Supporting Information

Stereoselective Synthesis of 1,2,3,4-Tetrasubstituted Dienes from Allenoates and Aldehydes: An Observation of Phosphine-Induced Chemoselectivity

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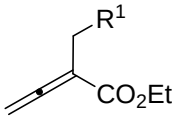
I. General Remarks

Unless otherwise noted, all reactions were carried out in nitrogen atmosphere. Liquid aldehydes were redistilled prior to use. Other reagents from commercial sources were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 400 spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard. NOESY spectra were obtained on a Variant 300 spectrometer in $CDCl_3$. Melting points were measured on a RY-I apparatus and uncorrected. High resolution ESI mass spectra were acquired with IonSpec QFT-ESI instrument. X-ray crystal diffraction data were collected on a Nonius Kappa CCD diffractometer with Mo Kα radiation (λ = 0.7107 Å) at room temperature. Column chromatography was performed on silica gel (200-300 mesh) using a mixture of petroleum ether/ethyl acetate as eluant.

II. Preparation of Allenoates



Diethyl 2-vinylidenesuccinate (R^1 = CO_2Et, **1a),** [1] ethyl 2-(cyanomethyl) buta-2,3-dienoate (R^1 = CN, **1b**),[2] ethyl 2-benzylbuta-2,3-dienoate (R^1 = Ph, **1c**),[3] (*E*)-ethyl 5-phenyl-2-vinylidenepent-4-enoate (R^1 = *E*-C_6H_4-CH=CH, **1d**),[3] ethyl 2-methylbuta-2,3-dienoate (R^1 = H, **1f**)[3] are known compounds and prepared according to the literatures.

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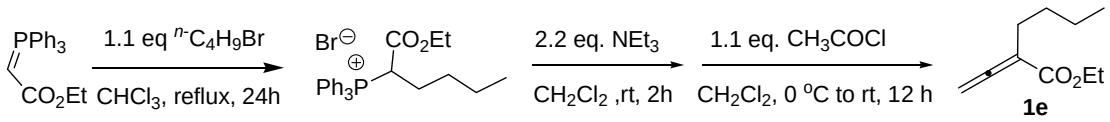
[1] H. Guo, Q. Xu, O. Kwon, *J. Am. Chem. Soc.* **2009**, *131*, 6318.

[2] Xu, S.; Zhou, L.; Ma, R.; Song, H.; He, Z. *Org. Lett.* **2010**, *12*, 544-547.

[3] Tran, Y. S.; Kwon, O. *J. Am. Chem. Soc.* **2007**, *129*, 12632..

Synthesis of ethyl 2-vinylidenehexanoate1e[4]



To a stirred solution of (carbethoxymethylene)triphenylphosphorane (17.43 g, 50 mmol) in chloroform (50 mL) was added 1.1 equivalent of 1-bromobutane (7.54 g, 55 mmol) at room temperature. The reaction mixture was refluxed for 24 h. Then the solvent and the excess of 1-bromobutane were evaporated under reduced pressure. To the resulting phosphonium salt was added anhydrous dichloromethane (200 mL) and 2.2 equivalent of triethylamine (11.11 g, 110 mmol). After stirred for 2 h, a solution of 1.1 equivalent of acetyl chloride (4.29 g, 55 mmol) in dichloromethane (50 mL) was dropwise added over 1 h at 0 ºC. Then the reaction mixture was allowed to warm up to room temperature and stirred for another 12 h. Most of the solvent was carefully distilled off, and the residue was thoroughly extracted with petroleum ether (bp 30-60 ºC, 5 × 100 mL). The combined extracting was concentrated and the residue was subjected to column chromatography on silica gel (eluant: 5% EtOAc in petroleum ether) to provide allenoate **1e** as colorless oil (4.32 g, 51% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 5.12 (t, *J* = 2.8 Hz, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.23 (m, 2H), 1.49-1.31 (m, 4H), 1.29 (t, *J* = 7.1 Hz), 0.91 (t, *J* = 7.1 Hz).; ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 213.7, 167.4, 100.4, 78.8, 60.9, 30.0, 27.7, 22.2, 14.2, 13.9; HRMS calcd for $C_{10}H_{16}O_2Na^+$ requires 192.1043, found 192.1049.

III. General Procedure for the Phosphine-Mediated Olefination

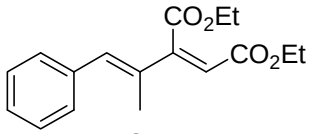
Under N_2 atmosphere and at room temperature, to a stirred solution of allenoate **1** (0.2 mmol) and aldehyde **2** (0.3 mmol) in $CHCl_3$ (5 mL) in a Schlenk tube (25 mL) was added the liquid phosphine (0.3 mmol) by the means of a microsyringe. The resulting reaction mixture was stirred till the aldehyde **2** was completely consumed, as

[4] **1e** was reported without being fully characterized: Maity, P.; Lepore, S. D. *J. Org. Chem.* **2009**, *74*, 158–162.

monitored by TLC. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (gradient eluant: petroleum ether/ethyl acetate 20:1–5:1) to afford dienes **4**.

IV. Analytical Data for Compounds 3[5], 4 and 5

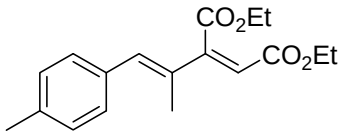
Table 2, entry 1. Following the general procedure, the reaction of allenoate **1a** (60 mg, 0.3 mmol), benzaldehyde (21 mg, 0.2 mmol) and PBu_3 (75 μL, 0.3 mmol) was performed for 24 h.



4a

4a: 96% yield (obtained as an inseparable mixture in 99% combined yield with a trace amount of cyclopropane (*trans*,*Z*)-**3a**), as colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.37 (m, 2H), 7.28 (m, 3H), 6.79 (s, 1H), 6.00 (s, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.06 (d, *J* = 1.0 Hz, 3H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 168.4, 165.3, 151.7, 136.4, 136.3, 131.9, 129.5, 128.2, 127.9, 116.2, 61.8, 60.7, 14.7, 14.2, 14.0; HRMS (ESI) calcd for $C_{17}H_{20}O_4Na^+$ requires 311.1254, found 311.1250.

Table 2, entry 2. Following the general procedure, the reaction of allenoate **1a** (60 mg, 0.3 mmol), 4-methylbenzaldehyde (24 mg, 0.2 mmol) and PBu_3 (75 μL, 0.3 mmol) was performed for 24 h.



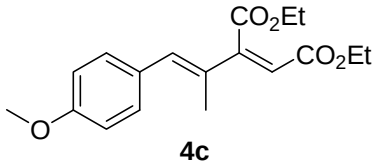
4b

4b: 85% yield (obtained as an inseparable mixture in 88% combined yield with a trace amount of cyclopropane (*trans*,*Z*)-**3b**), as a white solid, mp 79-81 °C; ^{1}H NMR

[5] Analytical data for **3a-d**, **3f**, **3g**, **3i-l** were reported: Xu, S.; Zhou, L.; Ma, R.; Song, H.; He, Z. *Org. Lett.* **2010**, *12*, 544-547.

($CDCl_3$, 400 MHz, TMS): δ 7.20 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 6.76 (s, 1H), 5.98 (s, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 2.06 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 168.4, 165.3, 151.9 137.9, 136.5, 133.5, 131.2, 129.5, 129.0, 115.7, 61.7, 60.7, 21.2, 14.7, 14.2, 14.0; HRMS calcd for $C_{18}H_{22}O_4Na^+$ requires 325.1410, found 325.1405.

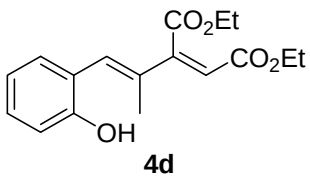
Table 2, entry 3. Following the general procedure, the reaction of allenoate **1a** (60 mg, 0.3 mmol), 4-methoxybenzaldehyde (27 mg, 0.2 mmol) and PBu_3 (75 μL, 0.3 mmol) was performed for 24 h.



4c

4c: 87% yield, as a white solid, mp 50-52 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.26 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.73 (s, 1H), 5.96 (s, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 2.07 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 168.6, 165.4, 159.3, 152.1, 136.3, 131.1, 130.2, 128.8, 115.3, 113.7, 61.7, 60.7, 55.3, 14.7, 14.2, 14.0; HRMS calcd for $C_{18}H_{22}O_5Na^+$ requires 341.1359, found 341.1355.

Table 2, entry 5. Following the general procedure, the reaction of allenoate **1a** (60 mg, 0.3 mmol), 2-hydroxybenzaldehyde (25 mg, 0.2 mmol) and PBu_3 (75 μL, 0.3 mmol) was performed for 1 h.

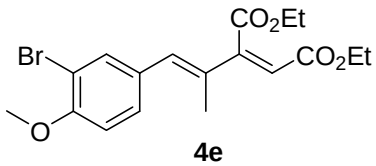


4d

4d: 72% yield, as a white solid, mp 137-138 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.19 (t, *J* = 7.7 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 6.90 (m, 2H), 6.81 (s, 1H), 6.01 (s, 1H), 5.83 (br s, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.97 (s, 3H),

1.38 (t, J = 7.1 Hz, 3H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 168.8, 165.3, 153.7, 151.1, 133.4, 131.6, 130.1, 129.7, 123.2, 120.1, 116.3, 115.8, 62.0, 60.9, 14.8, 14.1, 14.0; HRMS calcd for $C_{17}H_{20}O_5Na^+$ requires 327.1203, found 327.1204.

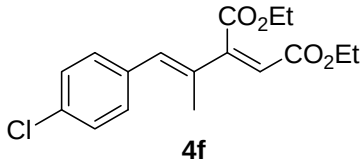
Table 2, entry 6. Following the general procedure, the reaction of allenoate **1a** (60 mg, 0.3 mmol), 3-bromo-4-methoxybenzaldehyde (43 mg, 0.2 mmol) and PBu_3 (75 μL, 0.3 mmol) was performed for 4 h.



4e

4e: 88% yield, as colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.51 (s, 1H), 7.23 (d, J = 8.4 Hz, 1H), 6.90 (d, J = 8.4 Hz, 1H), 6.65 (s, 1H), 5.99 (s, 1H), 4.43 (q, J = 7.0 Hz, 2H), 4.22 (q, J = 7.0 Hz, 2H), 3.92 (s, 3H), 2.06 (s, 3H), 1.40 (t, J = 7.0 Hz, 3H), 1.30 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 168.3, 165.2, 155.4, 151.5, 134.6, 134.3, 131.5, 130.1, 130.0, 116.1, 111.41, 111.38, 61.8, 60.8, 56.2, 14.7, 14.2, 14.0; HRMS calcd for $C_{18}H_{21}BrO_5Na^+$ requires 419.0465, found 419.0460.

Table 2, entry 7. Following the general procedure, the reaction of allenoate **1a** (60 mg, 0.3 mmol), 4-chlorobenzaldehyde (28 mg, 0.2 mmol) and PBu_3 (75 μL, 0.3 mmol) was run for 24 h.

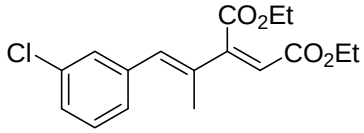


4f

4f: 90% yield (obtained in 99% combined yield as an inseparable mixture with a small amount of cyclopropane (*trans*,*Z*)-**3d**), as a white solid, mp 64-66 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.34 (d, J = 8.5 Hz, 2H), 7.22 (d, J = 8.5 Hz, 2H), 6.72 (s, 1H), 6.01 (s, 1H), 4.43 (q, J = 7.1 Hz, 2H), 4.22 (q, J = 7.1 Hz, 2H), 2.04 (d, J = 1.1 Hz, 3H), 1.40 (t, J = 7.1 Hz, 3H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100

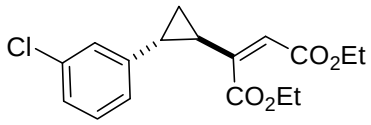
MHz, TMS): δ 168.2, 165.1, 151.3, 134.9, 134.7, 133.7, 132.4, 130.7, 128.5, 116.6, 61.8, 60.8, 14.7, 14.1, 14.0; HRMS calcd for $C_{17}H_{19}ClO_4Na^+$ requires 345.0864, found 345.0866.

Table 2, entry 8. Following the general procedure, the reaction of allenoate **1a** (60 mg, 0.3 mmol), 3-chlorobenzaldehyde (28 mg, 0.2 mmol) and PBu_3 (75 μL, 0.3 mmol) was performed for 24 h.



4g

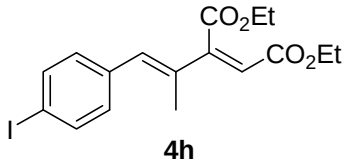
4g: 62% yield (obtained in 74% combined yield as an inseparable mixture with a small amount of cyclopropane (*trans*,*Z*)-**3e**), as colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.30 (m, 3H), 7.16 (m, 1H), 6.71 (s, 1H), 6.03 (s, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.05 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 168.1, 165.1, 151.2, 138.1, 134.6, 134.1, 133.0, 129.5, 129.2, 127.9, 127.5, 116.9, 61.8, 60.8, 14.7, 14.1, 14.0; HRMS calcd for $C_{17}H_{19}ClO_4Na^+$ requires 345.0864, found 345.0869.



(*trans*,*Z*)-**3e**

Selected ^{1}H NMR data for (*trans*,*Z*)-**3e**: δ 7.07 (s, 1H), 6.99 (d, *J* = 7.2 Hz, 1H), 5.84 (s, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.29 (m, 1H), 1.88 (m, 1H); selected ^{13}C NMR data for (*trans*,*Z*)-**3e**: δ 167.3, 164.6, 142.5, 129.7, 126.5, 126.1, 124.4, 117.7, 61.6, 60.7, 26.8, 25.6, 16.1, 14.1, 14.0.

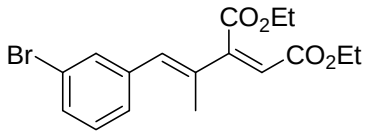
Table 2, entry 10. Following the general procedure, the reaction of allenoate **1a** (60 mg, 0.3 mmol), 4-iodobenzaldehyde (46 mg, 0.2 mmol) and PBu_3 (75 μL, 0.3 mmol) was run for 3 h.



4h

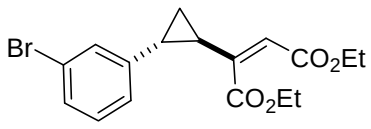
4h: 69% yield (obtained in 82% combined yield as an inseparable mixture with a small amount of cyclopropane (*trans*,*Z*)-**3g**), as a white solid, mp 50-53 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.68 (s, 1H), 6.01 (s, 1H), 4.43 (q, *J* = 7.2 Hz, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.03 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 168.2, 165.2, 151.3, 137.4, 135.8, 135.1, 132.6, 131.2, 116.7, 93.8, 61.8, 60.9, 14.7, 14.2, 14.0; HRMS calcd for $C_{17}H_{19}IO_4Na^+$ requires 437.0220, found 437.0218.

Table 2, entry 11. Following the general procedure, the reaction of allenoate **1a** (60 mg, 0.3 mmol), 3-bromobenzaldehyde (37 mg, 0.2 mmol) and PBu_3 (75 μL, 0.3 mmol) was performed for 1 h.



4i

4i: 72% yield (obtained in 86% combined yield as a mixture with a small amount of cyclopropane (*trans*,*Z*)-**3h**), as colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.35 (m, 2H), 7.16 (m, 2H), 6.63 (s, 1H), 5.95 (s, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 1.97 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 168.1, 165.1, 151.1, 138.4, 134.5, 133.1, 132.1, 130.8, 129.8, 128.0, 122.3, 116.9, 61.8, 60.9, 14.7, 14.1, 14.0; HRMS calcd for $C_{17}H_{19}BrO_4Na^+$ requires 389.0359, found 389.0359.

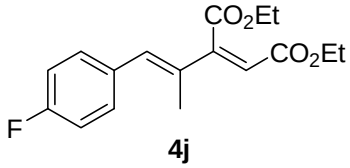


(*trans*,*Z*)-**3h**

Selected ^{1}H NMR data for (*trans*,*Z*)-**3h**: δ 7.25 (d, *J* = 7.8 Hz, 1H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 5.77 (s, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 4.10 (q, *J* = 7.1

Hz, 2H), 2.20 (m, 1H), 1.80 (m, 1H), 1.18 (t, J = 7.1 Hz, 3H); selected ^{13}C NMR data for (*trans*,*Z*)-**3h**: δ 167.3, 164.6, 142.8, 130.0, 129.4, 129.1, 124.9, 122.6, 117.7, 61.6, 60.7, 26.9, 25.5, 16.1, 14.1, 14.0.

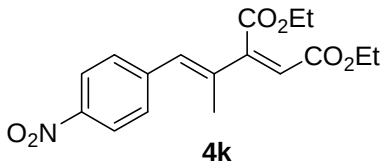
Table 2, entry 12. Following the general procedure, the reaction of allenoate **1a** (60 mg, 0.3 mmol), 4-fluorobenzaldehyde (25 mg, 0.2 mmol) and PBu_3 (75 μL, 0.3 mmol) was run for 2.5 h.



4j

4j: 84% yield (obtained in 92% combined yield as a mixture with a small amount of cyclopropane (*trans*,*Z*)-**3i**), as colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.27 (dd, J = 8.5, 5.5 Hz, 2H), 7.06 (t, J = 8.5 Hz, 2H), 6.74 (s, 1H), 6.00 (s, 1H), 4.44 (q, J = 7.1 Hz, 2H), 4.22 (q, J = 7.2 Hz, 2H), 2.04 (s, 3H), 1.40 (t, J = 7.2 Hz, 3H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 168.3, 165.2, 162.1 (d, $^1J_{CF}$ = 248.7 Hz), 151.5, 135.2, 132.3 (d, $^4J_{CF}$ = 3.3 Hz), 131.8, 131.2 (d, $^3J_{CF}$ = 8.1 Hz), 116.3, 115.3 (d, $^2J_{CF}$ = 21.6 Hz), 61.7, 60.8, 14.6, 14.1, 14.0; HRMS calcd for $C_{17}H_{19}FO_4Na^+$ requires 329.1160, found 329.1162.

Table 2, entry 13. Following the general procedure, the reaction of allenoate **1a** (60 mg, 0.3 mmol), 4-nitrobenzaldehyde (30 mg, 0.2 mmol) and PPh_2Me (56 μL, 0.3 mmol) was performed for 1 h.

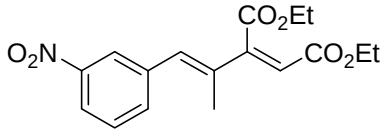


4k

4k: 63% yield (obtained in 65% combined yield as a mixture with a trace amount of cyclopropane (*trans*,*Z*)-**3j**), as a white solid, mp 70-71 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 8.24 (d, J = 8.6 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 6.80 (s, 1H), 6.09 (s, 1H), 4.45 (q, J = 7.1 Hz, 2H), 4.24 (q, J = 7.1 Hz, 2H), 2.07 (s, 3H), 1.41 (t, J = 7.1

Hz, 3H), 1.32 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 167.9, 164.9, 150.6, 146.9, 142.9, 135.0, 133.4, 130.2, 123.6, 118.1, 62.0, 61.0, 14.9, 14.1, 14.0; HRMS calcd for $C_{17}H_{19}NO_6Na^+$ requires 356.1104, found 356.1097.

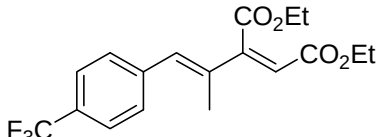
Table 2, entry 14. Following the general procedure, the reaction of allenoate **1a** (60 mg, 0.3 mmol), 3-nitrobenzaldehyde (30 mg, 0.2 mmol) and PPh_2Me (56 μL, 0.3 mmol) was run for 1.2 h.



4l

4l: 79% yield, as colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 8.16 (s, 2H), 7.59 (m, 2H), 6.80 (s, 1H), 6.09 (s, 1H), 4.45 (q, J = 7.1 Hz, 2H), 4.24 (q, J = 7.1 Hz, 2H), 2.08 (s, 3H), 1.41 (t, J = 7.1 Hz, 3H), 1.32 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 167.9, 164.9, 150.6, 148.1, 137.9, 135.3, 134.3, 133.1, 129.3, 124.0, 122.5, 117.8, 61.9, 61.0, 14.7, 14.1, 14.0; HRMS calcd for $C_{17}H_{19}NO_6Na^+$ requires 356.1104, found 356.1101.

Table 2, entry 15. Following the general procedure, the reaction of allenoate **1a** (60 mg, 0.3 mmol), 4-(trifluoromethyl)benzaldehyde (37 mg, 0.2 mmol) and PPh_2Me (56 μL, 0.3 mmol) was run for 6 h.

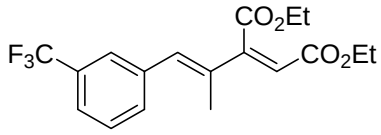


4m

4m: 95% yield (obtained in 99% combined yield as a mixture with a trace amount of cyclopropane (*trans*,*Z*)-**3k**), as colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.63 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 6.79 (s, 1H), 6.06 (s, 1H), 4.44 (q, J = 7.2 Hz, 2H), 4.23 (q, J = 7.1 Hz, 2H), 2.05 (d, J = 0.9 Hz, 3H), 1.40 (t, J = 7.2 Hz, 3H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 168.1, 165.1, 151.0, 139.9, 134.5, 133.7, 129.63, 129.62 (q, $^2J_{CF}$ = 32.8 Hz), 125.2 (q, $^3J_{CF}$ = 3.7

Hz), 123.9 (q, $^1J_{CF}$ = 272.0 Hz), 117.3, 61.9, 60.9, 14.7, 14.2, 14.0; HRMS calcd for $C_{18}H_{19}F_3O_4Na^+$ requires 379.1128, found 379.1125.

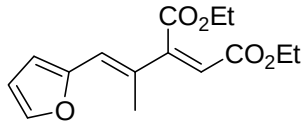
Table 2, entry 16. Following the general procedure, the reaction of allenoate **1a** (60 mg, 0.3 mmol), 3-(trifluoromethyl)benzaldehyde (37 mg, 0.2 mmol) and PPh_2Me (56 μL, 0.3 mmol) was performed for 6 h.



4n

4n: 96% yield, as colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.61-7.44 (m, 4H), 6.79 (s, 1H), 6.05 (s, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.05 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 168.1, 165.1, 151.0, 137.0, 134.4, 133.4, 132.6, 130.7 (q, $^2J_{CF}$ = 32.2 Hz), 128.8, 126.1 (q, $^3J_{CF}$ = 3.7 Hz), 124.5 (q, $^3J_{CF}$ = 3.7 Hz), 123.9 (q, $^1J_{CF}$ = 272.4 Hz) 117.2, 61.9, 60.9, 14.7, 14.2, 14.0; HRMS calcd for $C_{18}H_{19}F_3O_4Na^+$ requires 379.1128, found 379.1125.

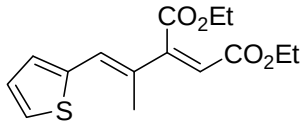
Table 2, entry 18. Following the general procedure, the reaction of allenoate **1a** (60 mg, 0.3 mmol), furfurylaldehyde (19 mg, 0.2 mmol) and PBu_3 (75 μL, 0.3 mmol) was performed for 4 h.



4o

4o: 88% yield, as a white solid, mp 78-80 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.50 (d, *J* = 1.4 Hz, 1H), 6.52 (s, 1H), 6.48 (m, 2H), 5.99 (s, 1H), 4.43 (q, *J* = 7.2 Hz, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.23 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 168.4, 165.3, 152.1, 151.6, 143.7, 128.6, 123.1, 115.5, 114.4, 112.0, 61.8, 60.7, 14.7, 14.2, 14.0; HRMS calcd for $C_{15}H_{18}O_5Na^+$ requires 301.1046, found 301.1041.

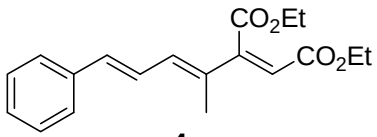
Table 2, entry 19. Following the general procedure, the reaction of allenoate **1a** (60 mg, 0.3 mmol), thiophene-2-carbaldehyde (22 mg, 0.2 mmol) and PBu_3 (75 μL, 0.3 mmol) was performed for 1 h.



4p

4p: 85% yield, as a white solid, mp 80-81 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.44 (d, *J* = 5.0 Hz, 1H), 7.15 (d, *J* = 3.6 Hz, 1H), 7.08 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.89 (s, 1H), 5.99 (s, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.20 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 168.4, 165.3, 151.7, 139.4, 131.2, 129.0, 128.9, 128.5, 127.3, 115.6, 61.8, 60.7, 15.1, 14.2, 14.0; HRMS calcd for $C_{15}H_{18}O_4SNa^+$ requires 317.0818, found 317.0815.

Table 2, entry 20. Following the general procedure, the reaction of allenoate **1a** (60 mg, 0.3 mmol), *E*-cinnamaldehyde (26 mg, 0.2 mmol) and PBu_3 (75 μL, 0.3 mmol) was performed for 24 h.

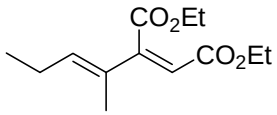


4q

4q: 80% yield, as a yellow solid, mp 106-107 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.46 (d, *J* = 7.3 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 2H), 7.29 (d, *J* = 7.1 Hz, 1H), 7.14 (dd, *J* = 15.3, 11.0 Hz, 1H), 6.75 (d, *J* = 15.3 Hz, 1H), 6.47 (d, *J* = 11.0 Hz, 1H), 5.93 (s, 1H), 4.45 (q, *J* = 7.0 Hz, 2H), 4.21 (q, *J* = 7.0 Hz, 2H), 2.05 (s, 3H), 1.41 (t, *J* = 7.0 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 168.4, 165.4, 151.3, 138.2, 136.7, 136.2, 130.8, 128.8, 128.6, 126.9, 124.3, 115.1, 61.7, 60.7, 14.2, 14.1, 13.6; HRMS calcd for $C_{19}H_{22}O_4Na^+$ requires 337.1410, found 337.1416.

Table 2, entry 21. Following the general procedure, the reaction of allenoate **1a** (60 mg, 0.3 mmol), propionaldehyde (12 mg, 0.2 mmol) and PBu_3 (75 μL, 0.3 mmol) was

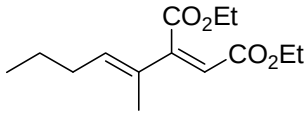
run for 40 h.



4r

4r: 98% yield, as colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 5.82 (s, 1H), 5.80 (t, *J* = 7.1 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.23 (p, *J* = 7.4 Hz, 2H), 1.83 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.02 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 168.5, 165.5, 151.6, 141.1, 130.0, 114.2, 61.5, 60.6, 22.4, 14.2, 14.0, 13.3, 13.0; HRMS calcd for $C_{13}H_{20}O_4Na^+$ requires 263.1254, found 263.1255.

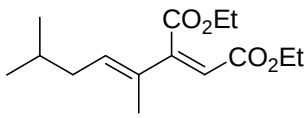
Table 2, entry 22. Following the general procedure, the reaction of allenoate **1a** (60 mg, 0.3 mmol), butyraldehyde (14 mg, 0.2 mmol) and PBu_3 (75 μL, 0.3 mmol) was performed for 24 h.



4s

4s: 99% yield, as colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 5.82 (m, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.20 (q, *J* = 7.3 Hz, 2H), 1.83 (s, 3H), 1.45 (m, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 168.6, 165.5, 151.6, 139.7, 130.5, 114.1, 61.5, 60.6, 31.1, 22.1, 14.2, 14.0, 13.8, 13.1; HRMS calcd for $C_{14}H_{22}O_4Na^+$ requires 277.1410, found 277.1412.

Table 2, entry 23. Following the general procedure, the reaction of allenoate **1a** (60 mg, 0.3 mmol), 3-methylbutanal (17 mg, 0.2 mmol) and PBu_3 (75 μL, 0.3 mmol) was performed for 24 h.

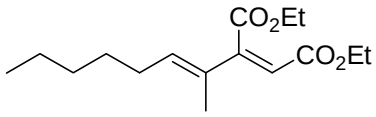


4t

4t: 97% yield, as colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 5.84 (t, *J* = 7.4

Hz, 1H), 5.82 (s, 1H), 4.39 (q, J = 7.2 Hz, 2H), 4.19 (q, J = 7.1 Hz, 2H), 2.11 (t, J = 7.4 Hz, 2H), 1.83 (s, 3H), 1.72 (m, 1H), 1.37 (t, J = 7.2 Hz, 3H), 1.28 (t, J = 7.1 Hz, 3H), 0.91 (d, J = 6.7 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 168.6, 165.5, 151.7, 138.8, 130.9, 114.1, 61.4, 60.6, 38.1, 28.6, 22.4, 14.2, 14.1, 13.2; HRMS calcd for $C_{15}H_{24}O_4Na^+$ requires 291.1567, found 291.1570.

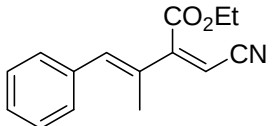
Table 2, entry 24. Following the general procedure, the reaction of allenoate **1a** (60 mg, 0.3 mmol), hexanal (20 mg, 0.2 mmol) and PBu_3 (75 μL, 0.3 mmol) was run for 24 h.



4u

4u: 87% yield, as colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 5.82 (t, J = 7.5 Hz, 1H), 5.81 (s, 1H), 4.38 (q, J = 7.2 Hz, 2H), 4.19 (q, J = 7.1 Hz, 2H), 2.21 (q, J = 7.3 Hz, 2H), 1.83 (s, 3H), 1.41 (m, 2H), 1.37 (t, J = 7.2 Hz, 3H), 1.28 (m, 7H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 168.5, 165.5, 151.6, 139.9, 130.3, 114.1, 61.5, 60.6, 31.4, 29.1, 28.5, 22.4, 14.1, 14.00, 13.95, 13.1; HRMS calcd for $C_{16}H_{26}O_4Na^+$ requires 305.1723, found 305.1729.

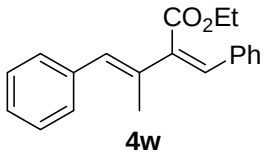
Table 2, entry 25. Following the general procedure, the reaction of allenoate **1b** (60 mg, 0.4 mmol), benzaldehyde (21 mg, 0.2 mmol) and PPh_2Me (75 μL, 0.4 mmol) was performed for 24 h.



4v

4v: 63% yield, as colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.39 (m, 2H), 7.32 (m, 3H), 6.88 (s, 1H), 5.59 (s, 1H), 4.46 (q, J = 7.1 Hz, 2H), 2.05 (s, 3H), 1.44 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 165.7, 156.8, 137.5, 135.7, 130.7, 129.5, 128.38, 128.35, 115.9, 96.6, 62.6, 14.5, 14.0; HRMS calcd for $C_{15}H_{15}NO_2Na^+$ requires 264.0995, found 264.0993.

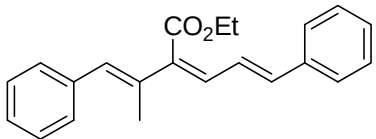
Table 2, entry 26. Following the general procedure, the reaction of allenoate **1c** (60 mg, 0.3 mmol), benzaldehyde (21 mg, 0.2 mmol) and PBu_3 (75 μL, 0.3 mmol) was performed for 24 h.



4w

4w: 91% yield, as colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.38-7.25 (m, 10H), 6.81 (s, 1H), 6.65 (s, 1H), 4.28 (d, *J* = 7.1 Hz, 2H), 2.14 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 170.1, 138.6, 137.4, 135.8, 133.6, 130.4, 129.4, 128.5, 128.4, 128.2, 128.1, 128.0, 126.9, 61.4, 15.1, 13.9; HRMS calcd for $C_{20}H_{20}O_2Na^+$ requires 315.1355, found 315.1357.

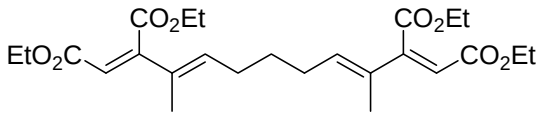
Table 2, entry 27. Following the general procedure, the reaction of allenoate **1d** (68 mg, 0.3 mmol), benzaldehyde (21 mg, 0.2 mmol) and PBu_3 (75 μL, 0.3 mmol) was performed for 4 h.



4x

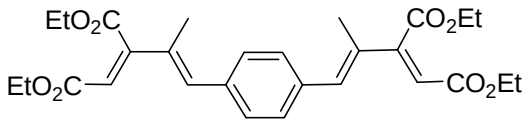
4x: 79% yield, as yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.44 (d, *J* = 7.7 Hz, 2H), 7.37-7.24 (m, 8H), 7.08 (dd, *J* = 15.4, 11.3 Hz, 1H), 6.78 (d, *J* = 15.4 Hz, 1H), 6.63 (d, *J* = 11.3 Hz, 1H), 6.58 (s, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 2.10 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 169.0, 138.3, 137.5, 137.0, 136.8, 133.9, 130.8, 130.2, 129.3, 128.7, 128.3, 128.1, 126.9, 126.1, 125.1, 61.1, 15.5, 14.4; HRMS calcd for $C_{22}H_{22}O_2Na^+$ requires 341.1512, found 341.1517.

