Supporting Information

For the article entitled

Access toward axially chirality by asymmetric alpha C-H alkenylations of aryl alkenes

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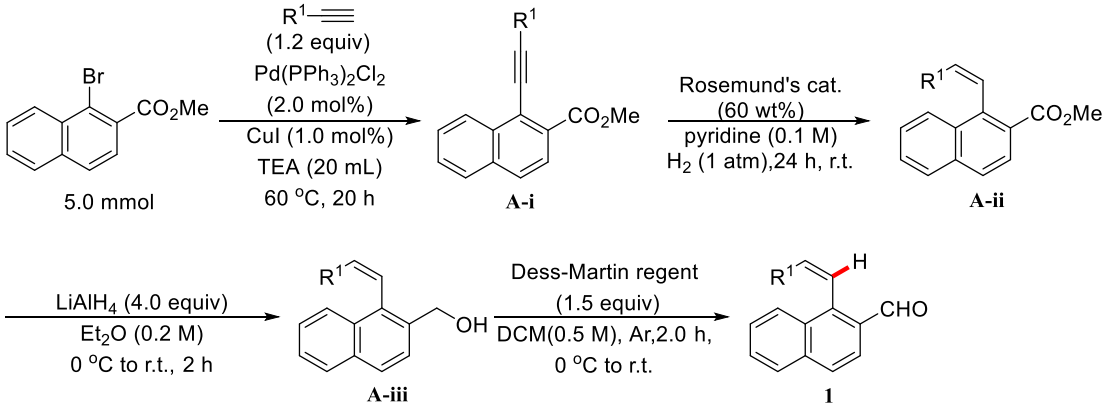
1.General Methods

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



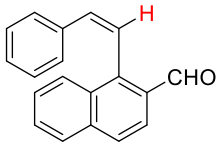
Alkynylation Reaction:[1] A solution of $Pd(PPh_3)_2Cl_2$ (1.0 mol%), CuI (1.0 mol%), methyl 2-bromobenzoate (5.0 mmol) and ethynylbenzene (6.0 mmol) in TEA (0.4 M) was stirred at 60 °C overnight, then cooled to rt and diluted with H_2O (20 mL) followed by extraction with EtOAc (30 mL × 3). The solvent was removed in vacuo, and the crud product was purified by silica gel chromatography (SiO_2, PE/EA) to obtain the corresponding product (**A-i)**.

Hydrogenation Reaction: Following a slight modification from a previously reported procedure, a solution of alkyne (**A-i)** (3.9 mmol, 1.0 equiv) in pyridine (39 mL) was vacuum purged three times, backfilling with N_2. Rosemund's catalyst (5% Pd on $BaSO_4$) 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 (monitored by TLC). The reaction was vacuum purged and backfilled with N_2, upon which the reaction was filtered through Celite, rinsing with EtOAc (200 mL). The organic solution was concentrated in vacuo to give an orange oil, which was dissolved in 50 mL EtOAc. The organic solution was washed with HCl (2 M, 30 mL × 2), water (50 mL), and brine (50 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 olefin (**A-ii)**

General Procedure for Ester Reduction:[2] To a solution of substituted ester **(A-ii)** 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., and 2 M HCl was added slowly until a clear solution was obtained. The Et_2O layer was separated and the aqueous phase was extracted with Et_2O (20 mL × 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 EtOAc and the resulting alcohol **(A-iii)** was used for the next step without further purification.

General Procedure for Aldehyde Preparation: To a solution of Dess-Martin reagent (1.5 equiv) in DCM (0.5 M) was added in dropwise substituted alcohol **(A-iii)** at 0°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 = 10 / 1) afforded aldehyde (**1)**.



(*Z*)-1-styryl-2-naphthaldehyde (1a)

Following the general procedure A, **1a** was obtained as a light yellow solid (0.72 g, 56% yield for four steps, m.p. = 67.3 °C).

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

δ 10.41 (s, 1H), 8.25 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.66 – 7.63 (m, 1H), 7.56 – 7.53 (m, 1H), 7.18 (d, *J* = 12.0 Hz, 1H), 7.08 – 7.01 (m, 4H), 6.88 – 6.86 (m, 2H).

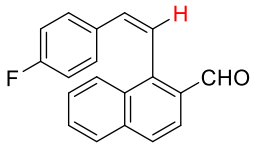
^{13}C NMR (125 MHz, $CDCl_3$)

δ 191.38, 141.32, 135.20, 135.18, 134.32, 130.21, 128.84, 128.10, 127.96, 127.56, 127.39, 127.19, 126.85, 126.07, 125.35, 122.13, 121.55.

HRMS (ESI) for $C_{19}H_{14}OK$ $[M+ K]^+$: 297.0676, found: 297.0664.

FTIR (KBr, cm^{-1})

3417.41, 2959.61, 1680.32, 1653.25, 1630.84, 1406.24, 1386.22, 1269.10, 1030.55.



(*Z*)-1-(4-fluorostyryl)-2-naphthaldehyde (1f)

Following the procedure A, **1f** was obtained as a yellow solid (0.80 g, 58% yield for four steps, m.p. =115.2 ^oC).

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

δ 10.39 (s, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.6 Hz, 1H), 7.89 (dd, *J* = 16.6, 8.4 Hz, 2H), 7.64 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 7.54 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.13 (d, *J* = 12.4 Hz, 1H), 7.05 (d, *J* = 12.4 Hz, 1H), 6.86 – 6.81 (m, 2H), 6.71 (t, *J* = 8.7 Hz, 2H).

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

δ 191.25, 161.01 (d, J_{CF} = 246.3 Hz), 140.94, 135.23, 133.95, 130.51 (d, J_{CF} = 3.8 Hz), 130.11, 129.66 (d, J_{CF} = 7.5 Hz), 128.90, 128.19, 127.63, 127.34, 126.17, 125.24, 121.95 (d, J_{CF} = 2.5 Hz), 121.61, 114.45 (d, J_{CF} = 21.3 Hz).

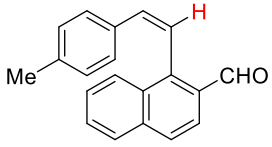
^{19}F NMR (471 MHz, $CDCl_3$)

δ-112.92

HRMS (ESI) for $C_{19}H_{13}OFNa$ $[M+ Na]^+$: 299.0843, found: 299.0829.

FTIR (KBr, cm^{-1})

3282.24, 3262.62, 2357.01, 1656.07, 1510.28, 1459.81.



(*Z*)-1-(4-methylstyryl)-2-naphthaldehyde (1g)

Following the procedure A, **1g** was obtained as a yellow solid (0.85 g, 63% yield for four

steps, m.p. = 114.2 °C).

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

δ 10.40 (s, 1H), 8.25 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.66 – 7.63 (m, 1H), 7.56 – 7.53 (m, 1H), 7.14 (d, *J* = 12.5 Hz, 1H), 7.00 (d, *J* = 12.5 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 8.0 Hz, 2H), 2.17 (s, 3H).

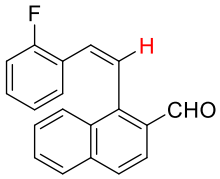
^{13}C NMR (125 MHz, $CDCl_3$)

δ 191.57, 141.67, 136.79, 135.22, 135.07, 131.50, 130.28, 128.82, 128.12, 128.07, 127.92, 127.53, 127.09, 126.03, 125.40, 121.52, 121.06, 20.09.

HRMS (ESI) for $C_{20}H_{16}ONa$ $[M+ Na]^+$: 295.1093, found: 295.1084.

FTIR (KBr, cm^{-1})

3287.85, 3226.17, 2354.21, 1653.27, 1636.45, 1504.67, 1454.21.



(*Z*)-1-(2-fluorostyryl)-2-naphthaldehyde (1h)

Following the procedure A, **1h** was obtained as a yellow solid (1.10 g, 80% yield for four steps, m.p. = 87.2 °C).

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

δ 10.38 (s, 1H), 8.22 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.66 – 7.62 (m, 1H), 7.57 – 7.54 (m, 1H), 7.37 (d, *J* = 12.5 Hz, 1H), 7.21 (d, *J* = 12.5 Hz, 1H), 7.06 – 7.02 (m, 1H), 6.97 – 6.93 (m, 1H), 6.60 – 6.57 (m, 1H), 6.50 (td, *J* = 8.0,2.0 Hz, 1H).

^{1}H NMR (500 MHz, Chloroform-*d*)

δ 10.37 (s, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 7.92 (d, *J* = 8.6 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.63 (ddd, *J* = 8.1, 6.9, 1.1

Hz, 1H), 7.55 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.36 (d, *J* = 12.3 Hz, 1H), 7.20 (d, *J* = 12.4 Hz, 1H), 7.06 – 7.01 (m, 1H), 6.97 – 6.91 (m, 1H), 6.58 (t, *J* = 8.0 Hz, 1H), 6.49 (td, *J* = 7.7, 1.6 Hz, 1H).

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

δ 191.08, 159.48(d, J_{CF} = 247.5 Hz), 140.55, 135.08, 130.15, 128.98, 128.60 (d, J_{CF} = 8.8Hz), 128.41 (d, J_{CF} = 2.5Hz), 128.08, 127.64 (d, J_{CF} = 6.3Hz), 127.45, 127.33, 126.14, 125.17, 124.11 (d, J_{CF} = 1.3Hz), 122.70 (d, J_{CF} = 3.8Hz), 122.22, 122.12, 121.56, 114.60 (d, J_{CF} = 21.3Hz).

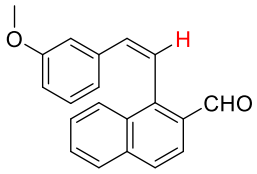
^{19}F NMR (471 MHz, $CDCl_3$)

δ -115.97.

HRMS (ESI) for $C_{19}H_{13}OFNa$ $[M+ Na]^+$: 299.0843, found: 299.0832.

FTIR (KBr, cm^{-1})

3170.09, 2351.40, 1681.31, 1647.66, 1454.21.



(*Z*)-1-(3-methoxystyryl)-2-naphthaldehyde (1i)

Following the procedure A, **1i** was obtained as a yellow oil (1.28 g, 89% yield for four steps).

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

δ 10.42 (s, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.6 Hz, 1H), 7.87 (dd, *J* = 16.1, 8.5 Hz, 2H), 7.65 – 7.61 (m, 1H), 7.53 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.13 (d, *J* = 12.4 Hz, 1H), 7.06 (d, *J* = 12.4 Hz, 1H), 6.96 (t, *J* = 8.0 Hz, 1H), 6.60 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.51 (d, *J* = 7.7 Hz, 1H), 6.36 – 6.32 (m, 1H), 3.32 (s, 3H).

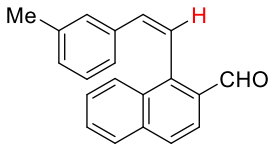
^{13}C NMR (125 MHz, $CDCl_3$)

δ 191.30, 158.22, 141.40, 135.57, 135.14, 135.01, 130.18, 128.95, 128.35, 128.12, 127.49, 127.15, 126.12, 125.39, 122.34, 121.48, 120.74, 113.21, 112.54, 53.63.

HRMS (ESI) for $C_{20}H_{16}O_2Na$ $[M+ Na]^+$: 311.1043, found: 311.1038.

FTIR (KBr, cm^{-1})

3242.99, 2354.21, 1650.47, 1636.45, 1499.07.



(*Z*)-1-(3-methylstyryl)-2-naphthaldehyde (1j)

Following the procedure A, **1j** was obtained as a yellow solid (1.07 g, 79% yield for four steps, m.p. = 70.6 °C).

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

δ 10.39 (s, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.6 Hz, 1H), 7.86 (dd, *J* = 17.4, 8.4 Hz, 2H), 7.62 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 7.52 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.12 (d, *J* = 12.4 Hz, 1H), 7.01 (d, *J* = 12.4 Hz, 1H), 6.87 – 6.84 (m, 2H), 6.74 (s, 1H), 6.60 – 6.55 (m, 1H), 2.07 (s, 3H).

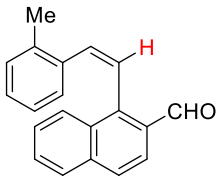
^{13}C NMR (125 MHz, $CDCl_3$)

δ 191.47, 141.52, 136.91, 135.30, 135.18, 134.23, 130.26, 129.04, 128.84, 128.06, 127.64, 127.52, 127.21, 127.12, 126.04, 125.38, 124.79, 121.87, 121.49, 20.20.

HRMS (ESI) for $C_{20}H_{16}ONa$ $[M+ Na]^+$: 295.1093, found: 295.1084.

FTIR (KBr, cm^{-1})

3240.19, 2351.40, 1684.11, 1619.63, 1459.81



(*Z*)-1-(2-methylstyryl)-2-naphthaldehyde (1k)

Following the procedure A, **1k** was obtained as a yellow solid (0.72 g, 53% yield for four steps, m.p. =111.8 ^{o}C).

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

δ 10.26 (s, 1H), 8.26 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.65 – 7.62 (m, 1H), 7.59 – 7.56 (m, 1H), 7.34 (d, *J* = 12.0 Hz, 1H), 7.17 (d, *J* = 12.0 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 6.96 (td, *J* = 7.5, 1.5 Hz, 1H), 6.63 (d, *J* = 15.0 Hz, 1H), 6.46 (d, *J* = 7.5 Hz, 1H), 2.38 (s, 3H).

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

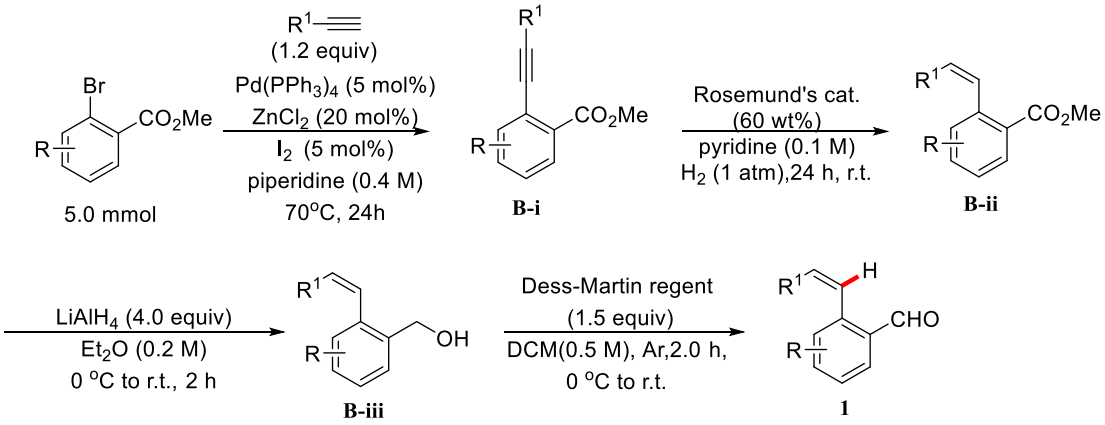
δ 191.04, 140.66, 135.46, 134.97, 134.39, 133.12, 130.67, 129.32, 129.05, 127.89, 127.76, 127.58, 126.97, 126.80, 125.99, 125.10, 124.51, 122.58, 121.57, 18.92.

HRMS (ESI) for $C_{20}H_{16}ONa$ $[M+ Na]^{+}$: 295.1093, found: 295.1083.

FTIR (KBr, cm^{-1})

3217.67, 2358.71, 1736.70, 1680.15, 1456.66.

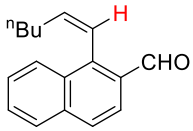
2.2 General Procedure B for Substrate Synthesis



Alkynylation Reaction： A solution of $Pd(PPh_3)_4$ (5.0 mol%), I_2 (1.0 mol%), $ZnCl_2$ (20.0 mol%), methyl 1-bromo-2-naphthoate (5.00 mmol) and ethynylbenzene (6.00 mmol) in piperidine (0.4 M) was stirred at 70 °C overnight, 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) to obtain the corresponding product **B-i**.

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



(*Z*)-1-(hex-1-en-1-yl)-2-naphthaldehyde (1l)

Following the procedure B, **1i** was obtained as a yellow oil (0.2 g, 17% yield for four steps).

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

δ 10.44 (s, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.65 – 7.62 (m, 1H), 7.58 – 7.54 (m, 1H), 6.87 (d, *J* = 11.5 Hz, 1H), 6.28 (dt, *J* = 11.5, 7.5 Hz, 1H), 1.84 (qd, J = 7.5, 1.5 Hz, 2H), 1.33 – 1.26 (m, 2H), 1.19 – 1.11 (m, 2H), 0.72 (t, *J* = 7.5 Hz, 3H).

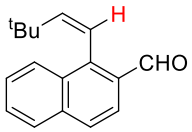
^{13}C NMR (125 MHz, $CDCl_3$)

δ 192.04, 141.29, 137.90, 135.03, 130.71, 129.77, 127.82, 127.38, 126.79, 125.67, 125.65, 121.31, 121.09, 29.95, 27.66, 21.17, 12.72.

HRMS (ESI) for $C_{17}H_{18}ONa$ $[M+ Na]^+$: 261.1250, found: 261.1252.

FTIR (KBr, cm^{-1})

3251.40, 3228.97, 2928.97, 1653.27, 1633.64, 1403.74.



(*Z*)-1-(3,3-dimethylbut-1-en-1-yl)-2-naphthaldehyde (1m)

Following the procedure B , **1j** was obtained as a yellow solid (0.8 g, 58% yield for four steps， m.p. = 46.9 °C).

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

δ 10.60 (s, 1H), 8.21 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.63 – 7.60 (m, 1H), 7.58 – 7.55 (m, 1H), 6.64 (d, *J* = 13.0 Hz, 1H), 6.16 (d, *J* = 13.0 Hz, 1H), 0.82 (s, 9H).

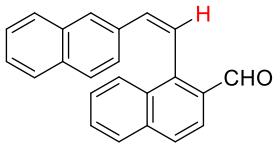
^{13}C NMR (125 MHz, $CDCl_3$)

δ 192.18, 146.01, 143.07, 134.85, 130.98, 129.57, 127.82, 127.29, 126.62, 126.40, 125.61, 120.80, 117.91, 33.96, 28.93.

HRMS (ESI) for $C_{17}H_{18}ONa$ $[M+ Na]^+$: 261.1250, found: 261.1258.

FTIR (KBr, cm^{-1})

3258.05, 223.36, 2354.21, 1681.31, 1650.47, 1398.13.



(*Z*)-1-(2-(naphthalen-2-yl)vinyl)-2-naphthaldehyde (1n)

Following the procedure B, **1k** was obtained as a white solid (1.1 g, 71% yield for four steps，m.p. = 156.3 °C).

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

δ 10.45 (s, 1H), 8.29 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.94 – 7.90 (m, 2H), 7.67 – 7.61 (m, 2H), 7.56 – 7.53 (m, 2H), 7.49 (s, 1H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.37 – 7.34 (m, 2H), 7.33 (s, 1H), 7.16 (d, *J* = 12.5 Hz, 1H), 6.82 (dd, *J* = 8.5, 1.5 Hz, 1H).

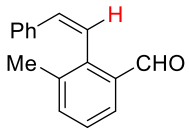
^{13}C NMR (125 MHz, $CDCl_3$)

δ 191.36, 141.37, 135.24, 135.21, 132.15, 131.99, 131.63, 130.28, 129.07, 128.22, 128.14, 127.59, 127.29, 127.03, 126.90, 126.46, 126.14, 125.43, 125.32, 125.12, 124.80, 122.38, 121.59.

HRMS (ESI) for $C_{23}H_{16}ONa$ $[M+ Na]^+$: 331.1093, found: 331.1083.

FTIR (KBr, cm^{-1})

3247.29, 2356.02, 1688.23, 1639.76, 1400.11.



(*Z*)-3-methyl-2-styrylbenzaldehyde (1o)

Following the procedure B, **1l** was obtained as a colorless oil (0.3 g, 27% yield for four steps).

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

δ 10.20 (s, 1H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.13 – 7.10 (m, 3H), 6.94 – 6.87 (m, 3H), 6.73 (d, *J* = 12.5 Hz, 1H), 2.28 (s, 3H).

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

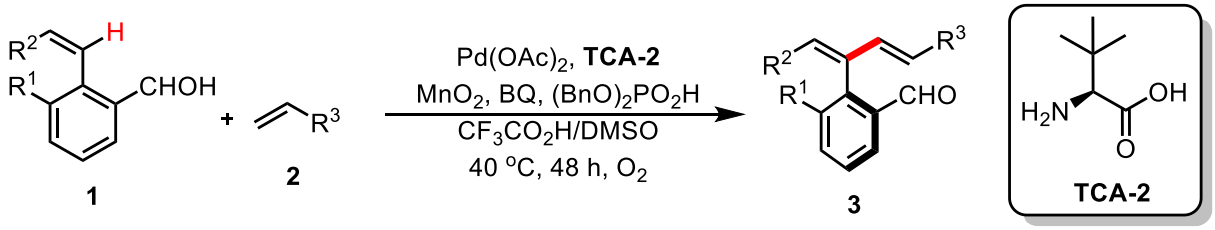
δ 191.56, 139.90, 136.22, 134.85, 134.72, 133.10, 132.10, 127.68, 127.39, 126.70, 126.54, 124.63, 123.73, 18.62.

HRMS (ESI) for $C_{16}H_{14}ONa$ $[M+ Na]^+$: 245.0937, found: 245.0928.

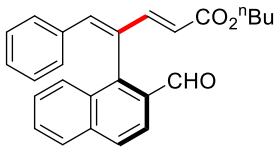
FTIR (KBr, cm^{-1})

3279.44, 2354.21, 1653.27, 1560.75, 1462.62.

3. General Procedure for Atroposelective α-C-H Alkenylation



A screw-cap vial was charged with $Pd(OAc)_2$ (15 mol%, 0.015 mmol), **TCA-2** (45 mol%, 0.045 mmol), MnO_2 (1.5 equiv, 0.15 mmol), BQ (1.0 equiv, 0.1 mmol), $(BnO)_2PO_2H$ (2.0 equiv, 0.1 mmol), CF_3CO_2H (0.5 mL), DMSO (0.5 mL). Then, 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 (2*E*,4*Z*)-4-(2-formylnaphthalen-1-yl)-5-phenylpenta-2,4-dienoate (3a)

Following the general procedure, **3a** was obtained as a light yellow oil (30.2 mg, 78% yield, 93% *ee*).

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

δ 10.11 (s, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.97 – 7.94 (m, 2H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.65 –7.62 (m, 1H), 7.49 – 7.46 (m, 2H), 7.11 – 7.08 (m, 1H), 7.01(t, *J* = 7.5 Hz, 2H), 6.74 (d, *J* = 7.5 Hz, 2H), 5.14 (d, *J* = 15.5 Hz, 1H), 4.12 – 4.03 (m, 2H), 1.60 – 1.54 (m, 2H), 1.37 – 1.29 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H).

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

δ 190.66, 165.78, 148.23, 141.50, 140.30, 135.55, 133.49, 131.32, 129.84, 129.48, 128.78, 128.43, 128.23, 128.09, 127.65, 127.59, 126.74, 125.21, 121.61, 120.56, 63.47, 29.61, 18.07, 12.65.

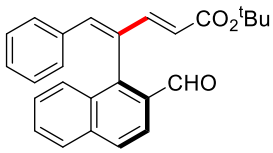
HRMS (ESI) for $C_{26}H_{24}O_3Na$ $[M+ Na]^+$: 407.1618, found: 407.1613.

FTIR (KBr, cm^{-1})

3442.06, 3383.18, 2957.01, 2354.21, 1689.72, 1656.07, 1636.45, 1557.94, 1541.12, 1510.28, 1406.54, 1398.13, 1033.64.

Opt. Rot. $[\alpha]^{20}D$ = -101.9 (c = 0.8, $CHCl_3$)

HPLC Daicel Chiralpak IA-H column, n-hexane/i-PrOH (98/2), 0.5 mL/min, 254 nm, 15.526 min (major enantiomer), 16.693 min (minor enantiomer)..



tert-Butyl (2*E*,4*Z*)-4-(2-formylnaphthalen-1-yl)-5-phenylpenta-

2,4-dienoate (3b)

Following the general procedure, **3b** was obtained as a yellow oil (26.8 mg, 70% yield, 89% *ee*).

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

δ 10.11 (s, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.94 (dd, *J* = 11.5, 8.5 Hz, 2H), 7.86 (d, *J* = 15.5 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.44 (s, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 2H), 6.73 (d, *J* = 7.5 Hz, 2H), 5.06 (d, *J* = 15.5 Hz, 1H), 1.42 (s, 9H).

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

δ 190.82, 165.00, 147.37, 140.95, 140.57, 135.54, 133.60, 131.40, 129.87, 129.47, 128.70, 128.40, 128.14, 127.94, 127.61, 127.56, 126.70, 125.32, 122.50, 121.56, 79.68, 27.03.

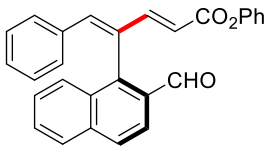
HRMS (ESI) for $C_{26}H_{24}O_3Na$ $[M+ Na]^+$: 407.1618, found: 407.1609.

FTIR (KBr, cm^{-1})

3321.50, 2914.95, 2359.81, 2320.56, 1667.29, 1625.34, 1459.81.

Opt. Rot. $[\alpha]^{20}D$ = -125.2 (c = 0.43, $CHCl_3$)

HPLC Daicel Chiralpak IA-H column, n-hexane/i-PrOH (98/2), 1.0 mL/min, 254 nm, 13.283 min (major enantiomer), 14.281 min (minor enantiomer).



Phenyl (2*E*,4*Z*)-4-(2-formylnaphthalen-1-yl)-5-phenylpenta-2,4-dienoate (3c)

Following the general procedure, **3c** was obtained as a white oil (37.1 mg, 92% yield, 89% *ee*).

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

δ 10.17 (s, 1H), 8.14 (d, *J* = 12.5 Hz, 1H), 8.12 (d, *J* = 6.0 Hz, 1H) 8.04 (d, *J* = 8.5 Hz, 1H), 7.97 (t, *J* = 8.5 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.55 (s, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.06 – 7.02 (m, 4H), 6.78 (d, *J* = 8.0 Hz, 2H), 5.32 (d, *J* = 15.5 Hz, 1H).

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

δ 190.57, 164.10, 150.04, 149.54, 142.50, 139.99, 135.60, 133.36, 131.21, 129.79, 129.52, 128.95, 128.54, 128.39, 128.37, 127.75, 127.67, 126.88, 125.14, 124.76, 121.71, 120.44, 119.50.

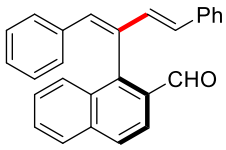
HRMS (ESI) for $C_{28}H_{20}O_3K$ $[M+K]^+$: 443.1044, found: 443.1050.

FTIR (KBr, cm^{-1})

3848.60, 3744.86, 3624.30, 3565.42, 3442.06, 3419.63, 2357.01, 1734.58, 1686.92, 1656.07, 1557.94, 1538.32, 1504.67, 1403.74, 1019.63, 806.54.

Opt. Rot. $[\alpha]^{20}D$ = -83.8 (c = 1.0, $CHCl_3$)

HPLC Daicel Chiralpak IA-H column, n-hexane/i-PrOH (95/5), 1.0 mL/min, 254 nm, 12.395 min (major enantiomer), 13.416 min (minor enantiomer).



1-((1*Z*,3*E*)-1,4-Diphenylbuta-1,3-dien-2-yl)-2-naphthaldehyde (3d)

Following the general procedure, **3d** was obtained as a yellow oil (25.3 mg, 71% yield, 94% *ee*).

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

δ 10.19 (s, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.27 – 7.16 (m, 6H), 7.20 – 7.16 (m, 1H), 7.03 –

6.96 (m, 3H), 6.68 (d, *J* = 7.5 Hz, 2H), 5.79 (d, *J* = 16.0 Hz, 1H).

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

δ 191.40, 142.04, 135.66, 135.49, 134.97, 134.54, 133.46, 133.38, 131.78, 130.33, 129.64, 128.25, 128.01, 127.80, 127.56, 127.48, 127.38, 126.89, 126.69, 126.49, 125.72, 125.50, 121.45.

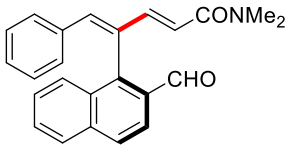
HRMS (ESI) for $C_{27}H_{20}OK$ $[M+K]^+$: 399.1146, found: 399.1145.

FTIR (KBr, cm^{-1})

3245.79, 2359.81, 1698.13, 1650.47, 1541.12, 1451.40.

Opt. Rot. $[\alpha]^{20}D$ = -25.7 (c = 0.16, $CHCl_3$)

HPLC Daicel Chiralpak IA-H column, n-hexane/i-PrOH (98/2), 1.0 mL/min, 254 nm, 13.965 min (major enantiomer), 16.944 min (minor enantiomer).



(2*E*,4*Z*)-4-(2-Formylnaphthalen-1-yl)-N,N-dimethyl-5-phenylpenta-2,4-dienamide (3e)

Following the general procedure, **3e** was obtained as a light yellow solid (31.9 mg, 90% yield, 88% *ee*, m.p. = 54.0 °C).

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

δ 10.12 (s, 1H), 8.09 (d, *J* = 9.0 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.96 (s, 1H), 7.94 (d, *J* = 9.0 Hz, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.49 – 7.46 (m, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 2H), 6.73 (d, *J* = 8.0 Hz, 2H), 5.56 (d, *J* = 15.0 Hz, 1H), 2.92 (s, 3H), 2.61 (s, 3H).

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

δ 190.96, 165.26, 146.19, 141.04, 140.32, 135.46, 133.76, 131.62, 129.93, 129.49, 128.61, 128.42, 128.05, 127.72, 127.54, 127.52, 126.67, 125.51, 121.46, 120.08, 36.03, 34.71.

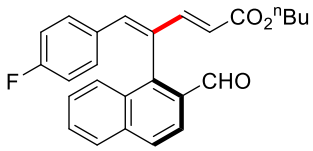
HRMS (ESI) for $C_{24}H_{21}NO_2K$ $[M+K]^+$: 394.1204, found: 394.1201.

FTIR (KBr, cm^{-1})

3851.40, 3739.25, 3649.53, 3629.91, 3565.42, 2348.60, 1737.38, 1684.11, 1650.47, 1563.55, 1541.12, 1510.28, 1398.13, 1386.92, 1028.04.

Opt. Rot. $[\alpha]^{20}D$ = -72.7 (c = 1.0, $CHCl_3$)

HPLC Daicel Chiralpak OD-H column, n-hexane/i-PrOH (90/10), 1.0 mL/min, 254 nm, 16.816 min (major enantiomer), 19.483 min (minor enantiomer).



Butyl (2*E*,4*Z*)-5-(4-fluorophenyl)-4-(2-formylnaphthalen-1-yl) penta-2,4-dienoate (3f)

Following the general procedure, **3f** was obtained as a light yellow oil (36.5 mg, 91% yield, 94% *ee*).

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

δ 10.10 (s, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.97 – 7.92 (m, 2H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.67 – 7.64 (m, 1H), 7.51 – 7.47 (m, 1H), 7.44 (s, 1H), 6.72 (s, 2H), 6.71 (d, *J* = 1.5 Hz, 2H), 5.14 (d, *J* = 15.5 Hz, 1H), 4.12 – 4.04 (m, 2H), 1.59 – 1.54 (m, 2H), 1.37 – 1.29 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H).

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

δ 190.52, 165.74, 161.72(d, J_{CF} = 251.3 Hz), 148.01, 139.97(d, J_{CF} = 12.5 Hz), 131.01(d, J_{CF} = 2.5 Hz), 130.59(d, J_{CF} = 7.5 Hz), 129.79(d,

J_{CF} = 2.5 Hz), 129.73, 129.54, 128.45(d, J_{CF} = 21.3 Hz), 127.73, 126.85, 125.06, 121.67, 120.62, 114.89, 114.71, 63.50, 29.60, 18.07, 12.64.

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

δ -110.32.

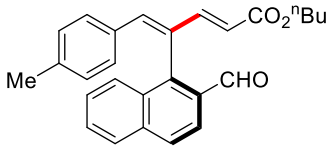
HRMS (ESI) for $C_{26}H_{23}FO_3Na$ $[M+ Na]^+$: 425.1523, found: 425.1501.

FTIR (KBr, cm^{-1})

3226.17, 2357.01, 1656.07, 1636.45, 1457.01, 1389.72.

Opt. Rot. $[\alpha]^{20}D$ = -352.9 (c = 0.12, $CHCl_3$)

HPLC Daicel Chiralpak IA-H column, n-hexane/i-PrOH (98/2), 1.0 mL/min, 254 nm, 17.686 min (major enantiomer), 19.934 min (minor enantiomer).



Butyl (2*E*,4*Z*)-4-(2-formylnaphthalen-1-yl)-5-(p-tolyl)penta -2,4-dienoate (3g)

Following the general procedure and extending the reaction time to 96 hours, **3g** was obtained as a yellow oil (32.7 mg, 82% yield, 83% *ee*).

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

δ 10.10 (s, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 4.0 Hz, 1H), 7.94 (d, *J* = 3.0 Hz, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.65 – 7.62 (m, 1H), 7.48 – 7.47 (m, 1H), 6.82 (d, *J* = 8.0 Hz, 2H), 6.63 (d, *J* = 8.0 Hz, 2H), 5.11 (d, *J* = 15.5 Hz, 1H), 4.10 – 4.04 (m, 2H), 2.16 (s, 3H), 1.59 – 1.53 (m, 2H), 1.35 – 1.31 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H).

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

δ 190.80, 165.89, 148.46, 141.61, 140.61, 138.52, 135.57, 130.77, 130.24, 129.85, 129.48, 128.83, 128.40, 128.38, 128.14, 127.62, 126.69, 125.23, 121.58, 119.93, 63.41, 29.62, 20.17, 18.07, 12.65.

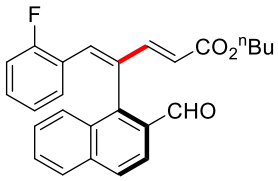
HRMS (ESI) for $C_{27}H_{26}O_3Na$ $[M+ Na]^+$: 421.1774, found: 421.1762.

FTIR (KBr, cm^{-1})

3259.81, 2357.01, 1656.07, 1636.45, 1400.93.

Opt. Rot. $[\alpha]^{20}D$ = -81.9 (c = 0.498, $CHCl_3$)

HPLC Daicel Chiralpak IA-H column, n-hexane/i-PrOH (99/1), 1.0 mL/min, 254 nm, 21.062 min (major enantiomer), 23.744 min (minor enantiomer).



Butyl (2*E*,4*Z*)-5-(2-fluorophenyl)-4-(2-formylnaphthalen-1-yl)penta-2,4-dienoate (3h)

Following the general procedure and extending the reaction time to 72 hours, **3h** was obtained as a light yellow oil (31.0 mg, 77% yield, 99% *ee*).

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

δ 10.12 (s, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 8.01 – 7.97 (m, 2H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.76 (s, 1H), 7.66 –7.63 (m, 1H), 7.52 –7.49 (m, 1H), 7.09 –7.05 (m, 1H), 7.00 –6.96 (m, 1H), 6.51 (t, *J* = 7.5 Hz, 1H), 6.16 (td, *J* = 8.0, 1.5 Hz, 1H), 5.18 (d, *J* = 15.5 Hz, 1H), 4.13 – 4.05 (m, 2H), 1.60 – 1.55 (m, 2H), 1.37 – 1.30 (m, 2H), 0.90 (t, *J* = 7.5 Hz, 3H).

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

δ 190.49, 165.62, 160.08(d, J_{CF} = 251.3 Hz), 147.83, 139.79, 135.46, 132.90(d, J_{CF} = 2.5 Hz), 132.32(d, J_{CF} = 6.3 Hz), 129.81, 129.72,

129.65, 129.58, 128.47, 128.35, 127.70, 127.49(d, J_{CF} = 2.5 Hz), 126.84, 125.16, 122.97(d, J_{CF} = 3.8 Hz), 121.60, 121.36, 114.65(d, J_{CF} = 21.3 Hz), 63.56, 29.60, 18.08, 12.65.

^{19}F NMR (471 MHz, $CDCl_3$) δ -114.98.

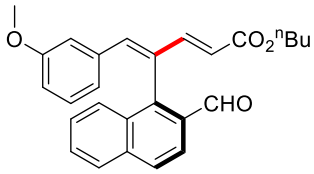
HRMS (ESI) for $C_{26}H_{23}FO_3Na$ $[M+ Na]^+$: 425.1523, found: 425.1554.

FTIR (KBr, cm^{-1})

3217.76, 2357.01, 1658.88, 1636.45, 1462.6, 1162.62.

Opt. Rot. $[\alpha]^{20}D$ = -77.8 (c = 0.512, $CHCl_3$)

HPLC Daicel Chiralpak IA-H column, n-hexane/i-PrOH (99/1), 1.0 mL/min, 254 nm, 15.198 min (major enantiomer), 17.346 min (minor enantiomer).



Butyl (2*E*,4*Z*)-4-(2-formylnaphthalen-1-yl)-5-(3-methoxyphenyl)penta-2,4-dienoate (3i)

Following the general procedure, **3i** was obtained as a yellow oil (37.2 mg, 90% yield, 87% *ee*).

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

δ 10.11 (s, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 9.5 Hz, 1H), 7.94 – 7.92 (m, 2H), 7.66 – 7.63 (m, 1H), 7.51 – 7.45 (m, 1H), 7.45 (s, 1H), 6.98 (t, *J* = 16.0 Hz, 1H), 6.65 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.51 (d, *J* = 7.5 Hz, 1H), 6.11 – 6.10 (m, 1H), 5.18 (d, *J* = 15.5 Hz, 1H), 4.12 – 4.04 (m, 2H), 3.19 (s, 3H), 1.60 – 1.54 (m, 2H), 1.37 – 1.30 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H).

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

δ 190.61, 165.76, 158.25, 148.11, 141.34, 140.38, 135.51, 134.70, 131.49, 129.95, 129.58, 128.51, 128.15, 127.57, 126.84, 125.27, 122.14, 121.63, 120.71, 115.09, 112.28, 63.49, 53.50, 29.61, 18.08, 12.65.

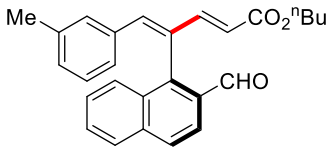
HRMS (ESI) for $C_{27}H_{26}O_4Na$ $[M+ Na]^+$: 437.1723, found: 437.1701.

FTIR (KBr, cm^{-1})

3234.58, 2357.01, 1650.47, 1633.64, 1392.52.

Opt. Rot. $[\alpha]^{20}D$ = -130.9 (c = 0.498, $CHCl_3$)

HPLC Daicel Chiralpak IC-H column, n-hexane/i-PrOH (90/10), 1.0 mL/min, 254 nm, 19.065 min (major enantiomer), 27.883 min (minor enantiomer).



Butyl (2*E*,4*Z*)-4-(2-formylnaphthalen-1-yl)-5-(m-tolyl)penta -2,4-dienoate (3j)

Following the general procedure, **3j** was obtained as a yellow oil (31.7 mg, 80% yield, 89% *ee*).

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

δ 10.10 (s, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.97 – 7.94 (m, 2H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.65 – 7.62 (m, 1H), 7.49 – 7.46 (m, 1H), 7.44 (s, 1H), 6.91 (d, *J* = 7.5 Hz, 1H), 6.85 (t, *J* = 7.5 Hz, 1H), 6.63 (s, 1H), 6.43 (d, *J* = 8.0 Hz, 1H), 5.14 (d, *J* = 15.5 Hz, 1H), 4.12 – 4.03 (m, 2H), 2.05 (s, 3H), 1.60 – 1.54 (m, 2H), 1.37 – 1.29 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H).

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

δ 190.74, 165.85, 148.33, 141.75, 140.51, 137.09, 135.53, 133.43, 131.11, 130.08, 129.88, 129.48, 128.93, 128.39, 128.12, 127.59, 127.44,

126.70, 125.52, 125.24, 121.55, 120.35, 63.45, 29.61, 20.15, 18.07, 12.65.

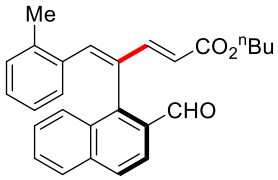
HRMS (ESI) for $C_{27}H_{26}O_3Na$ $[M+ Na]^+$: 421.1774, found: 421.1759.

FTIR (KBr, cm^{-1})

3320.56, 2357.01, 1650.47, 1633.64, 1395.33.

Opt. Rot. $[\alpha]^{20}D$ = -143.8 (c = 0.44, $CHCl_3$)

HPLC Daicel Chiralpak IA-H column, n-hexane/i-PrOH (98/2), 1.0 mL/min, 254 nm, 12.303 min (major enantiomer), 14.067 min (minor enantiomer).



Butyl (2*E*,4*Z*)-4-(2-formylnaphthalen-1-yl)-5-(o-tolyl)penta-2,4-dienoate (3k)

Following the general procedure and extending the reaction time to 72 hours, **3k** was obtained as a light yellow oil (33.2 mg, 83% yield, 97% *ee*).

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

δ 10.10 (d, *J* = 0.5 Hz, 1H), 8.01 – 7.98 (m, 2H), 7.94 – 7.91 (m, 3H), 7.71 (s, 1H), 7.64 – 7.61 (m, 1H), 7.53 – 7.49 (m, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 6.96 (t, *J* = 7.0 Hz, 1H), 6.55 (t, *J* = 7.5 Hz, 1H), 6.29 (d, *J* = 8.0 Hz, 1H), 5.16 (d, *J* = 15.5 Hz, 1H), 4.13 – 4.04 (m, 2H), 2.47 (s, 3H), 1.60 – 1.54 (m, 2H), 1.37 – 1.29 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H).

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

δ 190.61, 165.91, 148.09, 140.14, 139.67, 136.49, 135.32, 132.28, 131.84, 130.36, 129.65, 129.48, 128.23, 128.01, 127.82, 127.69, 126.81, 126.62, 125.43, 124.70, 121.51, 120.57, 63.51, 29.61, 19.23, 18.06, 12.65.

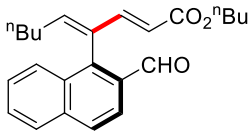
HRMS (ESI) for $C_{27}H_{26}O_3Na$ [M+ Na]$^+$: 421.1774, found: 421.1761.

FTIR (KBr, cm^{-1})

3203.74, 2354.21, 1650.47, 1628.04,1398.13.

Opt. Rot. $[\alpha]^{20}D$ = -116.3 (c = 0.544, $CHCl_3$)

HPLC Daicel Chiralpak IC-H column, n-hexane/i-PrOH (92/8), 1.0 mL/min, 254 nm, 14.602 min (major enantiomer), 16.477 min (minor enantiomer).



Butyl (3*E*,5*Z*)-5-(2-formylnaphthalen-1-yl)deca-3,5-dienoate (3l)

Following the general procedure and extending the reaction time to 72 hours, **3l** was obtained as a light yellow oil (23.5 mg, 65% yield, 85% *ee*).

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

δ 10.11 (s, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.94 – 7.91 (m, 2H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.77 (d, *J* = 15.5 Hz, 1H), 7.65 – 7.62 (m, 1H), 7.53 – 7.50 (m, 1H), 6.68 (t, *J* = 7.5 Hz, 1H), 5.06 (d, *J* = 15.5 Hz, 1H), 4.10 – 4.01 (m, 2H), 1.79 (q, *J* = 7.5 Hz, 2H), 1.58 – 1.52 (m, 2H), 1.34 – 1.28 (m, 4H), 1.18 – 1.11 (m, 2H), 0.88 (t, *J* = 7.5 Hz, 3H), 0.72 (t, *J* = 7.5 Hz, 3H).

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

δ 191.12, 165.96, 146.89, 146.00, 140.14, 135.41, 132.35, 130.06, 129.77, 128.16, 127.80, 127.52, 126.29, 125.37, 121.14, 119.45, 76.20, 63.36, 29.61, 28.94, 21.26, 18.06, 12.67, 12.63.

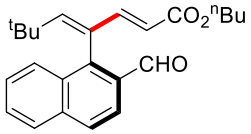
HRMS (ESI) for $C_{25}H_{30}O_3Na$ [M+ Na]$^+$: 401.2087, found: 401.2100.

FTIR (KBr, cm^{-1})

3226.17, 2354.21, 1653.27, 1633.64, 1538.32, 1457.01.

Opt. Rot. $[\alpha]^{20}D$ = -37.5 (c = 0.21, $CHCl_3$)

HPLC Daicel Chiralpak OD-H column, n-hexane/i-PrOH (98/2), 1.0 mL/min, 254 nm, 6.518 min (major enantiomer), 7.693 min (minor enantiomer).



Butyl (3*E*,5*Z*)-5-(2-formylnaphthalen-1-yl)-7,7-dimethylocta-3,5-dienoate (3m)

Following the general procedure and extending the reaction time to 72 hours, **3m** was obtained as a light yellow oil (15.4 mg, 42% yield, 33% *ee*).

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

δ 10.17 (s, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.92 – 7.89 (m, 3H), 7.72 (d, *J* = 15.5 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.54 – 7.51 (m, 1H), 6.61 (s, 1H), 4.96 (d, *J* = 15.5 Hz, 1H), 4.31 (t, *J* = 6.5 Hz, 1H), 4.08 – 4.00 (m, 2H), 1.56 – 1.51 (m, 2H), 1.33 – 1.29 (m, 2H), 0.88 (t, *J* = 7.5 Hz, 3H), 0.78 (s, 9H).

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

δ 191.35, 165.91, 154.91, 149.48, 140.56, 135.09, 130.93, 130.03, 129.88, 128.61, 128.06, 127.79, 127.43, 126.23, 125.93, 120.95, 119.29, 64.55, 63.34, 34.11, 29.60, 28.68, 18.06, 12.64.

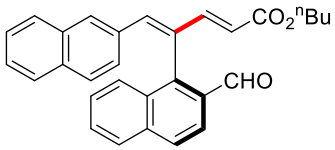
HRMS (ESI) for $C_{25}H_{30}O_3Na$ $[M+ Na]^+$: 401.2087, found: 401.2076.

FTIR (KBr, cm^{-1})

3232.78, 2351.40, 1650.47, 1625.23, 1507.48,1022.43.

Opt. Rot. $[\alpha]^{20}D$ = +0.3 (c = 0.12, $CHCl_3$)

HPLC Daicel Chiralpak OD-H column, n-hexane/i-PrOH (98/2), 1.0 mL/min, 254 nm, 5.636 min (major enantiomer), 6.204 min (minor enantiomer).



Butyl (3*E*,5*Z*)-5-(2-formylnaphthalen-1-yl)-6-(naphthalen-2-yl)hexa-3,5-dienoate (3n)

Following the general procedure and extending the reaction time to 96 hours, **3n** was obtained as a light yellow oil (35.0 mg, 81% yield, 85% *ee*).

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

δ 10.15 (s, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 8.05 – 8.00 (m, 2H), 7.96 (t, *J* = 8.4 Hz, 2H), 7.65 – 7.61 (m, 2H), 7.60 – 7.59 (m, 1H), 7.49 – 7.45 (m, 2H), 7.39 – 7.33 (m, 4H), 6.65 (dd, *J* = 8.5, 2.0 Hz, 1H), 5.20 (d, *J* = 15.5 Hz, 1H), 4.15 – 4.02 (m, 2H), 1.62 – 1.55 (m, 2H), 1.38 – 1.30 (m, 2H), 0.90 (t, *J* = 7.5 Hz, 3H).

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

δ 190.68, 165.83, 148.29, 141.59, 140.40, 135.57, 132.09, 131.91, 131.52, 131.12, 130.00, 129.97, 129.70, 128.48, 128.27, 127.65, 127.40, 127.20, 126.79, 126.37, 126.13, 125.41, 125.23, 124.75, 121.63, 120.51, 63.48, 29.62, 18.08, 12.66.

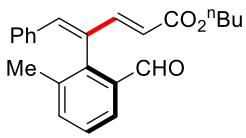
HRMS (ESI) for $C_{31}H_{28}O_3K$ $[M+K]^+$: 487.1670, found: 487.1654.

FTIR (KBr, cm^{-1})

3172.90, 2359.81, 1656.07, 1507.48, 1386.92.

Opt. Rot. $[\alpha]^{20}D$ = -171.3 (c = 0.592, $CHCl_3$)

HPLC Daicel Chiralpak IC-H column, n-hexane/i-PrOH (90/10), 1.0 mL/min, 254 nm, 19.763 min (major enantiomer), 23.790 min (minor enantiomer).



Butyl (3*E*,5*Z*)-5-(2-formyl-6-methylphenyl)-6-phenylhexa-3,5-die

noate (3o)

Following the general procedure and extending the reaction time to 96 hours, **3o** was obtained as a light yellow oil (31.7 mg, 91% yield, 95% *ee*).

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

δ 9.91 (s, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.79 (d, *J* = 16.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.21 (s, 1H), 7.19 – 7.16 (m, 1H), 7.15 – 7.11 (m, 2H), 6.85 – 6.83 (m, 2H), 5.25 (s, 1H), 4.15 – 4.10 (m, 2H), 2.14 (s, 3H), 1.63 – 1.60 (m, 2H), 1.40 – 1.36 (m, 2H), 0.93 (t, *J* = 7.5 Hz, 3H).

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

δ 190.90, 165.89, 147.71, 139.94, 138.86, 136.32, 135.54, 133.99, 132.67, 132.54, 128.49, 128.05, 127.68, 127.65, 124.91, 119.55, 63.48, 29.67, 18.12, 17.74, 12.69.

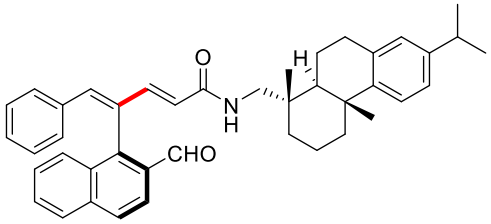
HRMS (ESI) for $C_{24}H_{26}O_3Na$ $[M+ Na]^+$: 385.1774, found: 385.1753.

FTIR (KBr, cm^{-1})

3245.79, 2357.01, 1653.27, 1633.64, 1457.01.

Opt. Rot. $[\alpha]^{20}D$ = + 1.8 (c = 0.498, $CHCl_3$)

HPLC Daicel Chiralpak OD-H column, n-hexane/i-PrOH (99/1), 1.0 mL/min, 254 nm, 14.244 min (major enantiomer), 16.127 min (minor enantiomer).



(2*E*,4*Z*)-4-(2-Formylnaphthalen-1-yl)-N-(((1*S*,4a*R*,10a*S*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-5-phenylpenta-2,4-dienamide (3p)

Following the general procedure, **3p** was obtained as a white solid (47.7 mg, 80% yield, 86% *ee*, m.p. = 92.5 ^{o}C).

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

δ 10.09 (s, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.94 – 7.91 (m, 3H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.47 – 7.44 (m, 2H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.08 – 7.05 (m, 1H), 7.01 – 6.95 (m, 3H), 6.85 (s, 1H), 6.70 (d, *J* = 8.0 Hz, 2H), 5.14 (t, *J* = 6.5 Hz, 1H), 5.05 (d, *J* = 15.0 Hz, 1H), 3.21 – 3.09 (m, 2H), 2.89 – 2.74 (m, 3H), 2.21 (d, *J* = 12.5 Hz, 1H), 1.84 – 1.59 (m, 6H), 1.26 – 1.16 (m, 8H), 1.16 (s, 3H), 0.88 (s, 3H).

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

δ 190.94, 164.62, 146.07, 145.41, 144.65, 140.90, 140.62, 135.49, 133.71, 133.68, 131.22, 129.93, 129.49, 128.61, 128.43, 128.07, 127.76, 127.54, 127.51, 126.78, 125.83, 125.56, 123.04, 122.90, 122.83, 121.62, 48.81, 43.94, 37.08, 36.45, 36.33, 34.85, 32.38, 28.89, 28.68, 24.18, 22.93, 17.79, 17.74, 17.41.

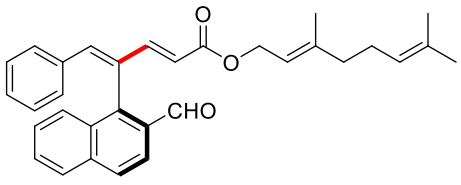
HRMS (ESI) for $C_{42}H_{45}NO_2Na$ $[M+ Na]^+$: 618.3343, found: 618.3315.

FTIR (KBr, cm^{-1})

3287.85, 2357.01, 1656.07, 1636.45, 1457.01.

Opt. Rot. $[\alpha]^{20}D$ = -307.6 (c = 0.054, $CHCl_3$)

HPLC Daicel Chiralpak IC-H column, n-hexane/i-PrOH (90/10), 1.0 mL/min, 254 nm, 28.443 min (major enantiomer), 48.025 min (minor enantiomer).



(*E*)-3,7-Dimethylocta-2,6-dien-1-yl (2*E*,4*Z*)-4-(2-formylnaphthalen-1-yl)-5-phenylpenta-2,4-dienoate (3q)

Following the general procedure, **3q** was obtained as a brown oil (39.2 mg, 84% yield, 88% *ee*).

