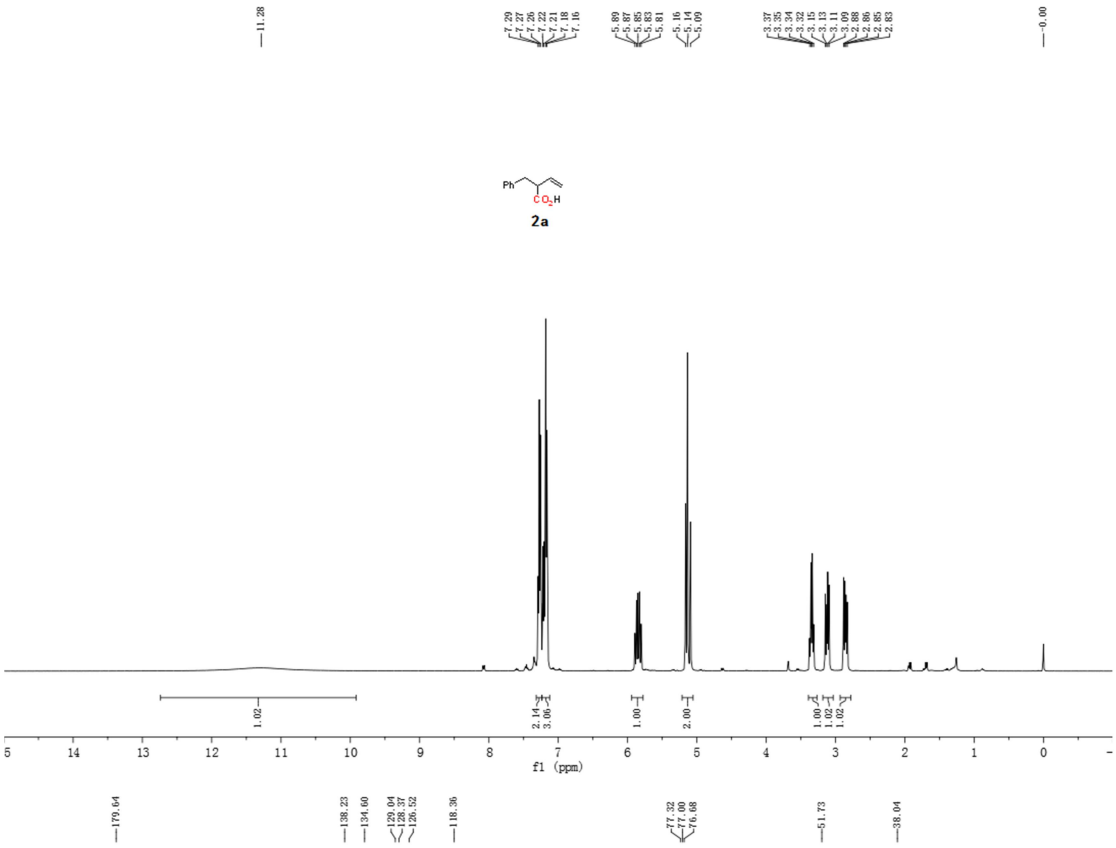
f1 (ppm)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7.18
7.16
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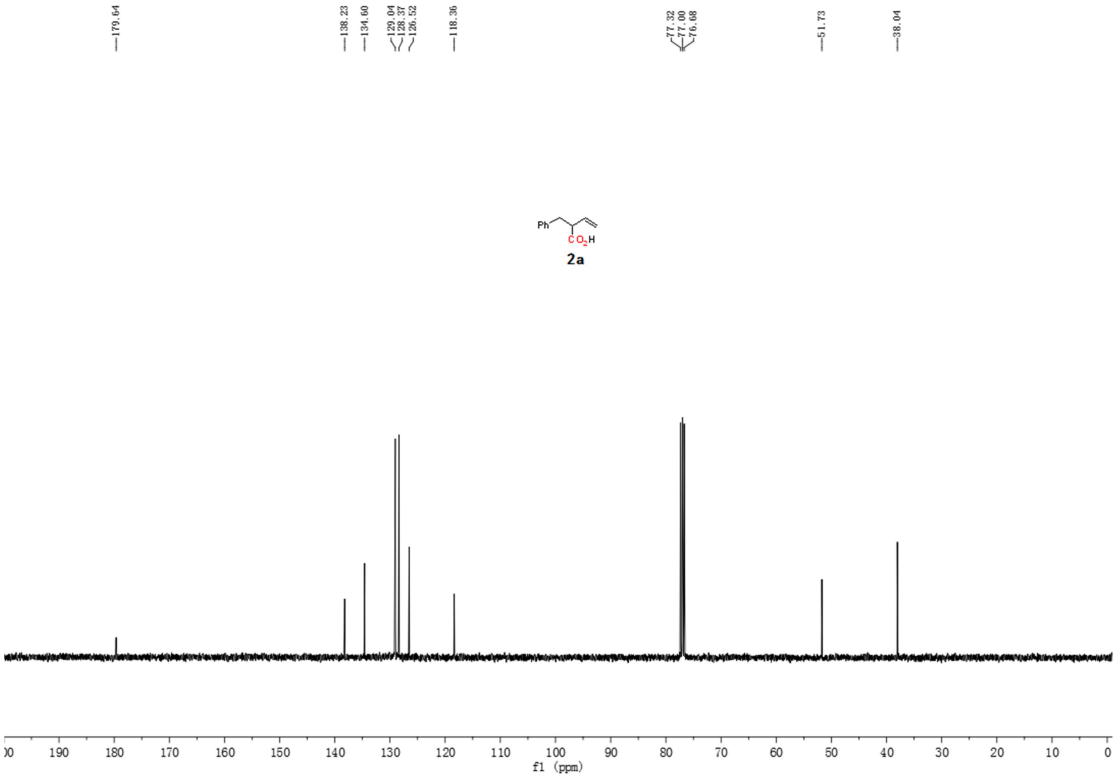
5.85
5.83
5.81
5.16
5.14
5.09
3.37
3.35
3.34
3.32
3.15
3.13
3.11
3.09
2.88
2.86
2.85
2.83
0.00
Ph
CO2H
2a
1.02
2.14
3.06
1.00
2.00
1.00
1.02
1.02
f1 (ppm)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129.04
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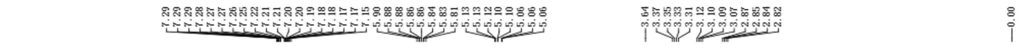
126.52
118.36
77.32
77.00
76.68
51.73
38.04
Ph
CO2H
2a
f1 (ppm)



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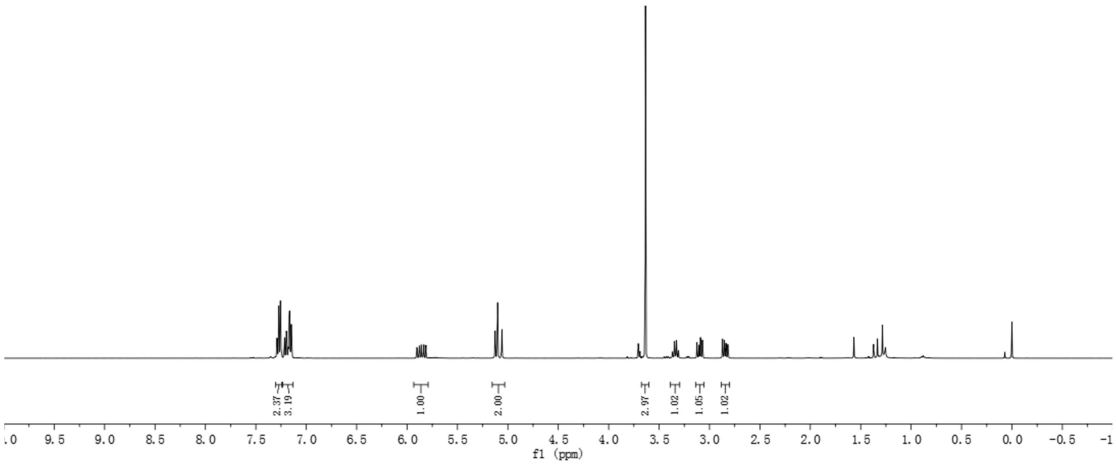

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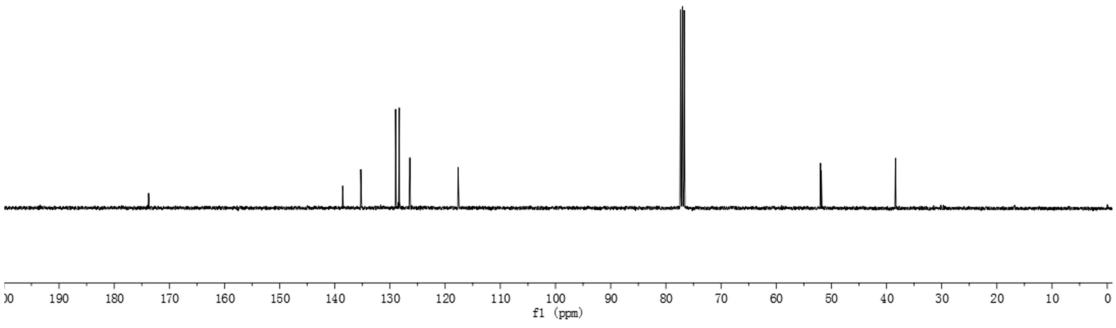

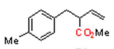

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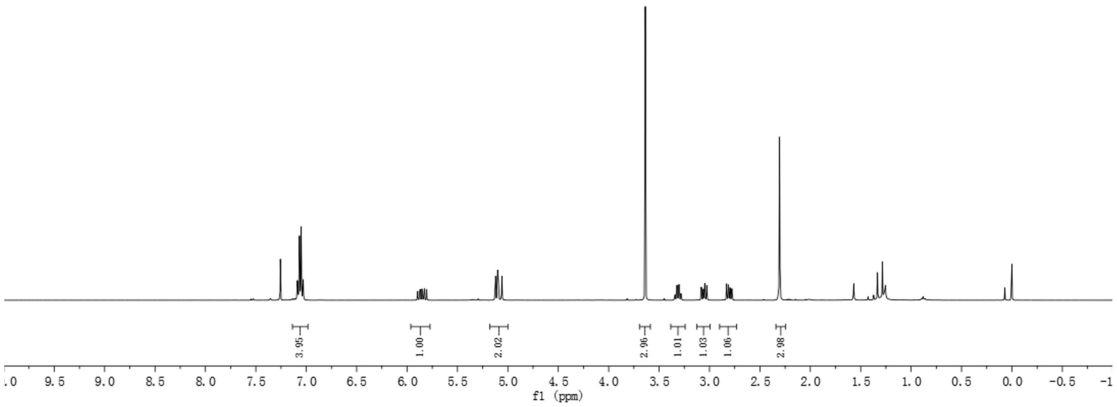

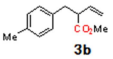

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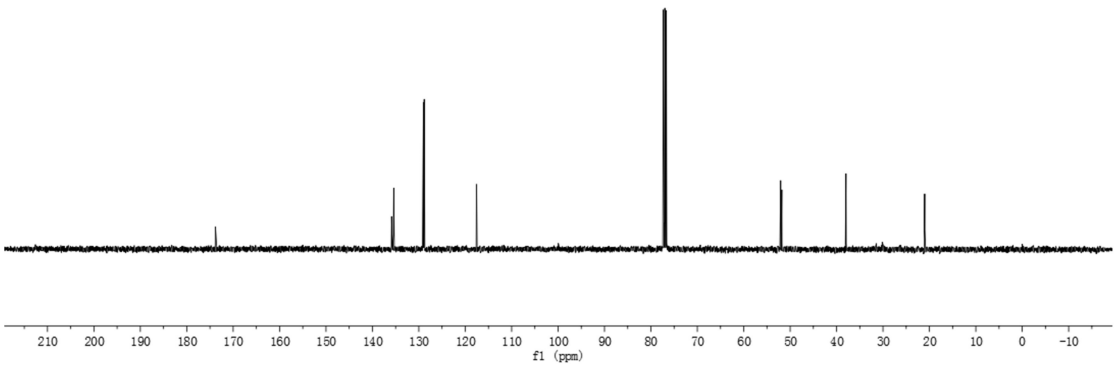