Scheme 2. Following the general procedure, the reaction of allenoate **1a** (120 mg, 0.6 mmol), the dialdehyde (0.2 mmol) and PBu_3 (150 μL, 0.6 mmol) was performed for 24 h.



5a

5a: 52% yield from glutaraldehyde, as colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 5.82 (s, 2H), 5.78 (t, *J* = 7.2 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 4H), 4.19 (q, *J* = 7.1 Hz, 4H), 2.22 (q, *J* = 7.3 Hz, 4H), 1.81 (s, 6H), 1.55 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 6H), 1.28 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 168.4, 165.4, 151.4, 138.3, 131.1, 114.6, 61.5, 60.6, 28.5, 28.0, 14.2, 14.0, 13.2; HRMS calcd for $C_{25}H_{36}O_8Na^+$ requires 487.2302, found 487.2305.

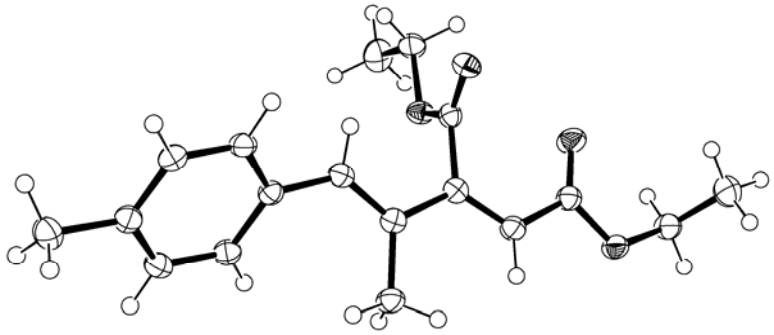


5b

5b: 61% yield from terephthalic aldehyde, as a white solid, mp 93-94 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.31 (s, 4H), 6.76 (s, 2H), 6.02 (s, 2H), 4.44 (q, *J* = 7.2 Hz, 4H), 4.23 (q, *J* = 7.1 Hz, 4H), 2.09 (s, 6H), 1.40 (t, *J* = 7.2 Hz, 6H), 1.31 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 168.3, 165.2, 151.6, 136.0, 135.7, 132.4, 129.5, 116.5, 61.8, 60.8, 14.8, 14.2, 14.0; HRMS calcd for $C_{28}H_{34}O_8Na^+$ requires 499.2326, found 499.2327.

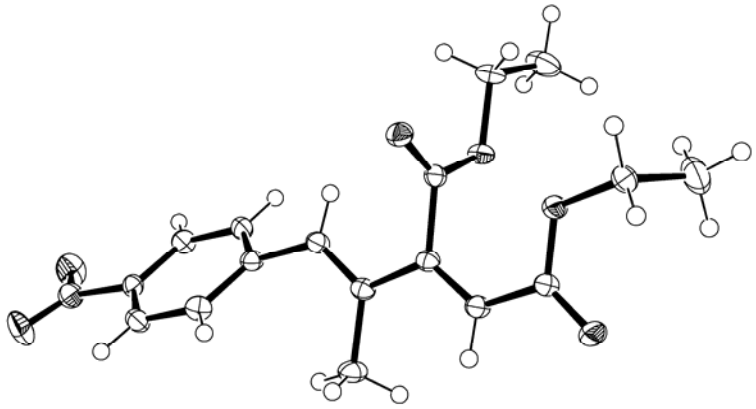
V. X-ray Crystallographic Data for 4b and 4k

Table 1. Crystal Data and Structure Refinement for Diene **4b**



Identification code	**4b**
Empirical formula	$C_{18}H_{22}O_4$
Formula weight	302.36
Temperature	113(2) K
Wavelength	1.54187 Å
Crystal system	Monoclinic
Space group	P 1 21/n 1
Unit cell dimensions	a = 14.985(3) Å, α = 90° b = 7.5030(14) Å, β = 108.888(11)° c = 15.386(3) Å, γ = 90°
Volume	1636.7(6) $Å^3$
Z	4
Calculated density	1.227 Mg/m^3
Absorption coefficient	0.696 mm^{-1}
F(000)	648
Crystal size	0.36 x 0.34 x 0.26 mm^3
θ range for data collection	3.58 to 72.64°
Limiting indices	-18<=h<=18, -8<=k<=9, -16<=l<=19
Reflections collected	16873
Independent reflections	3188 [R(int) = 0.0597]
Completeness to θ = 25.02°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8397 and 0.7877
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3188 / 0 / 204
Goodness-of-fit on F^2	1.121
Final R indices [I>2σ(I)]	R1 = 0.0523, wR2 = 0.1324
R indices (all data)	R1 = 0.0569, wR2 = 0.1479
Extinction coefficient	0.034(2)
Largest diff. peak and hole	0.364 and -0.464 e. $Å^{-3}$

Table 2. Crystal Data and Structure Refinement for Diene **4k**

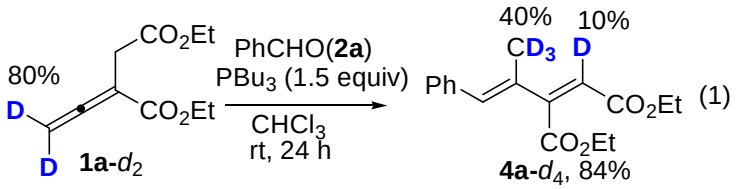


Identification code	**4k**
Empirical formula	$C_{17}H_{19}NO_6$
Formula weight	333.33
Temperature	113(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 8.8667(18) Å, α = 105.71(3)° b = 9.0480(18) Å, β = 98.61(3)° c = 11.101(2) Å, γ = 96.29(3)°
Volume	837.1(3) $Å^3$
Z	2
Calculated density	1.323 Mg/m^3
Absorption coefficient	0.101 mm^{-1}
F(000)	352
Crystal size	0.20 x 0.18 x 0.12 mm^3
θ range for data collection	2.35 to 27.88°
Limiting indices	-11<=h<=11, -11<=k<=11, -14<=l<=14
Reflections collected	10609
Independent reflections	3981 [R(int) = 0.0745]
Completeness to θ = 25.02°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9880 and 0.9801
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3981 / 0 / 221
Goodness-of-fit on F^2	0.613
Final R indices [I>2σ(I)]	R1 = 0.0618, wR2 = 0.1422
R indices (all data)	R1 = 0.0852, wR2 = .1508
Extinction coefficient	1.79(5)
Largest diff. peak and hole	0.721 and -0.432 e. $Å^{-3}$

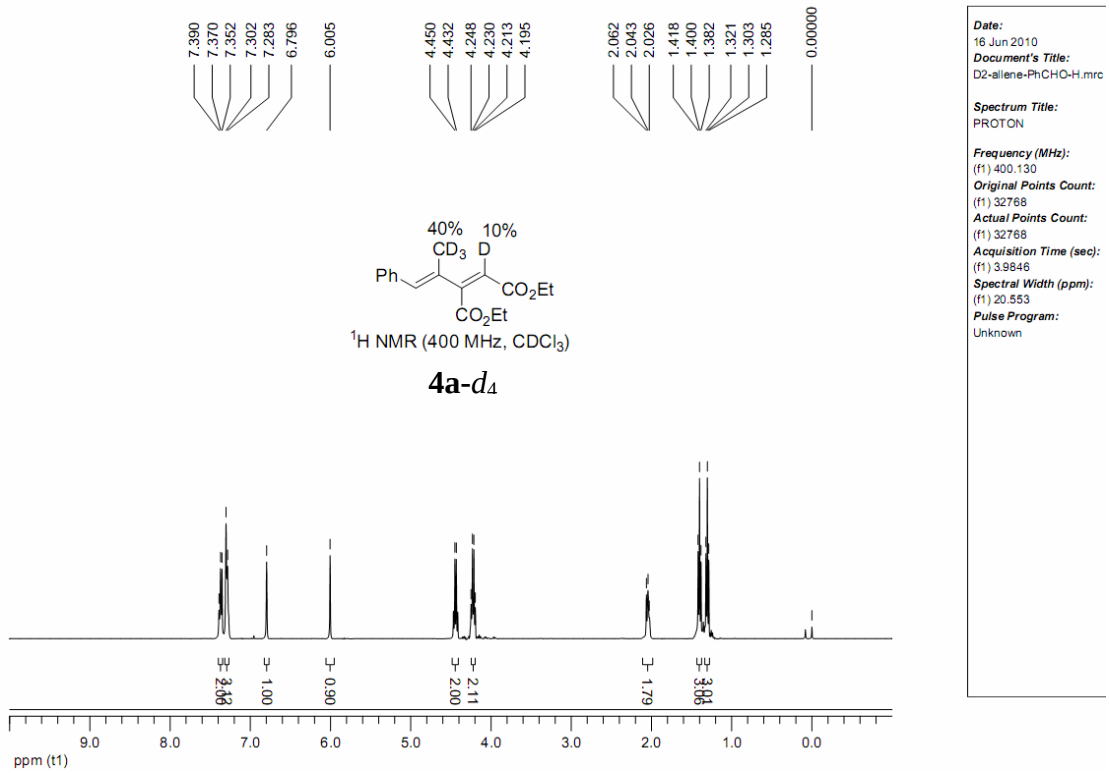
VI. Mechanistic Study

Deuterium-labeling experiments

(a) Following the general procedure, deuterated allenoate **1a**-d_2[6] (80% D, 60 mg, 0.3 mmol) was reacted with benzaldehyde **2a** (21 mg, 0.2 mmol) and Bu_3P (75μL, 0.3 mmol) for 24 h. Deuterated diene **4a**-d_4 were obtained in 84% yield with deuterium incorporations as shown in eq 1.

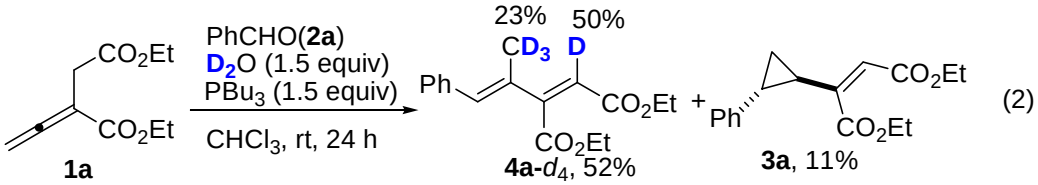


4a-d_4: 84% yield, as colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.37 (m, 2H), 7.29 (m, 3H), 6.80 (s, 1H), 6.01 (s, 0.90H), 4.44 (q, J = 7.2 Hz, 2H), 4.22 (q, J = 7.1 Hz, 2H), 2.04 (m, 1.79H), 1.40 (t, J = 7.2 Hz, 3H), 1.30 (t, J = 7.1 Hz, 3H).



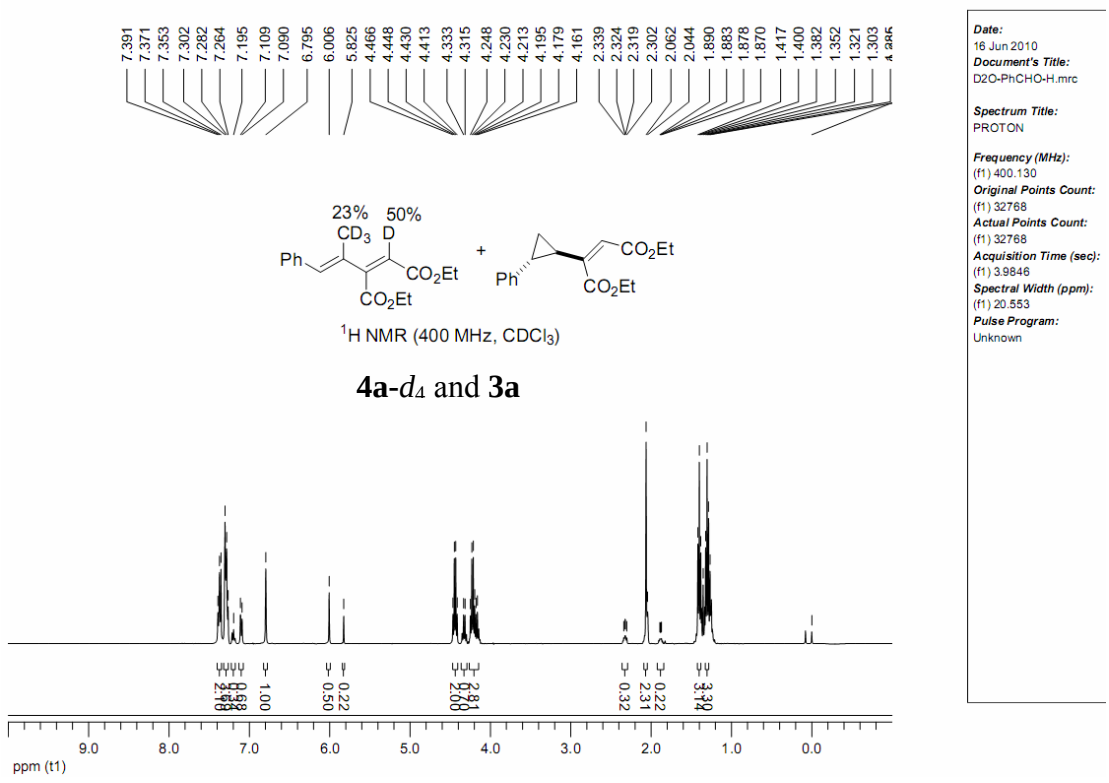
[6] Preparation of deuterated allenoate **1a**- d_2 (80% D) was reported: Xu, S.; Zhou, L.; Ma, R.; Song, H.; He, Z. *Org. Lett.* **2010**, *12*, 544-547.

(b) At room temperature and under nitrogen atmosphere, to a stirred solution of allenoate **1a** (60 mg, 0.3 mmol), benzaldehyde **2a** (21 mg, 0.2 mmol) and D_2O (6 mg, 0.3 mmol) in anhydrous $CHCl_3$ (5 mL) was added Bu_3P (75 μL, 0.3 mmol) by the means of microsyringe. The resulting mixture was further stirred for 24 h. After removal of solvent on a rotary evaporator, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 20:1–5:1) to afford an inseparable mixture of diene **4a**-d_4 (52% yield) and cyclopropane **3a**(11% yield), with deuterium incorporations shown in eq 2.

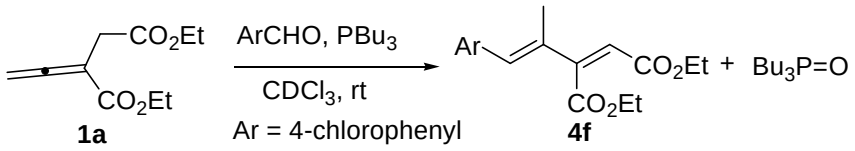


(2)

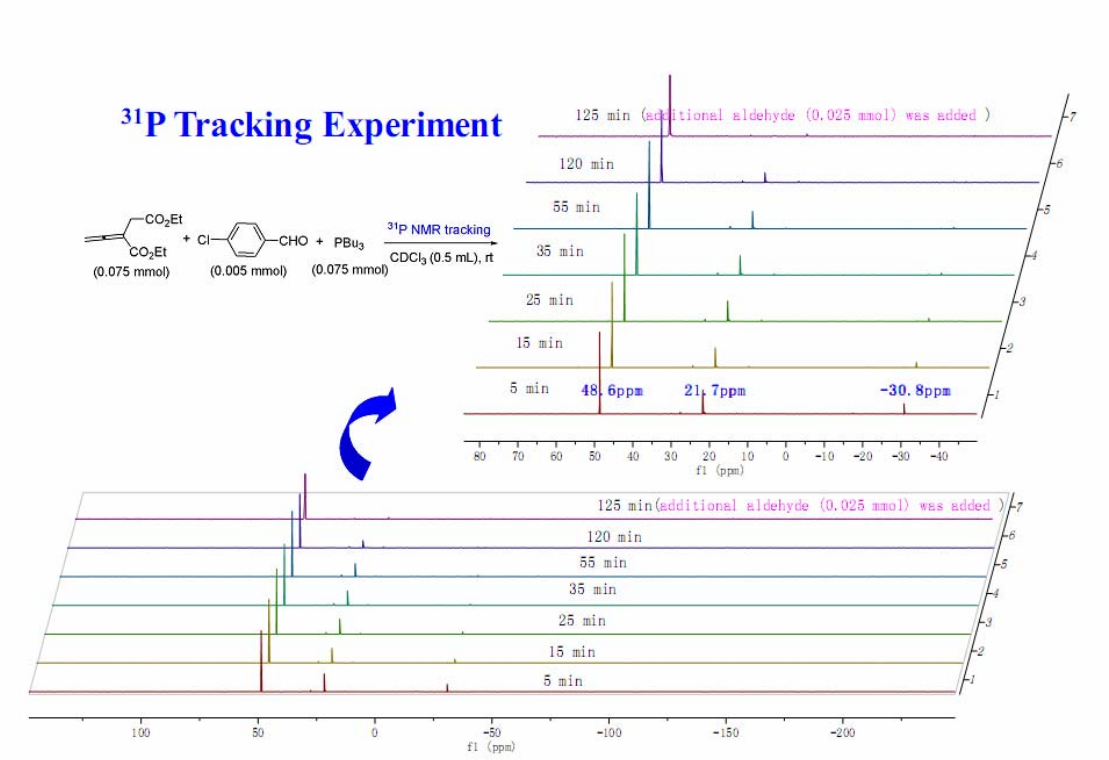
4a-d_4: 52% yield (obtained in 63% combined yield as a mixture with a small amount of cyclopropane **3a**), as colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 7.37 (m, 2H), 7.29 (m, 3H), 6.80 (s, 1H), 6.01 (s, 0.50H), 4.44 (q, J = 7.2 Hz, 2H), 4.22 (q, J = 7.1 Hz, 2H), 2.06 (m, 2.31 H), 1.40 (t, J = 7.2 Hz, 3H), 1.30 (t, J = 7.1 Hz, 3H).



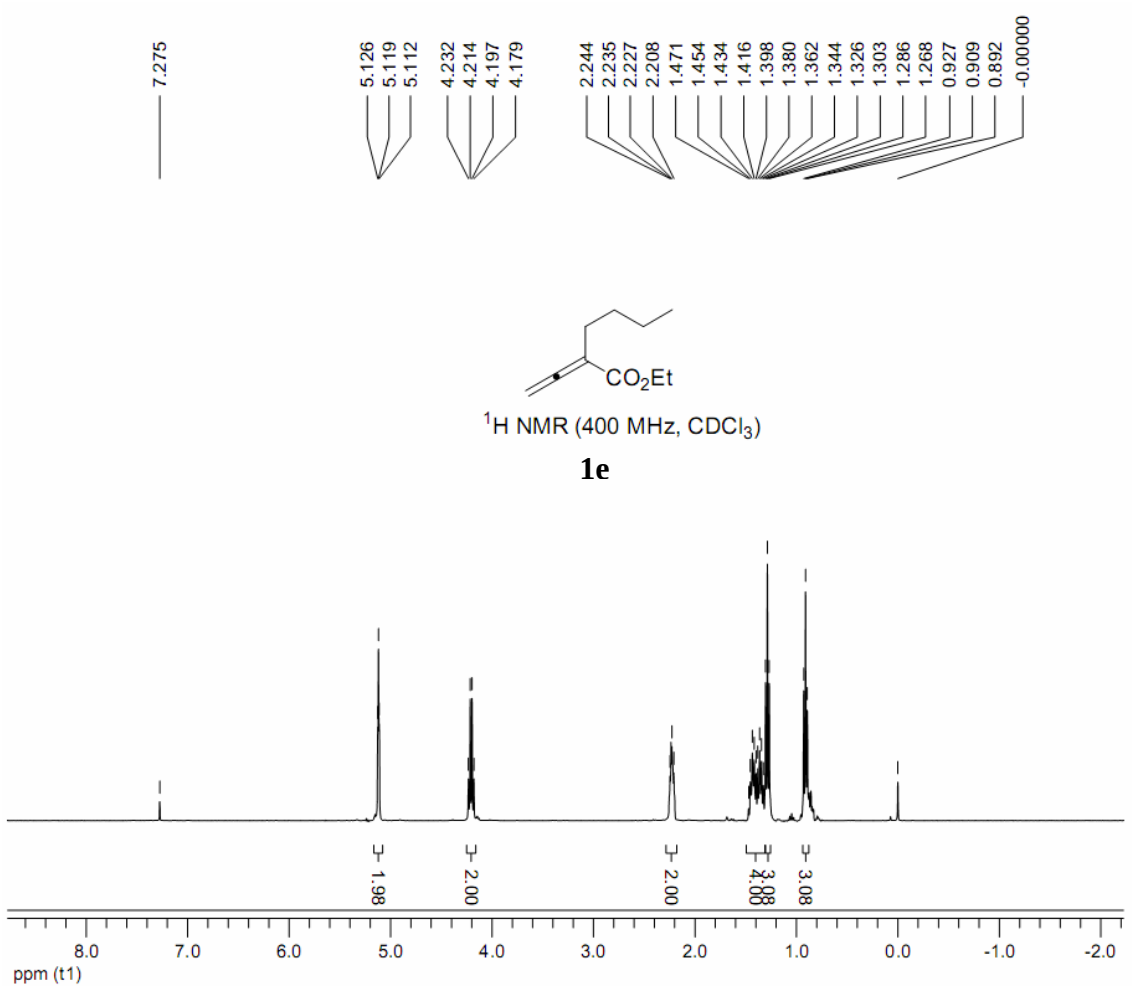
^{31}P NMR Tracking Experiment



To a solution of allenoate **1a** (15 mg, 0.075 mmol) and 4-chlorobenzaldehyde (7 mg, 0.05 mmol) in $CDCl_3$ (0.5 mL) in a N_2-filled NMR tube was added PBu_3 (19 μL, 0.075 mmol) by the means of microsyringe. The resulting mixture was shaken up and applied to ^{31}P NMR tracking. At the early stage, the sample was scanned at 10 min interval. An appreciable signal at δ 21.7 ppm emerged along with signals at δ 48.6 and δ -30.8 ppm which correspond to Bu_3PO and PBu_3, respectively. The signal at δ 21.7 ppm diappeared within 5 min upon addition of more 4-chlorobenzaldehyde (3 mg, 0.025 mmol) into the sample.



VII. ^{1}H and ^{13}C NMR Spectra of 1e, 3, 4 and 5



Date:
16 Jun 2010
Document's Title:
abutyl-allene-H.mrc

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Actual Points Count:
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Acquisition Time (sec):
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Spectral Width (ppm):
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Pulse Program:
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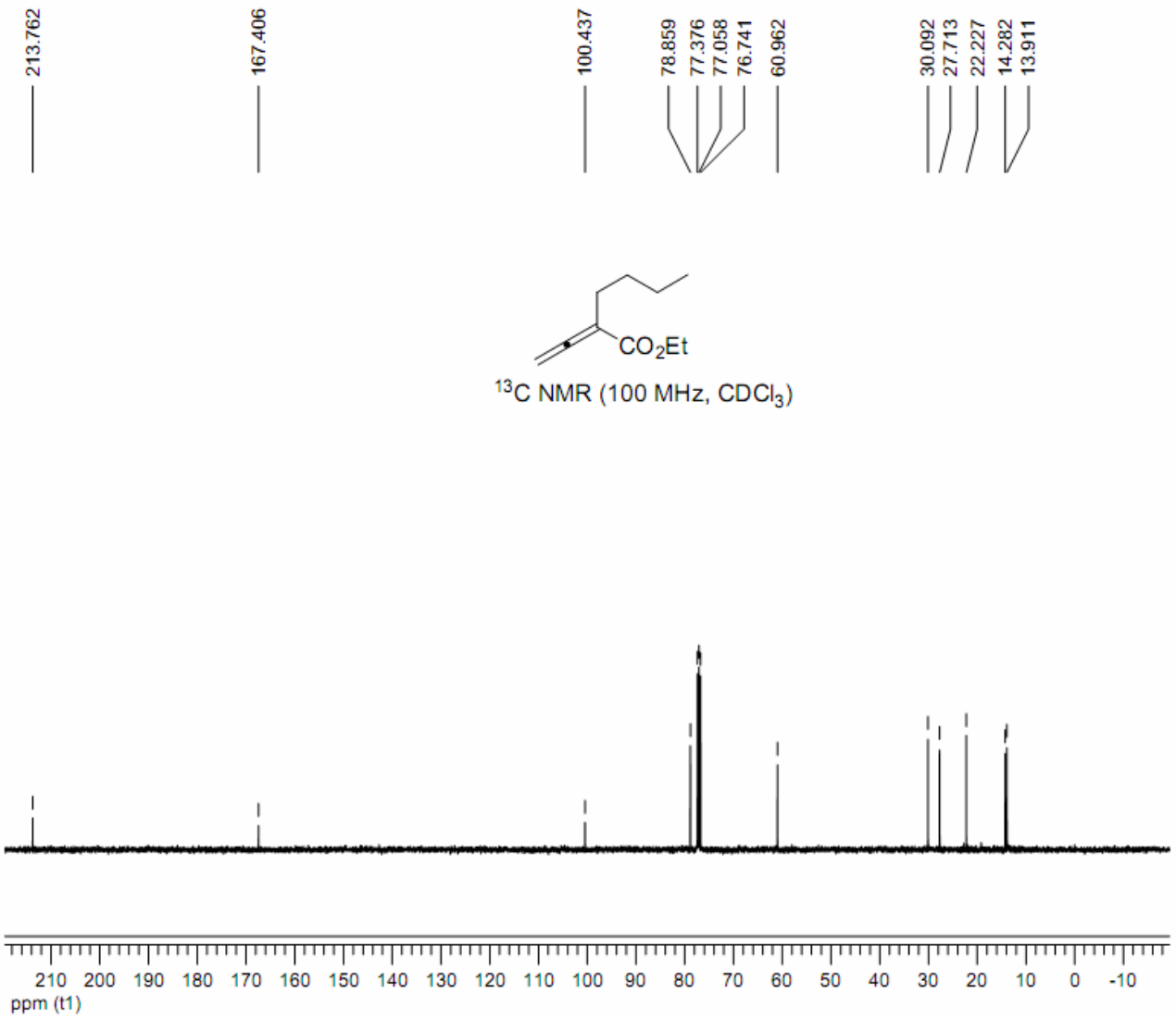

Date:
16 Jun 2010
Document's Title:
abutyl-allene-C.mrc

Spectrum Title:
C13CPD

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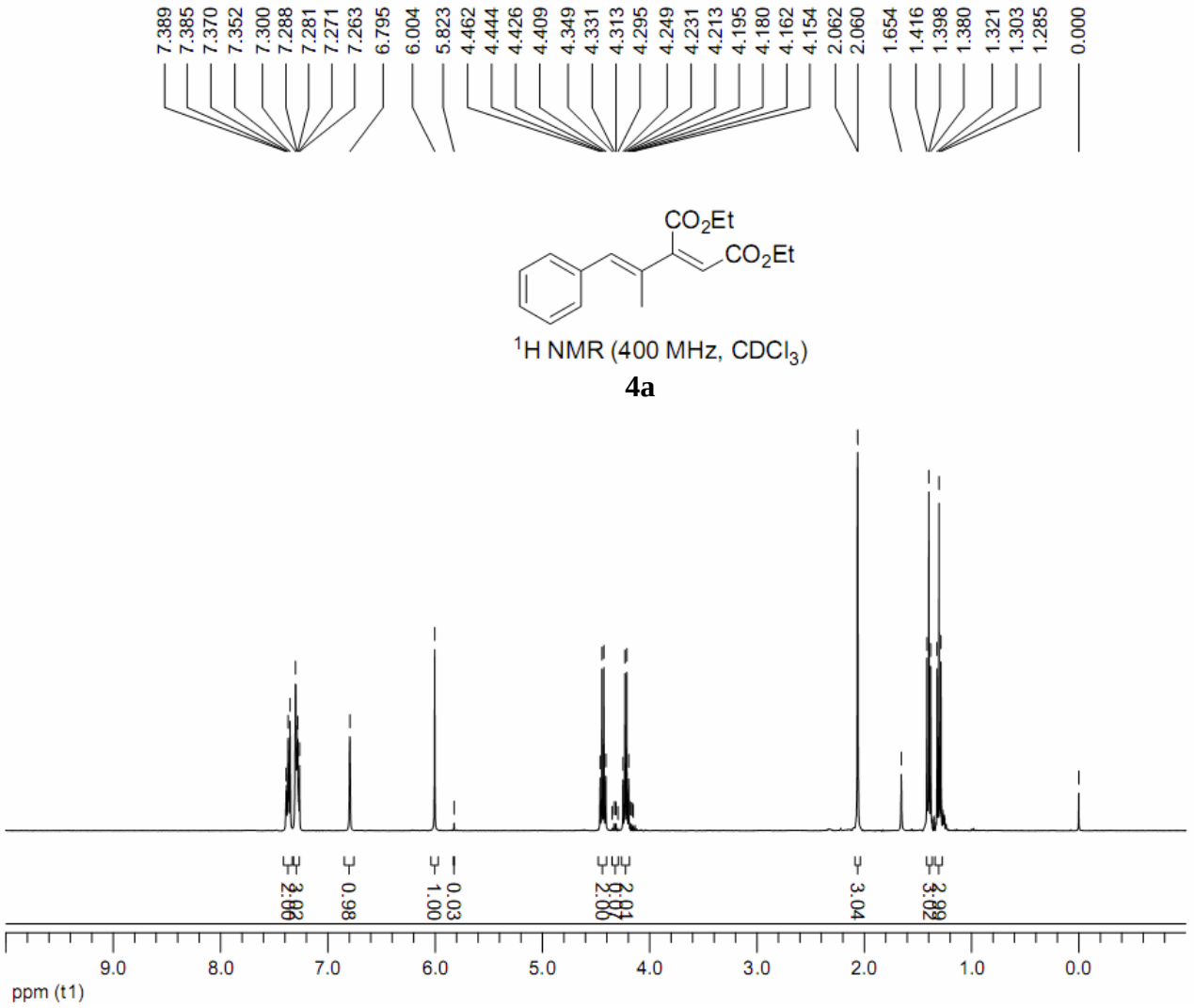

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15 Jun 2010
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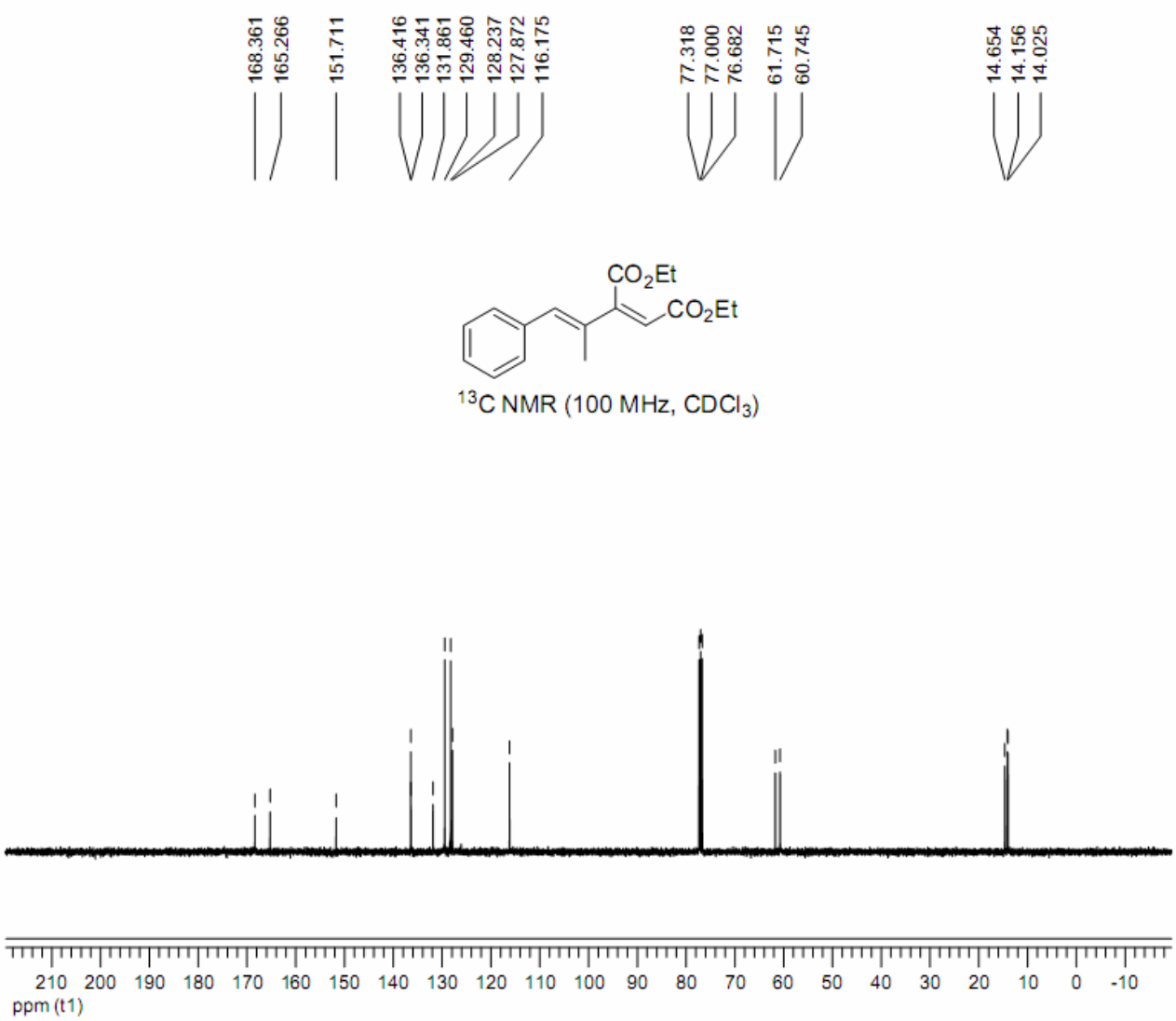