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

δ 10.10 (s, 1H), 8.07 (d, J = 8.5 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.98 – 7.94 (m, 2H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.64 – 7.62 (m, 1H), 7.49 – 7.46 (m, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 2H), 6.75 (d, *J* = 7.5 Hz, 2H), 7.30 – 7.27 (m, 1H), 5.15 (d, *J* = 15.5 Hz, 1H), 5.06 – 5.03 (m, 1H), 4.60 (d, *J* = 7.0 Hz, 2H), 2.09 – 2.04 (m, 2H), 2.02 – 1.99 (m, 2H), 1.66 (d, *J* = 6.5 Hz, 6H), 1.57 (s, 3H).

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

δ 190.64, 165.71, 148.33, 141.66, 141.52, 140.29, 135.55, 133.50, 131.34, 130.80, 129.83, 129.46, 128.79, 128.43, 128.21, 128.10, 127.65, 127.60, 126.73, 125.21, 122.66, 121.60, 120.56, 116.90, 60.46, 38.49, 25.21, 24.64, 16.65, 15.44.

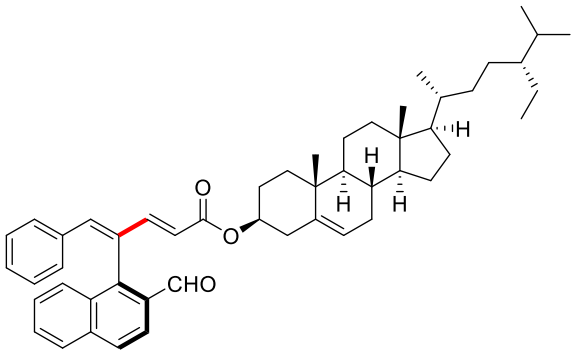
HRMS (ESI) for $C_{32}H_{32}O_3K$ $[M+K]^+$: 503.1983, found: 503.1976.

FTIR (KBr, cm^{-1})

3273.83, 2359.81, 2328.97, 1656.07, 1633.64, 1504.67, 1466.62.

Opt. Rot. $[\alpha]^{20}D$ = -147.9 (c = 0.276, $CHCl_3$)

HPLC Daicel Chiralpak IA-H column, n-hexane/i-PrOH (98/2), 1.0 mL/min, 254 nm, 12.494 min (major enantiomer), 13.771 min (minor enantiomer).



(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-17-((2*R*,5*R*)-5-Ethyl-6-methylheptan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl (2*E*,4*Z*)-4-(2-formylnaphthalen-1-yl)-5-phenylpenta-2,4-dienoate (3r)

Following the general procedure, **3r** was obtained as a white solid (54.7 mg, 75% yield, 98% *ee*, m.p. = 76.8 ^{o}C).

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

δ 10.11 (s, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.96 (s, 1H), 7.93 (dd, *J* = 10.5, 7.0 Hz, 2H), 7.65 – 7.62 (m, 1H), 7.50 – 7.46 (m, 2H), 7.09 (d, *J* = 14.5 Hz, 1H), 7.01 (d, *J* = 15.5 Hz, 2H), 6.74 (d, *J* = 7.5 Hz, 2H), 5.36 (d, *J* = 5.0 Hz, 1H), 5.12 (d, *J* = 15.5 Hz, 1H), 4.66 – 4.59 (m, 1H), 2.33 – 2.24 (m, 2H), 2.01 – 1.94 (m, 2H), 1.86 – 1.80 (m, 3H), 1.48 – 0.79 (m, 36H), 0.67 (d, *J* = 9.0 Hz, 3H).

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

δ 190.70, 165.08, 148.15, 141.42, 140.36, 138.51, 135.56, 133.52, 131.35, 129.84, 129.48, 128.77, 128.43, 128.20, 128.06, 127.64, 127.59, 126.73, 125.25, 121.70, 121.61, 120.98, 73.22, 55.65, 54.99, 48.98, 44.81, 41.27, 38.68, 35.93, 35.54, 35.12, 32.91, 30.82, 28.12, 27.21, 26.71, 25.04, 23.26, 22.04, 19.98, 18.80, 18.24, 18.01, 17.75, 17.23, 14.35, 10.96, 10.82.

HRMS (ESI) for $C_{51}H_{64}O_3Na$ $[M+ Na]^+$: 747.4748, found: 747.4703.

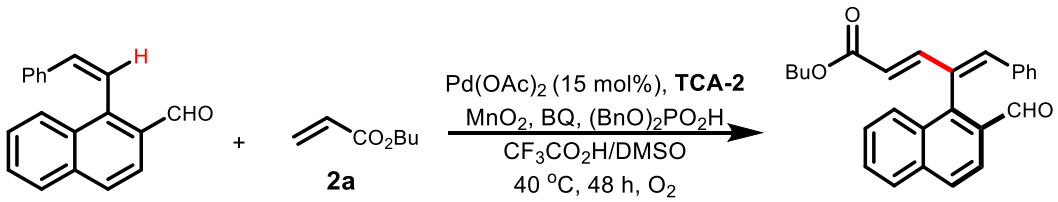
FTIR (KBr, cm^{-1})

3251.40, 2357.1, 1653.27, 1633.64, 1451.40.

Opt. Rot. $[\alpha]^{20}D$ = -111.9 (c = 0.36, $CHCl_3$)

HPLC Daicel Chiralpak IC-H column, n-hexane/i-PrOH (95/5), 1.0 mL/min, 254 nm, 14.550 min (major enantiomer), 16.680 min (minor enantiomer).

4. Gram-scaled preparation



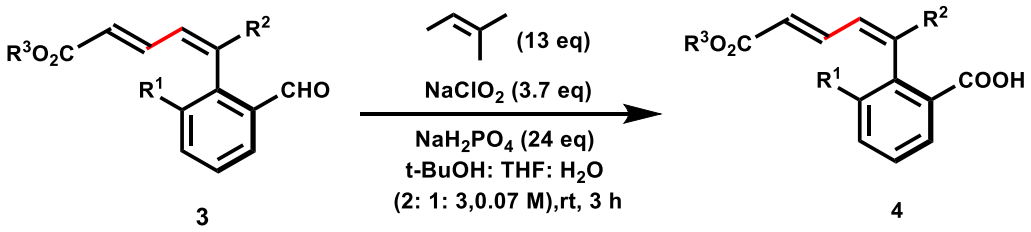
1a, 0.56 g

3a, 66%, 93% ee

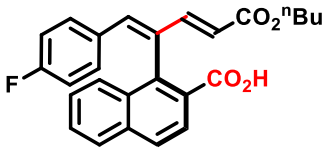
A screw-cap vial was charged with $Pd(OAc)_2$ (15 mol%,0.33 mmol), **TCA-2** (45 mol%, 0.99 mmol), MnO_2 (1.5 equiv, 3.3 mmol), BQ (1.0 equiv, 2.2 mmol), $(BnO)_2PO_2H$ (2.0 equiv, 4.4 mmol), CF_3CH_2OH (11 mL), DMSO (11 mL). Then, aldehyde **1** (1.0 equiv, 2.2 mmol,0.56g) and olefin **2** (4.0 equiv, 8.8 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 light yellow oil (0.56 g, 66% yield, 93% ee).

5. Further Elaboration

5.1 General procedure for the preparation of axial Chiral Carboxylic Acids 4（CCAs）:



To a solution of the aldehyde **3** (0.2 mmol) in a mixture of t-BuOH/THF/H_2O (3 mL, 2:1:3) at 0 ℃ 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 mixture either continued stirring at the same temperature for 3 h until of the carboxylic acid intermediates were 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 x 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 acid (**4**).



1-((1Z,3E)-5-butoxy-1-(4-fluorophenyl)-5-oxopenta-1,3-dien-2-yl)-2-naphthoic acid (4a)

Following the General procedure with **3a** (0.1 mmol), **4a** was obtained as a yellow liquid (38.9 mg, 93% yield, 92% *ee*,).

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

δ 8.17 (d, *J* = 8.7 Hz, 1H), 7.98 (d, *J* = 8.7 Hz, 1H), 7.95 – 7.84 (m, 3H), 7.61 – 7.54 (m, 1H), 7.43 (ddd, J = 8.2, 6.9, 1.1 Hz, 1H), 7.22 (s, 1H),

6.73 – 6.62 (m, 4H), 5.07 (d, *J* = 15.5 Hz, 4H), 4.06 (t, *J* = 6.8 Hz, 2H), 1.55 (dt, *J* = 14.6, 6.9 Hz, 3H), 1.31 (dt, *J* = 13.5, 6.8 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H).

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

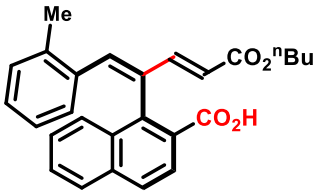
δ 171.24 , 167.43 , 163.32 , 161.34 , 149.38 , 138.19 , 138.07 , 135.80 , 135.68 (d, *J* = 2.3 Hz), 131.75 (d, *J* = 3.4 Hz), 131.08 (d, *J* = 8.1 Hz), 130.73 , 128.76 (d, *J* = 8.1 Hz), 128.32 , 127.64 , 126.79 (d, *J* = 2.5 Hz), 126.49 , 119.32 , 115.47 (d, *J* = 21.6 Hz), 64.39 , 30.65 , 19.13 , 13.71 .

FTIR (KBr, cm^{-1})

3448.85, 2960.44, 2831.32, 2716.53, 2359.81, 2343.55, 1597.12, 1364.17, 1068.5, 776.01, 556.91, 454.38

Opt. Rot. $[\alpha]^{20}D$ = -60.2 (c = 0.54, $CHCl_3$)

HPLC Daicel Chiralpak IA column, n-hexane/i-PrOH (60/40), 1 mL/min, 254 nm, 7.390 min (major enantiomer), 17.881 min (minor enantiomer).



1-((1Z,3E)-5-butoxy-5-oxo-1-(o-tolyl)penta-1,3-dien-2-yl) -2-naphthoic acid (4b)

Following the General procedure with **3b** (0.1 mmol), **4b** was obtained as a yellow liquid (37.3 mg, 90% yield, 96% *ee*).

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

δ 8.07 (d, *J* = 8.7 Hz, 1H), 7.94 (d, *J* = 15.6 Hz, 1H), 7.92 – 7.86 (m, 3H), 7.56 (d, *J* = 7.1 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.55 (t, *J* = 7.6 Hz, 1H), 6.37 (d, *J* = 7.8 Hz, 1H), 5.11 (d, *J* = 15.5 Hz, 1H), 4.08 (t, *J* = 6.5 Hz, 2H), 2.40 (s, 3H), 1.57 (dt, *J* = 14.7, 6.9 Hz, 2H), 1.33 (dq, *J* = 14.9, 7.5 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 3H).

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

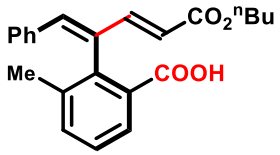
171.64 , 167.51 , 149.34 , 138.16 , 138.08 , 137.12 , 136.55 , 135.50 , 134.39 , 131.38 , 130.04 , 128.44 , 128.37 , 128.29 , 128.06 , 127.58 , 127.36 , 127.12 , 126.82 , 126.50 , 125.41 , 119.35 , 64.38 , 30.68 , 19.98 , 19.14 , 13.72 .

FTIR (KBr, cm^{-1})

2956.02, 2925.70, 2852.24, 1700.81, 1596.48, 1366.13, 1285.36, 1163.94, 744.50,

Opt. Rot. $[\alpha]^{20}D$ = -56.2 (c = 0.47, $CHCl_3$)

HPLC Daicel Chiralpak AD-H column, n-hexane/i-PrOH (60/40), 1 mL/min, 254 nm, 4.164 min (major enantiomer), 5.654 min (minor enantiomer).



2-((1Z,3E)-5-butoxy-5-oxo-1-phenylpenta-1,3-dien-2-yl)-3-methylbenzoic acid (4c)

Following the General procedure with **3c** (0.1 mmol), **4c** was obtained as a yellow liquid (32.1 mg, 88% yield, 94% *ee*).

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

δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 15.5 Hz, 1H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.15 – 7.07 (m, 3H), 6.98 (s, 1H), 6.84 (d, J = 7.0 Hz, 2H), 5.19 (d, *J* = 15.5 Hz, 1H), 4.10 (t, *J* = 6.7 Hz, 2H), 2.05 (s, 3H), 1.61 (dt, *J* = 14.7, 6.8 Hz, 2H), 1.37 (dq, *J* = 14.1, 7.1 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).

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

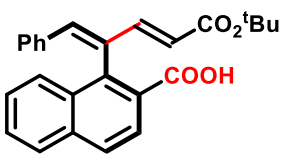
δ 171.14 , 167.51 , 149.03 , 138.17 , 137.89 , 137.33 , 137.27 , 135.88 , 135.52 , 129.69 , 129.42 , 129.13 , 128.43 , 128.29 , 128.05 , 118.22 , 64.34 , 30.71 , 19.52 , 19.18 , 13.75.

FTIR (KBr, cm^{-1})

2829.57, 1598.47, 1365.25, 1068.74, 774.96,

Opt. Rot. $[\alpha]^{20}D$ = -36.0 (c = 0.04, $CHCl_3$)

HPLC Daicel Chiralpak AD-H column, n-hexane/i-PrOH (60/40), 1 mL/min, 254 nm, 5.263min (major enantiomer), 11.326 min (minor enantiomer).



1-((1Z,3E)-5-(tert-butoxy)-5-oxo-1-phenylpenta-1,3-dien-2-yl) -2-naphthoic acid (4d)

Following the General procedure with **3d** (0.1 mmol), **4d** was obtained as a yellow liquid (36.8 mg, 92% yield, 88% *ee*).

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

δ 8.17 (d, *J* = 8.7 Hz, 1H), 7.97 (d, *J* = 8.7 Hz, 1H), 7.90 (t, *J* = 9.0 Hz, 2H), 7.80 (d, *J* = 15.5 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 17.0 Hz, 1H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 2H), 6.72 (d, *J* = 7.5 Hz, 2H), 4.98 (d, *J* = 15.5 Hz, 1H), 1.41 (s, 9H).

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

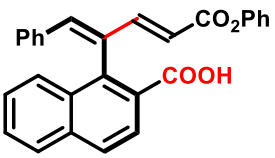
δ 170.70 , 166.62 , 148.56 , 139.06 , 138.59 , 136.09 , 135.75 , 135.57 , 130.88 , 129.29 , 128.57 , 128.31 , 128.18 , 128.15 , 127.49 , 127.10 , 126.80 , 126.29 , 121.22 , 80.31 , 28.12.

FTIR (KBr, cm^{-1})

2920.76, 1699.40, 1464.68, 1311.87, 1261.43, 1149.74, 1021.29, 804.21, 441.69

Opt. Rot. $[\alpha]^{20}D$ = -45.1 (c = 0.06, $CHCl_3$)

HPLC Daicel Chiralpak AD-H column, n-hexane/i-PrOH (60/40), 1 mL/min, 254 nm, 5.489min (major enantiomer), 23.947 min (minor enantiomer).



1-((1Z,3E)-5-oxo-5-phenoxy-1-phenylpenta-1,3-dien-2-yl)-2-naphthoic acid (4e)

Following the General procedure with **3e** (0.1 mmol), **4e** was obtained as a yellow liquid (36.1 mg, 86% yield, 90% *ee*).

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

δ 8.22 (d, *J* = 8.7 Hz, 1H), 8.09 (d, *J* = 15.5 Hz, 1H), 8.01 (d, *J* = 8.7 Hz, 1H), 7.93 (t, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.50 – 7.45 (m, 1H), 7.35 – 7.28 (m, 3H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.9 Hz, 3H), 6.99 (t, *J* = 7.5 Hz, 2H), 6.76 (d, *J* = 7.6 Hz, 2H), 5.25 (d, *J* = 15.5 Hz, 1H).

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

δ 170.82 , 165.66 , 151.41 , 150.73 , 140.59 , 138.20 , 135.95 , 135.84 , 135.31 , 130.81 , 129.53 , 129.32 , 128.84 , 128.74 , 128.59 , 128.43 , 128.34 , 127.69 , 126.87 , 126.85 , 126.32 , 125.61 , 121.60 , 118.30 .

HRMS (ESI) for $C_{28}H_{20}O_4Na$ $[M+Na]^+$: 443.1254, found: 443.1247； for $C_{28}H_{20}O_4$ K $[M+K]^+$: 459.0993, found: 459.2989.

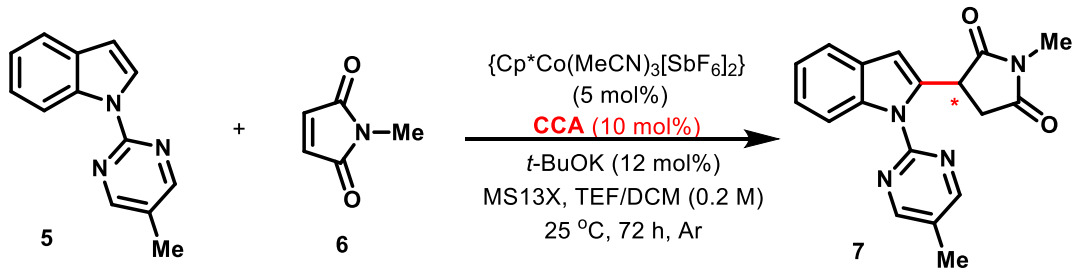
FTIR (KBr, cm^{-1})

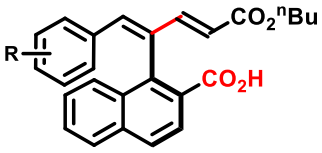
3433.27, 2925.12, 2830.89, 1715.79, 1592.59, 1363.77, 1124.14, 775.87

Opt. Rot. $[\alpha]^{20}D$ = -60.2 (c = 0.06, $CHCl_3$)

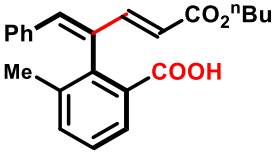
HPLC Daicel Chiralpak AD-H column, n-hexane/i-PrOH (60/40), 1 mL/min, 254 nm, 7.887min (major enantiomer), 9.044 min (minor enantiomer).

5.2 Application of 4 as CCA for Co^{III}-catalyzed enantioselective 1, 4-addition of indole and maleimides

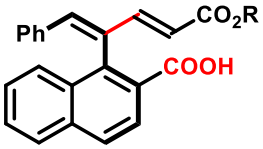




R = 4-F, **4a**, 71%, 74: 26 er
R = 2-Me, **4b**, 41%, 90:10 er

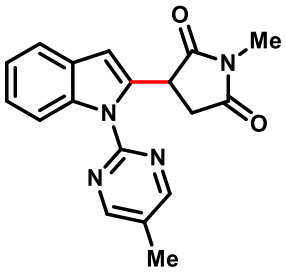


4c, **44%, 87:13 dr**



R = ^{t}Bu, **4d**, **40%, 92: 8 er**
R = Ph, **4e**, **41%, 83:17 er**

To an oven-dried 25 mL Schlenk tube was added N-5-methyl-pyrimidyl indole **5** (0.20 mmol, 1.0 equiv), maleimide **6** (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 **7** as white solid.



1-methyl-3-(1-(5-methylpyrimidin-2-yl)-1H-indol-2-yl)pyrrolidine-2,5-dione (7)

^{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).

6. Density Functional Theory (DFT) Calculations

6.1 Computational Details and Rotational Barrier Calculated by DFT

All density functional theory (DFT) calculations were carried out using Gaussian16 software package.[6] All geometry optimizations were performed with B3LYP[7,8]-D3[9] 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[10] 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[11] 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.

6.2 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.

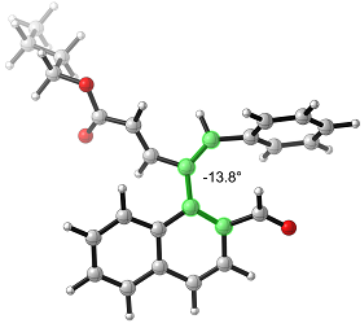
The epimerization of atropoisomer is a first order reaction, which makes the half-life only relates to the reaction rate constant:

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

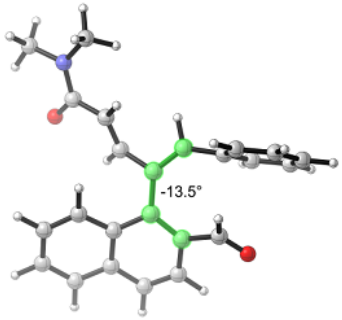
Based on Equations 1 and 2, the half-life at 40 $^{\mathrm{o}}$C (reaction conditions) and 25 $^{\mathrm{o}}$C (room temperature) was calculated.

Table of Energies and Figures

Structure	E	ZPE	H	T.S	T.qh-S	G(T)	qh-G(T)
3a-TS	-1230.900357	0.424751	-1230.448927	0.084702	0.079159	-1230.533629	-1230.528086
3a	-1230.951443	0.425198	-1230.498427	0.089616	0.082197	-1230.588043	-1230.580623
3e-TS	-1132.389275	0.379813	-1131.984727	0.080054	0.07509	-1132.064781	-1132.059816
3e	-1132.441378	0.380453	-1132.035128	0.084468	0.077903	-1132.119596	-1132.113031
5a-TS	-924.823022	0.355135	-924.445535	0.075135	0.070643	-924.52067	-924.516178
5a	-924.872508	0.354131	-924.494676	0.078712	0.073626	-924.573388	-924.568301
5e-TS	-806.868959	0.271208	-806.57951	0.064238	0.061691	-806.643748	-806.641201
5e	-806.918472	0.270186	-806.628684	0.067808	0.064679	-806.696492	-806.693363



3a-TS
$\Delta G^{\ddagger}$ = 30.5 kcal/mol
$t_{1/2}$ (25 °C) = 82 yrs
$t_{1/2}$ (40 °C) = 6 yrs



3e-TS
$\Delta G^{\ddagger}$ = 30.9 kcal/mol
$t_{1/2}$ (25 °C) = 162 yrs
$t_{1/2}$ (40 °C) = 12 yrs

3a-TS

C	3.068020	0.863098	0.340311
C	3.702557	1.971635	0.963444
C	3.085489	3.187123	1.080181
C	1.846510	3.402742	0.428702
C	1.184122	2.295842	-0.203920
C	1.722293	0.950733	-0.074688
C	0.769961	-0.208491	-0.202660
C	0.979685	-1.554750	-0.212278
C	-0.673994	0.133093	-0.045658
C	-1.700405	-0.430596	-0.703942
C	2.173994	-2.429728	-0.165435
C	2.784067	-2.719205	1.063509
C	3.861822	-3.602523	1.125490
C	4.328860	-4.222258	-0.033716
C	3.706214	-3.963163	-1.257444
C	2.629699	-3.079380	-1.322961
C	-3.088717	-0.047972	-0.376832
O	-3.421065	0.775207	0.457079
O	-3.964842	-0.737135	-1.150414
C	-7.956654	-1.786849	1.679578
C	-7.407079	-1.016586	0.474737
C	-5.902865	-1.237026	0.273561
C	-5.366046	-0.464382	-0.926367
H	4.710951	1.811280	1.330660
H	3.570778	4.013522	1.593116
H	0.063127	-2.141079	-0.178372
H	-0.923013	0.886749	0.698448
H	-1.557133	-1.153767	-1.501058
H	2.426926	-2.228003	1.964106
H	4.341931	-3.797840	2.080042
H	5.172890	-4.904409	0.014585
H	4.061411	-4.447496	-2.163080
H	2.148303	-2.873163	-2.275280
H	-9.030976	-1.613979	1.808736
H	-7.802163	-2.866277	1.560735
H	-7.453202	-1.479628	2.604116
H	-7.602313	0.056962	0.605421
H	-7.947870	-1.319687	-0.433387
H	-5.694308	-2.305565	0.129720
H	-5.355277	-0.915272	1.166747
H	-5.857461	-0.776194	-1.852505
H	-5.504359	0.612618	-0.789206
C	4.025697	-0.234665	0.007694

O	5.090143	-0.397277	0.577763
H	3.779305	-0.815107	-0.893230
C	0.054811	2.607554	-1.016458
C	-0.442074	3.888842	-1.111804
H	-1.295191	4.084097	-1.755187
C	0.156490	4.948979	-0.395114
H	-0.256081	5.951856	-0.459210
H	-0.403610	1.829617	-1.611282
C	1.287267	4.705896	0.347976
H	1.795106	5.516645	0.864500

3a

C	-1.597297	1.533696	-0.316131
C	-1.963777	2.735067	0.376568
C	-1.800842	2.803092	1.788633
C	-1.294448	1.738755	2.485095
C	-0.927622	0.541288	1.811256
C	-1.084191	0.425810	0.432447
C	-0.683229	-0.823799	-0.289810
C	-1.541871	-1.822665	-0.635920
C	0.713805	-0.948347	-0.677935
C	1.687968	-0.049646	-0.427602
C	-2.976765	-1.993928	-0.417994
C	-3.582639	-3.126583	-1.003224
C	-4.943933	-3.377524	-0.861942
C	-5.741002	-2.500665	-0.123513
C	-5.159753	-1.376790	0.469806
C	-3.799042	-1.122266	0.328096
C	3.066525	-0.310314	-0.883224
O	3.437407	-1.296874	-1.495840
O	3.884592	0.710821	-0.527603
C	8.298169	-1.269014	0.751154
C	7.527112	-0.389299	-0.238084
C	6.032894	-0.301802	0.095593
C	5.274897	0.574696	-0.895585
H	-2.083269	3.717690	2.304288
H	-1.089082	-2.648711	-1.184726
H	0.998096	-1.849288	-1.220427
H	1.504339	0.876679	0.105793
H	-2.968458	-3.815280	-1.578777
H	-5.381875	-4.257024	-1.325849
H	-6.804310	-2.691990	-0.008326
H	-5.771192	-0.691661	1.050664
H	-3.376966	-0.248350	0.804926

H	9.362232	-1.321767	0.494600
H	8.217859	-0.876731	1.772297
H	7.902604	-2.291816	0.757061
H	7.649467	-0.786722	-1.255382
H	7.961413	0.620817	-0.247785
H	5.895163	0.105029	1.106158
H	5.588057	-1.303405	0.084289
H	5.659577	1.598615	-0.896262
H	5.339819	0.163897	-1.907990
C	-0.393547	-0.579065	2.625526
O	-0.238491	-0.519431	3.832368
H	-0.137262	-1.499586	2.066745
H	-1.159200	1.771800	3.561284
C	-1.768920	1.482467	-1.726806
C	-2.273810	2.561310	-2.416961
H	-2.396963	2.504658	-3.494782
C	-2.634797	3.745525	-1.731377
H	-3.032933	4.589913	-2.287277
H	-1.496707	0.575718	-2.255743
C	-2.482364	3.827757	-0.365289
H	-2.757601	4.734866	0.167164

3e-TS

C	1.968817	1.542232	0.085942
C	2.263916	2.871801	0.491857
C	1.291291	3.827626	0.599299
C	-0.020615	3.538389	0.151345
C	-0.344775	2.199646	-0.259309
C	0.632243	1.131852	-0.106906
C	0.127584	-0.281072	0.033789
C	0.786237	-1.470880	0.118417
C	-1.318598	-0.409580	0.378104
C	-2.153170	-1.360653	-0.071910
C	2.200514	-1.900912	0.018136
C	3.035883	-1.840595	1.142709
C	4.346464	-2.313344	1.075194
C	4.830866	-2.872693	-0.107454
C	3.995044	-2.966130	-1.223204
C	2.685784	-2.490595	-1.159507
C	-3.575029	-1.364867	0.381053
O	-4.063741	-0.382435	0.942885
H	3.304768	3.097669	0.699178
H	1.528547	4.829983	0.946659
H	0.141085	-2.307848	0.380202

H	-1.733365	0.320033	1.069441
H	-1.814467	-2.073911	-0.816983
H	2.661993	-1.394702	2.059949
H	4.991381	-2.234955	1.945740
H	5.853818	-3.234397	-0.160966
H	4.364618	-3.405664	-2.145846
H	2.037202	-2.555321	-2.029275
C	3.193091	0.776674	-0.296515
O	4.310618	1.039965	0.112024
H	3.051001	0.034727	-1.095526
C	-1.613276	2.015262	-0.883674
C	-2.525628	3.040782	-0.997834
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H	-1.861421	1.055455	-1.314016
C	-0.994835	4.567607	0.056565
H	-0.727568	5.562323	0.404730
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C	-3.791323	-3.729829	-0.442852
H	-4.350494	-4.574755	-0.026432
H	-3.888682	-3.767459	-1.538075
H	-2.743167	-3.872352	-0.175139

3e

C	-0.697214	1.408376	-0.513620
C	-0.839302	2.746844	-0.016916
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C	-5.324313	-1.722383	0.202467
C	-4.524723	-0.729832	0.775551

C	-3.142066	-0.754376	0.619357
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H	-0.624866	4.044874	1.705102
H	-0.782670	-2.851077	-0.783342
H	1.417523	-2.420827	-0.916178
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H	-5.333907	-3.534827	-0.969636
H	-6.403328	-1.695814	0.327272
H	-4.981120	0.069685	1.352843
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C	0.560093	-0.329080	2.643223
O	0.923398	-0.077427	3.779104
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C	4.810317	0.645730	0.504141
H	5.800430	0.781588	0.947994
H	4.560977	1.560076	-0.053081
H	4.099238	0.527582	1.325926
C	6.151598	-0.957314	-0.832010
H	6.636900	-0.143766	-1.387658
H	6.802157	-1.241451	0.005575
H	6.016759	-1.815991	-1.488238

7. References

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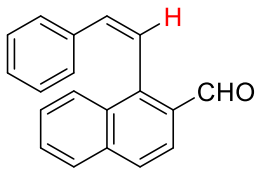
8. NMR Charts

8.1 ^{1}H / ^{13}C NMR Charts of The Substrates



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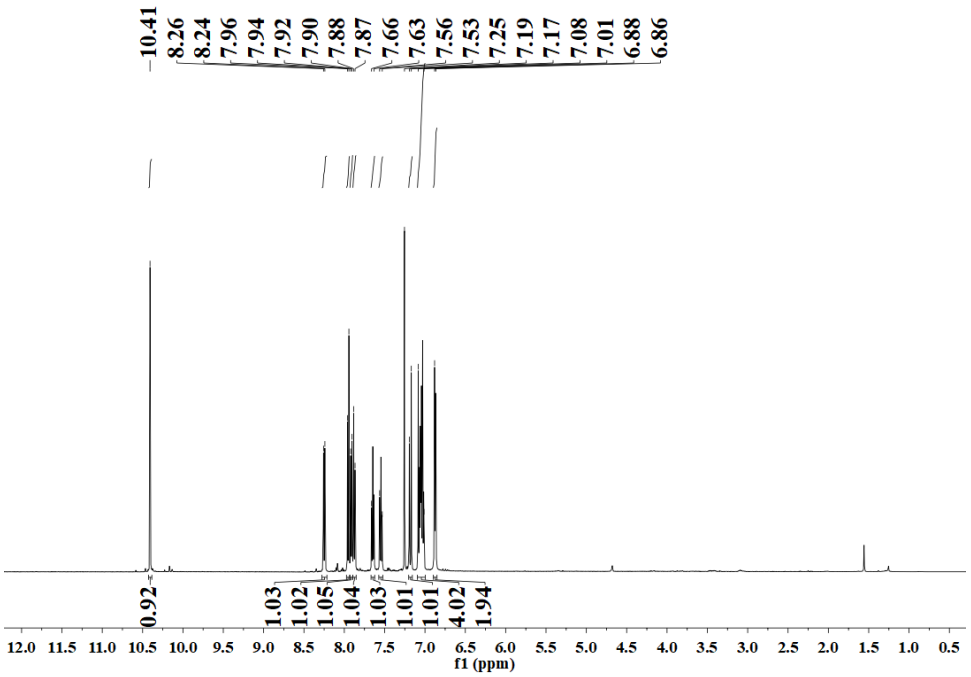

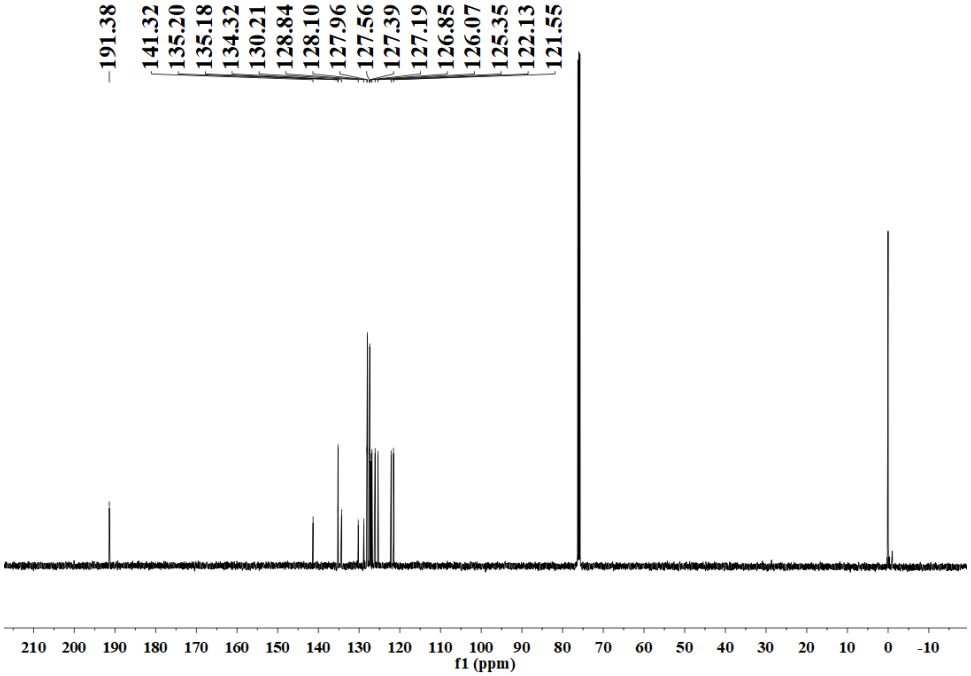

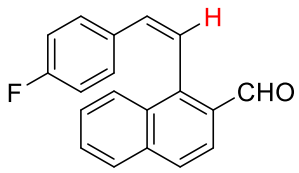
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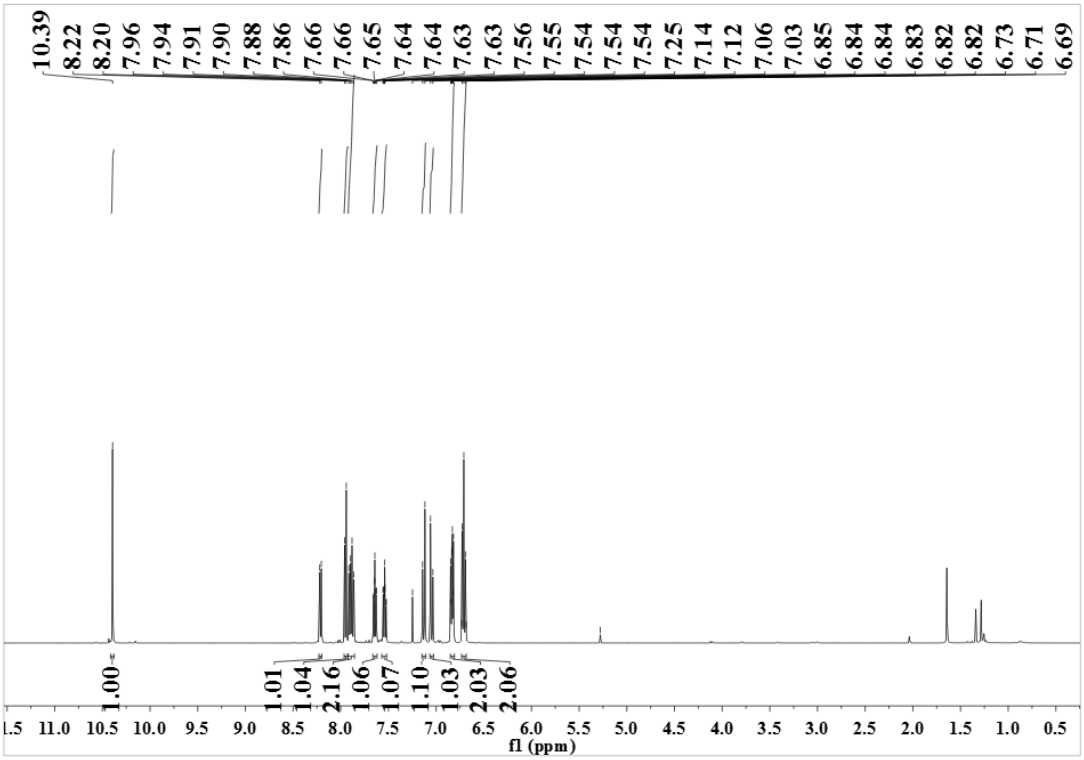
F
CHO

(1f)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7.64
7.63
7.63
7.56
7.55
7.54
7.54
7.54
7.25
7.14
7.12
7.06
7.03
6.85
6.84
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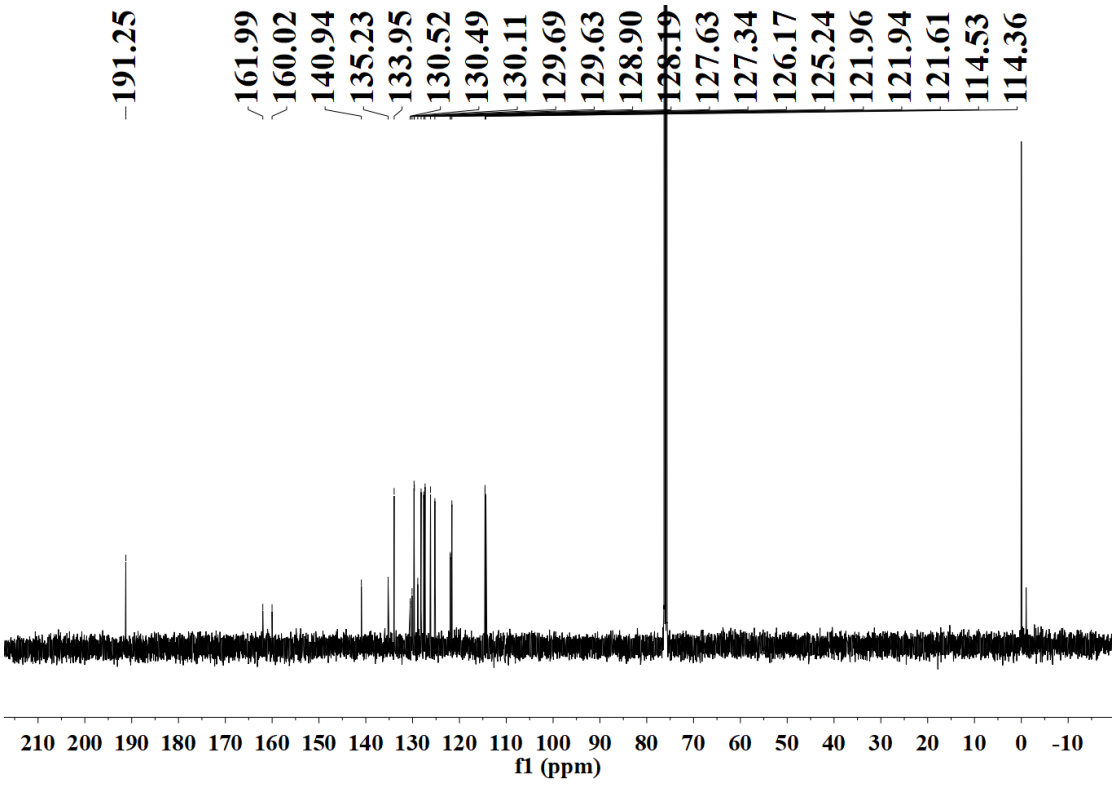
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135.23
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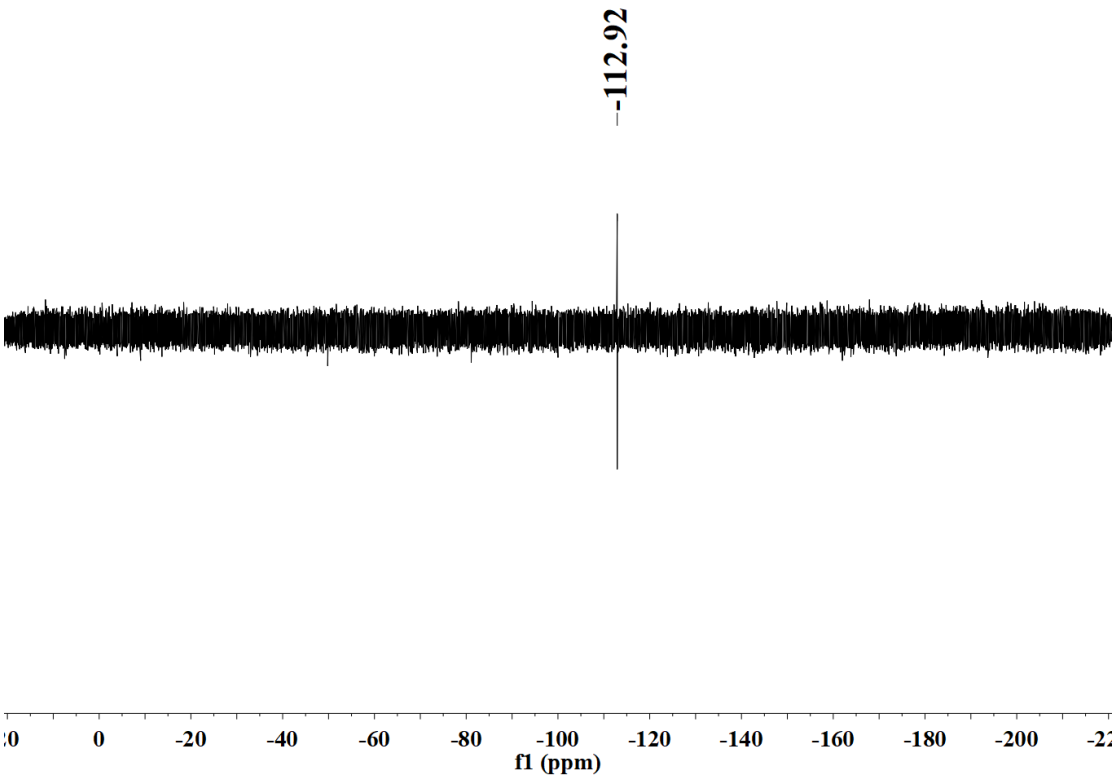
121.61
114.53
114.36
f1 (ppm)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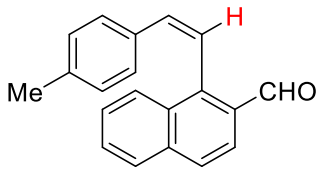
-200
f1 (ppm)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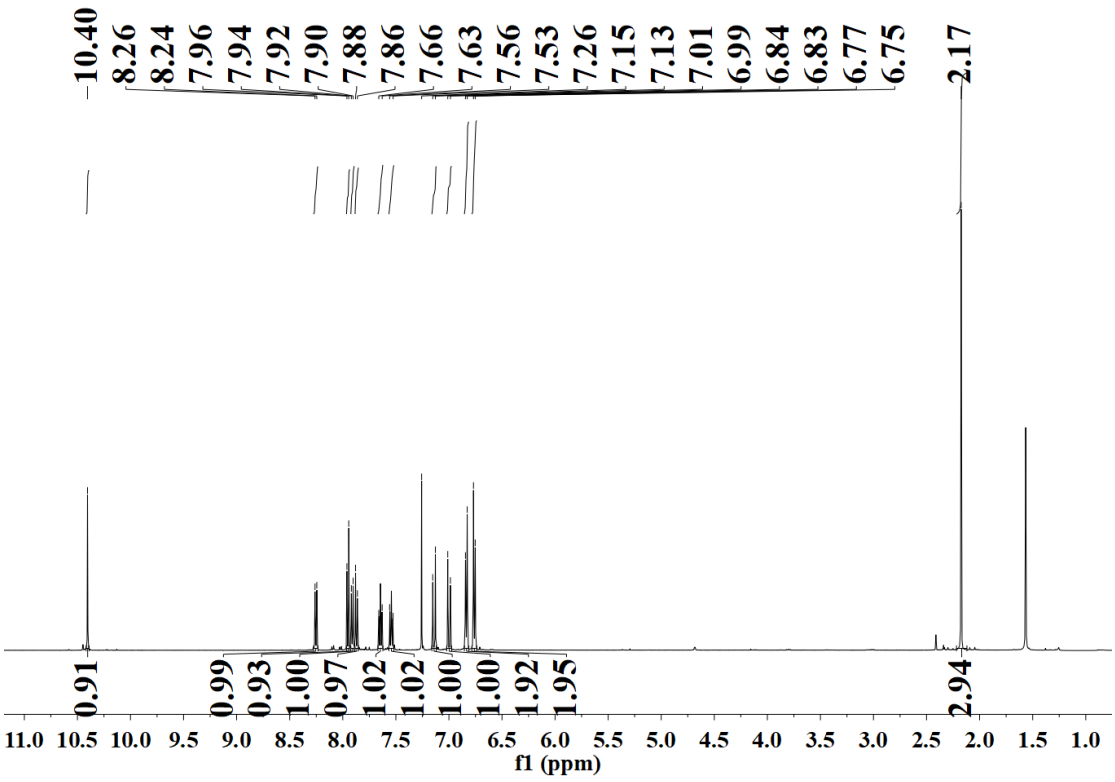
Me
CHO

(1g)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7.15
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7.01
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6.84
6.83
6.77
6.75
2.17
0.91
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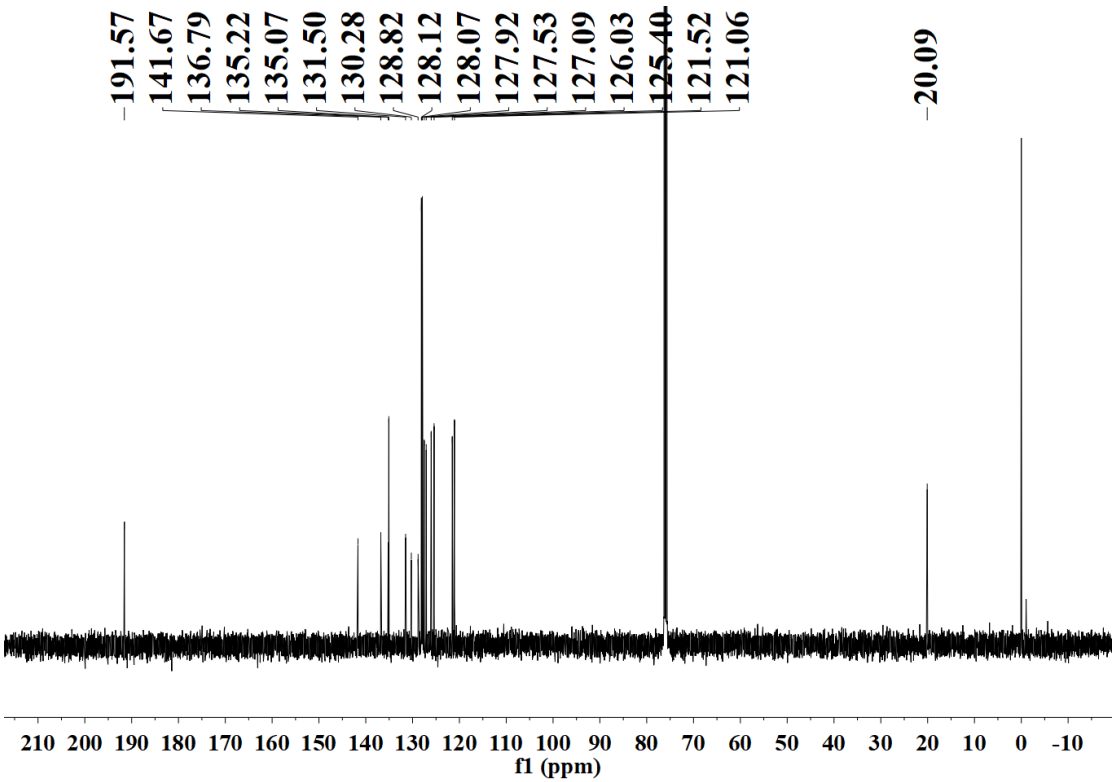
f1 (ppm)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20.09
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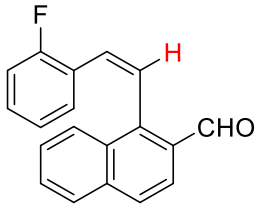
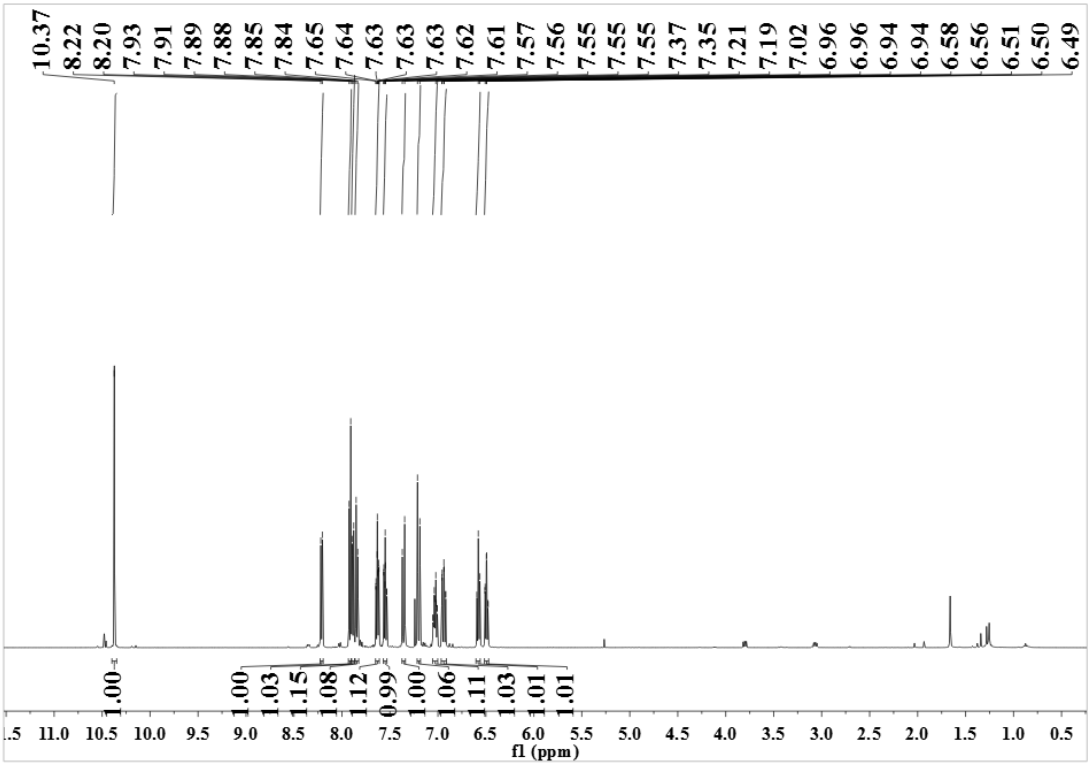
f1 (ppm)


