Efficient Trifluoromethylation via the Cyclopropanation of Allenes and Subsequent C-C Bond Cleavage

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Supporting Information

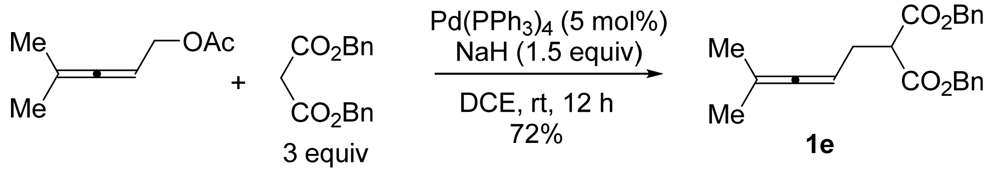
Table of Contents

General Information. NMR spectra were recorded on a commercial instrument at a Bruker-300 spectrometer (300 MHz for ^{1}H NMR, 75.4 MHz for ^{13}C NMR, 282 MHz for ^{19}F NMR) or an Agilent-400 spectrometer (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR, 376 MHz for ^{19}F NMR). ^{1}H NMR spectra were recorded in ppm relative to the residue of $CHCl_3$ (7.26 ppm) in $CDCl_3$ or TMS (0.00 ppm). ^{13}C NMR spectra were recorded in ppm relative to $CDCl_3$ (77.0 ppm). ^{19}F NMR spectra were recorded in ppm relative to $CFCl_3$ (0.00 ppm). All the reactions were carried out in oven dried Schlenk tubes. All solvents were distilled from the indicated drying reagents right before use: Na (benzophenone) for dioxane and THF; CaH_2 for $ClCH_2CH_2Cl$, 1,1,1-trichloroethane, 1,1,2-trichloroethane, MeCN, DMSO, DMF, and CH_2Cl_2.

1. **Synthesis of starting materials.**

The starting materials 1a, [1] **1b,**[1] **1c,**[2] **and 1d**[2] **were synthesized according to literatures.**

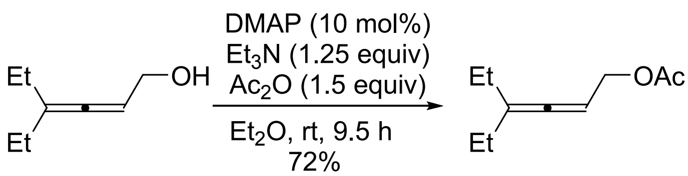
1) **Dibenzyl 2-(4-methyl-2,3-pentadienyl)malonate (1e)** [2] (tangy-5-174)



Typical Procedure 1: To a flame-dried Schlenk flask were added $Pd(PPh_3)_4$ (174.1 mg, 0.15 mmol), 4-methyl-2,3-pentadienyl acetate (421.3 mg, 3 mmol)/DCE (9 mL), dibenzyl malonate (2.5571 g, 9 mmol), and NaH (60% dispersion in mineral oil, 181.2 mg, 4.5 mmol) sequentially under argon. The resulting mixture was stirred at room temperature for 12 h as monitored by TLC. To the resulting mixture was added 10 mL of water, and the resulting mixture was extracted with Et_2O (10 mL × 3). The combined organic layer was washed with brine (10 mL), dried with $MgSO_4$, filtered, and concentrated under vacuum to afford **1e** (791.2 mg, 72%) via chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 15: 1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.26 (m, 10 H, Ar-H), 5.16 (d, J = 12.4 Hz, 2 H, one proton of OCH_2 × 2), 5.11 (d, J = 12.4 Hz, 2 H, one proton of OCH_2 × 2), 5.05-4.95 (m, 1 H, =CH), 3.59 (t, J = 7.4 Hz, 1 H, CH), 2.60 (t, J = 6.8 Hz, 2 H, CH_2), 1.60 (d, J = 2.8 Hz, 6 H, CH_3 × 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.7, 168.7, 135.3, 128.5, 128.3, 128.1, 97.6, 85.5, 67.0, 51.5, 28.1, 20.5; IR (neat, cm^{-1}) 1731, 1497, 1452, 1377, 1332, 1265, 1217, 1142, 1083, 1022; MS (ESI) *m/z* 382 ($M+NH_4^+$), 365 ($M+H^+$); HRMS calcd. for $C_{23}H_{28}O_4N$ [$M+NH_4^+$]: 382.2013; Found: 382.2011.

2) **Diethyl 2-(4-ethyl-2,3-hexadienyl)malonate (1f)**

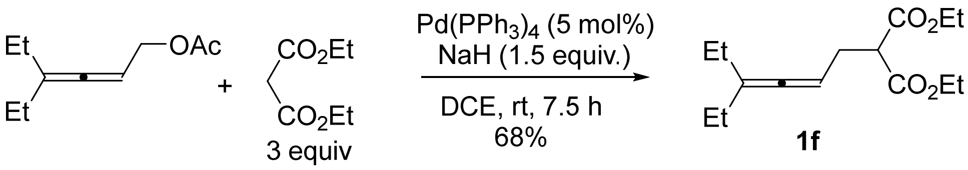
4-Ethyl-2,3-hexadienyl acetate (tangy-5-68)



Typical Procedure 2: To a round-bottom flask were added DMAP (61.2 mg, 0.5

mmol), 4-ethyl-2,3-hexadien-1-ol (631.3 mg, 5 mmol)/Et_2O (15 mL), Et_3N (0.9 mL, d = 0.73 g/mL, 657 mg, 6.25 mmol,), and Ac_2O (0.7 mL, d = 1.08 g/mL, 756 mg, 7.5 mmol) sequentially. The resulting mixture was stirred at room temperature for 9.5 h as monitored by TLC. After evaporation, the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6:1) to afford 4-ethyl-2,3-hexadienyl acetate (612.3 mg, 72%) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36-5.27 (m, 1 H, =CH), 4.53 (d, J = 6.4 Hz, 2 H, OCH_2), 2.07 (s, 3 H, CH_3), 1.98 (qd, J_1 = 7.5 Hz, J_2 = 2.8 Hz, 4 H, CH_2 × 2), 1.00 (t, J = 7.4 Hz, 6 H, CH_3 × 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 170.9, 110.3, 88.8, 63.5, 25.3, 21.0, 12.2; IR (neat, cm^{-1}) 2967, 1964, 1740, 1455, 1372, 1324, 1223, 1086, 1022.

Diethyl 2-(4-ethylhexa-2,3-dienyl)malonate (1f) [2] (tangy-5-172)

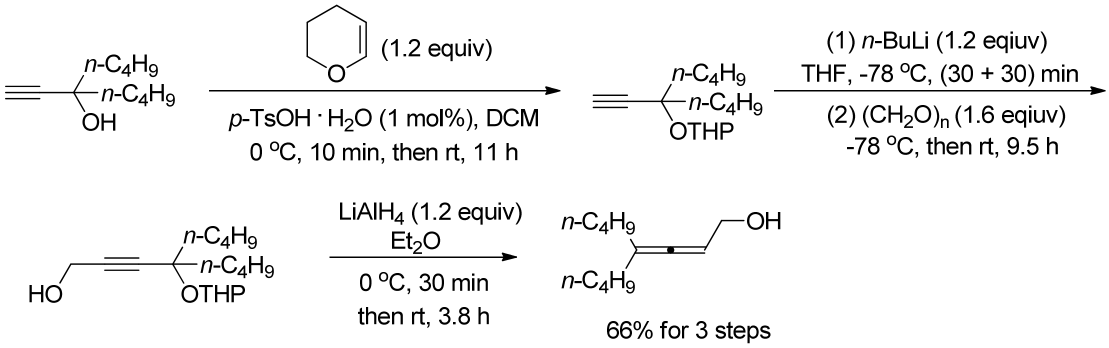


1f

Following **Typical Procedure 1**, the reaction of $Pd(PPh_3)_4$ (173.8 mg, 0.15 mmol), 4-ethyl-2,3-hexadienyl acetate (505.2 mg, 3 mmol)/DCE (9 mL), diethyl malonate (1.4 mL, d = 1.05 g/mL, 1.47 g, 9 mmol), and NaH (60% dispersion in mineral oil, 182.1 mg, 4.5 mmol) afforded **1f** (546.2 mg, 68%) as an oil (eluent: petroleum ether/ethyl acetate = 20:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.24-5.16 (m, 1 H, CH=), 4.26-4.13 (m, 4 H, OCH_2 × 2), 3.44 (t, J = 7.4 Hz, 1 H, CH), 2.58 (dd, J_1 = 7.2 Hz, J_2 = 6.0 Hz, 2 H, CH_2), 2.01-1.85 (m, 4 H, CH_2× 2), 1.27 (t, J = 7.0, 6 H, CH_3 × 2), 0.97 (t, J = 7.4 Hz, 6 H, CH_3 × 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 169.2, 110.2, 89.5, 61.3, 51.7, 28.5, 25.5, 14.0, 12.1; IR (neat, cm^{-1}) 2967, 2935, 2908, 1731, 1455, 1370, 1330, 1261, 1228, 1147, 1095, 1032; MS (EI) m/z (%) 268 (M^+, 45.41), 93 (100); HRMS calcd. for $C_{15}H_{24}O_4$ [M^+]: 268.1675; Found: 268.1682.

3) Diethyl 2-(4-butyl-2,3-octadienyl)malonate (1g)

4-Butyl-2,3-octadienol[3] (tangy-5-79, tangy-5-86, tangy-5-109)

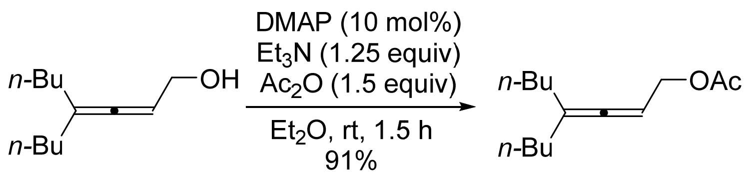


Typical Procedure 3: To a round-bottom flask were added *p*-TsOH·H_2O (38.5 mg, 0.2 mmol), 5-ethynylnonan-5-ol (3.3667 g, 20 mmol), and 40 mL of CH_2Cl_2 sequentially. Then 3,4-dihydro-2*H*-pyran (2.2 mL, d = 0.92 g/mL, 2.02 g, 24 mmol) was added dropwise within 10 min at 0 °C. The resulting mixture was stirred at room temperature for 11 h as monitored by TLC. To the mixture was added 1 mL of Et_3N, and then the solvent was evaporated under vacuum. The crude product was used in the next step without further purification.

To a three-neck flask were added the crude product prepared above and 20 mL of dry THF under argon. Then *n*-BuLi (10.4 mL, 26 mmol, 2.5 M in THF) was added dropwise to the mixture at -78 °C within 30 min. After addition, the resulting mixture was stirred at -78 °C for 30 min, which was followed by the addition of $(CH_2O)_n$ (970.2 mg, 32 mmol). The cooling bath was then removed and the mixture was stirred at room temperature for 9.5 h. After the reaction was complete as monitored by TLC, 10 mL of saturated aqueous NH_4Cl was added and the mixture was extracted with ethyl acetate (20 mL × 3). The combined organic layer was washed with 20 mL of brine, dried with $MgSO_4$, filtered, and concentrated under vacuum. The crude product was used in the next step without further purification.

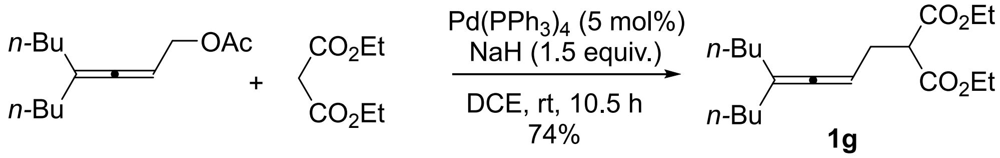
To a three-neck flask equipped with a condenser were added $LiAlH_4$ (911.3 mg, 24 mmol) and 10 mL of dry Et_2O at 0 °C under Ar. Then a solution of the crude product prepared above in 10 mL of Et_2O was added dropwise within 30 min. The ice bath was then removed and the resulting mixture was stirred at room temperature for 3.8 h. Then 1 mL of H_2O, 2 mL of 15% NaOH, and 3 mL of H_2O were added sequentially at 0 °C to quench the reaction. $MgSO_4$ was added and the mixture was stirred at room temperature for 5 min. After filtration and evaporation, the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 8:1) to afford 4-butyl-2,3-octadien-1-ol (2.4017 g, 66% for 3 steps) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36-5.29 (m, 1 H, CH=), 4.08 (t, J = 5.4 Hz, 2 H, OCH_2), 2.01-1.93 (m, 4 H, CH_2 × 2), 1.46-1.25 (m, 9 H, CH_2 × 4 and OH), 0.90 (t, J = 7.2 Hz, 6 H, CH_3 × 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 108.1, 92.6, 61.1, 32.2, 29.8, 22.4, 13.9; IR (neat, cm^{-1}) 3322, 2956, 2927, 2860, 1961, 1461, 1416, 1378, 1345, 1298, 1254, 1105, 1052, 1010. MS (ESI) *m/z*: 183 (M+H$^+$); HRMS calcd. for $C_{12}H_{23}O$ [M+H$^+$]: 183.1743; Found: 183.1744.

4-Butyl-2,3-octadienyl acetate (tangy-5-173)



Following **Typical Procedure 2**, the reaction of DMAP (61.3 mg, 0.5 mmol), 4-butyl-2,3-octadien-1-ol (912.1 mg, 5 mmol)/Et_2O (15 mL), Et_3N (0.9 mL, d = 0.73 g/mL, 657.0 mg, 6.25 mmol), and Ac_2O (0.7 mL, d = 1.08 g/mL, 756.0 mg, 7.5 mmol) for 1.5 h afforded 4-butyl-2,3-octadienyl acetate (1.0211 g, 91%) as an oil (eluent: petroleum ether/ethyl acetate = 15:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.27-5.18 (m, 1 H, CH=), 4.51 (d, J = 6.8 Hz, 2 H, OCH_2), 2.06 (s, 3 H, $O{=}CCH_3$), 1.95(td, J_1 = 7.2 Hz, J_2 = 2.4 Hz, 4 H, 2×CH_2), 1.44-1.24 (m, 8 H, 4×CH_2), 0.90 (t, J = 7.0 Hz, 6 H, 2 × CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.6, 170.9, 106.5, 87.4, 63.6, 31.9, 29.6, 22.3, 21.0, 13.9; IR (neat, cm^{-1}) 2957, 1970, 1742, 1461, 1373, 1222, 1022.

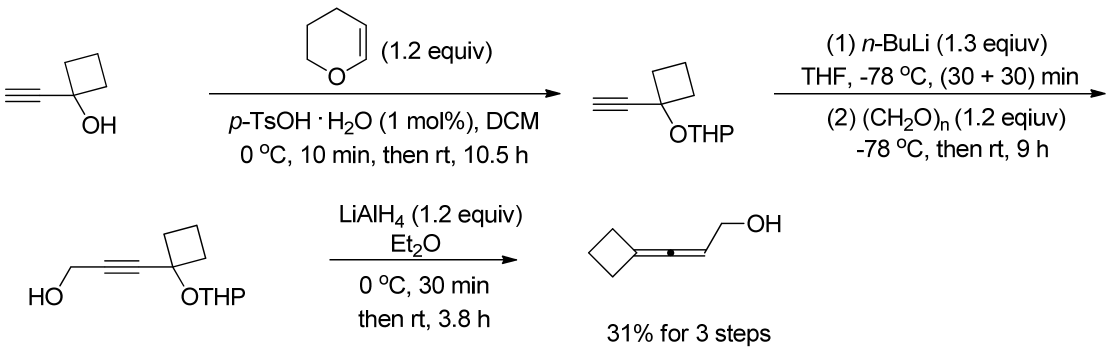
Diethyl 2-(4-butyl-2,3-octadienyl)malonate (1g)[2] (tangy-6-6)



Following **Typical Procedure 1**, the reaction of $Pd(PPh_3)_4$ (173.0 mg, 0.15 mmol), 4-butyl-2,3-octadienyl acetate (547.2 mg, 3 mmol)/DCE (9 mL), diethyl malonate (1.4 mL, d = 1.05 g/mL, 1.47 g, 9 mmol), and NaH (60% dispersion in mineral oil, 180.7 mg, 4.5 mmol) afforded **1g** (720.6 mg, 74%) as an oil (eluent: petroleum ether/ethyl acetate = 20:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.14-5.04 (m, 1 H, CH=), 4.26-4.11 (m, 4 H, $OCH_2 \times 2$), 3.43 (t, J = 7.6 Hz, 1 H, CH), 2.56 (dd, J_1 = 7.6 Hz, J_2 = 6.0 Hz, 2 H, CH_2), 1.97-1.82 (m , 4 H, $CH_2 \times 2$), 1.40-1.24 (m, 14 H, $CH_2 \times 4$ and $CH_3 \times 2$), 0.89 (t, J = 7.0 Hz, 6 H, $CH_3 \times 2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.9, 169.1, 106.4, 88.1, 61.3, 51.8, 32.3, 29.7, 28.5, 22.4, 14.03, 13.95; IR (neat, cm^{-1}) 2982, 1729, 1444, 1391, 1369, 1331, 1266, 1227, 1148, 1094, 1031; MS (EI) *m/z* (%) 324 (M^+, 3.35), 93 (100); HRMS calcd. for $C_{19}H_{32}O_4$ [M^+]: 324.2301; Found: 324.2289.

4) Diethyl 2-(4,4-trimethylene-2,3-butadienyl)malonate (1h)

4,4-Trimethylene-2,3-butadienol[3] (tangy-5-187, tangy-5-188, tangy-5-189)

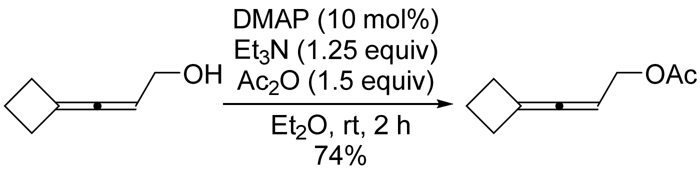


To a round-bottom flask were added 1-ethynylcyclobutanol (1.9205 g, 20 mmol)/ CH_2Cl_2 (40 mL) and p-TsOH·H_2O (38.1 mg, 0.2 mmol) sequentially. Then 3,4-dihydro-2*H*-pyran (2.2 mL, d = 0.92 g/mL, 2.02 g, 24 mmol,) was added dropwise within 10 min at 0 °C. The resulting mixture was stirred at room temperature for 10.5 h as monitored by TLC. To the mixture was added 1 mL of Et_3N and the solvent was evaporated under vacuum. The crude product was used without further purification.

To a three-neck flask were added the crude product prepared above and 20 mL of dry THF under argon. Then *n*-BuLi (10.4 mL, 26 mmol, 2.5 M in hexanes) was added dropwise to the mixture at -78 °C within 30 min. After addition, the resulting mixture was stirred at -78 °C for 30 min, and then $(CH_2O)_n$ (720.5 mg, 24 mmol) was added. The cooling bath was then removed and the mixture was stirred at room temperature for 9 h. After the reaction was complete (monitored by TLC), 10 mL of a saturated aqueous solution of NH_4Cl was added and the mixture was extracted with ethyl acetate (10 mL × 3). The combined organic layer was washed with 10 mL of brine, dried with $MgSO_4$, filtered and concentrated under vacuum. The crude product was used without further purification.

To a three-neck flask equipped with a condenser were added $LiAlH_4$ (911.5 mg, 24 mmol) and 10 mL of dry Et_2O at 0 °C under Ar. Then the crude product prepared above was dissolved in 10 mL of Et_2O and added dropwise into the mixture within 30 min. The ice bath was then removed and the resulting mixture was stirred at room temperature for 3.8 h. Then 1 mL of H_2O, 2 mL of 15% NaOH, and 3 mL of H_2O were added sequentially at 0 °C to quench the reaction. $MgSO_4$ was added and the resulting mixture was stirred at room temperature. After filtration and evaporation, the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6:1) to afford 4,4-trimethylene-2, 3-butadienol (681.7 mg, 31% for 3 steps) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40-5.30 (m, 1 H, CH=), 4.10 (d, J = 5.6 Hz, 2 H, OCH_2), 2.98-2.82 (m, 4 H, CH_2 × 2), 1.97 (quint, J = 8.0 Hz, 2 H, CH_2), 1.67 (brs, 1 H, OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 104.2, 94.1, 60.9, 29.8, 17.4; IR (neat, cm^{-1}) 3323, 2927, 1961, 1461, 1416, 1378, 1327, 1254, 1221, 1104, 1066, 1011.

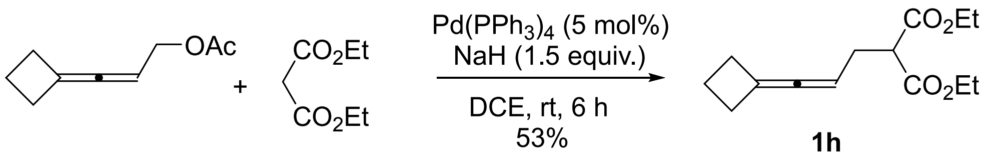
4,4-Trimethylene-2,3-butadienyl acetate (tangy-5-190)



Following **Typical Procedure 2**, the reaction of DMAP (61.5 mg, 0.5 mmol), 4,4-trimethylene-2, 3-butadien ol (551.2 mg, 5 mmol)/Et_2O (15 mL), Et_3N (0.9 mL, d = 0.73 g/mL, 657 mg, 6.25 mmol), and Ac_2O (0.7 mL, d = 1.08 g/mL, 756 mg, 7.5 mmol) for 2 h afforded 4,4-trimethylene-2,3-butadienyl acetate (561.3 mg, 74%) as an oil (eluent: petroleum ether/ethyl acetate = 10:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.29-5.20 (m, 1 H, =CH), 4.53 (d, J = 6.8 Hz, 2 H, OCH_2), 2.96-2.81 (m, 4 H, CH_2 × 2), 2.07 (s, 3 H, CH_3), 1.97 (quint, J = 7.9 Hz, 2 H, CH_2); ^{13}C NMR (100 MHz,

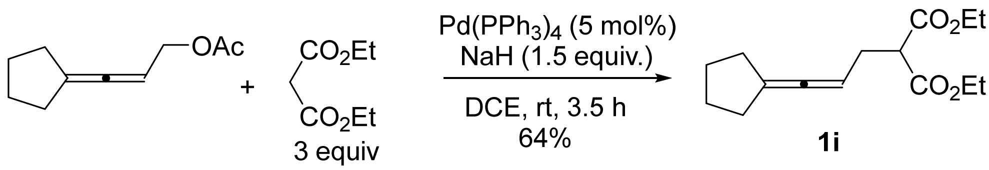
$CDCl_3$) δ 196.8, 170.7, 103.0, 88.8, 63.3, 29.5, 21.0, 17.5; IR (neat, cm^{-1}) 2967, 1964, 1741, 1454, 1372, 1324, 1223, 1086, 1022.

Diethyl 2-(4,4-trimethylene-2,3-butadienyl)malonate (**1h**)[2] (tangy-6-5)



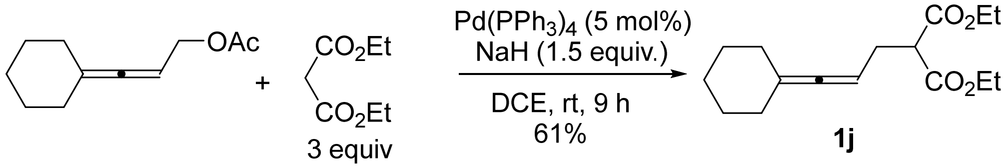
Following **Typical Procedure 1**, the reaction of $Pd(PPh_3)_4$ (115.9 mg, 0.1 mmol), 4,4-trimethylene-2,3-butadienyl acetate (302.3 mg, 2 mmol), DCE (6 mL), diethyl malonate (0.93 mL, d = 1.05 g/mL, 976.5 mg, 6 mmol), and NaH (60% dispersion in mineral oil, 121.3 mg, 3 mmol) afforded **1f** (269.1 mg, 53%) as an oil (eluent: petroleum ether/ethyl acetate = 10:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21-5.14 (m, 1 H, CH=), 4.27-4.13 (m, 4 H, $OCH_2 \times 2$), 3.50 (t, J = 7.4 Hz, 1 H, CH), 2.83 (td, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 4 H, $CH_2 \times 2$), 2.58 (dd, J_1 = 7.6 Hz, J_2 = 6.0 Hz, 2 H, CH_2), 1.98-1.87 (m, 2 H, CH_2), 1.28 (t, J = 7.0, 6 H, $CH_3 \times 2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 169.0, 103.3, 90.1, 61.3, 51.4, 29.8, 28.5, 17.4, 14.1; IR (neat, cm^{-1}) 2958, 2929, 2869, 1733, 1462, 1370, 1332, 1261, 1226, 1148, 1095, 1034; MS (EI) m/z (%) 252 (M^+, 57.38), 105 (100); HRMS calcd. for $C_{14}H_{20}O_4$ [M^+]: 252.1362; Found: 252.1366.

5) **Diethyl 2-(4,4-tetramethylene-2,3-butadienyl)malonate** (**1i**)[2] (tangy-5-12)



Following **Typical Procedure 1**, $Pd(PPh_3)_4$ (231.3 mg, 0.2 mmol), 4,4-tetramethylene-2, 3-butadienyl acetate (654.8 mg, 4.3 mmol), DCE (20 mL), diethyl malonate (2.0 mL, d = 1.05 g/mL, 2.10 g, 12.9 mmol), and NaH (60% dispersion in mineral oil, 261.0 mg, 6.5 mmol) afforded **1i** (737.0 mg, 64%) as an oil (eluent: petroleum ether/ethyl acetate = 20:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.15-5.06 (m, 1 H, CH=), 4.27-4.08 (m, 4 H, $2 \times OCH_2$), 3.47 (t, J = 7.4 Hz, 1 H, CH), 2.57 (dd, J_1 = 7.6 Hz, J_2 = 6.0 Hz, 2 H, CH_2), 2.40-2.24 (m, 4 H, CH_2 × 2), 1.70-1.55 (m, 4 H, CH_2 × 2), 1.27 (t, J = 7.2 Hz, 6 H, OCH_3 × 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 169.1, 106.0, 88.2, 61.3, 51.5, 31.1, 28.4, 27.0, 14.1; IR (neat, cm^{-1}) 2979, 1726, 1446, 1370, 1232, 1152, 1095, 1027; MS (EI) *m/z* (%) 266 (M^+, 100); HRMS calcd. for $C_{15}H_{22}O_4$ [M^+]: 266.1518; Found: 266.1522.

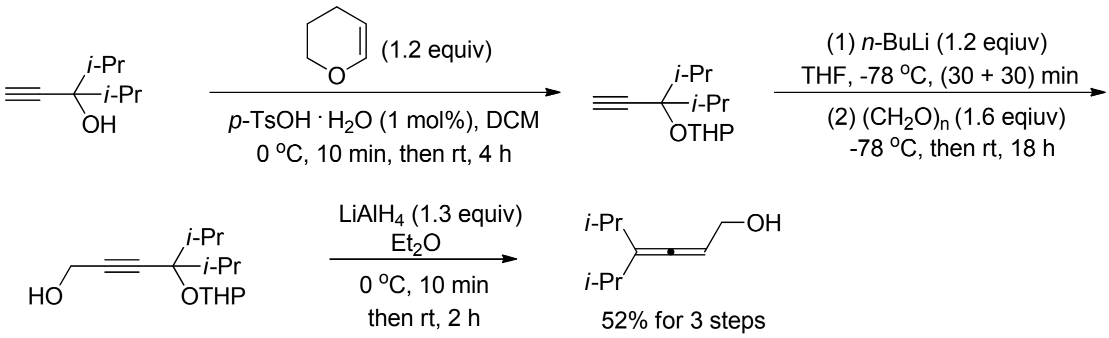
6) **Diethyl 2-(4,4-pentamethylene-2,3-butadienyl)malonate** (**1j**)[2] (tangy-5-22)



Following **Typical Procedure 1**, the reaction of $Pd(PPh_3)_4$ (173.8 mg, 0.15 mmol), 4,4-pentamethylene-2,3-butadienyl acetate (541.2 mg, 3 mmol), DCE (9 mL), diethyl malonate (1.4 mL, d = 1.05 g/mL, 1.47 g, 9 mmol), and NaH (60% dispersion in mineral oil, 180.3 mg, 4.5 mmol) afforded **1j** (513.9 mg, 61%) as an oil (eluent: petroleum ether/ethyl acetate = 15:1): ^1H NMR (400 MHz, $CDCl_3$) δ 5.05-4.98 (m, 1 H, =CH), 4.27-4.11 (m, 4 H, OCH_2 × 2), 3.47 (t, J = 7.6 Hz, 1 H, CH), 2.55 (t, J = 6.8 Hz, 2 H, CH_2), 2.11-1.98 (m, 4 H, CH_2 × 2), 1.64-1.39 (m, 6 H, CH_2 × 3), 1.27 (t, J = 7.0 Hz, 6 H, CH_3 × 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 169.1, 104.5, 85.4, 61.3, 51.5, 31.4, 28.2, 27.2, 26.0, 14.0; IR (neat, cm^{-1}) 2981, 2928, 2854, 1731, 1444, 1390, 1369, 1332, 1227, 1148, 1096, 1074, 1033; MS (EI) *m/z* (%) 280 (M^+, 39.04), 91 (100); HRMS calcd. for $C_{16}H_{24}O_4$ [M^+]: 280.1675; Found: 280.1678.

7) **Diethyl 2-(4-isopropyl-5-methyl-2,3-hexadienyl)malonate** (**1k**)

4-Isopropyl-5-methyl-2,3-hexadienol[3] (tangy-5-177)

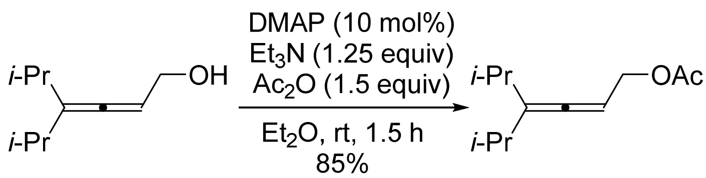


Following **Typical Procedure 3**, the reaction of 3-isopropyl-4-methylpent-1-yn-3-ol (2.8087 g, 20 mmol), *p*-TsOH·H_2O (38.3 mg, 0.2 mmol), 3,4-dihydro-2*H*-pyran (2.2 mL, d = 0.92 g/mL, 2.02 g, 24 mmol,) in 40 mL of CH_2Cl_2 afforded the crude product.

Then the reaction of the crude product, *n*-BuLi (10.4 mL, 26 mmol, 2.5 M in THF), and $(CH_2O)_n$ (720.5 mg, 24 mmol) in 20 mL of THF afforded the crude product.

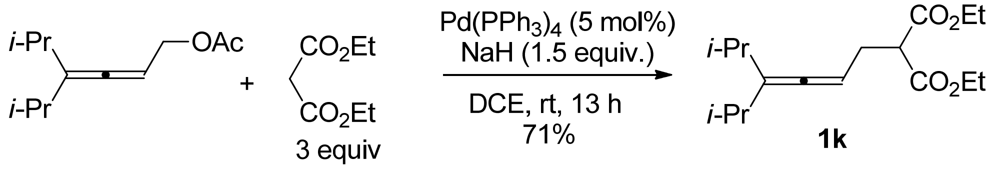
The reaction of the crude product/Et_2O (10 mL) and $LiAlH_4$ (911.5 mg, 24 mmol) in 10 mL of Et_2O for 2 h afforded 4-isopropyl-5-methyl-2,3-hexadien-1-ol as an oil (1.6146 g, 52% for 3 steps) (eluent: petroleum ether/ethyl acetate = 8:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.50-5.44 (m, 1 H, CH=), 4.08 (d, *J* = 5.6 Hz, 2 H, OCH_2), 2.26-2.13 (m, 2 H, CH × 2), 1.38 (brs, 1 H, OH), 1.03 (d, *J* = 6.8 Hz, 6 H, CH_3 × 2), 1.02 (d, *J* = 6.8 Hz, 6 H, CH_3 × 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 95.6, 61.1, 29.5, 22.6, 22.2; IR (neat, cm^{-1}) 3325, 2960, 2929, 2870, 1955, 1462, 1417, 1382, 1363, 1313, 1295, 1199, 1119, 1074, 1009.

4-Isopropyl-5-methyl-2,3-hexadienyl acetate (tangy-5-178)



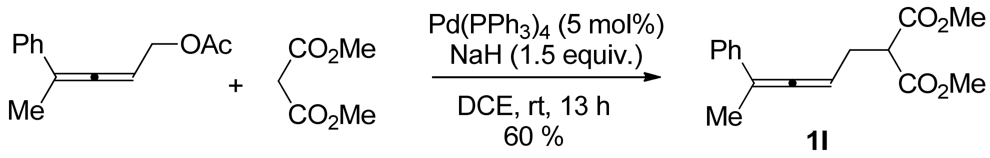
Following **Typical Procedure 2**, the reaction of DMAP (61.5 mg, 0.5 mmol), 4-isopropyl-5-methyl-2,3-hexadienol (770.5 mg, 5 mmol), Et_2O (15 mL), Et_3N (0.9 mL, d = 0.73 g/mL, 657 mg, 6.25 mmol), and Ac_2O (0.7 mL, d = 1.08 g/mL, 756 mg, 7.5 mmol) for 1.5 h afforded 4-isopropyl-5-methyl-2,3-hexadienyl acetate (718.8 mg, 85%) as an oil (eluent: petroleum ether/ethyl acetate = 15:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.34 (t, J = 6.4 Hz, 1 H, CH=), 4.52 (d, J = 6.4 Hz, 2 H, OCH_2), 2.17 (heptet, J = 6.7 Hz, 2 H, CH × 2), 2.06 (s, 3 H, CH_3C=O), 1.02 (d, J = 6.8 Hz, 6 H, CH_3 × 2), 1.01 (d, J = 6.8 Hz, 6 H, CH_3 × 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 170.9, 120.2, 90.3, 63.5, 29.4, 22.3, 22.1, 21.0; IR (neat, cm^{-1}): 2957, 2929, 2862, 1965, 1742, 1461, 1373, 1221, 1022.

Diethyl 2-(4-isopropyl-5-methyl-2,3-hexadienyl)malonate (**1k**)[2] (tangy-5-179)



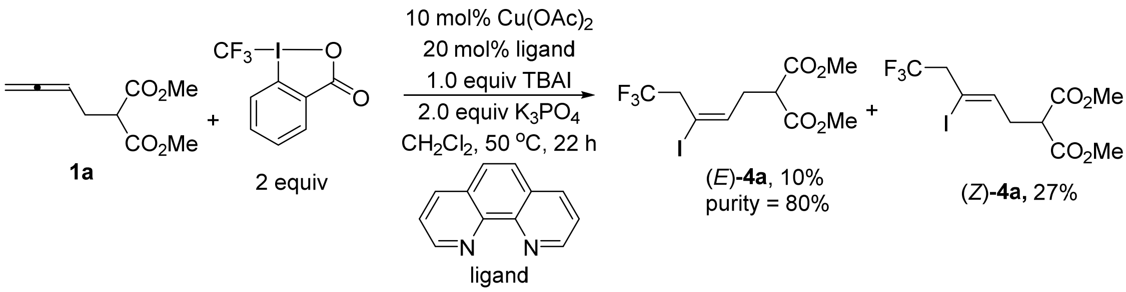
Following **Typical Procedure 1**, the reaction of $Pd(PPh_3)_4$ (173.8 mg, 0.15 mmol), 4-isopropyl-5-methyl-2,3-hexadienyl acetate (505.8 mg, 3 mmol), DCE (9 mL), diethyl malonate (1.4 mL, d = 1.05 g/mL, 1.47 g, 9 mmol), and NaH (60% dispersion in mineral oil, 181.1 mg, 4.5 mmol) afforded **1k** (631.5 mg, 71%) as an oil (eluent: petroleum ether/ethyl acetate = 20:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.24-5.18 (m, 1 H, =CH), 4.26-4.14 (m, 4 H, 2×OCH_2), 3.43 (t, J = 7.6 Hz, 1 H, O=CCH), 2.58 (dd, J_1 = 7.6 Hz, J_2 = 6.0 Hz, 2 H, =CCH_2), 2.20-2.08 (m, 2 H, CH × 2), 1.27 (t, J = 7.0 Hz, 6 H, CH_3 × 2), 0.99 (d, J = 8.8 Hz, 6 H, CH_3 × 2), 0.98 (d, J = 8.8 Hz, 6 H, CH_3 × 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 169.2, 119.7, 90.9, 61.3, 51.9, 29.4, 28.8, 22.4, 22.0, 14.0; IR (neat, cm^{-1}) 2962, 2933, 2871, 1956, 1732, 1463, 1368, 1332, 1263, 1225, 1148, 1095, 1031; MS (EI) m/z (%) 296 (M^+, 14.56), 93 (100); HRMS calcd. for $C_{17}H_{28}O_4$ [M^+]: 296.1988; Found: 296.1987.

8) Dimethyl 2-(4-phenyl-2,3-pentadienyl)malonate (1l)[2] (tangy-5-147)



To a flame-dried Schlenk flask were added $Pd(PPh_3)_4$ (232.0 mg, 0.2 mmol), 4-phenyl-2,3-pentadienyl acetate (811.2 mg, 4 mmol)/DCE (20 mL), and dimethyl malonate (1.8 mL, d = 1.05 g/mL, 1.89 g, 12 mmol) sequentially under argon. Then NaH (60% dispersion in mineral oil, 241.1 mg, 6 mmol) was added in portions within 10 min. The resulting mixture was stirred at room temperature for 13 h as monitored by TLC. To the mixture was added 20 mL of water, the resulting mixture was extracted with Et_2O (20 mL × 3). The combined organic layer was washed with brine (20 mL), dried with $MgSO_4$, filtered, and concentrated under vacuum to afford **1l** (658.2 mg, 60%) via chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10: 1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.27 (m, 4 H, ArH × 4), 7.23-7.16 (m, 1 H, ArH), 5.54-5.47 (m, 1 H, CH=), 3.72 (s, 3 H, OCH_3), 3.56 (s, 3 H, OCH_3), 3.55 (t, J = 7.6 Hz, 1 H, CH), 2.81-2.63 (m, 2 H, CH_2), 2.06 (d, J = 2.8 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.0, 169.3, 169.2, 136.7, 128.2, 126.7, 125.7, 102.8, 89.8, 52.6, 52.4, 50.9, 28.0, 17.0; IR (neat, cm^{-1}) 2954, 1730, 1685, 1599, 1493, 1436, 1340, 1264, 1235, 1199, 1152, 1070, 1025; MS (EI) *m/z* (%) 274 (M^+, 42.51), 142 (100); HRMS calcd. for $C_{16}H_{18}O_4$ [M^+]: 274.1205; Found: 274.1203.

2. Synthesis of (*E*)-dimethyl 2-(5,5,5-trifluoro-3-iodopent-2-enyl)-malonate (*E*)-4a and (*Z*)-dimethyl 2-(5,5,5-trifluoro-3-iodopent-2-enyl)malonate (*Z*)-4a.

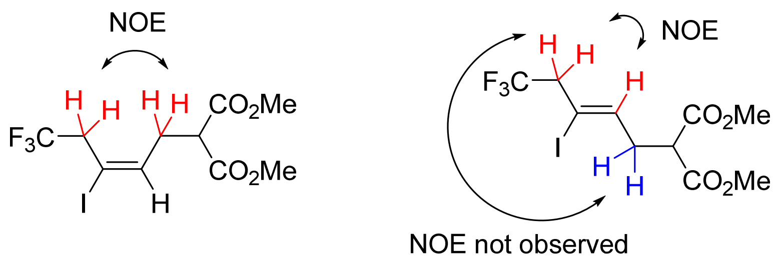


Typical Procedure 4: To a flame-dried Schlenk tube were added K_3PO_4 (425.7 mg, 2.0 mmol), $Cu(OAc)_2$ (18.1 mg, 0.10 mmol), ligand (36.3 mg, 0.20 mmol), Togni's reagent II (631.6 mg, 2.0 mmol), TBAI (369.5 mg, 1.0 mmol), **1a** (184.0 mg, 1.0 mmol), and 7 mL of CH_2Cl_2 under argon sequentially. After being stirred at 50 ^{o}C for

12 h, the crude reaction mixture was filtrated through a short pad of silica gel eluted with diethyl ether (50 mL). After evaporation, the residue was analyzed by ^{1}H NMR, and then purified by chromatography on silica gel (purified by chromatography for twice. First round eluent: petroleum ether/CH_2Cl_2 = 3 : 1, then petroleum ether : CH_2Cl_2 : ethyl acetate = 300 : 100 : 3; second round eluent: petroleum ether/ethyl acetate = 200:1) to afford impure (*E*)-**4a** (50.1 mg, 11%, purity = 80%) and pure (*Z*)-**4a** (103.5 mg, 27%).

(*E*)-**4a**: oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.52 (t, *J* = 7.8 Hz, 1 H, =CH), 3.76 (s, 6 H, $OCH_3 \times 2$), 3.53-3.43 (m, 3 H, CH_2CF_3 and CH), 2.65 (t, *J* = 7.8 Hz, 2 H, CH_2); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.6, 144.0, 125.0 (q, *J* = 276.6 Hz), 84.3 (q, *J* = 2.9 Hz), 52.9, 50.1, 43.0 (q, *J* = 30.15 Hz), 30.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.7 (s, 3 F); IR (neat, cm^{-1}) 2958, 1736, 1526, 1476, 1437, 1350, 1256, 1204, 1138, 1044, 1017; MS (EI) *m/z* (%) 380 (M^+, 1.95), 193 (100); HRMS calcd. for $C_{10}H_{12}F_3IO_4$ [M^+]: 379.9732; found: 379.9737. The configuration of (*E*)-**4a** was determined by NOE study.

(*Z*)-**4a**: oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.90 (t, *J* = 6.6 Hz, 1 H, =CH), 3.76 (s, 6 H, $CH_3 \times 2$), 3.54 (t, *J* = 7.2 Hz, 1 H, CH), 3.38 (q, *J* = 9.8 Hz, 2 H, CH_2CF_3), 2.75 (t, *J* = 7.2 Hz, 2 H, CH_2); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 139.4, 124.9 (q, *J* = 276.6 Hz), 91.6 (q, *J* = 3.4 Hz), 52.7, 49.8, 48.7 (q, *J* = 29.8 Hz), 35.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.6 (s, 3 F); IR (neat, cm^{-1}) 2957, 1733, 1437, 1349, 1252, 1120, 1069, 1047; MS (EI) *m/z* (%) 380 (M^+, 4.56), 193 (100); HRMS calcd. for $C_{10}H_{12}F_3IO_4$ [M^+]: 379.9732; found: 379.9721. The configuration of (*Z*)-**4a** was determined by NOE study.

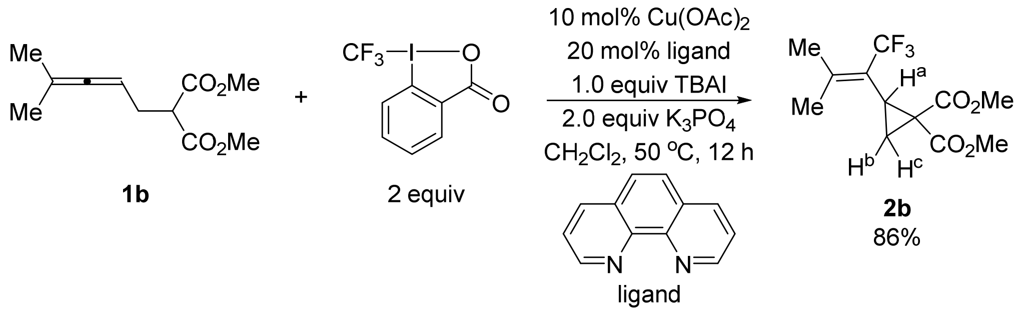


(*E*)-**4a** (*Z*)-**4a**

3. **Synthesis of cyclopropane-1,1-dicarboxylate 2**

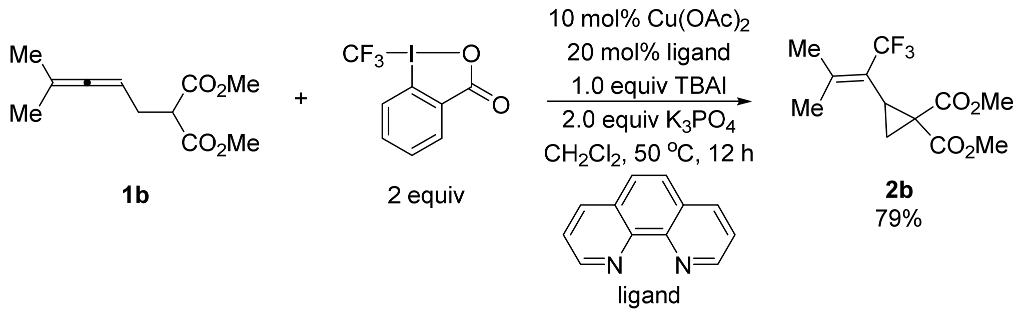
Unless otherwise specified, the following compounds were prepared according to **Typical Procedure 4**.

1) **Dimethyl 2-(2-methyl-1-trifluoromethyl-1-propenyl)cyclopropane-1,1-dicarboxylate 2b** (yq-8-113)



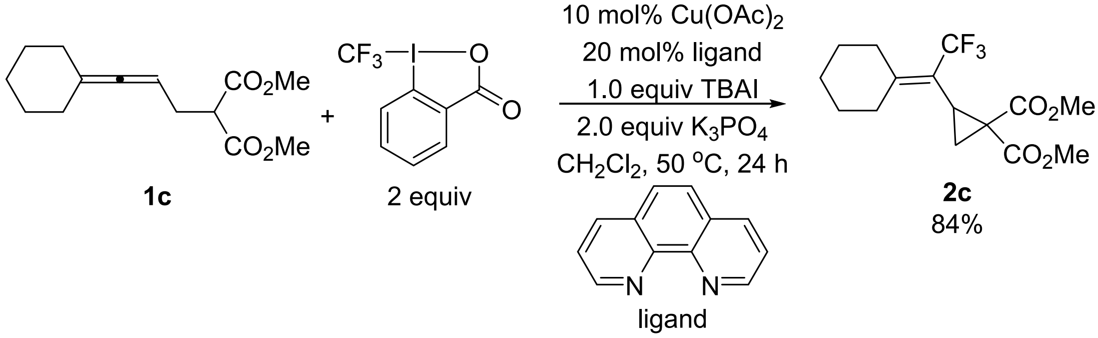
The reaction of K_3PO_4 (423.4 mg, 2.0 mmol), $Cu(OAc)_2$ (8.1 mg, 0.10 mmol), ligand (36.0 mg, 0.20 mmol), Togni's reagent II (632.2 mg, 2.0 mmol), TBAI (368.9 mg, 1.0 mmol), **1b** (212.5 mg, 1.0 mmol), and 7 mL of CH_2Cl_2 afforded **2b** (240.8 mg, 86%) as an oil (eluent: petroleum ether/CH_2Cl_2 = 3:1): ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.74 (s, 3 H, OCH_3), 3.62 (s, 3 H, OCH_3), 2.60 (t, $J_{H^b \text{ and } H^c \sim H^a}$ = 9.0 Hz, 1 H, =CCH), 2.01 (dd, $J_{H^a \sim H^b}$ = 8.0 Hz, $J_{H^c \sim H^b}$ = 5.6 Hz, 1 H, one proton of CH_2), 1.87 (s, 6 H, 2×CH_3), 1.66 (dd, $J_{H^a \sim H^c}$ = 9.8 Hz, $J_{H^b \sim H^c}$ = 5.3 Hz, 1 H, one proton of CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.8, 167.4, 148.7 (q, J = 3.0 Hz), 124.0 (q, J = 274.0 Hz), 118.6 (q, J = 28.6 Hz), 52.8, 52.2, 35.1, 27.6 (d, J = 2.6 Hz), 23.1, 21.9-21.5 (m, 2 C); ^{19}F NMR (282 MHz, $CDCl_3$): δ -56.7 (s, 3 F); IR (neat, cm^{-1}): 1730, 1655, 1439, 1378, 1320, 1286, 1220, 1110, 1063; MS (EI) *m/z* (%) 280 (M^+, 8.67), 141 (100); HRMS calcd. for $C_{12}H_{15}O_4F_3$ [M^+]: 280.0922; Found: 280.0924.

Synthesis of 2b on 5 mmol scale (yq-10-34)



To a flame-dried Schlenk tube were added K_3PO_4 (2.1202 g, 10.0 mmol), $Cu(OAc)_2$ (90.7 mg, 0.5 mmol), ligand (180.6 mg, 1 mmol), Togni's reagent II (3.1667 g, 10.0 mmol), TBAI (1.8462 g, 5 mmol), **1b** (1.0604 g, 5.0 mmol), and 35 mL of CH_2Cl_2 under argon sequentially. The resulting mixture was stirred at 50 ^{o}C for 12 h, the crude reaction mixture was filtrated through a short pad of silica gel eluted with diethyl ether (100 mL). After evaporation, the residue was analyzed by ^{1}H NMR, and then purified by chromatography on silica gel (eluent: petroleum ether/CH_2Cl_2 = 3:1) to afford **2b** (1.1061 g, 79%) as an oil: ^{1}H NMR (300 MHz, $CDCl_3$): 3.77 (s, 3 H, OCH_3), 3.66 (s, 3 H, OCH_3), 2.63 (t, J = 8.9 Hz, 1 H, =CCH), 2.05 (dd, J_1 = 8.4 Hz, J_2 = 5.4 Hz, 1 H, one proton of CH_2), 1.90 (s, 6 H, 2×CH_3), 1.70 (dd, J_1 = 9.8 Hz, J_2 = 5.3 Hz, 1 H, one proton of CH_2).

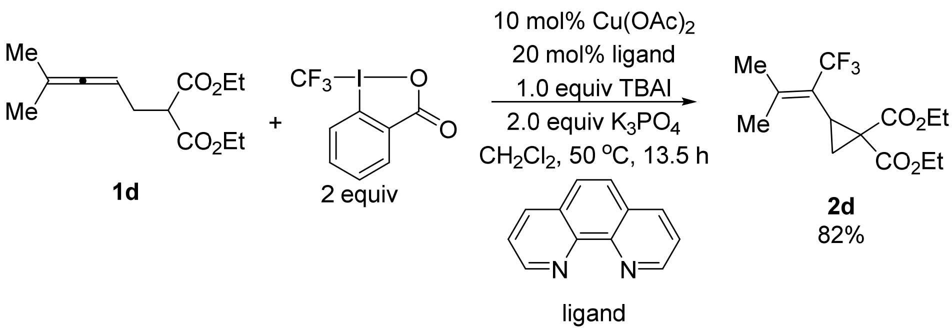
2) Dimethyl 2-(1-trifluoromethyl-1-cyclohexylidene)cyclopropane-1,1-dicarboxylate 2c (yq-11-64)



The reaction of K_3PO_4 (424.0 mg, 2.0 mmol), $Cu(OAc)_2$ (18.5 mg, 0.10 mmol), ligand (36.1 mg, 0.20 mmol), Togni's reagent II (631.3 mg, 2.0 mmol), TBAI (369.0 mg, 1.0 mmol), **1c** (246.8 mg, 0.98 mmol), and 7 mL of CH_2Cl_2 afforded **2c** (262.5 mg, 84%) as an oil (eluent: petroleum ether/ CH_2Cl_2 = 2:1): ^{1}H NMR (300 MHz,

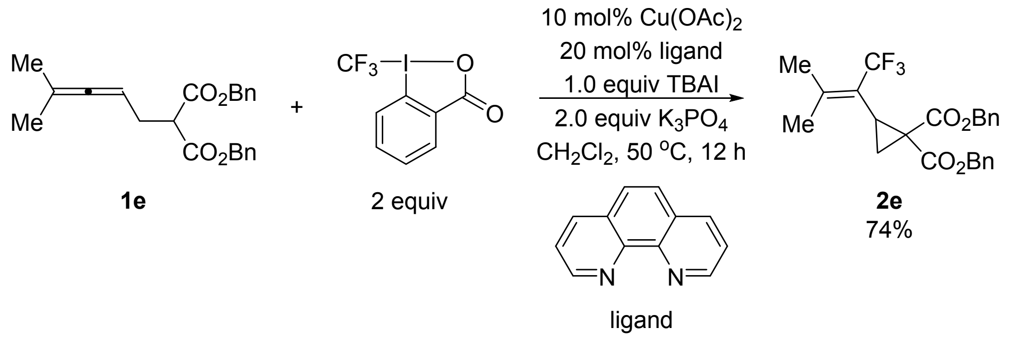
$CDCl_3$) δ 3.74 (s, 3 H, OCH_3), 3.62 (s, 3 H, OCH_3), 2.61 (t, J = 9.0 Hz, 1 H, =CCH), 2.50-2.35 (m, 2 H, CH_2), 2.27-2.12 (m, 2 H, CH_2), 1.99 (dd, J_1 = 8.6 Hz, J_2 = 5.3 Hz, 1 H, one proton of CH_2), 1.72-1.42 (m, 7 H, one proton of CH_2 and 3×CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.8, 167.3, 156.2 (q, J = 2.6 Hz), 124.2 (q, J = 274.7 Hz), 116.0 (q, J = 28.2 Hz), 52.8, 52.1, 35.1, 32.5, 32.3 (q, J = 2.5 Hz), 28.0, 27.9, 27.1 (q, J = 2.× Hz), 26.0, 22.2 (q, J = 2.4 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ = -55.3 (s, 3 F); IR (neat, cm^{-1}) 1729, 1443, 1316, 1218, 1113, 1001; MS (EI) *m/z* (%) 320 (M^+, 1.25), 159 (100); HRMS calcd. for $C_{15}H_{19}O_4F_3$ [M^+]: 320.1235; Found: 320.1239.

3) Diethyl 2-(2-methyl-1-trifluoromethyl-1-propenyl)cyclopropane-1,1-dicarboxylate 2d (yq-8-156)



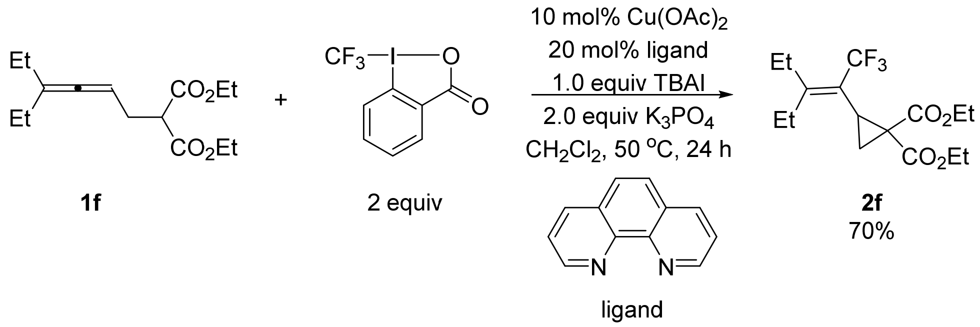
The reaction of K_3PO_4 (424.1 mg, 2.0 mmol), $Cu(OAc)_2$ (18.2 mg, 0.10 mmol), ligand (36.0 mg, 0.20 mmol), Togni's reagent II (632.3 mg, 2.0 mmol), TBAI (369.1 mg, 1.0 mmol), **1d** (238.7 mg, 1.0 mmol), and 7 mL of CH_2Cl_2 afforded **2d** (251.9 mg, 82%) as an oil ((purified by chromatography for twice: first round, petroleum ether/ CH_2Cl_2 = 2.5:1, second round: petroleum ether/ ethyl acetate = 30:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.28-4.14 (m, 2 H, OCH_2), 4.14-3.98 (m, 2 H, OCH_2), 2.56 (t, J = 9.2 Hz, 1 H, =CCH), 1.97 (ddq, J_1 = 8.6 Hz, J_2 = 5.4 Hz, J_3 = 1.0 Hz, 1 H, one proton of CH_2), 1.86 (s, 6 H, 2×CH_3), 1.61 (dd, J_1= 9.8 Hz, J_2= 5.3 Hz, 1 H, one proton of CH_2), 1.23 (t, J = 7.1 Hz, 3 H, CH_3), 1.17 (t, J = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 167.0, 148.4 (q, J = 3.2 Hz), 124.0 (q, J = 273.8 Hz), 118.6 (q, J = 28.7 Hz), 61.5, 61.2, 35.3, 27.1 (d, J = 2.6 Hz), 23.1, 21.7 (q, J = 2.6 Hz), 21.1 (q, J = 2.6 Hz), 13.9, 13.7; ^{19}F NMR (282 MHz, $CDCl_3$) δ -56.5 (s, 3 F); IR (neat, cm^{-1}) 1725, 1653, 1447, 1374, 1317, 1283, 1214, 1110, 1023; MS (EI) *m/z* (%) 308 (M^+, 13.71), 161 (100); HRMS calcd. for $C_{14}H_{19}O_4F_3$ [M^+]: 308.1235; Found: 308.1237.

4) Dibenzyl 2-(2-methyl-1-trifluoromethyl-1-propenyl)cyclopropane-1,1-dicarboxylate 2e (yq-9-159)



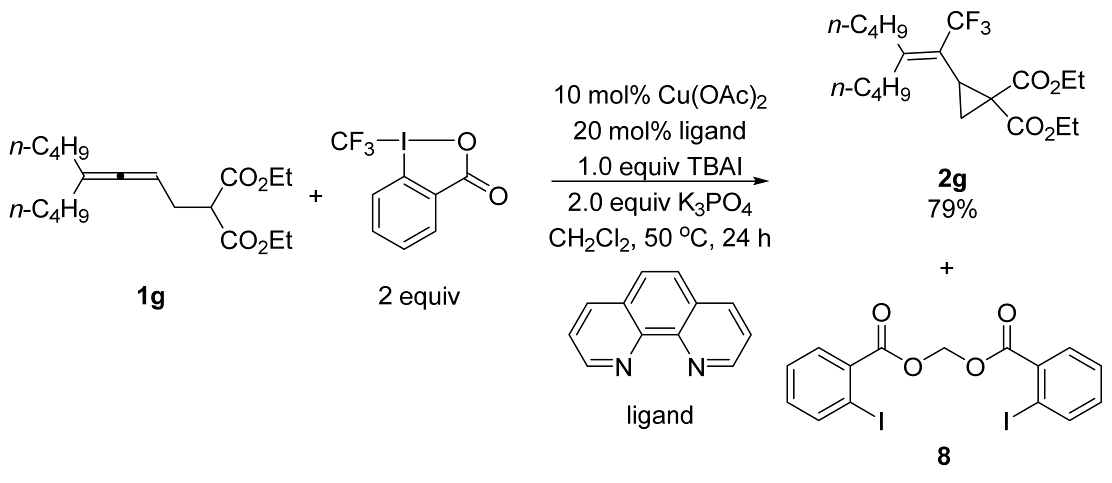
The reaction of K_3PO_4 (424.2 mg, 2.0 mmol), $Cu(OAc)_2$ (18.3 mg, 0.10 mmol), ligand (36.0 mg, 0.20 mmol), Togni's reagent II (632.3 mg, 2.0 mmol), TBAI (368.9 mg, 1.0 mmol), **1e** (364.5 mg, 1.0 mmol), and 7 mL of CH_2Cl_2 afforded **2e** (319.5 mg, 74%) as an oil (eluent: petroleum ether/ CH_2Cl_2 = 3:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.22 (m, 10 H, ArH), 5.28-5.01 (m, 4 H, 2×OCH_2), 2.65 (t, J = 9.2 Hz, 1 H, =CCH), 2.08 (dd, J_1 = 7.8 Hz, J_2 = 5.4 Hz, 1 H, one proton of CH_2), 1.82-1.65 (m, 7 H, 2×CH_3 and one proton of CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.1, 166.7, 148.7 (q, J = 3.0 Hz), 135.4, 135.2, 128.5, 128.4, 128.3, 128.2, 128.1, 127.8, 124.1 (q, J = 273.8 Hz), 118.3 (q, J = 28.7 Hz), 67.3, 67.2, 35.3, 27.7 (q, J = 2.4 Hz), 23.0, 21.6; ^{19}F NMR (282 MHz, $CDCl_3$) δ -56.6 (s, 3 F); IR (neat, cm^{-1}) 1727, 1654, 1455, 1380, 1311, 1278, 1208, 1111; MS (EI) *m/z* (%) 432 (M^+, 0.06), 91 (100); Anal. Calcd. for $C_{24}H_{23}O_4F_3$: C, 66.66; H, 5.36; Found: C, 66.61; H, 5.54.