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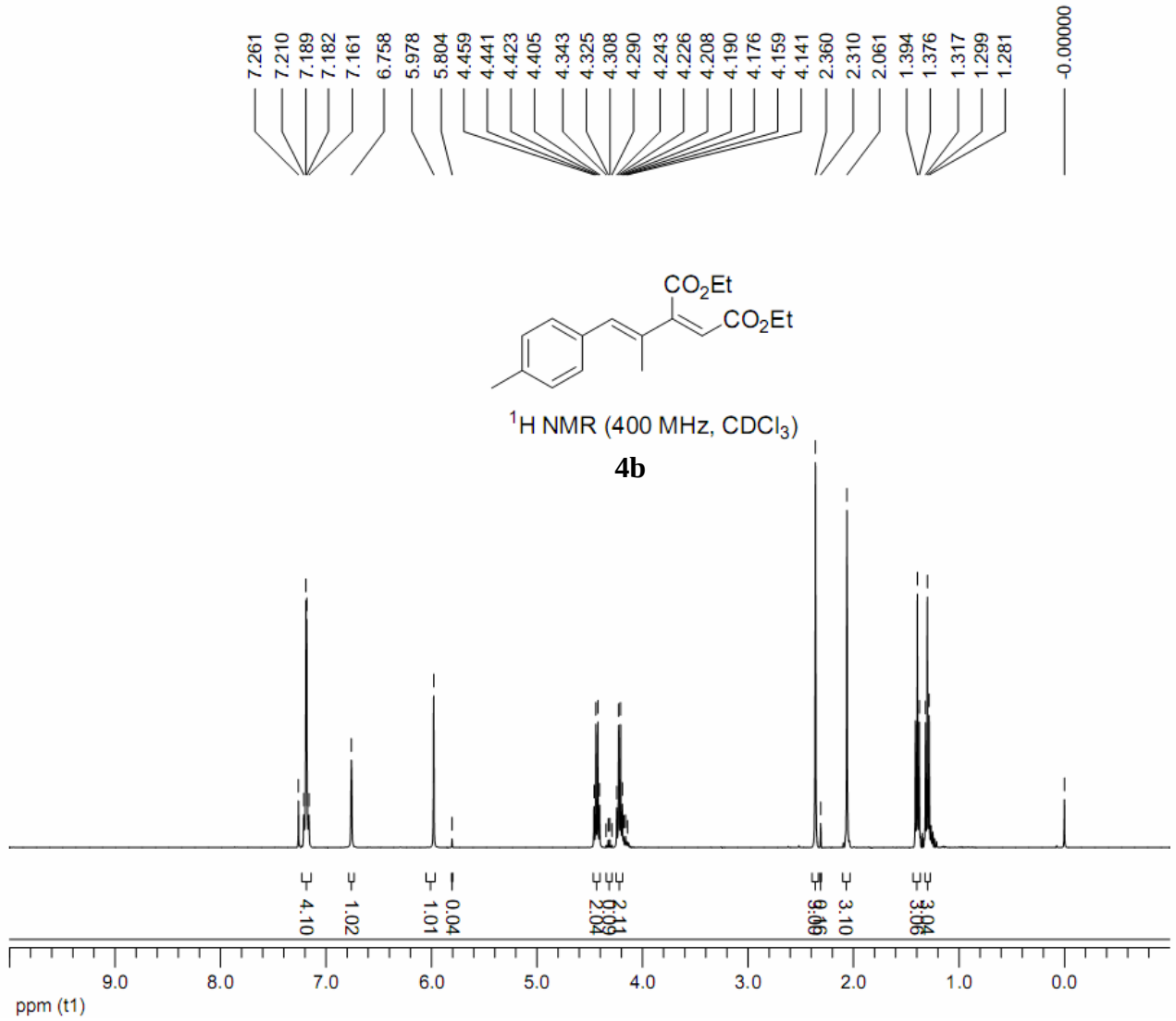

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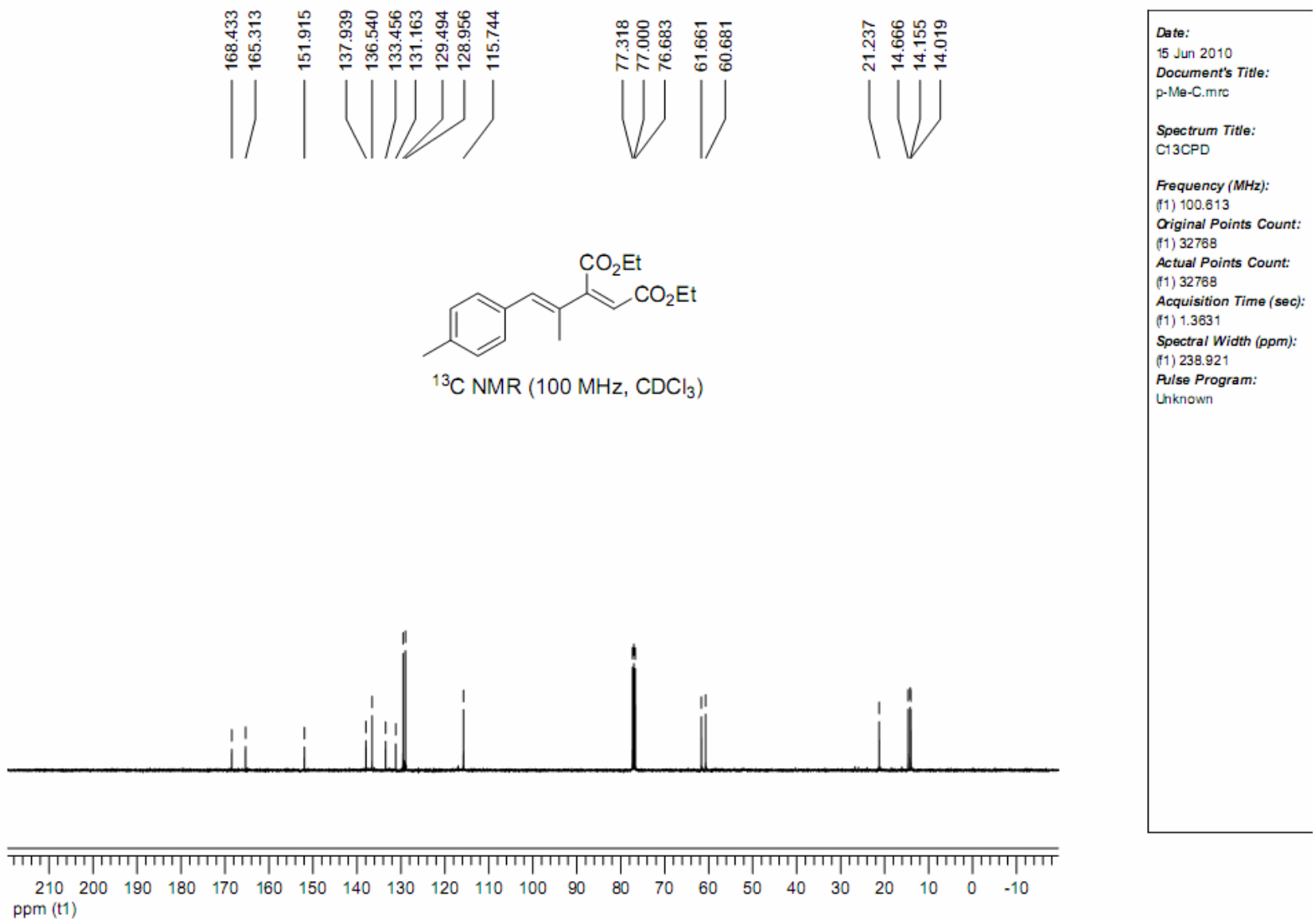

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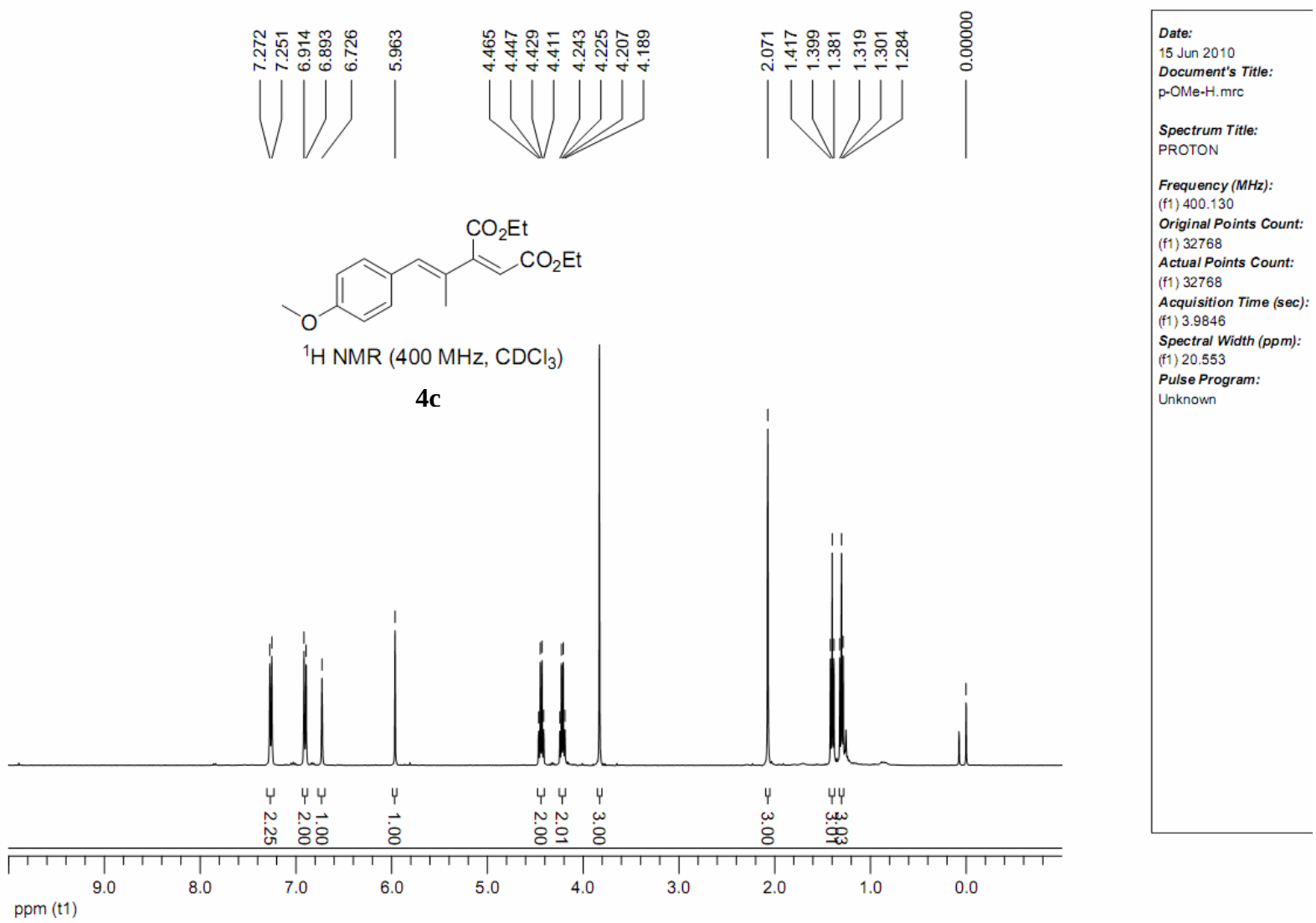

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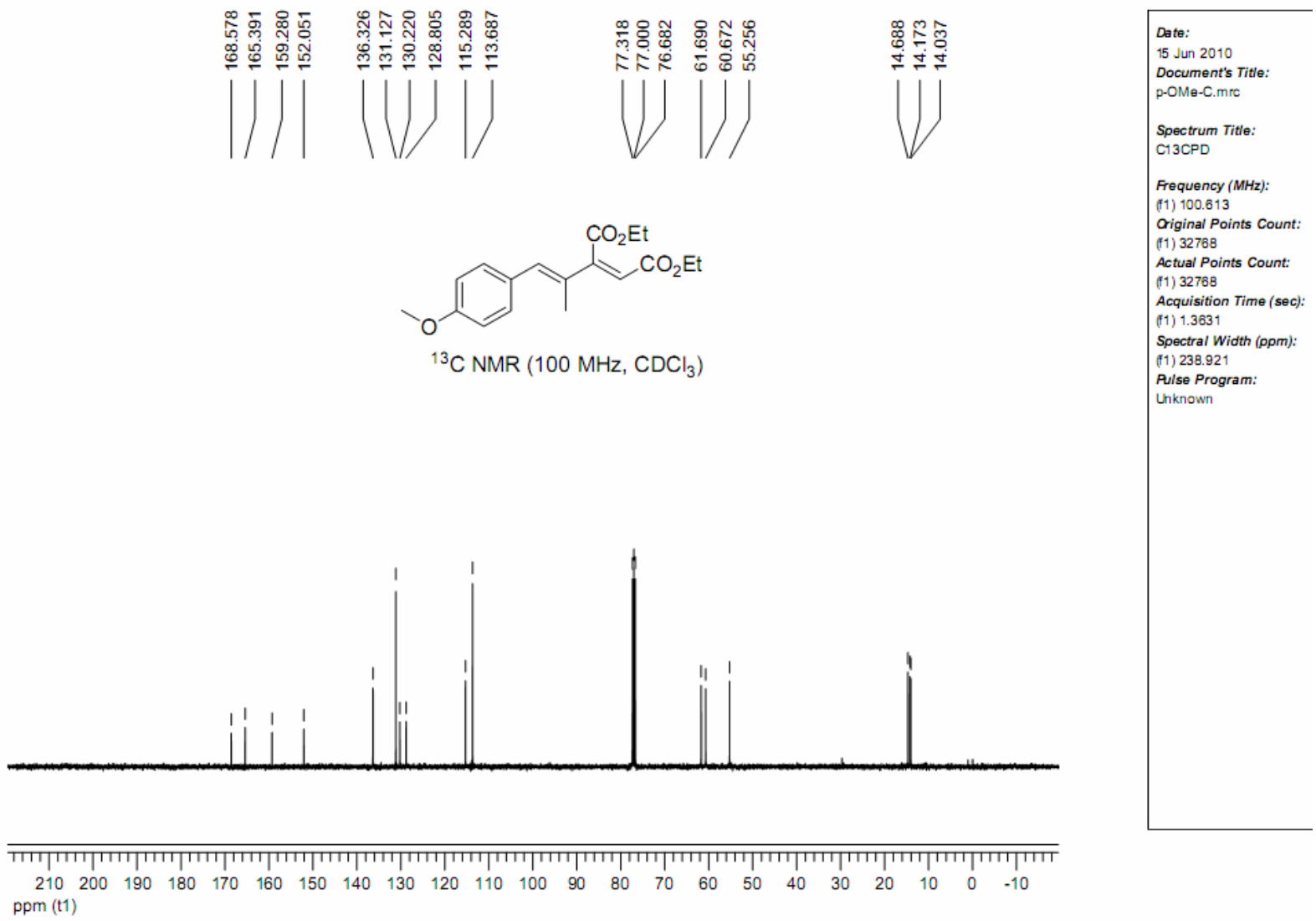

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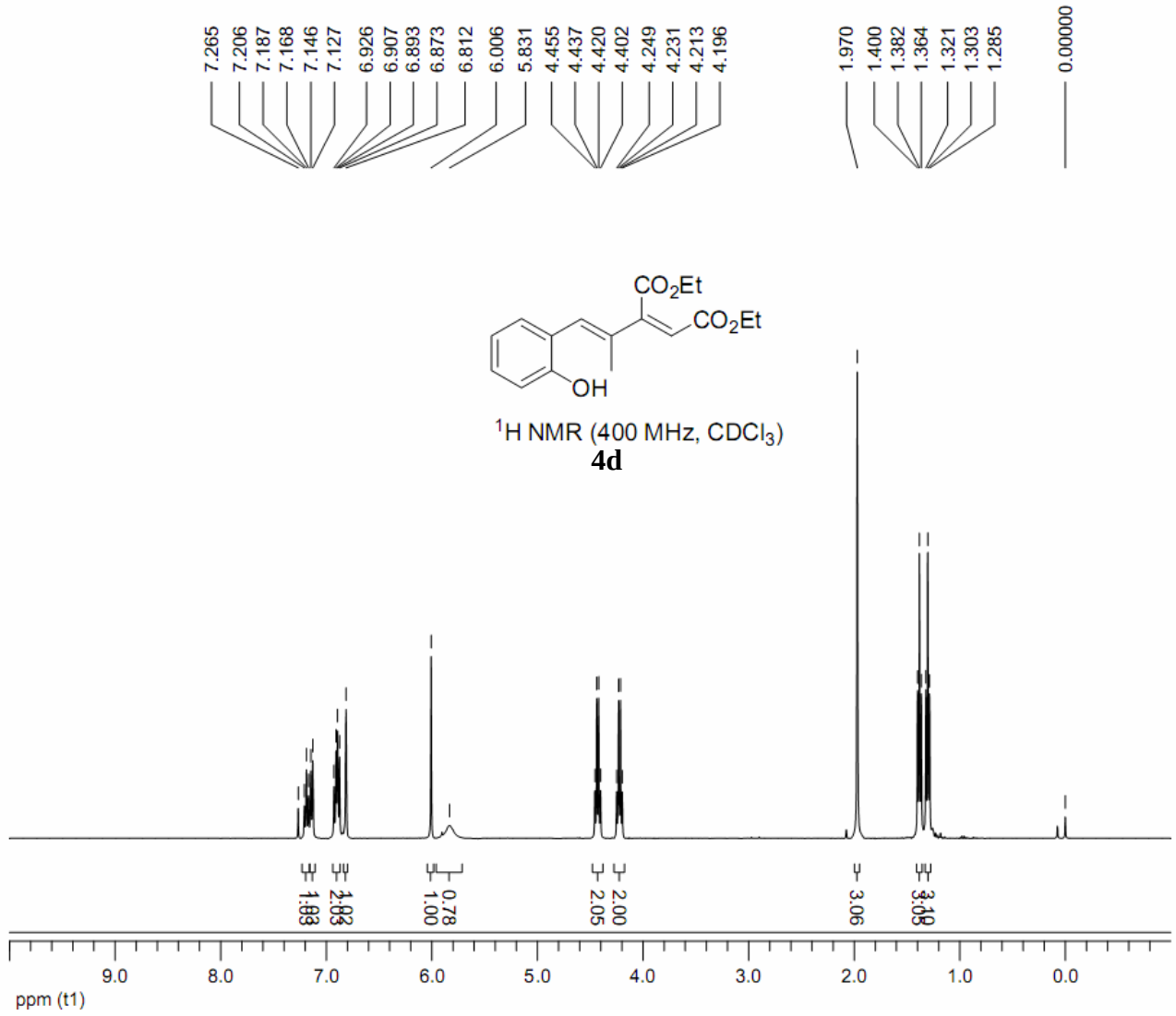

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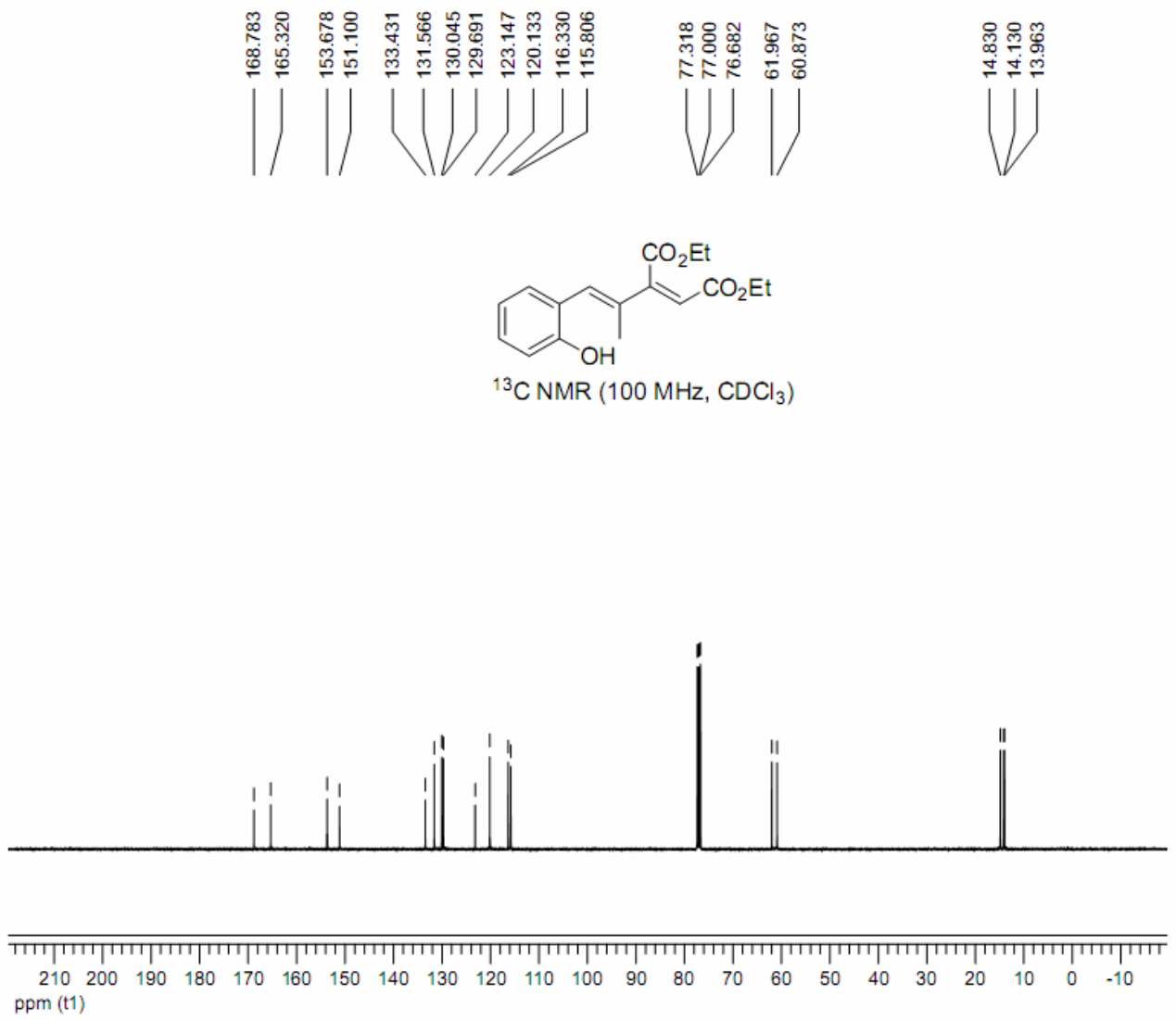

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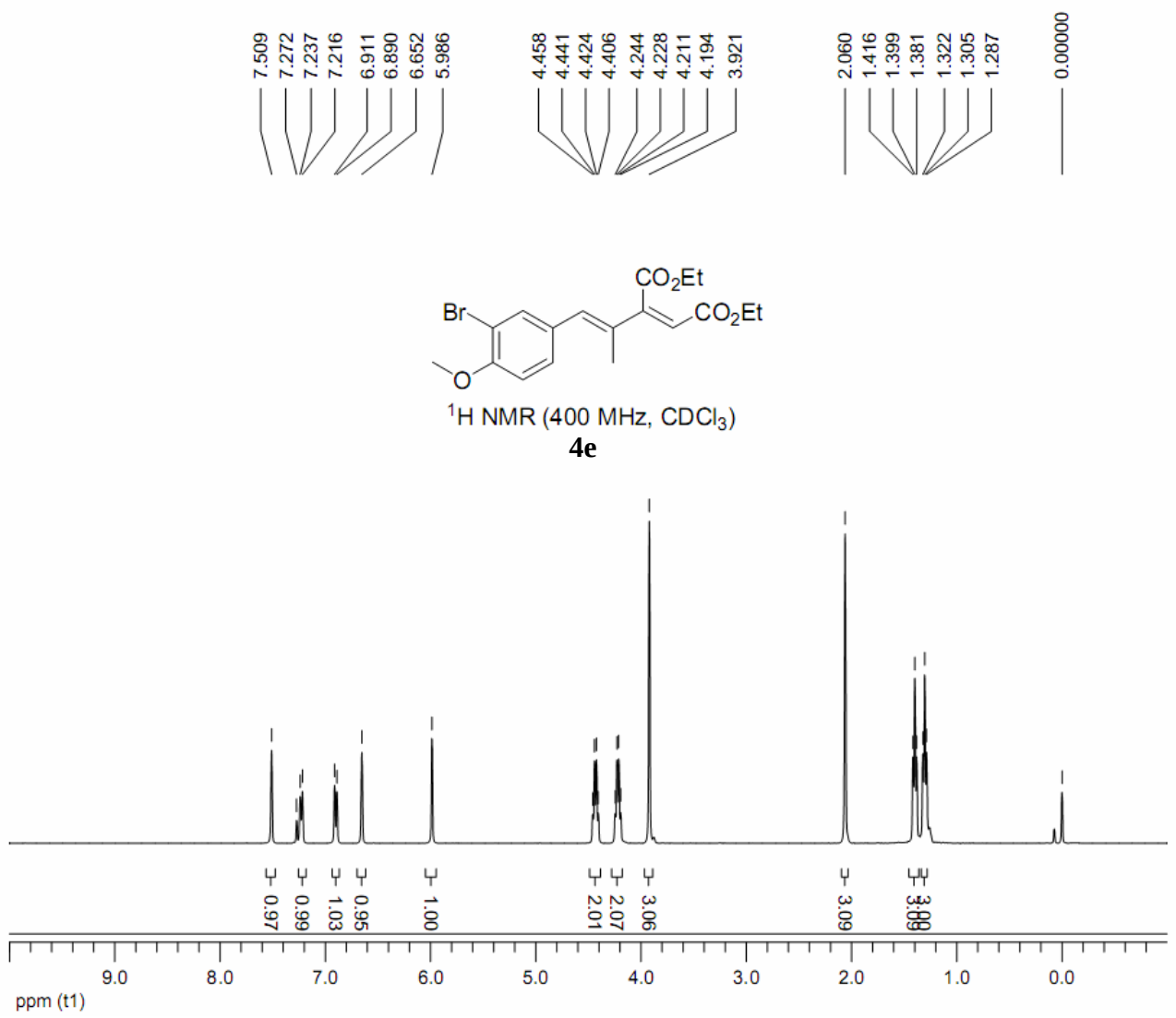

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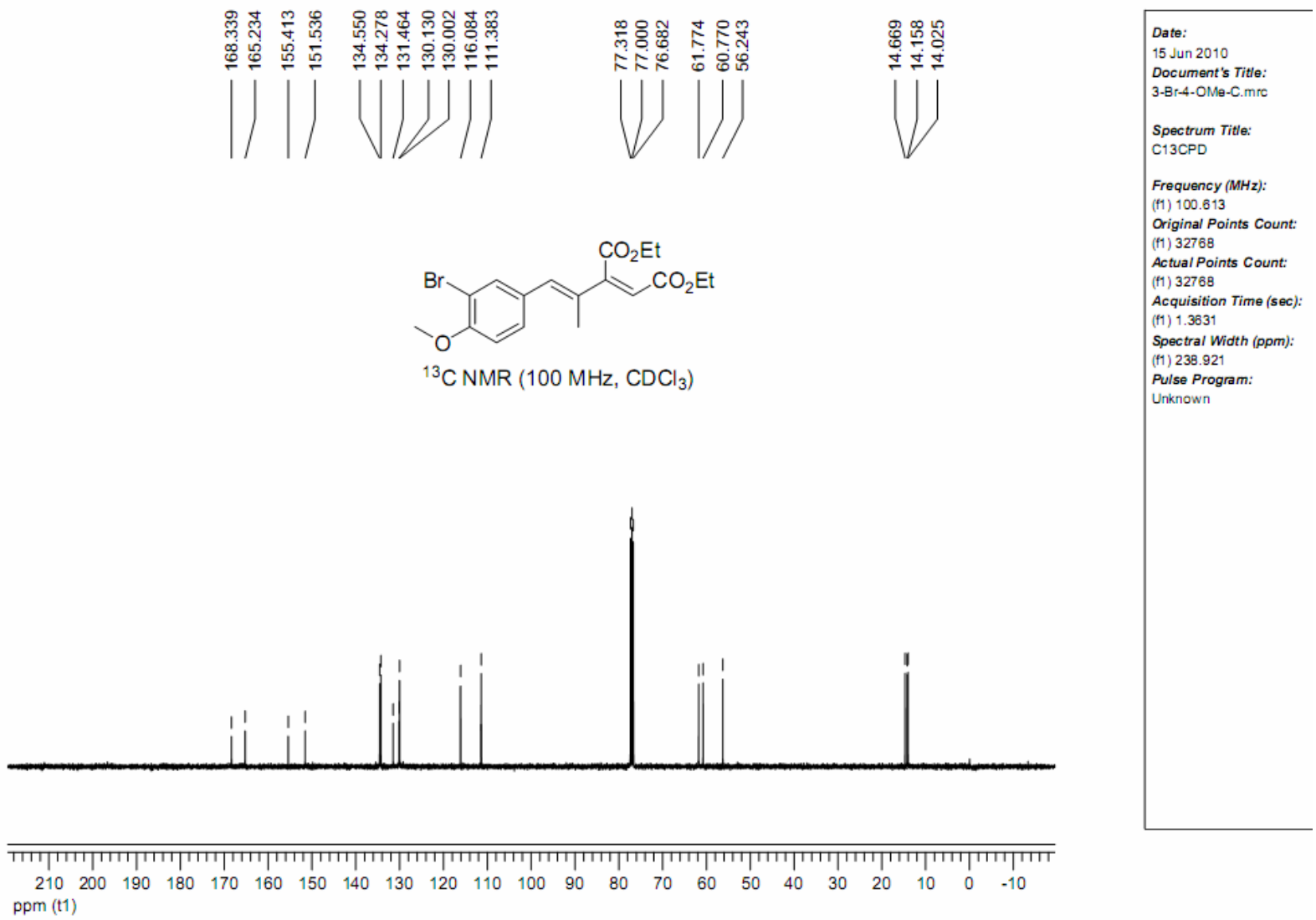

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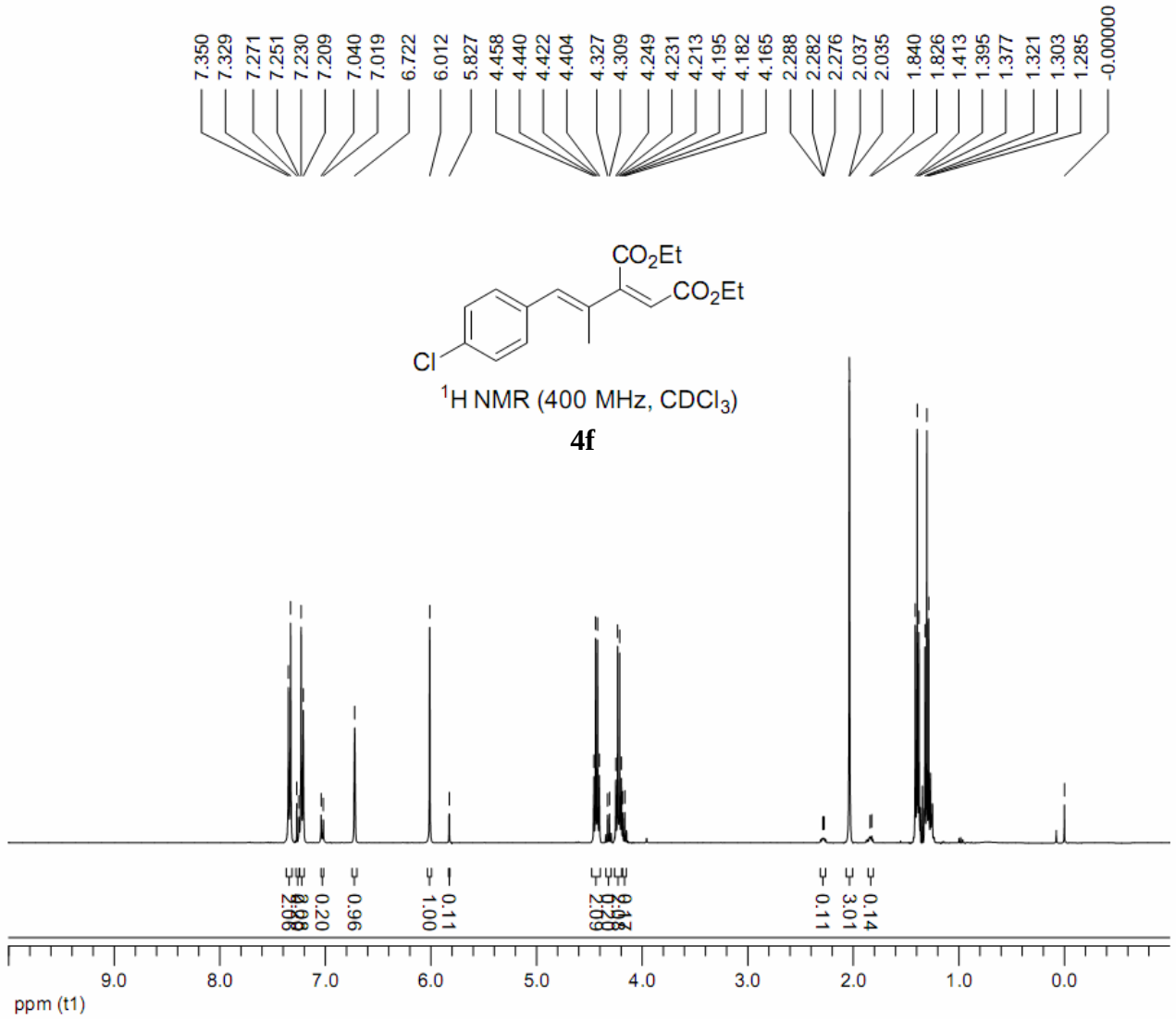