F
H
CHO

(1h)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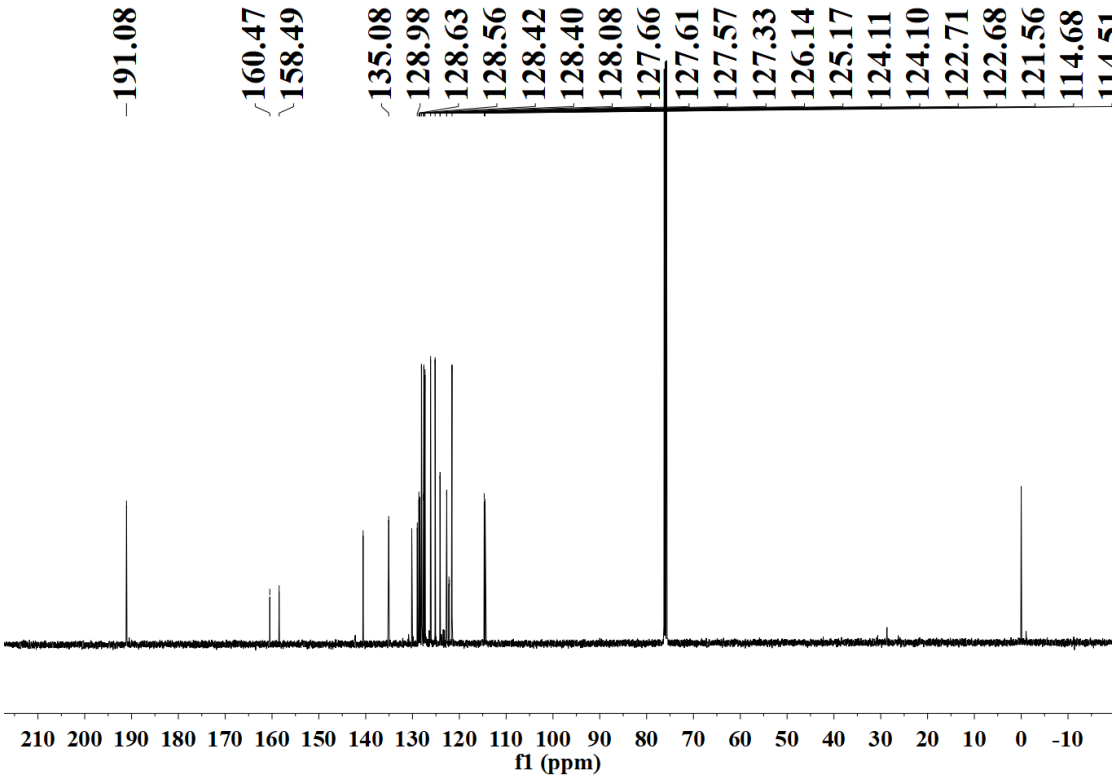
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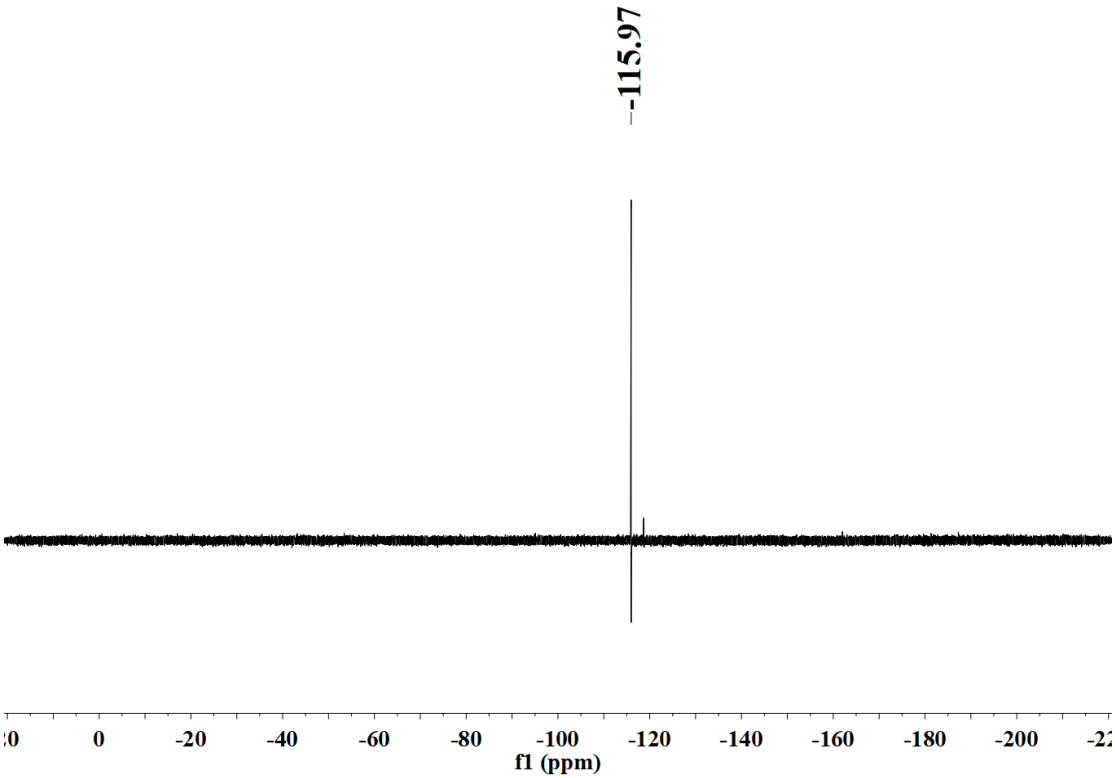
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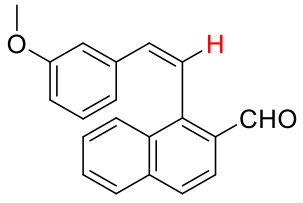
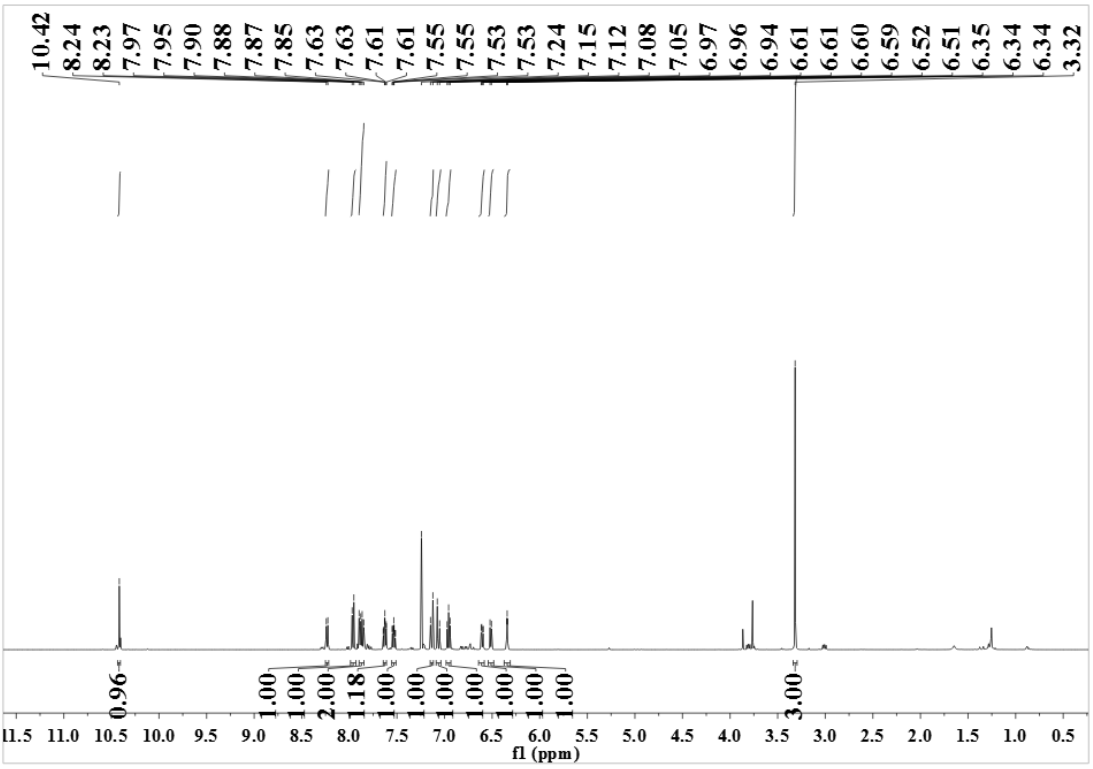

O
H
CHO

(1i)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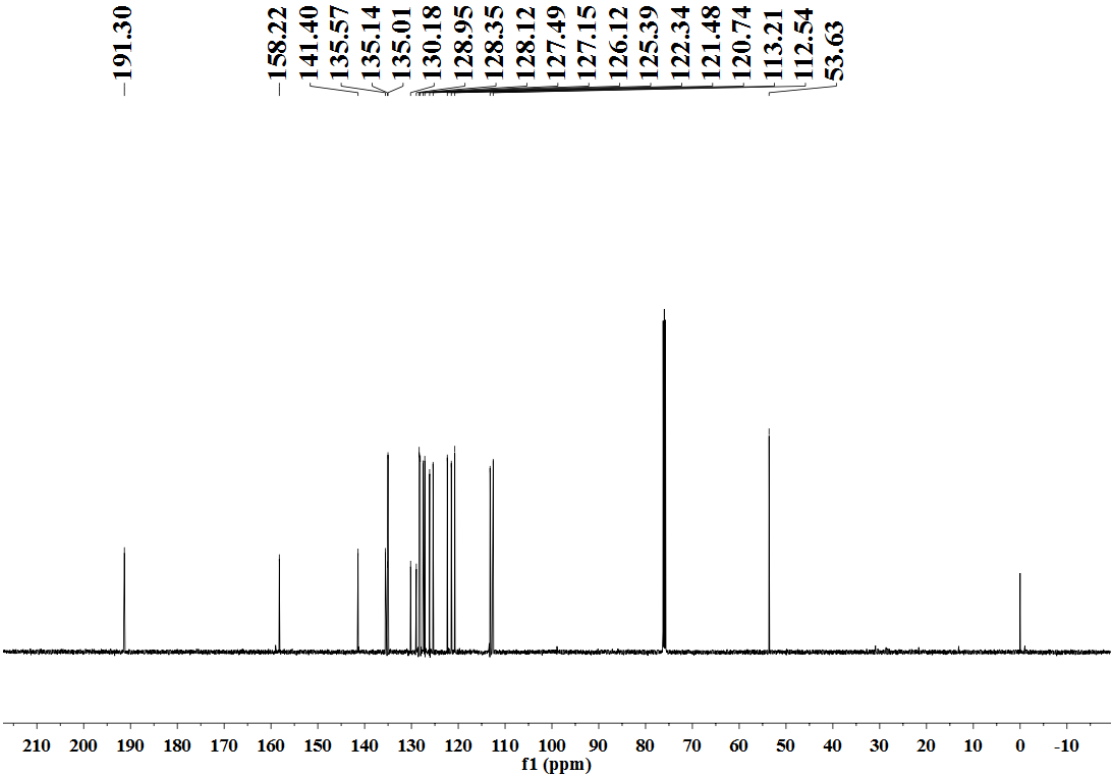
fl (ppm)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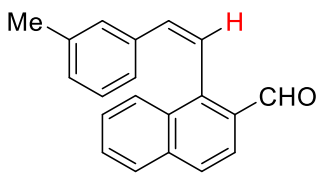
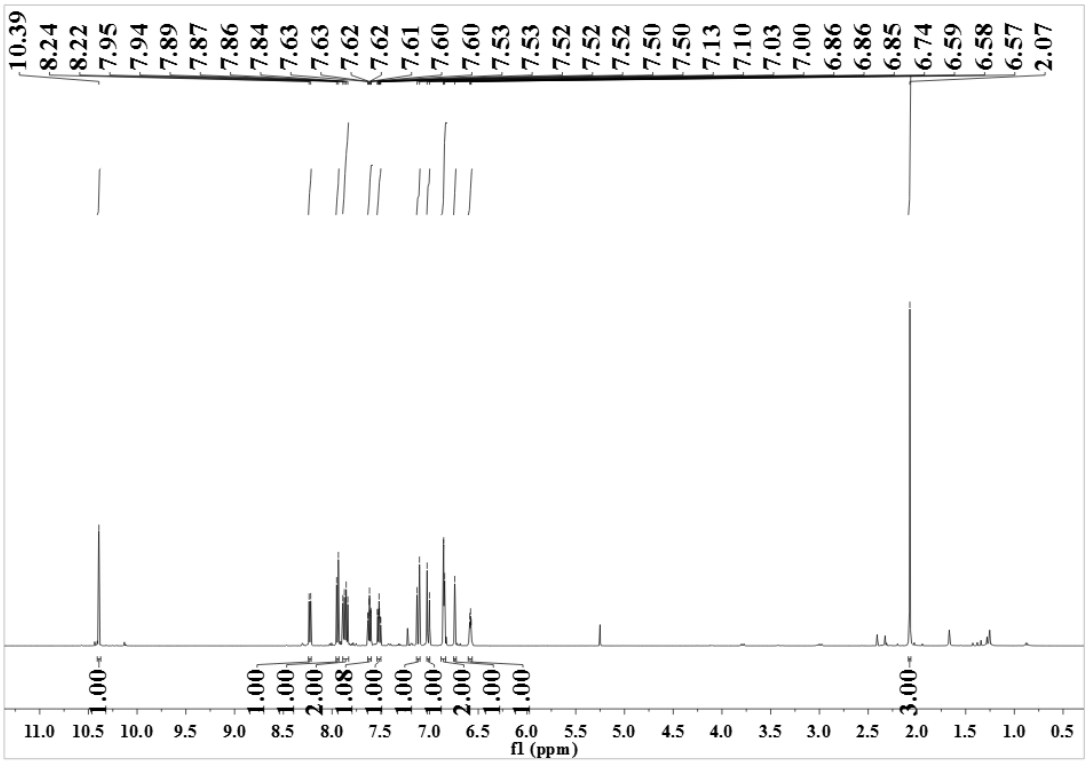

Me
H
CHO

(1j)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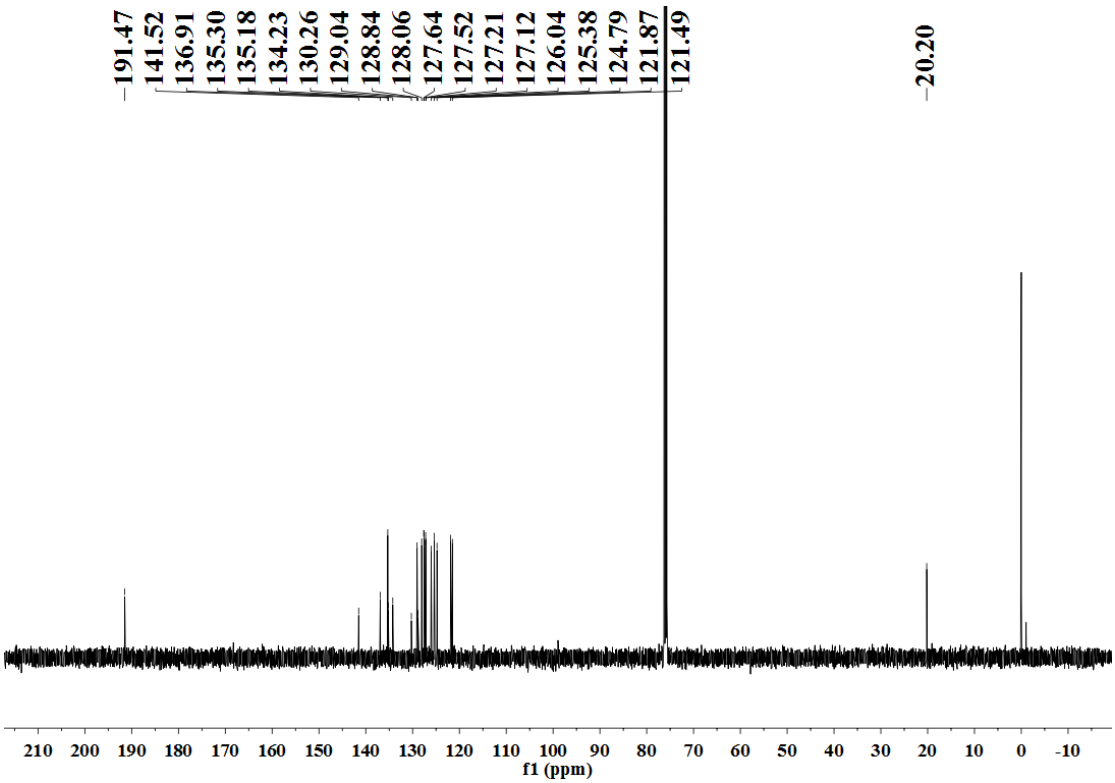
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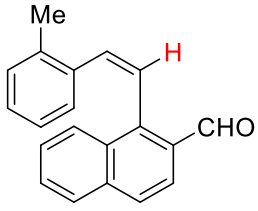
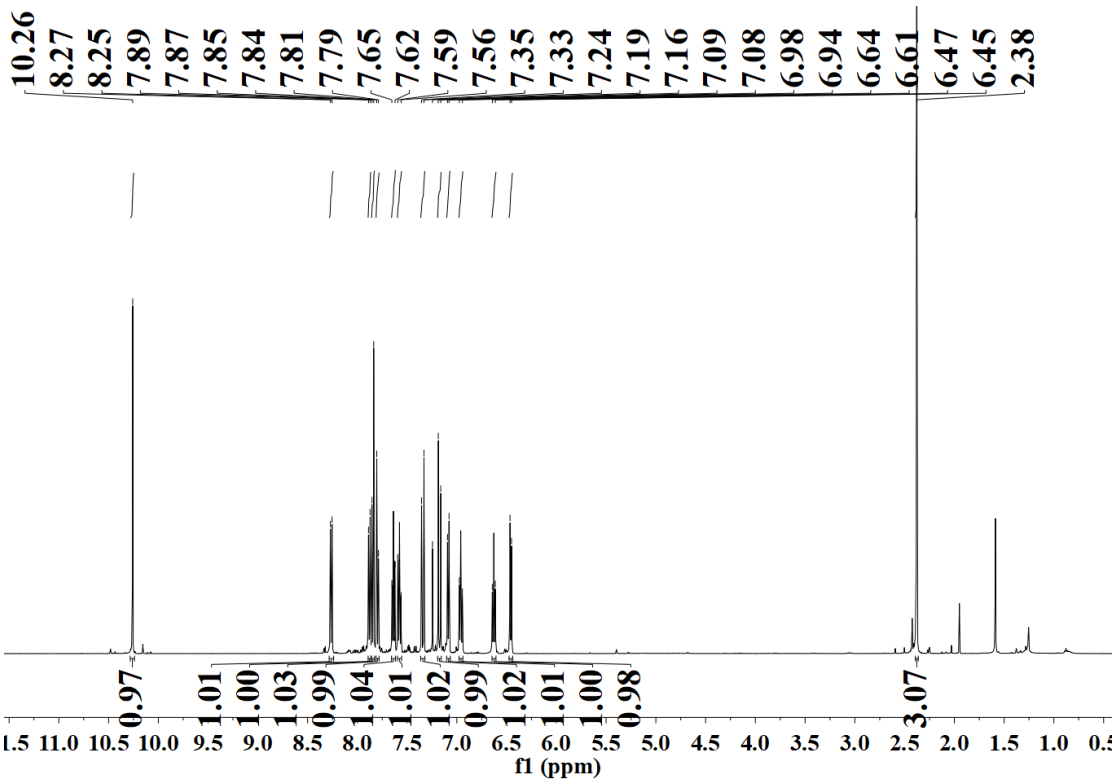
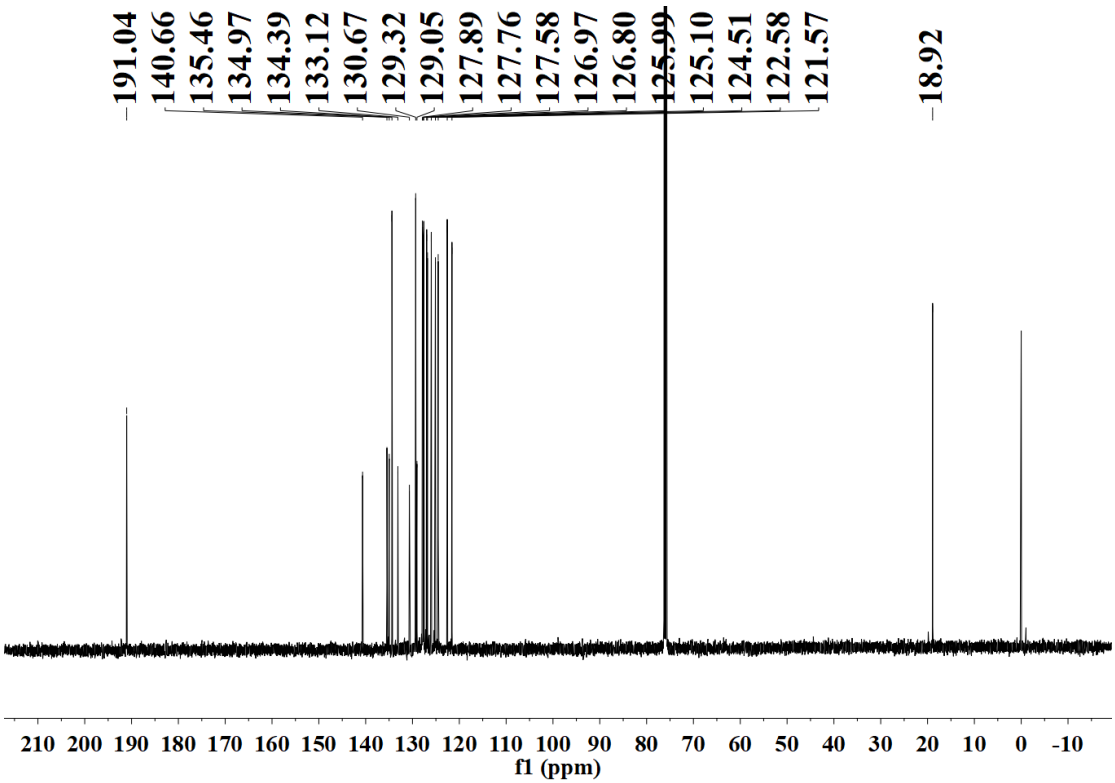
121.49
20.20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
H
CHO

(1k)


10.26
8.27
8.25
7.89
7.87
7.85
7.84
7.81
7.79
7.65
7.62
7.59
7.56
7.35
7.33
7.24
7.19
7.16
7.09
7.08
6.98
6.94
6.64
6.61
6.47
6.45
2.38
0.97
1.01
1.00
1.03
0.99
1.04
1.01
1.02
0.99
1.02
1.01
1.00
0.98
3.07
f1 (ppm)


191.04
140.66
135.46
134.97
134.39
133.12
130.67
129.32
129.05
127.89
127.76
127.58
126.97
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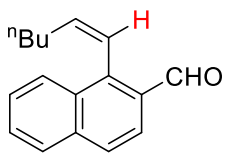
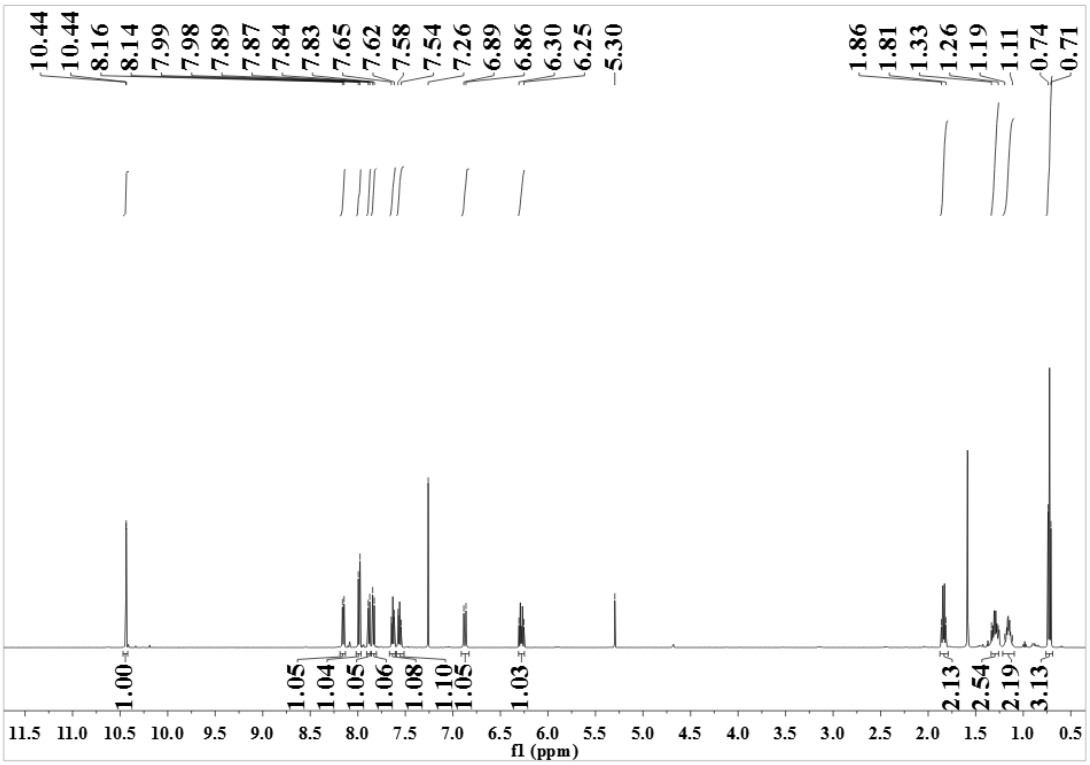
125.10
124.51
122.58
121.57
18.92
f1 (ppm)


nBu
H
CHO

(1l)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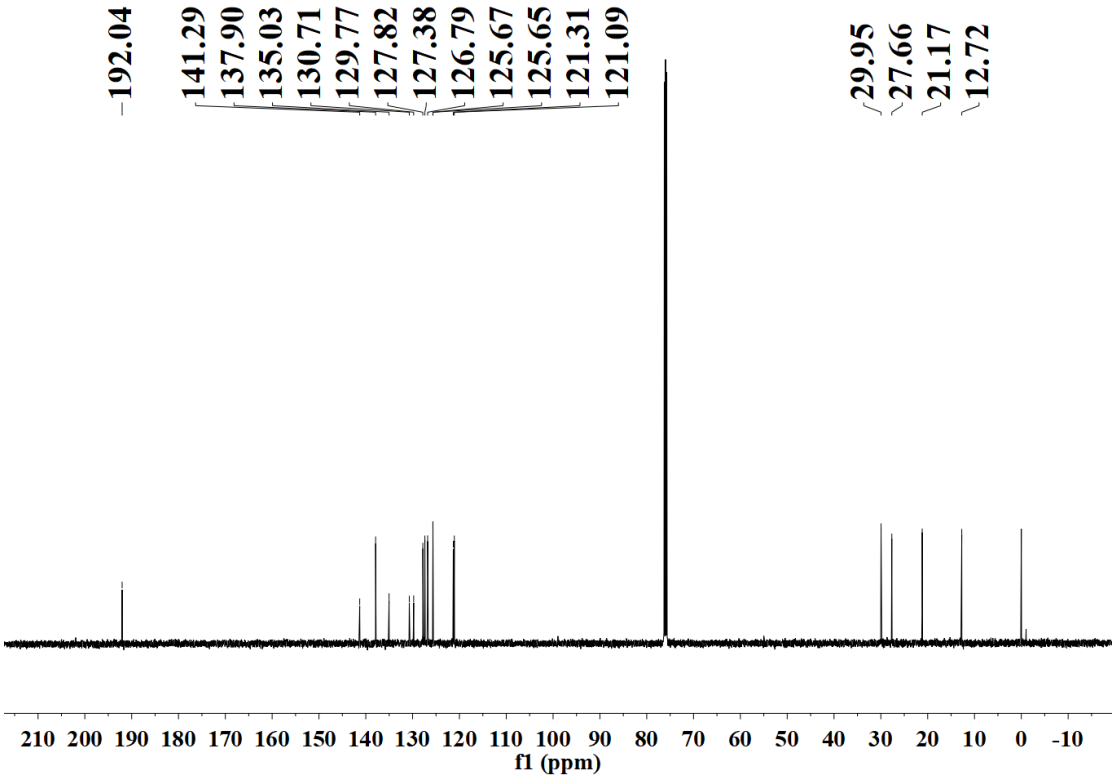
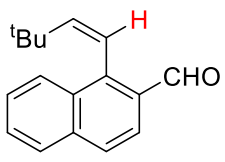
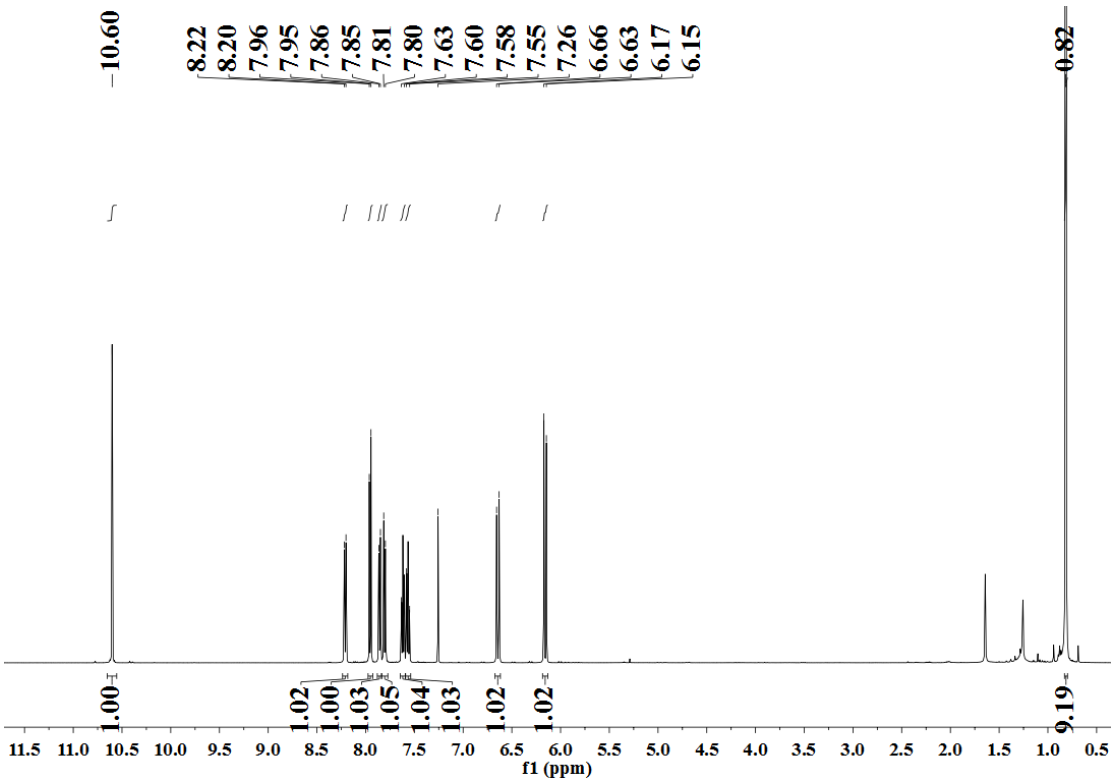
10.44
8.16
8.14
7.99
7.98
7.89
7.87
7.84
7.83
7.65
7.62
7.58
7.54
7.26
6.89
6.86
6.30
6.25
5.30
1.86
1.81
1.33
1.26
1.19
1.11
0.74
0.71
1.00
1.05
1.04
1.05
1.06
1.08
1.10
1.05
1.03
2.13
2.54
2.19
3.13
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


192.04
141.29
137.90
135.03
130.71
129.77
127.82
127.38
126.79
125.67
125.65
121.31
121.09
29.95
27.66
21.17
12.72
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)


tBu
H
CHO

(1m)


10.60
8.22
8.20
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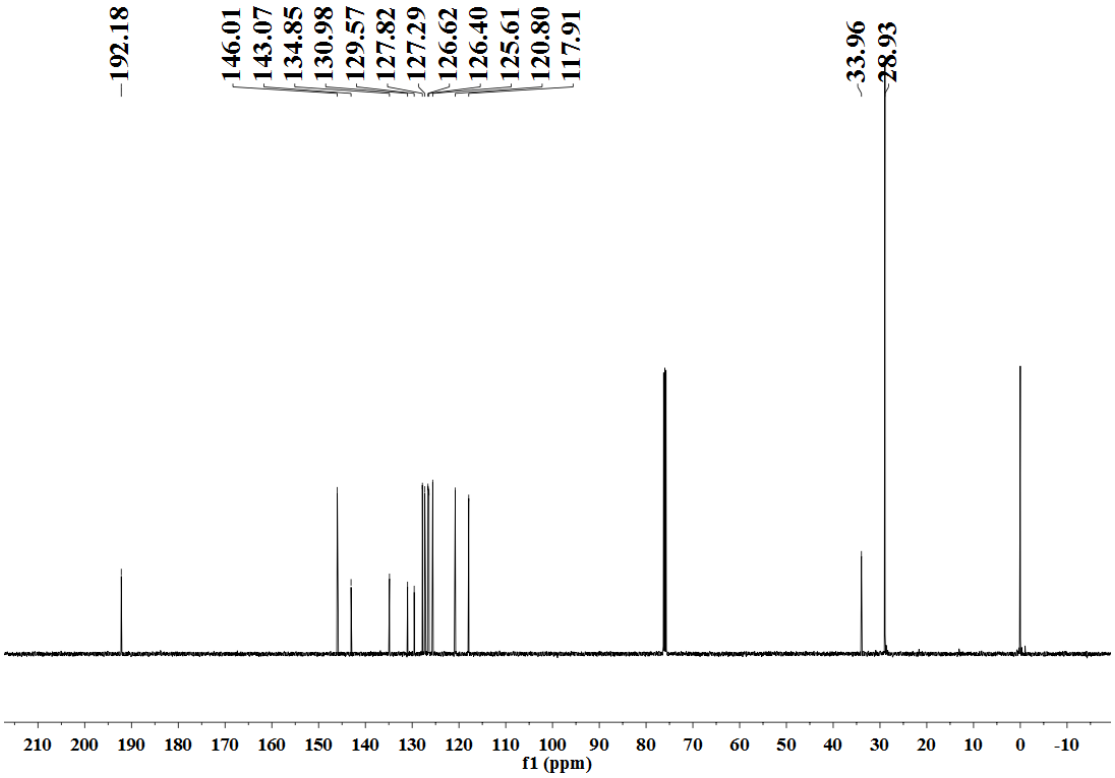
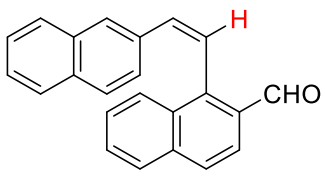
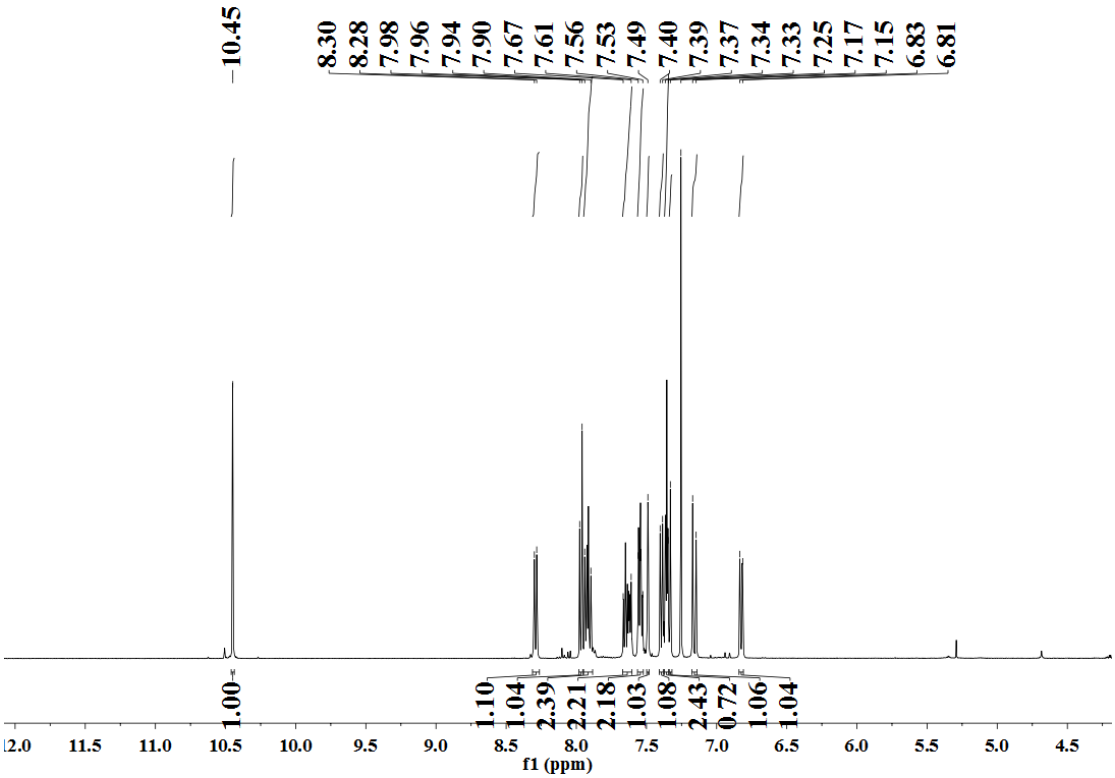
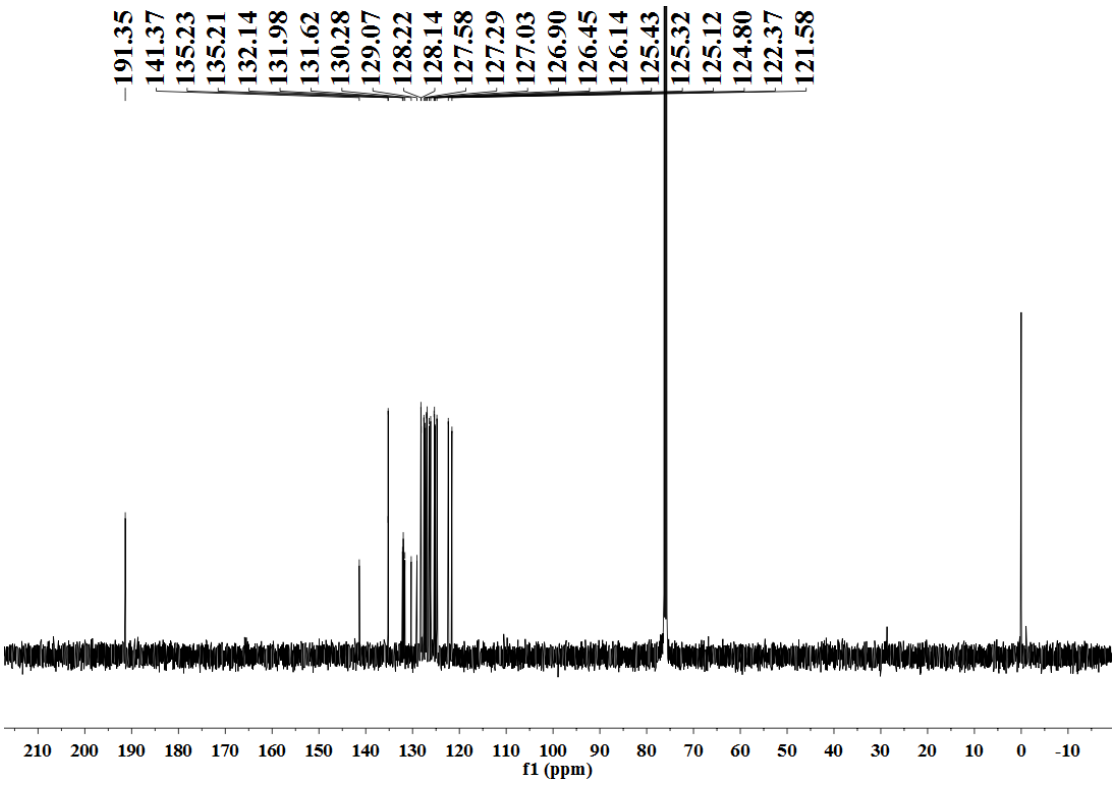
7.95
7.86
7.85
7.81
7.80
7.63
7.60
7.58
7.55
7.26
6.66
6.63
6.17
6.15
0.82
1.00
1.02
1.00
1.03
1.05
1.04
1.03
1.02
1.02
9.19
f1 (ppm)

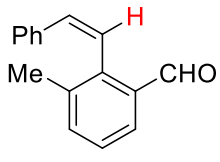

192.18
146.01
143.07
134.85
130.98
129.57
127.82
127.29
126.62
126.40
125.61
120.80
117.91
33.96
28.93
f1 (ppm)


H
CHO

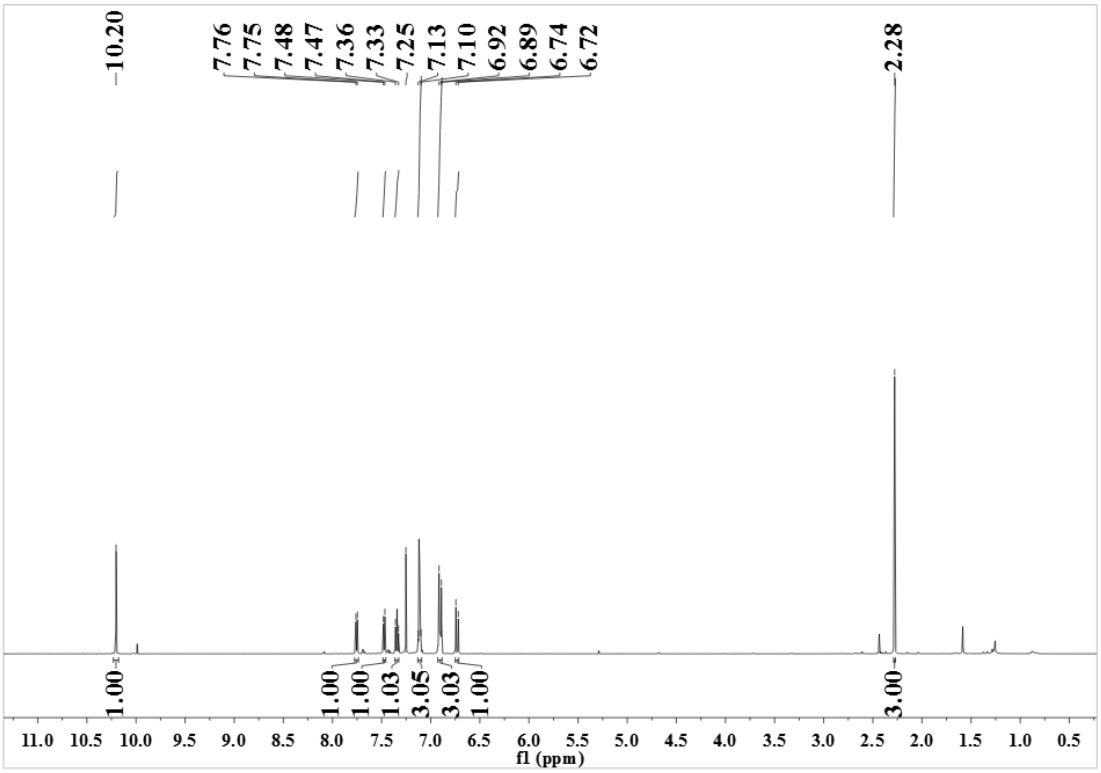
(1n)


10.45
8.30
8.28
7.98
7.96
7.94
7.90
7.67
7.61
7.56
7.53
7.49
7.40
7.39
7.37
7.34
7.33
7.25
7.17
7.15
6.83
6.81
1.00
1.10
1.04
2.39
2.21
2.18
1.03
1.08
2.43
0.72
1.06
1.04
f1 (ppm)


191.35
141.37
135.23
135.21
132.14
131.98
131.62
130.28
129.07
128.22
128.14
127.58
127.29
127.03
126.90
126.45
126.14
125.43
125.32
125.12
124.80
122.37
121.58
f1 (ppm)


Ph
H
Me
CHO

(1o)


10.20
7.76
7.75
7.48
7.47
7.36
7.33
7.25
7.13
7.10
6.92
6.89
6.74
6.72
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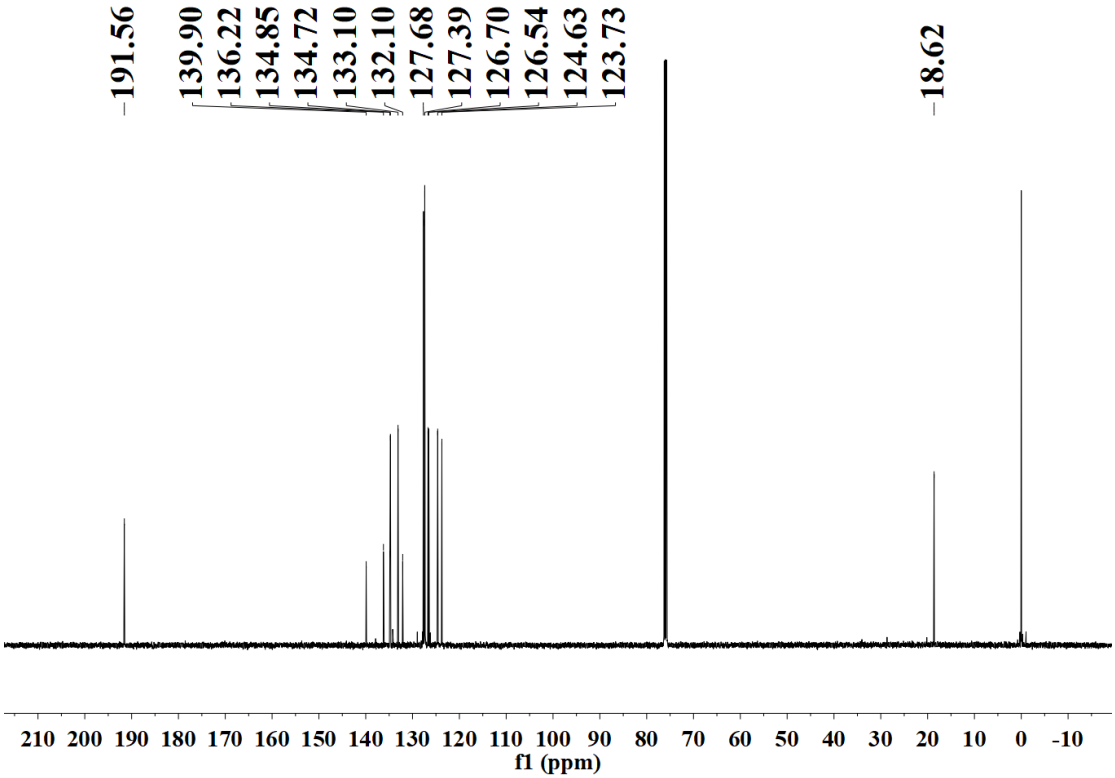
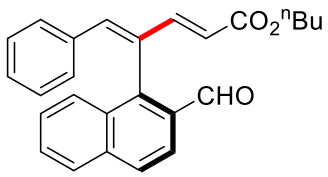
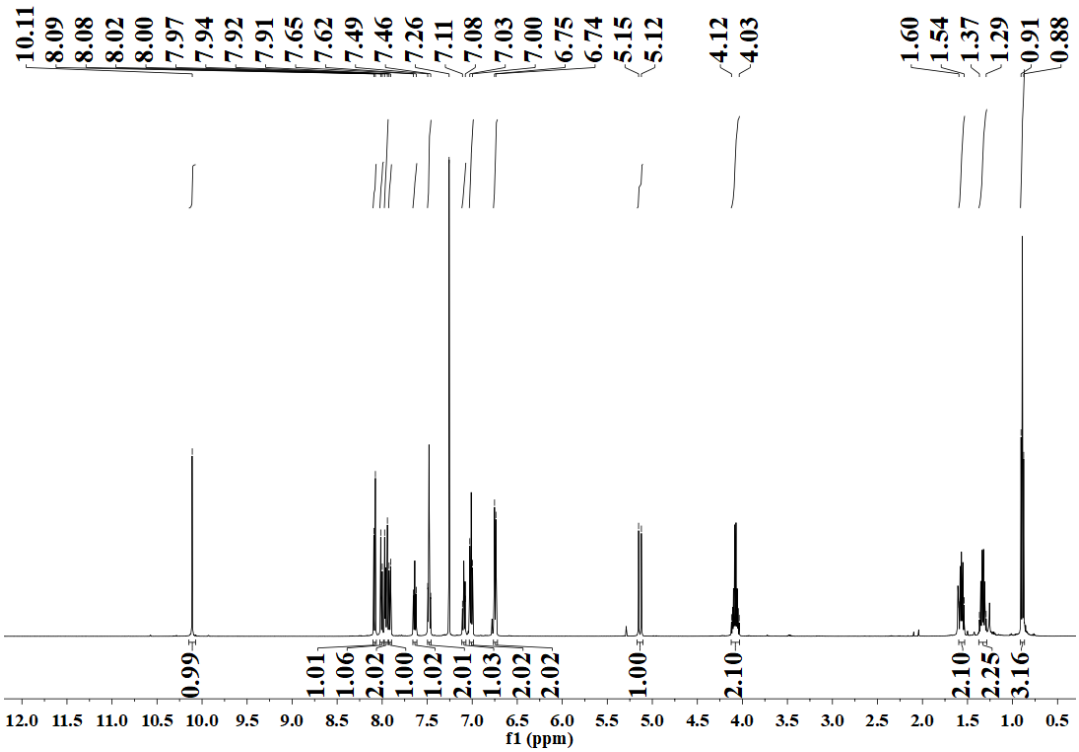
1.00
1.00
1.00
1.03
3.05
3.03
1.00
3.00
f1 (ppm)

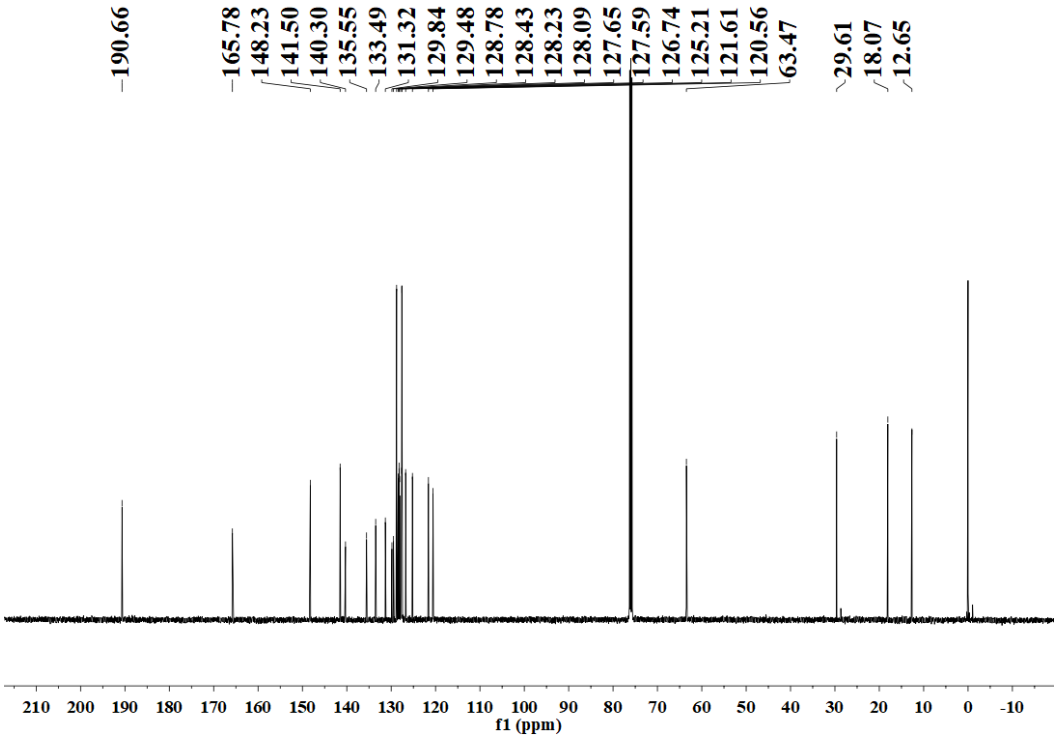

191.56
139.90
136.22
134.85
134.72
133.10
132.10
127.68
127.39
126.70
126.54
124.63
123.73
18.62
f1 (ppm)

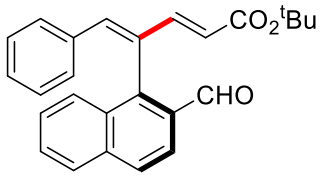
8.2 ^{1}H / ^{13}C NMR Charts of The Products



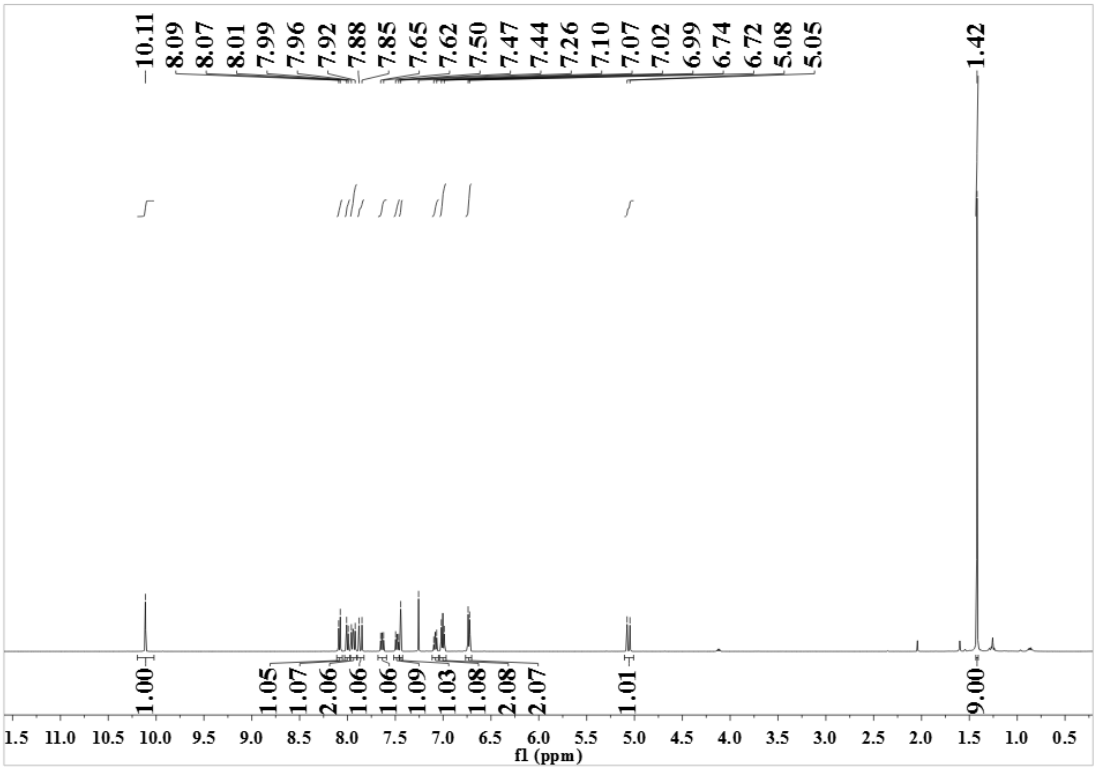
(3a)

