Supporting Information

Asymmetric Synthesis of Complex Tricyclo[3.2.2.0]nonenes from Racemic Norcaradienes: Kinetic Resolution via Diels–Alder Reaction

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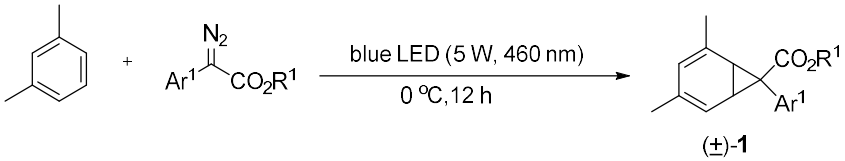
1. General

^{1}H NMR spectra were recorded on Bruker ASCEND (400 MHz or 600 MHz). Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.0; CD_3OD, 48.8). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constants (Hz), integration. $^{13}C\{^{1}H\}$ NMR data were collected on Bruker ASCEND (100 MHz or 150 MHz) with complete proton decoupling. $^{19}F\{^{1}H\}$ NMR spectra were collected on Bruker ASCEND (376 MHz or 565 MHz) with complete proton decoupling. Melting points (M.p.) were determined using OptiMelt automated melting point system. High resolution mass spectra (HRMS) analyses were recorded on Thermo Scientific Q Exactive hybrid quadrupole-Orbitrap mass spectrometer (ESI Source) and methanol were used to dissolve the sample. Enantiomeric excesses (ee) were determined by HPLC or UPC^2 analysis by using the corresponding commercial chiralpak column as stated in the experimental procedures at 25 °C, and SFC at 35 °C with PDA detector. Optical rotations were measured on a Rudolph Autopol V automatic polarimeter and are reported as follows: $[\alpha]^{T}_{\lambda}$ = (c = g/100 mL, in solvent). IR spectra were recorded on Bruker TENSOR II IR spectrophotometer. Unless otherwise indicated, reagents obtained from commercial sources were used without further purification. Solvents were dried and distilled prior to use according to the standard methods. Metal salts obtained from commercial sources were used without further purification. The chiral *N,N′*-dioxide ligands were synthesized by the same procedure in the literature.[1] (*E*)-ethyl 4-oxo-4-phenylbutenoates **3** were prepared according to literature procedure.[2] The α-diazoester were synthesized by following the literature procedure.[3] The norcaradienes were synthesized from *m*-xylene and α-diazoesters with Photoreactor following the literature procedure.[4] The β-nitroenones were synthesized following the literature procedure [5].

Note: 1,1,2,2-Tetrachloroethane is toxic by inhalation and in contact with skin, and should be used carefully.

2. Preparation of racemic norcaradienes

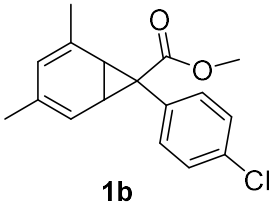
Starting materials of norcaradienes (NCDs) were prepared according to reported procedure [4]



(±)-**1**

The norcaradienes were synthesized from *m*-xylene and α-diazoesters with photoreactor following the literature procedure.[4] The reaction was conducted with *m*-xylene (6.0 mL) and the corresponding α-diazoester (0.3 mmol) in a quartz test tube and under air on the irradiation from 5 W blue LED (460 nm) at 0 °C[4]. After 12 hours, the complex was purified by column chromatography using petroleum ether/EtOAc as eluent to afford the racemic norcaradiene (±)-**1**.

1b: methyl 7-(4-chlorophenyl)-2,4-dimethylbicyclo[4.1.0]hepta-2,4-diene-7-carboxylate



1b

White solid, m.p. 82–84 °C.

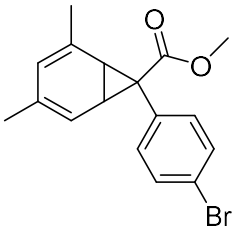
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.13 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 5.70 (d, *J* = 5.2 Hz, 1H), 5.39 (s, 1H), 3.63 (s, 3H), 3.09 (dd, *J* = 8.8, 5.6 Hz, 1H), 2.95 (d, *J* = 8.8 Hz, 1H), 2.04 (s, 3H), 1.50 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 176.8, 134.5, 134.0, 133.6, 132.4, 131.6, 127.4, 125.6, 116.8, 52.9, 41.3, 39.6, 26.0, 23.9, 21.2 ppm.

ESI-HRMS calcd for [$C_{17}H_{17}ClO_2$+Na^+] = 311.0809, 313.0780, found 311.0806, 313.0783.

IR $\tilde{\nu}$ (cm^{-1}) 2950, 1710,1493, 1433, 1335, 1237, 1090, 1015, 903, 836, 740, 560, 524, 476.

1c: methyl 7-(4-bromophenyl)-2,4-dimethylbicyclo[4.1.0]hepta-2,4-diene-7-carboxylate



1c

White solid, m.p. 115–117 °C.

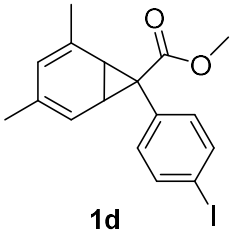
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.30 – 7.27 (m, 2H), 6.89 – 6.84 (m, 2H), 5.70 (d, *J* = 5.2 Hz, 1H), 5.40 (s, 1H), 3.63 (s, 3H), 3.11 – 3.07 (dd, *J* = 8.8, 6.4 Hz, 1H), 2.94 (d, *J* = 12.0 Hz, 1H), 2.04 (s, 3H), 1.51 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 176.7, 134.5, 134.3, 133.6, 132.2, 130.3, 125.6, 120.7, 116.8, 52.9, 41.3, 39.6, 26.1, 23.9, 21.2 ppm.

ESI-HRMS calcd for [$C_{17}H_{17}BrO_2$+Na^+] = 355.0304, 356.0338, 357.0284, found 355.0306, 356.0341, 357.0280.

IR $\tilde{\nu}$ (cm^{-1}) 2949, 1710, 1487, 1433, 1394, 1334, 1236, 1162, 1070, 1010, 970, 903, 807, 763, 738, 710, 555, 433.

1d: **methyl 7-(4-iodophenyl)-2,4-dimethylbicyclo[4.1.0]hepta-2,4-diene-7-carboxylate**



1d

White solid, m.p. 127–128 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.48 (d, *J* = 8.4 Hz, 2H), 6.74 (d, *J* = 8.4 Hz, 2H), 5.70 (d, *J* = 5.2 Hz, 1H), 5.40 (s, 1H), 3.62 (s, 3H), 3.13 – 3.04 (dd, *J* = 8.8, 5.6 Hz, 1H), 2.94 (d, *J* = 8.0 Hz, 1H), 2.03 (s, 3H), 1.51 (s, 3H) ppm.

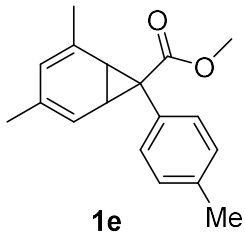
^{13}C NMR (101 MHz, $CDCl_3$) δ = 176.7, 136.37, 134.6, 134.5, 133.6, 132.9, 125.7,

116.8, 92.6, 52.9, 41.3, 39.7, 26.3, 23.9, 21.3 ppm.

ESI-HRMS calcd for [$C_{17}H_{17}BrO_2$+Na^+] = 403.0165, found 403.0163.

IR $\tilde{\nu}$ (cm^{-1}) 2949, 1710, 1493, 1433, 1335, 1237, 1090, 1015, 903, 836, 740, 560, 524, 476.

1e: methyl 2,4-dimethyl-7-(p-tolyl)bicyclo[4.1.0]hepta-2,4-diene-7-carboxylate



1e

White solid, m.p. 101–103 °C.

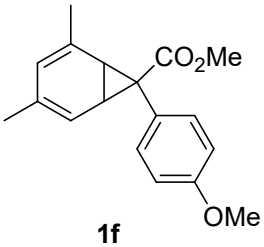
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 6.97 (d, *J* = 7.9 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 2H), 5.71 (d, *J* = 5.2 Hz, 1H), 5.39 (s, 1H), 3.63 (s, 3H), 3.09 (dd, *J* = 8.4, 5.6 Hz, 1H), 2.95 (d, *J* = 8.6 Hz, 1H), 2.28 (s, 3H), 2.04 (s, 3H), 1.50 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 177.5, 136.1, 134.2, 133.7, 132.3, 130.0, 127.8, 125.4, 117.1, 52.8, 41.9, 40.2, 26.5, 23.9, 21.3, 21.3 ppm.

ESI-HRMS calcd for [$C_{18}H_{20}O_2$+Na^+] = 291.1356, found 291.1359.

IR $\tilde{\nu}$ (cm^{-1}) 2949, 1709, 1517, 1433, 1335, 1238, 1002, 812, 714, 601, 546.

1f: methyl 7-(4-methoxyphenyl)-2,4-dimethylbicyclo[4.1.0]hepta-2,4-diene-7-carboxylate



1f

White solid, m.p. 72–73 °C.

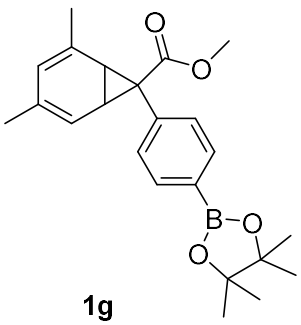
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 6.91 (d, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 8.0 Hz, 2H), 5.70 (d, *J* = 4.0 Hz, 1H), 5.39 (s, 1H), 3.75 (s, 3H), 3.63 (s, 3H), 3.07 (dd, *J* = 8.8, 5.6 Hz, 1H), 2.93 (d, *J* = 8.0 Hz, 1H), 2.04 (s, 3H), 1.50 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 177.6, 158.1, 134.3, 133.7, 133.6, 125.4, 125.1, 117.0, 112.5, 55.0, 52.8, 41.5, 39.9, 26.0, 23.9, 21.3 ppm.

ESI-HRMS calcd for [$C_{18}H_{20}O_3$+Na^+] = 307.1305, found 307.1307.

IR $\tilde{\nu}$ (cm^{-1}) 2950, 1705, 1611, 1513, 1434, 1335, 1291, 1232, 1174, 1107, 1032, 969, 902, 835, 813, 765, 738, 658, 626, 603, 555.

1g: methyl2,4-dimethyl-7-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)bicyclo[4.1.0]-hepta-2,4-diene-7-carboxylate



1g

White solid, m.p. 115–118 °C.

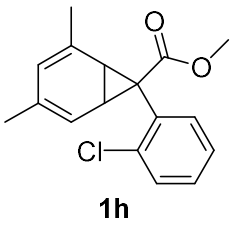
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.61 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 5.72 (d, *J* = 5.2 Hz, 1H), 5.36 (s, 1H), 3.61 (s, 3H), 3.11 (dd, *J* =8.8, 5.6 Hz, 1H), 2.97 (d, *J* = 12.0 Hz, 1H), 2.04 (s, 3H), 1.48 (s, 3H), 1.32 (s, 12H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 177.1, 136.4, 135.2, 134.3, 133.6, 133.5, 132.0, 129.7, 127.4, 125.5, 117.0, 83.7, 52.9, 41.8, 40.1, 26.9, 25.0, 24.9, 24.9, 23.8, 21.3 ppm.

ESI-HRMS calcd for [$C_{23}H_{29}BO_4$+Na^+] = 402.2087, found 403.2051.

IR $\tilde{\nu}$ (cm^{-1}) 2977, 1710, 1611, 1433, 1396, 1357, 1318, 1238, 1143, 1089, 1020, 962, 903, 857, 736, 658, 557.

1h: methyl 7-(2-chlorophenyl)-2,4-dimethylbicyclo[4.1.0]hepta-2,4-diene-7-carboxylate



1h

White solid, m.p. 105–108 °C.

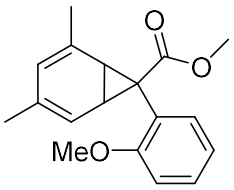
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.27 (d, *J* = 7.0 Hz, 1H), 7.11 (m, 1H), 7.04 – 6.92 (m, 2H), 5.80 (d, *J* = 4.8 Hz, 1H), 5.46 (s, 1H), 3.66 (s, 3H), 3.11 (m, 1H), 3.04 – 2.89 (m, 1H), 2.15 (s, 3H), 1.47 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 176.4, 137.0, 134.2, 131.2, 129.8, 129. 3, 128.2, 125.5, 125.0, 116.5, 52.9, 39.7, 38.5, 24.8, 24.2 21.1 ppm.

ESI-HRMS calcd for [$C_{17}H_{17}ClO_2$+Na^+] = 311.0809, 313.0780, found 311.0806, 313.0783.

IR $\tilde{\nu}$ (cm^{-1}) 2950, 1712, 1597, 1433, 1332, 1240, 1076, 794, 735, 693, 575.

1i: methyl 7-(2-methoxyphenyl)-2,4-dimethylbicyclo[4.1.0]hepta-2,4-diene-7-carboxylate



1i

White solid, m.p. 65–68 °C.

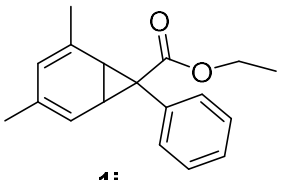
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.15 (m, 1H), 6.87 (d, *J* = 6.4 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.71 (m, 1H), 5.69 (d, *J* = 4.4 Hz, 1H), 5.35 (s, 1H), 3.75 (s, 3H), 3.63 (s, 3H), 2.99 (dd, *J* = 8.8, 5.2 Hz, 1H), 2.92 (d, *J* = 8.8 Hz, 1H), 2.03 (s, 3H), 1.48 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 177.6, 159.1, 134.1, 128.2, 124.4, 121.1, 118.8, 116.8, 110.0, 55.0, 52.7, 39.6, 37.4, 23.6, 22.1, 21.2 ppm.

ESI-HRMS calcd for [$C_{18}H_{20}O_3$+Na^+] = 307.1305, found 307.1307.

IR $\tilde{\nu}$ (cm^{-1}) 2948, 1708, 1601, 1495, 1434, 1335, 1235, 1161, 1120, 1029, 818, 752, 659, 536.

1j: ethyl 2,4-dimethyl-7-phenylbicyclo[4.1.0]hepta-2,4-diene-7-carboxylate



1j

Colorless oil.

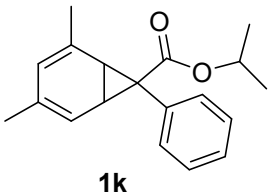
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.15 (m, 3H), 7.03 – 6.98 (m, 2H), 5.73 (d, *J* = 4.0 Hz, 1H), 5.38 (s, 1H), 4.10 (q, *J* = 8.0 Hz, 2H), 3.14 (dd, *J* = 8.4, 5.6 Hz, 1H), 3.00 (d, *J* = 8.0 Hz, 1H), 2.06 (s, 3H), 1.49 (s, 3H), 1.13 (m, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 175.6, 133.1, 132.7, 132.4, 131.4, 125.9, 125.5, 124.3, 116.2, 60.3, 41.5, 39.9, 26.4, 22.8, 20.2, 13.2 ppm.

ESI-HRMS calcd for [$C_{18}H_{20}O_2$+Na^+] = 305.1512, found 305.1511.

IR $\tilde{\nu}$ (cm^{-1}) 2975, 1704, 1446, 1366, 1333, 1230, 1160, 1070, 1027, 956, 911, 808, 735, 697, 663, 641, 553.

1k: isopropyl 2,4-dimethyl-7-phenylbicyclo[4.1.0]hepta-2,4-diene-7-carboxylate



1k

Yellow oil.

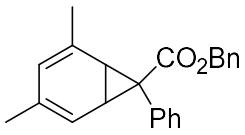
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.14 (m, 3H), 7.04 – 6.97 (m, 2H), 5.73 (d, *J* = 5.6 Hz, 1H), 5.39 (s, 1H), 4.99 – 4.91 (m, 1H), 3.18 (m, 1H), 3.03 (d, *J* = 8.2 Hz, 1H), 2.05 (s, 3H), 1.50 (s, 3H), 1.11 (m, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 175.9, 134.1, 133.8, 132.3, 130.0, 129.8, 128.9, 128.5, 127.9, 126.9, 126.4, 125.4, 117.5, 68.5, 42.6, 39.9, 23.9, 21.7, 21.3 ppm.

ESI-HRMS calcd for [$C_{19}H_{22}O_2$+Na^+] = 305.1512, found 305.1511.

IR $\tilde{\nu}$ (cm^{-1}) 2978, 1701, 1448, 1373, 1241, 1178, 1107, 965, 812, 781, 698, 556.

1l: benzyl 2,4-dimethyl-7-phenylbicyclo[4.1.0]hepta-2,4-diene-7-carboxylate



1l

Colorless oil.

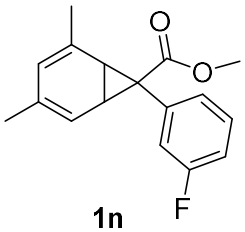
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.24 (s, 3H), 7.15 (m, 3H), 7.12 – 7.06 (m, 2H), 7.05 – 6.98 (m, 2H), 5.72 (d, *J* = 4.0 Hz, 1H), 5.38 (s, 1H), 5.08 (s, 2H), 3.15 (dd, *J* = 8.4, 5.6 Hz, 1H), 3.01 (d, *J* = 8.0 Hz, 1H), 2.04 (s, 3H), 1.48 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 175.4, 135.3, 133.3, 132.7, 132.2, 131.4, 127.3, 126.6, 126.0, 125.9, 125.60, 124.5, 116.1, 65.5, 41.5, 40.0, 26.4, 22.8, 20.2 ppm.

ESI-HRMS calcd for [$C_{23}H_{22}O_2$+Na^+] = 353.1512, found 353.1511.

IR $\tilde{\nu}$ (cm^{-1}) 3029, 1706, 1497, 1448, 1375, 1226, 1072, 966, 817, 736, 697, 664, 551.

1n: methyl 7-(3-fluorophenyl)-2,4-dimethylbicyclo[4.1.0]hepta-2,4-diene-7-carboxylate



1n

White solid, m.p.78–81 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.12 (m, 1H), 6.85 (m, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.71 (m, 1H), 5.72 (d, *J* = 5.2 Hz, 1H), 5.41 (s, 1H), 3.63 (s, 3H), 3.13 (dd, *J* = 8.4, 5.6 Hz, 1H), 2.98 (d, *J* = 8.0 Hz, 1H), 2.05 (s, 3H), 1.51 (s, 3H) ppm.

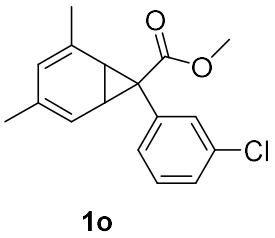
^{13}C NMR (101 MHz, $CDCl_3$) δ = 176.6, 163.0, 160.5, 135.5 (d, $J_{C\text{-}F}$ = 8.0 Hz), 134.49, 133.58, 128.3, 128.24 (d, $J_{C\text{-}F}$ = 8.0 Hz), 125.6, 119.4 (d, $J_{C\text{-}F}$ = 21.1 Hz), 116.9, 113.67 (d, $J_{C\text{-}F}$ = 20.9 Hz), 52.9, 42.0, 40.5, 26.6, 23.9, 21.2 ppm.

^{19}F NMR (377 MHz, $CDCl_3$) δ = -114.81 ppm.

ESI-HRMS calcd for [$C_{17}H_{17}FO_2$+Na^+] = 295.1110, found 295.1113,

IR $\tilde{\nu}$ (cm^{-1}) 2951, 1712, 1614, 1587, 1490, 1437, 1336, 1242, 1205, 983, 801, 760, 693.

1o: methyl 7-(3-chlorophenyl)-2,4-dimethylbicyclo[4.1.0]hepta-2,4-diene-7-carboxylate



1o

White solid, m.p.78–80 °C.

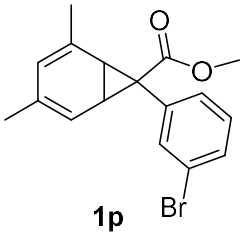
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.17 – 7.05 (m, 2H), 6.98 (s, 1H), 6.91 – 6.84 (m, 1H), 5.73 (d, *J* = 5.2 Hz, 1H), 5.41 (s, 1H), 3.64 (s, 3H), 3.11 (dd, *J* = 8.8, 5.6 Hz, 1H), 2.96 (d, *J* = 8.8 Hz, 1H), 2.05 (s, 3H), 1.51 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 176.6, 135.1, 134.6, 133.6, 132.8, 132.4, 130.8, 128.3, 126.9, 125.6, 116.8, 52.9, 41.6, 40.0, 26.4, 23.8, 21.2 ppm.

ESI-HRMS calcd for [$C_{17}H_{17}ClO_2$+Na^+] = 311.0809, 313.0780, found 311.0806, 313.0783.

IR $\tilde{\nu}$ (cm^{-1}) 2949, 1709, 1568, 1433, 1332, 1235, 1162, 1075, 1001, 974, 903, 817, 793, 733, 692.

1p: methyl 7-(3-bromophenyl)-2,4-dimethylbicyclo[4.1.0]hepta-2,4-diene-7-carboxylate



1p

White solid, m.p.107–110 °C.

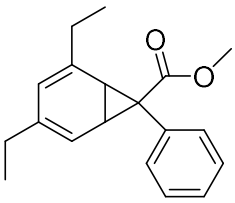
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.31 – 7.26 (m, 1H), 7.13 (m, 1H), 7.04 (m, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 5.73 (d, *J* = 5.2 Hz, 1H), 5.41 (s, 1H), 3.64 (s, 3H), 3.10 (dd, *J* = 8.4, 5.6 Hz, 1H), 2.96 (d, *J* = 8.0 Hz, 1H), 2.05 (s, 3H), 1.52 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 176.5, 135.7, 135.3, 134.6, 133.6, 131.3, 129.8, 128.6, 125.6, 120.4, 116.8, 52.9, 41.6, 39.9, 26.3, 23.8, 21.2 ppm.

ESI-HRMS calcd for [$C_{17}H_{17}BrO_2$+Na^+] = 355.0304, 356.0338, 357.0284, found 355.0306, 356.0341, 357.0280.

IR $\tilde{\nu}$ (cm^{-1}) 2949, 1711, 1564, 1433, 1332, 1239, 1065, 1000, 819, 792, 719, 692.

1q: methyl 2,4-diethyl-7-phenylbicyclo[4.1.0]hepta-2,4-diene-7-carboxylate



1q

Colorless oil.

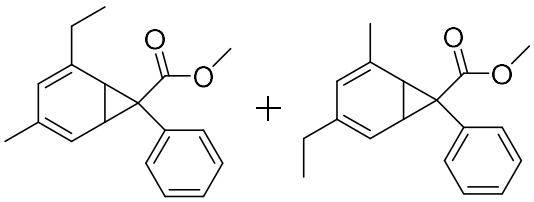
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.16 – 7.11 (m, 3H), 7.01 (m, 2H), 5.72 (d, *J* = 5.4 Hz, 1H), 5.41 (s, 1H), 3.64 (s, 3H), 3.17 (m, 1H), 3.07 (d, *J* = 8.6 Hz, 1H), 2.50 – 2.34 (m, 2H), 1.83 (m, 2H), 1.17 (t, *J* = 7.6 Hz, 3H), 0.58 (t, *J* = 7.6 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 177.3, 140.3, 139.2, 133.1, 132.8, 126.9, 126.6, 122.6, 122.6, 116.4, 116.4, 52.8, 52.8, 41.9, 40.7, 30.4, 28.8, 27.0, 13.0, 12.0 ppm.

ESI-HRMS calcd for [$C_{19}H_{22}O_2$+H^+] = 283.1693, found 283.1694.

IR $\tilde{\nu}$ (cm^{-1}) 2963, 1707, 1496, 1432, 1334, 1158, 1029, 923, 826, 735, 698.

1r: Regio-isomer mixture: **methyl 2-ethyl-4-methyl-7-phenylbicyclo[4.1.0]hepta-2,4-diene-7-carboxylate** and **methyl 4-ethyl-2-methyl-7-phenylbicyclo[4.1.0]hepta-2,4-diene-7-carboxylate**



1r

White solid, the mixture cannot be separated due to the same Rf value.

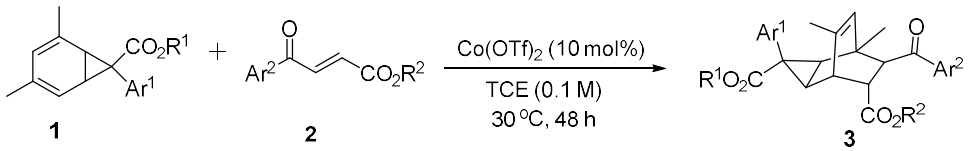
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.20 – 7.12 (m, 3H), 7.06 – 6.96 (m, 2H), 5.73 (m, 1H), 5.42 (s, 0.5 H), 5.37 (s, 0.5 H), 3.63 (d, *J* = 1.6 Hz, 3H), 3.15 (m, 1H), 3.07 (d, *J* = 8.6 Hz, 0.5 H), 2.98 (d, *J* = 8.6 Hz, 0.5 H), 2.51 – 2.30 (m, *J* = 7.9 Hz, 1H), 2.09 (s, 1.5 H), 1.89 – 1.74 (m, 1H), 1.51 (s, 1.5 H), 1.15 (t, *J* = 7.6 Hz, 1.5 H), 0.58 (t, *J* = 7.6 Hz, 1.5 H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 177.3, 177.2, 140.3, 139.1, 134.3, 133.8, 133.2, 133.0, 132.7, 132.7, 127.0, 126.9, 126.6, 126.6, 124.6, 124.6, 123.4, 123.4, 117.5, 116.0, 52.8, 52.8, 42.1, 41.7, 41.1, 39.8, 30.2, 28.7, 27.2, 26.7, 24.0, 21.3, 13.0, 12.0 ppm.

ESI-HRMS calcd for [$C_{18}H_{20}O_2$+Na^+] = 291.1361, found 291.1363.

3.General procedure for the preparation of the racemic products

General procedure for the preparation of the racemic tricyclo[3.2.2.0]nonene via Diels-Alder reaction of 4-oxo-4-arylbutenoates



A dry reaction tube was charged with $Co(OTf)_2$ (1.8 mg, 10 mol%), norcaradiene **1** (0.10 mmol), (*E*)-4-oxo-4-arylbutenoate **2** (0.05 mmol), followed by adding dry CCl_2HCCl_2H (1,1,2,2-Tetrachloroethane, TCE, 0.5 mL) under air atmosphere. The mixture was stirred for 48 h at 30 °C. Last, the reaction mixture was subjected to column chromatography on silica gel with eluent (petroleum ether /ethyl acetate = 10:1) to afford the racemic product **3.**

For the preparation of the racemic sample of 3ah, 3aj, 3ak, 3aq, 3ba, 3ca, 3da, and **3ea**

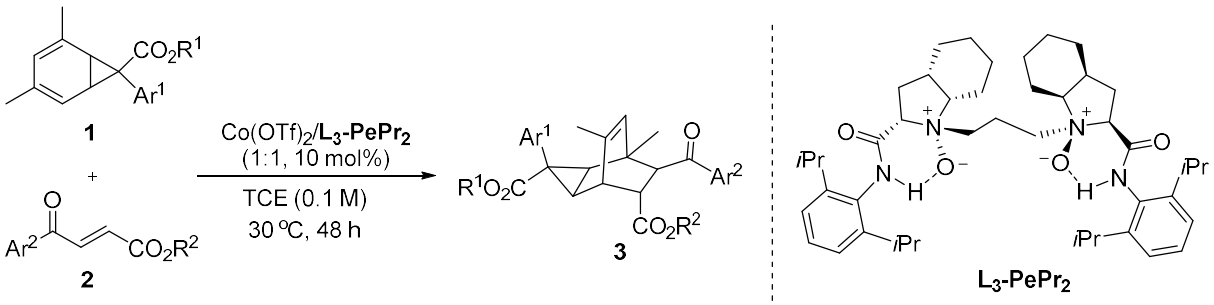
A dry reaction tube was charged with racemic ligand (±)-**L_3-PiPr$_2$** (3.3 mg, 10 mol%), $Co(OTf)_2$ (1.8 mg, 10 mol%), norcaradiene **1** (0.10 mmol), (*E*)-4-oxo-4-arylbutenoate **2** (0.05 mmol), followed by adding dry CCl_2HCCl_2H (1,1,2,2-Tetrachloroethane, TCE, 0.5 mL) under N_2 atmosphere. The mixture was stirred for 48 h at 30 °C. Last, the reaction mixture was subjected to column chromatography on silica gel with eluent (petroleum ether/ethyl acetate = 10:1) to afford the related racemic product **3.**

For the preparation of the racemic bicyclo[2,2,2]octene-based dienes 5

A dry reaction tube was charged with racemic ligand (±)-**L_3-PiPr$_2$** (6.5 mg, 10 mol%), $Co(OTf)_2$ (3.6 mg, 10 mol%), norcaradiene **1** (0.20 mmol), β-nitroenone **4** (0.10 mmol), followed by adding dry CH_2Cl_2 (1.0 mL) under N_2 atmosphere. The mixture was stirred at -10 °C. After reacted for 12 hours, added DBU (0.15 mmol) and continue to react for another 12 hours. Last, the reaction mixture was subjected to column chromatography on silica gel with eluent (petroleum ether /ethyl acetate = 10:1) to afford the corresponding product **5**.

4. General procedure for the asymmetric Diels–Alder reaction

Experimental procedure for the asymmetric Diels–Alder reaction of 4-oxo-4-arylbutenoates



A dry reaction tube was charged with chiral *N,N'*-dioxide ligand **L_3-PePr$_2$** (7.3mg, 10 mol%), $Co(OTf)_2$ (3.6 mg, 10 mol%), norcaradiene **1** (0.20 mmol), (*E*)-4-oxo-4-arylbutenoate **2** (0.10 mmol), followed by adding CCl_2HCCl_2H (1.0 mL) under air atmosphere. The mixture was stirred for 48 h at 30 °C. Last, the reaction mixture was subjected to column chromatography on silica gel with eluent (petroleum ether /ethyl acetate = 10:1) to afford the corresponding product **3**.

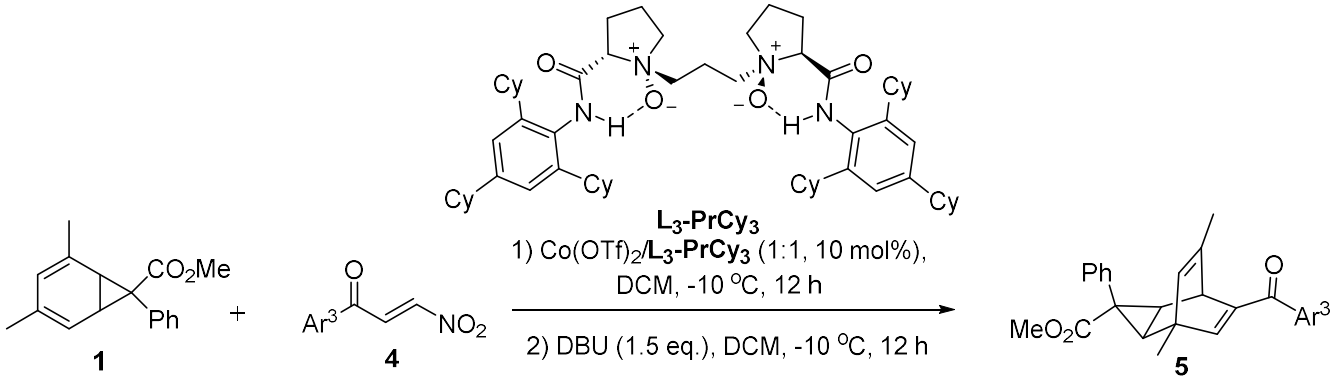
Experimental procedure for the synthesis of 3aj

A dry reaction tube was charged with ethyl (*E*)-4-(4-nitrophenyl)-4-oxobut-2-enoate **2j** (0.10 mmol), ligand **L_3-$PePr_2$** (7.3 mg, 10 mol%), $Co(OTf)_2$ (3.6 mg, 10 mol%), followed by adding dry CH_2Cl_2 (0.5 mL) under N_2 atmosphere. The CH_2Cl_2 was removed in vacuo after the mixture was stirred at 30 °C for 0.5 h. Norcaradiene **1a** (0.20 mmol) was added to the reaction tube, followed by the addition of dry CCl_2HCCl_2H (1.0 mL) under N_2 atmosphere, and the reaction mixture continued stirring at 30 °C for 72 h. Last, the reaction mixture was subjected to column chromatography on silica gel with eluent (petroleum ether /ethyl acetate = 10:1) to afford the corresponding product **3aj**.

Experimental procedure for the scale-up synthesis of 3aa

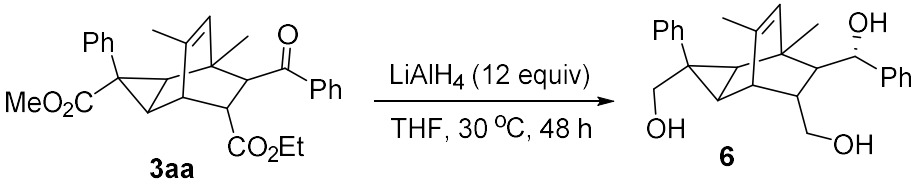
A dry reaction tube was charged with the ligand **L_3-$PePr_2$** (2.5 mmol, 182.5 mg), $Co(OTf)_2$ (10 mol%, 89.3 mg), (*E*)-ethyl 4-oxo-4-phenylbutenoate **2a** (2.5 mmol, 510 mg) and the norcaradiene **1a** (5.0 mmol, 1.27 g), followed by adding dry CCl_2HCCl_2H (25 mL). The mixture was stirred at 30 °C for 48 hours, and then subjected to column chromatography on silica gel with eluent (petroleum ether /ethyl acetate = 10:1) to afford the product **3aa** (0.92 g, 80% yield, >19:1 dr, 91% ee).

Experimental procedure for the asymmetric Diels–Alder reaction of β-nitroenones



A dry reaction tube was charged with ligand **L_3-$PrCy_3$** (9.5 mg, 10 mol%), $Co(OTf)_2$ (3.6 mg, 10 mol%), β-nitroenone **4** (0.10 mmol), followed by adding dry CH_2Cl_2 (0.5 mL) under N_2 atmosphere. The CH_2Cl_2 was removed in vacuo after the mixture was stirred at 30 °C for 0.5 h. Norcaradiene **1a** (0.20 mmol) was added to the reaction tube, followed by the addition of dry CH_2Cl_2 (1.0 mL) under N_2 atmosphere, and the reaction mixture continued stirring at -10 °C. After reacted for 12 hours, added DBU (0.15 mmol) and continue to react for another 12 hours. Last, the reaction mixture was subjected to column chromatography on silica gel with eluent (petroleum ether /ethyl acetate = 10:1) to afford the corresponding product **5**.

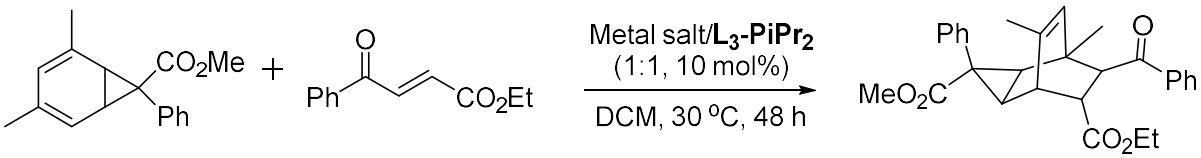
Experimental procedure for the further transformations.



The tricyclo[3.2.2.0]nonene **3aa** (1.0 mmol) was dissolved in the dry THF (1.0 mL) at the nitrogen atmosphere. Then this solution was added slowly to the dry reaction tube charged with $LiAlH_4$ (12.0 mmol) in the nitrogen atmosphere. The mixture was stirred at 30 °C for 48 hours and the reaction mixture was subjected to column chromatography on silica gel with eluent (petroleum ether /ethyl acetate = 3:1) to afford the derivative **6** (27.7mg, 71% yield).

5. Optimization of the reaction conditions

Table S1. Effect of the metal salts[a]

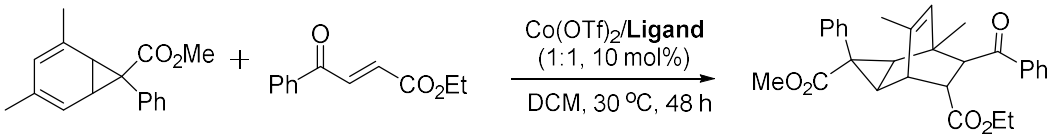


1a **2a** **3aa**

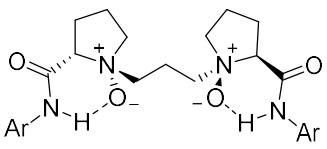
entry	Metal salt	Yield (%)[b]	dr [c]	ee (%)[d]
1	$La(OTf)_3$	trace	10:1	13/0
2	$Ce(OTf)_3$	trace	4:1	0/13
3	$Pr(OTf)_3$	trace	1:1	9/ 25
4	$Nd(OTf)_3$	trace	3:2	4/7
5	$Sm(OTf)_3$	trace	1:3	0/0
6	$Eu(OTf)_3$	trace	1:2	0/33
7	$Gd(OTf)_3$	trace	1:2	9/17
8	$Tb(OTf)_3$	trace	4:1	9/41
9	$Dy(OTf)_3$	trace	7:3	13/37
10	$Ho(OTf)_3$	trace	4:1	15/39
11	$Er(OTf)_3$	trace	3:1	39/33
12	$Tm(OTf)_3$	trace	3:1	17/35
13	$Al(OTf)_3$	trace	1:1	0/0
14	$In(OTf)_3$	trace	1:2	0/0
15	$Ca(OTf)_2$	trace	1:1	0/0
16	$Ba(OTf)_2$	trace	1:1	0/0
17	**$Co(OTf)_2$**	**26**	**19:1**	**35**
18	$Mg(OTf)_2$	trace	-	-
19	$Sc(OTf)_2$	27	19:1	27
20	$Ni(OTf)_2$	-	-	-
21	$Cu(OTf)_2$	-	-	-
22	$Zn(OTf)_2$	38	19:1	17
23	$Fe(OTf)_2$	-	-	-
24	$Fe(OTf)_3$	-	-	-
25	$Y(OTf)_3$	5	1:4	19/39
26	$Yb(OTf)_3$	30	1:3	30/30

[a]Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), **2a** (0.1 mmol), and metal salt/**L_3–PiPr$_2$** (1:1, 10 mol%) in DCM (1.0 mL) at 30 °C for 24 h. [b]Isolated yield of **3aa**. [c]Determined by ^{1}H NMR. [d]Determined by HPLC on a chiral stationary phase.

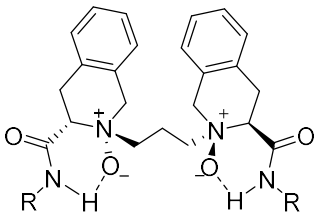
Table S2. Effect of the Ligand[a]



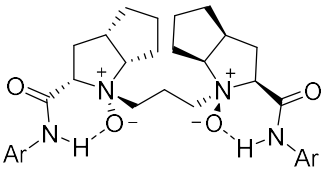
1a **2a** **3aa**



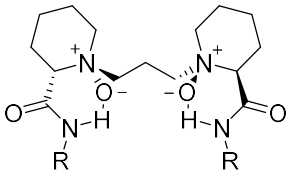
L_3-PrPr$_2$: Ar = 2,6-*i*Pr$_2$C$_6$H$_3$
L_3-PiEt$_3$: Ar = 2,4,6-*i*Pr$_3$C$_6$H$_2$



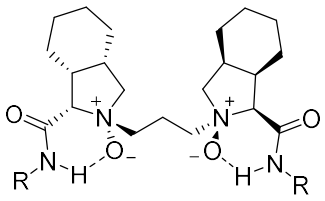
L_3-TQ-^{t}Bu: R = tert-butyl
L_3-TQ-Ad : R = adamantyl



L_3-RaMe$_2$: Ar = 2,6-Me$_2$C$_6$H$_3$
L_3-RaEt$_2$: Ar = 2,6-Et$_2$C$_6$H$_3$
L_3-RaPr$_2$: Ar = 2,6-*i*Pr$_2$C$_6$H$_3$
L_3-RaEt$_2$Me:Ar = 2,6-Et$_2$-4-Me-C$_6$H
L_3-Ra(OBu)$_2$: Ar = 2,6-(OBu)$_2$C$_6$H$_2$

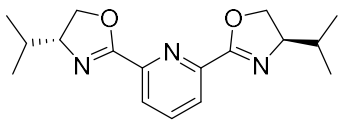


L_3-PiPr$_2$: R= 2,6-*i*Pr$_2$C$_6$H$_3$
L_3-Pi-Cy: R= cyclohexyl
L_3-Pi-(CH)$_2$Ph R = CH$_2$C$_6$H$_5$

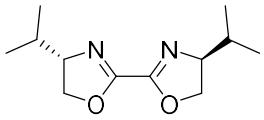


L_3-PePh: R = C$_6$H$_5$
L_3-PeMe$_2$: R = 2,6-Me$_2$C$_6$H$_3$
L_3-PeEt$_2$: R = 2,6-Et$_2$C$_6$H$_3$
L_3-PeMe$_3$: R = 2,4,6-Me$_3$C$_6$H$_2$
L_3-Pe-^{t}Bu: R = tert-butyl

L_3-PePr$_2$: R = 2,6-*i*Pr$_2$C$_6$H$_3$
L_3-PePr$_3$: R = 2,4,6-*i*-Pr$_2$C$_6$H$_2$
L_3-PeO^{i}Pr R = 2,6-O*i*PrC$_6$H$_3$
L_3-PePr$_2$Ad: R = 2,6-*i*Pr$_2$-4-Ad-C$_6$H$_2$
L_3-PePr$_2$ Me : R = 2,6-*i*Pr$_2$-4-Me-C$_6$H$_2$



^{i}Pr-PyBox
trace 3aa



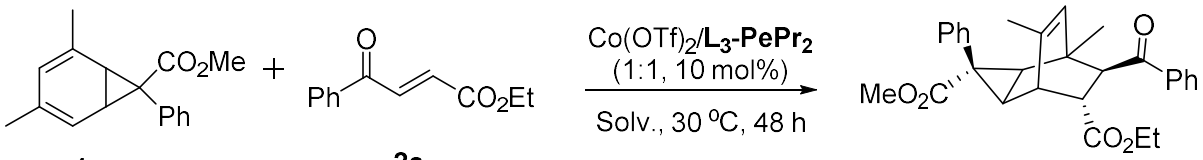
^{i}Pr-Box
trace 3aa

entry	Ligand	yield (%)[b]	dr[c]	solvent	ee (%)[d]
1	**L_3-PrPr$_2$**	28	19:1	DCM	65
2	**L_3-PrPr$_3$**	trace	8:1	DCM	35
3	**L_3-RaMe$_2$**	10	4:1	DCM	7/7
4	**L_3-RaEt$_2$**	20	19:1	DCM	53
5	**L_3-RaEt$_2$Me**	35	19:1	DCM	61
6	**L_3-Ra(OBu)$_2$**	20	19:1	DCM	37
7	**L_3-RaPr$_2$**	34	19:1	DCM	77
8	**L_3-TQ-^{t}Bu**	26	1:1	DCM	63/33
9	**L_3-TQ-Ad**	20	1:1	DCM	30/30
10	**L_3-PiPr$_2$**	30	19:1	DCM	69
11	**L_3-Pi-Cy**	trace	1:1	DCM	0/0

12	**L_3-Pi(CH)$_2$Ph**	trace	1:4	DCM	6
13	**L_3-PePr$_2$**	**35**	**19:1**	**DCM**	**89**
14	**L_3-PePr$_3$**	trace	7:1	DCM	65/7
15	**L_3-Pe(O^{i}Pr)$_2$**	35	19:1	DCM	75
16	**L_3-PePr$_2$Ad**	trace	9:1	DCM	59/3
17	**L_3-PeMe$_3$**	24	19:1	DCM	33
18	**L_3-Pe-^{t}Bu**	22	8:1	DCM	79/8
19	**L_3-PeNHPh**	20	7:1	DCM	60
20	**L_3-PeEt$_2$**	39	8:1	DCM	82/0
21	**L_3-PeMe$_2$**	38	9:1	DCM	74/0
22	**L_3-TQPr$_2$**	13	3:1	DCM	0/12

[a]Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), **2a** (0.1 mmol), and Co(OTf)$_2$/**Ligand** (1:1, 10 mol%) in DCM (1.0 mL) at 30 °C for 24 h. [b]Isolated yield of **3aa**. [c]Determined by ^{1}H NMR. [d]Determined by HPLC on a chiral stationary phase.

Table S3. Effect of the solvent[a]



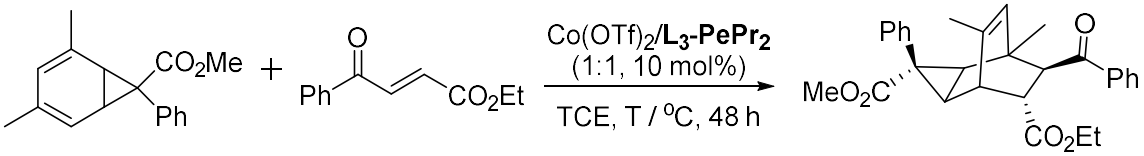
1a **2a** **3aa**

entry	Solvent	yield (%)[b]	dr[c]	ee (%)[d]
1	Toluene	trace	-	-
2	THF	trace	-	-
3	CH_3Cl	trace	-	-
4	EA	trace	-	-
5	MeOH	20	19:1	-79
6	MeCN	trace	-	-
7	Et_2O	trace	-	-
8	DCM	30	19:1	89
9	DCE	8	9:1	73
10	**1,1,2,2-Tetrachloroethane**	**32**	**19:1**	**92**
11	1,1,2-Trichloroethane	30	19:1	91
12	dichlorobenzene	10	19:1	90
13[e]	1,1,2-Trichloroethane	49	19:1	91
14[e]	1,1,2,2-Tetrachloroethane	67	19:1	91
15[e]	1-Bromo-3-chloropropane	66	19:1	91
16[e]	1,2-Dichlorobutane	12	19:1	91
17[e]	1,2-Dibromobutane	15	19:1	91
18[e]	1,1,2,2-Tetrabromoethane	-	-	-
19[e]	1,4-Dichlorobutane	57	19:1	91
20[f]	1,1,2,2-Tetrachloroethane	61	19:1	88

21[e,g]	**1,1,2,2-Tetrachloroethane**	**92**	**19:1**	**91**
22[e,g]	1-Bromo-3-chloropropane	90	19:1	90
23[e,g]	1,1,2,2-Tetrachloroethane	92	19:1	89
24[e,h]	1,1,2,2-Tetrachloroethane	trace	-	-
25[e,i]	1,1,2,2-Tetrachloroethane	trace	-	-
26[e,g]	1,1,2,2-Tetrachloroethane	20	3:1	0/12

[a]Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), **2a** (0.1 mmol), and $Co(OTf)_2$/**L_3-PePr$_2$** (1:1, 10 mol%) in solvent (1.0 mL) at 30 °C for 24 h. [b]Isolated yield of **3aa**. [c]Determined by ^{1}H NMR. [d]Determined by HPLC on a chiral stationary phase. [e]**1a** was 0.2 mmol. [f] 72 h. [g]48 h. [h]$Co(OTf)_2$/**^{i}Pr-PyBox**. [i]$Co(OTf)_2$/**^{i}Pr-Box**. [g]$Co(OTf)_2$/ **L_3-TQPr$_2$**.

Table S4. Effect of the temperature[a]

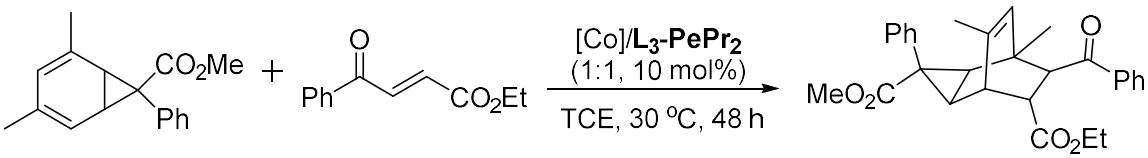


1a **2a** **3aa**

entry	T °C	yield (%)[b]	dr[c]	ee (%)[d]
1	40	94	19:1	83
2	35	69	19:1	86
3	**30**	**92**	**19:1**	**91**
4[e]	25	80	19:1	89
5	20	65	19:1	91
6[e]	20	71	19:1	91
7	10	30	19:1	93
8	0	13	19:1	92
9	-10	trace	19:1	91

[a]Unless otherwise noted, all reactions were carried out with **1a** (0.20 mmol), **2a** (0.1 mmol), and $Co(OTf)_2$/**L_3-PePr$_2$** (1:1, 10 mol%) in TCE (1.0 mL) at the set temperature for 24 h. [b]Isolated yield of **3aa**. [c]Determined by ^{1}H NMR. [d]Determined by HPLC on a chiral stationary phase. [e]72 h.

Table S5. Effect of the counterions of metal salts[a]



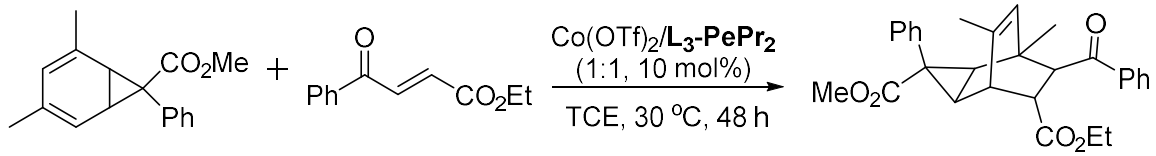
1a **2a** **3**

entry[a]	[Co]	yield (%)[b]	dr[c]	ee (%)[d]
1	$CoCl_2$	Trace	-	-
2	$Co(NTf_2)_2$	60	19:1	89
3	$Co(ClO_4)_2{\cdot}6H_2O$	46	19:1	88

4	$Co(BF_4)_2·6H_2O$	40	3:7	10/65
5	**$Co(OTf)_2$**	**92**	**19:1**	**91**

[a]Unless otherwise noted, all reactions were carried out with **1a** (0.20 mmol), **2a** (0.1 mmol), and Metal salt/**L_3-$PePr_2$** (1:1, 10 mol%) in TCE (1.0 mL) at 30 °C for 24 h. [b]Isolated yield of **3aa**. [c]Determined by ^{1}H NMR. [d]Determined by HPLC on a chiral stationary phase.

Table S6. Additive effect[a]



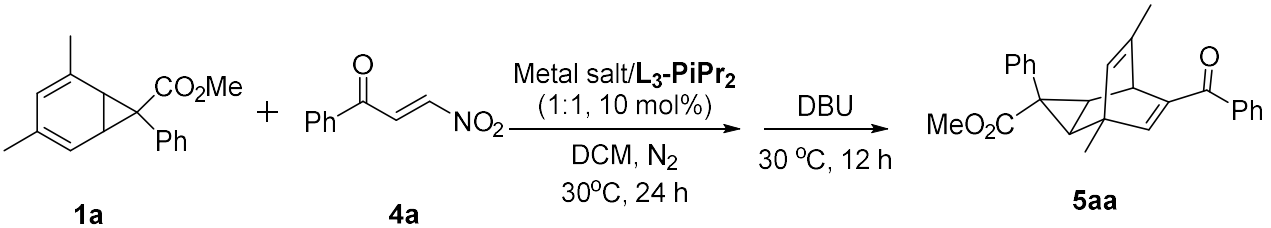
1a **2a** **3**

entry[a]	additives	yield (%)[b]	dr[c]	ee (%)[d]
1	3 Å MS (20 mg)	Trace	1:1	3/30
2	4 Å MS (20 mg)	Trace	1:3	15/53
3	5 Å MS (20 mg)	Trace	1: 2	0/53
4	LiNTf (10 mol %)	68	19:1	90
5	LiNTf (20 mol %)	85	19:1	89
6	LiNTf (30 mol %)	87	19:1	85
7	$NaBArF_4$ (10 mol %)	60	19:1	90
8	$NaBArF_4$ (20 mol %)	83	19:1	87
9	$NaBArF_4$ (30 mol %)	80	19:1	87
10	**-**	**92**	**19:1**	**91**
11	H_2O (1 μL)	32	9:1	86
12	H_2O (2 μL)	32	9:1	86
13	H_2O (5 μL)	32	9:1	86
14	H_2O (10 μL)	Trace	-	-

[a]Unless otherwise noted, all reactions were carried out with **1a** (0.20 mmol), **2a** (0.1 mmol), $Co(OTf)_2$/**L_3-$PePr_2$** (1:1, 10 mol%), and additives in TCE (1.0 mL) at 30 °C for 24 h. [b]Isolated yield of **3aa**. [c]Determined by ^{1}H NMR. [d]Determined by HPLC on a chiral stationary phase.

6. Optimization of the reaction conditions for β-nitroenone

Table S7. Effect of the metal salts[a]



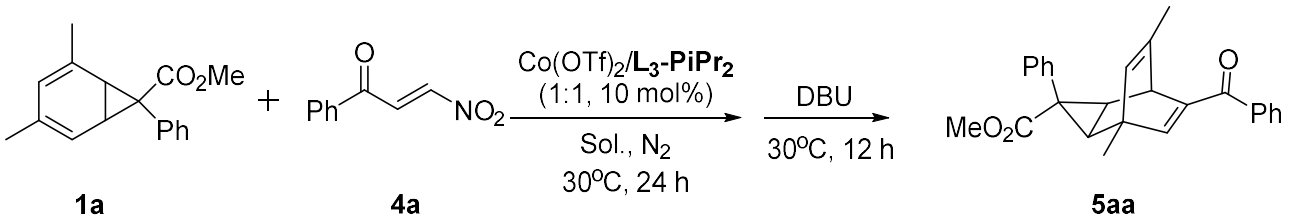
1a **4a** **5aa**

entry	metal salt	yield (%)[b]	dr[c]	ee[d]
1	**$Co(OTf)_2$**	**94**	**19:1**	**4**
2	$La(OTf)_3$	50	10:1	0

3	$Ce(OTf)_3$	42	12:1	0
4	$Pr(OTf)_3$	34	19:1	4
5	$Nd(OTf)_3$	56	10:1	5
6	$Sm(OTf)_3$	34	10:1	-
7	$Eu(OTf)_3$	46	4:1	0
8	$Gd(OTf)_3$	66	5:1	0
9	$Tb(OTf)_3$	66	10:1	6
10	$Dy(OTf)_3$	94	19:1	4
11	$Ho(OTf)_3$	50	10:1	0
12	$Er(OTf)_3$	42	12:1	0
13	$Tm(OTf)_3$	34	10:1	4
14	$Al(OTf)_3$	-	-	-
15	$In(OTf)_3$	-	-	-
16	$Ca(OTf)_2$	46	1:1	0
17	$Ba(OTf)_2$	66	3:1	0

[a]Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), **2a** (0.1 mmol), and metal salt/**L_3–PiPr$_2$** (1:1, 10 mol%) in DCM (1.0 mL) under nitrogen at 30 °C. After reacted for 24 h, added DBU (0.15 mmol) and continue to react for another 12 hours. [b]Isolated yield of **5aa**. [c]Determined by ^{1}H NMR. [d]Determined by HPLC on a chiral stationary phase.

Table S8. Effect of the solvent[a]

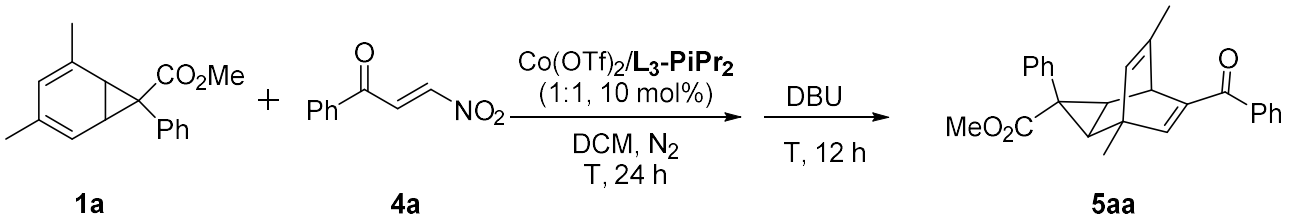


1a **4a** **5aa**

entry	solvent	yield (%)[b]	dr[c]	ee[d]
1	**DCM**	**95**	**19:1**	**4**
2	THF	20	1:1	0
3	Et_2O	60	1:1	0
4	Toluene	41	4:1	11
5	EA	38	3:2	4
6	MeOH	N.R.	-	-
7	CH_3CN	99	19:1	0
8	Acetone	trace	-	-
9	DCE	60	1:1	0
10	TCE	90	19:1	0
11	TeCA	93	19:1	0
12	1-Bromo-3-chloropropane	86	5:1	4
13	dichlorobenzene	trace	3:2	-

[a]Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), **2a** (0.1 mmol), and $Co(OTf)_2$/**L_3–PiPr$_2$** (1:1, 10 mol%) in solvent (1.0 mL) under nitrogen at 30 °C. After reacted for 24 h, added DBU (0.15 mmol) and continue to react for another 12 hours. [b]Isolated yield of **5aa**. [c]Determined by ^{1}H NMR. [d]Determined by HPLC on a chiral stationary phase.

Table S9. Effect of the temperature[a]

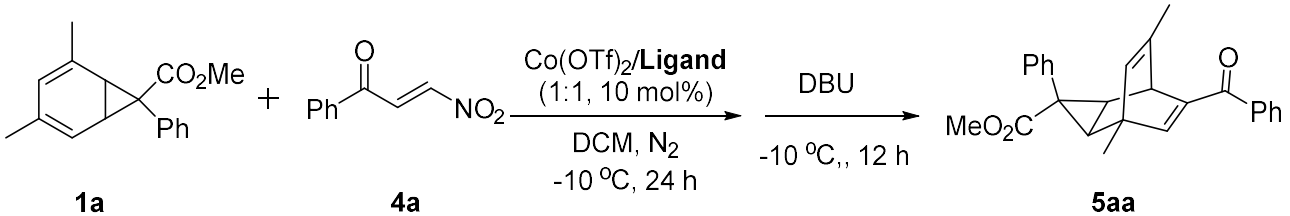


1a **4a** **5aa**

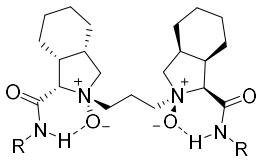
entry	*T* °C	yield (%)[b]	dr[c]	ee[d]
1	30	94	19:1	4
2	20	93	19:1	8
3	10	93	19:1	7
4	0	87	19:1	15
5	**-10**	**87**	**19:1**	**20**
6	-20	53	19:1	25
7	-30	44	19:1	30
8	-40	28	19:1	35

Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), **2a** (0.1 mmol), and $Co(OTf)_2$/**L_3–PiPr$_2$** (1:1, 10 mol%) in DCM (1.0 mL) under nitrogen at the set temperature. After reacted for 24 h, added DBU (0.15 mmol) and continue to react for another 12 hours. [b]Isolated yield of **5aa**. [c]Determined by ^{1}H NMR. [d]Determined by HPLC on a chiral stationary phase.

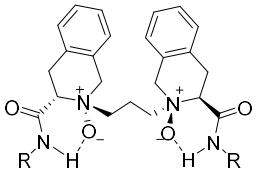
Table S10. Effect of the Ligands[a]



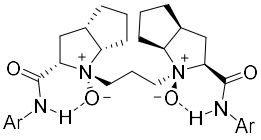
1a **4a** **5aa**



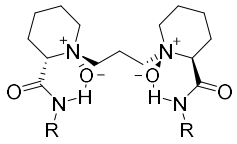
L_3-PePr$_2$: R = 2,6-*i*Pr$_2$C$_6$H$_3$



L_3-TQ-^{t}Bu: R = tert-butyl
L_3-TQ-Cy: R = cyclohexyl

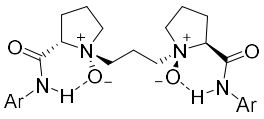


L_3-RaPr$_2$: Ar = 2,6-*i*Pr$_2$C$_6$H$_3$



L_3-PiMe$_2$: R = 2,6-Me$_2$C$_6$H$_3$
L_3-PiEt$_2$: R = 2,6-Et$_2$C$_6$H$_3$
L_3-PiPr$_2$: R = 2,6-*i*Pr$_2$C$_6$H$_3$
L_3-Pi(OMe)$_2$: R = 2,6-Me$_2$C$_6$H$_3$
L_3-PiEt$_3$:R = 2,4,6-Et$_3$C$_6$H$_2$
L_3-PiPr$_2$: R = 2,6-*i*Pr$_2$C$_6$H$_3$
L_3-Pi-m-^{t}Bu:R = 5-*t*BuC$_6$H$_4$
L_3-PiMe$_2$^{t}Bu:R=2,6-Me-4-^{t}Bu-C$_6$H$_2$

L_3-PiCHPh$_2$:R=CH$_2$-C$_6$H$_5$
L_3-(CH$_2$)$_2$-Ph:R=(CH$_2$)$_2$-C$_6$H$_5$
L_3-(CH$_2$)$_3$-Ph:R=(CH$_2$)$_3$-C$_6$H$_5$
L_3-Pi-Cy: R= cyclohexyl
L_3-PiAd: R=adamantyl
L_3-Pi-(1-Ad)Ph: R=1-Ad-C$_6$H$_4$
L_3-PiNaPhth: R=NaPhth



L_3-PrMe$_2$: R = 2,6-Me$_2$C$_6$H$_3$
L_3-PrEt$_2$: R = 2,6-Et$_2$C$_6$H$_3$
L_3-PrPr$_2$: R = 2,6-*i*Pr$_2$C$_6$H$_3$
L_3-Pr(OMe)$_2$: R = 2,6-Me$_2$C$_6$H$_3$
L_3-PrEt$_3$:R = 2,4,6-Et$_3$C$_6$H$_2$
L_3-PrPr$_3$: R = 2,4,6-*i*-Pr$_2$C$_6$H$_2$
L_3-PrCy$_3$: R = 2,4,6-Cy$_3$C$_6$H$_2$

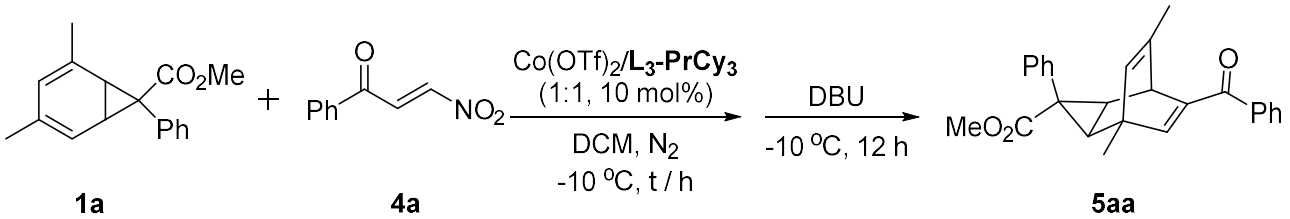
L_3-PrMe$_2$tBu: R=2,6-Me-4-^{t}Bu-C$_6$H$_2$
L_3-PrEt$_2$Ad: R = 2,6-Et$_2$-4-Ad-C$_6$H$_2$
L_3-PrEt$_2$CPh$_3$: R = 2,6-Et$_2$-4-(CPh$_3$)-C$_6$H$_2$
L_3-Pr(1-^{t}Bu)Ph: R=1-^{t}Bu-C$_6$H$_4$
L_3-PrCPh$_3$: R=C(C$_6$H$_5$)$_3$
L_3-PrCHPh$_2$: R=CH$_2$-C$_6$H$_5$

entry	**Ligand**	yield (%)[b]	dr[c]	ee[d]
1	**L_3-PiPr$_2$**	53	19:1	25
2	**L_3-PrPr$_2$**	56	19:1	5
3	**L_3-RaPr$_2$**	35	12:1	0
4	**L_3-PePr$_2$**	78	19:1	0
5	**L_3-TQ-^{t}Bu**	77	5:1	0
6	**L_3-TQ-Cy**	78	5:1	0
7	**L_3-PiMe$_2$**	50	19:1	3
8	**L_3-PiEt$_2$**	67	19:1	4
9	**L_3-PiPr$_2$**	53	19:1	20
10	**L_3-Pi(OMe)$_2$**	34	19:1	4
11	**L_3-PiEt$_3$**	81	19:1	13
12	***L_3-PiPr$_3$***	70	19:1	40
13	**L_3-Pi-*m*-^{t}Bu**	87	19:1	10
14	**L_3-PiMe$_2$^{t}Bu**	30	19:1	12
15	**L_3-PiCH$_2$Ph$_2$**	12	19:1	9
16	**L_3-PiBn**	60	19:1	12
17	**L_3-Pi(CH$_2$)$_3$-Ph**	45	19:1	4

18	**L_3-PiCy**	56	19:1	14
19	**L_3-PiAd**	93	19:1	5
20	**L_3-Pi-(1-Ad)Ph**	65	19:1	0
21	**L_3-Pi-$(CH_2)_2$Ph**	45	19:1	0
22	**L_3-PiNaPhth**	complex	-	-
23	**L_3-PrMe$_2$**	76	19:1	0
24	**L_3-PrEt$_2$**	65	19:1	0
25	**L_3-PrPr$_2$**	53	19:1	5
26	**L_3-Pr(OMe)$_2$**	50	19:1	4
27	**L_3-PrEt$_3$**	80	19:1	11
28	**L_3-PrPr$_3$**	36	19:1	5
29	**L_3-PrCy$_3$**	**48**	**19:1**	**80**
30	**L_3-PrMe$_2$^{t}Bu**	34	19:1	8
31	**L_3-PrEt$_2$Ad**	82	19:1	20
32	**L_3-PrEt$_2$CPh$_3$**	16	19:1	10
33	**L_3-Pr(1-^{t}Bu)Ph**	20	19:1	0
34	**L_3-PrCPh$_3$**	75	19:1	0
35	**L_3-PrCHPh$_2$**	12	19:1	0

Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), **2a** (0.1 mmol), and Co(OTf)$_2$/**Ligand** (1:1, 10 mol%) in DCM (1.0 mL) under nitrogen at -10^{o}C. After reacted for 24 h, added DBU (0.15 mmol) and continue to react for another 12 hours. [b]Isolated yield of **5aa**. [c]Determined by ^{1}H NMR. [d]Determined by HPLC on a chiral stationary phase.

Table S11. Effect of the reaction time[a]



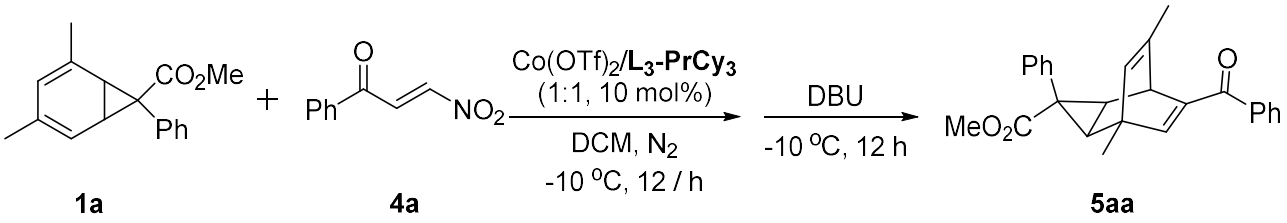
1a **4a** **5aa**

entry	t / h	yield (%)[b]	dr[c]	ee[d]
1	2	20	19:1	83
2	4	35	19:1	82

3	6	33	19:1	82
4	8	40	19:1	82
5	10	44	19:1	81
6	**12**	**48**	**19:1**	**81**
7[e]	**12**	**84**	**19:1**	**80**
8	14	53	19:1	76

Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), **2a** (0.1 mmol), and $Co(OTf)_2$/**L_3-PrCy$_3$** (1:1, 10 mol%) in DCM (1.0 mL) under nitrogen at -10°C. After reacted for the set time, added DBU (0.15 mmol) and continue to react for another 12 hours. [b]Isolated yield of **5aa**. [c]Determined by ^{1}H NMR. [d]Determined by HPLC on a chiral stationary phase. [e]**1a** was 0.2 mmol.

Table S12. Additive effect[a]

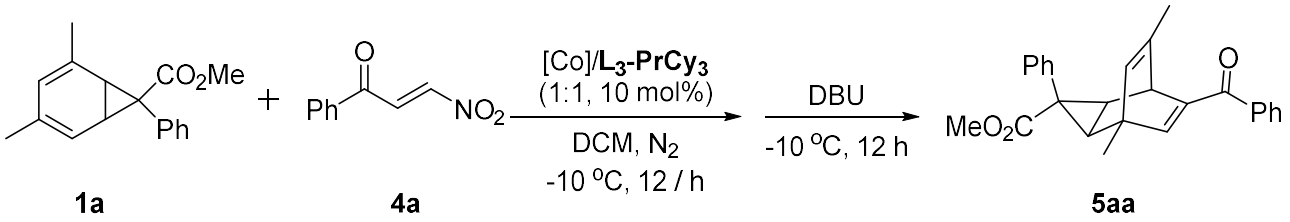


1a **4a** **5aa**

entry[a]	additives	yield (%)[b]	dr[c]	ee (%)[d]
1	3 Å MS (20 mg)	Trace	N.D	N.D
2	4 Å MS (20 mg)	Trace	N.D	N.D
3	5 Å MS (20 mg)	Trace	N.D	N.D
4	$LiNTf_2$	75	19:1	78
7	$NaBArF_4$ (10 mol %)	20	19:1	55
11	H_2O (1 μL)	67	19:1	75
12	H_2O (10 μL)	55	19:1	60

Unless otherwise noted, all reactions were carried out with **1a** (0.20 mmol), **2a** (0.1 mmol), additive and $Co(OTf)_2$/**L_3-PrCy$_3$** (1:1, 10 mol%) in DCM (1.0 mL) under nitrogen at -10°C. After reacted for 12 hours, added DBU (0.15 mmol) and continue to react for another 12 hours. [b]Isolated yield of **5aa**. [c]Determined by ^{1}H NMR. [d]Determined by HPLC on a chiral stationary phase.

Table S13. Effect of the counterions of metal salts[a]



1a **4a** **5aa**

entry[a]	[Co]	yield (%)[b]	dr[c]	ee (%)[d]
1	$CoCl_2$	Trace	-	-
2	$Co(NTf_2)_2$	61	19:1	69
3	$Co(ClO_4)_2 \cdot 6H_2O$	65	19:1	61

4	$Co(BF_4)_2·6H_2O$	43	8:1	55/61
5	**$Co(OTf)_2$**	**84**	**19:1**	**80**

Unless otherwise noted, all reactions were carried out with **1a** (0.20 mmol), **2a** (0.1 mmol), and Metal salt/**L_3-PrCy$_3$** (1:1, 10 mol%) in DCM (1.0 mL) under nitrogen at -10°C. After reacted for 12 hours, added DBU (0.15 mmol) and continue to react for another 12 hours. [b]Isolated yield of **5aa**. [c]Determined by ^{1}H NMR. [d]Determined by HPLC on a chiral stationary phase.

7. X-ray crystallography

7.1 The X-Ray diffraction of **3aa**

The colourless crystal in block-shape, with approximate dimensions of 0.348 × 0.678 × 0.777 mm^3, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2)K equipped with micro-focus Cu radiation source (K_α = 1.54178Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package[6-9]. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested[10]. CCDC 2155946 contains the supplementary crystallographic data which can be obtained free of charge from The Cambrige Crystallographic Data Centere via https://www.ccdc.cam.ac.uk/structures/

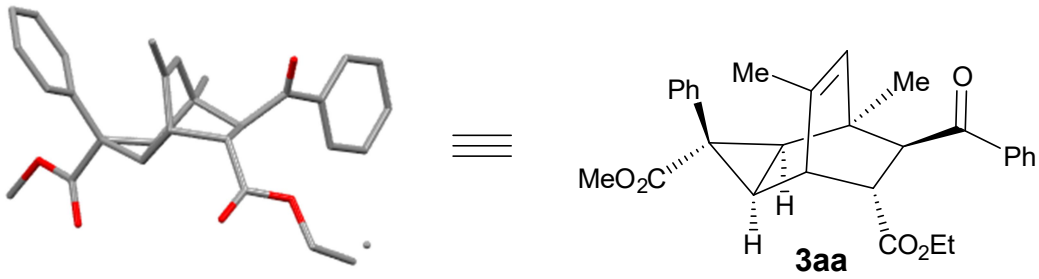


Figure S1. X-ray Crystal Structure of optical active product **3aa**.

The crystal of product **3aa** was obtained in the solvents of dichloromethane and petroleum ether. CCDC: 2155946. Crystallographic Data for C29 H30 O5

Formula	C29 H30 O5
Formula mass (amu)	458.53
Space group	P 43 21 2
a (Å)	9.9702(1)
b (Å)	9.9702(1)
c (Å)	48.7176(12)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	4842.77(15)
Z	8
λ (Å)	1.54178
T (K)	173 K

ρ_{calcd} (g cm^{-3})	1.258
μ (mm^{-1})	0.685
Transmission factors	0.709,0.873
θ_{max} (deg)	68.358
No. of unique data, including $F_o^2 < 0$	4386
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	4327
No. of variables	323
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0274
$R_w(F_o^2)$ [b]	0.0704
Goodness of fit	1.064

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

[b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

7.2 The X-Ray diffraction of **1a**

The colourless crystal in block-shape, with approximate dimensions of 0.486 × 0.445 × 0.345 mm^3, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2)K equipped with micro-focus Mo radiation source (K_α = 0.71073Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package[6-9].. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested[10]. CCDC 2070991contains the supplementary crystallographic data which can be obtained free of charge from The Cambrige Crystallographic Data Centere via https://www.ccdc.cam.ac.uk/structures/

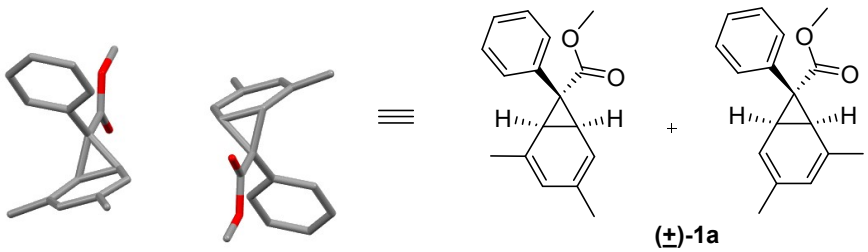


Figure S2. X-ray Crystal Structure of the racemic substrate **1a**.

The crystal of substrate **1a** was obtained in the solvents of dichloromethane and petroleum ether. CCDC: 2070991. Crystallographic Data for C17 H18 O2.

Formula	C17 H18 O2
Formula mass (amu)	254.31
Space group	P 21/c
a (Å)	9.7199(3)
b (Å)	17.3733(6)
c (Å)	8.5275(3)
α (deg)	90
β (deg)	106.832(1)

γ (deg)	90
V (Å^3)	1378.32(8)
Z	4
λ (Å)	0.71073
T (K)	173 K
ρ_{calcd} (g cm^{-3})	1.226
μ (mm^{-1})	0.079
Transmission factors	0.922,1.000
θ_{max} (deg)	25.371
No. of unique data, including $F_o^2 < 0$	2477
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	2012
No. of variables	175
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0402
$R_w(F_o^2)$ [b]	0.1102
Goodness of fit	1.087

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

[b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

7.3 The X-Ray diffraction of **5ab**

The colourless crystal in block-shape, with approximate dimensions of 0.322 × 0.335 × 0.704 mm^3, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2)K equipped with micro-focus Cu radiation source (K_α = 1.54178Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package[6-9]. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested[10].

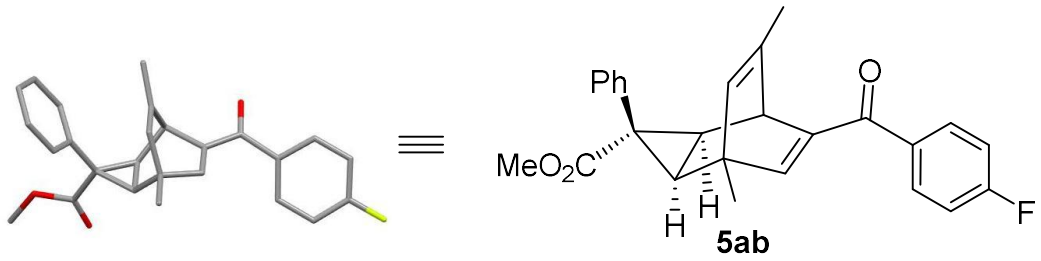


Figure S3. X-ray Crystal Structure of optical active product **5ab**

The crystal of substrate **5ab** was obtained in the solvents of dichloromethane and petroleum ether. CCDC: 2212551. Crystallographic Data for C26 H23 F O3.

Formula	C26 H23 F O3
Formula mass (amu)	402.44
Space group	P 21 21 21
a (Å)	8.7024(3)
b (Å)	13.0704(5)

c (Å)	18.7294(7)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	2130.35(14)
Z	4
λ (Å)	1.54178
T (K)	173 K
ρ_{calcd} (g cm^{-3})	1.255
μ (mm^{-1})	0.706
Transmission factors	0.682,0.844
θ_{max} (deg)	68.250
No. of unique data, including $F_o^2 < 0$	3883
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	3792
No. of variables	275
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0273
$R_w(F_o^2)$ [b]	0.0674
Goodness of fit	1.074

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

[b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

7.4 The X-Ray diffraction of L_3-$PePr_2$/$Co(BF_4)_2$•$6H_2O$ complex

The pink crystal in block-shape, with approximate dimensions of 0.422 × 0.436 × 0.583 mm^3, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2)K equipped with micro-focus Mo radiation source (K_α = 0.71073Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package[6-9]. The value observed herein is indicative of racemic twinning and was accommodated during the refinement (using the SHELXL TWIN instruction). In this case, the relatively large standard uncertainty indicates that the structural data alone should not be used to confirm absolute stereochemistry, but should be used in conjunction with the established stereochemistry of the precursor compound. Thus the Flack parameter is provided for informational purposes only. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested[10].

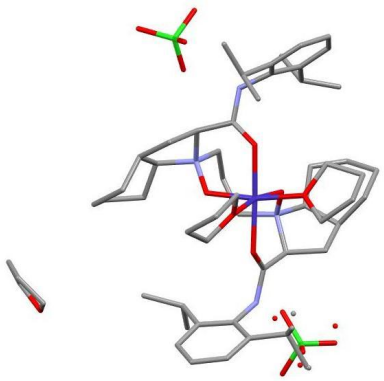


Figure S4. X-ray Crystal Structure of L_3-$PePr_2$/$Co(BF_4)_2$•$6H_2O$ complex

The crystal of the complex was obtained in the solvents of tetrahydrofuran and petroleum ether. CCDC: 2212550.

Crystallographic Data for C57 H92 Cl2 Co N4 O15

Formula	C57 H92 Cl2 Co N4 O15
Formula mass (amu)	1203.17
Space group	P 21 21 21
a (Å)	11.4334(7)
b (Å)	13.0191(8)
c (Å)	41.707(3)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	6208.1(7)
Z	4
λ (Å)	0.71073
T (K)	173 K
ρ_{calcd} (g cm^{-3})	1.287
μ (mm^{-1})	0.428
Transmission factors	0.780,0.910
θ_{max} (deg)	25.379
No. of unique data, including $F_o^2 < 0$	11374
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	10340
No. of variables	778
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0400
$R_w(F_o^2)$ [b]	0.1059
Goodness of fit	1.050

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

[b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

8. Control experiments and mechanistic studies

8.1 Mass spectrometry analysis of the reaction system

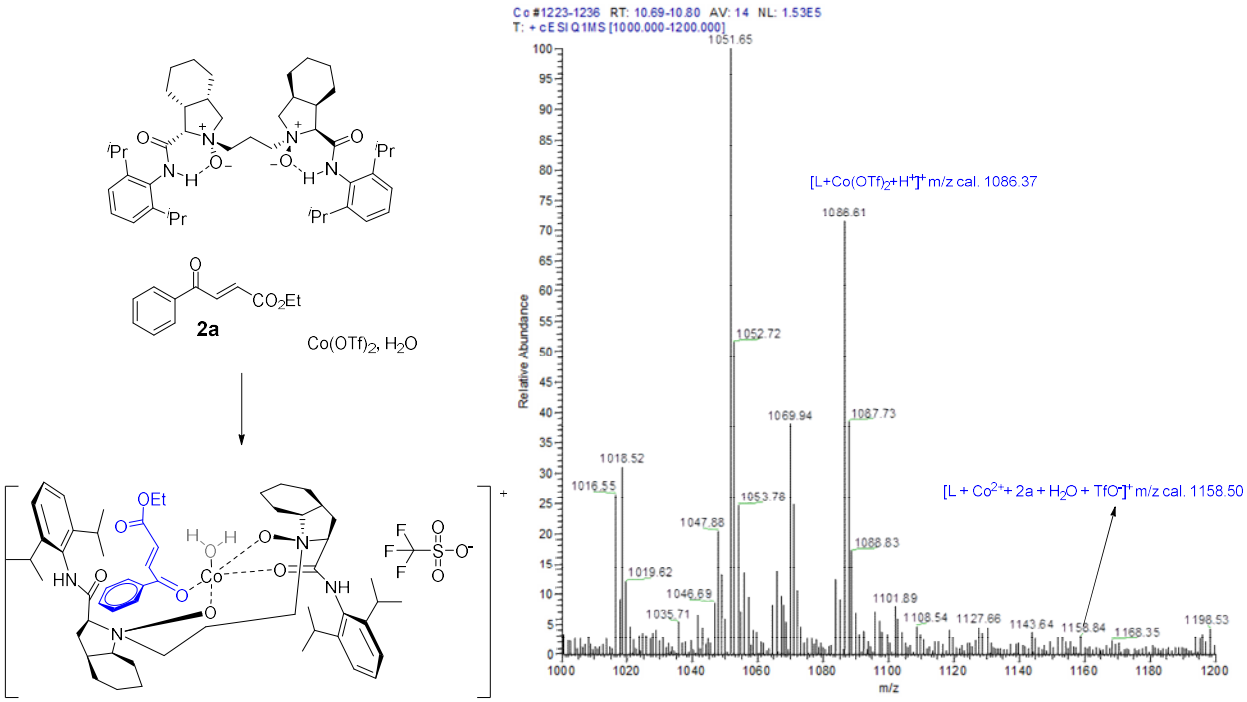
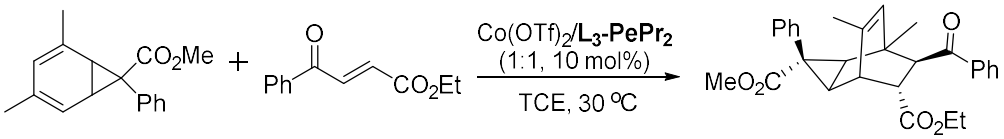


Figure S5. Mass spectrometry for the catalyst with enone **2a**

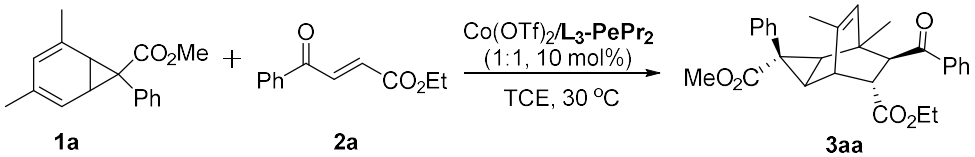
Table S14. Enantioselectivity-change of NCD 1a during the transformation[a]



Time (h)	ee (%)[b]	Time (h)	ee (%)[b]	Time (h)	ee (%)[b]	Time (h)	ee (%)[b]
4	15	24	43	48	55	72	56
8	20	28	44	52	53	76	56
12	33	32	49	56	54	80	58
16	43	36	50	60	55	84	57
20	42	40	52	64	56	88	57

[a]Unless otherwise noted, all reactions were carried out with **1a** (0.20 mmol), **2a** (0.1 mmol), and $Co(OTf)_2$/**L_3-PePr$_2$** (1:1, 10 mol%) in TCE (1.0 mL) at 30 °C. [b] Ee of the unreacted **1a**, determined by HPLC on a chiral stationary phase.

Table S15. Diastereo-, and enantioselectivity variation of the product 3aa during the reaction[a]



entry	Time	yield (%)[b]	dr[c]	ee (%)[d]
1	12 h	60	19:1	93

2	18 h	65	19:1	92
2	24 h	69	19:1	92
3	36 h	88	19:1	92
4	**48 h**	**94**	**19:1**	**91**
5	60 h	92	19:1	88
6	72 h	95	19:1	87

[a]Unless otherwise noted, all reactions were carried out with **1a** (0.20 mmol), **2a** (0.1 mmol), and $Co(OTf)_2$/**L_3-PePr$_2$** (1:1, 10 mol%) in TCE (1.0 mL) at 30 °C. [b]Isolated yield of **3aa**. [c]Determined by ^{1}H NMR. [d] Ee of the product **3aa**, determined by HPLC on a chiral stationary phase.

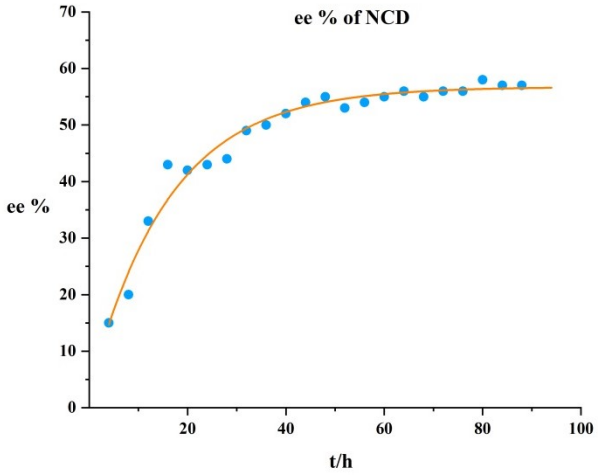


Figure S6. Variation of the ee of **1a** with the reaction time

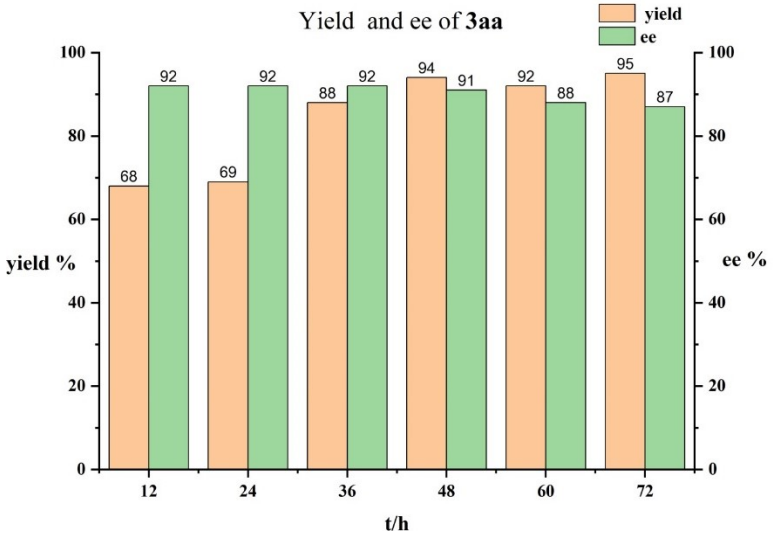
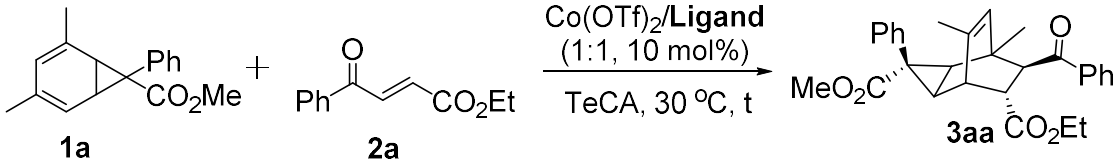


Figure S7. Variation of the yield and ee of the product **3aa** with the reaction time

Table S16 The control experiments on the racemization of the NCD 1a[a]



entry	**Ligand**	time	**1a** (ee%)[b]	**1a** (equiv.)	**1a** (recoverd) ee%, (rotation)	**3aa** Yield %[c]	**3aa** dr[d]	**3aa** Ee %[e]
1	**L_3-PePr$_2$**	48 h	0	1.02	53% ee; (+)	92	19:1	91
2	**L_3-PePr$_2$**	48 h	53% ee; (+)	1.98	60% ee; (+)	Trace	5:1	65 / 35
3[f]	**L_3-PePr$_2$**	48 h	53% ee; (+)	2.0	45% ee; (+)	—	—	—
4	**L_3-PePr$_2$**	48 h	52% ee; (-)	1.03	7 % ee; (-)	95	19:1	94
5[f]	**L_3-PePr$_2$**	48 h	27% ee; (-)	2.0	35 % ee; (-)	—	—	—
6	**L_3-PePr$_2$**	336 h	53% ee; (+)	1.03	83% ee; (+)	93	7:3	73 / 60
7	—	336 h	53% ee; (+)	1.96	47% ee; (+)	Trace	1:1	60 / 60
8	—	48 h	52% ee; (-)	1.98	45 % ee; (-)	Trace	1:1	45 / 35
9	***ent*-L_3-RaPr$_2$**	72 h	0	1.27	52% ee; (-)	70	19:1	79
10	***ent*-L_3-RaPr$_2$**	48 h	53% ee; (+)	0.98	23% ee; (+)	94	19:1	95
11[f]	***ent*-L_3-RaPr$_2$**	48 h	53% ee; (+)	2.0	45% ee; (+)	—	—	—
12[f]	***ent*-L_3-RaPr$_2$**	48 h	45% ee; (+)	2.0	45% ee; (+)	—	—	—
13[f]	***ent*-L_3-RaPr$_2$**	48 h	45% ee; (+)	2.0	45% ee; (+)	—	—	—
14[f]	***ent*-L_3-RaPr$_2$**	48 h	45% ee; (-)	2.0	45 % ee; (-)	—	—	—
15[f]	***ent*-L_3-RaPr$_2$**	48 h	45% ee; (-)	2.0	45 % ee; (-)	—	—	—
16	***ent*-L_3-RaPr$_2$**	48 h	27% ee; (-)	1.82	65 % ee; (-)	15	19:1	60 (-)
17[f]	***ent*-L_3-RaPr$_2$**	48 h	27% ee; (-)	2.0	35 % ee; (-)	—	—	—
18	**(±)-L_3-PiPr$_2$**	48 h	47% ee; (+)	1.30	43% ee; (+)	66	19:1	37

19	**(±)-L_3-$PiPr_2$**	48 h	50% ee; (-)	1.25	52% ee; (-)	71	19:1	50
20	**(±)-L_3-$PiPr_2$**	48 h	0	1.30	0 ee	64	19:1	0

[a]Unless otherwise noted, all reactions were carried out with **1a** (0.20 mmol), **2a** (0.1 mmol), and $Co(OTf)_2$/**L_3-$PePr_2$** (1:1, 10 mol%) in TCE (1.0 mL) at 30 °C for 24 h. [b]The ee of **1a** before react. [c]Isolated yield of **1a**. [d]Isolated yield of **3aa**. [e]Determined by ^{1}H NMR. [f]Without **2a**.

8.2 Computational studies

All computations were carried out using the Gaussian 09 D.01 software package[11]. The calculation of geometry optimization, frequency and Gibbs energy corrections were carried out for *exo*-**1a**, *endo*-**1a**, CHT-**a**, CHT-**b** at the temperature of 298.15K. All calculations were performed at M06-2X[12] level of theory with Grimme's D3 empirical dispersion correction[13] and SMD (dichloromethane) implicit solvation model[14]. The def-SVP basis set[15] was used for all atoms. Frequency calculations were calculated at the same level and no imaginary frequencies were observed. Single-point energies were obtained at the M06-2X, SMD (dichloromethane)/def2-TZVP[16] level of theory with GD3 empirical dispersion correction. The calculation of geometry optimization, frequency and Gibbs energy corrections were carried out for Co(II)-**L_3-$PrPr_2$**, Co(II)-**L_3-$PiPr_2$**, Co(II)-**L_3-$RaPr_2$**, Co(II)-**L_3-$TQPr_2$**, Co(II)-**L_3-$PePr_2$**, Co(II)-**L_3-$PePr_3$** at the temperature of 298.15K. All calculations were performed at B3LYP[17] level of theory with Grimme's D3 empirical dispersion correction[13] and SMD (dichloromethane) implicit solvation model[14]. The def-SVP basis set[16] was used for all atoms.

