Supporting Information

for

Lewis Acid-Catalyzed Unexpected Selective C-C Bond Cleavage : An Efficient and Mild Construction of Cyclopentenes

Qiong Yu and Shengming Ma*

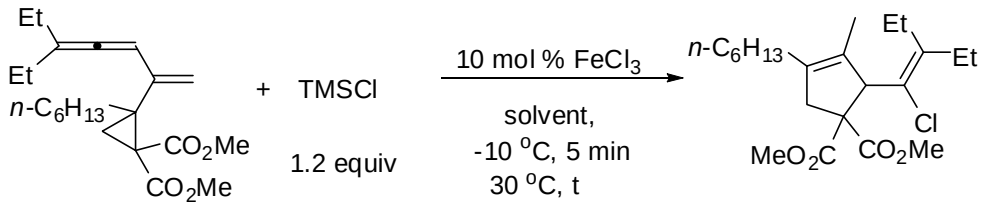
Shanghai Key Laboratory of Green Chemistry and Chemical Process, Department of Chemistry, East China Normal University, 3663 North Zhongshan Road, Shanghai 200062, P. R. China, and State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, P. R. China

masm@sioc.ac.cn

Supporting Information

Table of Contents

Table S1. Solvent effect on the reaction of **1a** with TMSCl forming cyclopentene **3a**.[a]



1a **3a**

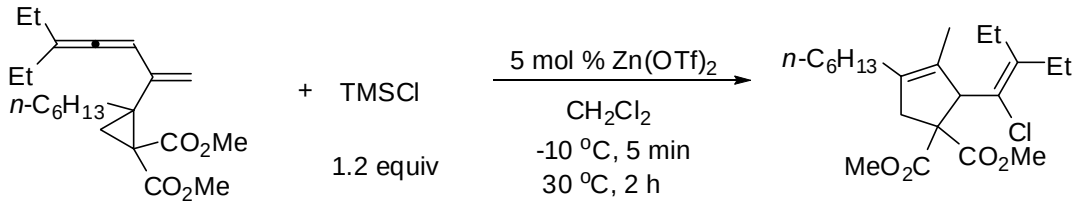
entry	solvent	time (h)	yield of **3a** (%)[b]	recovery of **1a**[b]
1	CH_2Cl_2	1	75[c]	-
2	CH_3CN	24	0	-
3	$ClCH_2CH_2Cl$	24	32	8
4	THF	24	0	100
5	DMF	24	0	100
6	1,1,1-trichloroethane	24	0	92
7	1,1,2-trichloroethane	27	62	7
8	DMSO	24	0	85
9	CH_3NO_2	24	20	0
10	dioxane	24	4 [c]	67

[a] Unless otherwise specified, the reaction was carried out using **1a** (0.2 mmol), TMSCl (31 μL, d = 0.846 g/mL, 26.2 mg, 0.24 mmol) and 10 mol% $FeCl_3$ in 5 mL of indicated solvent under nitrogen atmosphere. [b] NMR yield determined by ^{1}H NMR analysis using 1,3,5-trimethylbenzene as the internal standard. [c] Isolated yield.

General Information. All reactions were carried out in oven dried Schlenk tubes. All solvents were distilled from the indicated drying reagents right before use: dioxane, THF (over Na wire, benzophenone); $ClCH_2CH_2Cl$, 1,1,1-trichloroethane, 1,1,2-trichloroethane, MeCN, DMSO, DMF, CH_2Cl_2 (over CaH_2). TMSCl and TMSBr were distilled before use. The petroleum ether (30-60 ^oC) was distilled before use.

Synthesis of cyclopentenes 3

1. Dimethyl 2-(1-chloro-2-ethylbut-1-enyl)-4-hexyl-3-methylcyclopent-3-ene-1,1-dicarboxylate (3a) (yq-2-193)



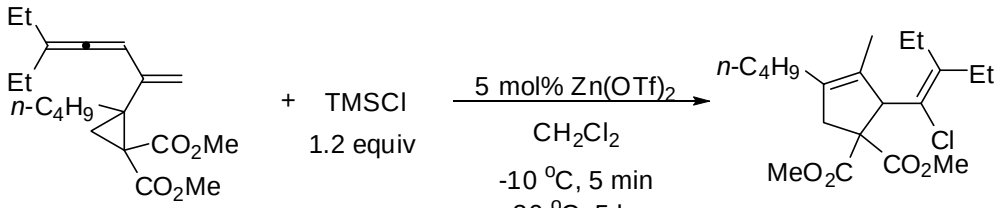
1a **3a** (94%)

Typical Procedure: Under an atmosphere of dry nitrogen, $Zn(OTf)_2$ (3.8 mg, 0.01 mmol) and 1 mL of CH_2Cl_2 were added to a reaction tube at -10 ^oC. TMSCl (31 μL, d = 0.846 g/mL, 26.2 mg, 0.24 mmol) was injected in one portion. Then a solution of **1a** (72.1 mg, 0.2 mmol) in 4 mL of CH_2Cl_2 was added dropwise slowly within 5 min. The resulting mixture was stirred at 30 ^oC. After the reaction was complete as monitored by TLC, the reaction mixture was quenched with 5 mL of water, extracted with EtOAc, and washed sequentially with water (3×5 mL) and an aqueous saturated solution of NaCl (3×5 mL). The organic layer was dried over anhydrous $MgSO_4$. After filtration and removal of the solvent under vacuum, the residue was purified by flash chromatography on silica gel (eluent: petroleum

ether/ethyl acetate = 20:1) to afford **3a** (74.5 mg , 94%) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.69 (s, 1 H, CH), 3.71 (s, 3 H, OCH_3), 3.62 (s, 3 H, OCH_3), 3.51 (d, *J* = 16.8 Hz, 1 H, one proton from CH_2), 2.56 (d, *J* = 16.8 Hz, 1 H, one proton from CH_2), 2.45-2.27 (m, 2 H, CH_2), 2.17-1.95 (m, 4 H, 2×CH_2), 1.50 (s, 3 H, =CCH_3), 1.43-1.17 (m, 8 H, 4×CH_2), 1.05 (t, *J* = 7.2 Hz, 3 H, CH_3), 0.97 (t, *J* = 7.2 Hz, 3 H, CH_3), 0.86 (t, *J* = 5.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 169.8, 143.5, 135.5, 129.4, 127.0, 62.0, 58.3, 52.8, 52.2, 42.9, 31.6, 28.8, 28.1, 27.4, 26.6, 25.4, 22.6, 14.0, 13.0, 12.11, 12.07; IR (neat) υ 2961, 2932, 2872, 2858, 1737, 1434, 1378, 1246, 1206 1160, 1121, 1078, 1048cm^{-1}; MS (EI) *m/z* (%) 400 (M(^{37}Cl)$^{+}$, 1.56), 398 (M(^{35}Cl)$^{+}$, 4.42), 303 (100); HRMS calcd. for $C_{22}H_{35}{}^{35}ClO_4$ [M^{+}]: 398.2224; Found: 398.2227.

The following compounds were prepared according to this Typical Procedure.

2. Dimethyl 4-butyl-2-(1-chloro-2-ethylbut-1-enyl)-3-methylcyclopent-3-ene-1,1-dicarboxylate (3b) (yq-3-86)

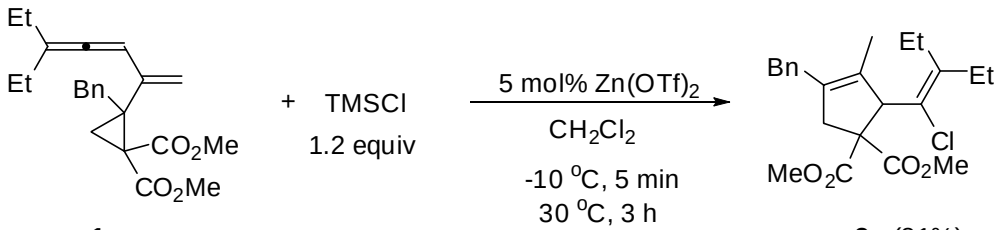


1b **3b** (87%)

The reaction of $Zn(OTf)_2$ (3.4 mg, 0.01 mmol), TMSCl (31 μL, d = 0.846 g/mL, 26.2 mg, 0.24 mmol), and **1b** (65.5 mg, 0.20 mmol) in 5 mL of CH_2Cl_2 afforded **3b** (63.1 mg, 87%) as an oil (eluent: petroleum ether/ethyl acetate = 40:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.69 (s, 1 H, CH), 3.71 (s, 3 H, OCH_3), 3.62 (s, 3 H, OCH_3), 3.52 (d, *J* = 16.8 Hz, 1 H, one proton from CH_2), 2.56 (d, *J* = 16.5 Hz, 1 H, one proton from

CH_2), 2.49-2.25 (m, 2 H, CH_2), 2.20-1.95 (m, 4 H, 2×CH_2), 1.50 (s, 3 H, =CCH_3), 1.43-1.15 (m, 4 H, 2×CH_2), 1.05 (t, J = 7.7 Hz, 3 H, CH_3), 0.97 (t, J = 7.5 Hz, 3 H, CH_3), 0.87 (t, J = 7.1 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 169.9, 143.5, 135.5, 129.4, 126.9, 61.9, 58.3, 52.9, 52.3, 42.9, 29.7, 27.9, 26.6, 25.4, 22.3, 13.9, 13.1, 12.2, 12.1; IR (neat) 2959, 2932, 2873, 1737, 1454, 1434, 1379, 1246, 1222, 1199, 1161, 1080, 1045 cm^{-1}; MS(EI) *m/z* (%) 372 ($M(^{37}Cl)^+$, 1.66), 370 ($M(^{35}Cl)^+$, 4.39), 275 (100); HRMS calcd. for $C_{20}H_{31}{}^{35}ClO_4$ [M^+]: 370.1911; Found: 370.1910

3. Dimethyl 4-benzyl-2-(1-chloro-2-ethylbut-1-enyl)-3-methylcyclopent-3-ene-1,1 –dicarboxylate (3c) (yq-3-41)

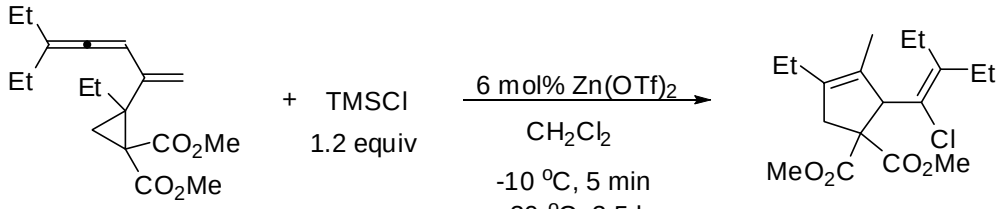


1c **3c** (81%)

The reaction of $Zn(OTf)_2$ (3.9 mg, 0.01 mmol), TMSCl (31 μL, d = 0.846 g/mL, 26.2 mg, 0.24 mmol), and **1c** (73.2 mg, 0.20 mmol) in 5 mL of CH_2Cl_2 afforded **3c** (64.7 mg, 81%) as an oil (eleuent: petroleum ether/ethyl acetate = 20:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28-7.20 (m, 2 H, Ar-H), 7.20-7.07 (m, 3 H, Ar-H), 4.78 (s, 1 H, CH), 3.64 (s, 3 H, OCH_3), 3.60 (s, 3 H, OCH_3), 3.52-3.35 (m, 3 H, one proton from CH_2 and CH_2 of Bn), 2.51-2.30 (m, 3 H, one proton from CH_2 and one CH_2), 2.19-2.01 (m, 2 H, CH_2), 1.66 (s, 3 H, =CCH_3), 1.09 (t, J = 7.5 Hz, 3 H, CH_3), 0.99 (t, J = 7.5 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.5, 169.6, 143.8, 139.1, 133.8, 131.4, 128.5, 128.3, 126.8, 125.9, 61.9, 58.3, 52.8, 52.2, 42.7, 34.5, 26.6, 25.4, 13.1, 12.3, 12.1; IR (neat) υ 2967, 2934, 2873, 1734, 1602, 1494, 1453, 1433, 1379,

1247, 1221, 1198, 1157, 1110, 1077, 1047, 1030 cm^{-1}; MS (EI) *m/z* (%) 406 ($M(^{37}Cl)^+$, 0.92), 404 ($M(^{35}Cl)^+$, 2.56), 91 (100); Anal. Calcd. for $C_{23}H_{29}ClO_4$: C, 68.22; H, 7.22; Found: C, 68.21; H, 7.22.

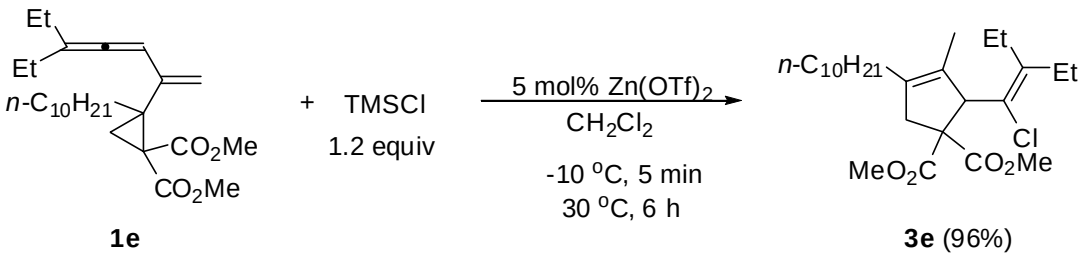
4. Dimethyl 2-(1-chloro-2-ethylbut-1-enyl)-4-ethyl-3-methylcyclopent-3-ene-1,1-dicarboxylate (3d) (yq-3-40)



1d **3d** (89%)

The reaction of $Zn(OTf)_2$ (4.2 mg, 0.012 mmol), TMSCl (31 μL, d = 0.846 g/mL, 26.2 mg, 0.24 mmol), and **1d** (61.5 mg, 0.20 mmol) in 5 mL of CH_2Cl_2 afforded **3d** (61.4 mg, 89%) as an oil (eluent: petroleum ether/ethyl acetate = 20:1): ^1H NMR (300 MHz, $CDCl_3$) δ 4.69 (s, 1 H, CH), 3.71 (s, 3 H, OCH_3), 3.62 (s, 3 H, OCH_3), 3.53 (d, *J* = 16.5 Hz, 1 H, one proton from CH_2), 2.57 (d, *J* = 16.5 Hz, 1 H, one proton from CH_2), 2.49-2.26 (m, 2 H, CH_2), 2.22-1.94 (m, 4 H, 2×CH_2), 1.50 (s, 3 H, =CCH_3), 1.05 (t, *J* = 7.5 Hz, 3 H, CH_3), 0.97 (t, *J* = 7.5 Hz, 6 H, 2×CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 169.9, 143.5, 136.8, 128.6, 127.0, 61.9, 58.3, 52.9, 52.3, 42.5, 26.6, 25.4, 21.4, 13.1, 12.22, 12.17, 11.9; IR (neat) υ 2966, 2935, 2874, 1736, 1453, 1434, 1378, 1243, 1203, 1162, 1121, 1079 cm^{-1}; MS(EI) *m/z* (%) 344 ($M(^{37}Cl)^+$, 0.52), 342 ($M(^{35}Cl)^+$, 1.25), 59 (100); HRMS calcd. for $C_{18}H_{27}{}^{35}ClO_4$ [M^+]: 342.1598; Found: 342.1594.

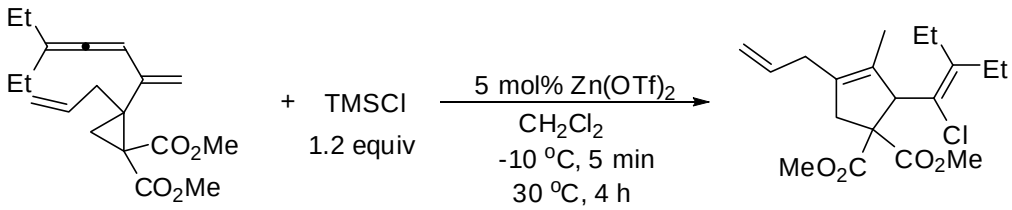
5. Dimethyl 2-(1-chloro-2-ethylbut-1-enyl)-4-decyl-3-methylcyclopent-3-ene-1,1-dicarboxylate (3e) (yq-4-22)



1e **3e** (96%)

The reaction of $Zn(OTf)_2$ (3.6 mg, 0.01 mmol), TMSCl (31 μL, d = 0.846 g/mL, 26.2 mg, 0.24 mmol), and **1e** (82.9 mg, 0.20 mmol) in 5 mL of CH_2Cl_2 afforded **3e** (86.6 mg, 96%) as an oil (eluent: petroleum ether/ethyl acetate = 40:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.69 (s, 1 H, CH), 3.71 (s, 3 H, OCH_3), 3.62 (s, 3 H, OCH_3), 3.51 (d, *J* = 16.8 Hz, 1 H, one proton from CH_2), 2.56 (d, *J* = 15.9 Hz, 1 H, one proton from CH_2), 2.49-2.27 (m, 2 H, CH_2), 2.19-1.93 (m, 4 H, 2×CH_2), 1.50 (s, 3 H, =CCH_3), 1.44-1.11 (m, 16 H, 8×CH_2), 1.05 (t, *J* = 7.5 Hz, 3 H, CH_3), 0.97 (t, *J* = 7.4 Hz, 3 H, CH_3), 0.87 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 169.9, 143.5, 135.5, 129.4, 127.0, 61.9, 58.3, 52.9, 52.3, 42.9, 31.9, 29.61, 29.59, 29.5, 29.3, 29.2, 28.1, 27.5, 26.6, 25.4, 22.7, 14.1, 13.1, 12.2, 12.1; IR (neat) υ 2966, 2927, 2856, 1738, 1456, 1435, 1378, 1246, 1204, 1159, 1077 cm^{-1}; MS(EI) *m/z* (%) 456 ($M(^{37}Cl)^+$, 0.42), 454 ($M(^{35}Cl)^+$, 1.07), 43 (100); HRMS calcd. for $C_{26}H_{43}{}^{35}ClO_4$ [M^+]: 454.2850; Found: 454.2849.

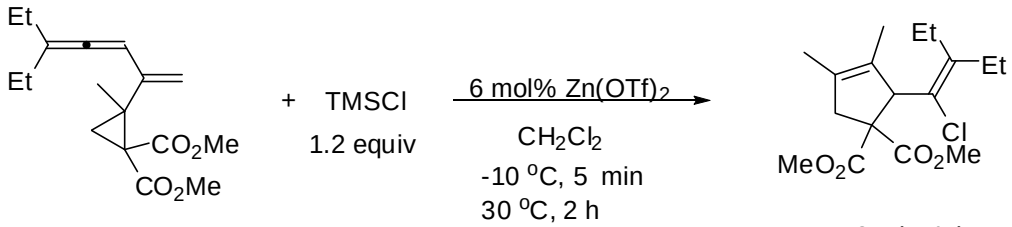
6. Dimethyl 4-allyl-2-(1-chloro-2-ethylbut-1-enyl)-3-methylcyclopent-3-ene-1,1-dicarboxylate (3f) (yq-4-44)



1f **3f** (44%)

The reaction of $Zn(OTf)_2$ (3.8 mg, 0.01 mmol), TMSCl (31 μL, d = 0.846 g/mL, 26.2 mg, 0.24 mmol), and **1f** (62.6 mg, 0.20 mmol) in 5 mL of CH_2Cl_2 afforded **3f** (30.9 mg, 44%) as an oil (eluent: petroleum ether/ethyl acetate = 40:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.81-5.65 (m, 1 H, =CH), 5.09-4.93 (m, 2 H, $=CH_2$), 4.73 (s, 1 H, CH), 3.70 (s, 3 H, OCH_3), 3.62 (s, 3 H, OCH_3), 3.51 (d, *J* = 16.5 Hz, 1 H, one proton from CH_2), 2.91-2.73 (m, 2 H, CH_2), 2.56 (d, *J* = 17.1 Hz, 1 H, one proton from CH_2), 2.49-2.23 (m, 2 H, CH_2), 2.19-2.01 (m, 2 H, CH_2), 1.52 (s, 3 H, CH_3), 1.05 (t, *J* = 7.5 Hz, 3 H, $=CCH_3$), 0.97 (t, *J* = 7.5 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 169.7, 143.7, 134.9, 132.8, 130.8, 126.8, 115.6, 61.8, 58.4, 53.0, 52.3, 43.0, 32.6, 26.6, 25.4, 13.1, 12.14, 12.08; IR (neat) υ 2968, 2875, 1736, 1639, 1435, 1379, 1249, 1203, 1163, 1078, 1047 cm^{-1}; MS(EI) *m/z* (%) 356 ($M(^{37}Cl)^+$, 1.27), 354 ($M(^{35}Cl)^+$, 3.79), 91 (100); HRMS calcd. for $C_{19}H_{27}{}^{35}ClO_4$ [M^+]: 354.1598; Found: 354.1596.

