Supporting Information for

Gold-Catalyzed Simultaneous Formation of C–C, C=O, and C–F bonds in the Presence of Selectfluor: A Synthesis of Fluoroindenes from Allene Esters

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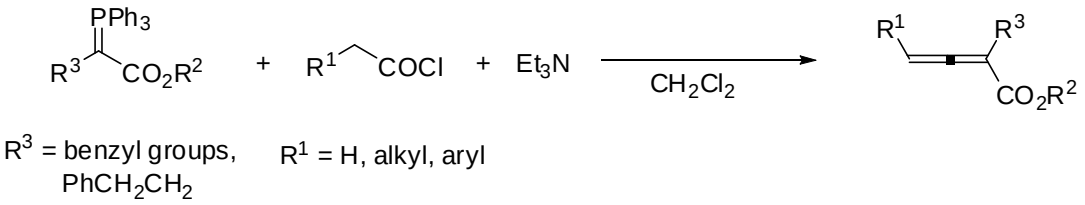
Contents

1. General Information: Melting points are uncorrected. The ^{1}H NMR and ^{13}C NMR spectra were recorded at 25 °C in $CDCl_3$ or DMSO-d_6 at 500 MHz and 125 MHz, respectively, with TMS as the internal standard. Chemical shifts (δ) are expressed in ppm and coupling constants J are given in Hz. The IR spectra were recorded on an FT-IR spectrometer. GC-MS experiments were performed with EI source, LC-MS experiments were performed with ESI source, and high resolution mass spectra (HRMS) were obtained on a TOF MS instrument with ESI or EI source.

2. The experimental procedures for the synthesis of 1a–1x



SCHEME S1

2,3-Allenoates **1a**–**1x** were synthesized according to the literature procedure (Scheme S1).[1] General procedure: A solution of (carbethoxymethylene)triphenylposphorane (1.7 g, 5 mmol) and the benzyl bromide (5.5 mmol) in CH_2Cl_2 (13 mL) was heated under reflux for 4-7 days. The mixture was concentrated and the crude oily foam was co-evaporated with CH_2Cl_2 (2 × 3 mL). The resultant crude phosphonium salt was dissolved in CH_2Cl_2 (13 mL) and Et_3N (1.4 mL, 10 mmol, 2 equiv) was added, followed by stirring for 30 min. AcCl (0.35 mL, 5 mmol) was then slowly added over 30 min with vigorous stirring. The resultant suspension was stirred for 16 h and concentrated. The thick slurry was stirred with Et_2O (30 mL) for 20 min and then organic fractions were concentrated. Column chromatography of the crude oil (EtOAc:hexane = 1:40) afforded the pure

ethyl-2-benzyl-2,3-butadienoate (**1a**).

Ethyl 2-benzylpenta-2,3-dienoate (**1a**).[1] Yellow oil; IR (neat): ν = 1709 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.31–7.19 (m, 5H), 5.50–5.44 (m, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.61 (dd, J_1 = 2.4 Hz, J_2 = 15.0 Hz, 1H), 3.55 (dd, J_1 = 2.4 Hz, J_2 = 15.0 Hz, 1H), 1.72 (d, J = 7.3 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 211.2, 167.2, 139.5, 128.8, 128.1, 126.1, 100.1, 90.0, 60.8, 35.3, 14.2, 13.0; GC-MS (EI): *m/z* (%) = 216.10(21) $[M]^+$.

Ethyl 2-benzylhexa-2,3-dienoate (**1b**).[1] Yellow oil; IR (neat): ν = 1709 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.31–7.21 (m, 5H), 5.55–5.53 (m, 1H), 4.22–4.17 (m, 2H), 3.61 (dd, J_1 = 2.4 Hz, J_2 = 15.0 Hz, 1H), 3.56 (dd, J_1 = 2.4 Hz, J_2 = 15.0 Hz, 1H), 2.08–2.05 (m, 2H), 1.27 (t, J = 7.1 Hz, 3H), 0.97 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 210.4, 167.3, 139.5, 128.9, 128.2, 126.2, 101.3, 97.1, 60.8, 35.4, 21.3, 14.2, 13.2; GC-MS (EI): *m/z* (%) = 230.28(28) $[M]^+$.

Ethyl 2-benzylhepta-2,3-dienoate (**1c**).[2] Yellow oil; IR (neat): ν = 1709 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.31–7.20 (m, 5H), 5.50–5.47 (m, 1H), 4.23–4.18 (m, 2H), 3.60 (dd, J = 2.4 Hz, J_2 = 15.0 Hz, 1H), 3.58 (dd, J_1 = 2.4 Hz, J_2 = 15.0 Hz, 1H), 2.06–2.03 (m, 2H), 1.43–1.41 (m, 2H), 1.28 (t, J = 7.2 Hz, 3H), 0.93 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 210.7, 167.3, 139.6, 128.9, 128.2, 126.2, 100.5, 95.1, 60.8, 35.4, 30.0, 22.1, 14.2, 13.5; GC-MS (EI): *m/z* (%) = 244.20(23) $[M]^+$.

Ethyl 2-benzylocta-2,3-dienoate (**1d**).[3] Yellow oil; IR (neat): ν = 1710 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.31–7.21 (m, 5H), 5.48–5.47 (m, 1H), 4.21–4.18 (m, 2H), 3.59 (dd, J = 2.4 Hz, J_2 = 15.0 Hz, 1H), 3.57 (dd, J_1 = 2.4 Hz, J_2 = 15.0 Hz, 1H),

2.06–2.05 (m, 2H), 1.35–1.26 (m, 7H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 210.6, 167.3, 139.5, 128.9, 128.1, 126.1, 100.5, 95.3, 60.8, 35.3, 30.9, 27.6, 21.9, 14.2, 13.7; GC-MS (EI): *m/z* (%) = 258.20(60) $[M]^+$.

Ethyl 2-benzylnona-2,3-dienoate (**1e**). Yellow oil; IR (neat): ν = 1710 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.31–7.19 (m, 5H), 5.50–5.47 (m, 1H), 4.23–4.18 (m, 2H), 3.60 (dd, J = 2.4 Hz, J_2 = 15.0 Hz, 1H), 3.56 (dd, J_1 = 2.4 Hz, J_2 = 15.0 Hz, 1H), 2.08–2.03 (m, 2H), 1.31–1.26 (m, 9H), 0.91 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 210.6, 167.3, 139.5, 128.9, 128.1, 126.1, 100.5, 95.3, 60.8, 35.3, 31.0, 28.4, 27.8, 22.3, 14.2, 13.9; GC-MS (EI): *m/z* (%) = 272.20(52) $[M]^+$.

Ethyl 2-benzyldeca-2,3-dienoate (**1f**).[2] Yellow oil; IR (neat): ν = 1710 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.30–7.19 (m, 5H), 5.50–5.46 (m, 1H), 4.23–4.16 (m, 2H), 3.60 (dd, J = 2.4 Hz, J_2 = 15.0 Hz, 1H), 3.55 (dd, J_1 = 2.4 Hz, J_2 = 15.0 Hz, 1H), 2.07–2.03 (m, 2H), 1.36–1.26 (m, 11H), 0.91 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 210.6, 167.3, 139.5, 128.9, 128.1, 126.1, 100.6, 95.4, 60.8, 35.4, 31.6, 28.8, 28.6, 27.9, 22.5, 14.2, 14.1; GC-MS (EI): *m/z* (%) = 286.20(49) $[M]^+$.

Ethyl 2-benzyl-5-phenylpenta-2,3-dienoate (**1g**).[1] Yellow oil; IR (neat): ν = 1709 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.32–7.16 (m, 10H), 5.66–5.64 (m, 1H), 4.27–4.22 (m, 2H), 3.60 (dd, J = 2.5 Hz, J_2 = 15.0 Hz, 1H), 3.59 (dd, J_1 = 2.5 Hz, J_2 = 15.0 Hz, 1H), 3.43–3.40 (m, 2H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 211.1, 167.0, 139.1, 138.9, 128.9, 128.6, 128.3, 128.2, 126.4, 126.2, 101.2, 94.8, 60.9, 35.2, 34.5, 14.2; GC-MS (EI): *m/z* (%) = 292.20(6) $[M]^+$.

Ethyl 2-benzyl-4-phenylbuta-2,3-dienoate (**1h**).[4] Yellow oil; IR (neat): ν = 1710 (C=O)

cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.29–7.14 (m, 10H), 6.47 (t, J = 2.3 Hz, 1H), 4.20–4.12 (m, 2H), 3.71 (dd, J = 2.5 Hz, J_2 = 14.8 Hz, 1H), 3.66 (dd, J_1 = 2.5 Hz, J_2 = 14.8 Hz, 1H), 1.19 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 213.1, 166.4, 139.1, 132.3, 129.0, 128.8, 128.4, 127.8, 127.4, 126.5, 104.4, 98.6, 61.3, 35.7; GC-MS (EI): *m/z* (%) = 278.20(5) $[M]^+$.

Methyl 2-benzylpenta-2,3-dienoate (**1i**). Yellow oil; IR (neat): ν = 1715 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.31–7.22 (m, 5H), 5.50–5.45 (m, 1H), 3.74 (s, 3H), 3.61 (dd, J = 2.5 Hz, J_2 = 15.0 Hz, 1H), 3.55 (dd, J_1 = 2.5 Hz, J_2 = 15.0 Hz, 1H), 1.72 (d, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 211.3, 167.7, 139.4, 128.8, 128.2, 126.2, 99.8, 90.2, 52.1, 35.4, 13.1; GC-MS (EI): *m/z* (%) = 202.10(23) $[M]^+$.

Propyl 2-benzylpenta-2,3-dienoate (**1j**). Yellow oil; IR (neat): ν = 1711 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.31–7.19 (m, 5H), 5.49–5.44 (m, 1H), 4.09 (t, J = 6.5 Hz, 2H), 3.60 (dd, J = 2.5 Hz, J_2 = 15.0 Hz, 1H), 3.55 (dd, J_1 = 2.5 Hz, J_2 = 15.0 Hz, 1H), 1.72–1.63 (m, 5H), 0.93 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 211.3, 167.3, 139.6, 128.8, 128.2, 126.2, 100.1, 90.0, 66.4, 35.4, 22.0, 13.0, 10.3; GC-MS (EI): *m/z* (%) = 230.20(9) $[M]^+$.

Isopropyl 2-benzylpenta-2,3-dienoate (**1k**). Yellow oil; IR (neat): ν = 1707 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.31–7.20 (m, 5H), 5.47–5.44 (m, 1H), 5.07–5.02 (m, 1H), 3.60 (dd, J = 2.0 Hz, J_2 = 15.0 Hz, 1H), 3.53 (dd, J_1 = 2.0 Hz, J_2 = 15.0 Hz, 1H), 1.72 (d, J = 7.0 Hz, 3H), 1.24 (d, J = 6.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 211.2, 166.7, 140.0, 128.9, 128.1, 126.1, 100.5, 89.9, 68.2, 35.4, 21.8, 21.77, 13.0; GC-MS (EI): *m/z* (%) = 230.10(1) $[M]^+$.

Butyl 2-benzylpenta-2,3-dienoate (**1l**). Yellow oil; IR (neat): ν = 1712 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.32–7.22 (m, 5H), 5.49–5.45 (m, 1H), 4.15 (t, J = 7.0 Hz, 2H), 3.62 (dd, J = 1.5 Hz, J_2 = 15.0 Hz, 1H), 3.56 (dd, J_1 = 1.5 Hz, J_2 = 15.0 Hz, 1H), 1.72 (d, J = 7.3 Hz, 3H), 1.66–1.61 (m, 2H), 1.40–1.36 (m, 2H), 0.95 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 211.3, 167.3, 139.6, 128.8, 128.2, 126.2, 100.1, 90.0, 64.8, 35.4, 30.7, 19.1, 13.7, 13.0; GC-MS (EI): *m/z* (%) = 244.20(8) $[M]^+$.

Allyl 2-benzylpenta-2,3-dienoate (**1m**). Yellow oil; IR (neat): ν = 1713 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.34–7.28 (m, 5H), 6.00–5.92 (m, 1H), 5.51–5.50 (m, 1H), 5.35–5.23 (m, 2H), 4.67 (d, J = 5.5 Hz, 2H), 3.65 (d, J = 15.0 Hz, 1H), 3.59 (d, J = 15.0 Hz, 1H), 1.74 (d, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 211.3, 166.8, 139.3, 132.3, 128.8, 128.1, 126.1, 117.5, 99.8, 90.1, 65.3, 35.3, 12.9; GC-MS (EI): *m/z* (%) = 228.10(1) $[M]^+$.

Methyl 2-benzylocta-2,3-dienoate (**1n**). Yellow oil; IR (neat): ν = 1713 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.30–7.19 (m, 5H), 5.50–5.47 (m, 1H), 3.74 (s, 3H), 3.60 (dd, J_1 = 2.5 Hz, J_2 = 15.0 Hz, 1H), 3.55 (dd, J_1 = 2.5 Hz, J_2 = 15.0 Hz, 1H), 2.08–2.03 (m, 2H), 1.33–1.32 (m, 4H), 0.93–0.86 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 210.7, 167.8, 139.4, 128.9, 128.2,126.2, 100.3, 95.5, 52.1, 35.4, 30.9, 27.6, 22.0, 13.8; GC-MS (EI): *m/z* (%) = 244.20(36) $[M]^+$.

Methyl 2-benzyl-4-phenylbuta-2,3-dienoate (**1o**). Yellow oil; IR (neat): ν = 1716 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.36–7.22 (m, 10H), 6.55 (t, J = 2.0 Hz, 1H), 3.76–3.73 (m, 5H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 213.1, 166.8, 138.9, 132.0, 128.9, 128.8, 128.3, 127.8, 127.3, 126.4, 104.0, 98.6, 52.4, 35.6; GC-MS (EI): *m/z* (%) =

264.20(7) $[M]^+$.

Ethyl 2-(3-methylbenzyl)penta-2,3-dienoate (**1p**). Yellow oil; IR (neat): ν = 1711 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.21–7.18 (m, 1H), 7.08–7.03 (m, 3H), 5.50–5.46 (m, 1H), 4.21–4.18 (m, 2H), 3.58 (dd, J_1 = 2.0 Hz, J_2 = 14.5 Hz, 1H), 3.52 (dd, J_1 = 2.0 Hz, J_2 = 14.5 Hz, 1H), 2.36 (s, 3H), 1.74 (d, J = 7.0 Hz, 3H), 1.28 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 211.3, 167.3, 139.5, 137.7, 129.7, 128.1, 126.9, 125.8, 100.1, 89.9, 60.9, 35.3, 21.4, 14.2, 13.1; GC-MS (EI): *m/z* (%) = 230.20(25) $[M]^+$.

Ethyl 2-(3-chlorobenzyl)penta-2,3-dienoate (**1q**). Yellow oil; IR (neat): ν = 1709 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.22–7.16 (m, 4H), 5.51–5.46 (m, 1H), 4.20–4.16 (m, 2H), 3.55 (d, J_1 = 2.5 Hz, J_2 = 15.0 Hz, 1H), 3.50 (dd, J_1 = 2.5 Hz, J_2 = 15.0 Hz, 1H), 1.72 (d, J = 7.0 Hz, 3H), 1.26 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 211.2, 167.0, 141.6, 133.9, 129.4, 129.0, 127.1, 126.4, 99.6, 90.4, 61.0, 35.1, 14.2, 13.0; GC-MS (EI): *m/z* (%) = 250.10(25) $[M]^+$.

Ethyl 2-(3-bromobenzyl)penta-2,3-dienoate (**1r**). Yellow oil; IR (neat): ν = 1712 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.38–7.30 (m, 2H), 7.16–7.11 (m, 2H), 5.50–5.46 (m, 1H), 4.20–4.15 (m, 2H), 3.54 (d, J_1 = 2.0 Hz, J_2 = 15.0 Hz, 1H), 3.49 (dd, J_1 = 2.0 Hz, J_2 = 15.0 Hz, 1H), 1.71 (d, J = 7.0 Hz, 3H), 1.25 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 211.1, 166.8, 141.8, 131.8, 129.6, 129.2, 127.4, 122.1, 99.5, 90.3, 60.9, 34.9, 14.1, 12.9; GC-MS (EI): *m/z* (%) = 294.10(6) $[M]^+$.

Ethyl 2-(2-methylbenzyl)penta-2,3-dienoate (**1s**). Yellow oil; IR (neat): ν = 1712 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.19–7.12 (m, 4H), 5.40–5.34 (m, 1H), 4.24–4.21 (m, 2H), 3.62 (d, J_1 = 2.5 Hz, J_2 = 15.5 Hz, 1H), 3.56 (dd, J_1 = 2.5 Hz, J_2 = 15.5 Hz, 1H), 2.33

(s, 3H), 1.62 (d, J = 7.0 Hz, 3H), 1.30 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 211.0, 167.3, 137.3, 136.5, 130.0, 129.7, 126.4, 125.7, 99.6, 90.3, 60.9, 32.7, 19.3, 14.3, 12.8; GC-MS (EI): *m/z* (%) = 230.20(52) $[M]^+$.

Ethyl 2-(4-methylbenzyl)penta-2,3-dienoate (**1t**). Yellow oil; IR (neat): ν = 1709 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.17 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 5.51–5.46 (m, 1H), 4.22–4.19 (m, 2H), 3.59 (d, J_1 = 2.0 Hz, J_2 = 14.5 Hz, 1H), 3.53 (dd, J_1 = 2.0 Hz, J_2 = 14.5 Hz, 1H), 2.36 (s, 3H), 1.75 (d, J = 7.0 Hz, 3H), 1.29 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 211.1, 167.2, 136.4, 135.5, 128.8, 128.6, 100.2, 89.8, 60.8, 34.9, 21.0, 14.2, 13.0; GC-MS (EI): *m/z* (%) = 230.20(17) $[M]^+$.

Ethyl 2-benzylbuta-2,3-dienoate (**1u**).[1] Yellow oil; IR (neat): ν = 1712 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.34–7.23 (m, 5H), 5.12 (d, J = 5.0 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 3.62 (d, J = 5.0 Hz, 1H), 1.30 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.7, 139.0, 128.7, 128.1, 126.2, 100.2, 79.0, 60.9, 34.8, 14.1; GC-MS (EI): *m/z* (%) = 202.10(2) $[M]^+$.

tert-Butyl 2-benzylpenta-2,3-dienoate (**1v**).[5] Colorless oil; IR (neat): ν = 1705 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.32–7.18 (m, 5H), 5.43–5.41 (m, 1H), 3.56 (d, J_1 = 2.3 Hz, J_2 = 15.0 Hz, 1H), 3.49 (dd, J_1 = 2.3 Hz, J_2 = 15.0 Hz, 1H), 1.70 (d, J = 7.3 Hz, 1H), 1.45 (s, 9H); GC-MS (EI): *m/z* (%) = 244.10(2) $[M]^+$.

Ethyl 2-benzyl-4-methylpenta-2,3-dienoate (**1w**). Yellow oil; IR (neat): ν = 1708 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.31–7.21 (m, 5H), 4.19 (q, J = 7.0 Hz, 2H), 3.57 (s, 2H), 1.72 (s, 6H), 1.27 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 208.7, 167.5, 139.8, 128.8, 128.0, 125.9, 99.8, 98.5, 60.5, 35.6, 19.2, 14.2; GC-MS (EI): *m/z* (%) =

230.20(40) $[M]^+$.

Ethyl 2-phenethylpenta-2,3-dienoate (**1x**). Yellow oil; IR (neat): ν = 1709 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.31–7.28 (m, 2H), 7.22–7.19 (m, 3H), 5.48–5.44 (m, 1H), 4.22 (q, J = 7.5 Hz, 2H), 2.80–2.76 (m, 2H), 2.61–2.54 (m, 2H), 1.66 (d, J = 7.0 Hz, 3H), 1.30 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 210.7, 167.5, 141.6, 128.6, 128.3, 125.8, 99.4, 90.0, 60.8, 34.3, 30.3, 14.3, 13.1; GC-MS (EI): *m/z* (%) = 230.20(29) $[M]^+$.

3. X-ray structural data for product 2q (CCDC 873586)

Crystal data

$C_{14}H_{12}ClFO_3$
M_r = 282.69
Monoclinic, P21
Hall synbol: P 2yb
a = 8.1890 (6) Å
b = 7.1850 (5) Å
c = 11.2590 (7) Å
α = 90.00°
β = 93.555 (2)°
γ = 90.00°
V = 661.18 (8) $Å^3$

F_{000} = 292
D_x = 1.42 Mg m^{-3}
Mo Kα radiation
Cell parameters from 3934 reflections
λ= 0.71073 Å
θ = 3.2-27.4°
μ = 0.301 mm^{-1}
T = 296 (1) K
Chunk, colourless
0.45 x 0.42 x 0.27 mmm
Z = 2

Data collection

Riguku RAXIS-RAPID diffractometer
Detector resolution: 10.00 pixels mm-1
ω scans
Absorption correction: multi-scan
(ABSCOR; Higashi, 1995)
T_{min} = 0.8764, T_{max} = 0.9231
6553 measured reflections

1454 reflections with $I > 2\sigma(I)$
R_{int} = 0.0217
θ_{max} = 27.48°
h = -10→10
k = -9→9
l = -14→14
2906 independent reflections

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0478
$wR(F^2)$ = 0.1494
S = 1.004
172 parameters
2906 reflections
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2)+(0.0405P)^2+0.6556P]$, $P=(F_o^2+2F_c^2)/3$
$(\triangle/\sigma)_{max} < 0.000$
$\triangle\rho_{max}$ = 0.439 e $Å^{-3}$
$\triangle\rho_{min}$ = -0.362 e $Å^{-3}$
Extinction correction: Larson (1970)

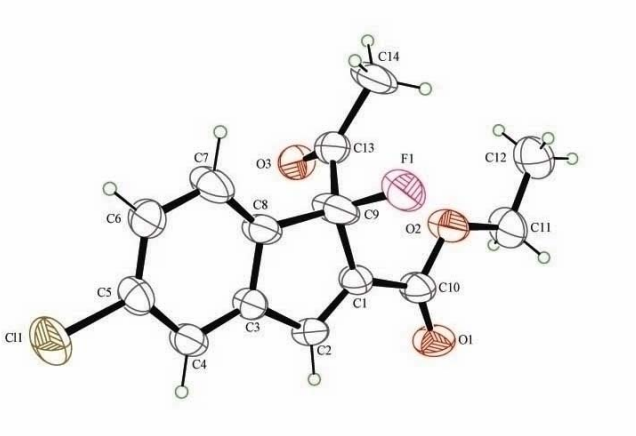
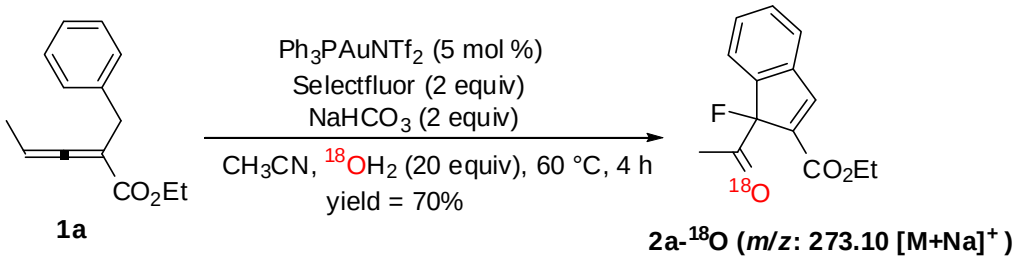


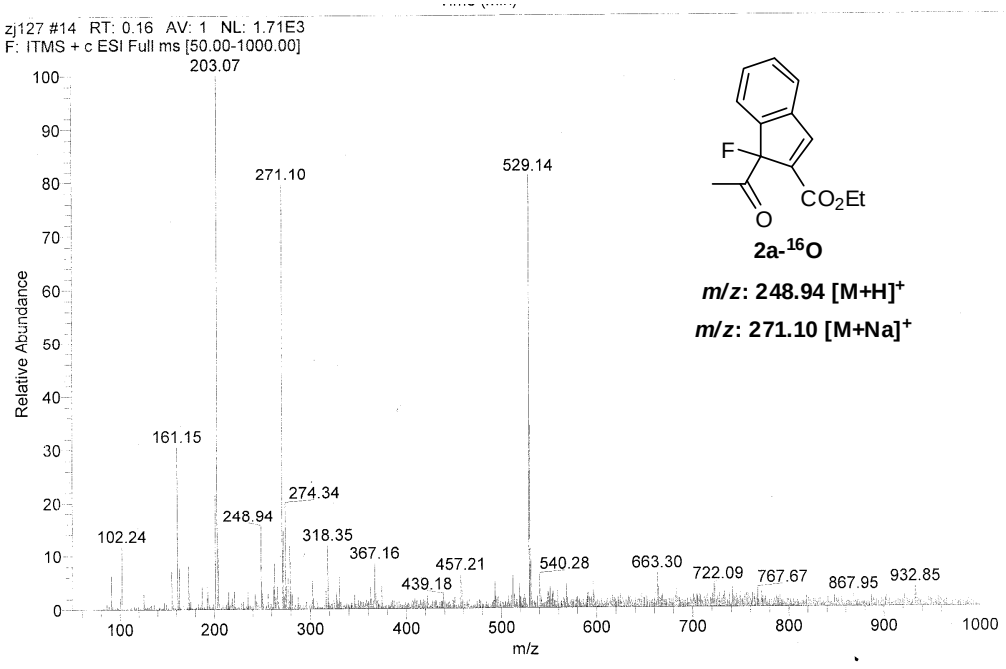
FIGURE S1. X-Ray crystal structure of **2q** (50% thermal ellipsoid)

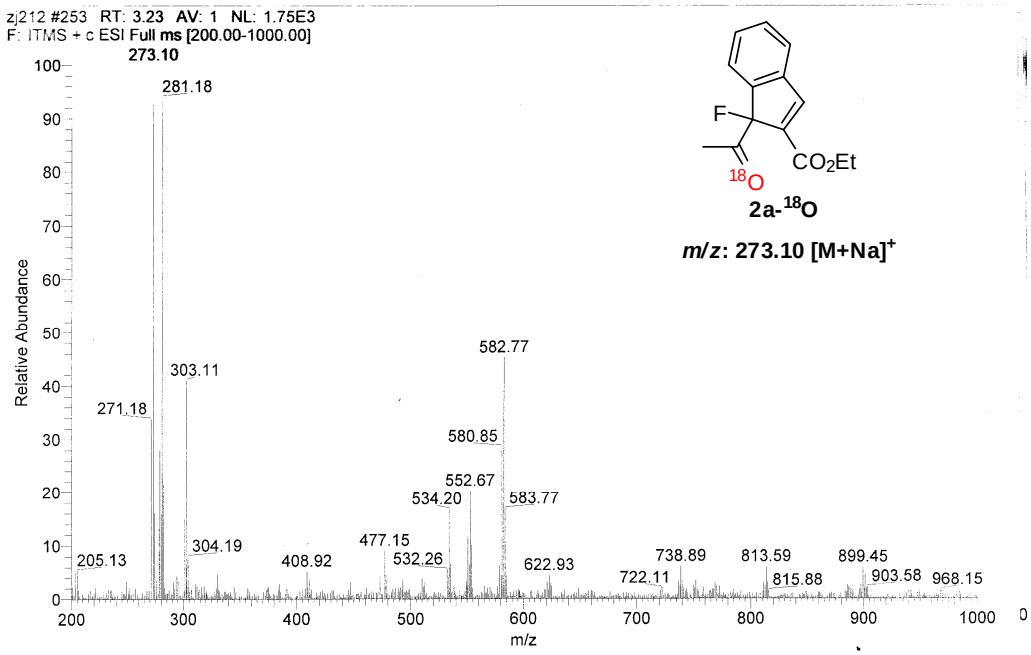
4. Preliminary Mechanistic Studies

4.1 O^{18}-Isotope Labelling Studies

SCHEME S2. O^{18}-Isotope Labelling Studies

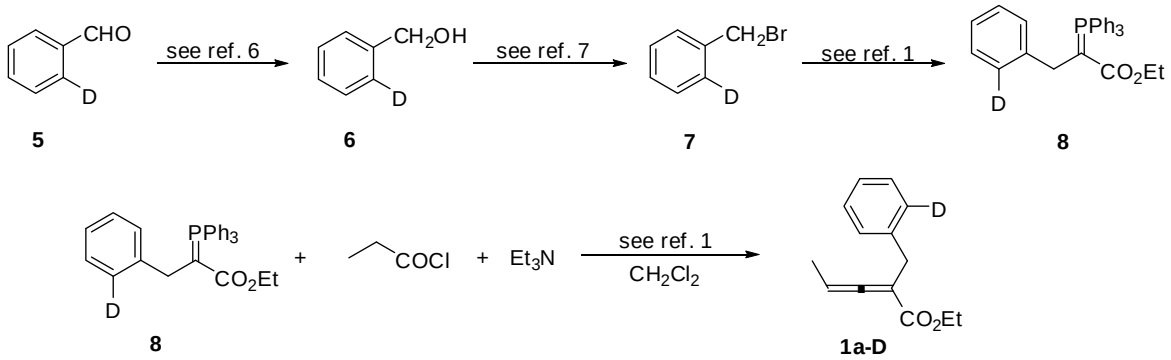






4.2 Determination of Intramolecular Kinetic Isotope Effect

Preparation of 1a-D



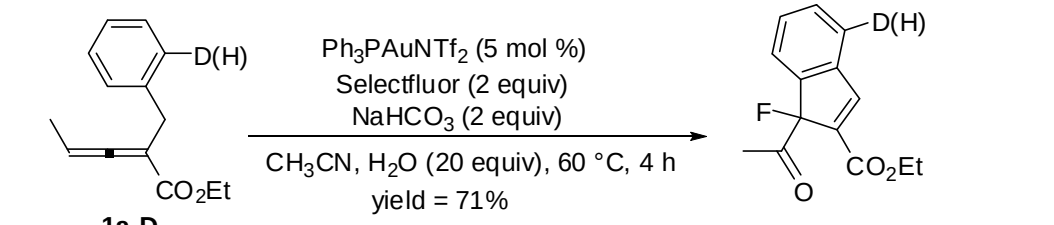
SCHEME S3

The synthesis of **1a-D** was according to the literature procedure (Scheme S3).[1] A solution of (carbethoxymethylene)triphenylposphorane (1.7 g, 5 mmol) and the d_1-benzyl bromide **7** (>99% D-enrichment, 0.95 g, 5.5 mmol) (synthesized from reduction of d_1-benzaldehyde **5**[6] followed by bromination of the resultant d_1-benzyl alcohol **6**[7]) in

CH_2Cl_2 (13 mL) was heated under reflux for 4 days. The mixture was concentrated and the crude oily foam was co-evaporated with CH_2Cl_2 (2 × 3 mL). The resultant crude phosphonium salt was dissolved in CH_2Cl_2 (13 mL) and Et_3N (1.4 mL, 10 mmol, 2 equiv) was added, followed by stirring for 30 min. AcCl (0.35 mL, 5 mmol) was then slowly added over 30 min with vigorous stirring. The resultant suspension was stirred for 16 h and concentrated. The thick slurry was stirred with Et_2O (30 mL) for 20 min and then organic fractions were concentrated. Column chromatography of the crude oil (EtOAc:hexane = 1:40) afforded the pure ethyl-2-benzyl-2,3-butadienoate-d_1 **1a-D** (>99% D-enrichment).