Coordinates

exo-**1a**

C	-1.44824000	-1.39921300	1.15681200
C	-1.49346400	-0.92450000	-1.67226200
C	-2.52993500	-0.54114800	-0.89389700
C	-2.48718900	-0.78682300	0.54671100
H	-1.56541100	-0.84593800	-2.75992100
H	-3.37436500	-0.52952500	1.13302300
C	-3.77842100	0.07484400	-1.45881000
H	-4.66830300	-0.50740800	-1.17255500
H	-3.92038700	1.09205100	-1.06026000
H	-3.73728400	0.13598800	-2.55446700
C	-1.46387900	-1.79631700	2.60194100
H	-2.41296800	-1.52766500	3.08408100
H	-1.31302000	-2.88332100	2.70355100
H	-0.64035600	-1.31191800	3.15169200
C	-0.22942500	-1.73375200	0.38785900
C	0.63594600	-0.62315600	-0.20264600

C	-0.25394100	-1.48121700	-1.10555600
H	0.35001000	-2.58952500	0.74331700
H	0.31575400	-2.17007300	-1.73233000
C	2.07562700	-1.01702000	-0.29861500
O	2.45732800	-2.14823300	-0.48163300
O	2.90394700	0.01620900	-0.16607300
C	4.29340100	-0.27574300	-0.26983600
H	4.81539300	0.68037300	-0.16092000
H	4.60345300	-0.96932300	0.52349000
H	4.52166400	-0.72377200	-1.24643500
C	0.33762300	0.82298400	0.04486000
C	0.20748700	1.71260900	-1.02613200
C	0.24095200	1.31464800	1.35069700
C	-0.01599000	3.07025400	-0.79781900
H	0.28297100	1.33293300	-2.04788700
C	0.01764600	2.67150900	1.58343500
H	0.34344500	0.62258600	2.18997300
C	-0.11358900	3.55185200	0.50867200
H	-0.11354100	3.75537900	-1.64197200
H	-0.05435500	3.04270700	2.60745000
H	-0.29055200	4.61377900	0.68933000

Zero-point correction = 0.309373

Thermal correction to Enthalpy = 0.3279

Thermal correction to Gibbs Free Energy = 0.263839

endo-**1a**

C	-1.73932200	-1.76595500	0.13640100
C	-1.81750100	0.53025300	-1.59685400
C	-2.88314200	0.20082100	-0.83588100
C	-2.82625700	-0.97277800	0.04080700
H	-1.89832300	1.33414100	-2.33272600
H	-3.73405800	-1.24137100	0.58907400
C	-4.18442600	0.95034400	-0.90463400
H	-5.01477000	0.27229700	-1.15684100
H	-4.42593900	1.39948900	0.07206800
H	-4.14771600	1.75285700	-1.65344700
C	-1.70672000	-3.02490200	0.94752200
H	-2.68265100	-3.23881300	1.40324400
H	-1.41129400	-3.88459000	0.32442500
H	-0.95567800	-2.93827200	1.74983600

C	-0.48425600	-1.39966500	-0.56287900
C	0.26515700	-0.14348100	-0.20838100
C	-0.52393800	-0.17500200	-1.48975100
H	0.15820500	-2.23676300	-0.85135100
H	0.08910600	-0.20476700	-2.39389600
C	-0.22214600	0.70680100	0.93932600
O	-0.52765900	0.29540600	2.02751400
O	-0.20235000	2.00073600	0.62319800
C	-0.62346000	2.90088000	1.64155500
H	-0.50921100	3.90876100	1.22967400
H	-1.67552700	2.71652800	1.90143000
H	-0.00576700	2.78557100	2.54234100
C	1.76896600	-0.15532300	-0.26857400
C	2.49125500	-1.00551100	0.57731800
C	2.46076200	0.71717200	-1.11478100
C	3.88526400	-0.99180400	0.56808800
H	1.95118300	-1.68242500	1.24396900
C	3.85567100	0.73016500	-1.12543500
H	1.89913500	1.38846600	-1.76830200
C	4.56987400	-0.12458600	-0.28490900
H	4.44022600	-1.66114300	1.22795800
H	4.38720000	1.41153600	-1.79230100
H	5.66126300	-0.11521200	-0.29447300

Zero-point correction = 0.309175

Thermal correction to Enthalpy = 0.327945

Thermal correction to Gibbs Free Energy = 0.262285

CHT-**a**

C	2.59242000	-0.30682500	0.22458000
C	2.41552400	-0.05205600	-1.10086700
C	1.38474700	-0.70149200	-1.90269700
C	1.83838200	-1.24469800	1.04782500
C	0.16272800	-1.07435800	-1.48038600
C	0.52412100	-1.50614500	0.87861900
C	-0.35894700	-0.76084000	-0.09544500
H	3.47427500	0.13827000	0.69959800
H	1.64431400	-0.89916400	-2.94847400
H	-0.49499800	-1.61825000	-2.16222800
H	0.04153000	-2.27188000	1.49080100
C	3.37189000	0.83943100	-1.84731200

H	4.14878800	1.24203500	-1.18404100
H	3.86067400	0.28777600	-2.66612900
H	2.83511700	1.68418300	-2.30765900
C	2.62384800	-1.93217600	2.13728800
H	3.47148000	-2.49686600	1.71988100
H	3.04498300	-1.18614800	2.83017800
H	1.99332500	-2.62022800	2.71544500
C	-1.80442500	-1.24557200	0.05975600
O	-2.24552800	-1.79655100	1.03378300
O	-2.54429000	-0.92943300	-0.99865400
C	-3.92935000	-1.25385900	-0.92185800
H	-4.39938500	-0.73259700	-0.07687200
H	-4.37469300	-0.92082300	-1.86461600
H	-4.06536700	-2.33666400	-0.79942900
C	-0.45695600	0.75061800	0.21295700
C	-0.60961100	1.70079400	-0.80119000
C	-0.49107500	1.17248500	1.54628600
C	-0.75890900	3.05222600	-0.48634200
H	-0.60516400	1.38577700	-1.84606700
C	-0.64251800	2.52230400	1.86163700
H	-0.39009500	0.43572600	2.34601600
C	-0.77121700	3.46876400	0.84475700
H	-0.86659500	3.78421800	-1.28910500
H	-0.65901500	2.83423800	2.90766400
H	-0.88454400	4.52666800	1.08835700

Zero-point correction = 0.308827

Thermal correction to Enthalpy = 0.327591

Thermal correction to Gibbs Free Energy = 0.263658

CHT-**b**

C	-2.73369900	-0.71940200	-0.16496800
C	-2.75686100	0.35099200	0.68099200
C	-1.75186600	0.55215900	1.71626400
C	-1.76300800	-1.80659200	-0.16812200
C	-0.44726800	0.23987200	1.60416900
C	-0.45204400	-1.62584900	0.10589900
C	0.15366000	-0.25775900	0.31207600
H	-3.60739500	-0.85822800	-0.81242700
H	-2.10541800	0.98224000	2.65924200
H	0.20634000	0.32453300	2.47545400

H	0.20369900	-2.49575600	0.19254500
C	-3.91703100	1.31065200	0.67297300
H	-4.68069900	1.01465300	-0.05817600
H	-4.38505600	1.36349300	1.66856200
H	-3.57566400	2.32891200	0.42740100
C	-2.30947200	-3.17699100	-0.48037600
H	-3.08241600	-3.47075900	0.24644300
H	-2.78471400	-3.18049200	-1.47400000
H	-1.51643400	-3.93636700	-0.47476100
C	1.68634000	-0.27096000	0.32562800
C	2.40473400	0.67722800	1.06331200
C	2.39206800	-1.16415800	-0.48937900
C	3.79864200	0.70414500	1.02006200
H	1.87472800	1.41324800	1.66999700
C	3.78563100	-1.13761200	-0.53324800
H	1.84916800	-1.88192300	-1.10669500
C	4.49461500	-0.20831200	0.22781200
H	4.34200400	1.44736600	1.60634900
H	4.31909700	-1.84650100	-1.16900600
H	5.58537900	-0.18934400	0.19633800
C	-0.16386500	0.65752300	-0.89485200
O	-0.26484800	0.27052200	-2.02729400
O	-0.19166300	1.94284900	-0.55471500
C	-0.37488700	2.86679100	-1.62159100
H	-0.33902700	3.86548600	-1.17451200
H	0.42199300	2.75798800	-2.37001400
H	-1.34761700	2.70411400	-2.10658200

Zero-point correction = 0.307947

Thermal correction to Enthalpy = 0.326984

Thermal correction to Gibbs Free Energy = 0.261945

Co(II)-**L_3-$PrPr_2$**

Co	-0.05609800	0.81196000	0.10583200
O	-0.07999300	-1.06443100	-0.67345300
O	-0.52955400	0.22205200	1.98084400
O	2.01945600	0.58548000	0.34778500
O	-2.11174000	1.21017000	-0.19723600
O	0.17099800	1.64581000	-1.82080300
O	0.28758800	2.79704700	0.76903400
N	-1.71074100	-0.44162100	2.26200900

C	-3.04543600	0.72449600	0.46157200
N	0.82103000	-2.02526200	-0.23763400
C	2.74499100	-0.38421300	0.06864600
C	-1.80468900	-0.50724900	3.76712100
C	-2.93046200	0.43045100	1.94853100
C	-1.83210100	-1.76677200	1.55220400
N	-4.22688100	0.42377800	-0.08746700
C	-4.46983500	0.51420300	-1.49853000
C	0.71510200	-2.30966500	1.24044100
C	0.62687900	-3.23184100	-1.12738800
C	2.24438700	-1.64559000	-0.60974400
N	4.05683200	-0.38583600	0.31801700
C	4.72838200	0.73954700	0.89808100
C	-0.66471700	-2.72710000	1.73599400
C	-2.14041600	0.93899300	4.17371000
C	-2.72853700	1.60584900	2.89934600
C	-4.64833000	1.77523400	-2.10625900
C	-4.50895000	-0.68792400	-2.23907400
C	-4.86927000	1.80798100	-3.49169100
C	-4.57990600	3.07957200	-1.32198800
C	-4.91820500	0.63329500	-4.24325700
C	-4.74147900	-0.60197900	-3.61959700
C	-4.28186400	-2.04582800	-1.58686300
C	-5.88089400	3.88937900	-1.43713500
C	-3.35998300	3.90834200	-1.75726300
C	-3.00192200	-2.70834700	-2.12061100
C	-5.50761000	-2.95962000	-1.72727900
C	1.21643500	-2.78989300	-2.47503700
C	2.19480600	-1.63371100	-2.13942900
C	4.83982100	0.81538600	2.30189200
C	5.24214400	1.73389800	0.03832100
C	5.15543100	1.56614700	-1.47417400
C	5.87162600	2.84030500	0.62627800
C	5.98327600	2.94517200	2.01489500
C	5.47740800	1.94256600	2.84335500
C	4.24953100	-0.26730300	3.19933700
C	5.05791600	2.89182700	-2.23713300
C	6.33061100	0.71157700	-1.98400500
C	5.13801100	-0.60406600	4.40431400
C	2.82947100	0.11846300	3.65452700

Cl	-5.64852500	-2.40726200	2.15708300
O	-6.04952800	-1.26485400	1.25271300
O	-4.90227900	-1.84364300	3.32944400
O	-6.86930200	-3.10175000	2.61505000
O	-4.76178400	-3.35265300	1.41713400
C	1.35939700	2.32730300	-2.26804500
C	-0.58785100	1.12863200	-2.94232300
C	1.09422400	2.62722300	-3.73744800
C	0.28542800	1.39407200	-4.16695900
C	-0.51161300	3.93623300	0.39682700
C	1.00654400	3.04518900	1.99947300
C	0.04255700	5.08510000	1.23082300
C	0.44894600	4.36594600	2.52453600
H	-4.90844600	-0.10197100	0.47964700
H	4.60077400	-1.23634900	0.09621400
H	-1.94664900	-1.52755300	0.49160800
H	-2.75605000	-2.22998600	1.91585900
H	-0.54449600	-2.97176200	2.80396500
H	-0.97053700	-3.66682400	1.24844500
H	1.02993200	-1.39400200	1.74641900
H	1.44032600	-3.10807700	1.44911900
H	-0.84369600	-0.87901100	4.13735400
H	-2.61040900	-1.20937200	4.01800900
H	-1.24292300	1.47279700	4.51167900
H	-2.86484700	0.93313800	4.99982100
H	-2.01582300	2.31342000	2.45912600
H	-3.68110200	2.12121100	3.07981700
H	-3.79693100	-0.16109400	2.26843900
H	-5.00519800	2.77121200	-3.98934400
H	-5.09449300	0.68158400	-5.32130200
H	-4.77725000	-1.51868800	-4.21316600
H	-4.45023100	2.82957900	-0.25923600
H	-2.44059100	3.31371200	-1.67238400
H	-3.25132000	4.80520300	-1.12520500
H	-3.46141600	4.24686400	-2.80182000
H	-6.75016900	3.30589400	-1.09325200
H	-6.07512900	4.20215600	-2.47610500
H	-5.82062500	4.80303900	-0.82267300
H	-4.13659900	-1.89694600	-0.51144800
H	-2.12396600	-2.06393200	-1.95581300

H	-3.07213500	-2.92666500	-3.19937400
H	-2.82443600	-3.66384400	-1.59929800
H	-5.33470700	-3.90687900	-1.19381700
H	-5.73058700	-3.19021900	-2.78246500
H	-6.39565000	-2.48997700	-1.27666100
H	-0.44111500	-3.46571300	-1.13817300
H	1.19320800	-4.06246100	-0.68566300
H	1.74478700	-3.63257500	-2.93941200
H	0.42656300	-2.44924300	-3.15691900
H	3.20040300	-1.79480400	-2.54267400
H	1.80910200	-0.66911900	-2.49009300
H	2.86886900	-2.48535900	-0.28157400
H	6.28252100	3.63081000	-0.00435800
H	6.47461300	3.81708100	2.45543700
H	5.57854500	2.03972000	3.92613100
H	4.23461300	1.00375300	-1.69025300
H	6.33300900	-0.29084400	-1.53088900
H	7.29349600	1.19929000	-1.75747900
H	6.26518100	0.57585900	-3.07627000
H	4.85435700	2.69826700	-3.30249800
H	5.99614600	3.46787800	-2.18620000
H	4.24691300	3.52725100	-1.84650500
H	2.85840500	1.02077300	4.28854100
H	6.16832900	-0.84350000	4.09589800
H	5.18309400	0.22632900	5.12772500
H	4.73164000	-1.47805100	4.93885900
H	2.17254000	0.33003100	2.80078200
H	2.37649300	-0.69491100	4.24562200
H	2.22731300	1.66230400	-2.13457900
H	1.50463300	3.21195900	-1.63286200
H	0.48520300	3.54116600	-3.83602000
H	2.02262300	2.76546700	-4.31064800
H	0.96138200	0.54285200	-4.34959200
H	-0.31272300	1.55716500	-5.07528900
H	-1.54637600	1.66815400	-2.98413000
H	-0.78842900	0.06530100	-2.75426800
H	-1.56650400	3.72299400	0.63219600
H	2.08059000	3.10717600	1.76333900
H	-0.42233200	4.07839000	-0.68842700
H	0.92808700	5.52177100	0.73965400

H	-0.69657800	5.88485300	1.38485800
H	-0.43936000	4.18505100	3.15209900
H	1.18579700	4.92035500	3.12381800
H	0.83422200	2.19126400	2.66686700
Cl	5.30361600	-3.54500100	-1.40862600
O	6.39609600	-4.53945500	-1.46367700
O	5.38511400	-2.80738700	-0.08607700
O	5.43858600	-2.56021900	-2.52119200
O	3.97677400	-4.22746500	-1.49107700
H	4.16355800	-1.18246400	2.59323400

Co(II)-**L_3-PiPr$_2$**

Co	-0.03167500	0.85327300	-0.25008000
O	-0.02043200	-1.09779600	-0.83750200
O	-0.34786100	0.48926100	1.71444500
O	2.05178600	0.74742800	-0.00287600
O	-2.12261700	1.01460500	-0.50966600
O	0.11577900	1.50051600	-2.25485600
O	0.21591500	2.92293600	0.16227300
N	-1.48605900	-0.15194200	2.16436200
C	-2.98735500	0.64415200	0.30244700
N	0.93321700	-1.98086900	-0.36378500
C	2.77042600	-0.26606400	-0.05888200
C	-1.39350200	-0.21721900	3.67890100
C	-2.74892400	0.64918600	1.80942800
C	-1.63307200	-1.54420500	1.57715000
N	-4.21112300	0.26905300	-0.07993600
C	-4.58380500	0.14428500	-1.45925900
C	0.89566900	-2.11404400	1.14924800
C	0.67645100	-3.32830200	-1.01926300
C	2.34238800	-1.54481400	-0.76749300
N	4.01788800	-0.27652100	0.41348200
C	4.63057900	0.89068300	0.97695500
C	-0.44933500	-2.48647500	1.76373500
C	-1.29401800	1.17537800	4.28415900
C	-2.47059900	2.06126200	3.86990900
C	-2.62353700	2.07290200	2.34771100
C	-4.87775000	1.29717300	-2.21745700
C	-4.63321100	-1.15354500	-2.01308500
C	-5.22142600	1.12090300	-3.56668600

C	-4.81307300	2.70060600	-1.62731300
C	-5.27879400	-0.15194500	-4.13609000
C	-4.99025000	-1.27769800	-3.36379100
C	-4.28836300	-2.38947800	-1.19214200
C	-6.15274900	3.44209500	-1.75893000
C	-3.66255800	3.50423900	-2.25595300
C	-3.01622600	-3.06836800	-1.72357400
C	-5.47183000	-3.36272300	-1.09961500
C	0.75270200	-3.23136000	-2.53581900
C	2.10276500	-2.68055000	-2.99913700
C	2.42080100	-1.36645800	-2.28472200
C	4.65225800	1.03662000	2.37766500
C	5.17733100	1.85486100	0.10120800
C	5.16311900	1.62250100	-1.40613900
C	5.75717200	2.99583000	0.67270800
C	5.78888000	3.16486100	2.05982300
C	5.24427700	2.19638400	2.90293900
C	4.00155700	0.00010800	3.28723400
C	5.19338000	2.91264900	-2.23276600
C	6.30478300	0.67290400	-1.81477900
C	4.81200400	-0.28608300	4.55813500
C	2.56037600	0.42130000	3.62982700
Cl	-5.40592000	-2.10483900	2.69519800
O	-5.91871900	-1.12357600	1.66696100
O	-4.53438100	-3.11985000	2.03236000
O	-4.60328600	-1.35035200	3.71136100
O	-6.55975000	-2.76390800	3.34074100
C	1.24258700	2.23028000	-2.78527900
C	-0.65592700	0.88384800	-3.31331200
C	0.95598300	2.35087700	-4.27777100
C	0.19943200	1.04558700	-4.56631800
C	-0.64587000	3.97790300	-0.31180900
C	1.05258900	3.37962600	1.24864900
C	-0.14112600	5.24184700	0.37987000
C	0.41608300	4.68882800	1.69928600
H	-4.83936400	-0.15032400	0.62216800
H	4.56518200	-1.15229500	0.37646100
H	-1.81032300	-1.40419100	0.50856300
H	-2.52841800	-1.98010800	2.03565100
H	-0.25109100	-2.65101300	2.83423000

H	-0.79069500	-3.46377100	1.38852800
H	1.21585500	-1.14893700	1.54692900
H	1.64487100	-2.87666400	1.40287900
H	-0.49578900	-0.80595800	3.89628800
H	-2.28386800	-0.75837000	4.02873300
H	-0.34465900	1.63141300	3.96713600
H	-1.25554300	1.05859300	5.37887500
H	-3.40107700	1.68050900	4.32522900
H	-2.32602400	3.08845300	4.24074700
H	-1.75375900	2.54205400	1.86958700
H	-3.52303100	2.62963900	2.04309900
H	-3.57312100	0.12795600	2.31134700
H	-5.44755100	1.99618500	-4.18036300
H	-5.55028200	-0.26646100	-5.18910400
H	-5.03404700	-2.27148400	-3.81627800
H	-4.60260400	2.60547200	-0.55234000
H	-2.70869600	2.97341400	-2.13479500
H	-3.57092900	4.49398500	-1.77858600
H	-3.83528600	3.66774900	-3.33283400
H	-6.97499200	2.87276900	-1.29623400
H	-6.41719600	3.62115300	-2.81397800
H	-6.09771500	4.42427400	-1.26085600
H	-4.07529900	-2.07495300	-0.16490600
H	-2.16225700	-2.37350100	-1.71294400
H	-3.14800900	-3.43399800	-2.75571900
H	-2.75606800	-3.93606300	-1.09436300
H	-5.21406500	-4.21082900	-0.44648000
H	-5.75756400	-3.76048800	-2.08780400
H	-6.34917100	-2.86541700	-0.65719700
H	-0.31978000	-3.63850700	-0.68907300
H	1.43017300	-4.02311500	-0.62109900
H	0.58071100	-4.24270900	-2.93745200
H	-0.06856800	-2.59318200	-2.89339900
H	2.09865000	-2.52195300	-4.08944600
H	2.90388900	-3.40131200	-2.77205000
H	3.43927300	-1.03178600	-2.52402100
H	1.71358900	-0.57671700	-2.56710100
H	2.99308500	-2.36663300	-0.45416600
H	6.19264600	3.76426100	0.03193000
H	6.24475100	4.06251400	2.48654900

H	5.27496900	2.34676200	3.98395700
H	4.21717200	1.11645500	-1.65085200
H	6.23775900	-0.29738700	-1.30145500
H	7.28469200	1.12189400	-1.58127000
H	6.27158600	0.47227900	-2.89862300
H	5.03425000	2.67975500	-3.29797500
H	6.16234700	3.43227100	-2.15520400
H	4.40514000	3.61561300	-1.91841200
H	2.55859000	1.36270600	4.20479200
H	5.85334900	-0.55744100	4.32174800
H	4.83203100	0.57965400	5.24031600
H	4.36037000	-1.12509300	5.11205400
H	1.94879900	0.57621800	2.73028100
H	2.06651900	-0.34927300	4.24518100
H	2.16231400	1.65926900	-2.58247000
H	1.31312800	3.19036100	-2.25563000
H	0.30636100	3.22027100	-4.47241600
H	1.87524100	2.46668300	-4.87037200
H	0.90818900	0.20693200	-4.66027600
H	-0.40829800	1.08559900	-5.48205600
H	-1.61723600	1.41475700	-3.39591000
H	-0.84997000	-0.15738000	-3.02287600
H	-1.68198000	3.73464800	-0.03209100
H	2.07700500	3.52444700	0.86844100
H	-0.58649300	4.01246400	-1.40868500
H	0.66704100	5.70479400	-0.20999500
H	-0.93808000	5.98756900	0.51568100
H	-0.40459600	4.49057900	2.40811400
H	1.13831700	5.36012100	2.18625000
H	1.06662800	2.59171800	2.01181900
Cl	5.39456100	-3.54535700	-0.77375900
O	6.59958600	-4.39816600	-0.83919200
O	5.47024500	-2.67448200	0.46394200
O	5.30853800	-2.66063900	-1.97206800
O	4.16472700	-4.39212100	-0.67789100
H	3.94190500	-0.94289300	2.72257900

Co(II)-**L_3-RaPr$_2$**

Co	0.07347800	0.06140100	0.44756700
O	-0.45912800	-1.40441300	-0.84831400

O	0.65479600	1.40011800	-0.94231200
O	2.06596700	-0.56911900	0.59112500
O	-1.96942300	0.61533800	0.47100300
O	0.46254100	1.60982700	1.87836000
O	-0.21111200	-1.19484100	2.13956200
N	-1.44515700	-1.21890700	-1.79650400
C	-2.91134900	0.17080800	-0.20948700
N	1.70434800	1.14975500	-1.79859200
C	3.05237500	-0.14866700	-0.03586000
C	-1.16037700	-0.04729800	-2.70724700
C	-2.80336600	-1.03030200	-1.13750600
C	-1.66732300	-2.55695300	-2.54655400
N	-4.14520700	0.68044200	-0.14854200
C	-4.56921800	1.67228800	0.79401300
C	1.46476800	-0.07428300	-2.65062800
C	3.01170500	0.98898700	-1.03796300
C	1.99690500	2.44158800	-2.60524700
N	4.28131900	-0.62849700	0.17279700
C	4.57699200	-1.57865200	1.20407200
C	0.16911000	-0.08218100	-3.45378800
C	-0.41849900	-3.43688500	-2.65516300
C	-2.69034500	-3.34337200	-1.66963400
C	-0.49160400	-4.39070000	-1.45383200
C	-1.99409500	-4.66690200	-1.29338900
C	-3.04263200	-2.39601200	-0.50640700
C	-4.12075500	3.00544600	0.66088500
C	-5.47076000	1.26883100	1.80406600
C	-5.85460000	2.22831700	2.75316800
C	-6.00358100	-0.16266600	1.84684300
C	-5.36965700	3.53445400	2.68524600
C	-4.52593900	3.92239100	1.64220500
C	-3.30036000	3.43376600	-0.55434300
C	-4.98043200	-1.11911300	2.48265000
C	-4.16660700	3.40742300	-1.83013600
C	0.77201700	3.33340800	-2.83087000
C	2.98086700	3.25992800	-1.71021300
C	0.79683200	4.34851000	-1.67789000
C	2.29372400	4.61662100	-1.46312400
C	3.22499400	2.38394100	-0.46670300
C	4.63664600	-2.94666100	0.87333200

C	4.80341200	-1.09889300	2.51320700
C	4.91786000	-3.85484200	1.90627600
C	5.13084400	-3.40812900	3.21054700
C	5.07664400	-2.04441800	3.51173400
C	4.77686400	0.40068100	2.79474400
C	6.07115200	1.07546300	2.29975300
C	4.34859400	-3.41506300	-0.54868000
C	2.84437300	-3.69567000	-0.72454700
Cl	6.54443300	1.41761600	-2.14815400
O	6.39333000	2.50948000	-1.14514100
O	7.86059200	1.50628800	-2.81520400
O	5.44726200	1.49770700	-3.16391900
O	6.44445400	0.08106900	-1.44304800
Cl	-6.40051400	-1.58173600	-2.16398500
O	-6.31571200	-2.39794000	-0.91735500
O	-5.31093400	-1.97365500	-3.10910200
O	-7.72101700	-1.75514700	-2.80353000
O	-6.21719000	-0.11968200	-1.80927500
C	-1.28437700	-1.09216000	3.09743700
C	0.35626400	-2.52789800	2.14601300
C	1.08946000	1.46456000	3.16430900
C	-0.31080600	2.81690100	1.90339100
C	-0.37211700	-3.27223400	3.26490500
C	-1.71478900	-2.53151300	3.34458800
C	0.15831800	2.18153100	4.17002600
C	-0.95406300	2.79045700	3.28480900
H	-4.87786000	0.27466900	-0.75431200
H	5.06079300	-0.29185100	-0.41675600
H	-1.20433700	0.83833600	-2.06755500
H	-1.98551100	-0.01450400	-3.43090400
H	0.15382500	0.77483400	-4.14521400
H	0.21170800	-0.97517800	-4.09691400
H	1.47877500	-0.92039000	-1.95781400
H	2.32350500	-0.14855100	-3.33199200
H	-2.08119500	-2.27393300	-3.52197600
H	-0.50760300	-4.00531700	-3.59598500
H	0.51603400	-2.86590400	-2.69837500
H	0.10264000	-5.30588500	-1.59940400
H	-0.10528600	-3.87204900	-0.56740900
H	-2.26601300	-5.00419000	-0.28056900

H	-2.30724600	-5.45813100	-1.99440600
H	-3.60860200	-3.51205700	-2.24561100
H	-4.08411200	-2.49994800	-0.18407900
H	-2.36910900	-2.52167100	0.35111000
H	-3.51953200	-0.89848700	-1.95984100
H	-6.54123200	1.95389400	3.55505700
H	-5.67071200	4.26610800	3.43991100
H	-4.19235100	4.95904900	1.59049100
H	-6.15535100	-0.49040700	0.80707000
H	-5.35340400	-2.15588000	2.46207100
H	-4.78709200	-0.84565200	3.53326700
H	-4.02181100	-1.10132200	1.94939600
H	-2.49297300	2.69661200	-0.68410100
H	-3.55098400	3.63707500	-2.71577200
H	-4.96722500	4.16322300	-1.77010300
H	-4.64020100	2.42833800	-1.99390700
H	2.46361300	2.09992600	-3.53664600
H	-0.16819000	2.77342800	-2.89995400
H	0.92466700	3.85126200	-3.79250700
H	0.22746600	5.26294500	-1.90354300
H	0.35990500	3.88354000	-0.78311800
H	2.52386700	5.02044200	-0.46452200
H	2.65267800	5.35157500	-2.20251400
H	3.94156500	3.36880700	-2.22931700
H	2.48766800	2.56505800	0.32757000
H	4.24258000	2.49398600	-0.07561100
H	3.77429400	0.80369600	-1.80581400
H	4.96849200	-4.92372000	1.69036100
H	5.34574100	-4.12974000	4.00348800
H	5.25449100	-1.71902900	4.53782800
H	3.94294900	0.82424500	2.21273400
H	6.02139100	2.16598900	2.45481000
H	6.25414900	0.90279700	1.22908500
H	6.94356200	0.69401400	2.85626600
H	4.61116300	-2.58520400	-1.22357400
H	2.62074300	-3.97476000	-1.76680200
H	2.22951900	-2.82386400	-0.46130700
H	2.53051300	-4.53118500	-0.07712500
H	1.44061000	-2.44503400	2.29420900
H	0.17196800	-2.96365600	1.15409700

H	-0.47619600	-4.34519600	3.04681600
H	0.17547900	-3.16725300	4.21570400
H	-2.39189300	-2.86849400	2.54406300
H	-2.23133200	-2.65665500	4.30732700
H	-2.05681500	-0.44447200	2.66723000
H	-0.89883500	-0.62504900	4.02016200
H	2.08455200	1.93617500	3.12771600
H	1.21440300	0.38989500	3.34019400
H	0.71044800	2.96419700	4.71156000
H	-0.25115300	1.48596300	4.91629600
H	-1.83504800	2.13140000	3.25610300
H	-1.28107700	3.78540300	3.61992900
H	-1.01520700	2.77807900	1.06800300
H	0.36105000	3.68589600	1.77549200
C	5.18416500	-4.62869200	-0.97464600
H	5.02865900	-4.83557000	-2.04583100
H	6.26073900	-4.45774900	-0.81501300
H	4.89839300	-5.54003400	-0.42441900
C	4.51143600	0.74956200	4.26269600
H	4.37481900	1.83716100	4.37196000
H	3.60346800	0.25459400	4.64193900
H	5.35338500	0.46203000	4.91330500
C	-7.36411500	-0.29158600	2.54152600
H	-8.10259700	0.41126100	2.12382700
H	-7.75443200	-1.31248600	2.40301600
H	-7.29697000	-0.11165900	3.62716600
C	-2.63774500	4.80675400	-0.40651800
H	-2.00536900	4.86945700	0.49246300
H	-2.00136000	5.00788200	-1.28031200
H	-3.38395500	5.61609800	-0.35540900

Co(II)-**L_3-$TQPr_2$**

Co	-0.03826100	0.09326200	0.89036100
O	0.41801600	1.43026900	-0.51881300
O	-0.33747200	-1.50424300	-0.24220500
O	1.98224700	-0.26903400	1.29473900
O	-2.05286600	0.57866900	0.62829500
N	-1.29649600	-1.49540900	-1.24857500
C	-2.91021500	0.03550700	-0.09097600
N	1.55842500	1.23783700	-1.27857600

C	2.89133900	0.01025100	0.48344300
C	-1.07828600	-0.37121100	-2.25291300
C	-1.22205800	-2.82833400	-1.94622300
C	-2.69847300	-1.36680900	-0.64955200
N	-4.07589600	0.61943000	-0.34852700
C	2.80434900	1.26401100	-0.38960500
C	1.65845900	2.39989900	-2.23219500
C	1.52514900	-0.07661200	-2.04391400
N	4.01090100	-0.69702800	0.37154200
C	0.29609100	-0.31146600	-2.91497400
C	-1.63823100	-3.97786800	-1.06648600
C	-2.44745200	-3.78098600	0.06087600
C	-1.22340000	-5.27235500	-1.41406300
C	-1.60884100	-6.37091500	-0.64554800
C	-2.41025400	-6.17715500	0.48651800
C	-2.82369600	-4.89038500	0.83279900
C	-2.87919600	-2.39552700	0.46484100
C	1.84755500	3.71141400	-1.51470300
C	2.42373500	3.76494300	-0.23562300
C	1.48596900	4.89984900	-2.16585400
C	1.69669400	6.13746300	-1.55500200
C	2.27030300	6.19381200	-0.27915200
C	2.62654100	5.01244600	0.37357200
C	2.75175200	2.49596000	0.50864500
Cl	-6.23468300	-2.12552200	-1.18282800
O	-7.59279800	-2.47185700	-1.65227000
O	-5.73806400	-0.92102700	-1.96637700
O	-5.29435000	-3.25771700	-1.41260800
O	-6.25845200	-1.76747700	0.26826400
Cl	5.39761900	0.10143200	-2.94287300
O	5.80934700	0.37182400	-1.50649300
O	4.61395000	-1.16758900	-2.98411100
O	6.60913200	-0.00124100	-3.77874700
O	4.53775300	1.23417200	-3.40627800
H	-4.77011200	0.12289800	-0.93308300
H	4.69822700	-0.37334400	-0.32875700
H	-1.25830500	0.56050000	-1.71519500
H	-1.85468200	-0.50220000	-3.01836600
H	0.21572900	0.46941200	-3.68693900
H	0.50329000	-1.23805000	-3.47191900

H	1.58893900	-0.86748500	-1.29323300
H	2.43582700	-0.10031400	-2.65486900
H	-1.86077700	-2.76084500	-2.83944600
H	-0.17989400	-2.94327600	-2.26457700
H	-0.58592300	-5.41468500	-2.29140400
H	-1.27973700	-7.37522700	-0.92377000
H	-2.71437800	-7.03098800	1.09755600
H	-3.45343100	-4.73511700	1.71333900
H	-2.31096600	-2.06854800	1.34951100
H	-3.94549500	-2.39627200	0.73008400
H	-3.39869900	-1.56614800	-1.46921700
H	2.49952100	2.19014000	-2.90865200
H	0.72589000	2.40109400	-2.80679200
H	1.03310500	4.85116800	-3.16001300
H	1.41150400	7.05672700	-2.07273800
H	2.43714300	7.15810600	0.20776900
H	3.07105800	5.05146000	1.37228200
H	1.99329100	2.32575100	1.28592300
H	3.72298900	2.58217900	1.01975900
H	3.65808600	1.31503500	-1.07307900
C	-4.41366900	1.87575800	0.25915700
C	-4.86526100	1.88498000	1.59591200
C	-4.22550100	3.05892500	-0.48471600
C	-5.13635100	3.13027300	2.18227900
C	-4.51504200	4.27924100	0.14400600
C	-4.96498700	4.31544400	1.46483200
H	-5.48003000	3.17238700	3.21842000
H	-4.37319700	5.21408300	-0.40269900
H	-5.17957900	5.27599200	1.94128700
C	4.43336000	-1.74643200	1.25638200
C	5.59448400	-1.50125700	2.02254200
C	3.73285300	-2.97515200	1.31148000
C	6.05785900	-2.52746600	2.85985600
C	4.23172300	-3.95884300	2.17812400
C	5.38178500	-3.74254600	2.94035500
H	6.95851700	-2.36891600	3.45670400
H	3.72242100	-4.92004600	2.25361400
H	5.75256900	-4.53150100	3.60032100
C	2.52651200	-3.25117000	0.41861300
C	1.61266300	-4.36683400	0.93584200

C	2.97661500	-3.53836600	-1.02518100
H	1.90781100	-2.34660700	0.39829500
H	1.30833100	-4.19274100	1.98063600
H	0.69870500	-4.40692300	0.32727300
H	2.08772900	-5.35995900	0.87912200
H	3.60383600	-2.73222400	-1.43263600
H	3.55629900	-4.47564200	-1.07515300
H	2.09929800	-3.65122400	-1.68431400
C	6.36024200	-0.18402400	1.93669400
C	7.65364100	-0.36166600	1.12246700
C	6.64550300	0.42105000	3.31975800
H	5.73462300	0.54222600	1.39808000
H	7.43613200	-0.72378900	0.10659500
H	8.18658900	0.59909100	1.02781700
H	8.33185300	-1.08020000	1.61230700
H	5.71922300	0.54487300	3.90416700
H	7.33604700	-0.20315900	3.90959200
H	7.11328500	1.41321900	3.21078000
C	-3.65172700	3.02559700	-1.89611400
C	-2.15842000	3.40239500	-1.87172400
C	-4.43359600	3.90519800	-2.88118900
H	-3.72288700	1.98865900	-2.25802500
H	-1.58194200	2.76340100	-1.18645900
H	-1.71821600	3.30529200	-2.87869600
H	-2.02306900	4.44771200	-1.54700000
H	-5.50309300	3.64042600	-2.89662100
H	-4.35311800	4.97551400	-2.63037900
H	-4.03748400	3.77851600	-3.90225300
C	-5.00860900	0.60007500	2.40362800
C	-6.39822800	0.46376500	3.04208100
C	-3.88857700	0.48606100	3.45380700
H	-4.90585500	-0.24439800	1.70983200
H	-7.19140100	0.52163200	2.28012200
H	-6.48956300	-0.51201500	3.54689300
H	-6.58825000	1.24555300	3.79604000
H	-2.89384000	0.53479800	2.98580800
H	-3.95665300	1.29848100	4.19733800
H	-3.96635400	-0.47124600	3.99603700
O	-0.20738100	1.31921300	2.53903800
C	0.61442500	1.26571700	3.73222200

C	-0.77355300	2.65190900	2.35394900
H	1.50797400	0.67234200	3.49682900
H	0.04039300	0.75902900	4.52654800
C	0.89048500	2.72443300	4.07062500
H	1.11965100	2.86861100	5.13636500
H	1.74283600	3.09651700	3.47950400
C	-0.40998000	3.40890300	3.62673300
H	-1.19372700	3.27334000	4.38989300
H	-0.29314700	4.48643700	3.44141900
H	-0.31090700	3.08146000	1.45189300
H	-1.85082200	2.54357100	2.17921800

Co(II)-**L_3-$PePr_2$**

Co	0.00451200	0.56504900	0.60168400
O	0.43138200	1.41823600	-1.17800600
O	2.04968700	0.49448200	1.00478300
O	-0.10402700	-1.35171900	-0.03049700
O	-2.05923200	0.67489700	0.32449800
N	1.55547200	1.08046500	-1.90028000
N	4.21004600	0.18819100	0.44417200
H	4.89874200	0.16853300	-0.32402300
N	-1.04617000	-1.74508500	-0.95907300
N	-4.17762100	0.00141400	-0.00970700
H	-4.80912000	-0.77997400	-0.24496900
C	1.57809500	-0.37644600	-2.30627200
H	1.74319200	-0.93222900	-1.37780500
H	2.45523500	-0.50339300	-2.94989800
C	0.33998300	-0.92378700	-3.00113100
H	0.13942100	-0.36702400	-3.92669700
H	0.61074800	-1.93520700	-3.33376800
C	-0.98408500	-0.95367600	-2.25023200
H	-1.26675400	0.06611900	-1.97503000
H	-1.76010300	-1.38022500	-2.89993700
C	1.69798800	2.09878300	-3.04980800
H	2.48743500	1.68529900	-3.69191400
C	0.41965300	2.33363100	-3.85076900
H	-0.44120000	2.32309000	-3.16740300
H	0.27375400	1.53439500	-4.58997200
C	0.51473900	3.68915200	-4.56623700
H	1.41729900	3.68486700	-5.20167400

H	-0.34038300	3.80311500	-5.25072100
C	0.57566500	4.87263100	-3.57387500
H	-0.43019100	5.30129100	-3.43148900
H	1.19749700	5.67623200	-4.00206600
C	1.13234300	4.44559600	-2.20423700
H	1.52672700	5.31722300	-1.65658200
H	0.32876200	4.01779100	-1.58725900
C	2.22307400	3.38045400	-2.33414900
H	3.04718100	3.77990000	-2.94534100
C	2.77373300	2.90085400	-0.97085800
H	3.76631600	3.30599600	-0.73508200
H	2.08018200	3.15567400	-0.15906300
C	2.83178600	1.38560500	-1.12101600
H	3.65542400	1.11368600	-1.78962300
C	2.97385500	0.62426400	0.18544500
C	4.56133400	-0.39623800	1.70470800
C	4.69054800	-1.79527900	1.79477600
C	5.05218100	-2.33778700	3.03922300
H	5.17293600	-3.41857900	3.14019700
C	5.25181900	-1.51637500	4.14722200
H	5.52766400	-1.95662300	5.10934700
C	5.09780800	-0.13054400	4.03730200
H	5.25504800	0.49443700	4.91776400
C	4.75273100	0.45970200	2.81469200
C	4.47000800	-2.69239900	0.58395700
H	3.96173000	-2.10058600	-0.18891100
C	5.81524500	-3.13257300	-0.01793400
H	6.40858300	-2.26156700	-0.33486100
H	5.65104800	-3.75687200	-0.91004500
H	6.40534000	-3.71282200	0.71175500
C	3.56901800	-3.89571400	0.89713200
H	2.60718600	-3.57496400	1.32717800
H	4.03963400	-4.59729600	1.60536500
H	3.35553200	-4.45766500	-0.02545300
C	4.62270500	1.97198200	2.65538900
H	3.78169300	2.15703500	1.97146700
C	4.28831400	2.71093100	3.95529900
H	4.08289800	3.77217100	3.74095500
H	5.12072700	2.68121800	4.67717200
H	3.39760200	2.28670200	4.44572300

C	5.88617600	2.55459300	1.99650300
H	5.76574100	3.63460500	1.80905200
H	6.10187600	2.06555500	1.03388200
H	6.76524000	2.41740600	2.64792300
C	-0.94425500	-3.27799400	-1.12420300
H	-1.55439300	-3.50322800	-2.00989900
C	0.47884900	-3.80045400	-1.30008000
H	1.15185100	-3.24084700	-0.63753400
H	0.82652200	-3.65020000	-2.33061100
C	0.51244600	-5.29563300	-0.95221100
H	1.50527200	-5.70380300	-1.19693800
H	-0.20383400	-5.82271300	-1.60595900
C	0.16716600	-5.56380600	0.53159800
H	-0.39299300	-6.51032300	0.61027200
H	1.08972300	-5.69866600	1.11941700
C	-0.65427200	-4.41681400	1.14563200
H	0.01379700	-3.60285700	1.46509900
H	-1.18782400	-4.76219400	2.04627700
C	-1.65410200	-3.83714000	0.14361000
H	-2.33478800	-4.63144400	-0.19512100
C	-2.49118600	-2.66936300	0.70893800
H	-3.53076500	-2.95153400	0.91531700
H	-2.03492100	-2.25913000	1.61908800
C	-2.45446900	-1.62600700	-0.39987600
H	-3.10957600	-1.93773400	-1.21876900
C	-2.85918800	-0.21738600	-0.00028800
C	-4.73390900	1.25144700	0.41553600
C	-5.30412000	1.32823300	1.70243100
C	-5.84524100	2.55930800	2.10528100
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C	-4.66382800	2.36245300	-0.45473200
C	-5.35052600	0.10095800	2.60498600
H	-4.52271600	-0.55725900	2.29881800
C	-6.65846100	-0.68004300	2.38517400
H	-6.78077600	-0.97528500	1.33207000
H	-7.52961500	-0.06709400	2.67147100

C	-5.13840000	0.42655700	4.08904700
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H	-5.98628900	0.98700800	4.51525300
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H	-3.17501900	1.56139200	-1.75263600
C	-5.04221800	1.54565800	-2.80688400
H	-5.34230200	0.54820600	-2.45226800
H	-4.58854600	1.41677200	-3.80393100
H	-5.95010800	2.16071700	-2.92450500
C	-3.52796300	3.54153700	-2.42848200
H	-2.84059200	4.04898500	-1.73287000
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O	-0.19979700	2.46223800	1.50648500
O	-0.22828000	-0.08557100	2.61508700
C	-1.09496700	3.47586800	1.00479700
H	-2.10578200	3.28311700	1.39898100
H	-1.12380700	3.38345100	-0.08893700
C	-0.51224300	4.78735700	1.51681500
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H	-1.27206500	5.57746100	1.60630300
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H	-0.69750200	4.27393400	3.62563400
C	0.66690300	2.98524500	2.53252000
H	1.69064500	3.04926800	2.12995500
H	0.67135800	2.27689200	3.37315500
C	-1.42629400	0.12165400	3.39013600
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H	-0.66187700	-0.07213900	5.41349300
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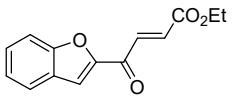
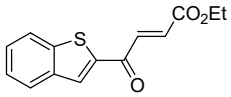
C	-0.32774700	-1.83645700	4.17966900
H	-0.94240000	-2.59447200	3.66856400
H	0.23508300	-2.33342500	4.98318500
C	0.58409200	-1.13767000	3.17841500
H	1.46199700	-0.68404900	3.66715700
H	0.93051600	-1.77248400	2.35234900

Cl	-5.44955800	-2.98288700	-1.81463000
O	-4.46746100	-4.08326100	-1.59924300
O	-6.71591400	-3.51169000	-2.36240600
O	-4.85983300	-1.96572600	-2.74272000
O	-5.72487700	-2.31075000	-0.48352000
Cl	5.42411600	-0.67955400	-2.98289100
O	4.49850400	-1.78068400	-2.58988400
O	6.55124800	-1.20744300	-3.77831000
O	4.66955200	0.34968100	-3.76823100
O	5.97396600	-0.01487300	-1.73726900
H	-6.67230000	-1.59867000	2.99543000

9. Substrates scope limitation



N. R.



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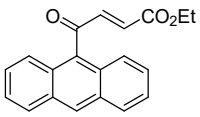

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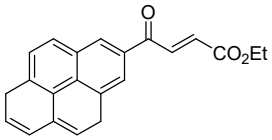

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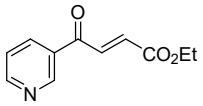

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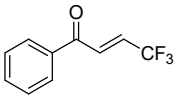
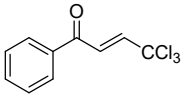


Trace



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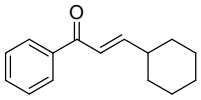

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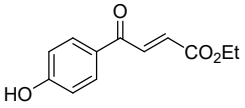

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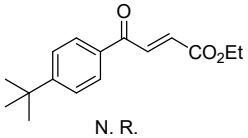

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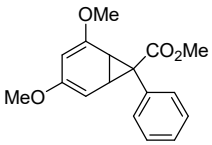

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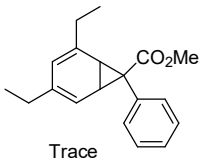
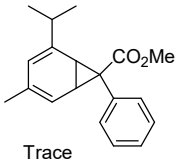


Trace



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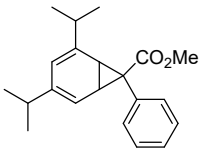

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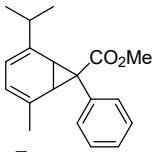

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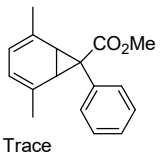
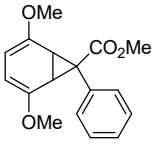
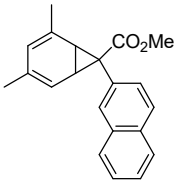


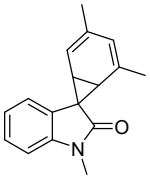
Trace



N. R.



N. R.



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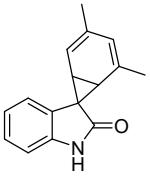
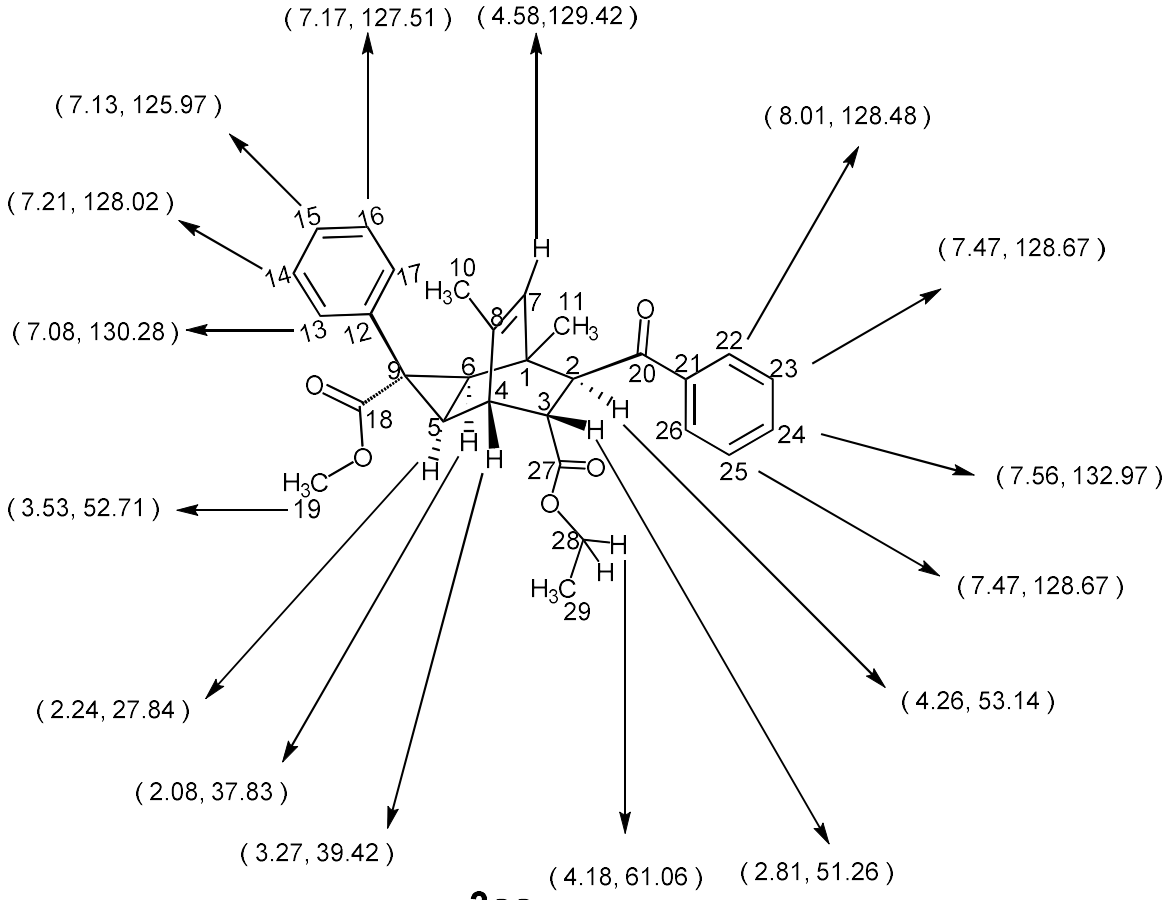


N. R.

10. Analysis Results of 2D NMR Spectra of the Product 3aa

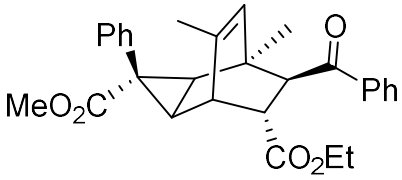


3aa

Number of Atom	H	C	Number of Atom	H	C
1	—	41.57	16	7.17 (m)	127.51
2	4.26 (d)	53.14	17	6.93 (d)	131.23
3	2.81 (d)	51.26	18	—	174.3
4	3.27	39.42	19	3.53	52.71
5	2.24 (m)	27.84	20	—	201.97
6	2.08 (d)	37.83	21	—	139.28
7	4.58	129.42	22	8.01 (d)	128.48
8	—	138.30	23	7.47	128.67
9	—	36.22	24	7.56	132.97
10	1.24	20.12	25	7.47	128.67
11	1.27,	23.70	26	8.01 (d)	128.48
12	—	137.1	27	—	173.19
13	7.08 (d)	130.28	28	4.18 (m)	61.06
14	7.21 (m)	128.02	29	1.23,	14.3
15	7.13 (m)	125.97			

11. Characterization of the product

3aa: 6-ethyl 3-methyl (1R,2R,3S,4R,5S,6R,7S)-7-benzoyl-1,9-dimethyl-3-phenyltricyclo[3.2.2.0^{2,4}]-non-8-ene-3,6-dicarboxylate



3aa

42.1 mg, 92% yield, 19:1 dr, 91% ee, light yellow solid, 132 – 134 °C,; $[\alpha]^{20}_{D}$ = -116.8 (*c* = 0.86, in CH_2Cl_2).

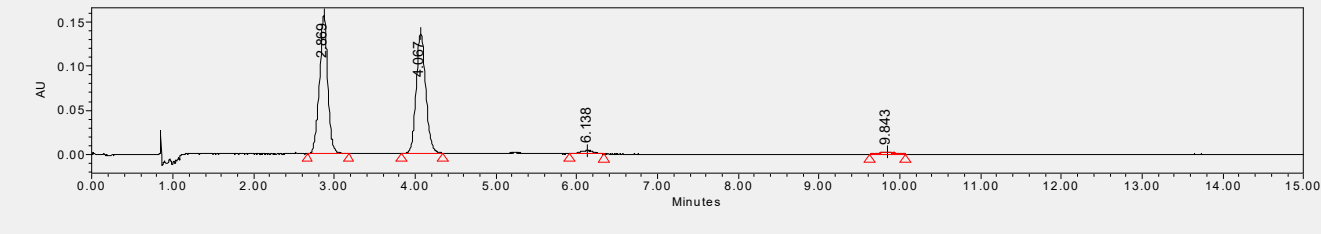
HPLC (Daicel chiralcel OX-3, CO_2/MeOH 90/10, 1.5 mL/min, λ = 254 nm), t_R(major) = 4.04 min, t_R(minor) = 2.86 min.

^{1}H NMR (600 MHz, Chloroform-*d*) δ = 8.01 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.20 (m, 2H), 7.13 (m, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 1H), 4.58 (s, 1H), 4.26 (d, *J* = 6.0 Hz, 1H), 4.17 (m, 2H), 3.53 (s, 3H), 3.27 (s, 1H), 2.80 (d, *J* = 5.4 Hz, 1H), 2.27 – 2.23 (m, 1H), 2.07 (d, *J* = 9.0 Hz, 1H), 1.25 (m, 9H) ppm.

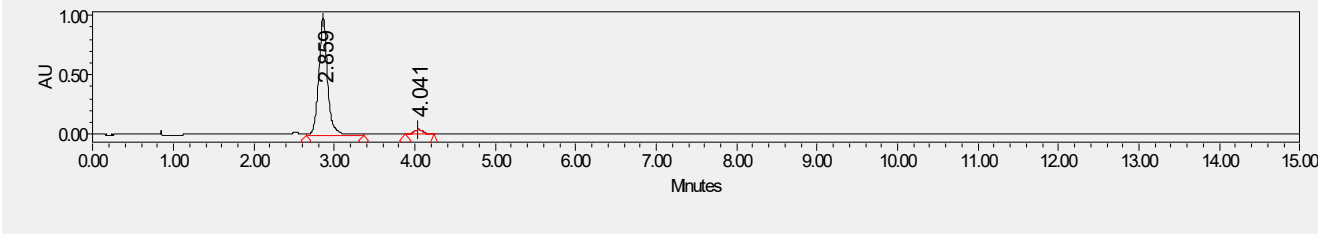
^{13}C NMR (151 MHz, $CDCl_3$) δ = 202.0, 174.3, 173.2, 139.3, 138.3, 137.1, 133.0, 131.2, 130.3, 129.4, 128.7, 128.5, 128.2, 127.5, 126.0, 61.1, 53.1, 52.7, 51.3, 41.6, 39.4, 37.8, 36.2, 27.8, 23.7, 20.1, 14.2 ppm.

ESI-HRMS calcd for [$C_{30}H_{32}O_5$+Na^+] = 458.2093, found 458.2092.

IR $\tilde{\nu}$ (cm^{-1}) 3059, 2959, 1722, 1677, 1446, 1374, 1300, 1230, 1024,961, 734, 697, 521.

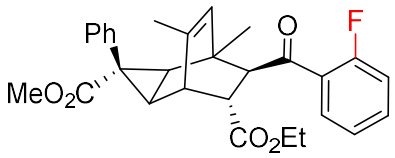


	Retention Time	Area	% Area
1	2.869	1130122	48.48
2	4.067	1132339	48.58
3	6.138	39799	1.71
4	9.843	28811	1.24



	Retention Time	Area	% Area
1	2.859	7491258	95.60
2	4.041	344750	4.40

3ab: 6-ethyl-3-methyl-7-(2-fluorobenzoyl)-1,9-dimethyl-3-phenyltricyclo[3.2.2.0^{2,4}]non-8-ene-3,6-dicarboxylate



3ab

42.8 mg, 86% yield, 19:1 dr, 90% ee; light yellow liquid, $[\alpha]^{22}_{D}$ = -137.7 (c = 0.57, in CH_2Cl_2).

HPLC (Daicel chiralcel OX-3, CO_2/MeOH 90/10, 1.5 mL/min, λ = 254 nm), t_R(major) = 2.99 min, t_R(minor) = 4.33 min

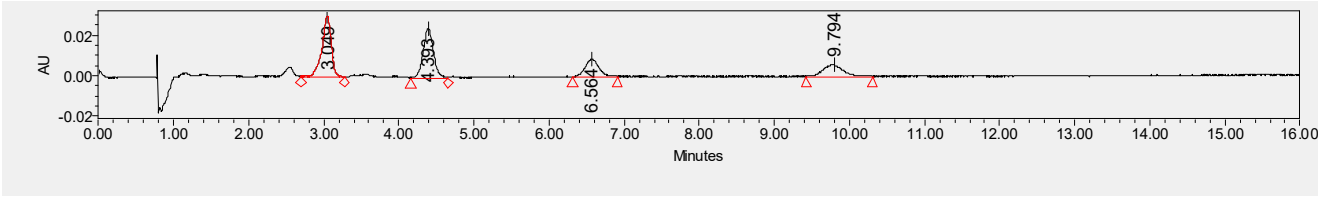
^{1}H NMR (600 MHz, Chloroform-d) δ = 7.78 (m, 1H), 7.49 (m, 1H), 7.23 – 7.10 (m, 5H), 7.07 (d, J = 7.2 Hz, 1H), 6.92 (d, J = 7.2 Hz, 1H), 4.56 (s, 1H), 4.22 – 4.13 (m, 3H), 3.51 (s, 3H), 3.28 – 3.23 (m, 1H), 2.88 (dd, J = 5.4, 1.8 Hz, 1H), 2.27 (dd, J = 9.0, 3.6, Hz, 1H), 2.05 (d, J = 9.0 Hz, 1H), 1.34 (s, 3H), 1.25 – 1.18 (m, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 200.2, 200.2, 174.2, 173.1, 161.7, 160.0, 138.8, 137.1, 134.0 ($J_{C\text{-}F}$ = 9.1 Hz), 131.2, 130. 6, 130.3, 129.1, 128.7 ($J_{C\text{-}F}$ = 12.1 Hz), 128.3, 127.5, 126.0, 124.4, 124.4, 117.1 ($J_{C\text{-}F}$ = 22.6 Hz), 116.9, 61.0, 57.4, 57.4, 52.7, 50.7, 42.0, 39.1, 37.9, 36.4, 27.7, 23.17, 20.1, 14.1 ppm.

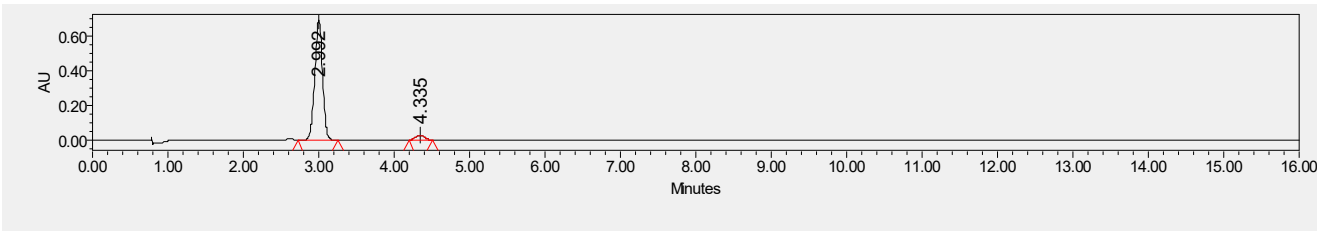
^{19}F NMR (565 MHz, $CDCl_3$) δ = -111.10 ppm.

ESI-HRMS calcd [$C_{29}H_{29}FO_5$+Na^+] = 477.2072, found 477.2070.

IR $\tilde{\nu}$ (cm^{-1}) 3058, 2874, 1718, 1606, 1577, 1481, 1448, 1373, 1228, 1193, 1127, 1024, 939, 768, 735, 643, 515

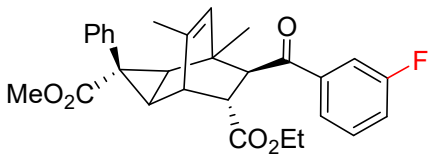


	Retention Time	Area	% Area
1	3.049	268424	37.30
2	4.393	232672	32.33
3	6.564	109849	15.27
4	9.794	108631	15.10



	Retention Time	Area	% Area
1	2.992	5080678	95.11
2	4.335	261247	4.89

3ac: 6-ethyl 3-methyl-7-(3-fluorobenzoyl)-1,9-dimethyl-3-phenyltricyclo[3.2.2.0^{2,4}]non-8-ene-3,6-dicarboxylate



3ac

38.6 mg, 90% yield, 19:1 dr, 91% ee.; light yellow liquid, $[\alpha]^{20}_{D}$ = -133.6 (*c* = 0.53, in CH_2Cl_2).

HPLC (Daicel chiralcel OXH, CO_2/EtOH 95/5, 1.0 mL/min, λ = 254 nm), t_R(major) = 14.03 min, t_R(minor) =15.82 min.

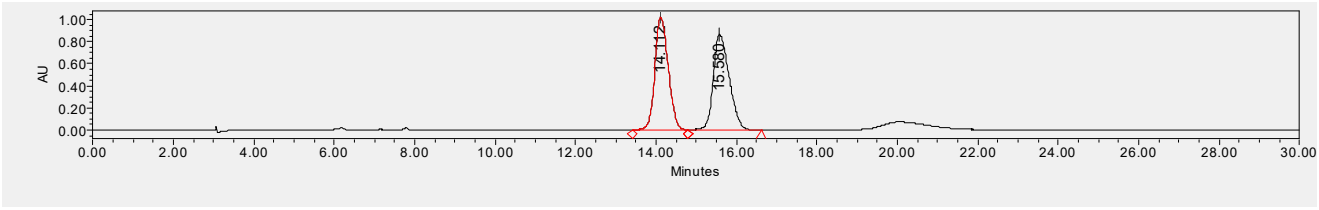
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.82 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 9.6 Hz, 1H), 7.46 (m, 1H), 7.30 – 7.06 (m, 5H), 6.92 (m, 1H), 4.57 (s, 1H), 4.27 – 4.12 (m, 3H), 3.53 (s, 3H), 3.32 – 3.23 (m, 1H), 2.78 (dd, *J* = 6.0, 2.0 Hz, 1H), 2.23 (dd, *J* = 8.8, 3.6 Hz, 1H), 2.06 (d, *J* = 9.2 Hz, 1H), 1.33 – 1.18 (m, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.9, 200.8, 174.2, 173.0, 164.1, 161. 7, 141.4 (J_{C-F} = 6.1Hz), 141.3, 138.5, 137.0, 131.2, 130.3 (J_{C-F} = 7.5Hz), 130.2, 129.2, 128.0, 127.5, 126.0, 124.3 124.3, 120.0 (J_{C-F} = 21.1Hz), 119.9, 115.1 (J_{C-F} = 22.2 Hz), 61.2, 53. 3, 52.7, 51.3, 41.7, 39.3, 37.70, 36.2, 27.8, 23.6, 20.1, 14.2 ppm.

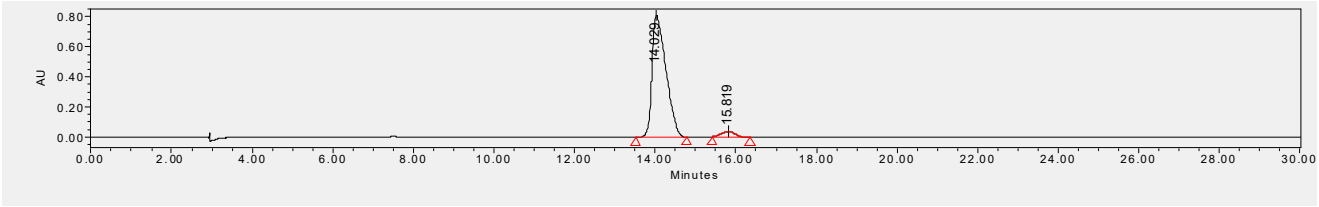
^{19}F NMR (377 MHz, $CDCl_3$) δ = -111.72 ppm.

ESI-HRMS calcd [$C_{29}H_{29}FO_5$+H^+] = 477.2072, found 477.2071.

IR $\tilde{\nu}$ (cm^{-1}) 2906, 1718, 1680, 1586, 1439, 1374, 1305, 1230, 1192, 1059, 1026, 897, 788, 734, 701, 518.

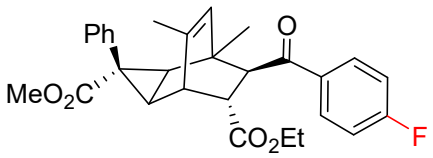


	Retention Time	Area	% Area
1	14.112	23490698	49.90
2	15.580	23582316	50.10



	Retention Time	Area	% Area
1	14.029	19531515	95.58
2	15.819	902403	4.42

3ad: 6-ethyl 3-methyl-7-(4-fluorobenzoyl)-1,9-dimethyl-3-phenyltricyclo[3.2.2.0^{2,4}]non-8-ene-3,6-dicarboxylate



3ad

41.5 mg, 90% yield, 19:1dr, 91% ee.; light yellow liquid, $[\alpha]^{22}_{D}$ = -116.0 (*c* = 0.50, in CH_2Cl_2).

HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm), t_R(major) = 7.27 min, t_R(minor) = 9.36 min.

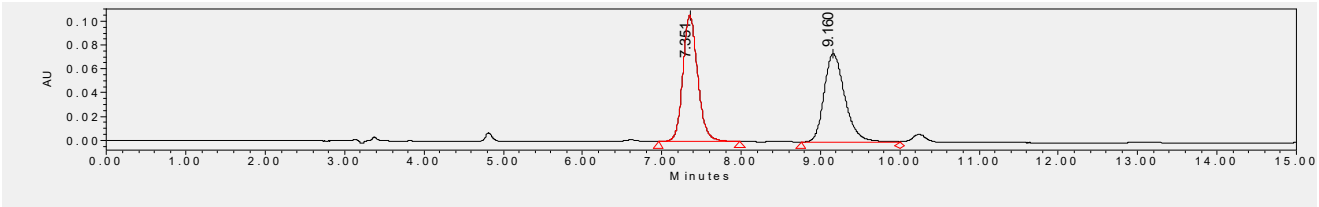
^{1}H NMR (600 MHz, Chloroform-*d*) δ = 8.05 (m, 2H), 7.24 – 7.11 (m, 5H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 4.58 (m, 1H), 4.23 – 4.15 (m, 3H), 3.53 (s, 3H), 3.28 – 3.25 (m, 1H), 2.76 (dd, *J* = 6.0, 1.8, Hz, 1H), 2.22 (dd, *J* = 7.2, 4.2, Hz, 1H), 2.06 (d, *J* = 9.0 Hz, 1H), 1.28 – 1.22 (m, 9H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 200.40, 174.20, 173.13, 165.8, 138.28, 137.01, 135.64 (J_{C-F} = 2.3 Hz), 131.2 (J_{C-F} = 8.8 Hz), 130.26, 129.39, 128.03, 127.53, 126.00, 115.8 (J_{C-F} = 21.6 Hz), 61.13, 53.1, 52.7, 51.38, 41.54, 39.43, 37.73, 36.19, 27.78, 23.65, 20.11, 14.25 ppm.

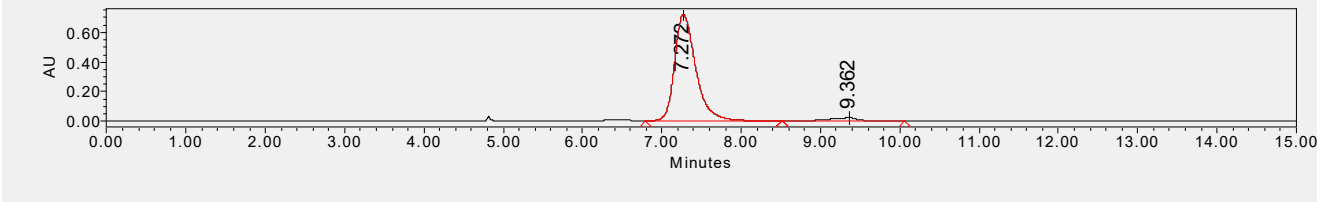
^{19}F NMR (565 MHz, $CDCl_3$) δ = -105.53 ppm.

ESI-HRMS calcd for [$C_{29}H_{29}FO_5$+Na^+] = 499.1891, found 499.1892.

IR $\tilde{\nu}$ (cm^{-1}) 2960, 2873, 1720, 1677, 1595, 1503, 1410, 1373, 1302, 1226, 1157, 1022, 961, 841, 800, 735, 603, 509.

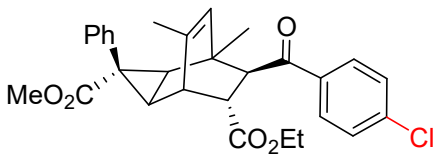


	Retention Time	Area	% Area
1	7.351	1383036	50.46
2	9.160	1357821	49.54



	Retention Time	Area	% Area
1	7.272	13481328	95.56
2	9.362	626282	4.44

3ae: 6-ethyl 3-methyl -7-(4-chlorobenzoyl)-1,9-dimethyl-3-phenyltricyclo[3.2.2.0^{2,4}]non-8-ene-3,6-dicarboxylate



3ae

33.1 mg, 91% yield, 19:1dr, 92% ee.; light yellow solid, 130 – 132 °C, $[\alpha]^{21}_{589}$ = -117.5 (*c* = 0.53, in CH_2Cl_2).

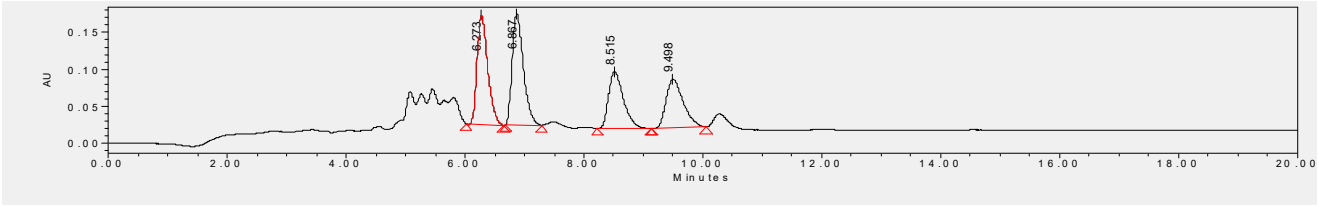
HPLC (Daicel chiralcel IB, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, λ = 254 nm), t_R(major) = 9.29 min, t_R(minor) =8.30 min.

^{1}H NMR (600 MHz, Chloroform-*d*) δ = 7.96 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 5.6 Hz, 2H), 7.20 (m, 2H), 7.13 (t, *J* = 4.0 Hz, 1H), 7.08 (d, *J* = 4.8 Hz, 1H), 6.92 (d, *J* = 7.2 Hz, 1H), 4.57 (s, 1H), 4.18 (m, 3H), 3.53 (s, 3H), 3.27 (s, 1H), 2.83 – 2.72 (m, 1H), 2.22 (dd, *J* = 9.0, 4.2 Hz, 1H), 2.05 (d, *J* = 9.0 Hz, 1H), 1.28 – 1.19 (m, 9H) ppm.

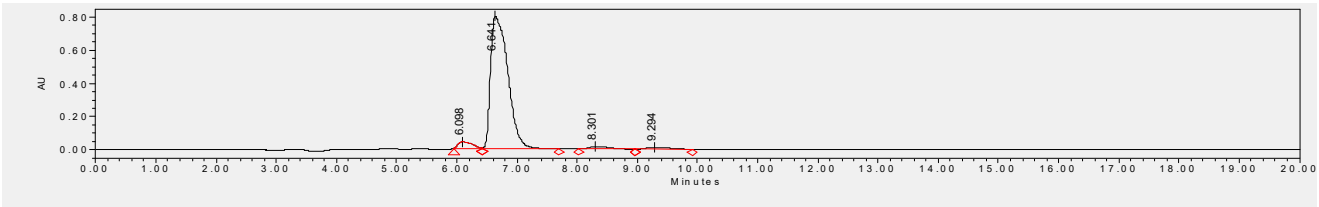
^{13}C NMR (151 MHz, $CDCl_3$) δ = 200.8, 174.2, 173.1, 139.5, 138.43 137.6, 137.0, 131.21 130.3, 129.90 129.3, 129.0, 128.1, 127.5, 126.0, 61.2, 53.2, 52.7, 51.4, 41.6, 39.4, 37.7, 36.2, 27.8, 23.7, 20.1, 14.3 ppm.

ESI-HRMS calcd [$C_{29}H_{29}ClO_5$+Na^+] = 515.1595, 517.1566, found 515.1605, 517.1570.

IR $\tilde{\nu}$ (cm^{-1}) 2959, 2906, 1720, 1677, 1588, 1490, 1442,1373, 1286, 1229, 1193, 1092, 1061, 961, 831, 735, 701, 527.

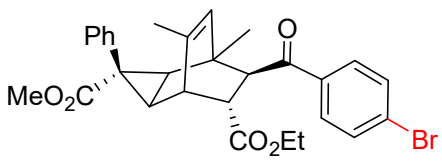


	Retention Time	Area	% Area
1	6.273	1862407	28.53
2	6.867	1978023	30.31
3	8.515	1352650	20.72
4	9.498	1333769	20.44



	Retention Time	Area	% Area
1	6.098	645042	3.77
2	6.641	15898521	92.80
3	8.301	312348	1.82
4	9.294	276253	1.61

3af: 6-ethyl 3-methyl -7-(4-bromobenzoyl)-1,9-dimethyl-3-phenyltricyclo[3.2.2.0^{2,4}]non-8–ene-3,6-dicarboxylate



3af

48.4 mg, 88% yield, 19:1dr, 91% ee.; light yellow solid, m.p. 137–138 °C, $[\alpha]^{20}_{D}$ = -144.0 (*c* = 0.60, in CH_2Cl_2).

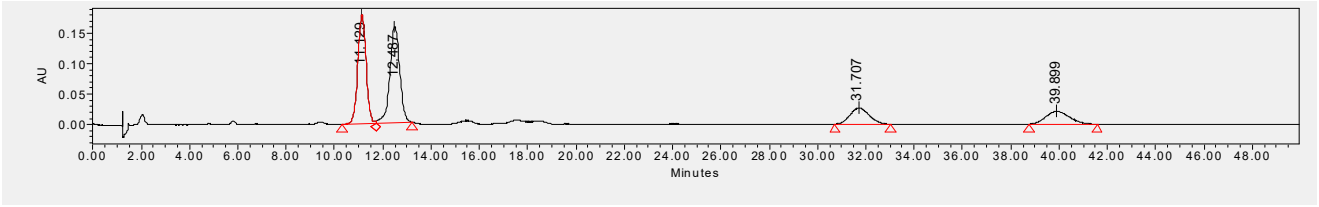
HPLC (Daicel chiralcel OX-3, CO_2/MeOH 95/5, 1.5 mL/min, λ = 254 nm), t_R(major) = 11.24 min, t_R(minor) = 12.66 min.

^{1}H NMR (600 MHz, Chloroform-*d*) δ = 7.88 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.23 – 7.16 (m, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 4.57 (s, 1H), 4.23 – 4.12 (m, 3H), 3.52 (s, 3H), 3.34 – 3.19 (m, 1H), 2.77 (dd, *J* = 6.0, 2.4 Hz, 1H), 2.22 (dd, *J* = 8.0, 3.6 Hz, 1H), 2.05 (d, *J* = 8.0 Hz, 1H), 1.28 – 1.20 (m, 9H) ppm.

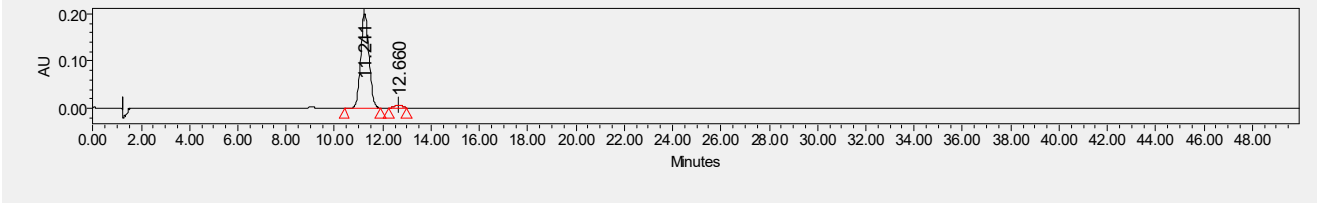
^{13}C NMR (151 MHz, $CDCl_3$) δ = 201.0, 174.2, 173.1, 138.4, 138.0, 137.0, 132.0, 131.2, 130.3, 130.0, 129.2, 128.3, 128.0, 127.53, 26.0, 61.2, 53.2, 52.7, 51.3, 41.6, 39.4, 37.7, 36.2, 27.8, 23.7, 20.1, 14.3 ppm.

ESI-HRMS calcd [$C_{29}H_{29}BrO_5$+Na^+] = 559.1091, 561.1070, found 559.1091, 561.1072.

IR $\tilde{\nu}$ (cm^{-1}) 2959, 1719, 1677, 1583, 1442, 1304, 1268, 1129, 1004, 961, 936, 735,701, 535.

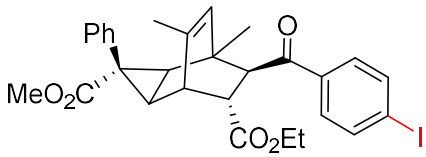


	Retention Time	Area	% Area
1	11.129	4302674	36.67
2	12.487	4458723	38.00
3	31.707	1493070	12.72
4	39.899	1479998	12.61



	Retention Time	Area	% Area
1	11.241	4874591	97.40
2	12.660	130056	2.60

3ag: 6-ethyl 3-methyl -7-(4-iodobenzoyl)-1,9-dimethyl-3-phenyltricyclo[3.2.2.0^{2,4}]non-8-ene-3,6-dicarboxylate



3ag

45.1 mg,77% yield, 19:1dr, 89% ee.; light yellow solid, m.p. 138 – 141 °C, $[\alpha]^{20}_{D}$ = -147.3 (*c* = 0.78, in CH_2Cl_2).

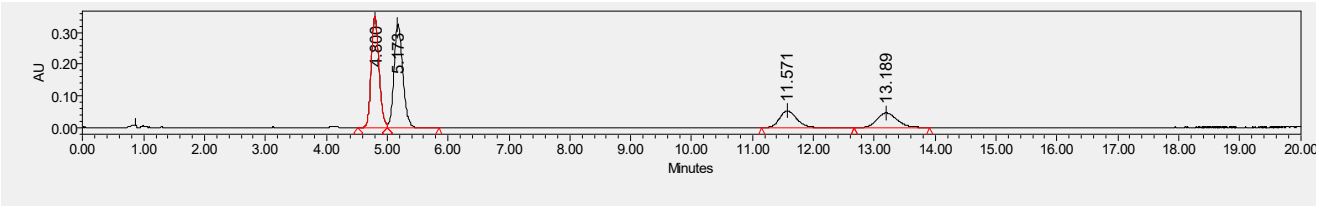
HPLC (Daicel chiralcel OX-3, CO_2/MeOH 95/5, 1.5 mL/min, λ = 254 nm), t_R(major) = 4.79 min, t_R(minor) =5.22 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.83 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.6 Hz, 2H), 7.24 – 7.04 (m, 4H), 6.91 (d, *J* = 8.4 Hz, 1H), 4.56 (s, 1H), 4.23 – 4.12 (m, 3H), 3.52 (s, 3H), 3.26 (m, 1H), 2.76 (dd, *J* = 6.0, 2.2 Hz, 1H), 2.22 (dd, *J* = 9.2, 4.0 Hz, 1H), 2.05 (d, *J* = 9.2 Hz, 1H), 1.28 – 1.20 (m, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 201.30 174.2, 173.1, 138.5, 138.4, 138.0, 136.9, 131.2, 130.23 129.9, 129.2, 128.02 127.52, 126.0, 101.12, 61.2, 53.1, 52.8, 51.3, 41.60 39.3, 37.72, 36.2, 27. 8, 23.7, 20.1, 14.3 ppm.

ESI-HRMS calcd [$C_{29}H_{29}IO_5$+Na^+] = 607.0952, found 607.0952.

IR $\tilde{\nu}$ (cm^{-1}) 2958, 1719, 1676, 1442, 1393, 1229, 1190, 1059, 1026, 961, 861, 735, 726, 626, 525.



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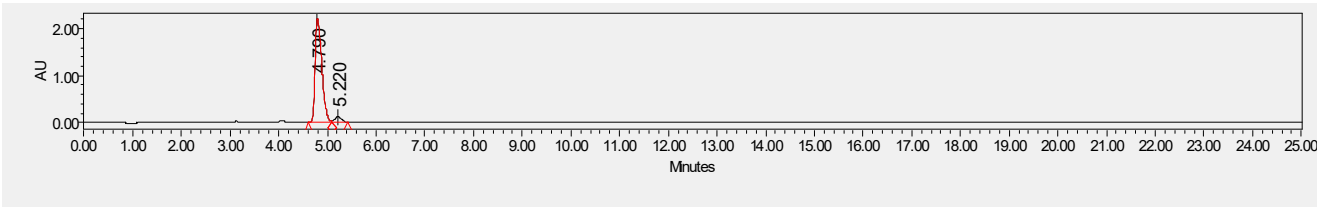
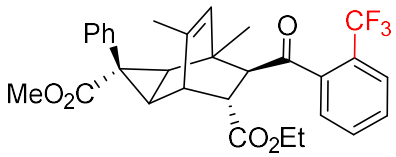
	Retention Time	Area	% Area
1	4.800	3173838	36.90
2	5.173	3305437	38.43
3	11.571	1066499	12.40
4	13.189	1055453	12.27



	Retention Time	Area	% Area
1	4.790	21566283	94.69
2	5.220	1209934	5.31

3ah: 6-ethyl-3-methyl-1,9-dimethyl-3-phenyl-7-(2-(trifluoromethyl)benzoyl)tricyclo[3.2.2.0^{2,4}]non-8-ene-3,6-dicarboxylate



3ah

33.1 mg,67% yield, 19:1dr, 87% ee.; light yellow liquid, $[\alpha]^{22}_{D}$ = -110.7 (*c* = 0.65, in CH_2Cl_2).

HPLC (Daicel chiralcel ODH, CO_2/MeOH 95/5, 1.0 mL/min, λ = 254 nm), t_R(major) = 10.75 min, t_R(minor) = 9.54 min.

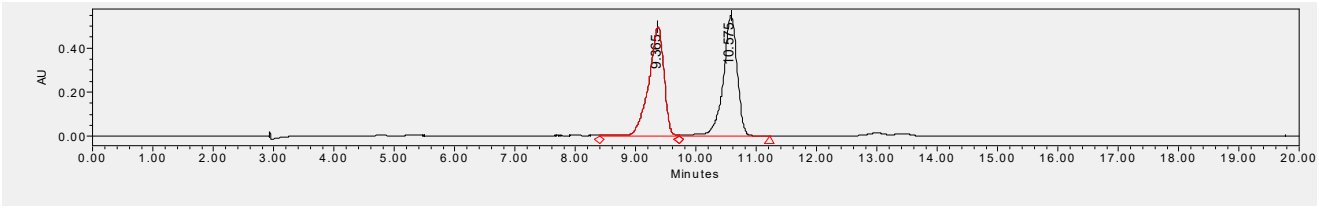
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.30 – 8.17 (m, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.24 – 7.06 (m, 4H), 6.92 (m 1H), 4.59 (s, 1H), 4.27 – 4.14 (m, 3H), 3.53 (s, 3H), 3.31 – 3.27 (m, 1H), 2.78 (dd, *J* = 6.0, 2.0 Hz, 1H), 2.25 (dd, *J* = 5.6, 2.0 Hz, 1H), 2.08 (d, *J* = 9.2 Hz, 1H), 1.30 – 1.21 (m, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.8, 174.2, 172.9, 139.7, 138.6, 136.9, 131.64 131.2, 130.2, 129.4, 129.20 128.1, 127.6, 126.1, 125.20 ($J_{C\text{-}F}$ = 5.1Hz), 61.3, 53.5, 52.8, 51.4, 41.7, 39.3, 37.6, 36.2, 27.7, 23.7, 20.1, 14.2 ppm.

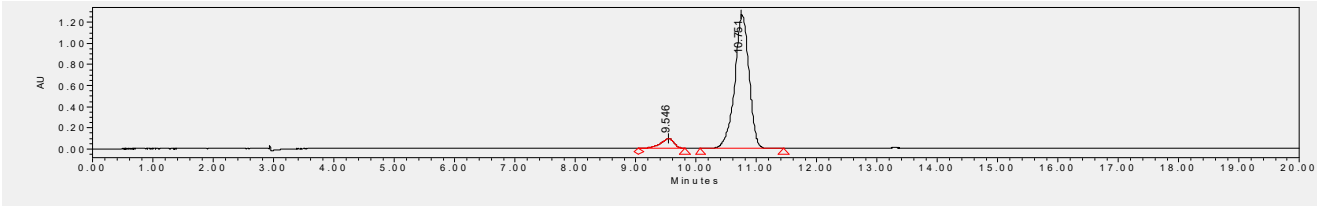
^{19}F NMR (377 MHz, $CDCl_3$) δ = -62.72 ppm.

ESI-HRMS calcd [$C_{30}H_{29}F_3O_5$+Na^+] = 549.1859, found 549.1859

IR $\tilde{\nu}$ (cm^{-1}) 3026, 2874, 1720, 1683, 1607, 1439, 1375, 1329, 1231, 1197, 1168, 1127, 1072, 998, 808, 780, 735, 697, 513.

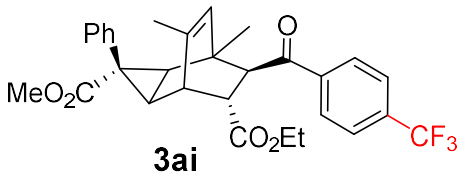


	Retention Time	Area	% Area
1	9.365	8586720	49.54
2	10.575	8746136	50.46



	Retention Time	Area	% Area
1	9.546	1452289	6.51
2	10.751	20866121	93.49

3ai: 6-ethyl-3-methyl-1,9-dimethyl-3-phenyl-7-(4-(trifluoromethyl)benzoyl)tricyclo[3.2.2.0^{2,4}]non-8-ene-3,6-dicarboxylate



3ai

32.4 mg, 61% yield, 19:1dr, 87% ee.; light yellow liquid, $[\alpha]^{22}_{D}$ = -129.7 (*c* = 0.48, in CH_2Cl_2).

HPLC (Daicel chiralcel ODH, CO_2/MeOH 95/5, 1.0 mL/min, λ = 254 nm), t_R(major) = 10.31 min, t_R(minor) = 9.15 min.

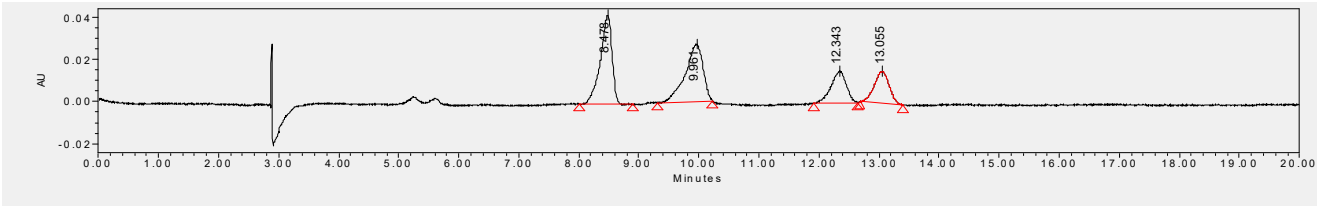
^{1}H NMR (600 MHz, Chloroform-*d*) δ = 8.11 (d, *J* = 7.8 Hz, 2H), 7.74 (d, *J* = 4.2 Hz, 2H), 7.20 (m, 2H), 7.13 (d, *J* = 7.2 Hz, 1H), 7.08 (d, *J* = 4.8 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 4.58 (s, 1H), 4.26 (d, *J* = 6.0 Hz, 1H), 4.19 (q, *J* = 5.6 Hz, 2H), 3.53 (s, 3H), 3.33 – 3.26 (m, 1H), 2.79 (dd, *J* = 6.0, 1.8 Hz, 1H), 2.23 (dd, *J* = 9.2, 4.2 Hz, 1H), 2.07 (d, *J* = 9.2 Hz, 1H), 1.28 – 1.23 (m, 9H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ = 201.3, 174.2, 173.00, 142.0, 138.8, 136.9, 134.1 (J_{C-F} = 31.7 Hz), 131.2, 130.3, 129.1, 128.7, 128.1, 127.6, 126.1, 125.8, (J_{C-F} = 3.0 Hz), 61.2, 53.6, 52.8, 51.4, 41.8, 39.3, 37.7, 36.2, 27.7, 23.7, 20.1, 14.2 ppm.

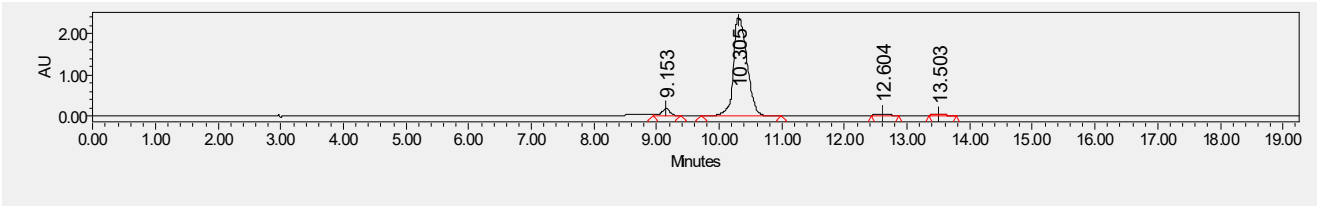
^{19}F NMR (565 MHz, $CDCl_3$) δ = -63.03 ppm.

ESI-HRMS calcd [$C_{30}H_{29}F_3O_5$+Na^+] = 549.1859, found 549.1862.

IR $\tilde{\nu}$ (cm^{-1}) 3058, 2874, 1721,1683, 1602, 1580,1507, 1444, 1376, 1322, 1268, 1230, 1169, 1129, 1066, 886, 774, 702.

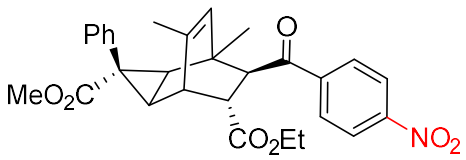


	Retention Time	Area	% Area
1	8.478	569766	34.33
2	9.961	560041	33.74
3	12.343	265838	16.02
4	13.055	264233	15.92



	Retention Time	Area	% Area
1	9.153	1709917	4.43
2	10.305	36081383	93.43
3	12.604	493935	1.28
4	13.503	333353	0.86

3aj: 6-ethyl-3-methyl-1,9-dimethyl-3-phenyl-7-(4-nitrobenzoyl)tricyclo[3.2.2.0^{2,4}]non-8-ene-3,6 – dicarboxylate



3aj

7.5 mg, 43% yield, 19:1 dr, 81% ee, yellow liquid, $[\alpha]^{21}_{D}$ = -135.4 (*c* = 0.21, in CH_2Cl_2).

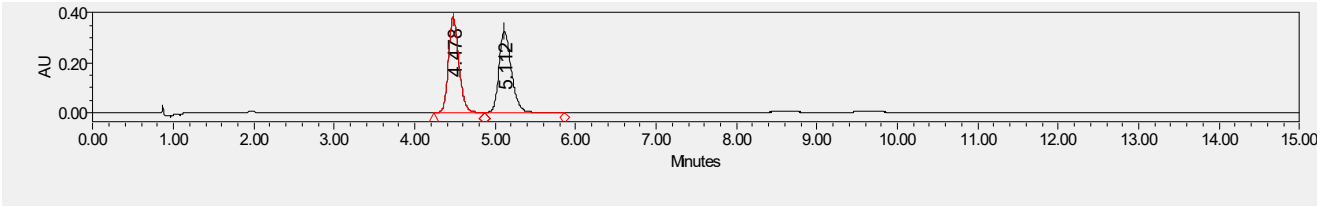
HPLC (Daicel chiralcel OX-3, CO_2/MeOH 90/10, 1.5 mL/min, λ = 254 nm), t_R(major) = 4.46 min, t_R(minor) = 5.13 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.32 (d, *J* = 8.8 Hz, 2H), 8.16 (d, *J* = 8.8 Hz, 2H), 7.25 – 7.11 (m, 3H), 7.08 (d, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 4.57 (s, 1H), 4.28 – 4.14 (m, 3H), 3.53 (s, 3H), 3.31 (m, 1H), 2.79 (dd, *J* = 6.0, 2.0 Hz, 1H), 2.22 (dd, *J* = 9.2, 4.0 Hz, 1H), 2.06 (d, *J* = 9.0 Hz, 1H), 1.30 – 1.22 (m, 9H) ppm.

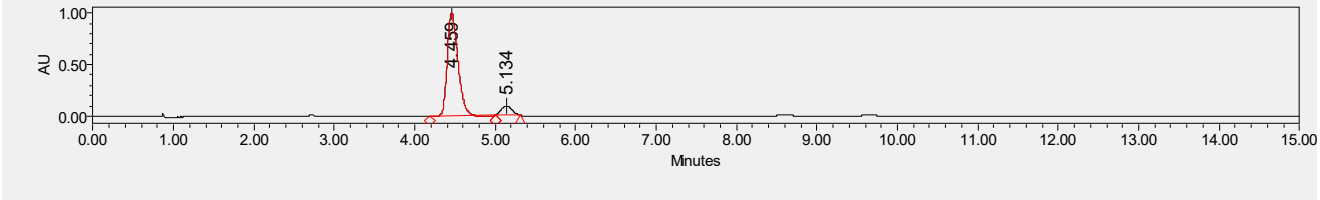
^{13}C NMR (101 MHz, $CDCl_3$) δ = 201.0, 174.1 172.9, 150.2, 143.9, 139.0, 136.8, 131.2, 130.3, 129.4, 128.9, 128.1, 127.6, 126.1, 124.0, 61.4, 54.1, 52.8, 51.5, 41.9, 39.3, 37.6, 36.2, 27.7, 23.8, 20.2, 14.3 ppm.

ESI-HRMS calcd [$C_{29}H_{29}NO_7$+Na^+] = 526.1836, found 526.1840.

IR $\tilde{\nu}$ (cm^{-1}) 2959, 1721, 1685, 1602, 1572, 1444, 1316,1268, 1060, 962, 888, 844, 724, 702, 507.

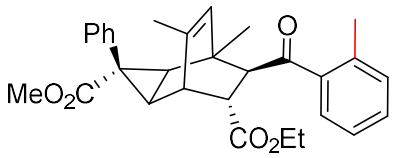


	Retention Time	Area	% Area
1	4.478	3457003	49.72
2	5.112	3495520	50.28



	Retention Time	Area	% Area
1	4.459	9206389	91.40
2	5.134	866333	8.60

3ak: 6-ethyl 3-methyl -1,9-dimethyl-7-(2-methylbenzoyl)-3-phenyltricyclo[3.2.2.0^{2,4}]non-8-ene-3,6-dicarboxylate



3ak

23.6 mg, 50% yield, 19:1dr, 90% ee.; light yellow liquid; $[\alpha]^{20}_{D}$ = -53.2 (*c* = 0.38, in CH_2Cl_2).

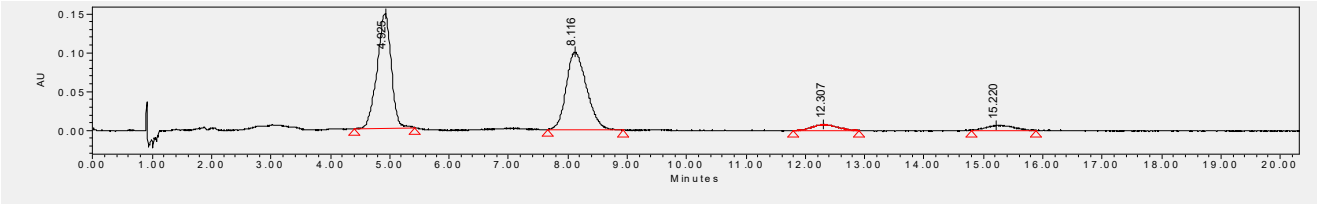
HPLC (Daicel chiralcel OX-3, CO_2/MeOH 95/5, 1.5 mL/min, λ = 254 nm), t_R(major) = 5.03 min, t_R(minor) = 8.42 min

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.90 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.24 – 7.06 (m, 5H), 6.91 (d, *J* = 7.6 Hz, 1H), 4.57 (s, 1H), 4.21 (q, *J* = 8.0 Hz, 2H), 4.13 (d, *J* = 5.8 Hz, 1H), 3.51 (s, 3H), 3.31 – 3.24 (m, 1H), 2.90 (dd, *J* = 5.6, 2.0 Hz, 1H), 2.37 (s, 3H), 2.23 (dd, *J* = 3.6, 4.0 Hz, 1H), 2.00 (d, *J* = 9.2 Hz, 1H), 1.31 – 1.23 (m, 9H) ppm.

