Unexpected Regioselectivity Switch: Organophosphine-Triggered Reactions of Cyclopropene-1,1-dicarboxylates with Aldehydes

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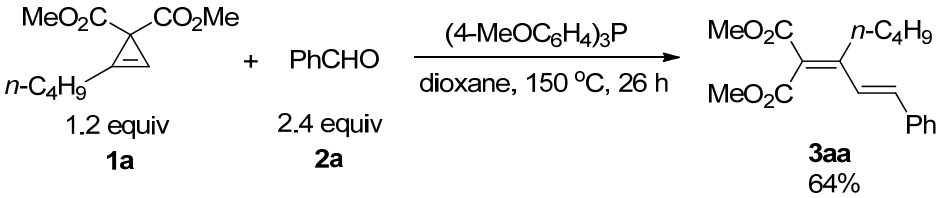
Supporting Information

General Information. ^{1}H NMR (300 or 400 MHz) and ^{13}C NMR (75 or 100 MHz) spectra were recorded with $CDCl_3$ as the solvent. Chemical shifts (δ) are given in parts per million (ppm). Infrared spectra were recorded with a Bruker Tensor 27 FT-IR Spectrometer. Mass and HRMS spectra were carried out in EI or ESI mode. Thin layer chromatography was performed on pre-coated glass-back plates and visualized with UV light at 254 nm. Flash column chromatography was performed with silica gel (10-40 μ). All reactions were carried out in oven dried Schlenk tubes with a screw cap. Dioxane used in experiment was refluxed over sodium wire using diphenyl ketone as indicator and distilled right before use. All the temperatures are referred to the oil baths applied. $(4\text{-}MeOC_6H_4)_3P$ (95 wt%) was purchased from Sigama-Aldrich. PhCHO was distilled before use. ^{19}F NMR experiments were measured with trifluoroacetic acid (-77.0 ppm) as the external reference.

Experimental procedures and characterization data

1. (*E*)-3-Butyl-2-(methoxycarbonyl)-5-phenyl-2,4-pentadienoic acid methyl ester 3aa (nsj-6-19):

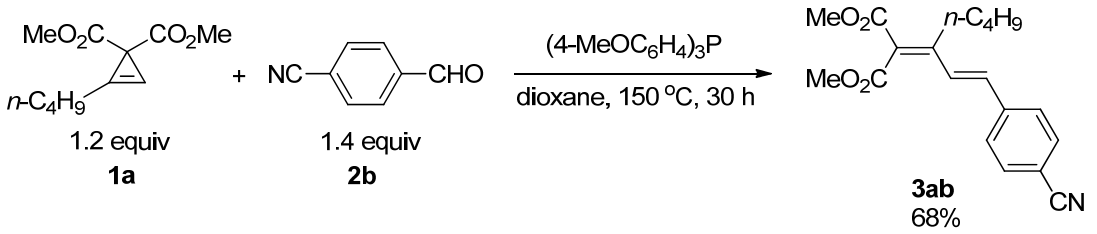


Typical Procedure: To a flame dried Schlenk tube with a screw cap were added $(4\text{-}MeOC_6H_4)_3P$ (95 wt%, 126.1 mg, 0.34 mmol), cyclopropene-1,1-dicarboxylate **1a** (84.8 mg, 0.4 mmol), dioxane (2 mL), benzaldehyde **2a** (84.9 mg, 0.8 mmol), and dioxane (2 mL) sequentially under Ar atmosphere. After being stirred at 150 °C for 26 h, the reaction was over as monitored by TLC. The mixture was exposed to air for one day to oxidize the remaining $(4\text{-}MeOC_6H_4)_3P$ to simplify the isolation. Evaporation and column chromatography on silica gel (eluent: petroleum ether/ethyl ether = 30/1) afforded the desired product **3aa** (65.8 mg, 64%): oil; ^{1}H NMR (400

MHz, $CDCl_3$) δ 7.57 (d, *J* = 16.4 Hz, 1 H, CH=), 7.50 (d, *J* = 7.6 Hz, 2 H, Ar-H), 7.39-7.27 (m, 3 H, Ar-H), 7.05 (d, *J* = 16.4 Hz, 1 H, CH=), 3.83 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3), 2.71-2.62 (m, 2 H, CH_2), 1.62-1.52 (m, 2 H, CH_2), 1.50-1.38 (m, 2 H, CH_2), 0.95 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.2, 166.0, 154.6, 137.0, 136.1, 129.1, 128.7, 127.4, 125.1, 123.6, 52.2, 52.1, 32.0, 29.8, 23.0, 13.8; MS (EI) *m/z* 303 (M^+ + 1, 9.27), 302 (M^+, 45.34), 141 (100); IR (neat, cm^{-1}) 2954, 2868, 1718, 1617, 1578, 1435, 1328, 1280, 1210, 1102, 1060, 1016; HRMS (EI) *m/z* calcd for $C_{18}H_{22}O_4$ [M^+]: 302.1518, found 302.1520.

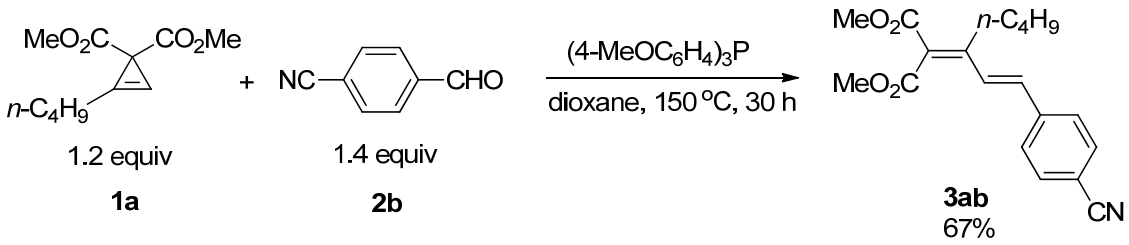
The following compounds were prepared according to this procedure. For the synthesis of **3ab**, **3ac**, **3ad** and **3af** the resulting reaction mixture was isolated without being exposed to air.

2. (*E*)-3-Butyl-5-(4-cyanophenyl)-2-(methoxycarbonyl)-2,4-pentadienoic acid methyl ester 3ab (nsj-6-47):



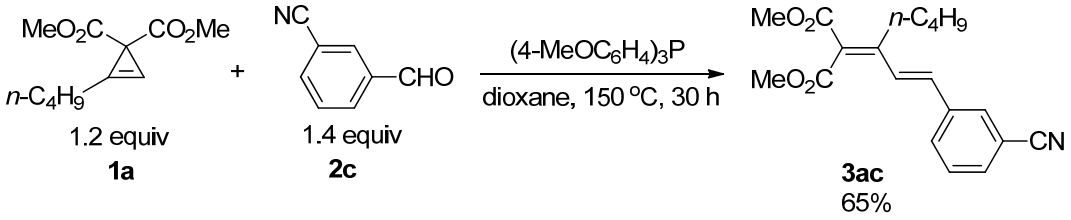
The reaction of $(4\text{-}MeOC_6H_4)_3P$ (95 wt%, 126.2 mg, 0.34 mmol), cyclopropene-1,1-dicarboxylate **1a** (84.8 mg, 0.4 mmol), dioxane (2 mL), 4-cyanobenzaldehyde **2b** (62.8 mg, 0.48 mmol), and dioxane (2 mL) afforded the desired product **3ab** (75.2 mg, 68%) (eluent: petroleum ether/ethyl acetate = 30/1): oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 16.4 Hz, 1 H, CH=), 7.64 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.58 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.00 (d, *J* = 16.4 Hz, 1 H, CH=), 3.83 (s, 6 H, 2×OCH_3), 2.65-2.58 (m, 2 H, CH_2), 1.61-1.51 (m, 2 H, CH_2), 1.49-1.37 (m, 2 H, CH_2), 0.95 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.1, 165.3, 153.2, 140.6, 134.4, 132.5, 128.6, 127.8, 125.4, 118.6, 112.0, 52.31, 52.27, 31.9, 30.0, 22.9, 13.7; MS (EI) *m/z* 328 (M^+ + 1, 21.93), 327 (M^+, 100); IR (neat, cm^{-1}) 2226, 1717, 1619, 1603, 1580, 1433, 1218, 1101, 1061, 1014; HRMS (EI) *m/z* calcd for $C_{19}H_{21}NO_4$ [M^+]: 327.1471, found 327.1473.

Gram scale synthesis (nsj-6-20):



The reaction of $(4\text{-}MeOC_6H_4)_3P$ (95 wt%, 1.5743 g, 4.25 mmol), cyclopropene-1,1-dicarboxylate **1a** (1.0609 g, 5.0 mmol), dioxane (25 mL), 4-cyanobenzaldehyde **2b** (0.7866 g, 6.0 mmol), and dioxane (25 mL) afforded the desired product **3ab** (0.9311 g, 67%) (eluent: petroleum ether/ethyl acetate = 30/1): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 15.9 Hz, 1 H, CH=), 7.65 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.58 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.00 (d, *J* = 16.2 Hz, 1 H, CH=), 3.83 (s, 6 H, 2×OCH_3), 2.66-2.57 (m, 2 H, CH_2), 1.62-1.36 (m, 4 H, 2×CH_2), 0.95 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.1, 165.3, 153.2, 140.6, 134.4, 132.4, 128.5, 127.8, 125.3, 118.6, 111.9, 52.32, 52.28, 31.9, 30.0, 22.9, 13.7.

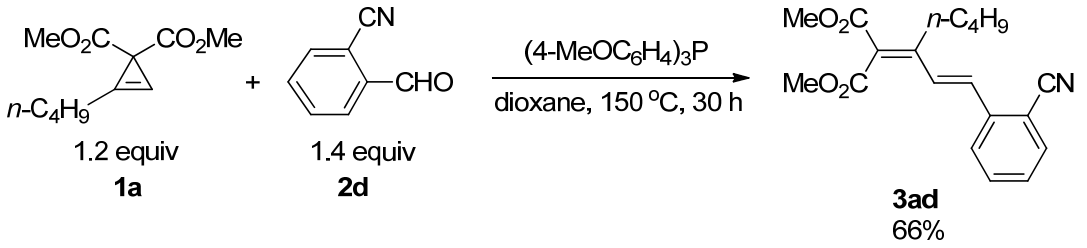
3. (*E*)-3-Butyl-5-(3-cyanophenyl)-2-(methoxycarbonyl)-2,4-pentadienoic acid methyl ester 3ac (nsj-5-172):



The reaction of $(4\text{-}MeOC_6H_4)_3P$ (95 wt%, 126.1 mg, 0.34 mmol), cyclopropene-1,1-dicarboxylate **1a** (84.4 mg, 0.4 mmol), dioxane (2 mL), 3-cyanobenzaldehyde **2c** (62.9 mg, 0.48 mmol), and dioxane (2 mL) afforded the desired product **3ac** (72.1 mg, 65%) (eluent: petroleum ether/ethyl acetate = 30/1): oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.67 (m, 3 H, CH= and Ar-H), 7.61-7.56 (m, 1 H, Ar-H), 7.48 (t, *J* = 7.6 Hz, 1 H, Ar-H), 6.99 (d, *J* = 16.4 Hz, 1 H, CH=), 3.84 (s, 3 H, OCH_3), 3.83 (s, 3 H, OCH_3), 2.65-2.58 (m, 2 H, CH_2), 1.61-1.51 (m, 2 H, CH_2),

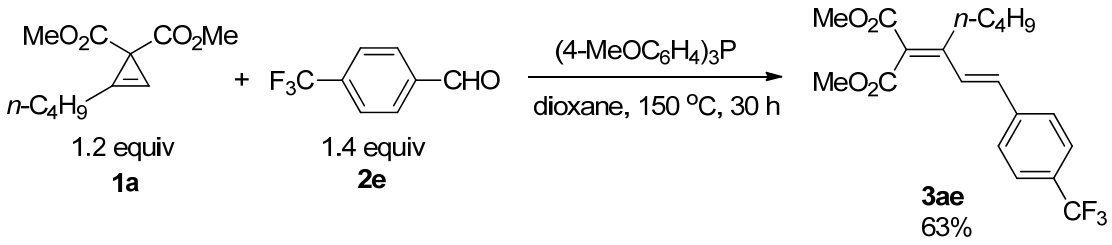
1.49-1.38 (m, 2 H, CH_2), 0.95 (t, J = 7.4 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.1, 165.4, 153.3, 137.5, 134.0, 132.0, 131.1, 130.8, 129.6, 127.6, 125.1, 118.3, 113.1, 52.32, 52.25, 31.9, 30.0, 22.9, 13.7; MS (EI) *m/z* 328 (M^+ + 1, 3.76), 327 (M^+, 15.26), 149 (100); IR (neat, cm^{-1}) 2961, 2231, 1718, 1258, 1214, 1090, 1061, 1014; HRMS (EI) *m/z* calcd for $C_{19}H_{21}NO_4$ [M^+]: 327.1471, found 327.1475.

4. (*E*)-3-Butyl-5-(2-cyanophenyl)-2-(methoxycarbonyl)-2,4-pentadienoic acid methyl ester 3ad (nsj-5-173):



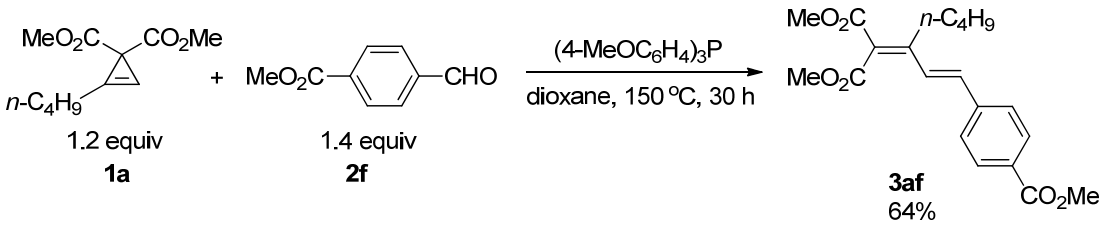
The reaction of $(4\text{-}MeOC_6H_4)_3P$ (95 wt%, 126.1 mg, 0.34 mmol), cyclopropene-1,1-dicarboxylate **1a** (84.3 mg, 0.4 mmol), dioxane (2 mL), 2-cyanobenzaldehyde **2d** (63.0 mg, 0.48 mmol), and dioxane (2 mL) afforded the desired product **3ad** (73.5 mg, 66%) (eluent: petroleum ether/ethyl acetate = 30/1): oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 16.4 Hz, 1 H, CH=), 7.79 (d, J = 7.6 Hz, 1 H, Ar-H), 7.69-7.65 (m, 1 H, Ar-H), 7.63-7.57 (m, 1 H, Ar-H), 7.43-7.36 (m, 2 H, CH= and Ar-H), 3.84 (s, 3 H, OCH_3), 3.83 (s, 3 H, OCH_3), 2.70-2.62 (m, 2 H, CH_2), 1.67-1.55 (m, 2 H, CH_2), 1.52-1.40 (m, 2 H, CH_2), 0.97 (t, J = 7.4 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.2, 165.3, 153.4, 139.3, 133.0, 132.9, 131.9, 129.3, 128.9, 126.0, 125.5, 117.4, 112.1, 52.33, 52.32, 31.9, 30.2, 22.9, 13.7; MS (EI) *m/z* 328 (M^+ + 1, 6.08), 327 (M^+, 26.42), 285 (100); IR (neat, cm^{-1}) 2958, 2220, 1725, 1711, 1620, 1585, 1475, 1451, 1433, 1226, 1065, 1014; HRMS (EI) *m/z* calcd for $C_{19}H_{21}NO_4$ [M^+]: 327.1471, found 327.1477.

5. (*E*)-3-Butyl-2-(methoxycarbonyl)-5-(4-trifluoromethylphenyl)-2,4-pentadie noic acid methyl ester 3ae (nsj-6-18):



The reaction of $(4\text{-}MeOC_6H_4)_3P$ (95 wt%, 126.0 mg, 0.34 mmol), cyclopropene-1,1-dicarboxylate **1a** (84.6 mg, 0.4 mmol), dioxane (2 mL), 4-(trifluoromethyl)benzaldehyde **2e** (83.6 mg, 0.48 mmol), and dioxane (2 mL) afforded the desired product **3ae** (79.3 mg, 63%) (eluent: petroleum ether/ethyl ether = 40/1): oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 16.0 Hz, 1 H, CH=), 7.65-7.55 (m, 4 H, Ar-H), 7.04 (d, *J* = 16.0 Hz, 1 H, CH=), 3.830 (s, 3 H, OCH_3), 3.825 (s, 3 H, OCH_3), 2.68-2.60 (m, 2 H, CH_2), 1.62-1.52 (m, 2 H, CH_2), 1.50-1.38 (m, 2 H, CH_2), 0.95 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.2, 165.6, 153.7, 139.7 (q, *J* = 1.5 Hz), 135.0, 130.5 (q, *J* = 32.3 Hz), 127.5, 125.7 (q, *J* = 3.7 Hz), 124.9, 123.9 (q, *J* = 270.6 Hz), 52.3, 52.2, 32.0, 30.0, 23.0, 13.7; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -62.7; MS (EI) *m/z* 371 (M^+ + 1, 11.10), 370 (M^+, 51.82), 306 (100); IR (neat, cm^{-1}) 1720, 1618, 1583, 1435, 1322, 1215, 1165, 1120, 1062, 1014; HRMS (EI) *m/z* calcd for $C_{19}H_{21}O_4F_3$ [M^+]: 370.1392, found 370.1389.

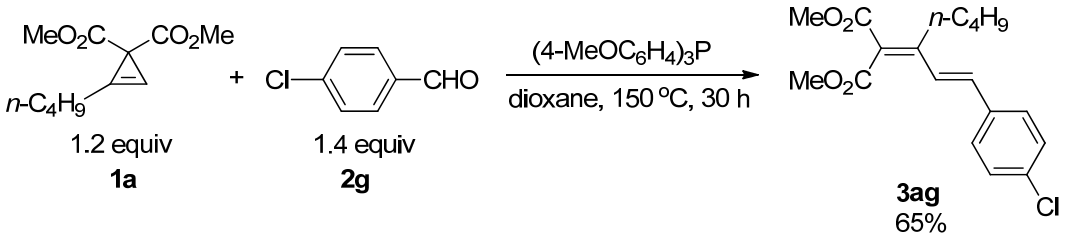
6. (*E*)-3-Butyl-2-(methoxycarbonyl)-5-(4-methoxycarbonylphenyl)-2,4-pentadienoic acid methyl ester 3af (nsj-5-186):



The reaction of $(4\text{-}MeOC_6H_4)_3P$ (95 wt%, 126.0 mg, 0.34 mmol), cyclopropene-1,1-dicarboxylate **1a** (84.7 mg, 0.4 mmol), dioxane (2 mL), methyl 4-formylbenzoate **2f** (78.7 mg, 0.48 mmol), and dioxane (2 mL) afforded the desired product **3af** (78.2 mg, 64%) (eluent: petroleum ether/ethyl acetate = 30/1): oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.72 (d, *J* = 16.0 Hz, 1 H, CH=), 7.56 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.05 (d, *J* = 16.0 Hz, 1 H, CH=), 3.93 (s, 3 H,

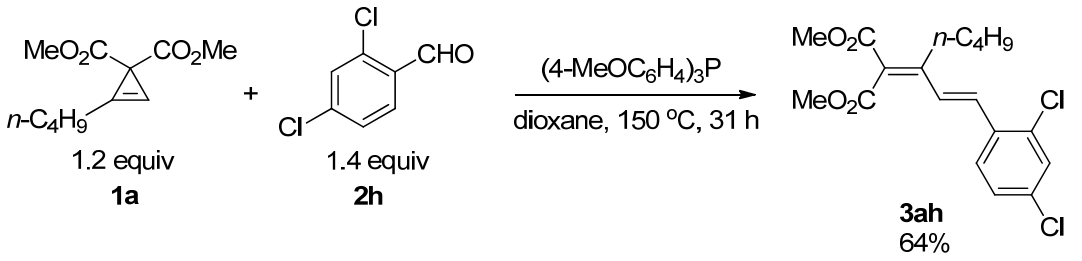
OCH_3), 3.84 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 2.69-2.62 (m, 2 H, CH_2), 1.62-1.52 (m, 2 H, CH_2), 1.50-1.39 (m, 2 H, CH_2), 0.96 (t, J = 7.2 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.5, 166.2, 165.6, 153.8, 140.6, 135.5, 130.2, 130.0, 127.5, 127.3, 124.8, 52.3, 52.2, 52.1, 32.0, 29.9, 23.0, 13.8; MS (EI) *m/z* 361 (M^+ + 1, 11.55), 360 (M^+, 50.60), 258 (100); IR (neat, cm^{-1}) 1716, 1580, 1434, 1276, 1217, 1107, 1061, 1016; HRMS (EI) *m/z* calcd for $C_{20}H_{24}O_6$ [M^+]: 360.1573, found 360.1569.

7. (*E*)-3-Butyl-5-(4-chlorophenyl)-2-(methoxycarbonyl)-2,4-pentadienoic acid methyl ester 3ag (nsj-6-45):



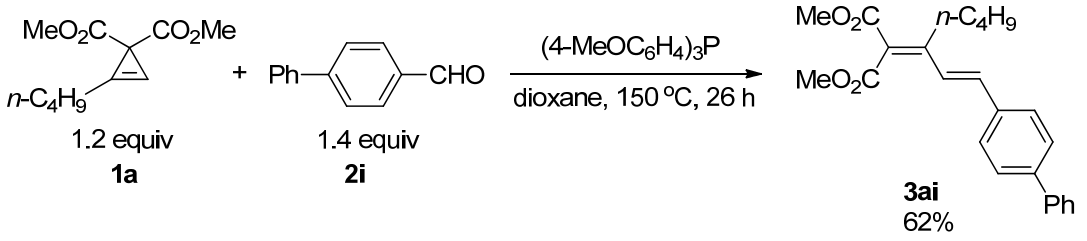
The reaction of $(4\text{-}MeOC_6H_4)_3P$ (95 wt%, 126.0 mg, 0.34 mmol), cyclopropene-1,1-dicarboxylate **1a** (84.8 mg, 0.4 mmol), dioxane (2 mL), 4-chlorobenzaldehyde **2g** (67.8 mg, 0.48 mmol), and dioxane (2 mL) afforded the desired product **3ag** (74.5 mg, 65%) (eluent: petroleum ether/ethyl ether = 30/1): oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 16.0 Hz, 1 H, CH=), 7.43 (d, J = 8.4 Hz, 2 H, Ar-H), 7.32 (d, J = 8.4 Hz, 2 H, Ar-H), 6.98 (d, J = 16.4 Hz, 1 H, CH=), 3.82 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3), 2.67-2.58 (m, 2 H, CH_2), 1.62-1.50 (m, 2 H, CH_2), 1.49-1.35 (m, 2 H, CH_2), 0.95 (t, J = 7.2 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.3, 165.8, 154.2, 135.5, 134.8, 134.7, 129.0, 128.6, 125.7, 124.0, 52.24, 52.18, 32.0, 29.9, 23.0, 13.8; MS (EI) *m/z* 339 (M^+ (^{35}Cl) + 1, 5.61), 338 (M^+ (^{37}Cl), 24.52), 337 (M^+ (^{35}Cl) + 1, 14.43), 336 (M^+ (^{35}Cl), 69.97), 245 (100); IR (neat, cm^{-1}) 1716, 1618, 1577, 1491, 1433, 1216, 1061; HRMS (EI) *m/z* calcd for $C_{18}H_{21}O_4{}^{35}Cl$ [M^+]: 336.1128, found 336.1130.