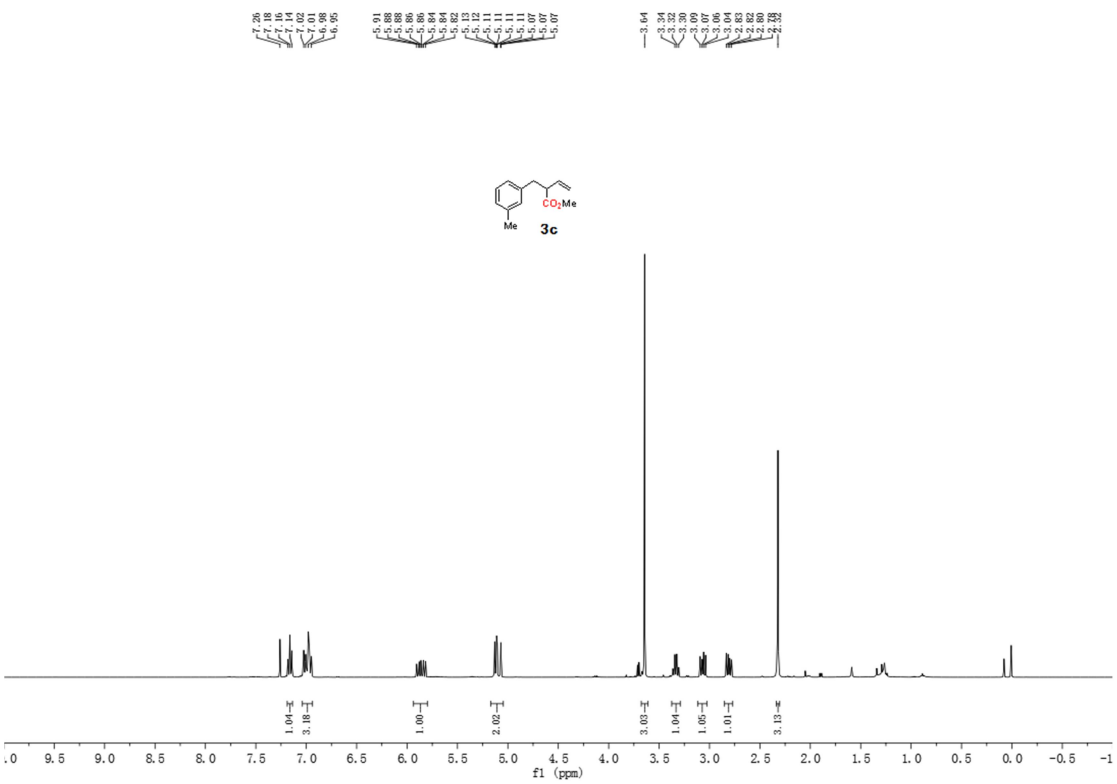
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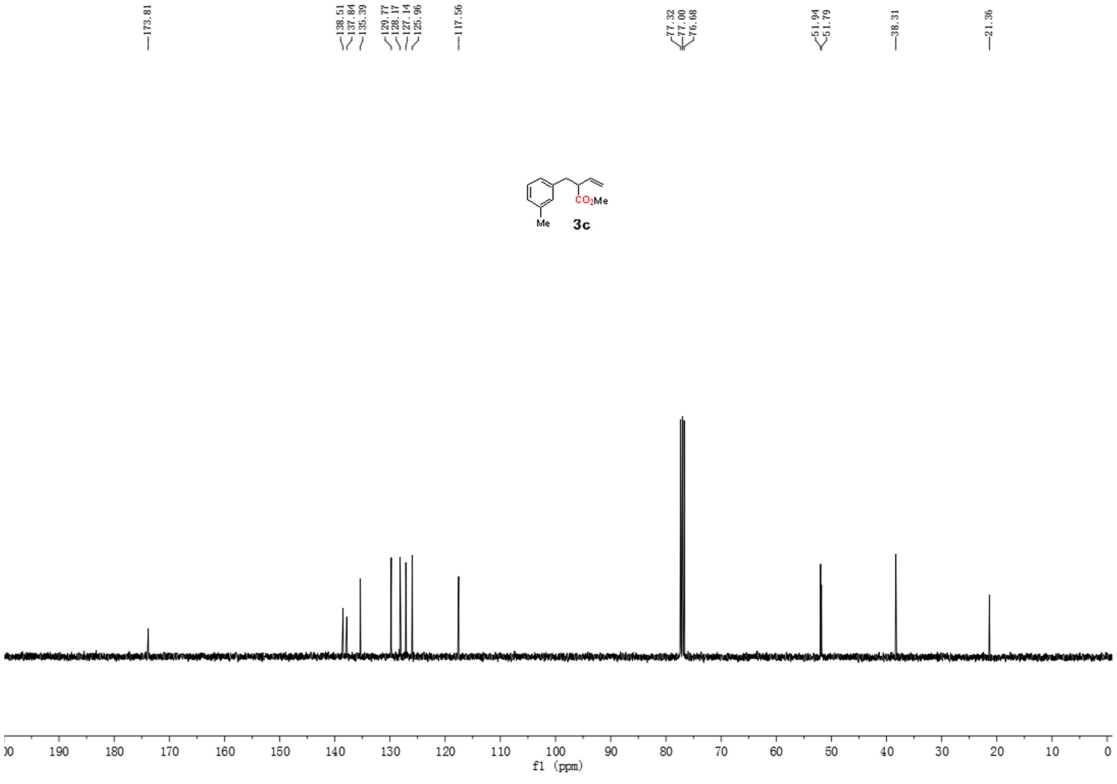
7.18
7.16
7.14
7.02
7.01
6.98
6.95
5.91
5.88
5.88
5.86
5.86
5.84
5.84
5.82
5.13
5.12
5.11
5.11
5.11
5.07
5.07
5.07
3.64
3.34
3.32
3.30
3.09
3.07
3.06
3.04
2.85
2.82
2.80
2.78
2.33
CO2Me
Me
3c
1.04
3.18
1.00
2.02
3.03
1.04
1.05
1.01
3.13
f1 (ppm)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128.17
127.14
125.96
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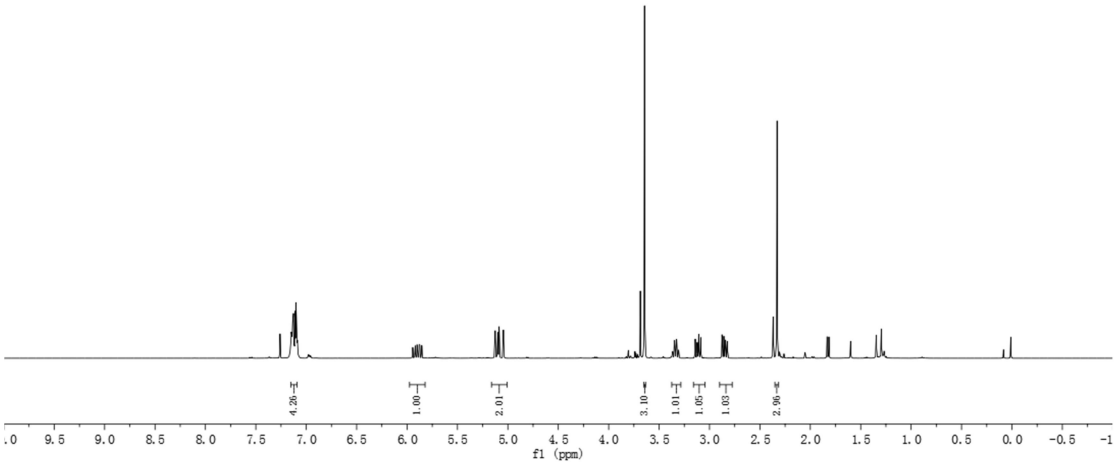
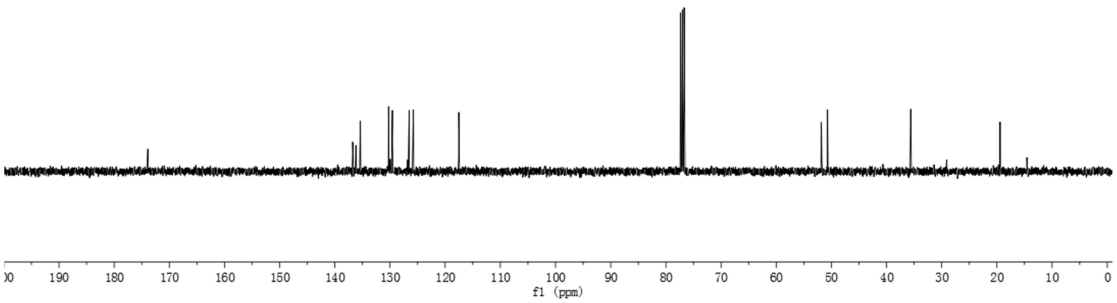
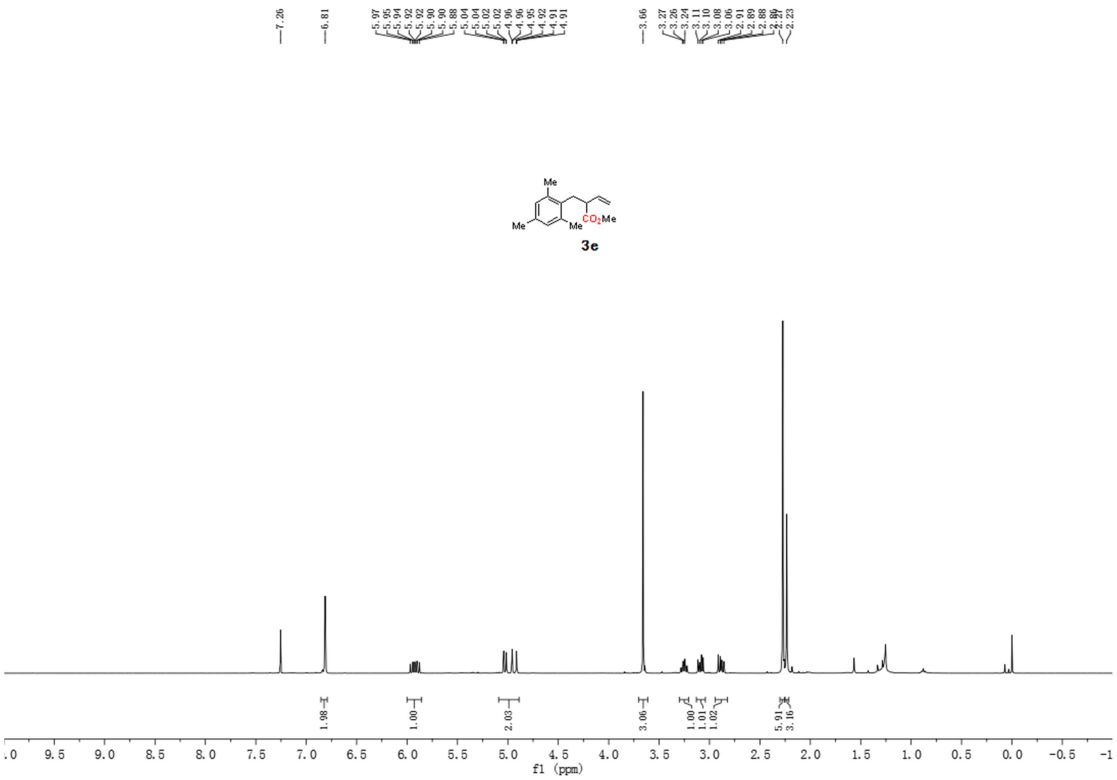
77.00
76.68
51.94
51.79
38.31
21.36
CO2Me
Me
3c
f1 (ppm)

3d



3d

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5.95
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5.92
5.92
5.90
5.88
5.04
5.02
5.02
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4.95
4.92
4.91
4.91
3.66
3.27
3.26
3.24
3.11
3.10
3.08
3.06
2.91
2.89
2.88
2.23
Me
Me
Me
CO2Me
3e
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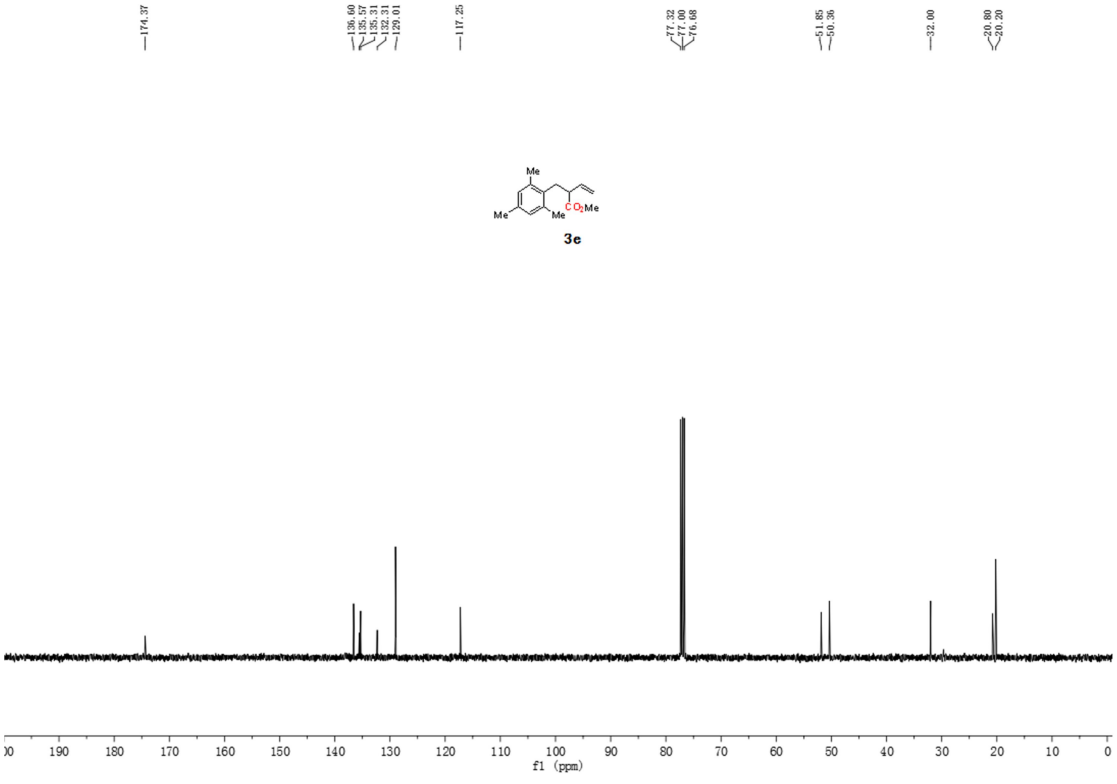
1.00
2.03
3.06
1.00
1.01
1.02
5.91
3.16
f1 (ppm)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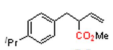
129.01
117.25
77.32
77.00
76.68
51.85
50.36
32.00
20.80
20.20
Me
Me
Me
CO2Me
3e
f1 (ppm)



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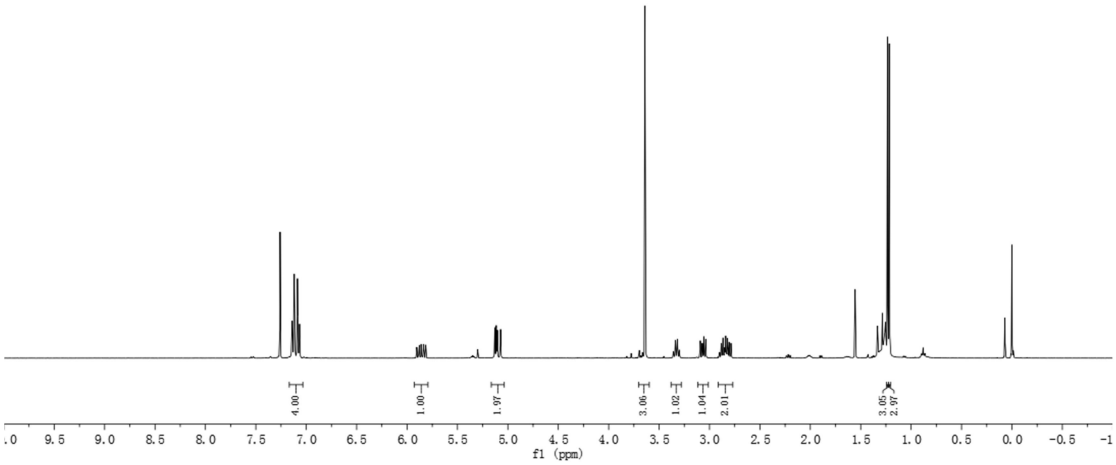
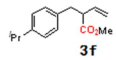
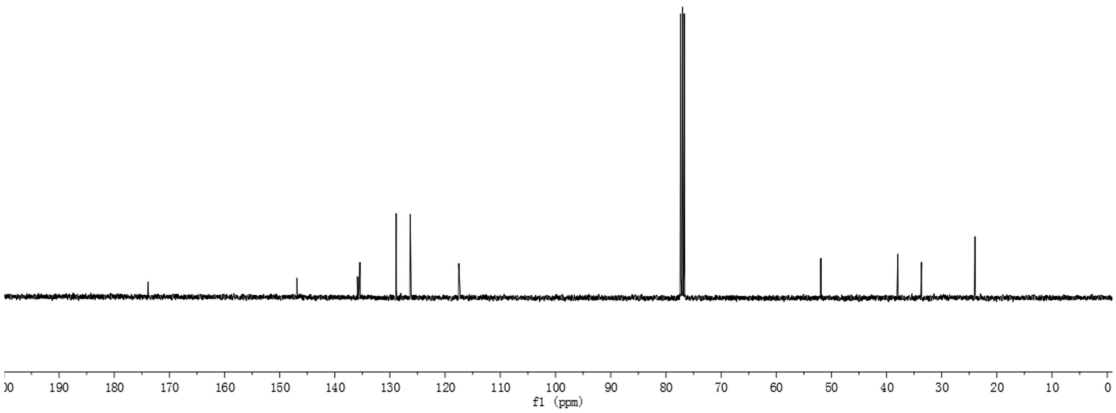
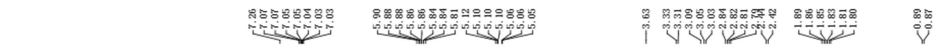
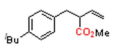