Analytical data of **1a-D** (>99% D-enrichment): Yellow oil; IR (neat): ν = 1712 (C=O) cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz): δ 7.28–7.19 (m, 4H), 5.64–5.60 (m, 1H), 4.13–4.07 (m, 2H), 3.52 (dd, J_1 = 2.0 Hz, J_2 = 15.0 Hz, 1H), 3.46 (dd, J_1 = 2.0 Hz, J_2 = 15.0 Hz, 1H), 1.64 (d, J = 7.5 Hz, 3H), 1.16 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 211.2, 167.2, 139.4, 128.8, 128.2, 128.0, 126.2, 100.1, 90.0, 60.9, 35.3, 14.2, 13.0; GC-MS (EI): m/z = 217.20(26) $[M]^+$.

Determination of Intramolecular Kinetic Isotope Effect

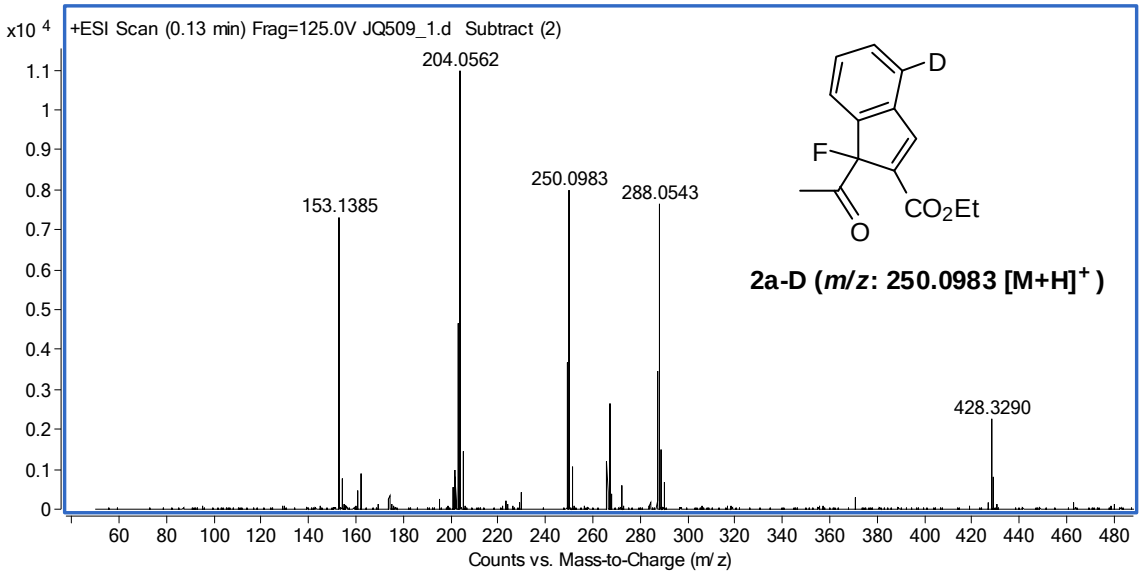


1a-D

(>99% D-enrichment)

2a-D (*m/z*: 250.0983 $[M+H]^+$)

(70% D-enrichment)



SCHEME S4

In a 10-mL flask, $Ph_3PAuNTf_2$ (7.4 mg, 0.01 mmol), Selectfluor (141 mg, 0.4 mmol), $NaHCO_3$ (34 mg, 0.4 mmol), H_2O (72 mg, 4 mmol), and CH_3CN (1 mL) were added. The mixture was stirred at rt for 5 min before a CH_3CN solution (1 mL) of **1a-D** (>99% Deuterium-enrichment, 43.4 mg, 0.2 mmol) was added. Then the mixture was stirred at 60 °C for 4 h. Upon completion, the resulting mixture was diluted with CH_2Cl_2 (10 mL) and filtered through Celite. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100-200 mesh) using petroleum ether-EtOAc (6:1, v/v) as an eluent to give a mixture of **2a-D** & **2a** (35.4 mg, 71% yield). ^{1}H NMR analysis of the isolated mixture showed the ration of **2a-D**:**2a** as 70:30. Based on this result, the kinetic isotope effect is caculated to be $k_H / k_D = 2.3$.

5. References

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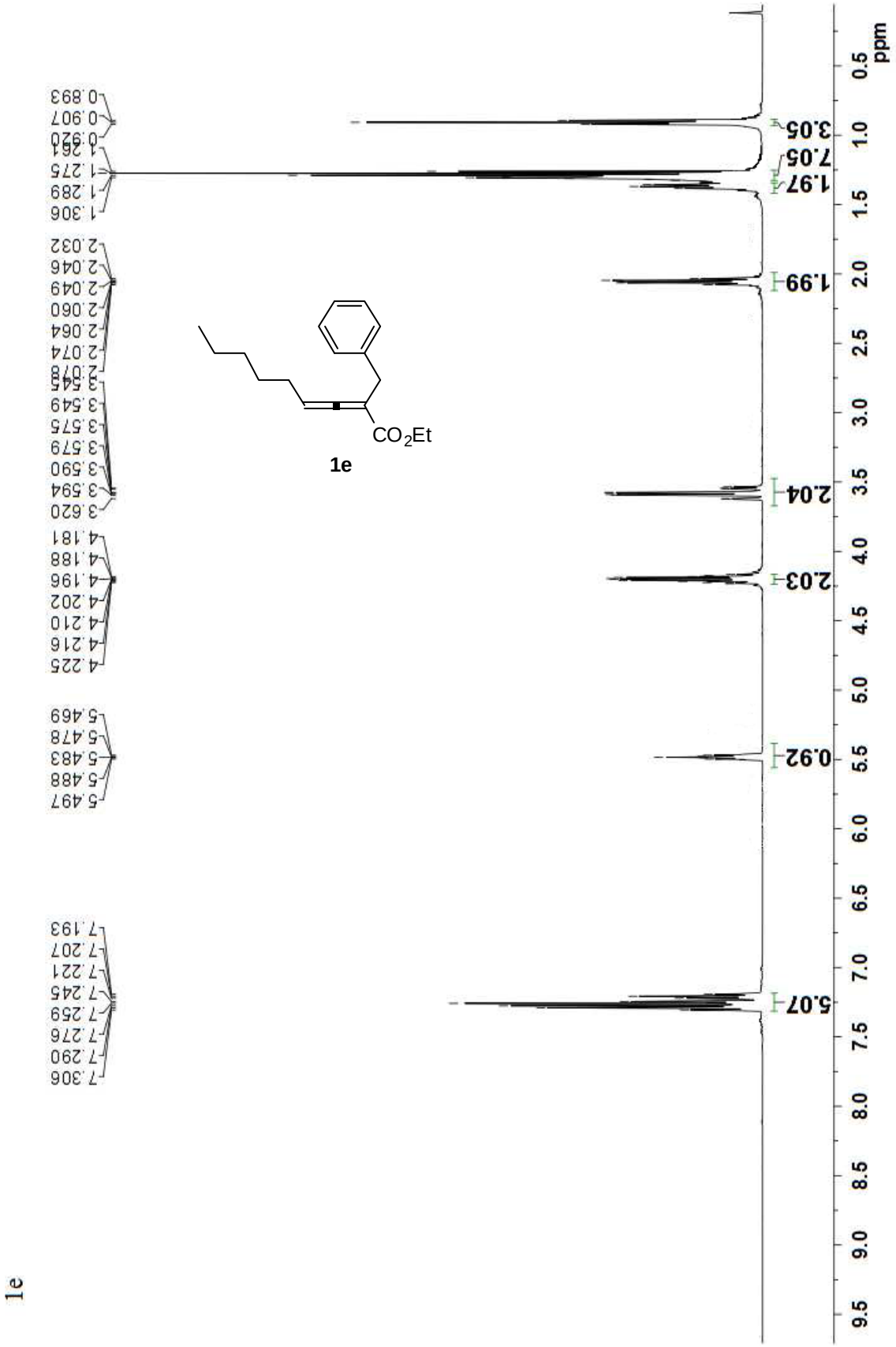
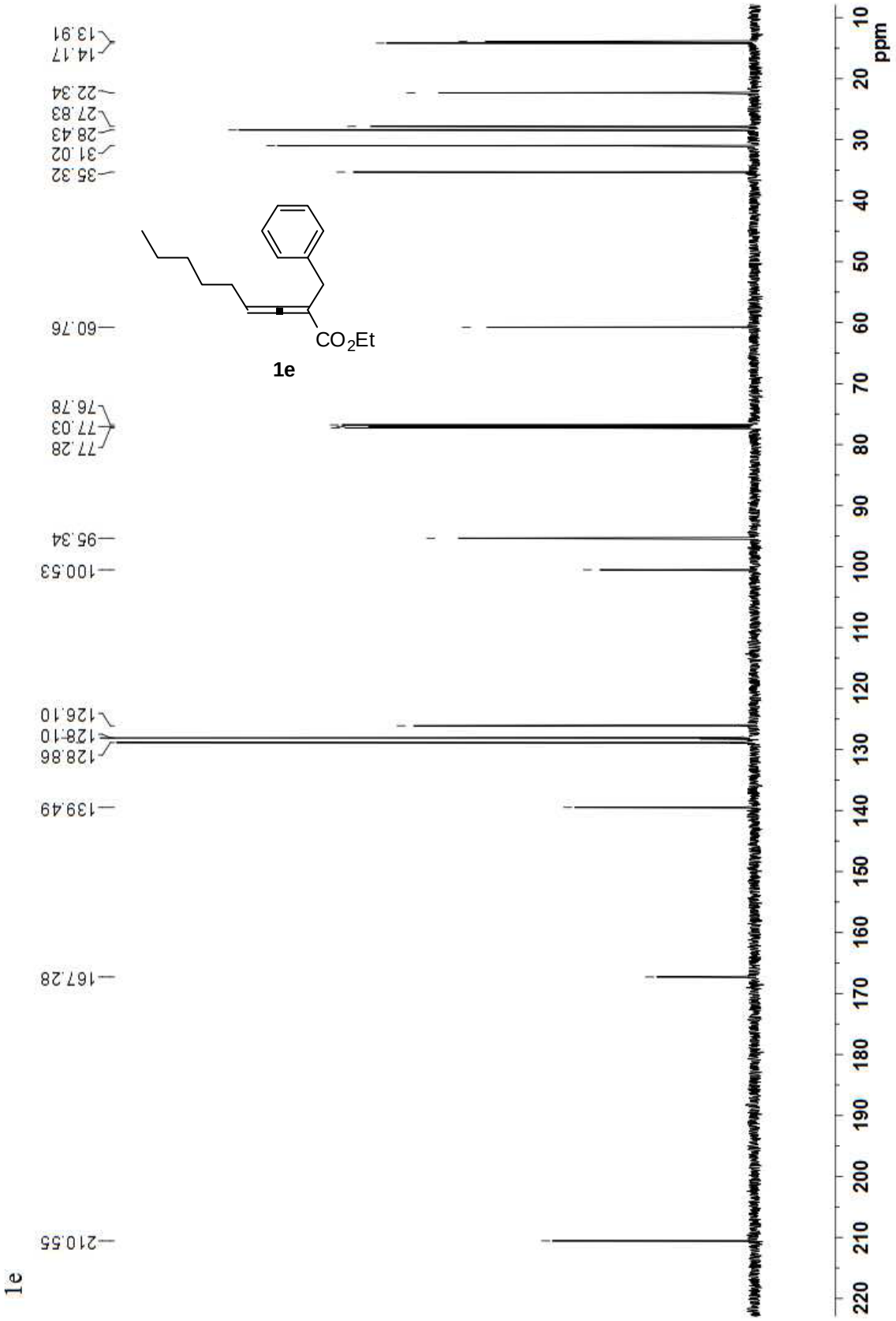
6. ^{1}H, ^{13}C, and ^{19}F NMR spectra of products

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100.53
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77.03
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60.76
35.32
31.02
28.43
27.83
22.34
14.17
13.91
CO2Et
1e
ppm
10
20
30
40
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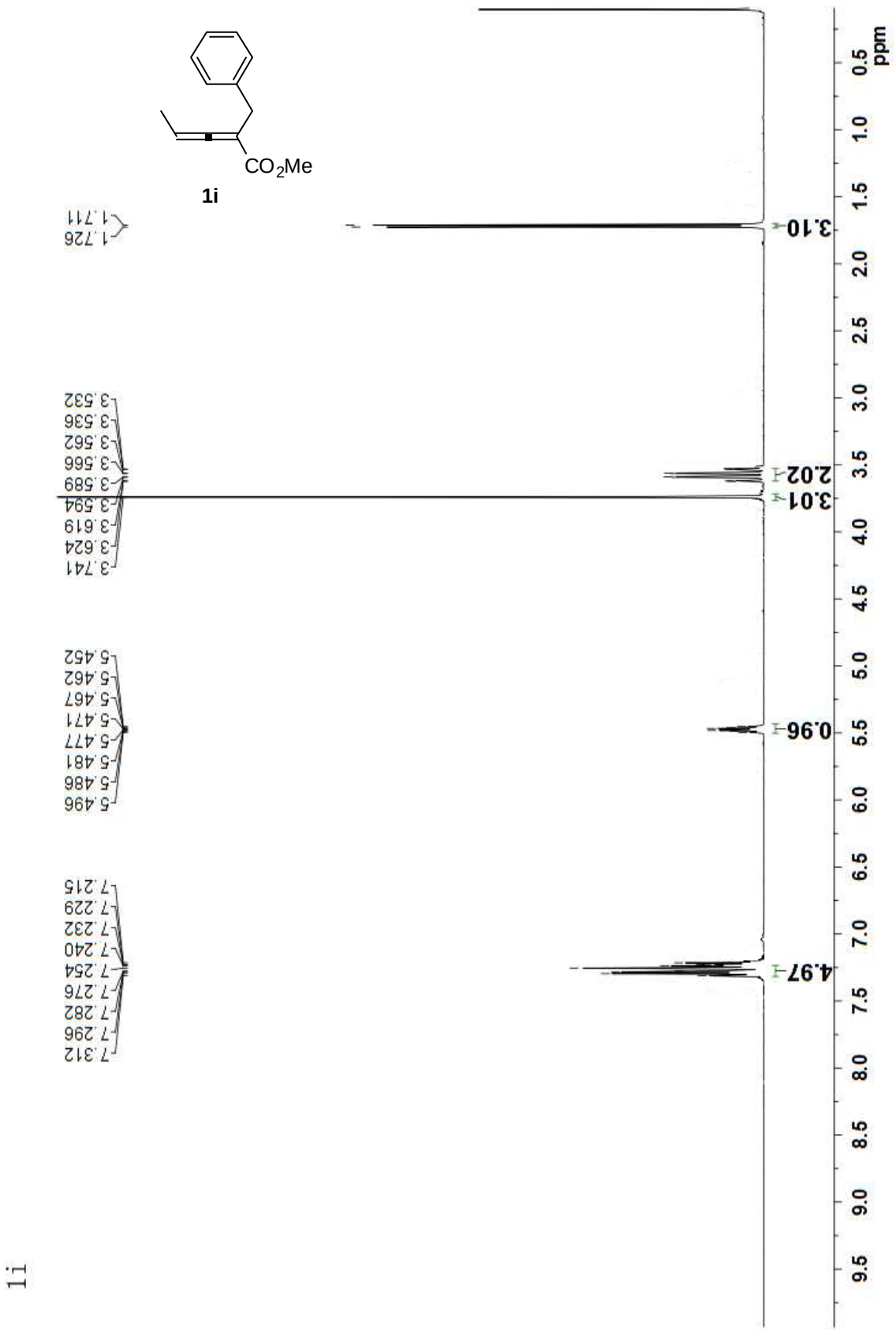
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220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3.741
5.452
5.462
5.467
5.471
5.477
5.481
5.486
5.496
7.215
7.229
7.232
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3.01
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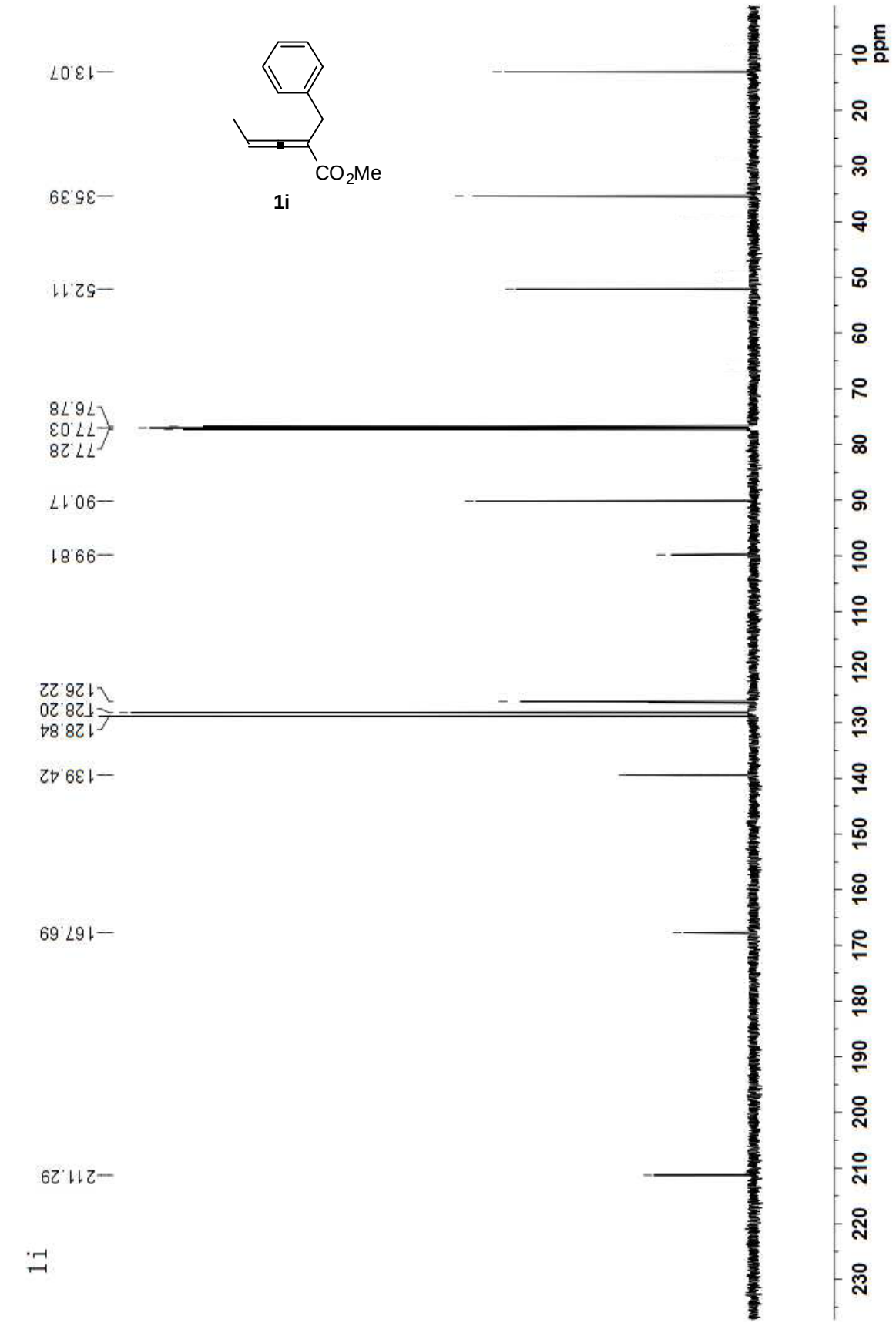
4.97
ppm