5) Diethyl 2-(2-ethyl-1-trifluoromethyl-1-butenyl)cyclopropane-1,1-dicarboxylate 2f (yq-10-84)



The reaction of K_3PO_4 (424.0 mg, 2.0 mmol), $Cu(OAc)_2$ (18.1 mg, 0.10 mmol), ligand (36.1 mg, 0.20 mmol), Togni's reagent II (632.1 mg, 2.0 mmol), TBAI (369.2 mg, 1.0 mmol), **1f** (268.9 mg, 1.0 mmol), and 7 mL of CH_2Cl_2 afforded **2f** (235.2 mg, 70%) as an oil (eluent: petroleum ether/ CH_2Cl_2 = 3:1): ^{1}H NMR (300 MHz, $CDCl_3$) ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.26-4.08 (m, 2 H, OCH_2), 4.08-3.96 (m, 2 H, OCH_2), 2.53 (t, J = 9.3 Hz, 1 H, =CCH), 2.47-2.25 (m, 2 H, CH_2), 2.20-2.03 (m, 2 H, CH_2), 1.99 (ddq, J_1 = 8.6 Hz, J_2 = 4.6 Hz, J_3 = 1.2 Hz, 1 H, one proton of CH_2), 1.61 (dd, J_1 = 9.9 Hz, J_2 = 5.4 Hz, 1 H, one proton of CH_2), 1.22 (t, J = 7.2 Hz, 3 H, CH_3), 1.17 (t, J = 7.1 Hz, 3 H, CH_3), 0.99 (t, J = 7.5 Hz, 3 H, CH_3), 0.94 (t, J = 7.7 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.3, 166.7, 159.1 (q, J = 2.8 Hz), 124.2 (q, J = 274.5 Hz), 117.8 (q, J = 28.3 Hz), 61.5, 61.2, 35.4, 26.5 (q, J = 2.9 Hz), 25.8, 25.2 (q, J = 2.5 Hz), 21.0 (q, J = 2.5 Hz), 13.8, 13.7, 12.9, 11.6; ^{19}F NMR (282 MHz, $CDCl_3$) δ -56.1 (s, 3 F); IR (neat, cm^{-1}) 1728, 1373, 1319, 1212, 1112, 1024; MS (EI) *m/z* (%) 336 (M^+, 2.88), 189 (100); HRMS calcd. for $C_{16}H_{23}O_4F_3$ [M^+]: 336.1548; Found: 336.1549.

6) Diethyl 2-(2-butyl-1-trifluoromethyl-1-hexenyl)cyclopropane-1,1-dicarboxylate 2f and methane-1,1-diyl bis(2-iodobenzoate) 4 (yq-10-68)



74%

The reaction of K_3PO_4 (424.7 mg, 2.0 mmol), $Cu(OAc)_2$ (18.2 mg, 0.10 mmol), ligand (36.1 mg, 0.20 mmol), Togni's reagent II (632.3 mg, 2.0 mmol), TBAI (369.7 mg, 1.0 mmol), **1g** (312.5 mg, 1.0 mmol), and 7 mL of CH_2Cl_2 afforded **2g** (300.4 mg, 79%) and **8** (374.9 mg, 74%) (eluent: petroleum ether/ ethyl acetate = 50:1).

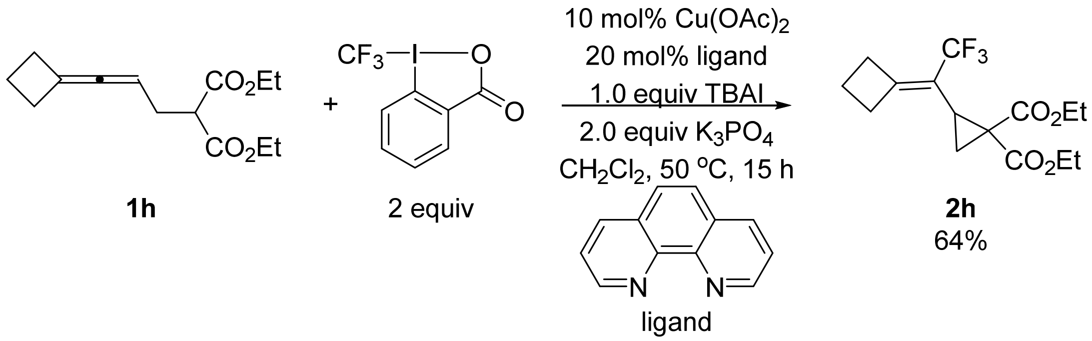
2g: oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.30-4.14 (m, 2 H, OCH_2), 4.14-4.00 (m, 2 H, OCH_2), 2.57 (t, J = 9.2 Hz, 1 H, =CCH), 2.50-2.27 (m, 2 H, CH_2), 2.17-2.00 (m, 3 H, CH_2 and one proton of CH_2), 1.65 (dd, J_1 = 9.8 Hz, J_2 = 5.3 Hz, 1 H, one proton of CH_2), 1.50-1.15 (m, 14 H, 7×CH_2), 0.91 (t, J = 6.6 Hz, CH_3), 0.88 (t, J = 7.2 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.4, 166.7, 157.2 (q, J = 3.0 Hz), 124.3 (q, J = 274.5 Hz), 118.1 (q, J = 28.1 Hz), 61.5, 61.2, 35.6, 33.4, 32.5 (q, J = 2.1 Hz), 30.9, 29.6, 26.8 (d, J = 3.2 Hz), 22.9, 22.8, 21.1, 13.9, 13.7, 13.6; ^{19}F NMR (282 MHz, $CDCl_3$): δ -55.8 (s, 3 F); IR (neat, cm^{-1}) 1728, 1466, 1372, 1318, 1207, 1109, 1024; MS (EI) *m/z* (%) 392 (M^+, 1.90), 57 (100); HRMS calcd. for $C_{20}H_{31}O_4F_3$ [M^+]: 392.2174; Found: 392.2176.

8:[4] solid; m.p. 71-72 °C (diethyl ether/ hexane) (lit.[4] 72-74 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, J = 7.8 Hz, 2 H, ArH), 7.93 (d, J = 7.8 Hz, 2 H, ArH), 7.42 (t, J = 7.5 Hz, 2 H, ArH), 7.19 (t, J = 7.7 Hz, 2 H, ArH), 6.24 (s, 2 H, OCH_2O); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.7, 141.7, 133.4, 133.0, 131.7, 128.0, 94.8, 80.4; IR (neat, cm^{-1}) 1744, 1581, 1425, 1231, 1153, 1064, 1037; MS (EI) *m/z* (%) 508 (M^+, 2.55), 231 (100).

Crystal data for compound **8**: $C_{15}H_{10}I_2O_4$, *MW* = 508.03, Monoclinic, space group

P2(1)/c, final *R* indices [$I > 2\sigma(I)$], $R1 = 0.0835$, $wR2 = 0.1766$, *R* indices (all data) $R1 = 0.1052$, $wR2 = 0.1859$, $a = 14.884$ (2) Å, $b = 4.3831$ (6) Å, $c = 27.390$ (3) Å, $\alpha = 90^{o}$, $\beta = 117.921(6)^{o}$, $\gamma = 90^{o}$, V = 1578.9(3) Å^3, $T = 296(2)$ K, $Z = 4$, reflections collected/unique 19434 / 3976 ($R_{int} = 0.0824$), number of observations [$> 2\sigma(I)$] 2985, parameters: 190. CCDC 1012501.

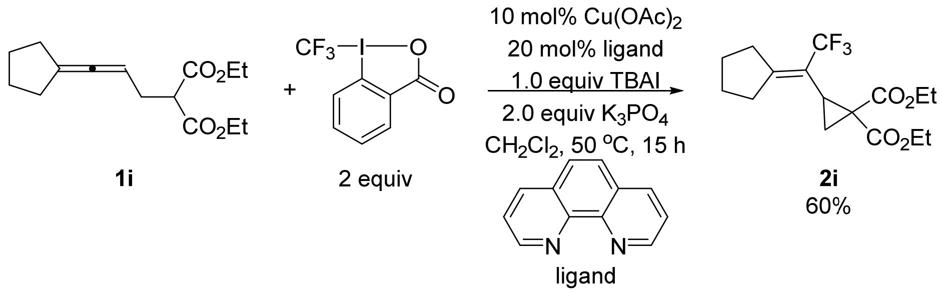
7) Diethyl 2-(2,2-trimethylene-1-trifluoromethylvinyl)cyclopropane-1,1-dicarbo-xylate 2h (yq-9-135)



The reaction of K_3PO_4 (424.3 mg, 2.0 mmol), $Cu(OAc)_2$ (18.1 mg, 0.10 mmol), ligand (36.4 mg, 0.20 mmol), Togni's reagent II (632.1 mg, 2.0 mmol), TBAI (369.1 mg, 1.0 mmol), **1h** (252.3 mg, 1.0 mmol), and 7 mL of CH_2Cl_2 afforded **2h** (206.4 mg, 64%) as an oil (purified by chromatography for twice: first round, petroleum ether/ CH_2Cl_2 = 3:1, second round: petroleum ether/ ethyl acetate = 30:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.26-4.03 (m, 4 H, 2×OCH_2), 3.04-2.72 (m, 4 H, 2×CH_2C=), 2.47 (t, J = 8.9 Hz, 1 H, =CCH), 2.10-1.88 (m, 3 H, CH_2 and one proton of CH_2), 1.47 (dd, J_1 = 9.5 Hz, J_1 = 5.3 Hz, 1 H, one proton of CH_2), 1.22 (t, J = 7.2 Hz, 3 H, CH_3), 1.20 (t, J = 6.9 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 166.9, 156.3 (q, J = 4.4 Hz), 124.0 (q, J = 273.0 Hz), 114.6 (q, J = 29.8 Hz), 61.6, 61.4, 34.7, 31.8, 30.9, 25.8 (q, J = 2.0 Hz), 18.5, 17.0 (q, J = 1.1 Hz), 13.93, 13.87; ^{19}F NMR (282 MHz, $CDCl_3$) δ -61.8 (s, 3 F); IR (neat, cm^{-1}) 2987, 1724, 1372, 1317, 1281, 1211, 1175, 1107, 1024; MS (EI) *m/z* (%) 320 (M^+, 11.73), 173 (100); HRMS calcd. for $C_{15}H_{19}O_4F_3$ [M^+]: 320.1235; Found: 320.1238.

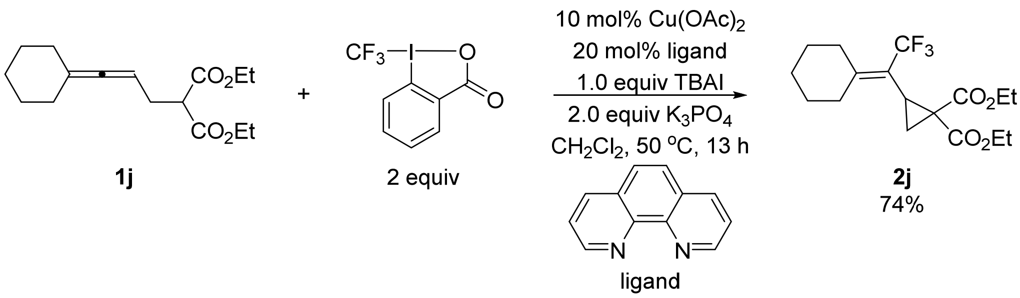
8) Diethyl 2-(2,2-tetramethylene-1-trifluoromethylvinyl)cyclopropane-1,1-

dicarboxylate 2h (yq-9-115)



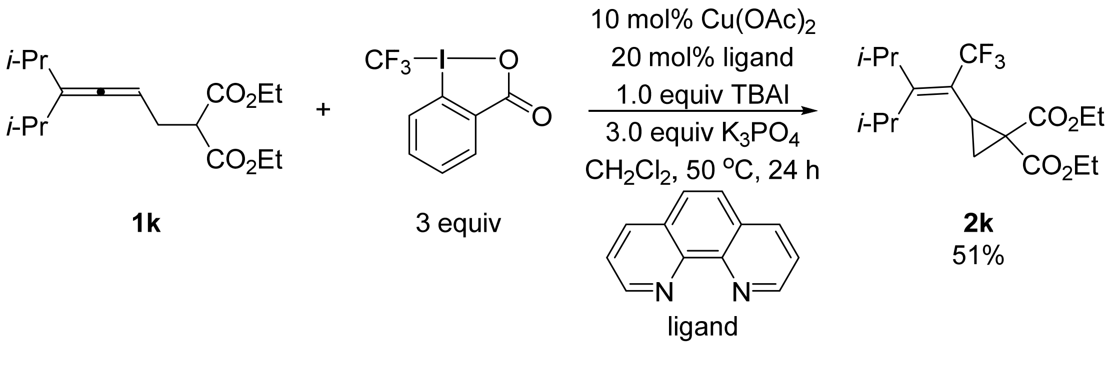
The reaction of K_3PO_4 (424.5 mg, 2.0 mmol), $Cu(OAc)_2$ (18.4 mg, 0.10 mmol), ligand (36.2 mg, 0.20 mmol), Togni's reagent II (631.3 mg, 2.0 mmol), TBAI (370.5 mg, 1.0 mmol), **1i** (265.4 mg, 1.0 mmol), and 7 mL of CH_2Cl_2 afforded **2i** (200.8 mg, 60%) as an oil (purified by chromatography for twice: first round, petroleum ether/ CH_2Cl_2 = 3:1, second round: petroleum ether/ ethyl acetate = 30:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.29-4.15 (m, 2 H, OCH_2), 4.15-4.01 (m, 2 H, OCH_2), 2.64-2.29 (m, 5 H, 2×CH_2 and =CCH), 2.09-2.02 (m, 1 H, one proton of CH_2), 1.76-1.54 (m, 5 H, 2×CH_2 and one proton of CH_2), 1.26 (t, J = 7.2 Hz, 3 H, CH_3), 1.18 (t, J = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6, 166.9, 159.8 (q, J = 3.4 Hz), 124.1 (q, J = 272.9 Hz), 114.5 (q, J = 29.6 Hz), 61.6, 61.3, 35.0, 33.5, 32.1 (q, J = 2.1 Hz), 27.8 (q, J = 2.2 Hz), 26.6, 25.4, 20.2, 14.0, 13.9; ^{19}F NMR (282 MHz, $CDCl_3$) δ -59.4 (s, 3 F); IR (neat, cm^{-1}) 2984, 2901, 1725, 1374, 1320, 1212, 1105, 1026; MS (EI) m/z (%) 334 (M^+, 1.98), 187 (100); HRMS calcd. for $C_{16}H_{21}O_4F_3$ [M^+]: 334.1392; Found: 334.1391.

9) Diethyl 2-(2,2-pentamethylene-1-trifluoromethylvinyl)cyclopropane-1,1-dicarboxylate 2j (yq-9-155)



The reaction of K_3PO_4 (424.7 mg, 2.0 mmol), $Cu(OAc)_2$ (18.1 mg, 0.10 mmol), ligand (36.0 mg, 0.20 mmol), Togni's reagent II (632.3 mg, 2.0 mmol), TBAI (369.1 mg, 1.0 mmol), **1j** (279.7 mg, 1.0 mmol), and 7 mL of CH_2Cl_2 afforded **2j** (258.0 mg, 74%) as an oil (eluent: petroleum ether/ CH_2Cl_2 = 3:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.27-3.96 (m, 4 H, 2×OCH_2), 2.55 (t , J = 9.2 Hz, 1 H, =CCH), 2.50-2.35 (m, 2 H, CH_2), 2.24-2.07 (m, 2 H, CH_2), 1.96-1.90 (m, 1 H, one proton of CH_2), 1.71-1.40 (m, 7 H, 3×CH_2 and one proton of CH_2), 1.23 (t, J = 7.2 Hz, 3 H, CH_3), 1.18 (t, J = 7.5 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 166.9, 155.9 (q, J = 2.7 Hz), 124.1 (q, J = 271.7 Hz), 116.0 (q, J = 28.2 Hz), 61.5, 61.2, 35.3, 32.5, 32.2 (q, J = 2.6 Hz), 27.9, 27.8, 26.5 (q, J = 2.3 Hz), 26.0, 21.6, 13.8, 13.7; ^{19}F NMR (282 MHz, $CDCl_3$) δ -55.2 (s, 3 F); IR (neat, cm^{-1}) 2936, 2858, 1726, 1646, 1448, 1371, 1316, 1207, 1109, 1023; MS (EI) *m/z* (%) 348 (M^+, 2.24), 159 (100); HRMS calcd. for $C_{17}H_{23}O_4F_3$ [M^+]: 348.1548; Found: 338.1550.

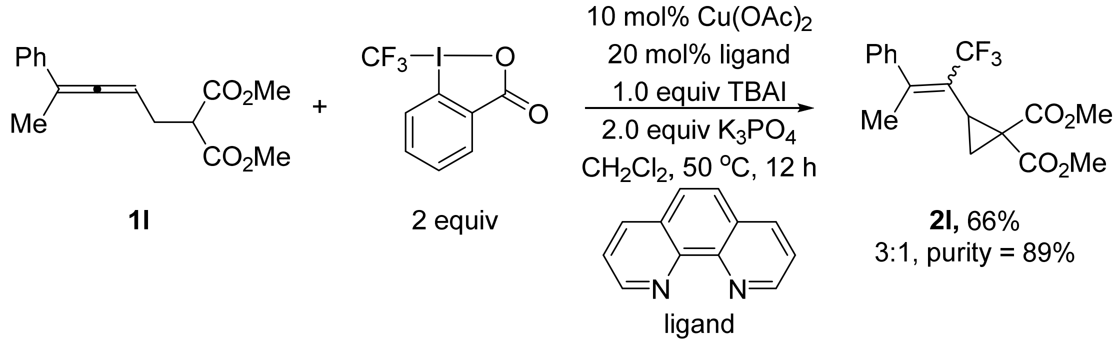
10) Diethyl 2-(2-isopropyl-3-methyl-1-trifluoromethyl-1-butenyl)cyclopropane-1,1-dicarboxylate 2k (yq-10-197)



The reaction of K_3PO_4 (636.1 mg, 3.0 mmol), $Cu(OAc)_2$ (18.2 mg, 0.10 mmol), ligand (36.1 mg, 0.20 mmol), Togni's reagent II (948.1 mg, 3.0 mmol), TBAI (369.2 mg, 1.0 mmol), **1k** (296.2 mg, 1.0 mmol), and 7 mL of CH_2Cl_2 afforded **2k** (184.9 mg, 51%) as an oil (eluent: petroleum ether/ CH_2Cl_2 = 3:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.32-4.01 (m, 4 H, 2×OCH_2), 3.18 (quint, J = 7.0 Hz, 1 H, MeCHMe), 2.96 (quint, J = 7.0 Hz, 1 H, MeCHMe), 2.57 (t , J = 9.3 Hz, 1 H, =CCH), 2.08 (ddq, J_1 = 8.7Hz, J_2 = 4.7 Hz, J_3 = 1.2 Hz, 1 H, one proton of CH_2), 1.68 (dd, J_1 = 9.8 Hz, J_2 = 5.4 Hz, 1 H, one proton of CH_2), 1.27 (t, J = 6.2 Hz, 3 H, CH_3), 1.23 (t, J = 6.0 Hz, 3 H, CH_3), 1.15-1.07 (m, 12 H, 4×CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6, 166.9, 165.5 (q, J

= 3.0 Hz), 124.2 (q, J = 272.1 Hz), 118.0 (q, J = 27.1 Hz), 61.6, 61.2, 35.8, 31.9, 30.3, 27.7 (q, J = 2.9 Hz), 21.8 (q, J = 1.7 Hz), 21.7 (q, J = 2.1 Hz), 21.1, 20.8, 20.6, 14.0, 13.8; ^{19}F NMR (282 MHz, $CDCl_3$) δ -54.3 (s, 3 F); IR (neat, cm^{-1}): 1727, 1467, 1371, 1317, 1214, 1105, 1024; MS (EI) *m/z* (%) 364 (M^+, 1.79), 160 (100); HRMS calcd. for $C_{18}H_{27}O_4F_3$ [M^+]: 364.1861; Found: 364.1863.

11) Dimethyl 2-(3-phenyl-1-trifluoromethyl-1-propanyl)cyclopropane-1,1-dicarboxylate (tangy-5-151)



The reaction of K_3PO_4 (425.0 mg, 2.0 mmol), $Cu(OAc)_2$ (18.3 mg, 0.10 mmol), ligand (36.2 mg, 0.20 mmol), Togni's II (630.9 mg, 2.0 mmol), TBAI (370.1 mg, 1.0 mmol), **1l** (276.1 mg, 1.0 mmol), and 7 mL of CH_2Cl_2 afforded **2l** (256.7 mg, 66%, 3 : 1, purity = 89%) as an oil (eluent: petroleum ether/ CH_2Cl_2 = 2 : 1, then petroleum ether : CH_2Cl_2 : ethyl acetate = 200 : 100 : 1). The product was a mixture of two stereoisomers.

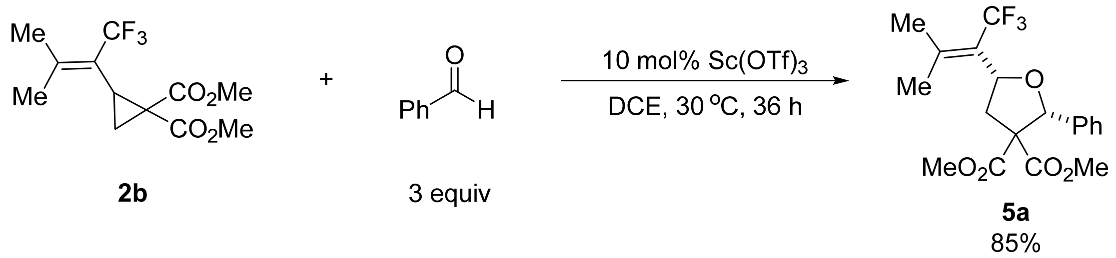
Major stereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.26 (m, 4 H, ArH), 7.20-7.14 (m, 1 H, ArH), 3.70 (s, 3 H, OCH_3), 3.68 (s, 3 H, OCH_3), 2.67 (t, J = 9.0 Hz, 1 H, CH=), 2.22 (t, J = 2.0 Hz, 3 H, CH_3), 1.19 (dd, J_1 = 8.8 Hz, J_2 = 5.2 Hz, 1 H, one proton of CH_2), 1.03 (dd, J_1 = 8.8 Hz, J_2 = 5.6 Hz, 1 H, one proton of CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.2 (s, 3 F); LC-MS (LC conditions: column: Agilent Eclipse × DF (4.6 × 250 mm, 5μm), eluent: CH_3CN : H_2O = 1 : 1, detector: 220 nm) (ESI) *m/z* 343 ($[M+H]^+$) (retention time: 29.7 min).

These signals are discernable for the minor stereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 3 H, OCH_3), 3.76 (s, 3 H, OCH_3), 2.82 (t, J = 9.4 Hz, 1 H, CH=), 2.19-2.16 (m, 3 H, CH_3), 1.76 (dd, J_1 = 10.0 Hz, J_2 = 5.2 Hz, 1 H, one proton of CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ -55.9 (s, 3 F); LC-MS (LC conditions: column: Agilent Eclipse × DF (4.6 × 250 mm, 5μm), eluent: CH_3CN : H_2O = 1 : 1, detector: 220 nm) (ESI) *m/z* 343 ($[M+H]^+$) (retention time: 10.0 min).

IR for the mixture of two isomers (neat, cm^{-1}): 2956, 2854, 1727, 1643, 1492, 1438, 1374, 1313, 1284, 1214, 1170, 1112, 1031, 1009.

4. Reactions of cyclopropane-1,1-dicarboxylate 2 with other compounds

1) Synthsis of dimethyl 2-phenyl-5-(2-methyl-1-trifluoromethyl-1-propenyl)-(*2H*)dihydrofuran-3,3-dicarboxylate 5a (yq-11-32)



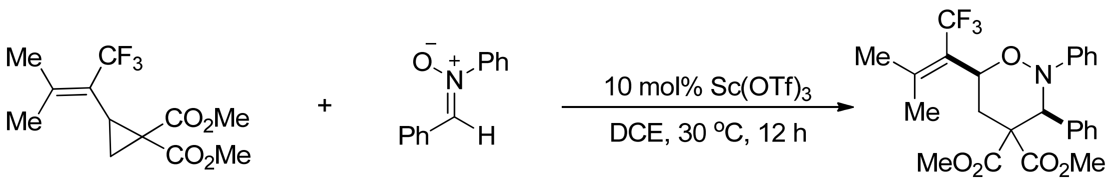
Typical Procedure 5: To a flame-dried Schlenk tube were added $Sc(OTf)_3$ (24.7 mg, 0.05 mmol), **2b** (136.9 mg, 0.49 mmol), 3 mL of DCE, and benzaldehyde (160.1 mg, 1.5 mmol), and 2 mL of DCE under argon sequentially. The resulting mixture was stirred at 30 °C for 36 hours. The crude reaction mixture was filtrated through a short pad of silica gel eluted with diethyl ether (50 mL). After evaporation, the residue was analyzed by NMR measurement, and then purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate =15:1) to afford **5a** (160.5 mg, 85%) as a solid: m.p.: 89-90 °C (diethyl ether/hexane): ^{1}H NMR (300 MHz, $CDCl_3$) 7.45-7.38 (m, 2 H, Ar-H), 7.32-7.20 (m, 3 H, ArH), 5.62 (s, 1 H, CHAr), 4.75 (dd, J_1 = 11.6 Hz, J_2 = 6.2 Hz, 1 H, one proton of CH_2), 3.81 (s, 3 H, CH_3), 3.16 (t, J = 12.5 Hz, 1 H, =CCH), 3.03 (s, 3 H, CH_3), 2.46 (dd, J_1 = 13.5 Hz, J_2 = 5.7 Hz, 1 H, one proton of CH_2), 2.09 (q, J = 1.8 Hz, 3 H, =CCH_3), 2.07 (q, J = 2.7 Hz, 3 H, =CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 169.0, 147.8 (q, J = 3.4 Hz), 137.0, 128.0, 127.8, 126.9, 124.4 (q, J =

274.8 Hz), 121.4 (q, J = 26.8 Hz), 84.3 (q, J = 2.9 Hz), 75.2, 65.8, 52.9 (q, J = 3.9 Hz), 52.1, 39.2, 22.9 (q, J = 2.7 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ -56.3 (s, 3 F); IR (neat, cm^{-1}): 2968, 2922, 1725, 1453, 1435, 1374, 1280, 1227, 1203, 1140, 1093, 1053; MS (EI) *m/z* (%) 386 (M^+, 6.89), 105 (100); Anal. Calcd. for $C_{19}H_{21}F_3O_5$: C, 59.06; H, 5.48; Found: C, 59.01; H, 5.45.

Crystal data for compound **5a**: $C_{19}H_{21}F_3O_5$, *MW* = 386.36, Triclinic, space group P-1, final R indices [$I > 2\sigma(I)$], $R1$ = 0.0615, $wR2$ = 0.1764, R indices (all data) $R1$ = 0.0740, $wR2$ = 0.1907, a = 8.5770 (4) Å, b = 11.2530 (5) Å, c = 11.3999 (5) Å, α = 83.2610°, β = 69.7150°, γ = 68.4110°, V = 959.58(7) Å^3, T = 173(2) K, Z = 2, reflections collected/unique 11222 / 3370 (Rint = 0.0209), number of observations [> $2\sigma(I)$] 2628, parameters: 244. CCDC 1012706.

The following compounds were prepared according to **Typical Procedure 5**.

2) Dimethyl 2,3-diphenyl-6-(1-trifluoromethyl-2-methyl-1-propenyl)-1,2-oxazinane-4,4-dicarboxylate 6a (yq-11-35)

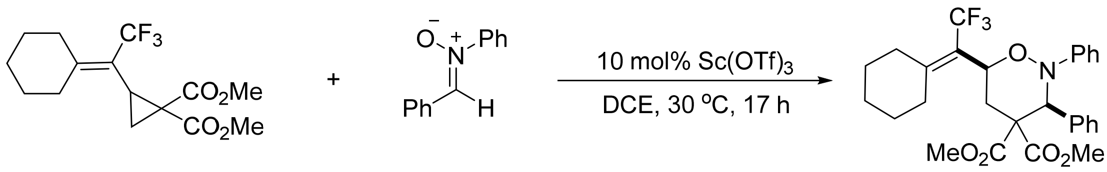


2b 2 equiv **6a** 81%

The reaction of $Sc(OTf)_3$ (24.7 mg, 0.05 mmol), **2b** (140.5 mg, 0.5 mmol), (*Z*)-*N*-benzylideneaniline oxide (191.2 mg, 1.0 mmol), and 5 mL of DCE afforded **6a** (192.8 mg, 81%) as a solid (eluent: petroleum ether/ ethyl acetate = 10:1): m.p.: 186-187 °C (diethyl ether/hexane): ^{1}H NMR (300 MHz, $CDCl_3$) 7.57-7.50 (m, 2 H, ArH), 7.20-7.07 (m, 5 H, ArH), 7.05-6.98 (m, 2 H, ArH), 6.78 (t, J = 7.4 Hz, 1 H, ArH), 5.77 (s, 1 H, CHAr), 4.93 (d, J = 12.3 Hz, 1 H, one proton of CH_2), 3.86 (s, 3 H, CH_3), 3.42 (s, 3 H, CH_3), 2.95 (t, J = 13.5 Hz, 1 H, OCH), 2.47 (d, J = 12.9 Hz, 1 H, one proton of CH_2), 2.01 (q, J = 2.8 Hz, 3 H, $=CCH_3$), 1.92 (q, J = 2.1 Hz, 3 H, $=CCH_3$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.1, 168.0, 148.4, 147.5 (q, J = 3.6 Hz), 134.7, 130.2, 128.5, 127.9, 127.8, 124.4 (q, J = 274.8 Hz), 123.1 (q, J = 27.9 Hz), 121.6, 115.7, 76.4, 66.0, 60.0, 53.3, 52.5, 29.1, 22.7, 22.7 (q, J = 2.9 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ -54.3 (s, 3 F); IR (neat, cm^{-1}) 1738, 1599, 1494, 1434, 1372, 1330, 1238, 1199, 1161, 1111; MS (EI) *m/z* (%) 477 (M^+, 8.79), 198 (100); Anal. Calcd. for $C_{25}H_{26}F_3O_5N$: C, 62.89; H, 5.49; N, 2.93; Found: C, 62.82; H, 5.47; N, 2.93.

Crystal data for compound **6a**: $C_{25}H_{26}F_3NO_5$, MW = 477.47, Monoclinic, space group P2(1)/c, final R indices [$I > 2\sigma(I)$], $R1$ = 0.0494, $wR2$ = 0.1183, R indices (all data) $R1$ = 0.0948, $wR2$ = 0.1463, a = 14.9433 (6) Å, b = 9.3141 (4) Å, c = 17.6377 (6) Å, α = 90°, β = 102.36°, γ = 90°, V = 2397.98(16) $Å^3$, T = 173(2) K, Z = 4, reflections collected/unique 27266 / 4219 (R_{int} = 0.0620), number of observations [> $2\sigma(I)$] 2480, parameters: 308. CCDC 1012812.

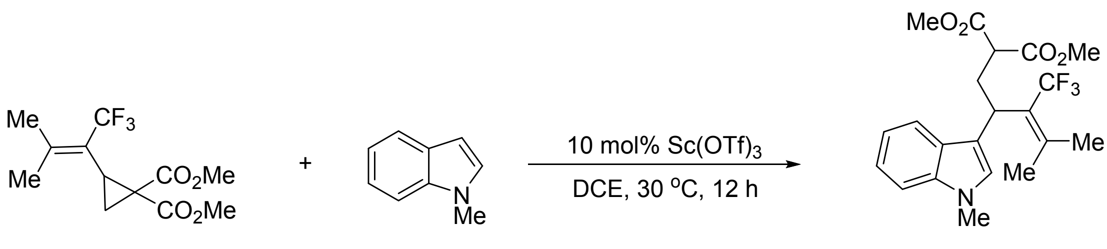
3) Dimethyl 2,3-diphenyl-6-(2,2-pentamethylene-1-trifluoromethylvinyl)-1,2-oxazinane-4,4-dicarboxylate 6b (yq-11-78)



The reaction of $Sc(OTf)_3$ (24.9 mg, 0.05 mmol), **2c** (160.0 mg, 0.5 mmol), (Z)-N-benzylideneaniline oxide (192.4 mg, 1.0 mmol), and 5 mL of DCE afforded **6b** (217.1 mg, 84%) as a solid (eluent: petroleum ether/ ethyl acetate = 20:1): m.p.:170-171 °C (diethyl ether/hexane): ^{1}H NMR (300 MHz, $CDCl_3$) 7.56-7.46 (m, 2 H, ArH), 7.22-7.10 (m, 5 H, ArH), 7.07-6.98 (m, 2 H, ArH), 6.81 (t, J = 7.2 Hz, 1 H, ArH), 5.79 (s, 1 H, CHAr), 5.00 (d, J = 12.6 Hz, 1 H, one proton of CH_2), 3.89 (s, 3 H, CH_3), 3.47 (s, 3 H, CH_3), 2.96 (t, J = 13.5 Hz, 1 H, OCH), 2.60-2.28 (m, 5 H, one proton of CH_2 and 2×CH_2), 1.85-1.56 (m, 6 H, 3×CH_2); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0, 168.0, 156.1 (q, J = 3.5 Hz), 148.3, 134.7, 130.0, 128.5, 127.9, 127.8, 124.4 (q, J = 275.6 Hz), 121.5, 120.0 (q, J = 27.6 Hz), 115.6, 75.8, 65.7, 59.9, 53.3, 52.6, 33.1 (q, J = 2.7 Hz), 32.7, 29.8, 28.7, 28.5, 26.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ -53.5

(s, 3 F); IR (neat, cm^{-1}) 1733, 1599, 1491, 1437, 1344, 1324, 1233, 1197, 1162, 1097, 1033; MS (EI) *m/z* (%) 517 (M^+, 2.13), 198 (100); Anal. Calcd. for $C_{28}H_{30}F_3O_5N$: C, 64.98; H, 5.84; N, 2.71; Found: C, 65.06; H, 5.92; N, 2.64.

4) Dimethyl 2-(4-methyl-2-(1-methyl-1*H*-indol-3-yl)-3-(trifluoromethyl) pent-3-en-1-yl)malonate 7a (yq-11-38)



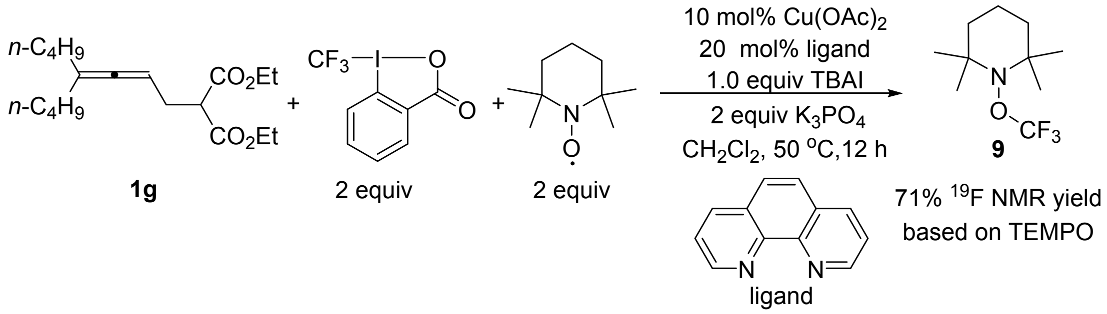
2b 2 equiv **7a** 90%

The reaction of $Sc(OTf)_3$ (25.2 mg, 0.05 mmol), **2b** (133.4 mg, 0.48 mmol), *N*-methylindole (131.3 mg, 1.0 mmol), and 5 mL of DCE afforded **7a** (176.4 mg, 90%) as a solid (eluent: petroleum ether/ ethyl acetate = 10:1): m.p.:110-111 °C (diethyl ether/hexane): ^{1}H NMR (300 MHz, $CDCl_3$) 7.43 (d, J = 8.1 Hz, 1 H, ArH), 7.27 (d, J = 8.1 Hz, 1 H, ArH), 7.23-7.15 (m, 1 H, ArH), 7.10-7.03 (m, 1 H, ArH), 6.93 (s, 1 H, =CHN), 4.37 (t, J = 8.0 Hz, 1 H, CH), 3.74 (s, 3 H, CH_3), 3.73 (s, 3 H, CH_3), 3.71 (s, 3 H, CH_3), 3.55 (t, J = 7.4 Hz, 1 H, CH), 2.80-2.68 (m, 1 H, one proton of CH_2), 2.60-2.48 (m, 1 H, one proton of CH_2), 2.03 (q, J = 2.1 Hz, 3 H, CH_3), 1.95 (q, J = 2.5 Hz, 3 H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.8, 169.7, 142.9 (q, J = 3.6 Hz), 136.7, 127.6, 126.5 (q, J = 25.0 Hz), 126.1 (q, J = 25.3 Hz), 125.2 (q, J = 276.7 Hz), 121.5, 118.9, 118.7, 113.8, 109.2, 52.54, 52.51, 49.7, 34.7, 32.7, 32.2 (q, J = 1.7 Hz), 22.6, 22.5 (q, J = 2.1 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ -53.9 (s, 3 F); IR (neat, cm^{-1}) 1736, 1458, 1437, 1375, 1315, 1274, 1242, 1200, 1168, 1097, 1016; MS (EI) *m/z* (%) 411 (M^+, 24.66), 226 (100); Anal. Calcd. for $C_{21}H_{24}F_3O_4N$: C, 61.31; H, 5.88; N, 3.40; Found: C, 61.30; H, 5.87; N, 3.38.

Crystal data for compound **7a**: $C_{21}H_{24}F_3NO_4$, *MW* = 411.41, Monoclinic, space group P2(1)/c, final R indices [$I > 2\sigma(I)$], $R1 = 0.0424$, $wR2 = 0.1036$, R indices (all data) $R1 = 0.0632$, $wR2 = 0.1171$, $a = 15.6855$ (6) Å, $b = 9.6366$ (3) Å, $c = 13.4345$ (5) Å, $\alpha = 90^o$, $\beta = 96.4^o$, $\gamma = 90^o$, $V = 2018.03(12)$ Å3, T = 173(2) K, Z = 4, reflections collected/unique 23009 / 3551 (Rint = 0.0567), number of observations [> $2\sigma(I)$] 2639, parameters: 262. CCDC 1012813.

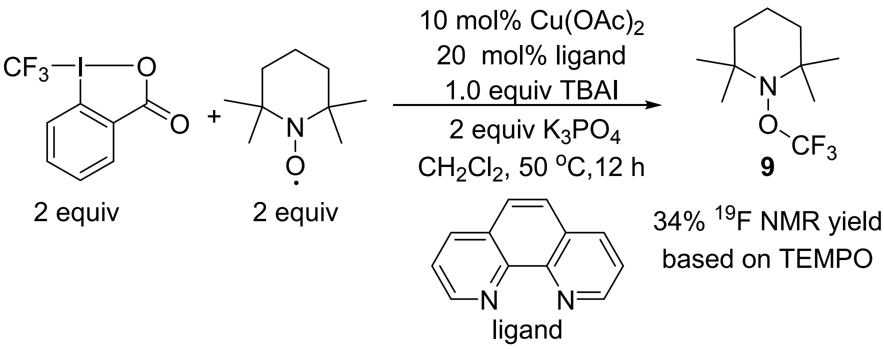
5. Mechanistic study

1) Reaction of 1f in the presence of TEMPO: Synthesis of 2,2,6,6-Tetramethyl-1-(trifluoromethoxy)piperidine 9 (yq-11-174)



To a flame-dried Schlenk tube were added K_3PO_4 (212.4 mg, 1.0 mmol), $Cu(OAc)_2$ (9.2 mg, 0.05 mmol), ligand (18.0 mg, 0.10 mmol), Togni's reagent II (316.7 mg, 1.0 mmol), TBAI (185.1 mg, 0.50 mmol), **1g** (162.1 mg, 0.5 mmol), TEMPO (156.3 mg, 1.0 mmol), and 4 mL of CH_2Cl_2 sequentially under argon. The resulting mixture was stirred at 50 ^oC for 12 h. The crude reaction mixture was filtrated through a short pad of silica gel eluted with diethyl ether (50 mL). After filtration and evaporation, the residue was analyzed by NMR measurement. ^{19}F NMR analysis of this reaction mixture showed that TEMPO-CF_3 **9**[5] was formed in 71% yield: ^1H NMR (300 MHz, $CDCl_3$) δ 1.74-1.50 (m, 5 H, 2×CH_2 and one proton of CH_2), 1.40-1.31 (m, 1 H, one proton of CH_2), 1.18 (s, 12 H, 4×CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) 123.7 (q, J = 254.1 Hz), 61.5, 40.0, 32.7 (q, J = 2.2 Hz), 20.4, 16.8; ^{19}F NMR (282 MHz, $CDCl_3$) δ -56.26 (s, 3 F).

2) Control reaction in the absence of 1g (yq-11-175)



To a flame-dried Schlenk tube were added K_3PO_4 (212.3 mg, 1.0 mmol), $Cu(OAc)_2$ (9.0 mg, 0.05 mmol), ligand (18.4 mg, 0.10 mmol), Togni's reagent II (317.0 mg, 1.0 mmol), TBAI (184.4 mg, 0.50 mmol), TEMPO (155.7 mg, 1.0 mmol), and 4 mL of CH_2Cl_2 under sequentially argon. The resulting mixture was stirred at 50 ^{o}C for 12 h. The crude reaction mixture was filtrated through a short pad of silica gel eluented with diethyl ether (50 mL). After filtration and evaporation, the residue was analyzed by NMR measurement. ^{19}F NMR analysis of this reaction mixture showed that TEMPO-CF_3 was formed in 34% yield: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.74-1.50 (m, 5 H, 2×CH_2 and one proton of CH_2), 1.43-1.32 (m, 1 H, one proton of CH_2), 1.19 (s, 12 H, 4×CH_3); ^{19}F NMR (282 MHz, $CDCl_3$) δ -56.26 (s, 3 F).

References:

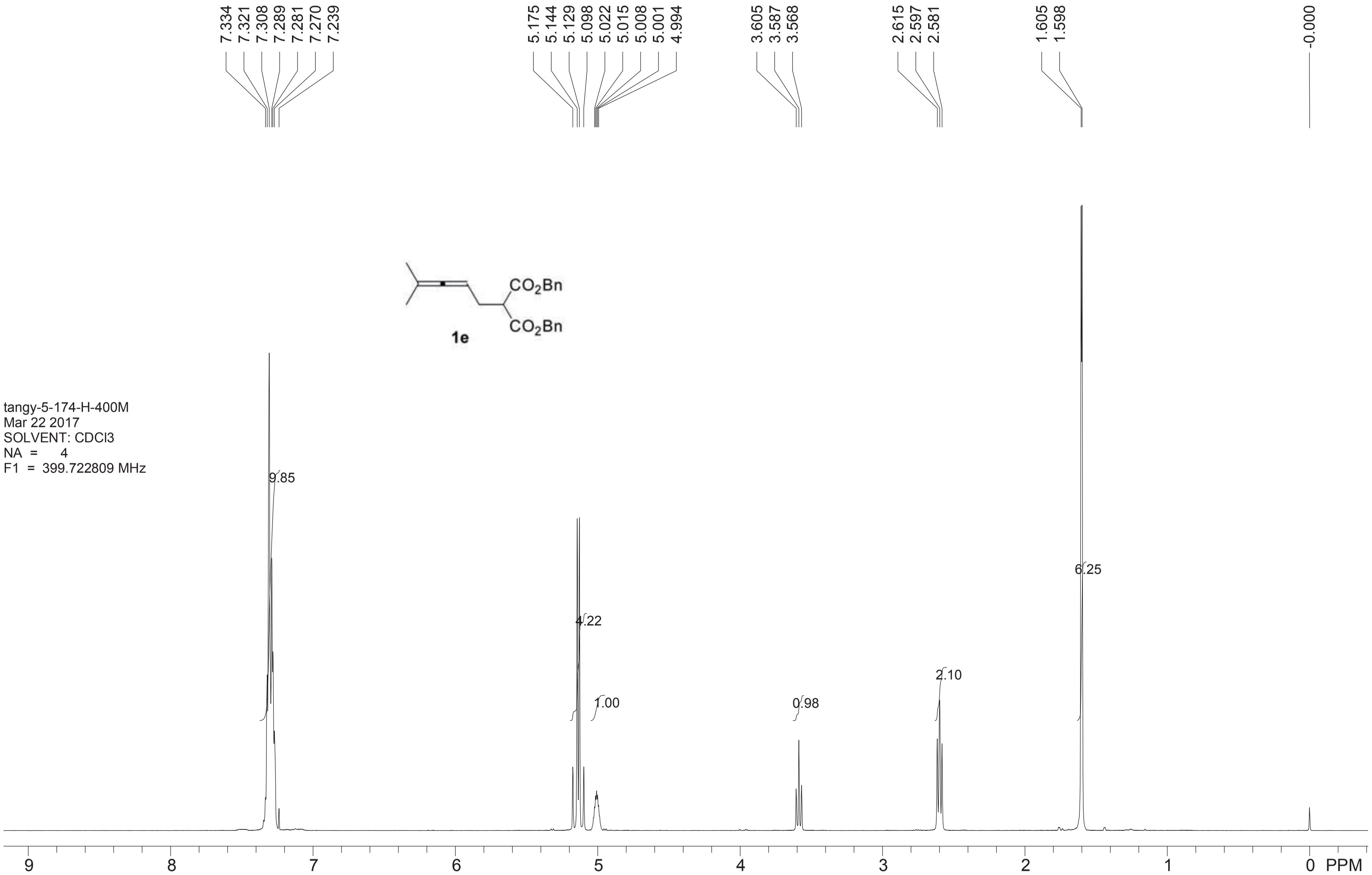
(1) Djahanbini, D.; Cazes, B.; Gore, J. *Tetrahedron* **1987**, *43*, 3441.

(2) Lu, P.; Ma, S. *Org. Lett.* **2007**, *9,* 2095.

(3) Zhang, Z.; Bender, C. F.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2007**, *129*, 14148.

(4) Zhang, Y.; H, J.; Xu, Y.; Wei, Y. *J. Chem. Res.* **2012**, *36*, 303.

(5) Yu, Q.; Ma, S. *Chem. Eur. J.* **2013**, *19*, 13304.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7.321
7.308
7.289
7.281
7.270
7.239
5.175
5.144
5.129
5.098
5.022
5.015
5.008
5.001
4.994
3.605
3.587
3.568
2.615
2.597
2.581
1.605
1.598
-0.000
CO2Bn
CO2Bn
1e
tangy-5-174-H-400M
Mar 22 2017
SOLVENT: CDCl3
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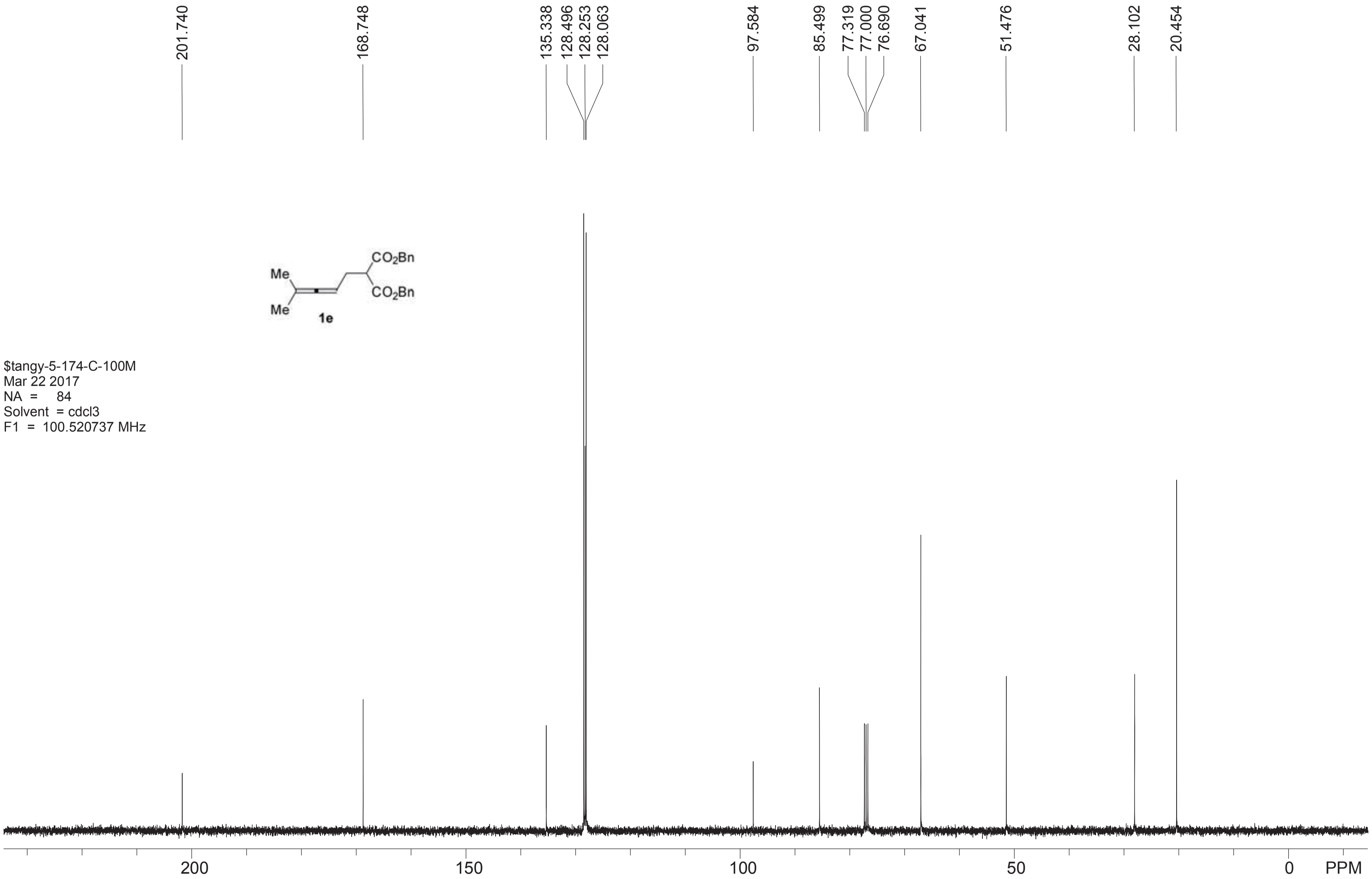
1.00
0.98
2.10
6.25
9
8
7
6
5
4
3
2
1
0 PPM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135.338
128.496
128.253
128.063
97.584
85.499
77.319
77.000
76.690
67.041
51.476
28.102
20.454
Me
Me
CO_2Bn
CO_2Bn
1e
$tangy-5-174-C-100M
Mar 22 2017
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Solvent = cdcl3
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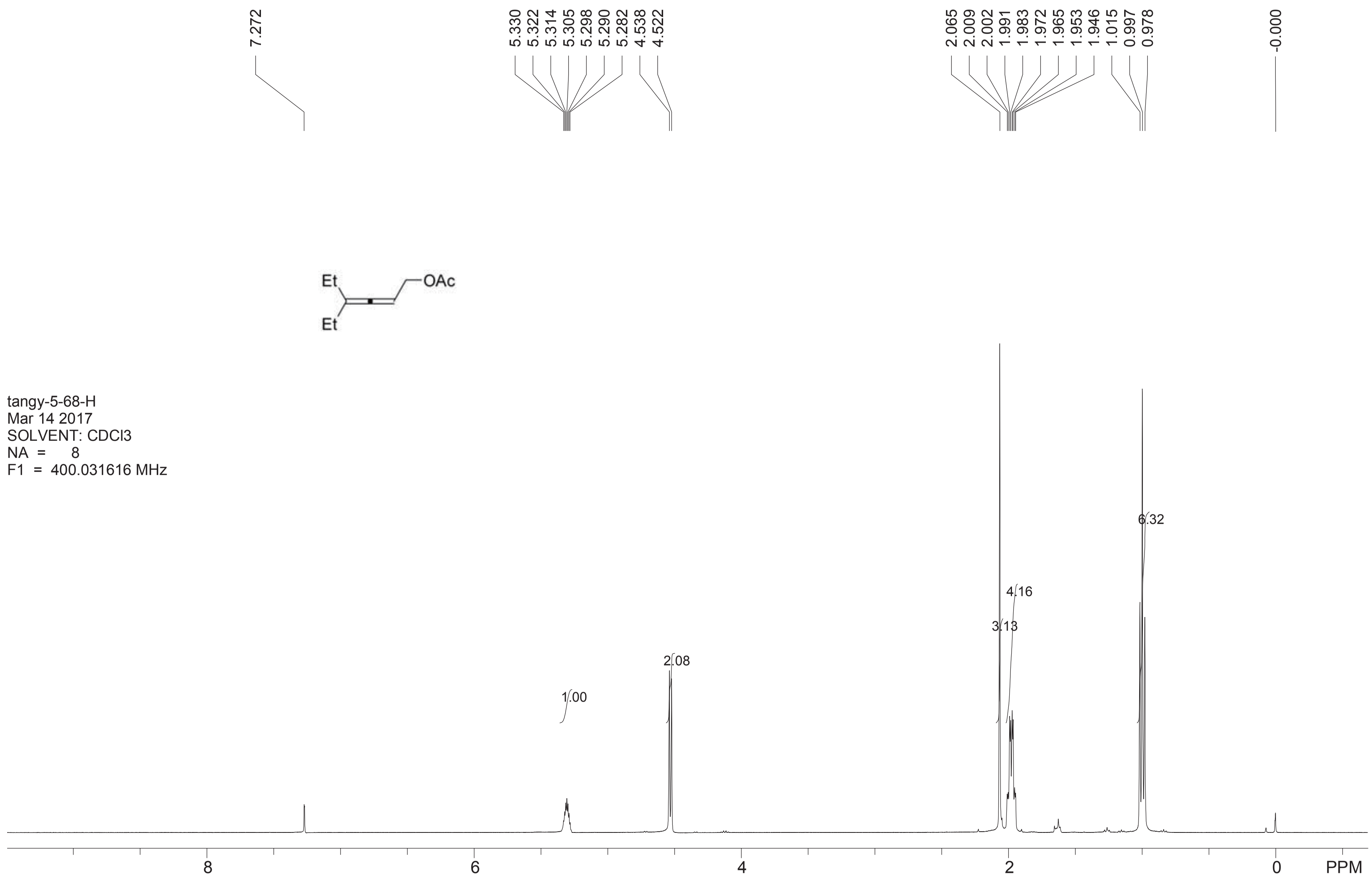
100
50
0
PPM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5.330
5.322
5.314
5.305
5.298
5.290
5.282
4.538
4.522
2.065
2.009
2.002
1.991
1.983
1.972
1.965
1.953
1.946
1.015
0.997
0.978
-0.000
Et
Et
OAc
tangy-5-68-H
Mar 14 2017
SOLVENT: CDCl3
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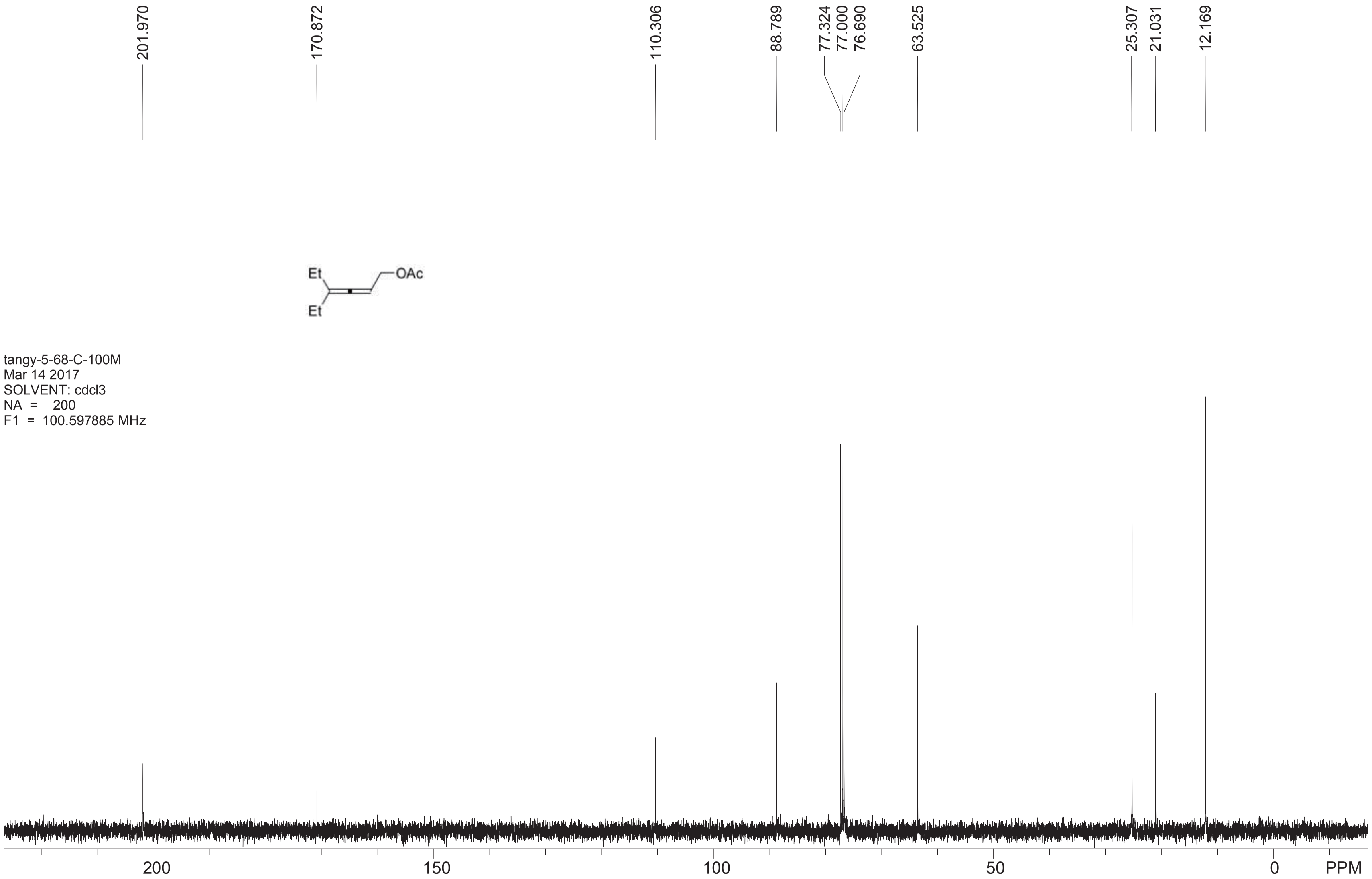
8
6
4
2
0
PPM



