Supporting information

Enantioselective Cyclopropanation of Enals by Oxidative N-heterocyclic Carbene Catalysis

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Experimental Section:

General: All reactions involving air or moisture-sensitive reagents or intermediates were carried out in heat-gun-dried glassware under an argon atmosphere. THF was freshly distilled from potassium under argon. All other solvents and reagents were used as received from Aldrich, Acros, ABCR and Fluka or were prepared according to standard procedures. Catalysts **2b**, **2c 2d** and ylides **3b**, **3c 3d** were prepared according to the reported procedures.[1,2] ^{1}H and ^{13}C NMR spectroscopy: *Bruker dpx 300, AV 400, Varian 600 unity plus*. Chemical shifts, δ (in ppm), are reported relative to TMS (δ (^{1}H) 0.0 ppm, δ (^{13}C) 0.0 ppm) which was used as the inner. Otherwise the solvents residual proton resonance and carbon resonance ($CHCl_3$, δ (^{1}H) 7.26 ppm, δ (^{13}C) 77.0 ppm were used for calibration. Additional NMR Spectra (NOE, ^{1}H/^{13}C gHSQC, ^{1}H/^{13}C gHMBC) were recorded on a *Varian 600 unity plus* (^{1}H: 600 MHz; ^{13}C: 151 MHz). TLC: Merck silica gel 60 F 254 plates; detection with UV light or by dipping into a solution of $KMnO_4$ (1.5 g in 400 mL H_2O, 5 g $NaHCO_3$) or a solution of $Ce(SO_4)_2$ x H_2O (10 g), phosphormolybdic acid hydrate (25 g), and conc. H_2SO_4 (60 mL) in H_2O (940 mL) followed by heating. Flash column chromatography (FC): Merck or Fluka silica gel 60 (40-63 μm) at approximately 0.4 bar. HPLC: *Hewlett Packard* Binary Pump, analyzed by *Hewlett Packard Series 1100 ChemStation* for LC. Column, eluent and retention times for HPLC analysis used for the determination of enantiomer ratios are given below with the details of the relevant experiment. Polarimetry: optical rotations were measured on *Perkin Elmer 341* polarimeter. IR: Infrared spectra were recorded on a *Varian Associates FT-IR 3100 Excalibur* and the wave numbers ($\tilde{\nu}$) of recorded IR signals are quoted in cm^{-1}. MS: Mass spectra were recorded on a *Bruker*

Daltonics MicroTof (ESI); and peaks are given in *m/z* (% of basis peak). Full characterization is provided for unknown compounds.

The following abbreviations are used for indicating multiplicities in nmr spectra: s= singlet, d = doublet, pt = pseudo triplet, dd = double doublet, pq = pseudo quintet, hept = heptet, m = multiplet.

General procedure for the synthesis of ylides (GP 1):

Tetrahydrothiophene (1.1 equiv) was added slowly to a well stirred solution of the corresponding bromide (1.0 equiv) in acetonitrile (2.0 M) at ambient temperature and the reaction mixture was stirred for 24 hours. The resulting precipitate was filtered and washed with dichloromethane and dried under vacuum.

General procedure for enantioselective cyclopropanation of enals by oxidative N-heterocyclic carbene catalysis (GP 2):

Base (110 mol%) was added to a solution of azolium salt **2b-2d** (5 mol%) in toluene (0.1 M) at room temperature. The mixture was stirred for 5 minutes, followed by the addition of the ylide (1.0 equiv) and 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (1.2 equiv). After stirring for 5 minutes, enal (1.2 equiv) and alcohol (1.2 equiv) were successively added. The resulting solution was stirred for 6-24 hours at room temperature. After completion of the reaction (checked by thin layer chromatography) the reaction mixture was directly subjected to flash silica gel column chromatography and the product was purified by using a mixture of pentane and methyl *tert*-butyl ether (MTBE) as eluents.

The racemic samples were prepared using the azolium salt **2a**, DBU as base and THF as solvent.

General procedure for intramolecular enantioselective cyclopropanation of enals by oxidative N-heterocyclic carbene catalysis (GP 3):

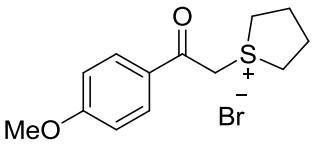
Base (110 mol%) was added to a solution of the azolium salt **2b-2d** (5 mol%) in toluene (0.1 M based on enal) as solvent at room temperature. The mixture was stirred for 5 minutes, followed by the addition of the ylide (1.5 equiv) and 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (1.0 equiv). After stirring for 5 minutes, enal (1.0 equiv) was added. The resulting solution

was stirred for 12-24 hours at room temperature. After completion of the reaction (checked by thin layer chromatography) the reaction mixture was directly subjected to flash silica gel column chromatography and the product was purified by using a mixture of pentane and methyl *tert*-butyl ether (MTBE) as eluents.

The racemic sample for **13a** was prepared using the azolium salt **2a**, Et_3N as base and toluene as solvent.

1-(2-(4-Methoxyphenyl)-2-oxoethyl)tetrahydro-1*H*-thiophen-1-ium bromide:

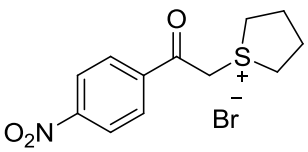
According to GP1 with 2-bromo-1-(4-methoxyphenyl)ethanone (2.3 g, 10 mmol) and tetrahydrothiophene (0.97 ml, 11.0 mmol) in acetonitrile (5 ml) for 24 hours afforded the title compound as white solid (54%, 1.8 g).



FTIR (neat): 1668, 1597, 1513, 1470, 1438, 1341, 1312, 1263, 1226, 1171, 1011, 954, 909, 832, 740, 591, 460 cm $^{-1}$. ^{1}H NMR (300 MHz, D_2O) δ 7.99-7.96 (m, 2H), 7.12-7.09 (m, 2H), 4.79 (s, 2H), 3.93 (s, 3H), 3.82 – 3.69 (m, 2H), 3.64 – 3.52 (m, 2H), 2.50-2.29 (m, 4H). ^{13}C NMR (75 MHz, D_2O) δ 193.5, 167.6, 134.1, 129.0, 117.1, 58.4, 45.6, 30.9. HRMS (ESI): Exact mass calculated for $C_{13}H_{17}O_2S$ (M^+): 237.0944, mass found: 237.0955.

1-(2-(4-Nitrophenyl)-2-oxoethyl)tetrahydro-1*H*-thiophen-1-ium bromide:

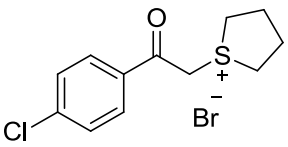
According to GP1 with 2-bromo-1-(4-nitrophenyl)ethanone (2.45 g, 10.0 mmol) and tetrahydrothiophene (0.97 l, 11.0 mmol) in acetonitrile (5 ml) for 24 hours afforded the title compound as faint yellow solid (54%, 1.80 g).



FTIR (neat): $\tilde{\nu}$ = 1684, 1601, 1413, 1344, 1324, 1205, 1002, 850, 745, 456 cm $^{-1}$. ^{1}H NMR (300 MHz, D_2O) δ 8.44-8.42 (m, 2H), 8.24-8.21 (m, 2H), 4.79 (s, 2H), 3.84 – 3.72 (m, 2H), 3.68 – 3.55 (m, 2H), 2.50 – 2.32 (m, 4H). ^{13}C NMR (75 MHz, D_2O) δ 191.7, 151.2, 138.1, 130.0, 124.3, 43.3, 28.4. HRMS (ESI): Exact mass calculated for $C_{12}H_{14}NO_3S$ (M^+): 252.0689, mass found: 252.0682.

1-(2-(4-Chlorophenyl)-2-oxoethyl)tetrahydro-1*H*-thiophen-1-ium bromide:

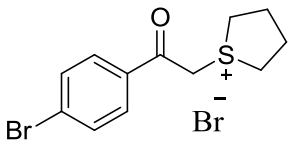
According to GP1 with 2-bromo-1-(4-chlorophenyl)ethanone (2.34 g, 10.0 mmol) and tetrahydrothiophene (0.97 ml, 11.0 mmol) in acetonitrile (5 ml) for 24 hours afforded the title compound as white solid (51%, 1.64 g).



FTIR (neat): $\tilde{\nu}$ = 1672, 1590, 1403, 1320, 1203, 1093, 824, 767, 650, 504 cm $^{-1}$. ^{1}H NMR (300 MHz, D_2O) δ 8.00-7.97 (m, 2H), 7.64-7.62 (m, 2H), 4.79 (d, *J* = 1.1 Hz, 2H), 3.89 – 3.68 (m, 2H), 3.66 – 3.52 (m, 2H), 2.49 – 2.31 (m, 4H). ^{13}C NMR (75 MHz, D_2O) δ 191.7, 141.4, 132.0, 130.3, 129.6, 43.4, 28.5. HRMS (ESI): Exact mass calculated for $C_{12}H_{14}ClOS$ (M^+): 241.0448, mass found: 241.0455.

1-(2-(4-Bromophenyl)-2-oxoethyl)tetrahydro-1*H*-thiophen-1-ium bromide:

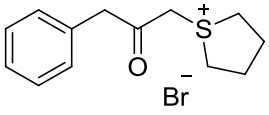
According to GP1 with 2-bromo-1-(4-bromophenyl)ethanone (2.78 g, 10.0 mmol) and tetrahydrothiophene (0.97 ml, 11.0 mmol) in acetonitrile (5 ml) for 24 hours afforded the title compound as faint yellowish white solid (54%, 1.97 g).



FTIR (neat): $\tilde{\nu}$ = 1669, 1585, 1361, 1318, 1202, 1176, 1070, 818, 759, 502, 486 cm $^{-1}$. ^{1}H NMR (300 MHz, D_2O) δ 7.91-7.88 (m, 2H), 7.81-7.78 (m, 2H), 4.79 (s, 2 H), 3.94 – 3.64 (m, 2H), 3.65 – 3.50 (m, 2H), 2.50 – 2.28 (m, 4H). ^{13}C NMR (75 MHz, D_2O) δ 192.0, 132.4, 132.4, 130.4, 130.2, 43.1, 28.4. HRMS (ESI): Exact mass calculated for $C_{12}H_{14}BrOS$ (M^+): 284.9949, mass found: 284.9949.

1-(2-Oxo-3-phenylpropyl)tetrahydro-1*H*-thiophen-1-ium bromide:

According to GP1 with 1-bromo-3-phenylpropan-2-one[3] (2.13 g, 10.0 mmol) and tetrahydrothiophene (0.97 ml, 11.0 mmol) in acetonitrile (5 ml) for 24 hours afforded the title compound as yellow solid (51%, 1.54g).



FTIR (neat): $\tilde{\nu}$ =1718, 1604, 1497, 1453, 1404, 1341, 1300, 1147, 1057, 937, 881, 700, 673, 522 cm^{-1}. ^{1}H NMR (300 MHz, D_2O) δ 8.23 – 8.09 (m, 3H), 8.07 – 7.98 (m, 2H), 5.50 (s, 2H), 4.79 (s, 2H), 4.45 – 4.25 (m, 2H), 4.22 – 4.04 (m, 2H), 3.23 – 2.86 (m, 4H). ^{13}C NMR (75 MHz, D_2O) δ 202.4, 132.3, 130.0, 129.2, 127.9, 47.9, 43.2, 28.4. HRMS (ESI): Exact mass calculated for $C_{13}H_{17}OS$ (M^+): 221.0995, mass found: 221.1002.

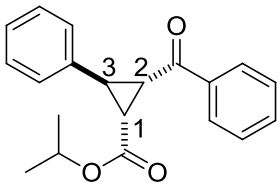
(1*R*,2*S*,3*S*)-Isopropyl 2-benzoyl-3-phenylcyclopropanecarboxylate (5a) and

(1*S*,2*S*,3*S*)-Isopropyl 2-benzoyl-3-phenylcyclopropanecarboxylate (5a'):

According to GP2 with (*E*)-cinnamaldehyde (38 µl, 0.30 mmol), DABCO (31.0 mg, 275 µmol), azolium salt **2b** (4.6 mg, 13 µmol), 1-(2-oxo-2-phenylethyl)tetrahydro-1*H*-thiophen-1-ium bromide (72 mg, 0.25 mmol), 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (123 mg, 300 µmol) and isopropanol (23 µl, 0.30 mmol) in toluene (2.5 ml) for 6 hours and SiO_2-chromatography (pentane: MTBE, 10:1) afforded **5a** and **5a'.** (overall yield 48 mg, 62%, dr 9:1).

5a' was first eluated and obtained as pure minor diastereomer (yellowish liquid, 5 mg) and then **5a** was isolated as pure major diastereomer (white solid, 43 mg).

Major diastereomer (5a):



$[\alpha]_D^{20}$ = -43.3° (c = 0.95 in $CHCl_3$). FTIR (neat): $\tilde{\nu}$ = 1723, 1674, 1448, 1370, 1312, 1287, 1210, 1181, 1107, 1009, 911, 879, 759, 699, 565, 512, 496 cm $^{-1}$. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 – 8.03 (m, 2H), 7.59 – 7.54 (m, 1H), 7.49 – 7.44 (m, 2H), 7.36 – 7.32 (m, 2H), 7.28 – 7.26 (m, 1H), 7.25 – 7.22 (m, 2H), 4.93 (pquin, J^1 = J^2 =6.3 Hz, 1H), 3.37 (pt, 1H), 3.06 (dd, *J* = 9.6, 6.4 Hz, 1H), 2.63 (dd, *J* = 9.6, 6.0 Hz, 1H), 1.12 (d, *J* = 6.3 Hz, 3H), 1.08 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.4, 168.5, 138.1, 136.9, 133.2, 128.6, 128.5, 128.3, 127.0, 126.5, 68.5, 35.1, 31.8, 29.2, 21.6, 21.5. HRMS (ESI): Exact mass calculated for $C_{20}H_{20}O_3Na$ ($[M+Na]^+$): 331.1305, mass found: 331.1291.
Assignment of 1D NMR data for **5a** was further supported by additional 2D NMR experiments (non-aromatic shifts listed only):

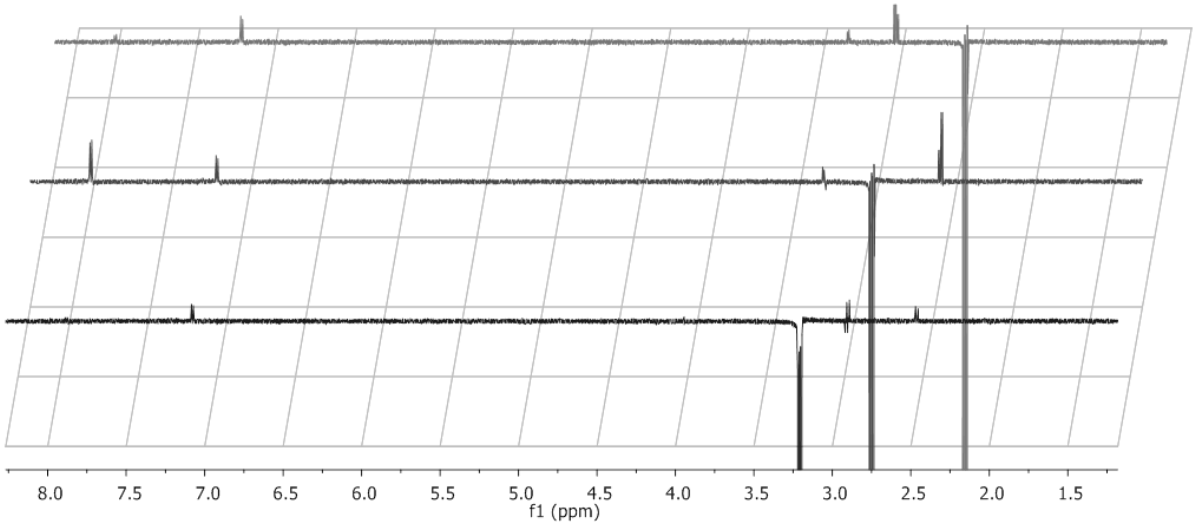
GHSQC (600 / 151 MHz, $CDCl_3$, 299 K): δ ^{1}H / δ ^{13}C = 4.93 / 68.6 (C*H*$(CH_3)_2$ / *C*H$(CH_3)_2$); 3.37 /29.3 (3-H / C3); 3.06 / 35.2 (2-H / C2); 2.62 / 31.9 (1-H /C 1); 1.12 / 21.5 (CH(C*H*$_3)_2$ / CH(*C*$H_3)_2$); 1.08 / 21.6 (CH(C*H*$_3)_2$ / CH(*C*$H_3)_2$).

GHMBC (600 / 151 MHz, $CDCl_3$, 299 K): δ ^{1}H / δ ^{13}C = 4.93 / 168.6, 21.6, 21.5 (C*H*$(CH_3)_2$ / -*C*(O)O*i*Pr, CH(*C*$H_3)_2$, CH(*C*$H_3)_2$); 3.37 / 193.5, 168.6, 126.6, 35.2, 31.9 (3-H / -*C*(O)Ph, -*C*(O)O*i*Pr, C_{ortho}^{Ph}, C2, C3); 3.06 / 168.6, 138.2, 31.9, 29.3 (2-H / -*C*(O)O*i*Pr, C_{ipso}^{Ph}, C1, C3);

2.62 / 193.5, 138.2, 35.2, 29.3 (1-H / -*C*(O)Ph, C_{ipso}^{Ph}, C2, C3); 1.12 / 68.6, 21.6 (CH(CH_3)$_2$ / -*C*(O)O*i*Pr, CH(*C*H$_3$)$_2$); 1.08 / 68.6, 21.5 (CH(CH_3)$_2$ / -*C*(O)O*i*Pr, CH(*C*H$_3$)$_2$).

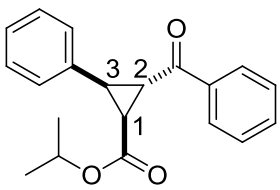
The determination of the relative configuration of **5a** was supported by additional 1D NOESY experiments:

NOESY (600 / 600 MHz, $CDCl_3$, 299 K): δ_{irr} / δ_{resp} 2.62 / 3.06, 3.37 (weak), 7.23, 8.04 (weak) (1-H / 2-H, 3-H, CH_{ortho}^{Ph}, CH_{ortho}^{Bz}); 3.06 / 2.62, 3.37 (weak), 7.23 (weak), 8.04 (2-H / 1-H, 3-H, CH_{ortho}^{Ph}, CH_{ortho}^{Bz}); 3.37 / 2.62 (weak), 3.06 (weak), 7.23 (3-H / 1-H. 2-H, CH_{ortho}^{Ph}).



Enantiomeric excess (89% ee) was determined by chiral HPLC. Column: Chiralcel OD-H; solvent: cyclohexane:2-propanol (99.5:0.5); flow: 1.0 mL/min; major enantiomer t_r = 21.023 min, minor enantiomer t_r = 19.169 min.

Minor diastereomer (5a'):



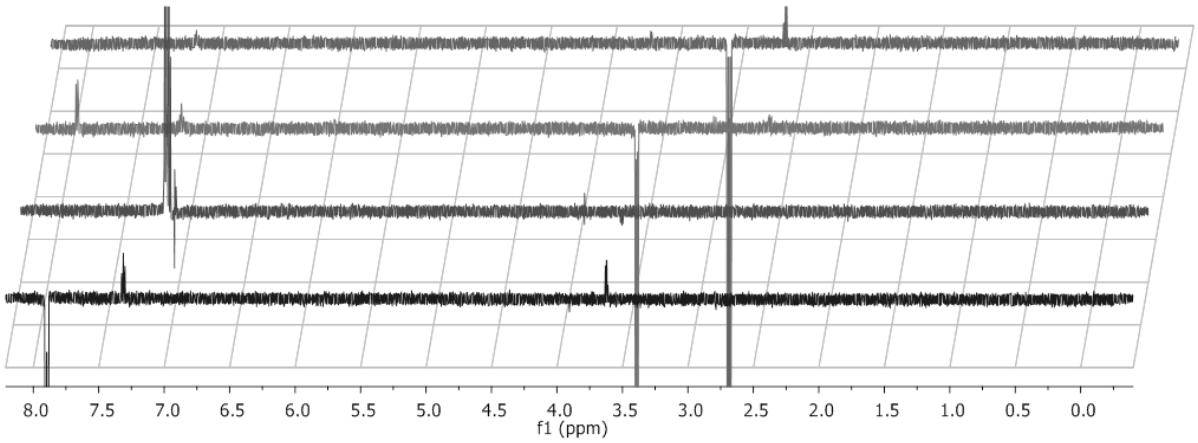
FTIR (neat): $\tilde{\nu}$ =1723, 1673, 1599, 1511, 1449, 1429, 1372, 1263, 1194, 1107, 1016, 740, 697, 496, 464 cm $^{-1}$. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 – 8.10 (m, 2H), 7.65 – 7.61 (m, 2H), 7.57 – 7.51 (m, 1H), 7.34 – 7.29 (m, 4H), 7.26 – 7.22 (m, 1H), 4.83 (pquin, J^1 = J^2 = 6.0 Hz, 1H), 3.84 (dd, *J* = 6.2, 4.8 Hz, 1H), 3.25 (dd, *J* = 10.0, 6.2 Hz, 1H), 2.83 (dd, *J* = 10.0, 4.7 Hz, 1H), 1.05 (d, *J* = 6.2 Hz, 3H), 1.03 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.7, 168.1, 137.0, 134.8, 133.4, 128.9, 128.7, 128.3, 128.1, 127.2, 68.4, 34.8, 32.4, 29.3, 21.7, 21.4. HRMS (ESI): Exact mass calculated for $C_{20}H_{20}O_3Na$ ([M+Na]$^+$): 331.1305, mass found: 331.1307.

Assignment of 1D NMR data for **5a'** was further supported by additional 2D NMR experiments (non-aromatic shifts listed only):

GHSQC (600 / 151 MHz, $CDCl_3$, 299 K): δ ^{1}H / δ ^{13}C = 4.83 / 68.4 (C*H*(CH_3)$_2$ / *C*H(CH_3)$_2$); 3.84 / 29.4 (2-H/ C2); 3.25/ 34.9 (3-H/ C3); 2.83/ 32.4 (1-H/ C1); 1.05 / 21.7 (CH(C*H*$_3$)$_2$ / CH(*C*H$_3$)$_2$); 1.03/ 21.4 (CH(C*H*$_3$)$_2$ / CH(*C*H$_3$)$_2$).

GHMBC (600 / 151 MHz, $CDCl_3$, 299 K): δ ^{1}H / δ ^{13}C = 4.83 / 168.2, 21.7, 21.4 (C*H*(CH_3)$_2$ / -*C*(O)O*i*Pr, CH(*C*H$_3$)$_2$, CH(*C*H$_3$)$_2$); 3.84 / 196.8, 168.2, 134.8 (2-H/ -*C*(O)Ph, -*C*(O)O*i*Pr, C_{ipso}^{Ph}); 3.25 / 196.8, 168.2, 128.9 (3-H/ -*C*(O)Ph, -*C*(O)O*i*Pr, C_{ipso}^{Ph}); 2.83 / 196.8 (1-H/ -*C*(O)Ph); 1.05 / 68.4, 21.7 (CH(C*H*$_3$)$_2$ / -*C*(O)O*i*Pr, CH(*C*H$_3$)$_2$); 1.03 / 68.4, 21.4 (CH(C*H*$_3$)$_2$ / -*C*(O)O*i*Pr, CH(*C*H$_3$)$_2$).

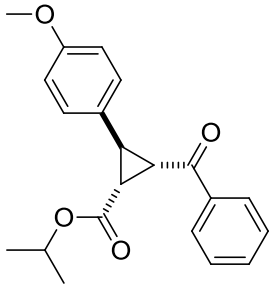
The determination of the relative configuration of **5a'** was supported by additional 1D NOESY experiments:
NOESY (600 / 600 MHz, $CDCl_3$, 299 K): δ_{irr} / δ_{resp} 3.23 / 2.81, 3.82 (weak), 7.30 (weak) (3-H / 1-H, 2-H, C_{ortho}^{Ph}); 3.82 / 2.81 (weak), 3.23 (weak), 7.30 (weak), 8.10 (2-H / 1-H, 3-H, C_{ortho}^{Ph}, C_{ortho}^{Bz}); 7.30 / 3.23 (weak), 3.82 (weak) (C_{ortho}^{Ph} / 3-H, 2-H); 8.10 / 3.82, 7.51 (C_{ortho}^{Bz} / 2-H, C_{meta}^{Bz}).



(1*R*,2*S*,3*S*)-Isopropyl 2-benzoyl-3-(4-methoxyphenyl) cyclopropane carboxylate (5b)

According to GP2 with (*E*)-3-(4-methoxyphenyl)acrylaldehyde (49 mg, 0.30 mmol), DABCO (31.0 mg, 27.5 µmol), azolium salt **2b** (4.6 mg, 13 µmol), dimethyl(2-oxo-2-phenylethyl)sulfonium bromide (65 mg, 0.25 mmol),3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (123 mg, 300 µmol) and isopropanol (23 µl, 0.30 mmol) in toluene (2.5 ml) for 6 hours and

SiO_2-chromatography (pentane: MTBE, 5:1) afforded **5b** as yellow solid. (yield 26 mg, 31%, dr 20:1).



$[\alpha]_D^{20}$ = -41.2° (c = 0.85 in $CHCl_3$). FTIR (neat): $\tilde{\nu}$ = 1724, 1682, 1518, 1451, 1373, 1283, 1250, 1179, 1109, 693, 631, 539, 458 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.09 – 7.98 (m, 2H), 7.61 – 7.52 (m, 1H), 7.50 – 7.41 (m, 2H), 7.17-7.14 (m, 2H), 6.89-6.86 (m, 2H), 4.92 (pquin, $J^1 = J^2$ = 6.2 Hz, 1H), 3.80 (s, 3H), 3.32 (pt, 1H), 3.00 (dd, *J* = 9.5, 6.5 Hz, 1H), 2.56 (dd, *J* = 9.5, 6.0 Hz, 1H), 1.11 (d, *J* = 6.3 Hz, 3H), 1.08 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.3, 168.5, 158.4, 136.8, 132.9, 129.9, 128.3, 128.1, 127.5, 113.9, 68.3, 55.0, 34.8, 31.5, 28.6, 21.4, 21.3. HRMS (ESI): Exact mass calculated for $C_{21}H_{22}O_4Na$ ($[M+Na]^+$): 361.1410, mass found: 361.1416

Enantiomeric excess (87% ee) was determined by chiral HPLC. Column: Chiralcel OD-H; solvent: cyclohexane:2-propanol (99.5:0.5); flow: 1.0 mL/min; major enantiomer t_r = 18.155 min, minor enantiomer t_r = 23.084 min.

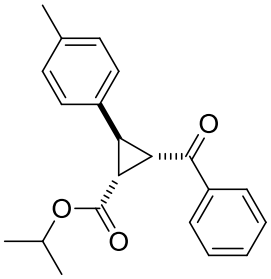
(1*R*,2*S*,3*S*)-Isopropyl 2-benzoyl-3-(*p*-tolyl)cyclopropanecarboxylate (5c) and

(1*S*,2*S*,3*S*)-Isopropyl 2-benzoyl-3-(*p*-tolyl)cyclopropanecarboxylate (5c'):

According to GP2 with (*E*)-3-(*p*-tolyl)acrylaldehyde (44 mg, 0.30 mmol), DABCO (31.0 mg, 275 µmol), azolium salt **2b** (4.6 mg, 13 µmol), 1-(2-oxo-2-phenylethyl)tetrahydro-1*H*-thiophen-1-ium bromide (72 mg, 0.25 mmol), 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (123 mg, 300 µmol) and isopropanol (23 µl, 0.30 mmol) in toluene (2.5 ml) for 16 hours and SiO_2-chromatography (pentane: MTBE, 10:1) afforded **5c** and **5c'.** (Overall yield 36 mg, 45%, dr 8:1.).

5c' was first eluated and obtained as pure minor diastereomer (yellow liquid, 4 mg) and then **5c** was isolated as pure major diastereomer (white solid, 32 mg).

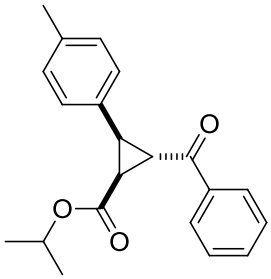
Major diastereomer (5c):



$[\alpha]_D^{20}$ = -32.8° (c = 0.8 in $CHCl_3$). FTIR (neat): $\tilde{\nu}$ = 1715, 1682, 1658, 1597, 1521, 1449, 1371, 1279, 1224, 1188, 1107, 1004, 804, 689, 491 cm $^{-1}$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 – 8.00 (m, 2H), 7.60 – 7.52 (m, 1H), 7.50 – 7.42 (m, 2H), 7.18 – 7.09 (m, 4H), 4.93 (pquin, $J^1 = J^2$ = 6.3 Hz, 1H), 3.33 (pt, 1H), 3.03 (dd, J = 9.5, 6.5 Hz, 1H), 2.58 (dd, J = 9.5, 6.0 Hz, 1H), 2.34 (s, 3H), 1.12 (d, J = 6.3 Hz, 3H), 1.08 (d, J = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.5, 168.6, 136.8, 136.6, 135.0, 133.0, 129.2, 128.4, 128.2, 126.3, 68.4, 35.0, 31.6, 29.0, 21.5, 21.4, 20.9. HRMS (ESI) Exact mass calculated for $C_{21}H_{22}O_3Na$ ($[M+Na]^+$): 345.1467, mass found: 345.1459.

Enantiomeric excess (81% ee) was determined by chiral HPLC. Column: Chiralpak AD-H; solvent: cyclohexane: 2-propanol (99.0:1.0); flow: 1.0 mL/min; major enantiomer t_r = 36.519 min, minor enantiomer t_r = 33.261 min.

Minor diastereomer (5c'):



FTIR (neat): 1727, 1674, 1450, 1373, 1296, 1194, 1108, 890, 631, 530, 490 cm $^{-1}$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 – 8.08 (m, 2H), 7.66 – 7.58 (m, 1H), 7.56 – 7.48 (m, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 7.9 Hz, 2H), 4.84 (pquin, $J^1 = J^2$ = 6.0 Hz,), 3.80 (dd, J = 6.0, 4.9 Hz, 1H), 3.21 (dd, J = 9.9, 6.2 Hz, 1H), 2.80 (dd, J = 9.9, 4.8 Hz, 1H), 2.32 (s, 3H), 1.08 (d, J = 1.8 Hz, 3H), 1.06 (d, J = 1.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.7, 168.1, 136.9, 136.6, 133.2, 131.5, 128.6, 128.5, 128.5, 128.1, 68.1, 34.5, 32.1, 29.3, 21.5, 21.2, 20.8. HRMS (ESI) Exact mass calculated for $C_{21}H_{22}O_3Na$ ($[M+Na]^+$): 345.1467, mass found: 345.1464.

(1*R*,2*S*,3*S*)-Isopropyl 2-benzoyl-3-(4-nitrophenyl)cyclopropanecarboxylate (5d) and (1*R*,2*R*,3*R*)-Isopropyl 2-benzoyl-3-(4-nitrophenyl)cyclopropanecarboxylate (5d')

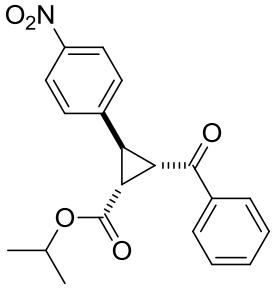
According to GP2 with (*E*)-3-(4-nitrophenyl)acrylaldehyde (45 mg, 0.30 mmol), DABCO (31.0 mg, 275 µmol), azolium salt **2b** (4.6 mg, 13 µmol), 1-(2-oxo-2-phenylethyl)tetrahydro-1*H*-thiophen-1-ium bromide (72 mg, 0.25 mmol), 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (123 mg, 300 µmol) and isopropanol (23 µl, 0.30 mmol) in toluene (2.5 ml) for 8 hours and

SiO_2-chromatography (pentane: MTBE, 5:1) afforded **5d**, **5d'** and **5d''.** (overall yield 58 mg, 65%, dr 8:4:1.).

5d' was first eluated and obtained as one of minor diastereomers (yellow solid, 17.5 mg), then **5d''** was isolated as another pure minor diastereomer (colorless liquid, 4.5 mg) and lastly **5d** was isolated as pure major diastereomer (yellow solid, 36 mg).

The relative configuration of third diastereomer (**5d''**) was not assigned.

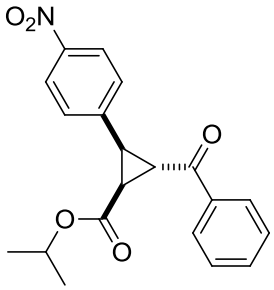
Major diastereomer (5d)



$[\alpha]_D^{20}$ = -24.0° (c = 1.0 in $CHCl_3$). FTIR (neat): $\tilde{\nu}$ = 1721, 1671, 1598, 1512, 1449, 1338, 1300, 1191, 1100, 1015, 853, 743, 691, 661, 512, 466 cm $^{-1}$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25-8.15 (m, 2H), 8.07 – 7.99 (m, 2H), 7.63-7.57 (m, 1H), 7.50-7.45 (m, 2H), 7.40-7.37 (m, 2H), 4.90 (pquin, $J^1 = J^2 =$ 6.3 Hz, 1H), 3.45 (pt, 1H), 3.13 (dd, J = 9.8, 6.4 Hz, 1H), 2.70 (dd, J = 9.8, 5.9 Hz, 1H), 1.10 (d, J = 6.3 Hz, 3H), 1.05 (d, J = 6.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.2, 167.4, 146.7, 145.7, 136.3, 133.3, 128.4, 128.1, 127.1, 123.7, 68.8, 35.3, 32.0, 28.2, 21.3, 21.2. HRMS (ESI): Exact mass calculated for $C_{20}H_{19}NO_5Na$ ($[M+Na]^+$): 376.1155, mass found: 376.1152.

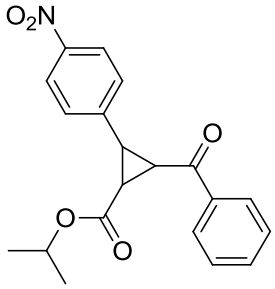
Enantiomeric excess (> 99% ee) was determined by chiral HPLC. Column: Chiralpak AD-H; solvent: cyclohexane:2-propanol (95.0:5.0); flow: 1.0 mL/min; major enantiomer t_r = 40.301 min, (minor enantiomer t_r = 46.634 min for racemic sample).

Minor diastereomer (5d')



FTIR (neat): $\tilde{\nu}$ = 1712, 1677, 1599, 1517, 1343, 1197, 809, 689, 509, 456 cm $^{-1}$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19-8.17 (m, 2H), 8.14 – 8.06 (m, 2H), 7.70 – 7.62 (m, 1H), 7.60 – 7.45 (m, 4H), 4.85 (pquin, $J^1 = J^2$ = 6.3 Hz, 1H), 3.87 (dd, J = 6.2, 4.8 Hz, 1H), 3.32 (dd, J = 9.9, 6.3 Hz, 1H), 2.86 (dd, J = 9.9, 4.8 Hz, 1H), 1.11 (d, J = 6.3 Hz, 3H), 1.06 (d, J = 6.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.5, 167.5, 146.9, 142.3, 136.4, 133.6, 129.7, 128.7, 128.1, 123.1, 68.8, 33.4, 32.3, 29.3, 21.6, 21.3. HRMS (ESI): Exact mass calculated for $C_{20}H_{19}NO_5Na$ ($[M+Na]^+$): 376.1155, mass found: 376.1156.

Minor diastereomer (5d'')*



FTIR (neat): $\tilde{\nu}$ = 1721, 1674, 1523, 1347, 1293, 1182, 1106, 907, 731, 631, 538 cm $^{-1}$.^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09-8.06 (m, 2H), 7.96 – 7.90 (m, 2H), 7.61 – 7.33 (m, 5H), 5.09 (pquin, J^1 = J^2 = 6.0 Hz, 1H), 3.65 (dd, *J* = 10.1, 4.9 Hz, 1H), 3.37 (dd, *J* = 10.1, 6.2 Hz, 1H), 3.25 – 3.20 (m, 1H), 1.36 – 1.27 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.5, 170.6, 141.3, 133.4, 129.5, 128.5, 127.9, 123.1, 69.09, 34.5, 34.5, 26.5, 21.6, 21.6 (2 aromatic resonances could not be detected). HRMS (ESI): Exact mass calculated for $C_{20}H_{19}NO_5Na$ ($[M+Na]^+$): 376.1155, mass found: 376.1155.

***relative configuration was not determined.

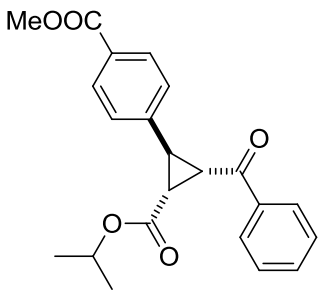
Methyl 4-((1*S*,2*S*,3*R*)-2-benzoyl-3-(isopropoxycarbonyl)cyclopropyl)benzoate (5e) and

Methyl 4-((1*S*,2*S*,3*S*)-2-benzoyl-3-(isopropoxycarbonyl)cyclopropyl)benzoate (5e'):

According to GP2 with (*E*)-methyl 4-(3-oxoprop-1-en-1-yl)benzoate (57 mg, 0.30 mmol), DABCO (31.0 mg, 275 µmol), azolium salt **2b** (4.6 mg, 13 µmol), 1-(2-oxo-2-phenylethyl)tetrahydro-1*H*-thiophen-1-ium bromide (72 mg, 0.25 mmol), 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (123 mg, 300 µmol) and isopropanol (23 µl, 0.30 mmol) in toluene (2.5 ml) for 12 hours and SiO_2-chromatography (pentane: MTBE, 10:1) afforded **5e** and **5e'.** (overall yield 52 mg, 57%, dr 5.5:1.).

5e' was first eluated as pure minor diastereomer (colurless gummy liquid liquid, 8 mg) and then **5e** was isolated as pure major diastereomer (white solid, 44 mg).

Major diastereomer (5e):

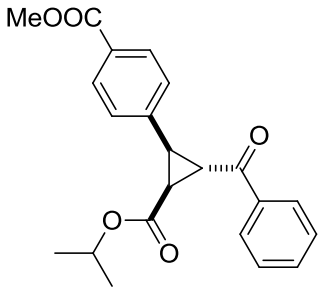


$[\alpha]_D^{20}$ = -28.3° (c = 1.0 in $CHCl_3$). FTIR (neat): $\tilde{\nu}$ = 1710, 1680, 1611, 1451, 1433, 1373, 1277, 1218, 1179, 1104, 1018, 769, 747, 693, 470 cm $^{-1}$.^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 – 7.96 (m, 4H), 7.60 – 7.52 (m, 1H), 7.50 – 7.41 (m, 2H), 7.27 – 7.24 (m, 2H), 4.90 (pquin, J^1 = J^2 = 6.3 Hz, 1H), 3.90 (s, 3H), 3.38 (pt, 1H), 3.08 (dd, *J* = 9.7, 6.4 Hz, 1H), 2.65 (dd, *J* = 9.7, 5.9 Hz, 1H), 1.09 (d, *J* = 6.3 Hz, 3H), 1.05 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.7, 167.9, 166.4,

143.3, 136.5, 133.1, 129.7, 128.7, 128.4, 128.1, 126.3, 68.6, 51.8, 35.2, 31.9, 28.7, 21.3, 21.3. HRMS (ESI): Exact mass calculated for $C_{22}H_{22}O_5Na$ ($[M+Na]^+$): 389.1359, mass found: 389.1352.

Enantiomeric excess (94% ee) was determined by chiral HPLC. Column: Chiralpak AD-H; solvent: cyclohexane:2-propanol (95.0:5.0); flow: 1.0 mL/min; major enantiomer t_r = 41.553 min, minor enantiomer t_r = 26.229 min.

Minor diastereomer (5e'):



FTIR (neat): $\tilde{\nu}$ = 1722, 1674, 1612, 1435, 1374, 1322, 1280, 1194, 1108, 1019, 703, 541, 460 cm $^{-1}$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 – 8.08 (m, 2H), 8.00-7.97 (m, 2H), 7.68 – 7.60 (m, 1H), 7.59 – 7.50 (m, 2H), 7.43-7.37 (m, 2H), 4.82 (pquin, J^1 = J^2 = 6.0 Hz, 1H), 3.91 (s, 3 H), 3.87 (dd, J = 6.0, 4.9 Hz, 1H), 3.28 (dd, J = 9.9, 6.3 Hz, 1H), 2.84 (dd, J = 10.0, 4.8 Hz, 1H), 1.05 (dd, J = 6.2, 4.3 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.1, 167.6, 166.5, 139.9, 136.7, 133.4, 129.2, 128.9, 128.8, 128.6, 128.1, 68.5, 51.8, 34.1, 32.3, 29.1, 21.5, 21.2. HRMS(ESI): Exact mass calculated for $C_{22}H_{22}O_5Na$ ($[M+Na]^+$): 389.1359, mass found: 389.1358.

(1*R*,2*S*,3*S*)-Isopropyl 2-(4-acetylphenyl)-3-benzoylcyclopropanecarboxylate (5f) and

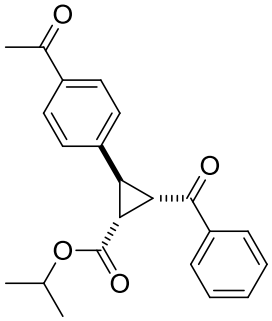
(1*S*,2*S*,3*S*)-Isopropyl 2-(4-acetylphenyl)-3-benzoylcyclopropanecarboxylate (5f')

According to GP2 with (*E*)-3-(4-acetylphenyl)acrylaldehyde (53 mg, 0.30 mmol), DABCO (31.0 mg, 275 µmol), azolium salt **2b** (4.6 mg, 13 µmol), 1-(2-oxo-2-phenylethyl)tetrahydro-1*H*-thiophen-1-ium bromide (72 mg, 0.25 mmol), 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (123 mg, 300 µmol) and isopropanol (23 µl, 0.30 mmol) in toluene (2.5 ml) for 8 hours and SiO_2-chromatography (pentane: MTBE, 5:1) afforded **5f** and **5f'.** (Overall yield 66 mg, 74%, dr 44.5:14.5:1.).

5f' was first eluated and obtained as a mixture of two minor diastereomers* (determined from ^{1}H NMR analysis, colorless liquid, 17 mg, dr 15:1) and then **5f** was isolated as pure major diastereomer (white solid, 49 mg).

* relative configuration of third diastereomer was not assigned.

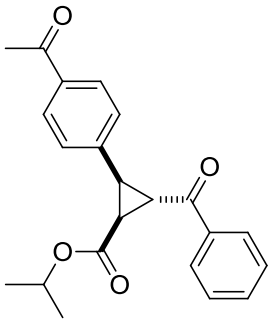
Major diastereomer (5f):



$[\alpha]_D^{20}$ = -27.9° (c = 0.8 in $CHCl_3$). FTIR (neat): $\tilde{\nu}$ = 1724, 1682, 1608, 1451, 1361, 1268, 1191, 1108, 756, 501 cm $^{-1}$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04-8.01 (m, 2 H), 7.94-7.91 (m, 2H), 7.62 – 7.53 (m, 1H), 7.52 – 7.42 (m, 2H), 7.32-7.29 (m, 2H), 4.91 (pquin, $J^1 = J^2$ = 6.0 Hz, 1H), 3.40 (pt, 1H), 3.10 (dd, J = 9.7, 6.4 Hz, 1H), 2.67 (dd, J = 9.7, 5.9 Hz, 1H), 2.59 (s, 3H), 1.10 (d, J = 6.3 Hz, 3H), 1.06 (d, J = 6.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.1, 192.6, 167.8, 143.5, 136.5, 135.7, 133.1, 128.5, 128.4, 128.1, 126.4, 68.6, 35.1, 31.8, 28.6, 26.3, 21.3, 21.2. HRMS (ESI): Exact mass calculated for $C_{22}H_{22}O_4Na$ ($[M+Na]^+$): 373.1410, mass found: 373.1407.

Enantiomeric excess (93% ee) was determined by chiral HPLC. Column: Chiralcel OD-H; solvent: cyclohexane: 2-propanol (95.0:5.0); flow: 1.0 mL/min; major enantiomer t_r = 19.254 min, minor enantiomer t_r = 32.588 min.

Minor diastereomer (5f')



FTIR (neat): $\tilde{\nu}$ = 1724, 1681, 1608, 1451, 1373, 1268, 1194, 1107, 631, 536, 469 cm $^{-1}$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 – 8.06 (m, 2H), 7.94 – 7.88 (m, 2H), 7.68 – 7.60 (m, 1H), 7.59 – 7.51 (m, 2H), 7.46-7.39 m, 2H), 4.83 (pquin, $J^1 = J^2$ = 6.3 Hz, 1H), 3.87 (dd, J = 6.2, 4.8 Hz, 1H), 3.29 (dd, J = 10.0, 6.3 Hz, 1H), 2.85 (dd, J = 10.0, 4.8 Hz, 1H), 2.59 (s, 3H), 1.08-1.04 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.3, 196.0, 167.7, 140.1, 136.6, 135.8.4, 129.0, 128.6, 128.1, 128.0, 68.5, 34.1, 32.2, 29.2, 26.3, 21.5, 21.2. HRMS (ESI): Exact mass calculated for $C_{22}H_{22}O_4Na$ ($[M+Na]^+$): 373.1410, mass found: 373.1412.

(1*R*,2*S*,3*S*)-Isopropyl 2-benzoyl-3-(4-chlorophenyl)cyclopropanecarboxylate (5g) and

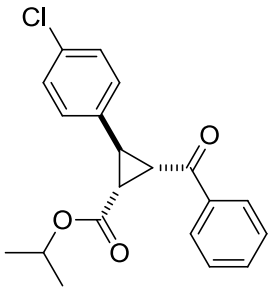
(1*S*,2*S*,3*S*)-Isopropyl 2-benzoyl-3-(4-chlorophenyl)cyclopropanecarboxylate (5g')

According to GP2 with (*E*)-3-(4-chlorophenyl)acrylaldehyde (50 mg, 0.30 mmol), DABCO (31.0 mg, 275 µmol), azolium salt **2b** (4.6 mg, 13 µmol), 1-(2-oxo-2-phenylethyl)tetrahydro-1*H*-thiophen-1-ium bromide (72 mg, 0.25 mmol), 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (123 mg, 300 µmol) and isopropanol (23 µl, 0.30 mmol) in toluene (2.5 ml) for 6 hours and

SiO_2-chromatography (pentane: MTBE, 10:1) afforded **5g** and **5g'.** (Overall yield 60 mg, 70%, dr 9:1.).

5g' was first eluated and obtained as pure minor diastereomer (colorless liquid, 6 mg) and then **5g** was isolated as pure major diastereomer (white solid, 54 mg).