8. (*E*)-3-Butyl-5-(2,4-dichlorophenyl)-2-(methoxycarbonyl)-2,4-pentadienoic acid methyl ester 3ah (nsj-6-17):



The reaction of $(4\text{-}MeOC_6H_4)_3P$ (95 wt%, 126.4 mg, 0.34 mmol), cyclopropene-1,1-dicarboxylate **1a** (84.6 mg, 0.4 mmol), dioxane (2 mL), 2,4-dichlorobenzaldehyde **2h** (84.1 mg, 0.48 mmol), and dioxane (2 mL) afforded the desired product **3ah** (81.1 mg, 64%) (eluent: petroleum ether/ethyl ether = 30/1): oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.56 (m, 2 H, Ar-H and CH=), 7.42-7.35 (m, 2 H, Ar-H and CH=), 7.24 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1 H, Ar-H), 3.83 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 2.64 (t, J = 8.0 Hz, 2 H, CH_2), 1.65-1.54 (m, 2 H, CH_2), 1.50-1.39 (m, 2 H, CH_2), 0.96 (t, J = 7.4 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.2, 165.5, 154.0, 134.9, 134.6, 133.0, 131.6, 129.6, 127.9, 127.7, 127.5, 124.7, 52.3, 52.2, 31.9, 30.1, 23.0, 13.7; MS (EI) *m/z* 374 (M^+ ($^{37}Cl^{37}Cl$), 7.59), 373 (M^+ ($^{37}Cl\,^{35}Cl$) + 1, 8.27), 372 (M^+ ($^{37}Cl\,^{35}Cl$), 41.60), 371 (M^+ ($^{35}Cl\,^{35}Cl$) + 1, 12.88), 370 (M^+ ($^{35}Cl\,^{35}Cl$), 62.74), 271 (100); IR (neat, cm^{-1}) 2958, 1719, 1578, 1468, 1433, 1256, 1215, 1140, 1100, 1061, 1014; HRMS (EI) *m/z* calcd for $C_{18}H_{20}O_4{}^{35}Cl_2$ [M^+]: 370.0739, found 370.0742.

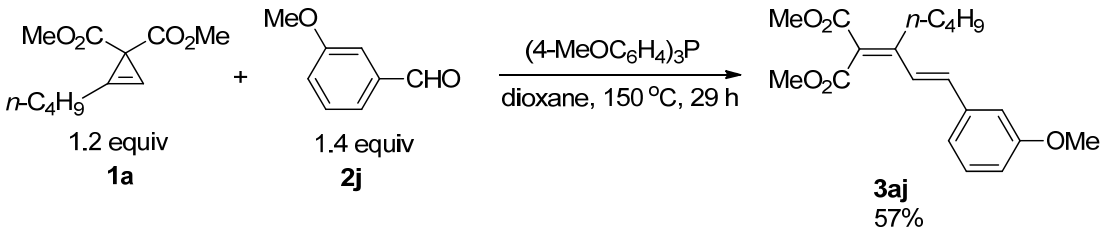
9. (*E*)-3-Butyl-2-(methoxycarbonyl)-5-(4-phenylphenyl)-2,4-pentadienoic acid methyl ester 3ai (nsj-6-48):



The reaction of $(4\text{-}MeOC_6H_4)_3P$ (95 wt%, 126.2 mg, 0.34 mmol), cyclopropene-1,1-dicarboxylate **1a** (84.6 mg, 0.4 mmol), dioxane (2 mL), 4-phenylbenzaldehyde **2i** (87.5 mg, 0.48 mmol), and dioxane (2 mL) afforded the desired product **3ai** (79.5 mg, 62%) (eluent: petroleum ether/ethyl ether = 30/1) and

recrystallization from hexane: solid; m.p. 155-157 ^{o}C (hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67-7.53 (m, 7 H, Ar-H and CH=), 7.44 (t, *J* = 7.6 Hz, 2 H, Ar-H), 7.40-7.32 (m, 1 H, Ar-H), 7.08 (d, *J* = 16.4 Hz, 1 H, CH=), 3.83 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3), 2.73-2.63 (m, 2 H, CH_2), 1.66-1.52 (m, 2 H, CH_2), 1.52-1.38 (m, 2 H, CH_2), 0.96 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.3, 166.0, 154.6, 141.8, 140.3, 136.5, 135.2, 128.8, 128.0, 127.6, 127.4, 126.9, 125.2, 123.7, 52.2, 52.1, 32.1, 29.8, 23.0, 13.8; MS (EI) m/z 379 (M^+ + 1, 21.30), 378 (M^+, 80.59), 287 (100); IR (neat, cm^{-1}) 1722, 1707, 1573, 1486, 1433, 1213, 1193, 1060, 1014; Anal. calcd for $C_{24}H_{26}O_4$: C 76.17; H 6.92. Found: C 75.94; H 6.97.

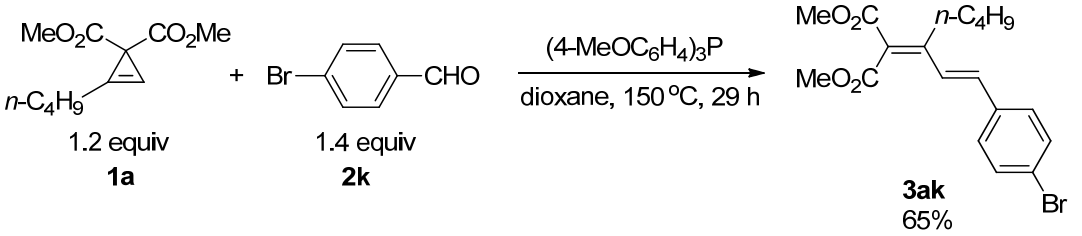
10. (*E*)-3-Butyl-2-(methoxycarbonyl)-5-(3-methoxyphenyl)-2,4-pentadienoic acid methyl ester 3aj (nsj-5-175):



The reaction of $(4\text{-}MeOC_6H_4)_3P$ (95 wt%, 126.2 mg, 0.34 mmol), cyclopropene-1,1-dicarboxylate **1a** (84.6 mg, 0.4 mmol), dioxane (2 mL), 3-methoxybenzaldehyde **2j** (65.5 mg, 0.48 mmol), and dioxane (2 mL) afforded the desired product **3aj** (63.8 mg, 57%) (eluent: petroleum ether/ethyl ether = 30/1): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 16.2 Hz, 1 H, CH=), 7.28 (t, *J* = 8.0 Hz, 1 H, Ar-H), 7.10 (d, *J* = 7.8 Hz, 1 H, Ar-H), 7.06-6.96 (m, 2 H, Ar-H and CH=), 6.87 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1 H, Ar-H), 3.83 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3), 2.71-2.61 (m, 2 H, CH_2), 1.63-1.37 (m, 4 H, 2×CH_2), 0.95 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.2, 166.0, 159.8, 154.5, 137.6, 136.9, 129.7, 125.5, 123.8, 120.1, 114.8, 112.7, 55.2, 52.2, 52.1, 32.0, 29.8, 23.0, 13.8; MS (EI) *m/z* 332 (M^+, 15.92), 272 (100); IR (neat, cm^{-1}) 1717, 1580, 1433, 1210, 1157, 1061, 1015; HRMS (EI) *m/z* calcd for $C_{19}H_{24}O_5$ [M^+]: 332.1624, found 332.1625.

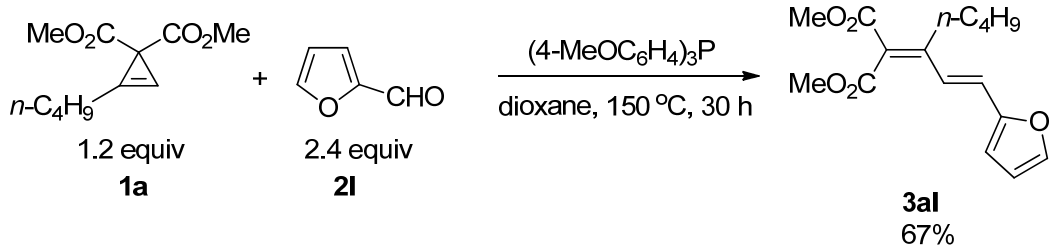
11. (*E*)-3-Butyl-5-(4-bromophenyl)-2-(methoxycarbonyl)-2,4-pentadienoic acid

methyl ester 3ak (nsj-5-176):



The reaction of $(4\text{-}MeOC_6H_4)_3P$ (95 wt%, 126.1 mg, 0.34 mmol), cyclopropene-1,1-dicarboxylate **1a** (84.5 mg, 0.4 mmol), dioxane (2 mL), 4-bromobenzaldehyde **2k** (88.8 mg, 0.48 mmol), and dioxane (2 mL) afforded the desired product **3ak** (84.1 mg, 65%) (eluent: petroleum ether/ethyl ether = 30/1): oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 16.4 Hz, 1 H, CH=), 7.48 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.36 (d, *J* = 8.4 Hz, 2 H, Ar-H), 6.96 (d, *J* = 16.4 Hz, 1 H, CH=), 3.82 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3), 2.67-2.57 (m, 2 H, CH_2), 1.61-1.50 (m, 2 H, CH_2), 1.49-1.37 (m, 2 H, CH_2), 0.95 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.3, 165.7, 154.2, 135.5, 135.1, 131.9, 128.8, 125.8, 124.1, 123.1, 52.23, 52.18, 32.0, 29.9, 23.0, 13.8; MS (EI) *m/z* 383 ($M^+(^{81}Br)$ + 1, 3.44), 382 ($M^+(^{81}Br)$, 15.68), 381 ($M^+(^{81}Br)$ + 1, 3.33), 380 ($M^+(^{79}Br)$, 16.87), 199 (100); IR (neat, cm^{-1}) 1717, 1617, 1576, 1487, 1433, 1216, 1100, 1062, 1008; HRMS (EI) *m/z* calcd for $C_{18}H_{21}O_4{}^{79}Br$ [M^+]: 380.0623, found 380.0625.

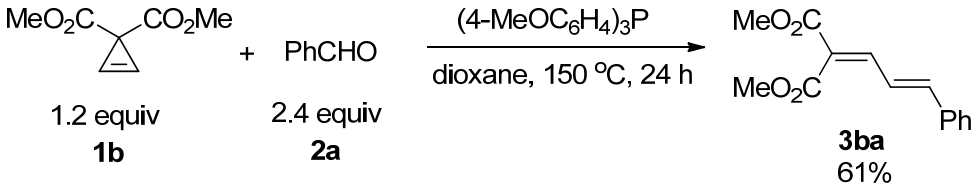
12. (*E*)-3-Butyl-5-(2-furyl)-2-(methoxycarbonyl)-2,4-pentadienoic acid methyl ester 3al (nsj-5-184):



The reaction of $(4\text{-}MeOC_6H_4)_3P$ (95 wt%, 126.0 mg, 0.34 mmol), cyclopropene-1,1-dicarboxylate **1a** (84.6 mg, 0.4 mmol), dioxane (2 mL), 2-furaldehyde **2l** (76.3 mg, 0.8 mmol), and dioxane (2 mL) afforded the desired product **3al** (66.1 mg, 67%) (eluent: petroleum ether/ethyl ether = 30/1): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (s, 1 H, Ar-H), 7.36 (d, *J* = 16.2 Hz, 1 H, CH=),

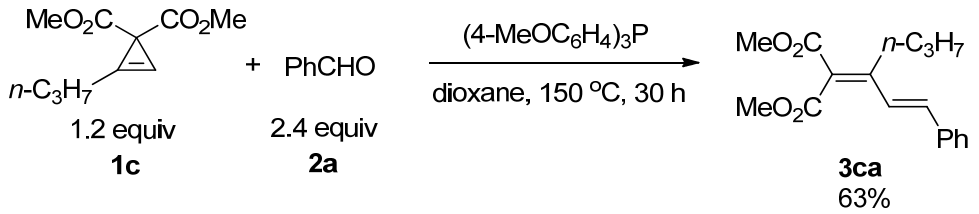
6.82 (d, J = 16.2 Hz, 1 H, CH=), 6.53-6.48 (m, 1 H, Ar-H), 6.47-6.41 (m, 1 H, Ar-H), 3.83 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 2.68-2.58 (m, 2 H, CH_2), 1.61-1.35 (m, 4 H, 2×CH_2), 0.94 (t, J = 7.1 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.1, 165.9, 154.2, 152.3, 143.8, 123.9, 123.4, 123.3, 112.3, 112.0, 52.2, 52.0, 32.0, 29.3, 23.0, 13.7; MS (EI) *m/z* 293 (M^+ + 1, 18.46), 292 (M^+, 98.03), 118 (100); IR (neat, cm^{-1}) 1777, 1719, 1618, 1584, 1434, 1260, 1222, 1201, 1099, 1061, 1014; HRMS (EI) *m/z* calcd for $C_{16}H_{20}O_5$ [M^+]: 292.1311, found 292.1310.

13. (*E*)-2-(methoxycarbonyl)-5-phenyl-2,4-pentadienoic acid methyl ester 3ba (nsj-5-180):



The reaction of (4-$MeOC_6H_4$)$_3$P (95 wt%, 126.0 mg, 0.34 mmol), cyclopropene-1,1-dicarboxylate **1b** (62.0 mg, 0.4 mmol), dioxane (2 mL), benzaldehyde **2a** (84.8 mg, 0.8 mmol), and dioxane (2 mL) afforded the desired product **3ba**[1](51.2 mg, 61%) (eluent: petroleum ether/ethyl acetate = 30/1): oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, J = 11.1 Hz, 1 H, CH=), 7.53-7.44 (m, 2 H, Ar-H), 7.42-7.30 (m, 3 H, Ar-H), 7.29-7.21 (m, 1 H, CH=), 7.05 (d, J = 15.3 Hz, 1 H, CH=), 3.90 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.6, 165.1, 146.2, 145.1, 135.5, 129.9, 128.8, 127.8, 124.0, 123.2, 52.33, 52.27; MS (EI) *m/z* 247 (M^+ + 1, 7.27), 246 (M^+, 46.22), 214 (100); IR (neat, cm^{-1}) 2962, 1714, 1614, 1435, 1260, 1020.

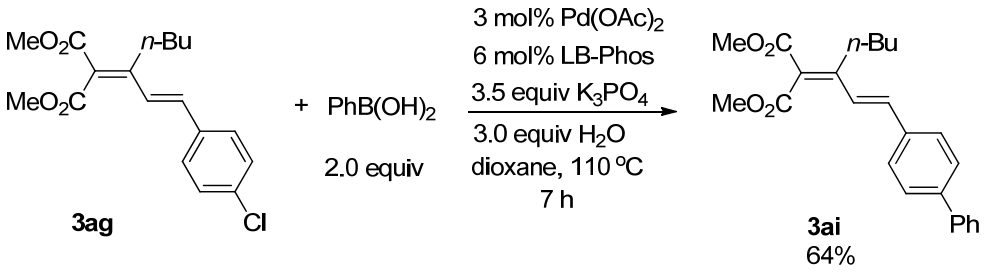
14. (*E*)-2-(methoxycarbonyl)-5-phenyl-3-propyl-2,4-pentadienoic acid methyl ester 3ca (nsj-5-181):



The reaction of (4-$MeOC_6H_4$)$_3$P (95 wt%, 126.0 mg, 0.34 mmol),

cyclopropene-1,1-dicarboxylate **1c** (78.8 mg, 0.4 mmol), dioxane (2 mL), benzaldehyde **2a** (84.8 mg, 0.8 mmol), and dioxane (2 mL) afforded the desired product **3ca** (62.1 mg, 63%) (eluent: petroleum ether/ethyl ether = 30/1): oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 16.4 Hz, 1 H, CH=), 7.52-7.46 (d, *J* = 6.8 Hz, 2 H, Ar-H), 7.39-7.27 (m, 3 H, Ar-H), 7.04 (d, *J* = 16.0 Hz, 1 H, CH=), 3.82 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 2.70-2.60 (m, 2 H, CH_2), 1.68-1.55 (m, 2 H, CH_2), 1.02 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.2, 165.9, 154.4, 137.0, 136.1, 129.1, 128.7, 127.4, 125.1, 123.7, 52.2, 52.1, 31.9, 23.3, 14.3; MS (EI) *m/z* 289 (M^+ + 1, 12.74), 288 (M^+, 67.84), 224 (100); IR (neat, cm^{-1}) 1717, 1617, 1580, 1433, 1277, 1209, 1061; HRMS (EI) *m/z* calcd for $C_{17}H_{20}O_4$ [M^+]: 288.1362, found 288.1366.

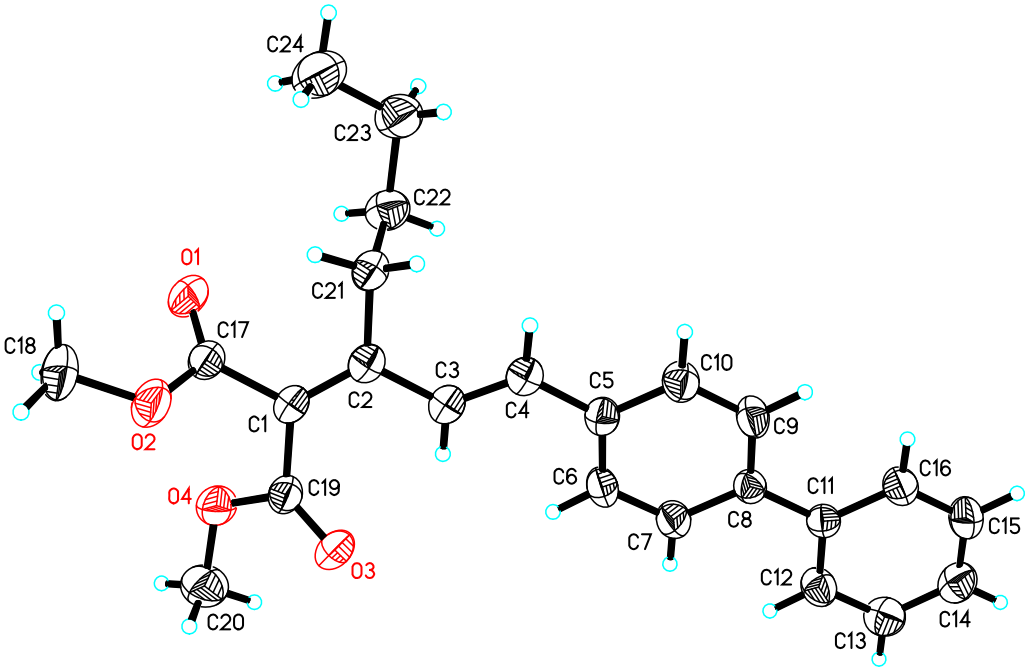
Coupling of 3ag with phenylboronic acid (nsj-5-92):[2]

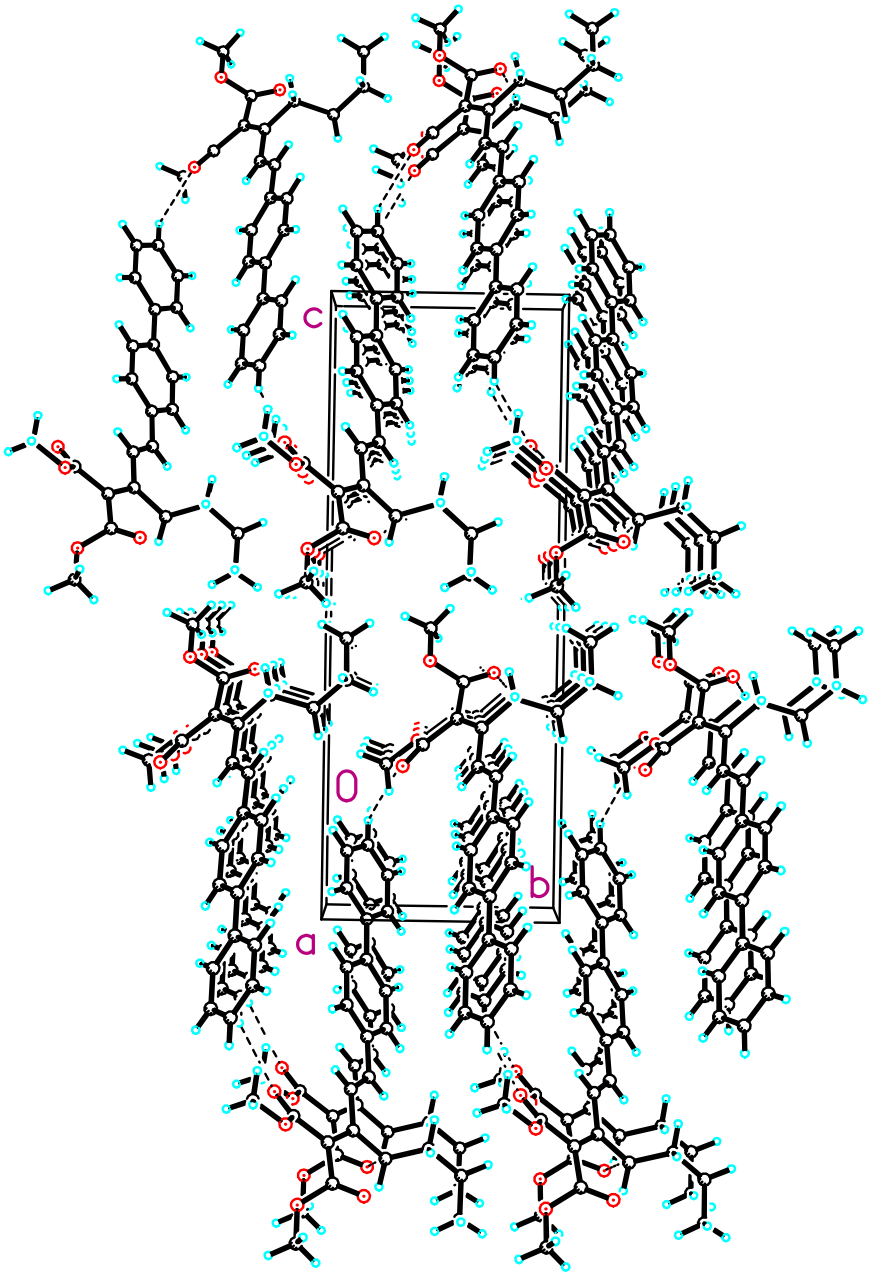


To a flame dried Schlenk tube with a screw cap were added K_3PO_4 (303.9 mg, 1.4 mmol), $Pd(OAc)_2$ (2.7 mg, 0.012 mmol), LB-Phos·HBF_4 (10.8 mg, 0.024 mmol), phenylboronic acid (97.5 mg, 0.8 mmol), dioxane (1 mL), **3ag** (135.1 mg, 0.4 mmol), dioxane (1 mL), and H_2O (21.6 μL, 21.6 mg, 1.2 mmol). The resulting mixture was stirred at 110 °C. After 7 h the reaction was over as monitored by TLC. The reaction mixture was filtrated through a short column of silica gel (2 cm) to remove the inorganic salts (eluent: 80 mL of Et_2O). After evaporation of the solvent, chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 40/1) afforded the desired product **3ai** (96.7 mg, 64%): solid; m.p. 155-157 °C (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.54 (m, 7 H, Ar-H and CH=), 7.47-7.40 (m, 2 H, Ar-H), 7.38-7.32 (m, 1 H, Ar-H), 7.08 (d, *J* = 16.0 Hz, 1 H, CH=), 3.83 (s, 3 H, OCH_3), 3.81

(s, 3 H, OCH_3), 2.72-2.63 (m, 2 H, CH_2), 1.65-1.53 (m, 2 H, CH_2), 1.51-1.39 (m, 2 H, CH_2), 0.96 (t, J = 7.4 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.2, 165.9, 154.6, 141.7, 140.2, 136.5, 135.1, 128.7, 127.9, 127.5, 127.3, 126.8, 125.1, 123.5, 52.13, 52.05, 32.0, 29.7, 23.0, 13.8.