7. Dimethyl 2-(1-chloro-2-ethylbut-1-enyl)-3,4-dimethylcyclopent-3-ene-1,1-dicarboxylate (3g) (yq-4-102)

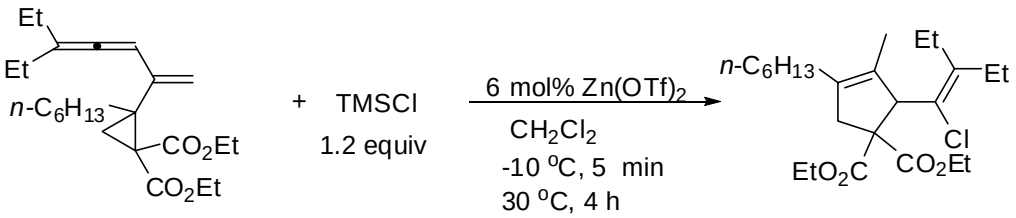


1g **3g** (74%)

The reaction of $Zn(OTf)_2$ (4.5 mg, 0.012 mmol), TMSCl (31 μL, d = 0.846 g/mL,

26.2 mg, 0.24 mmol), and **1g** (58.4 mg, 0.20 mmol) in 5 mL of CH_2Cl_2 afforded **3g** (48.8 mg, 74%) as an oil (eluent: petroleum ether/ethyl acetate = 40:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.70 (s, 1 H, CH), 3.71 (s, 3 H, OCH_3), 3.62 (s, 3 H, OCH_3), 3.50 (d, *J* = 16.5 Hz, 1 H, one proton from CH_2), 2.54 (d, *J* = 16.8 Hz, 1 H, one proton from CH_2), 2.48-2.25 (m, 2 H, CH_2), 2.18-2.00 (m, 2 H, CH_2), 1.65 (s, 3 H, CH_3), 1.50 (s, 3 H, CH_3), 1.05 (t, *J* = 7.5 Hz, 3 H, CH_3), 0.97 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 169.8, 143.6, 131.0, 129.3, 127.1, 61.8, 58.4, 52.9, 52.3, 45.1, 26.6, 25.4, 13.6, 13.1, 12.2, 12.1; IR (neat) υ 2968, 2874, 1736, 1435, 1245, 1206, 1163, 1081 cm^{-1}; MS(EI) *m/z* (%) 330 (M(^{37}Cl)$^+$, 1.44), 328 (M(^{35}Cl)$^+$, 3.90), 173 (100); HRMS calcd. for $C_{17}H_{25}{}^{35}ClO_4$ [M^+]: 328.1441; Found: 328.1440.

8. Diethyl 2-(1-chloro-2-ethylbut-1-enyl)-4-hexyl-3-methylcyclopent-3-ene-1,1-dicarboxylate (3h) (yq-3-79)

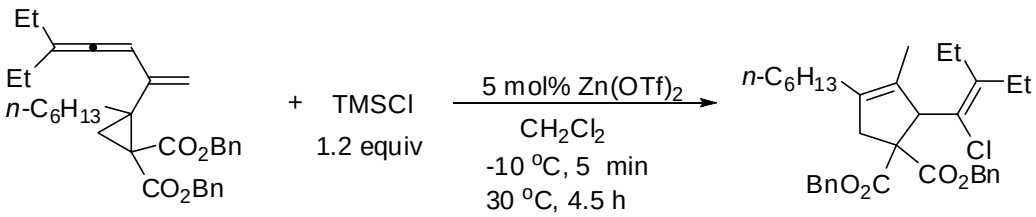


1h **3h** (90%)

The reaction of $Zn(OTf)_2$ (4.3 mg, 0.012 mmol), TMSCl (31 μL, d = 0.846 g/mL, 26.2 mg, 0.24 mmol), and **1h** (78.1 mg, 0.20 mmol) in 5 mL of CH_2Cl_2 afforded **3h** (77.2 mg, 90%) as an oil (eluent: petroleum ether/ethyl acetate = 40:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.69 (s, 1 H, CH), 4.27-4.04 (m, 3 H, OCH_2 and one proton from another OCH_2), 4.04-3.91 (m, 1 H, one proton from OCH_2), 3.51 (d, *J* = 16.2 Hz, 1 H, one proton from CH_2), 2.55 (d, *J* = 16.5 Hz, 1 H, one proton from CH_2), 2.49-2.20 (m, 2 H, CH_2), 2.20-1.94 (m, 4 H, 2×CH_2), 1.50 (s, 3 H, =CCH_3), 1.45-1.13 (m, 14 H, 4

×CH_2 and 2×CH_3), 1.06 (t, *J* = 7.5 Hz, 3 H, CH_3), 0.97 (t, *J* = 7.5 Hz, 3 H, CH_3), 0.86 (t, *J* = 6.2 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.2, 169.4, 143.1, 135.5, 129.4, 127.3, 61.9, 61.6, 61.2, 58.2, 42.9, 31.7, 28.9, 28.1, 27.5, 26.7, 25.6, 22.6, 14.05, 13.95, 13.86, 13.2, 12.1, 12.0; IR (neat) υ 2964, 2931, 2872, 2858, 1734, 1464, 1379, 1366, 1299, 1243, 1205, 1156, 1075, 1046, 1018 cm^{-1}; MS(EI) *m/z* (%) 428 ($M(^{37}Cl)^+$, 1.54), 426 ($M(^{35}Cl)^+$, 4.04), 317 (100); HRMS calcd. for $C_{24}H_{39}{}^{35}ClO_4$ [M^+]: 426.2537; Found: 426.2538.

9. Dibenzyl 2-(1-chloro-2-ethylbut-1-enyl)-4-hexyl-3-methylcyclopent-3-ene-1,1-dicarboxylate (3i) (yq-4-16)

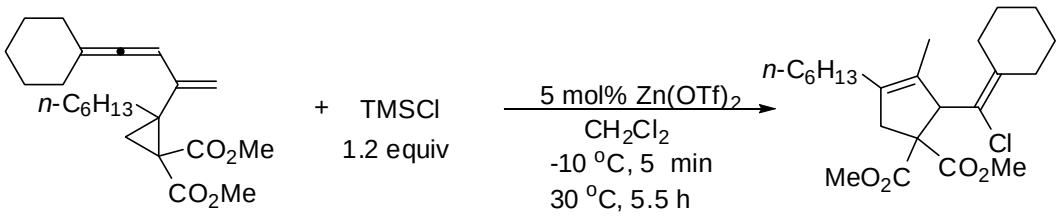


1i **3i** (76%)

The reaction of $Zn(OTf)_2$ (3.5 mg, 0.01 mmol), TMSCl (31 μL, d = 0.846 g/mL, 26.2 mg, 0.24 mmol), and **1i** (102.3 mg, 0.20 mmol) in 5 mL of CH_2Cl_2 afforded **3i** (82.8 mg, 76%) as an oil (eluent: petroleum ether/ethyl acetate = 50:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.13 (m, 10 H, Ar-H), 5.14 (d, *J* = 12.3 Hz, 1 H, one proton from OCH_2), 5.12 (d, *J* = 12.3 Hz, 1 H, one proton from OCH_2), 5.03 (d, *J* = 12.3 Hz, 1 H, one proton from OCH_2), 4.88 (d, *J* = 12.3 Hz, 1 H, one proton from OCH_2), 4.73 (s, 1 H, CH), 3.56 (d, *J* = 16.8 Hz, 1 H, one proton from CH_2), 2.61 (d, *J* = 16.5 Hz, 1 H, one proton from CH_2), 2.41-1.84 (m, 6 H, 3×CH_2), 1.50 (s, 3 H, =CCH_3), 1.41-1.09 (m, 8 H, 4×CH_2), 0.98-0.81 (m, 9 H, 3×CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 169.1, 143.4, 135.5, 135.4, 135.3, 129.4, 128.4, 128.3, 128.2, 128.1, 128.0,

127.9, 126.9, 67.3, 67.1, 62.0, 58.3, 42.9, 31.6, 28.8, 28.1, 27.4, 26.7, 25.5, 22.6, 14.1, 13.0, 12.11, 12.07; IR (neat) υ 2968, 2932. 1733, 1455, 1377, 1235, 1154, 1067 cm^{-1}; MS(EI) *m/z* (%) 552 ($M(^{37}Cl)^+$, 0.09) 550 ($M(^{35}Cl)^+$, 0.29), 91 (100); Anal. Calcd. for $C_{34}H_{43}ClO_4$: C, 74.09; H, 7.86; Found: C, 74.35; H, 7.97.

10. Dimethyl 2-(chloro(cyclohexylidene)methyl)-4-hexyl-3-methylcyclopent-3-ene-1,1-dicarboxylate (3j) (yq-3-83)

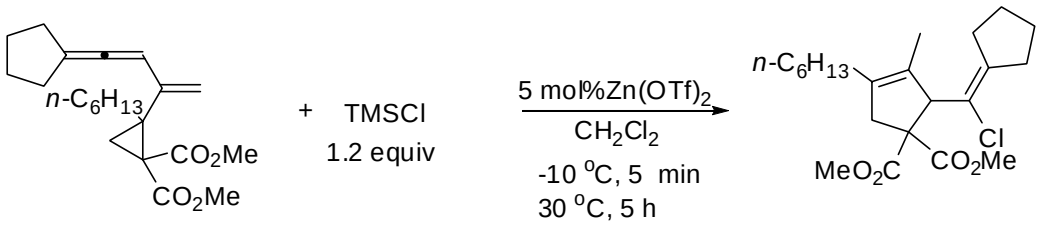


1j **3j** (74%)

The reaction of $Zn(OTf)_2$ (3.8 mg, 0.01 mmol), TMSCl (31 μL, d = 0.846 g/mL, 26.2 mg, 0.24 mmol), and **1j** (76.2 mg, 0.20 mmol) in 5 mL of CH_2Cl_2 afforded **3j** (61.5 mg, 74%) as an oil (eluent: petroleum ether/ethyl acetate = 50:1): ^1H NMR (300 MHz, $CDCl_3$) δ 4.83 (s, 1 H, CH), 3.71 (s, 3 H, OCH_3), 3.65 (s, 3 H, OCH_3), 3.52 (d, *J* = 16.5 Hz, 1 H, one proton from CH_2), 2.56 (d, *J* = 16.8 Hz, 1 H, one proton from CH_2), 2.48-2.28 (m, 4 H, 2×CH_2), 2.20-1.93 (m, 2 H, CH_2), 1.65-1.42 (m, 9 H, 3× CH_2 and CH_3), 1.41-1.20 (m, 8 H, 4×CH_2), 0.96 (t, *J* = 6.5 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 170.0, 139.7, 135.4, 129.6, 124.0, 61.9, 58.0, 52.9, 52.4, 43.0, 32.2, 31.7, 31.6, 28.9, 28.1, 27.8, 27.5, 27.4, 26.5, 22.6, 14.1, 12.1; IR (neat) υ 2928, 2855, 1737, 1449, 1434, 1379, 1244, 1206, 1160, 1081, 1044 cm^{-1}; MS(EI) *m/z* (%) 412 ($M(^{37}Cl)^+$, 1.53), 410 ($M(^{35}Cl)^+$, 4.08), 249 (100); HRMS calcd. for $C_{23}H_{35}{}^{35}ClO_4$ [M^+]: 410.2224; Found: 410.2224.

11. Dimethyl 2-(chloro(cyclopentylidene)methyl)-4-hexyl-3-methylcyclopent-3-

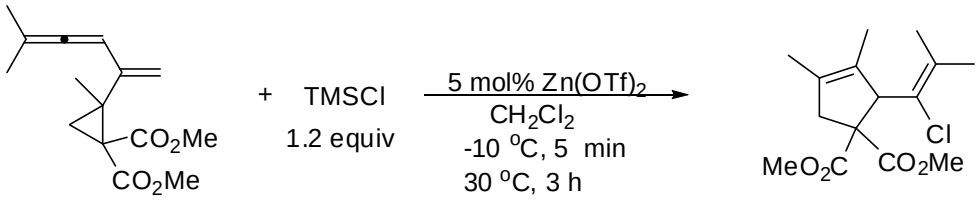
ene-1,1-dicarboxylate (3k) (yq-3-156)



1k **3k** (50%)

The reaction of $Zn(OTf)_2$ (3.9 mg, 0.011 mmol), TMSCl (31 μL, d = 0.846 g/mL, 26.2 mg, 0.24 mmol), **1k** (72.5 mg, 0.20 mmol) in 5 mL of CH_2Cl_2 afforded **3k** (39.9 mg, 50%) as an oil (petroleum ether/ethyl acetate = 40:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.54 (s, 1 H, CH), 3.71 (s, 3 H, OCH_3), 3.63 (s, 3 H, OCH_3), 3.49 (d, J = 16.8 Hz, 1 H, one proton from CH_2), 2.55 (d, J = 16.5 Hz, 1 H, one proton from CH_2), 2.50-2.20 (m, 4 H, 2×CH_2), 2.18-1.94 (m, 2 H, CH_2), 1.86-1.61 (m, 4 H, 2×CH_2), 1.51 (s, 3 H, =CCH_3), 1.43-1.15 (m, 8 H, 4×CH_2), 0.86 (t, J = 6.6 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 170.0, 144.7, 135.4, 129.5, 122.8, 62.0, 60.5, 52.9, 52.3, 42.7, 33.3, 31.9, 31.7, 28.8, 28.1, 27.6, 27.5, 26.1, 22.6, 14.1, 12.2; IR (neat) υ 2953, 2931, 2858, 1738, 1658, 1452, 1433, 1379, 1246, 1207, 1195, 1160, 1084, 1047 cm^{-1}; MS(EI) *m/z* (%) 398 (M(^{37}Cl)$^+$, 0.27), 396 (M(^{35}Cl)$^+$, 0.81), 43 (100); Anal. Calcd. for $C_{22}H_{33}ClO_4$: C, 66.57; H, 8.38; Found: C, 66.30; H, 8.49.

12. Dimethyl 2-(1-chloro-2-methylprop-1-enyl)-3,4-dimethylcyclopent-3-ene-1,1-dicarboxylate (3l) (yq-4-103)

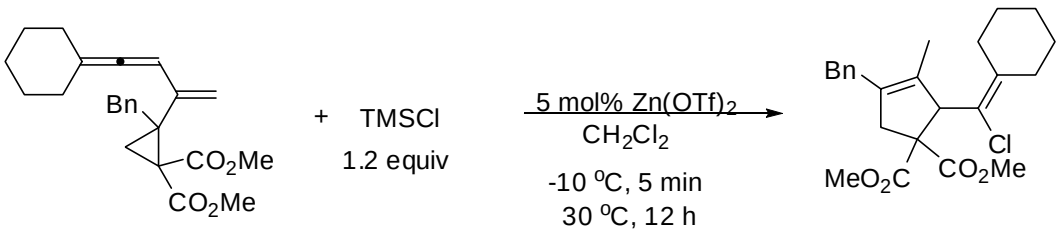


1l **3l** (79%)

The reaction of $Zn(OTf)_2$ (3.8 mg, 0.01 mmol), TMSCl (31 μL, d = 0.846 g/mL,

26.2 mg, 0.24 mmol), and **1l** (52.4 mg, 0.20 mmol) in 5 mL of CH_2Cl_2 afforded **3l** (42.9 mg, 79%) as an oil (petroleum ether/ethyl acetate = 40:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.77 (s, 1 H, CH), 3.71 (s, 3 H, OCH_3), 3.62 (s, 3 H, OCH_3), 3.48 (d, J = 16.5 Hz, 1 H, one proton from CH_2), 2.53 (d, J = 16.5 Hz, 1 H, one proton from CH_2), 1.88 (s, 3 H, CH_3), 1.84 (s, 3 H, CH_3), 1.64 (s, 3 H, CH_3), 1.49 (s, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 169.9, 132.3, 131.0, 129.6, 126.7, 61.9, 58.6, 52.9, 52.3, 45.0, 22.4, 21.0, 13.6, 12.2; IR (neat) υ 2924, 2858, 1736, 1435, 1381, 1246, 1206, 1161, 1080 cm^{-1}; MS(EI) *m/z* (%) 302 (M(^{37}Cl)$^+$, 2.01), 300 (M(^{35}Cl)$^+$, 5.78), 205 (100); HRMS calcd. for $C_{15}H_{21}{}^{35}ClO_4$ [M^+]: 300.1128; Found: 300.1127.

13. Dimethyl 4-benzyl-2-(chloro(cyclohexylidene)methyl)-3-methylcyclopent-3-ene-1,1-dicarboxylate (3m) (yq-4-9)

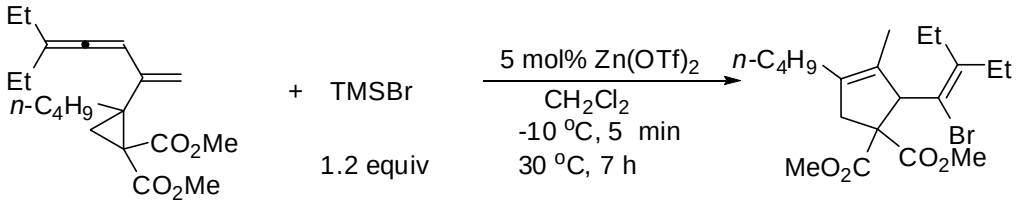


1m **3m** (62%)

The reaction of $Zn(OTf)_2$ (3.4 mg, 0.01 mmol), TMSCl (31 μL, d = 0.846 g/mL, 26.2 mg, 0.24 mmol), and **1m** (75.1 mg, 0.20 mmol) in 5 mL of CH_2Cl_2 afforded **3m** (51.1 mg, 62%) as an oil (eluent: petroleum ether/ethyl acetate = 40:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29-7.20(m, 2 H, Ar-H), 7.20-7.11 (m, 3 H, Ar-H), 4.91 (s, 1 H, CH), 3.65 (s, 3 H, OCH_3), 3.63 (s, 3 H, OCH_3), 3.52-3.33 (m, 3 H, one proton from CH_2 and Bn), 2.50-2.30 (m, 5 H, one proton from CH_2 and 2×CH_2), 1.70-1.45 (m, 9 H, 3×CH_2 and CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6, 169.8, 140.0, 139.2, 133.6, 131.6, 128.5, 128.3, 125.9, 123.7, 61.9, 58.0, 52.9, 52.4, 42.8, 34.5, 32.2, 31.6, 27.9,

27.5, 26.4, 12.3; IR (neat) υ 2970, 2932, 1735, 1495, 1452, 1379, 1247, 1158, 1077 cm^{-1}; MS(EI) *m/z* (%) 418 ($M(^{37}Cl)^+$, 0.80), 416 ($M(^{35}Cl)^+$, 2.25), 91 (100); HRMS calcd. for $C_{24}H_{29}{}^{35}ClO_4$ [M^+]: 416.1754; Found: 416.1752.

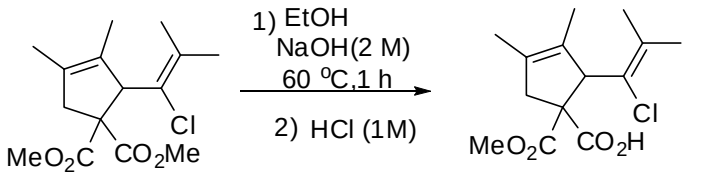
14. Dimethyl 2-(1-bromo-2-ethylbut-1-enyl)-4-butyl-3-methylcyclopent-3-ene-1,1-dicarboxylate (3n) (yq-5-18)



1b **3n** (62%)

The reaction of $Zn(OTf)_2$ (3.8 mg, 0.01 mmol), TMSBr (31.5 μL, d = 1.16 g/mL, 36.5 mg, 0.24 mmol), and **1b** (67.1 mg, 0.20 mmol) in 5 mL of CH_2Cl_2 afforded **3n** (51.7 mg, 62%) as an oil (eluent: petroleum ether/ethyl acetate = 40:1): ^1H NMR (300 MHz, $CDCl_3$) δ 4.72 (s, 1 H, CH), 3.71 (s, 3 H, OCH_3), 3.63 (s, 3 H, OCH_3), 3.55 (d, *J* = 16.8 Hz, 1 H, one proton from CH_2), 2.55 (d, *J* = 15.6 Hz, 1 H, one proton from CH_2), 2.51-2.28 (m, 2 H, CH_2), 2.19-1.92 (m, 4 H, 2×CH_2), 1.50 (s, 3 H, =CCH_3), 1.44-1.16 (m, 4 H, 2×CH_2), 1.06 (t, *J* = 7.5 Hz, 3 H, CH_3), 0.98 (t, *J* = 7.5 Hz, 3 H, CH_3), 0.88 (t, *J* = 7.1 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 169.7, 146.4, 135.5, 130.3, 121.5, 62.2, 59.3, 53.0, 52.3, 42.9, 29.9, 29.7, 27.9, 25.9, 22.5, 13.9, 13.0, 12.3, 12.1; IR (neat) υ 2957, 2873, 1734, 1434, 1379, 1248, 1199, 1162, 1080, 1036 cm^{-1}; MS(EI) *m/z* (%) 416 ($M(^{81}Br)^+$, 0.37), 414 ($M(^{79}Br)^+$, 0.39), 335 (100); Anal. Calcd. for $C_{20}H_{31}BrO_4$: C, 57.83; H, 7.52; Found: C, 57.82; H, 7.41.