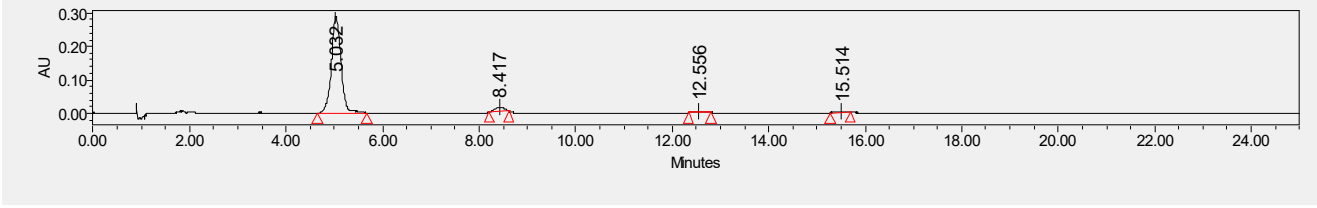
^{13}C NMR (101 MHz, $CDCl_3$) δ = 204.7, 174.2, 173.4, 140.3, 138.6, 137.5, 137.1, 131.9, 131.2, 131.2, 130.3, 129.2, 129.1, 128.1, 127.5, 126.0, 125.7, 61.1, 56.4, 52.7, 50.3, 41.9, 39.2, 38.1, 36.3, 28.0, 23.6, 21.0, 20.3, 14.3 ppm.

ESI-HRMS calcd [$C_{30}H_{32}O_5$+Na^+] = 495.2142, found 495.2142.

IR $\tilde{\nu}$ (cm^{-1}) 2960, 2872, 1722, 1680, 1600, 1447, 1374, 1231, 1194, 1027, 775, 735, 702, 532.

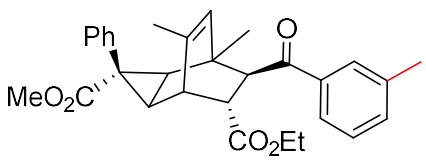


	Retention Time	Area	% Area
1	4.925	2445410	46.29
2	8.116	2414241	45.70
3	12.307	222238	4.21
4	15.220	200905	3.80



	Retention Time	Area	% Area
1	5.032	4008880	93.59
2	8.417	185118	4.32
3	12.556	51734	1.21
4	15.514	37533	0.88

3al: 6-ethyl 3-methyl -1,9-dimethyl-7-(3-methylbenzoyl)-3-phenyltricyclo[3.2.2.0^{2,4}]non-8-ene-3,6-dicarboxylate



3al

354.2 mg, 75% yield, 19:1 dr, 91% ee.; light yellow liquid; $[\alpha]^{20}_{D}$ = -132.6 (*c* = 0.56, in CH_2Cl_2).

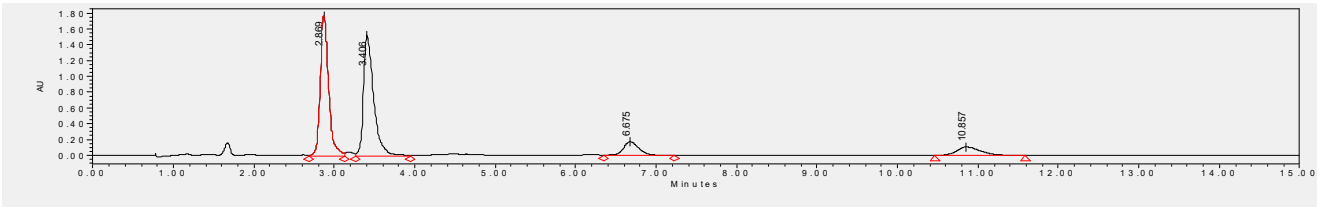
HPLC (Daicel chiralcel OX-3, CO_2/MeOH 90/10, 1.5 mL/min, λ = 254 nm), t_R(major) = 2.86 min, t_R(minor) = 3.45 min

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.81 (d, *J* = 10.4 Hz, 2H), 7.36 (m, 2H), 7.24 – 7.05 (m, 4H), 6.92 (m, 1H), 4.57 (s, 1H), 4.24 (d, *J* = 6.0 Hz, 1H), 4.17 (m, 2H), 3.52 (s, 3H), 3.29 – 3.23 (m, 1H), 2.80 (dd, *J* = 6.0, 2.4 Hz, 1H), 2.42 (s, 3H), 2.25 (dd, *J* = 9.2, 4.0 Hz, 1H), 2.08 (d, *J* = 9.2 Hz, 1H), 1.28 – 1.21 (m, 9H) ppm.

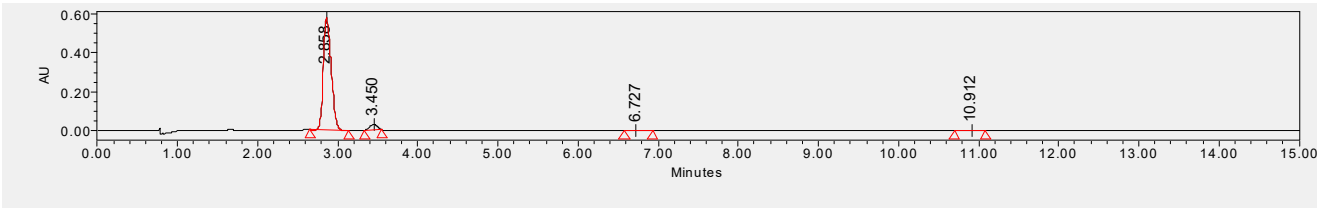
^{13}C NMR (101 MHz, $CDCl_3$) δ = 202.1, 174.3, 173.2, 139.3, 138.4, 138.3, 137.1, 133.8, 131.2, 130.3, 129.4, 128.9, 128.5, 128.0, 127.5, 125.94, 125.7, 61.0, 53.1, 52.7, 51.2, 41.5, 39.4, 37.9, 36.2, 27.9, 23.7, 21.5, 20.1, 14.2 ppm.

ESI-HRMS calcd [$C_{30}H_{32}O_5$+Na^+] = 495.2142, found 495.2142.

IR $\tilde{\nu}$ (cm^{-1}) 2958, 2906, 1719, 1674, 1601, 1494, 1444, 1373, 1230, 1188, 1026, 892, 786, 733, 700, 515.

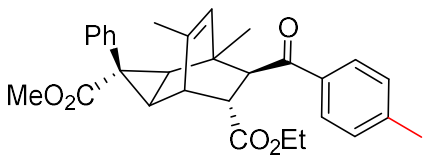


	Retention Time	Area	% Area
1	2.869	13055161	41.71
2	3.406	13666272	43.66
3	6.675	2399852	7.67
4	10.857	2180315	6.97



	Retention Time	Area	% Area
1	2.858	3945017	94.63
2	3.450	185509	4.45
3	6.727	22102	0.53
4	10.912	16391	0.39

3am: 6-ethyl 3-methyl-1,9-dimethyl-7-(4-methylbenzoyl)-3-phenyltricyclo[3.2.2.0^{2,4}]non-8-ene-3,6-dicarboxylate



3am

330.3 mg, 70% yield, 19:1dr, 91% ee.; light yellow liquid; $[\alpha]^{20}_{D}$ = -126.7 (*c* = 0.57, in CH_2Cl_2).

HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH, 90/10, 1.0mL/min, λ = 254 nm), t_R(major) = 11.38 min, t_R(minor) = 13.57 min.

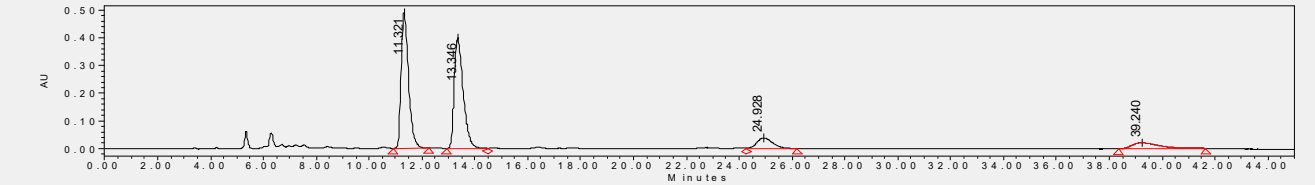
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.81 (d, *J* = 10.0 Hz, 2H), 7.36 (m, 2H), 7.15 (m, 4H), 6.92 (d, *J* = 7.6 Hz, 1H), 4.57 (s, 1H), 4.31 – 4.07 (m, 3H), 3.53 (s, 3H), 3.26 (s, 1H), 2.80 (d, *J* = 5.6 Hz, 1H), 2.42 (s, 3H), 2.25 (dd, *J* = 9.2, 3.6 Hz, 1H), 2.08 (d, *J* = 5.2, Hz, 1H), 1.31 – 1.18 (m, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.1, 174.3, 173.2, 139.3, 138.4, 138.3, 137.1, 133.7, 131.2, 130.3, 129.4, 129.0, 128.5, 128.0, 127.5, 126.0, 125.8, 61.0, 53.2, 52.7, 51.2, 41.5, 39.4, 37.9, 36.2, 27.9, 23.7, 21.4, 20.1, 14.2 ppm.

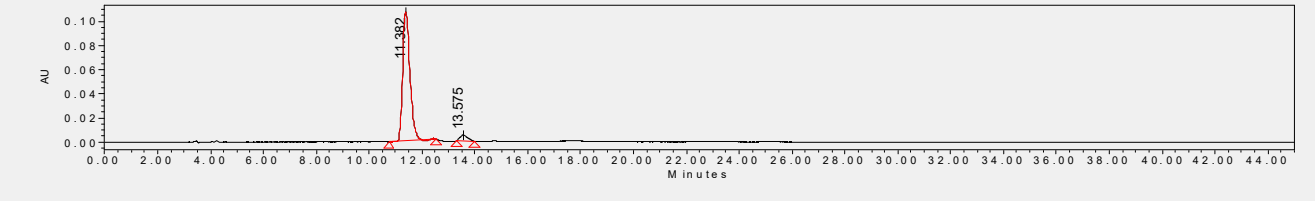
ESI-HRMS calcd $[C_{30}H_{32}O_5+Na^+]$ = 495.2142, found 495.2143.

IR $\tilde{\nu}$ (cm^{-1}) 3026, 2872, 1720, 1675, 1584, 1442, 1303, 1231, 1190, 1056, 1026, 997, 734, 700, 661, 515.

.

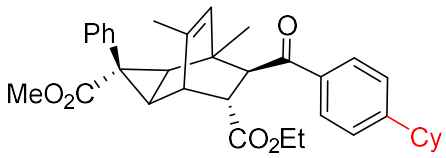


	Retention Time	Area	% Area
1	11.321	9490817	42.82
2	13.346	9450531	42.64
3	24.928	1641032	7.40
4	39.240	1579995	7.13



	Retention Time	Area	% Area
1	11.382	2036957	95.55
2	13.575	94854	4.45

3an: 6-ethyl3-methyl-7-(4-cyclohexylbenzoyl)-1,9-dimethyl-3-phenyltricyclo[3.2.2.0^{2,4}]non-8 ene -3,6-dicarboxylate



3an

36.8 mg, 68% yield, 19:1 dr, 93% ee.; light yellow solid, 143 – 144 °C, $[\alpha]^{20}_{D}$ = -141.2 (*c* = 0.61, in CH_2Cl_2).

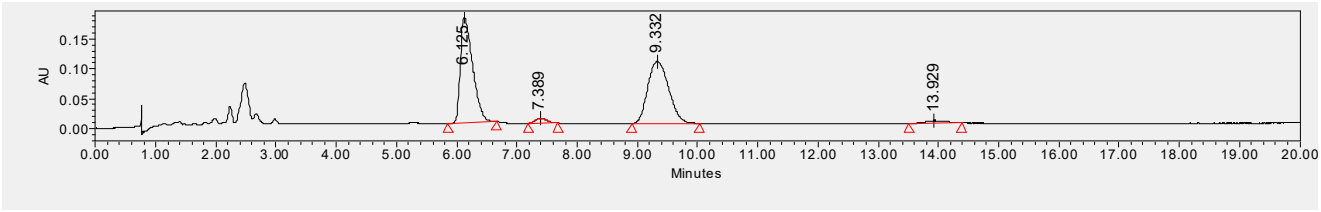
HPLC (Daicel chiralcel IA, CO_2/MeOH 90/10, 1.5 mL/min, λ = 254 nm), t_R(major) = 5.81min, t_R(minor) = 9.11 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.94 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.06 (m, 4H), 6.93 (m, 1H), 4.59 (s, 1H), 4.24 (d, *J* = 6.0 Hz, 1H), 4.16 (m, 2.0 Hz, 2H), 3.53 (s, 3H), 3.25 (m, 1H), 2.77 (dd, *J* = 6.0, 2.4 Hz, 1H), 2.56 (m,1H), 2.24 (dd, *J* = 6.0, 2.4 Hz, 1H), 2.10 – 2.05 (m, 1H), 1.87 (s, 4H), 1.76 (d, *J* = 12.4 Hz, 1H), 1.42 (m, 4H), 1.31 – 1.20 (m, 10H) ppm.

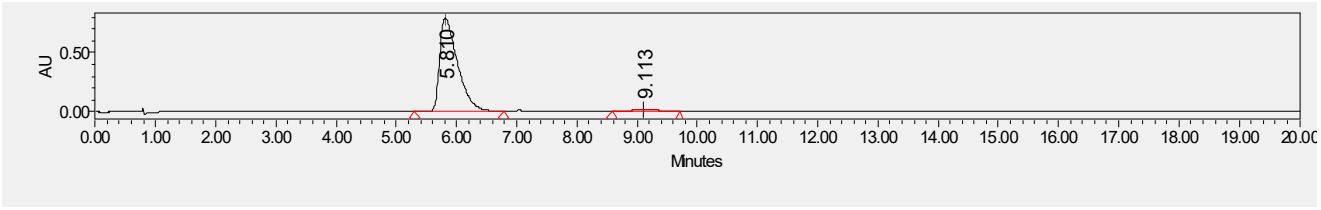
^{13}C NMR (101 MHz, $CDCl_3$) δ = 201.5, 174.3, 173.2, 153.7, 138.0, 137.13, 136.9, 131.2, 130.2, 129.6, 128.7, 128.0, 127.5, 127.1, 125.9, 61.0, 52.8, 52.7, 51.3, 44.6, 41.5, 39.4, 37.9, 36.1, 34.1, 34.1, 27.9, 26.7, 26.0, 23.7, 20.1, 14.2 ppm.

ESI-HRMS calcd [$C_{35}H_{40}O_5$+Na^+] = 563.2768, found 563.2767.

IR $\tilde{\nu}$ (cm-1) 2926, 2852, 1722, 1673,1567, 1446, 1267, 1228, 1188, 1028, 994, 937, 828,735, 701, 529.

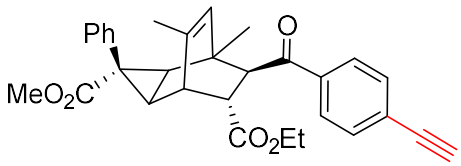


	Retention Time	Area	% Area
1	6.125	2507779	48.03
2	7.389	104398	2.00
3	9.332	2505765	47.99
4	13.929	103105	1.97



	Retention Time	Area	% Area
1	5.810	16522069	96.70
2	9.113	564686	3.30

3ao: 6-ethyl3-methyl-7-(4-ethynylbenzoyl)-1,9-dimethyl-3-phenyltricyclo[3.2.2.0^{2,4}]non-8-ene-3,6--dicarboxylate



3ao

29.5 mg,61% yield, 19:1dr, 87% ee.; light yellow liquid, $[\alpha]^{20}_{D}$ = -160.9 (*c* = 0.77, in CH_2Cl_2).

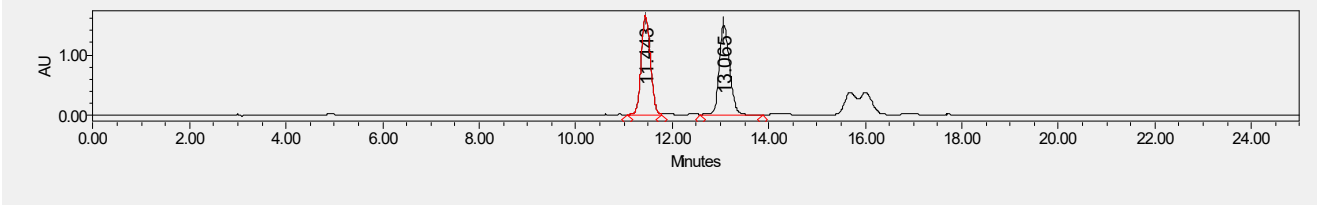
HPLC (Daicel chiralcel ODH, CO_2/MeOH 90/10, 1.0 mL/min, λ = 254 nm), t_R(major) = 13.73 min, t_R(minor) =12.01 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.96 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.23 – 7.05 (m, 4H), 6.92 (d, *J* = 7.6 Hz, 1H), 4.57 (s, 1H), 4.26 – 4.11 (m, 3H), 3.52 (s, 3H), 3.33 – 3.21 (m, 2H), 2.78 (dd, *J* = 6.0, 2.4 Hz, 1H), 2.23 (dd, *J* = 7.6, 4.0 Hz, 1H), 2.06 (d, *J* = 8.8 Hz, 1H), 1.28 – 1.20 (m, 9H) ppm.

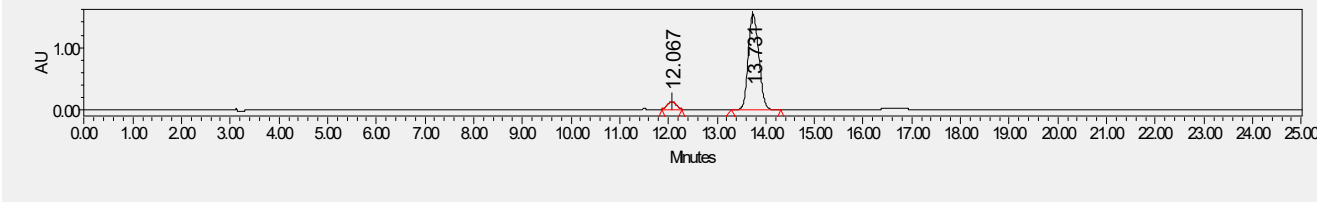
^{13}C NMR (101 MHz, $CDCl_3$) δ = 201.2, 174.2, 173.1, 138.9, 138.5, 137.0, 132.4 131.2, 130.2, 129.2, 128.3, 128.0, 127.5, 126.8, 126.0, 82.8, 80.5, 61.1, 53.2, 52.7, 51.2, 41.6, 39.3, 37.7, 36.2, 27.8, 23.7, 20.1, 14.2 ppm.

ESI-HRMS calcd [$C_{31}H_{30}O_5$+Na^+] = 505.1985, found 505.1985.

IR $\tilde{\nu}$ (cm^{-1}) 3026, 2906, 1718, 1676, 1601,1444, 1227, 1193, 1026, 937, 838, 809, 735, 702, 532, 511.

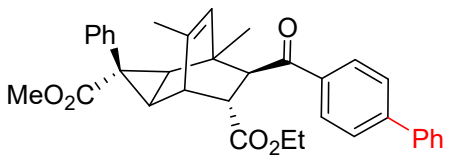


	Retention Time	Area	% Area
1	11.443	22162838	49.41
2	13.065	22693477	50.59



	Retention Time	Area	% Area
1	12.067	1491367	6.06
2	13.731	23101340	93.94

3ap: 6-ethyl 3-methyl -7-([1,1'-biphenyl]-4-carbonyl)-1,9-dimethyl-3-phenyltricyclo [3.2.2.0^{2,4}] non-8-ene-3,6-dicarboxylate



3ap

47.5 mg, 89% yield, 19:1dr, 93% ee.; light yellow solid, 91 – 92 °C, $[\alpha]^{20}_{D}$ = -160.4 (*c* = 0.71, in CH_2Cl_2)

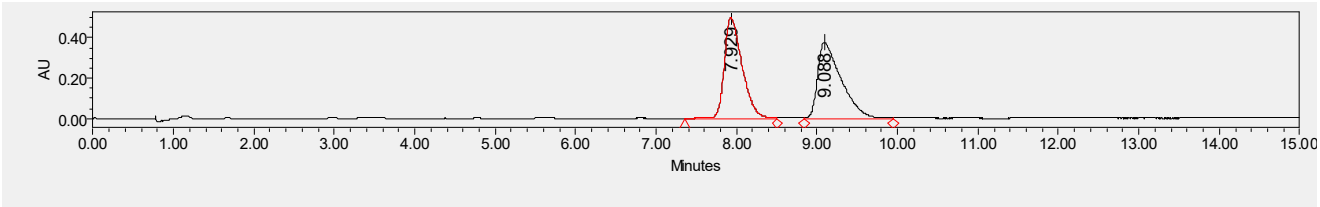
HPLC (Daicel chiralcel OX-3, CO_2/MeOH 90/10, 1.5 mL/min, λ = 254 nm), t_R(major) = 7.90 min, t_R(minor) =9.35 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.10 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.68 – 7.62 (m, 2H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.40 (m, 1H), 7.26 – 7.08 (m, 4H), 6.95 (d, *J* = 7.6 Hz, 1H), 4.61 (s, 1H), 4.31 (d, *J* = 6.0 Hz, 1H), 4.19 (m, 2H), 3.54 (s, 3H), 3.32 – 3.26 (m, 1H), 2.83 (dd, *J* = 5.6, 2.0 Hz, 1H), 2.27 (dd, *J* = 8.4, 4.0 Hz, 1H), 2.11 (d, *J* = 8.8 Hz, 1H), 1.34 – 1.23 (m, 9H) ppm.

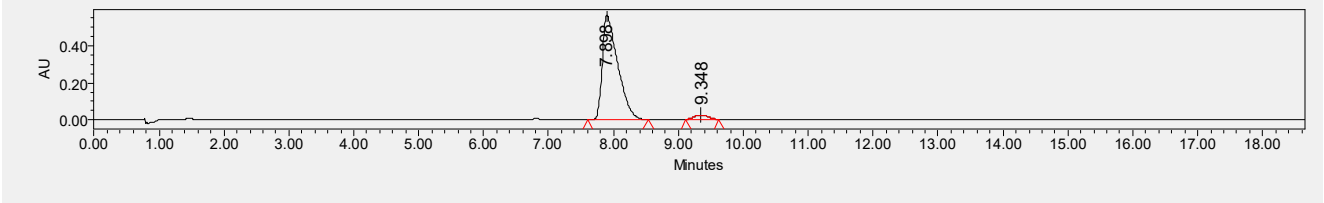
^{13}C NMR (101 MHz, $CDCl_3$) δ = 201.5, 174.3, 173.2, 145.6, 139.8, 138.3, 137.8, 137.1, 131.2, 130.2, 129.4, 129.1, 129.0, 128.2, 128.0, 127.5, 127.3, 126.0, 61.1, 53.1, 52.7, 51.3, 41.6, 39.4, 37.9, 36.2, 27.9, 23.7, 20.1, 14.2 ppm.

ESI-HRMS calcd [$C_{35}H_{34}O_5$+Na^+] = 557.2298, found 557.2297.

IR $\tilde{\nu}$ (cm-1) 3029, 2958, 2872, 1720, 1673, 1601, 1445, 1373, 1228, 1192, 1027, 1002, 841, 808, 737, 699, 521.

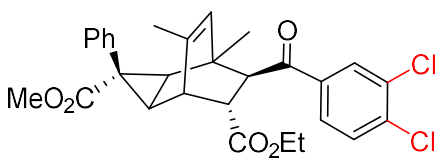


	Retention Time	Area	% Area
1	7.929	7644058	50.09
2	9.088	7616266	49.91



	Retention Time	Area	% Area
1	7.898	9355395	96.15
2	9.348	374849	3.85

3aq: 6-ethyl 3-methyl -7-(3,4-dichlorobenzoyl)-1,9-dimethyl-3-phenyltricyclo[3.2.2.0^{2,4}]non-8-ene -3,6-dicarboxylate



3aq

47.5 mg, 92% yield, 19:1 dr, 86% ee.; light yellow liquid, $[\alpha]^{22}_{D}$ = -135.2 (*c* = 0.89, in CH_2Cl_2).

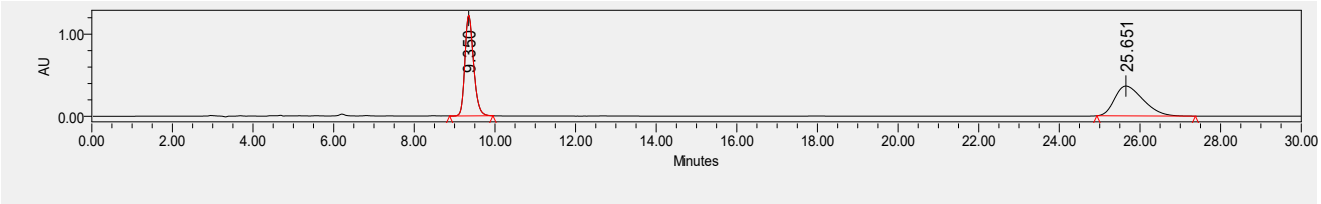
HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm), t_R(major) = 25.64 min, t_R(minor) = 9.42 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.07 (d, *J* = 1.8 Hz, 1H), 7.85 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.24 – 7.06 (m, 4H), 6.91 (d, *J* = 7.6 Hz, 1H), 4.56 (s, 1H), 4.23 – 4.11 (m, 3H), 3.53 (s, 3H), 3.30 – 3.25 (m, 1H), 2.74 (dd, *J* = 5.6, 2.0 Hz, 1H), 2.22 (dd, *J* = 8.4, 4.0 Hz, 1H), 2.05 (d, *J* = 5.2 Hz, 1H), 1.28 – 1.21 (m, 9H) ppm.

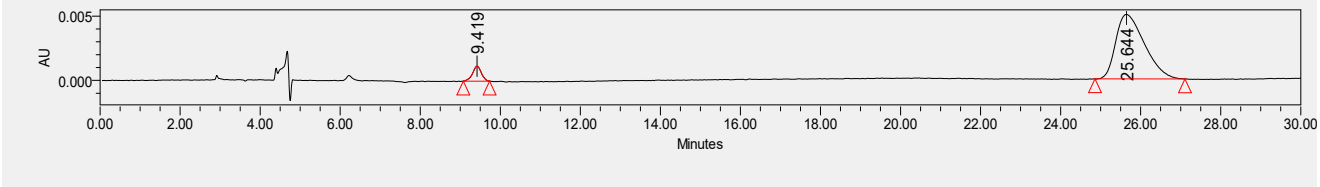
^{13}C NMR (101 MHz, $CDCl_3$) δ = 199.9, 174.1, 172.9, 138.7, 138.6, 137.6, 136.9, 133.4, 131.2, 130.8, 130.4, 130.2, 129.1, 128.0, 127.5, 127.5, 126.0, 61.3, 53.4, 52.8, 51.4, 41.7, 39.3, 37.6, 36.2, 27.7, 23.7, 20.1, 14.2 ppm.

ESI-HRMS calcd $[C_{29}H_{28}Cl_2O_5+Na^+]$ = 549.1206, 551.1176, 553.1147, found 549.1211, 551.1173, 553.1151.

IR $\tilde{\nu}$ (cm-1) 2959, 2873, 1720, 1681, 1582, 1555, 1442, 1377, 1230, 1198, 1028, 830, 735, 701.

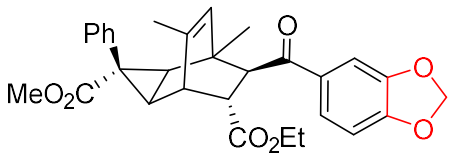


	Retention Time	Area	% Area
1	9.350	18256339	50.64
2	25.651	17793405	49.36



	Retention Time	Area	% Area
1	9.419	17693	6.61
2	25.644	250020	93.39

3ar: 6-ethyl 3-methyl-7-(benzo*[d]*[1,3]dioxole-5-carbonyl)-1,9-dimethyl-3-phenyltricyclo [3.2.2.0^{2,4}] -non-8-ene-3,6-dicarboxylate



3ar

35.4 mg, 87% yield, 19:1 dr, 87% ee.; light yellow solid, 164 – 166 °C, $[\alpha]^{20}_{D}$ = -126.6 (*c* = 0.58, in CH_2Cl_2).

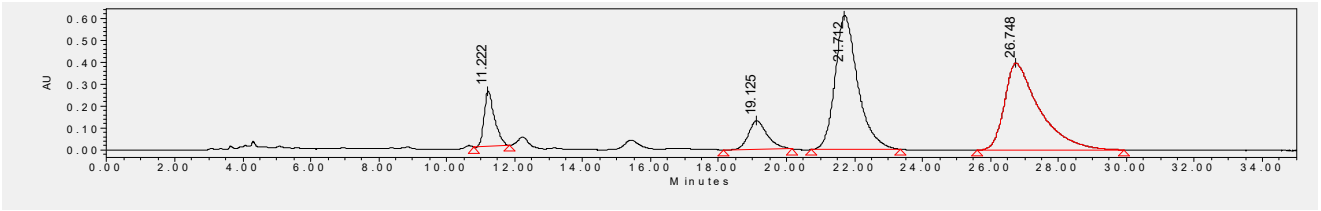
HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm), t_R(major) = 26.84 min, t_R(minor) = 21.7 min.

^{1}H NMR (400 MHz, Chloroform-d) δ = 7.69 (d, J = 4.8 Hz, 1H), 7.44 (s, 1H), 7.23 – 7.05 (m, 4H), 6.92 (d, J = 7.6 Hz, 1H), 6.87 (d, J = 8.0 Hz, 1H), 4.57 (s, 1H), 4.22 – 4.12 (m, 3H), 3.52 (s, 3H), 3.25 (s, 1H), 2.76 (dd, J = 5.6, 1.2 Hz, 1H), 2.22 (dd, J =9.2, 4.0 Hz, 1H), 2.05 (d, J = 9.2 Hz, 1H), 1.30 – 1.20 (m, 9H) ppm.

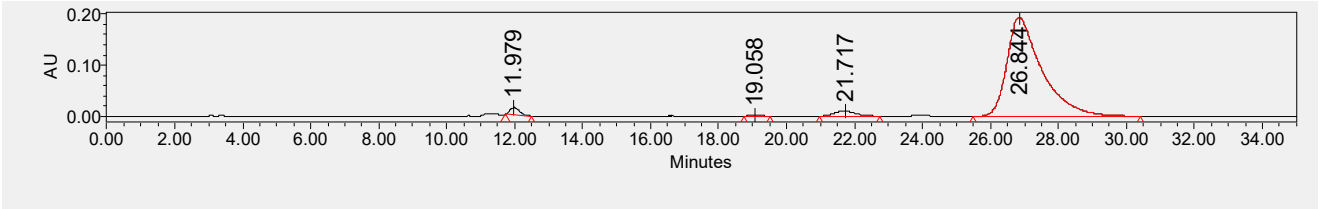
^{13}C NMR (101 MHz, CDCl3) δ = 199.8, 174.3, 173.2, 151.8, 148.3, 138.1, 137.1, 134.1, 131.2, 130.2, 129.5, 128.0, 127.5, 126.0, 125.0, 108.1, 107.9, 101.9, 61.0, 52.8, 52.7, 51.3, 41.5, 39.4, 37.8, 36.14, 27.8, 23.6, 20.1, 14.3 ppm.

ESI-HRMS calcd [$C_{30}H_{30}O_7$+H^+] =503.2064, found 503.2065

IR $\tilde{\nu}$ (cm^{-1}) 2959, 2905, 1719, 1667, 1439, 1372, 1233, 1191, 1128, 1098, 1034, 961, 933, 796, 701.

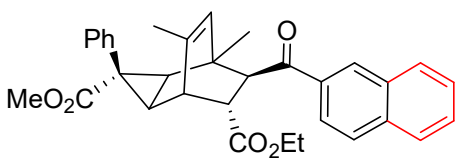


	Retention Time	Area	% Area
1	11.222	5361483	7.99
2	19.125	5022466	7.49
3	21.712	28404838	42.36
4	26.748	28272165	42.16



	Retention Time	Area	% Area
1	11.979	272900	1.88
2	19.058	41242	0.28
3	21.717	426657	2.94
4	26.844	13755144	94.89

3as: 6-ethyl-3-methyl-7-(2-naphthoyl)-1,9-dimethyl-3-phenyltricyclo[3.2.2.0^{2,4}]non-8-ene-3,6-dicarboxylate



3as

45.7 mg, 90% yield, 19:1dr, 87% ee.; light yellow liquid, $[\alpha]^{20}_{D}$ = -125.7 (*c* = 0.75, in CH_2Cl_2).

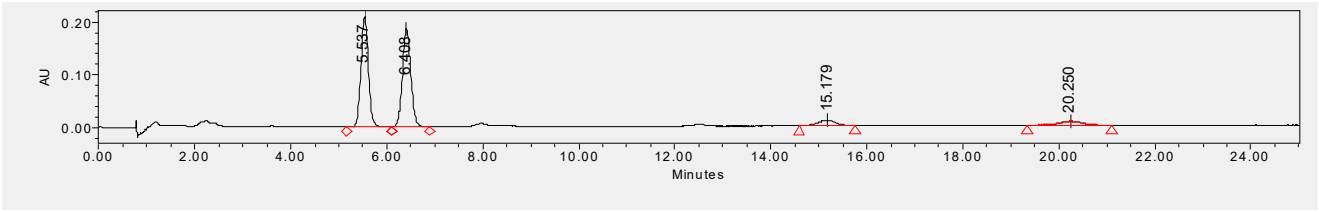
HPLC (Daicel chiralcel OX-3, CO_2/MeOH 90/10, 1.5 mL/min, λ = 254 nm), t_R(major) = 5.42 min, t_R(minor) = 6.37 min.

^{1}H NMR (600 MHz, Chloroform-*d*) δ = 8.61 (s, 1H), 8.03 (t, *J* = 7.8 Hz, 2H), 7.89 (t, *J* = 9.0 Hz, 2H), 7.64 – 7.56 (m, 2H), 7.21 (m, 2H), 7.16 – 7.09 (m, 2H), 6.94 (d, *J* = 7.2 Hz, 1H), 4.62 (s, 1H), 4.44 (d, *J* = 6.0 Hz, 1H), 4.23 – 4.11 (m, 2H), 3.54 (s, 3H), 3.34 – 3.29 (m, 1H), 2.88 (dd, *J* = 6.0, 1.8 Hz, 1H), 2.30 (dd, *J* = 9.0, 4.2, Hz, 1H), 2.15 (d, *J* = 6.0 Hz, 1H), 1.30 – 1.25 (m, 6H), 1.23 (m, 3H) ppm.

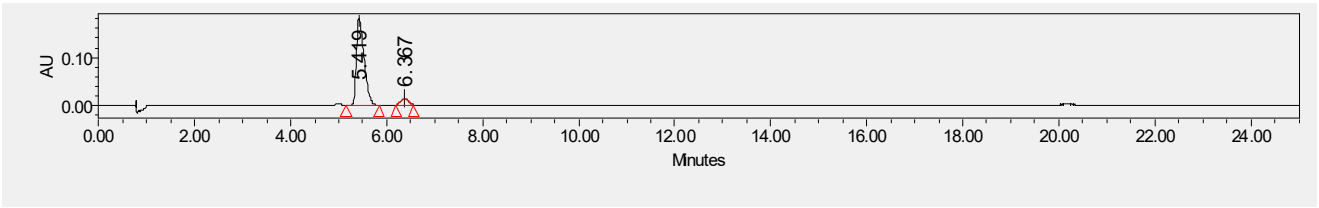
^{13}C NMR (151 MHz, $CDCl_3$) δ = 201.8, 174.3, 173.3, 138.4, 137.0, 136.5, 135.5, 132.6, 131.2, 130.4, 130.3, 129.8, 129.4, 128.6, 128.5, 128.0, 127.7, 127.5, 126.8, 126.0, 124.1, 61.1, 53.1, 52.8, 51.2, 41.7, 39.4, 38.0, 36.2, 28.0, 23.8, 20.2, 14.2 ppm.

ESI-HRMS calcd [$C_{33}H_{32}O_5$+Na^+] = 531.2142, found 513.2147.

IR $\tilde{\nu}$ (cm-1) 3057, 3025, 2957, 1718, 1671, 1626, 1440, 1376, 1271, 1230, 1187, 1058, 1025, 961,863, 735, 701, 514, 476.

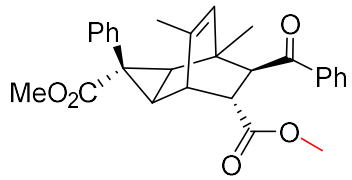


	Retention Time	Area	% Area
1	5.537	2301514	44.94
2	6.408	2272436	44.37
3	15.179	285822	5.58
4	20.250	261547	5.11



	Retention Time	Area	% Area
1	5.419	2011529	93.16
2	6.367	147735	6.84

3at: dimethyl-7-benzoyl-1,9-dimethyl-3-phenyltricyclo[3.2.2.0^{2,4}]non-8-ene-3,6-dicarboxylate



3at

22.2 mg, 88% yield, 19:1 dr, 88% ee.; light yellow liquid, $[\alpha]^{21}_{D}$ = -123.8 (c = 0.52, in CH_2Cl_2).

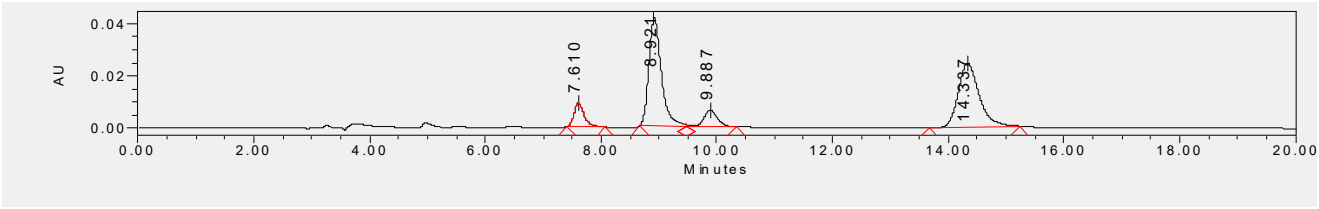
HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm), t_R(major) =14.31 min, t_R(minor) = 8.93 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.01 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 8.0 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.24 – 7.05 (m, 4H), 6.92 (d, J = 7.4 Hz, 1H), 4.57 (s, 1H), 4.27 (d, J = 6.0 Hz, 1H), 3.72 (s, 3H), 3.53 (s, 3H), 3.32 – 3.24 (m, 1H), 2.84 (dd, J = 6.0, 1.8 Hz, 1H), 2.23 (dd, J = 9.0, 4.2 Hz, 1H), 2.07 (d, J = 9.1 Hz, 1H), 1.25 (d, J = 11.4 Hz, 6H).

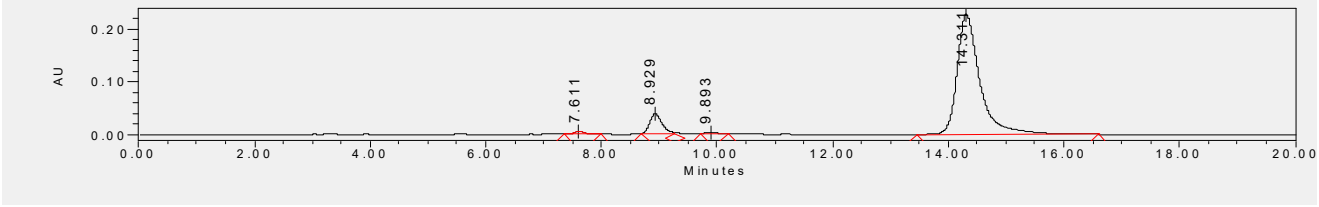
^{13}C NMR (151 MHz, $CDCl_3$) δ = 201.9, 174.2, 173.3, 139.2, 138.3, 137.10, 133.0, 131.2, 130.3, 129.4, 128.7, 128.5, 128.02, 127.5, 126.0, 65.0, 53.1, 52.7, 51.3, 41.6, 39.4, 37.8, 36.2, 30.6, 27.8, 23.7, 20.1, 19.2, 13.7 ppm.

ESI-HRMS calcd [$C_{28}H_{28}O_5$+Na^+] = 467.1829, found 467.1828.

IR $\tilde{\nu}$ (cm^{-1}) 3057, 2955, 1718, 1674, 1597, 1439, 1374, 1301, 1267, 1225, 1128, 1058, 1018, 961, 850, 732, 696, 628.

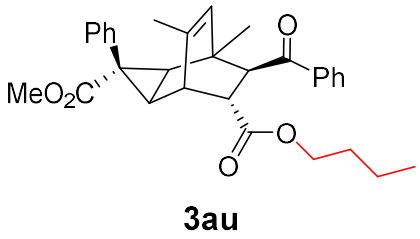


	Retention	Area	% Area
1	7.610	111150	7.60
2	8.921	627567	42.90
3	9.887	104721	7.16
4	14.337	619323	42.34



	Retention	Area	% Area
1	7.611	67787	0.98
2	8.929	541955	7.86
3	9.893	37968	0.55
4	14.311	6245987	90.60

3au: 6-butyl 3-methyl -7-benzoyl-1,9-dimethyl-3-phenyltricyclo[3.2.2.0^{2,4}]non-8-ene-3,6-dicarbo -xylate



3au

44.2 mg, 91% yield, 19:1 dr, 93% ee.; light yellow solid, 96 – 98 °C, $[\alpha]^{21}_{D}$ = -143.5 (*c* = 0.48, in CH_2Cl_2).

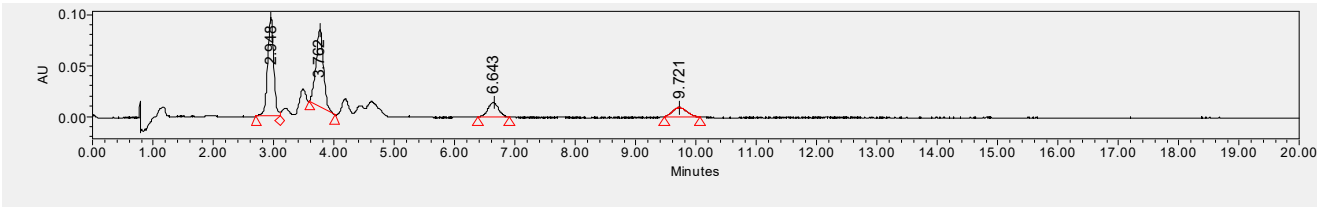
HPLC (Daicel chiralcel OX-3, CO_2/MeOH 90/10, 1.5 mL/min, λ = 254 nm), t_R(major) = 2.95 min, t_R(minor) = 3.79 min.

^{1}H NMR (600 MHz, Chloroform-*d*) δ = 8.01 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 6.0 Hz, 2H), 7.20 (m, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.08 (d, *J* = 5.2 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 4.58 (s, 1H), 4.26 (d, *J* = 6.0 Hz, 1H), 4.12 (m, 2H), 3.53 (s, 3H), 3.28 – 3.24 (m, 1H), 2.81 (dd, *J* =6.0, 1.8 Hz, 1H), 2.25 (dd, *J* = 9.0, 4.2 Hz, 1H), 2.07 (d, *J* = 6.0 Hz, 1H), 1.57 (m, 2H), 1.32 – 1.26 (m, 5H), 1.24 (d, *J* = 1.2 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H) ppm.

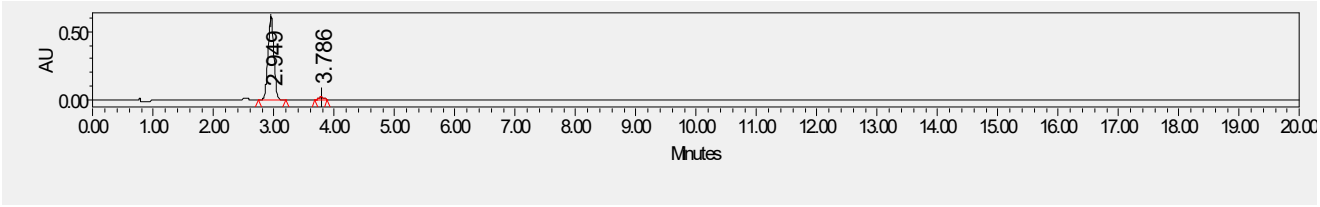
^{13}C NMR (151 MHz, $CDCl_3$) δ = 201.9, 174.2, 173.3, 139.2, 138.3, 137.10, 133.0, 131.2, 130.3, 129.4, 128.7, 128.5, 128.02, 127.5, 126.0, 65.0, 53.1, 52.7, 51.3, 41.6, 39.4, 37.8, 36.2, 30.6, 27.8, 23.7, 20.1, 19.2, 13.7 ppm.

ESI-HRMS calcd [$C_{31}H_{34}O_5$+Na^+] = 509.2299, found509.2299.

IR $\tilde{\nu}$ (cm-1) 3058, 3026, 1719, 1676, 1496, 1446, 1374, 1301, 1267, 1225, 1128, 961, 891, 808, 780, 696, 515.

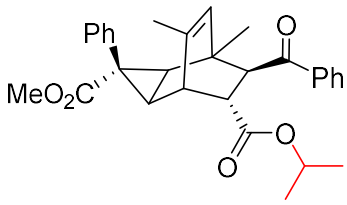


	Retention Time	Area	% Area
1	2.948	675678	40.44
2	3.762	672807	40.27
3	6.643	171620	10.27
4	9.721	150536	9.01



	Retention Time	Area	% Area
1	2.949	4361148	96.76
2	3.786	146098	3.24

3av: 6-isopropyl 3-methyl -7-benzoyl-1,9-dimethyl-3-phenyltricyclo[3.2.2.0^{2,4}]non-8–ene-3,6-dicarboxylate



3av

37.4 mg, 79% yield, 19:1 dr, 93% ee.; light yellow liquid, $[\alpha]^{22}_{D}$ = -126.7 (*c* = 0.42, in CH_2Cl_2).

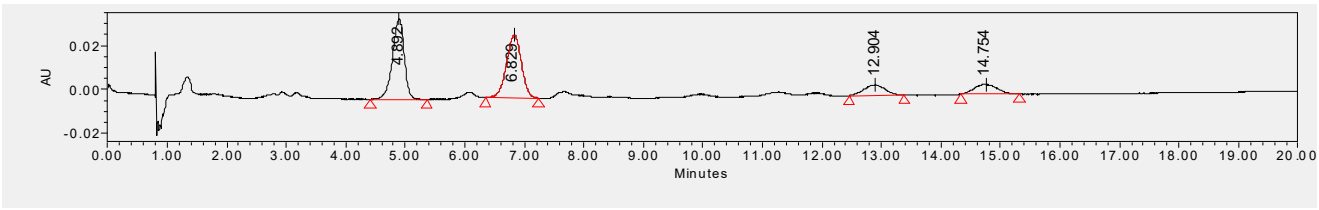
HPLC (Daicel chiralcel OX-3, CO_2/MeOH 95/5, 1.5 mL/min, λ = 254 nm), t_R(major) = 4.42 min, t_R(minor) = 6.42 min.

^{1}H NMR (600 MHz, Chloroform-*d*) δ = 8.01 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 5.2 Hz, 2H), 7.20 (m, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.09 (d, *J* =4.0 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 5.05 (m, 1H), 4.58 (s, 1H), 4.26 (d, *J* = 4.8 Hz, 1H), 3.53 (s, 3H), 3.28 – 3.21 (m, 1H), 2.76 (dd, *J* = 5.4, 1.8 Hz, 1H), 2.24 (dd, *J* = 7.2, 4.2 Hz, 1H), 2.07 (d, *J* = 7.2 Hz, 1H), 1.28 – 1.19 (m, 12H) ppm.

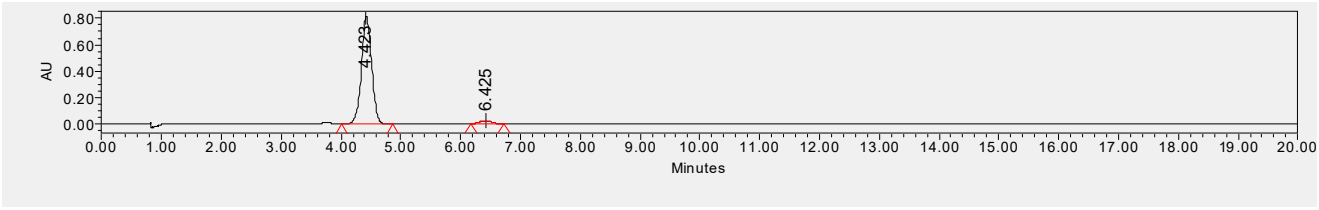
^{13}C NMR (151 MHz, $CDCl_3$) δ = 202.1, 174.3, 172.7, 139.2, 138.3, 137.1, 133.0, 131.2, 130.3, 129.4, 128.6, 128.5, 128.0, 127.5, 126.0, 68.5, 53.1, 52.7, 51.4, 41.5, 39.4, 37.8, 36.1, 27.9, 23.9, 21.9, 21.9, 20.1 ppm.

ESI-HRMS calcd [$C_{30}H_{32}O_5$+Na^+] = 495.2142, found 495.2142.

IR $\tilde{\nu}$ (cm-1) 3058, 3026, 1720, 1677, 1598, 1447, 1374, 1374, 1268, 1229, 1106, 1058, 962, 940, 807, 780, 697.

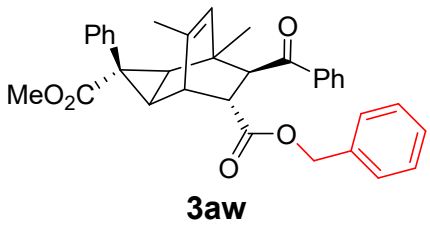


	Retention Time	Area	% Area
1	4.892	508044	41.01
2	6.829	499016	40.28
3	12.904	116420	9.40
4	14.754	115470	9.32



	Retention Time	Area	% Area
1	4.423	9738475	96.50
2	6.425	352741	3.50

3aw: 6-benzyl 3-methyl -7-benzoyl-1,9-dimethyl-3-phenyltricyclo[3.2.2.0^{2,4}]non-8-ene-3,6-dicarbo -xylate



3aw

48.1 mg, 92% yield, 19:1 dr, 94% ee.; light yellow liquid, $[\alpha]^{22}_{D}$ = -105.3 (*c* = 0. 66, in CH_2Cl_2).

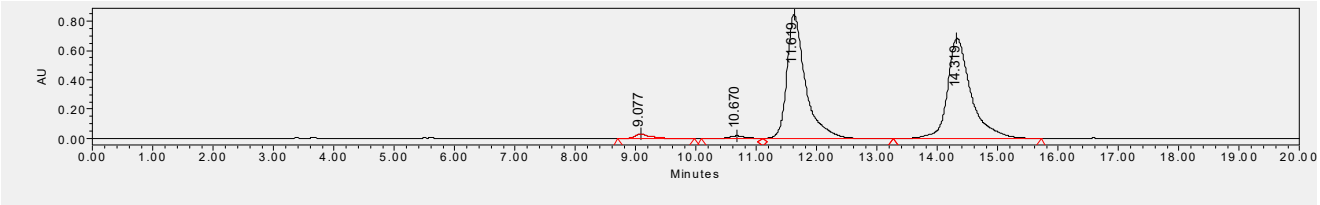
HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 90/10, 1.5 mL/min, λ = 254 nm), t_R(major) = 11.68 min, t_R(minor) = 14.39 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.94 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.34 – 7.05 (m, 10H), 6.92 (d, *J* = 7.4 Hz, 1H), 5.22 – 5.08 (m, 2H), 4.57 (s, 1H), 4.27 (d, *J* = 5.6 Hz, 1H), 3.52 (s, 3H), 3.29 (s, 1H), 2.88 (d, *J* = 6.0 Hz, 1H), 2.24 (dd, *J* = 9.0, 4.0 Hz, 1H), 2.08 (d, *J* = 9.2 Hz, 1H), 1.24 (d, *J* = 14.4 Hz, 6H) ppm.

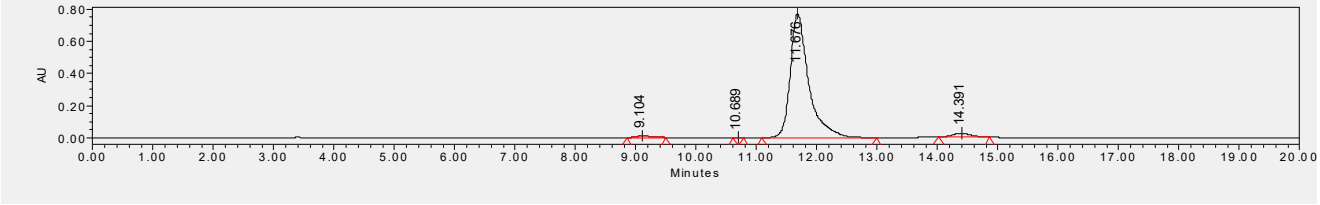
^{13}C NMR (101 MHz, $CDCl_3$) δ = 201.8, 174.2, 173.1, 139.1, 138.2, 137.01, 135.6, 132.9, 131.1, 130.2, 129.4, 128.6, 128.6, 128.5, 128.3, 128.0, 127.5, 126.0, 66.9, 53.1, 52.7, 51.1, 41.6, 39.3, 37.7, 36.2, 27.8, 23.7, 20.1 ppm.

ESI-HRMS calcd [$C_{35}H_{34}O_5$+Na^+] = 557.2298, found 557.2300.

IR $\tilde{\nu}$ (cm-1) 3029, 2837, 1722, 1677, 1598, 1447, 1373, 1220, 1099, 1025, 808, 721, 696, 508.

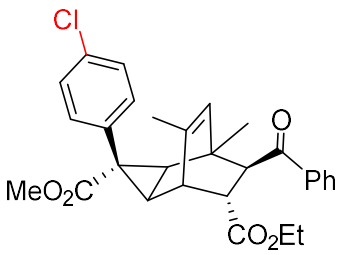


	Retention Time	Area	% Area
1	9.077	538650	1.45
2	10.670	330802	0.89
3	11.619	17962459	48.32
4	14.319	18344199	49.34



	Retention Time	Area	% Area
1	9.104	191991	1.13
2	10.689	1295	0.01
3	11.676	16355488	96.17
4	14.391	458683	2.70

3ba: 6-ethyl 3-methyl -7-benzoyl-3-(4-chlorophenyl)-1,9-dimethyltricyclo[3.2.2.0^{2,4}]non-8-ene-3,6-dicarboxylate



3ba

28.6 mg, 58% yield, 19:1 dr, 91% ee.; light yellow solid, 135 – 138 °C, $[\alpha]^{20}_{D}$ = -221.7 (*c* = 0. 30, in CH_2Cl_2).

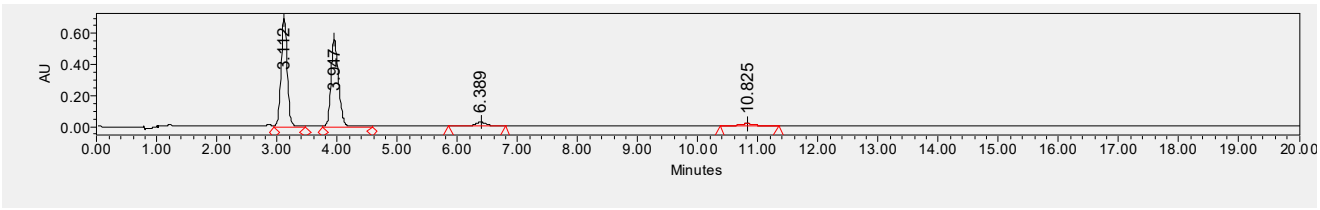
HPLC (Daicel chiralcel OX-3, CO_2/MeOH 90/10, 1.5 mL/min, λ = 254 nm), t_R(major) = 3.10 min, t_R(minor) = 3.98 min.

^{1}H NMR (600 MHz, Chloroform-*d*) δ = 8.00 (d, *J* = 1.8 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.18 (m, Hz, 2H), 7.01 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.85 (dd, *J* = 8.4, 1.8 Hz, 1H), 4.61 (s, 1H), 4.25 (d, *J* = 6.0 Hz, 1H), 4.17 (m, 2H), 3.53 (s, 3H), 3.28 – 3.23 (m, 1H), 2.81 (dd, *J* = 6.0, 1.8 Hz, 1H), 2.24 (dd, *J* =9.0, 3.6 Hz, 1H), 2.08 (d, *J* = 9.6 Hz, 1H), 1.28 – 1.21 (m, 9H) ppm.

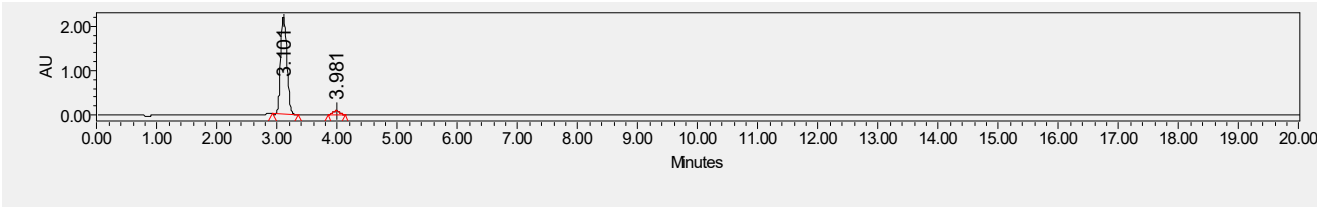
^{13}C NMR (151 MHz, $CDCl_3$) δ = 201.8, 173.8, 173.1, 139.1, 138.4, 135.8, 133.1, 132.5, 131.7, 131.4, 129.7, 128.7, 128.5, 128.1, 127.8, 61.1, 53.0, 52.8, 51.2, 41.5, 39.3, 37.9, 35.5, 27.9, 23.7, 20.2, 14.2 ppm.

ESI-HRMS calcd [$C_{29}H_{29}ClO_5$+Na^+] = 515.1595, 517.1566, found 515.1595, 517.1566.

IR $\tilde{\nu}$ (cm-1) 2906, 1723, 1677, 1596, 1492, 1446, 1374, 1301, 1269, 1230, 1193, 1092, 962, 838, 718, 525.

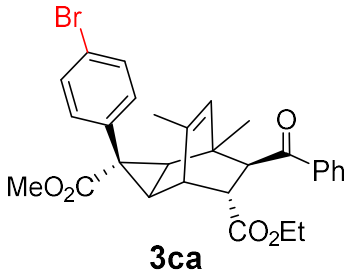


	Retention Time	Area	% Area
1	3.112	5130351	46.91
2	3.947	5112293	46.75
3	6.389	376199	3.44
4	10.825	316630	2.90



	Retention Time	Area	% Area
1	3.101	16265457	95.89
2	3.981	696305	4.11

3ca: 6-ethyl 3-methyl -7-benzoyl-3-(4-bromophenyl)-1,9-dimethyltricyclo[3.2.2.0^{2,4}]non-8-ene-3,6-dicarboxylate



3ca

47.2 mg, 88% yield, 19:1 dr, 93% ee.; light yellow solid, 145 – 146 °C, $[\alpha]^{20}_{D}$ = -144.8 (*c* = 0.59, in CH_2Cl_2).

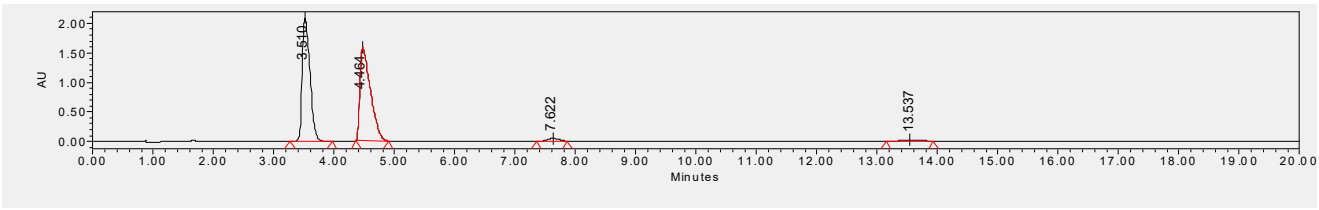
HPLC (Daicel chiralcel OX-3, CO_2/MeOH 90/10, 1.5 mL/min, λ = 254 nm), t_R(major) = 3.52 min, t_R(minor) = 4.61 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.05 – 7.97 (m, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.32 (ddd, *J* = 15.8, 8.2, 2.0 Hz, 2H), 6.95 (dd, *J* = 8.0, 2.4 Hz, 1H), 6.80 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.61 (s, 1H), 4.25 (d, *J* = 6.0 Hz, 1H), 4.17 (m, 2H), 3.52 (s, 3H), 3.29 – 3.21 (m, 1H), 2.80 (dd, *J* = 5.6, 2.0 Hz, 1H), 2.24 (dd, *J* = 8.8, 4.0 Hz, 1H), 2.07 (d, *J* = 9.2 Hz, 1H), 1.30 – 1.19 (m, 9H) ppm.

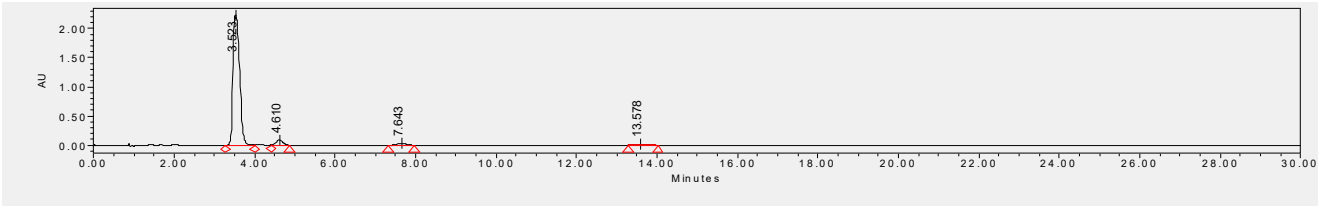
^{13}C NMR (101 MHz, $CDCl_3$) δ = 201.8, 173.7 173.1, 139.1, 138.3, 136.4, 133.0, 132.9, 131.8, 131.0, 130.7, 129.8, 128.7, 128.5, 119.7, 61.1, 53.0, 52.8, 51.2, 41.5, 39.3, 37.9, 35.6, 27.9, 23.7, 20.2, 14.2 ppm.

ESI-HRMS calcd [$C_{29}H_{29}BrO_5$+Na^+] = 559.1091, 561.1070, found 559.1090, 561.1069.

IR $\tilde{\nu}$ (cm^{-1}) 2906, 1720, 1676, 1488, 1445, 1373, 1268, 1228, 1192, 1067, 1009, 826, 766, 721, 691, 515.

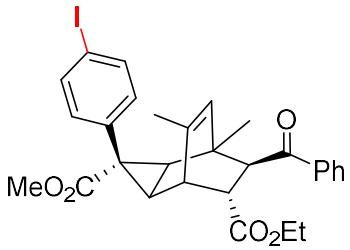


	Retention Time	Area	% Area
1	3.510	18372113	47.52
2	4.464	19011227	49.18
3	7.622	664456	1.72
4	13.537	612139	1.58



	Retention Time	Area	% Area
1	3.523	25849325	93.12
2	4.610	1068868	3.85
3	7.643	479449	1.73
4	13.578	361762	1.30

3da: 6-ethyl 3-methyl -7-benzoyl-3-(4-iodophenyl)-1,9-dimethyltricyclo[3.2.2.$0_{2,4}$]non-8-ene-3,6-dicarboxylate



3da

47.2 mg, 88% yield, 19:1 dr, 95% ee.; light yellow solid, 146 – 148 °C,, $[\alpha]^{21}_{D}$ = -150.3 (*c* = 0.79, in CH_2Cl_2).

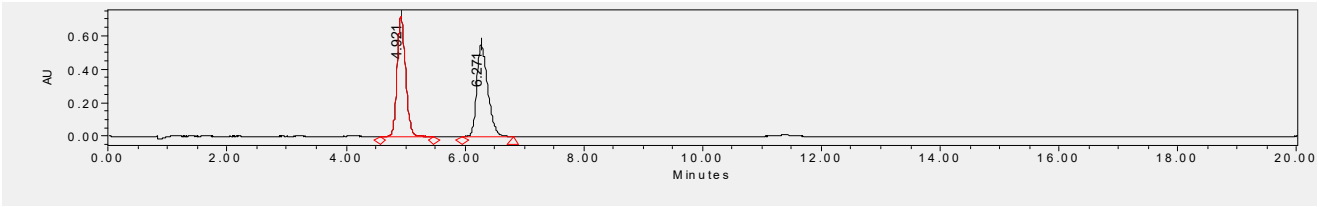
HPLC (Daicel chiralcel OX-3, CO_2/MeOH 90/10, 1.5 mL/min, λ = 254 nm), t_R(major) = 4.76 min, t_R(minor) = 6.10 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.00 (d, *J* = 7.2 Hz, 2H), 7.67 – 7.41 (m, 5H), 6.82 (dd, *J* = 8.0, 2.4 Hz, 1H), 6.67 (dd, *J* = 6.0, 2.0 Hz, 1H), 4.61 (s, 1H), 4.25 (d, *J* = 6.0 Hz, 1H), 4.16 (m, 2H), 3.52 (s, 3H), 3.30 – 3.19 (m, 1H), 2.80 (dd, *J* = 6.0, 2.0 Hz, 1H), 2.23 (dd, *J* = 9.2, 4.0 Hz, 1H), 2.07 (d, *J* = 9.2 Hz, 1H), 1.30 – 1.20 (m, 9H) ppm.

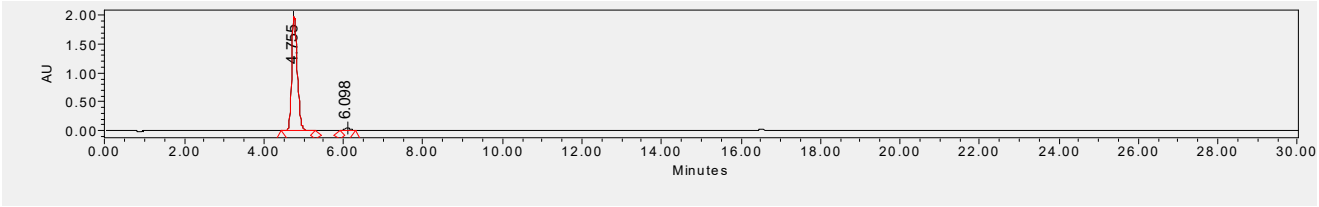
^{13}C NMR (101 MHz, $CDCl_3$) δ = 201.8, 173.7, 173.0, 139.1, 138.4, 137.1, 137.0, 136.6, 133.2, 133.0, 132.1, 129.8, 128.7, 128.5, 91.1, 61.1, 53.0, 52.8, 51.1, 41.5, 39.2, 37.9, 35.7, 27.9, 23.7, 20.2, 14.2 ppm.

ESI-HRMS calcd [$C_{29}H_{29}IO_5$+Na^+] = 607.0952, found 607.0952.

IR $\tilde{\nu}$ (cm^{-1}) 2955, 2872, 1723, 1677, 1595, 1446, 1373, 1230, 1193, 1060, 1029, 961, 822, 764, 720.

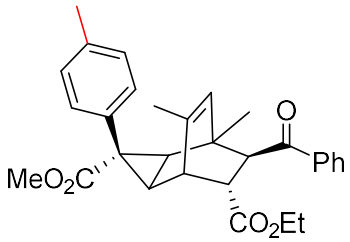


	Retention Time	Area	% Area
1	4.921	7064060	50.07
2	6.271	7044599	49.93



	Retention Time	Area	% Area
1	4.755	19427944	97.77
2	6.098	443277	2.23

3ea: 6-ethyl 3-methyl -7-benzoyl-1,9-dimethyl-3-(p-tolyl)tricyclo[3.2.2.0^{2,4}]non-8-ene-3,6-dicarboxylate



3ea

45.1 mg, 98% yield, 19:1 dr, 85% ee.; light yellow liquid, $[\alpha]^{20}_{D}$ = -146.1 (*c* = 0.66, in CH_2Cl_2).

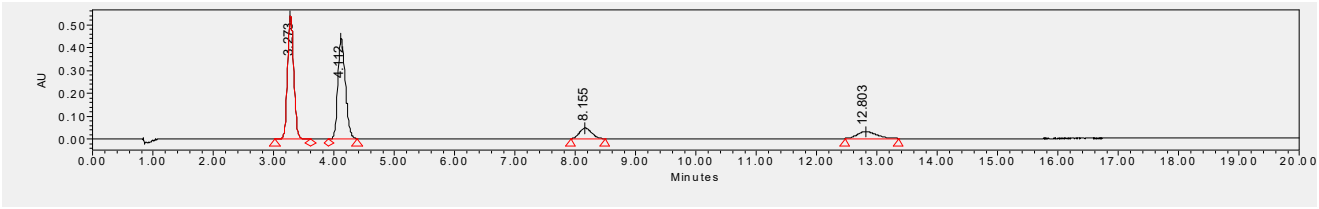
HPLC (Daicel chiralcel OX-3, CO_2/MeOH 90/10, 1.5 mL/min, λ = 254 nm), t_R(major) = 3.38, min, t_R(minor) = 4.30 min

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.01 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 2H), 6.99 (m, 3H), 6.84 – 6.77 (m, 1H), 4.58 (s, 1H), 4.26 (d, *J* = 6.0 Hz, 1H), 4.23 – 4.11 (m, 2H), 3.52 (s, 3H), 3.29 – 3.24 (m, 1H), 2.80 (dd, *J* = 6.0, 2.4 Hz, 1H), 2.30 (s, 3H), 2.22 (dd, *J* =9.2, 4.0 Hz, 1H), 2.04 (d, *J* = 9.2 Hz, 1H), 1.30 – 1.20 (m, 9H) ppm.

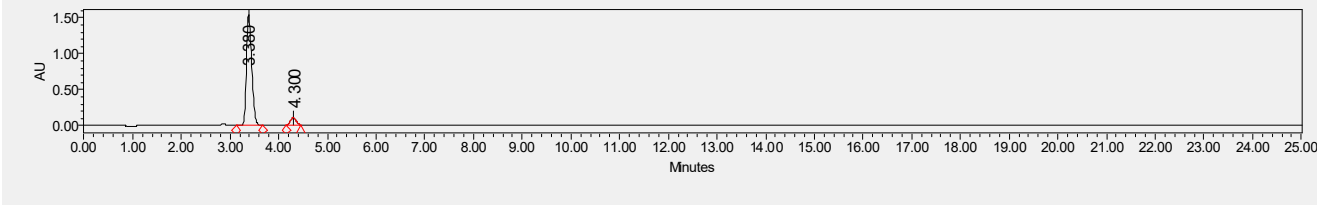
^{13}C NMR (101 MHz, $CDCl_3$) δ = 202.0, 174.4, 173.2, 139.3, 138.2, 135.3, 133.8, 132.9, 131.0, 130.1, 129.1, 128.6, 128.6, 128.4, 128.3, 61.0, 53.1, 52.7, 51.26, 41.6, 39.4, 37.7, 35.8, 27.7, 23.7, 21.2, 20.1, 14.2 ppm.

ESI-HRMS calcd [$C_{30}H_{32}O_5$+Na^+] = 495.2142, found 495.2143.

IR $\tilde{\nu}$ (cm^{-1}) 2958, 1719, 1676, 1445, 1373, 1226, 1190, 1022, 999, 938, 896, 819, 760, 691, 617, 522.

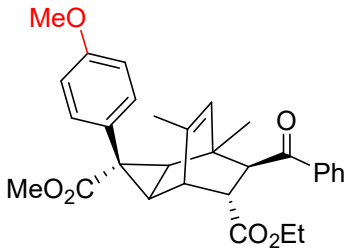


	Retention Time	Area	% Area
1	3.273	3806681	42.72
2	4.112	3789900	42.53
3	8.155	664212	7.45
4	12.803	650394	7.30



	Retention Time	Area	% Area
1	3.380	11512842	92.97
2	4.300	870022	7.03

3fa: 6-ethyl 3-methyl -7-benzoyl-3-(4-methoxyphenyl)-1,9-dimethyltricyclo[3.2.2.0^{2,4}]non-8-ene-3,6-dicarboxylate



3fa

43.1 mg, 89% yield, 19:1 dr, 89% ee.; light yellow liquid, $[\alpha]^{20}_{D}$ = -165.1 (c = 0.64, in CH_2Cl_2).

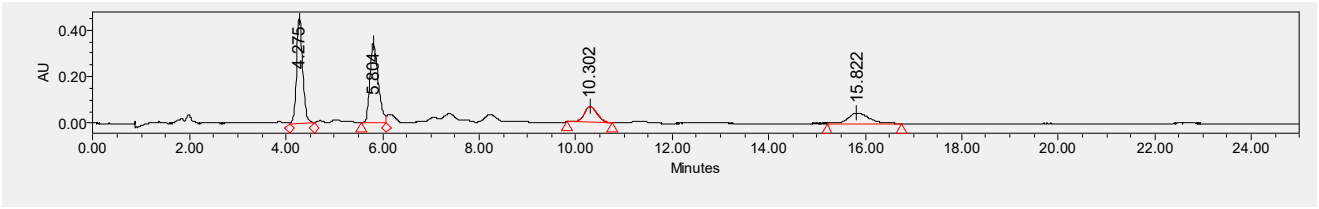
HPLC (Daicel chiralcel OX-3, CO_2/MeOH 90/10, 1.5 mL/min, λ = 254 nm), t_R(major) = 4.16 min, t_R(minor) = 5.70 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.01 (d, J = 5.2 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.04 – 6.97 (m, 1H), 6.85 – 6.72 (m, 3H), 4.61 (s, 1H), 4.25 (d, J = 6.0 Hz, 1H), 4.17 (m, 2H), 3.78 (s, 3H), 3.52 (s, 3H), 3.32 – 3.22 (m, 1H), 2.80 (dd, J = 6.0, 2.0 Hz, 1H), 2.21 (dd, J = 9.2, 4.0 Hz, 1H), 2.03 (d, J = 9.2 Hz, 1H), 1.29 – 1.18 (m, 9H) ppm.

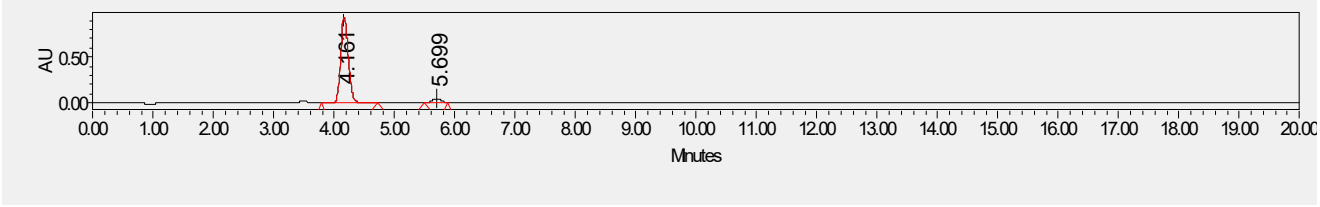
^{13}C NMR (101 MHz, $CDCl_3$) δ = 202.0, 174.5, 173.2, 157.7, 139.2, 138.3, 133.0, 132.1, 131.0, 129.1, 128.8, 128.6, 128.4, 113.4, 113.1, 61.0, 55.2, 53.1, 52.7, 51.2, 41.6, 39.4, 37.7, 35.5, 27.8, 23.7, 20.2, 14.2 ppm.

ESI-HRMS calcd [$C_{30}H_{32}O_6$+Na^+] = 511.2091, found 511.2092.

IR $\tilde{\nu}$ (cm-1) 2957, 2837, 1718, 1675, 1611, 1445, 1373, 1268, 1225, 1185, 1030, 838, 719, 692, 536.

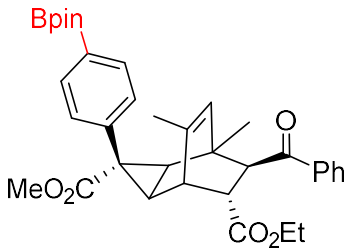


	Retention Time	Area	% Area
1	4.275	4100846	38.08
2	5.804	4089480	37.97
3	10.302	1277972	11.87
4	15.822	1300866	12.08



	Retention Time	Area	% Area
1	4.161	8192583	94.82
2	5.699	447490	5.18

3ga: 6-ethyl 3-methyl -7-benzoyl-1,9-dimethyl-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaboro -lan-2-yl) phenyl)tricyclo[3.2.2.0^{2,4}]non-8-ene-3,6-dicarboxylate



3ga

38.1 mg, 65% yield, 19:1 dr, 89% ee.; light yellow solid, 138 – 141 °C,, $[\alpha]^{20}_{D}$ = -163.6 (*c* = 0.33, in CH_2Cl_2).

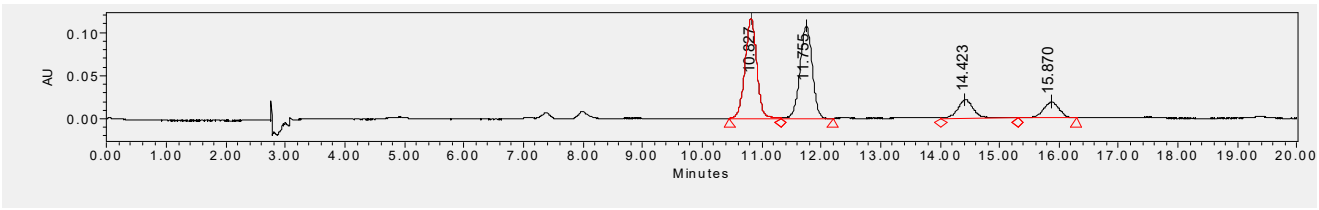
HPLC (Daicel chiralcel ODH, CO_2/MeOH 90/10, 1.0 mL/min, λ = 254 nm), t_R(major) = 10.81, min, t_R(minor) = 11.77 min

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.06 – 7.96 (m, 2H), 7.61 (m, 3H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.08 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.94 (dd, *J* = 7.6, 1.2 Hz, 1H), 4.57 (s, 1H), 4.26 (d, *J* = 6.0 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.60 (s, 1H), 3.50 (s, 3H), 3.31 – 3.24 (m, 1H), 2.80 (dd, *J* = 6.0, 2.0 Hz, 1H), 2.23 (dd, *J* = 10.0, 4.0 Hz, 1H), 2.08 (d, *J* = 7.2 Hz, 1H), 1.34 (s, 12H), 1.26 – 1.21 (m, 9H) ppm.

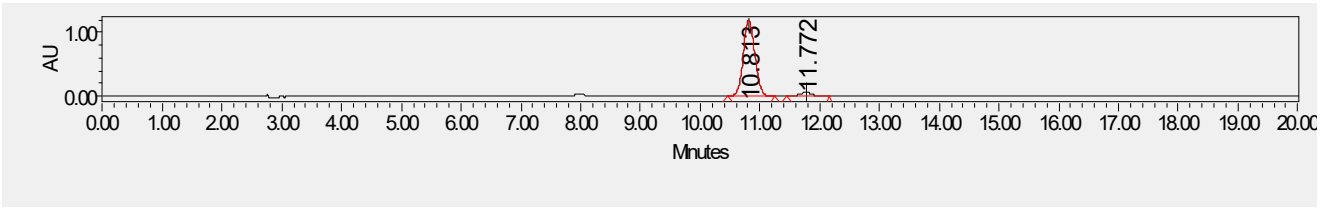
^{13}C NMR (101 MHz, $CDCl_3$) δ = 202.0, 174.0, 173.2, 140.4, 139.2, 138.4, 134.5, 133.9, 133.5, 133.0, 132.0, 130.6, 129.7, 129.7, 128.7, 128.5, 83.7, 61.1, 53.0, 52.7, 51.2, 41.5, 39.3, 38.0, 36.2, 28.0, 25.0, 24.9, 23.8, 23.6, 21.3, 20.3, 14.2 ppm.

ESI-HRMS calcd for [$C_{35}H_{41}BO_7$+Na^+] = 607.2838, found 607.2839.

IR $\tilde{\nu}$ (cm^{-1}) 2977, 1721, 1678, 1518, 1446, 1397, 1359, 1319, 1229, 1061, 1020, 962, 898, 775, 720, 659.

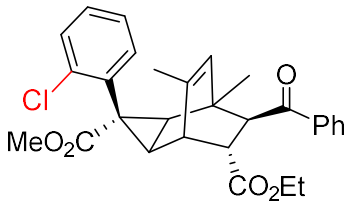


	Retention Time	Area	% Area
1	10.827	1595053	40.85
2	11.755	1543502	39.53
3	14.423	410404	10.51
4	15.870	355804	9.11



	Retention Time	Area	% Area
1	10.813	16234755	94.72
2	11.772	904909	5.28

3ha: 6-ethyl 3-methyl -7-benzoyl-3-(2-chlorophenyl)-1,9-dimethyltricyclo[3.2.2.0^{2,4}]non-8 -ene-3,6 -dicarboxylate



3ha

35.1 mg, 71% yield, 2:3 dr, 89/ 91% ee.; light yellow liquid, $[\alpha]^{21}_{D}$ = -108.7 (*c* = 0.24, in CH_2Cl_2).

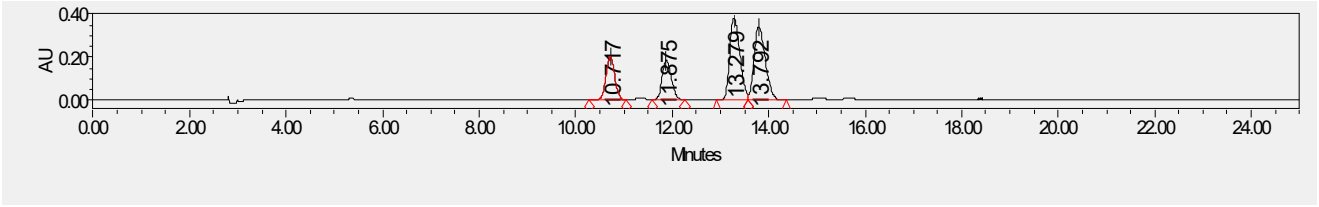
HPLC (Daicel chiralcel ODH, CO_2/MeOH 90/10, 1.0 mL/min, λ = 254 nm), t_1 = 10.71, t_2 = 11.92, t_3 = 13.31, t_4 = 13.88.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.07 – 7.96 (m, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.27 – 6.92 (m, 4H), 4.80 (m, 0.5H), 4.63 (m, 0.4 H) 4.32 – 4.09 (m, 3H), 3.54 (d, *J* = 7.6 Hz, 3H), 3.42 – 3.36 (m, 0.4 H), 3.31 (s, 0.6 H), 2.79 (m, 1H), 2.47 (dd, *J* = 8.8, 4.0 Hz, 0.4 H), 2.29 (d, *J* = 9.2 Hz, 0.6 H), 2.23 (dd, *J* = 8.8, 3.2 Hz, 0.6 H), 2.09 (d, *J* = 9.2 Hz, 0.4 H), 1.35 – 1.18 (m, 9H) ppm.

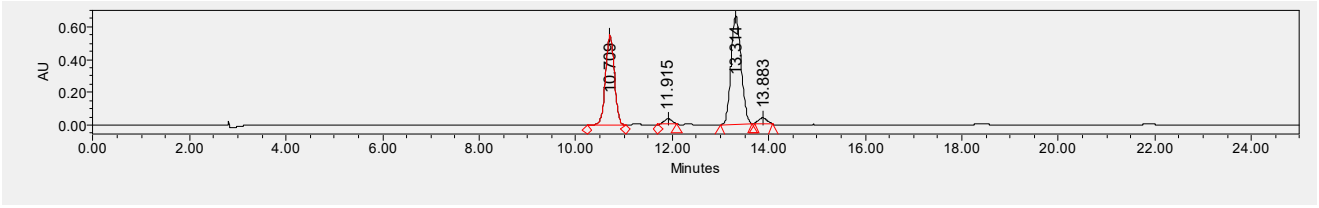
^{13}C NMR (101 MHz, $CDCl_3$) δ = 202.3, 202.1, 173.4, 173.2, 173.1, 140.1, 139.2, 139.2, 138.2, 135.8, 135.7, 135.2, 134.7, 133.8, 133.0, 133.0, 132.7, 129.8, 129.5, 129.1, 128.7, 128.6, 128.5, 127.5, 127.4, 127.4, 126.2, 125.8, 61.1, 53.3, 52.8, 52.6, 51.4, 51.3, 41.8, 41.6, 40.4, 39.9, 39.8, 38.4, 34.5, 34.3, 30.5, 28.1, 23.8, 23.0, 20.1, 19.6, 14.2, 14.2 ppm.

ESI-HRMS calcd [$C_{29}H_{29}ClO_5$+Na^+] = 515.1595, 517.1566, found 515.1590, 517.1560.

IR $\tilde{\nu}$ (cm^{-1}) 2959, 1721, 1676, 1476, 1441, 1373, 1268, 1228, 1191, 1069, 1071, 691, 657.

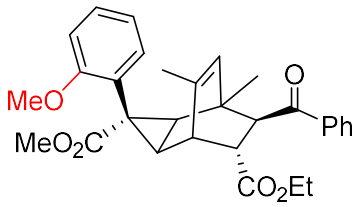


	Retention Time	Area	% Area
1	10.717	2551842	15.70
2	11.875	2523436	15.53
3	13.279	5626588	34.63
4	13.792	5546987	34.14



	Retention Time	Area	% Area
1	10.709	6899647	39.66
2	11.915	379216	2.18
3	13.314	9671287	55.60
4	13.883	445391	2.56

3ia: 6-ethyl 3-methyl -7-benzoyl-3-(2-methoxyphenyl)-1,9-dimethyltricyclo[3.2.2.0^{2,4}]non-8-ene -3,6-dicarboxylate



3ia

44.0 mg, 89% yield, 1:1 dr, 80 /80 % ee.; light yellow liquid, $[\alpha]^{20}_{D}$ = -114.2 (*c* = 0.74, in CH_2Cl_2).

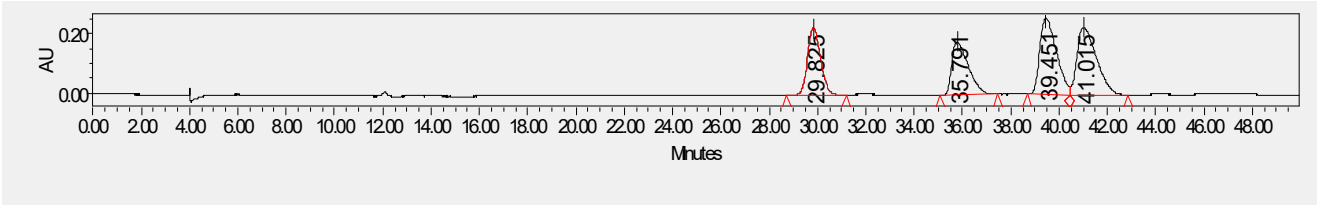
HPLC (Daicel chiralcel OXH, CO_2/MeOH 95/5, 0.8 mL/min, λ = 254 nm), t_1 = 30.10, t_2 = 36.65, t_3 = 39.78, t_4 = 41.98.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.08 – 7.98 (m, 2H), 7.60 – 7.52 (m, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.17 – 7.10 (m, 1H), 7.03 – 6.68 (m, 3H), 4.61 (s, 1H), 4.28 – 4.10 (m, 3H), 3.79 (m, 1.4 H), 3.71 (m, 1.5 H), 3.51 (d, *J* = 5.2 Hz, 3H), 3.24 (m, 1H), 2.81 (dd, *J* = 6.0, 2.0 Hz, 1H), 2.75 (dd, *J* = 6.0, 2.0 Hz, 0.4 H), 2.34 (dd, *J* = 8.8, 4.0 Hz, 0.5H), 2.20 (dd, *J* = 8.8, 4.0 Hz, 0.5H), 2.09 (d, *J* = 9.2 Hz, 0.5H), 2.01 (d, *J* = 9.2 Hz, 0.5H), 1.29 – 1.16 (m, 9H) ppm.

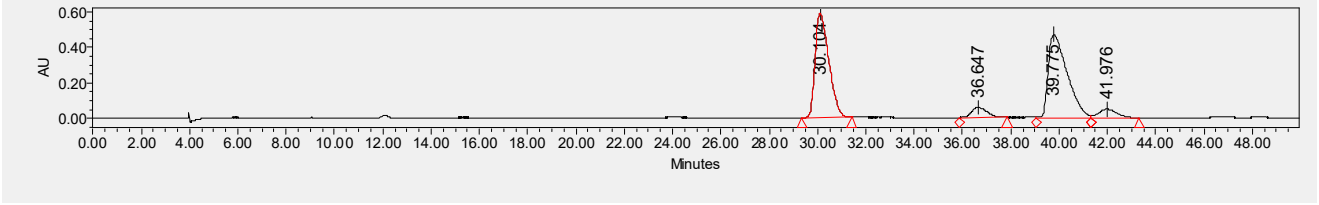
^{13}C NMR (101 MHz, $CDCl_3$) δ = 202.4, 202.3, 174.4, 174.3, 173.3, 157.6, 157.1, 139.9, 139.4, 139.3, 137.2, 132.9, 132.9, 132.8, 131.7, 129.7, 128.6, 128.6, 128.5, 127.6, 127.2, 127.0, 126.0, 125.4, 120.1, 119.6, 110.2, 109.4, 61.0 55.1, 54.5, 53.4, 52.9, 52.6, 51.4, 51.2, 41.9, 41.6, 40.0, 39.7, 39.5, 37.4, 31.4, 31.3, 29.3, 27.2, 23.8, 22.6, 19.8, 19.6, 14.2 ppm.

ESI-HRMS calcd [$C_{30}H_{32}O_6$+Na^+] = 511.2091, found 511.2094.

IR $\tilde{\nu}$ (cm^{-1}) 2957, 2873, 1719, 1676, 1496, 1447, 1372, 1227, 1189, 1028, 963, 755, 719, 692, 516.

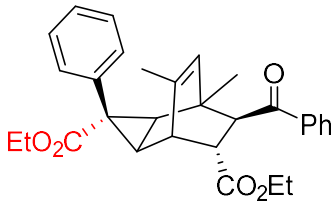


	Retention Time	Area	% Area
1	29.825	8427667	20.15
2	35.791	8458284	20.22
3	39.451	12300516	29.40
4	41.015	12644984	30.23



	Retention Time	Area	% Area
1	30.104	23220900	43.01
2	36.647	2563569	4.75
3	39.775	25603196	47.42
4	41.976	2603856	4.82

3ja: diethyl -7-benzoyl-1,9-dimethyl-3-phenyltricyclo[3.2.2.0^{2,4}]non-8-ene-3,6-dicarboxylate



3ja

42.5 mg, 90% yield, 19:1 dr, 85 % ee; light yellow liquid, $[\alpha]^{20}_{D}$ = -115.6 (*c* = 0.69, in CH_2Cl_2).

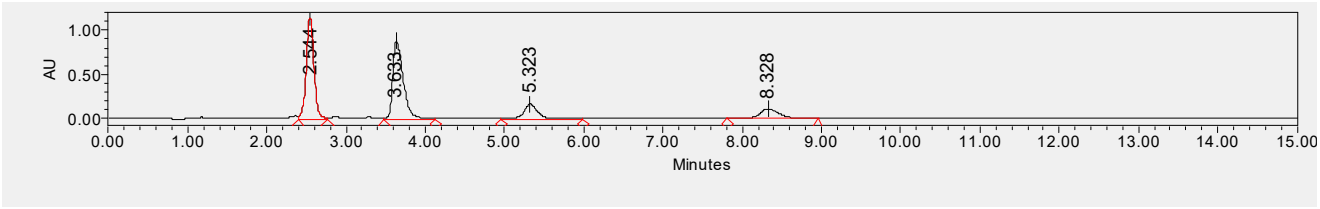
HPLC (Daicel chiralcel OX-3, CO_2/MeOH 90/10, 1.5 mL/min, λ = 254 nm), t_R(major) = 2.55 min, t_R(minor) = 3.72 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.01 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.14 (m, 4H), 6.92 (d, *J* = 7.2 Hz, 1H), 4.58 (s, 1H), 4.27 (d, *J* = 6.0 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.98 (m, 2H), 3.33 – 3.24 (m, 1H), 2.81 (dd, *J* = 6.0, 2.0 Hz, 1H), 2.22 (dd, *J* = 8.8, 3.6 Hz, 1H), 2.05 (d, *J* = 9.0 Hz, 1H), 1.29 – 1.20 (m, 9H), 1.06 (t, *J* = 6.0 Hz, 3H) ppm.

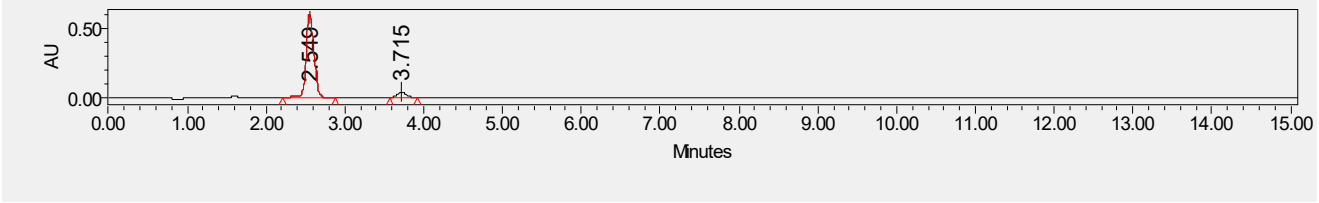
^{13}C NMR (101 MHz, $CDCl_3$) δ = 202.0, 173.7, 173.2, 139.2, 138.3, 137.2, 133.0, 131.2, 130.2, 129.4, 128.6, 128.5, 127.9, 127.4, 125.8, 61.3, 61.0, 53.1, 51.2, 41.5, 39.4, 37.4, 36.4, 27.5, 23.7, 20.1, 14.2, 14.0 ppm.

ESI-HRMS calcd [$C_{30}H_{32}O_5$+Na^+] = 495.2142, found 495.2142.

IR $\tilde{\nu}$ (cm^{-1}) 2963, 1719, 1677, 1446, 1369, 1223, 1191, 1059, 1027, 939,719, 525.

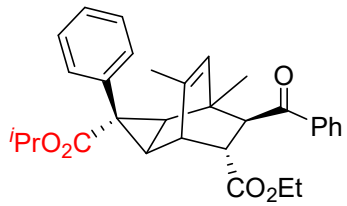


	Retention Time	Area	% Area
1	2.544	8029132	39.06
2	3.633	8292118	40.34
3	5.323	2372295	11.54
4	8.328	1861473	9.06



	Retention Time	Area	% Area
1	2.549	4130763	92.71
2	3.715	324946	7.29

3ka: 6-ethyl 3-isopropyl -7-benzoyl-1,9-dimethyl-3-phenyltricyclo[3.2.2.0^{2,4}]non-8-ene-3,6-dicar -boxylate



3ka

42.3mg, 89% yield, 19:1 dr, 90% ee.; light yellow liquid, $[\alpha]^{21}_{D}$ = -130.6 (*c* = 0. 53, in CH_2Cl_2).