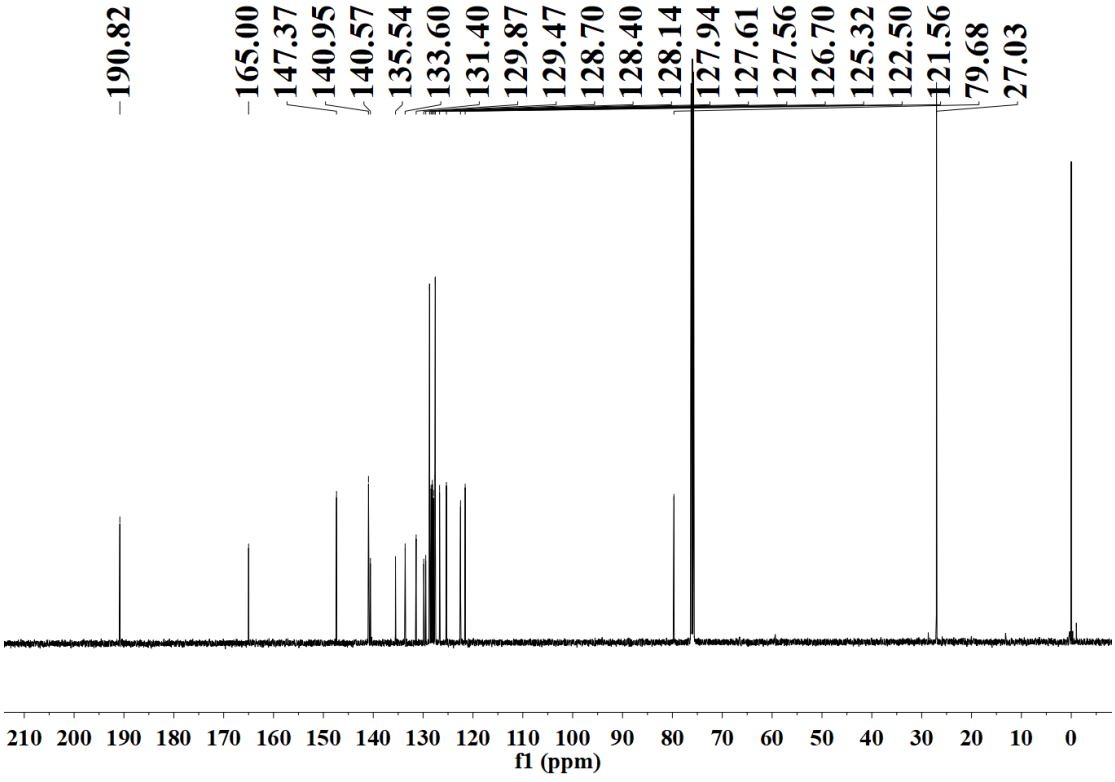


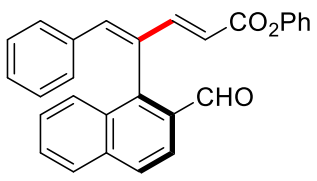



CO2tBu
CHO

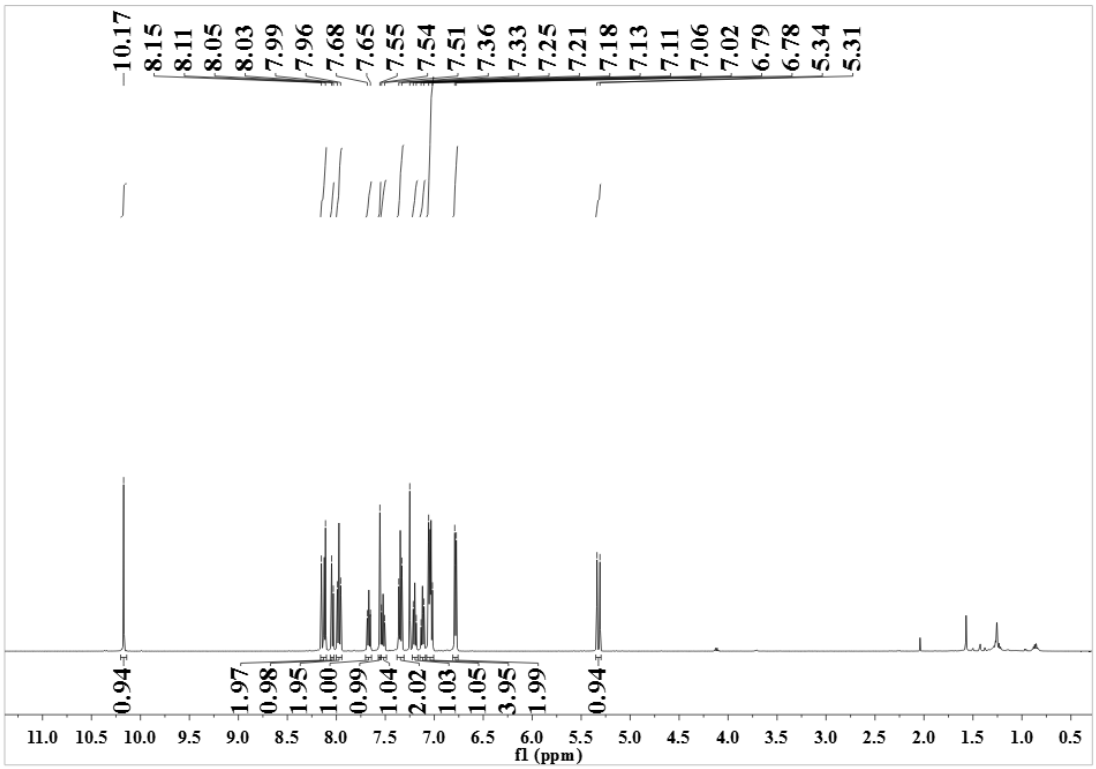
(3b)

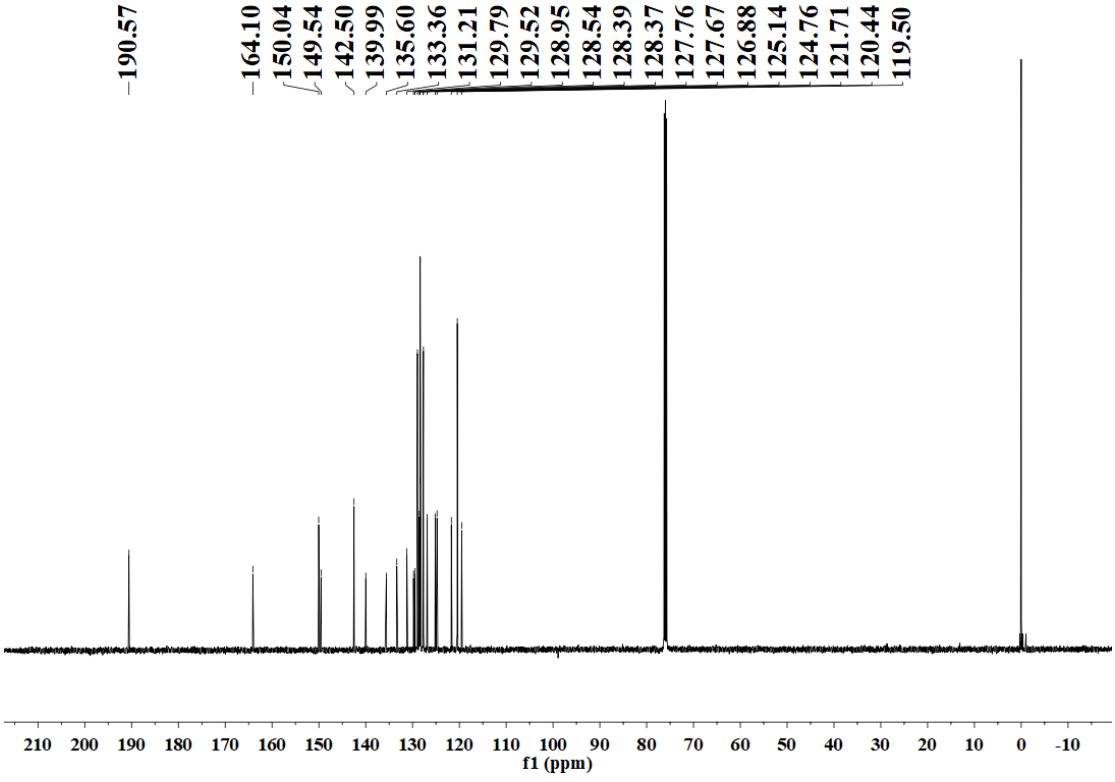

10.11
8.09
8.07
8.01
7.99
7.96
7.92
7.88
7.85
7.65
7.62
7.50
7.47
7.44
7.26
7.10
7.07
7.02
6.99
6.74
6.72
5.08
5.05
1.42
1.00
1.05
1.07
2.06
1.06
1.06
1.09
1.03
1.08
2.08
2.07
1.01
9.00
1.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

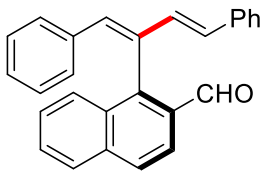

190.82
165.00
147.37
140.95
140.57
135.54
133.60
131.40
129.87
129.47
128.70
128.40
128.14
127.94
127.61
127.56
126.70
125.32
122.50
121.56
79.68
27.03
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CO2Ph
CHO

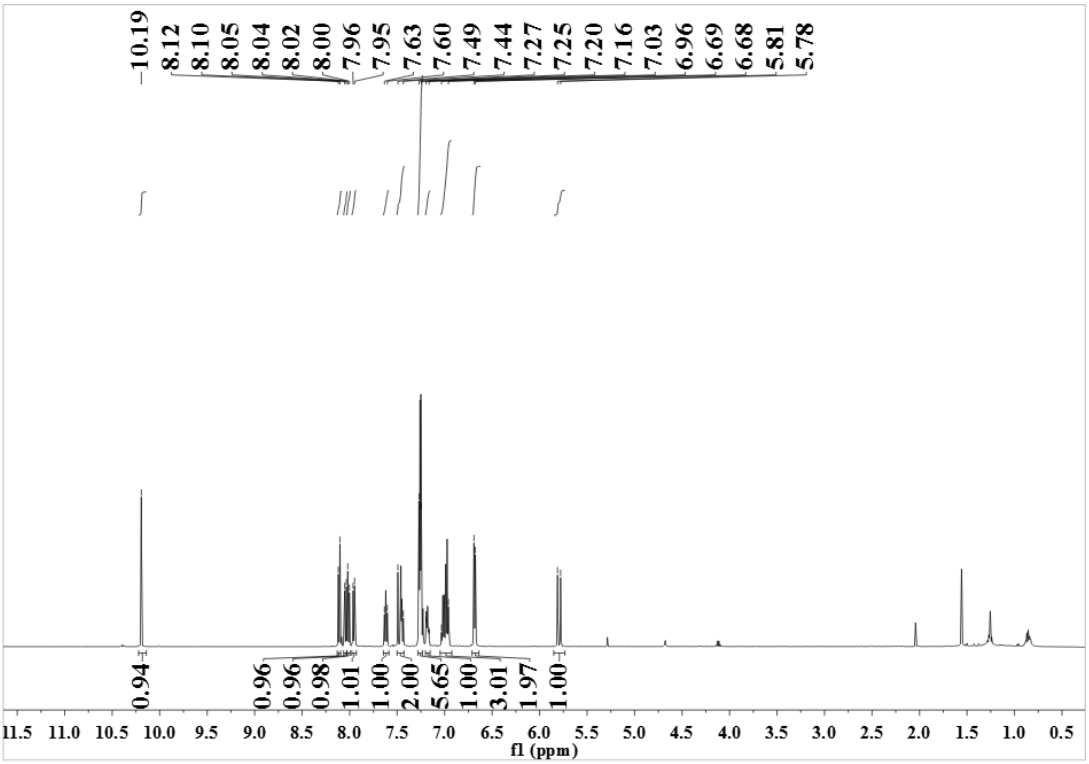
(3c)

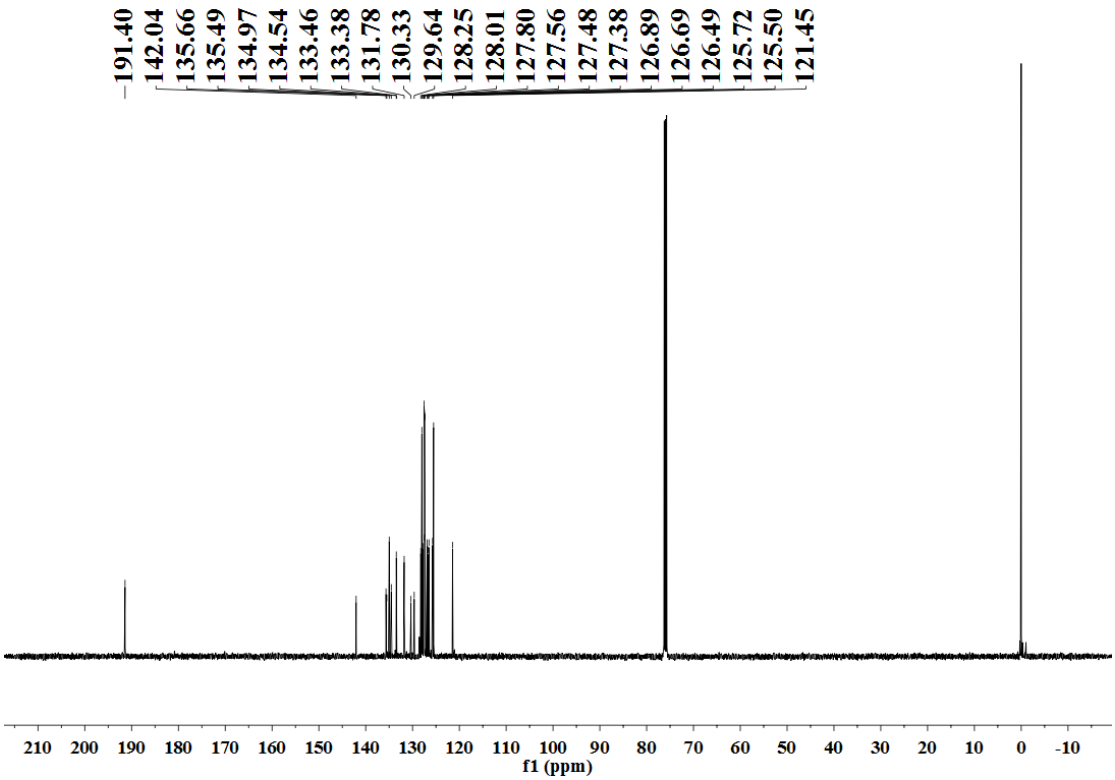

10.17
8.15
8.11
8.05
8.03
7.99
7.96
7.68
7.65
7.55
7.54
7.51
7.36
7.33
7.25
7.21
7.18
7.13
7.11
7.06
7.02
6.79
6.78
5.34
5.31
0.94
1.97
0.98
1.95
1.00
0.99
1.04
2.02
1.03
1.05
3.95
1.99
0.94
f1 (ppm)


190.57
164.10
150.04
149.54
142.50
139.99
135.60
133.36
131.21
129.79
129.52
128.95
128.54
128.39
128.37
127.76
127.67
126.88
125.14
124.76
121.71
120.44
119.50
f1 (ppm)


Ph
CHO

(3d)


10.19
8.12
8.10
8.05
8.04
8.02
8.00
7.96
7.95
7.63
7.60
7.49
7.44
7.27
7.25
7.20
7.16
7.03
6.96
6.69
6.68
5.81
5.78
0.94
0.96
0.96
0.98
1.01
1.00
2.00
5.65
1.00
3.01
1.97
1.00
f1 (ppm)


191.40
142.04
135.66
135.49
134.97
134.54
133.46
133.38
131.78
130.33
129.64
128.25
128.01
127.80
127.56
127.48
127.38
126.89
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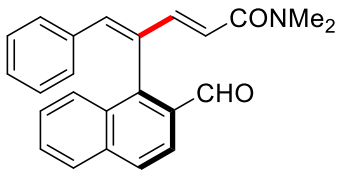
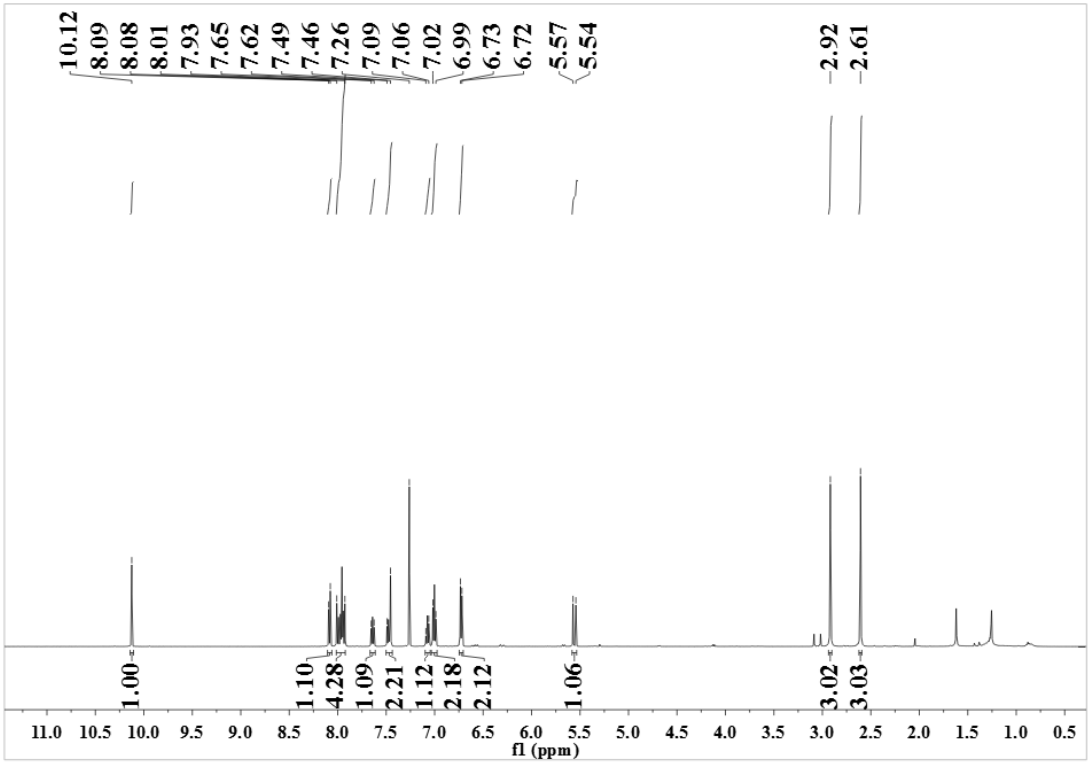
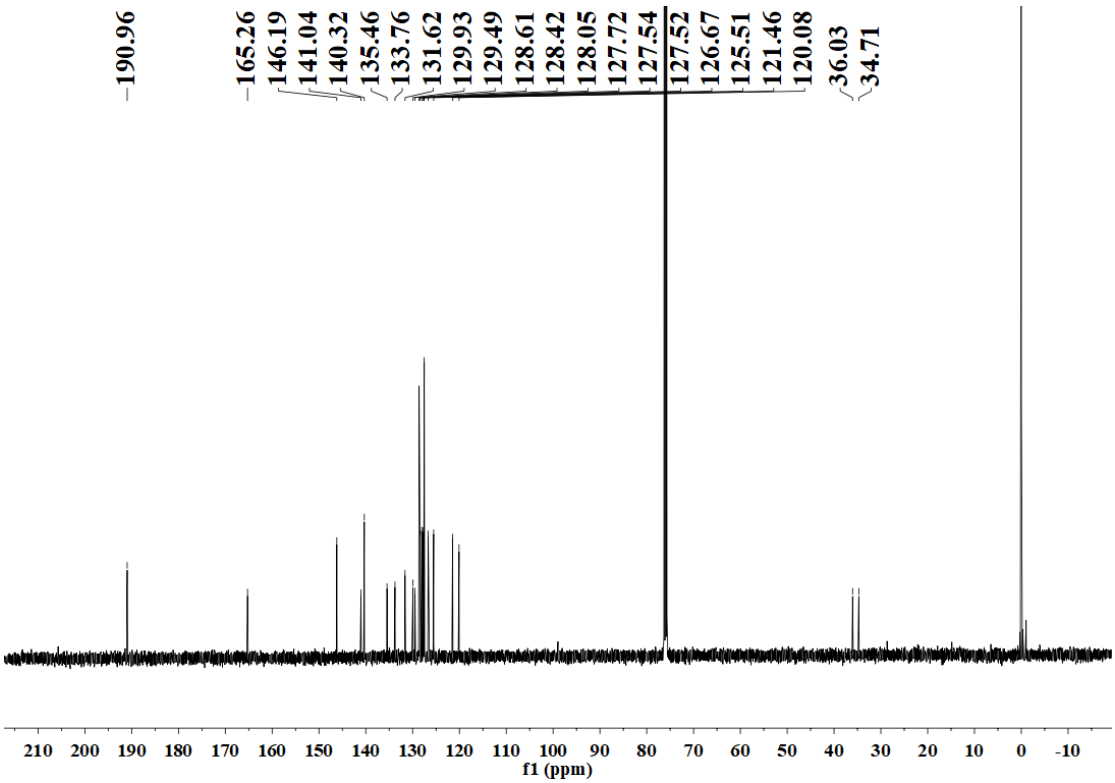
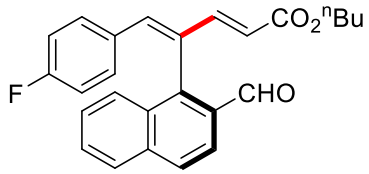
125.72
125.50
121.45
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


CONMe2
CHO

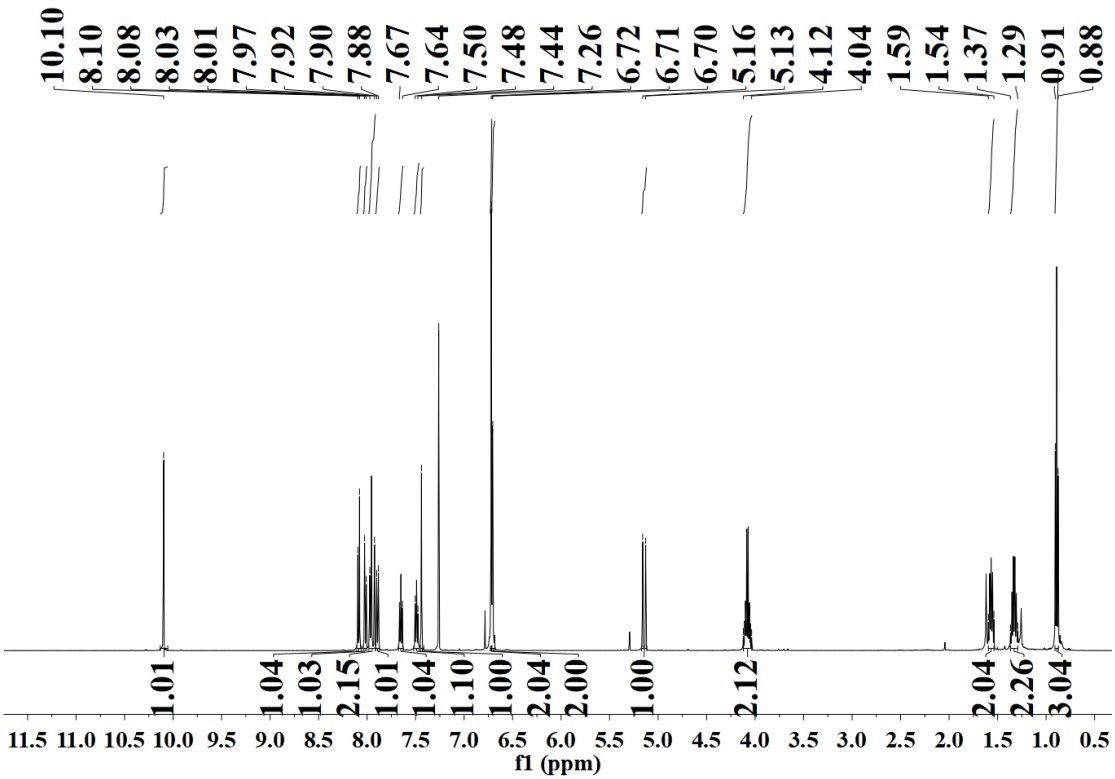
(3e)

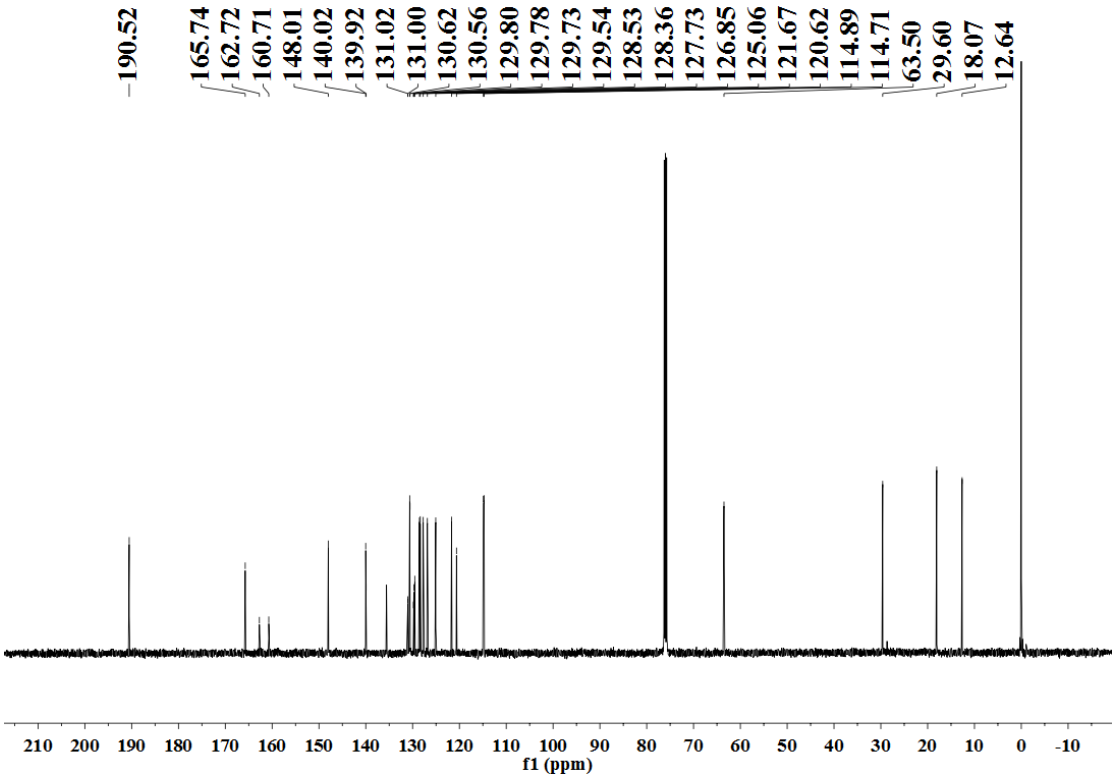

10.12
8.09
8.08
8.01
7.93
7.65
7.62
7.49
7.46
7.26
7.09
7.06
7.02
6.99
6.73
6.72
5.57
5.54
2.92
2.61
1.00
1.10
4.28
1.09
2.21
1.12
2.18
2.12
1.06
3.02
3.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

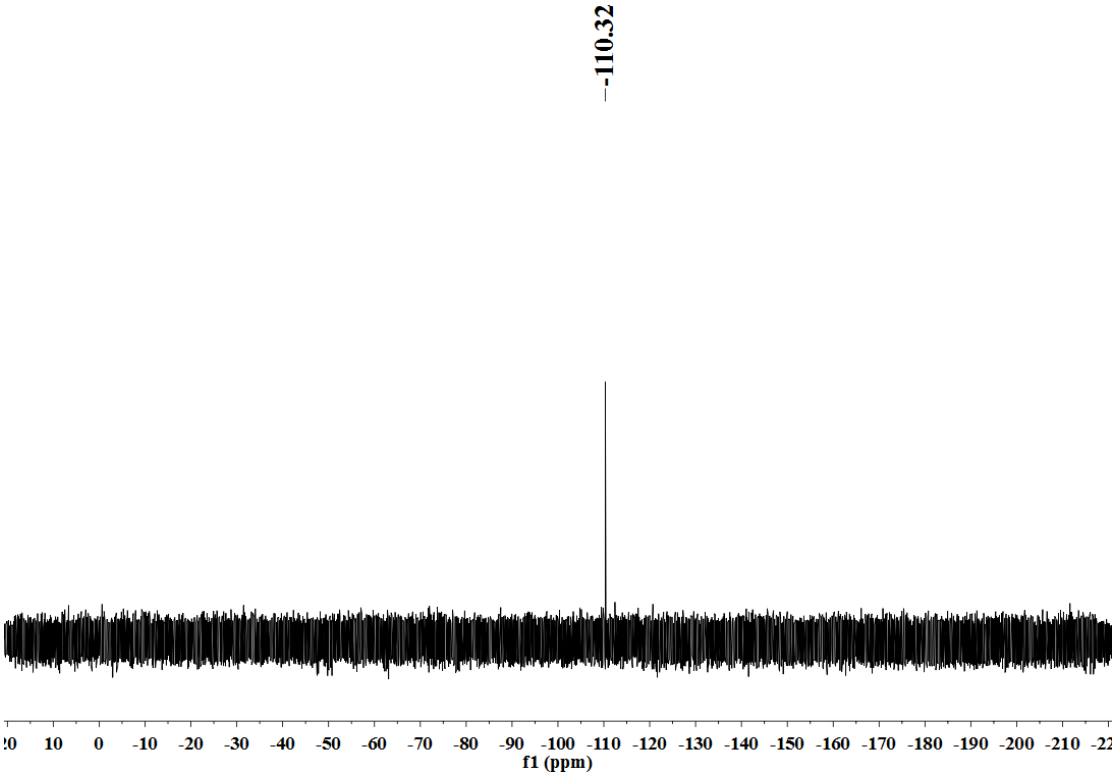

190.96
165.26
146.19
141.04
140.32
135.46
133.76
131.62
129.93
129.49
128.61
128.42
128.05
127.72
127.54
127.52
126.67
125.51
121.46
120.08
36.03
34.71
f1 (ppm)

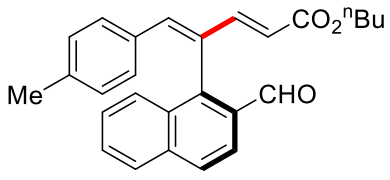

CO2nBu
F
CHO

(3f)

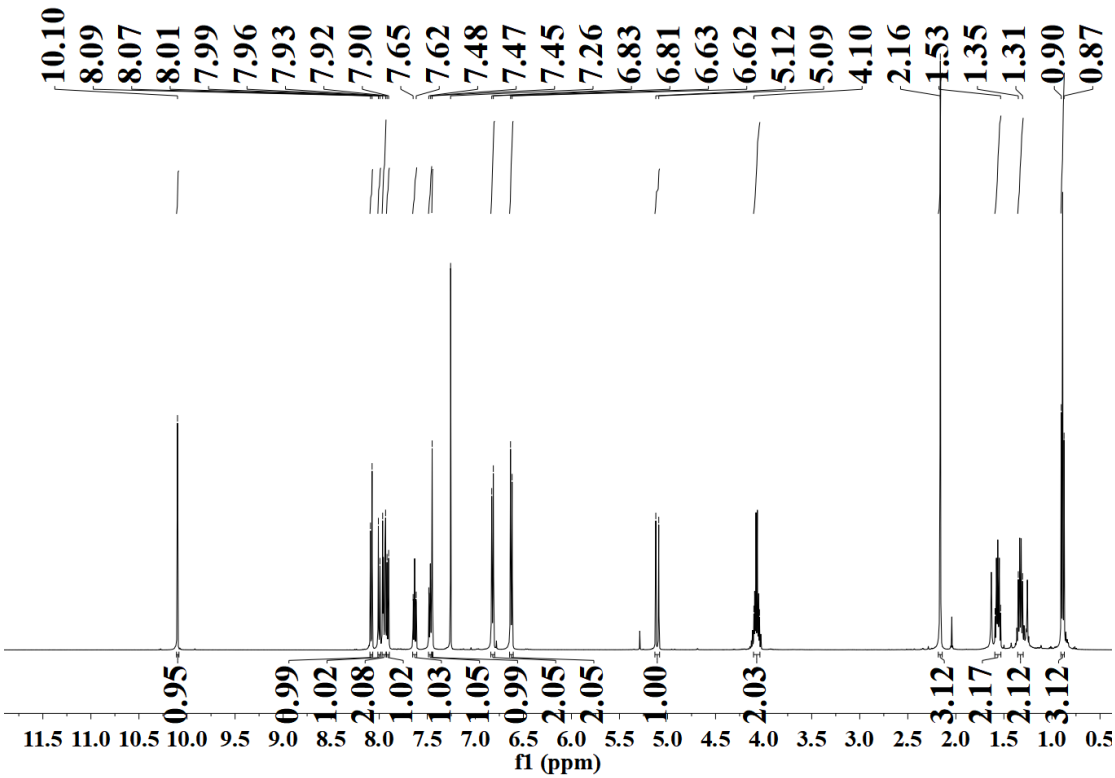

10.10
8.10
8.08
8.03
8.01
7.97
7.92
7.90
7.88
7.67
7.64
7.50
7.48
7.44
7.26
6.72
6.71
6.70
5.16
5.13
4.12
4.04
1.59
1.54
1.37
1.29
0.91
0.88
1.01
1.04
1.03
2.15
1.01
1.04
1.10
1.00
2.04
2.00
1.00
2.12
2.04
2.26
3.04
f1 (ppm)

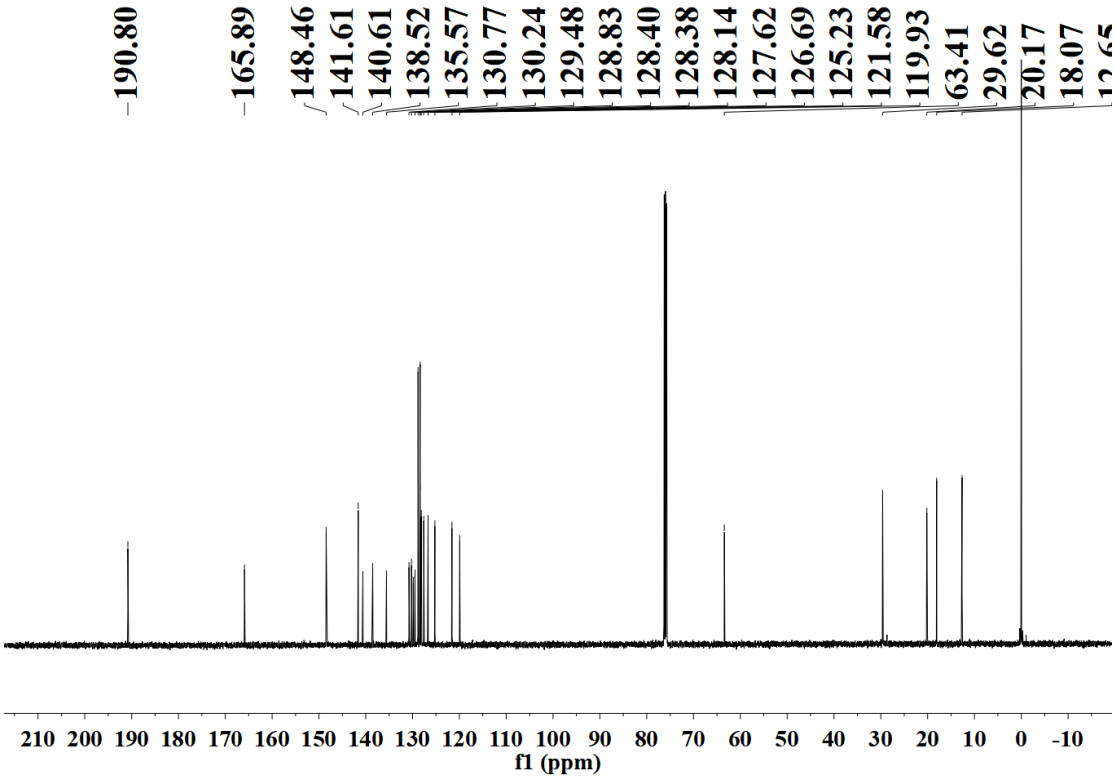

190.52
165.74
162.72
160.71
148.01
140.02
139.92
131.02
131.00
130.62
130.56
129.80
129.78
129.73
129.54
128.53
128.36
127.73
126.85
125.06
121.67
120.62
114.89
114.71
63.50
29.60
18.07
12.64
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

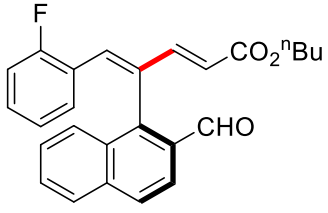

-110.32
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


CO2nBu
Me
CHO

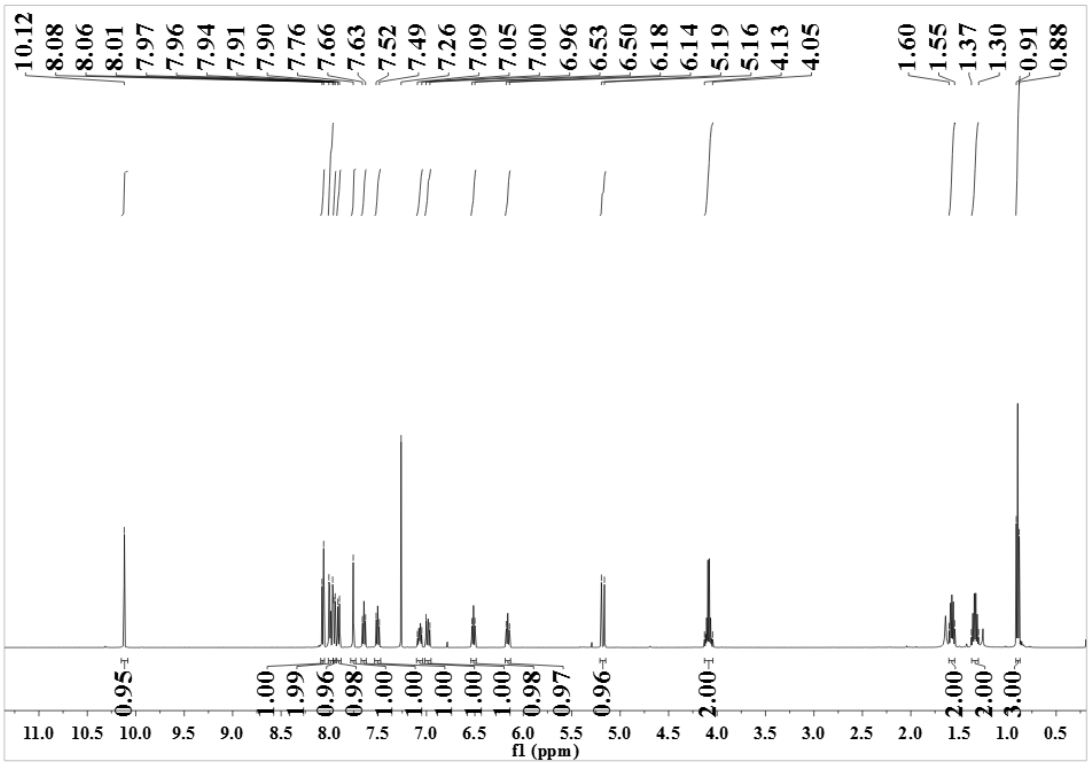
(3g)


10.10
8.09
8.07
8.01
7.99
7.96
7.93
7.92
7.90
7.65
7.62
7.48
7.47
7.45
7.26
6.83
6.81
6.63
6.62
5.12
5.09
4.10
2.16
1.53
1.35
1.31
0.90
0.87
0.95
0.99
1.02
2.08
1.02
1.03
1.05
0.99
2.05
2.05
1.00
2.03
3.12
2.17
2.12
3.12
f1 (ppm)


190.80
165.89
148.46
141.61
140.61
138.52
135.57
130.77
130.24
129.48
128.83
128.40
128.38
128.14
127.62
126.69
125.23
121.58
119.93
63.41
29.62
20.17
18.07
f1 (ppm)


F
CO2nBu
CHO

(3h)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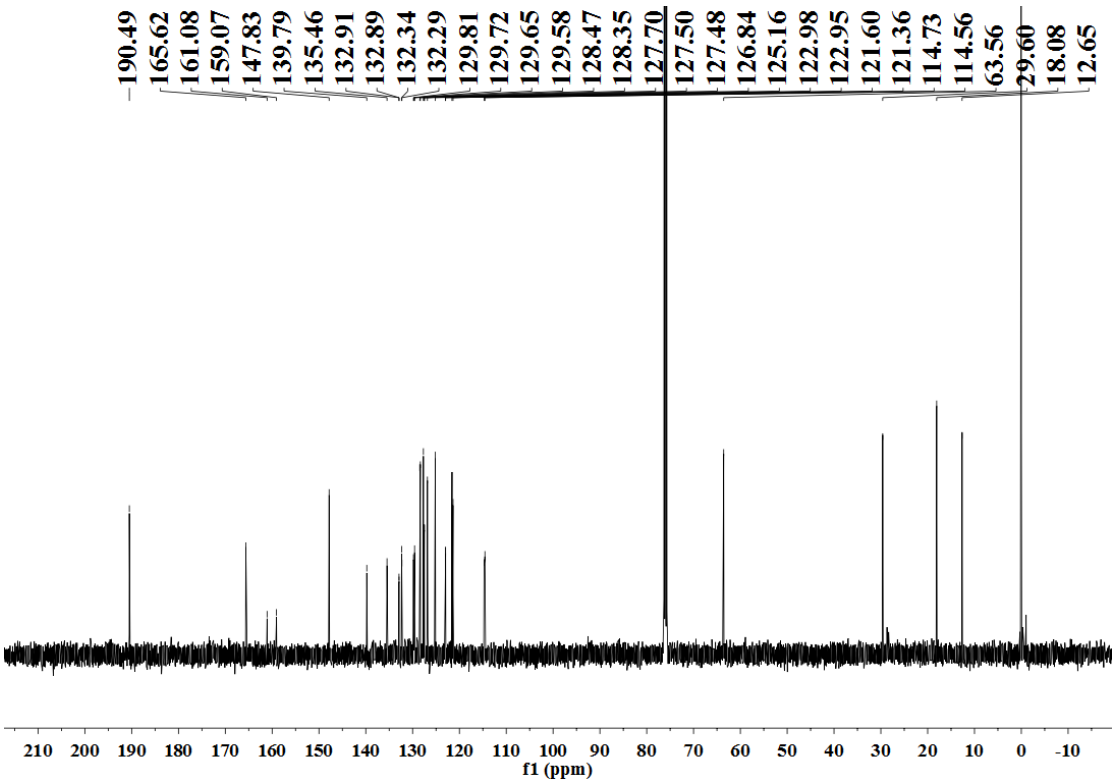
8.08
8.06
8.01
7.97
7.96
7.94
7.91
7.90
7.76
7.66
7.63
7.52
7.49
7.26
7.09
7.05
7.00
6.96
6.53
6.50
6.18
6.14
5.19
5.16
4.13
4.05
1.60
1.55
1.37
1.30
0.91
0.88
0.95
1.00
1.99
0.96
0.98
1.00
1.00
1.00
1.00
1.00
0.98
0.97
0.96
2.00
2.00
2.00
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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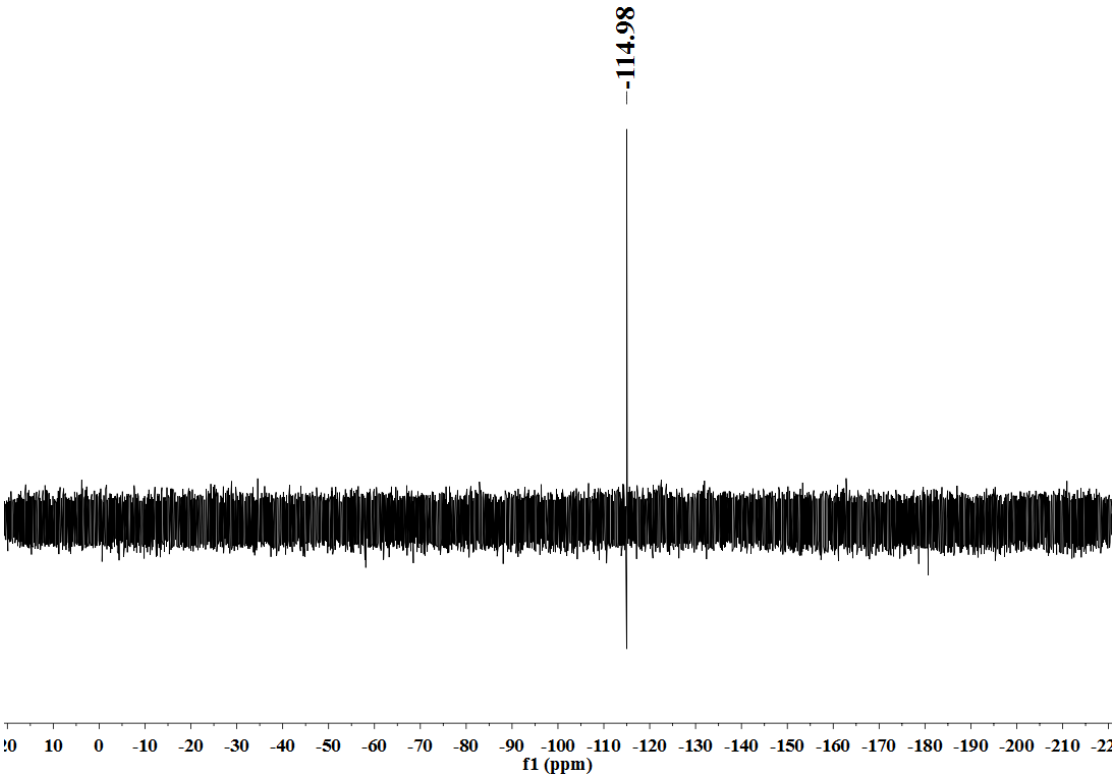
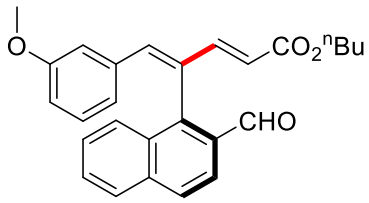
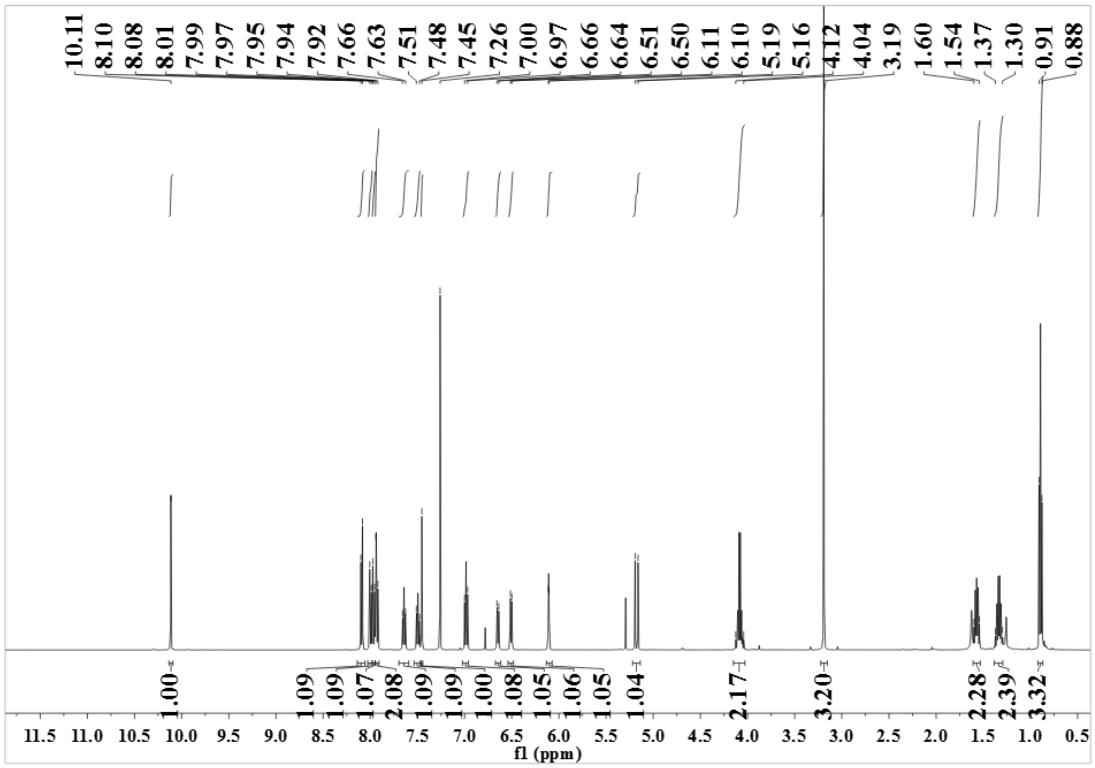
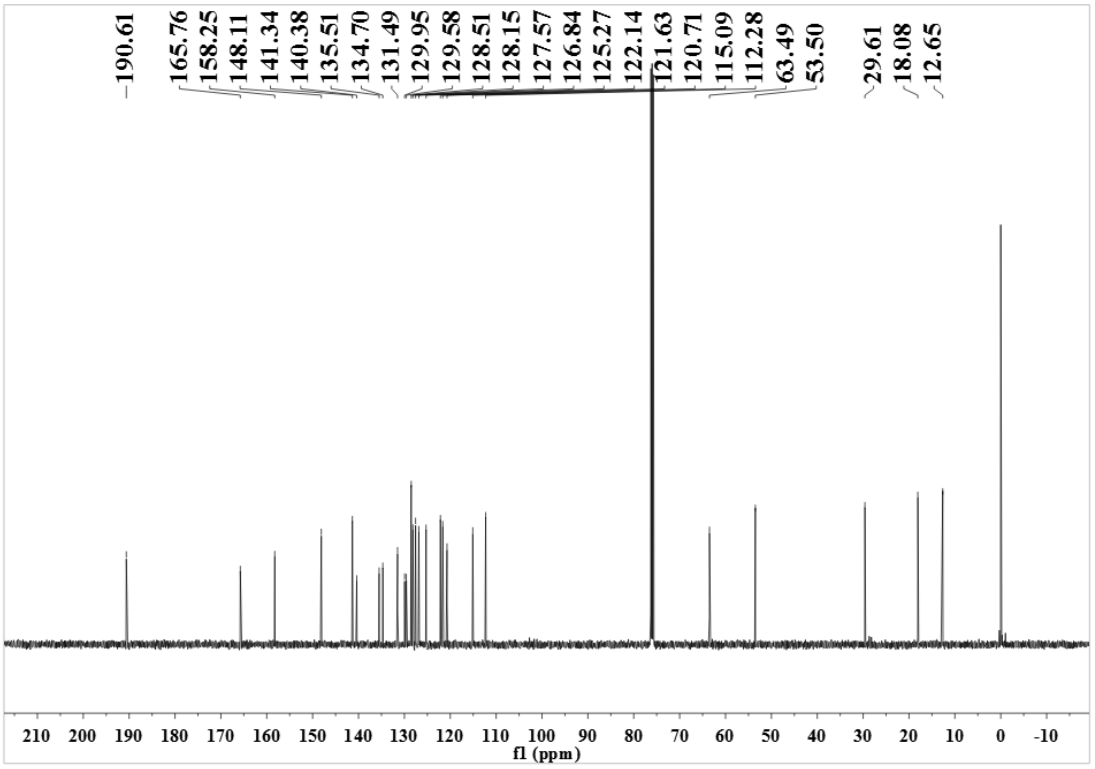
165.62
161.08
159.07
147.83
139.79
135.46
132.91
132.89
132.34
132.29
129.81
129.72
129.65
129.58
128.47
128.35
127.70
127.50
127.48
126.84
125.16
122.98
122.95
121.60
121.36
114.73
114.56
63.56
29.60
18.08
12.65
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