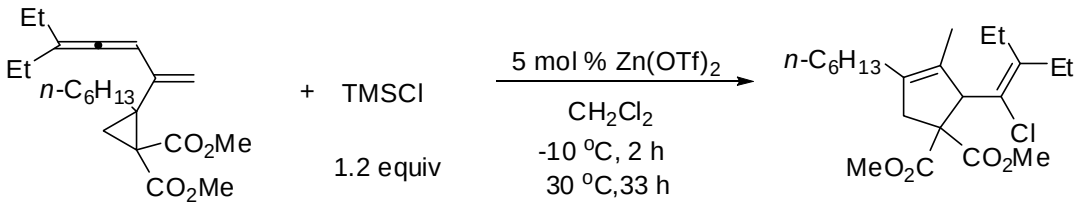
Synthesis of 2-(1-chloro-2-methylprop-1-en-1-yl)-3,4-dimethyl-3-cyclopentene -1,1-dicarboxylic acid-1-methyl ester 4 (yq-4-177)



3l **4** 94% yield

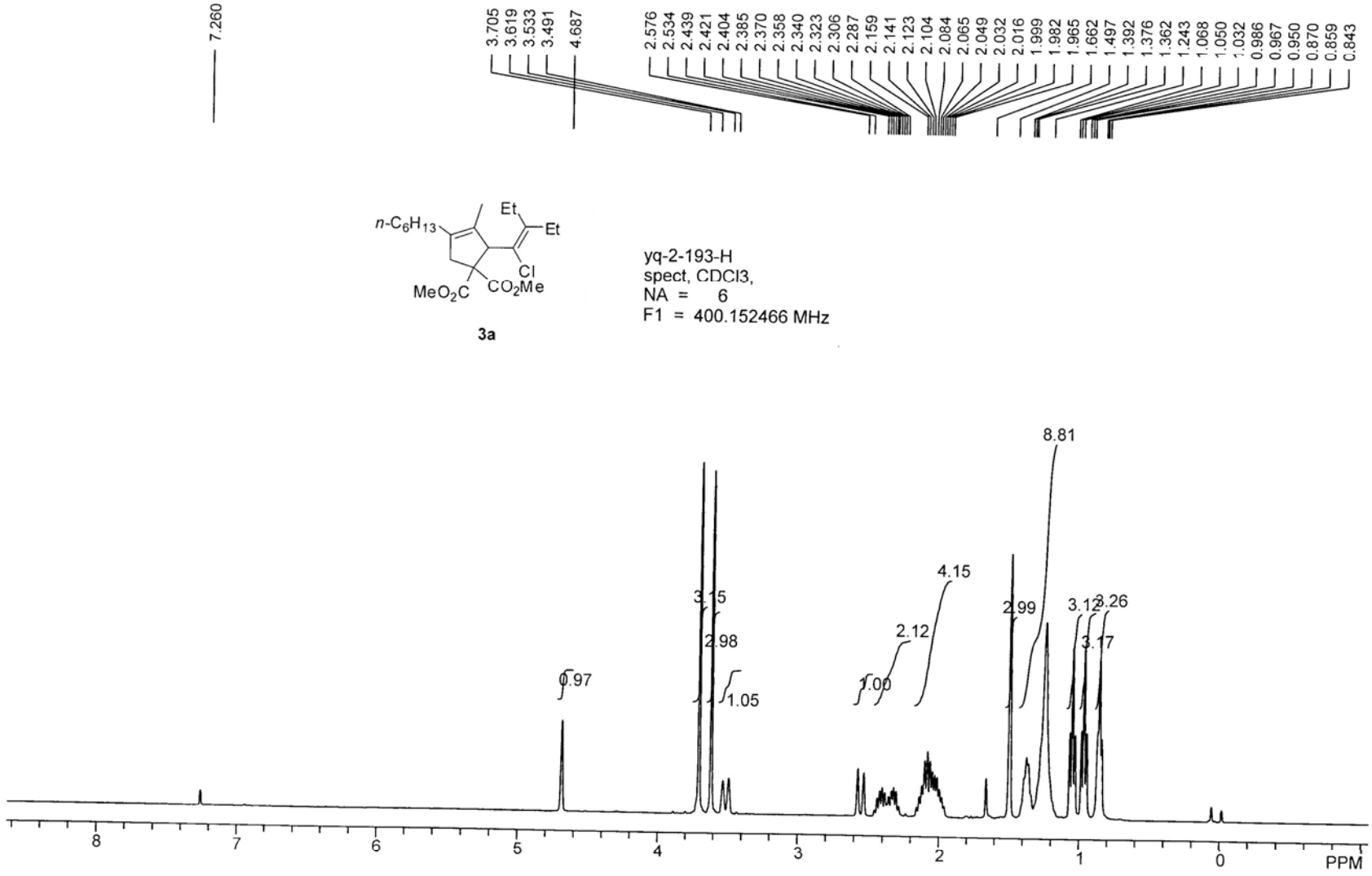
3l (186.3 mg, 0.6 mmol) and 3 mL of EtOH were added to a reaction tube. Then NaOH (2 mol/L, 2 mL) was injected in one portion. Then the mixture was stirred at 60 °C. After the reaction was complete as monitored by TLC, the reaction mixture was quenched with 5 mL of hydrochloric acid (1 M), extracted with EtOAc, and washed with water (3×8 mL) and an aqueous saturated solution of NaCl (3×8 mL). The organic layer was dried over anhydrous Na_2SO_4. After filtration and removal of the solvent under vacuum, the residue was purified with flash chromatography on silica gel (diethyl ether/dichloromethane = 1:1.5) to afford **4** (166.4 mg, 94%) as a solid: m.p.: 143-145 °C (diethyl ether): ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.40-10.60 (bs, 1 H, COOH), 4.69 (s, 1 H, CH), 3.65 (s, 3 H, OCH_3), 3.50 (d, *J* = 16.8 Hz, 1 H, one proton from CH_2), 2.66 (d, *J* = 16.8 Hz, 1 H, one proton from CH_2), 1.87 (s, 3 H, CH_3), 1.83 (s, 3 H, CH_3), 1.66 (s, 3 H, CH_3), 1.48 (s, 3 H, one =C-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.1, 169.5, 132.5, 131.2, 129.5, 126.4, 62.1, 58.4, 52.5, 45.0, 22.3, 20.9, 13.5, 12.1; IR (KBr) υ 3075, 2798, 1755, 1746, 1704, 1437, 1340, 1383, 1272, 1243, 1211, 1188, 1174, 1079, 1048, 1025 cm^{-1}; MS(EI) *m/z* (%) 288 (M(^{37}Cl)$^+$, 1.32), 286 (M(^{35}Cl)$^+$, 4.76), 91(100); Anal. Calcd. for $C_{14}H_{19}ClO_4$: C, 58.64; H, 6.68; Found: C, 58.57; H, 6.91.

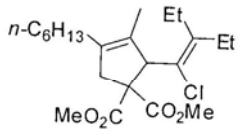
Synthesis of cyclopentenes 3a on 4.7 mmol scale (yq-5-161)



1a **3a** (83%)

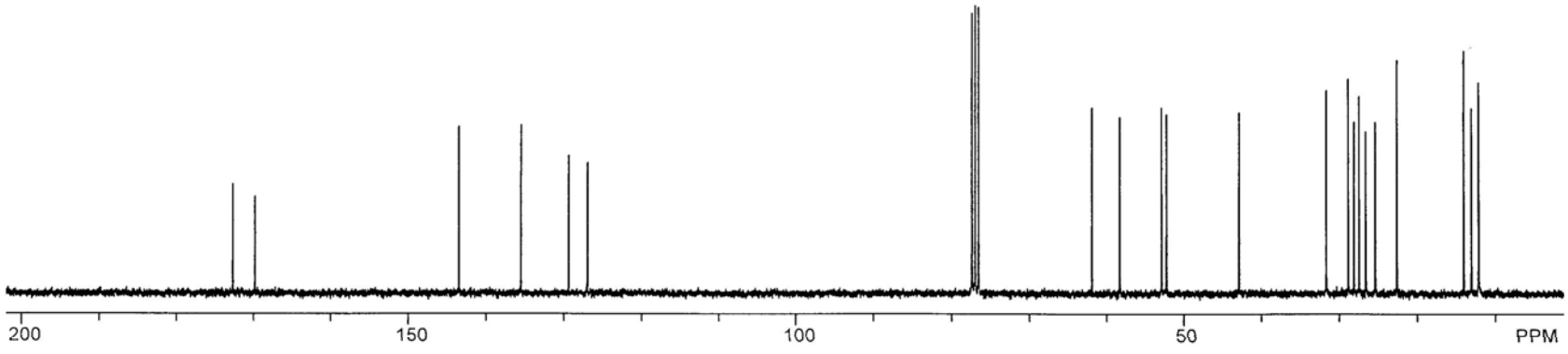
Under an atmosphere of dry argon, $Zn(OTf)_2$ (85.9 mg, 0.237 mmol) and 15 mL of CH_2Cl_2 were added to a two-necked round bottom flask at -10 °C. TMSCl (720 μL, d = 0.846 g/mL, 609.1 mg, 5.64 mmol) was injected in one portion. Then a solution of **1a** (1.7014 g, 4.7 mmol) in 20 mL of CH_2Cl_2 was added dropwise slowly by syringe pump within 2 h . The mixture was stirred at 30 °C. After the reaction was complete as monitored by TLC, the reaction mixture was quenched with 20 mL of water, extracted with EtOAc and washed sequentially with water (3×15 mL) and an aqueous saturated solution of NaCl (3×15 mL). The organic layer was dried over anhydrous $MgSO_4$. After filtration and removal of the solvent under vacuum, the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30:1) to afford **3a** (1.5376 g, 83%) as an oil. δ 4.68 (s, 1 H, CH), 3.70 (s, 3 H, OCH_3), 3.61 (s, 3 H, OCH_3), 3.50 (d, J = 16.5 Hz, 1 H, one proton from CH_2), 2.55 (d, J = 16.8 Hz, 1 H, one proton from CH_2), 2.48-2.24 (m, 2 H, CH_2), 2.20-1.95 (m, 4 H, 2× CH_2), 1.49 (s, 3 H, =CCH_3), 1.41-1.16 (m, 8 H, 4×CH_2), 1.04 (t, J = 7.5 Hz, 3 H, CH_3), 0.96 (t, J = 7.5 Hz, 3 H, CH_3), 0.85 (t, J = 6.9 Hz, 3 H, CH_3).

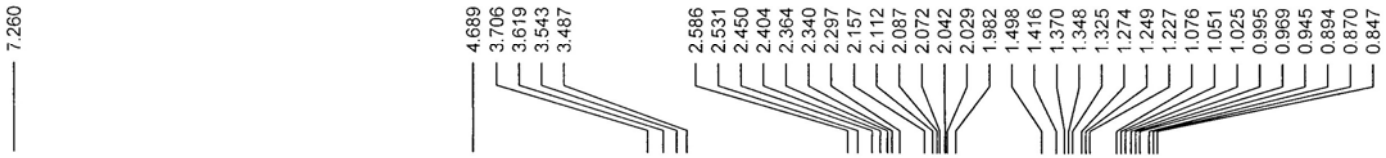

7.260
3.705
3.619
3.533
3.491
4.687
2.576
2.534
2.439
2.421
2.404
2.385
2.370
2.358
2.340
2.323
2.306
2.287
2.159
2.141
2.123
2.104
2.084
2.065
2.049
2.032
2.016
1.999
1.982
1.965
1.662
1.497
1.392
1.376
1.362
1.243
1.068
1.050
1.032
0.986
0.967
0.950
0.870
0.859
0.843
n-C6H13
Et
Et
Cl
MeO2C
CO2Me
3a
yq-2-193-H
spect, CDCl3,
NA = 6
F1 = 400.152466 MHz
8.81
4.15
3.15
2.98
2.12
2.99
3.12
3.26
3.17
0.97
1.00
1.05
8
7
6
5
4
3
2
1
0
PPM

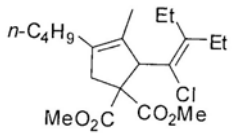


3a

yq-2-193-C
spect, CDCl3,
Thu Jun 28 14:47:18 2012
NA = 189
F1 = 75.475296 MHz

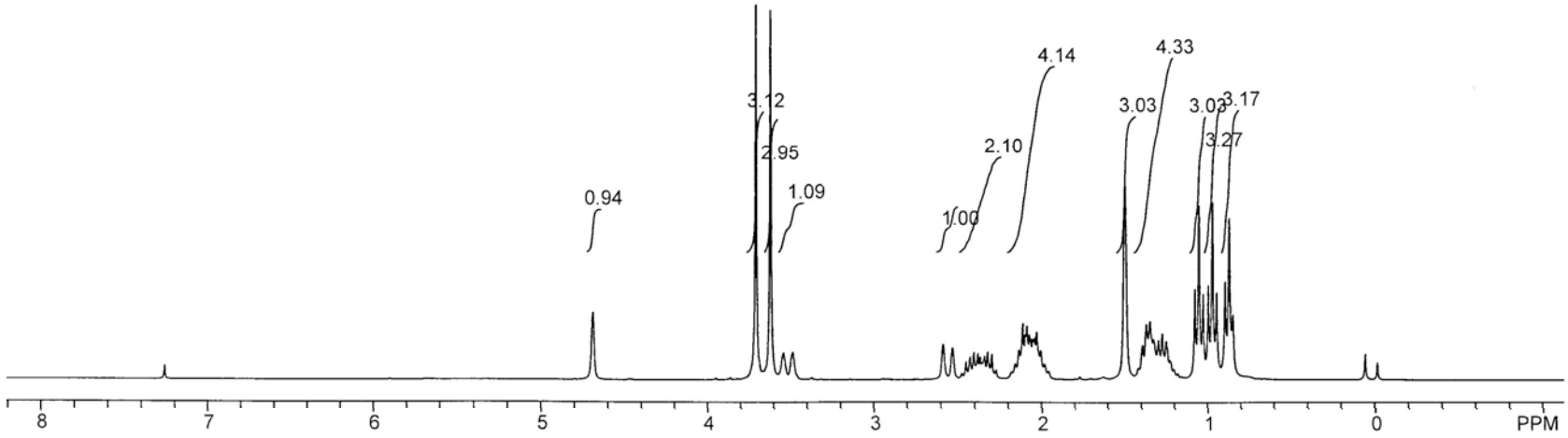


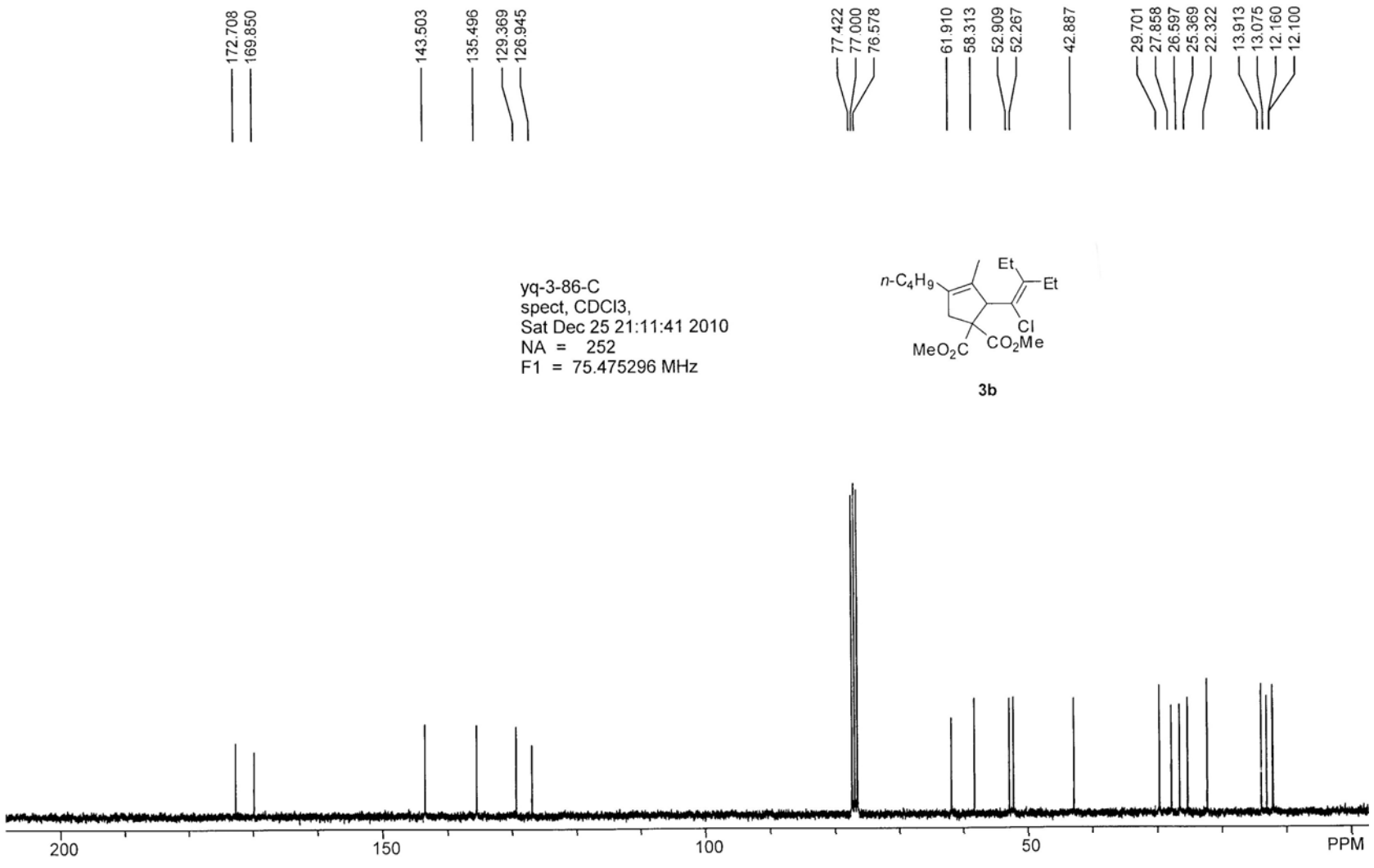


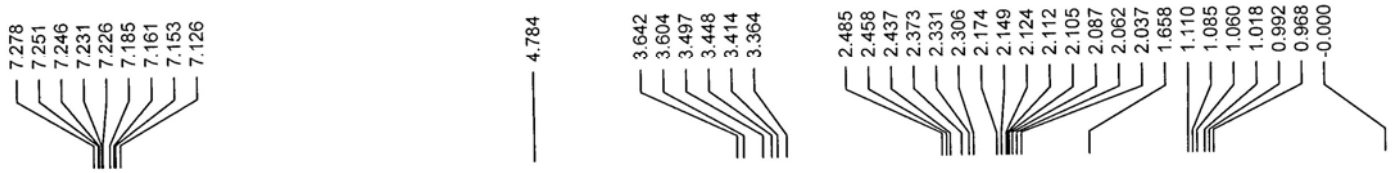


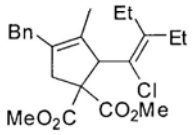
3b

yq-3-86-H
spect, CDCl3,
Sat Dec 25 21:02:53 2010
NA = 8
F1 = 300.131866 MHz



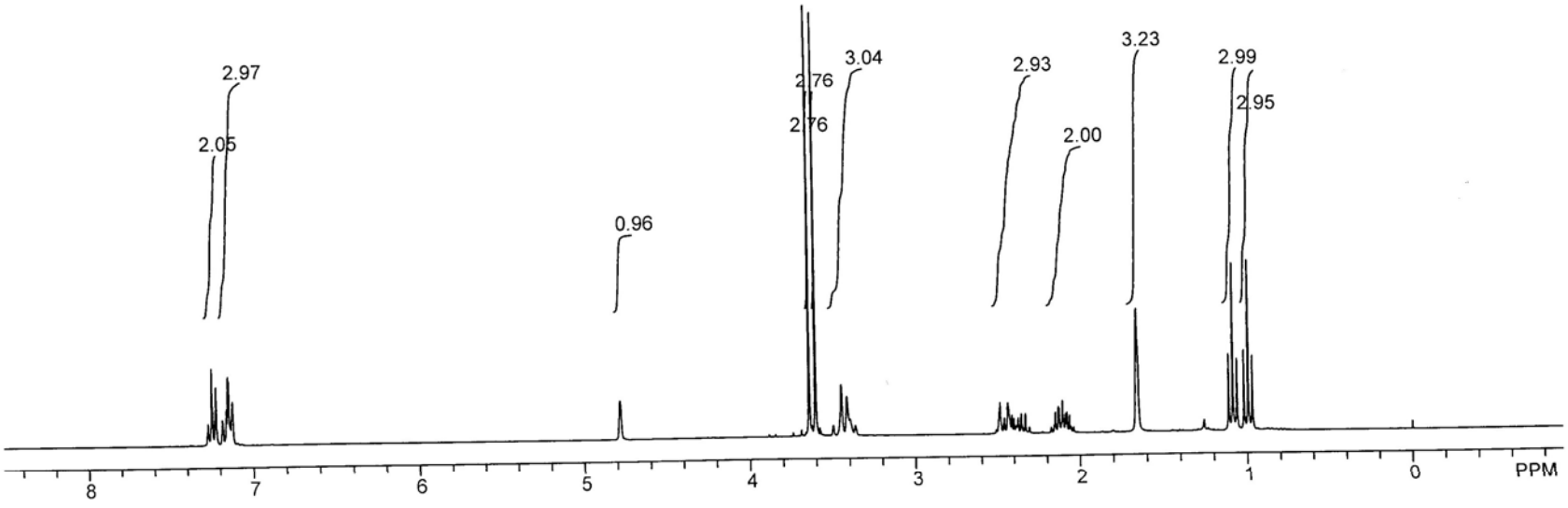

172.708
169.850
143.503
135.496
129.369
126.945
77.422
77.000
76.578
61.910
58.313
52.909
52.267
42.887
29.701
27.858
26.597
25.369
22.322
13.913
13.075
12.160
12.100
yq-3-86-C
spect, CDCl3,
Sat Dec 25 21:11:41 2010
NA = 252
F1 = 75.475296 MHz
n-C4H9
Et
Et
Cl
MeO2C
CO2Me
3b
200
150
100
50
PPM

