Supporting Information

For the article entitled

Access to Axially Chiral Aryl 1, 3-Dienes by Transient Group Directed Asymmetric C-H Alkenylations

Cong Shen, Yuhang Zhu, Wenzhou Shen, Shuqi Jin, Guofu Zhong,* Shuxin Luo, Lixia Xu, Liangjun Zhong, and Jian Zhang*
zgf@hznu.edu.cn; zhangjian@hznu.edu.cn

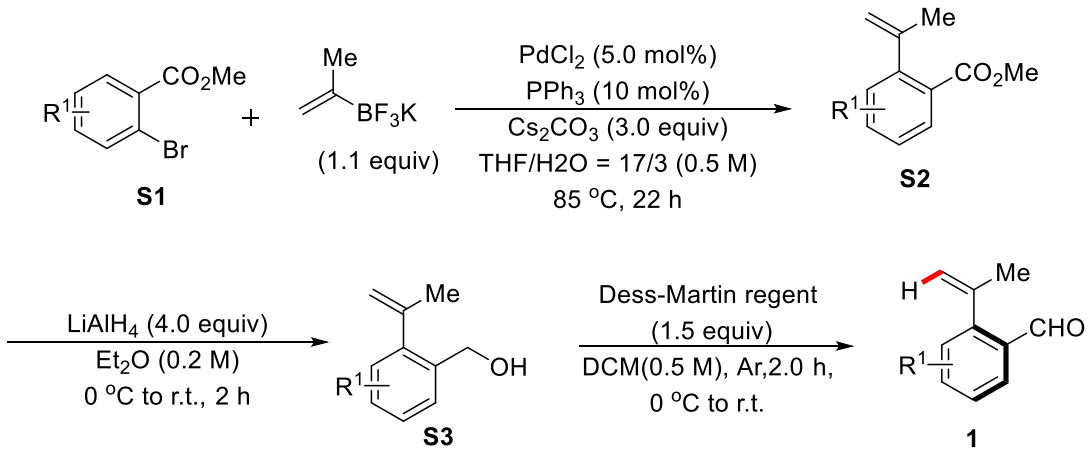
Table of Contents

1. General Methods

Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate. Flash column chromatography was performed using Merck aluminium oxide 90 active neutral with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on Bruker AMX 400 spectrophotometer ($CDCl_3$ as solvent), and Bruker AMX 500 spectrophotometer ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 7.26, singlet). Multiplicities were given as: s (singlet), d (doublet), t (triplet), dd (doublets of doublet) or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a J value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 77.0, triplet). Mass spectrometry was performed by Waters Q-Tof Premier Micromass instrument, using Electro Spray Ionization (ESI) mode. IR spectra were recorded as thin films on KBr plates on a Bio-Rad FTS 165 FTIR spectrometer and are reported in frequency of absorption (cm^{-1}). The enantiomeric excesses (ee) of the products were determined by chiral stationary phase HPLC with Chiralpak (AD-H, OD-H, IA-H, IC-H, IB-H). Optical rotations were measured with Rudolph Autopol IVT. The single crystal X-ray diffraction studies were carried out on a Bruker D8 Venture diffractometer. $Pd(OAc)_2$ were purchased from TCI and used directly. Other reagents, unless otherwise noted below, are commercially available from TCI, Energy Chemical, Alfa Aesar (China) Chemical Co. Ltd. and used without further purification.

2. General Procedure for Substrate Synthesis

2.1 General Procedure A for Substrate Synthesis

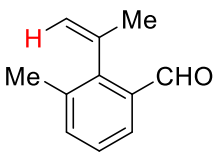


General Procedure for Heck Reaction: A solution of potassium vinyl trifluoro borate (1.1 equiv), $PdCl_2$ (5.0 mol%), PPh_3 (10 mol%), Cs_2CO_3 (3.0 equiv), and substituted ester **(S1)** (5.00 mmol) in THF/H_2O (17:3) (0.5 M) was heated at 85 °C under N_2 atmosphere in a sealed tube. The reaction mixture was stirred at 85 °C for 22 h, then cooled to r.t. and diluted with H_2O (3 mL) followed by extraction with EtOAc (30 mL × 3). The solvent was removed in vacuo, and the crud product was purified by silica gel chromatography (SiO_2, PE/EA = 98/2) to obtain the corresponding product Ester **(S2)**.

General Procedure for Ester Reduction[1] : To a solution of substituted Ester **(S2)** in Et_2O (0.2 M) was added dropwise $LiAlH_4$ (4.0 equiv) over 30 min at 0°C and stirred for 2 h at r.t. 2 M HCl was added slowly to until a clear solution was obtained. The Et_2O layer was separated and the aqueous phase was extracted with Et_2O (20 mL x 3). Combined the organic layers and dried over Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with PE/EA to obtain the corresponding product alcohol **(S3).**

General Procedure for Aldehyde Preparation[2] : To a solution of Dess-Martin regent (1.5 equiv)in DCM (0.5 M) was added dropwise substituted alcohol **(S3)** at 0°C and stirred at r.t. for 2 h. The solvent was removed in vacuo, and the resulting residue was purified by silica gel column chromatography to obtain the

corresponding product benzaldehyde derivatives **(1)**.



3-methyl-2-(prop-1-en-2-yl) benzaldehyde (1a)

Following the general procedure A, **1a** was obtained as a yellow oil (0.6 g, 75% yield for three steps).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.19 (s, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.29 (t, J = 7.5 Hz, 1H), 5.48 (t, J = 1.5 Hz, 1H), 4.92 – 4.91 (m, 1H), 2.33 (s, 3H), 2.08 (s, 3H).

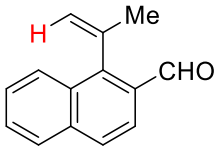
^{13}C NMR (125 MHz, $CDCl_3$)

δ 191.85, 146.24, 140.31, 134.89, 134.60, 132.02, 126.04, 123.85, 117.01, 24.39, 17.76.

HRMS (ESI) for $C_{11}H_{13}O$ $[M+H]^+$: 161.0961, found: 161.0969.

FTIR (KBr, cm^{-1})

3441.54, 3423.43, 2354.21, 1650.47, 1630.84, 1557.94, 1504.67, 1398.13, 1022.43.



1-(prop-1-en-2-yl)-2-naphthaldehyde (1b)

Following the general procedure A, **1b** was obtained as a reddish brown oil (0.68 g, 69% yield for three steps).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.42 (s, 1H), 8.11 (dd, J = 8.5, 1.0 Hz, 1H), 7.97 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.5 Hz, 1H), 7.64 – 7.61 (m, 1H), 7.58 – 7.55 (m, 1H), 5.74 (t, J = 1.5 Hz, 1H), 5.16 (s, 1H), 2.27 (s, 3H).

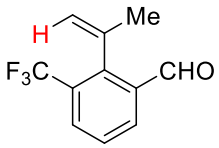
^{13}C NMR (125 MHz, $CDCl_3$)

δ 191.65, 147.75, 138.86, 135.25, 129.83, 128.33, 127.81, 127.38, 126.75, 125.87, 125.68, 121.12, 118.84, 25.75.

HRMS (ESI) for $C_{14}H_{13}O$ $[M+H]^+$: 197.0961, found: 197.0962.

FTIR (KBr, cm^{-1})

3473.23, 3442.38, 3417.86, 2982.24, 2931.78, 1675.70, 1653.27, 1630.84, 1605.61, 1409.35, 1386.92, 1266.36, 1106.54, 1025.23, 798.13.



2-(prop-1-en-2-yl)-3-(trifluoromethyl) benzaldehyde (1c)

Following the general procedure A, **1c** was obtained as a light yellow oil (0.44 g, 55% yield for three steps).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.24 (s, 1H), 8.12 (dd, J = 7.5, 1.0 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.53 (t, J = 7.5 Hz, 1H), 5.55 (t, J = 1.5 Hz, 1H), 5.08 (s, 1H), 2.16 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 190.12, 145.12 (d, J_{CF} = 1.8 Hz), 137.32, 133.00, 130.38 (q, J_{CF} = 5.3 Hz), 129.65, 128.25 (q, J_{CF} = 29.9 Hz), 126.58, 122.67 (q, J_{CF} = 272.4 Hz), 119.00 (d, J_{CF} = 1.4 Hz), 25.76.

^{19}F NMR (471 MHz, $CDCl_3$)

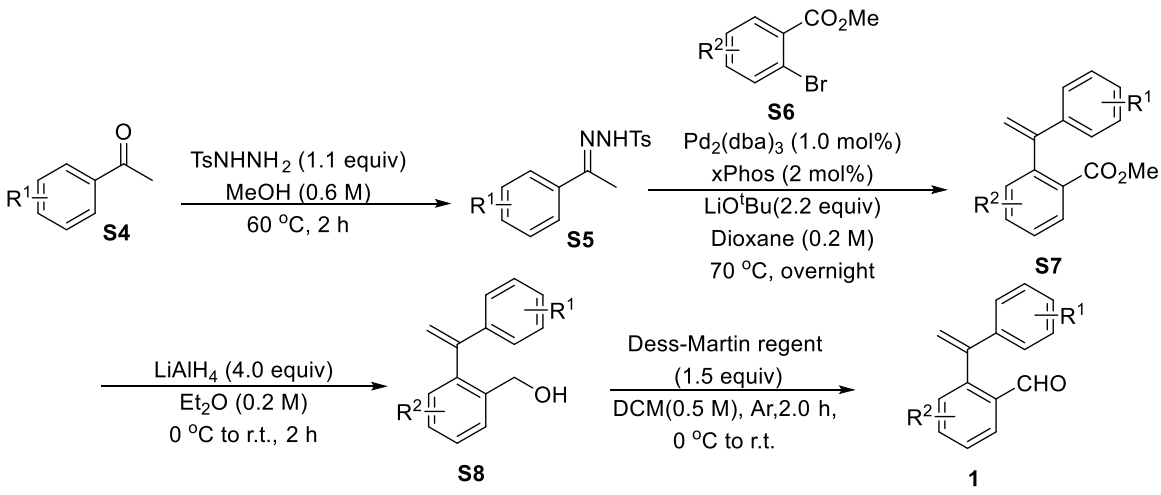
δ -58.32.

HRMS (ESI) for $C_{11}H_{10}OF_3$ $[M+H]^+$: 215.0678, found: 215.0687.

FTIR (KBr, cm^{-1})

3424.87, 2923.36, 2357.01, 1664.49, 1653.27, 1639.25, 1400.93, 1386.92, 1028.04, 798.13, 666.36.

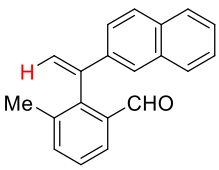
2.2 General Procedure B for Substrate Synthesis



General Procedure for Hydrazide Preparation[3]: To a solution of $TsNHNH_2$ (1.1 equiv) in MeOH (0.5 M) was added dropwise substituted ketone **(S4)** at 60°C and stirred for 2 h. The solvent was removed in vacuo, and the resulting residue was purified by silica gel column chromatography (PE / EA = 1 / 1) to obtain the corresponding product **(S5)**.

General Procedure for Heck Reaction: A solution of $Pd_2(dba)_3$ (1.0 mol%), X-Phos (2.0 mol%), LiO^tBu (2.2 equiv), substituted ester **(S6)** (5.00 mmol) and Hydrazide (**S5**) (5.00 mmol) in Dioxane (0.2 M) was heated stirred at 85 °C overnight under Ar atmosphere in a sealed tube. Then cooled to r.t. and diluted with H_2O (20 mL) followed by extraction with EtOAc (30 mL × 3). The solvent was removed in vacuo, and the crud product was purified by silica gel chromatography (SiO_2, PE/EA = 98/2) to obtain the corresponding product **(S7)**.

Ester Reduction and **Aldehyde Preparation** were conducted following the general procedure A.



3-methyl-2-(1-(naphthalen-2-yl) vinyl) benzaldehyde (1d)

Following the general procedure B, **1d** was obtained as a yellow oil (0.33 g, 24% yield for four steps).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.11 (s, 1H), 7.92 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.80 (dd, *J* = 8.0,

1.5 Hz, 1H), 7.68 – 7.65 (m, 2H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.45 – 7.42 (m, 3H), 7.39 (d, *J* = 2.0 Hz, 1H), 6.28 (s, 1H), 5.29 (s, 1H), 2.17 (s, 3H).

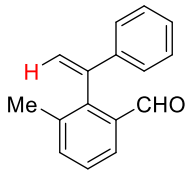
^{13}C NMR (125 MHz, $CDCl_3$)

δ 192.08, 143.70, 142.65, 136.55, 135.61, 134.76, 133.80, 132.28, 132.03, 127.51, 127.35, 126.78, 126.52, 125.45, 125.40, 125.14, 123.73, 122.21, 116.93, 18.34.

HRMS (ESI) for $C_{20}H_{16}ONa$ $[M+ Na]^+$: 295.1093, found: 295.1095.

FTIR (KBr, cm^{-1})

3447.66, 3385.98, 1686.92, 1653.27, 1633.64, 1557.94, 1406.54, 1395.33, 1025.23.



3-methyl-2-(1-phenylvinyl) benzaldehyde (1e)

Following the general procedure B, **1e** was obtained as a yellow oil (0.31 g, 28% yield for four steps).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.08 (s, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.32 – 7.29 (m, 3H), 7.27 – 7.26 (m, 2H), 6.15 (s, 1H), 5.21 (s, 1H), 2.15 (s, 3H).

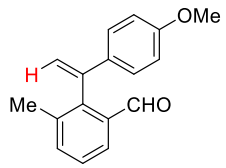
^{13}C NMR (125 MHz, $CDCl_3$)

δ 192.13, 143.71, 142.74, 138.30, 136.48, 134.69, 133.72, 127.71, 127.25, 126.69, 125.09, 123.69, 116.48, 18.35.

HRMS (ESI) for $C_{16}H_{15}O$ $[M+ H]^+$: 223.1117, found: 223.1127.

FTIR (KBr, cm^{-1})

3472.92, 3443.15, 3417.11, 3395.61, 3385.11, 2359.81, 2334.58, 1650.47, 1633.64, 1395.33, 1263.55, 1022.43.



2-(1-(4-methoxyphenyl)vinyl)-3-methylbenzaldehyde (1f)

Following the general procedure B, **1f** was obtained as a yellow oil (0.37 g, 29%

yield for four steps).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.07 (s, 1H), 7.86 (d, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.03 (s, 1H), 5.09 (s, 1H), 3.79 (s, 3H), 2.16 (s, 3H).

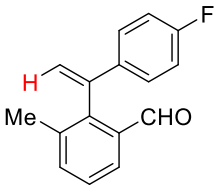
^{13}C NMR (125 MHz, $CDCl_3$)

δ 192.25, 158.64, 144.04, 142.04, 136.44, 134.63, 133.66, 131.04, 126.57, 126.38, 123.55, 114.40, 113.03, 54.27, 18.26.

HRMS (ESI) for $C_{17}H_{17}O_2$ $[M+H]^+$: 253.1223, found: 253.1217.

FTIR (KBr, cm^{-1})

3417.50, 3386.70, 2962.62, 2923.36, 2856.07, 1653.27, 1630.84, 1400.93, 1263.55, 1028.04, 798.13.



2-(1-(4-fluorophenyl)vinyl)-3-methylbenzaldehyde (1g)

Following the general procedure B, **1g** was obtained as a colorless oil (0.54 g, 45% yield for four steps).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.07 (s, 1H), 7.86 (d, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.02 – 6.98 (m, 2H), 6.09 (s, 1H), 5.19 (s, 1H), 2.15 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 191.88, 161.68 (d, J_{CF} = 247.0 Hz), 143.35, 141.70, 136.38, 134.78, 134.49 (d, J_{CF} = 3.4 Hz), 133.63, 126.84, 126.82 (d, J_{CF} = 8.1 Hz), 123.90, 116.17 (d, J_{CF} = 1.6 Hz), 114.66 (d, J_{CF} = 21.5 Hz), 18.29.

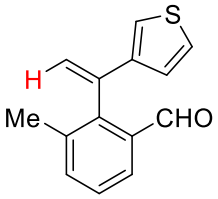
^{19}F NMR (471 MHz, $CDCl_3$)

δ-113.46

HRMS (ESI) for $C_{16}H_{14}OF$ $[M+H]^+$: 241.1023, found: 241.1019.

FTIR (KBr, cm^{-1})

3445.33, 3422.81, 2959.81, 2357.01, 1675.70, 1647.66, 1560.75, 1504.67, 1395.33, 1384.11, 1025.23, 795.33.



3-methyl-2-(1-(thiophen-3-yl)vinyl)benzaldehyde (1h)

Following the general procedure B, **1h** was obtained as a yellow oil (0.33g, 24% yield for four steps).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.06 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.49 – 7.48 (m, 1H), 7.40 – 7.37 (m, 1H), 7.34 – 7.32 (m, 2H), 6.68 (dd, *J* = 3.0, 1.5 Hz, 1H), 6.04 (s, 1H), 5.15 (s, 1H), 2.21 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

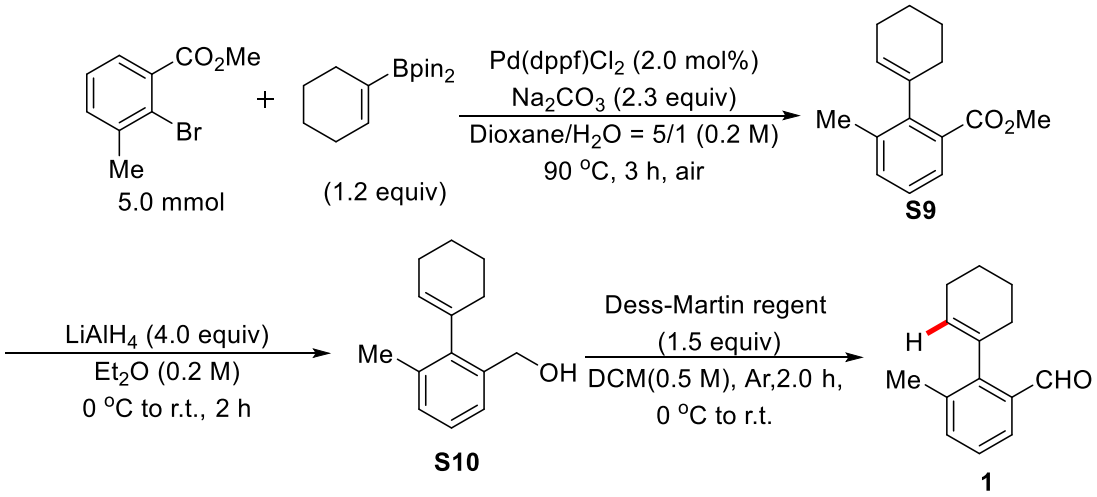
δ 192.02, 143.68, 141.13, 137.89, 136.25, 135.22, 134.69, 126.71, 125.59, 123.68, 123.50, 122.74, 115.09, 18.10.

HRMS (ESI) for $C_{14}H_{12}OSNa$ $[M+ Na]^+$: 251.0501, found: 251.0499.

FTIR (KBr, cm^{-1})

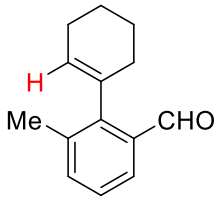
3444.86, 3414.02, 2351.40, 2328.97, 1734.58, 1686.92, 1653.27, 1636.25, 1563.55, 1504.67, 1406.54, 1022.43, 669.16.

2.3 General Procedure C for Substrate Synthesis



General Procedure for Suzuki Reaction: A solution of $Pd(dppf)Cl_2$ (0.1 mmol, 2.0 mol%), Na_2CO_3 (11.5 mmol, 2.3 equiv), methyl 2-bromo-3-methylbenzoate (5.0 mmol, 1.0 equiv) and 2-(cyclohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.00 mmol, 1.2 equiv) in Dioxane/H_2O (5/1, 0.2M) was heated at 90 °C under N_2 atmosphere in a sealed tube. The reaction mixture was stirred at 90 °C for 3 h, then cooled to rt and diluted with H_2O (20 mL) followed by extraction with EtOAc (30 mL × 3). The solvent was removed in vacuo, and the crude product was purified by silica gel chromatography (SiO_2, PE/EtOAc) to obtain the corresponding product (**S9**).

Ester Reduction and **Aldehyde Preparation** were conducted following the general procedure A.



6-Methyl-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-carbaldehyde (1i)

Following the procedure C, **1i** was obtained as a light yellow oil (0.7 g, 70% yield for three steps).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.17 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.28 – 7.25 (m, 1H), 5.63 – 5.60 (m, 1H), 2.29 (s, 3H), 2.26 – 2.21 (m, 3H), 2.10 – 2.03 (m, 1H), 1.84 – 1.78 (m, 2H), 1.77 – 1.70 (m, 2H).

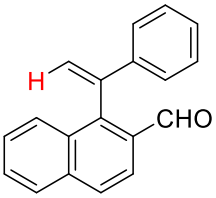
^{13}C NMR (125 MHz, $CDCl_3$)

δ 192.30, 147.08, 135.65, 134.48, 133.31, 132.66, 128.17, 125.77, 123.48, 30.41, 24.35, 21.73, 20.96, 17.80.

HRMS (ESI) for $C_{14}H_{17}O$ $[M+H]^+$: 201.1274, found: 201.1265.

FTIR (KBr, cm^{-1})

3473.28, 3442.36, 3422.95, 1653.27, 1633.64, 1538.32, 1507.48, 1403.74, 1022.43.



1-(1-phenylvinyl)-2-naphthaldehyde (1j)

Following the general procedure C, **1j** was obtained as an orange oil (0.67 g, 26% yield for four steps).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.31 (s, 1H), 8.06 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.91 (dd, *J* = 12.5, 8.5 Hz, 2H), 7.61 – 7.58 (m, 1H), 7.46 – 7.43 (m, 1H), 7.33 – 7.27 (m, 5H), 6.38 (s, 1H), 5.42 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 191.90, 144.78, 141.54, 139.05, 135.29, 131.02, 130.28, 127.82, 127.77, 127.43, 127.38, 127.27, 126.42, 126.01, 125.18, 121.14, 118.13.

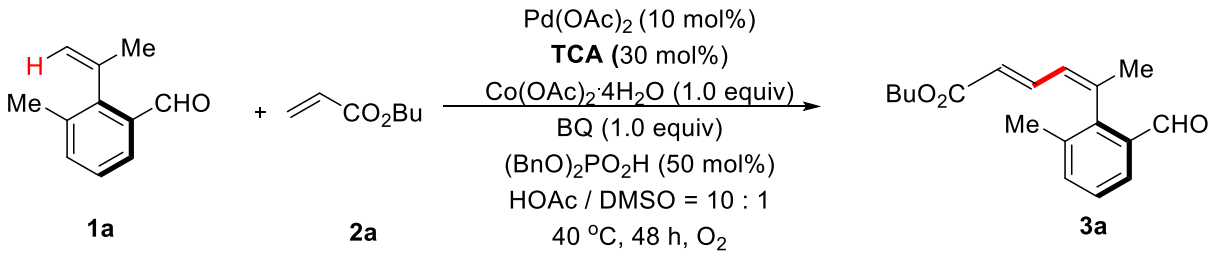
HRMS (ESI) for $C_{19}H_{14}OK$ $[M+K]^+$: 297.0676, found: 297.0691.

FTIR (KBr, cm^{-1})

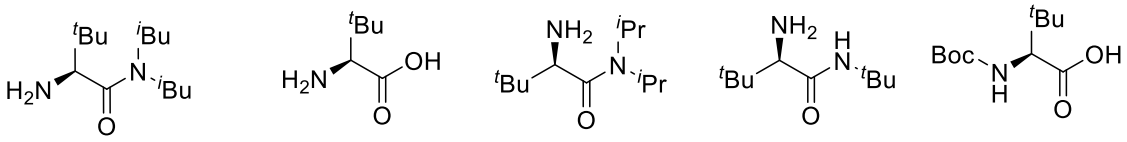
3474.05, 3441.95, 3422.82, 2959.81, 2926.17, 1656.07, 1639.25, 1538.32, 145421, 1398.13, 1022.43.

3. Optimization of Reaction Conditions

Table S1. Preliminary Screening of TCAs [a]



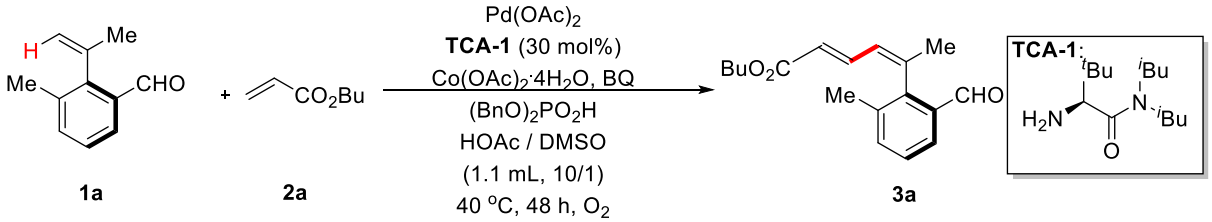
TCAs:



TCA-1	TCA-2	TCA-3	TCA-4	TCA-5
52%, 98% ee	16%, 99% ee	19%, 72% ee	16%, 98% ee	0%

[a] Reactions conditions: **1a** (0.1 mmol), **2a** (0.4 mmol), $Pd(OAc)_2$ (10 mol %), **TCA** (30 mol%), $Co(OAc)_2{\cdot}4H_2O$ (1.0 equiv), BQ (1.0 equiv), $(BnO)_2PO_2H$ (50 mol%) in HOAc/DMSO (10:1, v/v,1.1 mL) under O_2 at 40 °C for 48 h. Isolated yields. The ee value was determined by HPLC .

Table S2. Preliminary Screening of Additives [a]

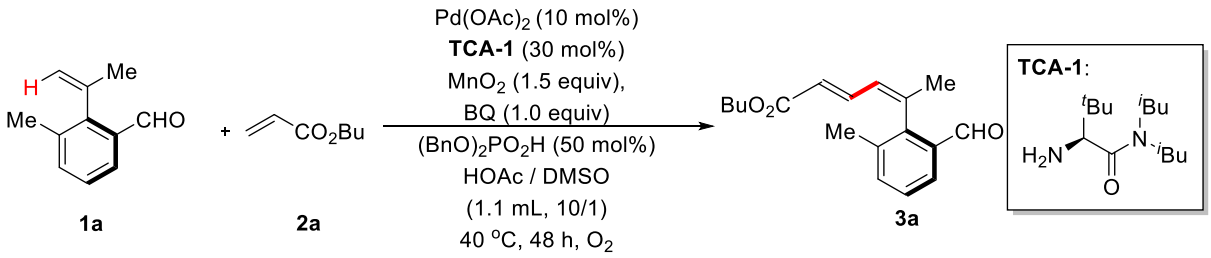


entry	additive	yield (%)[b]	*ee* (%)[c]
1	$Co(OAc)_2{\cdot}4H_2O$ (0.5equiv)	42	98
2	$Co(OAc)_2{\cdot}4H_2O$ (1.5equiv)	33	98
3	BQ (0.5equiv)	33	98
4	BQ (1.5equiv)	29	98
5	$(BnO)_2PO_2H$ (25 mol%)	27	98
6	$(BnO)_2PO_2H$ (75 mol%)	34	98
7	$(BnO)_2PO_2H$ (100 mol%)	36	98
8	**MnO_2 (1.5 equiv) Instead of $Co(OAc)_2{\cdot}4H_2O$(1.0**	**82**	**98**

	equiv)		
9	$Pd(OAc)_2$ (15 mol%)	80	98

[a] Reactions conditions: **1a** (0.1 mmol), **2a** (0.4 mmol), $Pd(OAc)_2$ (10 mol%), **TCA-1** (30 mol%), additives in HOAc/DMSO (10:1, v/v, 1.1 mL) under O_2 at 40 °C for 48 h. [b] Isolated yields. [c] The ee value was determined by HPLC.

Table S3. Further Optimization of Reaction Conditions [a]

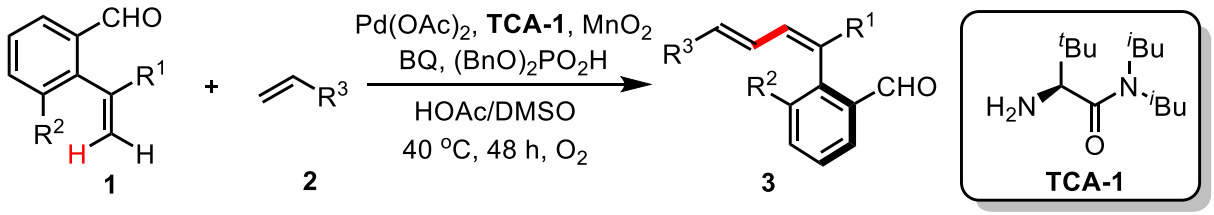


entry	deviation from standard conditions	yield (%)[b]	ee (%)[c]
1	**none**	**82**	**98**
2	MnO_2(1.0 equiv)	69	98
3	MnO_2(2.0 equiv)	60	98
4	25 °C	45	98
5	25 °C, 72 h	38	97
6	(S)-diphenyl(pyrrolidin-2-yl)methanol as ligand	23	13
7	$Pd(OAc)_2$ (5 mol%) **TCA-1** (15 mol%)	48	97

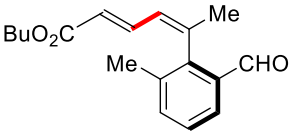
[a] Reactions conditions: **1a** (0.1 mmol), **2a** (0.4 mmol), $Pd(OAc)_2$ (10 mol %), **TCA-1** (30 mol%), MnO_2 (1.5 equiv), BQ (1.0 equiv), $(BnO)_2PO_2H$ (50 mol%) in HOAc/DMSO (v/v, 10:1, 1.1 mL) under O_2 at 40 °C for 48 h. [b] Isolated yields. [c] The ee value was determined by HPLC.

4. General Procedures D for the Cross-Couplings

General Procedure for Atroposelective Cross-Coupling by β-C-H Alkenylation



An screw-cap vial was charged with $Pd(OAc)_2$ (10 mol%, 0.01 mmol) , MnO_2 (1.5 equiv, 0.15 mmol), BQ (1.0 equiv, 0.1 mmol), $(BnO)_2PO_2H$ (0.5 equiv, 0.05 mmol), HOAc (1.0 mL), DMSO (0.1 mL). Then, **TCA-1** (30 mol%, 0.03 mmol), aldehyde **1** (1.0 equiv, 0.1 mmol) and olefin **2** (4.0 equiv, 0.4 mmol) were added into the solution in sequence. The vial was sealed under O_2 and heated to 40 °C with stirring for 48 h. After cooling down, the mixture was directly applied to a flash column chromatography (PE / EA).



Butyl (*R*)-(2*E*,4*Z*)-5-(2-formyl-6-methylphenyl)hexa-2,4-dienoate (3a)

Following the General Procedures D, **3a** was obtained as a yellow oil (23.4 mg, 82% yield, 98% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.00 (s, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 6.71 (dd, *J* = 15.0, 11.5 Hz, 1H), 6.50 (d, *J* = 12.5 Hz, 1H), 5.87 (d, *J* = 15.0 Hz, 1H), 4.05 (t, *J* = 6.5 Hz, 2H), 2.22 (s, 3H), 2.17 (s, 3H), 1.58 – 1.53 (m, 2H), 1.35 – 1.28 (m, 2H), 0.88 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 190.87, 165.95, 143.59, 142.02, 139.30, 135.06, 134.92, 132.05, 127.22, 126.96, 125.57, 120.52, 63.18, 29.60, 25.39, 18.09, 17.74, 12.66.

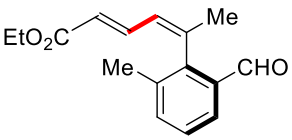
HRMS (ESI) for $C_{18}H_{23}O_3$ $[M+H]^+$: 287.1642, found: 287.1632.

FTIR (KBr, cm^{-1})

3444.17, 3417.83, 3383.41, 2923.36, 2354.21, 1731.78, 1681.31, 1653.27, 1633.64, 1538.32, 1400.93, 1022.43.

Opt. Rot. $[\alpha]^{20}D$ = - 20.7 (c = 0.4, $CHCl_3$)

HPLC Daicel Chiralpak OD-H column, n-hexane/i-PrOH (60/40), 1.0 mL/min, 254 nm, 15.763 min (major enantiomer), 23.606 min (minor enantiomer).



Ethyl (*R*)-(2*E*,4*Z*)-5-(2-formyl-6-methylphenyl)hexa-2,4-dienoate (3b)

Following the General Procedures D, **3b** was obtained as a brown oil (17.4 mg, 67% yield, 98% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.00 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 6.71 (dd, *J* = 15.0, 11.5 Hz, 1H), 6.50 (d, *J* = 12.5 Hz, 1H), 5.87 (d, *J* = 15.0 Hz, 1H), 4.10 (q, *J* = 7.0 Hz, 2H), 2.22 (s, 3H), 2.17 (s, 3H), 1.21 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 190.86, 165.86, 143.55, 142.01, 139.24, 135.52, 135.08, 132.04, 127.25, 126.97, 125.58, 120.59, 59.25, 25.42, 17.74, 13.19.

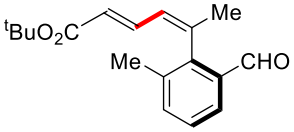
HRMS (ESI) for $C_{16}H_{19}O_3$ $[M+H]^+$: 259.1329, found: 259.1326.

FTIR (KBr, cm^{-1})

3473.40, 3441.43, 3422.79, 2957.01, 2923.36, 2853.27, 2354.21, 2331.78, 1681.31, 1653.27, 1636.45, 1398.13, 1028.04, 798.13, 669.16.

Opt. Rot. $[\alpha]^{20}D$ = - 30.7 (c = 0.4, $CHCl_3$)

HPLC Daicel Chiralpak OD-H column, n-hexane/i-PrOH (60/40), 1.0 mL/min, 254 nm, 17.331 min (major enantiomer), 24.726 min (minor enantiomer).



Tert-Butyl (*R*)-(2*E*,4*Z*)-5-(2-formyl-6-methylphenyl)hexa-2,4-dienoate (3c)

Following the General Procedures D, **3c** was obtained as a yellow oil (21.5 mg, 76% yield,98% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.99 (s, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 6.65 (dd, *J* = 15.0, 11.5 Hz, 1H), 6.47 (d, *J* = 12.5 Hz, 1H), 5.81 (d, *J* = 15.0 Hz, 1H), 2.22 (s, 3H), 2.16 (s, 3H), 1.40 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 190.95, 165.28, 142.85, 142.19, 138.40, 135.04, 134.92, 132.03, 127.25, 126.89, 125.43, 122.38, 79.25, 27.07, 25.38, 17.74.

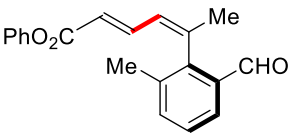
HRMS (ESI) for $C_{18}H_{23}O_3$ $[M+H]^+$: 287.1642, found: 287.1635.

FTIR (KBr, cm^{-1})

3444.95, 3416.76, 3405.25, 3384.98, 2968.22, 2923.36, 2359.81, 2334.58, 1684.11, 1647.66, 1633.64, 1403.74, 1028.04, 803.74, 666.36.

Opt. Rot. $[\alpha]^{20}D$ = - 14.0 (c = 0.4, $CHCl_3$)

HPLC Daicel Chiralpak OD-H column, n-hexane/i-PrOH (98/2), 0.5 mL/min, 254 nm, 18.950 min (major enantiomer), 21.680 min (minor enantiomer).



Phenyl (*R*)-(2*E*,4*Z*)-5-(2-formyl-6-methylphenyl)hexa-2,4-dienoate (3d)

Following the General Procedures D, **3d** was obtained as a yellow solid (21.5 mg, 70% yield, 99% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.02 (s, 1H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.0 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 2H), 6.88 (dd, *J* = 15.0, 11.5 Hz, 1H), 6.59 (d, *J* = 12.0 Hz, 1H), 6.07 (d, *J* = 15.5 Hz, 1H), 2.25 (s, 3H), 2.21 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 190.77, 164.22, 149.64, 145.25, 141.61, 141.16, 135.14, 134.86, 132.06, 128.26, 127.11, 127.05, 125.96, 124.61, 120.51, 119.50, 25.45, 17.76.

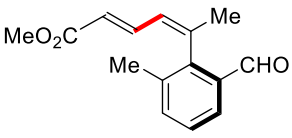
HRMS (ESI) for $C_{20}H_{18}O_3Na$ $[M+ Na]^+$: 329.1148, found: 329.1138.

FTIR (KBr, cm^{-1})

3441.51, 3417.85, 3384.07, 2959.81, 2920.56, 2847.66, 2357.01, 2337.38, 1678.50, 1653.27, 1633.64, 1398.13, 1260.75, 1103.74, 1022.43, 803.74, 669.16.

Opt. Rot. $[\alpha]^{20}D$ = - 25.4 (c = 0.4, $CHCl_3$)

HPLC Daicel Chiralpak IB-H column, n-hexane/i-PrOH (95/5), 0.5 mL/min, 254 nm, 26.432 min (major enantiomer), 28.410 min (minor enantiomer).



Methyl (*R*)-(2*E*,4*Z*)-5-(2-formyl-6-methylphenyl)hexa-2,4-dienoate (3e)

Following the General Procedures D, **3e** was obtained as a yellow solid

(21.5 mg, 76% yield, 98% *ee*, m.p. = 65.0 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.99 (s, 1H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 6.71 (dd, *J* = 15.0, 11.5 Hz, 1H), 6.50 (d, *J* = 12.0 Hz, 1H), 5.87 (d, *J* = 15.5 Hz, 1H), 3.64 (s, 3H), 2.22 (s, 3H), 2.17 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 190.83, 166.23, 143.79, 141.95, 139.44, 135.10, 134.91, 132.04, 127.22, 127.00, 125.62, 120.14, 50.45, 25.41, 17.73.

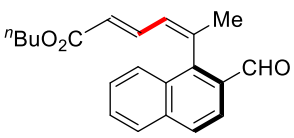
HRMS (ESI) for $C_{15}H_{16}O_3Na$ $[M+ Na]^+$: 267.0992, found: 267.0984.

FTIR (KBr, cm^{-1})

3441.07, 3417.58, 340521, 3384.21, 2957.01, 2920.56, 2351.40, 1647.66, 1633.64, 1400.93, 1384.11, 1022.43.

Opt. Rot. $[\alpha]^{20}D$ = - 2.7 (c = 0.4, $CHCl_3$)

HPLC Daicel Chiralpak OD-H column, n-hexane/i-PrOH (60/40), 1.0 mL/min, 254 nm, 23.133 min (major enantiomer), 34.742 min (minor enantiomer).



butyl (*R*)-(2*E*,4*Z*)-5-(2-formylnaphthalen-1-yl)hexa-2,4-dienoate (3f)

Following the general procedure D, **3f** was obtained as a reddish brown oil (27.5 mg, 85% yield, >99% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.21 (s, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.93 – 7.87 (m, 3H), 7.66 – 7.63 (m, 1H), 7.57 – 7.53 (m, 1H), 6.79 – 6.77 (m, 1H), 6.66 (dd, *J* = 15.0, 11.5 Hz, 1H), 5.91 (d, *J* = 15.0 Hz, 1H), 3.98 (t, *J* = 6.5 Hz, 2H), 2.35 (s, 3H), 1.53 – 1.47 (m, 2H), 1.24 – 1.21 (m, 2H), 0.82 (d, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 190.67, 165.68, 143.89, 141.58, 139.12, 135.43, 129.39, 129.28, 128.68, 128.14, 127.65, 127.64, 126.45, 125.25, 121.52, 121.26, 63.19, 29.54, 26.73, 18.03, 12.60.

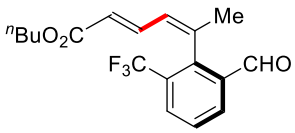
HRMS (ESI) for $C_{21}H_{23}O_3$ [M+ H]$^+$: 323.1642, found: 323.1649.

FTIR (KBr, cm^{-1})

3473.23, 3442.38, 3417.86, 3383.18, 2982.24, 2931.78, 2853.27, 1674.70, 1653.27, 1630.84, 1605.61, 1532.71, 1504.67, 1409.35, 1386.92, 1266.36, 1106.54, 1025.23, 798.13, 669.16.

Opt. Rot. $[\alpha]^{20}D = 73.5$ (c = 0.4, $CHCl_3$)

HPLC Daicel Chiralpak OD-H column, n-hexane/i-PrOH (60/40), 1.0 mL/min, 254 nm, 7.371 min (major enantiomer), 13.580 min (minor enantiomer).



Butyl (*R*)-(2*E*,4*Z*)-5-(2-formyl-6-(trifluoromethyl)phenyl)hexa-2,4-dienoate (3g)

Following the general procedure D, **3g** was obtained as a yellow oil (23.8 mg, 70% yield, > 99% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.99 (s, 1H), 8.11 (d, *J* = 7.5 Hz, 1H), 7.90 (d, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 6.59 (dd, *J* = 15.0, 11.5 Hz, 1H), 6.49 (d, *J* = 11.5 Hz, 1H), 5.82 (d, *J* = 15.0 Hz, 1H), 4.00 – 3.95 (m, 2H), 2.18 (s, 3H), 1.50 – 1.46 (m, 2H), 1.28 – 1.21 (m, 2H), 0.81 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 189.21, 165.65, 141.50 (d, J_{CF} = 1.9 Hz), 141.48, 139.18, 138.77, 132.92, 130.80 (q, J_{CF} = 5.1 Hz), 129.33 (d, J_{CF} = 1.0 Hz), 128.44 (q, J_{CF} = 30.3 Hz), 127.53, 122.38 (q, J_{CF} = 272.6 Hz), 121.29, 63.27, 29.57, 26.52, 18.07, 12.65.

^{19}F NMR (471 MHz, $CDCl_3$)

δ -59.30.

HRMS (ESI) for $C_{18}H_{20}O_3F_3$ [M+ H]$^+$: 341.1359, found: 341.1356.

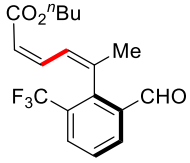
FTIR (KBr, cm^{-1})

3473.34, 3443.73, 3423.12, 2954.21, 2917.76, 2853.27, 2348.62, 2331.78, 1656.07,

1628.04, 1608.41, 1541.12, 1504.67, 1400.93, 1016.82, 669.16.

Opt. Rot. $[\alpha]^{20}D$ = - 46.5 (c = 2.0, $CHCl_3$)

HPLC Daicel Chiralpak OD-H column, n-hexane/i-PrOH (60/40), 1.0 mL/min, 254 nm, 9.301 min (major enantiomer), 26.712 min (minor enantiomer).



Butyl (*R*)-(2Z,4Z)-5-(2-formyl-6-(trifluoromethyl)phenyl)hexa-2,4-dienoate (3 g')

Following the general procedure D, **3g'** was obtained as a light yellow oil (8.0 mg, 23% yield, >99% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.06 (s, 1H), 8.18 (d, *J* = 7.4 Hz, 1H), 7.97 (d, *J* = 7.5 Hz, 1H), 7.82 (d, *J* = 11.5 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 5.97 (t, *J* = 11.5 Hz, 1H), 5.52 (d, *J* = 11.5 Hz, 1H), 4.14 (t, *J* = 6.5 Hz, 2H), 2.29 (s, 3H), 1.68 – 1.61 (m, 2H), 1.45 – 1.37 (m, 2H), 0.95 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 189.42, 165.23, 141.97 (q, J_{CF} = 1.6 Hz), 139.30, 138.54, 133.09, 130.71 (q, J_{CF} = 5.0 Hz), 130.13 (d, J_{CF} = 0.5 Hz), 128.46 (q, J_{CF} = 30.4 Hz), 127.61 (d, J_{CF} = 0.8 Hz), 127.36, 122.36 (q, J_{CF} = 272.6 Hz), 117.45, 63.08, 29.67, 26.66, 18.18, 12.70.

^{19}F NMR (471 MHz, $CDCl_3$)

δ -59.44.

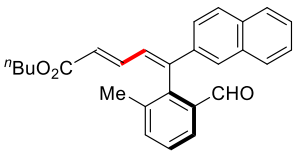
HRMS (ESI) for $C_{18}H_{20}O_3F_3$ $[M+H]^+$: 341.1359, found: 341.1369.

FTIR (KBr, cm^{-1})

3473.29, 3441.49, 3417.39, 3385.39, 2957.01, 2926.17, 2357.01, 2337.38, 1650.47, 1630.84, 1541.12, 1507.48, 1457.01, 1400.93, 1386.92, 1016.82.

Opt. Rot. $[\alpha]^{20}D$ = 49.2 (c = 0.4, $CHCl_3$)

HPLC Daicel Chiralpak OD-H column, n-hexane/i-PrOH (92/8), 1.0 mL/min, 254 nm, 6.403 min (major enantiomer), 4.757 min (minor enantiomer).



Butyl (*R*)-(2*E*,4*Z*)-5-(2-formyl-6-methylphenyl)-5-(naphthalen-2-yl)penta -2,4-dienoate (3h)

Following the general procedure D, **3h** was obtained as a yellow oil (28.2 mg, 71% yield, >99% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.92 (s, 1H), 7.95 (d, *J* = 7.5 Hz, 1H), 7.84 (d, *J* = 9.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.69 – 7.66 (m, 2H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.45 – 7.42 (m, 1H), 7.41 (d, *J* = 1.0 Hz, 1H), 7.33 (d, *J* = 10.5 Hz, 1H), 6.89 (dd, *J* = 15.0, 11.5 Hz, 1H), 6.13 (d, *J* = 15.0 Hz, 1H), 4.09 (d, *J* = 13.0 Hz, 2H), 2.14 (s, 3H), 1.60 – 1.57 (m, 2H), 1.37 – 1.30 (m, 2H), 0.90 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 191.04, 165.65, 143.63, 139.80, 139.36, 136.76, 135.21, 135.15, 133.68, 132.47, 132.27, 127.76, 127.65, 127.58, 126.56, 126.32, 126.27, 126.01, 125.64, 124.74, 122.90, 122.01, 63.31, 29.61, 18.18, 18.11, 12.68.

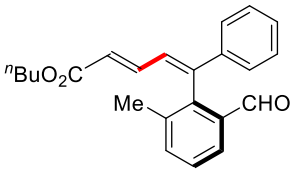
HRMS (ESI) for $C_{27}H_{26}O_3Na$ $[M+ Na]^+$: 421.1774, found: 421.1766.

FTIR (KBr, cm^{-1})

3456.07, 3414.02, 3385.98, 3231.78, 2957.01, 2357.01, 1684.11, 1656.07, 1633.64, 1560.75, 1541.12, 1510.28, 1406.54, 1395.33, 1030.84, 666.36.

Opt. Rot. $[\alpha]^{20}D$ = - 4.9 (c = 0.4, $CHCl_3$)

HPLC Daicel Chiralpak OD-H column, n-hexane/i-PrOH (85/15), 1.0 mL/min, 254 nm, 11.377 min (major enantiomer), 6.578 min (minor enantiomer).



Butyl (*R*)-(2E,4Z)-5-(2-formyl-6-methylphenyl)-5-phenylpenta-2,4-dieno ate (3i)

Following the general procedure D, **3i** was obtained as a yellow oil (30.8 mg, 89% yield, 99% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.89 (s, 1H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.34 – 7.31 (m, 3H), 7.29 – 7.26 (m, 2H), 7.19 (d, *J* = 11.5 Hz, 1H), 6.86 (dd, *J* = 15.0, 11.5 Hz, 1H), 6.08 (d, *J* = 15.0 Hz, 1H), 4.07 (t, *J* = 6.5 Hz, 2H), 2.12 (s, 3H), 1.58 (p, *J* = 7.0 Hz, 2H), 1.37 – 1.29 (m, 2H), 0.90 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 191.03, 165.64, 143.74, 139.79, 139.32, 137.80, 136.65, 135.13, 133.56, 128.19, 127.94, 127.56, 125.89, 125.53, 124.68, 122.86, 63.30, 29.60, 18.17, 18.10, 12.68.

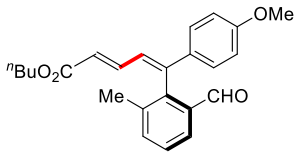
HRMS (ESI) for $C_{23}H_{25}O_3$ $[M+H]^+$: 349.1798, found: 349.1801.

FTIR (KBr, cm^{-1})

3473.04, 3441.86, 3416.71, 3395.58, 3385.80, 2957.01, 2354.21, 1653.27, 1636.45, 1614.02, 1541.12, 1504.67, 1406.54, 1019.63.

Opt. Rot. $[\alpha]^{20}D$ = - 18.1 (c = 0.8, $CHCl_3$)

HPLC Daicel Chiralpak OD-H column, n-hexane/i-PrOH (95/5), 0.5 mL/min, 254 nm, 19.882 min (major enantiomer), 18.111 min (minor enantiomer).



Butyl (*R*)-(2*E*,4*Z*)-5-(2-formyl-6-methylphenyl)-5-(4-methoxyphenyl)penta-2,4-dienoate (3j)

Following the general procedure D, **3j** was obtained as a yellow oil (29.6 mg, 78% yield, 98% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.87 (s, 1H), 7.90 (d, *J* = 7.5 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 9.0 Hz, 2H), 7.10 (d, *J* = 11.5 Hz, 1H), 6.86 – 6.80 (m, 3H), 6.03 (d, *J* = 15.0 Hz, 1H), 4.06 (t, *J* = 6.5 Hz, 2H), 3.80 (s, 3H), 2.11 (s, 3H), 1.59 – 1.56 (m, 2H), 1.36 – 1.30 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 191.18, 165.82, 159.49, 143.28, 140.11, 139.70, 136.59, 135.08, 133.53, 130.44, 127.46, 127.00, 124.46, 123.93, 121.71, 113.36, 63.21, 54.34, 29.62, 28.68, 18.08, 12.68.

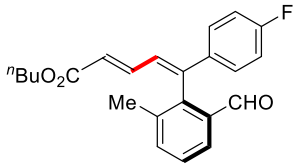
HRMS (ESI) for $C_{24}H_{27}O_4$ $[M+H]^+$: 379.1904, found: 379.1911.

FTIR (KBr, cm^{-1})

3444.52, 3422.80, 3404.70, 3383.99, 2965.42, 2923.36, 2853.27, 2354.21, 2328.97, 1670.09, 1653.27, 1630.84, 1400.93, 1384.11, 1263.55, 1100.93, 1028.04, 800.93, 666.36.

Opt. Rot. $[\alpha]^{20}D$ = - 12.4 (c = 0.4, $CHCl_3$)

HPLC Daicel Chiralpak OD-H column, n-hexane/i-PrOH (80/20), 1.0 mL/min, 254 nm, 7.150 min (major enantiomer), 5.690 min (minor enantiomer).



Butyl (*R*)-(2*E*,4*Z*)-5-(4-fluorophenyl)-5-(2-formyl-6-methylphenyl)penta-2,4-dienoate (3k)

Following the general procedure D, **3k** was obtained as a white oil (30.6 mg, 84% yield, > 99% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.88 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 3.5 Hz, 1H), 7.25 (d, *J* = 5.5 Hz, 1H), 7.11 (d, *J* = 11.5 Hz, 1H), 7.02 (t, *J* = 8.5 Hz, 2H), 6.85 – 6.80 (m, 1H), 6.08 (d, *J* = 15.0 Hz, 1H), 4.07 (t, *J* = 6.5 Hz, 2H), 2.11 (s, 3H), 1.61 – 1.55 (m, 2H), 1.33 – 1.29 (m, 2H), 0.90 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 190.82, 165.60, 162.17 (d, J_{CF} = 249.3 Hz), 142.63, 139.37, 139.18, 136.59, 135.23, 134.02 (d, J_{CF} = 3.4 Hz), 133.49, 127.72, 127.34 (d, J_{CF} = 9.4 Hz), 125.57 (d, J_{CF} = 1.8 Hz), 125.09, 122.90, 114.64 (d, J_{CF} = 21.6 Hz), 76.20, 63.33, 29.59, 18.12, 18.10, 12.67.

^{19}F NMR (471 MHz, $CDCl_3$)

δ-111.51

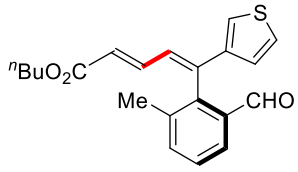
HRMS (ESI) for $C_{24}H_{24}O_3F$ $[M+H]^+$: 367.1665, found: 367.1668.

FTIR (KBr, cm^{-1})

3445.33, 3422.81, 3383.81, 2959.81, 2920.56, 2842.0,6 2357.01, 2326.17, 1675.70, 1647.66,, 1560.75, 1535.51, 1504.67, 1395.33, 1384.11, 1260.75, 1103.74, 1025.23, 795.33, 666.36.

Opt. Rot. $[\alpha]^{20}D$ = - 19.3 (c = 0.8, $CHCl_3$)

HPLC Daicel Chiralpak AD-H column, n-hexane/i-PrOH (95/5), 0.5 mL/min, 254 nm, 19.725 min (major enantiomer), 21.934 min (minor enantiomer).



Butyl (*R*)-(2*E*,4*E*)-5-(2-formyl-6-methylphenyl)-5-(thiophen-3-yl)penta-2, 4-dienoate (3l)

Following the general procedure D, **3l** was obtained as a yellow oil (29.3 mg, 83% yield, >99% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.88 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 2.0 Hz, 2H), 7.08 (d, *J* = 11.5 Hz, 1H), 6.87 – 6.79 (m, 1H), 6.74 (t, *J* = 2.0 Hz, 1H), 6.05 (d, *J* = 15.0 Hz, 1H), 4.07 (t, *J* = 6.5 Hz, 2H), 2.15 (s, 3H), 1.60 – 1.55 (m, 2H), 1.36 – 1.29 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 191.03, 165.66, 141.04, 139.84, 139.27, 138.75, 136.40, 135.10, 133.25, 127.57, 126.09, 124.98, 124.74, 124.38, 123.33, 122.25, 63.27, 29.60, 18.10, 17.98, 12.67.

HRMS (ESI) for $C_{21}H_{22}O_3SNa$ $[M+Na]^+$: 377.1182, found: 377.1172.

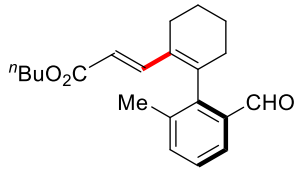
FTIR (KBr, cm^{-1})

3565.42, 2351.40, 1681.31, 1650.47, 1636.45, 1560.75, 1541.12, 1504.67, 666.36.

Opt. Rot. $[\alpha]^{20}D$ = - 7.7 (c = 0.4, $CHCl_3$)

HPLC Daicel Chiralpak IA-H column, n-hexane/i-PrOH (98/2), 1.0 mL/min, 254 nm, 15.699

min (major enantiomer), 13.717 min (minor enantiomer).



Butyl (*R*)-(*E*)-3-(2'-formyl-6'-methyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)acrylate (3m)

Following the general procedure D, **3m** was obtained as a colorless oil (28.9 mg, 89% yield, >99% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 9.98 (s, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 15.5 Hz, 1H), 5.86 (d, *J* = 15.5 Hz, 1H), 4.05 – 4.00 (m, 2H), 2.38 – 2.35 (m, 3H), 2.30 – 2.25 (m, 1H), 2.18 (s, 3H), 1.88 – 1.76 (m, 4H), 1.56 – 1.51 (m, 2H), 1.31 – 1.26 (m, 2H), 0.87 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 191.08, 166.21, 143.72, 141.80, 141.62, 135.25, 134.95, 132.31, 131.37, 126.67, 125.15, 116.02, 63.04, 33.06, 29.59, 23.80, 21.46, 21.21, 18.10, 17.74, 12.66.

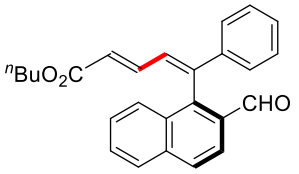
HRMS (ESI) for $C_{21}H_{27}O_3$ $[M+ H]^+$: 327.1955, found: 327.1947.

FTIR (KBr, cm^{-1})

3441.17, 3417.14, 3404.98, 3383.83, 2965.42, 2931.78, 2354.21, 2340.19, 1647.66, 1633.64, 1398.13, 1392.52, 1260.75, 1028.04, 812.15, 669.16.

Opt. Rot. $[\alpha]^{20}D$ = - 6.9 (c = 0.4, $CHCl_3$)

HPLC Daicel Chiralpak OD-H column, n-hexane/i-PrOH (97/3), 1.0 mL/min, 254 nm, 13.743 min (major enantiomer), 15.202 min (minor enantiomer).