tangy-5-68-C-100M
Mar 14 2017
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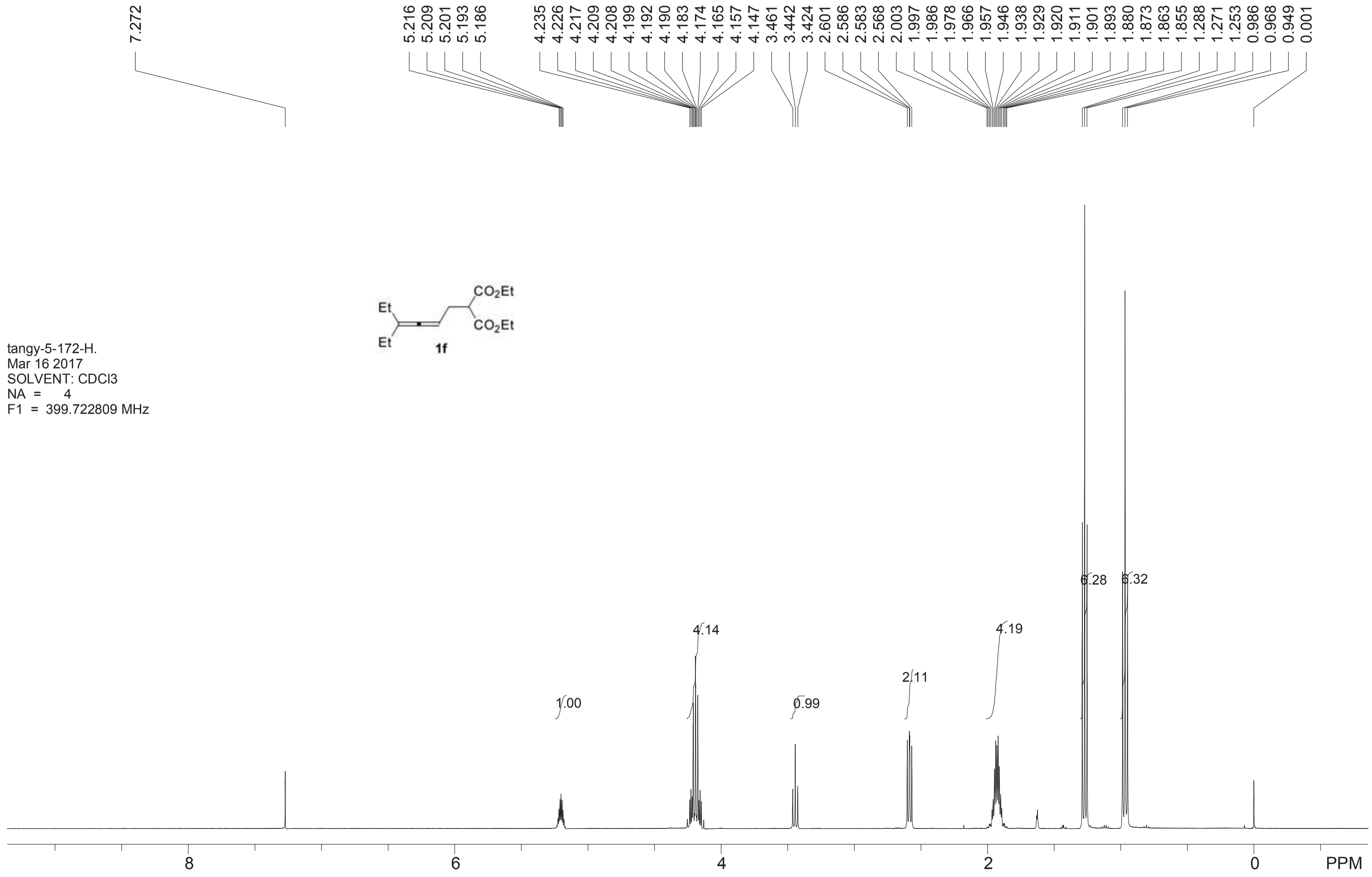
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5.209
5.201
5.193
5.186
4.235
4.226
4.217
4.209
4.208
4.199
4.192
4.190
4.183
4.174
4.165
4.157
4.147
3.461
3.442
3.424
2.601
2.586
2.583
2.568
2.003
1.997
1.986
1.978
1.966
1.957
1.946
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1.929
1.920
1.911
1.901
1.893
1.880
1.873
1.863
1.855
1.288
1.271
1.253
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0.968
0.949
0.001
tangy-5-172-H.
Mar 16 2017
SOLVENT: CDCl3
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Et
CO2Et
CO2Et
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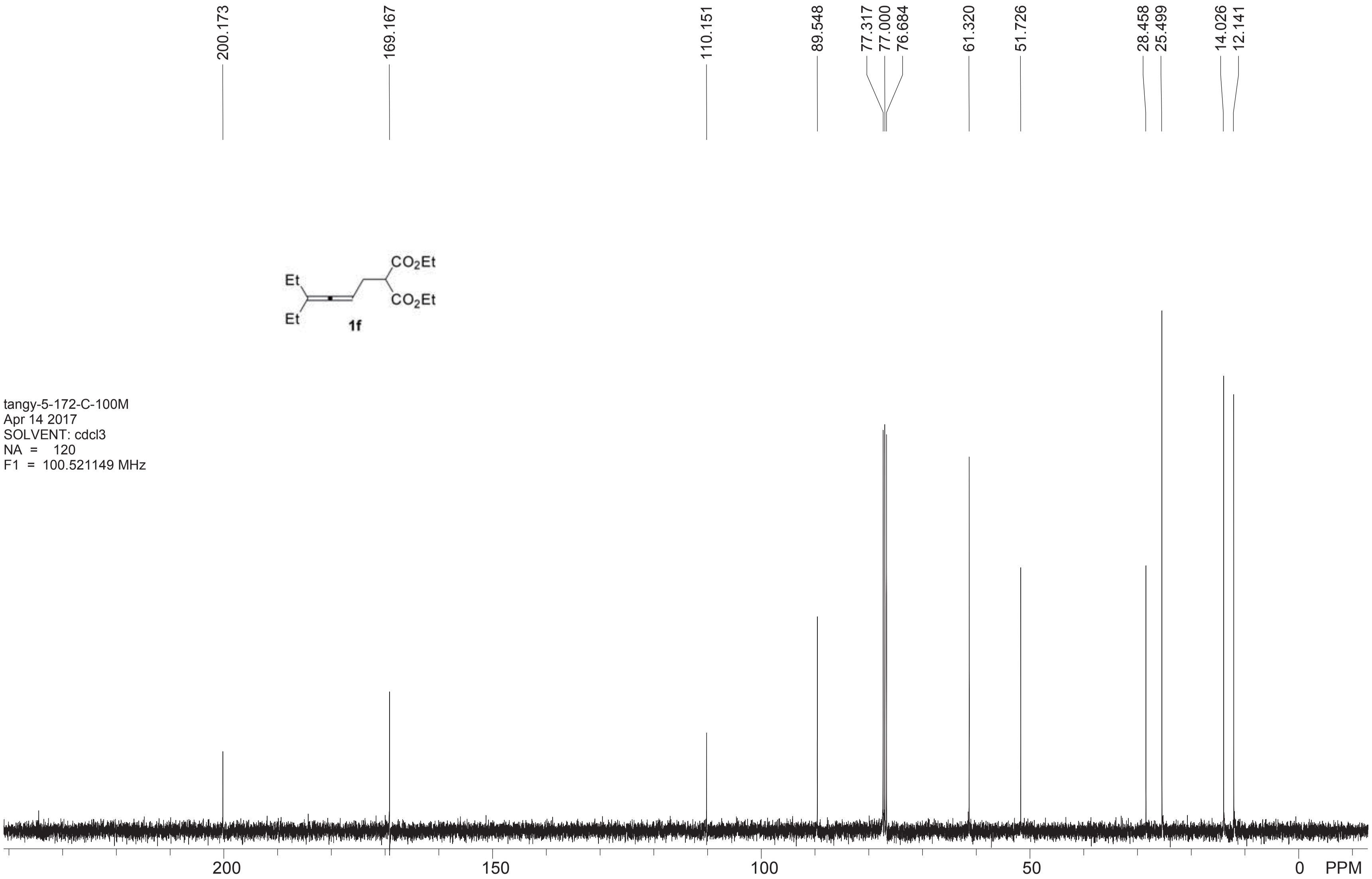
0.99
2.11
4.19
6.28
6.32
8
6
4
2
0
PPM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110.151
89.548
77.317
77.000
76.684
61.320
51.726
28.458
25.499
14.026
12.141
Et
Et
CO2Et
CO2Et
1f
tangy-5-172-C-100M
Apr 14 2017
SOLVENT: cdcl3
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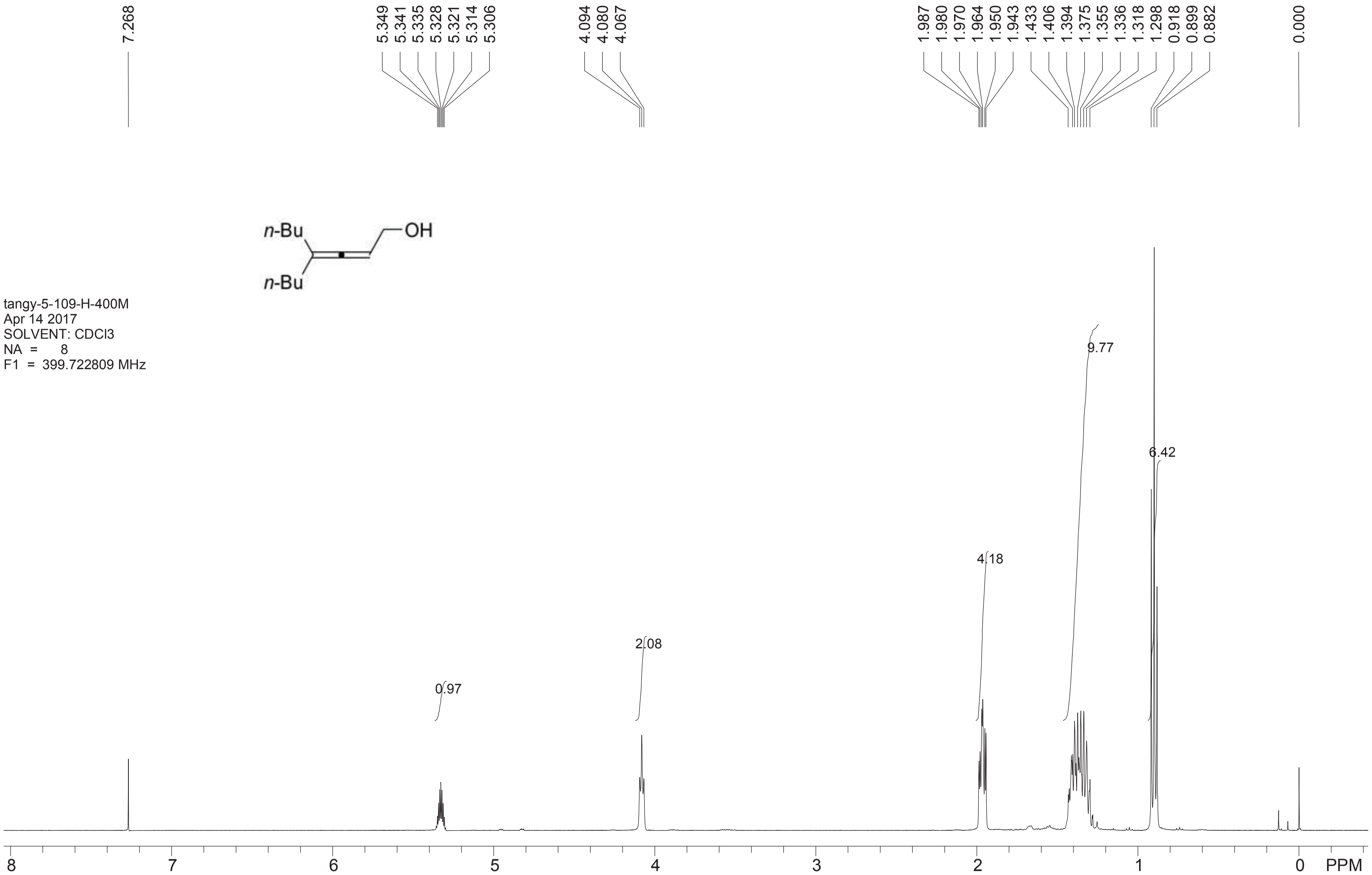
100
50
0
PPM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5.314
5.306
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4.080
4.067
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1.980
1.970
1.964
1.950
1.943
1.433
1.406
1.394
1.375
1.355
1.336
1.318
1.298
0.918
0.899
0.882
0.000
n-Bu
n-Bu
OH
tangy-5-109-H-400M
Apr 14 2017
SOLVENT: CDCl3
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F1 = 399.722809 MHz
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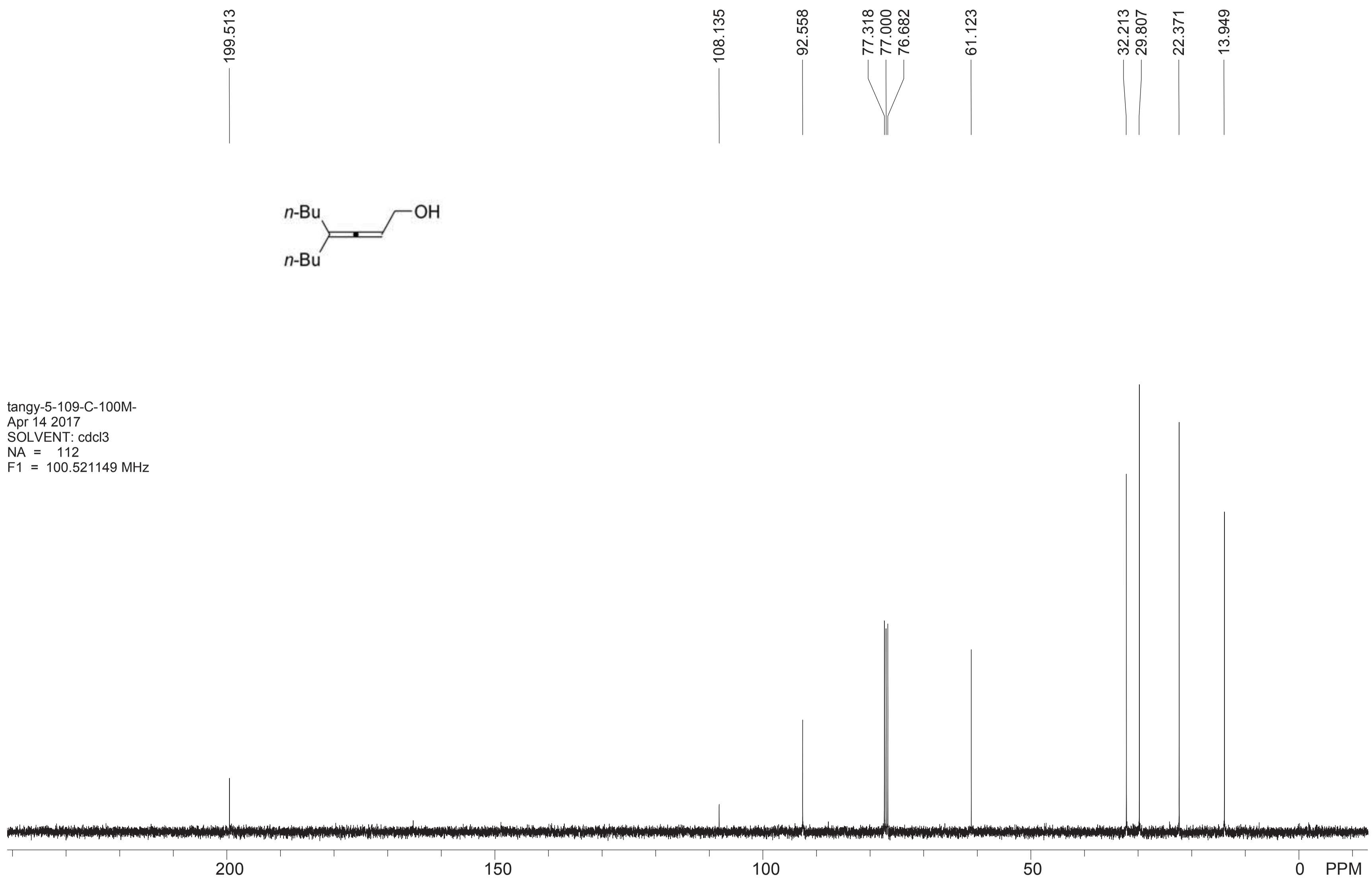
9.77
6.42
8
7
6
5
4
3
2
1
0
PPM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108.135
92.558
77.318
77.000
76.682
61.123
32.213
29.807
22.371
13.949
n-Bu
n-Bu
OH
tangy-5-109-C-100M-
Apr 14 2017
SOLVENT: cdcl3
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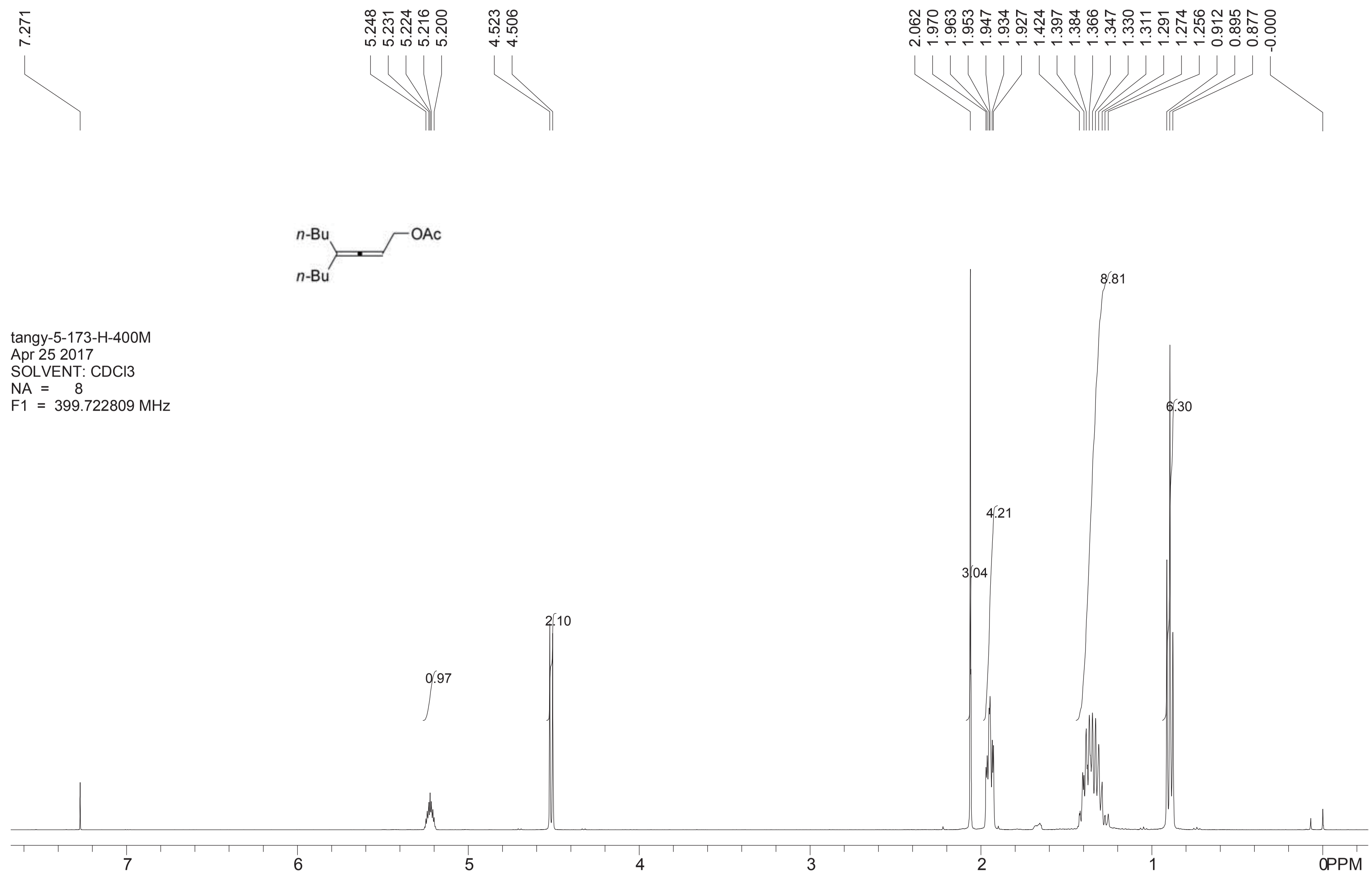
150
100
50
0
PPM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4.523
4.506
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1.963
1.953
1.947
1.934
1.927
1.424
1.397
1.384
1.366
1.347
1.330
1.311
1.291
1.274
1.256
0.912
0.895
0.877
-0.000
n-Bu
n-Bu
OAc
tangy-5-173-H-400M
Apr 25 2017
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz
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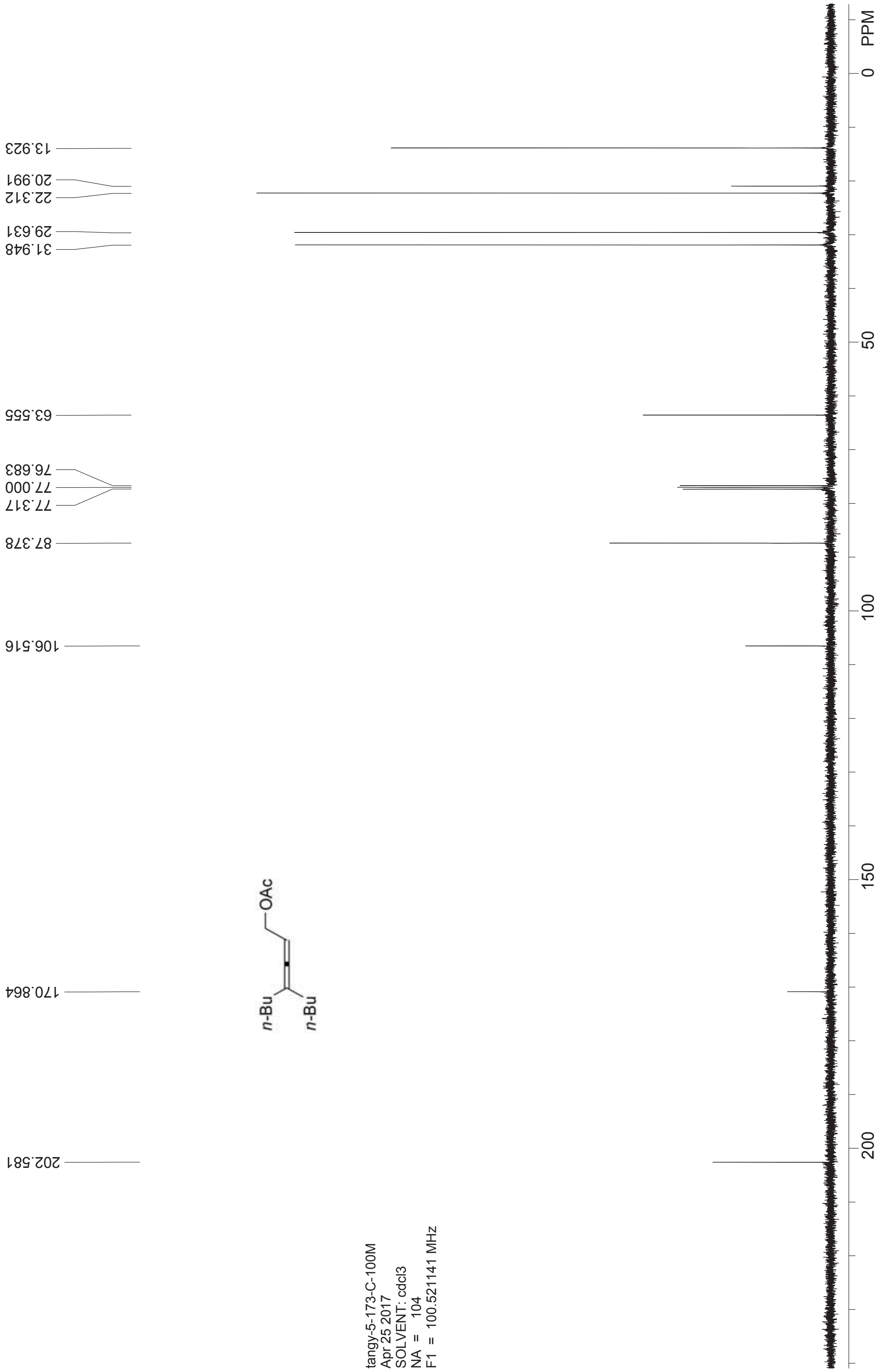
6.30
4.21
3.04
2.10
0.97
7
6
5
4
3
2
1
0PPM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202.581
OAc
n-Bu
n-Bu
tangy-5-173-C-100M
Apr 25 2017
SOLVENT: cdcl3
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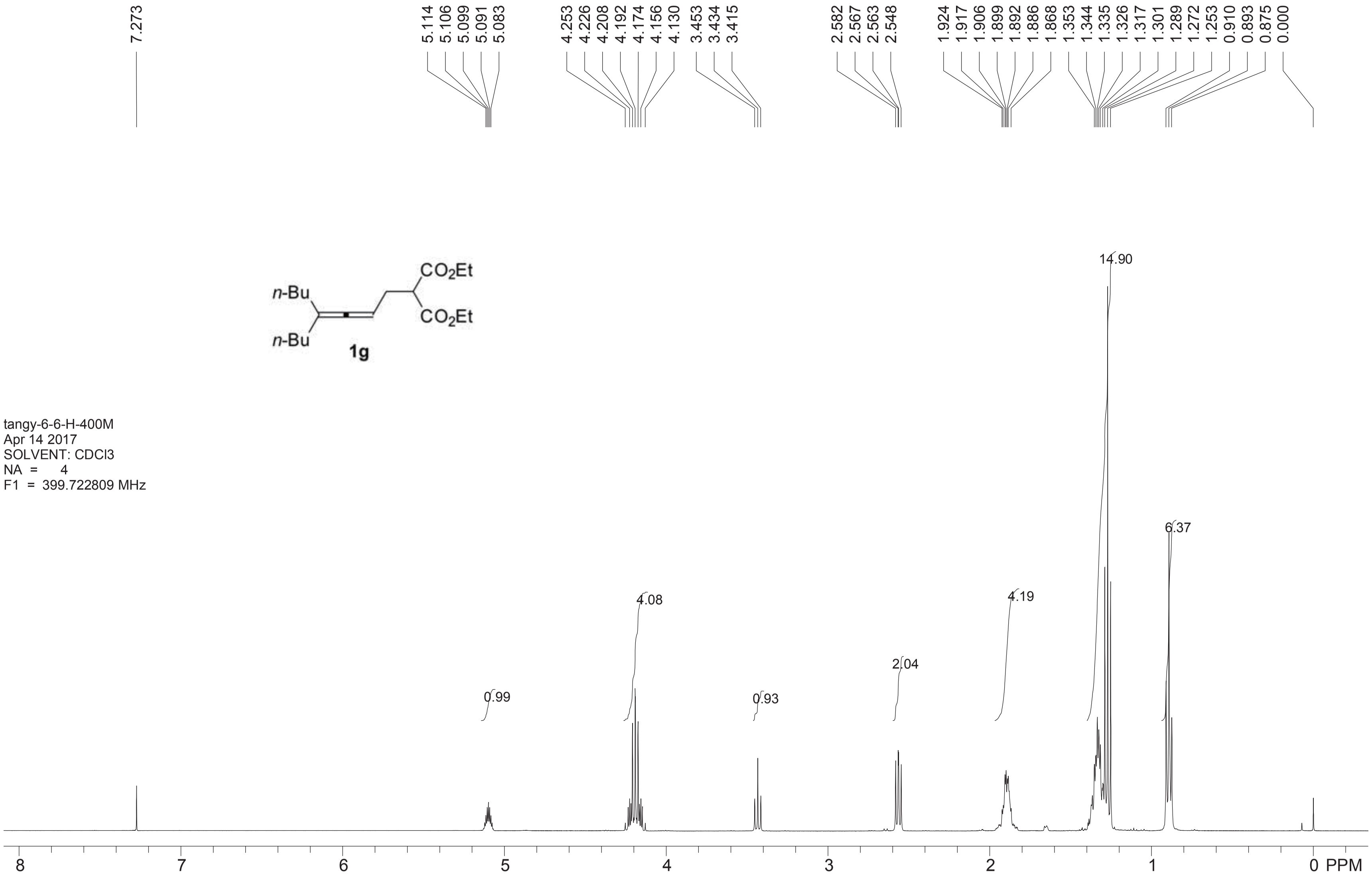
150
200



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5.091
5.083
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4.208
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3.453
3.434
3.415
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2.563
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1.917
1.906
1.899
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1.886
1.868
1.353
1.344
1.335
1.326
1.317
1.301
1.289
1.272
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0.910
0.893
0.875
0.000
14.90
6.37
4.19
4.08
2.04
0.99
0.93
tangy-6-6-H-400M
Apr 14 2017
SOLVENT: CDCl3
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F1 = 399.722809 MHz
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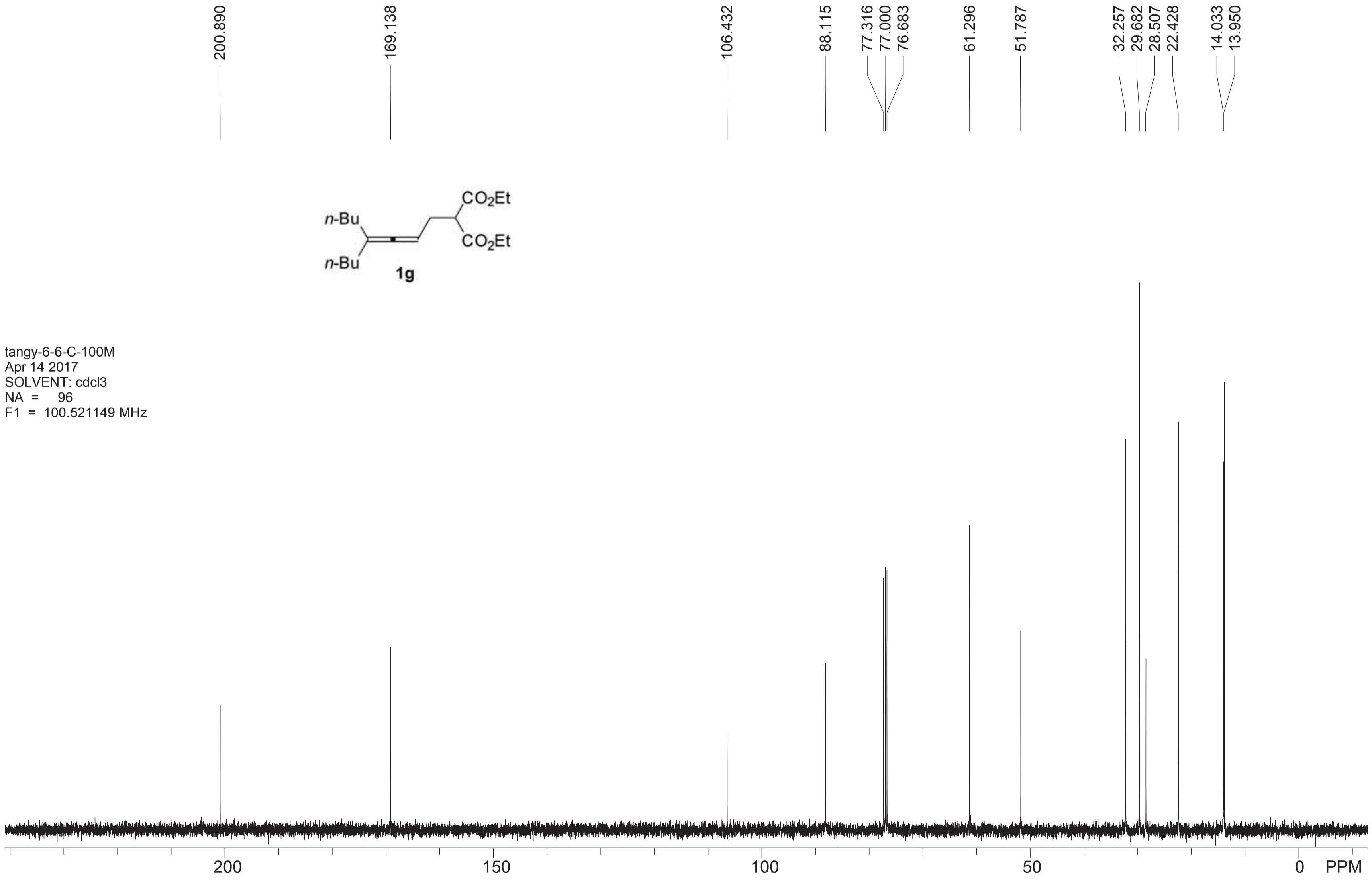
6
5
4
3
2
1
0 PPM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n-Bu
n-Bu
CO2Et
CO2Et
1g
tangy-6-6-C-100M
Apr 14 2017
SOLVENT: cdcl3
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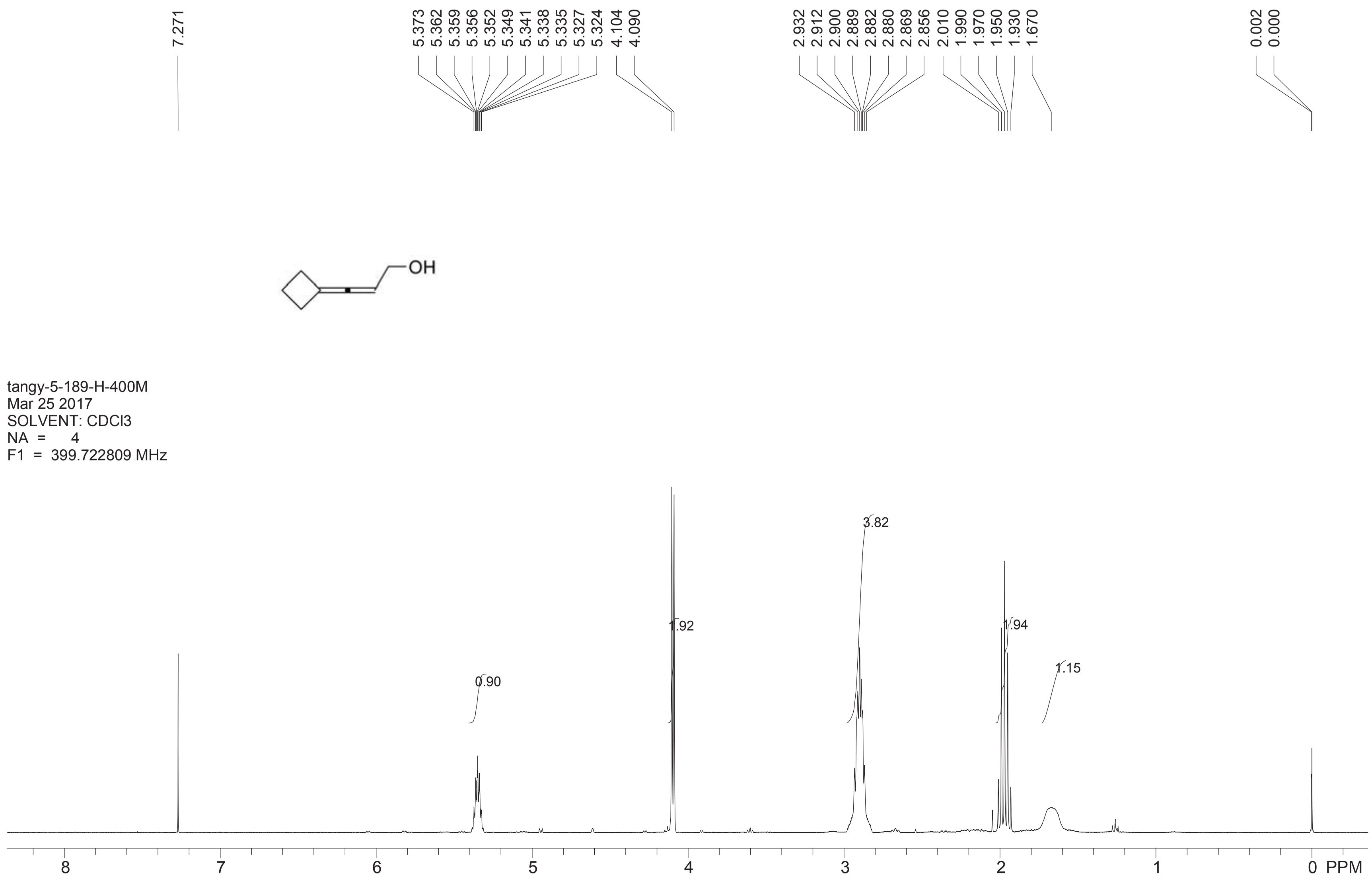
PPM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2.889
2.882
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2.869
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1.950
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tangy-5-189-H-400M
Mar 25 2017
SOLVENT: CDCl3
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2
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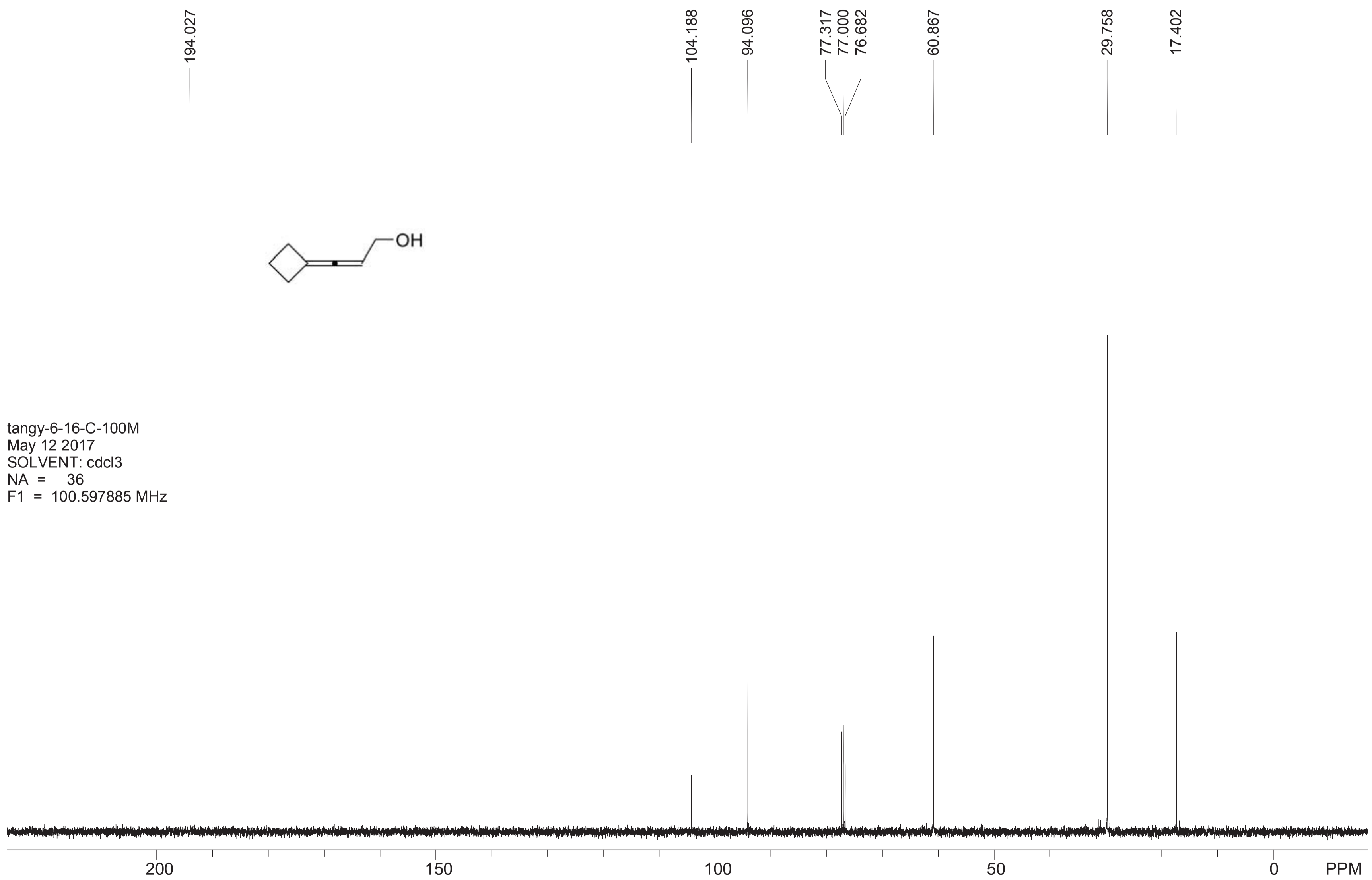

tangy-6-16-C-100M
May 12 2017
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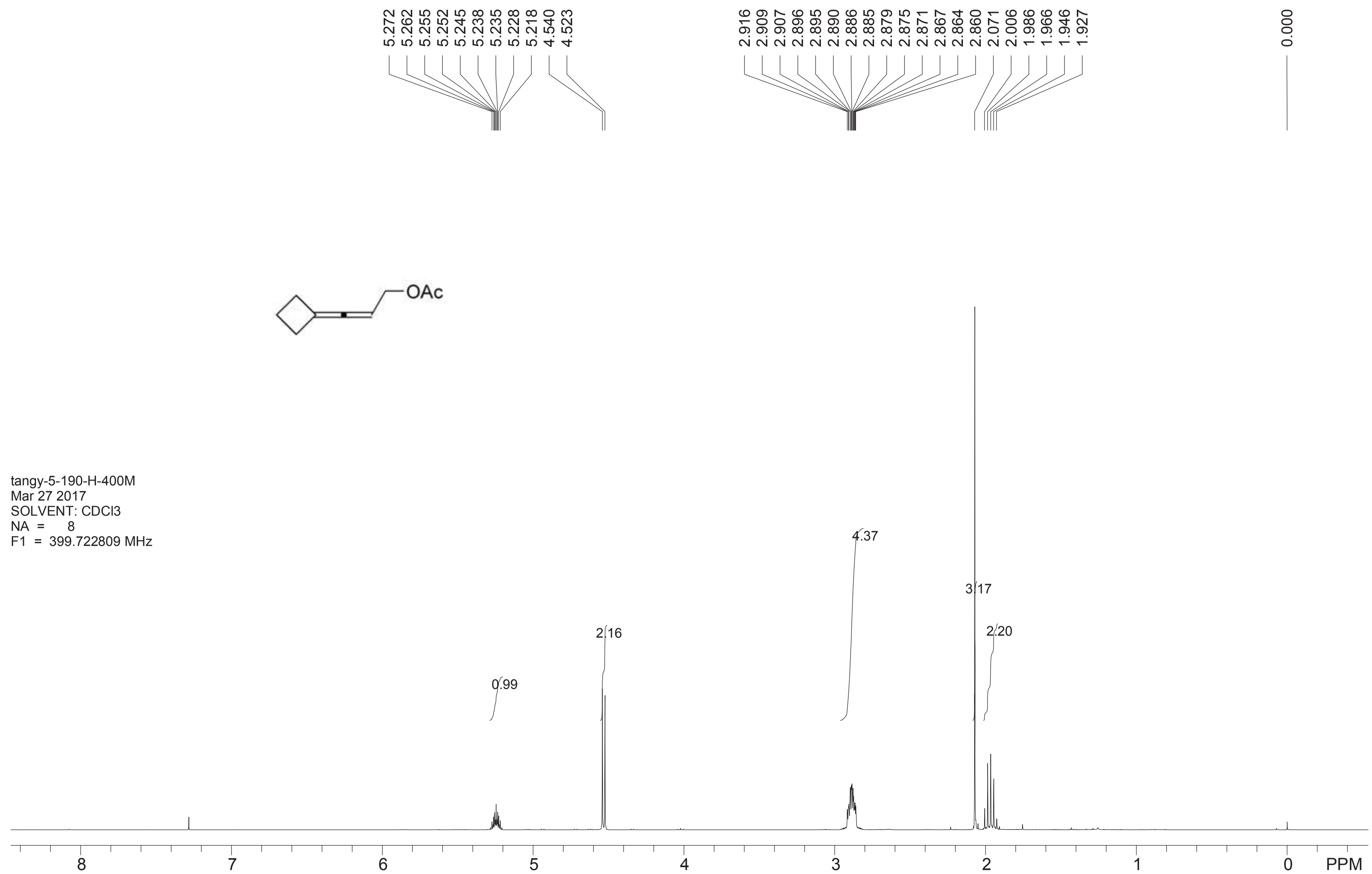
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4.523
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2.875
2.871
2.867
2.864
2.860
2.071
2.006
1.986
1.966
1.946
1.927
0.000
OAc
tangy-5-190-H-400M
Mar 27 2017
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz
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4.37
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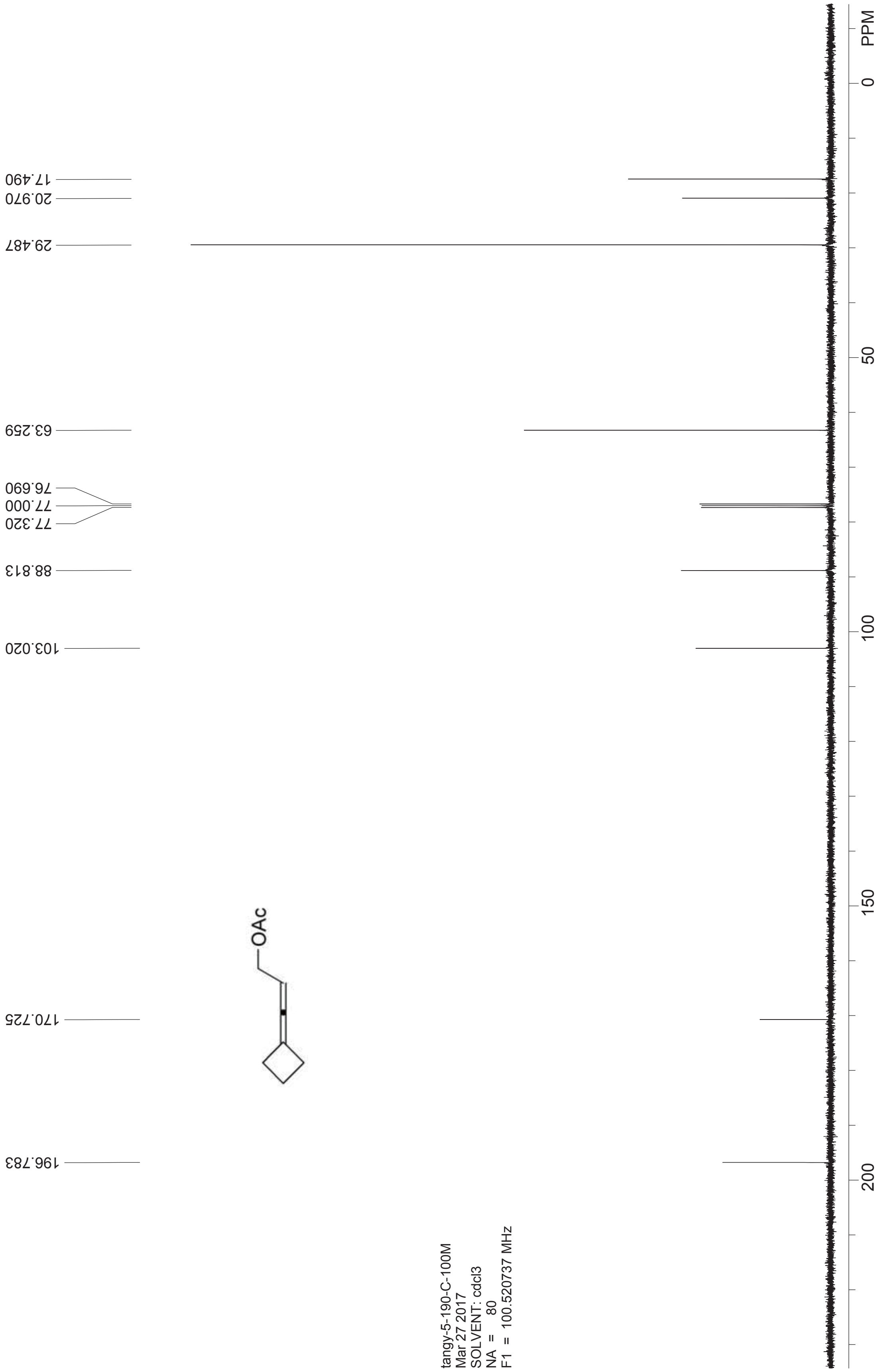
6
5
4
3
2
1
0
PPM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77.000
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88.813
103.020
170.725
196.783
OAc
PPM
0
50
100
150
200
tangy-5-190-C-100M
Mar 27 2017
SOLVENT: cdcl3
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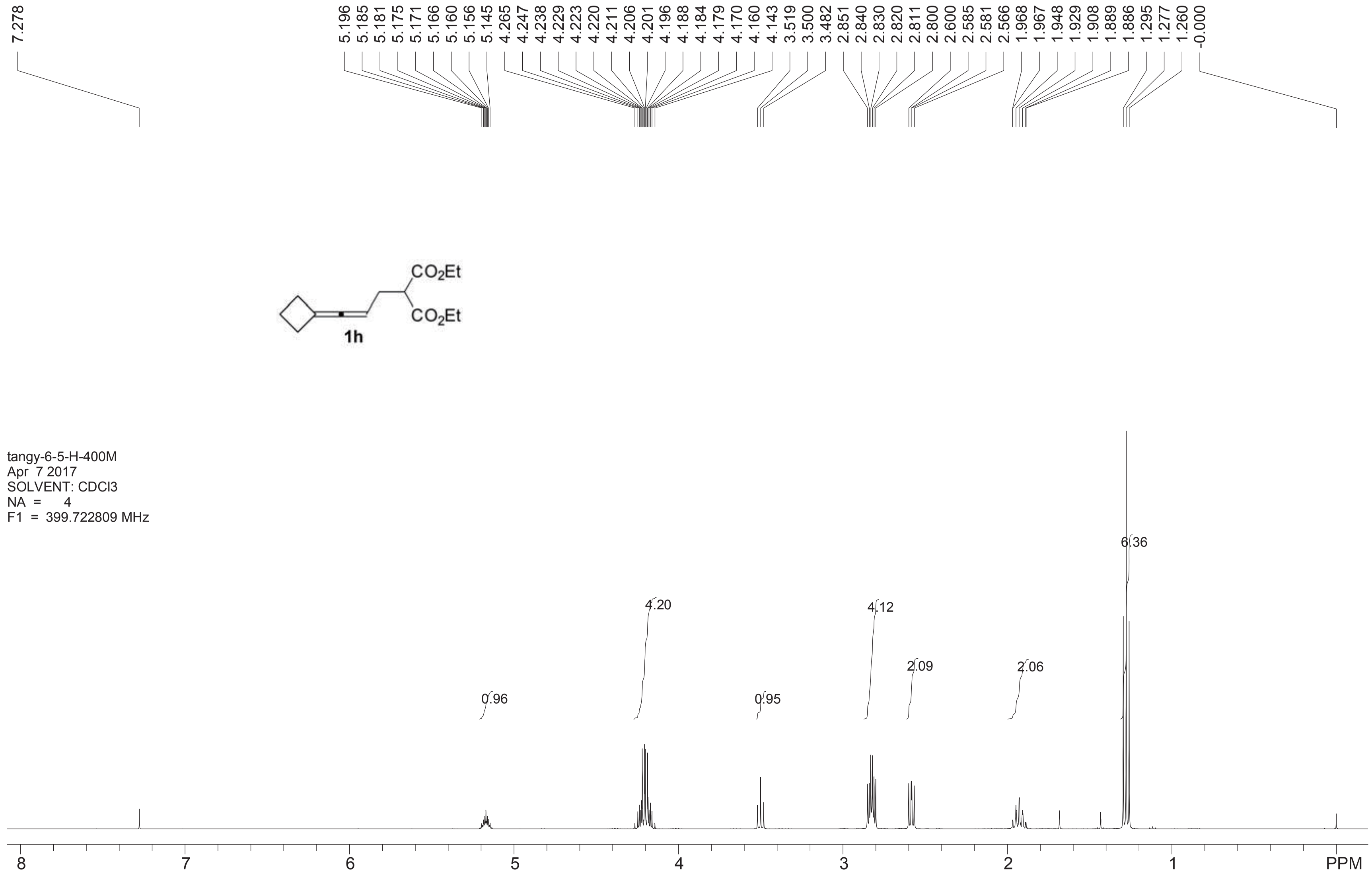
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5.160
5.156
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4.238
4.229
4.223
4.220
4.211
4.206
4.201
4.196
4.188
4.184
4.179
4.170
4.160
4.143
3.519
3.500
3.482
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2.820
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2.600
2.585
2.581
2.566
1.968
1.967
1.948
1.929
1.908
1.889
1.886
1.295
1.277
1.260
-0.000
CO2Et
CO2Et
1h
tangy-6-5-H-400M
Apr 7 2017
SOLVENT: CDCl3
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F1 = 399.722809 MHz
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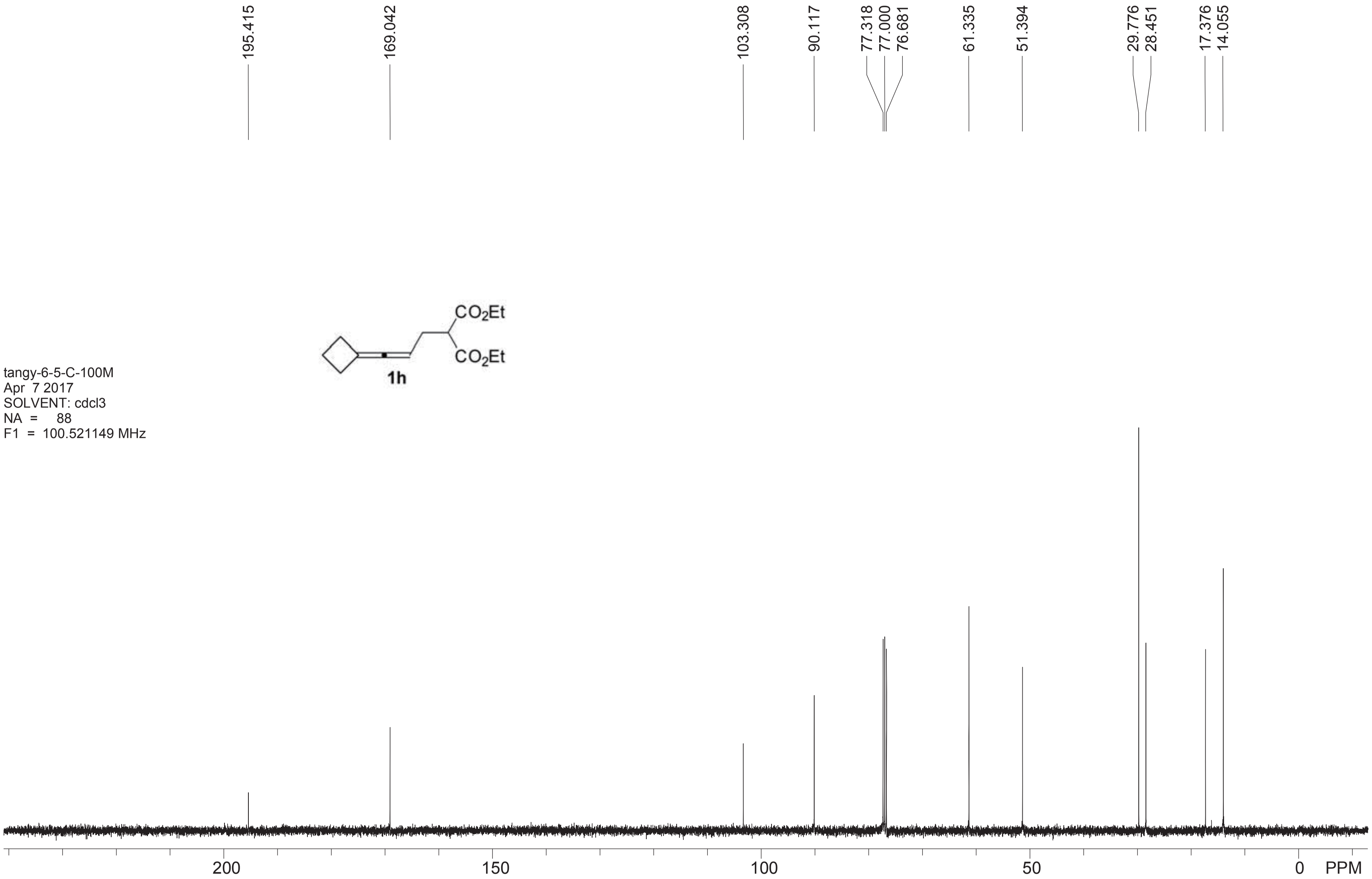
6
5
4
3
2
1
PPM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14.055
tangy-6-5-C-100M
Apr 7 2017
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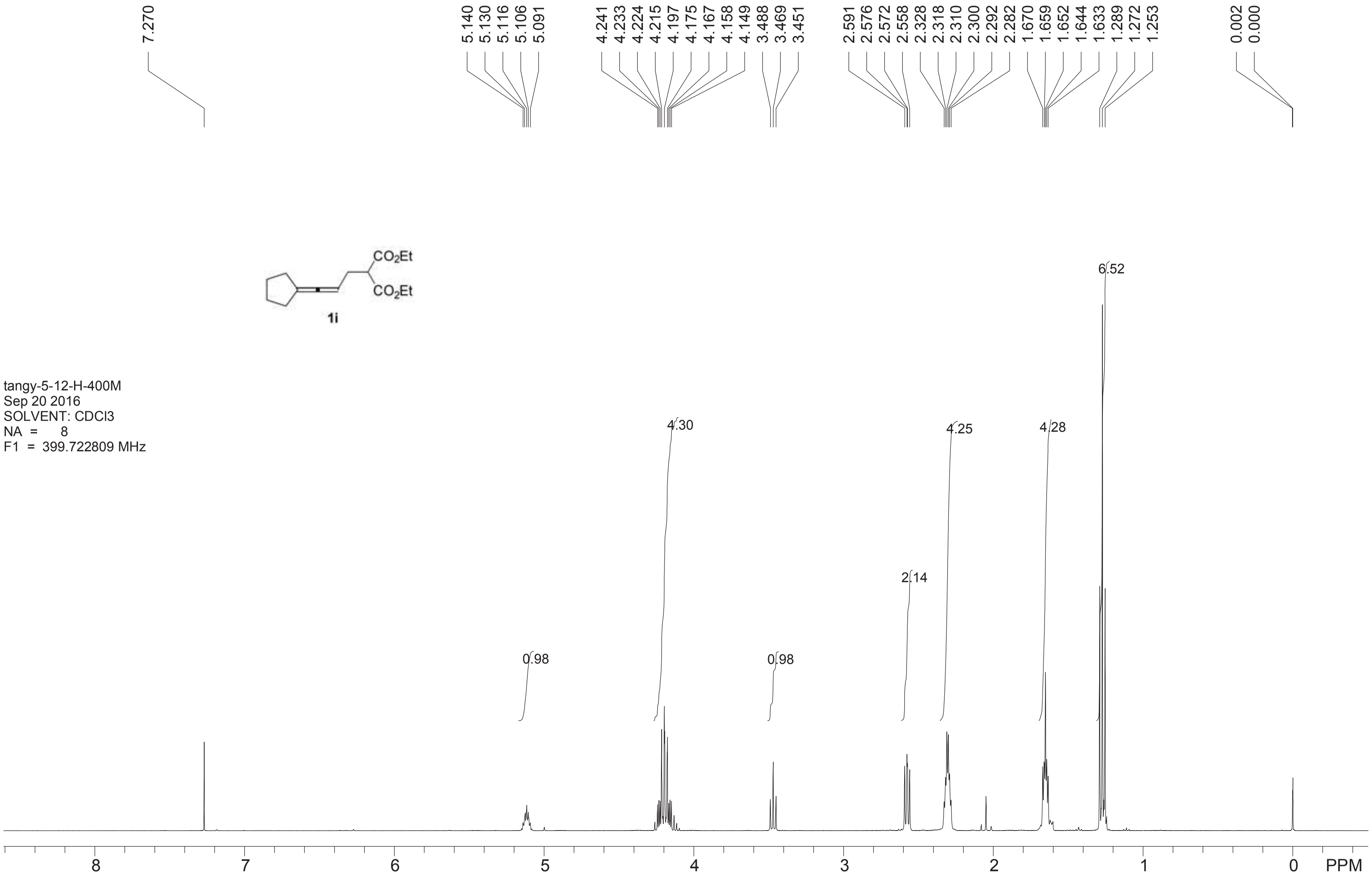
50
0
PPM
CO2Et
CO2Et