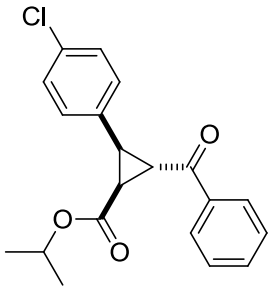
Major diastereomer (5g):



$[\alpha]_D^{20}$ = -37.9° (c = 0.65 in $CHCl_3$). FTIR (neat): $\tilde{\nu}$ = 1713, 1680, 1583, 1449, 1372, 1300, 1222, 1191, 1107, 1007, 809, 688, 482 cm $^{-1}$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 – 7.98 (m, 2H), 7.62 – 7.52 (m, 1H), 7.51 – 7.42 (m, 2H), 7.35-7.29 (m, 2H), 7.21-7.11 (m, 2H), 4.91 (pquin, J^1 = J^2 = 6.2 Hz, 1H), 3.33 (pt, 1H), 3.02 (dd, *J* = 9.7, 6.4 Hz, 1H), 2.58 (dd, *J* = 9.7, 6.0 Hz, 1H), 1.11 (d, *J* = 6.3 Hz, 3H), 1.06 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ 193.0, 168.0, 136.6, 136.5, 133.1, 132.6, 128.6, 128.4, 128.1, 127.7, 68.5, 34.8, 31.6, 28.2, 21.3, 21.3. HRMS (ESI): Exact mass calculated for $C_{20}H_{19}ClO_3Na$ ($[M+Na]^+$): 365.0915, mass found: 365.0906.

Enantiomeric excess (95% ee) was determined by chiral HPLC. Column: Chiralpak AD-H; solvent: cyclohexane:2-propanol (99.0:1.0); flow: 1.0 mL/min; major enantiomer t_r = 41.286 min, minor enantiomer t_r = 46.323 min.

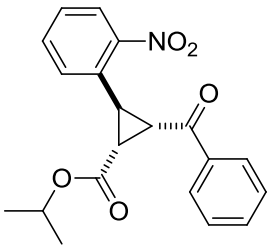
Minor diastereomer (5g'):



FTIR (neat): $\tilde{\nu}$ = 1724, 1674, 1598, 1495, 1450, 1373, 1295, 1194, 1107, 1025, 782, 534, 481 cm $^{-1}$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 – 8.09 (m, 2H), 7.66 – 7.61 (m, 1H), 7.60 – 7.56 (m, 2H), 7.30 – 7.23 (m, 4H), 4.85 (pquin, J^1 = J^2 = 6.0 Hz, 1H), 3.79 (dd, *J* = 6.1, 4.8 Hz, 1H), 3.21 (dd, *J* = 9.9, 6.2 Hz, 1H), 2.79 (dd, *J* = 9.0, 3.0 Hz 1H), 1.09 (d, *J* = 3.1 Hz, 3H), 1.07 (d, *J* = 3.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.1, 167.8, 136.7, 133.3, 133.1, 132.9, 130.0, 128.6, 128.1, 128.1, 68.4, 33.7, 32.2, 29.3, 21.6, 21.3. HRMS (ESI): Exact mass calculated for $C_{20}H_{19}ClO_3Na$ ($[M+Na]^+$): 365.0920, mass found: 365.0910.

(1*R*,2*S*,3*S*)-Isopropyl 2-benzoyl-3-(2-nitrophenyl)cyclopropanecarboxylate (5h):

According to GP2 with (*E*)-3-(2-nitrophenyl)acrylaldehyde (53 mg, 0.30 mmol), DABCO (31.0 mg, 275 µmol), azolium salt **2b** (4.6 mg, 13 µmol), 1-(2-oxo-2-phenylethyl)tetrahydro-1*H*-thiophen-1-ium bromide (72 mg, 0.25 mmol), 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (123 mg, 300 µmol) and isopropanol (23 µl, 0.30 mmol) in toluene (2.5 ml) for 6 hours and SiO_2-chromatography (pentane: MTBE, 10:1) afforded **5h** as white solid. (yield 28 mg, 32%, dr 20:1.).



$[\alpha]_D^{20}$= -42.3° (c = 0.6 in $CHCl_3$). FTIR (neat): $\tilde{\nu}$ = 1724, 1682, 1529, 1471, 1350, 1289, 1216, 731, 651, 461 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 – 7.97 (m, 3H), 7.63 – 7.53 (m, 2H), 7.51 – 7.42 (m, 3H),7.39-7.36 (m, 1H), 4.92 (pquin, J^1 = J^2 = 6.3 Hz, 1H), 3.80 (pt, 1H), 3.13 (dd, *J* = 9.7, 6.8 Hz, 1H), 2.51 (dd, *J* = 9.7, 6.3 Hz, 1H), 1.13 – 1.06 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.5, 167.7, 150.0, 136.5, 133.1, 132.9, 132.8, 129.2, 128.4, 128.1, 128.1, 124.7, 68.6, 32.8, 31.0, 26.8, 21.3, 21.2. HRMS (ESI): Exact mass calculated for $C_{20}H_{19}NO_5Na$ ($[M+Na]^+$): 376.1155, mass found: 376.1165.

Enantiomeric excess was determined by comparing the HPLC spectra of the reactions with the ylides **3b** and **3c**.

Enantiomeric excess (94% ee, with ylide **3b**) was determined by chiral HPLC. Column: Chiralcel OD-H; solvent: cyclohexane:2-propanol (95.0:5.0); flow: 1.0 mL/min; major enantiomer t_r = 11.897 min, minor enantiomer t_r = 20.823 min.

Enantiomeric excess (99% ee, with ylide **3c**) was determined by chiral HPLC. Column: Chiralcel OD-H; solvent: cyclohexane:2-propanol (95.0:5.0); flow: 1.0 mL/min; major enantiomer t_r = 12.144 min, minor enantiomer t_r = 21.663 min.

(1*R*,2*S*,3*S*)-Isopropyl-2-benzoyl-3-(naphthalen-2yl)cyclopropanecarboxylate (5i) and

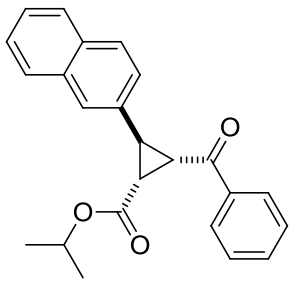
(1*S*,2*S*,3*S*)-Isopropyl 2-benzoyl-3-(naphthalen-2-yl)cyclopropanecarboxylate (5i')

According to GP2 with (*E*)-3-(naphthalen-2-yl)acrylaldehyde (55 mg, 0.30 mmol), DABCO (31.0 mg, 275 µmol), azolium salt **2b** (4.6 mg, 13 µmol), 1-(2-oxo-2-phenylethyl)tetrahydro-1*H*-thiophen-1-ium bromide (72 mg, 0.25 mmol), 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (123 mg, 300 µmol) and isopropanol (23 µl, 0.30 mmol) in toluene (2.5 ml) for 16 hours and

SiO_2-chromatography (pentane: MTBE, 10:1) afforded **5i** and **5i'.** (overall yield 49 mg, 55%, dr 5.2:1.).

5i' was first eluated and obtained as pure minor diastereomer (colorless gummy liquid, 8 mg) and then **5i** was isolated as pure major diastereomer (white solid, 41mg).

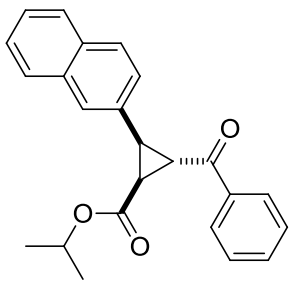
Major diastereomer (5i):



$[\alpha]_D^{20}$ = -34.5° (c = 1.0 in $CHCl_3$). FTIR (neat): $\tilde{\nu}$ = 1722, 1674, 1636, 1450, 1374, 1294, 1188, 1107, 747, 631, 541, 462 cm $^{-1}$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 – 8.03 (m, 2H), 7.87 – 7.75 (m, 3H), 7.73-7.68 (m, 1H), 7.62 – 7.53 (m, 1H), 7.53 – 7.39 (m, 4H), 7.38 – 7.30 (m, 1H), 4.94 (pquin, $J^1 = J^2$ = 6.0 Hz, 1H), 3.53 (pt, 1H), 3.17 (dd, J = 9.6, 6.5 Hz, 1H), 2.74 (dd, J = 9.6, 6.0 Hz, 1H), 1.13 (d, J = 6.3 Hz, 3H), 1.10 (d, J = 6.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ192.0, 168.2, 139.4, 137.7, 135.0, 131.0, 129.5, 128.8, 128.6, 128.4, 128.2, 126.9, 126.3, 68.4, 34.7, 31.5, 29.0, 21.3, 21.3. HRMS (ESI): Exact mass calculated for $C_{24}H_{22}O_3Na$ ($[M+Na]^+$) :381.1461, mass found: 381.1458.

Enantiomeric excess (91% ee) was determined by chiral HPLC. Column: Chiralpak AD-H; solvent: cyclohexane:2-propanol (98.5:1.5); flow: 1.0 mL/min; major enantiomer t_r = 42.828 min, minor enantiomer t_r = 38.494 min.

Minor diastereomer (5i'):



FTIR (neat): $\tilde{\nu}$ = 1724, 1673, 1450, 1374, 1294, 1187, 1107, 1017, 781, 683, 487 cm $^{-1}$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 – 8.11 (m, 2H), 7.84-7.74 (m, 4H), 7.69 – 7.61 (m, 1H), 7.60 – 7.51 (m, 2H), 7.49 – 7.40 (m, 3H), 4.80 (pquin, $J^1 = J^2$ = 6.0 Hz, 1H), 3.97 (dd, J = 6.1, 4.8 Hz, 1H), 3.42 (dd, J = 9.9, 6.2 Hz, 1H), 2.89 (dd, J = 10.0, 4.8 Hz, 1H), 1.03-0.98 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.5, 167.9, 136.9, 133.3, 132.9, 132.4, 132.1, 128.6, 128.2, 127.6, 127.5, 127.4, 127.4, 126.8, 125.9, 125.6, 68.2, 34.7, 32.4, 29.4, 21.5, 21.2. HRMS (ESI): Exact mass calculated for $C_{24}H_{22}O_3Na$ ($[M+Na]^+$): 381.1467, mass found: 381.1448.

(1*R*,2*S*,3*S*)-Isopropyl-2-benzoyl-3-(furan-2-yl)cyclopropanecarboxylate (5j) and

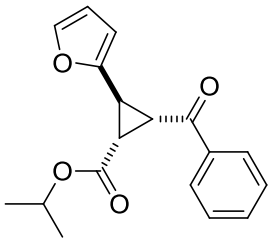
(1*S*,2*S*,3*S*)-Isopropyl-2-benzoyl-3-(furan-2-yl)cyclopropanecarboxylate (5j')

According to GP2 with (*E*)-3-(furan-2-yl)acrylaldehyde (37 mg, 0.30 mmol), DABCO (31.0 mg, 27.5 µmol), azolium salt **2b** (4.6 mg, 13 µmol), 1-(2-oxo-2-phenylethyl)tetrahydro-1*H*-thiophen-1-ium bromide (72 mg, 0.25 mmol),3,3´,5,5´-tetra-tert-butyldiphenoquinone (123 mg, 300 µmol) and isopropanol (23 µl, 0.30 mmol) in toluene (2.5 ml) for 12 hours and SiO_2-chromatography (pentane: MTBE, 10:1) afforded **5j** and **5j'**. (overall yield 38 mg, 51%, dr 15:3:1.).

5j' was first eluated as mixture of two minor diastereomers[a,b](colurless gummy liquid, 8 mg, dr 3.1:1.0) and then **5j** was isolated as pure major diastereomer (colorless gummy liquid, 30 mg).

a) analysed from 1H nmr spectra, b) configuration of third diastereomer was not determined.

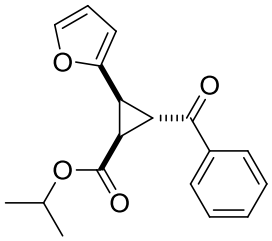
Major diastereomer (5j):



$[\alpha]_D^{20}$ = -26.3° (c = 0.95 in $CHCl_3$). FTIR (neat): $\tilde{\nu}$ = 1726, 1682, 1450, 1374, 1296, 1106, 907, 694, 536 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.07 – 7.99 (m, 2H), 7.62 – 7.52 (m, 1H), 7.51 – 7.42 (m, 2H), 7.31 – 7.28 (m, 1H), 6.35 – 6.31 (m, 1H), 6.25-6.24 (m, 1H), 4.90 (pquin, J^1 = J^2 = 6.3 Hz, 1H), 3.34 (pt, 1H), 3.20 (dd, *J* = 9.7, 6.3 Hz, 1H), 2.70 (dd, *J* = 9.7, 5.8 Hz, 1H), 1.10 (d, *J* = 6.3 Hz, 3H), 1.06 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (75 MHz, CDCl3) δ 192.8, 167.9, 151.1, 141.1, 136.6, 133.0, 128.3, 128.2, 110.5, 106.4, 68.5, 32.8, 30.0, 22.5, 21.3, 21.2. HRMS (ESI): Exact mass calculated for $C_{18}H_{18}O_4Na$ ($[M+Na]^+$) : 321.1097, mass found: 321.1102.

Enantiomeric excess (90% ee) was determined by chiral HPLC. Column: Chiralpak AD-H; solvent: cyclohexane:2-propanol (99.5: 0.5); flow: 1.0 mL/min; major enantiomer t_r = 58.325 min, minor enantiomer t_r = 56.582 min.

Minor diastereomer (5j'):



FTIR (neat): $\tilde{\nu}$ = 1726, 1675, 1598, 1451, 1298, 1106, 632, 504, 478 cm $^{-1}$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 – 8.06 (m, 2H), 7.66 – 7.42 (m, 3H), 7.35 – 7.31 (m, 1H), 6.34 – 6.31 (m, 1H), 6.26 – 6.22 (m, 1H), 4.94 (pquin, $J^1 = J^2$ = 6.0 Hz, 1H), 3.81-3.78 (m, 1H), 3.12-3.04 (m, 1H), 2.76 (dd, *J* = 9.5, 5.2 Hz, 1H), 1.16 (d, *J* = 3.9 Hz, 3H), 1.14 (d, *J* = 3.9 Hz, 3H). **For second minor diastereomer:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03.-7.95 (m, 2H), 7.67 – 7.42 (m, 3H), 7.20-7.16 (m, 1H), 6.22 – 6.18 (m, 1H), 6.12 – 6.09 (m, 1H), 5.13 – 5.02 (m, 1H), 3.46 (dd, *J* = 9.7, 5.2 Hz, 1H), 3.22 (dd, *J* = 9.7, 6.0 Hz, 1H), 3.12-3.04 (m,1H), 1.31-1.26 (m,6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.7, 167.7, 149.1, 141.5, 133.3, 132.9, 128.5, 128.5, 128.3, 128.2, 128.1, 110.3, 110.1, 107.8, 68.4, 30.9, 29.2, 27.5, 26.5, 25.7, 21.6, 21.5, 21.4, 21.3. Exact mass calculated for $C_{18}H_{18}O_4Na$ ($[M+Na]^+$) : 321.1097, mass found: 321.1097.

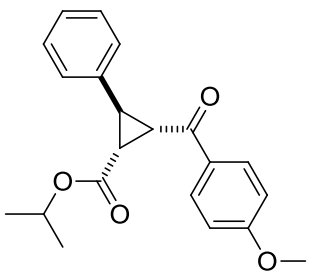
(1*R*,2*S*,3*S*)-Isopropyl2-(4-methoxybenzoyl)-3-phenylcyclopropanecarboxylate (6a) and

(1*S*,2*S*,3*S*)-Isopropyl 2-(4-methoxybenzoyl)-3-phenylcyclopropanecarboxylate (6a'):

According to GP2 with (*E*)-cinnamaldehyde (38 µl, 0.30 mmol), DABCO (31.0 mg, 275 µmol), azolium salt **2b** (4.6 mg, 13 µmol), 1-(2-(4-methoxyphenyl)-2-oxoethyl)tetrahydro-1*H*-thiophen-1-ium bromide (80 mg, 0.25 mmol), 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (123 mg, 300 µmol) and isopropanol (23 µl, 0.30 mmol) in toluene (2.5 ml) for 12 hours and SiO_2-chromatography (pentane: MTBE, 10:1) afforded **6a** and **6a'.** (overall yield 41 mg, 48%, dr 7:1.).

6a' was first eluated and obtained as pure minor diastereomer (colorless gummy liquid, 5 mg) and then **6a** was isolated as pure major diastereomer (white solid, 36 mg).

Major diastereomer (6a):

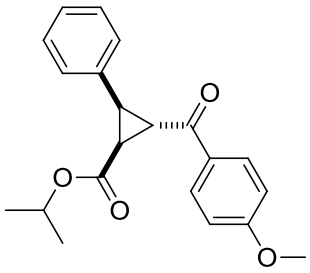


$[\alpha]_D^{20}$ = -38.7° (c = 0.9 in $CHCl_3$). FTIR (neat): $\tilde{\nu}$ = 1712, 1667, 1600, 1573, 1511, 1365, 1255, 1223, 1170, 1109, 1024, 837, 811, 749, 697, 608, 458 cm $^{-1}$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 – 8.00 (m, 2H), 7.40 – 7.30 (m, 2H), 7.28 – 7.19 (m, 3H), 6.95-6.92 (m, 2H), 4.93 (pquin, $J^1 = J^2$ = 6.3 Hz, 1H), 3.87 (s, 3H), 3.34 (pt, 1H), 3.02 (dd, *J* = 9.6, 6.5 Hz, 1H), 2.58 (dd, *J* = 9.6, 5.9 Hz, 1H), 1.13-1.08 (m, 6H). ^{13}C NMR (75

MHz, $CDCl_3$) δ 191.6, 168.5, 163.4, 138.2, 130.4, 129.9, 128.4, 126.7, 126.3, 113.5, 68.2, 55.2, 34.8, 31.4, 28.9, 21.4, 21.3. HRMS (ESI): Exact mass calculated for $C_{21}H_{22}O_4Na$ ($[M+Na]^+$): 361.1410, mass found: 361.1410.

Enantiomeric excess (82% ee) was determined by chiral HPLC. Column: Chiralcel OD-H; solvent: cyclohexane:2-propanol (98.0:2.0); flow: 1.0 mL/min; major enantiomer t_r = 19.048 min, minor enantiomer t_r = 16.478 min.

Minor diastereomer (6a'):



FTIR (neat): $\tilde{\nu}$ = 1721, 1664, 1601, 1467, 1375, 1263, 1174, 1107, 906, 730, 651, 536, 468 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.12-8.09 (m, 2H), 7.37 – 7.28 (m, 4H), 7.28 – 7.21 (m, 1H), 7.02-6.99 (m, 2H), 4.82 (pquin, $J^1 = J^2$ = 6.0 Hz, 1H), 3.90 (s, 3H), 3.79 (dd, *J* = 6.1, 4.8 Hz, 1H), 3.22 (dd, *J* = 9.9, 6.2 Hz, 1H), 2.79 (dd, *J* = 10.0, 4.8 Hz, 1H), 1.05 (d, *J* = 2.9 Hz, 3H), 1.03 (d, *J* = 2.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.88, 168.1, 163.6, 134.9, 130.4, 130.0, 128.7, 127.9, 126.9, 113.7, 68.1, 55.3, 34.3, 31.8, 28.8, 21.5, 21.2. HRMS (ESI): Exact mass calculated for $C_{21}H_{22}O_4Na$ ($[M+Na]^+$) : 361.1410, mass found: 361.1410.

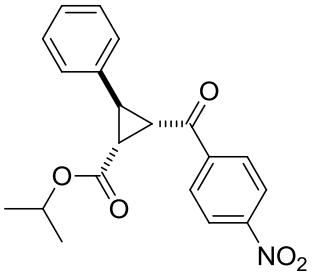
(1*R*,2*S*,3*S*)-Isopropyl 2-(4-nitrobenzoyl)-3-phenylcyclopropanecarboxylate (6b) and

(1*S*,2*S*,3*S*)-Isopropyl2-(4-nitrobenzoyl)-3-phenylcyclopropane carboxylate (6b')

According to GP2 with (*E*)-cinnamaldehye (38 µl, 0.30 mmol), DABCO (31.0 mg, 275 µmol), azolium salt **2b** (4.6 mg, 13 µmol), 1-(2-(4-nitrophenyl)-2-oxoethyl)tetrahydro-1*H*-thiophen-1-ium bromide (83 mg, 0.25 mmol), 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (123 mg, 300 µmol) and isopropanol (23 µl, 0.30 mmol) in toluene (2.5 ml) for 6 hours and SiO_2-chromatography (pentane: MTBE, 10:1) afforded **6b** and **6b'.** (Overall yield 50 mg, 56%, dr 10:1.).

6b' was first eluated and obtained as pure minor diastereomer (yellow liquid, 4.5 mg) and then **6b** was isolated as pure major diastereomer (white solid, 45.5 mg).

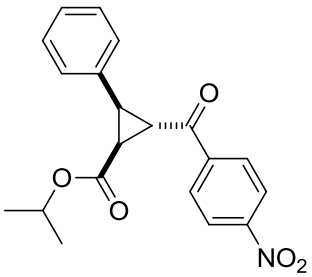
Major diastereomer (6b):



$[\alpha]_D^{20}$ = -32.2° (c = 0.95 in $CHCl_3$). FTIR (neat): $\tilde{\nu}$ = 1714, 1603, 1518, 1340, 1199, 1107, 910, 848, 744, 701, 466 cm $^{-1}$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34-8.31 (m, 2H), 8.19-8.17 (m, 2H), 7.40 – 7.28 (m, 3H), 7.25 – 7.20 (m, 2H), 4.93 (pquin, $J^1 = J^2$ = 6.3 Hz, 1H), 3.38 (pt, 1H), 3.03 (dd, J = 9.5, 6.4 Hz, 1H), 2.70 (dd, J = 9.4, 6.0 Hz, 1H), 1.15 (d, J = 6.3 Hz, 3H), 1.10 (d, J = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.2, 168.2, 150.1, 141.2, 137.3, 129.2, 128.7, 127.3, 126.4, 123.7, 68.8, 35.0, 32.0, 29.6, 21.5, 21.4. HRMS (ESI): Exact mass calculated for $C_{20}H_{19}NO_5Na$ ($[M+Na]^+$): 376.1155, mass found: 376.1146.

Enantiomeric excess (65% ee) was determined by chiral HPLC. Column: Chiralpak AD-H; solvent: cyclohexane: 2-propanol (98.5:1.5); flow: 1.0 mL/min; major enantiomer t_r = 8.313 min, minor enantiomer t_r = 9.759 min.

Minor diastereomer (6b'):



FTIR (neat): $\tilde{\nu}$ = 1724, 1680, 1604, 1528, 1374, 1347, 1318, 1284, 1197, 1107, 790, 740, 544, 477 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40-8.37 (m, 2H), 8.27-8.24 (m, 2H),7.38-7.29 (m, 1H), 4.84 (pquin, $J^1 = J^2$ = 6.3 Hz, 1H), 3.82 (pt, 1H), 3.30 (dd, J = 10.0, 6.1 Hz, 1H), 2.88 (dd, J = 10.0, 4.7 Hz, 1H), 1.09 – 0.99 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.4, 141.2, 129.1, 128.5, 128.1, 127.3, 123.8, 68.6, 35.2, 32.9, 29.6, 21.5, 21.2. HRMS(ESI): Exact mass calculated for $C_{20}H_{19}NO_5Na$ ($[M+Na]^+$): 376.1155, mass found: 376.1154.

(1*R*,2*S*,3*S*)-Isopropyl 2-(4-chlorobenzoyl)-3-phenylcyclopropanecarboxylate (6c) and

(1*S*,2*S*,3*S*)-Isopropyl 2-(4-chlorobenzoyl)-3-phenylcyclopropanecarboxylate (6c'):

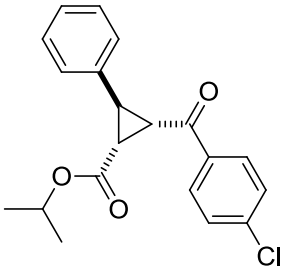
According to GP2 with (*E*)-cinnamaldehyde (38 µl, 0.30 mmol), DABCO (31.0 mg, 275 µmol), azolium salt **2b** (4.6 mg, 13 µmol), 1-(2-(4-chlorophenyl)-2-oxoethyl)tetrahydro-1*H*-thiophen-1-ium bromide (80 mg, 0.25 mmol), 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (123 mg, 300 µmol) and isopropanol (23 µl, 0.30 mmol) in toluene (2.5 ml) for 24 hours and SiO_2-

chromatography (pentane: MTBE, 10:1) afforded **6c** and **6c'.** (Overall yield 39.2 mg, 46%, dr 8:1.).

6c' was first eluated and obtained as minor diastereomer* (yellow liquid, 5 mg) and then **6c** was isolated as major diastereomer (yellow solid, 35 mg).

*It was obtained as mixture with isopropyl cinnamate (minor diastereomer: isopropyl cinnamate 1.0:0.2). So the mixture contains 4.2 mg of minor diastereomer.

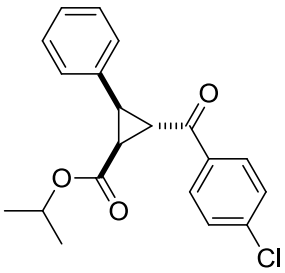
Major diastereomer (6c):



$[\alpha]_D^{20}$ = -29.4° (c = 0.5 in $CHCl_3$). FTIR (neat): $\tilde{\nu}$ = 1721, 1674, 1626, 1588, 1451, 1432, 1372, 1334, 1282, 1190, 1009, 749, 696456 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.02 – 7.93 (m, 2H), 7.45-7.39 (m, 3H), 7.38 – 7.19 (m, 4H), 4.93 (pquin, $J^1 = J^2$ = 6.2 Hz, 1H), 3.35 (pt, 1H), 3.00 (dd, *J* = 9.5, 6.4 Hz, 1H), 2.63 (dd, *J* = 9.6, 6.0 Hz, 1H), 1.13 (d, *J* = 6.3 Hz, 3H), 1.09 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.2, 168.4, 136.8, 135.4, 133.1, 133.0, 132.3, 128.4, 128.2, 128.2, 127.4, 127.3, 126.2, 125.6, 125.1, 124.5, 68.4, 35.0, 31.5, 29.3, 21.4, 21.3. HRMS (ESI): Exact mass calculated for $C_{20}H_{19}ClO_3Na$ ($[M+Na]^+$): 365.0915, mass found: 365.0907.

Enantiomeric excess (> 99% ee) was determined by chiral HPLC. Column: Chiralpak AD-H; solvent: cyclohexane:2-propanol (98.5:1.5); flow: 1.0 mL/min; major enantiomer t_r = 42.311 min, (minor enantiomer t_r = 26.096 min. for racemic sample)

Minor diastereomer (6c'):



FTIR (neat): $\tilde{\nu}$ = 1722, 1673, 1589, 1283, 1195, 1106, 906, 805, 732, 546 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.09 – 8.02 (m, 2H), 7.55 – 7.44 (m, 3H), 7.33 – 7.27 (m, 4H), 4.83 (pquin, $J^1 = J^2$ = 6.0 Hz, 1H), 3.81 – 3.74 (m, 1H), 3.25 (dd, *J* = 10.0, 6.1 Hz, 1H), 2.82 (dd, *J* = 10.0, 4.7 Hz, 1H), 1.04 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.3, 167.8, 144.0, 139.8, 135.1, 134.4, 130.1, 129.8, 129.5, 129.0, 128.9, 128.6, 128.6, 128.0, 127.7, 127.1, 118.6, 68.3, 67.5, 34.7, 32.3, 30.0, 29.1, 21.7, 21.5, 21.2. HRMS (ESI): Exact mass calculated for $C_{20}H_{19}ClO_3Na$ ($[M+Na]^+$): 365.0915, mass found: 365.0911.

(1*R*,2*S*,3*S*)-Isopropyl 2-(4-bromobenzoyl)-3-phenylcyclopropanecarboxylate (6d) and

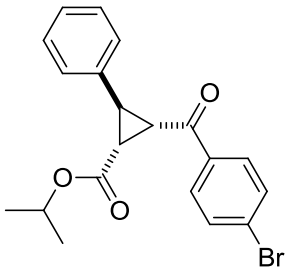
(1*S*,2*S*,3*S*)-Isopropyl 2-(4-bromobenzoyl)-3-phenylcyclopropanecarboxylate (6d')

According to GP2 with (*E*)-cinnamaldehdye (38 µl, 0.30 mmol), DABCO (3.0 mg, 275 µmol), azolium salt **2b** (4.6 mg, 13 µmol), 1-(2-(4-bromophenyl)-2-oxoethyl)tetrahydro-1*H*-thiophen-1-ium bromide (92 mg, 0.25 mmol), 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (123 mg, 300 µmol) and isopropanol (23 µl, 0.30 mmol) in toluene (2.5 ml) for 12 hours and SiO_2-chromatography (pentane: MTBE, 10:1) afforded **6d** and **6d'.** (Overall yield 59.5 mg, 61%, dr 16:1.).

6d' was first eluated and obtained as a mixture* of minor diastereomer and isopropyl cinnamate (yellow liquid, 10 mg) and then **6d** was isolated as pure major diastereomer (yellow solid, 56 mg).

*The mixture contains minor diastereomer and isopropyl cinnamate at a weight ratio of 1.73:1. The minor diastereomer amounts to 3.5 mg.

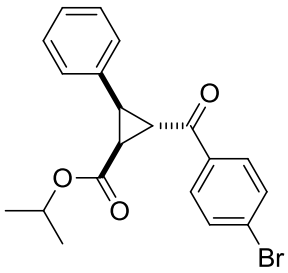
Major diastereomer(6d):



$[\alpha]_D^{20}$ = -23.8° (c = 0.8 in $CHCl_3$). FTIR (neat): $\tilde{\nu}$ = 1706, 1676, 1584, 1371, 1217, 1069, 1007, 826, 745, 644, 509 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.91-7.88 (m, 2H), 7.62-7.59 (m, 2H), 7.39 – 7.18 (m, 5H), 4.93 (pquin, $J^1 = J^2$ = 6.2 Hz, 1H), 3.35 (pt, 1H), 2.99 (dd, *J* = 9.5, 6.4 Hz, 1H), 2.63 (dd, *J* = 9.5, 6.0 Hz, 1H), 1.13 (d, *J* = 6.3 Hz, 3H), 1.10 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.3, 168.2, 137.7, 135.5, 131.7, 129.6, 128.5, 128.2, 126.9, 126.3, 68.5, 34.7, 31.5, 29.1, 21.4, 21.3. HRMS (ESI): Exact mass calculated for $C_{20}H_{19}BrO_3Na$ ($[M+Na]^+$): 409.0415, mass found: 409.0405.

Enantiomeric excess (82% ee) was determined by chiral HPLC. Column: Chiralpak AD-H; solvent: cyclohexane:2-propanol (98.0:2.0); flow: 1.0 mL/min; major enantiomer t_r = 23.602 min, minor enantiomer t_r = 42.481 min.

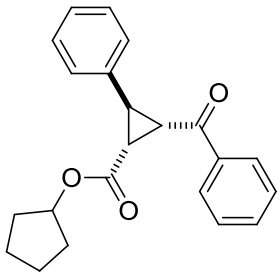
Minor diastereomer (6d', mixture with isopropyl cinnamate**):**



FTIR (neat): $\tilde{\nu}$ = 1704, 1639, 1375, 1282, 1107, 906, 730, 651, 542 cm $^{-1}$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 – 7.94 (m, 2H), 7.57 – 7.48 (m, 3H), 7.33 – 7.27 (m, 4H), 4.83 (pquin, $J^1 = J^2$ = 6.0 Hz, 1H), 3.77 (dd, *J* = 6.1, 4.8 Hz, 1H), 3.25 (dd, *J* = 10.0, 6.1 Hz, 1H), 2.82 (dd, *J* = 10.0, 4.7 Hz, 1H), 1.05-1.03 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.6, 167.8, 166.3, 144.0, 135.5, 134.3, 134.3, 131.8, 129.9, 129.6, 128.6, 128.6, 128.5, 128.0, 127.7, 127.1, 118.5, 68.3, 67.5, 34.7, 32.4, 29.0, 21.7, 21.5, 21.2. HRMS (ESI): Exact mass calculated for $C_{20}H_{19}BrO_3Na$ ($[M+Na]^+$): 409.0415, mass found: 409.0415.

(1*R*,2*S*,3*S*)-Cyclopentyl 2-benzoyl-3-phenylcyclopropanecarboxylate (7a):

According to GP2 with (*E*)-cinnamaldehyde (38 µl, 0.30 mmol), DABCO (31.0 mg, 275 µmol), azolium salt **2b** (4.6 mg, 13 µmol), 1-(2-oxo-2-phenylethyl)tetrahydro-1*H*-thiophen-1-ium bromide (72 mg, 0.25 mmol), 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (123 mg, 300 µmol) and cyclopentanol (27µl, 0.30 mmol) in toluene (2.5 ml) for 6 hours and SiO_2-chromatography (pentane: MTBE, 10:1) afforded **7a** as white solid. (Yield 39 mg, 46%, dr 20:1.)

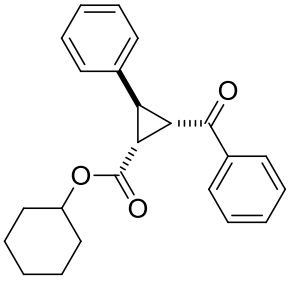


$[\alpha]_D^{20}$ = -25.3° (c = 1.0 in $CHCl_3$). FTIR (neat): $\tilde{\nu}$ = 1723, 1679, 1449, 1280, 1220, 1164, 696, 631, 536 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 – 8.00 (m, 2H), 7.62 – 7.53 (m, 1H), 7.52 – 7.43 (m, 2H), 7.40 – 7.27 (m, 3H), 7.25 – 7.20 (m, 2H), 5.12 – 5.04 (m, 1H), 3.35(pt, 1H), 3.05 (dd, *J* = 9.6, 6.5 Hz, 1H), 2.62 (dd, *J* = 9.6, 6.0 Hz, 1H), 1.79 – 1.64 (m, 2H), 1.64 – 1.43 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.2, 168.6, 138.0, 136.7, 133.0, 128.4, 128.3, 128.1, 126.8, 126.4, 77.8, 34.9, 32.3, 32.1, 31.6, 29.0, 23.3. HRMS (ESI) Exact mass calculated for $C_{22}H_{22}O_3Na$ ($[M+Na]^+$): 357.1461, mass found: 357.1066.

Enantiomeric excess (86% ee) was determined by chiral HPLC. Column: Chiralcel OD-H; solvent: cyclohexane:2-propanol (99.0:1.0); flow: 1.0 mL/min; major enantiomer t_r = 17.653 min, minor enantiomer t_r = 15.105 min.

(1*R*,2*S*,3*S*)-Cyclohexyl 2-benzoyl-3-phenylcyclopropanecarboxylate (7b):

According to GP2 with (*E*)-cinnamaldehyde (38 µl, 0.30 mmol), DABCO (31.0 mg, 27.5 µmol), azolium salt **2b** (4.6 mg, 13 µmol), 1-(2-oxo-2-phenylethyl)tetrahydro-1*H*-thiophen-1-ium bromide (72 mg, 0.25 mmol), 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (123 mg, 300 µmol) and cyclohexanol (31 µl, 0.30 mmol) in toluene (2.5 ml) for 6 hours and SiO_2-chromatography (pentane: MTBE, 10:1) afforded **7b** as yellow solid. (Yield 42 mg, 48%, dr 20:1.).

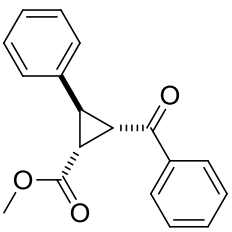


$[\alpha]_D^{20}$ = -26.5° (c = 1.0 in $CHCl_3$). FTIR (neat): $\tilde{\nu}$ = 1712, 1678, 1448, 1288, 1176, 1122, 903, 695, 505, 468 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.05-8.03 (m, 2H), 7.61 – 7.53 (m, 1H), 7.51 – 7.43 (m, 2H), 7.37 – 7.30 (m, 2H), 7.30 – 7.21 (m, 2H), 4.75 – 4.64 (m, 1H), 3.37 (pt, 1H), 3.06 (dd, *J* = 9.6, 6.5 Hz, 1H), 2.64 (dd, *J* = 9.6, 6.0 Hz, 1H), 1.80 – 1.36 (m, 6H), 1.32 – 1.18 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.3, 168.3, 138.0, 136.8, 132.9, 128.4, 128.3, 128.1, 126.8, 126.3, 73.2, 34.9, 31.7, 31.1, 31.1, 29.1, 25.0, 23.4. HRMS (ESI): Exact mass calculated for $C_{23}H_{24}O_3Na$ ($[M+Na]^+$): 371.1618, mass found: 371.1619.

Enantiomeric excess (86% ee) was determined by chiral HPLC. Column: Chiralpak AD-H; solvent: cyclohexane:2-propanol (98.5:1.5); flow: 1.0 mL/min; major enantiomer t_r = 19.763 min, minor enantiomer t_r = 23.441 min.

(1*R*,2*S*,3*S*)-Methyl 2-benzoyl-3-phenylcyclopropanecarboxylate (7c)

According to GP2 with (*E*)-cinnamaldehyde (38 µl, 0.30 mmol), DABCO (31.0 mg, 27.5 µmol), azolium salt **2b** (4.6 mg, 13 µmol), 1-(2-oxo-2-phenylethyl)tetrahydro-1*H*-thiophen-1-ium bromide (72 mg, 0.25 mmol), 3,3´,5,5´-tetra-tert-butyldiphenoquinone (123 mg, 300 µmol) and methanol (12 µl, 0.30 mmol) in toluene (2.5 ml) for 6 hours and SiO_2-chromatography (pentane: MTBE, 4:1) afforded **7c** as yellow solid. (Yield 18 mg, 26%, dr 98:2).



$[\alpha]_D^{20}$ = -30.8° (c = 0.3 in $CHCl_3$). FTIR (neat): $\tilde{\nu}$ = 1735, 1680, 1449, 1362, 1279, 1220, 1173, 837, 631, 534, 494 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.10 – 7.97 (m, 2H), 7.62 – 7.53 (m, 1H), 7.51 – 7.42 (m, 2H), 7.39 – 7.27 (m, 3H), 7.25 – 7.20 (m, 2H), 3.66 (s, 3H), 3.37 (pt, 1H), 3.11

(dd, *J* = 9.4, 6.4 Hz, 1H), 2.65 (dd, *J* = 9.4, 6.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.6, 169.4, 137.7, 136.7, 133.0, 128.5, 128.4, 128.1, 127.0, 126.3, 51.9, 34.7, 31.3, 29.8. HRMS (ESI): Exact mass calculated for $C_{18}H_{16}O_3Na$ ($[M+Na]^+$): 303.0992, mass found: 303.0989.

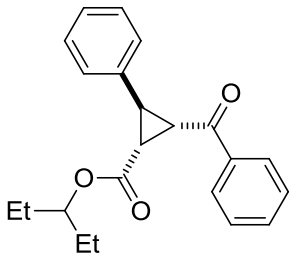
Enantiomeric excess (67% ee) was determined by chiral HPLC. Column: Chiralcel OD-H; solvent: cyclohexane:2-propanol (95.0: 5.0); flow: 1.0 mL/min; major enantiomer t_r = 17.418 min, minor enantiomer t_r = 9.46 min.

(1*R*,2*S*,3*S*)-Pentan-3-yl 2-benzoyl-3-phenylcyclopropanecarboxylate (7d) and (1*S*,2*S*,3*S*)-Pentan-3-yl 2-benzoyl-3-phenylcyclopropanecarboxylate (7d'):

According to GP2 with (*E*)-cinnamaldehyde (38 µl, 0.30 mmol), DABCO (31.0 mg, 27.5 µmol), azolium salt **2b** (4.6 mg, 13 µmol), 1-(2-oxo-2-phenylethyl)tetrahydro-1*H*-thiophen-1-ium bromide (72 mg, 0.25 mmol), 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (123 mg, 300 µmol) and 3-pentanol (64 µl, 0.30 mmol) in toluene (2.5 ml) for 24 hours and SiO_2-chromatography (pentane: MTBE, 10:1) afforded **7c** and **7c'**. (Overall yield 19.7 mg, 24%, dr 11:1.).

7d' was first eluated as pure minor diastereomer (yellow liquid, 1.7 mg,) and then **7d** was isolated as pure major diastereomer (colorless gummy liquid, 18 mg).

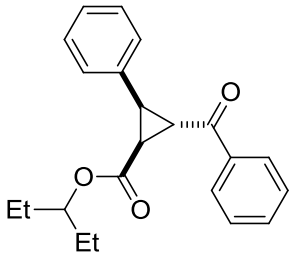
Major diastereomer (7d):



$[\alpha]_D^{20}$ = -22.3° (c = 0.6 in $CHCl_3$). FTIR (neat): $\tilde{\nu}$ = 1726, 1683, 1450, 1282, 1189, 1107, 903, 742, 697, 631, 536, 478 cm $^{-1}$.^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 – 8.02 (m, 2H), 7.60 – 7.51 (m, 1H), 7.50 – 7.41 (m, 2H), 7.38 – 7.31 (m, 2H), 7.30 – 7.22 (m, 3H), 4.68 (p, *J* = 6.2 Hz, 1H), 3.39 (pt, 1H), 3.08 (dd, *J* = 9.6, 6.5 Hz, 1H), 2.65 (dd, *J* = 9.6, 5.9 Hz, 1H), 1.51 – 1.44 (m, 2H), 1.44 – 1.38 (m, 2H), 0.78 (t, *J* = 6.3 Hz, 3H), 0.73 (t, *J* = 6.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.1, 168.7, 138.0, 136.7, 132.9, 128.4, 128.3, 128.1, 126.8, 126.4, 77.5, 34.8, 31.8, 29.0, 25.8, 25.8, 9.2, 9.0. HRMS (ESI): Exact mass calculated for $C_{22}H_{24}O_3Na$ ($[M+Na]^+$): 359.1615, mass found: 359.1615

Enantiomeric excess (97% ee) was determined by chiral HPLC. Column: Chiralpak AD-H; solvent: cyclohexane: 2-propanol (98.0:2.0); flow: 1.0 mL/min; major enantiomer t_r = 17.054 min, minor enantiomer t_r = 16.423 min.

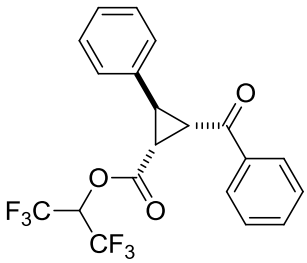
Minor diastereomer (7d'):



FTIR (neat): $\tilde{\nu}$ = 1723, 1674, 1599, 1450, 1324, 1196, 908, 734, 632, 538, 492 cm $^{-1}$. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 – 8.10 (m, 2H), 7.66 – 7.61 (m, 1H), 7.57 – 7.50 (m, 2H), 7.34 – 7.32 (m, 2H), 7.31 – 7.28 (m, 2H), 7.26 – 7.22 (m, 1H), 4.62 – 4.56 (m, 1H), 3.87 (dd, *J* = 6.2, 4.8 Hz, 1H), 3.26 (dd, *J* = 10.0, 6.1 Hz, 1H), 2.87 (dd, *J* = 10.1, 4.8 Hz, 1H), 1.44 – 1.36 (m, 4H), 0.75 (t, *J* = 7.5 Hz, 3H), 0.67 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.8, 168.4, 137.0, 134.7, 133.4, 128.8, 128.7, 128.3, 128.2, 127.2, 77.6, 34.9, 32.3, 29.3, 26.1, 26.1, 9.5, 9.1. HRMS (ESI): Exact mass calculated for $C_{22}H_{24}O_3Na$ ($[M+Na]^+$): 359.1618, mass found: 359.1614.

(1*R*,2*S*,3*S*)-1,1,1,3,3,3-Hexafluoropropan-2-yl 2-benzoyl-3-phenylcyclopropane carboxylate (7e):

According to GP2 with (*E*)-cinnamaldehyde (38 µl, 0.30 mmol), DABCO (31 mg, 27.5 µmol), azolium salt **2b** (4.6 mg, 12.5 µmol), 1-(2-oxo-2-phenylethyl)tetrahydro-1*H*-thiophen-1-ium bromide (72 mg, 0.25 mmol), 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (123 mg, 300 µmol) and hexafluoroisopropanol (32 µl, 0.30 mmol) in toluene (2.5 ml) for 6 hours and SiO_2-chromatography (pentane: MTBE, 20:1) afforded **7e** as yellow solid. (Yield 73 mg, 70%, dr 98:2).



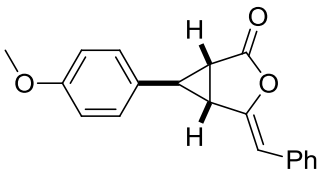
$[\alpha]_D^{20}$ = -17.9° (c = 0.6 in $CHCl_3$). FTIR (neat): $\tilde{\nu}$ = 1777, 1680, 1599, 1450, 1384, 1366, 1288, 1232, 1203, 1112, 904, 726, 650 cm $^{-1}$. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 – 7.96 (m, 2H), 7.64 – 7.56 (m, 1H), 7.52 – 7.44 (m, 2H), 7.42 – 7.28 (m, 3H), 7.26-7.21 (m,2H), 5.72 (pquin, $J^1 = J^2$ = 6.0 Hz, 1H), 3.46 (pt, 1H), 3.32 (dd, *J* = 9.4, 6.6 Hz, 1H), 2.78 (dd, *J* = 9.4, 6.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.1, 166.0, 136.5, 136.1, 133.4, 128.7, 128.5, 128.1, 127.4, 126.3, 66.7 (pquin, J = 138.0 Hz), 35.4, 30.4, 29.6, (*C*F_3-resonances could not be detected). HRMS (ESI): Exact mass calculated for $C_{20}H_{14}F_6O_3Na$ $(M + Na)^+$: 439.0739, mass found: 439.0734.

Enantiomeric excess (62% ee) was determined by chiral HPLC. Column: Chiralcel OD-H; solvent: cyclohexane:2-propanol (99.5:0.5); flow: 1.0 mL/min; major enantiomer t_r = 14.852 min, minor enantiomer t_r = 16.687 min

(1*S*,5*R*,6*R*,*Z*)-4-Benzylidene-6-(4-methoxyphenyl)-3-oxabicyclo[3.1.0]

hexan -2-one (13a):

According to GP3 with (*E*)-3-(4-methoxyphenyl)acrylaldehyde (41 mg, 0.25 mmol), DABCO (31 mg, 27.5 µmol), azolium salt **2d** (4.6 mg, 13 µmol), 1-(2-oxo-3-phenylpropyl)tetrahydro-1*H*-thiophen-1-ium bromide (113 mg, 375 µmol), 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (102 mg, 250 µmol) in toluene (2.5 ml) for 12 hours and SiO_2-chromatography (pentane: MTBE, 5:1) afforded **13a** as a colorless gummy liquid**.** (yield 31 mg, 43%, dr 10: 1)

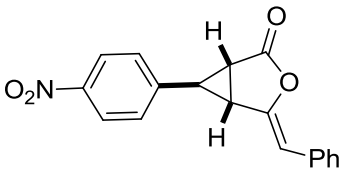


$[\alpha]_D^{20}$ = + 74.3° (c = 0.9 in $CHCl_3$). FTIR (neat): $\tilde{\nu}$ = 1801, 1731, 1689, 1612, 1583, 1517, 1497, 1451, 1250, 1224, 1184, 1121, 1033, 1009, 946, 831, 697, 627, 493 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 2H), 7.37 – 7.29 (m, 2H), 7.24 – 7.17 (m, 1H), 7.05-6.99 (m, 2H), 6.88-6.85 (m, 2H), 5.66 (s, 1H), 3.80 (s, 3H), 3.01 (dd, *J* = 5.4, 3.4 Hz, 1H), 2.64 (dd, *J* = 5.5, 3.0 Hz, 1H), 2.54 (pt, 1H). **For minor diastereomer**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.58-7.51 (m, 2H), 7.37 – 7.29 (m, 2H), 7.24 – 7.17 (m, 1H), 6.95 – 6.90 (m, 2H), 6.81-6.76 (m, 2H), 5.66 (s, 1H), 3.77 (s, 3H), 3.12 (pt, 1H), 2.46 (dd, *J* = 9.4, 6.2 Hz, 1H), 2.35 (dd, *J* = 9.4, 6.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3, 158.8, 158.5, 147.0, 133.4, 129.4, 129.3, 129.3, 128.5, 128.2, 128.1, 127.5, 126.8, 126.7, 126.6, 113.7, 114.0, 104.2, 55.1, 55.0, 36.1, 31.5, 31.1, 31.0, 29.9, 27.1. HRMS (ESI): Exact mass calculated for $C_{19}H_{16}O_3Na$ ($[M+Na]^+$): 315.0992, mass found: 315.0996.