Butyl (*R*)-(2*E*,4*Z*)-5-(2-formylnaphthalen-1-yl)-5-phenylpenta-2,4-dienoate (3n)

Following the general procedure D, **3n** was obtained as a yellow oil (28.9 mg, 75% yield, 99% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.12 (s, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.61 (d, *J* = 16.0 Hz, 1H), 7.47 – 7.44 (m, 1H), 7.42 (d, *J* = 11.5 Hz, 1H), 7.32 – 7.28 (m, 5H), 6.78 – 6.73 (m, 1H), 6.10 (d, *J* = 15.0 Hz, 1H), 4.00 (t, *J* = 6.5 Hz, 2H), 1.54 – 1.48 (m, 2H), 1.25 (dd, *J* = 7.5, 1.5 Hz, 2H), 0.84 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 191.00, 165.42, 142.26, 141.06, 139.27, 138.63, 135.51, 135.42, 130.77, 130.50, 128.26, 128.18, 127.97, 127.74, 127.53, 126.59, 125.95, 125.62, 123.34, 121.31, 63.28, 29.51, 18.03, 12.62.

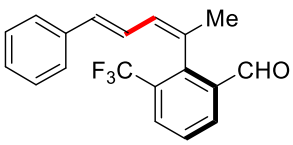
HRMS (ESI) for $C_{26}H_{25}O_3$ $[M+H]^+$: 385.1798, found: 385.1789.

FTIR (KBr, cm^{-1})

3451.97, 3417.41, 3383.93, 2959.81, 2926.17, 2354.21, 2326.17, 1681.31, 1653.27, 1630.84, 1405.54, 1386.92, 1269.16, 1030.84, 809.35, 666.36.

Opt. Rot. $[\alpha]^{20}D$ = 83.7 (c = 0.8, $CHCl_3$)

HPLC Daicel Chiralpak IB-H column, n-hexane/i-PrOH (98/2), 0.5 mL/min, 254 nm, 25.445 min (major enantiomer), 24.646 min (minor enantiomer).



(*R*)-(2-((2*Z*,4*E*)-5-phenylpenta-2,4-dien-2-yl)-3-(trifluoromethyl)benzaldehyde (3o)

Following the general procedure D, **3o** was obtained as a yellow oil (25.9 mg, 82% yield, 95% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.13 (s, 1H), 8.20 (d, *J* = 7.5 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.23 – 7.22 (m, 2H), 7.17 – 7.14 (m, 3H), 6.60 (d, *J* = 11.0 Hz, 1H), 6.56 (d, *J* = 15.5 Hz, 1H), 6.09 (dd, *J* = 15.5, 11.0 Hz, 1H), 2.23 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 190.16, 135.88, 133.28, 132.46, 131.68, 131.68, 130.79 (q, J_{CF} = 5.3 Hz), 130.00, 129.96, 127.42 (q, J_{CF} = 16.8 Hz), 127.46, 127.00, 126.71, 124.32 (q, J_{CF} = 288.0 Hz), 125.43, 124.02, 26.23.

^{19}F NMR (471 MHz, $CDCl_3$)

δ -59.60.

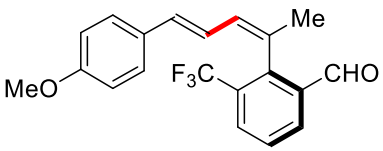
HRMS (ESI) for $C_{19}H_{16}O_3F_3$ $[M+H]^+$: 317.1148, found: 317.1144.

FTIR (KBr, cm^{-1})

3441.47, 3422.54, 3383.74, 2962.62, 2923.36, 2354.21, 1681.31, 1650.47, 1543.93, 1403.74, 1381.31, 1260.75, 1028.04, 795.33.

Opt. Rot. $[\alpha]^{20}D$ = - 75.9 (c = 2, $CHCl_3$)

HPLC Daicel Chiralpak OD-H column, n-hexane/i-PrOH (98/2), 0.5 mL/min, 254 nm, 11.147 min (major enantiomer), 12.985 min (minor enantiomer).



(*R*)-(2-((2*Z*,4*E*)-5-(4-methoxyphenyl)penta-2,4-dien-2-yl)-3-(trifluoromethyl)benzaldehyde (3p)

Following the general procedure D, **3p** was obtained as an orange yellow oil (27.2 mg, 79% yield, > 99% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.12 (s, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.75 (d, *J* = 8.5 Hz, 2H), 6.56 (d, *J* = 11.0 Hz, 1H), 6.50 (d, *J* = 15.5 Hz, 1H), 5.96 (dd, *J* = 15.5, 11.0 Hz, 1H), 3.75 (s, 3H), 2.21 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 190.32, 158.33, 143.52 (d, J_{CF} = 1.9 Hz),133.33, 132.01, 131.86 (d, J_{CF} = 0.9 Hz), 130.77 (q, J_{CF} = 4.3 Hz), 129.98, 128.89 (q, J_{CF} = 30.3 Hz), 128.73, 128.62, 126.90, 126.68, 122.56 (q, J_{CF} = 272.6 Hz), 122.09, 112.93, 54.23, 26.17.

^{19}F NMR (471 MHz, $CDCl_3$)

δ -59.64.

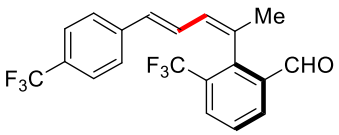
HRMS (ESI) for $C_{20}H_{17}O_2F_3Na$ [M+ Na]$^+$: 369.1073, found: 369.1072.

FTIR (KBr, cm^{-1})

3447.66, 3419.63, 3385.98, 2351.40, 2328.97, 1684.11, 1656.07, 1533.64, 1510.28, 1406.54, 1384.11, 1025.23, 671.96.

Opt. Rot. $[\alpha]^{20}D$ = - 123.7 (c = 0.4, $CHCl_3$)

HPLC Daicel Chiralpak OD-H column, n-hexane/i-PrOH (95/5), 1.0 mL/min, 254 nm, 6.247 min (major enantiomer), 9.032 min (minor enantiomer).



(*R*)-(3-(Trifluoromethyl)-2-((2Z,4E)-5-(4-(trifluoromethyl)phenyl)penta-2,4-dien-2-yl)benzaldehyde (3q)

Following the general procedure D, **3q** was obtained as an orange yellow oil (29.2 mg, 76% yield, >99% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 10.12 (s, 1H), 8.21 (d, *J* = 7.5 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.61 (d, *J* = 11.0 Hz, 1H), 6.57 (d, *J* = 15.5 Hz, 1H), 6.16 (dd, *J* = 15.5, 11.0 Hz, 1H), 2.25 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 189.86, 142.74 (d, J_{CF} = 1.8 Hz), 139.32 (q, J_{CF} = 1.3 Hz), 133.23, 132.16, 131.18, 130.83 (q, J_{CF} = 5.3 Hz), 130.78, 130.23, 128.74 (q, J_{CF} = 30.3 Hz), 128.33 (q, J_{CF} = 22.6 Hz), 127.21, 126.94 (d, J_{CF} = 7.9 Hz), 126.29, 125.50, 124.40 (q, J_{CF} = 3.8 Hz), 124.22 (q, J_{CF} = 3.8 Hz), 123.05 (q, J_{CF} = 270.1 Hz), 122.51 (q, J_{CF} = 272.5 Hz), 26.32.

^{19}F NMR (471 MHz, $CDCl_3$)

δ -59.55, -62.61.

HRMS (ESI) for $C_{20}H_{15}OF_6$ [M+ H]$^+$: 385.0982, found: 385.0972.

FTIR (KBr, cm^{-1})

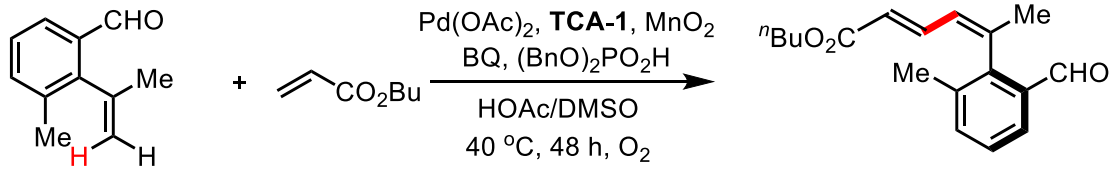
3447.56, 3429.32, 3377.68, 2323.40, 2320.07, 1683.21, 1646.08, 1555.54, 1510.38,

1406.67, 1382.01, 1035.25, 666.96.

Opt. Rot. $[\alpha]^{20}D = 108.7$ (c = 0.4, $CHCl_3$)

HPLC Daicel Chiralpak AD-H column, n-hexane/i-PrOH (99.2/0.8), 1.0 mL/min, 254 nm, 6.952 min (major enantiomer), 8. 784 min (minor enantiomer).

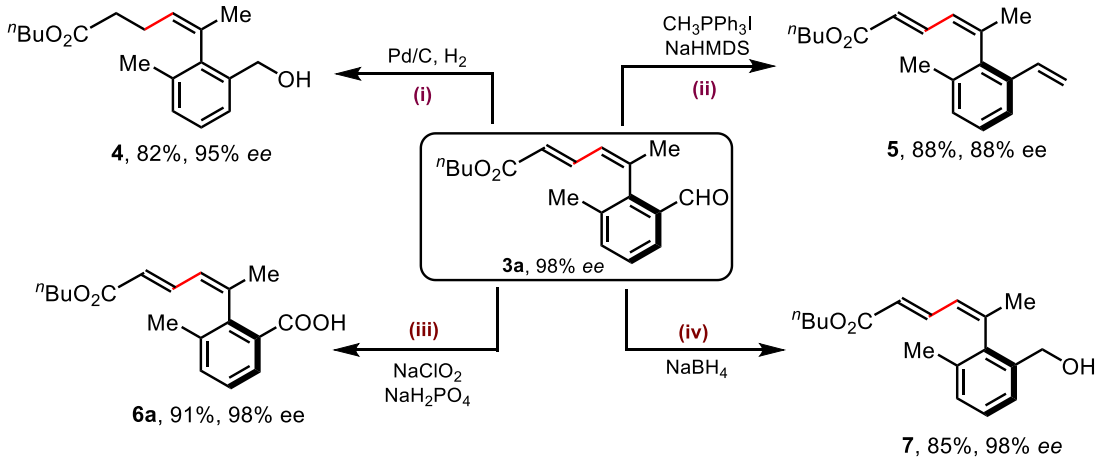
5. Gram-Scaled Synthesis



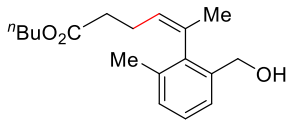
1a, 0.75 g **2a** **3a**, 74%, 99% *ee*

An screw-cap vial was charged with $Pd(OAc)_2$ (10 mol%, 0.47 mmol) , MnO_2 (1.5 equiv, 7.05 mmol), BQ (1.0 equiv, 4.7 mmol), $(BnO)_2PO_2H$ (0.5 equiv, 2.35 mmol), HOAc (47 mL), DMSO (4.7 mL). Then, **TCA-1** (30 mol%, 1.41 mmol), aldehyde **1a** (1.0 equiv, 4.7 mmol, 0.75g) and acrylate **2a** (4.0 equiv, 18.8 mmol) were added into the solution in sequence. The vial was sealed under O_2 and heated to 40 °C with stirring for 48 h. After cooling down, the mixture was directly applied to a flash column chromatography (PE / EA). Product **3a** was obtained as a yellow oil (1.0 g, 74% yield, 99% *ee*).

6. Further Elaboration



Hydrogenation Reaction (i): A solution of aldehyde (**3a)** (0.2 mmol, 1.0 equiv) in EtOAc (2 mL) was vacuum purged three times, backfilling with Ar. Pd/C (5% on carbon (wetted with cal. 55% water), 10 wt%) was added and the solution was vacuumed purged once more, backfilling with H_2. The solution was allowed to stir at room temperature for 4 h until reaction completion (moitored by TLC). The reaction was vacuum purged and backfilled with N_2, upon which the reaction was filtered through Celite, rinsing with EtOAc (10 mL). The organic solution was concentrated in vacuo to give an orange oil, which was dissolved in 10 mL EtOAc. The organic solution was washed with HCl (2 M, 10 mL × 2), water (10 mL), and brine (10 mL). The organic layer was then dried with Na_2SO_4 and concentrated in vacuo to afford the crude olefin. Purification by column chromatography (PE/EA) afforded styrene **(4)**.



Butyl 5-(2-(hydroxymethyl)-6-methylphenyl)-4-ene-hexanoate (4)

Following the procedure, **4** was obtained as a colorless oil (48.0 mg, 82% yield, 95% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.33 (d, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 15.0 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 5.52 (t, *J* = 6.5 Hz, 1H), 4.56 (q, *J* = 7.5 Hz, 2H), 4.05 – 4.03 (m, 2H), 2.31 – 2.27 (m, 2H), 2.19 (s, 3H), 2.02 – 1.94 (m, 2H), 1.91 (s, 3H), 1.61 – 1.55 (m, 4H), 1.37 – 1.31 (m, 3H), 0.92 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 172.50, 138.45, 136.79, 134.66, 133.95, 128.22, 126.02, 125.69, 124.58, 63.37, 62.05, 32.54, 29.60, 23.59, 23.42, 18.12, 18.09, 12.68.

HRMS (ESI) for $C_{18}H_{28}O_3Na$ $[M+ Na]^+$: 315.1931, found: 315.1928.

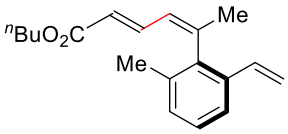
FTIR (KBr, cm^{-1})

3383.18, 2348.60, 1656.07, 1636.45, 1560.7,5 1538.32, 1507.48, 1403.74, 1016.82.

Opt. Rot. $[\alpha]^{20}D = 1.9$ (c = 0.4, $CHCl_3$)

HPLC Daicel Chiralpak OD-H column, n-hexane/i-PrOH (97/3), 1.0 mL/min, 210 nm, 9.896 min (major enantiomer), 11.192 min (minor enantiomer).

Wittig olefination (ii): Methyl triphenylphosphonium bromide (0.2 mmol, 1.1 equiv) was suspended in THF (0.5 M) and cooled to 0 °C. A solution of NaHMDS (1.3 equiv, 0.26 mmol) in THF (2.0 M) was added dropwise. The mixture was stirred for 1 h until an orange suspension formed. The mixture was then further cooled to – 78 °C, and the aldehyde **3a** (1.0 equiv, 0.2 mmol) was added over 20 min. After addition was completed, the reaction was gradually warmed to room temperature and stirred overnight. The reaction was quenched with sat. NH_4Cl (aq.) solution, then extracted with EA. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo, and the resulting residue was purified using silica gel column chromatography (PE / EA) afforded ester **(5)**.



Butyl (2*E*,4*Z*)-5-(2-methyl-6-vinylphenyl)hexa-2,4-dienoate (5)

Following the procedure, **5** was obtained as a white oil (50.0 mg, 88% yield, 88% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.43 (d, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 6.79 (dd, *J* = 15.5, 11.5 Hz, 1H), 6.63 (dd, *J* = 17.5, 11.0 Hz, 1H), 6.36 (d, *J* = 11.5 Hz, 1H), 5.82 (d, *J* = 15.5 Hz, 1H), 5.65 (d, *J* = 17.5 Hz, 1H), 5.18 (d, *J* = 11.0 Hz, 1H), 4.04 (t, *J* = 6.5 Hz, 2H), 2.14 (s, 3H), 2.06 (s, 3H), 1.59 – 1.53 (m, 2H), 1.36 – 1.28 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 166.24, 146.75, 140.49, 137.45, 133.90, 133.78, 133.65, 128.46, 126.45, 125.91, 121.65, 119.32, 114.12, 63.00, 29.65, 24.32, 18.43, 18.10, 12.68.

HRMS (ESI) for $C_{19}H_{24}O_2Na$ $[M+ Na]^+$: 307.1669, found: 307.1675.

FTIR (KBr, cm^{-1})

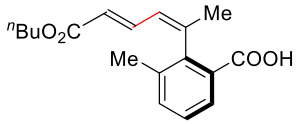
3851.40, 3744.86, 3643.93, 3629.91, 3562.62, 1689.72, 1653.27, 1636.45, 1538.32, 1507.48, 1400.93, 1028.04.

Opt. Rot. $[\alpha]^{20}D$ = - 101.3 (c = 0.4, $CHCl_3$)

HPLC Daicel Chiralpak OB-H column, n-hexane/i-PrOH (99.2/0.8), 0.5 mL/min, 254 nm,

16.436 min (major enantiomer), 11.784 min (minor enantiomer).

Oxidation Reaction (iii)[4] **:** To a solution of the aldehyde **3a** (0.2 mmol) in a mixture of t-BuOH/THF/H_2O (3 mL, 2:1:3) at 0 °C were added NaH_2PO_4 (4.8 mmol, 24.0 equiv), 2-methyl-2-butene (2.6 mmol, 13.0 equiv), and followed by $NaClO_2$ (0.74 mmol, 3.7 equiv). The mixture was allowed to warm to room temperature. The reaction was stirred at the same temperature for 8 h until the aldehyde was consumed. The organic solution was concentrated in vacuo to give an orange oil, which was dissolved in 10 mL EtOAc. The organic solution was washed with HCl (2 M, 10 mL × 2), water (10 mL), and brine (10 mL). The organic layer was then dried with Na_2SO_4 and concentrated in vacuo to afford the crude product. Purification by column chromatography (PE/EA) afforded acid **(6a)**.



2-((2*Z*,4*E*)-6-butoxy-6-oxohexa-2,4-dien-2-yl)-3-methylbenzoic acid (6a)

Following the procedure, **6a** was obtained as a yellow solid (54.8 mg, 91% yield, 98% *ee*, m.p. = 83.5 °C).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.94 (d, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 6.71 (dd, *J* = 15.0, 11.5 Hz, 1H), 6.28 (d, *J* = 12.0 Hz, 1H), 5.80 (d, *J* = 15.0 Hz, 1H), 4.03 (t, *J* = 6.5 Hz, 2H), 2.20 (s, 3H), 2.17 (s, 3H), 1.58 – 1.52 (m, 2H), 1.33 – 1.29 (m, 2H), 0.88 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 170.52, 166.40, 147.49, 140.72, 140.26, 135.01, 134.05, 128.21, 127.01, 126.38, 124.42, 118.88, 63.01, 29.62, 24.08, 18.48, 18.10, 12.67.

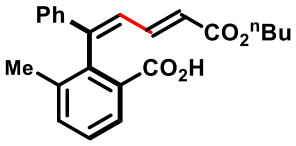
HRMS (ESI) for $C_{18}H_{22}O_4$ Na $[M+ Na]^+$: 325.1410, found: 325.1407.

FTIR (KBr, cm^{-1})

3425.23, 3385.98, 3332.71, 3265.42, 3142.06, 3004.67, 2957.01, 2351.40, 1653.27, 1636.45, 1535.51, 1510.28, 1392.52, 1019.63.

Opt. Rot. $[\alpha]^{20}D$ = - 65.6 (c = 2, $CHCl_3$)

HPLC Daicel Chiralpak OD-H column, n-hexane/i-PrOH (60/40), 1.0 mL/min, 254 nm, 5.768 min (major enantiomer), 27.319 min (minor enantiomer).



2-((1Z,3E)-5-butoxy-5-oxo-1-phenylpenta-1,3-dien-1-yl)-3-methylbenzoic acid(6b)

Following the **Oxidation Reaction** (**iii**) in **Further Elaboration,** with 0.1 mmol **3i**, **6b** was obtained as a yellow liquid (33.2 mg, 91% yield, 99% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.95 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.29 – 7.21 (m, 5H), 6.95 – 6.82 (m, 2H), 6.00 (d, *J* = 14.3 Hz, 1H), 4.06 (t, *J* = 6.6 Hz, 2H), 2.10 (s, 3H), 1.57 (dt, *J* = 14.5, 6.7 Hz, 2H), 1.32 (dt, *J* = 14.8, 7.5 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 169.94 , 166.09 , 147.45 , 140.17 , 138.17 , 138.00 , 136.82 , 133.93 , 128.68 , 128.20 , 127.40 , 127.38 , 126.96 , 125.64 , 123.32 , 121.24 , 63.12 , 29.63 , 18.95 , 18.11 , 12.69 .

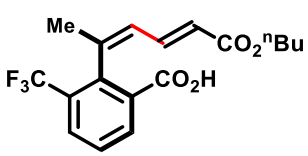
HRMS (ESI) for $C_{23}H_{24}O_4Na$ $[M+Na]^+$: 387.1567, found: 387.1577；for $C_{23}H_{24}O_4K$ $[M+K]^+$: 403.1306, found: 403.1308.

FTIR (KBr, cm^{-1})

3447.47, 2832.28, 1596.46, 1363.56, 1068.81, 776.04.

Opt. Rot. $[\alpha]^{20}D$ = -32.5 (c = 0.08, $CHCl_3$)

HPLC Daicel Chiralpak OD-H column, n-hexane/i-PrOH (50/50), 1 mL/min, 254 nm, 9.719 min (major enantiomer), 56.533 min (minor enantiomer).



2-((2Z,4E)-6-butoxy-6-oxohexa-2,4-dien-2-yl)-3-(trifluoromethyl)benzoic acid (6c)

Following the **Oxidation Reaction** (**iii**) in **Further Elaboration**, with 0.1 mmol **3g**, **6c** was obtained as a yellow liquid (30.6 mg, 86% yield, 99% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 8.23 (d, *J* = 7.8 Hz, 1H), 7.94 (d, *J* = 7.7 Hz, 1H), 7.57 (t, *J* = 7.9 Hz, 1H), 6.64 (dd, *J* = 15.1, 11.7 Hz, 1H), 6.34 (d, *J* = 11.6 Hz, 1H), 5.81 (d, *J* = 15.2 Hz, 1H), 4.04 (t, *J* = 6.6 Hz, 2H), 2.24 (s, 3H), 1.55 (dt, *J* = 14.5, 6.7 Hz, 2H), 1.35 – 1.28 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 168.86 , 166.30 , 143.21 , 139.98 , 133.62 , 129.70 (q, J_{CF} = 5.4 Hz), 129.57 , 128.83 , 128.59 , 126.98 , 126.74 , 122.46 (d, J_{CF} = 272.5 Hz), 119.46 , 63.16 , 29.59 , 25.01 , 18.08 , 12.65 .

HRMS (ESI) for $C_{18}H_{19}F_3O_4Na$ $[M+Na]^+$: 379.1128, found: 379.1128；for $C_{18}H_{19}F_3O_4K$ $[M+K]^+$: 395.0867, found: 395.0864.

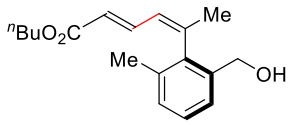
FTIR (KBr, cm^{-1})

2960.83, 2919.57, 2829.16, 1595.29, 1364.40, 1311.09, 1260.03, 1088.41, 1025.86, 797.61, 775.42

Opt. Rot. $[\alpha]^{20}D$ = -102.7 (c = 0.29, $CHCl_3$)

HPLC Daicel Chiralpak AD-H column, n-hexane/i-PrOH (60/40), 1 mL/min, 254 nm, 5.918 min (major enantiomer), 4.552 min (minor enantiomer).

Reduction Reaction[5]: To a solution of aldehyde **3a** (0.2 mmol) in MeOH (0.2 M) was added dropwise $NaBH_4$ (2.0 equiv) over 30 min at 0°C and stirred at r.t. for 8 h. 2 M HCl was added slowly until a clear solution was obtained. The layer was separated and the aqueous phase was extracted with Et_2O (10 mL × 3). The organic layers were combined and dried over Na_2SO_4. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel to afford the resulting alcohol **(7)**.



Butyl (2*E*,4*Z*)-5-(2-(hydroxymethyl)-6-methylphenyl)hexa-2,4-dienoate (7)

Following the procedure, **7** was obtained as a colorless oil (54.9 mg, 95% yield, 98% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.32 (d, J = 7.5 Hz, 1H), 7.23 (s, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 6.77 (dd, *J* = 15.5, 11.5 Hz, 1H), 6.37 (d, *J* = 11.5 Hz, 1H), 5.84 (d, *J* = 15.5 Hz, 1H), 4.50 (d, *J* = 3.0 Hz, 2H), 4.05 (t, *J* = 6.5 Hz, 2H), 2.16 (s, 3H), 2.11 (s, 3H), 1.59 – 1.54 (m, 3H), 1.36 – 1.29 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 166.19, 146.45, 140.07, 137.30, 136.37, 133.75, 128.58, 126.76, 125.83, 124.38, 119.60, 63.09, 62.25, 29.63, 24.34, 18.21, 18.10, 12.67.

HRMS (ESI) for $C_{18}H_{24}O_3Na$ $[M+ Na]^+$: 311.1618, found: 311.1614.

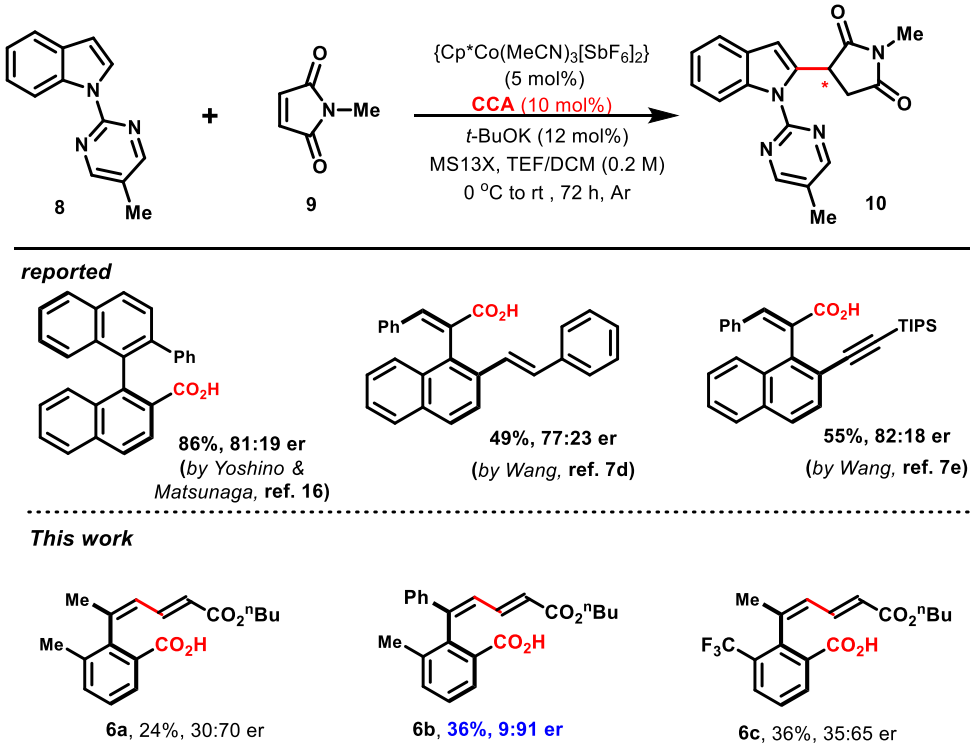
FTIR (KBr, cm^{-1})

3854.21, 3744.86, 3629.91, 3568.22, 3456.07, 3414.02, 2354.21, 1656.07, 1633.64, 1560.75, 1504.67, 1457.01, 1406.54, 1386.92, 1025.23, 803.74.

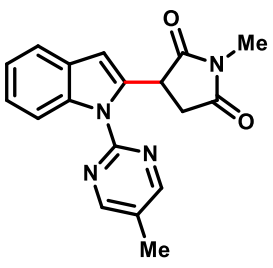
Opt. Rot. $[\alpha]^{20}D$ = - 2.9 (c = 0.8, $CHCl_3$)

HPLC Daicel Chiralpak OD-H column, n-hexane/i-PrOH (60/40), 1.0 mL/min, 254 nm, 6.121 min (major enantiomer), 15.077 min (minor enantiomer).

7. Co^{III}-catalyzed Enantioselective 1,4-Addition of Indoles and Maleimides [6]



To an oven-dried 25 mL Schlenk tube was added N-(5-methyl)-pyrimidyl indole **8** (0.20 mmol, 1.0 equiv), maleimide **9** (0.4 mmol, 2 equiv), **CCA** (0.02 mmol, 10 mol %), $[Cp^*Co(MeCN)_3][SbF_6]_2$ (0.01 mmol), activated MS13X (40 mg). To the mixture were added t-BuOK in TFE (0.1 M, 240 μL, 0.024 mmol, 12 mol %), TFE (560 μL), and DCM (200 μL) at 0 ºC, and the mixture was stirred at 25 ºC. After 72 hours, the reaction mixture was filtered through a short pad of silica gel and purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1 to 2/1) to afford **10** as white solid.



1-methyl-3-(1-(5-methylpyrimidin-2-yl)-1H-indol-2-yl)pyrrolidine-2,5-dione (10)

^{1}H NMR (500 MHz, $CDCl_3$)

δ 8.55 (d, *J* = 7.8 Hz, 1H), 8.43 (s, 2H), 7.56 (d, *J* = 7.1 Hz, 1H), 7.31 (t, *J* = 7.0 Hz, 1H), 7.23 (q, *J* = 9.1, 6.8 Hz, 1H), 6.67 (s, 1H), 4.77 (s, 1H), 3.17 – 3.05 (m, 4H), 2.97 – 2.84 (m, 1H), 2.30 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$)

δ 175.99 , 175.44 , 156.71 , 154.84 , 136.26 , 132.53 , 127.52 , 125.21 , 122.96 , 121.29 , 119.30 , 114.48 , 109.57 , 41.18 , 35.50 , 24.05 , 14.02 .

HRMS (ESI) for $C_{18}H_{16}O_2N_4$ H $[M+ H]^+$: 321.1346, found: 321.1137.

FTIR 2925.20, 2828.58, 1699.93, 1591.69, 1365.93, 775.34

HPLC Daicel Chiralpak IA column, n-hexane/i-PrOH (80/20), 1.0 mL/min, 254 nm, 17.130 min (major enantiomer), 37.385 min (minor enantiomer).

8. Density Functional Theory (DFT) Calculations

8.1 Computational Details and Rotational Barrier Calculated by DFT

All density functional theory (DFT) calculations were carried out using Gaussian16 software package.[7] All geometry optimizations were performed with B3LYP[8-9] -D3[10] functional and 6-31G (d) basis set. The vibrational frequencies were computed at the same level of theory as for the geometry optimizations, and to evaluate the zero-point vibrational energy (ZPVE) and thermal corrections at 298 K. The single-point energies were computed based on the gas-phase optimized structures, using M06-2x[11] functional and 6-311+G (d, p) basis set, with the inclusion of solvation energy corrections using a self-consistent reaction field (SCRF) based on SMD implicit solvent model[17] with DMSO as solvent. I Free energies were corrected using Truhlar's quasiharmonic correction, by raising vibrational frequencies that are below 100 cm^{-1}.[12] All reported energies were computed at 298.15K. DFT-optimized structures are illustrated using CYLView.

8.2 Enantiomeric conversion half-life calculation strategy

The Eyring Equation relates the activation free energy and rate constant:

$$k = \frac{k_b T}{h} e^{-\frac{\Delta G^{\ddagger}}{RT}} \qquad (1)$$

In this equation, $\Delta G^{\ddagger}$ is the Gibbs energy of activation, κ is the transmission coefficient, k_{b} is Boltzmann's constant, and h is Planck's constant. The transmission coefficient is often assumed to be equal to one as it reflects what fraction of the flux through the transition state proceeds to the product without recrossing the transition state.

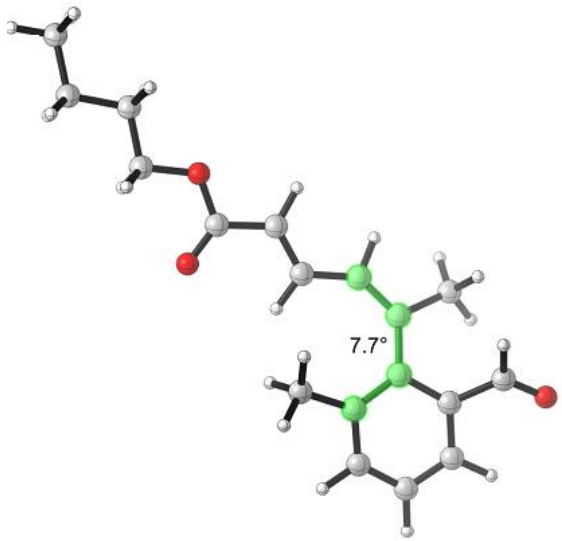
The epimerization of atropoisomer is a first order reaction, which makes the half-life only relates to the reaction rate constant:

$$t_{1/2} = \ln 2 / k \qquad (2)$$

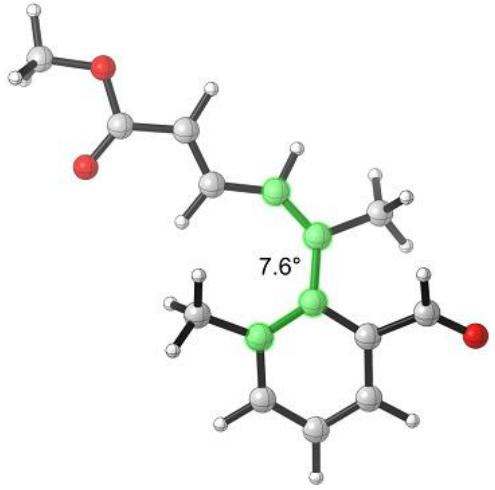
Based on Equations 1 and 2, the half-life at 40 $^{\mathrm{o}}$C (reaction conditions) and 25 $^{\mathrm{o}}$C (room temperature) was calculated.

Table S4. Table of Energies and Figures

Structure	E	ZPE	H	T.S	T.qh-S	G(T)	qh-G(T)
3a-TS	-924.823022	0.355135	-924.445535	0.075135	0.070643	-924.52067	-924.516178
3a	-924.872508	0.354131	-924.494676	0.078712	0.073626	-924.573388	-924.568301
3c-TS	-806.868959	0.271208	-806.57951	0.064238	0.061691	-806.643748	-806.641201
3c	-806.918472	0.270186	-806.628684	0.067808	0.064679	-806.696492	-806.693363



3a-TS
$\Delta G^{\ddagger}$ = 32.4 kcal/mol
$t_{1/2}$ (25 °C) = 2043 yrs
$t_{1/2}$ (40 °C) = 141 yrs



3e-TS
$\Delta G^{\ddagger}$ = 32.5 kcal/mol
$t_{1/2}$ (25 °C) = 2419 yrs
$t_{1/2}$ (40 °C) = 166 yrs

3a-TS

C	-2.889902	1.451963	0.112028
C	-3.903114	2.391083	-0.143530
C	-5.223851	2.036232	-0.379501
C	-5.573801	0.704631	-0.204413
C	-4.595898	-0.257560	0.060088
C	-3.189481	0.056409	0.048259
C	-2.215100	-1.070543	-0.140083
C	-0.841876	-1.136557	-0.164930
C	-1.574585	2.067105	0.535349
H	-3.630065	3.443696	-0.135680
H	-5.972624	2.790184	-0.603738
H	-6.610154	0.382878	-0.211920
H	-0.489815	-2.159555	-0.296320
H	-0.917877	2.308492	-0.307388
H	-1.030548	1.433616	1.236783
H	-1.778879	3.012605	1.047761
C	-2.816175	-2.440521	-0.505947
H	-3.734251	-2.353779	-1.091488
H	-3.033046	-3.061818	0.369493
H	-2.112415	-3.004306	-1.122000
C	-5.171883	-1.531744	0.592491
O	-6.293056	-1.935004	0.346396
H	-4.546983	-2.053186	1.342030
C	0.291048	-0.244244	-0.140917
H	0.188017	0.821612	-0.239208
C	1.562399	-0.701167	-0.074537
H	1.802297	-1.757946	0.005332
C	2.687237	0.251435	-0.105428
O	2.589479	1.463601	-0.194278
O	3.873174	-0.398027	-0.021222
C	5.048039	0.439668	-0.041727
H	4.994688	1.150907	0.790868
H	5.054323	1.024223	-0.969148
C	6.262397	-0.467775	0.064654
H	6.187113	-1.057969	0.987444
H	6.247273	-1.183239	-0.768062
C	7.577017	0.322187	0.053343
H	7.577669	1.041829	0.884060
H	7.636858	0.918310	-0.868083
C	8.807630	-0.583938	0.158767
H	9.735098	-0.000707	0.149481
H	8.787934	-1.168368	1.086707
H	8.848015	-1.292015	-0.677892

3a

C	3.060514	1.039979	1.210658
C	3.631468	2.240151	0.771317
C	4.183693	2.366756	-0.505907
C	4.165409	1.282139	-1.371204
C	3.597308	0.067775	-0.959767
C	3.044424	-0.063486	0.332095
C	2.493505	-1.375237	0.802335
C	1.168198	-1.636837	0.824840
C	2.456753	0.943247	2.593253
H	3.641071	3.093305	1.445501
H	4.619069	3.311911	-0.817737
H	4.574782	1.343001	-2.374612
H	0.835535	-2.602329	1.205651
H	2.840011	0.076888	3.144471
H	1.367786	0.828682	2.542011
H	2.674073	1.840790	3.179725
C	3.515169	-2.367408	1.296160
H	4.093033	-1.942542	2.128198
H	4.242214	-2.604442	0.508340
H	3.050867	-3.299041	1.634381
C	3.569716	-1.058609	-1.926593
O	4.079510	-1.020597	-3.031805
H	3.032255	-1.967292	-1.586442
C	0.140028	-0.715616	0.391349
H	0.448953	0.248958	-0.007608
C	-1.181984	-0.969867	0.456842
H	-1.571760	-1.910017	0.837349
C	-2.161744	0.037244	0.005133
O	-1.896306	1.143041	-0.430602
O	-3.427106	-0.429649	0.140074
C	-4.473268	0.473445	-0.274628
H	-4.321404	0.737326	-1.327757
H	-4.397694	1.399797	0.306897
C	-5.802627	-0.228600	-0.052132
H	-5.811099	-1.165977	-0.623776
H	-5.887229	-0.505671	1.006985
C	-6.993998	0.646069	-0.461925
H	-6.893977	0.926700	-1.519820
H	-6.970002	1.585810	0.107566
C	-8.339181	-0.052904	-0.241706
H	-9.176115	0.588092	-0.540282
H	-8.401461	-0.979616	-0.825098
H	-8.477989	-0.316135	0.814006

3e-TS

C	-1.399828	1.468385	0.099310
C	-2.363126	2.452779	-0.178060
C	-3.695647	2.159403	-0.431315
C	-4.111410	0.847365	-0.252188
C	-3.184722	-0.158264	0.033948
C	-1.764872	0.088301	0.041402
C	-0.842687	-1.085228	-0.123251
C	0.526112	-1.217055	-0.126453
C	-0.062704	2.023397	0.537019
H	-2.040224	3.491192	-0.173771
H	-4.404166	2.946388	-0.672218
H	-5.161743	0.575430	-0.273278
H	0.830559	-2.256890	-0.243612
H	0.616719	2.225655	-0.297988
H	0.440122	1.370694	1.251517
H	-0.228552	2.982069	1.038694
C	-1.502850	-2.428217	-0.486994
H	-2.406693	-2.303159	-1.087524
H	-1.762371	-3.030328	0.390224
H	-0.817568	-3.030552	-1.087157
C	-3.829224	-1.399360	0.566360
O	-4.964148	-1.750852	0.304699
H	-3.242076	-1.943628	1.330052
C	1.700009	-0.379917	-0.093303
H	1.649667	0.688757	-0.201701
C	2.946946	-0.897047	-0.005112
H	3.134561	-1.963294	0.086819
C	4.115435	0.000083	-0.028137
O	4.081116	1.214350	-0.128637
O	5.269455	-0.705019	0.078717
C	6.467088	0.085830	0.065459
H	7.289783	-0.623876	0.160967
H	6.548754	0.646552	-0.870497
H	6.470735	0.794420	0.899141

3e

C	1.682055	1.320506	0.947237
C	2.308717	2.351437	0.237369
C	2.939492	2.121764	-0.988029
C	2.945405	0.843055	-1.526909
C	2.322927	-0.209137	-0.839834
C	1.690456	0.020086	0.400828
C	1.078605	-1.109801	1.171779

C	-0.251979	-1.344626	1.177336
C	0.994346	1.608130	2.262488
H	2.299644	3.355521	0.654744
H	3.416741	2.943019	-1.515162
H	3.415604	0.625648	-2.480720
H	-0.632155	-2.167212	1.782815
H	1.323272	0.922393	3.051729
H	-0.092015	1.491097	2.174720
H	1.197432	2.630048	2.595906
C	2.042222	-1.938599	1.981957
H	2.579822	-1.307993	2.703039
H	2.808915	-2.387739	1.337078
H	1.534212	-2.738608	2.529486
C	2.324821	-1.555627	-1.465393
O	2.900267	-1.823302	-2.504587
H	1.745667	-2.333518	-0.927065
C	-1.227205	-0.567774	0.443342
H	-0.869171	0.249462	-0.180290
C	-2.556973	-0.784271	0.486988
H	-2.993841	-1.582237	1.080963
C	-3.479089	0.069519	-0.285178
O	-3.161935	1.012686	-0.986531
O	-4.764076	-0.332437	-0.113774
C	-5.740167	0.438142	-0.830212
H	-6.704806	-0.009777	-0.588197
H	-5.711891	1.485628	-0.515290
H	-5.553269	0.391868	-1.907236

9. References

[1] M. Liu, P. Yang, M. K. Karunananda, Y. Wang, P. Liu and K. M. Engle, C(alkenyl)–H Activation via Six-Membered Palladacycles: Catalytic 1,3-Diene Synthesis, *J. Am. Chem. Soc.*, 2018**, 140,** 5805-5813.

[2] B. Bradshaw, P. Evans, J. Fletcher, A. T. L. Lee, P. G. Mwashimba, D. Oehlrich, E. J. Thomas, R. H. Davies, B. C. P. Allen, K. J. Broadley, A. Hamrouni and C. Escargueil, Synthesis of 5-hydroxy-2,3,4,5-tetrahydro-[1H]-2-benzazepin-4-ones: selective antagonists of muscarinic (M_3) receptors, *Org. Biomol. Chem*., 2008**, 6,** 2138–2157.

[3] B.-H. Zhang, L.-S. Lei, S.-Z. Liu, X.-Q. Mou, W.-T. Liu, .-H. Wang, J. Wang, W. Bao and K. Zhang, Zinc-promoted cyclization of tosylhydrazones and 2-(dimethylamino)malononitrile: an efficient strategy for the synthesis of substituted 1-tosyl-1H-pyrazoles, *Chem. Commun.*, 2017**, 53,** 8545-8548.

[4] J. Li, E. Chin, A. S. Lui and L. Chen, One-pot synthesis of phthalides via regioselective intramolecular cyclization from ortho-alkynylbenzaldehydes, *Tetrahedron. Lett.*, 2010**, 51,** 5937-5939.

[5] P. Zheng, X. Han, J. Hu, X. Zhao, and T. Xu, Enantioselective Copper-Catalyzed Desymmetrization of 1,3-Diketones Involving Borylation of Styrenes, *Org. Lett.*, 2019**, 21,** 6040−6044.

[6] T. Urihara, M. Kojima, T. Yoshino and S. Matsunaga, Cp*Co^{III}/Chiral Carboxylic Acid-Catalyzed Enantioselective 1, 4-Addition Reactions of Indoles to Maleimides, *Asian. J. Org. Chem.*, 2020**, 9,** 368-371.

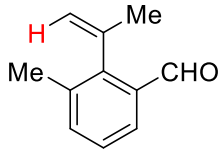
[7] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams- Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd,

E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. *Gaussian 16,* Revision A.03, Gaussian, Inc., Wallingford CT, **2016**.

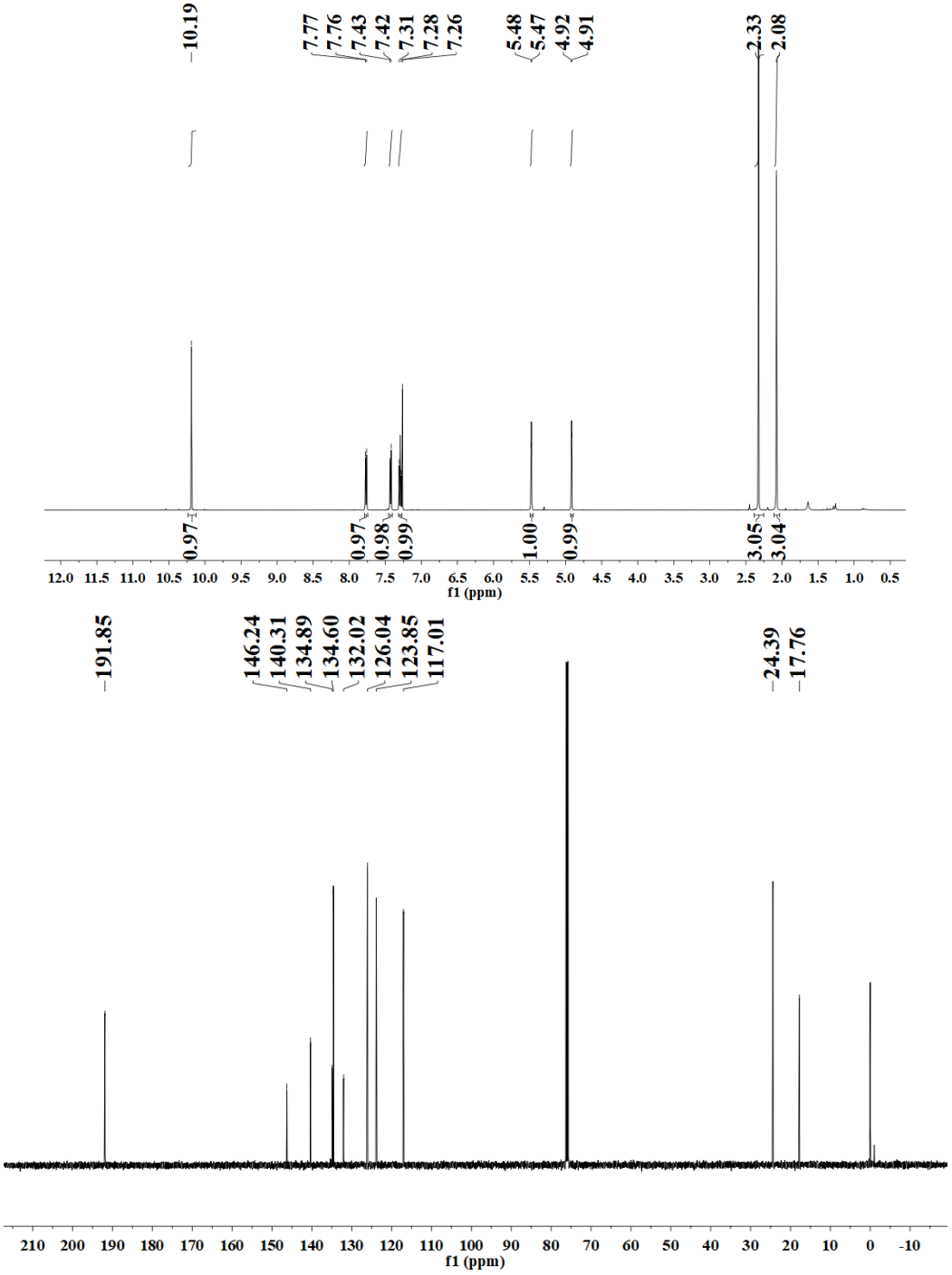
[8] M. Head-Gordon, J. A. Pople, M. J. Frisch, MP_2 energy evaluation by direct methods. *Chem. Phys. Lett*., 1988**, 153,** 503-506.

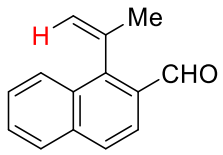
[9] C. Lee, W. Yang and R. G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1988**, 37,** 785.

10. NMR Charts

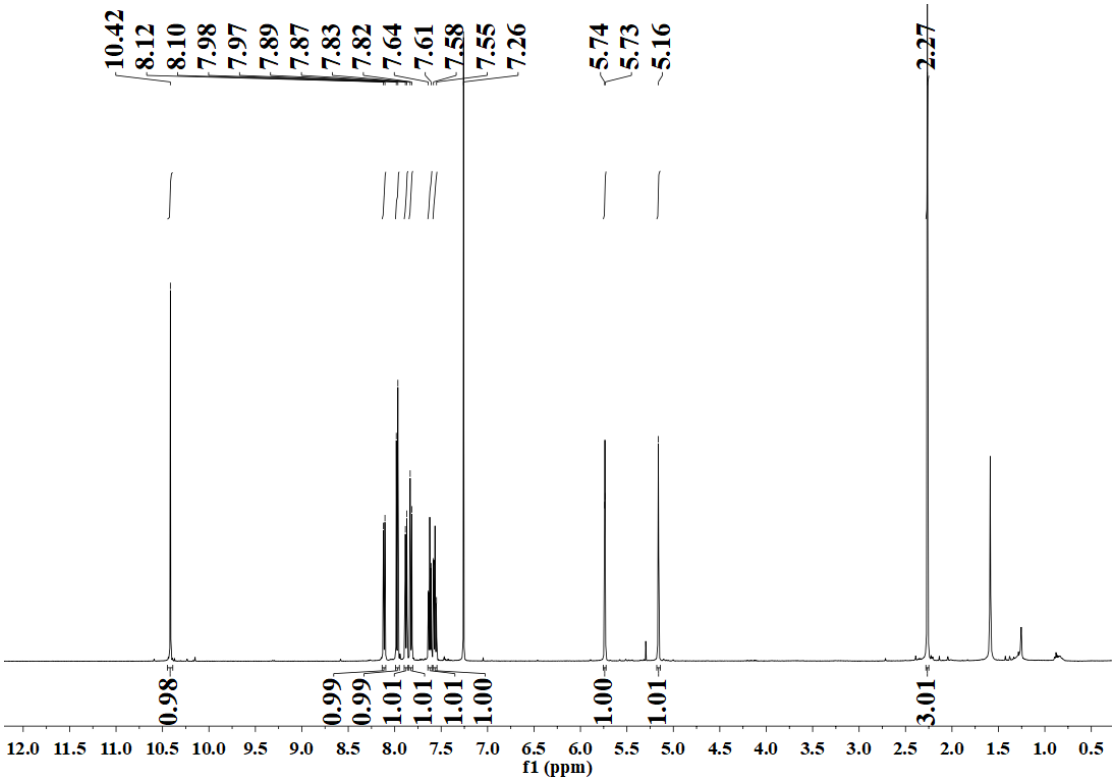


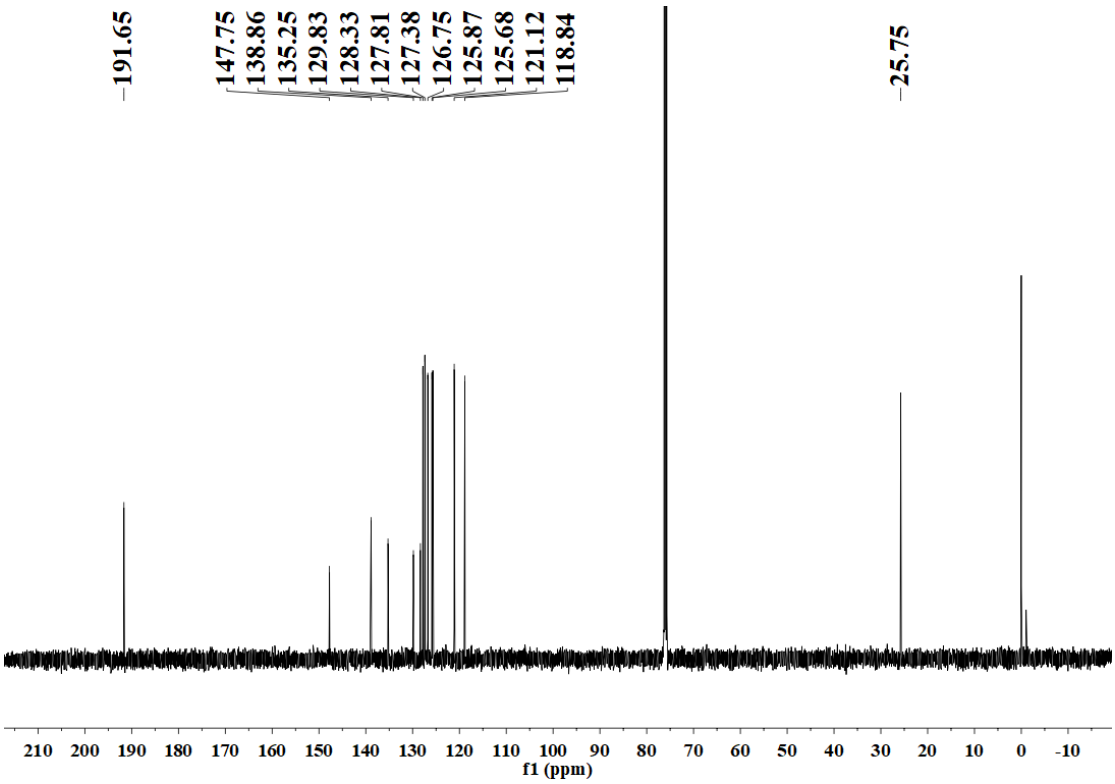
(1a)

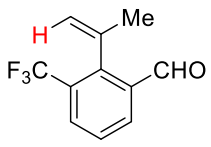



H
Me
CHO

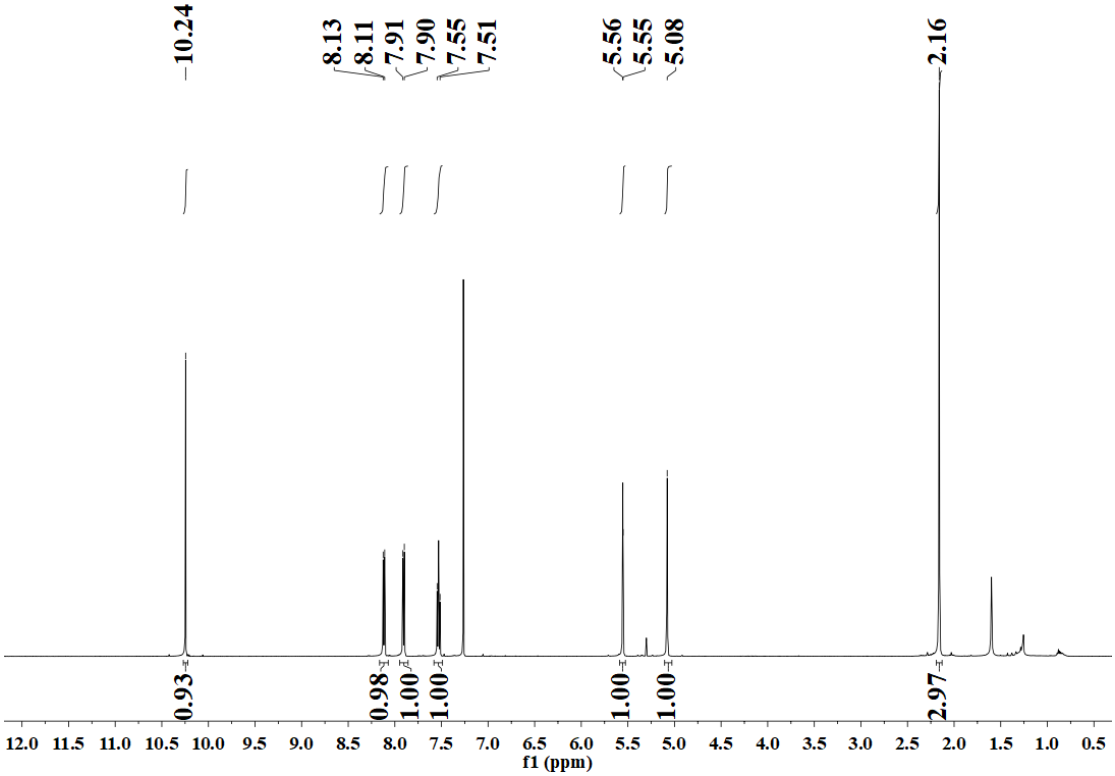
(1b)