1h


tangy-5-12-H-400M
Sep 20 2016
SOLVENT: CDCl3
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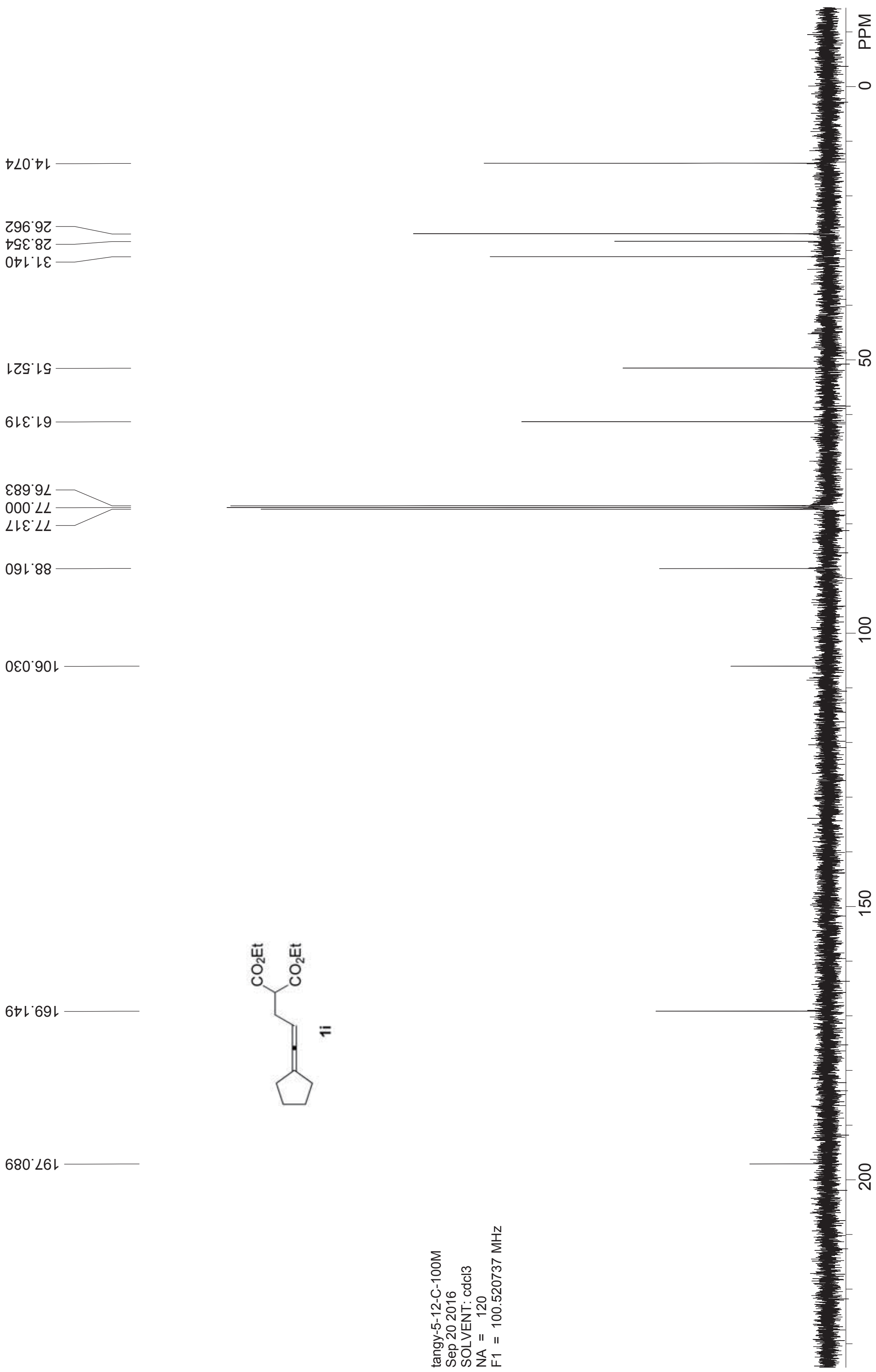
F1 = 399.722809 MHz
1i
PPM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61.319
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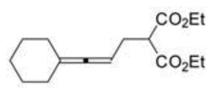
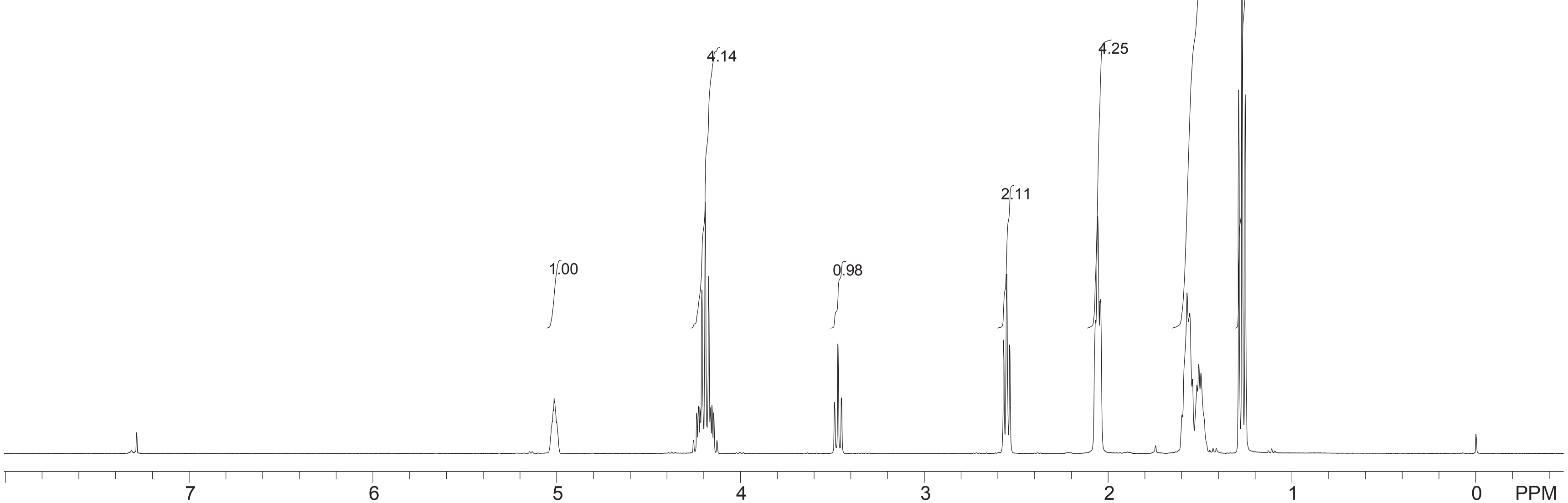
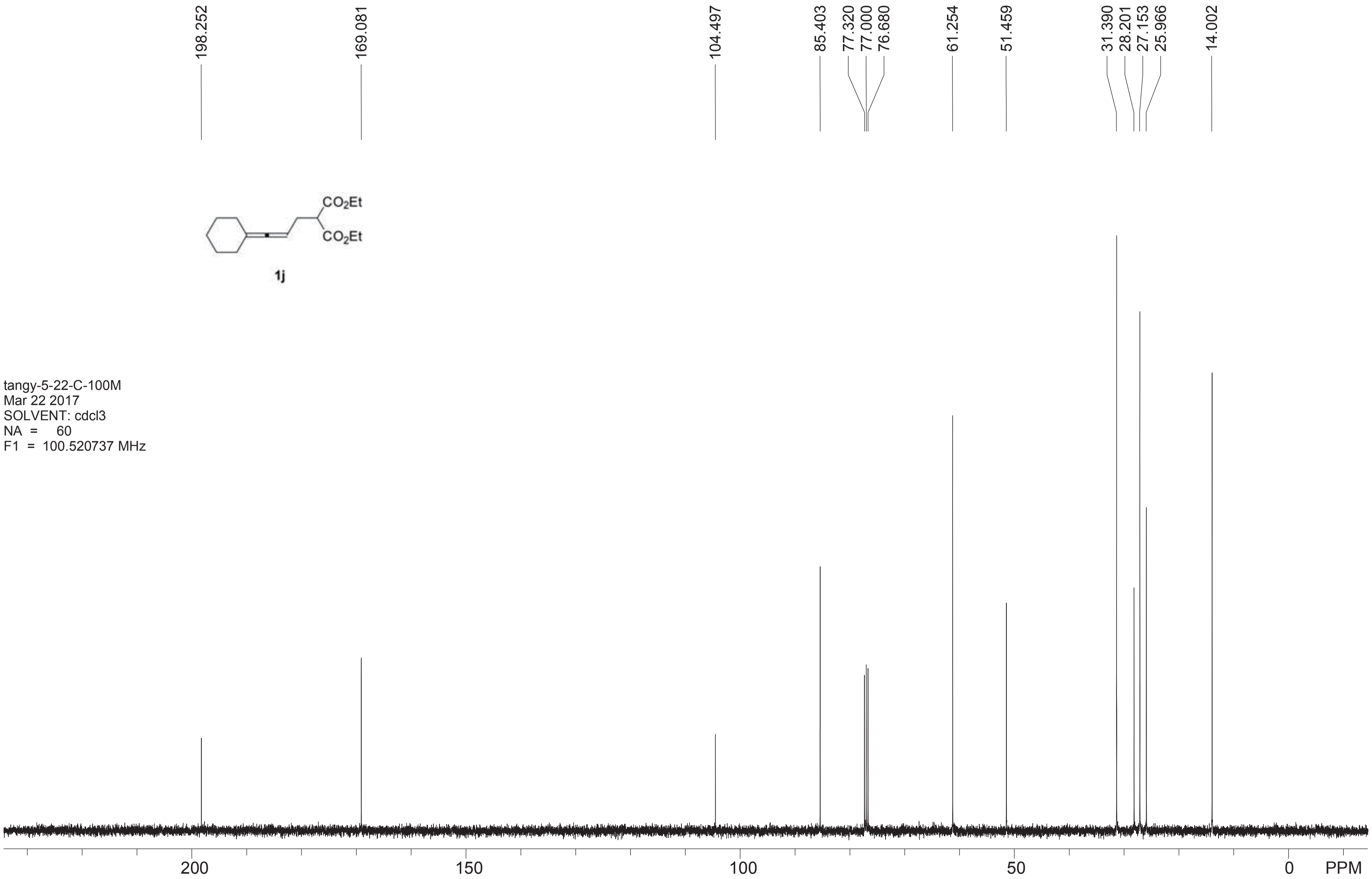
77.000
77.317
88.160
106.030
169.149
197.089
CO_2Et
CO_2Et
1i
PPM
0
50
100
150
200
tangy-5-12-C-100M
Sep 20 2016
SOLVENT: cdcl3
NA = 120
F1 = 100.520737 MHz

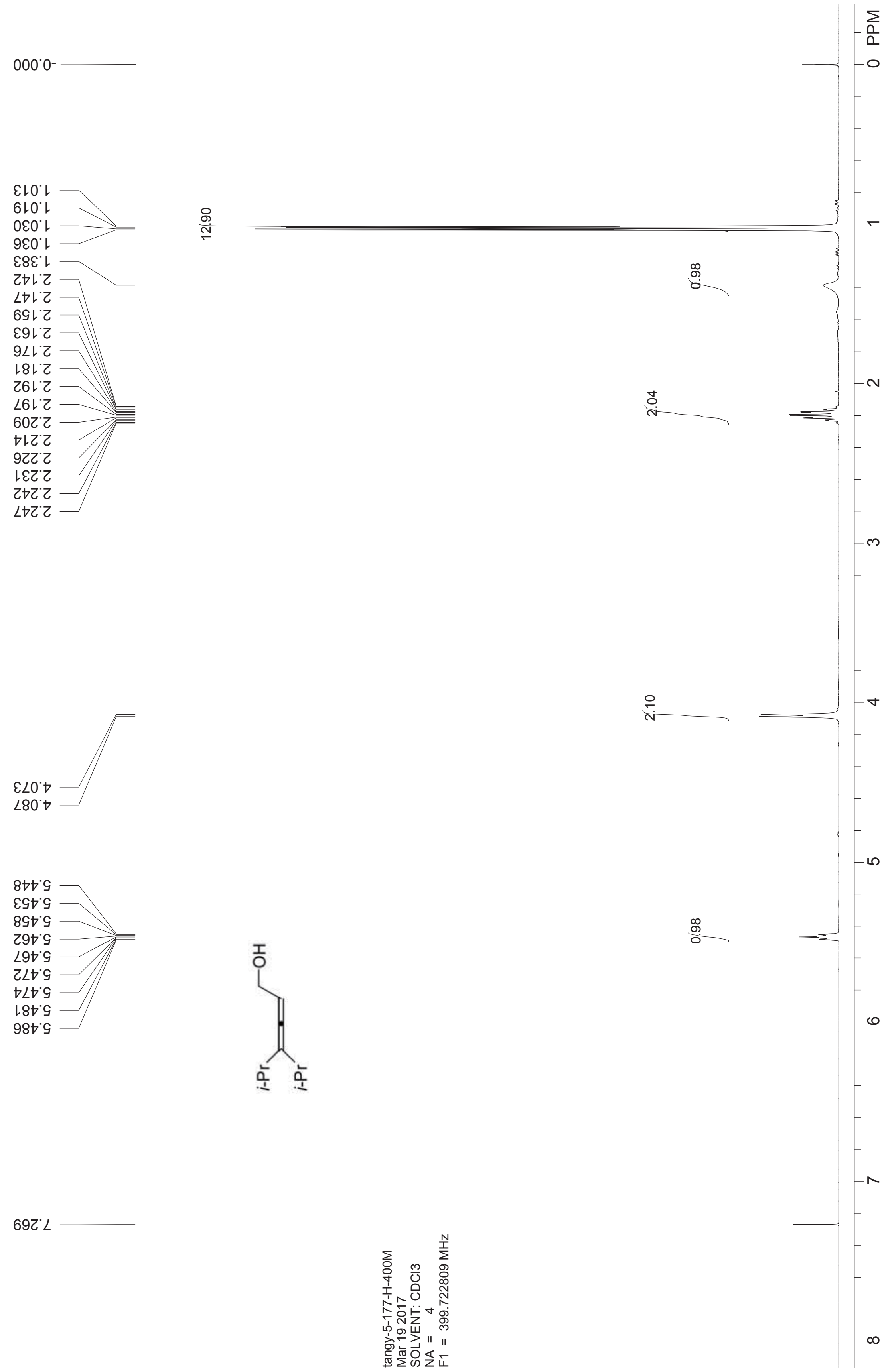


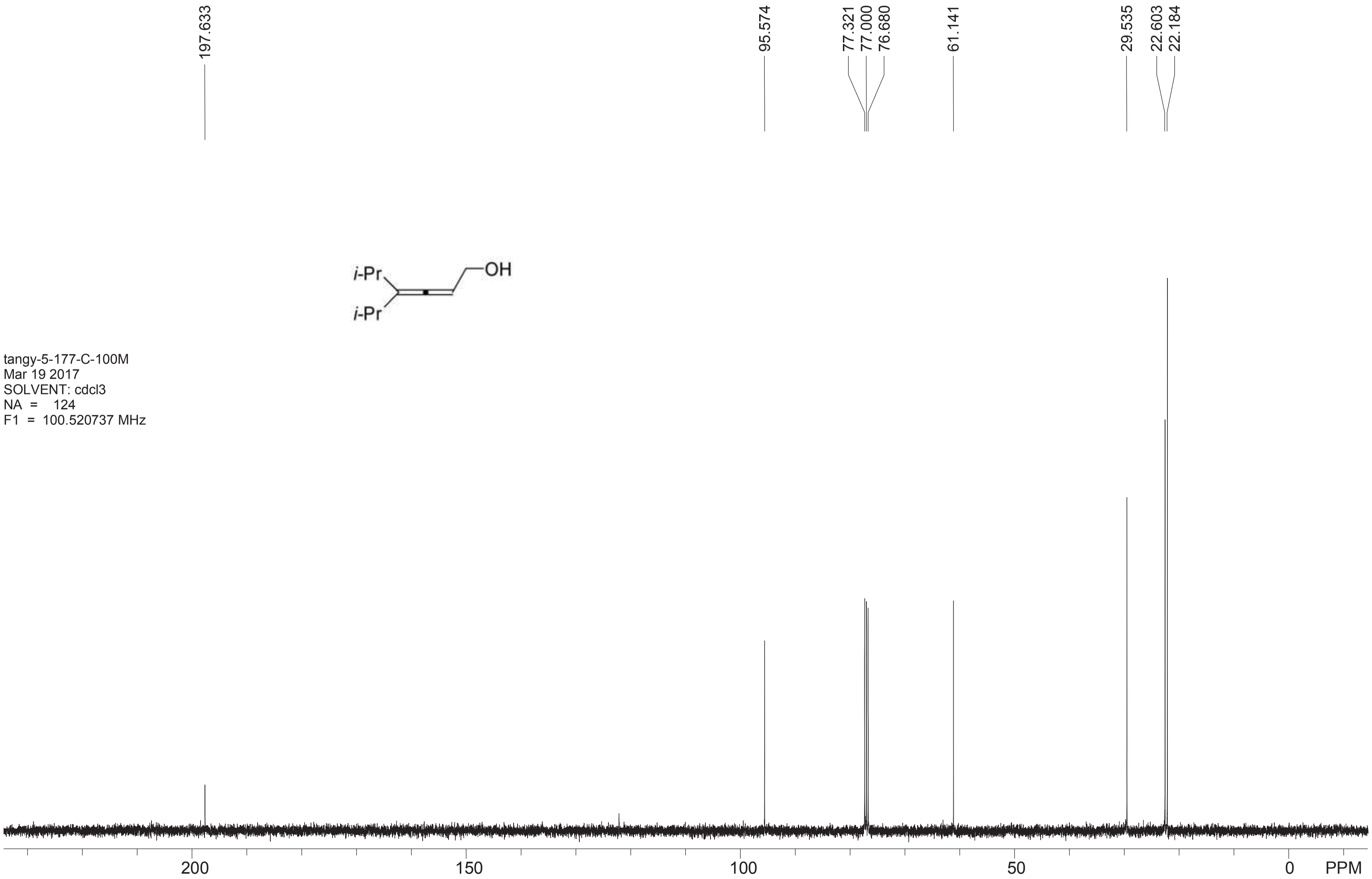
1j

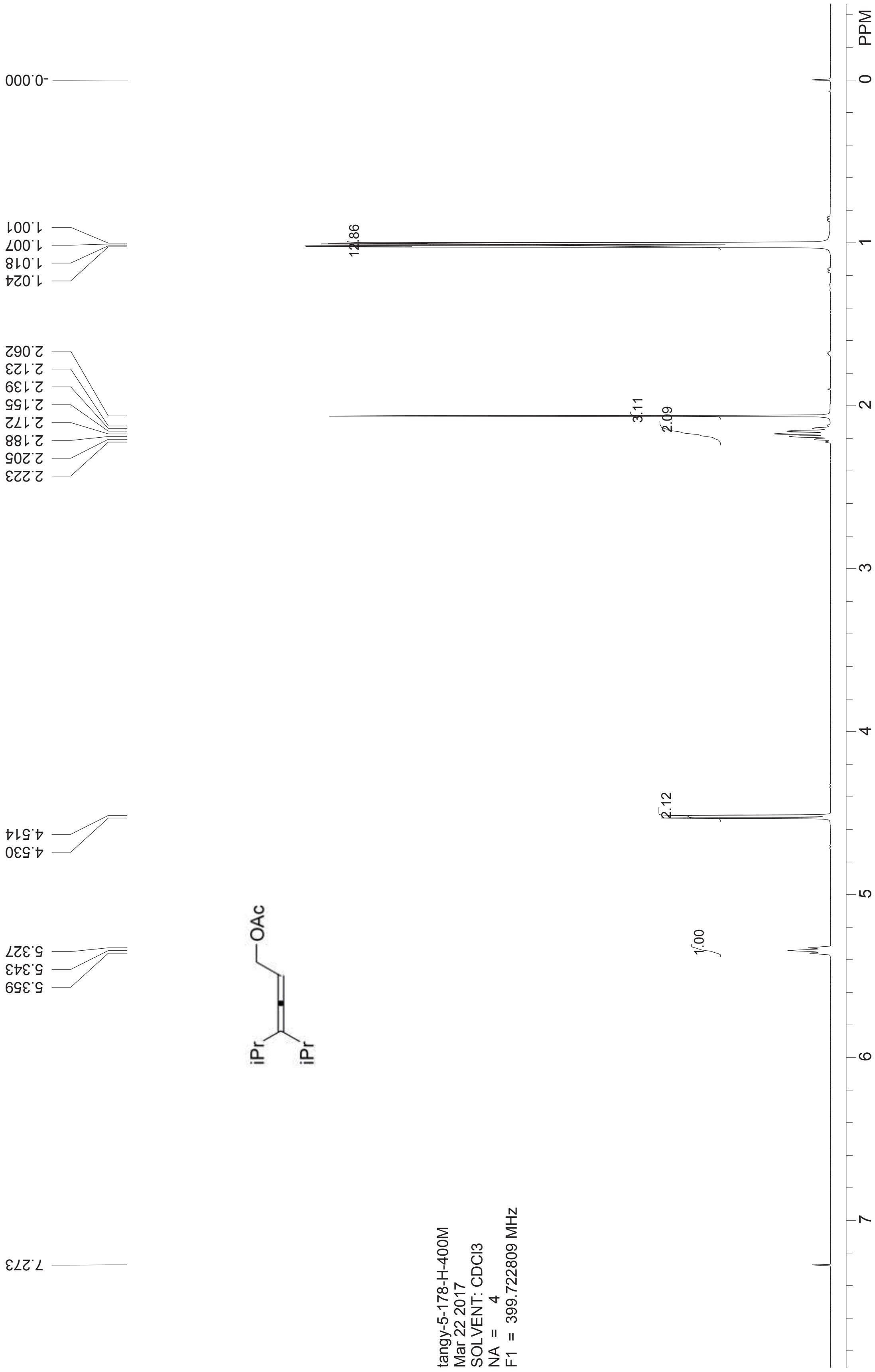
tangy-5-22-H-400M
Mar 22 2017
SOLVENT: CDCl3
NA = 4
F1 = 399.722809 MHz



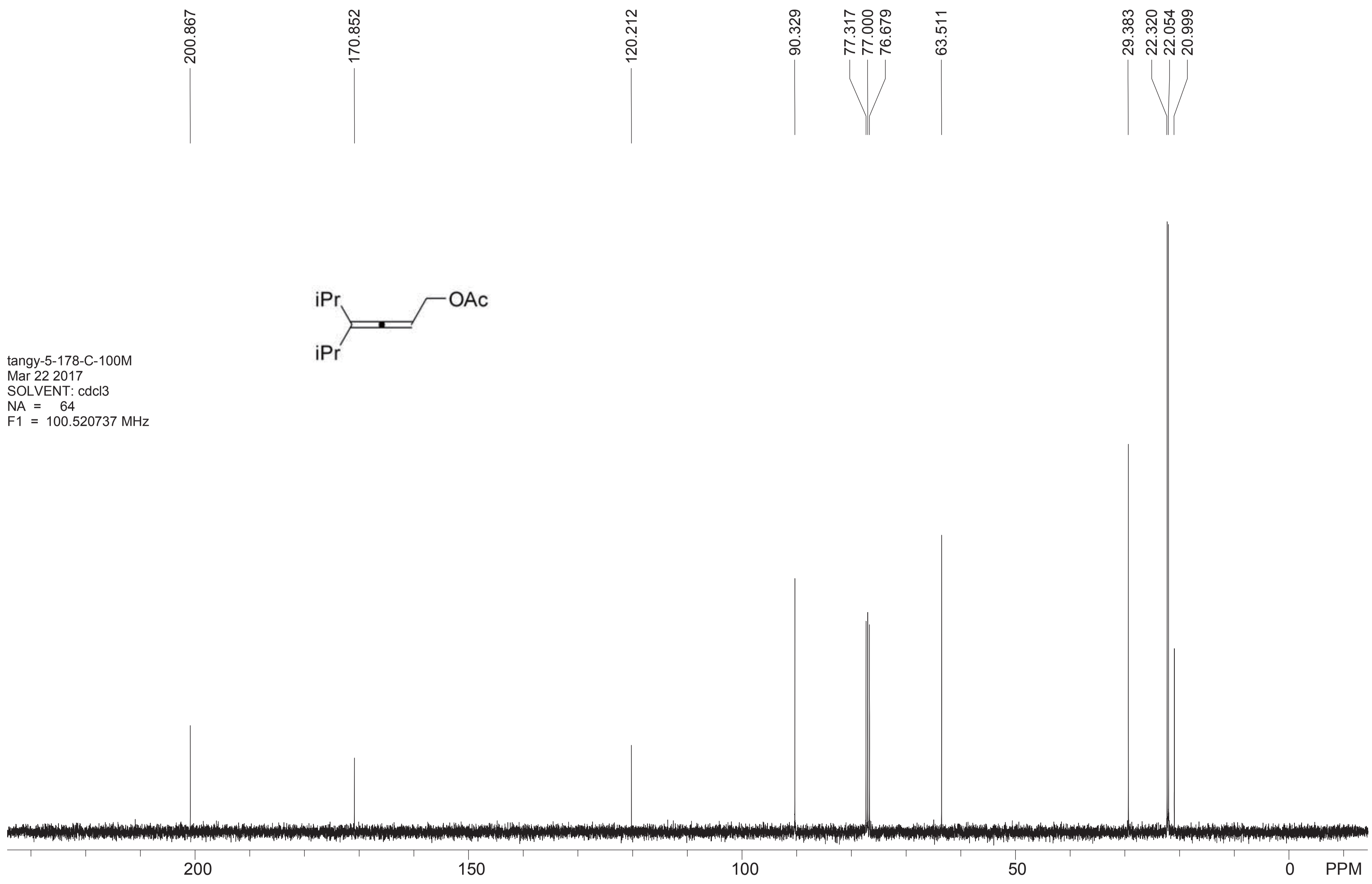

1j
198.252
169.081
104.497
85.403
77.320
77.000
76.680
61.254
51.459
31.390
28.201
27.153
25.966
14.002
tangy-5-22-C-100M
Mar 22 2017
SOLVENT: cdcl3
NA = 60
F1 = 100.520737 MHz
200
150
100
50
0
PPM

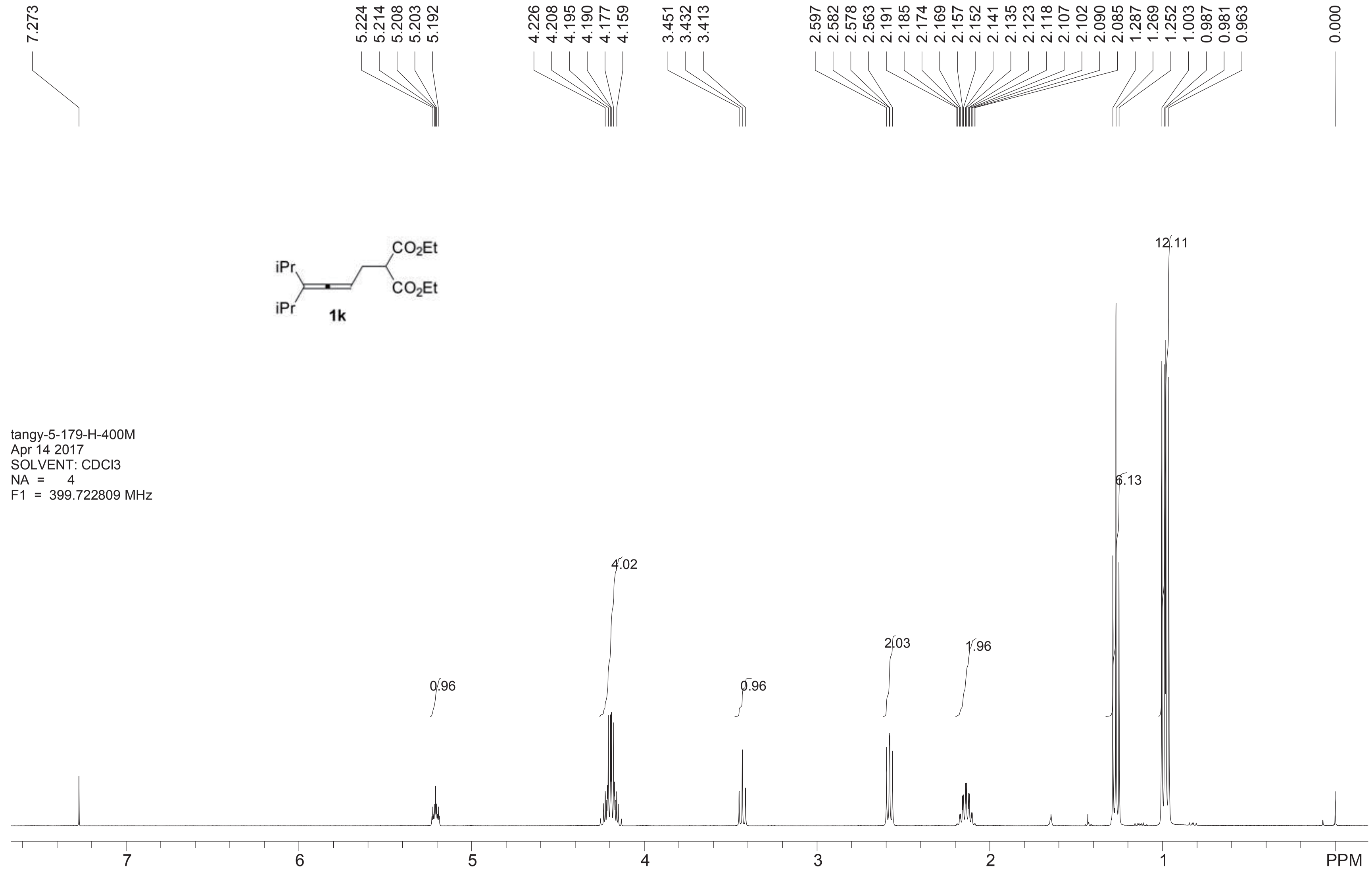

-0.000
1.013
1.019
1.030
1.036
1.383
2.142
2.147
2.159
2.163
2.176
2.181
2.192
2.197
2.209
2.214
2.226
2.231
2.242
2.247
4.073
4.087
5.448
5.453
5.458
5.462
5.467
5.472
5.474
5.481
5.486
7.269
12.90
0.98
2.04
2.10
0.98
OH
i-Pr
i-Pr
tangy-5-177-H-400M
Mar 19 2017
SOLVENT: CDCl3
NA = 4
F1 = 399.722809 MHz
0
1
2
3
4
5
6
7
8
PPM

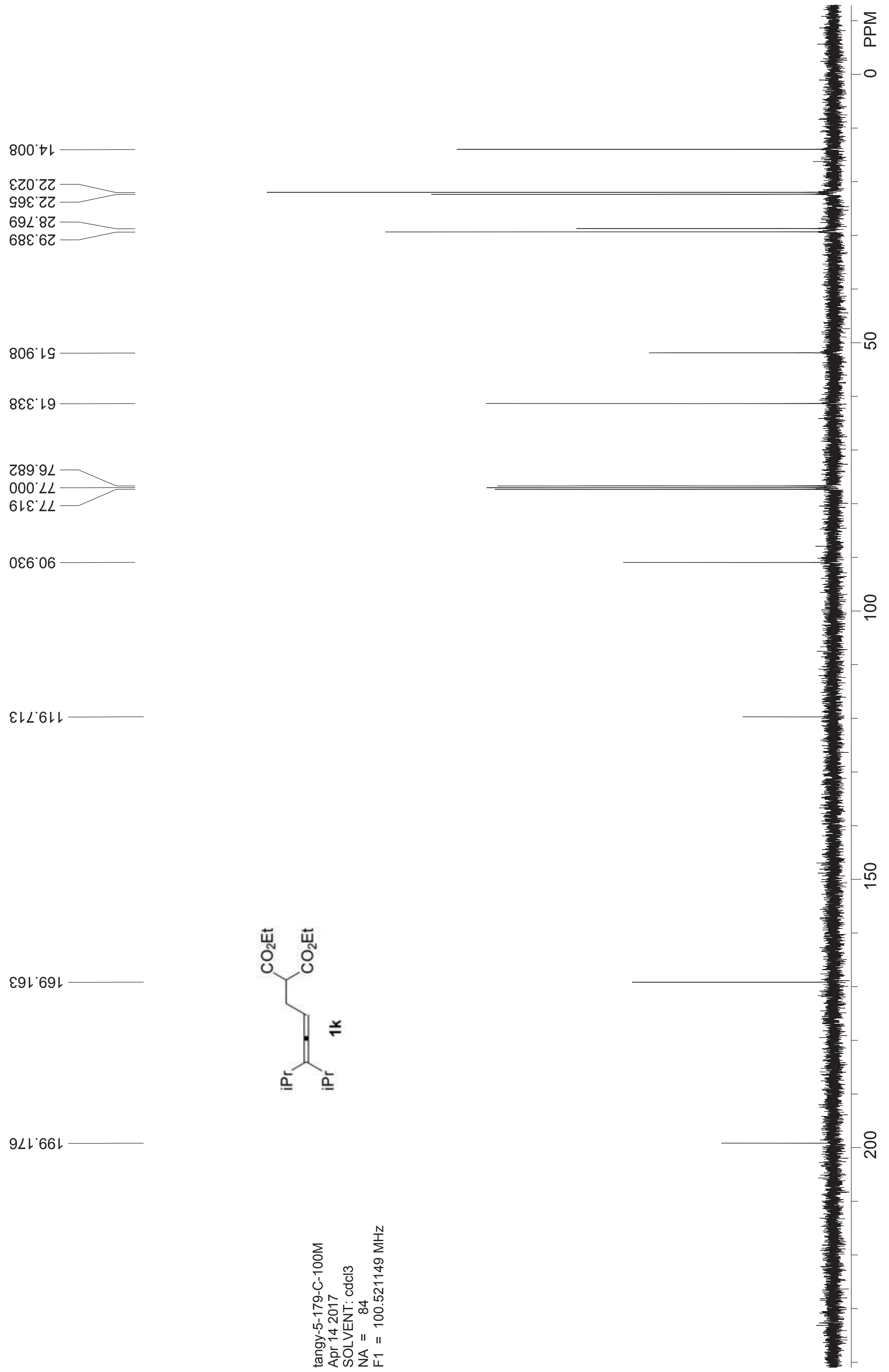

197.633
95.574
77.321
77.000
76.680
61.141
29.535
22.603
22.184
i-Pr
i-Pr
OH
tangy-5-177-C-100M
Mar 19 2017
SOLVENT: cdcl3
NA = 124
F1 = 100.520737 MHz
200
150
100
50
0
PPM

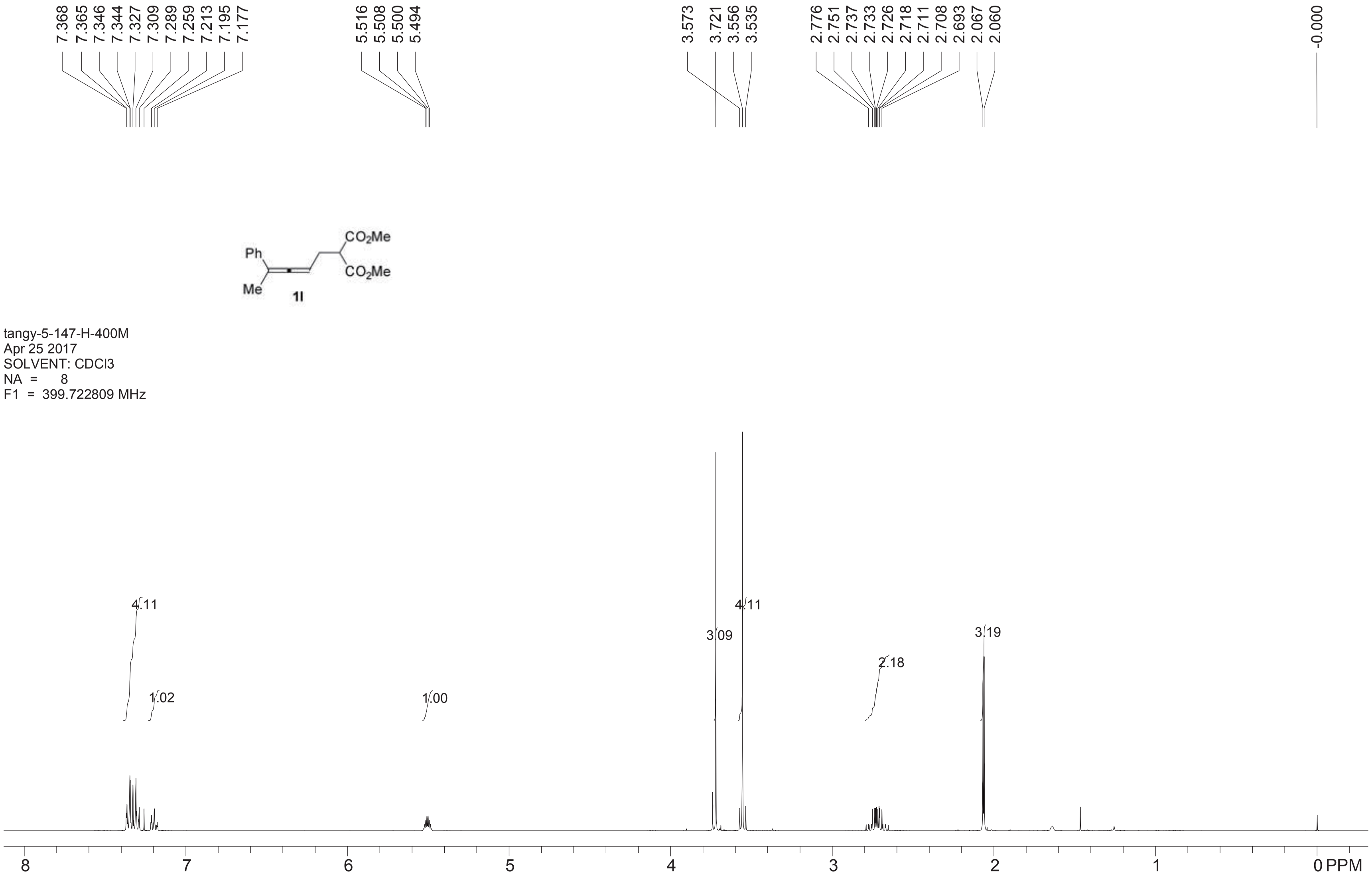


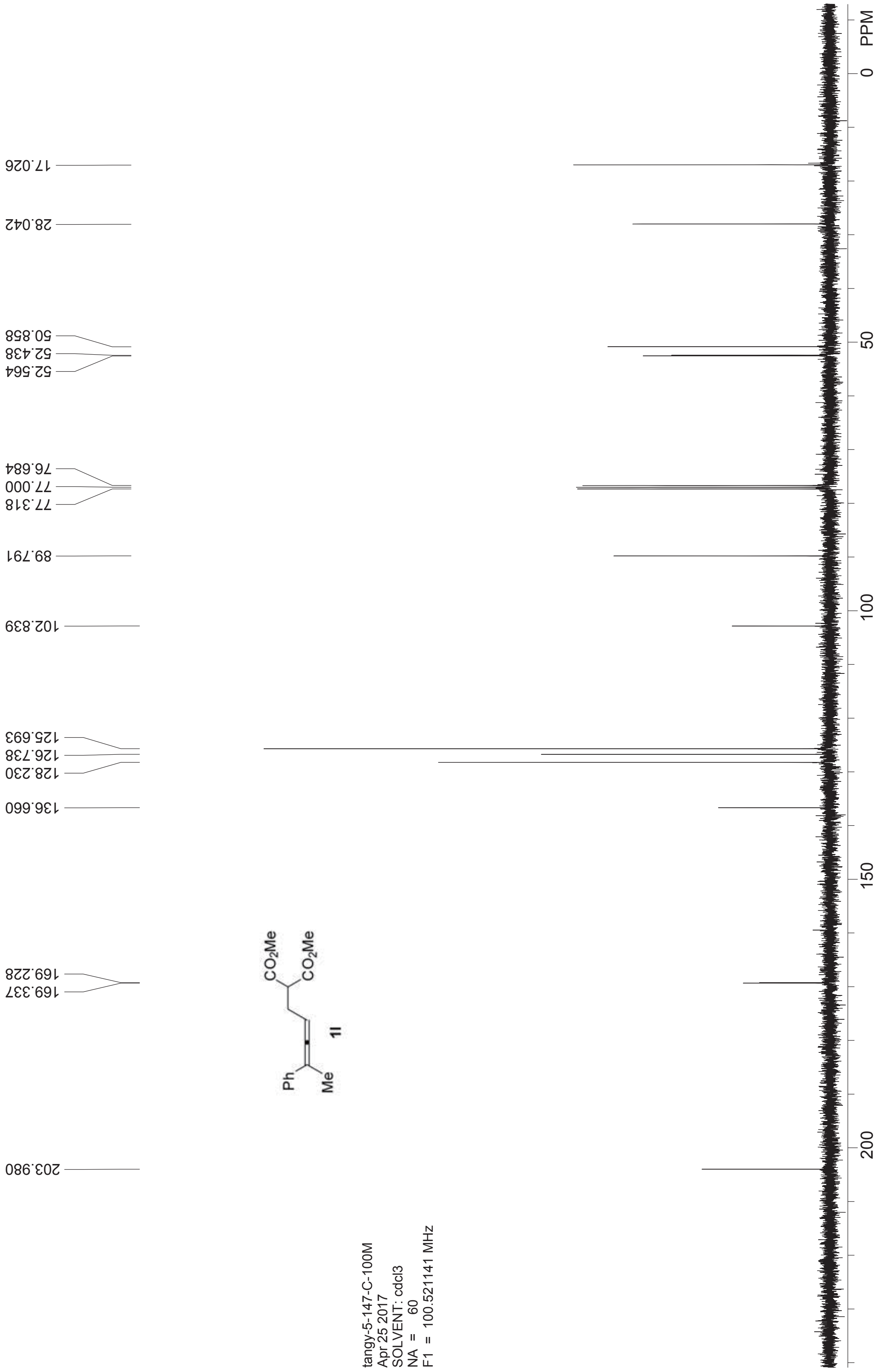
-0.000
1.001
1.007
1.018
1.024
2.062
2.123
2.139
2.155
2.172
2.188
2.205
2.223
4.514
4.530
5.327
5.343
5.359
7.273
OAc
iPr
iPr
12.86
3.11
2.09
2.12
1.00
tangy-5-178-H-400M
Mar 22 2017
SOLVENT: CDCl3
NA = 4
F1 = 399.722809 MHz
PPM
0
1
2
3
4
5
6
7

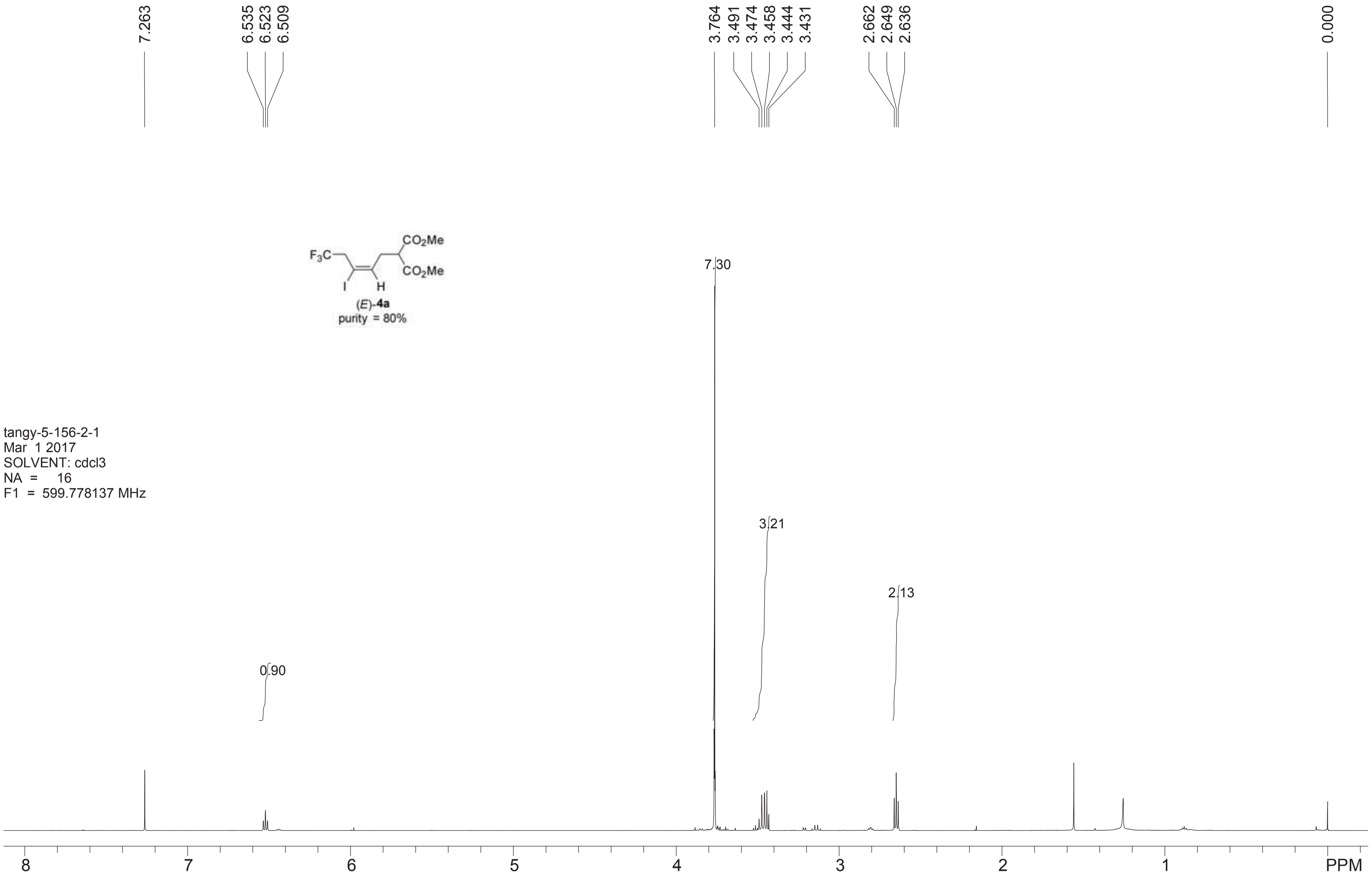

200.867
170.852
120.212
90.329
77.317
77.000
76.679
63.511
29.383
22.320
22.054
20.999
iPr
iPr
OAc
tangy-5-178-C-100M
Mar 22 2017
SOLVENT: cdcl3
NA = 64
F1 = 100.520737 MHz
200
150
100
50
0
PPM


7.273
5.224
5.214
5.208
5.203
5.192
4.226
4.208
4.195
4.190
4.177
4.159
3.451
3.432
3.413
2.597
2.582
2.578
2.563
2.191
2.185
2.174
2.169
2.157
2.152
2.141
2.135
2.123
2.118
2.107
2.102
2.090
2.085
1.287
1.269
1.252
1.003
0.987
0.981
0.963
0.000
iPr
iPr
CO_2Et
CO_2Et
1k
tangy-5-179-H-400M
Apr 14 2017
SOLVENT: CDCl3
NA = 4
F1 = 399.722809 MHz
12.11
6.13
4.02
2.03
1.96
0.96
0.96
7
6
5
4
3
2
1
PPM

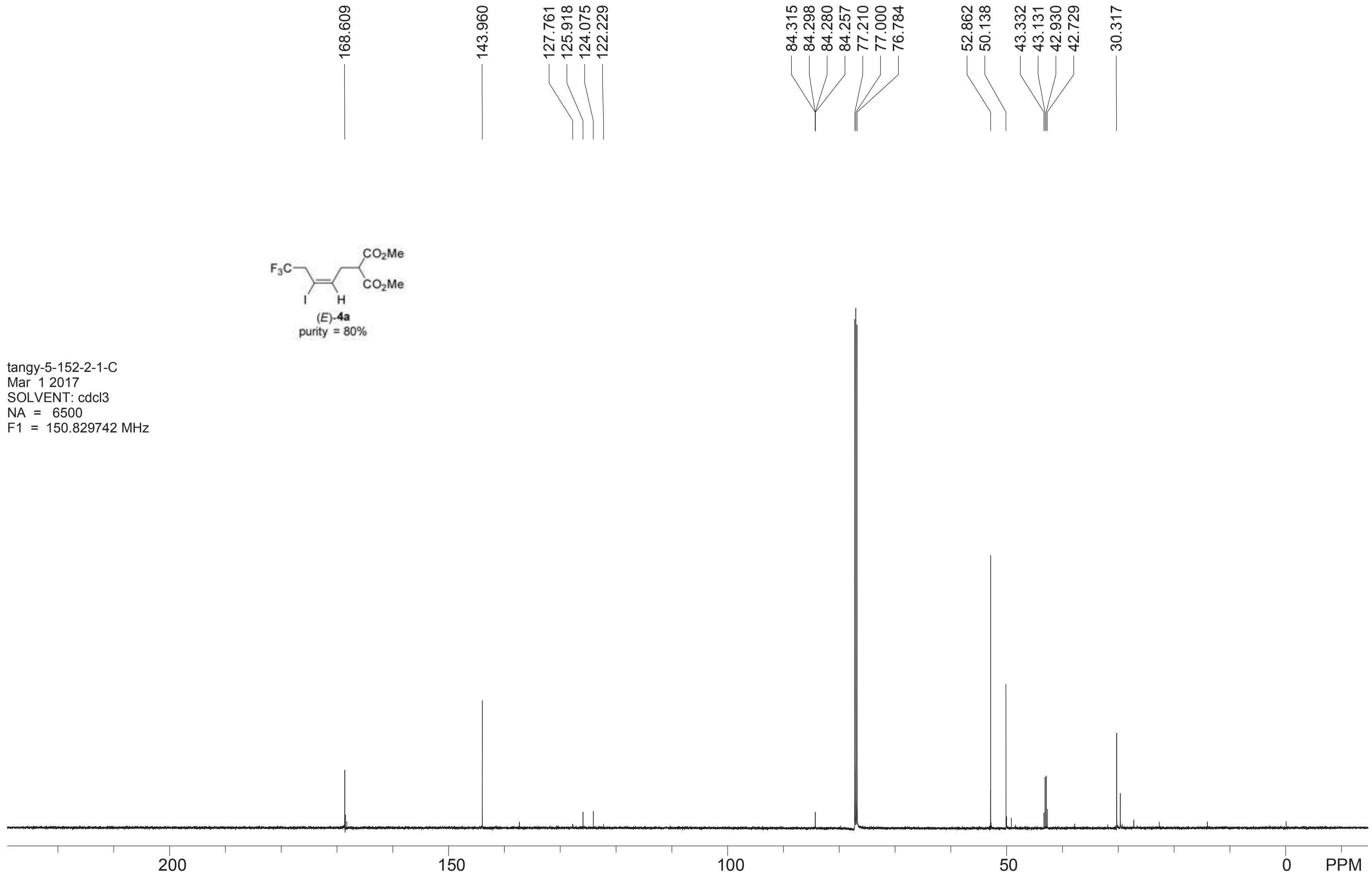

14.008
22.023
22.365
28.769
29.389
51.908
61.338
76.682
77.000
77.319
90.930
119.713
169.163
199.176
PPM
0
50
100
150
200
CO2Et
CO2Et
iPr
iPr
1k
tangy-5-179-C-100M
Apr 14 2017
SOLVENT: cdcl3
NA = 84
F1 = 100.521149 MHz


7.368
7.365
7.346
7.344
7.327
7.309
7.289
7.259
7.213
7.195
7.177
5.516
5.508
5.500
5.494
3.573
3.721
3.556
3.535
2.776
2.751
2.737
2.733
2.726
2.718
2.711
2.708
2.693
2.067
2.060
-0.000
Ph
Me
CO_2Me
CO_2Me
1l
tangy-5-147-H-400M
Apr 25 2017
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz
4.11
1.02
1.00
3.09
4.11
2.18
3.19
8
7
6
5
4
3
2
1
0 PPM


17.026
28.042
50.858
52.438
52.564
76.684
77.000
77.318
89.791
102.839
125.693
126.738
128.230
136.660
169.228
169.337
203.980
CO_2Me
CO_2Me
Ph
Me
1l
tangy-5-147-C-100M
Apr 25 2017
SOLVENT: cdcl3
NA = 60
F1 = 100.521141 MHz
PPM
0
50
100
150
200

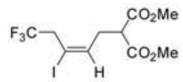


tangy-5-156-2-1
Mar 1 2017
SOLVENT: cdcl3
NA = 16
F1 = 599.778137 MHz



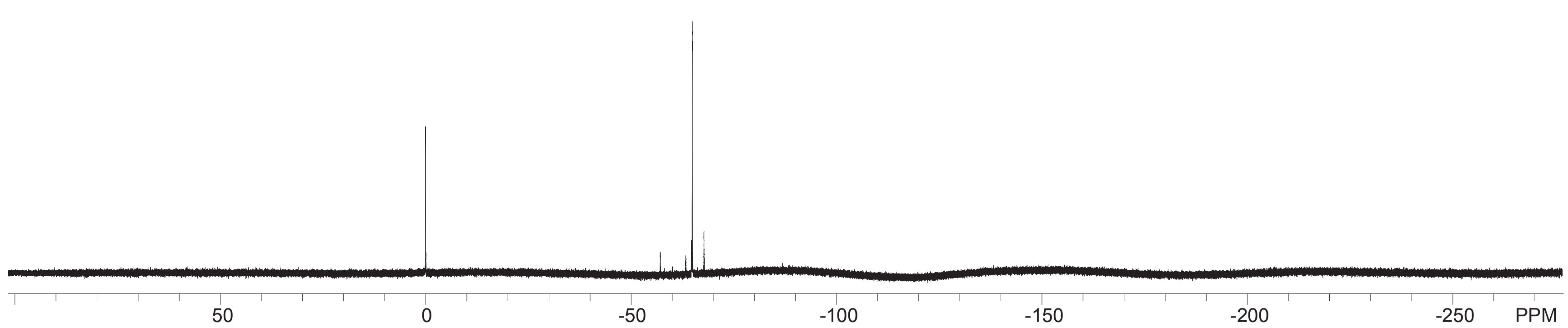
(E)-**4a**
purity = 80%

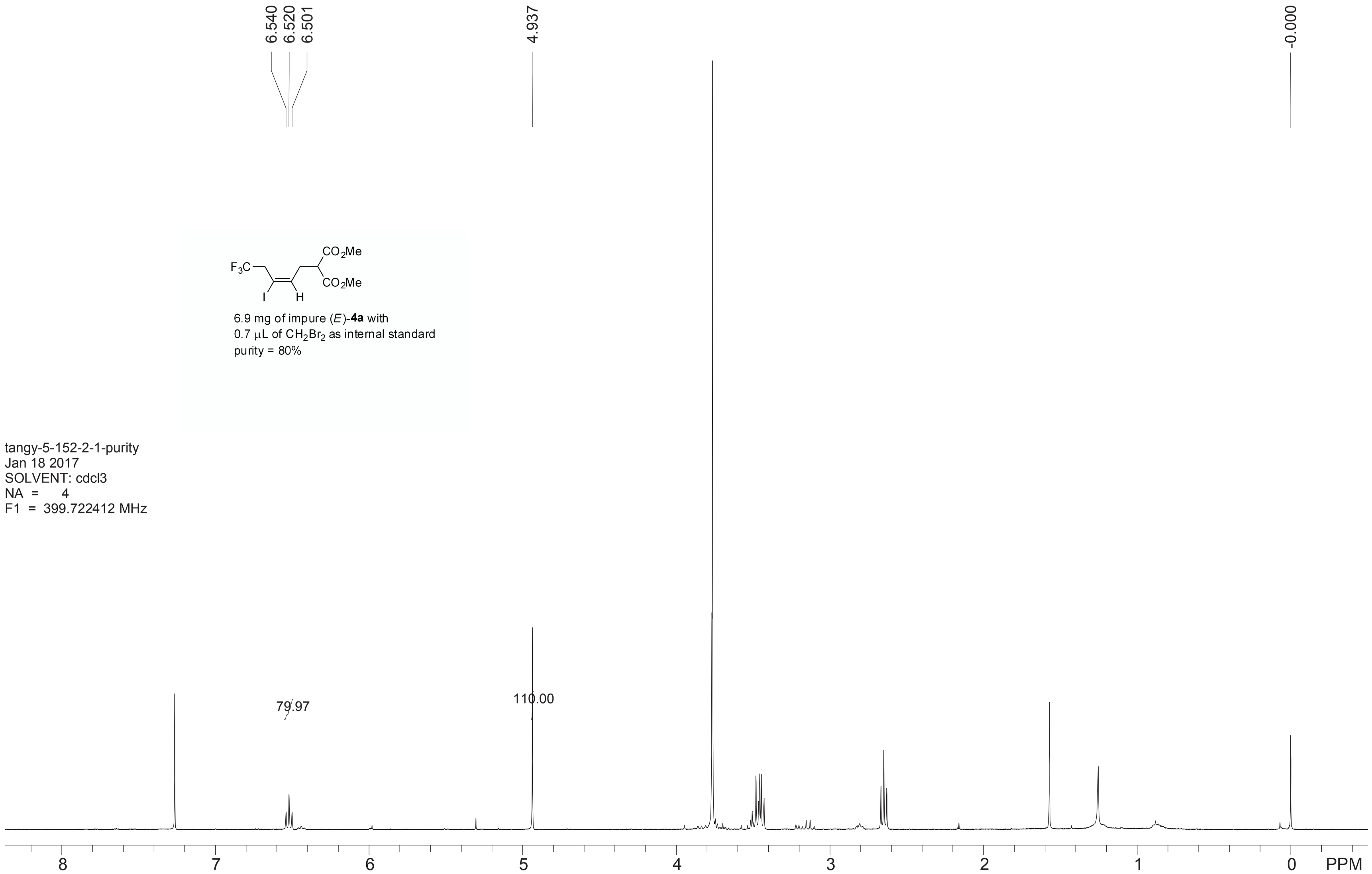
tangy-5-152-2-1-C
Mar 1 2017
SOLVENT: cdcl3
NA = 6500
F1 = 150.829742 MHz