Enantiomeric excess (-76% ee, with catalyst **2d**) was determined by chiral HPLC. Column: Chiralpak AD-H; solvent: cyclohexane:2-propanol (98.0:2.0); flow: 1.0 mL/min; major enantiomer t_r = 24.896 min, minor enantiomer t_r = 22.35min.

(1*S*,5*R*,6*R*,*Z*)-4-Benzylidene-6-(4-nitrophenyl)-3-oxabicyclo[3.1.0]hexan-2-one (13b):

According to GP3 with (*E*)-3-(4-nitrophenyl)acrylaldehyde (44 mg, 0.25 mmol), DABCO (31.0 mg, 27.5 µmol), azolium salt **2d** (4.6 mg, 13 µmol), 1-(2-oxo-3-phenylpropyl)tetrahydro-1*H*-thiophen-1-ium bromide (113 mg, 375 µmol),3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (102 mg, 250 µmol) in toluene (2.5 ml) for 12 hours and SiO_2-chromatography (pentane: MTBE, 4:1) afforded **13b** as a yellow gummy liquid**.** (Yield 23 mg, 30%, dr 98:2)



$[\alpha]_D^{20}$ = + 69.7° (c = 0.65 in $CHCl_3$). FTIR (neat): $\tilde{\nu}$ = 1802, 1690, 1601, 1522, 1347, 1225, 1187, 1124, 947, 906, 729, 631, 529, 460 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.25 – 8.18 (m, 2H), 7.60 – 7.51 (m, 2H), 7.39-7.28 (m, 3H), 7.25 – 7.21 (m, 2H), 5.74 (s, 1H), 3.15 (dd, *J* = 5.6, 3.3 Hz, 1H), 2.82 (dd, *J* = 5.6, 3.0 Hz, 1H), 2.65 (pt, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1, 147.0, 145.8, 143.8, 132.9, 128.4, 128.3, 127.1, 126.2, 123.9, 105.5, 32.1, 30.7, 27.8. HRMS (ESI): Exact mass calculated for $C_{18}H_{13}NO_4Na$ ($[M+Na]^+$): 330.0737, mass found: 330.0736.

Enantiomeric excess (-82% ee, with catalyst **2d**) was determined by chiral HPLC. Column: Chiralpak AD-H; solvent: cyclohexane:2-propanol (95.0:5.0); flow: 1.0 mL/min; major enantiomer t_r = 34.136 min, minor enantiomer t_r = 44.815 min.

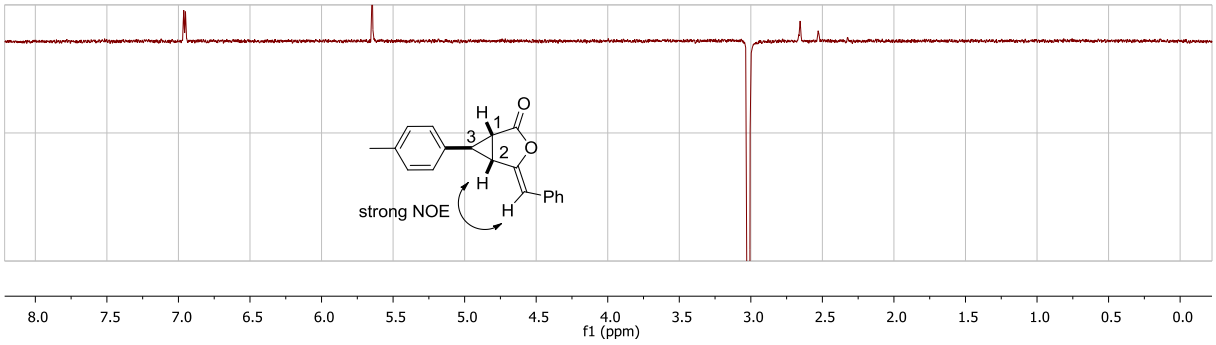
Enantiomeric excess (+59% ee, with catalyst **2b**) was determined by chiral HPLC. Column: Chiralpak AD-H; solvent: cyclohexane:2-propanol (95.0:5.0); flow: 1.0 mL/min; major enantiomer t_r = 43.306 min, minor enantiomer t_r = 34.030 min.

(1*S*,5*R*,6*R*,*Z*)-4-Benzylidene-6-(*p*-tolyl)-3-oxabicyclo[3.1.0]hexan-2-one (13c)

According to GP3 with (*E*)-3-(p-tolyl)acrylaldehyde (37 mg, 0.25 mmol), DABCO (31.0 mg, 27.5 µmol), azolium salt **2d** (4.6 mg, 13 µmol), 1-(2-oxo-3-phenylpropyl)tetrahydro-1*H*-thiophen-1-ium bromide (113 mg, 375 µmol), 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (102 mg, 250 µmol) in toluene (2.5 ml) for 12 hours and SiO_2-chromatography (pentane: MTBE, 5:1) afforded **13c** as a yellow solid**.** (Yield 24 mg, 35%)

$[\alpha]_D^{20}$ = + 144° (c = 0.7 in $CHCl_3$). FTIR (neat): $\tilde{\nu}$ = 1801, 1690, 1225, 1122, 906, 749, 731, 651, 561 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ 7.57 – 7.54 (m, 2H), 7.35 – 7.31 (m, 2H), 7.24 – 7.20 (m, 1H), 7.16-7.14 (m, 2H), 6.99 – 6.96 (m, 2H), 5.67 (s, 1H), 3.04 (ddd, *J* = 5.5, 3.4, 0.5 Hz, 1H), 2.68 (dd, *J* = 5.5, 3.0 Hz, 1H), 2.55 (pt,1H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.5, 147.2, 137.3, 133.6, 133.4, 129.5, 128.5, 128.4, 126.9, 125.6, 104.4, 31.6, 31.5, 27.4, 21.0. HRMS (ESI): Exact mass calculated for $C_{19}H_{16}O_2Na$ ($[M+Na]^+$): 299.1043, mass found: 299.1045.

Stereochemistry of the C-C double bond was determined by an NOESY experiment.



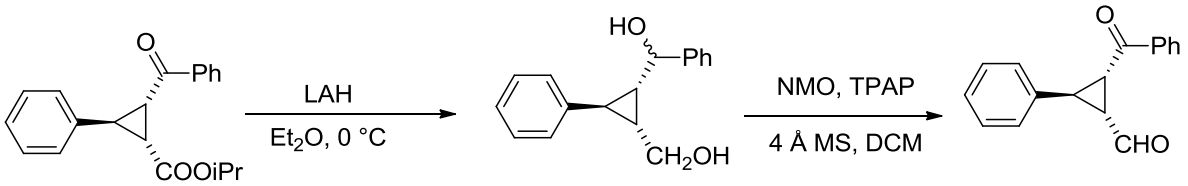
NOESY (600 / 600 MHz, $CDCl_3$, 299 K): δ_{irr} / δ_{resp} 3.02 / 2.53, 2.66, 5.64, 6.96 (2-H / 3-H, 1-H, C*H*$_{vinylic}$, C*H*$_{tolyl}$)

Enantiomeric excess (-87% ee, with catalyst **2d**) was determined by chiral HPLC. Column: Chiralpak AD-H; solvent: cyclohexane:2-propanol (98.0:2.0); flow: 1.0 mL/min; major enantiomer t_r = 9.558 min, minor enantiomer t_r = 8.869 min.

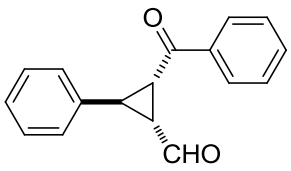
Enantiomeric excess (+62% ee, with catalyst **2b**) was determined by chiral HPLC. Column: Chiralpak AD-H; solvent: cyclohexane:2-propanol (98.0:2.0); flow: 1.0 mL/min; major enantiomer t_r = 8.691 min, minor enantiomer t_r = 9.414 min.

Determination of absolute configuration of 5a:

The isopropyl ester group of the compound **5a** was converted to the corresponding aldehyde via reduction followed by oxidation[4]. ^{1}H and ^{13}C NMR spectra exactly matches with the previously reported diastereomer.[5] Absolute configuration was assigned by comparing the optical rotation with the reported value.



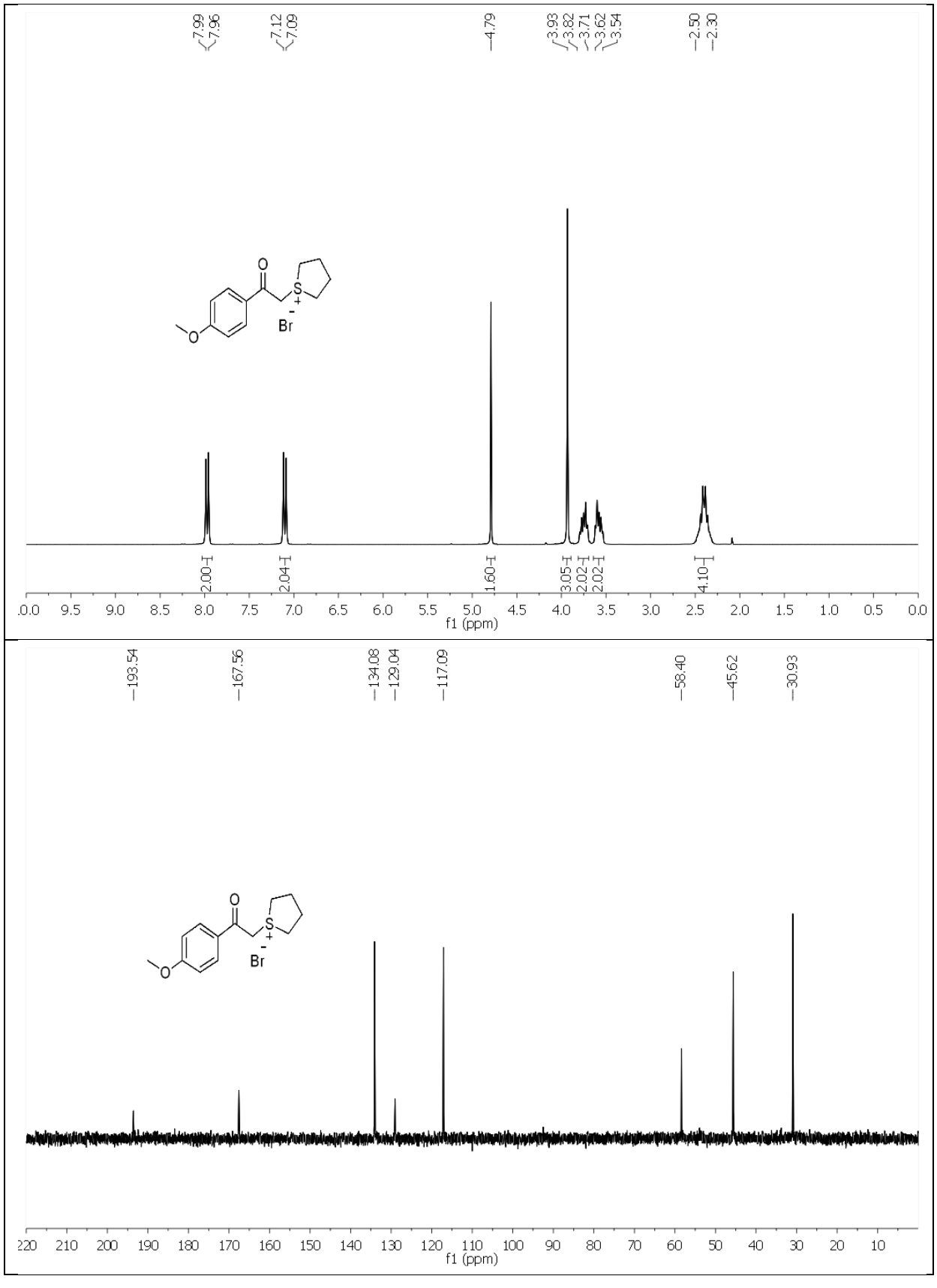
(1*R*,2*S*,3*R*)-2-benzoyl-3-phenylcyclopropanecarbaldehyde:



$[\alpha]_D^{20}$ = -154.0° (c = 0.3 in $CHCl_3$).