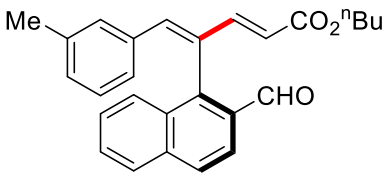

-114.98
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


O
CO2nBu
CHO

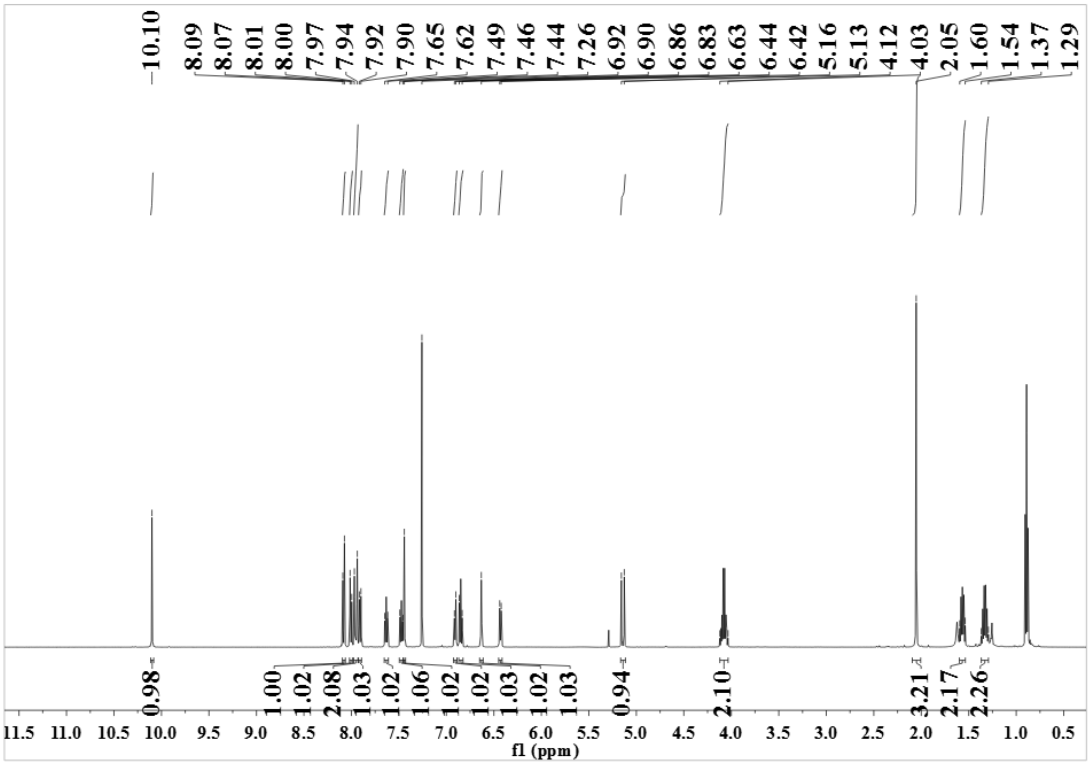
(3i)

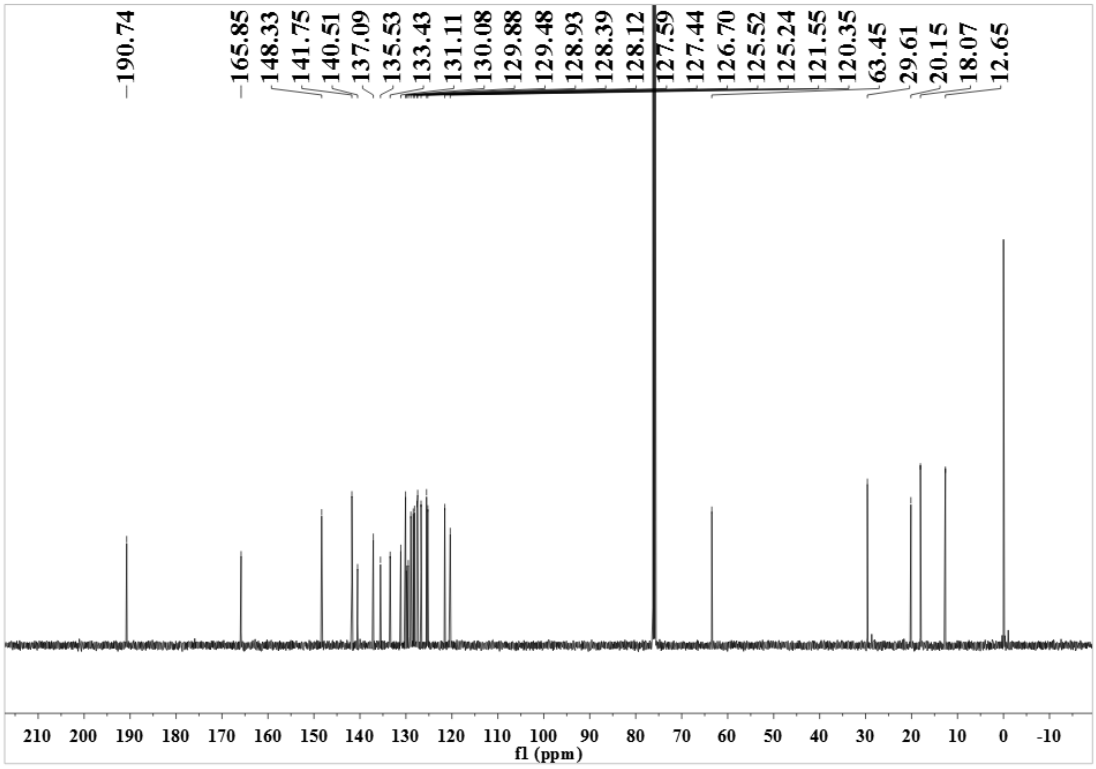

10.11
8.10
8.08
8.01
7.99
7.97
7.95
7.94
7.92
7.66
7.63
7.51
7.48
7.45
7.26
7.00
6.97
6.66
6.64
6.51
6.50
6.11
6.10
5.19
5.16
4.12
4.04
3.19
1.60
1.54
1.37
1.30
0.91
0.88
1.00
1.09
1.09
1.07
2.08
1.09
1.09
1.00
1.08
1.05
1.06
1.05
1.04
2.17
3.20
2.28
2.39
3.32
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 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)


190.61
165.76
158.25
148.11
141.34
140.38
135.51
134.70
131.49
129.95
129.58
128.51
128.15
127.57
126.84
125.27
122.14
121.63
120.71
115.09
112.28
63.49
53.50
29.61
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)


Me
CO2nBu
CHO

(3j)


10.10
8.09
8.07
8.01
8.00
7.97
7.94
7.92
7.90
7.65
7.62
7.49
7.46
7.44
7.26
6.92
6.90
6.86
6.83
6.63
6.44
6.42
5.16
5.13
4.12
4.03
2.05
1.60
1.54
1.37
1.29
0.98
1.00
1.02
2.08
1.03
1.02
1.06
1.02
1.02
1.03
1.02
1.03
0.94
2.10
3.21
2.17
2.26
fl (ppm)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165.85
148.33
141.75
140.51
137.09
135.53
133.43
131.11
130.08
129.88
129.48
128.93
128.39
128.12
127.59
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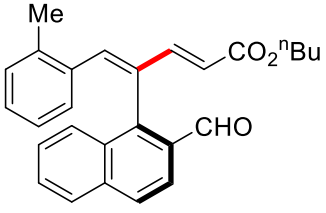
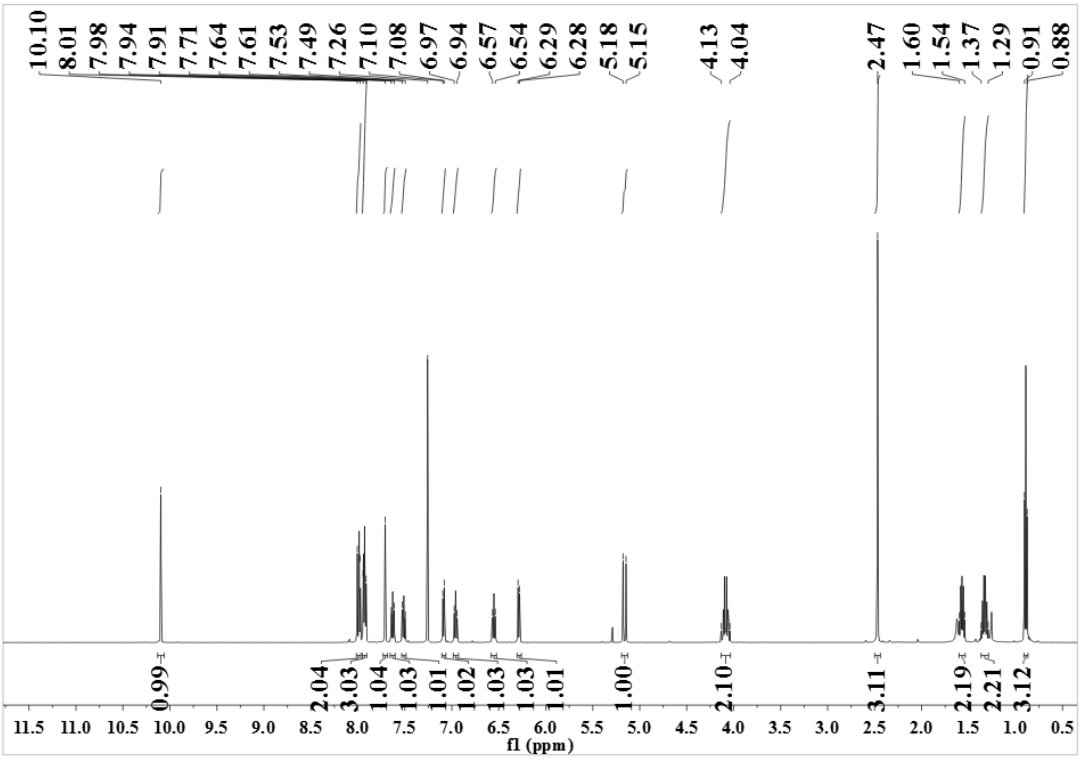
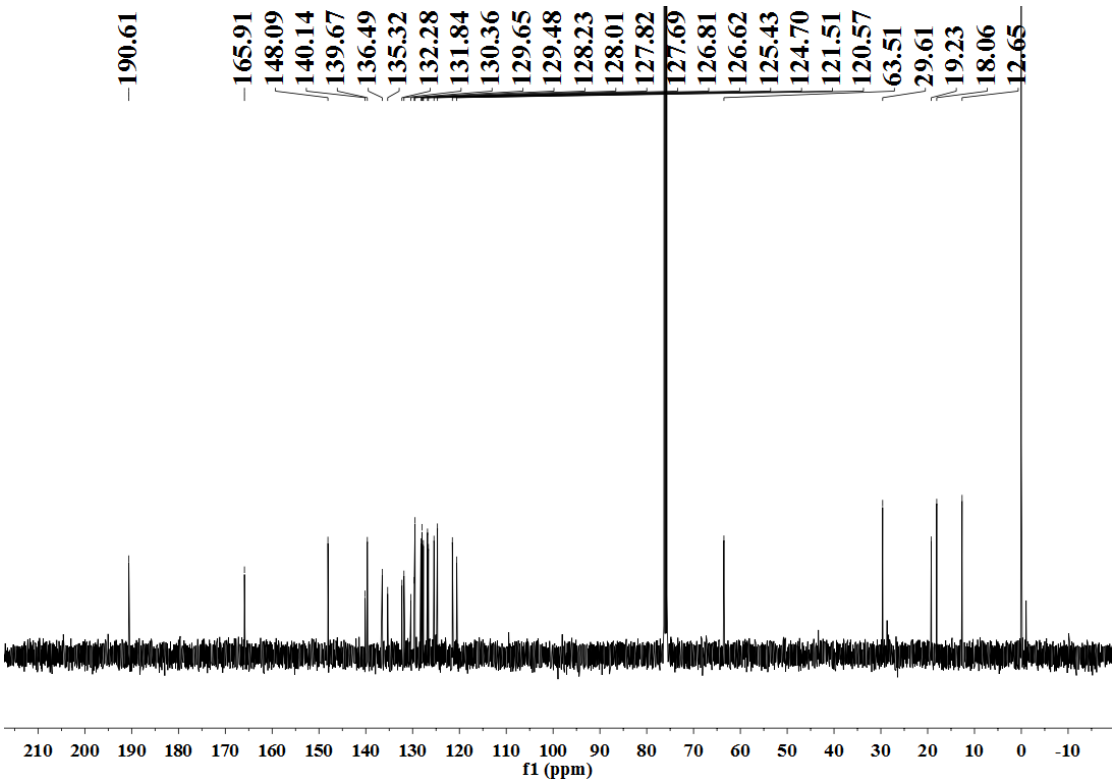
121.55
120.35
63.45
29.61
20.15
18.07
12.65
fl (ppm)


Me
CO2nBu
CHO

(3k)


10.10
8.01
7.98
7.94
7.91
7.71
7.64
7.61
7.53
7.49
7.26
7.10
7.08
6.97
6.94
6.57
6.54
6.29
6.28
5.18
5.15
4.13
4.04
2.47
1.60
1.54
1.37
1.29
0.91
0.88
0.99
2.04
3.03
1.04
1.03
1.01
1.02
1.03
1.03
1.01
1.00
2.10
3.11
2.19
2.21
3.12
f1 (ppm)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165.91
148.09
140.14
139.67
136.49
135.32
132.28
131.84
130.36
129.65
129.48
128.23
128.01
127.82
127.69
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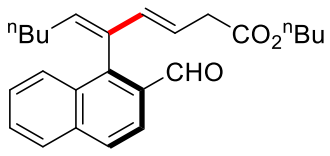
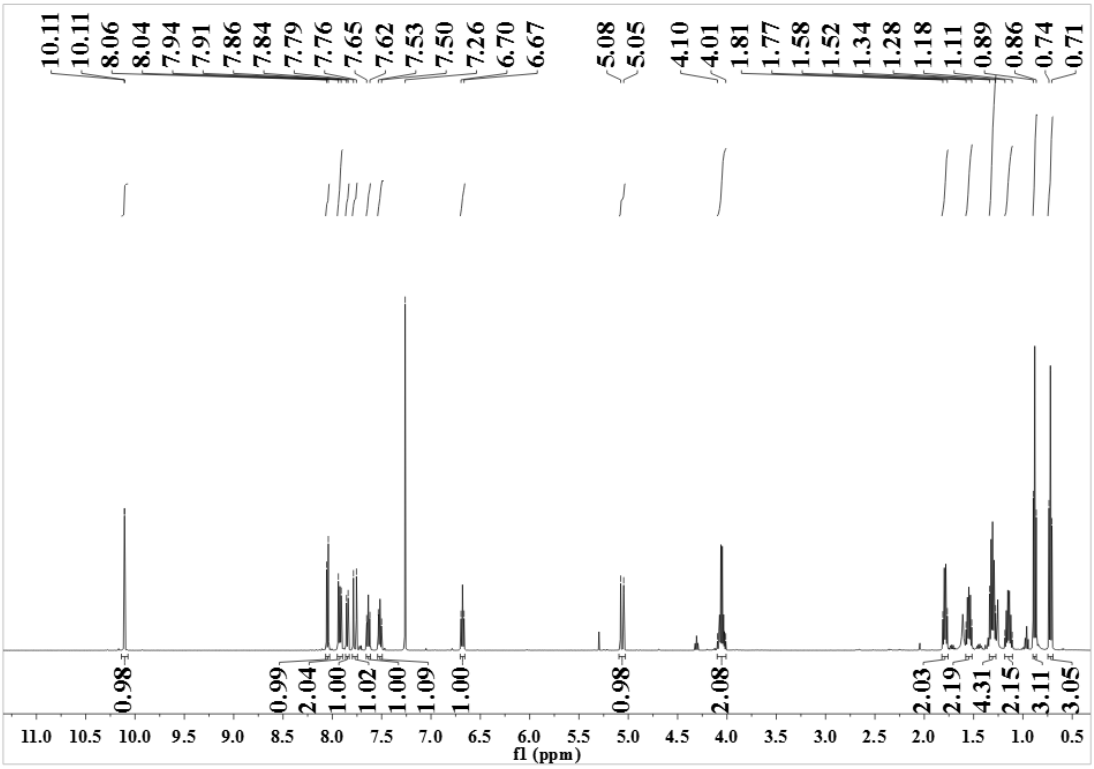
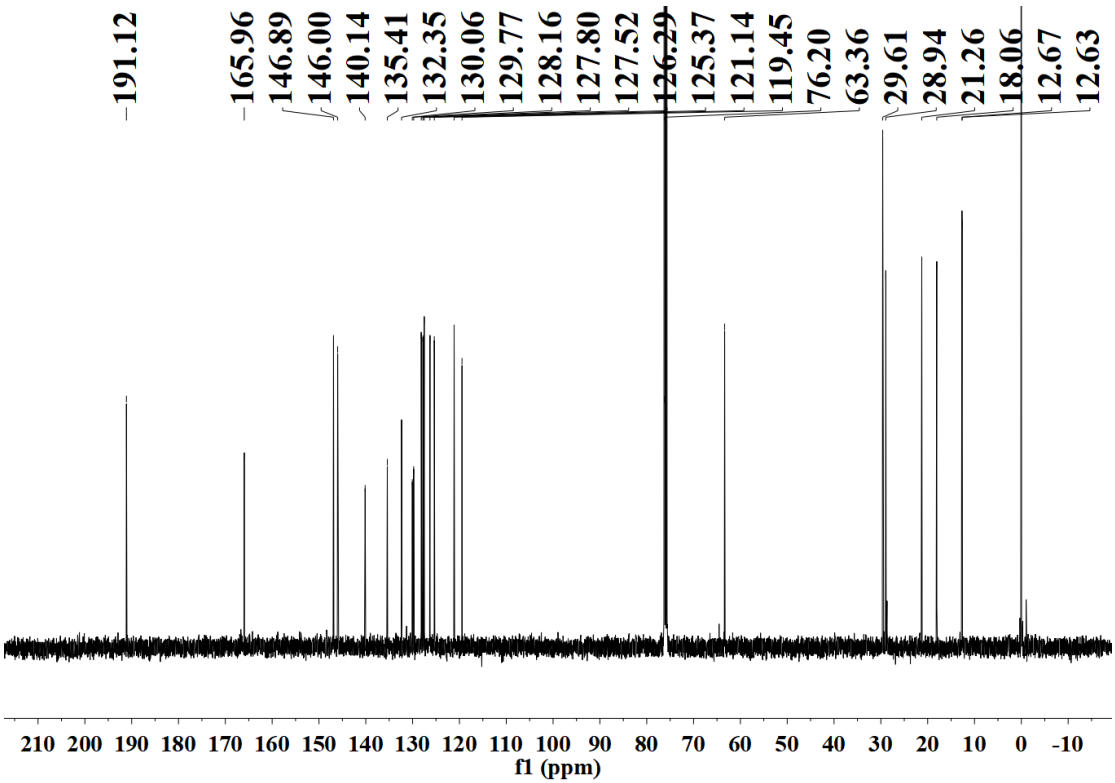
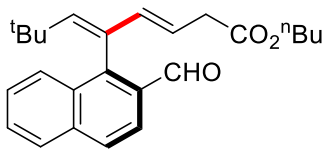
121.51
120.57
63.51
29.61
19.23
18.06
12.65
f1 (ppm)


nBu
CO2nBu
CHO

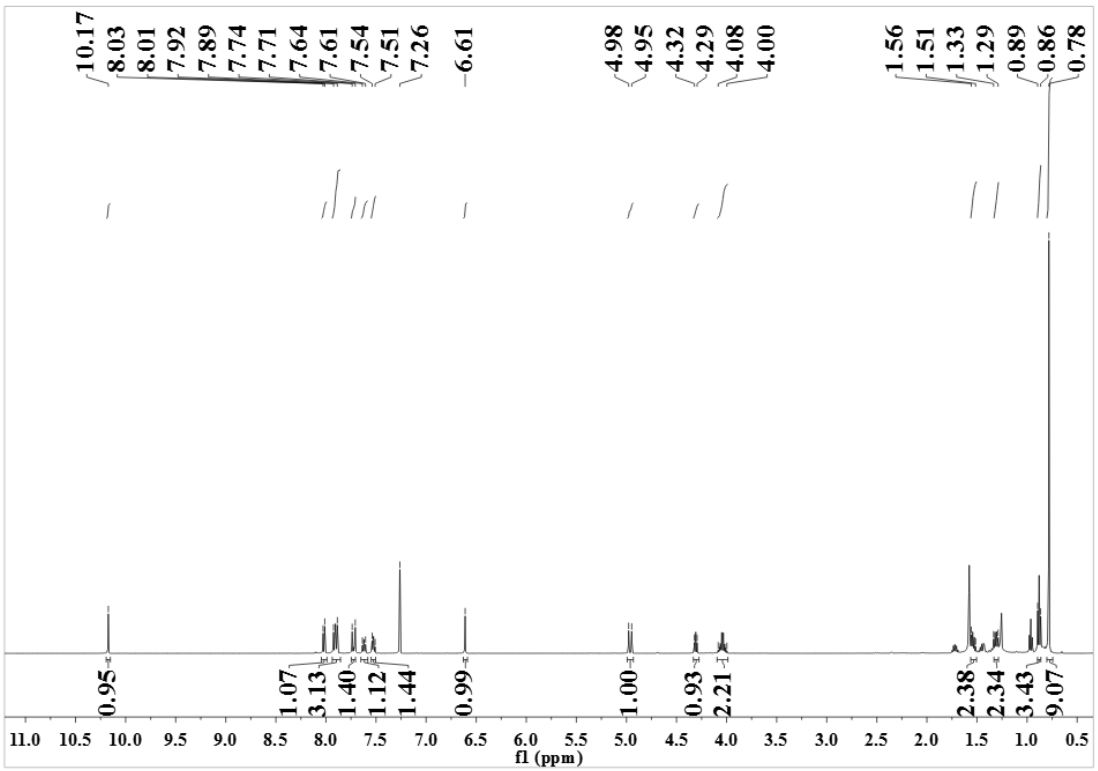
(3l)

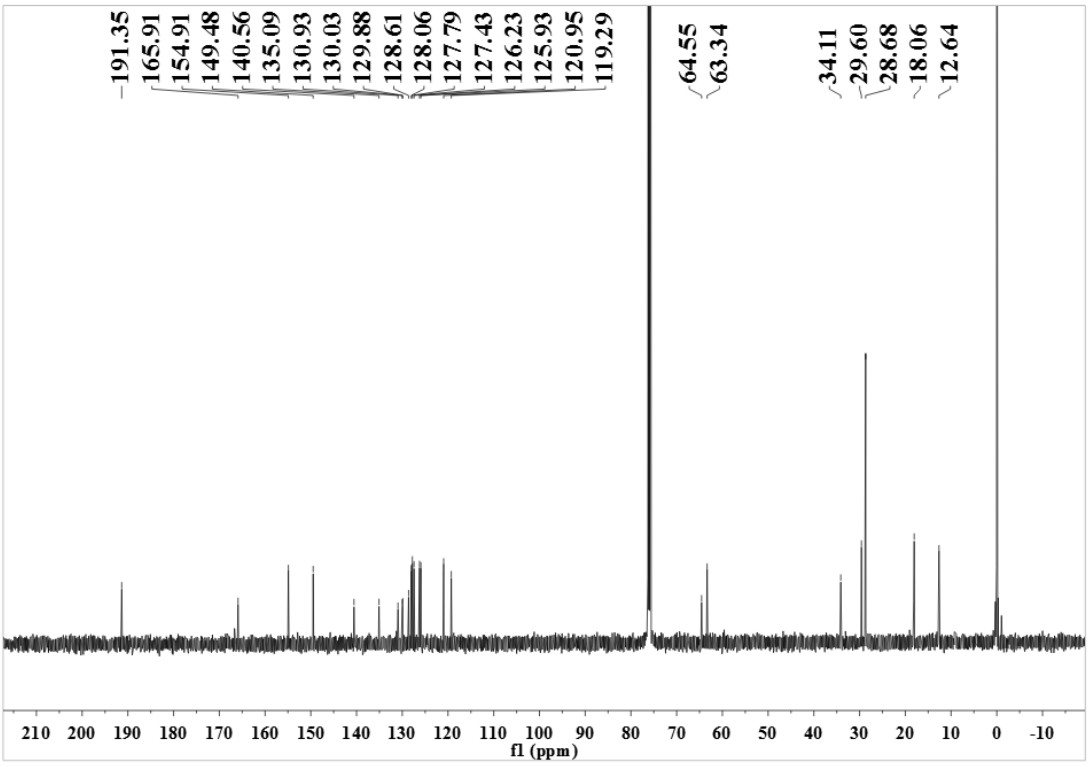

10.11
10.11
8.06
8.04
7.94
7.91
7.86
7.84
7.79
7.76
7.65
7.62
7.53
7.50
7.26
6.70
6.67
5.08
5.05
4.10
4.01
1.81
1.77
1.58
1.52
1.34
1.28
1.18
1.11
0.89
0.86
0.74
0.71
0.98
0.99
2.04
1.00
1.02
1.00
1.09
1.00
0.98
2.08
2.03
2.19
4.31
2.15
3.11
3.05
f1 (ppm)

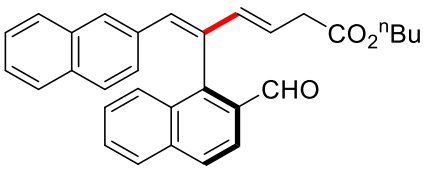

191.12
165.96
146.89
146.00
140.14
135.41
132.35
130.06
129.77
128.16
127.80
127.52
126.29
125.37
121.14
119.45
76.20
63.36
29.61
28.94
21.26
18.06
12.67
12.63
f1 (ppm)


tBu
CO2nBu
CHO

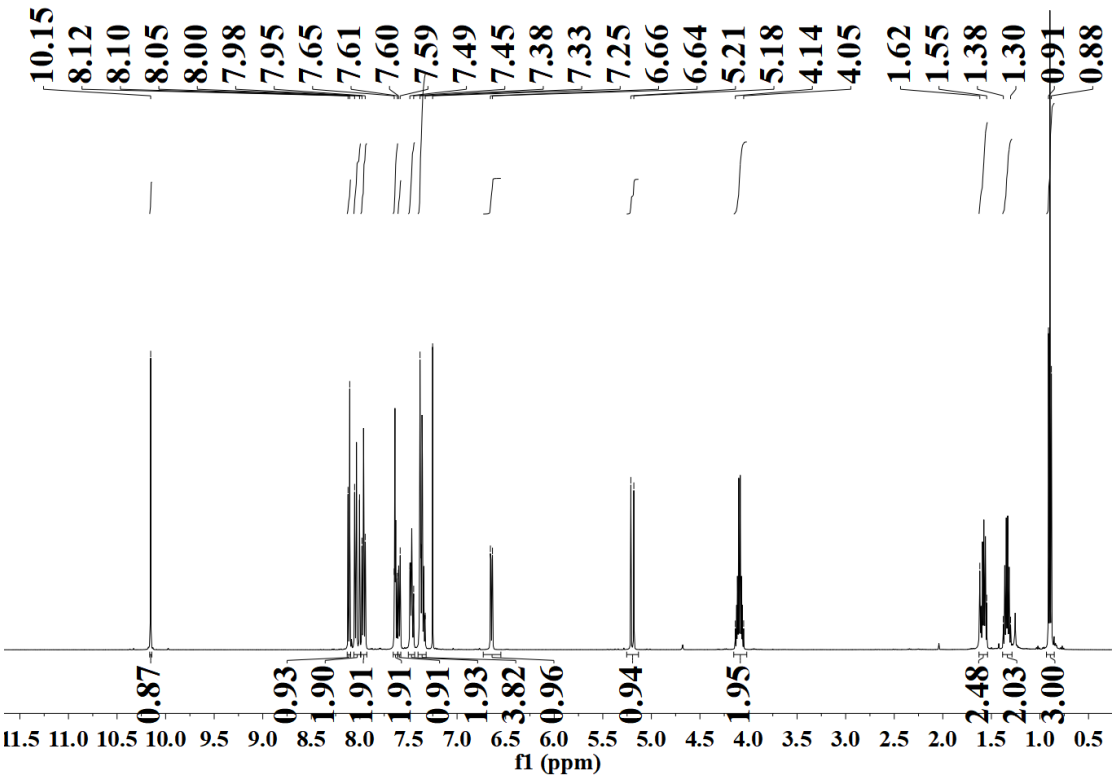
(3m)

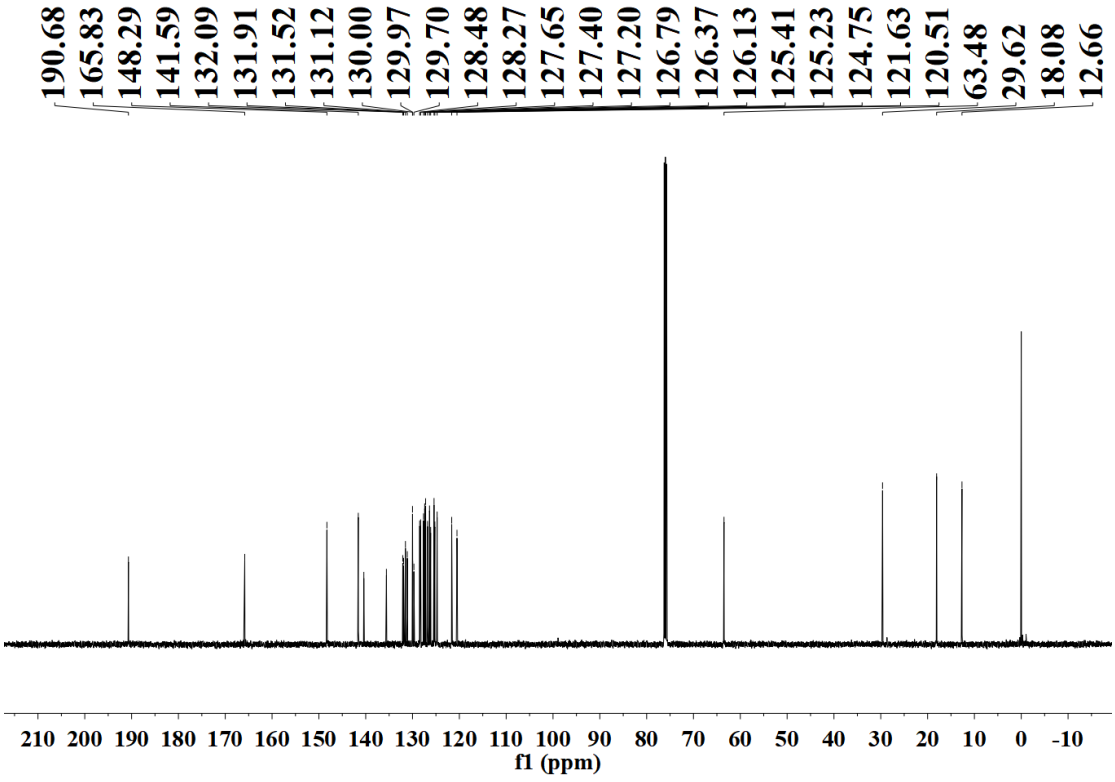

10.17
8.03
8.01
7.92
7.89
7.74
7.71
7.64
7.61
7.54
7.51
7.26
6.61
4.98
4.95
4.32
4.29
4.08
4.00
1.56
1.51
1.33
1.29
0.89
0.86
0.78
0.95
1.07
3.13
1.40
1.12
1.44
0.99
1.00
0.93
2.21
2.38
2.34
3.43
9.07
fl (ppm)


191.35
165.91
154.91
149.48
140.56
135.09
130.93
130.03
129.88
128.61
128.06
127.79
127.43
126.23
125.93
120.95
119.29
64.55
63.34
34.11
29.60
28.68
18.06
12.64
fl (ppm)


CO2nBu
CHO

(3n)


10.15
8.12
8.10
8.05
8.00
7.98
7.95
7.65
7.61
7.60
7.59
7.49
7.45
7.38
7.33
7.25
6.66
6.64
5.21
5.18
4.14
4.05
1.62
1.55
1.38
1.30
0.91
0.88
0.87
0.93
1.90
1.91
1.91
0.91
1.93
3.82
0.96
0.94
1.95
2.48
2.03
3.00
f1 (ppm)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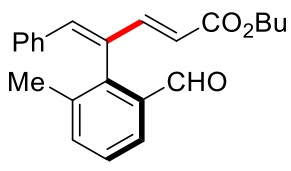
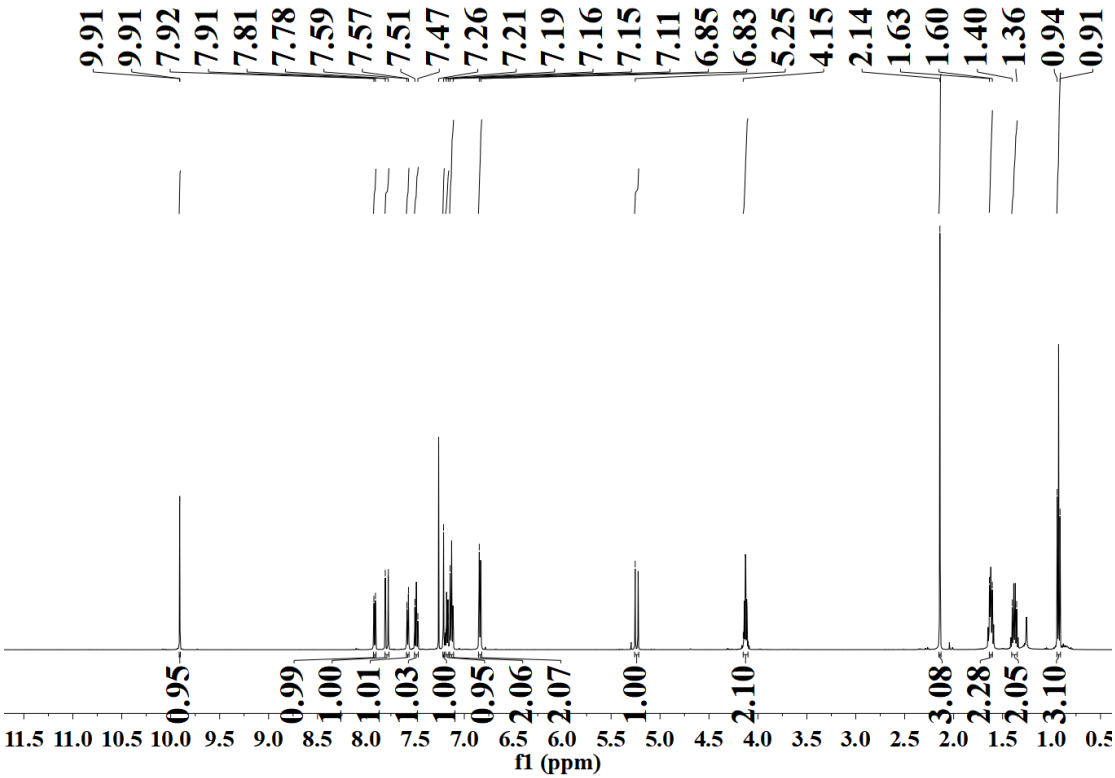
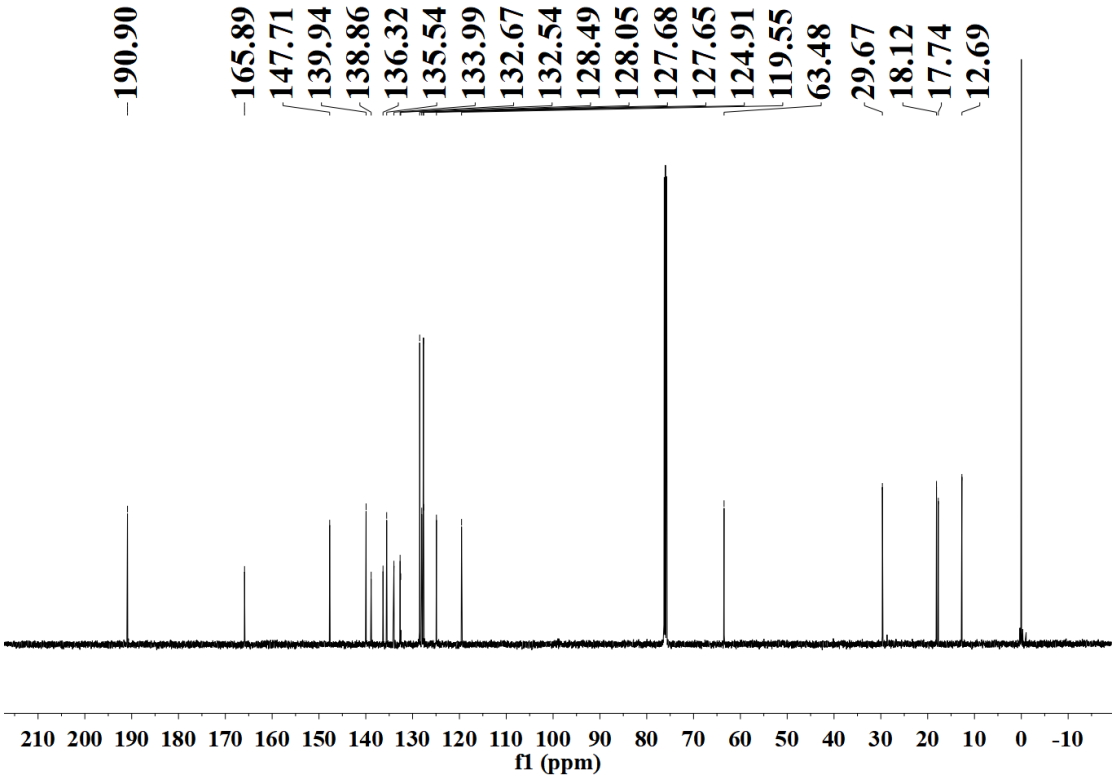
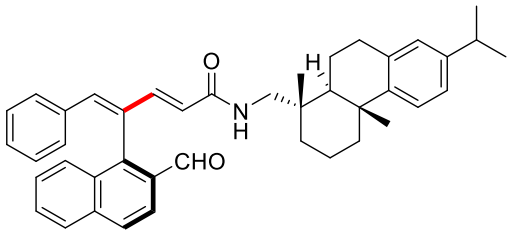
141.59
132.09
131.91
131.52
131.12
130.00
129.97
129.70
128.48
128.27
127.65
127.40
127.20
126.79
126.37
126.13
125.41
125.23
124.75
121.63
120.51
63.48
29.62
18.08
12.66
f1 (ppm)


Ph
CO2Bu
Me
CHO

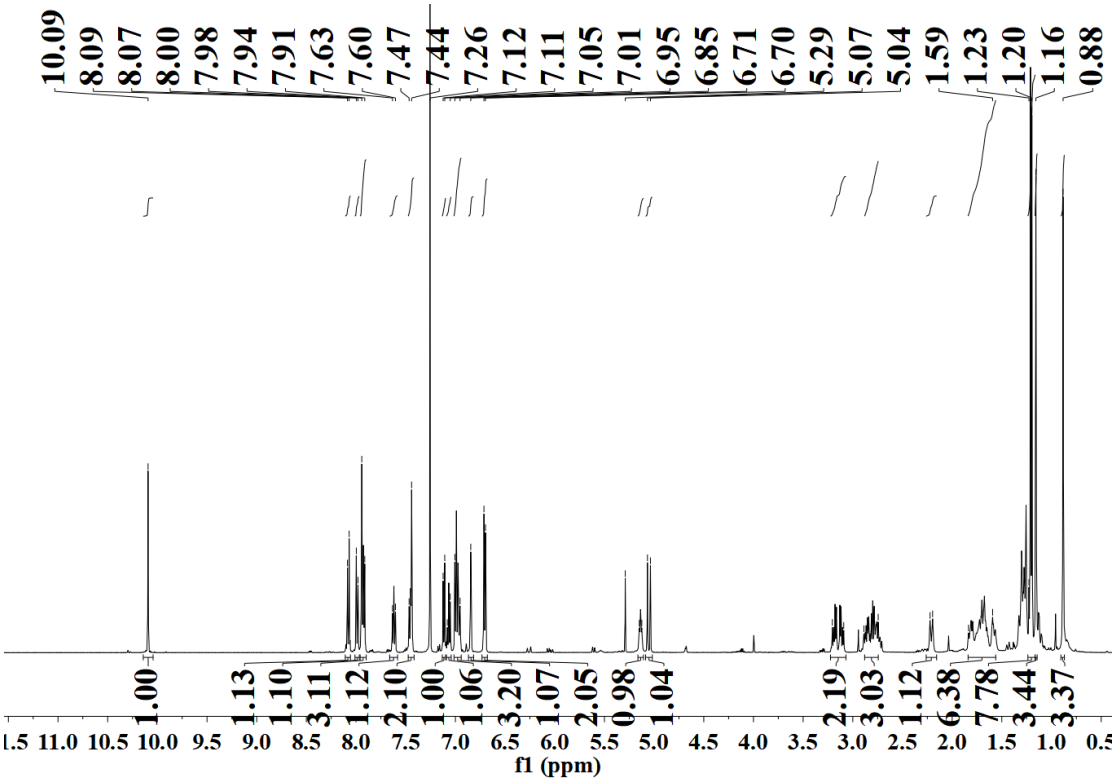
(3o)

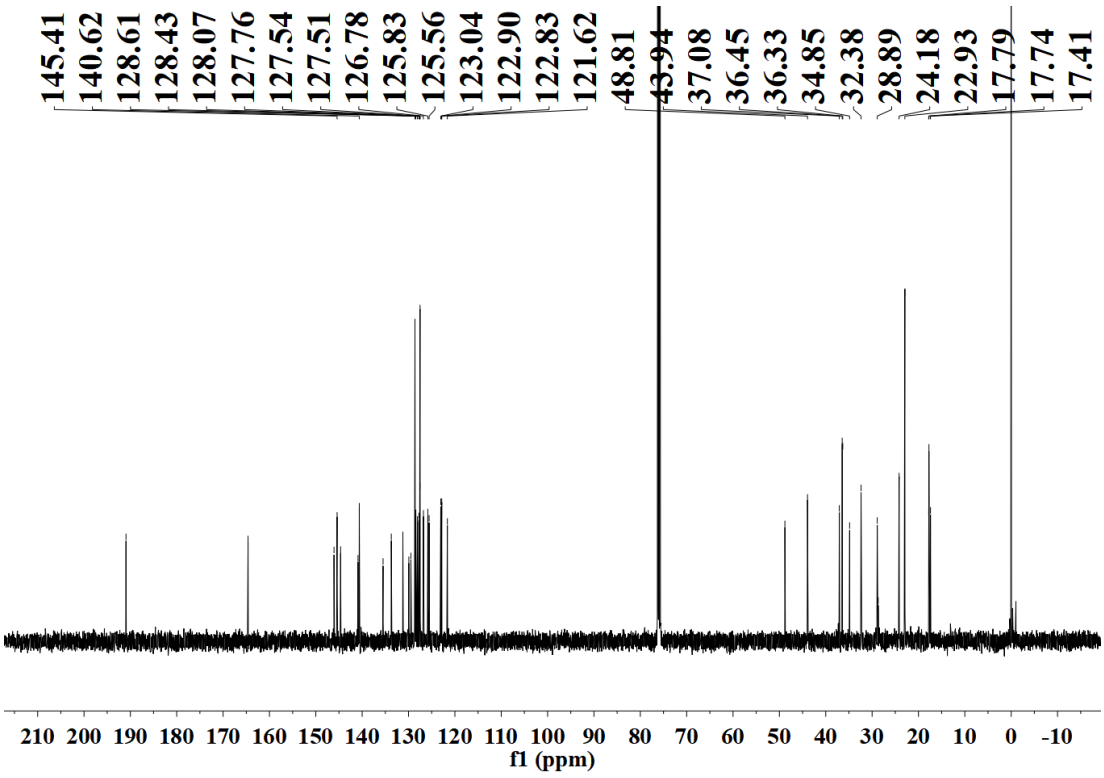

9.91
9.91
7.92
7.91
7.81
7.78
7.59
7.57
7.51
7.47
7.26
7.21
7.19
7.16
7.15
7.11
6.85
6.83
5.25
4.15
2.14
1.63
1.60
1.40
1.36
0.94
0.91
0.95
0.99
1.00
1.01
1.03
1.00
0.95
2.06
2.07
1.00
2.10
3.08
2.28
2.05
3.10
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

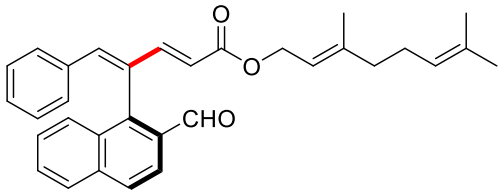

190.90
165.89
147.71
139.94
138.86
136.32
135.54
133.99
132.67
132.54
128.49
128.05
127.68
127.65
124.91
119.55
63.48
29.67
18.12
17.74
12.69
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
H
N
H
CHO

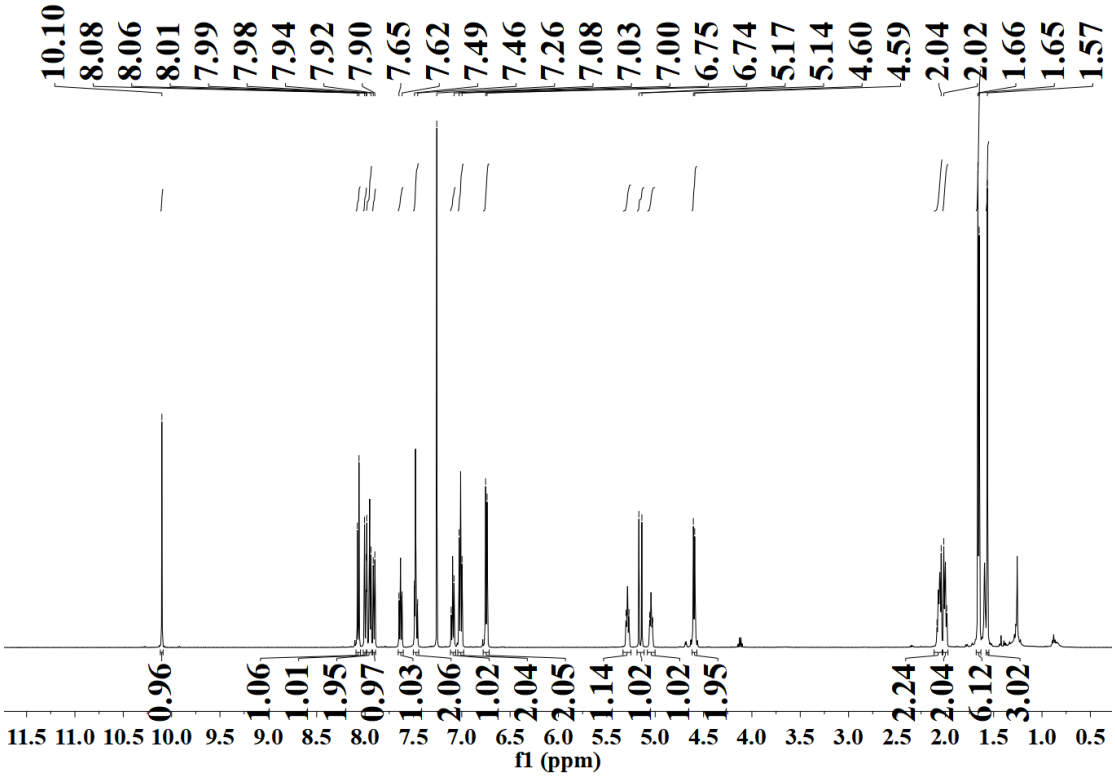
(3p)

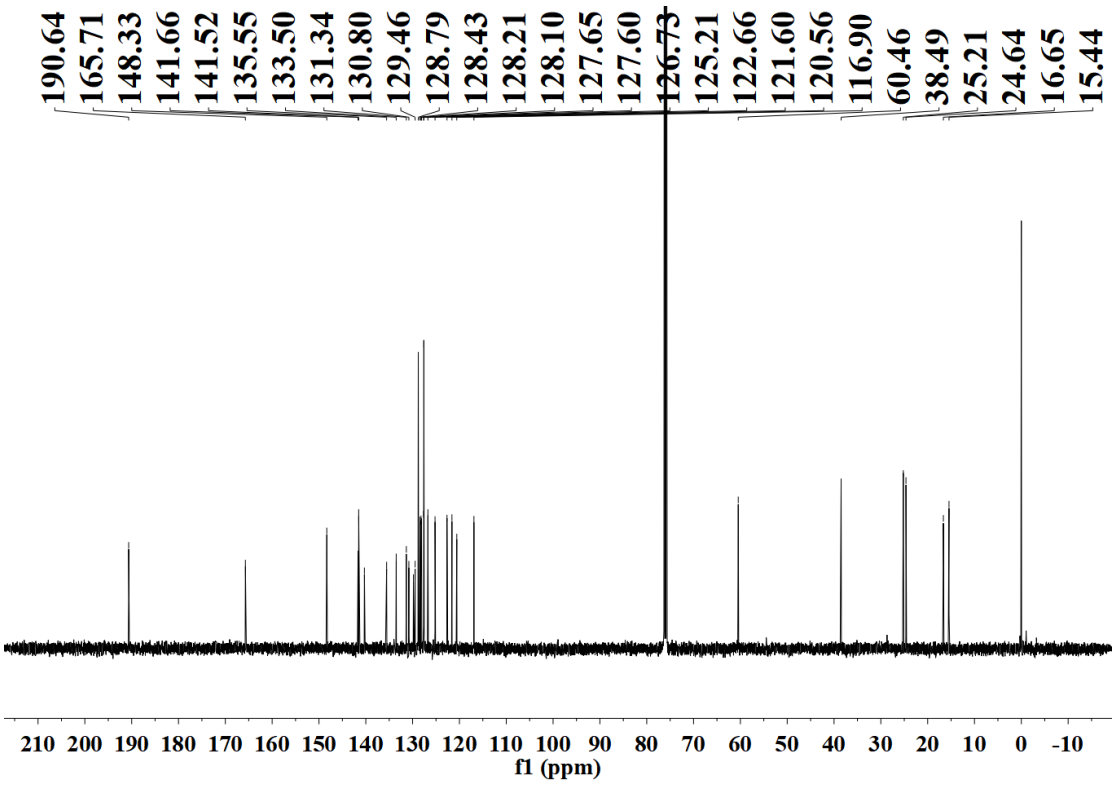

10.09
8.09
8.07
8.00
7.98
7.94
7.91
7.63
7.60
7.47
7.44
7.26
7.12
7.11
7.05
7.01
6.95
6.85
6.71
6.70
5.29
5.07
5.04
1.59
1.23
1.20
1.16
0.88
1.00
1.13
1.10
3.11
1.12
2.10
1.00
1.06
3.20
1.07
2.05
0.98
1.04
2.19
3.03
1.12
6.38
7.78
3.44
3.37
f1 (ppm)

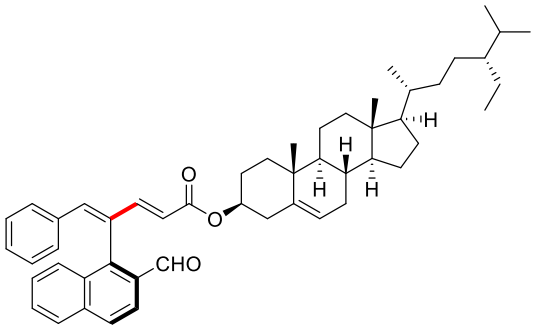

145.41
140.62
128.61
128.43
128.07
127.76
127.54
127.51
126.78
125.83
125.56
123.04
122.90
122.83
121.62
48.81
43.94
37.08
36.45
36.33
34.85
32.38
28.89
24.18
22.93
17.79
17.74
17.41
f1 (ppm)


O
O
CHO

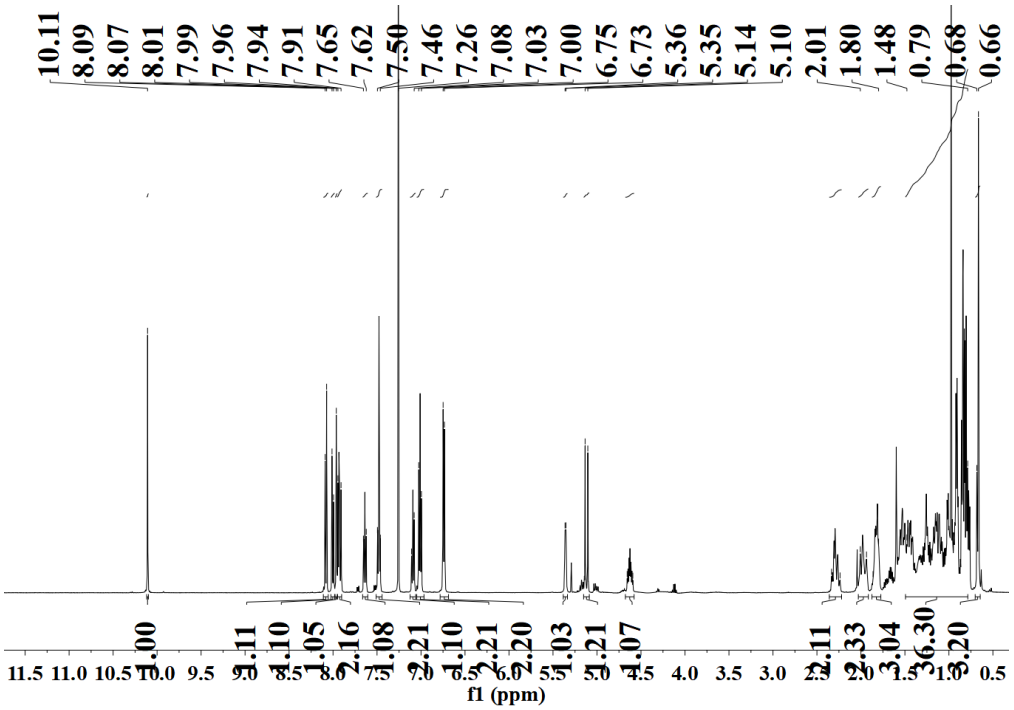
(3q)