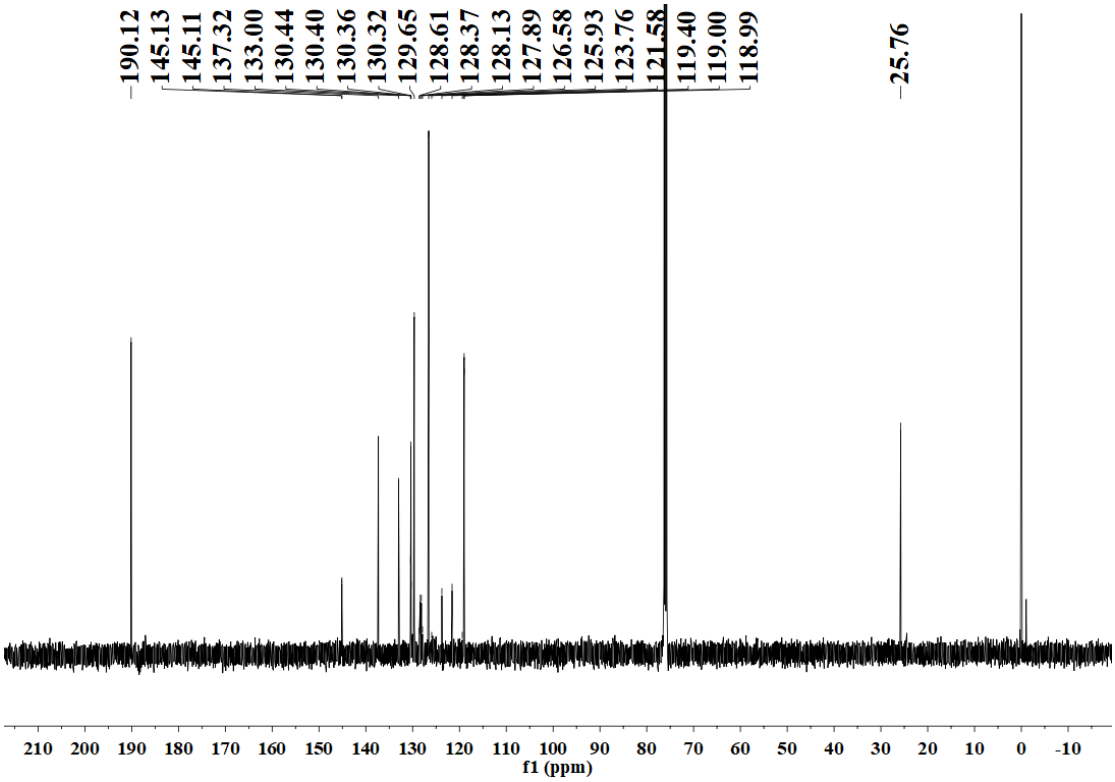

10.42
8.12
8.10
7.98
7.97
7.89
7.87
7.83
7.82
7.64
7.61
7.58
7.55
7.26
5.74
5.73
5.16
2.27
0.98
0.99
0.99
1.01
1.01
1.01
1.00
1.00
1.01
3.01
f1 (ppm)

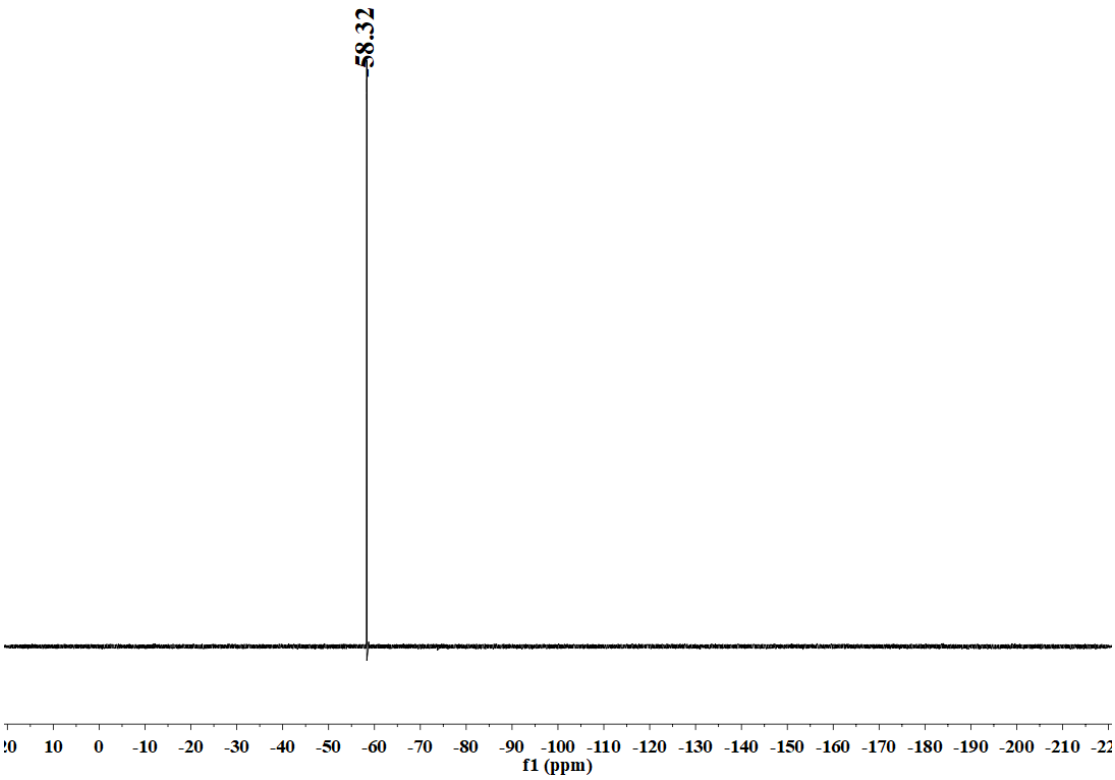

191.65
147.75
138.86
135.25
129.83
128.33
127.81
127.38
126.75
125.87
125.68
121.12
118.84
25.75
f1 (ppm)

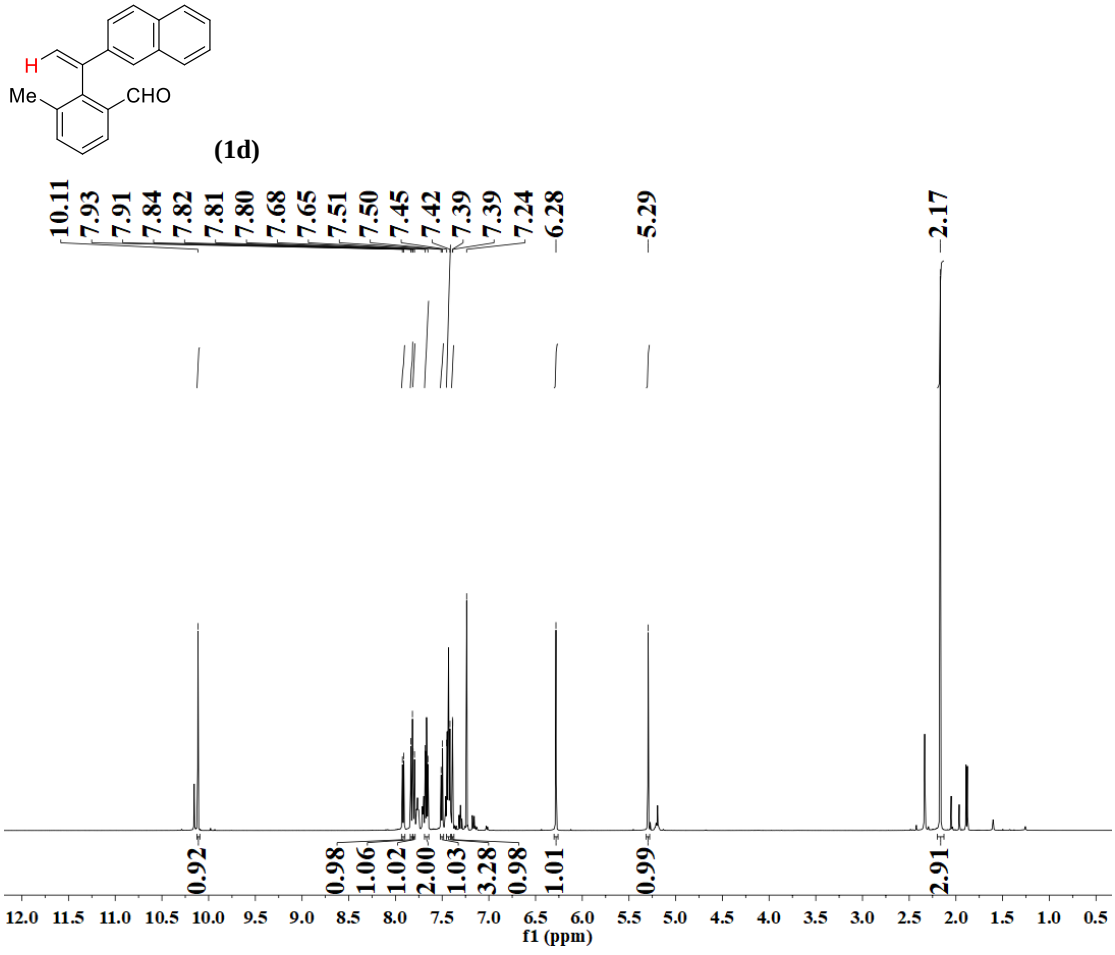

H
Me
F3C
CHO

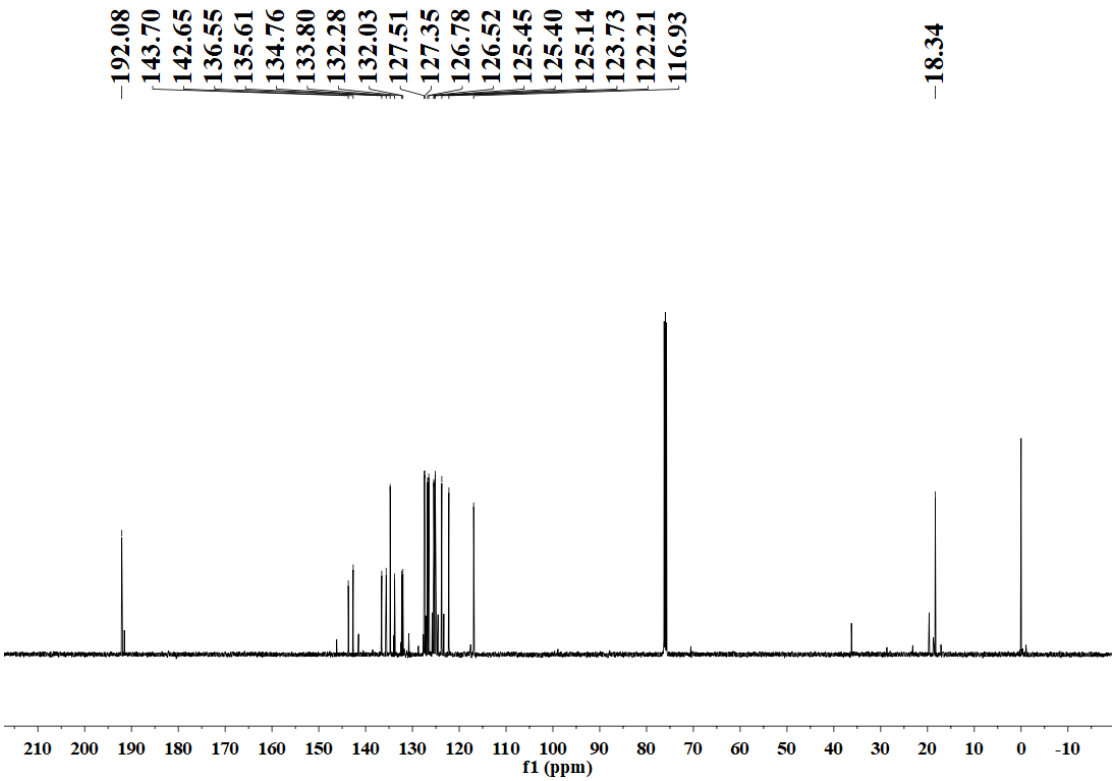
(1c)

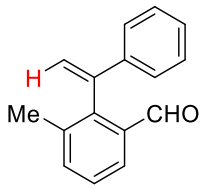

10.24
8.13
8.11
7.91
7.90
7.55
7.51
5.56
5.55
5.08
2.16
0.93
0.98
1.00
1.00
1.00
1.00
2.97
f1 (ppm)


190.12
145.13
145.11
137.32
133.00
130.44
130.40
130.36
130.32
129.65
128.61
128.37
128.13
127.89
126.58
125.93
123.76
121.58
119.40
119.00
118.99
25.76
f1 (ppm)

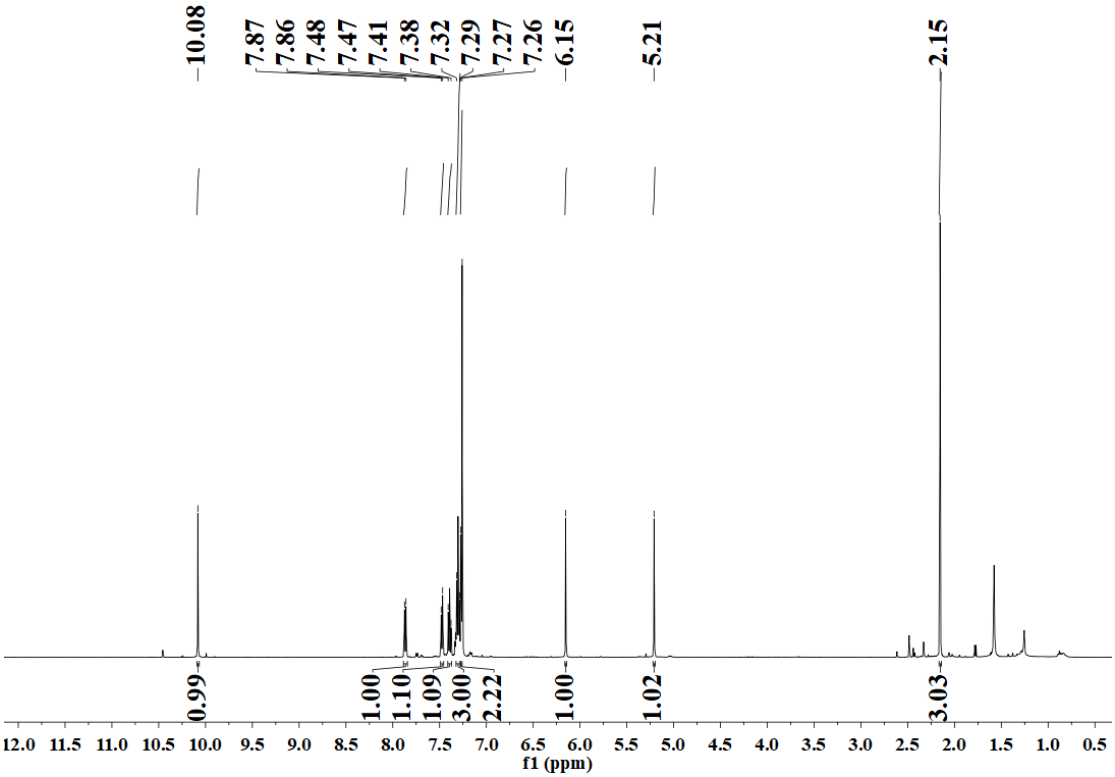

58.32
f1 (ppm)

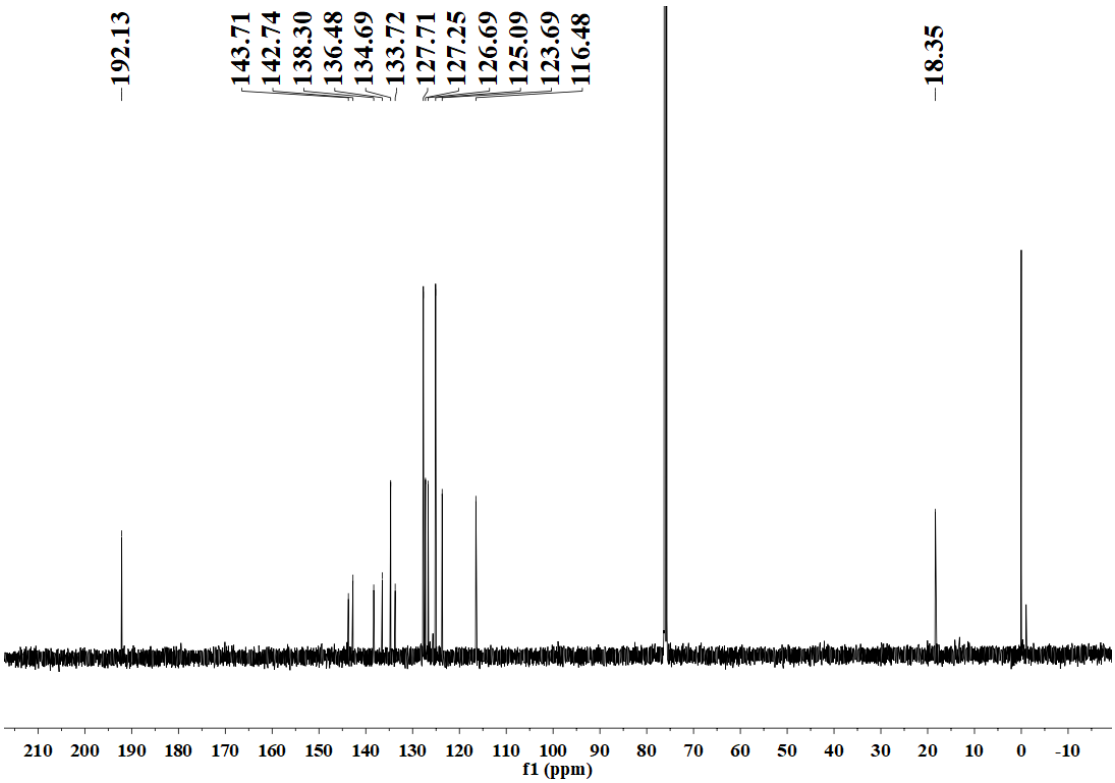

H
Me
CHO
(1d)
10.11
7.93
7.91
7.84
7.82
7.81
7.80
7.68
7.65
7.51
7.50
7.45
7.42
7.39
7.39
7.24
6.28
5.29
2.17
0.92
0.98
1.06
1.02
2.00
1.03
3.28
0.98
1.01
0.99
2.91
f1 (ppm)

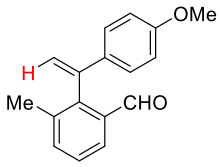

192.08
143.70
142.65
136.55
135.61
134.76
133.80
132.28
132.03
127.51
127.35
126.78
126.52
125.45
125.40
125.14
123.73
122.21
116.93
18.34
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


H
Me
CHO

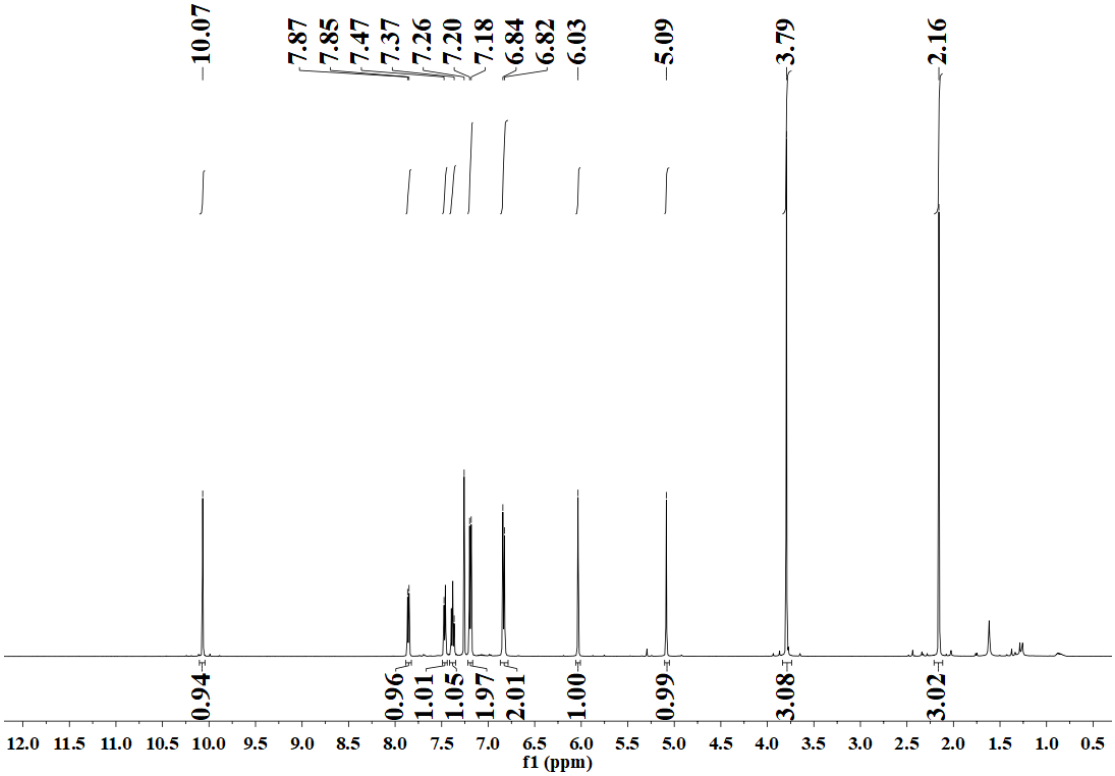
(1e)

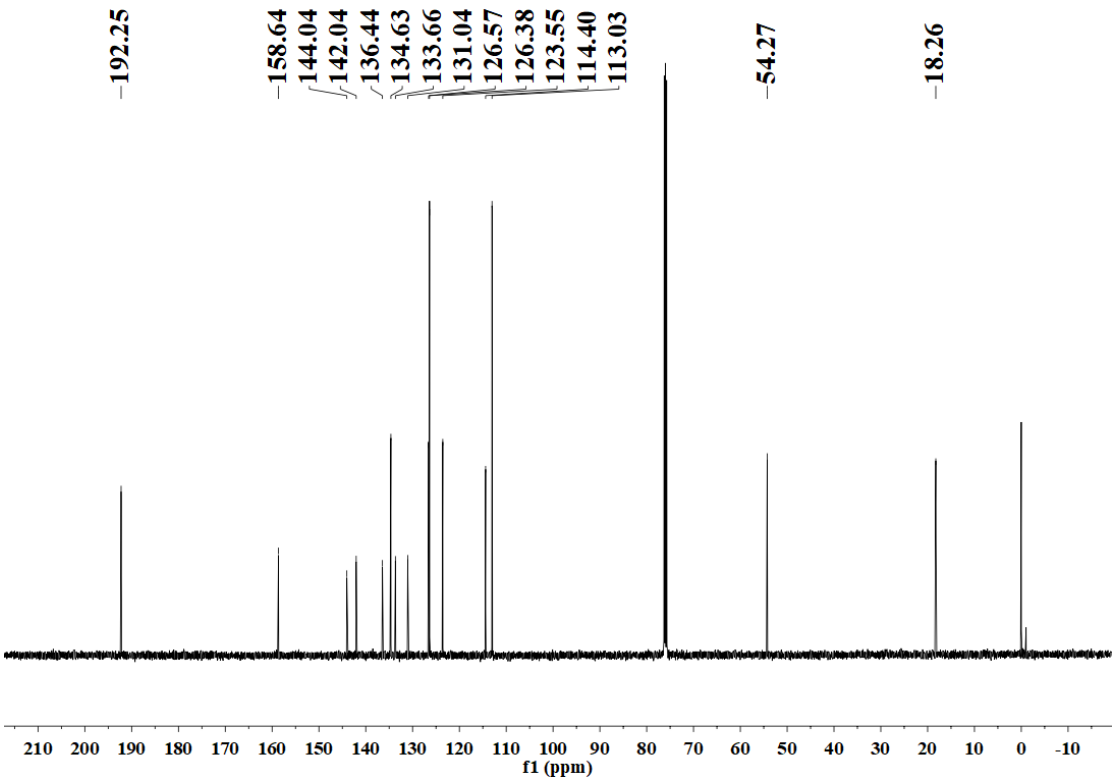

10.08
7.87
7.86
7.48
7.47
7.41
7.38
7.32
7.29
7.27
7.26
6.15
5.21
2.15
0.99
1.00
1.10
1.09
3.00
2.22
1.00
1.02
3.03
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

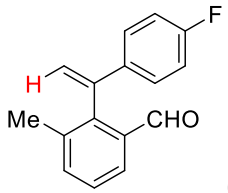

192.13
143.71
142.74
138.30
136.48
134.69
133.72
127.71
127.25
126.69
125.09
123.69
116.48
18.35
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


OMe
H
Me
CHO

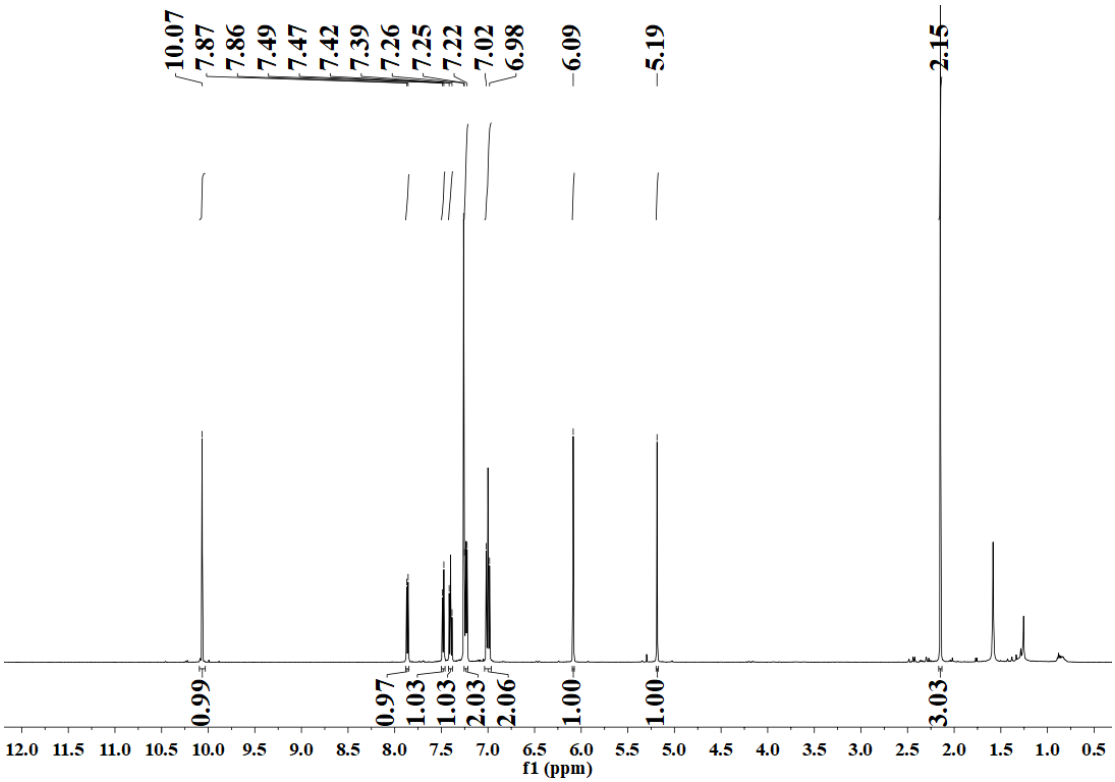
(1f)

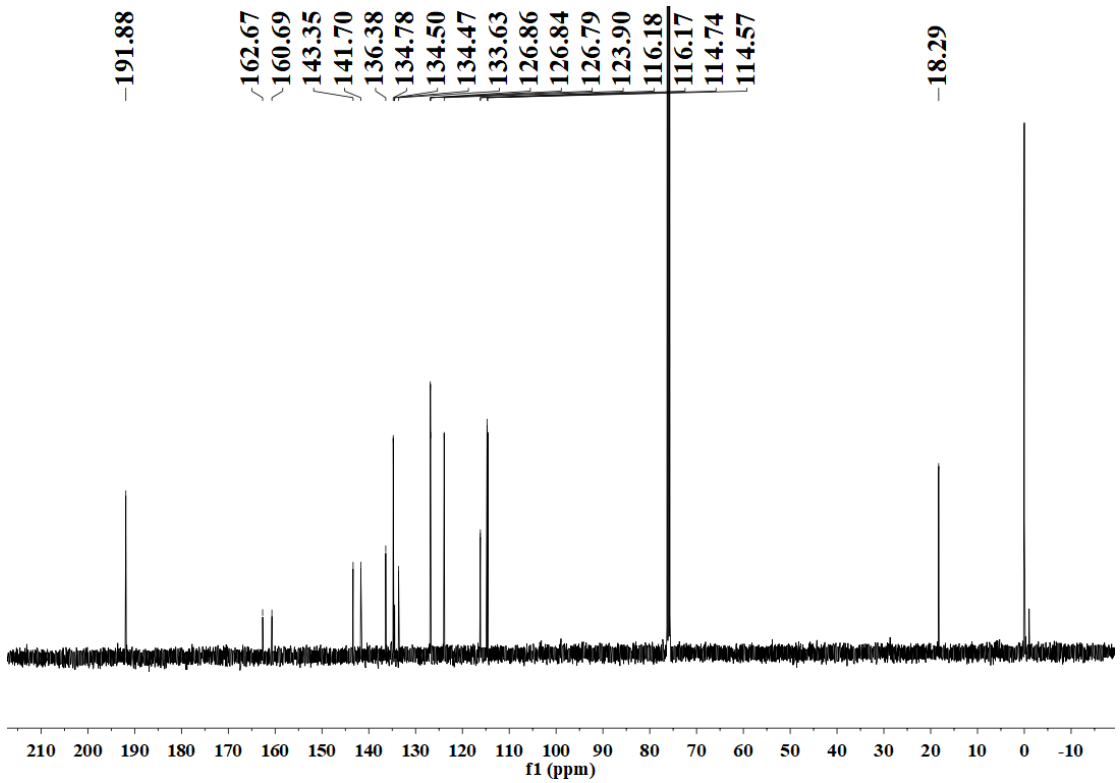

10.07
7.87
7.85
7.47
7.37
7.26
7.20
7.18
6.84
6.82
6.03
5.09
3.79
2.16
0.94
0.96
1.01
1.05
1.97
2.01
1.00
0.99
3.08
3.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

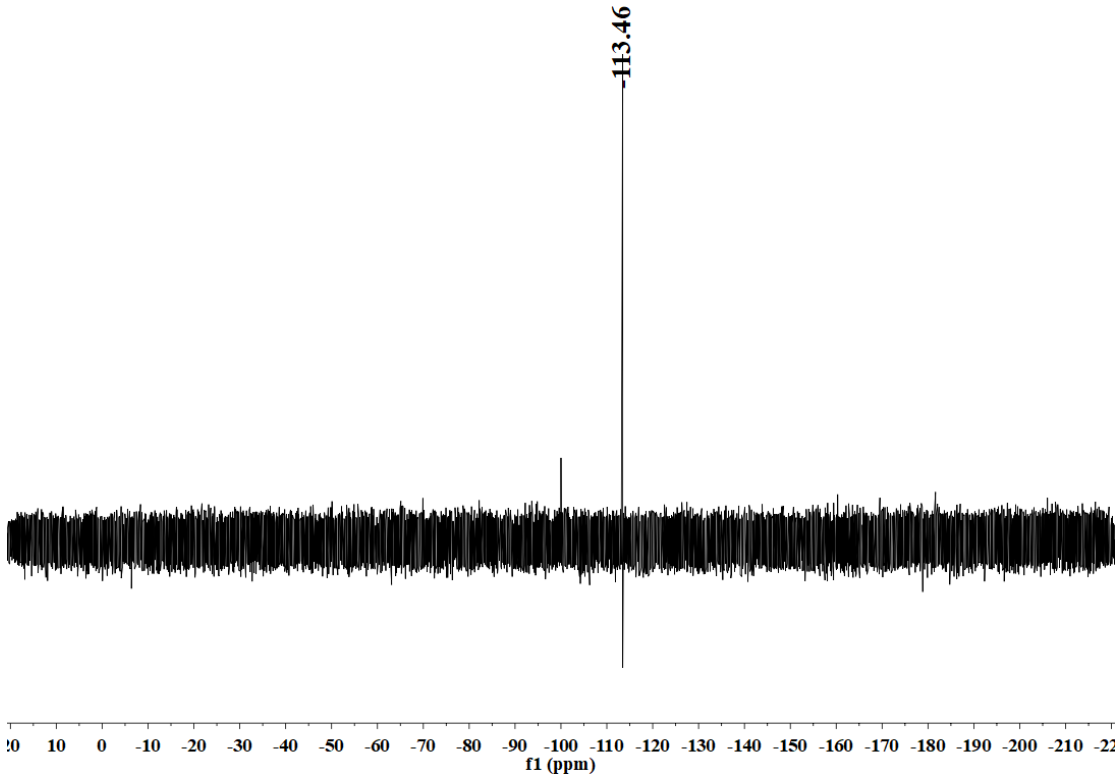

192.25
158.64
144.04
142.04
136.44
134.63
133.66
131.04
126.57
126.38
123.55
114.40
113.03
54.27
18.26
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

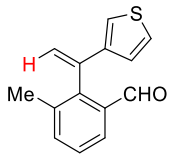

F
H
Me
CHO

(1g)

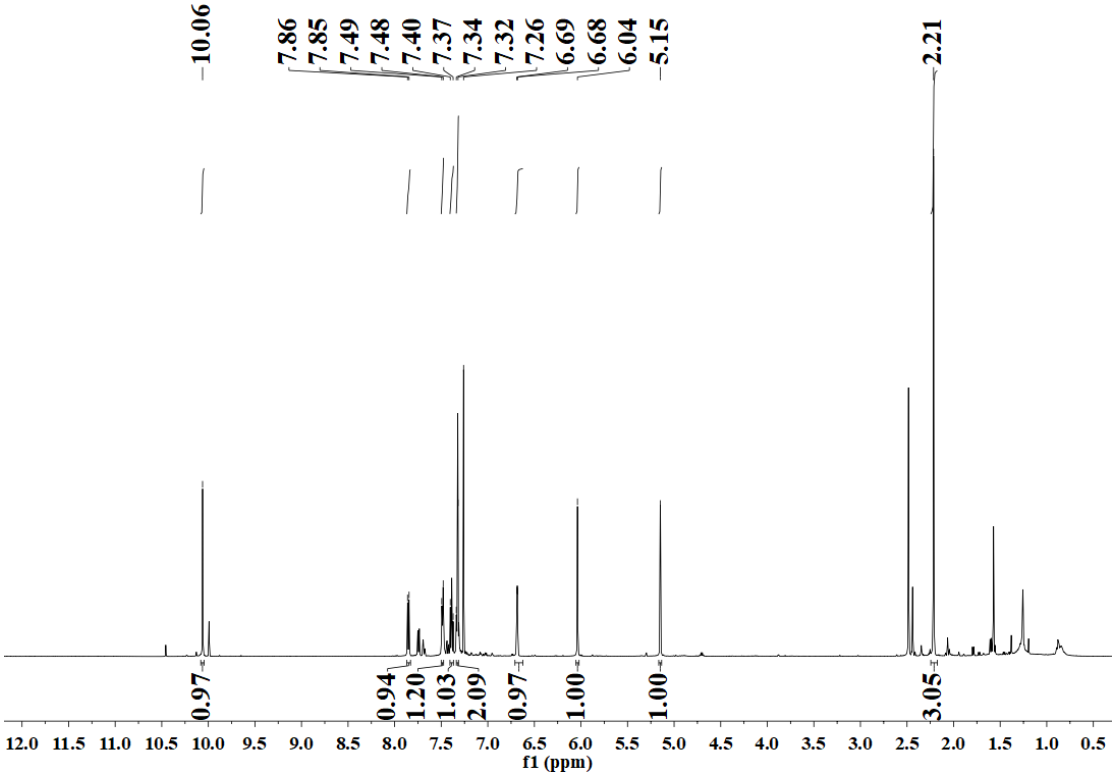

10.07
7.87
7.86
7.49
7.47
7.42
7.39
7.26
7.25
7.22
7.02
6.98
6.09
5.19
2.15
0.99
0.97
1.03
1.03
2.03
2.06
1.00
1.00
3.03
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

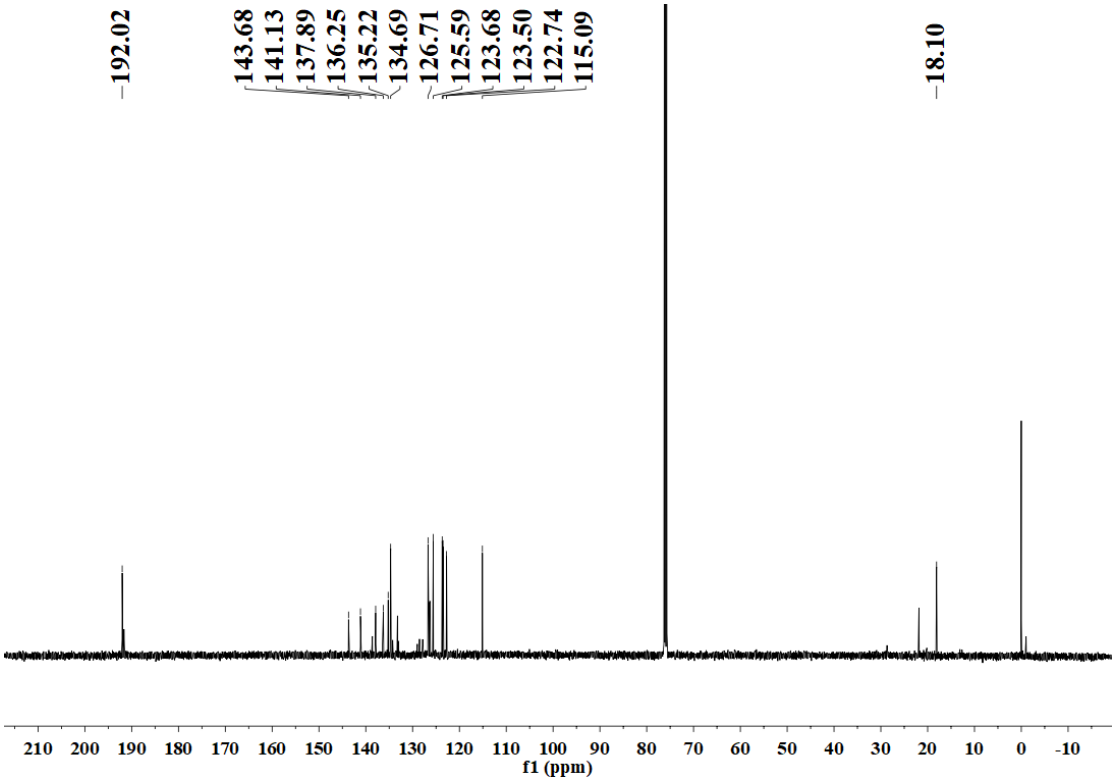

191.88
162.67
160.69
143.35
141.70
136.38
134.78
134.50
134.47
133.63
126.86
126.84
126.79
123.90
116.18
116.17
114.74
114.57
18.29
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

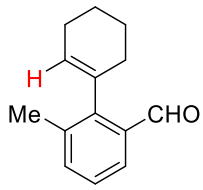

-113.46
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


S
H
Me
CHO

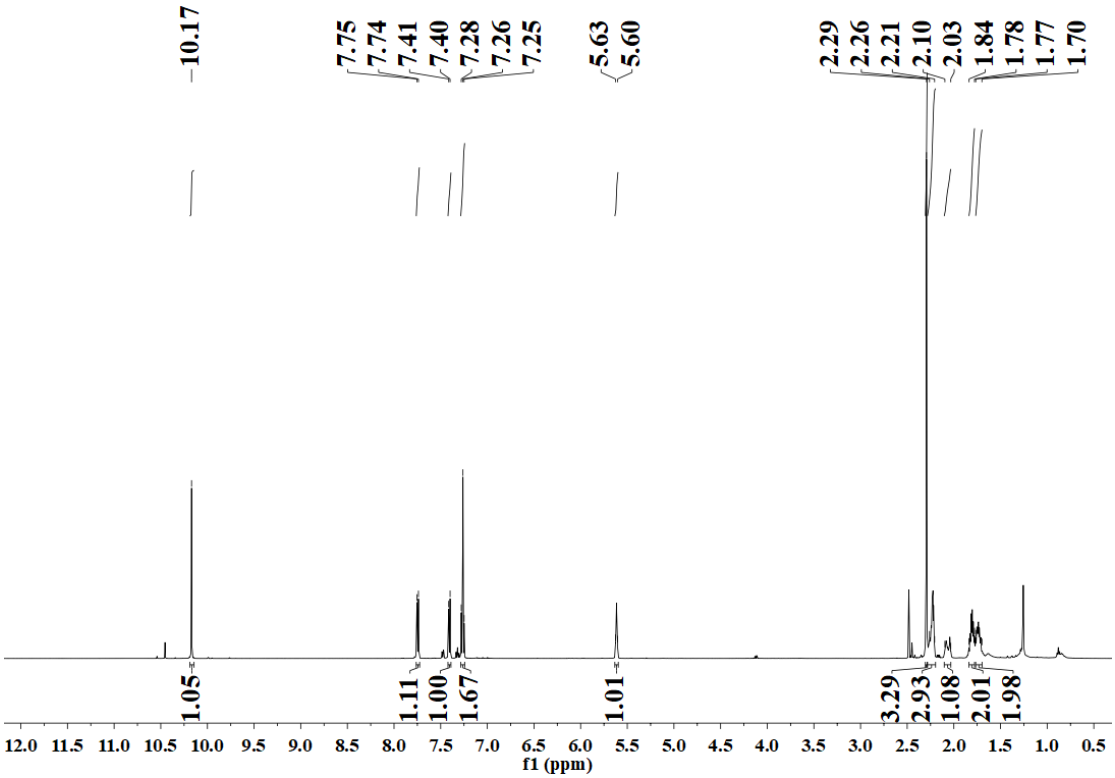
(1h)

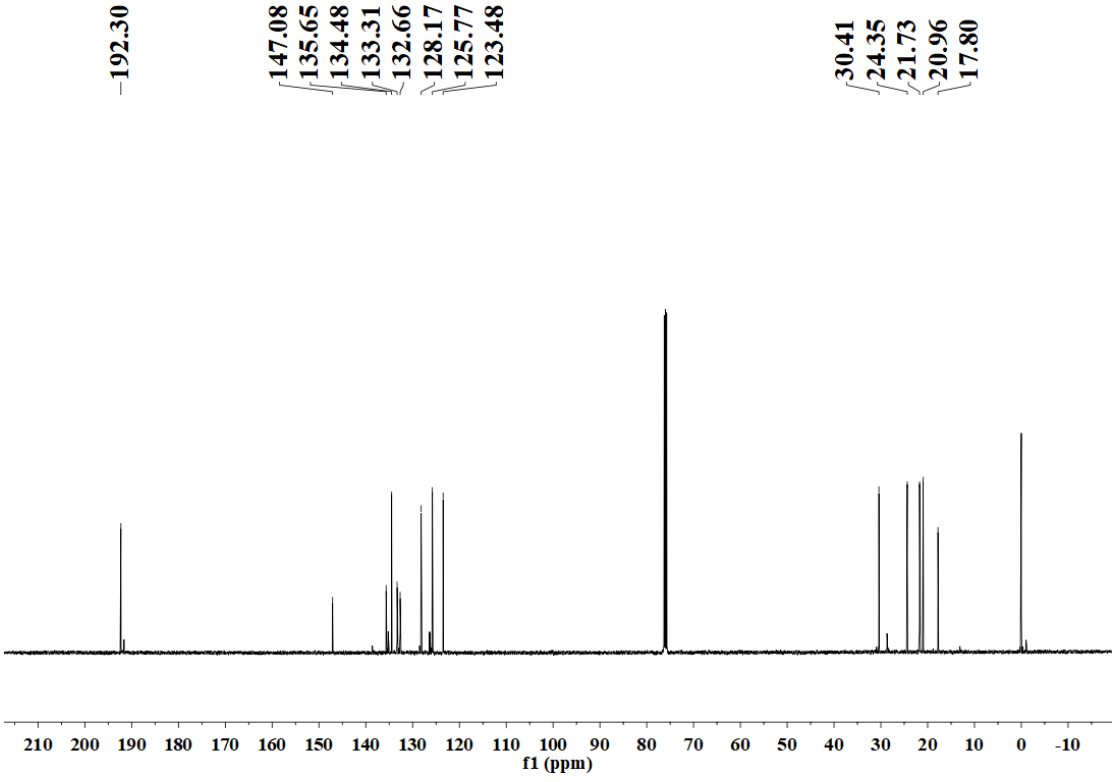

10.06
7.86
7.85
7.49
7.48
7.40
7.37
7.34
7.32
7.26
6.69
6.68
6.04
5.15
2.21
0.97
0.94
1.20
1.03
2.09
0.97
1.00
1.00
3.05
f1 (ppm)

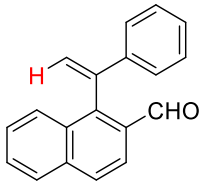

192.02
143.68
141.13
137.89
136.25
135.22
134.69
126.71
125.59
123.68
123.50
122.74
115.09
18.10
f1 (ppm)


H
Me
CHO

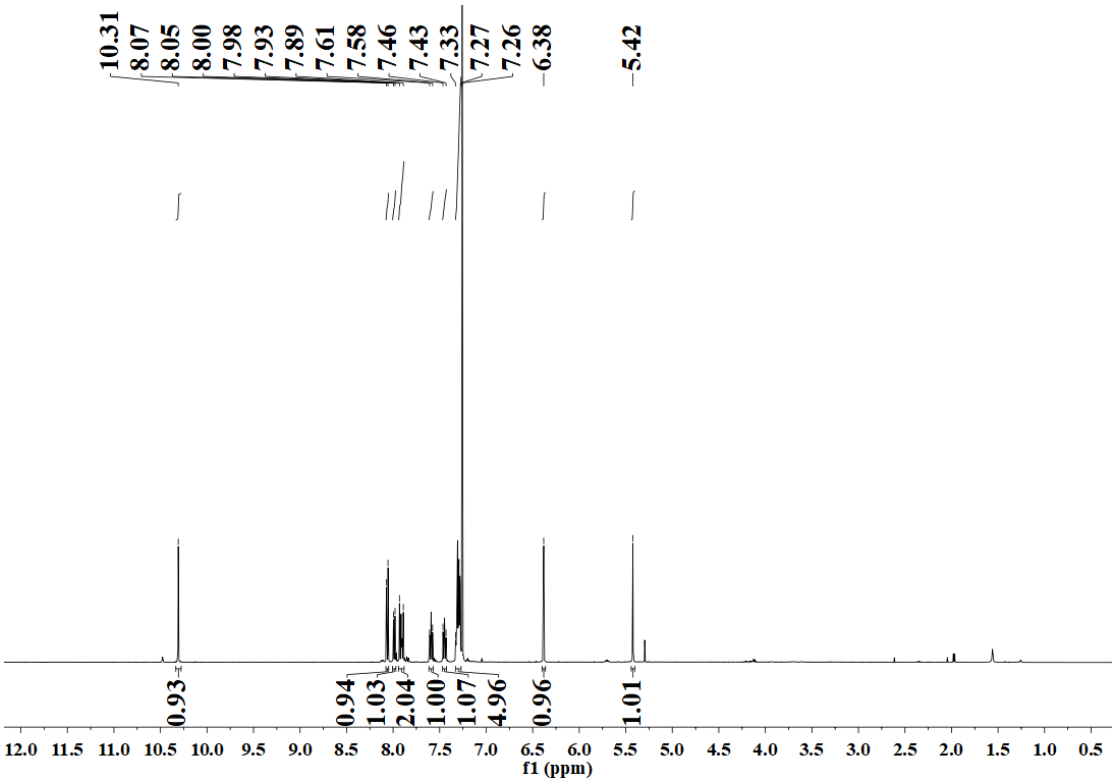
(1i)

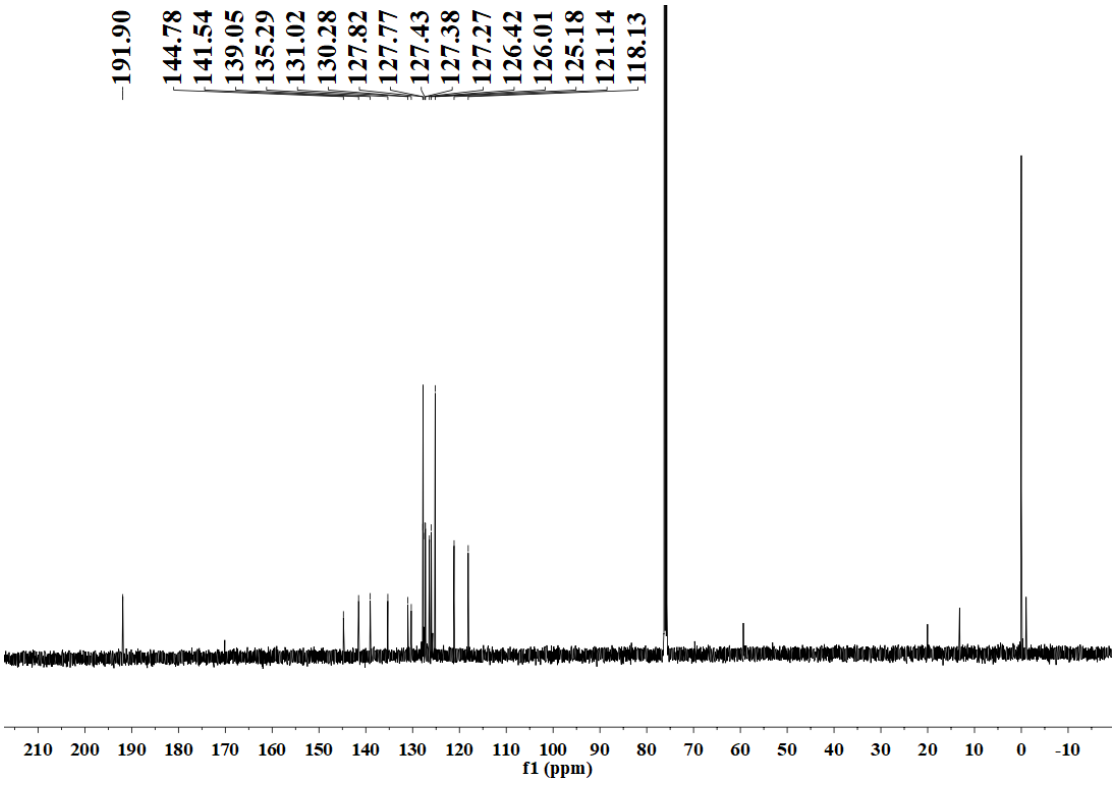

10.17
7.75
7.74
7.41
7.40
7.28
7.26
7.25
5.63
5.60
2.29
2.26
2.21
2.10
2.03
1.84
1.78
1.77
1.70
1.05
1.11
1.00
1.67
1.01
3.29
2.93
1.08
2.01
1.98
f1 (ppm)

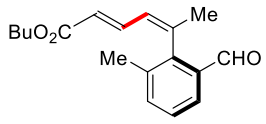

192.30
147.08
135.65
134.48
133.31
132.66
128.17
125.77
123.48
30.41
24.35
21.73
20.96
17.80
f1 (ppm)


H
CHO

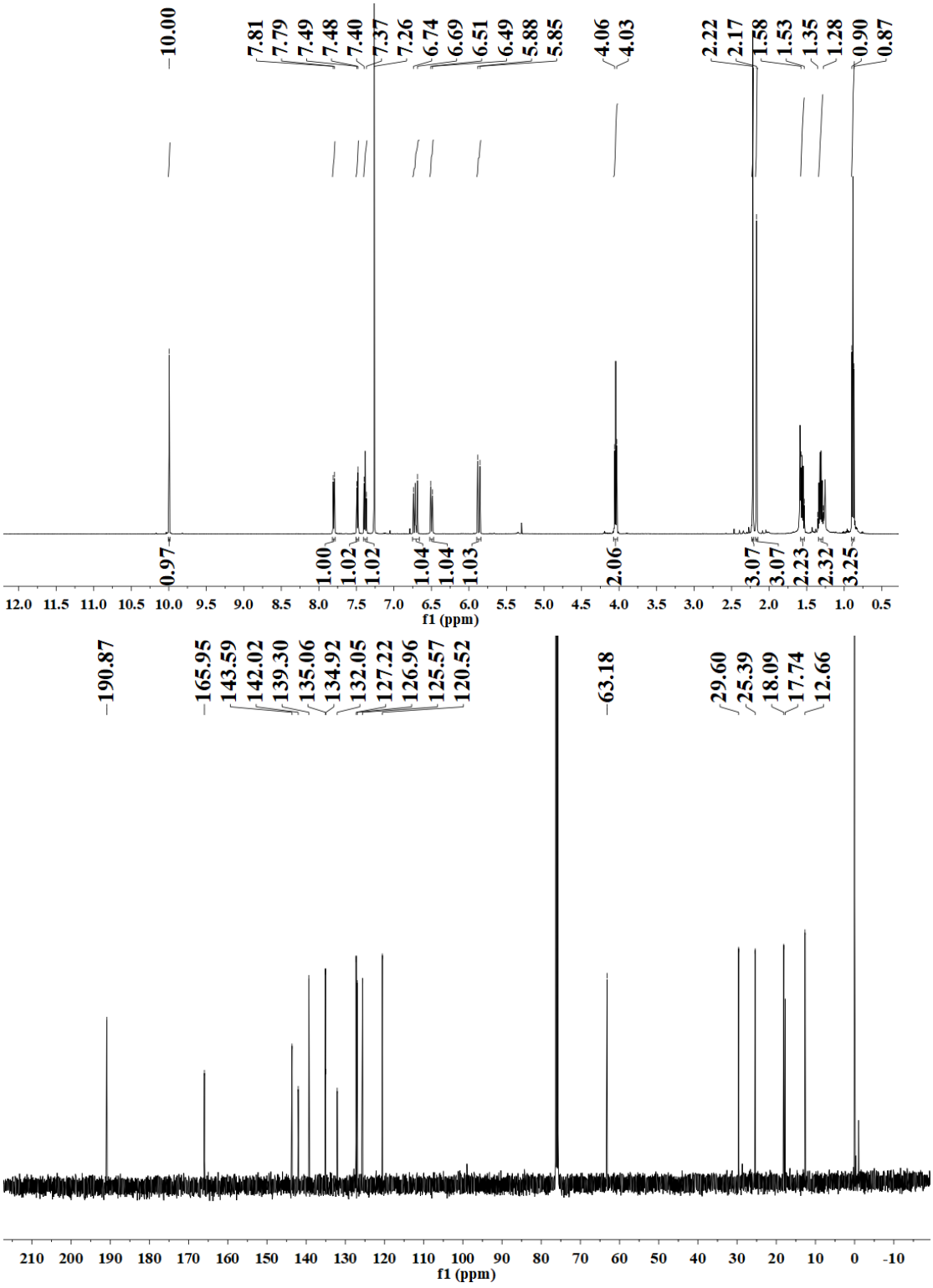
(1j)

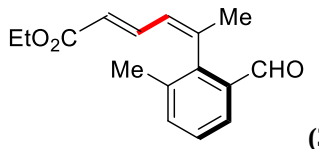

10.31
8.07
8.05
8.00
7.98
7.93
7.89
7.61
7.58
7.46
7.43
7.33
7.27
7.26
6.38
5.42
0.93
0.94
1.03
2.04
1.00
1.07
4.96
0.96
1.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


191.90
144.78
141.54
139.05
135.29
131.02
130.28
127.82
127.77
127.43
127.38
127.27
126.42
126.01
125.18
121.14
118.13
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