Literature value[5]: $[\alpha]_D^{20}$ = -165.7° (c = 1.0 in $CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.59 (d, *J* = 6.1 Hz, 1H), 8.04 – 7.95 (m, 2H), 7.66 – 7.56 (m, 1H), 7.54 – 7.45 (m, 2H), 7.42 – 7.28 (m, 4H), 7.25 – 7.19 (m, 2H), 3.61 (pt, 1H), 3.48 (dd, *J* = 8.9, 6.1 Hz, 1H), 2.68 (dt, *J* = 8.9, 6.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.7, 194.9, 136.7, 136.5, 133.5, 128.7, 128.6, 128.2, 127.4, 126.3, 40.6, 36.5, 32.2.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2.02
2.02
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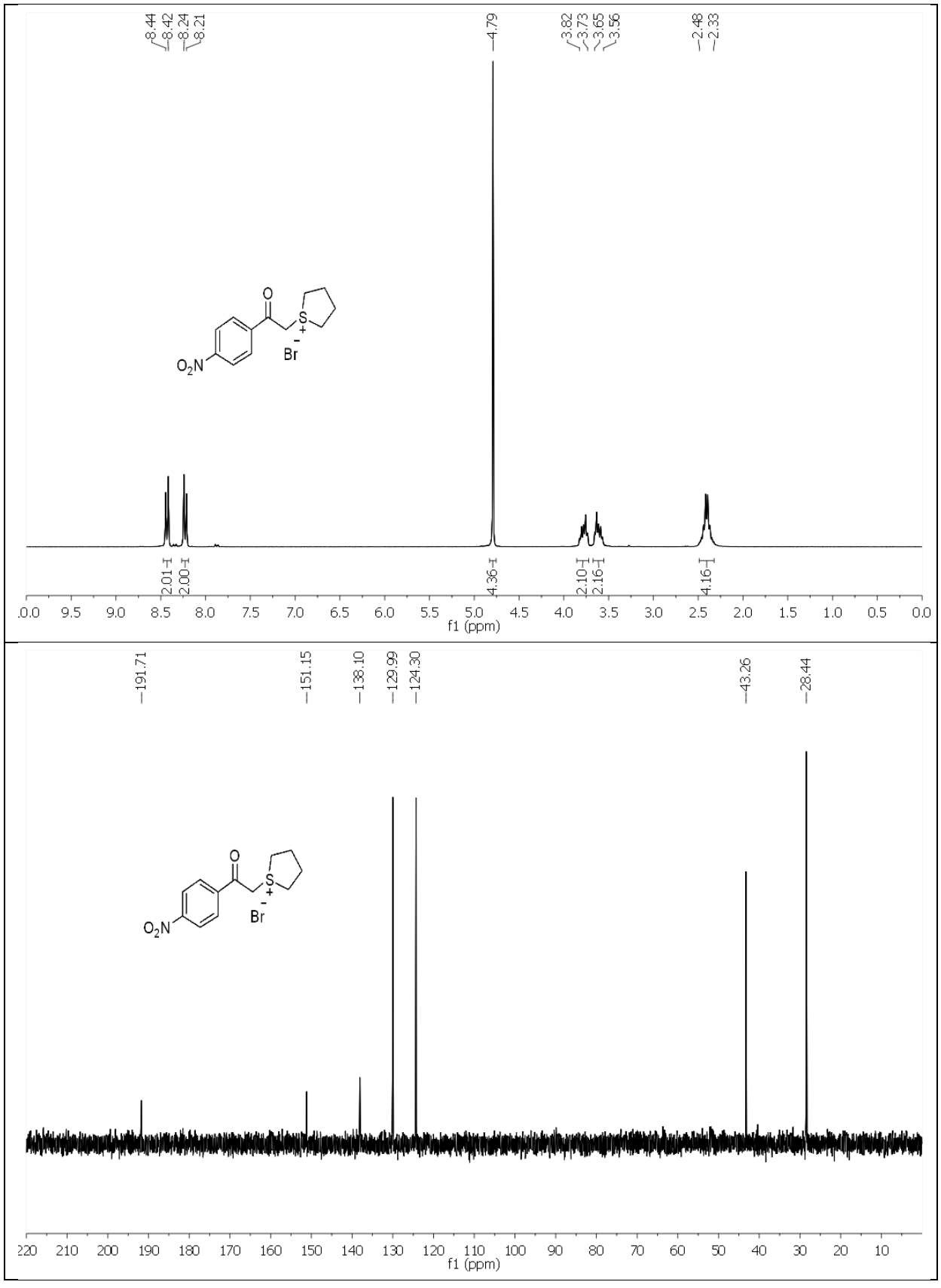
30.93
f1 (ppm)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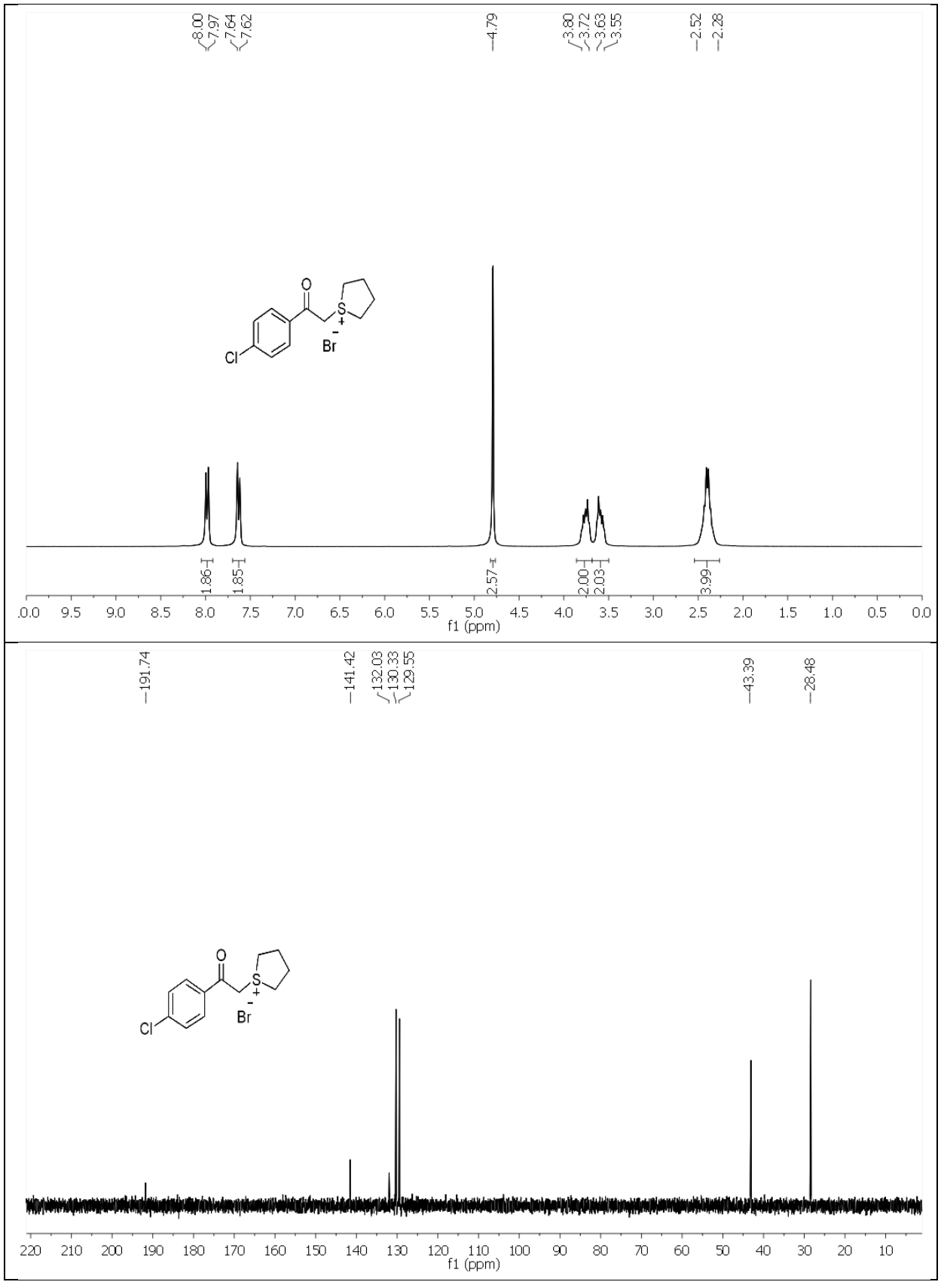
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-
Br
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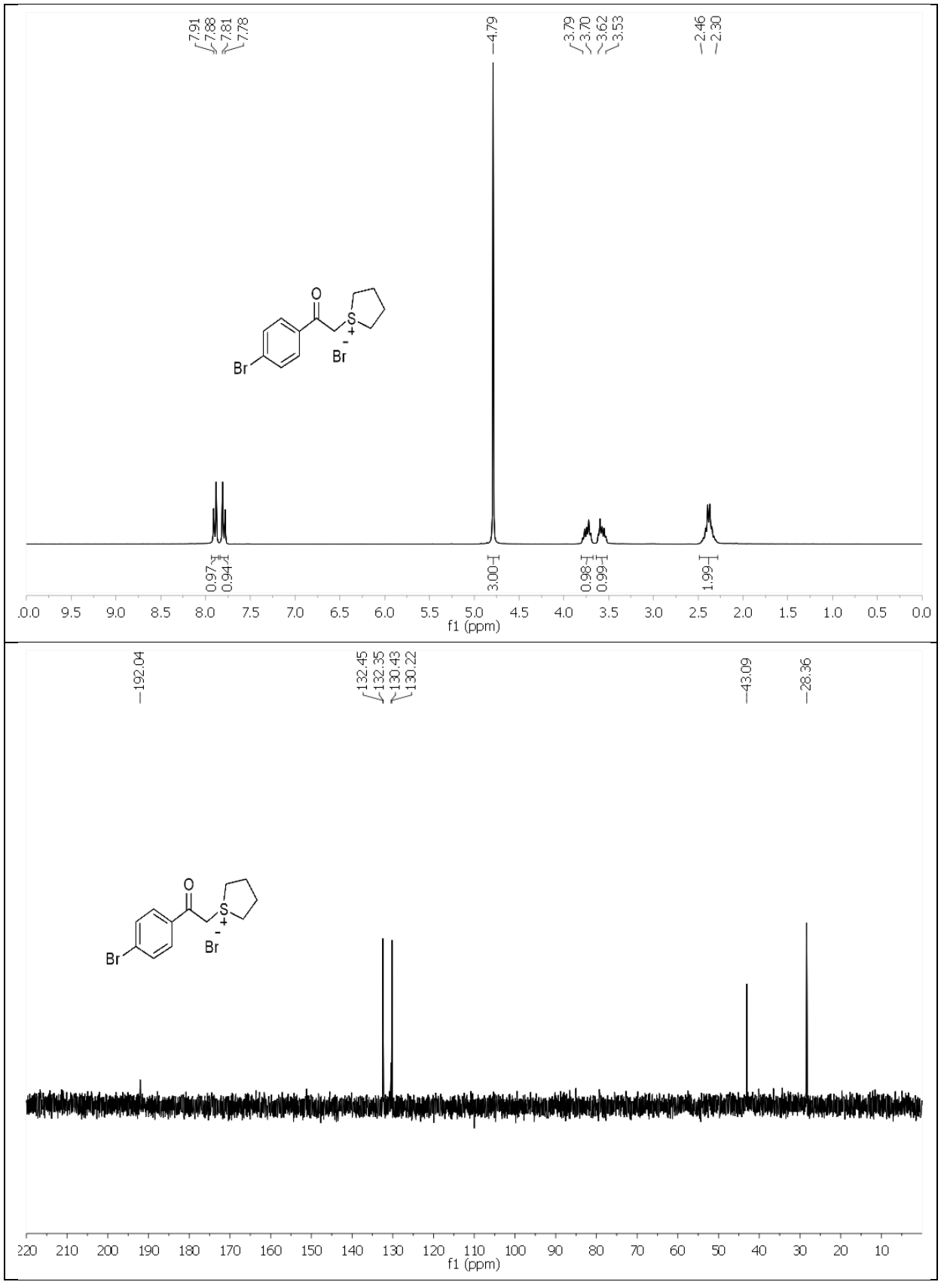
Br
Cl
f1 (ppm)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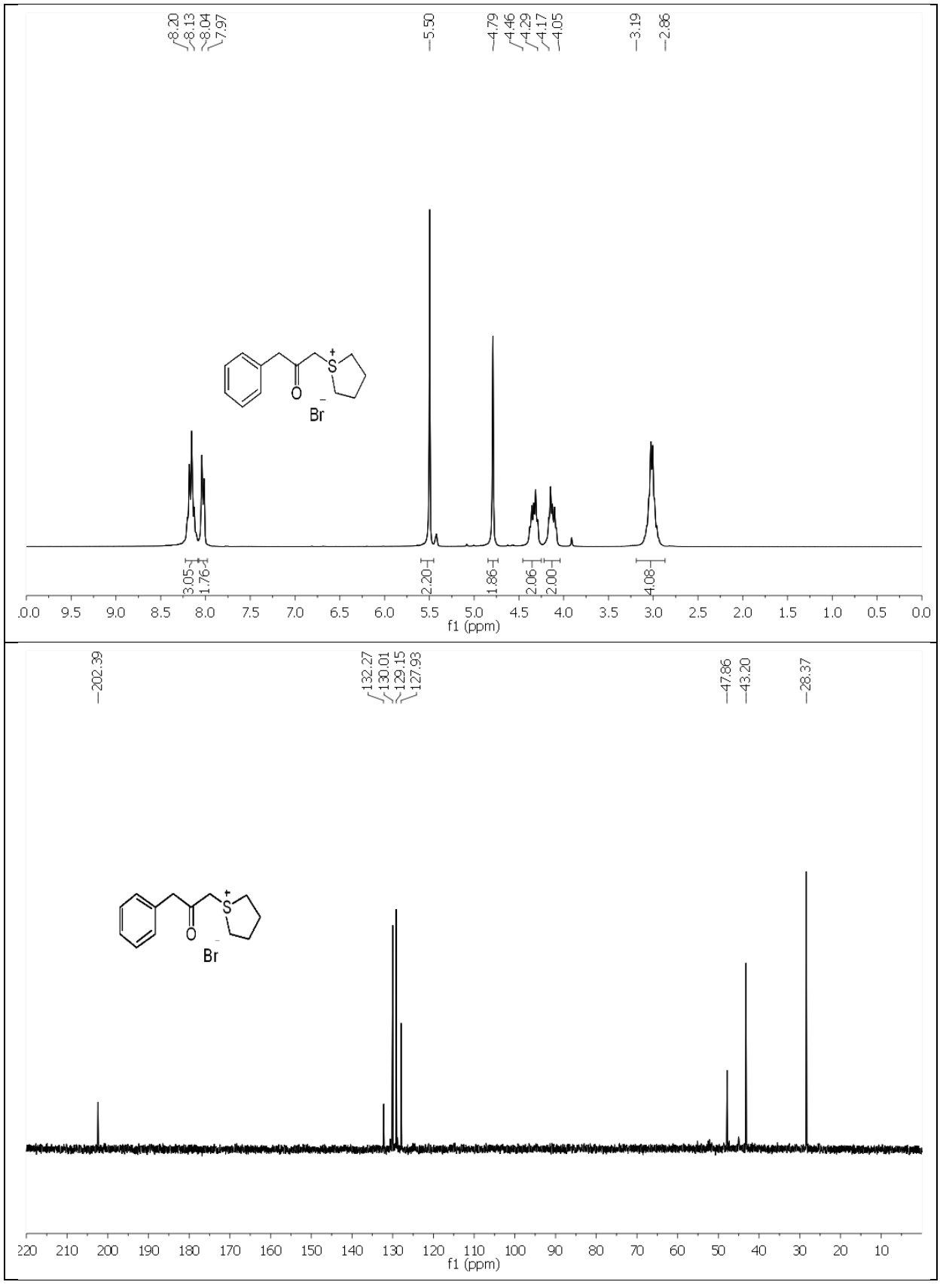
f1 (ppm)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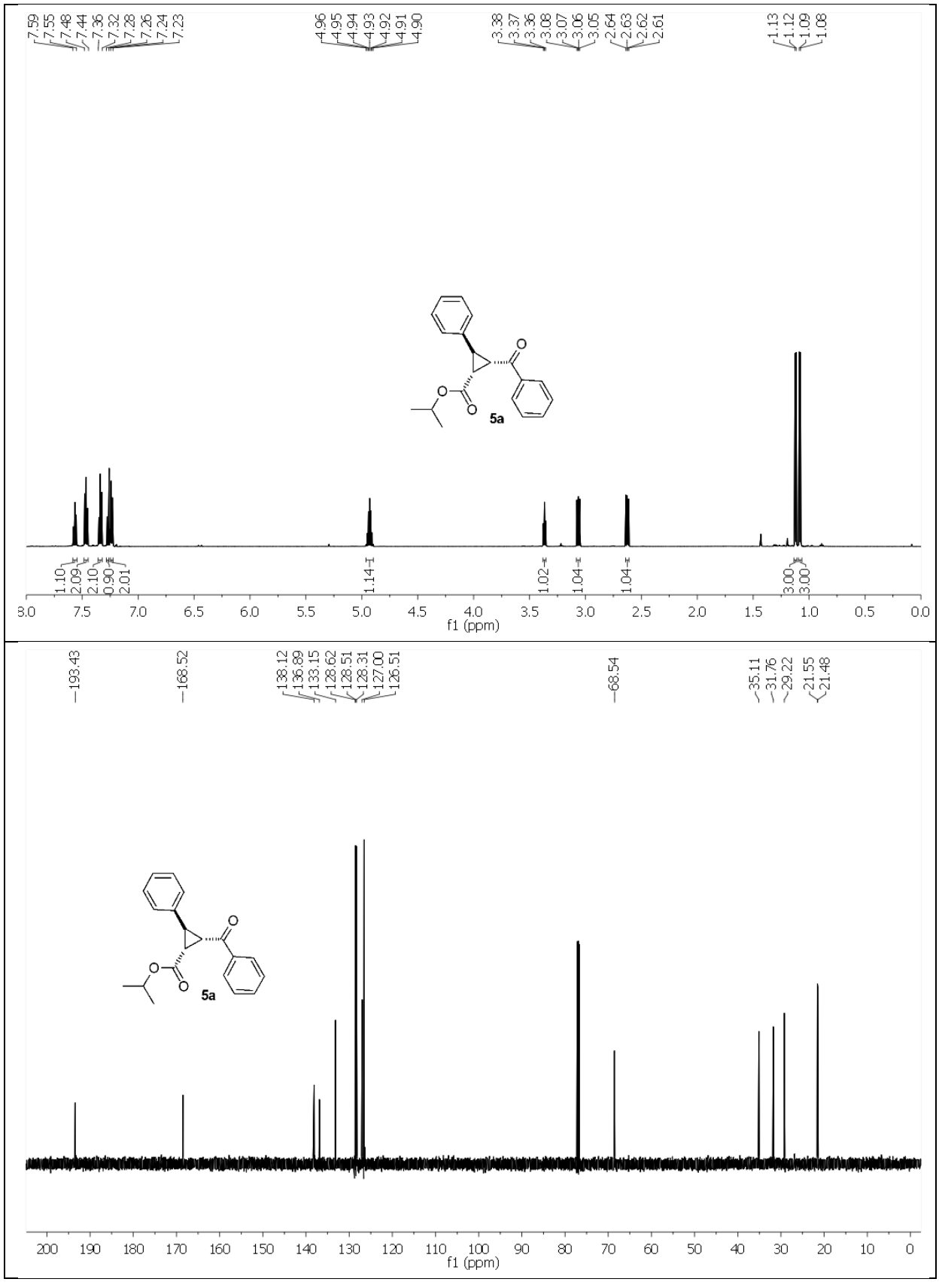
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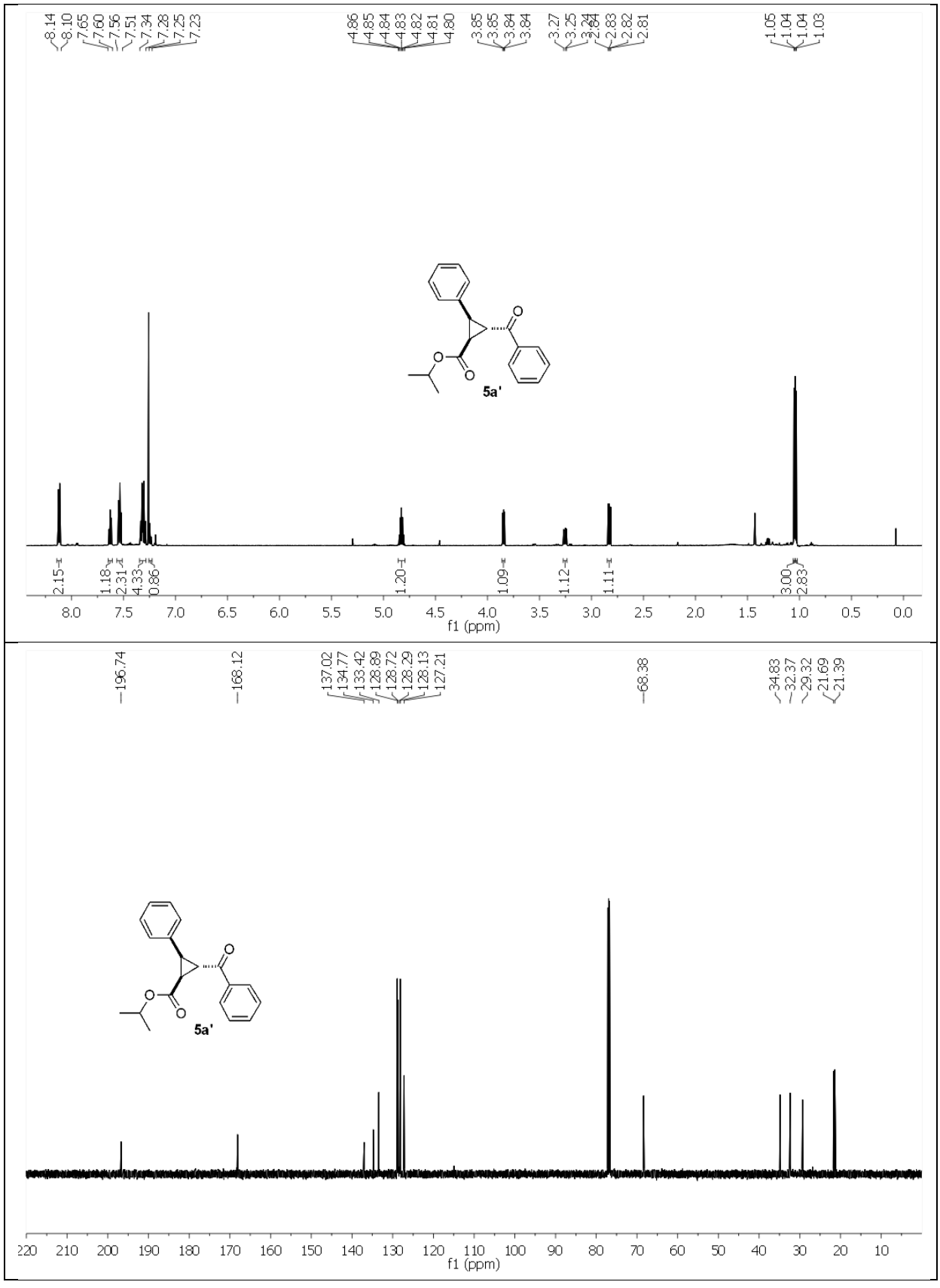
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1.03
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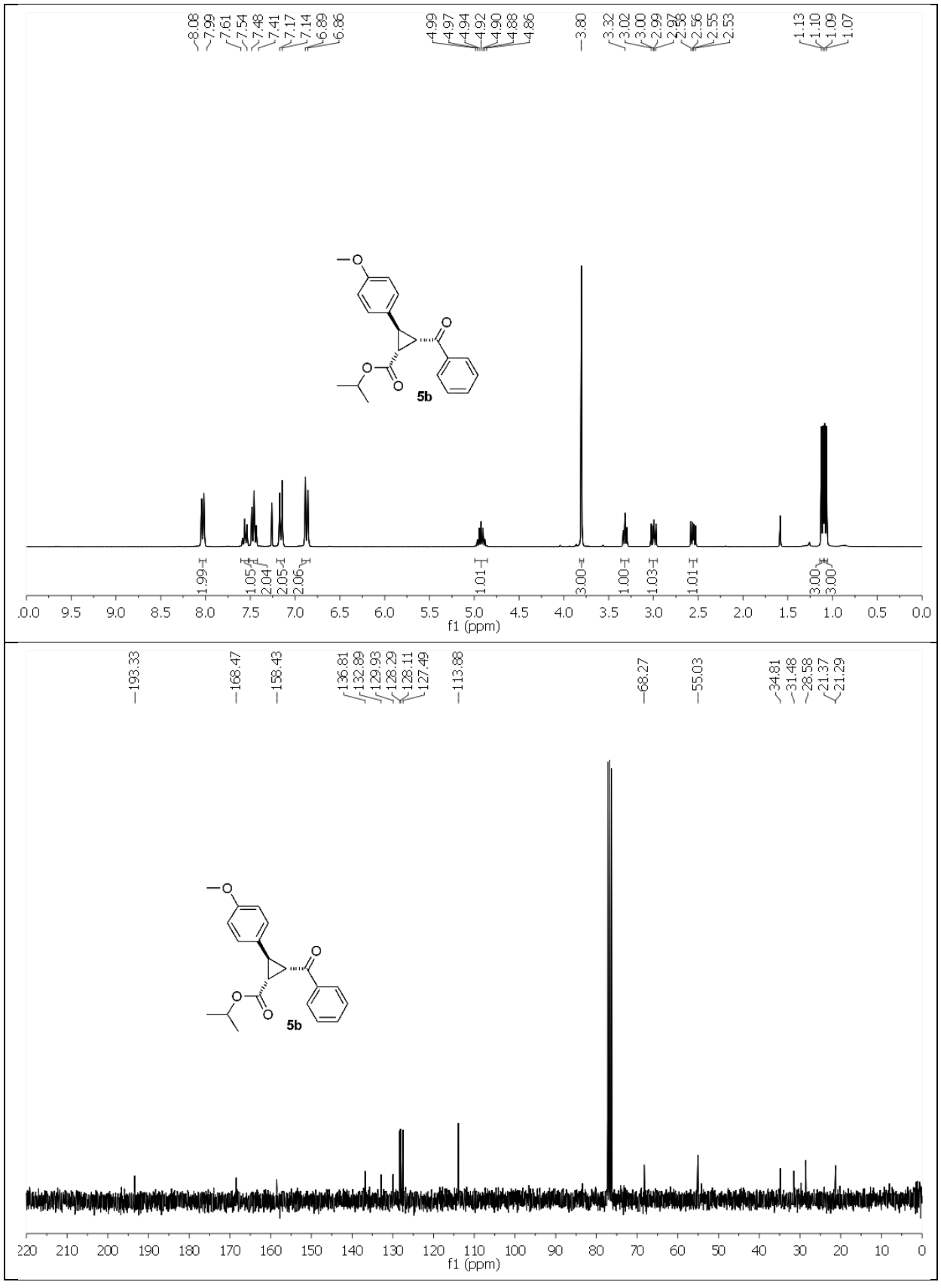
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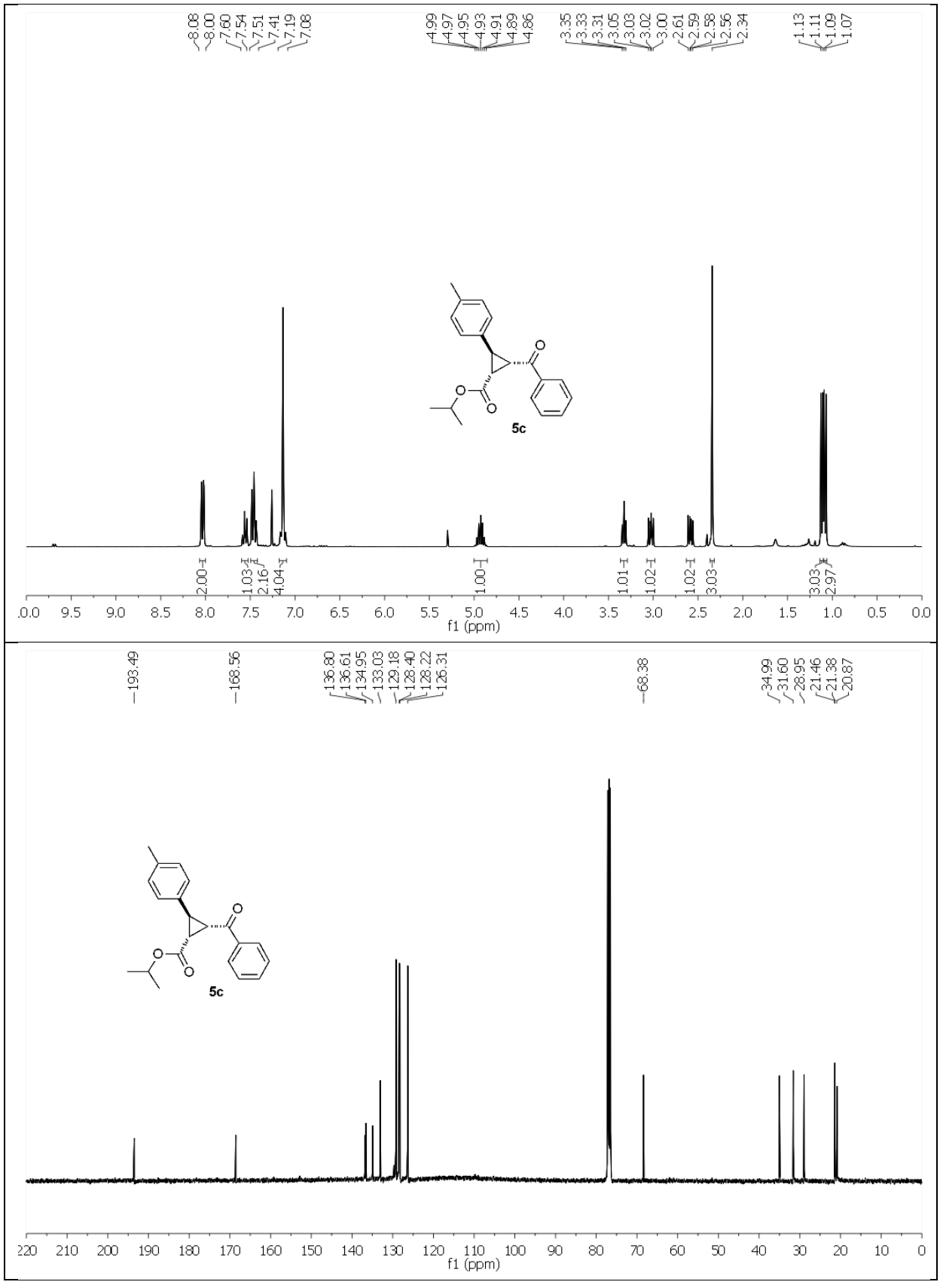
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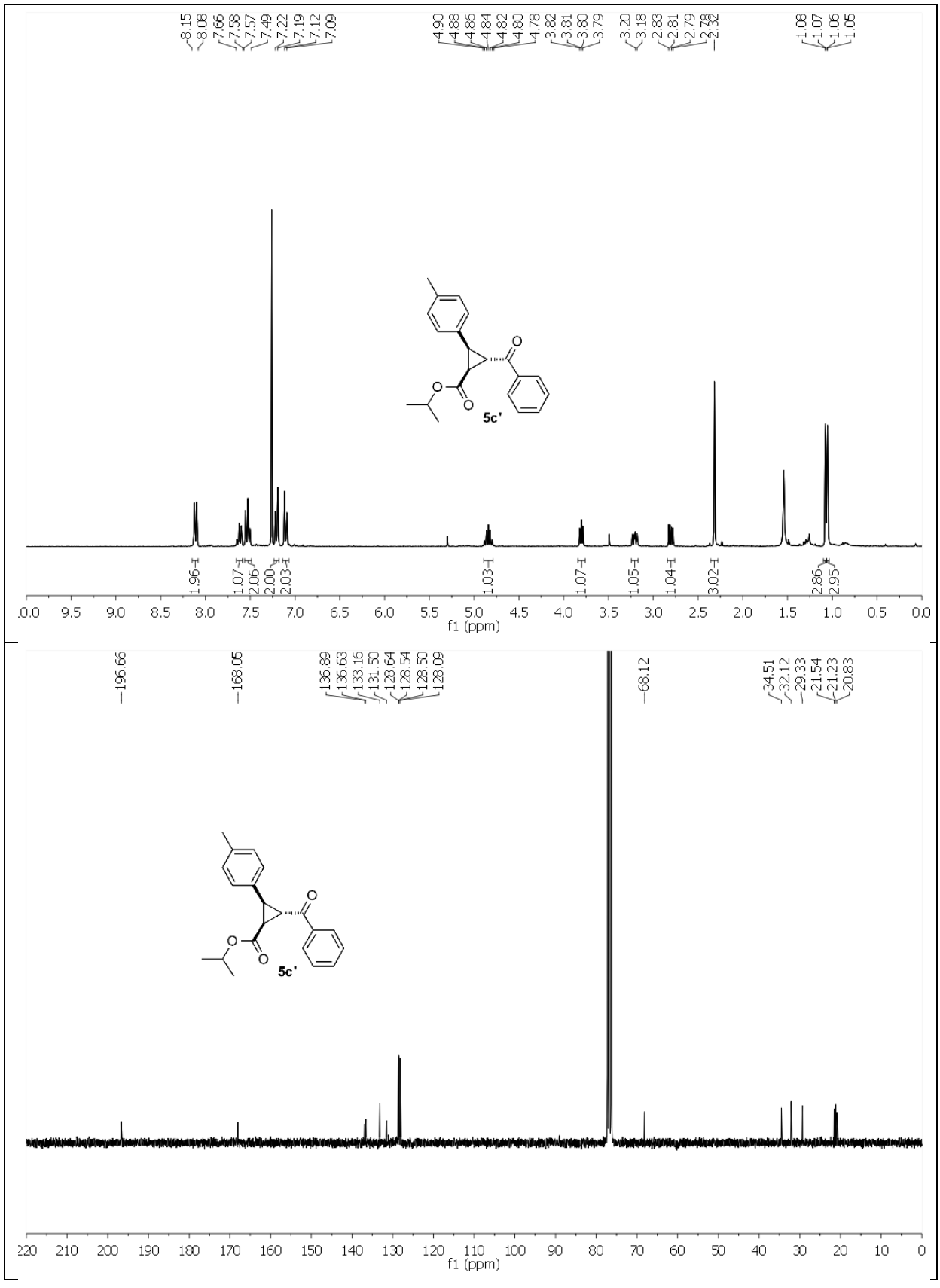
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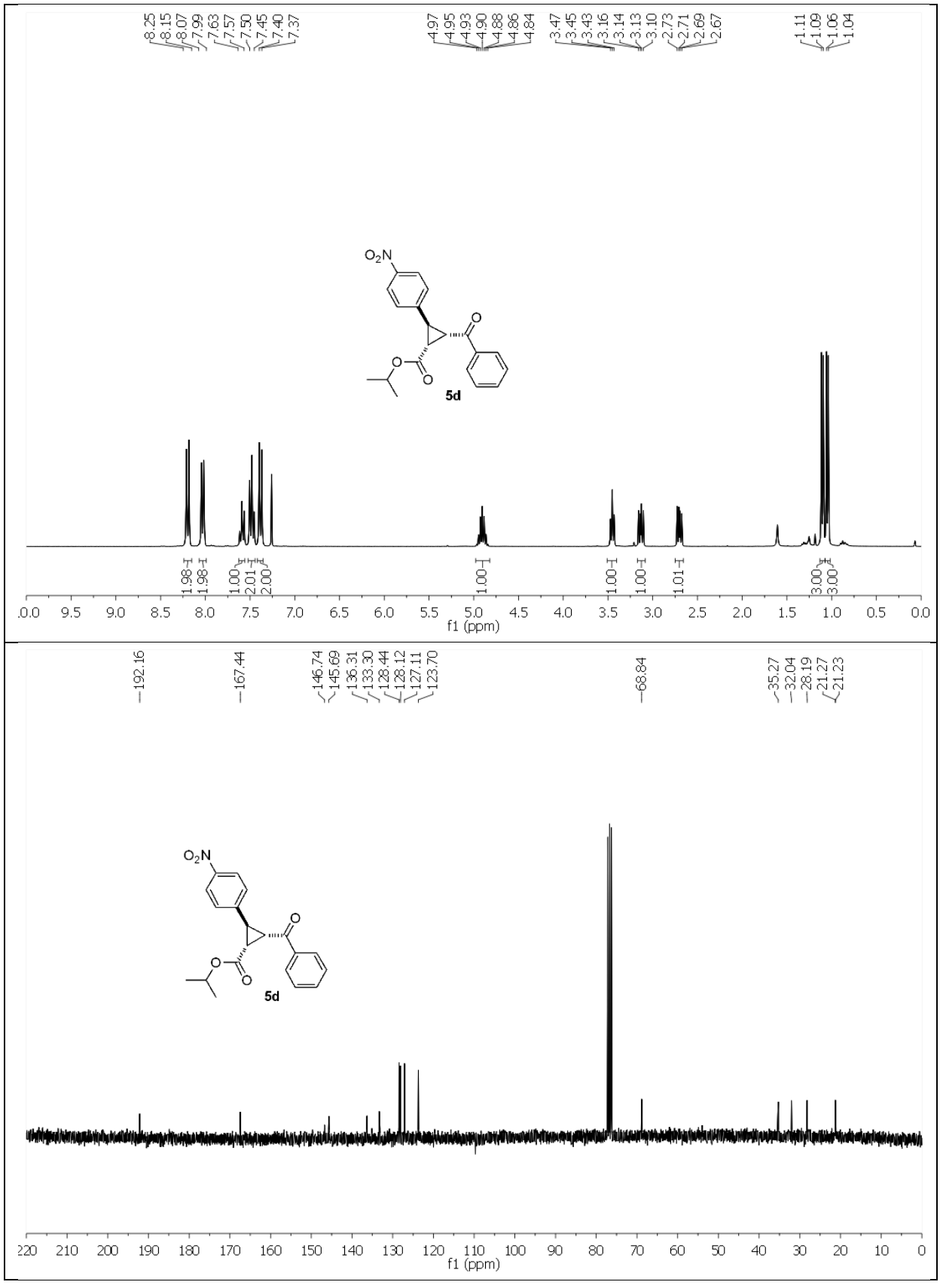
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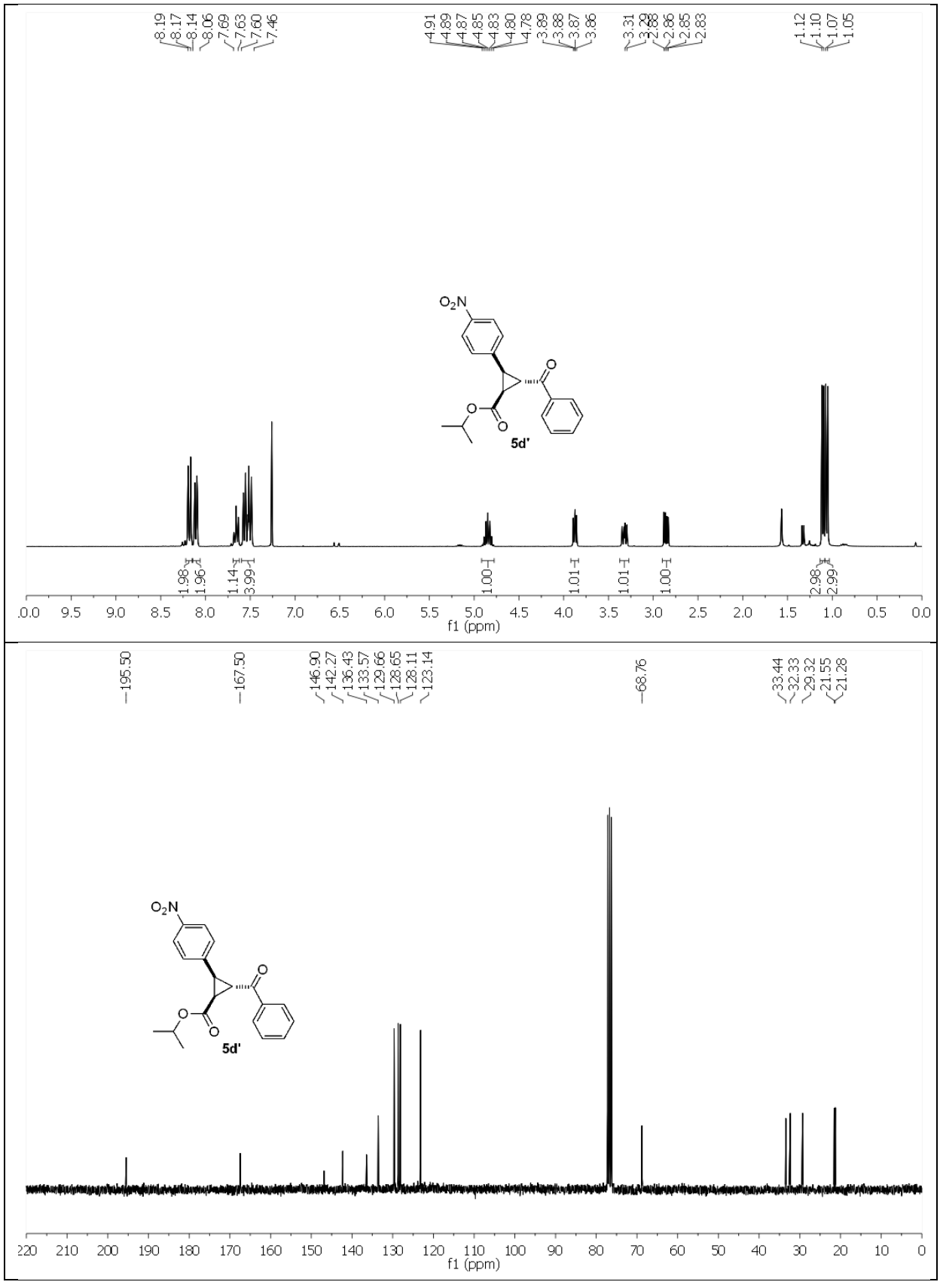
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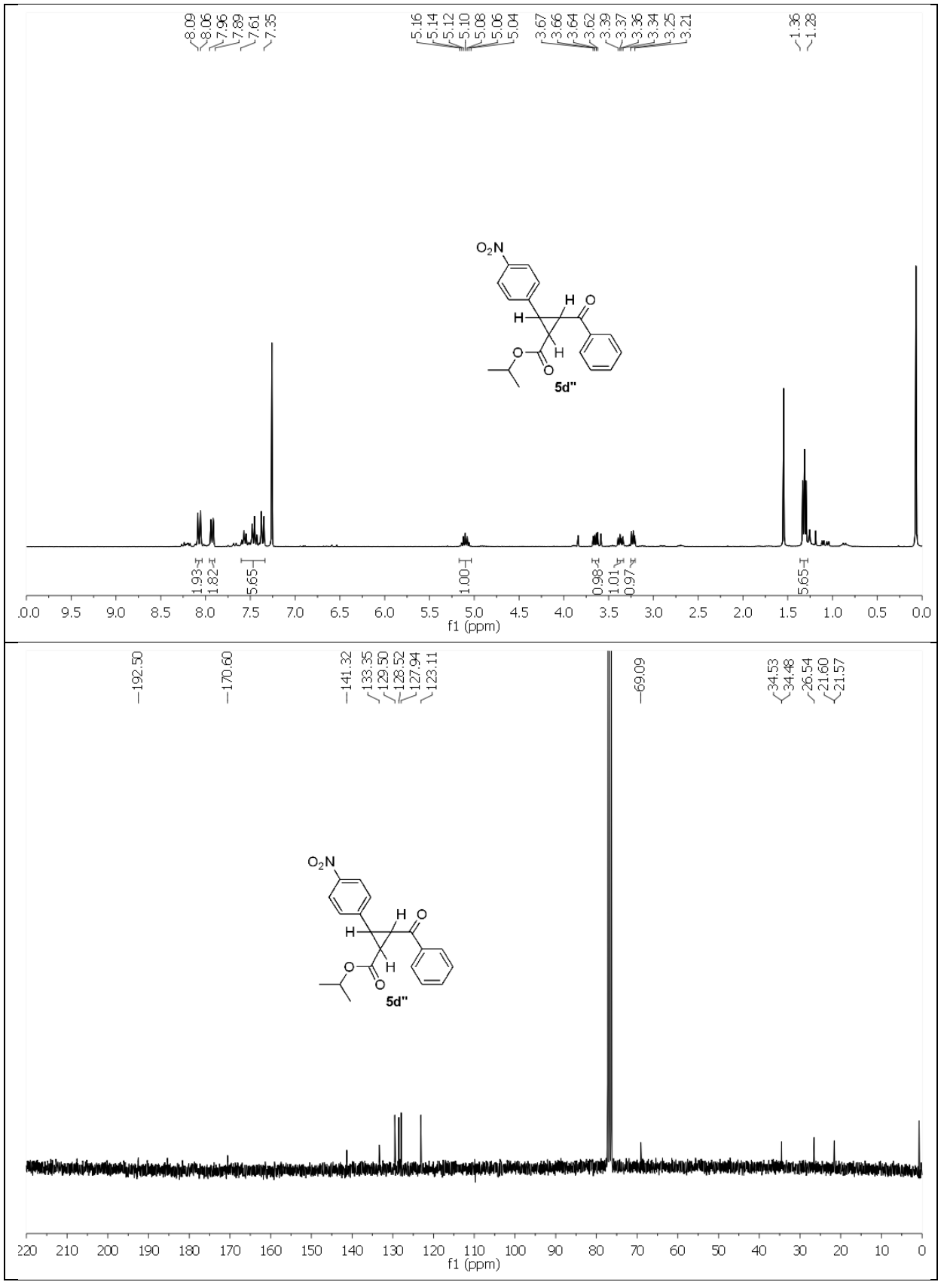
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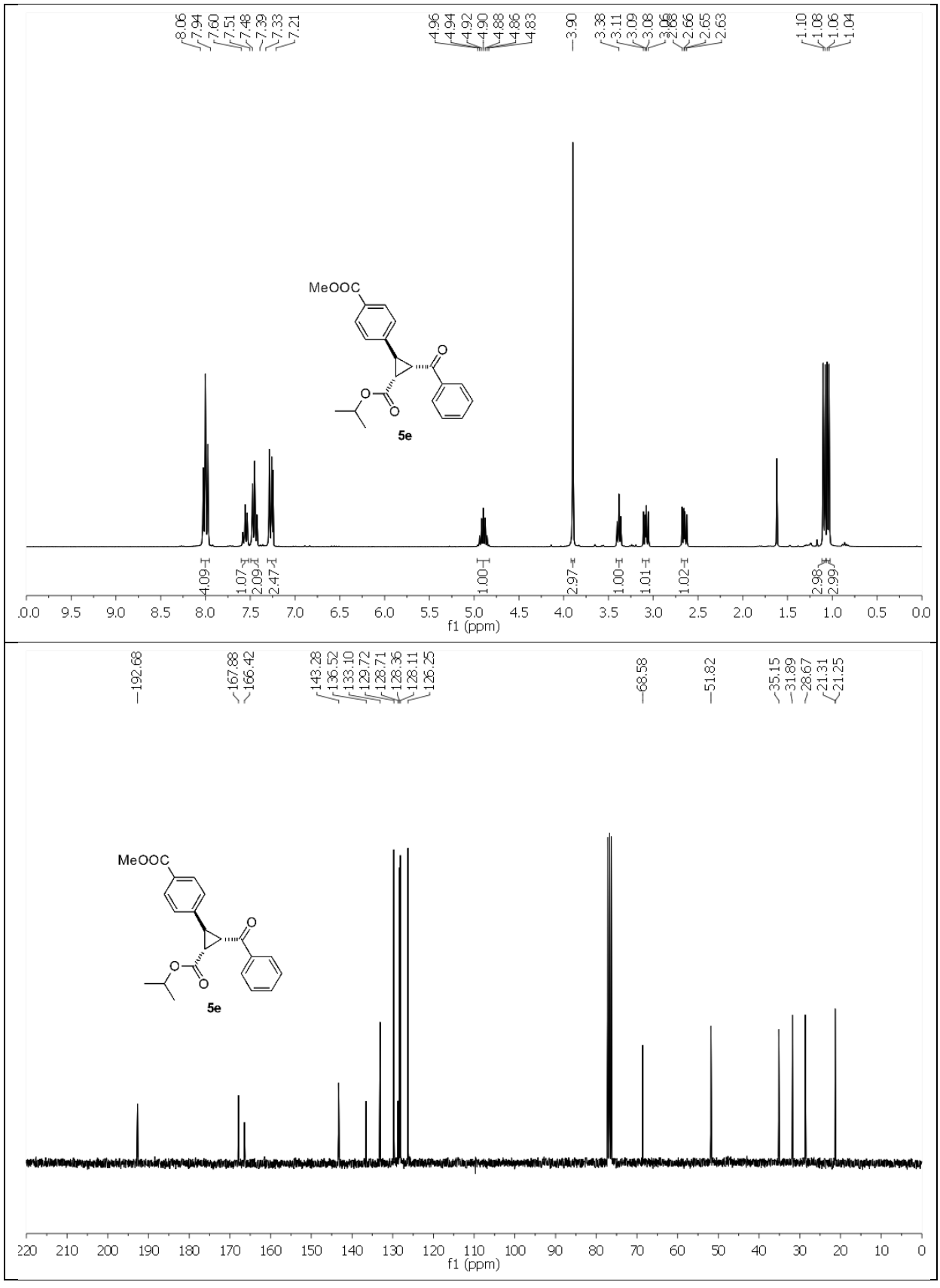
5d"
f1 (ppm)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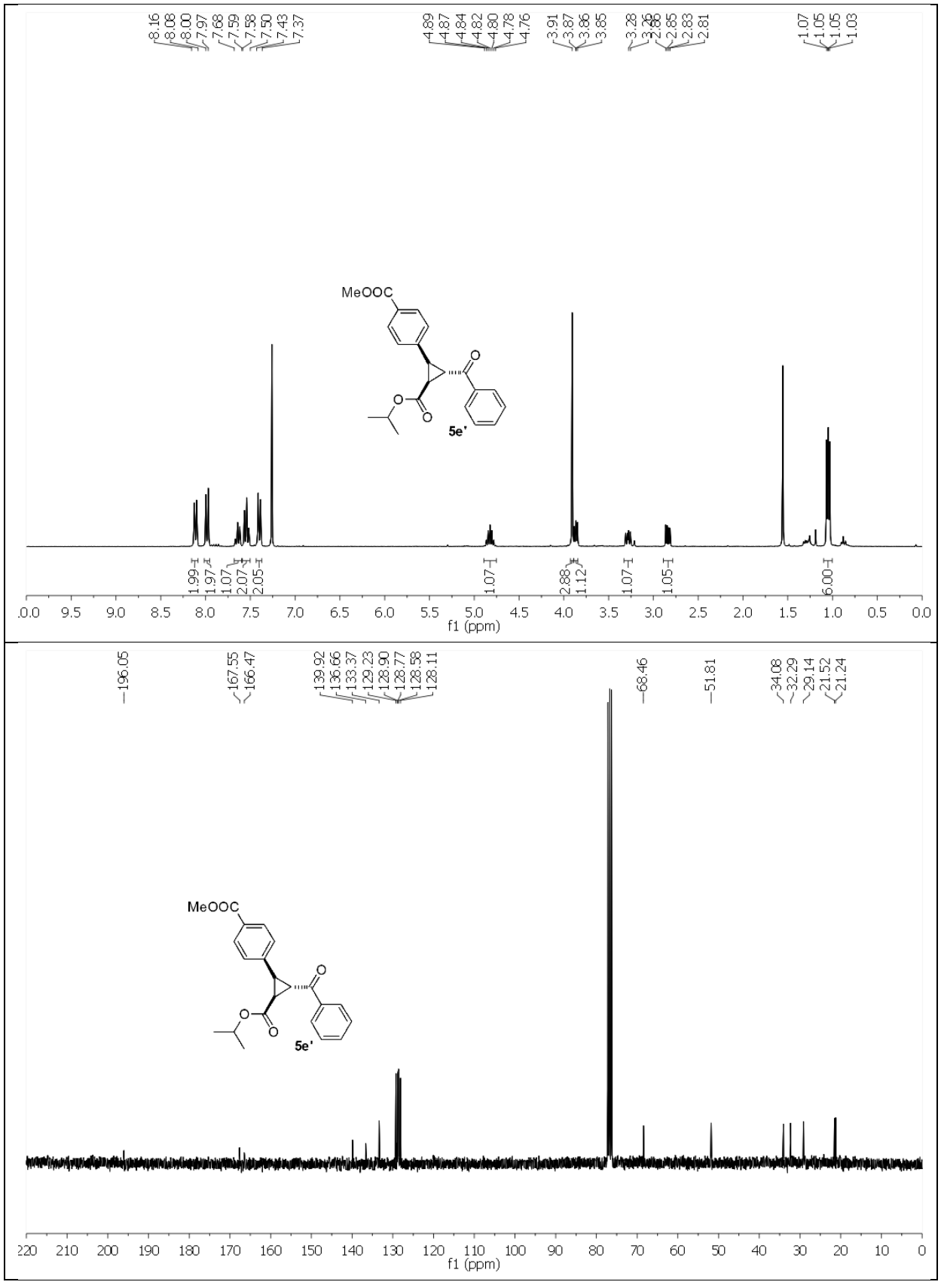
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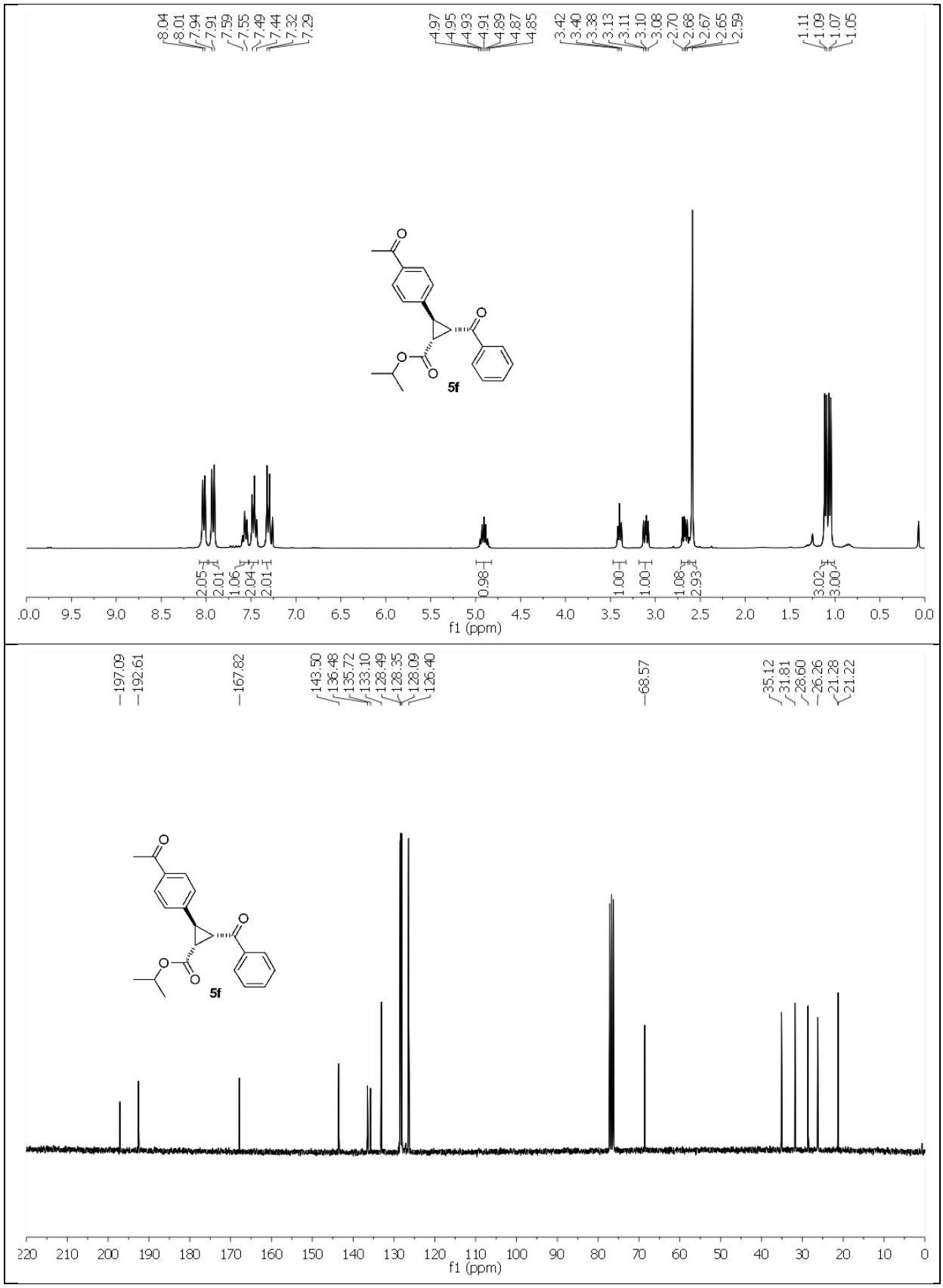
7.97
7.68
7.59
7.58
7.50
7.43
7.37
4.89
4.87
4.84
4.82
4.80
4.78
4.76
3.91
3.87
3.86
3.85
3.28
2.85
2.83
2.81
1.07
1.05
1.05
1.03
MeOOC
O
O
O
5e'
1.99
1.97
1.07
2.07
2.05
1.07
2.88
1.12
1.07
1.05
6.00
f1 (ppm)
196.05
167.55
166.47
139.92
136.66
133.37
129.23
128.90
128.77
128.58
128.11
68.46
51.81
34.08
32.29
29.14
21.52
21.24
MeOOC
O
O
O
5e'
f1 (ppm)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8.01
7.94
7.91
7.59
7.55
7.49
7.44
7.32
7.29
4.97
4.95
4.93
4.91
4.89
4.87
4.85
3.42
3.40
3.38
3.13
3.11
3.10
3.08
2.70
2.68
2.67
2.65
2.59
1.11
1.09
1.07
1.05
5f
2.05
2.01
1.06
2.04
2.01
0.98
1.00
1.00
1.08
2.93
3.02
3.00
f1 (ppm)
197.09
192.61
167.82
143.50
136.48
135.72
133.10
128.49
128.35
128.09
126.40
68.57
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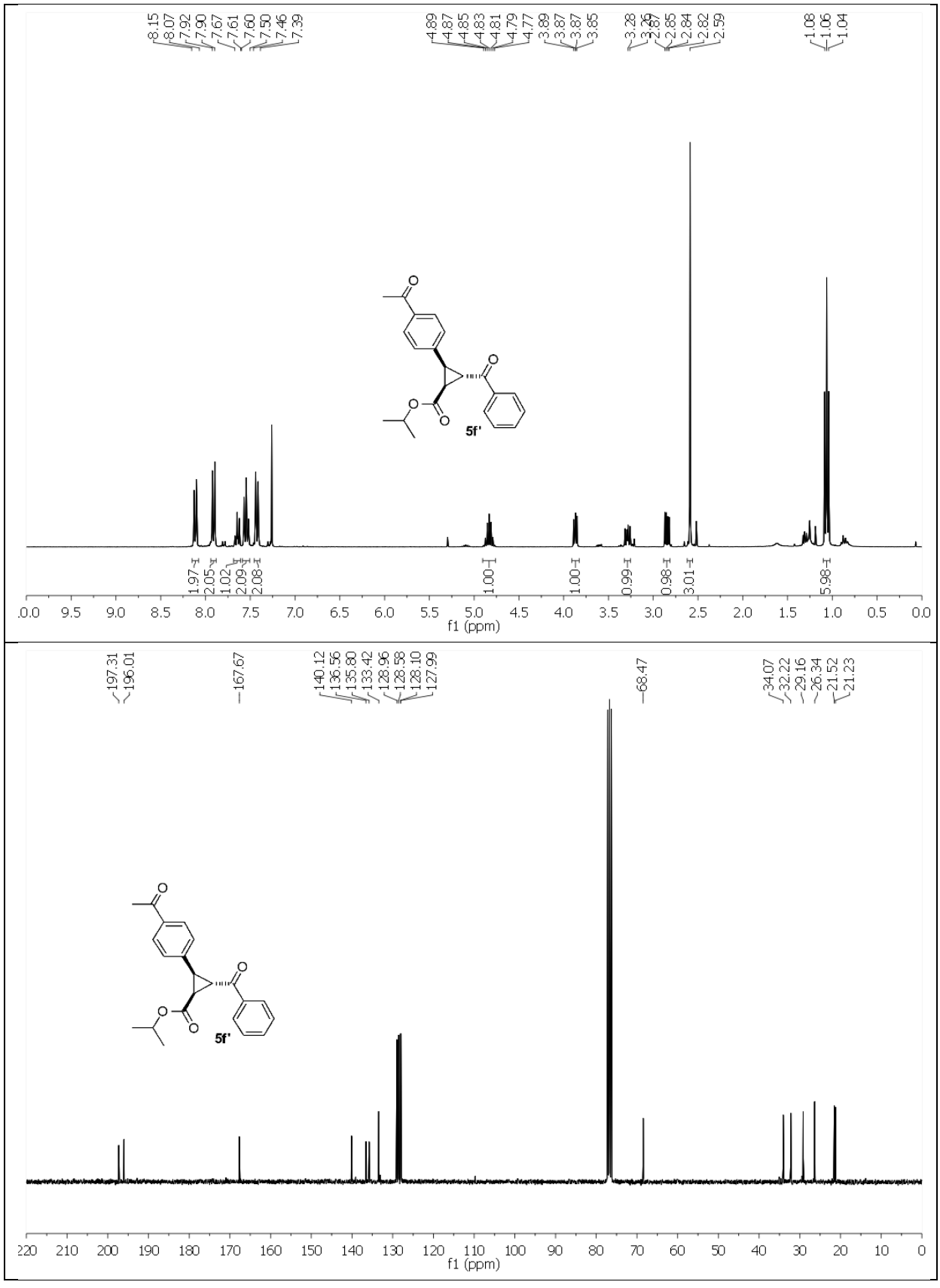
21.28
21.22
5f
f1 (ppm)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8.07
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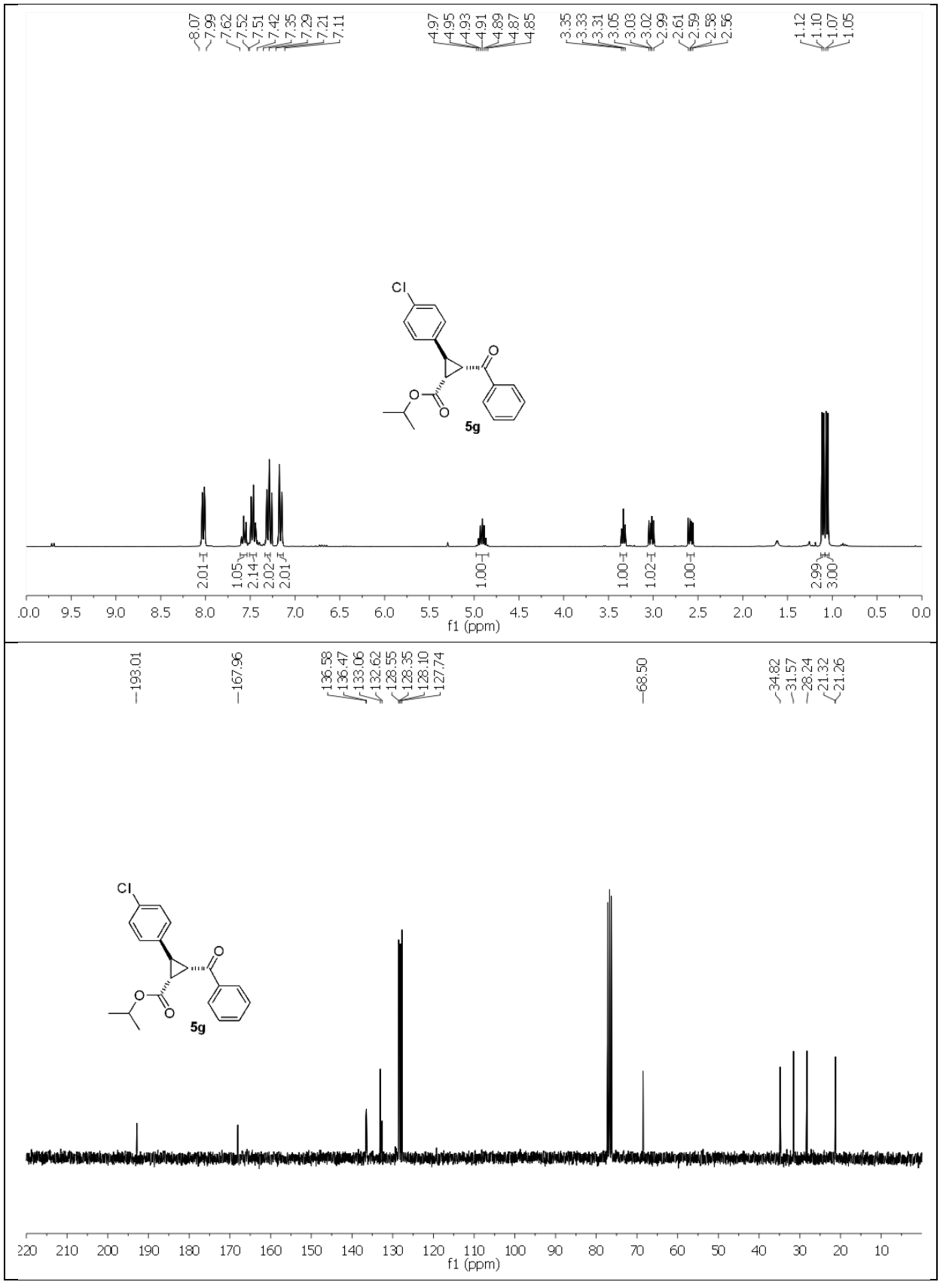
7.60
7.50
7.46
7.39
4.89
4.87
4.85
4.83
4.81
4.79
4.77
3.89
3.87
3.87
3.85
3.28
3.26
2.87
2.85
2.84
2.82
2.59
1.08
1.06
1.04
5f'
1.97
2.05
1.02
2.09
2.08
1.00
1.00
0.99
0.98
3.01
5.98
f1 (ppm)
197.31
196.01
167.67
140.12
136.56
135.80
133.42
128.96
128.58
128.10
127.99
68.47
34.07
32.22
29.16
26.34
21.52
21.23
5f'
f1 (ppm)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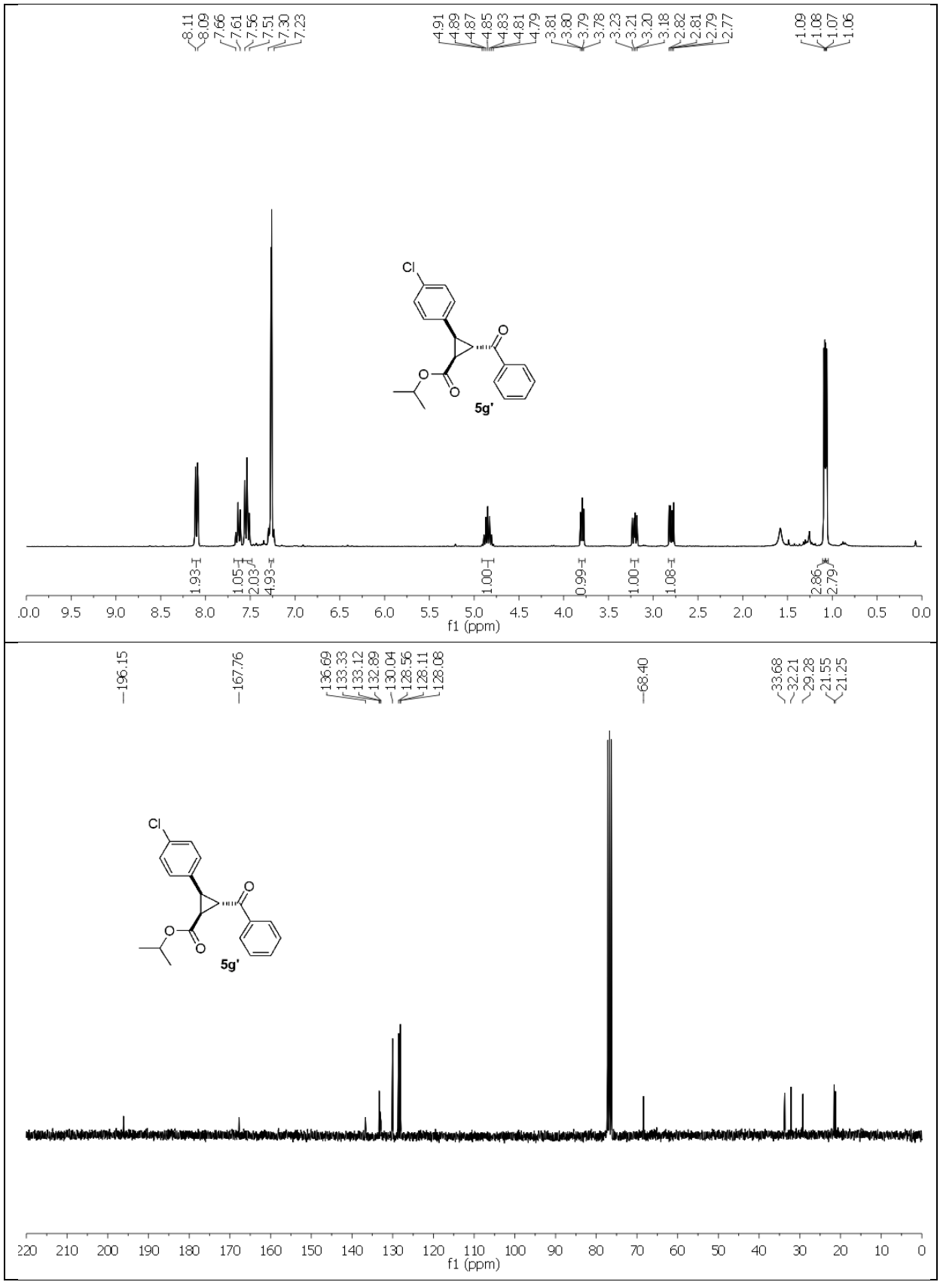
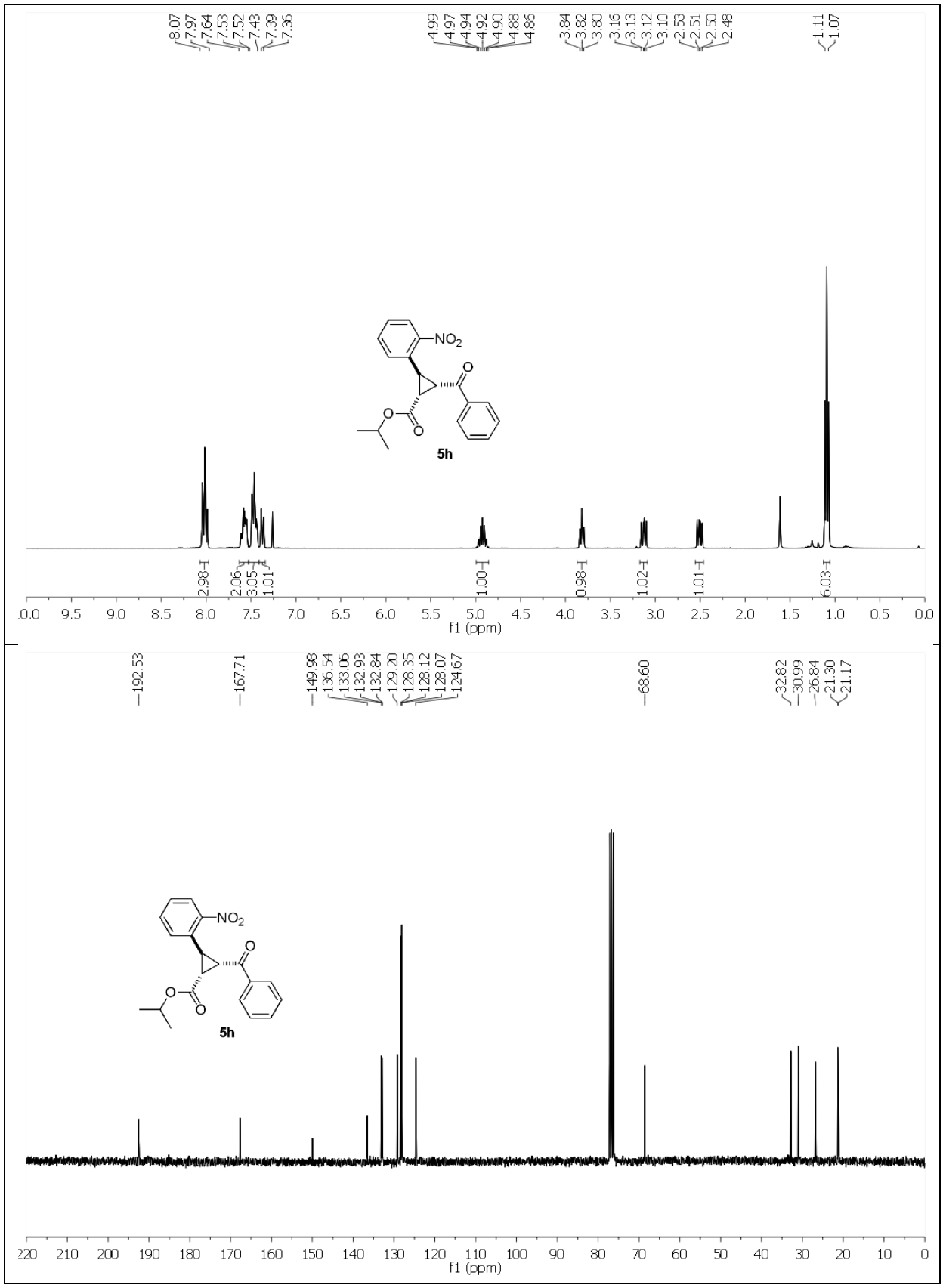
7.51
7.42
7.35
7.29
7.21
7.11
4.97
4.95
4.93
4.91
4.89
4.87
4.85
3.35
3.33
3.31
3.05
3.03
3.02
2.99
2.61
2.59
2.58
2.56
1.12
1.10
1.07
1.05
Cl
O
O
O
5g
2.01
1.05
2.14
2.02
2.01
1.00
1.00
1.02
1.00
2.99
3.00
f1 (ppm)
193.01
167.96
136.58
136.47
133.06
132.62
128.55
128.35
128.10
127.74
68.50
34.82
31.57
28.24
21.32
21.26
Cl
O
O
O
5g
f1 (ppm)