(*E*)-**4a**
purity = 80%

tangy-5-152-2-1-F
Apr 15 2017
SOLVENT: CDCl3
NA = 12
F1 = 376.072876 MHz




6.540
6.520
6.501
4.937
-0.000
CO2Me
F3C
CO2Me
I
H
6.9 mg of impure (E)-4a with
0.7 μL of CH2Br2 as internal standard
purity = 80%
tangy-5-152-2-1-purity
Jan 18 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.722412 MHz
79.97
110.00
8
7
6
5
4
3
2
1
0
PPM

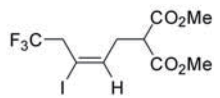
tangy-5-152-2-1-NOESY

Sample Name:
tangy-5-152-2-1-NOESY
Data Collected on:
OMC-NMR600-vnmrs600
Archive directory:
/home/omc/vnmrsys/data
Sample directory:
tangy-5-152-2-1-NOESY_20170301_01
FidFile: NOESY_01

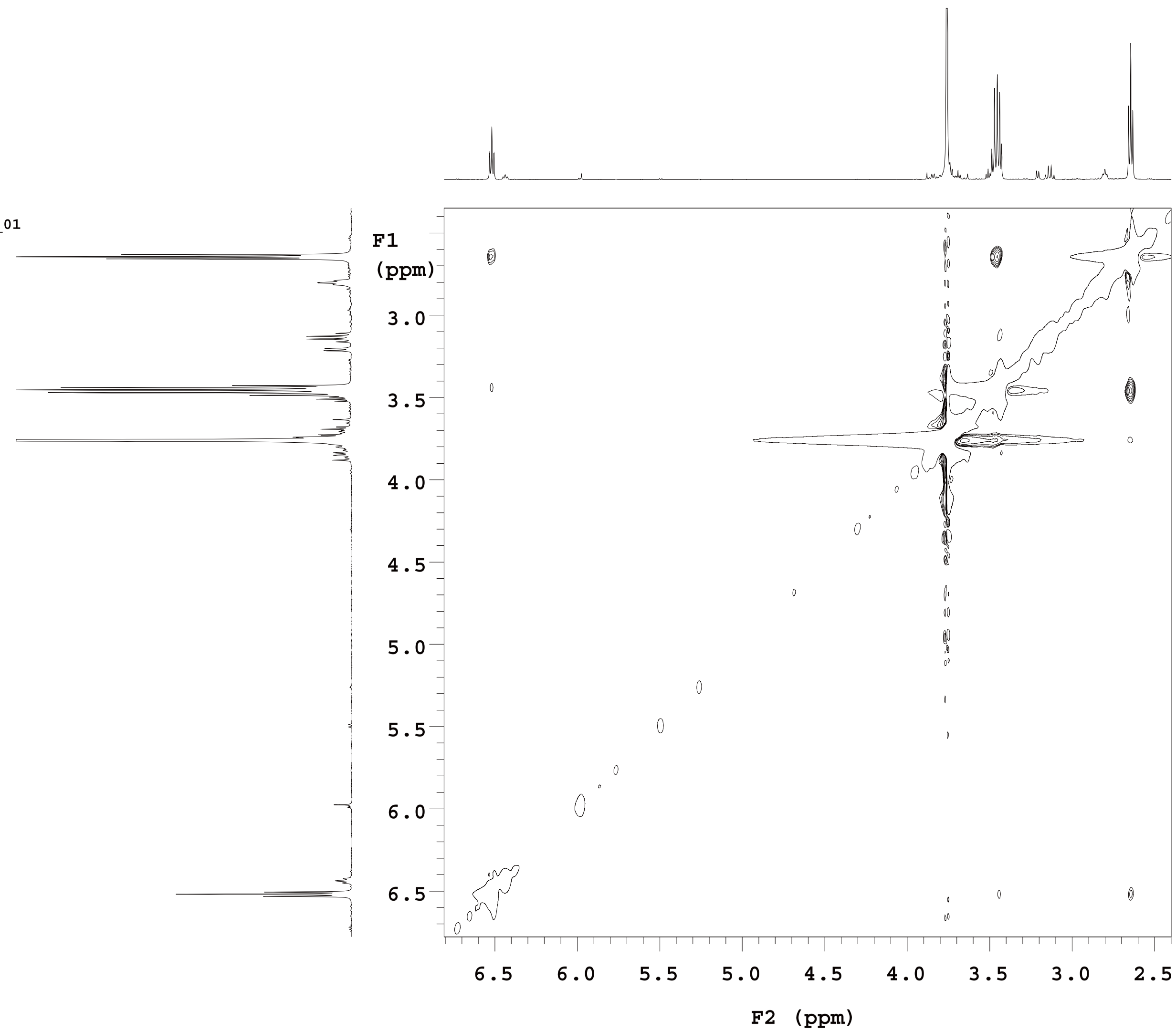
Pulse Sequence: NOESY
Solvent: cdcl3
Data collected on: Mar 1 2017

Temp. 25.0 C / 298.1 K
Operator: omc

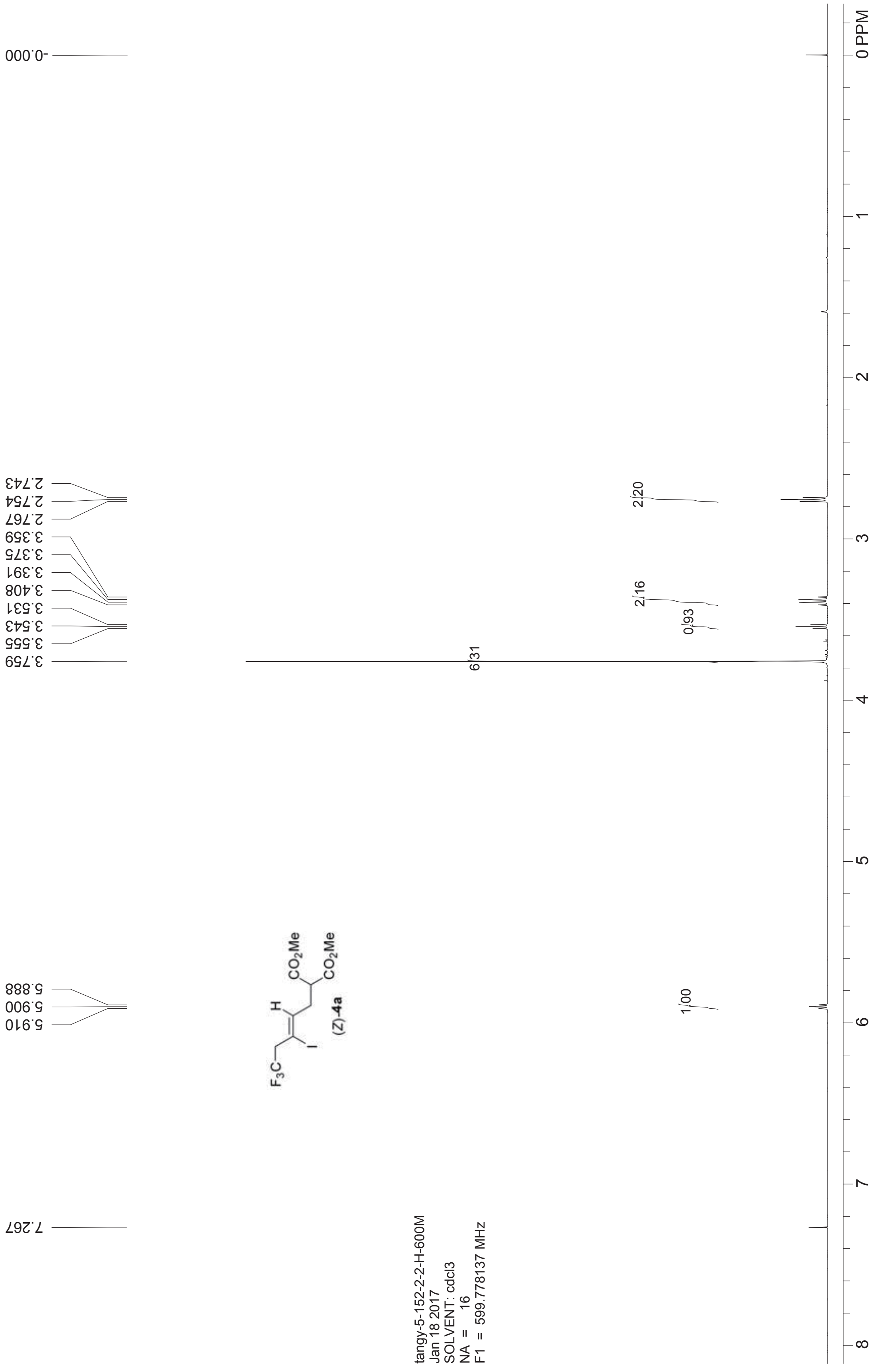
Relax. delay 1.500 sec
Acq. time 0.333 sec
Width 6068.0 Hz
2D Width 6068.0 Hz
8 repetitions
2 x 128 increments
OBSERVE H1, 599.7751422 MHz
DATA PROCESSING
Line broadening 3.0 Hz
Gauss apodization 0.049 sec
F1 DATA PROCESSING
Gauss apodization 0.012 sec
FT size 4096 x 2048
Total time 1 hr, 19 min

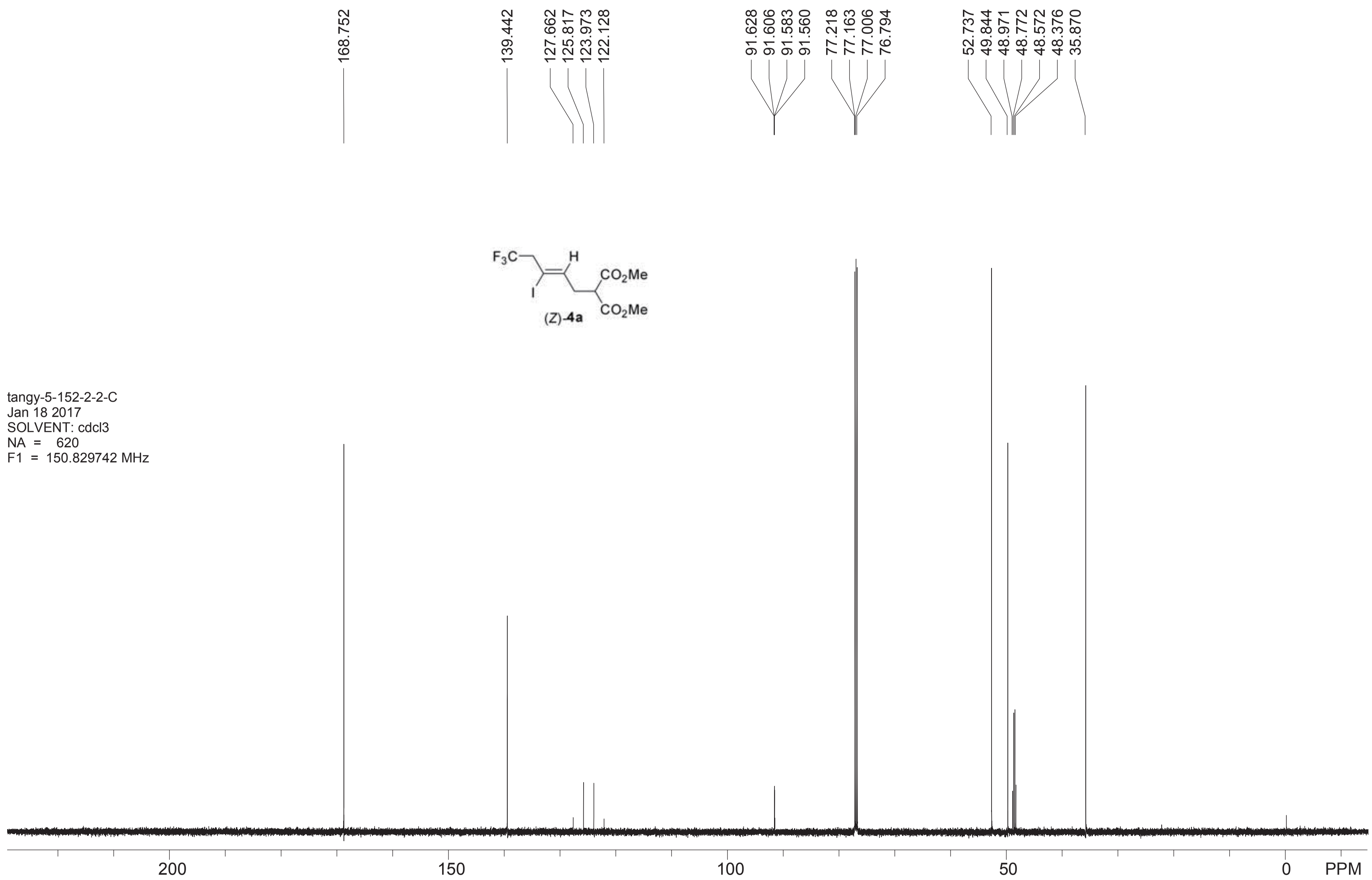


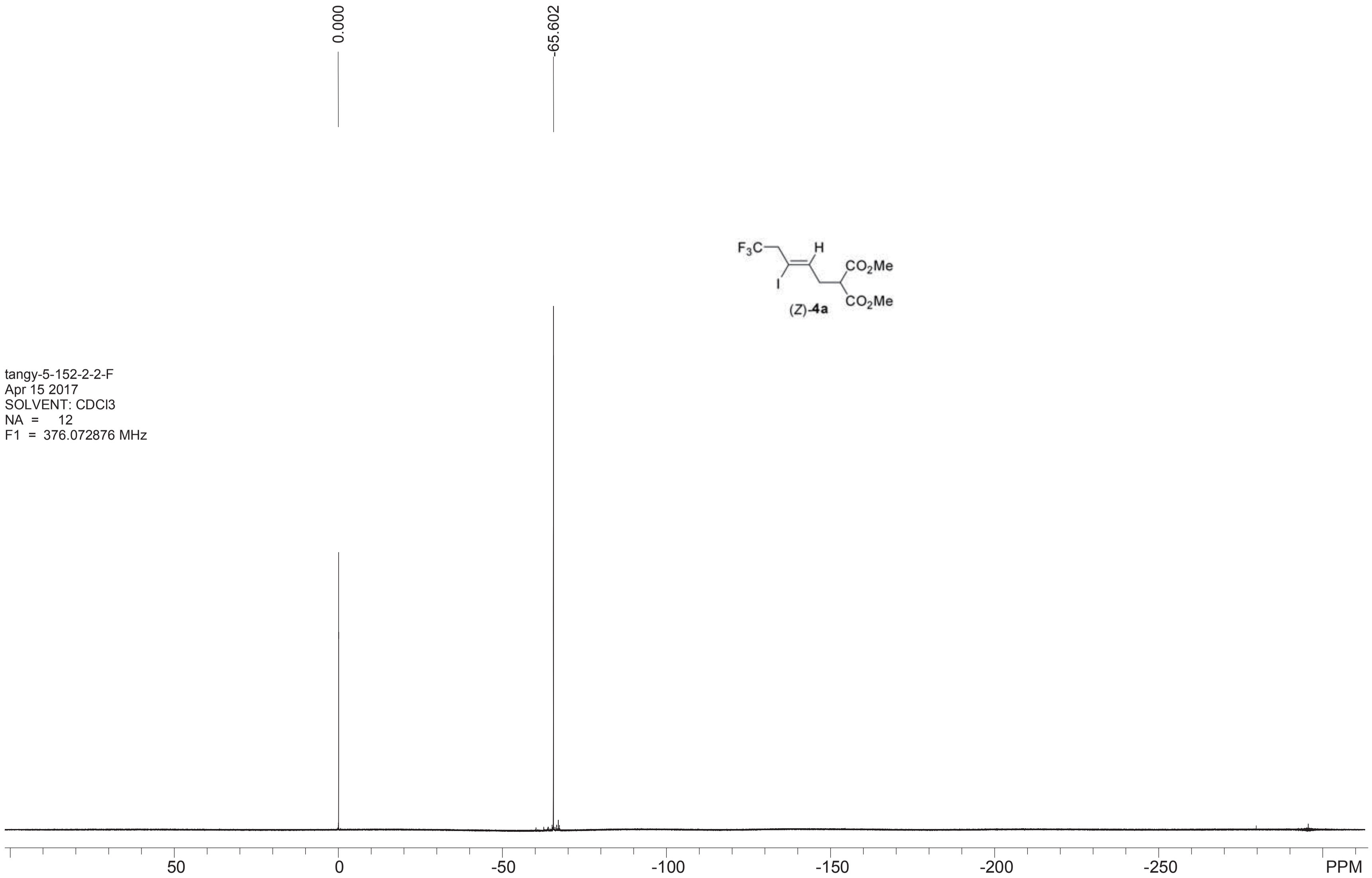
(*E*)-**4a**
purity = 80%



Plotname: --Not assigned--


-0.000
2.743
2.754
2.767
3.359
3.375
3.391
3.408
3.531
3.543
3.555
3.759
5.888
5.900
5.910
7.267
(Z)-4a
tangy-5-152-2-2-H-600M
Jan 18 2017
SOLVENT: cdcl3
NA = 16
F1 = 599.778137 MHz
2.20
2.16
0.93
6.31
1.00
0 PPM
1
2
3
4
5
6
7
8


168.752
139.442
127.662
125.817
123.973
122.128
91.628
91.606
91.583
91.560
77.218
77.163
77.006
76.794
52.737
49.844
48.971
48.772
48.572
48.376
35.870
F3C
H
CO2Me
I
CO2Me
(Z)-4a
tangy-5-152-2-2-C
Jan 18 2017
SOLVENT: cdcl3
NA = 620
F1 = 150.829742 MHz
200
150
100
50
0
PPM



0.000
-65.602
F_3C
H
I
CO_2Me
CO_2Me
tangy-5-152-2-2-F
Apr 15 2017
SOLVENT: CDCl3
NA = 12
F1 = 376.072876 MHz
50
0
-50
-100
-150
-200
-250
PPM

(*Z*)-**4a**

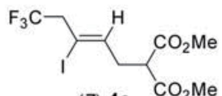
tangy-5-152-3-2-NOESY

Sample Name:
tangy-5-152-3-2-NOESY
Data Collected on:
OMC-NMR600-vnmrs600
Archive directory:
/home/omc/vnmrsys/data
Sample directory:
tangy-5-152-3-2-NOESY_20170118_02
FidFile: NOESY_01

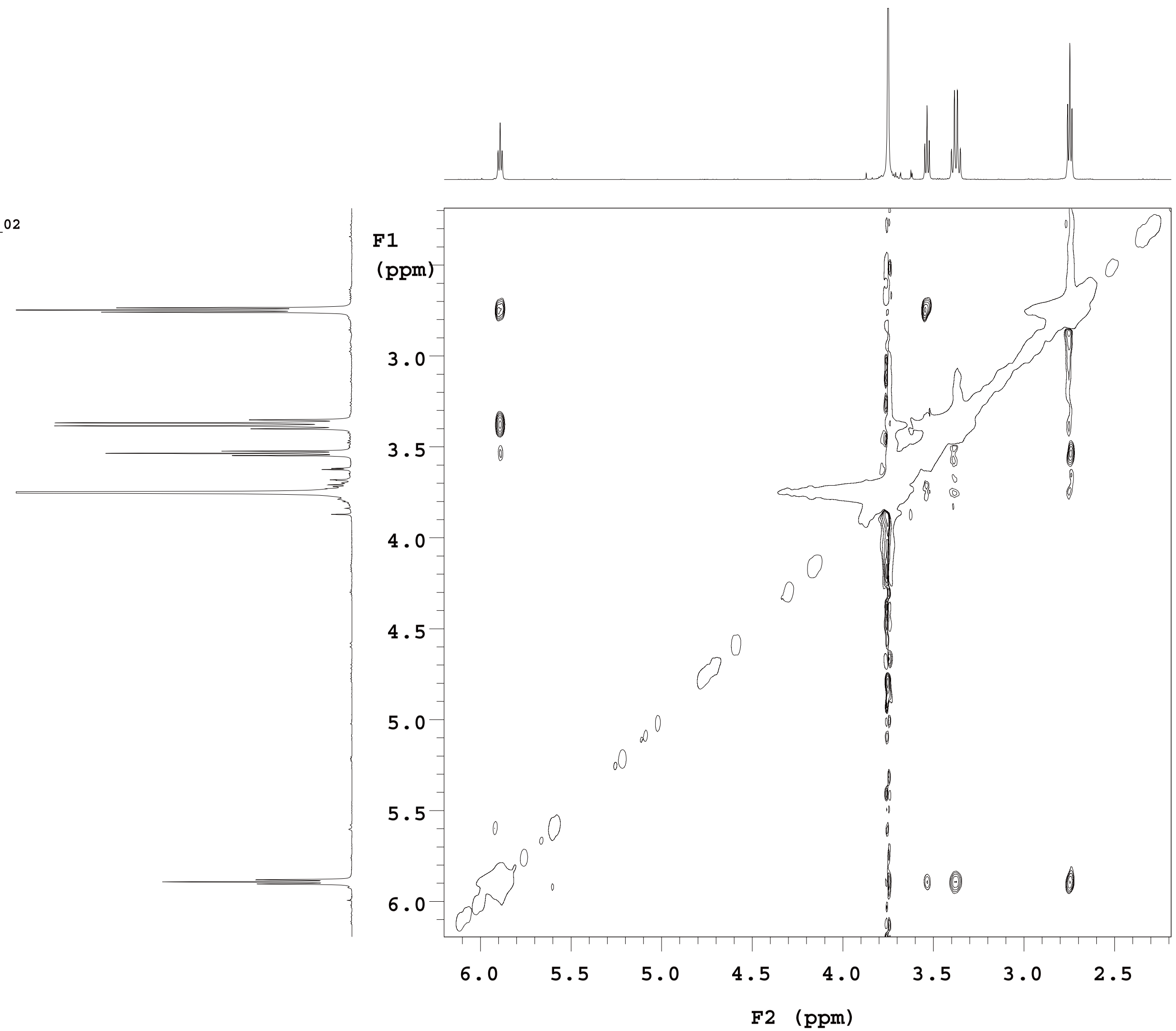
Pulse Sequence: NOESY
Solvent: cdcl3
Data collected on: Jan 18 2017

Temp. 25.0 C / 298.1 K
Operator: omc

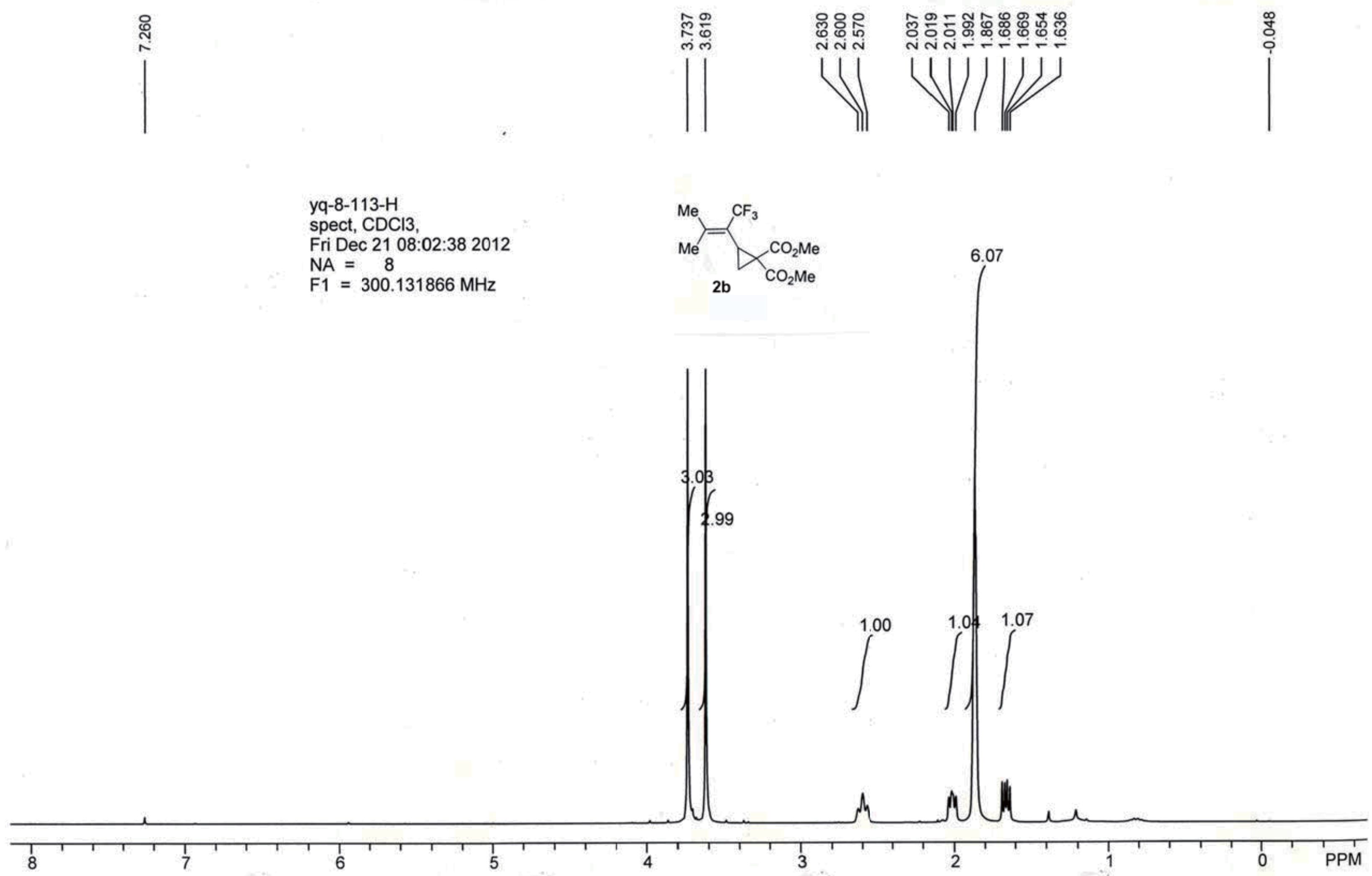
Relax. delay 1.500 sec
Acq. time 0.278 sec
Width 7267.4 Hz
2D Width 7267.4 Hz
4 repetitions
2 x 128 increments
OBSERVE H1, 599.7751422 MHz
DATA PROCESSING
Line broadening 3.0 Hz
Gauss apodization 0.057 sec
F1 DATA PROCESSING
Gauss apodization 0.012 sec
FT size 4096 x 4096
Total time 39 min

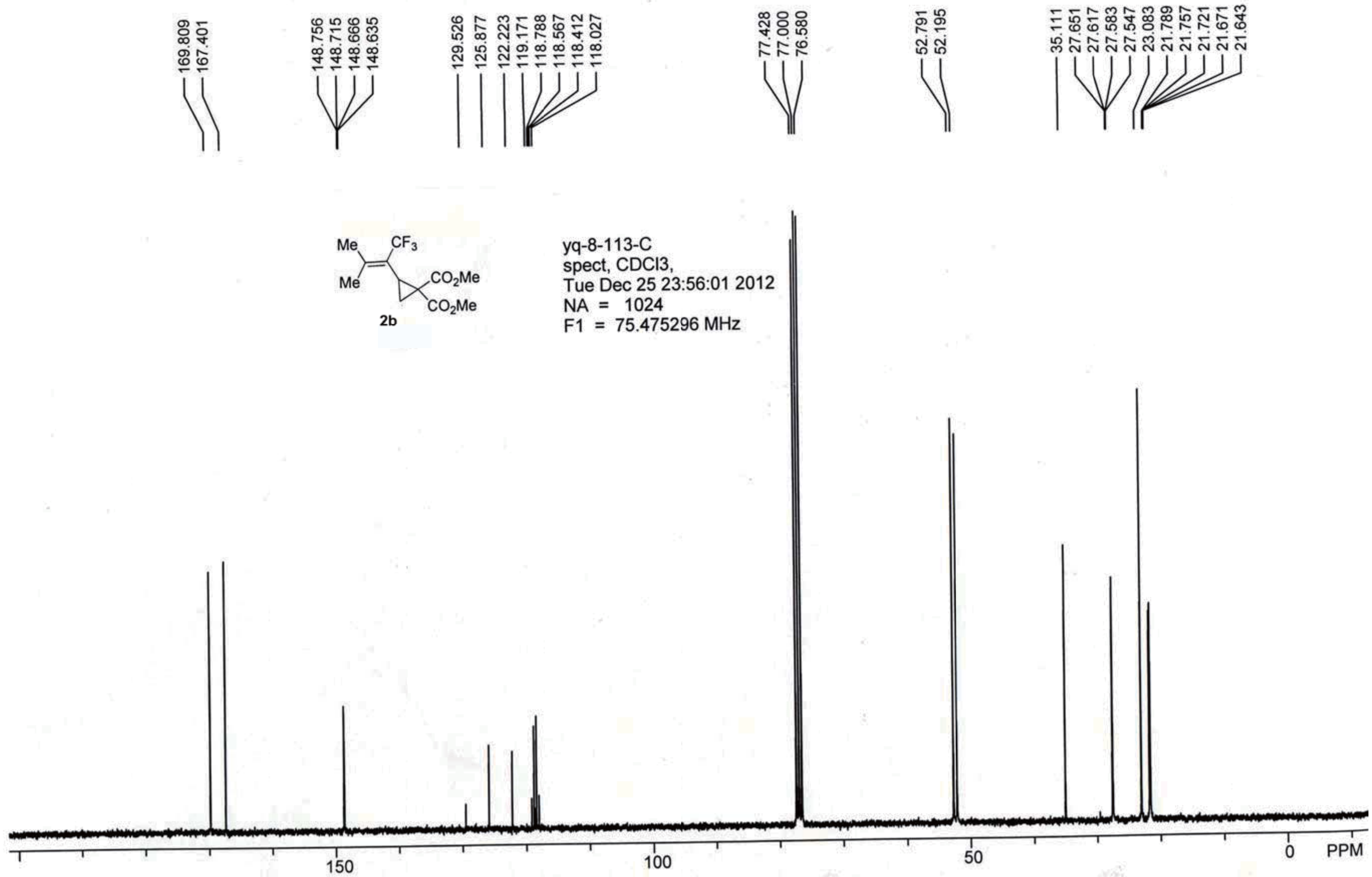


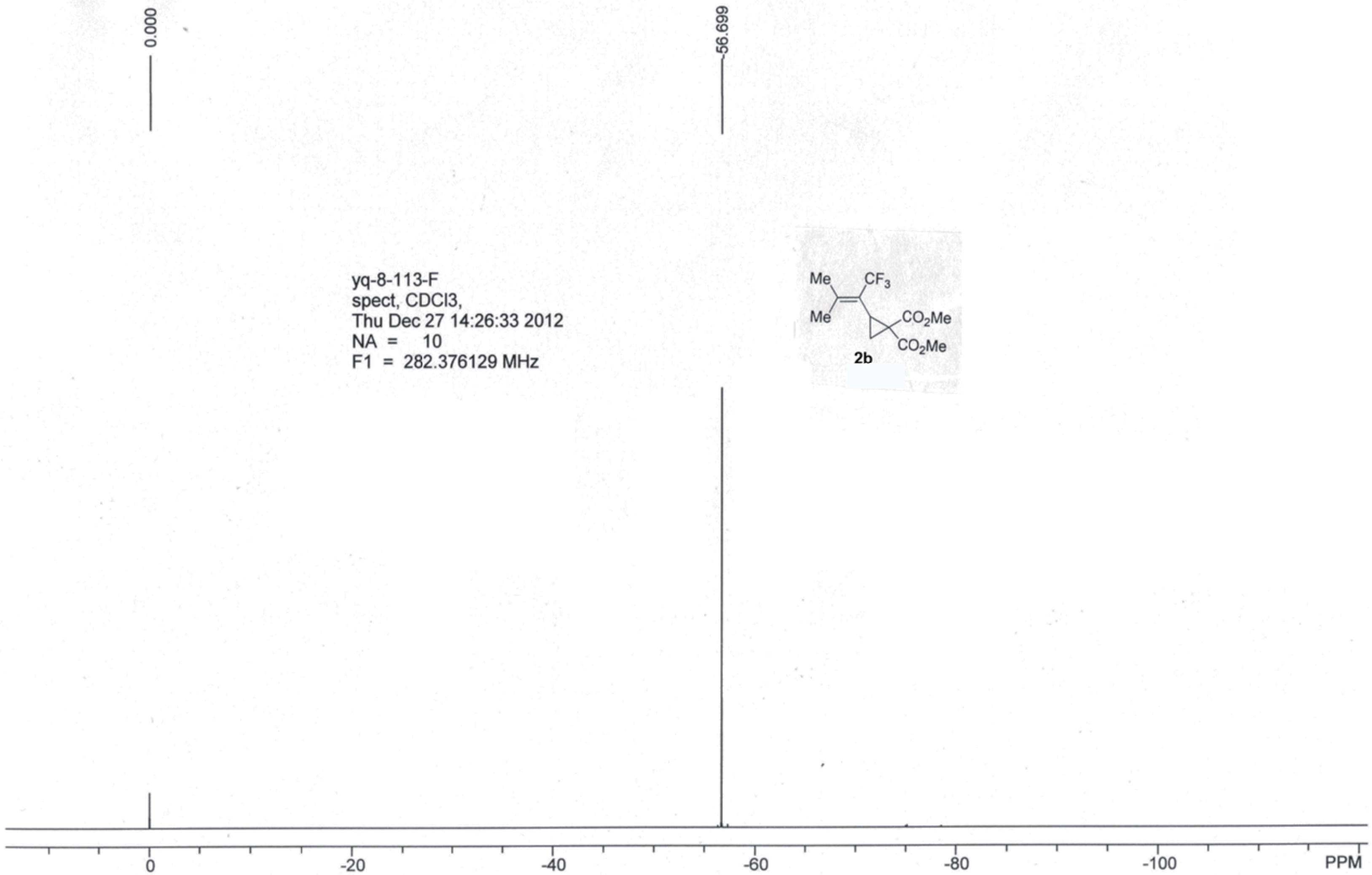
(*Z*)-**4a**



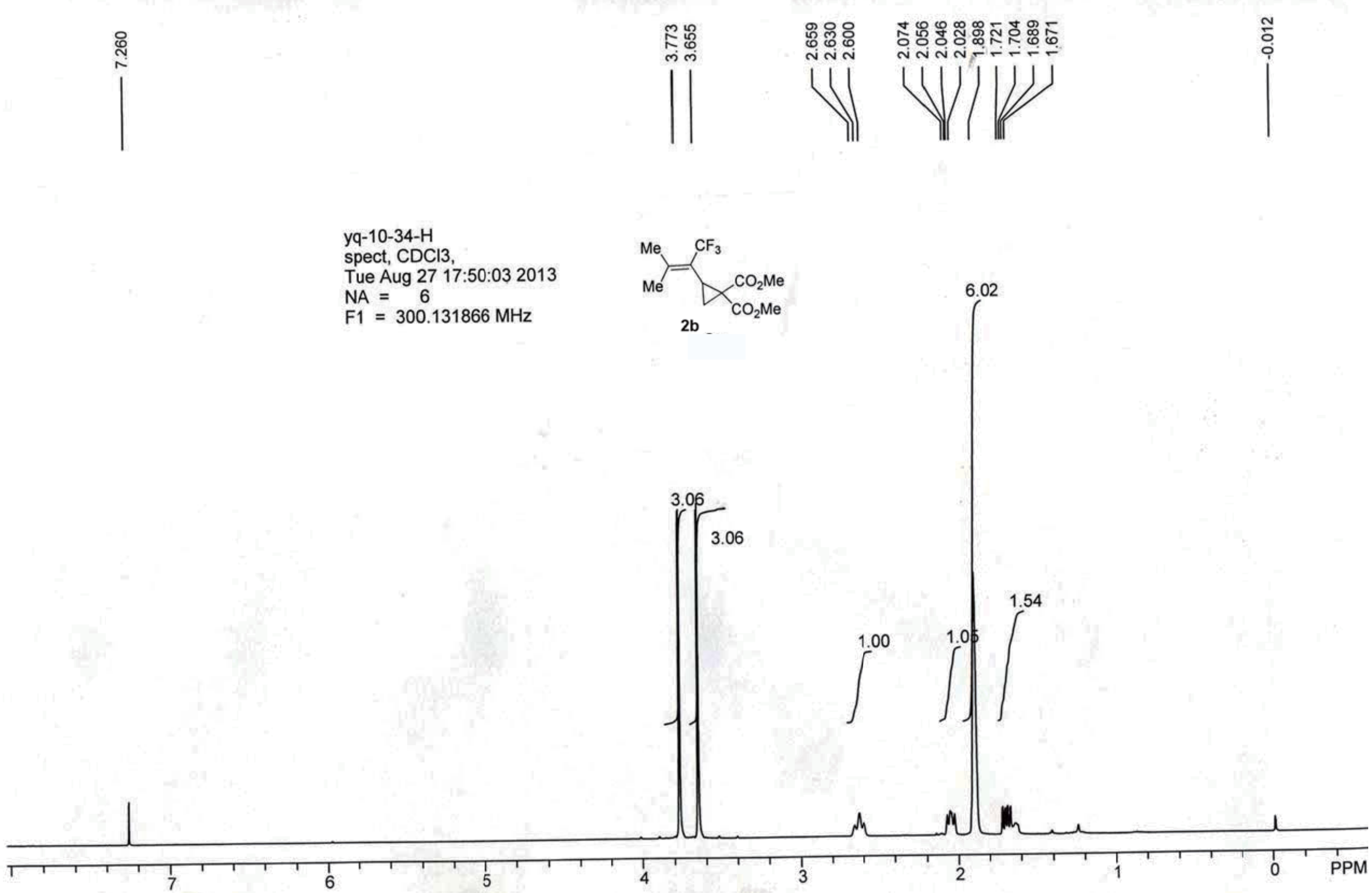
Plotname: --Not assigned--

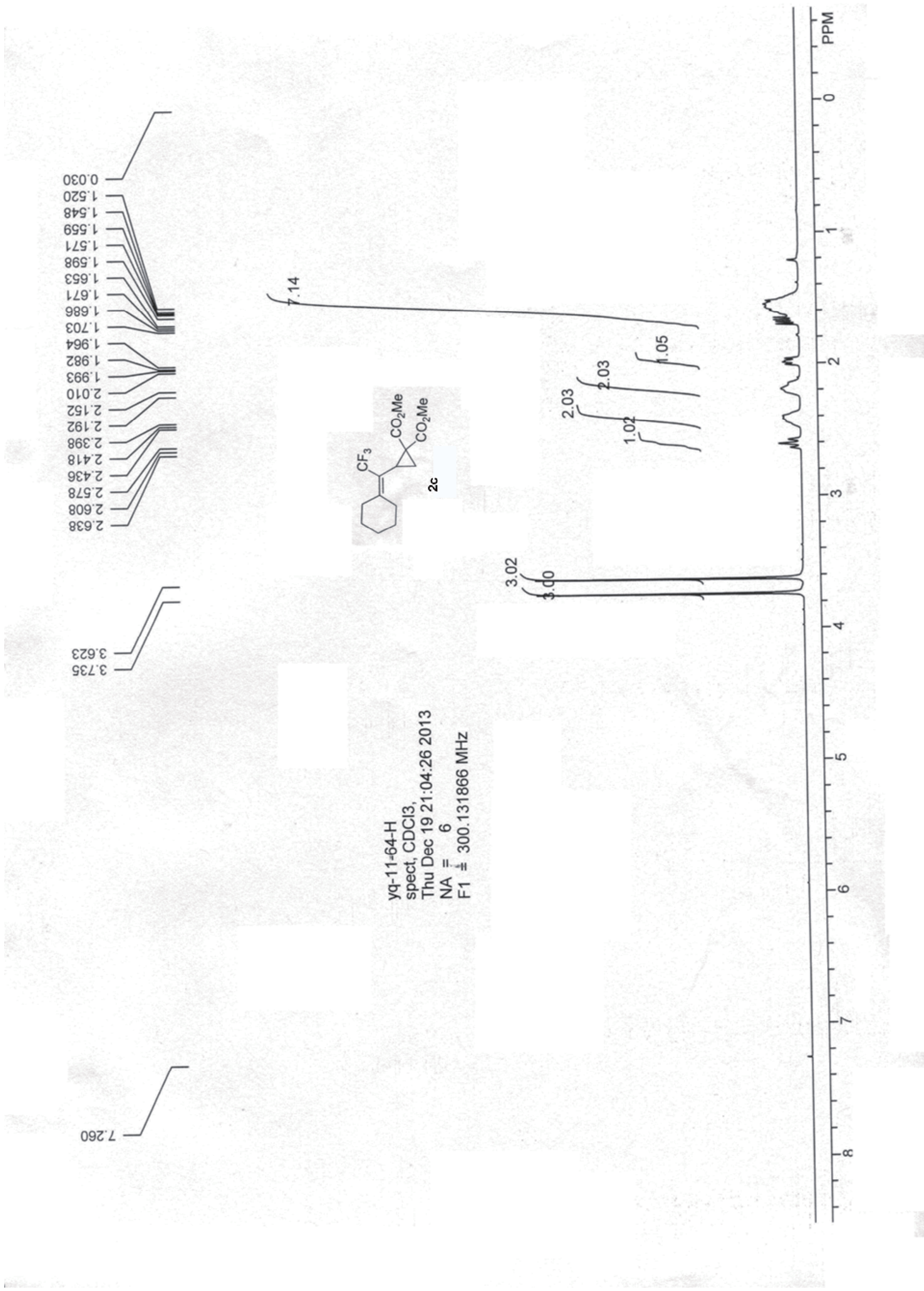

7.260
3.737
3.619
2.630
2.600
2.570
2.037
2.019
2.011
1.992
1.867
1.686
1.669
1.654
1.636
-0.048
yq-8-113-H
spect, CDCl3,
Fri Dec 21 08:02:38 2012
NA = 8
F1 = 300.131866 MHz
Me
CF3
CO2Me
CO2Me
2b
6.07
3.03
2.99
1.00
1.04
1.07
8
7
6
5
4
3
2
1
0
PPM

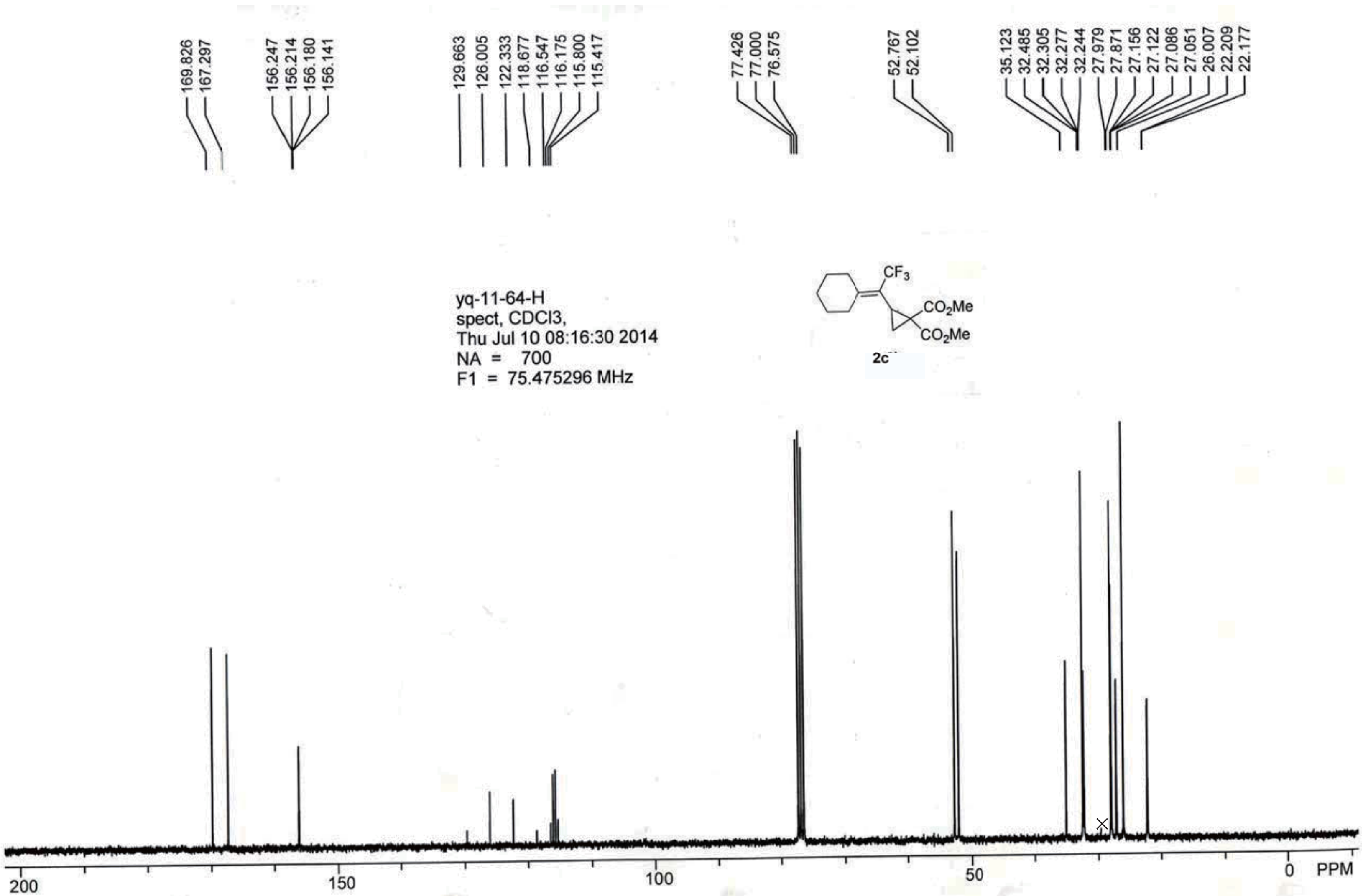

169.809
167.401
148.756
148.715
148.666
148.635
129.526
125.877
122.223
119.171
118.788
118.567
118.412
118.027
77.428
77.000
76.580
52.791
52.195
35.111
27.651
27.617
27.583
27.547
23.083
21.789
21.757
21.721
21.671
21.643
Me
CF3
Me
CO2Me
CO2Me
2b
yq-8-113-C
spect, CDCl3,
Tue Dec 25 23:56:01 2012
NA = 1024
F1 = 75.475296 MHz
150
100
50
0
PPM

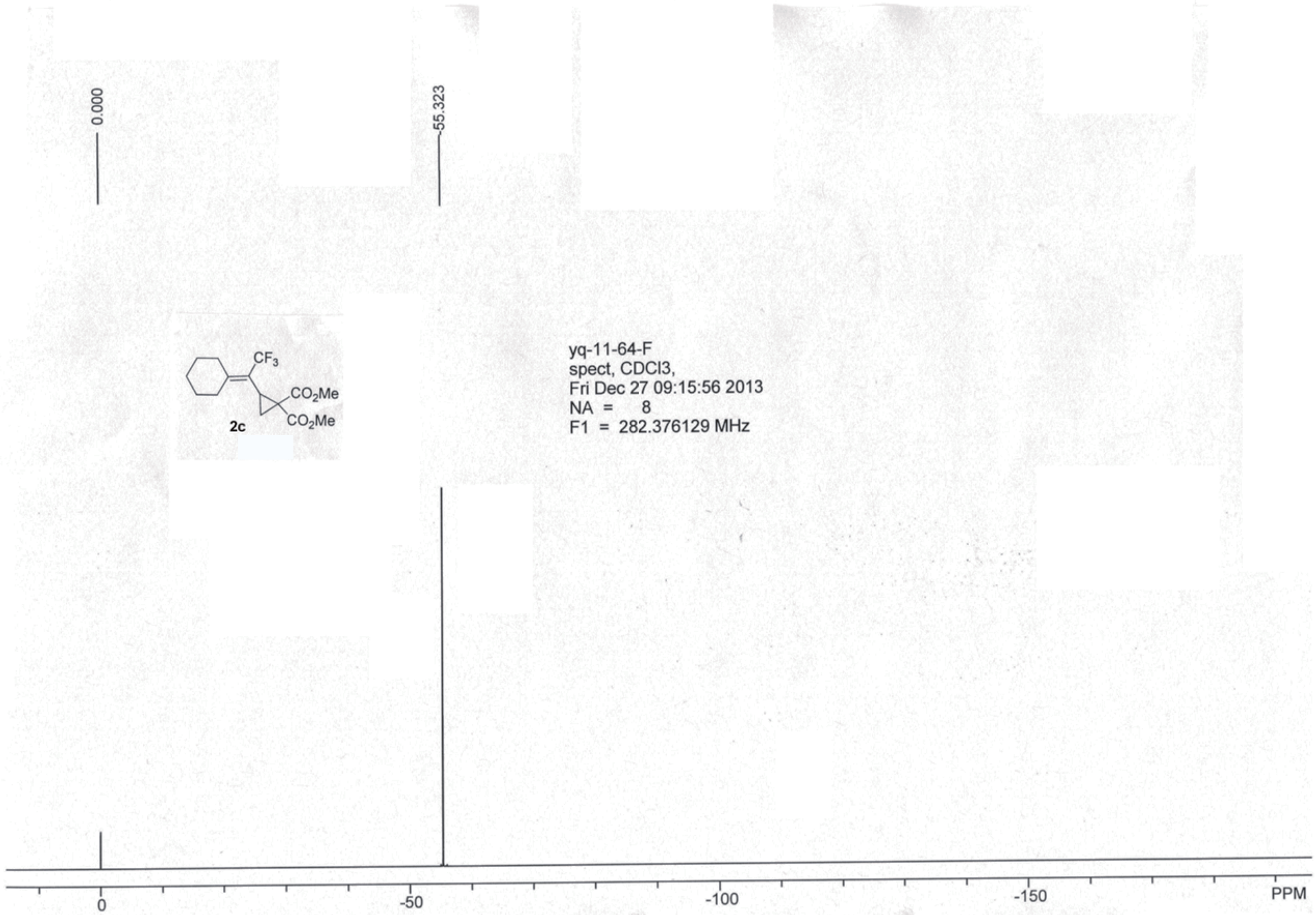

0.000
56.699
yq-8-113-F
spect, CDCl3,
Thu Dec 27 14:26:33 2012
NA = 10
F1 = 282.376129 MHz
0
-20
-40
-60
-80
-100
PPM
Me
CF3
Me
CO2Me
CO2Me

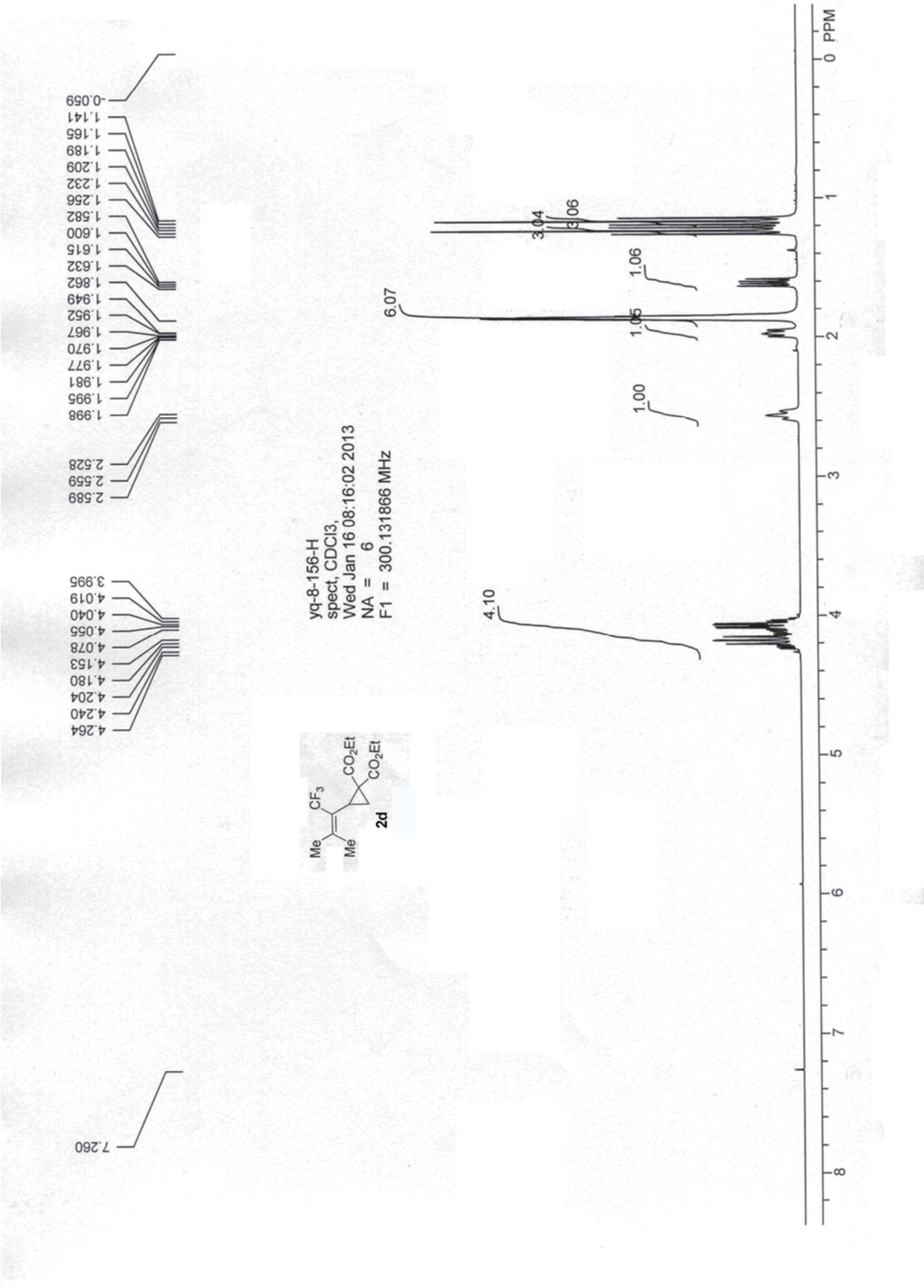
2b

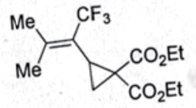

7.260
3.773
3.655
2.659
2.630
2.600
2.074
2.056
2.046
2.028
1.898
1.721
1.704
1.689
1.671
-0.012
yq-10-34-H
spect, CDCl3,
Tue Aug 27 17:50:03 2013
NA = 6
F1 = 300.131866 MHz
Me
CF3
Me
CO2Me
CO2Me
2b
6.02
3.06
3.06
1.54
1.00
1.05
7
6
5
4
3
2
1
0
PPM


yq-11-64-H
spect, CDCl3,
Thu Dec 19 21:04:26 2013
NA = 6
F1 = 300.131866 MHz
7.260
3.735
3.623
2.638
2.608
2.578
2.436
2.418
2.398
2.192
2.152
2.010
1.993
1.982
1.964
1.703
1.686
1.671
1.653
1.598
1.571
1.559
1.548
1.520
0.030
CF3
CO2Me
CO2Me
2c
3.02
3.00
2.03
1.02
2.03
1.05
7.14
PPM

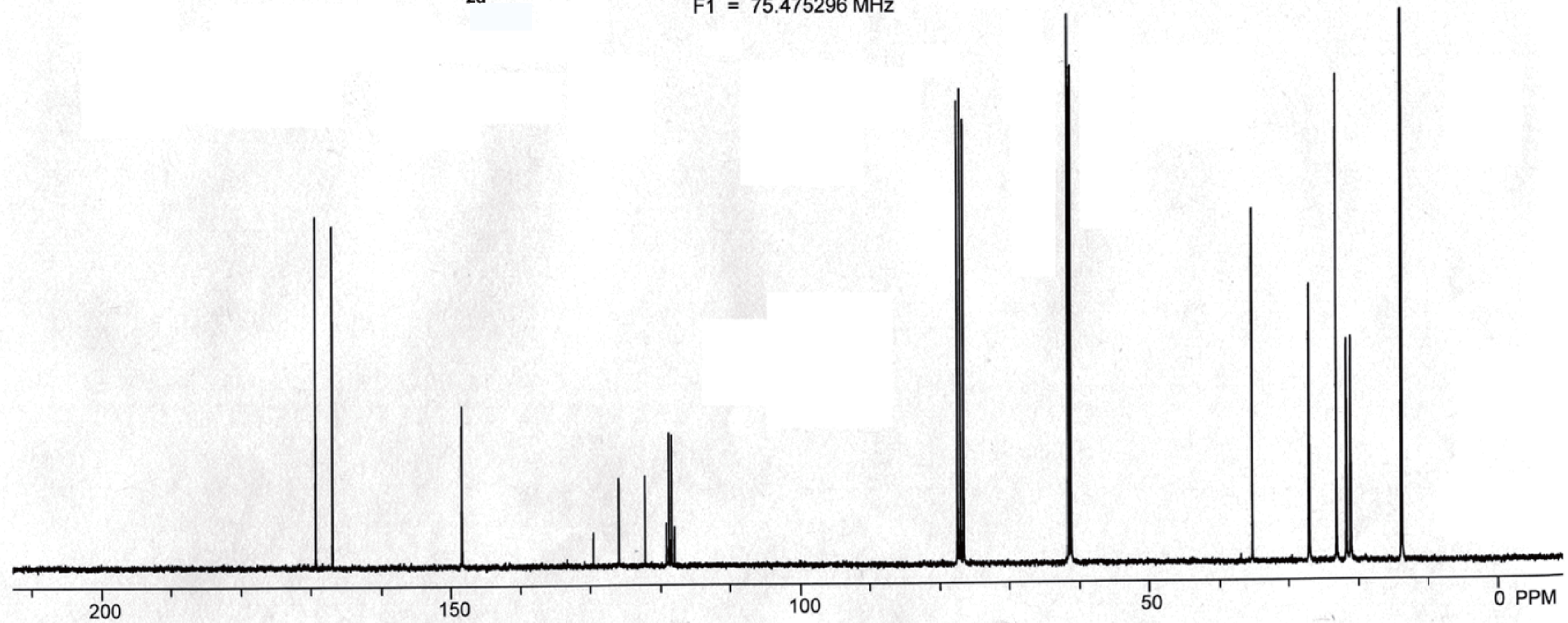

169.826
167.297
156.247
156.214
156.180
156.141
129.663
126.005
122.333
118.677
116.547
116.175
115.800
115.417
77.426
77.000
76.575
52.767
52.102
35.123
32.485
32.305
32.277
32.244
27.979
27.871
27.156
27.122
27.086
27.051
26.007
22.209
22.177
yq-11-64-H
spect, CDCl3,
Thu Jul 10 08:16:30 2014
NA = 700
F1 = 75.475296 MHz
CF3
CO2Me
CO2Me
2c
200
150
100
50
0
PPM