X-ray structure of (*E*)-2-[1-Butyl-3-(4-trifluoromethylphenyl)-allylidene]-malonic acid dimethyl ester (**3ai**) [CCDC 918034 contains the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk /data request/cif.]

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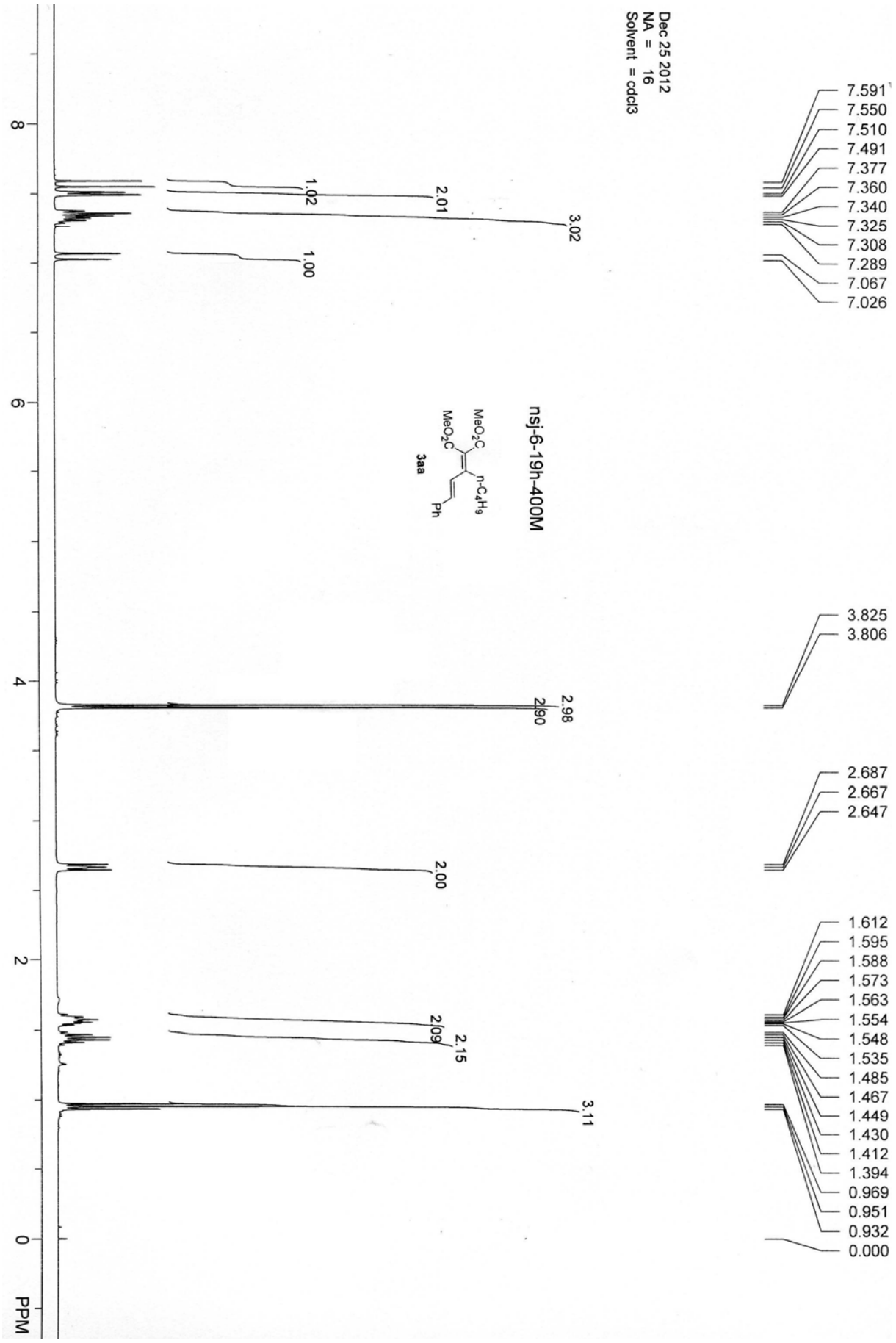
0
b
a

References:

1. a) Nigmatov, A. G.; Komilova, I. N. and Serebryakov, E. P. *Russ. Chem. BulL* **1996**, *45*, 144. b) Lenhert, W. *Tetrohedron Lett.* **1970**, *11,* 4723. c) Lenhert, W. *Tetrahedron* **1973**, *29,* 635. d) Mikami, K.; Ohmura, H. *Org. Lett.* **2002**, *4*, 3355.
2. Lü, B.; Fu, C.; Ma, S. *Tetrahedron Lett.* **2010**, *51*, 1284.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7.308
7.289
7.067
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3.825
3.806
2.687
2.667
2.647
1.612
1.595
1.588
1.573
1.563
1.554
1.548
1.535
1.485
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0.951
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2.00
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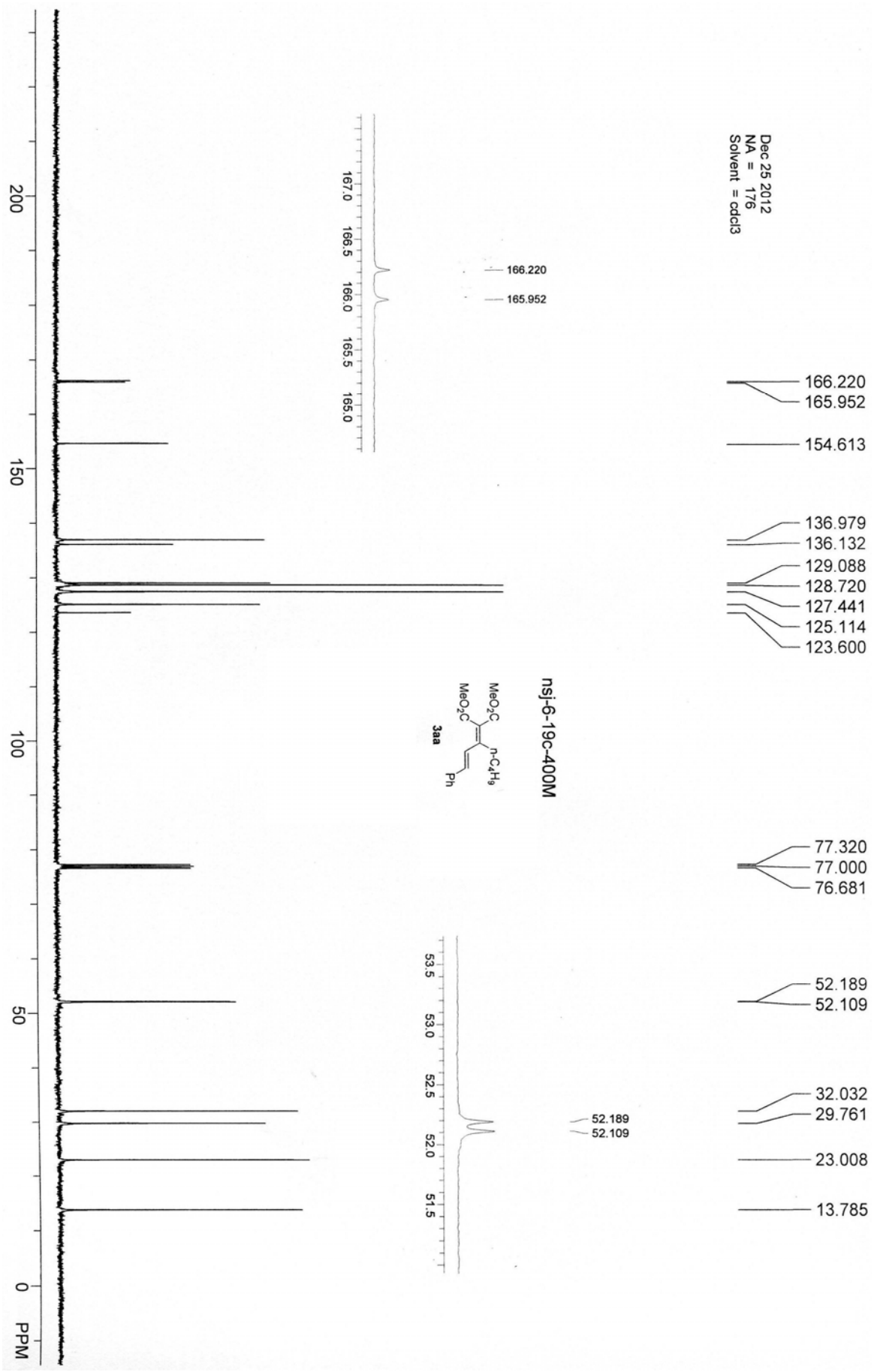
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136.979
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129.088
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127.441
125.114
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77.320
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52.109
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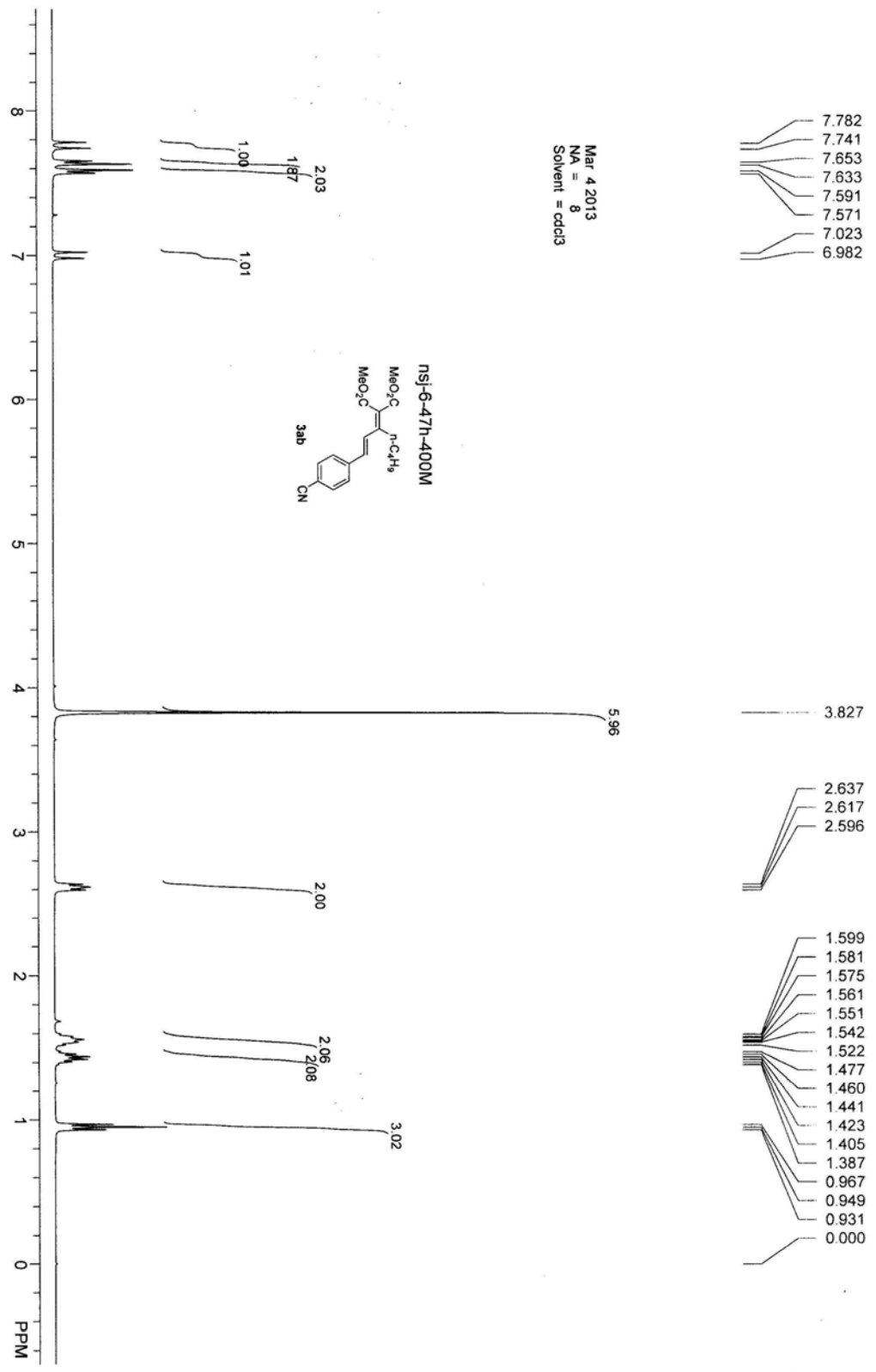
50
0
PPM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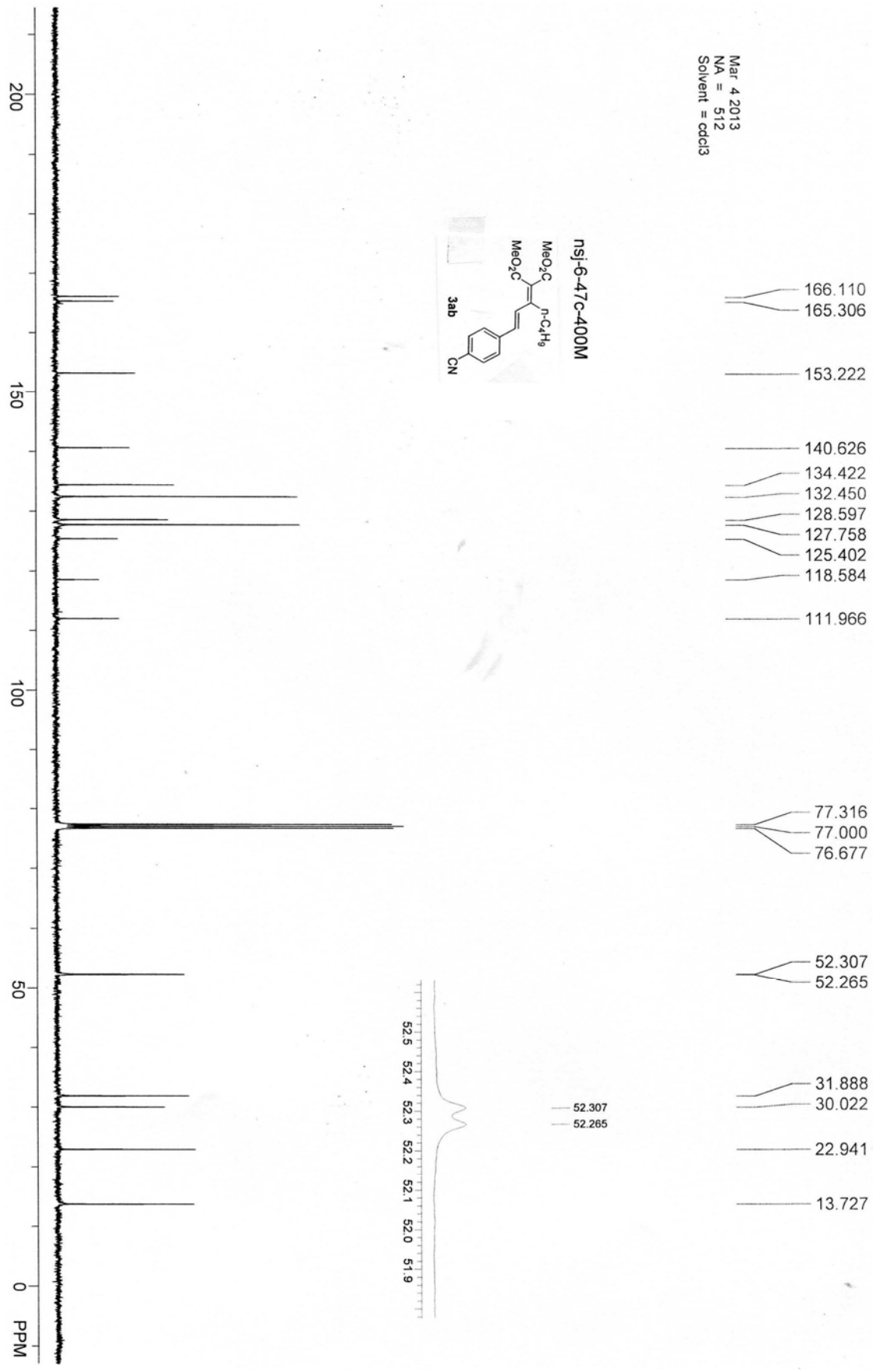
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52.307
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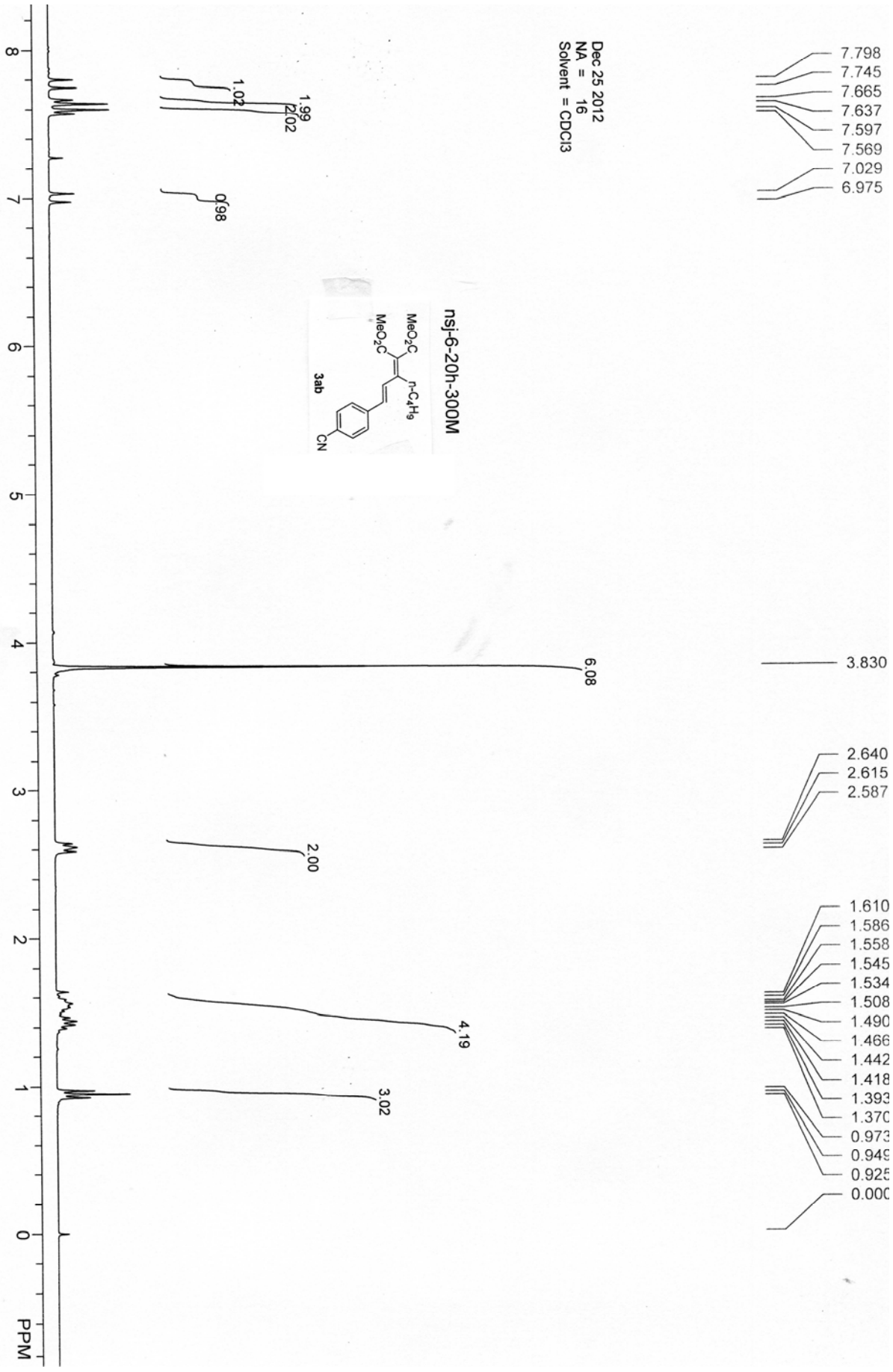
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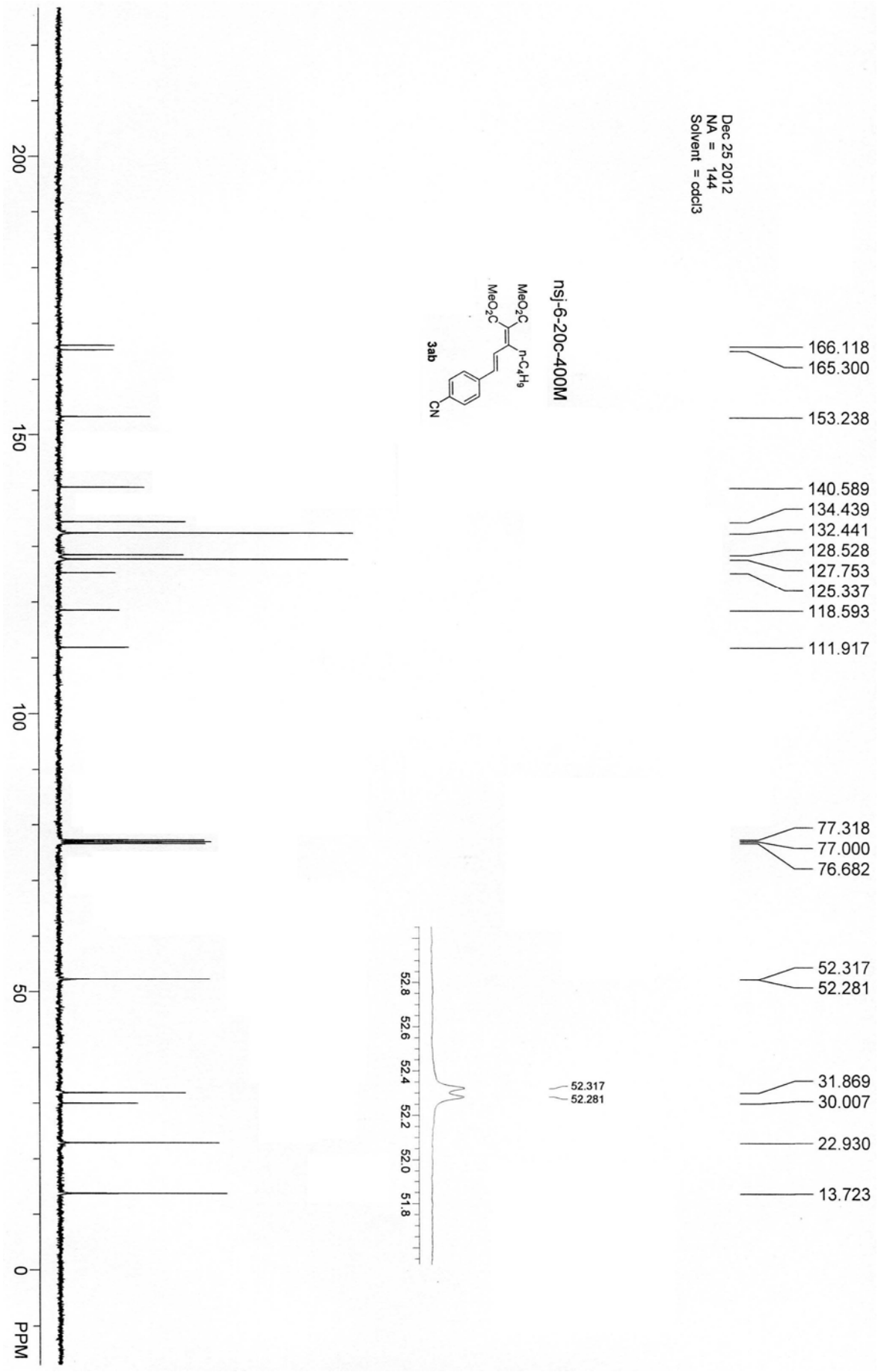
PPM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150
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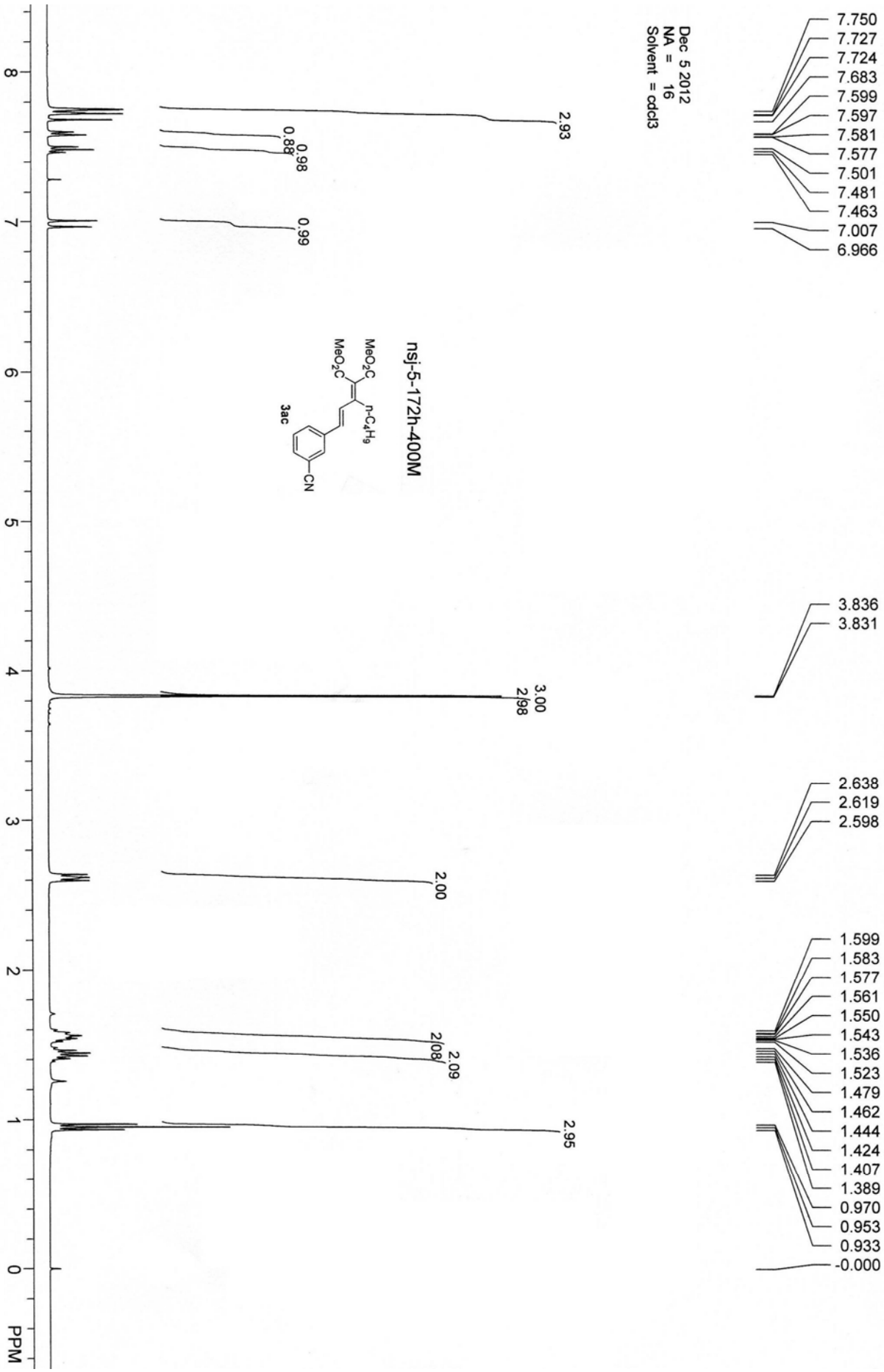
50
0
PPM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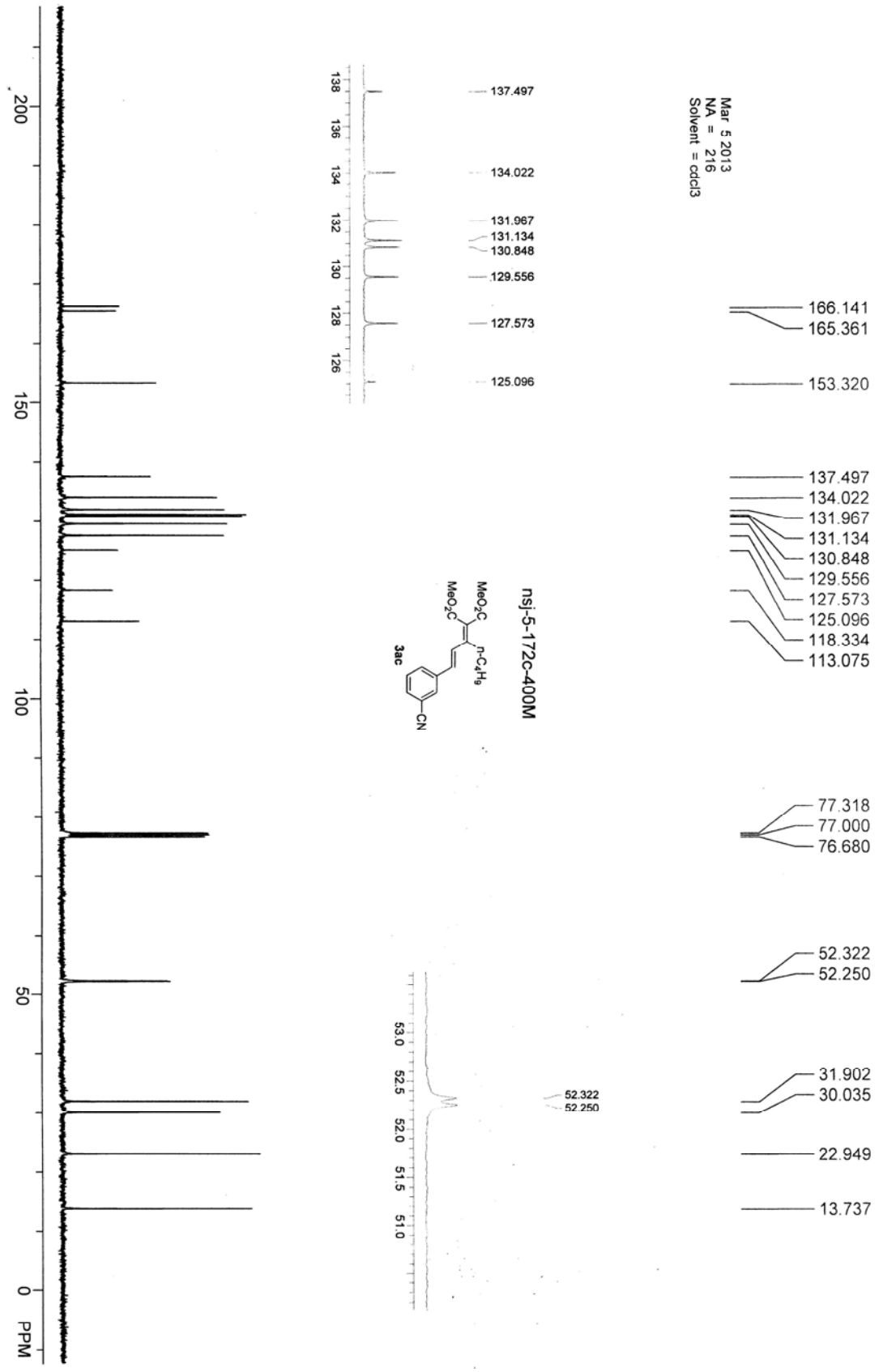
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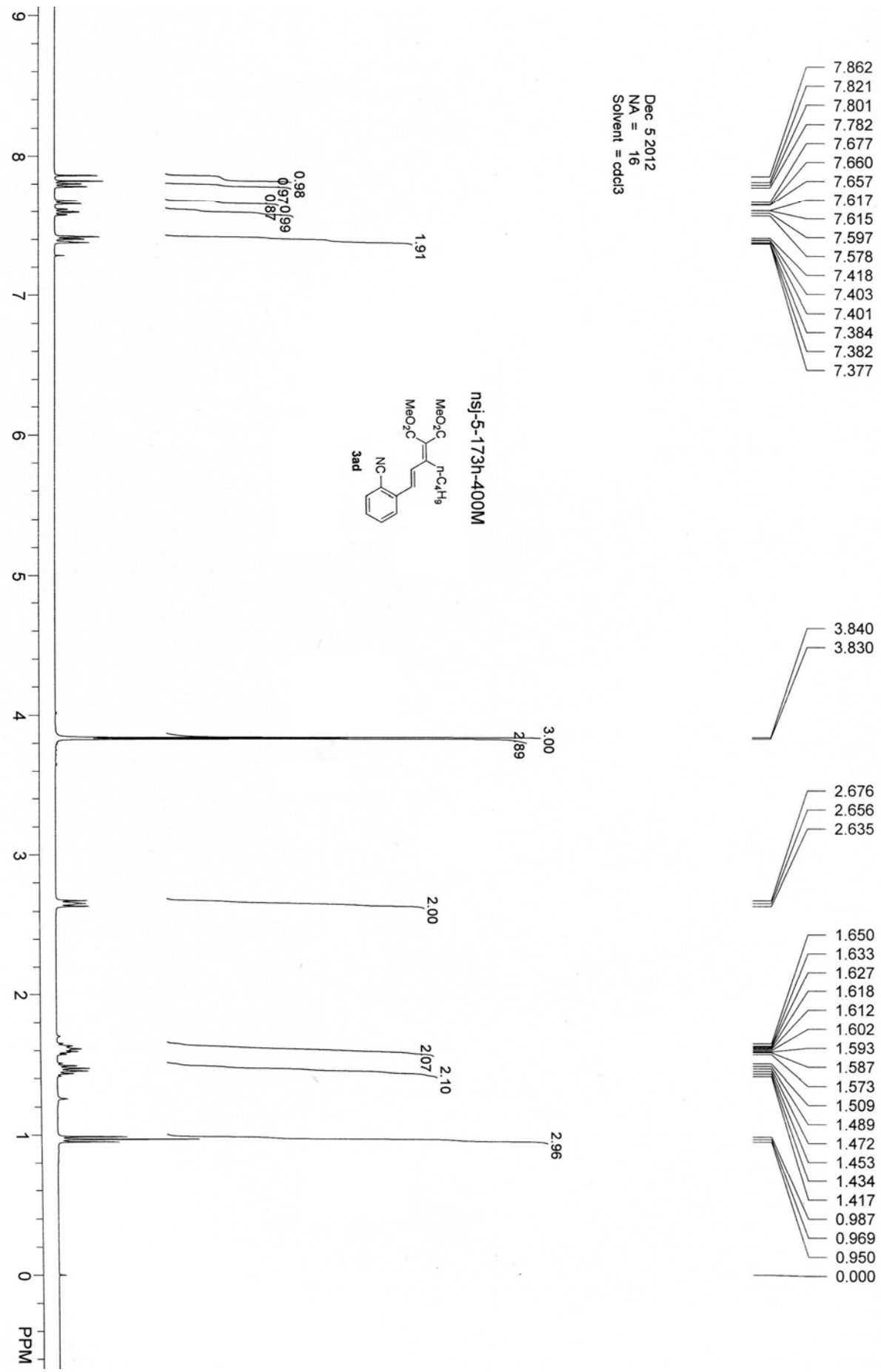
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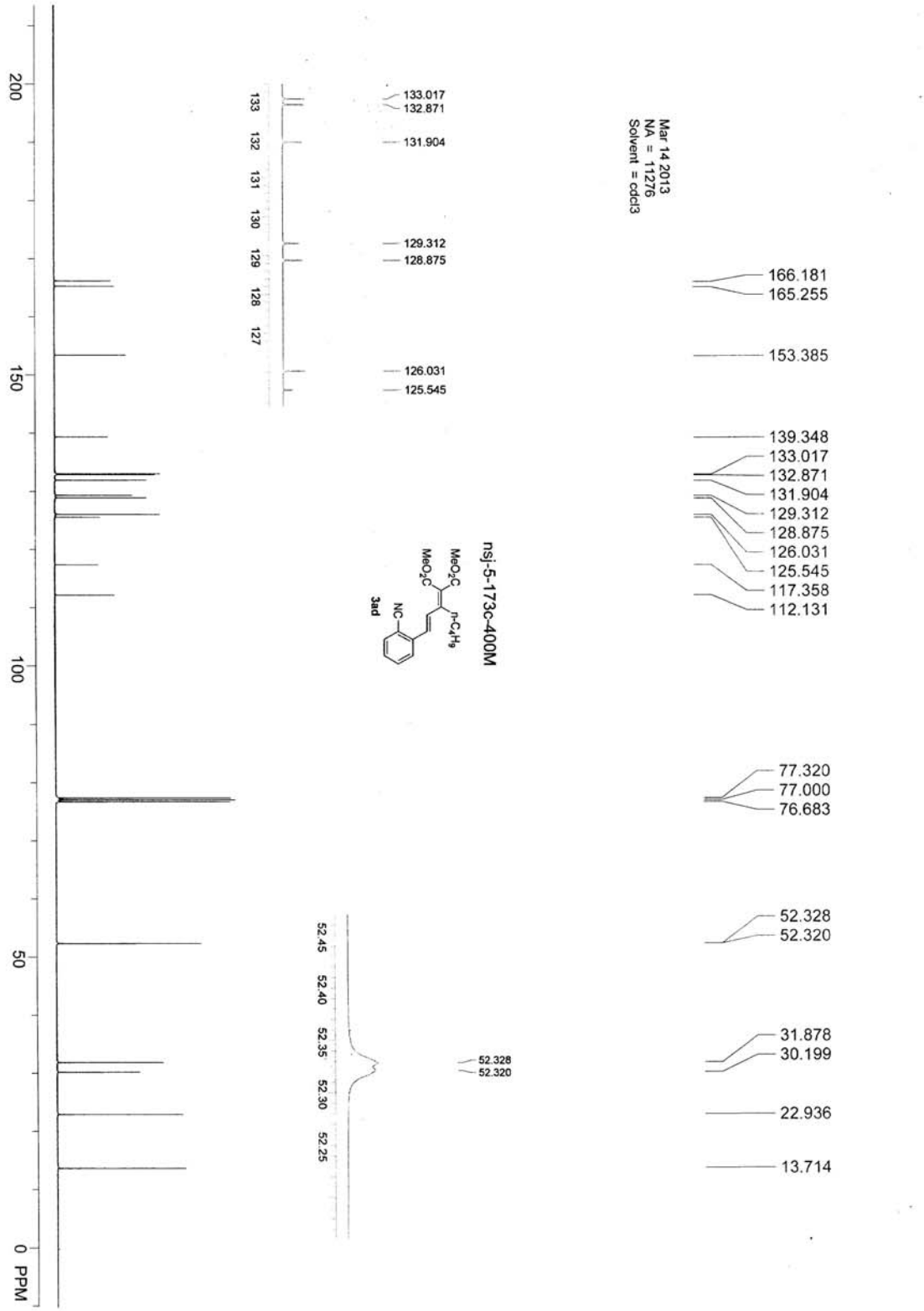
PPM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50
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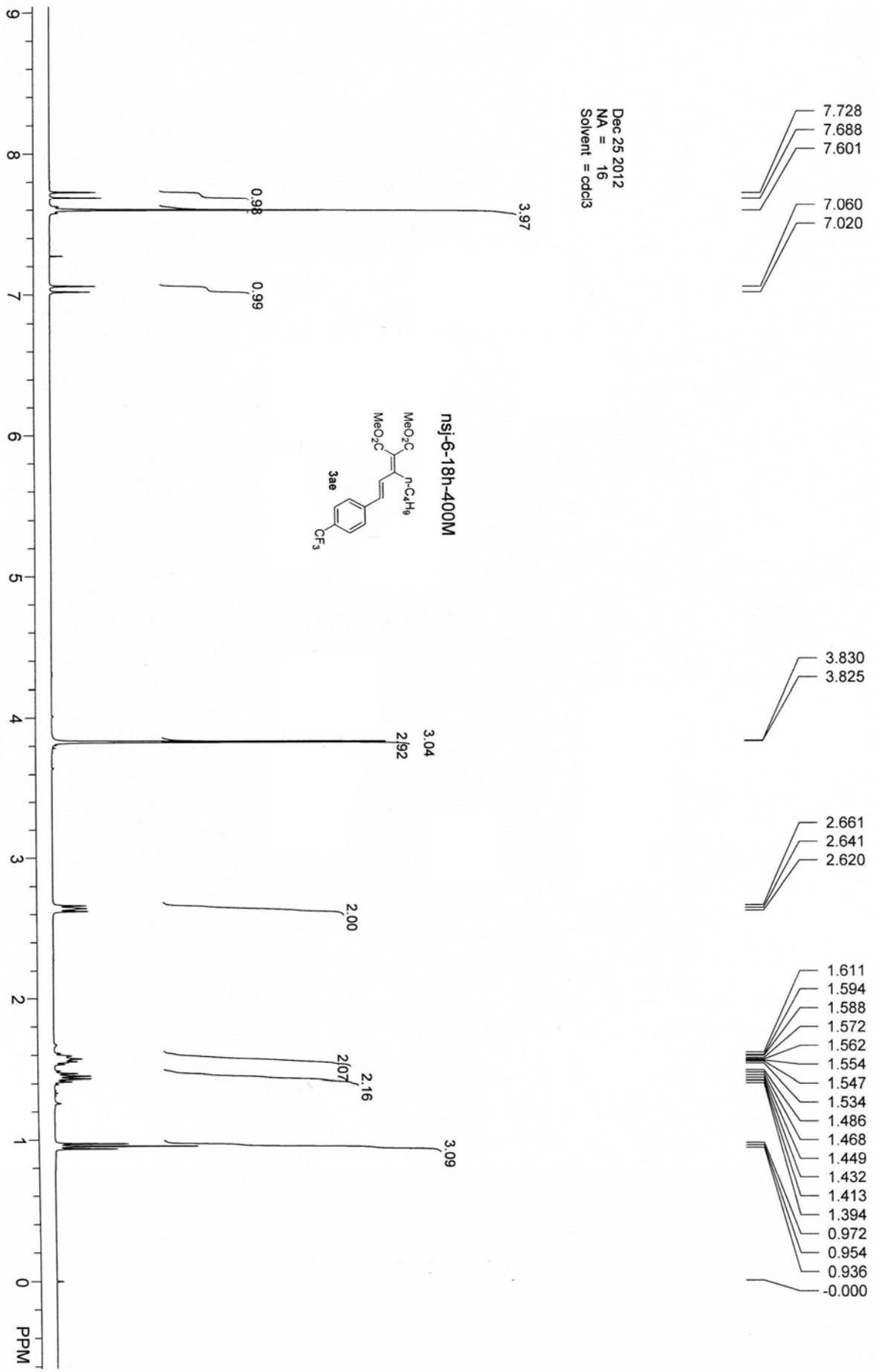
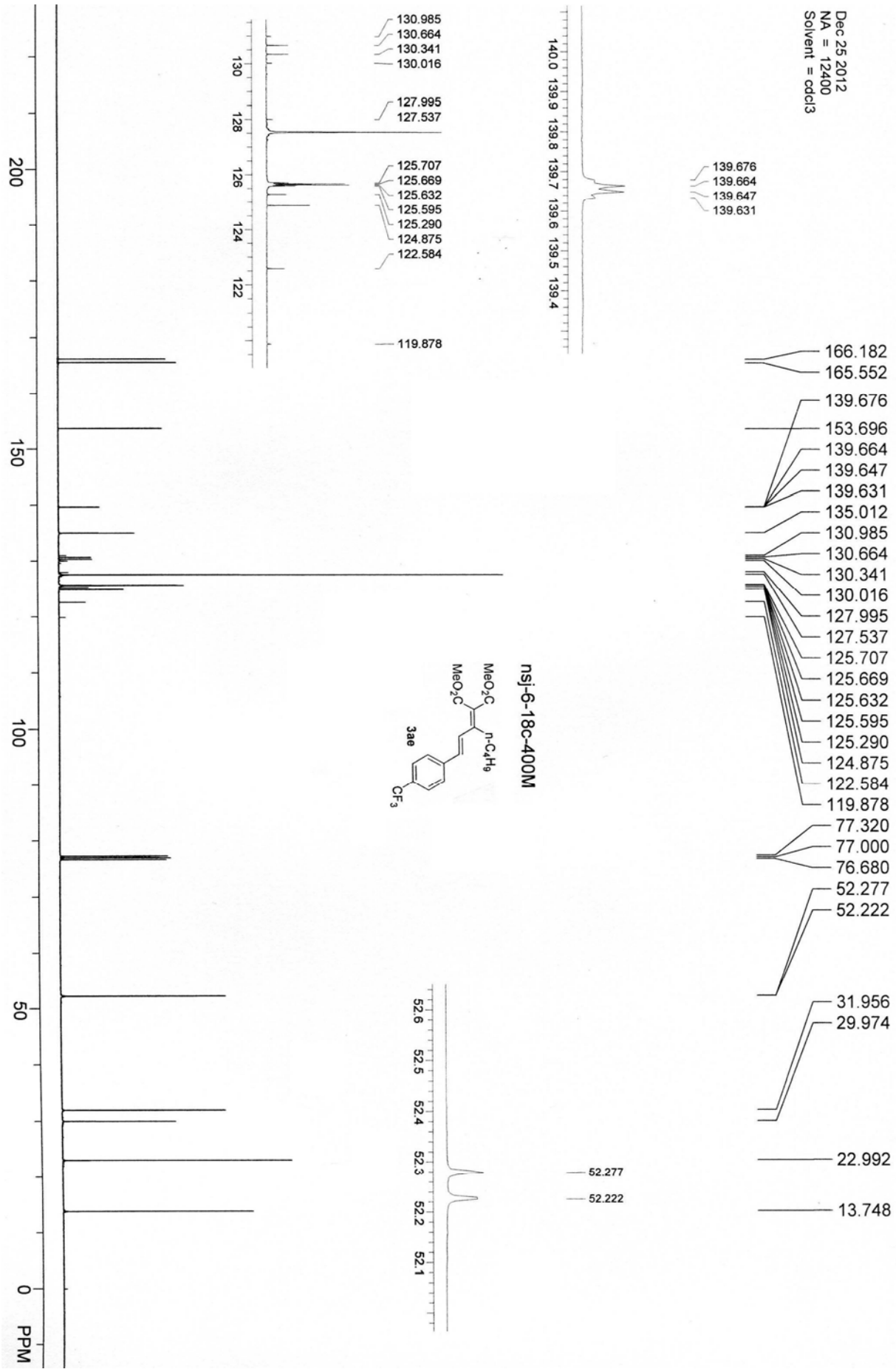
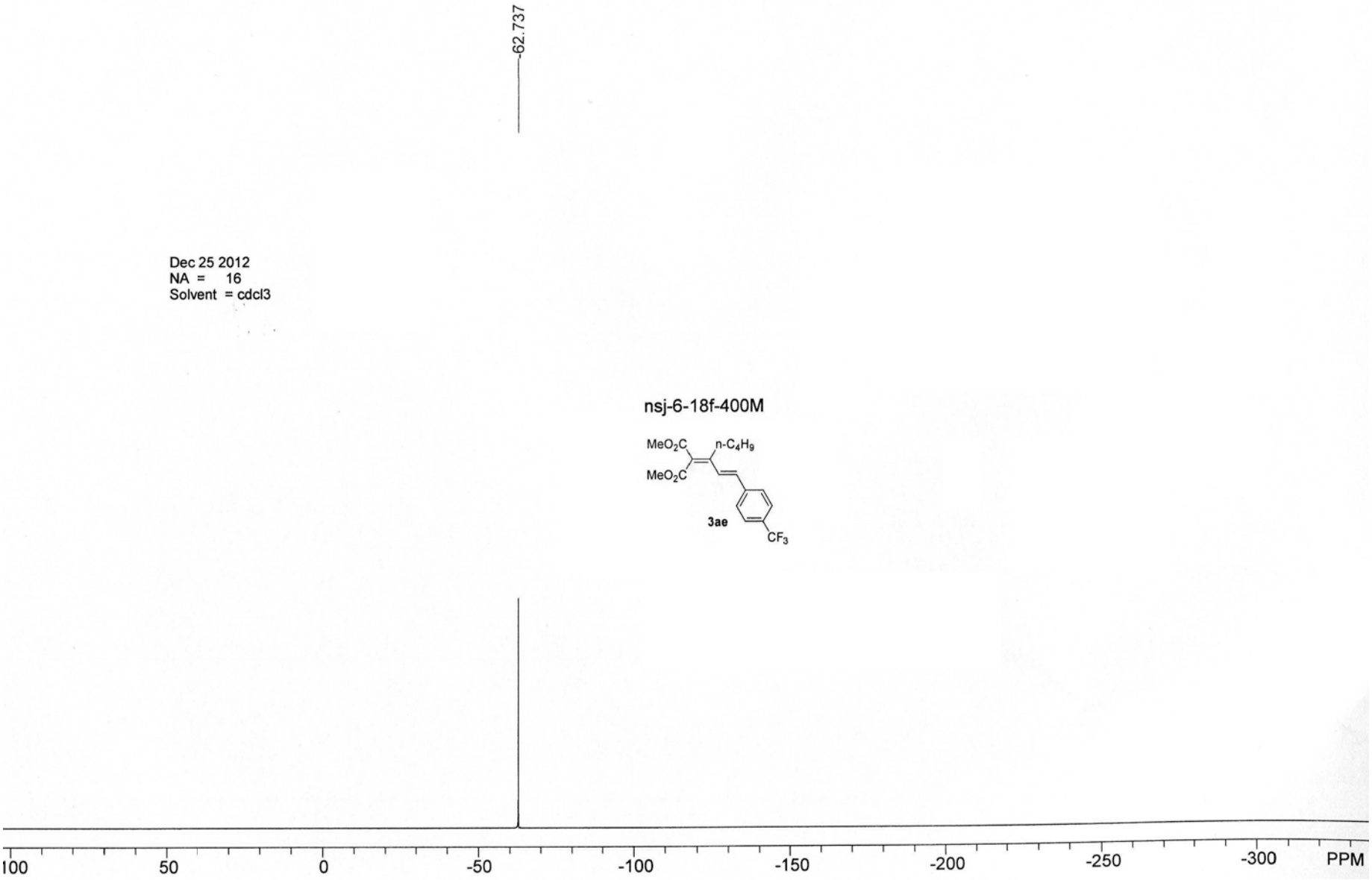
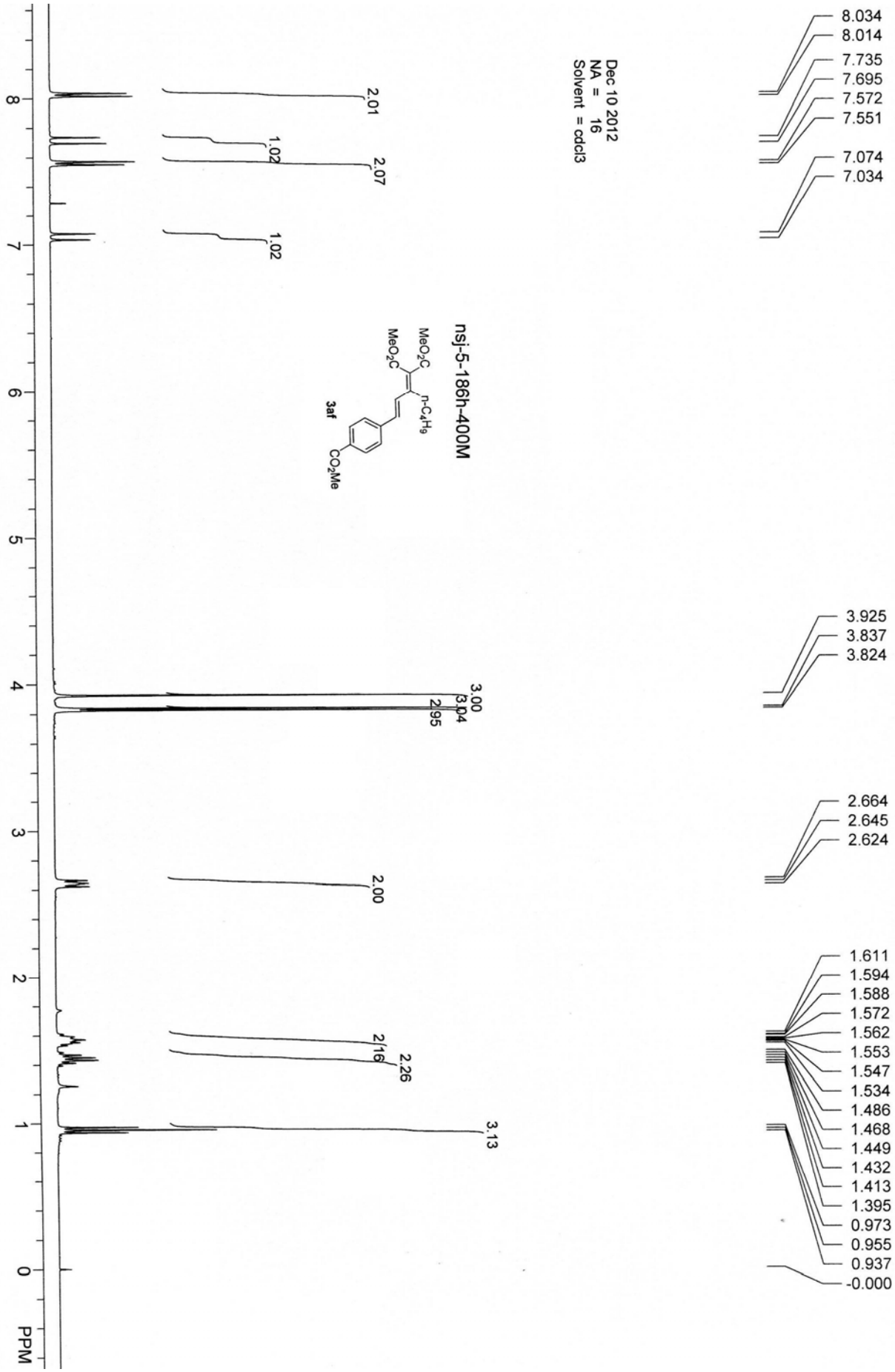
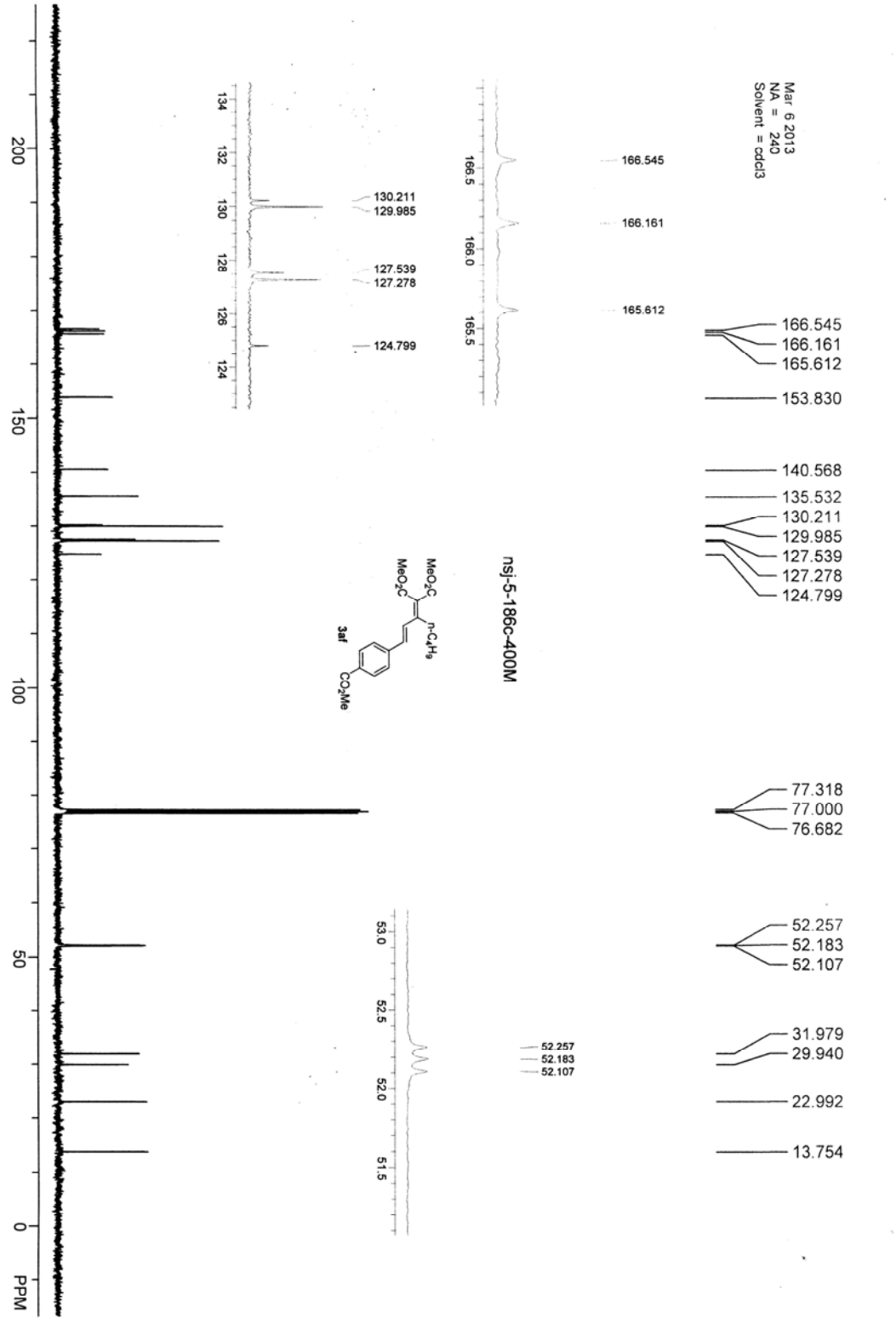
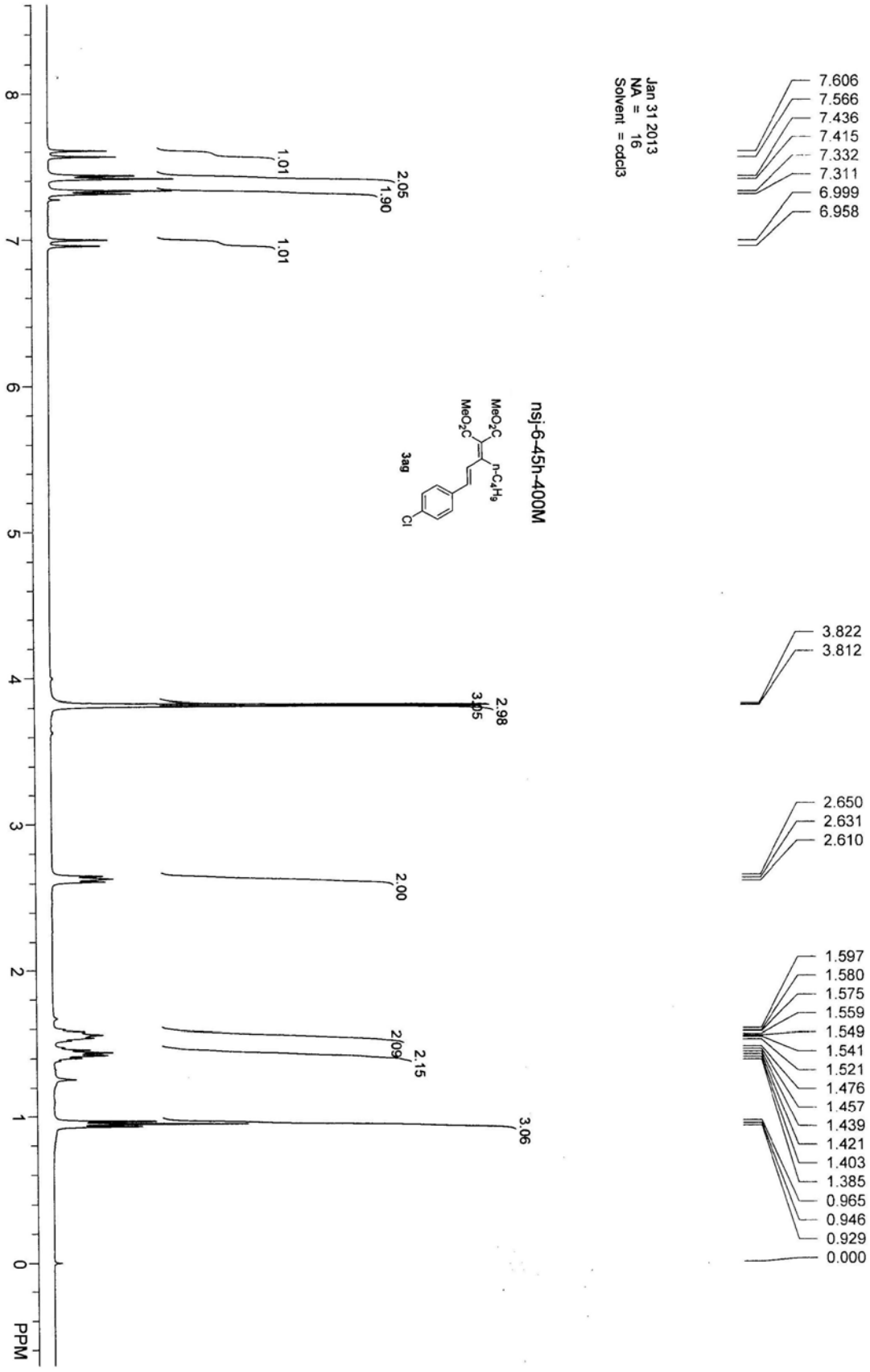