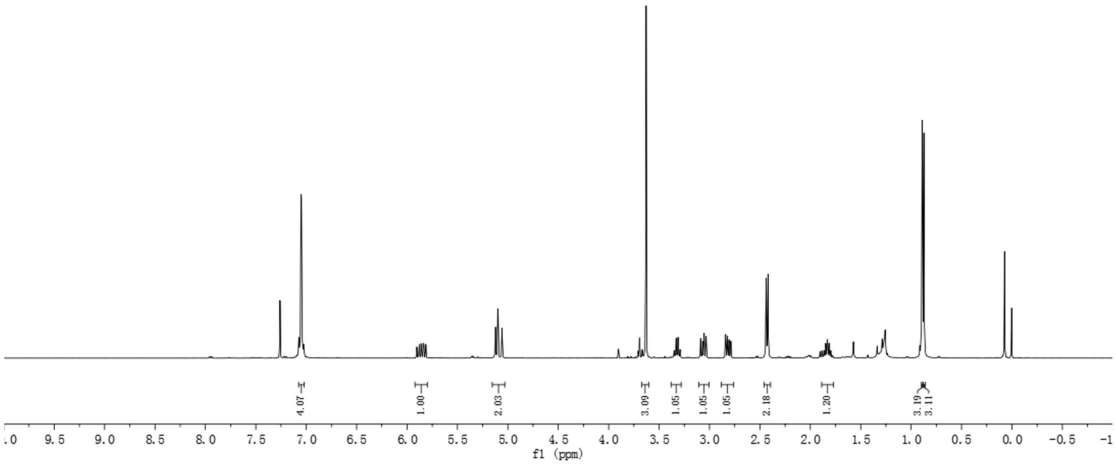
3f

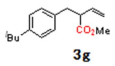




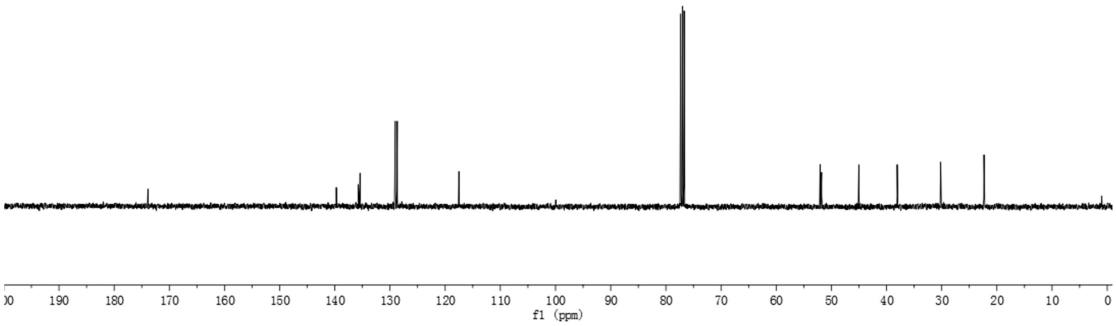


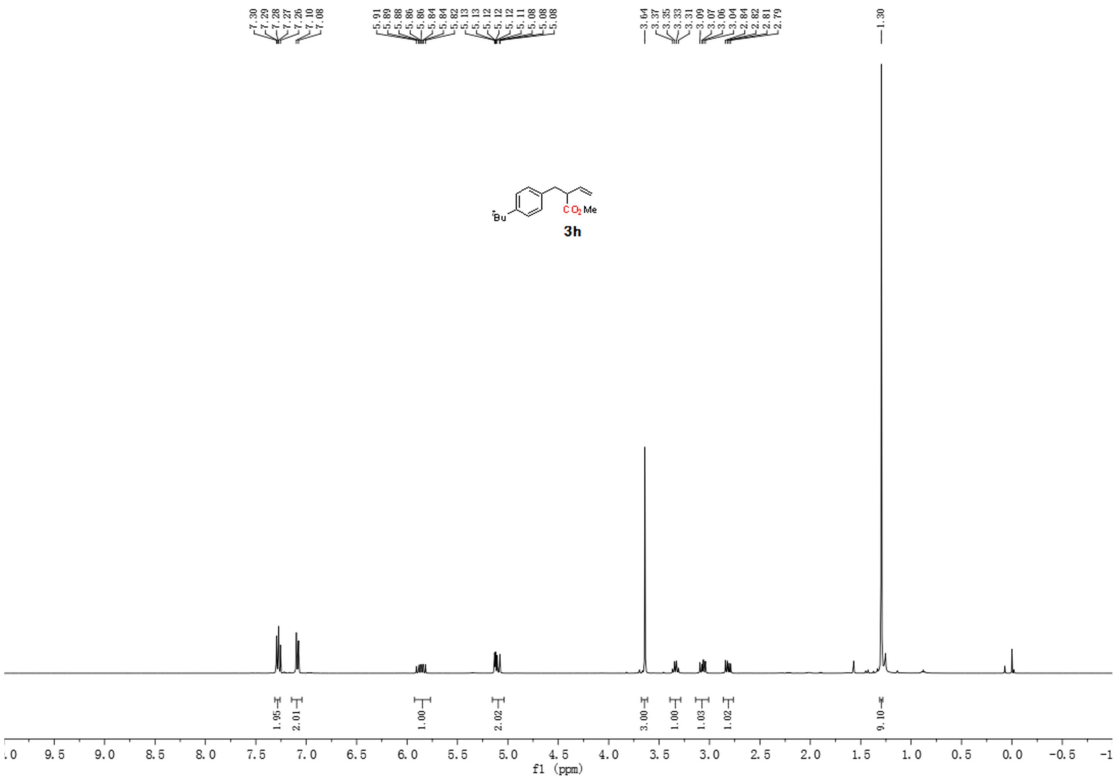
3g





3g

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5.88
5.86
5.86
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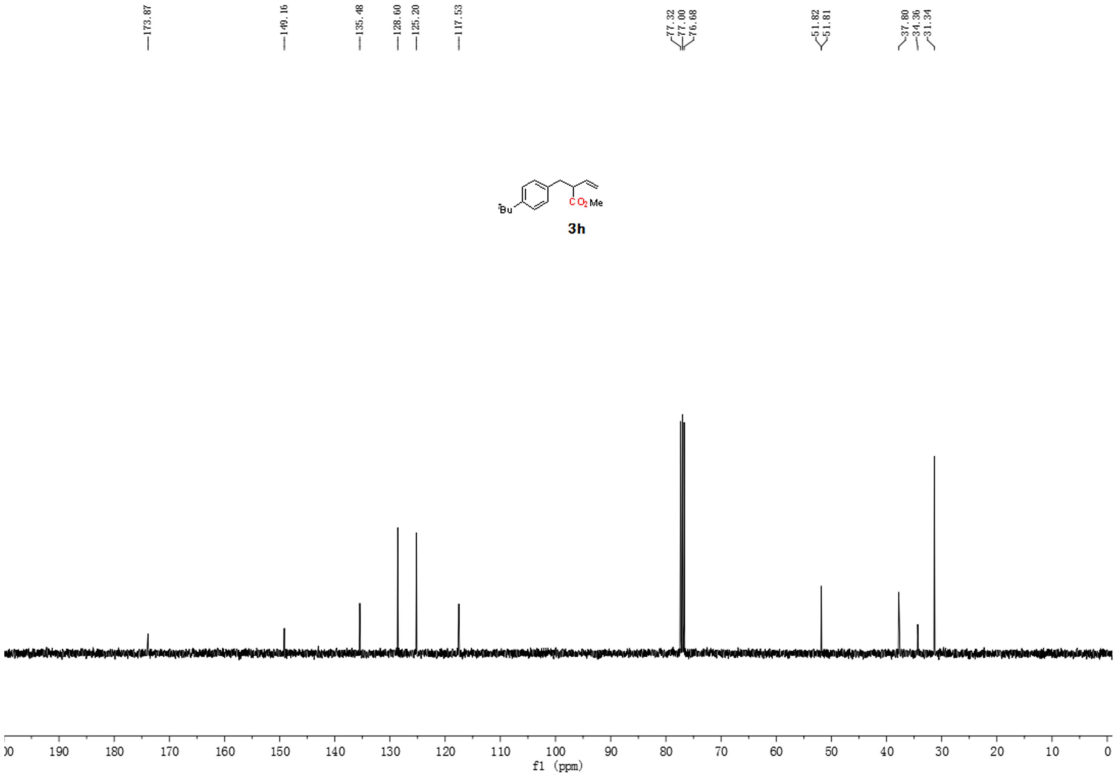
5.82
5.13
5.12
5.12
5.12
5.11
5.08
5.08
3.64
3.37
3.35
3.33
3.31
3.09
3.07
3.06
3.04
2.84
2.82
2.81
2.79
1.30
tBu
CO2Me
3h
1.95
2.01
1.00
2.02
3.00
1.00
1.03
1.02
9.10
f1 (ppm)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117.53
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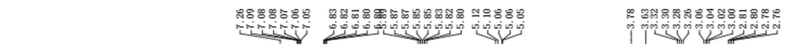
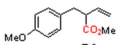
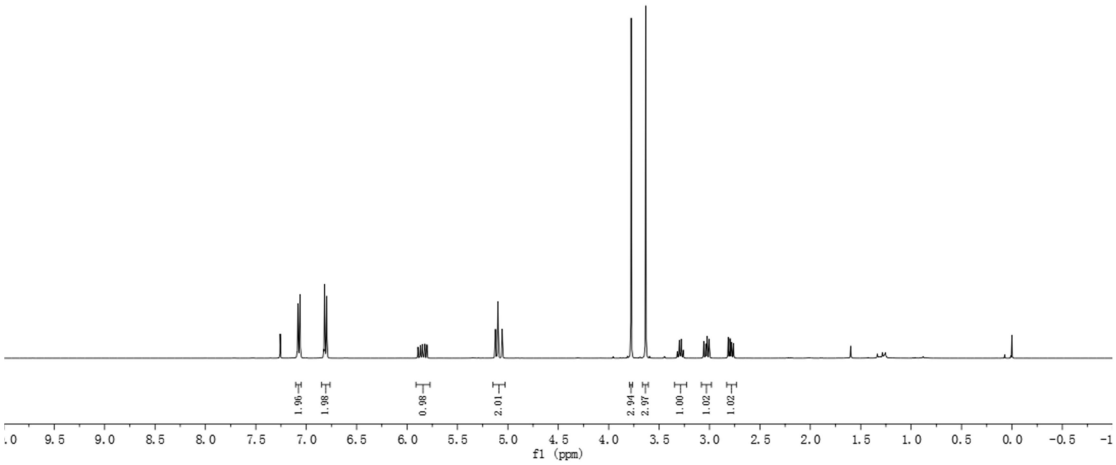
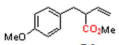
77.00
76.68
51.82
51.81
37.80
34.36
31.34
tBu
CO2Me
3h
f1 (ppm)



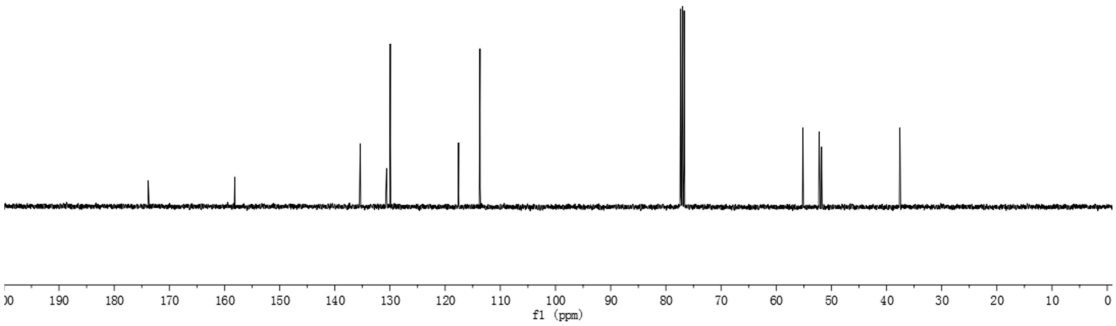


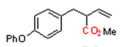
3i



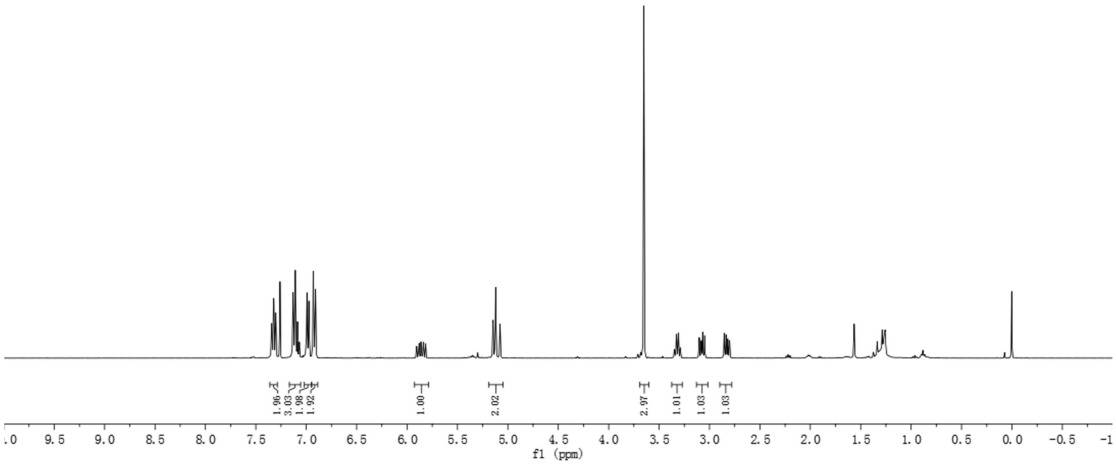


3i

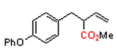



PhO
CO2Me

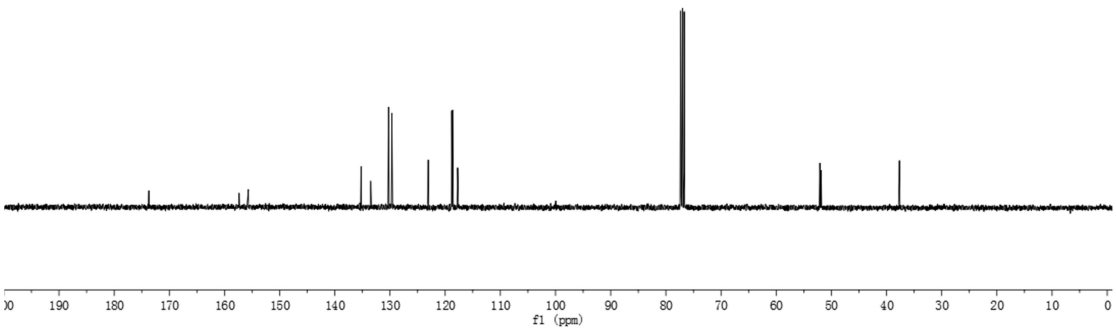
3j

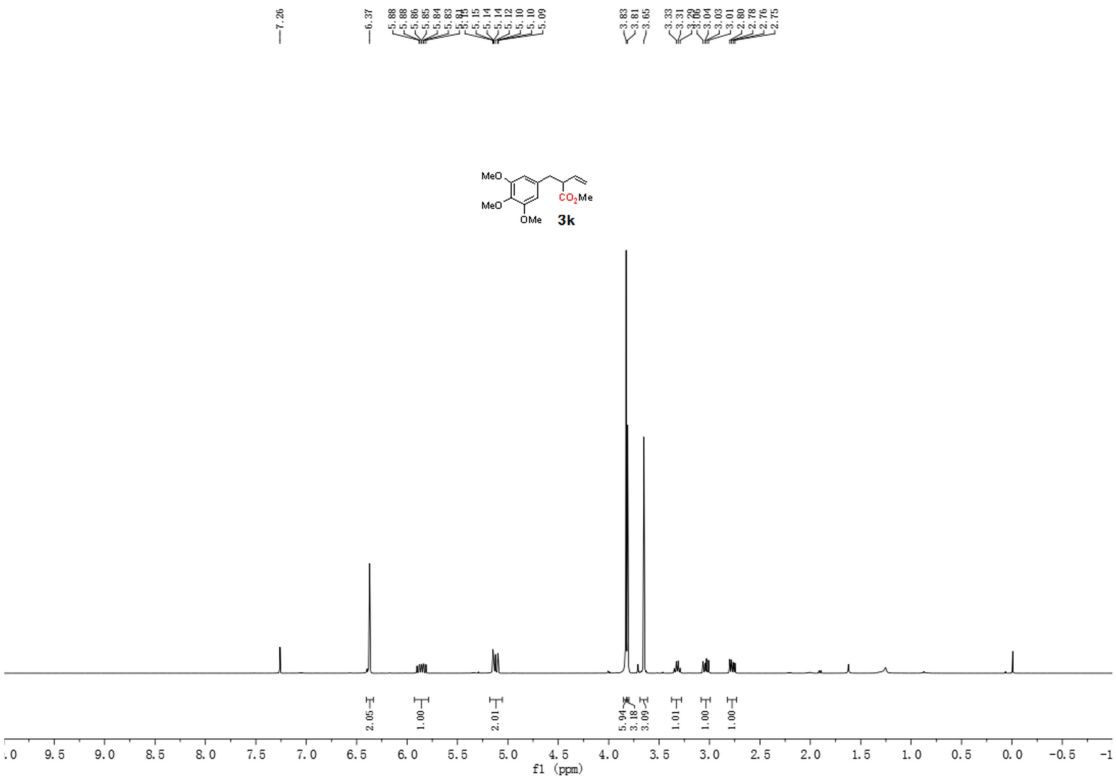

1.96
3.03
1.98
1.92
1.00
2.02
2.97
1.01
1.03
1.03
f1 (ppm)


173.71
157.35
155.67
135.24
133.50
130.27
129.67
123.07
118.82
118.67
117.74
77.32
77.00
76.68
52.09
51.85
37.67