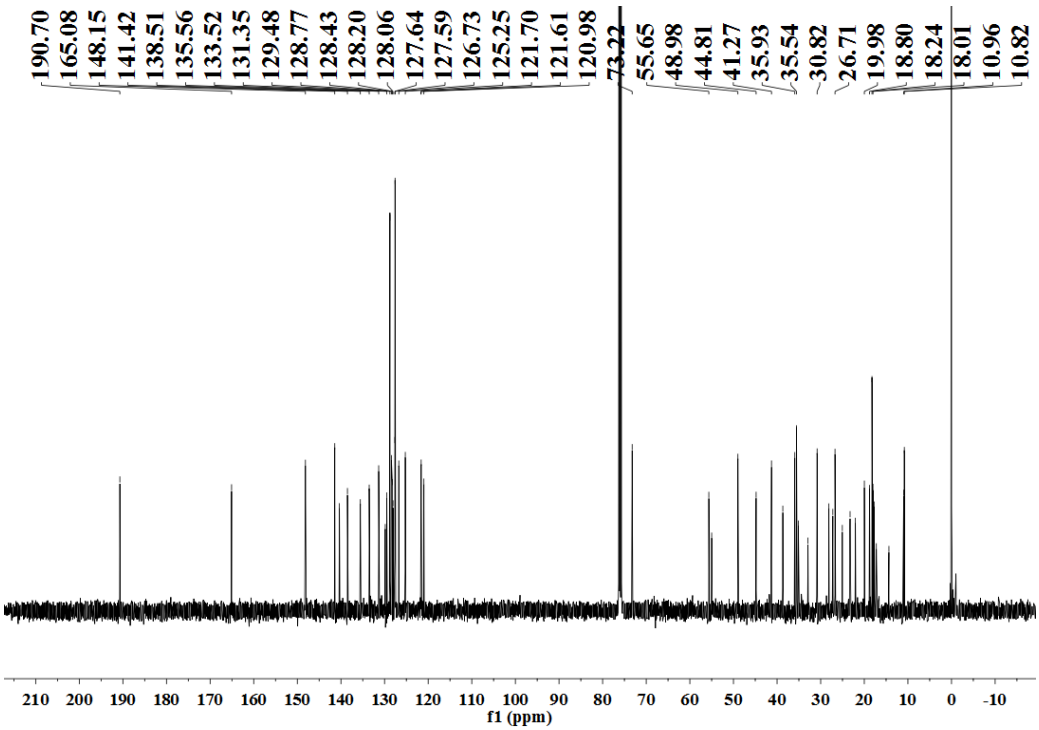

10.10
8.08
8.06
8.01
7.99
7.98
7.94
7.92
7.90
7.65
7.62
7.49
7.46
7.26
7.08
7.03
7.00
6.75
6.74
5.17
5.14
4.60
4.59
2.04
2.02
1.66
1.65
1.57
0.96
1.06
1.01
1.95
0.97
1.03
2.06
1.02
2.04
2.05
1.14
1.02
1.02
1.95
2.24
2.04
6.12
3.02
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


190.64
165.71
148.33
141.66
141.52
135.55
133.50
131.34
130.80
129.46
128.79
128.43
128.21
128.10
127.65
127.60
126.73
125.21
122.66
121.60
120.56
116.90
60.46
38.49
25.21
24.64
16.65
15.44
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)

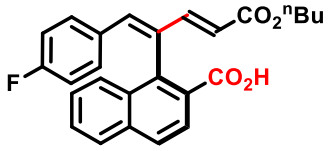

O
O
H
H
H
H
CHO

(3r)

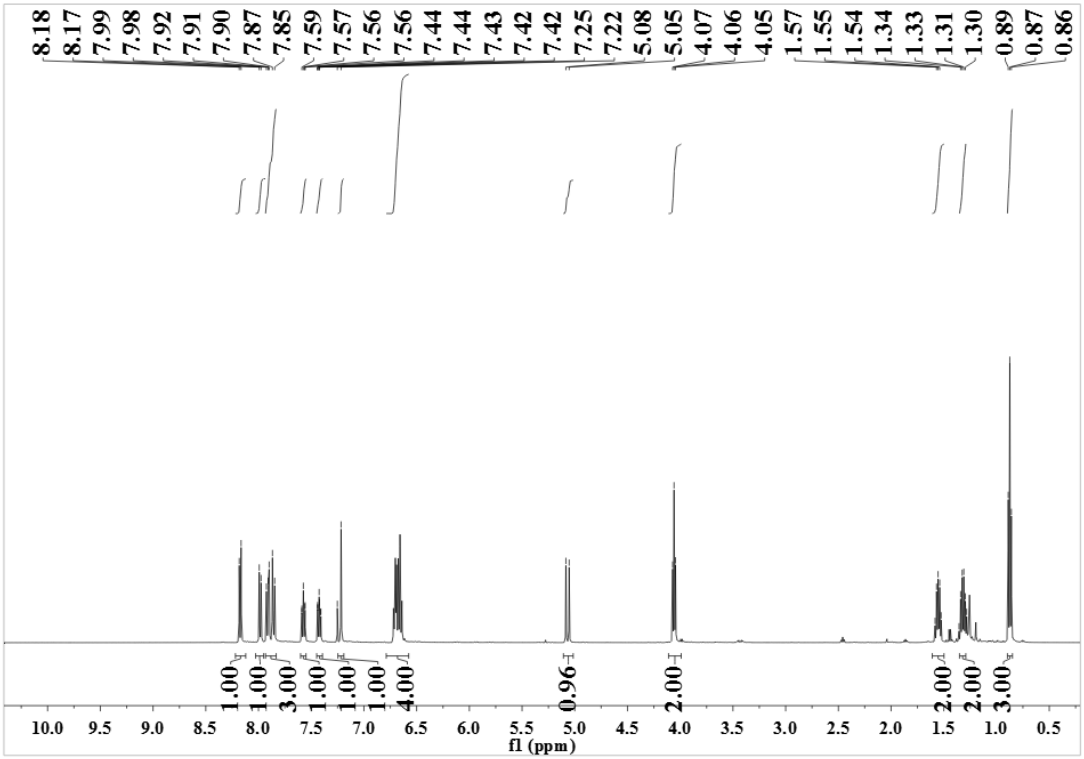

10.11
8.09
8.07
8.01
7.99
7.96
7.94
7.91
7.65
7.62
7.50
7.46
7.26
7.08
7.03
7.00
6.75
6.73
5.36
5.35
5.14
5.10
2.01
1.80
1.48
0.79
0.68
0.66
1.00
1.11
1.10
1.05
2.16
1.08
2.21
1.10
2.21
2.20
1.03
1.21
1.07
2.11
2.33
3.04
36.30
3.20
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

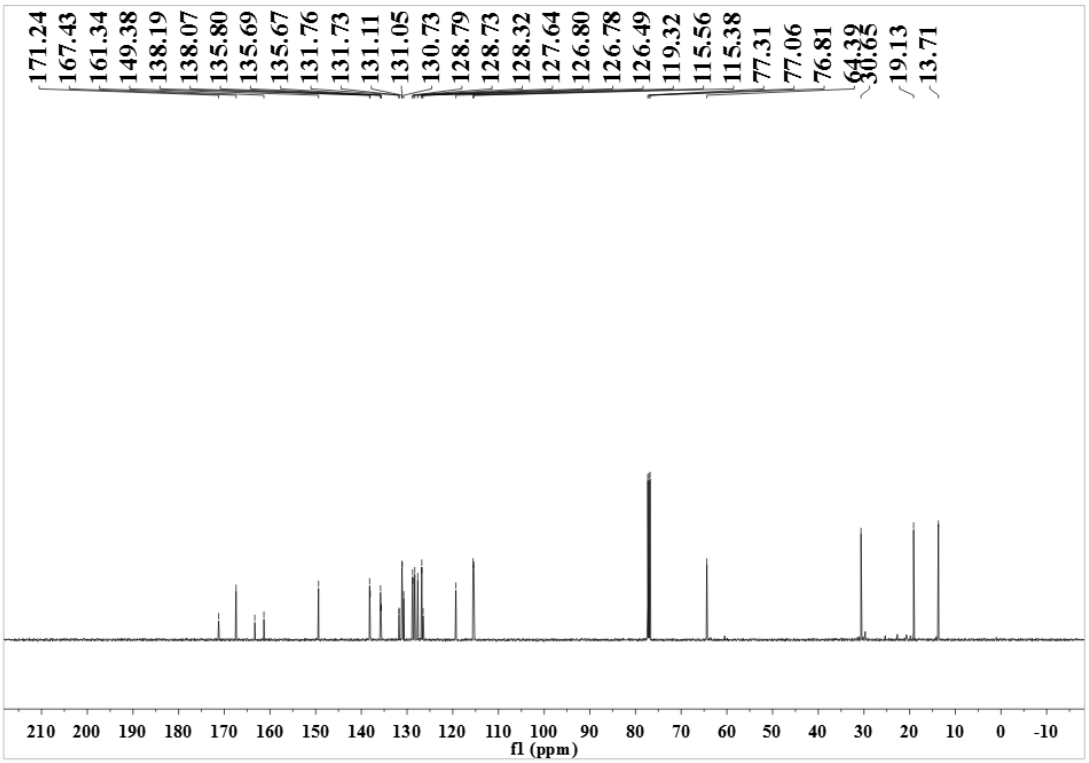

190.70
165.08
148.15
141.42
138.51
135.56
133.52
131.35
129.48
128.77
128.43
128.20
128.06
127.64
127.59
126.73
125.25
121.70
121.61
120.98
73.22
55.65
48.98
44.81
41.27
35.93
35.54
30.82
26.71
19.98
18.80
18.24
18.01
10.96
10.82
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

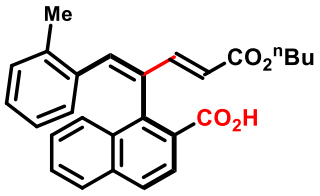
8.3 ^{1}H / ^{13}C NMR Charts of CCAs



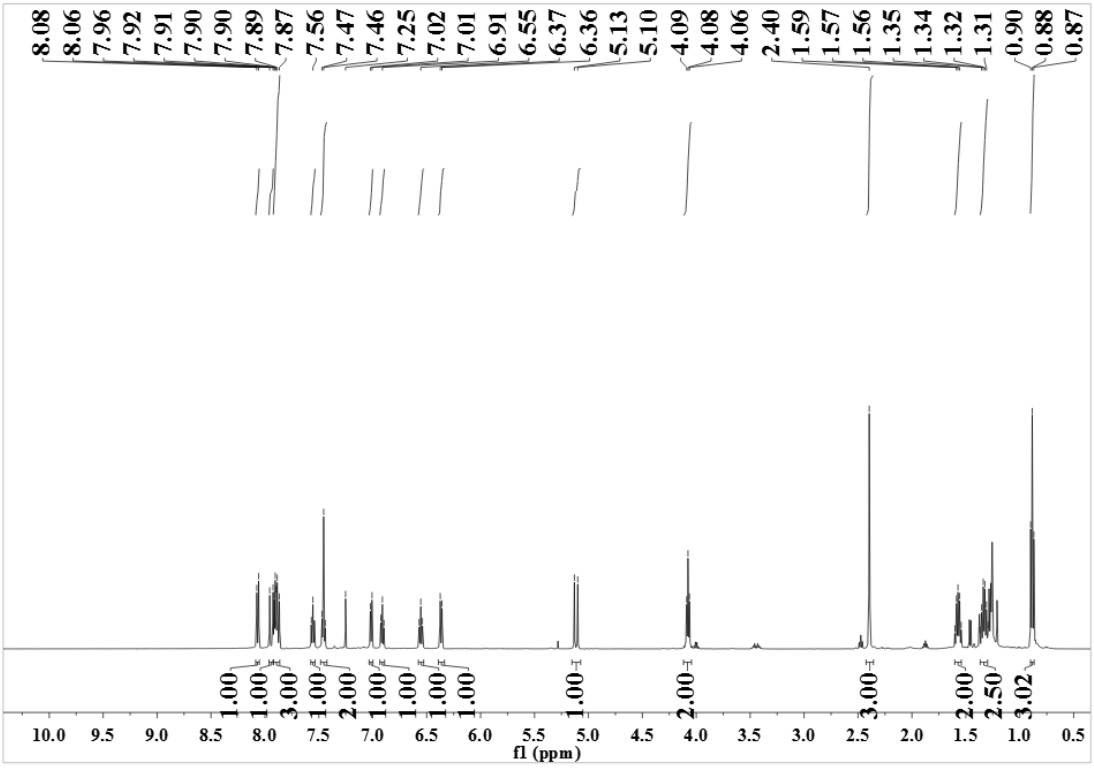
(4a)

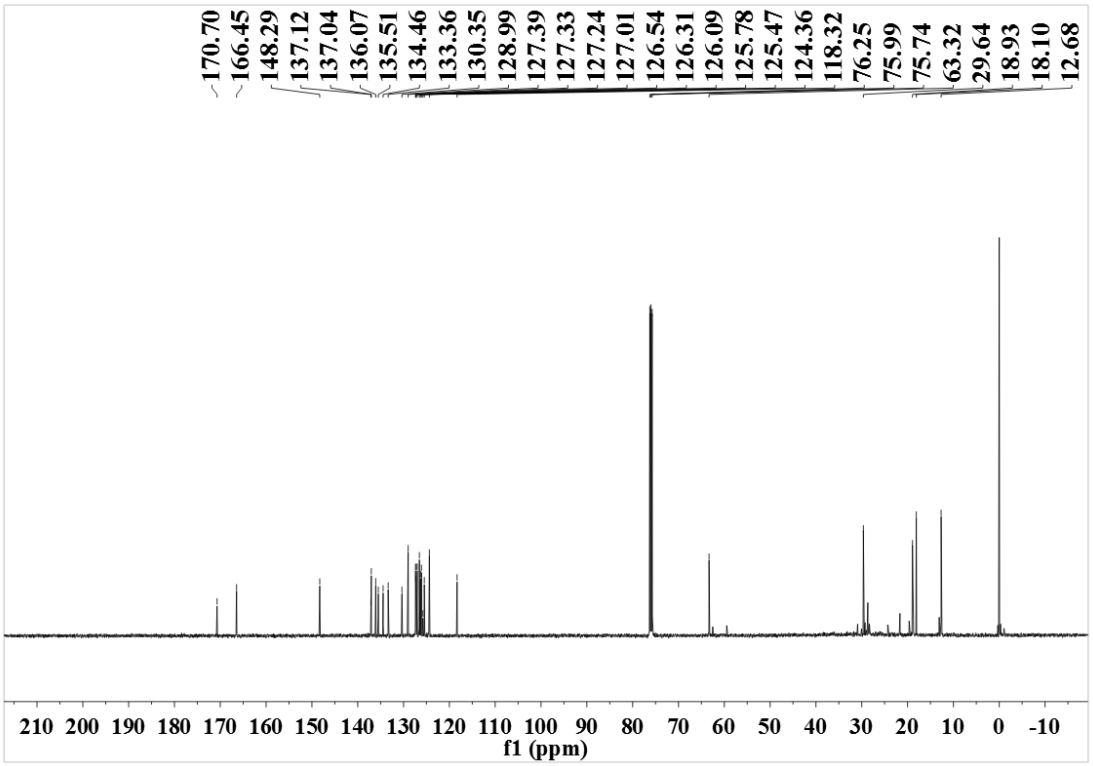


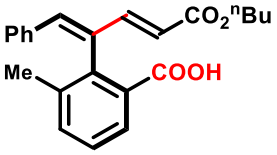

171.24
167.43
161.34
149.38
138.19
138.07
135.80
135.69
135.67
131.76
131.73
131.11
131.05
130.73
128.79
128.73
128.32
127.64
126.80
126.78
126.49
119.32
115.56
115.38
77.31
77.06
76.81
64.39
30.65
19.13
13.71
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
CO2nBu
CO2H

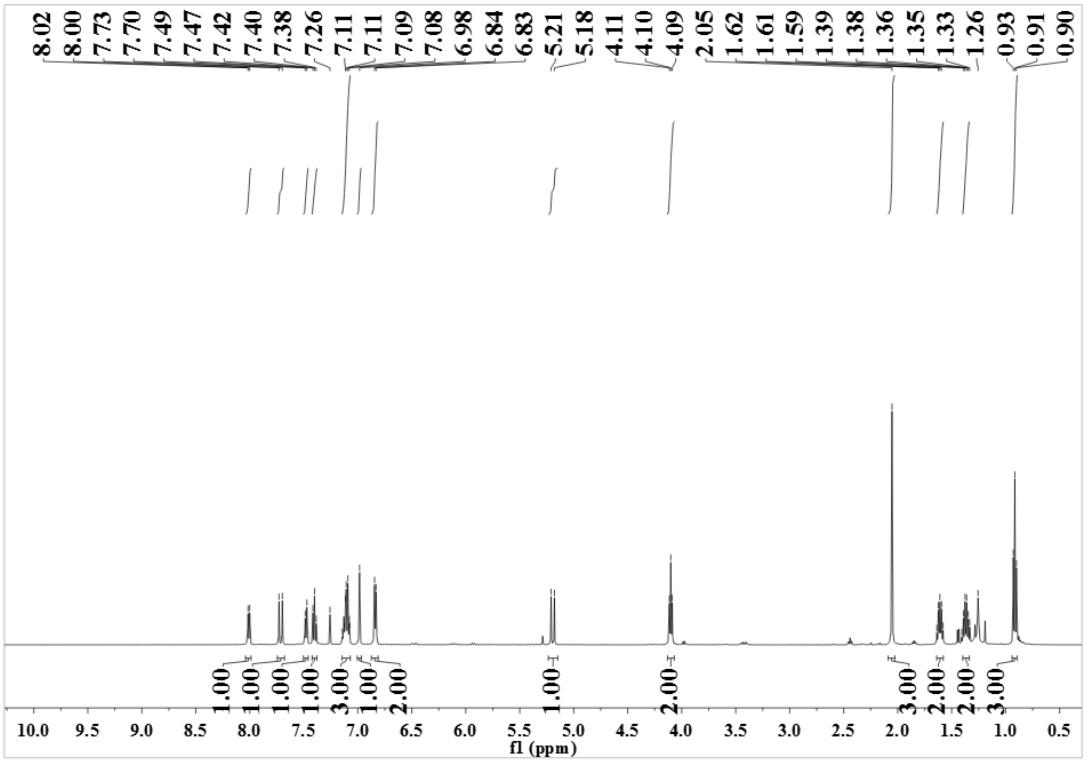
(4b)

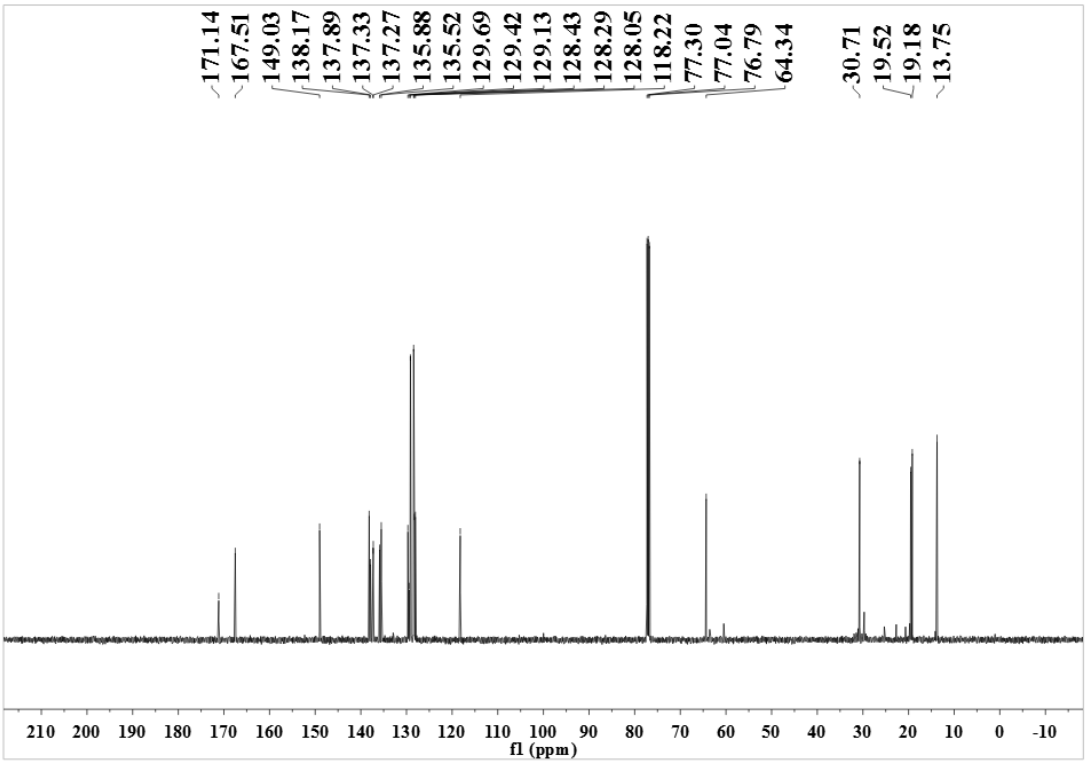

8.08
8.06
7.96
7.92
7.91
7.90
7.90
7.89
7.87
7.56
7.47
7.46
7.25
7.02
7.01
6.91
6.55
6.37
6.36
5.13
5.10
4.09
4.08
4.06
2.40
1.59
1.57
1.56
1.35
1.34
1.32
1.31
0.90
0.88
0.87
1.00
1.00
3.00
1.00
2.00
1.00
1.00
1.00
1.00
2.00
3.00
2.00
2.50
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

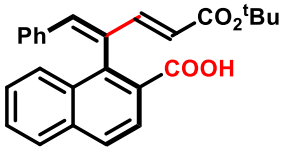

170.70
166.45
148.29
137.12
137.04
136.07
135.51
134.46
133.36
130.35
128.99
127.39
127.33
127.24
127.01
126.54
126.31
126.09
125.78
125.47
124.36
118.32
76.25
75.99
75.74
63.32
29.64
18.93
18.10
12.68
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ph
Me
CO2nBu
COOH

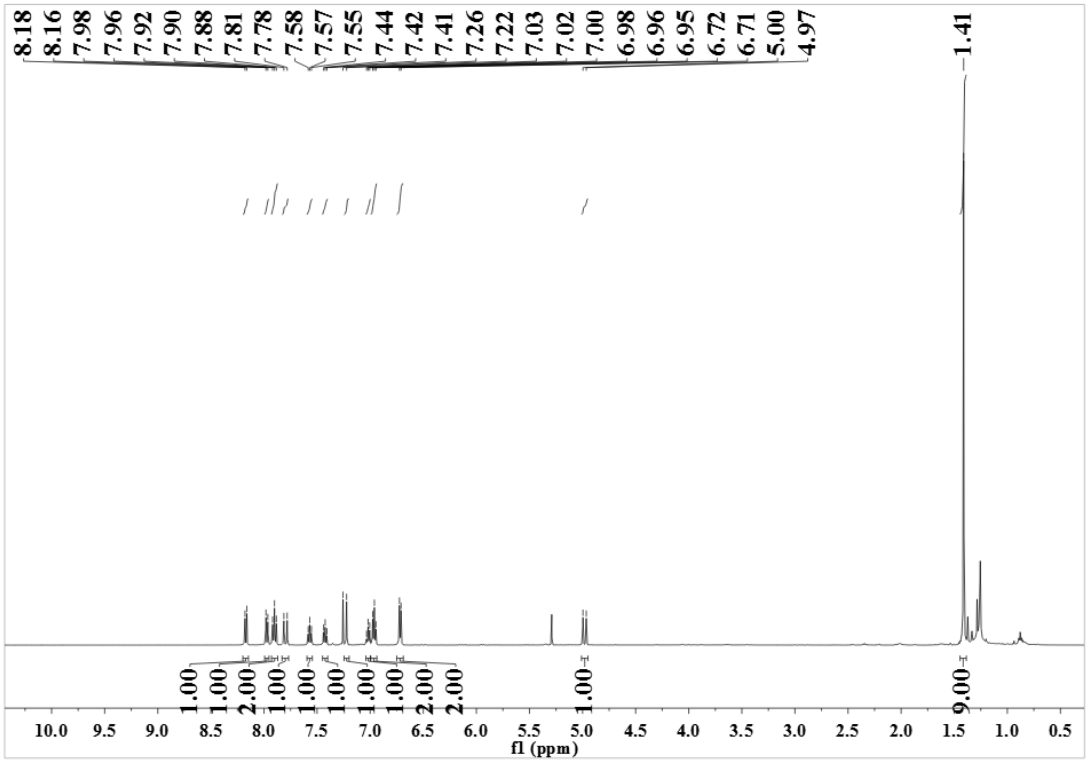
(4c)

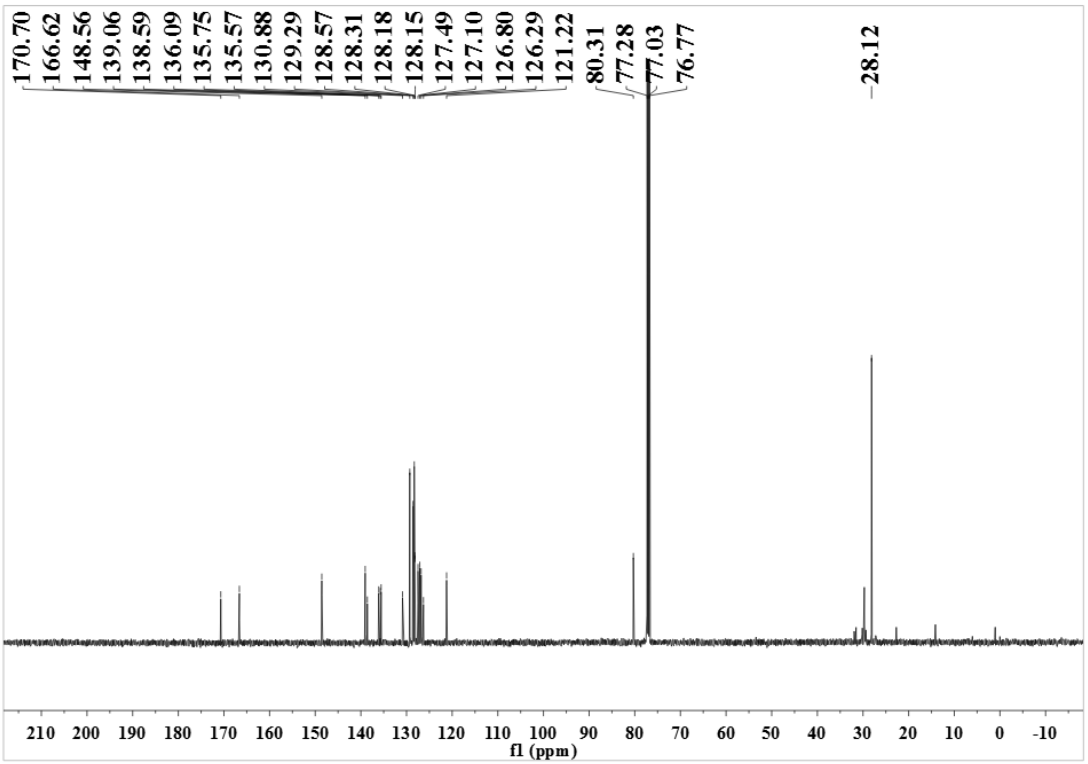

8.02
8.00
7.73
7.70
7.49
7.47
7.42
7.40
7.38
7.26
7.11
7.11
7.09
7.08
6.98
6.84
6.83
5.21
5.18
4.11
4.10
4.09
2.05
1.62
1.61
1.59
1.39
1.38
1.36
1.35
1.33
1.26
0.93
0.91
0.90
1.00
1.00
1.00
1.00
3.00
1.00
2.00
1.00
2.00
3.00
2.00
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

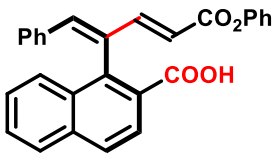

171.14
167.51
149.03
138.17
137.89
137.33
137.27
135.88
135.52
129.69
129.42
129.13
128.43
128.29
128.05
118.22
77.30
77.04
76.79
64.34
30.71
19.52
19.18
13.75
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ph
CO2tBu
COOH

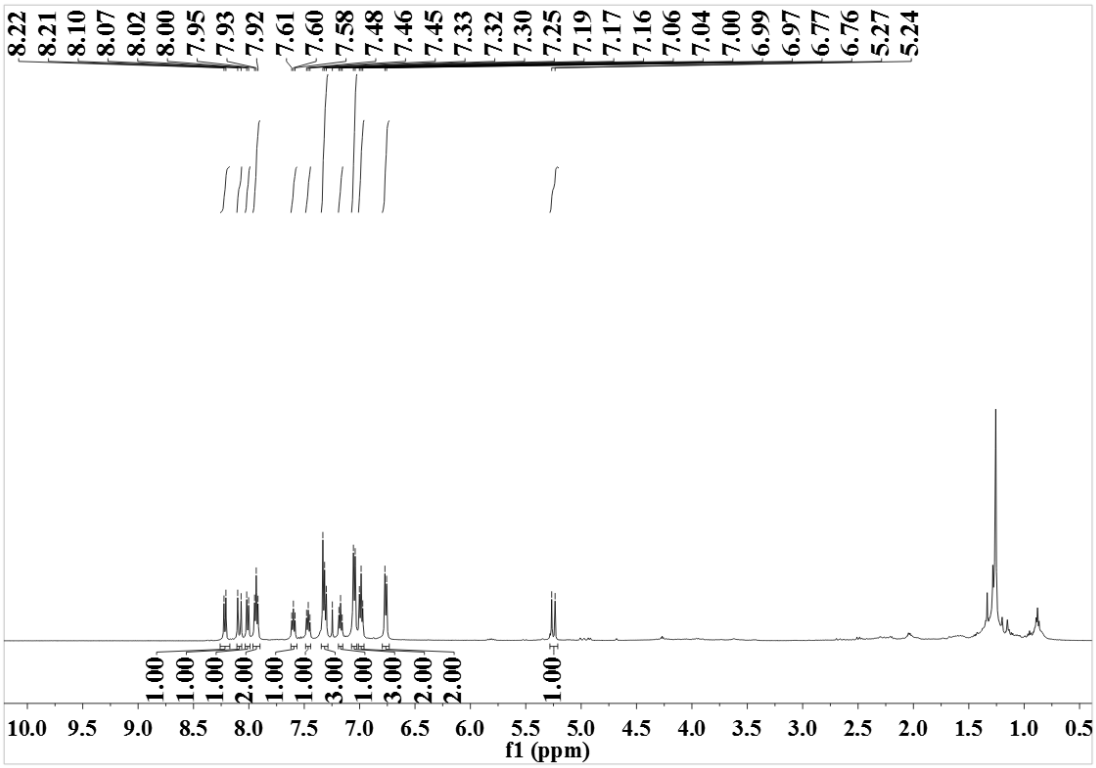
(4d)

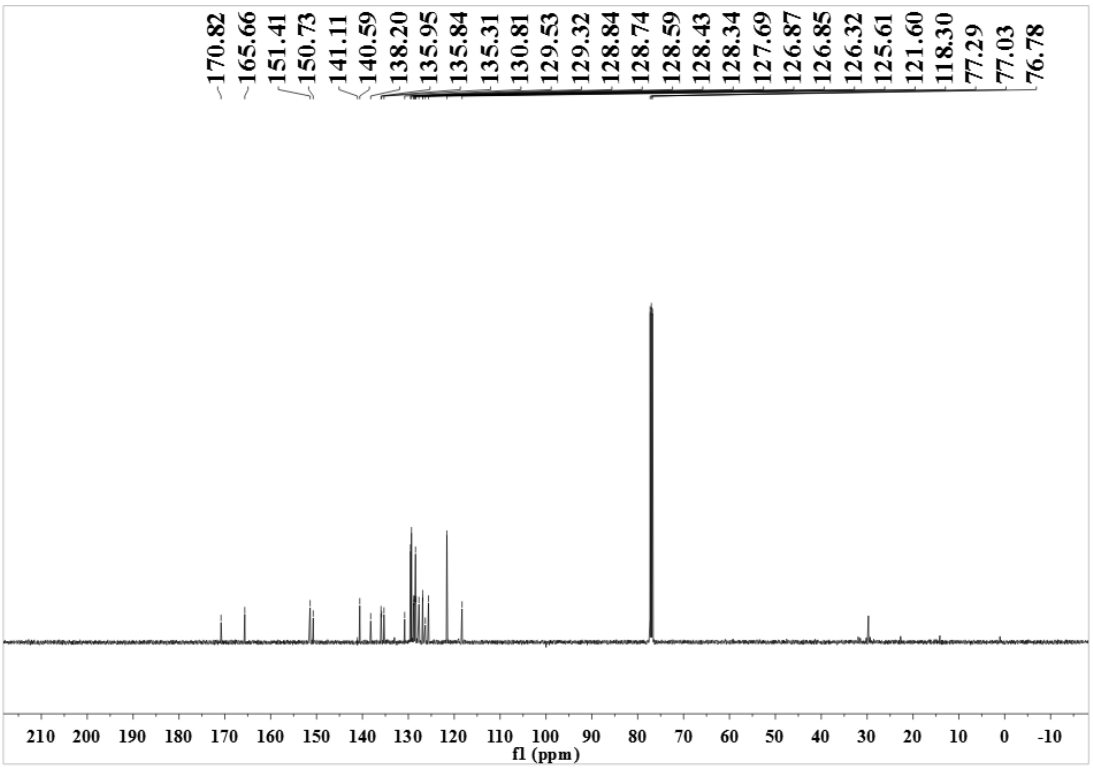

8.18
8.16
7.98
7.96
7.92
7.90
7.88
7.81
7.78
7.58
7.57
7.55
7.44
7.42
7.41
7.26
7.22
7.03
7.02
7.00
6.98
6.96
6.95
6.72
6.71
5.00
4.97
1.41
1.00
1.00
2.00
1.00
1.00
1.00
1.00
1.00
2.00
2.00
1.00
9.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

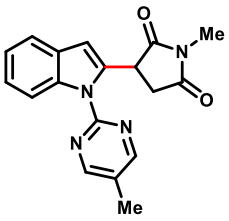

170.70
166.62
148.56
139.06
138.59
136.09
135.75
135.57
130.88
129.29
128.57
128.31
128.18
128.15
127.49
127.10
126.80
126.29
121.22
80.31
77.28
77.03
76.77
28.12
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ph
CO2Ph
COOH

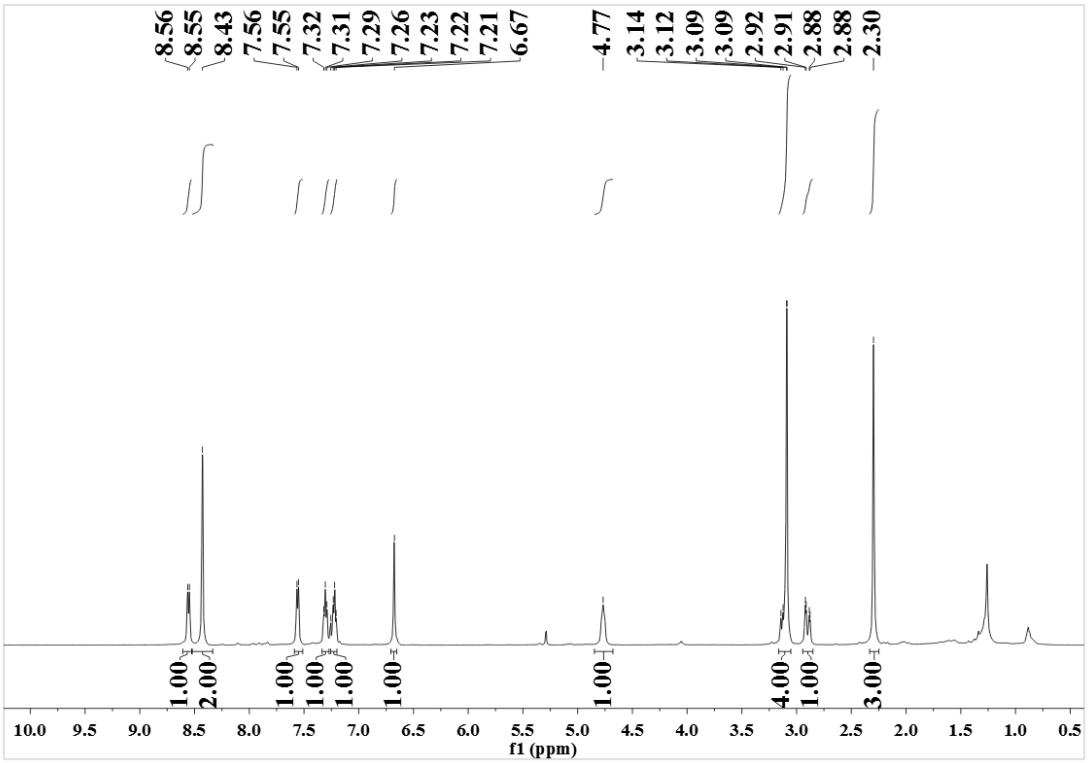
(4e)

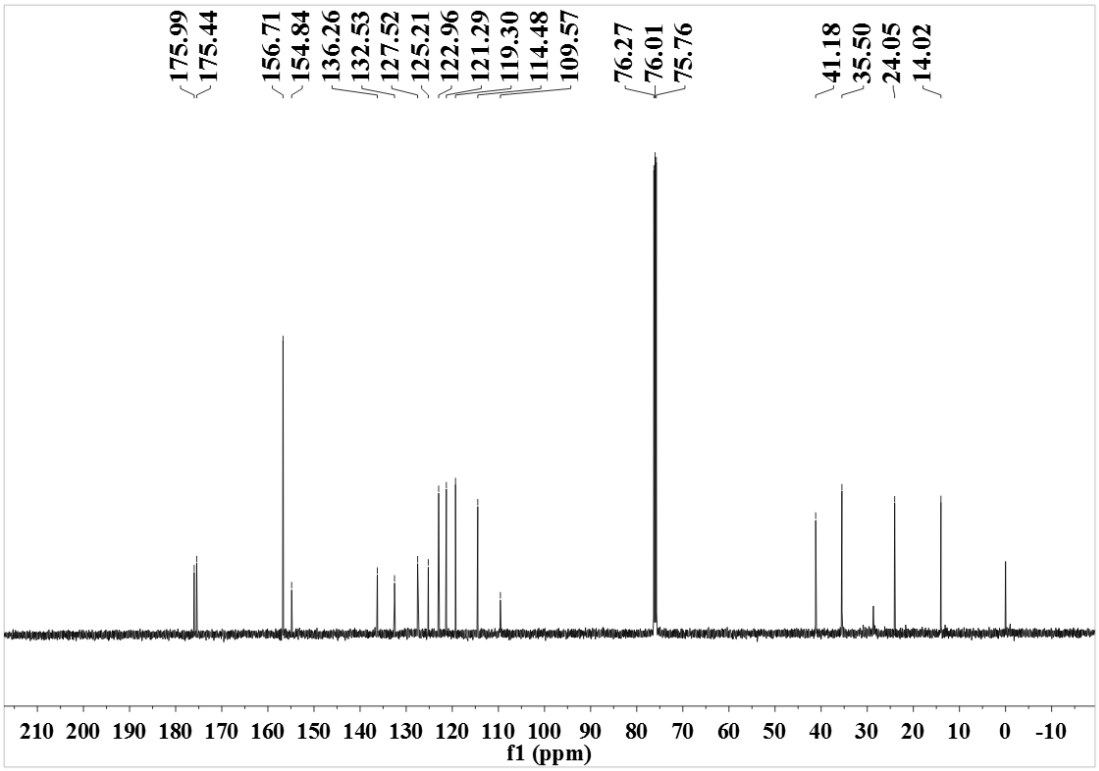

8.22
8.21
8.10
8.07
8.02
8.00
7.95
7.93
7.92
7.61
7.60
7.58
7.48
7.46
7.45
7.33
7.32
7.30
7.25
7.19
7.17
7.16
7.06
7.04
7.00
6.99
6.97
6.77
6.76
5.27
5.24
1.00 1.00 1.00 2.00 1.00 1.00 3.00 1.00 3.00 2.00 2.00 1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


170.82
165.66
151.41
150.73
141.11
140.59
138.20
135.95
135.84
135.31
130.81
129.53
129.32
128.84
128.74
128.59
128.43
128.34
127.69
126.87
126.85
126.32
125.61
121.60
118.30
77.29
77.03
76.78
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)


O
N
Me
O
N
N
N
Me

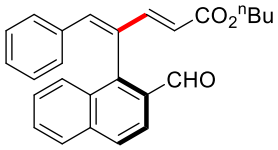
(7)


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)

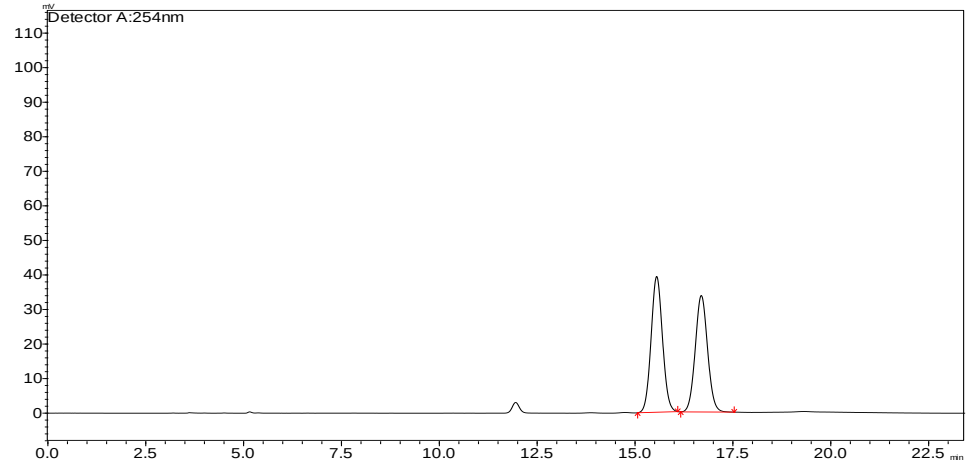
9. Copies of HPLC Analysis

9.1 HPLC Analysis of Products

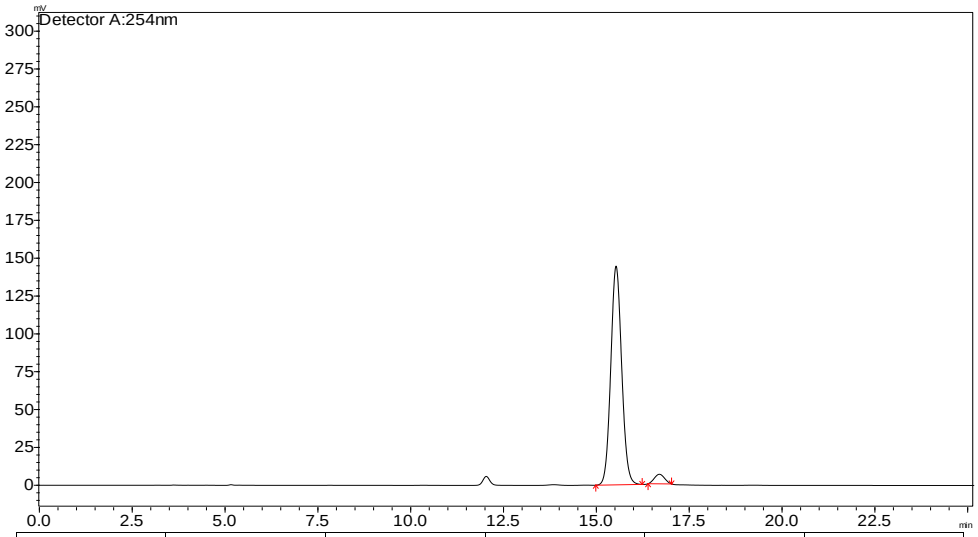


3a
78%, 93% ee

Daicel Chiralpak IA-H column, n-hexane/i-PrOH (98/2), 1.0 mL/min, 254 nm, 15.526 min (major enantiomer), 16.693 min (minor enantiomer).

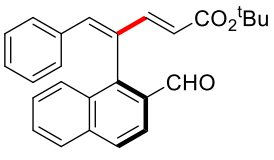


Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.548	798038	39311	51.937	53.822
2	16.688	738520	33729	48.063	46.178
Total		1536558	73040	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %

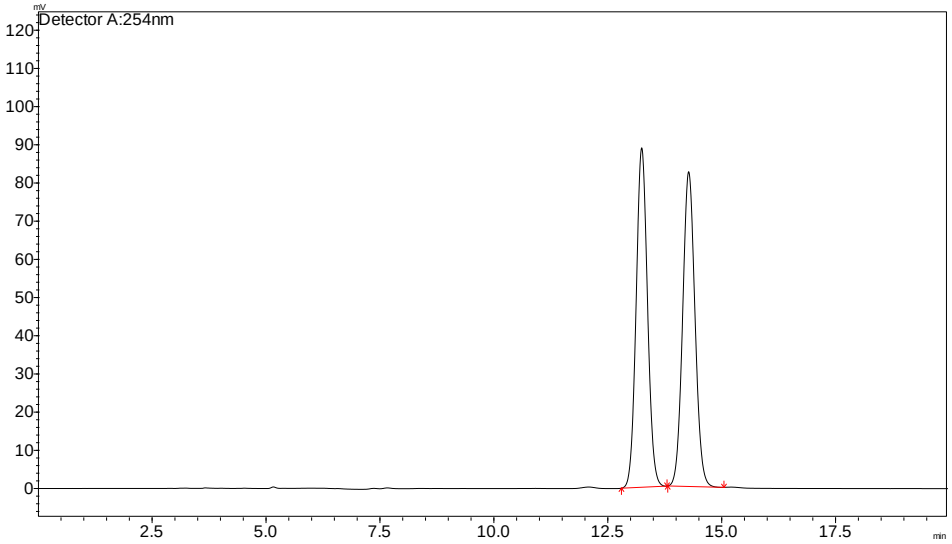
1	15.526	2952019	144542	96.063	95.812
2	16.693	120999	6318	3.937	4.188
Total		3073018	150860	100.000	100.000



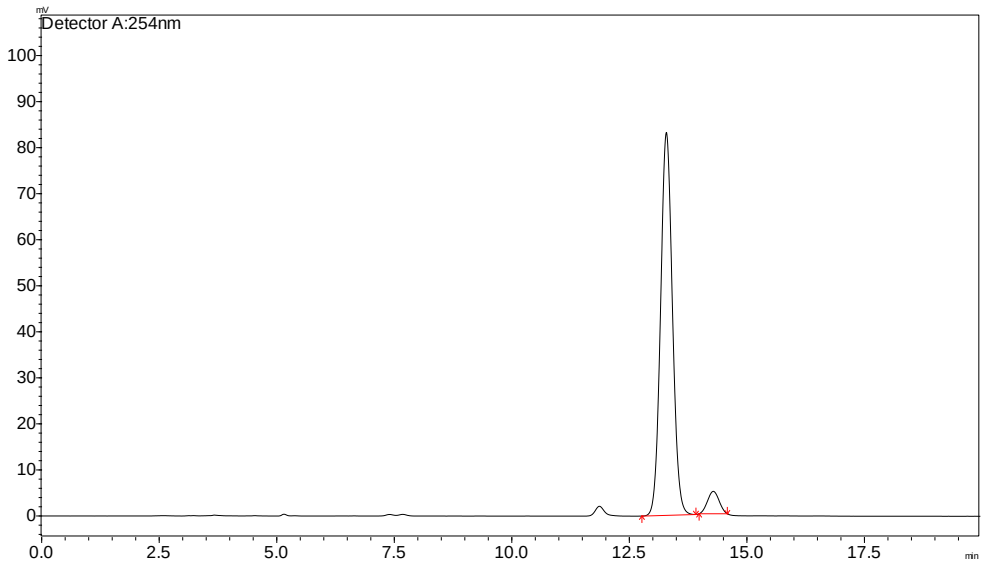
3b

70%, 89% ee

Daicel Chiralpak IA-H column, n-hexane/i-PrOH (98/2), 1.0 mL/min, 254 nm, 13.283 min (major enantiomer), 14.281 min (minor enantiomer).

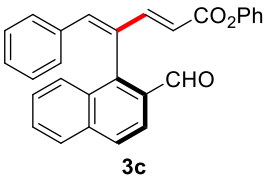


Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.240	1540444	88885	49.810	51.885
2	14.272	1552191	82427	50.190	48.115
Total		3092635	171312	100.000	100.000



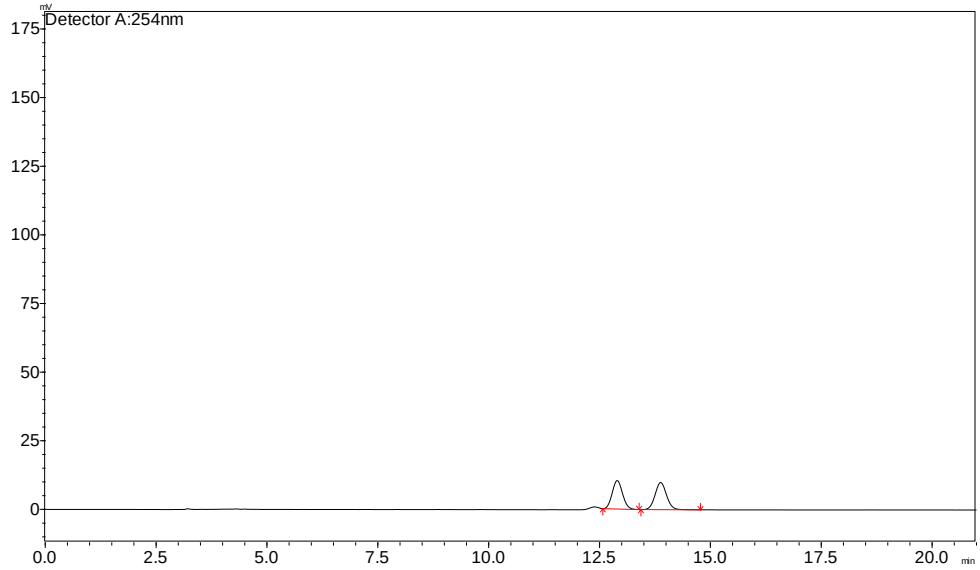
Peak#	Ret. Time	Area	Height	Area %	Height %

1	13.283	1457625	83157	94.588	94.472
2	14.281	83394	4866	5.412	5.528
Total		1541020	88022	100.000	100.000

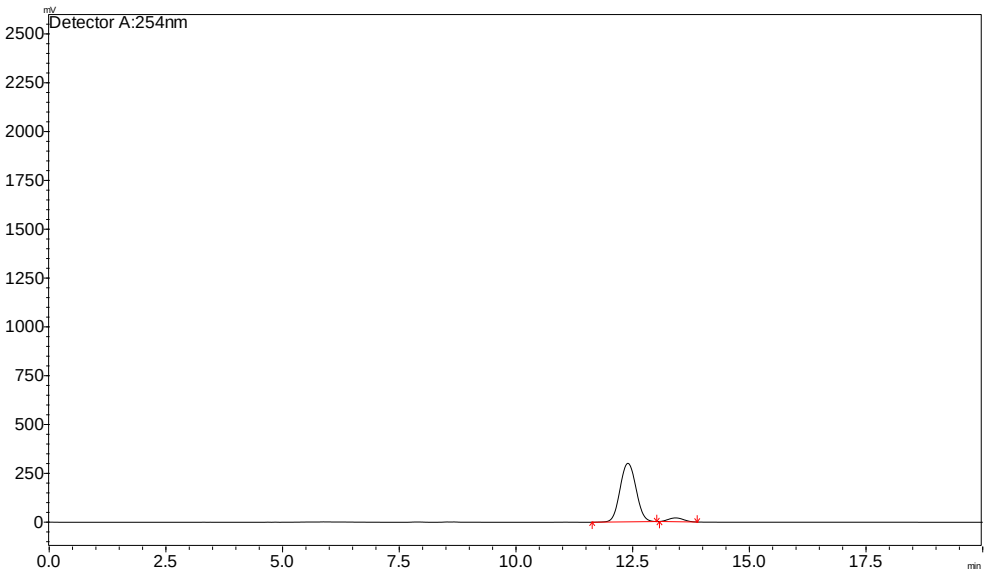


3c
92%, 89% ee

Daicel Chiralpak IA-H column, n-hexane/i-PrOH (95/5), 1.0 mL/min, 254 nm, 12.395 min (major enantiomer), 13.416 min (minor enantiomer).