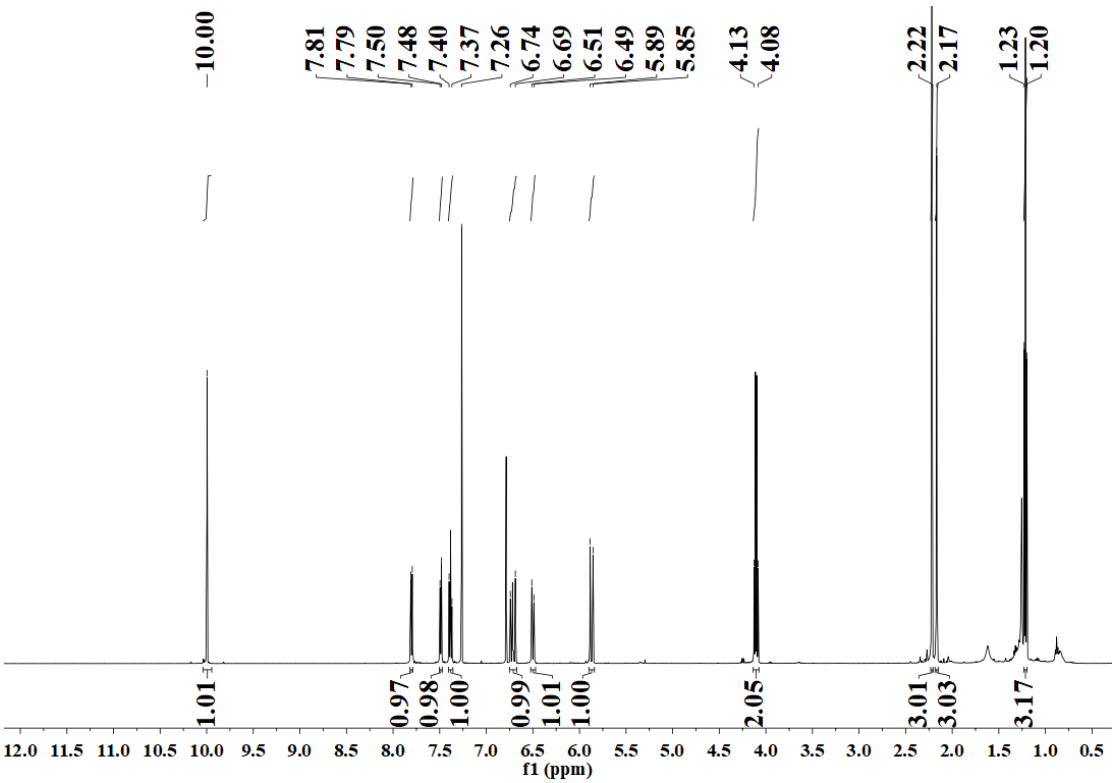

BuO2C
Me
Me
CHO

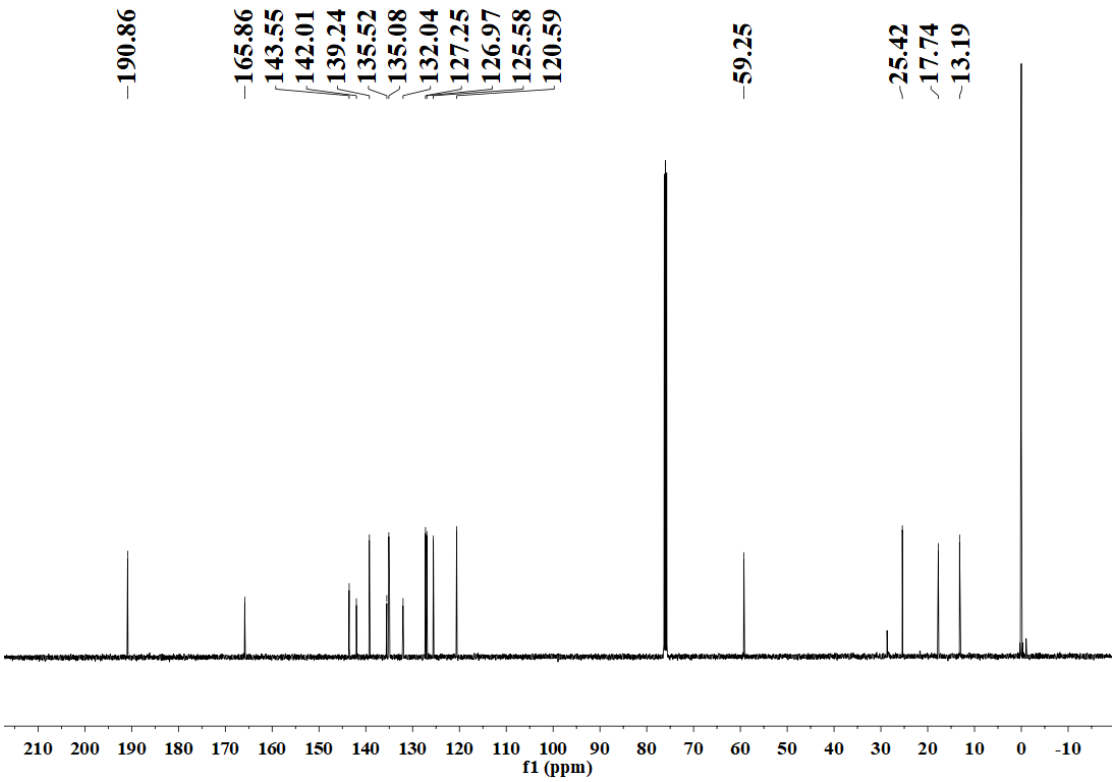
(3a)

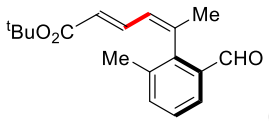

10.00
7.81
7.79
7.49
7.48
7.40
7.37
7.26
6.74
6.69
6.51
6.49
5.88
5.85
4.06
4.03
2.22
2.17
1.58
1.53
1.35
1.28
0.90
0.87
0.97
1.00
1.02
1.02
1.04
1.04
1.03
2.06
3.07
3.07
2.23
2.32
3.25
f1 (ppm)
190.87
165.95
143.59
142.02
139.30
135.06
134.92
132.05
127.22
126.96
125.57
120.52
63.18
29.60
25.39
18.09
17.74
12.66
f1 (ppm)


EtO2C
Me
Me
CHO

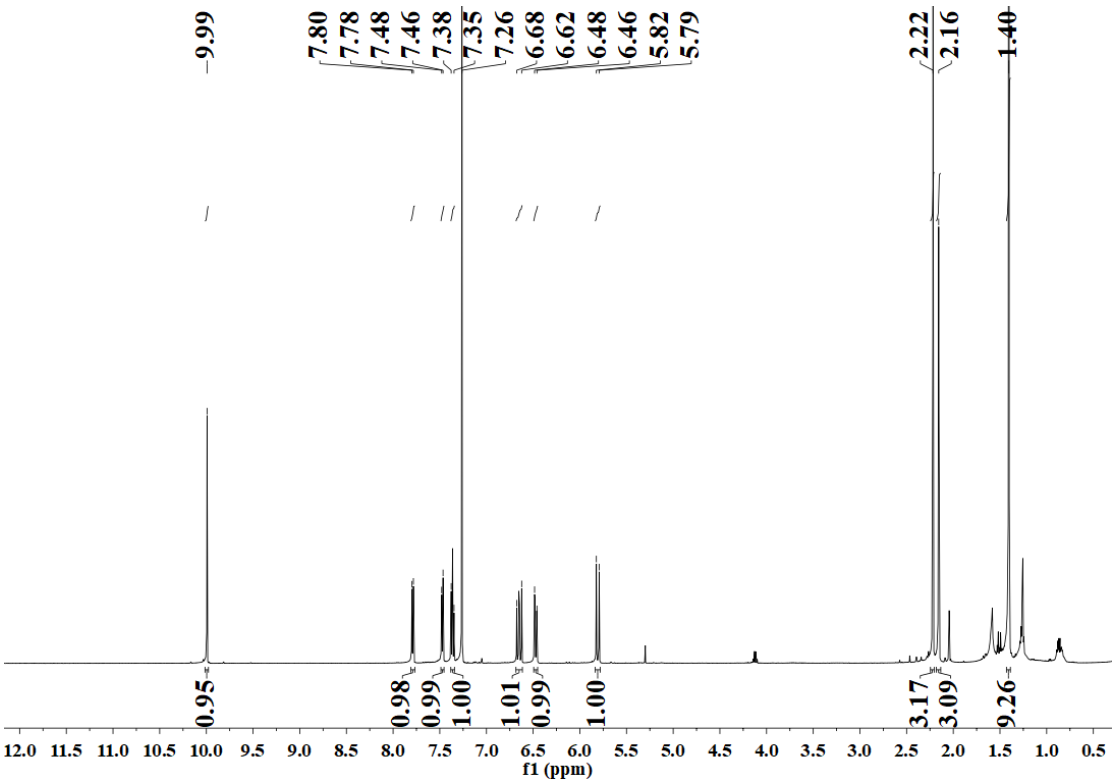
(3b)

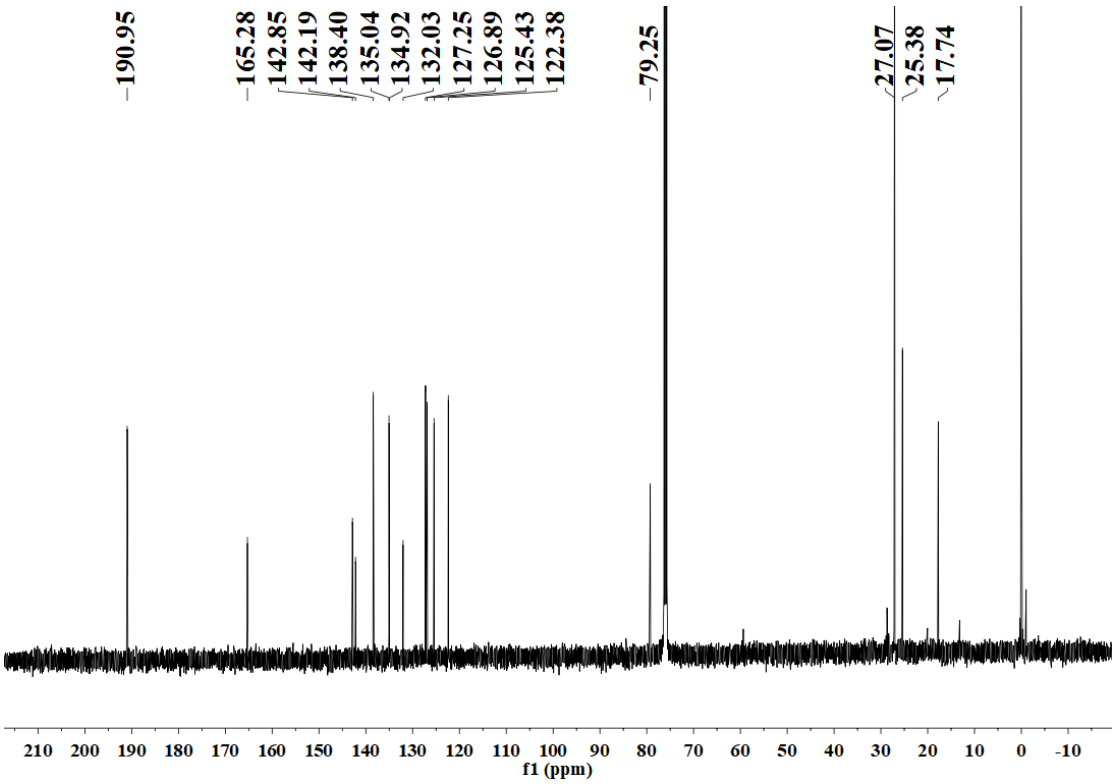

10.00
7.81
7.79
7.50
7.48
7.40
7.37
7.26
6.74
6.69
6.51
6.49
5.89
5.85
4.13
4.08
2.22
2.17
1.23
1.20
1.01
0.97
0.98
1.00
0.99
1.01
1.00
2.05
3.01
3.03
3.17
f1 (ppm)

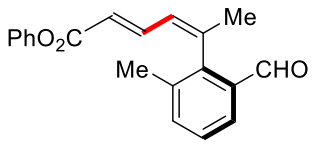

190.86
165.86
143.55
142.01
139.24
135.52
135.08
132.04
127.25
126.97
125.58
120.59
59.25
25.42
17.74
13.19
f1 (ppm)


tBuO2C
Me
Me
CHO

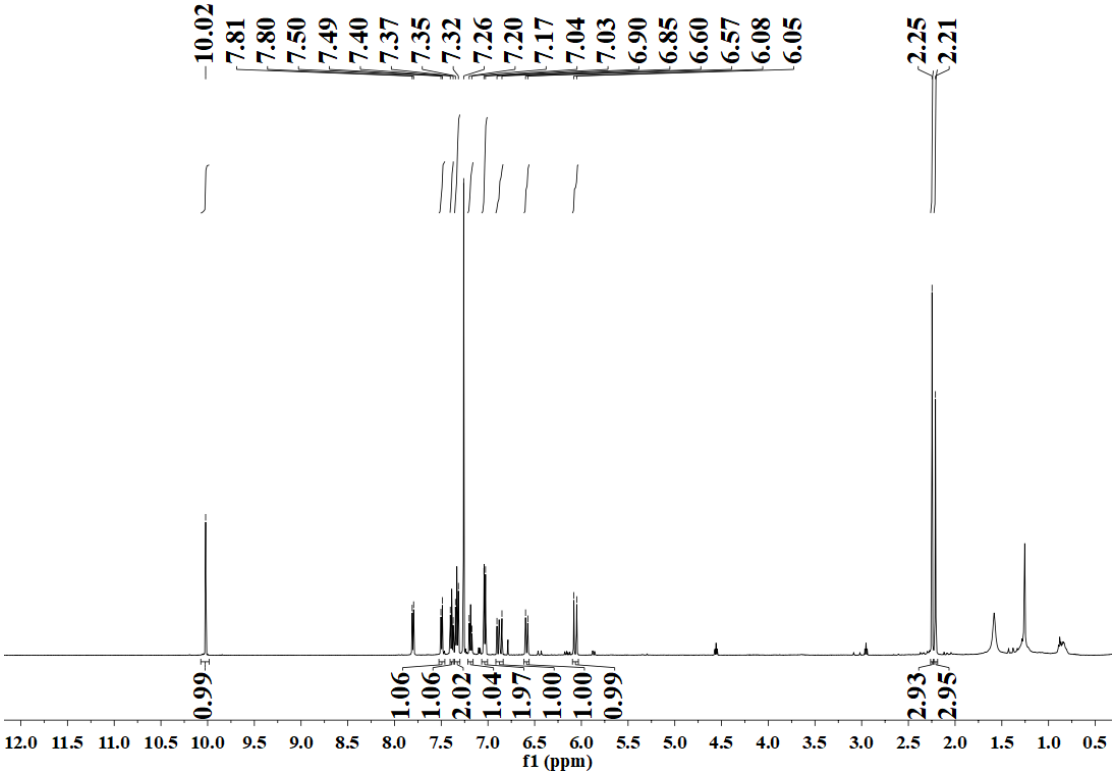
(3c)

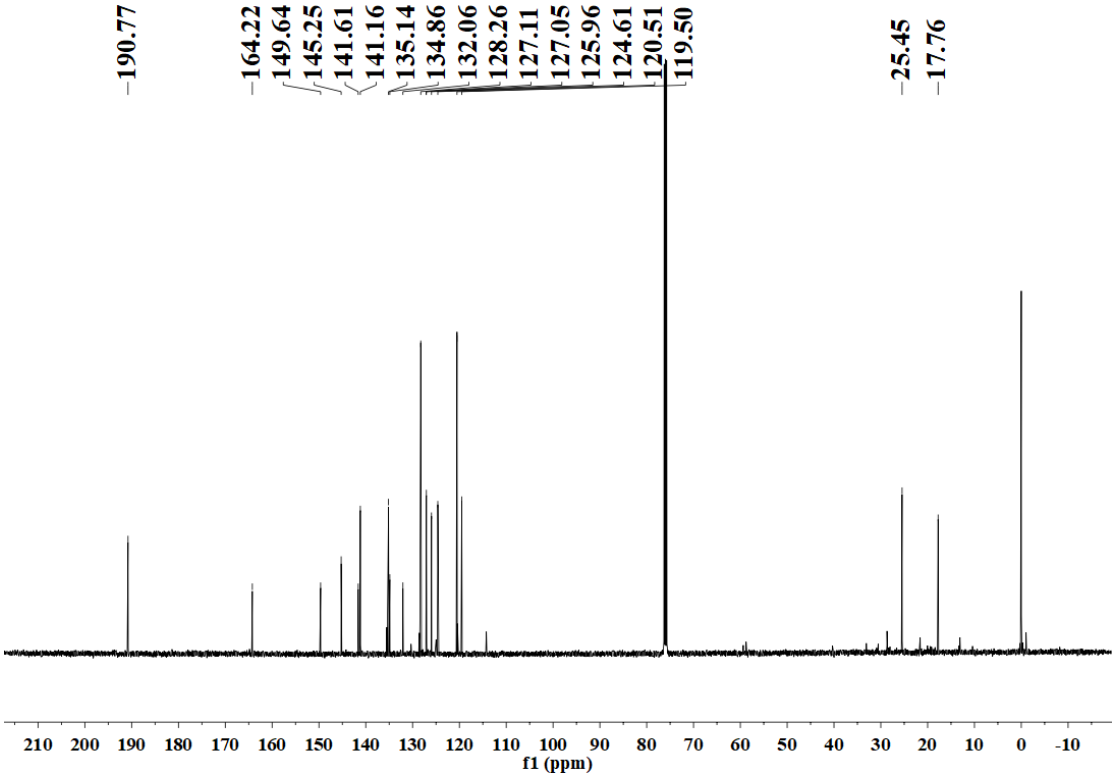

9.99
7.80
7.78
7.48
7.46
7.38
7.35
7.26
6.68
6.62
6.48
6.46
5.82
5.79
2.22
2.16
1.40
0.95
0.98
0.99
1.00
1.01
0.99
1.00
3.17
3.09
9.26
f1 (ppm)

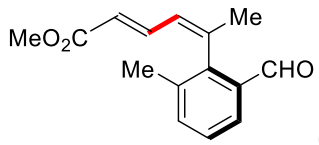

190.95
165.28
142.85
142.19
138.40
135.04
134.92
132.03
127.25
126.89
125.43
122.38
79.25
27.07
25.38
17.74
f1 (ppm)


PhO2C
Me
Me
CHO

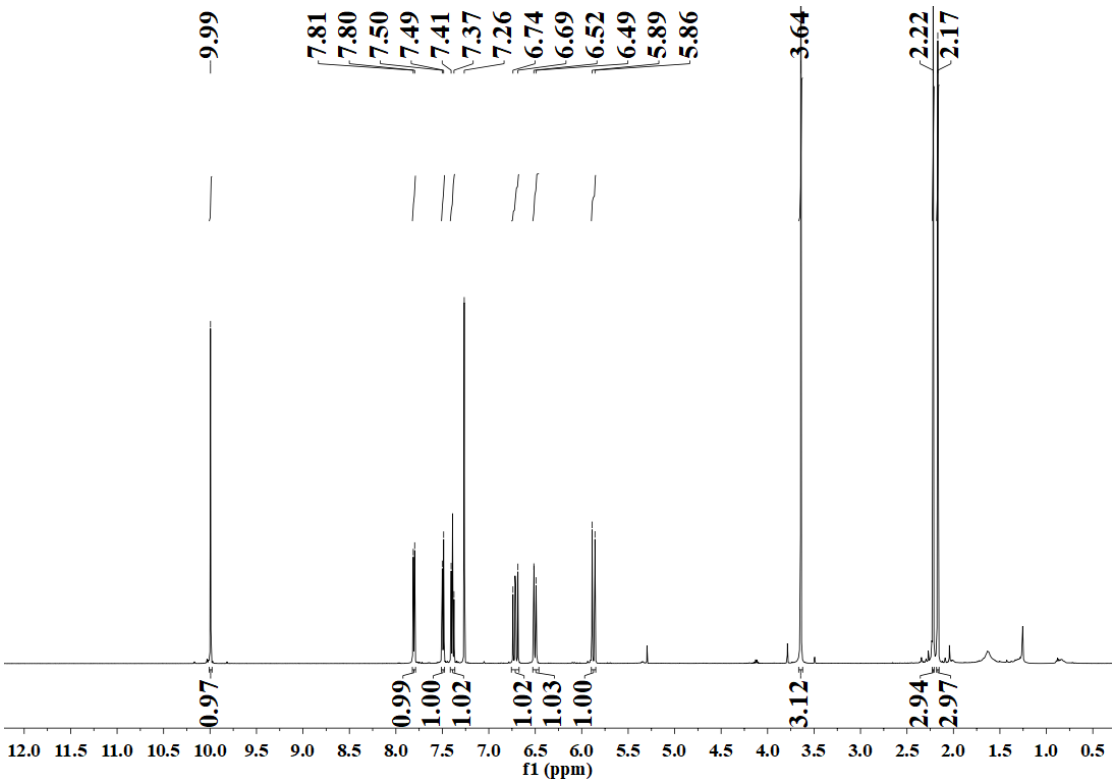
(3d)

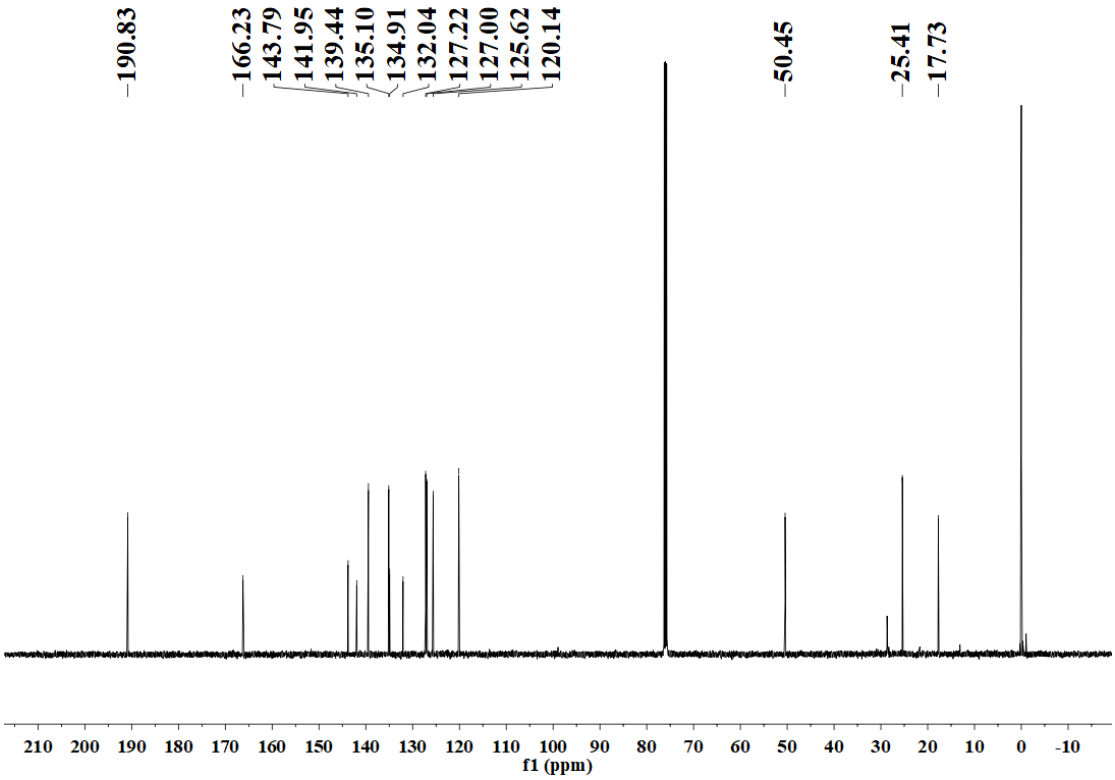

10.02
7.81
7.80
7.50
7.49
7.40
7.37
7.35
7.32
7.26
7.20
7.17
7.04
7.03
6.90
6.85
6.60
6.57
6.08
6.05
2.25
2.21
0.99
1.06
1.06
2.02
1.04
1.97
1.00
1.00
0.99
2.93
2.95
f1 (ppm)

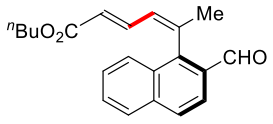

190.77
164.22
149.64
145.25
141.61
141.16
135.14
134.86
132.06
128.26
127.11
127.05
125.96
124.61
120.51
119.50
25.45
17.76
f1 (ppm)


MeO2C
Me
Me
CHO

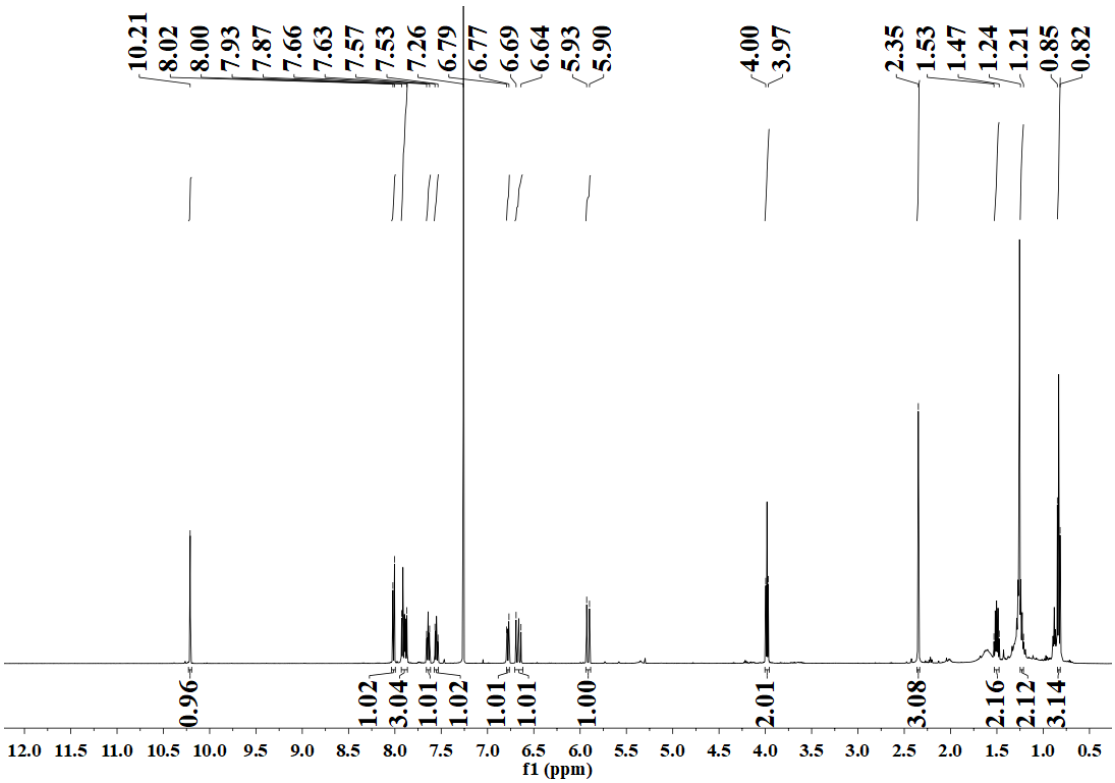
(3e)

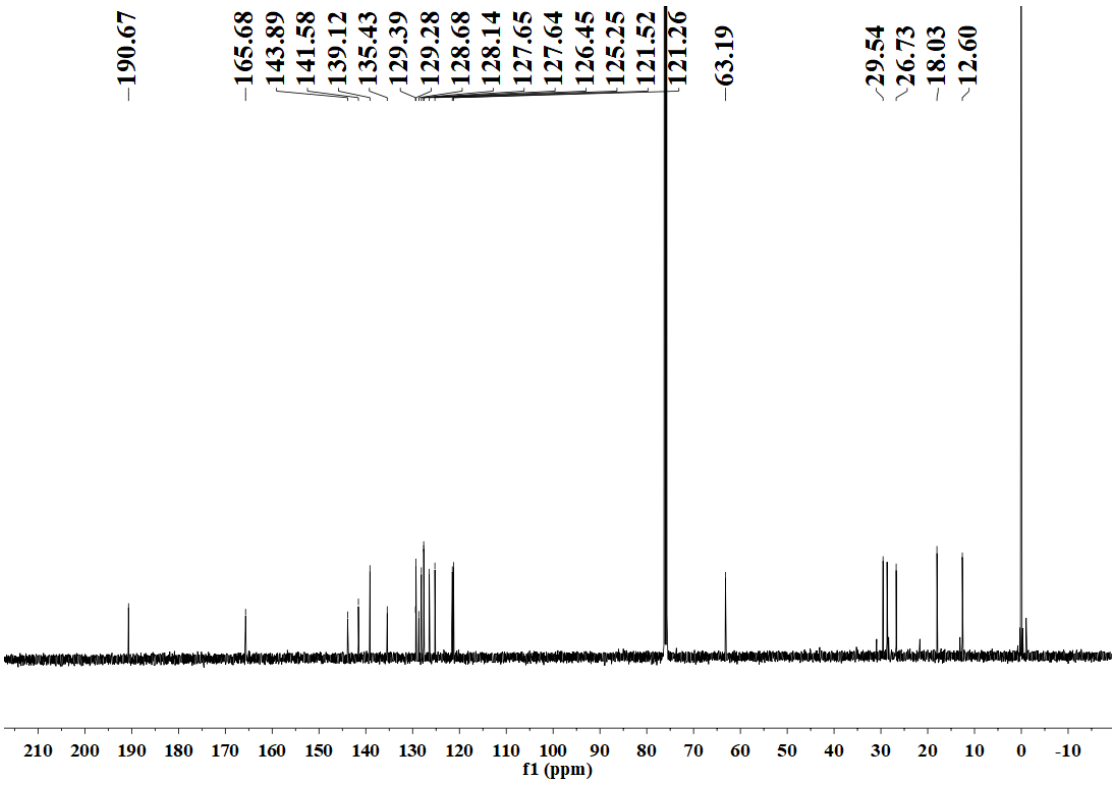

9.99
7.81
7.80
7.50
7.49
7.41
7.37
7.26
6.74
6.69
6.52
6.49
5.89
5.86
3.64
2.22
2.17
0.97
0.99
1.00
1.02
1.02
1.03
1.00
3.12
2.94
2.97
f1 (ppm)

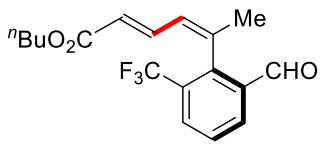

190.83
166.23
143.79
141.95
139.44
135.10
134.91
132.04
127.22
127.00
125.62
120.14
50.45
25.41
17.73
f1 (ppm)


nBuO2C
Me
CHO

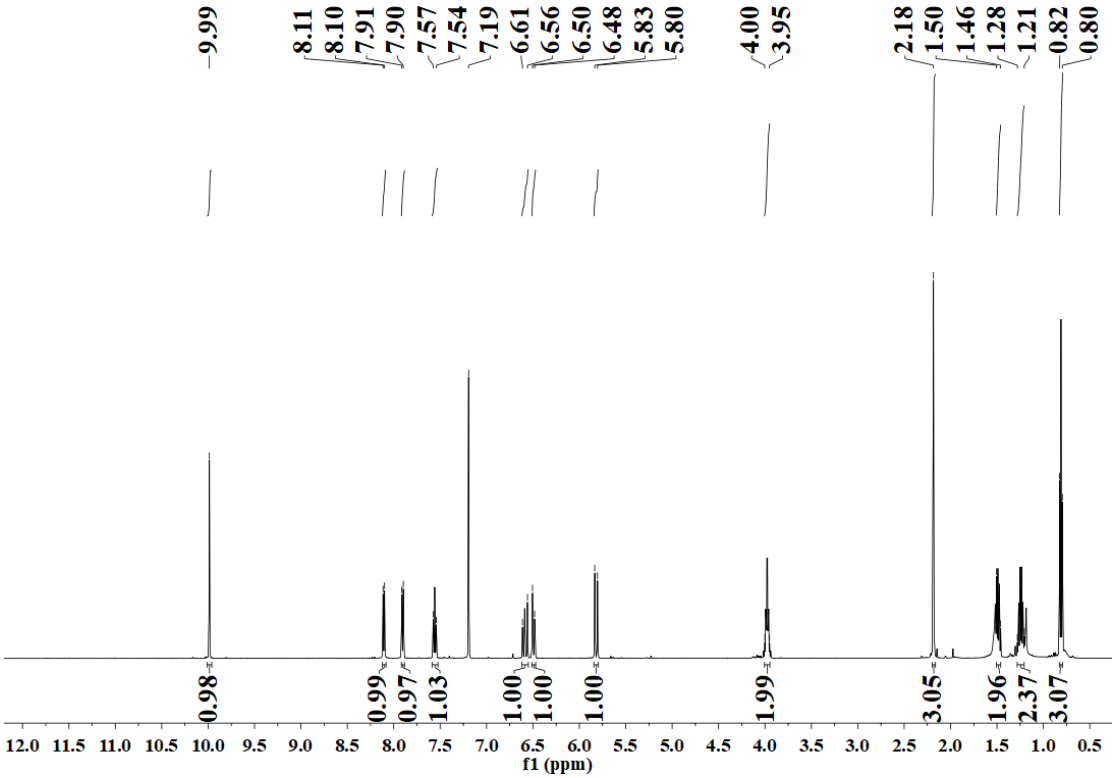
(3f)

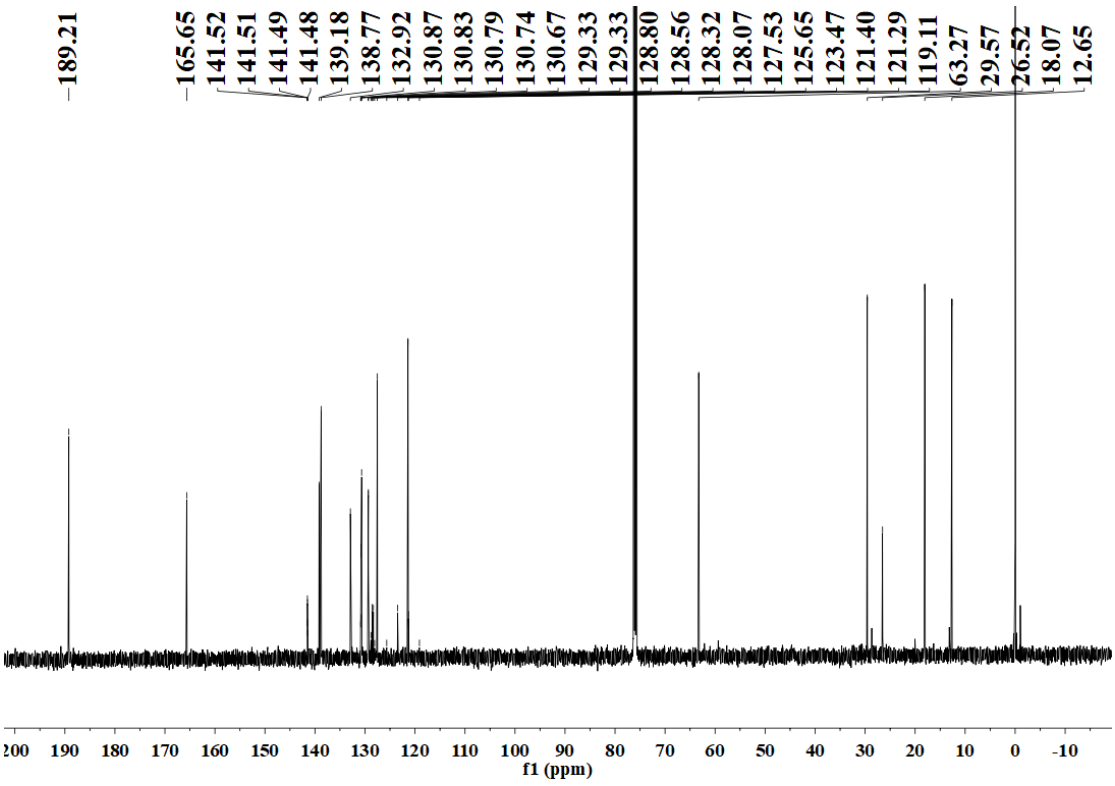

10.21
8.02
8.00
7.93
7.87
7.66
7.63
7.57
7.53
7.26
6.79
6.77
6.69
6.64
5.93
5.90
4.00
3.97
2.35
1.53
1.47
1.24
1.21
0.85
0.82
0.96
1.02
3.04
1.01
1.02
1.01
1.01
1.00
2.01
3.08
2.16
2.12
3.14
f1 (ppm)

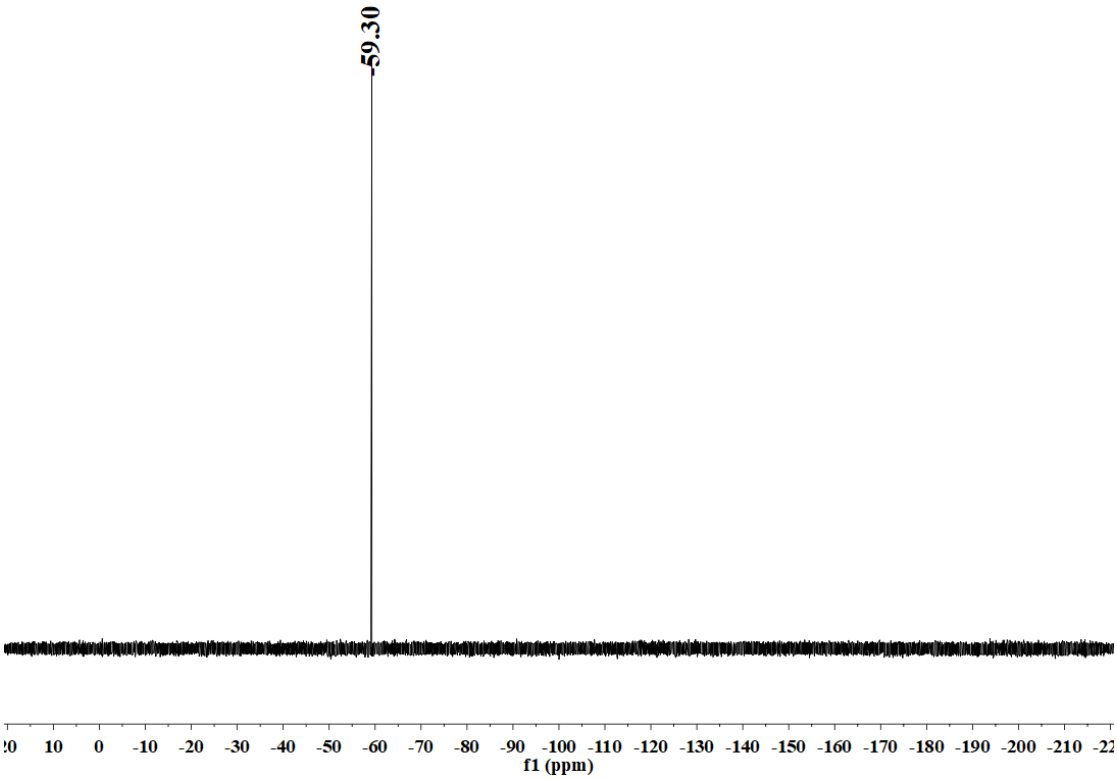

190.67
165.68
143.89
141.58
139.12
135.43
129.39
129.28
128.68
128.14
127.65
127.64
126.45
125.25
121.52
121.26
63.19
29.54
26.73
18.03
12.60
f1 (ppm)

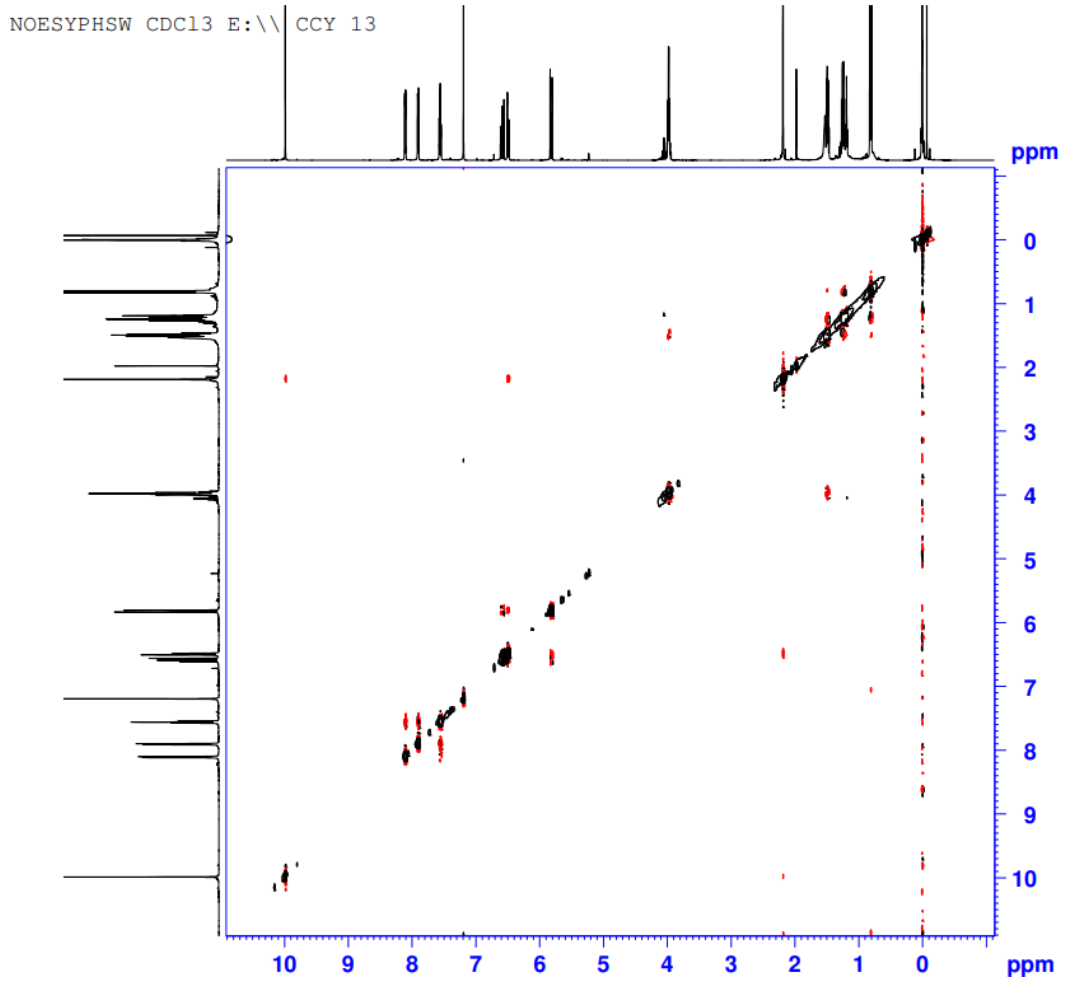

nBuO2C
Me
F3C
CHO

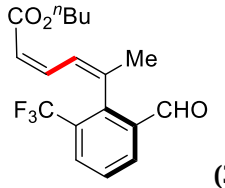
(3g)


9.99
8.11
8.10
7.91
7.90
7.57
7.54
7.19
6.61
6.56
6.50
6.48
5.83
5.80
4.00
3.95
2.18
1.50
1.46
1.28
1.21
0.82
0.80
0.98
0.99
0.97
1.03
1.00
1.00
1.00
1.99
3.05
1.96
2.37
3.07
f1 (ppm)

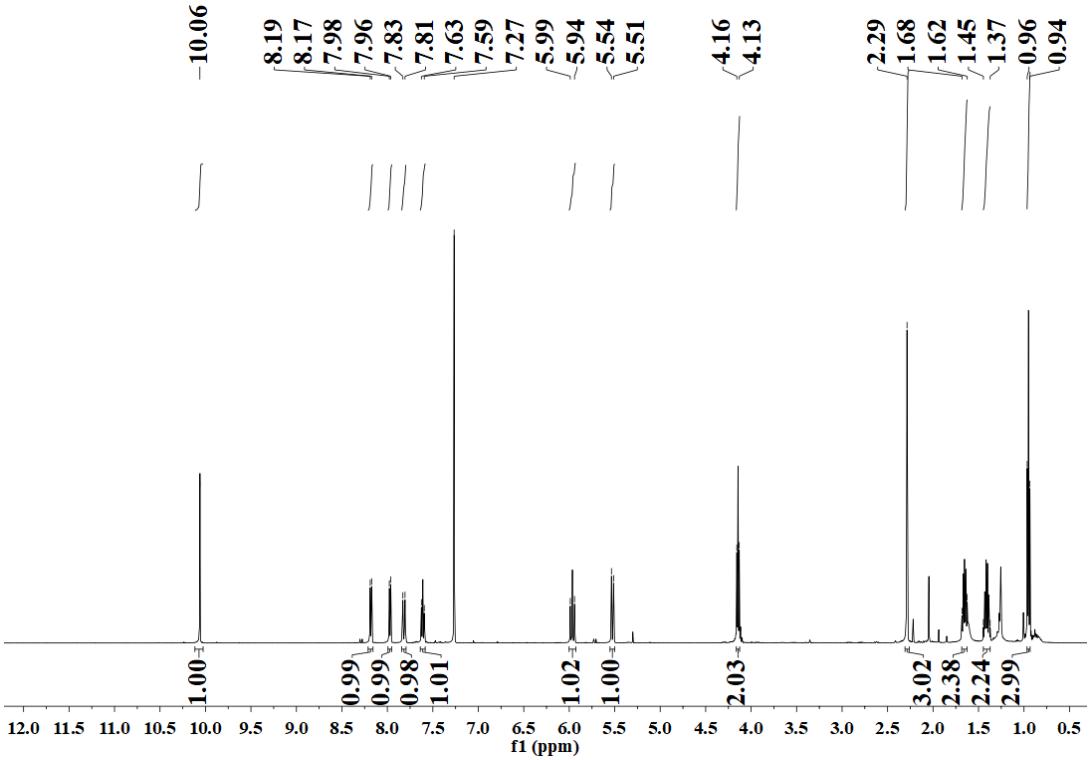

189.21
165.65
141.52
141.51
141.49
141.48
139.18
138.77
132.92
130.87
130.83
130.79
130.74
130.67
129.33
129.33
128.80
128.56
128.32
128.07
127.53
125.65
123.47
121.40
121.29
119.11
63.27
29.57
26.52
18.07
12.65
f1 (ppm)

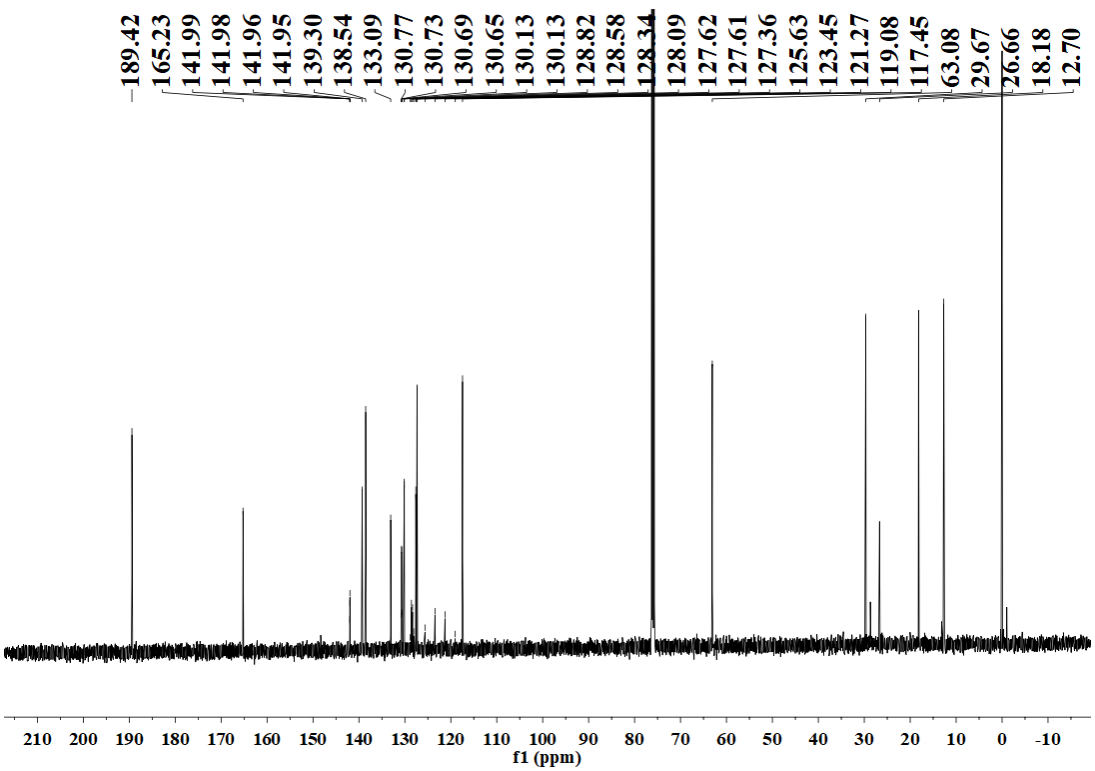

-59.30
f1 (ppm)

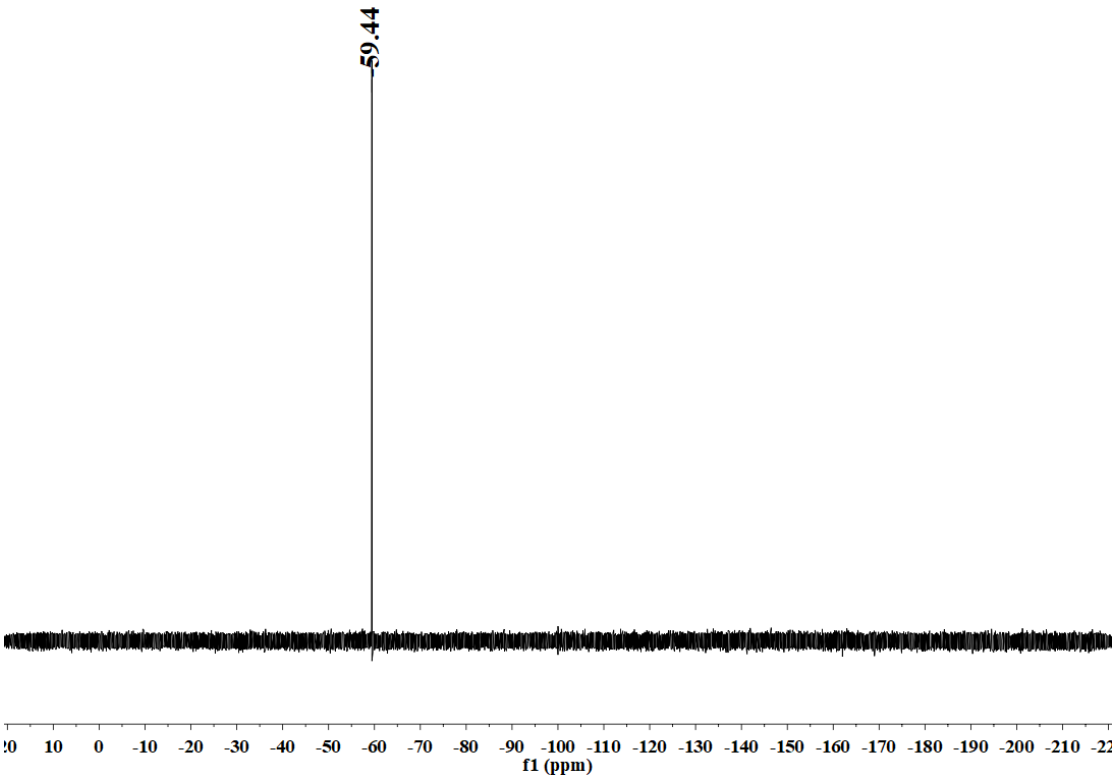

NOESYPHSW CDCl3 E:\\ CCY 13
ppm
ppm

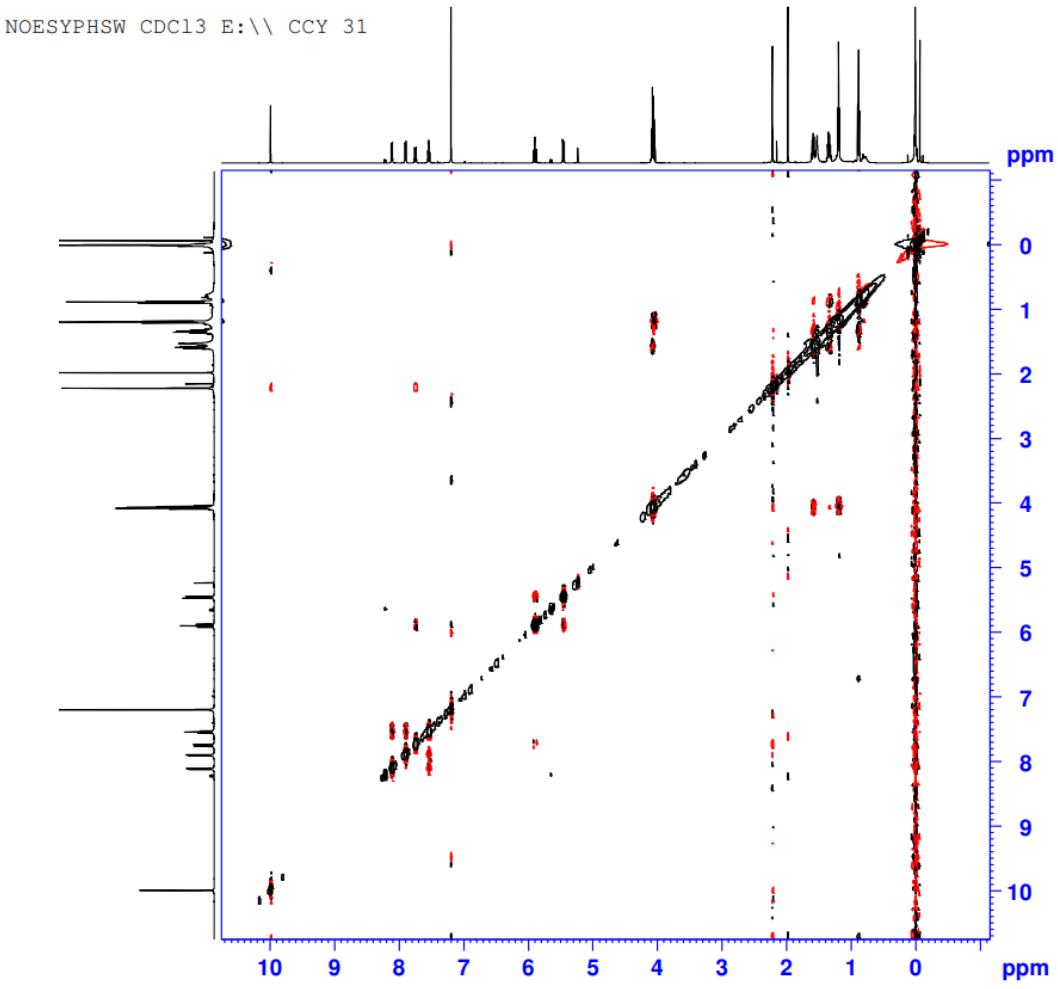

CO2nBu
Me
F3C
CHO

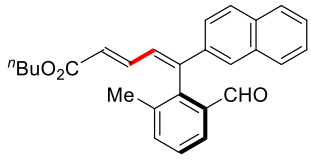
(3g')


10.06
8.19
8.17
7.98
7.96
7.83
7.81
7.63
7.59
7.27
5.99
5.94
5.54
5.51
4.16
4.13
2.29
1.68
1.62
1.45
1.37
0.96
0.94
1.00
0.99
0.99
0.98
1.01
1.02
1.00
2.03
3.02
2.38
2.24
2.99
f1 (ppm)

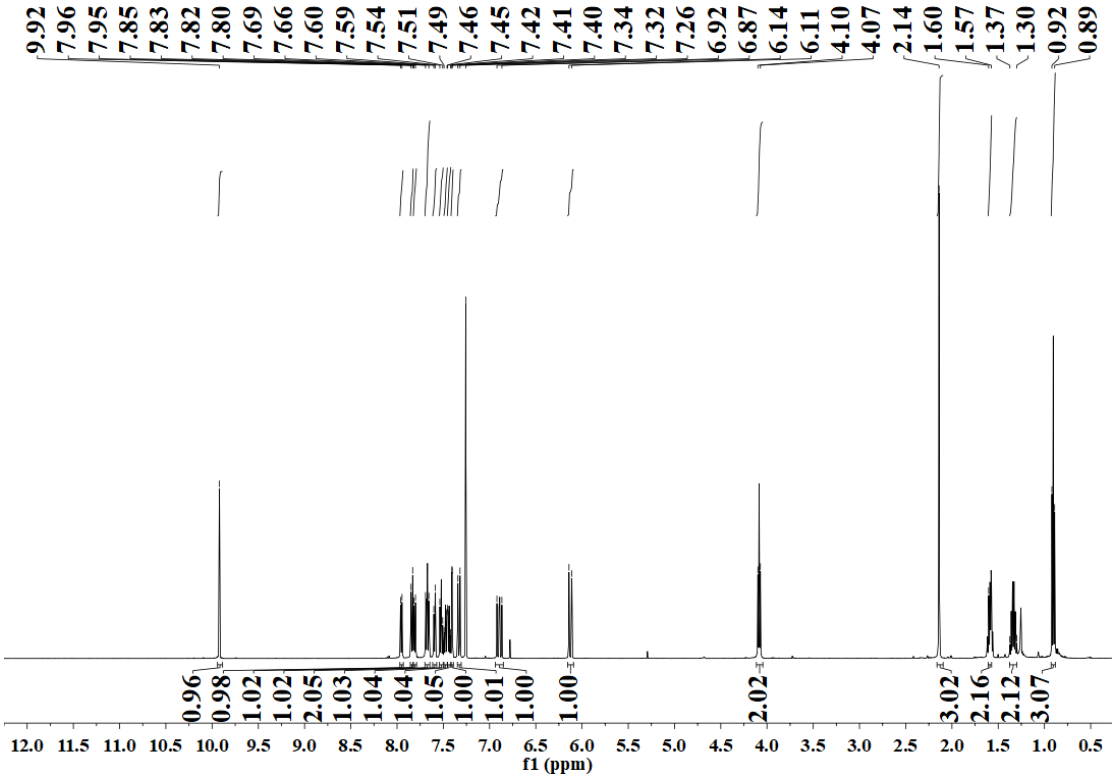

189.42
165.23
141.99
141.98
141.96
141.95
139.30
138.54
133.09
130.77
130.73
130.69
130.65
130.13
130.13
128.82
128.58
128.34
128.09
127.62
127.61
127.36
125.63
123.45
121.27
119.08
117.45
63.08
29.67
26.66
18.18
12.70
f1 (ppm)