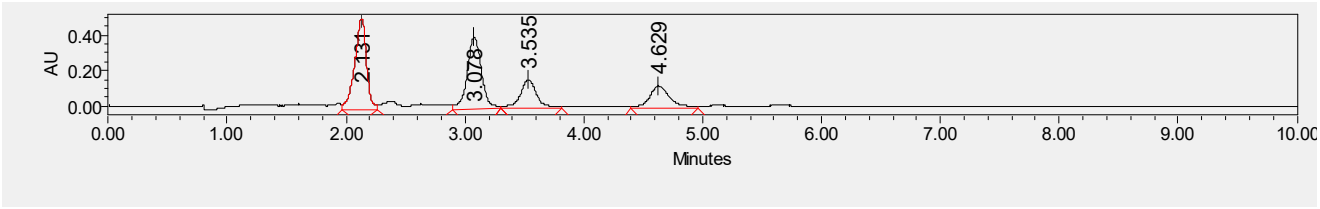
HPLC (Daicel chiralcel OX-3, CO_2/MeOH 90/10, 1.5 mL/min, λ = 254 nm), t_R(major) = 2.12 min, t_R(minor) = 3.09 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.05 – 7.99 (m, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.47 (m, 2H), 7.21 – 7.04 (m, 4H), 6.90 (d, *J* = 9.2 Hz, 1H), 4.82 (m, 1H), 4.58 (s, 1H), 4.27 (d, *J* = 5.6 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.26 (m, 1H), 2.81 (dd, *J* = 6.0, 2.2 Hz, 1H), 2.19 (dd, *J* = 9.2, 4.0Hz, 1H), 2.02 (d, *J* = 8.8 Hz, 1H), 1.29 – 1.21 (m, 9H), 1.04 (m, 6H) ppm.

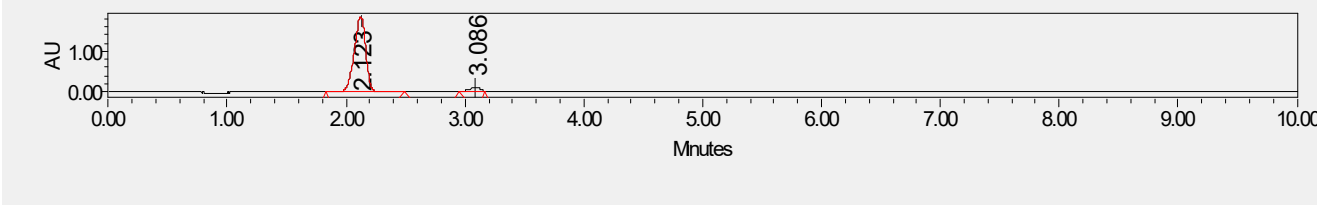
^{13}C NMR (101 MHz, $CDCl_3$) δ = 202.1, 173.3 173.1, 139.3, 138.3, 137.3, 132.9, 131.1, 130.2, 129.4, 128.6, 128.5, 127.8, 127.3, 125.7, 68.5, 61.0, 53.1, 51.2, 41.5, 39.4, 37.0, 36.6, 27.1, 23.7, 21.5, 21.5, 20.1, 14.2 ppm.

ESI-HRMS calcd [$C_{31}H_{34}O_5$+Na$^+$] = 509.2299, found 509.2295.

IR $\tilde{\nu}$ (cm^{-1}) 2977, 2873, 1721, 1677, 1447, 1373, 1229, 1187, 1107, 807, 780, 719, 695.

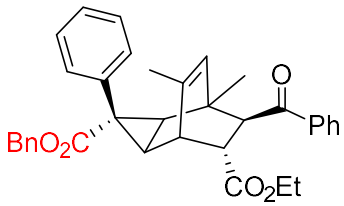


	Retention Time	Area	% Area
1	2.131	3531479	34.57
2	3.078	3394585	33.23
3	3.535	1702301	16.66
4	4.629	1586659	15.53



	Retention Time	Area	% Area
1	2.123	12399457	95.35
2	3.086	604065	4.65

3la: 3-benzyl 6-ethyl-7-benzoyl-1,9-dimethyl-3-phenyltricyclo[3.2.2.0^{2,4}]non-8-ene-3,6-dicarboxy -late



3la

36.6 mg, 68% yield, 19:1 dr, 88 % ee; light yellow liquid, $[\alpha]^{22}_{D}$ = -105.3 (c = 0. 66, in CH_2Cl_2).

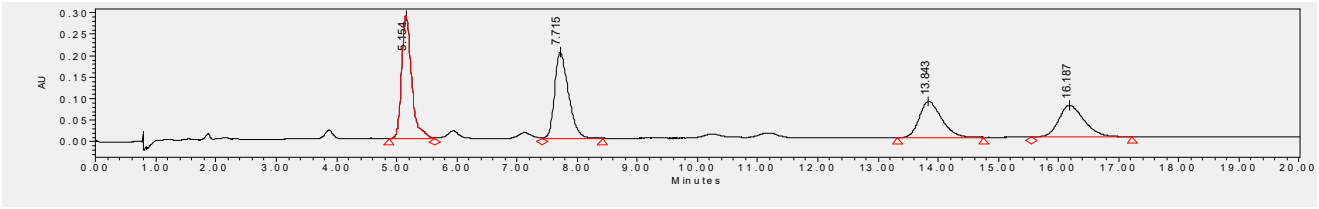
HPLC (Daicel chiralcel OX-3, CO_2/MeOH 90/10, 1.5 mL/min, λ = 254 nm), t_R(major) = 5.24 min, t_R(minor) = 7.93 min

^{1}H NMR (600 MHz, Chloroform-*d*) δ = 8.02 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 5.2 Hz, 1H), 7.48 (m, 2H), 7.22 (m, 5H), 7.14 (m, 2H), 7.04 – 6.91 (m, 3H), 5.00 (s, 2H), 4.61 (s, 1H), 4.28 (d, J = 6.0 Hz, 1H), 4.17 (q, J = 7.2 Hz, 2H), 3.34 – 3.26 (m, 1H), 2.82 (dd, J = 4.0, 1.6 Hz, 1H), 2.27 (dd, J = 6.4, 3.6 Hz, 1H), 2.10 (d, J = 6.0 Hz, 1H), 1.30 – 1.20 (m, 9H) ppm.

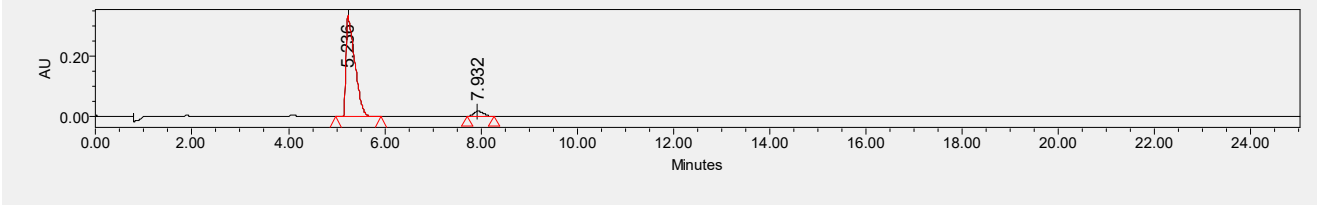
^{13}C NMR (151 MHz, $CDCl_3$) δ = 202.0, 173.4, 173.1, 139.2, 138.3, 137.0, 136.1, 133.0, 131.2, 130.2, 129.5, 128.6, 128.5, 128.3, 128.0, 127.6, 127.5, 126.7, 125.9, 66.4, 61.0, 53.0, 51.2, 41.5, 39.3, 37.8, 36.3, 27.8, 23.7, 20.1, 14.2 ppm.

ESI-HRMS calcd [$C_{35}H_{34}O_5^+Na^+$] = 557.2298, found 557.2300.

IR $\tilde{\nu}$ (cm^{-1}) 3029, 2837, 1722, 1677, 1598, 1447, 1373, 1220, 1099, 1025, 808, 721, 696, 508.

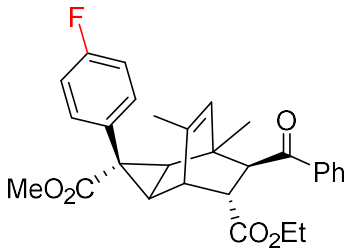


	Retention Time	Area	% Area
1	5.154	3313609	30.58
2	7.715	3187767	29.42
3	13.843	2159216	19.93
4	16.187	2176042	20.08



	Retention Time	Area	% Area
1	5.236	4243279	94.09
2	7.932	266760	5.91

3ma: 6-ethyl 3-methyl -7-benzoyl-3-(4-fluorophenyl)-1,9-dimethyltricyclo[3.2.2.0^{2,4}]non-8-ene -3,6-dicarboxylate



3ma

37.2 mg, 78% yield; light yellow liquid, $[\alpha]^{22}_{D}$ = -105.3 (*c* = 0. 66, in CH_2Cl_2). The racemates of this compound cannot be separated by the generally used column.

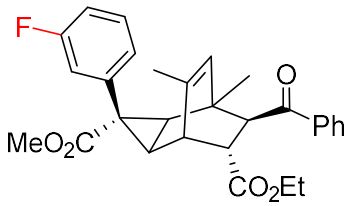
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.07 – 7.96 (m, 2H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.10 – 7.00 (m, 1H), 6.94 – 6.83 (m, 3H), 4.60 (s, 1H), 4.25 (d, *J* = 6.0 Hz, 1H), 4.17 (m, 2H), 3.53 (s, 3H), 3.30 – 3.21 (m, 1H), 2.80 (dd, *J* = 6.0, 2.0 Hz, 1H), 2.24 (dd, *J* = 6.0, 2.0 Hz, 1H), 2.07 (d, *J* = 7.2 Hz, 1H), 1.31 – 1.19 (m, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 201.9, 174.1, 173.1, 162.4, 160.0, 139.12, 138.3, 133.0 ($J_{C\text{-}F}$ = 4.04 Hz), 132.5 ($J_{C\text{-}F}$ = 8.1 Hz), 131.4 ($J_{C\text{-}F}$ = 6.1 Hz), 129.3, 128.7, 128.5, 114.8, 114.6, 61.1, 53.1, 52.8, 51.2, 41.5, 39.3, 37.8, 35.4, 27.9, 23.7, 20.2, 14.2 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.75 ppm.

ESI-HRMS calcd [$C_{29}H_{29}FO_5$+Na^+] = 477.2072, found 477.2070.

3na: 6-ethyl 3-methyl -7-benzoyl-3-(3-fluorophenyl)-1,9-dimethyltricyclo[3.2.2.0^{2,4}]non-8 -ene-3,6-dicarboxylate



3na

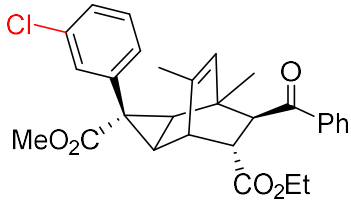
42.9 mg, 90 % yield, light yellow liquid, the racemates of this compound cannot be separated by the generally used column.

^{1}H NMR (600 MHz, Chloroform-*d*) δ = 8.00 (d, *J* = 7.6 Hz, 2H), 7.61 – 7.54 (m, 1H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.16 (m, 1H), 6.89 – 6.60 (m, 3H), 4.66 (s, 0.5H), 4.59 (s, 0.5H), 4.31 – 4.11 (m, 3H), 3.54 (d, *J* = 4.8 Hz, 3H), 3.32 – 3.21 (m, 1H), 2.81 (d, *J* = 6.0 Hz, 1H), 2.26 (dd, *J* = 9.6, 3.6 Hz, 0.5H), 2.22 (dd, *J* = 9.0, 4.2 Hz, 0.5H), 2.10 (d, *J* = 6.0 Hz, 0.5H), 2.07 (d, *J* = 6.0 Hz, 0.5H), 1.34 – 1.21 (m, 9H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ = 201.8 , 201.8, 173.4, ($J_{C\text{-}F}$ = 4.5 Hz),173.3, 162.3, 162.3, 139.8($J_{C\text{-}F}$ = 5.1 Hz), 139.7($J_{C\text{-}F}$ = 9.1 Hz), 139.2($J_{C\text{-}F}$ = 3.1 Hz),138.4, 138.0, 133.0, 129.7, 129.6, 129.2, 129.2, 128.7, 128.5, 126.8($J_{C\text{-}F}$ = 2.3 Hz), 126.0($J_{C\text{-}F}$ = 2.3 Hz), 117.6 ($J_{C\text{-}F}$ = 19.6 Hz) 117.5 ($J_{C\text{-}F}$ = 21.1 Hz), 113.2 ($J_{C\text{-}F}$ = 21.1 Hz), 112.9 ($J_{C\text{-}F}$ = 21.2 Hz), 61.1, 53.1, 53.0, 52.8, 51.2, 41.5, 41.4, 39.3, 38.0, 28.0, 23.6, 20.2, 20.0, 14.2 ppm.

^{19}F NMR (565 MHz, $CDCl_3$) δ = -114.36, -114.59 ppm.

3oa: 6-ethyl 3-methyl -7-benzoyl-3-(3-chlorophenyl)-1,9-dimethyltricyclo[3.2.2.0^{2,4}]non-8 -ene-3,6-dicarboxylate



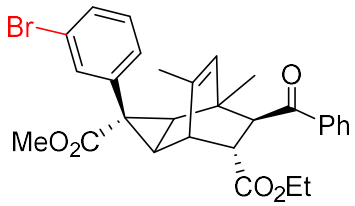
3oa

44.3 mg, 90 % yield, yellow liquid, the racemates of this compound cannot be separated by the generally used column.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.00 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.47 (m, 2H), 7.18 – 7.08 (m, 2H), 7.04 – 6.82 (m, 2H), 4.66 (s, 0H), 4.56 (s, 1H), 4.26 (d, *J* = 5.8 Hz, 1H), 4.22 – 4.11 (m, 2H), 3.54 (d, *J* = 2.0 Hz, 3H), 3.32 – 3.22 (m, 1H), 2.85 – 2.78 (m, 1H), 2.28 – 2.19 (m, 1H), 2.08 (dd, *J* =2.8, 3.6 Hz, 1H), 1.33 – 1.20 (m, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 202.3, 202.1, 173.4 173.2, 173.1, 140.1, 139.2, 139.2, 138.2, 135.8, 135.7, 135.2, 134.7, 133.8, 133.0, 133.0, 132.7, 129.8, 129.5, 129.1, 128.7, 128.6, 128.5, 127.5, 127.4, 127.4, 126.2, 125.8, 61.1, 53.3, 52.8, 52.6, 51.4, 51.32, 41.8, 41.6, 40.4, 39.9, 39.8, 38.4, 34.5, 34.3, 30.5, 28.1, 23.8, 23.0, 20.1, 19.6, 14.2, 14.2 ppm.

3pa: 6-ethyl 3-methyl -7-benzoyl-3-(3-bromophenyl)-1,9-dimethyltricyclo[3.2.2.0^{2,4}]non-8 -ene-3,6-dicarboxylate



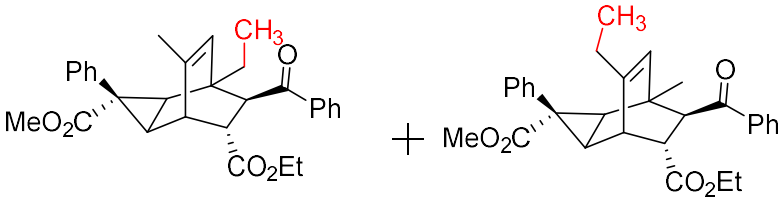
3pa

48.2 mg, 90 % yield, yellow solid, the racemates of this compound cannot be separated by the generally used column.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.00 (d, *J* = 7.4 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.29 – 7.16 (m, 2H), 7.11 – 7.03 (m, 1H), 6.94 (m, 1H), 4.66 (m, 0.4H), 4.56 (m, 0.6H), 4.25 (d, *J* = 5.8 Hz, 1H), 4.17 (m, 2H), 3.53 (s, 3H), 3.34 – 3.23 (m, 1H), 2.88 – 2.74 (m, 1H), 2.23 (m, 1H), 2.08 (d, *J* = 7.2 Hz, 1H), 1.34 – 1.17 (m, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 201.8, 201.7, 173.6, 173.5, 173.0, 139.6, 139.6, 139.2, 139.1, 138.1, 138.2, 134.0, 133.2, 133.0, 129.8, 129.6, 129.5, 129.4, 129.1, 129.0, 128.8, 128.7, 128.4, 128.4, 122.1, 121.4, 61.1, 53.0, 52.8, 51.1, 41.5, 41.4, 39.2, 39.2, 37.9, 37.9, 35.7, 35.6, 28.1, 28.0, 23.7, 23.6, 20.2, 19.9, 14.2 ppm.

3ra: Regio-isomer mixture **6-ethyl 3-methyl-7-benzoyl-1-ethyl-9-methyl-3-phenyltricyclo[3.2.2.0^{2,4}]non-8-ene-3,6-dicarboxylate** and **6-ethyl 3-methyl -7-benzoyl-9-ethyl-1-methyl-3-phenyltricyclo[3.2.2.0^{2,4}]non-8-ene-3,6-dicarboxylate**



3ra

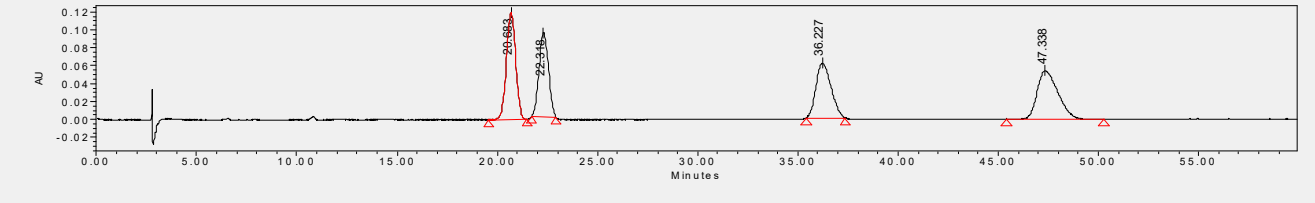
10.4 mg, total recovery: 22%, the mixture cannot be separated due to the same Rf value. 19:1dr / 19:1 dr, 88% ee / 86% ee; light yellow liquid.

HPLC (Daicel chiralcel OXH, CO_2/MeOH 95/5, 1.0 mL/min, λ = 254 nm), t_1 = 20.37, t_2 = 22.03, t_3 = 36.33, t_4 = 47.56.

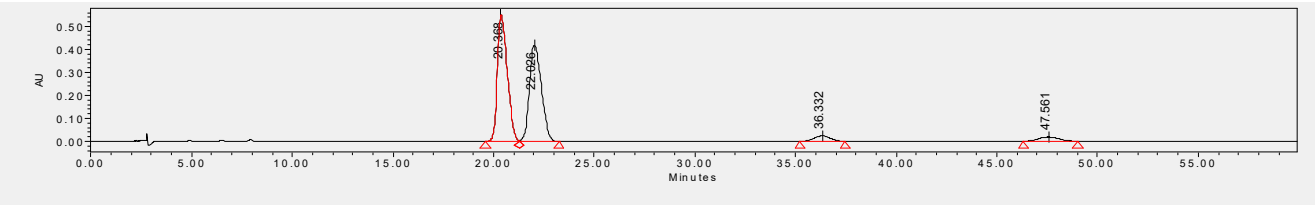
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.01 (d, *J* = 7.6 Hz, 2H), 7.55 (dd, *J* = 7.0, 4.9 Hz, 1H), 7.46 (m, 2H), 7.23 – 6.92 (m, 5H), 4.79 (s, 0.5 H), 4.53 (s, 0.5 H), 4.28 (m, 1H), 4.18 (m, 2H), 3.52 (d, *J* = 2.8 Hz, 3H), 3.32 – 3.21 (m, 1H), 2.79 (dd, *J* = 6.0, 2.0 Hz, 0.5 H), 2.69 (dd, *J* = 6.0, 2.0 Hz, 0.5 H), 2.24 (m, 1H), 2.07 (t, *J* = 8.8 Hz, 1H), 1.60 (m, 2H), 1.30 – 1.20 (m, 6H), 1.00 (t, *J* = 7.6 Hz, 1.5 H), 0.44 (t, *J* = 7.6 Hz, 1.5 H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 202.7, 201.9, 174.3, 173.2, 173.2, 143.0, 139.3, 139.1, 138.68, 137.0, 132.9, 131.2, 131.1, 130.5, 129.9, 128.6, 128.6, 128.5, 128.4, 128.2, 128.0, 127.9, 127.4, 126.8, 126.0, 125.9, 61.0, 53.2, 52.7, 52.2, 51.8, 51.6, 46.2, 41.4, 39.9, 39.0, 37.9, 36.2, 35.9, 35.3, 28.9, 27.6, 27.0, 26.4, 23.9, 20.0, 14.2, 10.6, 9.8.

ESI-HRMS calcd [$C_{30}H_{32}O_5^{+}Na^{+}$] = 495.2142, found 495.2143.

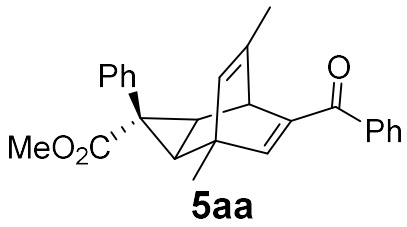


	Retention Time	Area	% Area
1	20.683	3851454	27.49
2	22.318	3115623	22.24
3	36.227	3183888	22.72
4	47.338	3859561	27.55



	Retention Time	Area	% Area
1	20.368	18880767	48.62
2	22.026	17300165	44.55
3	36.332	1357737	3.50
4	47.561	1298149	3.34

5aa: methyl -8-benzoyl-1,6-dimethyl-3-phenyltricyclo[3.2.2.0^{2,4}]nona-6,8-diene-3-carboxylate



5aa

32.6 mg, 84% yield, 19:1 dr, 80% ee; yellow solid, solid, m. p. 173–174 °C, $[\alpha]^{22}_{D} = 23.3$ (c = 0.56, in CH_2Cl_2).

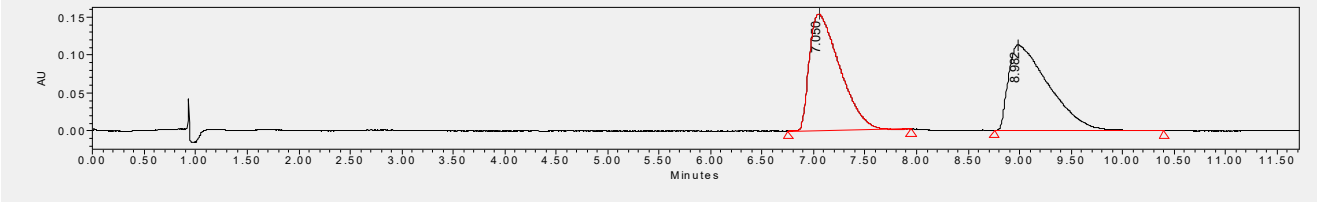
HPLC (Daicel chiralcel ID-3, CO_2/EtOH 95/10, 1.5 mL/min, λ = 254 nm), t_R(major) = 7.10 min, t_R(minor) = 9.46 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.68 – 7.62 (m, 2H), 7.52 (m, 1H), 7.42 (m, 2H), 7.27 – 7.21 (m, 2H), 7.17 (m, 2H), 7.06 – 7.01 (m, 2H), 4.84 (s, 1H), 4.35 (m, 1H), 3.51 (s, 3H), 2.51 (dd, J = 9.2, 4.0 Hz, 1H), 2.14 (d, J = 9.6 Hz, 1H), 1.74 (s, 3H), 1.21 (d, J = 1.6Hz, 3H) ppm.

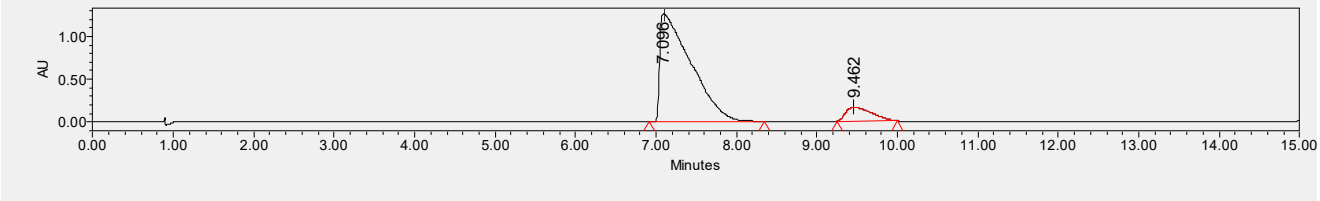
^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.5, 173.1, 161.6, 153.5, 143.4, 138.2, 136.8, 134.3, 131.9, 131.1, 130.4, 129.1, 128.2, 128.0, 127.2, 126.1, 52.7, 50.6, 46.5, 44.2, 42.7, 39.2, 22.3, 20.1 ppm.

ESI-HRMS calcd [$C_{26}H_{24}O_3^+Na^+$] = 407.1618, found 407.1615.

IR $\tilde{\nu}$ (cm^{-1}) 3025, 2959, 2871, 1713, 1636, 1597, 1487, 1434, 1325, 1235, 1153, 1057, 1023, 755, 746.

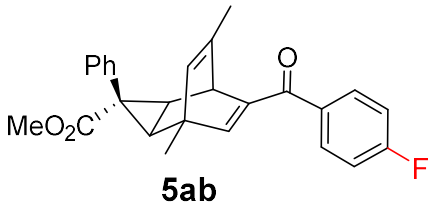


	Retention Time	Area	% Area
1	7.050	3161020	50.62
2	8.982	3083202	49.38



	Retention Time	Area	% Area
1	7.096	33890459	90.43
2	9.462	3587951	9.57

5ab: methyl-8-(4-fluorobenzoyl)-1,6-dimethyl-3-phenyltricyclo[3.2.2.0^{2,4}]nona-6,8-diene-3-carboxylate



5ab

26.7 mg, 66% yield, 19:1dr, 60% ee.; yellow solid, m. p. 170 – 172 °C, $[\alpha]^{21}_{D}$ =3.2 (*c* = 0.54, in CH_2Cl_2).

HPLC (Daicel chiralcel IE-3, CO_2/MeOH 90/10, 1.5 mL/min, λ = 254 nm), t_R(major) = 4.88 min, t_R(minor) = 5.74 min.

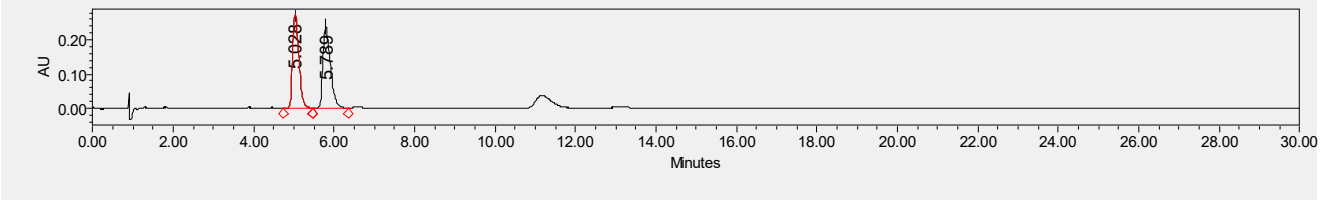
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 – 7.61 (m, 2H), 7.24 (m, 2H), 7.21 – 7.14 (m, 2H), 7.09 (m, 2H), 7.03 (d, *J* = 7.4 Hz, 2H), 4.84 (s, 1H), 4.39 – 4.23 (m, 1H), 3.50 (s, 3H), 2.50 (dd, *J* = 8.8, 4.2 Hz, 1H), 2.14 (d, *J* = 9.6 Hz, 1H), 1.74 (s, 3H), 1.20 (d, *J* = 1.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.1, 173., 166.3, 163.8, 161.3, 153.4, 143.4, 136.7, 134.2 (d, $J_{C\text{-}F}$ = 4.9 Hz), 131.5 (d, $J_{C\text{-}F}$ = 9.0 Hz), 131.0, 130.3, 127.9, 127.2, 126.1, 115.3 (d, $J_{C\text{-}F}$ = 21.6 Hz), 52.67, 50.61, 46.47, 44.34, 42.69, 39.19, 22.29, 20.09 ppm.

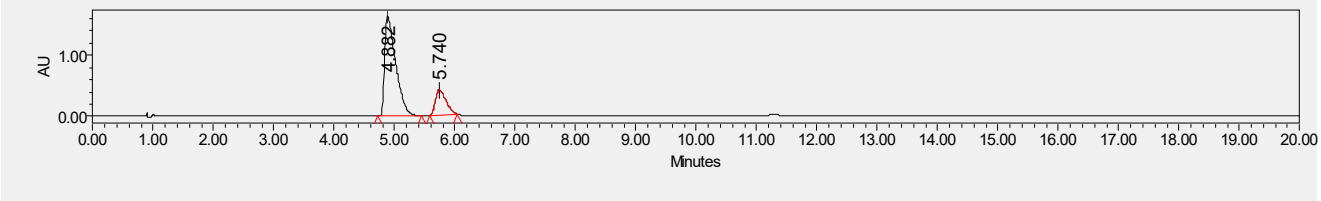
^{19}F NMR (377 MHz, $CDCl_3$) δ = -107.14 PPm.

ESI-HRMS calcd [$C_{26}H_{23}FO_3^+Na^+$] = 425.1532, found 425.1529.

IR $\tilde{\nu}$ (cm^{-1}) 3025, 2960, 2851, 1714, 1636, 1593, 1504, 1407, 1366, 1319, 1225, 1154, 844, 756, 754, 684.

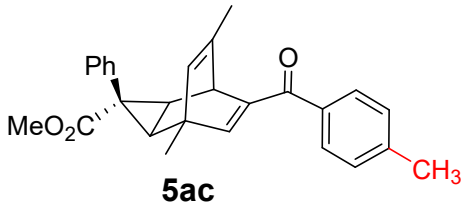


	Retention Time	Area	% Area
1	5.028	3026096	49.12
2	5.789	3134406	50.88



	Retention Time	Area	% Area
1	4.882	20709300	80.67
2	5.740	4962212	19.33

5ac: methyl-1,6-dimethyl-8-(4-methylbenzoyl)-3-phenyltricyclo[3.2.2.0^{2,4}]nona -6,8-diene-3-carboxylate



5ac

30.8 mg, 77% yield, 19:1dr, 70% ee.; yellow solid, m. p. 173 – 175°C, $[\alpha]^{21}_{D}$ =5.5 (*c* = 0.56, in CH_2Cl_2).

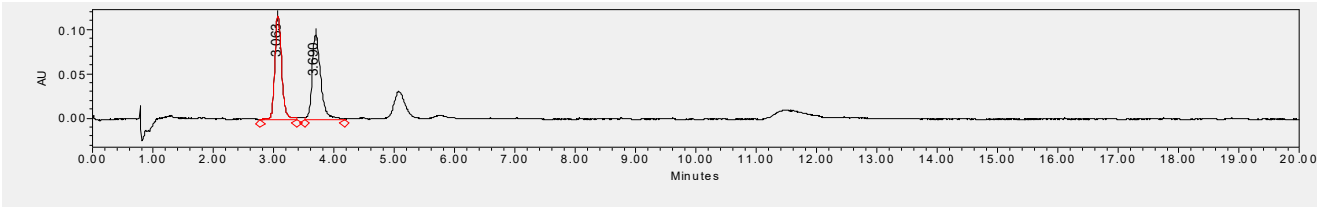
HPLC (Daicel chiralcel IA-3, CO_2/MeOH 90/10, 1.5 mL/min, λ = 254 nm), t_R(major) = 2.92 min, t_R(minor) = 3.55 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.20 (m, 4H), 7.19 – 7.14 (m, 2H), 7.06 – 7.00 (m, 2H), 4.83 (s, 1H), 4.33 (m, 1H), 3.51 (s, 3H), 2.51 (dd, *J* = 9.2, 4.4 Hz, 1H), 2.40 (s, 3H), 2.14 (d, *J* = 9.4 Hz, 1H), 1.73 (s, 3H), 1.20 (d, *J* = 1.2 Hz, 3H) ppm.

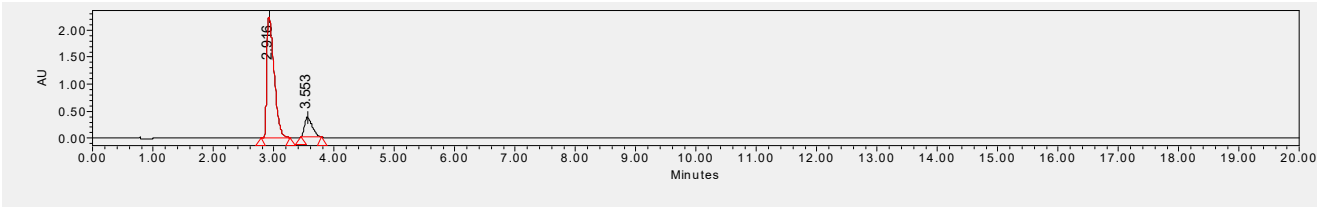
^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 173.1, 160.9, 153.5, 143.4, 142.5, 136.8, 135.4, 134.3, 131.1, 130.4, 129.3, 128.9, 127.9, 127.2, 126.1, 52.6, 50.6, 46.4, 44.3, 42.8, 39.2, 22.3, 21.6, 20.1 ppm.

ESI-HRMS calcd $[C_{27}H_{26}O_3{}^{+}Na^{+}]$ = 421.1774, found 425.1775.

IR $\tilde{\nu}$ (cm^{-1}) 3025, 2959, 2871, 2361, 2340, 1713, 1635, 1596, 1582, 1435, 1323, 1232, 962, 754, 734.

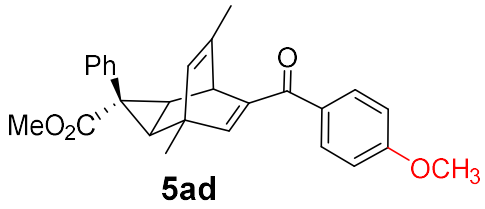


	Retention Time	Area	% Area
1	3.063	927120	49.38
2	3.690	950419	50.62



	Retention Time	Area	% Area
1	2.916	18665314	85.01
2	3.553	3291283	14.99

5ad: methyl-8-(4-methoxybenzoyl)-1,6-dimethyl-3-phenyltricyclo[3.2.2.0^{2,4}] nona-6,8-diene-3-carboxylate



5ad

29.3mg, 70% yield, 19:1dr, 66% ee.; yellow solid, m. p. 176 – 178°C, $[\alpha]^{21}_{D}$ =8.8 (*c* = 0.49, in CH_2Cl_2).

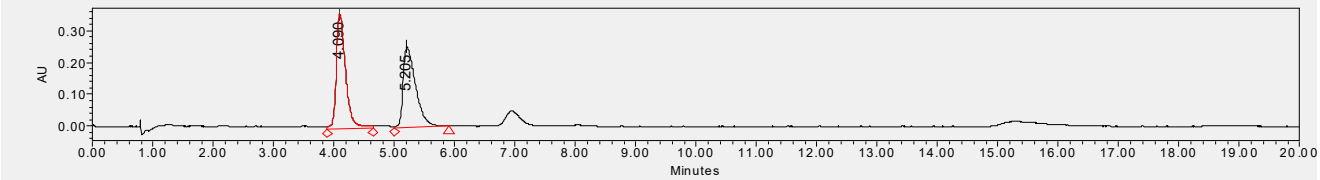
HPLC (Daicel chiralcel IA-3, CO_2/MeOH 90/10, 1.5 mL/min, λ = 254 nm), t_R(major) = 3.91 min, t_R(minor) = 5.09 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.72 – 7.65 (m, 2H), 7.22–7.25 (m, 2H), 7.19 – 7.13 (m, 2H), 7.05 – 7.01 (m, 1H), 6.99 (d, *J* = 1.2 Hz, 1H), 6.93 – 6.88 (m, 2H), 4.84 (s, 1H), 4.30 (m, 1H), 3.86 (s, 3H), 3.50 (s, 3H), 2.51 (dd, *J* = 9.4, 4.2 Hz, 1H), 2.14 (d, *J* = 9.4 Hz, 1H), 1.74 (s, 3H), 1.20 (d, *J* = 1.5 Hz, 3H) ppm.

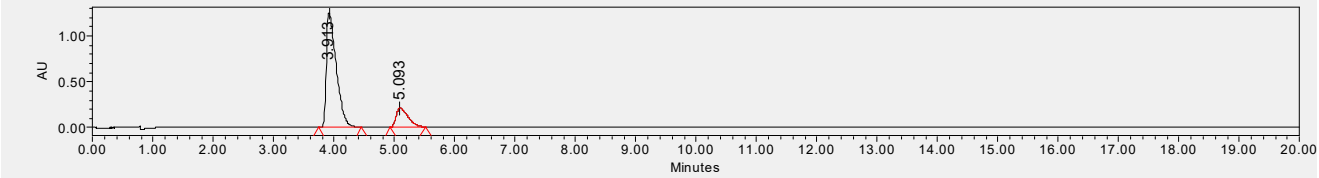
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.5, 173.1, 162.8, 159.9, 153.5, 143.4, 136.8, 134.3, 131.4, 131.1, 130.7, 130.4, 127.9, 127.2, 126.1, 113.4, 55.4, 52.6, 50.6, 46.3, 44.7, 42.8, 39.3, 22.3, 20.1 ppm.

ESI-HRMS calcd [$C_{27}H_{26}O_4^+Na^+$] = 437.1723, found 437.1721.

IR $\tilde{\nu}$ (cm^{-1}) 2958, 1713, 1630, 1598, 1508, 1443, 1324, 1234, 1168, 1027, 962, 840, 814, 757, 734, 703.

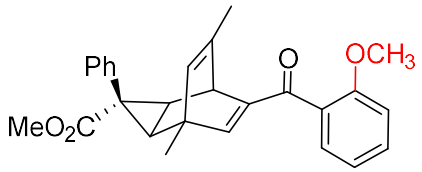


-	Retention Time	Area	% Area
1	4.090	3919390	51.97
2	5.205	3622855	48.03



	Retention Time	Area	% Area
1	3.913	14400580	83.21
2	5.093	2906623	16.79

5ae: methyl-8-(2-methoxybenzoyl)-1,6-dimethyl-3-phenyltricyclo[3.2.2.0^{2,4}] nona-6,8-diene-3-carboxylate



5ae

36.5 mg, 88% yield, 19:1dr, 81% ee.; yellow solid, m. p. 179 – 181°C, $[\alpha]^{21}_{D}$ =26.8 (*c* = 0.54, in CH_2Cl_2).

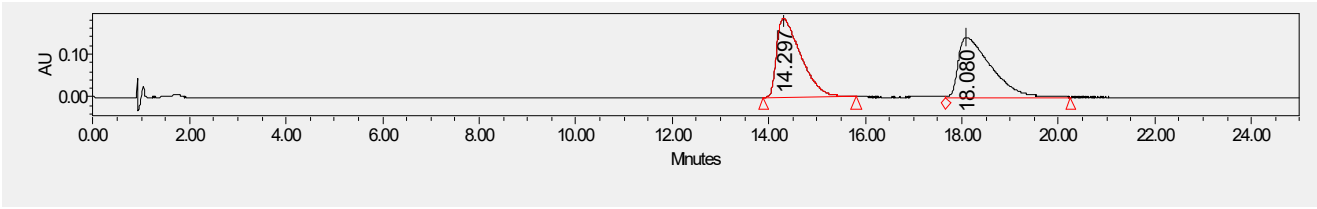
HPLC (Daicel chiralcel ID-3, CO_2/MeOH 95/5, 1.5 mL/min, λ = 254 nm), t_R(major) = 13.25 min, t_R(minor) = 17.95 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.42 – 7.36 (m, 1H), 7.26 – 7.20 (m, 2H), 7.20 – 7.13 (m,3H), 7.04 – 6.99 (m, 1H), 6.98 – 6.91 (m, 2H), 6.89 (d, *J* = 1.2 Hz, 1H), 4.77 (s, 1H), 4.36 (dt, *J* = 3.7, 1.7 Hz, 1H), 3.77 (s, 3H), 3.50 (s, 3H), 2.48 (dd, *J* = 9.4, 4.2 Hz, 1H), 2.10 (d, *J* = 9.4 Hz, 1H), 1.67 (s, 3H), 1.20 (d, *J* = 1.2 Hz, 3H) ppm.

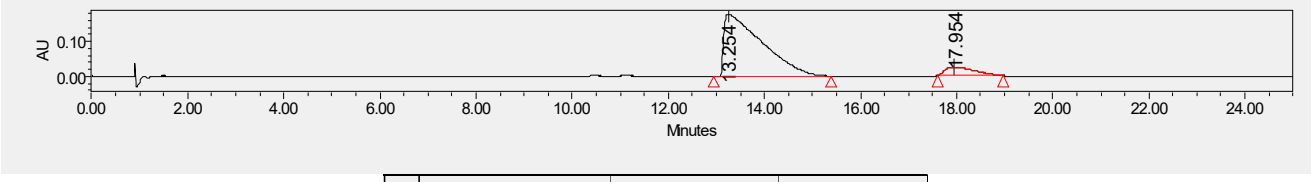
^{13}C NMR (101 MHz, $CDCl_3$) δ = 192. 1, 173.2 161.8, 157.1, 155.0, 143.3, 136.8, 134.2, 131.2, 131.0, 130.3, 129.1, 129.1, 127.9, 127.2, 126.0, 119.9, 111.5, 55.7, 52.6, 50.5, 46.3, 42.9, 42.6, 39.1, 22.2, 20.0 ppm.

ESI-HRMS calcd $[C_{27}H_{26}O_4^+Na^+]$ = 437.1723, found 437.1721.

IR $\tilde{\nu}$ (cm^{-1}) 2958, 2359, 1714, 1644, 1597, 1487, 1434, 1326, 1236, 1077, 1047, 1023, 755, 733.

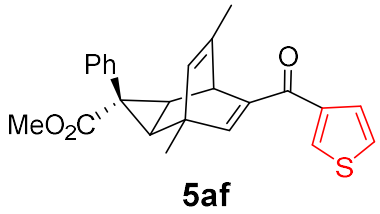


	Retention Time	Area	% Area
1	14.297	6436994	49.73
2	18.080	6507223	50.27



	Retention Time	Area	% Area
1	13.254	9937692	90.51
2	17.954	1041618	9.49

5af: methyl-1,6-dimethyl-3-phenyl-8-(thiophene-3-carbonyl)tricyclo[3.2.2.0^{2,4}]nona-6,8-diene-3-carboxylate



5af

24.6 mg, 63% yield, 19:1dr, 53% ee.; yellow solid, m. p. 169 – 171°C, $[\alpha]^{21}_{D}$ =6.3 (*c* = 0.52, in CH_2Cl_2).

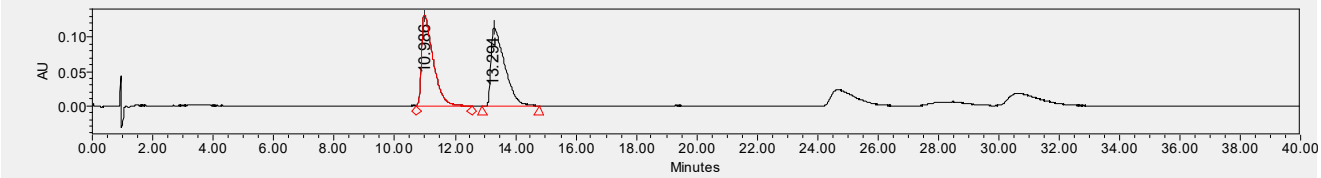
HPLC (Daicel chiralcel ID-3, CO_2/MeOH 95/5, 1.5 mL/min, λ = 254 nm), t_R(major) = 10.56 min, t_R(minor) = 13.22 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.61 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.58 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.30 (d, *J* = 1.2 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.19 – 7.12 (m, 2H), 7.09 (m, 1H), 7.06 – 7.01 (m, 1H), 4.84 (s, 1H), 4.28 (m, 1H), 3.50 (s, 3H), 2.51 (dd, *J* = 9.4, 4.2 Hz, 1H), 2.15 (d, *J* = 9.4 Hz, 1H), 1.78 (s, 3H), 1.19 (d, *J* = 1.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 183.8, 173.0, 159.1, 153.5, 143.3, 143.2, 136.7, 134.3, 133.0, 132.6, 131.0, 130.3, 127.9, 127.7, 127.2, 126.1, 52.6, 50.7, 46.4, 44.8, 42.7, 39.2, 22.4, 20.0 ppm.

ESI-HRMS calcd $[C_{24}H_{22}O_3S^+Na^+]$ = 413.1182, found 413.1183.

IR $\tilde{\nu}$ (cm^{-1}) 2959, 2358, 1713, 1614, 1582, 1513, 1414, 1368, 1234, 1050, 961, 861, 798, 758, 701.



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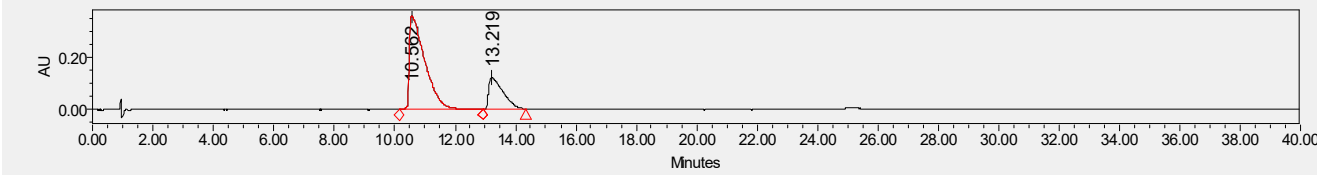
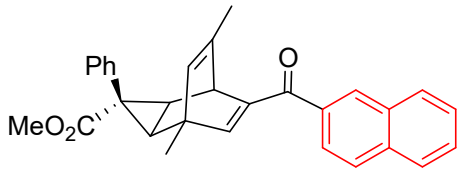
2	13.294	3627138	50.24



	Retention Time	Area	% Area
1	10.562	12805918	76.26
2	13.219	3987432	23.74

5ag: methyl--8-(2-naphthoyl)-1,6-dimethyl-3-phenyltricyclo[3.2.2.0^{2,4}]nona-6,8-diene-3-carboxylate



5ag

34.3mg, 63% yield, 19:1dr, 63% ee.; yellow solid, m. p. 182 – 183°C, $[\alpha]^{21}_{D}$ =2.1 (*c* = 0.76, in CH_2Cl_2).

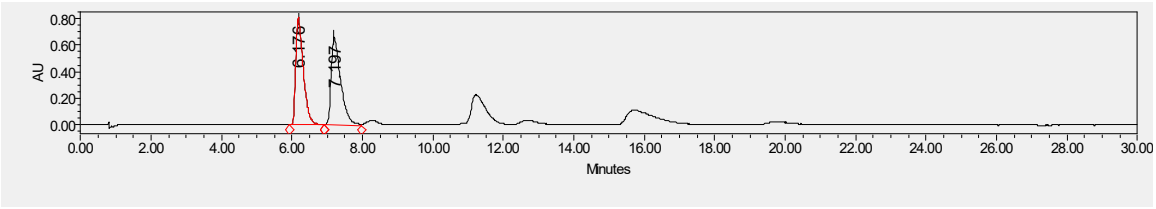
HPLC (Daicel chiralcel IA-3, CO_2/MeOH 90/10, 1.5 mL/min, λ = 254 nm), t_R(major) = 5.92 min, t_R(minor) = 7.09 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (s, 1H), 7.97 – 7.85 (m, 3H), 7.77 (m, 1H), 7.62 – 7.51 (m, 2H), 7.30 – 7.26 (m, 1H), 7.26 – 7.23 (m, 1H), 7.22 – 7.16 (m, 2H), 7.12 (s, 1H), 7.06 (m, 1H), 4.89 (s, 1H), 4.53 – 4.32 (m, 1H), 3.52 (s, 3H), 2.57 (dd, *J* = 9.4, 4.2 Hz, 1H), 2.19 (d, *J* = 9.4 Hz, 1H), 1.75 (s, 3H), 1.25 (d, *J* = 1.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.5, 173.1, 161.6, 153.7, 143.4, 136.8, 135.4, 135.0, 134.3, 132.3, 131.1, 130.4, 130.0, 129.2, 128.2, 128.0, 127.9, 127.8, 127.2, 126.7, 126.1, 125.4, 52.7, 50.6, 46.5, 44.3, 42.8, 39.3, 22.3, 20.2 ppm.

ESI-HRMS calcd $[C_{30}H_{26}O_3Na^+]$ = 457.1774, found 457.1775.

IR $\tilde{\nu}$ (cm^{-1}) 2959, 2328, 1714, 1624, 1581, 1434, 1364, 1321, 1233, 1128, 961, 824, 798, 760, 731, 480.



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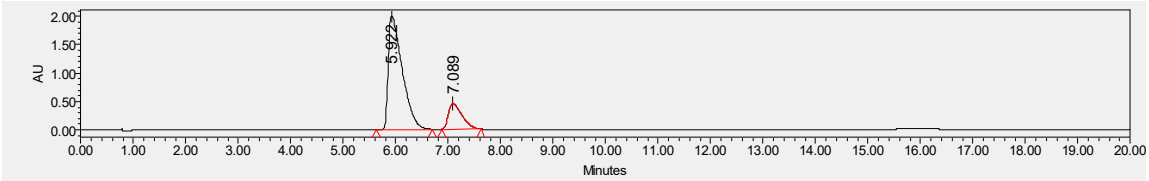
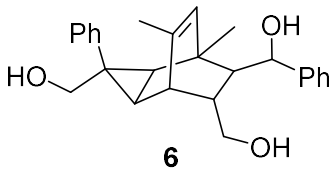


	Retention Time	Area	% Area
1	5.922	37051687	81.95
2	7.089	8160612	18.05

6：(-7-(hydroxy(phenyl)methyl)-1,9-dimethyl-3-phenyltricyclo[3.2.2.0^{2,4}]non-8-ene- 3,6-diyl)di -methanol



6

27.7 mg, 71% yield, 19:1dr, 90% ee.; white solid, m. p. 186 – 187 °C, $[\alpha]^{21}_{D}$ = -25.5 (*c* = 0.42, in CH_2Cl_2).

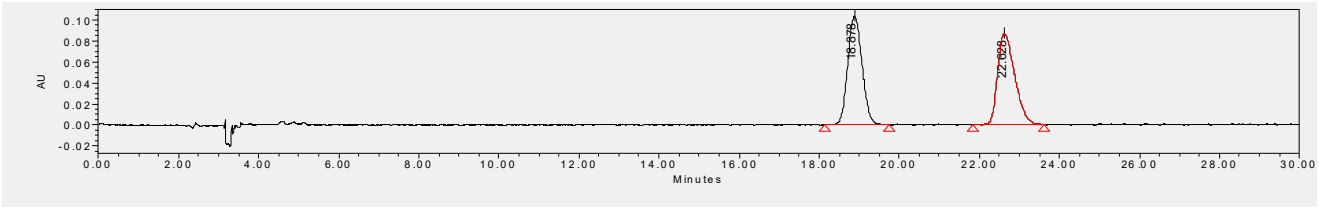
HPLC (Daicel chiralcel ODH, CO_2/MeOH 80/20, 1.0 mL/min, λ = 254 nm), t_R(major) = 18.50 min, t_R(minor) = 22.50 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 – 7.11 (m, 6H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 4.74 (d, *J* = 4.8 Hz, 1H), 4.20 (s, 1H), 3.64 (m, 1H), 3.57 – 3.37 (m, 3H), 3.28 (dd, *J* = 10.8, 6.0 Hz, 1H), 3.16 (dd, *J* = 10.8, 6.0 Hz, 1H), 2.61 – 2.43 (m, 1H), 1.80 – 1.75 (m, 1H), 1.70 – 1.48 (m, 5H), 1.32 (dd, *J* = 8.8, 4.0 Hz, 1H), 1.14 (d, *J* = 8.8 Hz, 1H), 0.78 (d, *J* = 1.6 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 140.1, 136.5, 129.9, 128.9, 128.4, 127.1, 126.8, 126.6, 126.5, 126.1, 124.3, 73.4, 72.1, 65.1, 56.8, 42.9, 38.1, 37.0, 34.4, 33.0, 23.6, 21.2, 18.8.

ESI-HRMS calcd [$C_{26}H_{30}O_3^+Na^+$] = 413.2087, found 413.2086.

IR $\tilde{\nu}$ (cm^{-1}) 3293, 2927, 2868, 1600, 1493, 1446, 1374, 1264, 1088, 1027, 915, 816, 762, 734, 701, 558, 531 ppm.



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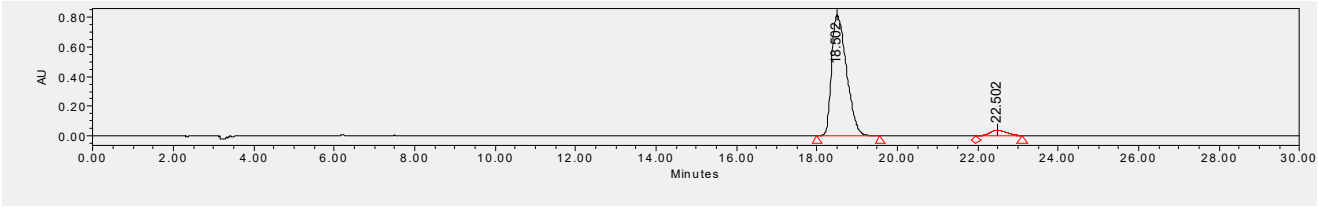
2	22.628	2564536	50.16



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2	22.502	1055334	4.77

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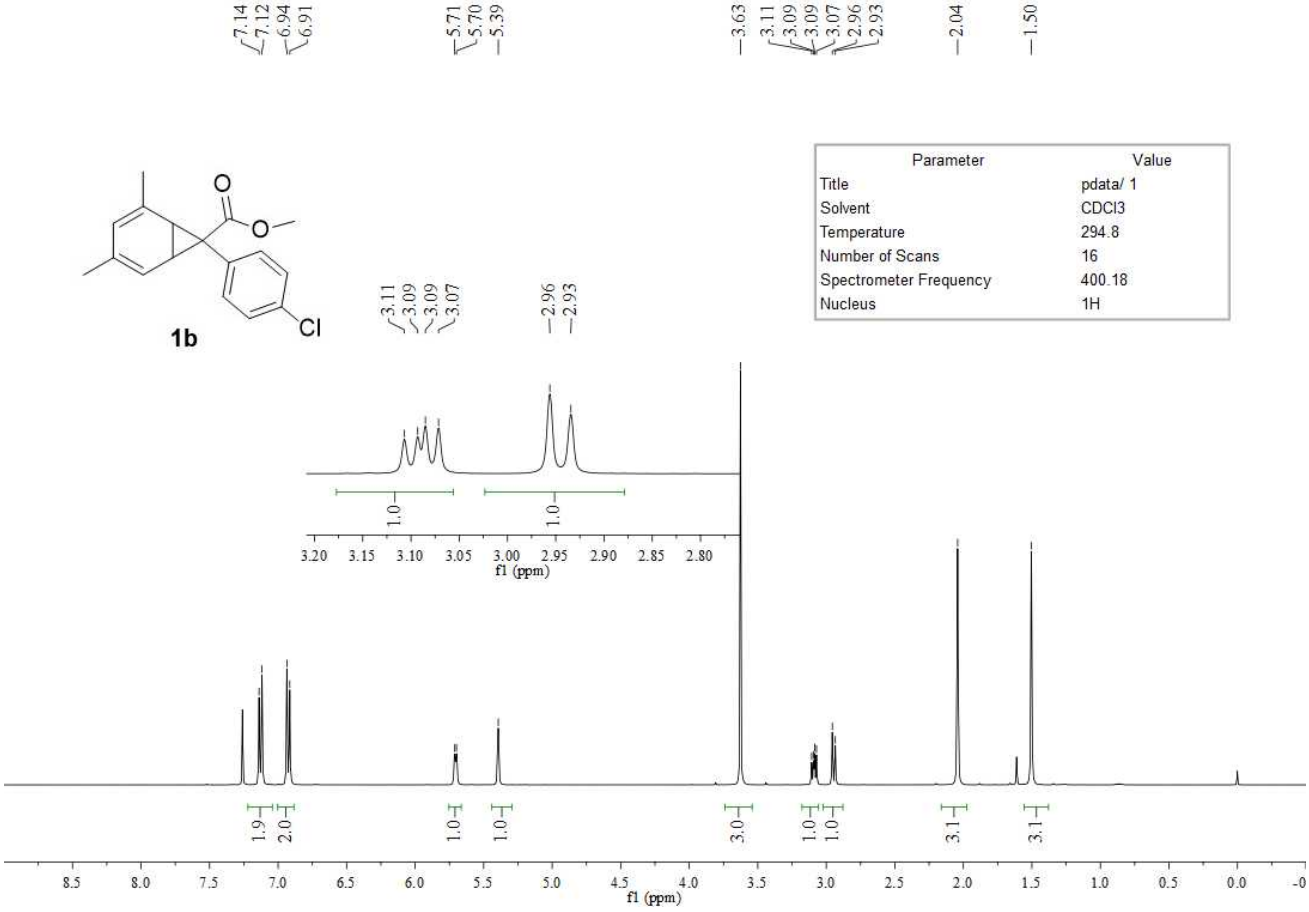
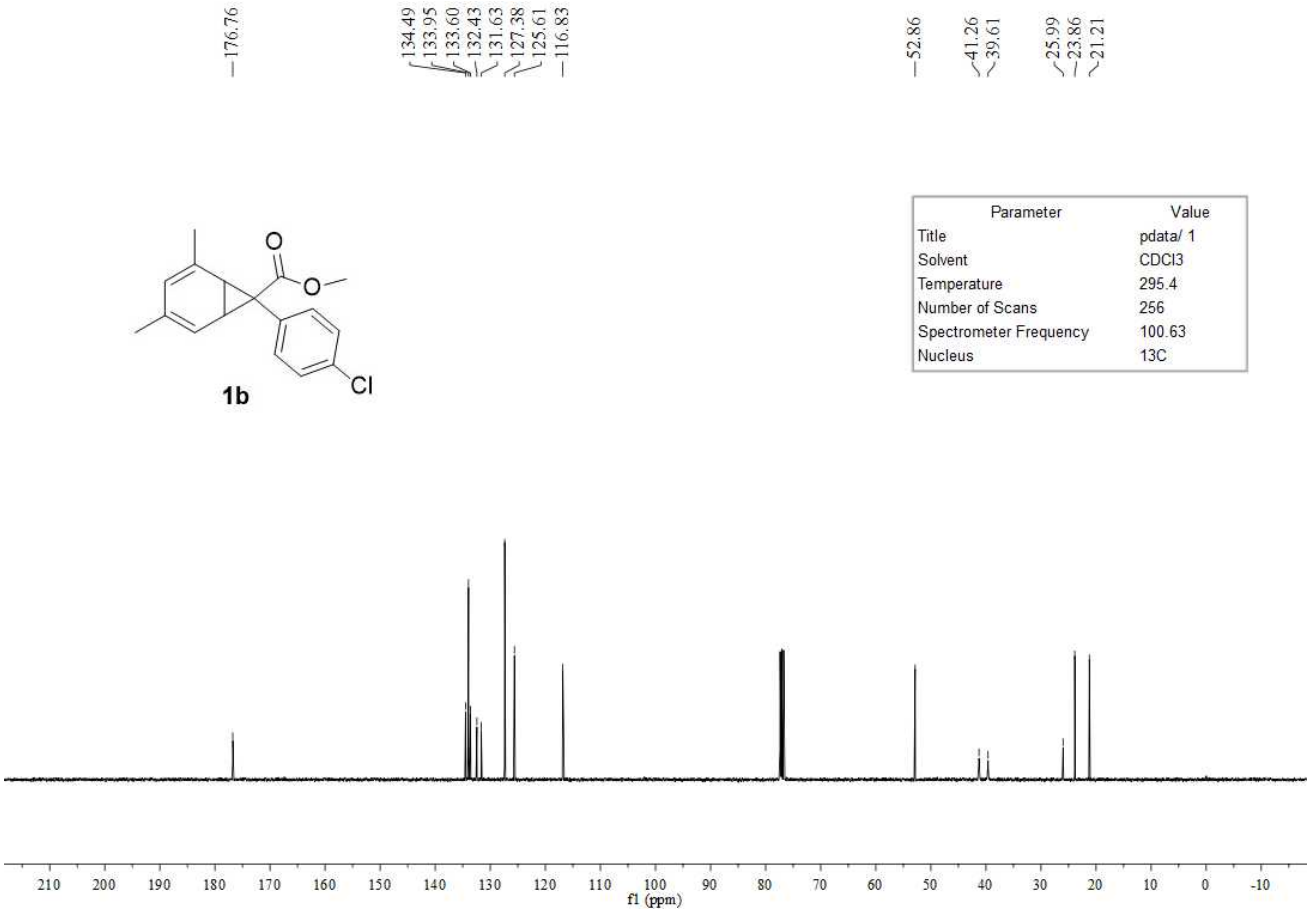
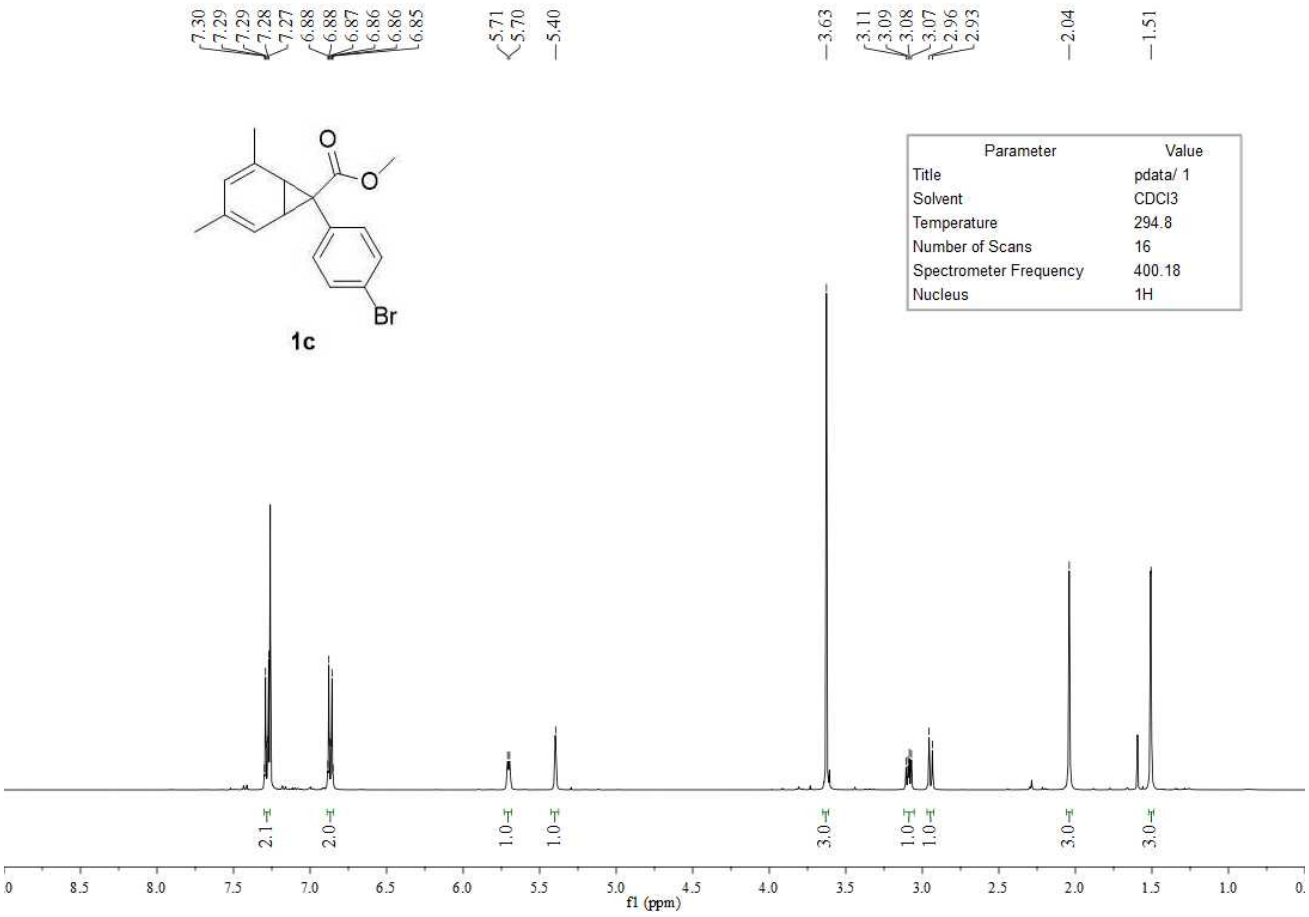
13. Copies of NMR spectra



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3.08
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2.04
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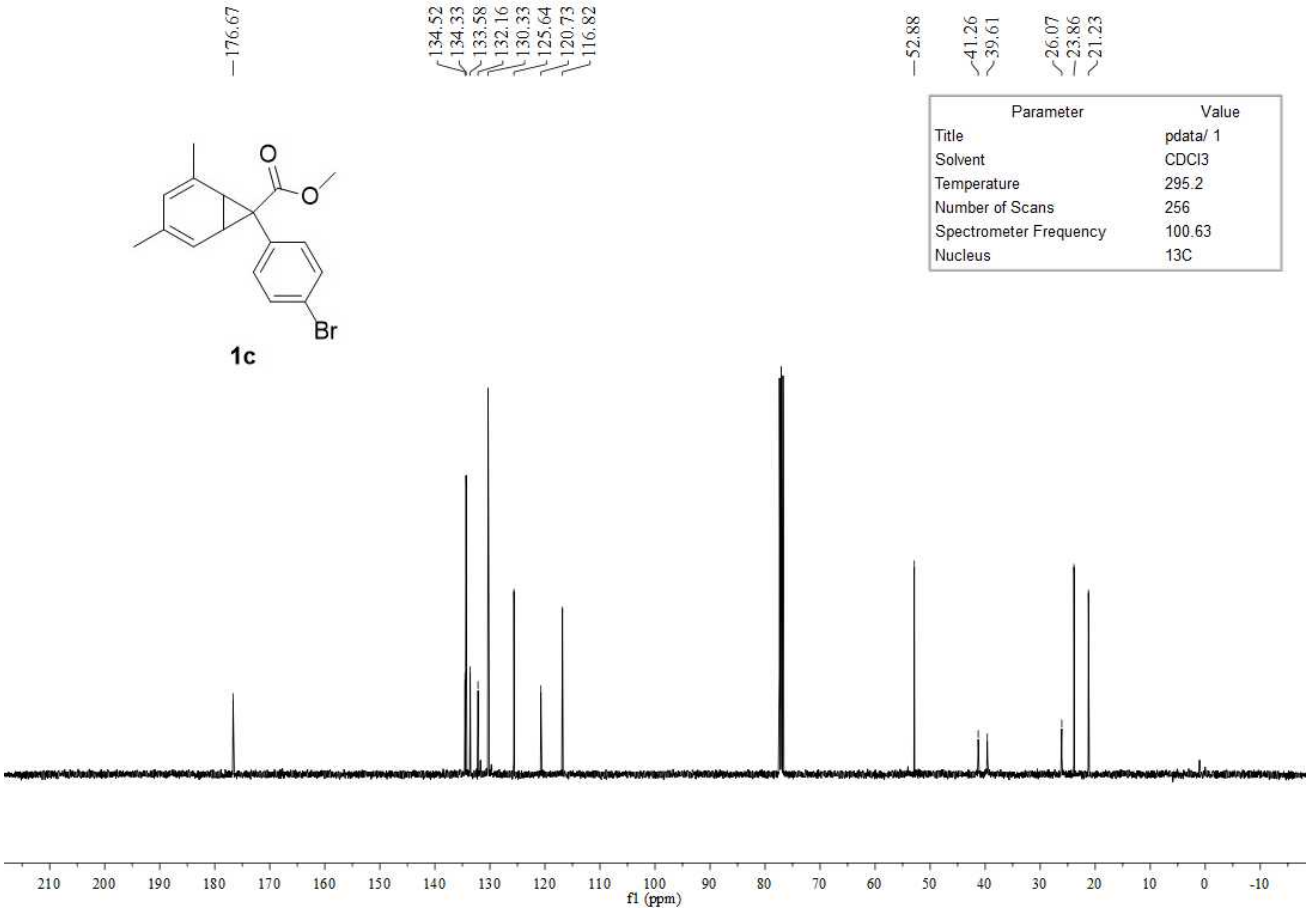
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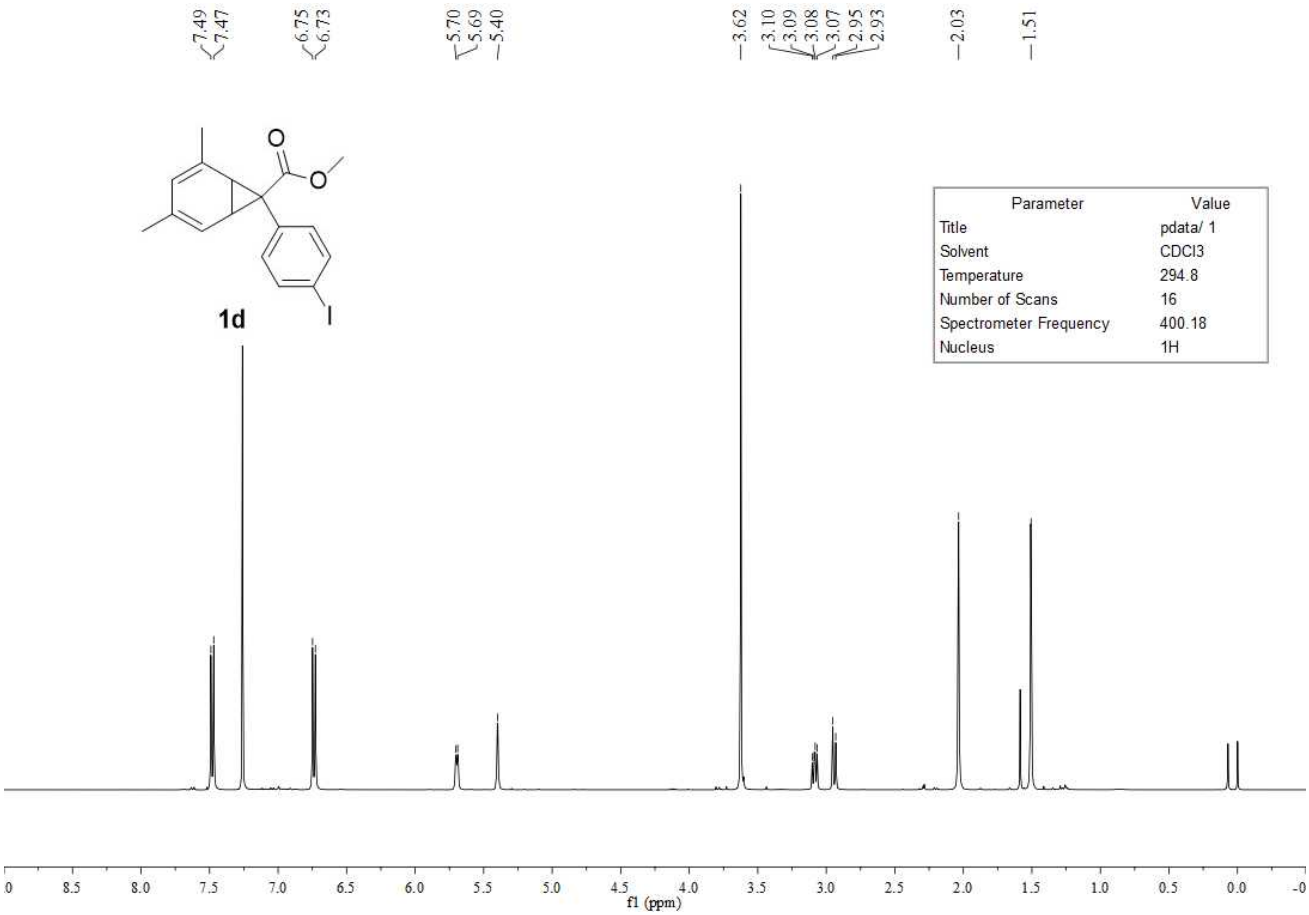
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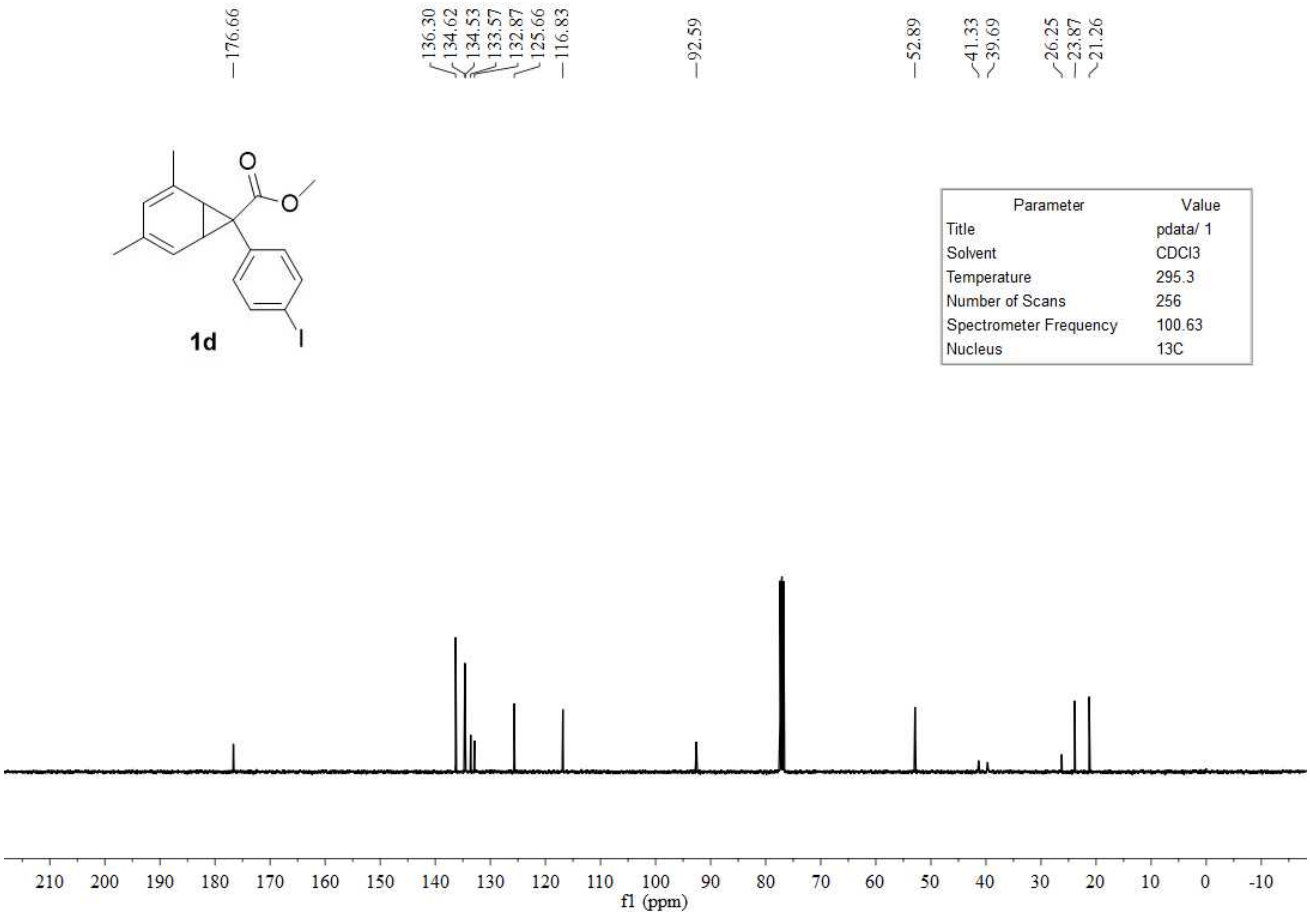
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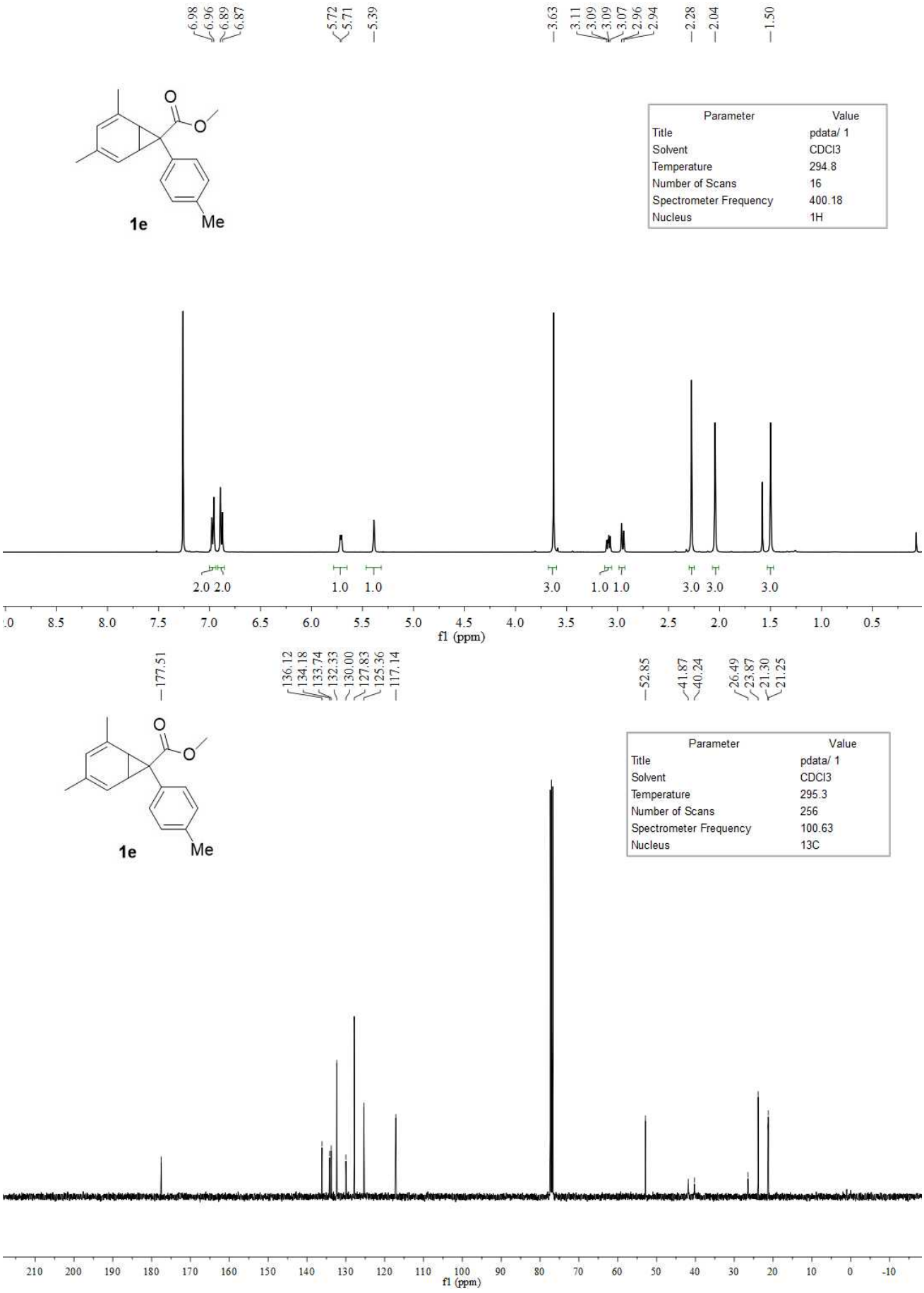
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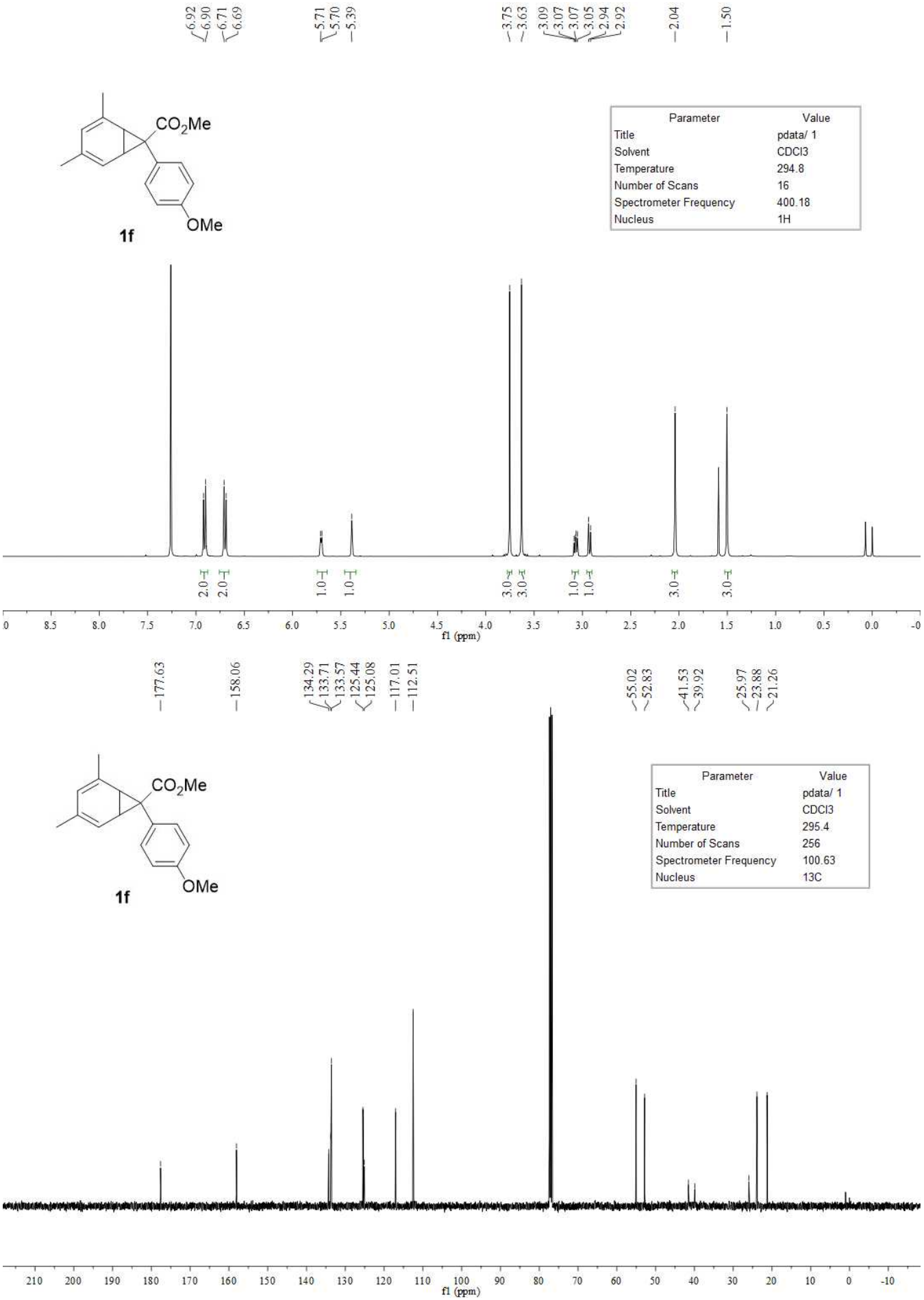
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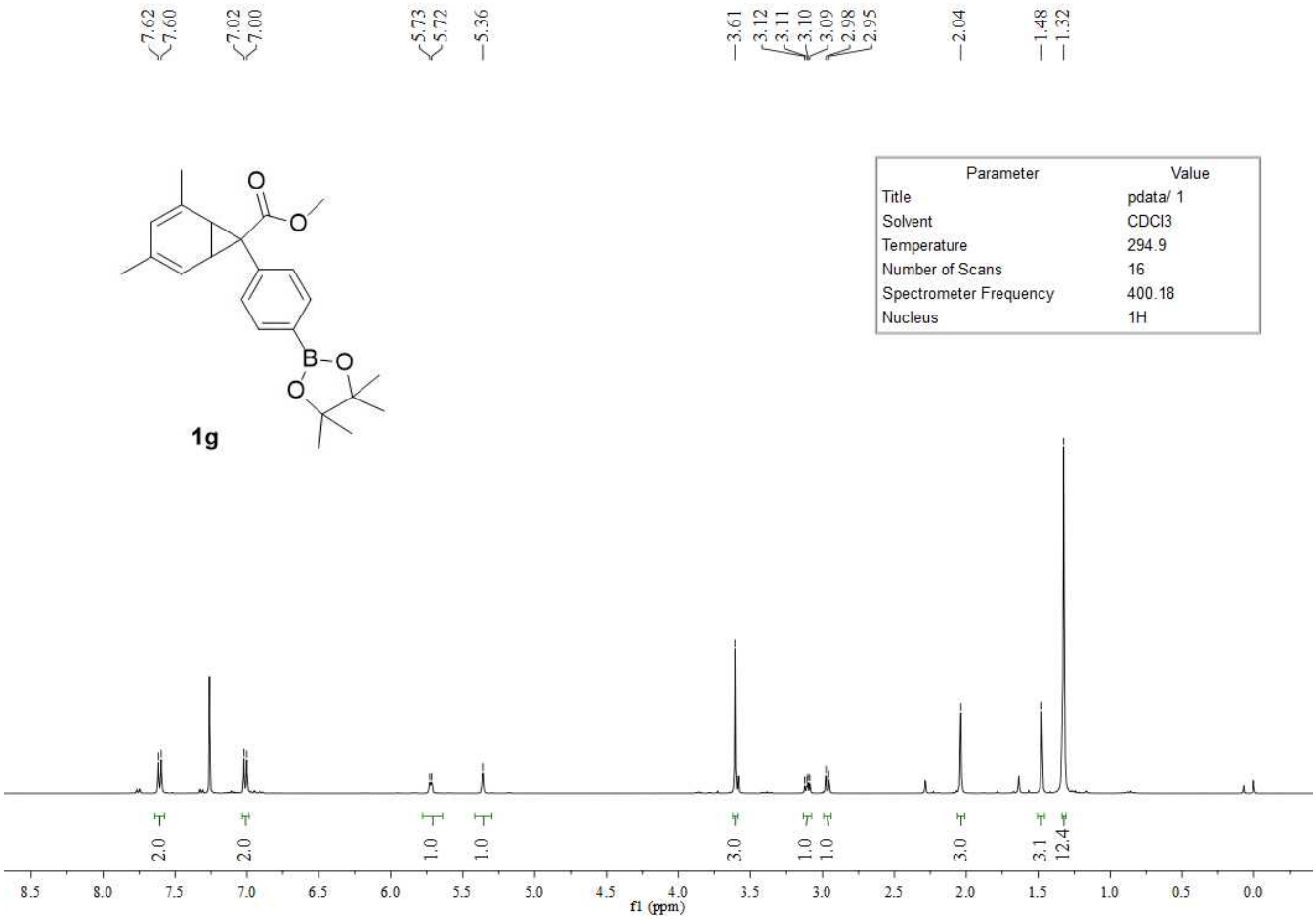
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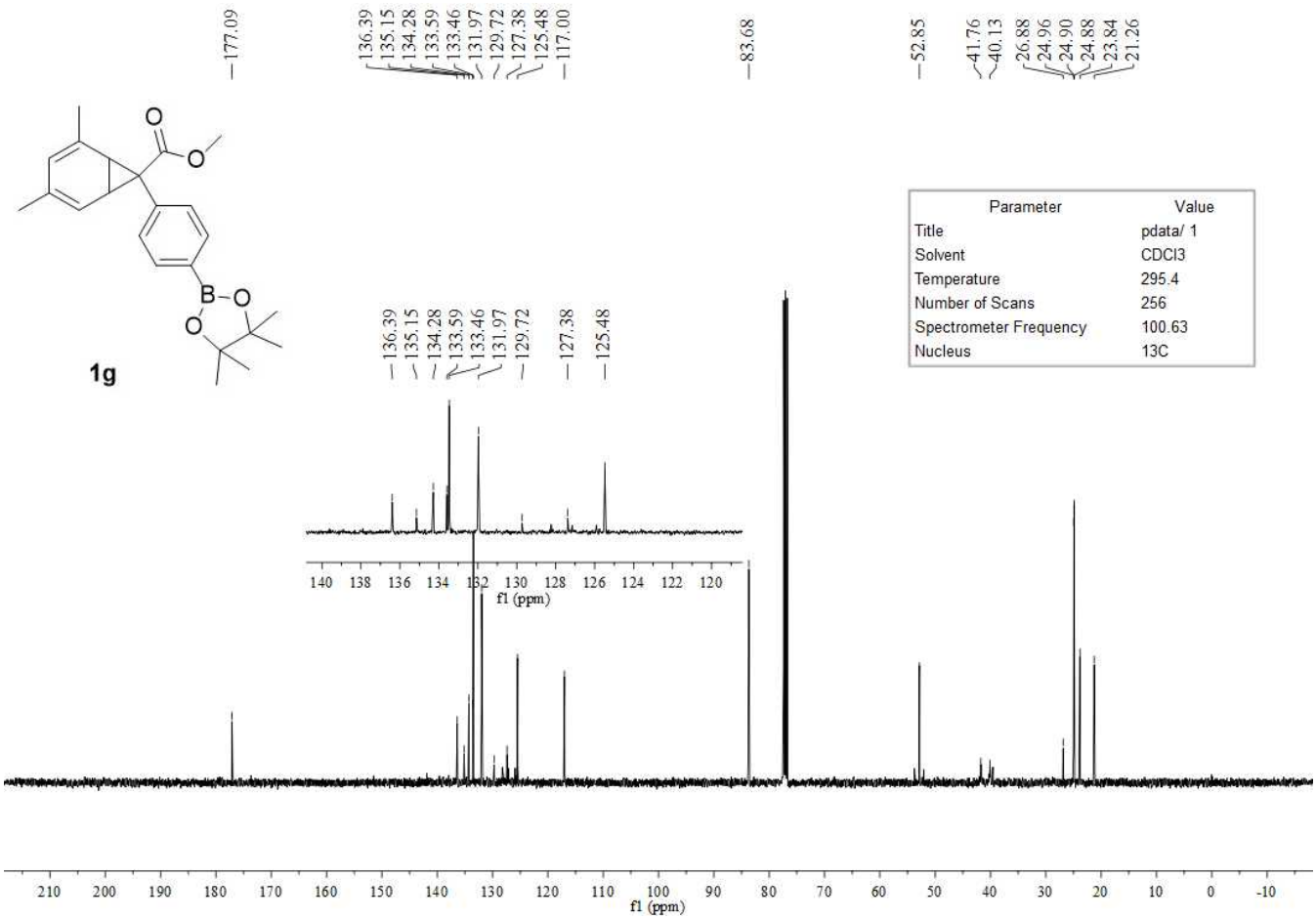
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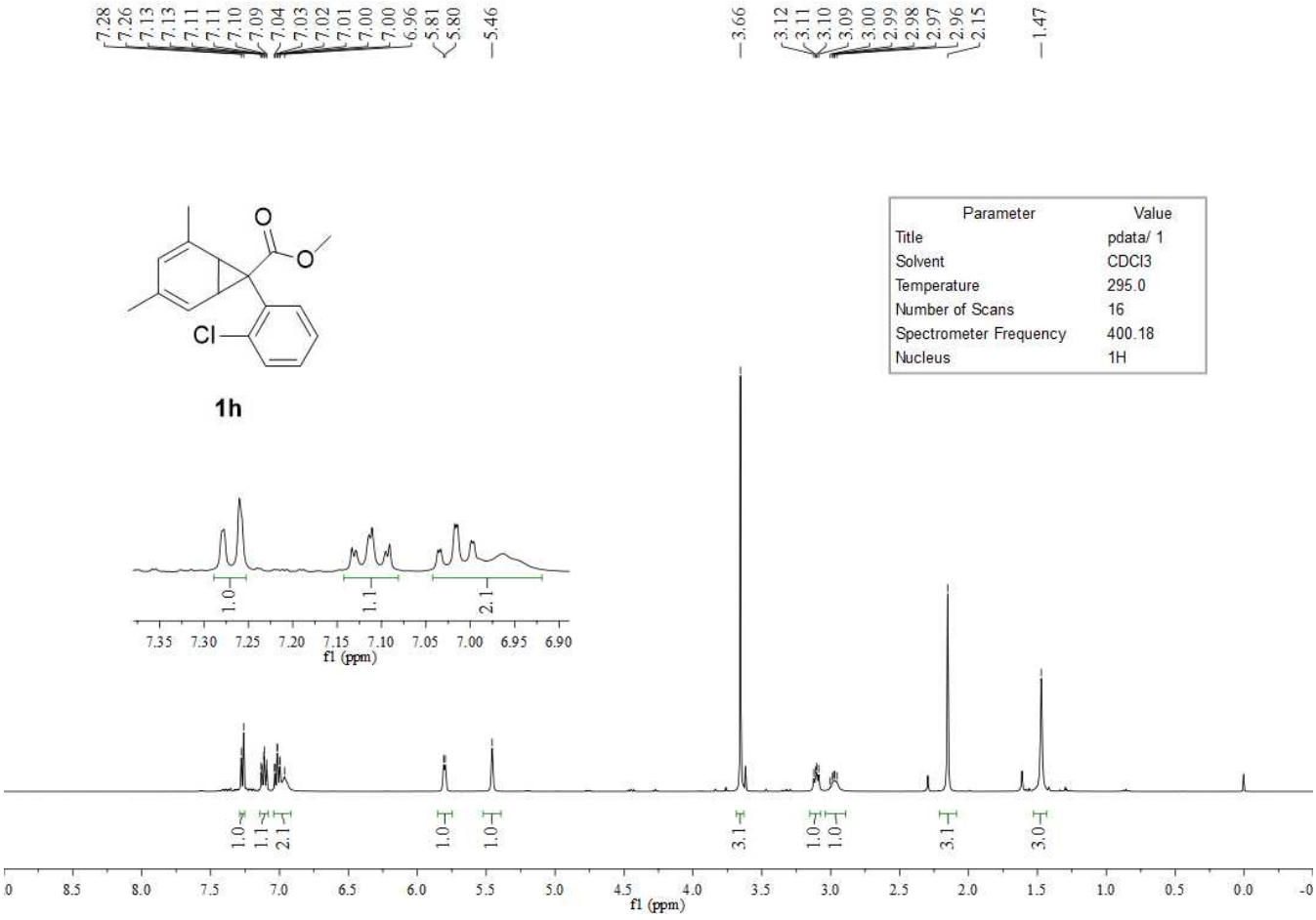
f1 (ppm)
f1 (ppm)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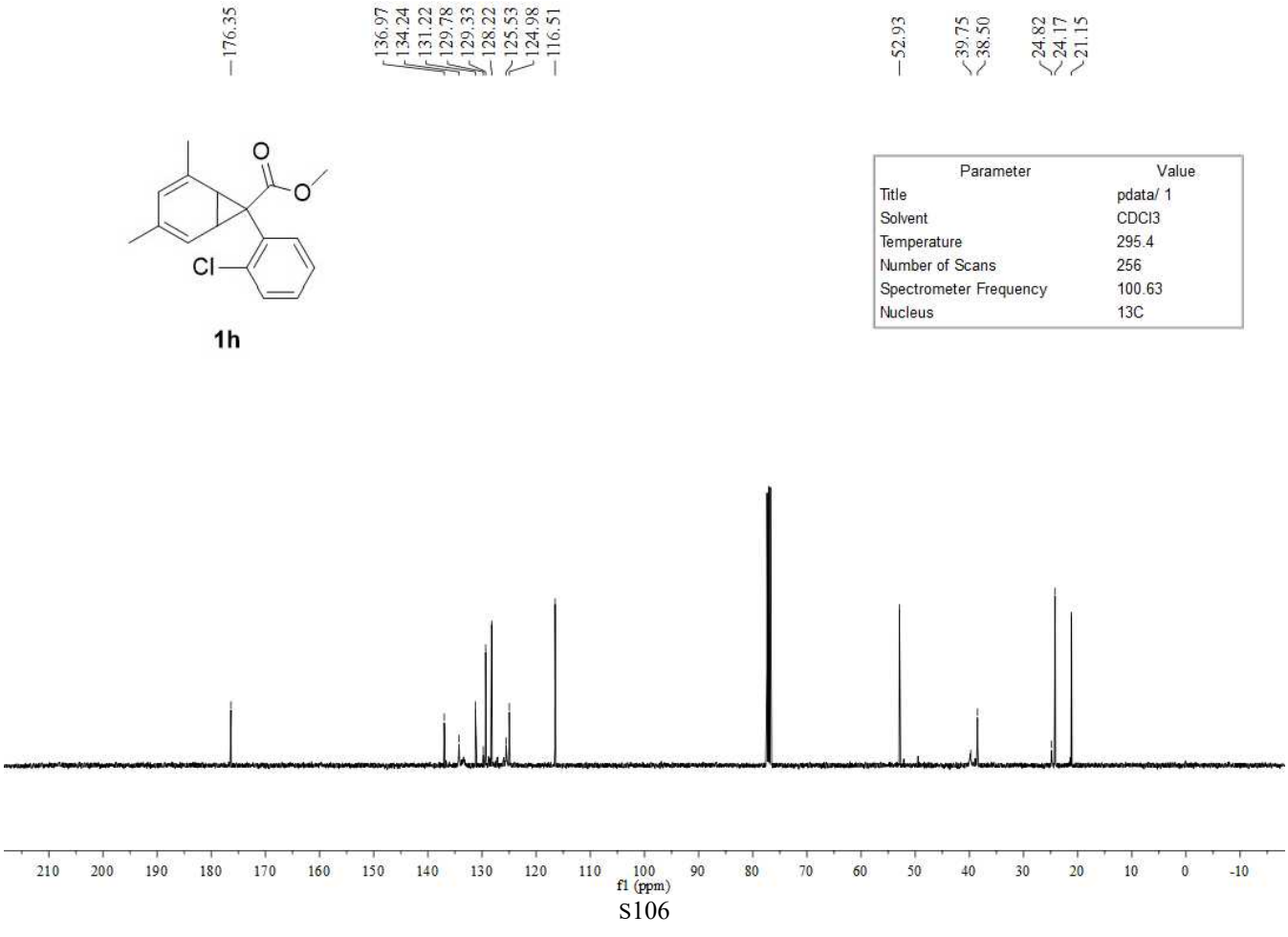
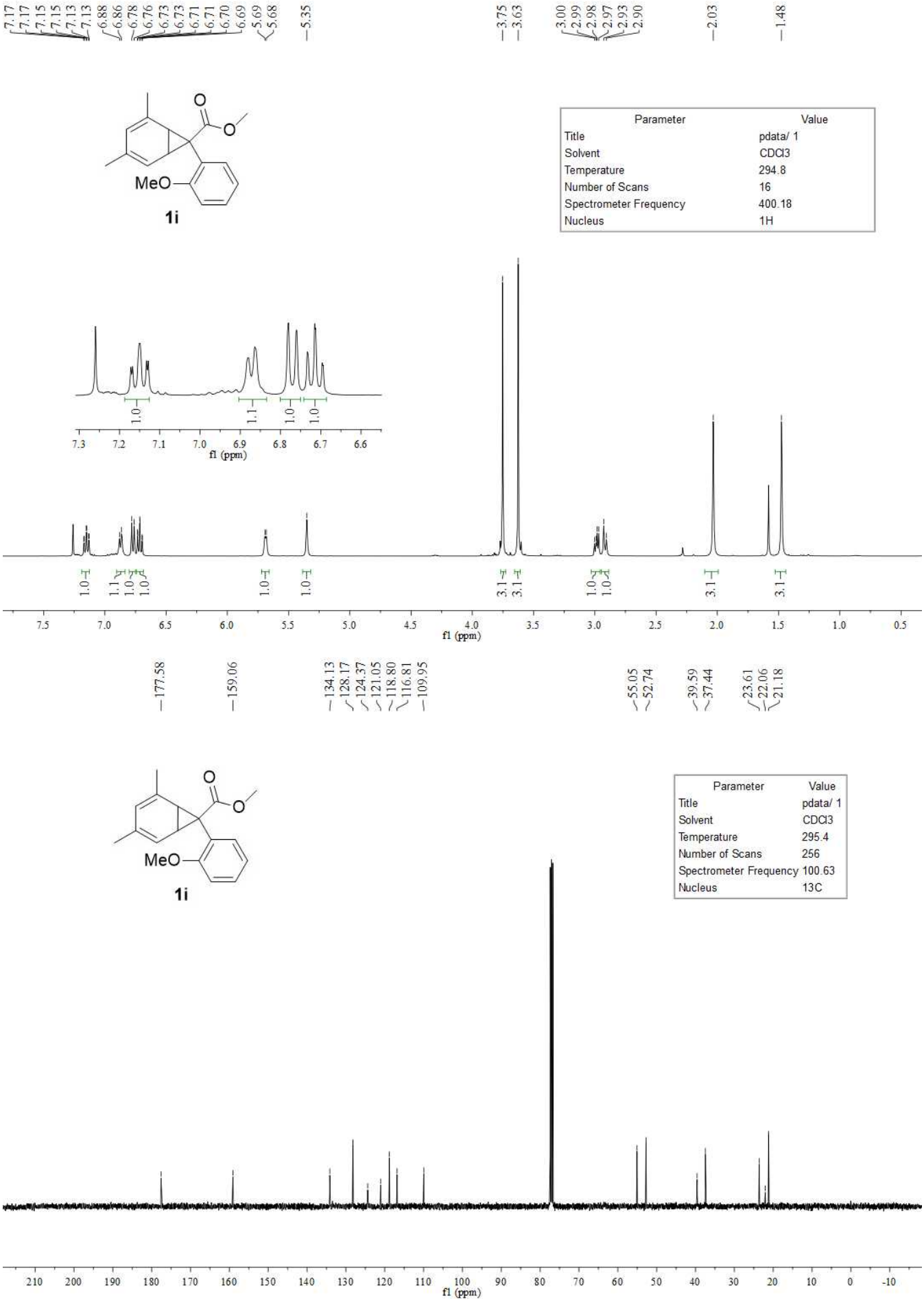
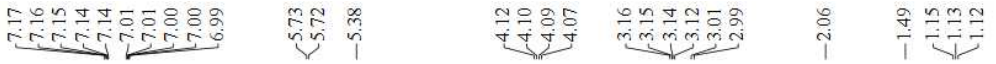
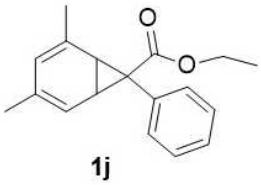
1.0
3.1
3.0
f1 (ppm)