1i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77.03
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139.42
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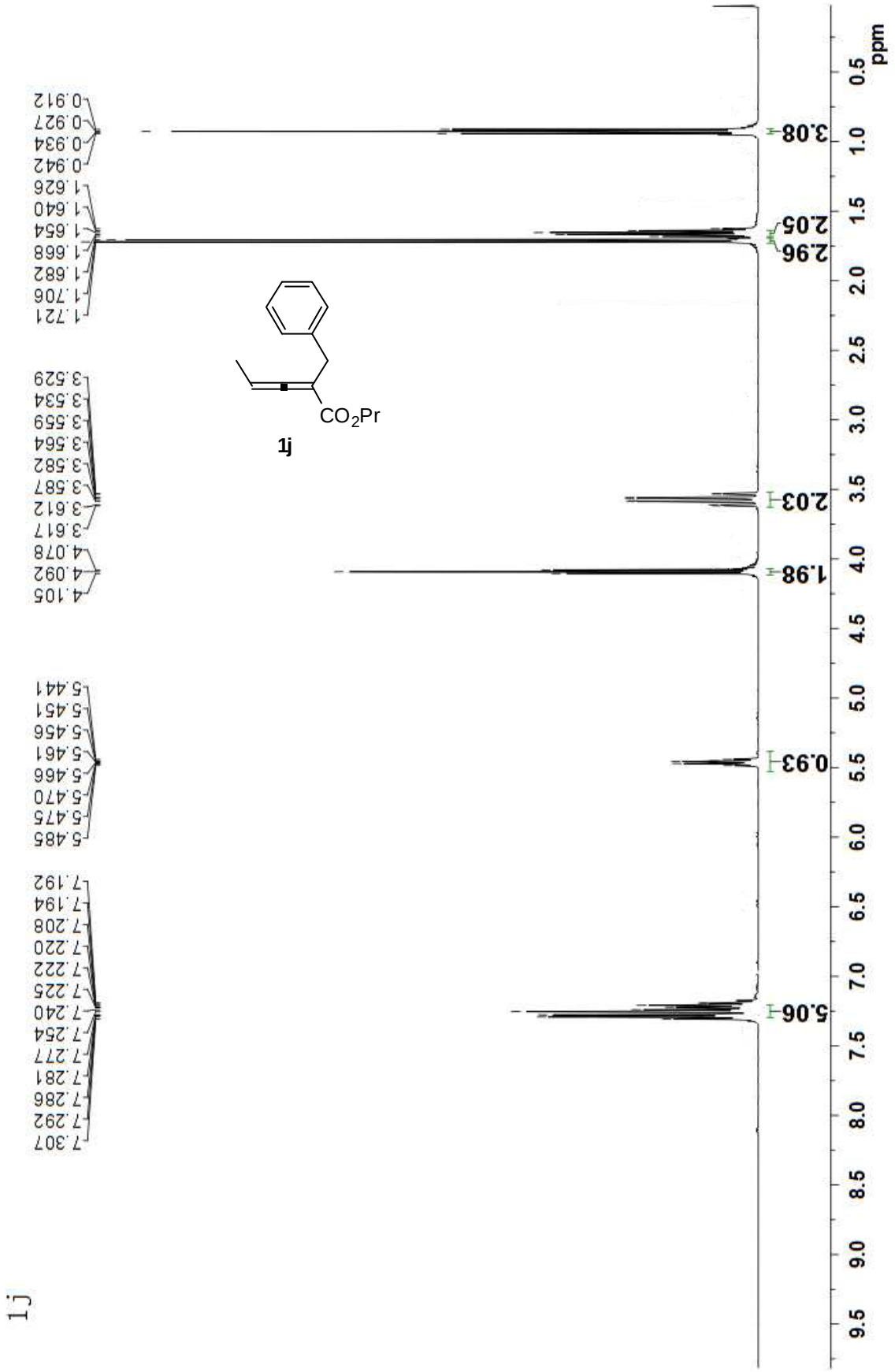
CO2Me
1i
ppm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1.682
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1.721
3.529
3.534
3.559
3.564
3.582
3.587
3.612
3.617
4.078
4.092
4.105
5.441
5.451
5.456
5.461
5.466
5.470
5.475
5.485
7.192
7.194
7.208
7.220
7.222
7.225
7.240
7.254
7.277
7.281
7.286
7.292
7.307
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2.96
2.03
1.98
0.93
5.06
ppm
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1.5
2.0
2.5
3.0
3.5
4.0
4.5
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6.0
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7.0
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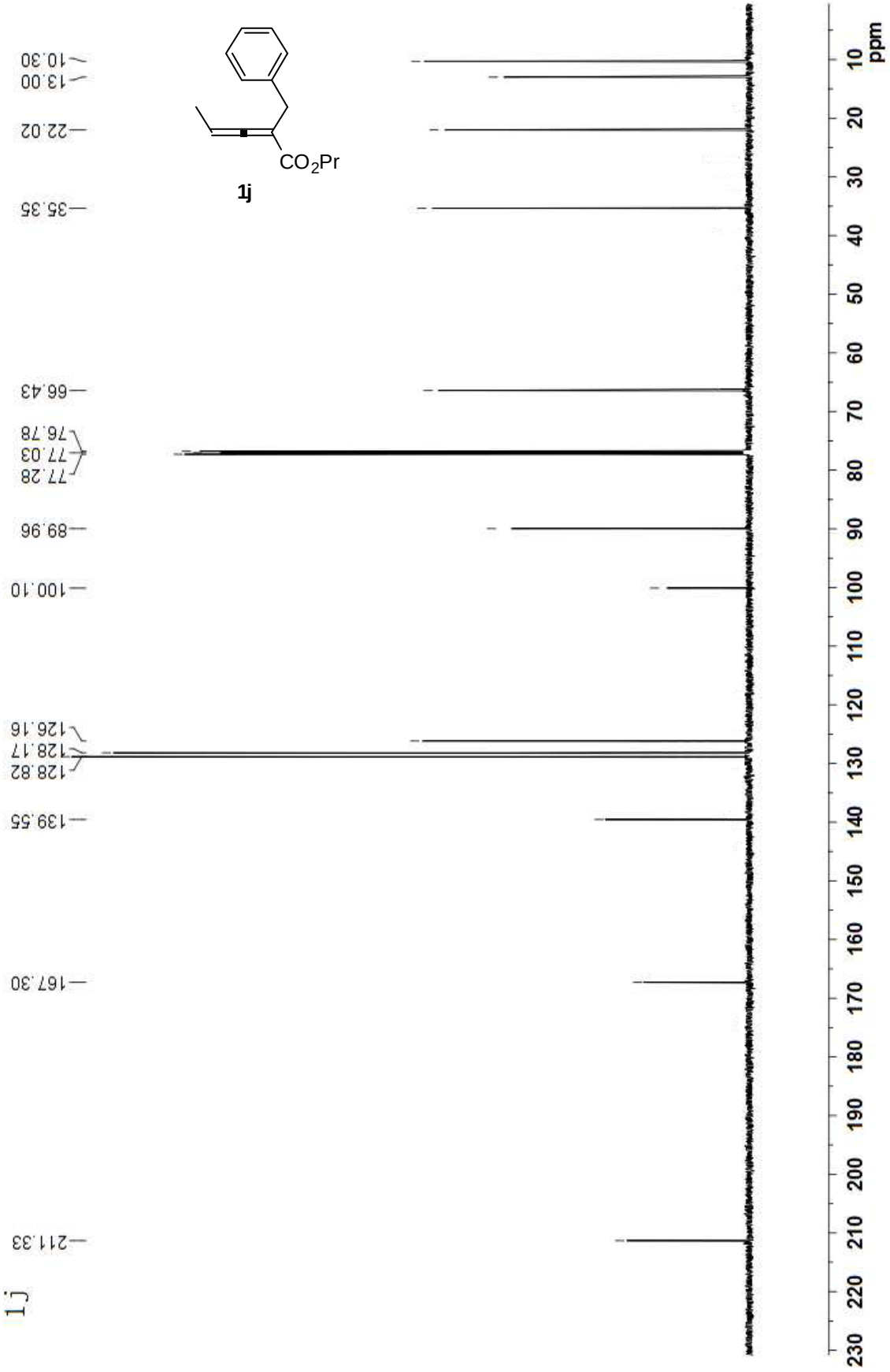
8.5
9.0
9.5
CO2Pr
1j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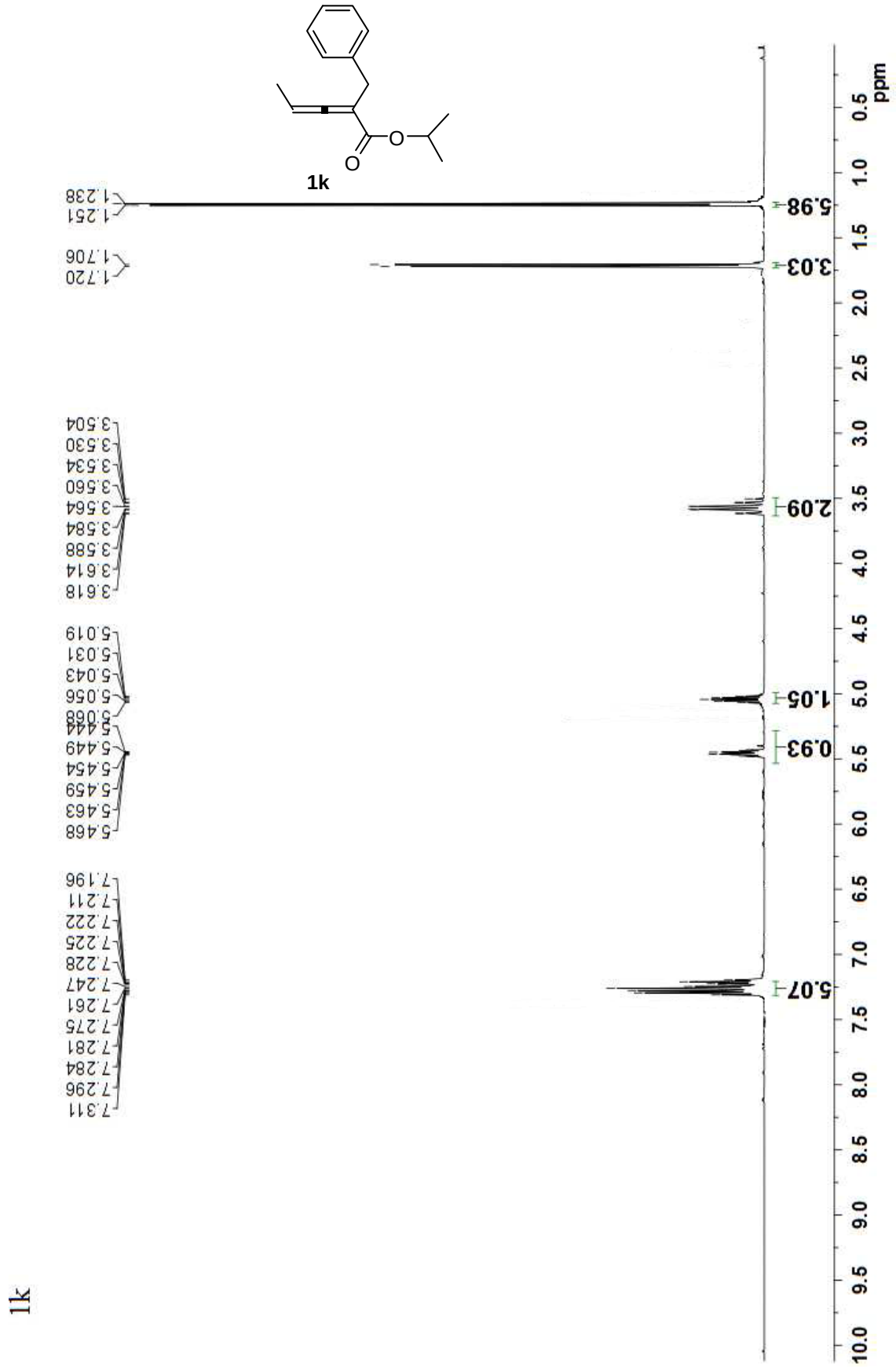
1j
CO2Pr
1j
ppm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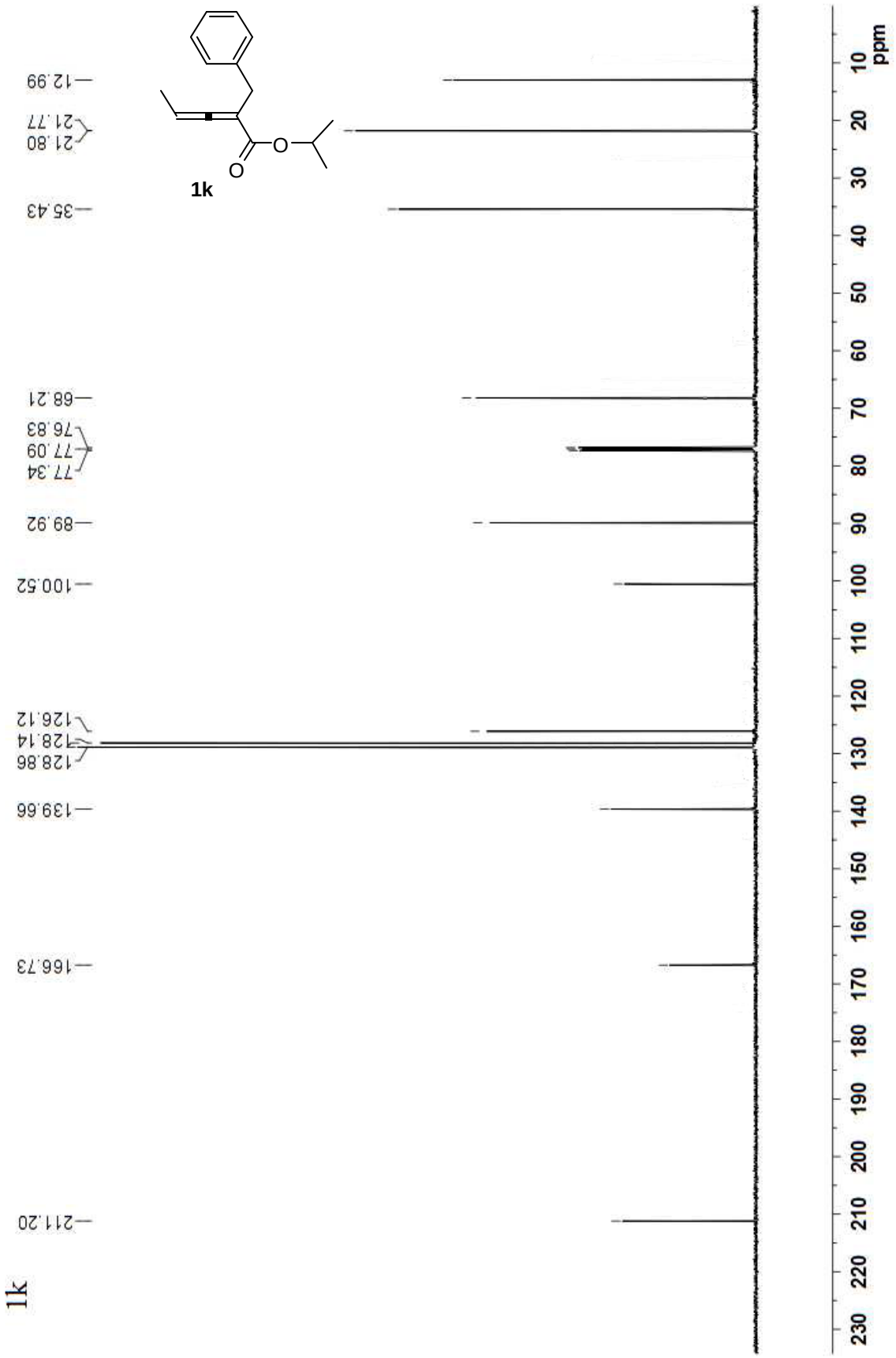
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128.86
139.66
166.73
211.20
O
O
1k
ppm
10
20
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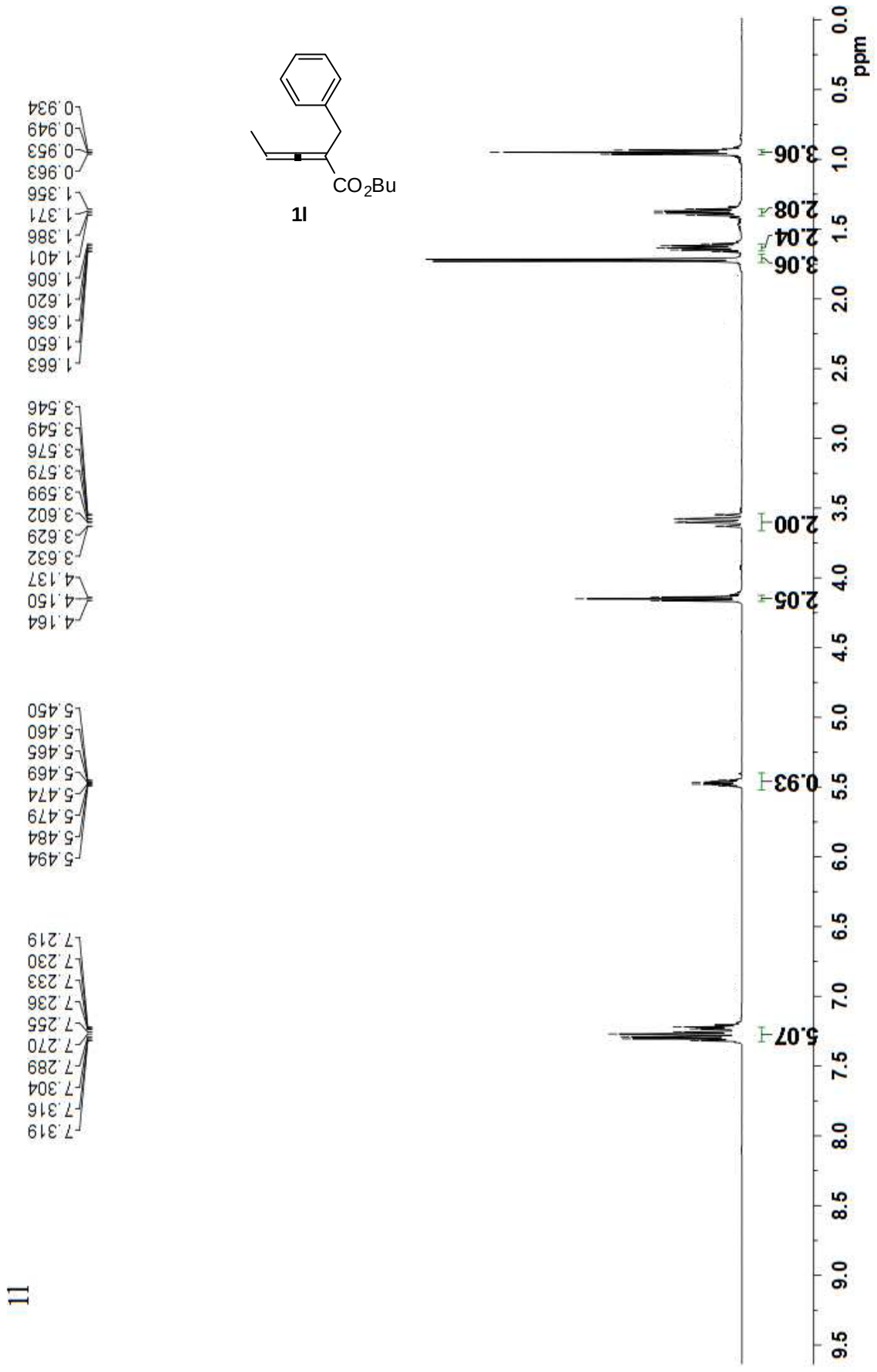
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1.636
1.650
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3.549
3.576
3.579
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3.629
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4.150
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5.465
5.469
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5.479
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7.233
7.236
7.255
7.270
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2.00
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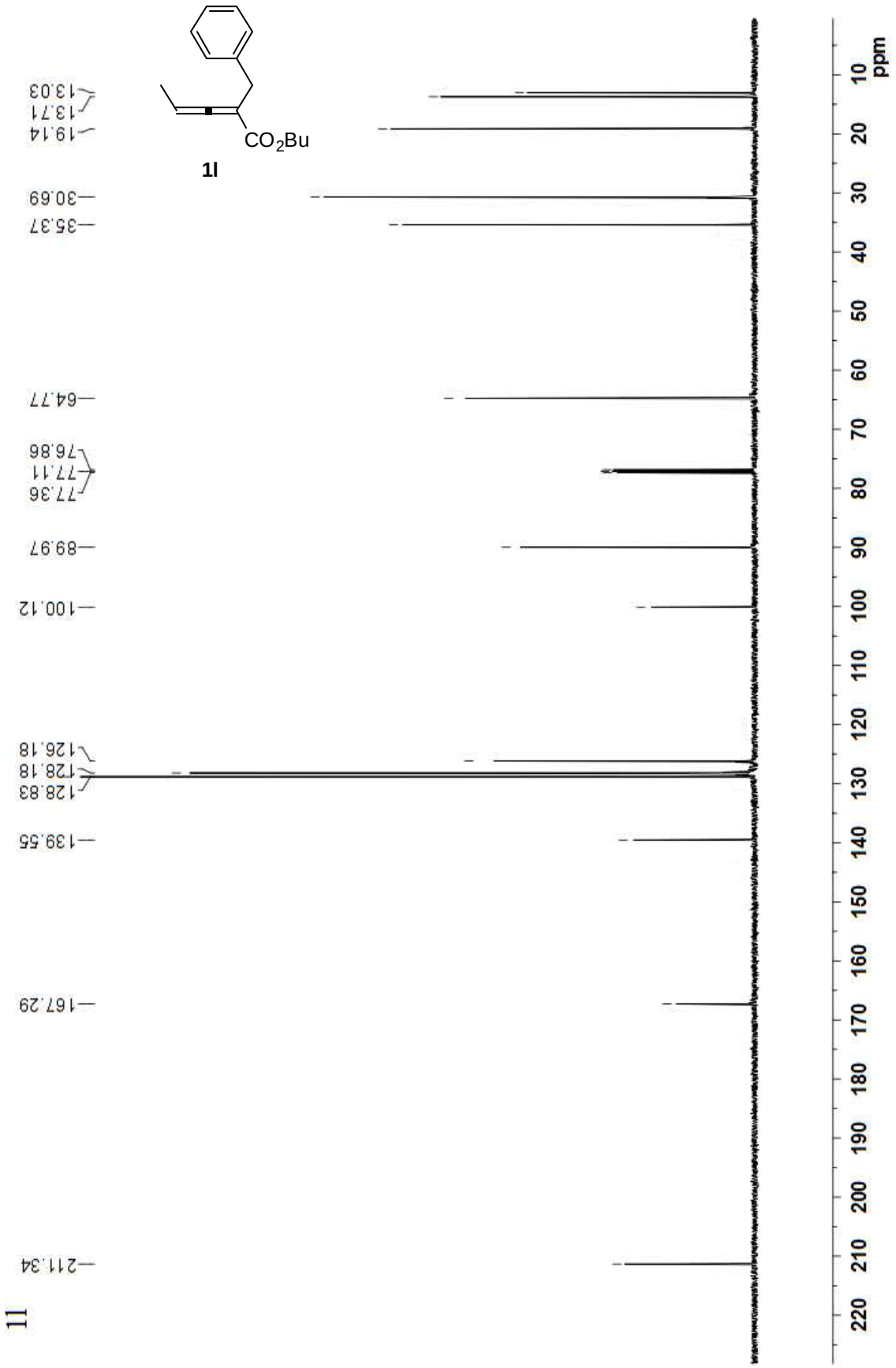
ppm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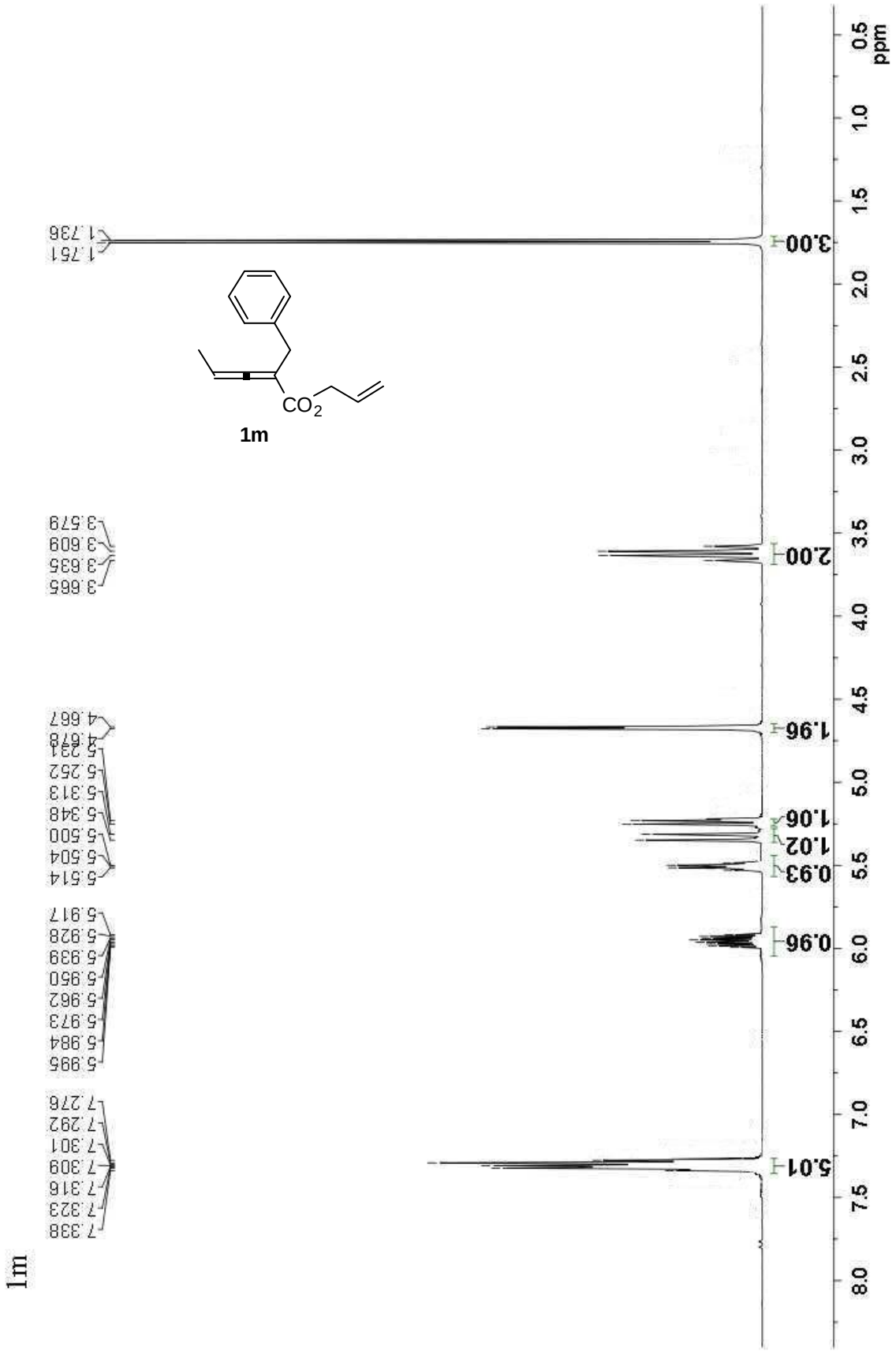
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7.338
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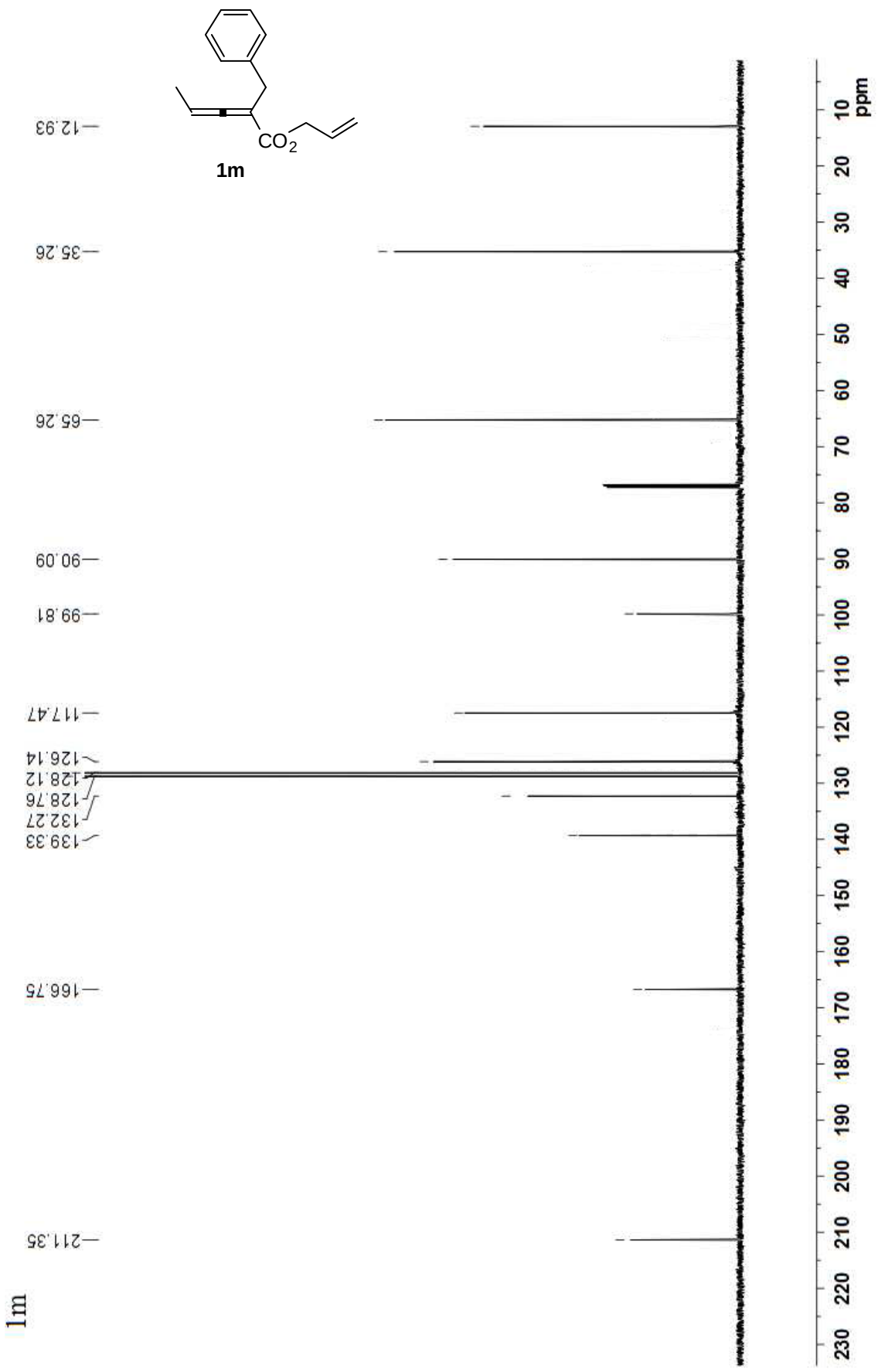
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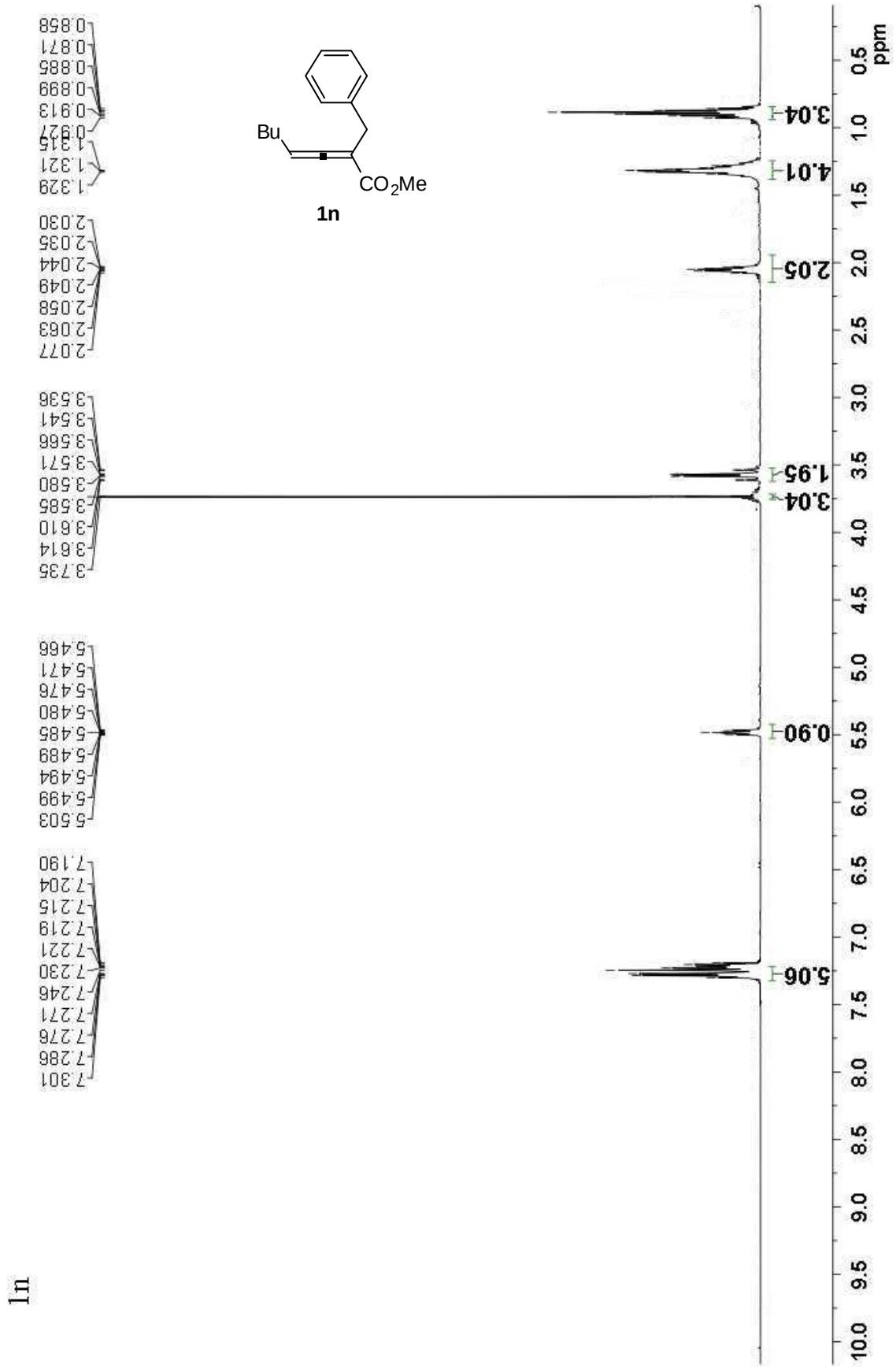
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2.049
2.058
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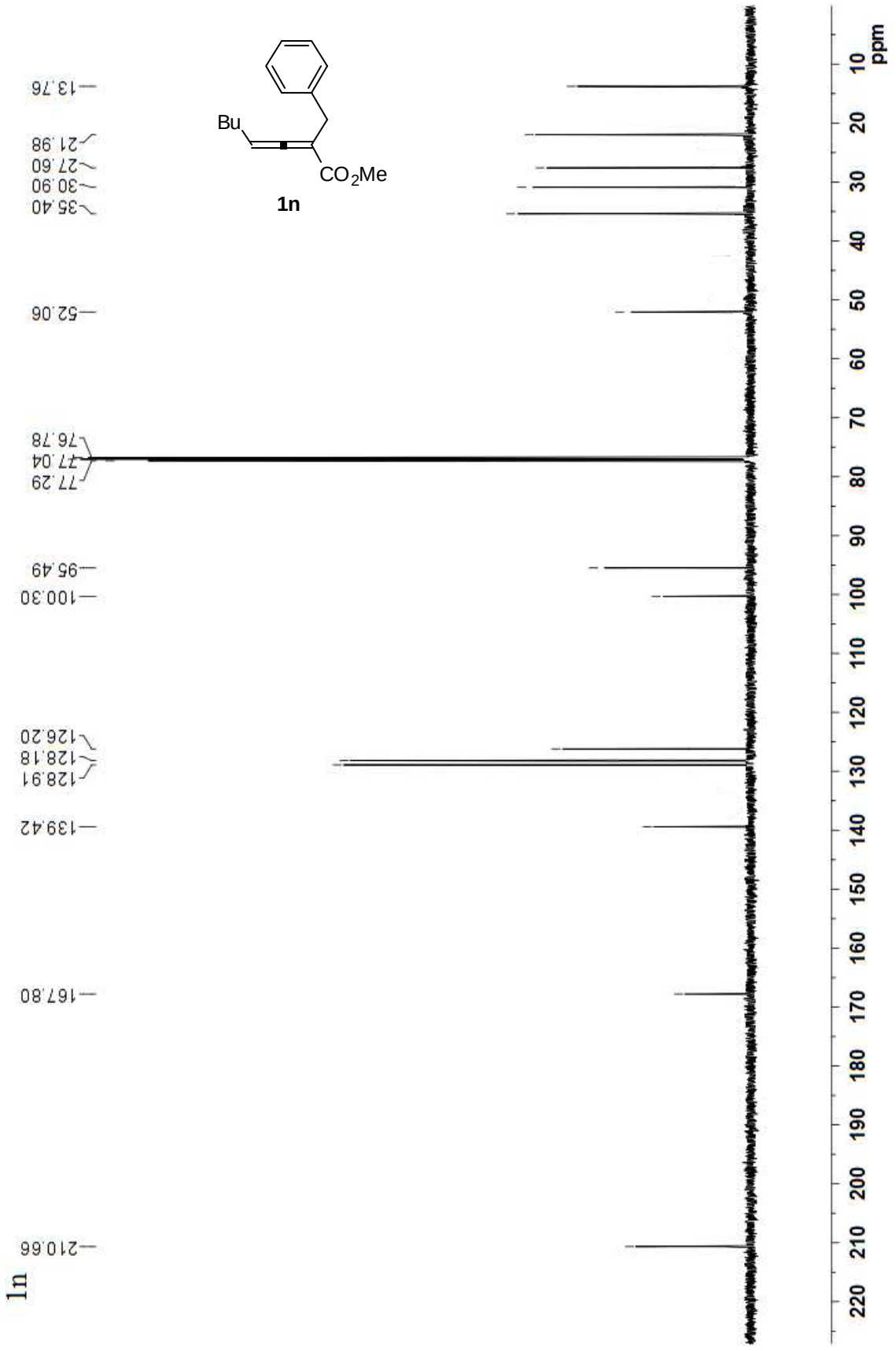
ppm