Dec 25 2012
NA = 16
Solvent = cdcl3
nsj-6-18h-400M
3ae
MeO2C
MeO2C
n-C4H9
CF3
7.728
7.688
7.601
7.060
7.020
3.830
3.825
2.661
2.641
2.620
1.611
1.594
1.588
1.572
1.562
1.554
1.547
1.534
1.486
1.468
1.449
1.432
1.413
1.394
0.972
0.954
0.936
-0.000
3.97
0.98
0.99
3.04
2.92
2.00
2.07
2.16
3.09
PPM

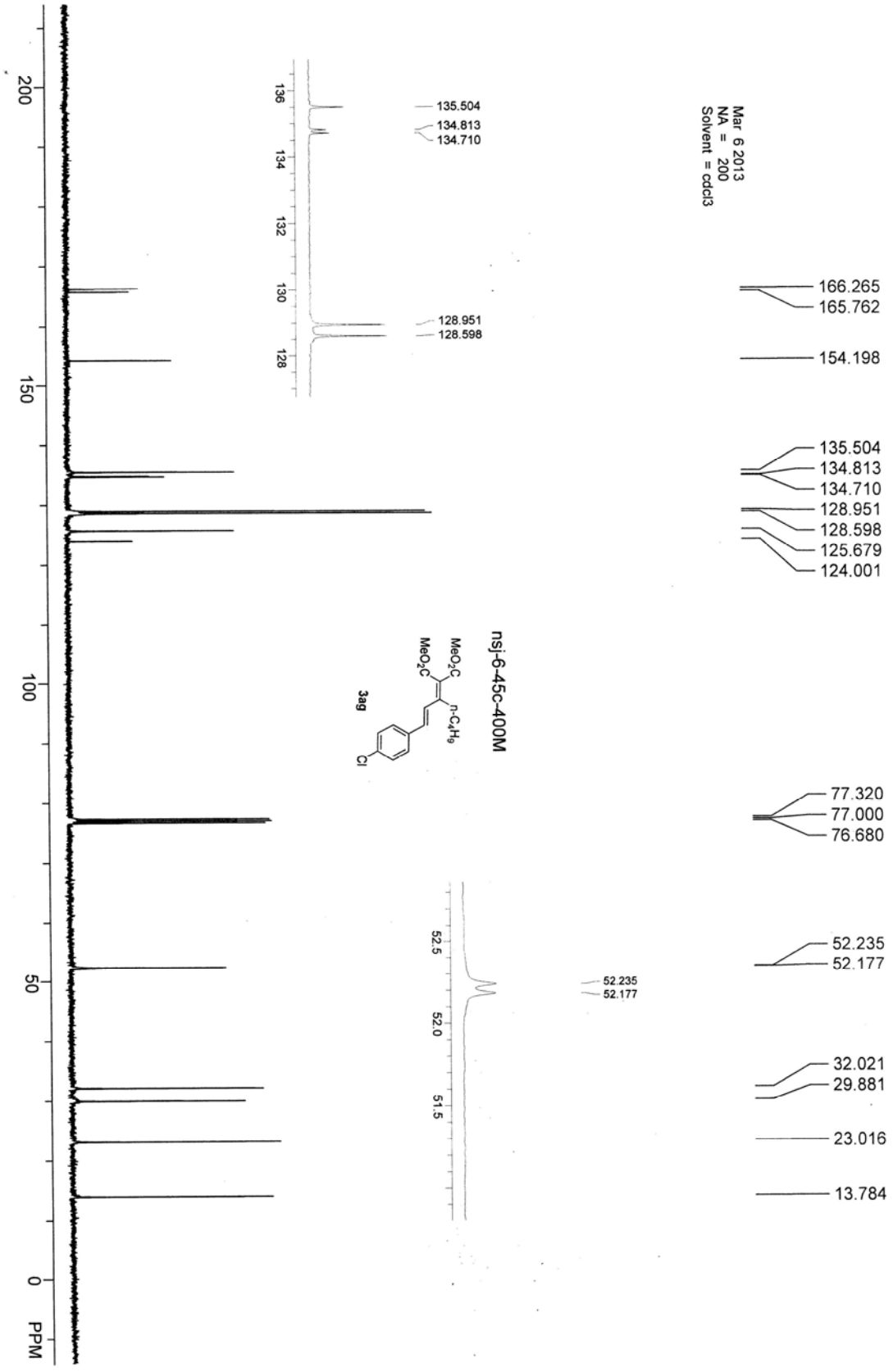

Dec 25 2012
NA = 12400
Solvent = cdcl3
nsj-6-18c-400M
3ae
MeO2C
MeO2C
n-C4H9
CF3
166.182
165.552
139.676
153.696
139.664
139.647
139.631
135.012
130.985
130.664
130.341
130.016
127.995
127.537
125.707
125.669
125.632
125.595
125.290
124.875
122.584
119.878
77.320
77.000
76.680
52.277
52.222
31.956
29.974
22.992
13.748
PPM