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7.97
7.64
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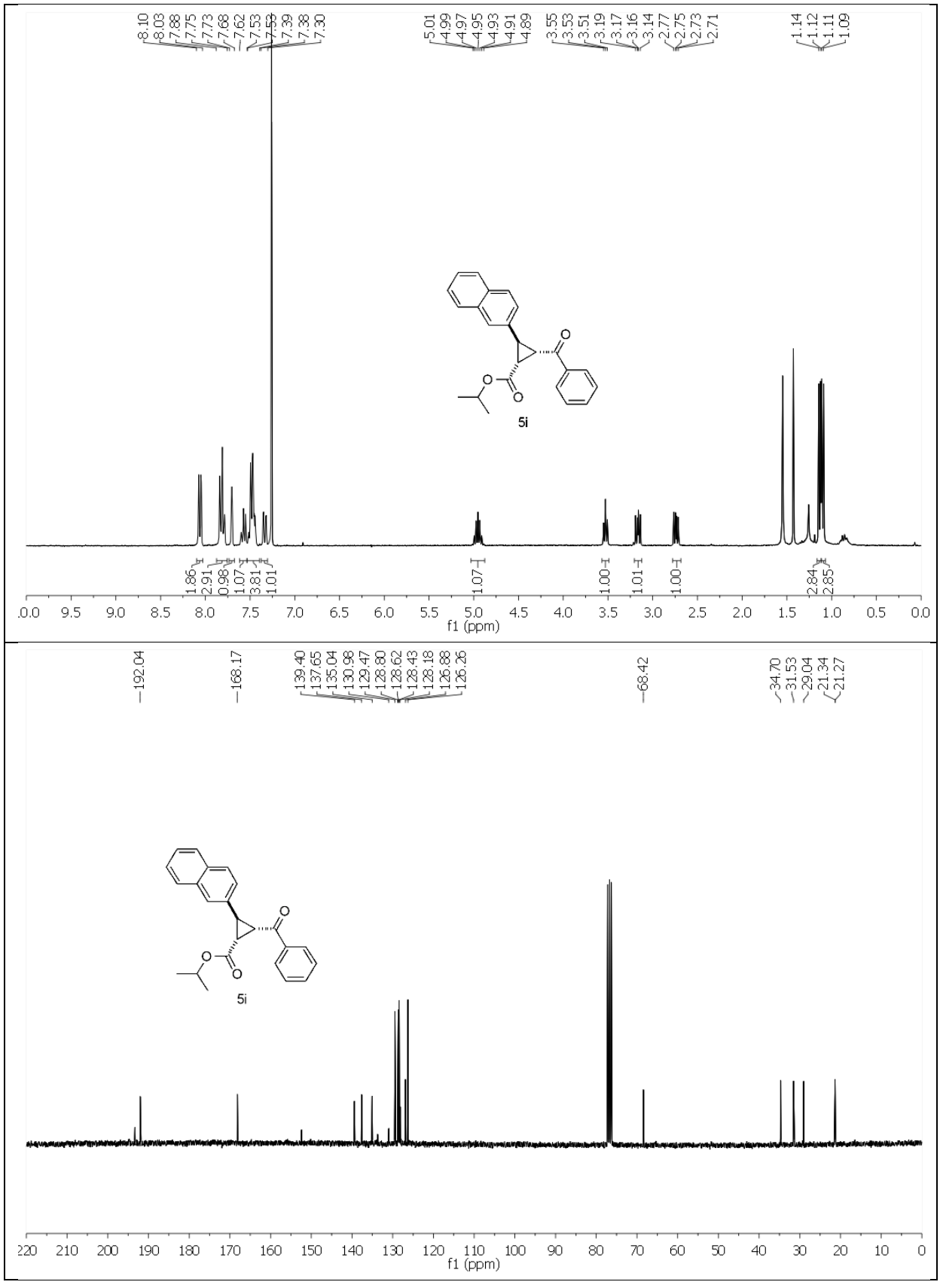
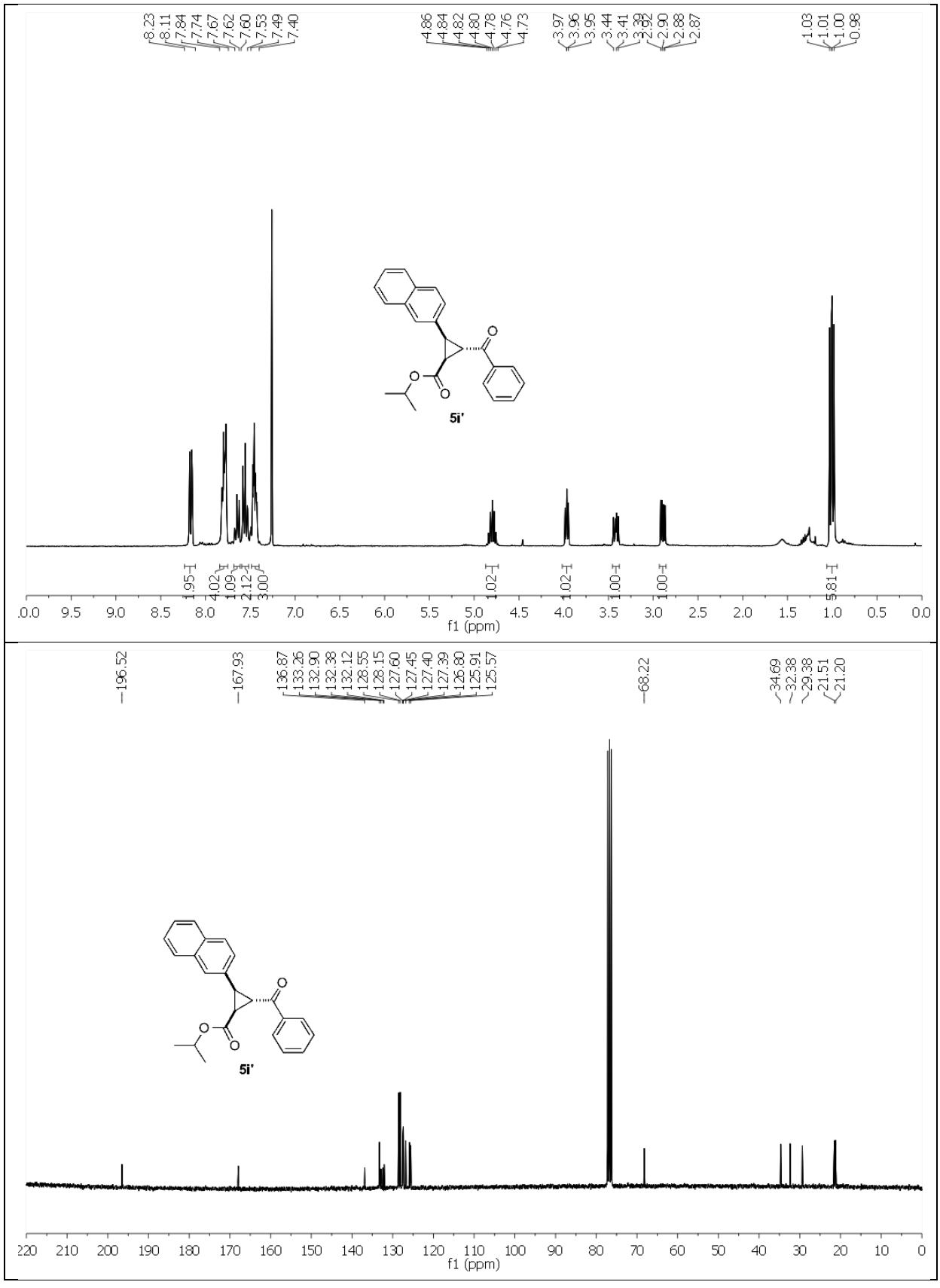
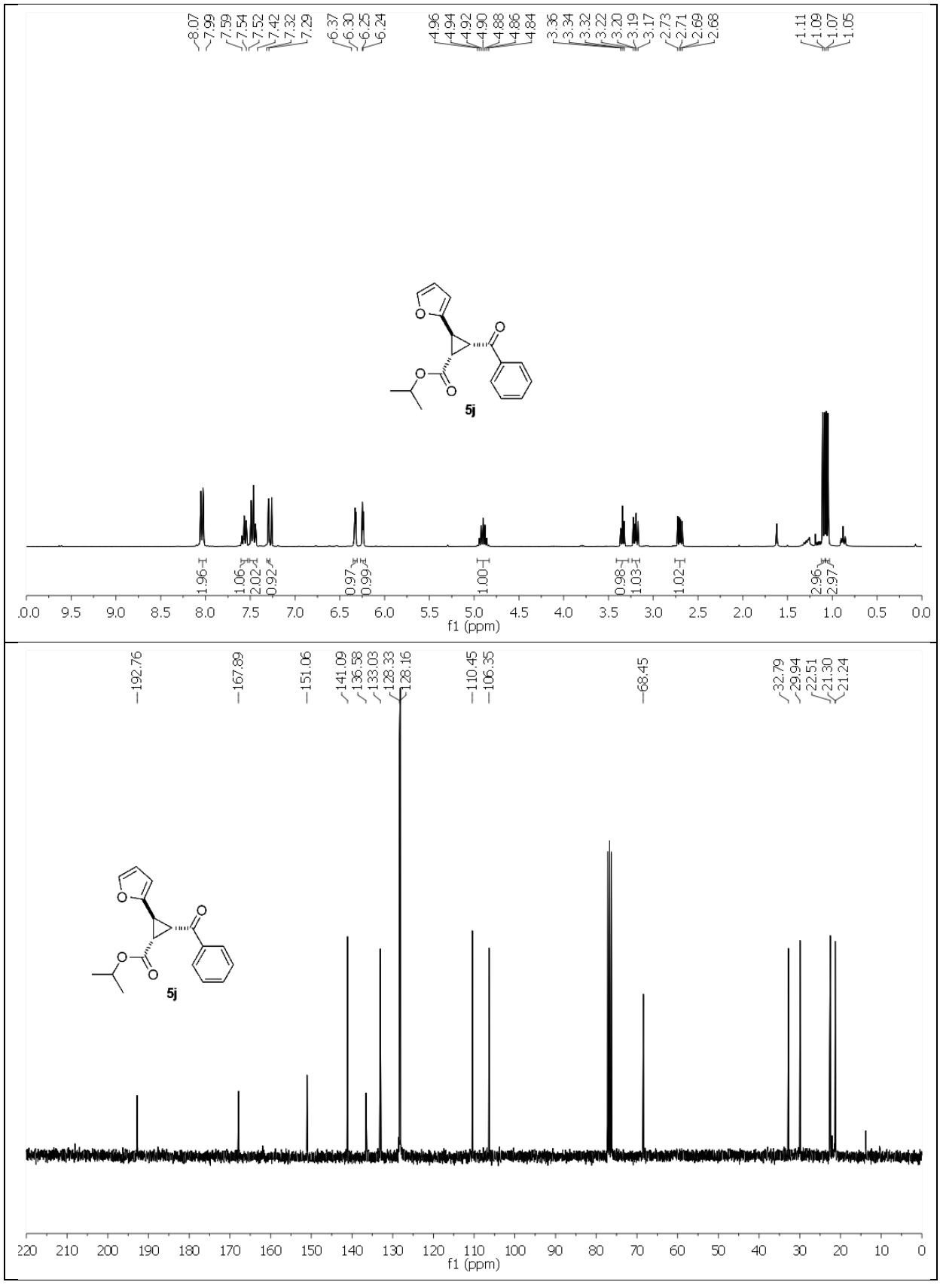
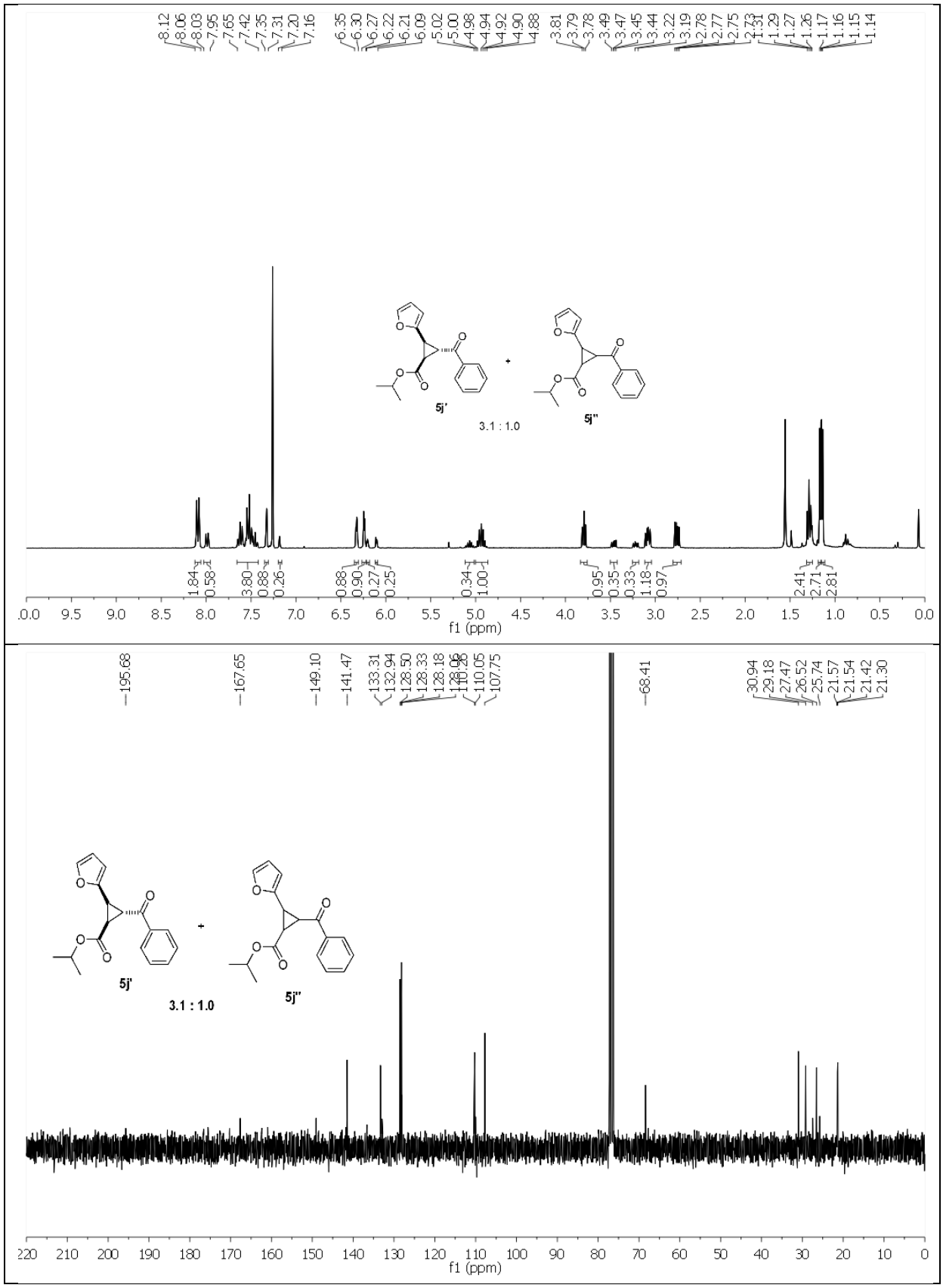
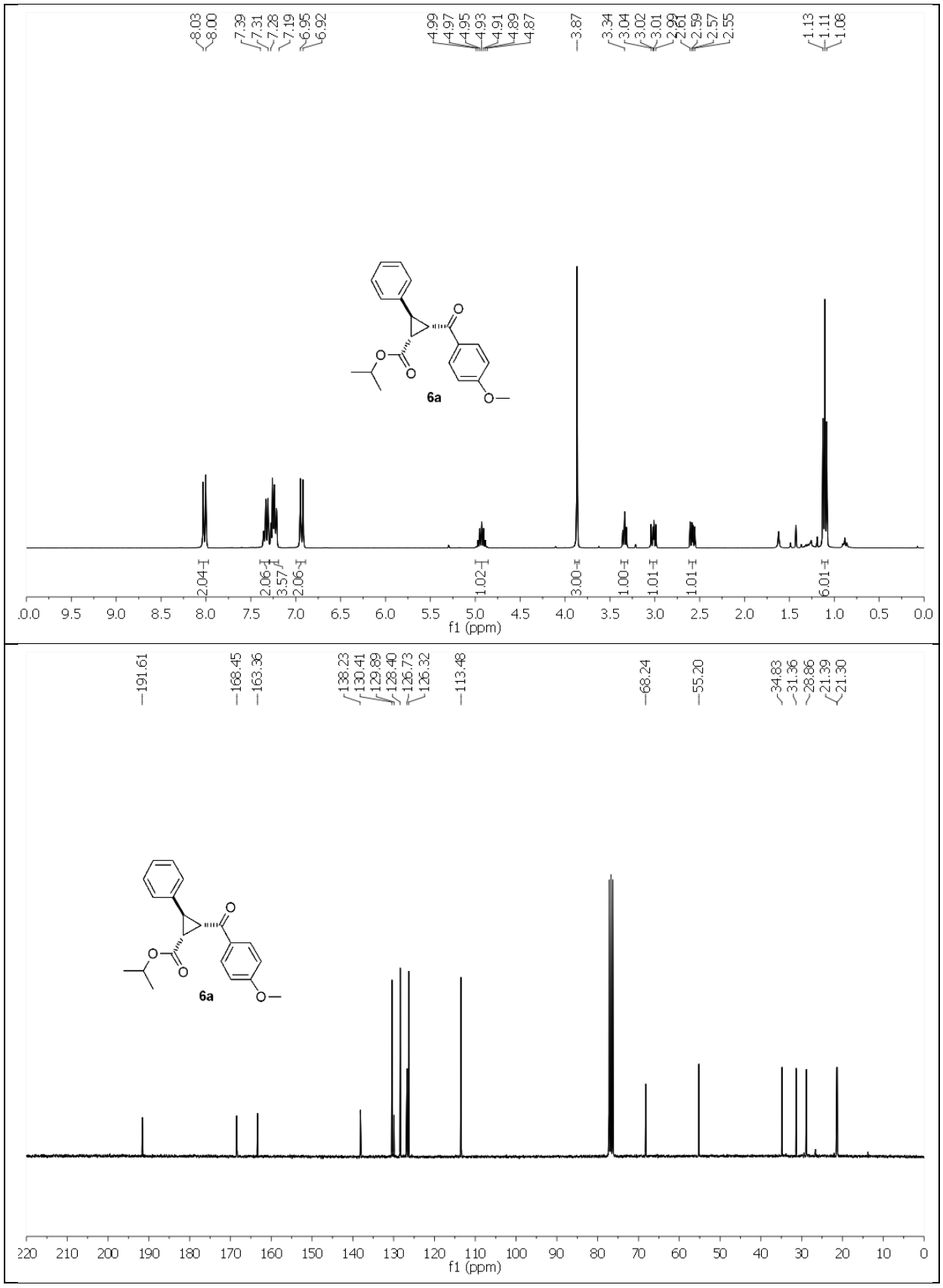
7.43
7.39
7.36
4.99
4.97
4.94
4.92
4.90
4.88
4.86
3.84
3.82
3.80
3.16
3.13
3.12
3.10
2.53
2.51
2.50
2.48
1.11
1.07
NO2
O
O
O
5h
2.98
2.06
3.05
1.01
1.00
0.98
1.02
1.01
6.03
f1 (ppm)
192.53
167.71
149.98
136.54
133.06
132.93
132.84
129.20
128.35
128.12
128.07
124.67
68.60
32.82
30.99
26.84
21.30
21.17
NO2
O
O
O
5h
f1 (ppm)

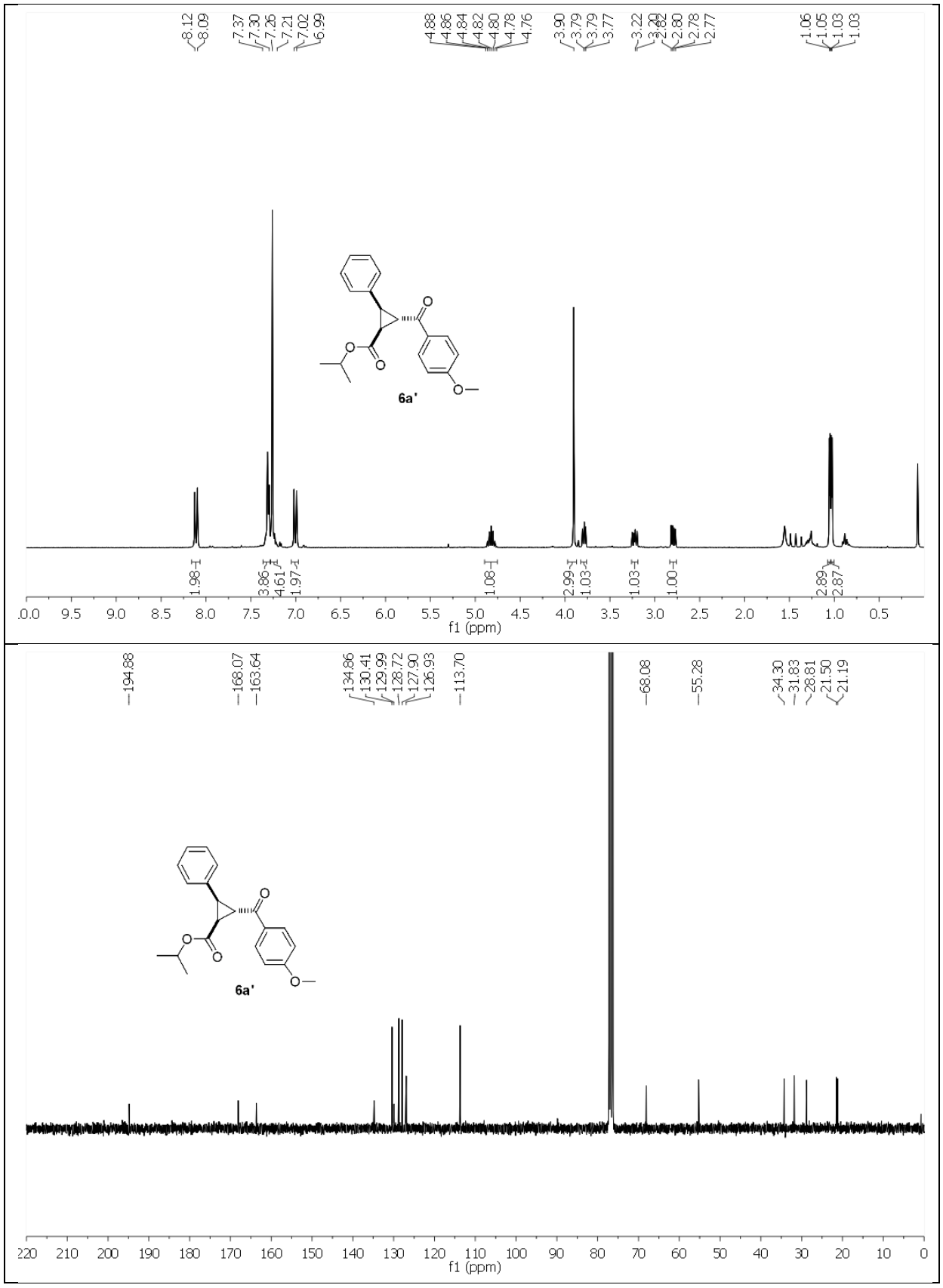

8.10
8.03
7.88
7.75
7.73
7.68
7.62
7.53
7.52
7.39
7.38
7.30
5.01
4.99
4.97
4.95
4.93
4.91
4.89
3.55
3.53
3.51
3.19
3.17
3.16
3.14
2.77
2.75
2.73
2.71
1.14
1.12
1.11
1.09
1.86
2.91
0.98
1.07
3.81
1.01
1.07
1.00
1.01
1.00
2.84
2.85
f1 (ppm)
5i
192.04
168.17
139.40
137.65
135.04
130.98
129.47
128.80
128.62
128.43
128.18
126.88
126.26
68.42
34.70
31.53
29.04
21.34
21.27
f1 (ppm)
5i

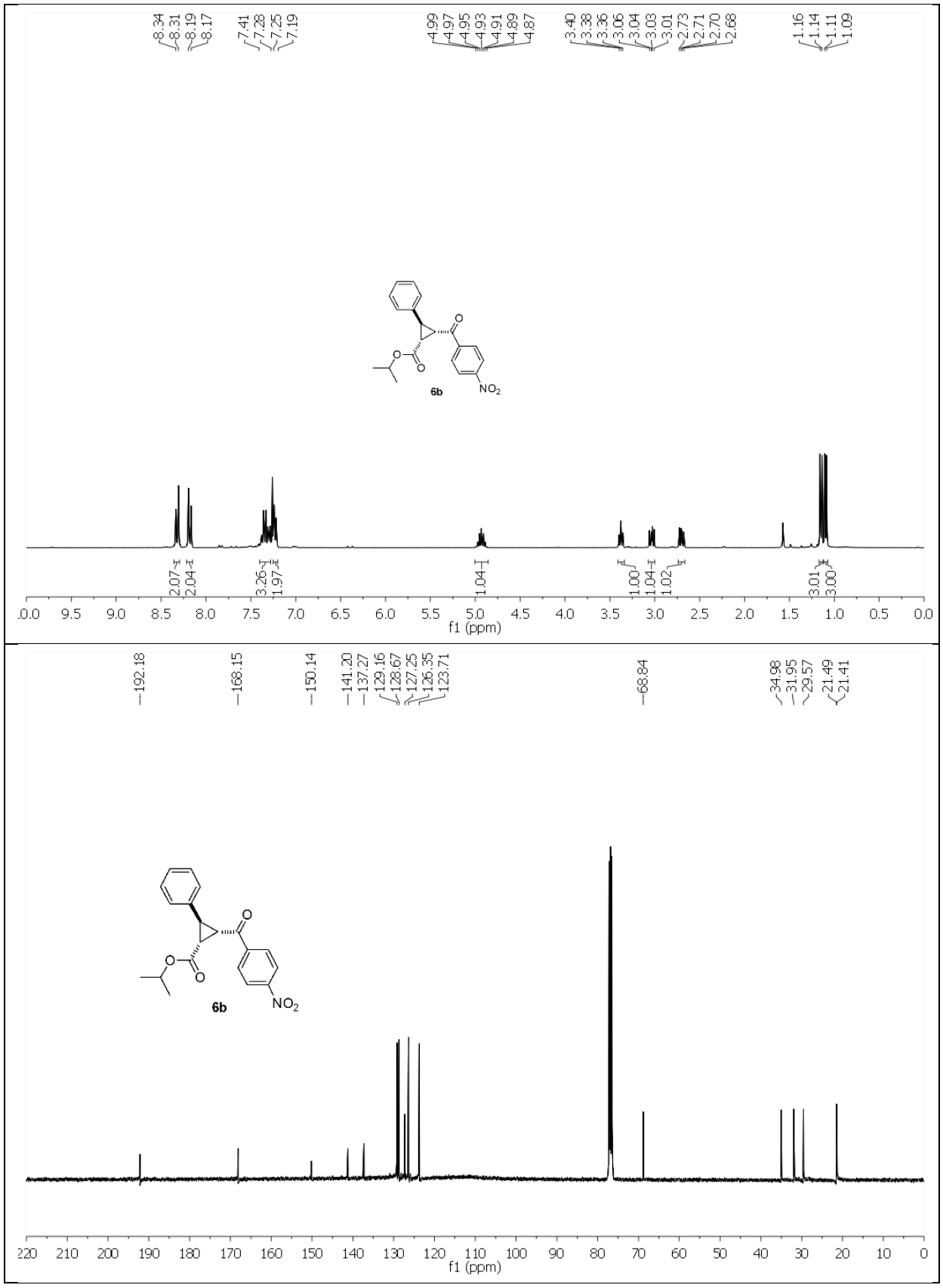

8.23
8.11
7.84
7.74
7.67
7.62
7.60
7.53
7.49
7.40
4.86
4.84
4.82
4.80
4.78
4.76
4.73
3.97
3.96
3.95
3.44
3.41
3.39
3.92
2.90
2.88
2.87
1.03
1.01
1.00
0.98
5i'
1.95
4.02
1.09
2.12
3.00
1.02
1.02
1.00
1.00
5.81
f1 (ppm)
196.52
167.93
136.87
133.26
132.90
132.38
132.12
128.55
128.15
127.60
127.45
127.40
127.39
126.80
125.91
125.57
68.22
34.69
32.38
29.38
21.51
21.20
5i'
f1 (ppm)


8.07
7.99
7.59
7.54
7.52
7.42
7.32
7.29
6.37
6.30
6.25
6.24
4.96
4.94
4.92
4.90
4.88
4.86
4.84
3.36
3.34
3.32
3.22
3.20
3.19
3.17
2.73
2.71
2.69
2.68
1.11
1.09
1.07
1.05
5j
1.96
1.06
2.02
0.92
0.97
0.99
1.00
0.98
1.03
1.02
2.96
2.97
f1 (ppm)
192.76
167.89
151.06
141.09
136.58
133.03
128.33
128.16
110.45
106.35
68.45
32.79
29.94
22.51
21.30
21.24
5j
f1 (ppm)


8.12
8.06
8.03
7.95
7.65
7.42
7.35
7.31
7.20
7.16
6.35
6.30
6.27
6.22
6.21
6.09
5.02
5.00
4.98
4.94
4.92
4.90
4.88
3.81
3.79
3.78
3.49
3.47
3.45
3.44
3.22
3.19
2.78
2.77
2.75
2.73
1.31
1.29
1.27
1.26
1.17
1.16
1.15
1.14
5j'
3.1 : 1.0
5j''
1.84
0.58
3.80
0.88
0.26
0.88
0.90
0.27
0.25
0.34
1.00
0.95
0.35
0.33
1.18
0.97
2.41
2.71
2.81
f1 (ppm)
195.68
167.65
149.10
141.47
133.31
132.94
128.50
128.33
128.18
128.06
110.26
110.05
107.75
68.41
30.94
29.18
27.47
26.52
25.74
21.57
21.54
21.42
21.30
5j'
3.1 : 1.0
5j''
f1 (ppm)


8.03
8.00
7.39
7.31
7.28
7.19
6.95
6.92
4.99
4.97
4.95
4.93
4.91
4.89
4.87
3.87
3.34
3.04
3.02
3.01
2.99
2.61
2.59
2.57
2.55
1.13
1.11
1.08
6a
2.04
2.06
3.57
2.06
1.02
3.00
1.00
1.01
1.01
6.01
f1 (ppm)
191.61
168.45
163.36
138.23
130.41
129.89
128.40
126.73
126.32
113.48
68.24
55.20
34.83
31.36
28.86
21.39
21.30
6a
f1 (ppm)


8.12
8.09
7.37
7.30
7.26
7.21
7.02
6.99
4.88
4.86
4.84
4.82
4.80
4.78
4.76
3.90
3.79
3.79
3.77
3.22
3.20
2.80
2.78
2.77
1.06
1.05
1.03
1.03
6a'
1.98
3.86
4.61
1.97
1.08
2.99
1.03
1.03
1.00
2.89
2.87
f1 (ppm)
194.88
168.07
163.64
134.86
130.41
129.99
128.72
127.90
126.93
113.70
68.08
55.28
34.30
31.83
28.81
21.50
21.19
6a'
f1 (ppm)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8.31
8.19
8.17
7.41
7.28
7.25
7.19
4.99
4.97
4.95
4.93
4.91
4.89
4.87
3.40
3.38
3.36
3.06
3.04
3.03
3.01
2.73
2.71
2.70
2.68
1.16
1.14
1.11
1.09
6b
NO2
2.07
2.04
3.26
1.97
1.04
1.00
1.04
1.02
3.01
3.00
f1 (ppm)
192.18
168.15
150.14
141.20
137.27
129.16
128.67
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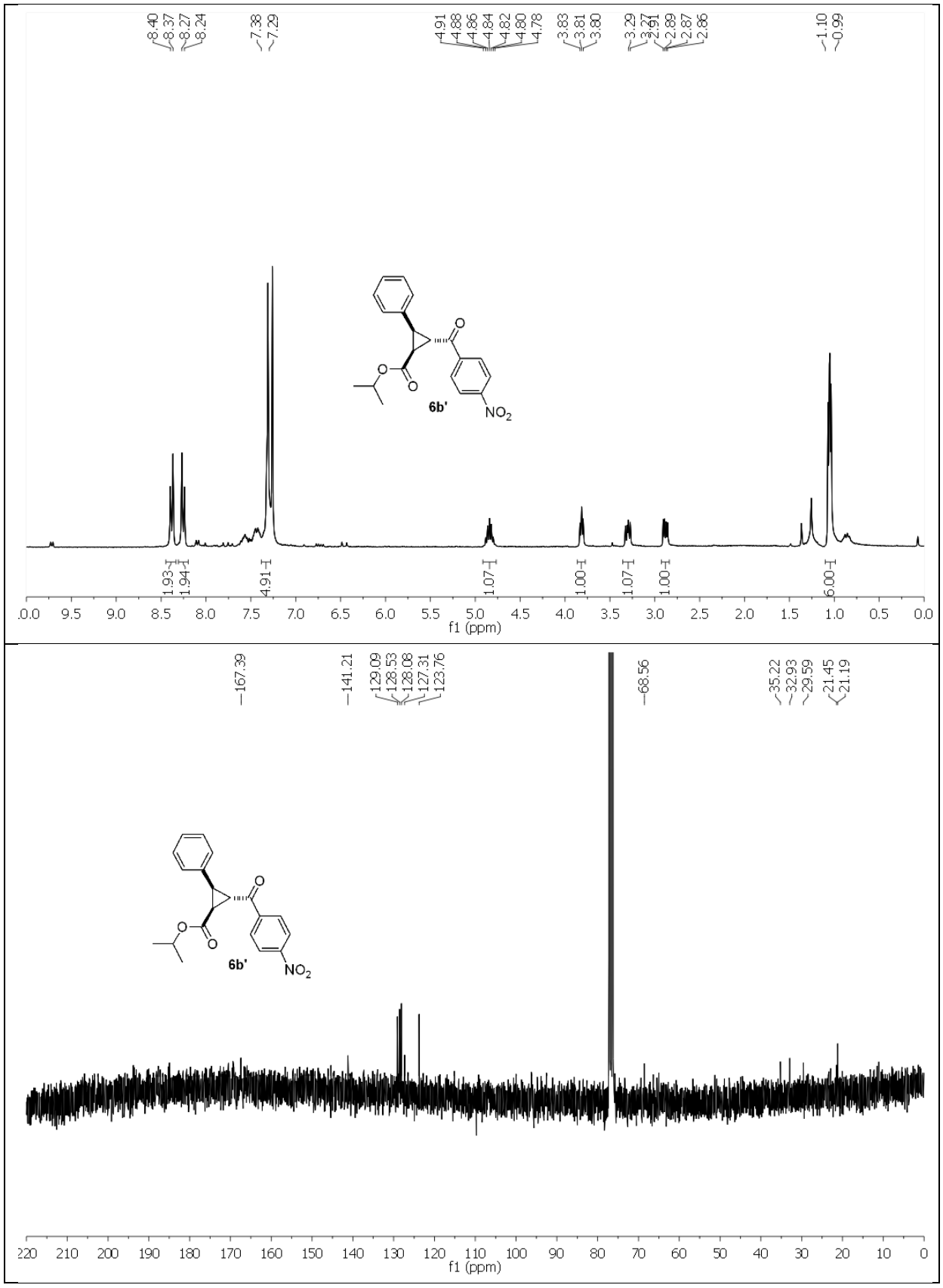
126.35
123.71
68.84
34.98
31.95
29.57
21.49
21.41
6b
NO2
f1 (ppm)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8.37
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8.24
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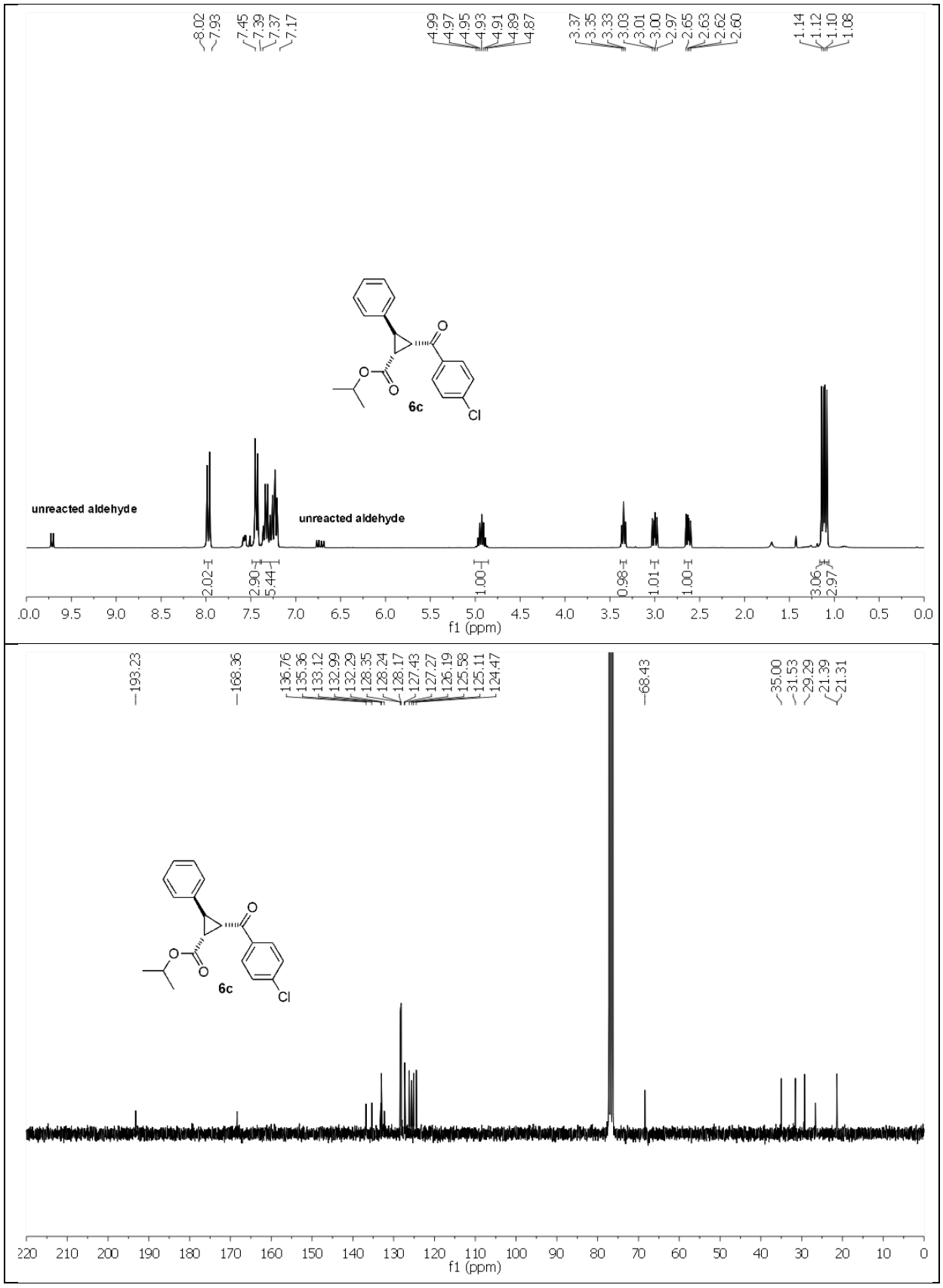
7.29
4.91
4.88
4.86
4.84
4.82
4.80
4.78
3.83
3.81
3.80
3.29
3.27
2.91
2.89
2.87
2.86
1.10
0.99
6b'
NO2
1.93
1.94
4.91
1.07
1.00
1.07
1.00
6.00
f1 (ppm)
167.39
141.21
129.09
128.53
128.08
127.31
123.76
68.56
35.22
32.93
29.59
21.45
21.19
6b'
NO2
f1 (ppm)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7.45
7.39
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7.17
4.99
4.97
4.95
4.93
4.91
4.89
4.87
3.37
3.35
3.33
3.03
3.01
3.00
2.97
2.65
2.63
2.62
2.60
1.14
1.12
1.10
1.08
6c
Cl
unreacted aldehyde
unreacted aldehyde
2.02
2.90
5.44
1.00
0.98
1.01
1.00
3.06
2.97
f1 (ppm)
193.23
168.36
136.76
135.36
133.12
132.99
132.29
128.35
128.24
128.17
127.43
127.27
126.19
125.58
125.11
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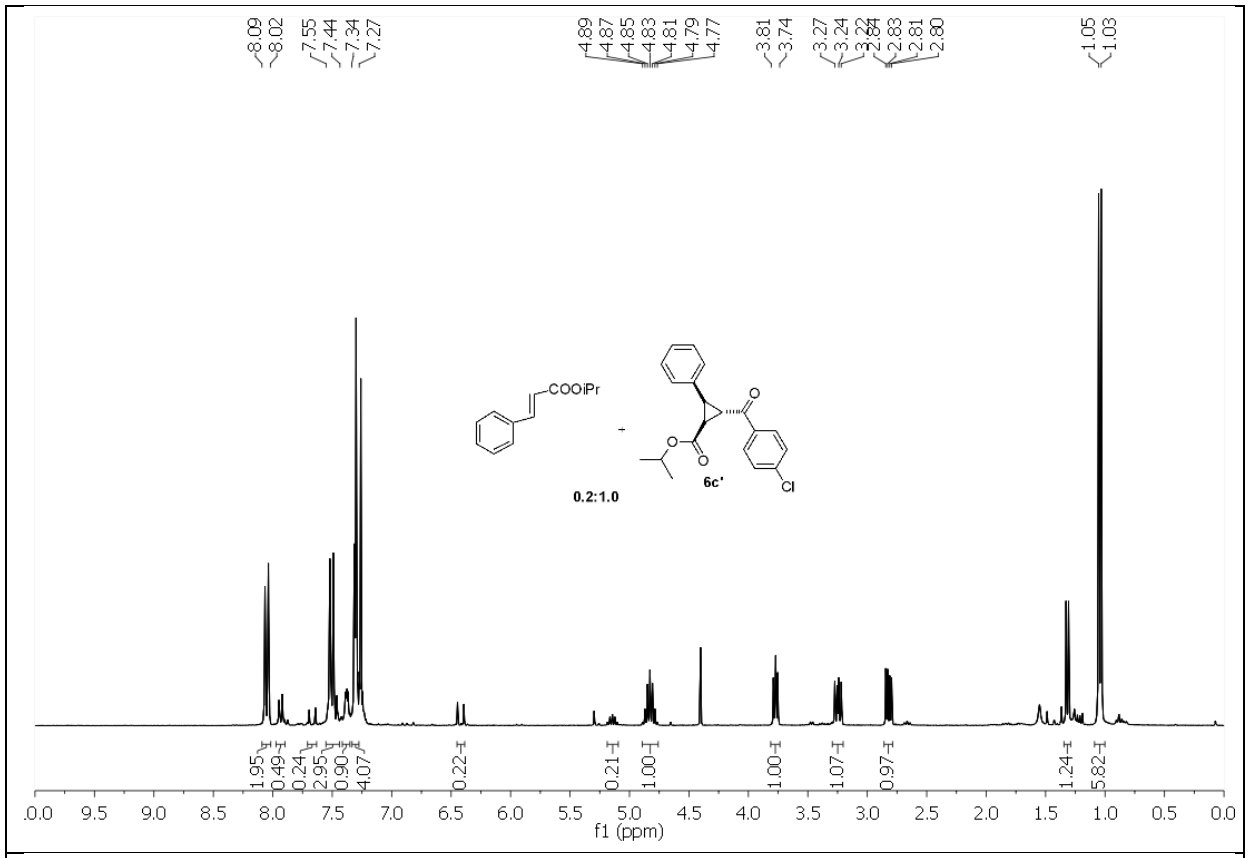
29.29
21.39
21.31
6c
Cl
f1 (ppm)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7.27
4.89
4.87
4.85
4.83
4.81
4.79
4.77
3.81
3.74
3.27
3.24
3.22
2.83
2.81
2.80
1.05
1.03
COOiPr
O
O
O
Cl
6c'
0.2:1.0
1.95
0.49
0.24
2.95
0.90
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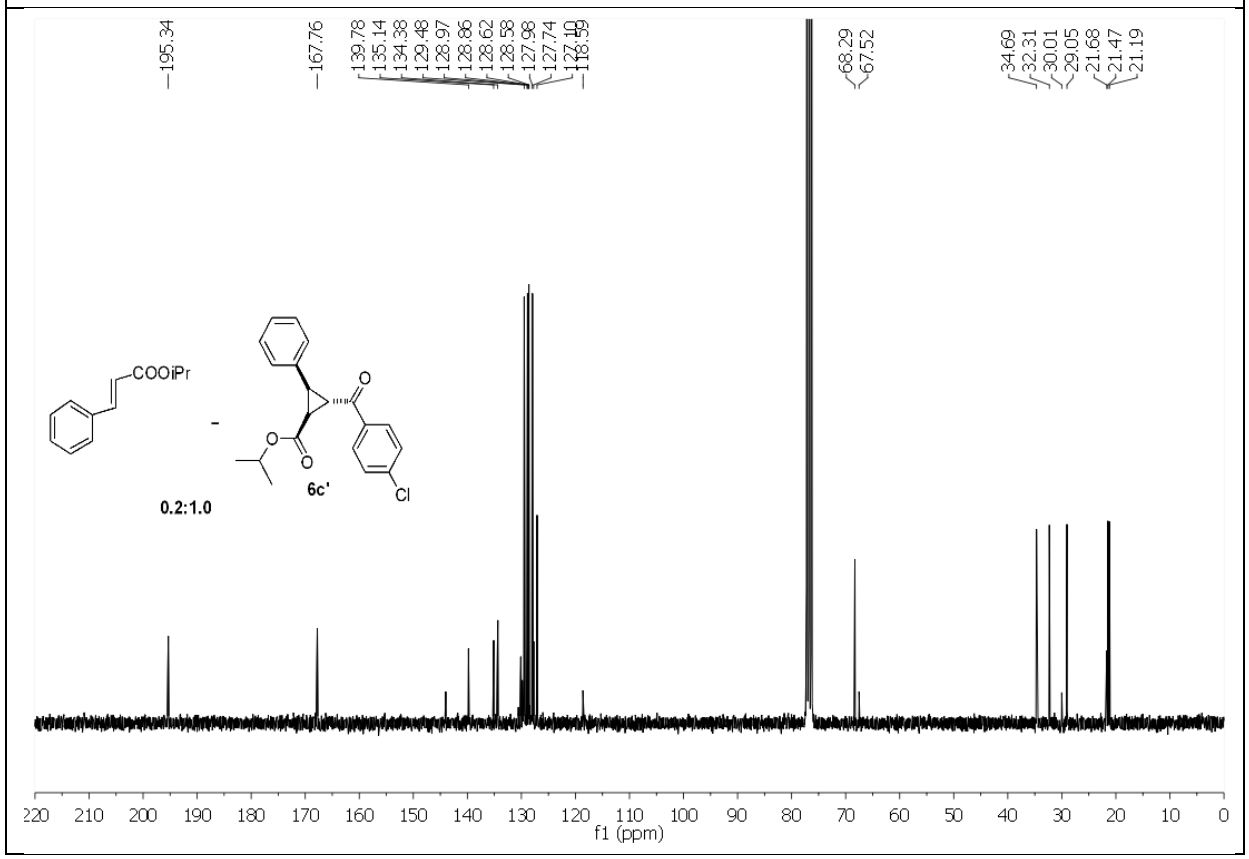
0.22
0.21
1.00
1.00
1.07
0.97
1.24
5.82
f1 (ppm)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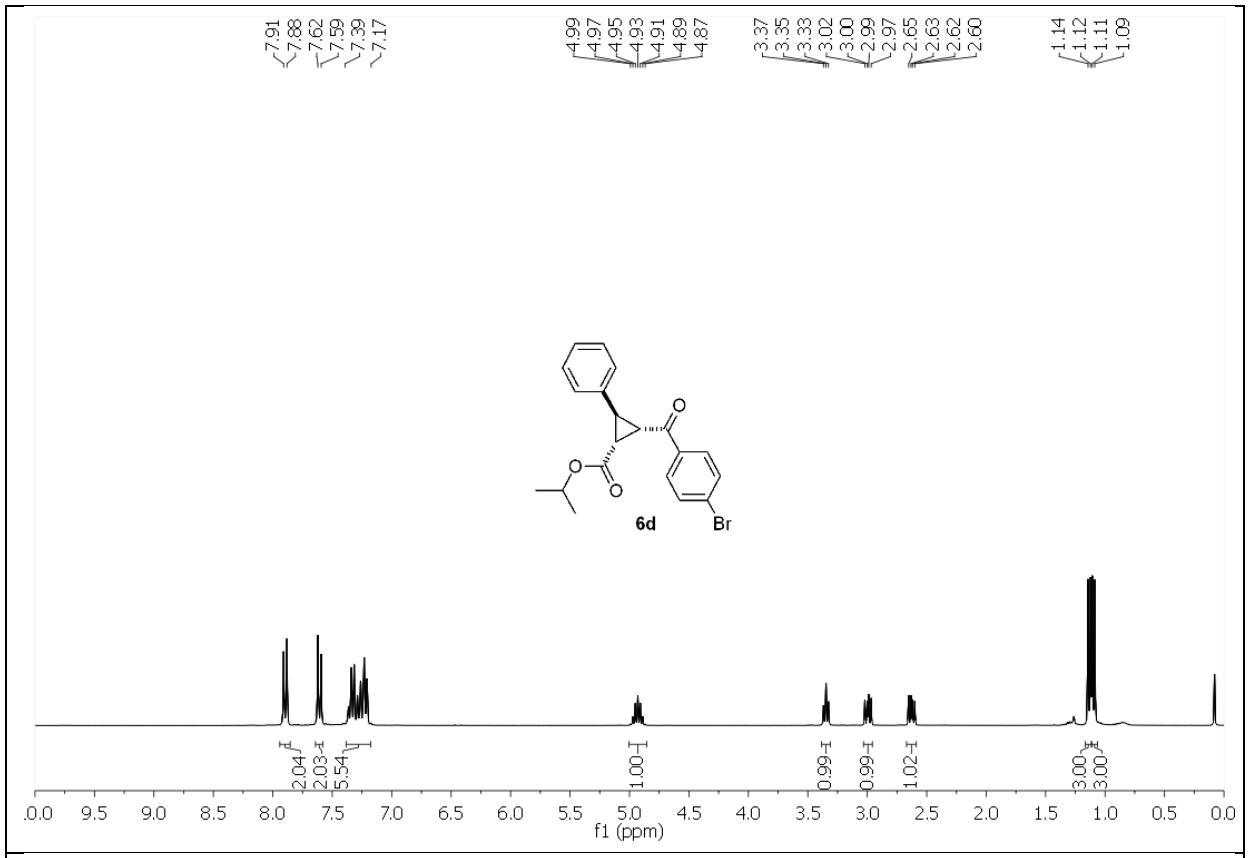
167.76
139.78
135.14
134.38
129.48
128.97
128.86
128.62
128.58
127.98
127.74
68.29
67.52
34.69
32.31
30.01
29.05
21.68
21.47
21.19
COOiPr
O
O
O
Cl
6c'
0.2:1.0
f1 (ppm)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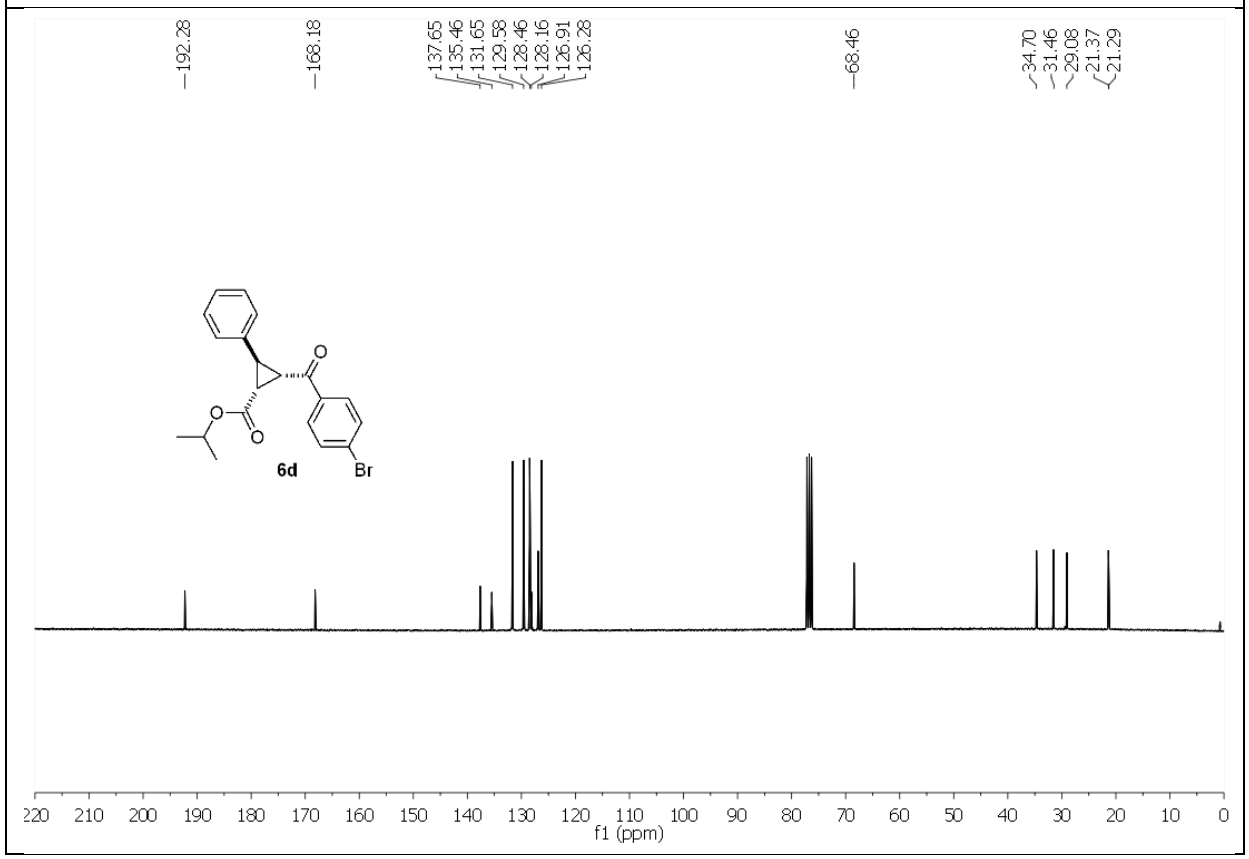
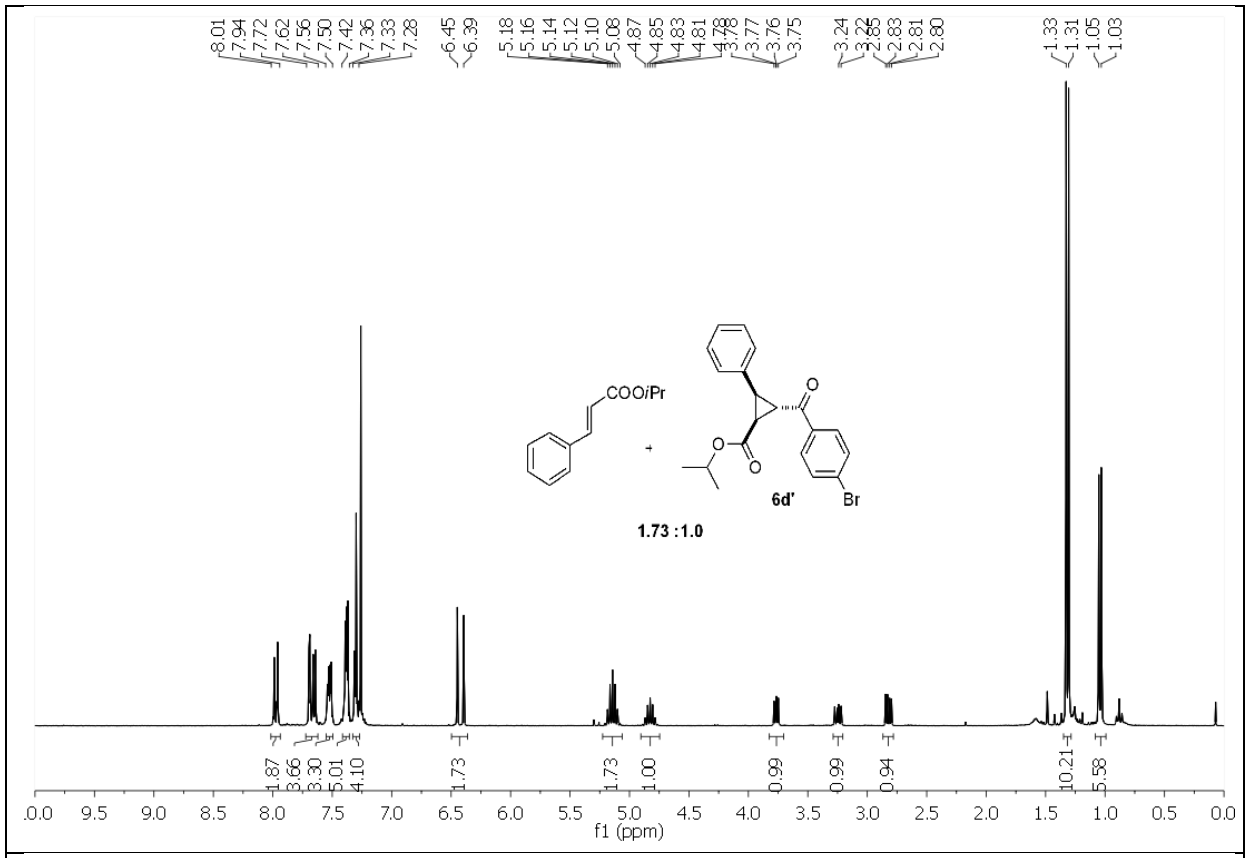
7.17
4.99
4.97
4.95
4.93
4.91
4.89
4.87
3.37
3.35
3.33
3.02
3.00
2.99
2.97
2.65
2.63
2.62
2.60
1.14
1.12
1.11
1.09
6d
Br
2.04
2.03
5.54
1.00
0.99
0.99
1.02
3.00
3.00
f1 (ppm)