1n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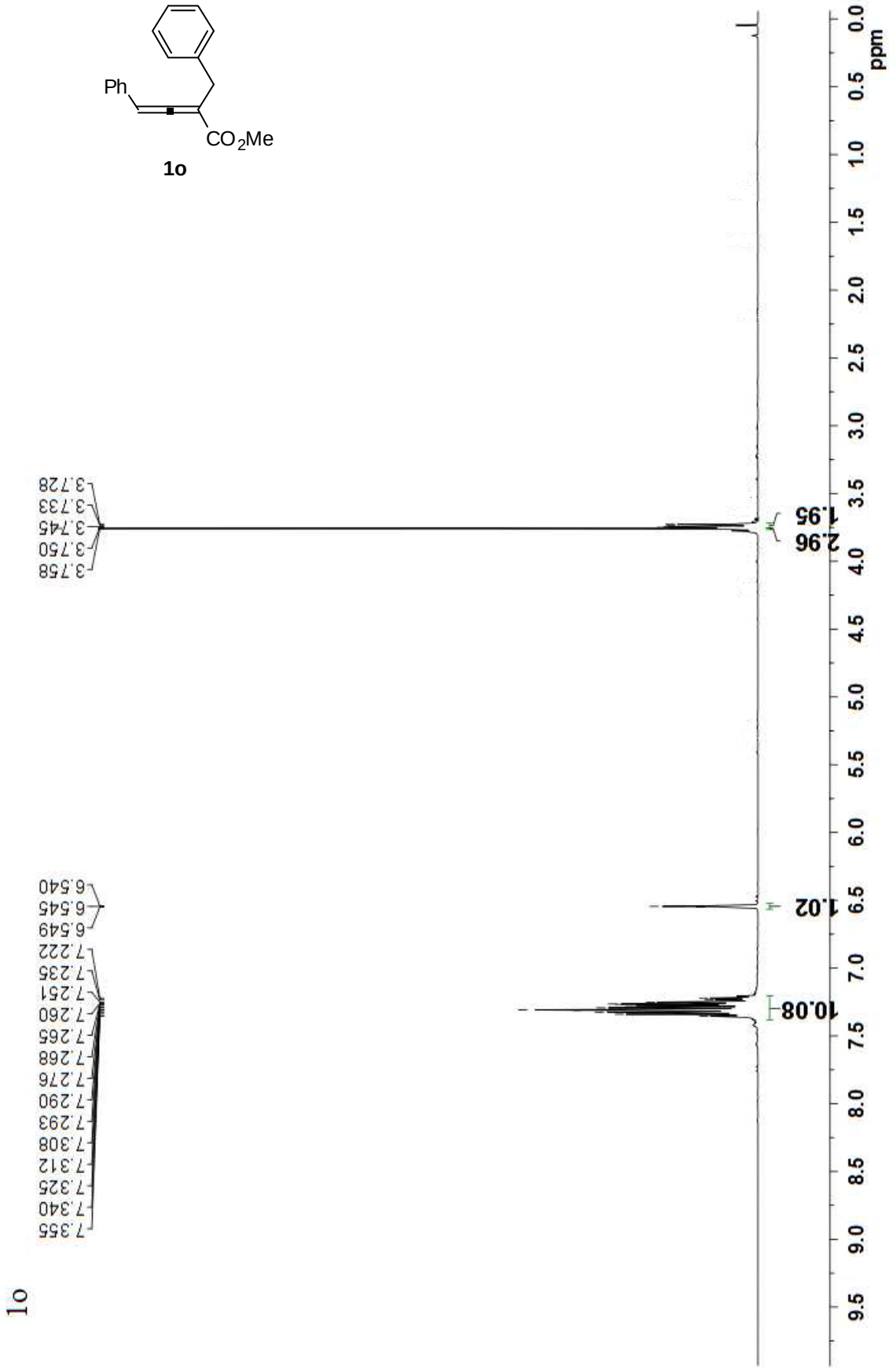
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7.325
7.340
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2.96
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10.08
ppm
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0.5
1.0
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2.0
2.5
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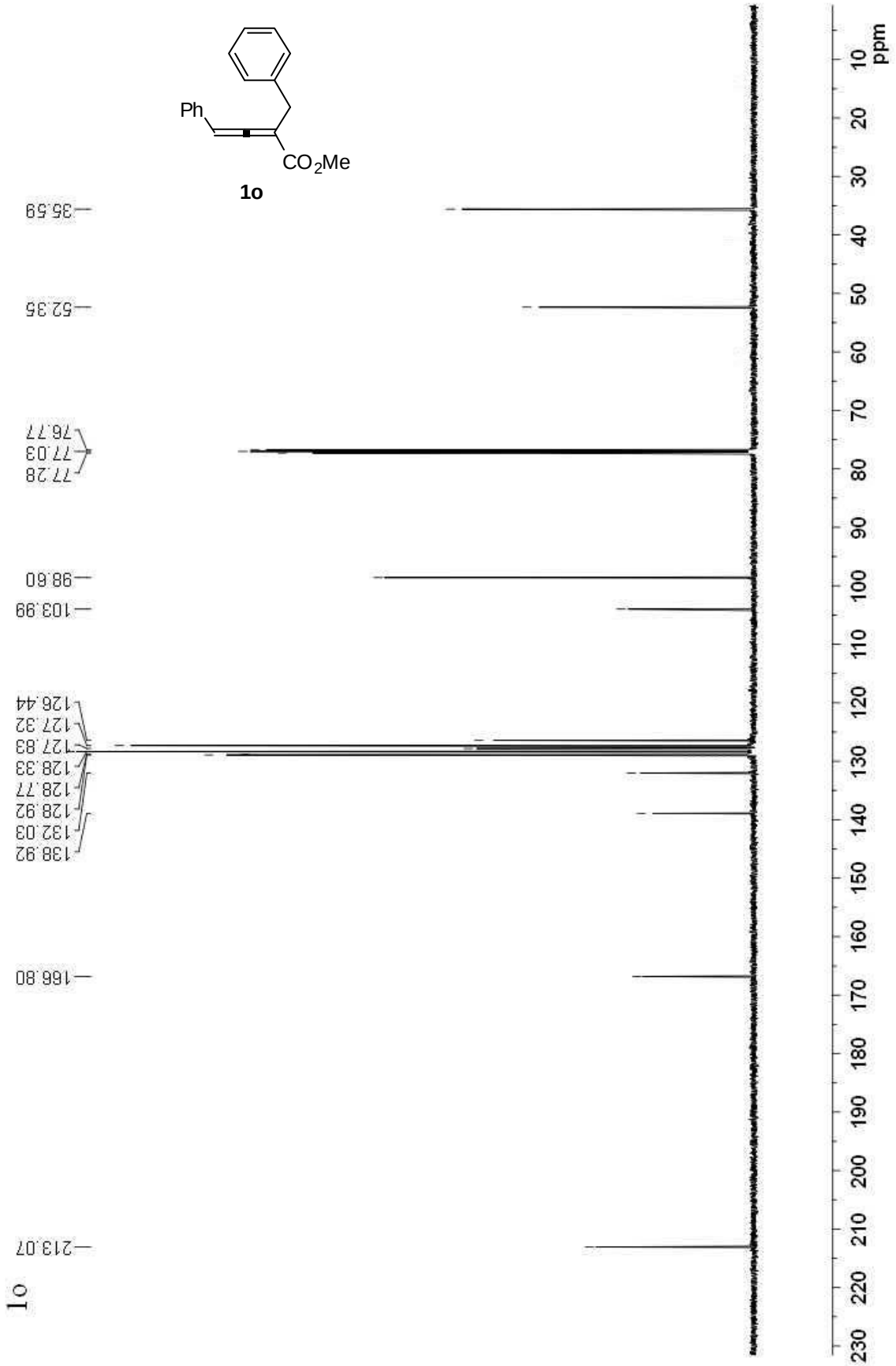
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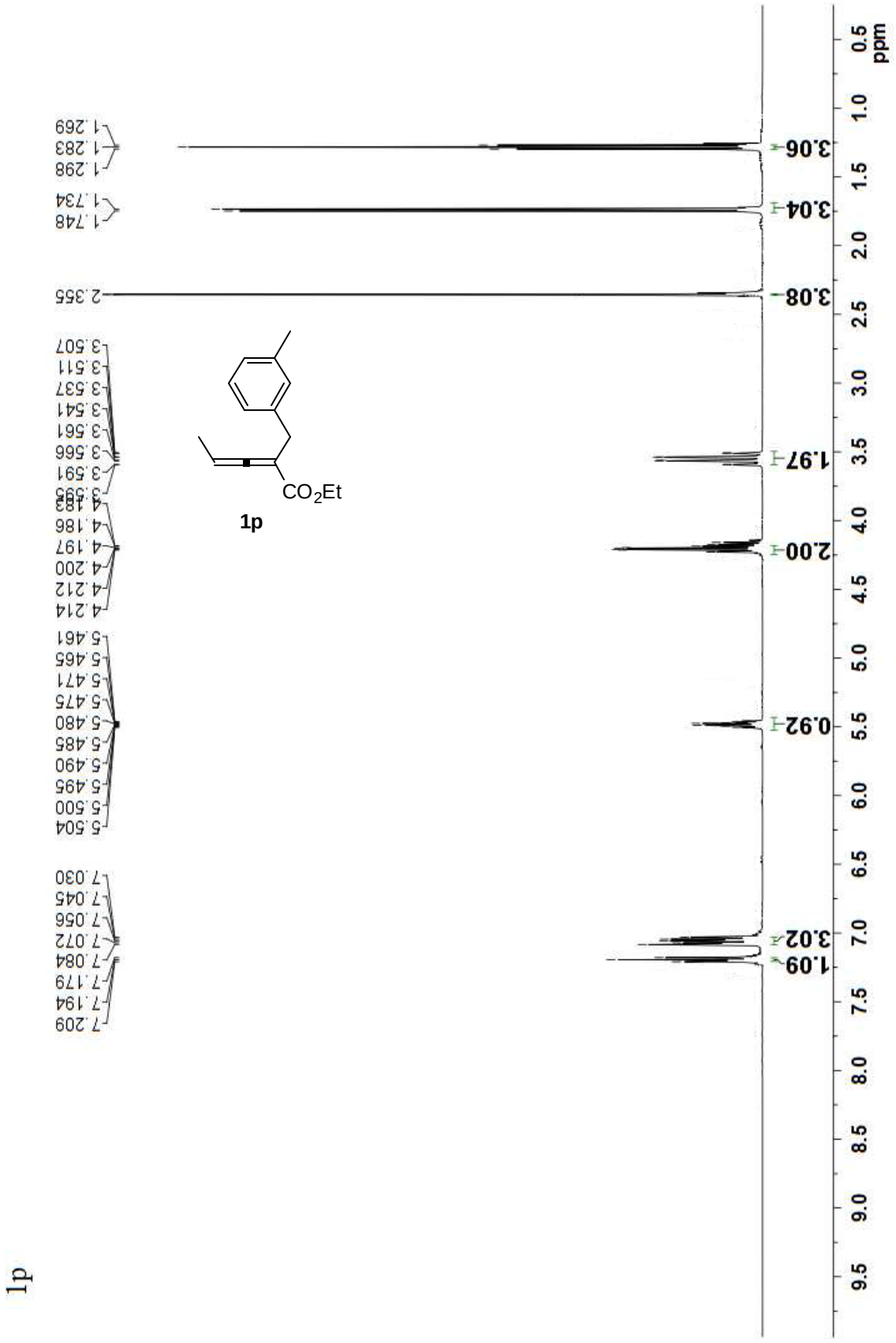
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5.480
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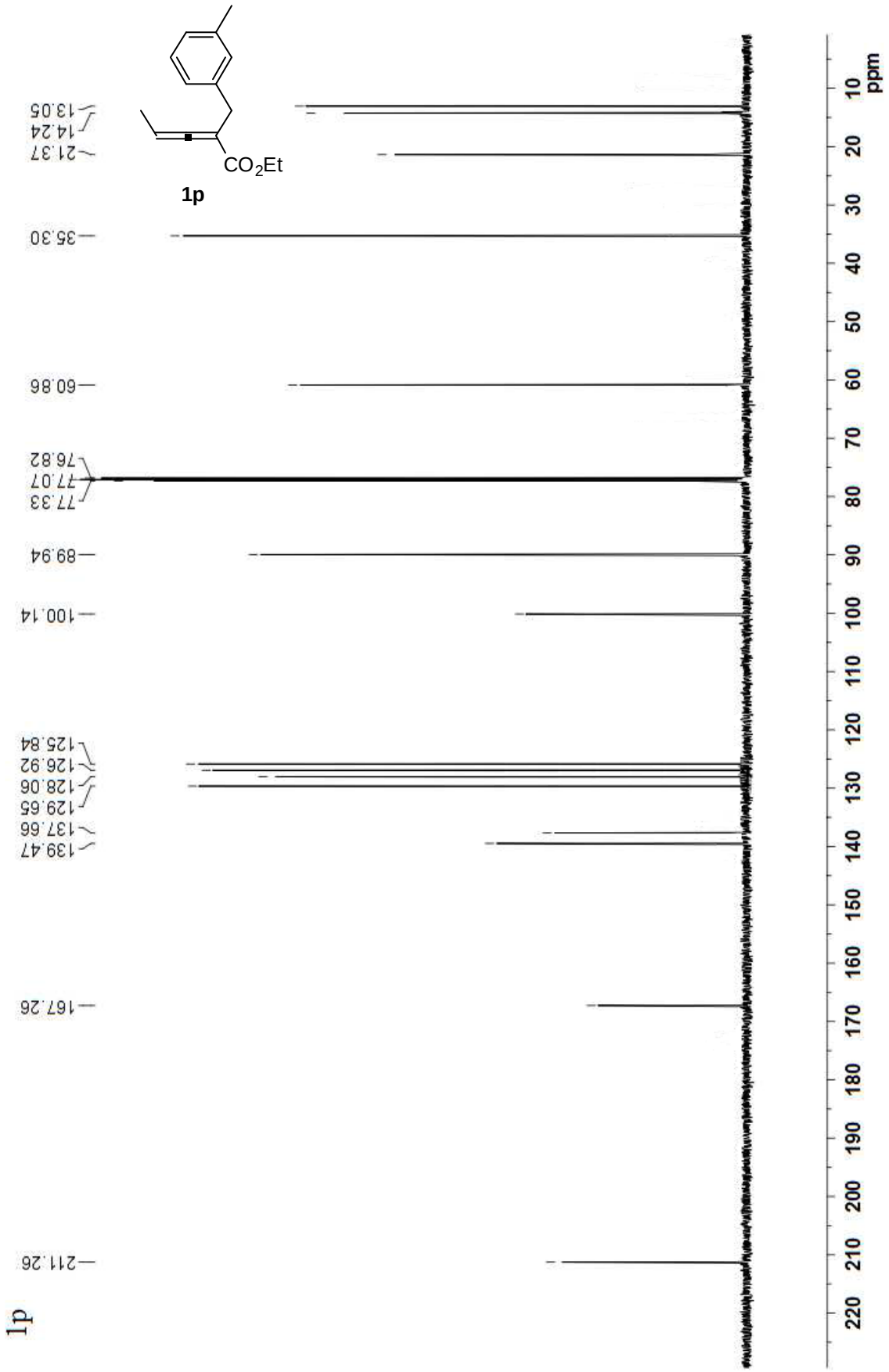
CO2Et
1p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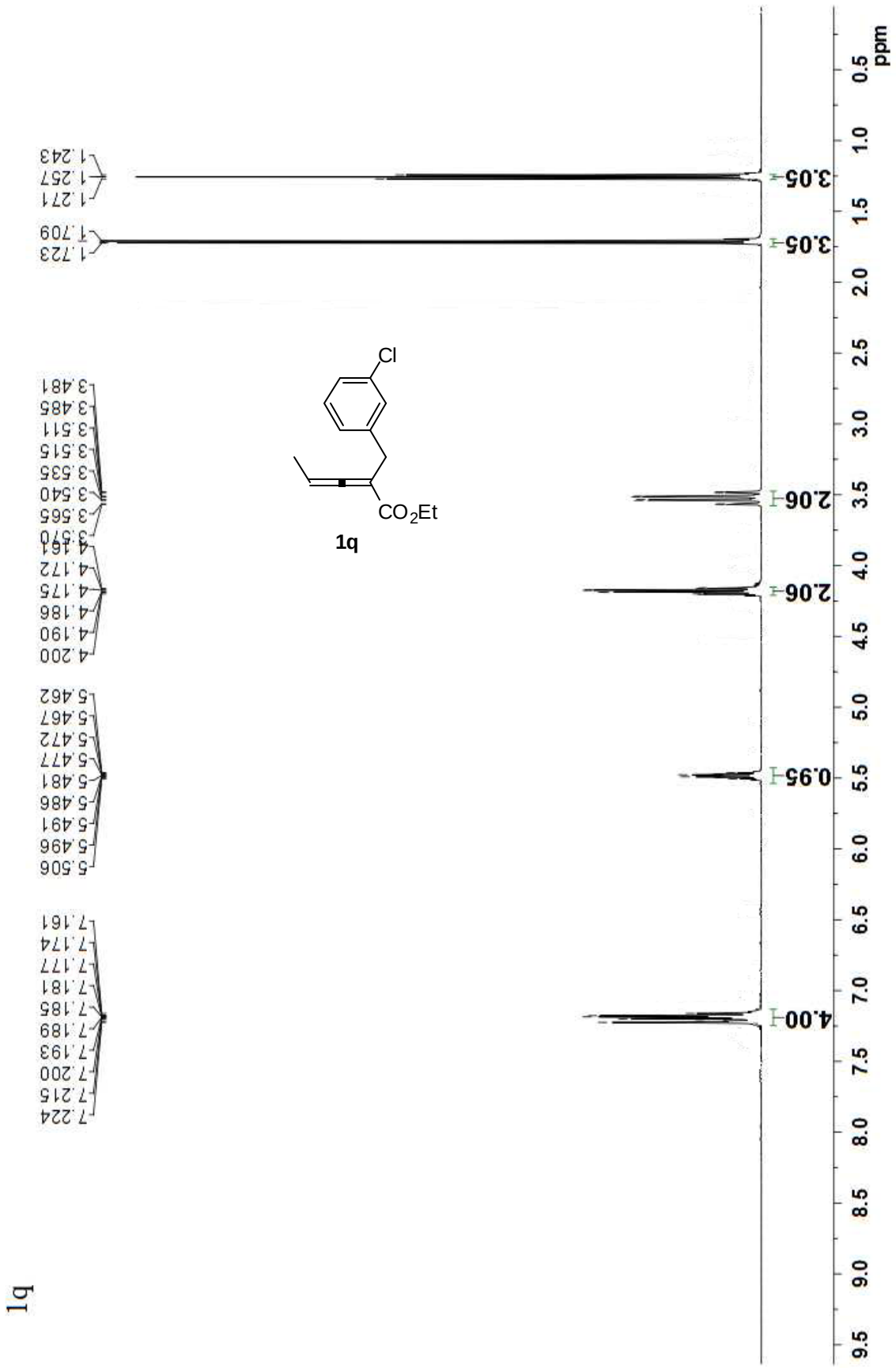
1p
ppm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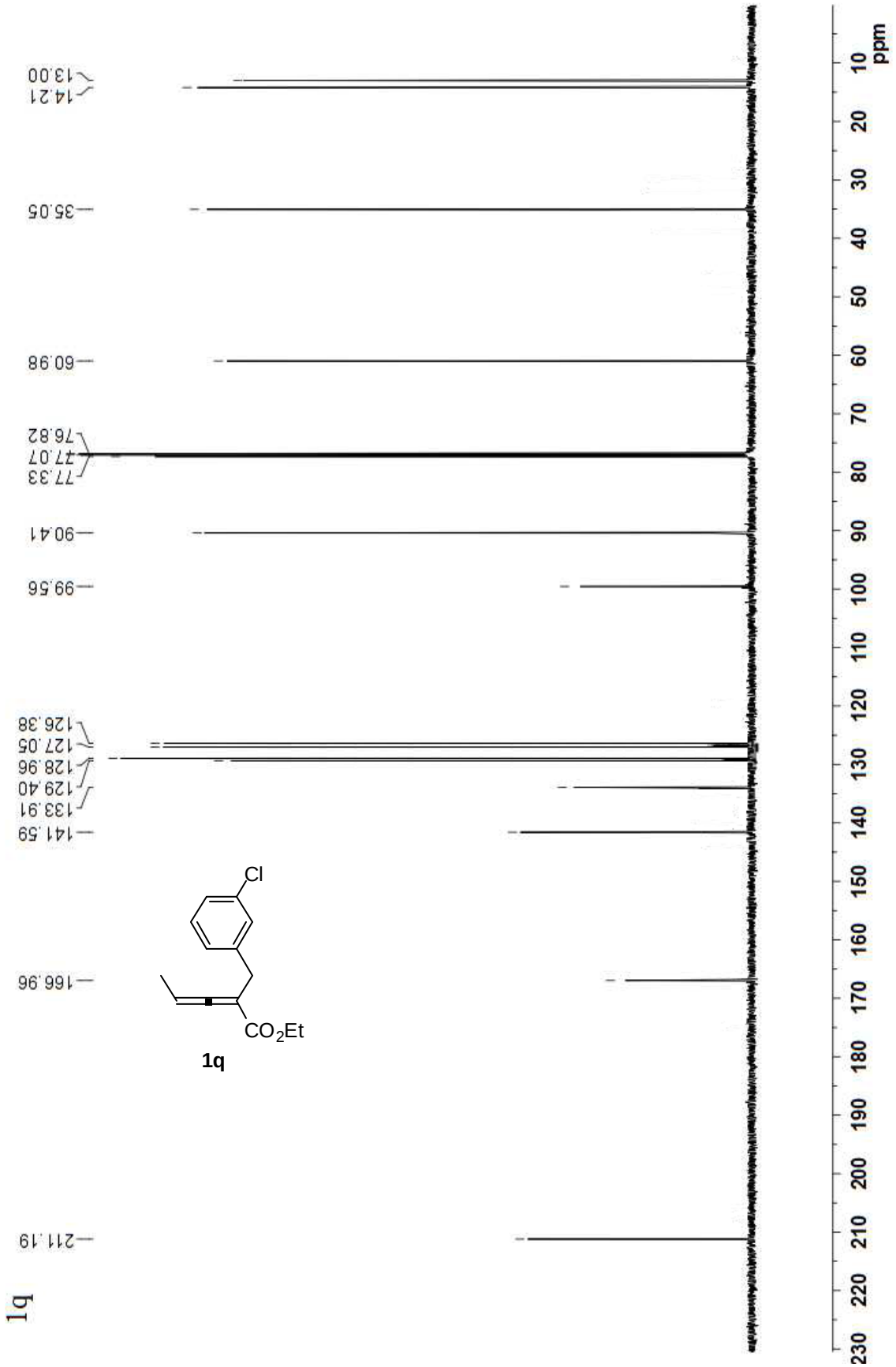
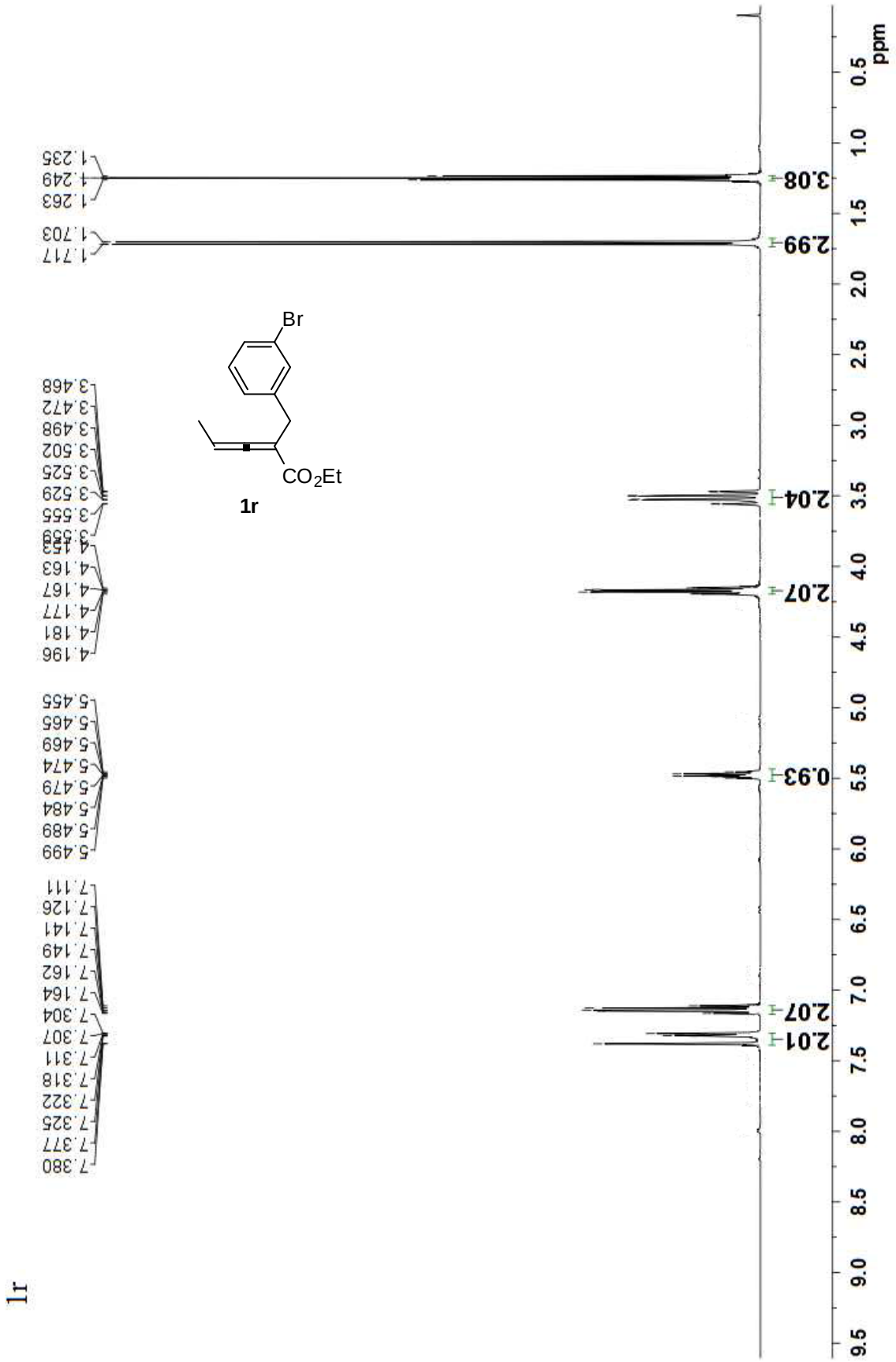
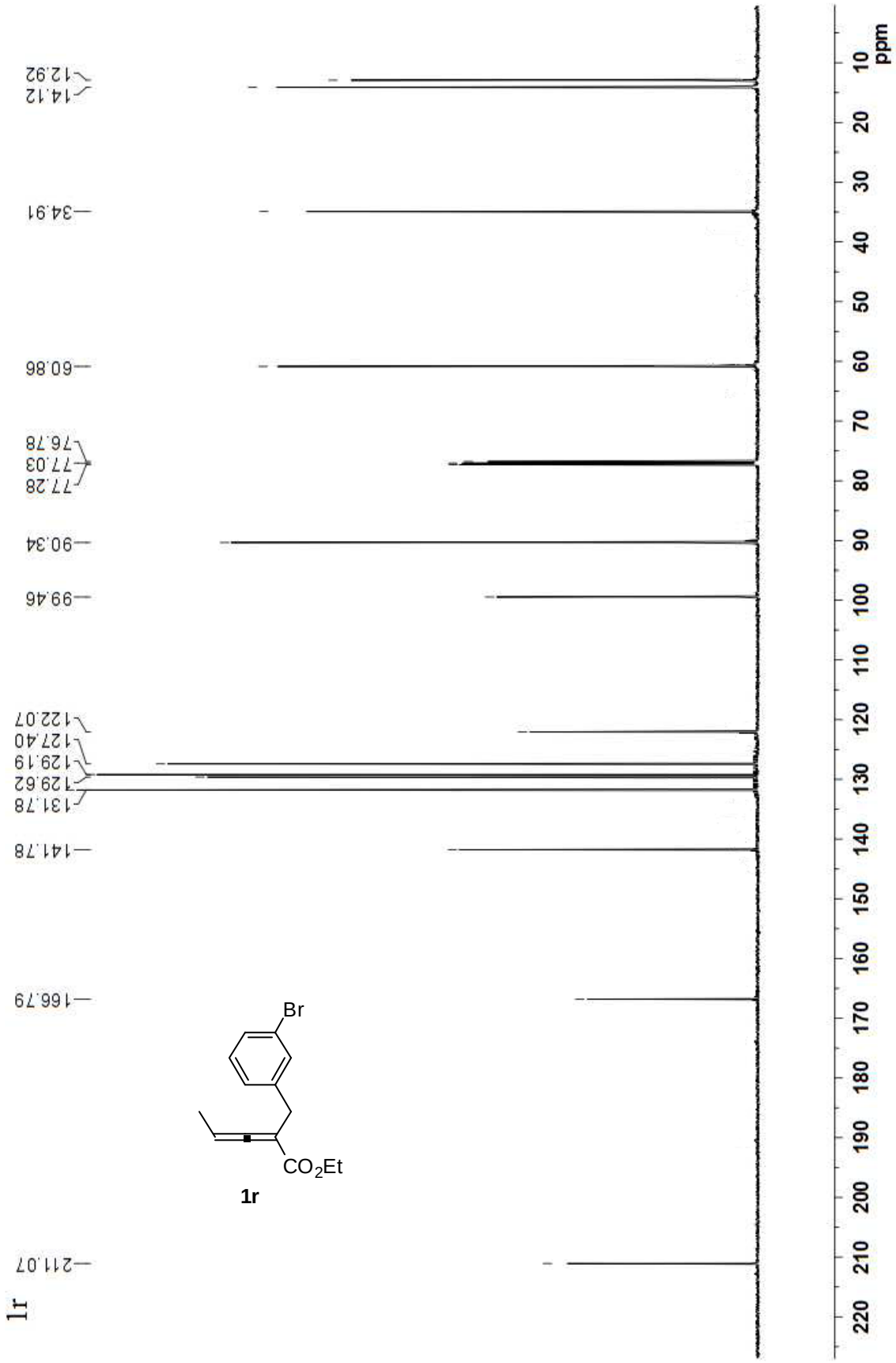
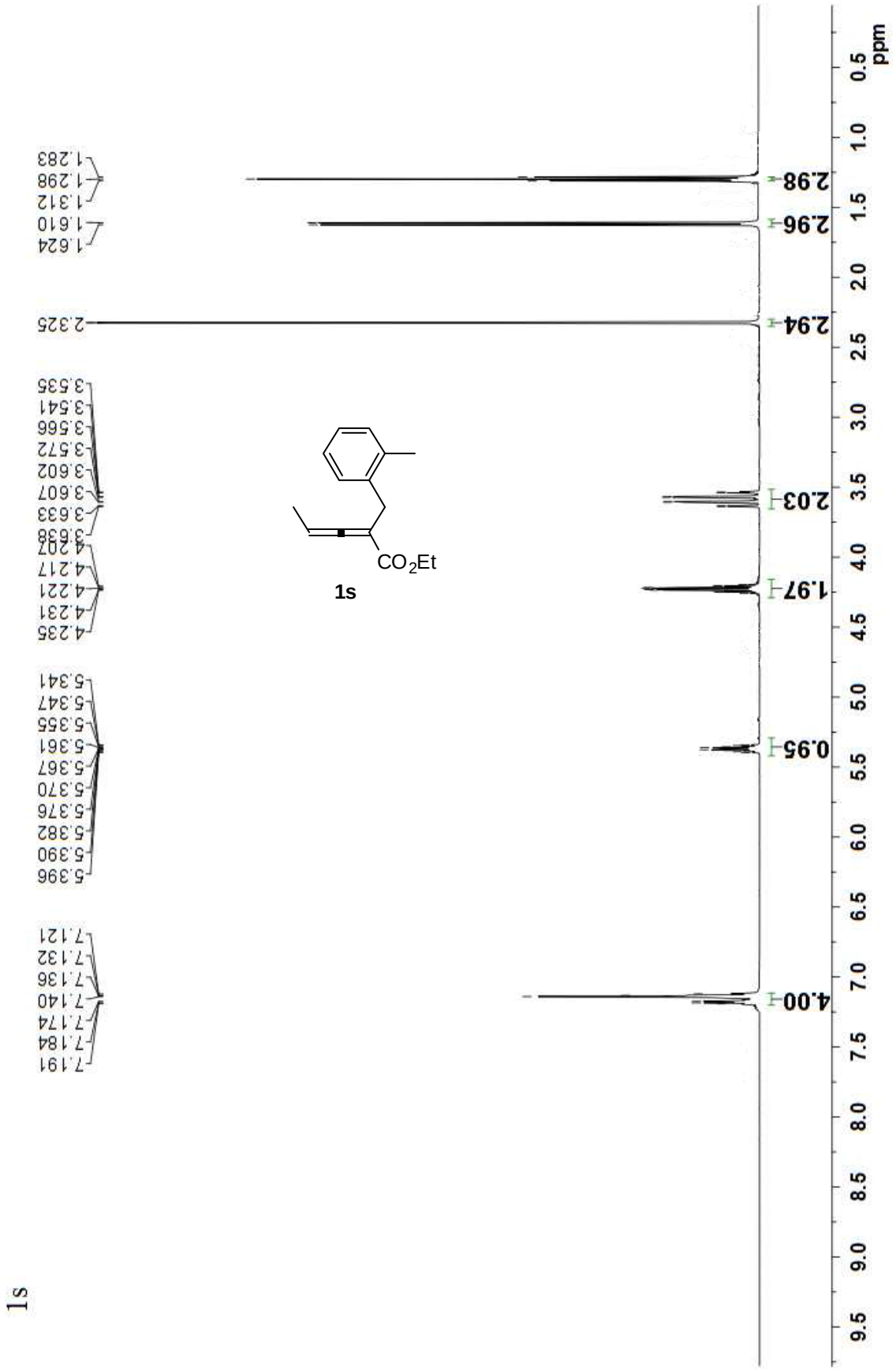
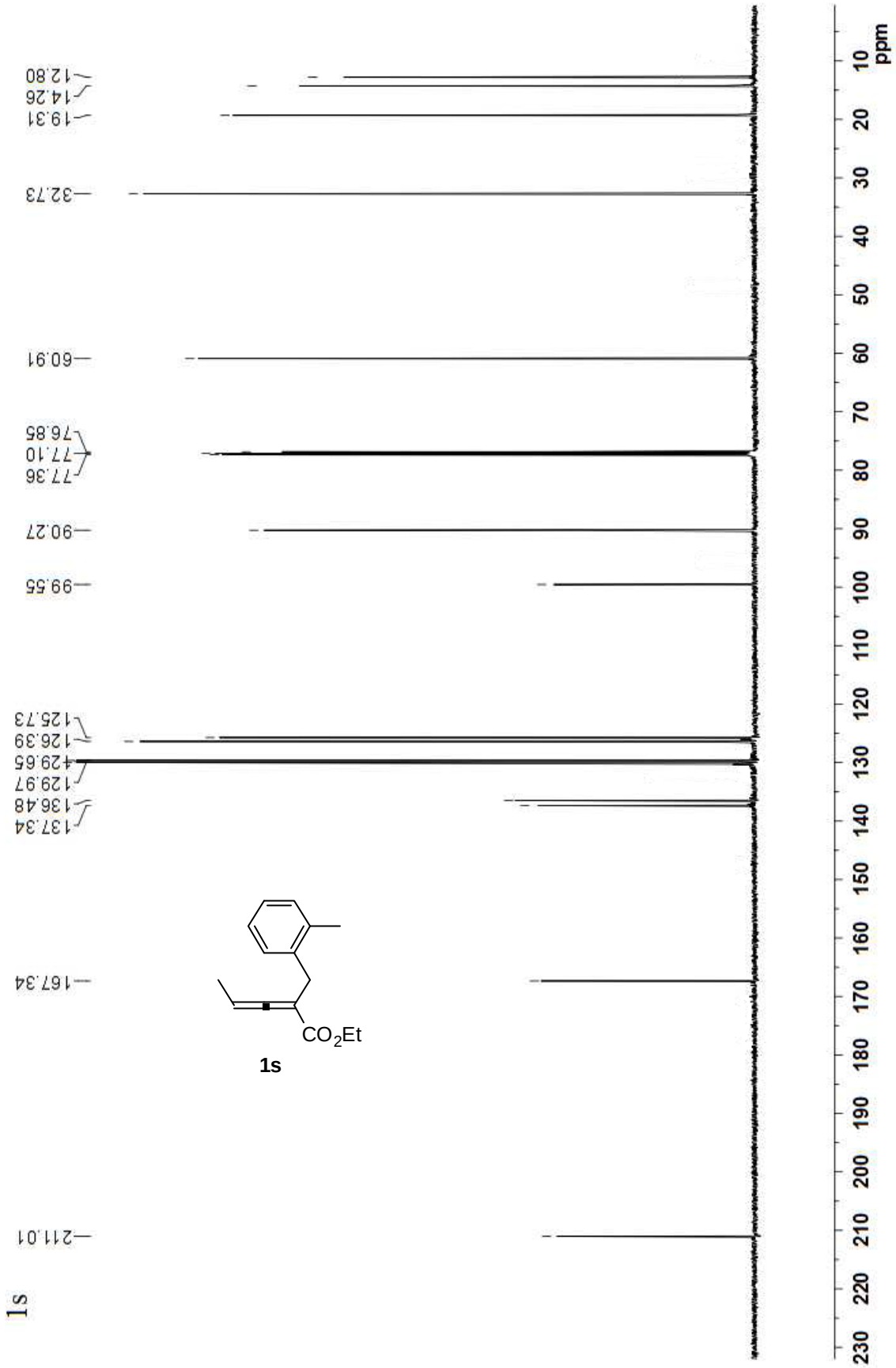
7.181
7.185
7.189
7.193
7.200
7.215
7.224
3.05
3.05
2.06
2.06
0.95
4.00
Cl
CO2Et
1q
ppm