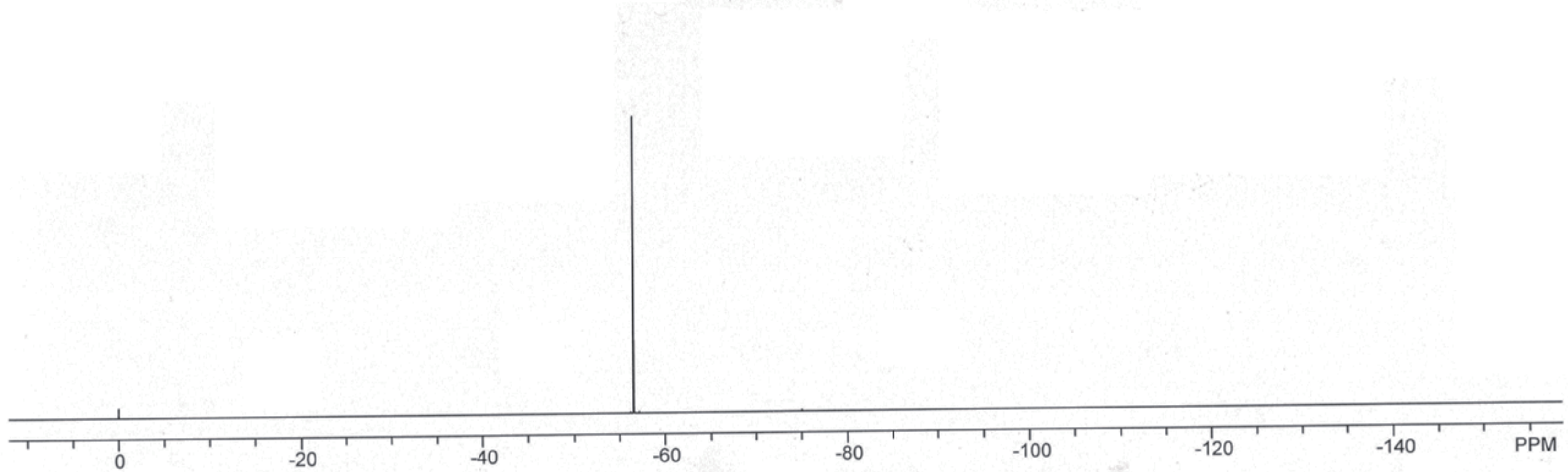

0.000
-55.323
CF3
CO2Me
CO2Me
2c
yq-11-64-F
spect, CDCl3,
Fri Dec 27 09:15:56 2013
NA = 8
F1 = 282.376129 MHz
0
-50
-100
-150
PPM


yq-8-156-H
spect, CDCl3,
Wed Jan 16 08:16:02 2013
NA = 6
F1 = 300.131866 MHz
2d
PPM

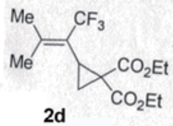


2d

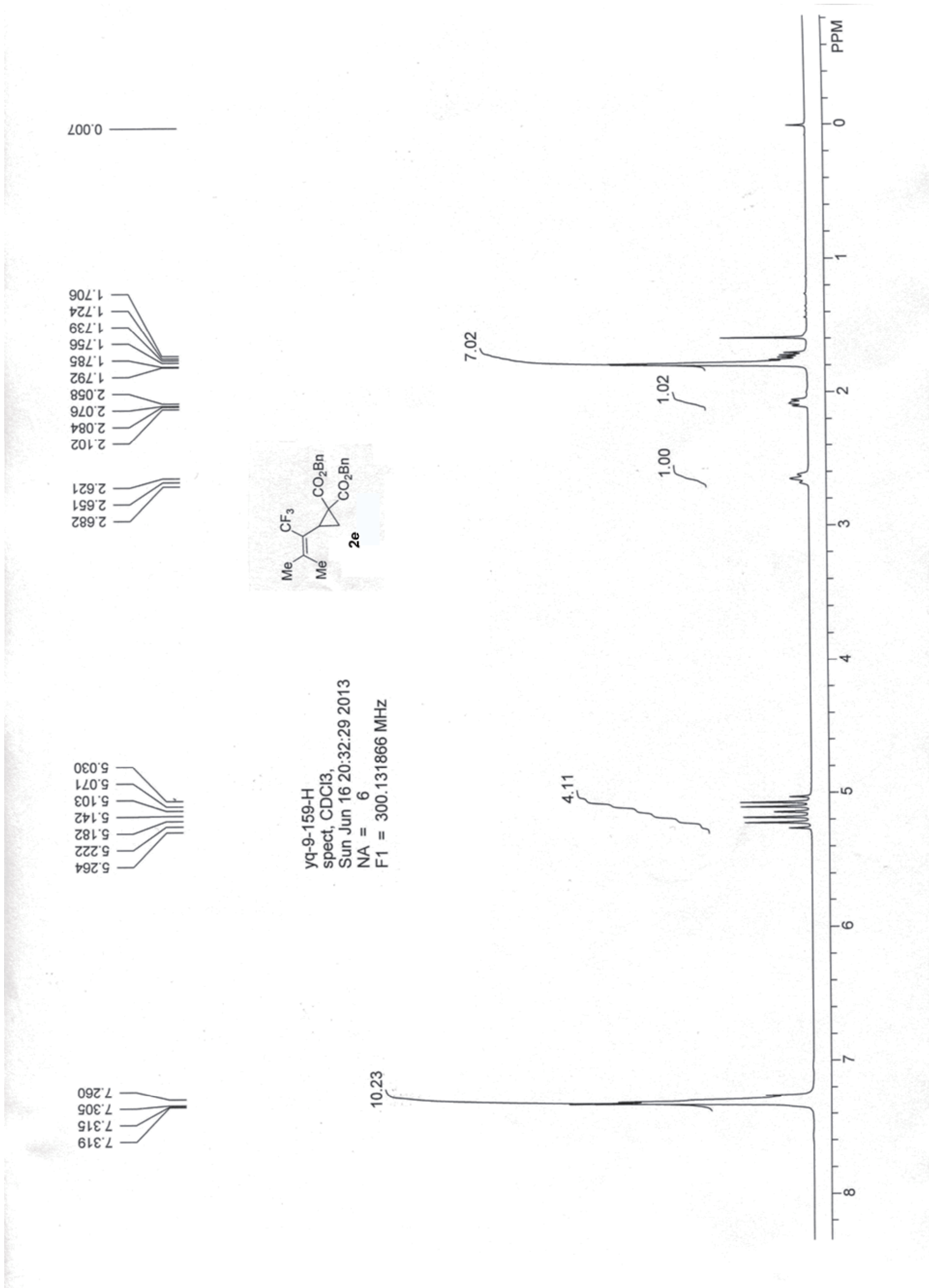

yq-8-156-C
spect, CDCl3,
Wed Jan 16 17:37:01 2013
NA = 916
F1 = 75.475296 MHz
169.328
166.951
148.438
148.387
148.356
148.310
129.525
125.877
122.230
119.197
118.817
118.574
118.435
118.047
77.425
77.000
76.574
61.541
61.192
35.322
27.109
27.077
27.045
27.004
23.101
21.682
21.656
21.071
21.039
13.880
13.744
200
150
100
50
0 PPM

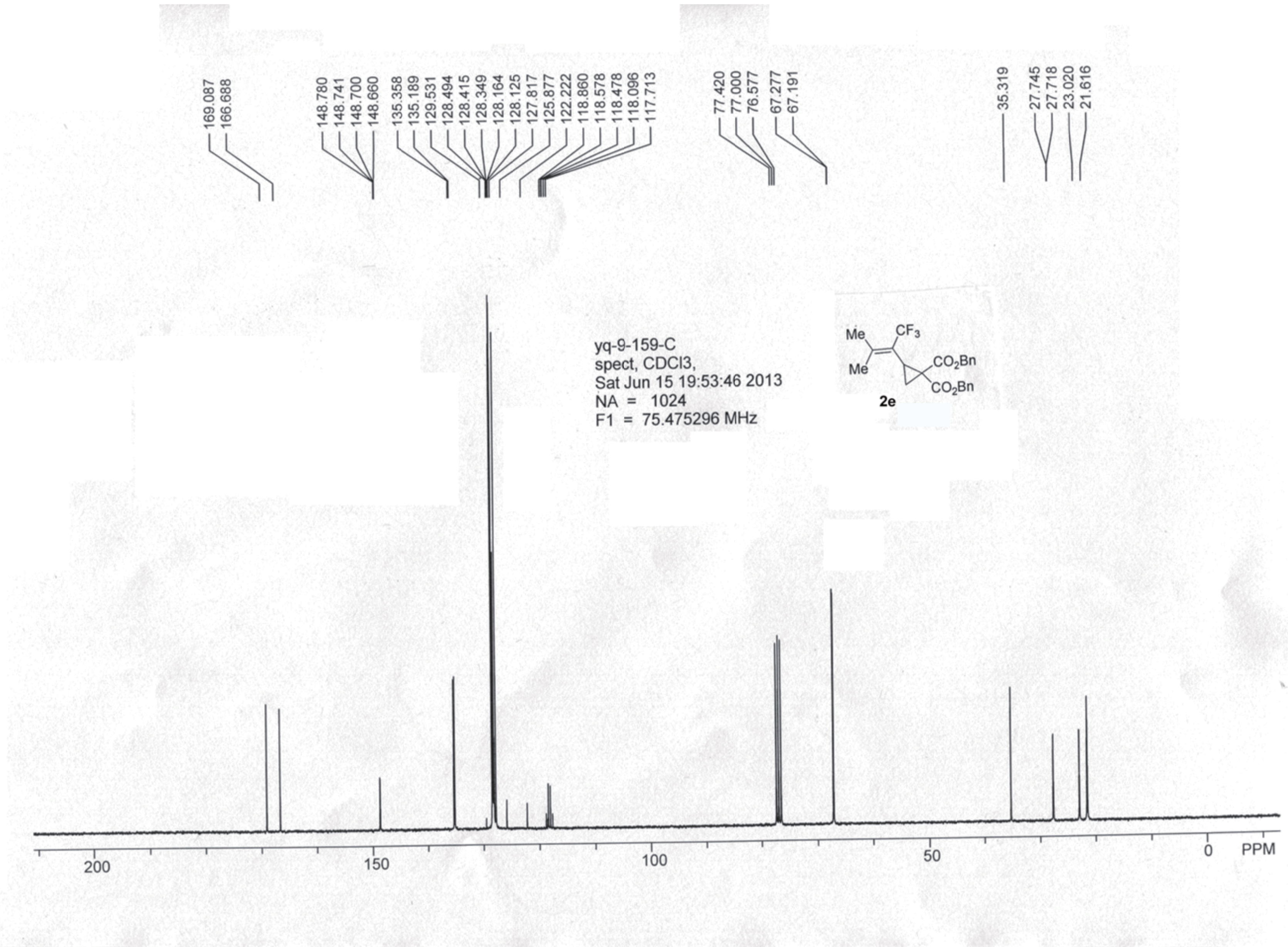


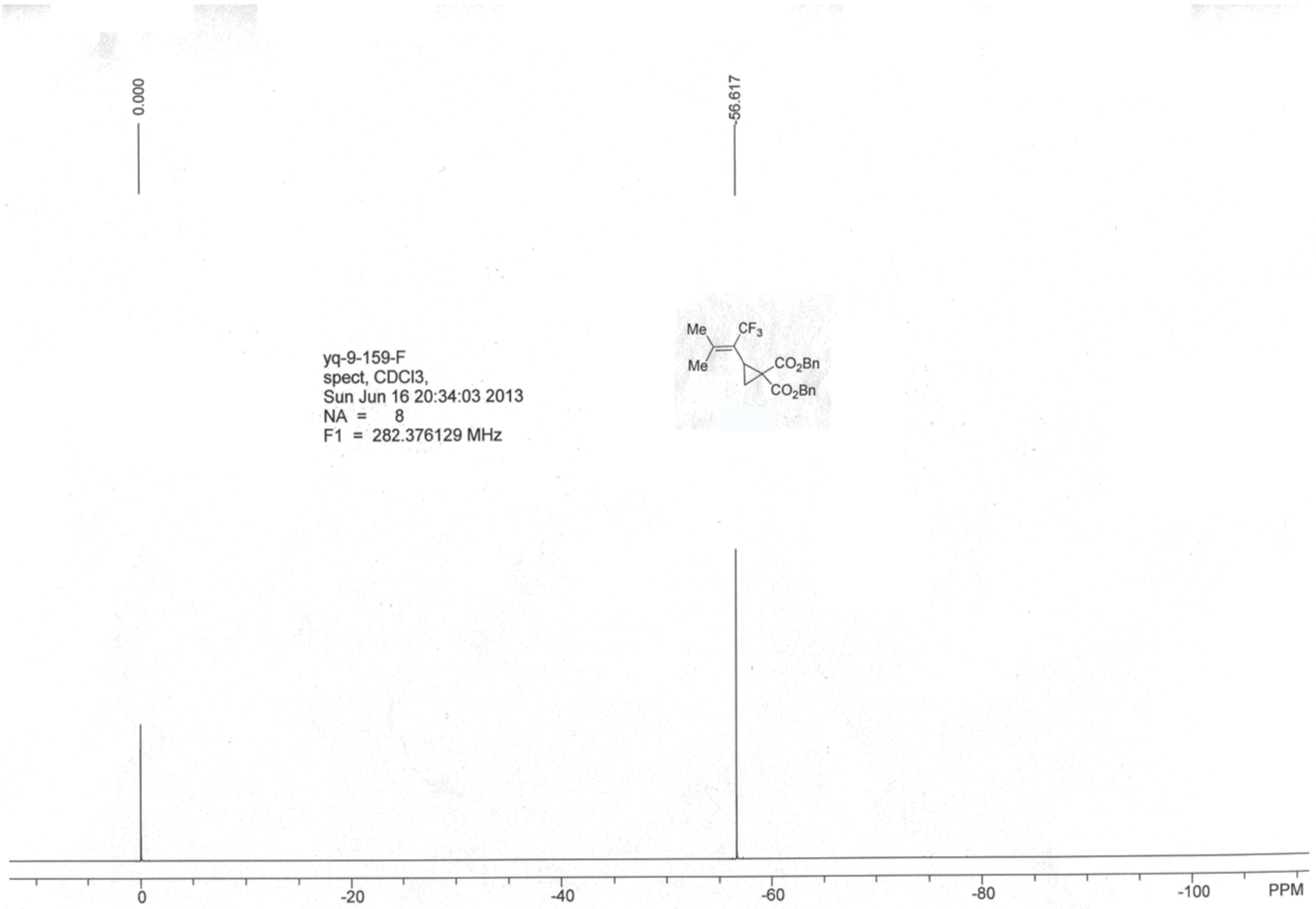
yq-8-156-F
spect, CDCl3,
Fri Jan 18 10:16:00 2013
NA = 16
F1 = 282.376129 MHz

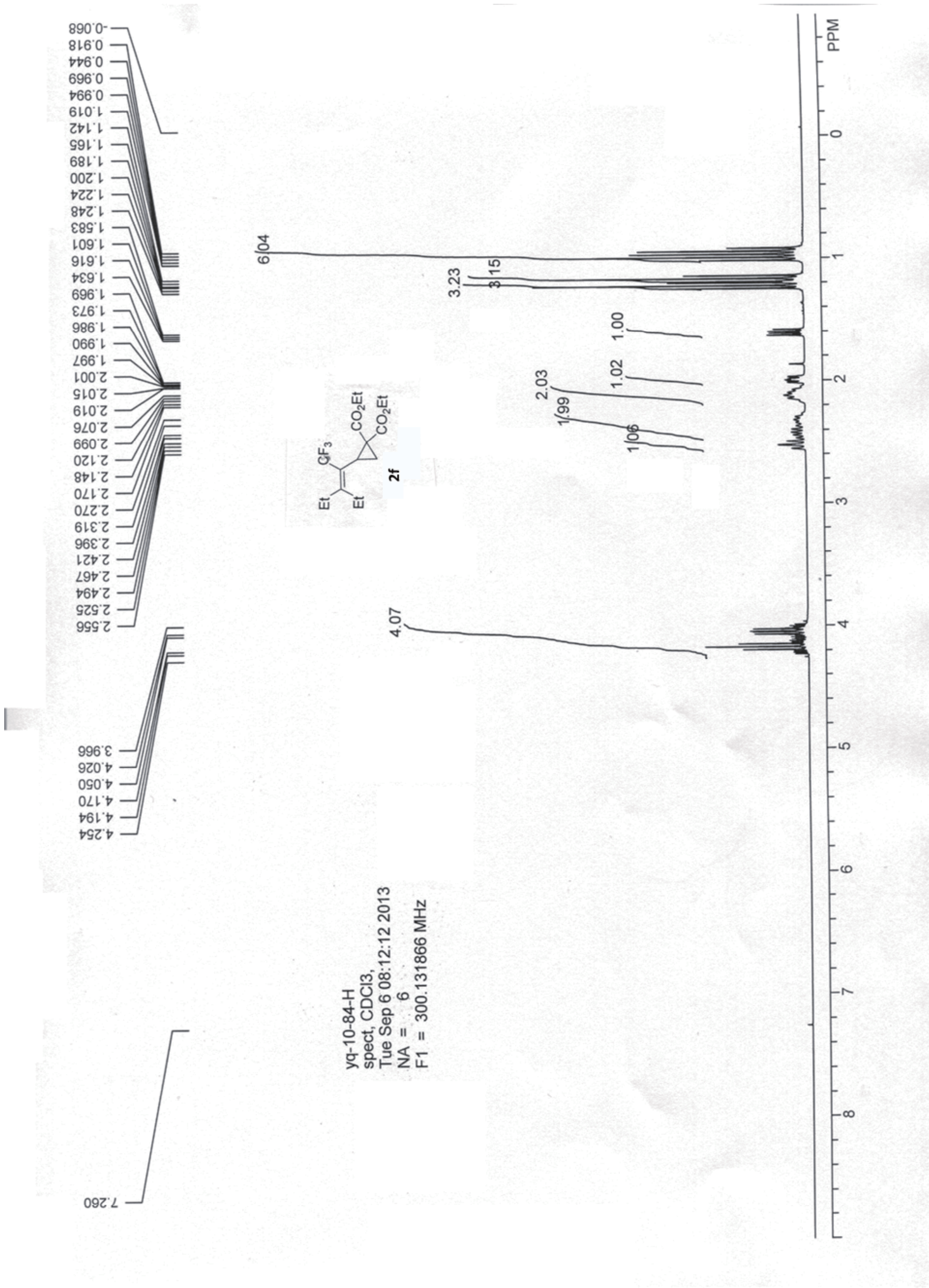


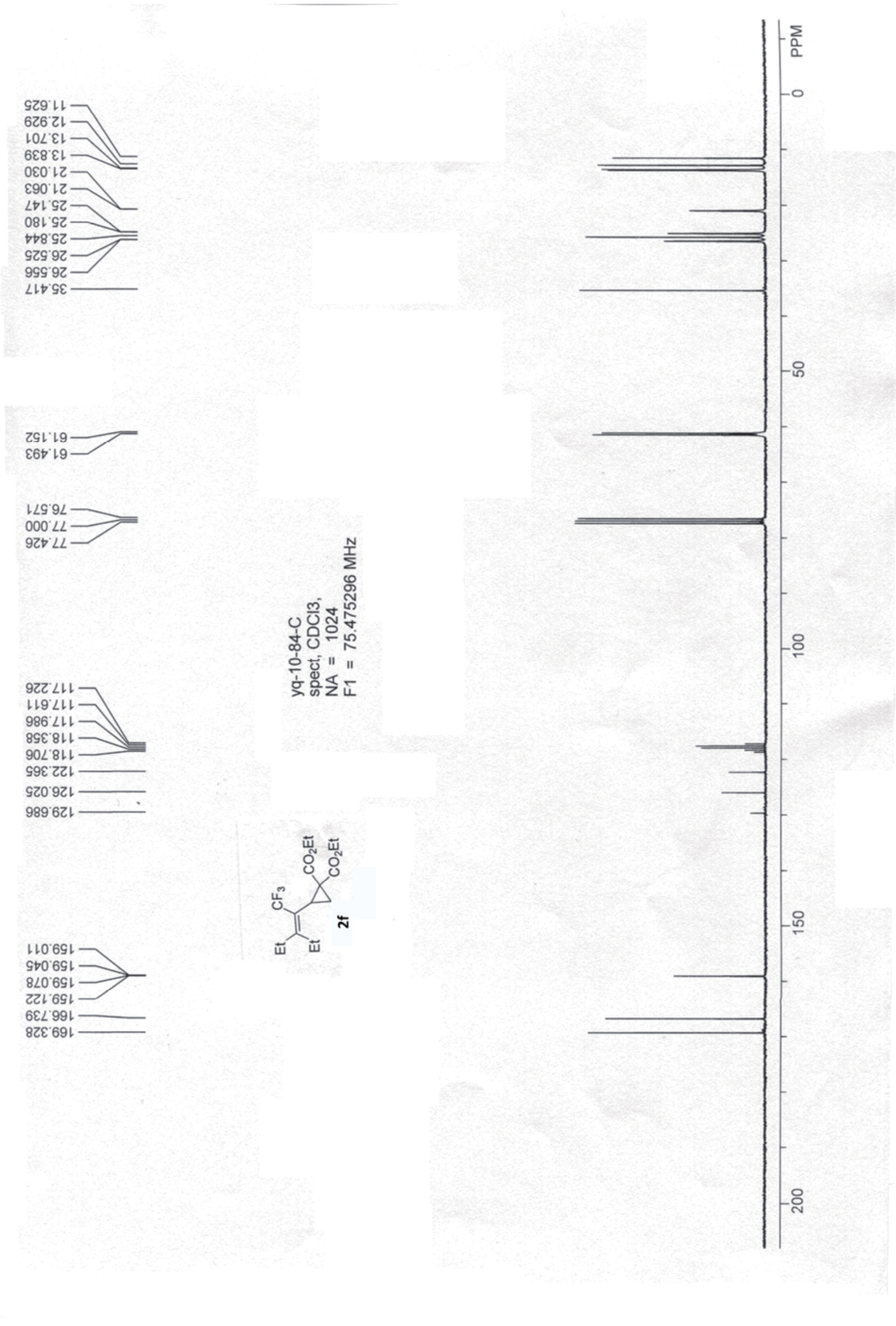
2d


yq-9-159-H
spect, CDCl3,
Sun Jun 16 20:32:29 2013
NA = 6
F1 = 300.131866 MHz
2e
7.319
7.315
7.305
7.260
5.264
5.222
5.182
5.142
5.103
5.071
5.030
2.682
2.651
2.621
2.102
2.084
2.076
2.058
1.792
1.785
1.756
1.739
1.724
1.706
0.007
10.23
4.11
1.00
1.02
7.02
PPM

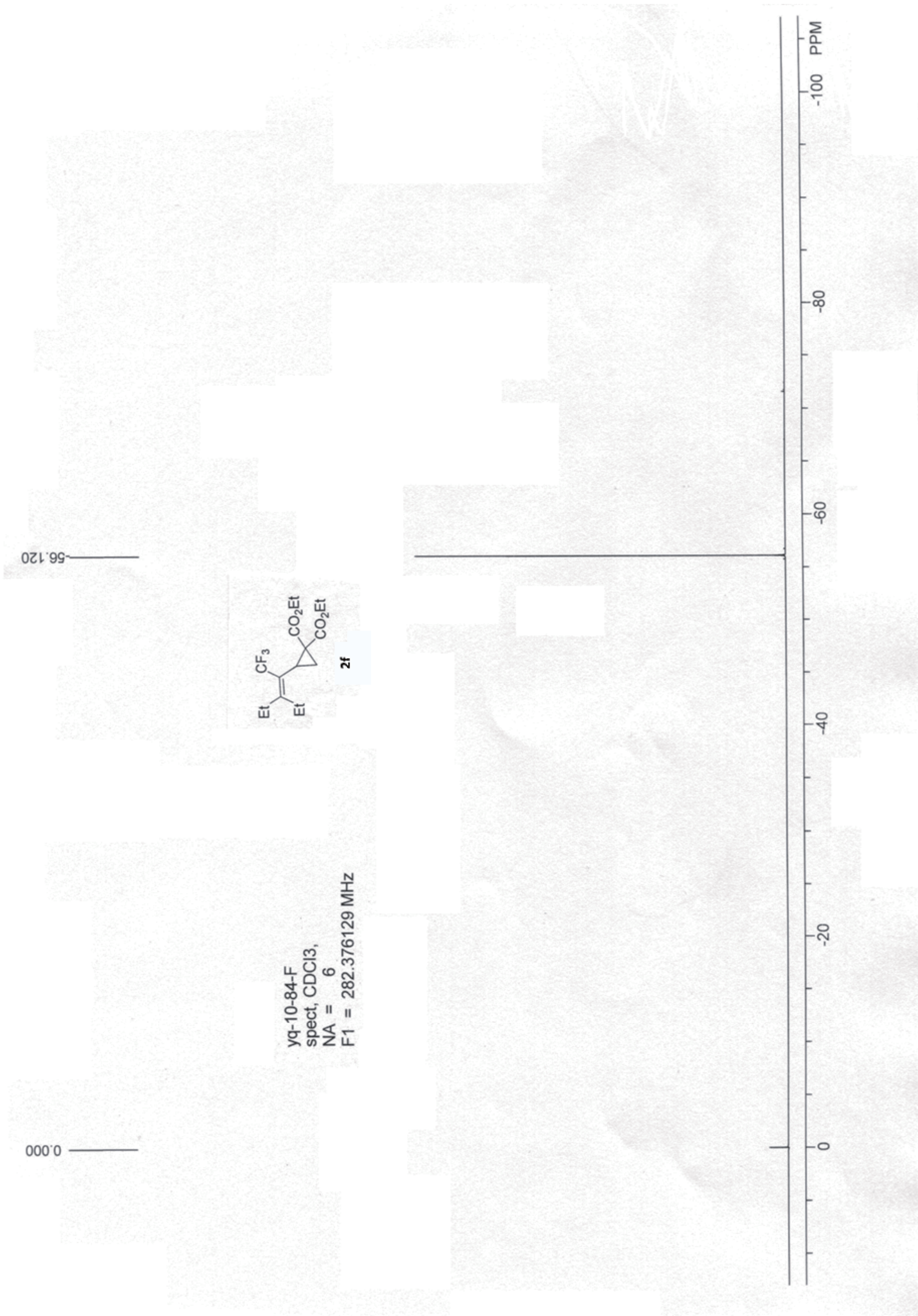

169.087
166.688
148.780
148.741
148.700
148.660
135.358
135.189
129.531
128.494
128.415
128.349
128.164
128.125
127.817
125.877
122.222
118.860
118.578
118.478
118.096
117.713
77.420
77.000
76.577
67.277
67.191
35.319
27.745
27.718
23.020
21.616
yq-9-159-C
spect, CDCl3,
Sat Jun 15 19:53:46 2013
NA = 1024
F1 = 75.475296 MHz
Me
Me
CF3
CO2Bn
CO2Bn
2e
200
150
100
50
0
PPM

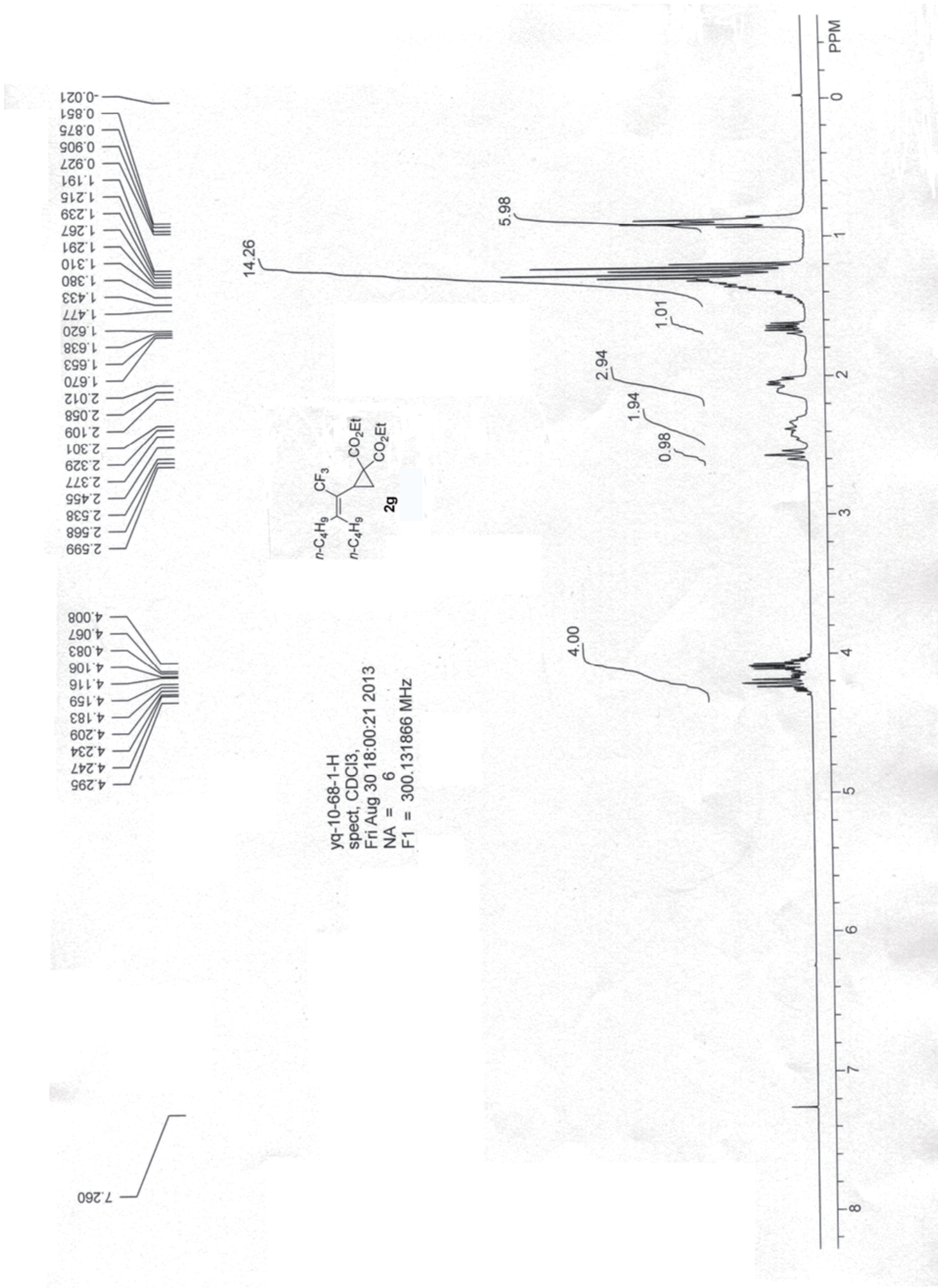

0.000
-56.617
yq-9-159-F
spect, CDCl3,
Sun Jun 16 20:34:03 2013
NA = 8
F1 = 282.376129 MHz
Me
Me
CF3
CO2Bn
CO2Bn
0
-20
-40
-60
-80
-100
PPM


yq-10-84-H
spect, CDCl3,
Tue Sep 6 08:12:12 2013
NA = 6
F1 = 300.131866 MHz
2f
PPM

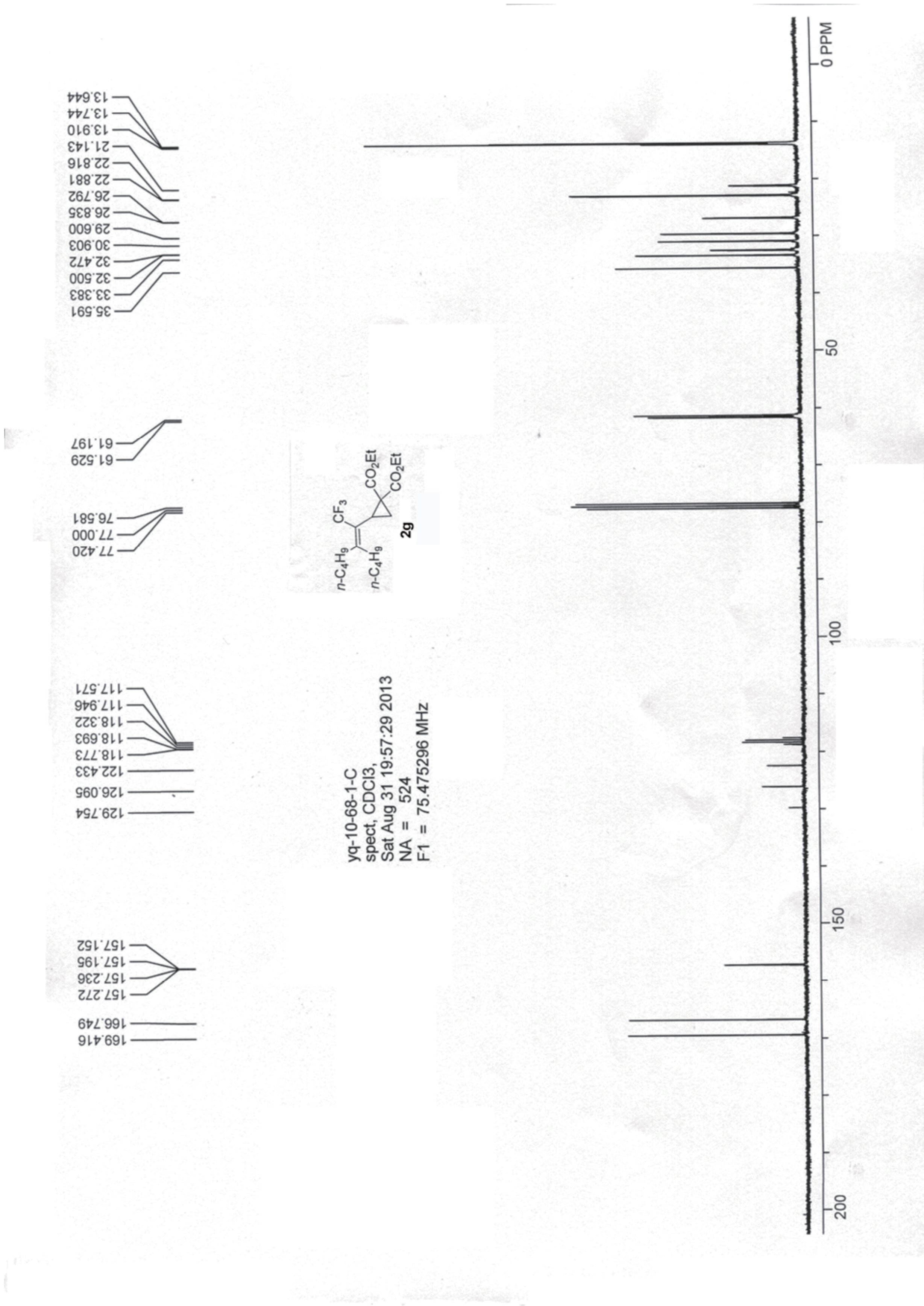


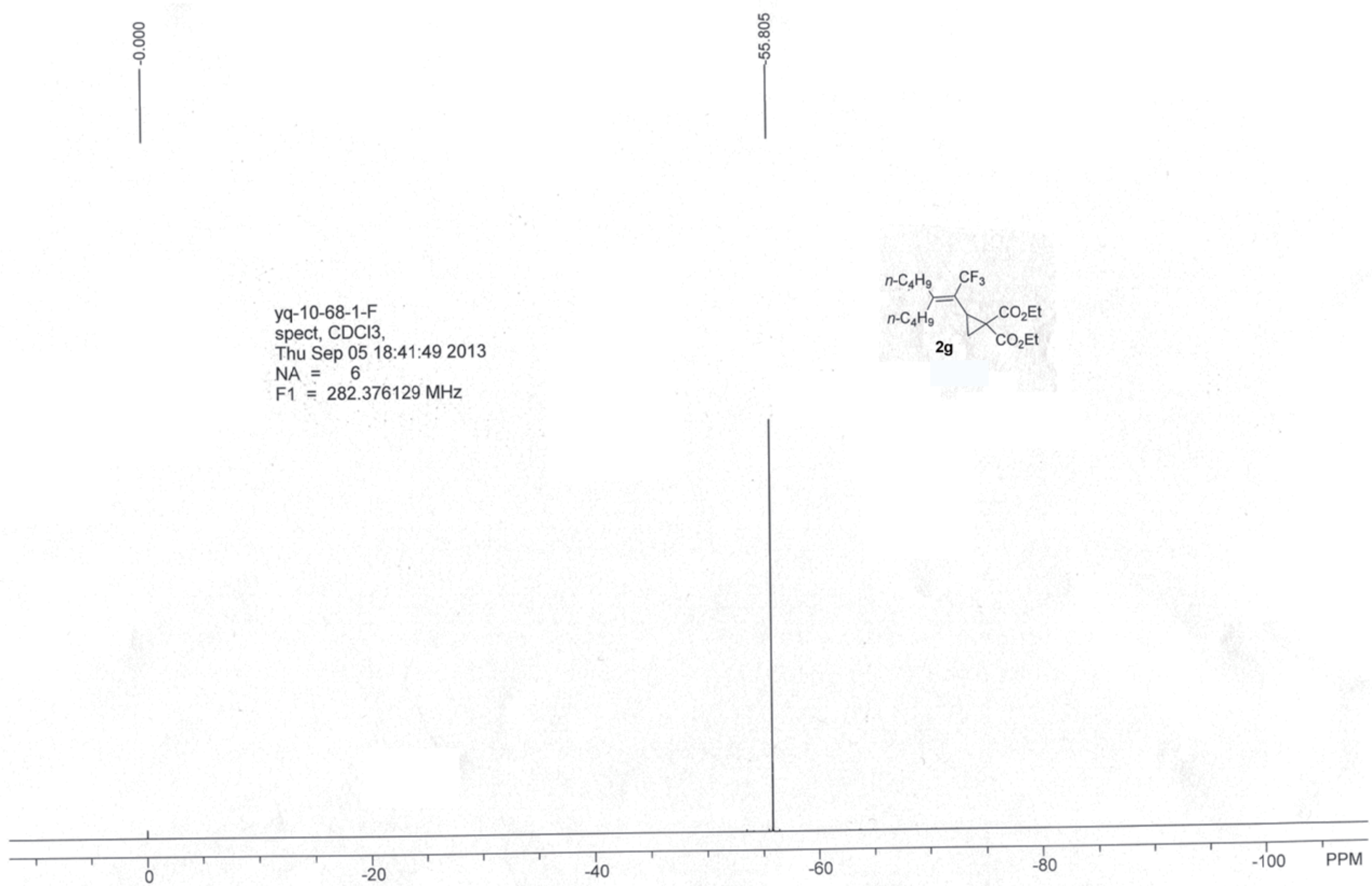
yq-10-84-C
spect, CDCl3,
NA = 1024
F1 = 75.475296 MHz
2f
11.625
12.929
13.701
13.839
21.030
21.063
25.147
25.180
25.844
26.525
26.556
35.417
61.152
61.493
76.571
77.000
77.426
117.226
117.611
117.986
118.358
118.706
122.365
126.025
129.686
159.011
159.045
159.078
159.122
166.739
169.328
PPM

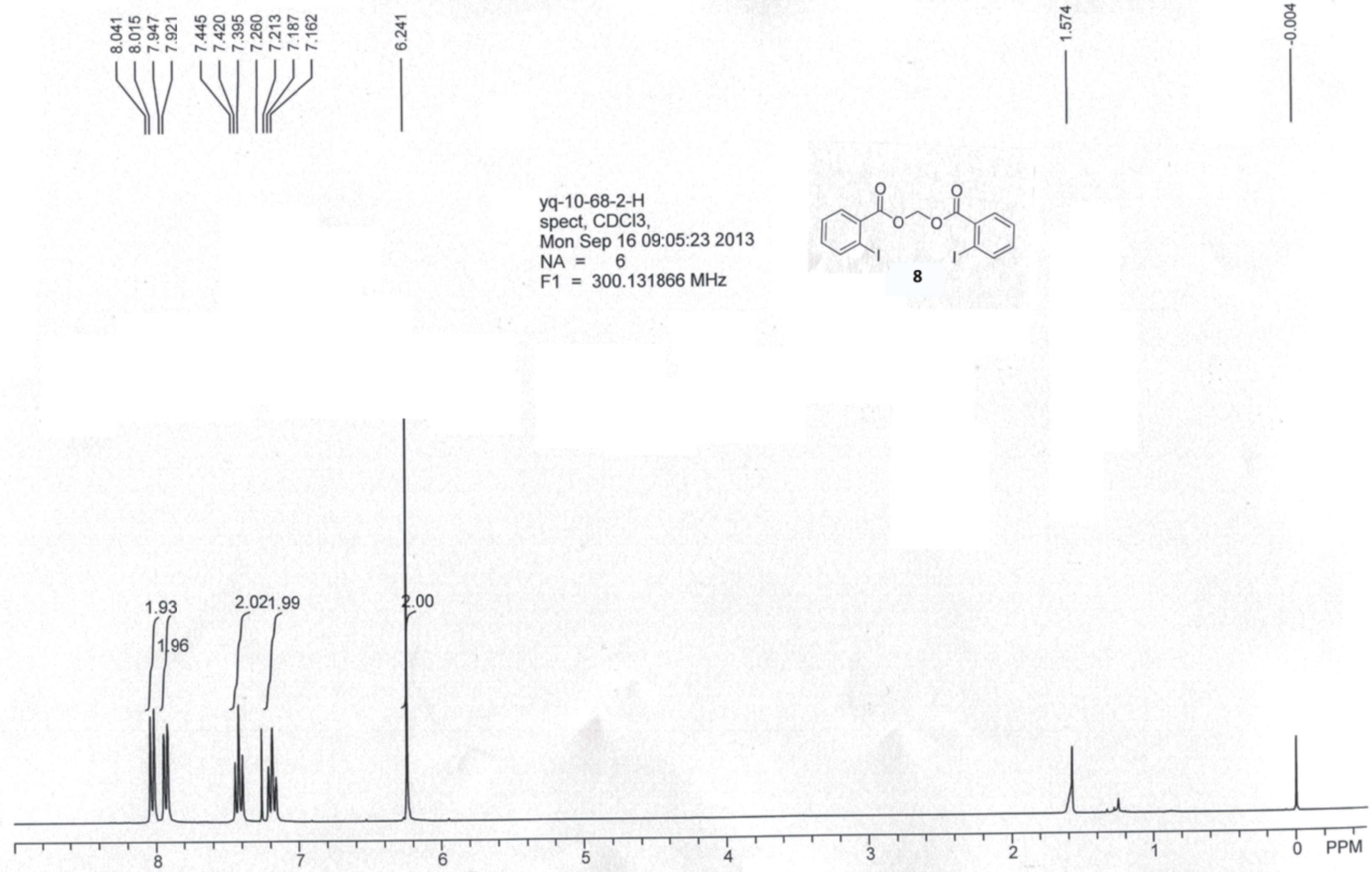

yq-10-84-F
spect, CDCl3,
NA = 6
F1 = 282.376129 MHz
-56.120
0.000
2f
CF3
Et
Et
CO2Et
CO2Et
PPM
-100
-80
-60
-40
-20
0



yq-10-68-1-H
spect, CDCl3,
Fri Aug 30 18:00:21 2013
NA = 6
F1 = 300.131866 MHz
n-C4H9
CF3
CO2Et
2g
14.26
5.98
1.01
2.94
1.94
0.98
4.00
PPM

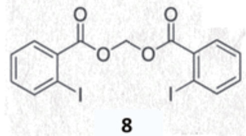

yq-10-68-1-C
spect, CDCl3,
Sat Aug 31 19:57:29 2013
NA = 524
F1 = 75.475296 MHz
n-C4H9
n-C4H9
CF3
CO2Et
CO2Et
2g
169.416
166.749
157.272
157.236
157.195
157.152
129.754
126.095
122.433
118.773
118.693
118.322
117.946
117.571
77.420
77.000
76.581
61.529
61.197
35.591
33.383
32.500
32.472
30.903
29.600
26.835
26.792
22.881
22.816
21.143
13.910
13.744
13.644
200
150
100
50
0 PPM


-0.000
-55.805
yq-10-68-1-F
spect, CDCl3,
Thu Sep 05 18:41:49 2013
NA = 6
F1 = 282.376129 MHz
n-C4H9
CF3
n-C4H9
CO2Et
CO2Et
2g
0
-20
-40
-60
-80
-100
PPM

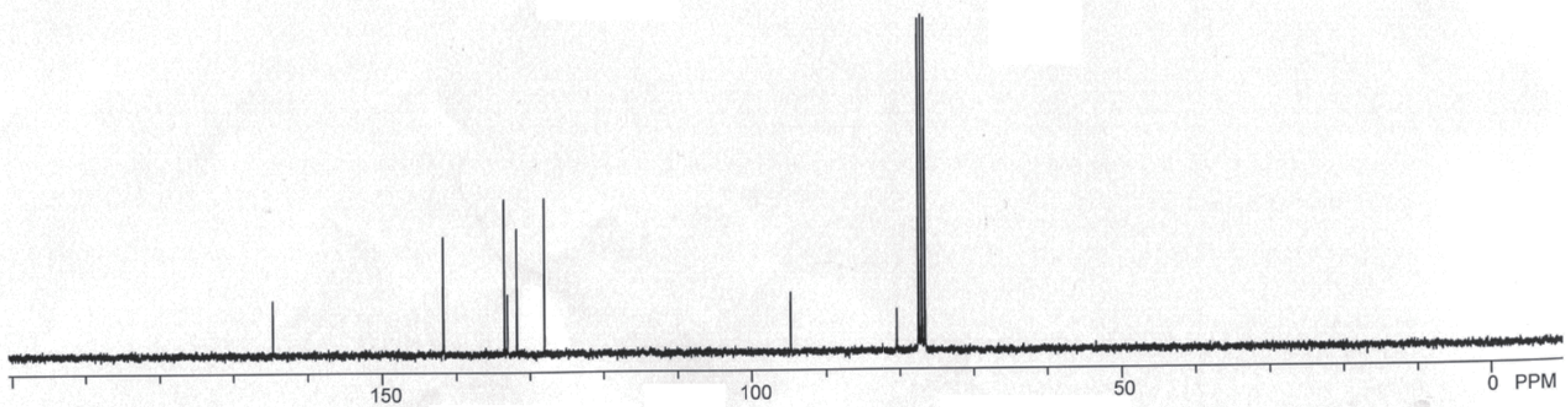

8.041
8.015
7.947
7.921
7.445
7.420
7.395
7.260
7.213
7.187
7.162
6.241
1.574
-0.004
yq-10-68-2-H
spect, CDCl3,
Mon Sep 16 09:05:23 2013
NA = 6
F1 = 300.131866 MHz
O
O
O
O
I
I
8
1.93
1.96
2.02
1.99
2.00
8
7
6
5
4
3
2
1
0
PPM

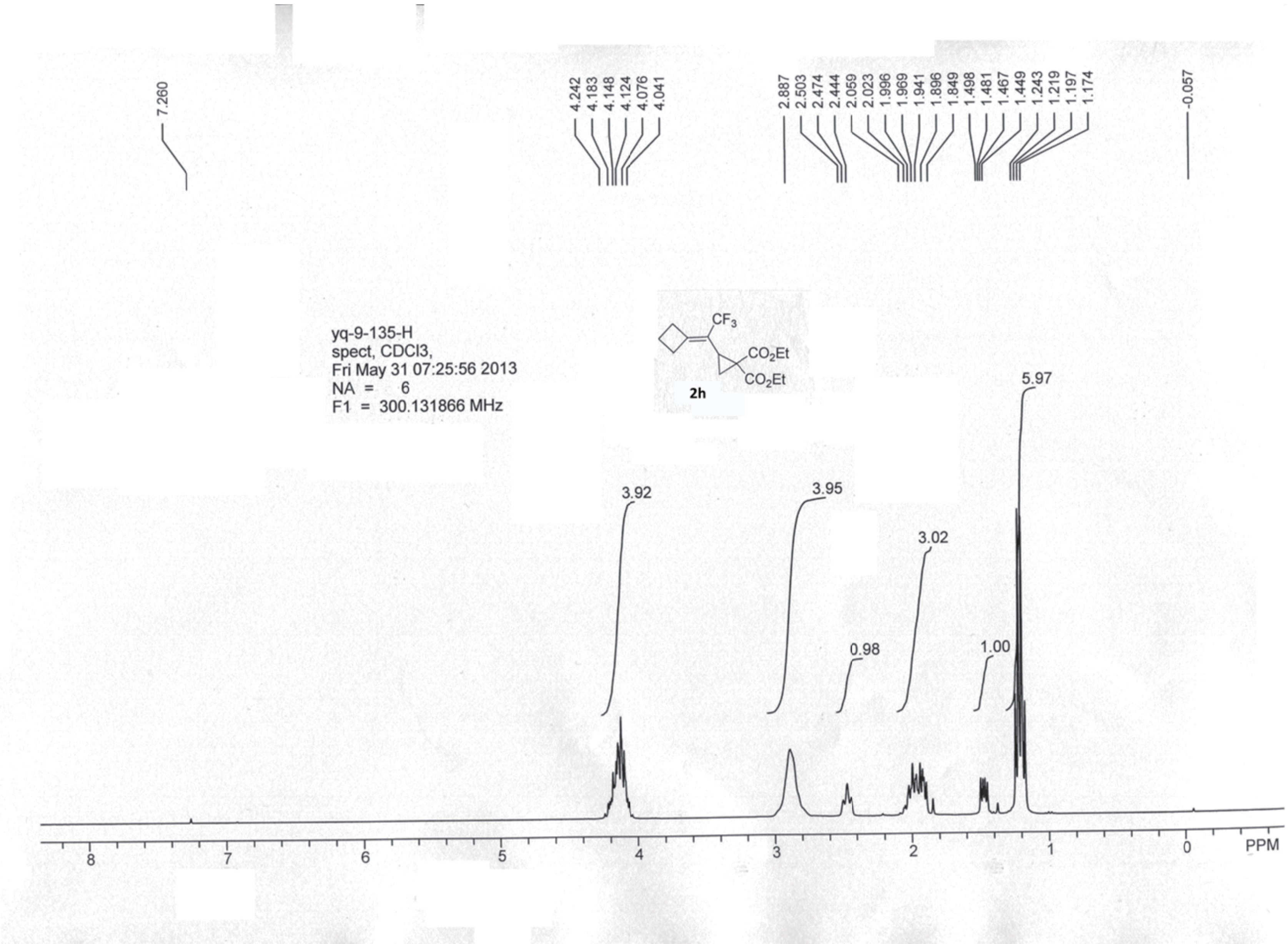
164.679
141.736
133.441
133.025
131.749
128.016
94.766
80.391
77.424
77.000
76.575

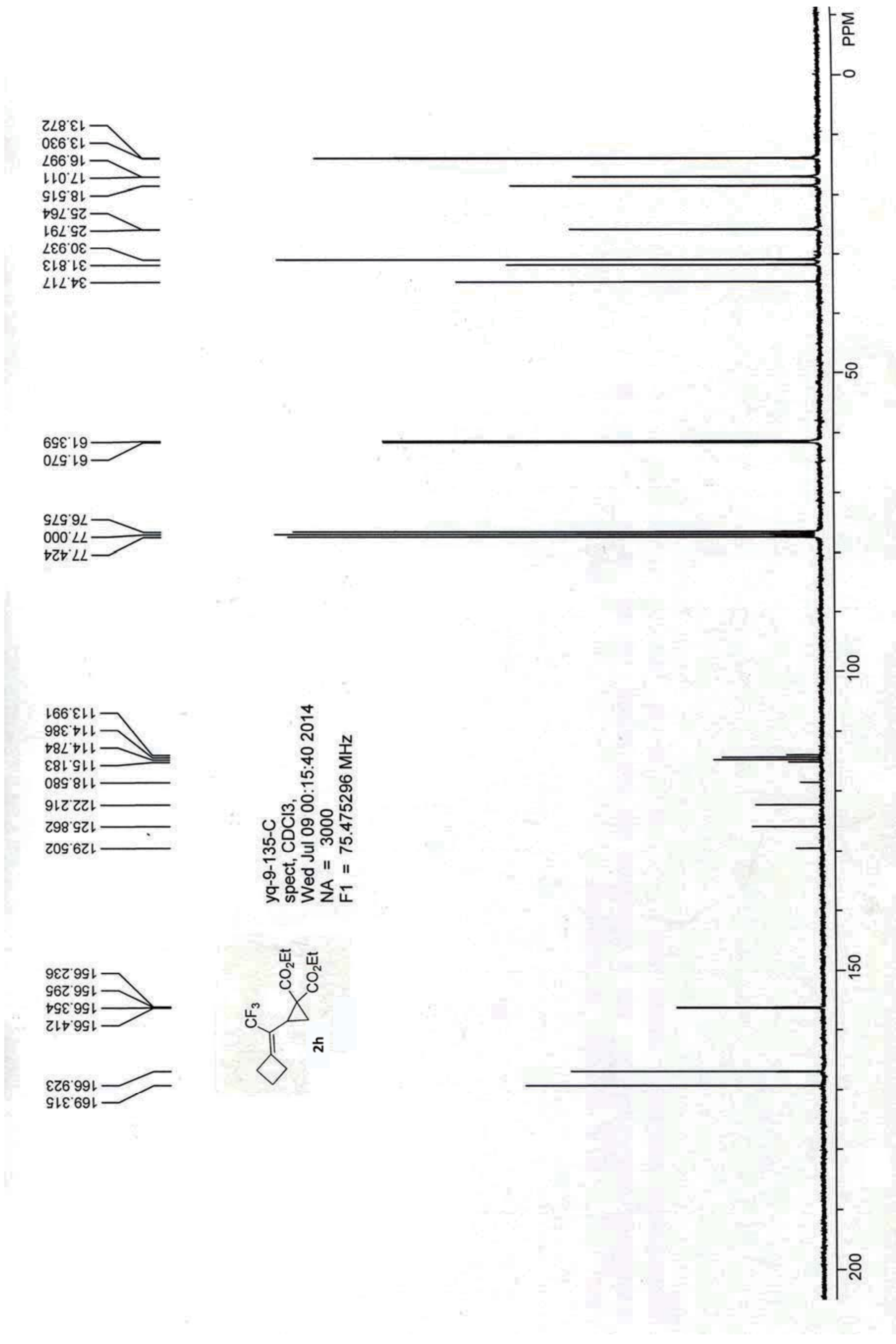
yq-10-68-2
spect, CDCl3,
Mon Sep 16 09:09:12 2013
NA = 500
F1 = 75.475296 MHz