176.35
136.97
134.24
131.22
129.78
129.33
128.22
125.53
124.98
116.51
52.93
39.75
38.50
24.82
24.17
21.15
O
O
Cl
1h
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 295.4
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
f1 (ppm)

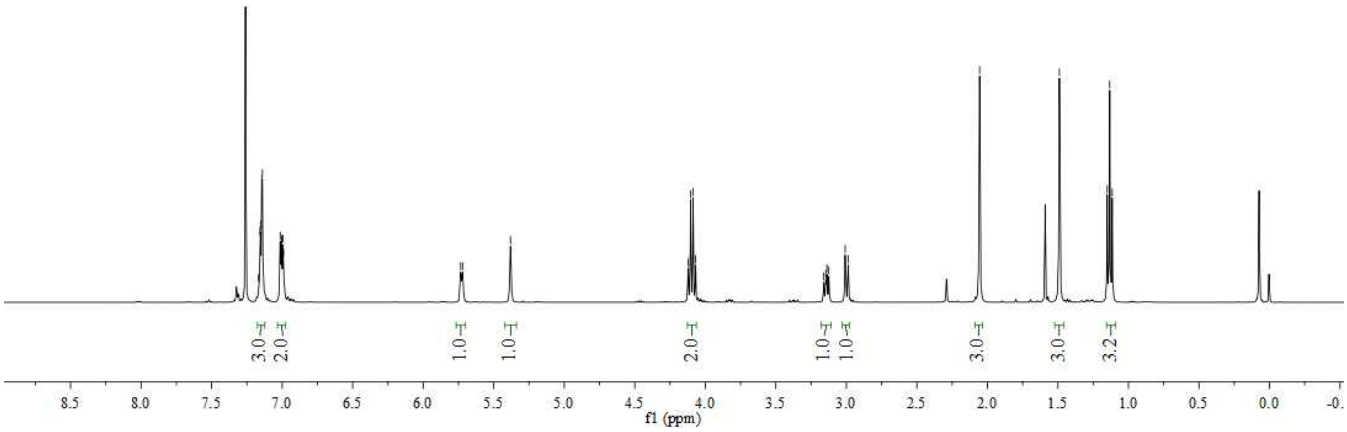

7.17
7.17
7.15
7.15
7.13
7.13
6.88
6.86
6.78
6.76
6.73
6.73
6.71
6.70
6.69
5.69
5.68
5.35
3.75
3.63
3.00
2.99
2.98
2.97
2.93
2.90
2.03
1.48
O
O
MeO
1i
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.8
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
1.0
1.1
1.0
1.0
7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
f1 (ppm)
1.0
1.1
1.0
1.0
1.0
1.0
3.1
3.1
1.0
1.0
3.1
3.1
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
177.58
159.06
134.13
128.17
124.37
121.05
118.80
116.81
109.95
55.05
52.74
39.59
37.44
23.61
22.06
21.18
O
O
MeO
1i
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 295.4
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

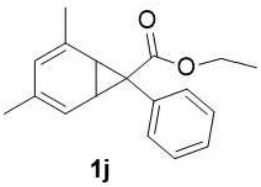




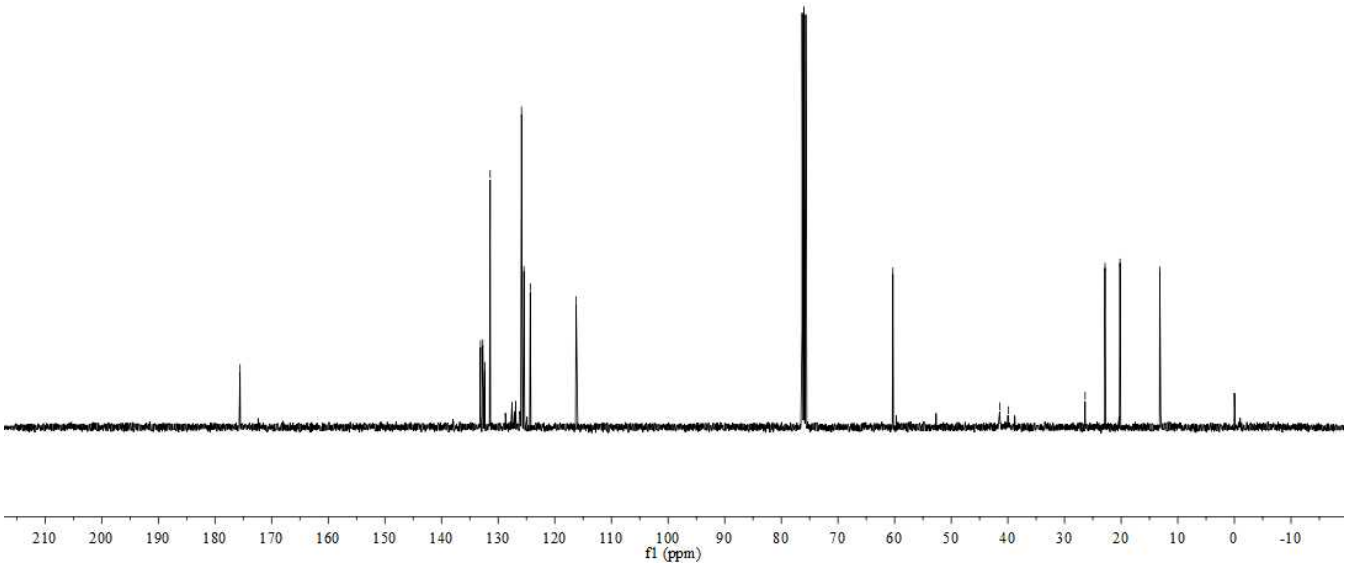
1j

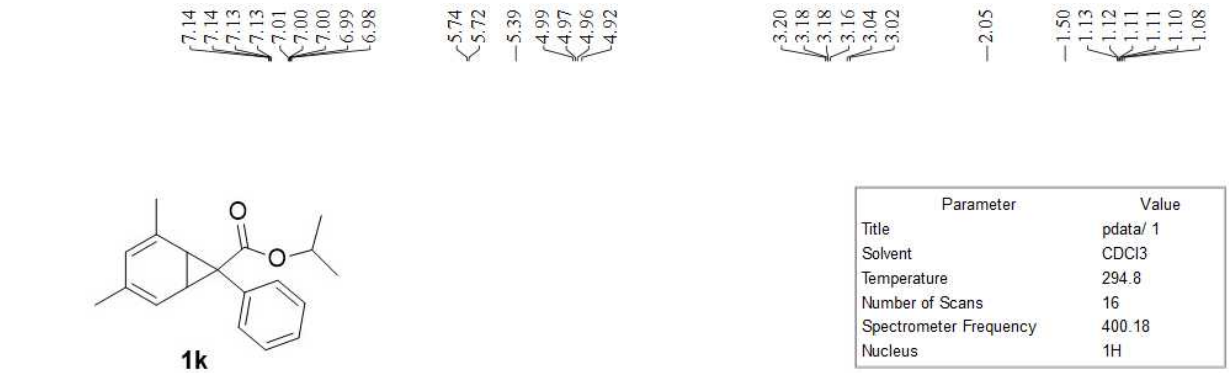
Parameter	Value
Title	pdata/ 1
Solvent	CDCl3
Temperature	294.9
Number of Scans	16
Spectrometer Frequency	400.18
Nucleus	1H





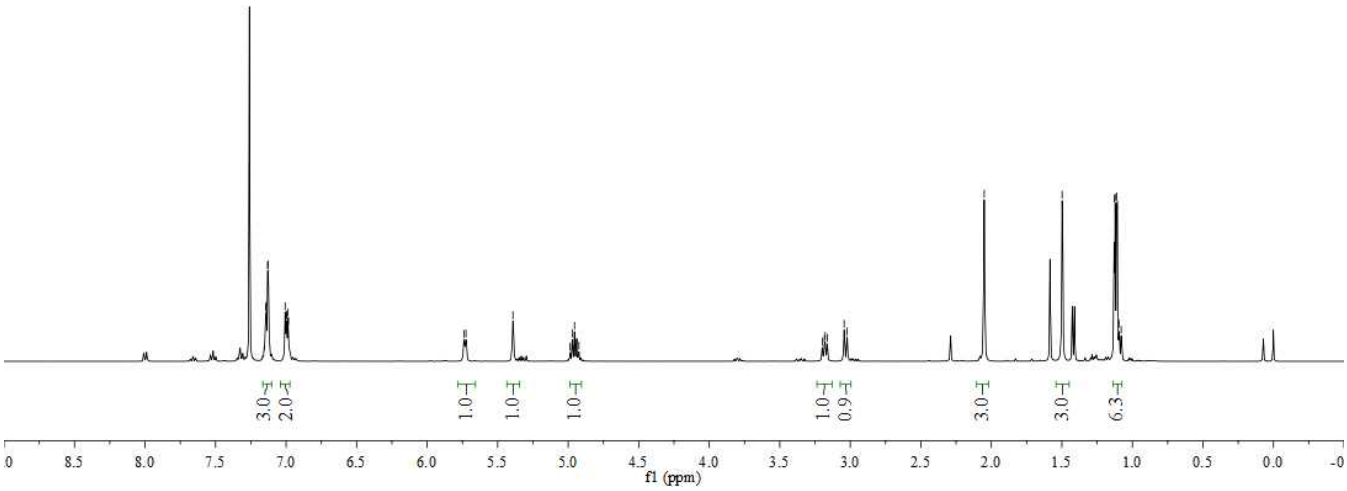
1j

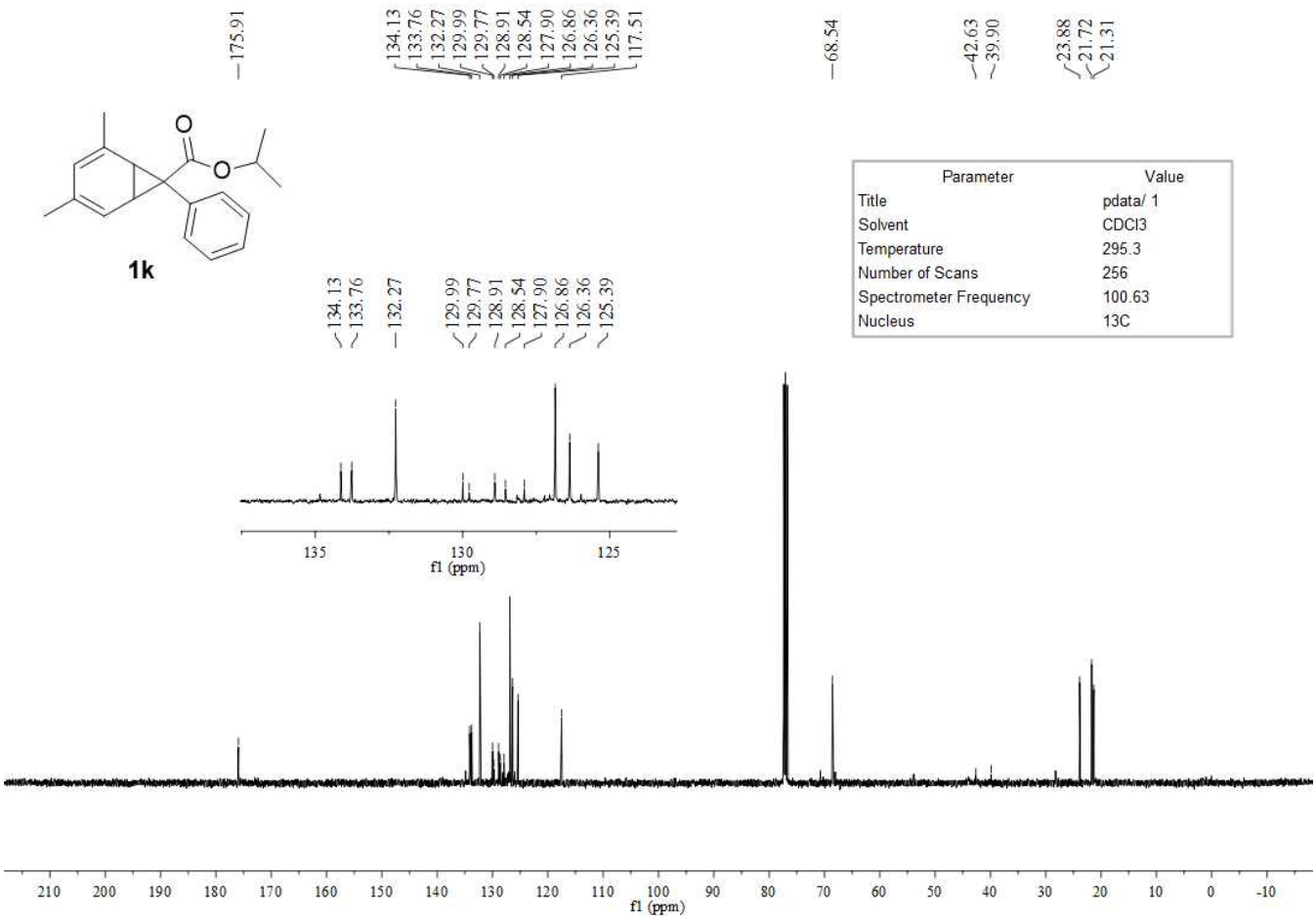




1k

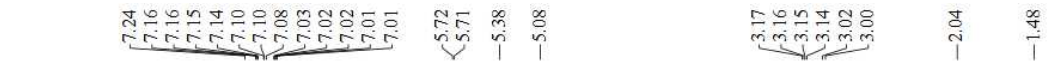
Parameter	Value
Title	pdata/ 1
Solvent	CDCl3
Temperature	294.8
Number of Scans	16
Spectrometer Frequency	400.18
Nucleus	1H

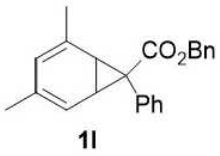




1k

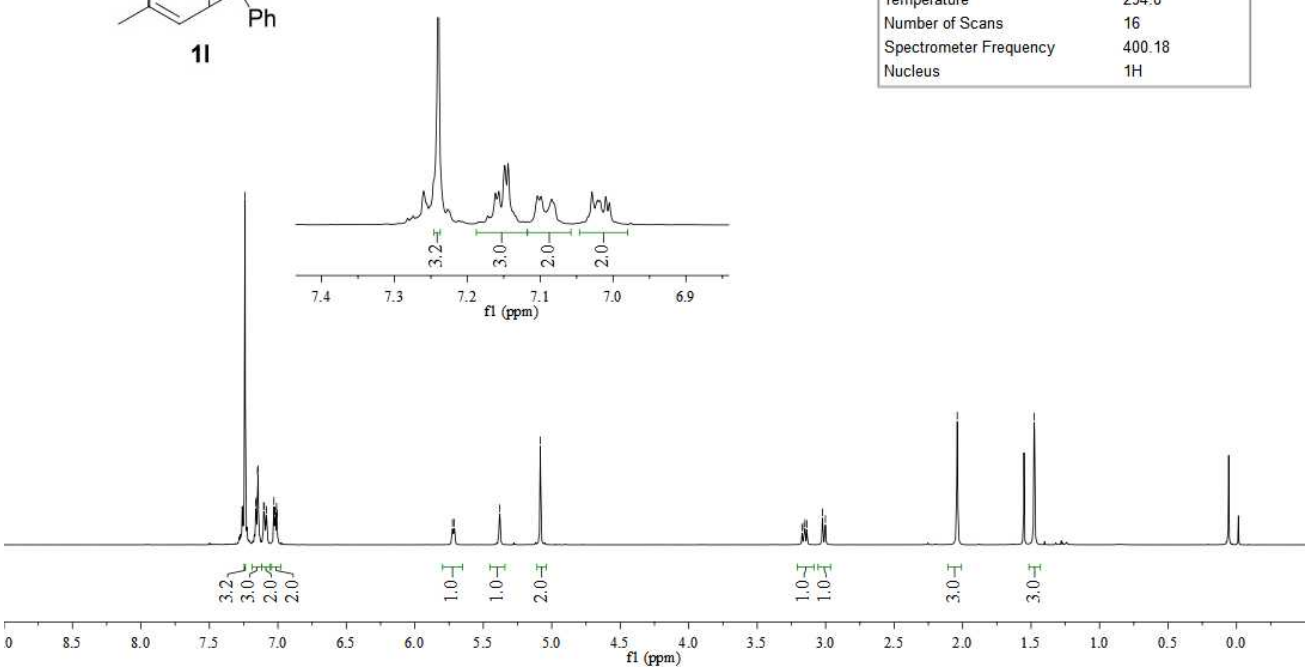
Parameter	Value
Title	pdata/ 1
Solvent	CDCl3
Temperature	295.3
Number of Scans	256
Spectrometer Frequency	100.63
Nucleus	13C

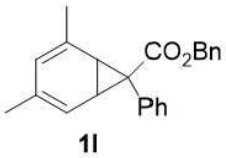




1l

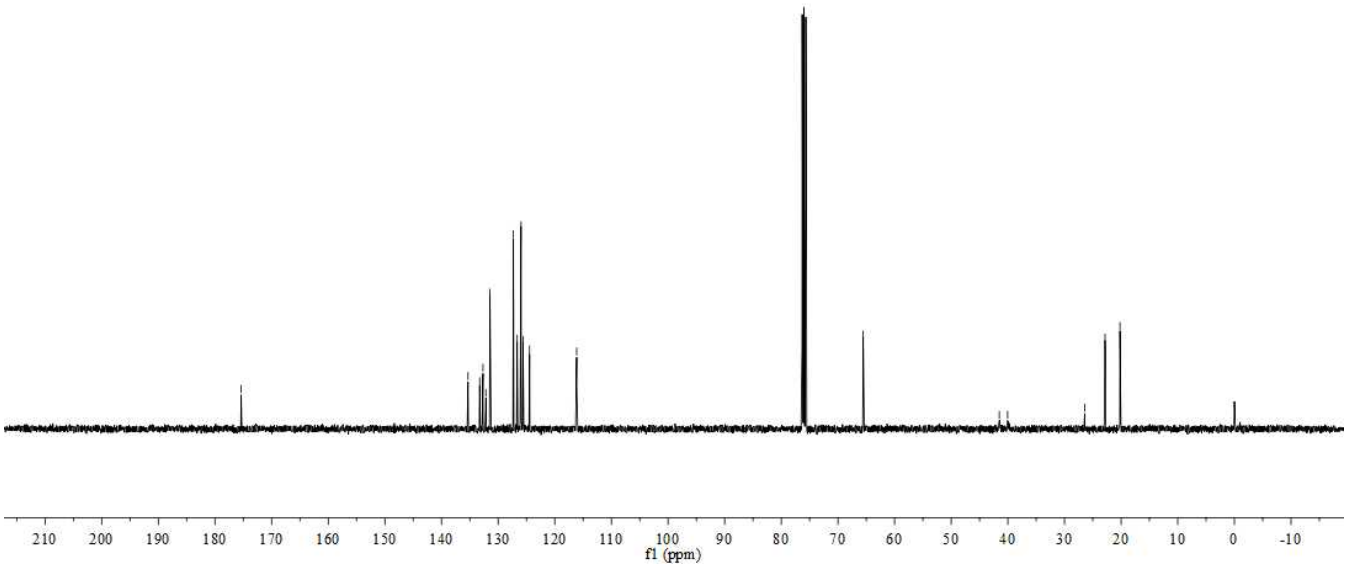
Parameter	Value
Title	pdata/ 1
Solvent	CDCl3
Temperature	294.8
Number of Scans	16
Spectrometer Frequency	400.18
Nucleus	1H

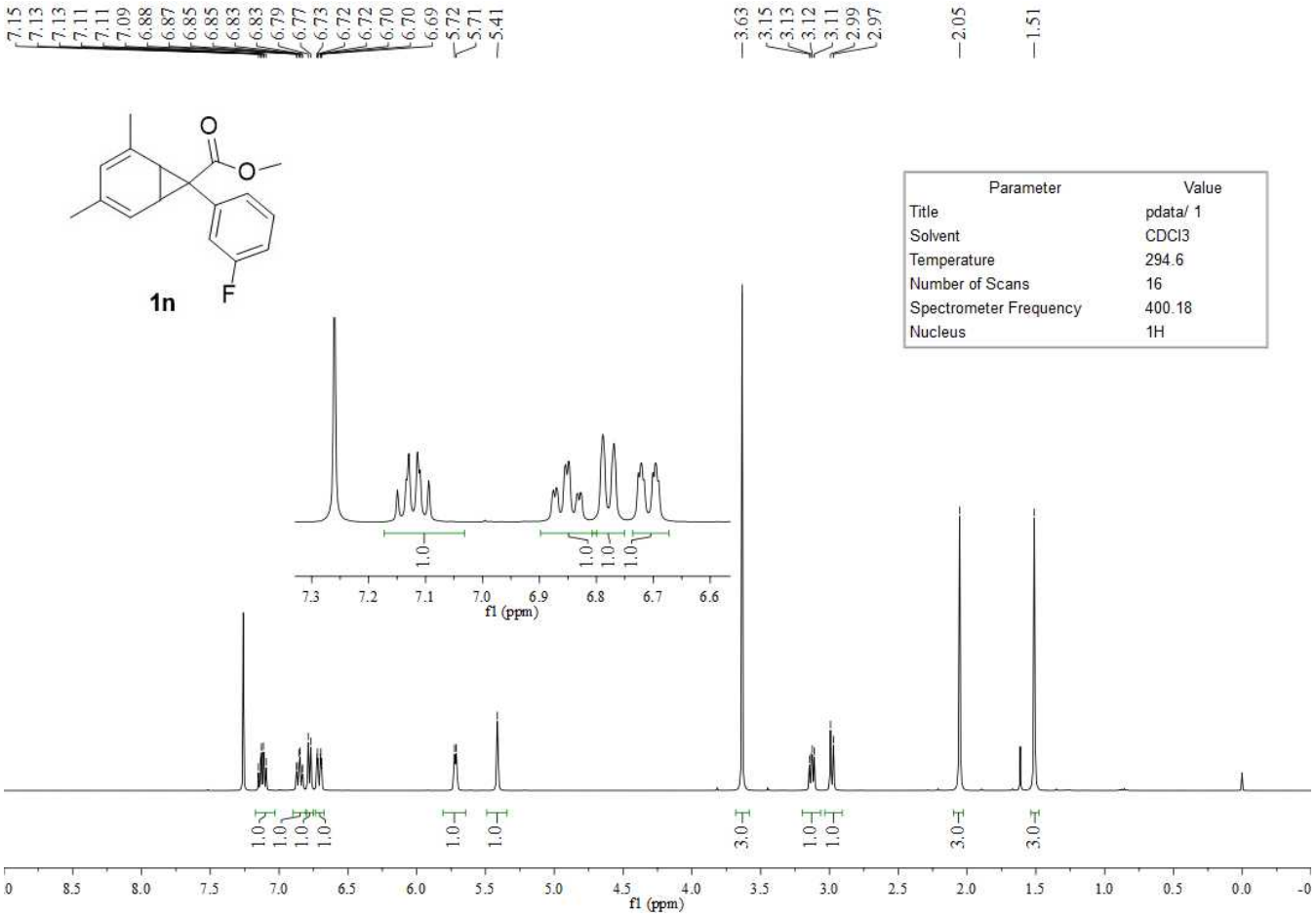


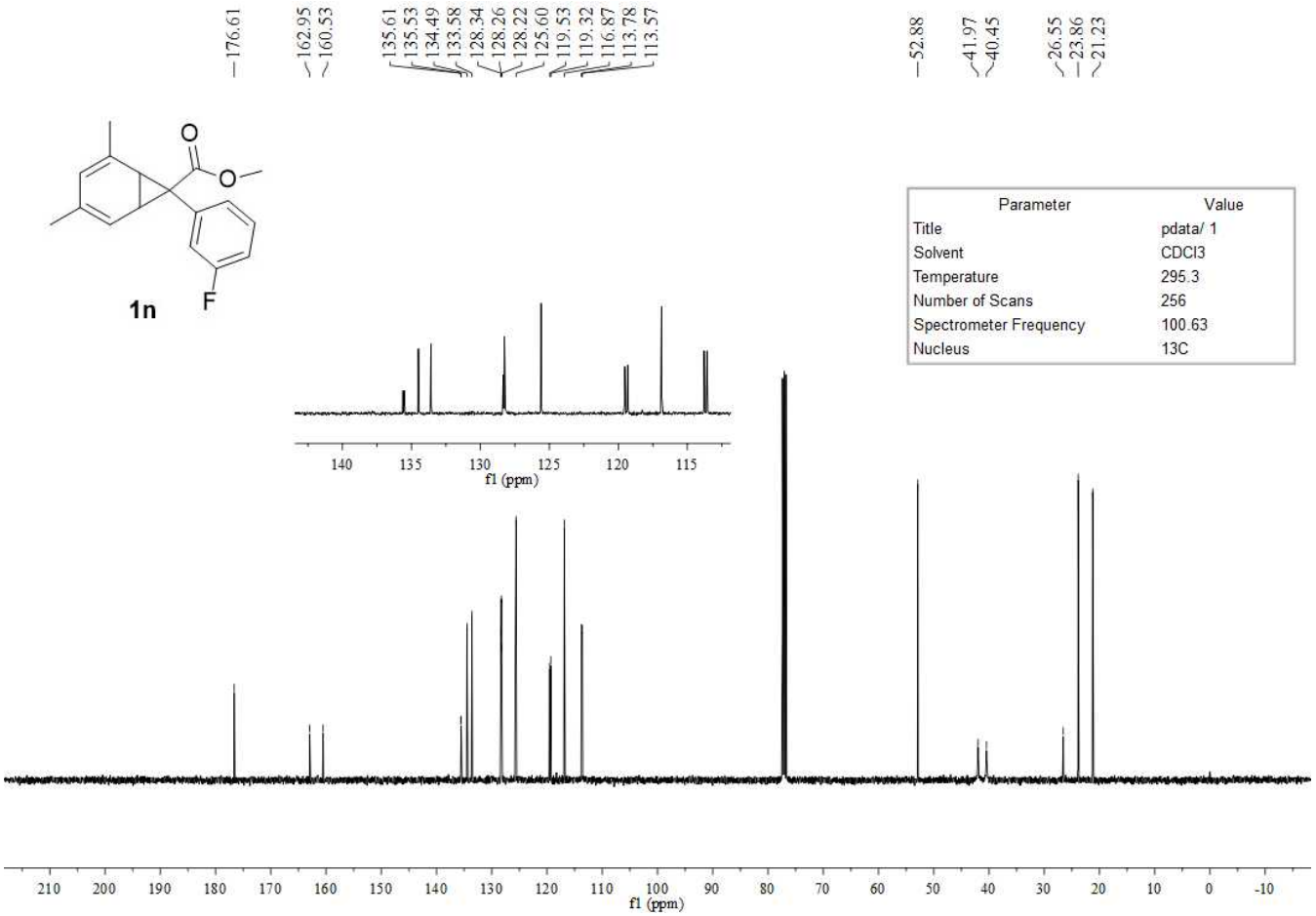


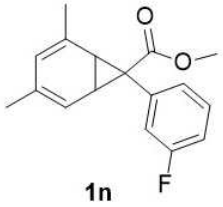
1l

Parameter	Value
Title	pdata/ 1
Solvent	CDCl3
Temperature	295.4
Number of Scans	256
Spectrometer Frequency	100.63
Nucleus	13C




7.15
7.13
7.13
7.11
7.11
7.09
6.88
6.87
6.85
6.85
6.83
6.83
6.79
6.77
6.73
6.72
6.72
6.70
6.70
6.69
5.72
5.71
5.41
3.63
3.15
3.13
3.12
3.11
2.99
2.97
2.05
1.51
O
O
F
1n
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.6
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
f1 (ppm)

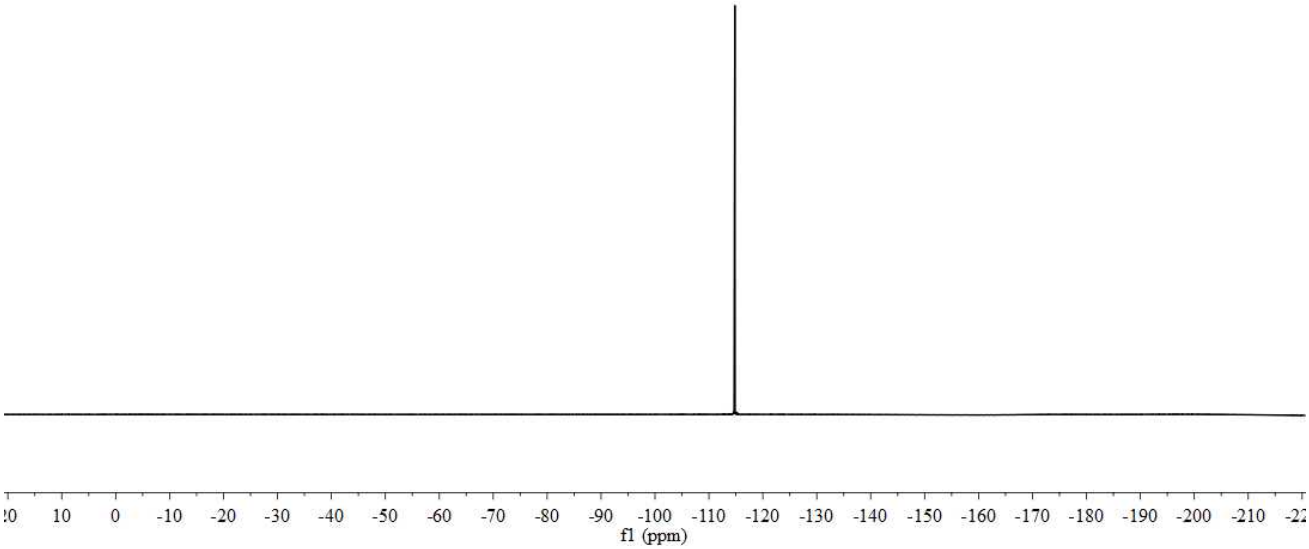

176.61
162.95
160.53
135.61
135.53
134.49
133.58
128.34
128.26
128.22
125.60
119.53
119.32
116.87
113.78
113.57
52.88
41.97
40.45
26.55
23.86
21.23
O
O
F
1n
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 295.3
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
f1 (ppm)

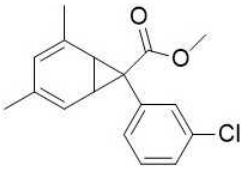


1n

-114.81

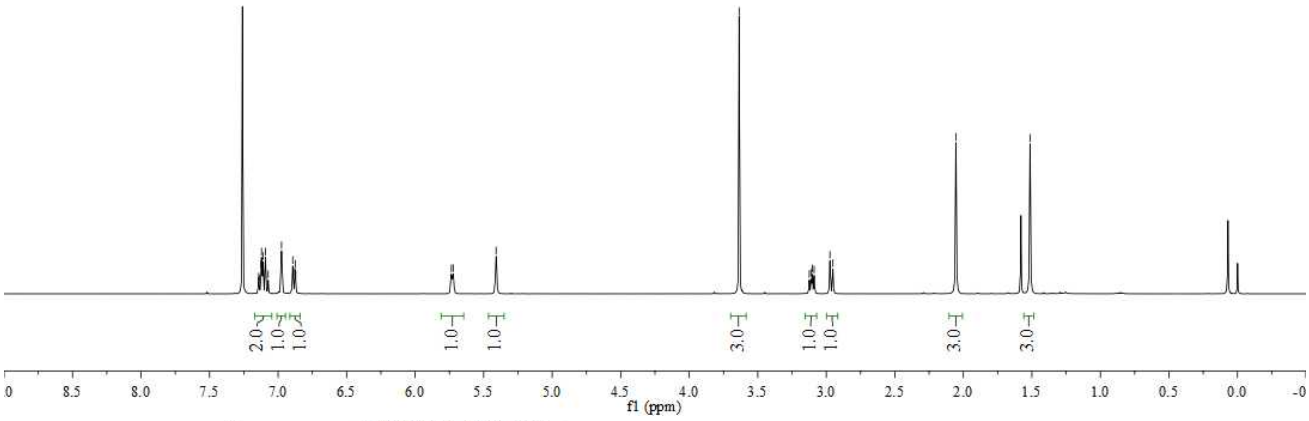
Parameter	Value
Title	pdata/ 1
Solvent	CDCl3
Temperature	294.9
Number of Scans	16
Spectrometer Frequency	376.55
Nucleus	19F

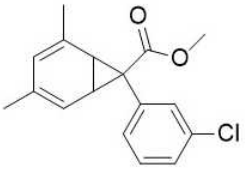




1o

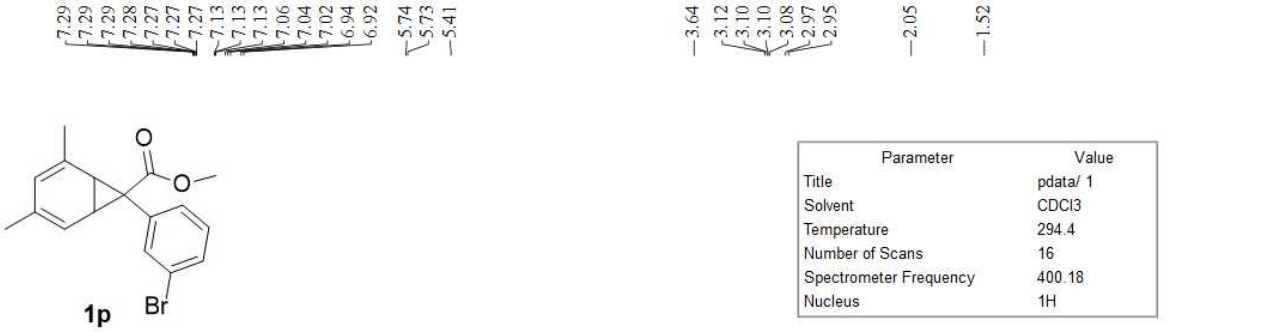
Parameter	Value
Title	pdata/ 1
Solvent	CDCl3
Temperature	294.6
Number of Scans	16
Spectrometer Frequency	400.18
Nucleus	1H





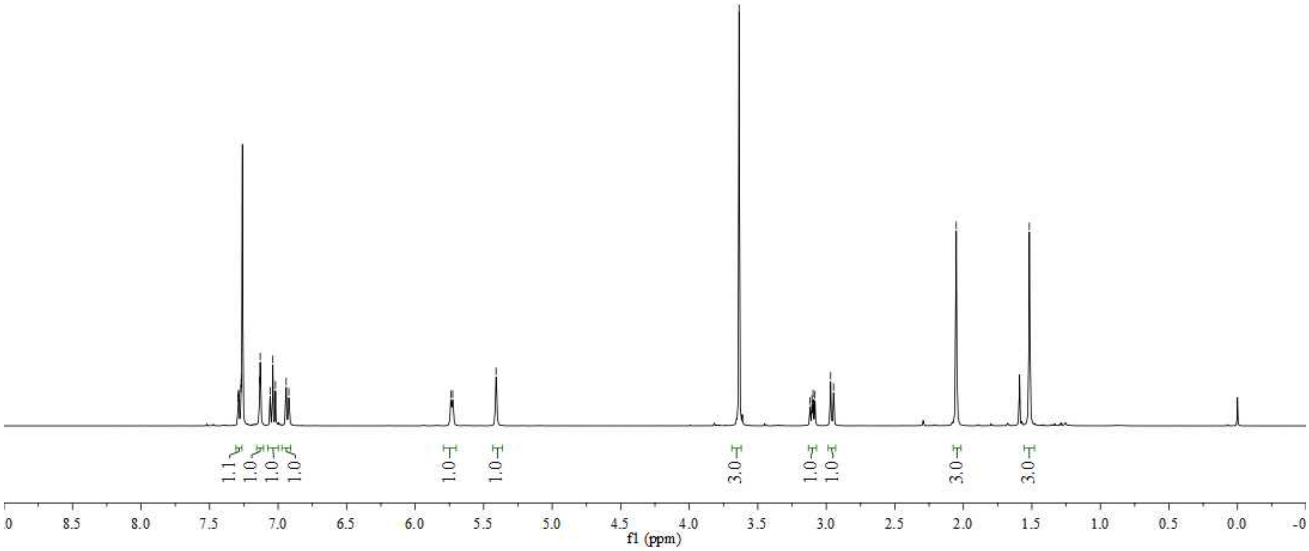
1o

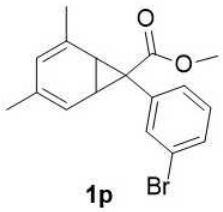
Parameter	Value
Title	pdata/ 1
Solvent	CDCl3
Temperature	295.2
Number of Scans	256
Spectrometer Frequency	100.63
Nucleus	13C



1p

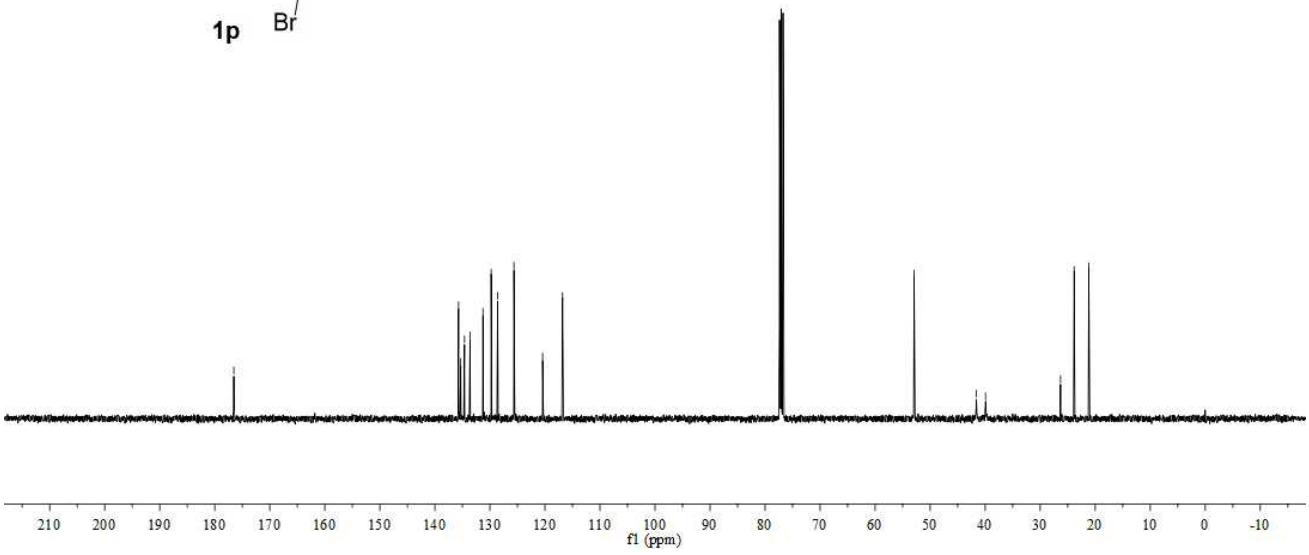
Parameter	Value
Title	pdata/ 1
Solvent	CDCl3
Temperature	294.4
Number of Scans	16
Spectrometer Frequency	400.18
Nucleus	1H

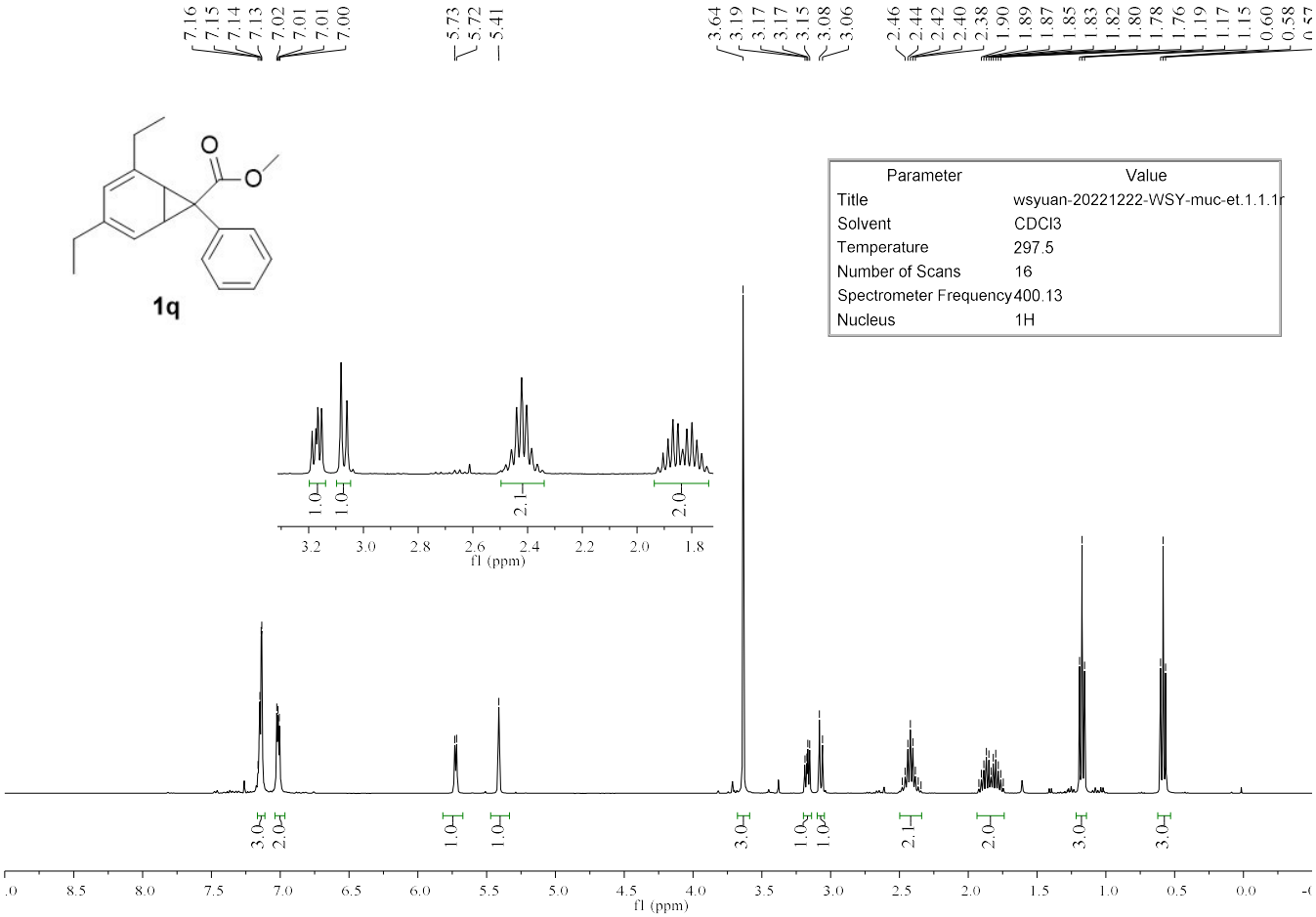


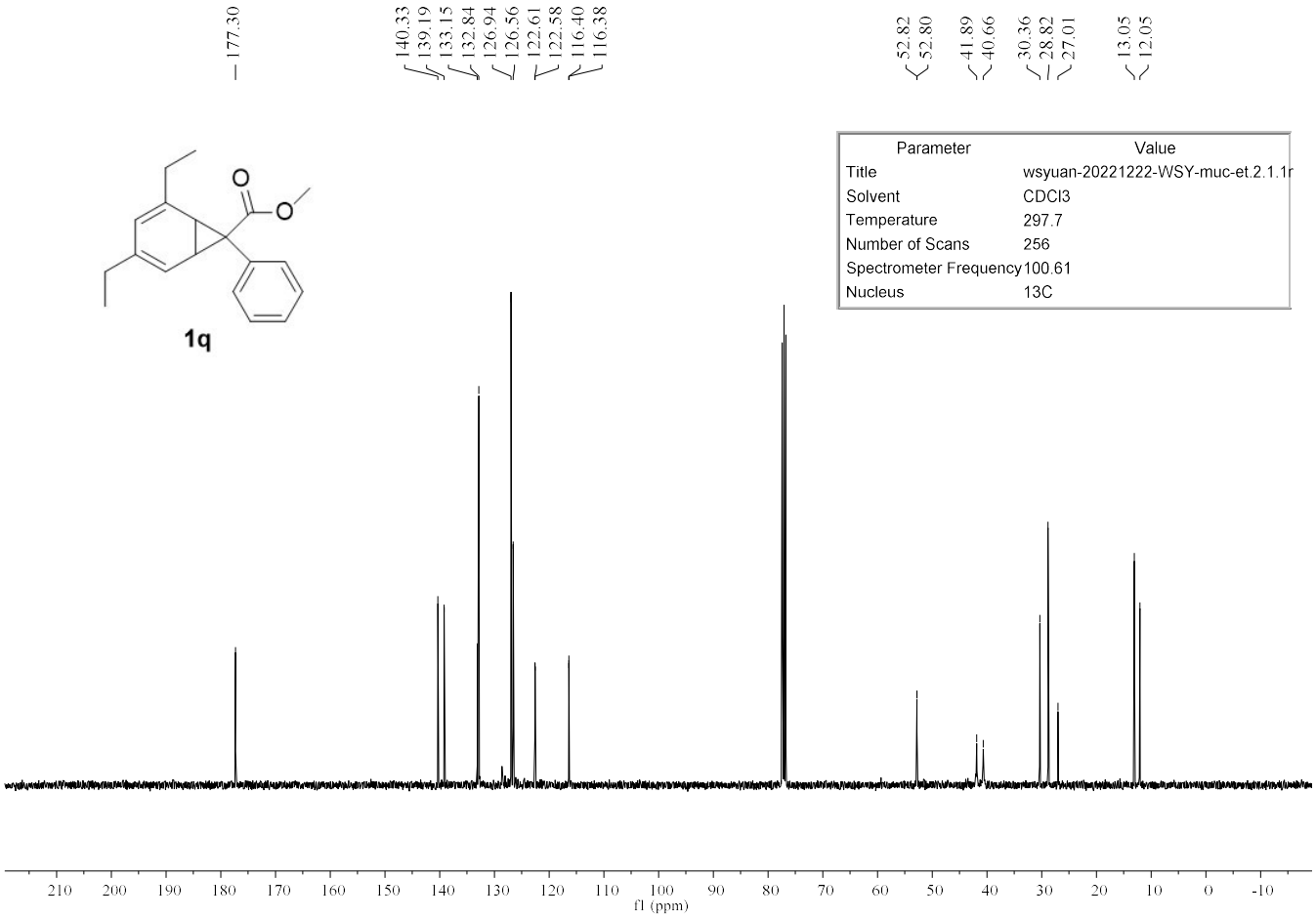


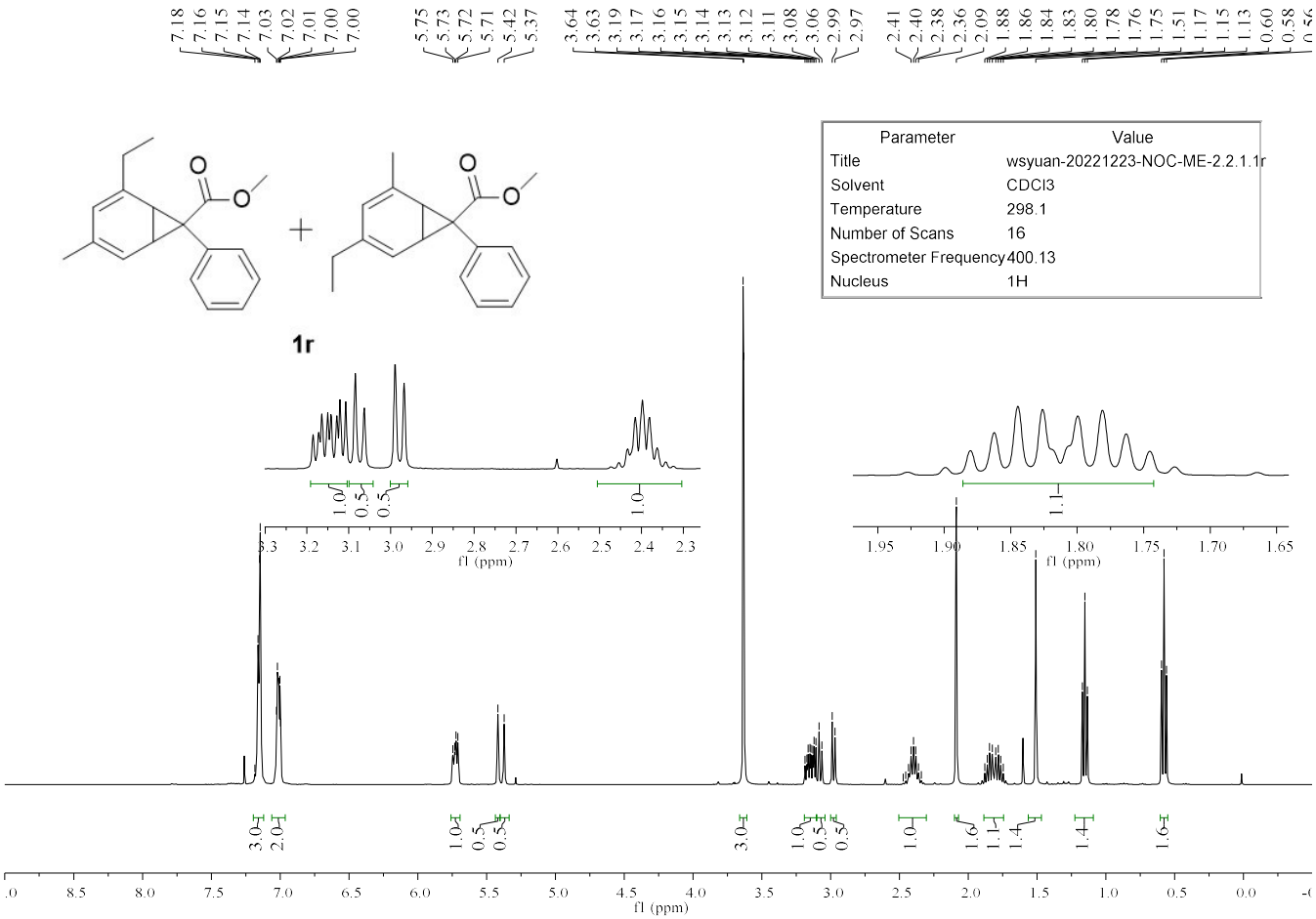
1p

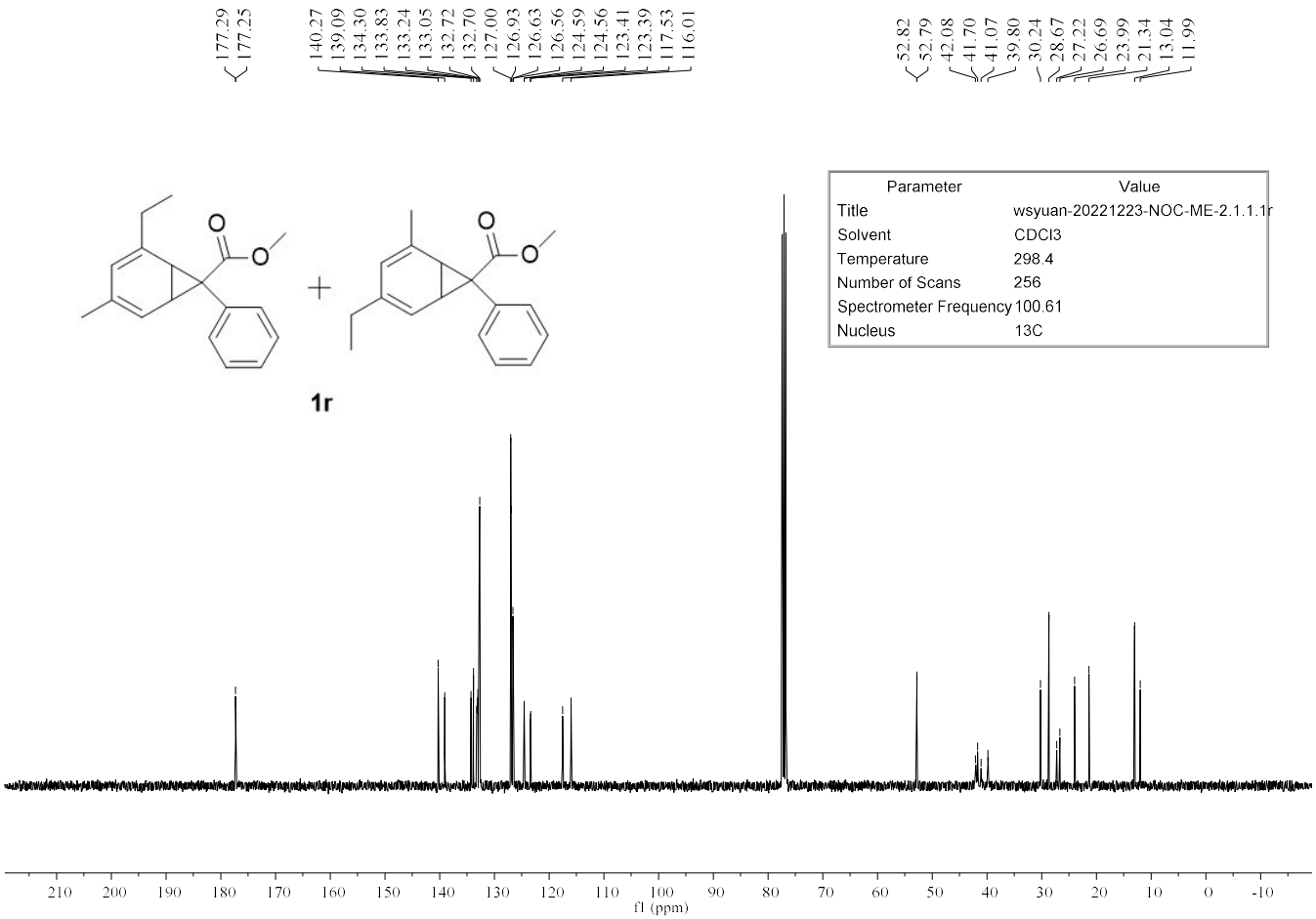
Parameter	Value
Title	pdata/ 1
Solvent	CDCl3
Temperature	295.1
Number of Scans	256
Spectrometer Frequency	100.63
Nucleus	13C



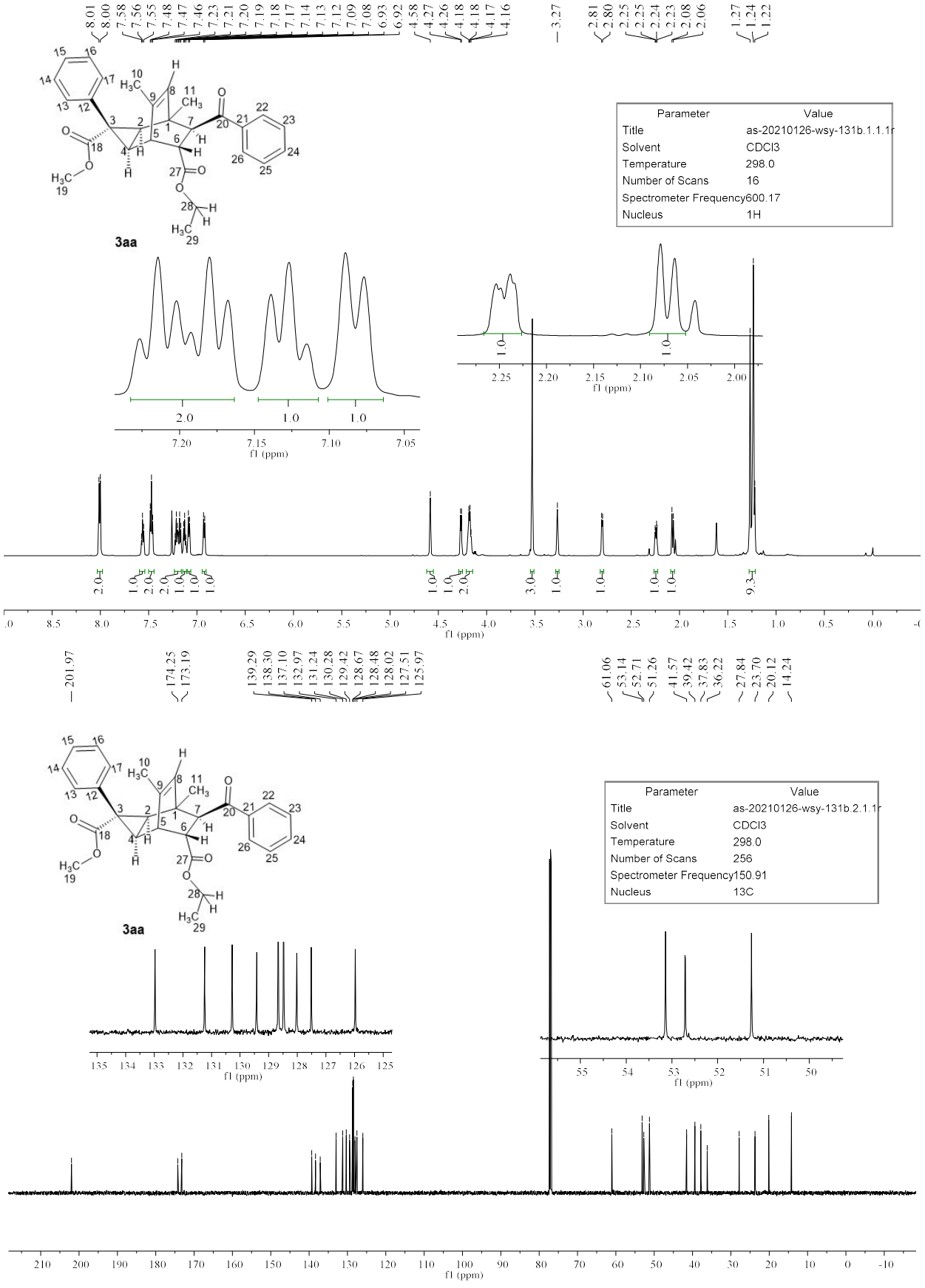

7.16
7.15
7.14
7.13
7.02
7.01
7.01
7.00
5.73
5.72
5.41
3.64
3.19
3.17
3.17
3.15
3.08
3.06
2.46
2.44
2.42
2.40
2.38
1.90
1.89
1.87
1.85
1.83
1.82
1.80
1.78
1.76
1.19
1.17
1.15
0.60
0.58
1q
Parameter Value
Title wsyuan-20221222-WSY-muc-et.1.1.1r
Solvent CDCl3
Temperature 297.5
Number of Scans 16
Spectrometer Frequency 400.13
Nucleus 1H
f1 (ppm)

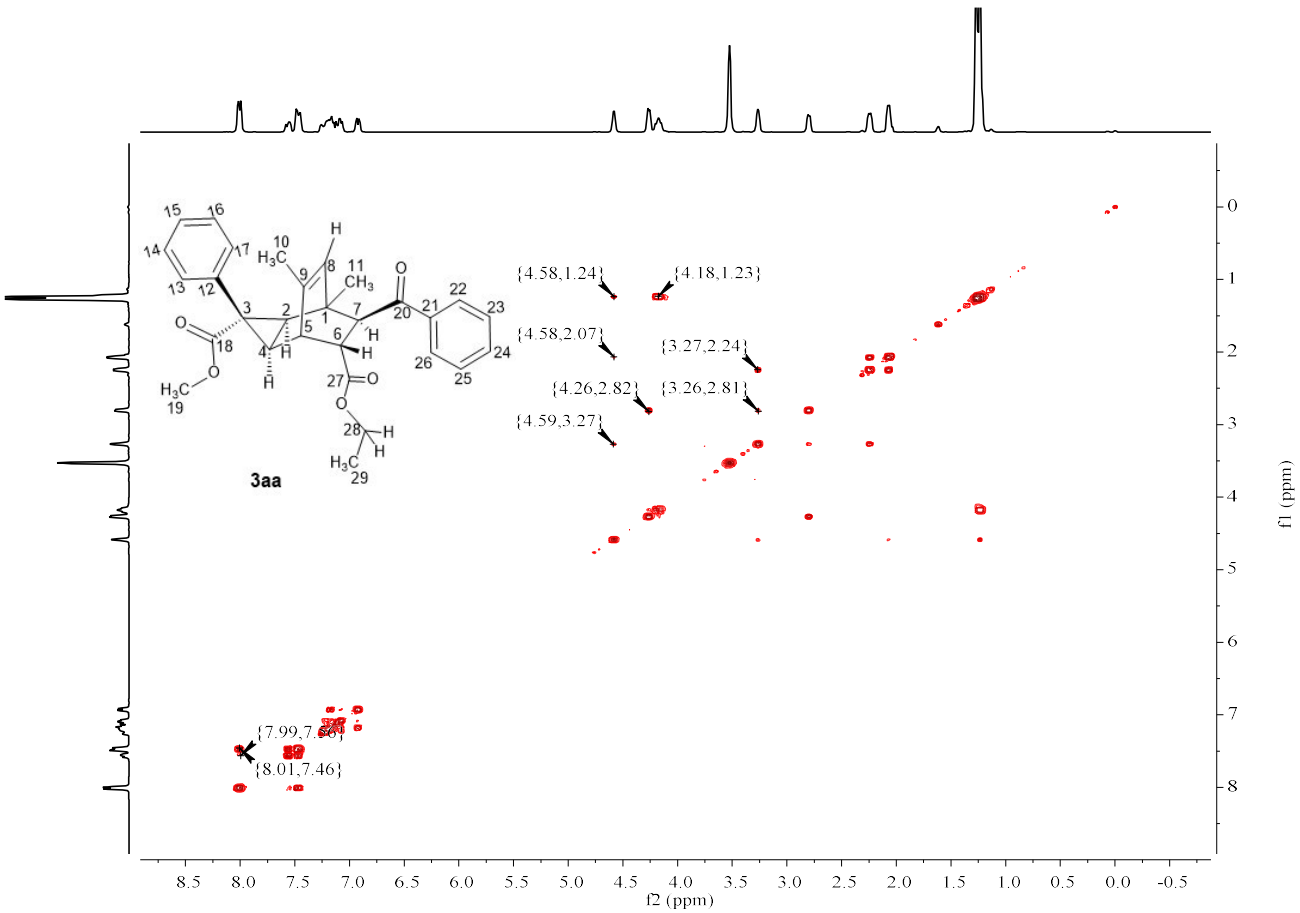

177.30
140.33
139.19
133.15
132.84
126.94
126.56
122.61
122.58
116.40
116.38
52.82
52.80
41.89
40.66
30.36
28.82
27.01
13.05
12.05
1q
Parameter Value
Title wsyuan-20221222-WSY-muc-et.2.1.1r
Solvent CDCl3
Temperature 297.7
Number of Scans 256
Spectrometer Frequency 100.61
Nucleus 13C
f1 (ppm)


7.18 7.16 7.15 7.14 7.03 7.02 7.01 7.00 7.00
5.75 5.73 5.72 5.71 5.42 5.37
3.64 3.63 3.19 3.17 3.16 3.15 3.14 3.13 3.12 3.11 3.08 3.06 2.99 2.97
2.41 2.40 2.38 2.36 2.09 1.88 1.86 1.84 1.83 1.80 1.78 1.76 1.75 1.51 1.17 1.15 1.13 0.60 0.58
Parameter Value
Title wsyuan-20221223-NOC-ME-2.2.1.1r
Solvent CDCl3
Temperature 298.1
Number of Scans 16
Spectrometer Frequency 400.13
Nucleus 1H
1r
f1 (ppm)


177.29 177.25
140.27 139.09 134.30 133.83 133.24 133.05 132.72 132.70 127.00 126.93 126.63 126.56 124.59 124.56 123.41 123.39 117.53 116.01
52.82 52.79 42.08 41.70 41.07 39.80 30.24 28.67 27.22 26.69 23.99 21.34 13.04 11.99
Parameter Value
Title wsyuan-20221223-NOC-ME-2.1.1.1r
Solvent CDCl3
Temperature 298.4
Number of Scans 256
Spectrometer Frequency 100.61
Nucleus 13C
1r
f1 (ppm)

3aa


8.01 8.00 7.58 7.56 7.55 7.48 7.47 7.46 7.23 7.21 7.20 7.19 7.18 7.17 7.14 7.13 7.12 7.09 7.08 6.93 6.92 4.58 4.27 4.26 4.18 4.18 4.17 4.16 3.27 2.81 2.80 2.25 2.25 2.24 2.23 2.08 2.06 1.27 1.24 1.22
Parameter Value
Title as-20210126-wsy-131b.1.1.1r
Solvent CDCl3
Temperature 298.0
Number of Scans 16
Spectrometer Frequency 600.17
Nucleus 1H
3aa
f1 (ppm)
201.97 174.25 173.19 139.29 138.30 137.10 132.97 131.24 130.28 129.42 128.67 128.48 128.02 127.51 125.97 61.06 53.14 52.71 51.26 41.57 39.42 37.83 36.22 27.84 23.70 20.12 14.24
Parameter Value
Title as-20210126-wsy-131b.2.1.1r
Solvent CDCl3
Temperature 298.0
Number of Scans 256
Spectrometer Frequency 150.91
Nucleus 13C
3aa
f1 (ppm)


3aa
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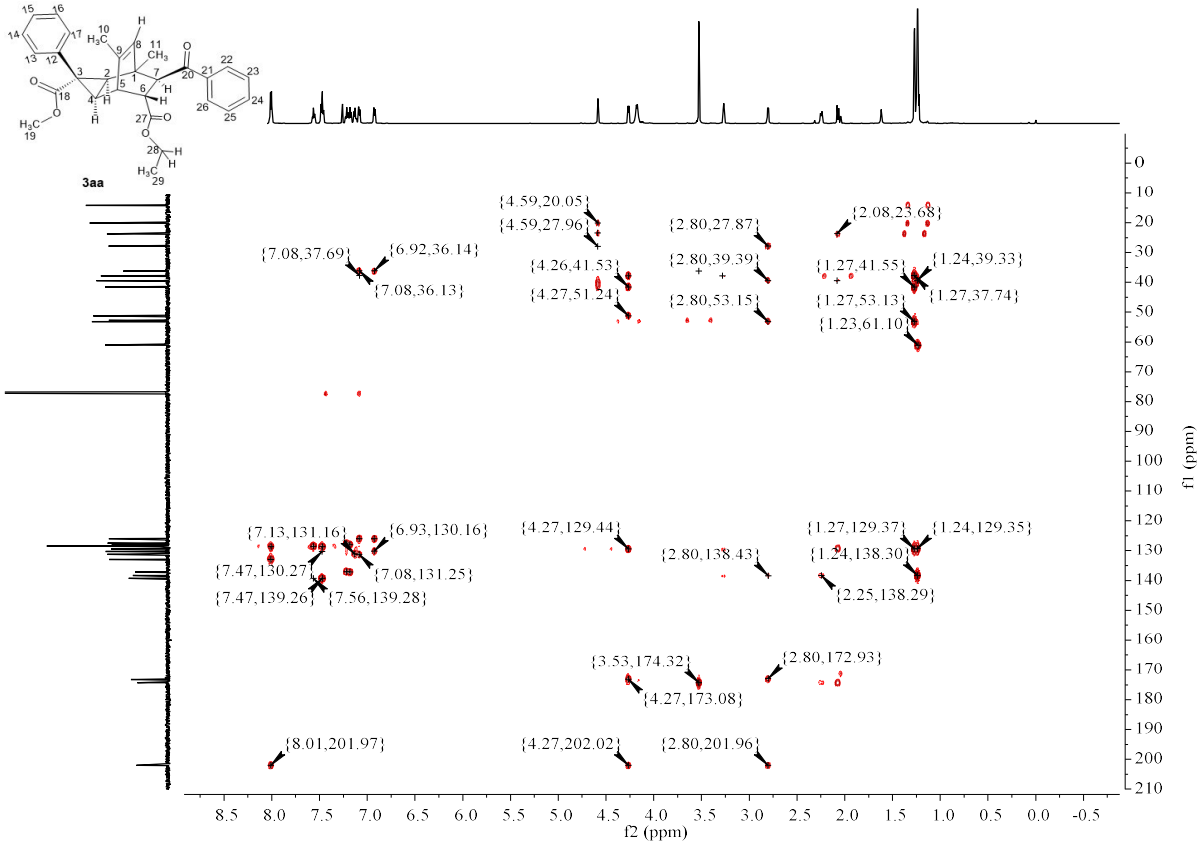
{4.18,1.23}
{4.58,2.07}
{3.27,2.24}
{4.26,2.82}
{3.26,2.81}
{4.59,3.27}
{7.99,7.46}
{8.01,7.46}
f2 (ppm)
f1 (ppm)


3aa
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{4.59,27.96}
{2.80,27.87}
{2.08,25.68}
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{4.27,51.24}
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{2.80,53.15}
{1.27,41.55}
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{1.27,53.13}
{1.27,37.74}
{1.23,61.10}
{7.13,131.16}
{6.93,130.16}
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{2.80,172.93}
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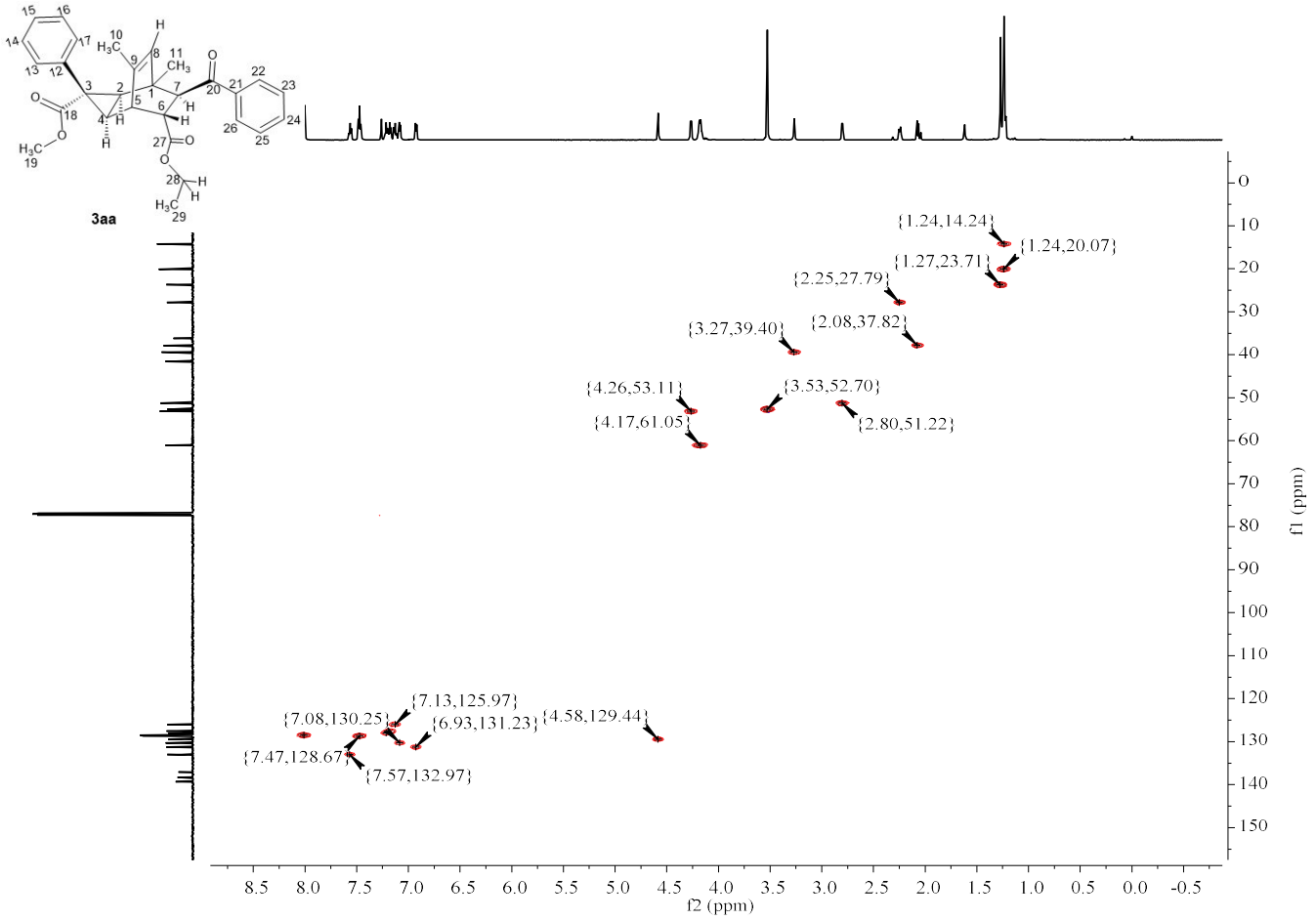
{8.01,201.97}
{4.27,202.02}
{2.80,201.96}
f2 (ppm)
f1 (ppm)


3aa
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{2.08,37.82}
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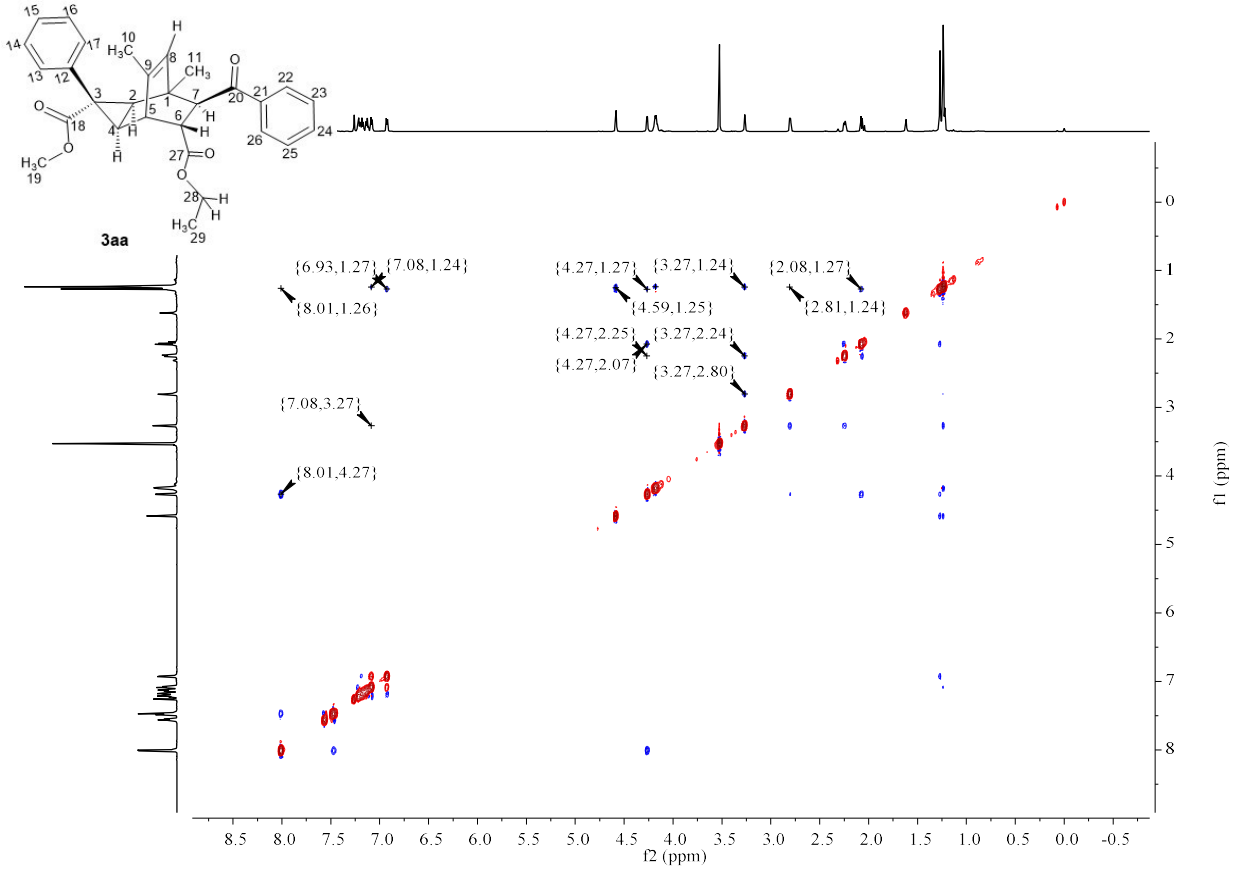
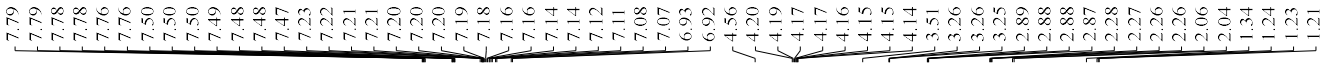
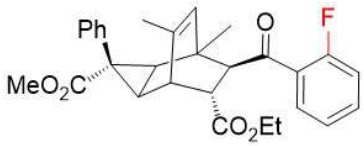
{7.13,125.97}
{7.08,130.25}
{6.93,131.23}
{4.58,129.44}
{7.47,128.67}
{7.57,132.97}
f2 (ppm)
f1 (ppm)

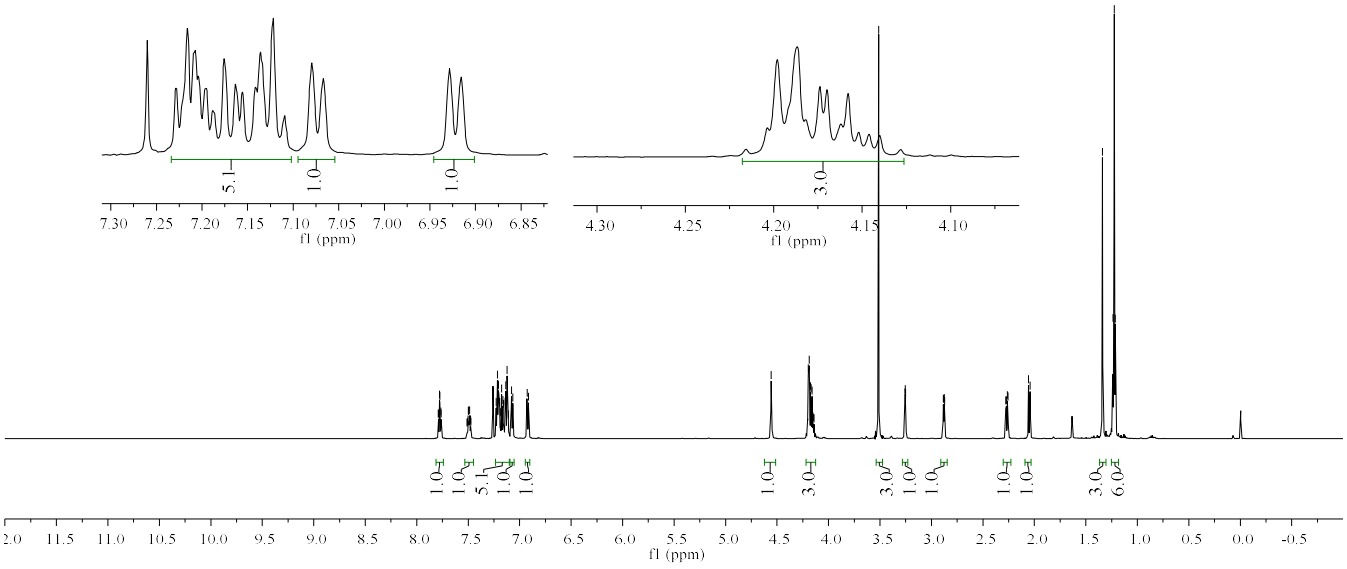

3aa
{6.93,1.27}
{7.08,1.24}
{8.01,1.26}
{4.27,1.27}
{3.27,1.24}
{4.59,1.25}
{2.08,1.27}
{2.81,1.24}
{4.27,2.25}
{4.27,2.07}
{3.27,2.24}
{3.27,2.80}
{7.08,3.27}
{8.01,4.27}
f2 (ppm)
f1 (ppm)

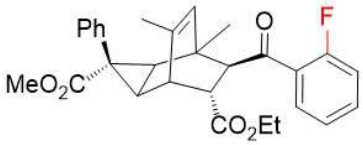




3ab

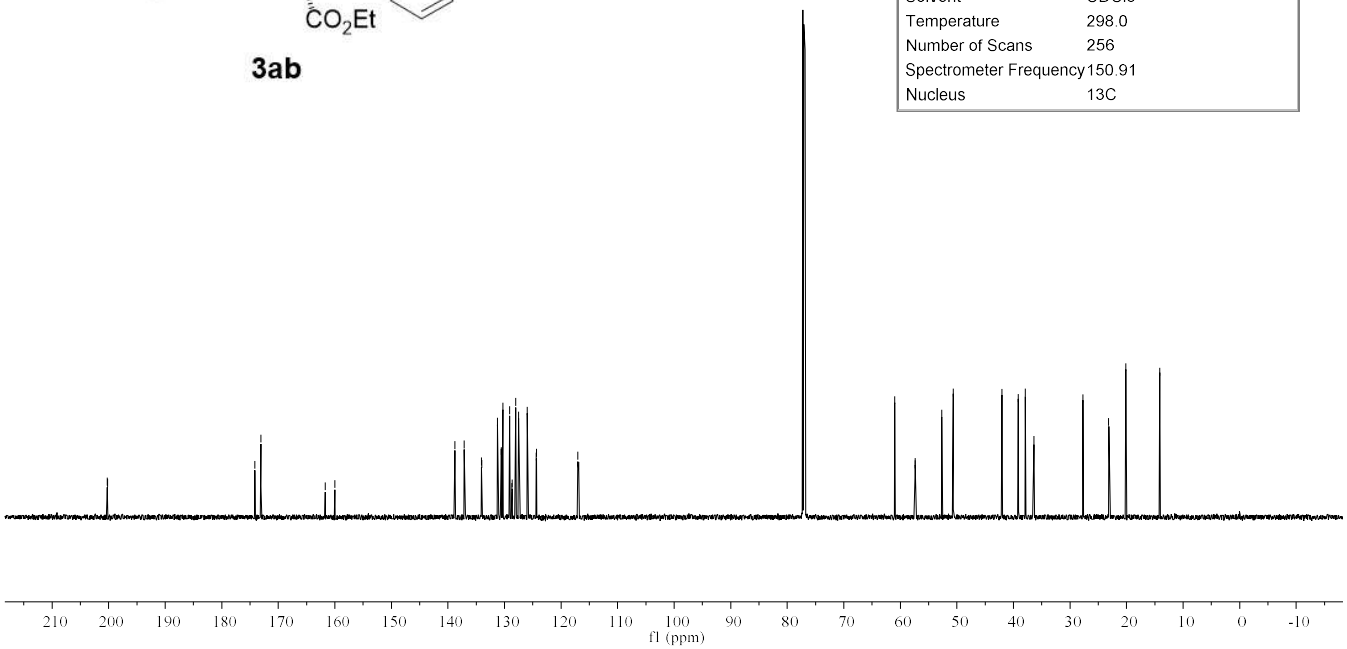
Parameter	Value
Title	as-20211201-WSY-388.1.1.1r
Solvent	CDCl3
Temperature	297.1
Number of Scans	16
Spectrometer Frequency	600.17
Nucleus	1H

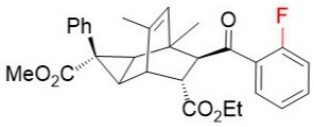




3ab

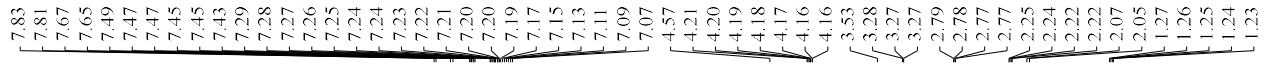
Parameter	Value
Title	as-20211201-WSY-388.2.1.1r
Solvent	CDCl3
Temperature	298.0
Number of Scans	256
Spectrometer Frequency	150.91
Nucleus	13C

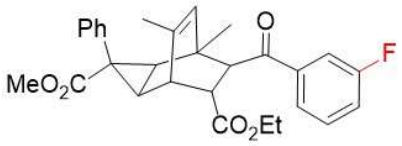




3ab

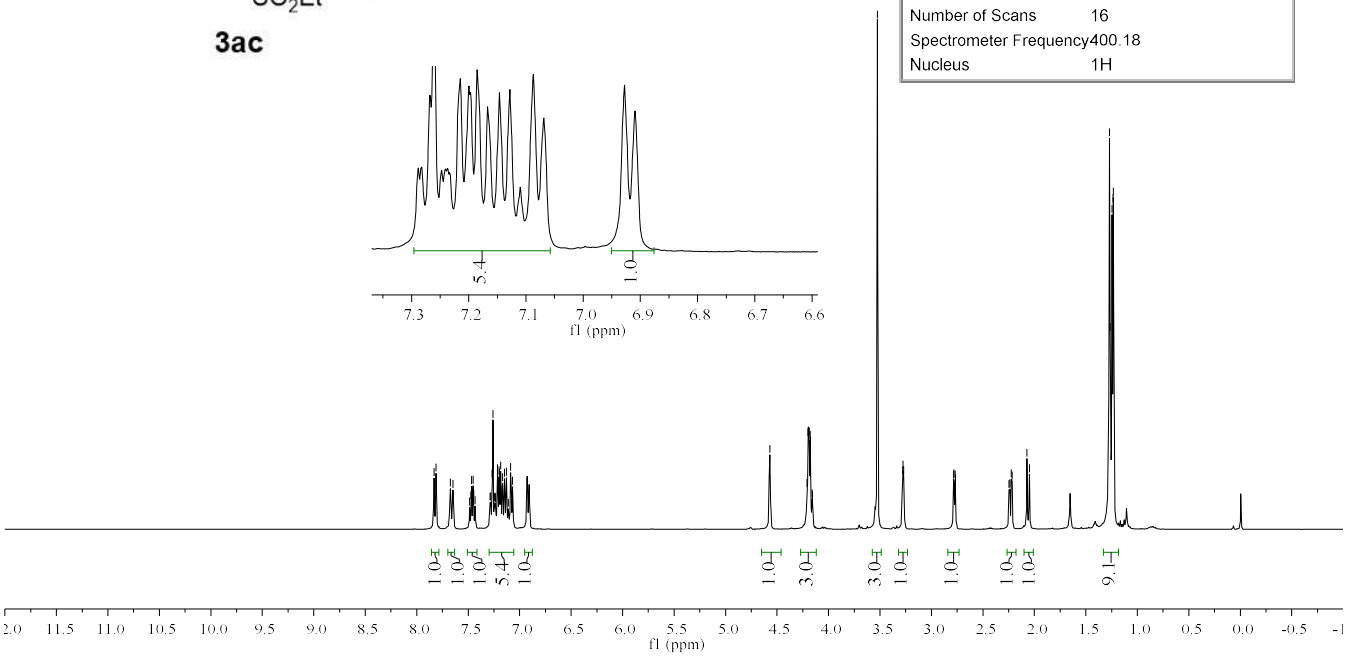
Parameter	Value
Title	as-20211201-WSY-388.3.1.1r
Solvent	CDCl3
Temperature	297.4
Number of Scans	16
Spectrometer Frequency	564.72
Nucleus	19F

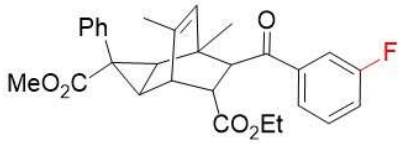




3ac

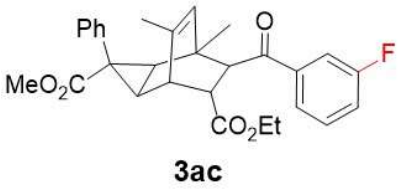
Parameter	Value
Title	as-20211210-wsy-395.7.1.1r
Solvent	CDCl3
Temperature	292.7
Number of Scans	16
Spectrometer Frequency	400.18
Nucleus	1H





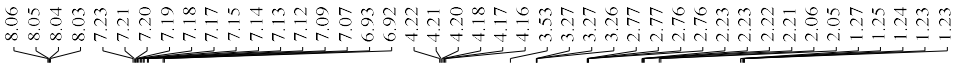
3ac

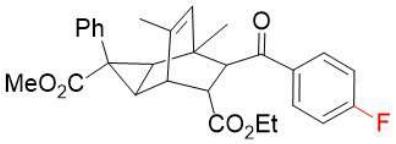
Parameter	Value
Title	as-20211210-wsy-395.8.1.1r
Solvent	CDCl3
Temperature	293.3
Number of Scans	256
Spectrometer Frequency	100.63
Nucleus	13C