192.28
168.18
137.65
135.46
131.65
129.58
128.46
128.16
126.91
126.28
68.46
34.70
31.46
29.08
21.37
21.29
6d
Br
f1 (ppm)


8.01
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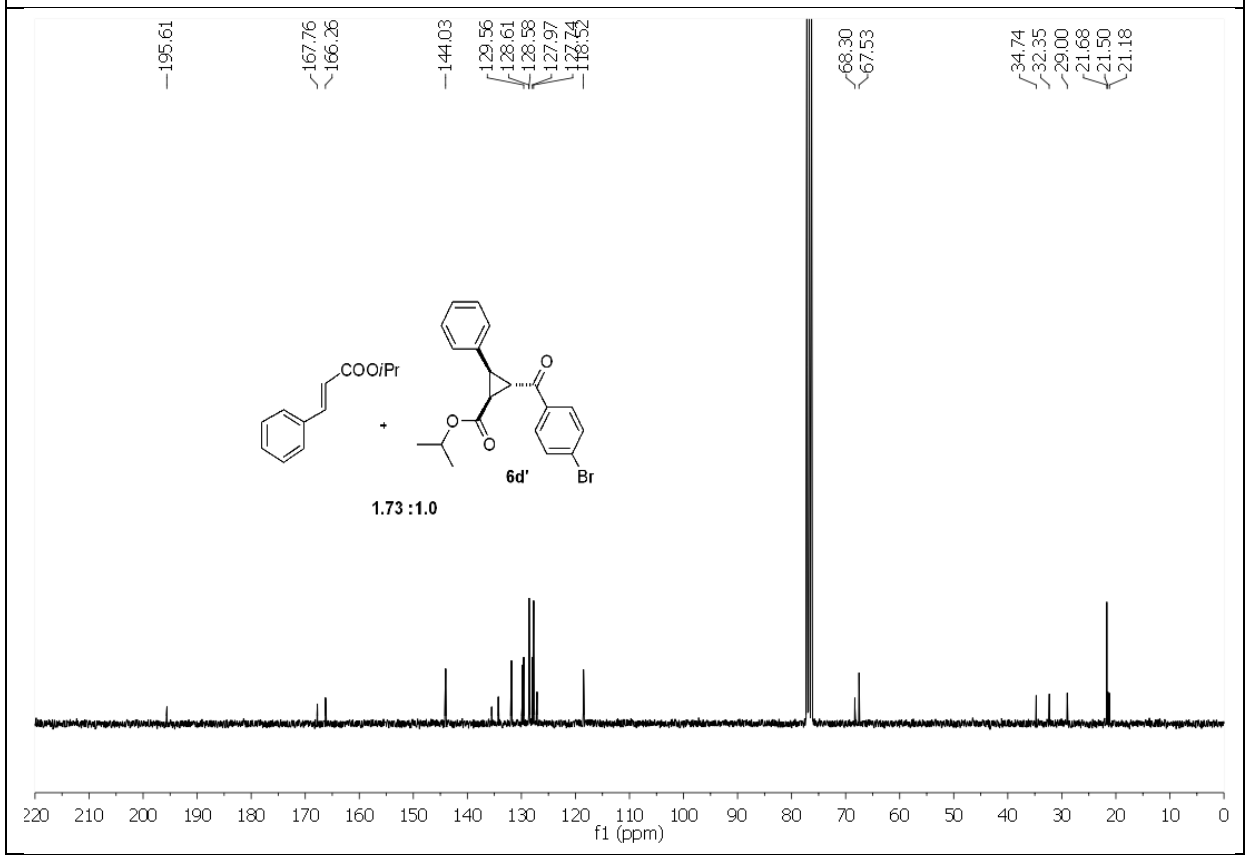
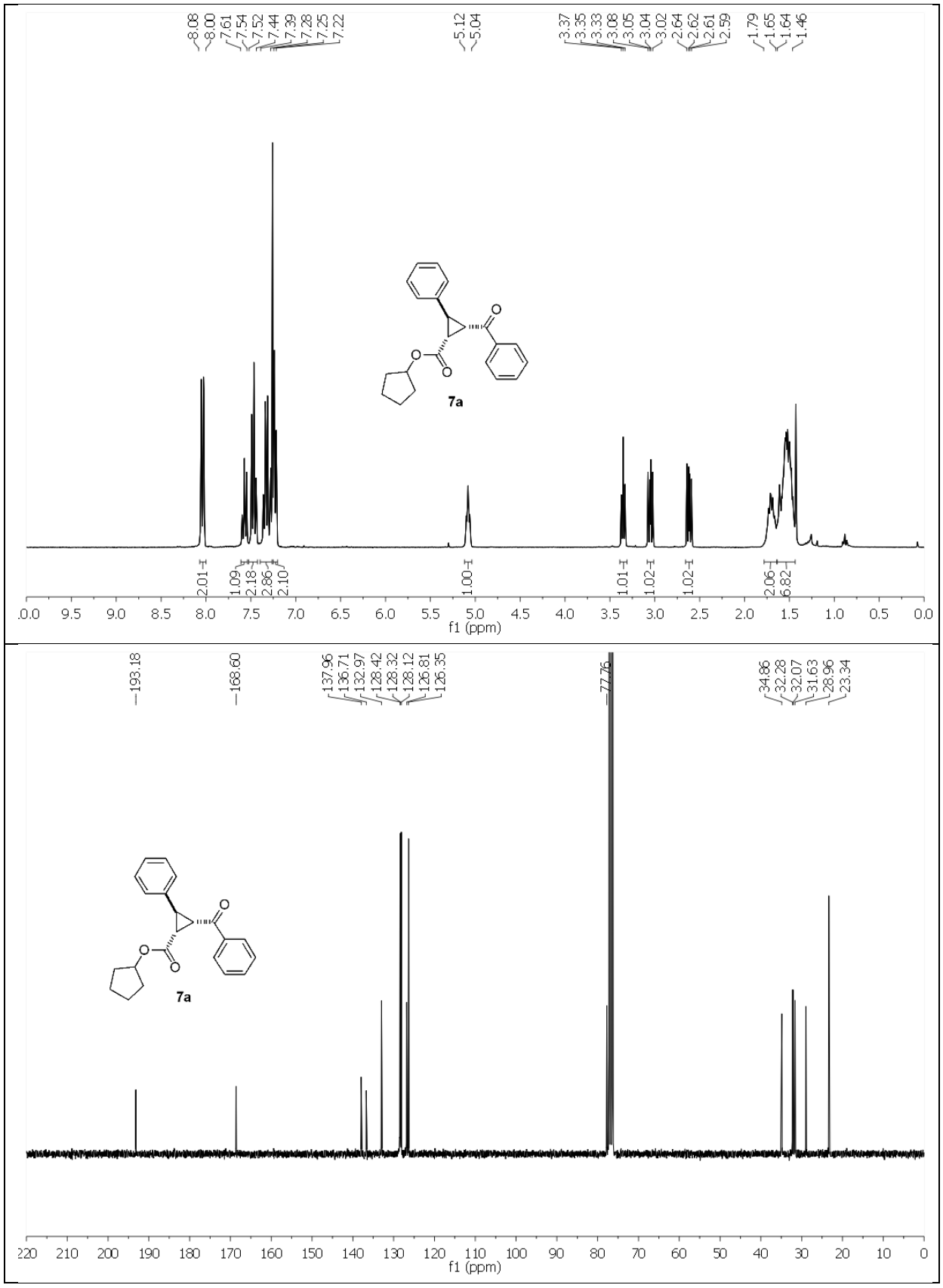
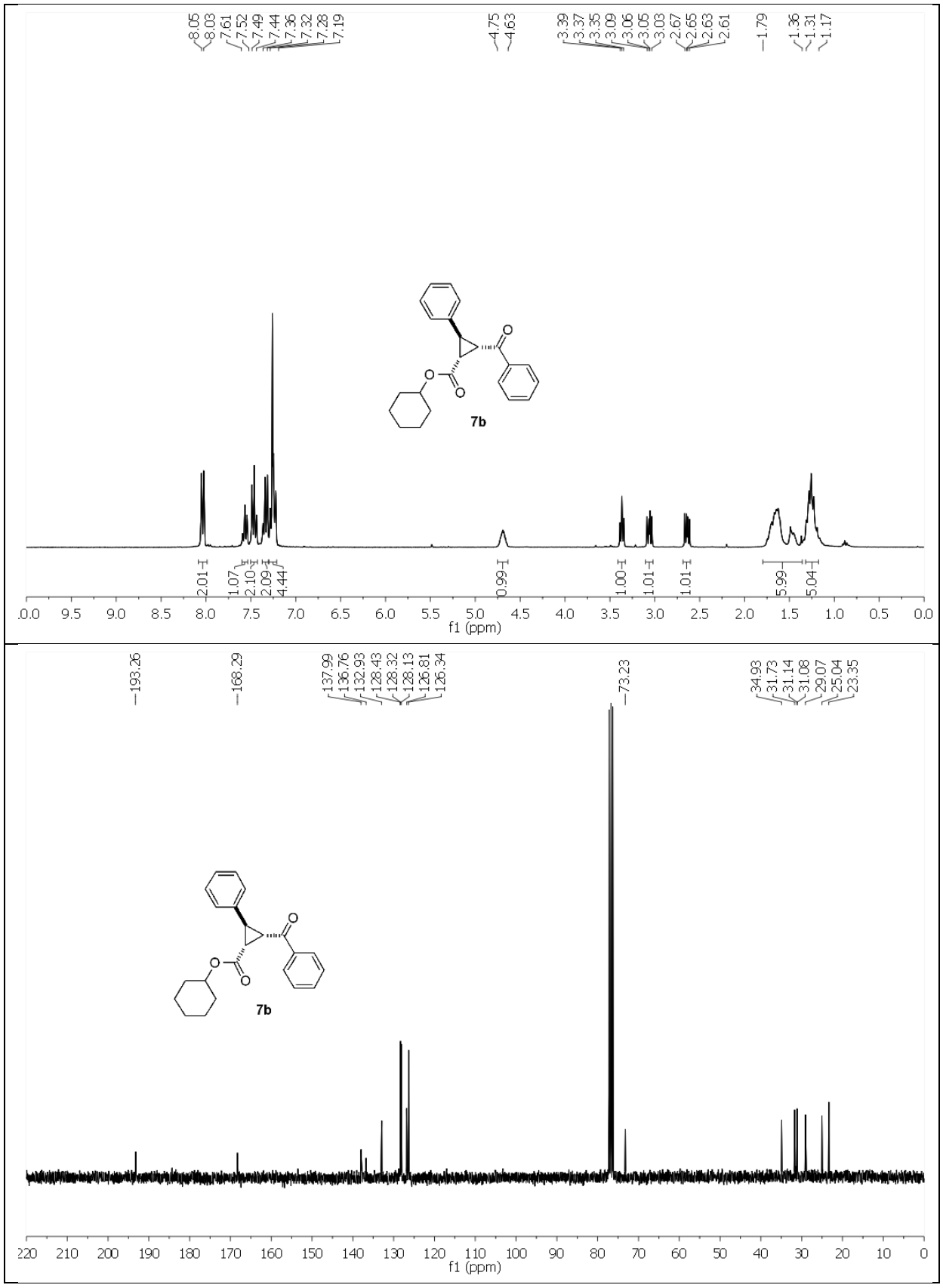
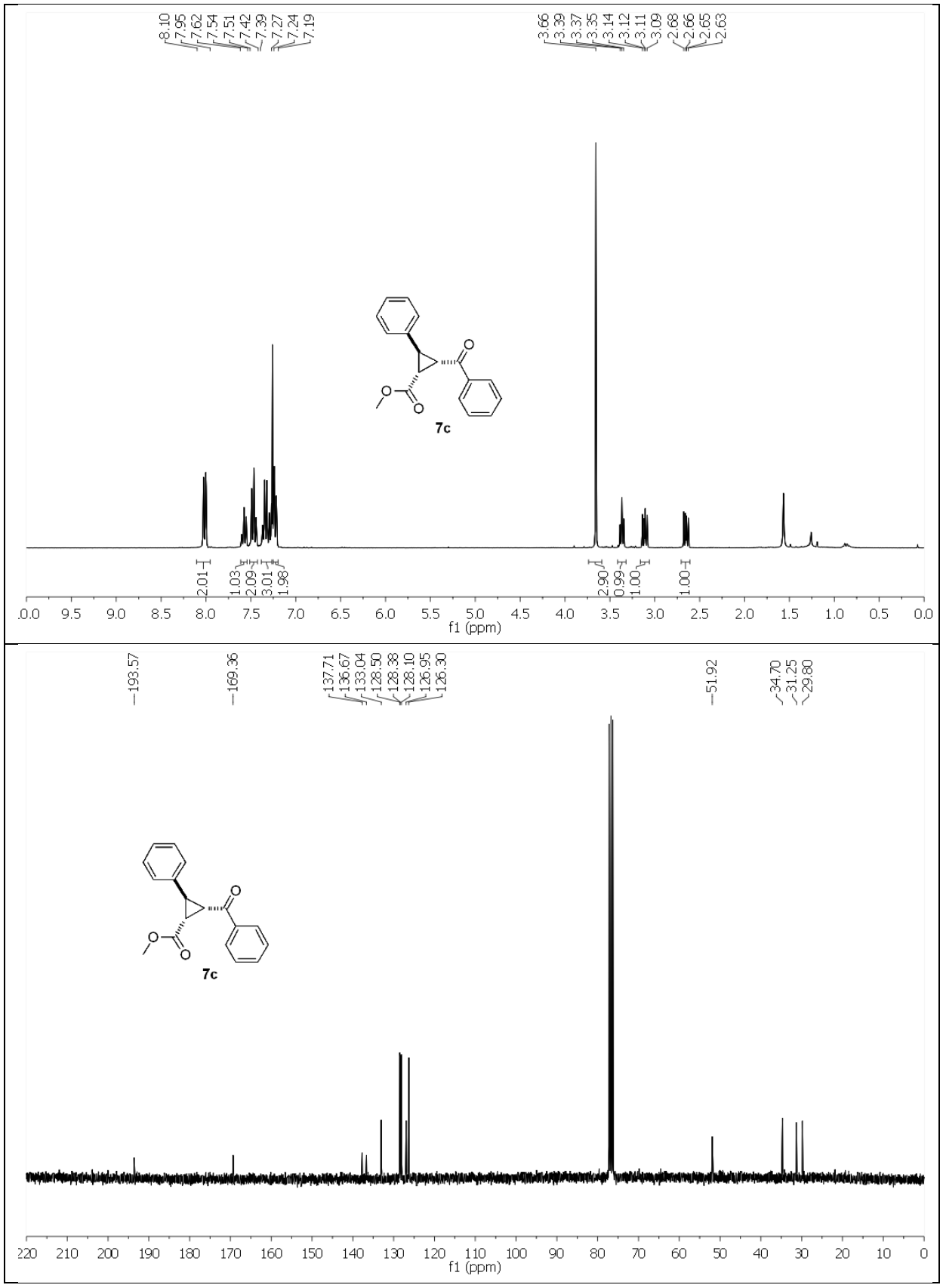
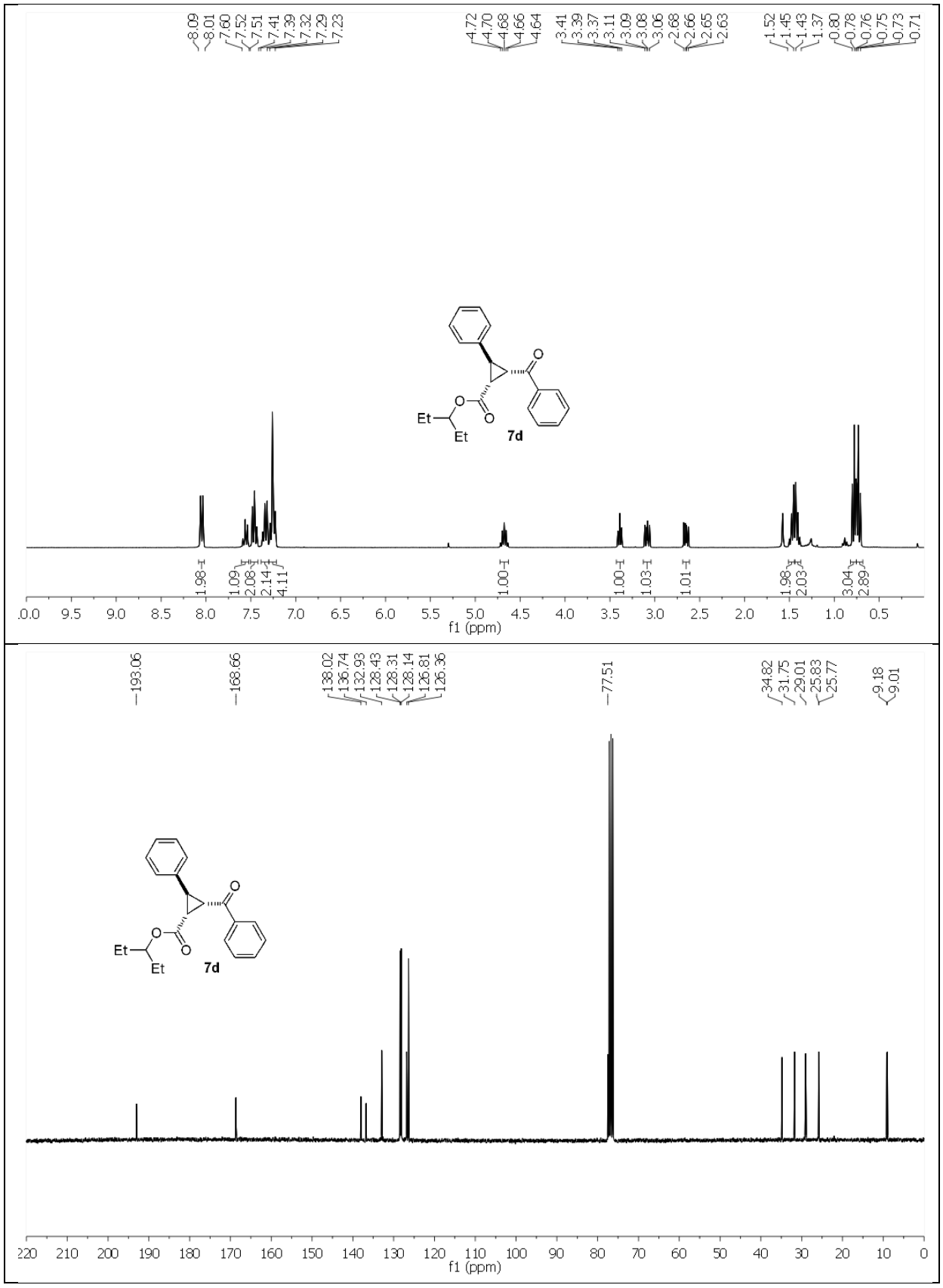
7.62
7.56
7.50
7.42
7.36
7.33
7.28
6.45
6.39
5.18
5.16
5.14
5.12
5.10
5.08
4.87
4.85
4.83
4.81
4.78
3.78
3.77
3.76
3.75
3.24
3.22
2.85
2.83
2.81
2.80
1.33
1.31
1.05
1.03
COO*i*Pr
O
O
O
6d'
Br
1.73 :1.0
1.87
3.66
3.30
5.01
4.10
1.73
1.73
1.00
0.99
0.99
0.94
10.21
5.58
f1 (ppm)

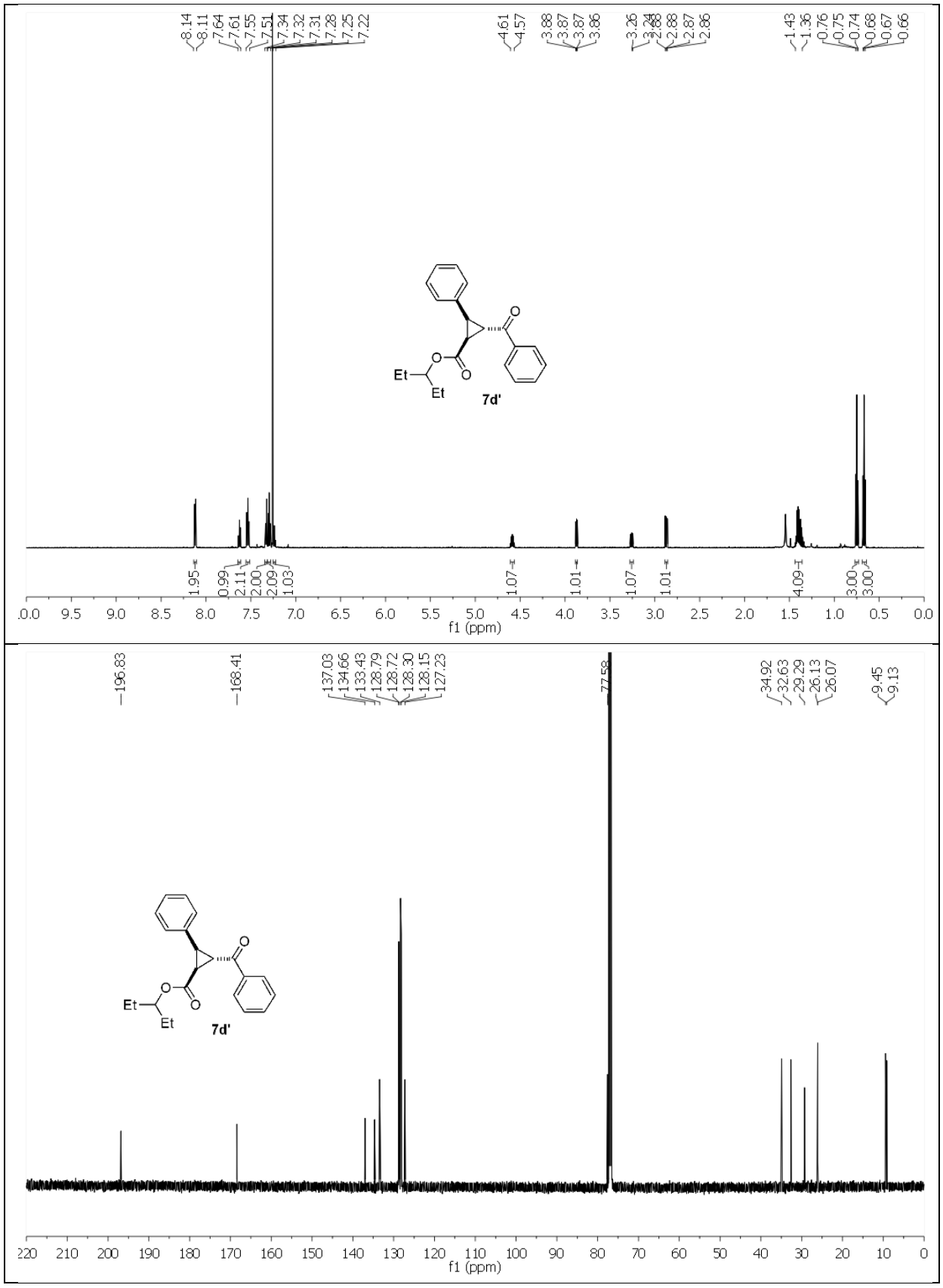

195.61
167.76
166.26
144.03
129.56
128.61
128.58
127.97
127.74
118.52
68.30
67.53
34.74
32.35
29.00
21.68
21.50
21.18
COO*i*Pr
O
O
O
6d'
Br
1.73 :1.0
f1 (ppm)

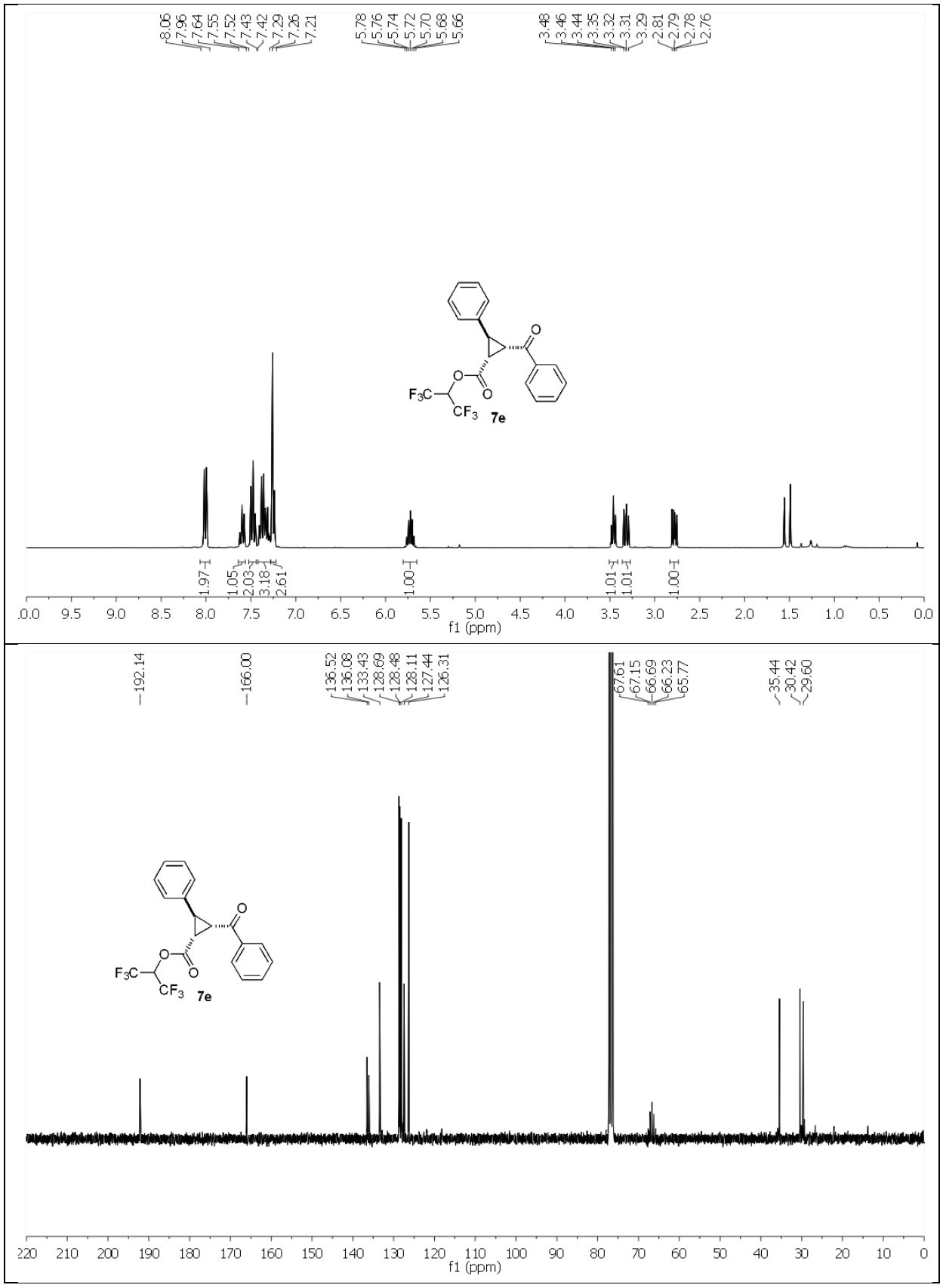

8.08
8.00
7.61
7.54
7.52
7.44
7.39
7.28
7.25
7.22
5.12
5.04
3.37
3.35
3.33
3.08
3.05
3.04
3.02
2.64
2.62
2.61
2.59
1.79
1.65
1.64
1.46
7a
2.01
1.09
2.18
2.86
2.10
1.00
1.01
1.02
1.02
2.06
6.82
f1 (ppm)
193.18
168.60
137.96
136.71
132.97
128.42
128.32
128.12
126.81
126.35
77.46
34.86
32.28
32.07
31.63
28.96
23.34
7a
f1 (ppm)

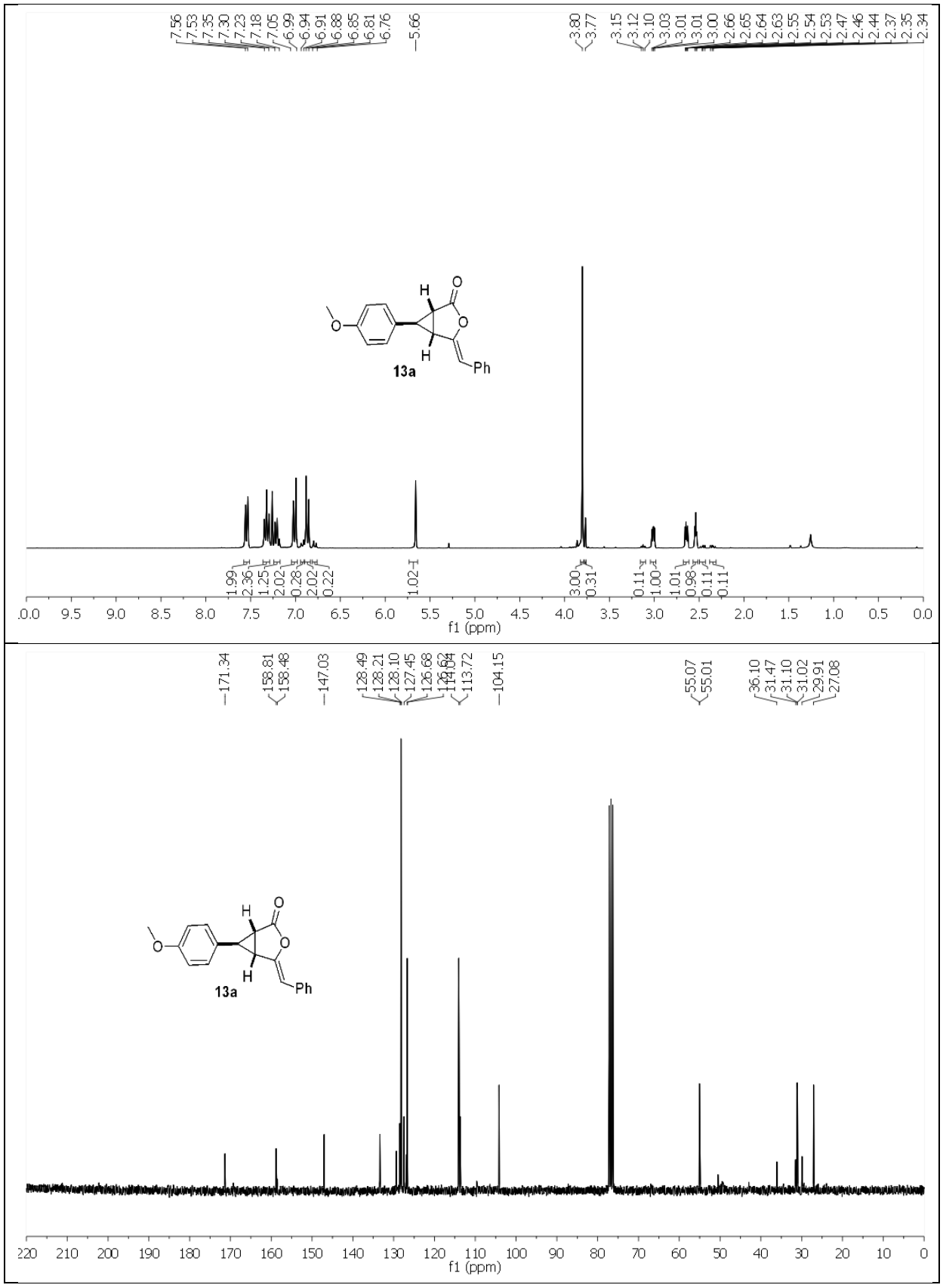

8.05
8.03
7.61
7.52
7.49
7.44
7.36
7.32
7.28
7.19
4.75
4.63
3.39
3.37
3.35
3.09
3.06
3.05
3.03
2.67
2.65
2.63
2.61
1.79
1.36
1.31
1.17
7b
2.01
1.07
2.10
2.09
4.44
0.99
1.00
1.01
1.01
5.99
5.04
f1 (ppm)
193.26
168.29
137.99
136.76
132.93
128.43
128.32
128.13
126.81
126.34
73.23
34.93
31.73
31.14
31.08
29.07
25.04
23.35
7b
f1 (ppm)

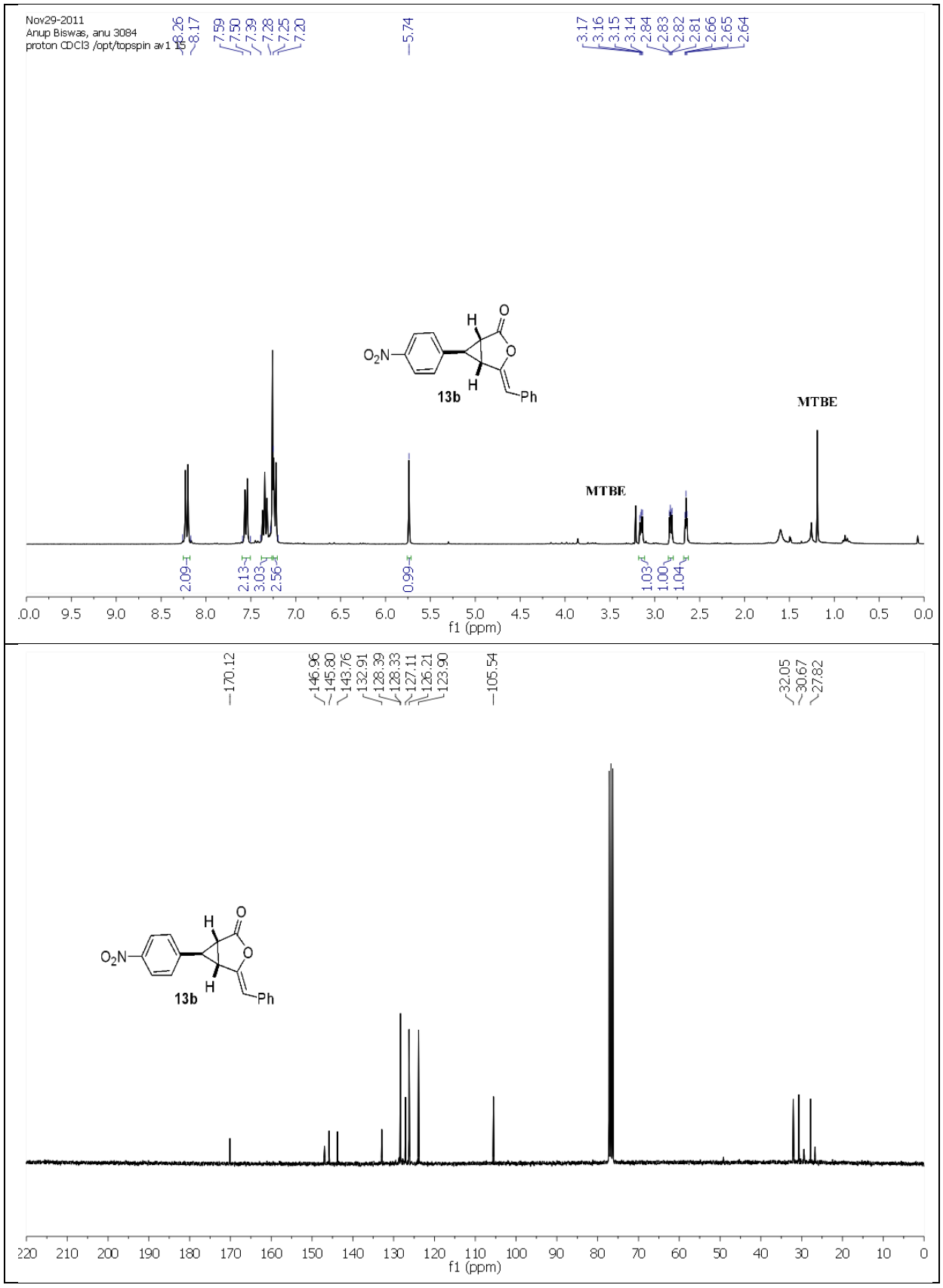

8.10
7.95
7.62
7.54
7.51
7.42
7.39
7.27
7.24
7.19
3.66
3.39
3.37
3.35
3.14
3.12
3.11
3.09
2.68
2.66
2.65
2.63
2.01
1.03
2.09
3.01
1.98
2.90
0.99
1.00
1.00
7c
f1 (ppm)
193.57
169.36
137.71
136.67
133.04
128.50
128.38
128.10
126.95
126.30
51.92
34.70
31.25
29.80
7c
f1 (ppm)


8.09
8.01
7.60
7.52
7.51
7.41
7.39
7.32
7.29
7.23
4.72
4.70
4.68
4.66
4.64
3.41
3.39
3.37
3.11
3.09
3.08
3.06
2.68
2.66
2.65
2.63
1.52
1.45
1.43
1.37
0.80
0.78
0.76
0.75
0.73
0.71
1.98
1.09
2.08
2.14
4.11
1.00
1.00
1.03
1.01
1.98
2.03
3.04
2.89
Et
Et
O
O
O
7d
f1 (ppm)
193.06
168.66
138.02
136.74
132.93
128.43
128.31
128.14
126.81
126.36
77.51
34.82
31.75
29.01
25.83
25.77
9.18
9.01
Et
Et
O
O
O
7d
f1 (ppm)

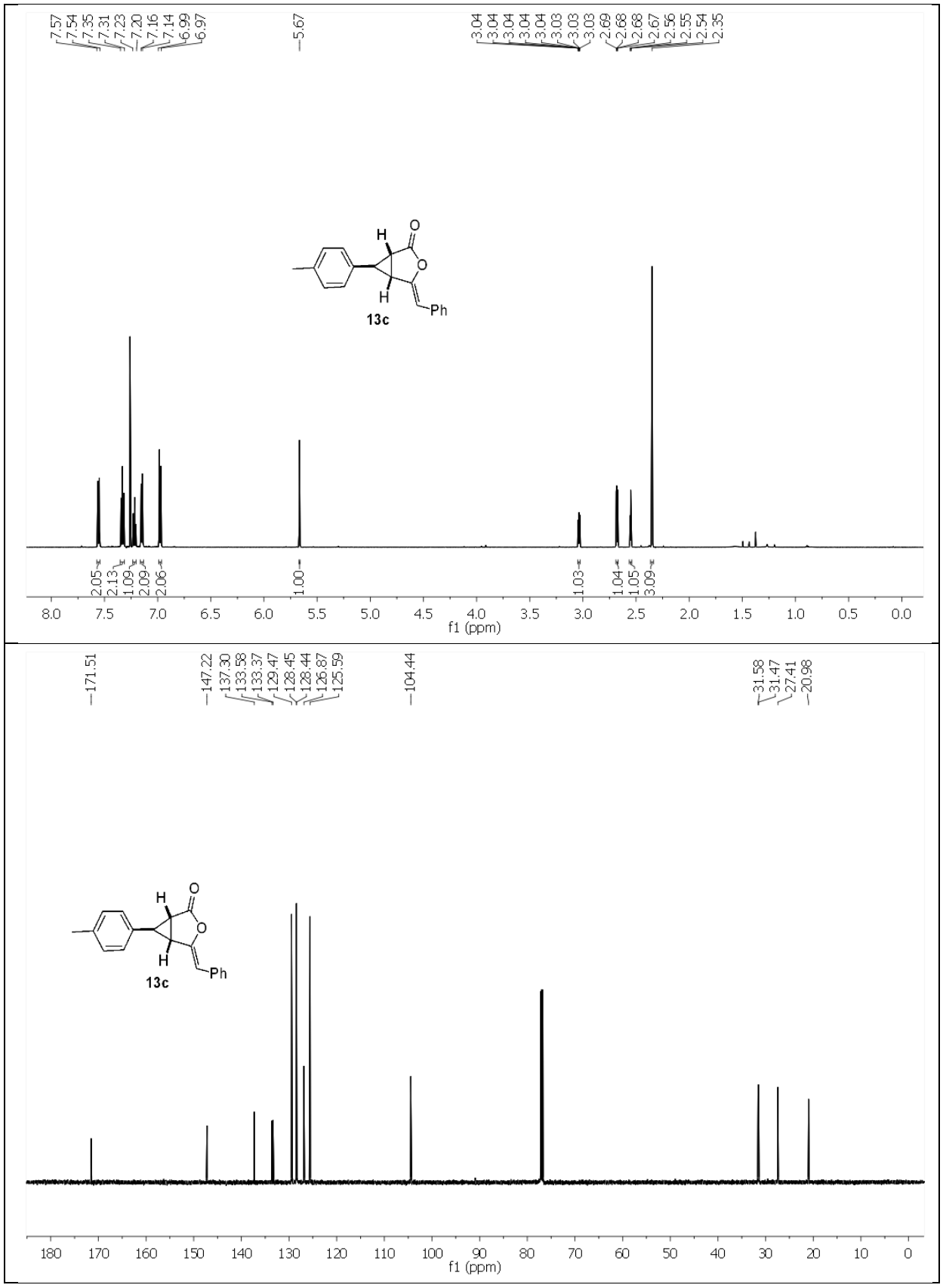

8.14
8.11
7.64
7.61
7.55
7.51
7.34
7.32
7.31
7.28
7.25
7.22
4.61
4.57
3.88
3.87
3.87
3.86
3.26
3.24
2.88
2.87
2.86
1.43
1.36
0.76
0.75
0.74
0.68
0.67
0.66
1.95
0.99
2.11
2.00
2.09
1.03
1.07
1.01
1.07
1.01
4.09
3.00
3.00
f1 (ppm)
Et
Et
7d'
196.83
168.41
137.03
134.66
133.43
128.79
128.72
128.30
128.15
127.23
77.58
34.92
32.63
29.29
26.13
26.07
9.45
9.13
f1 (ppm)
Et
Et
7d'