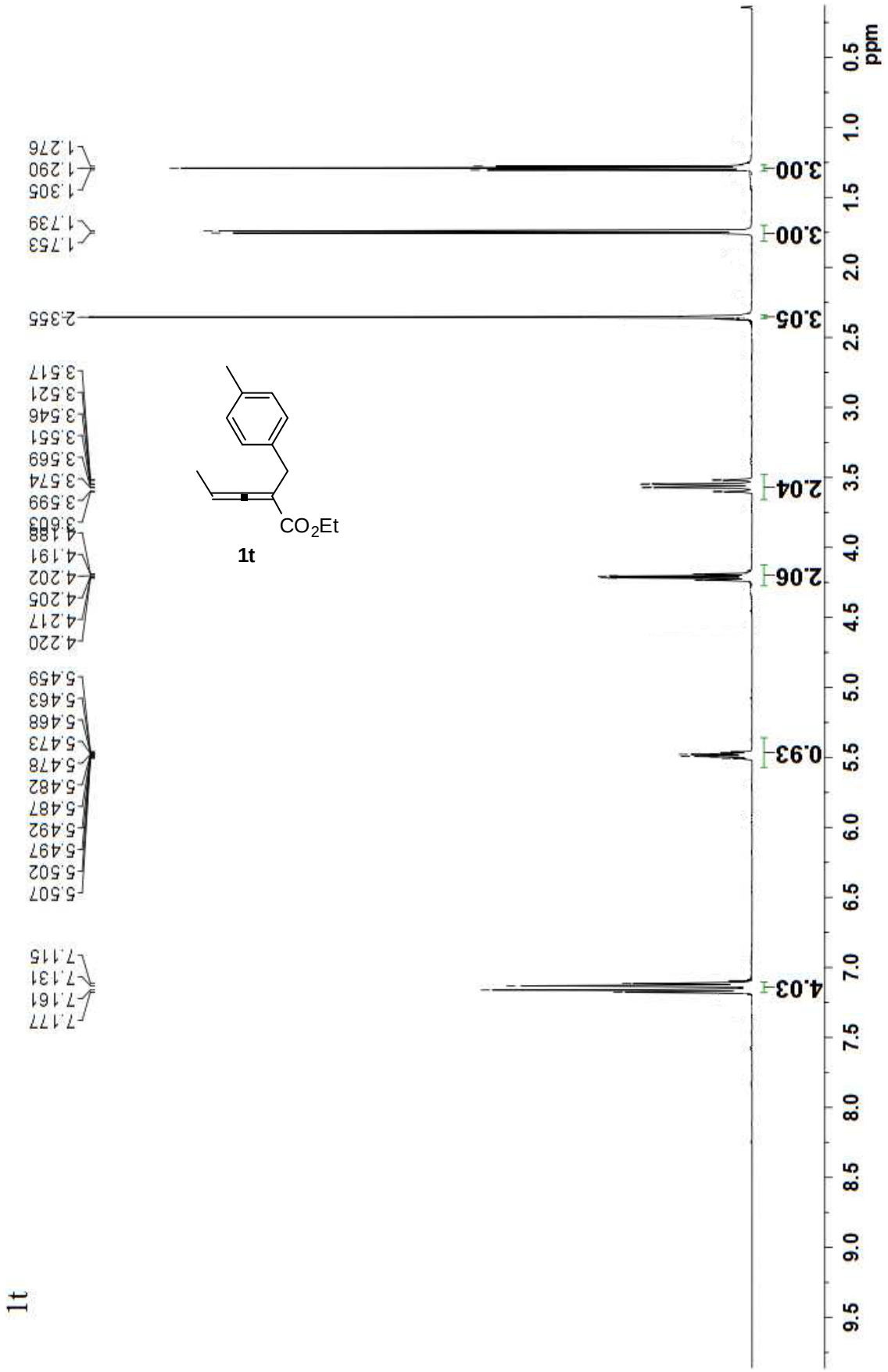

1q
211.19
166.96
141.59
133.91
129.40
128.96
127.05
126.38
99.56
90.41
77.33
77.07
76.82
60.98
35.05
14.21
13.00
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
Cl
CO2Et
1q

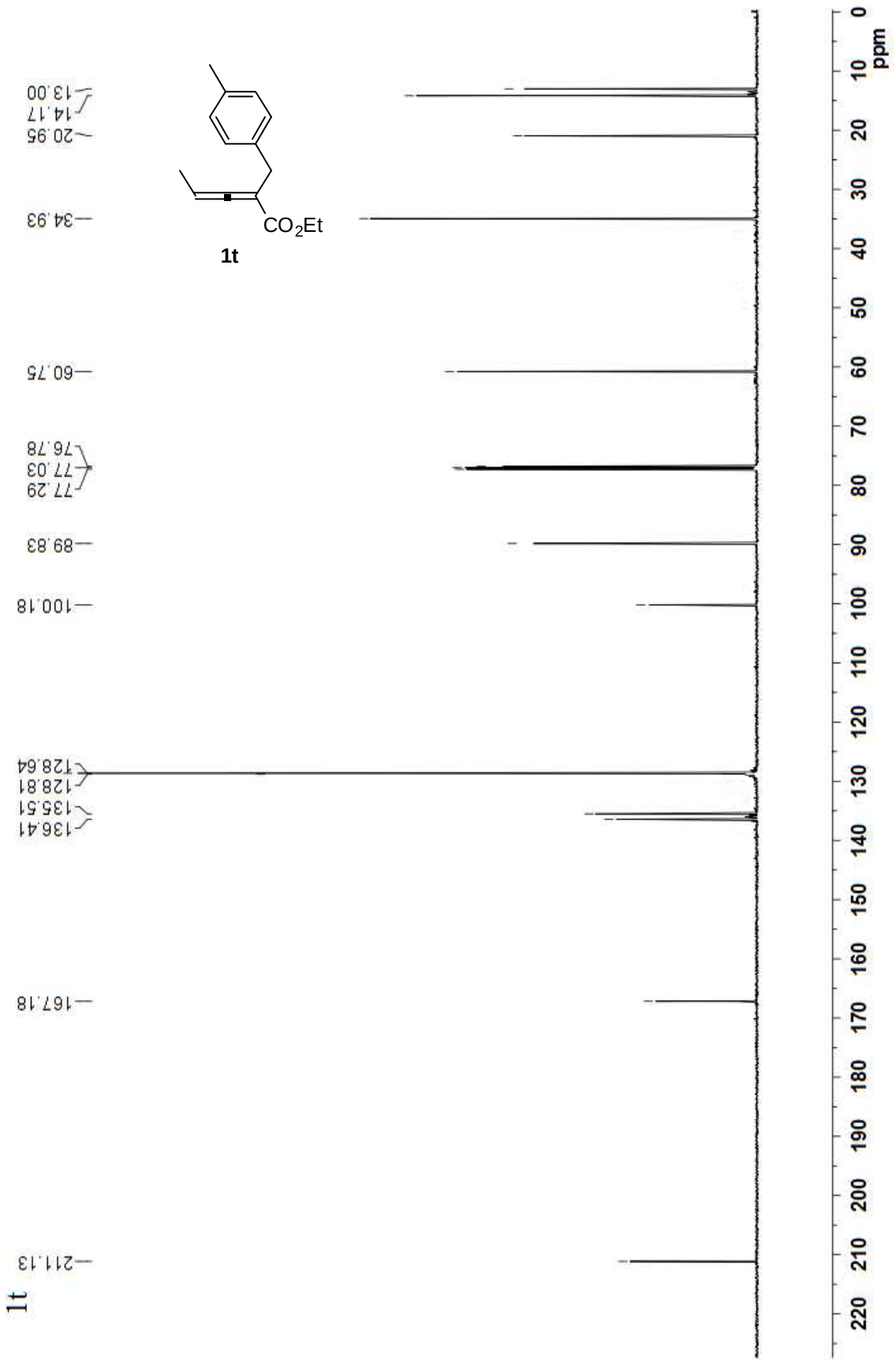

1r
1.235
1.249
1.263
1.703
1.717
3.468
3.472
3.498
3.502
3.525
3.529
3.555
3.559
4.153
4.163
4.167
4.177
4.181
4.196
5.455
5.465
5.469
5.474
5.479
5.484
5.489
5.499
7.111
7.126
7.141
7.149
7.162
7.164
7.304
7.307
7.311
7.318
7.322
7.325
7.377
7.380
3.08
2.99
2.04
2.07
0.93
2.07
2.01
ppm
Br
CO2Et
1r

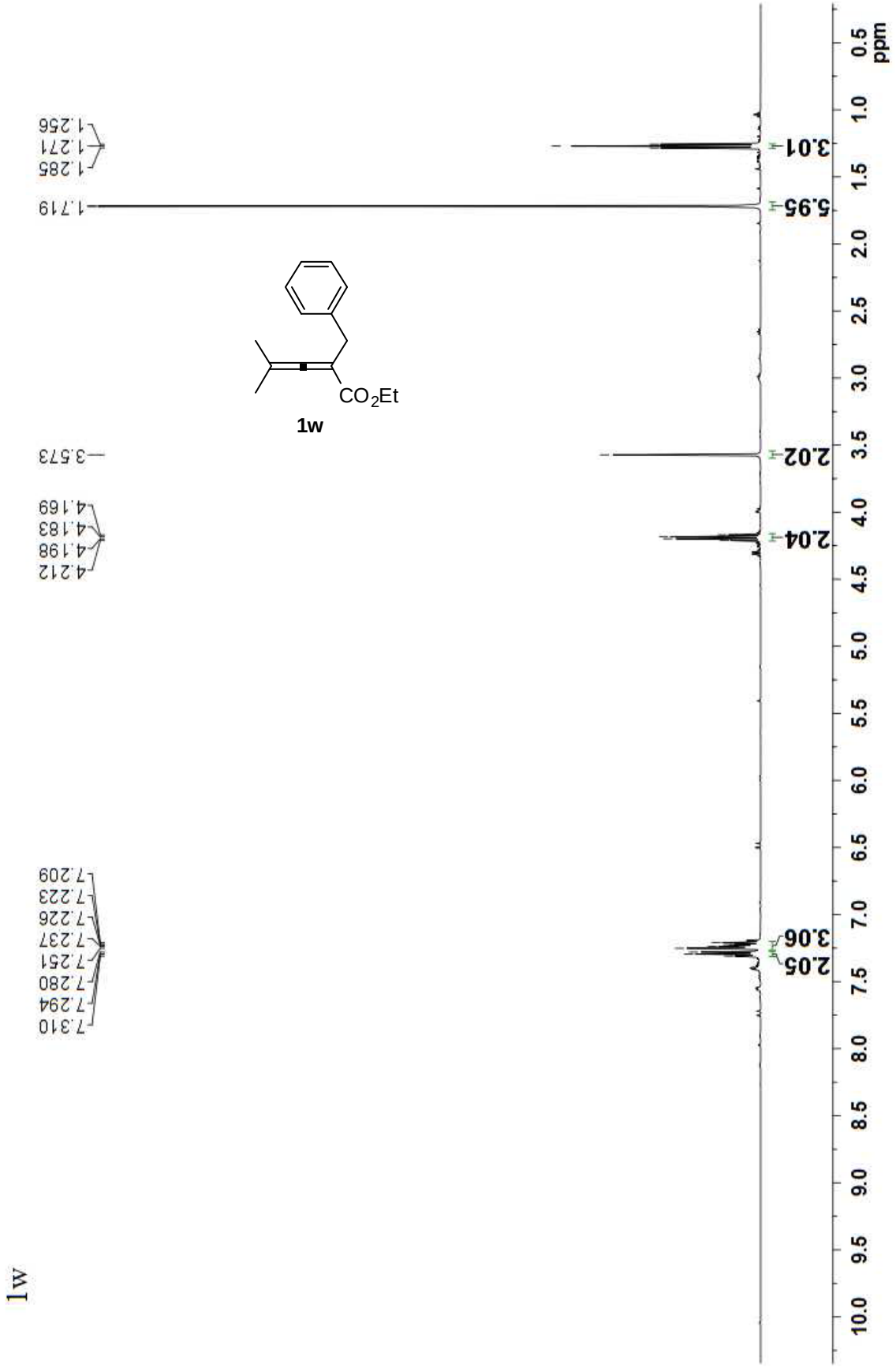

14.12
34.91
60.86
77.03
90.34
99.46
122.07
127.40
129.19
129.62
131.78
141.78
166.79
211.07
1r
Br
CO2Et
1r
ppm

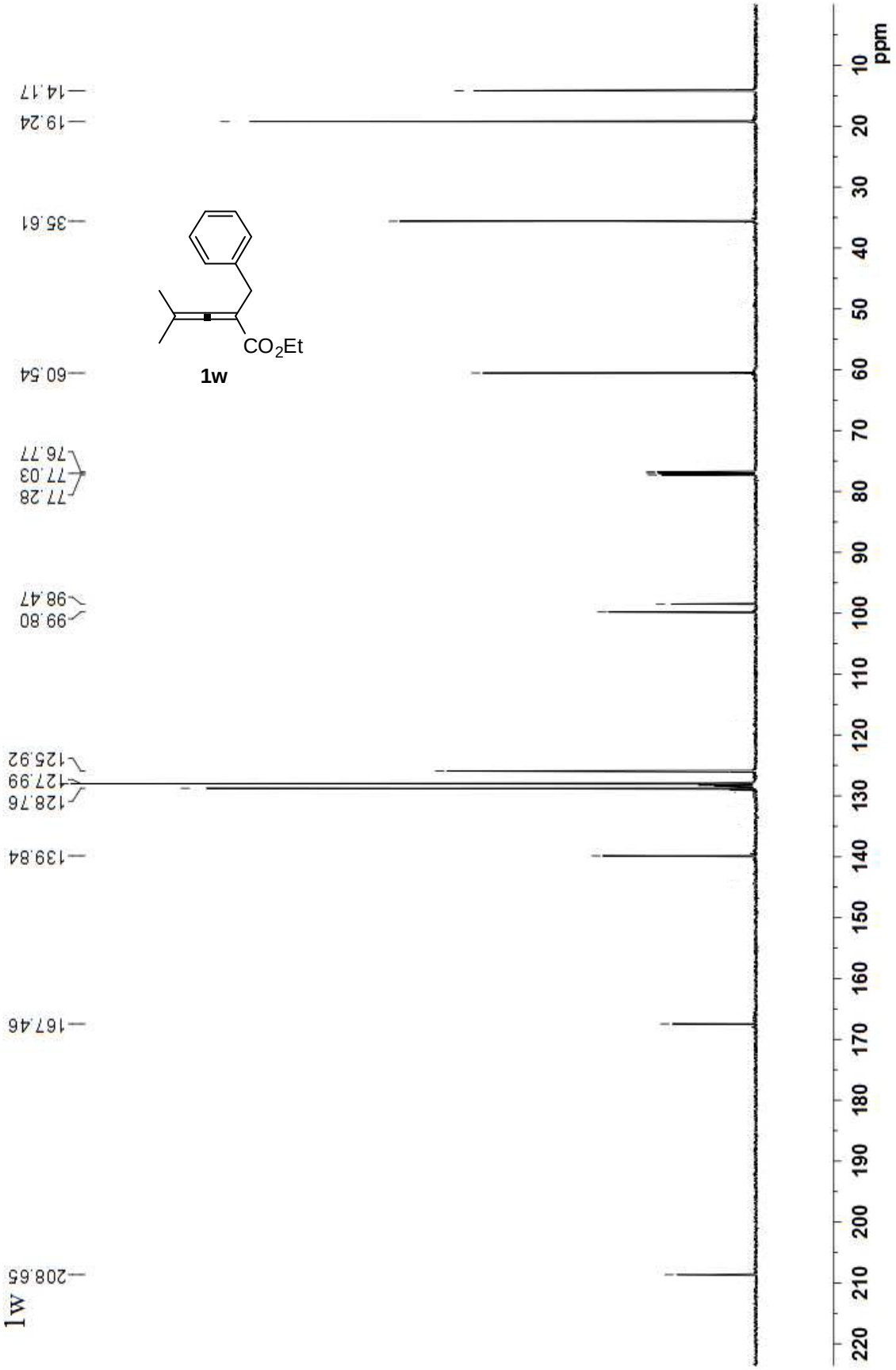

1s
1.283
1.298
1.312
1.610
1.624
2.325
3.535
3.541
3.566
3.572
3.602
3.607
3.633
3.638
4.207
4.217
4.221
4.231
4.235
5.341
5.347
5.355
5.361
5.367
5.370
5.376
5.382
5.390
5.396
7.121
7.132
7.136
7.140
7.174
7.184
7.191
2.98
2.96
2.94
2.03
1.97
0.95
4.00
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
CO2Et
1s