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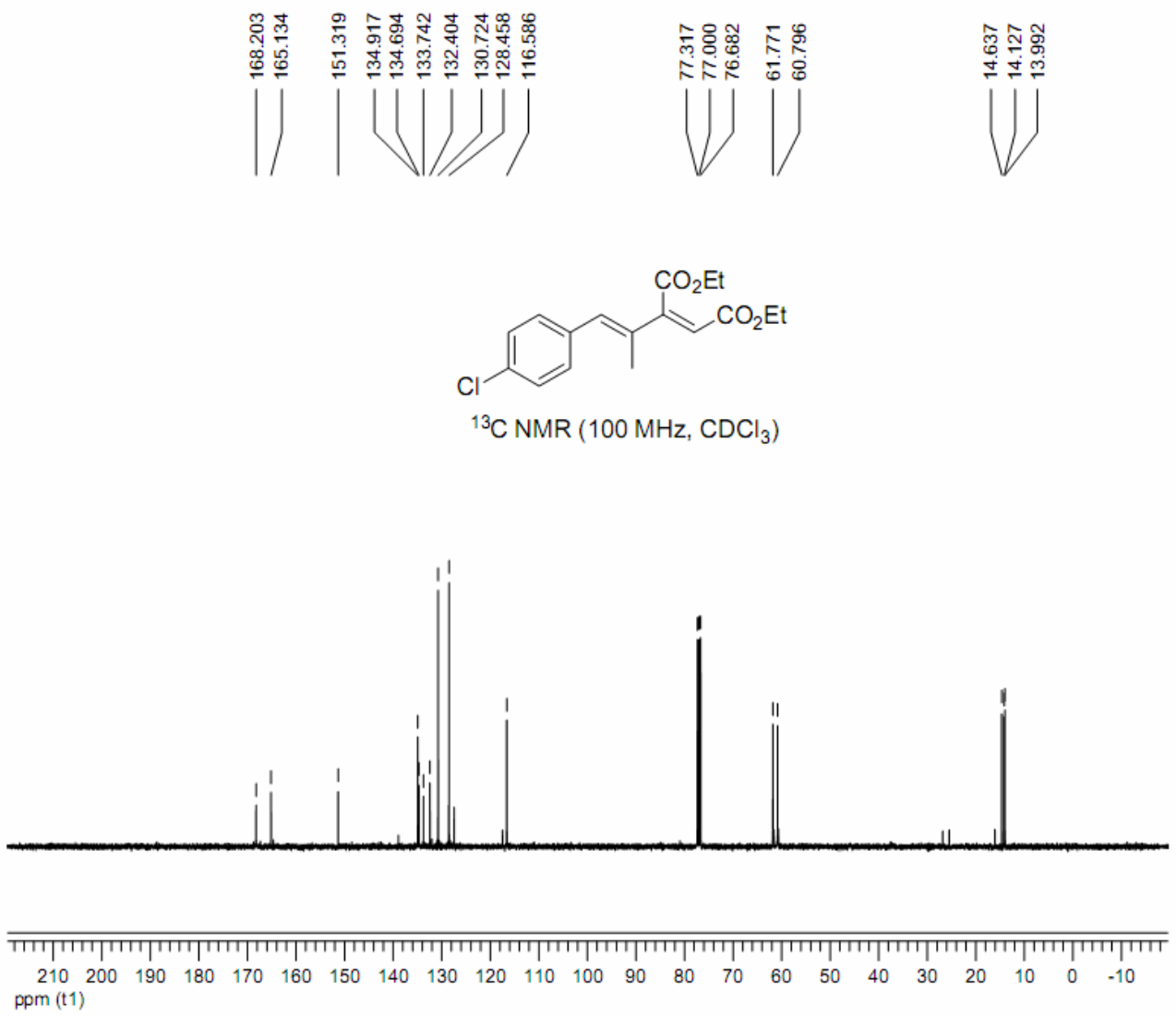

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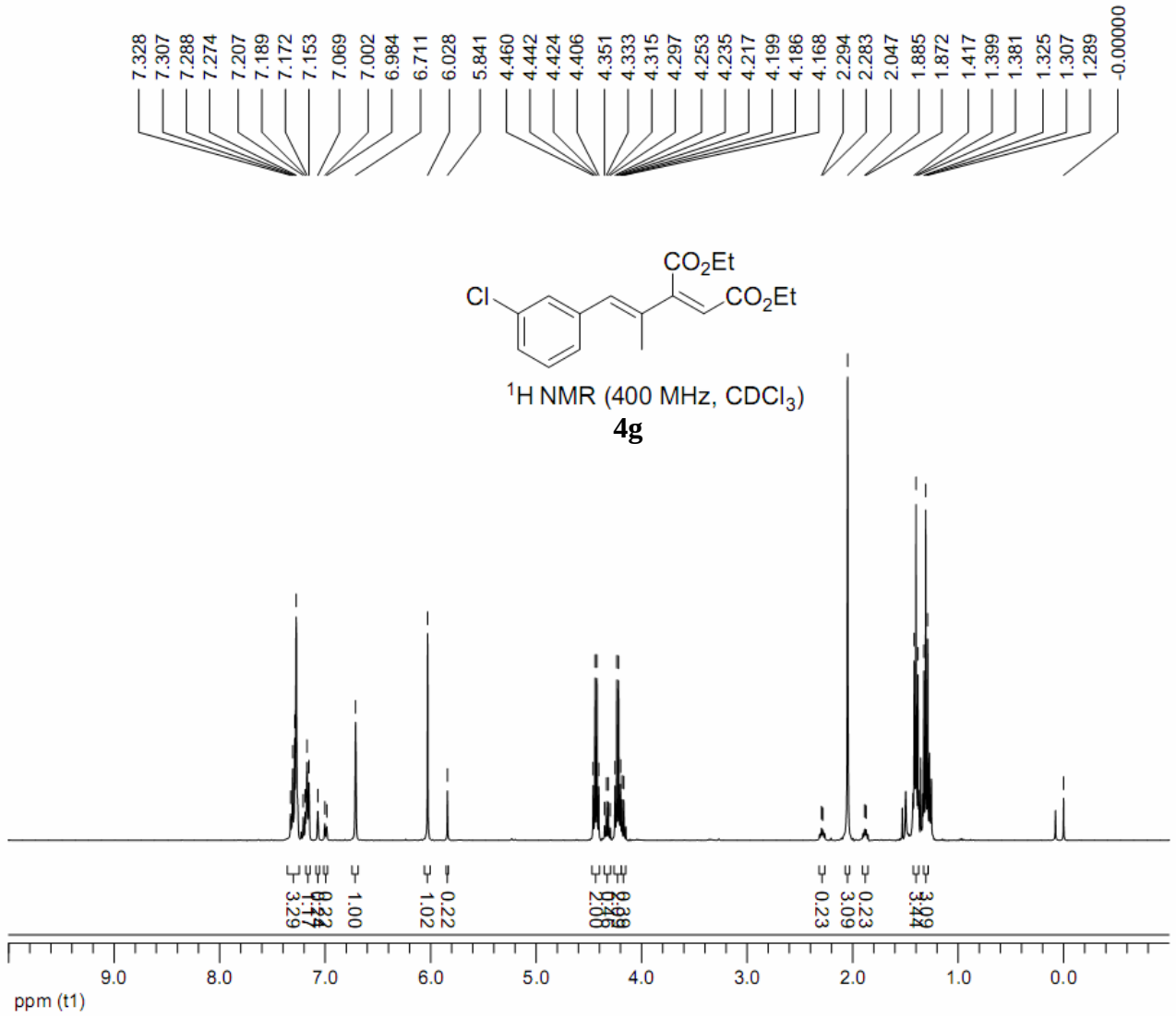

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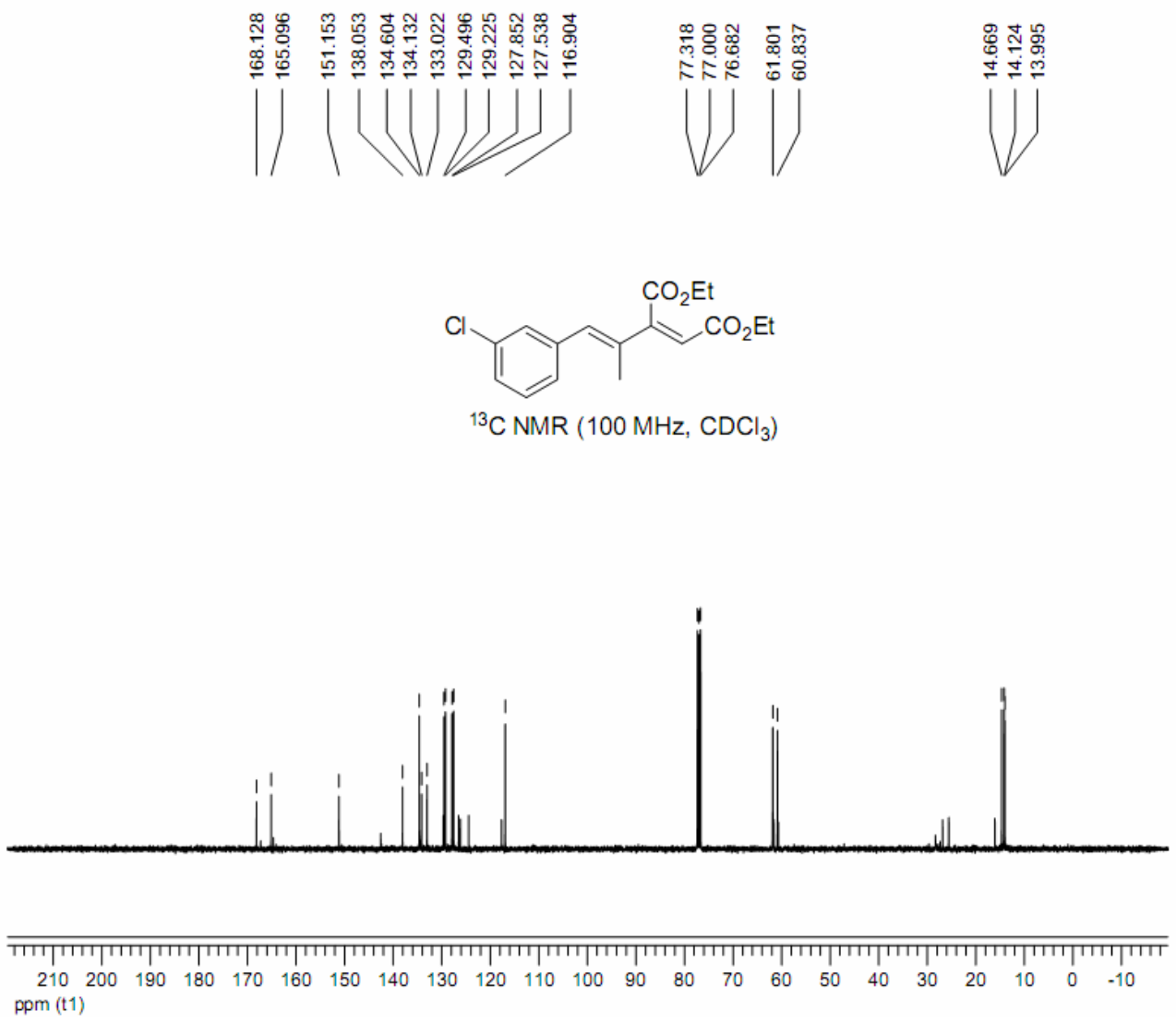

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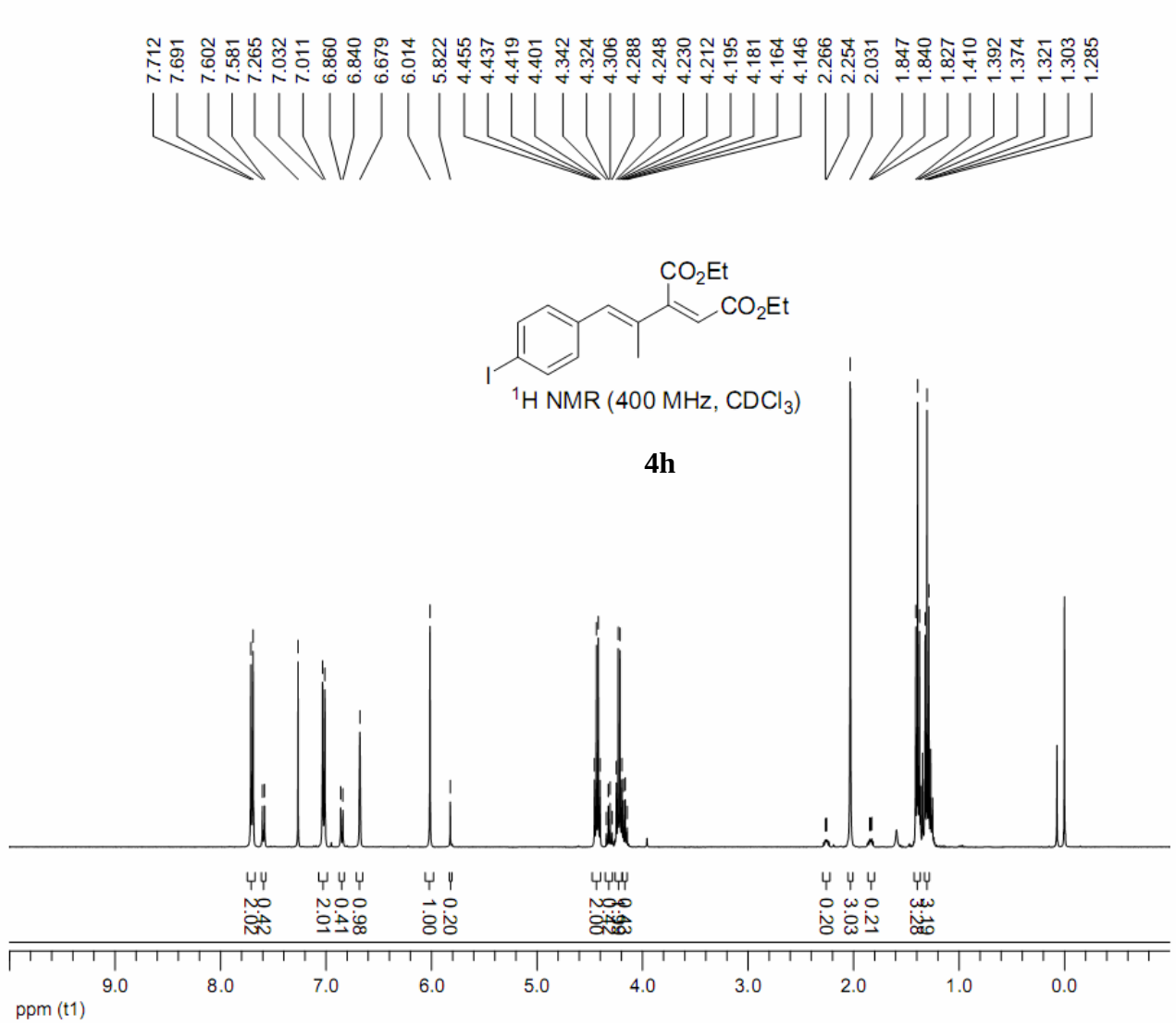

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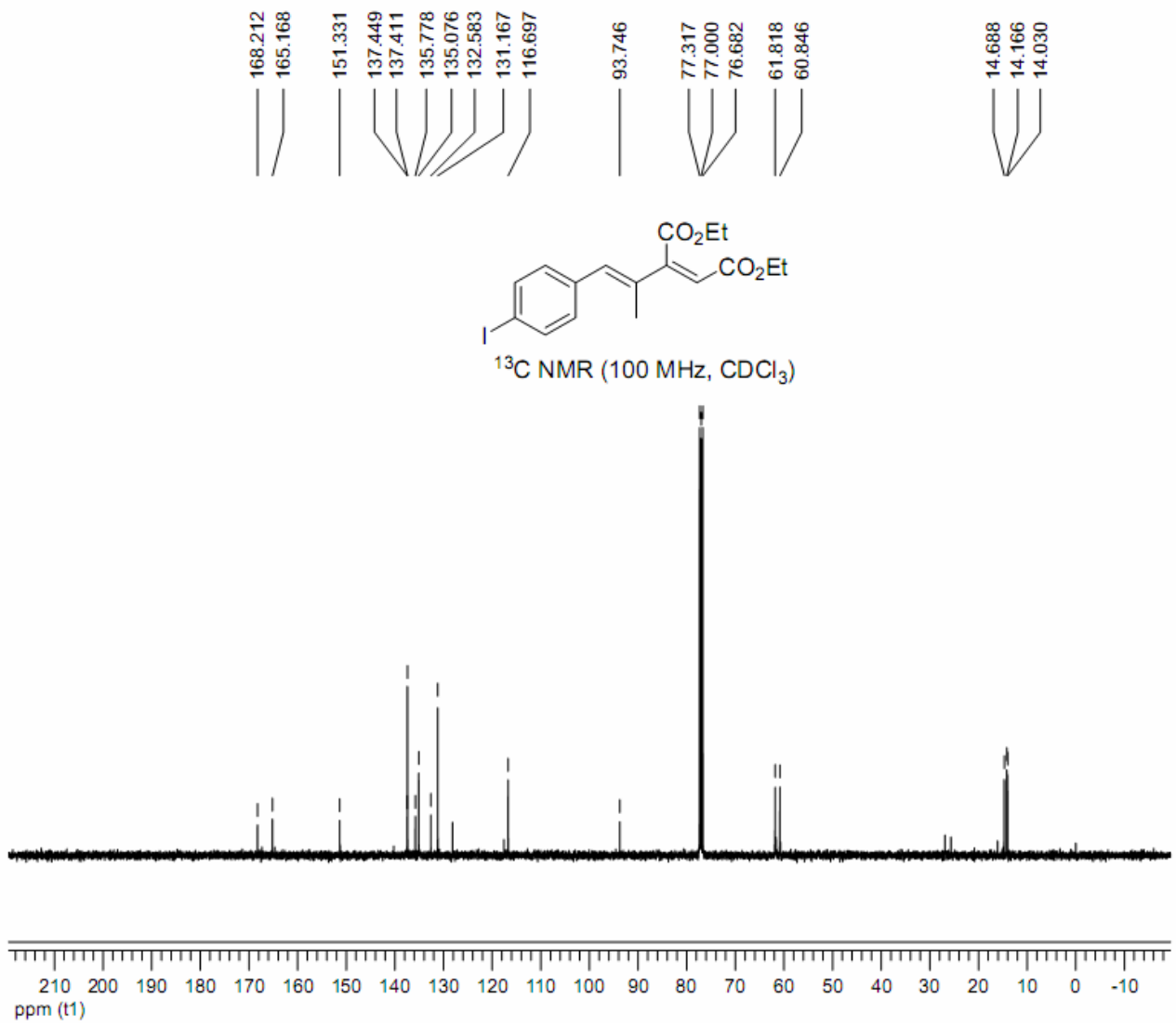

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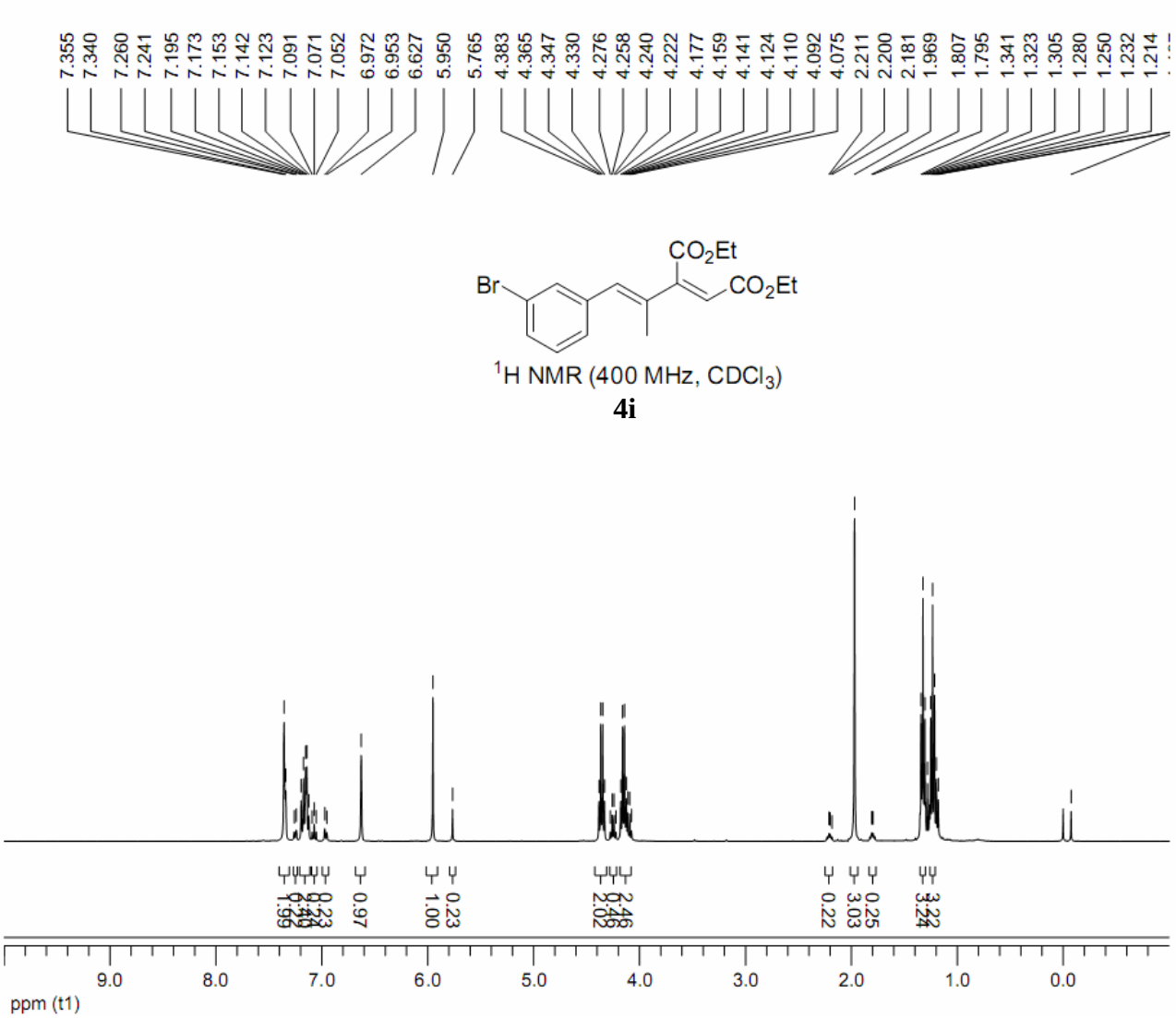

Date:
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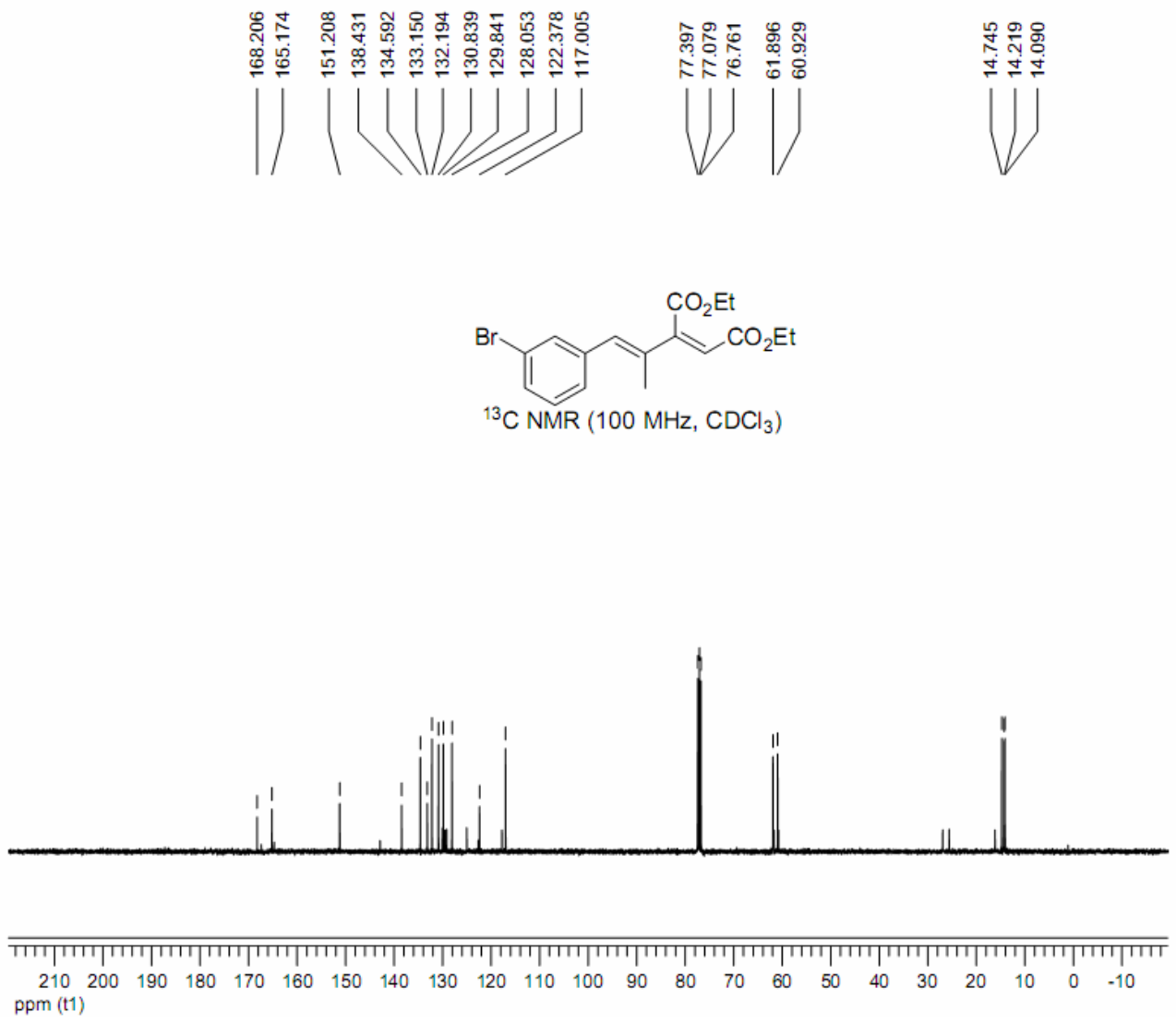

Date:
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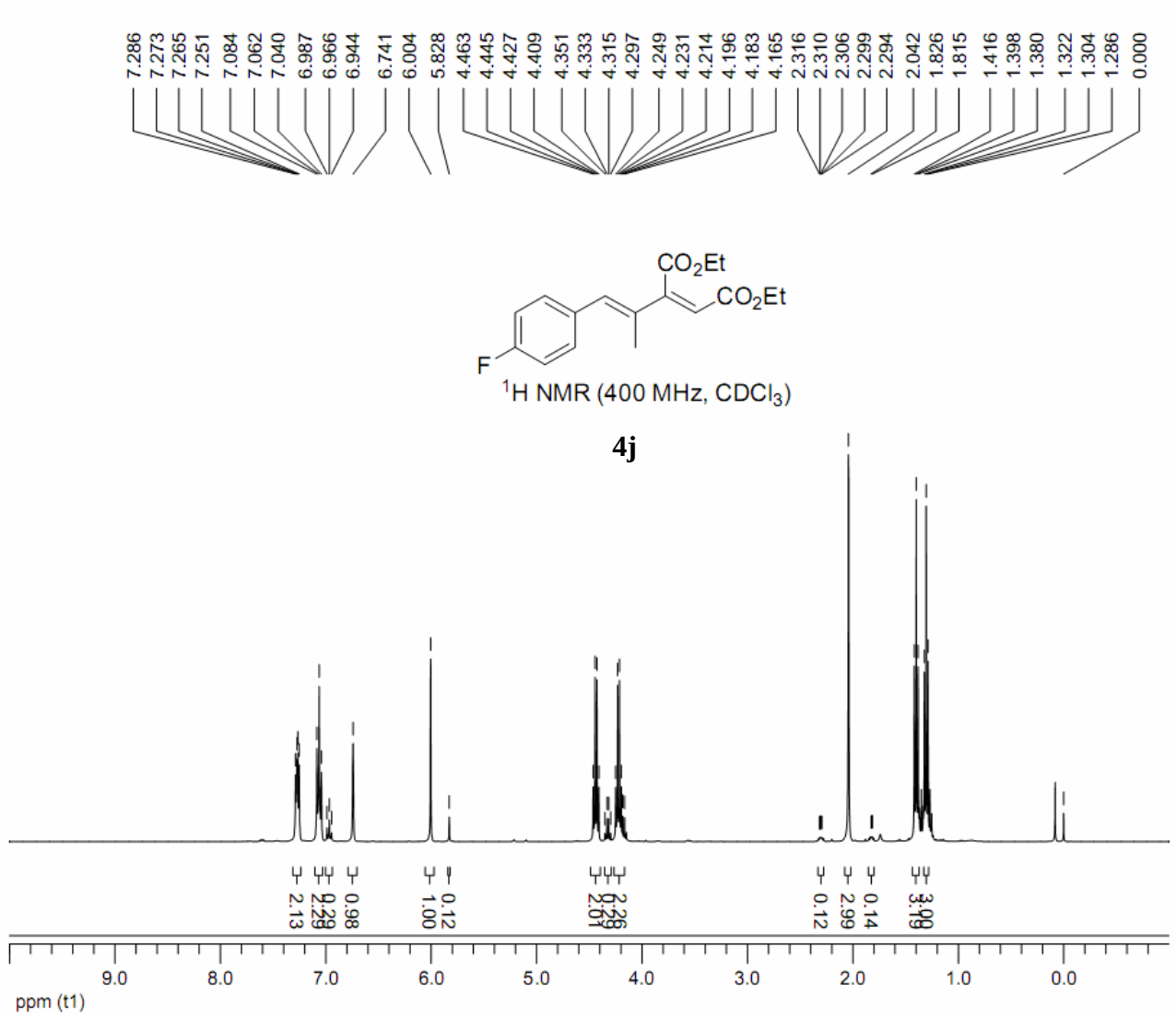