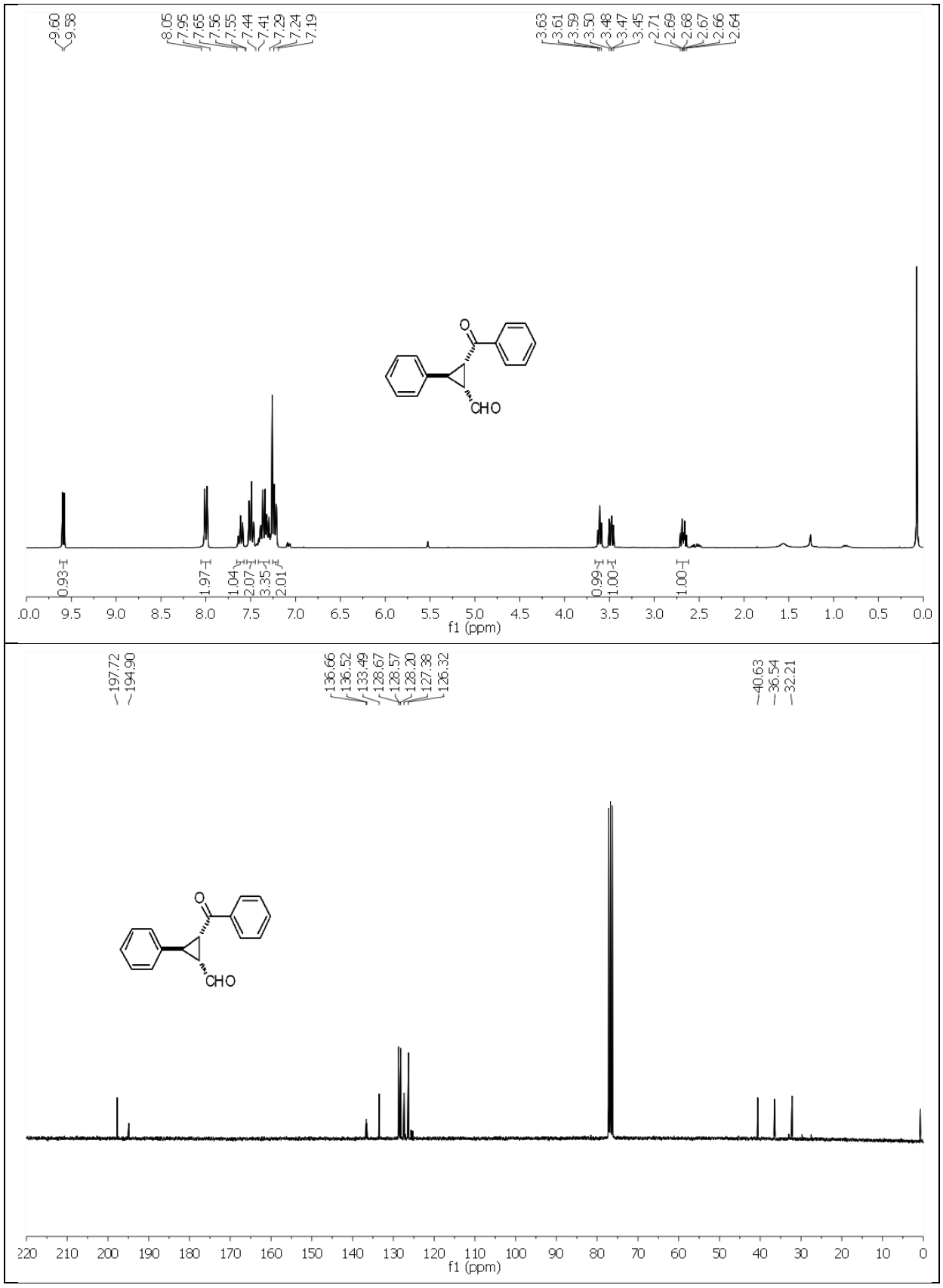

8.06
7.96
7.64
7.55
7.52
7.43
7.42
7.29
7.26
7.21
5.78
5.76
5.74
5.72
5.70
5.68
5.66
3.48
3.46
3.44
3.35
3.32
3.31
3.29
2.81
2.79
2.78
2.76
F3C
CF3
7e
1.97
1.05
2.03
3.18
2.61
1.00
1.01
1.01
1.00
f1 (ppm)
192.14
166.00
136.52
136.08
133.43
128.69
128.48
128.11
127.44
126.31
67.61
67.15
66.69
66.23
65.77
35.44
30.42
29.60
f1 (ppm)


7.56
7.53
7.35
7.30
7.23
7.18
7.05
6.99
6.94
6.91
6.88
6.85
6.81
6.76
5.66
3.80
3.77
3.15
3.12
3.10
3.03
3.01
3.01
3.00
2.66
2.65
2.64
2.63
2.55
2.54
2.53
2.47
2.46
2.44
2.37
2.35
2.34
13a
1.99
2.36
1.25
2.02
0.28
2.02
0.22
1.02
3.00
0.31
0.11
1.00
1.01
0.98
0.11
0.11
f1 (ppm)
171.34
158.81
158.48
147.03
128.49
128.21
128.10
127.45
126.68
114.04
113.72
104.15
55.07
55.01
36.10
31.47
31.10
31.02
29.91
27.08
13a
f1 (ppm)

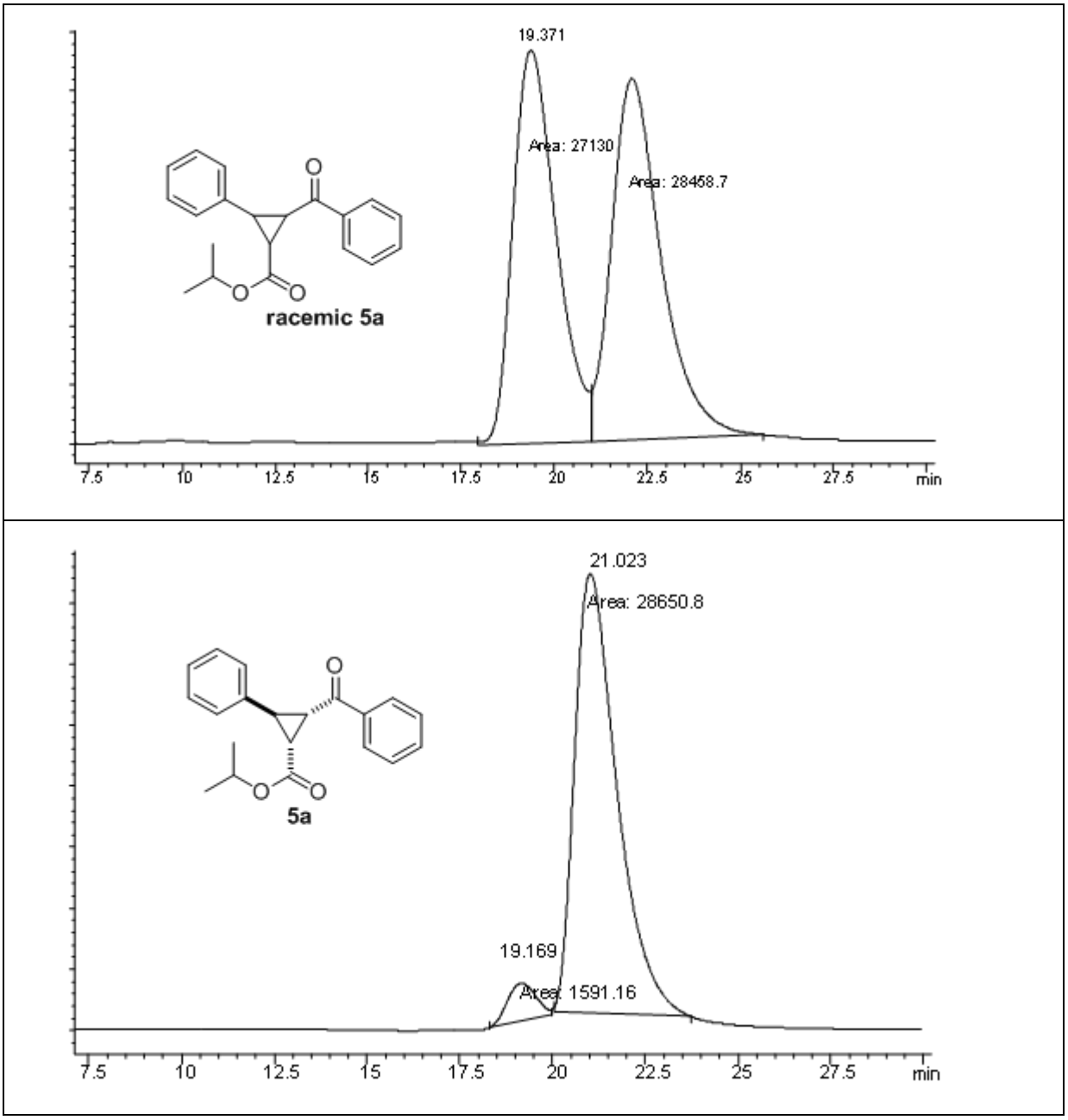

Nov29-2011
Anup Biswas, anu 3084
proton CDCl3 /opt/topspin av1 15
8.26
8.17
7.59
7.50
7.39
7.28
7.25
7.20
5.74
3.17
3.16
3.15
3.14
2.84
2.83
2.82
2.81
2.66
2.65
2.64
MTBE
MTBE
13b
2.09
2.13
3.03
2.56
0.99
1.03
1.00
1.04
f1 (ppm)
170.12
146.96
145.80
143.76
132.91
128.39
128.33
127.11
126.21
123.90
105.54
32.05
30.67
27.82
13b
f1 (ppm)

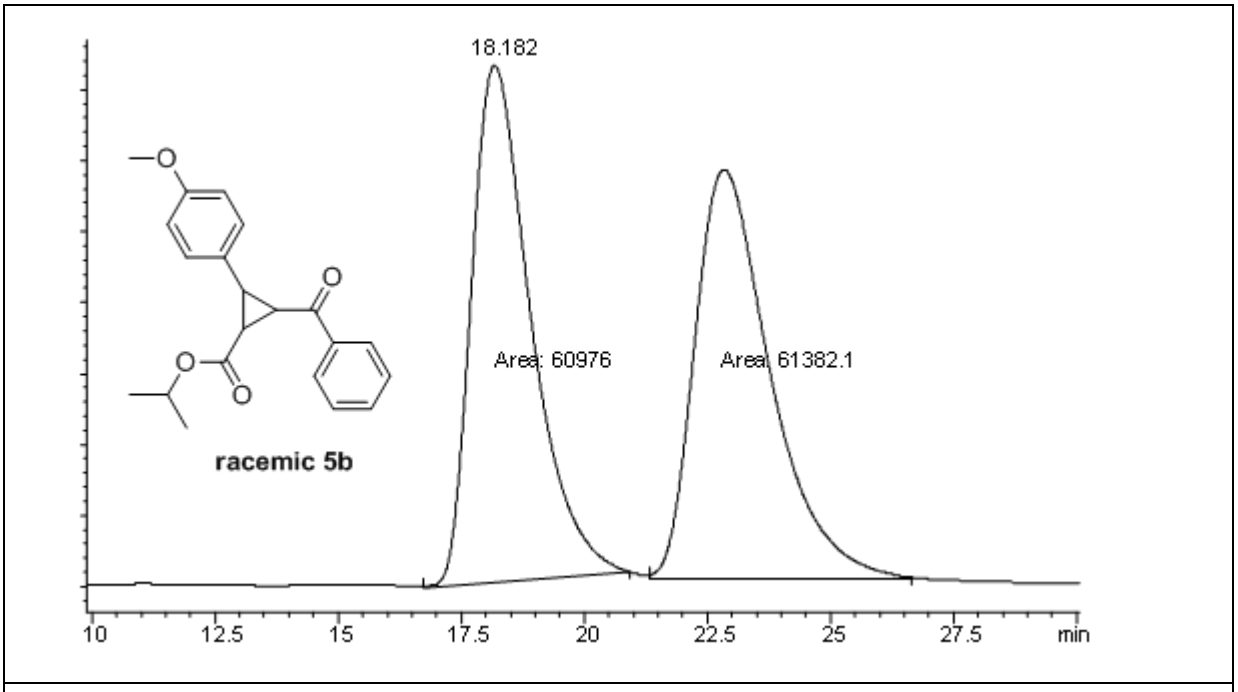
MTBE = methyl *tert*-butyl ether

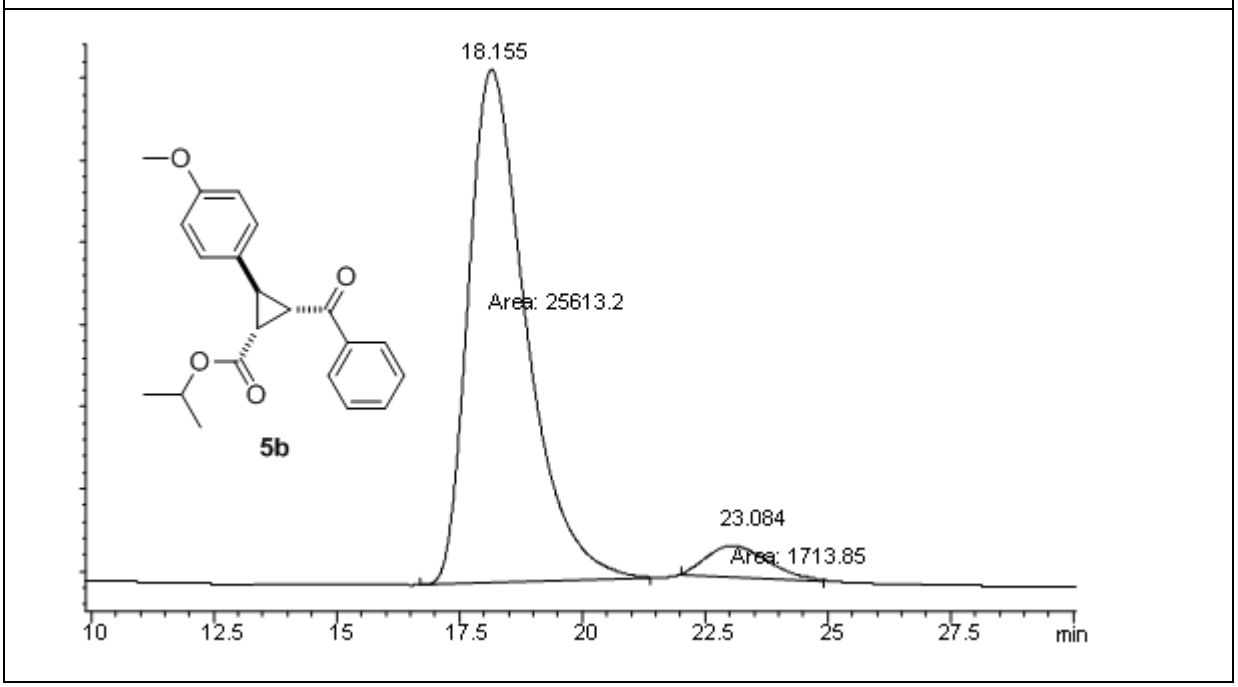


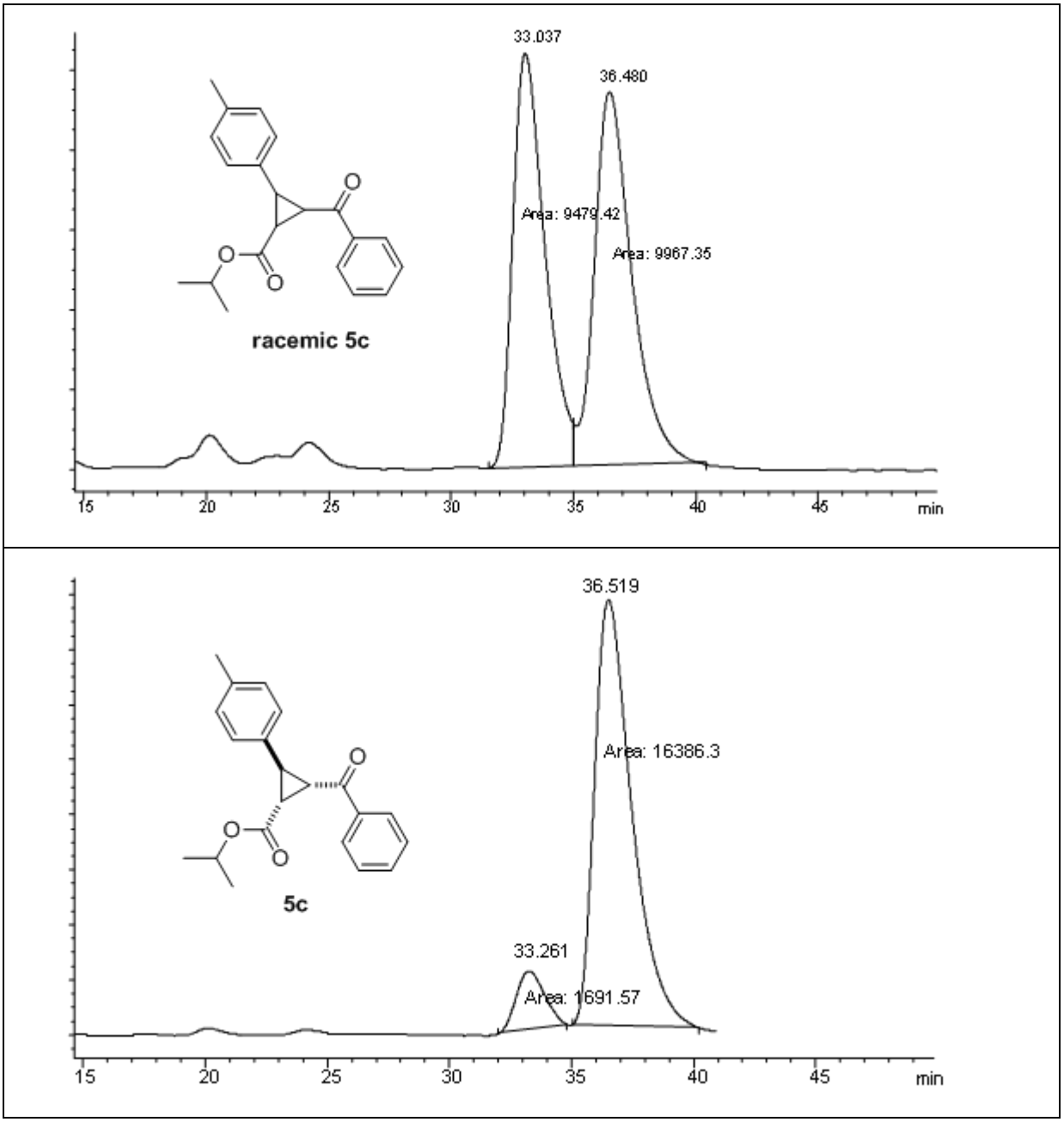

9.60
9.58
8.05
7.95
7.65
7.56
7.55
7.44
7.41
7.29
7.24
7.19
3.63
3.61
3.59
3.50
3.48
3.47
3.45
2.71
2.69
2.68
2.67
2.66
2.64
O
CHO
0.93
1.97
1.04
2.07
3.35
2.01
0.99
1.00
1.00
f1 (ppm)
197.72
194.90
136.66
136.52
133.49
128.67
128.57
128.20
127.38
126.32
40.63
36.54
32.21
O
CHO
f1 (ppm)

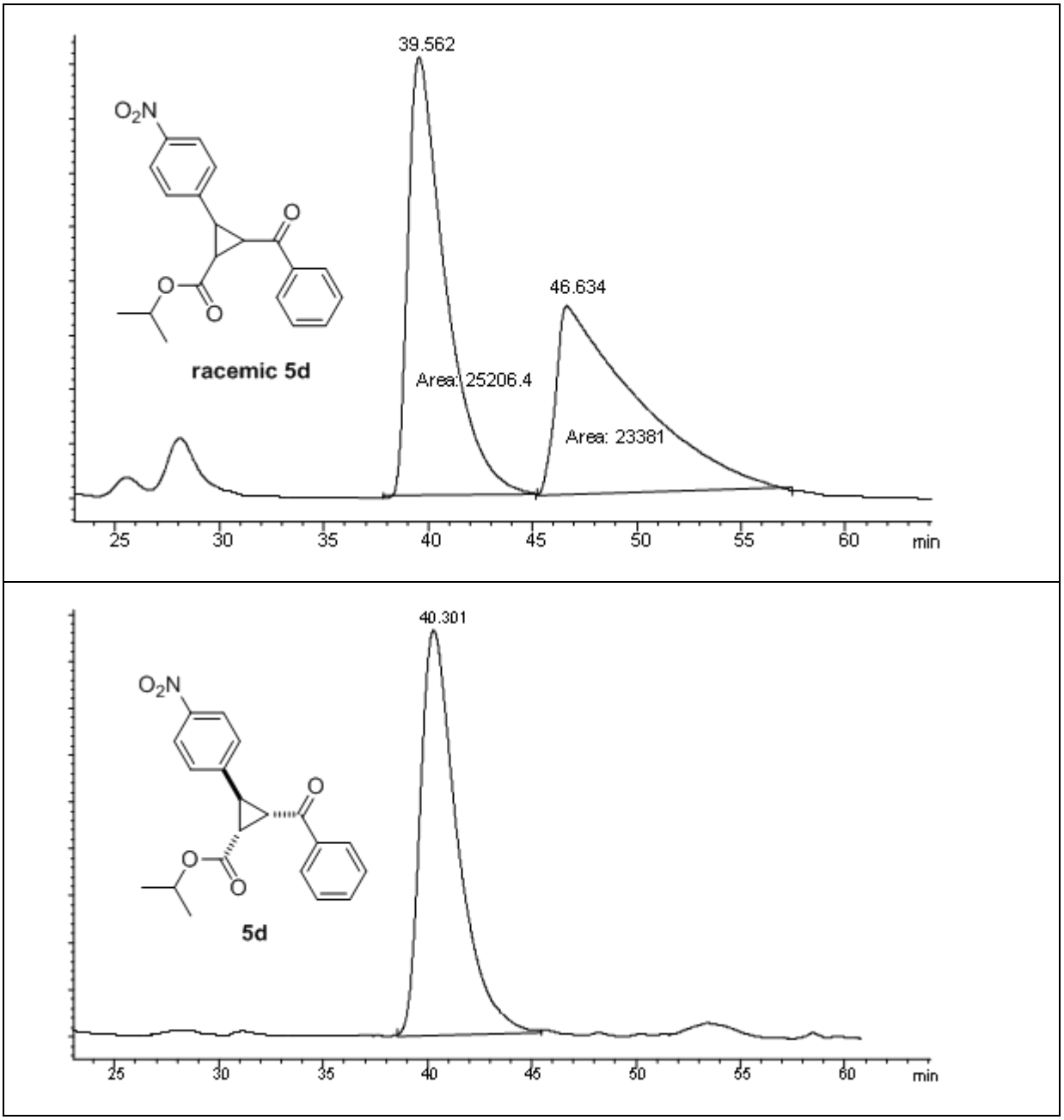
HPLC spectras:

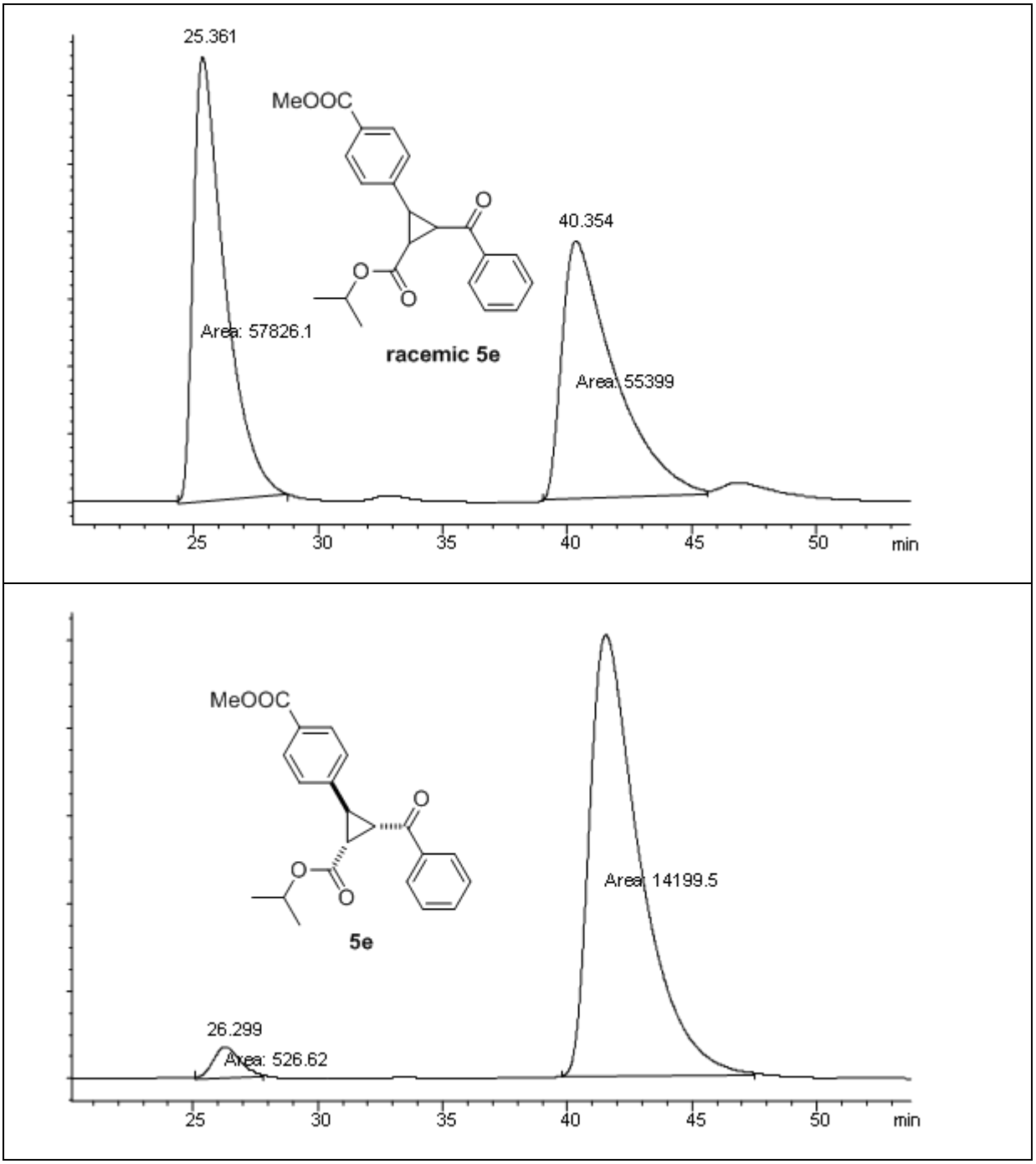


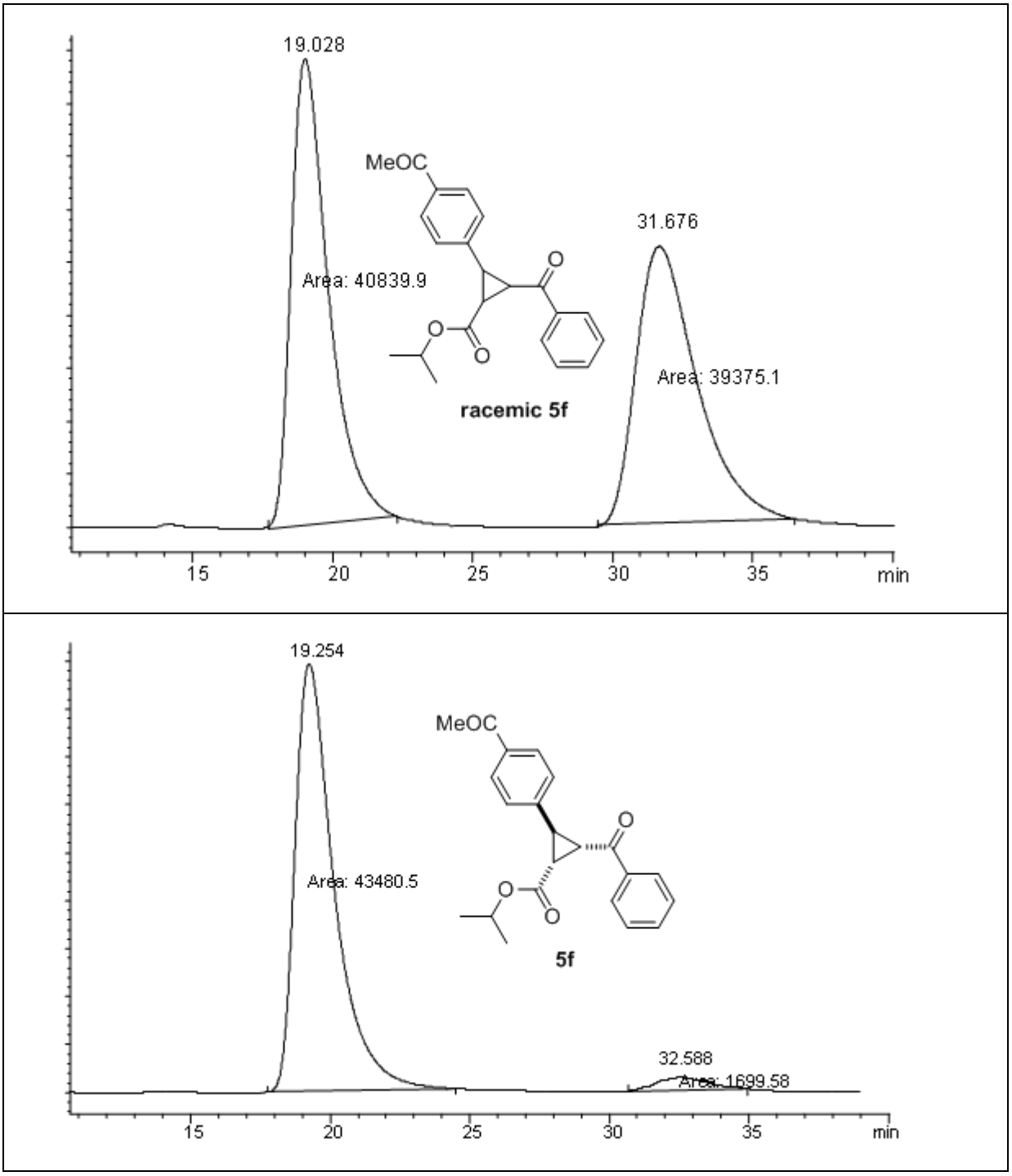

18.182
Area: 60976
Area: 61382.1
racemic 5b
10
12.5
15
17.5
20
22.5
25
27.5
min

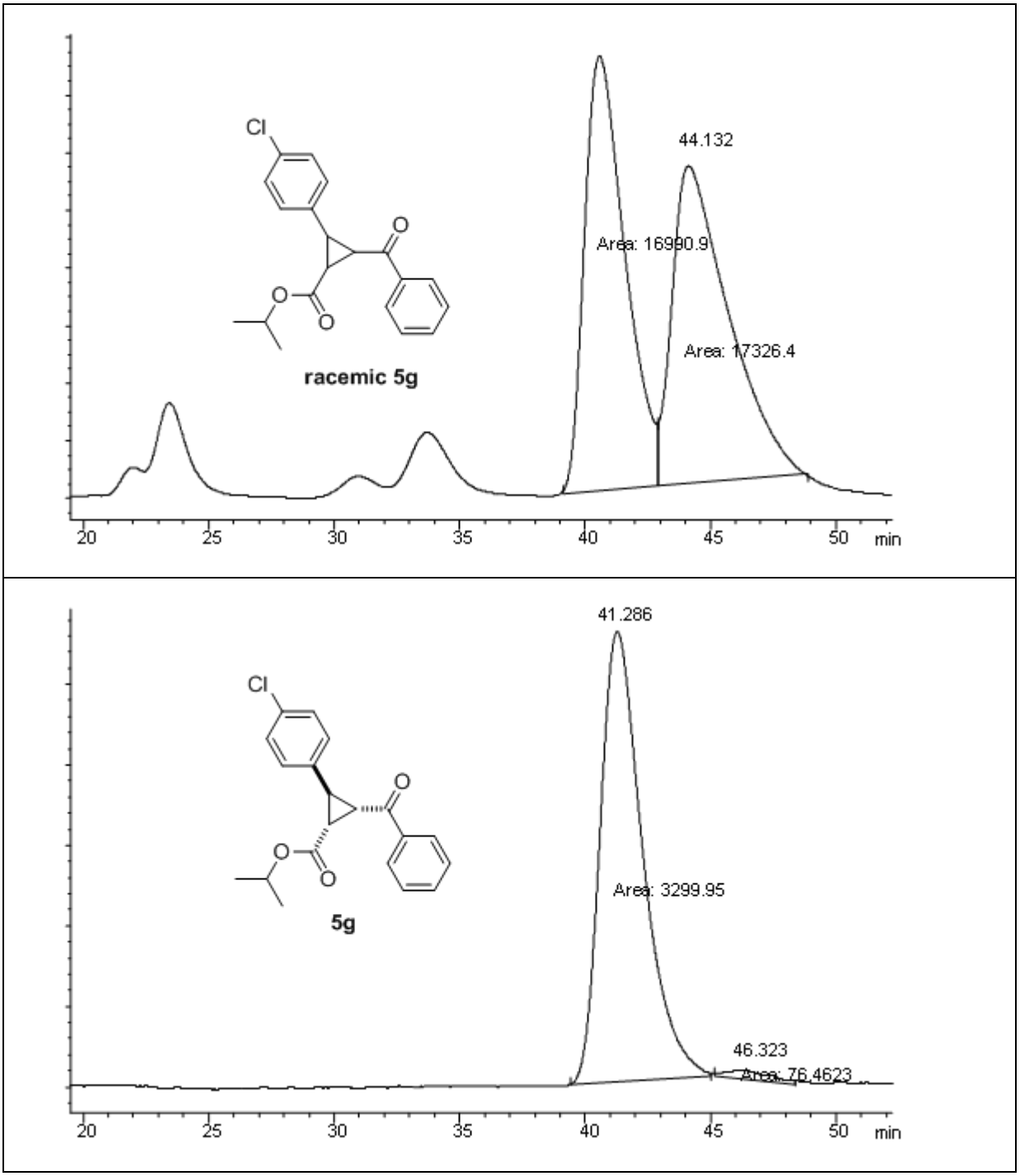

18.155
Area: 25613.2
5b
23.084
Area: 1713.85
10
12.5
15
17.5
20
22.5
25
27.5
min

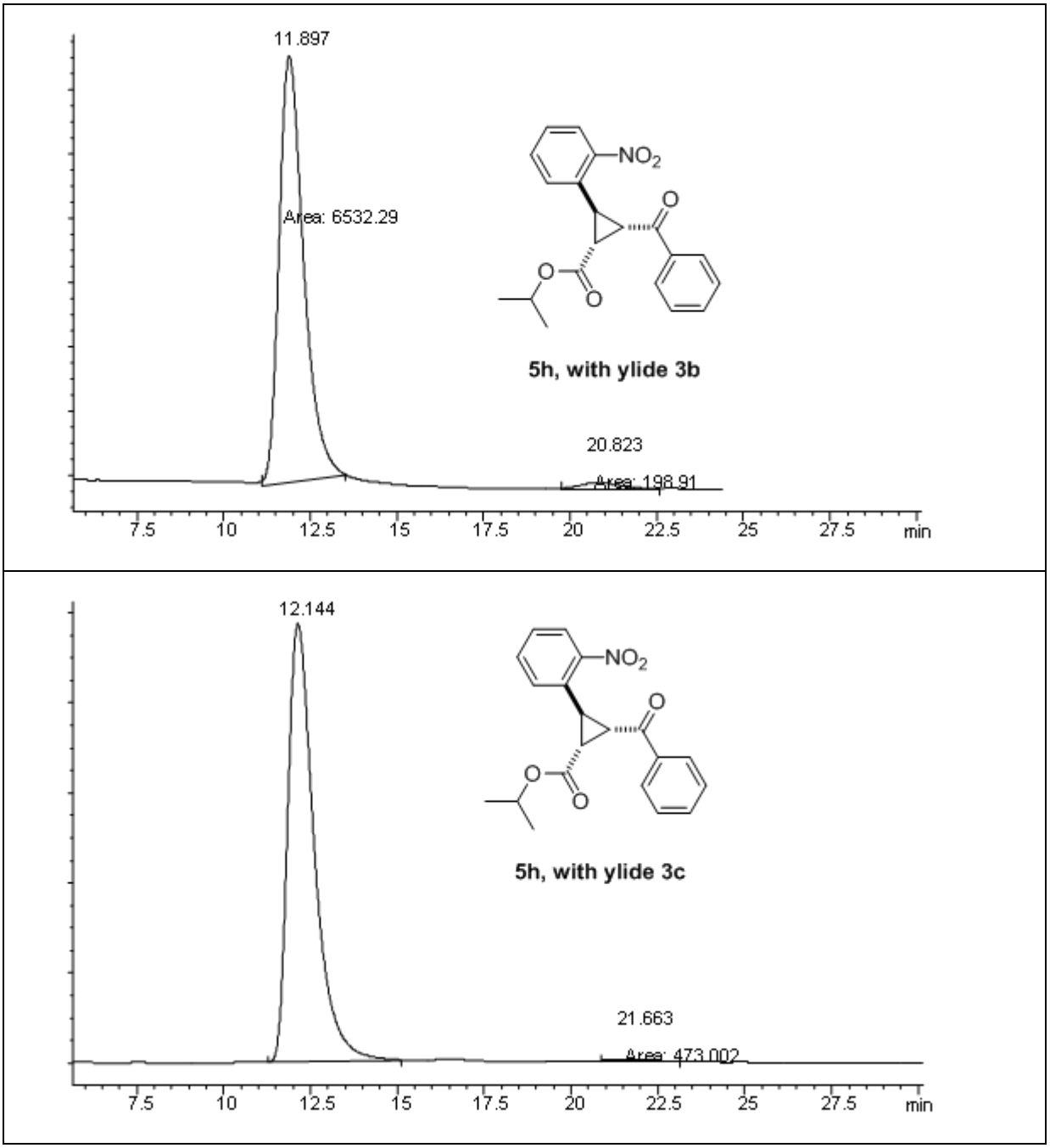

33.037
36.480
Area: 9479.42
Area: 9967.35
racemic 5c
15
20
25
30
35
40
45
min
36.519
Area: 16386.3
5c
33.261
Area: 1691.57
15
20
25
30
35
40
45
min

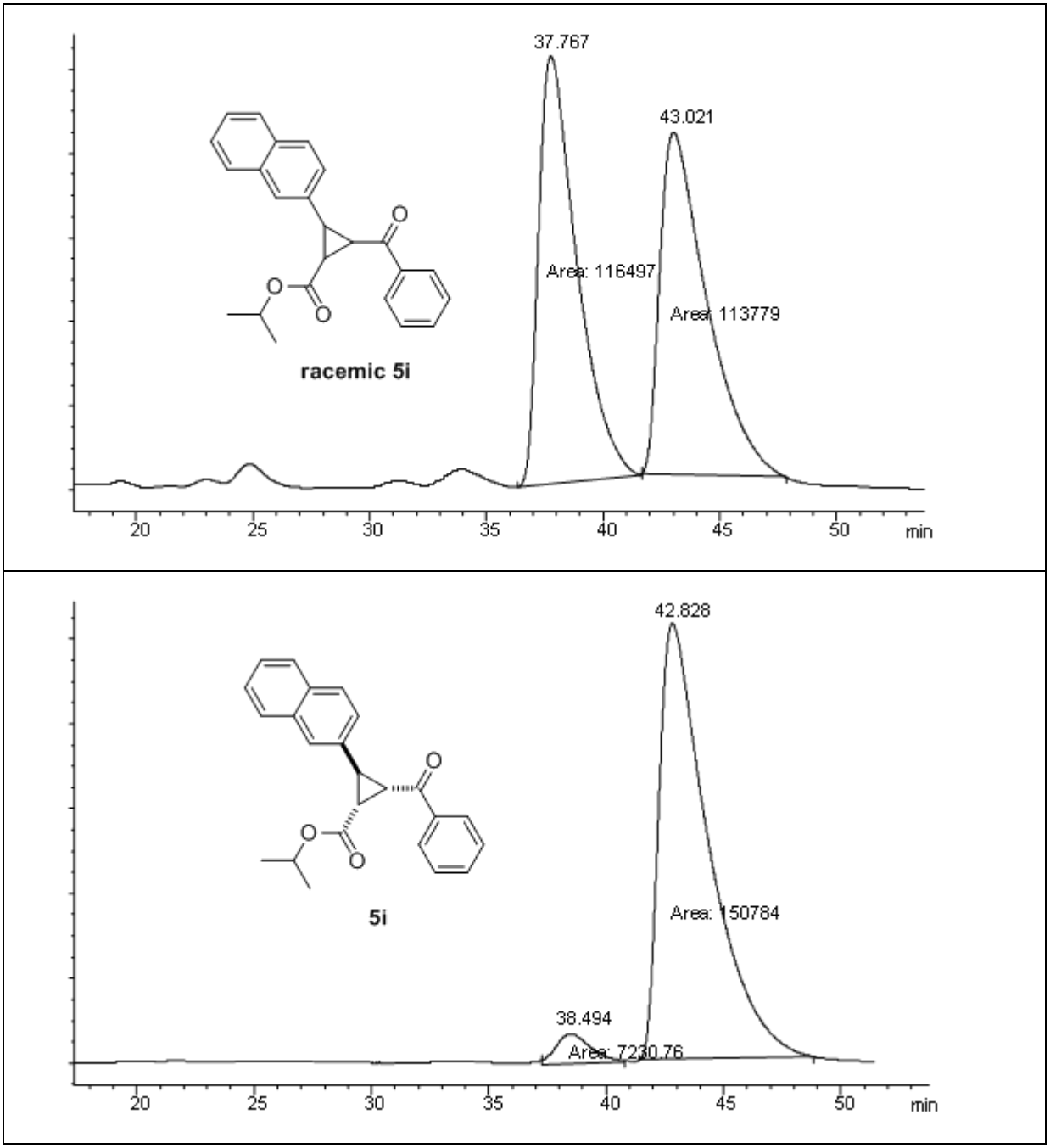

39.562
46.634
racemic 5d
Area: 25206.4
Area: 23381
25
30
35
40
45
50
55
60
min
40.301
5d
25
30
35
40
45
50
55
60
min

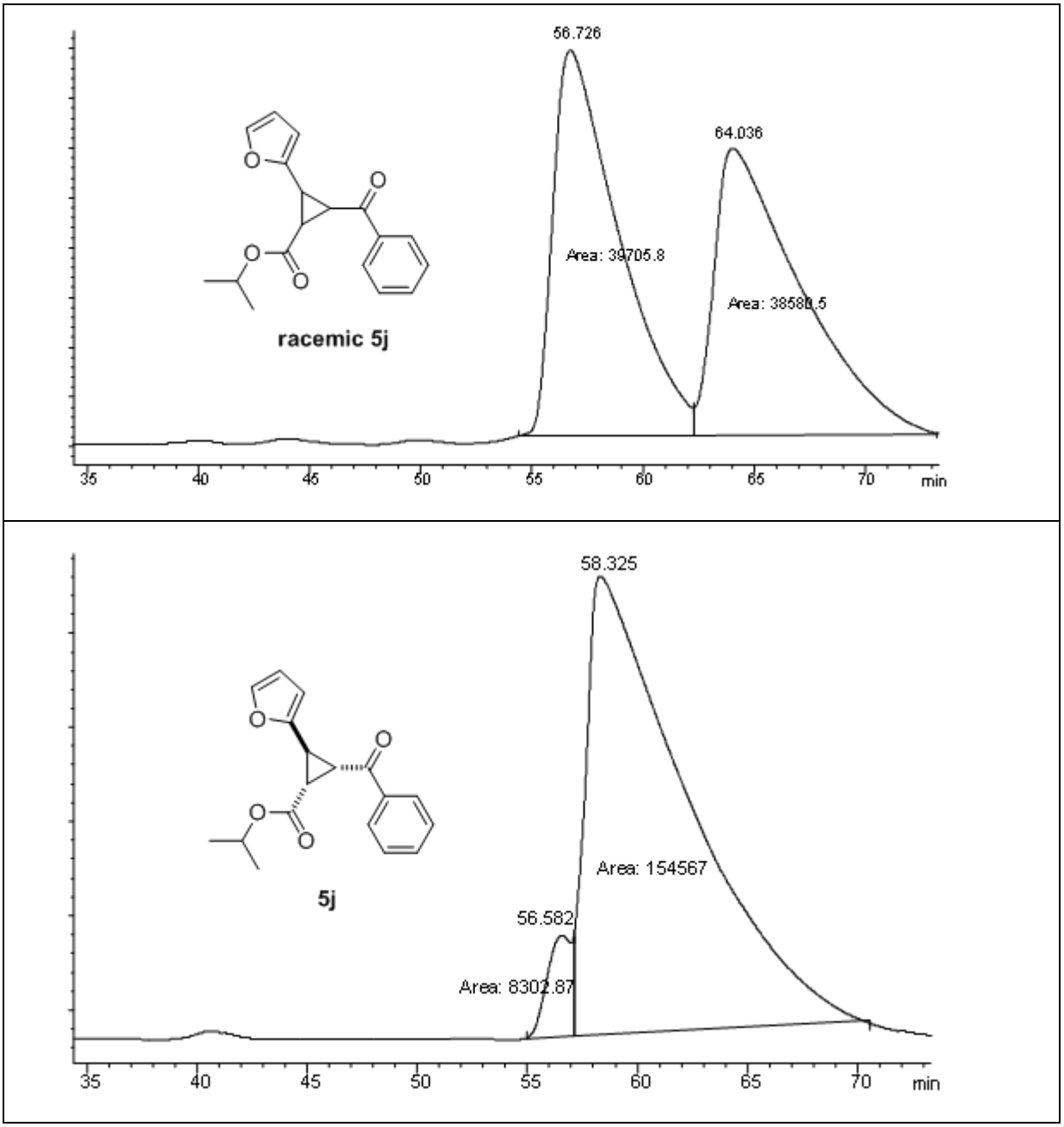

25.361
MeOOC
O
40.354
O
O
Area: 57826.1
racemic 5e
Area: 55399
25
30
35
40
45
50
min
MeOOC
O
O
O
5e
Area: 14199.5
26.299
Area: 526.62
25
30
35
40
45
50
min

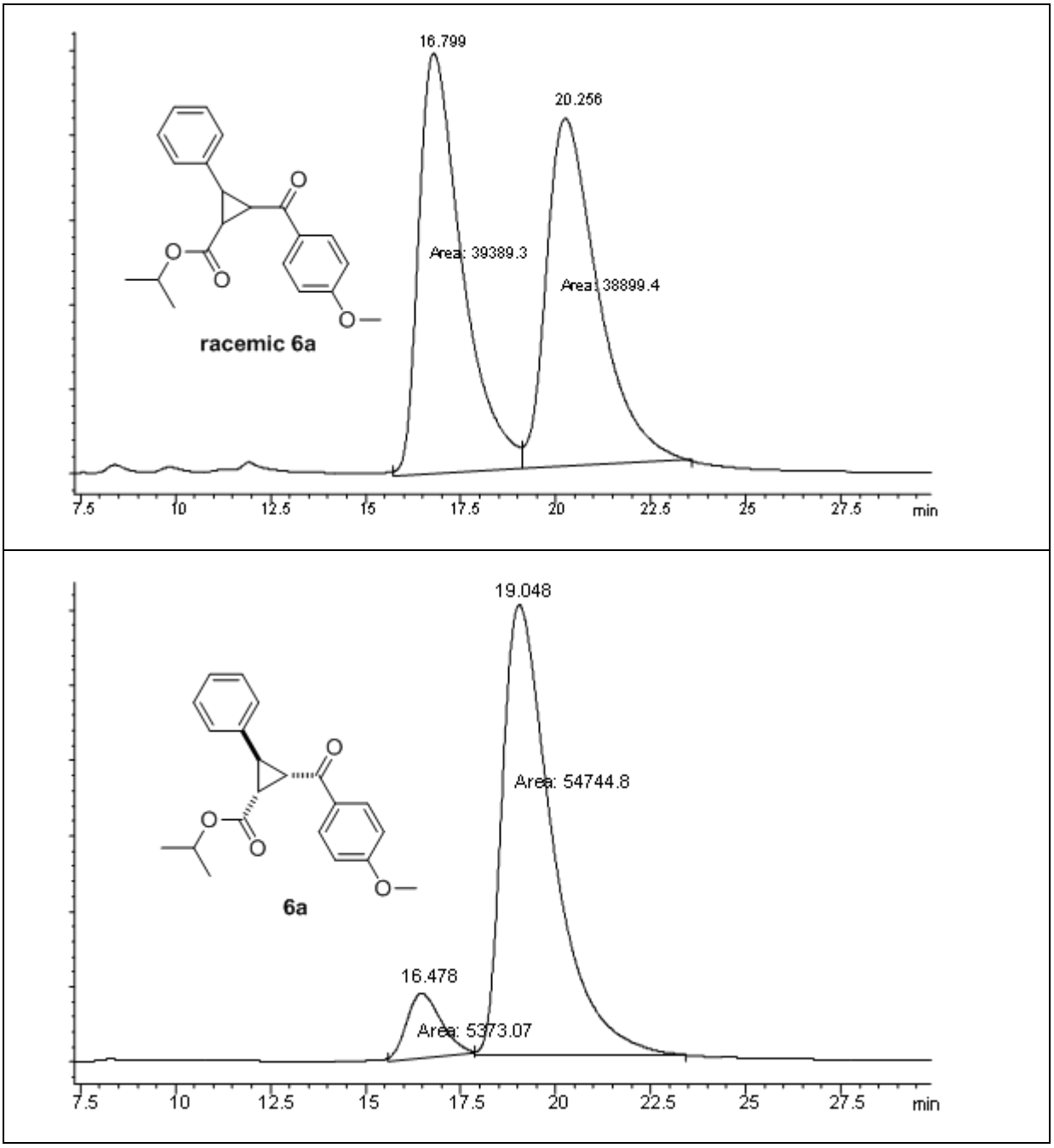

19.028
Area: 40839.9
MeOC
O
O
O
31.676
Area: 39375.1
racemic 5f
15
20
25
30
35
min
19.254
Area: 43480.5
MeOC
O
O
O
5f
32.588
Area: 1699.58
15
20
25
30
35
min