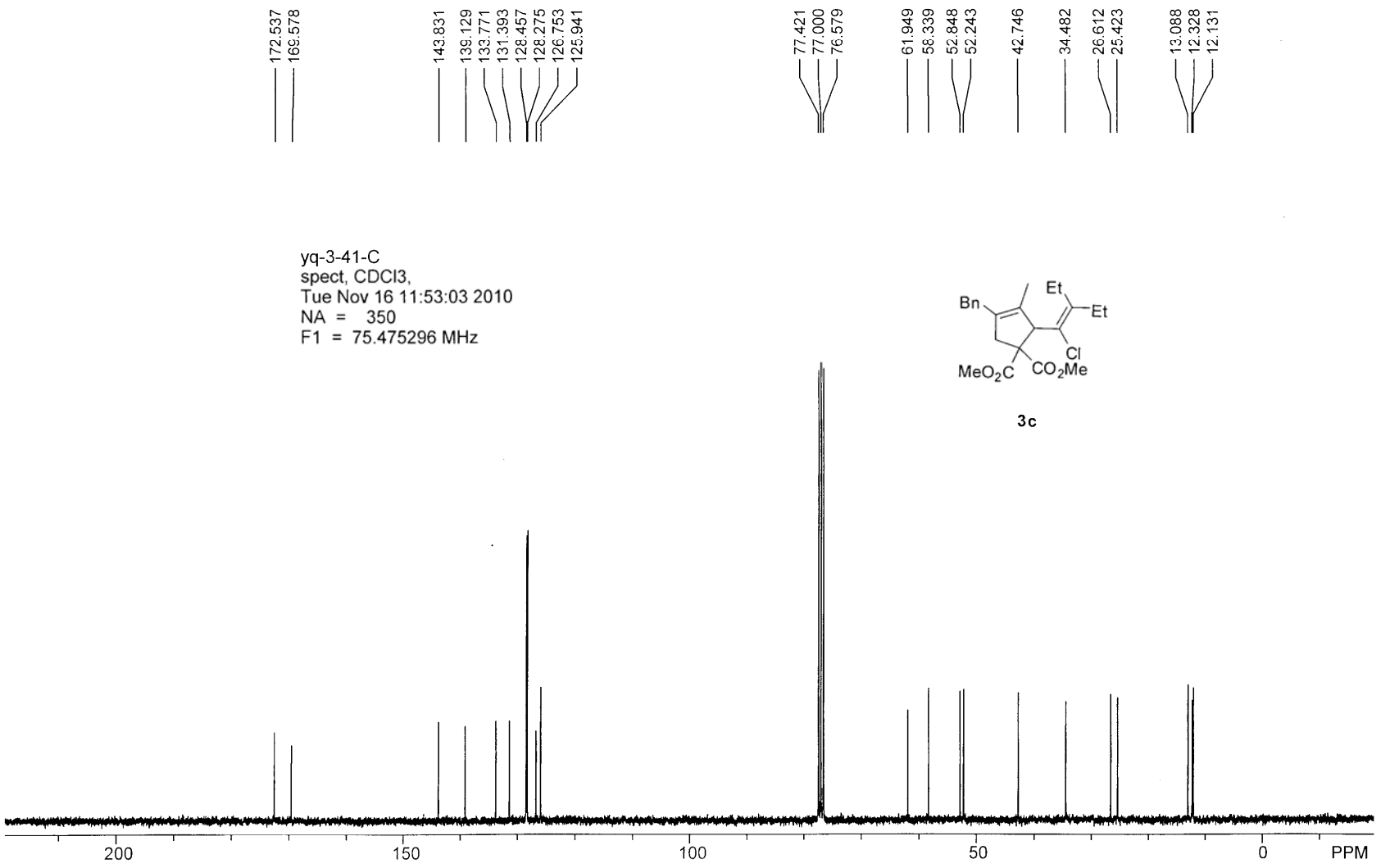


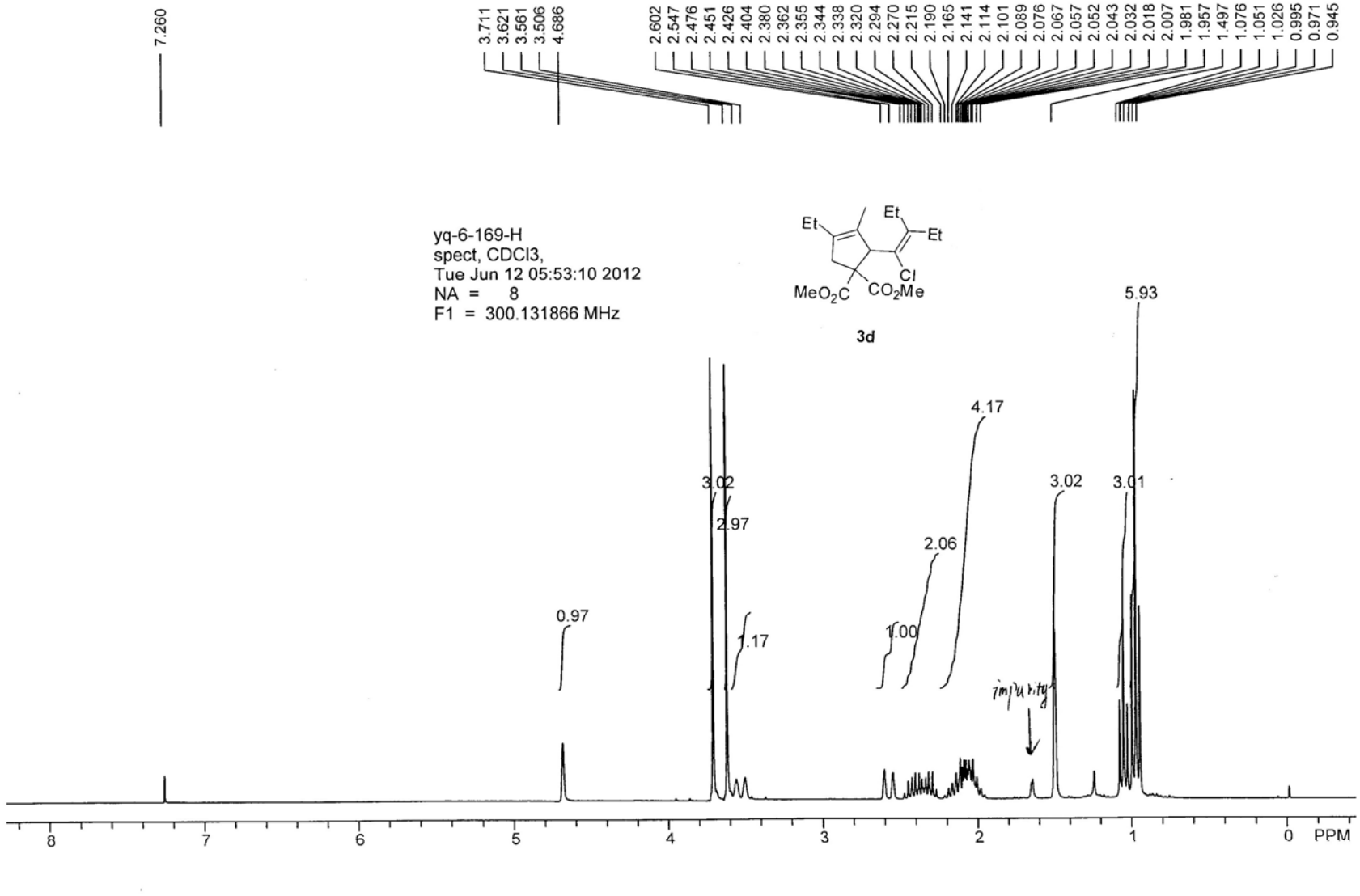


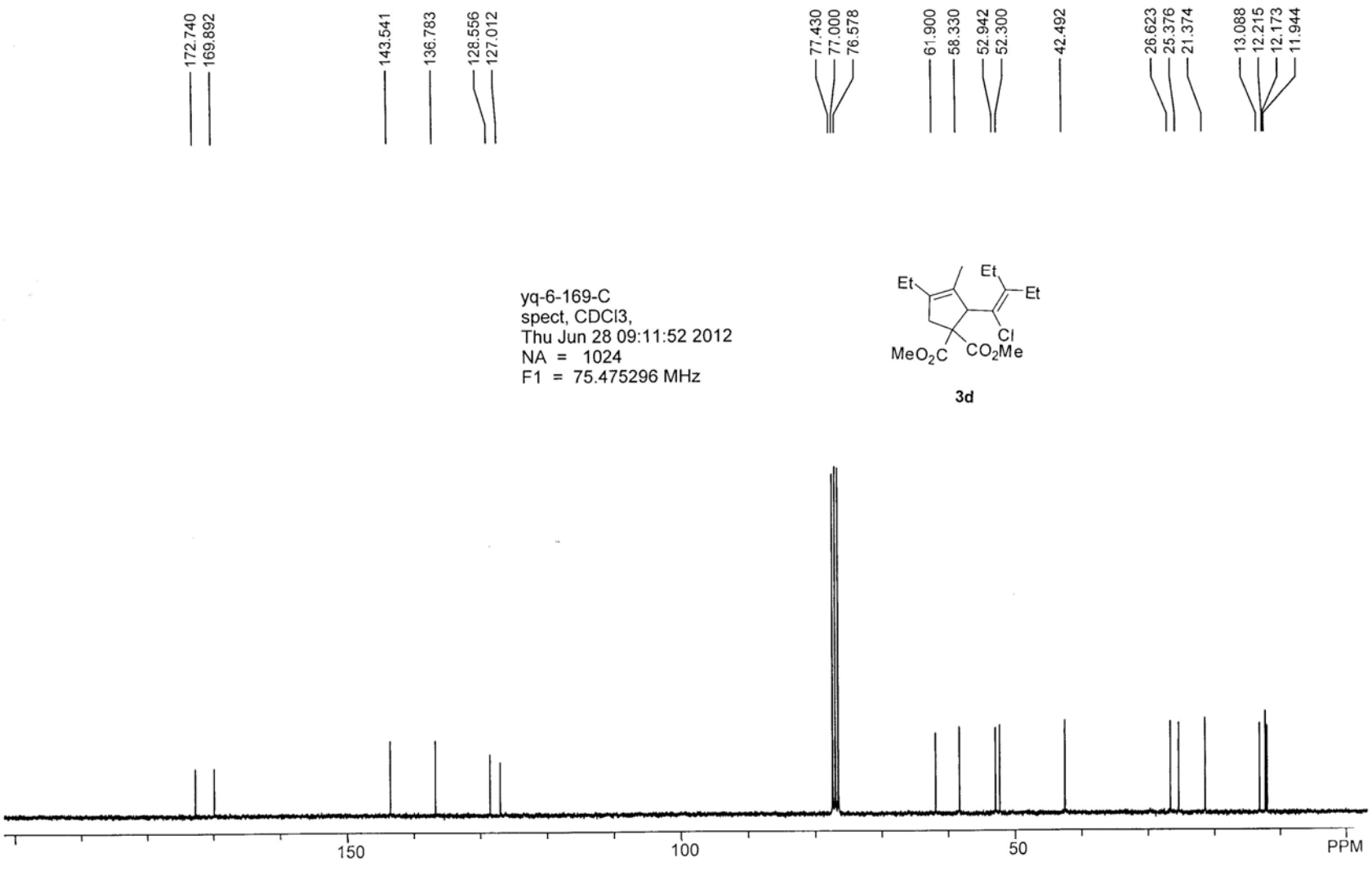
3c

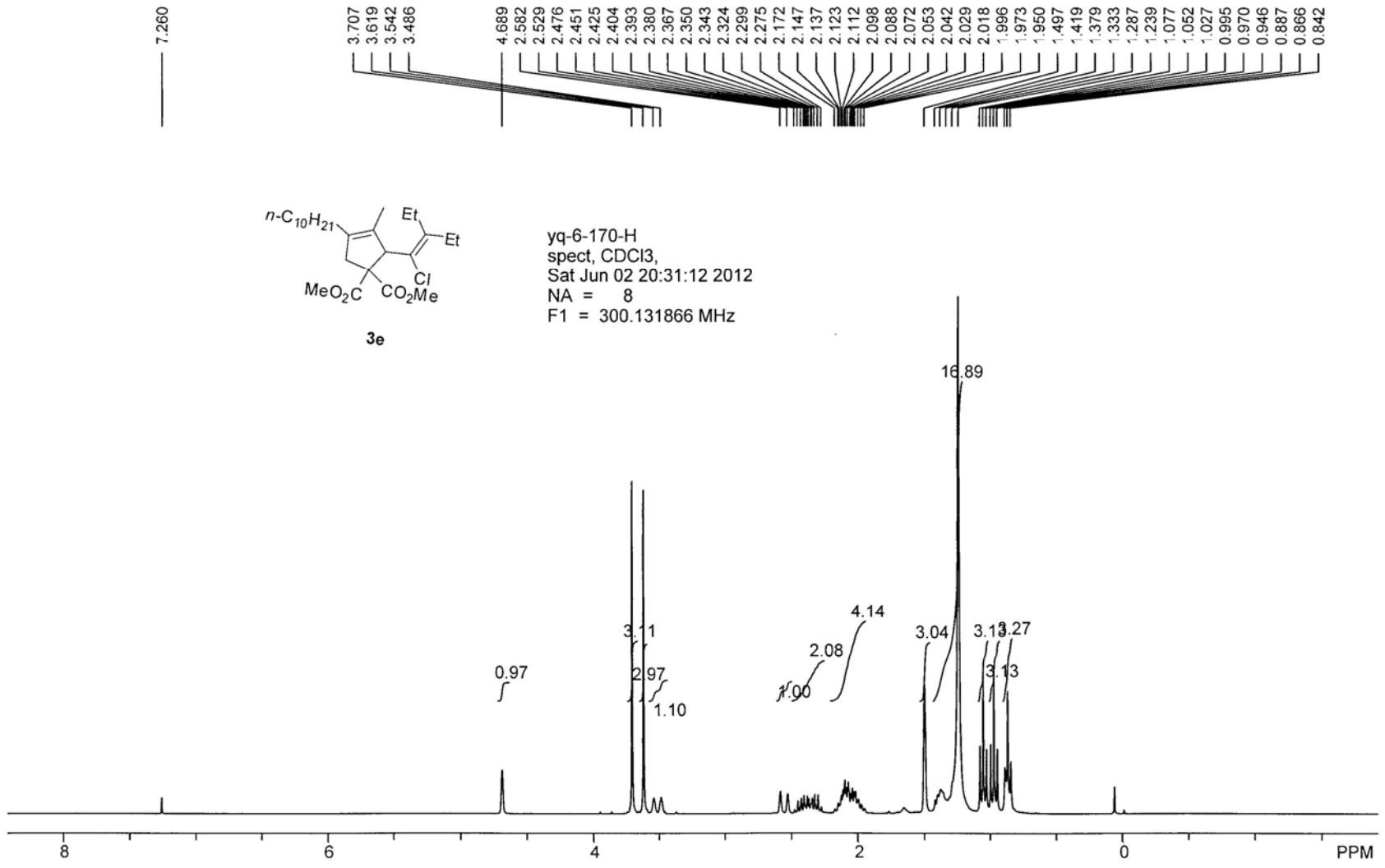
yq-3-41-H
spect, CDCl3,
Tue Jun 19 06:40:31 2012
NA = 8
F1 = 300.131866 MHz

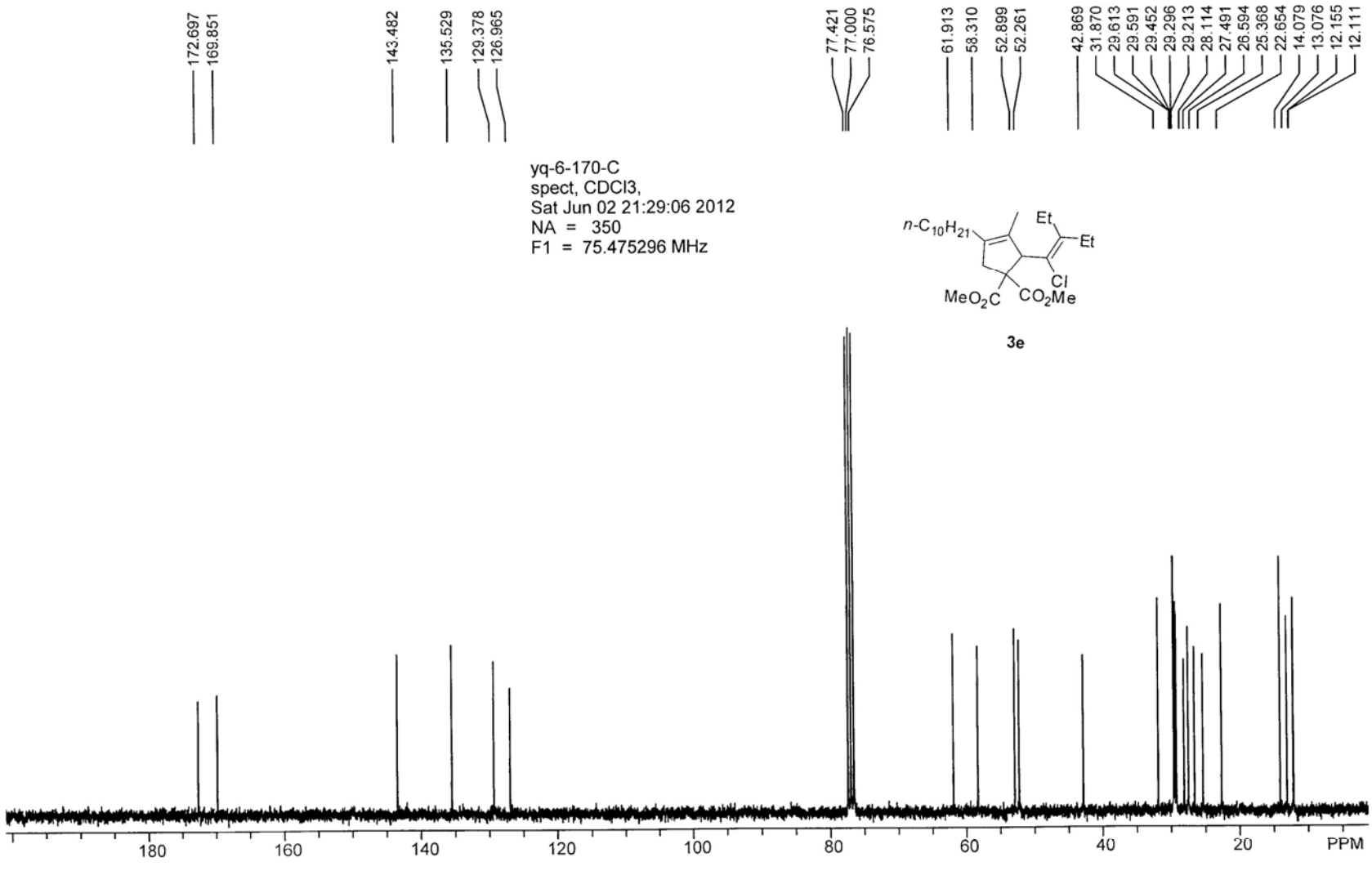


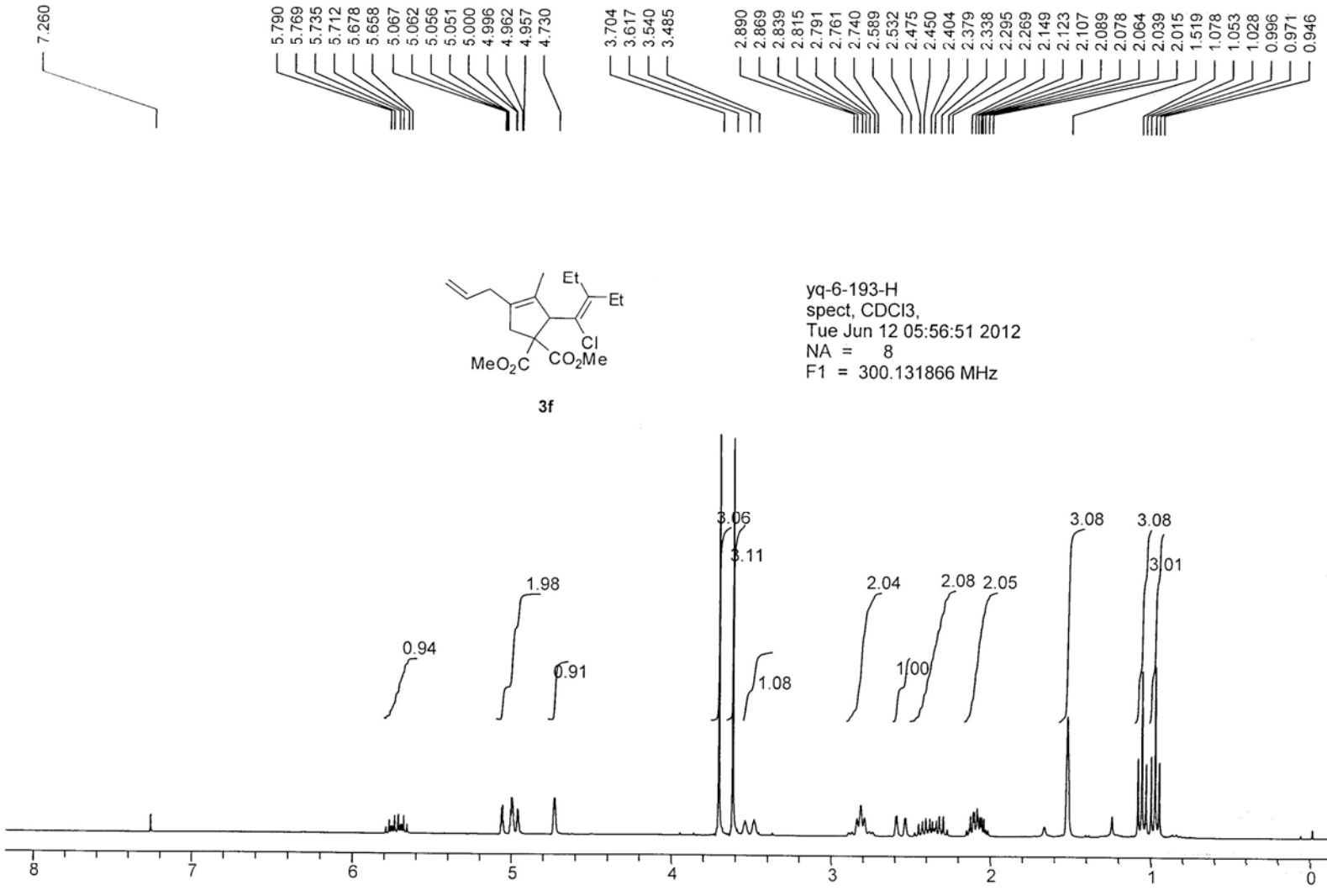

172.537
169.578
143.831
139.129
133.771
131.393
128.457
128.275
126.753
125.941
77.421
77.000
76.579
61.949
58.339
52.848
52.243
42.746
34.482
26.612
25.423
13.088
12.328
12.131
yq-3-41-C
spect, CDCl3,
Tue Nov 16 11:53:03 2010
NA = 350
F1 = 75.475296 MHz
Bn
Et
Et
Cl
MeO2C
CO2Me
3c
200
150
100
50
0
PPM