3ac

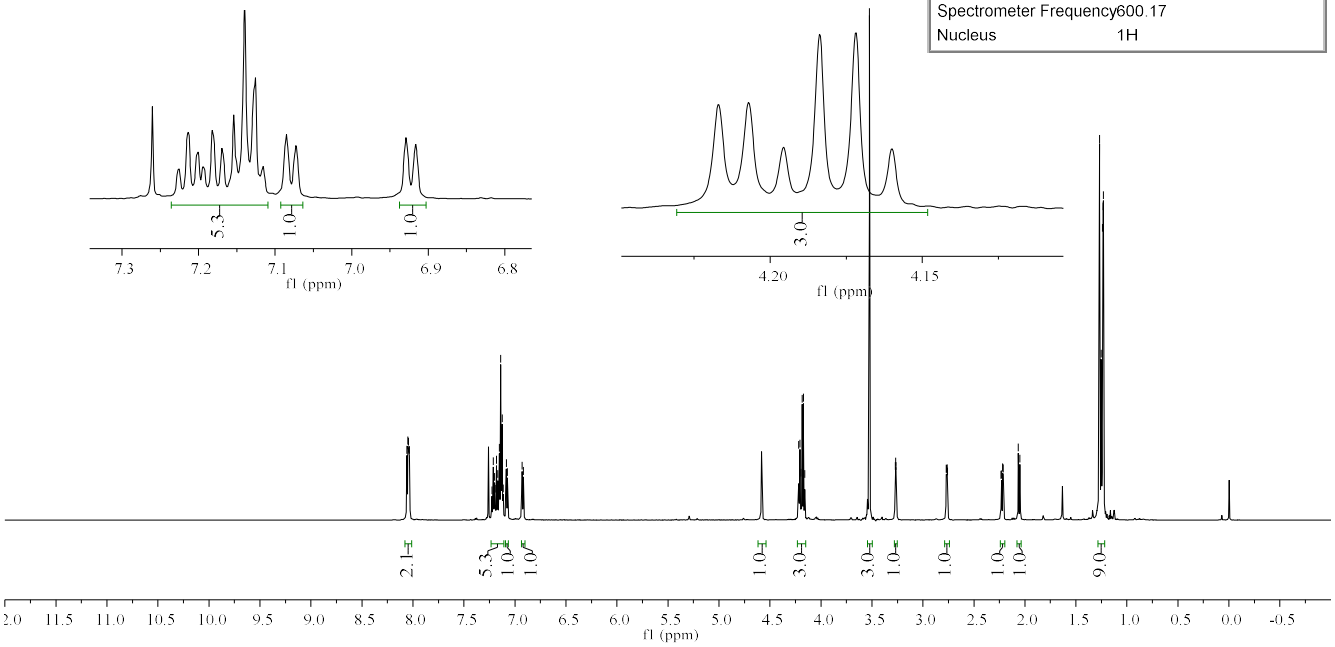
Parameter	Value
Title	as-20211210-wsy-395.9.1.1r
Solvent	CDCl3
Temperature	293.0
Number of Scans	16
Spectrometer Frequency	376.55
Nucleus	19F

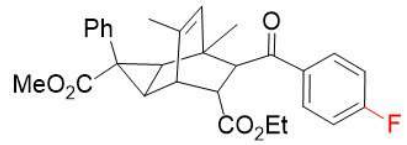




3ad

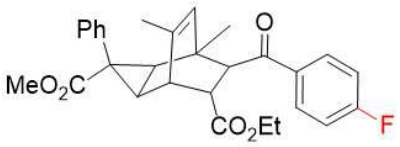
Parameter	Value
Title	as-20211129-WSY-384.1.1.1r
Solvent	CDCl3
Temperature	296.7
Number of Scans	16
Spectrometer Frequency	600.17
Nucleus	1H





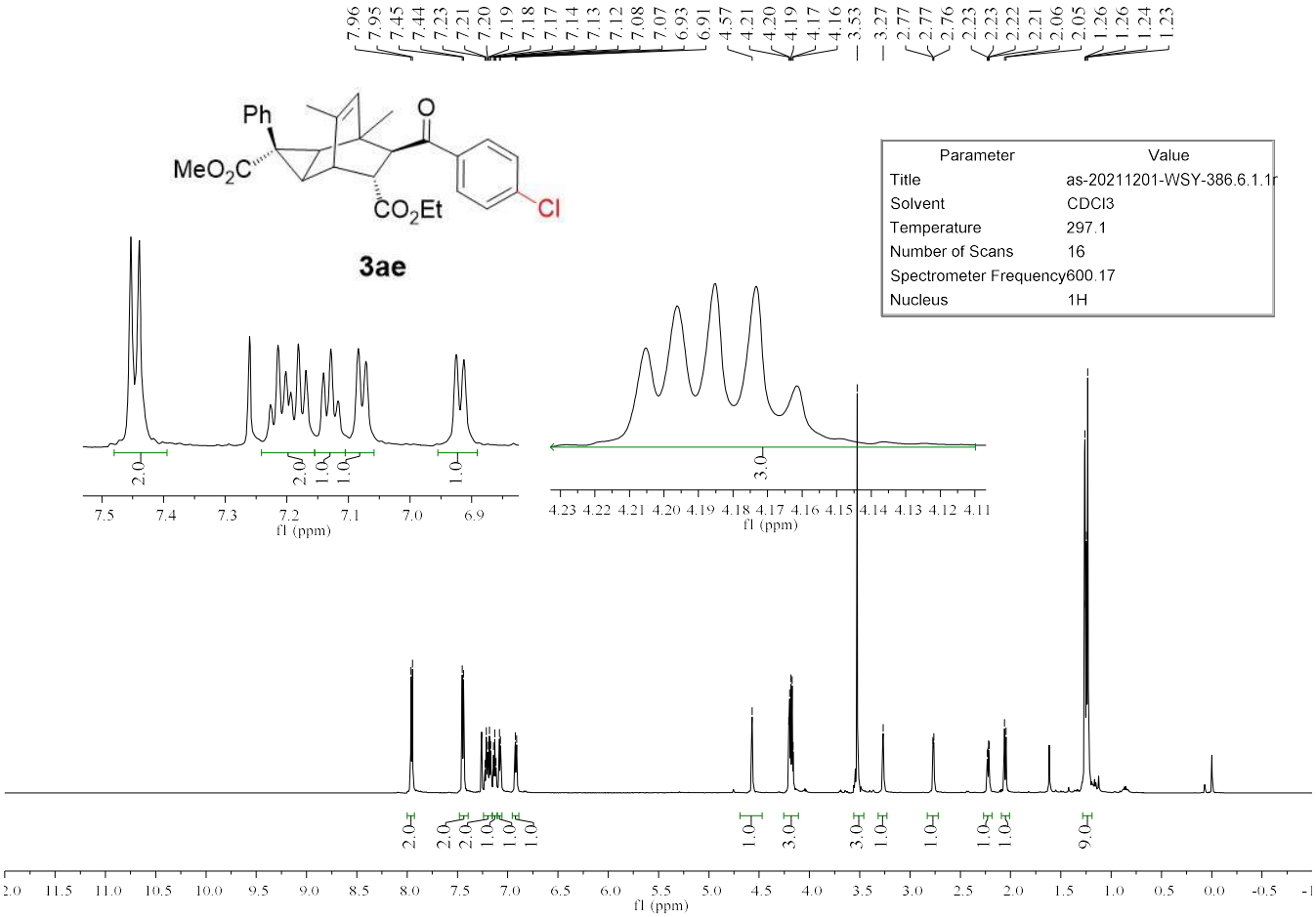
3ad

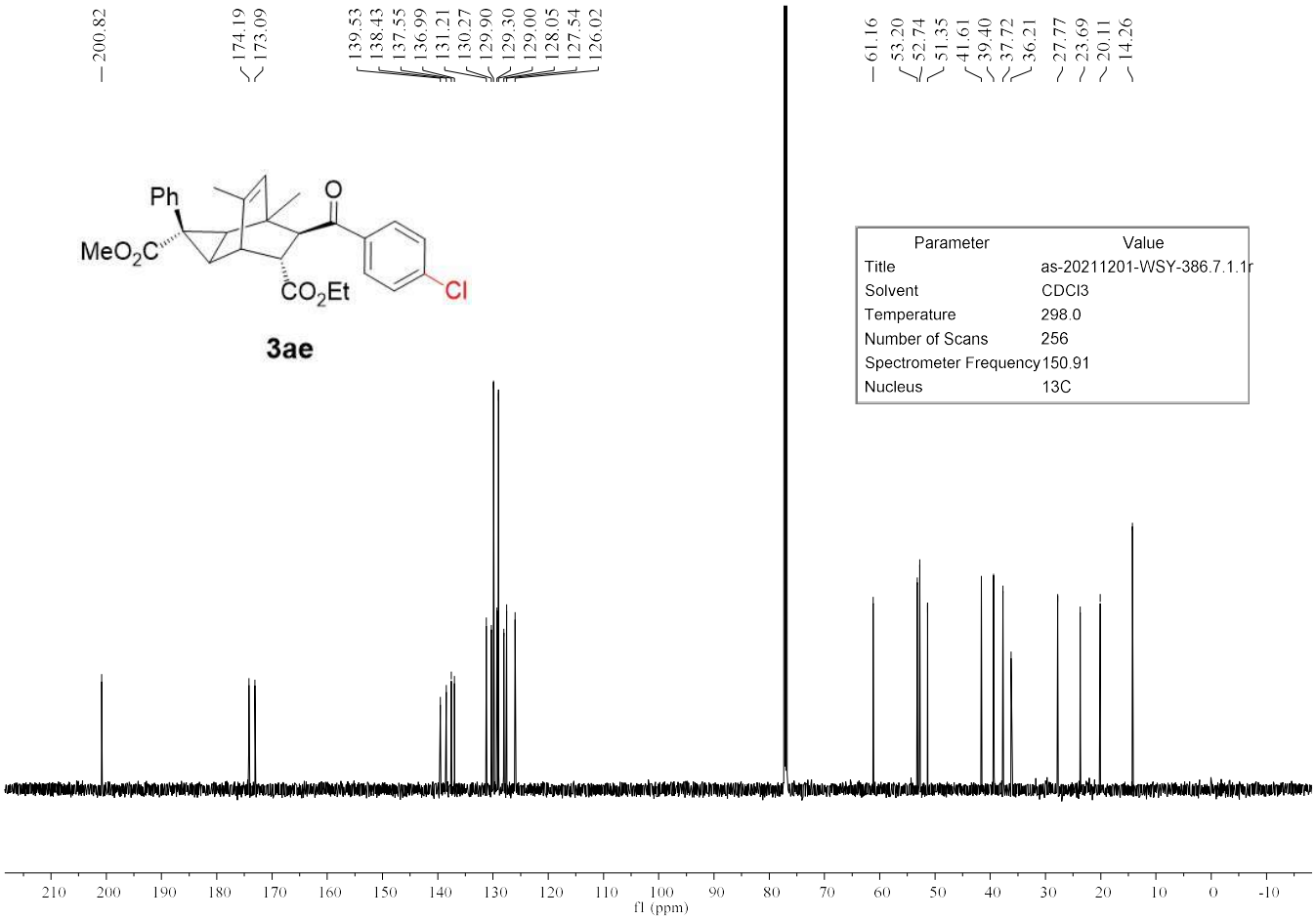
Parameter	Value
Title	as-20211129-WSY-384.2.1.1r
Solvent	CDCl3
Temperature	297.6
Number of Scans	256
Spectrometer Frequency	150.91
Nucleus	13C

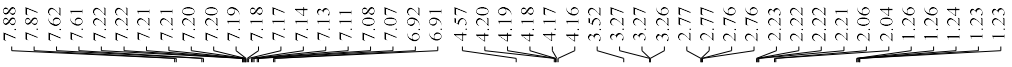


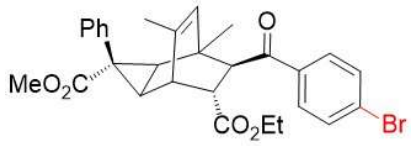
3ad

Parameter	Value
Title	as-20211129-WSY-384.3.1.1r
Solvent	CDCl3
Temperature	297.0
Number of Scans	16
Spectrometer Frequency	564.72
Nucleus	19F


7.96 7.95 7.45 7.44 7.23 7.21 7.20 7.19 7.18 7.17 7.14 7.13 7.12 7.08 7.07 6.93 6.91 4.57 4.21 4.20 4.19 4.17 4.16 3.53 3.27 2.77 2.76 2.23 2.23 2.22 2.21 2.06 2.05 1.26 1.26 1.24 1.23
Ph
O
MeO2C
CO2Et
Cl
3ae
Parameter Value
Title as-20211201-WSY-386.6.1.1r
Solvent CDCl3
Temperature 297.1
Number of Scans 16
Spectrometer Frequency 600.17
Nucleus 1H
f1 (ppm)

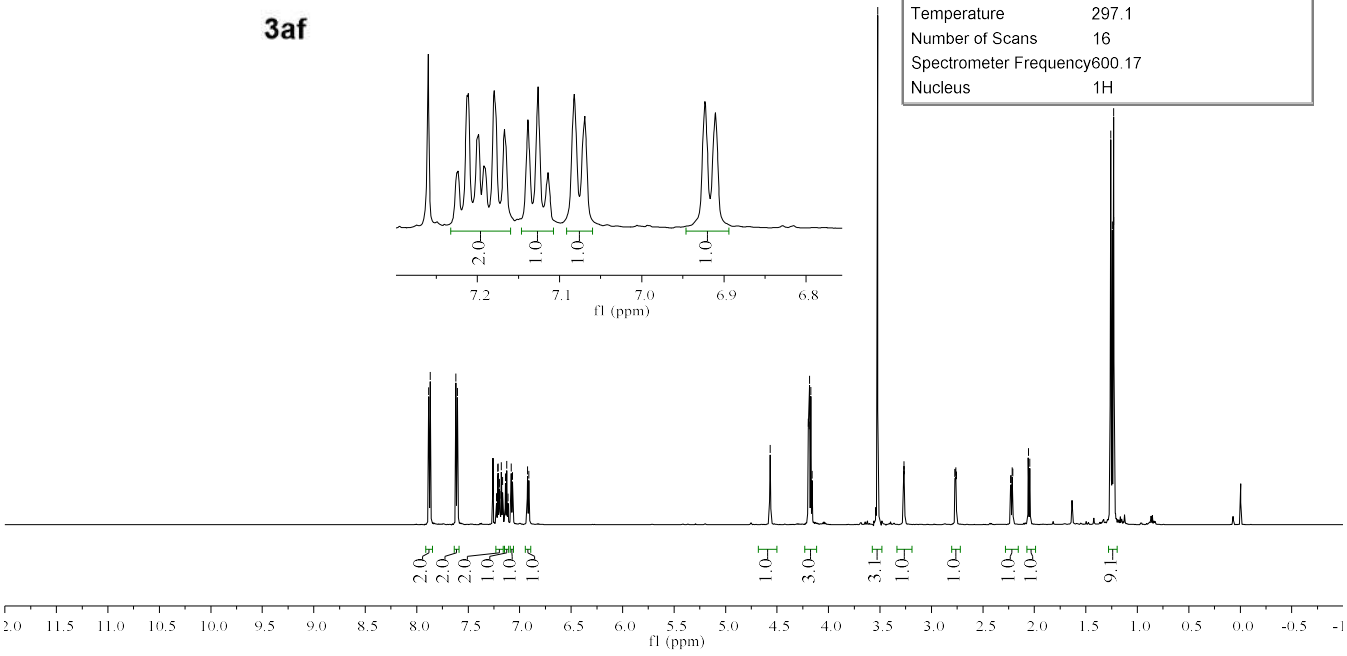

200.82 174.19 173.09 139.53 138.43 137.55 136.99 131.21 130.27 129.90 129.30 129.00 128.05 127.54 126.02 61.16 53.20 52.74 51.35 41.61 39.40 37.72 36.21 27.77 23.69 20.11 14.26
Ph
O
MeO2C
CO2Et
Cl
3ae
Parameter Value
Title as-20211201-WSY-386.7.1.1r
Solvent CDCl3
Temperature 298.0
Number of Scans 256
Spectrometer Frequency 150.91
Nucleus 13C
f1 (ppm)

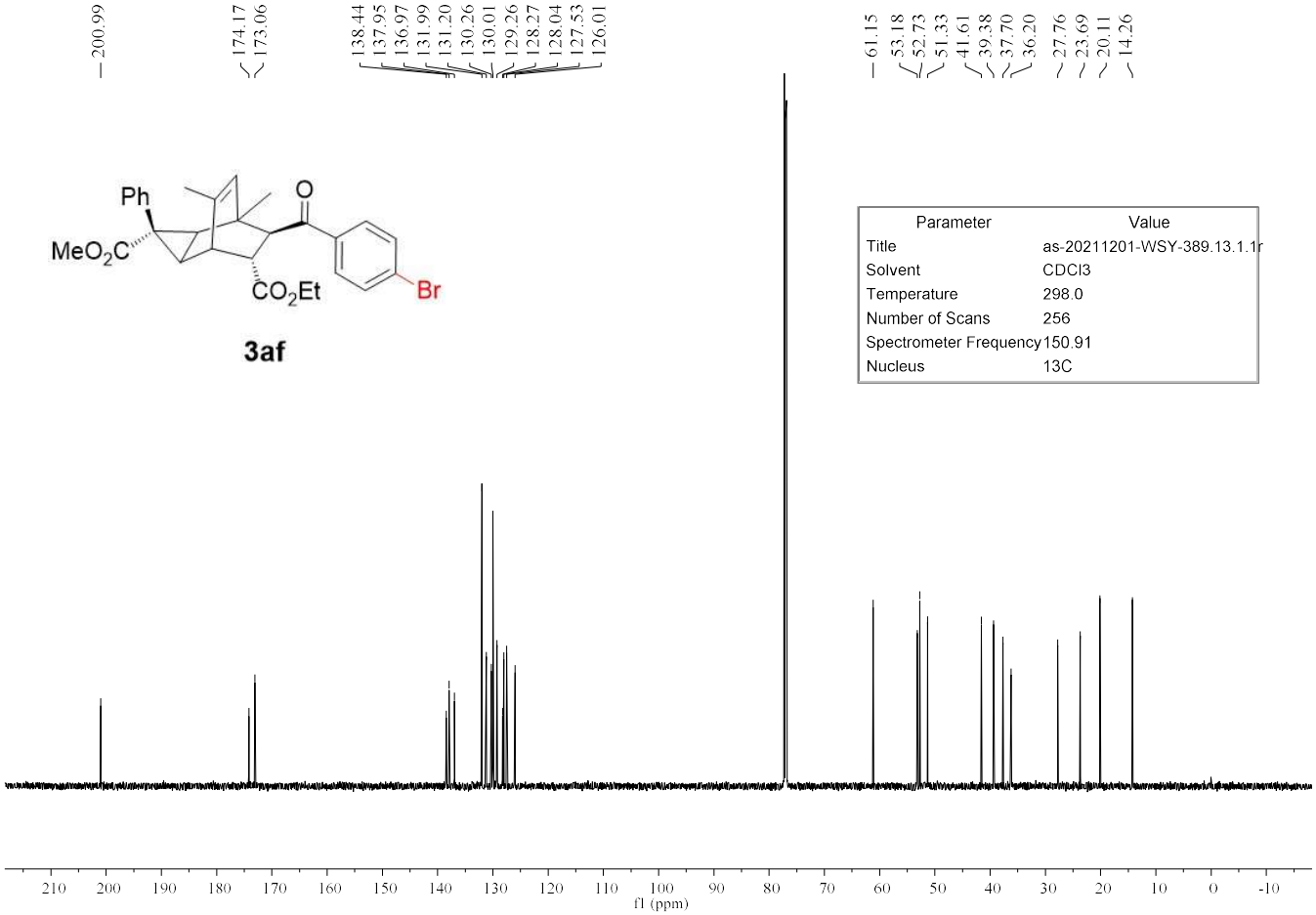




3af

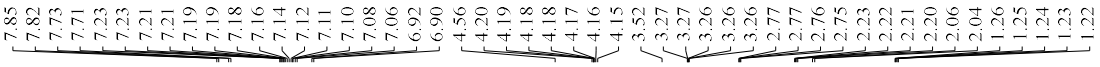
Parameter	Value
Title	as-20211201-WSY-389.12.1.1r
Solvent	CDCl3
Temperature	297.1
Number of Scans	16
Spectrometer Frequency	600.17
Nucleus	1H

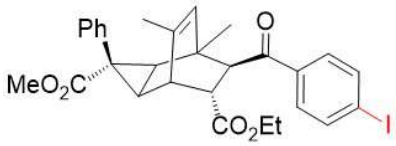




3af

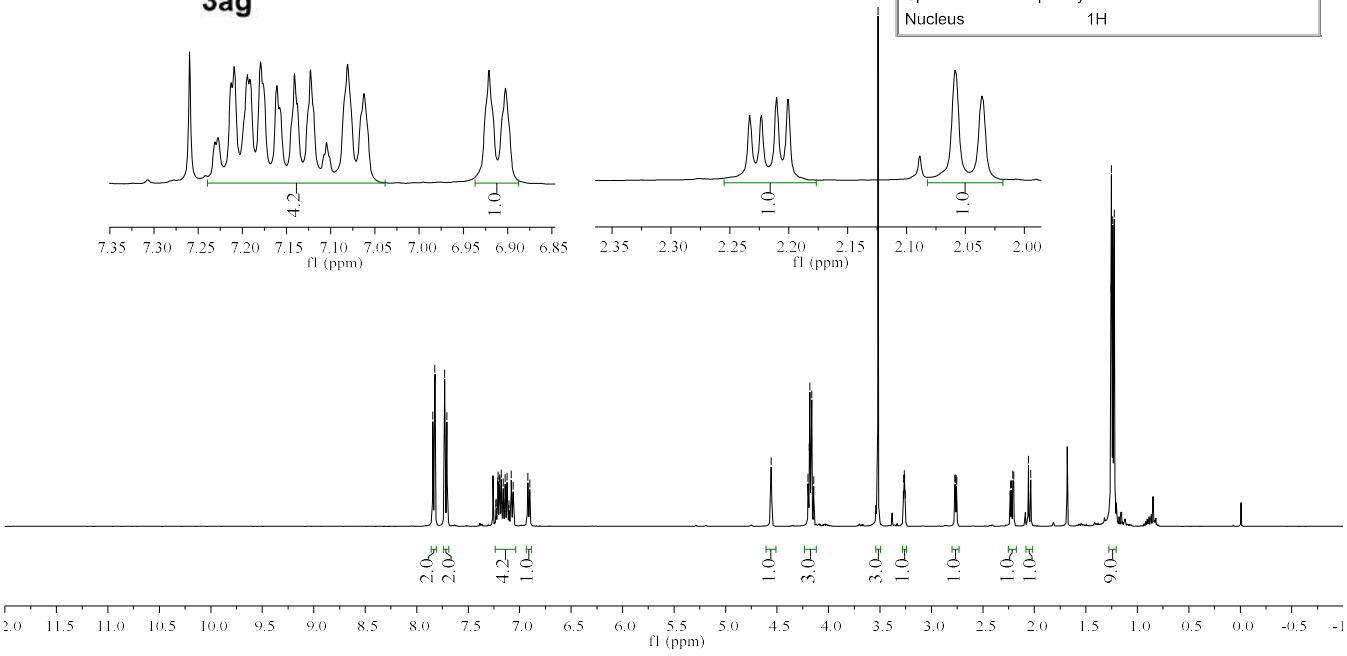
Parameter	Value
Title	as-20211201-WSY-389.13.1.1r
Solvent	CDCl3
Temperature	298.0
Number of Scans	256
Spectrometer Frequency	150.91
Nucleus	13C

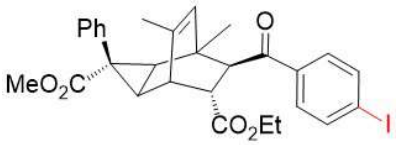




3ag

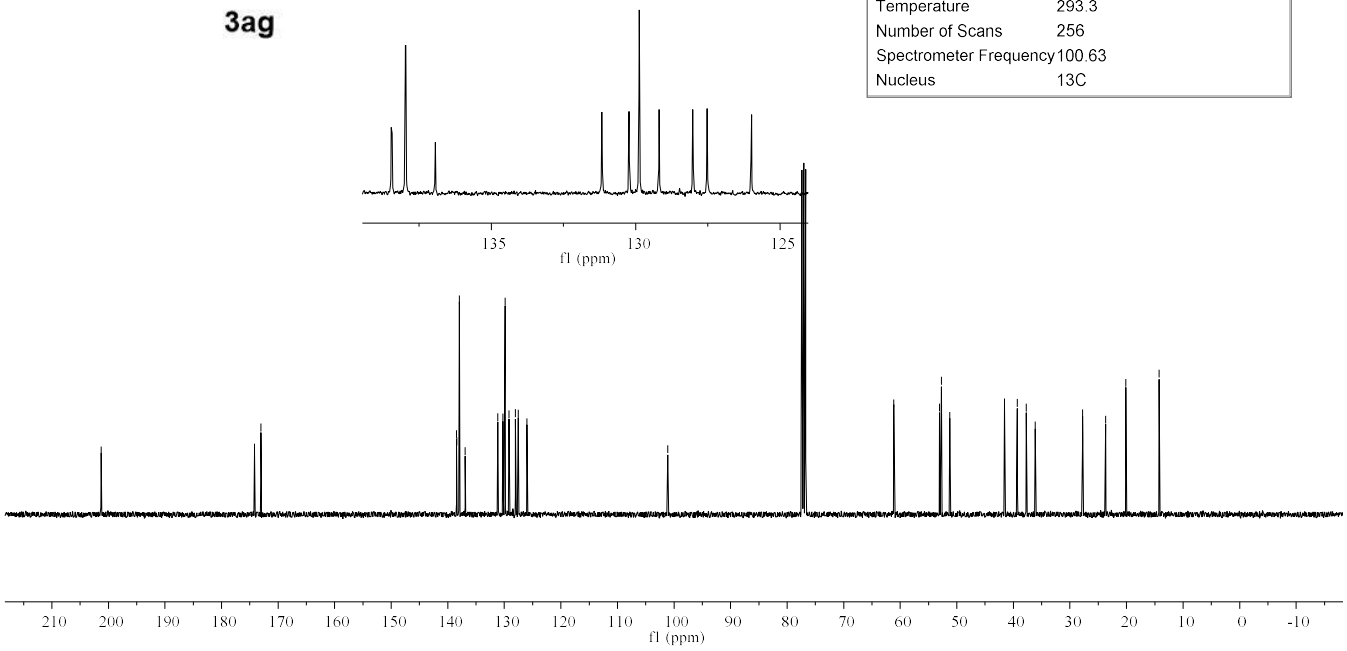
Parameter	Value
Title	wangsyuan-20220126-414.1.1.1r
Solvent	CDCl3
Temperature	292.7
Number of Scans	16
Spectrometer Frequency	400.18
Nucleus	1H

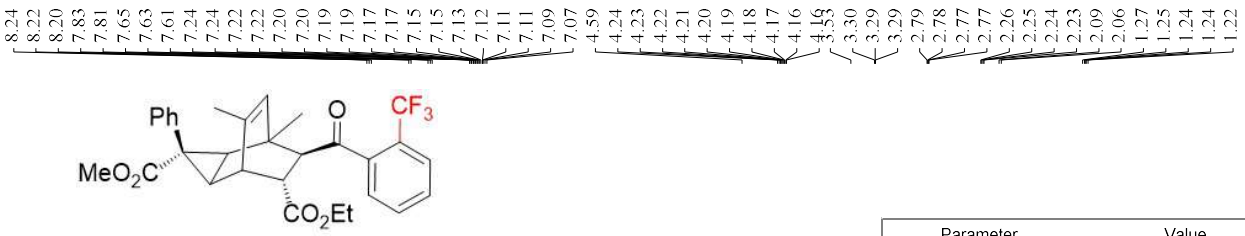




3ag

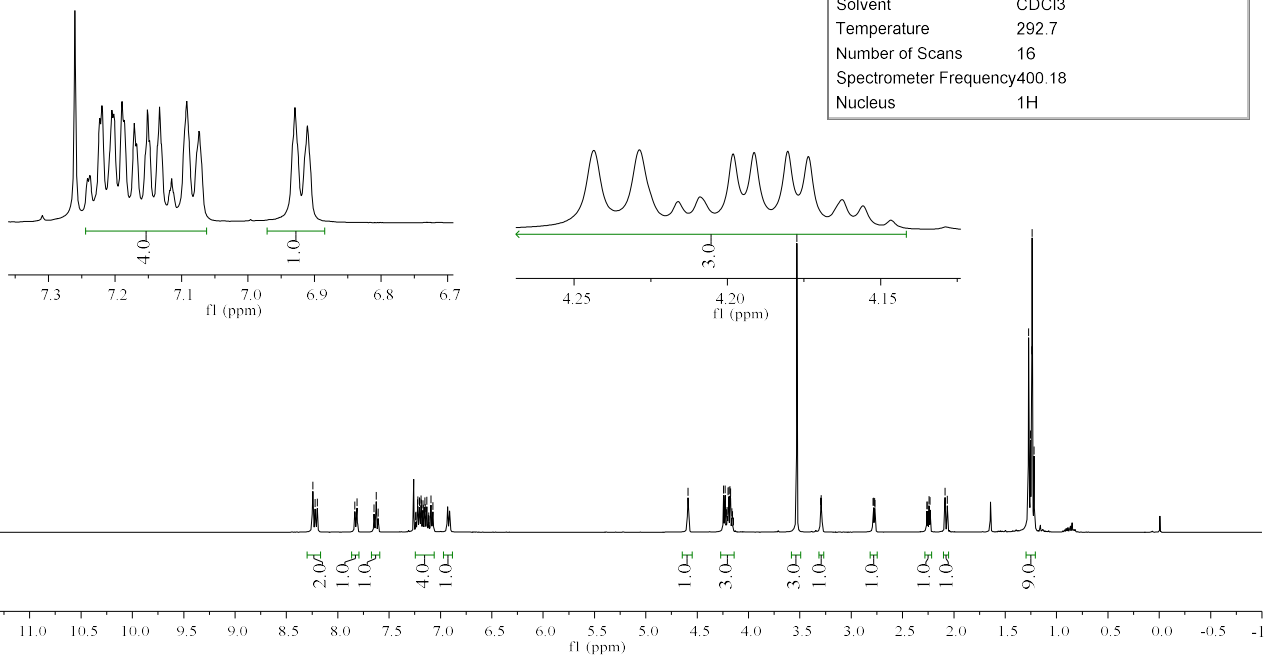
Parameter	Value
Title	wangsyuan-20220126-414.2.1.1r
Solvent	CDCl3
Temperature	293.3
Number of Scans	256
Spectrometer Frequency	100.63
Nucleus	13C

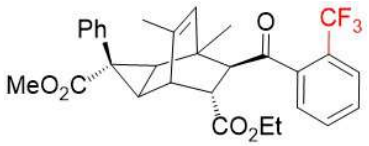




3ah

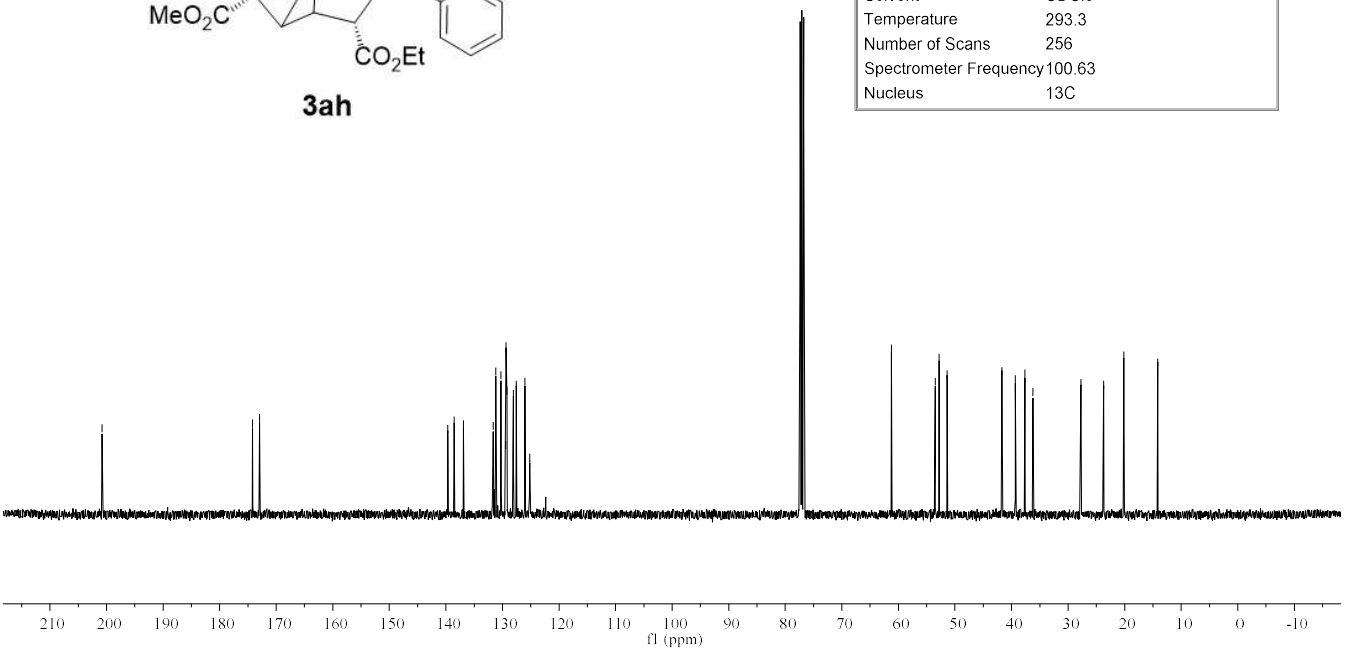
Parameter	Value
Title	wangsyuan-20220122-411.1.1.1r
Solvent	CDCl3
Temperature	292.7
Number of Scans	16
Spectrometer Frequency	400.18
Nucleus	1H

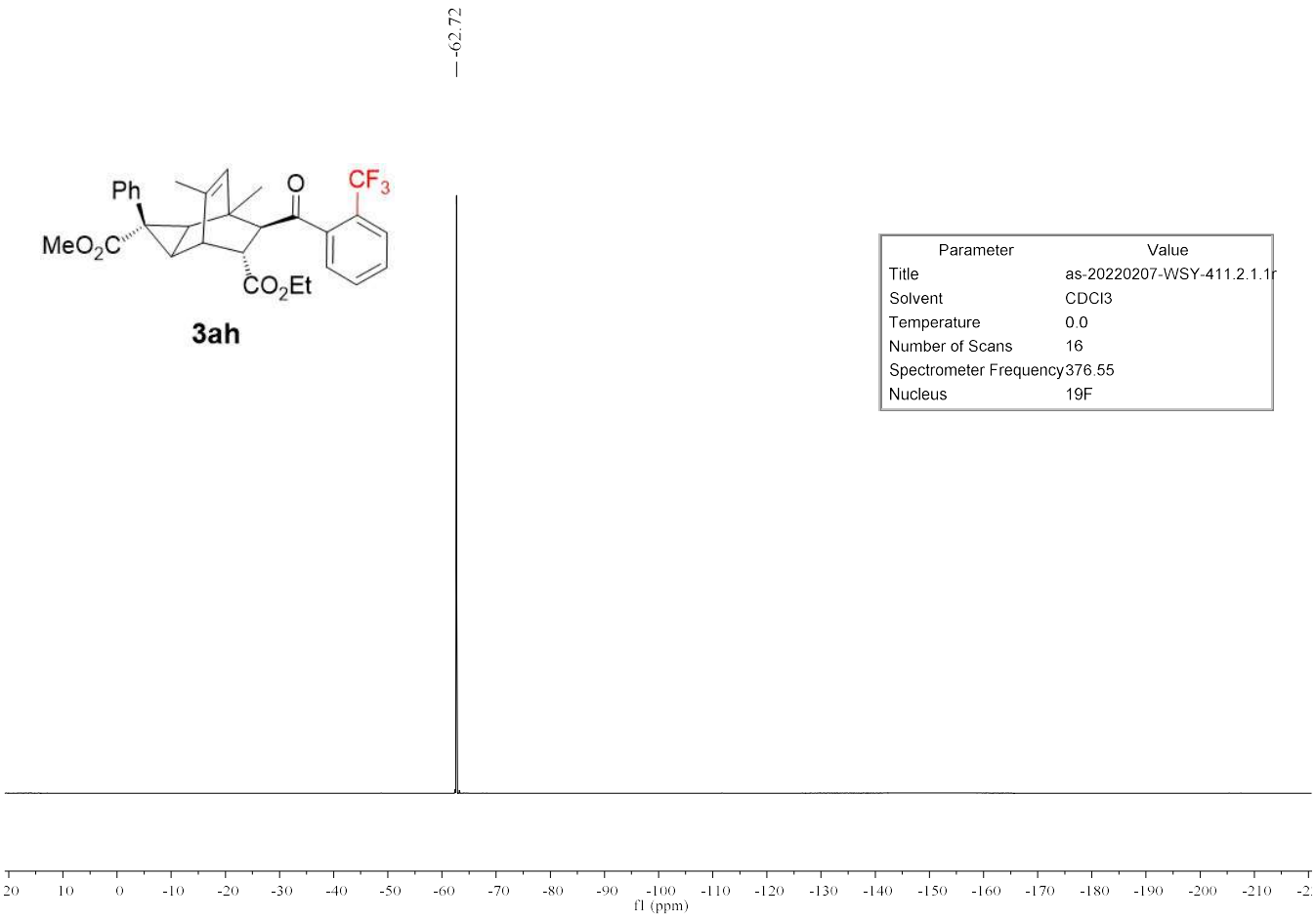


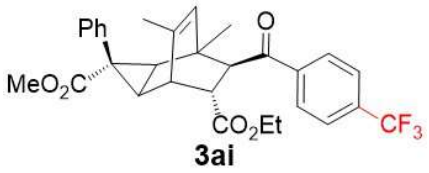


3ah

Parameter	Value
Title	wangsyuan-20220122-411.2.1.1r
Solvent	CDCl3
Temperature	293.3
Number of Scans	256
Spectrometer Frequency	100.63
Nucleus	13C

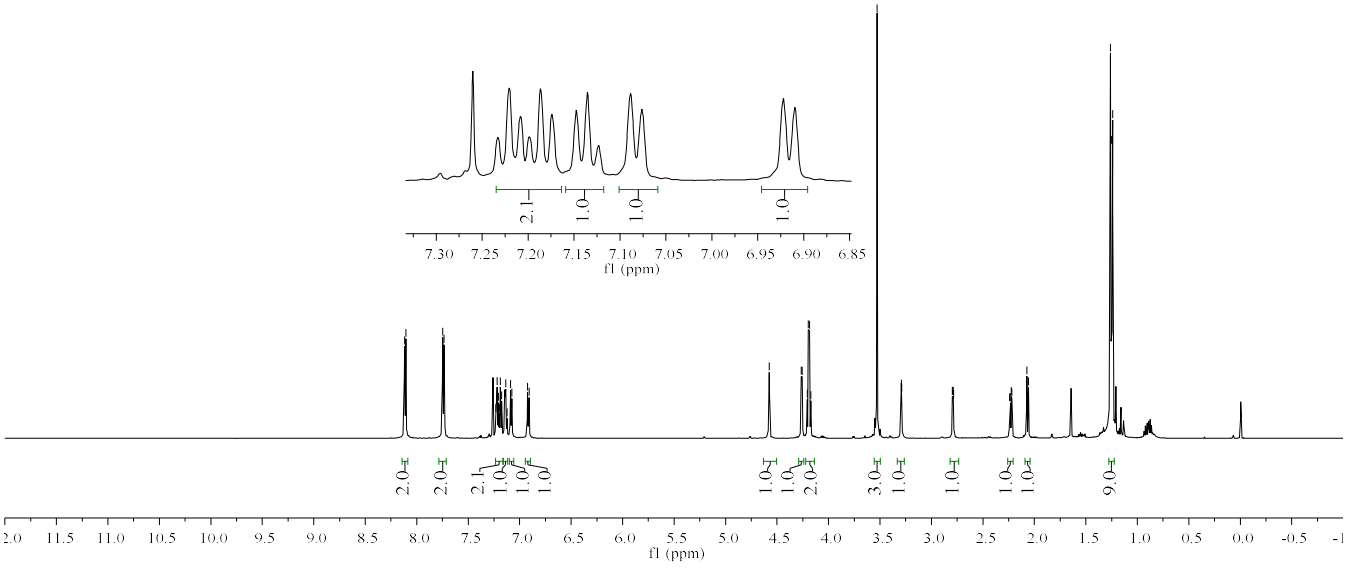


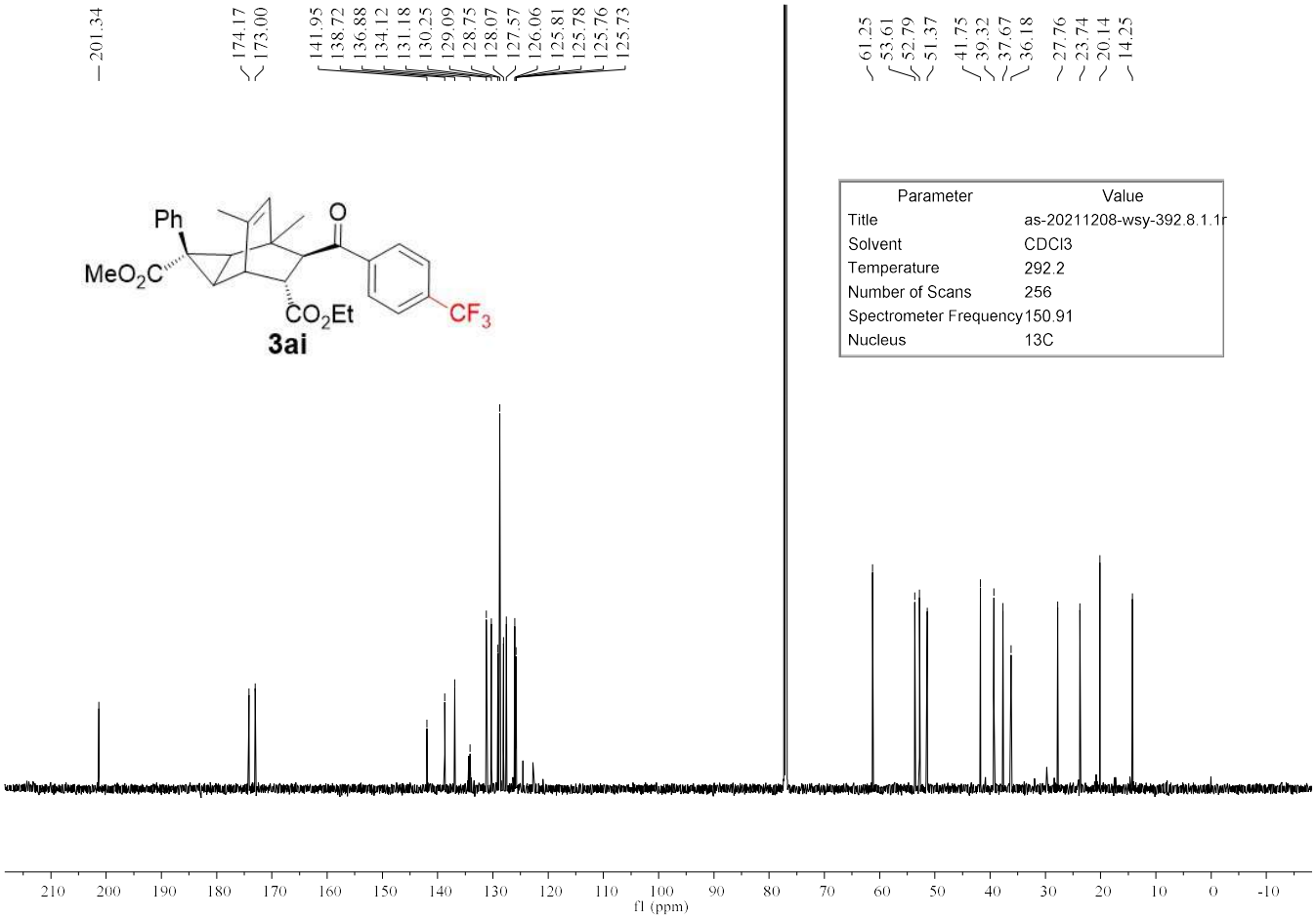

-62.72
Ph
O
CF3
MeO2C
CO2Et
3ah
Parameter
Value
Title
as-20220207-WSY-411.2.1.1r
Solvent
CDCl3
Temperature
0.0
Number of Scans
16
Spectrometer Frequency
376.55
Nucleus
19F
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)



3ai

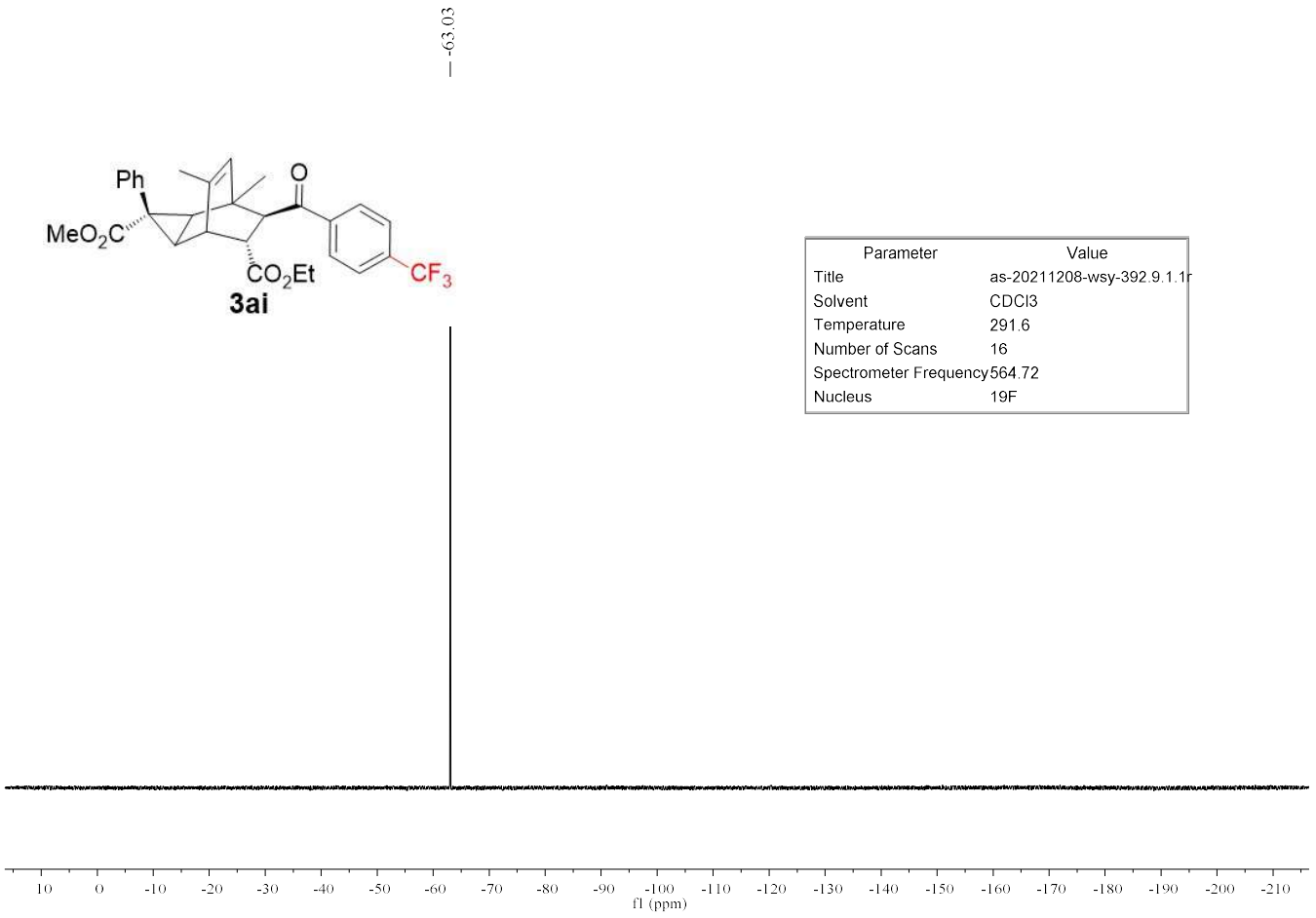
Parameter	Value
Title	as-20211208-wsy-392.7.1.1r
Solvent	CDCl3
Temperature	291.1
Number of Scans	16
Spectrometer Frequency	600.17
Nucleus	1H

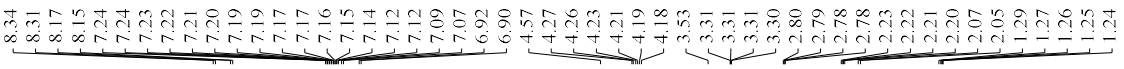


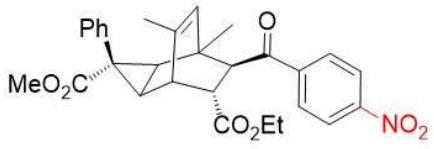


3ai

Parameter	Value
Title	as-20211208-wsy-392.8.1.1r
Solvent	CDCl3
Temperature	292.2
Number of Scans	256
Spectrometer Frequency	150.91
Nucleus	13C

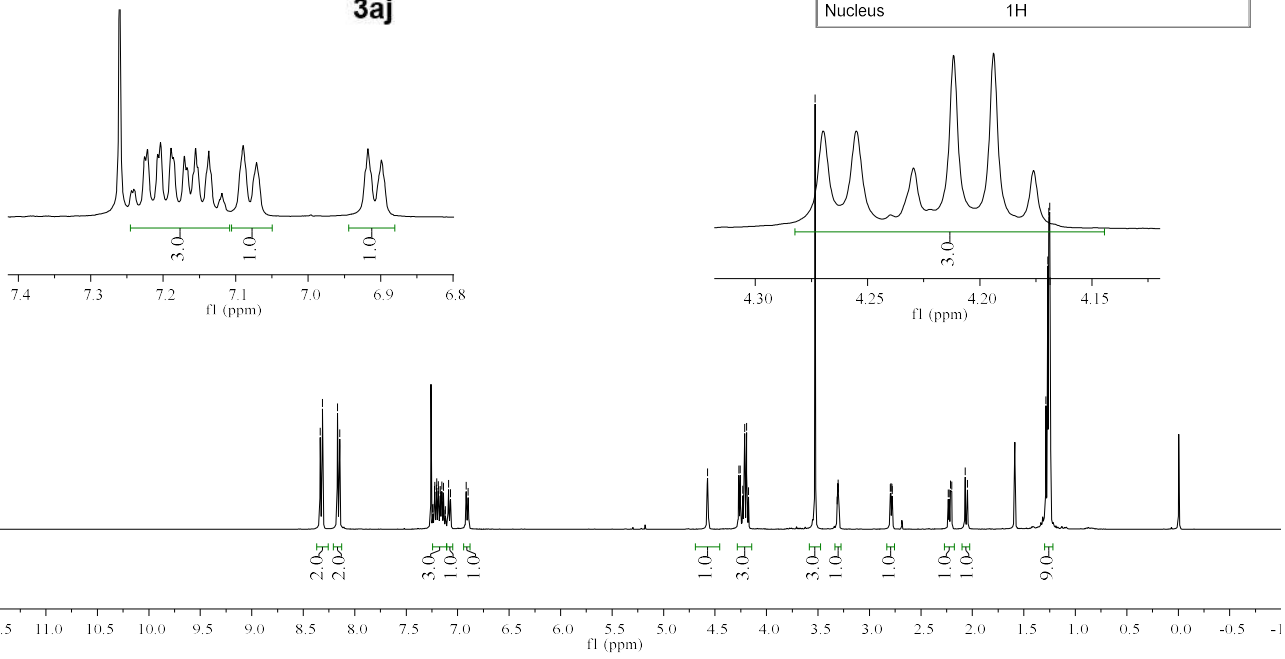

-63.03
Ph
O
MeO2C
CO2Et
CF3
3ai
Parameter Value
Title as-20211208-wsy-392.9.1.1r
Solvent CDCl3
Temperature 291.6
Number of Scans 16
Spectrometer Frequency 564.72
Nucleus 19F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

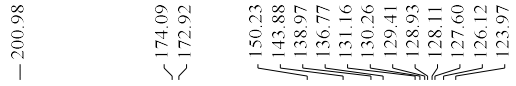




3aj

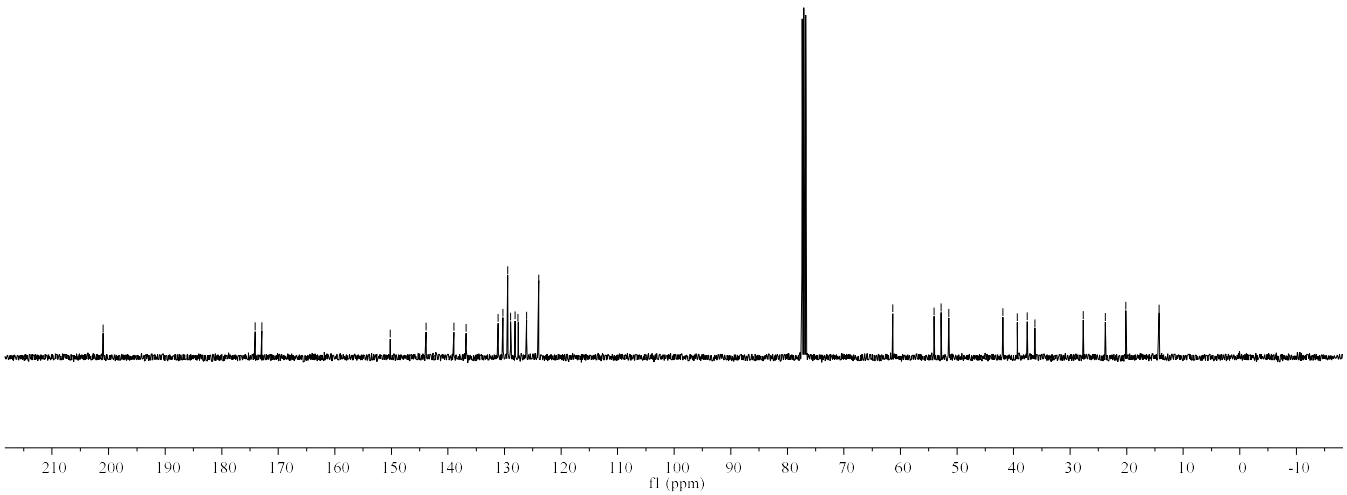
Parameter	Value
Title	wangsyuan-20211221-400B.1.1.1r
Solvent	CDCl3
Temperature	292.5
Number of Scans	16
Spectrometer Frequency	400.18
Nucleus	1H

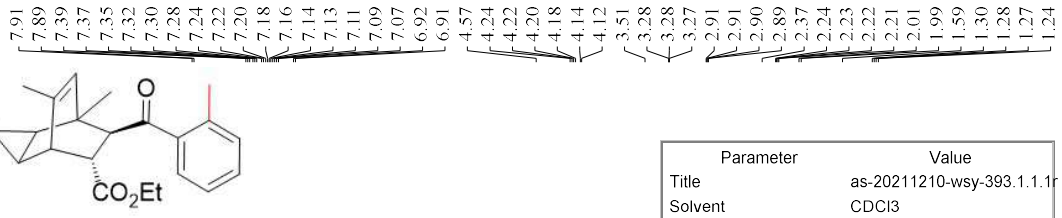




3aj

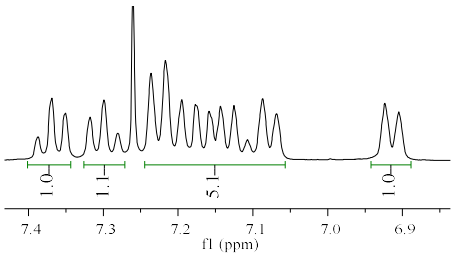
Parameter	Value
Title	wangsyuan-20211216-400B.12.1.1r
Solvent	CDCl3
Temperature	293.3
Number of Scans	256
Spectrometer Frequency	100.63
Nucleus	13C

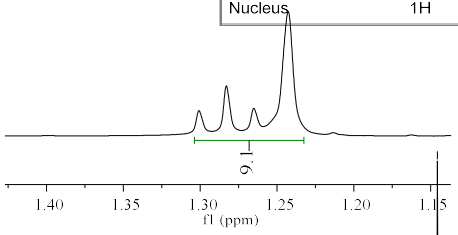


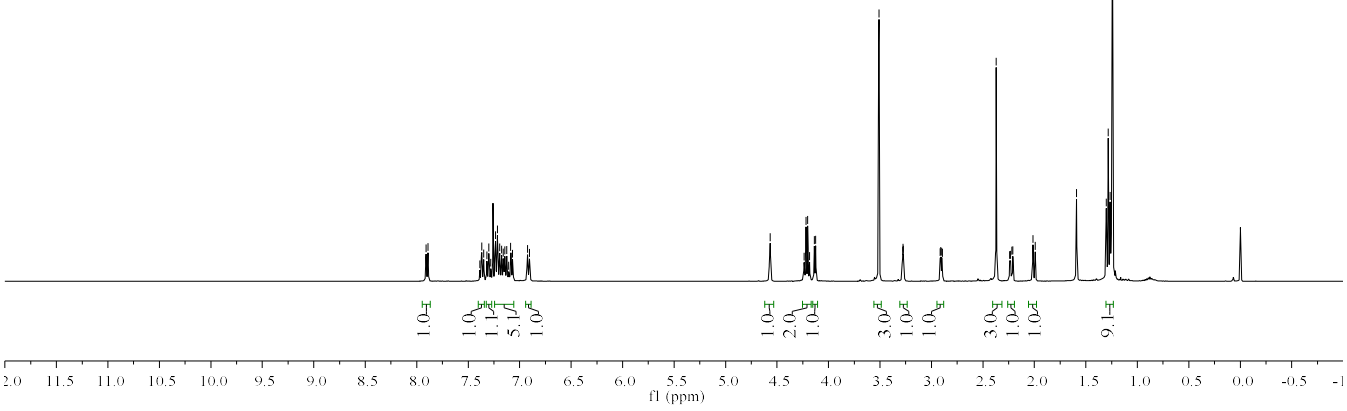


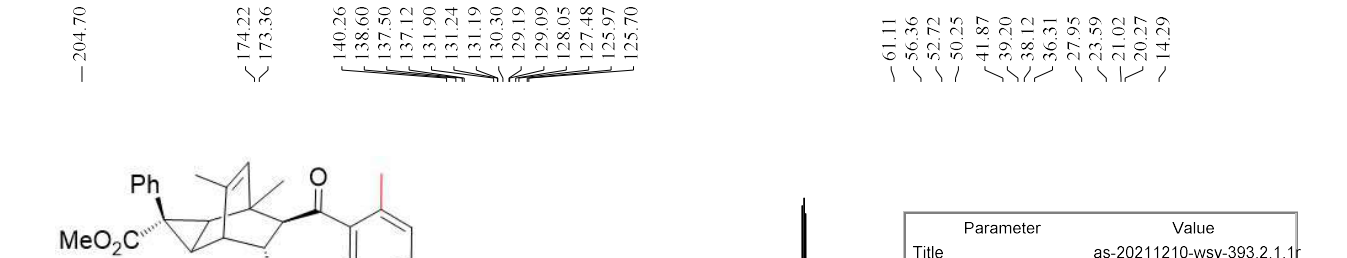
3ak

Parameter	Value
Title	as-20211210-wsy-393.1.1.1r
Solvent	CDCl3
Temperature	292.9
Number of Scans	16
Spectrometer Frequency	400.18
Nucleus	1H



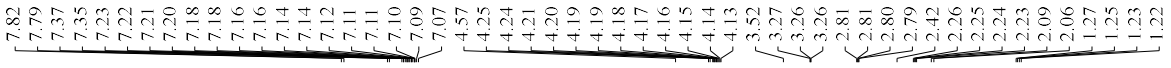


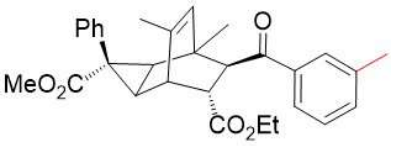




3ak

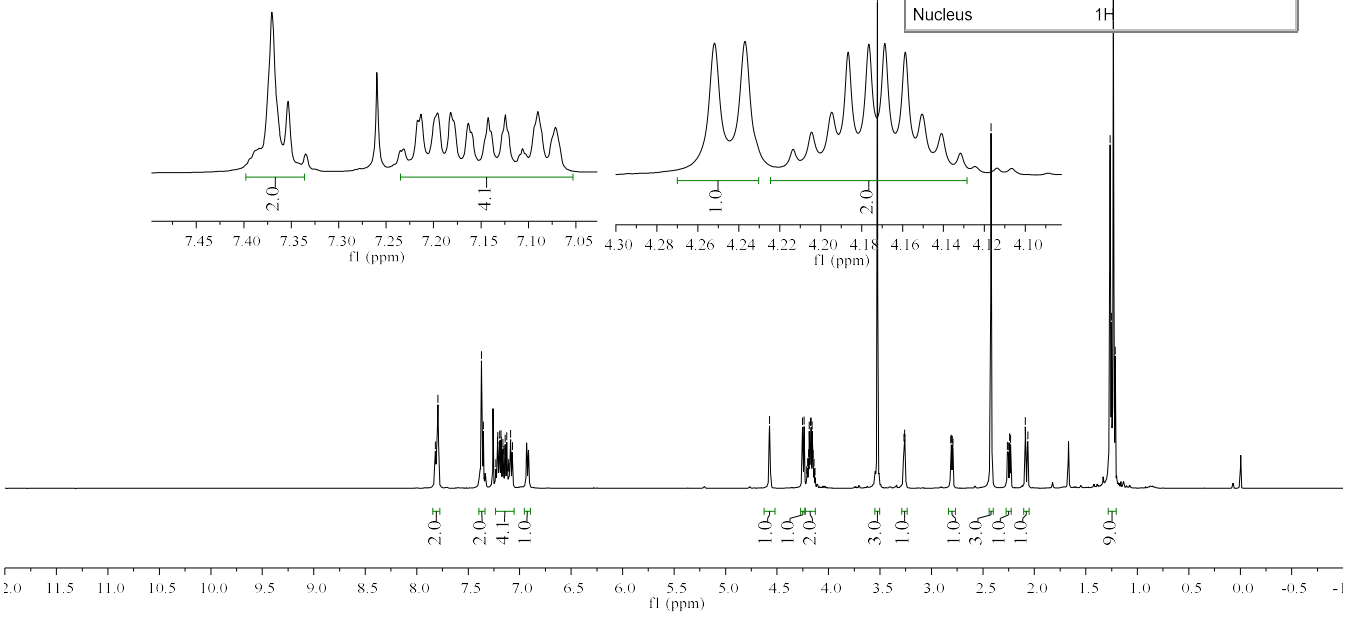
Parameter	Value
Title	as-20211210-wsy-393.2.1.1r
Solvent	CDCl3
Temperature	293.6
Number of Scans	256
Spectrometer Frequency	100.63
Nucleus	13C

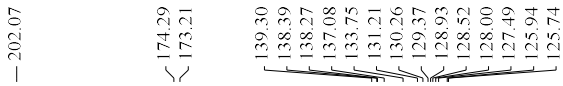


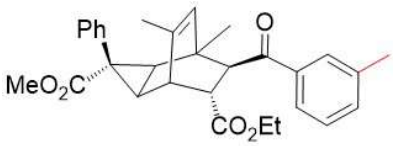


3al

Parameter	Value
Title	as-20211210-wsy-394.5.1.1r
Solvent	CDCl3
Temperature	292.8
Number of Scans	16
Spectrometer Frequency	400.18
Nucleus	1H

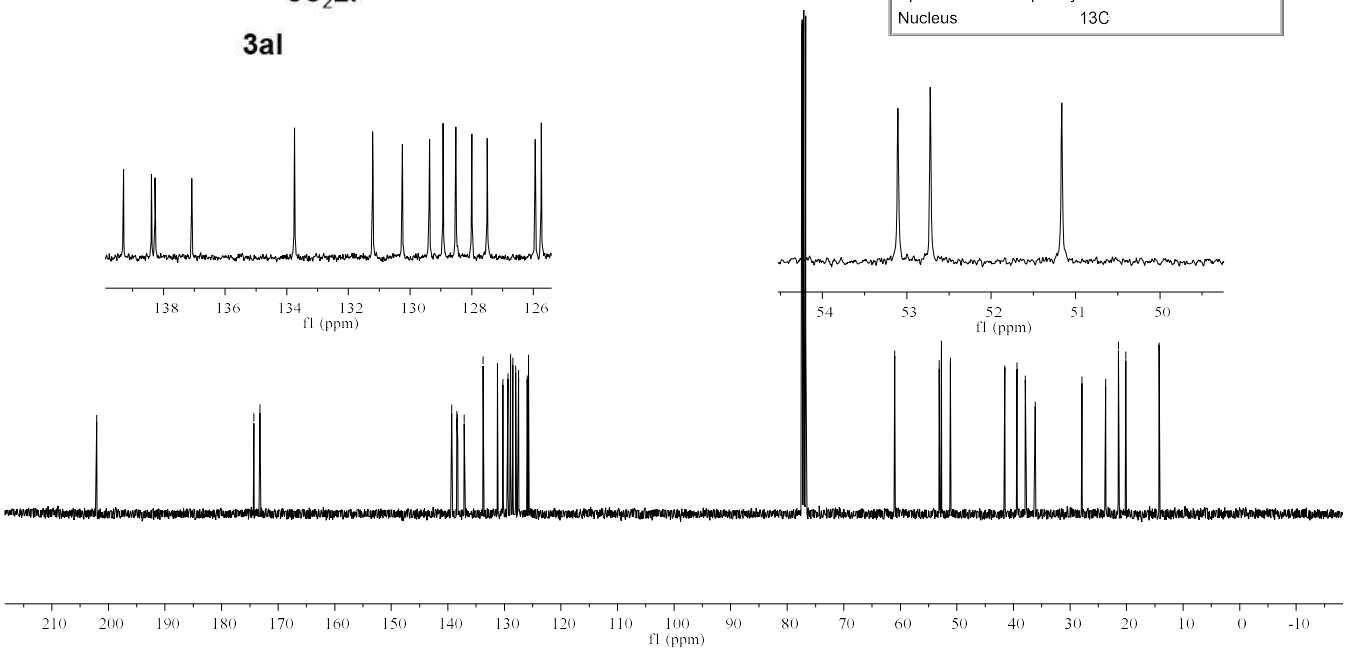


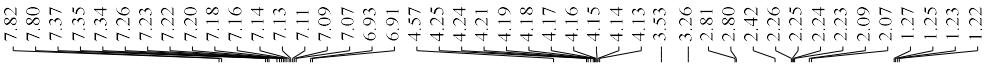


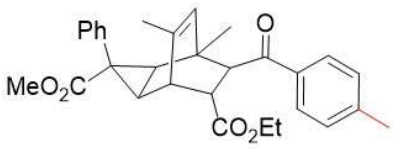


3al

Parameter	Value
Title	as-20211210-wsy-394.6.1.1r
Solvent	CDCl3
Temperature	293.4
Number of Scans	256
Spectrometer Frequency	100.63
Nucleus	13C

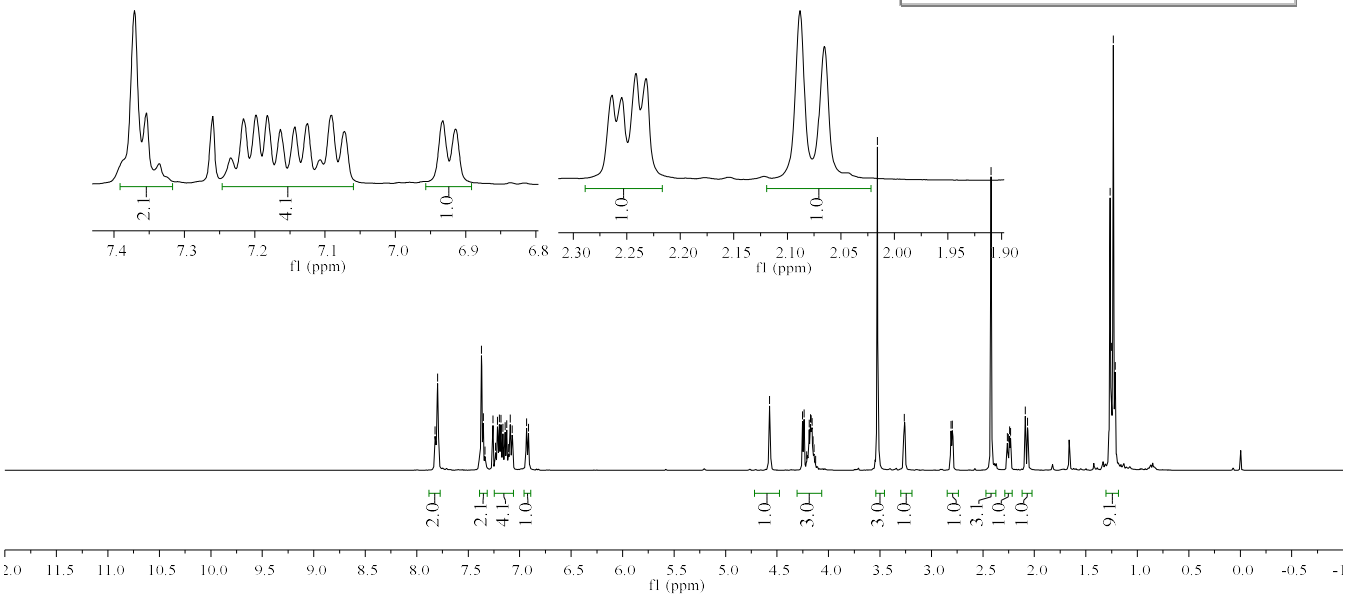


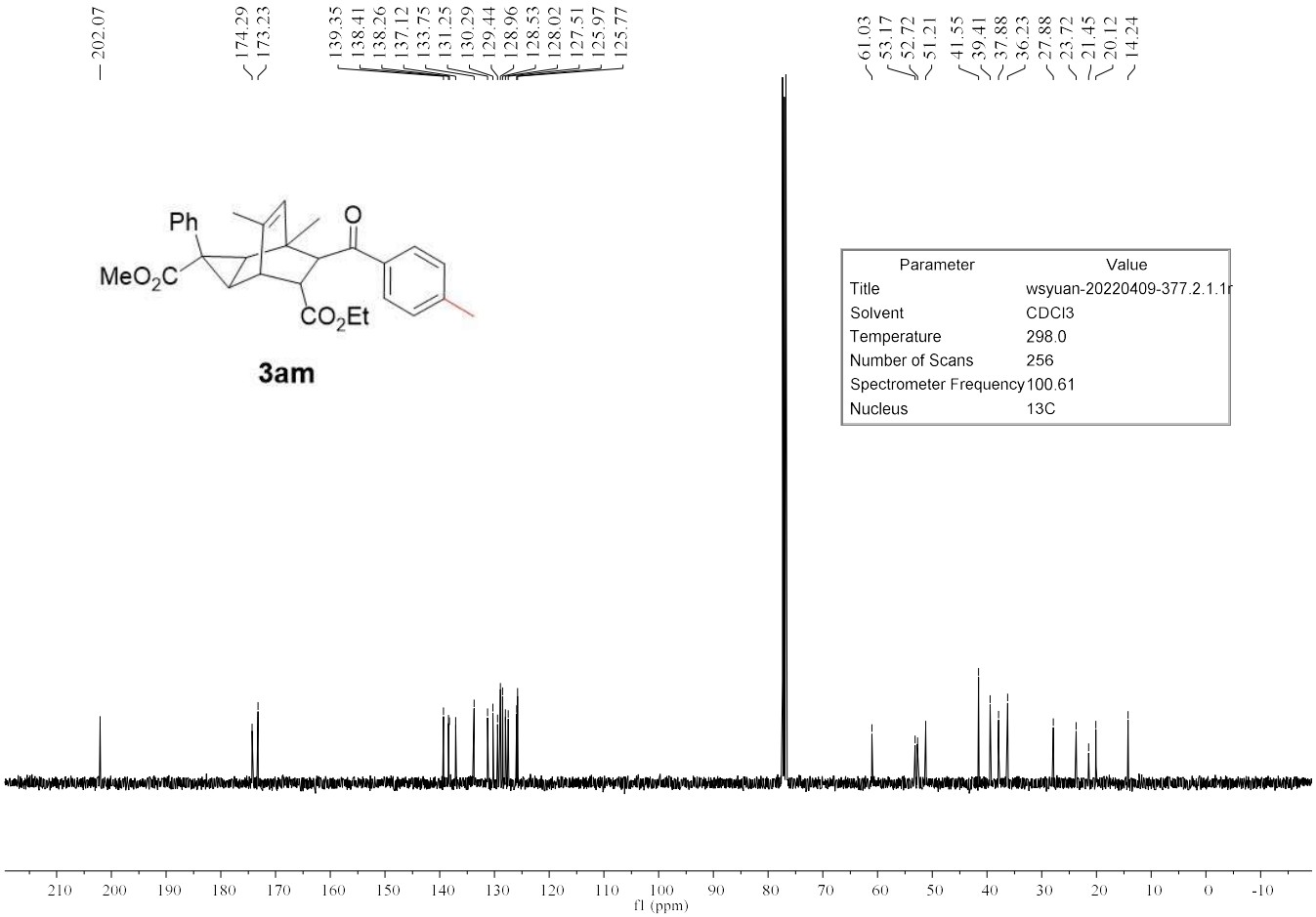




3am

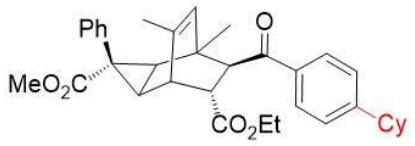
Parameter	Value
Title	wsyuan-20211124-377.1.1.1r
Solvent	CDCl3
Temperature	292.9
Number of Scans	16
Spectrometer Frequency	400.13
Nucleus	1H





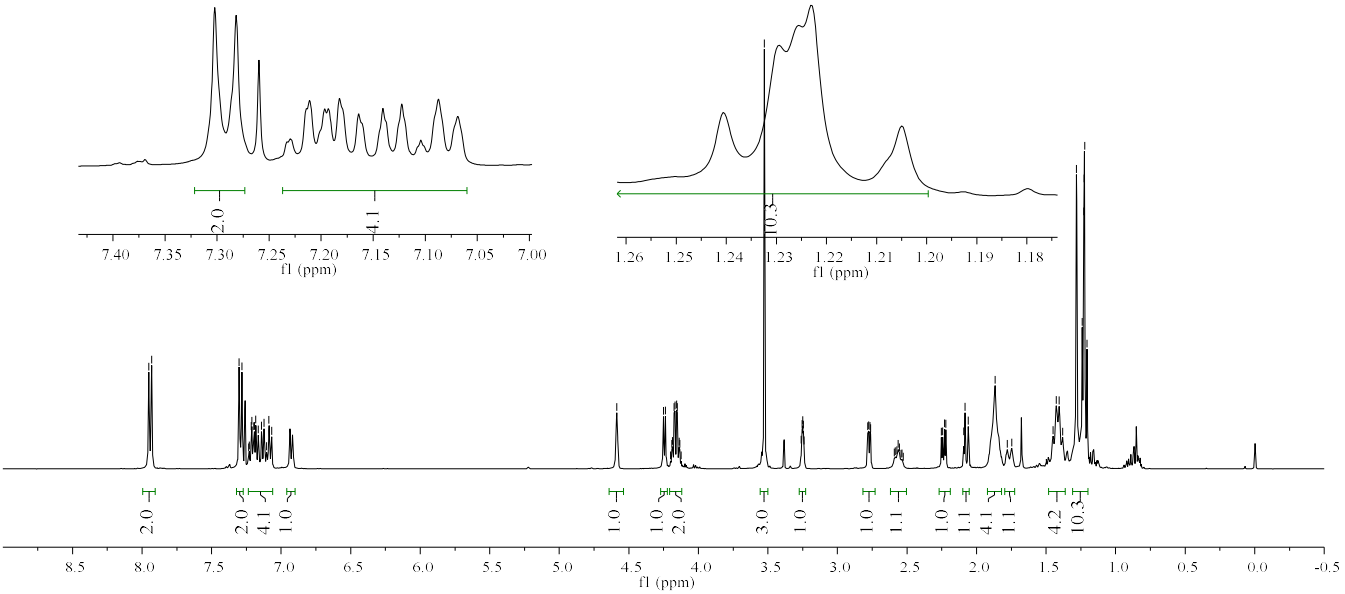
3am

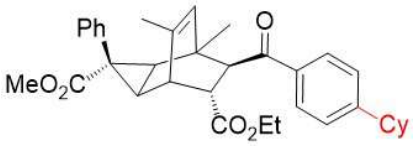
Parameter	Value
Title	wsyuan-20220409-377.2.1.1r
Solvent	CDCl3
Temperature	298.0
Number of Scans	256
Spectrometer Frequency	100.61
Nucleus	13C



3an

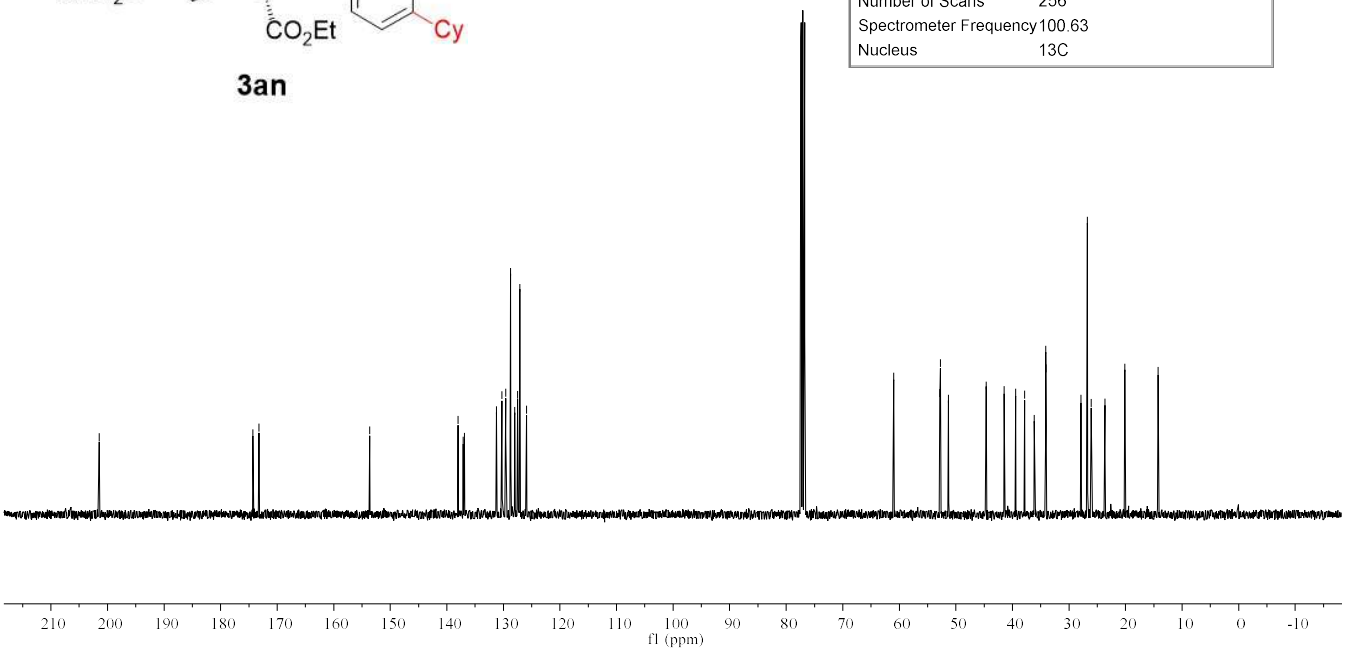
Parameter	Value
Title	wangsyuan-20220122-409.1.1.1r
Solvent	CDCl3
Temperature	292.5
Number of Scans	16
Spectrometer Frequency	400.18
Nucleus	1H

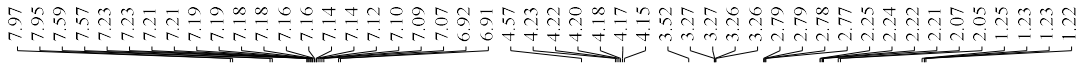


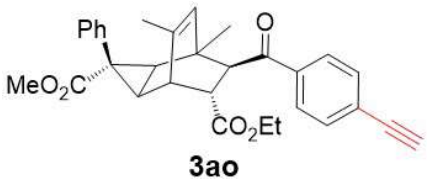


3an

Parameter	Value
Title	wangsyuan-20220122-409.2.1.1r
Solvent	CDCl3
Temperature	293.2
Number of Scans	256
Spectrometer Frequency	100.63
Nucleus	13C

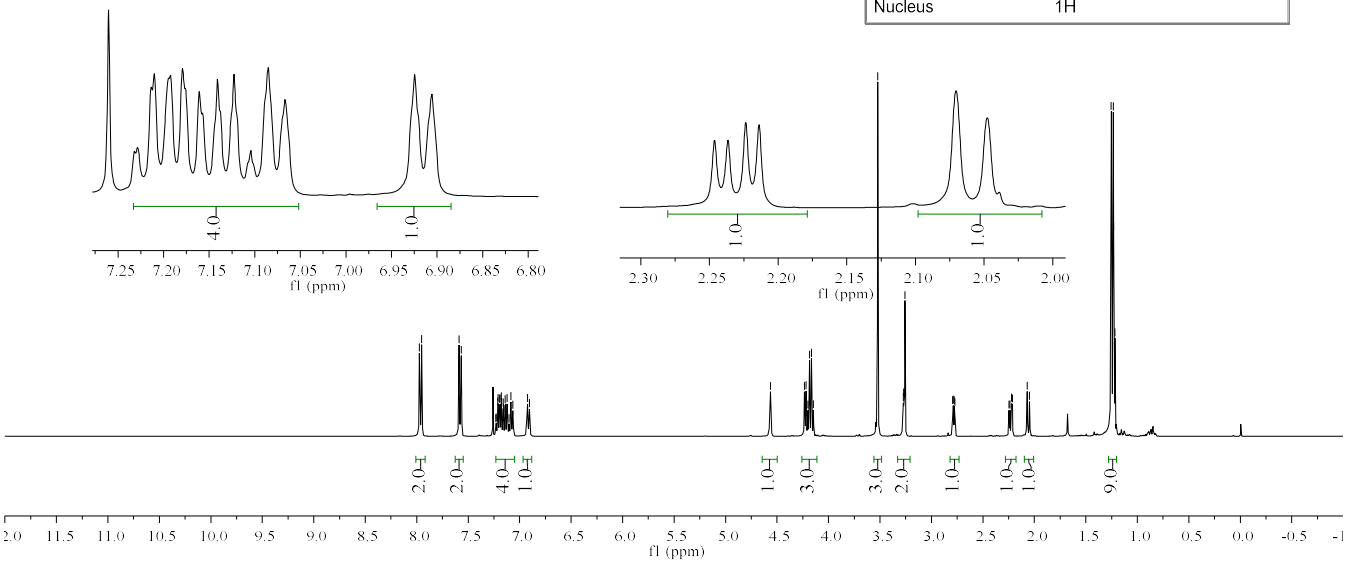


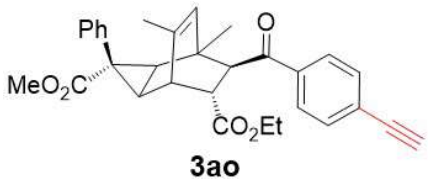




3ao

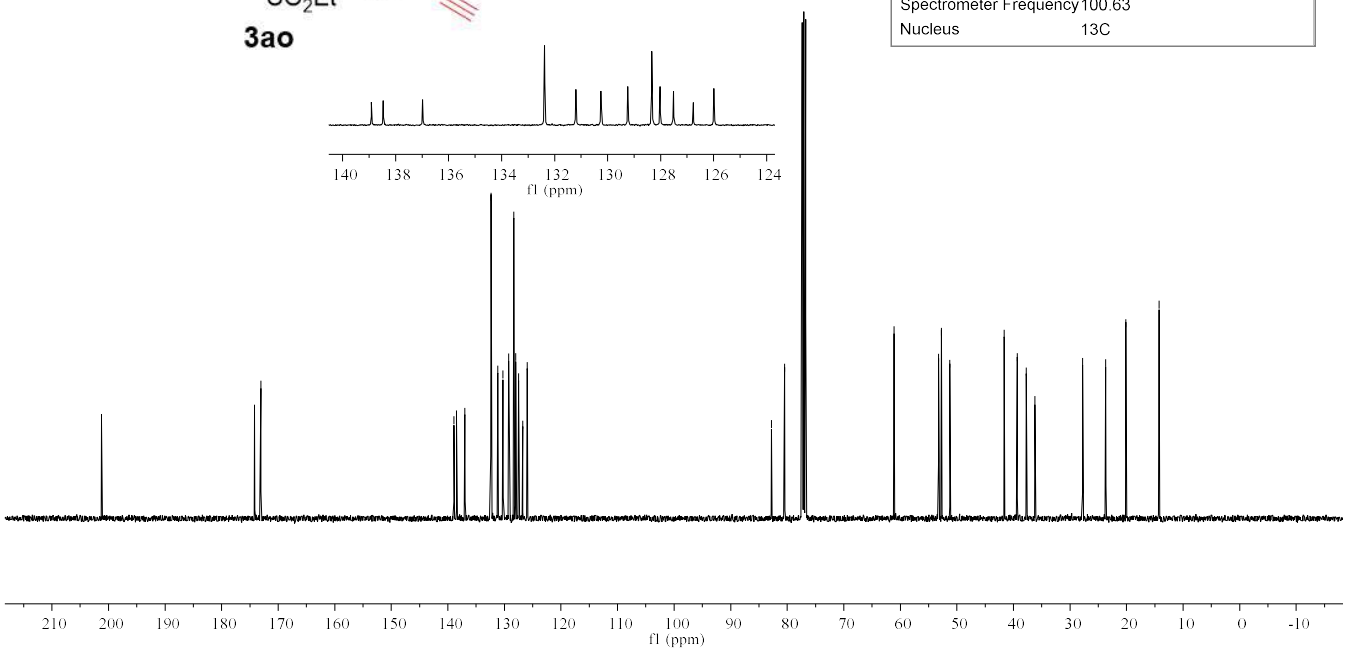
Parameter	Value
Title	wangsyuan-20220304-423.3.1.1r
Solvent	CDCl3
Temperature	295.0
Number of Scans	16
Spectrometer Frequency	400.18
Nucleus	1H

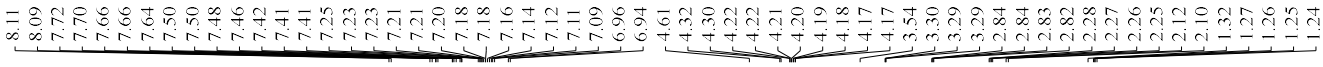


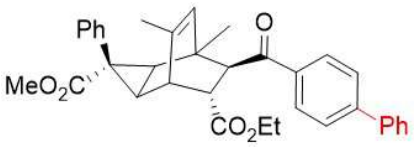


3ao

Parameter	Value
Title	wangsyuan-20220304-423.4.1.1r
Solvent	CDCl3
Temperature	295.8
Number of Scans	512
Spectrometer Frequency	100.63
Nucleus	13C

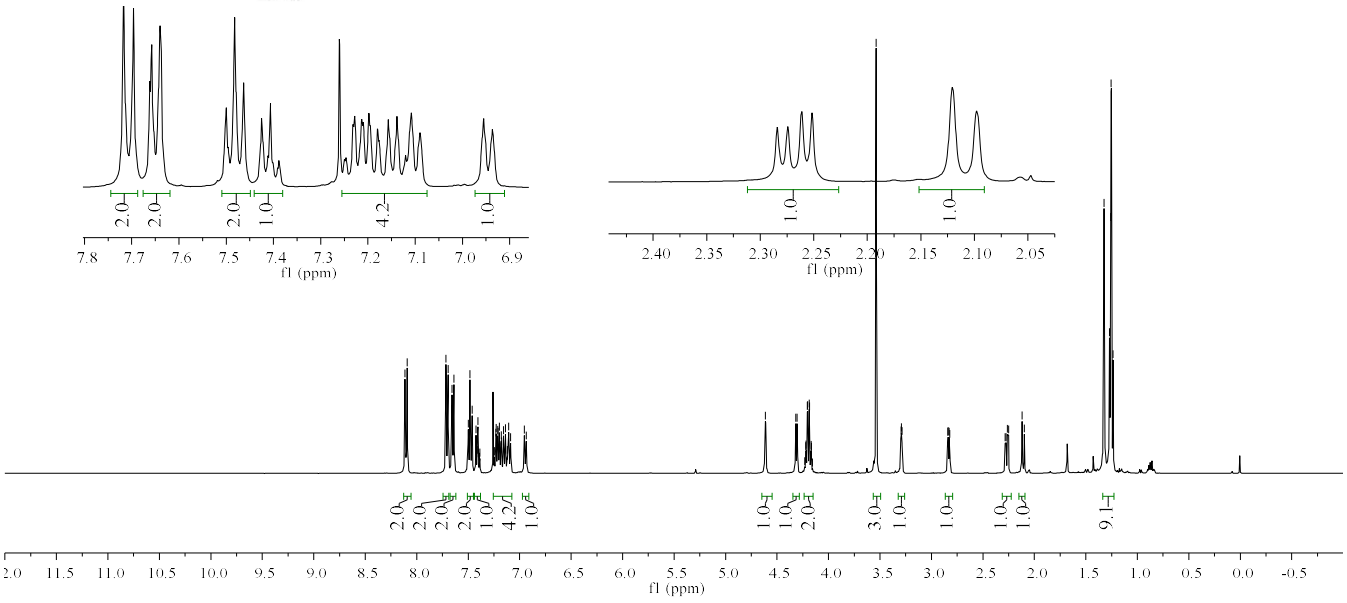


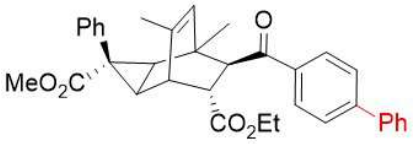




3ap

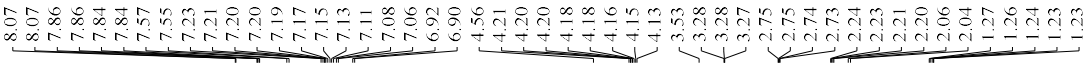
Parameter	Value
Title	wangsyuan-20211216-399.7.1.1r
Solvent	CDCl3
Temperature	292.7
Number of Scans	16
Spectrometer Frequency	400.18
Nucleus	1H

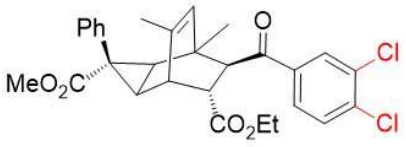




3ap

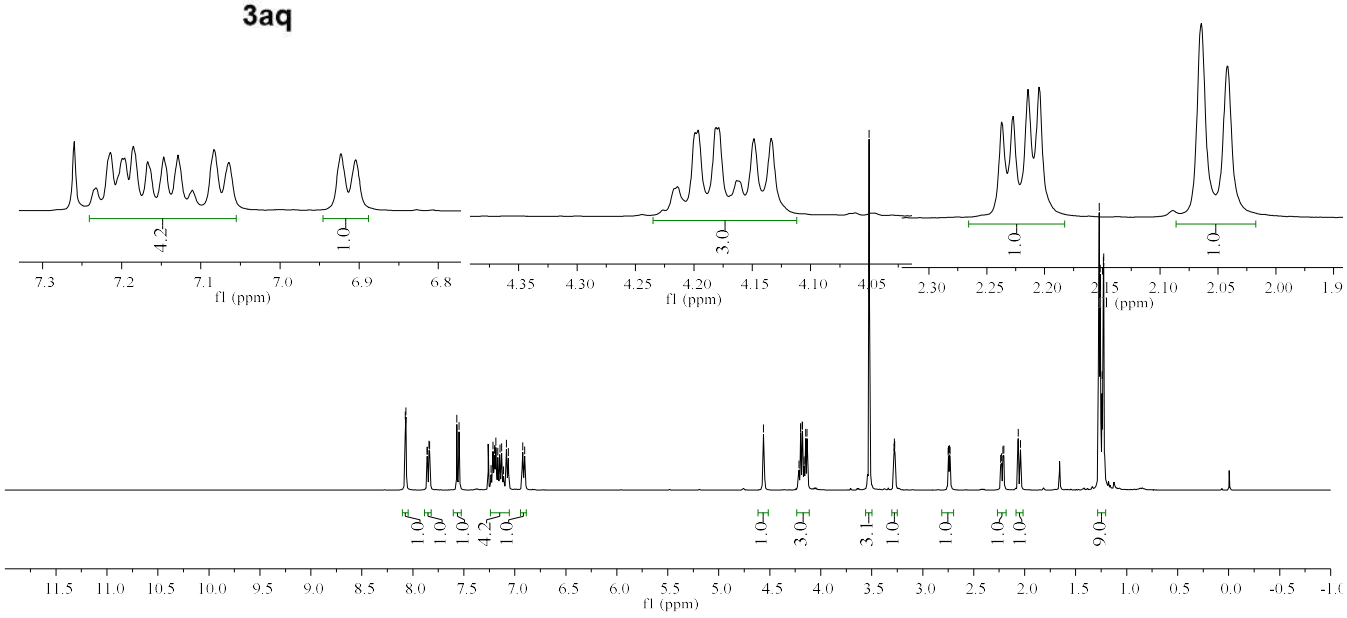
Parameter	Value
Title	wangsyuan-20211216-399.8.1.1r
Solvent	CDCl3
Temperature	293.4
Number of Scans	256
Spectrometer Frequency	100.63
Nucleus	13C

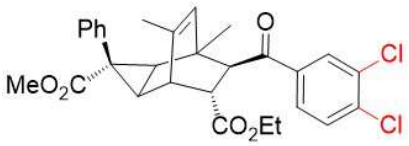




3aq

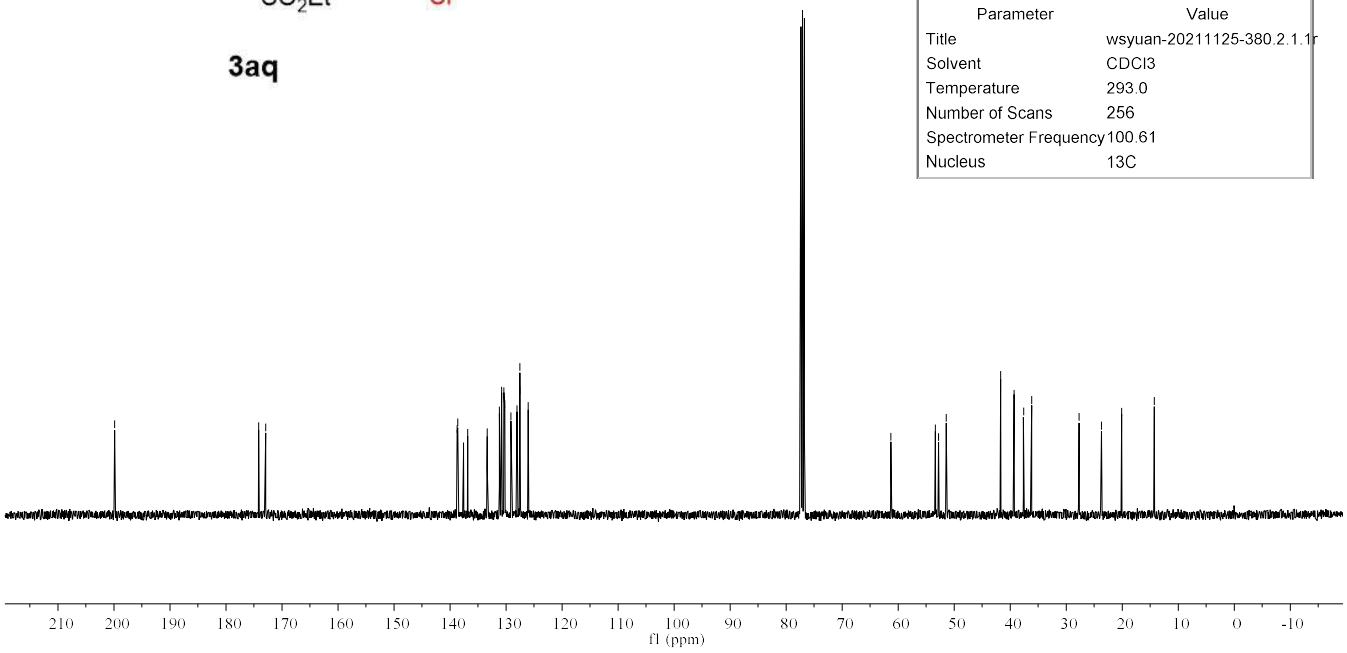
Parameter	Value
Title	wsyuan-20211125-380.1.1.1r
Solvent	CDCl3
Temperature	292.8
Number of Scans	16
Spectrometer Frequency	400.13
Nucleus	1H