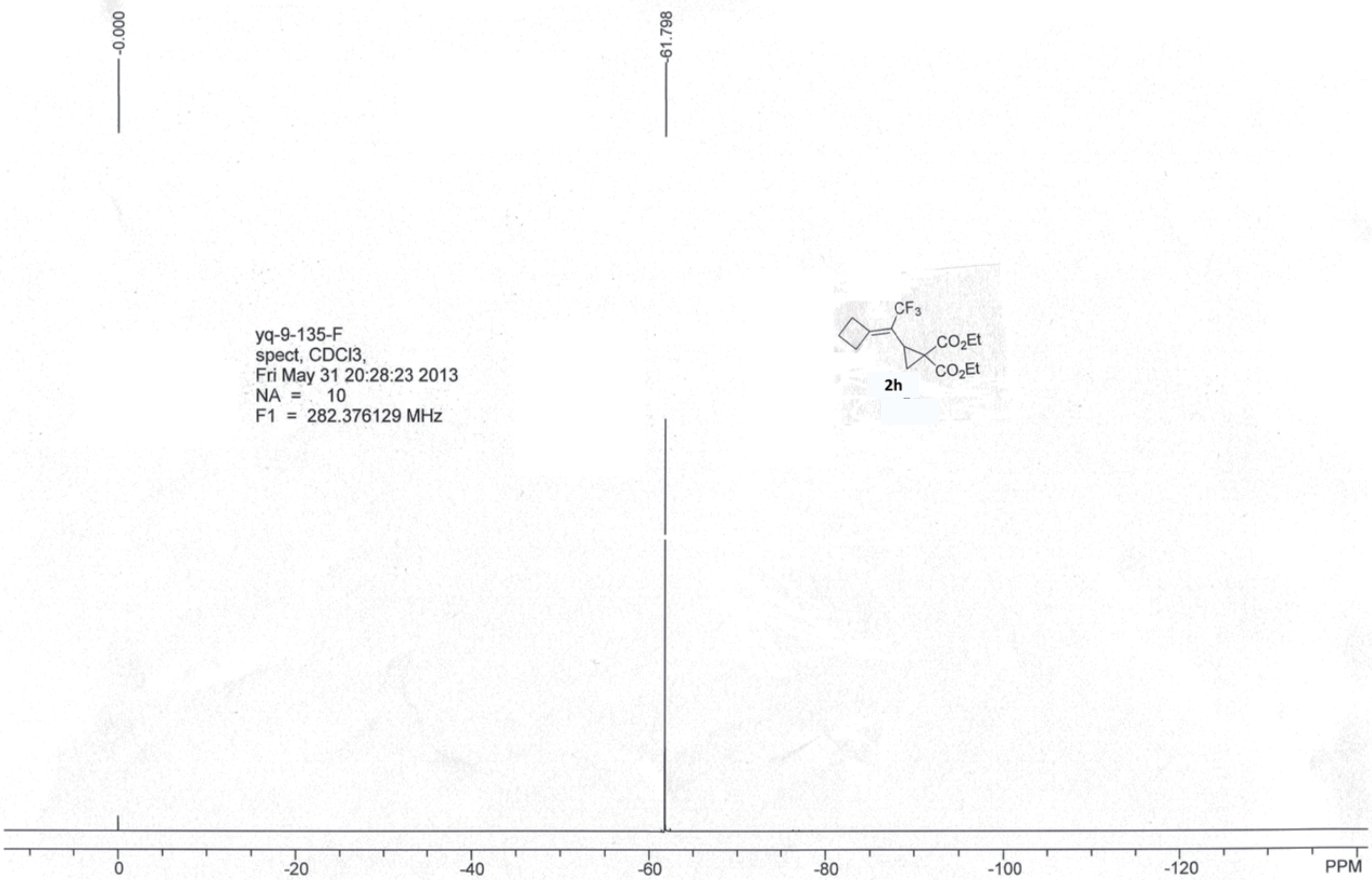
8

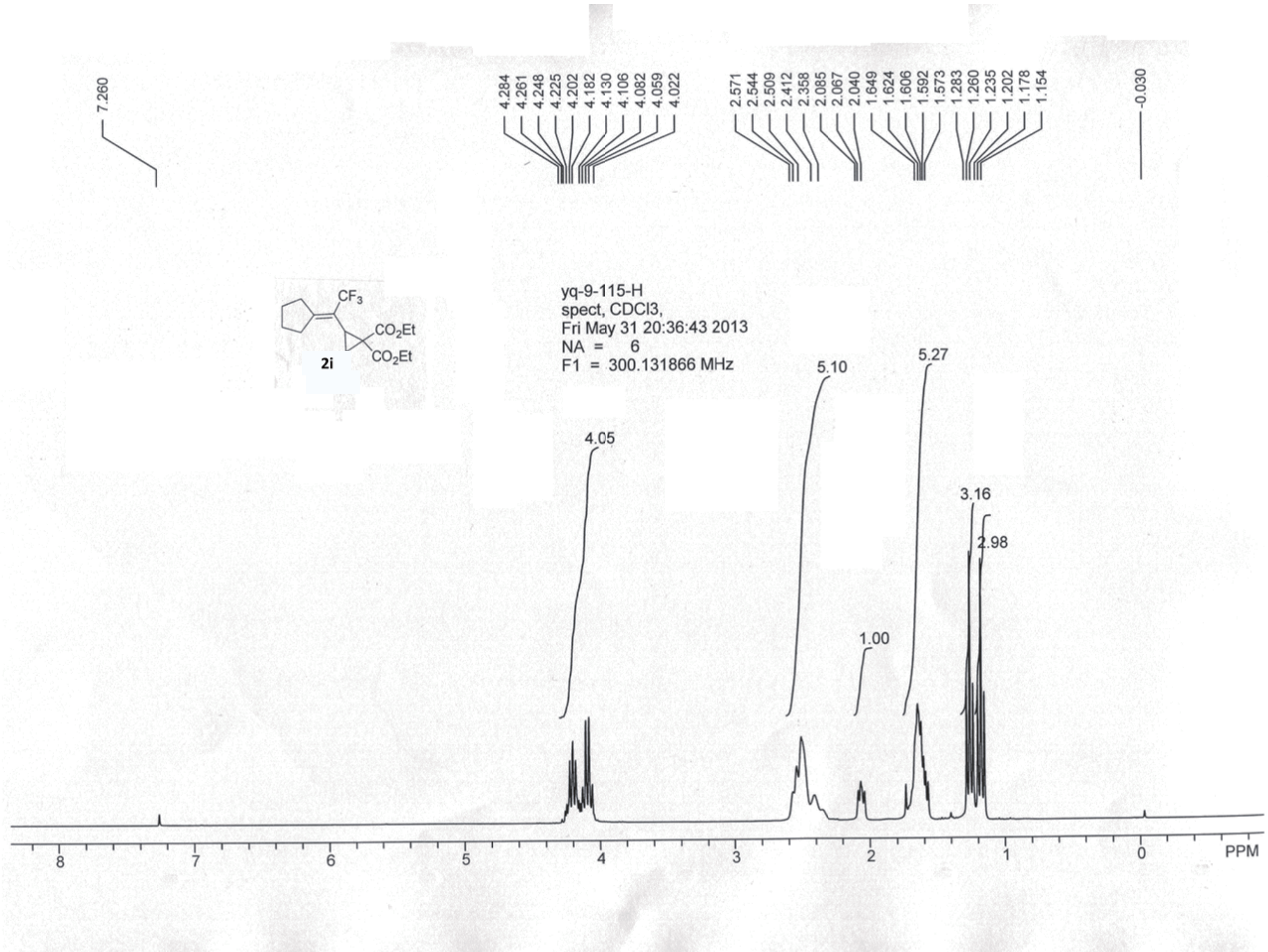


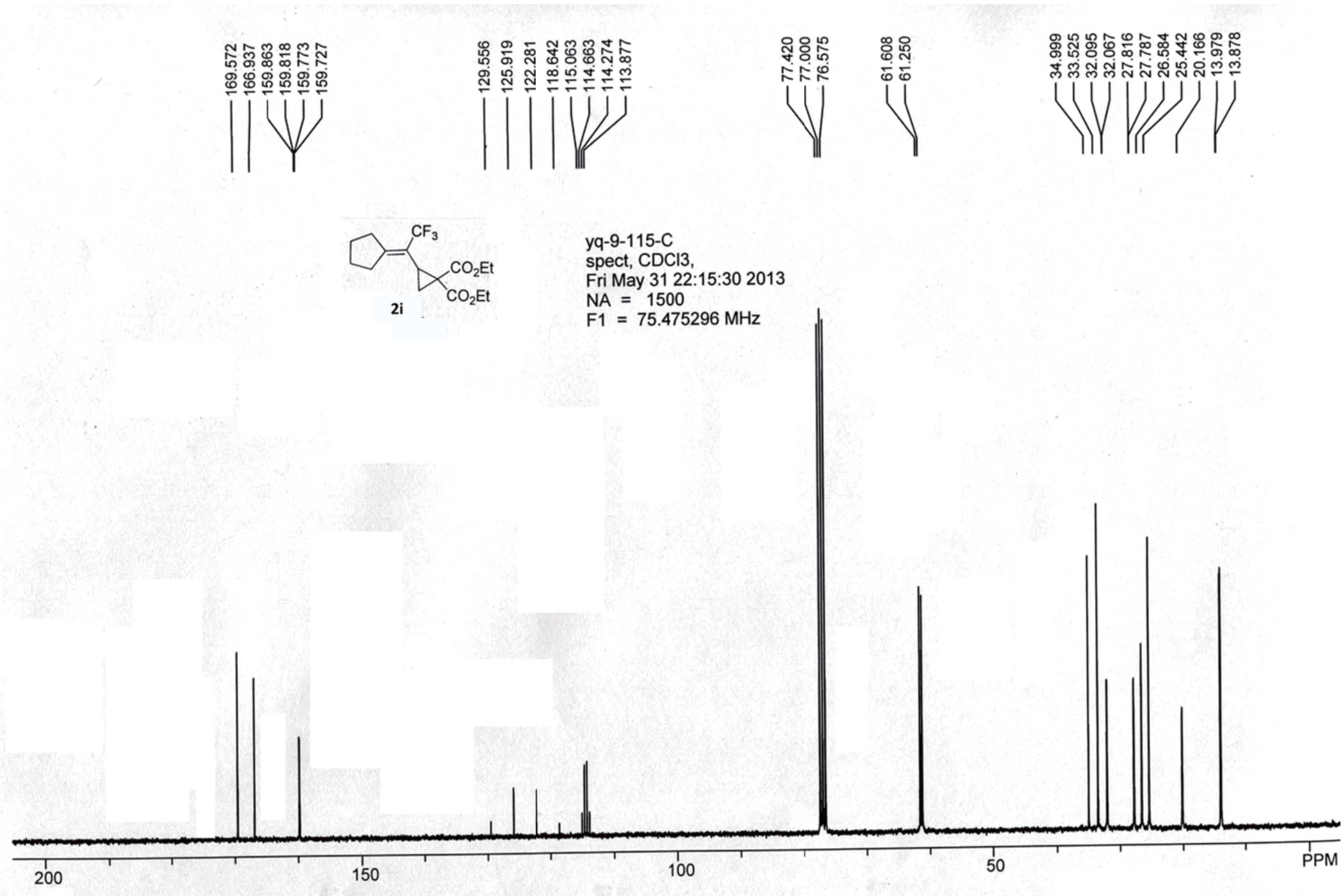

7.260
4.242
4.183
4.148
4.124
4.076
4.041
2.887
2.503
2.474
2.444
2.059
2.023
1.996
1.969
1.941
1.896
1.849
1.498
1.481
1.467
1.449
1.243
1.219
1.197
1.174
-0.057
yq-9-135-H
spect, CDCl3,
Fri May 31 07:25:56 2013
NA = 6
F1 = 300.131866 MHz
CF3
CO2Et
CO2Et
2h
5.97
3.92
3.95
3.02
0.98
1.00
8
7
6
5
4
3
2
1
0
PPM

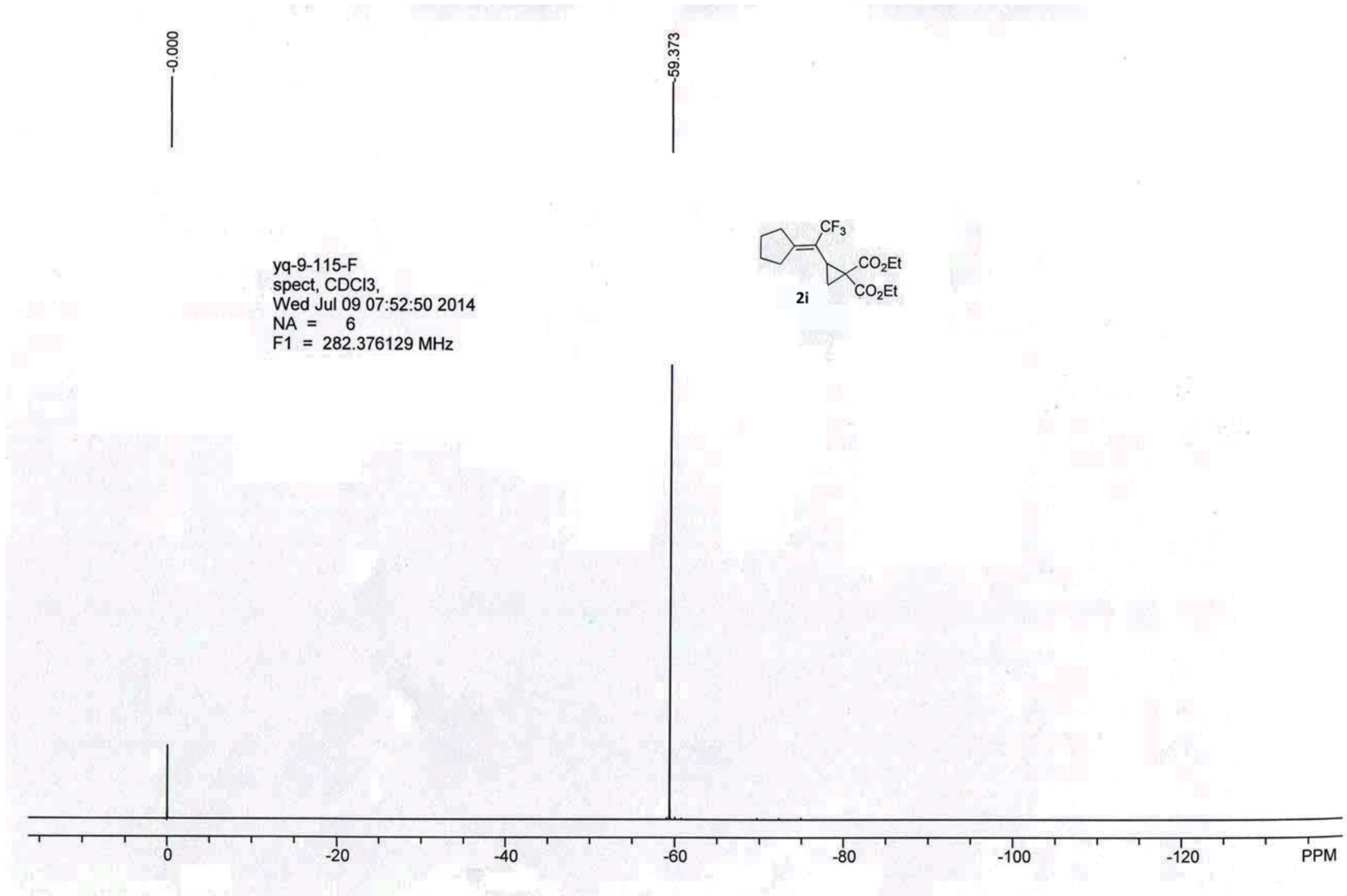


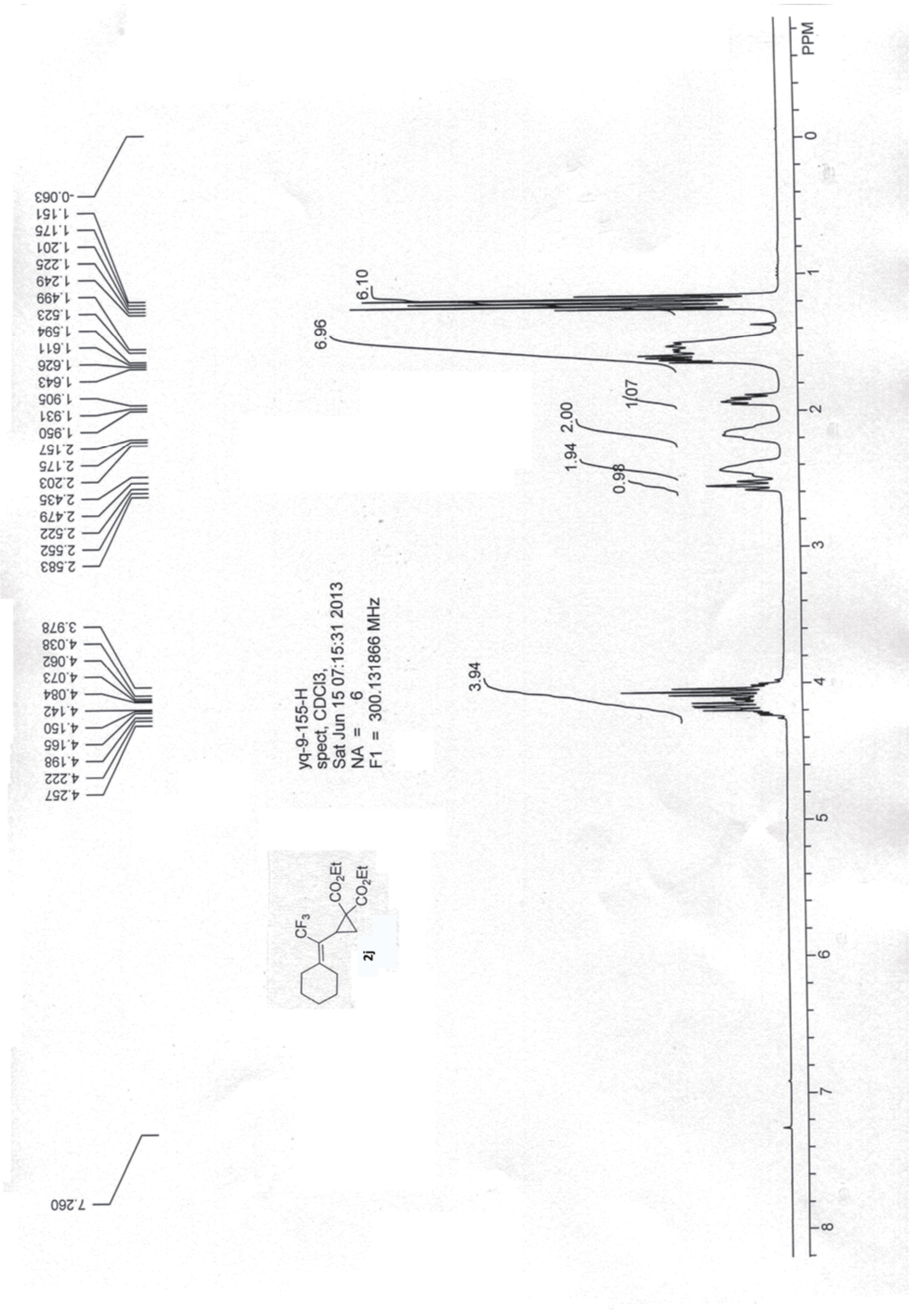
13.872
13.930
16.997
17.011
18.515
25.764
25.791
30.937
31.813
34.717
61.359
61.570
76.575
77.000
77.424
113.991
114.386
114.784
115.183
118.580
122.216
125.862
129.502
156.236
156.295
156.354
156.412
166.923
169.315
CF3
CO2Et
CO2Et
2h
yq-9-135-C
spect, CDCl3,
Wed Jul 09 00:15:40 2014
NA = 3000
F1 = 75.475296 MHz
PPM
0
50
100
150
200


-0.000
-61.798
yq-9-135-F
spect, CDCl3,
Fri May 31 20:28:23 2013
NA = 10
F1 = 282.376129 MHz
CF3
CO2Et
CO2Et
2h
0
-20
-40
-60
-80
-100
-120
PPM

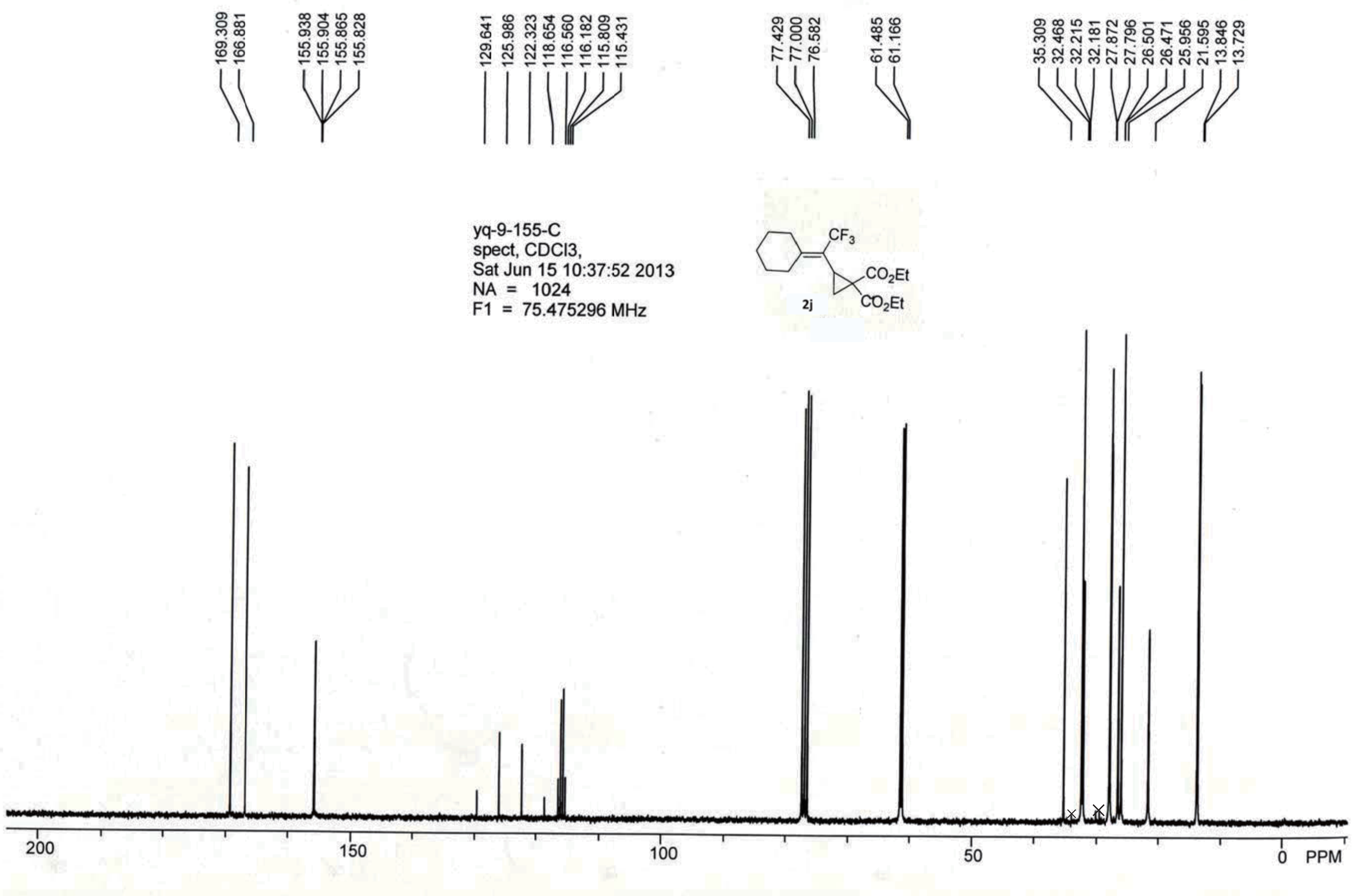

7.260
4.284
4.261
4.248
4.225
4.202
4.182
4.130
4.106
4.082
4.059
4.022
2.571
2.544
2.509
2.412
2.358
2.085
2.067
2.040
1.649
1.624
1.606
1.592
1.573
1.283
1.260
1.235
1.202
1.178
1.154
-0.030
CF_3
CO_2Et
CO_2Et
2i
yq-9-115-H
spect, CDCl3,
Fri May 31 20:36:43 2013
NA = 6
F1 = 300.131866 MHz
4.05
5.10
1.00
5.27
3.16
2.98
8
7
6
5
4
3
2
1
0
PPM

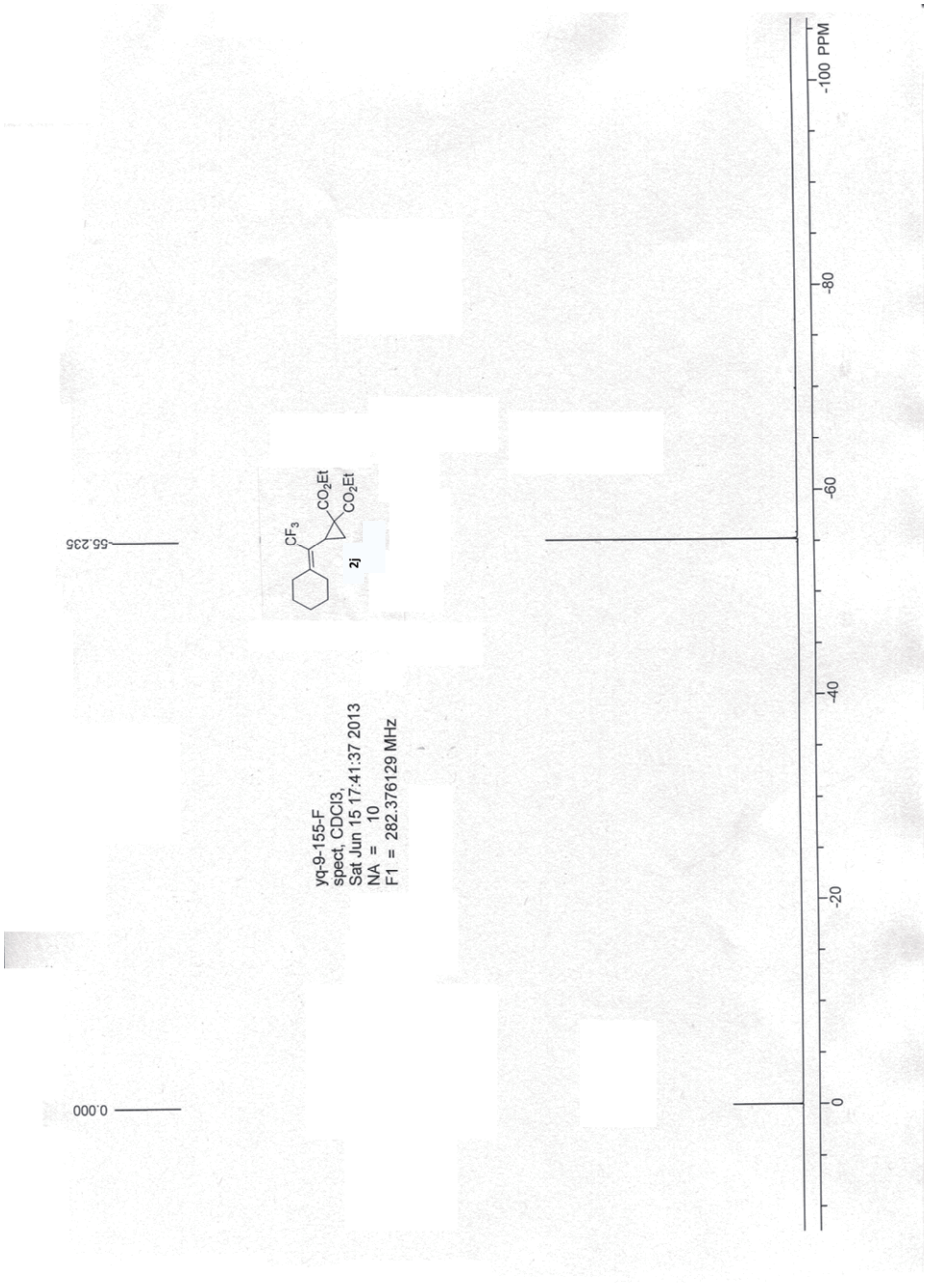

169.572
166.937
159.863
159.818
159.773
159.727
129.556
125.919
122.281
118.642
115.063
114.663
114.274
113.877
77.420
77.000
76.575
61.608
61.250
34.999
33.525
32.095
32.067
27.816
27.787
26.584
25.442
20.166
13.979
13.878
CF3
CO2Et
CO2Et
2i
yq-9-115-C
spect, CDCl3,
Fri May 31 22:15:30 2013
NA = 1500
F1 = 75.475296 MHz
200
150
100
50
PPM

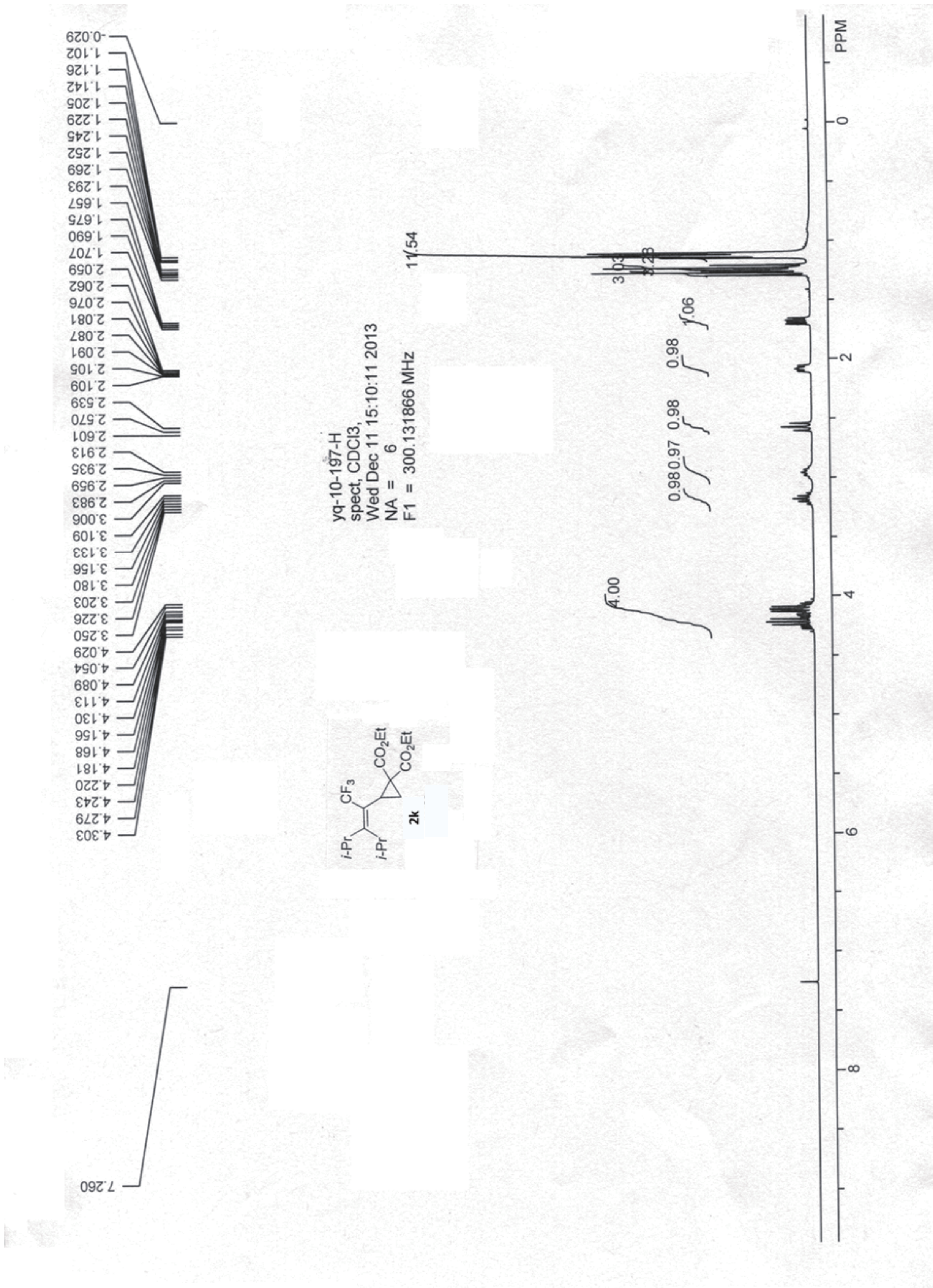

-0.000
-59.373
yq-9-115-F
spect, CDCl3,
Wed Jul 09 07:52:50 2014
NA = 6
F1 = 282.376129 MHz
CF3
CO2Et
CO2Et
2i
0
-20
-40
-60
-80
-100
-120
PPM



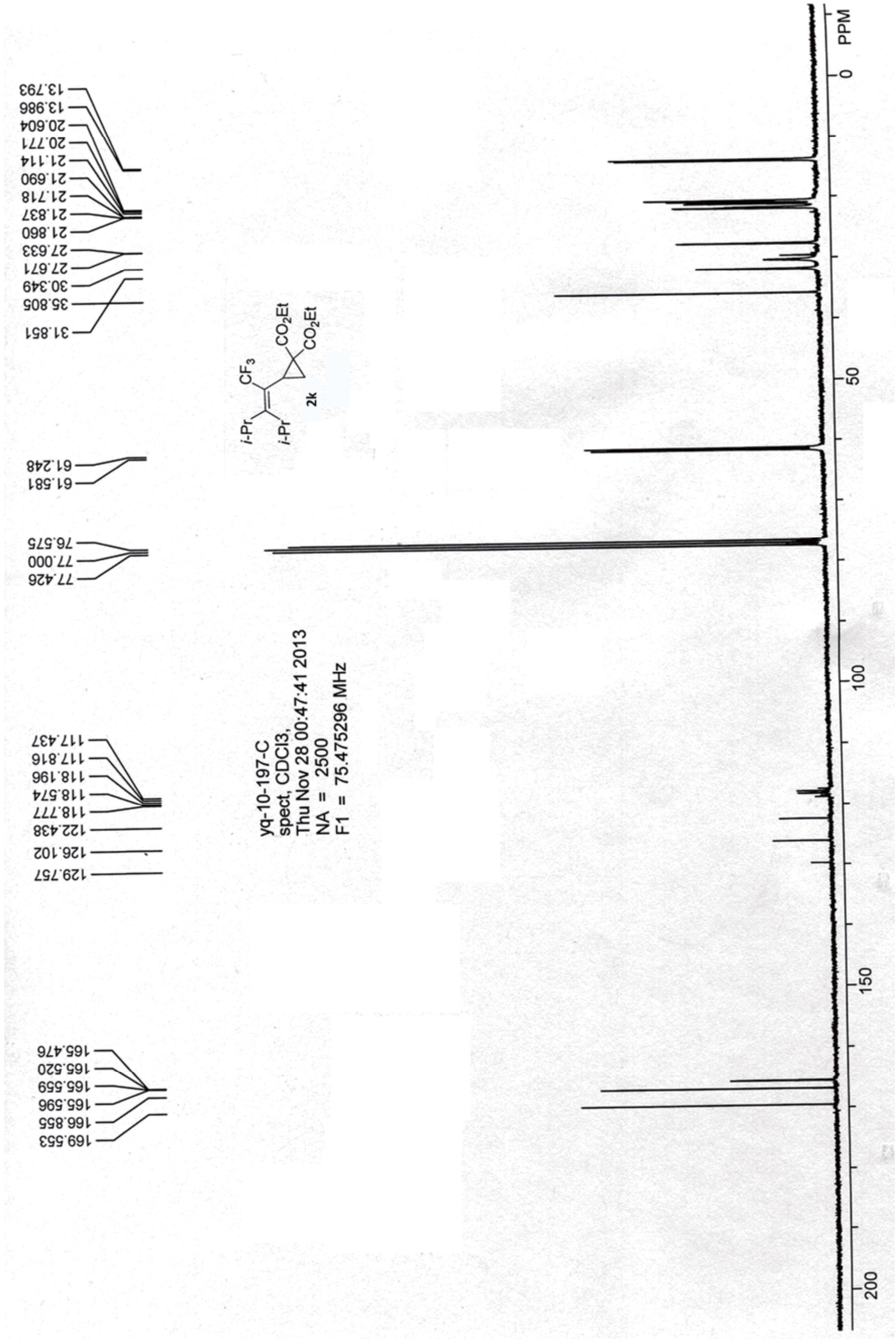
yq-9-155-H
spect, CDCl3,
Sat Jun 15 07:15:31 2013
NA = 6
F1 = 300.131866 MHz
2j
7.260
4.257
4.222
4.198
4.165
4.150
4.142
4.084
4.073
4.062
4.038
3.978
2.583
2.552
2.522
2.479
2.435
2.203
2.175
2.157
1.950
1.931
1.905
1.643
1.626
1.611
1.594
1.523
1.499
1.249
1.225
1.201
1.175
1.151
-0.063
3.94
0.98
1.94
2.00
1.07
6.96
6.10
PPM


169.309
166.881
155.938
155.904
155.865
155.828
129.641
125.986
122.323
118.654
116.560
116.182
115.809
115.431
77.429
77.000
76.582
61.485
61.166
35.309
32.468
32.215
32.181
27.872
27.796
26.501
26.471
25.956
21.595
13.846
13.729
yq-9-155-C
spect, CDCl3,
Sat Jun 15 10:37:52 2013
NA = 1024
F1 = 75.475296 MHz
CF3
CO2Et
CO2Et
2j
200
150
100
50
0
PPM

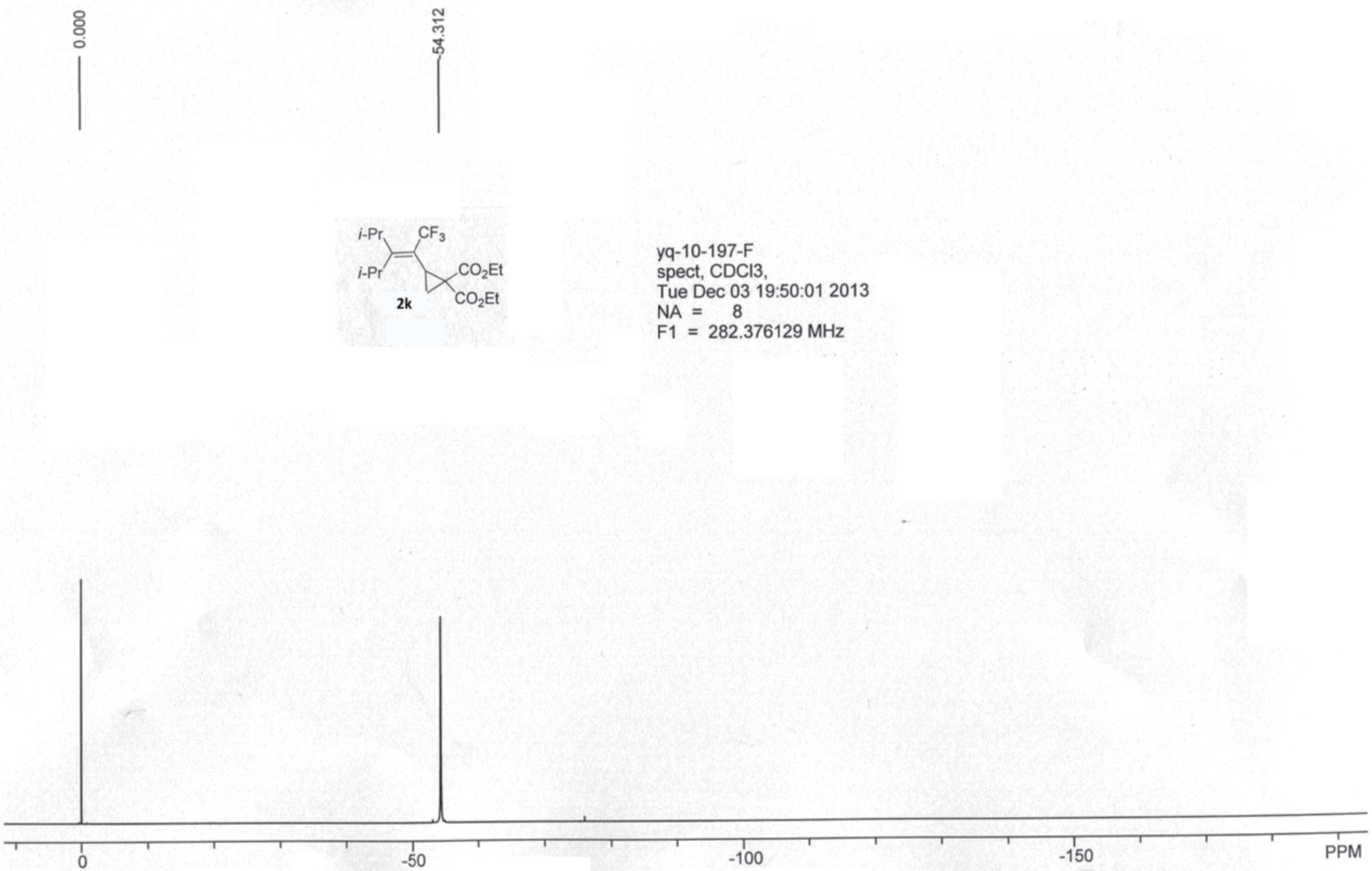

-55.235
0.000
CF3
CO2Et
CO2Et
2j
yq-9-155-F
spect, CDCl3,
Sat Jun 15 17:41:37 2013
NA = 10
F1 = 282.376129 MHz
-100 PPM
-80
-60
-40
-20
0



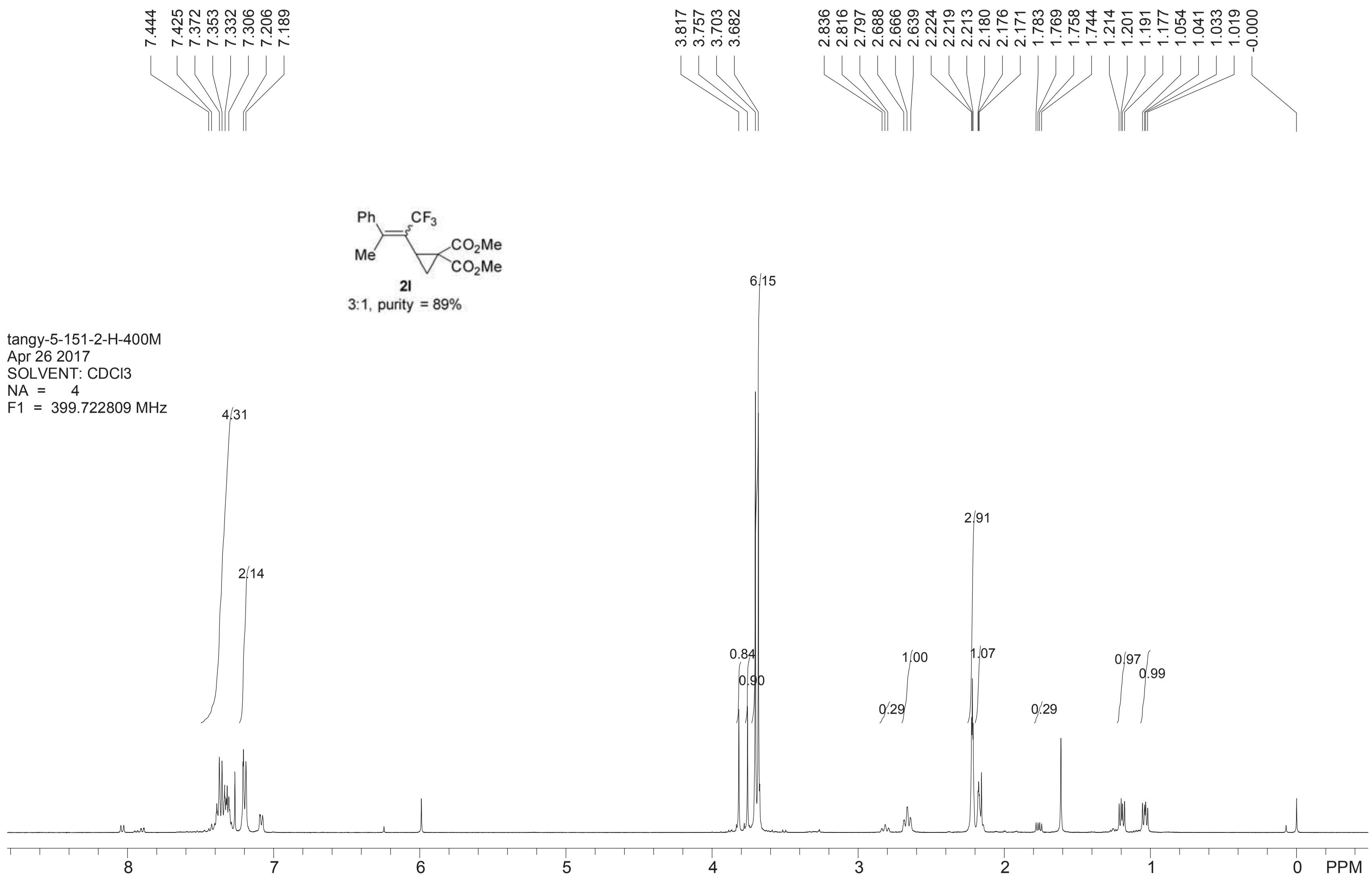
yq-10-197-H
spect, CDCl3,
Wed Dec 11 15:10:11 2013
NA = 6
F1 = 300.131866 MHz
7.260
4.303
4.279
4.243
4.220
4.181
4.168
4.156
4.130
4.113
4.089
4.054
4.029
3.250
3.226
3.203
3.180
3.156
3.133
3.109
3.006
2.983
2.959
2.935
2.913
2.601
2.570
2.539
2.109
2.105
2.091
2.087
2.081
2.076
2.062
2.059
1.707
1.690
1.675
1.657
1.293
1.269
1.252
1.245
1.229
1.205
1.142
1.126
1.102
-0.029
4.00
0.98
0.97
0.98
0.98
1.06
3.03
3.23
11.54
CF3
CO2Et
CO2Et
i-Pr
i-Pr
2k
PPM



yq-10-197-C
spect, CDCl3,
Thu Nov 28 00:47:41 2013
NA = 2500
F1 = 75.475296 MHz
2k
i-Pr
i-Pr
CF3
CO2Et
CO2Et
13.793
13.986
20.604
20.771
21.114
21.690
21.718
21.837
21.860
27.633
27.671
30.349
35.805
31.851
61.248
61.581
76.575
77.000
77.426
117.437
117.816
118.196
118.574
118.777
122.438
126.102
129.757
165.476
165.520
165.559
165.596
166.855
169.553
PPM
0
50
100
150
200

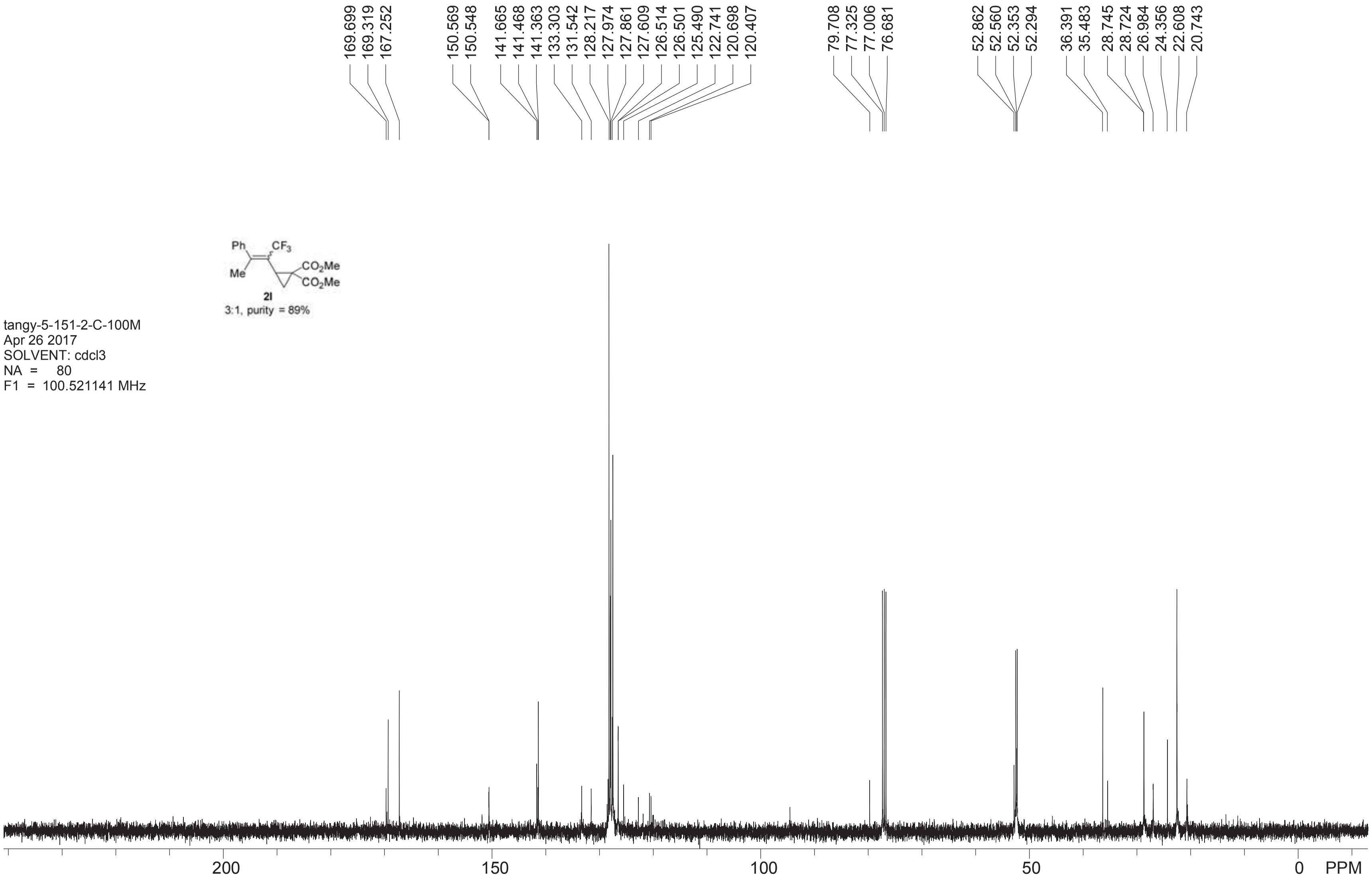


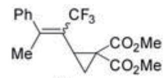
0.000
-54.312
i-Pr
i-Pr
CF3
CO2Et
CO2Et
2k
yq-10-197-F
spect, CDCl3,
Tue Dec 03 19:50:01 2013
NA = 8
F1 = 282.376129 MHz
0
-50
-100
-150
PPM



2l

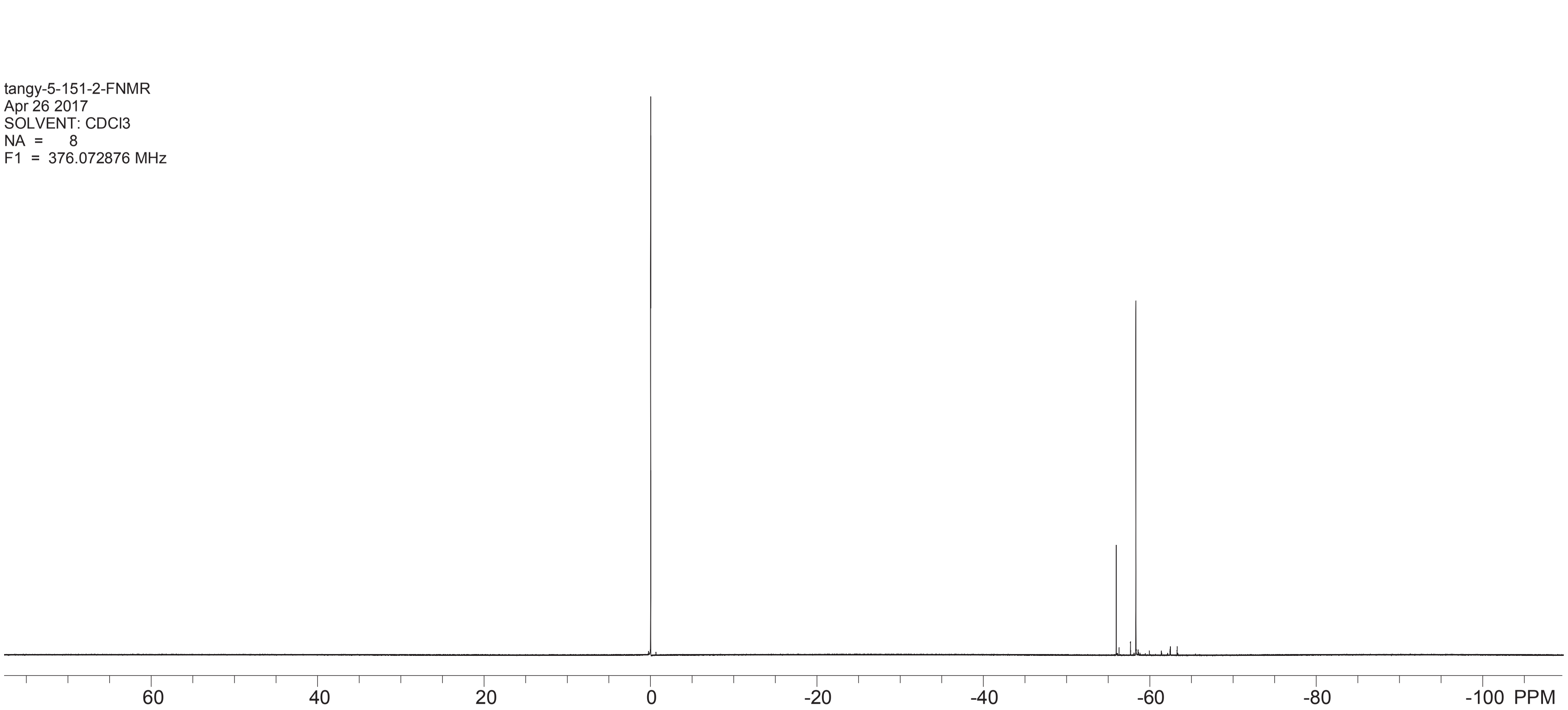
3:1, purity = 89%

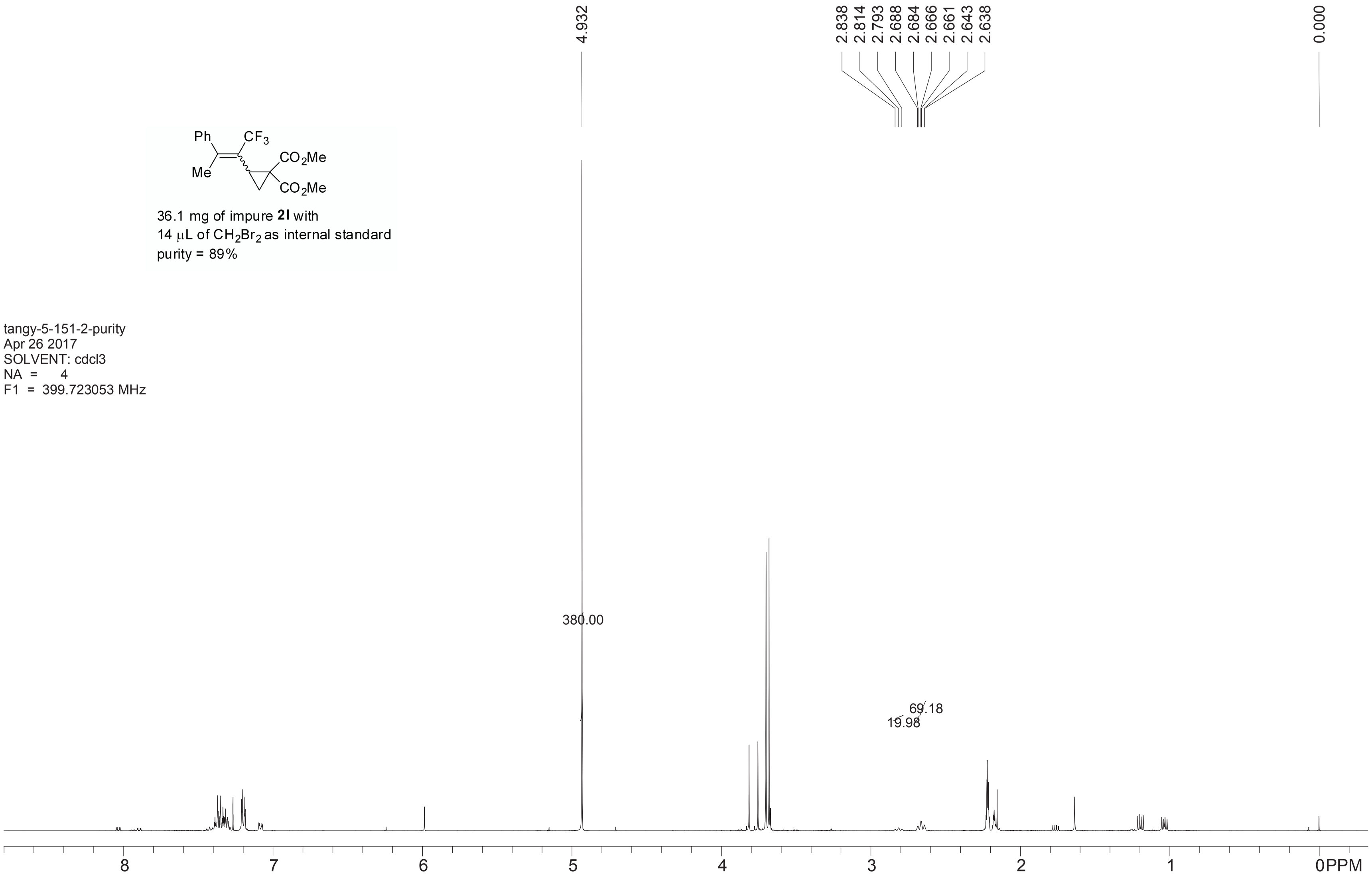

169.699
169.319
167.252
150.569
150.548
141.665
141.468
141.363
133.303
131.542
128.217
127.974
127.861
127.609
126.514
126.501
125.490
122.741
120.698
120.407
79.708
77.325
77.006
76.681
52.862
52.560
52.353
52.294
36.391
35.483
28.745
28.724
26.984
24.356
22.608
20.743
Ph
CF3
Me
CO2Me
CO2Me
2l
3:1, purity = 89%
tangy-5-151-2-C-100M
Apr 26 2017
SOLVENT: cdcl3
NA = 80
F1 = 100.521141 MHz
200
150
100
50
0
PPM