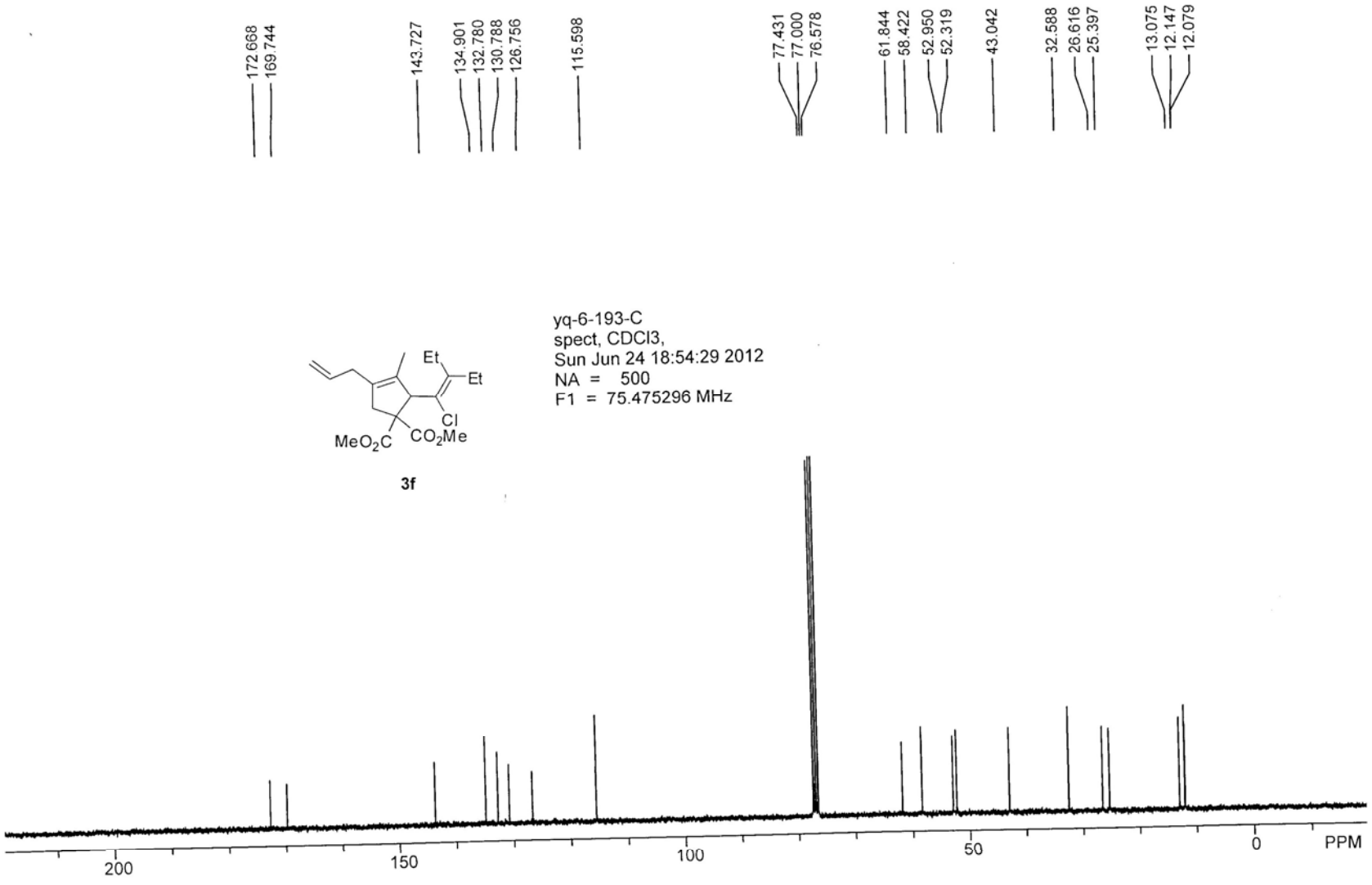

7.260
3.711
3.621
3.561
3.506
4.686
2.602
2.547
2.476
2.451
2.426
2.404
2.380
2.362
2.355
2.344
2.338
2.320
2.294
2.270
2.215
2.190
2.165
2.141
2.114
2.101
2.089
2.076
2.067
2.057
2.052
2.043
2.032
2.018
2.007
1.981
1.957
1.497
1.076
1.051
1.026
0.995
0.971
0.945
yq-6-169-H
spect, CDCl3,
Tue Jun 12 05:53:10 2012
NA = 8
F1 = 300.131866 MHz
Et
Et
Et
Cl
MeO2C
CO2Me
3d
5.93
4.17
3.02
3.01
3.02
2.97
2.06
0.97
1.00
1.17
impurity
8
7
6
5
4
3
2
1
0
PPM

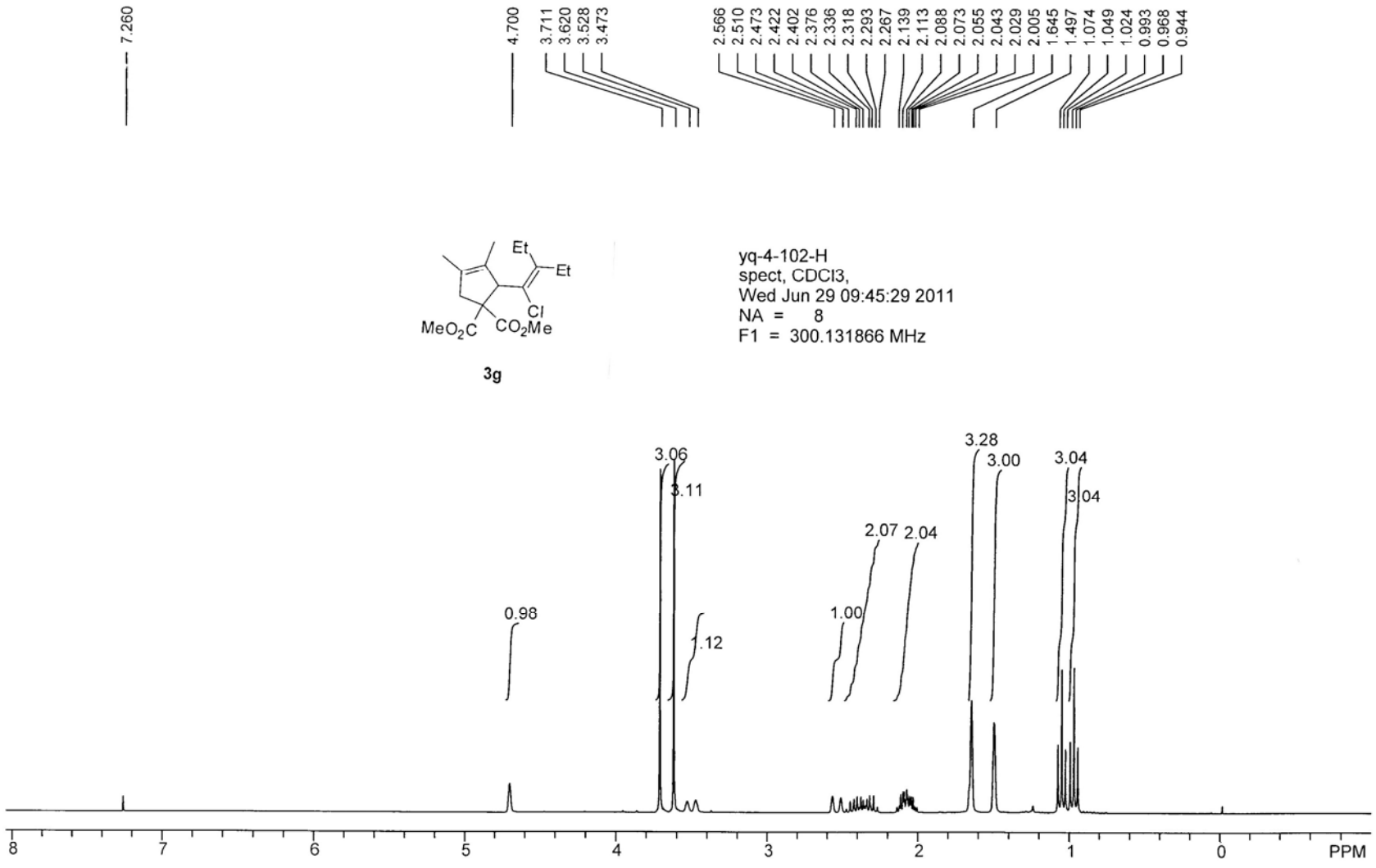


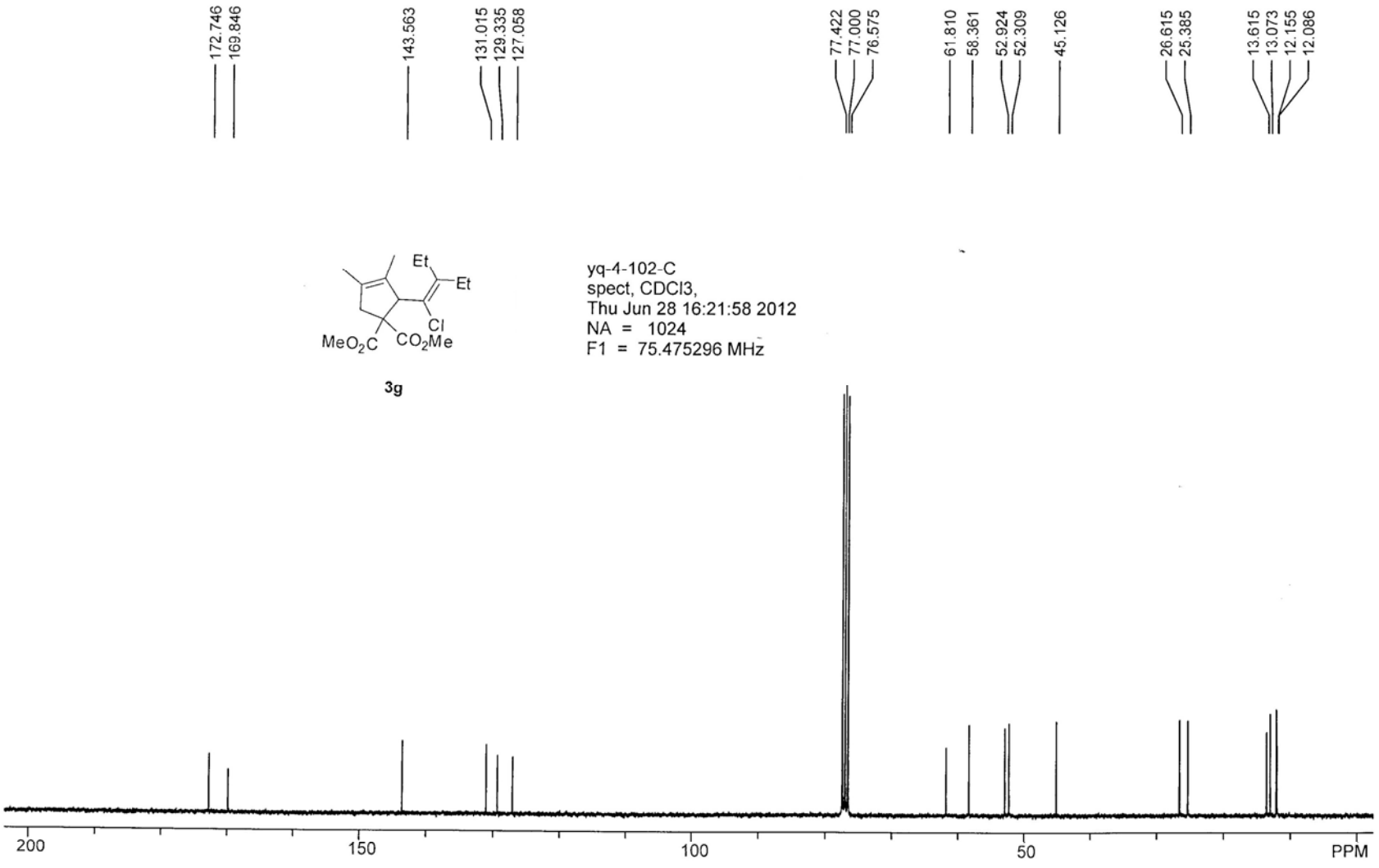

7.260
3.707
3.619
3.542
3.486
4.689
2.582
2.529
2.476
2.451
2.425
2.404
2.393
2.380
2.367
2.350
2.343
2.324
2.299
2.275
2.172
2.147
2.137
2.123
2.112
2.098
2.088
2.072
2.053
2.042
2.029
2.018
1.996
1.973
1.950
1.497
1.419
1.379
1.333
1.287
1.239
1.077
1.052
1.027
0.995
0.970
0.946
0.887
0.866
0.842
n-C10H21
Et
Et
Cl
MeO2C
CO2Me
3e
yq-6-170-H
spect, CDCl3,
Sat Jun 02 20:31:12 2012
NA = 8
F1 = 300.131866 MHz
16.89
4.14
3.11
3.04
3.27
2.08
0.97
2.97
1.10
1.00
3.13
8
6
4
2
0
PPM

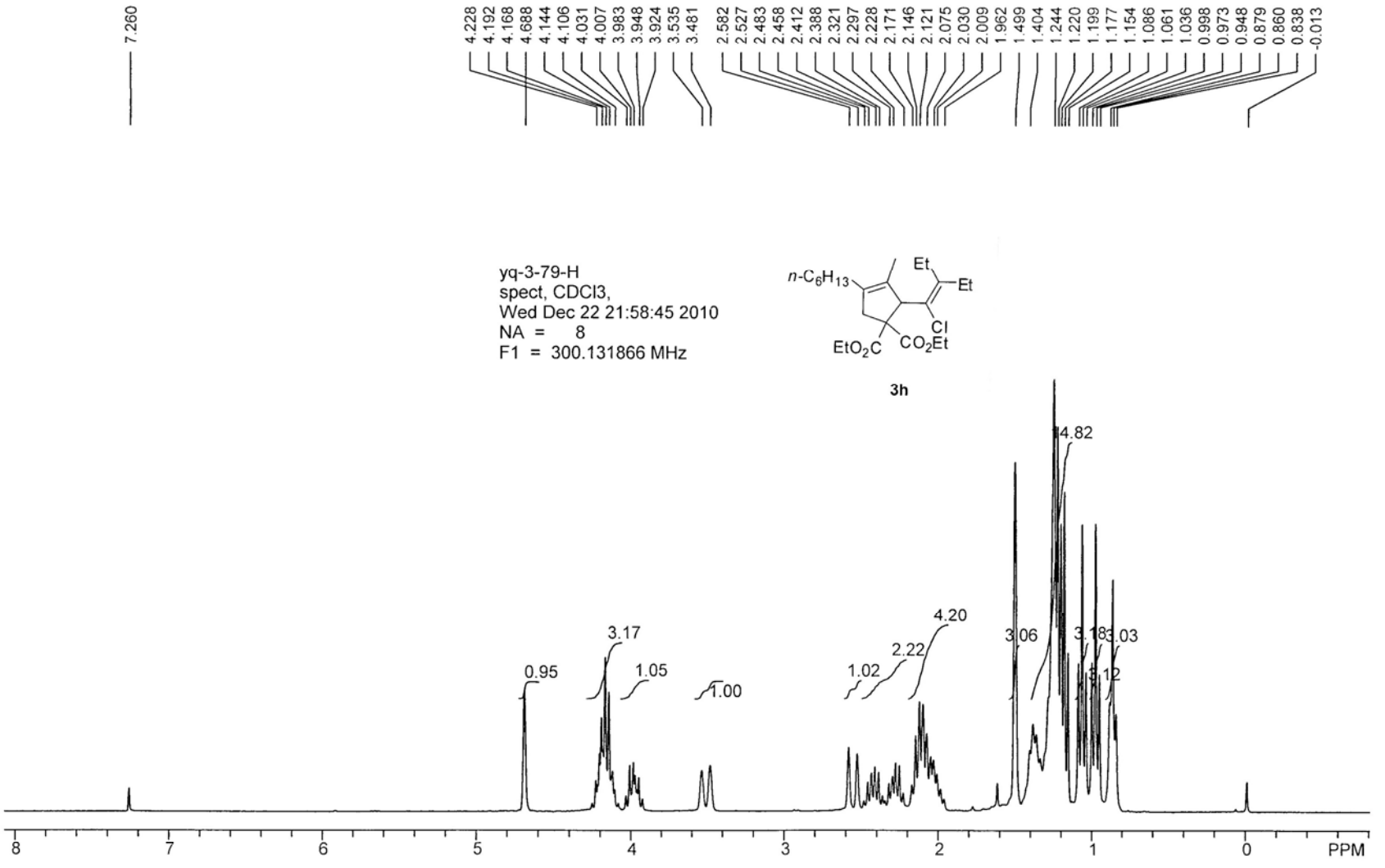

172.697
169.851
143.482
135.529
129.378
126.965
77.421
77.000
76.575
61.913
58.310
52.899
52.261
42.869
31.870
29.613
29.591
29.452
29.296
29.213
28.114
27.491
26.594
25.368
22.654
14.079
13.076
12.155
12.111
yq-6-170-C
spect, CDCl3,
Sat Jun 02 21:29:06 2012
NA = 350
F1 = 75.475296 MHz
n-C10H21
Et
Et
Cl
MeO2C
CO2Me
3e
180
160
140
120
100
80
60
40
20
PPM

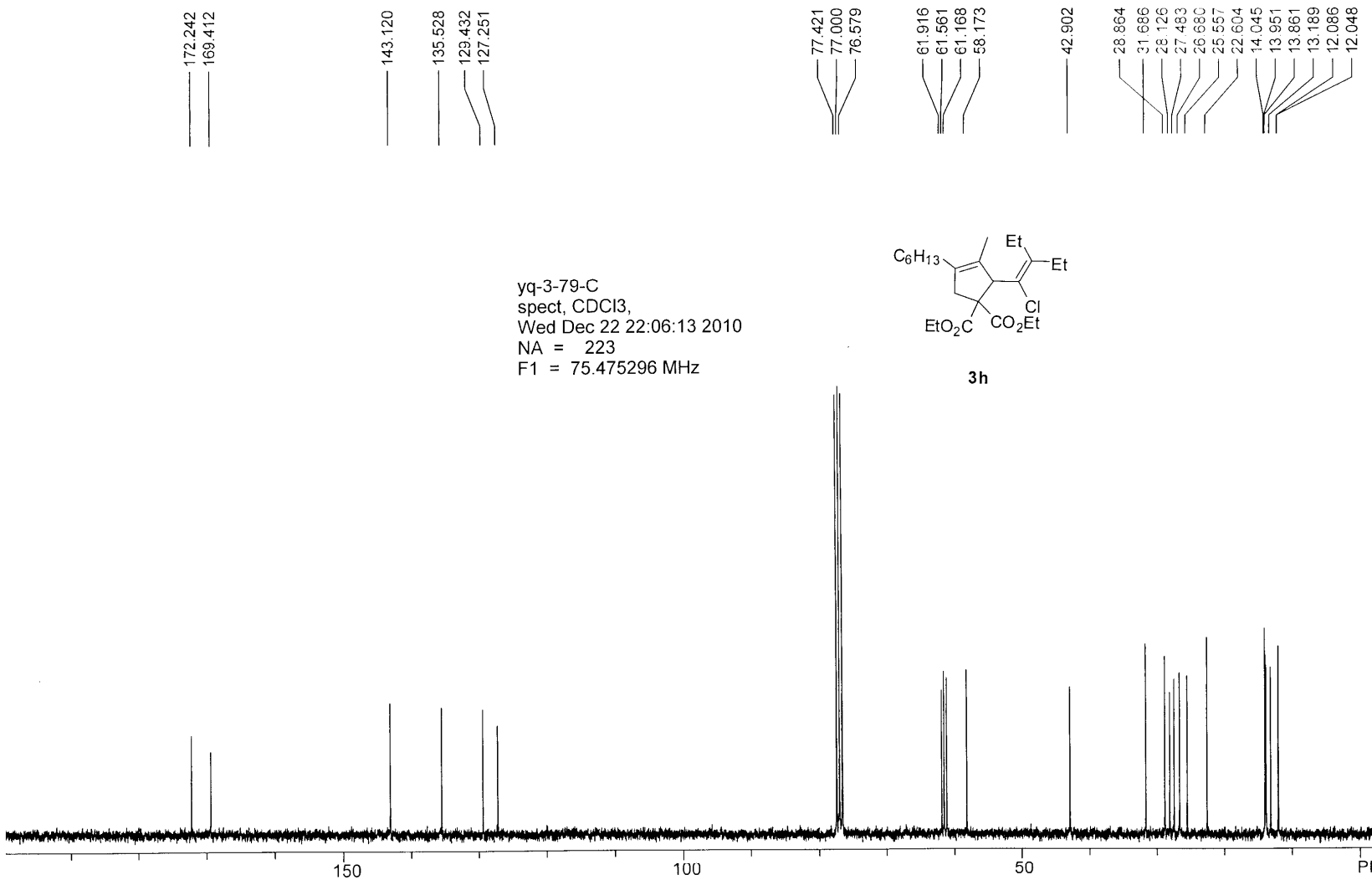

7.260
5.790
5.769
5.735
5.712
5.678
5.658
5.067
5.062
5.056
5.051
5.000
4.996
4.962
4.957
4.730
3.704
3.617
3.540
3.485
2.890
2.869
2.839
2.815
2.791
2.761
2.740
2.589
2.532
2.475
2.450
2.404
2.379
2.338
2.295
2.269
2.149
2.123
2.107
2.089
2.078
2.064
2.039
2.015
1.519
1.078
1.053
1.028
0.996
0.971
0.946
Et
Et
Cl
MeO2C
CO2Me
3f
yq-6-193-H
spect, CDCl3,
Tue Jun 12 05:56:51 2012
NA = 8
F1 = 300.131866 MHz
0.94
1.98
0.91
3.06
3.11
1.08
2.04
1.00
2.08
2.05
3.08
3.08
3.01
8
7
6
5
4
3
2
1
0
PPM