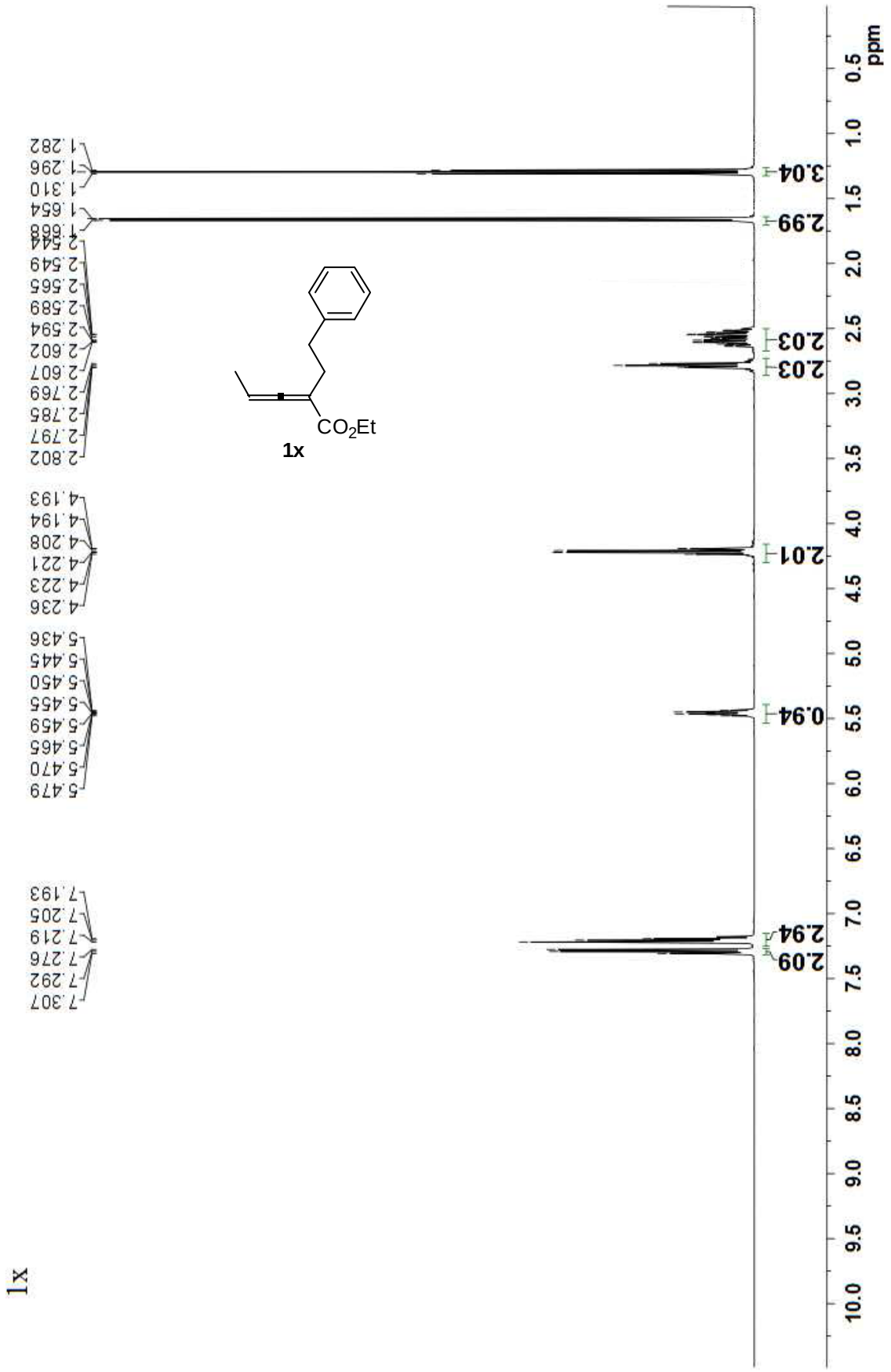

1s
211.01
167.34
137.34
136.48
129.97
129.65
126.39
125.73
99.55
90.27
77.36
77.10
76.85
60.91
32.73
19.31
14.26
12.80
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
CO2Et
1s

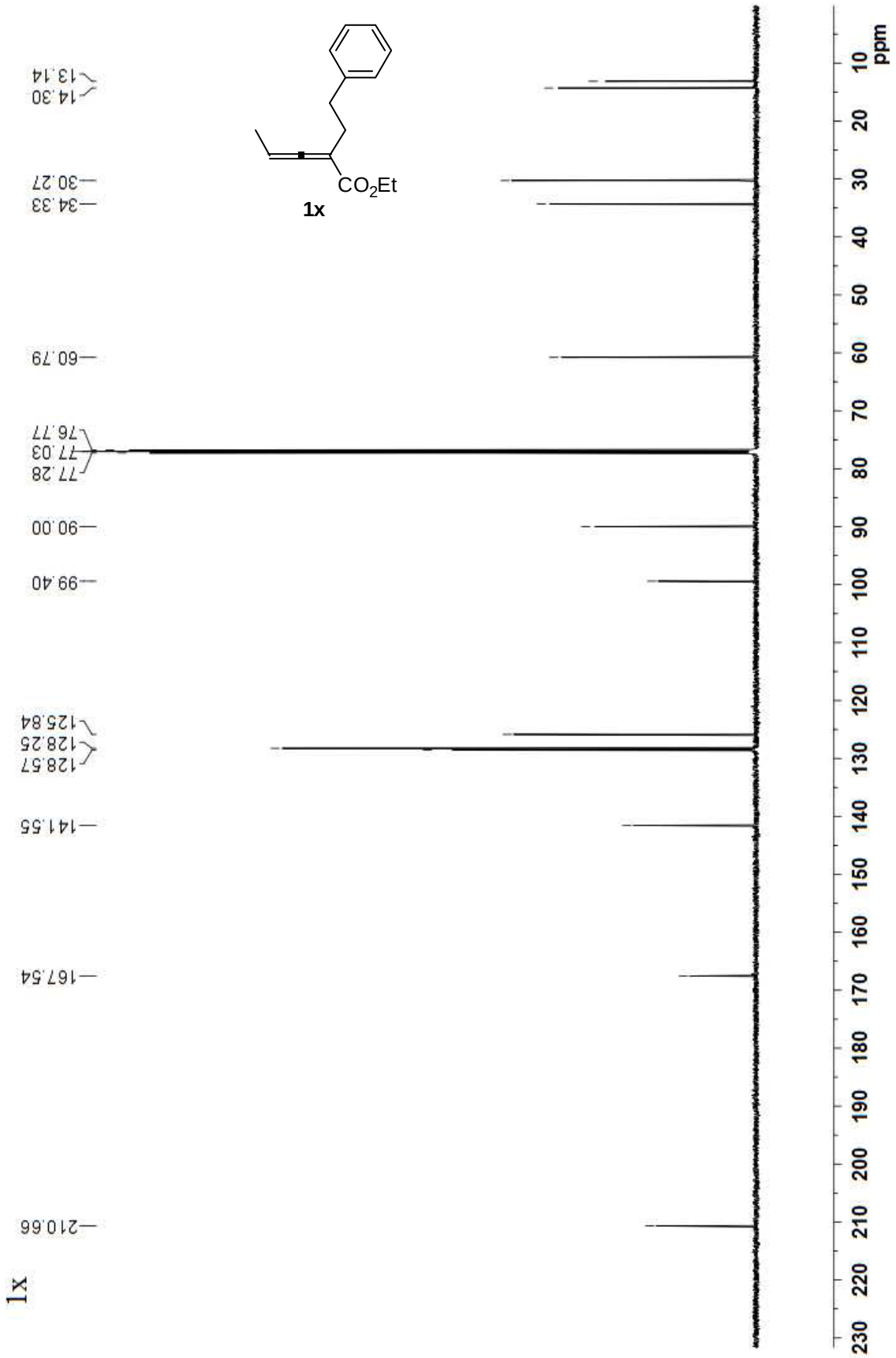

1t
1.276
1.290
1.305
1.739
1.753
2.355
3.517
3.521
3.546
3.551
3.569
3.574
3.599
3.603
4.188
4.191
4.202
4.205
4.217
4.220
5.459
5.463
5.468
5.473
5.478
5.482
5.487
5.492
5.497
5.502
5.507
7.115
7.131
7.161
7.177
3.00
3.00
3.05
2.04
2.06
0.93
4.03
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
CO2Et
1t

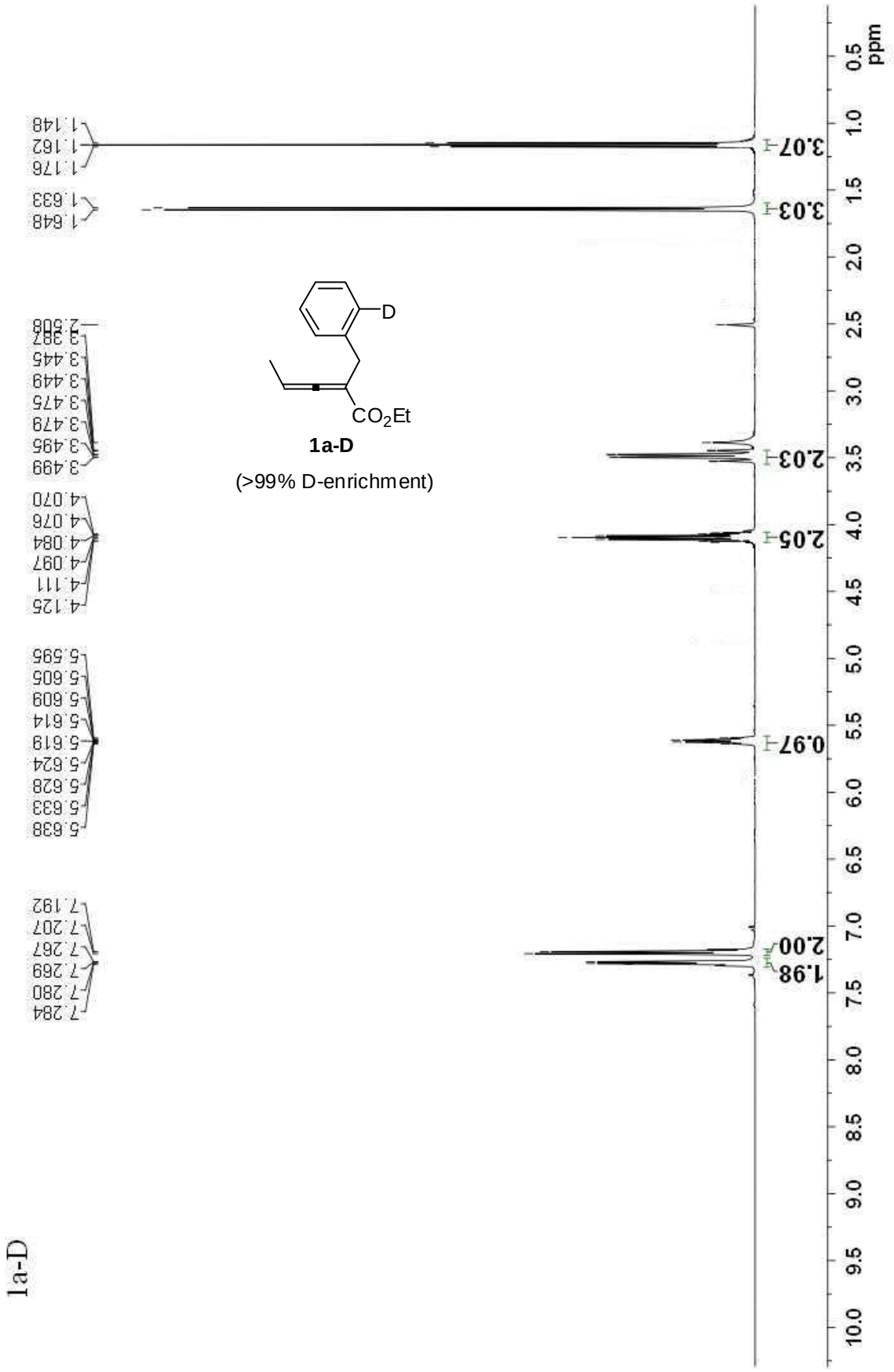

1t
211.13
167.18
136.41
135.51
128.81
128.64
100.18
89.83
77.29
77.03
76.78
60.75
34.93
20.95
14.17
13.00
CO2Et
1t
ppm

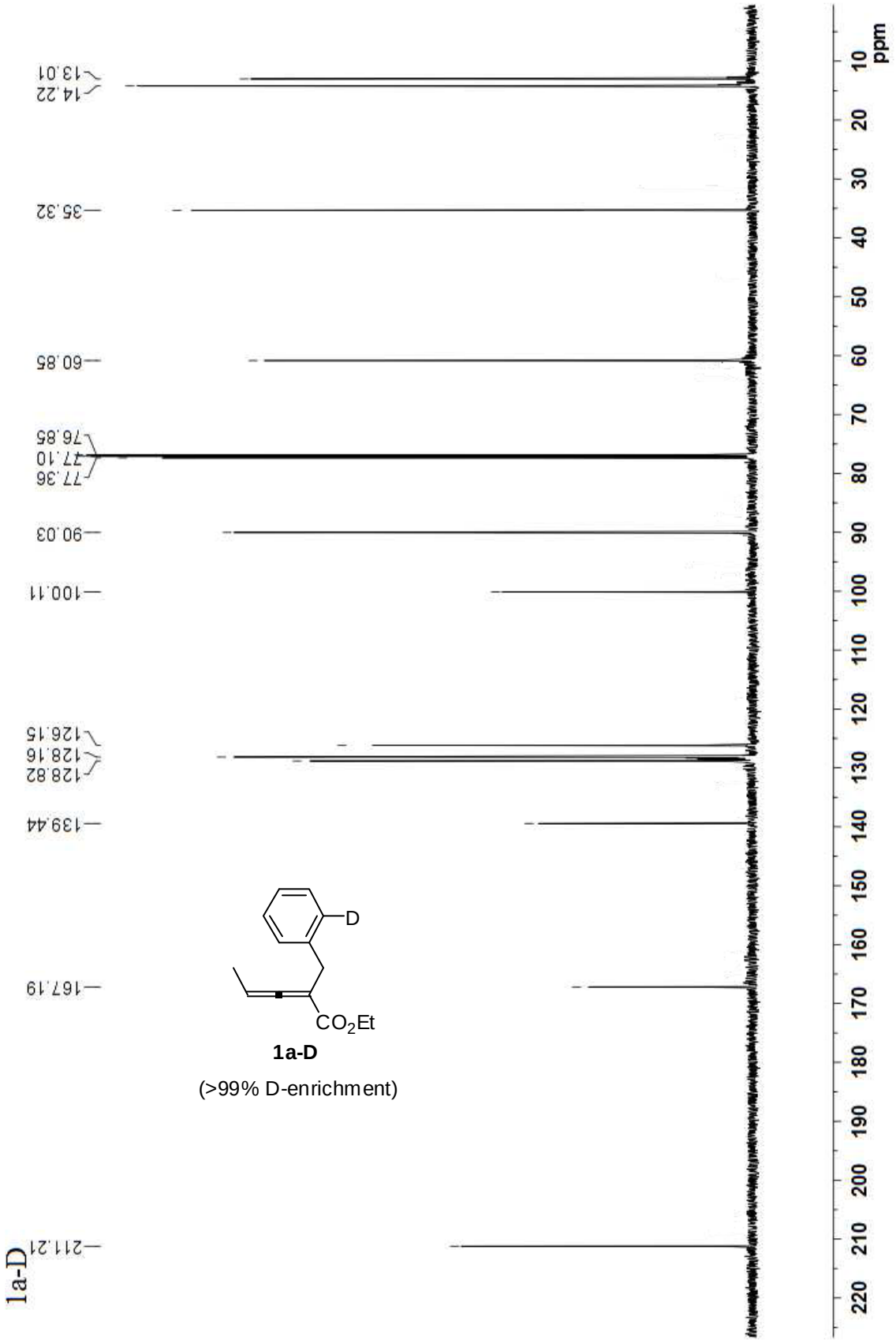

1w
1.256
1.271
1.285
1.719
3.573
4.169
4.183
4.198
4.212
7.209
7.223
7.226
7.237
7.251
7.280
7.294
7.310
3.01
5.95
2.02
2.04
3.06
2.05
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
CO2Et
1w


14.17
19.24
35.61
60.54
76.77
77.03
77.28
98.47
99.80
125.92
127.99
128.76
139.84
167.46
208.65
1w
CO2Et
1w
ppm


1x
1.282
1.296
1.310
1.654
1.668
2.544
2.549
2.565
2.589
2.594
2.602
2.607
2.769
2.785
2.797
2.802
4.193
4.194
4.208
4.221
4.223
4.236
5.436
5.445
5.450
5.455
5.459
5.465
5.470
5.479
7.193
7.205
7.219
7.276
7.292
7.307
CO2Et
1x
3.04
2.99
2.03
2.03
2.01
0.94
2.94
2.09
ppm

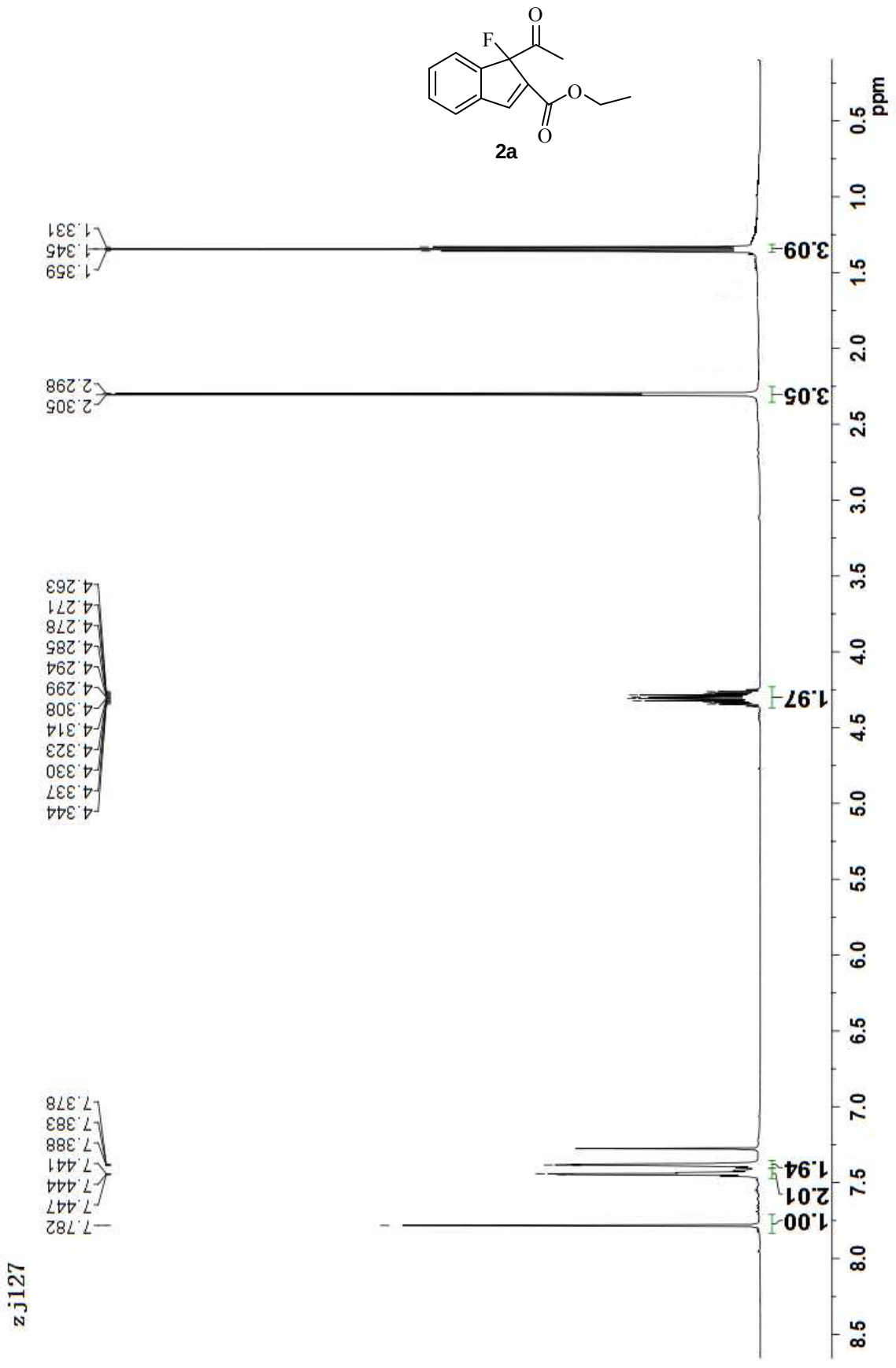

1x
210.66
167.54
141.55
128.57
128.25
125.84
99.40
90.00
77.28
77.03
76.77
60.79
34.33
30.27
14.30
13.14
CO2Et
1x
ppm

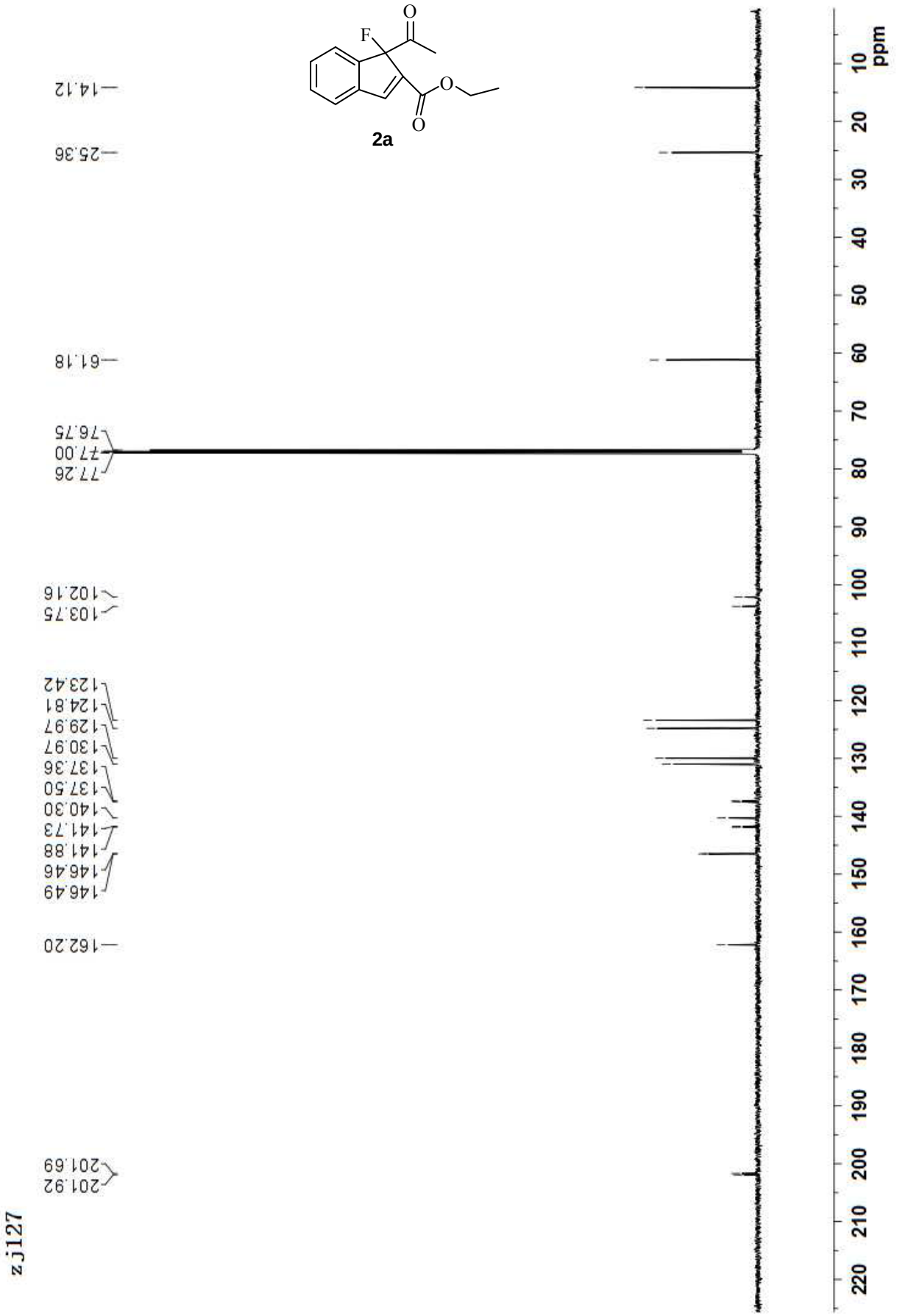

1a-D
D
CO2Et
1a-D
(>99% D-enrichment)
3.07
3.03
2.03
2.05
0.97
2.00
1.98
ppm

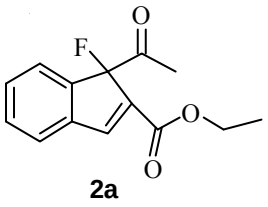


1a-D

(>99% D-enrichment)