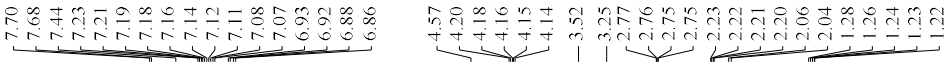


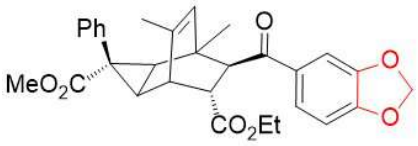


3aq

Parameter	Value
Title	wsyuan-20211125-380.2.1.1r
Solvent	CDCl3
Temperature	293.0
Number of Scans	256
Spectrometer Frequency	100.61
Nucleus	13C

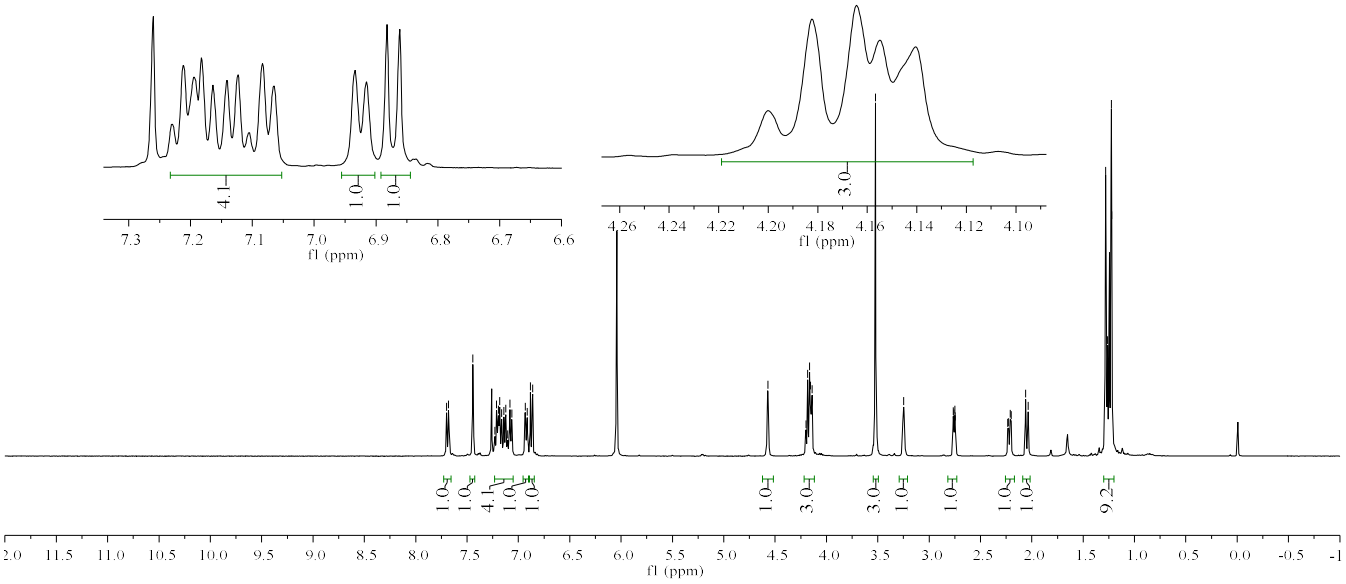


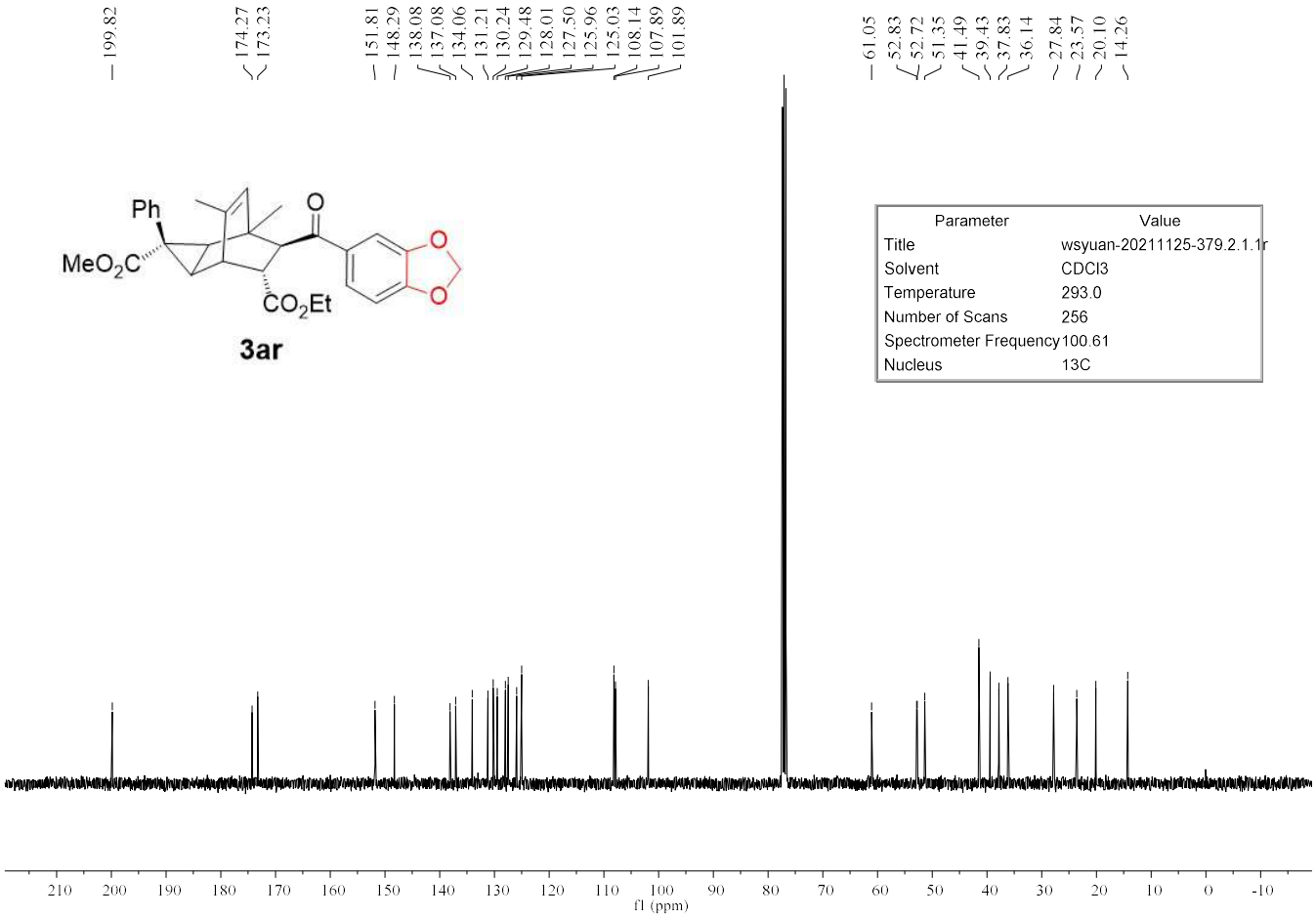




3ar

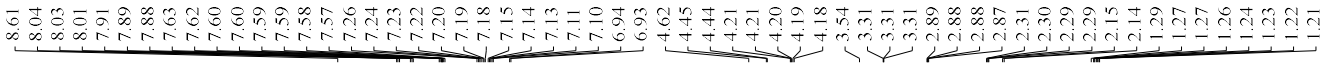
Parameter	Value
Title	wsyuan-20211125-379.1.1.1r
Solvent	CDCl3
Temperature	292.7
Number of Scans	16
Spectrometer Frequency	400.13
Nucleus	1H

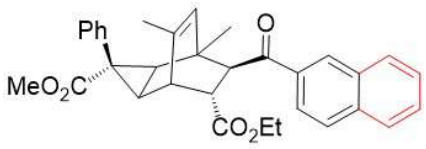




3ar

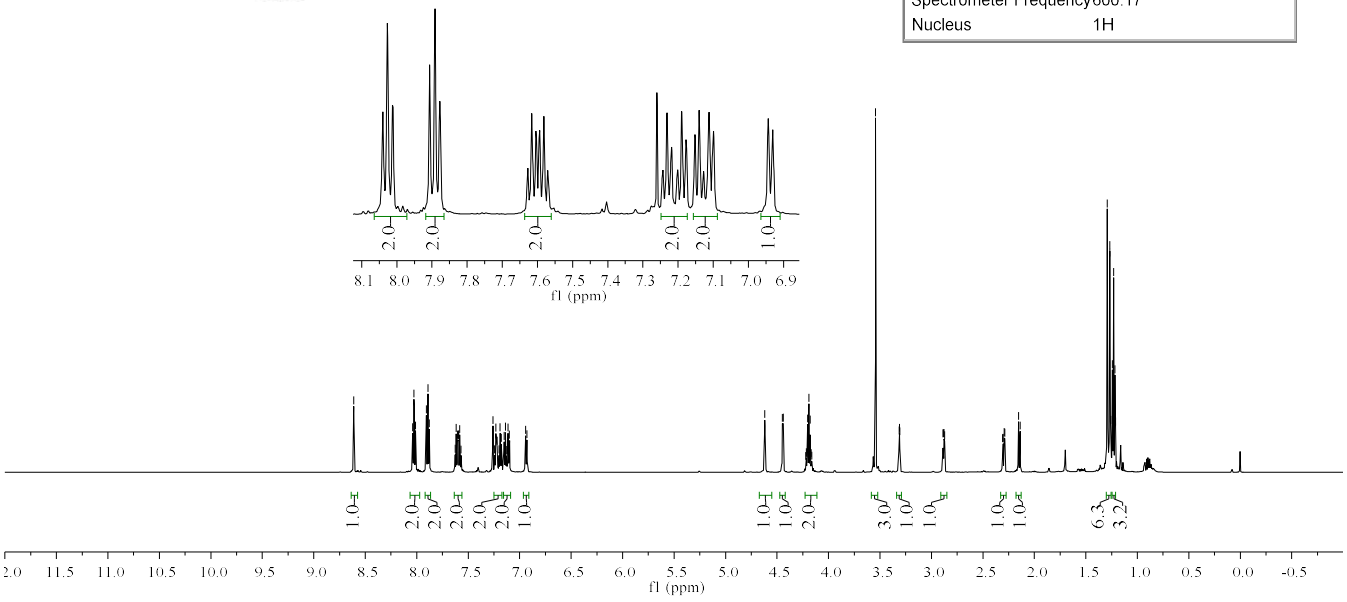
Parameter	Value
Title	wsyuan-20211125-379.2.1.1r
Solvent	CDCl3
Temperature	293.0
Number of Scans	256
Spectrometer Frequency	100.61
Nucleus	13C

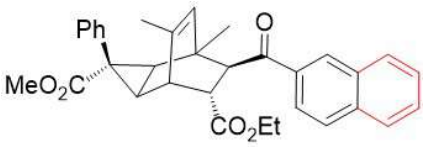




3as

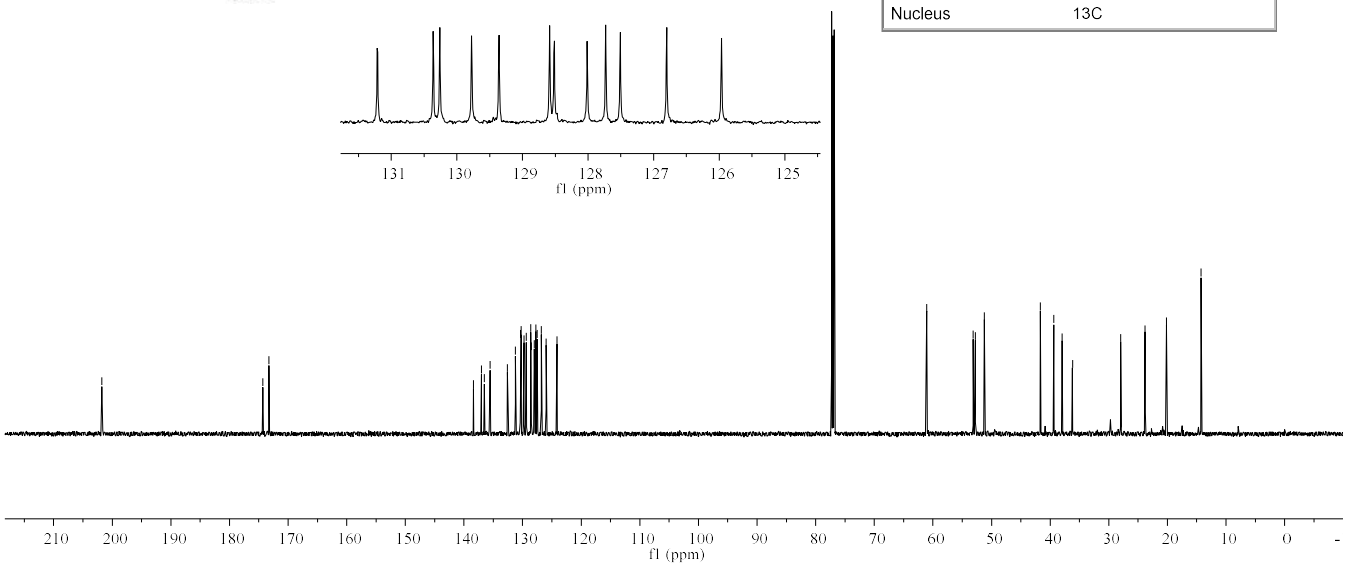
Parameter	Value
Title	as-20211208-wsy-390.1.1.1r
Solvent	CDCl3
Temperature	291.5
Number of Scans	16
Spectrometer Frequency	600.17
Nucleus	1H

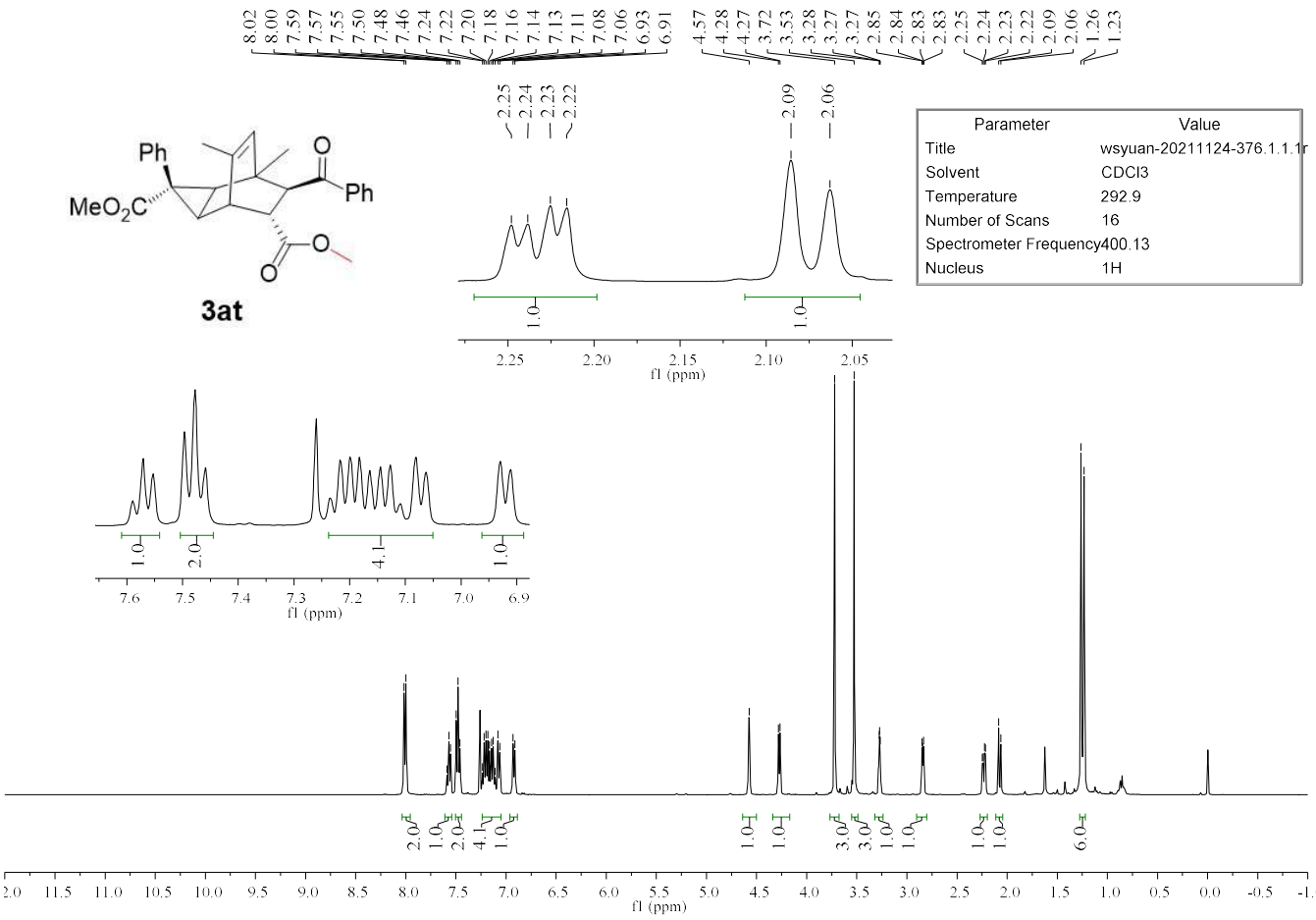


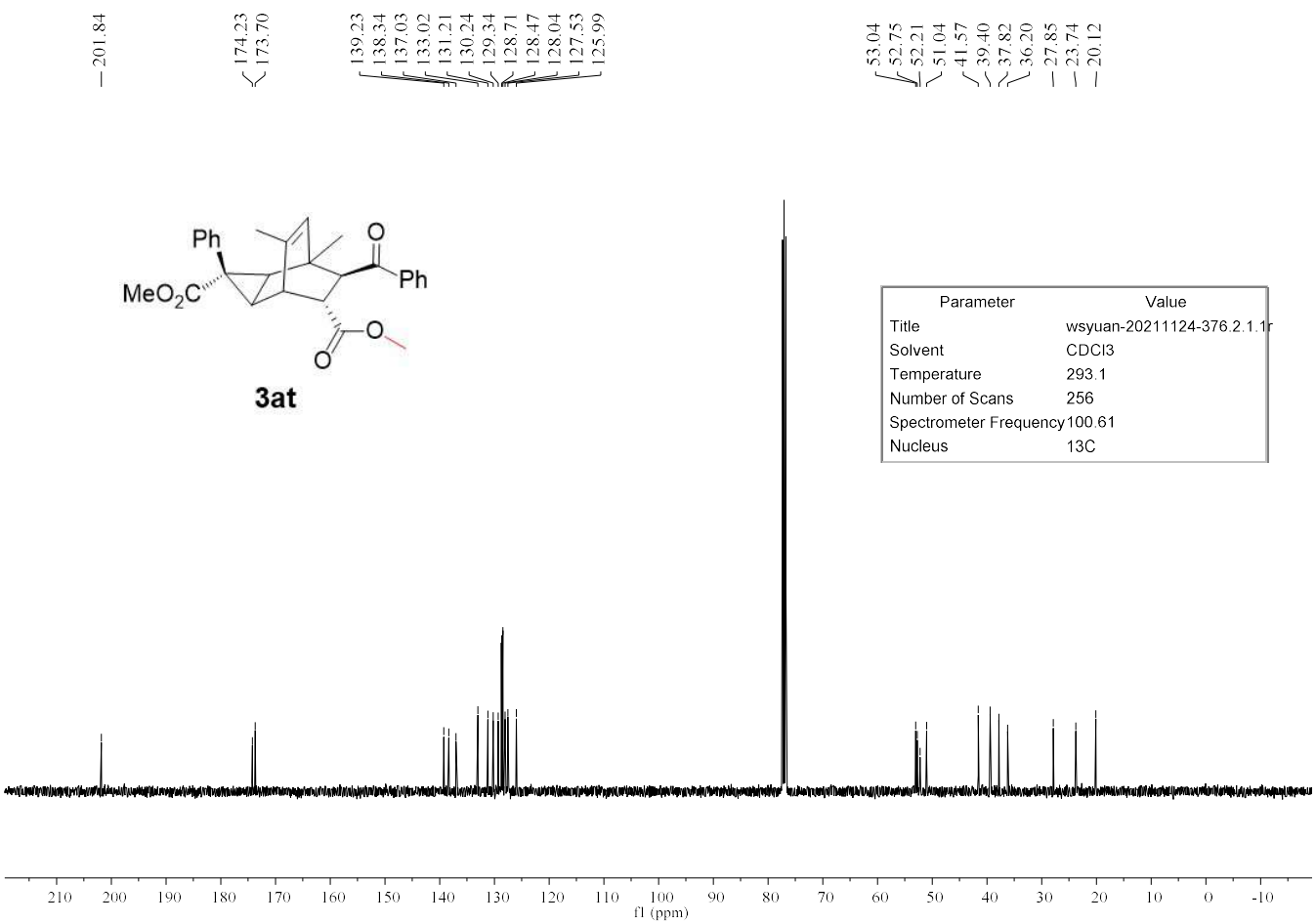


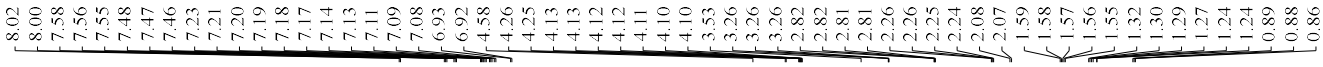
3as

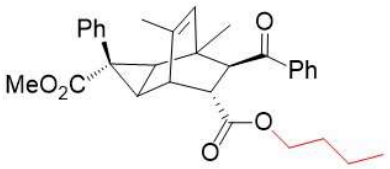
Parameter	Value
Title	as-20211208-wsy-390.2.1.1r
Solvent	CDCl3
Temperature	292.4
Number of Scans	256
Spectrometer Frequency	150.91
Nucleus	13C




8.02 8.00 7.59 7.57 7.55 7.50 7.48 7.46 7.24 7.22 7.20 7.18 7.16 7.14 7.13 7.11 7.08 7.06 6.93 6.91
4.57 4.28 4.27 3.72 3.53 3.28 3.27 3.27 2.85 2.84 2.83 2.83 2.25 2.24 2.23 2.22 2.09 2.06 1.26 1.23
Ph
O
Ph
MeO2C
O
O
3at
Parameter Value
Title wsyuan-20211124-376.1.1.1r
Solvent CDCl3
Temperature 292.9
Number of Scans 16
Spectrometer Frequency 400.13
Nucleus 1H
f1 (ppm)

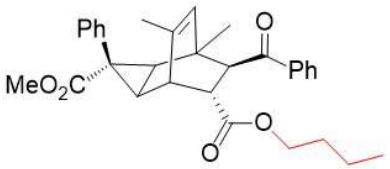

201.84
174.23 173.70
139.23 138.34 137.03 133.02 131.21 130.24 129.34 128.71 128.47 128.04 127.53 125.99
53.04 52.75 52.21 51.04 41.57 39.40 37.82 36.20 27.85 23.74 20.12
Ph
O
Ph
MeO2C
O
O
3at
Parameter Value
Title wsyuan-20211124-376.2.1.1r
Solvent CDCl3
Temperature 293.1
Number of Scans 256
Spectrometer Frequency 100.61
Nucleus 13C
f1 (ppm)





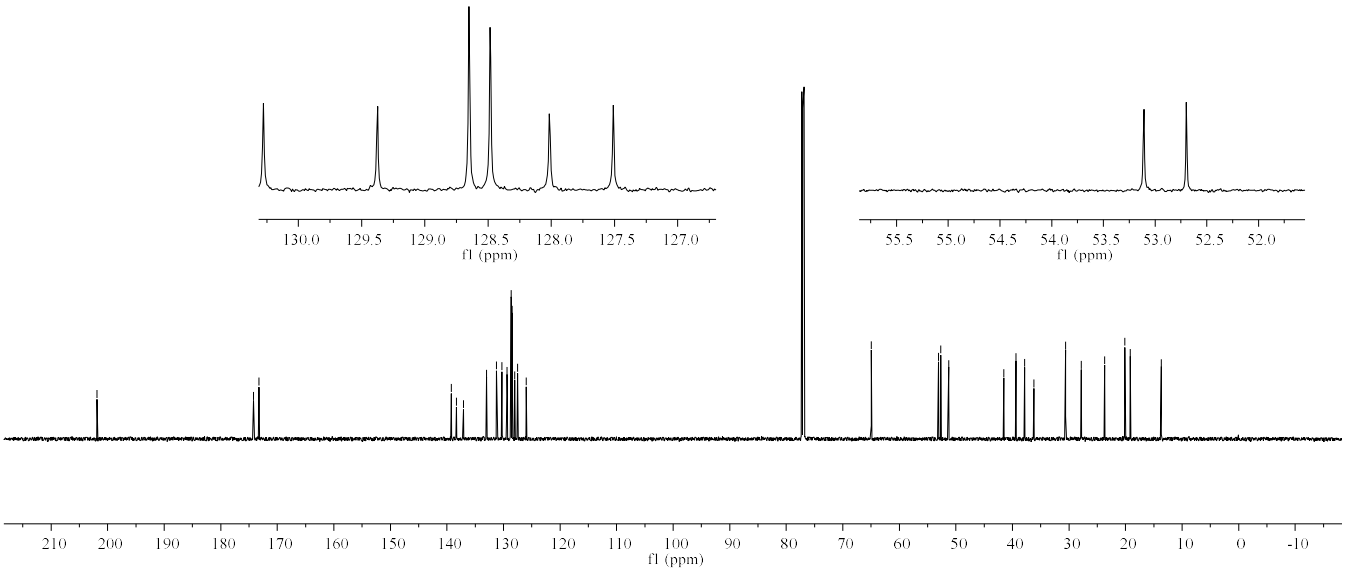
3au

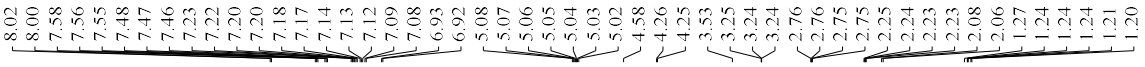
Parameter	Value
Title	as-20211201-WSY-387.10.1.1r
Solvent	CDCl3
Temperature	297.1
Number of Scans	16
Spectrometer Frequency	600.17
Nucleus	1H

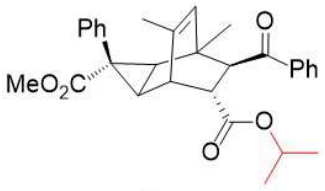


3au

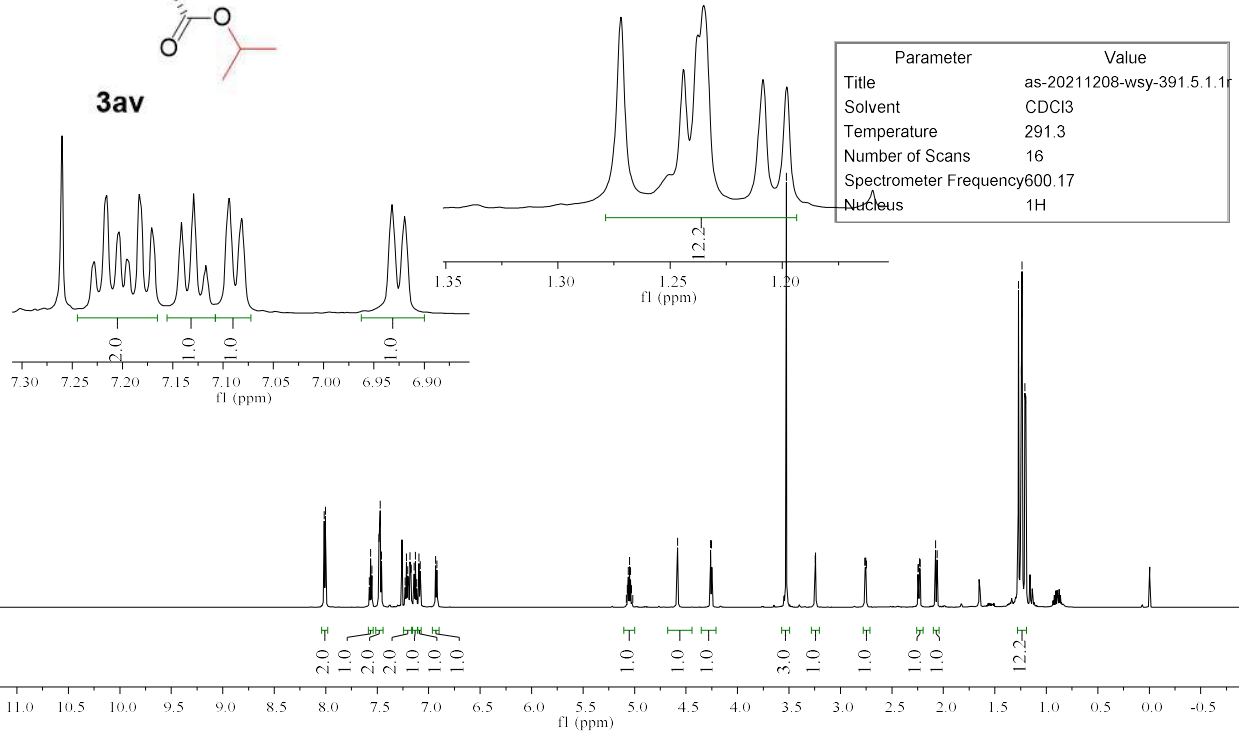
Parameter	Value
Title	as-20211201-WSY-387.11.1.1r
Solvent	CDCl3
Temperature	298.0
Number of Scans	256
Spectrometer Frequency	150.91
Nucleus	13C

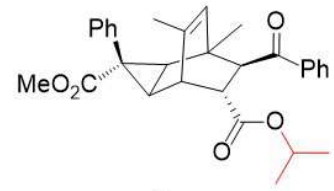






3av


Parameter Value
Title as-20211208-wsy-391.5.1.1r
Solvent CDCl3
Temperature 291.3
Number of Scans 16
Spectrometer Frequency 600.17
Nucleus 1H
fl (ppm)

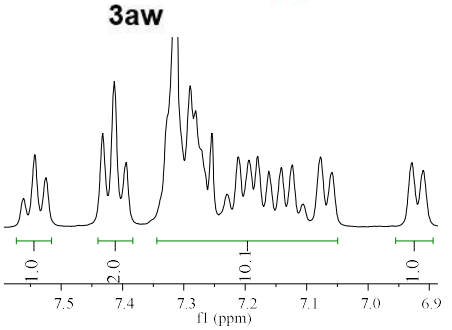


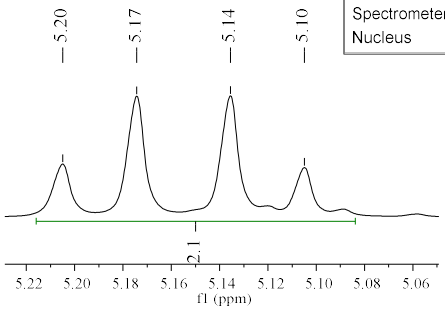
3av

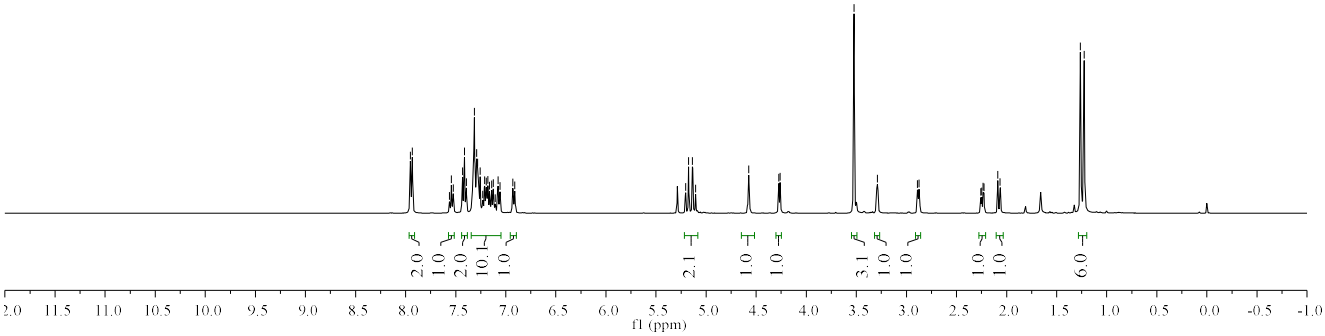
Parameter Value
Title as-20211208-wsy-391.6.1.1r
Solvent CDCl3
Temperature 292.2
Number of Scans 256
Spectrometer Frequency 150.91
Nucleus 13C
fl (ppm)

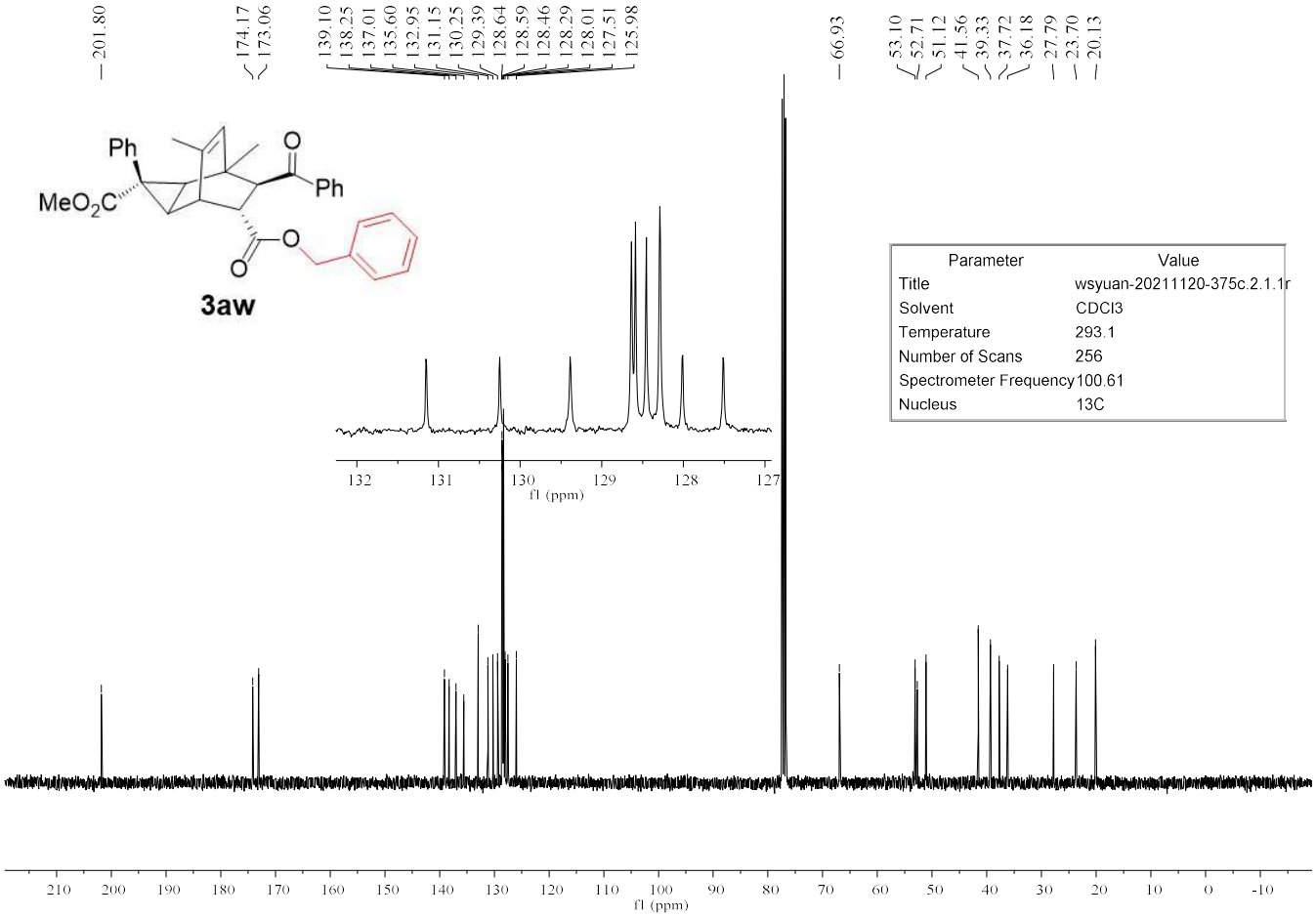
3aw

Parameter	Value
Title	wsyuan-20211120-375b.1.1.1r
Solvent	CDCl3
Temperature	292.9
Number of Scans	16
Spectrometer Frequency	400.13
Nucleus	1H







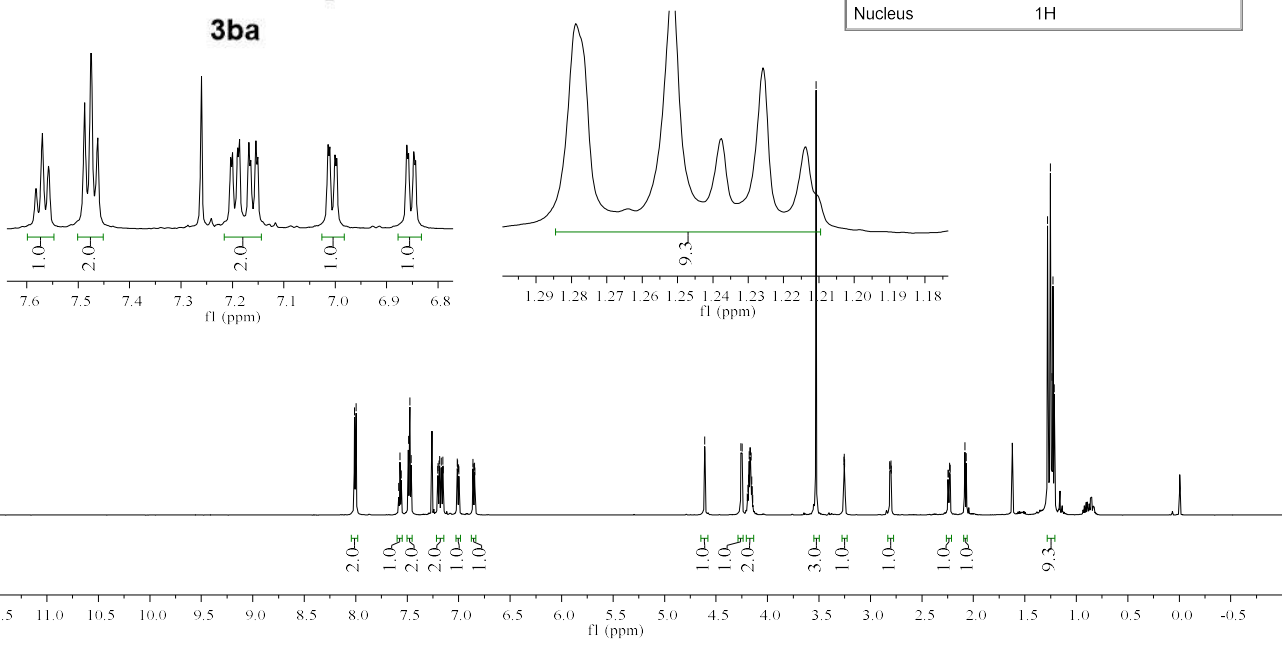


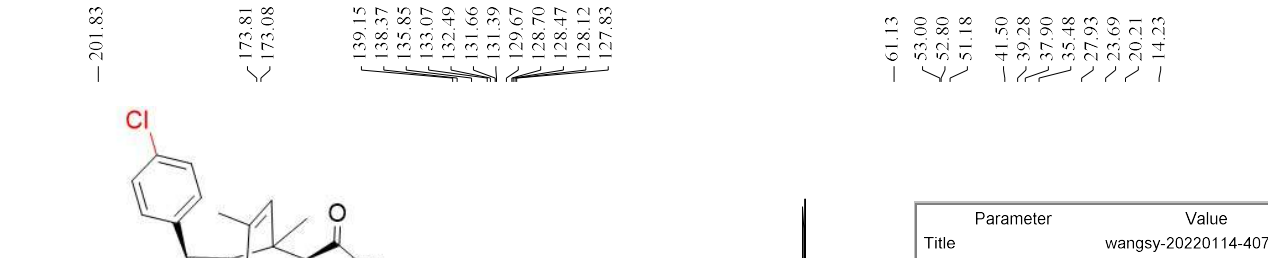
3aw

Parameter	Value
Title	wsyuan-20211120-375c.2.1.1r
Solvent	CDCl3
Temperature	293.1
Number of Scans	256
Spectrometer Frequency	100.61
Nucleus	13C

3ba

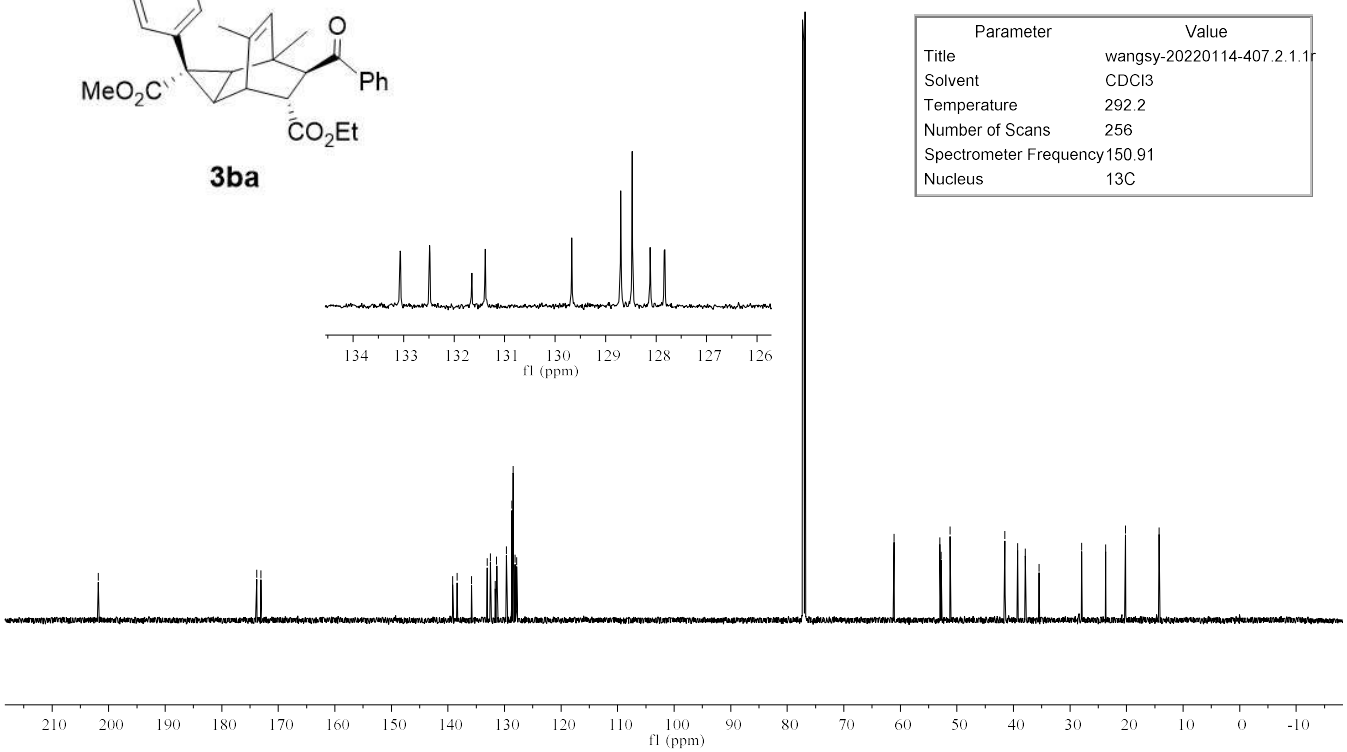
Parameter	Value
Title	wangsy-20220114-407.1.1.1r
Solvent	CDCl3
Temperature	291.3
Number of Scans	16
Spectrometer Frequency	600.17
Nucleus	1H

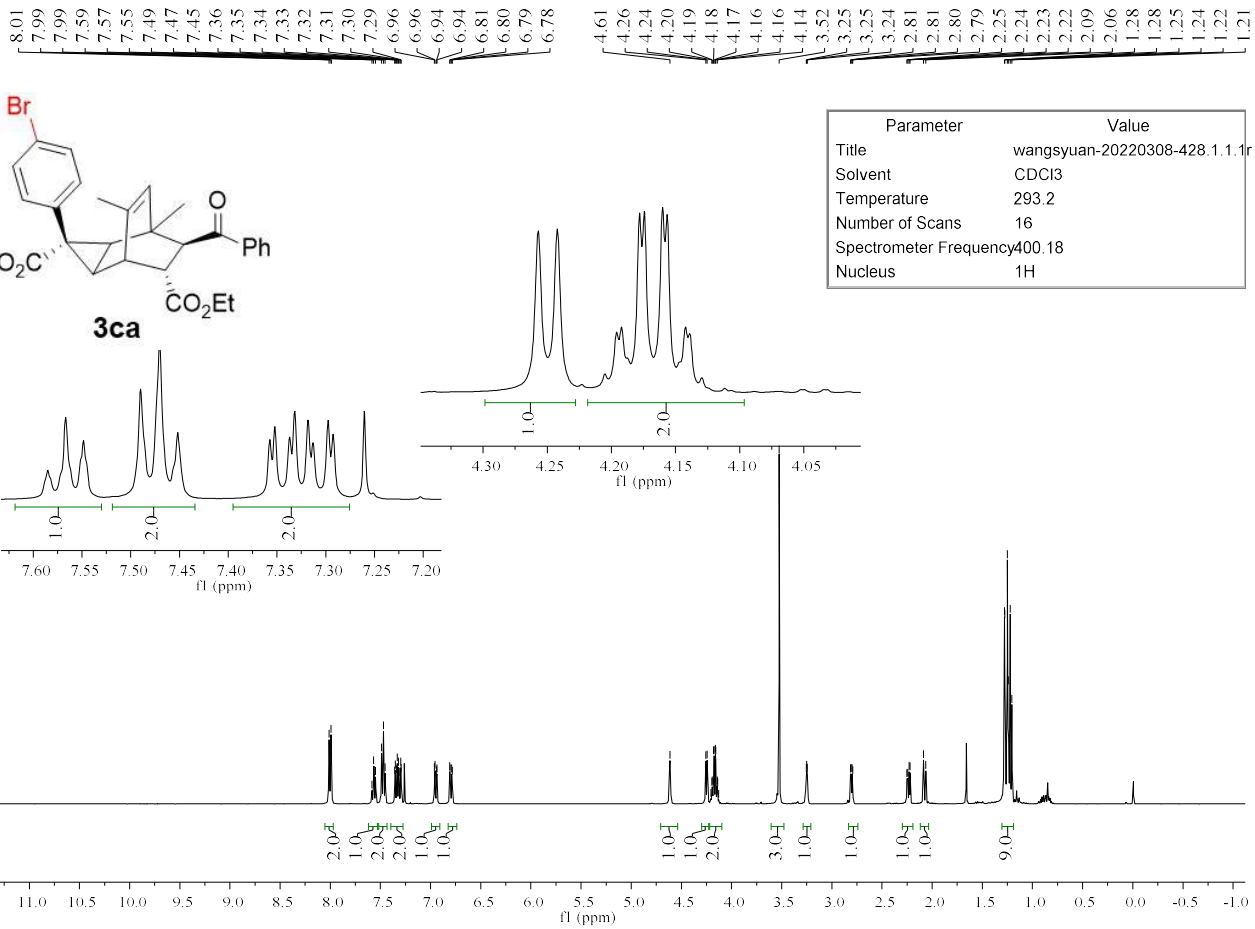


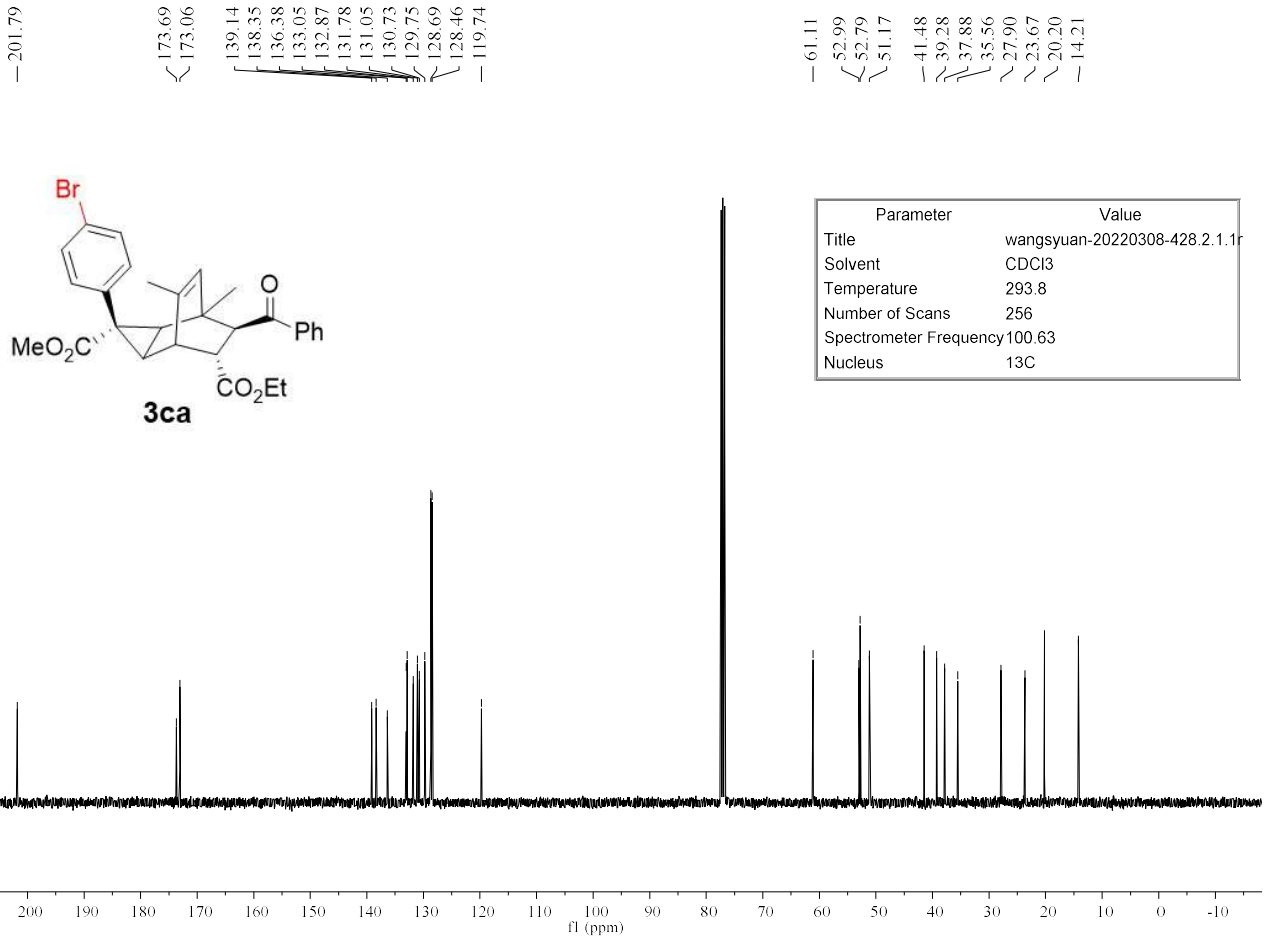


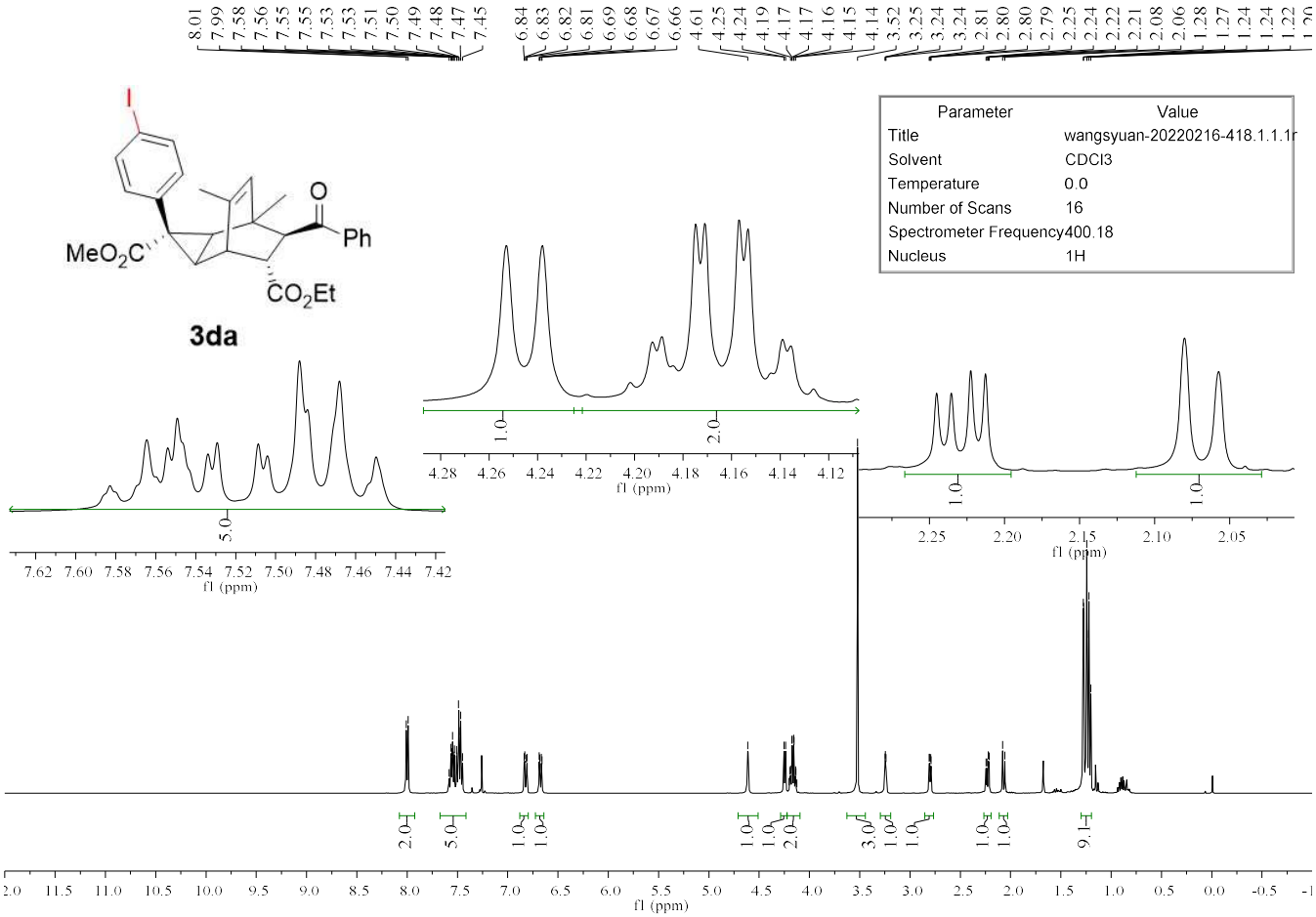
3ba

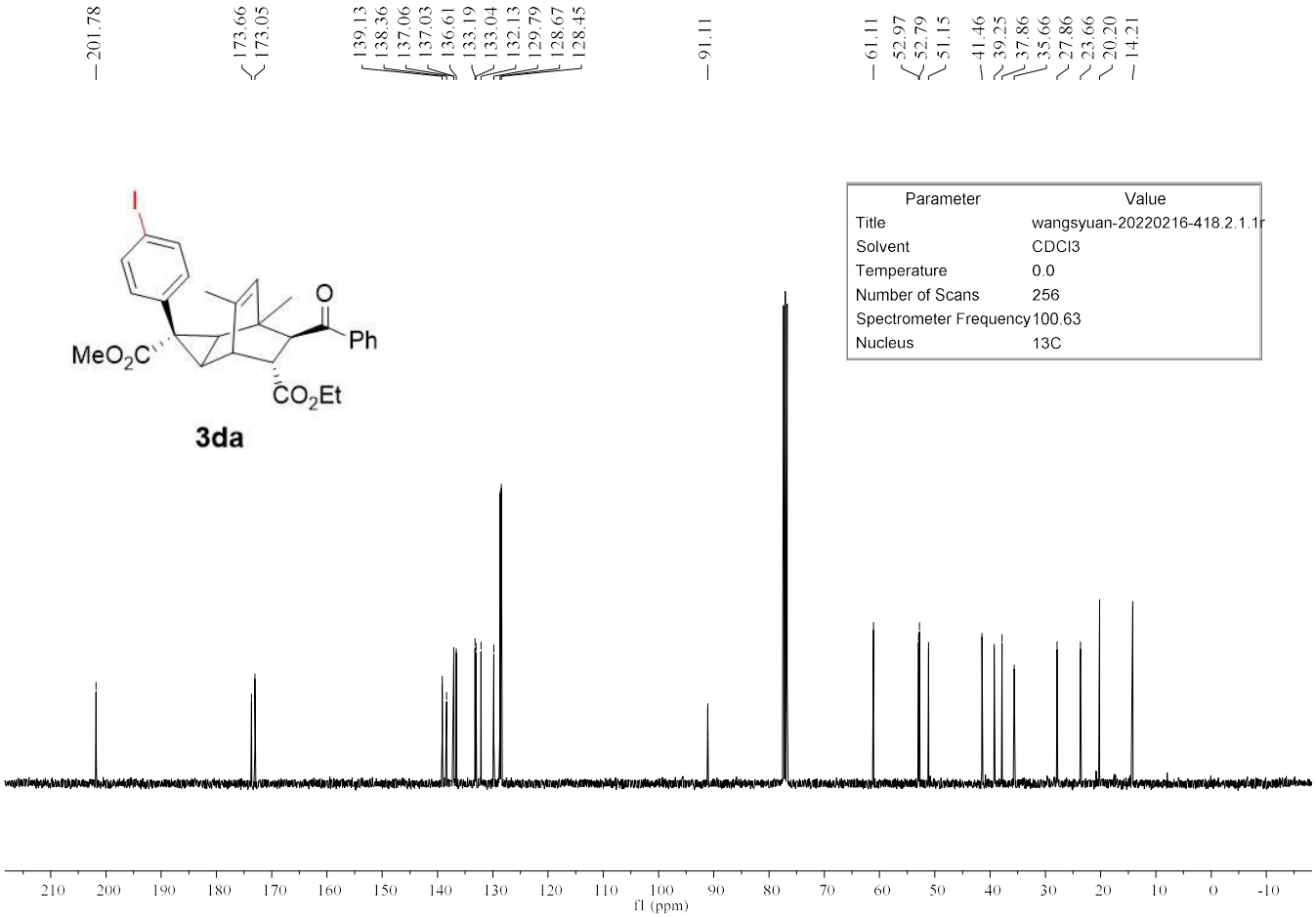
Parameter	Value
Title	wangsy-20220114-407.2.1.1r
Solvent	CDCl3
Temperature	292.2
Number of Scans	256
Spectrometer Frequency	150.91
Nucleus	13C

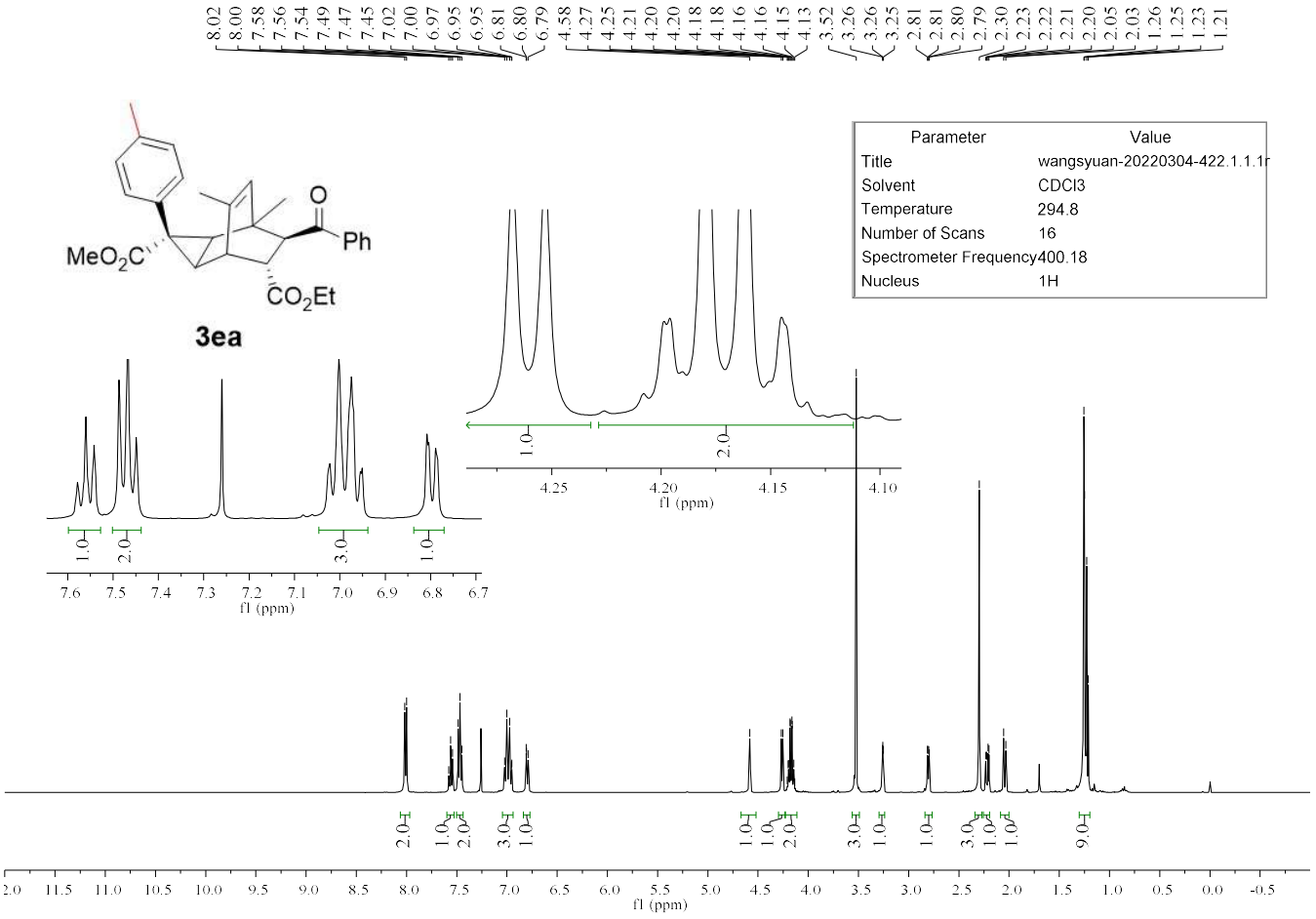


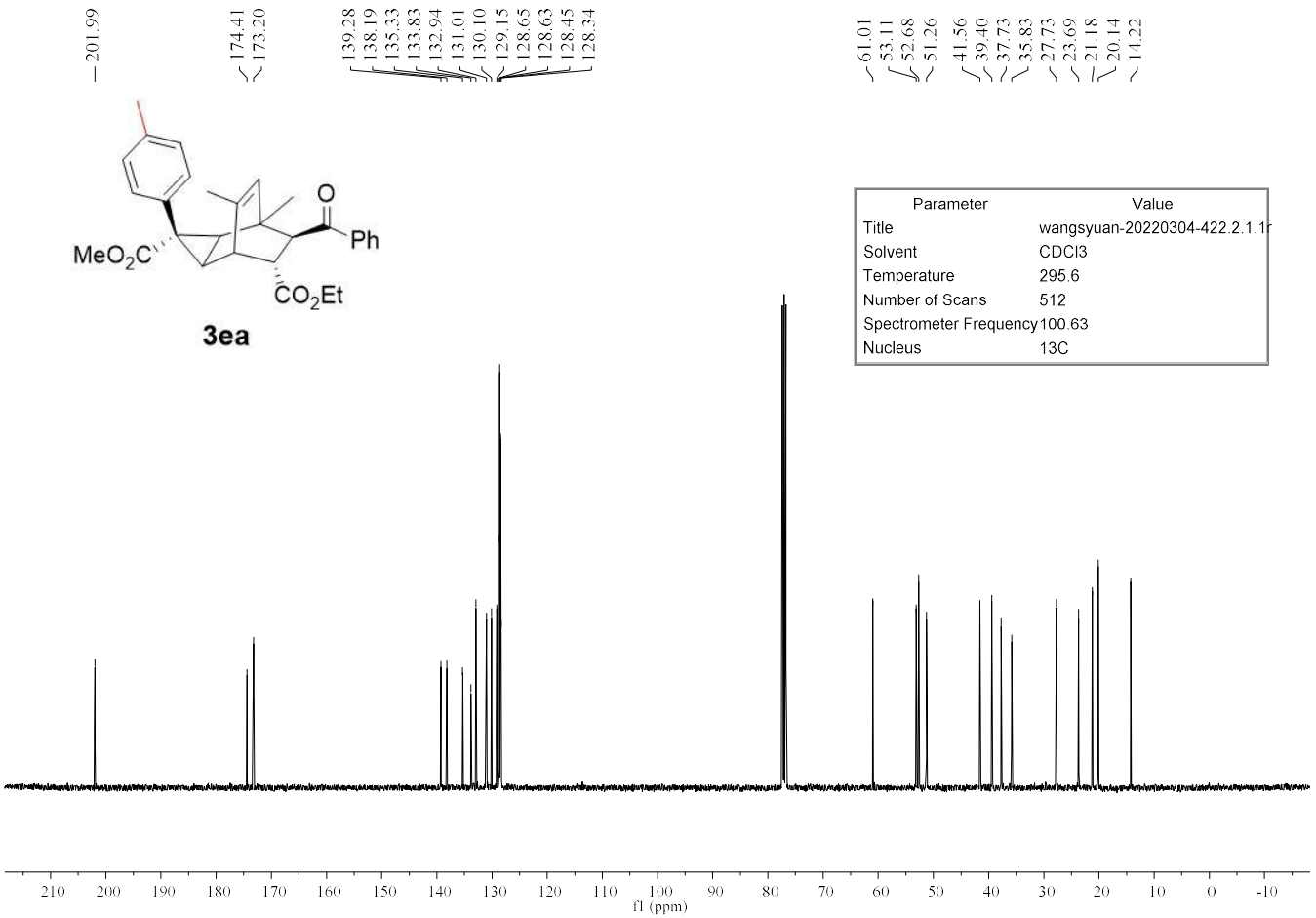

8.01 7.99 7.99 7.59 7.57 7.55 7.49 7.47 7.45 7.36 7.35 7.34 7.33 7.32 7.31 7.30 7.29 6.96 6.94 6.94 6.81 6.80 6.79 6.78
4.61 4.26 4.24 4.20 4.19 4.18 4.17 4.16 4.16 4.14 3.52 3.25 3.25 3.24 2.81 2.81 2.80 2.79 2.25 2.24 2.23 2.22 2.09 2.06 1.28 1.28 1.25 1.24 1.22 1.21
Br
O
Ph
MeO2C
CO2Et
3ca
Parameter Value
Title wangsyuan-20220308-428.1.1.1r
Solvent CDCl3
Temperature 293.2
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
1.0 2.0 2.0
7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20
f1 (ppm)
1.0 2.0
4.30 4.25 4.20 4.15 4.10 4.05
f1 (ppm)
2.0 1.0 2.0 2.0 1.0 1.0 1.0 1.0 2.0 3.0 1.0 1.0 1.0 1.0 9.0
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

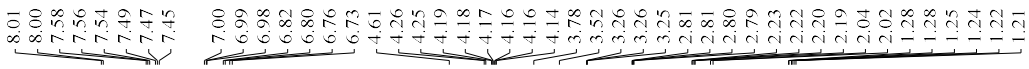

201.79
173.69 173.06
139.14 138.35 136.38 133.05 132.87 131.78 131.05 130.73 129.75 128.69 128.46
119.74
61.11
52.99 52.79
51.17
41.48 39.28 37.88 35.56 27.90 23.67 20.20
14.21
Br
O
Ph
MeO2C
CO2Et
3ca
Parameter Value
Title wangsyuan-20220308-428.2.1.1r
Solvent CDCl3
Temperature 293.8
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

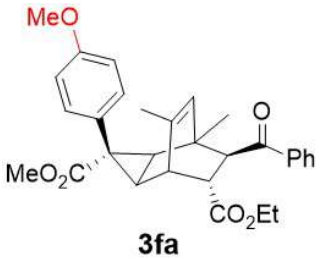

8.01 7.99 7.58 7.56 7.55 7.55 7.53 7.53 7.51 7.50 7.49 7.48 7.47 7.45
6.84 6.83 6.82 6.81 6.69 6.68 6.67 6.66
4.61 4.25 4.24 4.19 4.17 4.17 4.16 4.15 4.14
3.52 3.25 3.24 3.24 2.81 2.80 2.80 2.79 2.25 2.24 2.22 2.21 2.08 2.06 1.28 1.27 1.24 1.24 1.22
O
Ph
MeO2C
CO2Et
3da
Parameter Value
Title wangsyuan-20220216-418.1.1.1r
Solvent CDCl3
Temperature 0.0
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
fl (ppm)
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


201.78
173.66 173.05
139.13 138.36 137.06 137.03 136.61 133.19 133.04 132.13 129.79 128.67 128.45
91.11
61.11 52.97 52.79 51.15 41.46 39.25 37.86 35.66 27.86 23.66 20.20 14.21
O
Ph
MeO2C
CO2Et
3da
Parameter Value
Title wangsyuan-20220216-418.2.1.1r
Solvent CDCl3
Temperature 0.0
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
fl (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

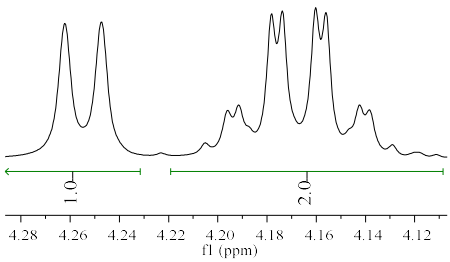

8.02 8.00 7.58 7.56 7.54 7.49 7.47 7.45 7.02 7.00 6.97 6.95 6.95 6.81 6.80 6.79 4.58 4.27 4.25 4.21 4.20 4.20 4.18 4.18 4.16 4.16 4.15 4.13 3.52 3.26 3.26 3.25 2.81 2.81 2.80 2.79 2.30 2.23 2.22 2.21 2.20 2.05 2.03 1.26 1.25 1.23 1.21
MeO2C
O
Ph
CO2Et
3ea
Parameter Value
Title wangsyuan-20220304-422.1.1.1r
Solvent CDCl3
Temperature 294.8
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
f1 (ppm)


201.99 174.41 173.20 139.28 138.19 135.33 133.83 132.94 131.01 130.10 129.15 128.65 128.63 128.45 128.34 61.01 53.11 52.68 51.26 41.56 39.40 37.73 35.83 27.73 23.69 21.18 20.14 14.22
MeO2C
O
Ph
CO2Et
3ea
Parameter Value
Title wangsyuan-20220304-422.2.1.1r
Solvent CDCl3
Temperature 295.6
Number of Scans 512
Spectrometer Frequency 100.63
Nucleus 13C
f1 (ppm)

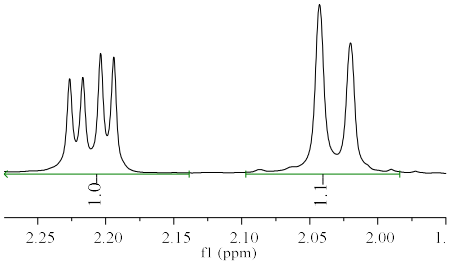


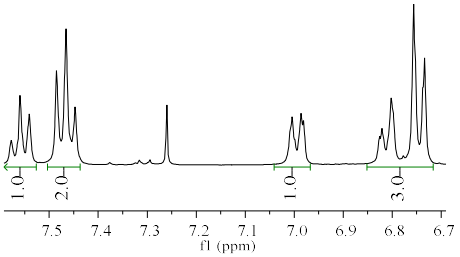


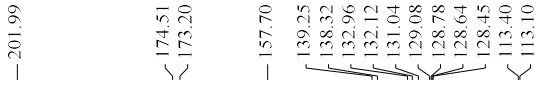
3fa

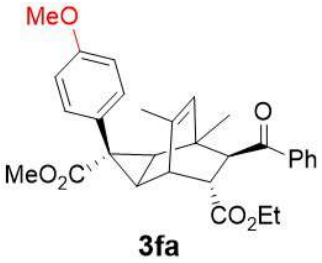


Parameter	Value
Title	wangsyuan-20220310-430.1.1.1r
Solvent	CDCl3
Temperature	293.2
Number of Scans	16
Spectrometer Frequency	400.18
Nucleus	1H



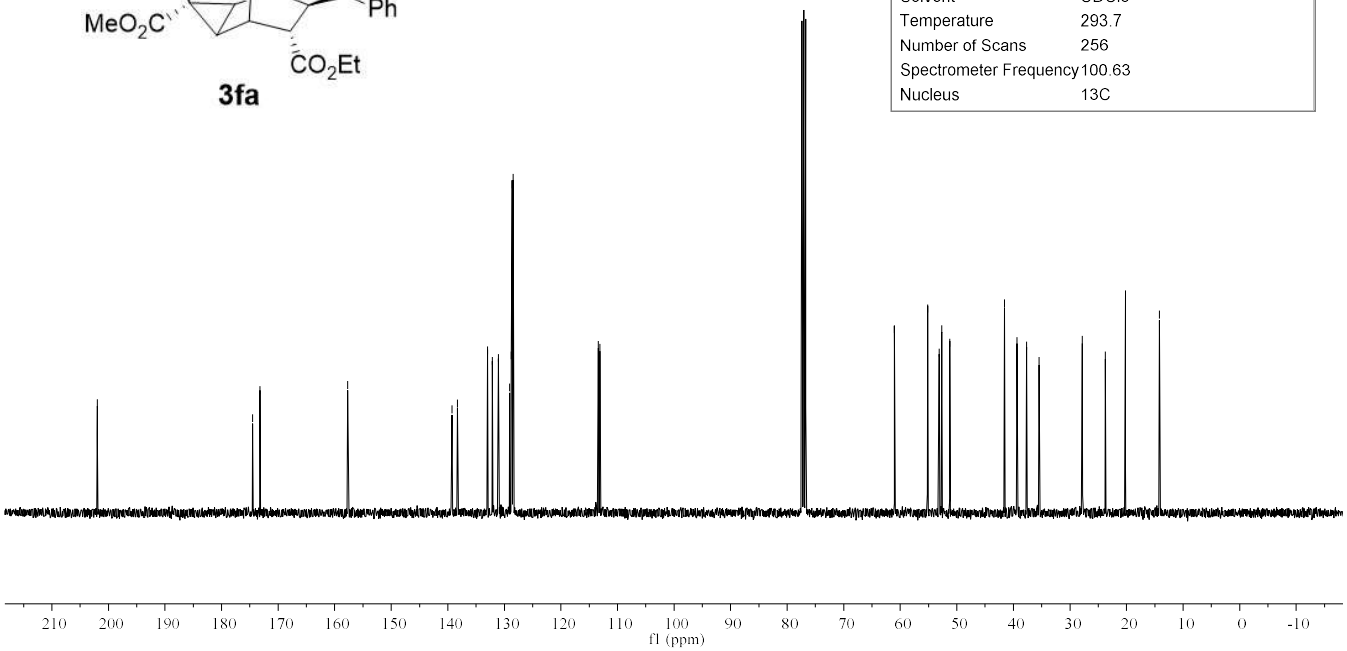


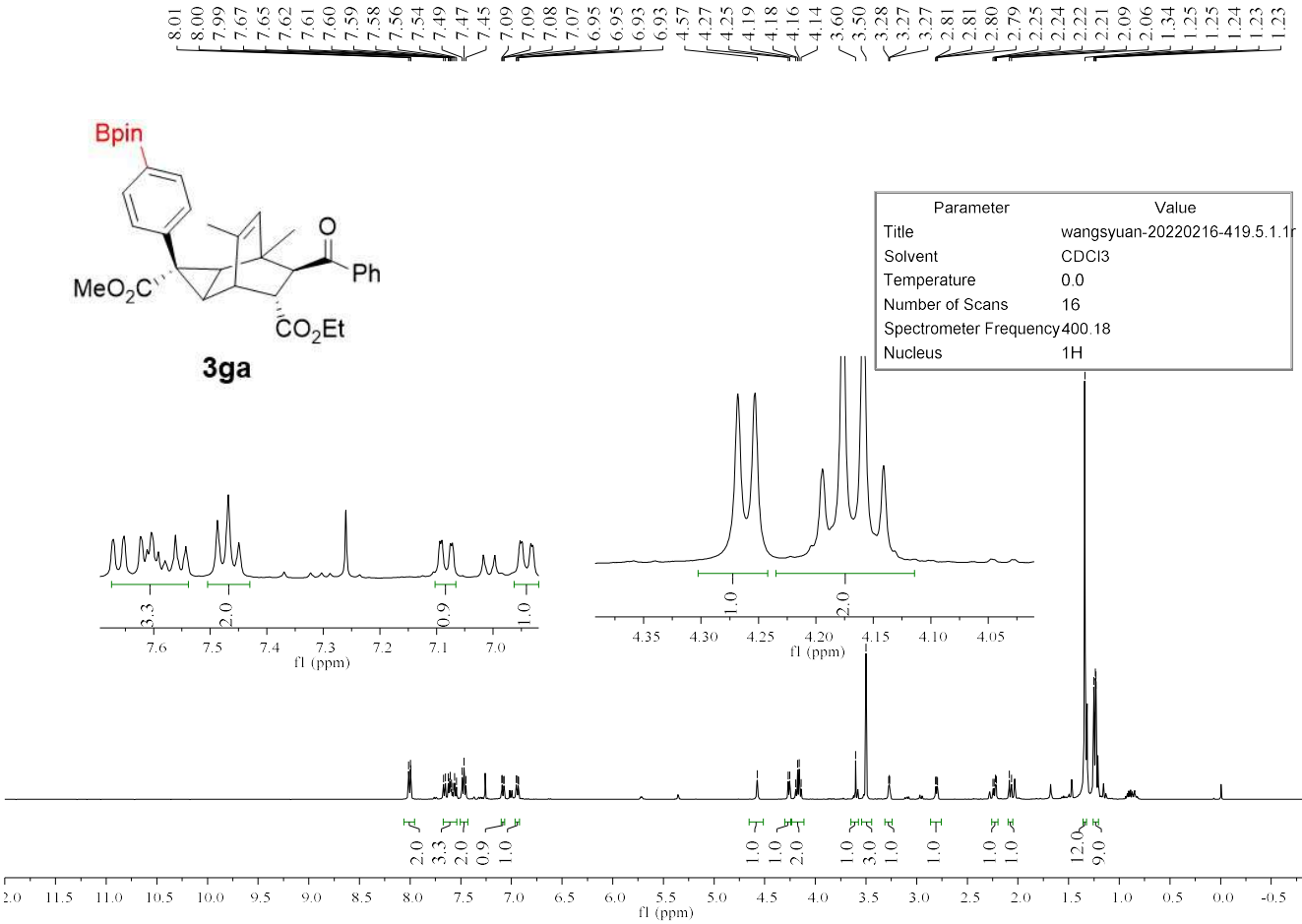


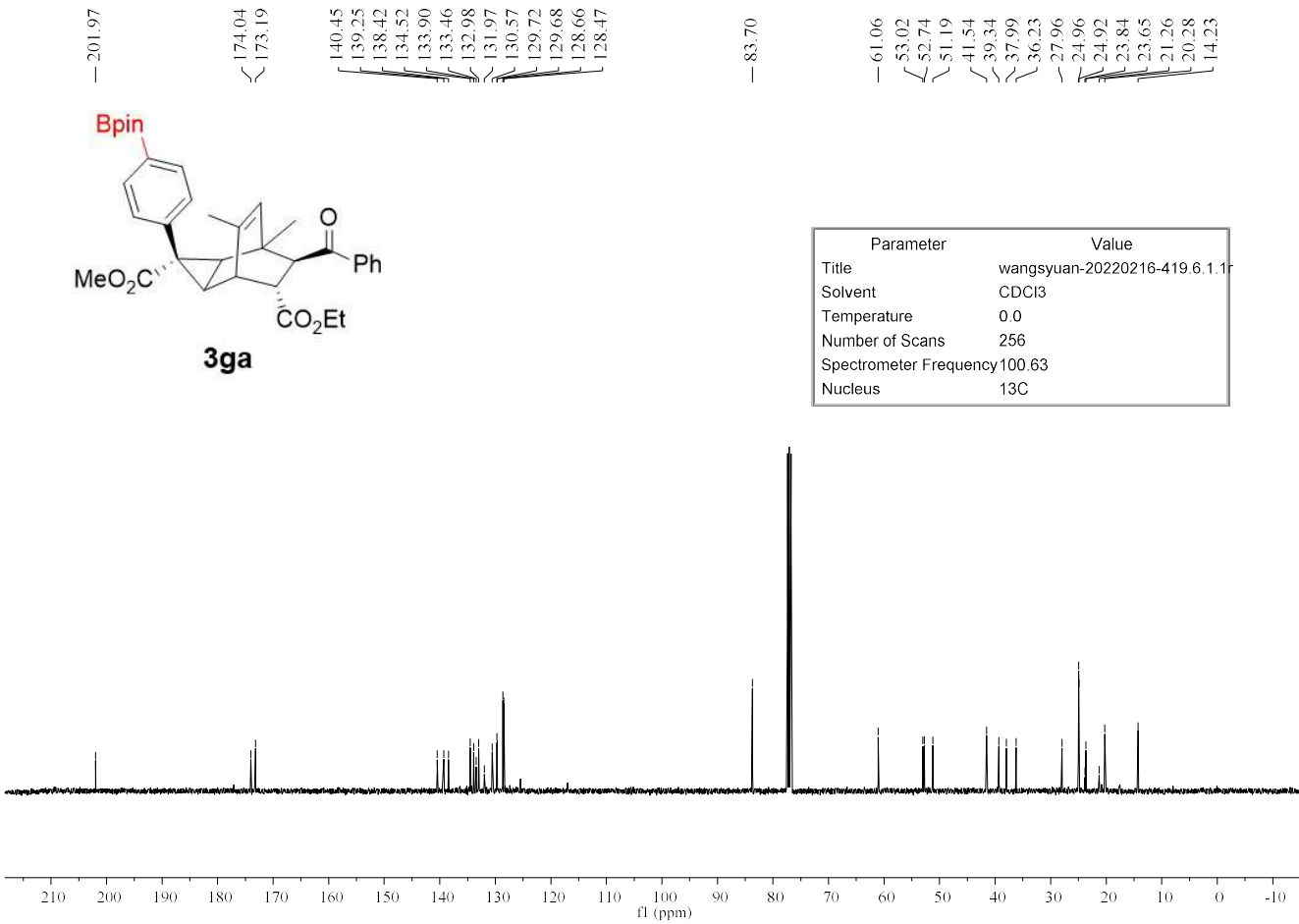


3fa

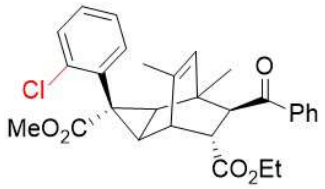
Parameter	Value
Title	wangsyuan-20220310-430.2.1.1r
Solvent	CDCl3
Temperature	293.7
Number of Scans	256
Spectrometer Frequency	100.63
Nucleus	13C



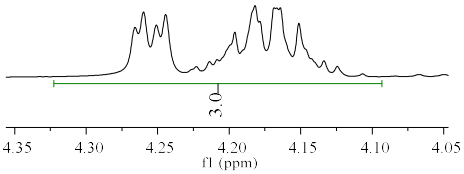

Bpin
O
Ph
MeO2C
CO2Et
3ga
Parameter Value
Title wangsyuan-20220216-419.5.1.1r
Solvent CDCl3
Temperature 0.0
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
f1 (ppm)

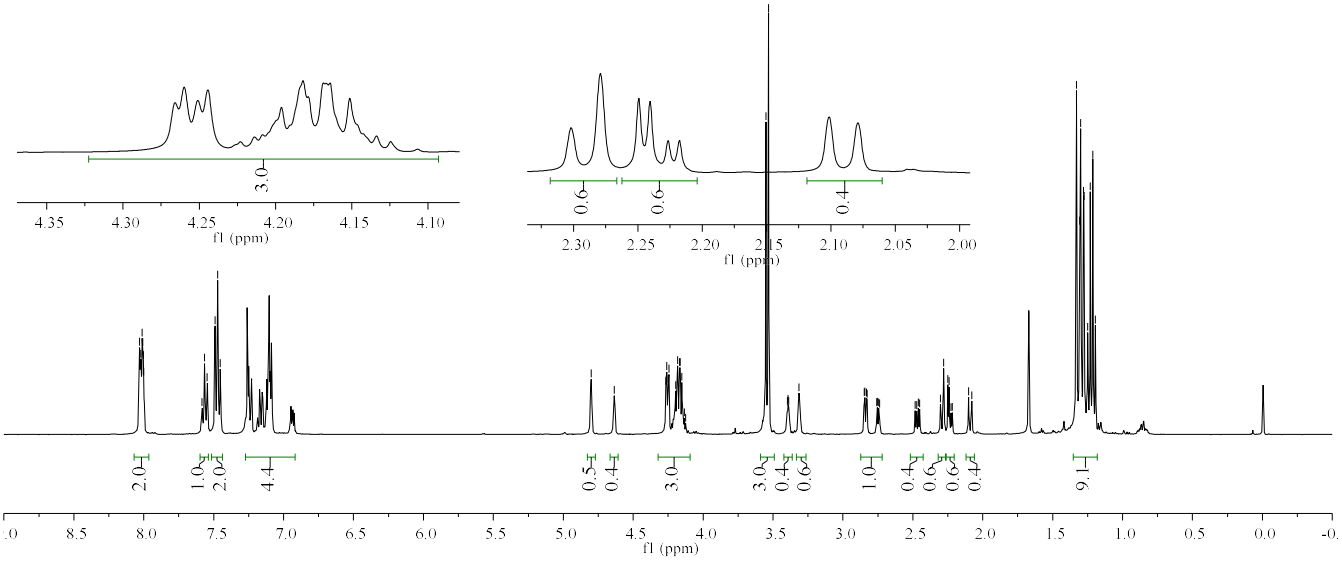

Bpin
O
Ph
MeO2C
CO2Et
3ga
Parameter Value
Title wangsyuan-20220216-419.6.1.1r
Solvent CDCl3
Temperature 0.0
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
f1 (ppm)

Parameter	Value
Title	as-20220317-WSY-434.1.1.1r
Solvent	CDCl3
Temperature	293.4
Number of Scans	16
Spectrometer Frequency	400.18
Nucleus	1H

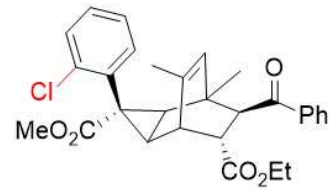


3ha

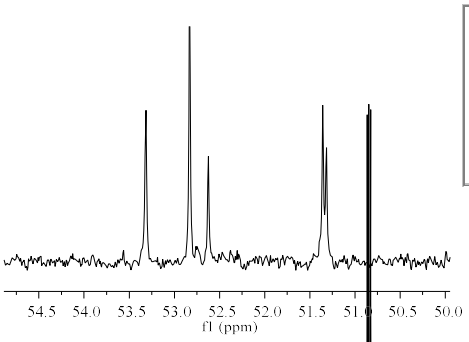


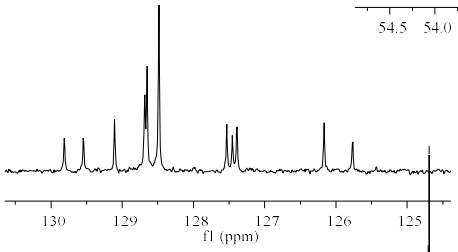


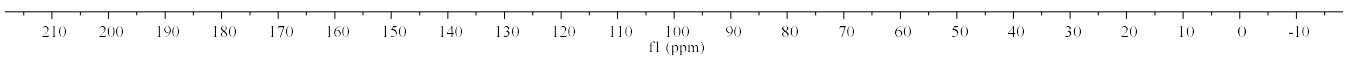
Parameter	Value
Title	as-20220317-WSY-434.2.1.1r
Solvent	CDCl3
Temperature	294.1
Number of Scans	256
Spectrometer Frequency	100.63
Nucleus	13C

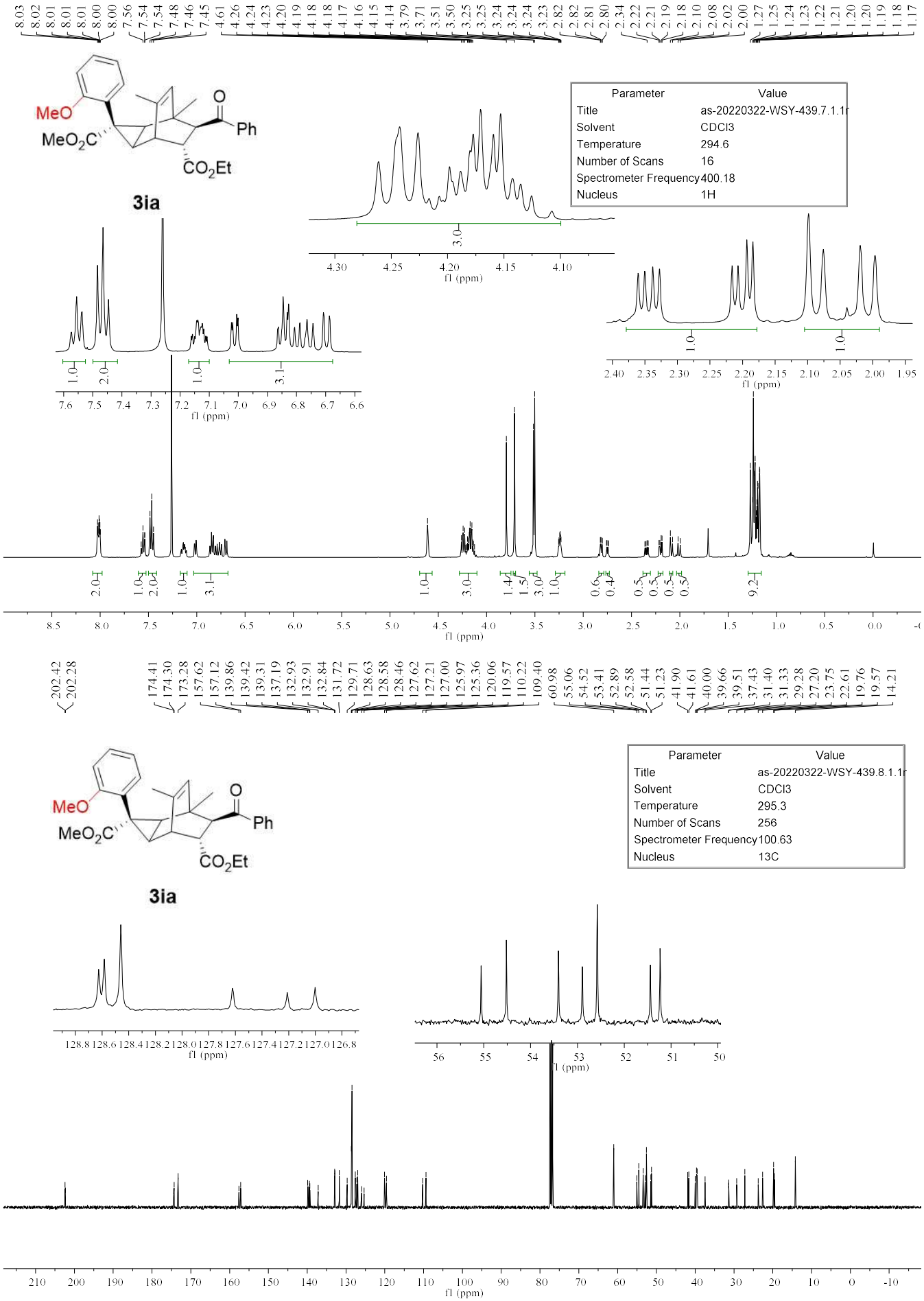


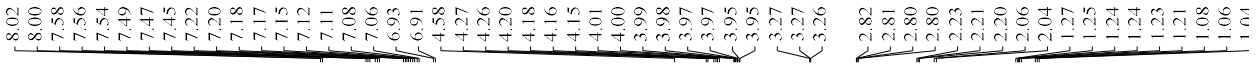
3ha

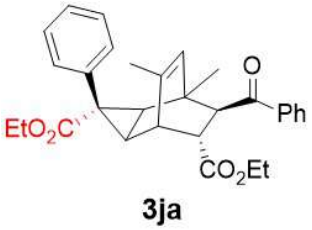




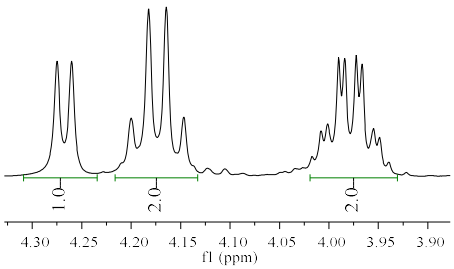



MeO
MeO2C
O
Ph
CO2Et
3ia
Parameter Value
Title as-20220322-WSY-439.7.1.1r
Solvent CDCl3
Temperature 294.6
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
f1 (ppm)
Parameter Value
Title as-20220322-WSY-439.8.1.1r
Solvent CDCl3
Temperature 295.3
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C