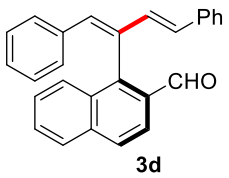


Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.894	167921	10352	48.572	51.170
2	13.874	177793	9879	51.428	48.830
Total		345713	20231	100.000	100.000



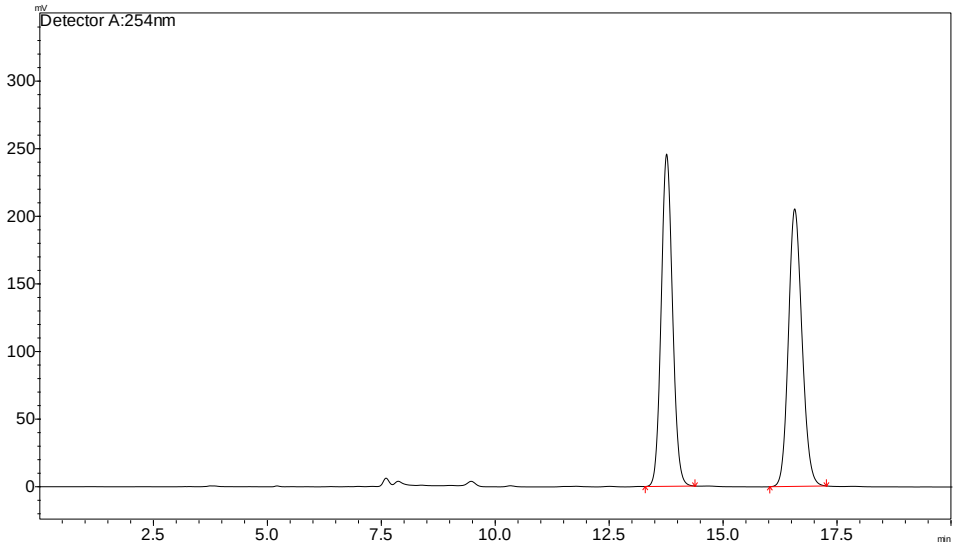
Peak#	Ret. Time	Area	Height	Area %	Height %

1	12.395	7140568	299680	94.211	93.905
2	13.416	438801	19451	5.789	6.095
Total		7579369	319131	100.000	100.000

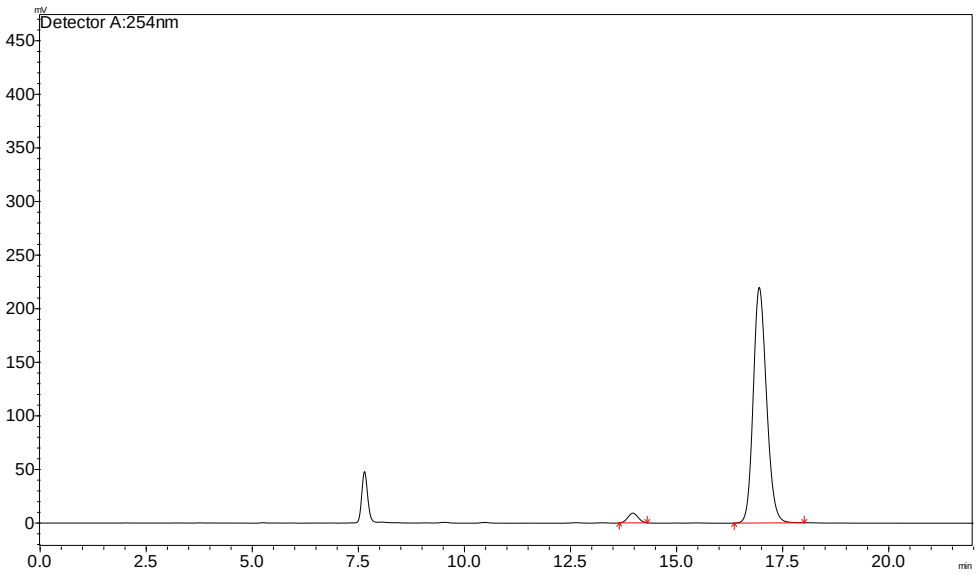


3d
71%, 94% ee

Daicel Chiralpak IA-H column, n-hexane/i-PrOH (98/2), 1.0 mL/min, 254 nm, 13.965 min (major enantiomer), 16.944 min (minor enantiomer).

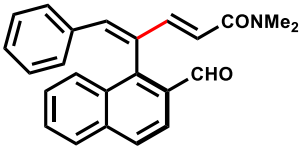


Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.757	4249850	245725	49.923	54.494
2	16.567	4262877	205195	50.077	45.506
Total		8512727	450920	100.000	100.000



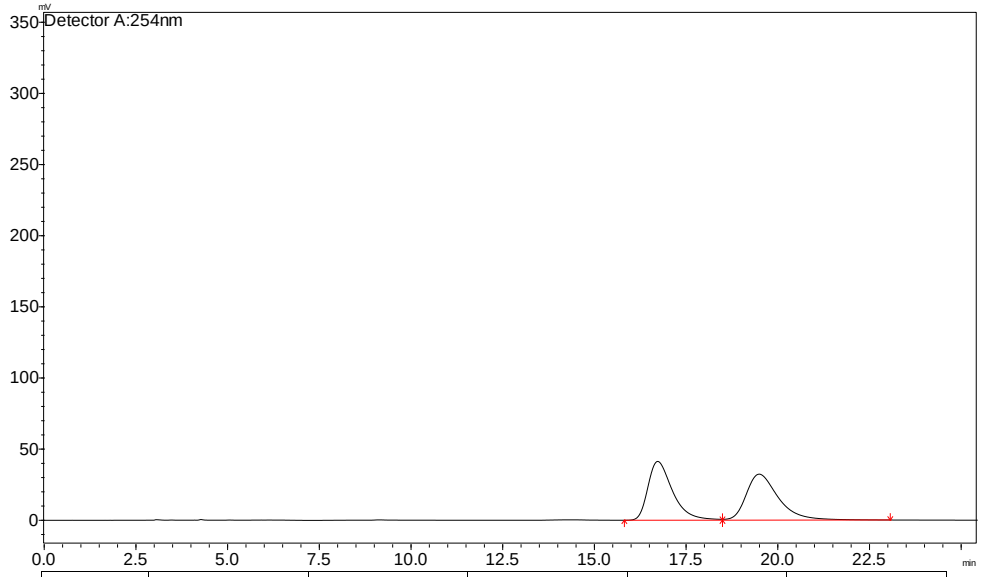
Peak#	Ret. Time	Area	Height	Area %	Height %

1	13.965	152572	9052	3.090	3.955
2	16.944	4784447	219842	96.910	96.045
Total		4937019	228894	100.000	100.000

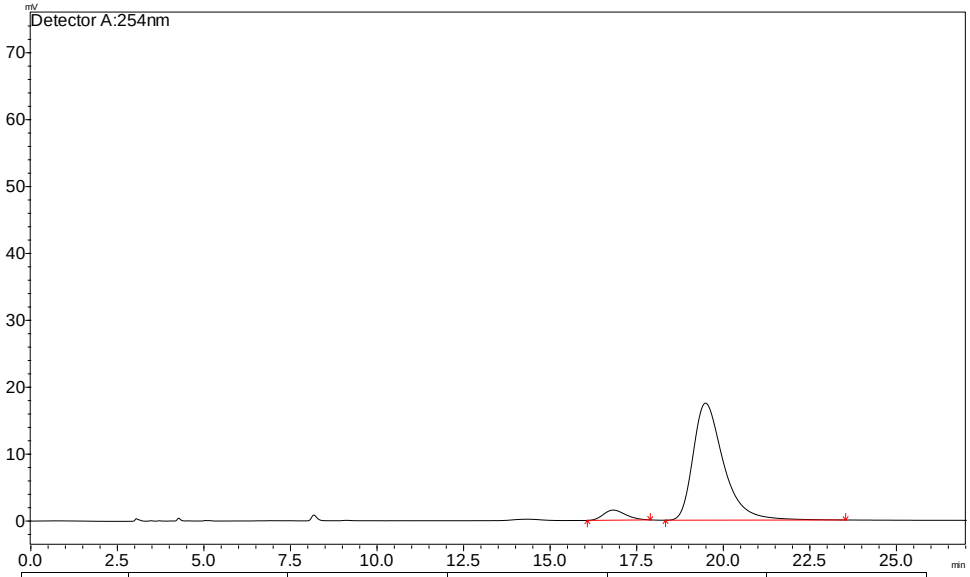


3e
90%,88% ee

Daicel Chiralpak OD-H column, n-hexane/i-PrOH (90/10), 1.0 mL/min, 254 nm, 16.816 min (major enantiomer), 19.483 min (minor enantiomer).

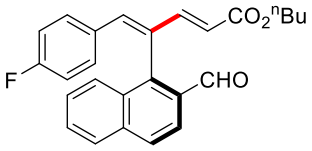


Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.722	1929336	41307	49.448	56.115
2	19.489	1972399	32304	50.552	43.885
Total		3901734	73612	100.000	100.000



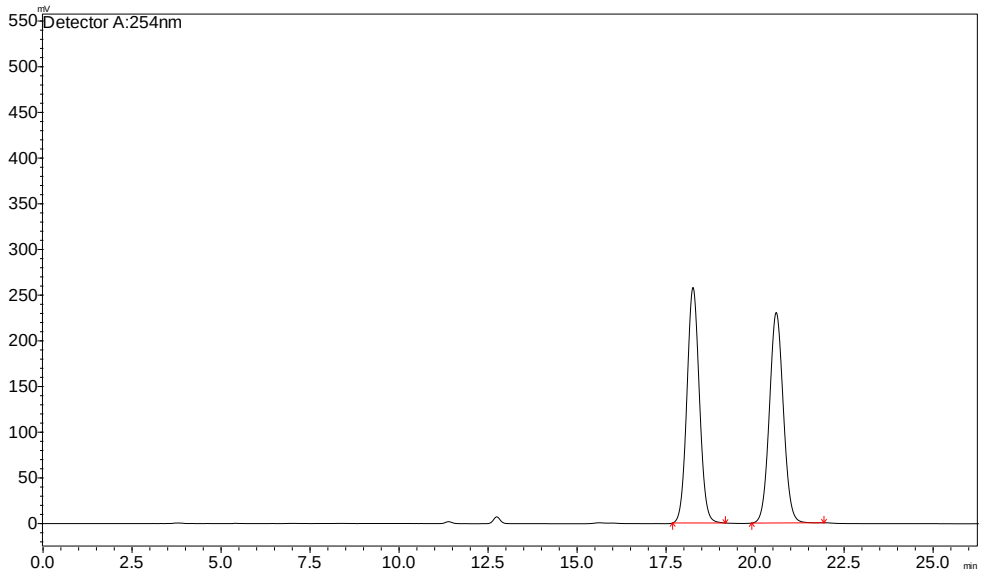
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.816	67875	1510	5.965	7.946

2	19.483	1070105	17498	94.035	92.054
Total		1137980	19008	100.000	100.000

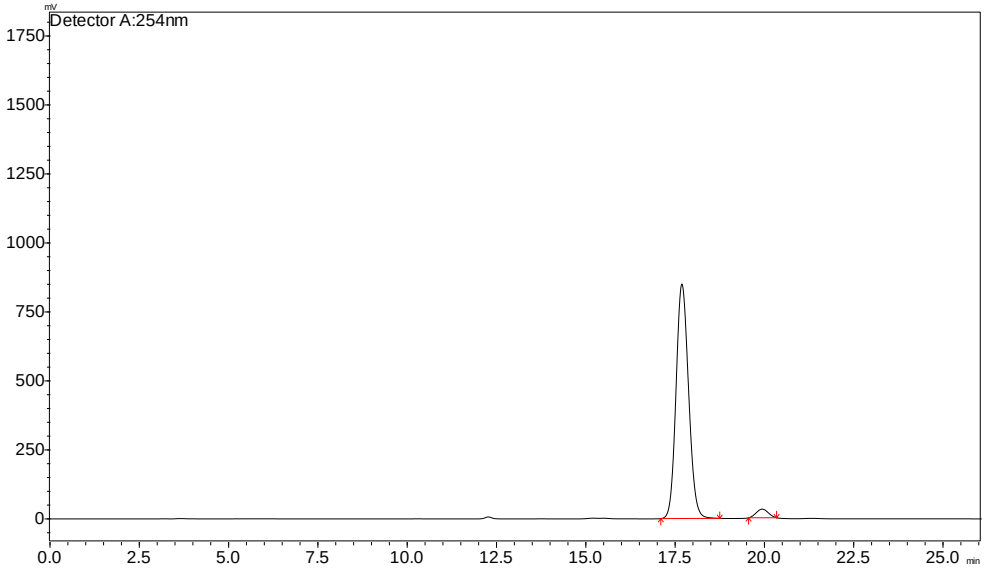


3f
91%, 94% ee

Daicel Chiralpak IA-H column, n-hexane/i-PrOH (98/2), 1.0 mL/min, 254 nm, 17.686 min (major enantiomer), 19.934 min (minor enantiomer).

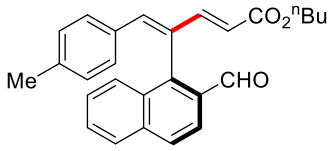


Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.252	6261635	257767	49.963	52.812
2	20.589	6270953	230320	50.037	47.188
Total		12532588	488087	100.000	100.000



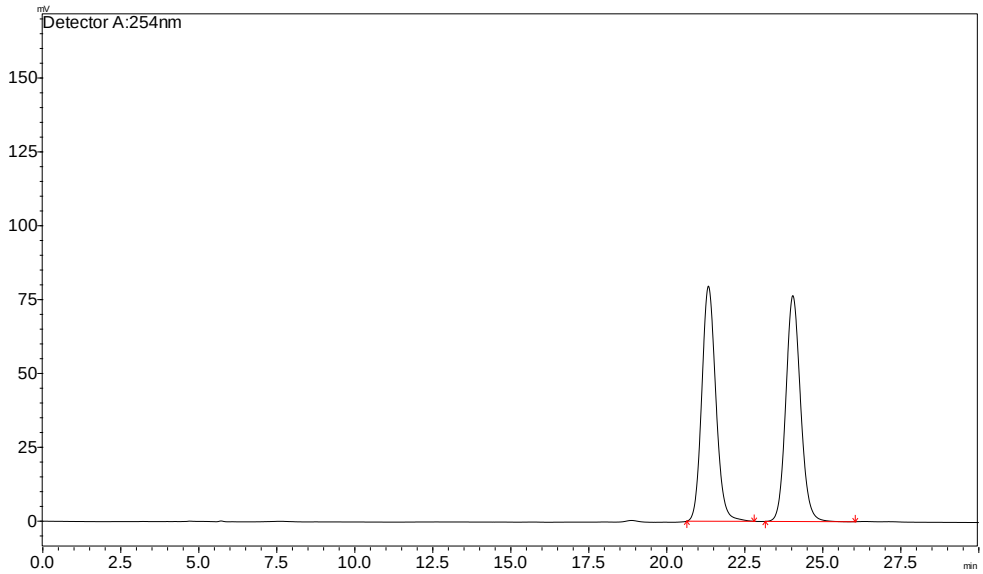
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.686	20773374	849917	96.613	96.446

2	19.934	728182	31318	3.387	3.554
Total		21501556	881235	100.000	100.000

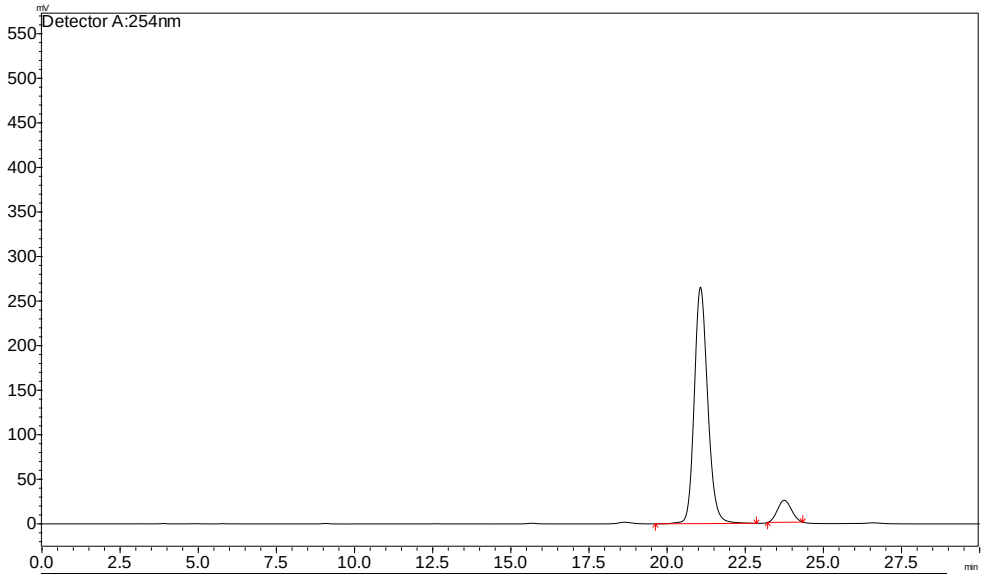


3g
82%, 83% ee

Daicel Chiralpak IA-H column, n-hexane/i-PrOH (99/1), 1.0 mL/min, 254 nm, 21.062 min (major enantiomer), 23.744 min (minor enantiomer).

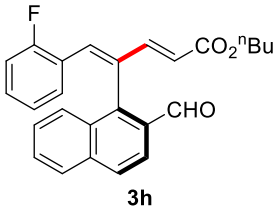


Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.330	2500738	79591	49.908	51.000
2	24.035	2510007	76471	50.092	49.000
Total		5010745	156061	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.062	7934544	265384	91.207	91.498

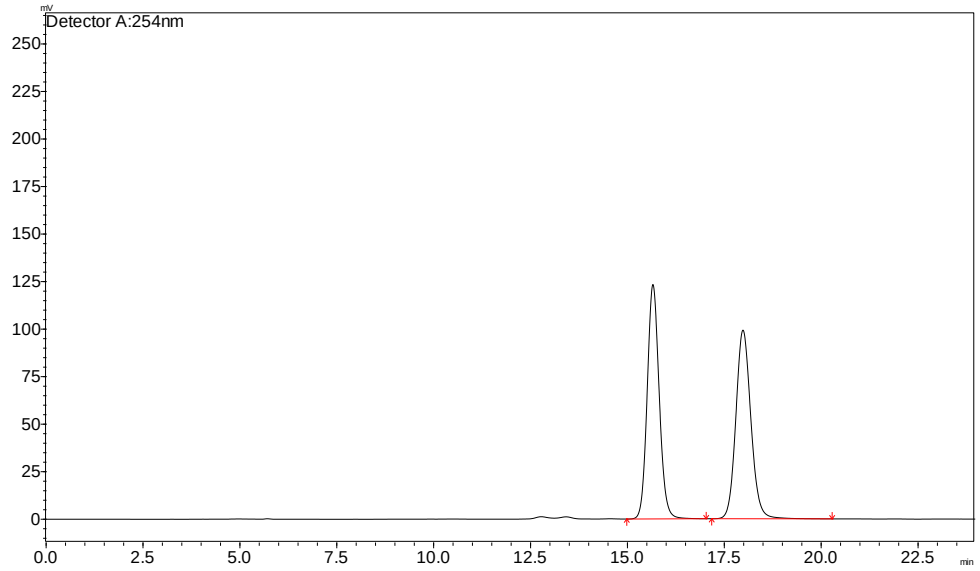
2	23.744	764926	24659	8.793	8.502
Total		8699470	290043	100.000	100.000



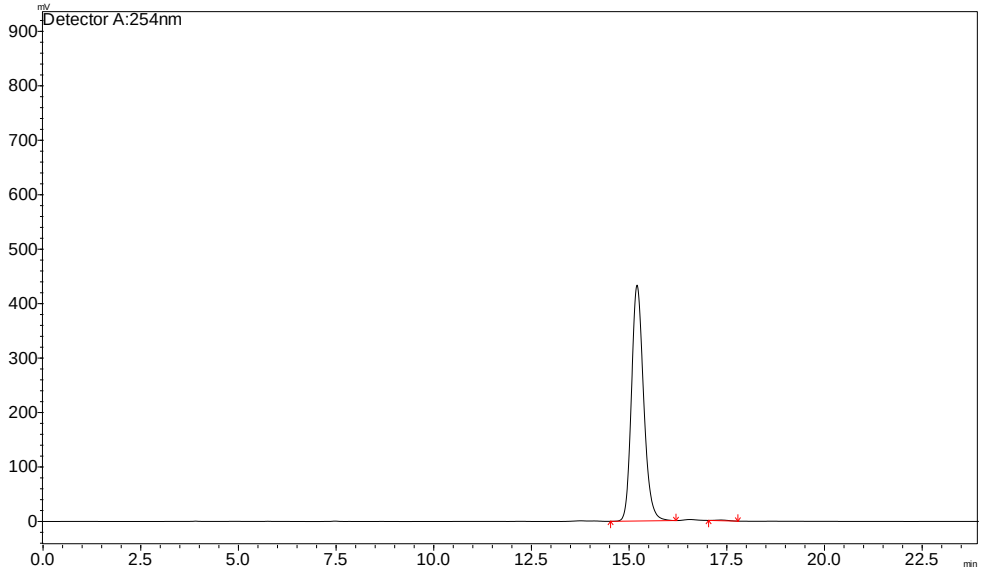
3h

77%, 99% ee

Daicel Chiralpak IA-H column, n-hexane/i-PrOH (99/1), 1.0 mL/min, 254 nm, 15.198 min (major enantiomer), 17.346 min (minor enantiomer).

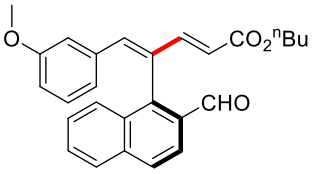


Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.654	2658802	123325	49.862	55.414
2	17.978	2673478	99227	50.138	44.586
Total		5332281	222552	100.000	100.000



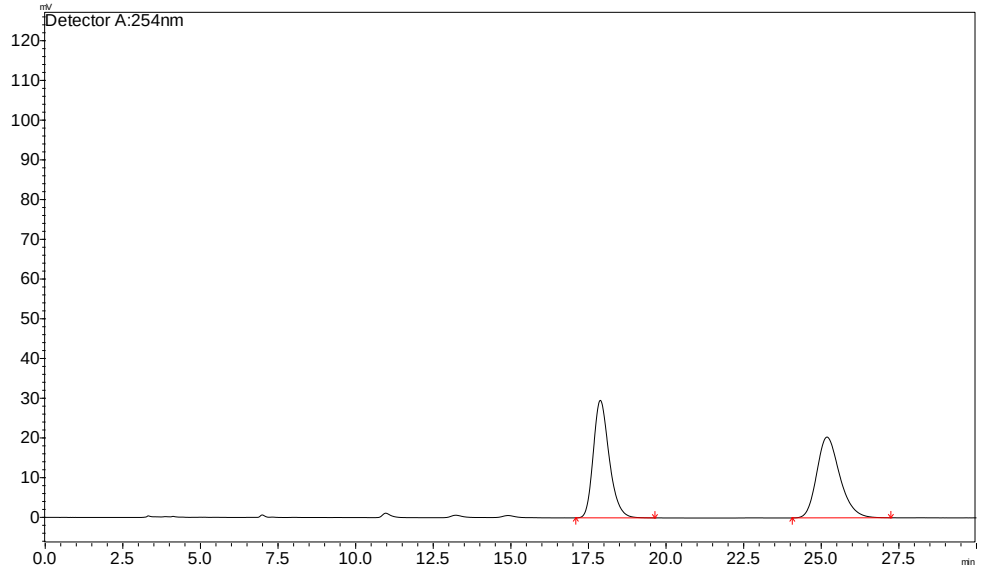
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.198	9373485	433244	99.715	99.718

2	17.346	26838	1225	0.285	0.282
Total		9400322	434469	100.000	100.000

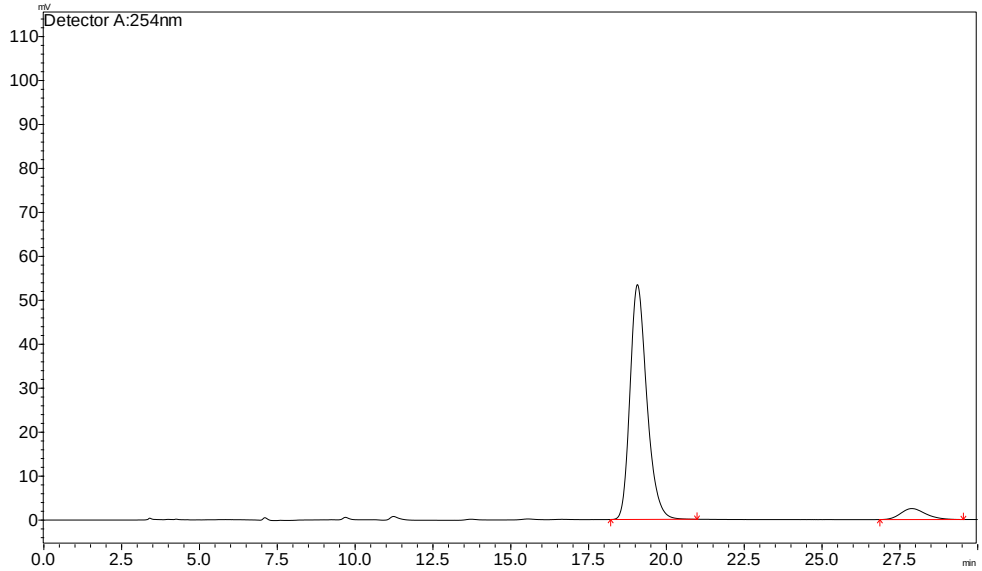


3i
90%, 87% ee

Daicel Chiralpak IC-H column, n-hexane/i-PrOH (90/10), 1.0 mL/min, 254 nm, 19.065 min (major enantiomer), 27.883 min (minor enantiomer).

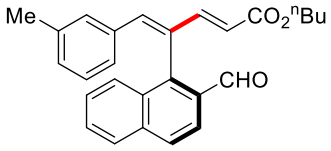


Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.878	1053989	29578	50.098	59.257
2	25.181	1049886	20337	49.902	40.743
Total		2103875	49914	100.000	100.000



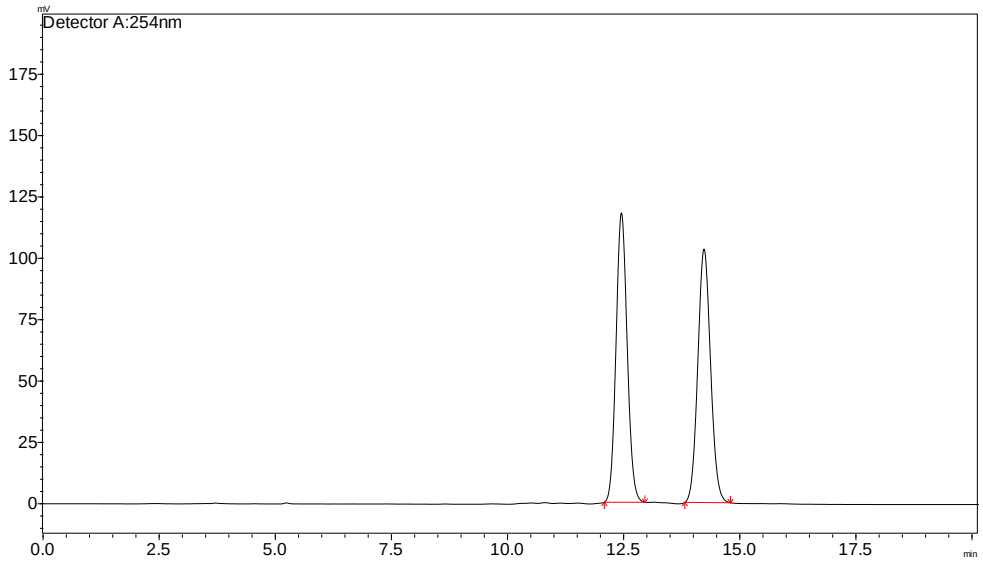
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.065	2005137	53420	93.475	95.531

2	27.883	139968	2499	6.525	4.469
Total		2145105	55919	100.000	100.000

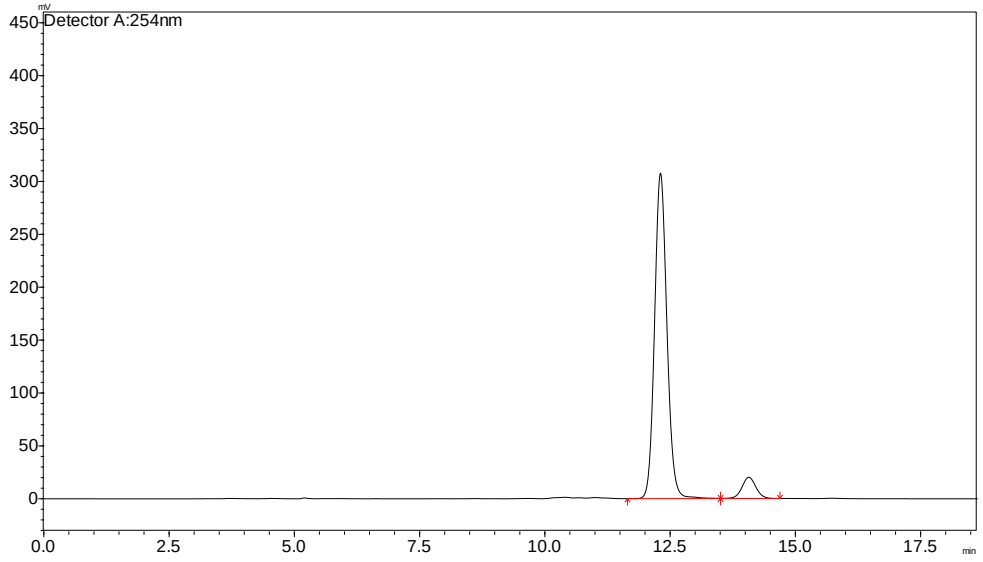


3j
80%, 89% ee

Daicel Chiralpak IA-H column, n-hexane/i-PrOH (98/2), 1.0 mL/min, 254 nm, 12.303 min (major enantiomer), 14.067 min (minor enantiomer).

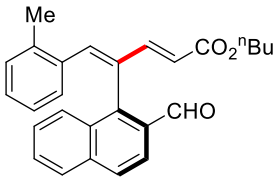


Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.448	1971262	117916	49.901	53.309
2	14.226	1979079	103279	50.099	46.691
Total		3950341	221195	100.000	100.000



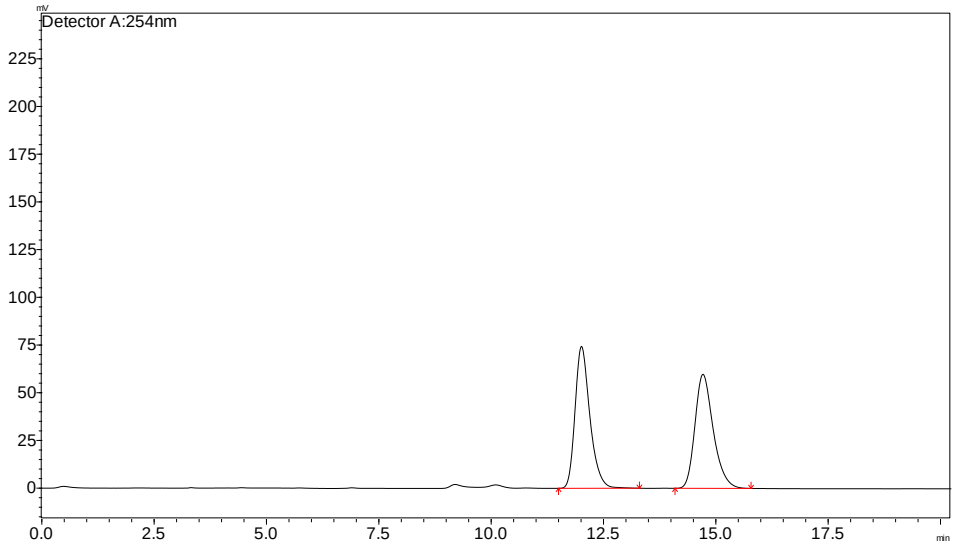
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.303	5272406	307790	93.133	93.886

2	14.067	388769	20044	6.867	6.114
Total		5661175	327834	100.000	100.000

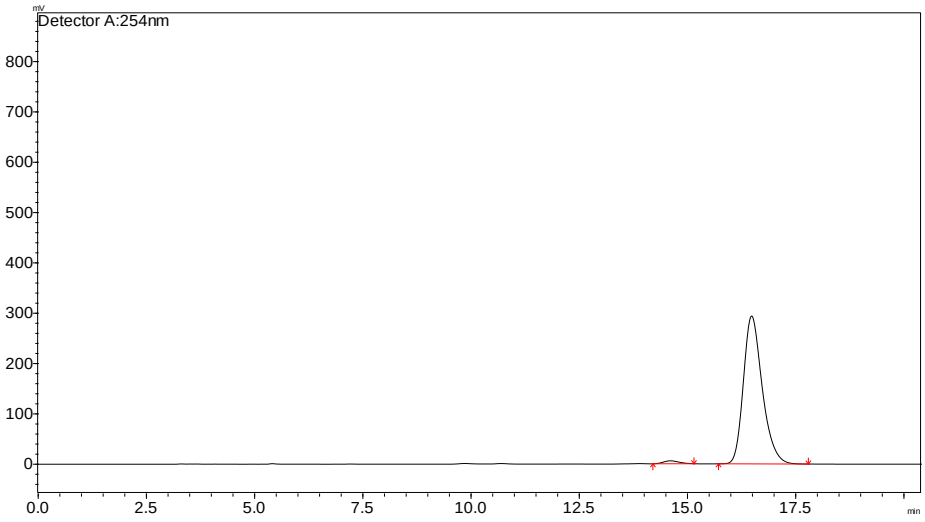


3k
83%, 97% ee

Daicel Chiralpak IC-H column, n-hexane/i-PrOH (92/8), 1.0 mL/min, 254 nm, 14.602 min (major enantiomer), 16.477 min (minor enantiomer).

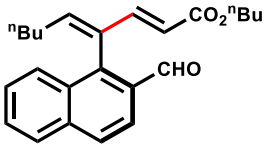


Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.006	1707606	74360	50.202	55.446
2	14.709	1693851	59751	49.798	44.554
Total		3401456	134111	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.602	148687	5906	1.642	1.971

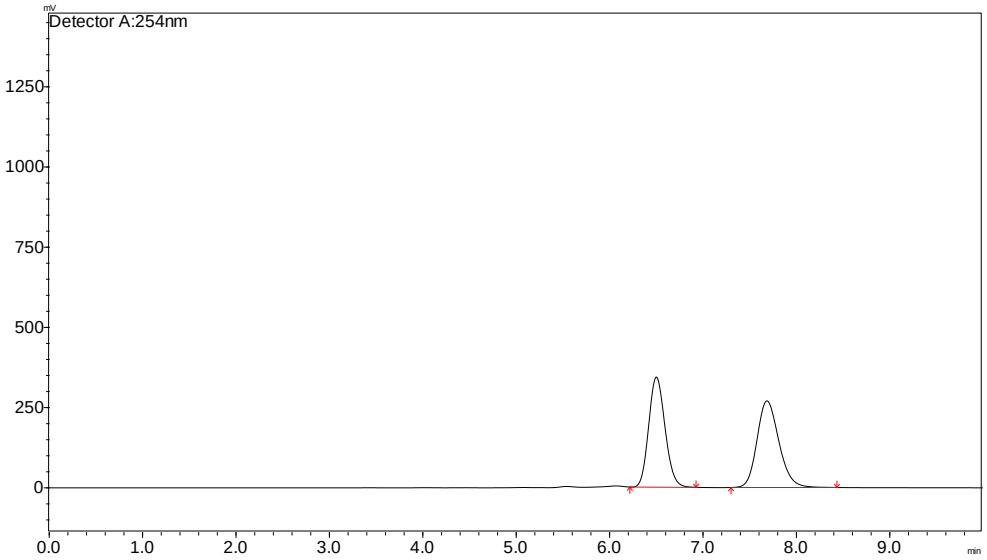
2	16.477	8906591	293804	98.358	98.029
Total		9055278	299711	100.000	100.000



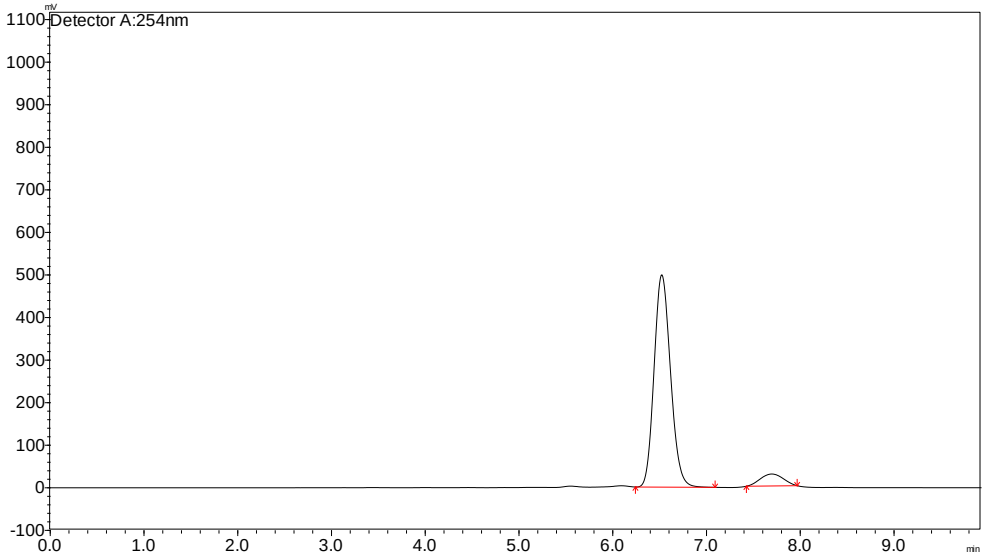
3l

65%,85% ee

Daicel Chiralpak OD-H column, n-hexane/i-PrOH (98/2), 1.0 mL/min, 254 nm, 6.518 min (major enantiomer), 7.693 min (minor enantiomer).

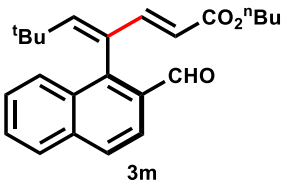


Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.496	4177985	343499	48.699	55.984
2	7.680	4401245	270063	51.301	44.016
Total		8579230	613561	100.000	100.000



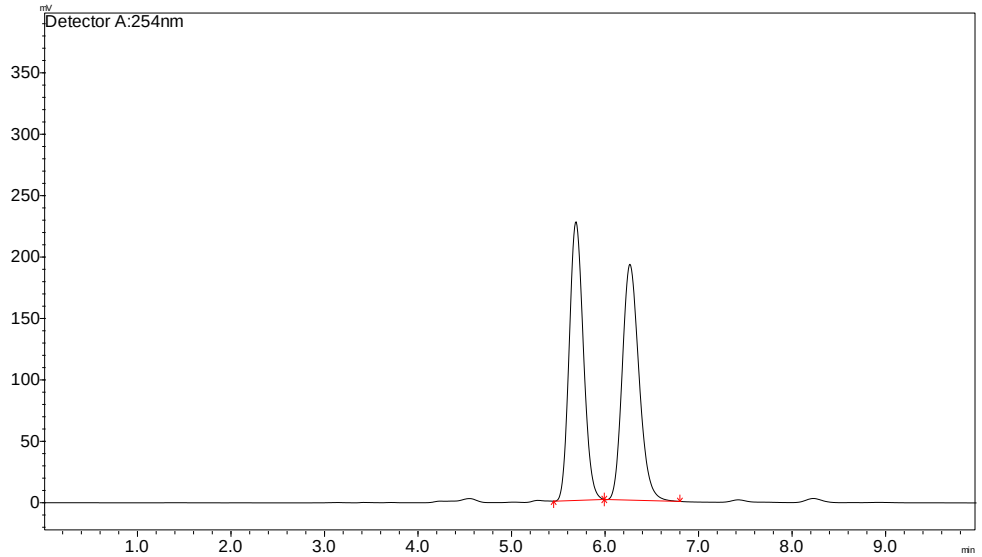
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.518	6080216	498913	92.699	94.685
2	7.693	478875	28006	7.301	5.315

Total		6559091	526920	100.000	100.000

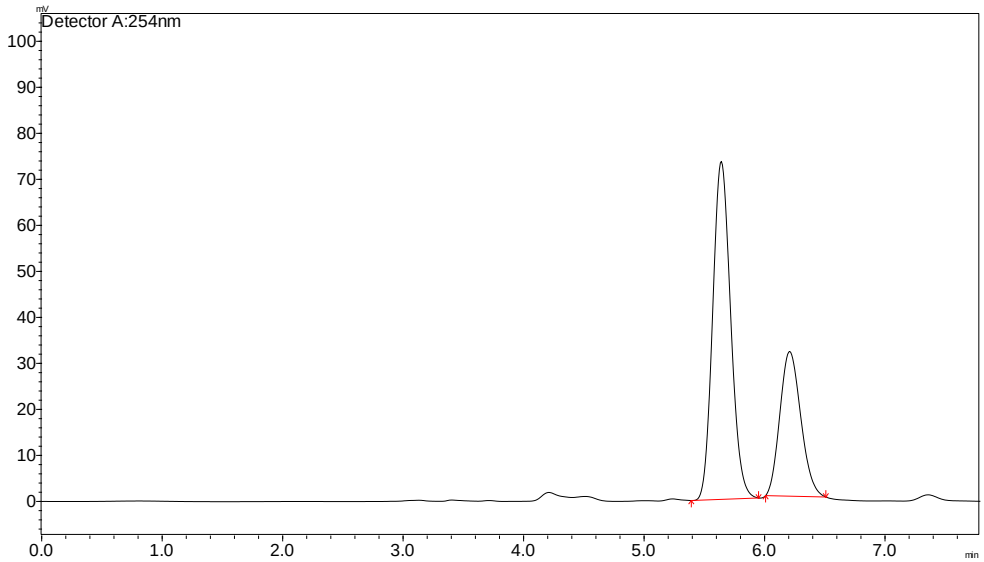


3m
42%,33% ee

Daicel Chiralpak OD-H column, n-hexane/i-PrOH (98/2), 1.0 mL/min, 254 nm, 5.636 min (major enantiomer), 6.204 min (minor enantiomer).

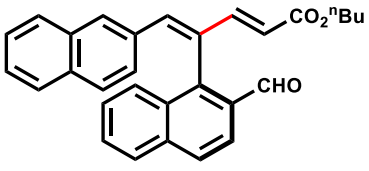


Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.684	2389287	226813	49.952	54.154
2	6.262	2393845	192020	50.048	45.846
Total		4783132	418833	100.000	100.000



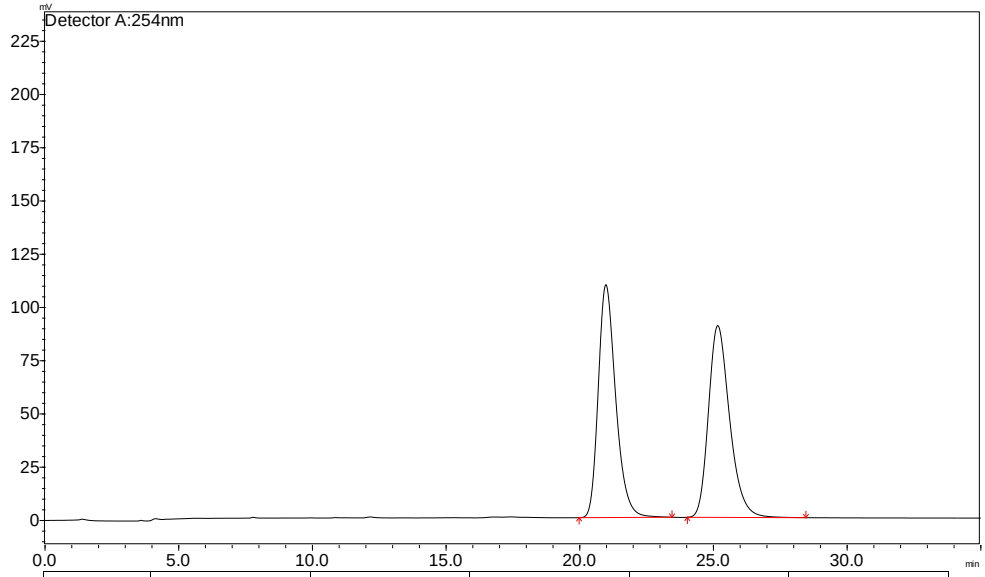
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.636	762232	73467	66.750	70.021
2	6.204	379688	31455	33.250	29.979

Total		1141920	104921	100.000	100.000

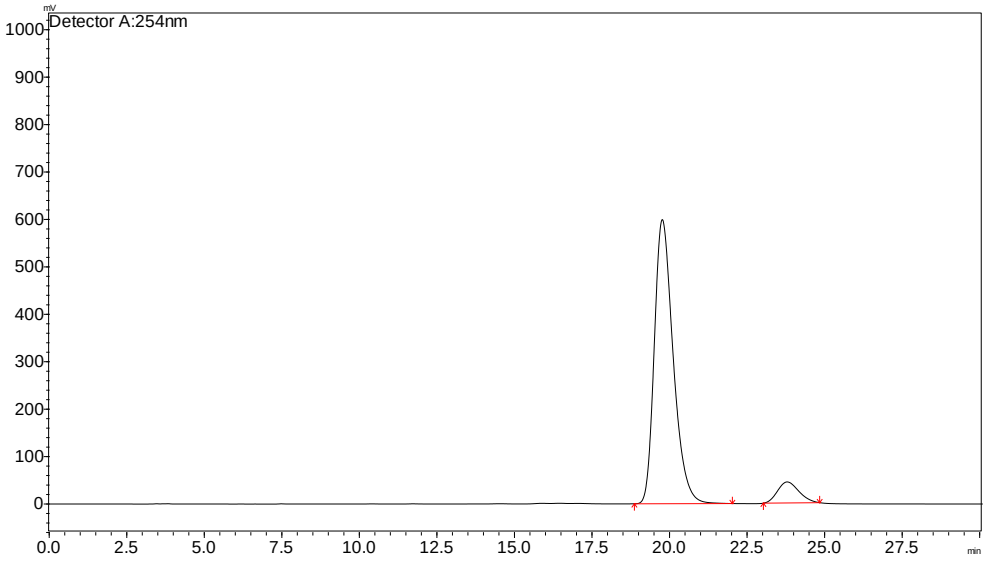


3n
81%,85% ee

Daicel Chiralpak IC-H column, n-hexane/i-PrOH (90/10), 1.0 mL/min, 254 nm, 19.763 min (major enantiomer), 23.790 min (minor enantiomer).

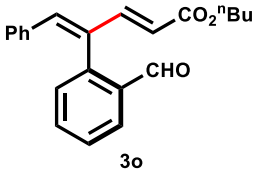


Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.973	4974614	109323	50.037	54.832
2	25.156	4967336	90055	49.963	45.168
Total		9941951	199378	100.000	100.000



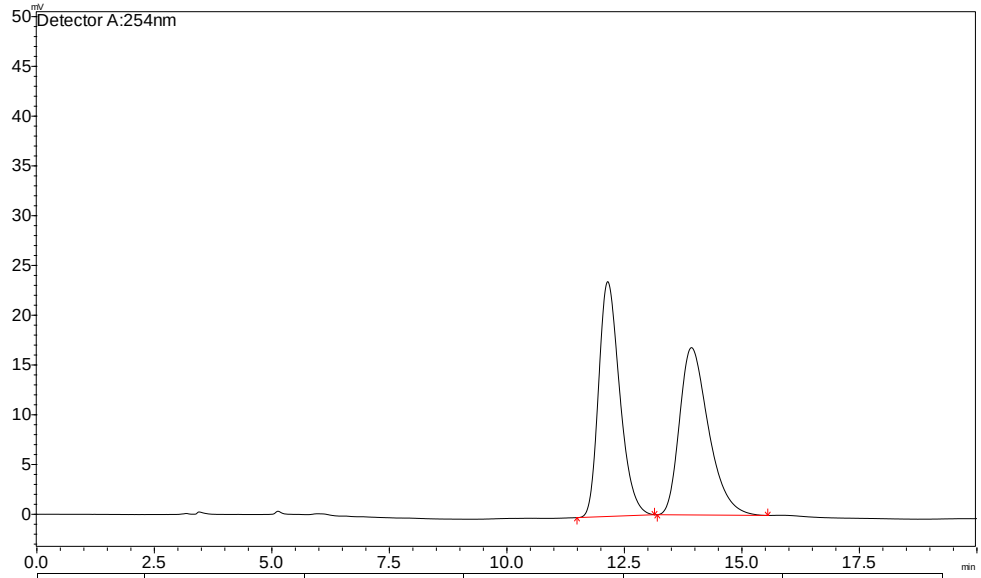
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.763	25319603	599181	92.261	93.109
2	23.790	2123927	44343	7.739	6.891

Total		27443529	643524	100.000	100.000

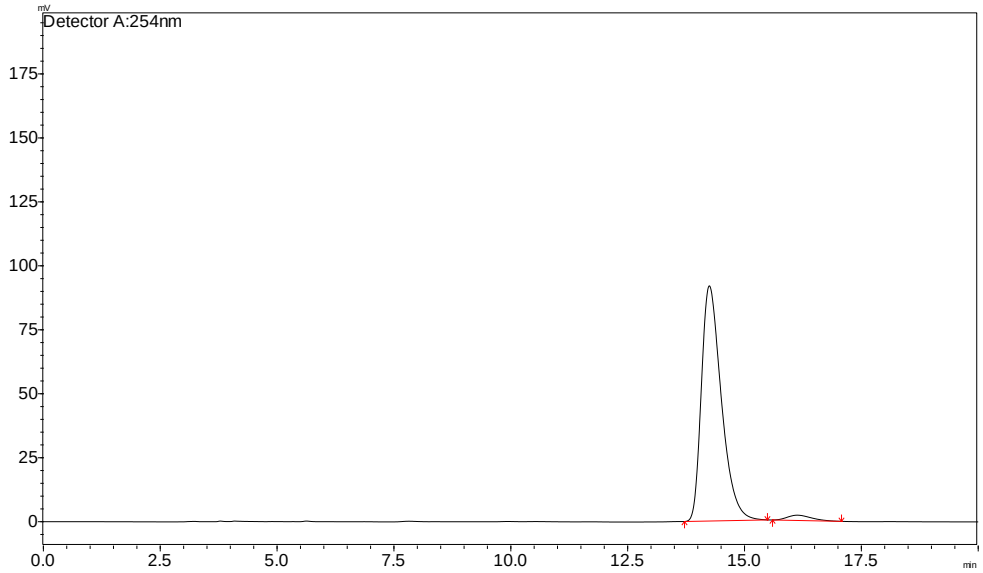


3o
91%,95% ee

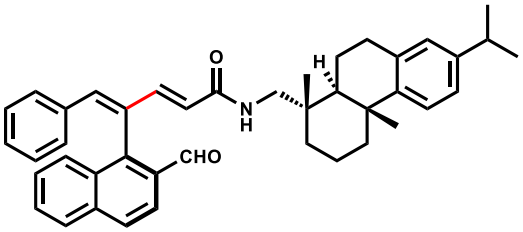
Daicel Chiralpak OD-H column, n-hexane/i-PrOH (99/1), 1.0 mL/min, 254 nm, 14.244 min (major enantiomer), 16.127 min (minor enantiomer).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.141	736985	23594	50.495	58.393
2	13.924	722530	16811	49.505	41.607
Total		1459515	40406	100.000	100.000

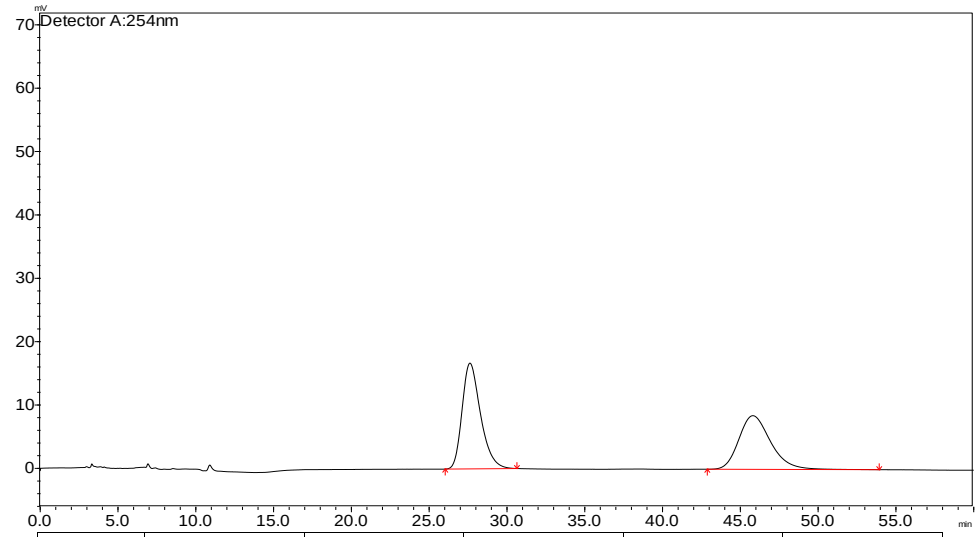


Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.244	2730672	91917	97.355	97.804
2	16.127	74196	2063	2.645	2.196
Total		2804868	93981	100.000	100.000

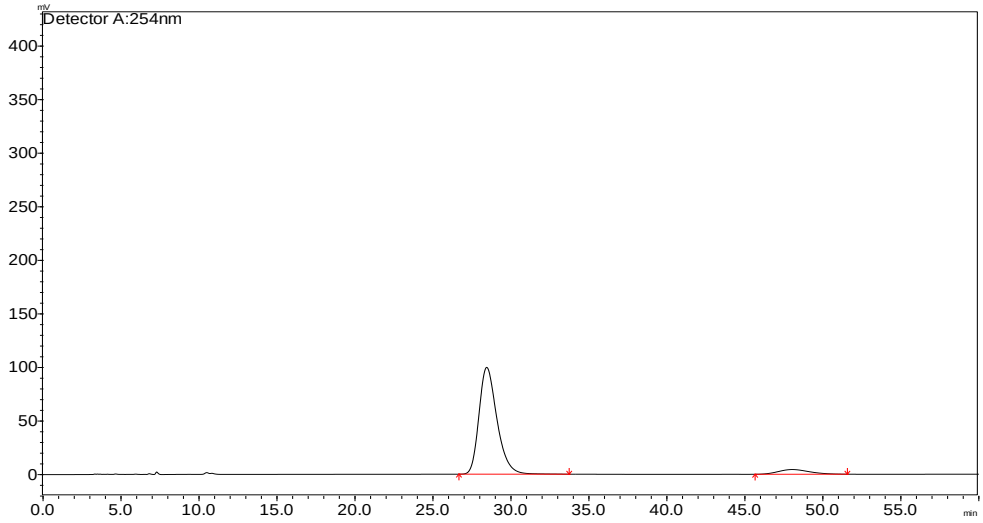


3p
80%,86% ee

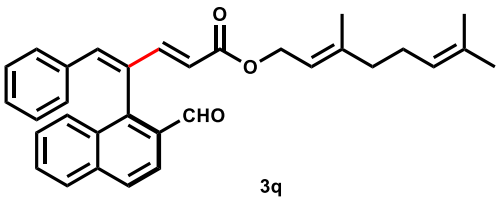
Daicel Chiralpak IC-H column, n-hexane/i-PrOH (90/10), 1.0 mL/min, 254 nm, 28.443 min (major enantiomer), 48.025 min (minor enantiomer).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.616	1376921	16694	53.330	66.333
2	45.801	1204944	8473	46.670	33.667
Total		2581865	25166	100.000	100.000