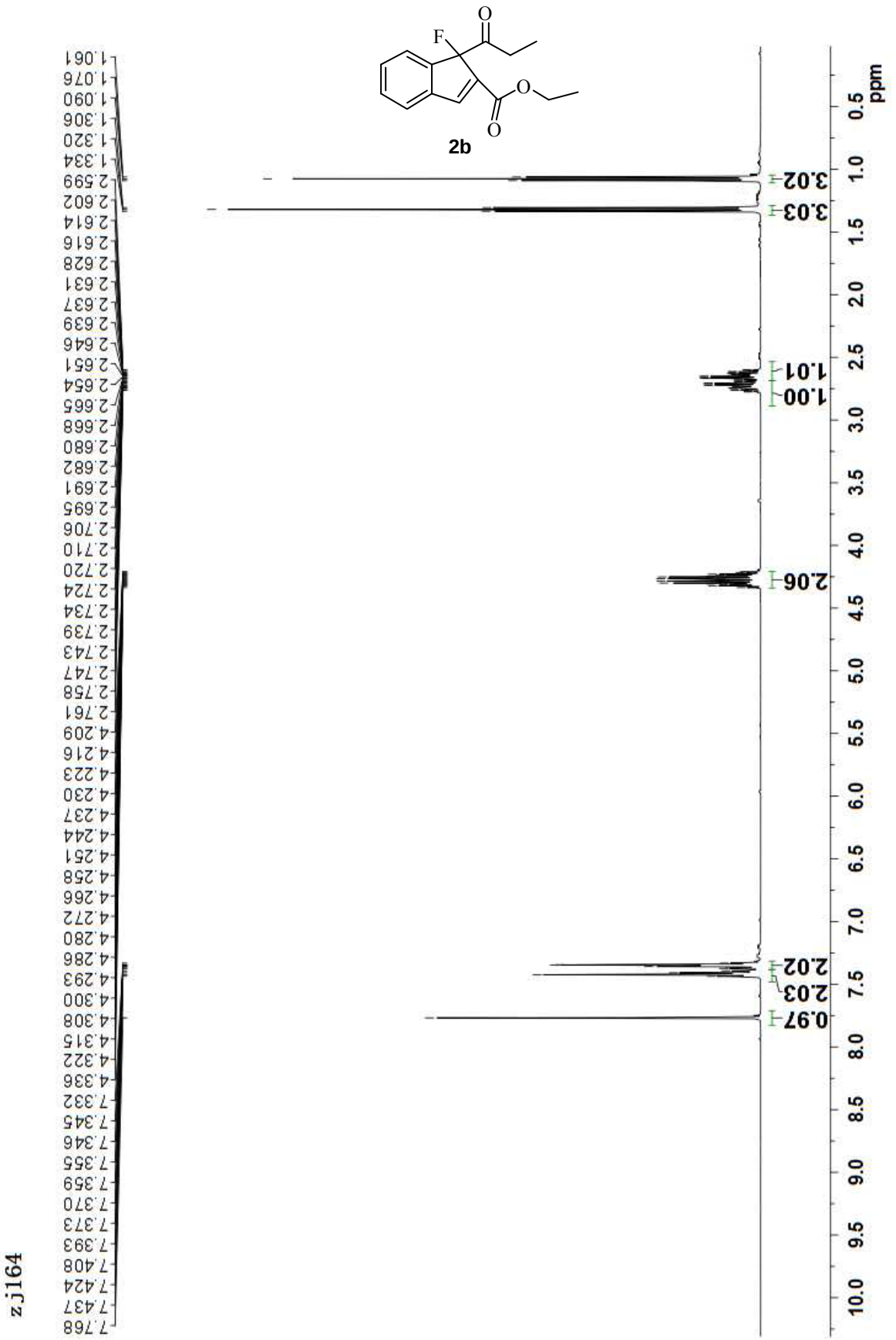

O
F
O
O
O
2a
zj127
7.782
7.447
7.444
7.441
7.388
7.383
7.378
4.344
4.337
4.330
4.323
4.314
4.308
4.299
4.294
4.285
4.278
4.271
4.263
2.305
2.298
1.359
1.345
1.331
1.00
2.01
1.94
1.97
3.05
3.09
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5

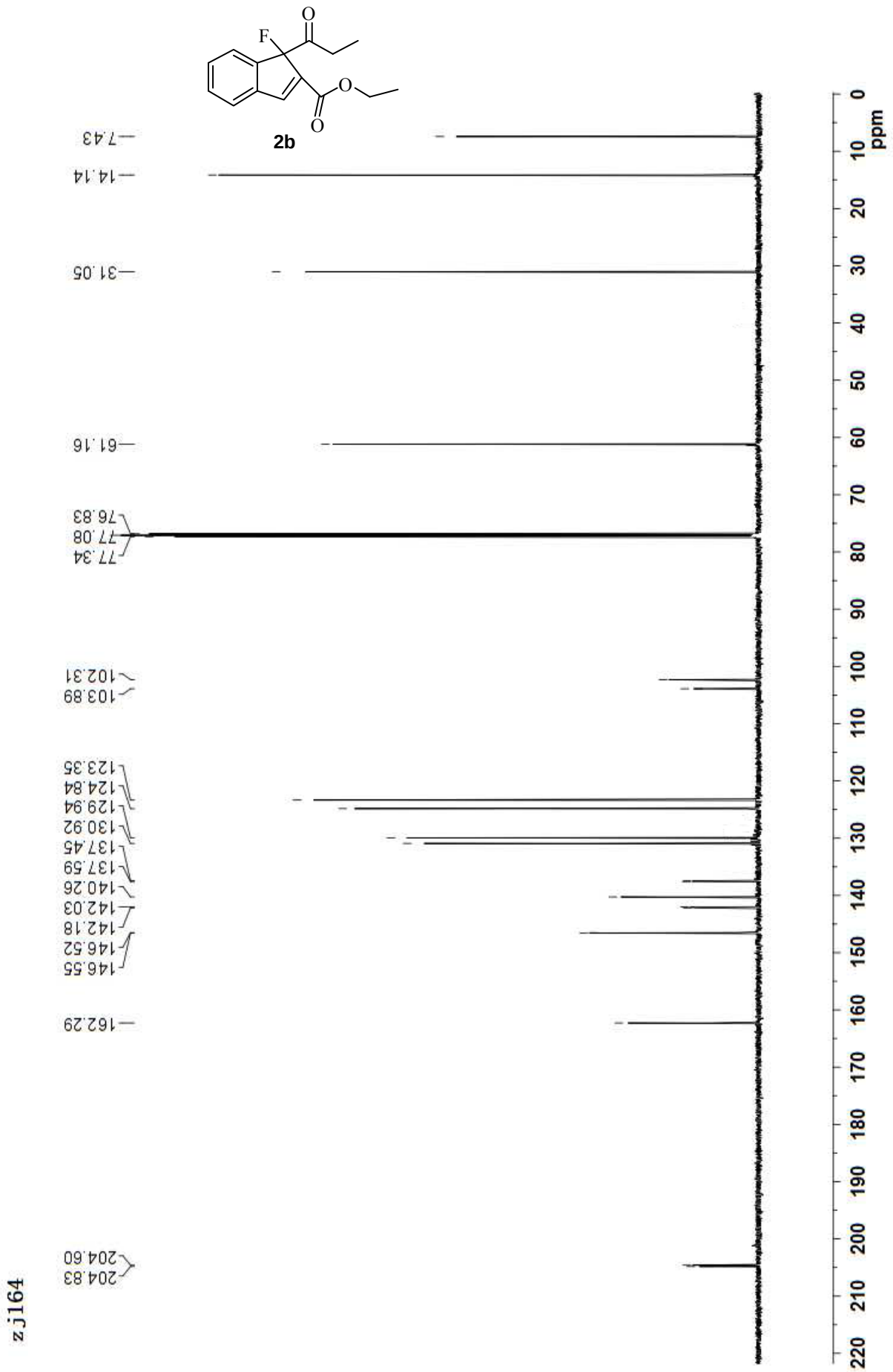

F
O
O
O
2a
zj127
14.12
25.36
61.18
76.75
77.00
77.26
102.16
103.75
123.42
124.81
129.97
130.97
137.36
137.50
140.30
141.73
141.88
146.46
146.49
162.20
201.69
201.92
ppm

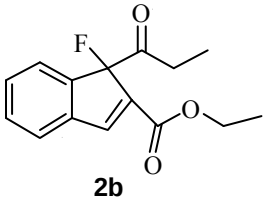

O
F
O
O

2a

-176.993
1.00
ppm
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
zj127 CDCl3 F19
Pulse Sequence: s2pul

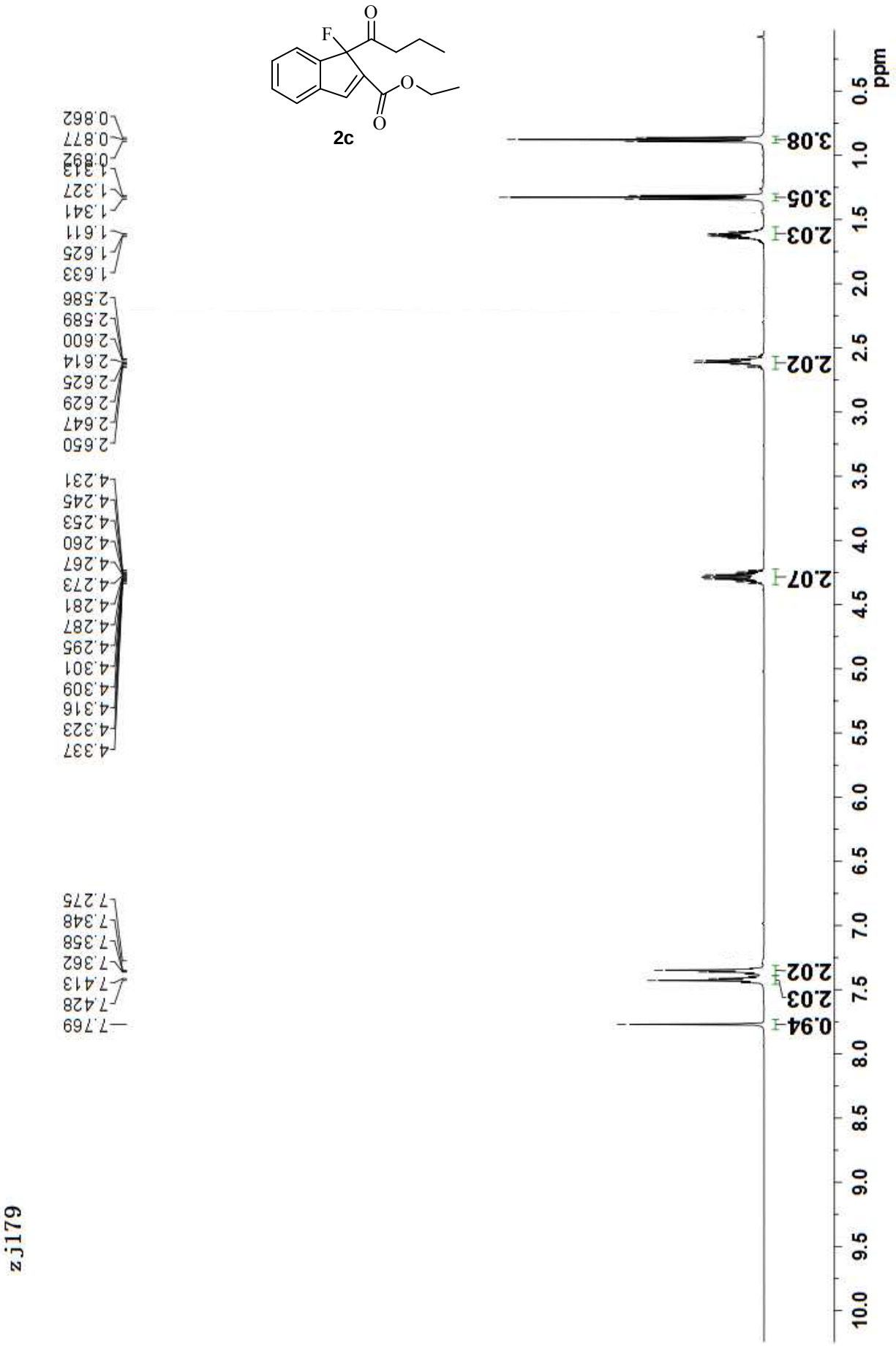

zj164
2b
F
O
O
O
3.02
3.03
1.01
1.00
2.06
2.02
2.03
0.97
ppm

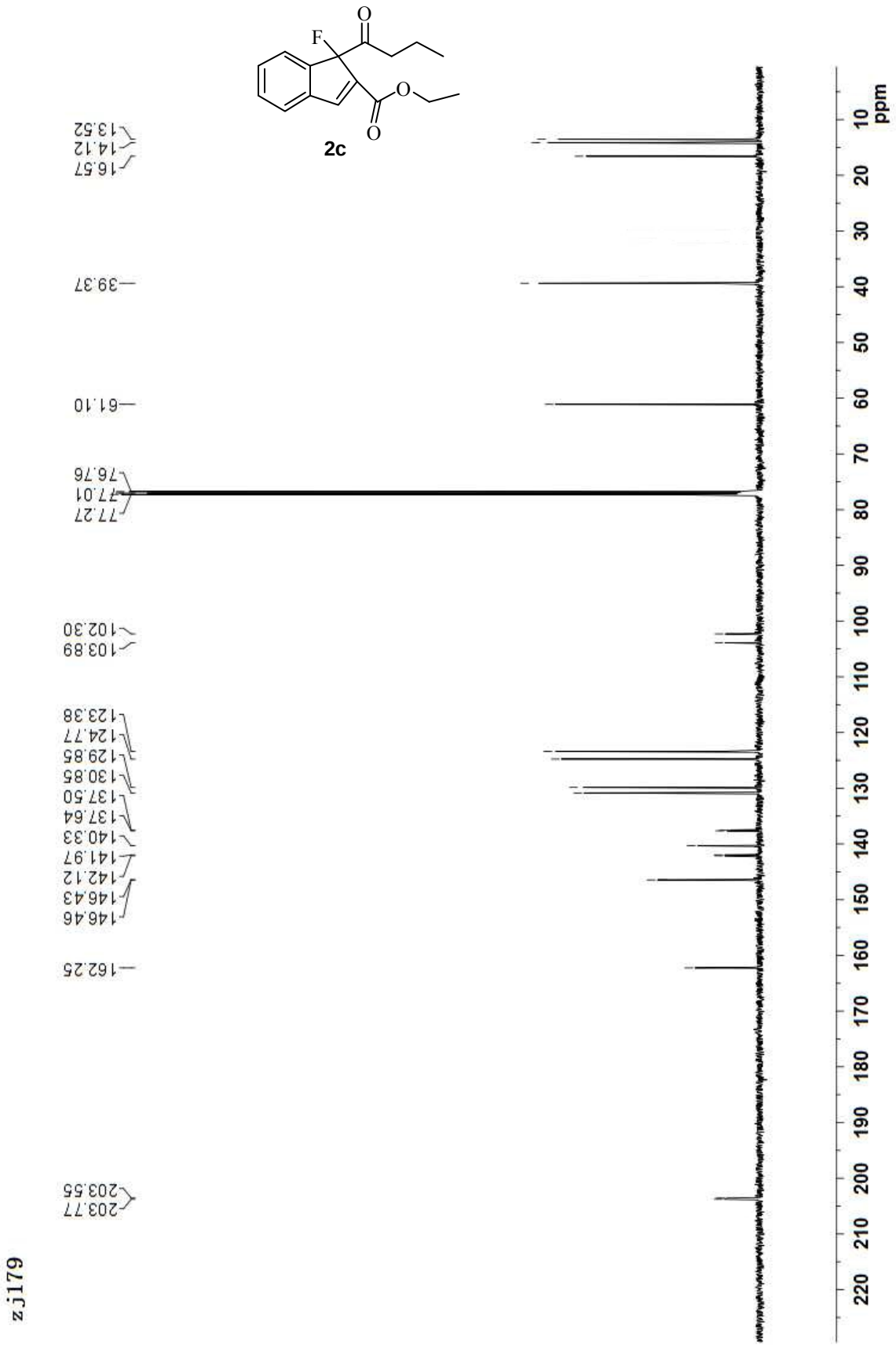

F
O
O
O
2b
7.43
14.14
31.05
61.16
76.83
77.08
77.34
102.31
103.89
123.35
124.84
129.94
130.92
137.45
137.59
140.26
142.03
142.18
146.52
146.55
162.29
204.60
204.83
zj164
ppm


F
O
O
O

2b

-178.355
1.00
ppm
-180
-160
-140
-120
-100
-80
-60
-40
-20
0
zj164 CDCl3 F19
Pulse Sequence: s2pul

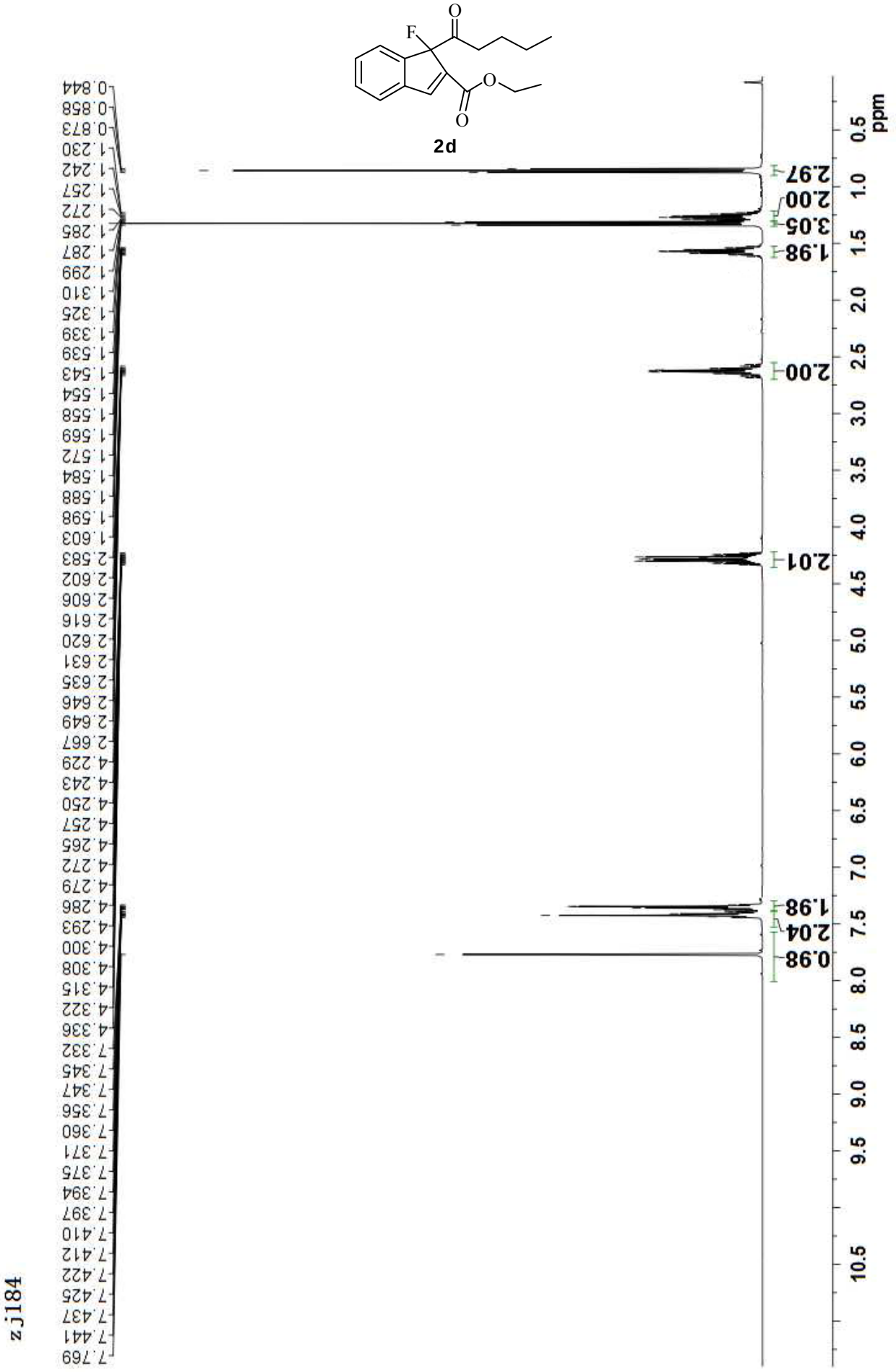

F
O
O
O
2c
zj179
0.862
0.877
0.892
1.313
1.327
1.341
1.611
1.625
1.633
2.586
2.589
2.600
2.614
2.625
2.629
2.647
2.650
4.231
4.245
4.253
4.260
4.267
4.273
4.281
4.287
4.295
4.301
4.309
4.316
4.323
4.337
7.275
7.348
7.358
7.362
7.413
7.428
7.769
3.08
3.05
2.03
2.02
2.07
2.02
2.03
0.94
ppm

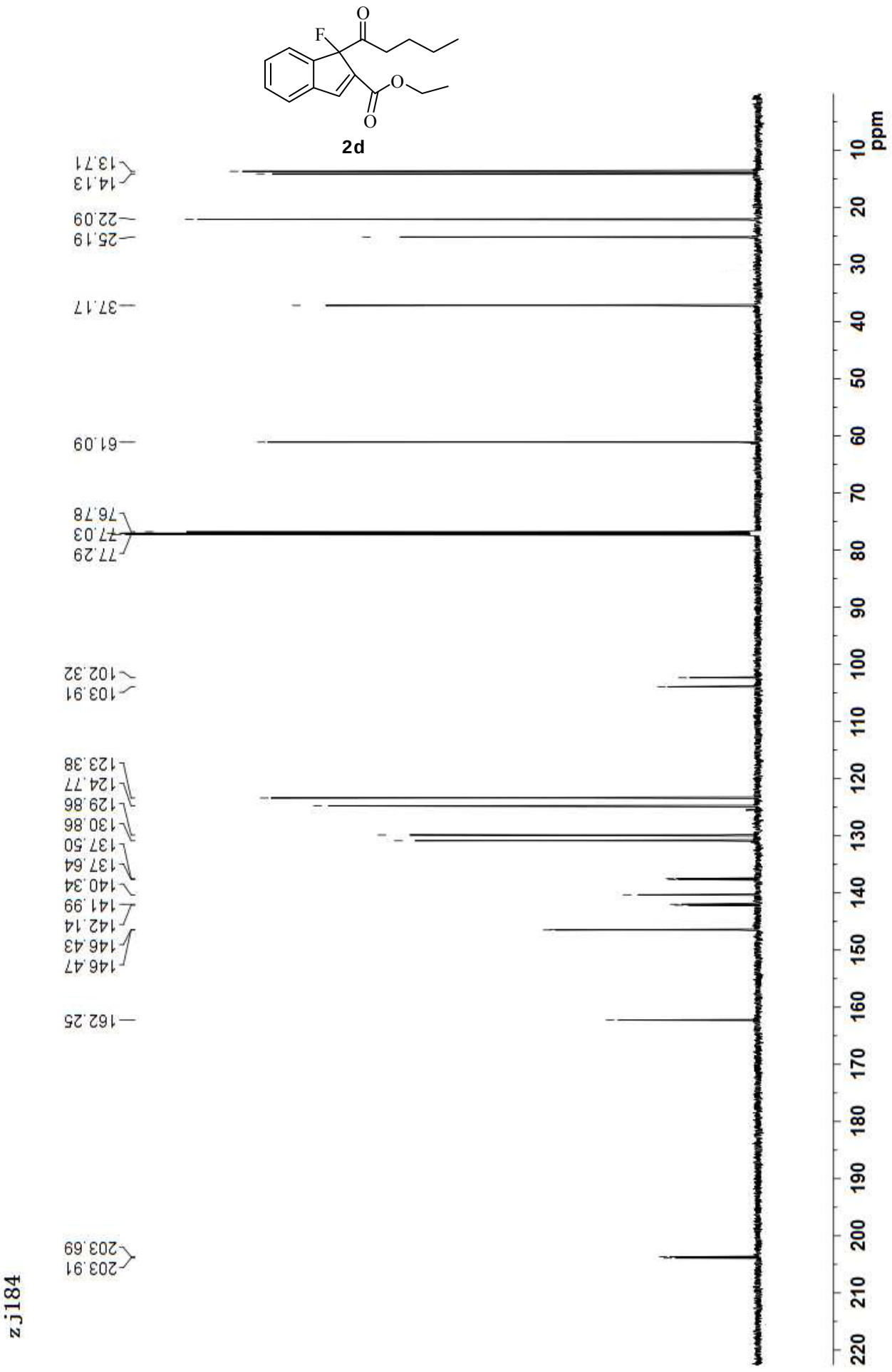

2c
zj179
13.52
14.12
16.57
39.37
61.10
76.76
77.01
77.27
102.30
103.89
123.38
124.77
129.85
130.85
137.50
137.64
140.33
141.97
142.12
146.43
146.46
162.25
203.77
203.55
ppm