2l

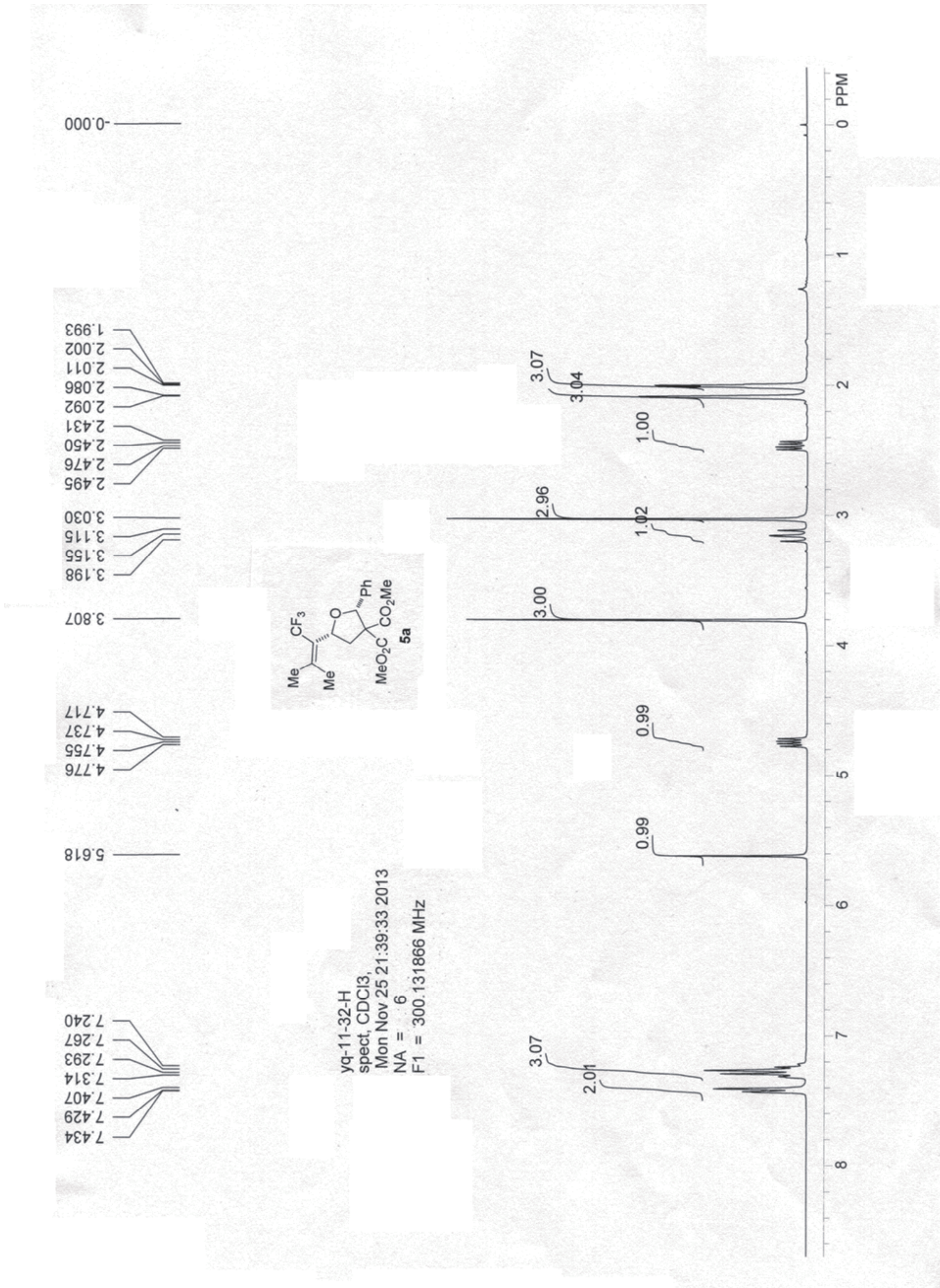
3:1, purity = 89%

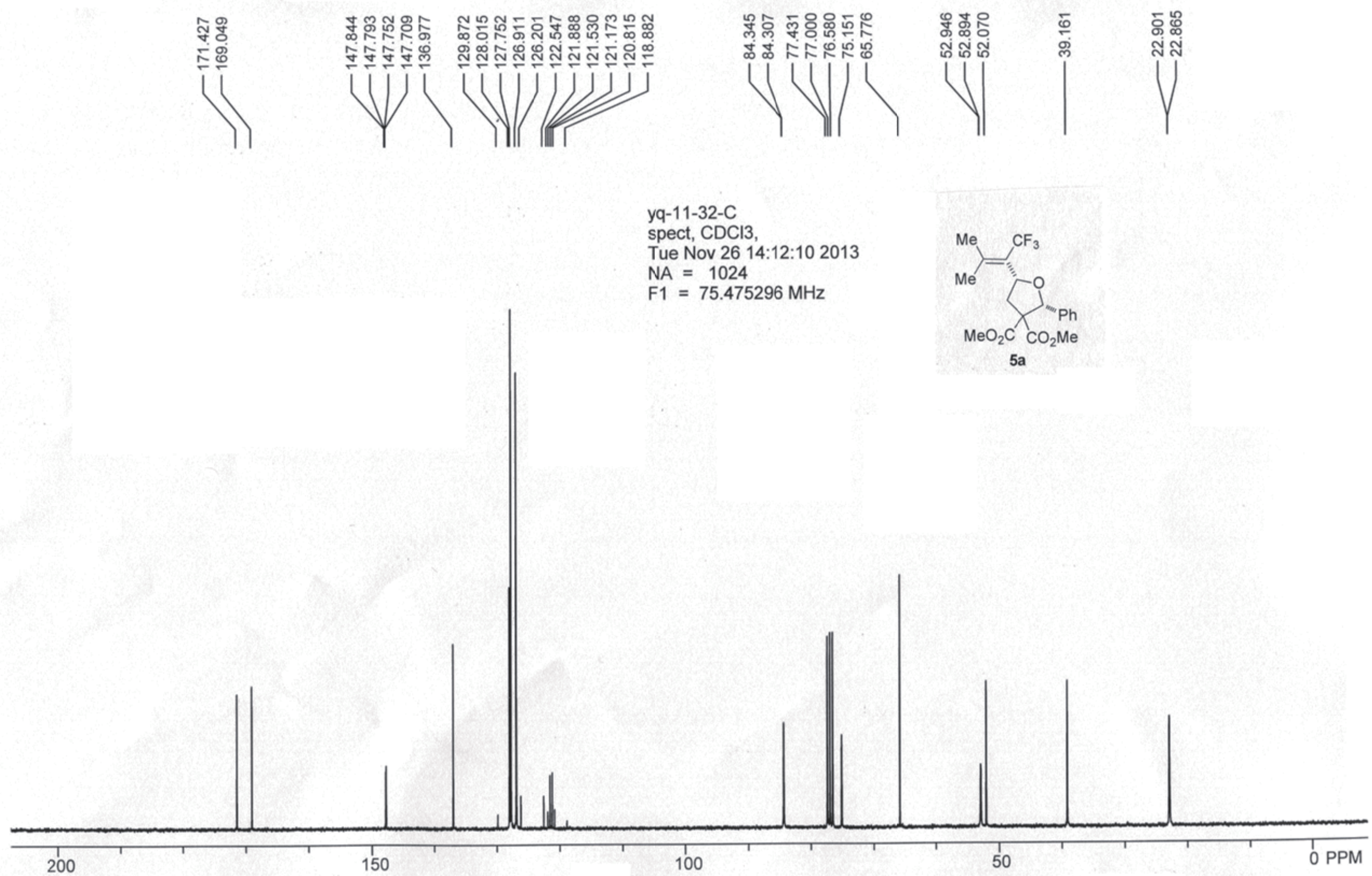


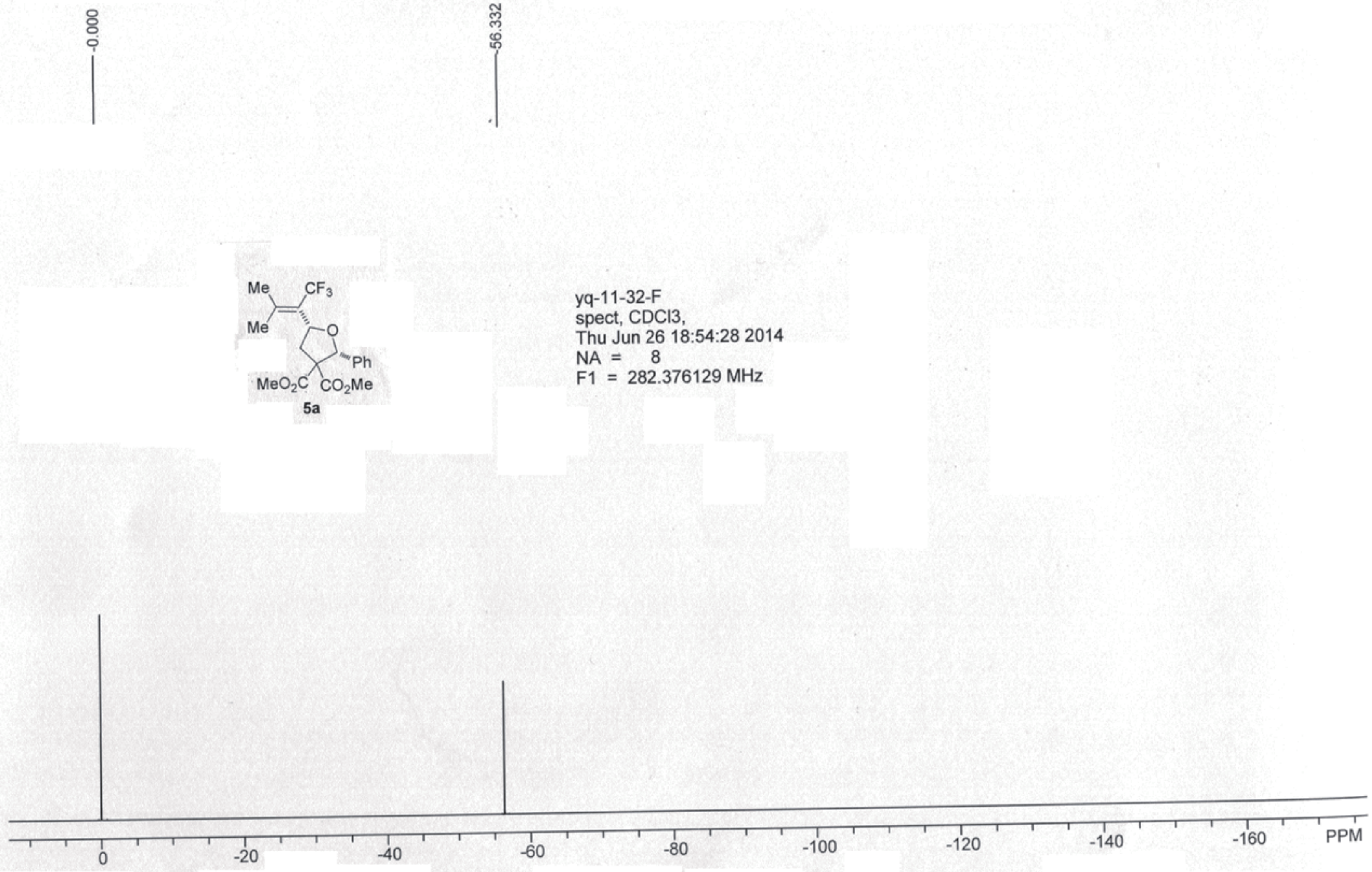


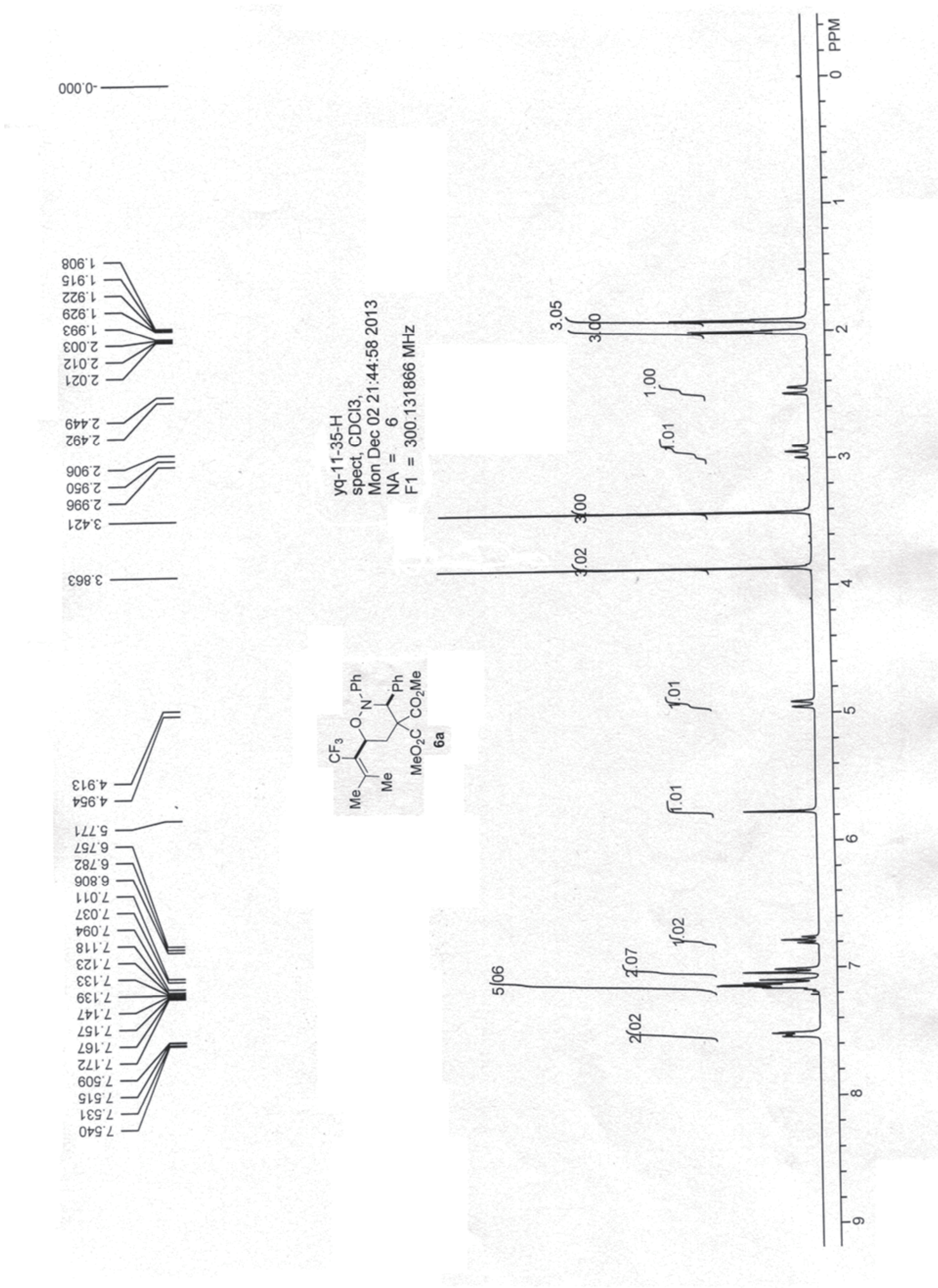
36.1 mg of impure **2l** with
14 µL of CH_2Br_2 as internal standard
purity = 89%

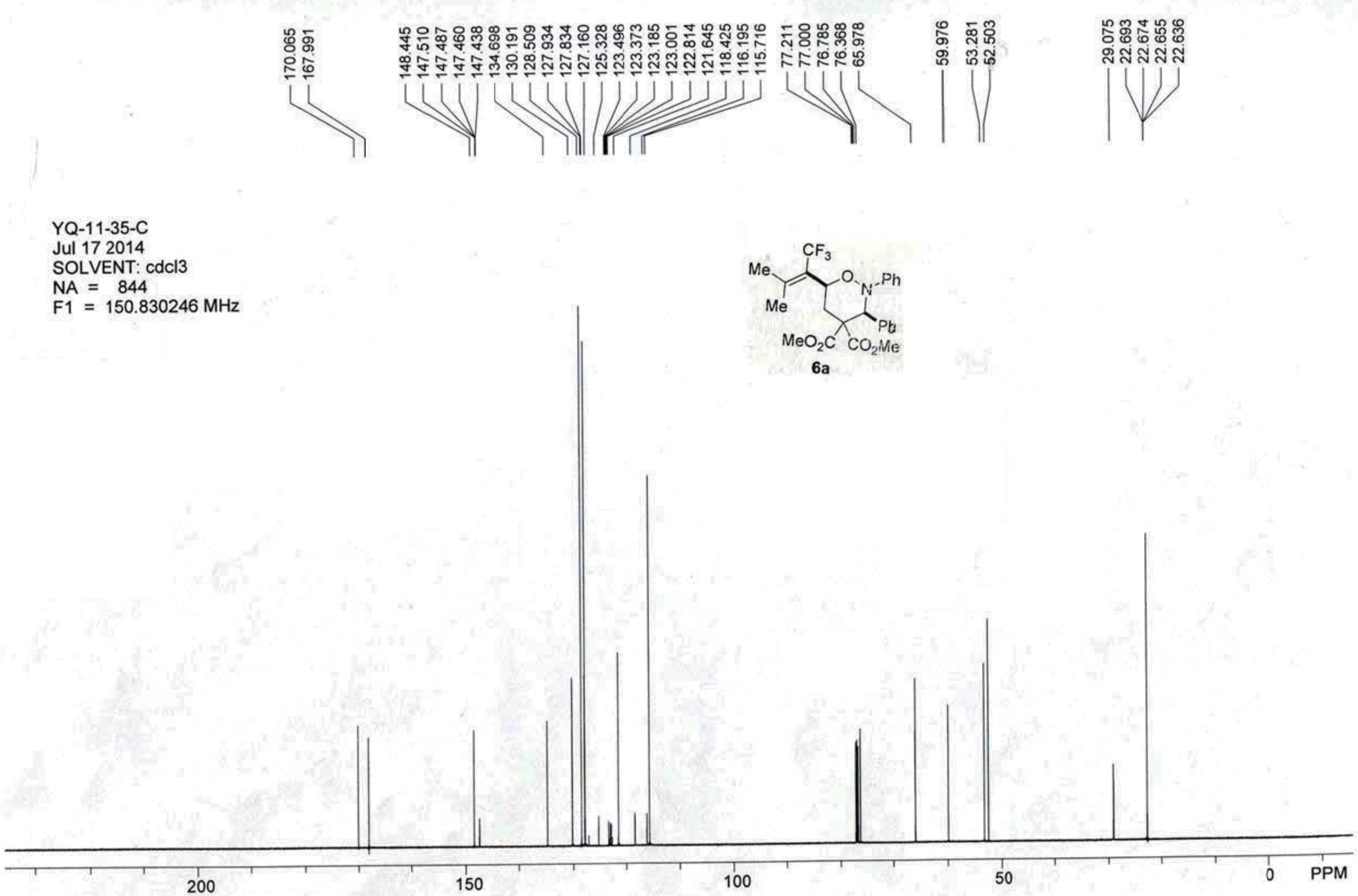
tangy-5-151-2-purity
Apr 26 2017
SOLVENT: cdcl3
NA = 4
F1 = 399.723053 MHz

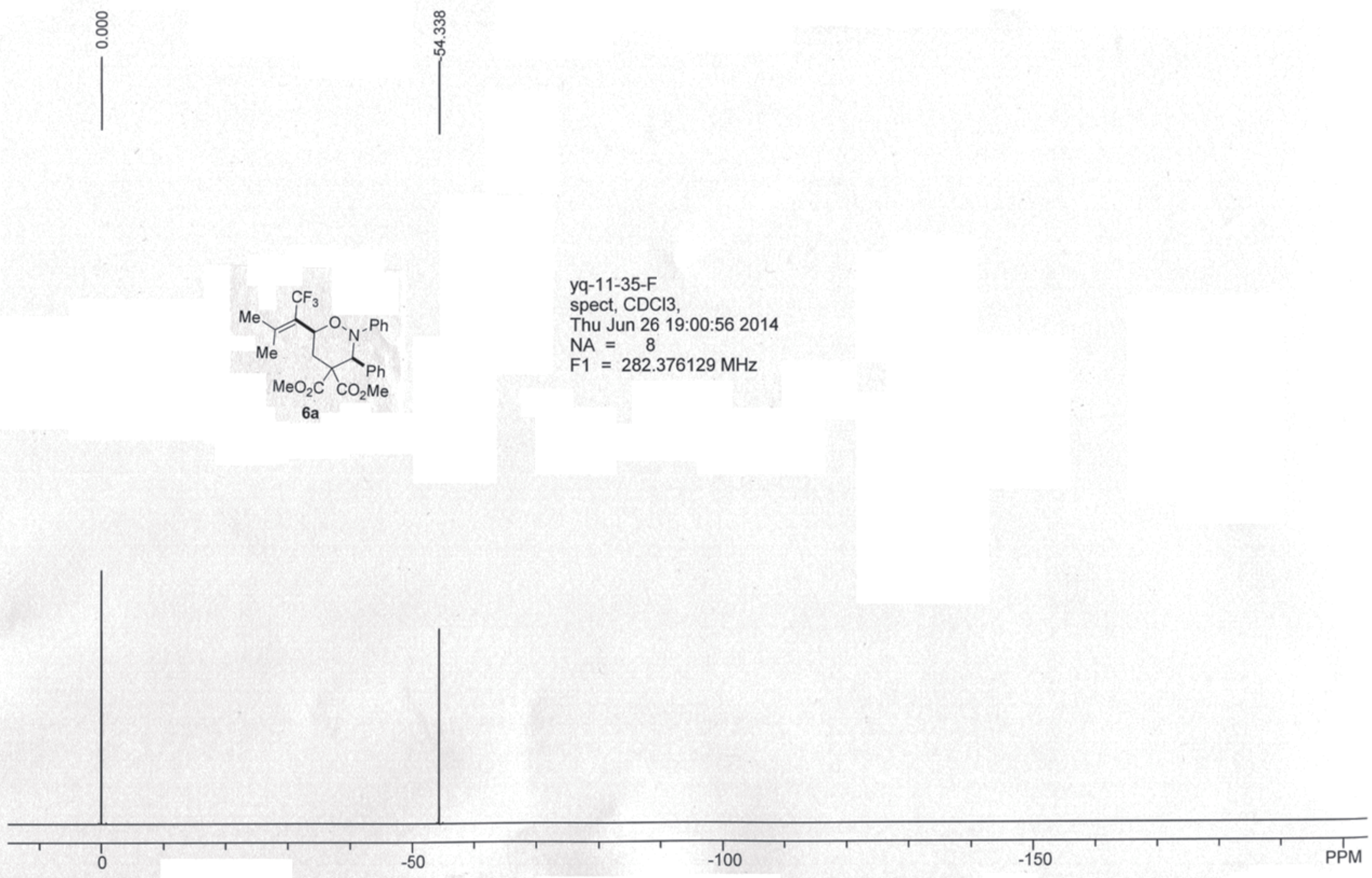

yq-11-32-H
spect, CDCl3,
Mon Nov 25 21:39:33 2013
NA = 6
F1 = 300.131866 MHz
5a
7.434
7.429
7.407
7.314
7.293
7.267
7.240
5.618
4.776
4.755
4.737
4.717
3.807
3.198
3.155
3.115
3.030
2.495
2.476
2.450
2.431
2.092
2.086
2.011
2.002
1.993
-0.000
3.07
2.01
0.99
0.99
3.00
1.02
2.96
1.00
3.04
3.07
PPM


171.427
169.049
147.844
147.793
147.752
147.709
136.977
129.872
128.015
127.752
126.911
126.201
122.547
121.888
121.530
121.173
120.815
118.882
84.345
84.307
77.431
77.000
76.580
75.151
65.776
52.946
52.894
52.070
39.161
22.901
22.865
yq-11-32-C
spect, CDCl3,
Tue Nov 26 14:12:10 2013
NA = 1024
F1 = 75.475296 MHz
Me
CF3
Me
O
Ph
MeO2C
CO2Me
5a
200
150
100
50
0 PPM

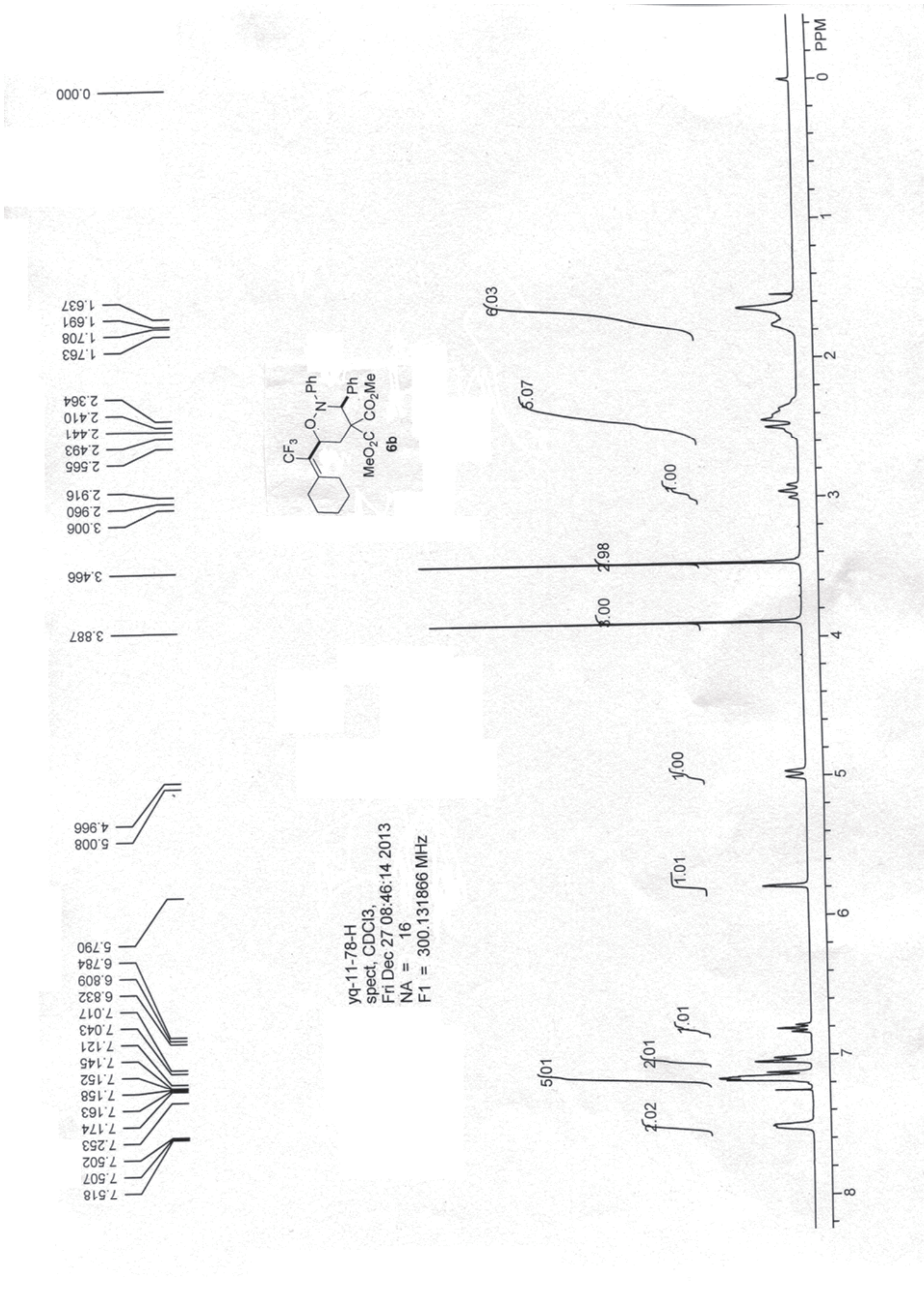

-0.000
-56.332
Me
CF3
Me
O
Ph
MeO2C
CO2Me
5a
yq-11-32-F
spect, CDCl3,
Thu Jun 26 18:54:28 2014
NA = 8
F1 = 282.376129 MHz
0
-20
-40
-60
-80
-100
-120
-140
-160
PPM


yq-11-35-H
spect, CDCl3,
Mon Dec 02 21:44:58 2013
NA = 6
F1 = 300.131866 MHz
6a
-0.000
1.908
1.915
1.922
1.929
1.993
2.003
2.012
2.021
2.449
2.492
2.906
2.950
2.996
3.421
3.863
4.913
4.954
5.771
6.757
6.782
6.806
7.011
7.037
7.094
7.118
7.123
7.133
7.139
7.147
7.157
7.167
7.172
7.509
7.515
7.531
7.540
PPM

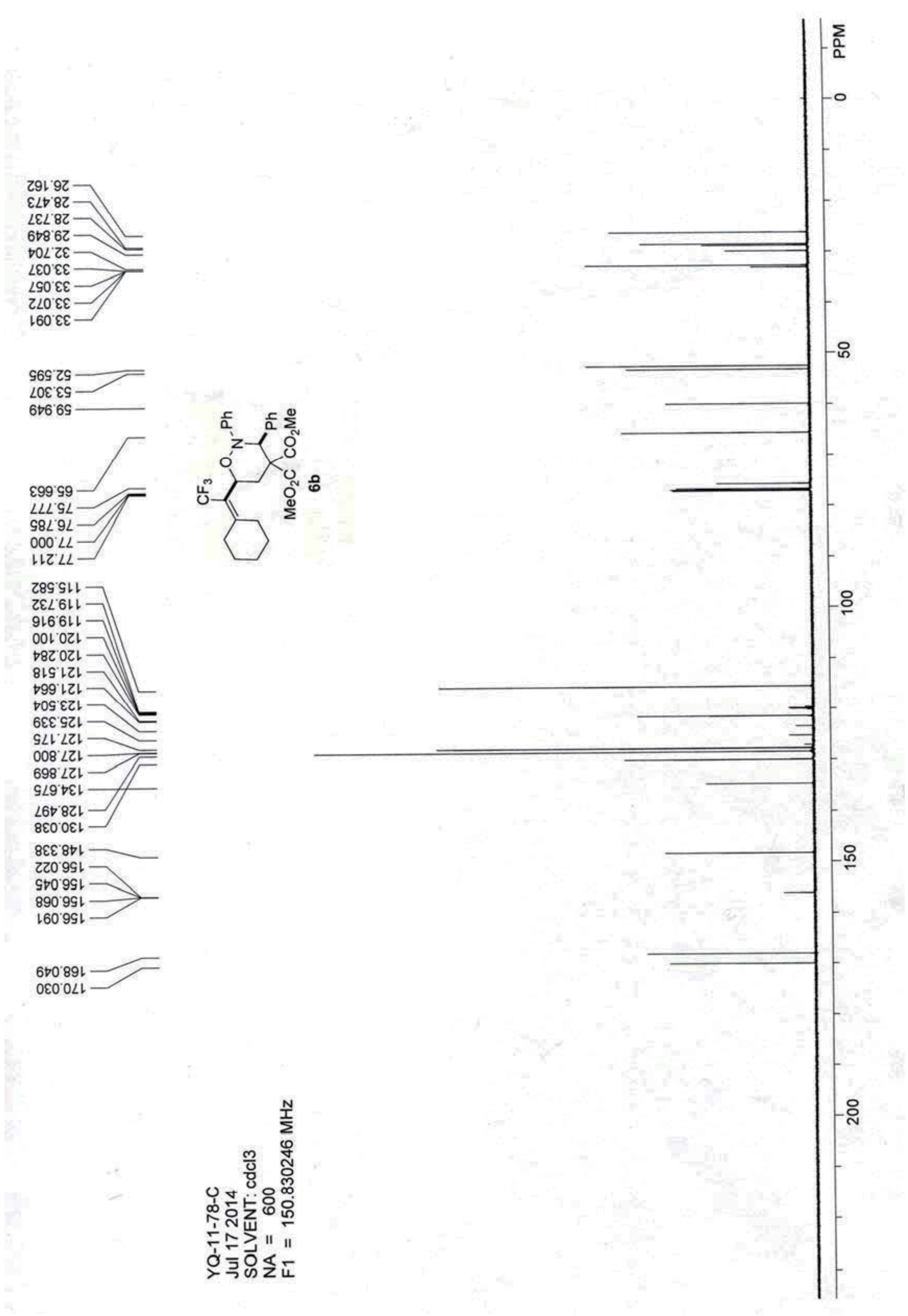

YQ-11-35-C
Jul 17 2014
SOLVENT: cdcl3
NA = 844
F1 = 150.830246 MHz
170.065
167.991
148.445
147.510
147.487
147.460
147.438
134.698
130.191
128.509
127.934
127.834
127.160
125.328
123.496
123.373
123.185
123.001
122.814
121.645
118.425
116.195
115.716
77.211
77.000
76.785
76.368
65.978
59.976
53.281
52.503
29.075
22.693
22.674
22.655
22.636
CF3
Me
Me
O
N
Ph
Ph
MeO2C
CO2Me
6a
200
150
100
50
0
PPM

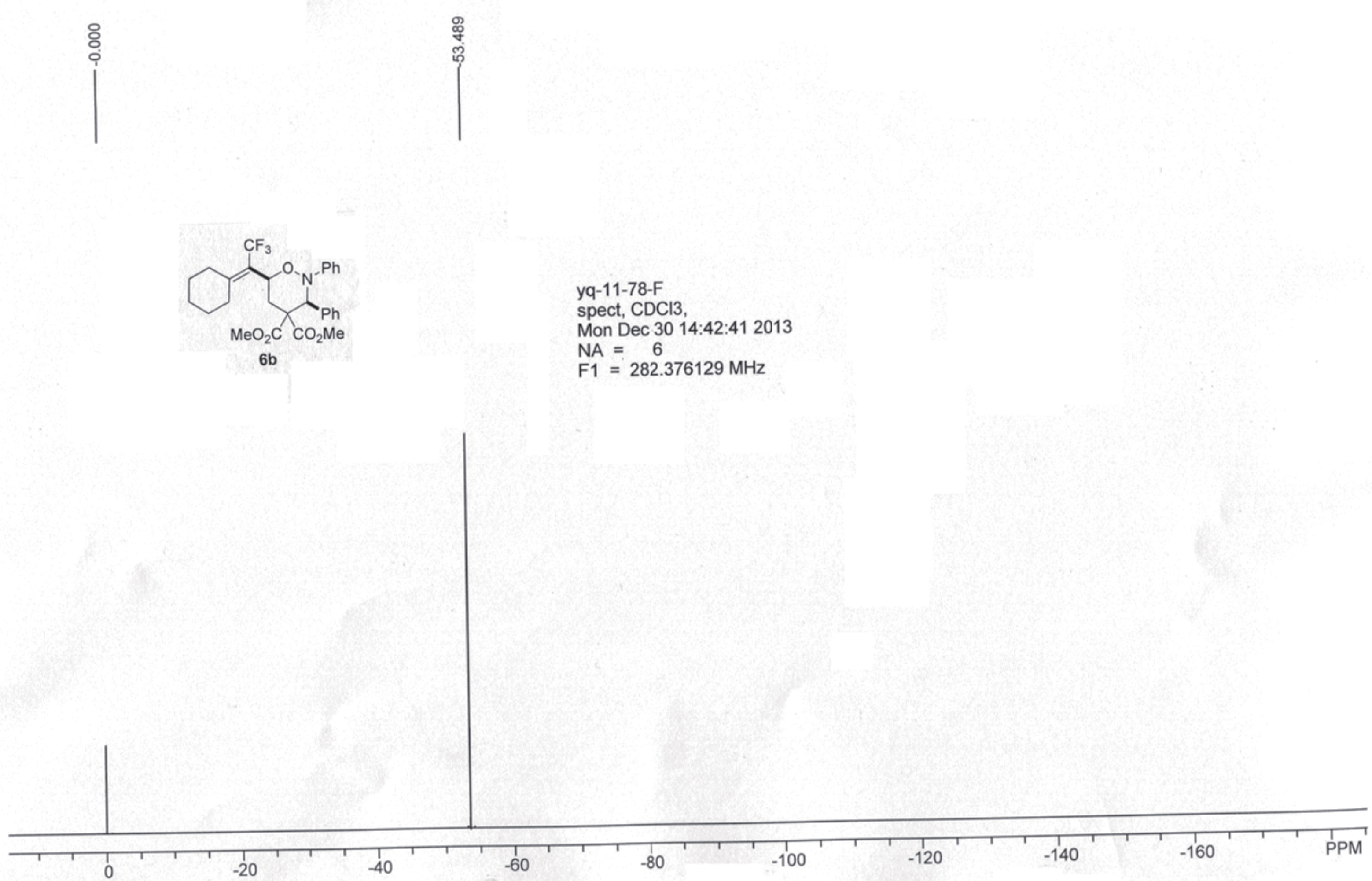


0.000
-54.338
CF3
Me
Me
O
N
Ph
Ph
MeO2C
CO2Me
6a
yq-11-35-F
spect, CDCl3,
Thu Jun 26 19:00:56 2014
NA = 8
F1 = 282.376129 MHz
0
-50
-100
-150
PPM



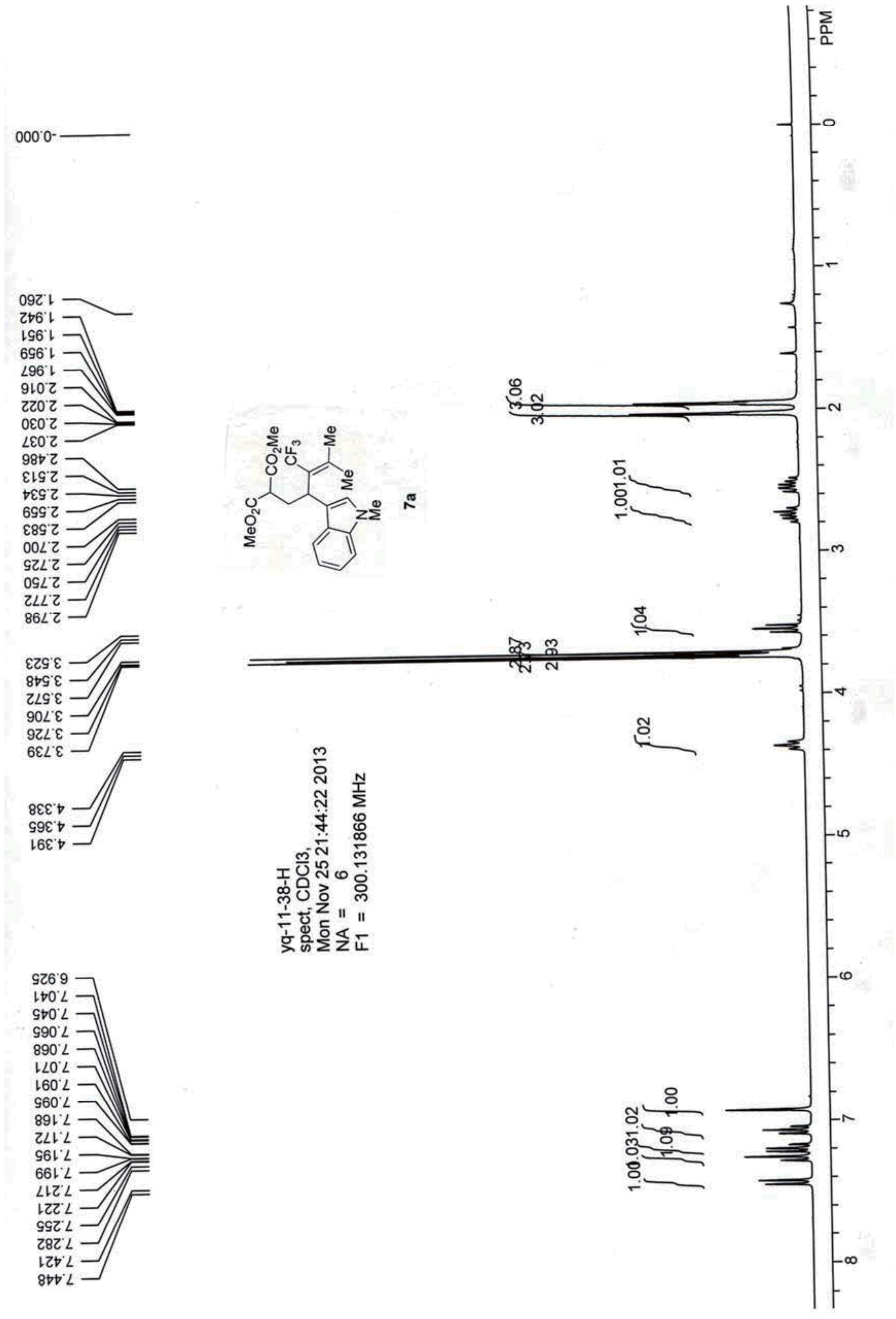
7.518
7.507
7.502
7.253
7.174
7.163
7.158
7.152
7.145
7.121
7.043
7.017
6.832
6.809
6.784
5.790
5.008
4.966
3.887
3.466
3.006
2.960
2.916
2.565
2.493
2.441
2.410
2.364
1.763
1.708
1.691
1.637
0.000
CF_3
O
N
Ph
Ph
MeO_2C
CO_2Me
6b
yq-11-78-H
spect, CDCl3,
Fri Dec 27 08:46:14 2013
NA = 16
F1 = 300.131866 MHz
2.02
5.01
2.01
1.01
1.01
1.00
3.00
2.98
1.00
5.07
6.03
PPM


YQ-11-78-C
Jul 17 2014
SOLVENT: cdcl3
NA = 600
F1 = 150.830246 MHz
170.030
168.049
156.091
156.068
156.045
156.022
148.338
130.038
128.497
134.675
127.869
127.800
127.175
125.339
123.504
121.664
121.518
120.284
120.100
119.916
119.732
115.582
77.211
77.000
76.785
75.777
65.663
59.949
53.307
52.595
33.091
33.072
33.057
33.037
32.704
29.849
28.737
28.473
26.162
CF3
O
N
Ph
Ph
MeO2C
CO2Me
6b
PPM
0
50
100
150
200



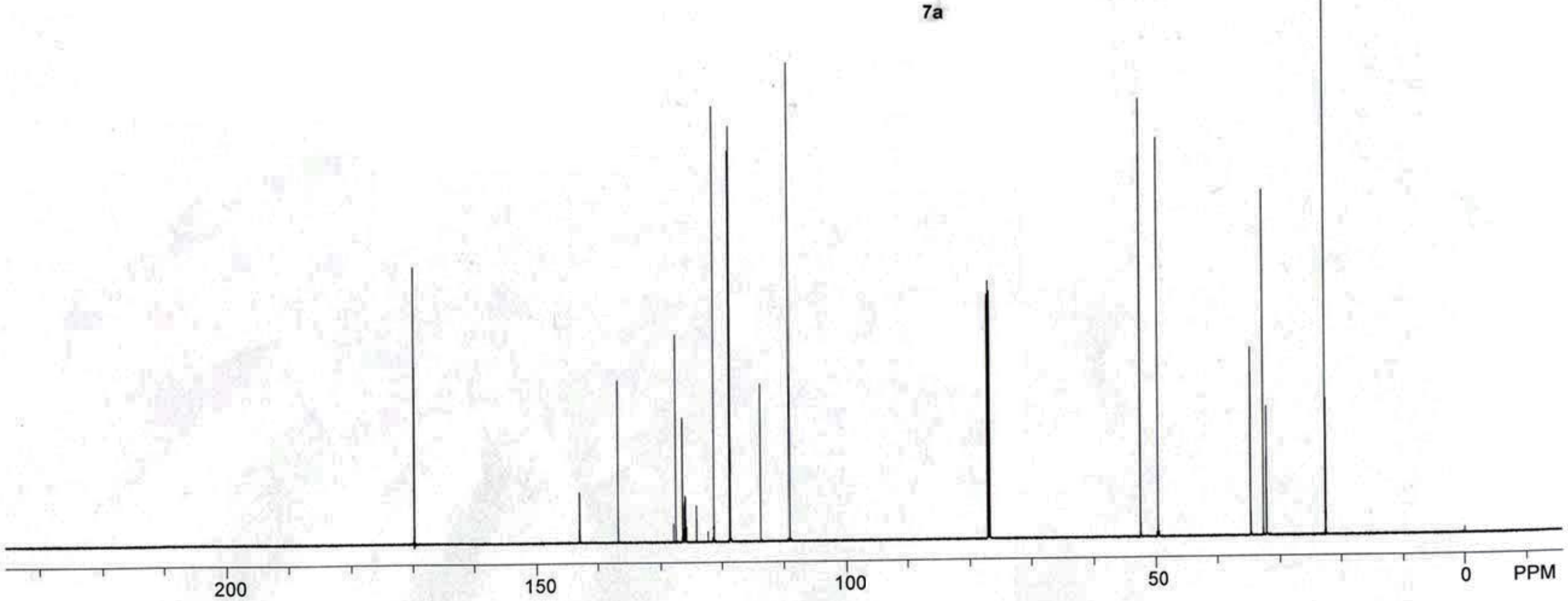
6b

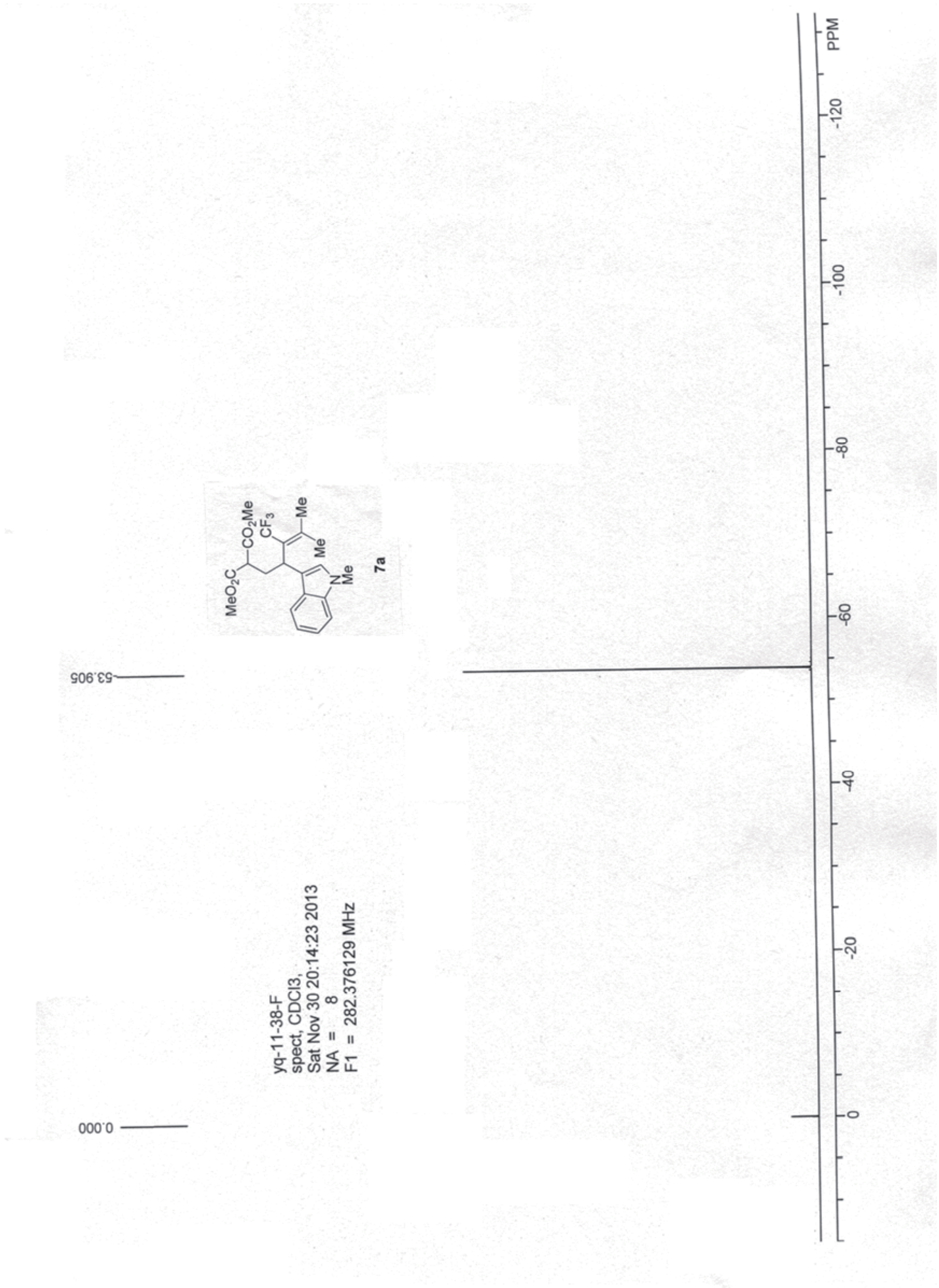
-0.000
-53.489
yq-11-78-F
spect, CDCl3,
Mon Dec 30 14:42:41 2013
NA = 6
F1 = 282.376129 MHz
0
-20
-40
-60
-80
-100
-120
-140
-160
PPM


yq-11-38-H
spect, CDCl3,
Mon Nov 25 21:44:22 2013
NA = 6
F1 = 300.131866 MHz
7a
PPM

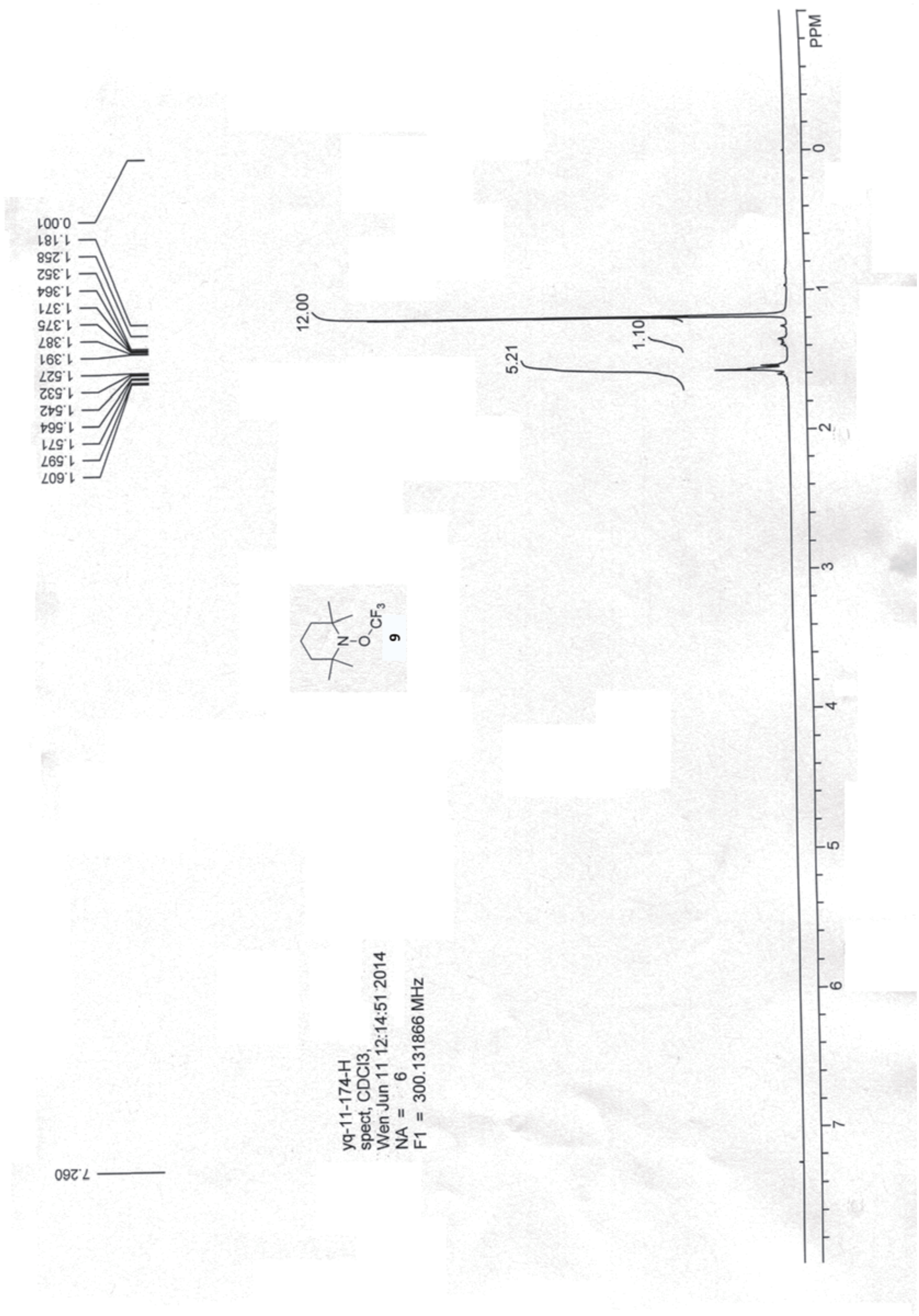
YQ-11-38-c
Jul 17 2014
SOLVENT: cdcl3
NA = 1824
F1 = 150.830246 MHz

7a

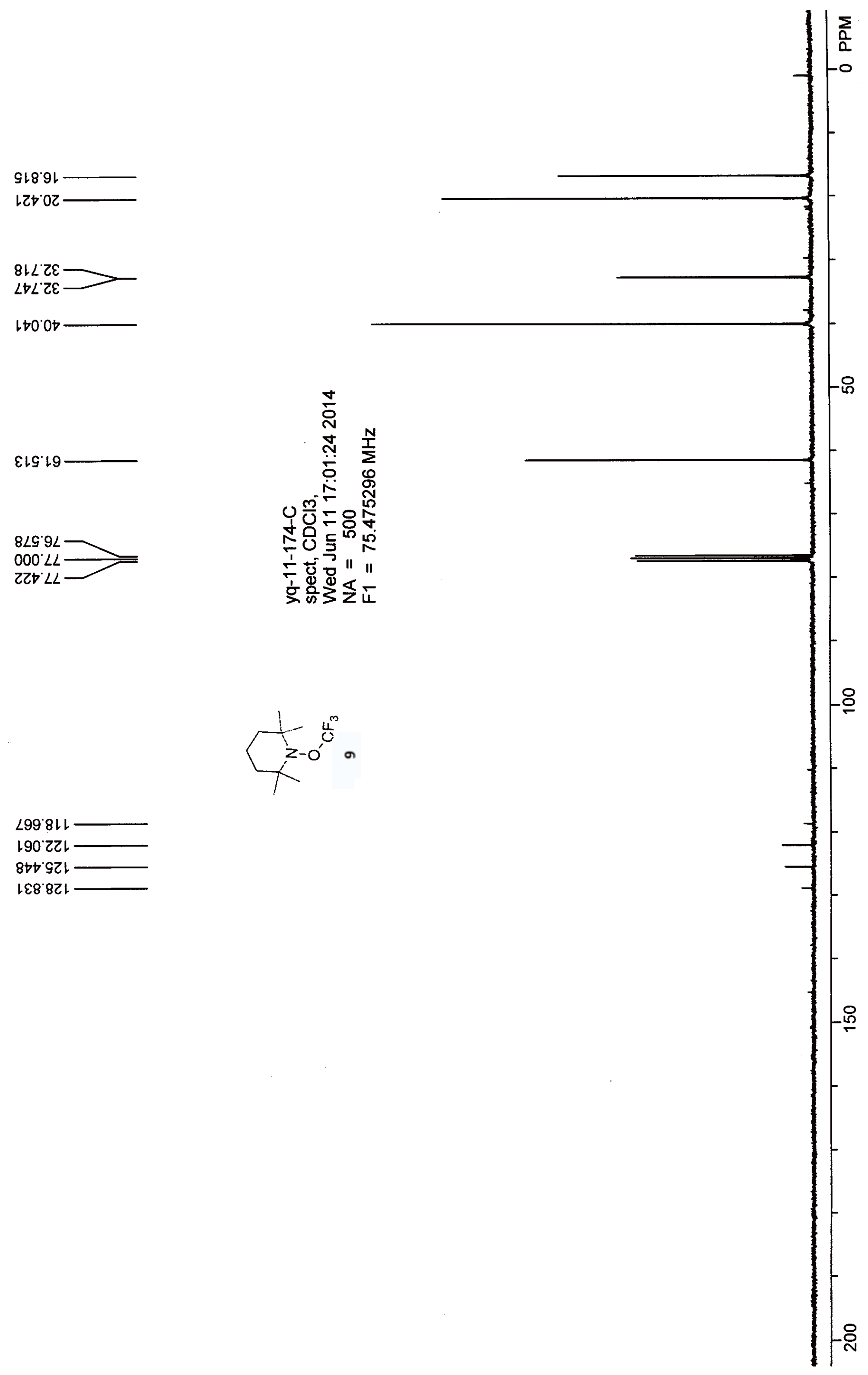


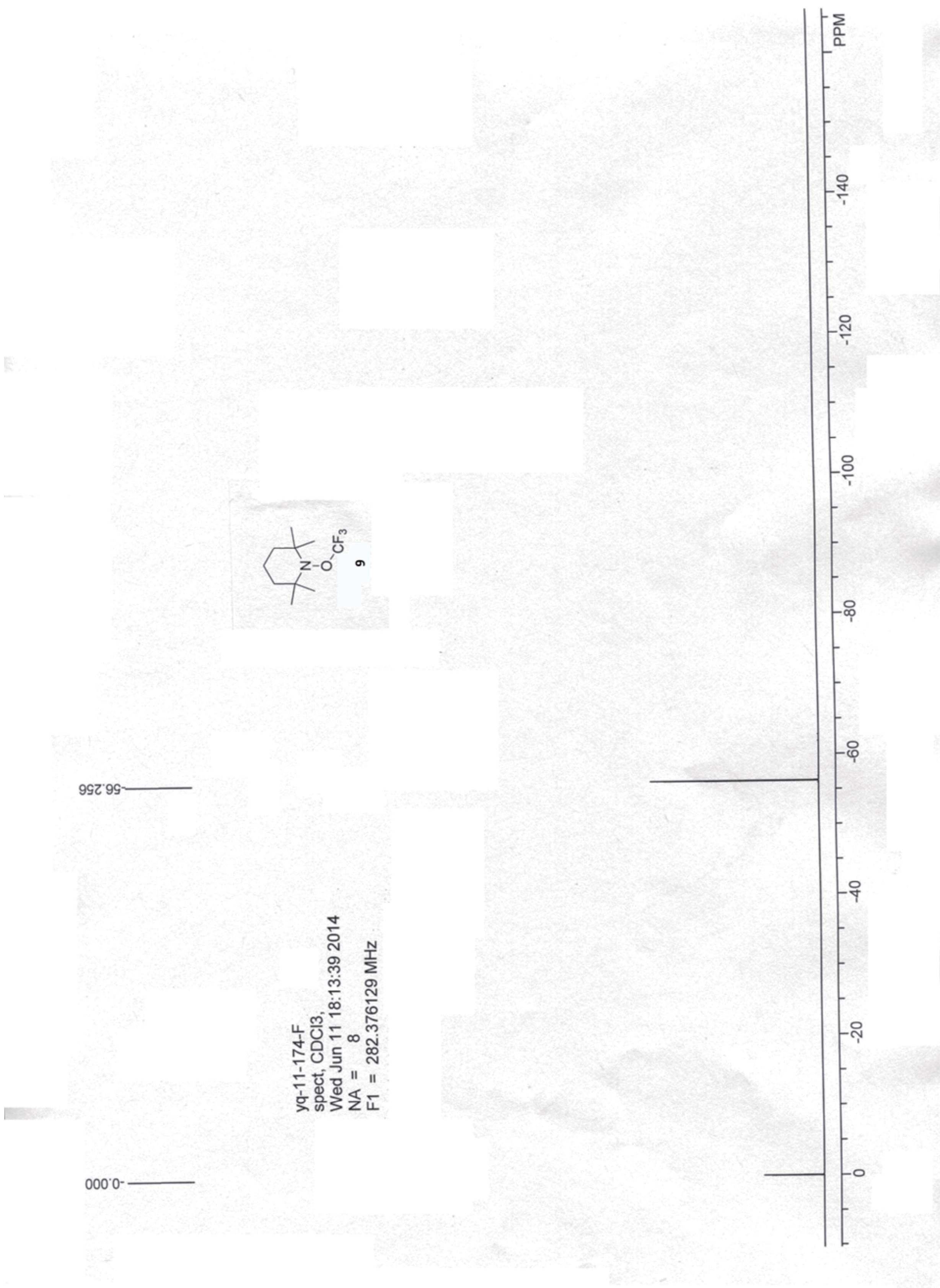


yq-11-38-F
spect, CDCl3,
Sat Nov 30 20:14:23 2013
NA = 8
F1 = 282.376129 MHz
-53.905
0.000
MeO2C
CO2Me
CF3
Me
Me
N
Me
7a
PPM
-120
-100
-80
-60
-40
-20
0

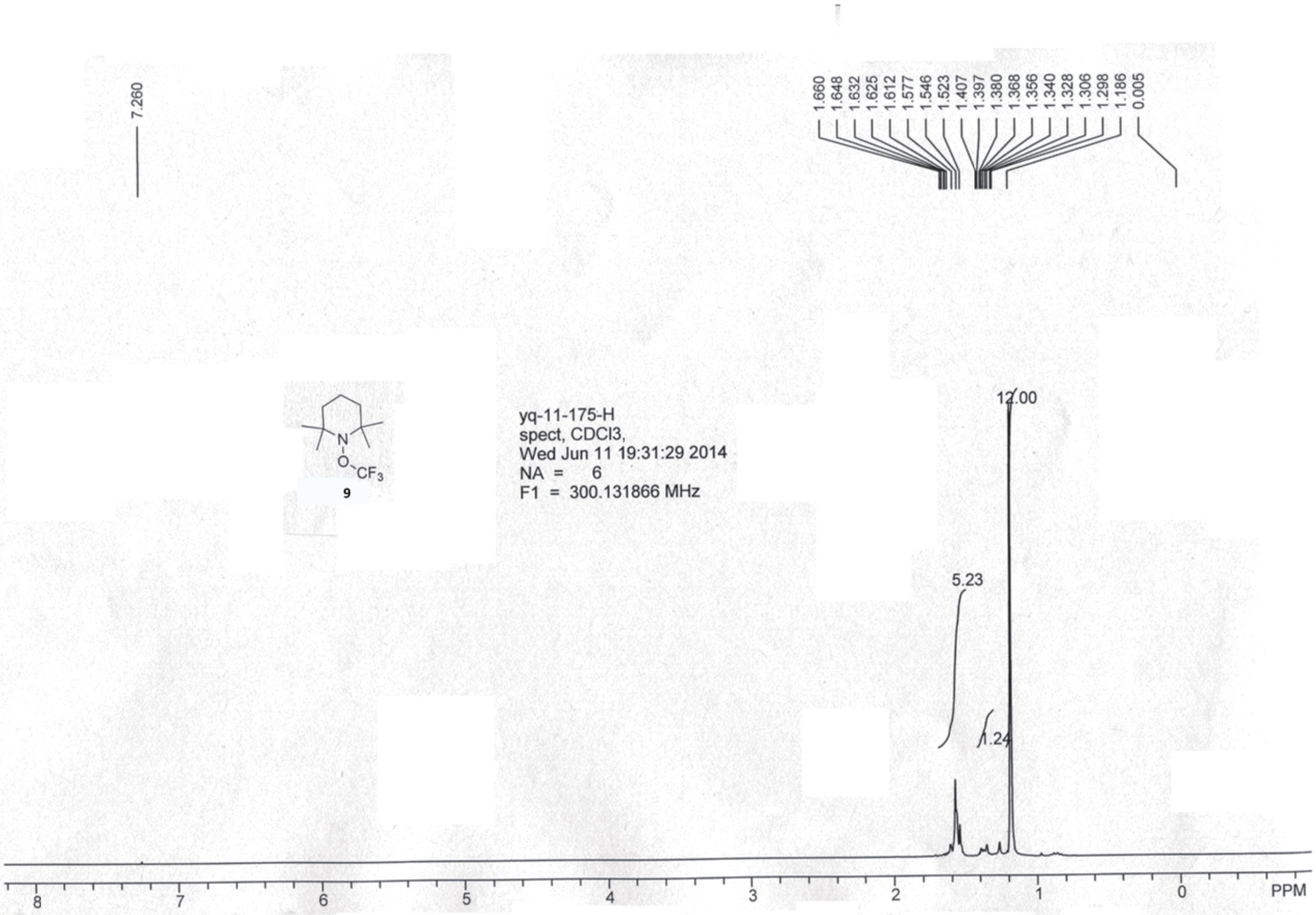


yq-11-174-H
spect, CDCl3,
Wen Jun 11 12:14:51 2014
NA = 6
F1 = 300.131866 MHz
7.260
1.607
1.597
1.571
1.564
1.542
1.532
1.527
1.391
1.387
1.375
1.371
1.364
1.352
1.258
1.181
0.001
12.00
5.21
1.10
N
O
CF3
9
PPM


16.815
20.421
32.718
32.747
40.041
61.513
76.578
77.000
77.422
118.667
122.061
125.448
128.831
yq-11-174-C
spect, CDCl3,
Wed Jun 11 17:01:24 2014
NA = 500
F1 = 75.475296 MHz
N
O
CF3
9
0 PPM
50
100
150
200



-56.256
-0.000
yq-11-174-F
spect, CDCl3,
Wed Jun 11 18:13:39 2014
NA = 8
F1 = 282.376129 MHz
9
PPM
-140
-120
-100
-80
-60
-40
-20
0


7.260
1.660
1.648
1.632
1.625
1.612
1.577
1.546
1.523
1.407
1.397
1.380
1.368
1.356
1.340
1.328
1.306
1.298
1.186
0.005
N
O
CF3
9
yq-11-175-H
spect, CDCl3,
Wed Jun 11 19:31:29 2014
NA = 6
F1 = 300.131866 MHz
12.00
5.23
1.24
8
7
6
5
4
3
2
1
0
PPM