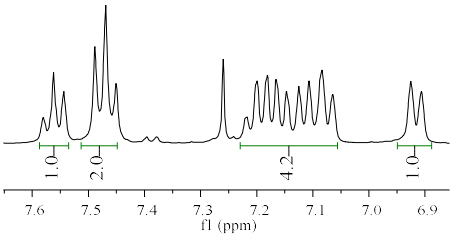


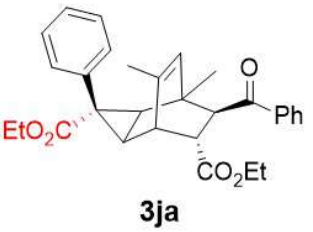


3ja



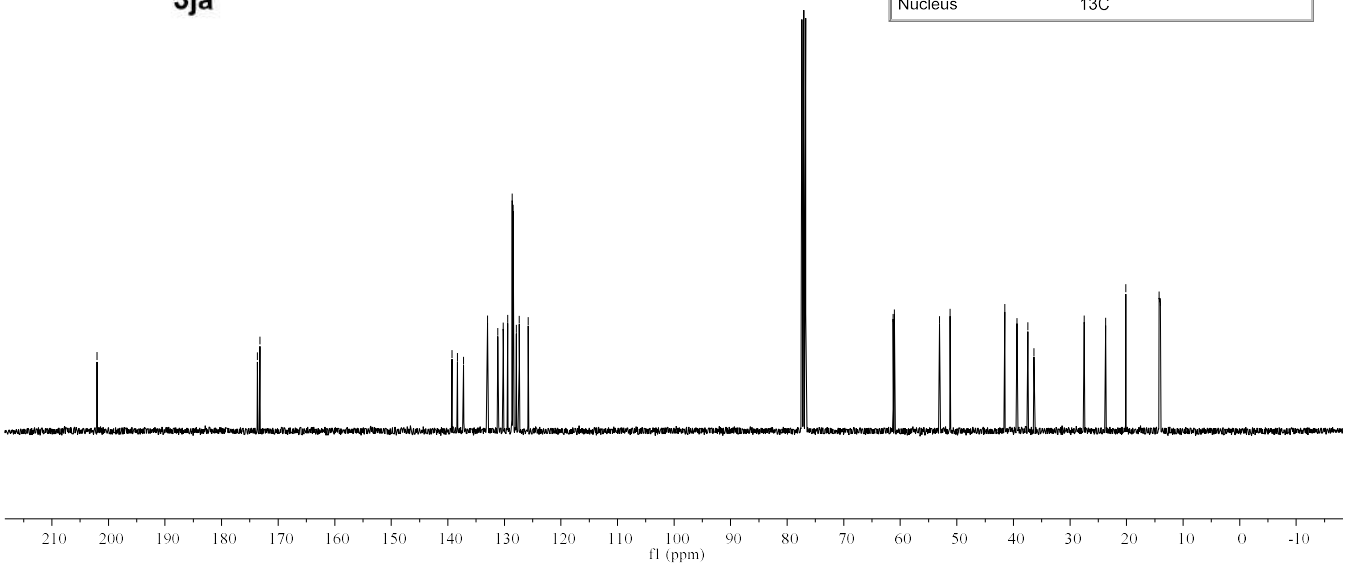
Parameter	Value
Title	wangsyuan-20220126-412.1.1.1r
Solvent	CDCl3
Temperature	292.5
Number of Scans	16
Spectrometer Frequency	400.18
Nucleus	1H

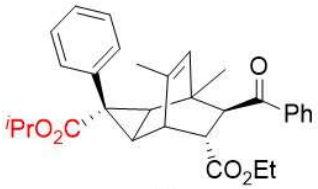




3ja

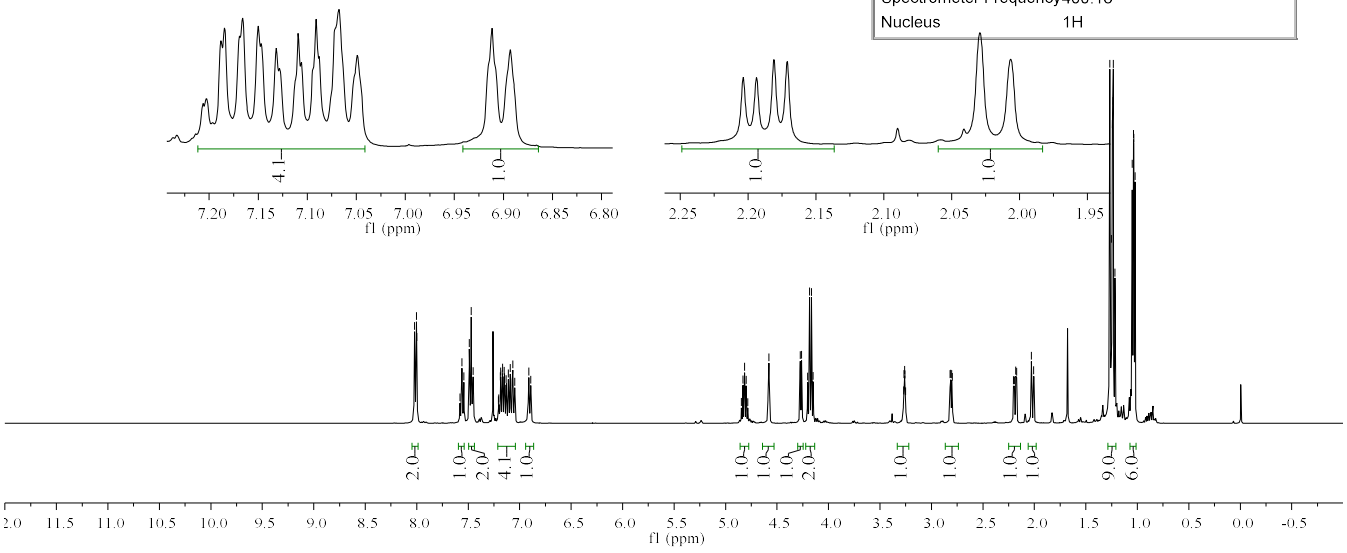
Parameter	Value
Title	wangsyuan-20220126-412.2.1.1r
Solvent	CDCl3
Temperature	293.1
Number of Scans	256
Spectrometer Frequency	100.63
Nucleus	13C

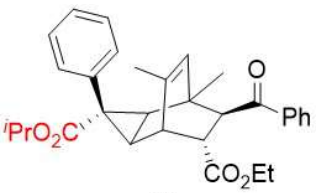




3ka

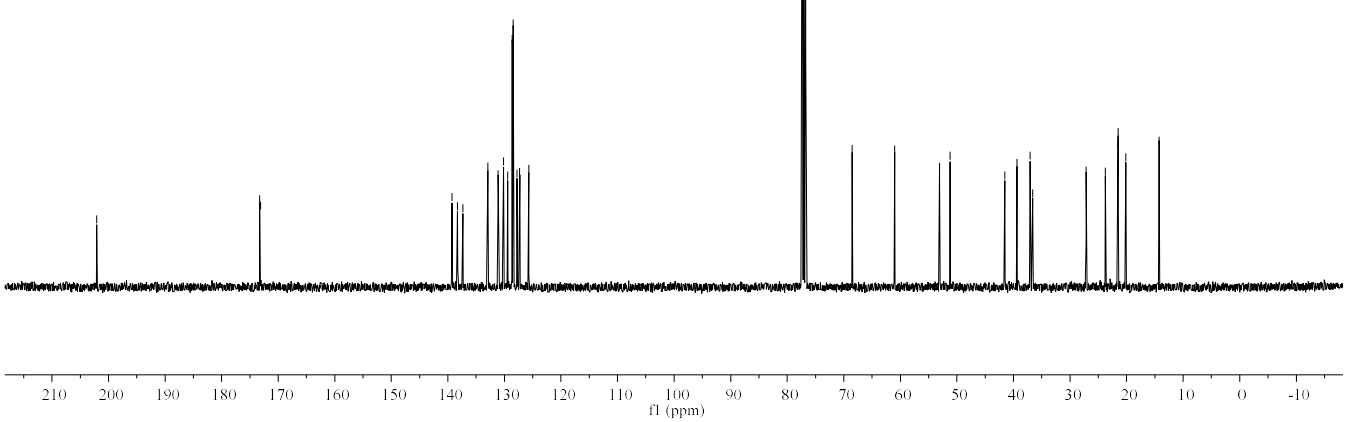
Parameter	Value
Title	wangsyuan-20220126-413.1.1.1r
Solvent	CDCl3
Temperature	292.6
Number of Scans	16
Spectrometer Frequency	400.18
Nucleus	1H

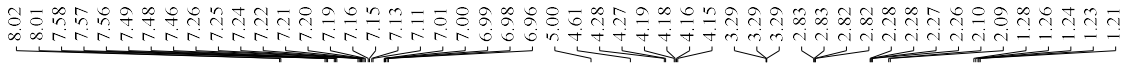


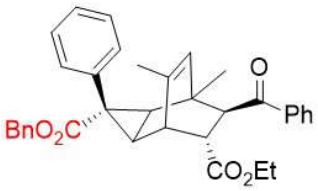


3ka

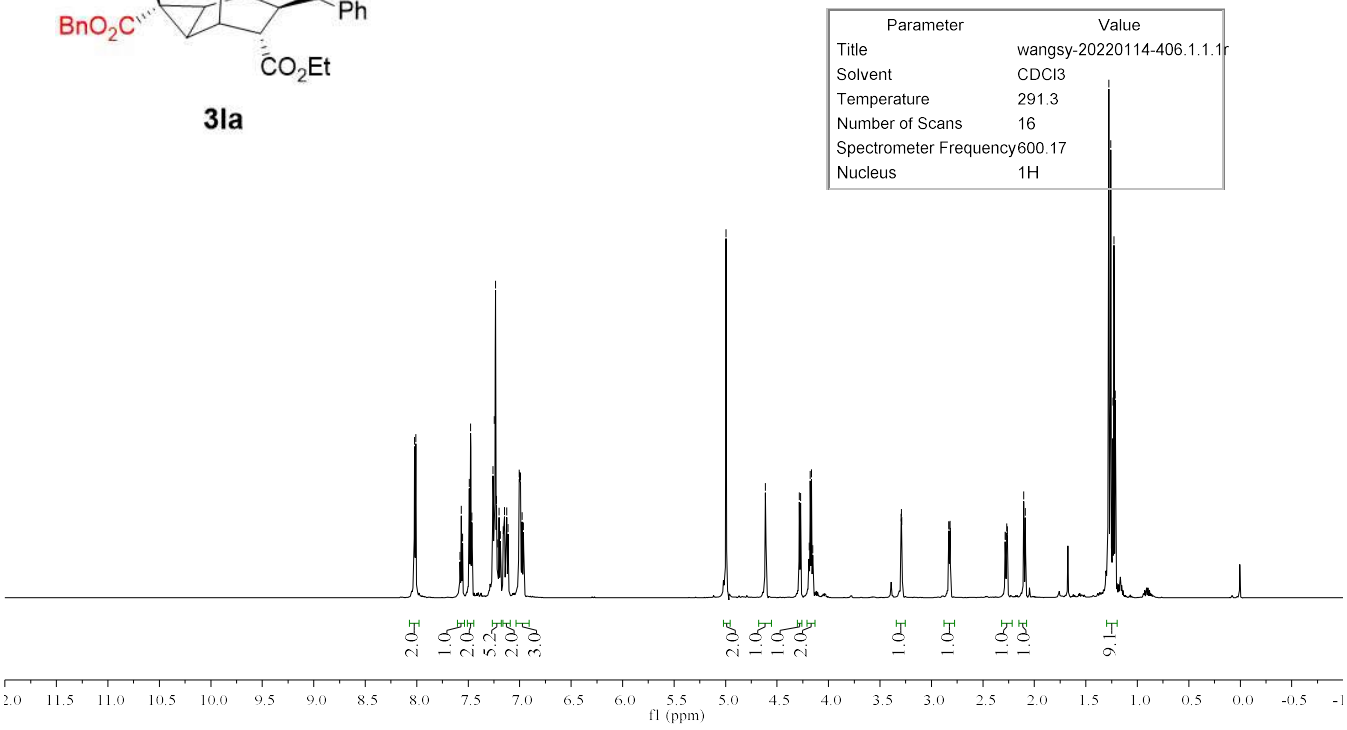
Parameter	Value
Title	wangsyuan-20220126-413.2.1.1r
Solvent	CDCl3
Temperature	293.2
Number of Scans	256
Spectrometer Frequency	100.63
Nucleus	13C



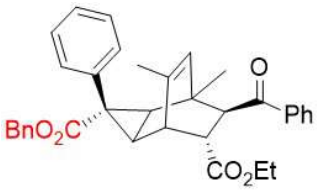

8.02
8.01
7.58
7.57
7.56
7.49
7.48
7.46
7.26
7.25
7.24
7.22
7.21
7.20
7.19
7.16
7.15
7.13
7.11
7.01
7.00
6.99
6.98
6.96
5.00
4.61
4.28
4.27
4.19
4.18
4.16
4.15
3.29
3.29
3.29
2.83
2.83
2.82
2.82
2.28
2.28
2.27
2.26
2.10
2.09
1.28
1.26
1.24
1.23
1.21


O
Ph
BnO2C
CO2Et

3la

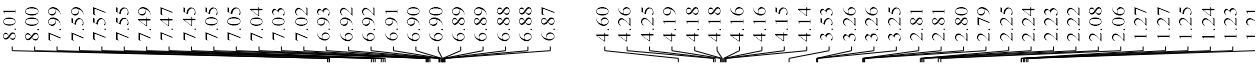

Parameter Value
Title wangsy-20220114-406.1.1.1r
Solvent CDCl3
Temperature 291.3
Number of Scans 16
Spectrometer Frequency 600.17
Nucleus 1H
2.0
1.0
2.0
5.2
2.0
3.0
2.0
1.0
1.0
2.0
1.0
1.0
1.0
1.0
9.1
f1 (ppm)

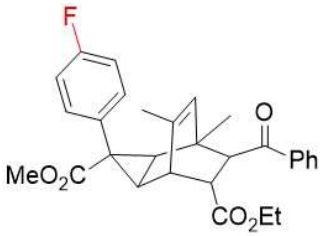

201.98
173.44
173.14
139.22
138.32
137.03
136.12
132.98
131.21
130.25
129.46
128.65
128.46
128.29
127.97
127.63
127.52
126.74
125.95
66.42
61.05
53.03
51.19
41.55
39.33
37.76
36.35
27.79
23.70
20.13
14.22


O
Ph
BnO2C
CO2Et

3la

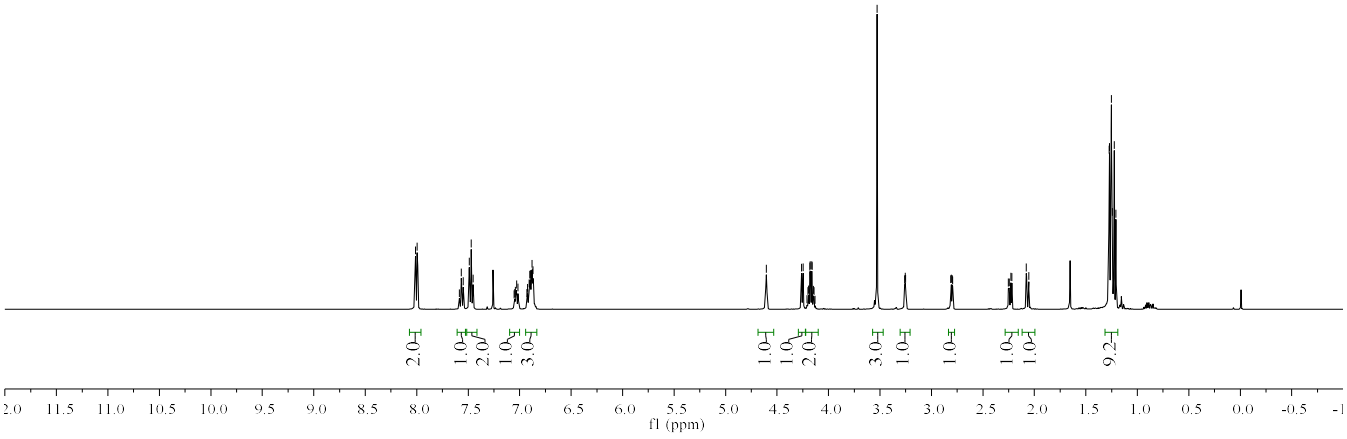
Parameter Value
Title wangsy-20220114-406.2.1.1r
Solvent CDCl3
Temperature 292.4
Number of Scans 256
Spectrometer Frequency 150.91
Nucleus 13C
f1 (ppm)

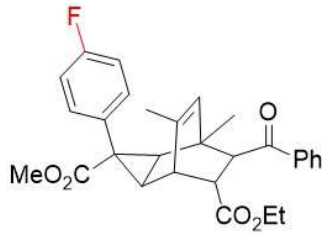




3ma

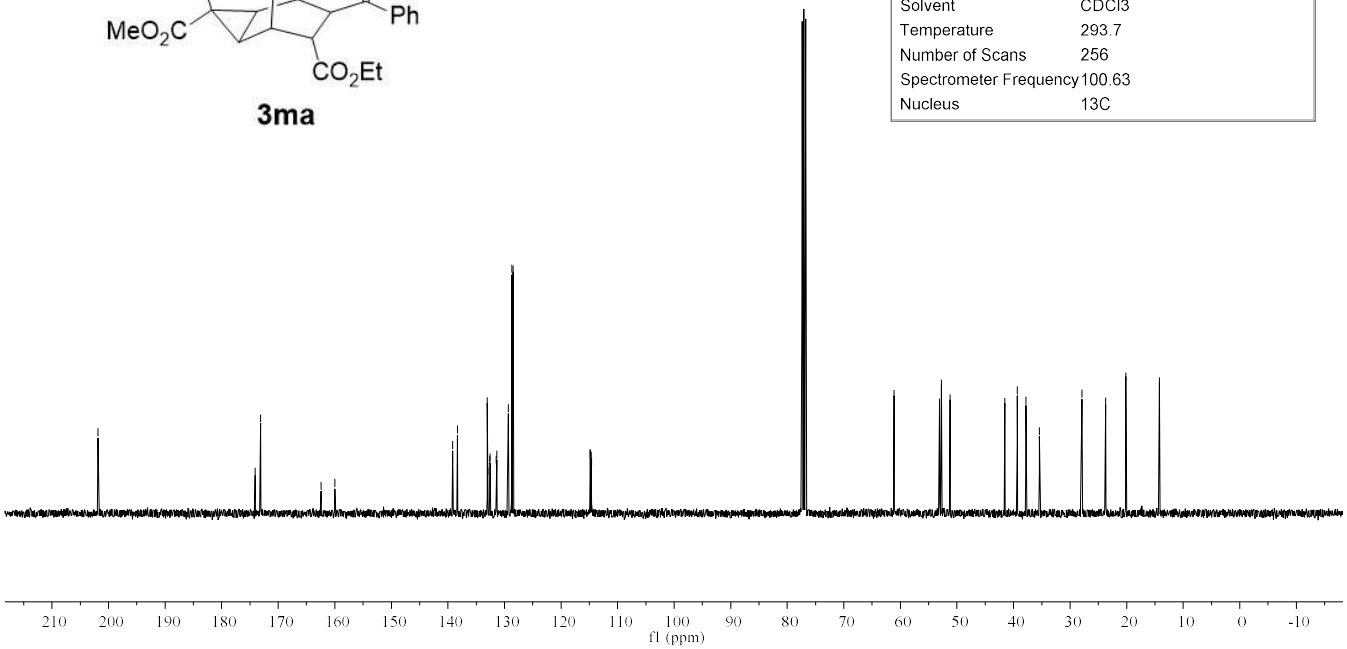
Parameter	Value
Title	wangsyuan-20220308-427.1.1.1r
Solvent	CDCl3
Temperature	293.1
Number of Scans	16
Spectrometer Frequency	400.18
Nucleus	1H

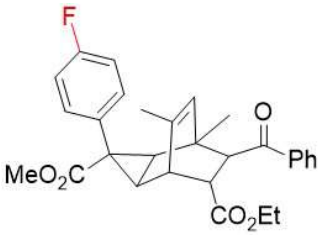




3ma

Parameter	Value
Title	wangsyuan-20220308-427.2.1.1r
Solvent	CDCl3
Temperature	293.7
Number of Scans	256
Spectrometer Frequency	100.63
Nucleus	13C

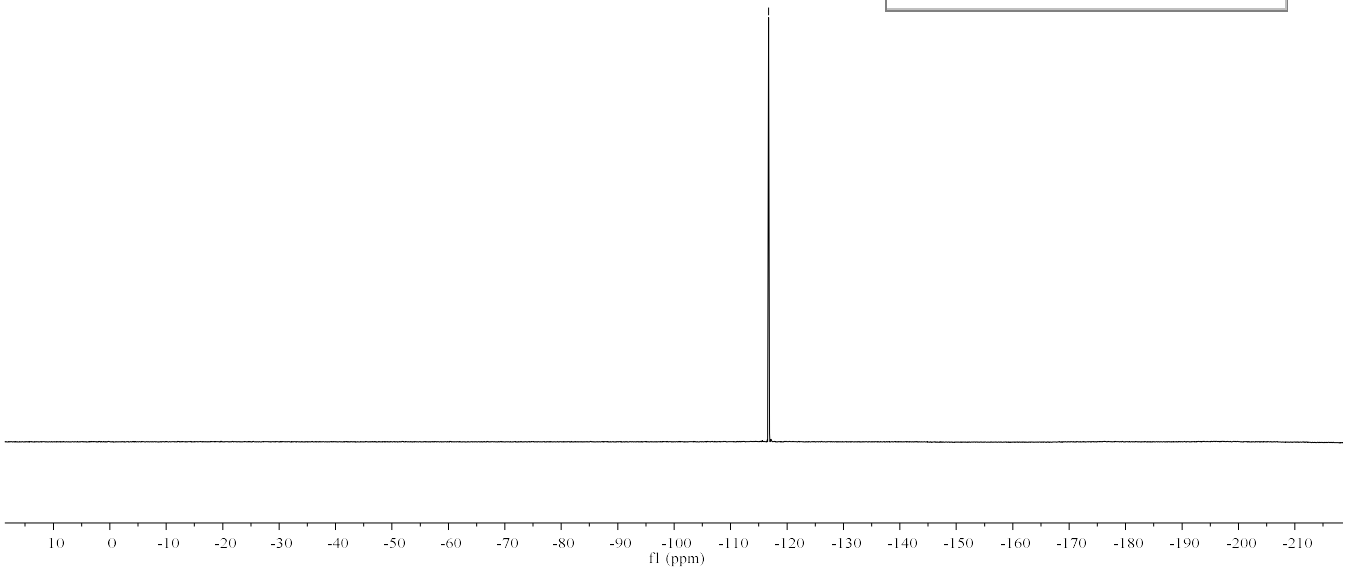


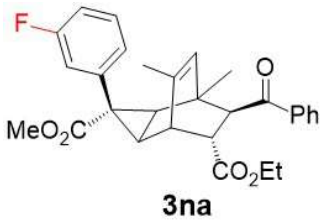


3ma

-116.75

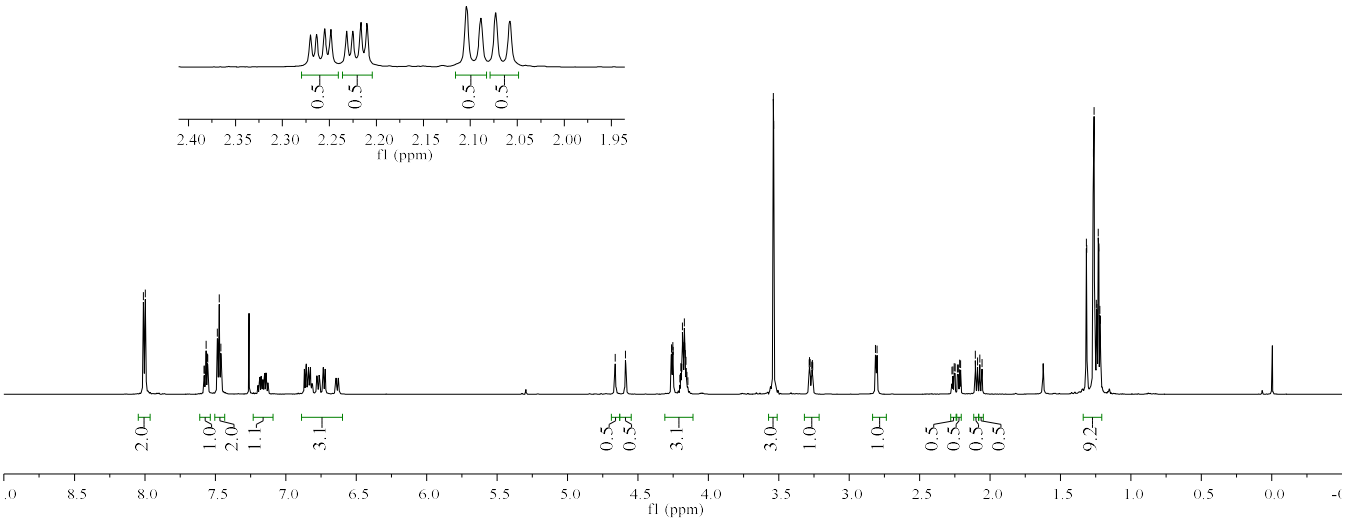
Parameter	Value
Title	as-20220411-WSY-427.1.1.1r
Solvent	CDCl3
Temperature	298.7
Number of Scans	16
Spectrometer Frequency	376.50
Nucleus	19F

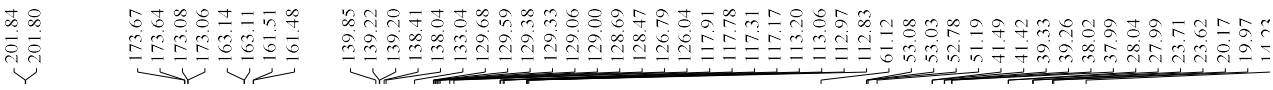


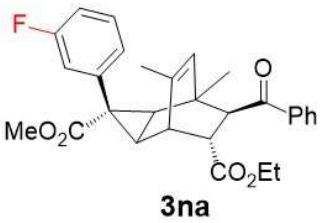


3na

Parameter	Value
Title	as-20211129-WSY-383.1.1.1r
Solvent	CDCl3
Temperature	296.8
Number of Scans	16
Spectrometer Frequency	600.17
Nucleus	1H

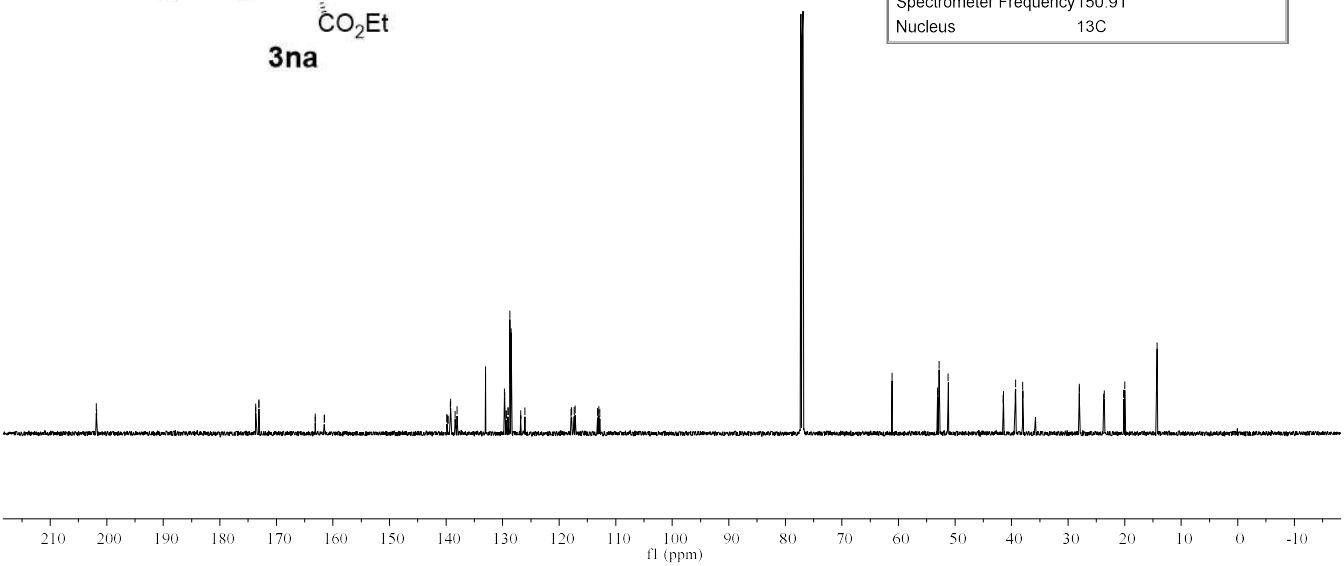


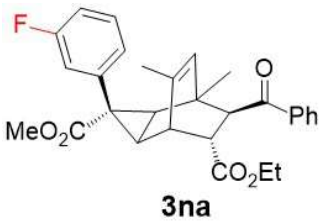




3na

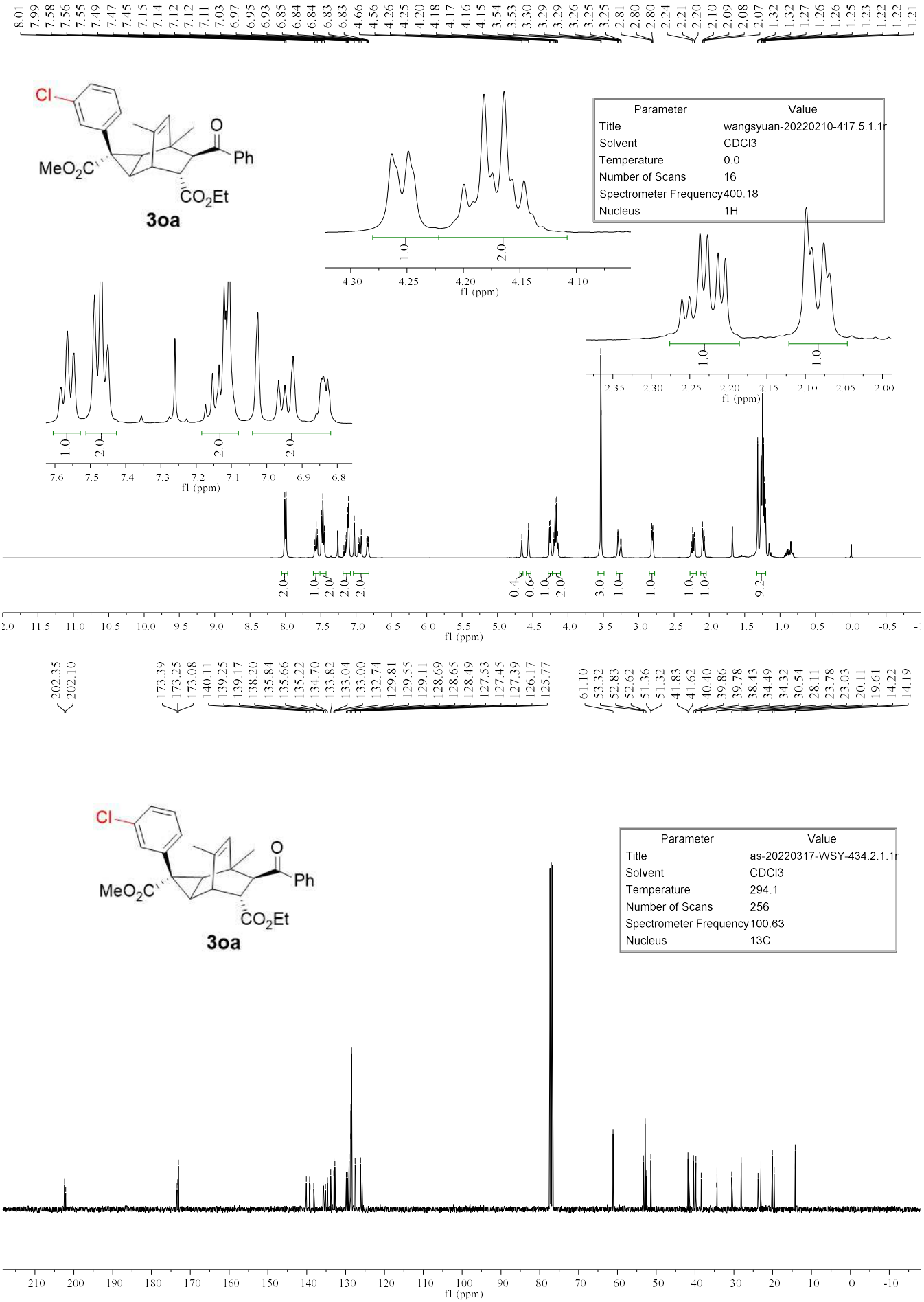
Parameter	Value
Title	as-20211129-WSY-383.2.1.1r
Solvent	CDCl3
Temperature	297.6
Number of Scans	256
Spectrometer Frequency	150.91
Nucleus	13C



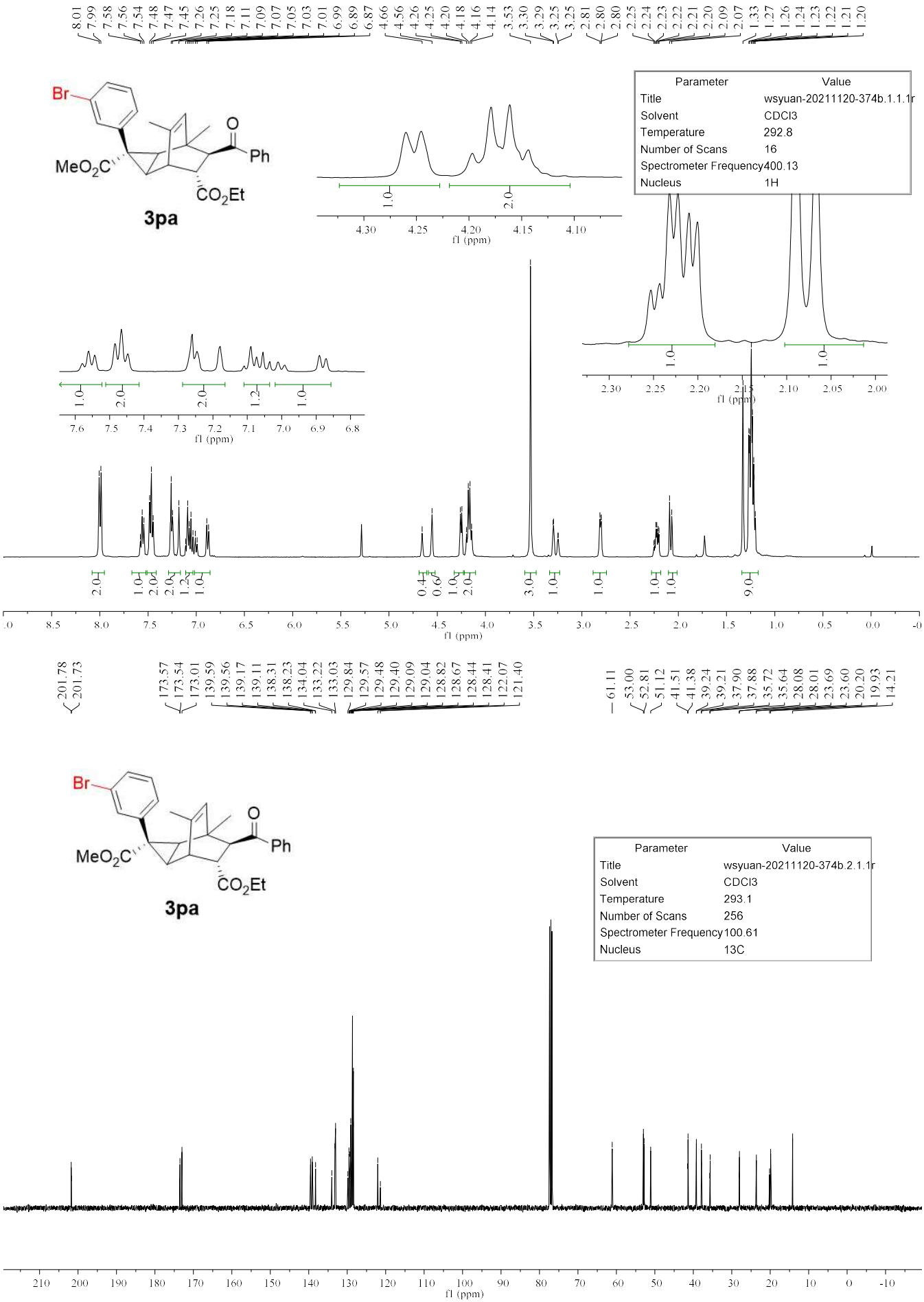


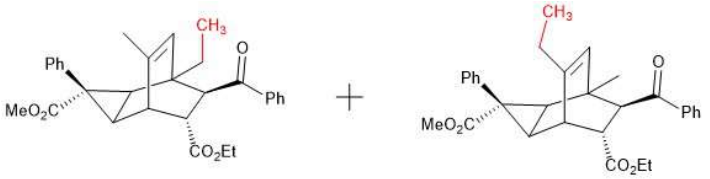
3na

Parameter	Value
Title	as-20211129-WSY-383.3.1.1r
Solvent	CDCl3
Temperature	297.0
Number of Scans	16
Spectrometer Frequency	564.72
Nucleus	19F


Cl
O
Ph
MeO2C
CO2Et
3oa
Parameter Value
Title wangsyuan-20220210-417.5.1.1r
Solvent CDCl3
Temperature 0.0
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
f1 (ppm)

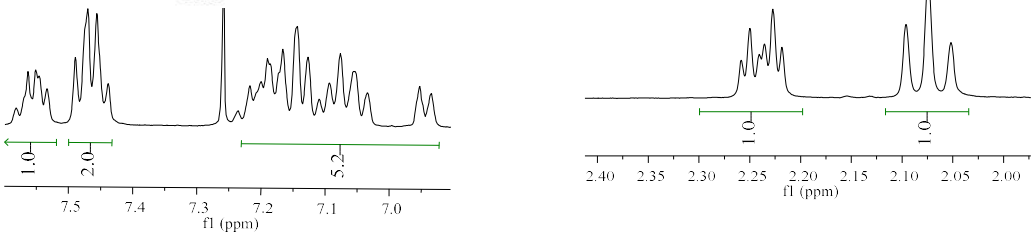
Cl
O
Ph
MeO2C
CO2Et
3oa
Parameter Value
Title as-20220317-WSY-434.2.1.1r
Solvent CDCl3
Temperature 294.1
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
f1 (ppm)

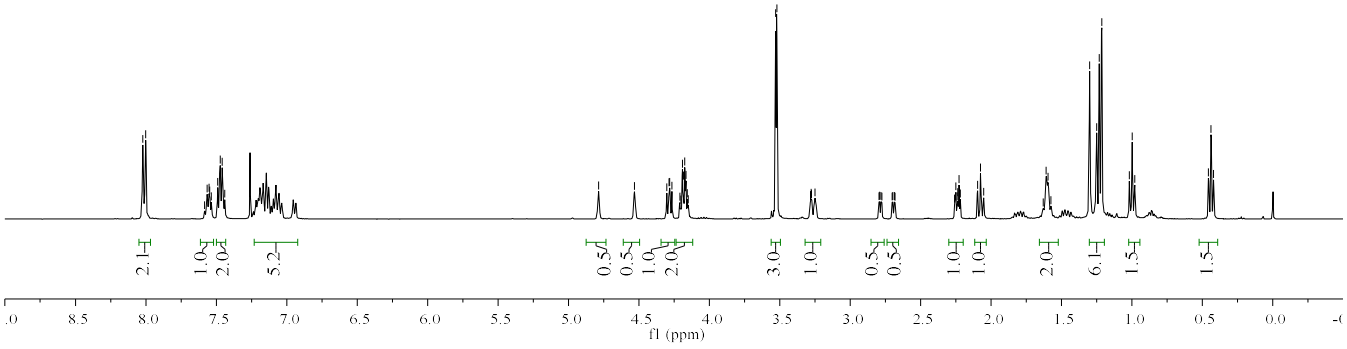

Br
O
Ph
MeO2C
CO2Et
3pa
Parameter Value
Title wsyuan-20211120-374b.1.1.1r
Solvent CDCl3
Temperature 292.8
Number of Scans 16
Spectrometer Frequency 400.13
Nucleus 1H
f1 (ppm)
Br
O
Ph
MeO2C
CO2Et
3pa
Parameter Value
Title wsyuan-20211120-374b.2.1.1r
Solvent CDCl3
Temperature 293.1
Number of Scans 256
Spectrometer Frequency 100.61
Nucleus 13C
f1 (ppm)

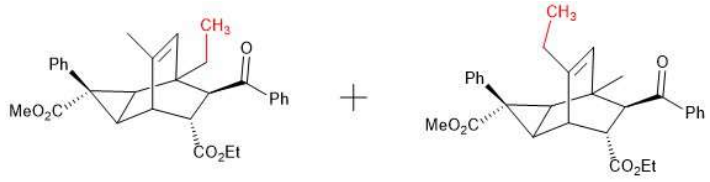


3ra

Parameter	Value
Title	wsyuan-20221222-WSY-Cat.1.1.1r
Solvent	CDCl3
Temperature	297.4
Number of Scans	16
Spectrometer Frequency	400.13
Nucleus	1H

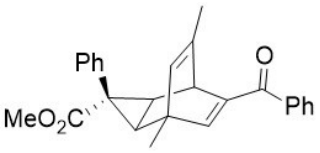






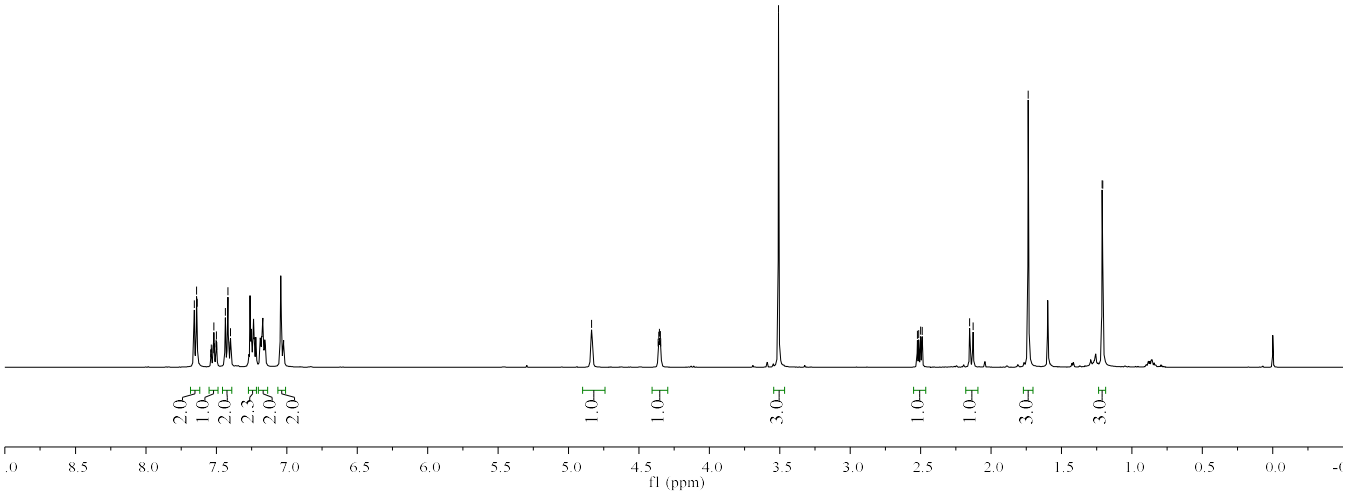
3ra

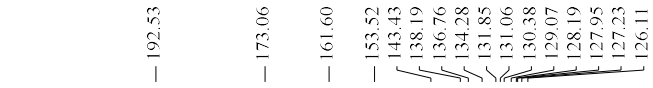
Parameter	Value
Title	wsyuan-20221222-WSY-Cat.2.1.1r
Solvent	CDCl3
Temperature	297.6
Number of Scans	256
Spectrometer Frequency	100.61
Nucleus	13C

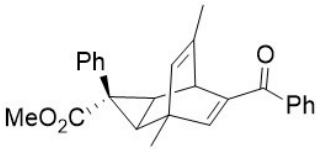


5aa

Parameter	Value
Title	wsyuan-20220421-N-1.1.1.1r
Solvent	CDCl3
Temperature	297.4
Number of Scans	16
Spectrometer Frequency	400.13
Nucleus	1H

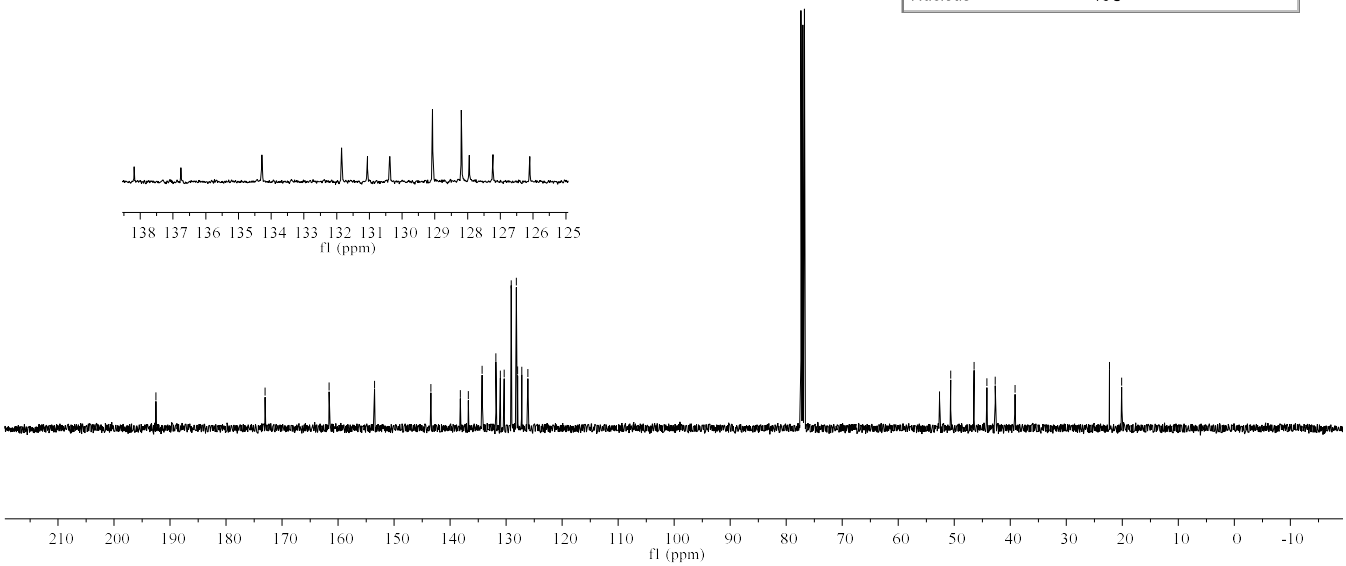


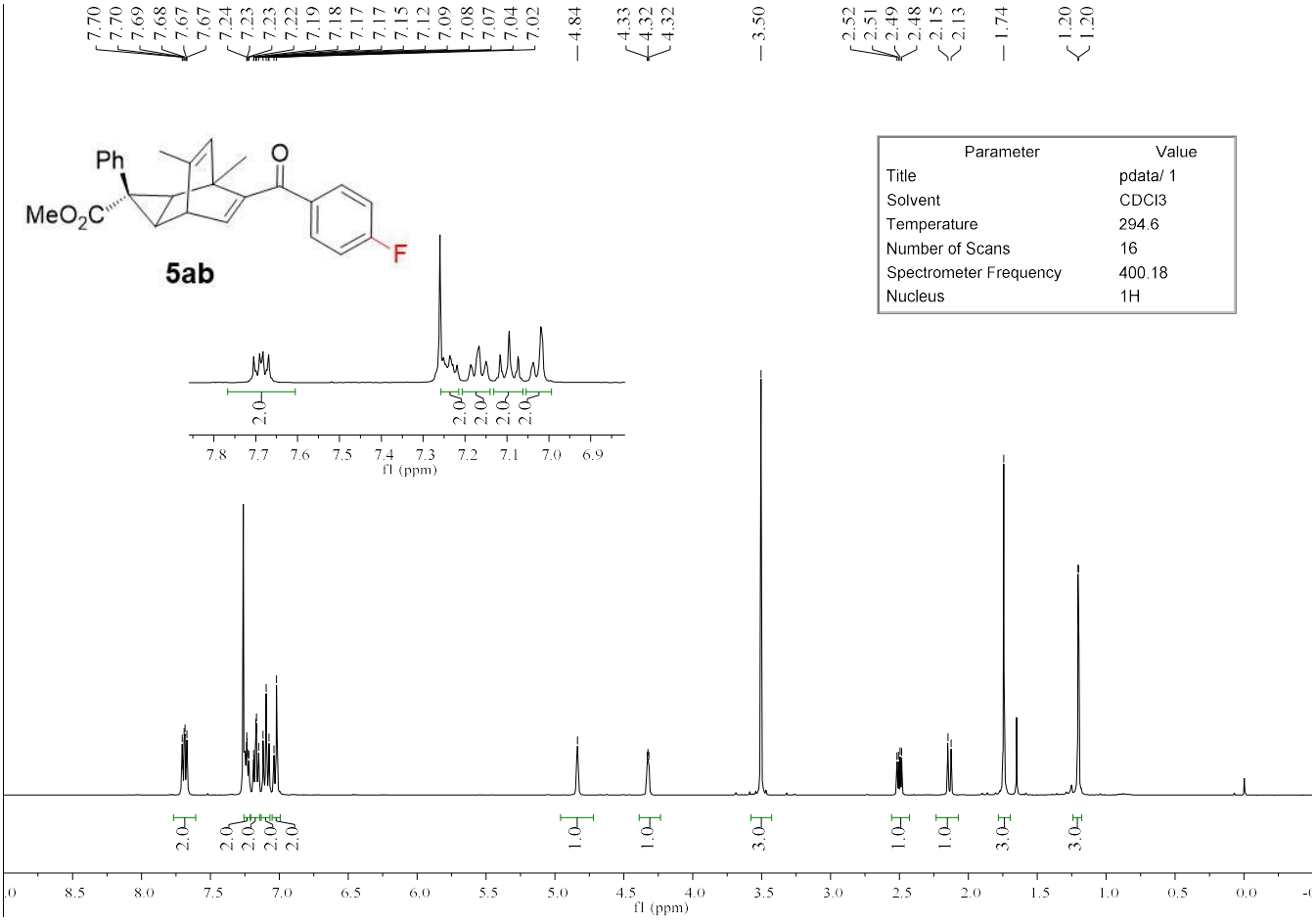


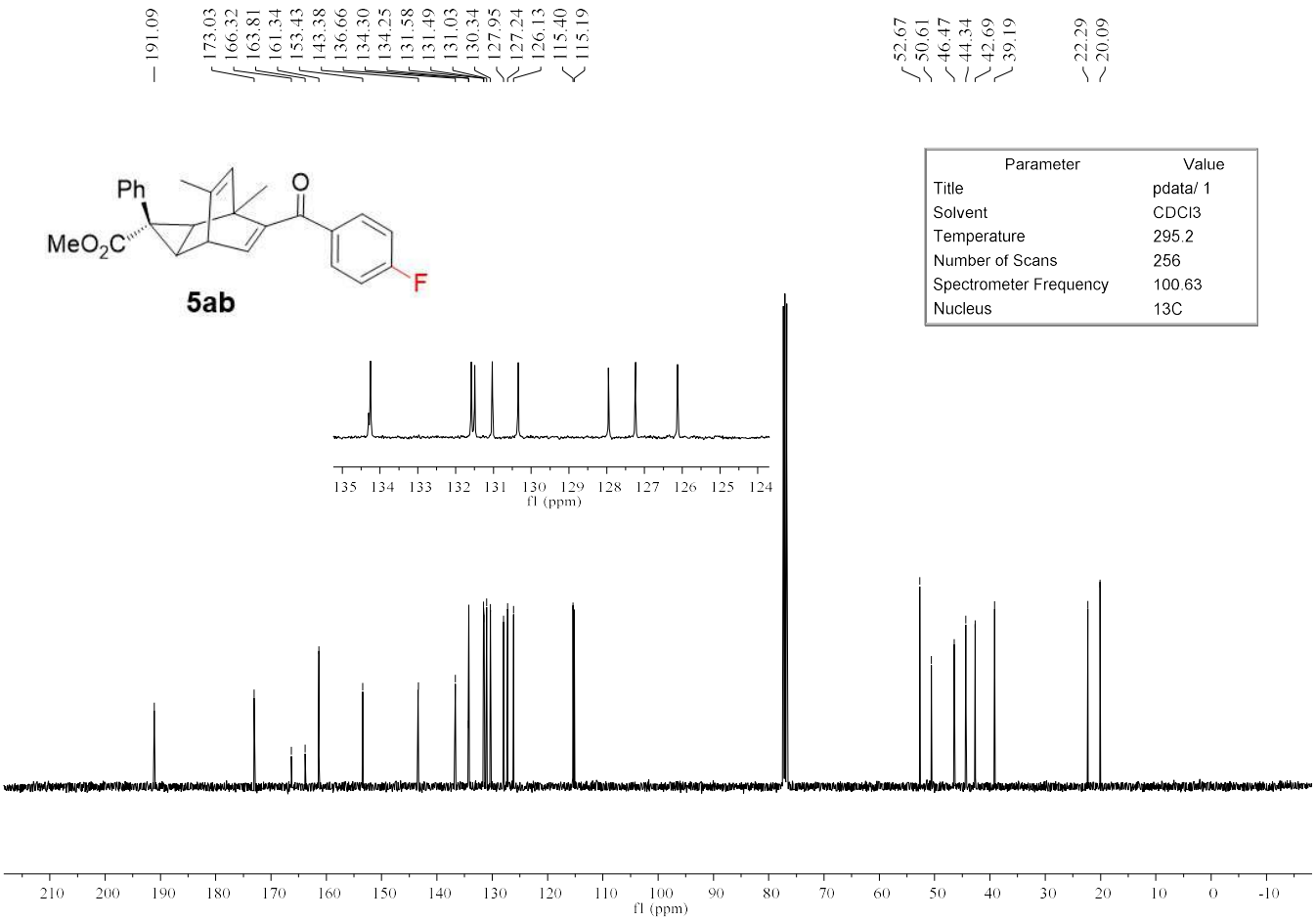


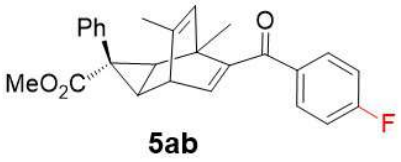
5aa

Parameter	Value
Title	wsyuan-20220421-N-1.2.1.1r
Solvent	CDCl3
Temperature	297.5
Number of Scans	256
Spectrometer Frequency	100.61
Nucleus	13C



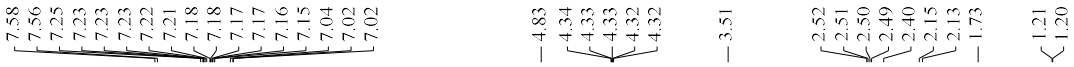

7.70 7.70 7.69 7.68 7.67 7.67 7.24 7.23 7.23 7.22 7.19 7.18 7.17 7.17 7.15 7.12 7.09 7.08 7.07 7.04 7.02
4.84
4.33 4.32 4.32
3.50
2.52 2.51 2.49 2.48 2.15 2.13
1.74
1.20 1.20
Ph
O
MeO2C
F
5ab
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 294.6
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
f1 (ppm)

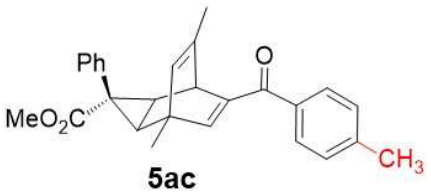

191.09
173.03 166.32 163.81 161.34 153.43 143.38 136.66 134.30 134.25 131.58 131.49 131.03 130.34 127.95 127.24 126.13 115.40 115.19
52.67 50.61 46.47 44.34 42.69 39.19
22.29 20.09
Ph
O
MeO2C
F
5ab
Parameter Value
Title pdata/ 1
Solvent CDCl3
Temperature 295.2
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
f1 (ppm)



5ab

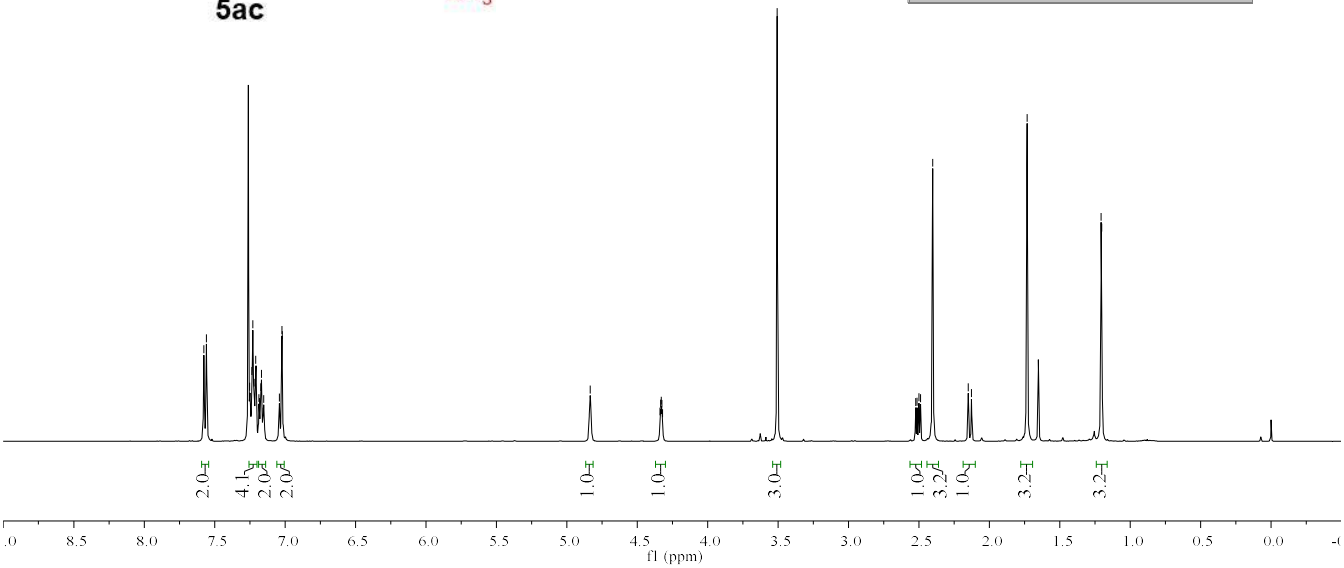
Parameter	Value
Title	pdata/ 1
Solvent	CDCl3
Temperature	294.9
Number of Scans	16
Spectrometer Frequency	376.55
Nucleus	19F

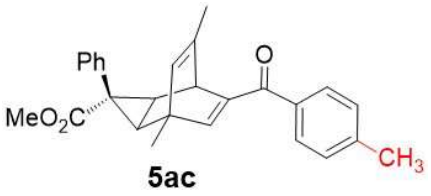




5ac

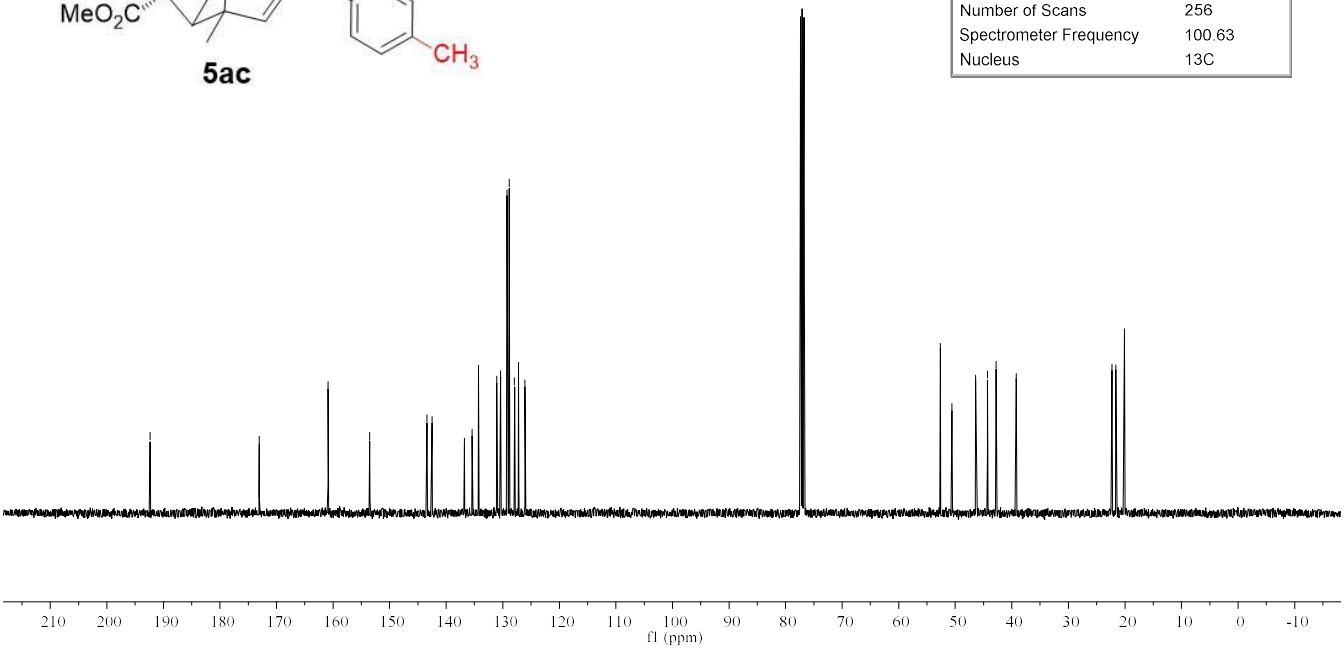
Parameter	Value
Title	pdata/ 1
Solvent	CDCl3
Temperature	294.6
Number of Scans	16
Spectrometer Frequency	400.18
Nucleus	1H

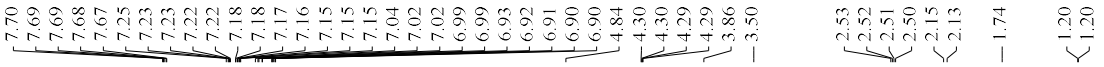




5ac

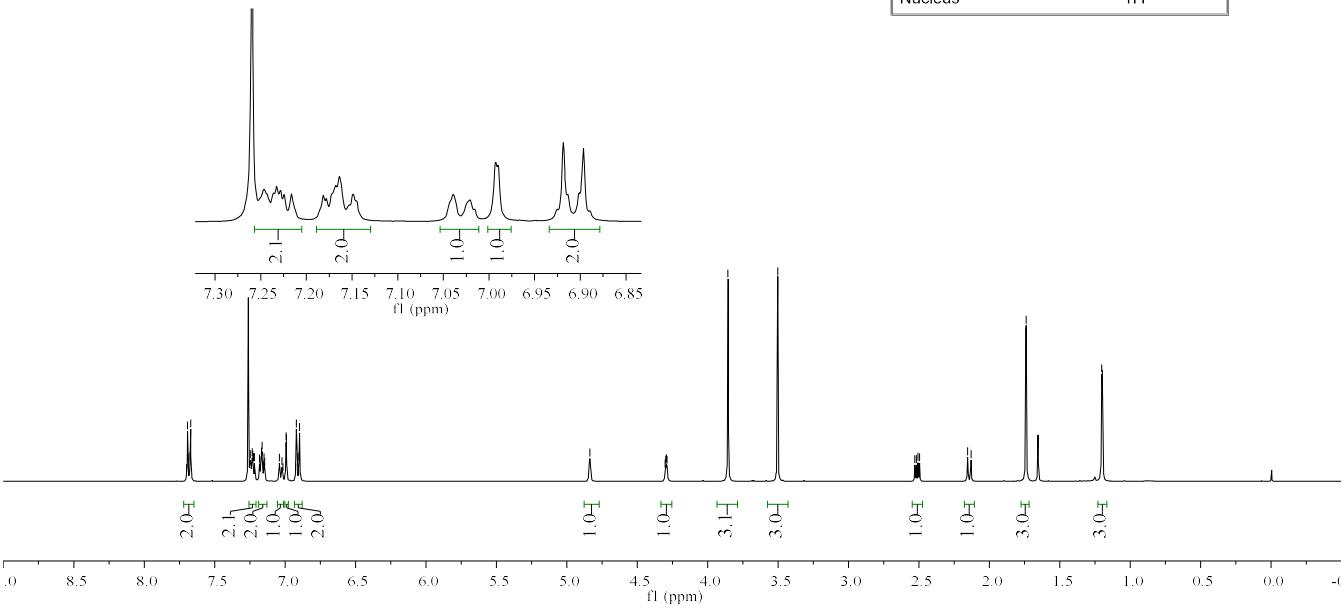
Parameter	Value
Title	pdata/ 1
Solvent	CDCl3
Temperature	295.2
Number of Scans	256
Spectrometer Frequency	100.63
Nucleus	13C





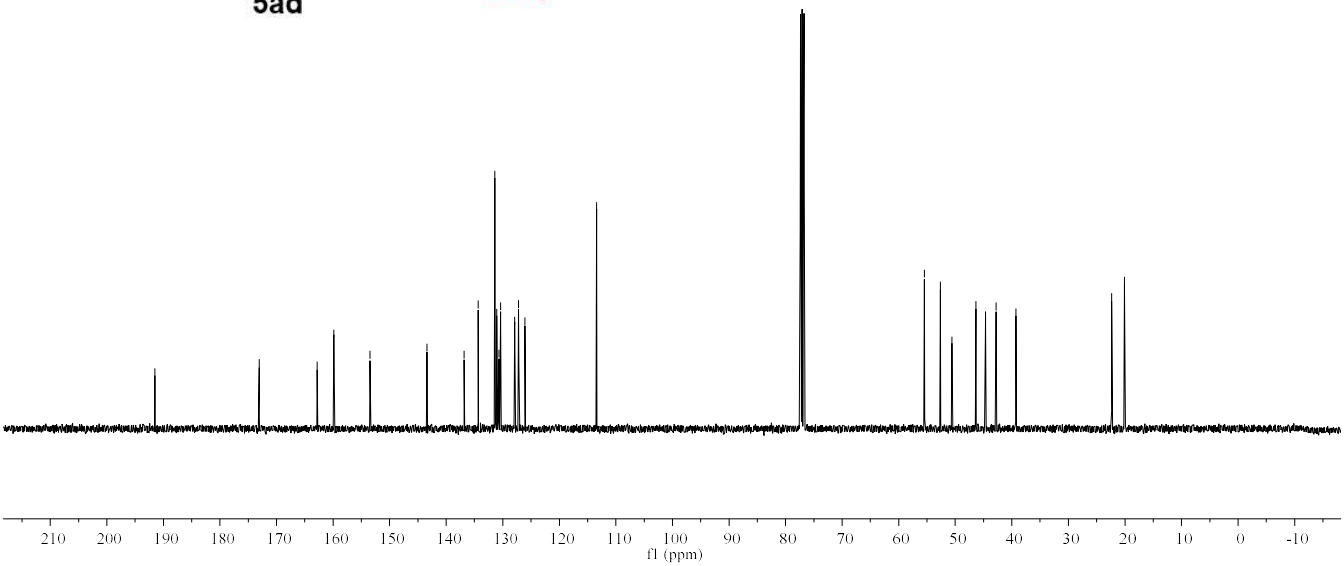
5ad

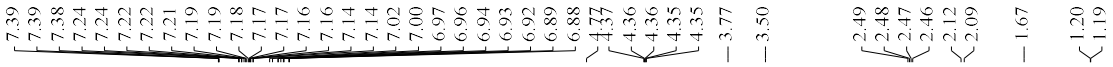
Parameter	Value
Title	pdata/ 1
Solvent	CDCl3
Temperature	294.8
Number of Scans	16
Spectrometer Frequency	400.18
Nucleus	1H

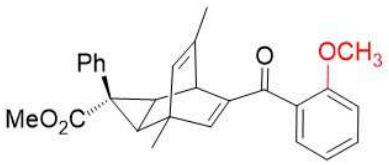


5ad

Parameter	Value
Title	pdata/ 1
Solvent	CDCl3
Temperature	295.4
Number of Scans	256
Spectrometer Frequency	100.63
Nucleus	13C

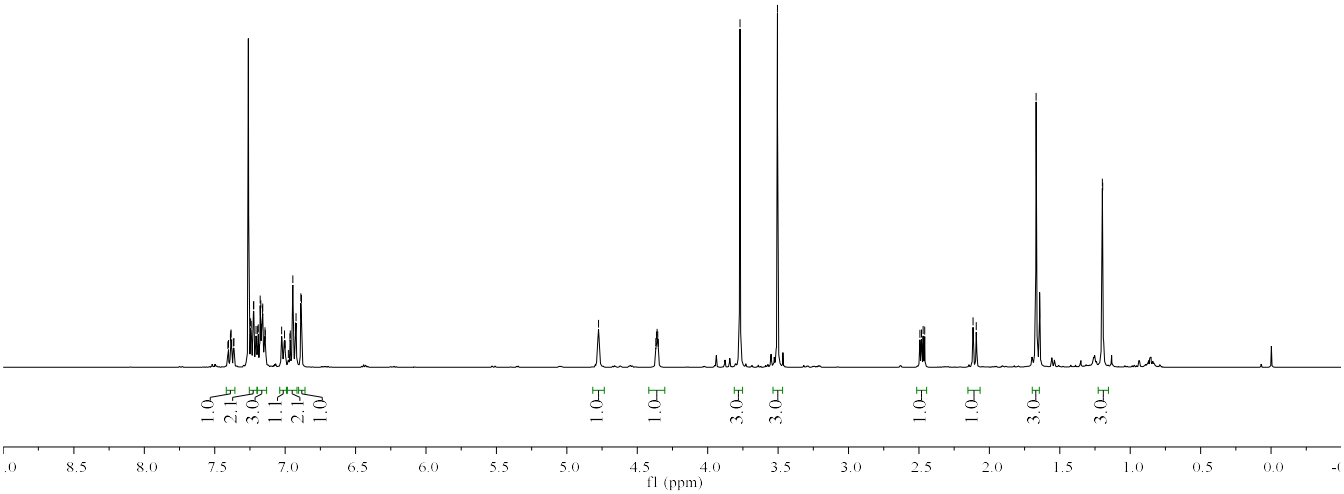


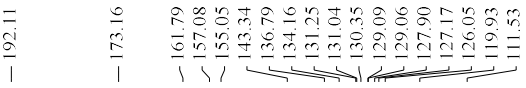


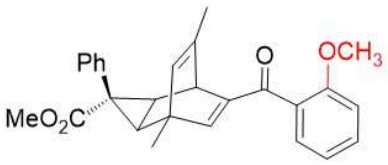


5ae

Parameter	Value
Title	pdata/ 1
Solvent	CDCl3
Temperature	294.8
Number of Scans	16
Spectrometer Frequency	400.18
Nucleus	1H

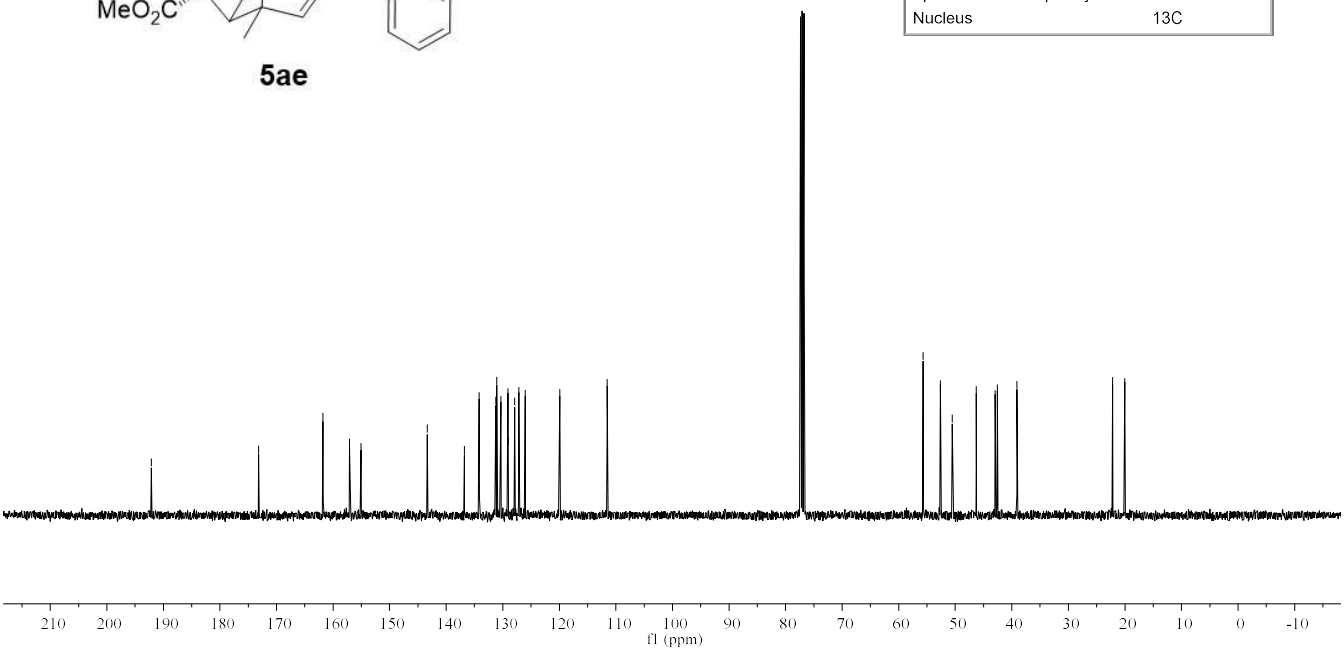


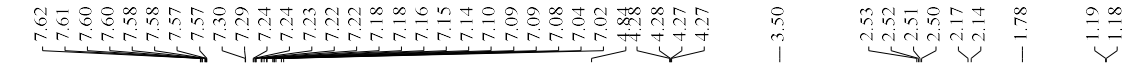


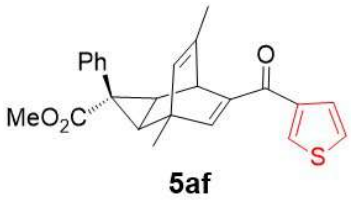


5ae

Parameter	Value
Title	pdata/ 1
Solvent	CDCl3
Temperature	295.3
Number of Scans	256
Spectrometer Frequency	100.63
Nucleus	13C

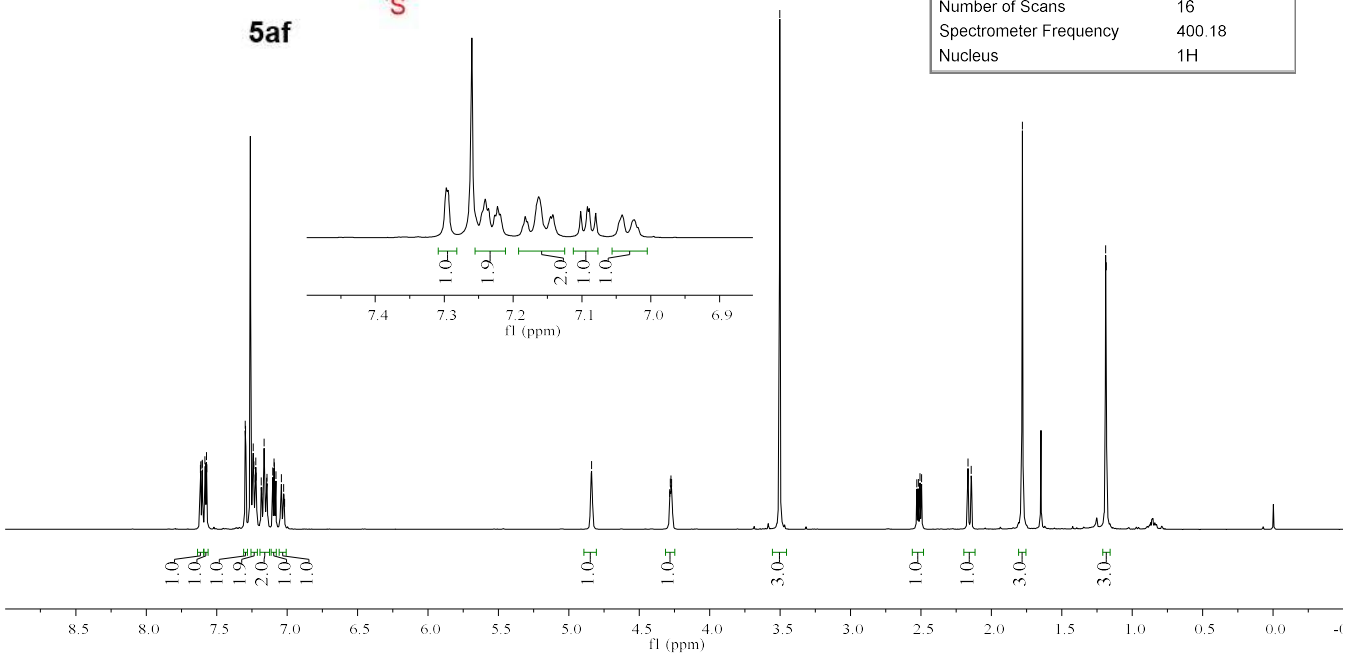


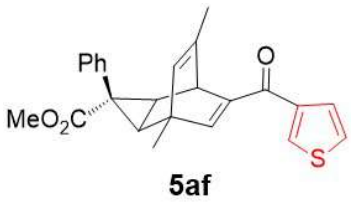




5af

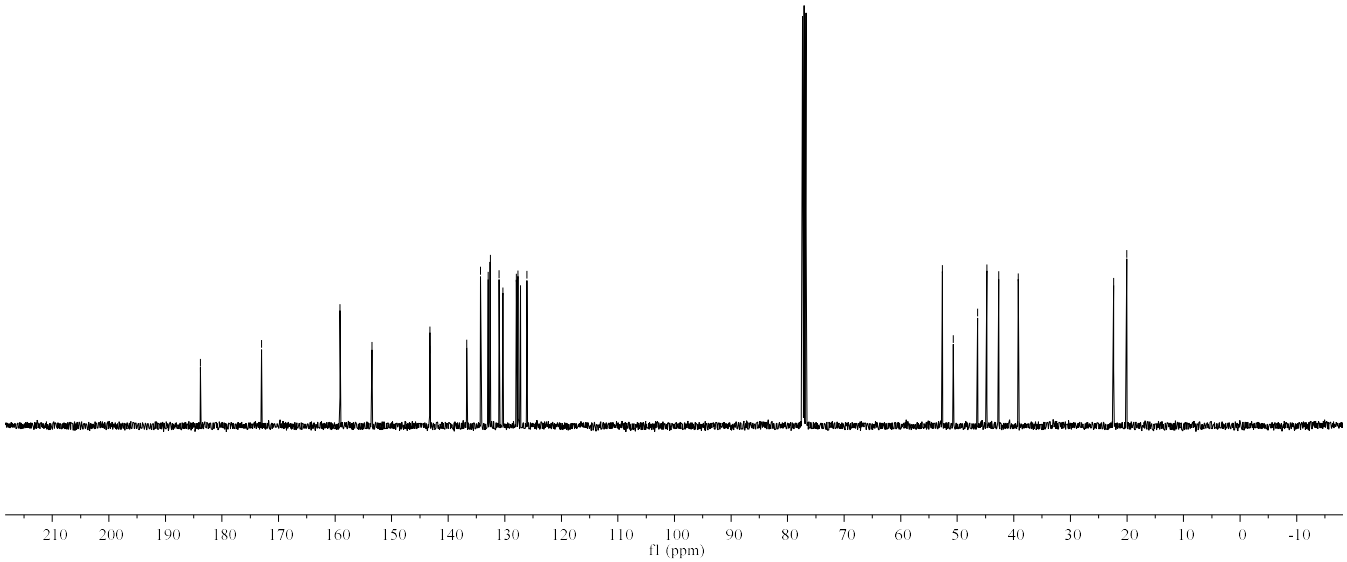
Parameter	Value
Title	pdata/ 1
Solvent	CDCl3
Temperature	294.8
Number of Scans	16
Spectrometer Frequency	400.18
Nucleus	1H

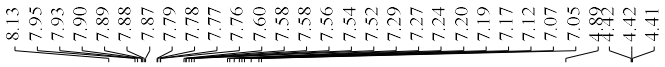


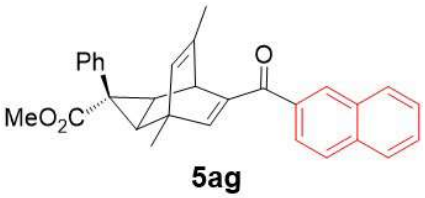


5af

Parameter	Value
Title	pdata/ 1
Solvent	CDCl3
Temperature	295.4
Number of Scans	256
Spectrometer Frequency	100.63
Nucleus	13C

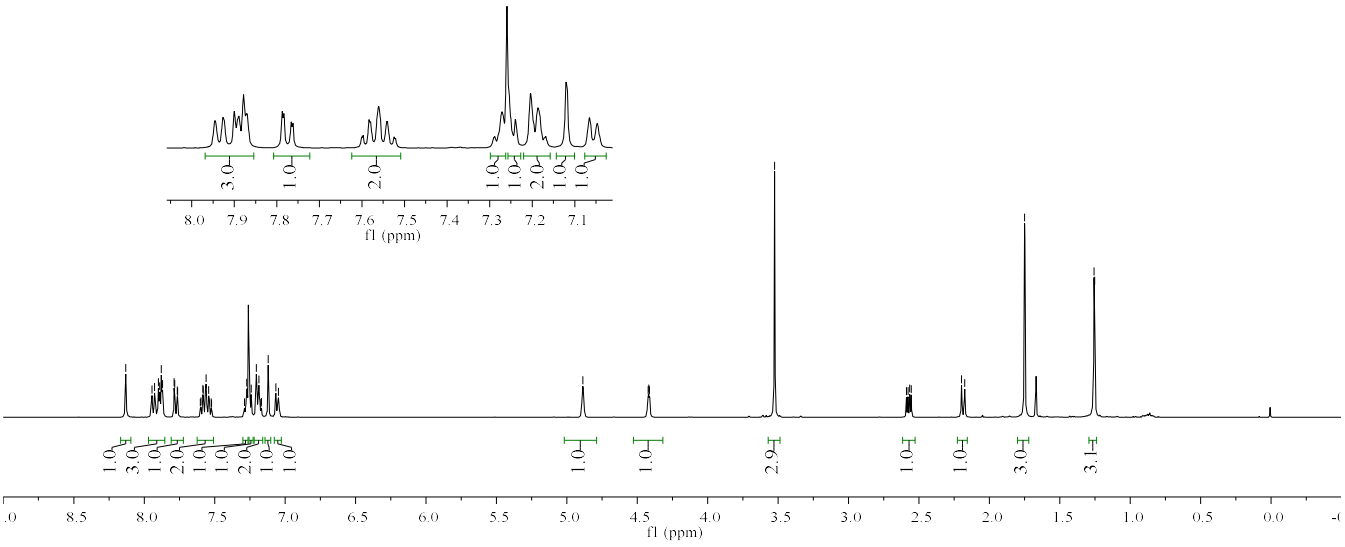


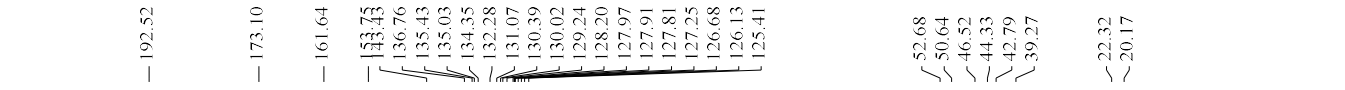


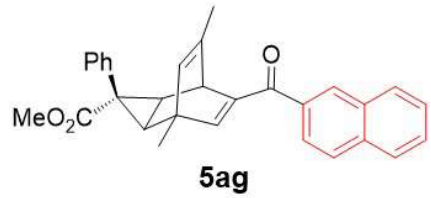


5ag

Parameter	Value
Title	pdata/ 1
Solvent	CDCl3
Temperature	294.6
Number of Scans	16
Spectrometer Frequency	400.18
Nucleus	1H

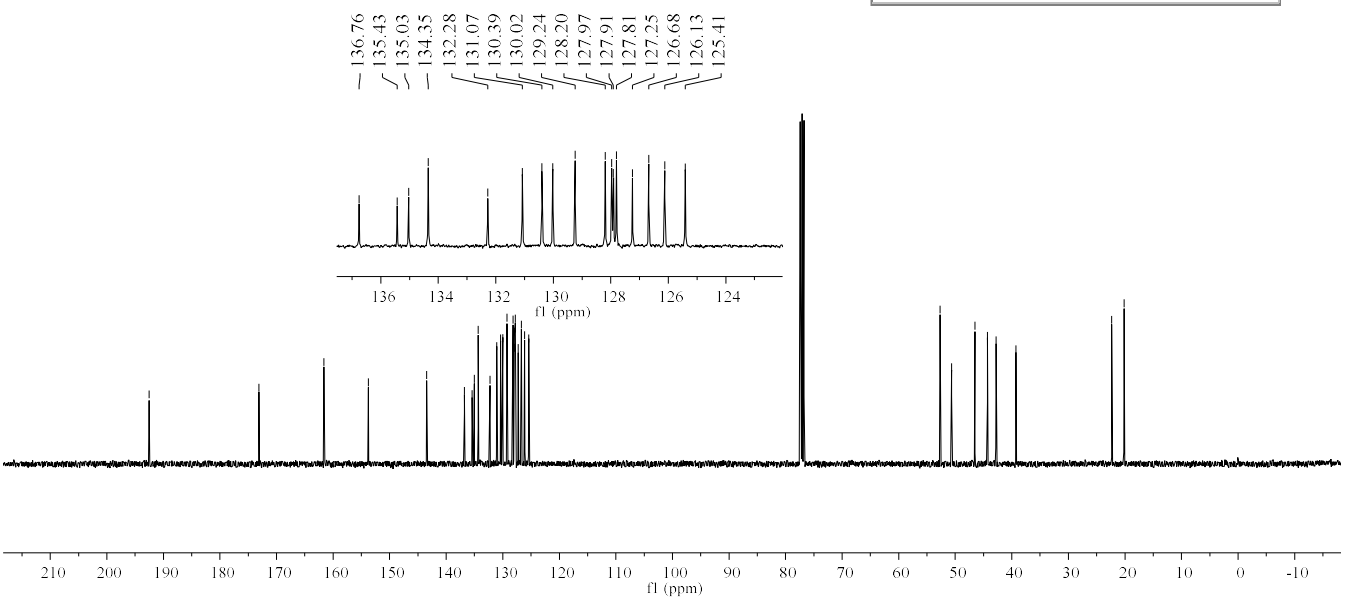


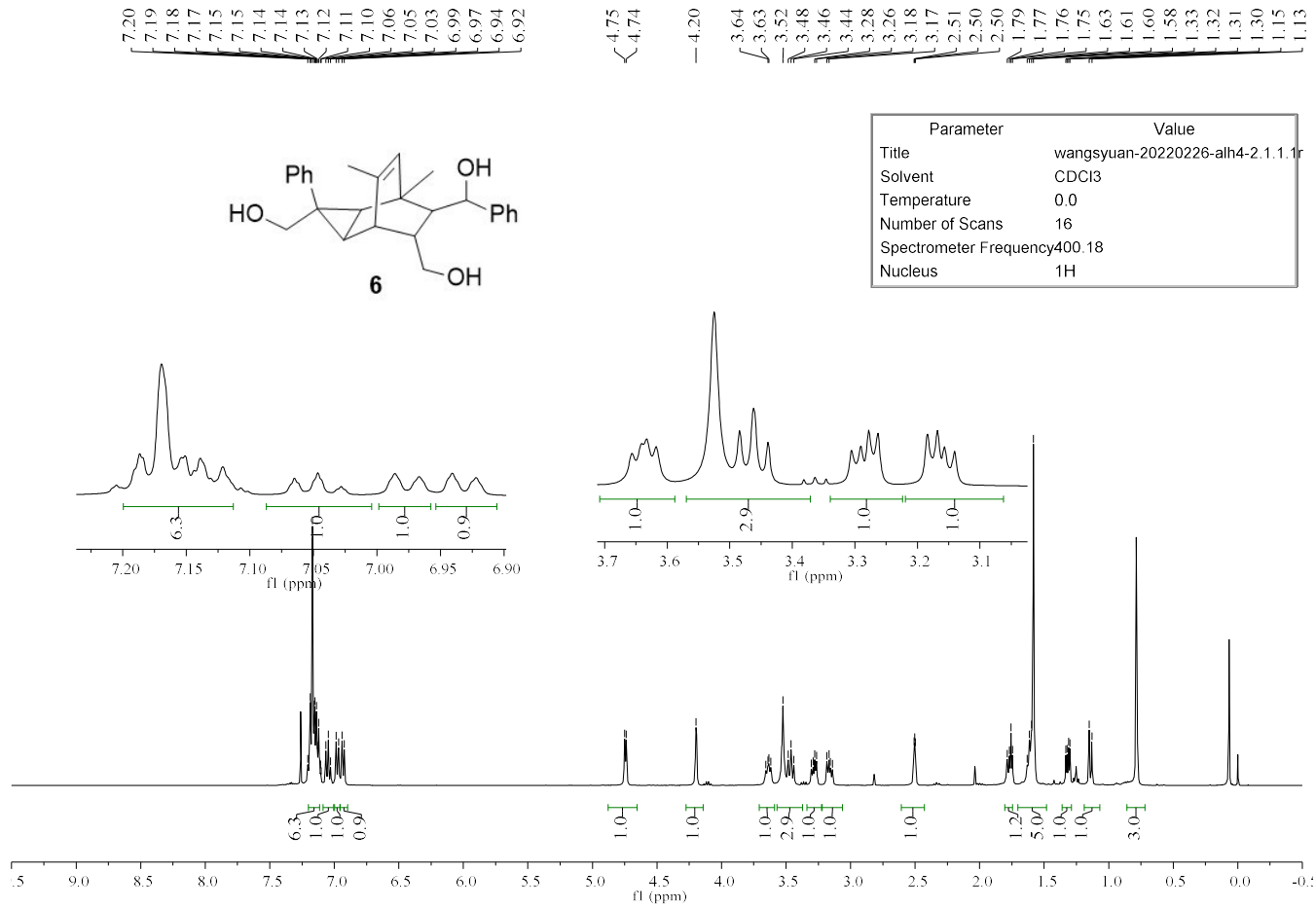


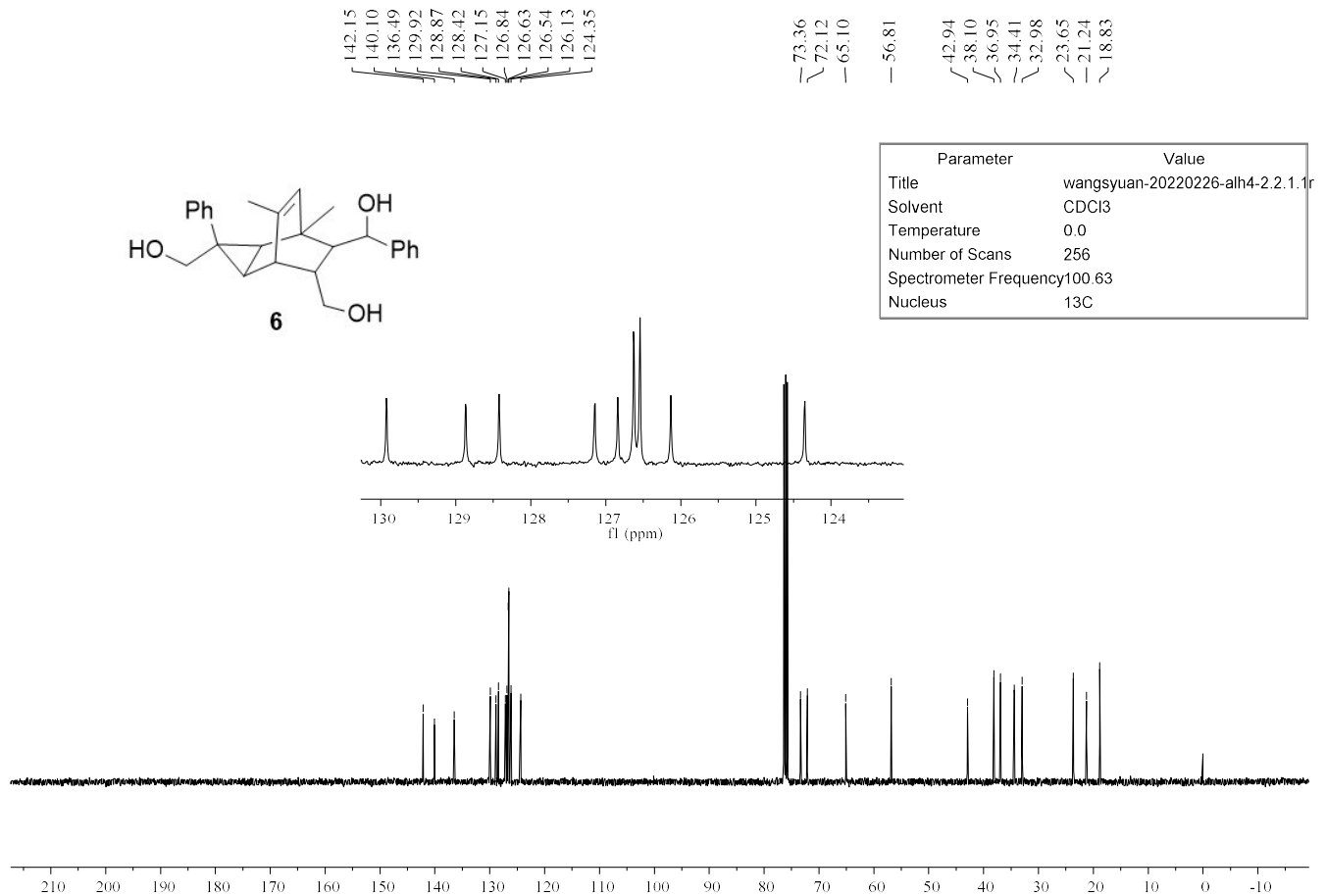


5ag

Parameter	Value
Title	pdata/ 1
Solvent	CDCl3
Temperature	295.2
Number of Scans	256
Spectrometer Frequency	100.63
Nucleus	13C




7.20 7.19 7.18 7.17 7.15 7.15 7.14 7.14 7.13 7.12 7.11 7.10 7.06 7.05 7.03 6.99 6.97 6.94 6.92
4.75 4.74
4.20
3.64 3.63 3.52 3.48 3.46 3.44 3.28 3.26 3.18 3.17 2.51 2.50 2.50
1.79 1.77 1.76 1.75 1.63 1.61 1.60 1.58 1.33 1.32 1.31 1.30 1.15 1.13
Ph
OH
HO
Ph
OH
6
Parameter Value
Title wangsyuan-20220226-alh4-2.1.1.1r
Solvent CDCl3
Temperature 0.0
Number of Scans 16
Spectrometer Frequency 400.18
Nucleus 1H
6.3 1.0 1.0 0.9
1.0 2.9 1.0 1.0
f1 (ppm)


142.15 140.10 136.49 129.92 128.87 128.42 127.15 126.84 126.63 126.54 126.13 124.35
73.36 72.12 65.10 56.81
42.94 38.10 36.95 34.41 32.98 23.65 21.24 18.83
Ph
OH
HO
Ph
OH
6
Parameter Value
Title wangsyuan-20220226-alh4-2.2.1.1r
Solvent CDCl3
Temperature 0.0
Number of Scans 256
Spectrometer Frequency 100.63
Nucleus 13C
f1 (ppm)