Date:
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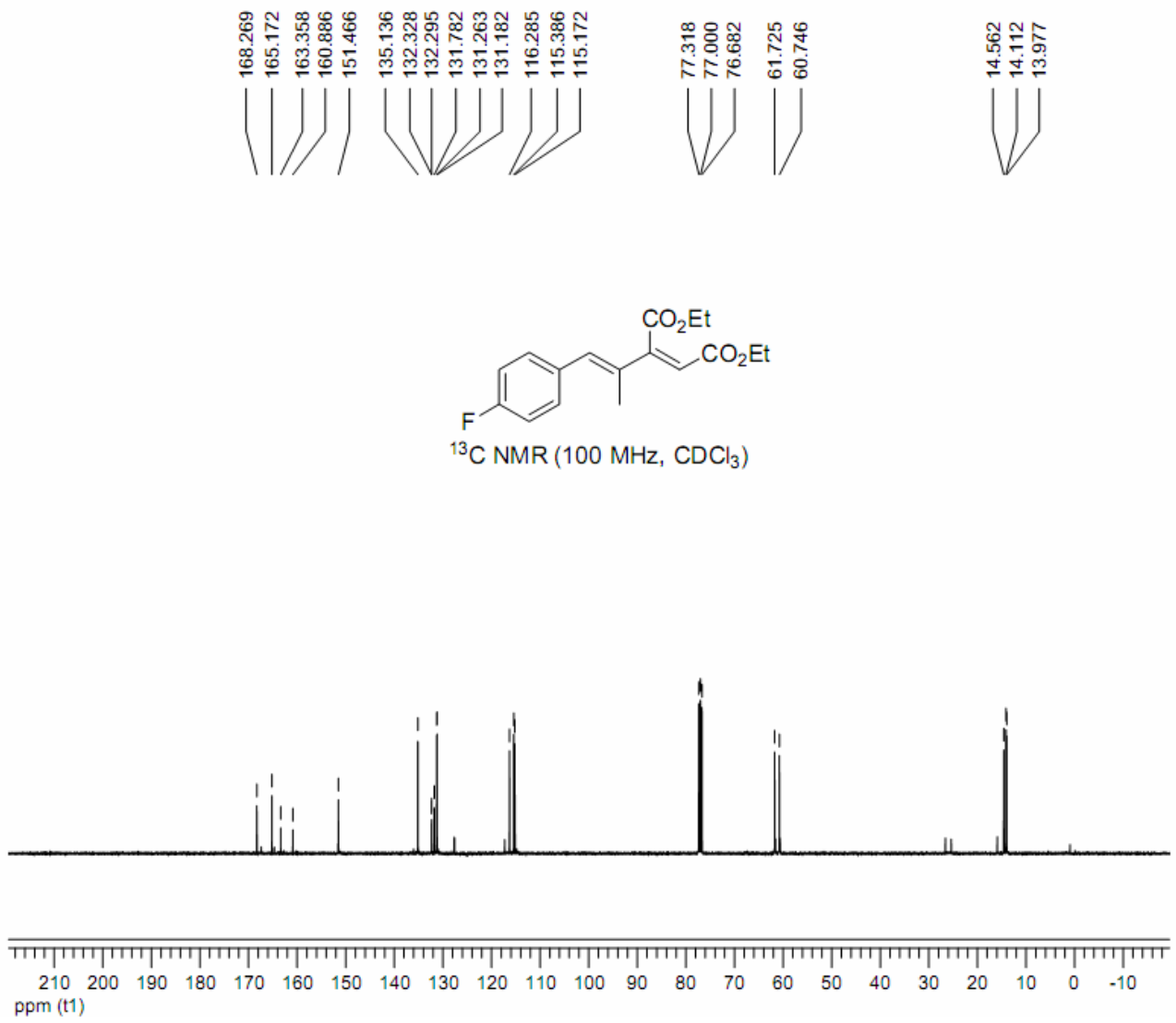

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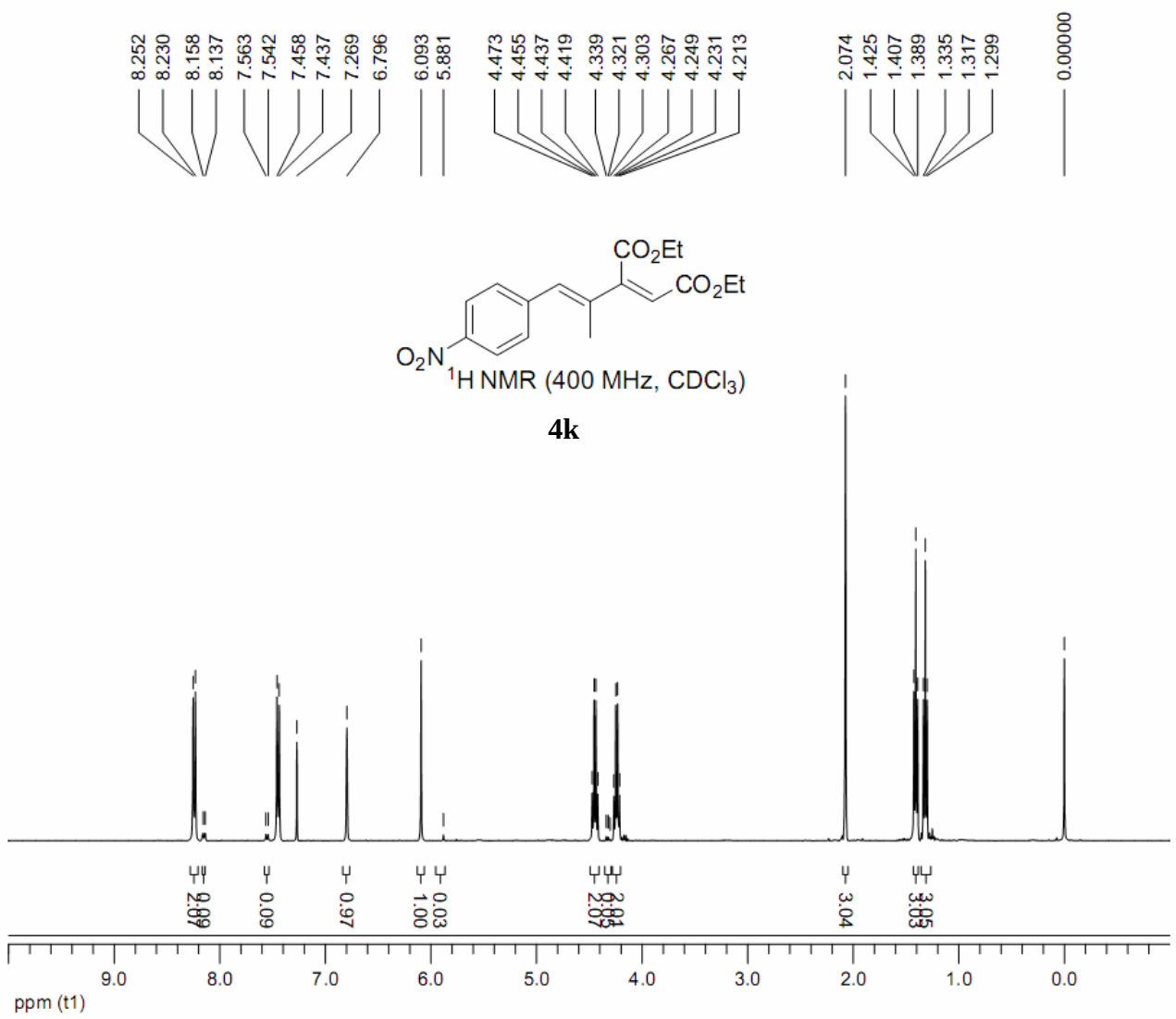

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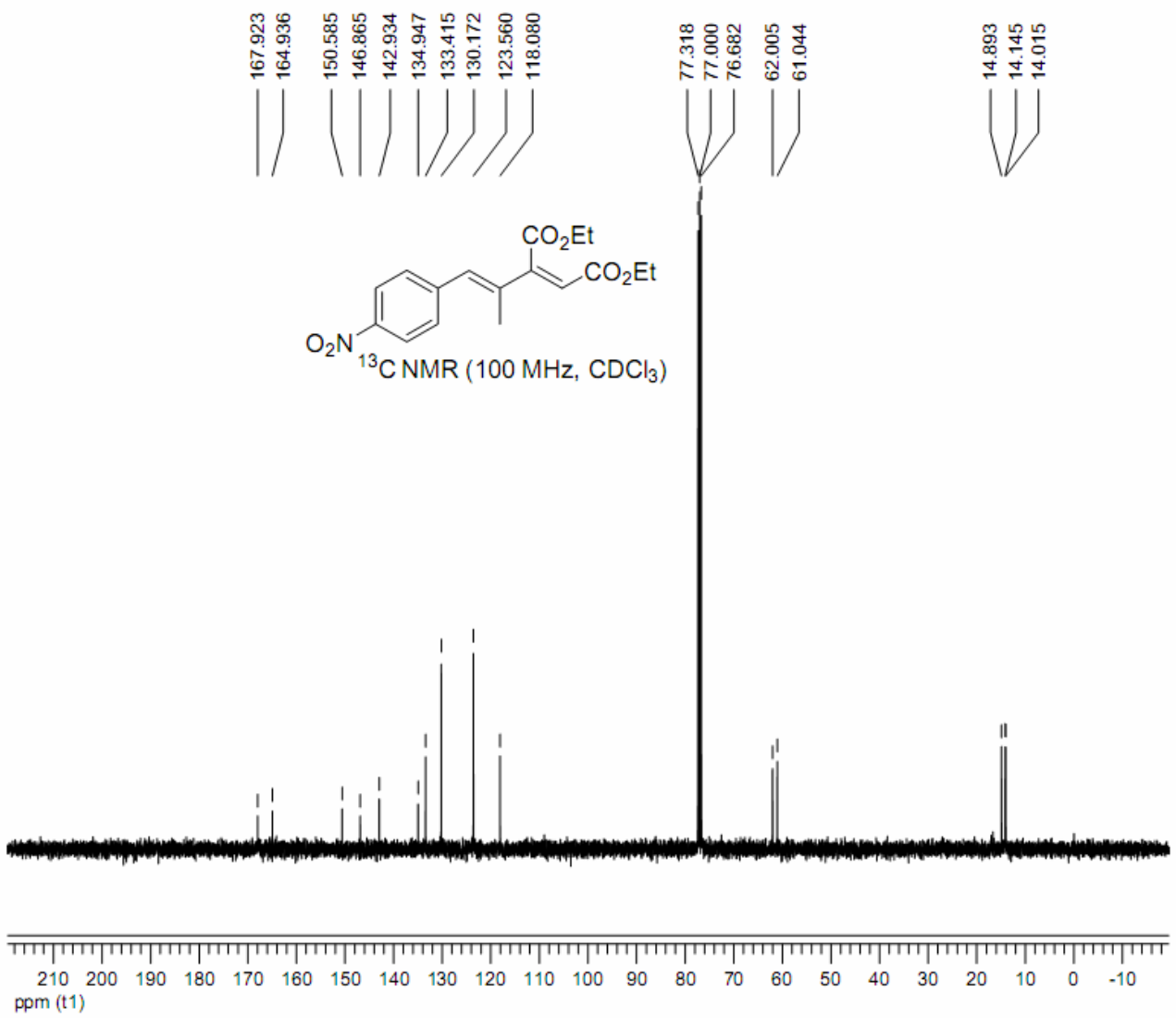

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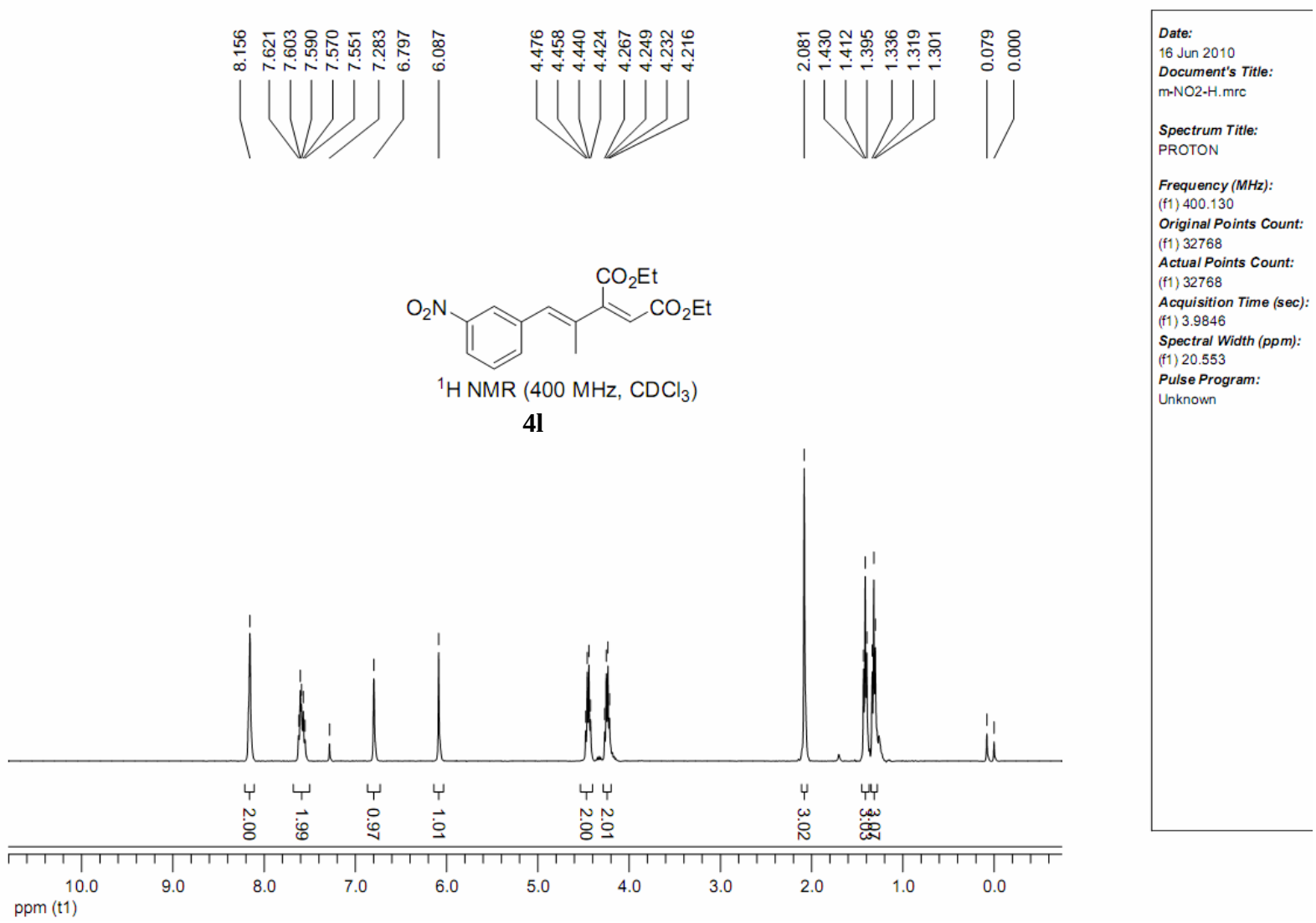

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Original Points Count:
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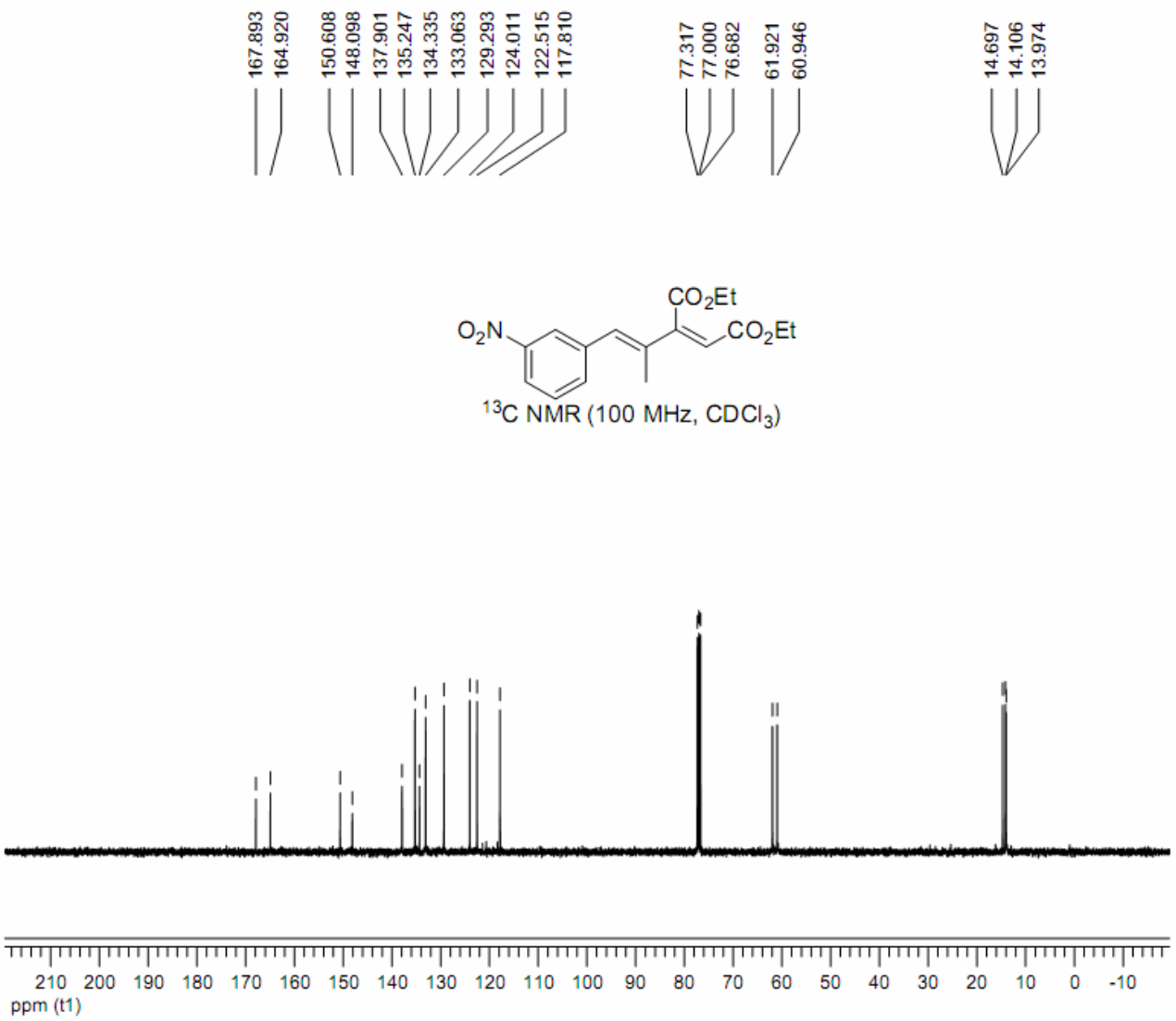
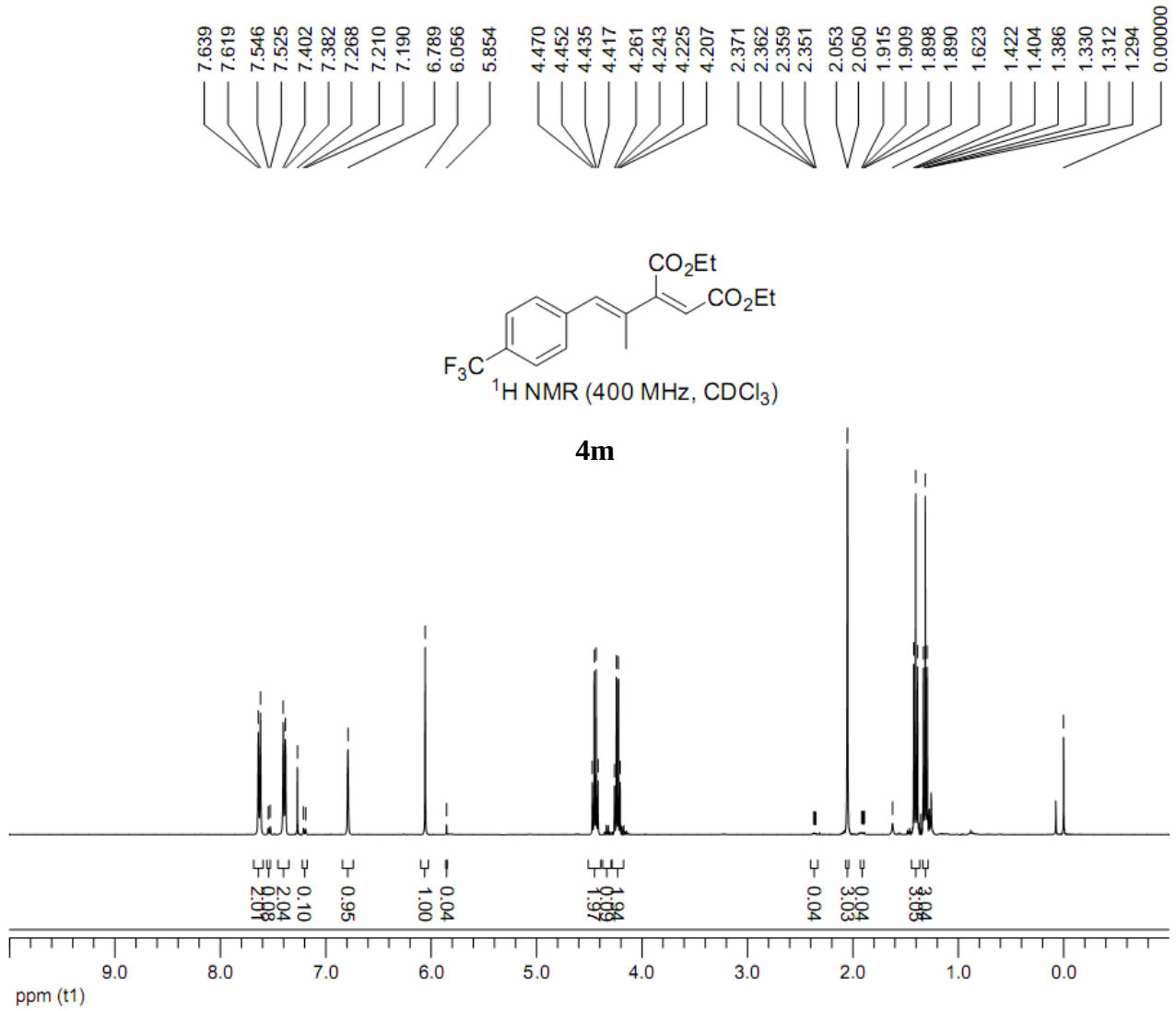
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 3.9846
Spectral Width (ppm):
(f1) 20.553
Pulse Program:
Unknown



Date:
16 Jun 2010
Document's Title:
m-NO2-C.mrc

Spectrum Title:
C13CPD

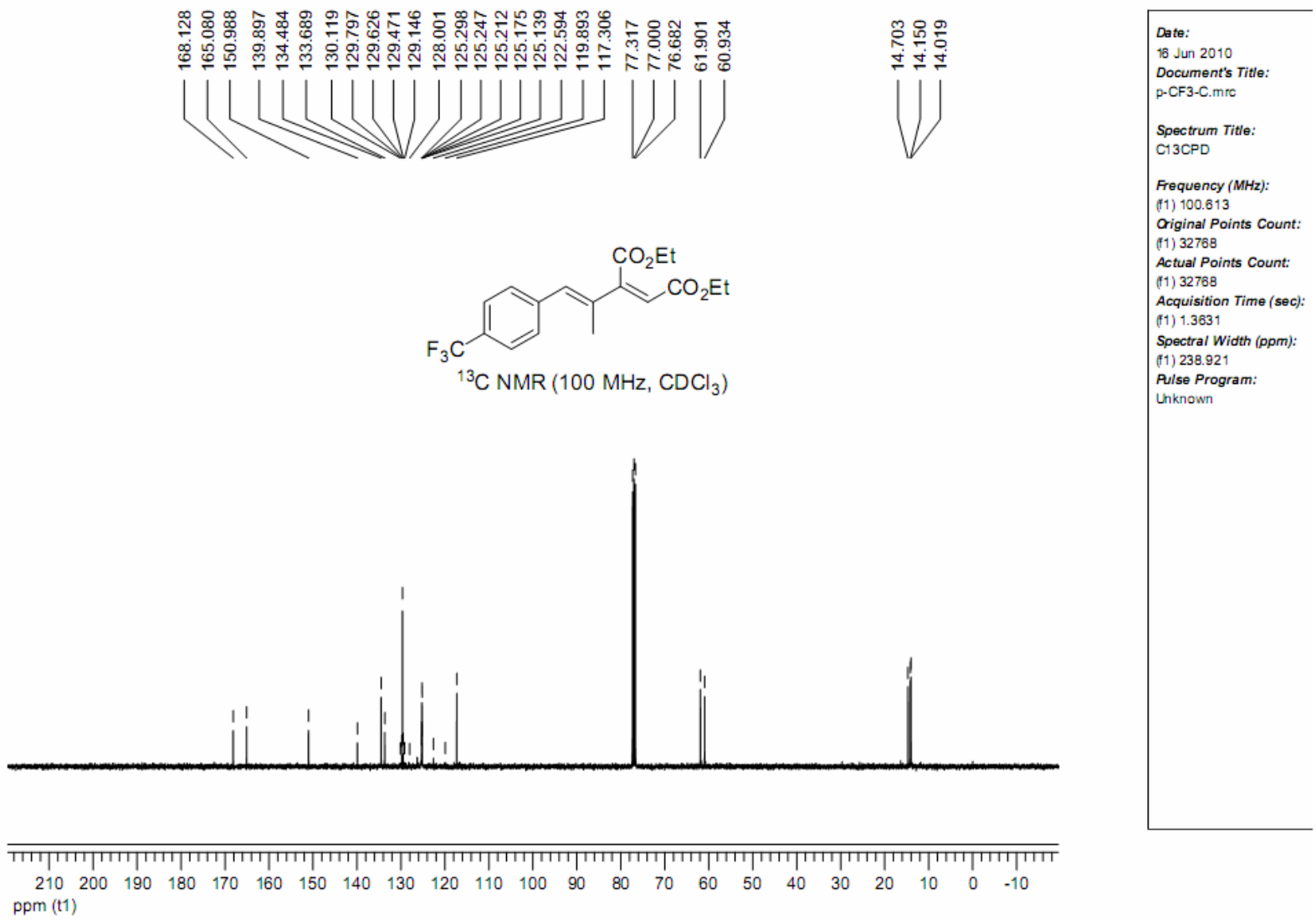
Frequency (MHz):
(f1) 100.613
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 1.3631
Spectral Width (ppm):
(f1) 238.921
Pulse Program:
Unknown



Date:
16 Jun 2010
Document's Title:
p-CF3-H.mrc

Spectrum Title:
PROTON

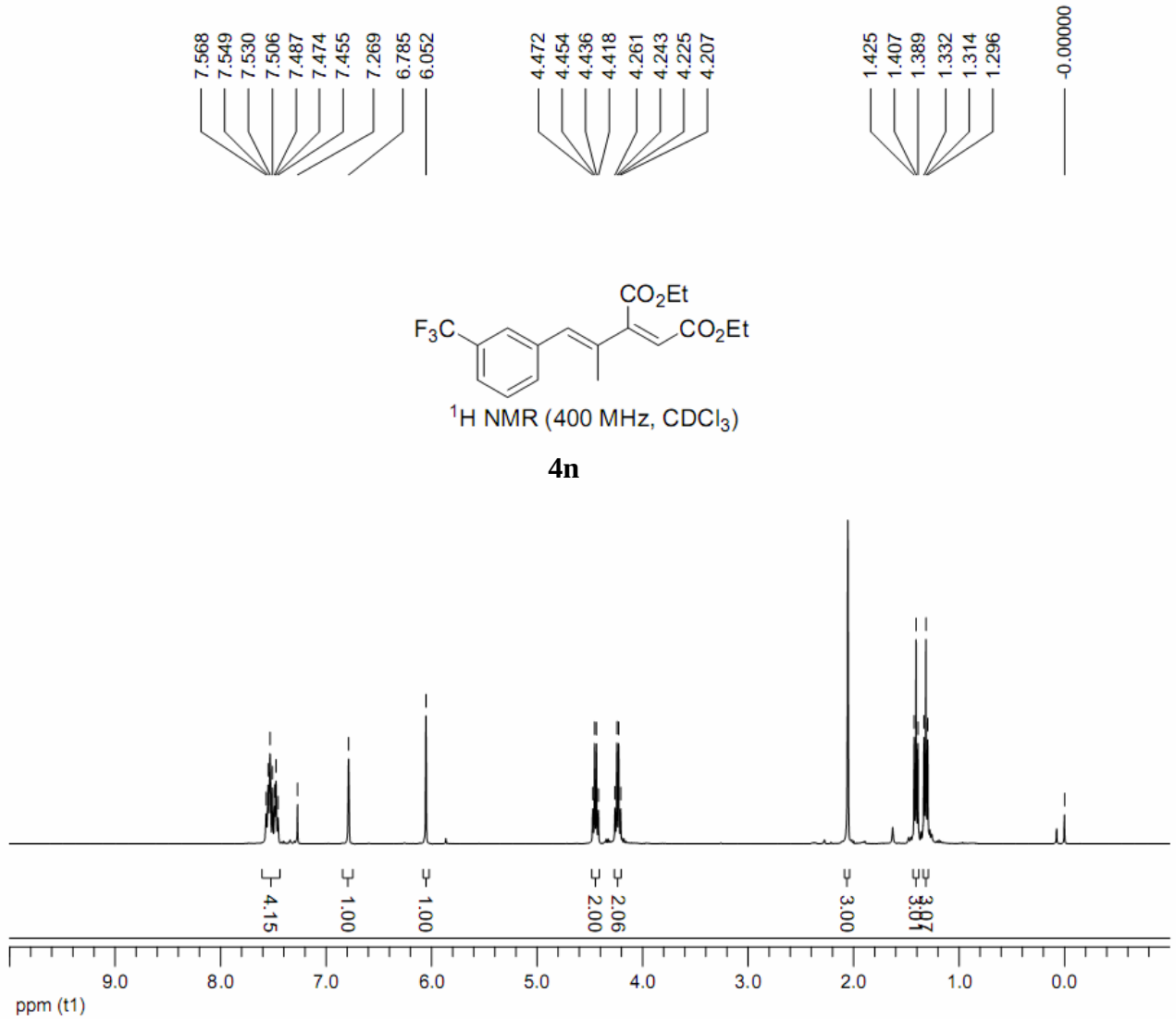
Frequency (MHz):
(f1) 400.130
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 3.9846
Spectral Width (ppm):
(f1) 20.553
Pulse Program:
Unknown



Date:
16 Jun 2010
Document's Title:
p-CF3-C.mrc

Spectrum Title:
C13CPD

Frequency (MHz):
(f1) 100.613
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 1.3631
Spectral Width (ppm):
(f1) 238.921
Pulse Program:
Unknown

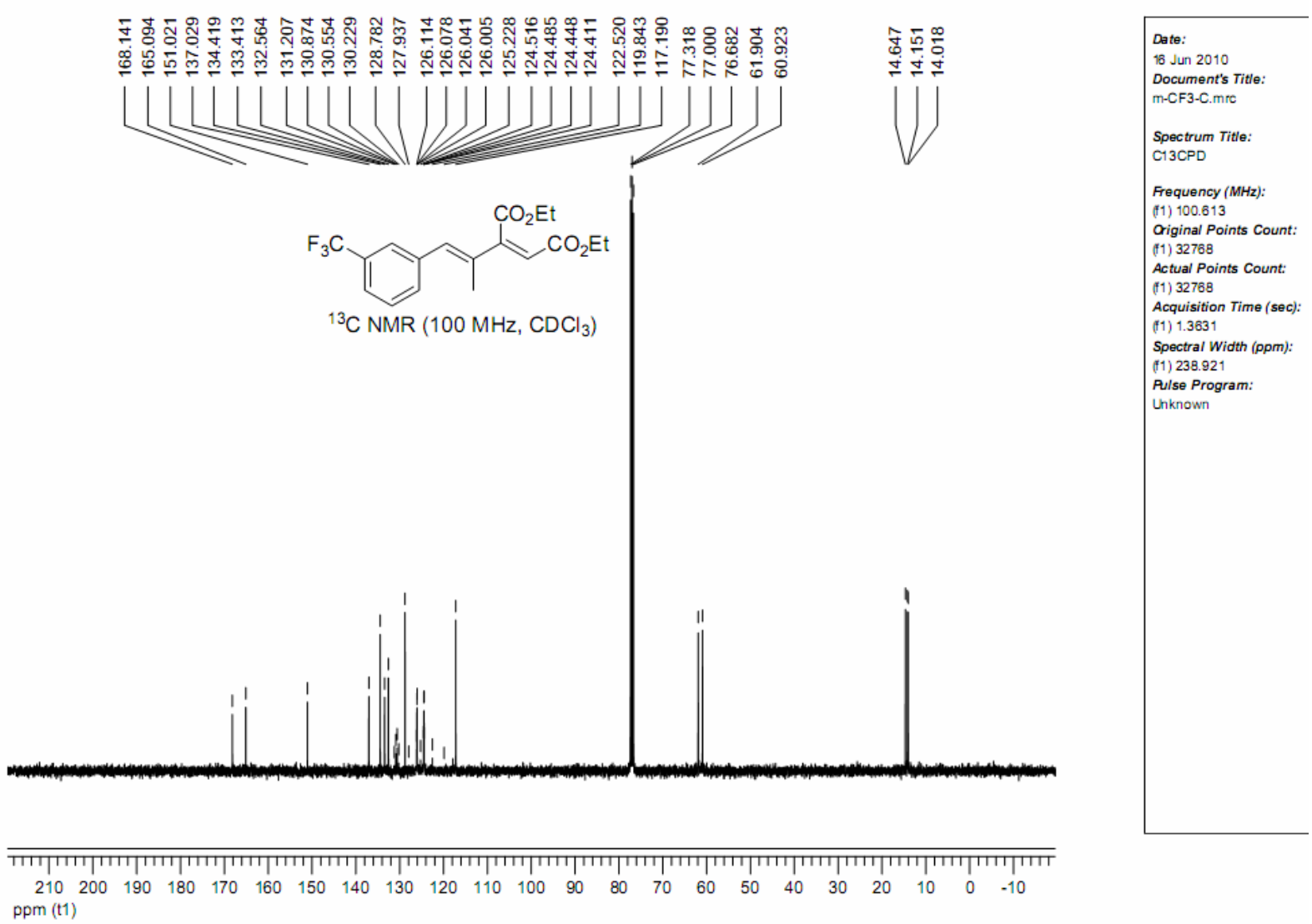


4n

Date:
16 Jun 2010
Document's Title:
m-CF3-H.mrc

Spectrum Title:
PROTON

Frequency (MHz):
(f1) 400.130
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 3.9846
Spectral Width (ppm):
(f1) 20.553
Pulse Program:
Unknown