PhO
CO2Me

3j


f1 (ppm)


7.26
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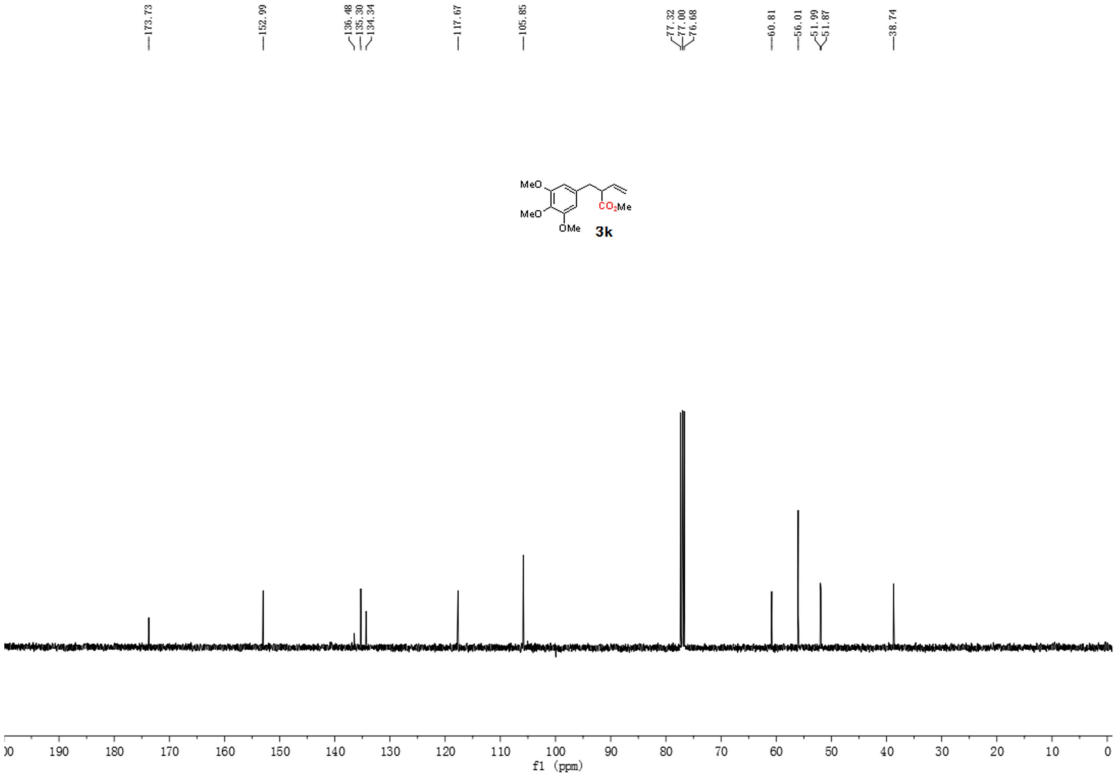
5.84
5.83
5.15
5.14
5.12
5.10
5.09
3.83
3.81
3.65
3.33
3.31
3.04
3.03
3.01
2.78
2.76
2.75
MeO
MeO
OMe
CO2Me
3k
2.05
1.00
2.01
5.94
3.18
3.09
1.01
1.00
1.00
f1 (ppm)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117.67
105.85
77.32
77.00
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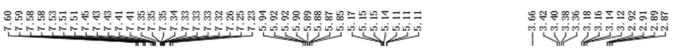
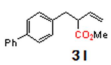
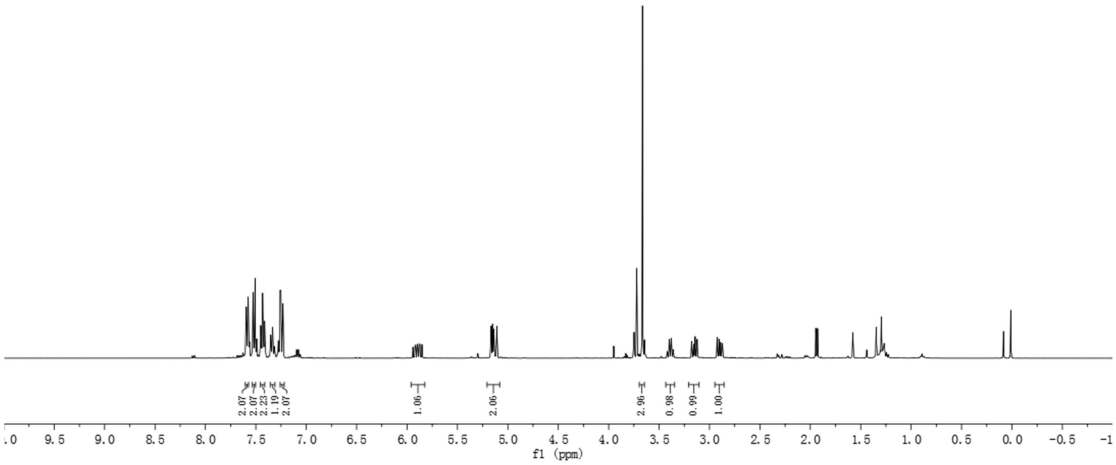
60.81
56.01
51.99
51.87
38.74
MeO
MeO
OMe
CO2Me
3k
f1 (ppm)




Ph
CO2Me

3l


2.07
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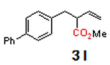
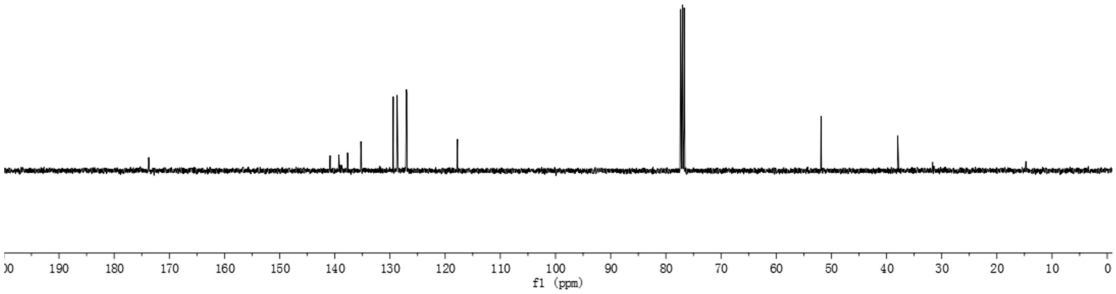
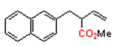
1.19
2.07
1.06
2.06
2.96
0.98
0.99
1.00
f1 (ppm)

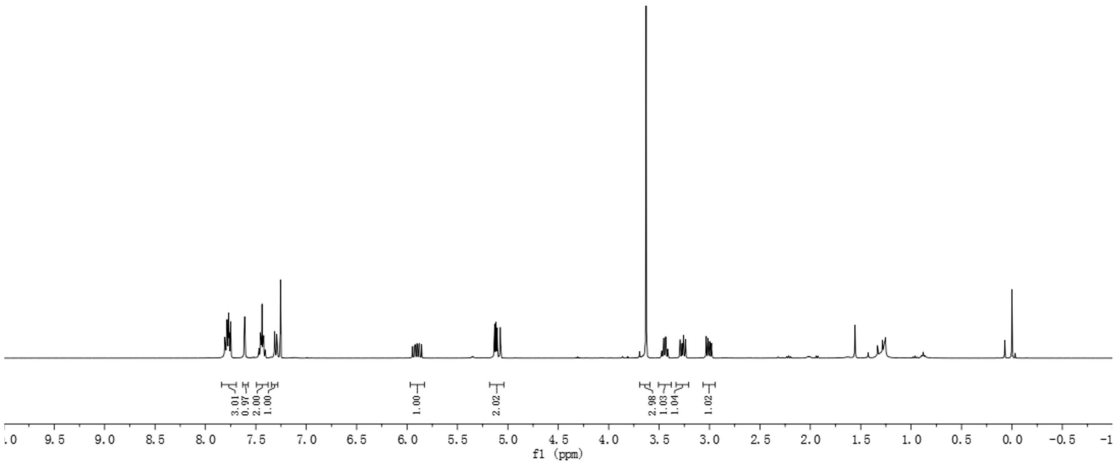

Ph
CO2Me

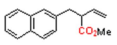
3l


f1 (ppm)

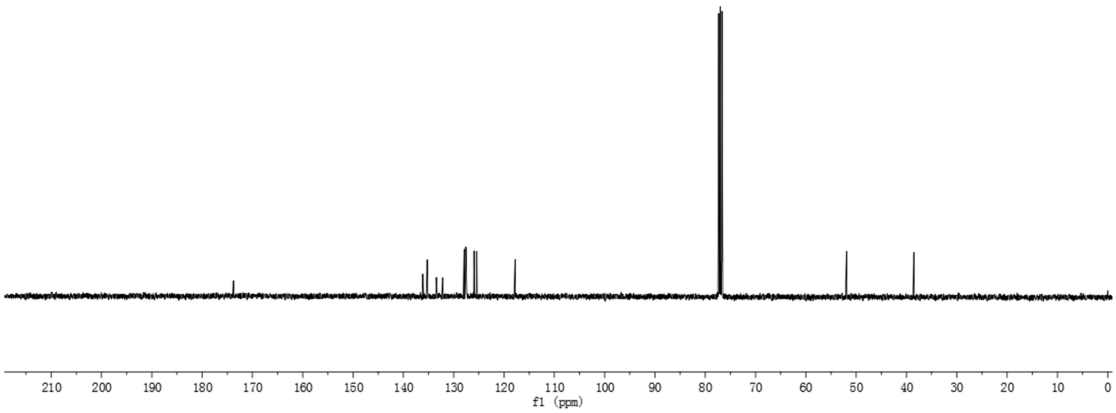

CO2Me

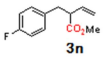
3m


3.01
0.97
2.00
1.00
1.00
2.02
2.98
1.03
1.04
1.02
f1 (ppm)

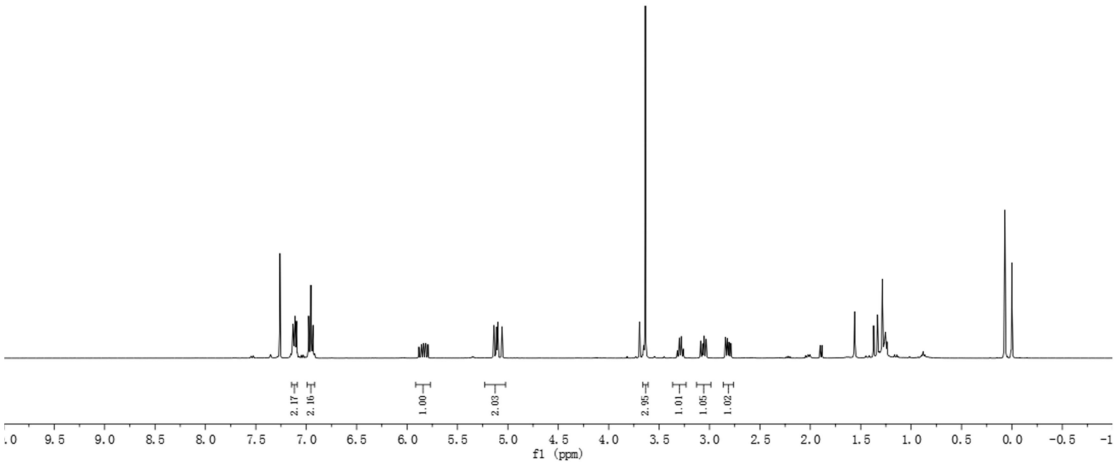

CO2Me

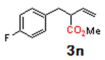
3m


f1 (ppm)