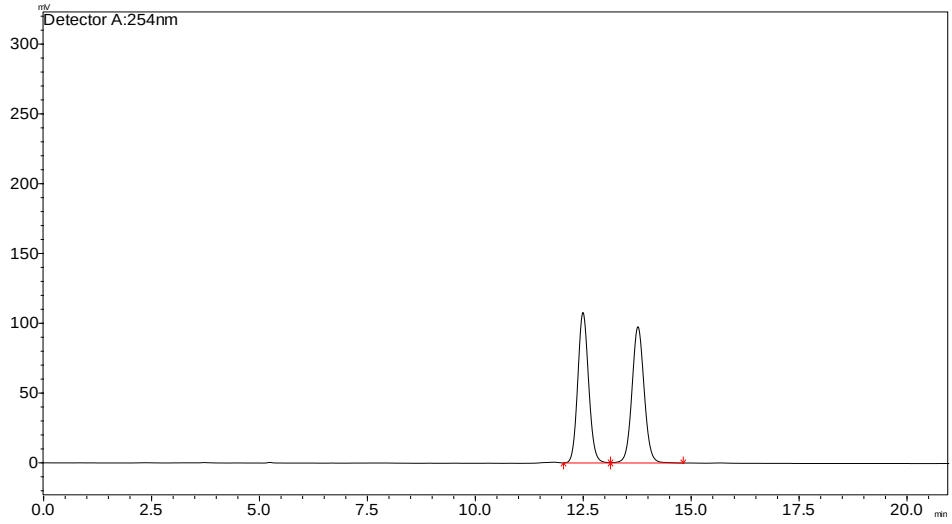


Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.443	8007764	99701	92.986	95.795
2	48.025	604027	4376	7.014	4.205
Total		8611791	104077	100.000	100.000

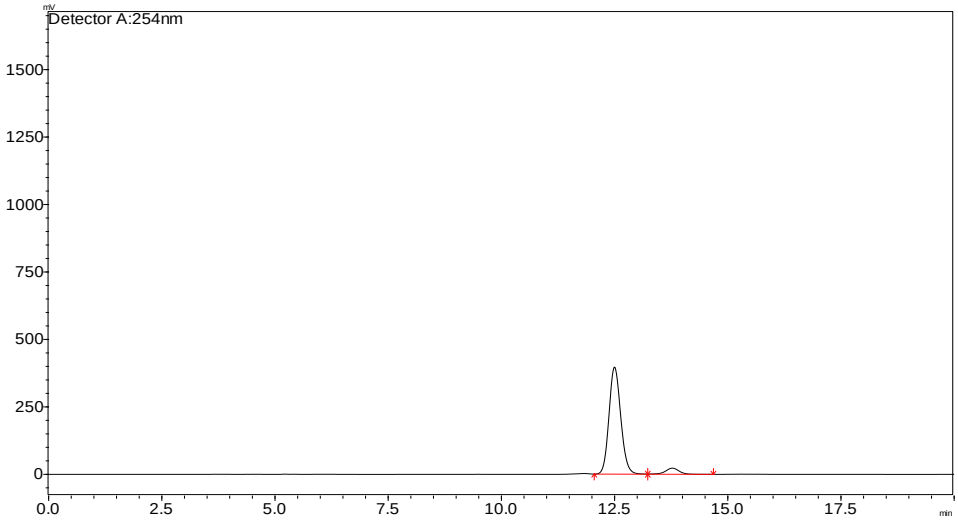


3q
84%,88% ee

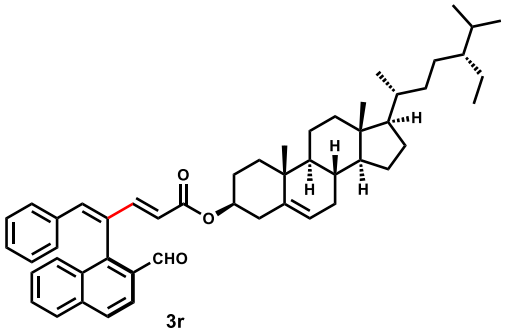
Daicel Chiralpak IA-H column, n-hexane/i-PrOH (98/2), 1.0 mL/min, 254 nm, 12.494 min (major enantiomer), 13.771 min (minor enantiomer).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.489	1889756	107813	49.579	52.475
2	13.763	1921865	97642	50.421	47.525
Total		3811621	205455	100.000	100.000



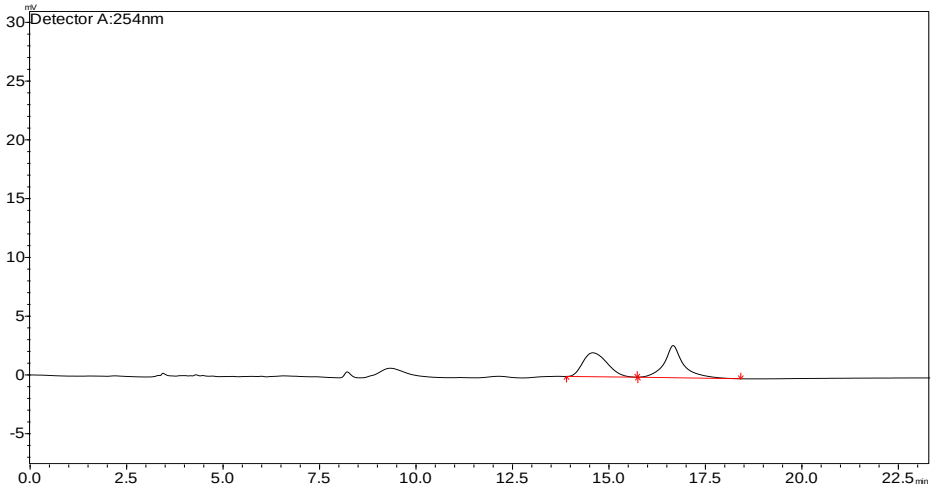
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.494	7173083	396778	93.853	94.606
2	13.771	469788	22621	6.147	5.394
Total		7642871	419399	100.000	100.000



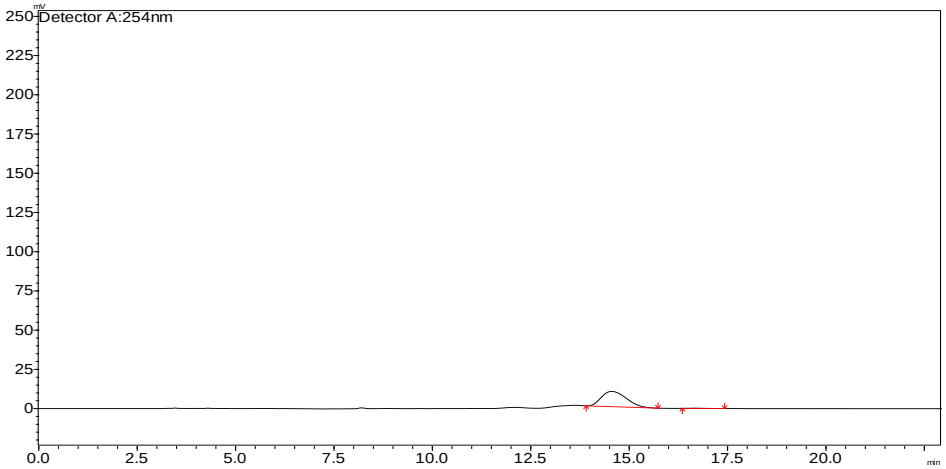
3r

75%98% ee

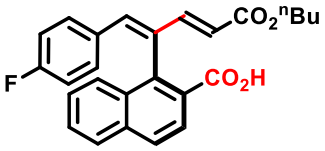
Daicel Chiralpak IC-H column, n-hexane/i-PrOH (95/5), 1.0 mL/min, 254 nm, 14.550 min (major enantiomer), 16.680 min (minor enantiomer).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.581	90007	2038	48.440	42.687
2	16.658	95806	2736	51.560	57.313
Total		185813	4774	100.000	100.000

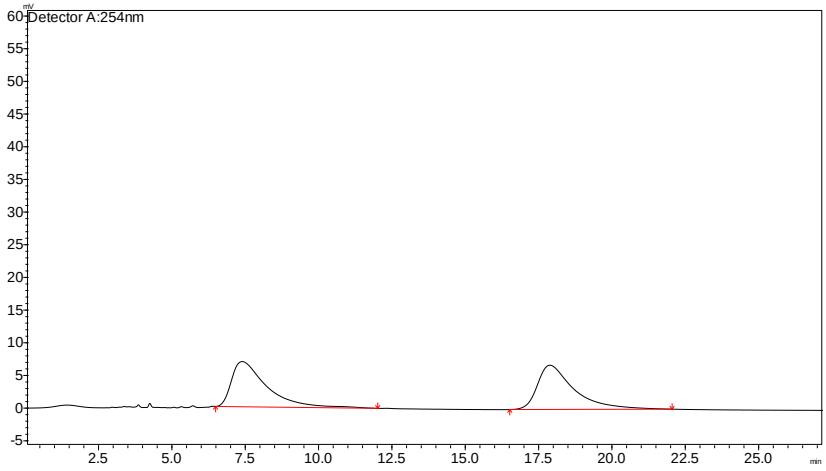


Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.550	428975	9716	99.152	98.698
2	16.680	3671	128	0.848	1.302
Total		432646	9844	100.000	100.000

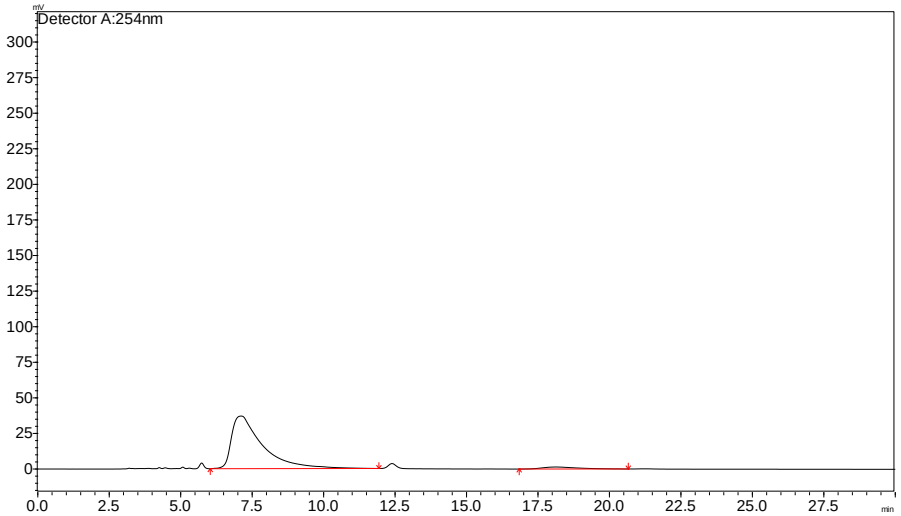


4a, 93%, 92% ee

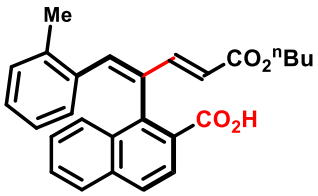
Daicel Chiralpak IA column, n-hexane/i-PrOH (60/40), 1 mL/min, 254 nm, 7.113 min (major enantiomer), 18.107 min (minor enantiomer).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.390	581497	6919	49.662	50.525
2	17.881	589420	6775	50.338	49.475
Total		1170916	13694	100.000	100.000

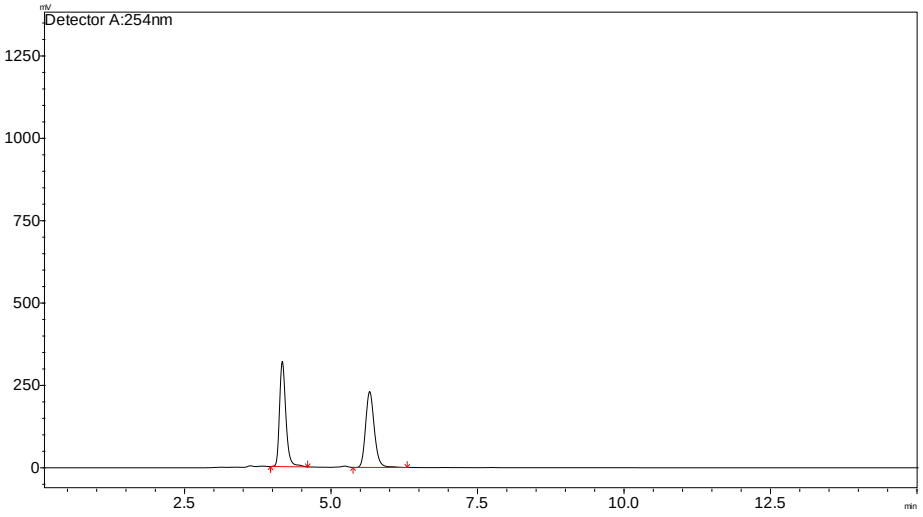


Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.113	2801293	36978	95.838	96.328
2	18.107	121651	1409	4.162	3.672
Total		2922943	38387	100.000	100.000

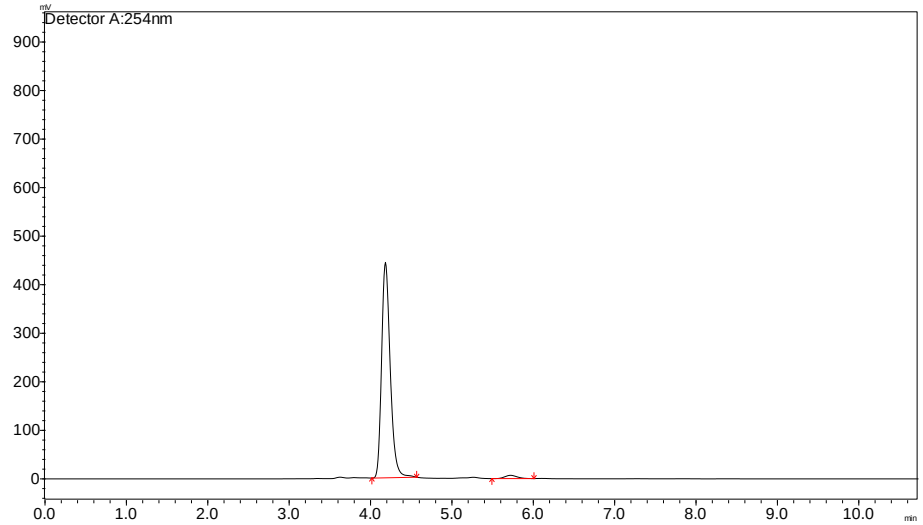


4b, 90%, 96% ee

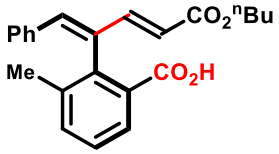
Daicel Chiralpak AD-H column, n-hexane/i-PrOH (60/40), 1 mL/min, 254 nm, 4.179 min (major enantiomer), 5.716 min (minor enantiomer).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.164	2407075	319860	50.259	58.136
2	5.654	2382292	230336	49.741	41.864
Total		4789368	550196	100.000	100.000

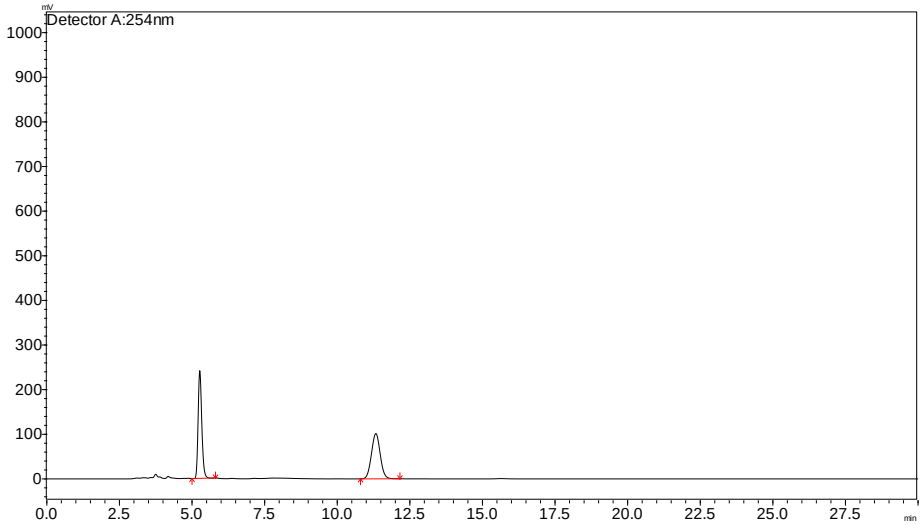


Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.179	3275942	443886	97.911	98.518
2	5.716	69888	6679	2.089	1.482
Total		3345829	450565	100.000	100.000

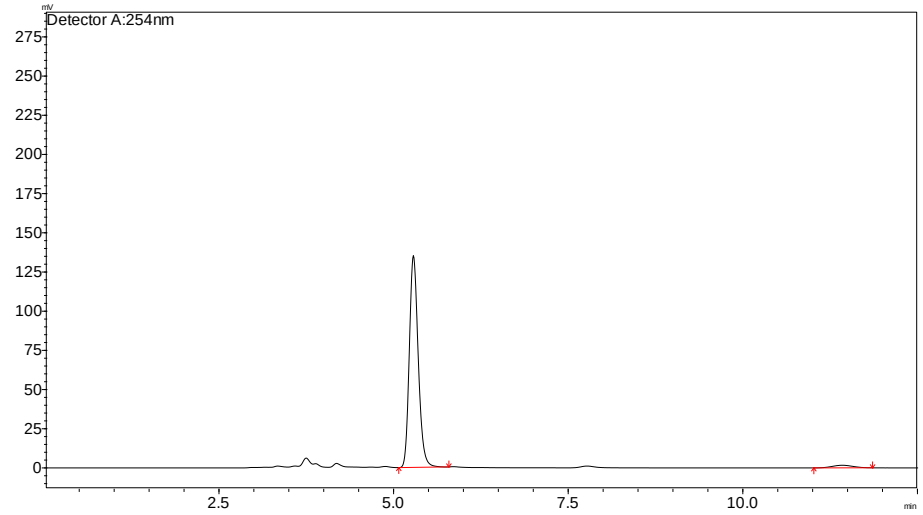


4c, 88%, 94% ee

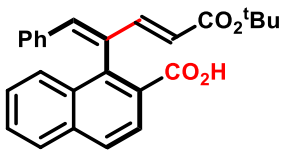
Daicel Chiralpak AD-H column, n-hexane/i-PrOH (60/40), 1 mL/min, 254 nm, 5.280 min (major enantiomer), 11.521 min (minor enantiomer).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.263	2104871	241276	49.699	70.385
2	11.326	2130395	101518	50.301	29.615
Total		4235266	342794	100.000	100.000

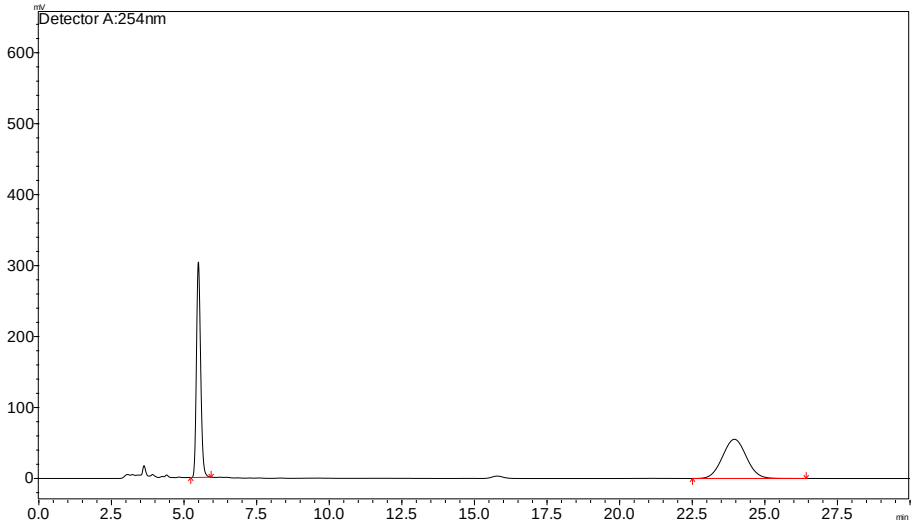


Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.280	1197303	135119	97.217	98.784
2	11.421	34280	1664	2.783	1.216
Total		1231583	136782	100.000	100.000



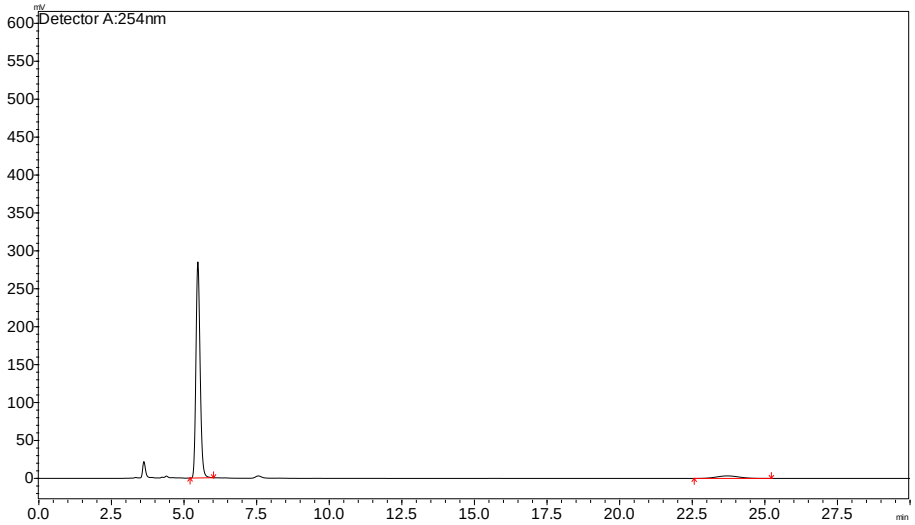
4d, 92%, 88% ee

Daicel Chiralpak AD-H column, n-hexane/i-PrOH (60/40), 1 mL/min, 254 nm, 5.471 min (major enantiomer), 23.709 min (minor enantiomer).

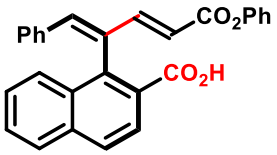


3.

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.489	3061516	303616	49.167	84.611
2	23.947	3165246	55223	50.833	15.389
Total		6226762	358839	100.000	100.000

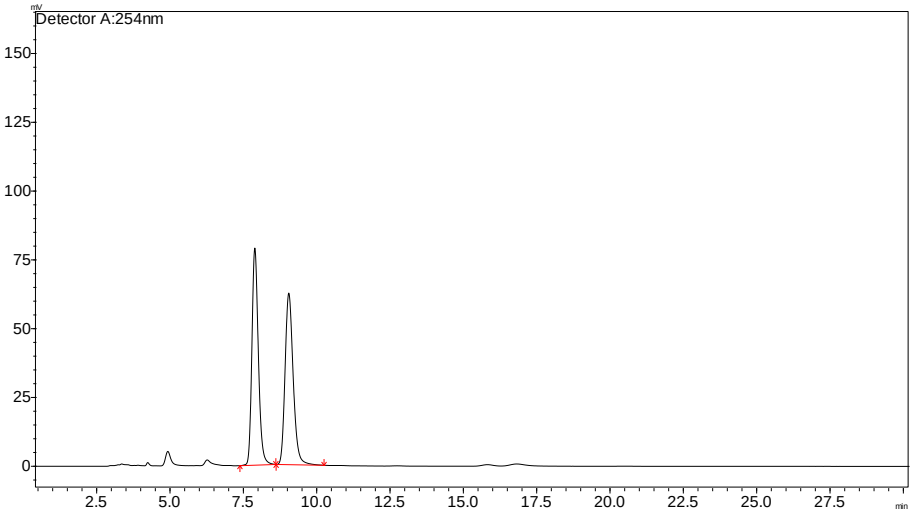


Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.471	2850763	284879	94.005	98.850
2	23.709	181814	3315	5.995	1.150
Total		3032577	288195	100.000	100.000

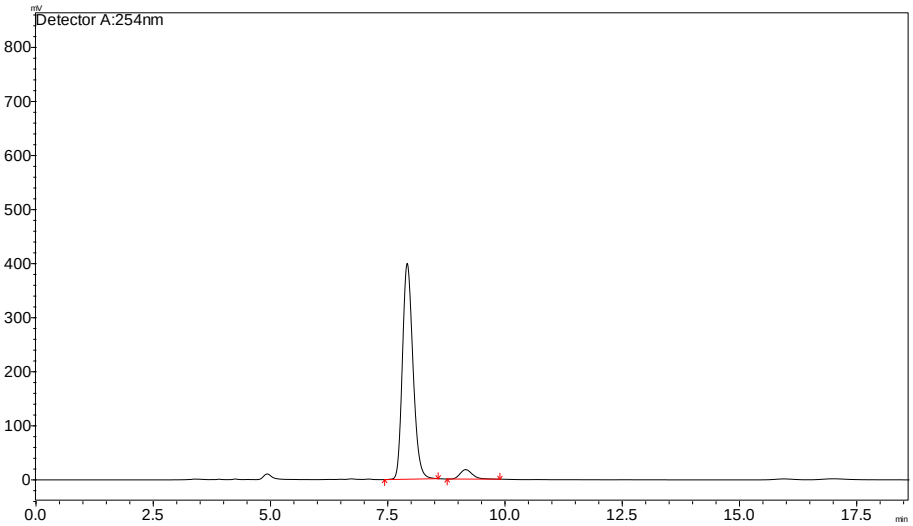


4e, 86%, 90% ee

Daicel Chiralpak AD-H column, n-hexane/i-PrOH (60/40), 1 mL/min, 254 nm, 7.911 min (major enantiomer), 9.157 min (minor enantiomer).



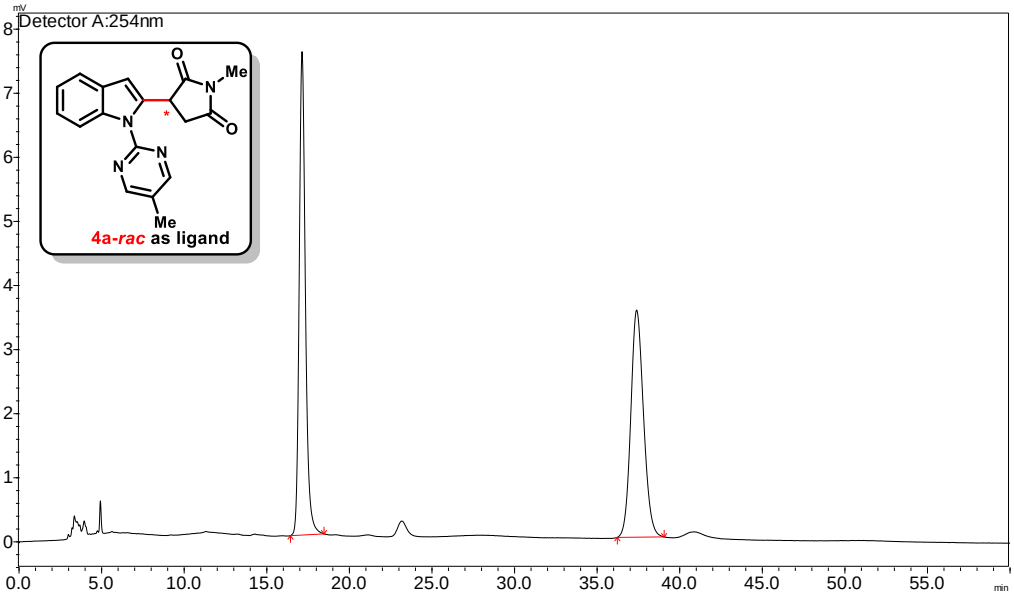
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.887	1206066	78926	50.112	55.863
2	9.044	1200678	62358	49.888	44.137
Total		2406744	141284	100.000	100.000



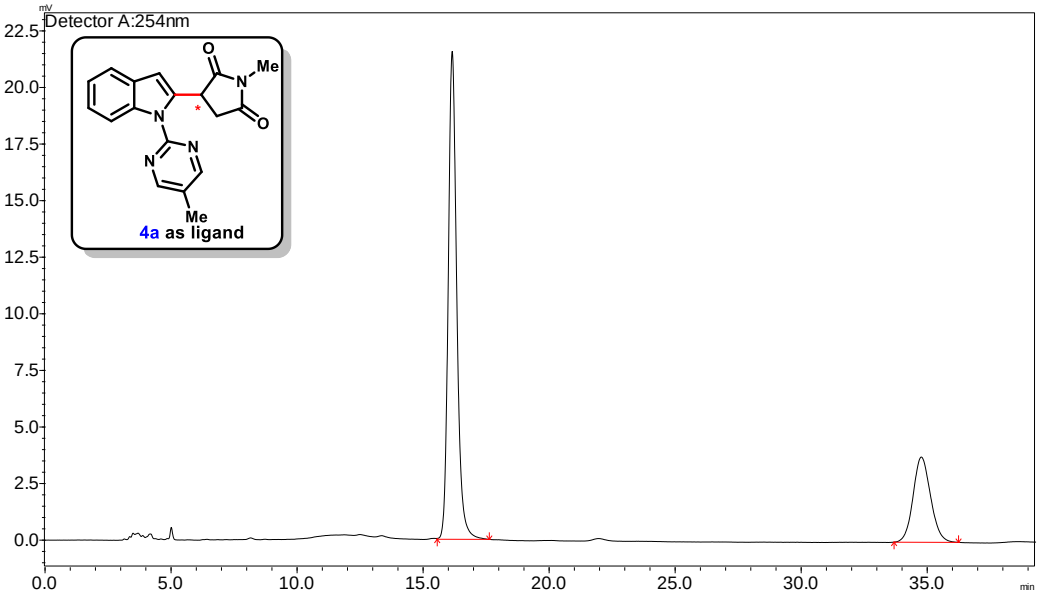
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.911	6251934	399293	95.131	95.808
2	9.157	319973	17471	4.869	4.192
Total		6571908	416765	100.000	100.000

9.2 HPLC Analysis of Products 7 with different CCAs

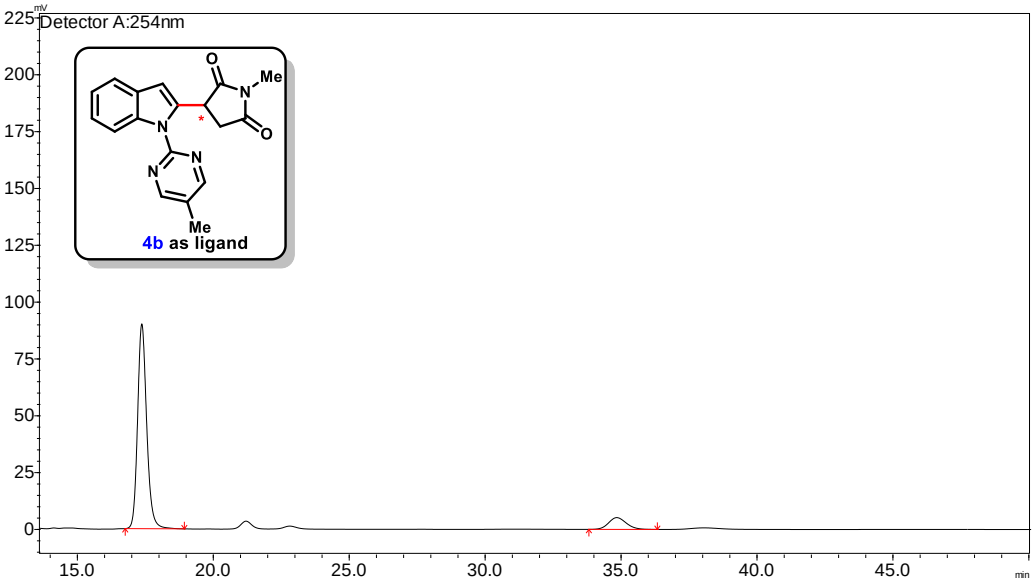
Daicel Chiralpak IA column, n-hexane/i-PrOH (80/20), 1.0 mL/min, 254 nm, 17.130min (major enantiomer), 37.385 min (minor enantiomer).



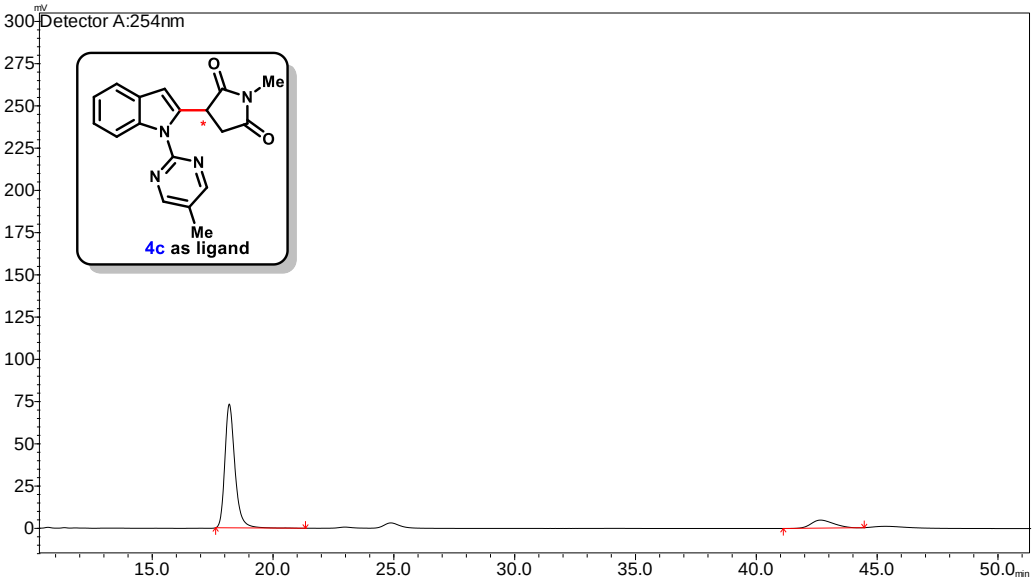
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.130	197209	7543	50.911	68.037
2	37.385	190152	3544	49.089	31.963
Total		387361	11087	100.000	100.000



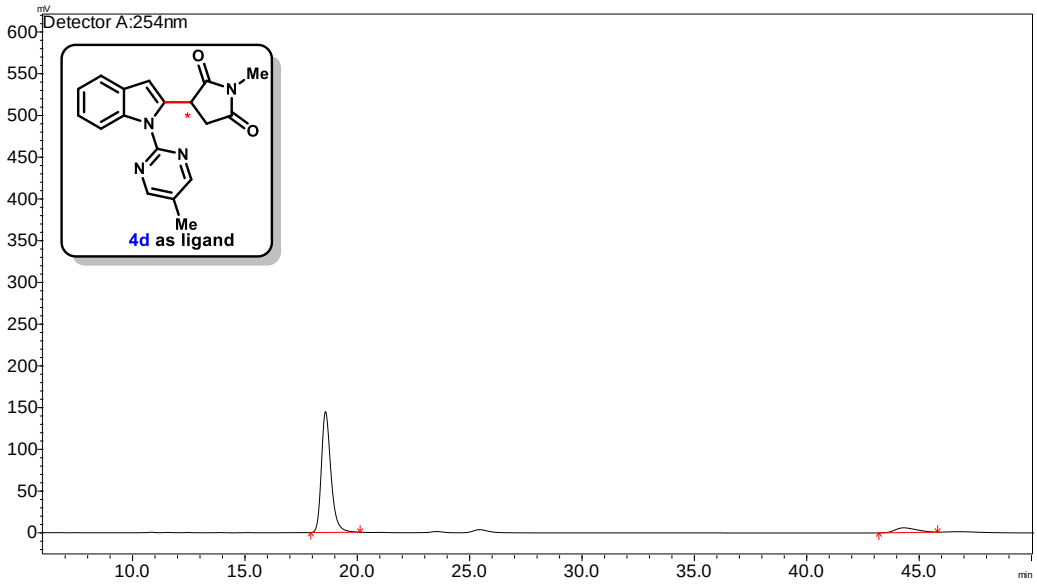
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.149	506081	21555	73.543	85.127
2	34.760	182066	3766	26.457	14.873
Total		688147	25321	100.000	100.000



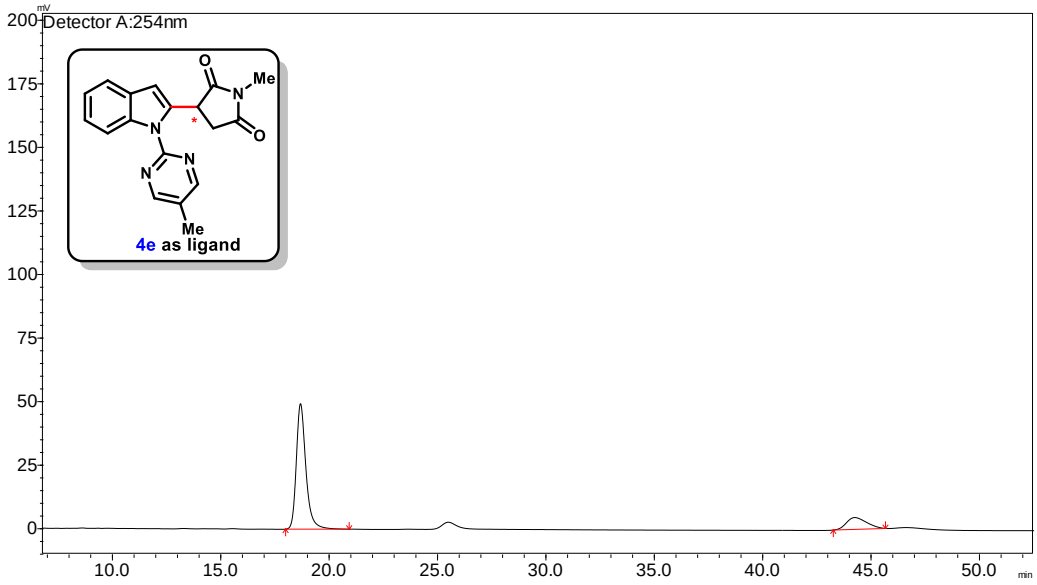
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.365	2087108	90029	89.998	94.585
2	34.836	231945	5154	10.002	5.415
Total		2319053	95183	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.184	2139674	73479	87.281	93.887
2	42.654	311790	4784	12.719	6.113
Total		2451464	78263	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.581	4312134	144911	92.233	96.262
2	44.310	363107	5627	7.767	3.738
Total		4675241	150538	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.673	1519938	49397	82.972	91.264
2	44.244	311920	4728	17.028	8.736
Total		1831858	54126	100.000	100.000

10. X-ray Crystallography

Single crystal of compound **3e**:

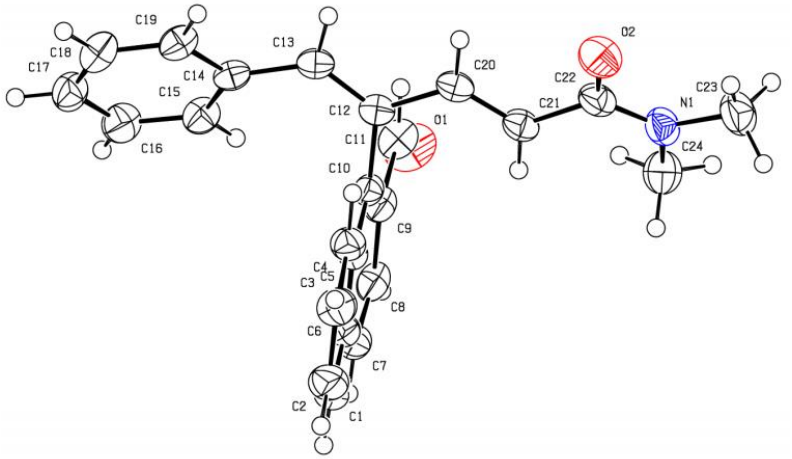


Table 1 Crystal data and structure refinement for 3e.

Empirical formula	$C_{24}H_{21}NO_2$
Formula weight	355.42
Temperature/K	170.0
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.726(2)
b/Å	12.5790(16)
c/Å	14.755(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1990.9(6)
Z	4
ρ_{calc}g/cm^3	1.186
μ/mm^{-1}	0.593
F(000)	752.0
Crystal size/mm^3	0.42 × 0.36 × 0.29
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.238 to 136.458
Index ranges	$-12 \le h \le 12$, $-14 \le k \le 15$, $-15 \le l \le 17$
Reflections collected	18353
Independent reflections	3644 [R_{int} = 0.0218, R_{sigma} = 0.0163]
Data/restraints/parameters	3644/0/247
Goodness-of-fit on F^2	1.070

Final R indexes [I>=2σ (I)]	R_1 = 0.0277, wR_2 = 0.0741
Final R indexes [all data]	R_1 = 0.0279, wR_2 = 0.0744
Largest diff. peak/hole / e Å^{-3}	0.15/-0.15
Flack parameter	0.00(5)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) 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	6748.2(15)	371.3(11)	4907.3(9)	61.7(4)
O2	1053.4(11)	2285.3(10)	3763.6(10)	54.3(3)
N1	1365.2(11)	512.0(12)	3808.0(10)	41.7(3)
C1	6477.4(17)	1582.7(14)	667.6(12)	46.2(4)
C2	5785(2)	2347.8(14)	249.5(12)	51.2(5)
C3	5078.9(19)	3071.8(13)	762.1(12)	46.3(4)
C4	5076.5(15)	3016.2(12)	1688.9(11)	37.0(3)
C5	5762.8(13)	2215.8(12)	2148.1(10)	31.8(3)
C6	6471.1(14)	1476.0(12)	1626.3(11)	36.4(3)
C7	7096.5(14)	628.6(13)	2070.8(12)	40.7(4)
C8	7006.7(14)	504.8(12)	2981.9(12)	39.7(4)
C9	6319.4(14)	1246.3(12)	3516.7(11)	34.7(3)
C10	5729.3(13)	2100.0(11)	3114.6(10)	30.6(3)
C11	6263.3(17)	1111.3(13)	4507.0(12)	43.2(4)
C12	4975.2(13)	2887.9(11)	3644.9(10)	31.9(3)
C13	5408.6(14)	3851.2(12)	3893.0(10)	33.9(3)
C14	6653.4(14)	4317.1(11)	3778.1(10)	33.5(3)
C15	7772.5(15)	3739.9(13)	3792.2(12)	40.1(3)
C16	8910.1(16)	4245.2(14)	3691.6(13)	46.6(4)
C17	8967.8(16)	5331.2(14)	3564.6(11)	45.5(4)
C18	7876.3(17)	5918.9(13)	3544.6(12)	45.5(4)
C19	6738.3(15)	5421.9(13)	3666.7(11)	39.6(4)
C20	3668.2(14)	2623.3(12)	3804.1(10)	34.8(3)
C21	3140.8(13)	1687.1(12)	3628.4(10)	34.9(3)
C22	1777.3(14)	1519.2(14)	3745.9(11)	39.1(3)
C23	26.2(16)	303.9(19)	3781.1(14)	58.3(5)
C24	2179.3(18)	-411.3(15)	3853.3(14)	50.6(4)

Table 3 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	78.9(10)	47.8(7)	58.4(8)	10.0(6)	-20.6(7)	15.0(7)
O2	35.3(6)	57.9(7)	69.7(8)	-7.1(7)	2.6(6)	14.4(5)
N1	31.8(6)	53.0(8)	40.2(7)	0.8(6)	-0.2(6)	-3.2(6)
C1	47.3(9)	44.9(8)	46.4(9)	-12.8(7)	15.7(7)	-7.9(8)
C2	69.4(13)	48.3(9)	36.1(9)	-1.6(7)	11.2(8)	-10.5(9)
C3	61.8(11)	38.7(8)	38.5(8)	5.1(7)	0.6(8)	-3.1(8)
C4	39.9(8)	33.4(7)	37.6(8)	-1.2(6)	3.4(6)	1.3(6)
C5	28.4(7)	30.8(7)	36.2(8)	-4.0(6)	3.6(6)	-2.5(6)
C6	29.4(7)	34.1(7)	45.7(8)	-9.8(6)	6.8(6)	-3.7(6)
C7	26.6(7)	35.6(8)	59.9(10)	-15.2(7)	4.0(7)	2.6(6)
C8	27.8(7)	30.0(8)	61.1(10)	-6.4(7)	-8.7(7)	3.9(6)
C9	29.2(7)	30.1(7)	44.7(8)	-2.5(6)	-5.1(6)	1.8(6)
C10	26.7(7)	28.6(7)	36.5(8)	-3.9(6)	-1.2(5)	-0.7(6)
C11	47.0(10)	36.9(8)	45.8(9)	2.1(7)	-11.2(7)	3.6(7)
C12	34.5(7)	32.3(7)	29.0(7)	0.9(6)	-0.4(6)	6.5(6)
C13	37.8(7)	33.3(7)	30.7(7)	-1.8(6)	0.2(6)	7.8(6)
C14	40.8(7)	32.7(7)	27.0(7)	-3.3(6)	-4.7(6)	3.6(6)
C15	40.2(8)	35.7(8)	44.4(8)	-1.7(7)	-5.4(7)	3.7(6)
C16	38.1(8)	49.0(9)	52.9(10)	-4.8(8)	-6.8(8)	4.7(7)
C17	42.2(8)	50.9(9)	43.4(9)	-3.2(8)	-5.9(7)	-8.0(8)
C18	53.0(10)	36.4(8)	47.2(9)	0.0(7)	-10.7(8)	-5.5(7)
C19	43.3(8)	34.0(7)	41.6(8)	-5.2(6)	-8.3(7)	4.6(6)
C20	35.2(7)	37.1(7)	32.1(7)	-0.8(6)	3.4(6)	8.9(6)
C21	30.7(7)	39.2(8)	34.7(7)	-0.8(6)	2.0(6)	7.6(6)
C22	31.5(7)	50.7(9)	35.2(7)	-3.0(7)	2.1(6)	5.9(6)
C23	36.2(9)	85.2(14)	53.6(10)	-3.7(10)	3.2(8)	-14.3(9)
C24	50.2(9)	46.9(9)	54.6(10)	5.3(8)	-1.4(8)	-2.5(8)

Table 4 Bond Lengths for 3e.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C11	1.219(2)	C9	C10	1.381(2)
O2	C22	1.238(2)	C9	C11	1.472(2)
N1	C22	1.345(2)	C10	C12	1.500(2)
N1	C23	1.460(2)	C12	C13	1.349(2)
N1	C24	1.455(2)	C12	C20	1.460(2)

Table 4 Bond Lengths for 3e.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.363(3)	C13	C14	1.468(2)
C1	C6	1.421(2)	C14	C15	1.403(2)
C2	C3	1.405(3)	C14	C19	1.402(2)
C3	C4	1.369(2)	C15	C16	1.384(2)
C4	C5	1.419(2)	C16	C17	1.380(3)
C5	C6	1.427(2)	C17	C18	1.385(3)
C5	C10	1.434(2)	C18	C19	1.383(2)
C6	C7	1.420(2)	C20	C21	1.332(2)
C7	C8	1.357(3)	C21	C22	1.488(2)
C8	C9	1.427(2)			

Table 5 Bond Angles for 3e.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C22	N1	C23	119.35(16)	C9	C10	C12	122.49(13)
C22	N1	C24	123.91(14)	O1	C11	C9	123.47(17)
C24	N1	C23	116.65(16)	C13	C12	C10	123.34(13)
C2	C1	C6	120.96(16)	C13	C12	C20	119.49(13)
C1	C2	C3	120.50(16)	C20	C12	C10	116.82(13)
C4	C3	C2	120.36(17)	C12	C13	C14	129.86(13)
C3	C4	C5	120.79(15)	C15	C14	C13	124.75(13)
C4	C5	C6	118.77(14)	C19	C14	C13	117.92(13)
C4	C5	C10	122.26(13)	C19	C14	C15	117.32(15)
C6	C5	C10	118.93(14)	C16	C15	C14	121.01(15)
C1	C6	C5	118.56(16)	C17	C16	C15	120.57(16)
C7	C6	C1	121.90(15)	C16	C17	C18	119.55(16)
C7	C6	C5	119.46(15)	C19	C18	C17	120.13(15)
C8	C7	C6	120.68(14)	C18	C19	C14	121.37(15)
C7	C8	C9	120.64(15)	C21	C20	C12	125.32(13)
C8	C9	C11	119.65(14)	C20	C21	C22	121.36(14)
C10	C9	C8	120.51(15)	O2	C22	N1	121.72(15)
C10	C9	C11	119.83(14)	O2	C22	C21	120.57(16)
C5	C10	C12	117.73(13)	N1	C22	C21	117.70(14)
C9	C10	C5	119.67(13)				

Table 6 Torsion Angles for 3e.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C3	C4	-0.1(3)	C10	C5	C6	C7	1.7(2)
C1	C6	C7	C8	-175.56(16)	C10	C9	C11	O1	179.07(16)
C2	C1	C6	C5	-2.5(3)	C10	C12	C13	C14	-4.5(2)
C2	C1	C6	C7	174.34(16)	C10	C12	C20	C21	9.7(2)
C2	C3	C4	C5	-1.3(3)	C11	C9	C10	C5	-178.62(14)
C3	C4	C5	C6	0.8(2)	C11	C9	C10	C12	-2.6(2)
C3	C4	C5	C10	-176.68(16)	C12	C13	C14	C15	-32.6(2)
C4	C5	C6	C1	1.1(2)	C12	C13	C14	C19	148.92(16)
C4	C5	C6	C7	-175.88(14)	C12	C20	C21	C22	-175.10(14)
C4	C5	C10	C9	173.83(14)	C13	C12	C20	C21	-176.84(15)
C4	C5	C10	C12	-2.4(2)	C13	C14	C15	C16	-179.03(16)
C5	C6	C7	C8	1.3(2)	C13	C14	C19	C18	-179.28(14)
C5	C10	C12	C13	-83.36(18)	C14	C15	C16	C17	-0.7(3)
C5	C10	C12	C20	89.81(16)	C15	C14	C19	C18	2.1(2)
C6	C1	C2	C3	2.1(3)	C15	C16	C17	C18	0.5(3)
C6	C5	C10	C9	-3.7(2)	C16	C17	C18	C19	1.1(3)
C6	C5	C10	C12	-179.88(13)	C17	C18	C19	C14	-2.4(2)
C6	C7	C8	C9	-2.3(2)	C19	C14	C15	C16	-0.6(2)
C7	C8	C9	C10	0.3(2)	C20	C12	C13	C14	-177.51(14)
C7	C8	C9	C11	-178.36(15)	C20	C21	C22	O2	20.1(2)
C8	C9	C10	C5	2.7(2)	C20	C21	C22	N1	-161.57(15)
C8	C9	C10	C12	178.74(13)	C23	N1	C22	O2	7.8(2)
C8	C9	C11	O1	-2.3(3)	C23	N1	C22	C21	-170.49(15)
C9	C10	C12	C13	100.54(18)	C24	N1	C22	O2	-175.61(17)
C9	C10	C12	C20	-86.29(17)	C24	N1	C22	C21	6.1(2)
C10	C5	C6	C1	178.65(14)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3e.

Atom	*x*	*y*	*z*	U(eq)
H1	6971.45	1114.01	312.76	55
H2	5779.06	2391.77	-393.18	61
H3	4600.85	3602.8	464.03	56
H4	4609.84	3519.43	2028.7	44
H7	7582.74	143.3	1726.67	49
H8	7405.17	-81.23	3266.54	48

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3e.

Atom	*x*	*y*	*z*	U(eq)
H11	5826.12	1628.35	4852.37	52
H13	4818.37	4296.27	4187.07	41
H15	7748.95	2990.81	3871.97	48
H16	9657.91	3841.05	3710.11	56
H17	9751.02	5673.31	3491.3	55
H18	7909.21	6664.85	3446.91	55
H19	5998.96	5837.55	3675.25	48
H20	3151.87	3162.75	4053.33	42
H21	3645.56	1114.86	3423.74	42
H23A	-424.44	976.38	3709.04	87
H23B	-231.71	-39.14	4347.13	87
H23C	-163.8	-165	3269.02	87
H24A	2394.97	-639.81	3238.06	76
H24B	1749.72	-990.59	4169.11	76
H24C	2941.59	-225.49	4183.39	76

Table 8 Solvent masks information for 3e.

Number	X	Y	Z	Volume	Electron count	Content
1	-0.051	0.260	0.208	24	3	
2	0.051	0.760	0.292	24	3	
3	0.449	0.240	0.792	24	3	
4	0.551	0.740	0.708	24	3	