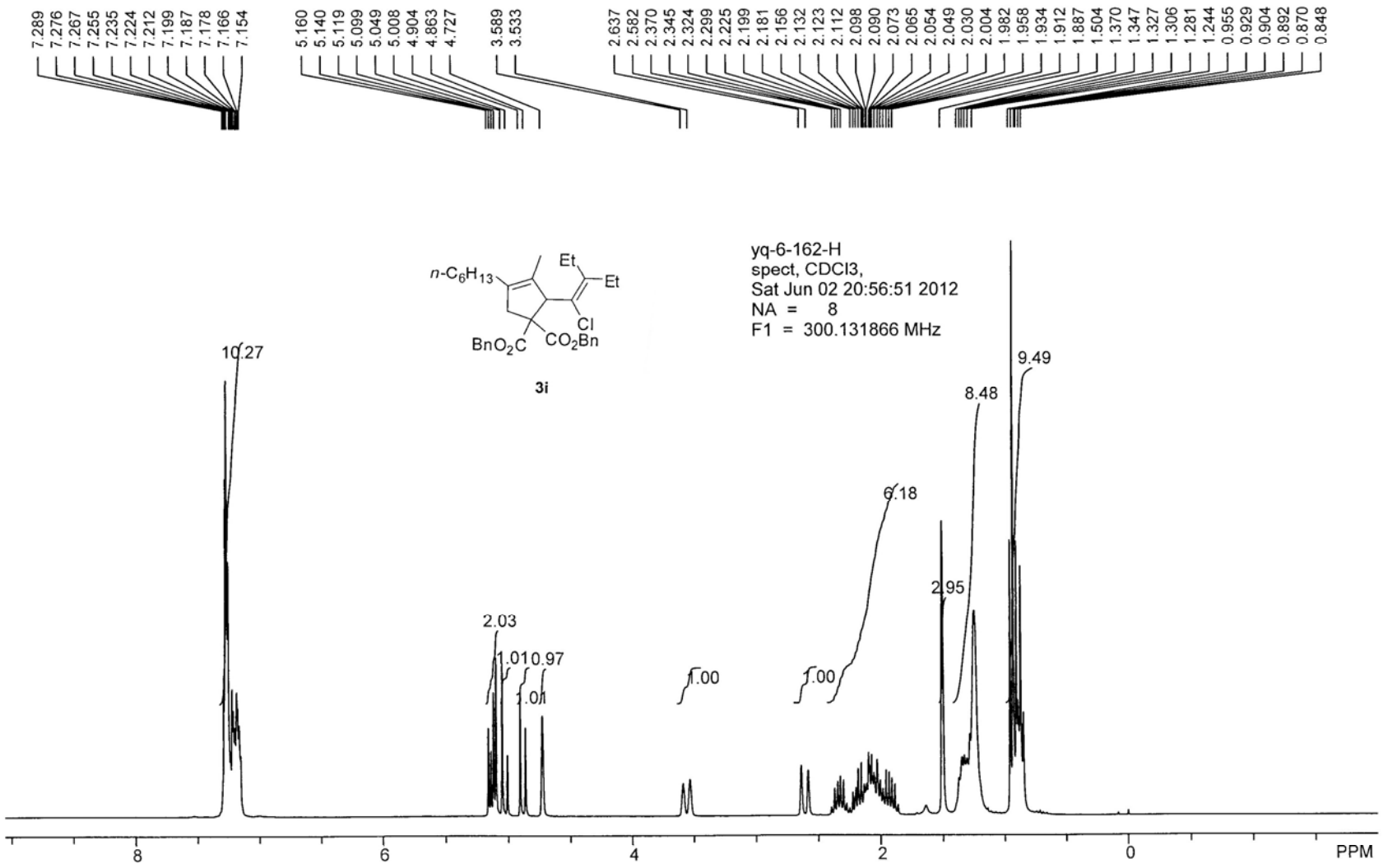

172.668
169.744
143.727
134.901
132.780
130.788
126.756
115.598
77.431
77.000
76.578
61.844
58.422
52.950
52.319
43.042
32.588
26.616
25.397
13.075
12.147
12.079
yq-6-193-C
spect, CDCl3,
Sun Jun 24 18:54:29 2012
NA = 500
F1 = 75.475296 MHz
Et
Et
Cl
MeO2C
CO2Me
3f
200
150
100
50
0
PPM

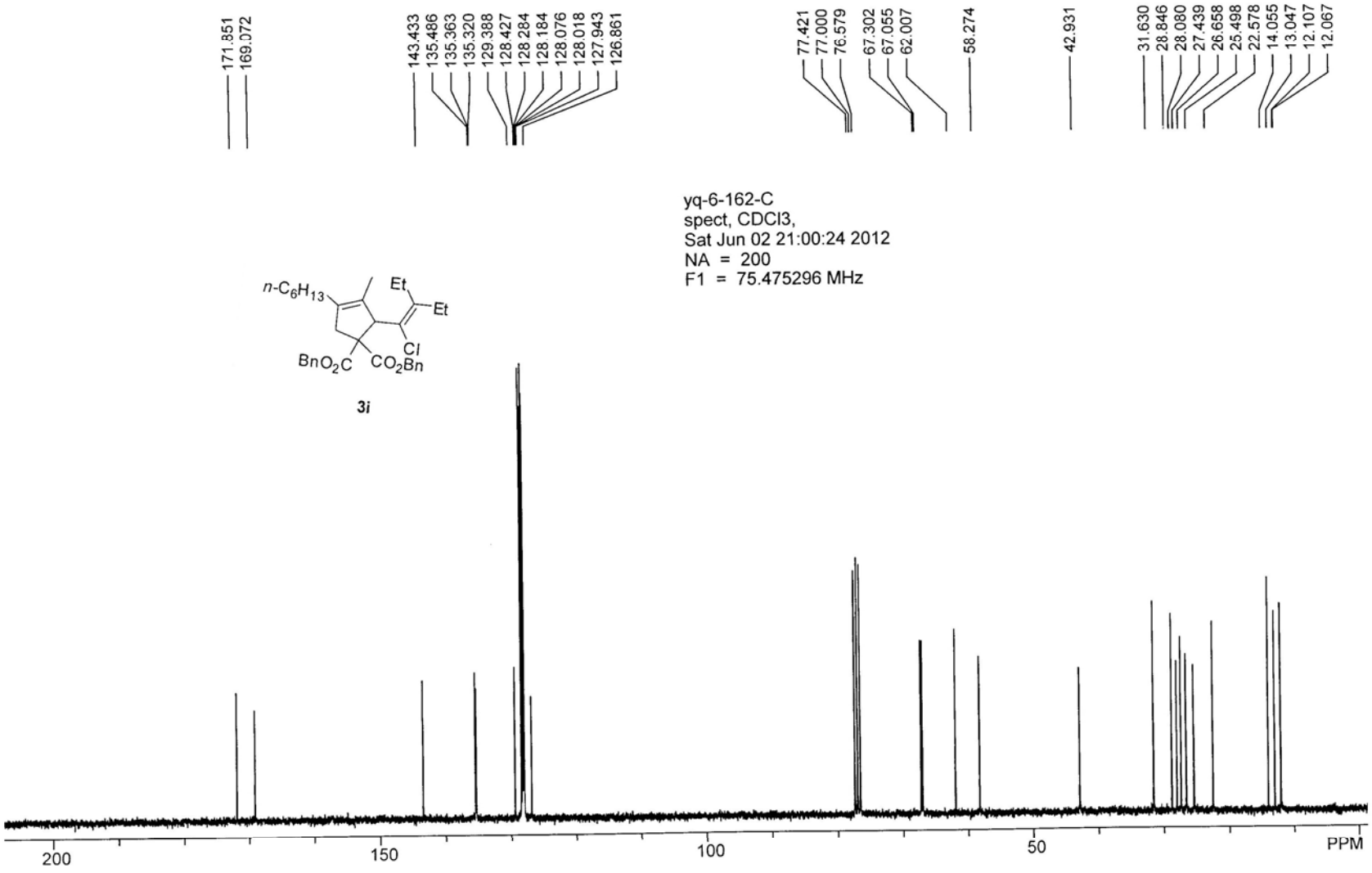

7.260
4.700
3.711
3.620
3.528
3.473
2.566
2.510
2.473
2.422
2.402
2.376
2.336
2.318
2.293
2.267
2.139
2.113
2.088
2.073
2.055
2.043
2.029
2.005
1.645
1.497
1.074
1.049
1.024
0.993
0.968
0.944
Et
Et
Cl
MeO2C
CO2Me
3g
yq-4-102-H
spect, CDCl3,
Wed Jun 29 09:45:29 2011
NA = 8
F1 = 300.131866 MHz
3.06
3.11
3.28
3.00
3.04
3.04
2.07
2.04
0.98
1.00
1.12
8
7
6
5
4
3
2
1
0
PPM

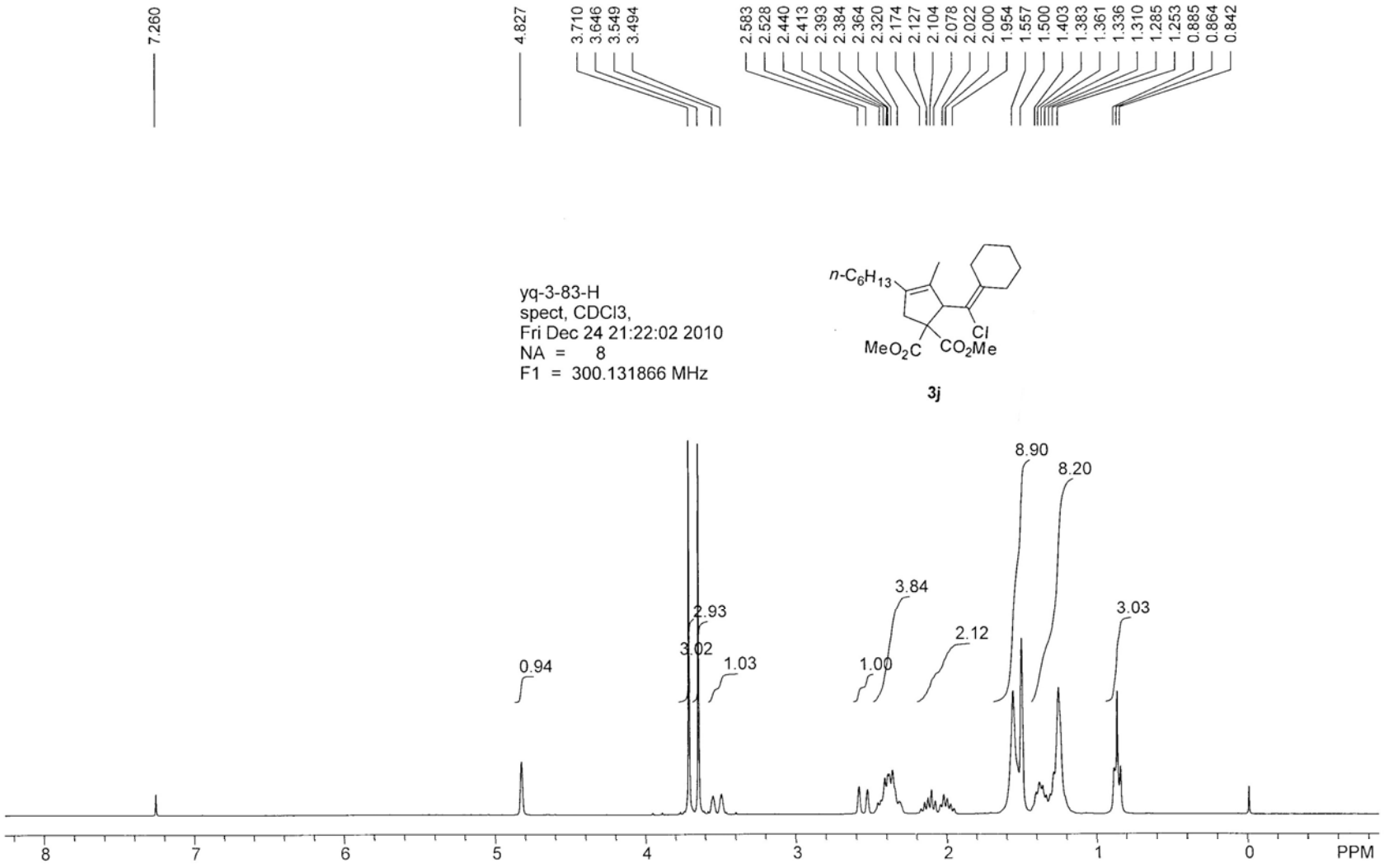

172.746
169.846
143.563
131.015
129.335
127.058
77.422
77.000
76.575
61.810
58.361
52.924
52.309
45.126
26.615
25.385
13.615
13.073
12.155
12.086
Et
Et
Cl
MeO2C
CO2Me
3g
yq-4-102-C
spect, CDCl3,
Thu Jun 28 16:21:58 2012
NA = 1024
F1 = 75.475296 MHz
200
150
100
50
PPM

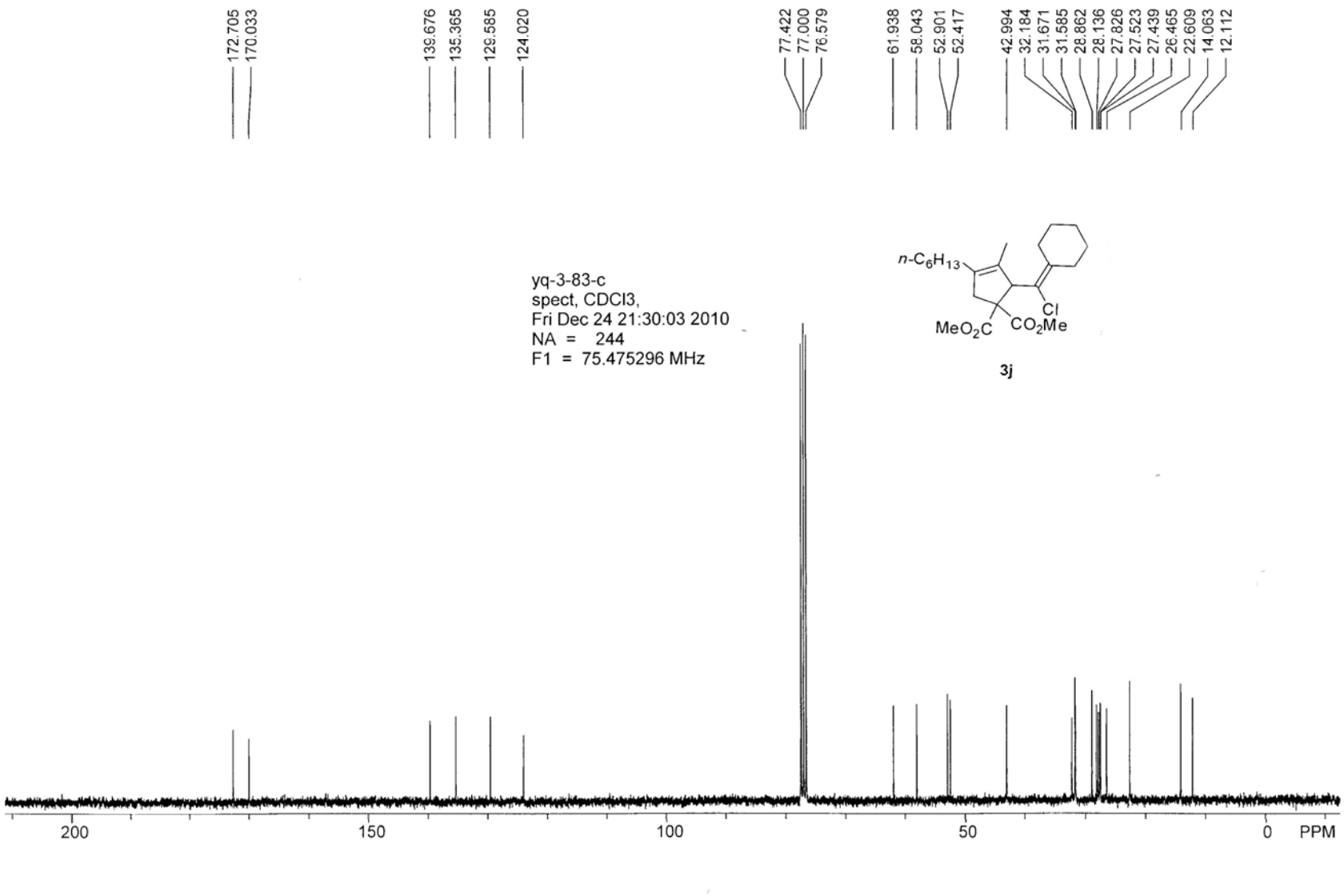

7.260
4.228
4.192
4.168
4.688
4.144
4.106
4.031
4.007
3.983
3.948
3.924
3.535
3.481
2.582
2.527
2.483
2.458
2.412
2.388
2.321
2.297
2.228
2.171
2.146
2.121
2.075
2.030
2.009
1.962
1.499
1.404
1.244
1.220
1.199
1.177
1.154
1.086
1.061
1.036
0.998
0.973
0.948
0.879
0.860
0.838
-0.013
yq-3-79-H
spect, CDCl3,
Wed Dec 22 21:58:45 2010
NA = 8
F1 = 300.131866 MHz
n-C6H13
Et
Et
Cl
EtO2C
CO2Et
3h
0.95
3.17
1.05
1.00
1.02
2.22
4.20
3.06
4.82
3.18
3.03
3.12
8
7
6
5
4
3
2
1
0
PPM

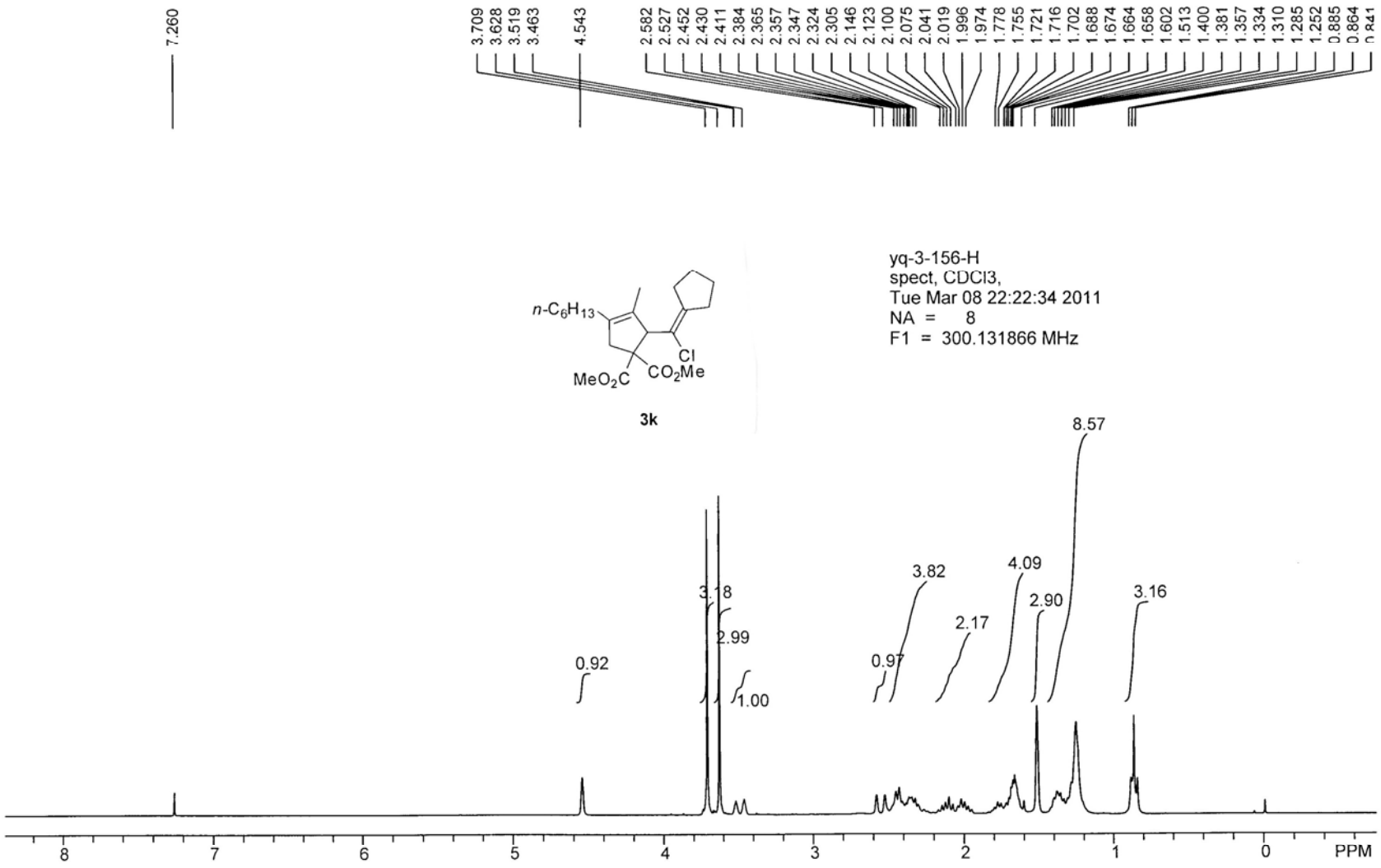

172.242
169.412
143.120
135.528
129.432
127.251
77.421
77.000
76.579
61.916
61.561
61.168
58.173
42.902
28.864
31.686
28.126
27.483
26.680
25.557
22.604
14.045
13.951
13.861
13.189
12.086
12.048
yq-3-79-C
spect, CDCl3,
Wed Dec 22 22:06:13 2010
NA = 223
F1 = 75.475296 MHz
C6H13
Et
Et
Cl
EtO2C
CO2Et
3h
150
100
50
PPM