3n





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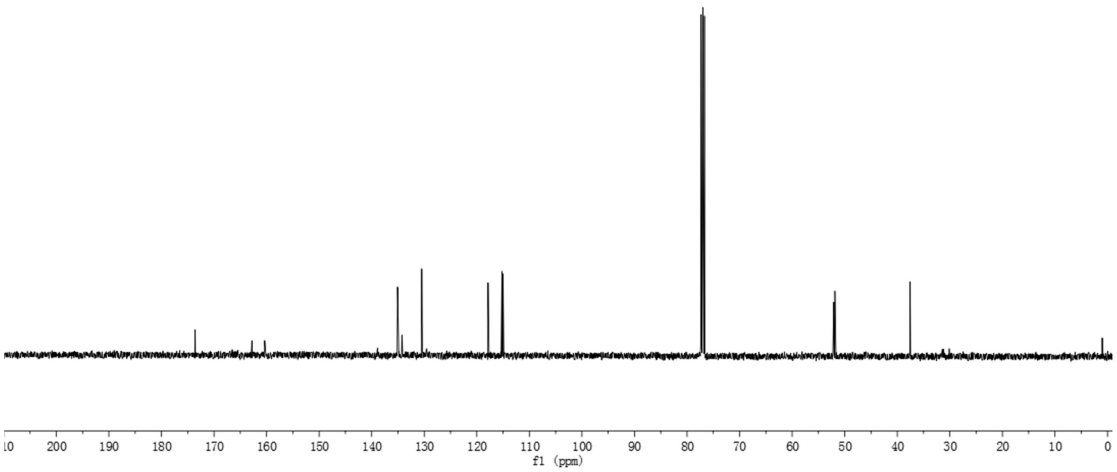
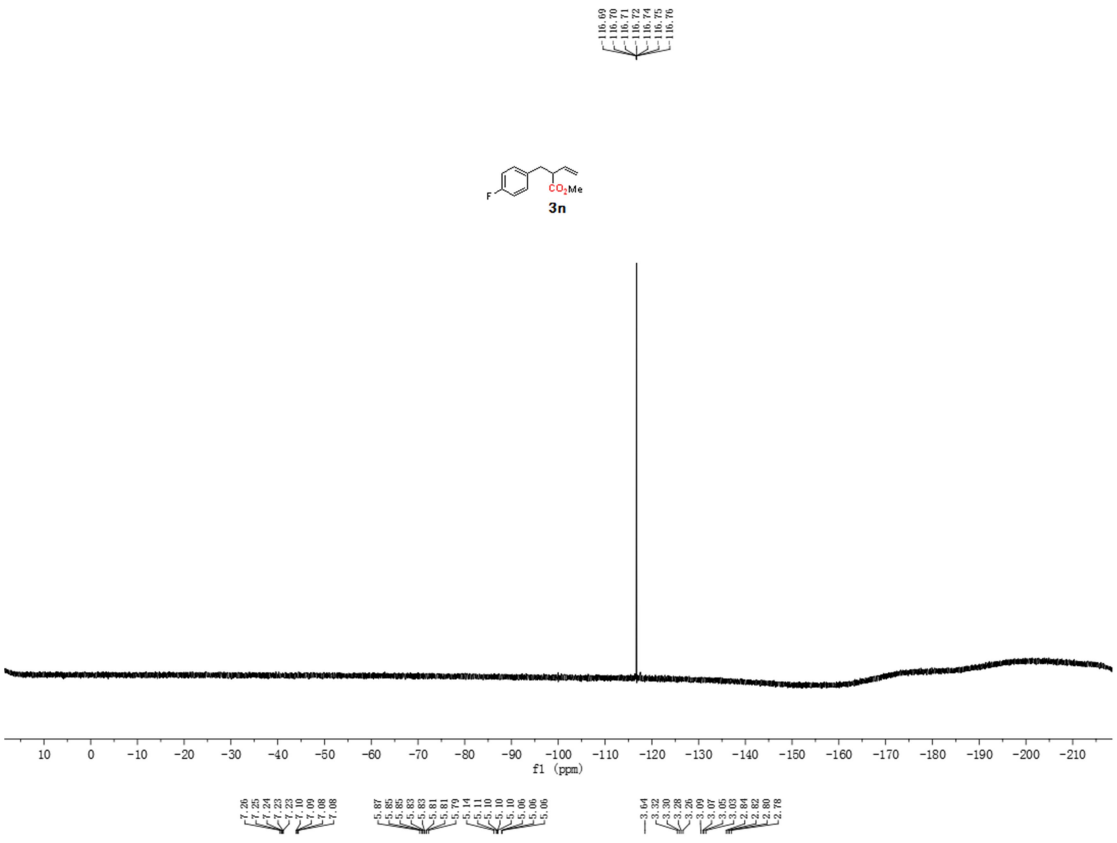
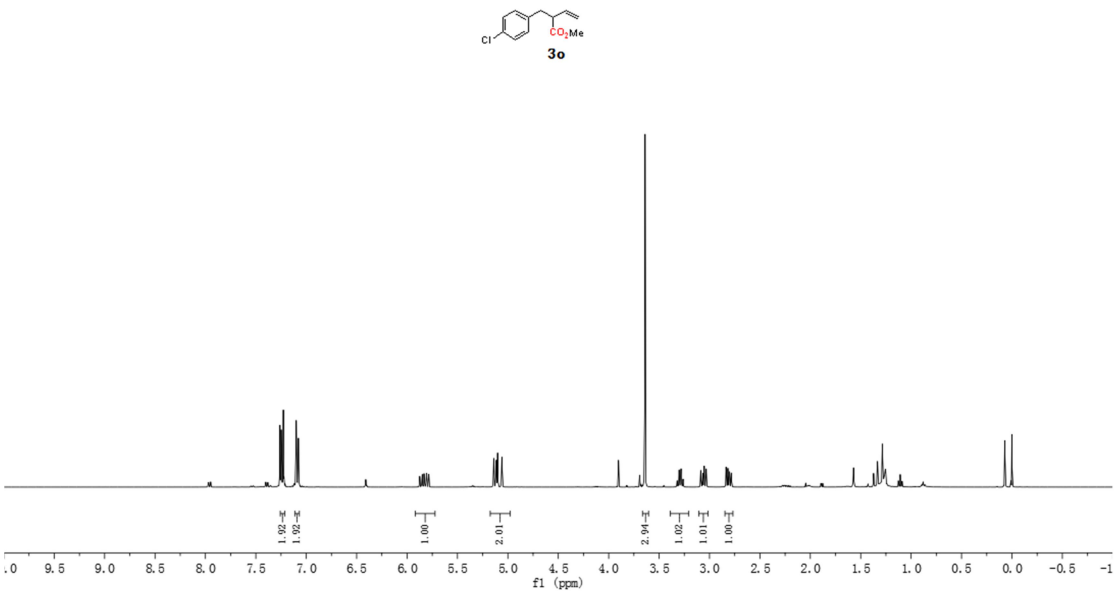
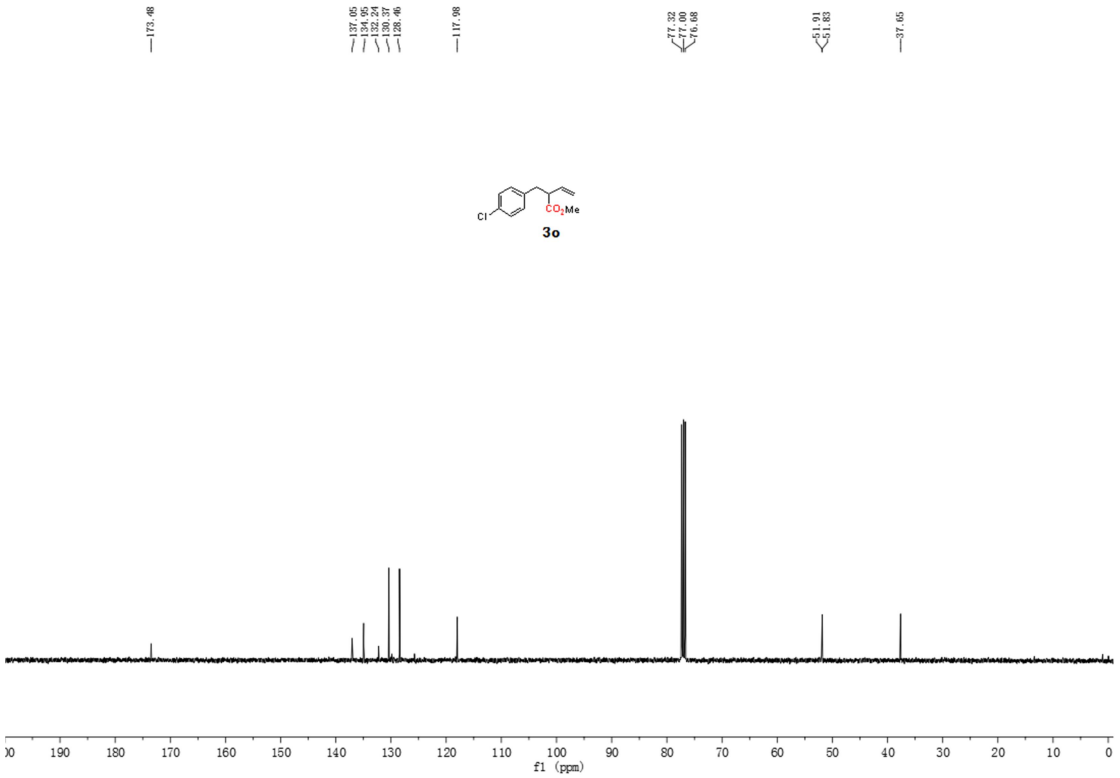
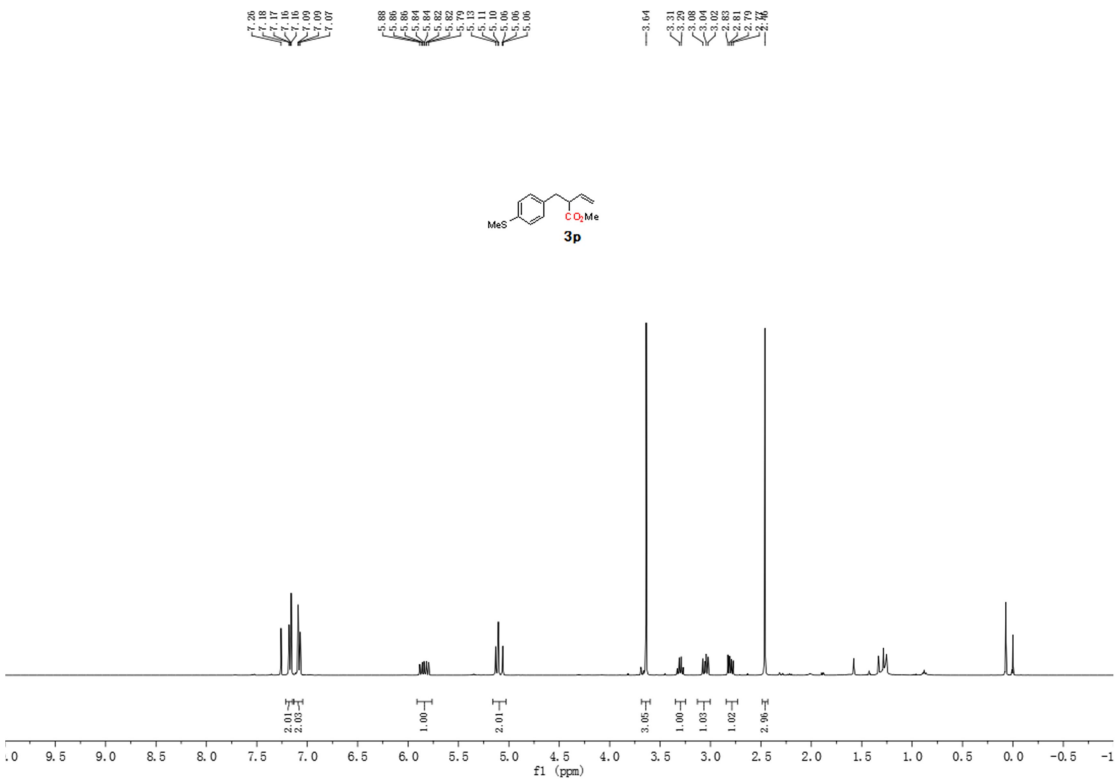
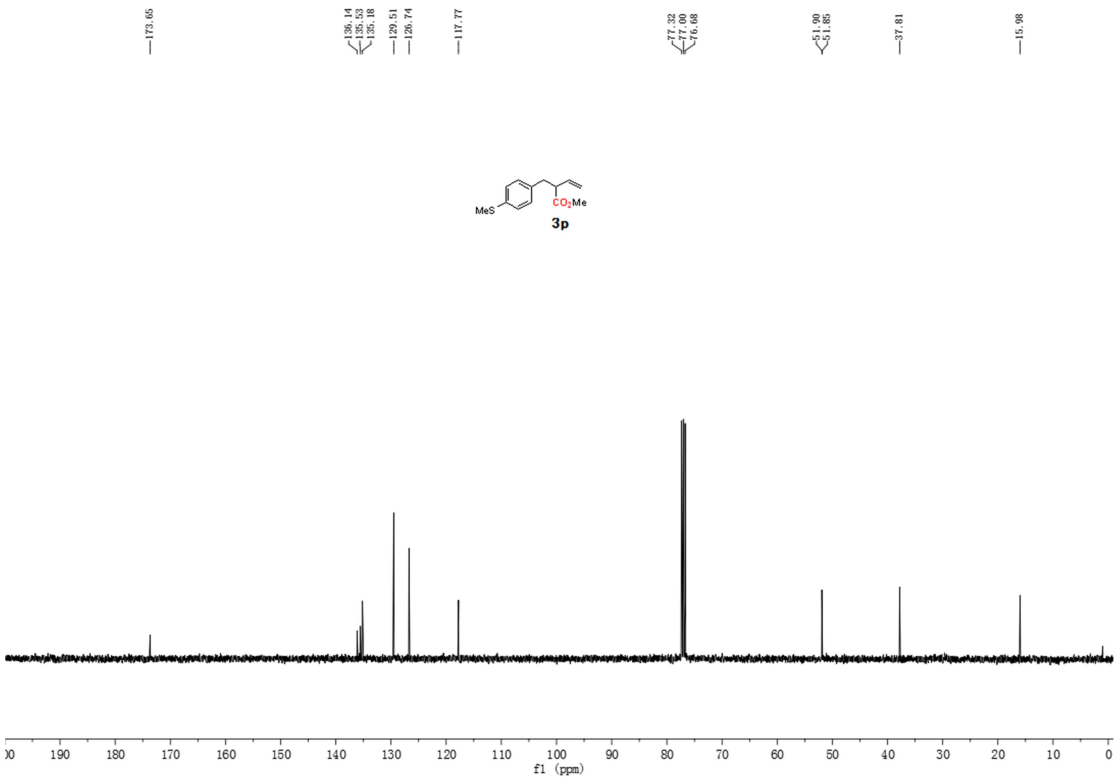



-116.69
-116.70
-116.71
-116.72
-116.74
-116.75
-116.76
F
CO2Me
3n
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
7.26
7.25
7.24
7.23
7.23
7.10
7.09
7.08
7.08
5.87
5.85
5.85
5.83
5.83
5.81
5.81
5.79
5.14
5.11
5.10
5.10
5.06
5.06
5.06
3.64
3.32
3.30
3.28
3.26
3.09
3.07
3.05
3.03
2.84
2.82
2.80
2.78


Cl
CO2Me
3o
1.92
1.92
1.00
2.01
2.94
1.02
1.01
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


173.48
137.05
134.65
132.24
130.37
128.46
117.98
77.32
77.00
76.68
51.91
51.83
37.65
Cl
CO2Me
3o
f1 (ppm)


7.26
7.18
7.17
7.16
7.16
7.09
7.09
7.07
5.88
5.86
5.86
5.84
5.84
5.82
5.82
5.79
5.13
5.11
5.10
5.06
5.06
5.06
3.64
3.31
3.29
3.08
3.04
3.02
2.83
2.81
2.79
2.77
2.76
MeS
CO2Me
3p
2.01
2.03
1.00
2.01
3.05
1.00
1.03
1.02
2.96
f1 (ppm)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136.14
135.53
135.18
129.51
126.74
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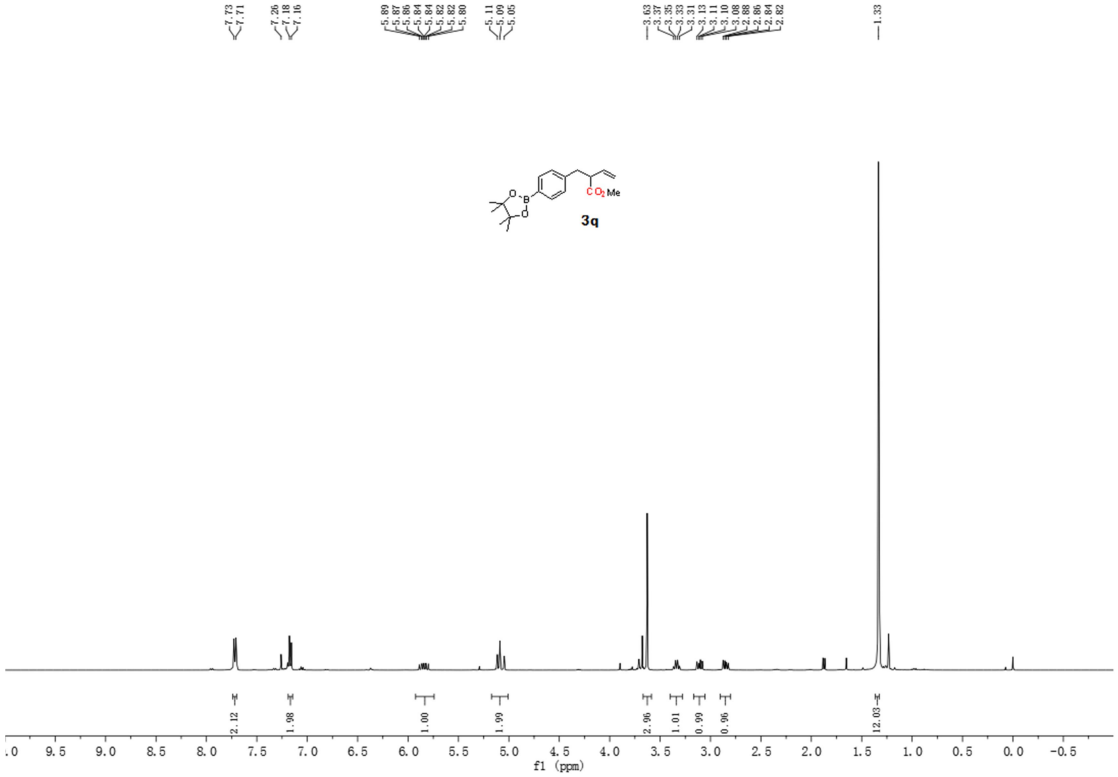
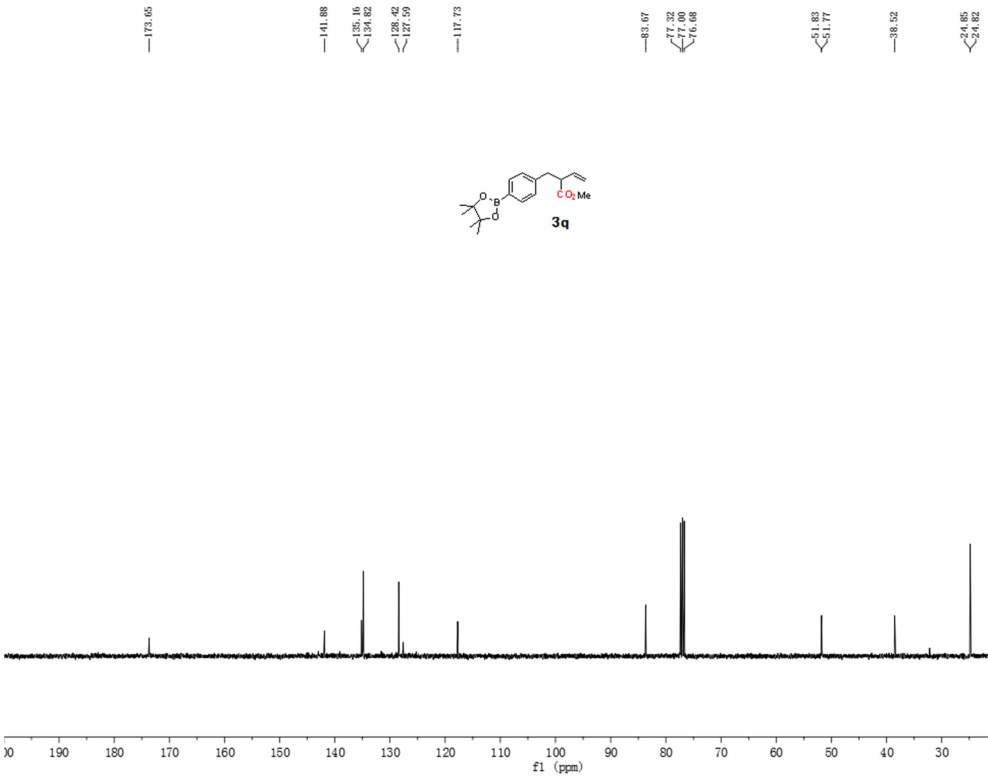
77.32
77.00
76.68
51.90
51.85
37.81
15.98
MeS
CO2Me
3p
f1 (ppm)