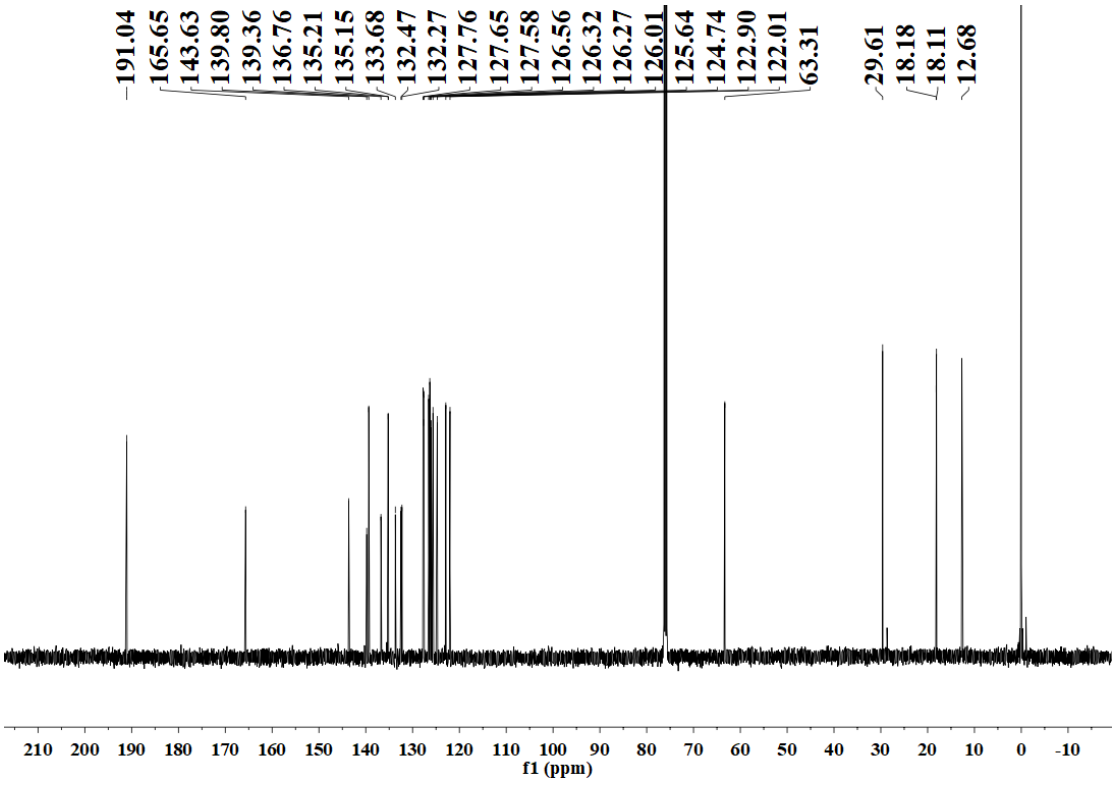

59.44
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

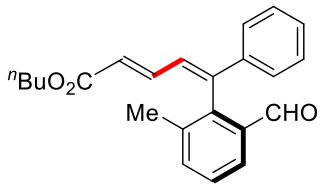

NOESYPHSW CDCl3 E:\\ CCY 31
ppm
0
1
2
3
4
5
6
7
8
9
10
10 9 8 7 6 5 4 3 2 1 0
ppm


nBuO2C
Me
CHO

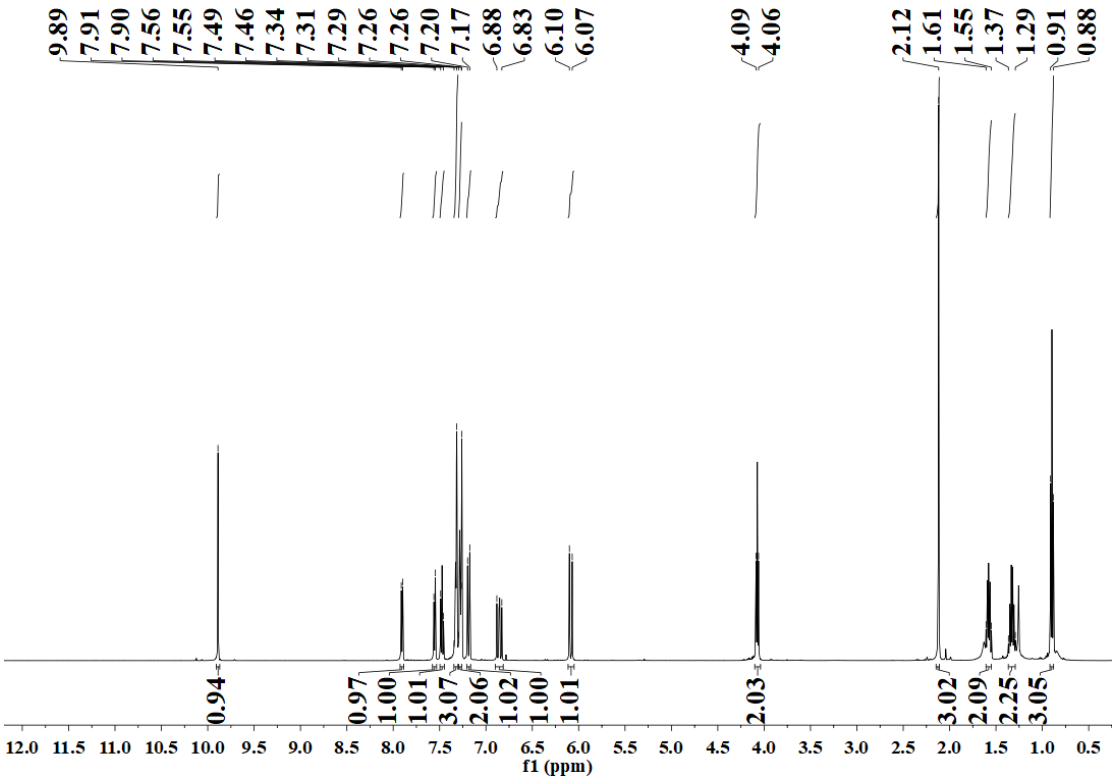
(3h)

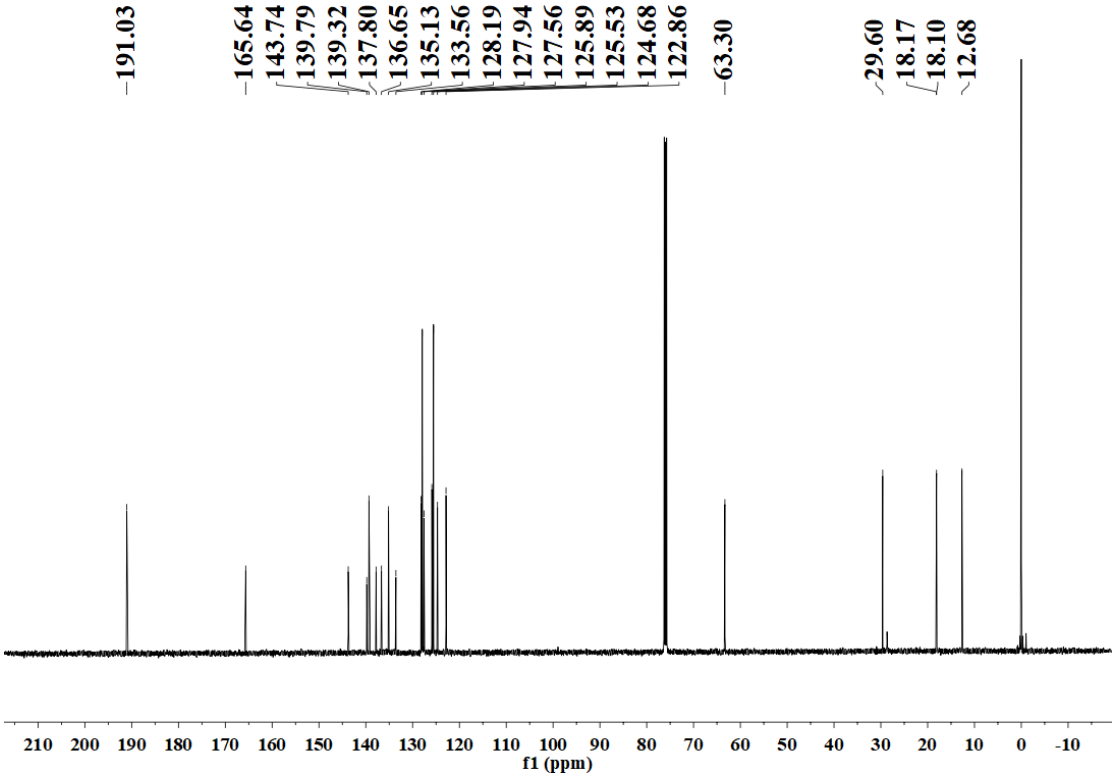

9.92 7.96 7.95 7.85 7.83 7.82 7.80 7.69 7.66 7.60 7.59 7.54 7.51 7.49 7.46 7.45 7.42 7.41 7.40 7.34 7.32 7.26 6.92 6.87 6.14 6.11 4.10 4.07 2.14 1.60 1.57 1.37 1.30 0.92 0.89
0.96 0.98 1.02 1.02 2.05 1.03 1.04 1.04 1.05 1.00 1.01 1.00 1.00 2.02 3.02 2.16 2.12 3.07
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

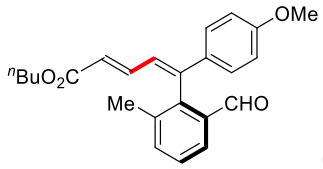

191.04 165.65 143.63 139.80 139.36 136.76 135.21 135.15 133.68 132.47 132.27 127.76 127.65 127.58 126.56 126.32 126.27 126.01 125.64 124.74 122.90 122.01 63.31 29.61 18.18 18.11 12.68
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


^{n}BuO$_2$C
Me
CHO

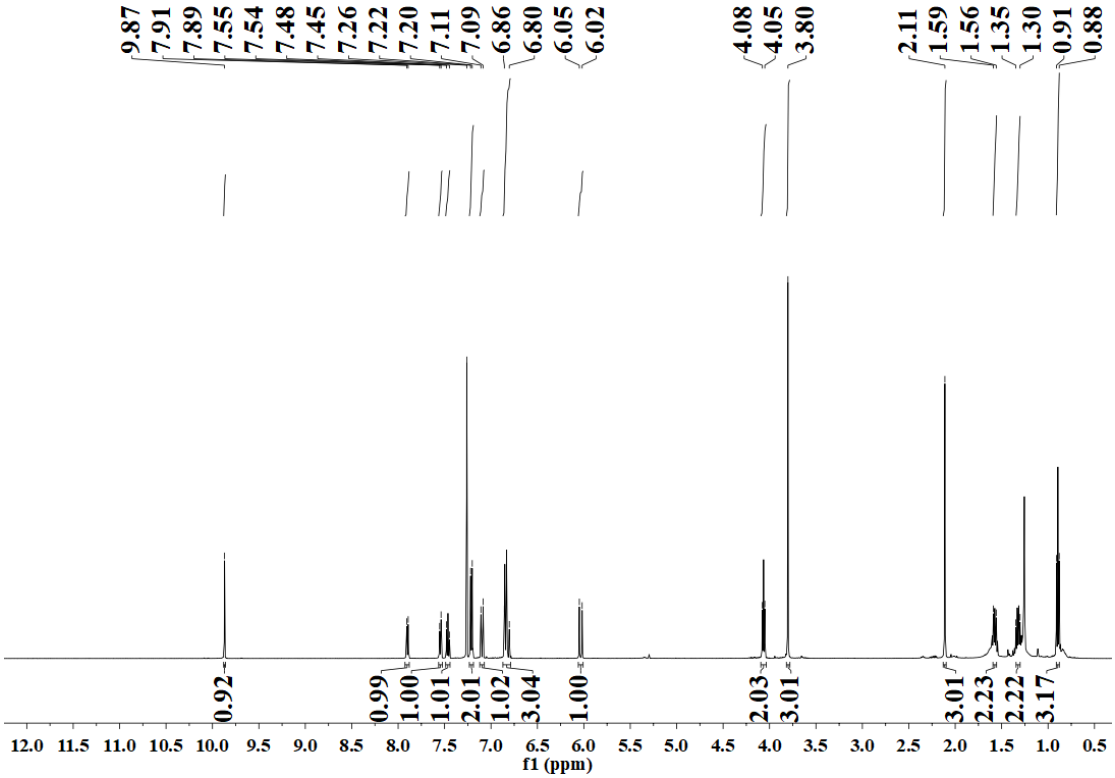
(3i)

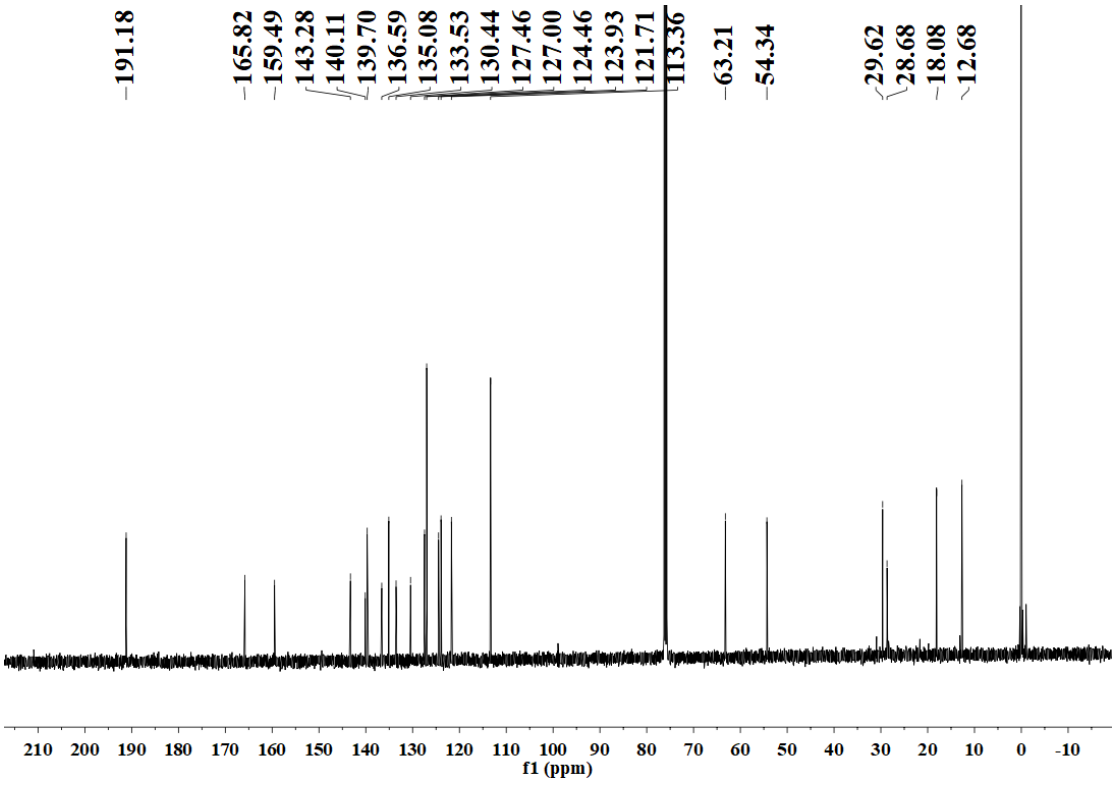

9.89
7.91
7.90
7.56
7.55
7.49
7.46
7.34
7.31
7.29
7.26
7.26
7.20
7.17
6.88
6.83
6.10
6.07
4.09
4.06
2.12
1.61
1.55
1.37
1.29
0.91
0.88
0.94
0.97
1.00
1.01
3.07
2.06
1.02
1.00
1.01
2.03
3.02
2.09
2.25
3.05
f1 (ppm)

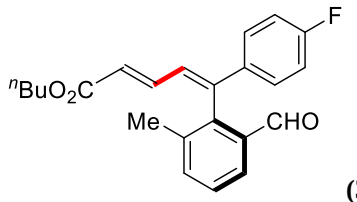

191.03
165.64
143.74
139.79
139.32
137.80
136.65
135.13
133.56
128.19
127.94
127.56
125.89
125.53
124.68
122.86
63.30
29.60
18.17
18.10
12.68
f1 (ppm)


OMe
nBuO2C
Me
CHO

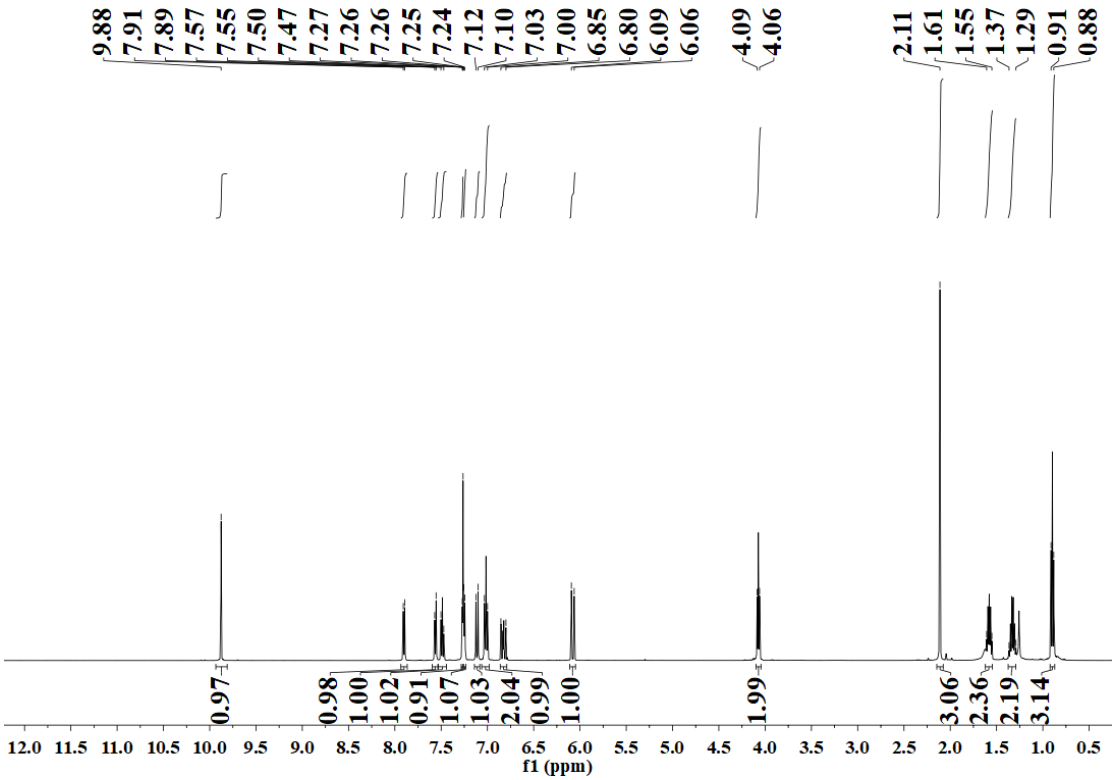
(3j)

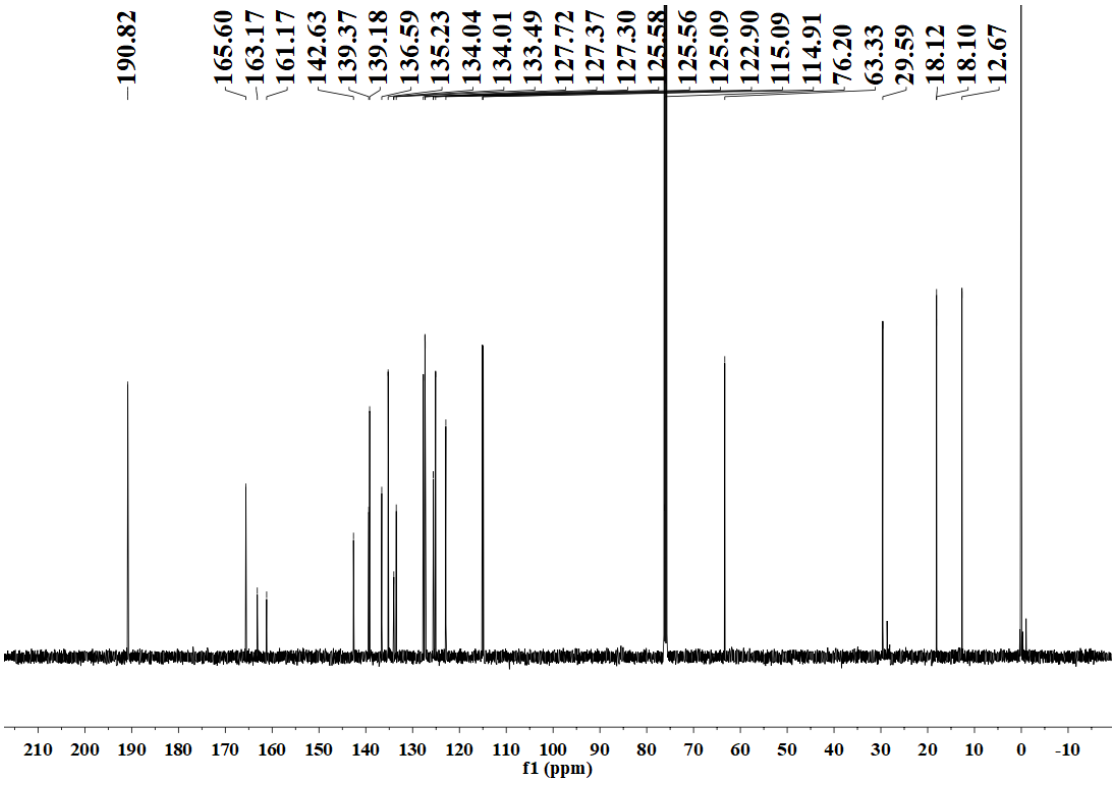

9.87
7.91
7.89
7.55
7.54
7.48
7.45
7.26
7.22
7.20
7.11
7.09
6.86
6.80
6.05
6.02
4.08
4.05
3.80
2.11
1.59
1.56
1.35
1.30
0.91
0.88
0.92
0.99
1.00
1.01
2.01
1.02
3.04
1.00
2.03
3.01
3.01
2.23
2.22
3.17
f1 (ppm)

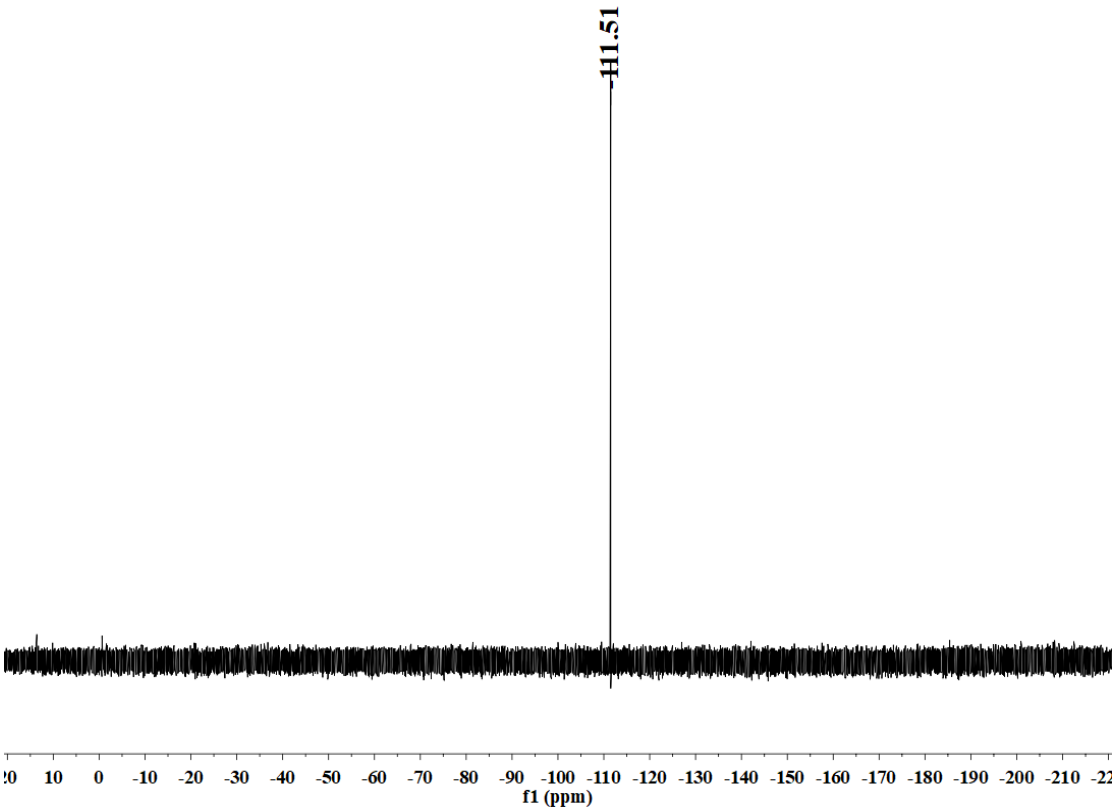

191.18
165.82
159.49
143.28
140.11
139.70
136.59
135.08
133.53
130.44
127.46
127.00
124.46
123.93
121.71
113.36
63.21
54.34
29.62
28.68
18.08
12.68
f1 (ppm)

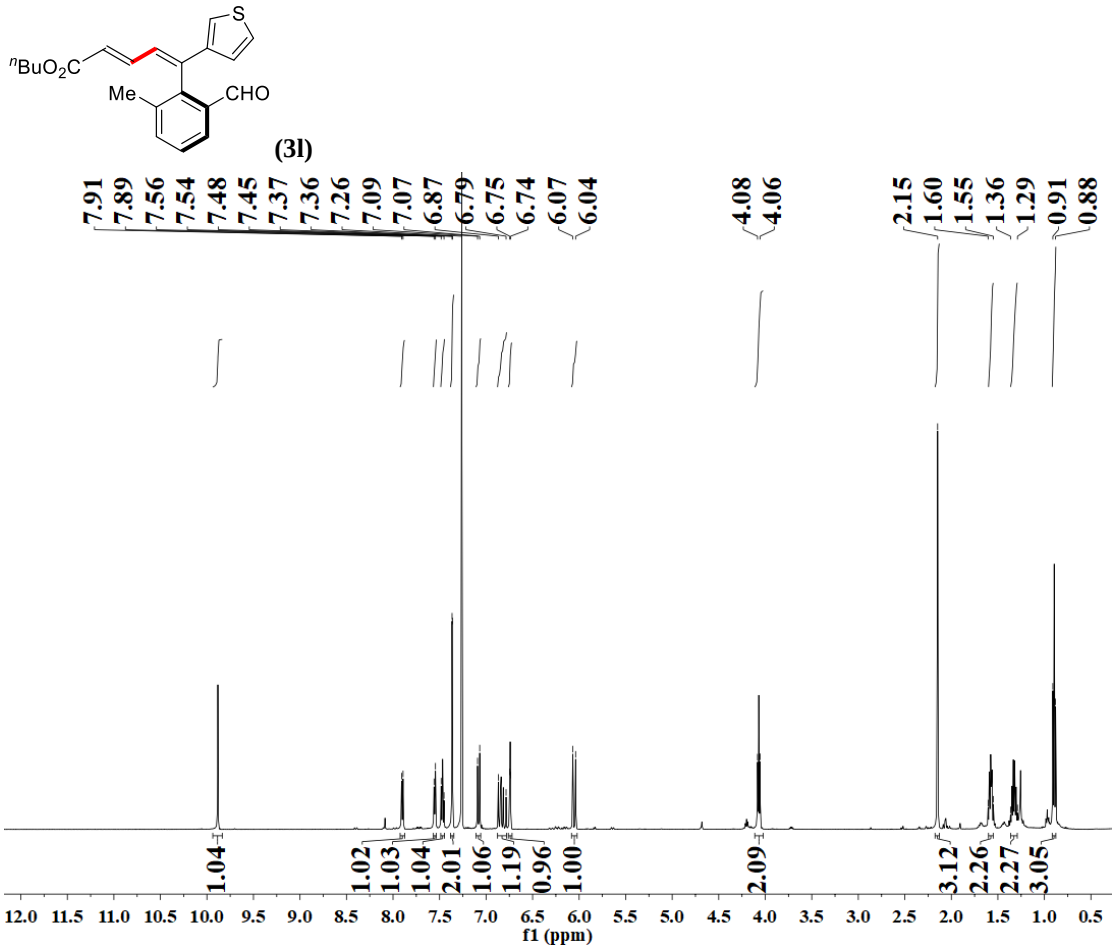

F
^{n}BuO$_2$C
Me
CHO

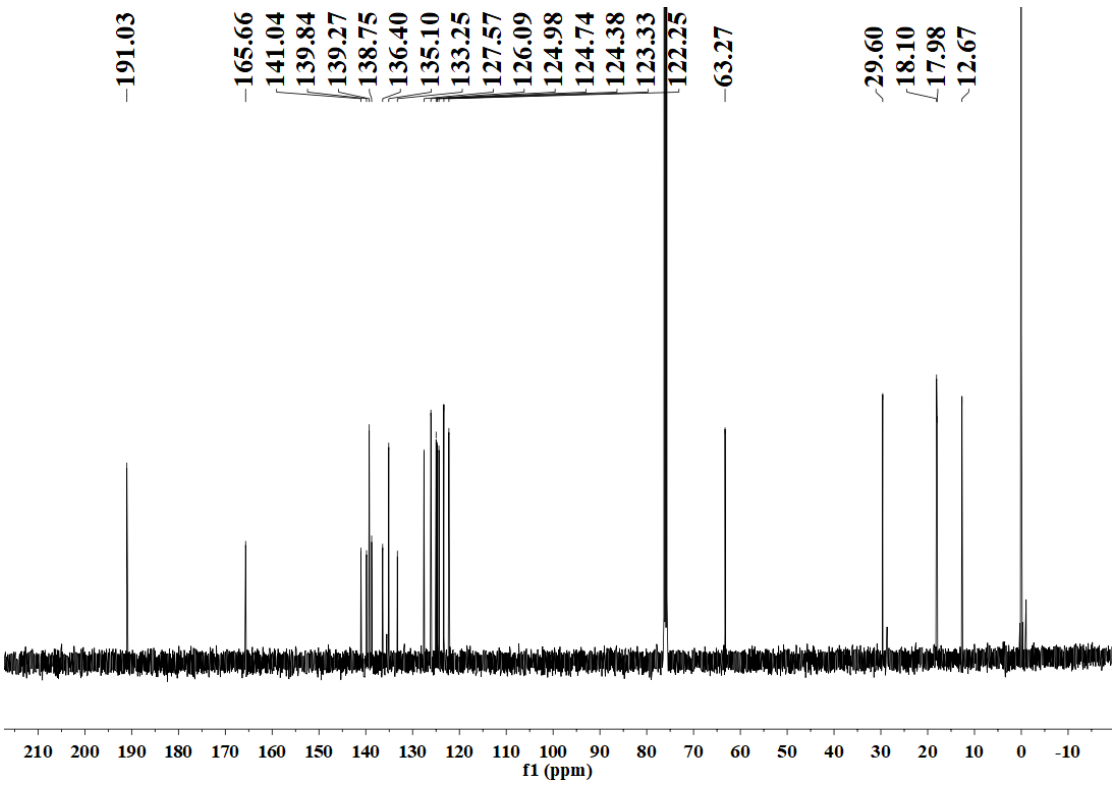
(3k)

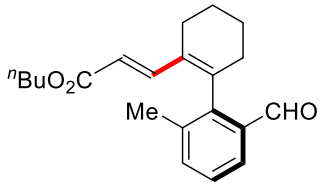

9.88 7.91 7.89 7.57 7.55 7.50 7.47 7.27 7.26 7.26 7.25 7.24 7.12 7.10 7.03 7.00 6.85 6.80 6.09 6.06 4.09 4.06 2.11 1.61 1.55 1.37 1.29 0.91 0.88
0.97 0.98 1.00 1.02 0.91 1.07 1.03 2.04 0.99 1.00 1.99 3.06 2.36 2.19 3.14
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


190.82 165.60 163.17 161.17 142.63 139.37 139.18 136.59 135.23 134.04 134.01 133.49 127.72 127.37 127.30 125.58 125.56 125.09 122.90 115.09 114.91 76.20 63.33 29.59 18.12 18.10 12.67
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

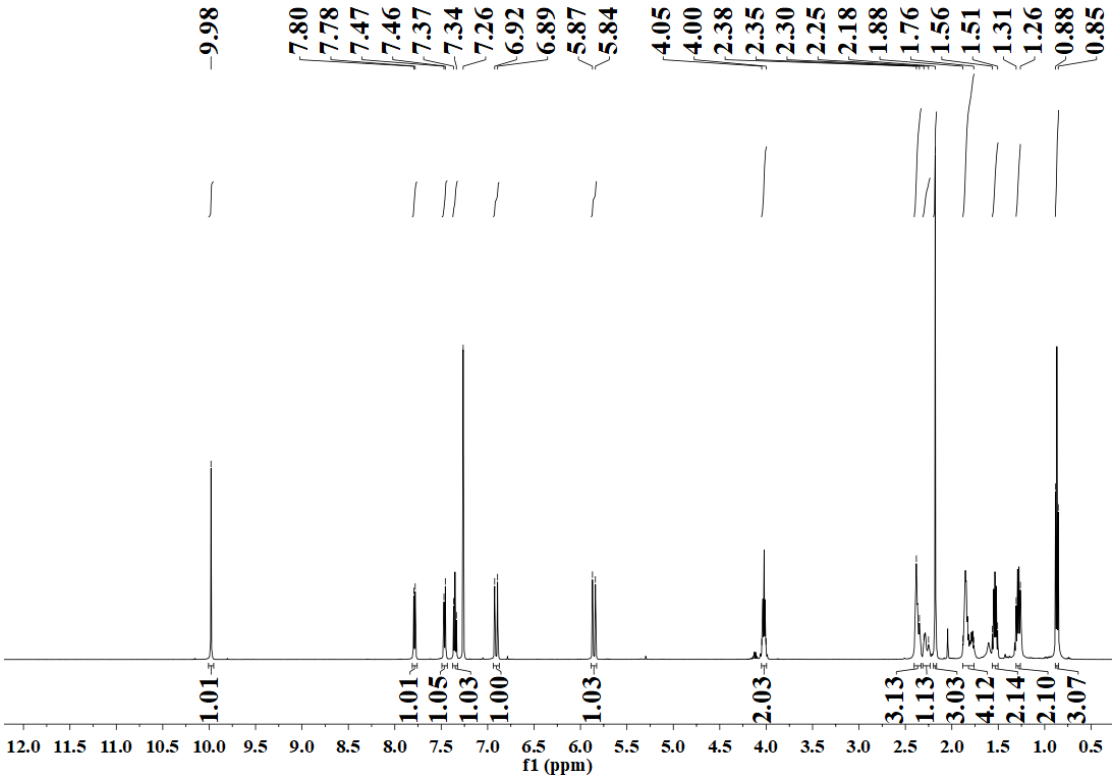

-111.51
f1 (ppm)

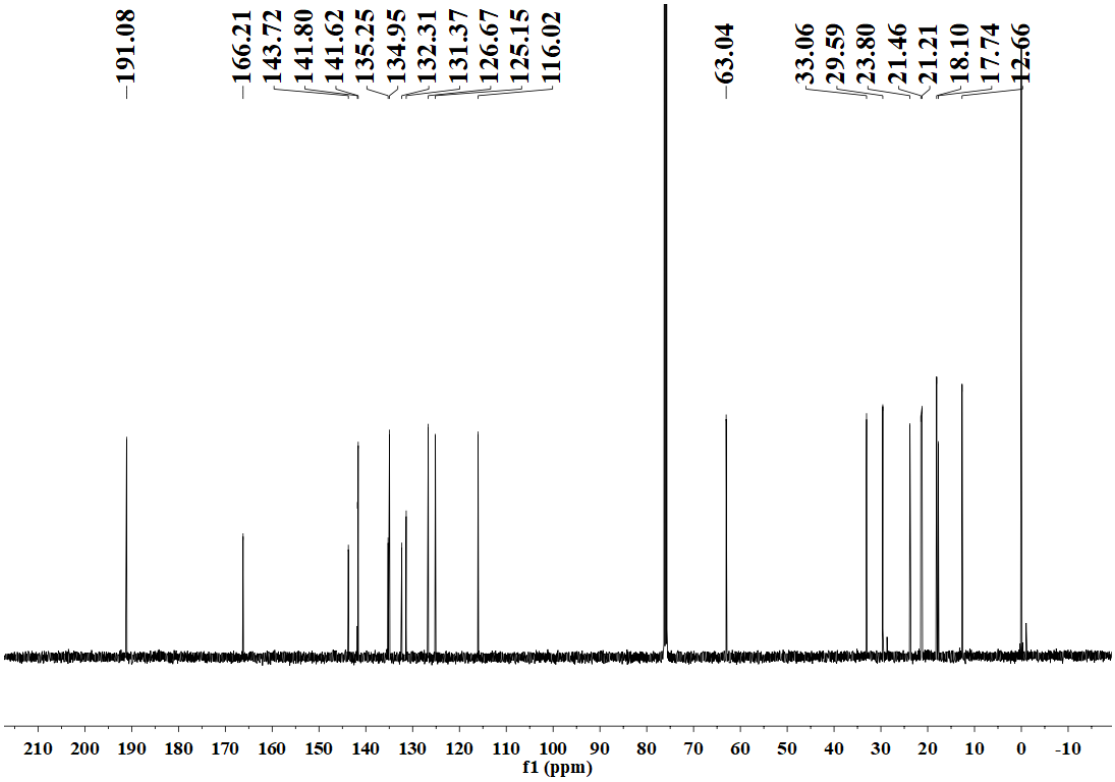

S
nBuO2C
Me
CHO
(3l)
7.91
7.89
7.56
7.54
7.48
7.45
7.37
7.36
7.26
7.09
7.07
6.87
6.79
6.75
6.74
6.07
6.04
4.08
4.06
2.15
1.60
1.55
1.36
1.29
0.91
0.88
1.04
1.02
1.03
1.04
2.01
1.06
1.19
0.96
1.00
2.09
3.12
2.26
2.27
3.05
f1 (ppm)

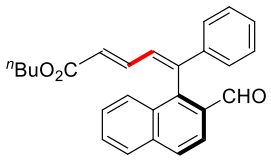

191.03
165.66
141.04
139.84
139.27
138.75
136.40
135.10
133.25
127.57
126.09
124.98
124.74
124.38
123.33
122.25
63.27
29.60
18.10
17.98
12.67
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


nBuO2C
Me
CHO

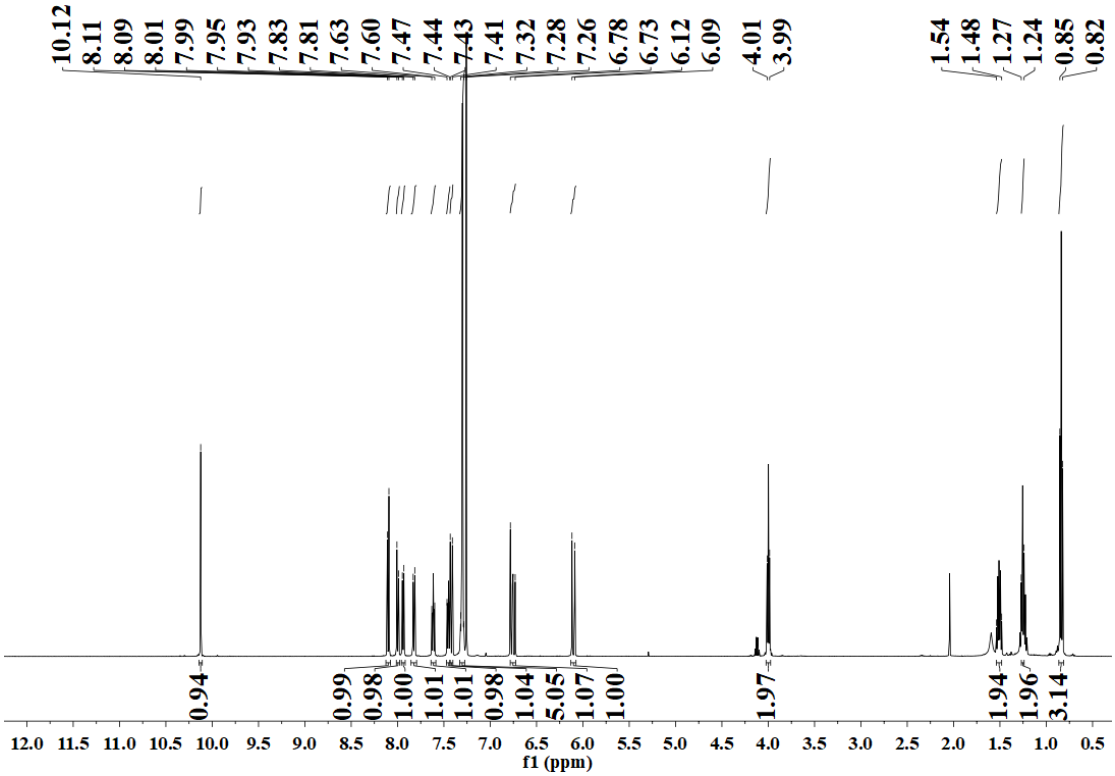
(3m)

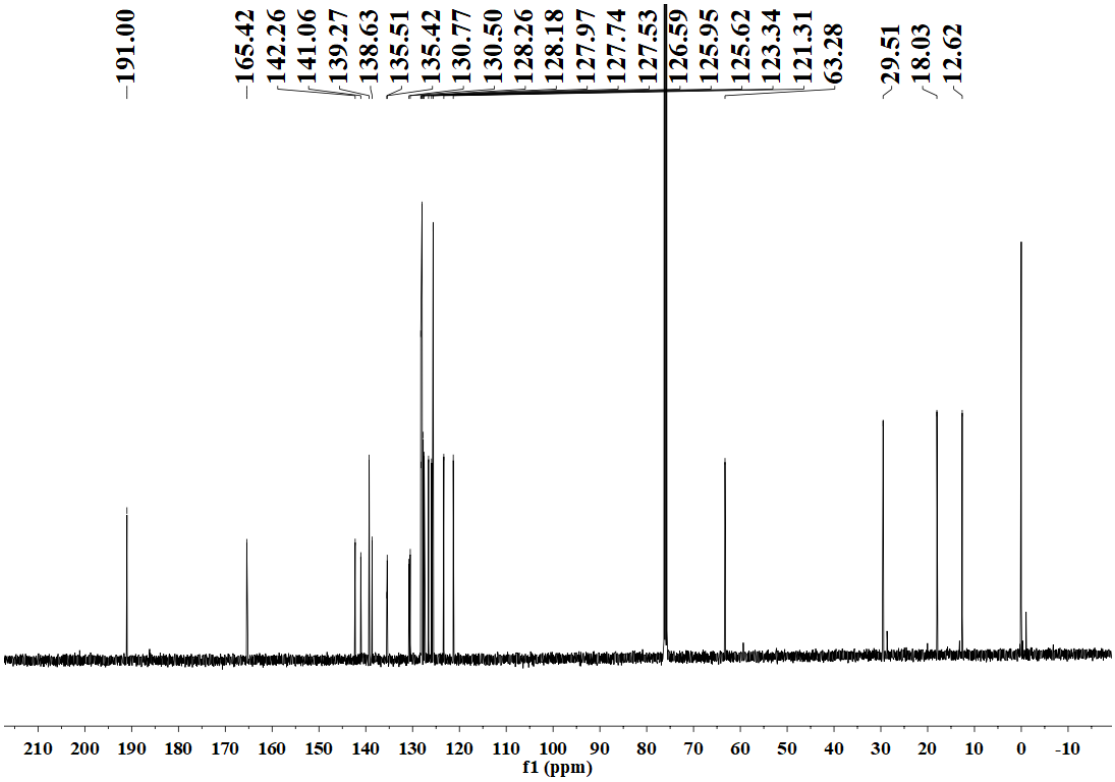

9.98
7.80
7.78
7.47
7.46
7.37
7.34
7.26
6.92
6.89
5.87
5.84
4.05
4.00
2.38
2.35
2.30
2.25
2.18
1.88
1.76
1.56
1.51
1.31
1.26
0.88
0.85
1.01
1.01
1.05
1.03
1.00
1.03
2.03
3.13
1.13
3.03
4.12
2.14
2.10
3.07
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

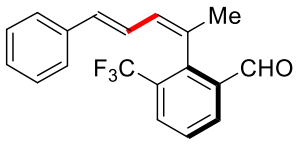

191.08
166.21
143.72
141.80
141.62
135.25
134.95
132.31
131.37
126.67
125.15
116.02
63.04
33.06
29.59
23.80
21.46
21.21
18.10
17.74
12.66
f1 (ppm)


nBuO2C
CHO

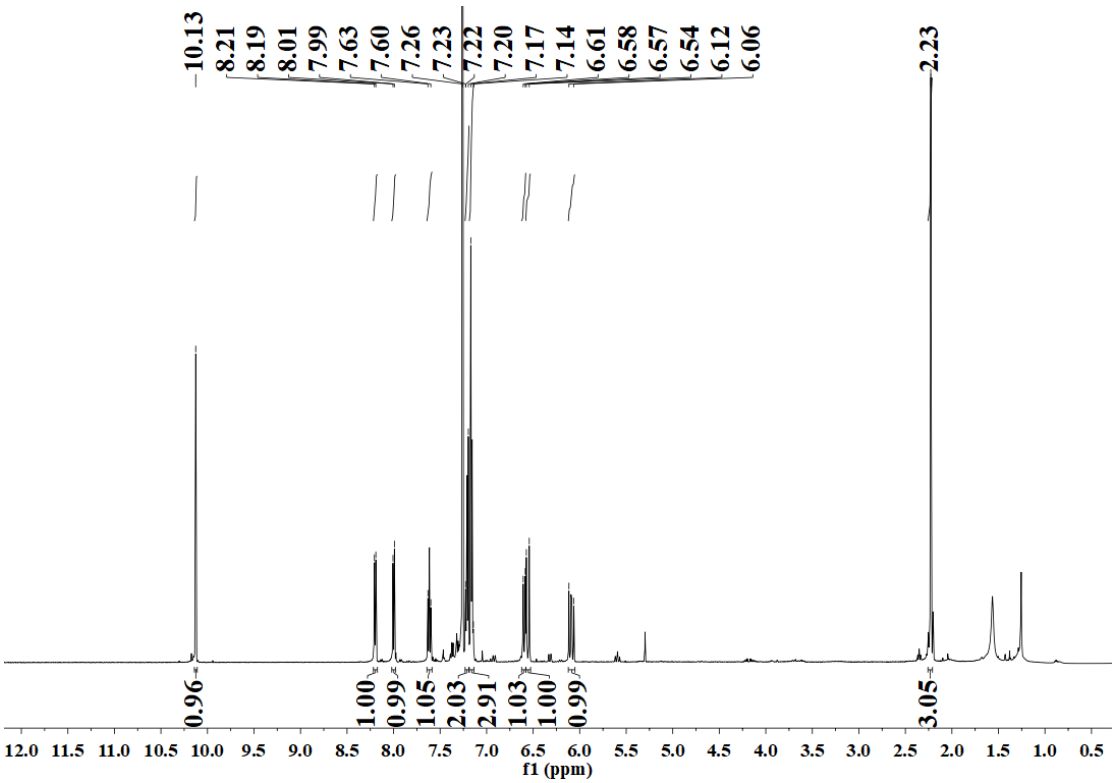
(3n)

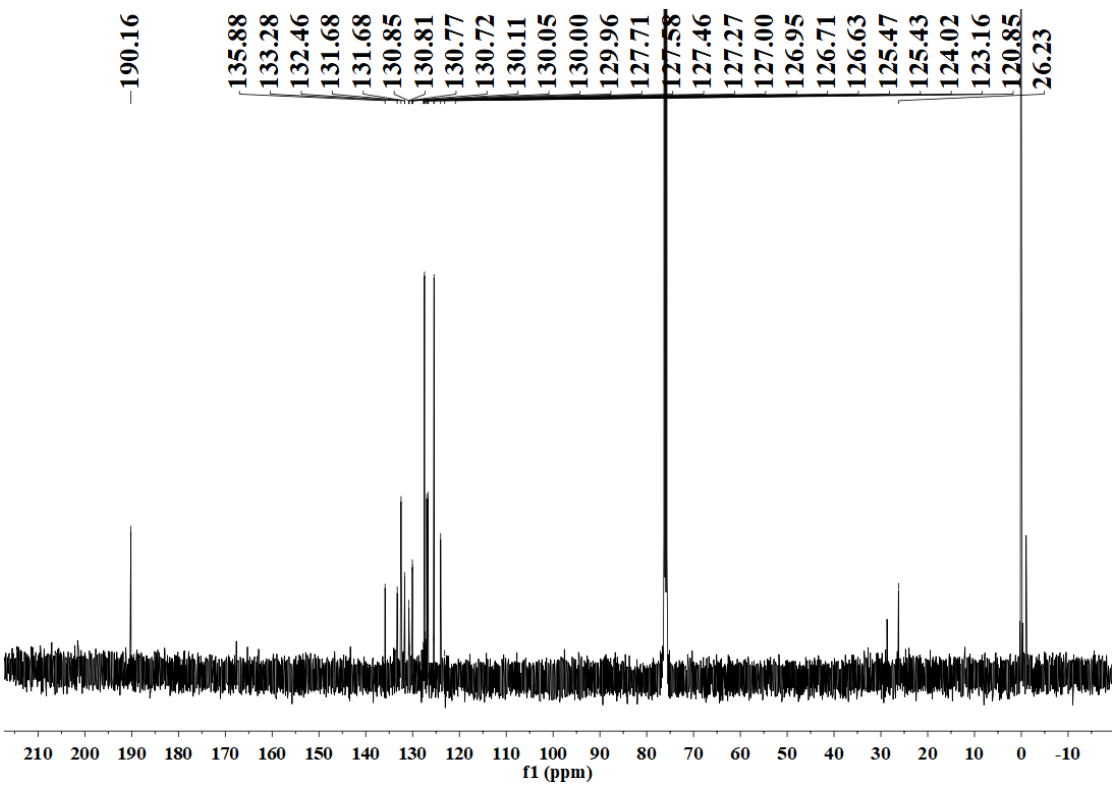

10.12
8.11
8.09
8.01
7.99
7.95
7.93
7.83
7.81
7.63
7.60
7.47
7.44
7.43
7.41
7.32
7.28
7.26
6.78
6.73
6.12
6.09
4.01
3.99
1.54
1.48
1.27
1.24
0.85
0.82
0.94
0.99
0.98
1.00
1.01
1.01
0.98
1.04
5.05
1.07
1.00
1.97
1.94
1.96
3.14
f1 (ppm)

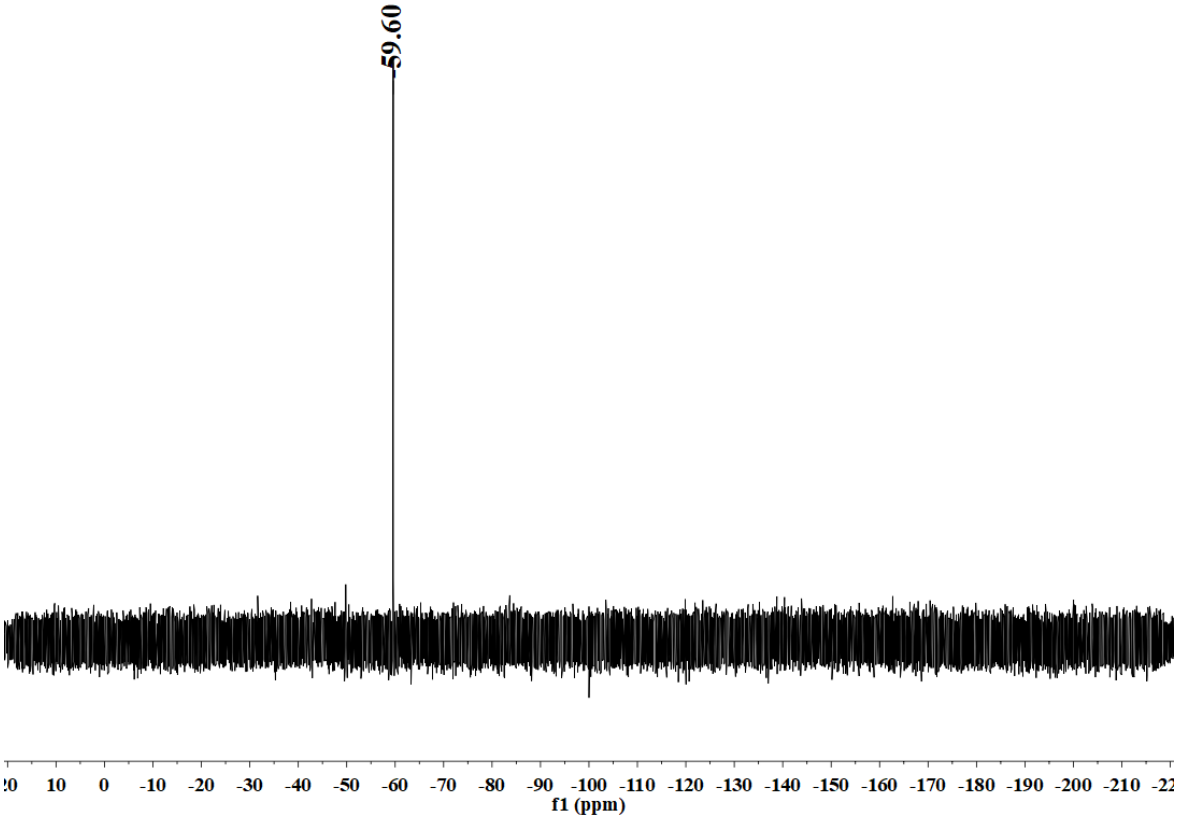

191.00
165.42
142.26
141.06
139.27
138.63
135.51
135.42
130.77
130.50
128.26
128.18
127.97
127.74
127.53
126.59
125.95
125.62
123.34
121.31
63.28
29.51
18.03
12.62
f1 (ppm)

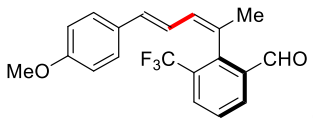

Me
F3C
CHO

(3o)

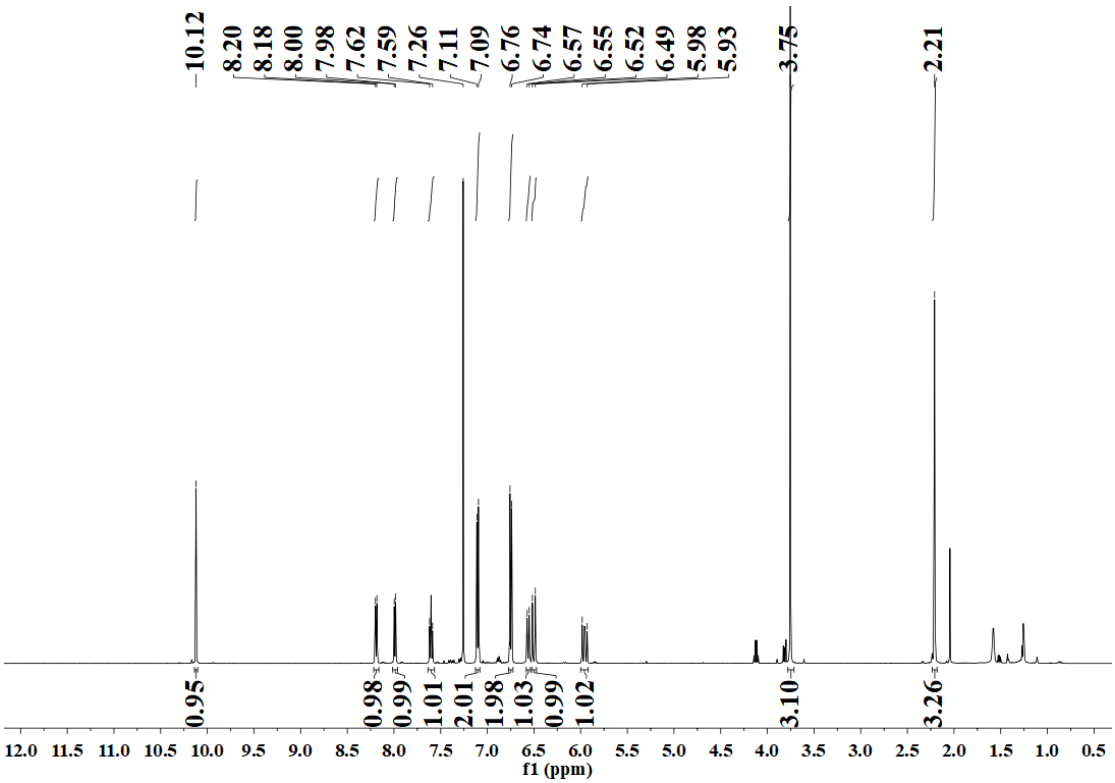

10.13
8.21
8.19
8.01
7.99
7.63
7.60
7.26
7.23
7.22
7.20
7.17
7.14
6.61
6.58
6.57
6.54
6.12
6.06
2.23
0.96
1.00
0.99
1.05
2.03
2.91
1.03
1.00
0.99
3.05
f1 (ppm)