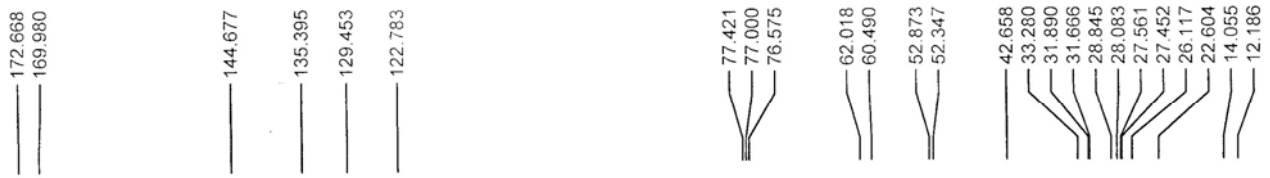


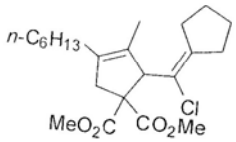

171.851
169.072
143.433
135.486
135.363
135.320
129.388
128.427
128.284
128.184
128.076
128.018
127.943
126.861
77.421
77.000
76.579
67.302
67.055
62.007
58.274
42.931
31.630
28.846
28.080
27.439
26.658
25.498
22.578
14.055
13.047
12.107
12.067
yq-6-162-C
spect, CDCl3,
Sat Jun 02 21:00:24 2012
NA = 200
F1 = 75.475296 MHz
n-C6H13
Et
Et
Cl
BnO2C
CO2Bn
3i
200
150
100
50
PPM


7.260
4.827
3.710
3.646
3.549
3.494
2.583
2.528
2.440
2.413
2.393
2.384
2.364
2.320
2.174
2.127
2.104
2.078
2.022
2.000
1.954
1.557
1.500
1.403
1.383
1.361
1.336
1.310
1.285
1.253
0.885
0.864
0.842
yq-3-83-H
spect, CDCl3,
Fri Dec 24 21:22:02 2010
NA = 8
F1 = 300.131866 MHz
n-C6H13
Cl
MeO2C
CO2Me
3j
0.94
2.93
3.02
1.03
1.00
3.84
2.12
8.90
8.20
3.03
8
7
6
5
4
3
2
1
0
PPM


172.705
170.033
139.676
135.365
129.585
124.020
77.422
77.000
76.579
61.938
58.043
52.901
52.417
42.994
32.184
31.671
31.585
28.862
28.136
27.826
27.523
27.439
26.465
22.609
14.063
12.112
yq-3-83-c
spect, CDCl3,
Fri Dec 24 21:30:03 2010
NA = 244
F1 = 75.475296 MHz
n-C6H13
Cl
MeO2C
CO2Me
3j
200
150
100
50
0
PPM

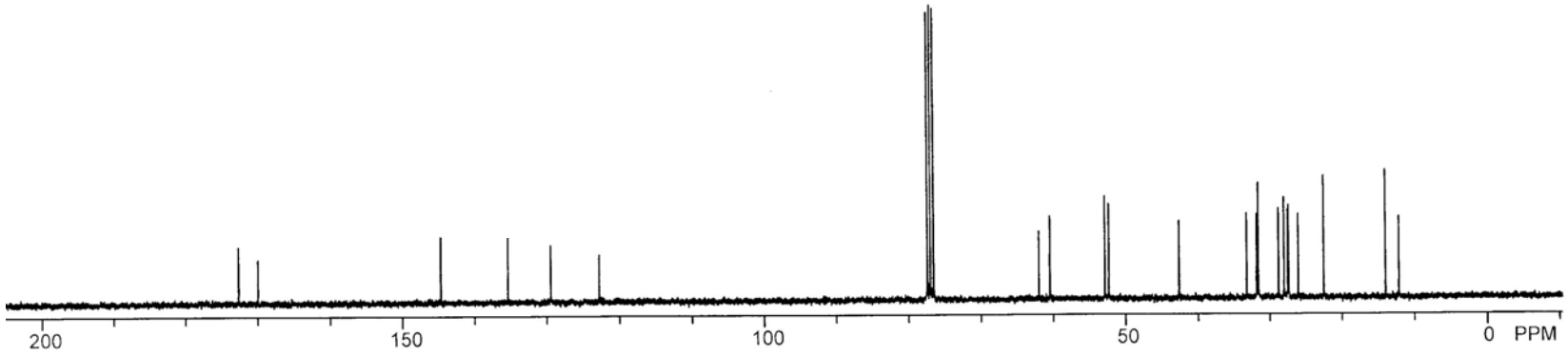

7.260
3.709
3.628
3.519
3.463
4.543
2.582
2.527
2.452
2.430
2.411
2.384
2.365
2.357
2.347
2.324
2.305
2.146
2.123
2.100
2.075
2.041
2.019
1.996
1.974
1.778
1.755
1.721
1.716
1.702
1.688
1.674
1.664
1.658
1.602
1.513
1.400
1.381
1.357
1.334
1.310
1.285
1.252
0.885
0.864
n-C6H13
Cl
MeO2C
CO2Me
3k
yq-3-156-H
spect, CDCl3,
Tue Mar 08 22:22:34 2011
NA = 8
F1 = 300.131866 MHz
8.57
3.82
4.09
3.18
2.90
3.16
2.17
2.99
0.92
0.97
1.00
8
7
6
5
4
3
2
1
0
PPM

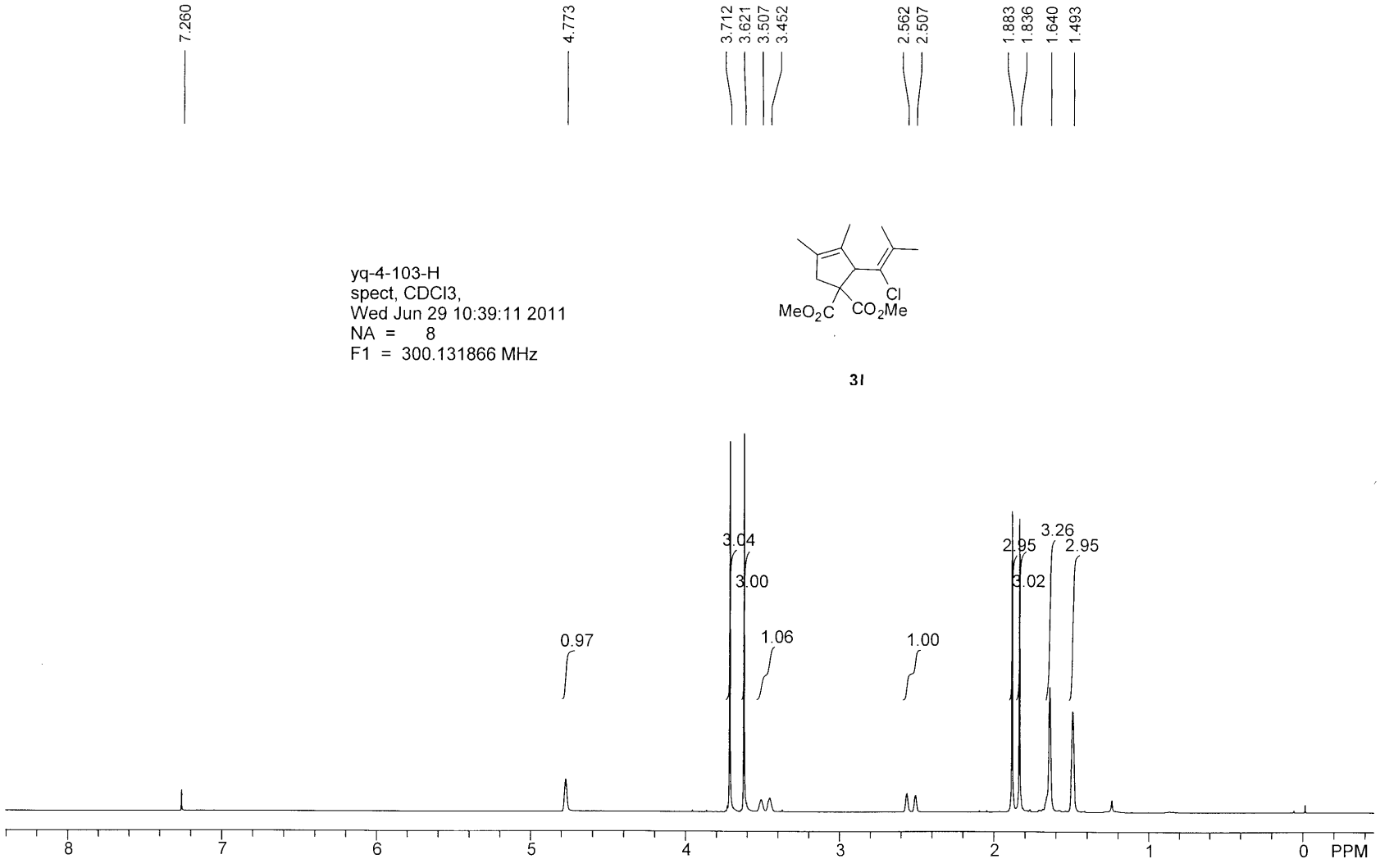


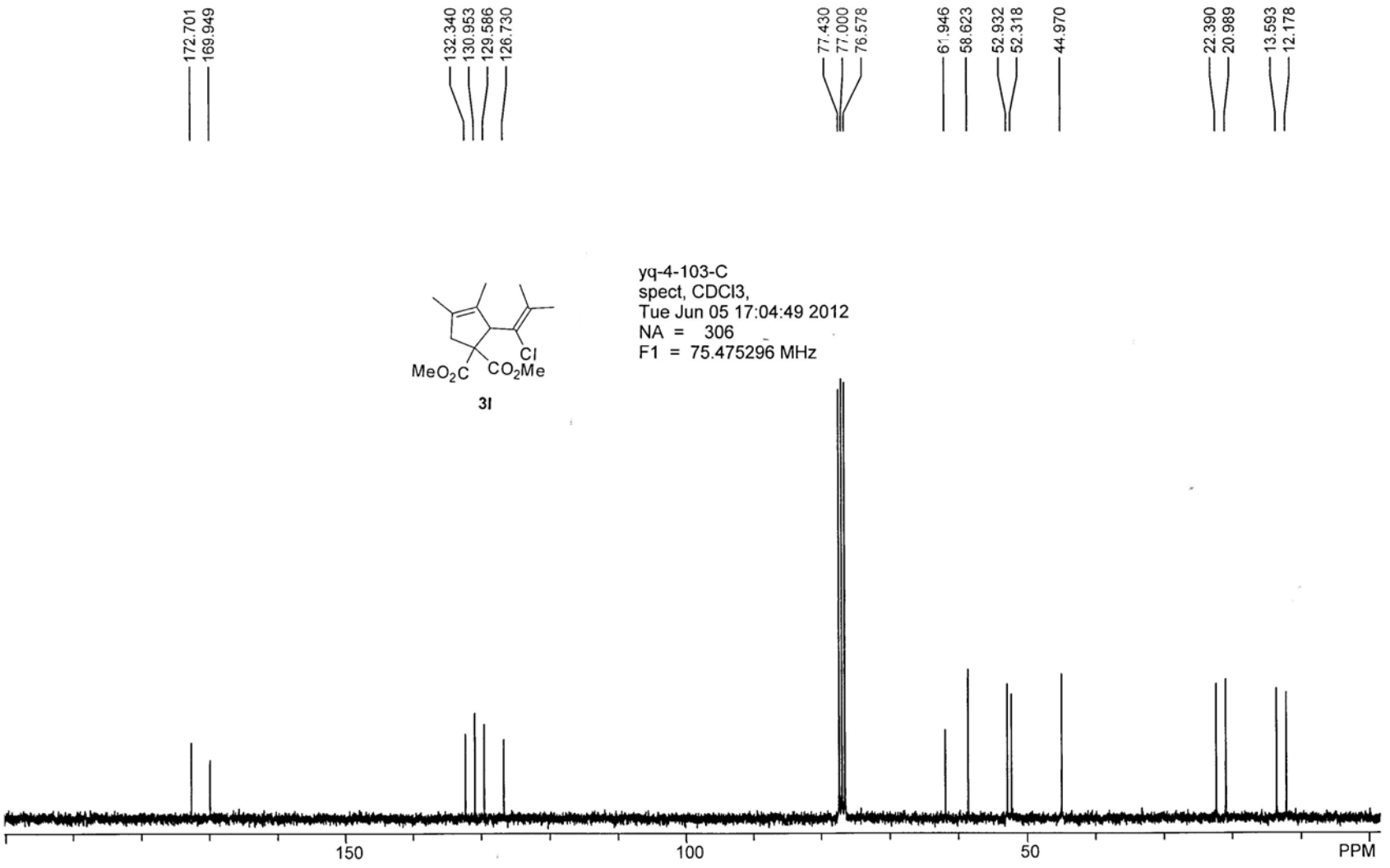


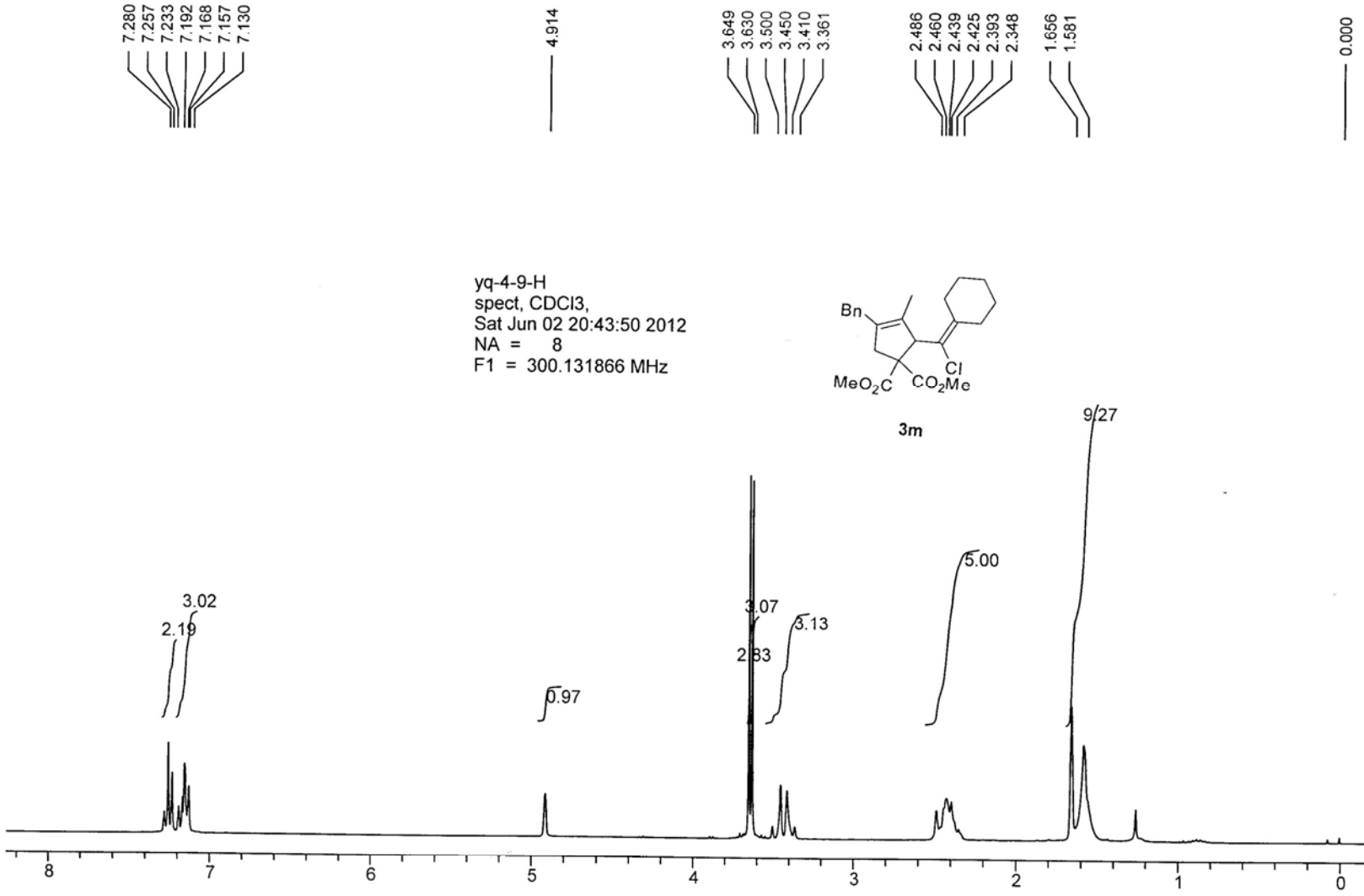
3k

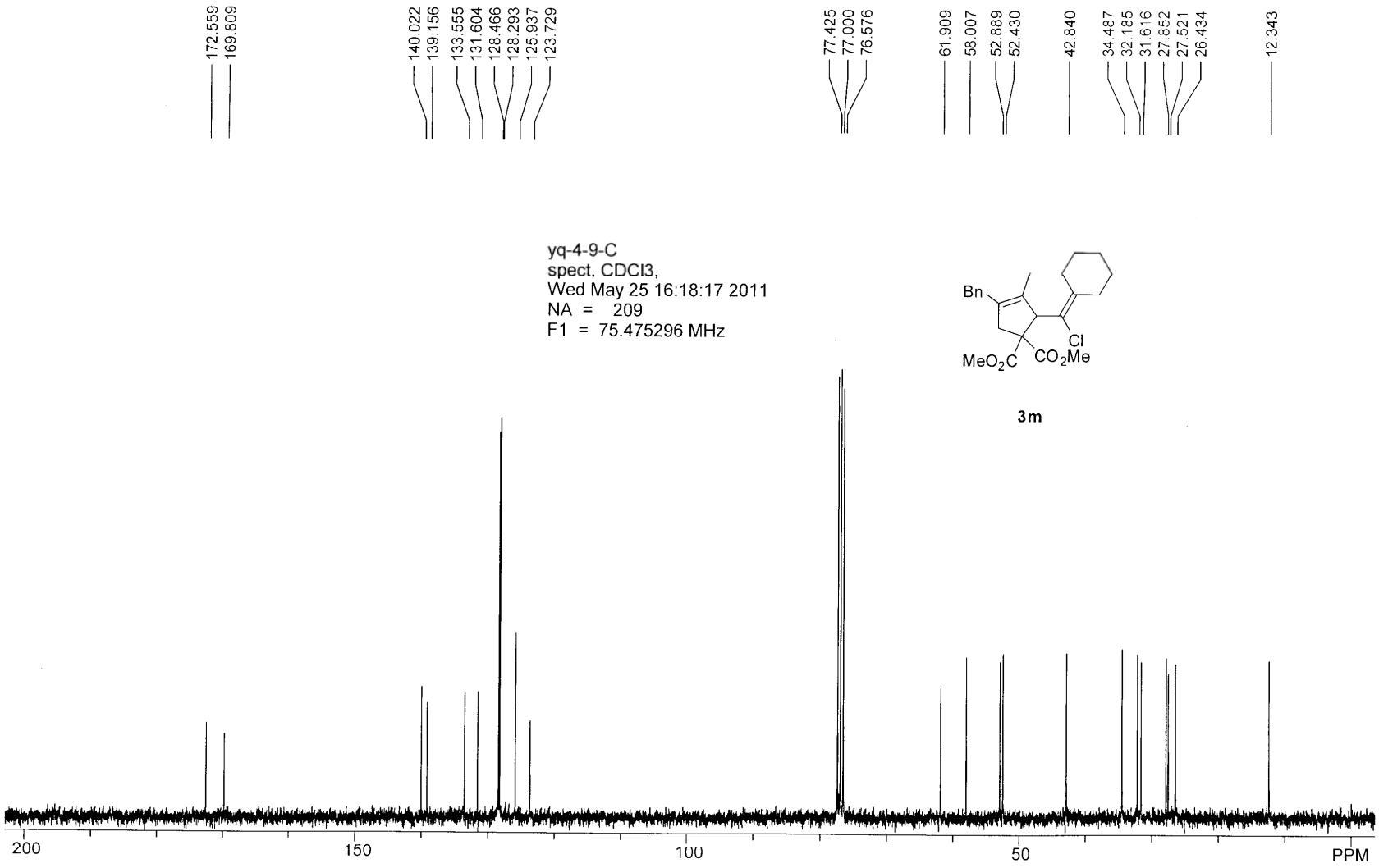
yq-3-156-C
spect, CDCl3,
Tue Mar 08 22:50:01 2011
NA = 400
F1 = 75.475296 MHz