7.73
7.71
7.26
7.18
7.16
5.89
5.87
5.86
5.84
5.82
5.82
5.80
5.11
5.09
5.05
3.63
3.37
3.35
3.33
3.31
3.13
3.11
3.10
3.08
2.88
2.86
2.84
2.82
1.33
CO2Me
3q
2.12
1.98
1.00
1.99
2.96
1.01
0.99
0.96
12.03
f1 (ppm)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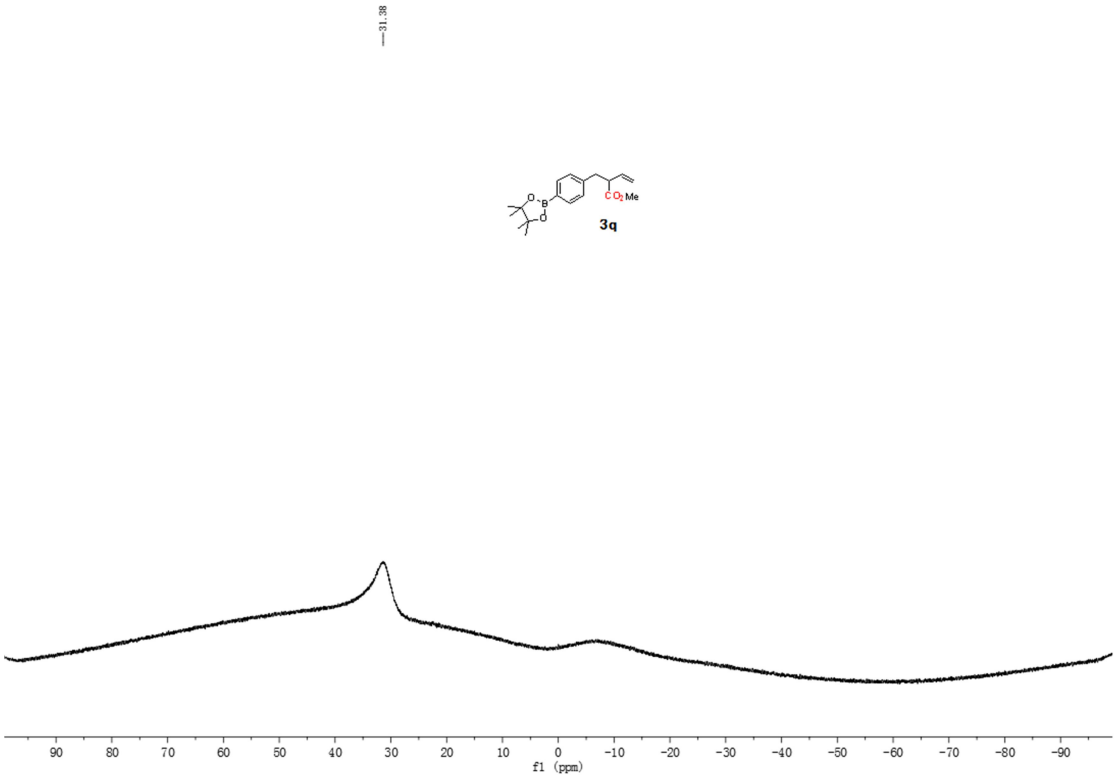
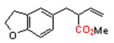
141.88
135.16
134.82
128.42
127.59
117.73
83.67
77.32
77.00
76.68
51.83
51.17
38.52
24.85
24.82
CO2Me
3q
f1 (ppm)


31.38
CO2Me
3q
f1 (ppm)



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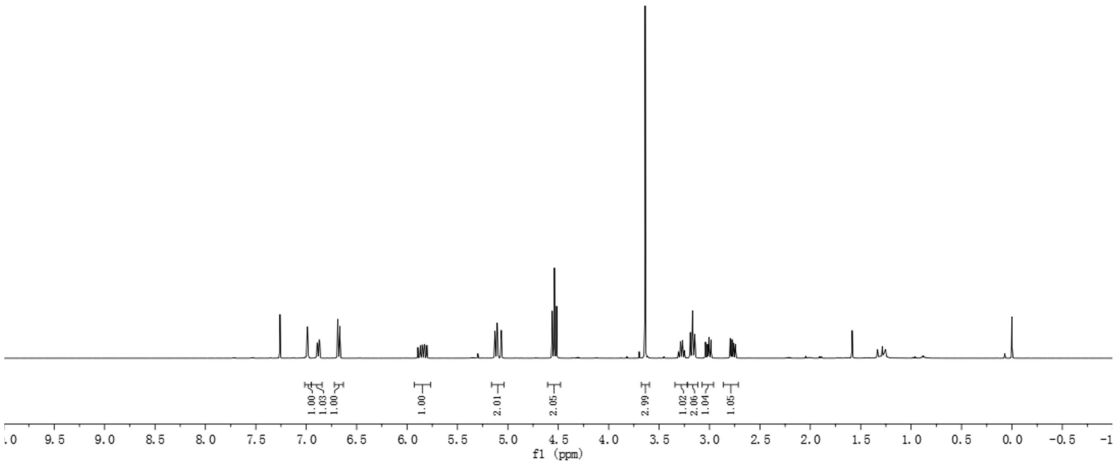
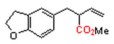
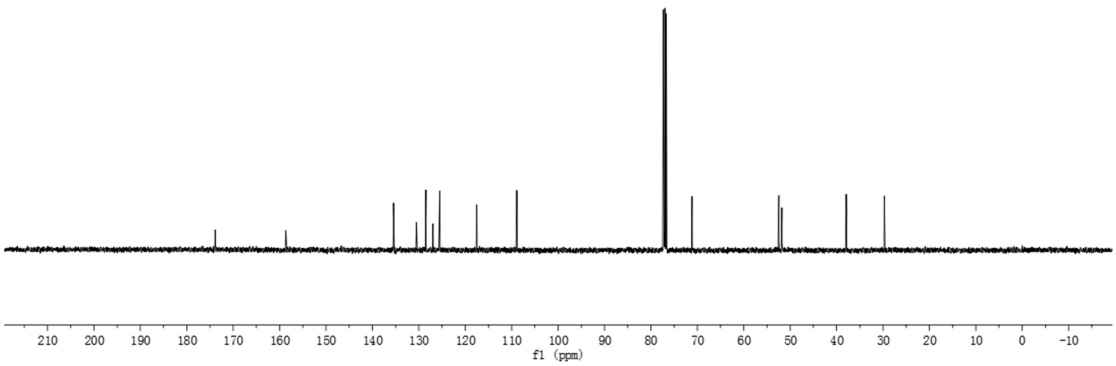




3r




7.26
6.72
6.70
6.66
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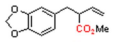
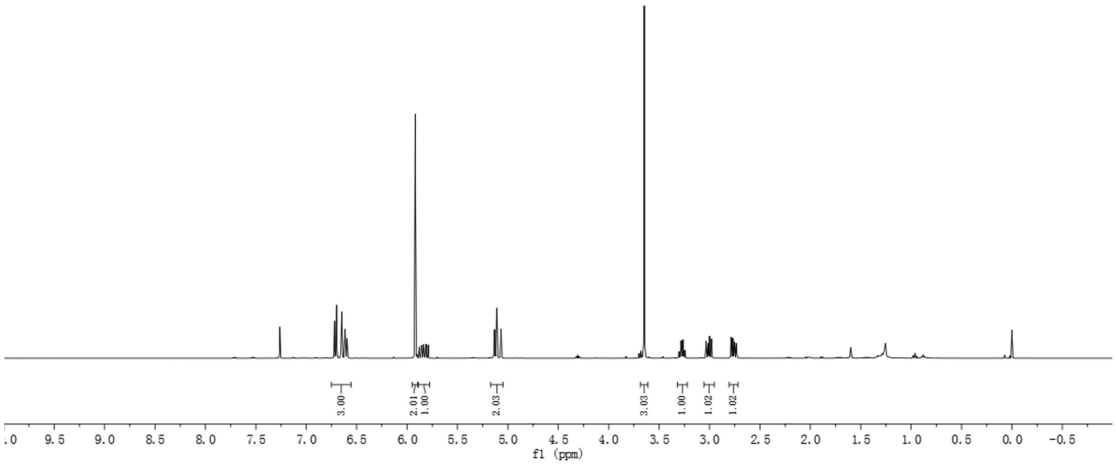
6.62
6.61
6.60
6.59
5.92
5.85
5.84
5.83
5.82
5.81
5.13
5.13
5.11
5.11
5.07
5.07
3.65
3.30
3.28
3.26
3.24
3.03
3.01
3.00
2.98
2.79
2.77
2.75
2.73
0.00


CO2Me

3s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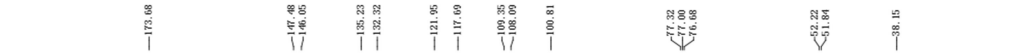
2.01
1.00
2.03
3.03
1.00
1.02
1.02
f1 (ppm)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146.05
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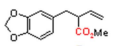
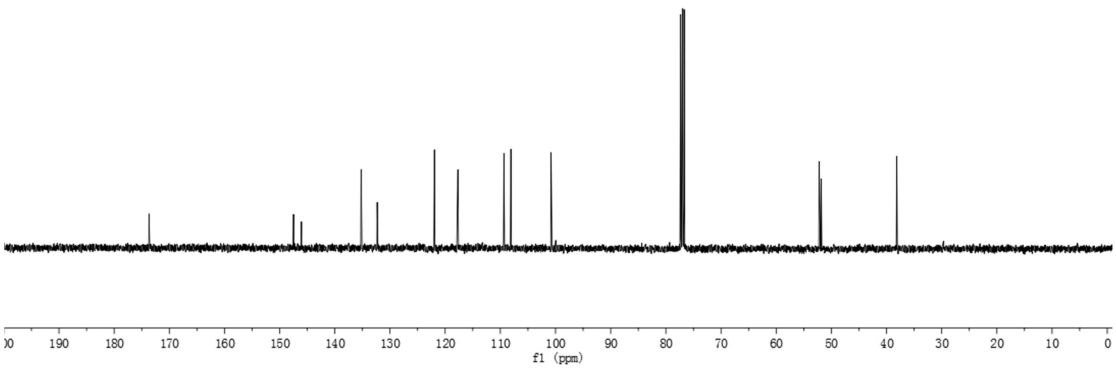
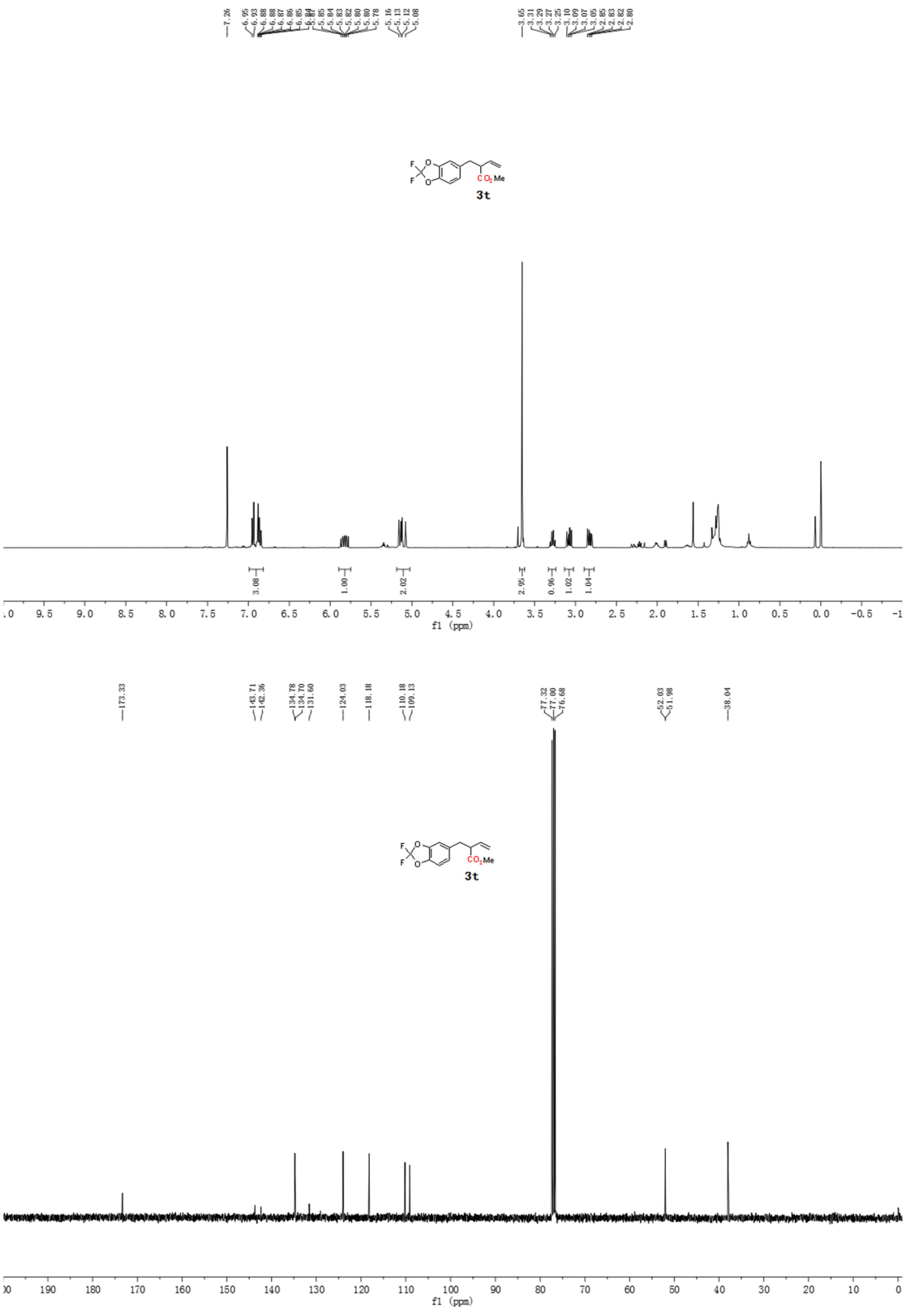
132.32
121.95
117.69
109.35
108.09
100.81
77.32
77.00
76.68
52.22
51.84
38.15