168.141
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137.029
134.419
133.413
132.564
131.207
130.874
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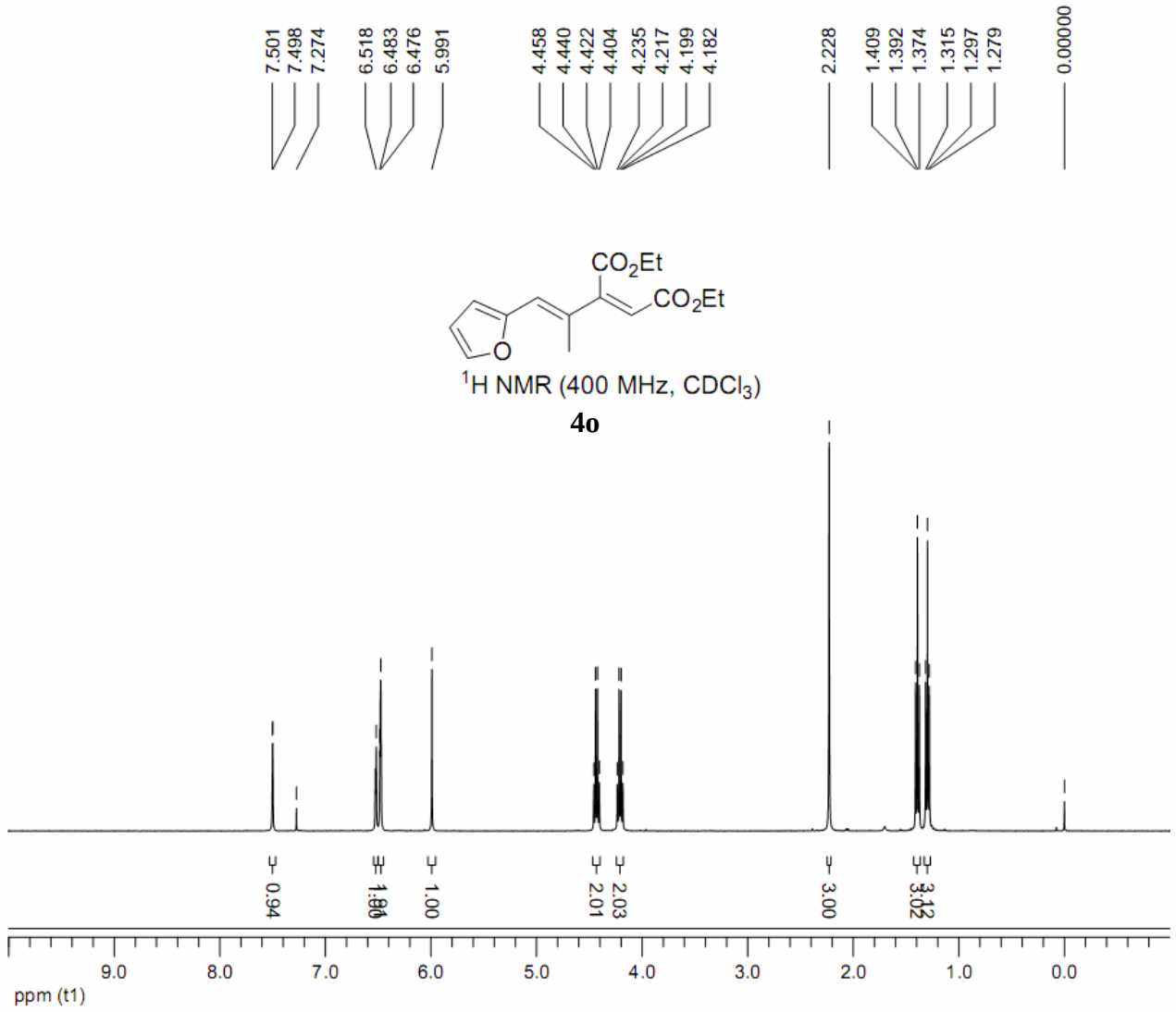
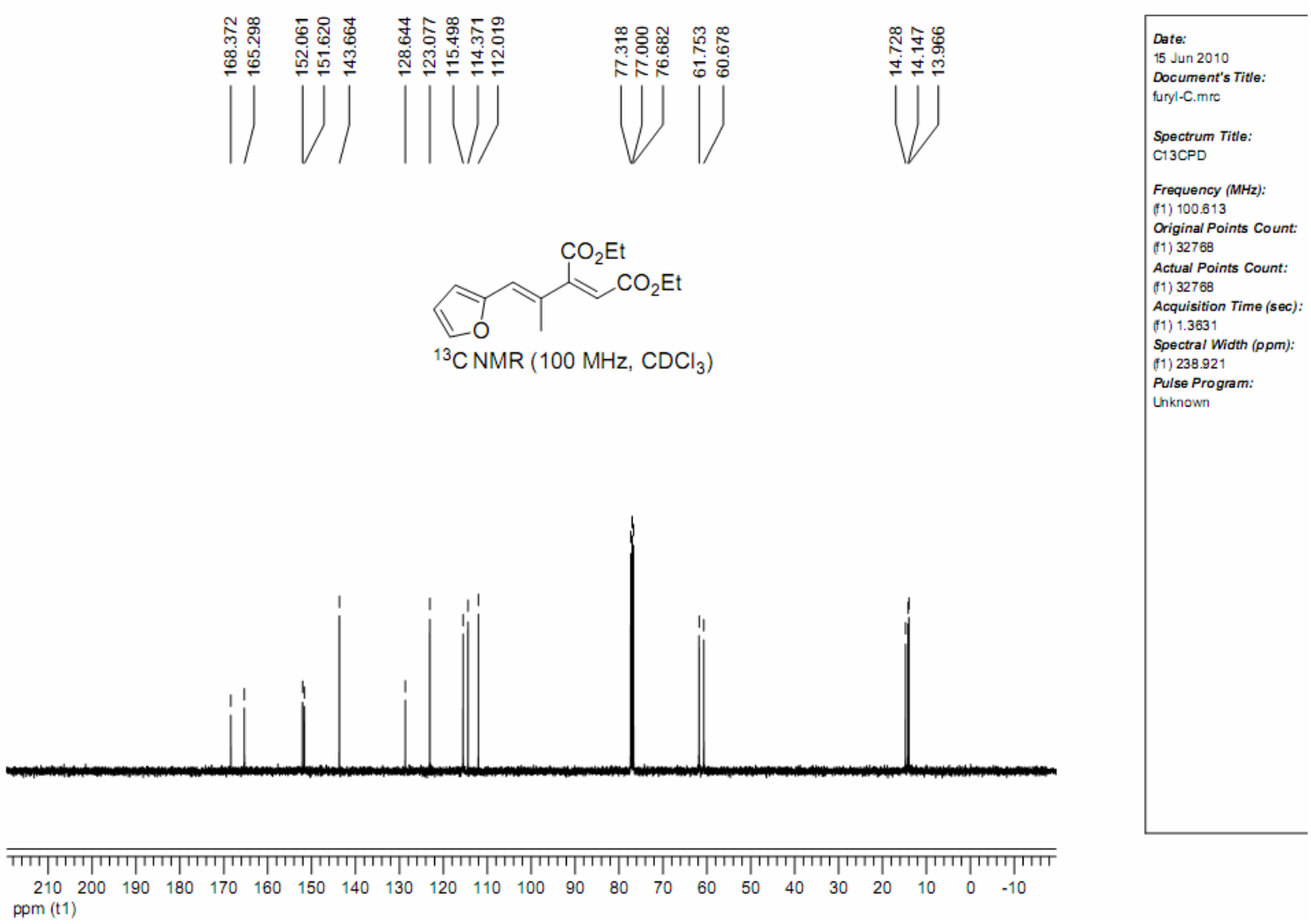
130.229
128.782
127.937
126.114
126.078
126.041
126.005
125.228
124.516
124.485
124.448
124.411
122.520
119.843
117.190
77.318
77.000
76.682
61.904
60.923
14.647
14.151
14.018
CO2Et
F3C
CO2Et
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm (t1)
Date:
16 Jun 2010
Document's Title:
m-CF3-C.mrc
Spectrum Title:
C13CPD
Frequency (MHz):
(f1) 100.613
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 1.3631
Spectral Width (ppm):
(f1) 238.921
Pulse Program:
Unknown



Date:
15 Jun 2010
Document's Title:
furyl-H.mrc

Spectrum Title:
PROTON

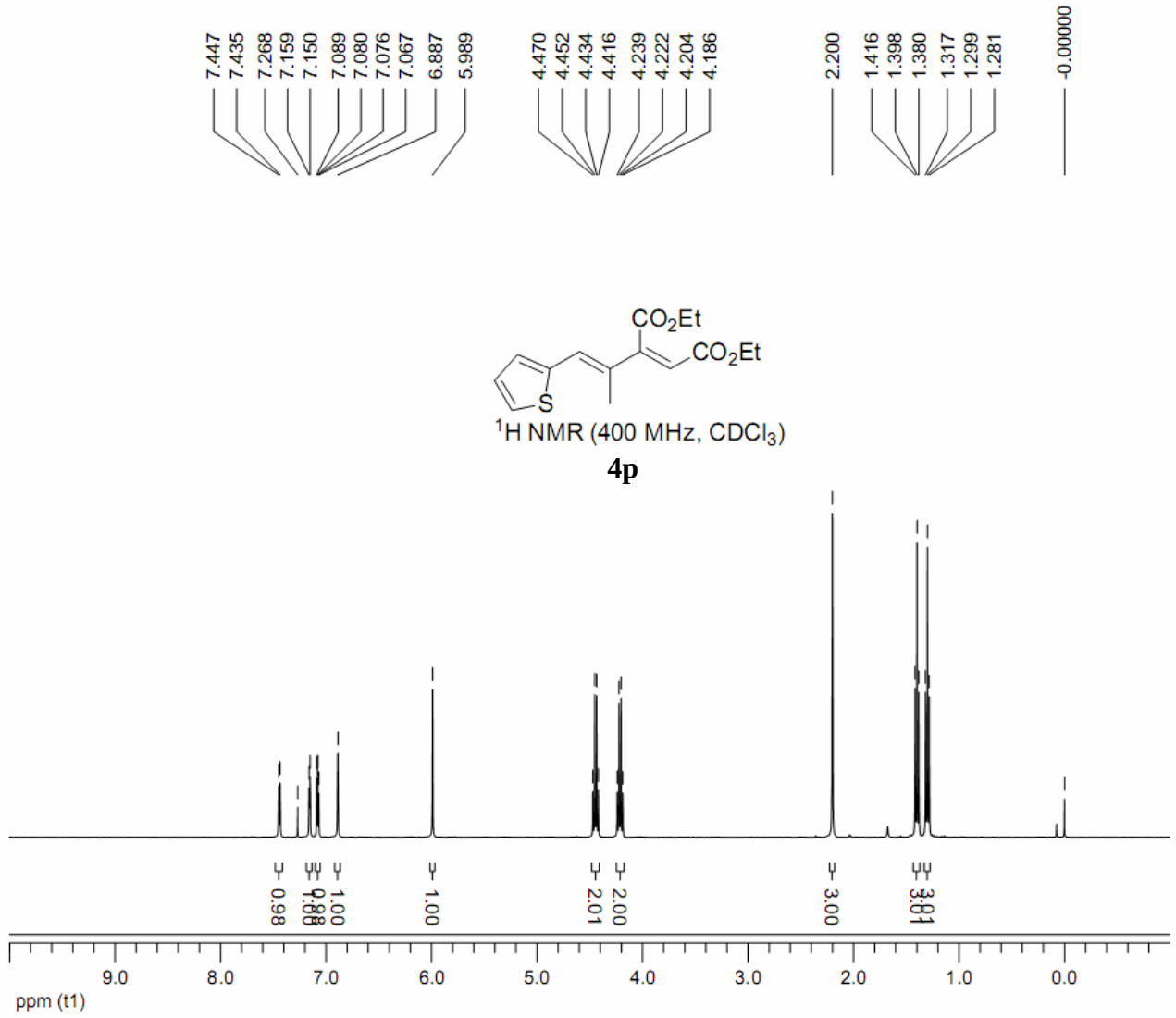
Frequency (MHz):
(f1) 400.130
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 3.9846
Spectral Width (ppm):
(f1) 20.553
Pulse Program:
Unknown



Date:
15 Jun 2010
Document's Title:
furyl-C.mrc

Spectrum Title:
C13CPD

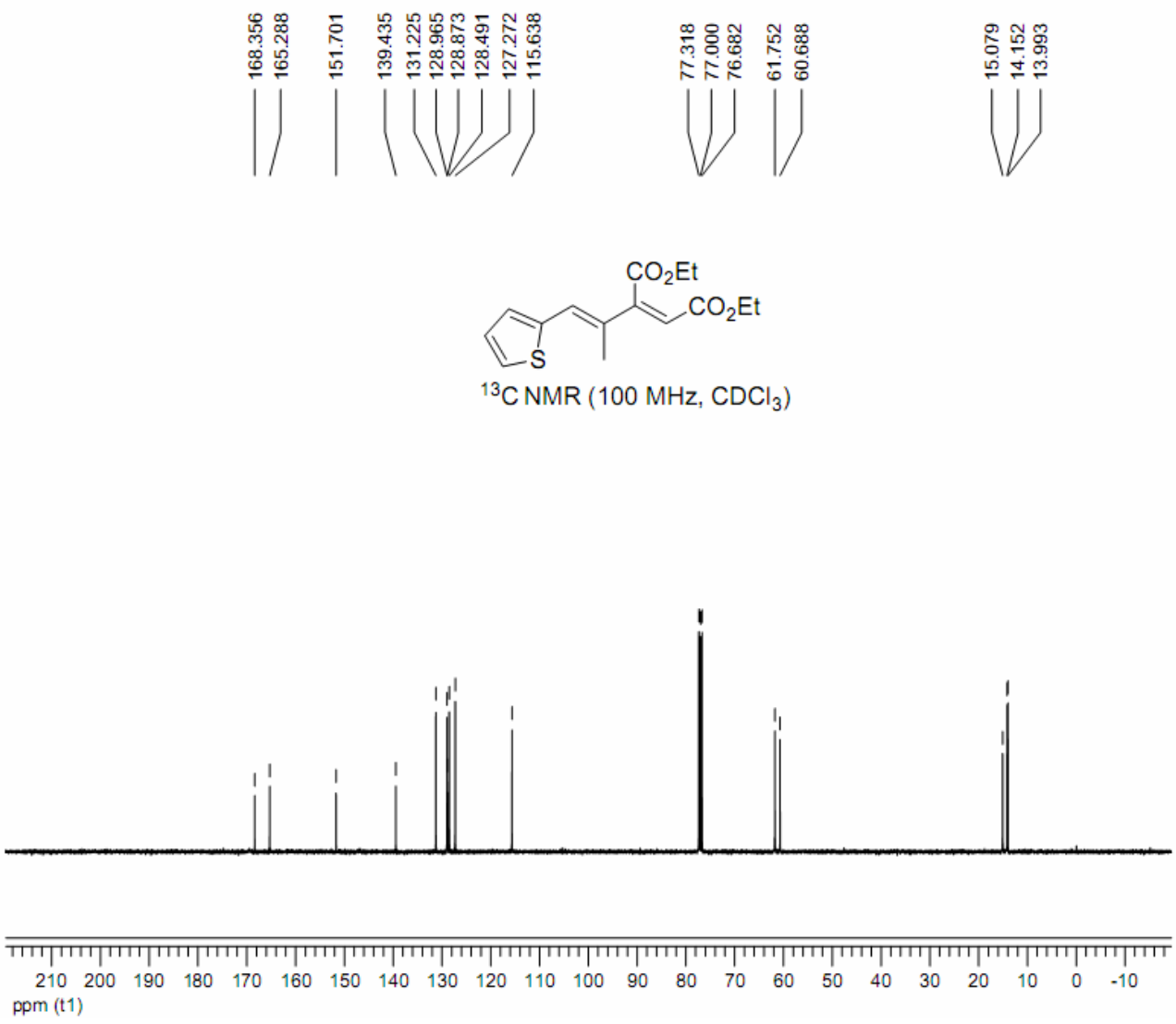
Frequency (MHz):
(f1) 100.613
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 1.3631
Spectral Width (ppm):
(f1) 238.921
Pulse Program:
Unknown



Date:
15 Jun 2010
Document's Title:
thiofuryl-H.mrc

Spectrum Title:
PROTON

Frequency (MHz):
(f1) 400.130
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 3.9846
Spectral Width (ppm):
(f1) 20.553
Pulse Program:
Unknown



Date:
15 Jun 2010
Document's Title:
thiofuryl-C.mrc

Spectrum Title:
C13CPD

Frequency (MHz):
(f1) 100.613
Original Points Count:
(f1) 32768
Actual Points Count:
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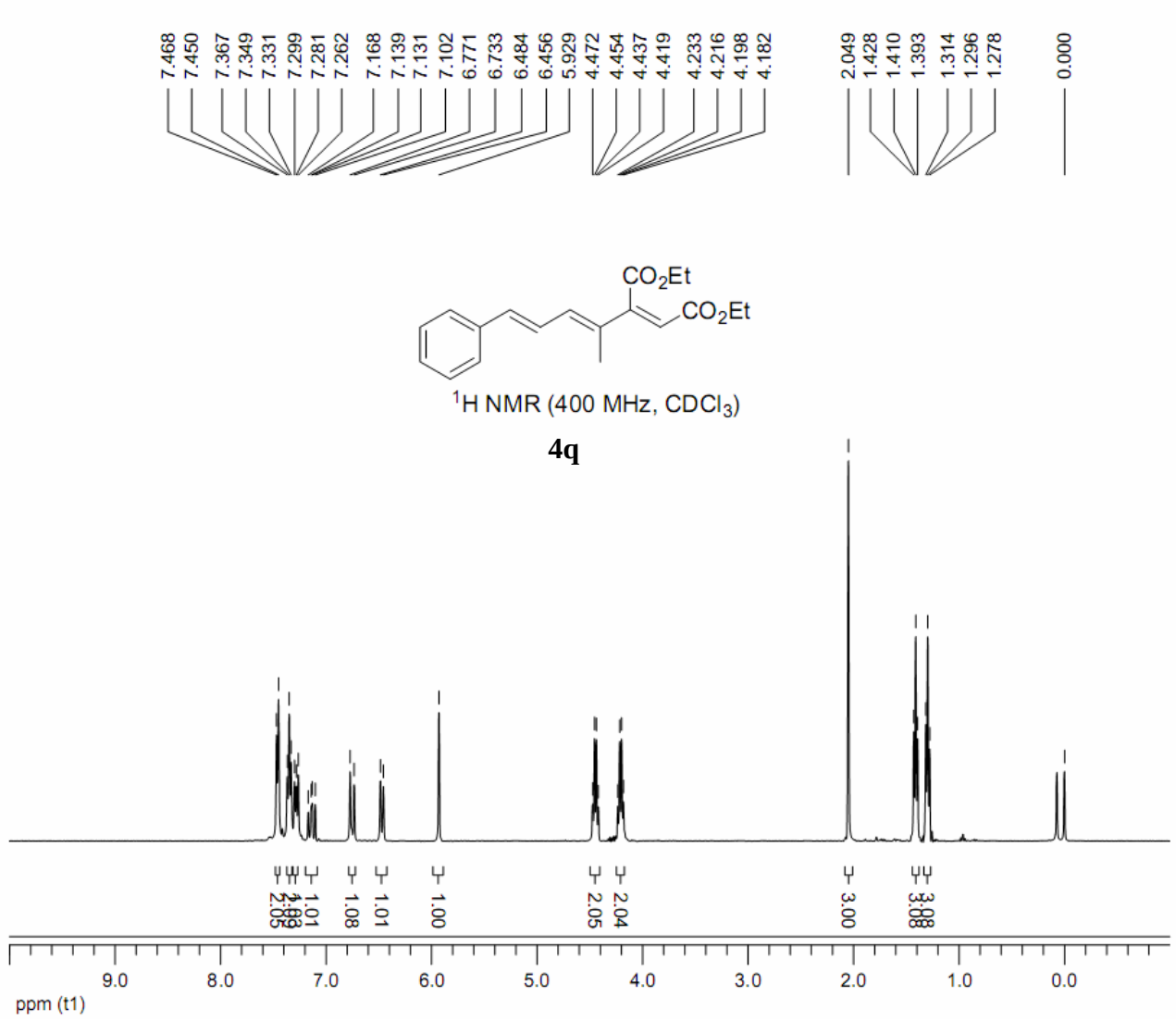
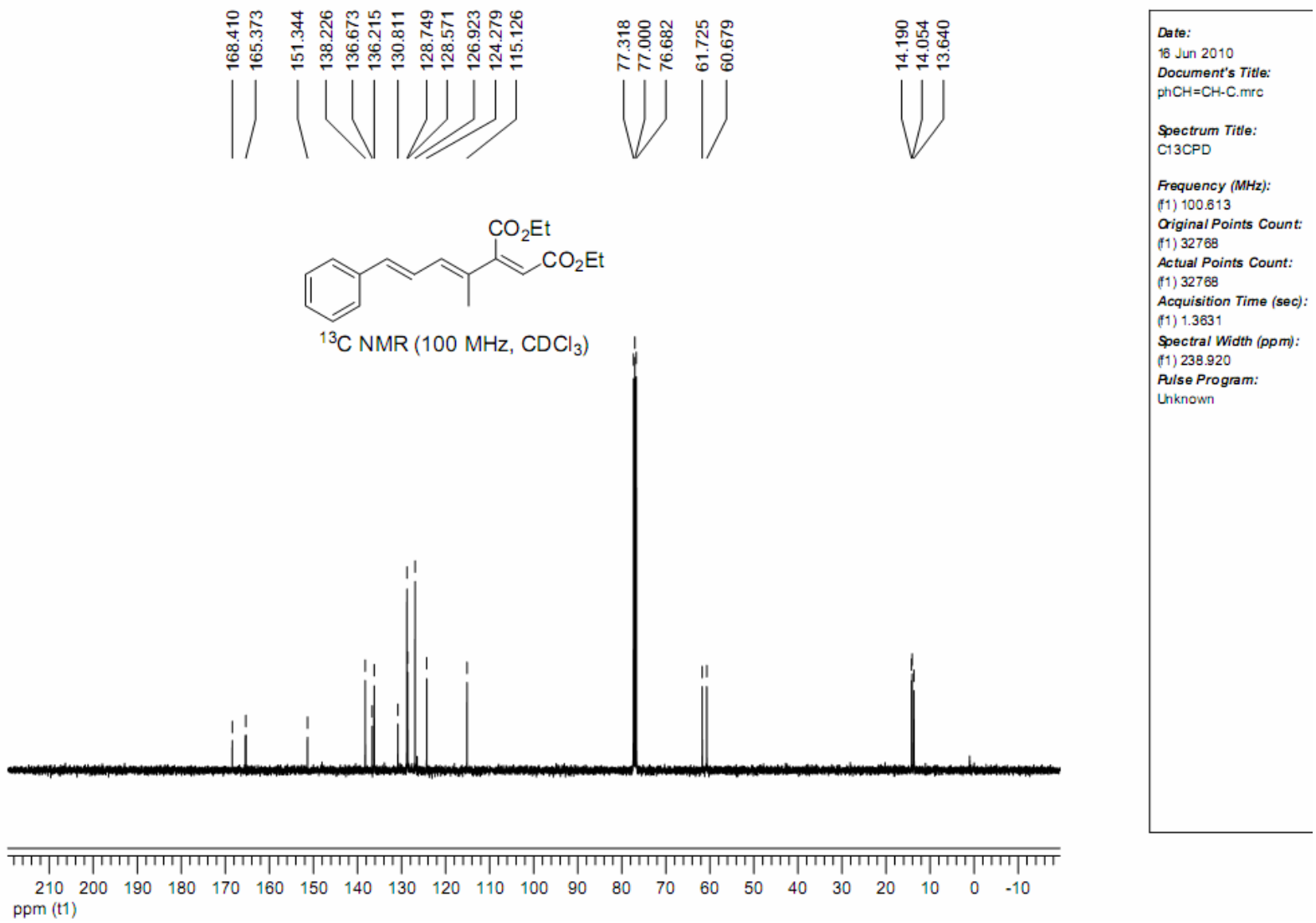
Acquisition Time (sec):
(f1) 1.3631
Spectral Width (ppm):
(f1) 238.921
Pulse Program:
Unknown



Date:
16 Jun 2010
Document's Title:
phCH=CH-H.mrc

Spectrum Title:
PROTON

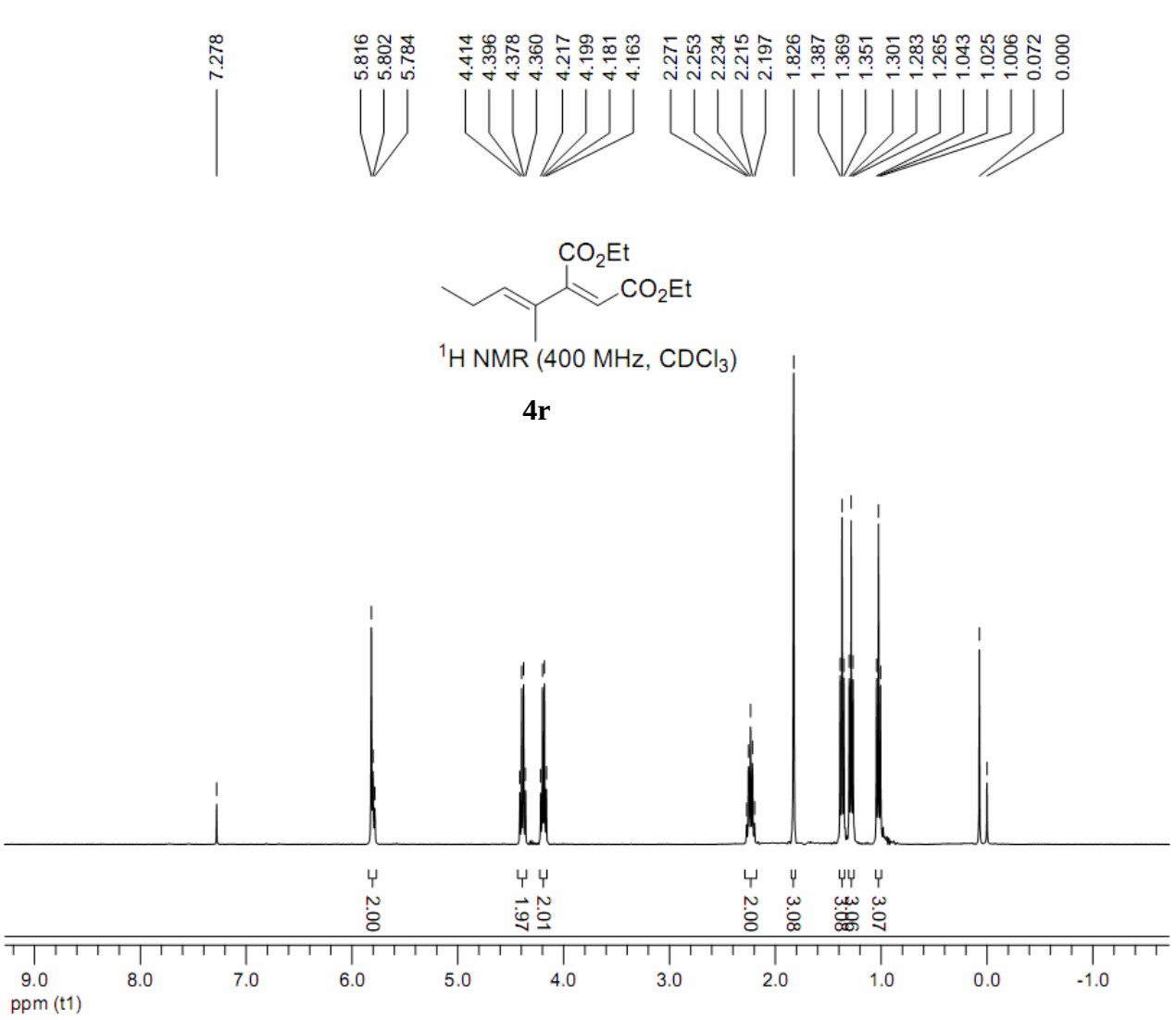
Frequency (MHz):
(f1) 400.130
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 3.9846
Spectral Width (ppm):
(f1) 20.553
Pulse Program:
Unknown



Date:
16 Jun 2010
Document's Title:
phCH=CH-C.mrc

Spectrum Title:
C13CPD

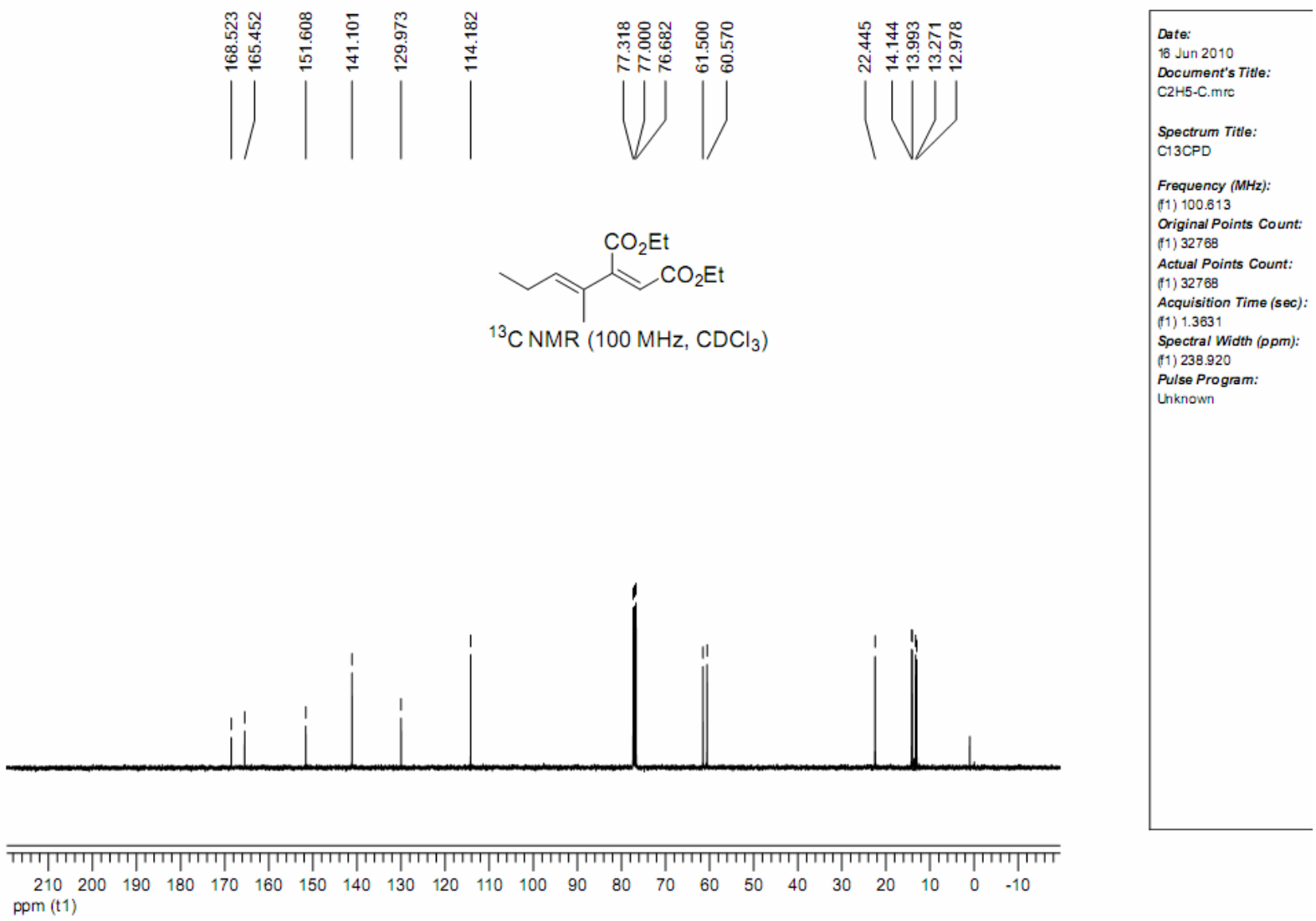
Frequency (MHz):
(f1) 100.613
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 1.3631
Spectral Width (ppm):
(f1) 238.920
Pulse Program:
Unknown