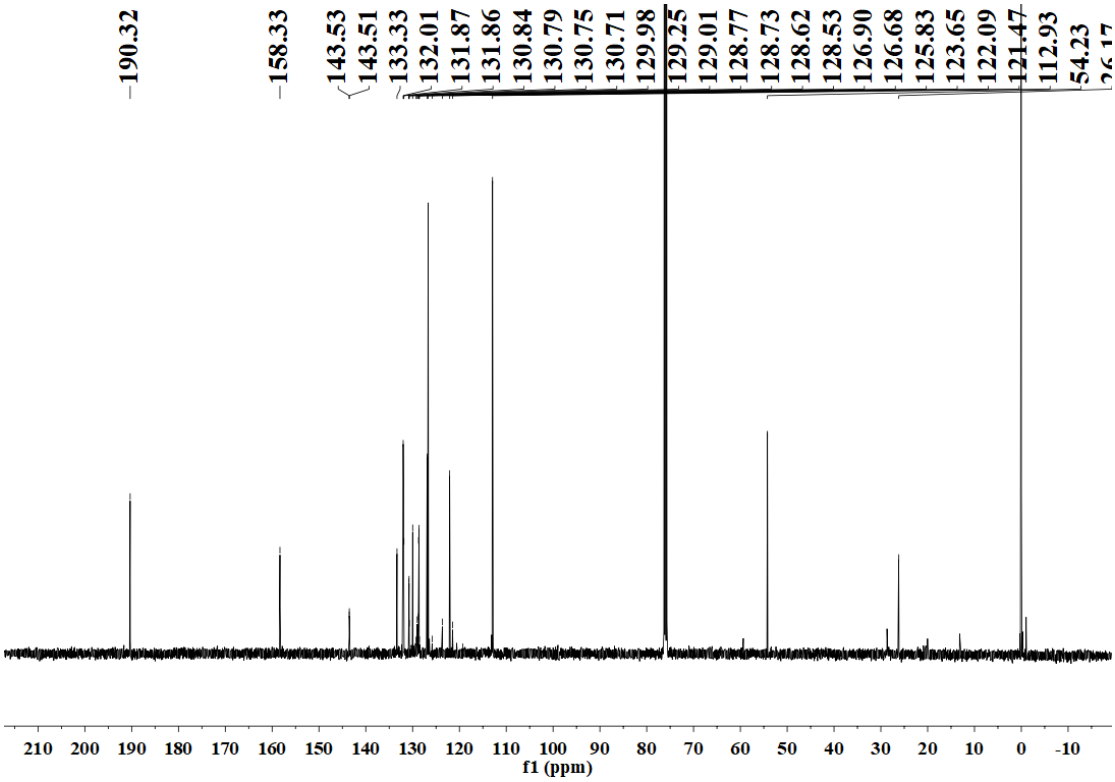

190.16
135.88
133.28
132.46
131.68
131.68
130.85
130.81
130.77
130.72
130.11
130.05
130.00
129.96
127.71
127.58
127.46
127.27
127.00
126.95
126.71
126.63
125.47
125.43
124.02
123.16
120.85
26.23
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

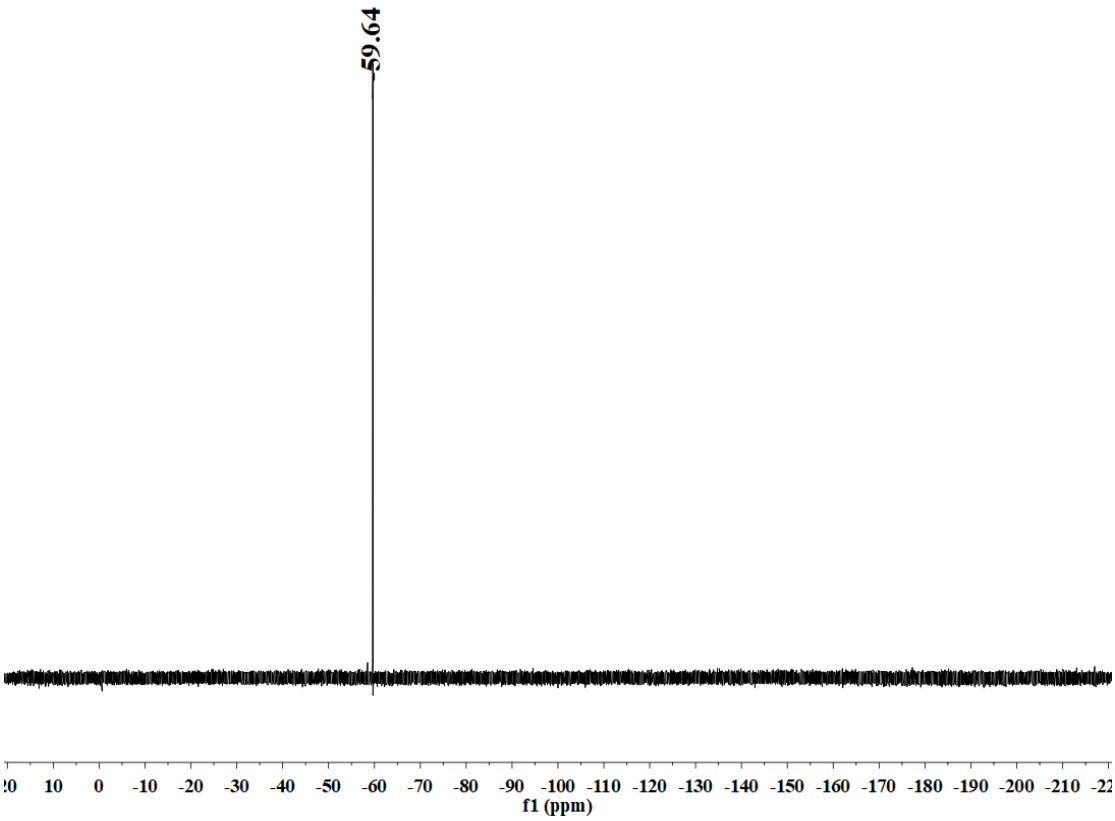

59.60
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

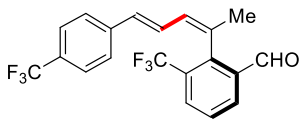

Me
MeO
F3C
CHO

(3p)

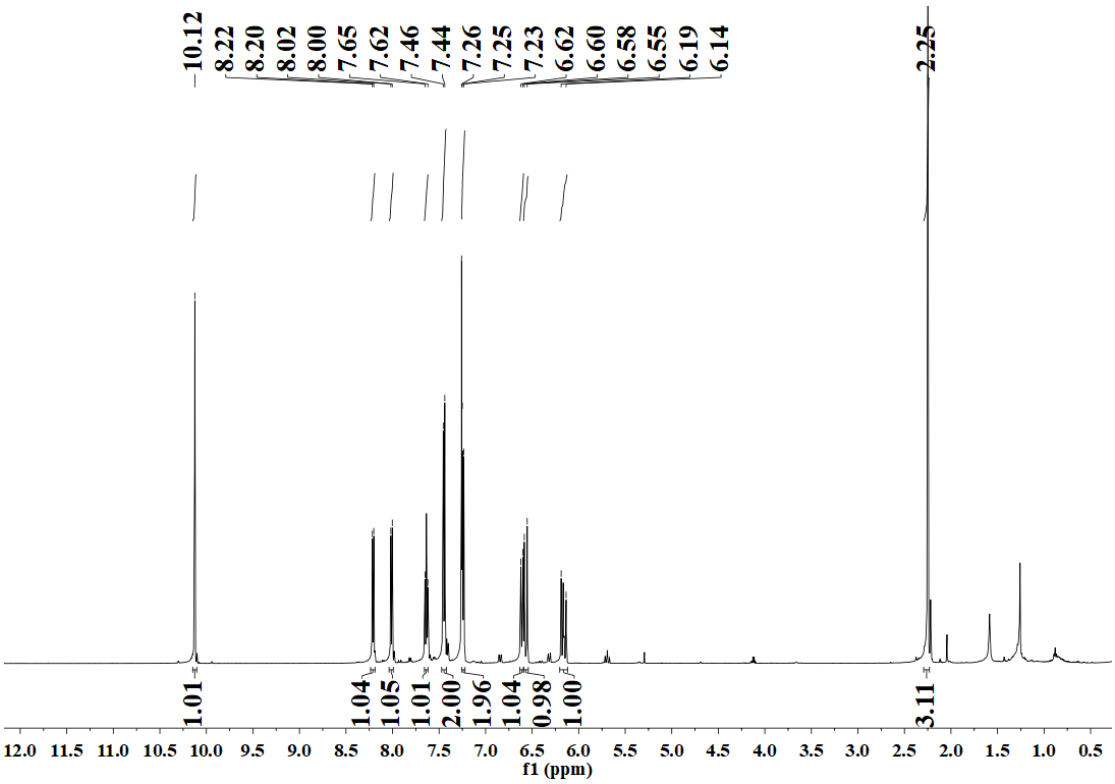

10.12
8.20
8.18
8.00
7.98
7.62
7.59
7.26
7.11
7.09
6.76
6.74
6.57
6.55
6.52
6.49
5.98
5.93
3.75
2.21
0.95
0.98
0.99
1.01
2.01
1.98
1.03
0.99
1.02
3.10
3.26
f1 (ppm)

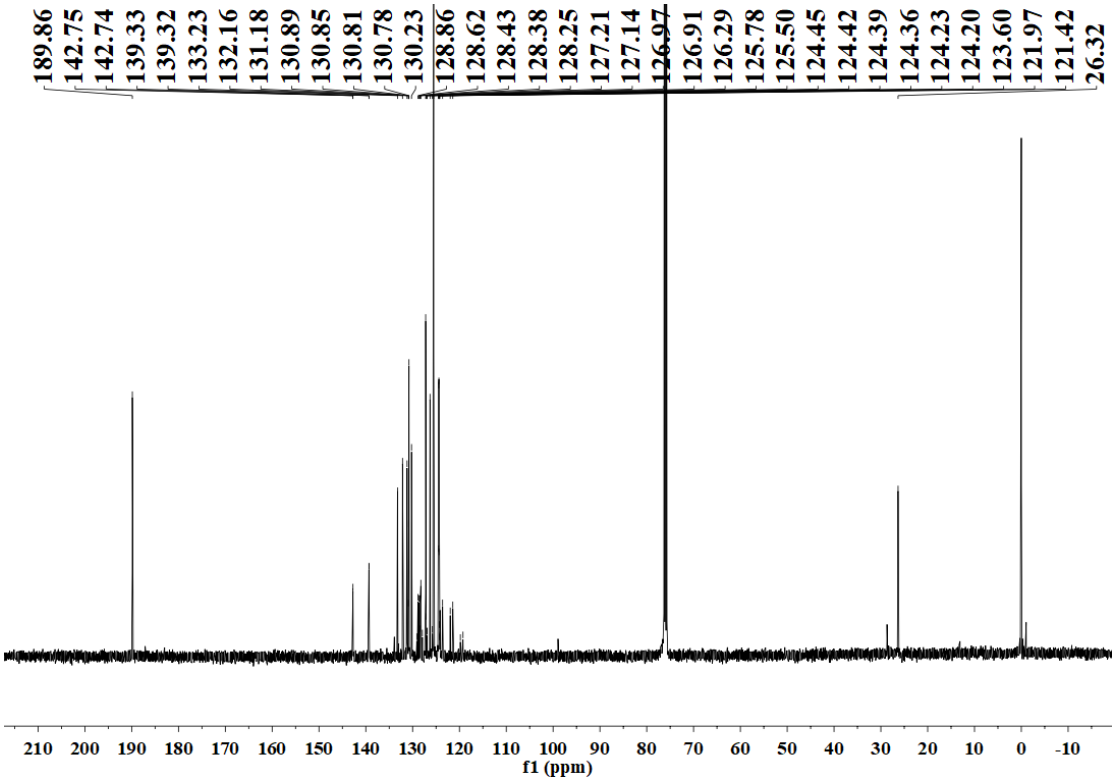

190.32
158.33
143.53
143.51
133.33
132.01
131.87
131.86
130.84
130.79
130.75
130.71
129.98
129.25
129.01
128.77
128.73
128.62
128.53
126.90
126.68
125.83
123.65
122.09
121.47
112.93
54.23
f1 (ppm)

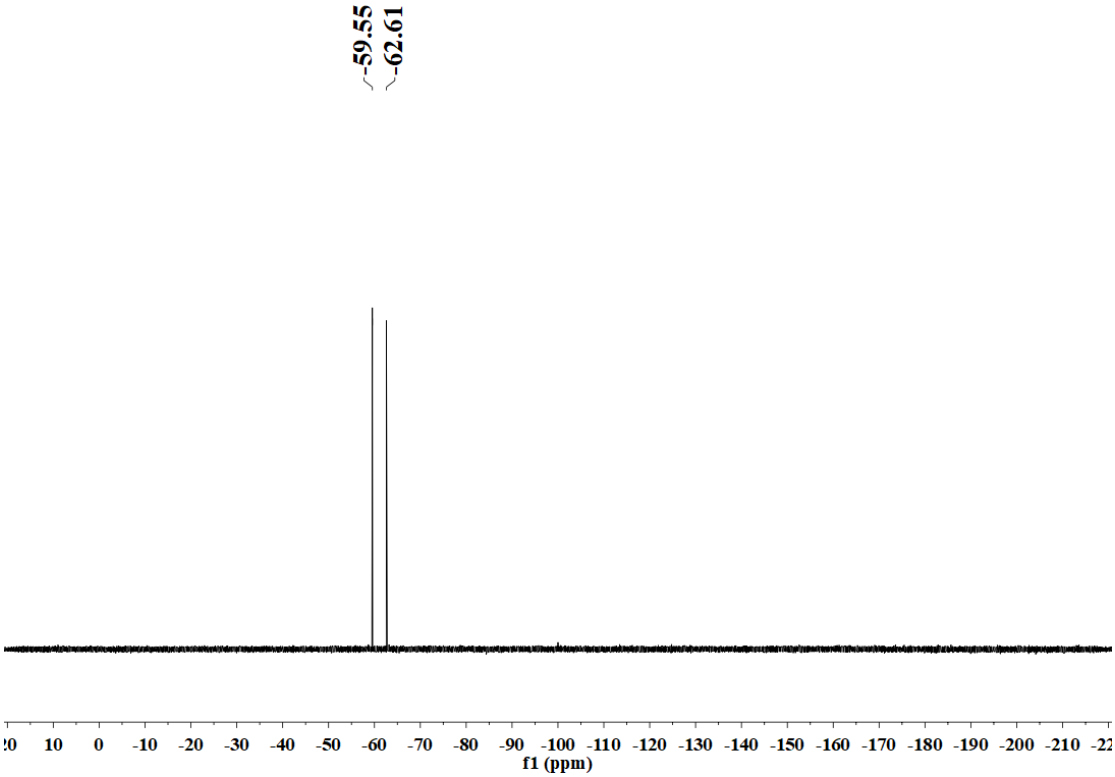

59.64
f1 (ppm)

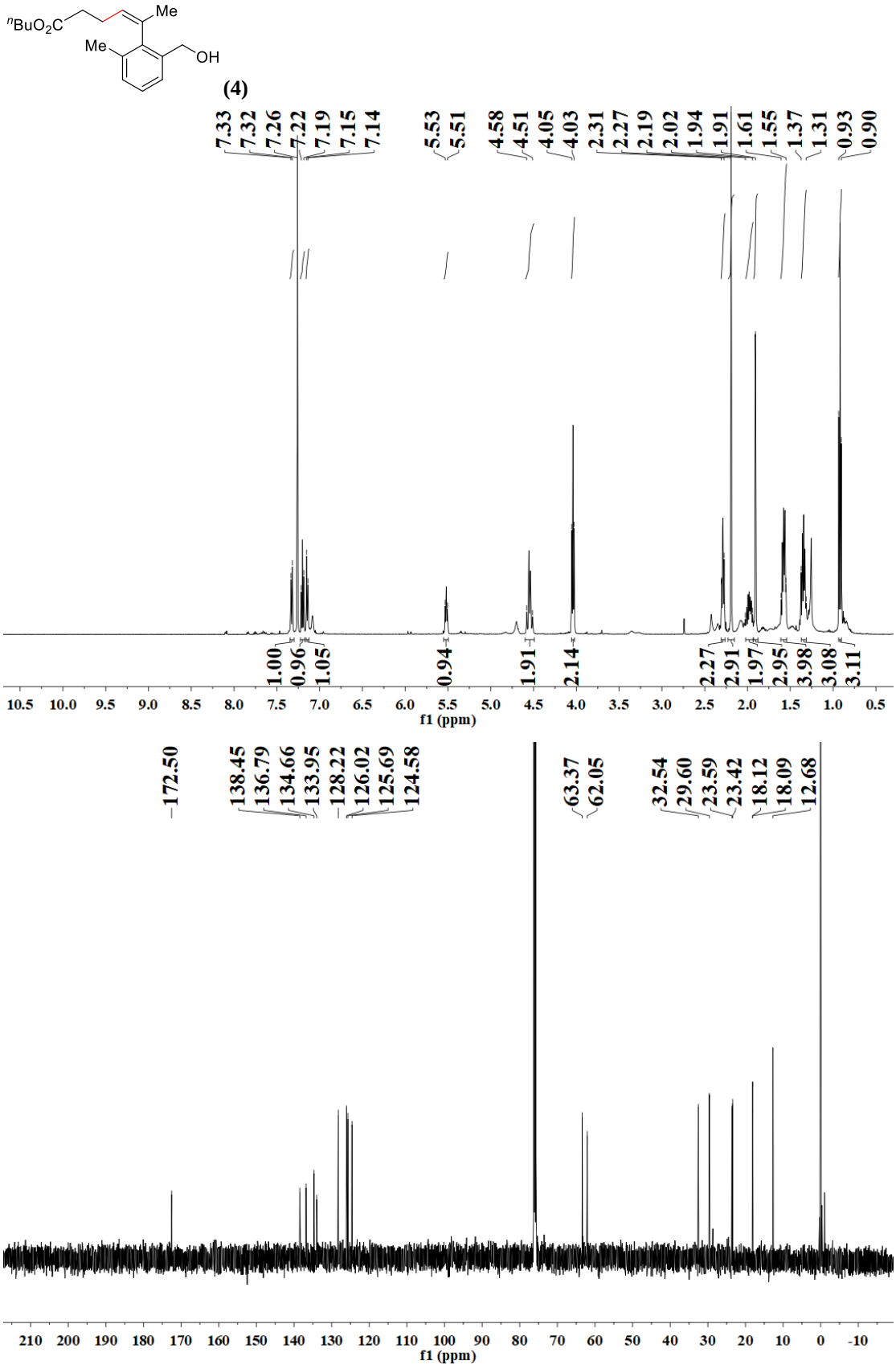

Me
F3C
F3C
CHO

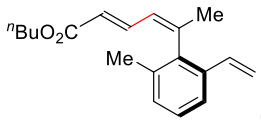
(3q)


10.12
8.22
8.20
8.02
8.00
7.65
7.62
7.46
7.44
7.26
7.25
7.23
6.62
6.60
6.58
6.55
6.19
6.14
2.25
1.01
1.04
1.05
1.01
2.00
1.96
1.04
0.98
1.00
3.11
f1 (ppm)

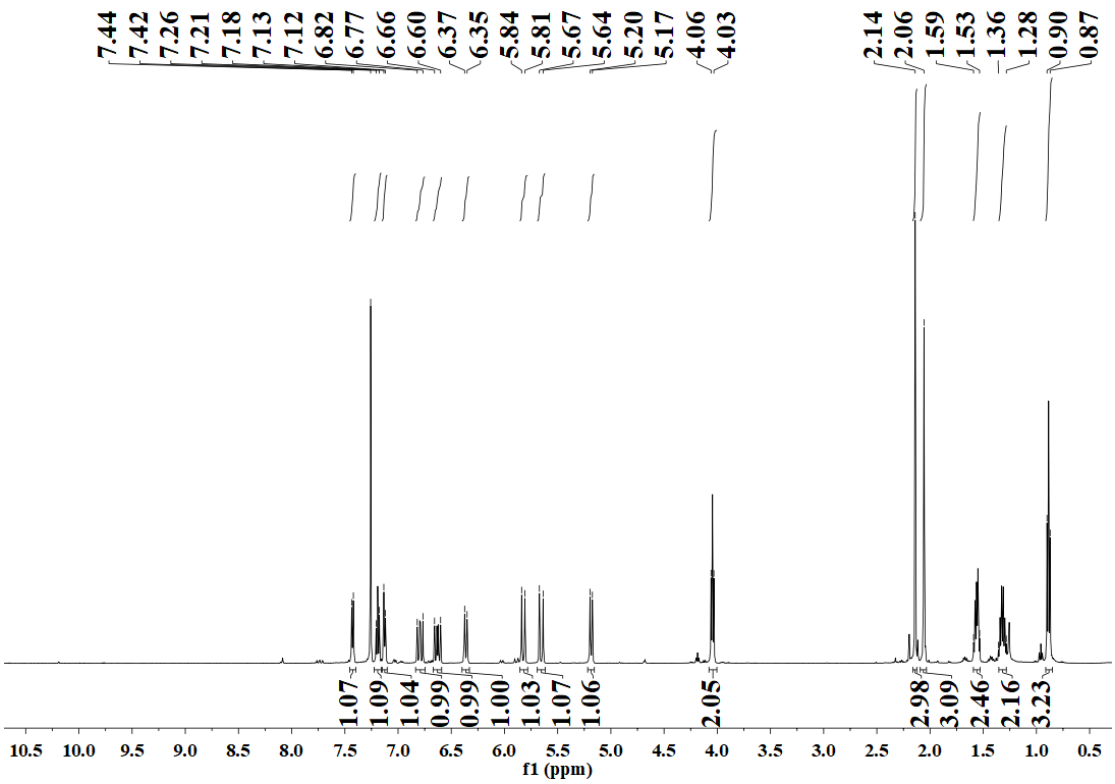

189.86
142.75
142.74
139.33
139.32
133.23
132.16
131.18
130.89
130.85
130.81
130.78
130.23
128.86
128.62
128.43
128.38
128.25
127.21
127.14
126.97
126.91
126.29
125.78
125.50
124.45
124.42
124.39
124.36
124.23
124.20
123.60
121.97
121.42
26.32
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

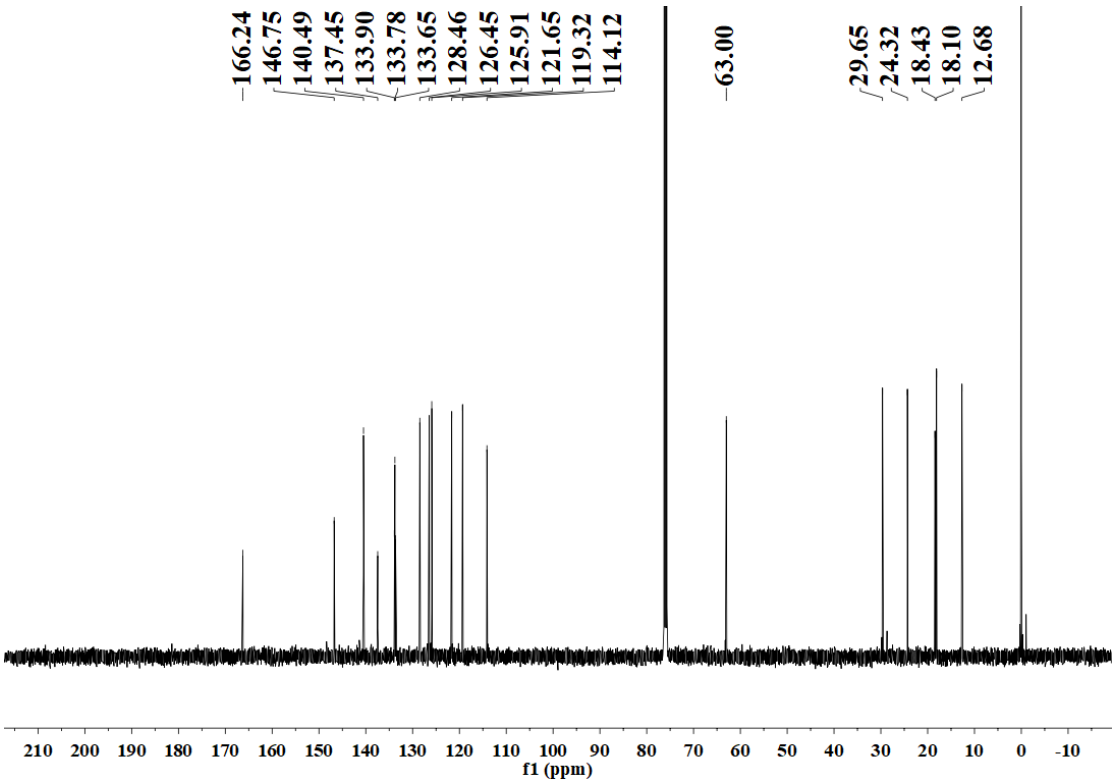

-59.55
-62.61
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

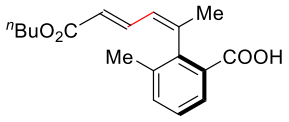

nBuO2C
Me
Me
OH
(4)
7.33
7.32
7.26
7.22
7.19
7.15
7.14
5.53
5.51
4.58
4.51
4.05
4.03
2.31
2.27
2.19
2.02
1.94
1.91
1.61
1.55
1.37
1.31
0.93
0.90
1.00
0.96
1.05
0.94
1.91
2.14
2.27
2.91
1.97
2.95
3.98
3.08
3.11
f1 (ppm)
172.50
138.45
136.79
134.66
133.95
128.22
126.02
125.69
124.58
63.37
62.05
32.54
29.60
23.59
23.42
18.12
18.09
12.68
f1 (ppm)


^{n}BuO$_2$C
Me
Me

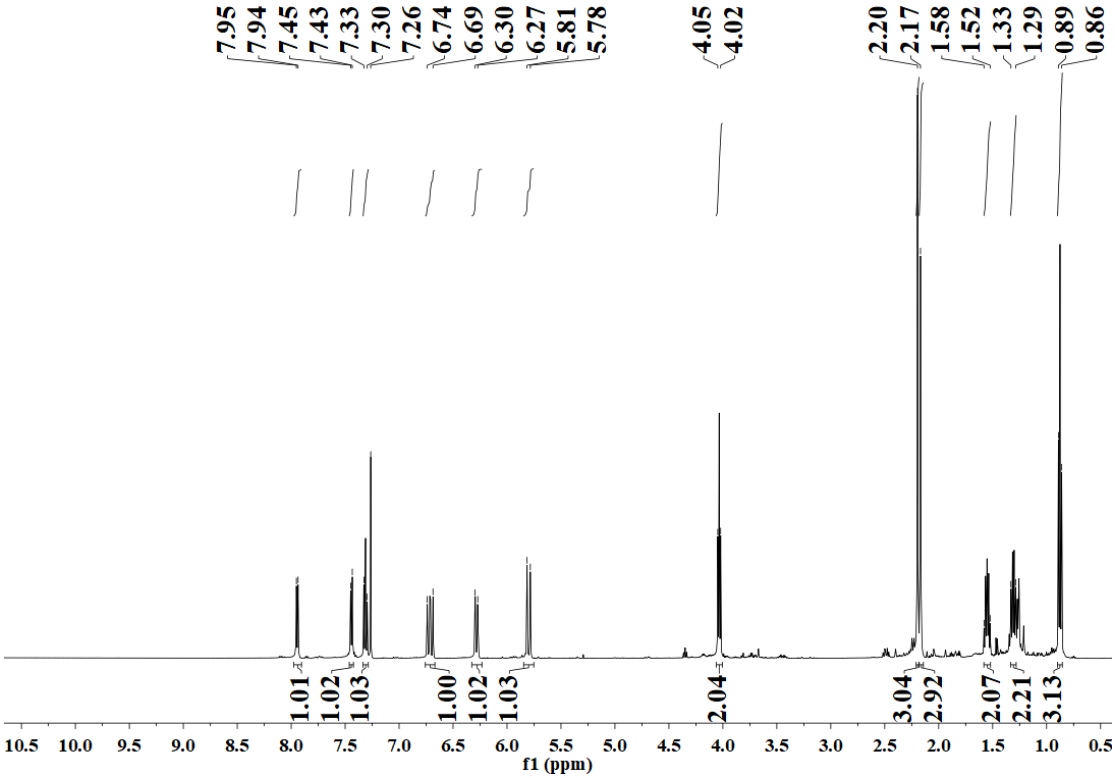
(5)

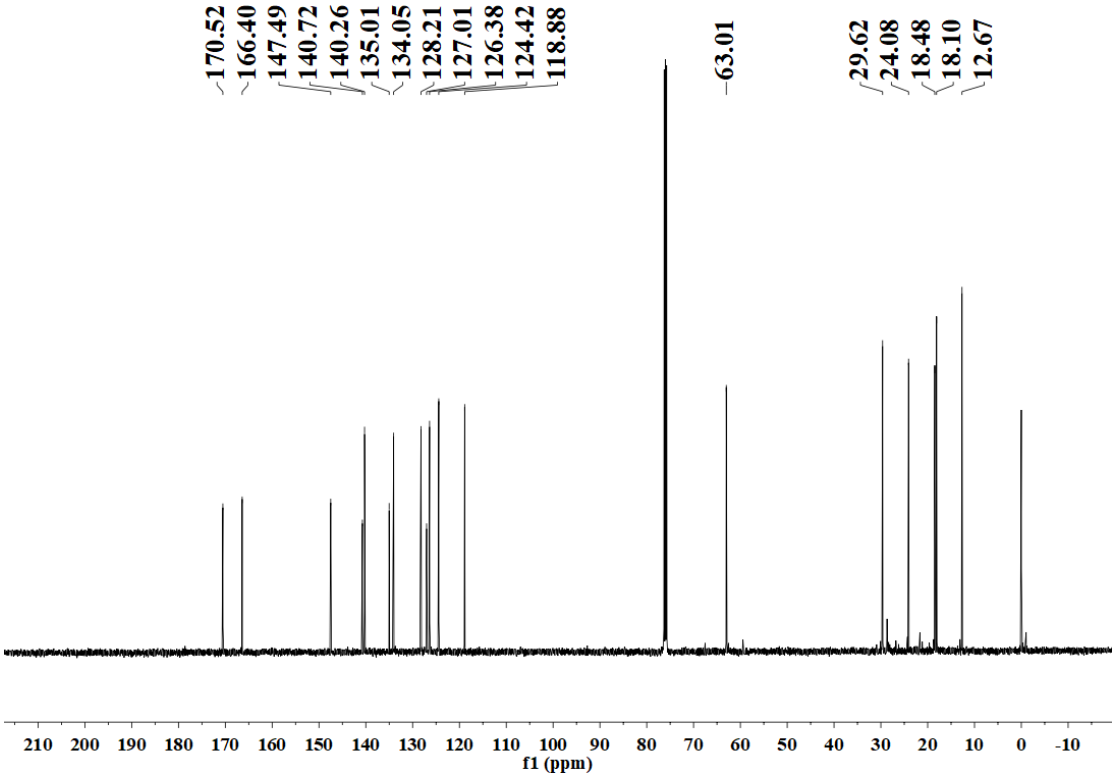

7.44
7.42
7.26
7.21
7.18
7.13
7.12
6.82
6.77
6.66
6.60
6.37
6.35
5.84
5.81
5.67
5.64
5.20
5.17
4.06
4.03
2.14
2.06
1.59
1.53
1.36
1.28
0.90
0.87
1.07
1.09
1.04
0.99
0.99
1.00
1.03
1.07
1.06
2.05
2.98
3.09
2.46
2.16
3.23
f1 (ppm)

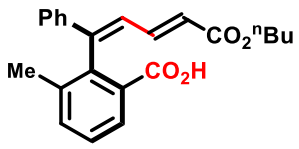

166.24
146.75
140.49
137.45
133.90
133.78
133.65
128.46
126.45
125.91
121.65
119.32
114.12
63.00
29.65
24.32
18.43
18.10
12.68
f1 (ppm)


nBuO2C
Me
Me
COOH

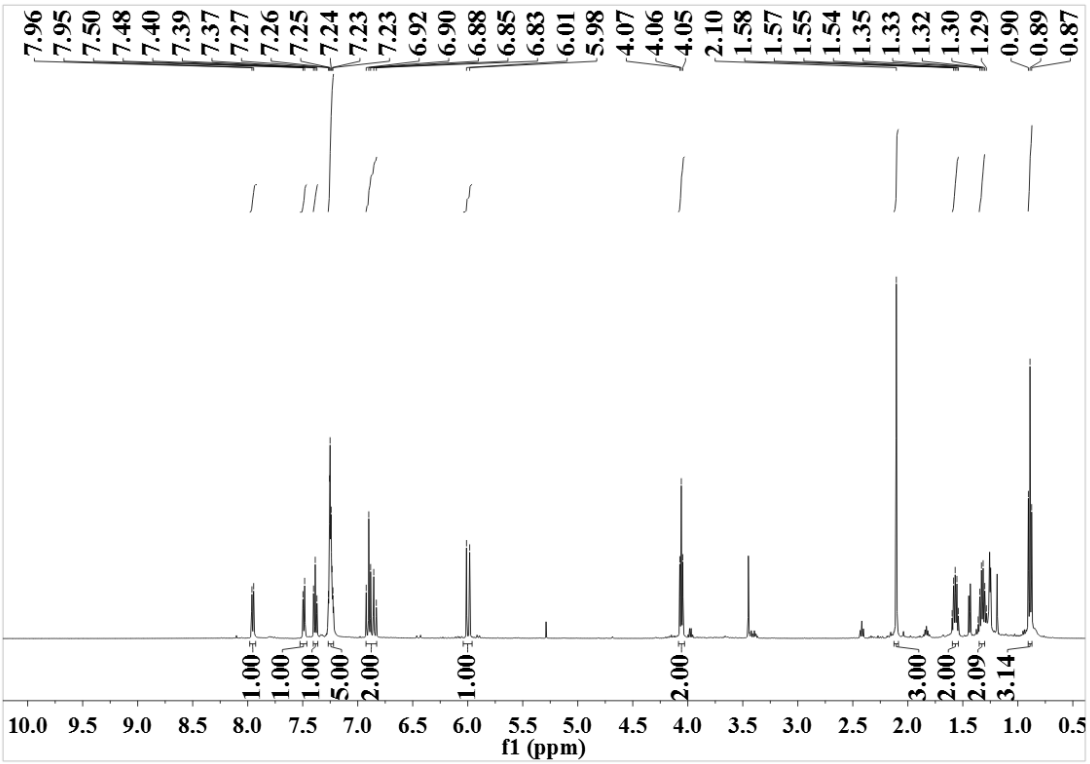
(6a)

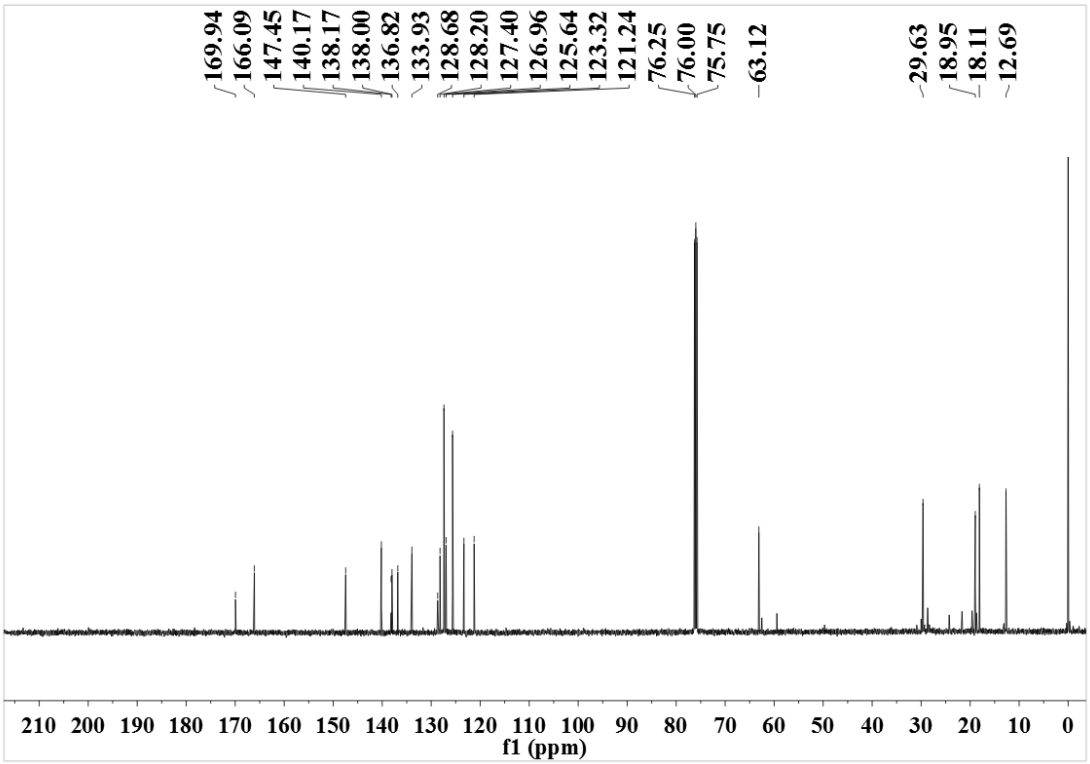

7.95
7.94
7.45
7.43
7.33
7.30
7.26
6.74
6.69
6.30
6.27
5.81
5.78
4.05
4.02
2.20
2.17
1.58
1.52
1.33
1.29
0.89
0.86
1.01
1.02
1.03
1.00
1.02
1.03
2.04
3.04
2.92
2.07
2.21
3.13
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

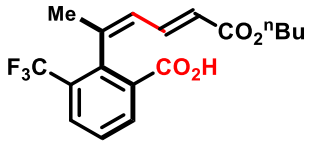

170.52
166.40
147.49
140.72
140.26
135.01
134.05
128.21
127.01
126.38
124.42
118.88
63.01
29.62
24.08
18.48
18.10
12.67
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ph
CO2nBu
Me
CO2H

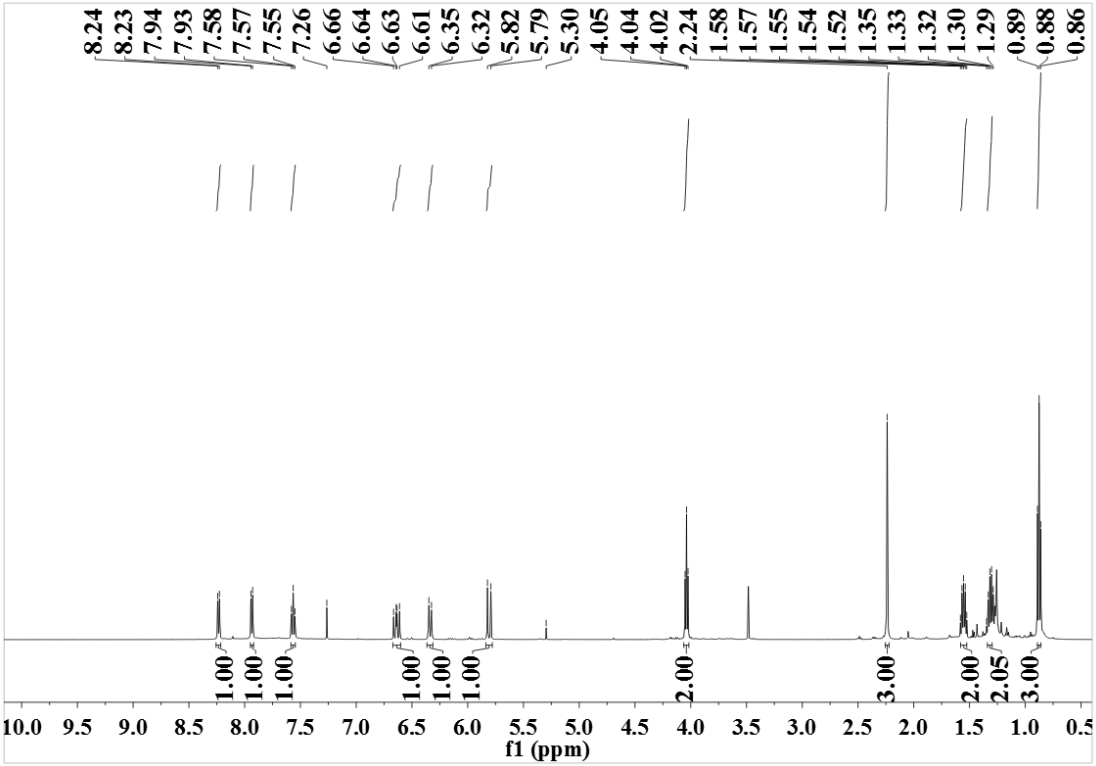
(6b)

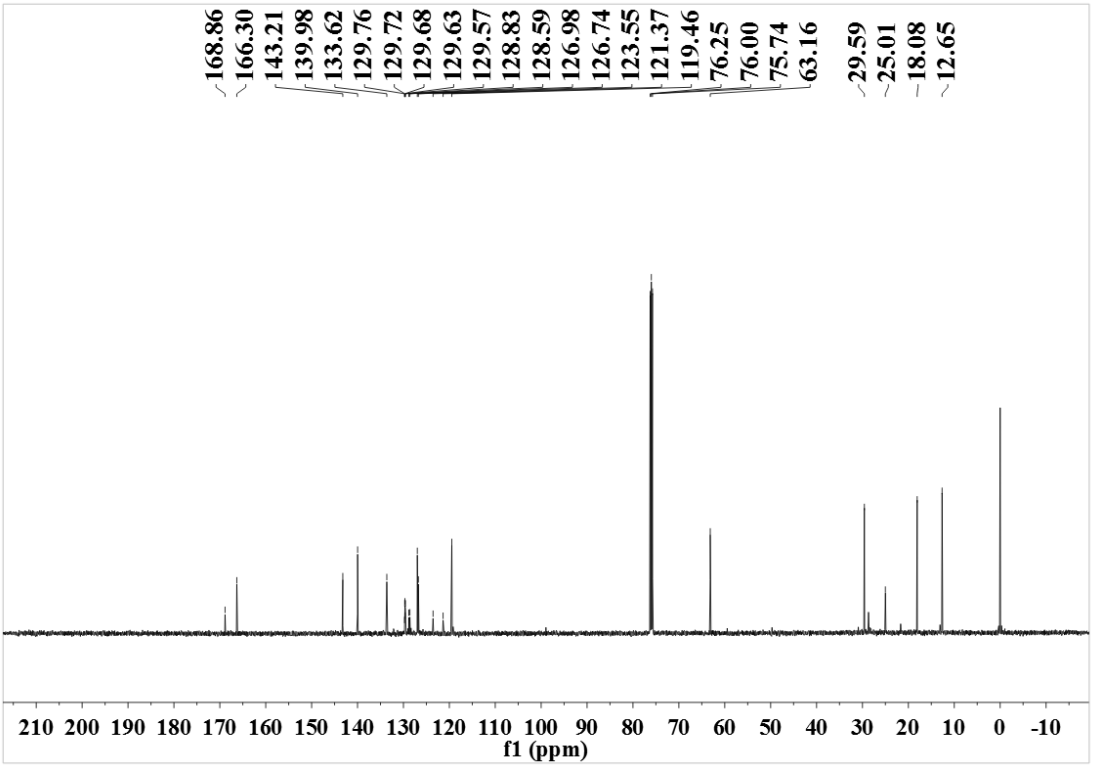

7.96 7.95 7.50 7.48 7.40 7.39 7.37 7.27 7.26 7.25 7.24 7.23 7.23 6.92 6.90 6.88 6.85 6.83 6.01 5.98 4.07 4.06 4.05 2.10 1.58 1.57 1.55 1.54 1.35 1.33 1.32 1.30 1.29 0.90 0.89 0.87
1.00 1.00 1.00 5.00 2.00 1.00 2.00 3.00 2.00 2.09 3.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

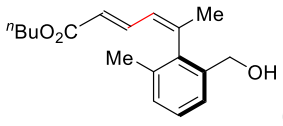

169.94 166.09 147.45 140.17 138.17 138.00 136.82 133.93 128.68 128.20 127.40 126.96 125.64 123.32 121.24 76.25 76.00 75.75 63.12 29.63 18.95 18.11 12.69
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
$CO_2{}^nBu$
F_3C
CO_2H

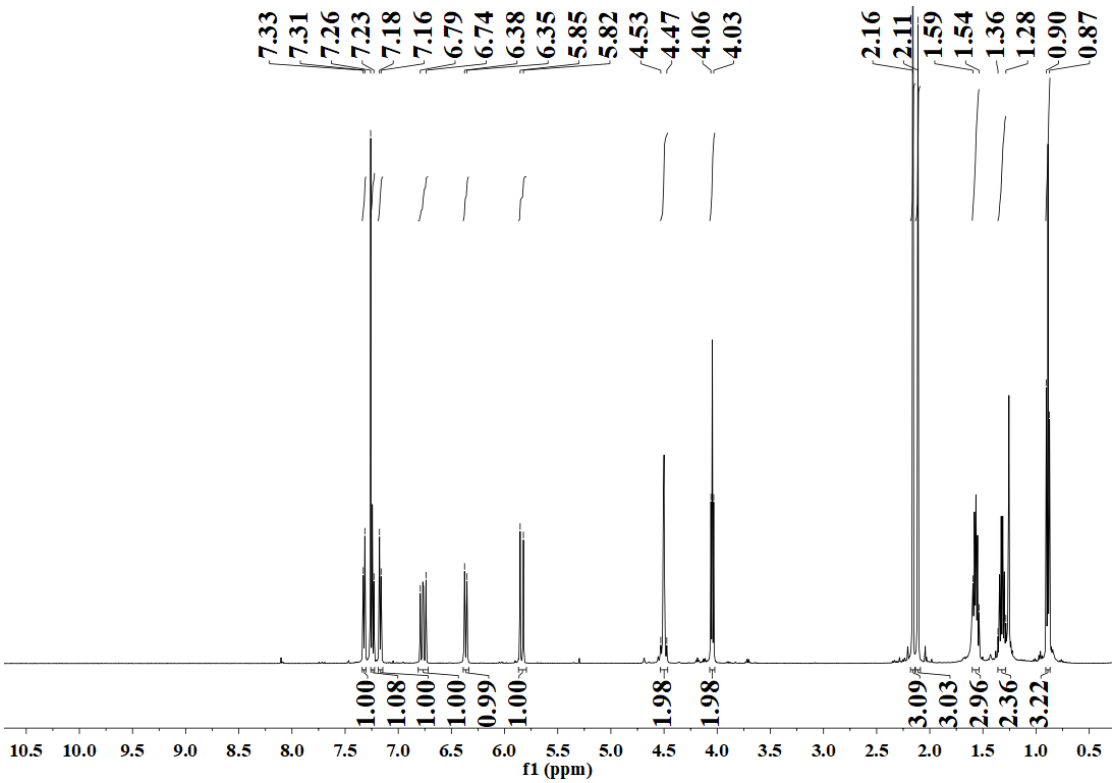
(6c)

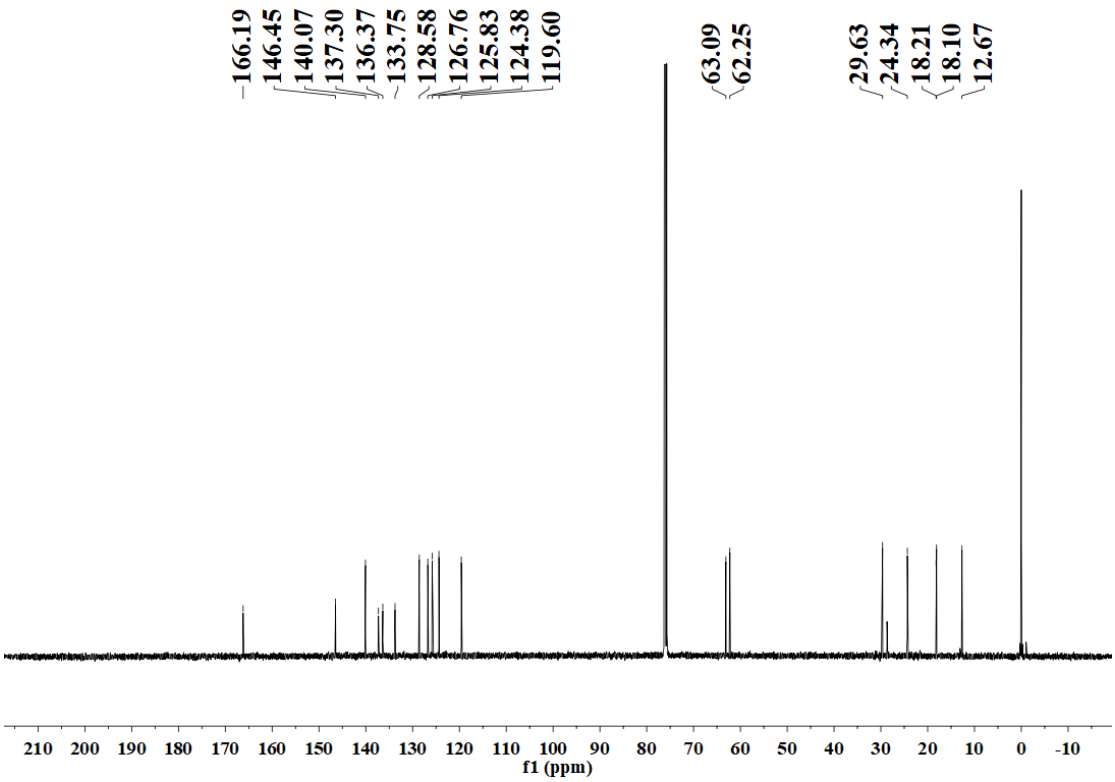

8.24 8.23 7.94 7.93 7.58 7.57 7.55 7.26 6.66 6.64 6.63 6.61 6.35 6.32 5.82 5.79 5.30 4.05 4.04 4.02 2.24 1.58 1.57 1.55 1.54 1.52 1.35 1.33 1.32 1.30 1.29 0.89 0.88 0.86
1.00 1.00 1.00 1.00 1.00 1.00 2.00 3.00 2.00 2.05 3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

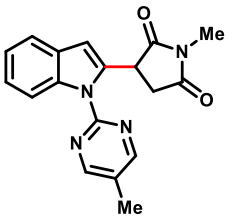

168.86 166.30 143.21 139.98 133.62 129.76 129.72 129.68 129.63 129.57 128.83 128.59 126.98 126.74 123.55 121.37 119.46 76.25 76.00 75.74 63.16 29.59 25.01 18.08 12.65
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


nBuO2C
Me
Me
OH

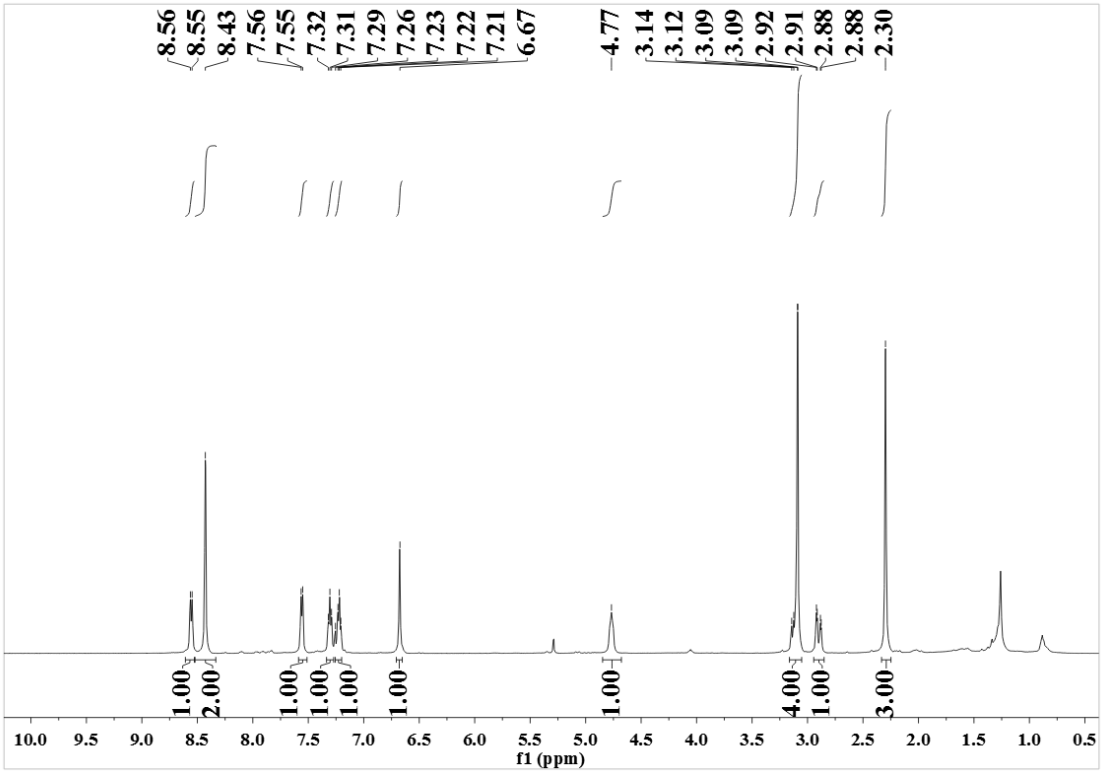
(7)

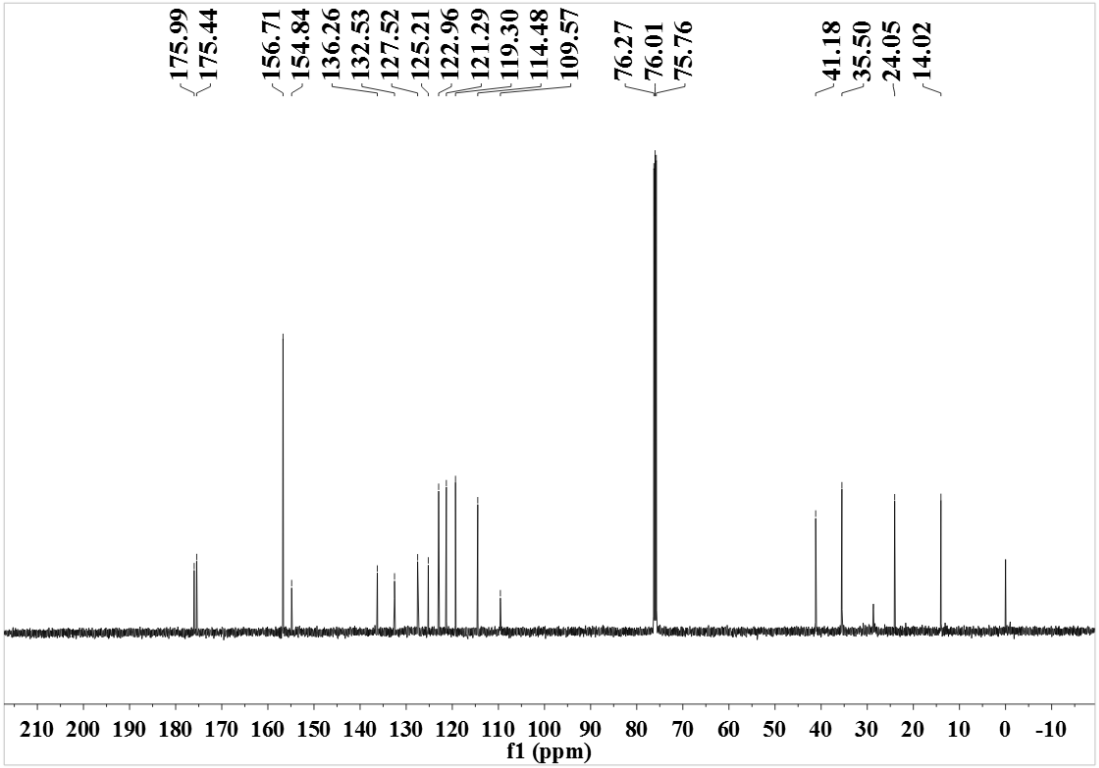

7.33
7.31
7.26
7.23
7.18
7.16
6.79
6.74
6.38
6.35
5.85
5.82
4.53
4.47
4.06
4.03
2.16
2.11
1.59
1.54
1.36
1.28
0.90
0.87
1.00
1.08
1.00
1.00
0.99
1.00
1.98
1.98
3.09
3.03
2.96
2.36
3.22
f1 (ppm)