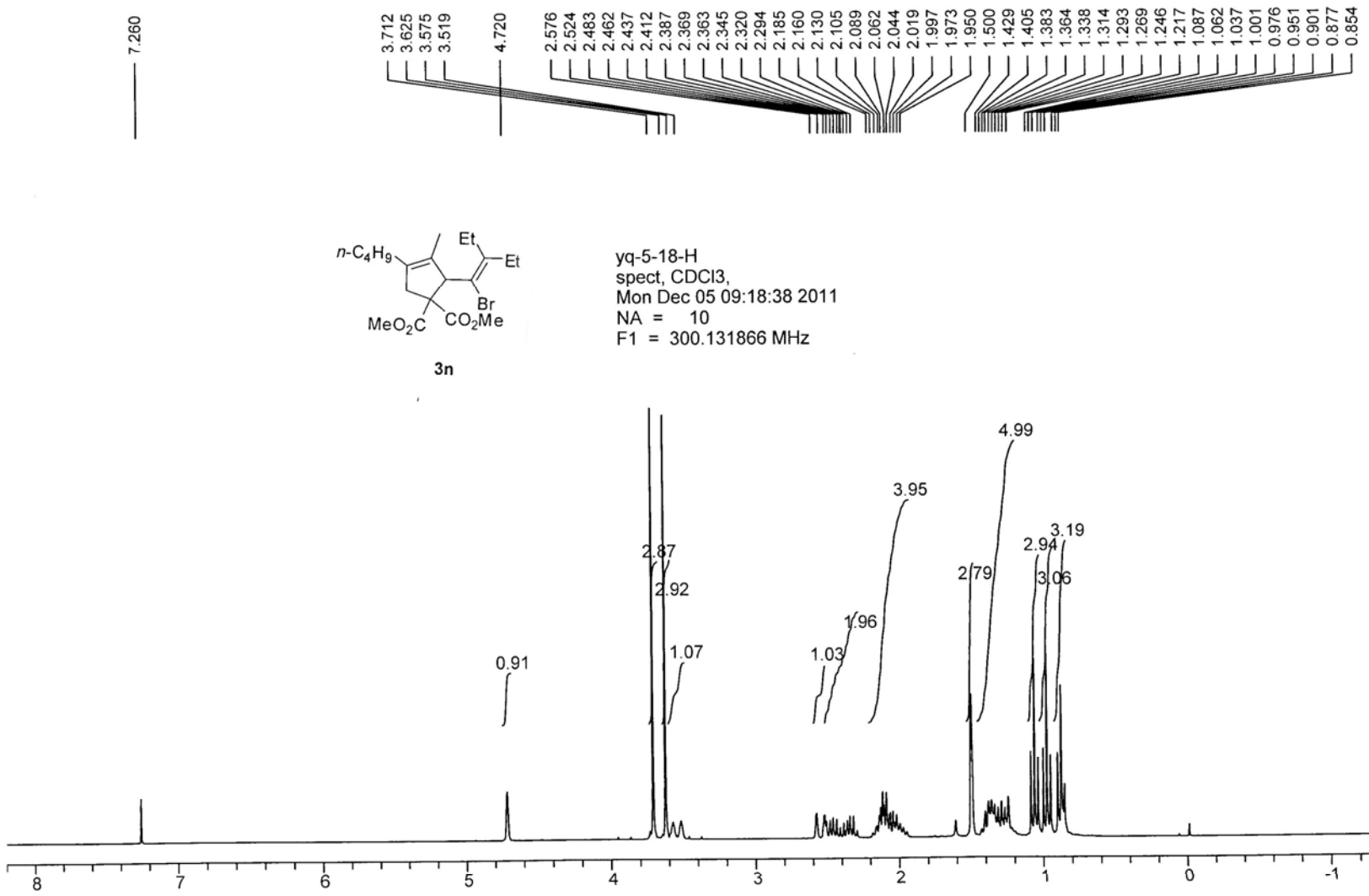


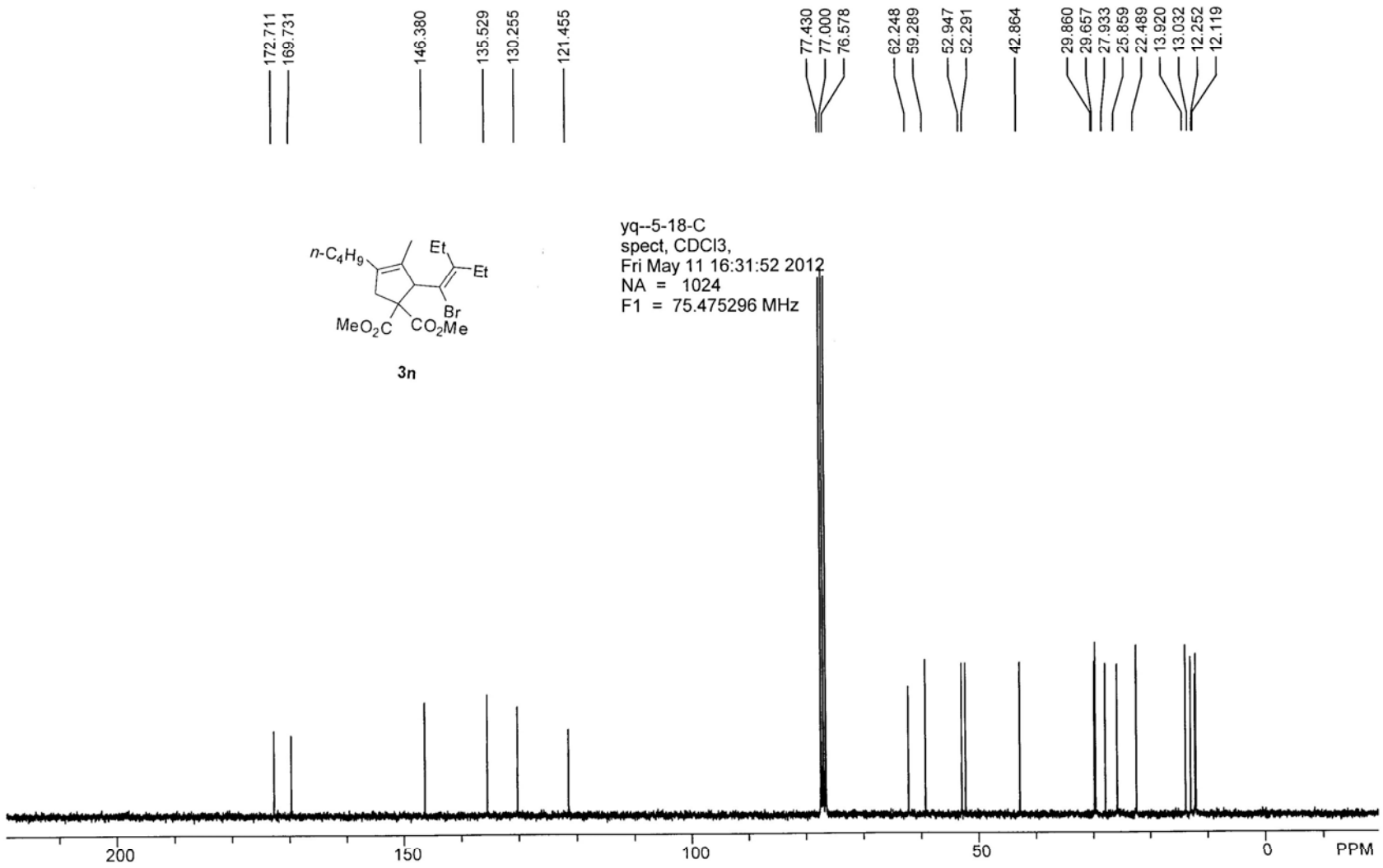

7.260
4.773
3.712
3.621
3.507
3.452
2.562
2.507
1.883
1.836
1.640
1.493
yq-4-103-H
spect, CDCl3,
Wed Jun 29 10:39:11 2011
NA = 8
F1 = 300.131866 MHz
MeO2C
CO2Me
Cl
3I
0.97
3.04
3.00
1.06
1.00
2.95
3.02
3.26
2.95
8
7
6
5
4
3
2
1
0
PPM

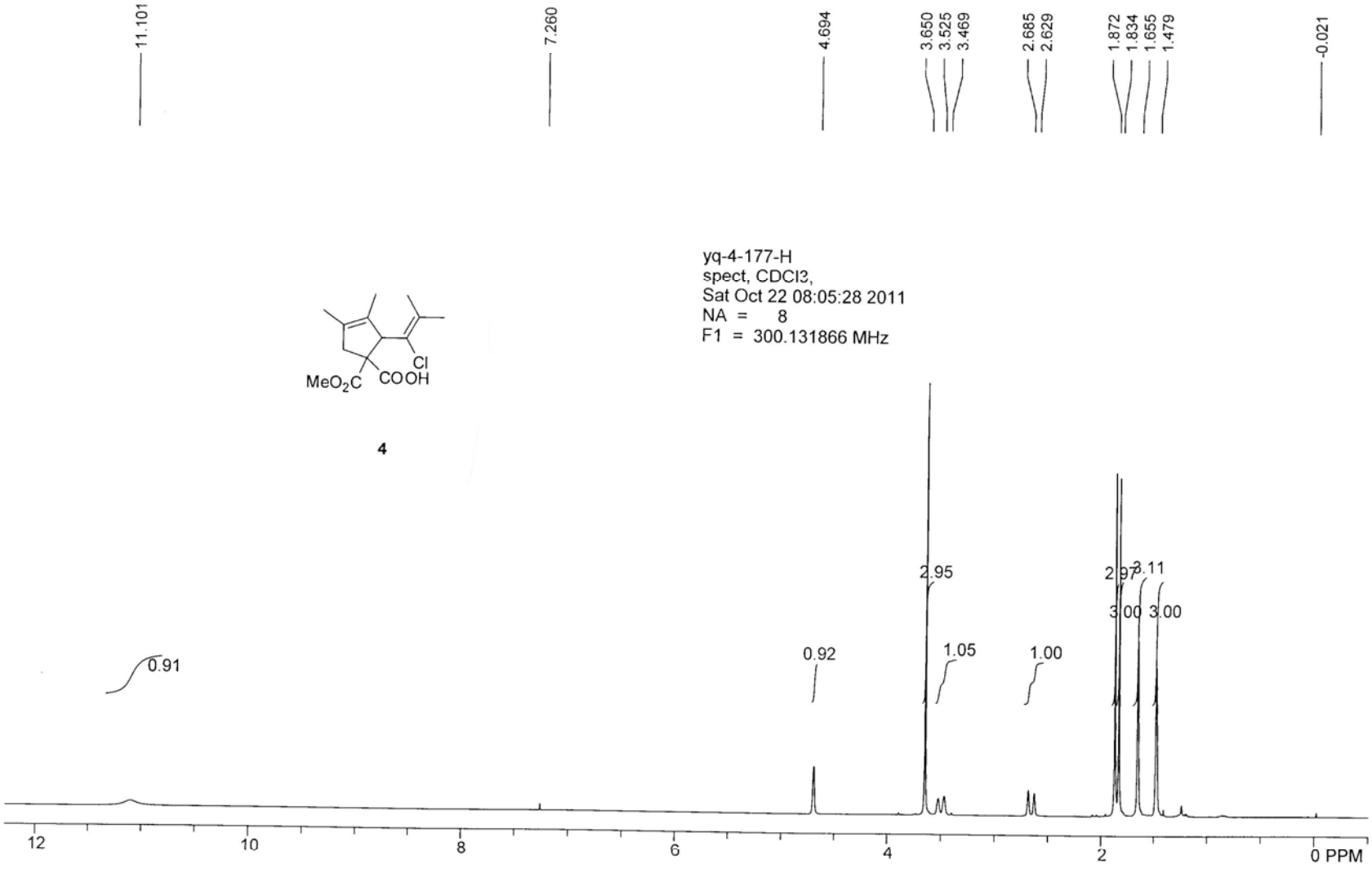

172.701
169.949
132.340
130.953
129.586
126.730
77.430
77.000
76.578
61.946
58.623
52.932
52.318
44.970
22.390
20.989
13.593
12.178
yq-4-103-C
spect, CDCl3,
Tue Jun 05 17:04:49 2012
NA = 306
F1 = 75.475296 MHz
MeO2C
CO2Me
Cl
3l
150
100
50
PPM

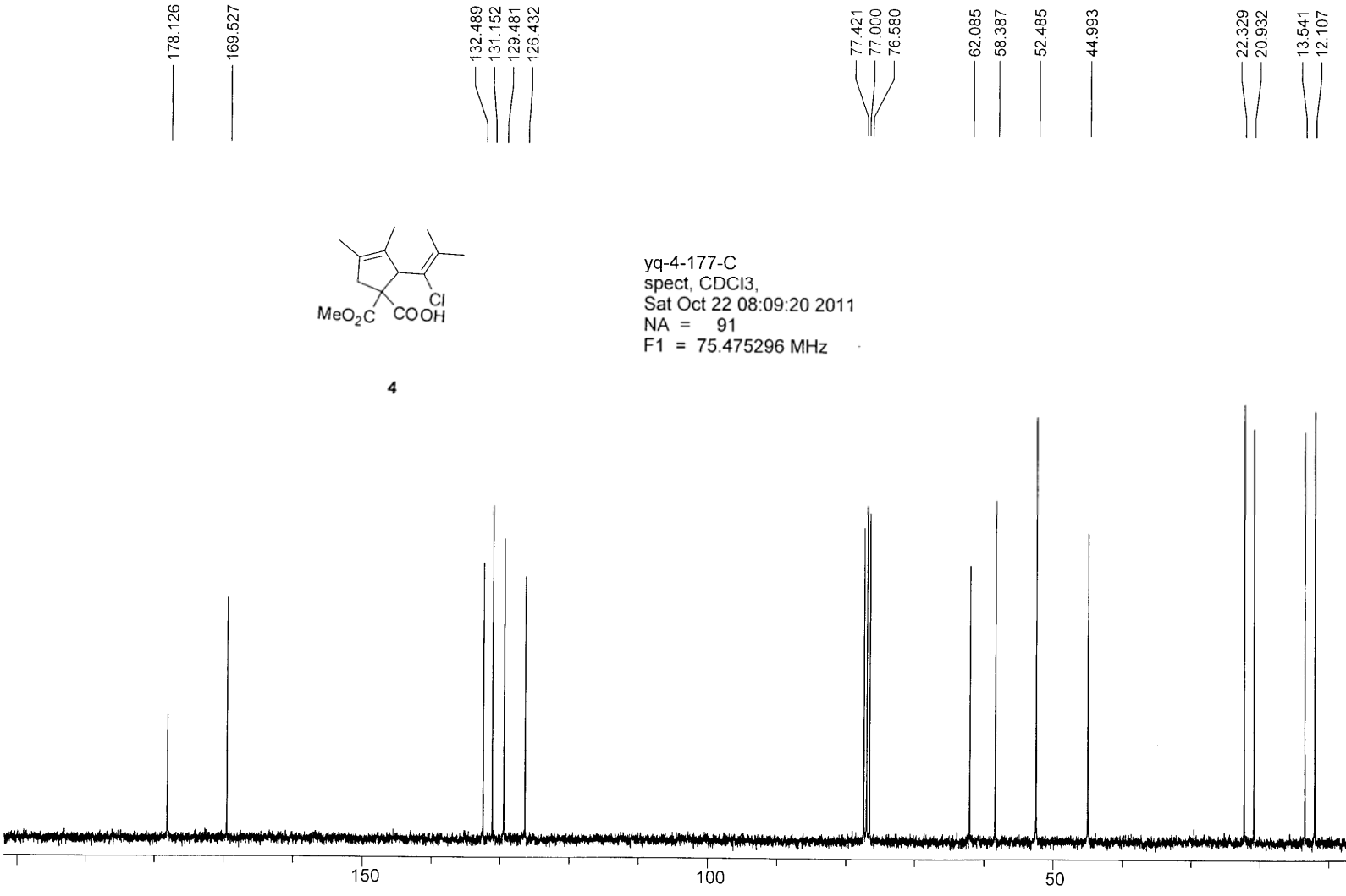

7.280
7.257
7.233
7.192
7.168
7.157
7.130
4.914
3.649
3.630
3.500
3.450
3.410
3.361
2.486
2.460
2.439
2.425
2.393
2.348
1.656
1.581
0.000
yq-4-9-H
spect, CDCl3,
Sat Jun 02 20:43:50 2012
NA = 8
F1 = 300.131866 MHz
Bn
Cl
MeO2C
CO2Me
3m
3.02
2.19
0.97
3.07
2.83
3.13
5.00
9.27
8
7
6
5
4
3
2
1
0
PPM



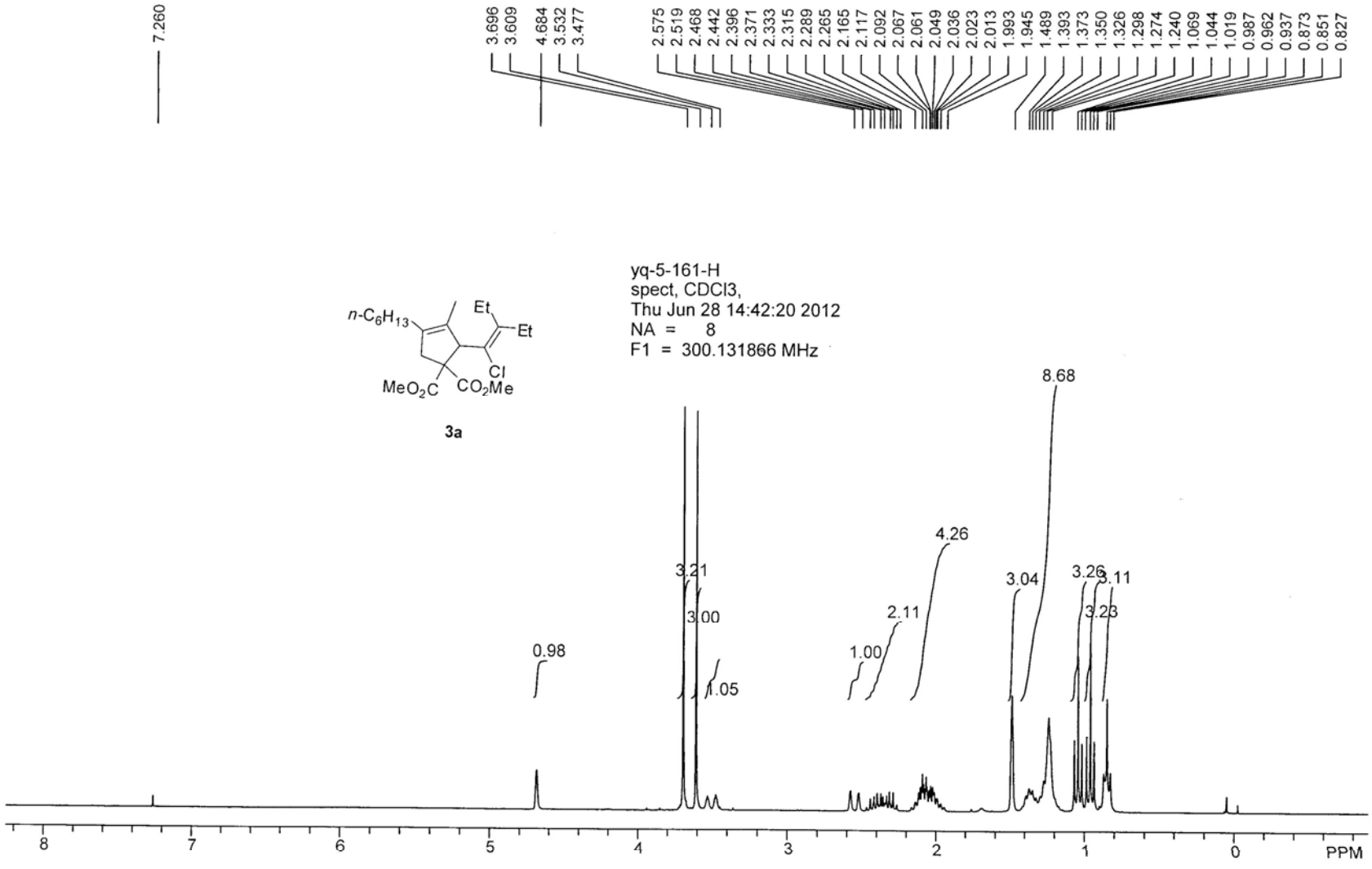

7.260
3.712
3.625
3.575
3.519
4.720
2.576
2.524
2.483
2.462
2.437
2.412
2.387
2.369
2.363
2.345
2.320
2.294
2.185
2.160
2.130
2.105
2.089
2.062
2.044
2.019
1.997
1.973
1.950
1.500
1.429
1.405
1.383
1.364
1.338
1.314
1.293
1.269
1.246
1.217
1.087
1.062
1.037
1.001
0.976
0.951
0.901
0.877
0.854
n-C4H9
Et
Et
Br
MeO2C
CO2Me
3n
yq-5-18-H
spect, CDCl3,
Mon Dec 05 09:18:38 2011
NA = 10
F1 = 300.131866 MHz
4.99
3.95
3.19
2.94
2.87
2.92
2.79
3.06
1.96
1.07
1.03
0.91
8
7
6
5
4
3
2
1
0
-1
PPM


172.711
169.731
146.380
135.529
130.255
121.455
77.430
77.000
76.578
62.248
59.289
52.947
52.291
42.864
29.860
29.657
27.933
25.859
22.489
13.920
13.032
12.252
12.119
n-C4H9
Et
Et
Br
MeO2C
CO2Me
3n
yq--5-18-C
spect, CDCl3,
Fri May 11 16:31:52 2012
NA = 1024
F1 = 75.475296 MHz
200
150
100
50
0
PPM


11.101
7.260
4.694
3.650
3.525
3.469
2.685
2.629
1.872
1.834
1.655
1.479
-0.021
yq-4-177-H
spect, CDCl3,
Sat Oct 22 08:05:28 2011
NA = 8
F1 = 300.131866 MHz
Cl
MeO2C
COOH
4
0.91
0.92
2.95
1.05
1.00
2.97
3.11
3.00
3.00
12
10
8
6
4
2
0 PPM


178.126
169.527
132.489
131.152
129.481
126.432
77.421
77.000
76.580
62.085
58.387
52.485
44.993
22.329
20.932
13.541
12.107
MeO2C
COOH
Cl
yq-4-177-C
spect, CDCl3,
Sat Oct 22 08:09:20 2011
NA = 91
F1 = 75.475296 MHz
150
100
50
PPM

4


7.260
3.696
3.609
4.684
3.532
3.477
2.575
2.519
2.468
2.442
2.396
2.371
2.333
2.315
2.289
2.265
2.165
2.117
2.092
2.067
2.061
2.049
2.036
2.023
2.013
1.993
1.945
1.489
1.393
1.373
1.350
1.326
1.298
1.274
1.240
1.069
1.044
1.019
0.987
0.962
0.937
0.873
0.851
0.827
n-C6H13
Et
Et
Cl
MeO2C
CO2Me
3a
yq-5-161-H
spect, CDCl3,
Thu Jun 28 14:42:20 2012
NA = 8
F1 = 300.131866 MHz
8.68
4.26
3.21
3.04
3.26
3.11
3.23
3.00
2.11
0.98
1.00
1.05
8
7
6
5
4
3
2
1
0
PPM