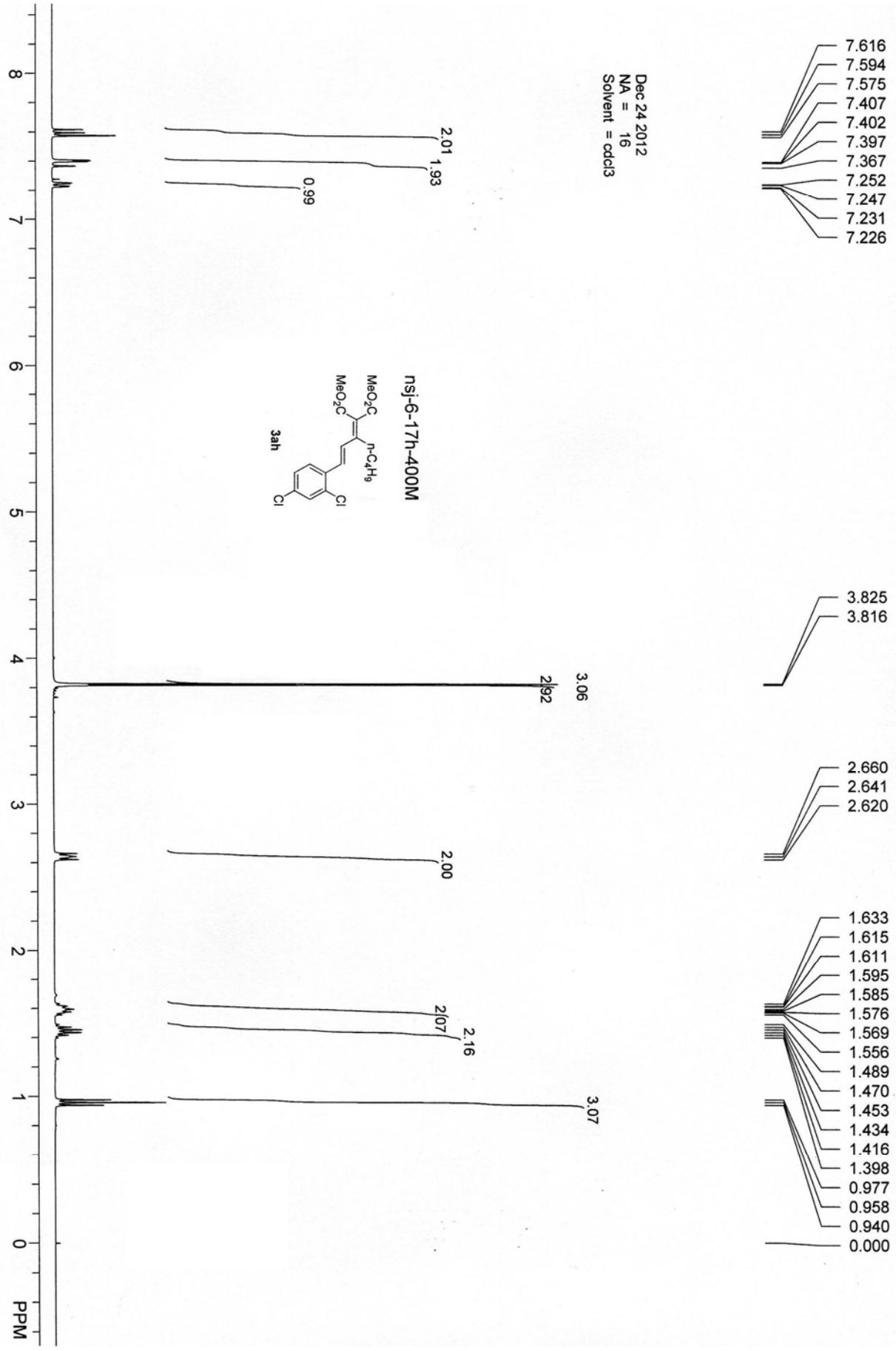

-62.737
Dec 25 2012
NA = 16
Solvent = cdcl3
nsj-6-18f-400M
MeO2C
n-C4H9
MeO2C
3ae
CF3
100
50
0
-50
-100
-150
-200
-250
-300
PPM

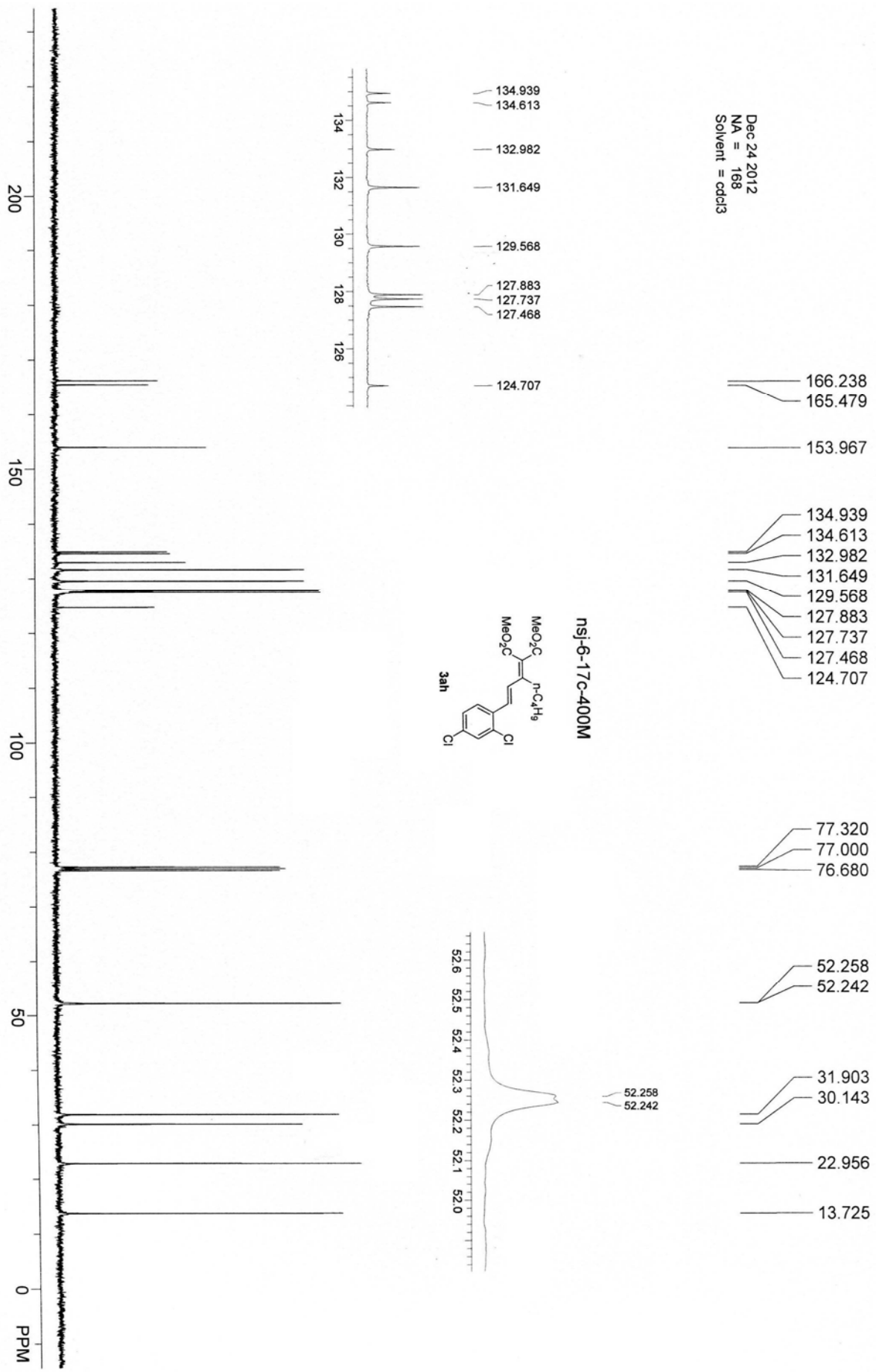

nsj-5-186h-400M
Dec 10 2012
NA = 16
Solvent = cdcl3
3af
8.034
8.014
7.735
7.695
7.572
7.551
7.074
7.034
3.925
3.837
3.824
2.664
2.645
2.624
1.611
1.594
1.588
1.572
1.562
1.553
1.547
1.534
1.486
1.468
1.449
1.432
1.413
1.395
0.973
0.955
0.937
-0.000
2.01
1.02
2.07
1.02
3.00
3.04
2.95
2.00
2.16
2.26
3.13
PPM

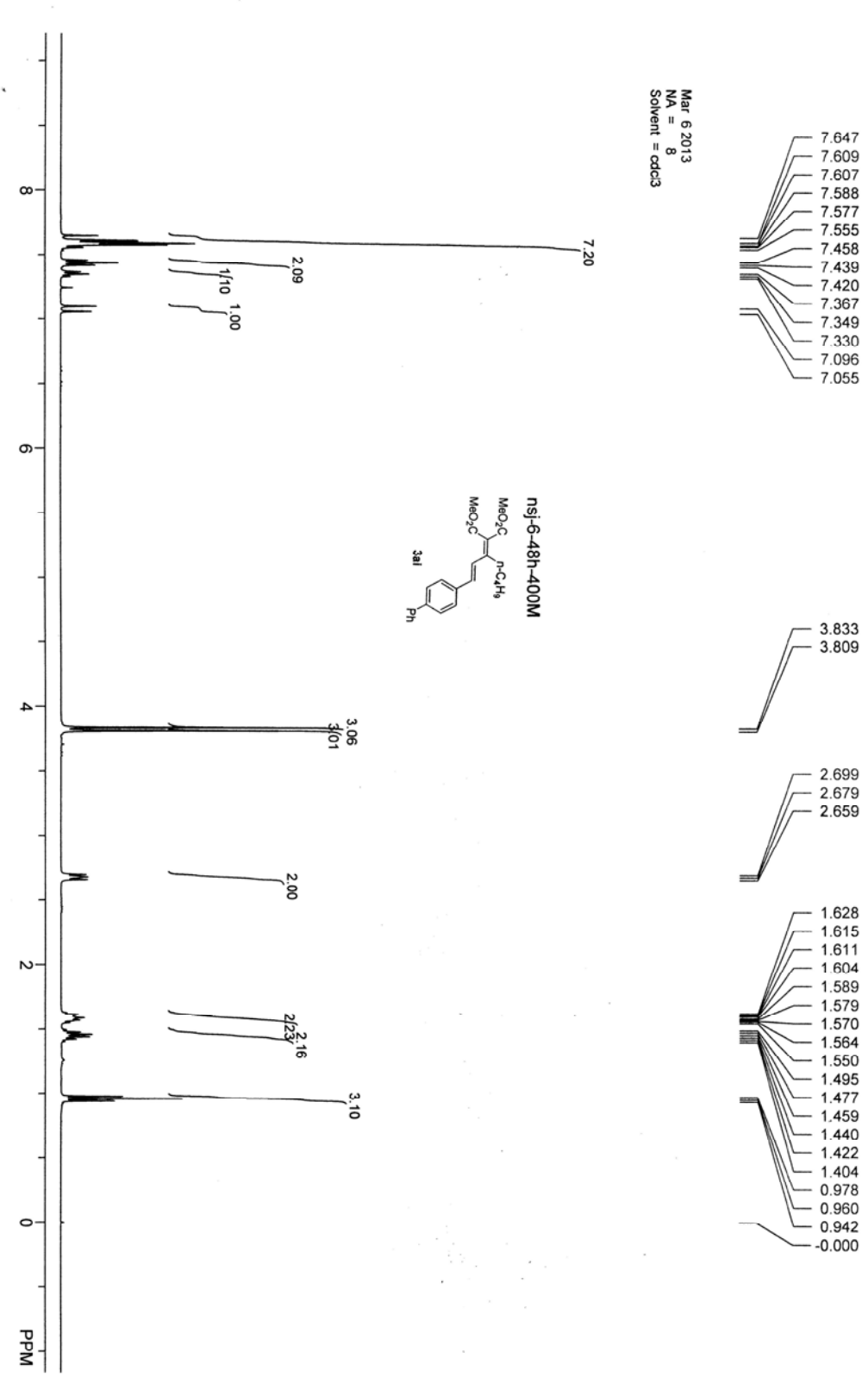

Mar 6 2013
NA = 240
Solvent = cdcl3
166.545
166.161
165.612
153.830
140.568
135.532
130.211
129.985
127.539
127.278
124.799
77.318
77.000
76.682
52.257
52.183
52.107
31.979
29.940
22.992
13.754
nsj-5-186c-400M
3af
PPM

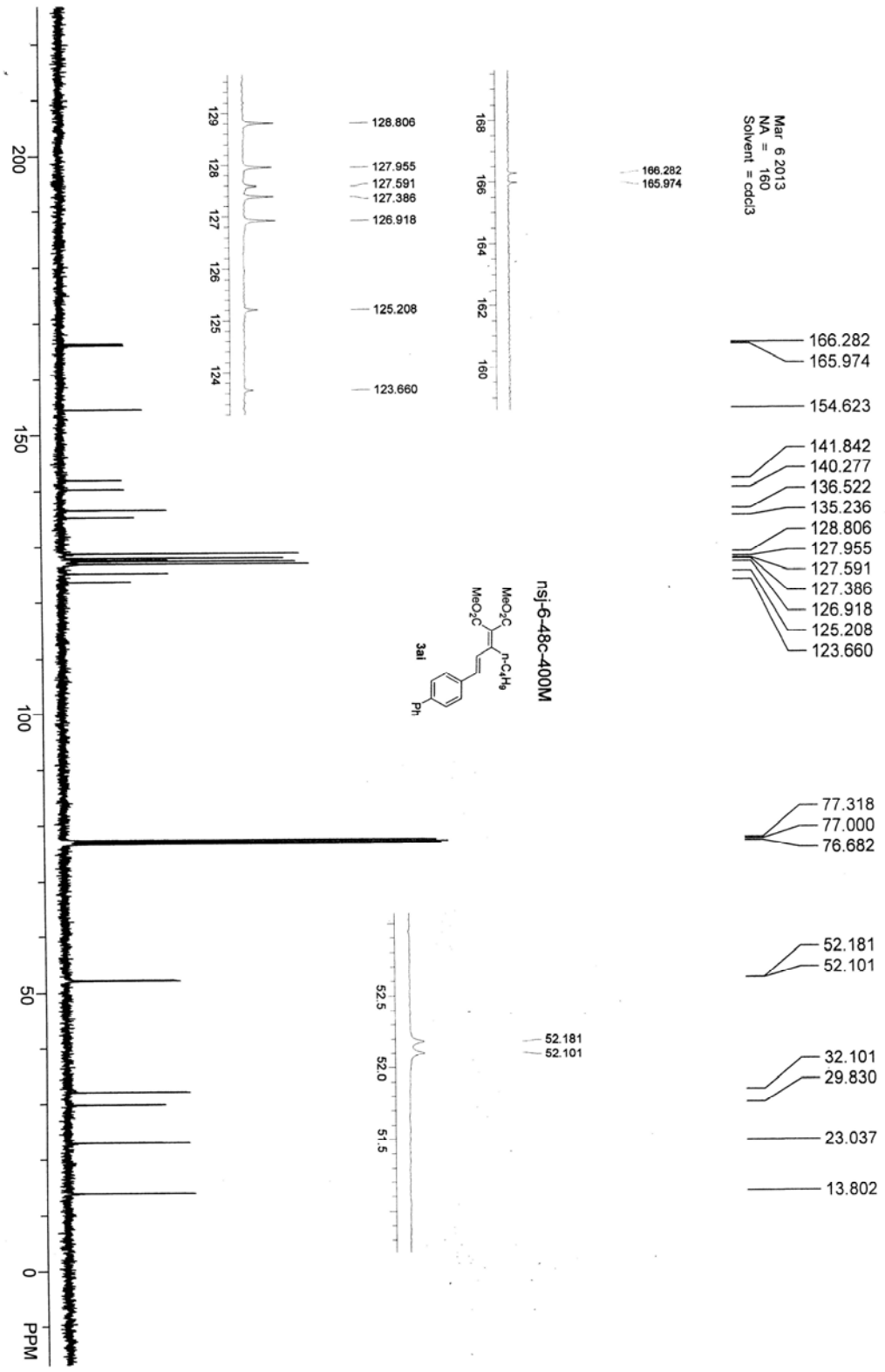

Jan 31 2013
NA = 16
Solvent = cdcl3
nsj-6-45h-400M
3ag
MeO2C
MeO2C
n-C4H9
Cl
7.606
7.566
7.436
7.415
7.332
7.311
6.999
6.958
3.822
3.812
2.650
2.631
2.610
1.597
1.580
1.575
1.559
1.549
1.541
1.521
1.476
1.457
1.439
1.421
1.403
1.385
0.965
0.946
0.929
0.000
1.01
2.05
1.90
1.01
2.98
3.05
2.00
2.09
2.15
3.06
PPM

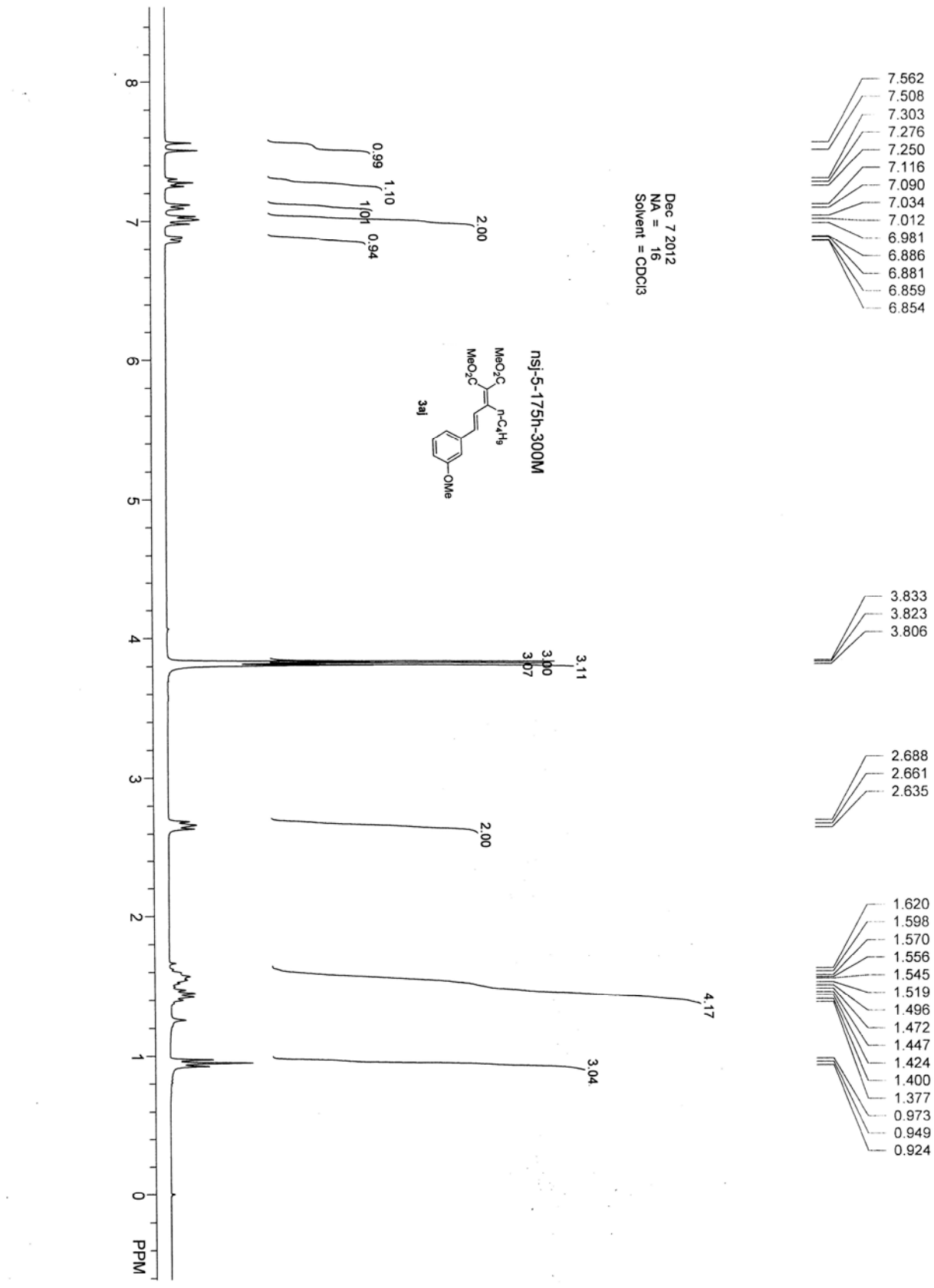

Mar 6 2013
NA = 200
Solvent = cdcl3
166.265
165.762
154.198
135.504
134.813
134.710
128.951
128.598
125.679
124.001
77.320
77.000
76.680
52.235
52.177
32.021
29.881
23.016
13.784
nsj-6-45c-400M
3ag
PPM

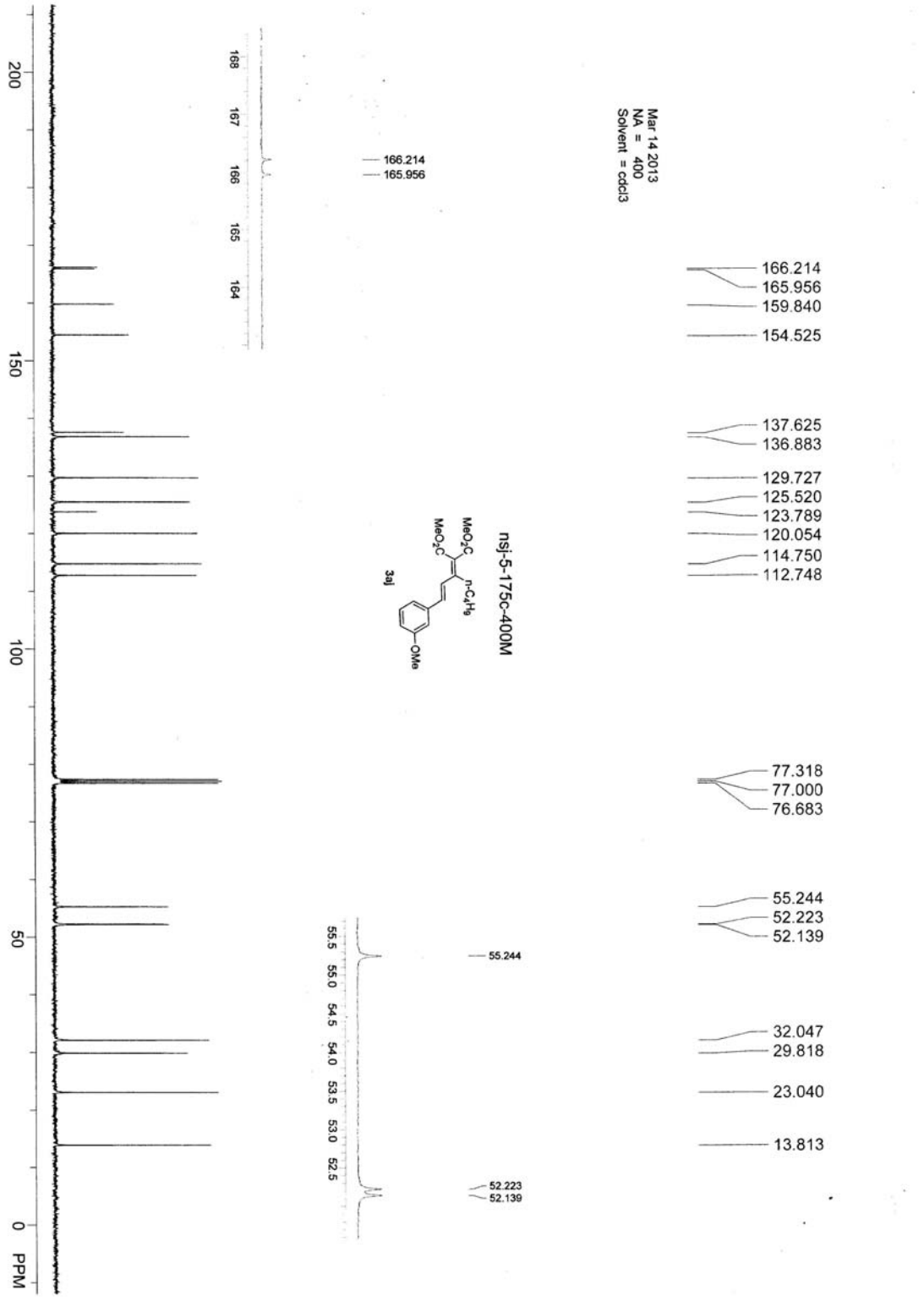

Dec 24 2012
NA = 16
Solvent = cdcl3
nsj-6-17h-400M
3ah
MeO2C
MeO2C
n-C4H9
Cl
Cl
7.616
7.594
7.575
7.407
7.402
7.397
7.367
7.252
7.247
7.231
7.226
3.825
3.816
2.660
2.641
2.620
1.633
1.615
1.611
1.595
1.585
1.576
1.569
1.556
1.489
1.470
1.453
1.434
1.416
1.398
0.977
0.958
0.940
0.000
2.01
1.93
0.99
3.06
2.92
2.00
2.07
2.16
3.07
PPM