Date:
16 Jun 2010
Document's Title:
C2H5-H.mrc

Spectrum Title:
PROTON

Frequency (MHz):
(f1) 400.130
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 3.9846
Spectral Width (ppm):
(f1) 20.553
Pulse Program:
Unknown



Date:
16 Jun 2010
Document's Title:
C2H5-C.mrc

Spectrum Title:
C13CPD

Frequency (MHz):
(f1) 100.613
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 1.3631
Spectral Width (ppm):
(f1) 238.920
Pulse Program:
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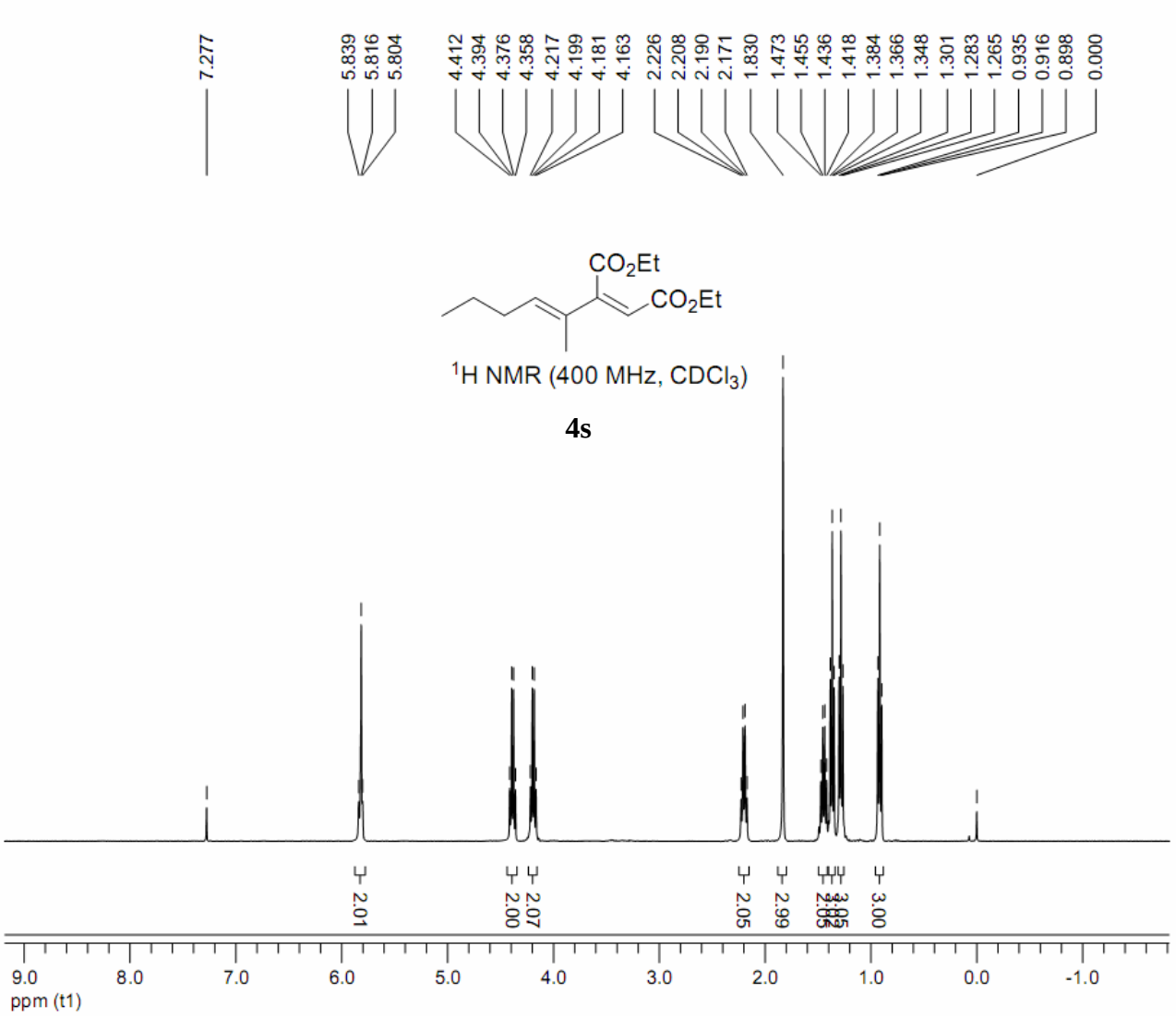

Date:
16 Jun 2010
Document's Title:
C3H7-H.mrc

Spectrum Title:
PROTON

Frequency (MHz):
(f1) 400.130
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 3.9846
Spectral Width (ppm):
(f1) 20.553
Pulse Program:
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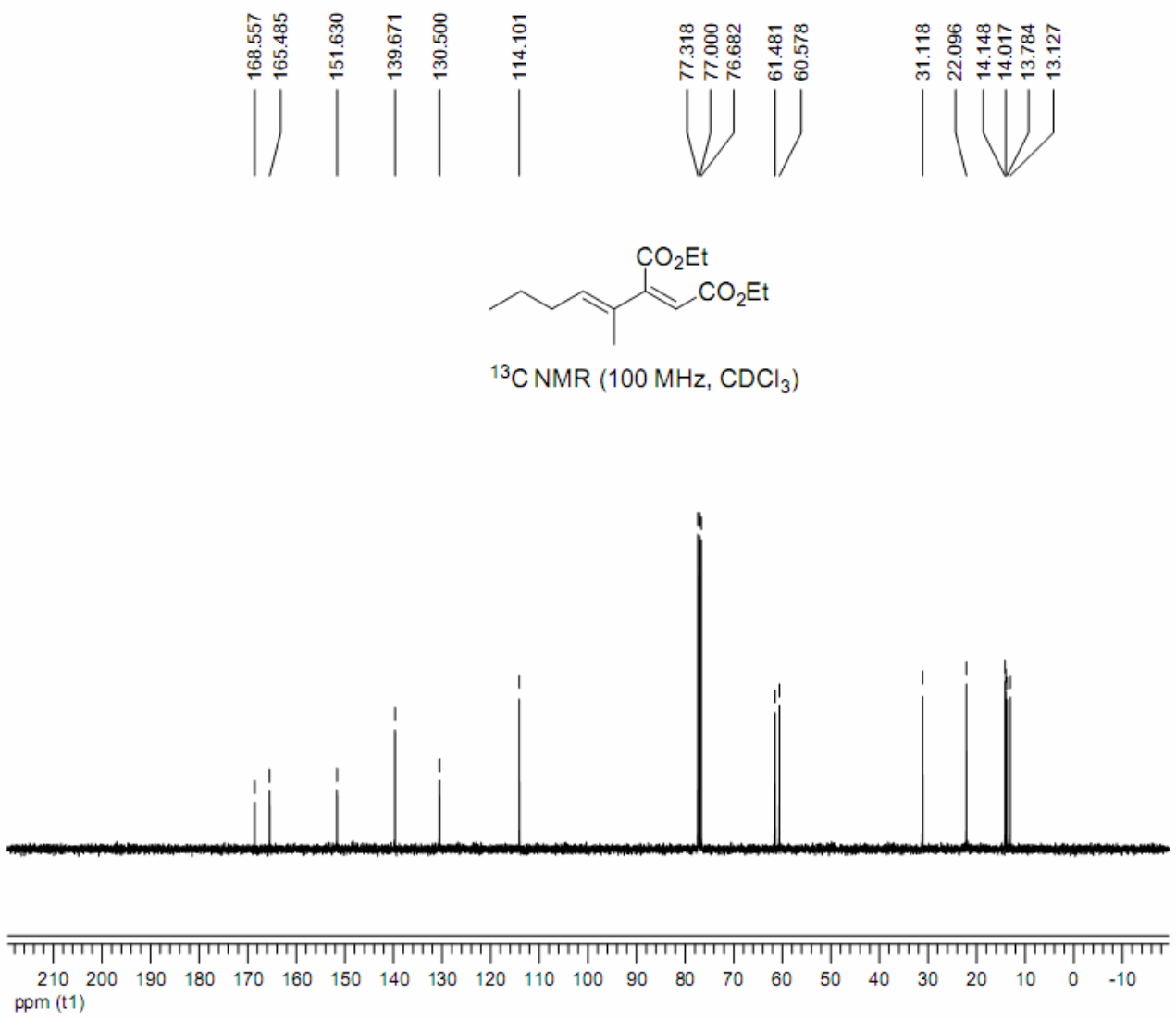

Date:
16 Jun 2010
Document's Title:
C3H7-C.mrc

Spectrum Title:
C13CPD

Frequency (MHz):
(f1) 100.613
Original Points Count:
(f1) 32768
Actual Points Count:
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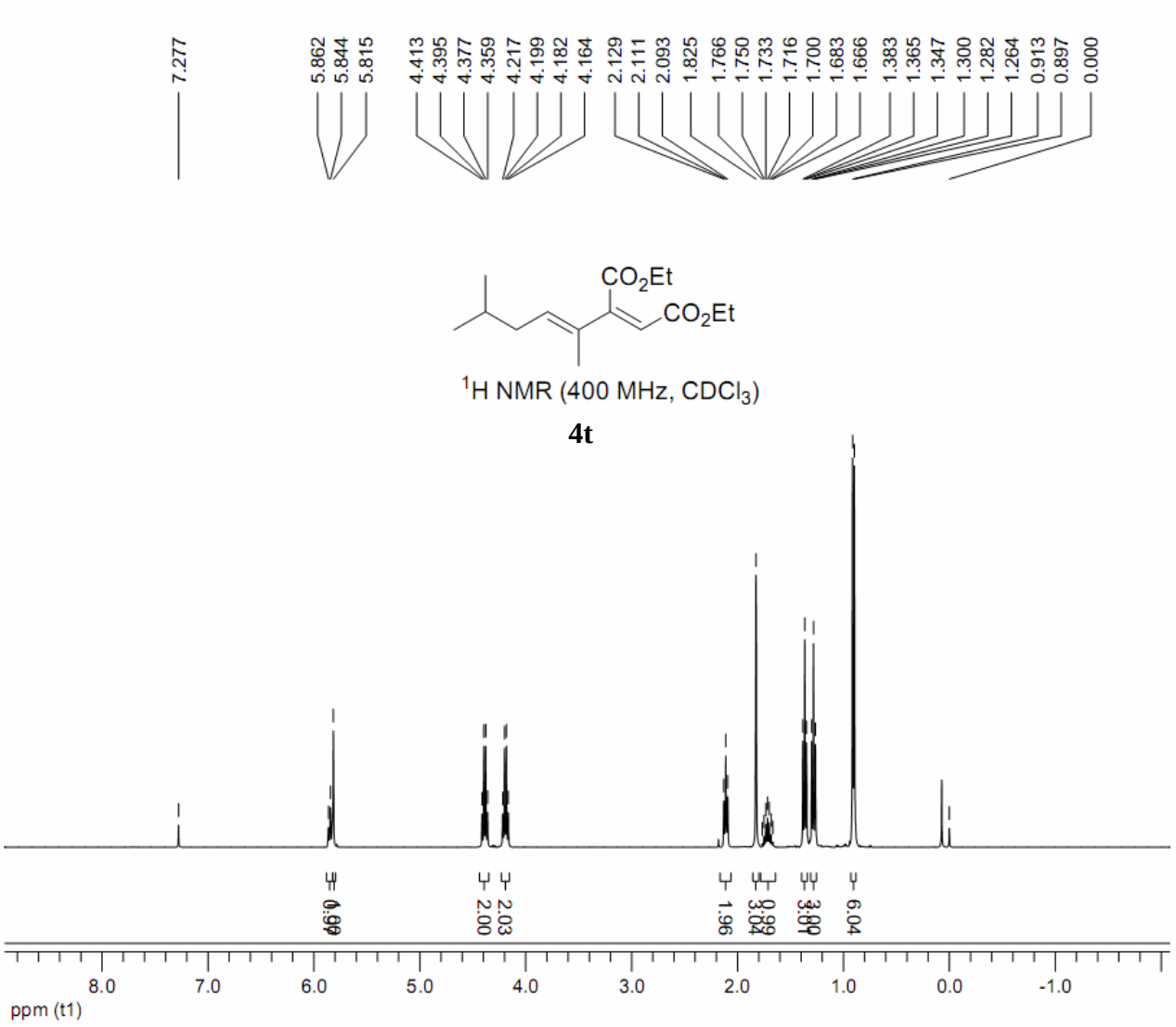
Acquisition Time (sec):
(f1) 1.3631
Spectral Width (ppm):
(f1) 238.921
Pulse Program:
Unknown



Date:
16 Jun 2010
Document's Title:
iso-C4H9-H.mrc

Spectrum Title:
PROTON

Frequency (MHz):
(f1) 400.130
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 3.9846
Spectral Width (ppm):
(f1) 20.553
Pulse Program:
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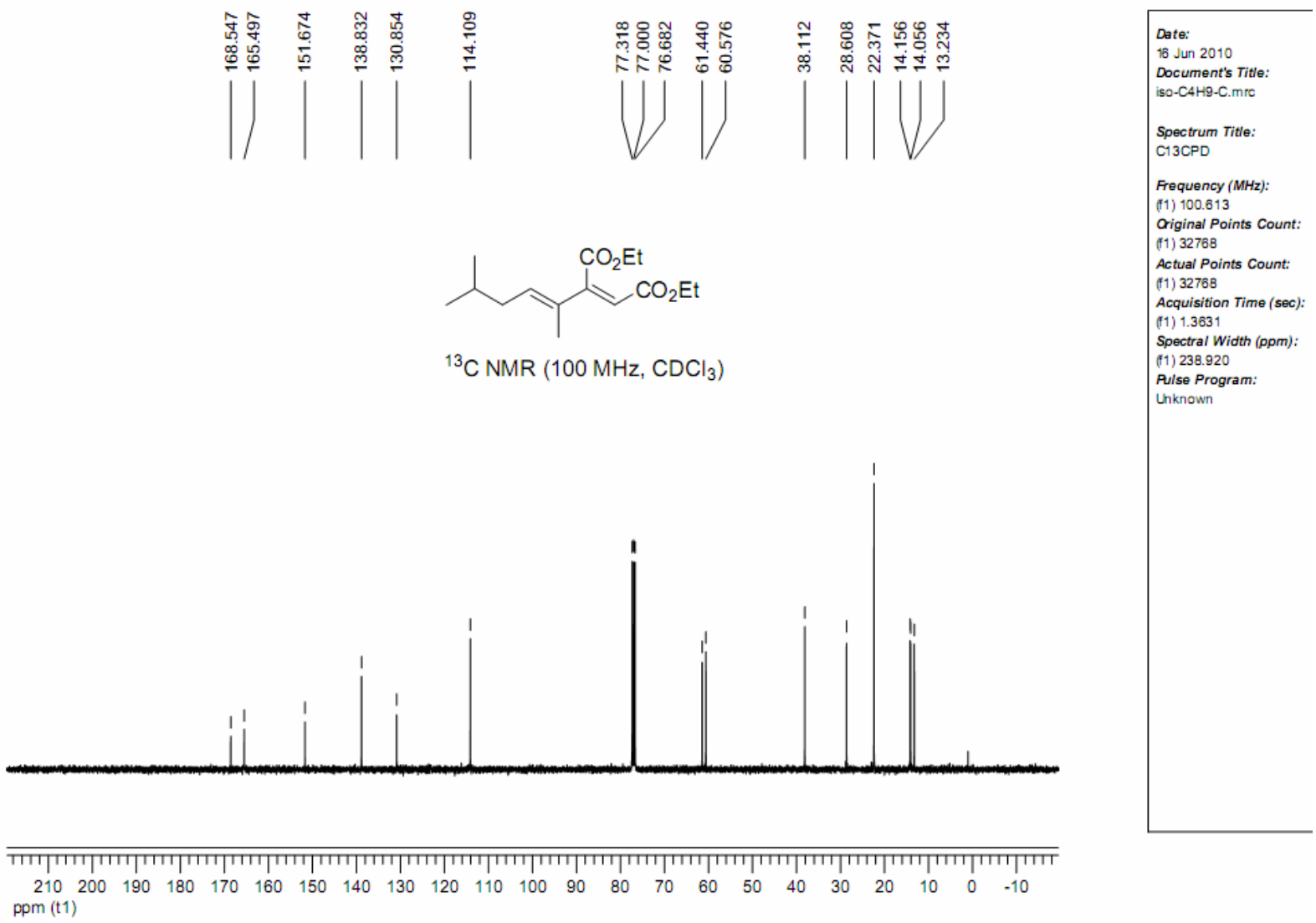

Date:
16 Jun 2010
Document's Title:
iso-C4H9-C.mrc

Spectrum Title:
C13CPD

Frequency (MHz):
(f1) 100.613
Original Points Count:
(f1) 32768
Actual Points Count:
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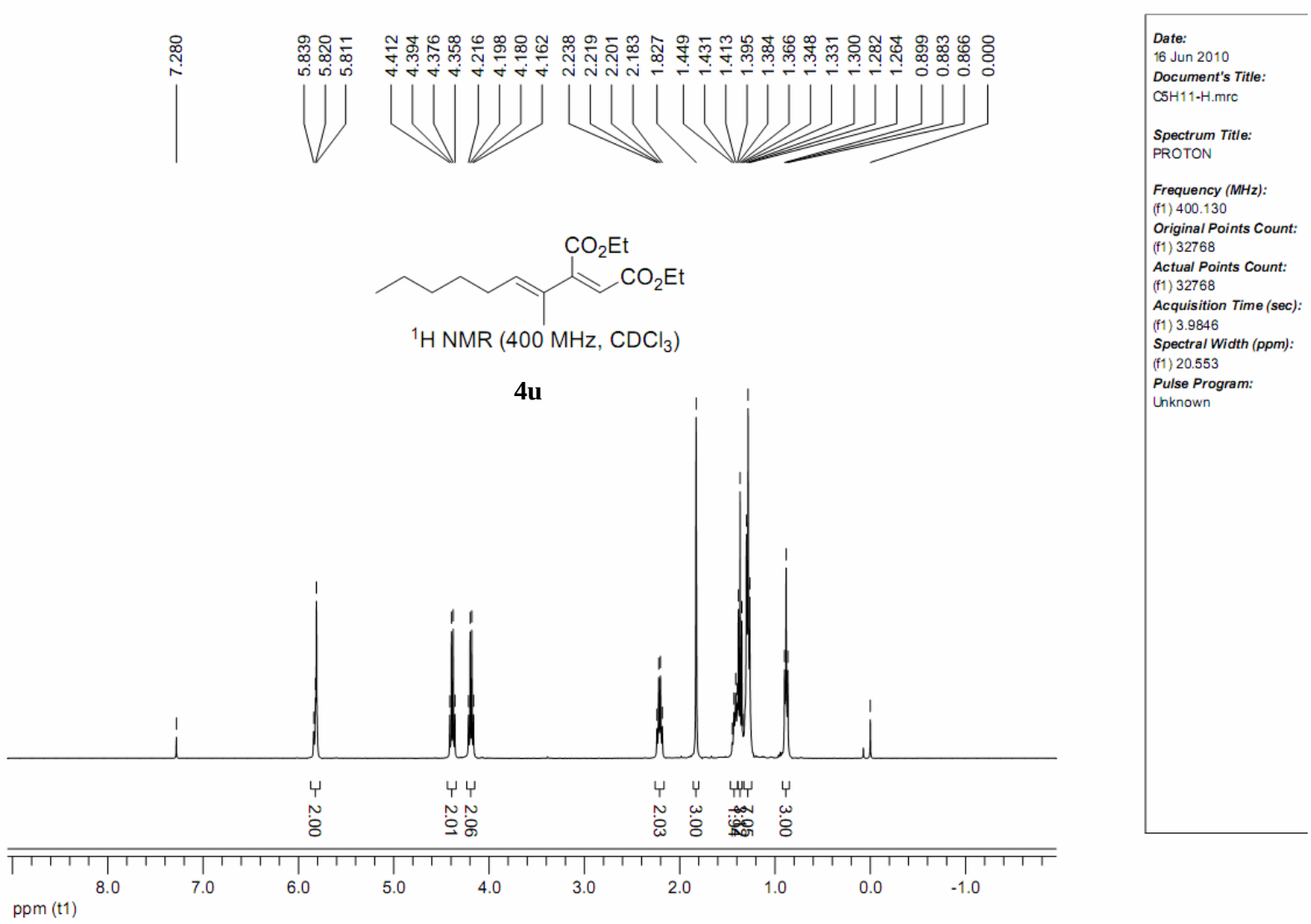
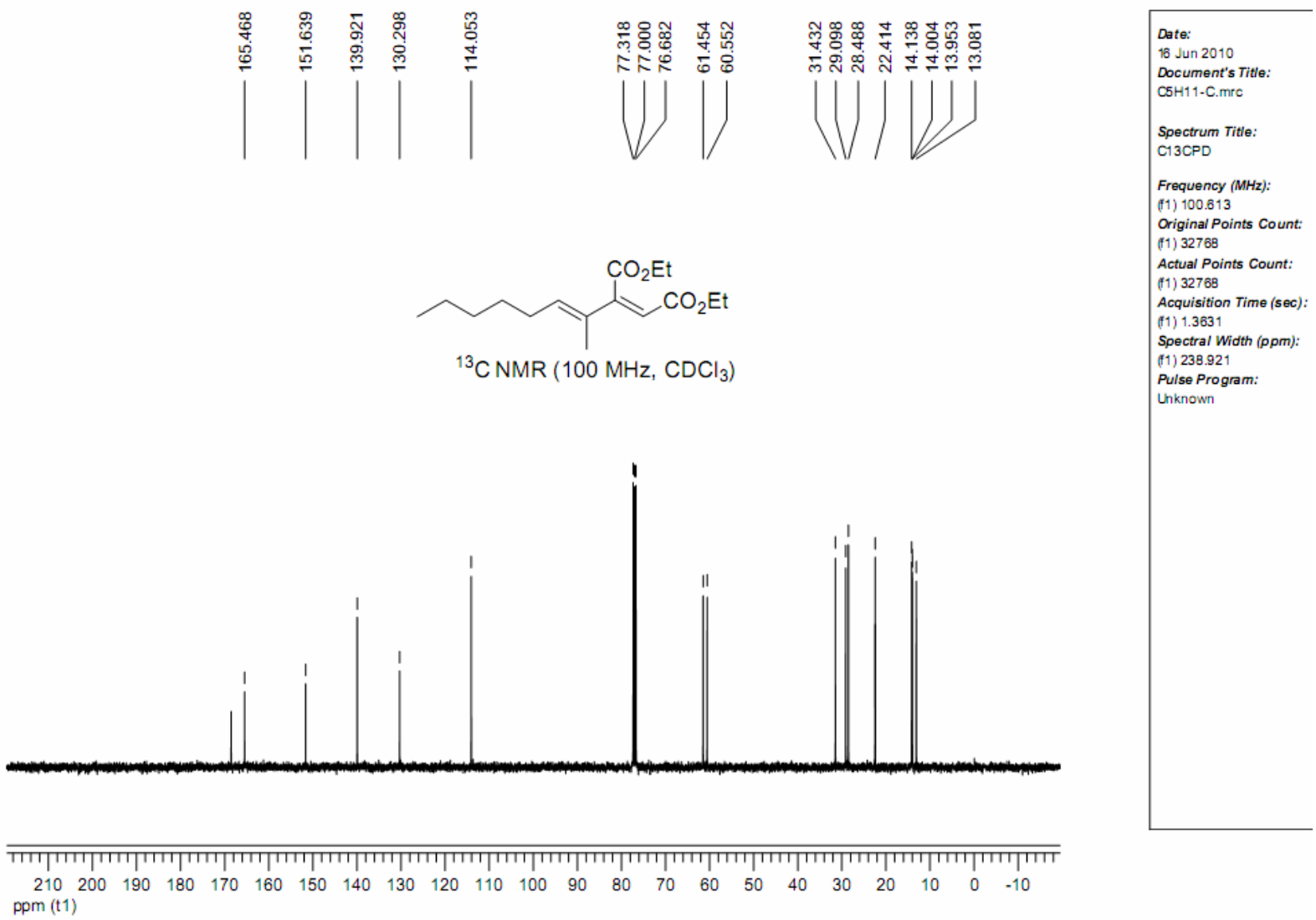
Acquisition Time (sec):
(f1) 1.3631
Spectral Width (ppm):
(f1) 238.920
Pulse Program:
Unknown



Date:
16 Jun 2010
Document's Title:
C5H11-H.mrc

Spectrum Title:
PROTON

Frequency (MHz):
(f1) 400.130
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 3.9846
Spectral Width (ppm):
(f1) 20.553
Pulse Program:
Unknown



Date:
16 Jun 2010
Document's Title:
C5H11-C.mrc

Spectrum Title:
C13CPD

Frequency (MHz):
(f1) 100.613
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 1.3631
Spectral Width (ppm):
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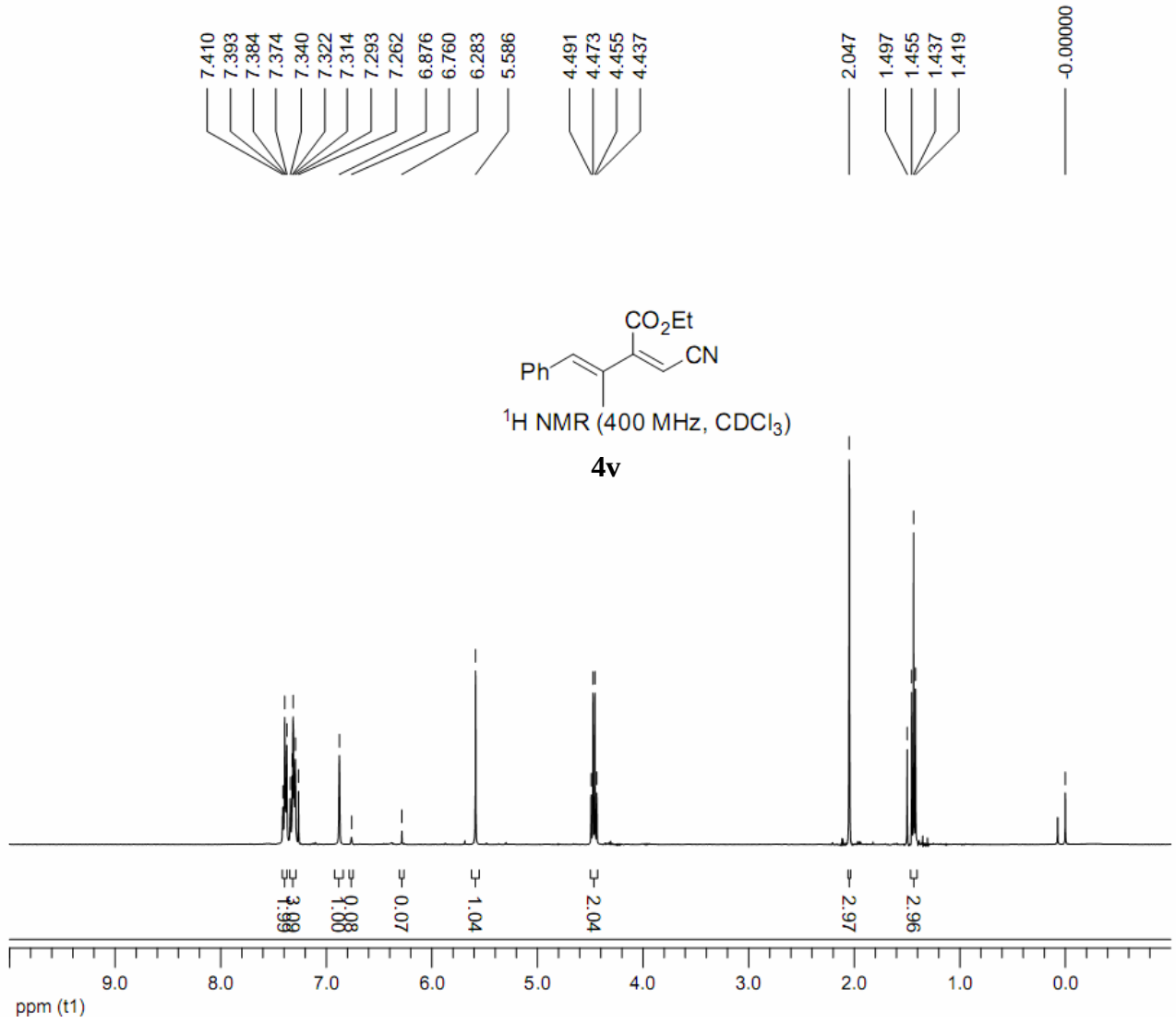
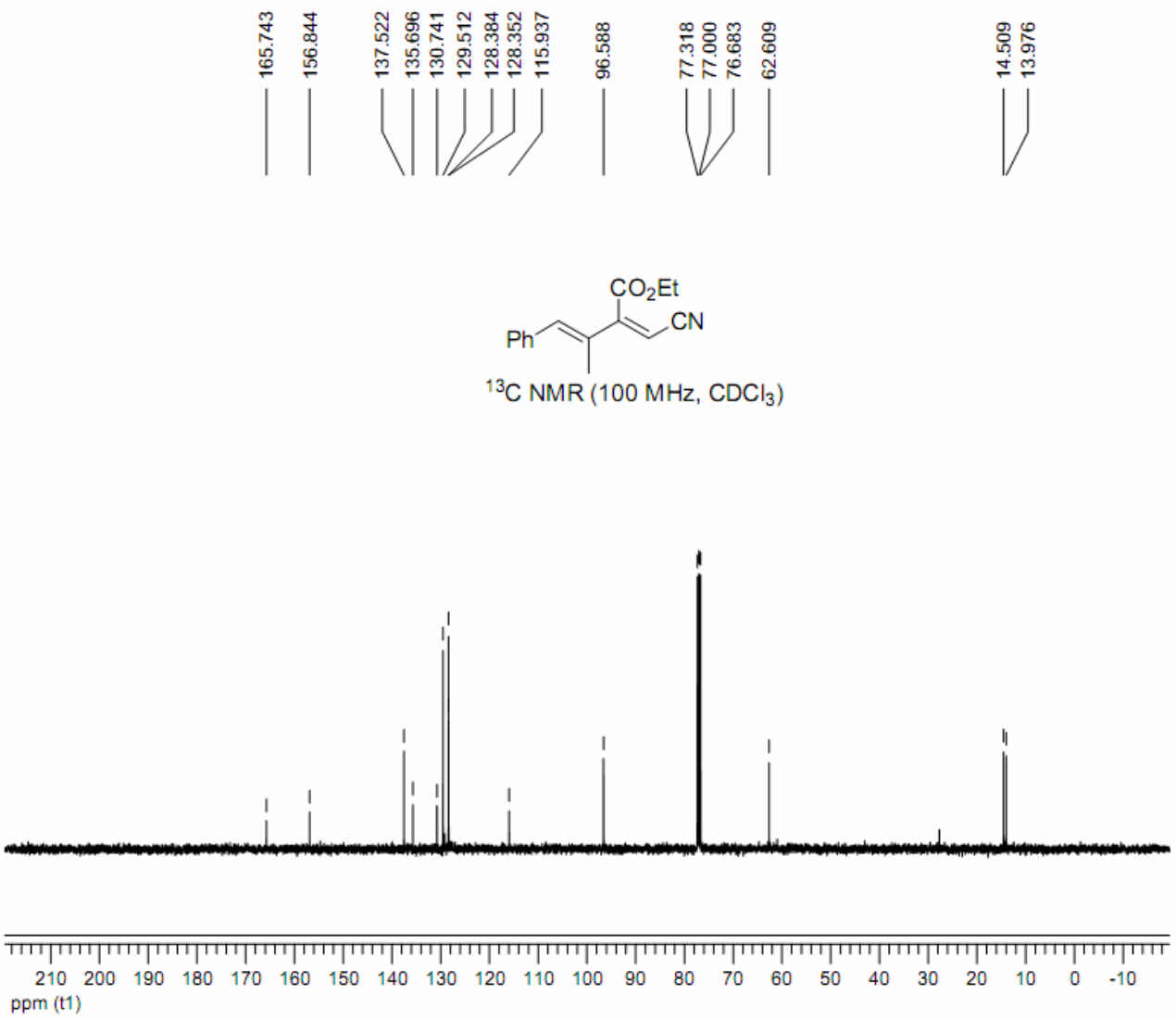
Pulse Program:
Unknown