CO2Me

3s


f1 (ppm)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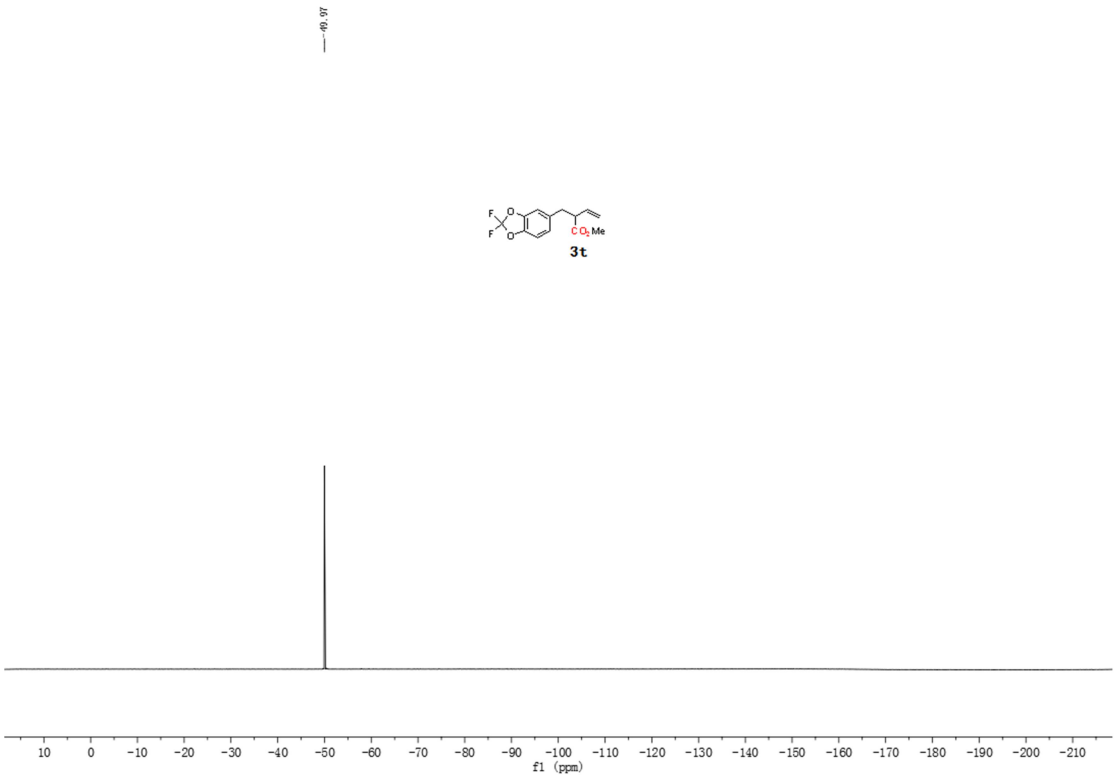
6.87
6.86
6.85
6.84
5.85
5.84
5.82
5.82
5.80
5.80
5.78
5.16
5.13
5.13
5.08
3.65
3.31
3.29
3.27
3.25
3.10
3.09
3.07
3.05
2.85
2.83
2.82
2.80
CO2Me
3t
3.08
1.00
2.02
2.95
0.96
1.02
1.04
f1 (ppm)
173.33
143.71
142.36
134.78
134.70
131.60
124.03
118.18
110.18
109.13
77.32
77.00
76.68
52.03
51.98
38.04
CO2Me
3t
f1 (ppm)


-49.97
3t
f1 (ppm)


7.26
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7.13
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7.12
7.12
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6.81
6.81
6.81
6.80
6.80
5.88
5.88
5.86
5.86
5.84
5.83
5.19
5.19
5.18
5.16
5.15
5.15
3.68
3.39
3.37
3.36
3.36
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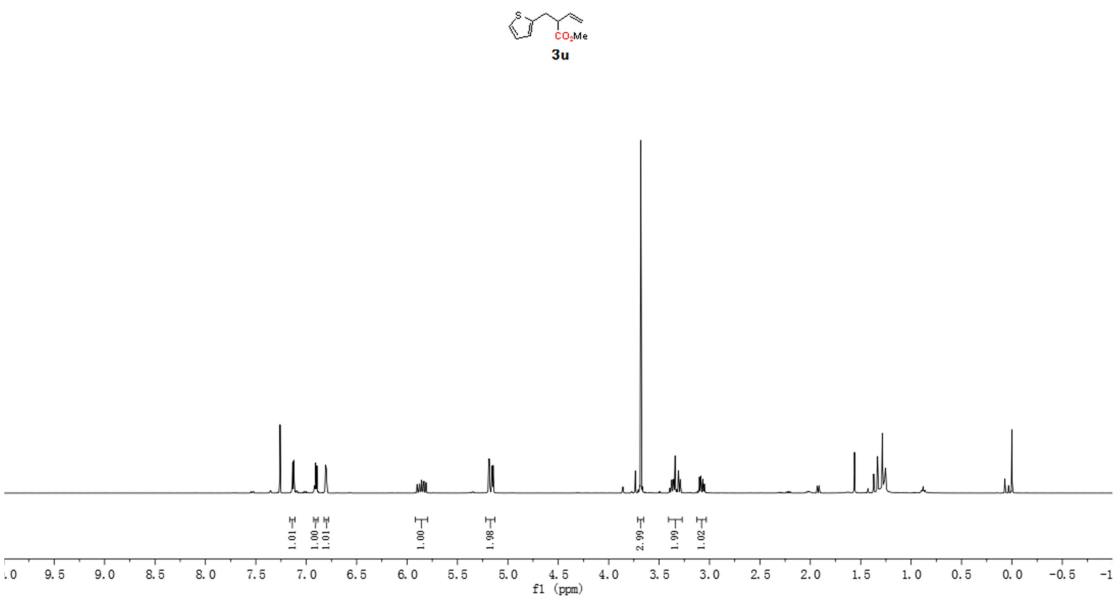
3.32
3.31
3.31
3.29
3.29
3.12
3.10
3.09
3.07
3.05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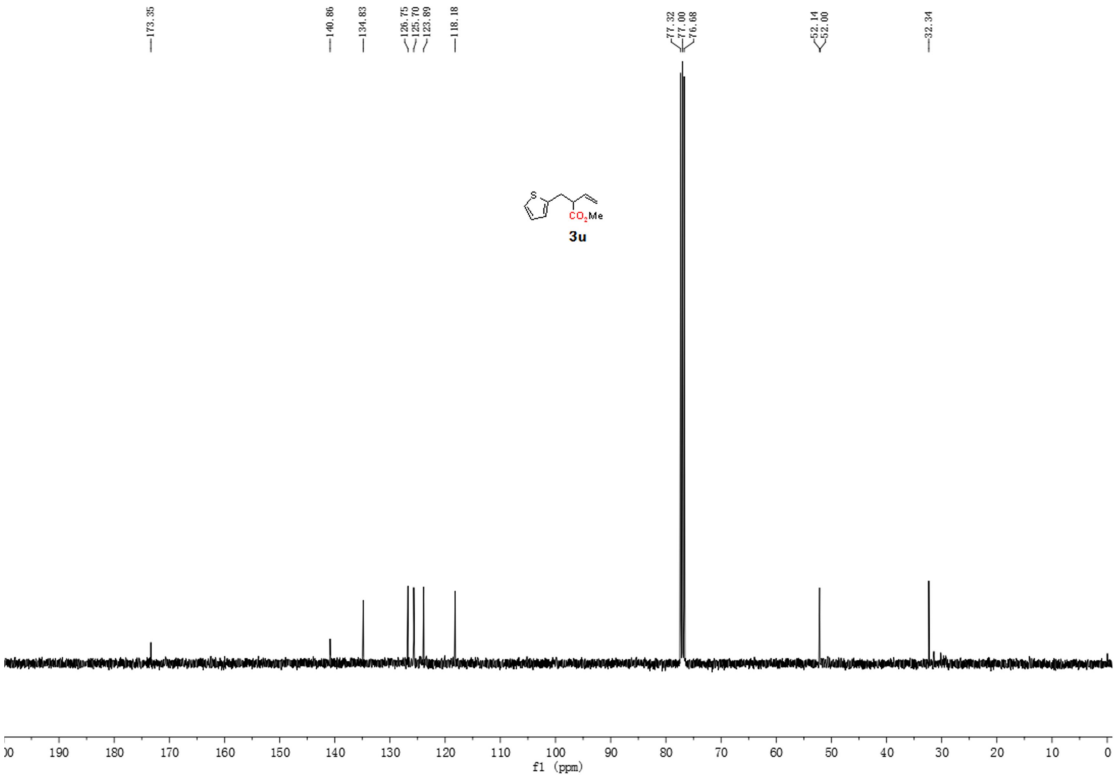
1.00
1.01
1.00
1.98
2.99
1.99
1.02
f1 (ppm)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125.70
123.89
118.18
77.32
77.00
76.68
52.14
32.00
32.34
CO2Me
3u
f1 (ppm)


7.41
7.40
7.26
7.24
7.22
7.04
7.04
7.02
7.01
6.42
6.41
6.41
5.92
5.90
5.90
5.88
5.88
5.11
5.11
5.11
5.10
5.09
5.06
5.06
5.06
3.77
3.63
3.42
3.40
3.38
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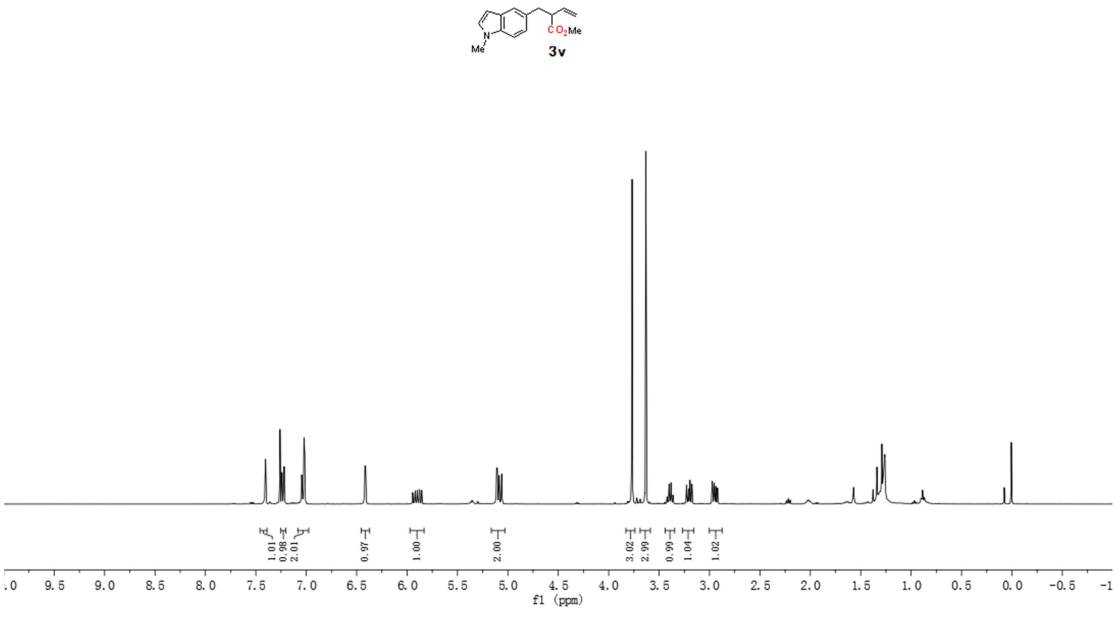
3.23
3.21
3.19
3.17
2.97
2.95
2.94
2.92