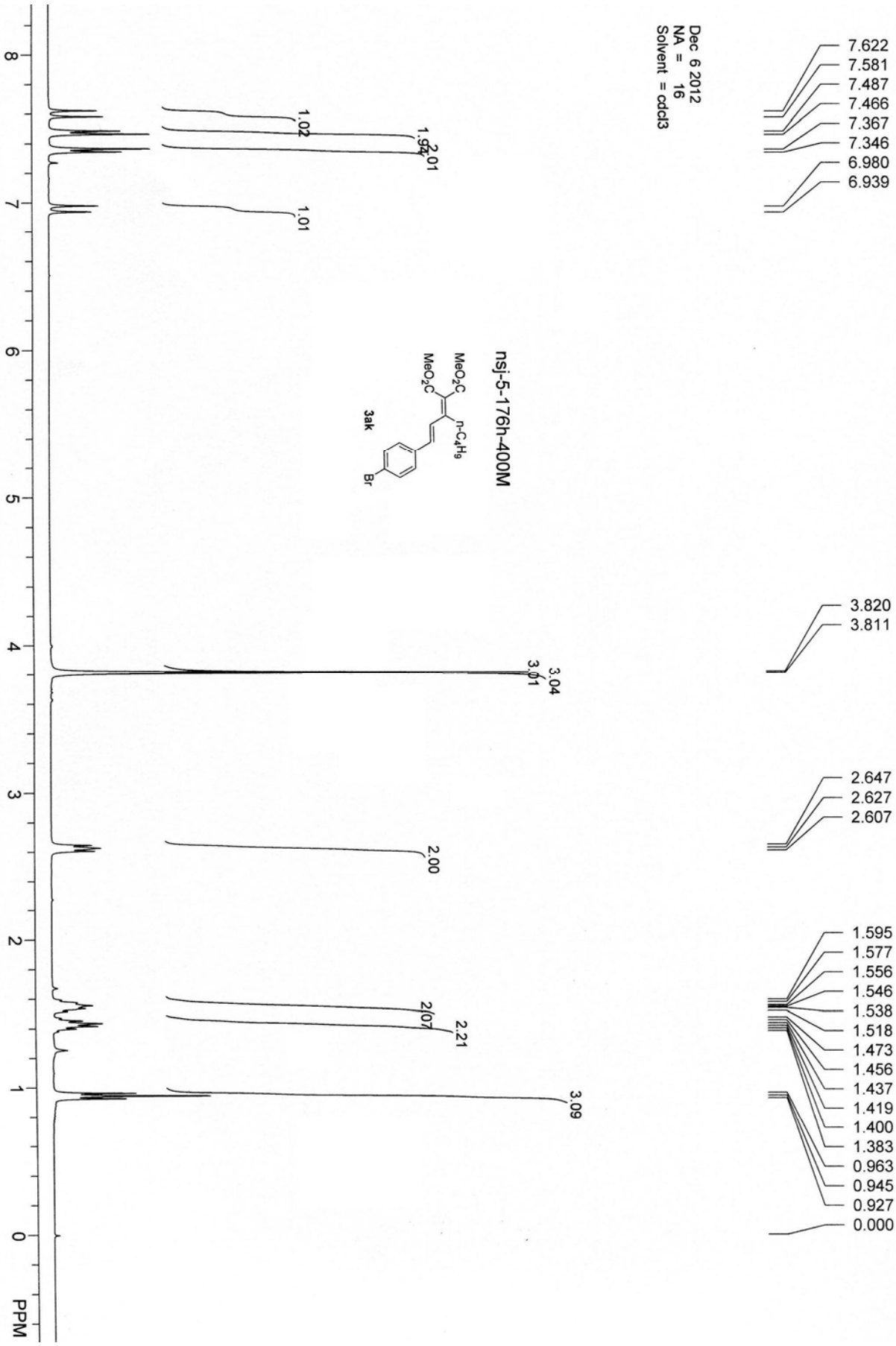

Dec 24 2012
NA = 168
Solvent = cdcl3
nsj-6-17c-400M
3ah
MeO2C
MeO2C
n-C4H9
Cl
Cl
166.238
165.479
153.967
134.939
134.613
132.982
131.649
129.568
127.883
127.737
127.468
124.707
77.320
77.000
76.680
52.258
52.242
31.903
30.143
22.956
13.725
PPM

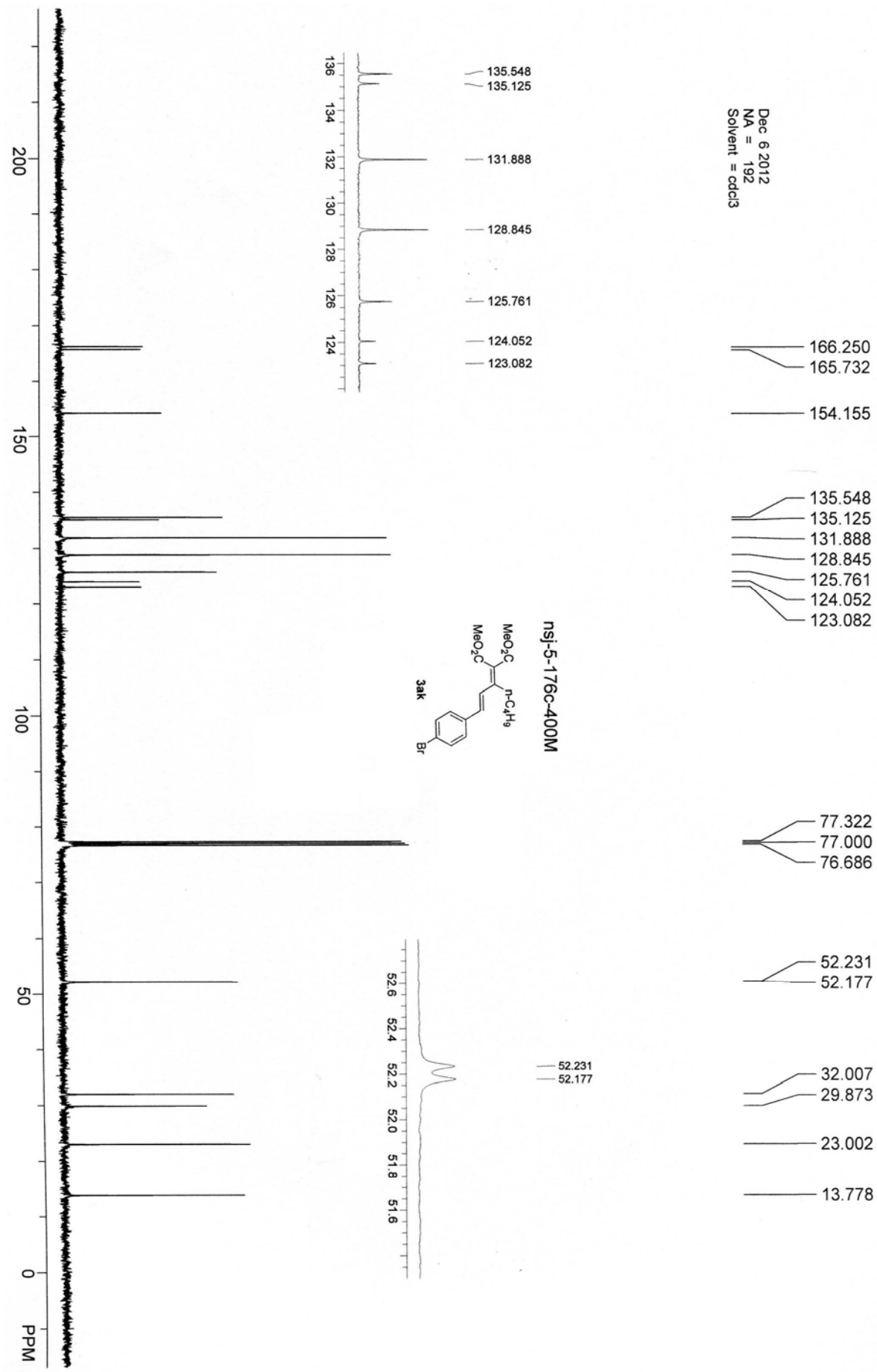

Mar 6 2013
NA = 8
Solvent = cdcl3
nsj-6-48h-400M
3al
Ph
MeO2C
MeO2C
n-C4H9
7.647
7.609
7.607
7.588
7.577
7.555
7.458
7.439
7.420
7.367
7.349
7.330
7.096
7.055
3.833
3.809
2.699
2.679
2.659
1.628
1.615
1.611
1.604
1.589
1.579
1.570
1.564
1.550
1.495
1.477
1.459
1.440
1.422
1.404
0.978
0.960
0.942
-0.000
7.20
2.09
1.10
1.00
3.06
3.01
2.00
2.16
2.23
3.10
8
6
4
2
0
PPM

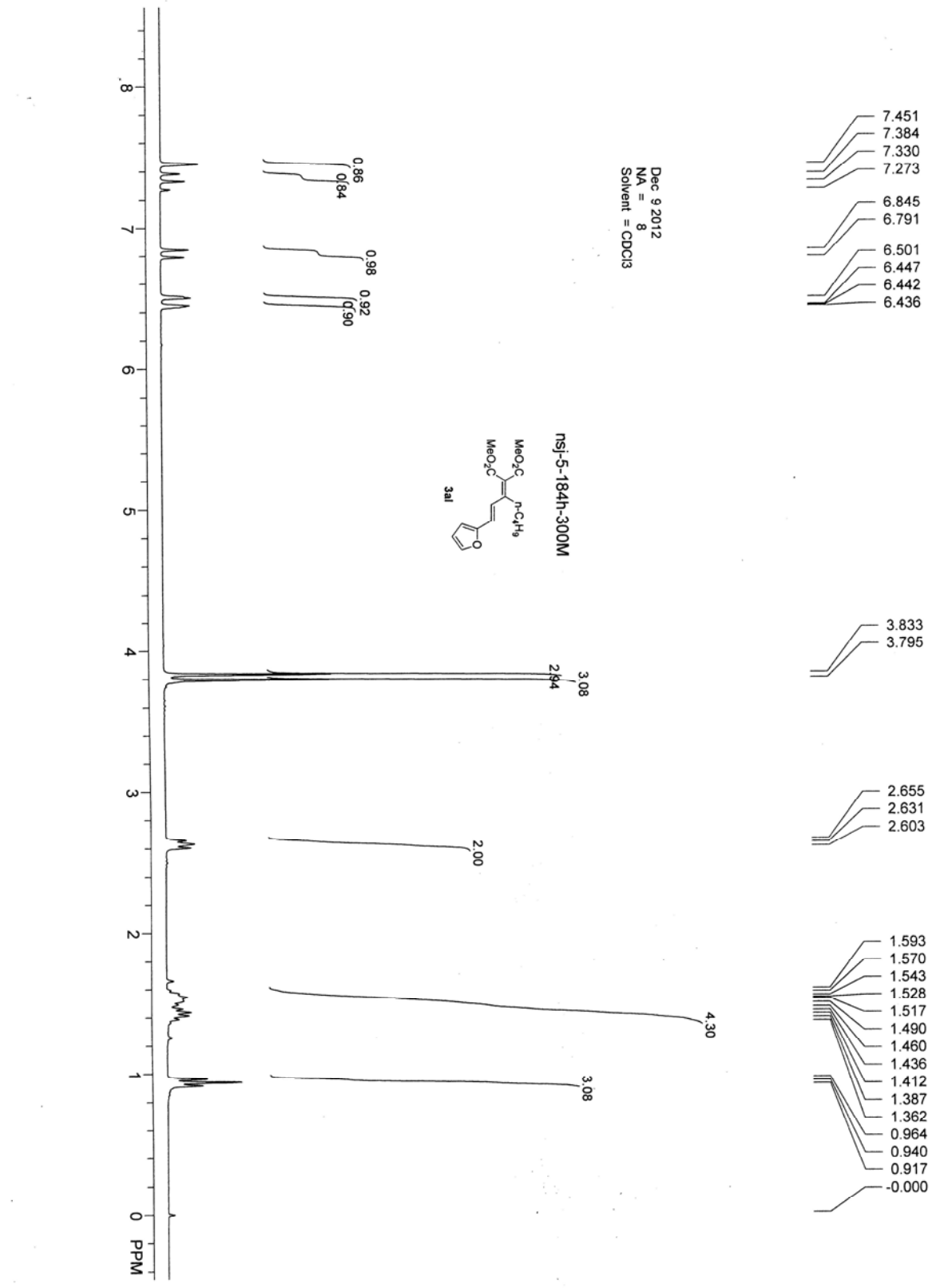

Mar 6 2013
NA = 160
Solvent = cdcl3
166.282
165.974
154.623
141.842
140.277
136.522
135.236
128.806
127.955
127.591
127.386
126.918
125.208
123.660
77.318
77.000
76.682
52.181
52.101
32.101
29.830
23.037
13.802
nsj-6-48c-400M
3ai
Ph
n-C4H9
MeO2C
MeO2C
PPM

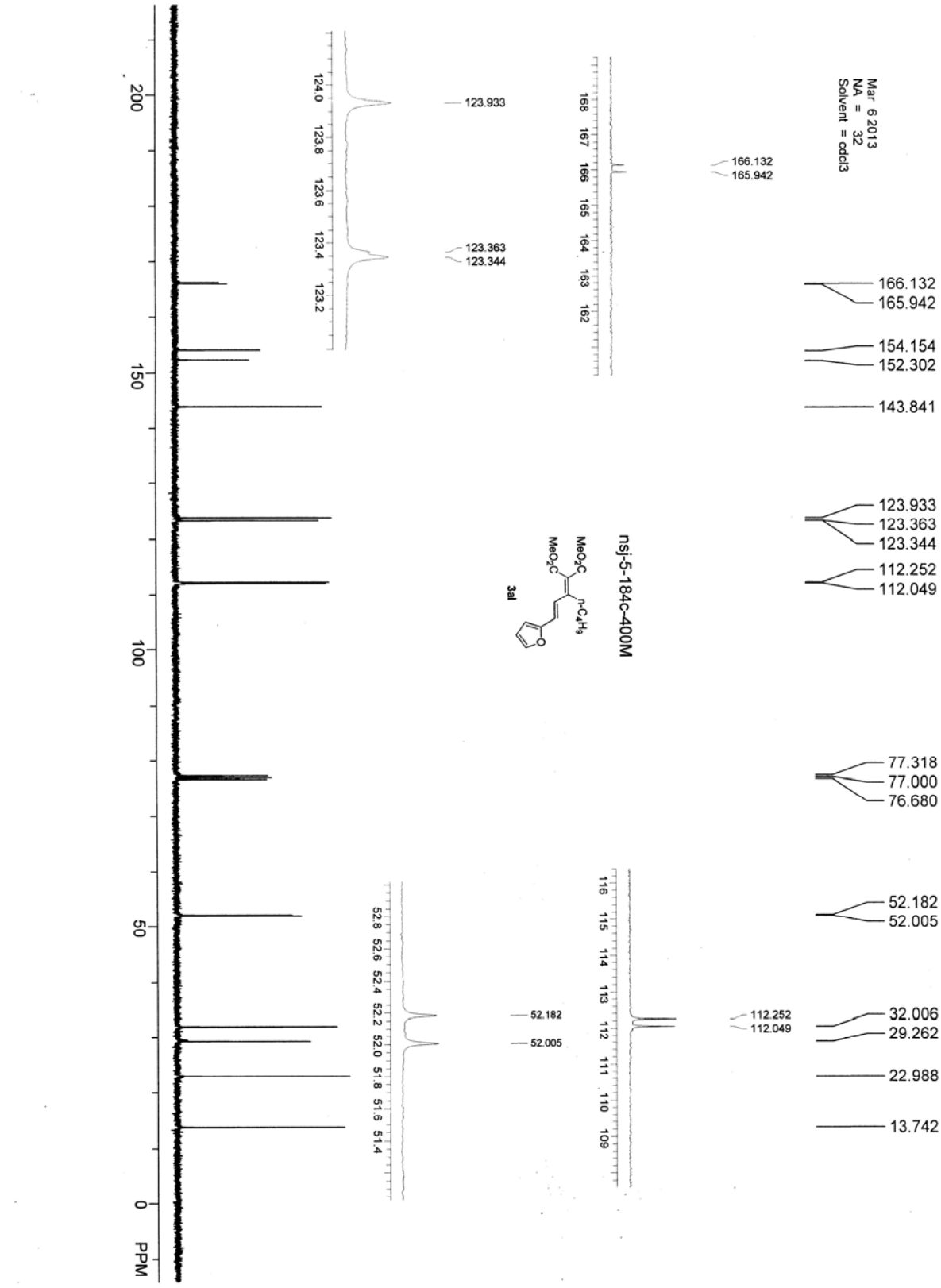

nsj-5-175h-300M
Dec 7 2012
NA = 16
Solvent = CDCl3
3aj
MeO2C
MeO2C
n-C4H9
OMe
7.562
7.508
7.303
7.276
7.250
7.116
7.090
7.034
7.012
6.981
6.886
6.881
6.859
6.854
3.833
3.823
3.806
2.688
2.661
2.635
1.620
1.598
1.570
1.556
1.545
1.519
1.496
1.472
1.447
1.424
1.400
1.377
0.973
0.949
0.924
0.99
1.10
1.01
2.00
0.94
3.11
3.00
3.07
2.00
4.17
3.04
PPM

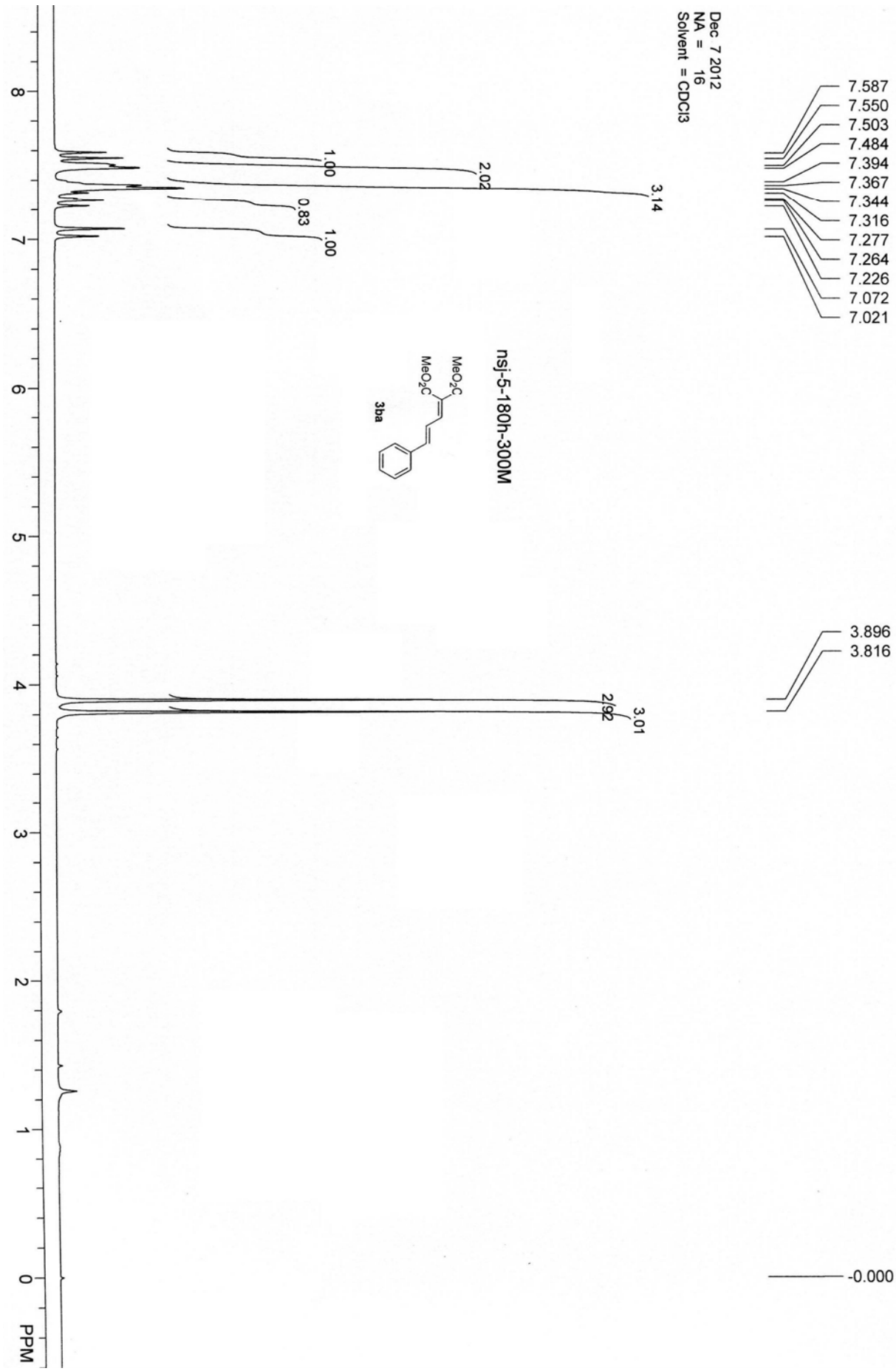

Mar 14 2013
NA = 400
Solvent = cdcl3
nsj-5-175c-400M
3aj
166.214
165.956
159.840
154.525
137.625
136.883
129.727
125.520
123.789
120.054
114.750
112.748
77.318
77.000
76.683
55.244
52.223
52.139
32.047
29.818
23.040
13.813
PPM