166.19
146.45
140.07
137.30
136.37
133.75
128.58
126.76
125.83
124.38
119.60
63.09
62.25
29.63
24.34
18.21
18.10
12.67
f1 (ppm)


O
N
Me
O
N
N
N
Me

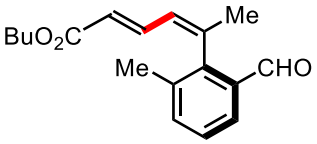
(10)


8.56
8.55
8.43
7.56
7.55
7.32
7.31
7.29
7.26
7.23
7.22
7.21
6.67
4.77
3.14
3.12
3.09
3.09
2.92
2.91
2.88
2.88
2.30
1.00
2.00
1.00
1.00
1.00
1.00
1.00
4.00
1.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


175.99
175.44
156.71
154.84
136.26
132.53
127.52
125.21
122.96
121.29
119.30
114.48
109.57
76.27
76.01
75.76
41.18
35.50
24.05
14.02
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

11. Copies of HPLC Analysis

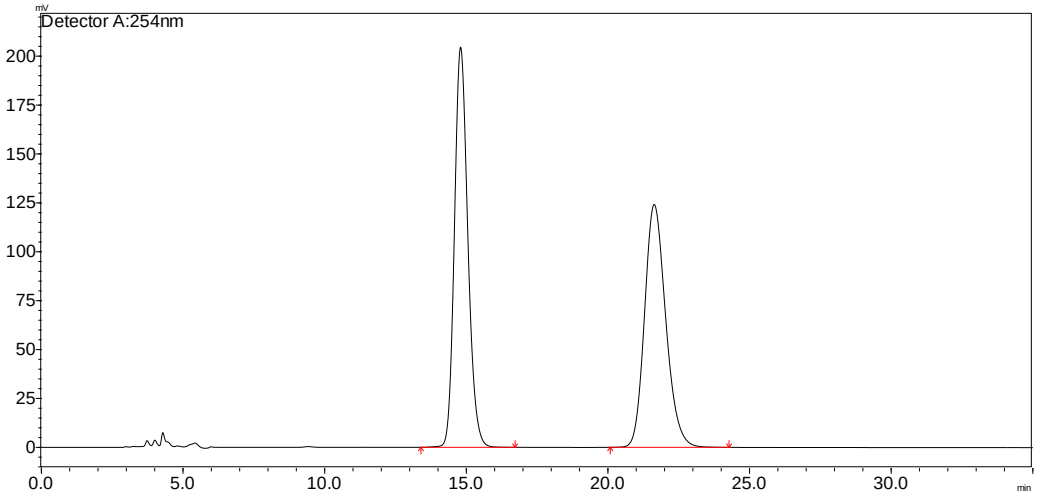
11.1 Copies of HPLC Analysis for β-C-H Alkenylation product



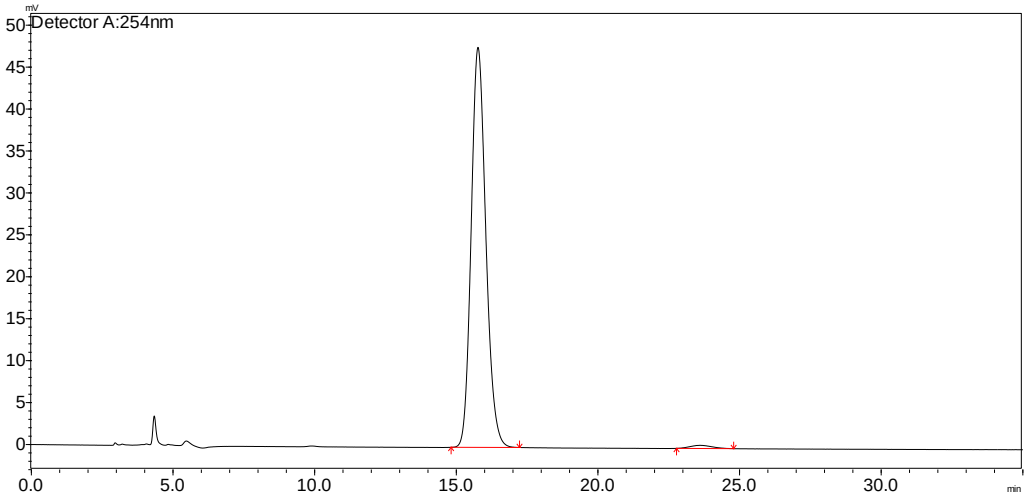
3a

82%, 98% *ee*

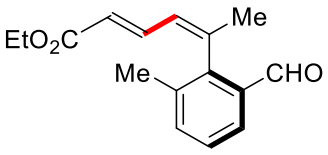
Daicel Chiralpak OD-H column, n-hexane/i-PrOH (60/40), 1.0 mL/min, 254 nm, 15.763 min (major enantiomer), 23.606 min (minor enantiomer).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.796	6722363	204590	51.011	62.233
2	21.630	6455973	124158	48.989	37.767
Total		13178336	328748	100.000	100.000



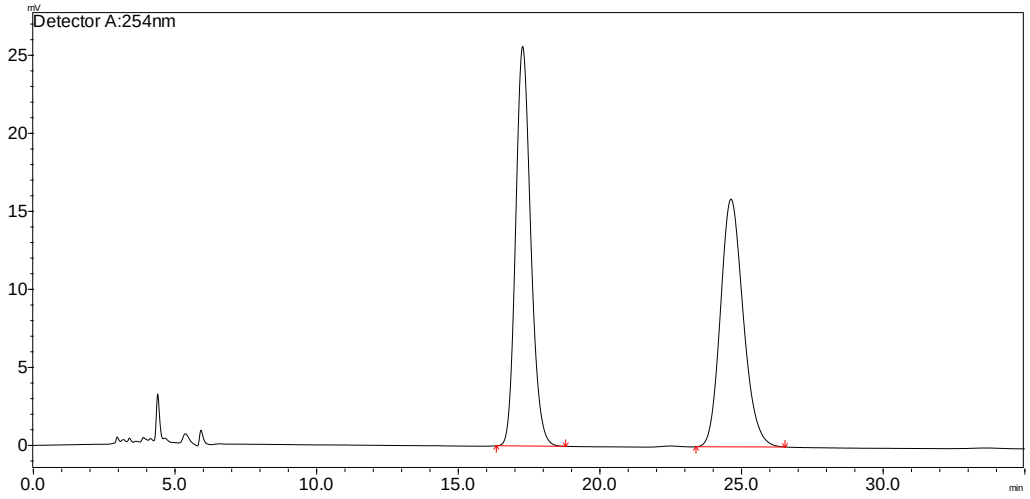
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.763	1718651	47698	98.834	99.220
2	23.606	20278	375	1.166	0.780
Total		1738929	48073	100.000	100.000



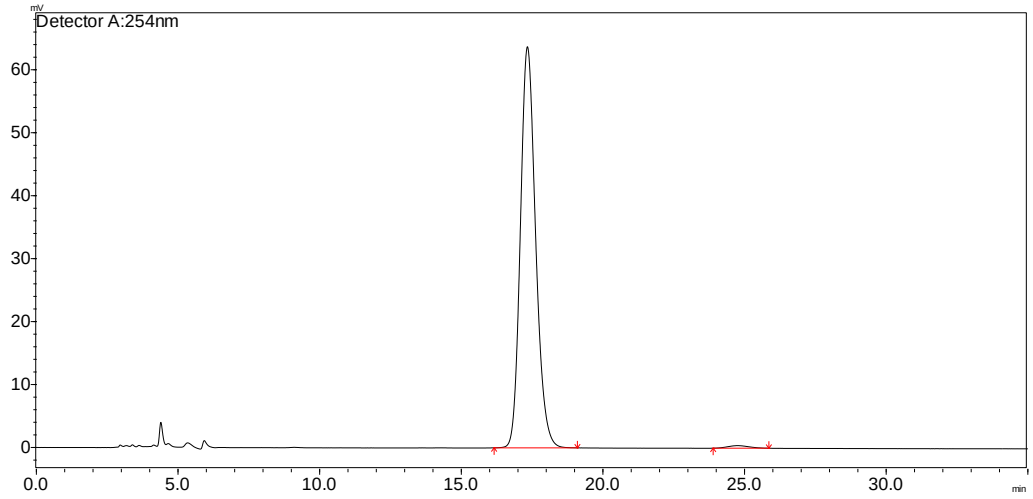
3b

67%, 98% *ee*

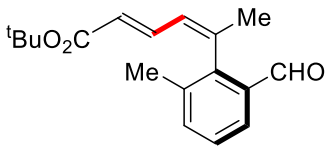
Daicel Chiralpak OD-H column, n-hexane/i-PrOH (60/40), 1.0 mL/min, 254 nm, 17.331 min (major enantiomer), 24.726 min (minor enantiomer).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.268	949791	25600	51.666	61.717
2	24.622	888548	15880	48.334	38.283
Total		1838339	41480	100.000	100.000



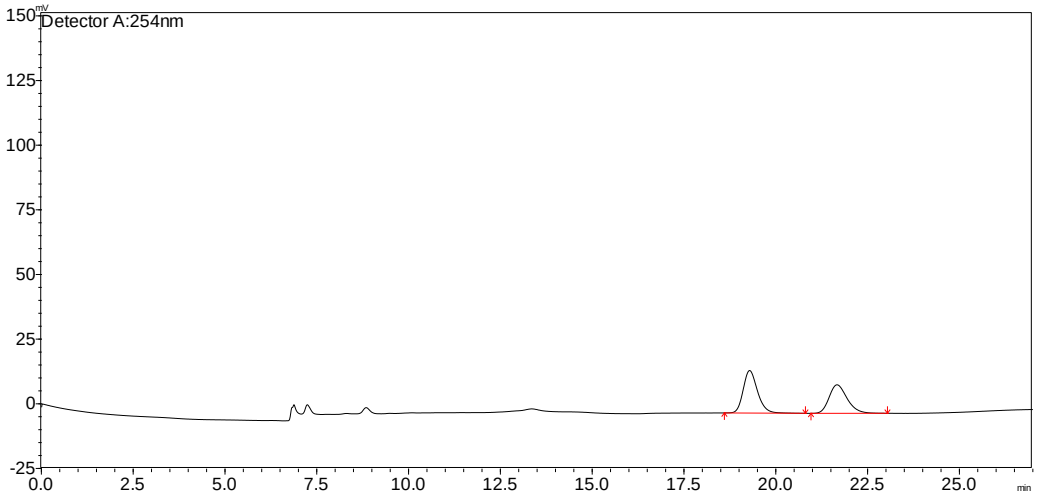
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.331	2385656	63731	99.102	99.362
2	24.726	21607	409	0.898	0.638
Total		2407263	64140	100.000	100.000



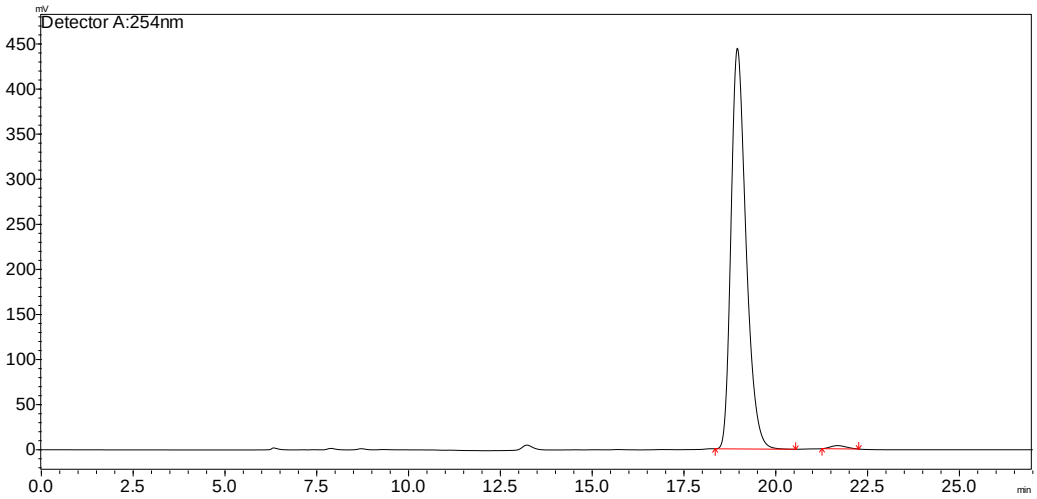
3c

69%, 98% *ee*

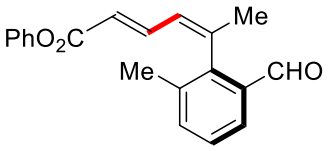
Daicel Chiralpak OD-H column, n-hexane/i-PrOH 98/2), 0.5 mL/min, 254 nm, 18.950 min (major enantiomer), 21.680 min (minor enantiomer).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.283	444756	16427	54.190	59.841
2	21.664	375975	11024	45.810	40.159
Total		820732	27452	100.000	100.000



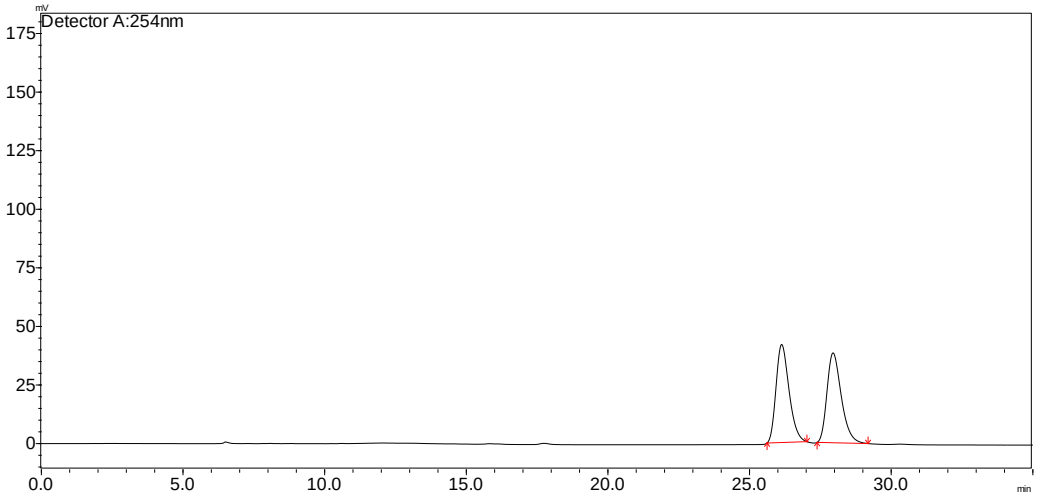
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.950	12648880	444292	99.152	99.206
2	21.680	108178	3558	0.848	0.794
Total		12757059	447850	100.000	100.000



3d

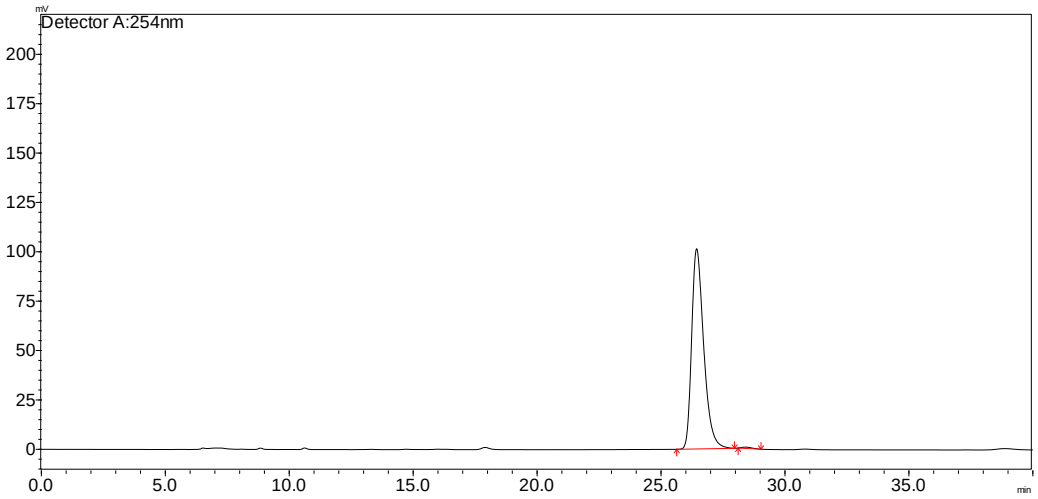
70%, 99% *ee*

Daicel Chiralpak IB-H column, n-hexane/i-PrOH (95/5), 0.5 mL/min, 254 nm, 26.432 min (major enantiomer), 28.410 min (minor enantiomer).

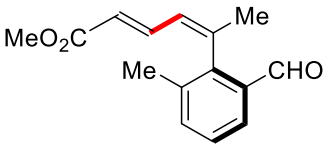


Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.129	1340278	41847	49.854	52.185
2	27.943	1348151	38343	50.146	47.815

Total		2688429	80190	100.000	100.000



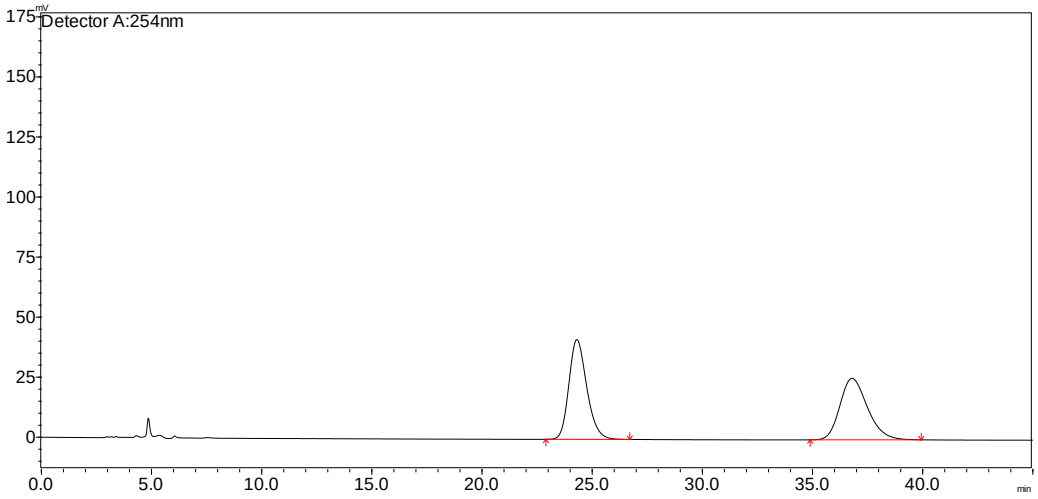
Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.432	3430976	101384	99.455	99.338
2	28.410	18799	675	0.545	0.662
Total		3449775	102059	100.000	100.000



3e

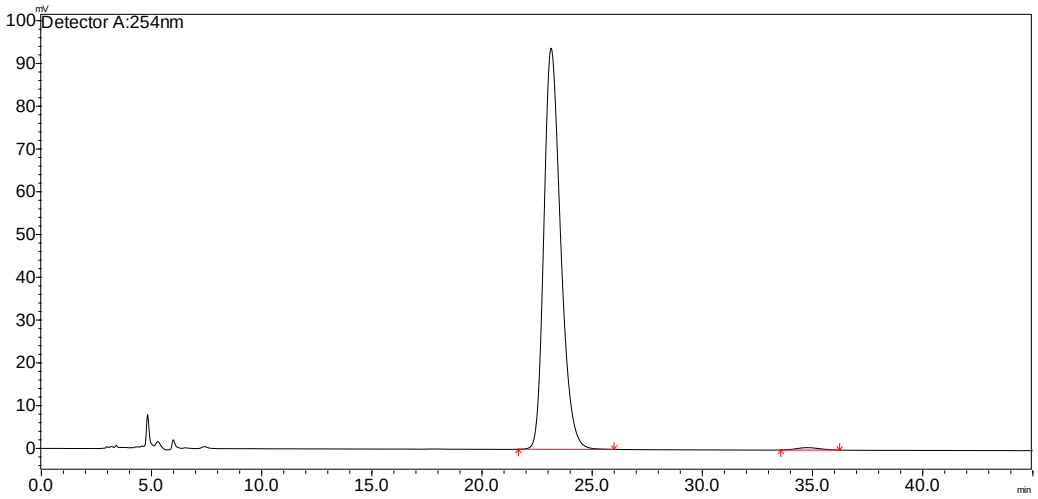
76%, 98% *ee*

Daicel Chiralpak OD-H column, n-hexane/i-PrOH (60/40), 1.0 mL/min, 254 nm, 23.133 min (major enantiomer), 34.742 min (minor enantiomer).

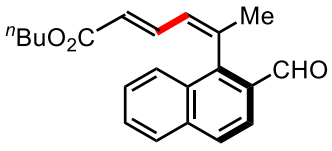


Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.299	2345774	41519	51.274	61.858
2	36.792	2229169	25601	48.726	38.142

Total		4574944	67120	100.000	100.000



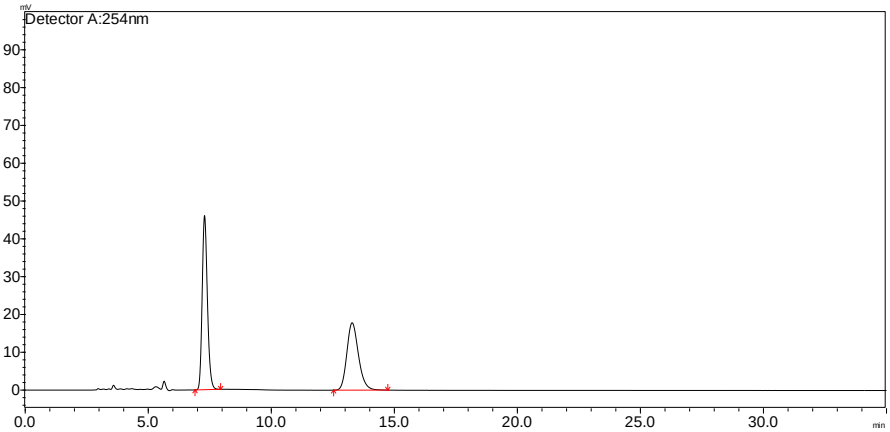
Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.133	4955220	93759	99.176	99.411
2	34.742	41177	555	0.824	0.589
Total		4996398	94314	100.000	100.000



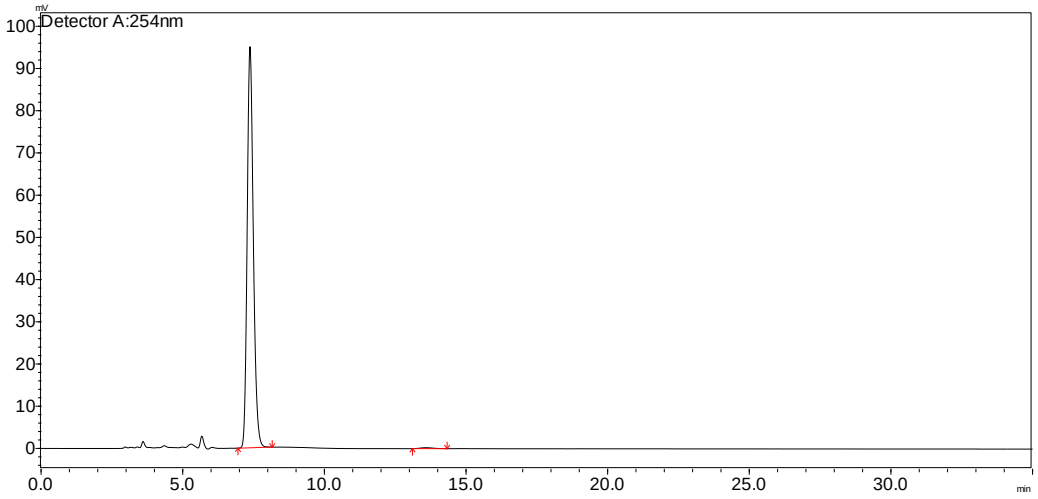
3f

85%, > 99% *ee*

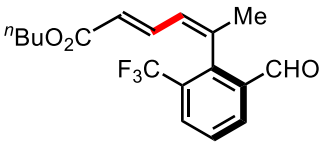
Daicel Chiralpak OD-H column, n-hexane/i-PrOH (60/40), 1.0 mL/min, 254 nm, 7.371 min (major enantiomer), 13.580 min (minor enantiomer).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.284	680589	46051	53.782	72.093
2	13.281	584863	17826	46.218	27.907
Total		1265453	63877	100.000	100.000

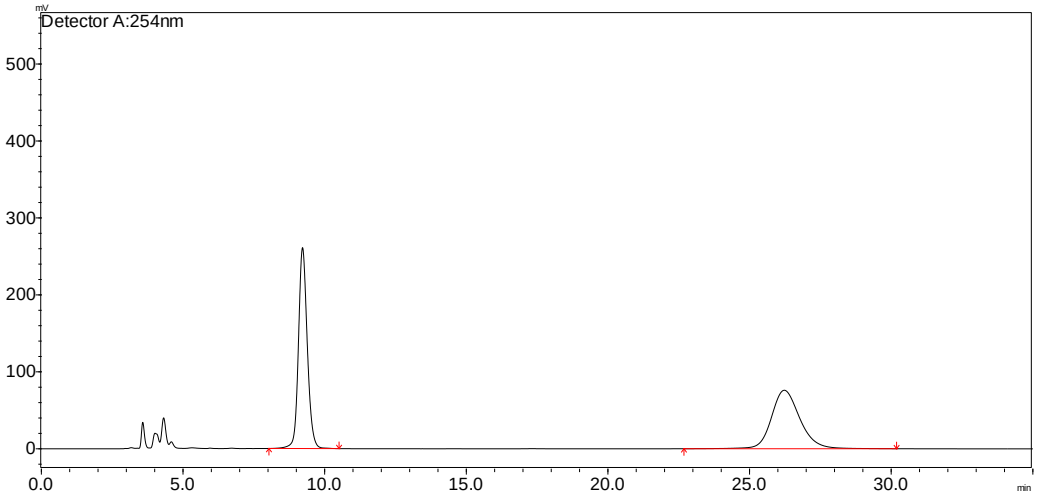


Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.371	1435341	95024	99.502	99.760
2	13.580	7188	229	0.498	0.240
Total		1442529	95253	100.000	100.000

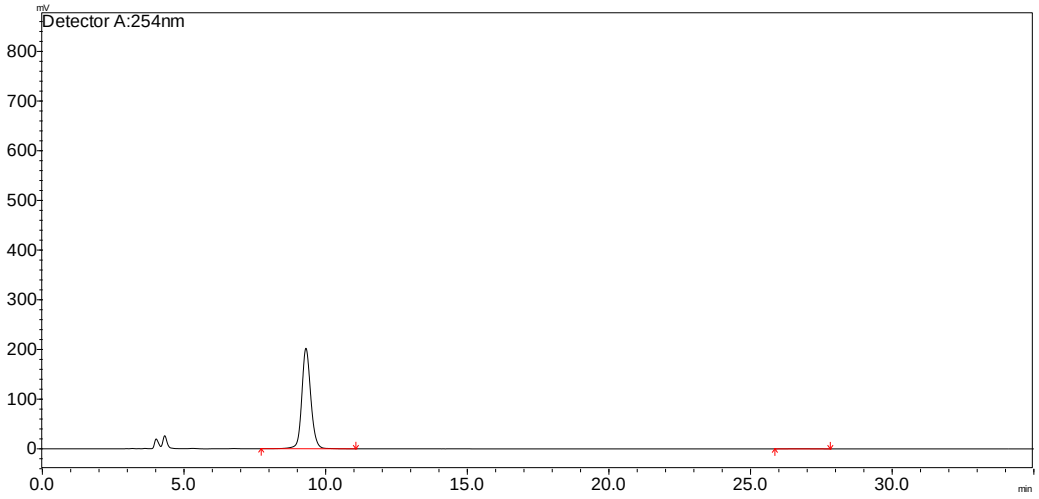


3g, 70%, > 99% *ee*

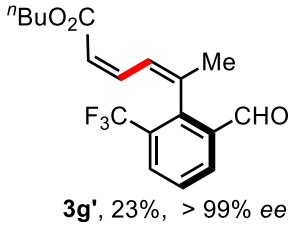
Daicel Chiralpak OD-H column, n-hexane/i-PrOH (60/40), 1.0 mL/min, 254 nm, 9.301 min (major enantiomer), 26.712 min (minor enantiomer).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.216	5665406	261063	51.577	77.452
2	26.222	5318952	76000	48.423	22.548
Total		10984358	337063	100.000	100.000

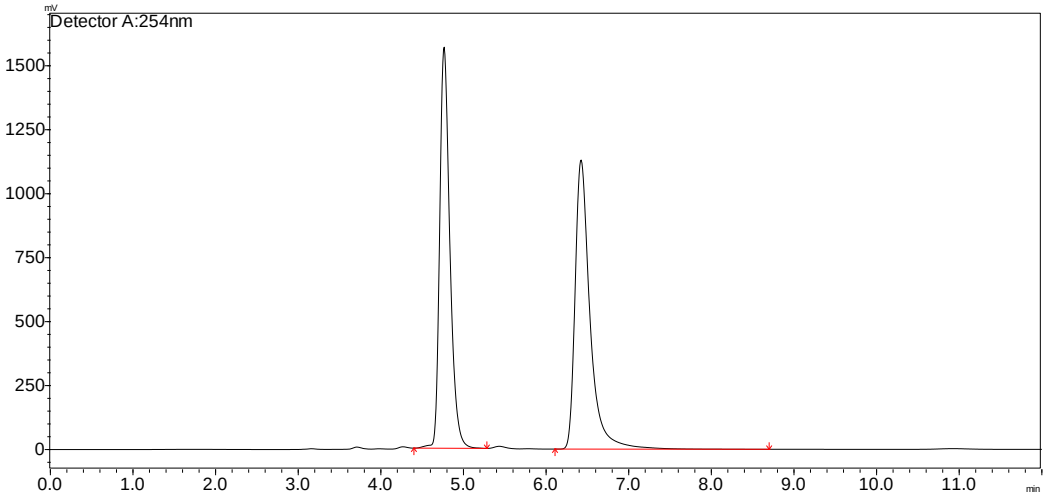


Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.301	4476780	202215	99.662	99.873
2	26.712	15198	257	0.338	0.127
Total		4491978	202472	100.000	100.000



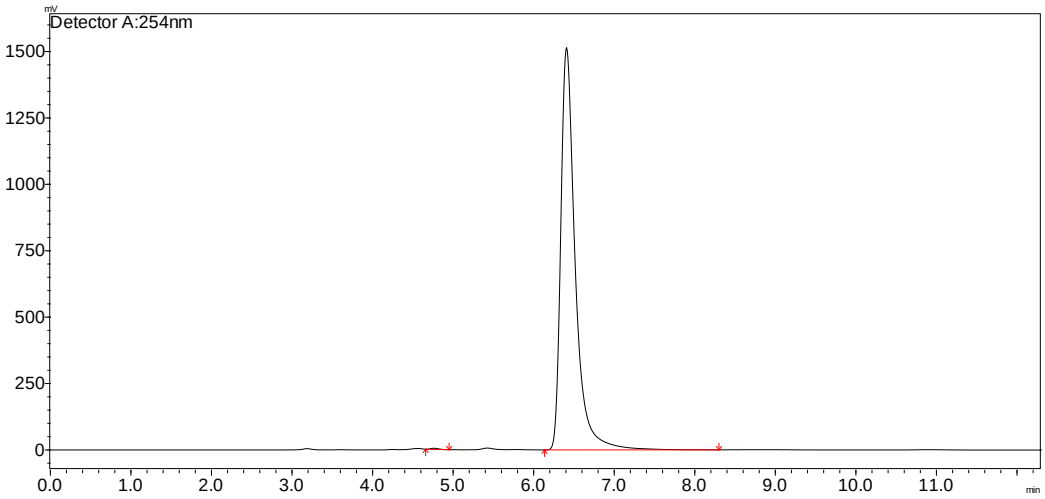
3g', 23%, > 99% *ee*

Daicel Chiralpak OD-H column, n-hexane/i-PrOH (92/8), 1.0 mL/min, 254 nm, 6.403 min (major enantiomer), 4.757 min (minor enantiomer).

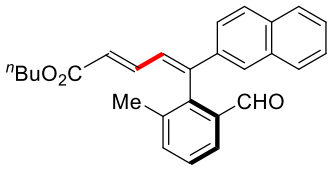


Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.760	13451490	1568113	48.642	58.119
2	6.418	14202507	1129980	51.358	41.881

Total		27653997	2698093	100.000	100.000



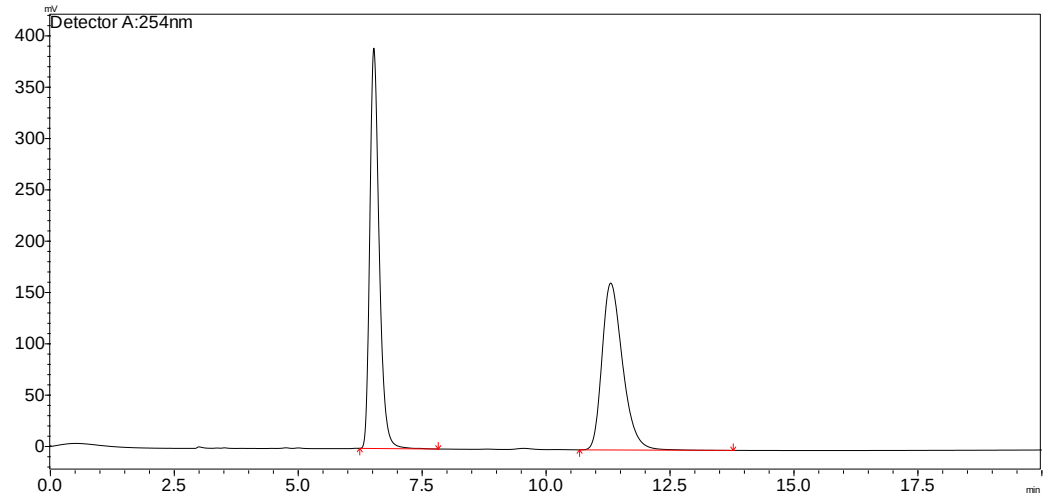
Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.757	29218	4320	0.155	0.284
2	6.403	18869501	1514443	99.845	99.716
Total		18898719	1518762	100.000	100.000



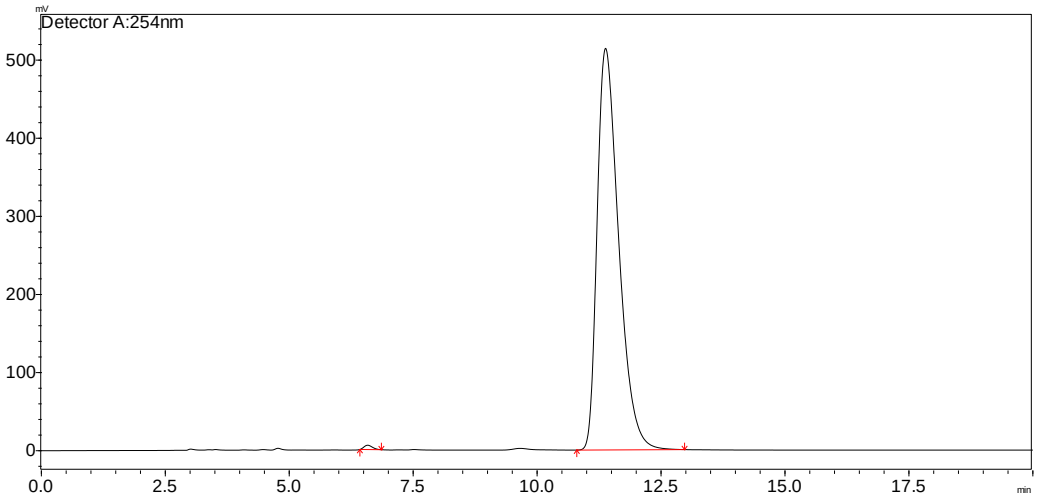
3h

71%, > 99% *ee*

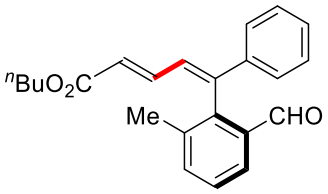
Daicel Chiralpak OD-H column, n-hexane/i-PrOH (85/15), 1.0 mL/min, 254 nm, 11.377 min (major enantiomer), 6.578 min (minor enantiomer).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.521	5134802	390072	52.220	70.580
2	11.299	4698235	162592	47.780	29.420
Total		9833037	552664	100.000	100.000



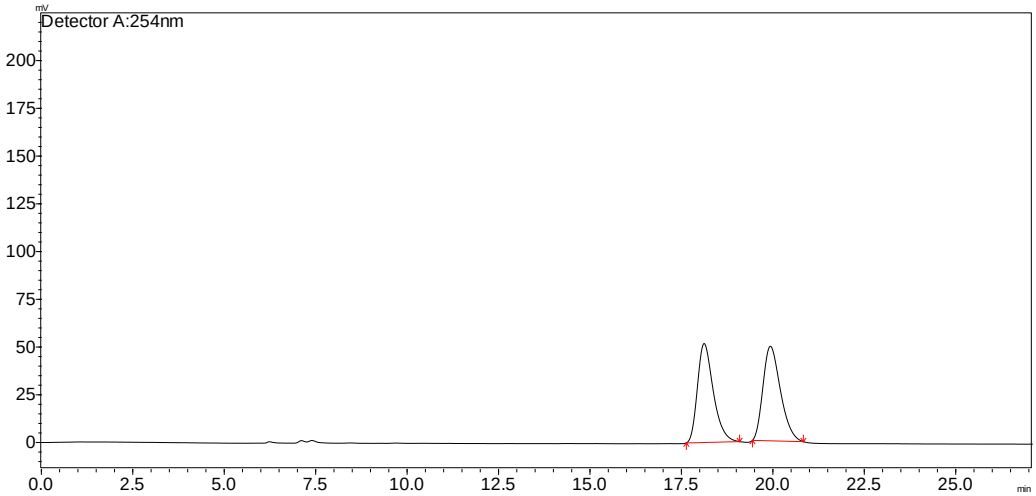
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.578	65761	5590	0.421	1.075
2	11.377	15537636	514194	99.579	98.925
Total		15603397	519784	100.000	100.000



3i

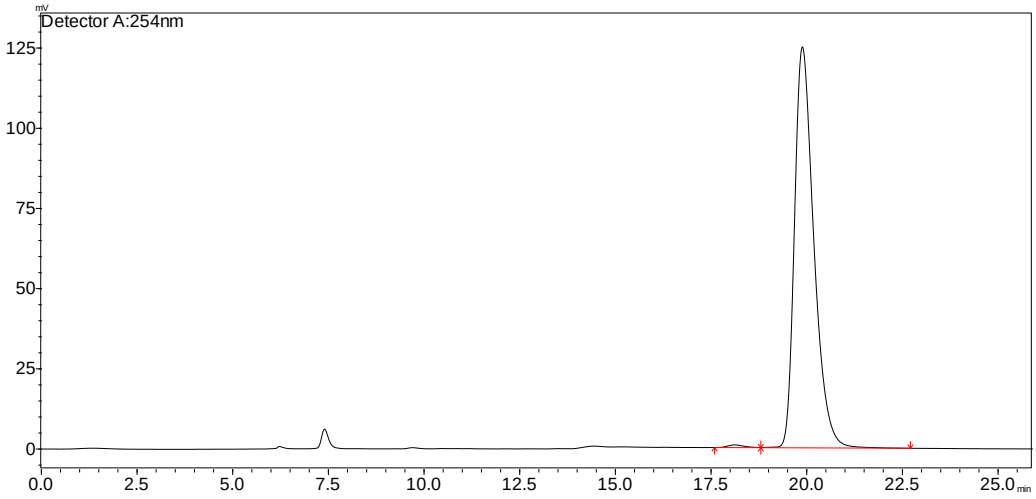
89%, 99% *ee*

Daicel Chiralpak OD-H column, n-hexane/i-PrOH (95/5), 0.5 mL/min, 254 nm, 19.882 min (major enantiomer), 18.111 min (minor enantiomer).

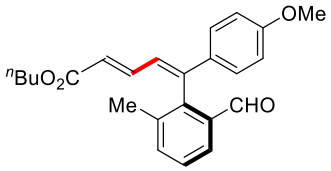


Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.117	1562875	51796	48.642	51.112

2	19.928	1650149	49541	51.358	48.888
Total		3213023	101337	100.000	100.000

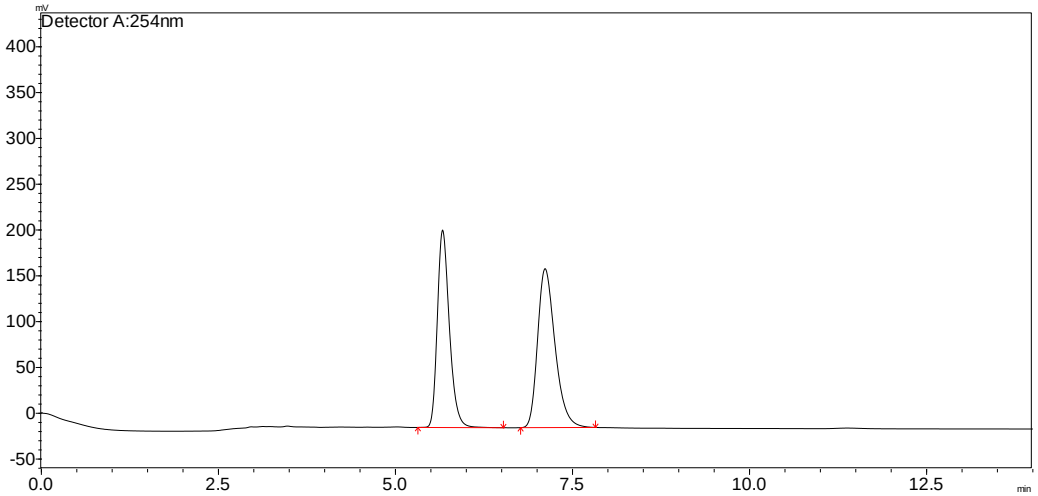


Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.111	26160	857	0.592	0.681
2	19.882	4396054	124998	99.408	99.319
Total		4422215	125855	100.000	100.000

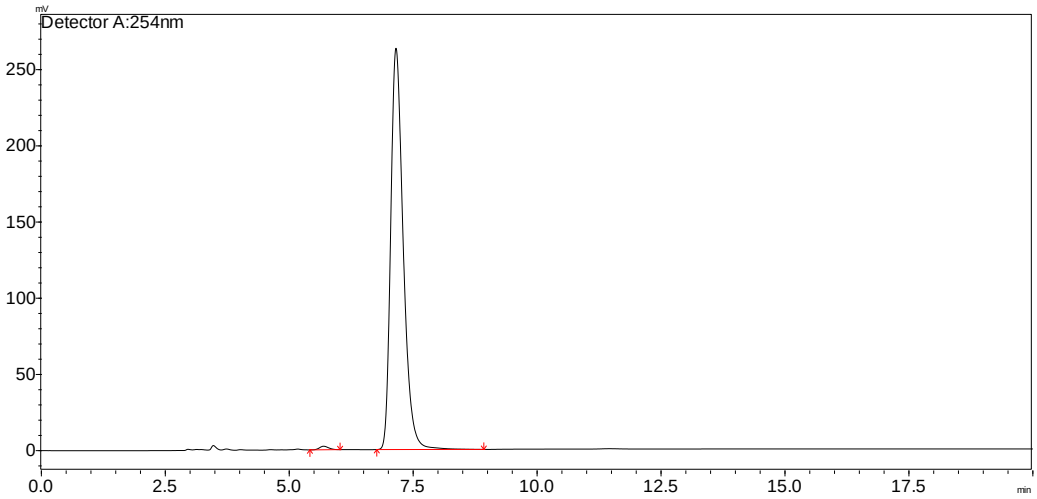


3j
78%, 99% ee

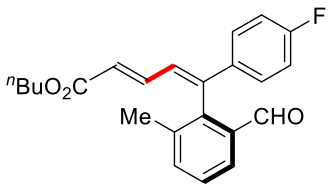
Daicel Chiralpak OD-H column, n-hexane/i-PrOH (80/20), 1.0 mL/min, 254 nm, 7.150 min (major enantiomer), 5.690 min (minor enantiomer).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.661	2546292	215549	46.116	55.421
2	7.109	2975190	173382	53.884	44.579
Total		5521482	388932	100.000	100.000

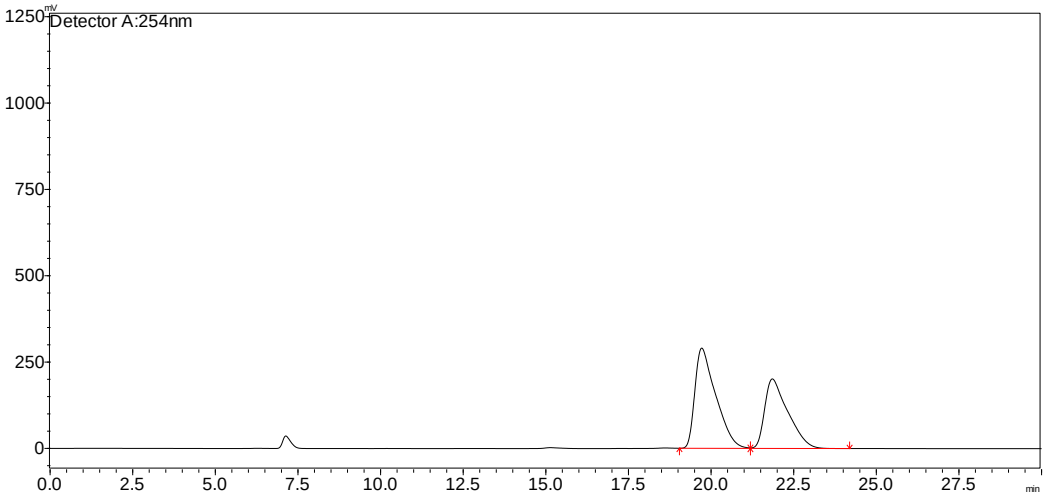


Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.690	29876	2325	0.642	0.875
2	7.150	4626772	263272	99.358	99.125
Total		4656648	265597	100.000	100.000

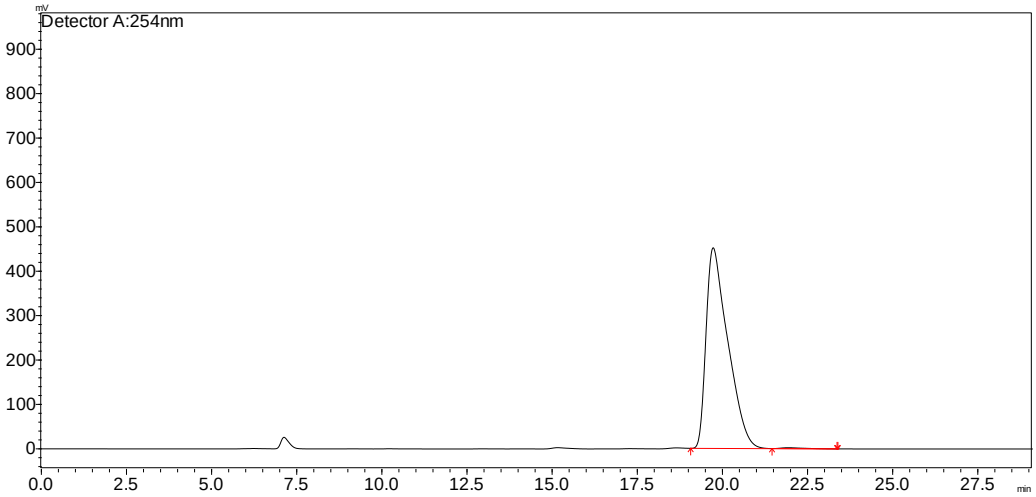


3k
84%, >99% ee

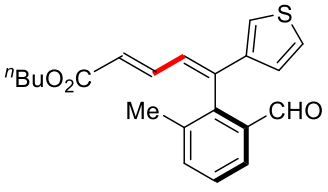
Daicel Chiralpak AD-H column, n-hexane/i-PrOH (95/5), 0.5 mL/min, 254 nm, 19.725 min (major enantiomer), 21.934 min (minor enantiomer).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.714	12742432	290100	56.573	59.048
2	21.849	9781434	201197	43.427	40.952
Total		22523866	491297	100.000	100.000



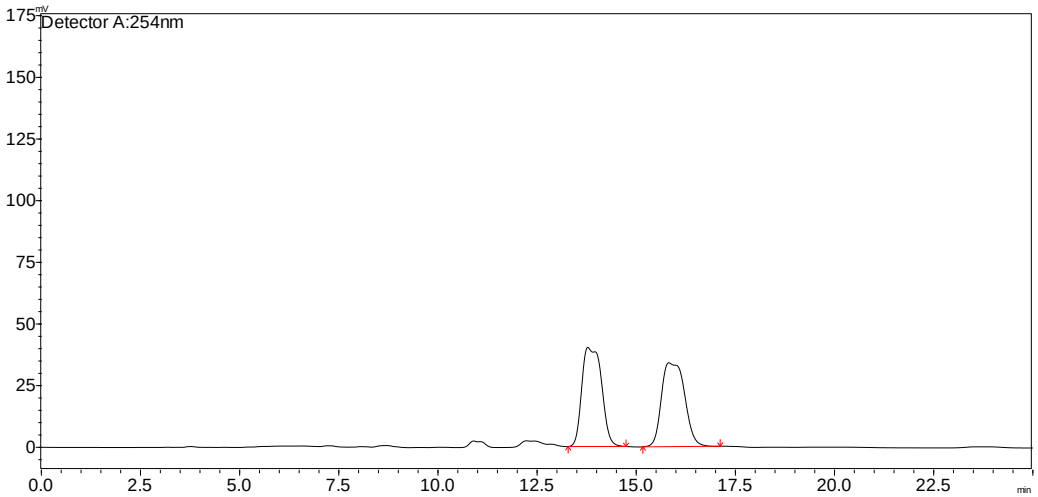
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.725	20092675	451923	99.528	99.537
2	21.934	95242	2104	0.472	0.463
Total		20187917	454026	100.000	100.000



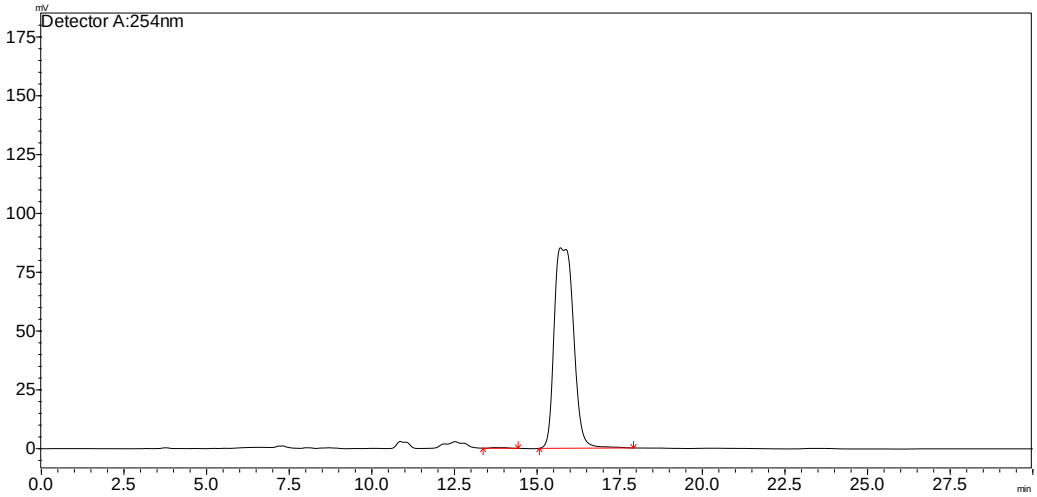
3l

83%, > 99% *ee*

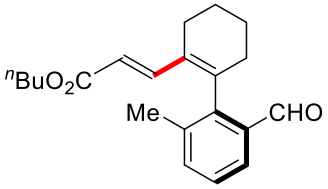
Daicel Chiralpak IA-H column, n-hexane/i-PrOH (98/2), 1.0 mL/min, 254 nm, 15.699 min (major enantiomer), 13.717 min (minor enantiomer).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.774	1390985	40184	50.223	54.166
2	15.817	1378619	34002	49.777	45.834
Total		2769604	74185	100.000	100.000

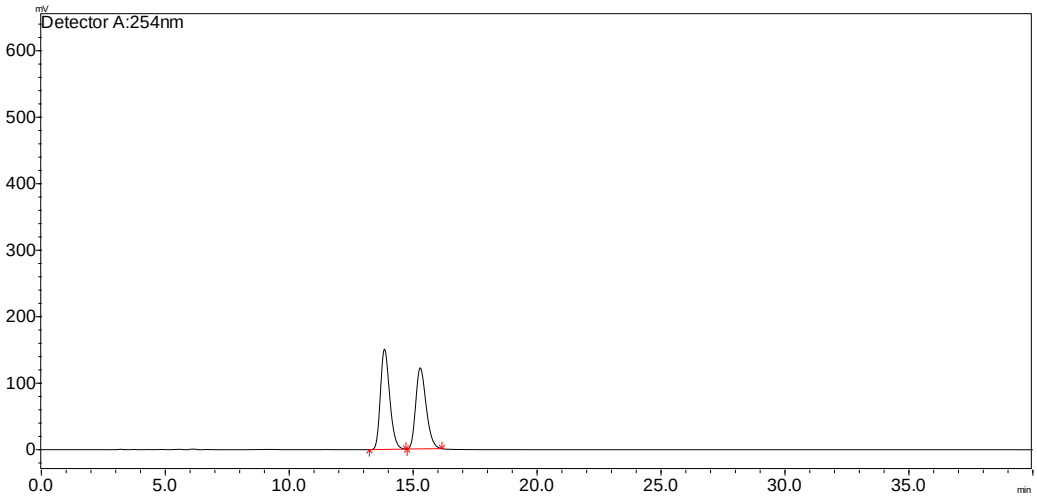


Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.717	9416	281	0.270	0.328
2	15.699	3475404	85197	99.730	99.672
Total		3484820	85478	100.000	100.000

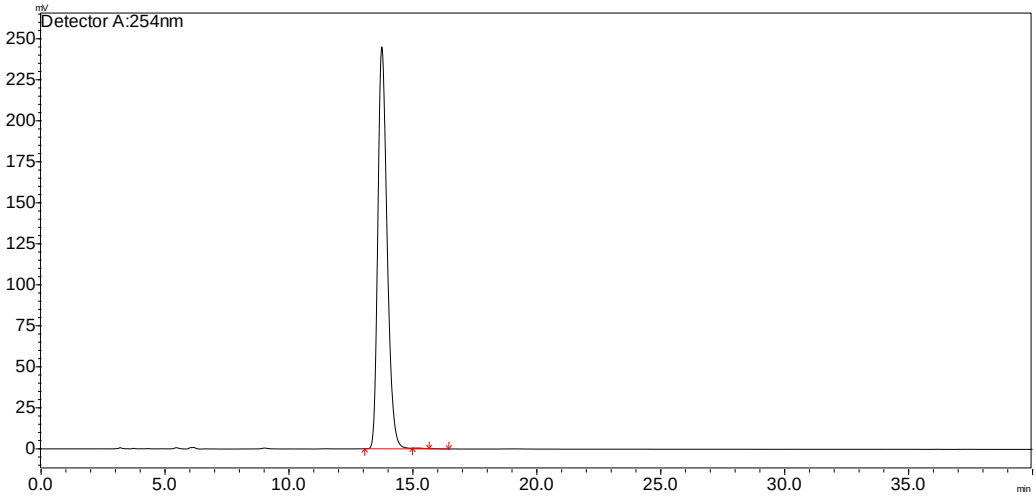


3m, 89%, > 99% *ee*

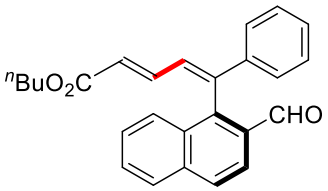
Daicel Chiralpak OD-H column, n-hexane/i-PrOH (97/3), 1.0 mL/min, 254 nm, 13.743 min (major enantiomer), 15.202 min (minor enantiomer).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.839	3932061	150774	52.423	55.309
2	15.282	3568575	121830	47.577	44.691
Total		7500636	272604	100.000	100.000