N
Me
CO2Me
3v
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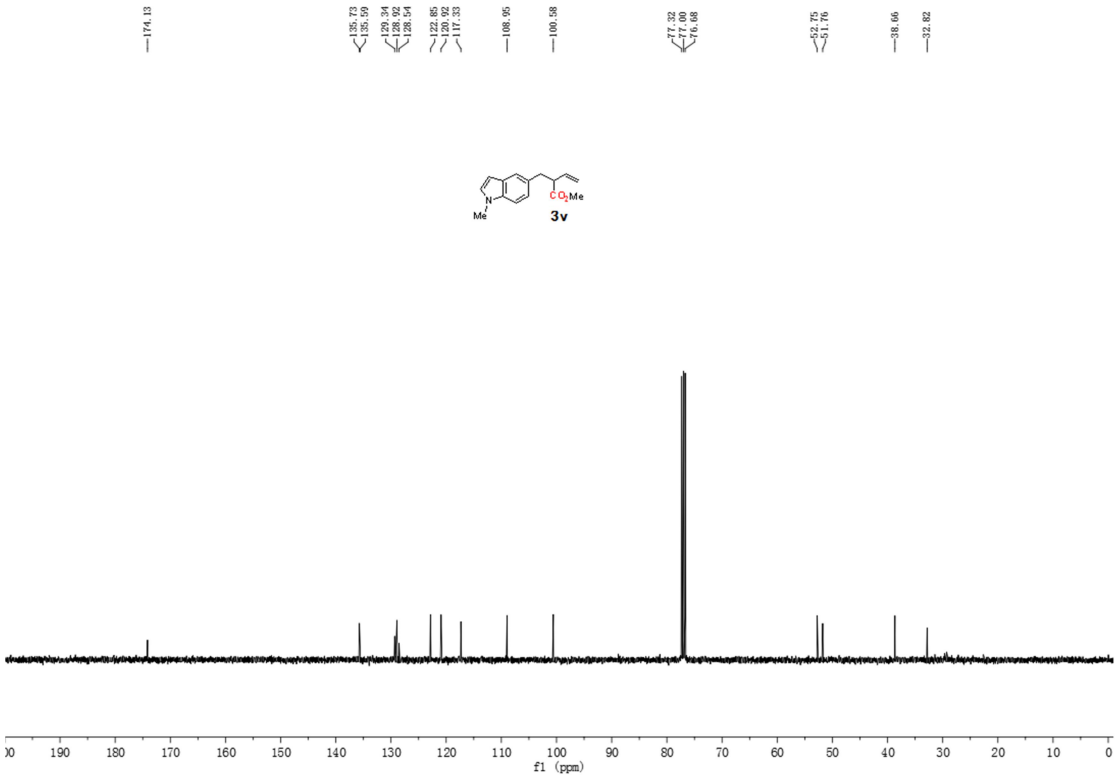
0.98
2.01
0.97
1.00
2.00
3.02
2.99
0.99
1.04
1.02
f1 (ppm)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120.92
117.33
108.95
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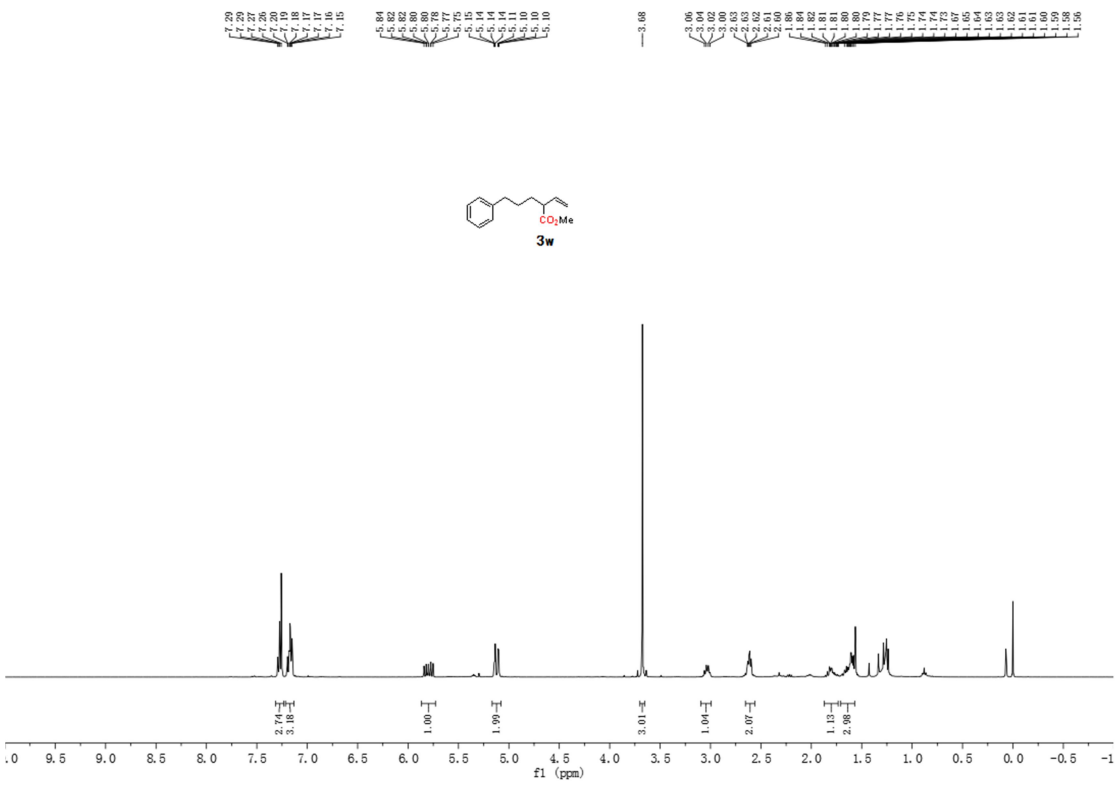
77.00
76.68
52.75
51.76
38.66
32.82
N
Me
CO2Me
3v
f1 (ppm)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7.17
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7.16
7.15
5.84
5.82
5.82
5.80
5.80
5.78
5.77
5.75
5.15
5.14
5.14
5.11
5.10
5.10
5.10
3.68
3.06
3.04
3.02
3.00
2.63
2.62
2.61
2.60
1.86
1.84
1.82
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1.81
1.80
1.80
1.79
1.79
1.77
1.77
1.76
1.75
1.75
1.74
1.74
1.73
1.67
1.65
1.64
1.63
1.63
1.62
1.61
1.61
1.60
1.59
1.58
1.56
CO2Me
3w
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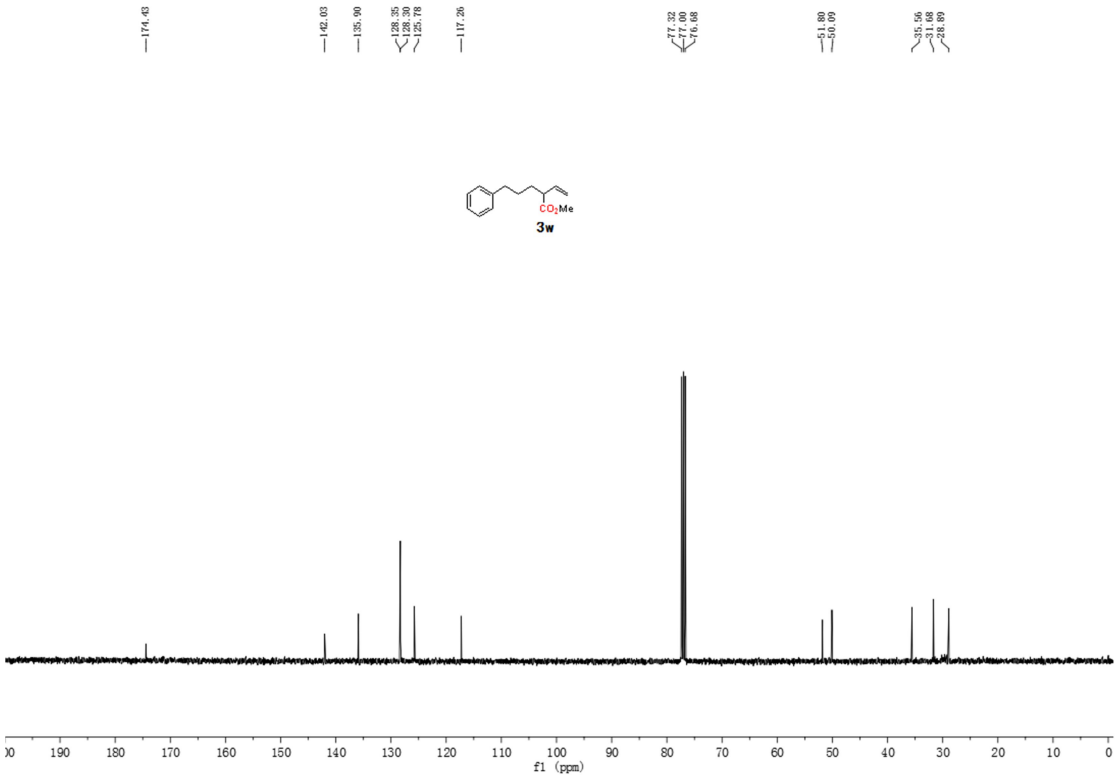
3.01
1.04
2.07
1.13
2.98
f1 (ppm)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125.78
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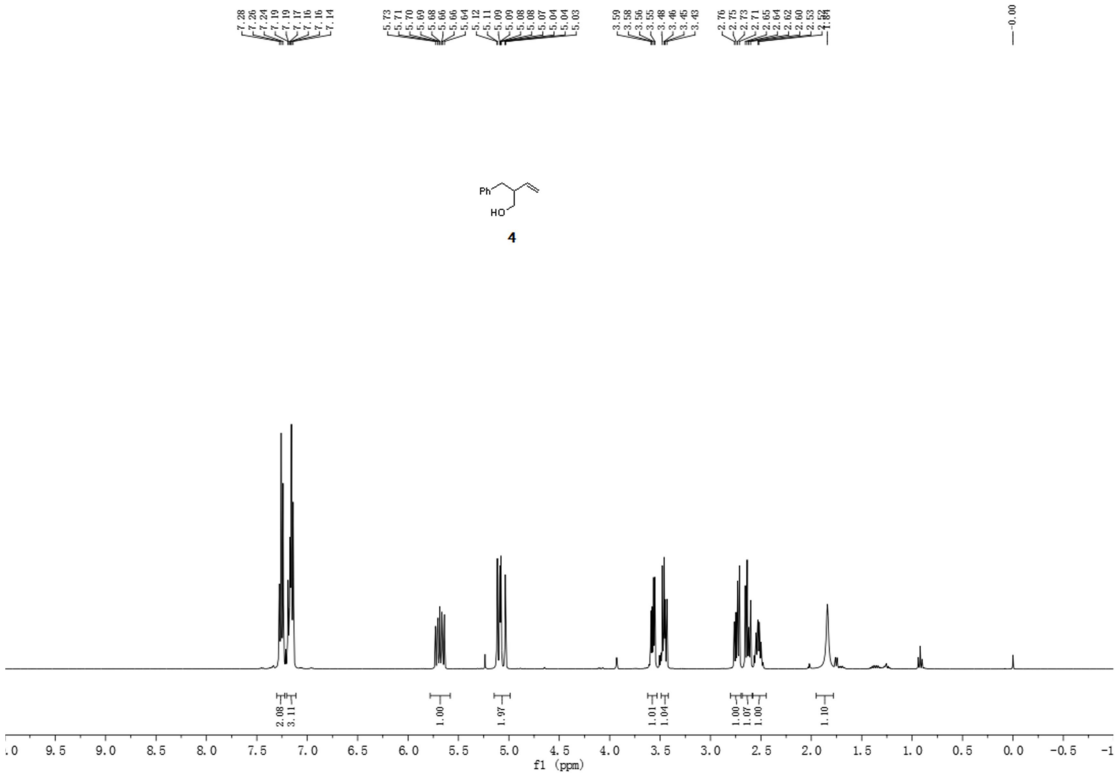
77.00
76.68
51.80
50.09
35.56
31.68
28.89
CO2Me
3w
f1 (ppm)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5.09
5.08
5.08
5.07
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3.58
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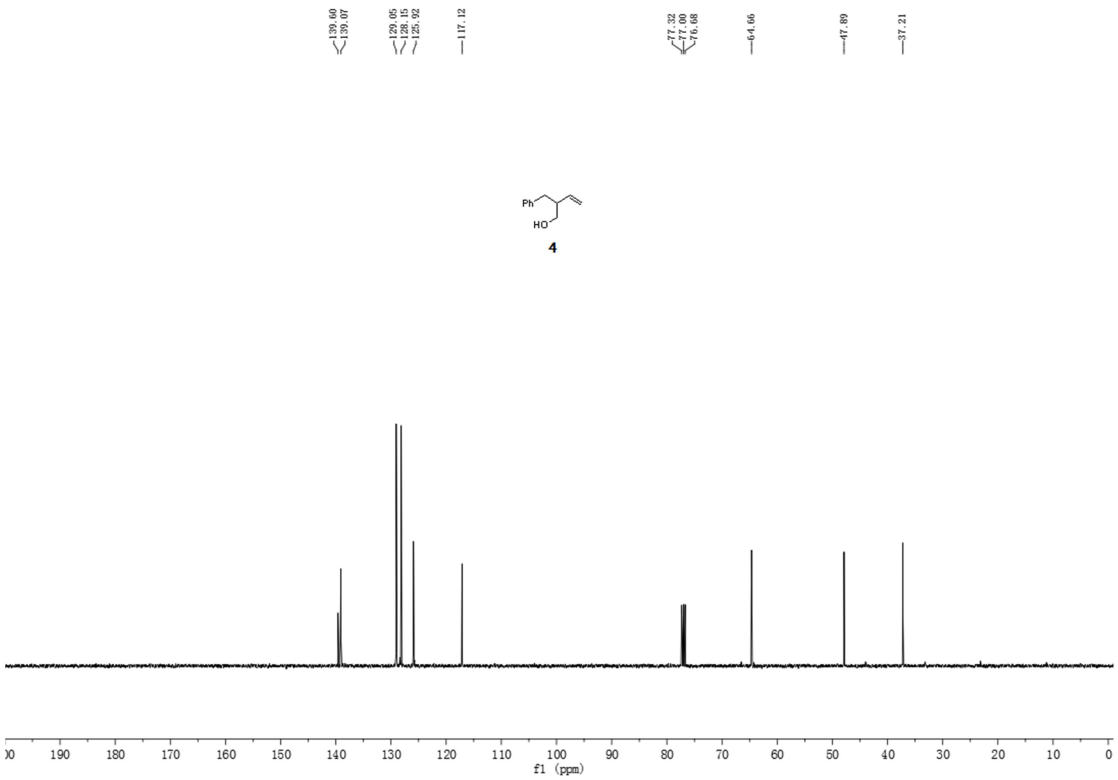
3.43
2.76
2.75
2.73
2.71
2.65
2.64
2.62
2.60
2.53
2.52
1.84
0.00
Ph
HO
4
2.08
3.11
1.00
1.97
1.01
1.04
1.00
1.07
1.00
1.10
f1 (ppm)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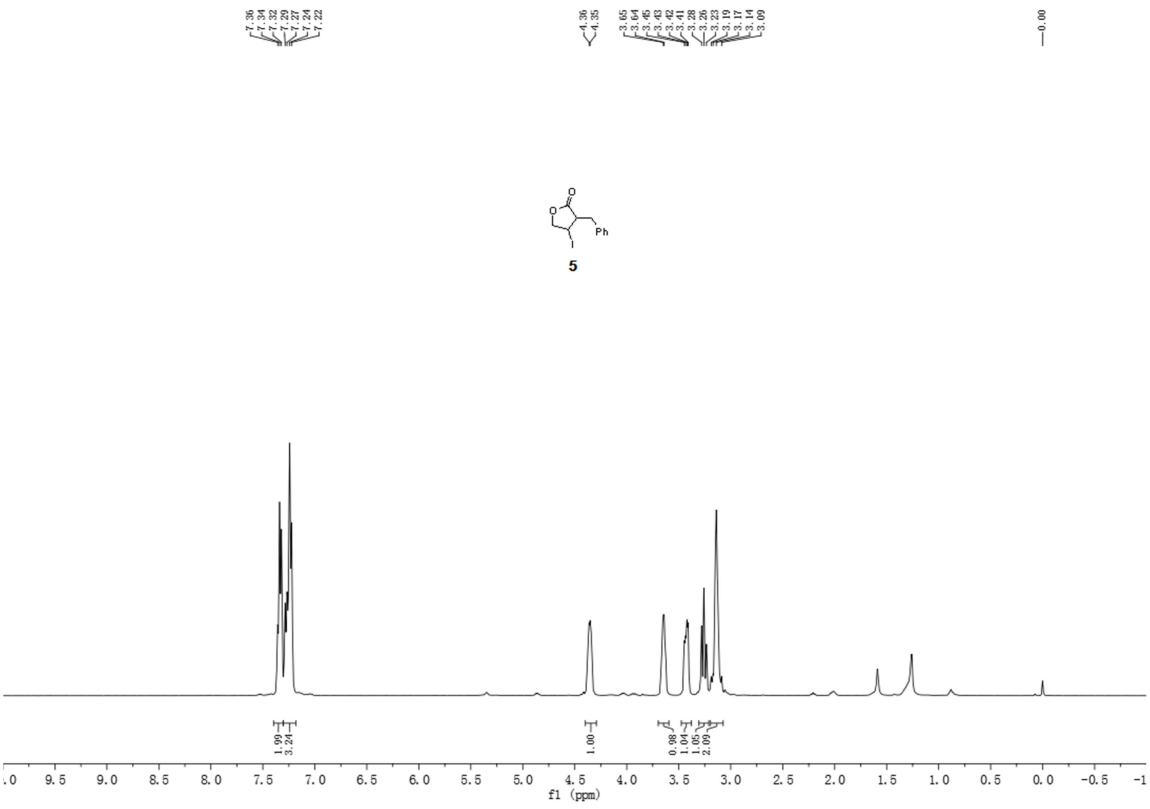
77.32
77.00
76.68
64.66
47.89
37.21
Ph
HO
4
f1 (ppm)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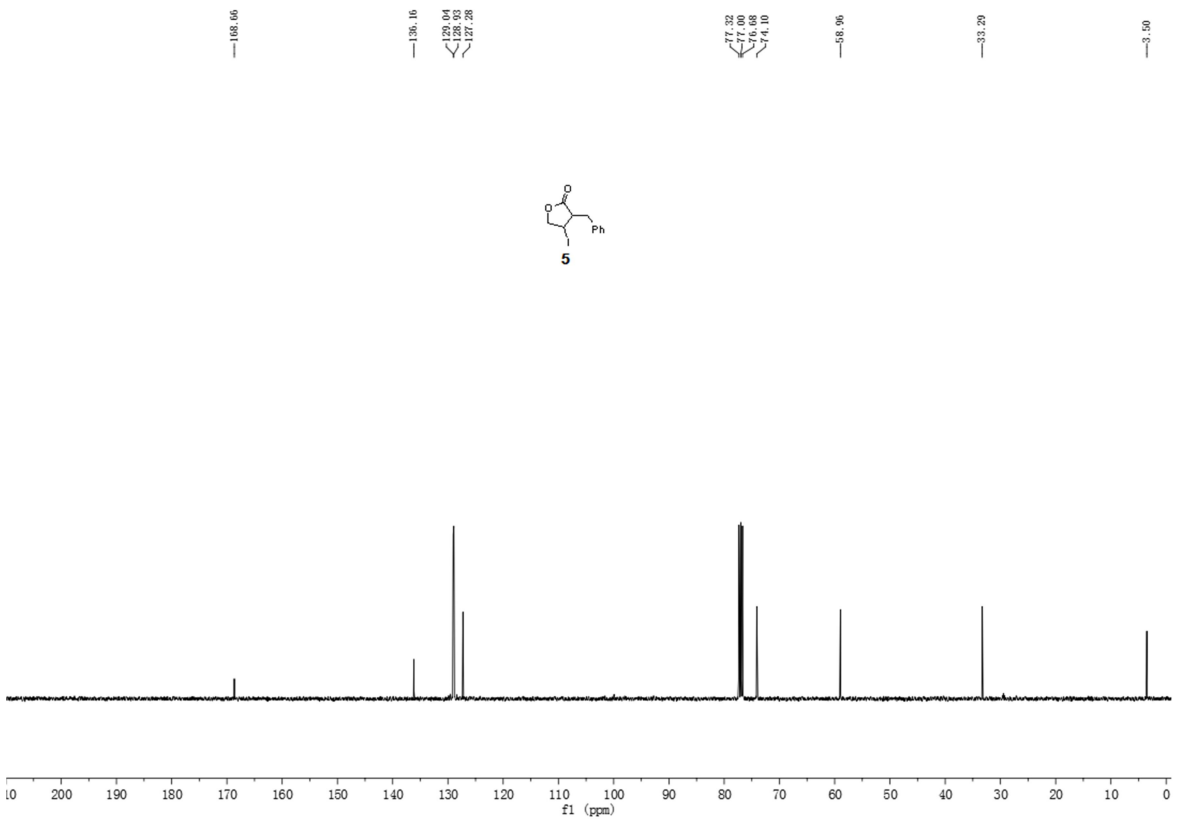
3.65
3.64
3.43
3.42
3.41
3.28
3.25
3.23
3.19
3.17
3.14
3.09
0.00
O
O
I
Ph
5
1.99
3.24
1.00
0.98
1.04
1.05
2.09
f1 (ppm)


168.66
136.16
129.04
128.93
127.28
77.32
77.00
76.68
74.10
58.96
33.29
3.50
O
O
O
Ph
I
5
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)