Date:
17 Jun 2010
Document's Title:
a-CH2CN-allene-Ph-H.m

Spectrum Title:
PROTON

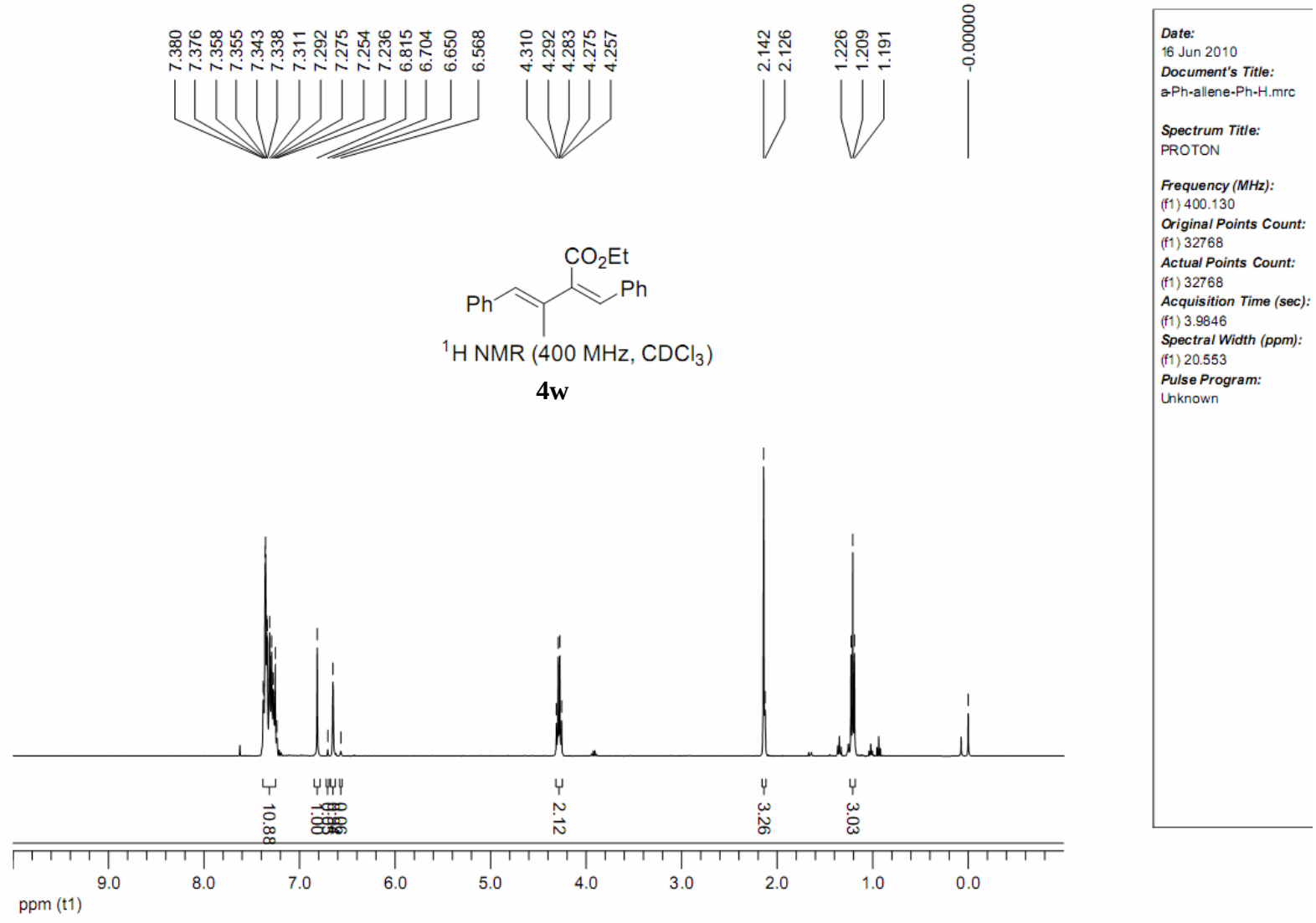
Frequency (MHz):
(f1) 400.130
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 3.9846
Spectral Width (ppm):
(f1) 20.553
Pulse Program:
Unknown



Date:
16 Jun 2010
Document's Title:
a-CH2CN-allene-Ph-C.m

Spectrum Title:
C13CPD

Frequency (MHz):
(f1) 100.613
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 1.3631
Spectral Width (ppm):
(f1) 238.921
Pulse Program:
Unknown



Date:
16 Jun 2010
Document's Title:
a-Ph-allene-Ph-H.mrc

Spectrum Title:
PROTON

Frequency (MHz):
(f1) 400.130
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 3.9846
Spectral Width (ppm):
(f1) 20.553
Pulse Program:
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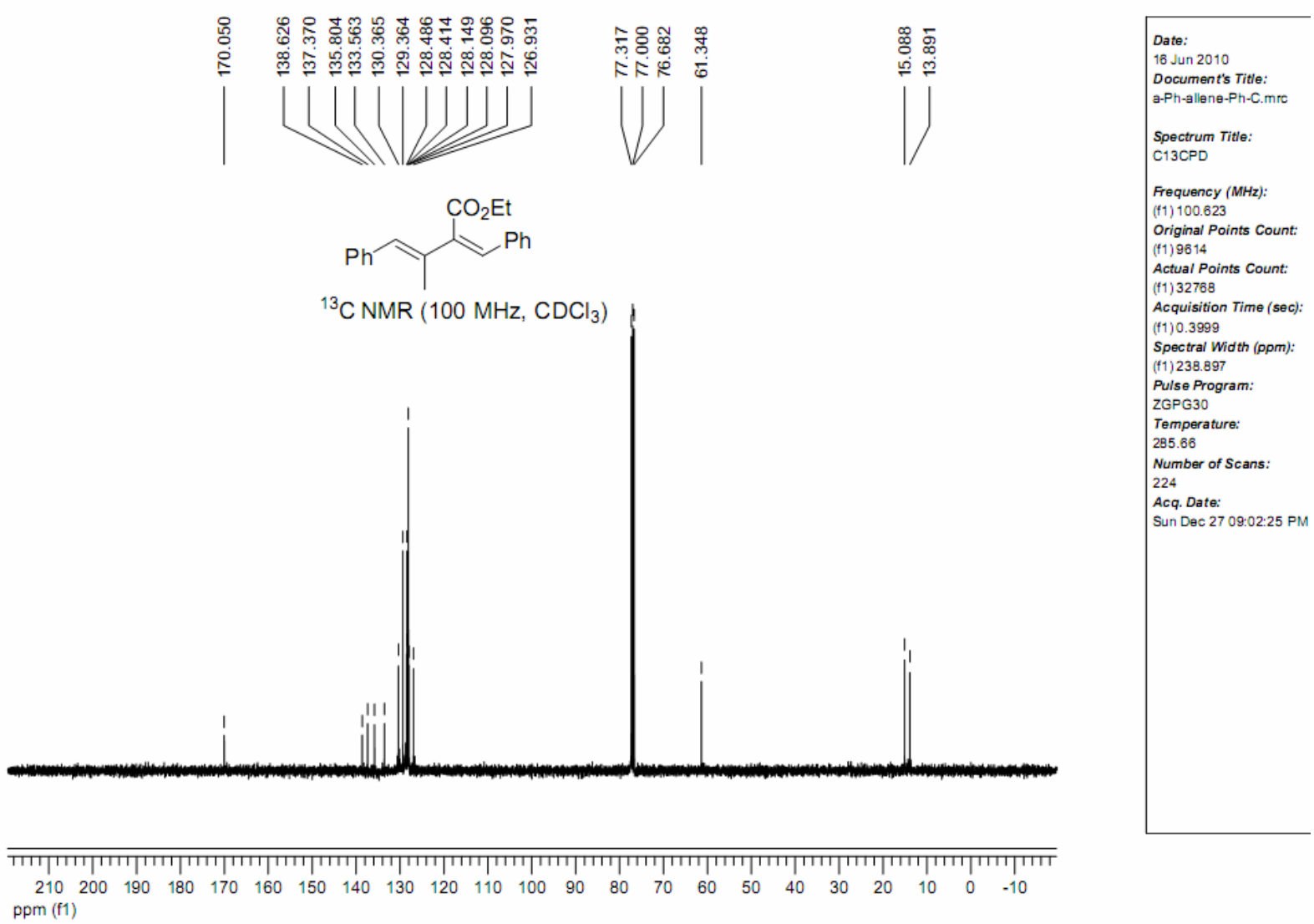

Date:
16 Jun 2010
Document's Title:
a-Ph-allene-Ph-C.mrc

Spectrum Title:
C13CPD

Frequency (MHz):
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Original Points Count:
(f1) 9614
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 0.3999
Spectral Width (ppm):
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Pulse Program:
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Temperature:
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Number of Scans:
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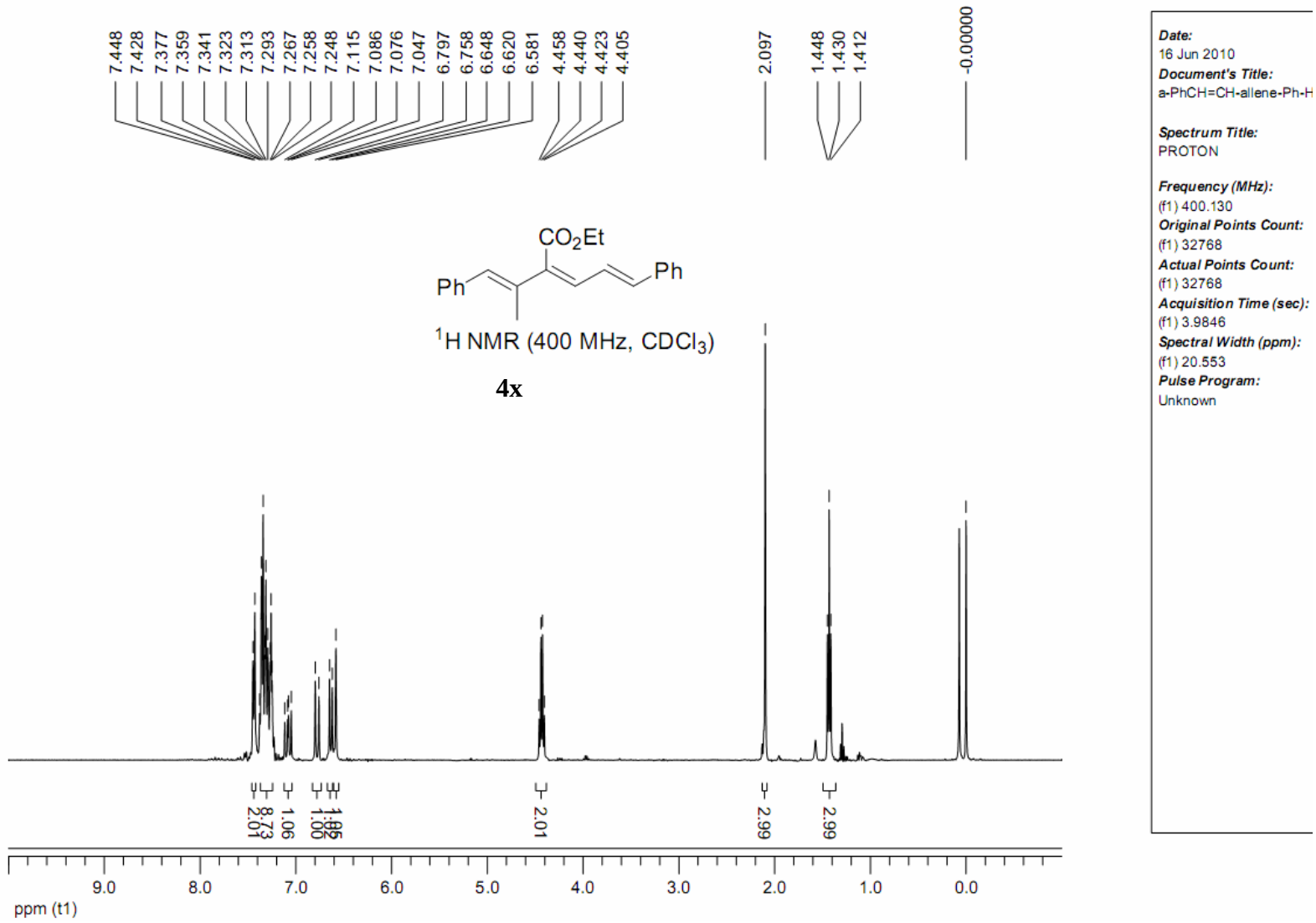
Acq. Date:
Sun Dec 27 09:02:25 PM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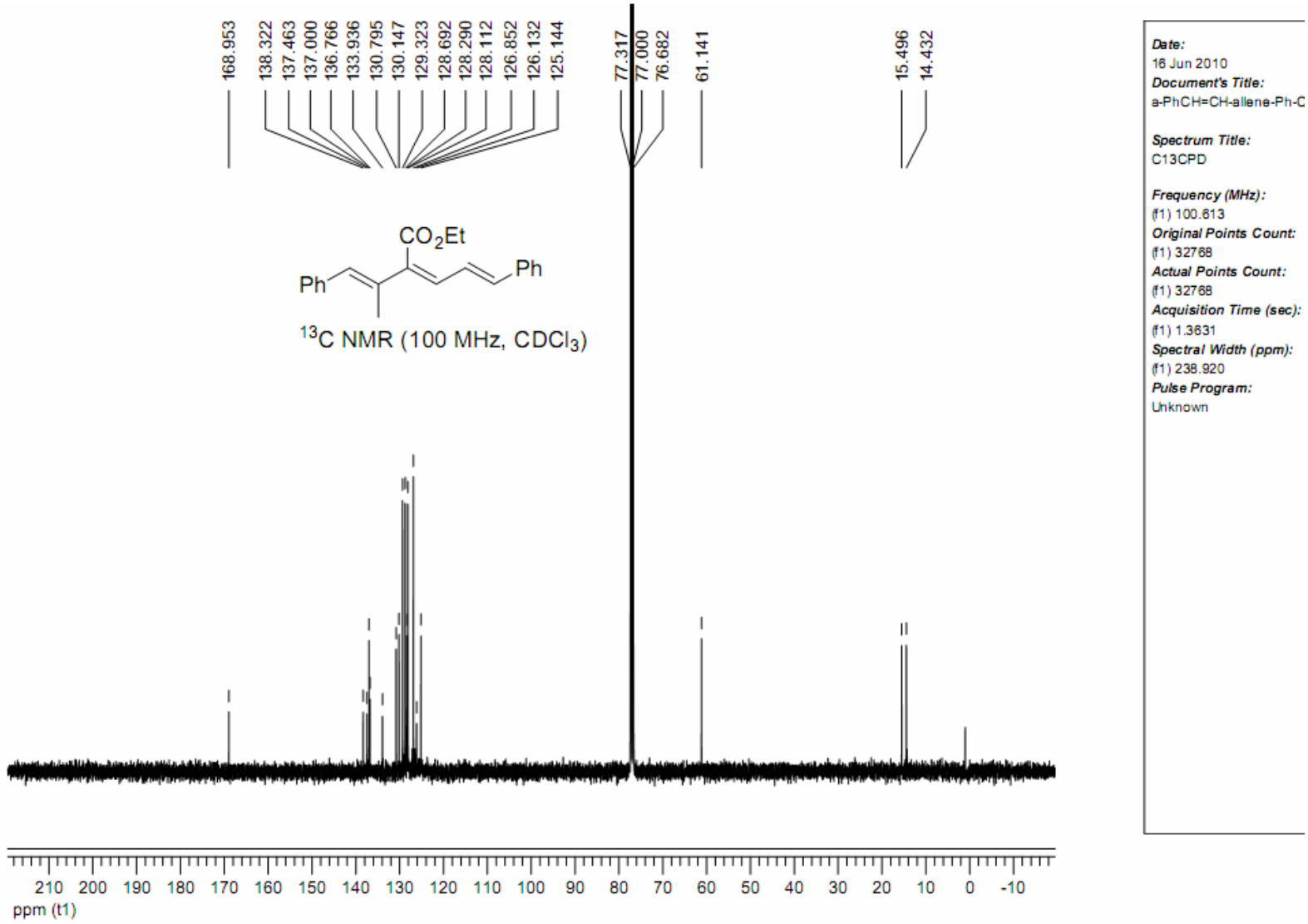
7.428
7.377
7.359
7.341
7.323
7.313
7.293
7.267
7.258
7.248
7.115
7.086
7.076
7.047
6.797
6.758
6.648
6.620
6.581
4.458
4.440
4.423
4.405
2.097
1.448
1.430
1.412
-0.00000
CO2Et
Ph
Ph
1H NMR (400 MHz, CDCl3)
4x
2.01
1.06
2.01
2.99
2.99
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
Date:
16 Jun 2010
Document's Title:
a-PhCH=CH-allene-Ph-H
Spectrum Title:
PROTON
Frequency (MHz):
(f1) 400.130
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 3.9846
Spectral Width (ppm):
(f1) 20.553
Pulse Program:
Unknown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138.322
137.463
137.000
136.766
133.936
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130.147
129.323
128.692
128.290
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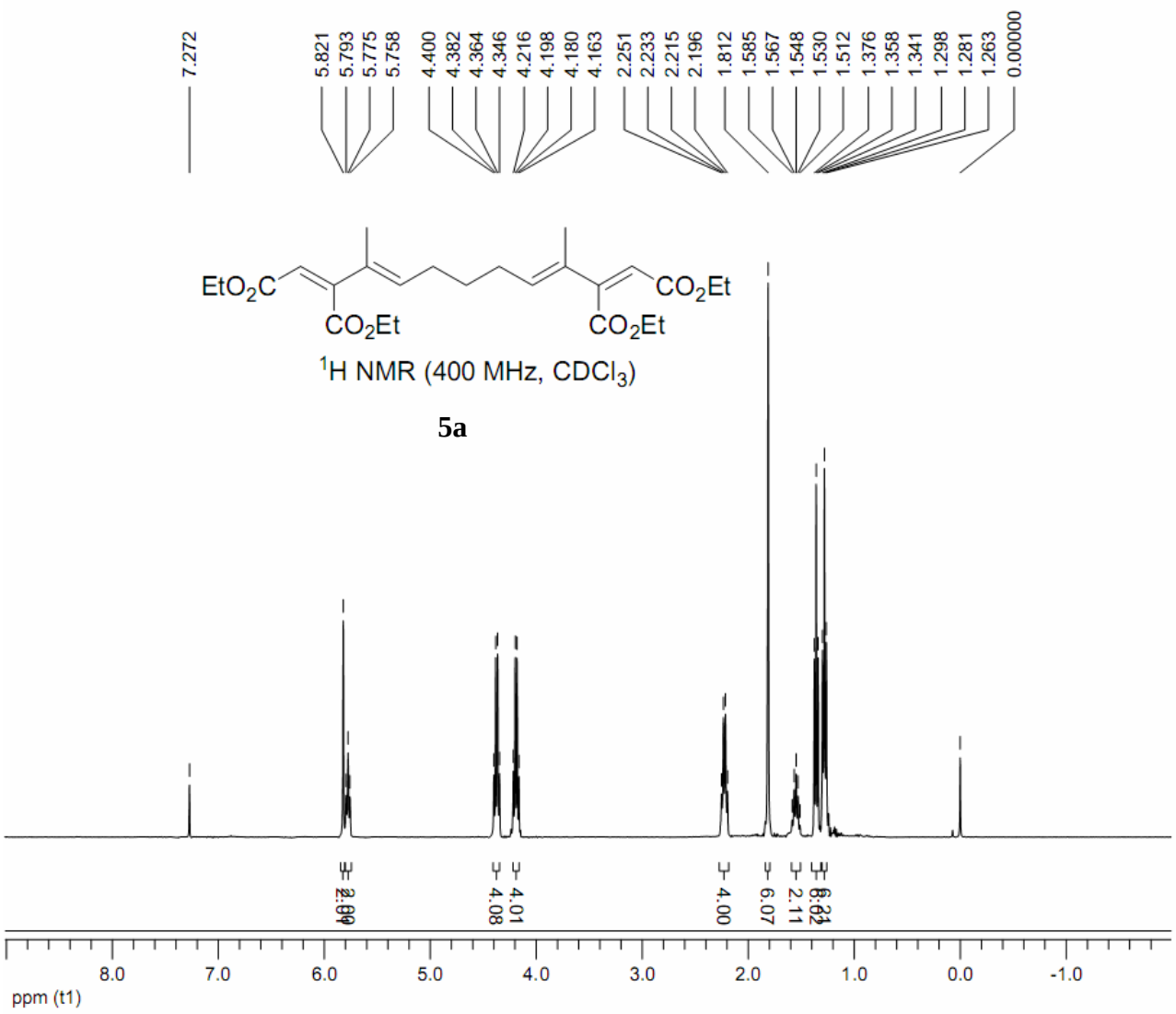
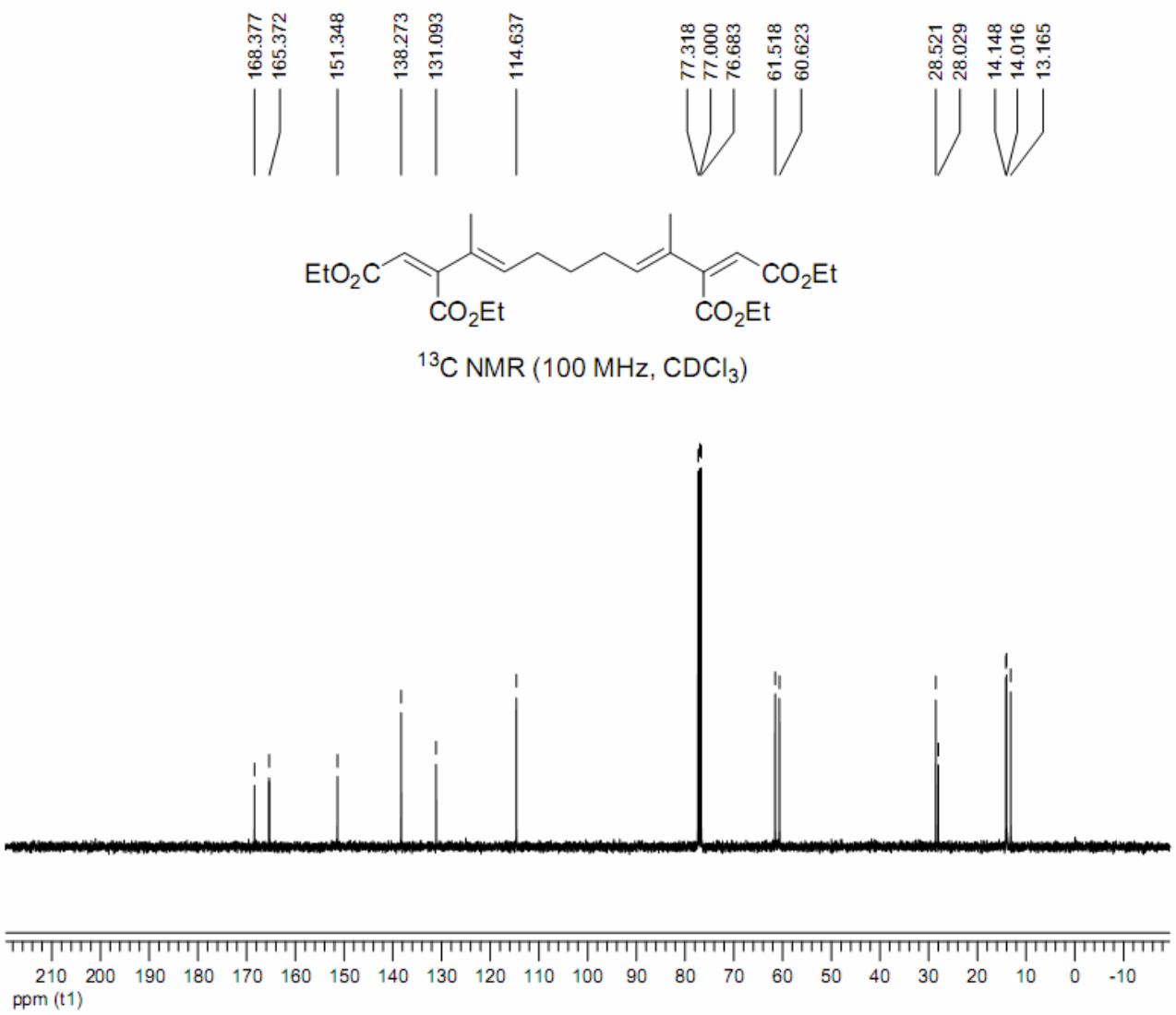
126.852
126.132
125.144
77.317
77.000
76.682
61.141
15.496
14.432
CO2Et
Ph
Ph
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm (t1)
Date:
16 Jun 2010
Document's Title:
a-PhCH=CH-allene-Ph-C
Spectrum Title:
C13CPD
Frequency (MHz):
(f1) 100.613
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 1.3631
Spectral Width (ppm):
(f1) 238.920
Pulse Program:
Unknown



Date:
16 Jun 2010
Document's Title:
di-CH2CH2CH2-H.mrc

Spectrum Title:
PROTON

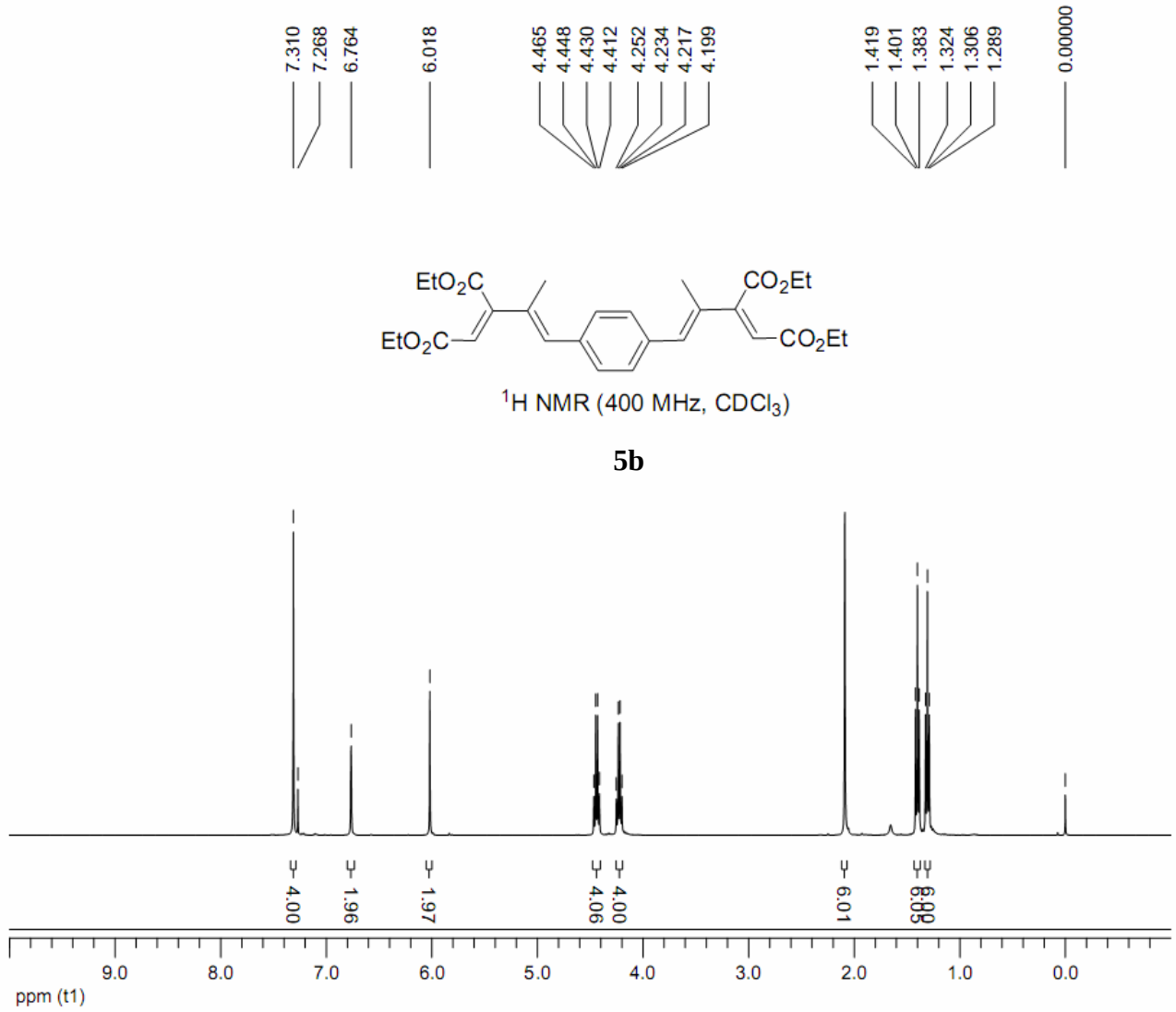
Frequency (MHz):
(f1) 400.130
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 3.9846
Spectral Width (ppm):
(f1) 20.553
Pulse Program:
Unknown



Date:
16 Jun 2010
Document's Title:
di-CH2CH2CH2-C.mrc

Spectrum Title:
C13CPD

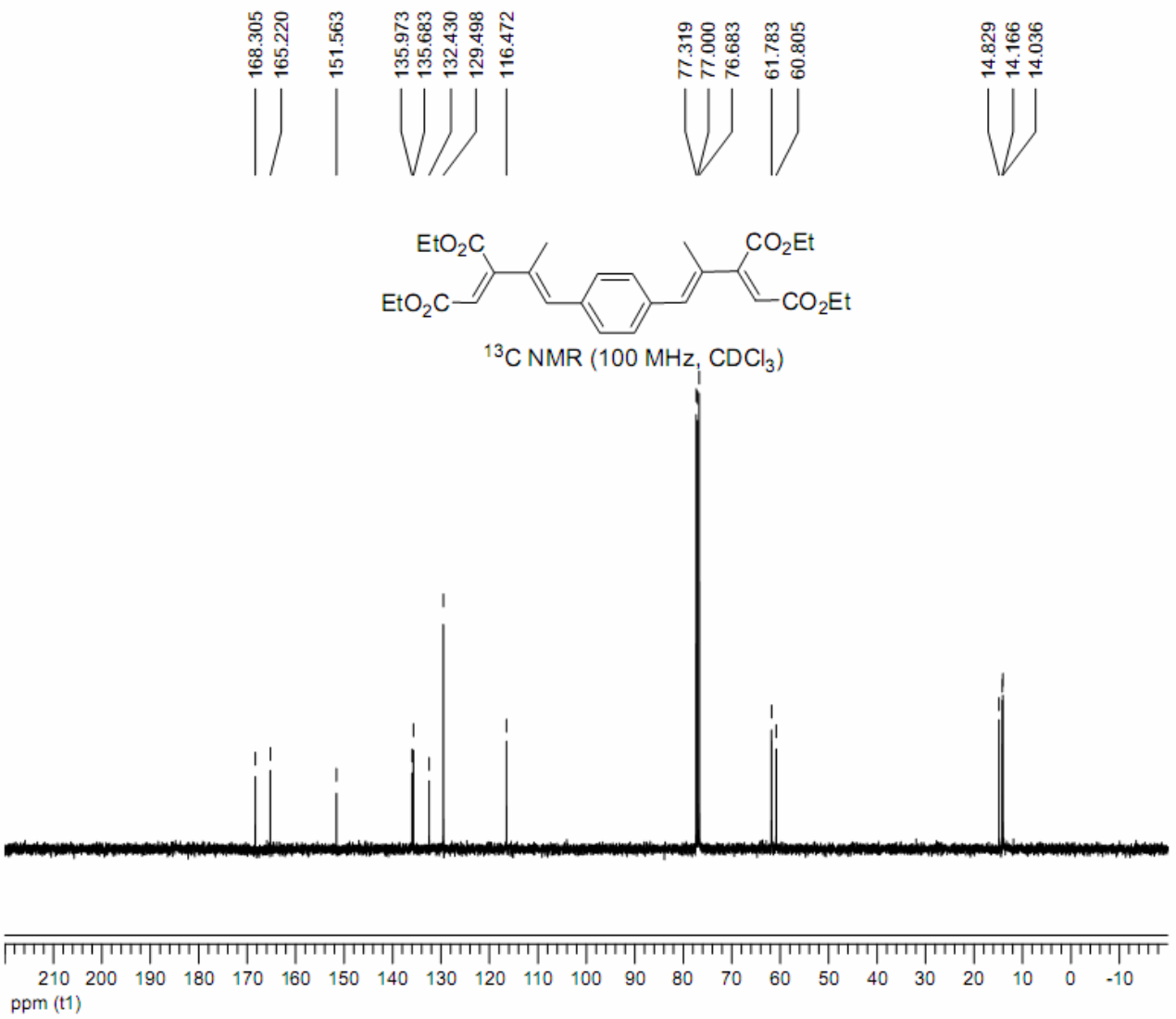
Frequency (MHz):
(f1) 100.613
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 1.3631
Spectral Width (ppm):
(f1) 238.921
Pulse Program:
Unknown



Date:
16 Jun 2010
Document's Title:
di-C6H4-H.mrc

Spectrum Title:
PROTON

Frequency (MHz):
(f1) 400.130
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 3.9846
Spectral Width (ppm):
(f1) 20.553
Pulse Program:
Unknown



Date:
16 Jun 2010
Document's Title:
di-C6H4-C.mrc

Spectrum Title:
C13CPD

Frequency (MHz):
(f1) 100.613
Original Points Count:
(f1) 32768
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
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Spectral Width (ppm):
(f1) 354.968
Pulse Program:
Unknown

VIII. NOESY Spectrum of 4a