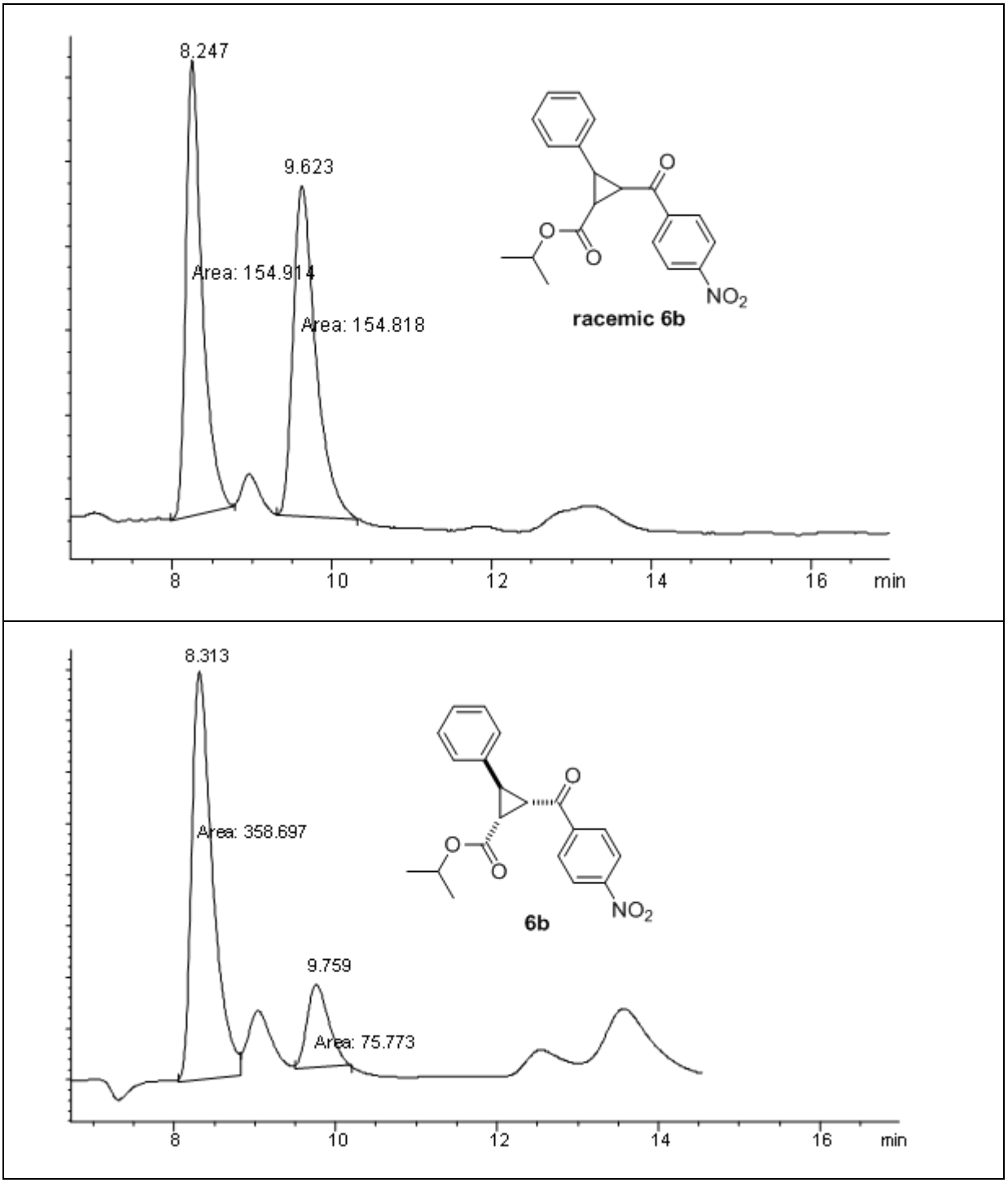

Cl
O
O
O
racemic 5g
44.132
Area: 16990.9
Area: 17326.4
20
25
30
35
40
45
50
min
Cl
O
O
O
5g
41.286
Area: 3299.95
46.323
Area: 76.4623
20
25
30
35
40
45
50
min

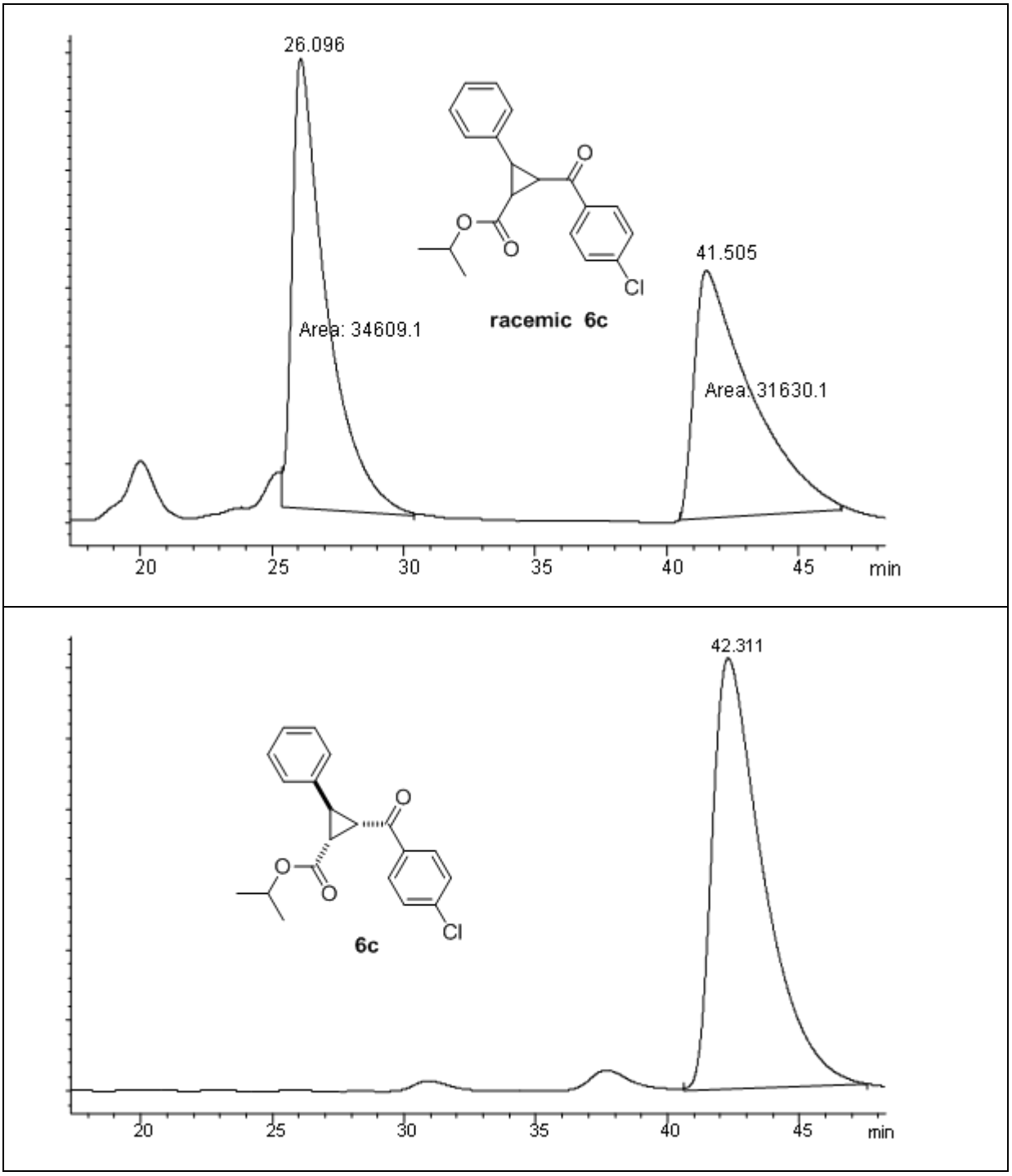

11.897
Area: 6532.29
NO2
O
O
O
5h, with ylide 3b
20.823
Area: 198.91
7.5
10
12.5
15
17.5
20
22.5
25
27.5
min
12.144
NO2
O
O
O
5h, with ylide 3c
21.663
Area: 473.002
7.5
10
12.5
15
17.5
20
22.5
25
27.5
min

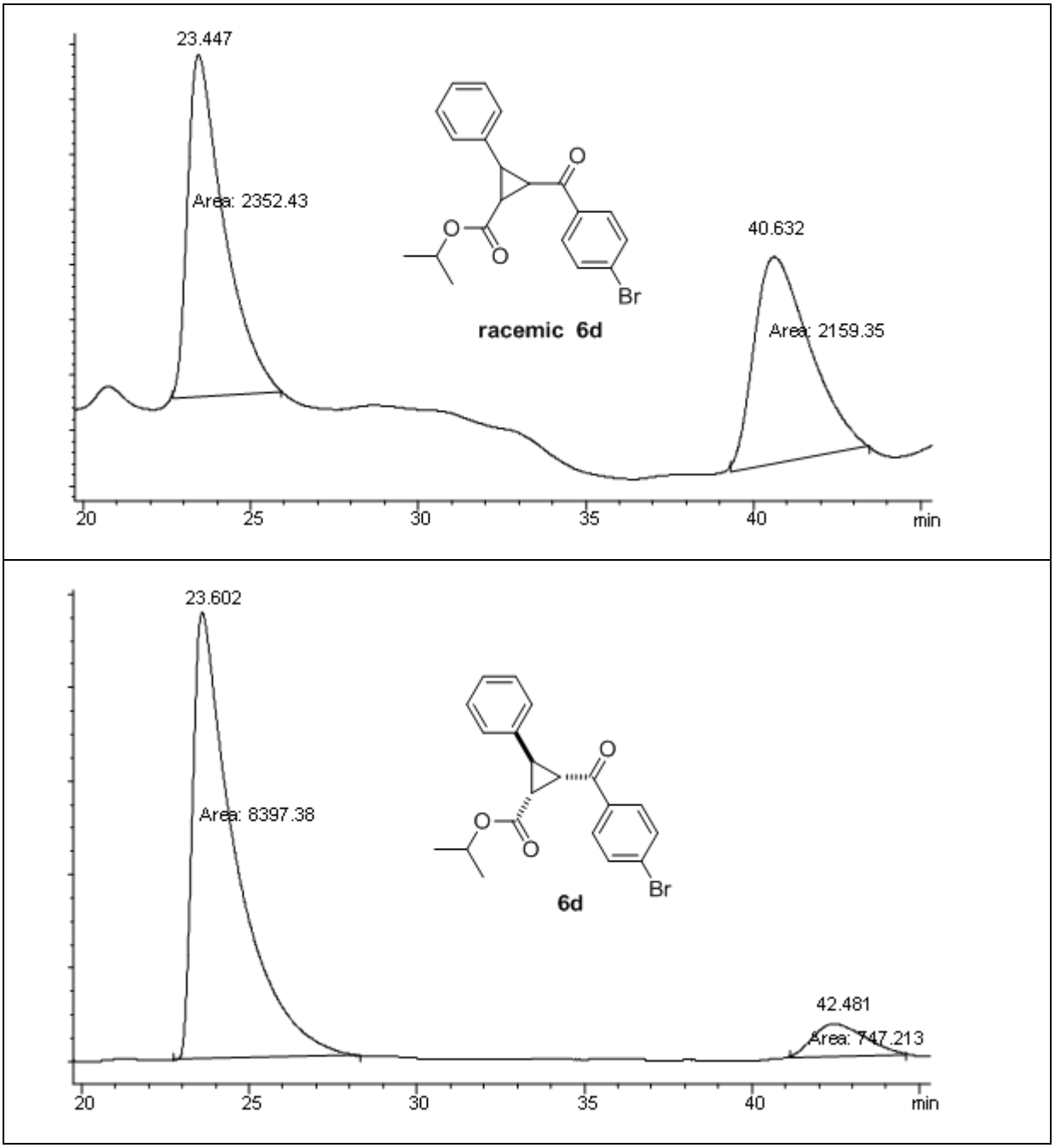

37.767
43.021
Area: 116497
Area: 113779
racemic 5i
20
25
30
35
40
45
50
min
42.828
Area: 150784
38.494
Area: 7230.76
5i
20
25
30
35
40
45
50
min

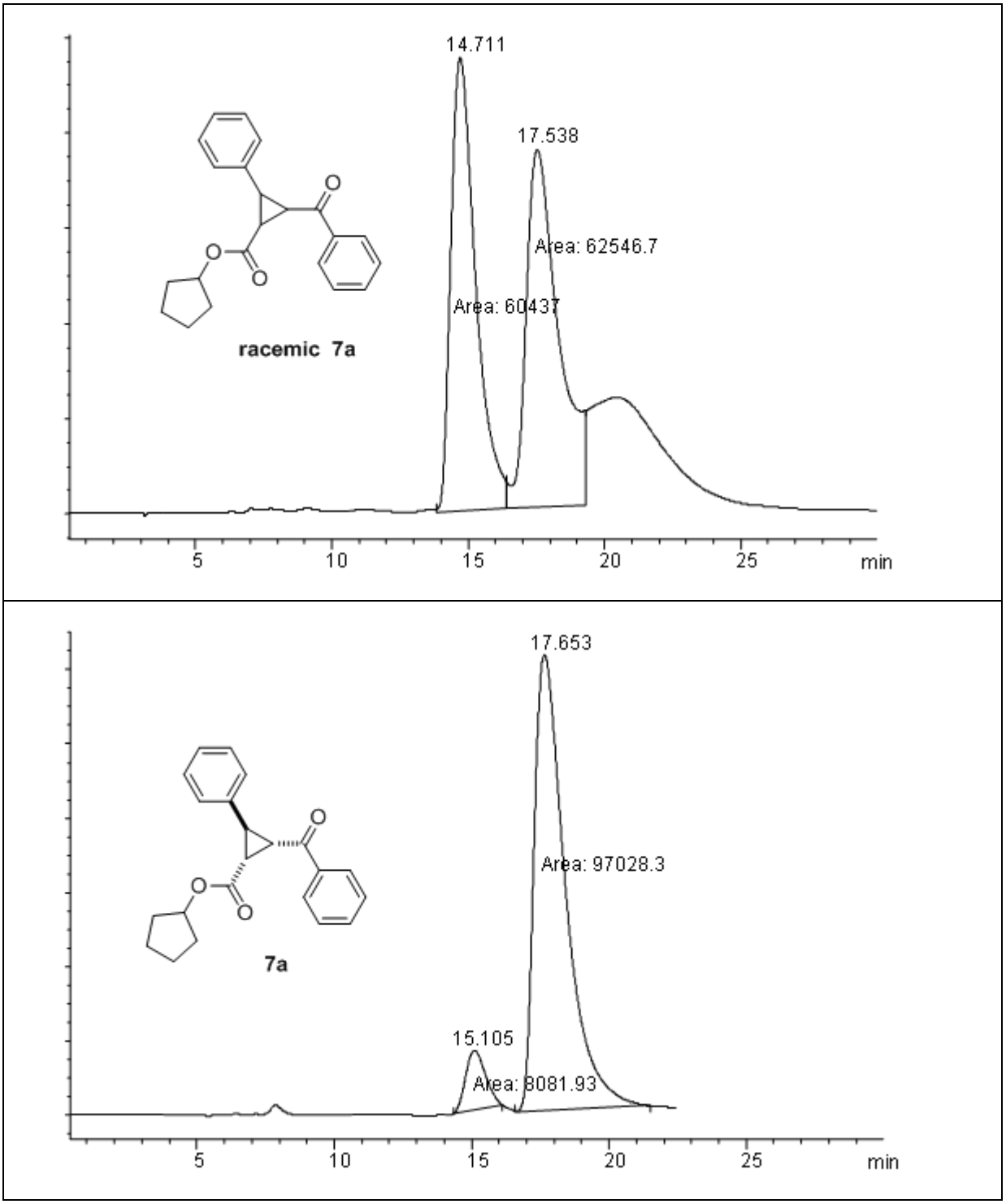

56.726
64.036
Area: 39705.8
Area: 38580.5
racemic 5j
35
40
45
50
55
60
65
70
min
58.325
Area: 154567
56.582
Area: 8302.87
5j
35
40
45
50
55
60
65
70
min

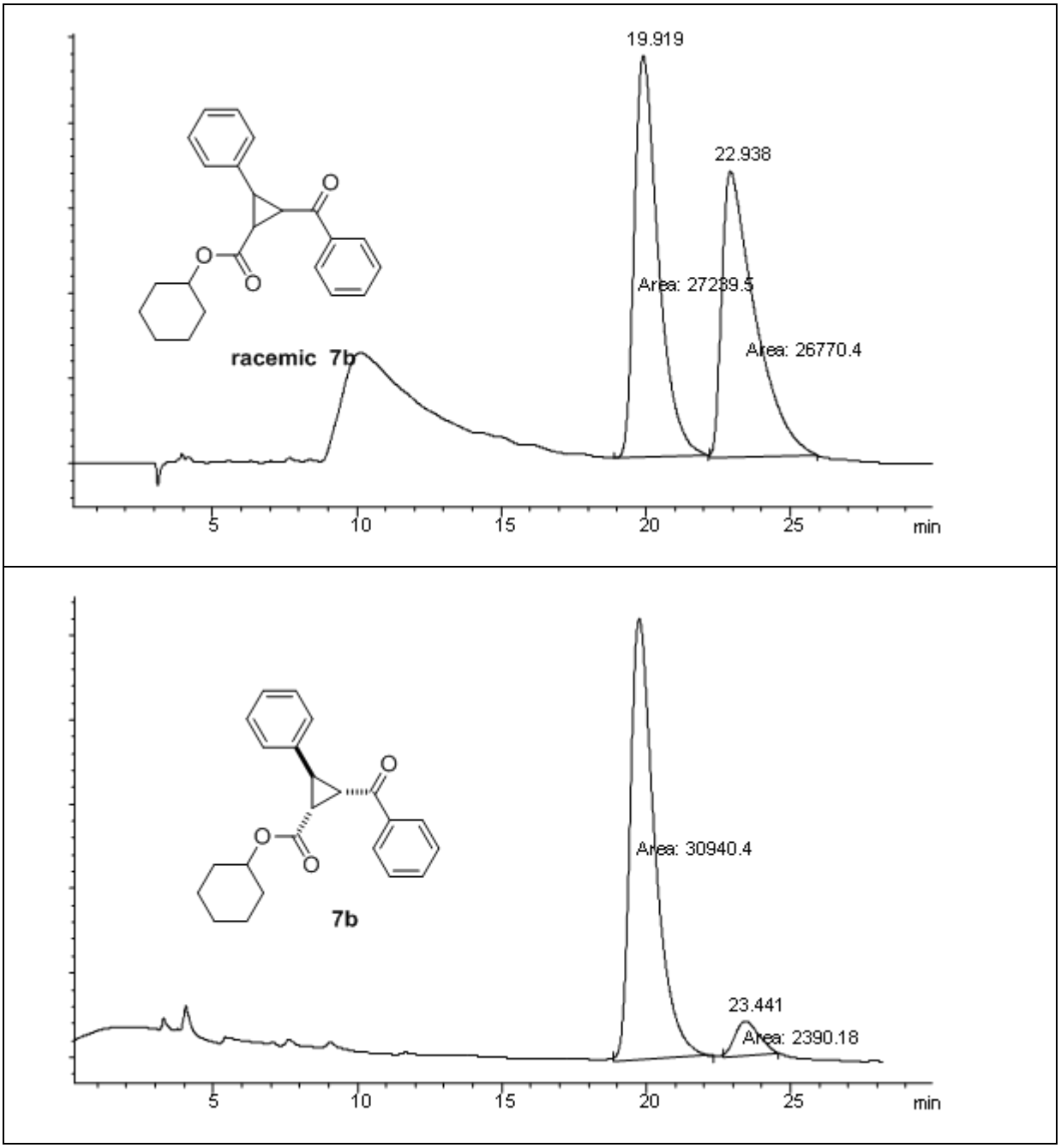


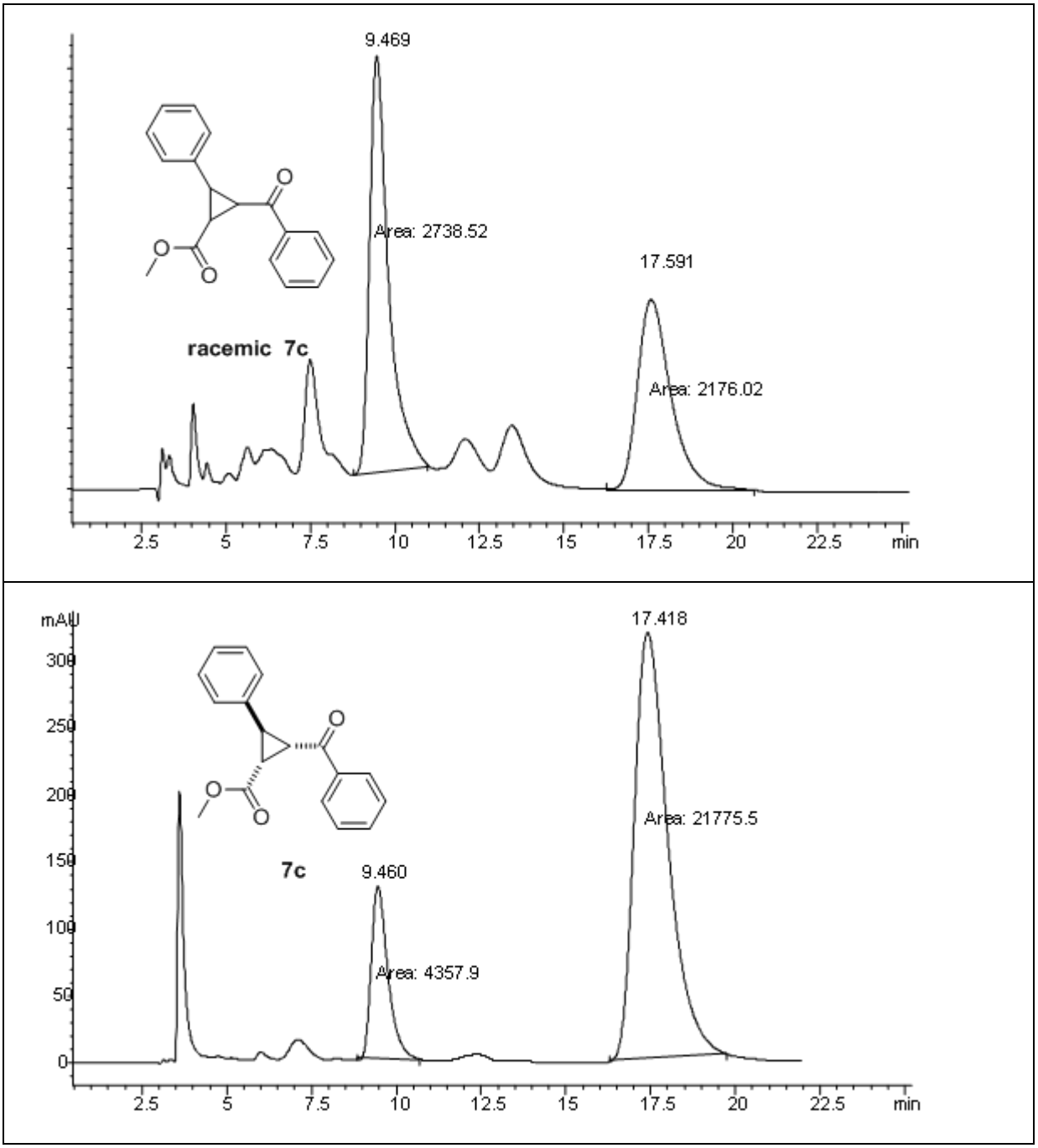

8.247
9.623
Area: 154.914
Area: 154.818
racemic 6b
8
10
12
14
16
min
8.313
Area: 358.697
6b
9.759
Area: 75.773
8
10
12
14
16
min

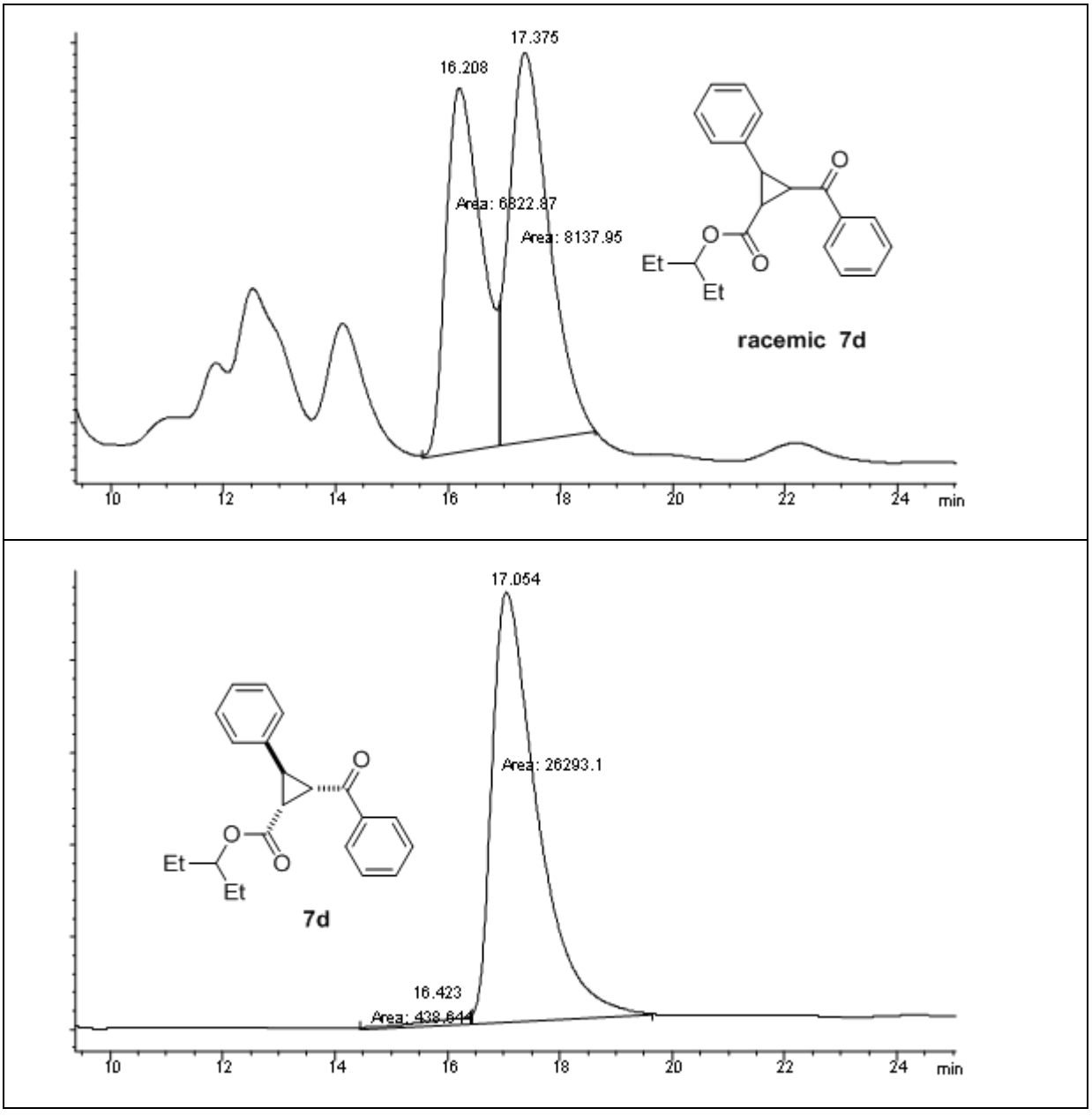

26.096
Area: 34609.1
racemic 6c
41.505
Area: 31630.1
20
25
30
35
40
45
min
42.311
6c
20
25
30
35
40
45
min

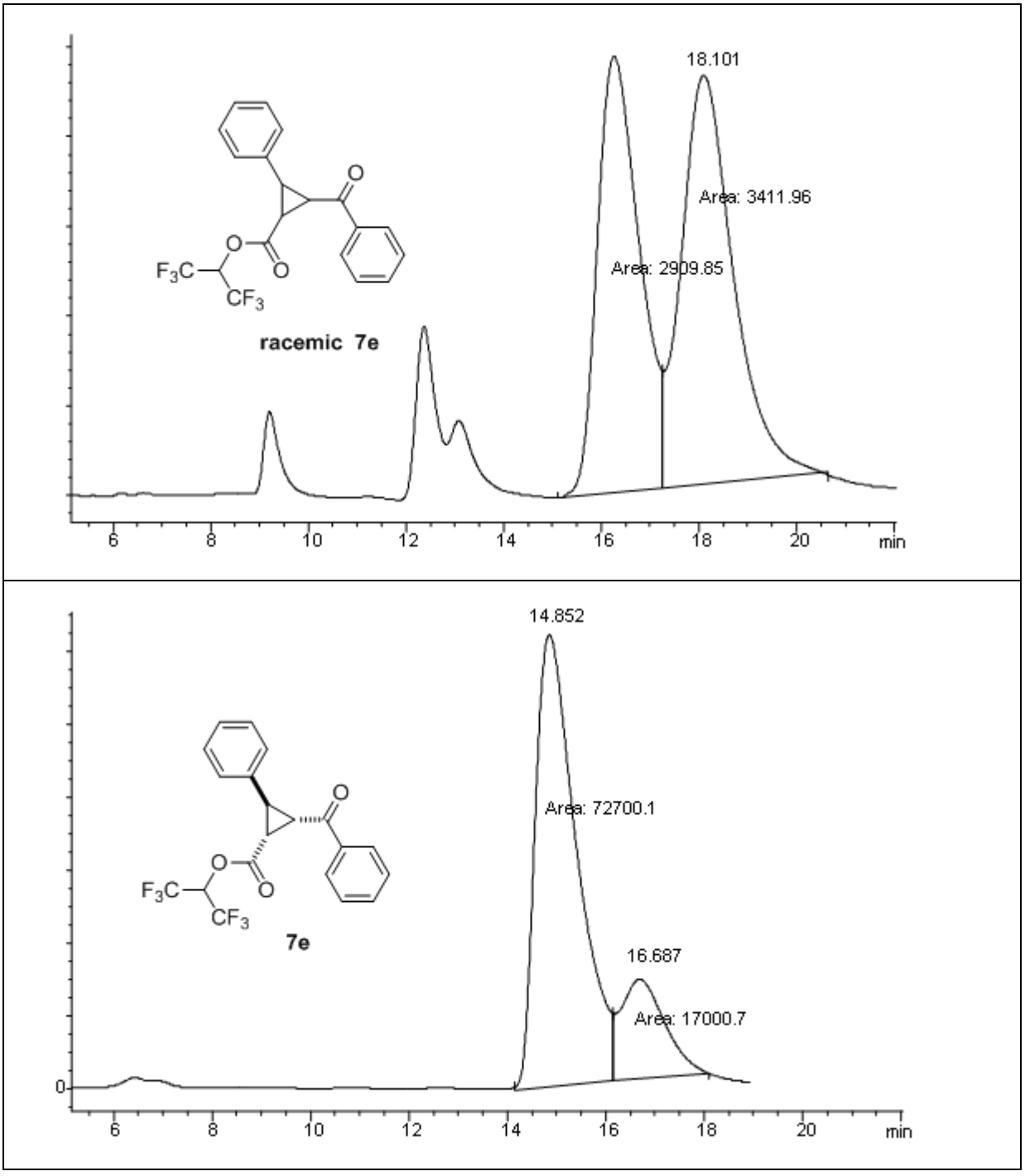

23.447
Area: 2352.43
racemic 6d
40.632
Area: 2159.35
20
25
30
35
40
min
23.602
Area: 8397.38
6d
42.481
Area: 747.213
20
25
30
35
40
min

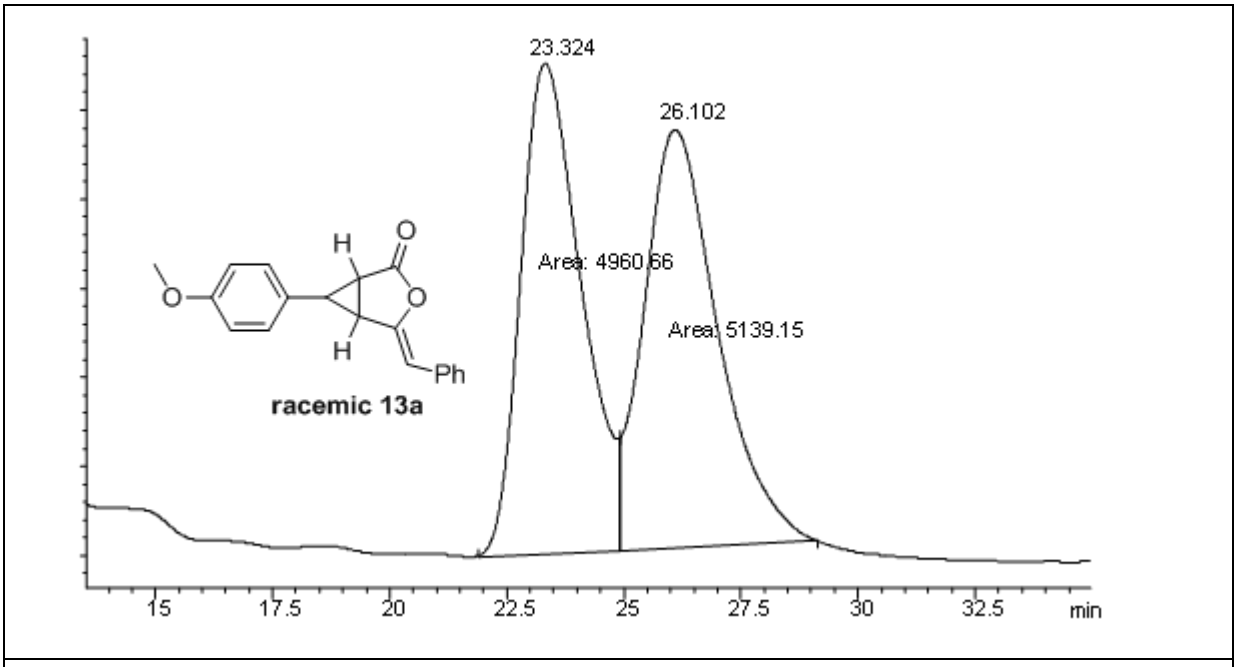


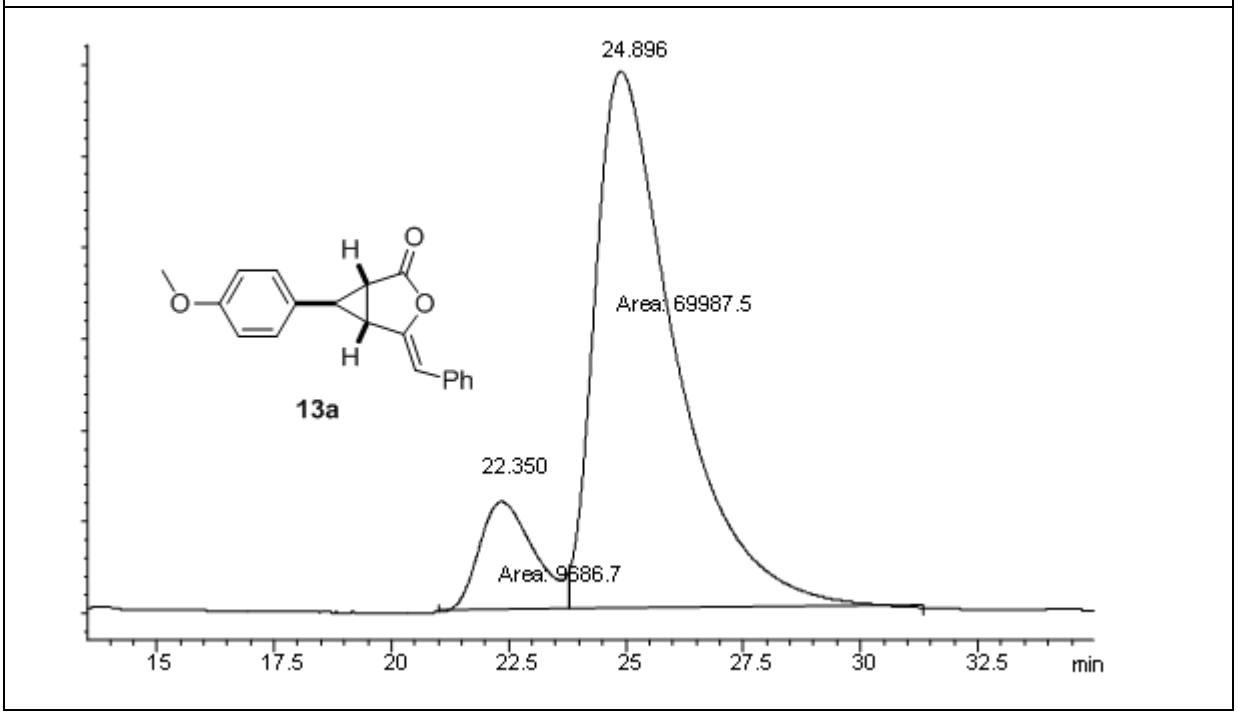

19.919
22.938
Area: 27239.5
Area: 26770.4
racemic 7b
5
10
15
20
25
min
Area: 30940.4
7b
23.441
Area: 2390.18
5
10
15
20
25
min

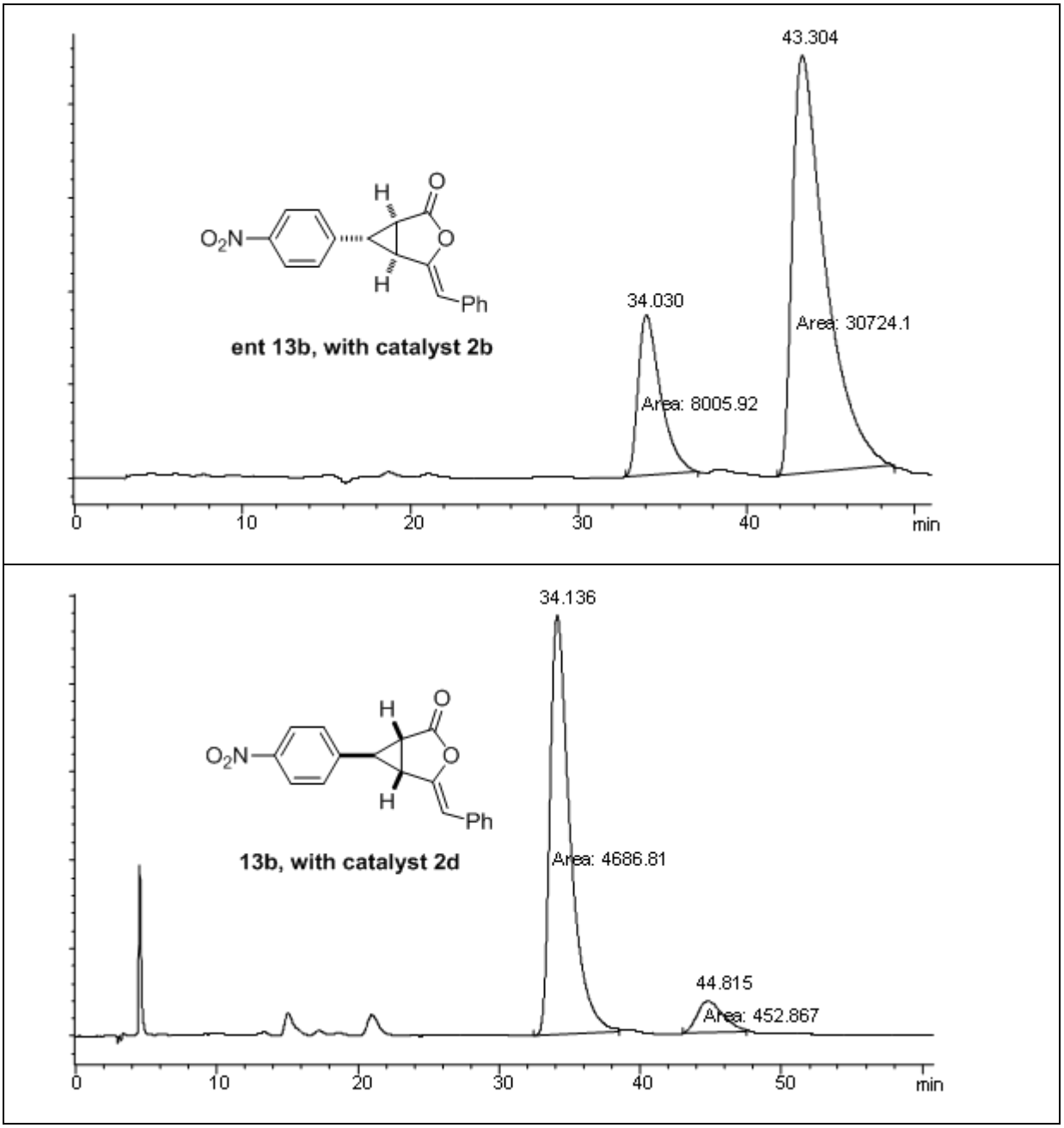


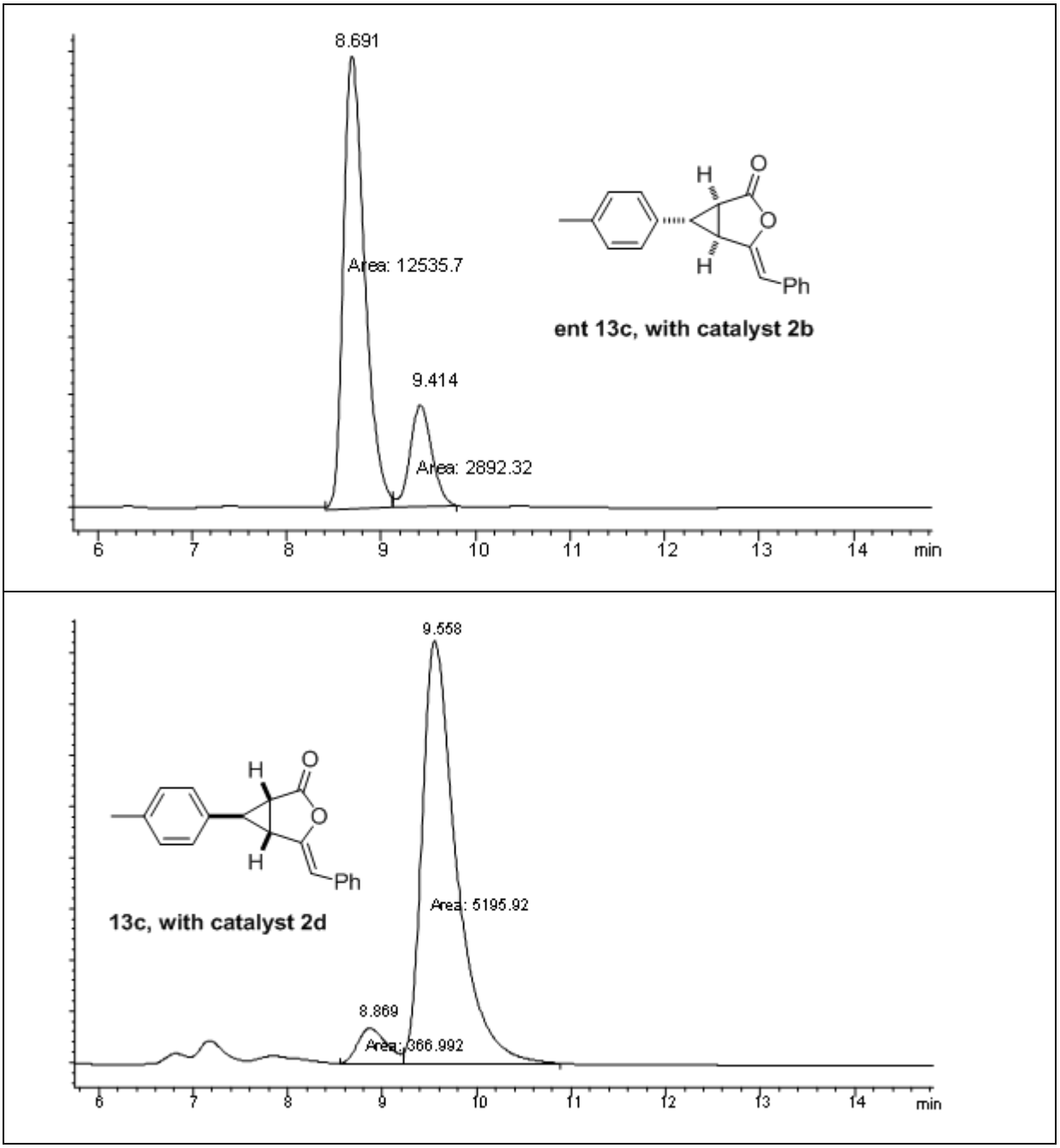

17.375
16.208
Area: 6822.87
Area: 8137.95
racemic 7d
10
12
14
16
18
20
22
24
min
17.054
Area: 26293.1
7d
16.423
Area: 438.644
10
12
14
16
18
20
22
24
min




23.324
26.102
Area: 4960.66
Area: 5139.15
racemic 13a
15
17.5
20
22.5
25
27.5
30
32.5
min


24.896
Area: 69987.5
13a
22.350
Area: 9686.7
15
17.5
20
22.5
25
27.5
30
32.5
min


43.304
34.030
Area: 30724.1
Area: 8005.92
ent 13b, with catalyst 2b
0
10
20
30
40
min
34.136
Area: 4686.81
44.815
Area: 452.867
13b, with catalyst 2d
0
10
20
30
40
50
min


8.691
Area: 12535.7
9.414
Area: 2892.32
ent 13c, with catalyst 2b
6
7
8
9
10
11
12
13
14
min
9.558
Area: 5195.92
8.869
Area: 366.992
13c, with catalyst 2d
6
7
8
9
10
11
12
13
14
min

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