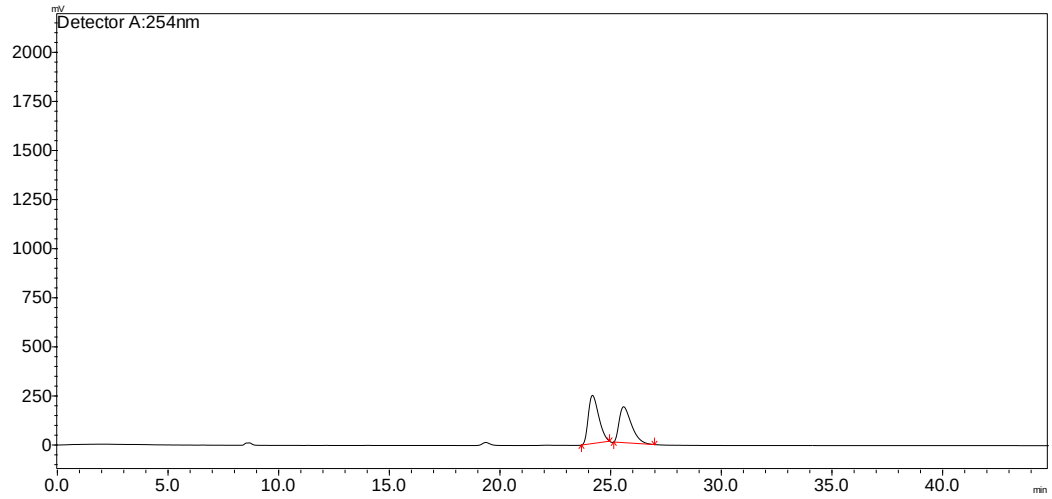
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.743	6415936	245007	99.956	99.943
2	15.202	2825	139	0.044	0.057
Total		6418761	245146	100.000	100.000



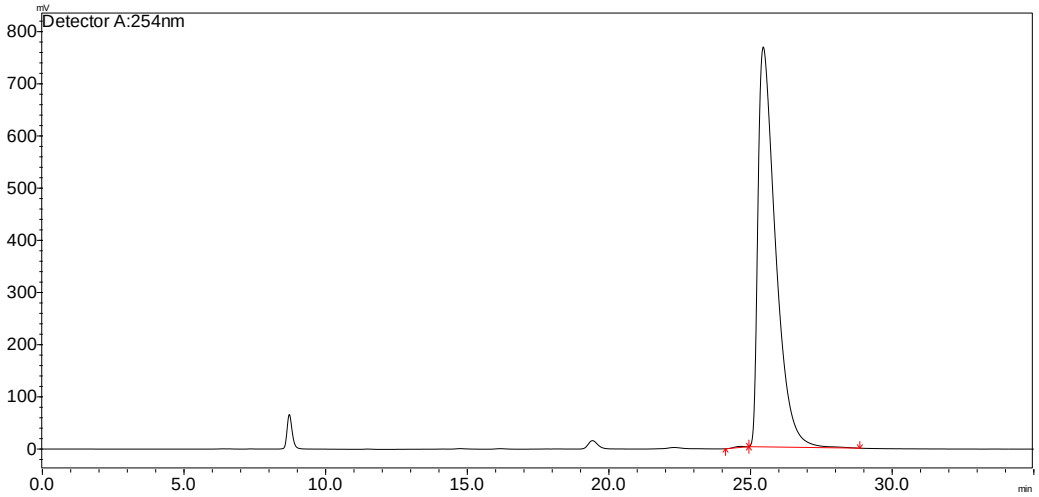
3n

75%, 99% *ee*

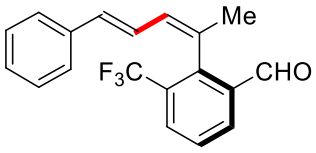
Daicel Chiralpak IB-H column, n-hexane/i-PrOH (98/2), 0.5 mL/min, 254 nm, 25.445 min (major enantiomer), 24.646 min (minor enantiomer).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.175	8049665	245523	53.396	57.339
2	25.581	7025697	182670	46.604	42.661
Total		15075362	428192	100.000	100.000



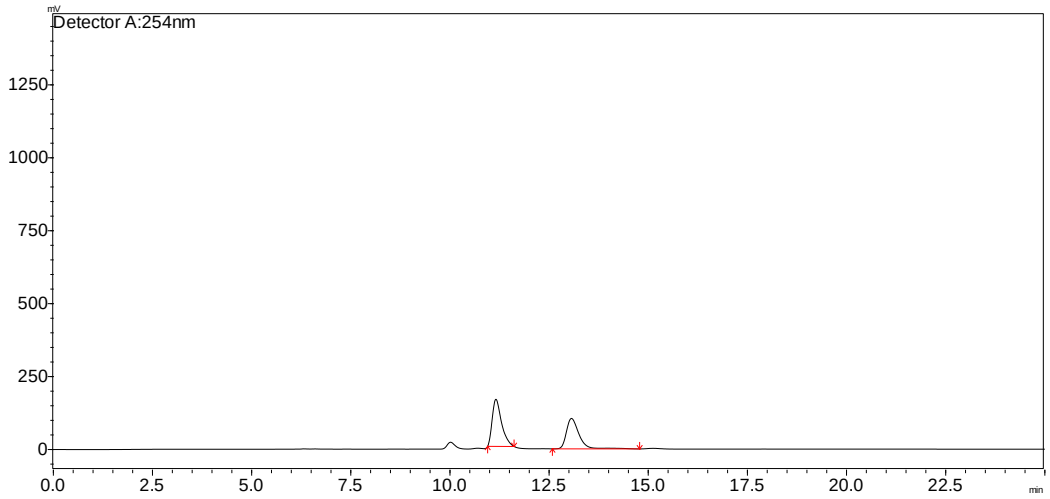
Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.646	47470	2037	0.143	0.265
2	25.445	33066362	766455	99.857	99.735
Total		33113832	768492	100.000	100.000



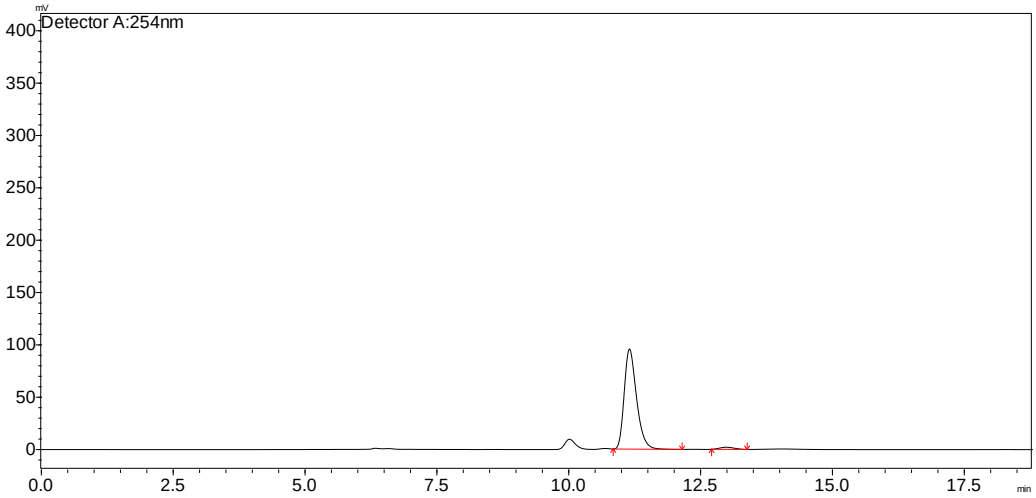
3o

82%, 95% *ee*

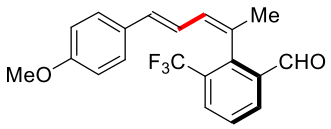
Daicel Chiralpak OD-H column, n-hexane/i-PrOH (98/2), 0.5 mL/min, 254 nm, 11.147 min (major enantiomer), 12.985 min (minor enantiomer).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.155	2646575	161502	53.305	60.751
2	13.060	2318387	104342	46.695	39.249
Total		4964962	265845	100.000	100.000

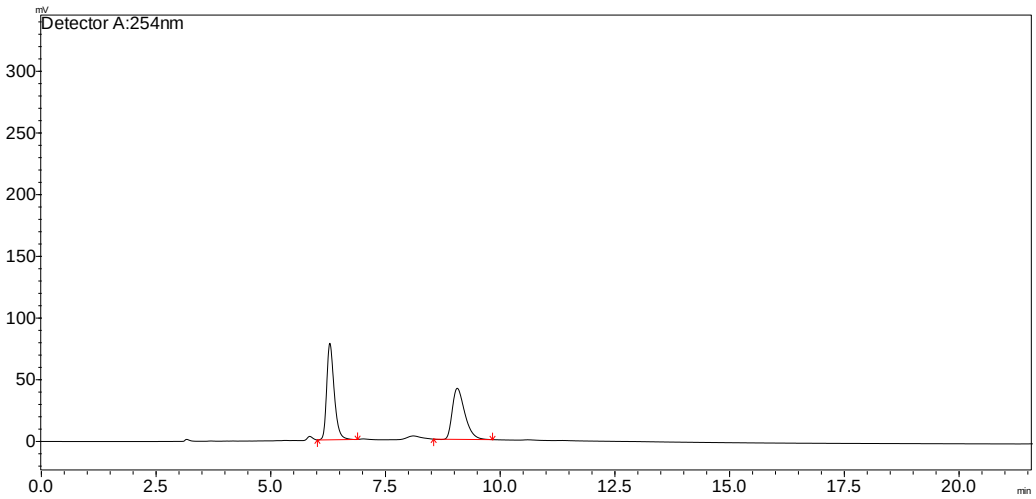


Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.147	1552971	95611	97.590	97.936
2	12.985	38355	2015	2.410	2.064
Total		1591326	97626	100.000	100.000

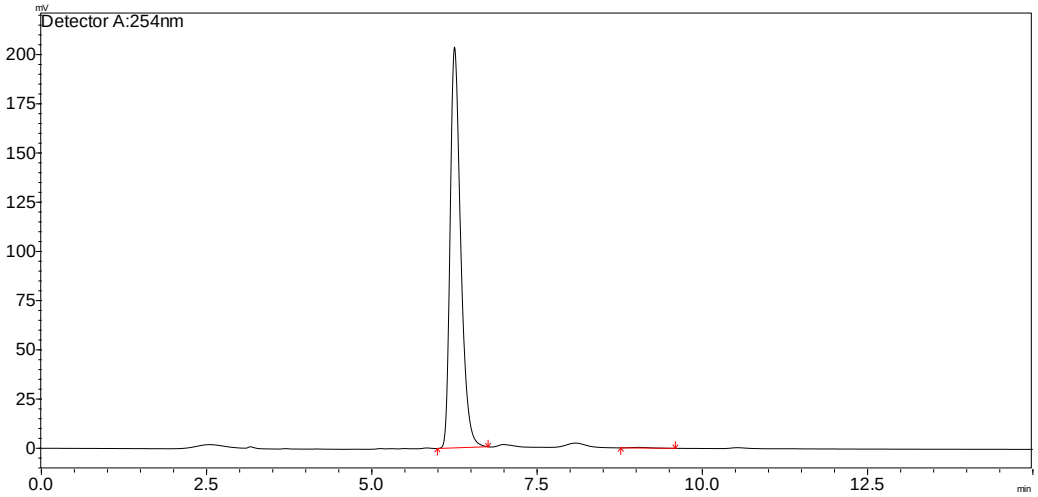


3p
79%, > 99% *ee*

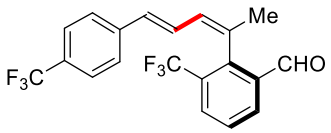
Daicel Chiralpak OD-H column, n-hexane/i-PrOH (95/5), 1.0 mL/min, 254 nm, 6.247 min (major enantiomer), 9.032 min (minor enantiomer).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.283	888322	78209	53.167	65.394
2	9.060	782489	41387	46.833	34.606
Total		1670812	119596	100.000	100.000

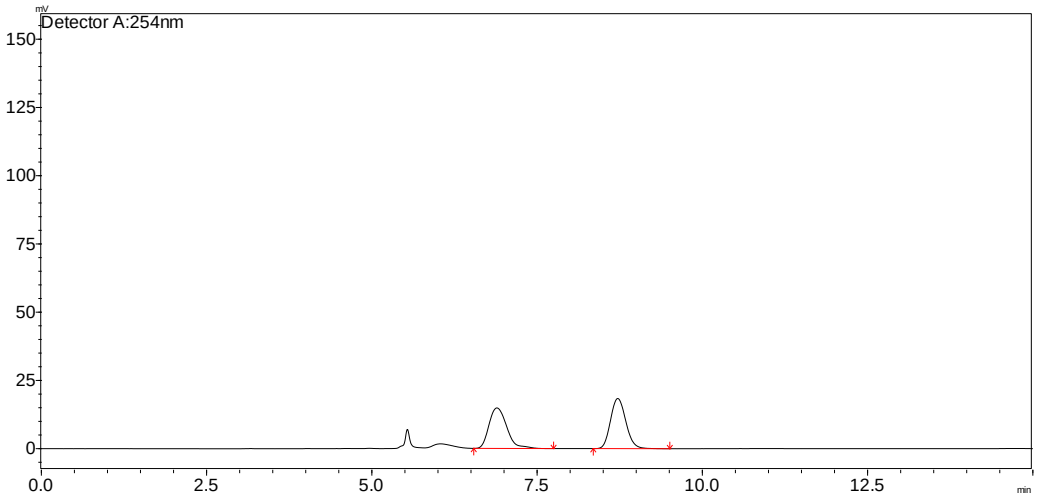


Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.247	2266521	203698	99.729	99.839
2	9.032	6162	329	0.271	0.161
Total		2272683	204027	100.000	100.000

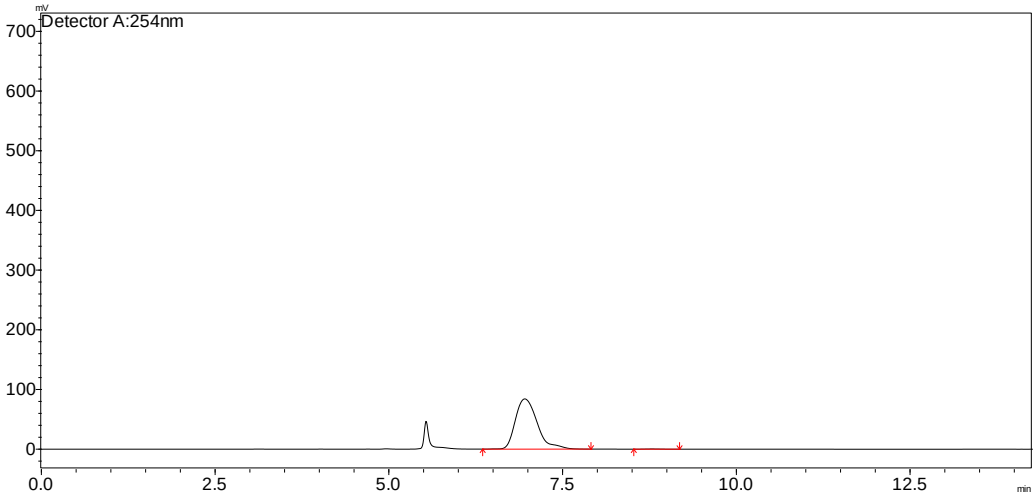


3q
76%, > 99% *ee*

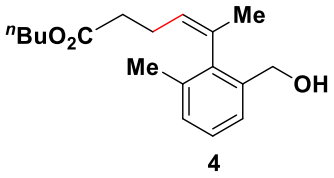
Daicel Chiralpak AD-H column, n-hexane/i-PrOH (99.2/0.8), 1.0 mL/min, 254 nm, 6.952 min (major enantiomer), 8. 784 min (minor enantiomer).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.887	278351	14849	48.438	44.704
2	8.716	296303	18367	51.562	55.296
Total		574654	33216	100.000	100.000



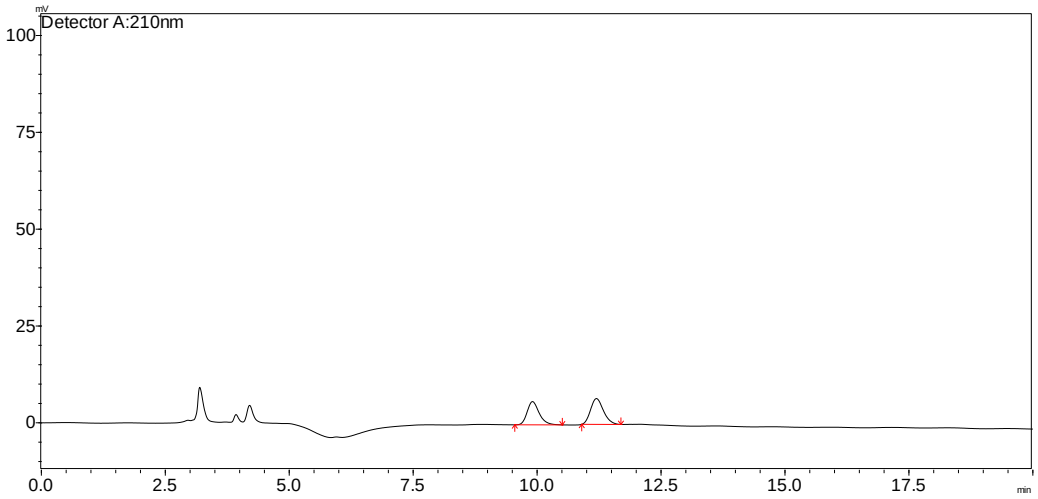
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.952	1840832	84104	99.746	99.637
2	8.784	4687	306	0.254	0.363
Total		1845519	84410	100.000	100.000



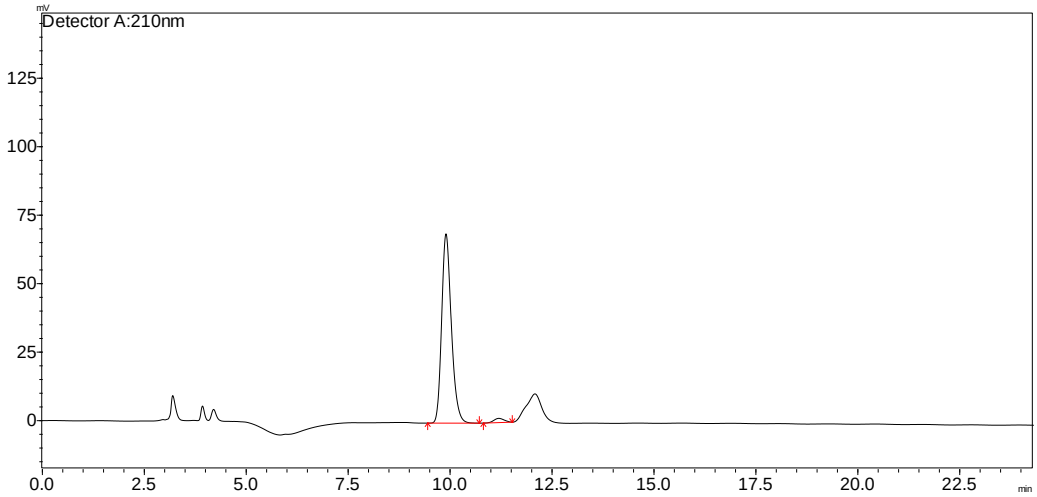
4

82%, 95% *ee*

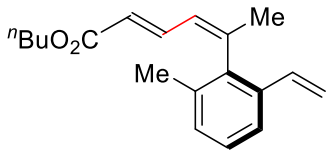
Daicel Chiralpak OD-H column, n-hexane/i-PrOH (97/3), 1.0 mL/min, 210 nm, 9.896 min (major enantiomer), 11.192 min (minor enantiomer).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.903	101256	6005	45.656	47.387
2	11.192	120526	6668	54.344	52.613
Total		221782	12673	100.000	100.000



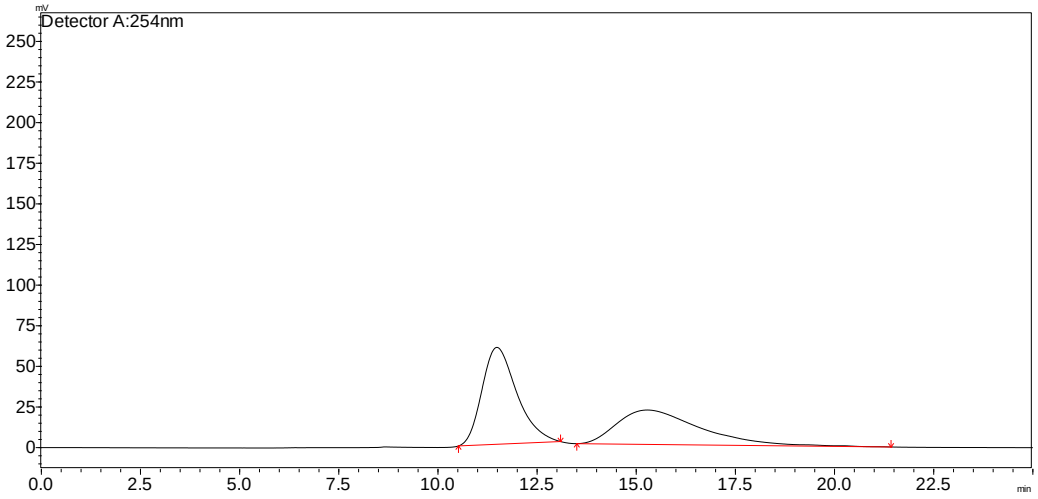
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.896	1143407	69119	97.656	97.815
2	11.192	27443	1544	2.344	2.185
Total		1170850	70663	100.000	100.000



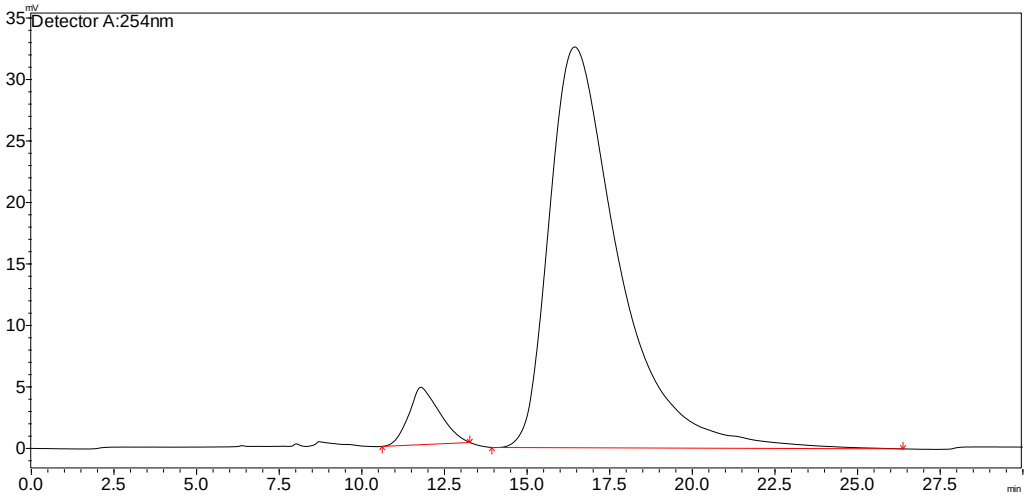
5

88%, 88% *ee*

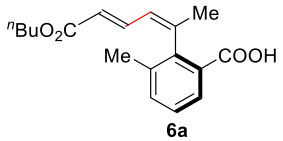
Daicel Chiralpak OB-H column, n-hexane/i-PrOH (99.2/0.8), 0.5 mL/min, 254 nm, 16.436 min (major enantiomer), 11.784 min (minor enantiomer).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.482	3653776	59645	54.167	73.818
2	15.275	3091634	21155	45.833	26.182
Total		6745410	80800	100.000	100.000



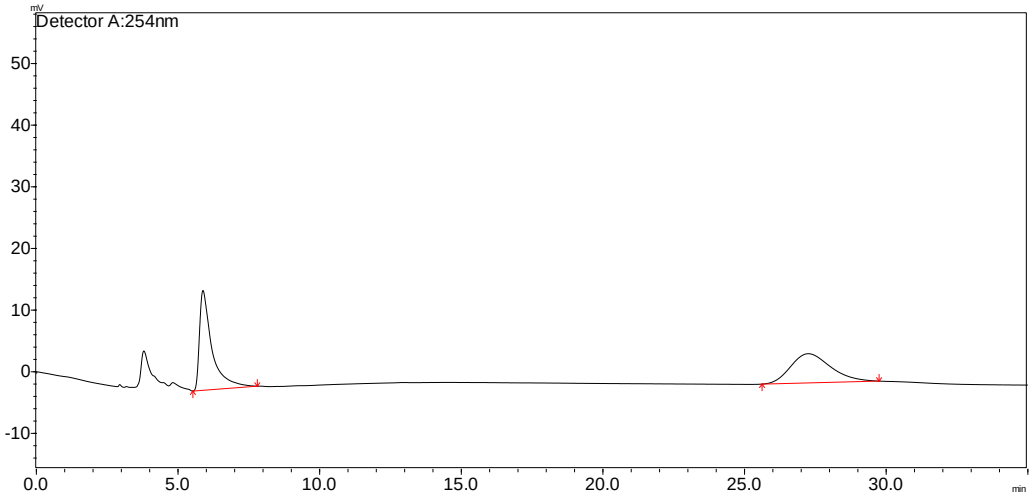
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.784	302091	4667	5.951	12.527
2	16.436	4774257	32592	94.049	87.473
Total		5076348	37259	100.000	100.000



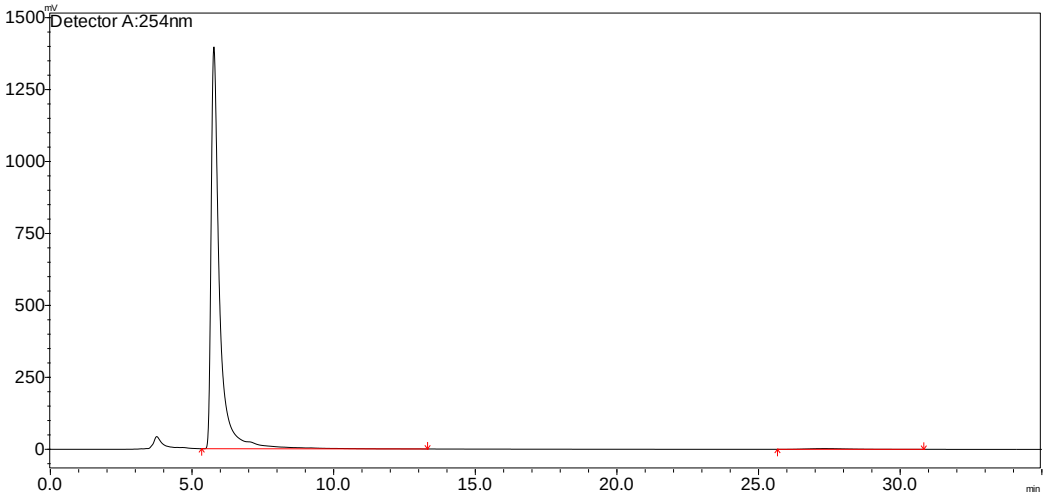
6a

91%, 98% ee

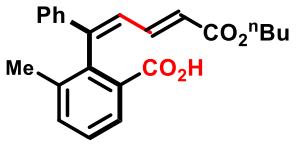
Daicel Chiralpak OD-H column, n-hexane/i-PrOH (60/40), 1.0 mL/min, 254 nm, 5.768 min (major enantiomer), 27.319 min (minor enantiomer).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.878	497022	16196	51.585	77.359
2	27.248	466471	4740	48.415	22.641
Total		963493	20935	100.000	100.000

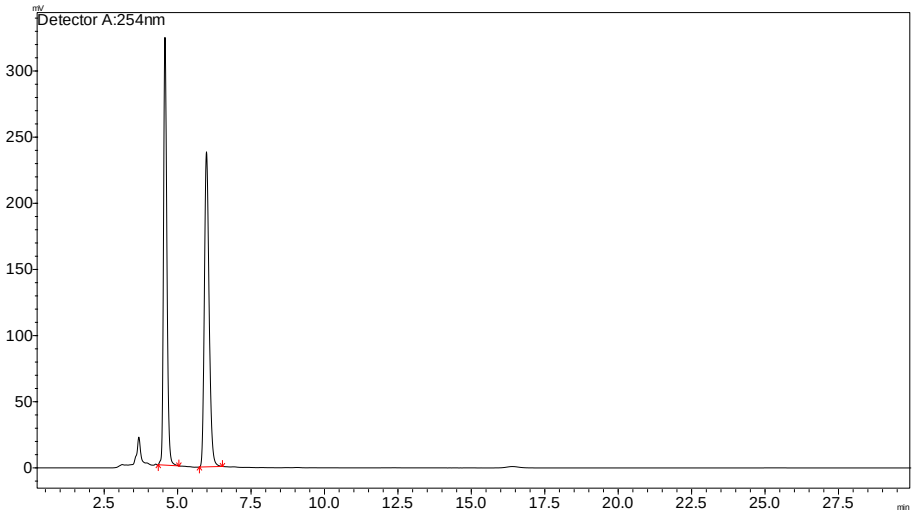


Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.768	28987269	1396035	99.074	99.819
2	27.319	270933	2533	0.926	0.181
Total		29258202	1398569	100.000	100.000

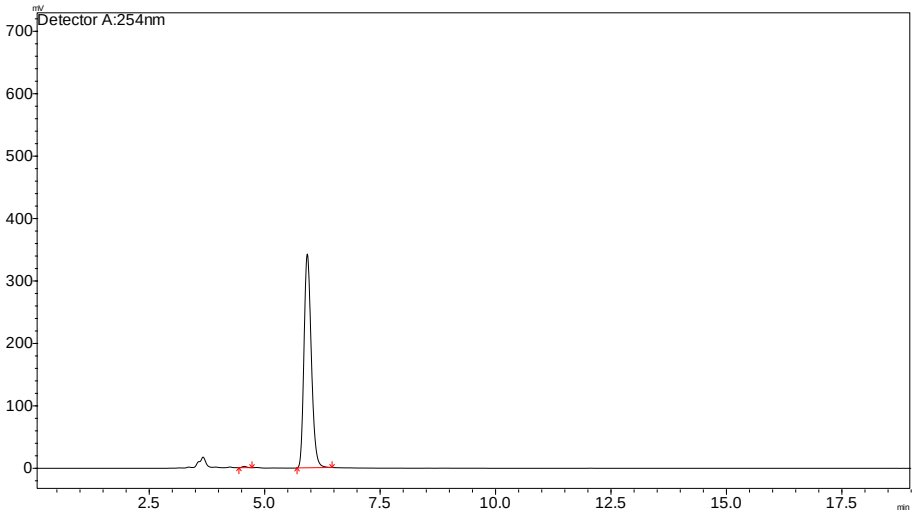


6b, **86%, 99% ee**

Daicel Chiralpak AD-H column, n-hexane/i-PrOH (60/40), 1 mL/min, 254 nm, 5.918 min (major enantiomer), 4.552 min (minor enantiomer).

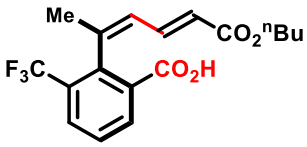


Peak #	Ret. Time	Area	Height	Area %	Height %
1	4.566	2555938	323322	48.902	57.593
2	5.978	2670727	238072	51.098	42.407
Total		5226664	561393	100.000	100.000



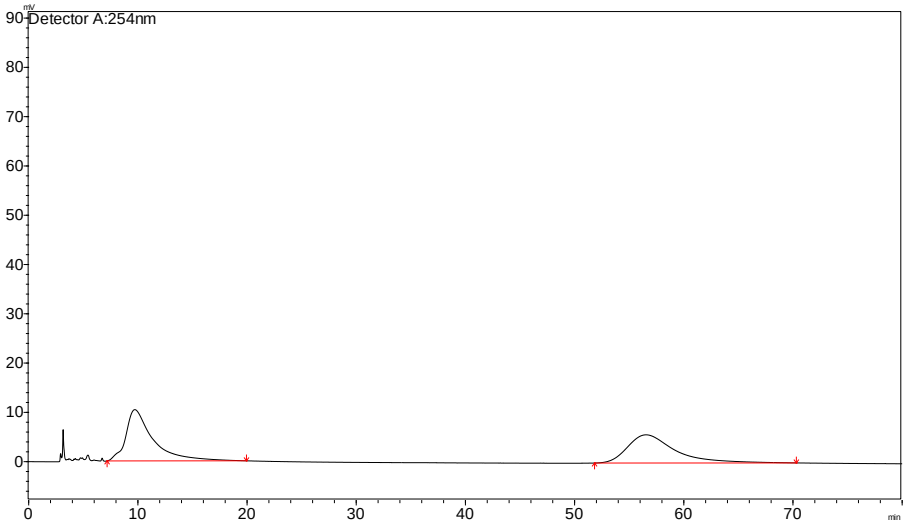
Peak #	Ret. Time	Area	Height	Area %	Height %

1	4.552	13999	2072	0.370	0.601
2	5.918	3768907	342439	99.630	99.399
Total		3782906	344510	100.000	100.000

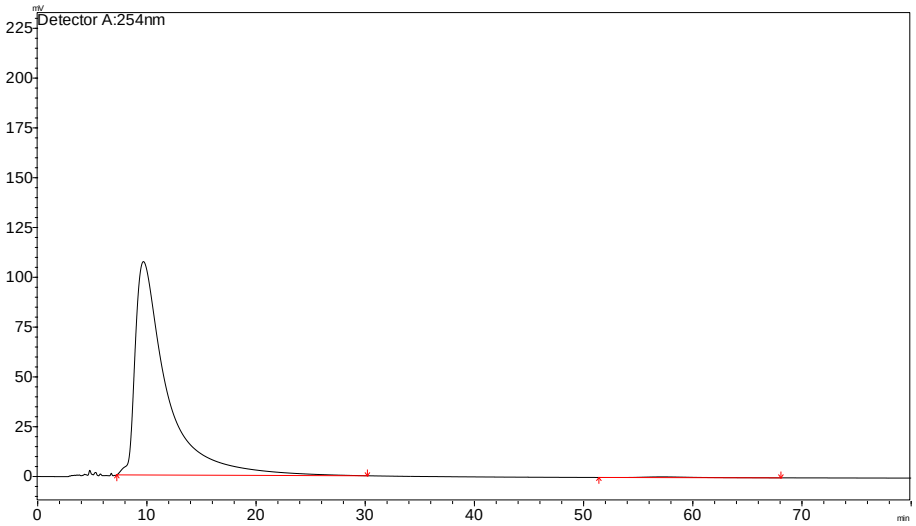


6c, 91%, 99% ee

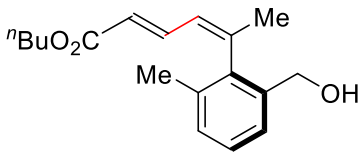
Daicel Chiralpak OD-H column, n-hexane/i-PrOH (50/50), 1 mL/min, 254 nm, 9.684 min (major enantiomer), 57.209 min (minor enantiomer).



Peak #	Ret. Time	Area	Height	Area %	Height %
1	9.719	1802538	10405	51.024	64.523
2	56.533	1730182	5721	48.976	35.477
Total		3532720	16127	100.000	100.000



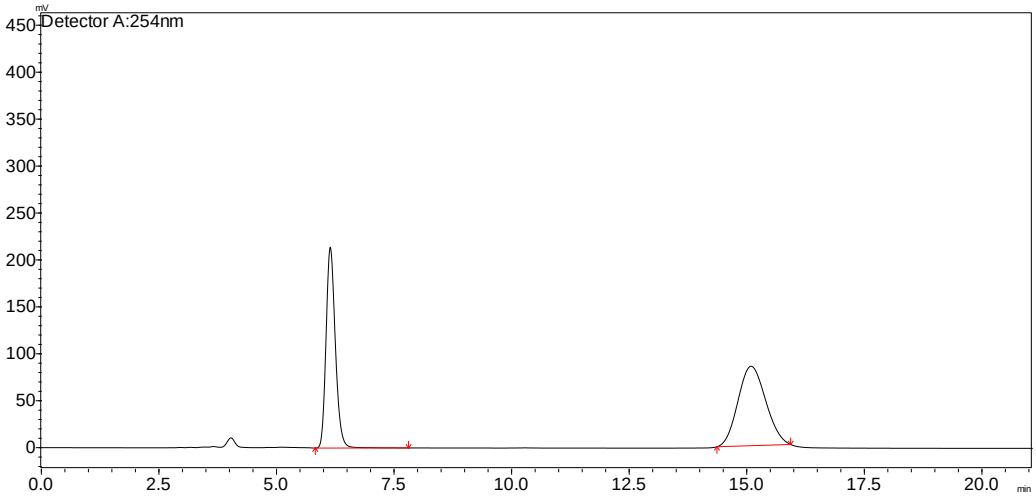
Peak #	Ret. Time	Area	Height	Area %	Height %
1	9.684	21607297	107118	99.505	99.662
2	57.209	107444	363	0.495	0.338
Total		21714740	107481	100.000	100.000



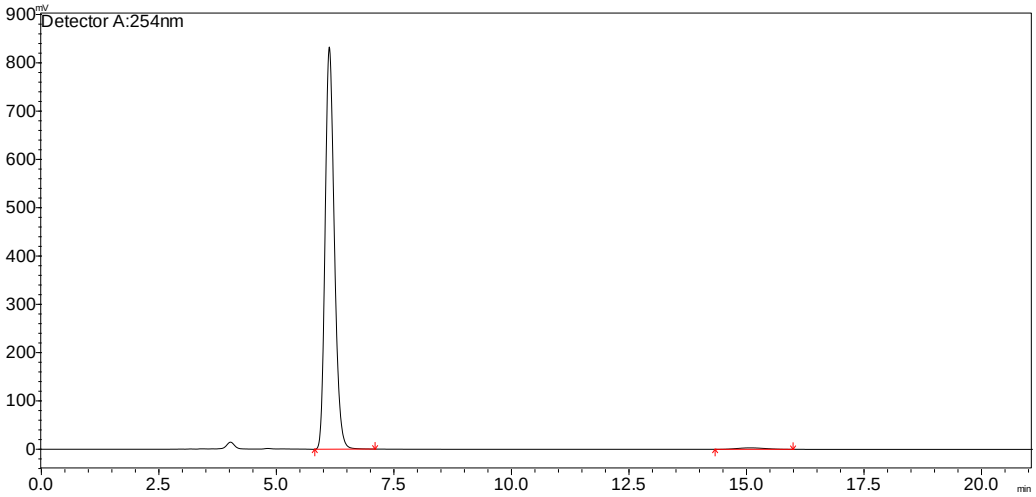
7

85%, 98% ee

Daicel Chiralpak OD-H column, n-hexane/i-PrOH (60/40), 1.0 mL/min, 254 nm, 6.121 min (major enantiomer), 15.077 min (minor enantiomer).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.139	2941922	214011	45.901	71.653
2	15.088	3467414	84665	54.099	28.347
Total		6409336	298676	100.000	100.000

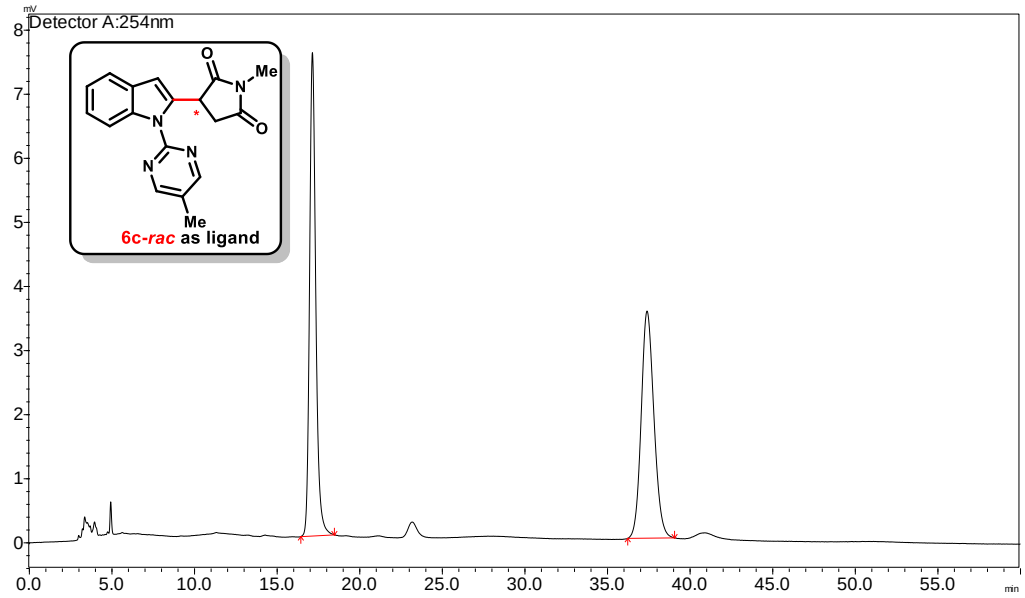


Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.121	11333655	832826	98.903	99.640
2	15.077	125669	3011	1.097	0.360
Total		11459323	835837	100.000	100.000

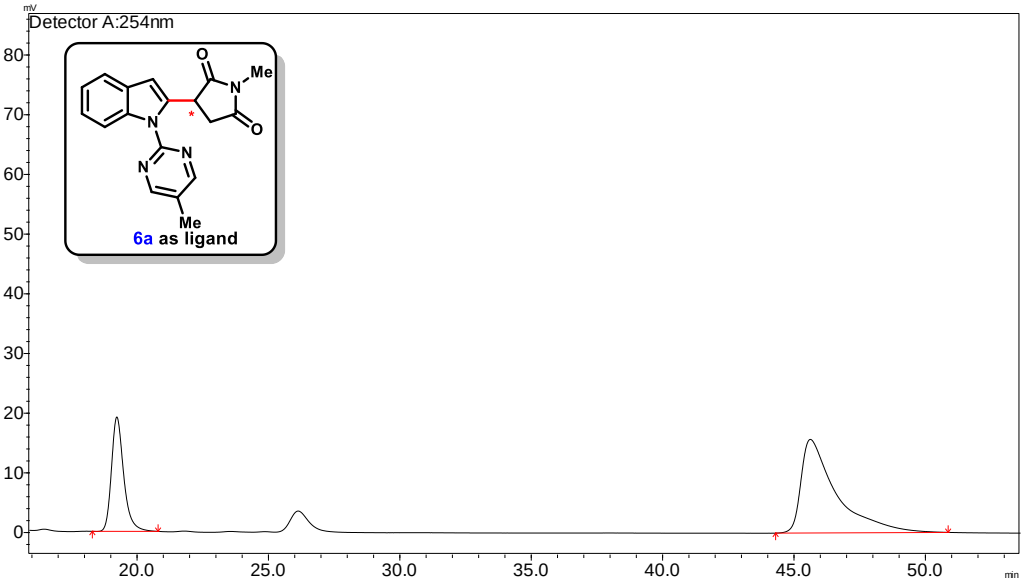
11.2 Copies of HPLC Analysis for 12 with different CCAs

6c-rac as ligand

Daicel Chiralpak IA column, n-hexane/i-PrOH (80/20), 1.0 mL/min, 254 nm, 17.130min (major enantiomer), 37.385 min (minor enantiomer).

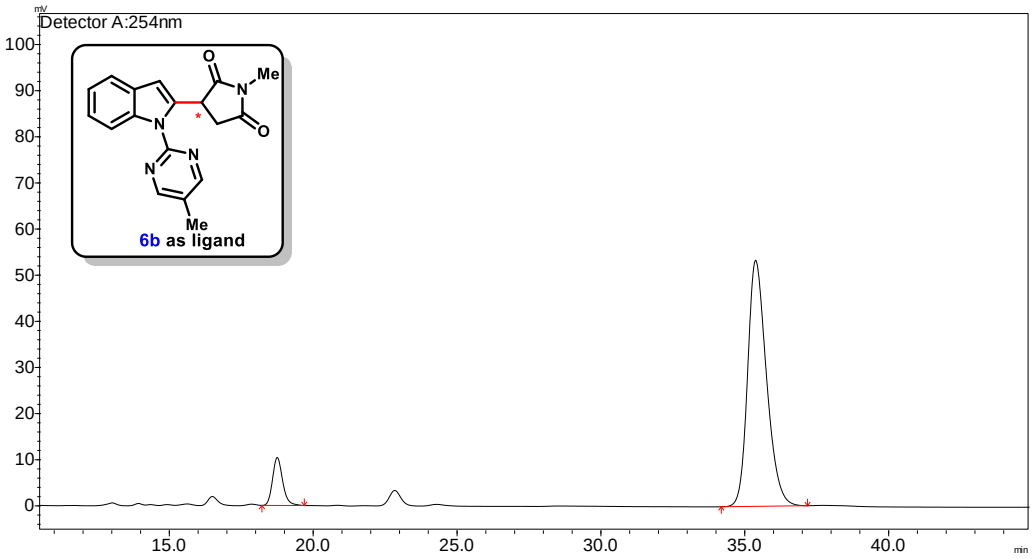


Peak #	Ret. Time	Area	Height	Area %	Height %
1	17.130	197209	7543	50.911	68.037
2	37.385	190152	3544	49.089	31.963
Total		387361	11087	100.000	100.000

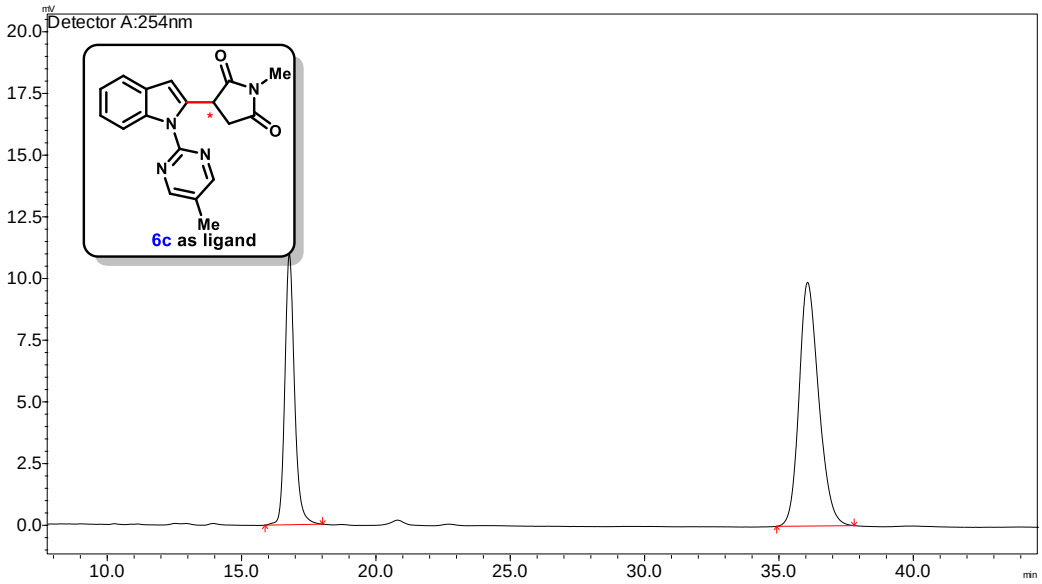


P	Ret.	Area	Height	Area %	Height

ea k #	Time				%
1	19.227	628966	19198	30.125	55.053
2	45.617	1458904	15674	69.875	44.947
Total		2087870	34872	100.000	100.000



Peak #	Ret. Time	Area	Height	Area %	Height %
1	18.746	248725	10326	9.270	16.218
2	35.375	2434312	53346	90.730	83.782
Total		2683037	63672	100.000	100.000



Peak #	Ret. Time	Area	Height	Area %	Height %
1	16.773	274479	10968	35.269	52.615
2	36.063	503764	9878	64.731	47.385
Total		778243	20846	100.000	100.000

12. X-ray Crystallography

Single crystal of compound **3e**:

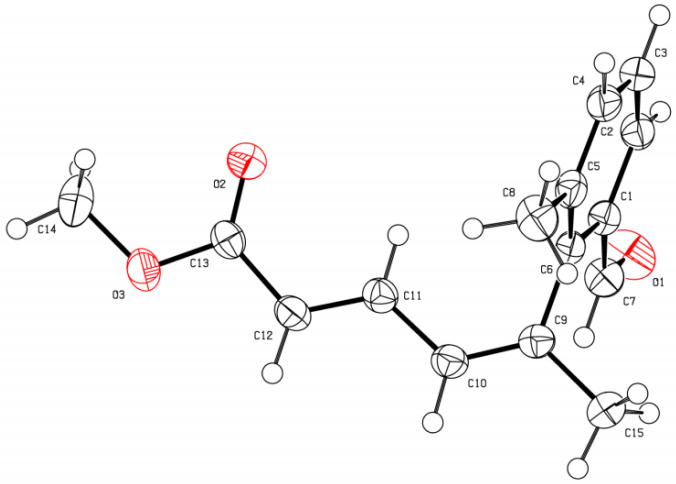


Table S5 Crystal data and structure refinement for 3e.

Empirical formula	$C_{15}H_{16}O_3$
Formula weight	244.28
Temperature/K	170.0
Crystal system	orthorhombic
Space group	$P2_12_12$
a/Å	8.8975(4)
b/Å	21.5517(9)
c/Å	6.9771(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1337.90(10)
Z	4
ρ_{calc}g/cm^3	1.213
μ/mm^{-1}	0.679
F(000)	520.0
Crystal size/mm^3	0.48 × 0.32 × 0.07
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	10.756 to 145.002
Index ranges	$-11 \leq h \leq 9$, $-20 \leq k \leq 26$, $-8 \leq l \leq 7$
Reflections collected	11542
Independent reflections	2628 [R_{int} = 0.0309, R_{sigma} = 0.0246]
Data/restraints/parameters	2628/0/166
Goodness-of-fit on F^2	1.070
Final R indexes [I>=2σ (I)]	R_1 = 0.0294, wR_2 = 0.0732
Final R indexes [all data]	R_1 = 0.0308, wR_2 = 0.0744
Largest diff. peak/hole / e Å^{-3}	0.11/-0.14
Flack parameter	-0.04(6)

Table S6. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3e. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	3276.7(17)	1601.0(6)	6478(2)	51.5(4)
O2	5389.9(15)	4233.2(6)	10909.4(18)	36.4(3)
O3	7391.1(15)	4731.4(6)	9701(2)	38.7(3)
C1	1951.7(18)	2546.7(7)	6897(2)	27.5(3)
C2	1007.2(19)	2305.1(8)	8309(2)	31.5(4)
C3	-40(2)	2681.4(9)	9175(2)	35.0(4)
C4	-160.0(19)	3299.6(8)	8636(3)	33.7(4)

C5	758.5(18)	3553.3(8)	7224(2)	29.7(4)
C6	1843.7(18)	3172.6(7)	6349(2)	25.4(3)
C7	3082(2)	2133.4(8)	6008(3)	34.0(4)
C8	580(2)	4223.1(8)	6667(3)	41.2(4)
C9	2829.6(19)	3430.1(7)	4800(2)	27.8(3)
C10	4096(2)	3743.3(8)	5190(3)	30.5(4)
C11	4595.6(19)	3888.4(7)	7113(2)	28.7(3)
C12	5811.4(19)	4227.9(8)	7541(3)	32.5(4)
C13	6139.5(19)	4385.5(7)	9543(3)	29.3(4)
C14	7769(2)	4920.3(10)	11628(3)	46.5(5)
C15	2275(2)	3334.7(9)	2796(3)	35.7(4)

Table S7. Anisotropic Displacement Parameters ($Å^2×10^3$) for 3e. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	52.7(8)	31.3(7)	70.5(10)	6.5(7)	11.5(8)	10.5(6)
O2	39.0(7)	37.3(6)	33.0(6)	2.2(5)	2.6(5)	-5.0(5)
O3	31.0(7)	40.5(7)	44.7(7)	-6.5(6)	0.2(5)	-9.0(5)
C1	27.9(8)	27.4(8)	27.2(7)	-2.2(6)	-0.9(6)	-1.7(6)
C2	32.1(9)	31.3(8)	31.0(8)	1.4(6)	-2.3(7)	-5.2(7)
C3	32.6(9)	44.1(9)	28.2(8)	-2.8(7)	2.7(7)	-8.2(7)
C4	28.5(8)	39.0(9)	33.6(8)	-11.9(7)	3.7(7)	-1.1(7)
C5	28.4(8)	28.2(8)	32.5(8)	-7.5(6)	-2.2(7)	-0.7(6)
C6	24.7(8)	26.7(7)	24.8(7)	-3.8(6)	-1.4(6)	-2.6(6)
C7	34.6(9)	30.1(8)	37.3(9)	-1.7(7)	1.8(8)	3.0(7)
C8	41.9(10)	27.6(8)	54.2(11)	-7.2(8)	4.6(9)	3.5(8)
C9	31.4(9)	25.0(7)	27.1(8)	-0.1(6)	2.0(6)	1.8(7)
C10	32.9(9)	29.9(8)	28.8(8)	1.8(6)	3.3(6)	-2.0(7)
C11	31.0(8)	25.0(7)	30.3(8)	1.1(6)	2.0(7)	-1.3(6)
C12	30.0(8)	33.4(8)	34.2(9)	1.4(7)	5.3(7)	-5.3(7)
C13	26.8(8)	24.5(7)	36.7(9)	1.0(6)	0.5(7)	-0.2(6)
C14	41.7(11)	44.7(11)	53.2(11)	-12.8(9)	-12.4(9)	-3.0(8)
C15	38.6(9)	40.2(9)	28.2(8)	-2.2(7)	-0.8(7)	-1.3(8)

Table S8. Bond Lengths for 3e.

Atom	Atom	Length/Å	Atom	Atom	Length/Å

O1	C7	1.206(2)	C4	C5	1.392(2)
O2	C13	1.209(2)	C5	C6	1.406(2)
O3	C13	1.344(2)	C5	C8	1.503(2)
O3	C14	1.445(2)	C6	C9	1.498(2)
C1	C2	1.396(2)	C9	C10	1.342(2)
C1	C6	1.405(2)	C9	C15	1.497(2)
C1	C7	1.480(2)	C10	C11	1.447(2)
C2	C3	1.375(3)	C11	C12	1.340(2)
C3	C4	1.389(3)	C12	C13	1.467(2)

Table S9. Bond Angles for 3e.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C13	O3	C14	115.13(15)	C5	C6	C9	119.94(14)
C2	C1	C6	120.60(15)	O1	C7	C1	123.78(17)
C2	C1	C7	118.73(15)	C10	C9	C6	122.12(15)
C6	C1	C7	120.67(15)	C10	C9	C15	122.37(15)
C3	C2	C1	119.87(16)	C15	C9	C6	115.47(14)
C2	C3	C4	119.94(16)	C9	C10	C11	123.69(15)
C3	C4	C5	121.56(16)	C12	C11	C10	124.92(16)
C4	C5	C6	118.77(15)	C11	C12	C13	119.96(15)
C4	C5	C8	119.85(16)	O2	C13	O3	122.91(16)
C6	C5	C8	121.38(16)	O2	C13	C12	125.32(15)
C1	C6	C5	119.25(15)	O3	C13	C12	111.76(14)
C1	C6	C9	120.77(14)				

Table S10. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3e.

Atom	*x*	*y*	*z*	U(eq)
H2	1087.66	1881.46	8671.7	38
H3	-680.4	2518.63	10141.81	42
H4	-886.37	3555.5	9245.42	40
H7	3689.99	2296.97	5008.76	41
H8A	1480.27	4454.75	7043.62	62
H8B	-300.01	4397.62	7318.75	62
H8C	441.66	4253.62	5277.03	62
H10	4699.46	3877.36	4145.86	37

H11	4017.61	3731.05	8149.74	34
H12	6460.75	4366.46	6548.68	39
H14A	8648.92	5193.48	11595.61	70
H14B	7996.51	4552.72	12402.64	70
H14C	6917.06	5142.85	12194.71	70
H15A	2212.63	2889.28	2525.53	53
H15B	2973.14	3530.24	1892.59	53
H15C	1277.88	3522.22	2658.56	53