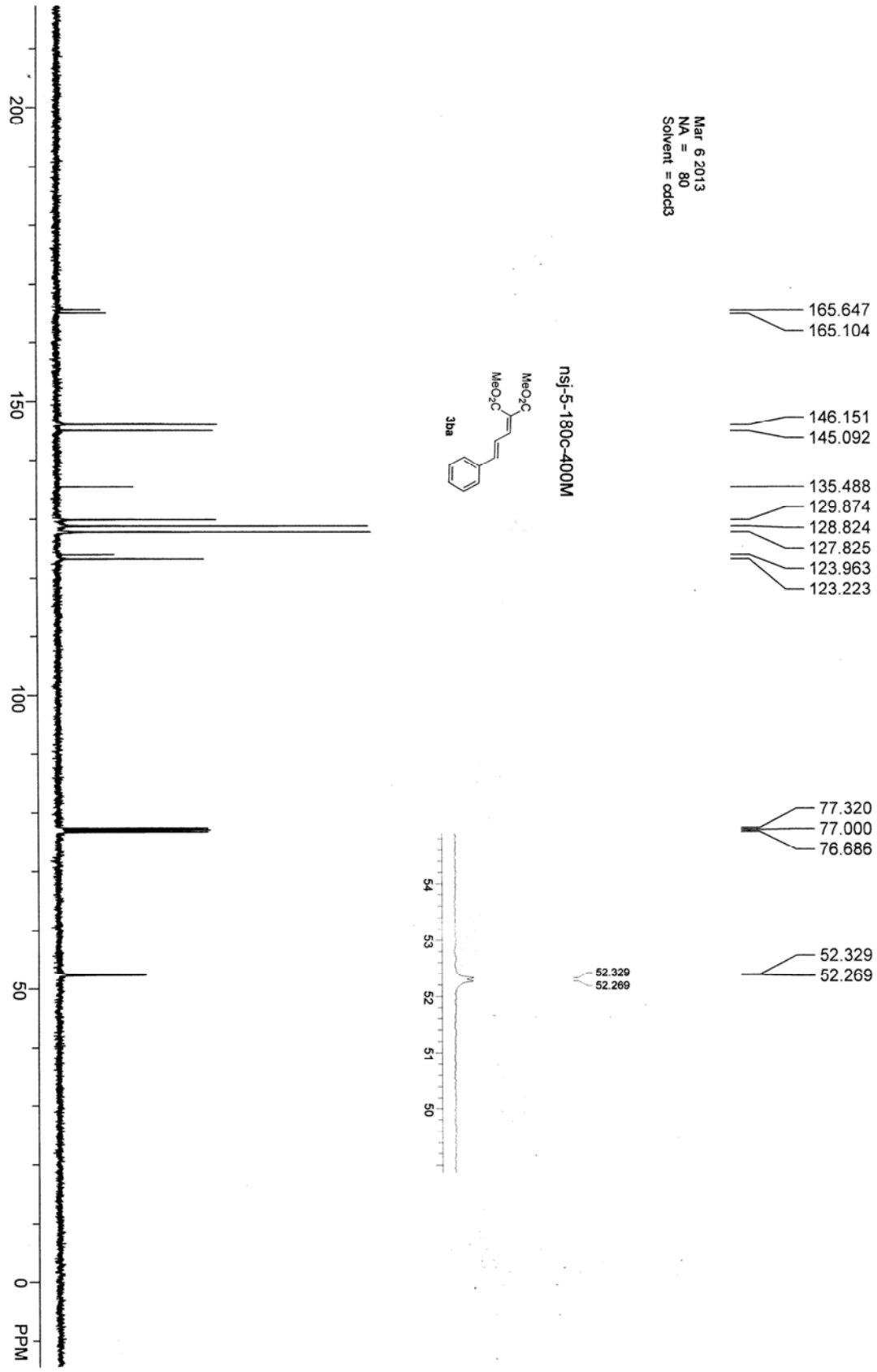

Dec 6 2012
NA = 16
Solvent = cdcl3
nsj-5-176h-400M
3ak
MeO2C
MeO2C
n-C4H9
Br
7.622
7.581
7.487
7.466
7.367
7.346
6.980
6.939
3.820
3.811
2.647
2.627
2.607
1.595
1.577
1.556
1.546
1.538
1.518
1.473
1.456
1.437
1.419
1.400
1.383
0.963
0.945
0.927
0.000
1.02
2.01
1.01
3.04
3.01
2.00
2.07
2.21
3.09
PPM

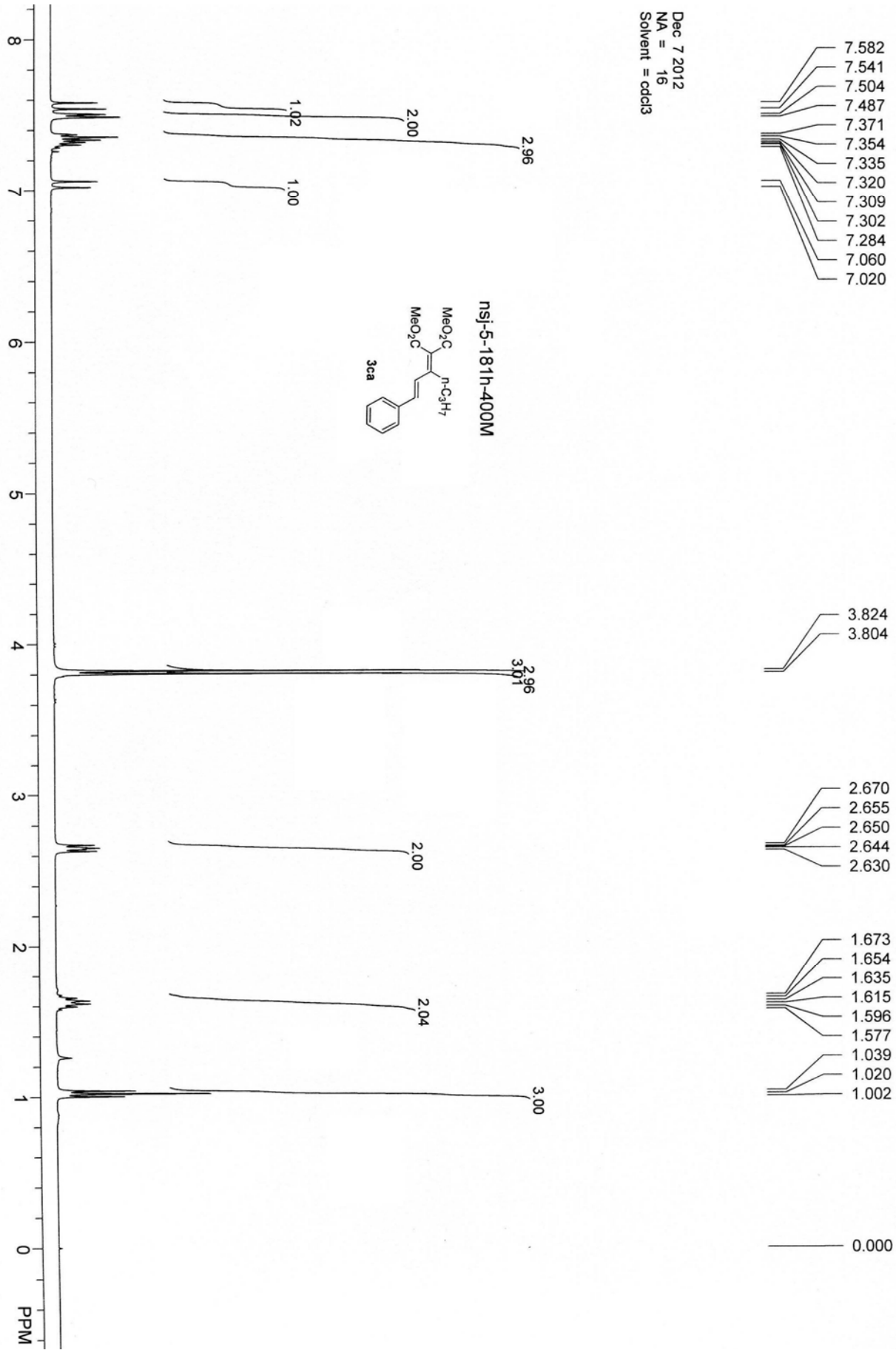

Dec 6 2012
NA = 192
Solvent = cdcl3
nsj-5-176c-400M
3ak
MeO2C
MeO2C
n-C4H9
Br
166.250
165.732
154.155
135.548
135.125
131.888
128.845
125.761
124.052
123.082
77.322
77.000
76.686
52.231
52.177
32.007
29.873
23.002
13.778
PPM

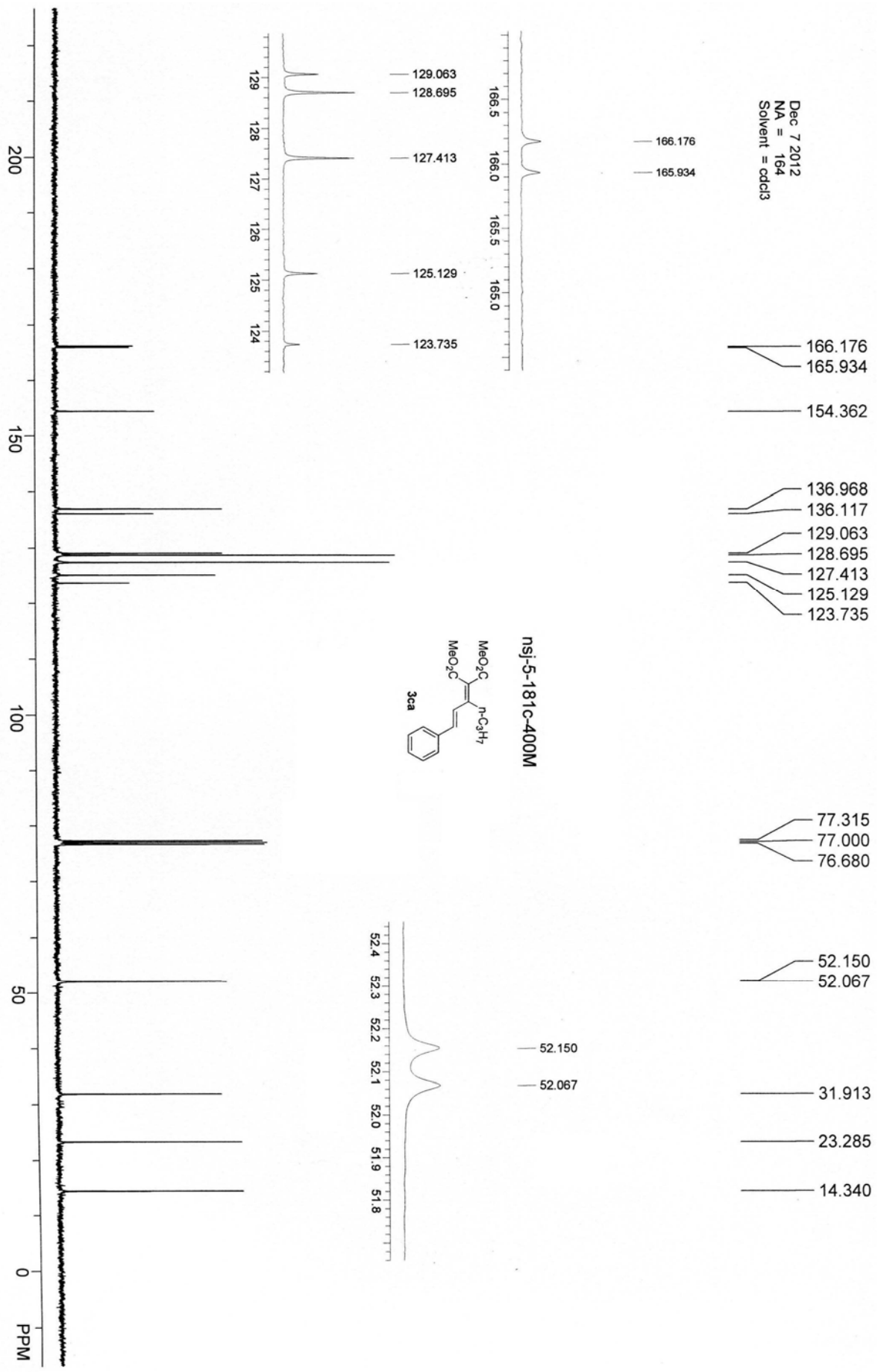

Dec 9 2012
NA = 8
Solvent = CDCl3
nsj-5-184h-300M
3al
MeO2C
MeO2C
n-C4H9
O
7.451
7.384
7.330
7.273
6.845
6.791
6.501
6.447
6.442
6.436
3.833
3.795
2.655
2.631
2.603
1.593
1.570
1.543
1.528
1.517
1.490
1.460
1.436
1.412
1.387
1.362
0.964
0.940
0.917
-0.000
0.86
0.84
0.98
0.92
0.90
3.08
2.94
2.00
4.30
3.08
8
7
6
5
4
3
2
1
0 PPM

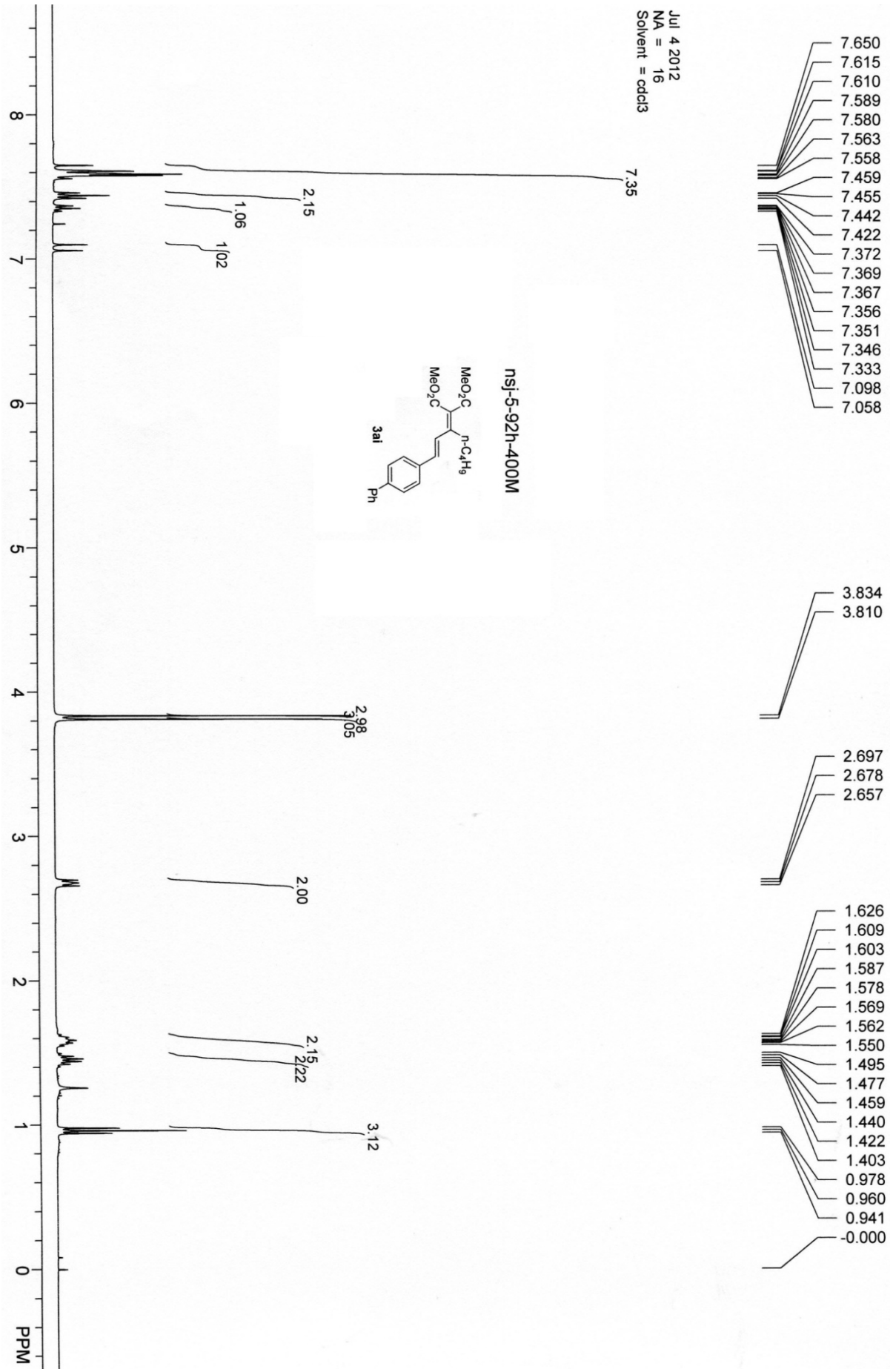

Mar 6 2013
NA = 32
Solvent = cdcl3
nsj-5-184c-400M
3al
MeO2C
MeO2C
n-C4H9
166.132
165.942
154.154
152.302
143.841
123.933
123.363
123.344
112.252
112.049
77.318
77.000
76.680
52.182
52.005
32.006
29.262
22.988
13.742
PPM

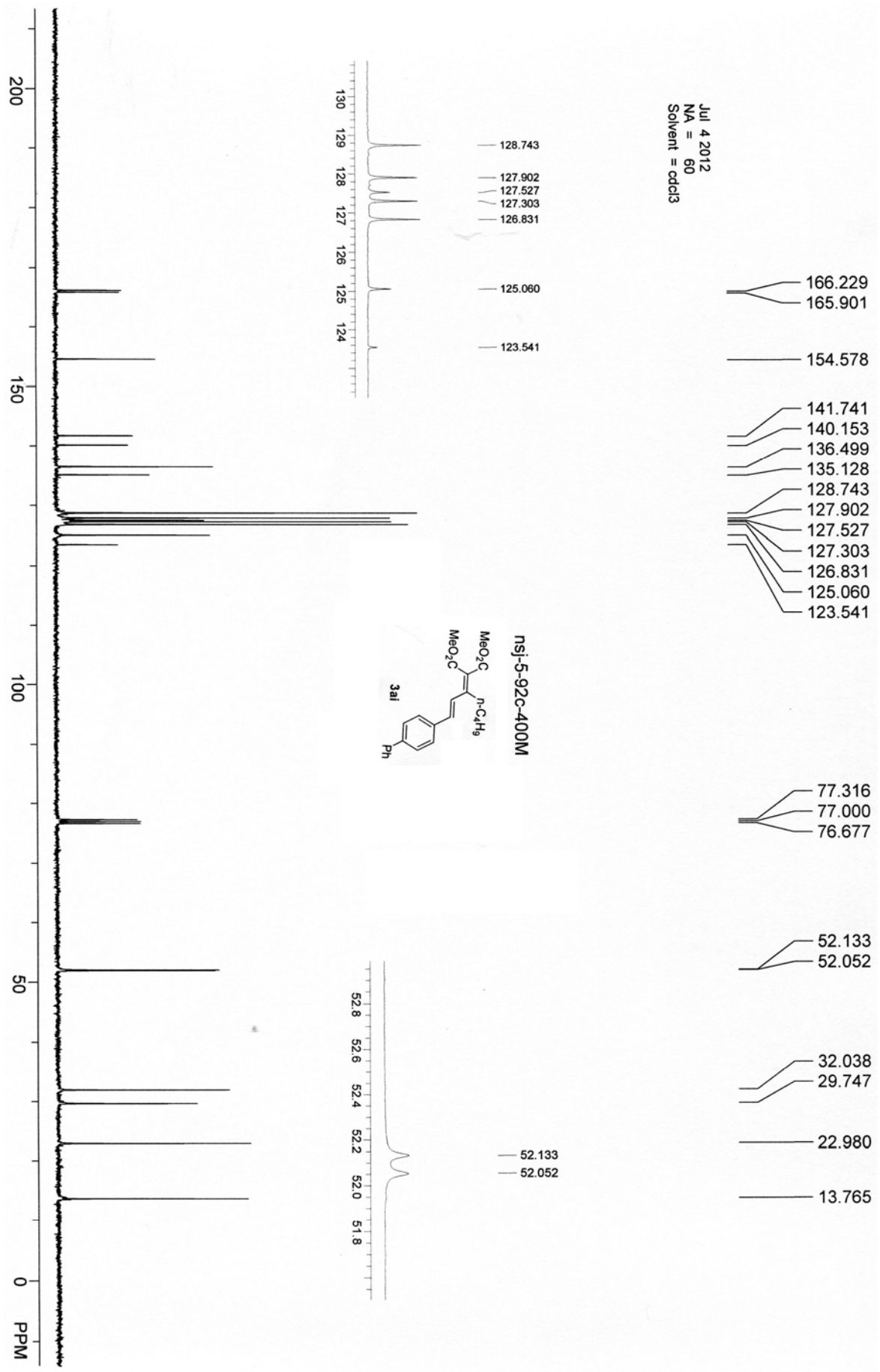

Dec 7 2012
NA = 16
Solvent = CDCl3
nsj-5-180h-300M
3ba
MeO2C
MeO2C
7.587
7.550
7.503
7.484
7.394
7.367
7.344
7.316
7.277
7.264
7.226
7.072
7.021
3.896
3.816
-0.000
1.00
2.02
3.14
0.83
1.00
2.92
3.01
PPM


Mar 6 2013
NA = 80
Solvent = cdcl3
nsj-5-180c-400M
3ba
MeO2C
MeO2C
165.647
165.104
146.151
145.092
135.488
129.874
128.824
127.825
123.963
123.223
77.320
77.000
76.686
52.329
52.269
52.329
52.269
200
150
100
50
0
PPM
54
53
52
51
50


Dec 7 2012
NA = 16
Solvent = cdcl3
nsj-5-181h-400M
3ca
7.582
7.541
7.504
7.487
7.371
7.354
7.335
7.320
7.309
7.302
7.284
7.060
7.020
3.824
3.804
2.670
2.655
2.650
2.644
2.630
1.673
1.654
1.635
1.615
1.596
1.577
1.039
1.020
1.002
0.000
2.96
2.00
1.02
1.00
2.96
3.01
2.00
2.04
3.00
PPM


Dec 7 2012
NA = 164
Solvent = cdcl3
nsj-5-181c-400M
3ca
166.176
165.934
154.362
136.968
136.117
129.063
128.695
127.413
125.129
123.735
77.315
77.000
76.680
52.150
52.067
31.913
23.285
14.340
PPM


Jul 4 2012
NA = 16
Solvent = cdcl3
nsj-5-92h-400M
3ai
MeO2C
MeO2C
n-C4H9
Ph
7.650
7.615
7.610
7.589
7.580
7.563
7.558
7.459
7.455
7.442
7.422
7.372
7.369
7.367
7.356
7.351
7.346
7.333
7.098
7.058
3.834
3.810
2.697
2.678
2.657
1.626
1.609
1.603
1.587
1.578
1.569
1.562
1.550
1.495
1.477
1.459
1.440
1.422
1.403
0.978
0.960
0.941
-0.000
7.35
2.15
1.06
1.02
2.98
3.05
2.00
2.15
2.22
3.12
PPM


Jul 4 2012
NA = 60
Solvent = cdcl3
166.229
165.901
154.578
141.741
140.153
136.499
135.128
128.743
127.902
127.527
127.303
126.831
125.060
123.541
77.316
77.000
76.677
52.133
52.052
32.038
29.747
22.980
13.765
nsj-5-92c-400M
3al
MeO2C
MeO2C
n-C4H9
Ph
PPM