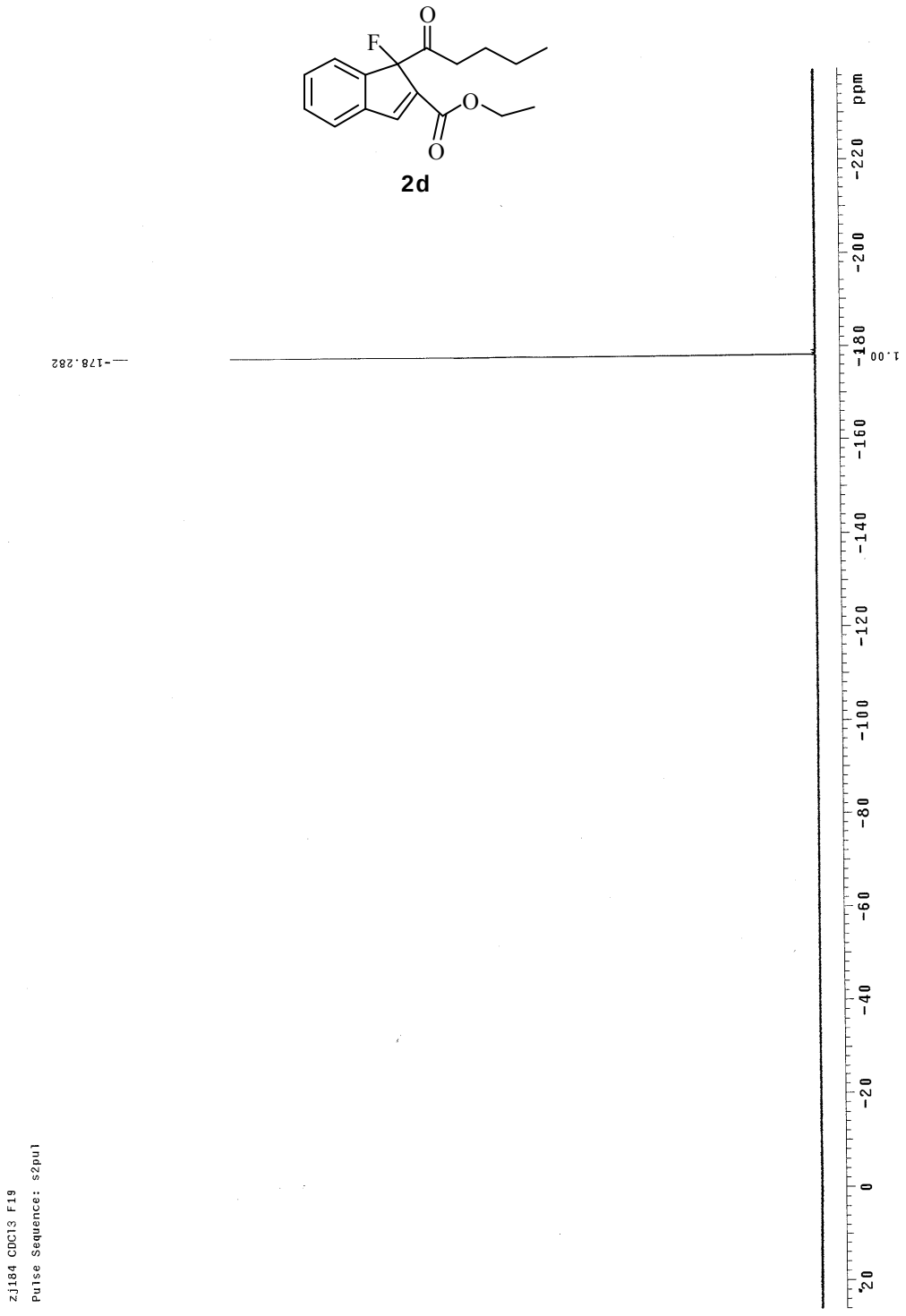
F
O
O
O

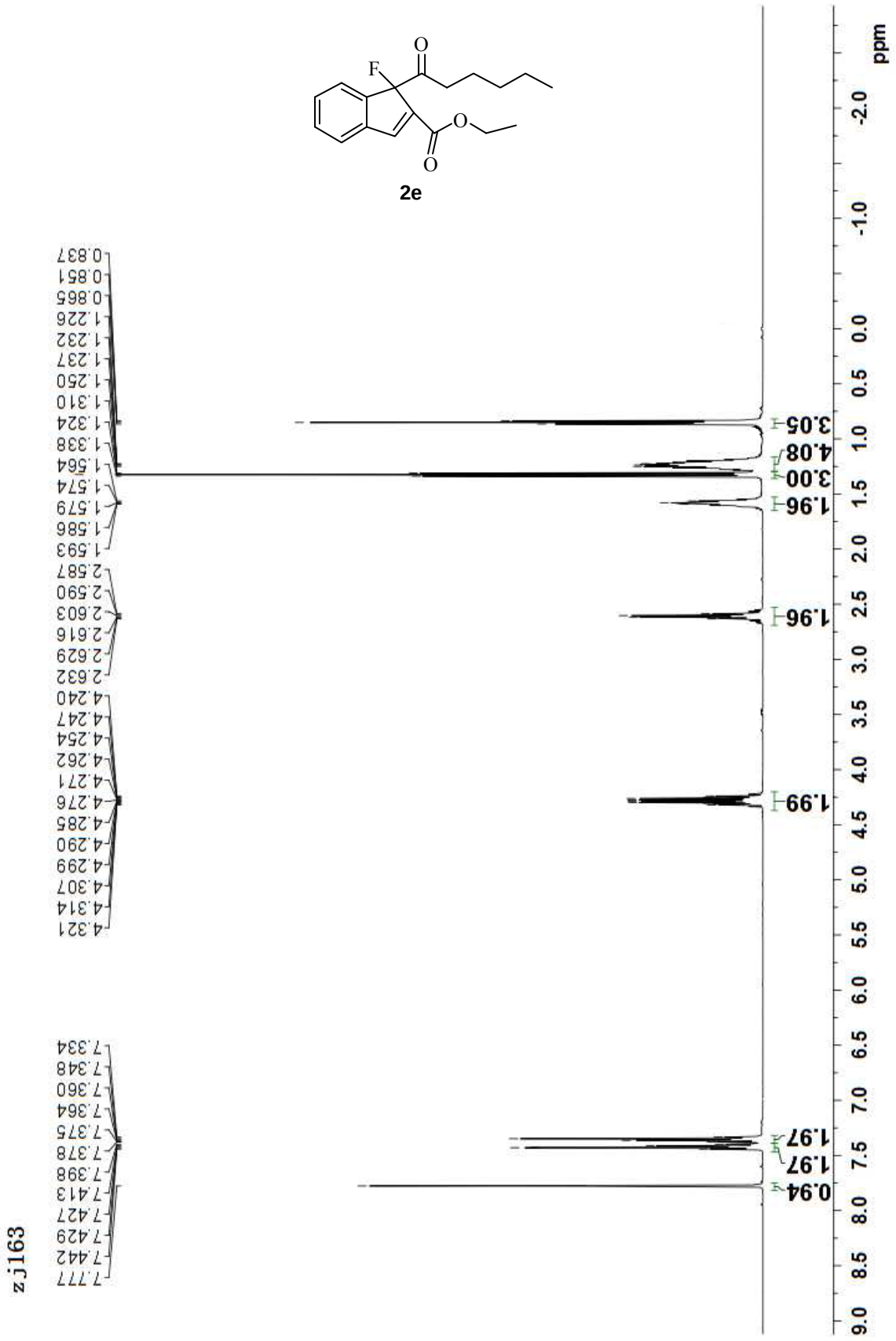
2c

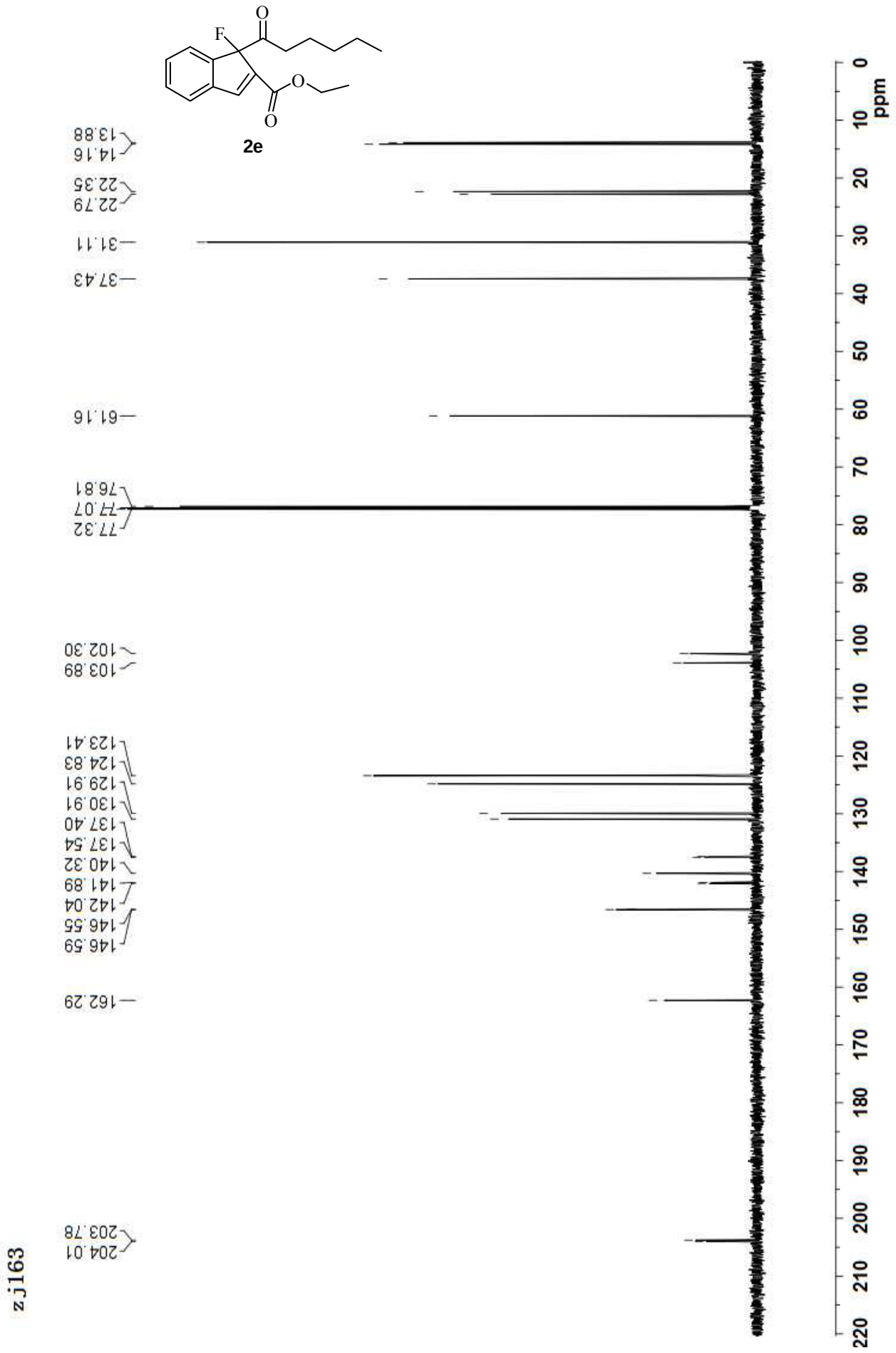
-178.428
1.00
ppm
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
zj179 CDCl3 F19
Pulse Sequence: s2pul

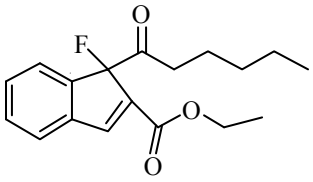

F
O
O
O
2d
zj184
0.844
0.858
0.873
1.230
1.242
1.257
1.272
1.285
1.287
1.299
1.310
1.325
1.339
1.539
1.543
1.554
1.558
1.569
1.572
1.584
1.588
1.598
1.603
2.583
2.602
2.606
2.616
2.620
2.631
2.635
2.646
2.649
2.667
4.229
4.243
4.250
4.257
4.265
4.272
4.279
4.286
4.293
4.300
4.308
4.315
4.322
4.336
7.332
7.345
7.347
7.356
7.360
7.371
7.375
7.394
7.397
7.410
7.412
7.422
7.425
7.437
7.441
7.769
2.97
2.00
3.05
1.98
2.00
2.01
1.98
2.04
0.98
ppm


O
F
O
O
O
2d
13.71
14.13
22.09
25.19
37.17
61.09
76.78
77.03
77.29
102.32
103.91
123.38
124.77
129.86
130.86
137.50
137.64
140.34
141.99
142.14
146.43
146.47
162.25
203.69
203.91
zj184
ppm


O
F
O
O
2d
-178.282
1.00
ppm
-220
-200
-180
-160
-140
-120
-100
-80
-60
-40
-20
0
20
zj184 CDCl3 F19
Pulse Sequence: s2pul

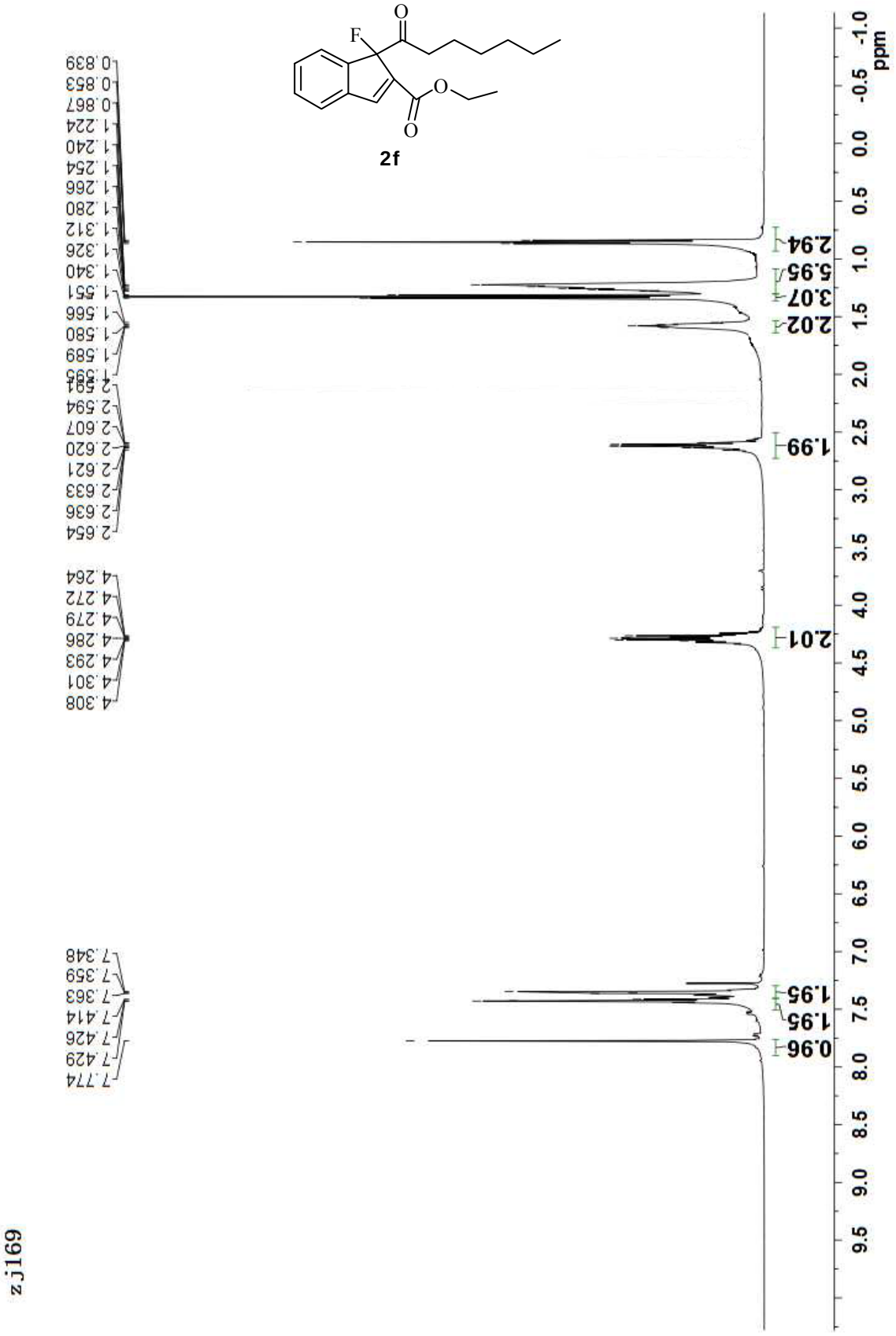

F
O
O
O
2e
zj163
ppm
0.94
1.97
1.97
3.05
4.08
3.00
1.96
1.96
1.99

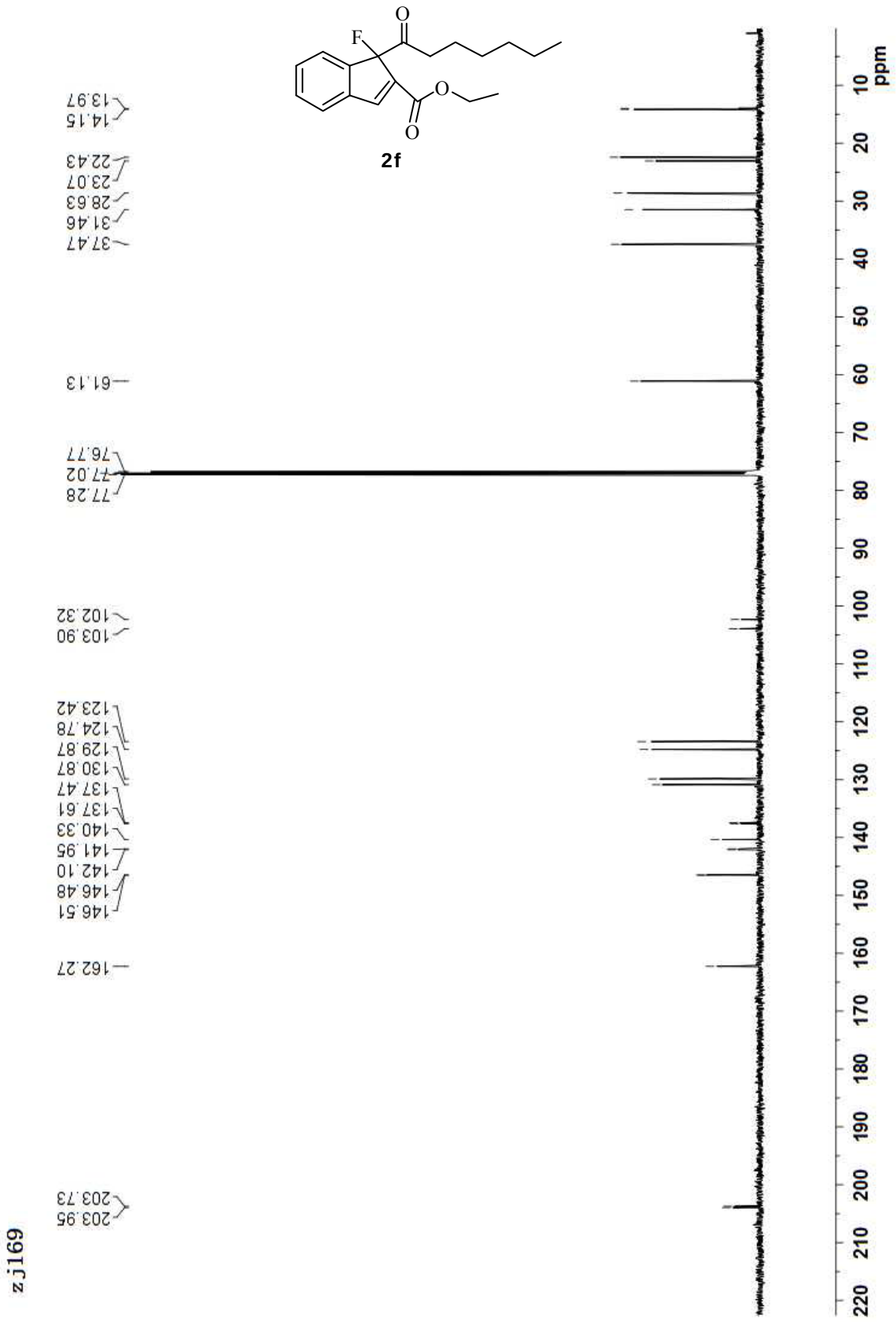

F
O
O
O
2e
13.88
14.16
22.35
22.79
31.11
37.43
61.16
76.81
77.07
77.32
102.30
103.89
123.41
124.83
129.91
130.91
137.40
137.54
140.32
141.89
142.04
146.55
146.59
162.29
203.78
204.01
zj163
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220

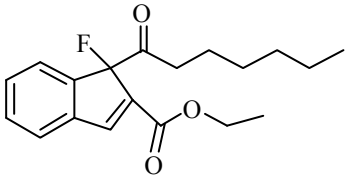


2e

-178.343
1.00
ppm
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
zj163 CDCl3 F19
Pulse Sequence: s2pul

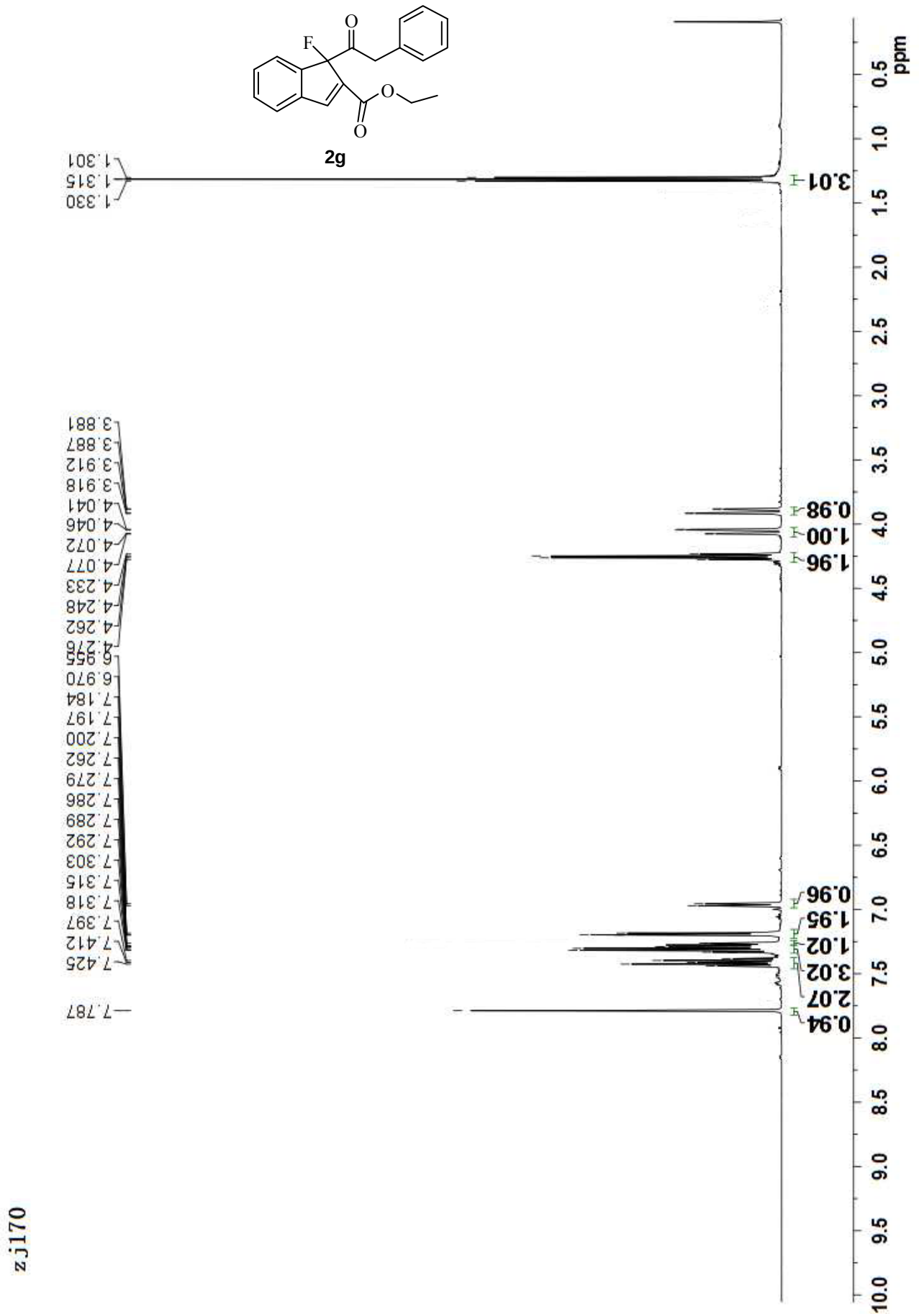

zj169
2f
F
O
O
O
0.839
0.853
0.867
1.224
1.240
1.254
1.266
1.280
1.312
1.326
1.340
1.551
1.566
1.580
1.589
2.591
2.594
2.607
2.620
2.621
2.633
2.636
2.654
4.264
4.272
4.279
4.286
4.293
4.301
4.308
7.348
7.359
7.363
7.414
7.426
7.429
7.774
2.94
5.95
3.07
2.02
1.99
2.01
1.95
1.95
0.96
ppm

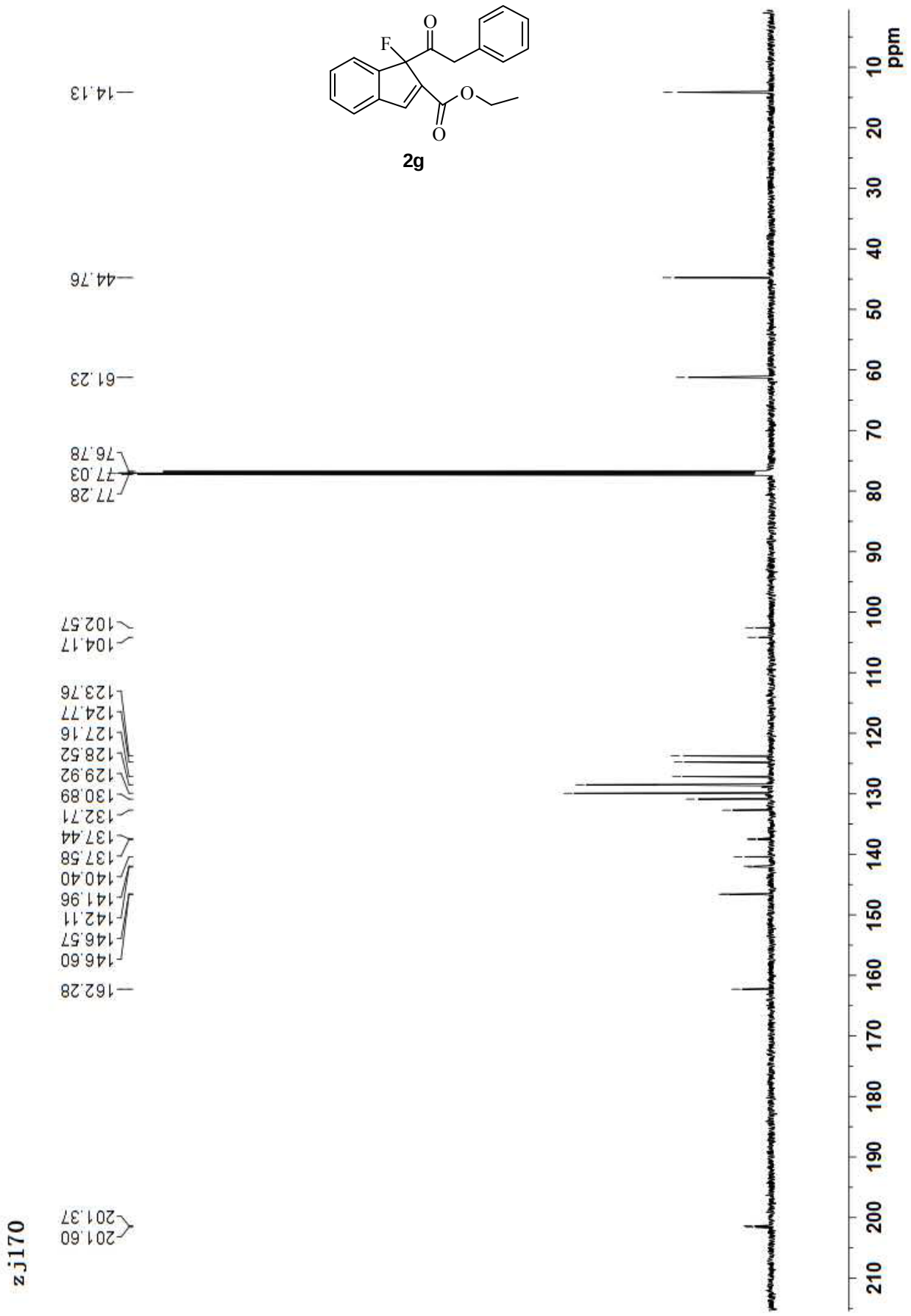

F
O
O
O
2f
zj169
13.97
14.15
22.43
23.07
28.63
31.46
37.47
61.13
76.77
77.02
77.28
102.32
103.90
123.42
124.78
129.87
130.87
137.47
137.61
140.33
141.95
142.10
146.48
146.51
162.27
203.73
203.95
ppm

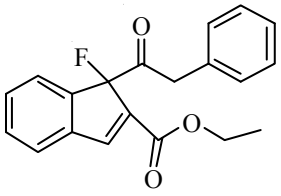


2f

-178.367
1.00
ppm
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
zj169 CDCl3 F19
Pulse Sequence: s2pul

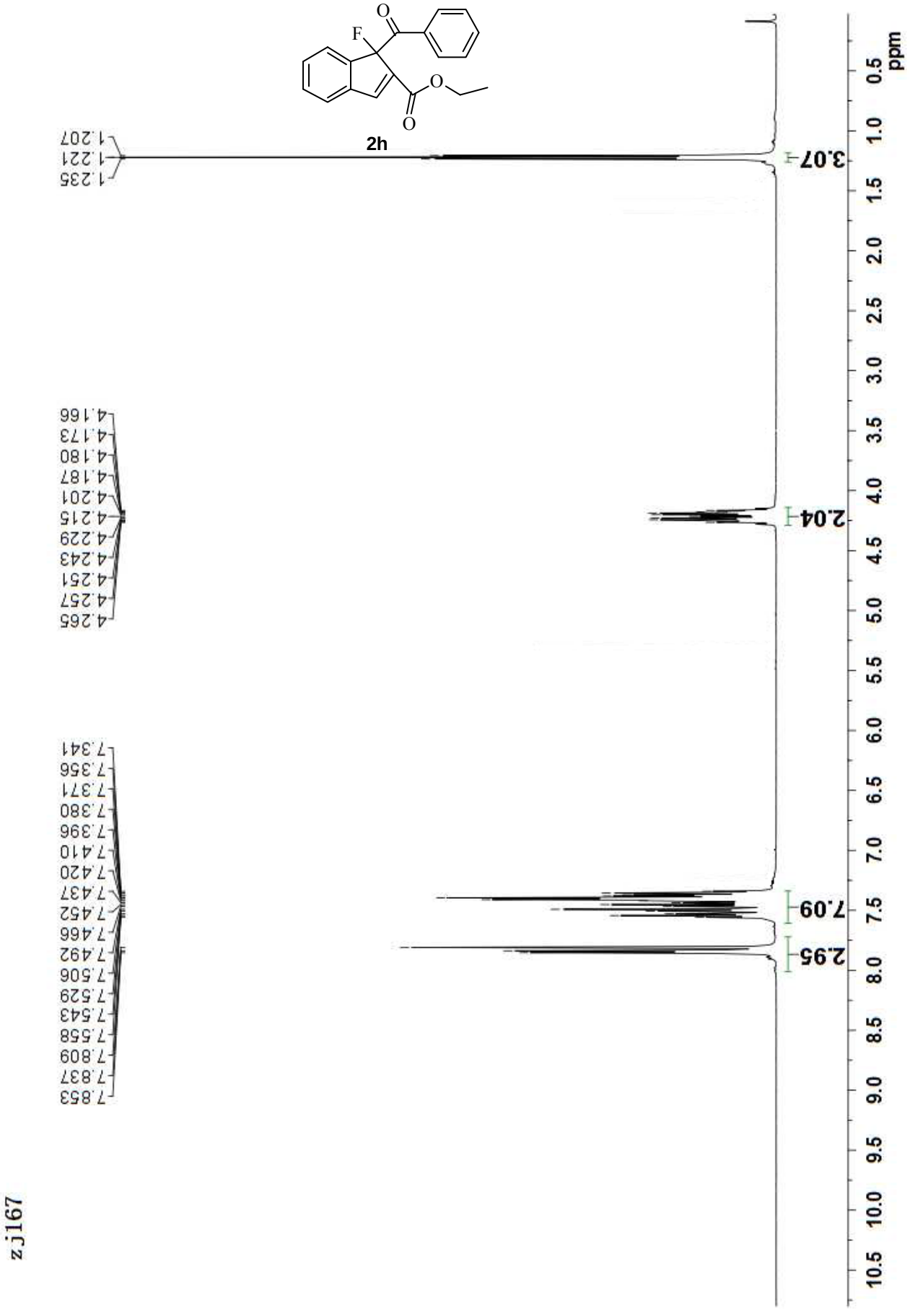

F
O
O
O
2g
zj170
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
3.01
0.98
1.00
1.96
0.96
1.95
1.02
3.02
2.07
0.94
1.301
1.315
1.330
3.881
3.887
3.912
3.918
4.041
4.046
4.072
4.077
4.233
4.248
4.262
4.276
6.955
6.970
7.184
7.197
7.200
7.262
7.279
7.286
7.289
7.292
7.303
7.315
7.318
7.397
7.412
7.425
7.787

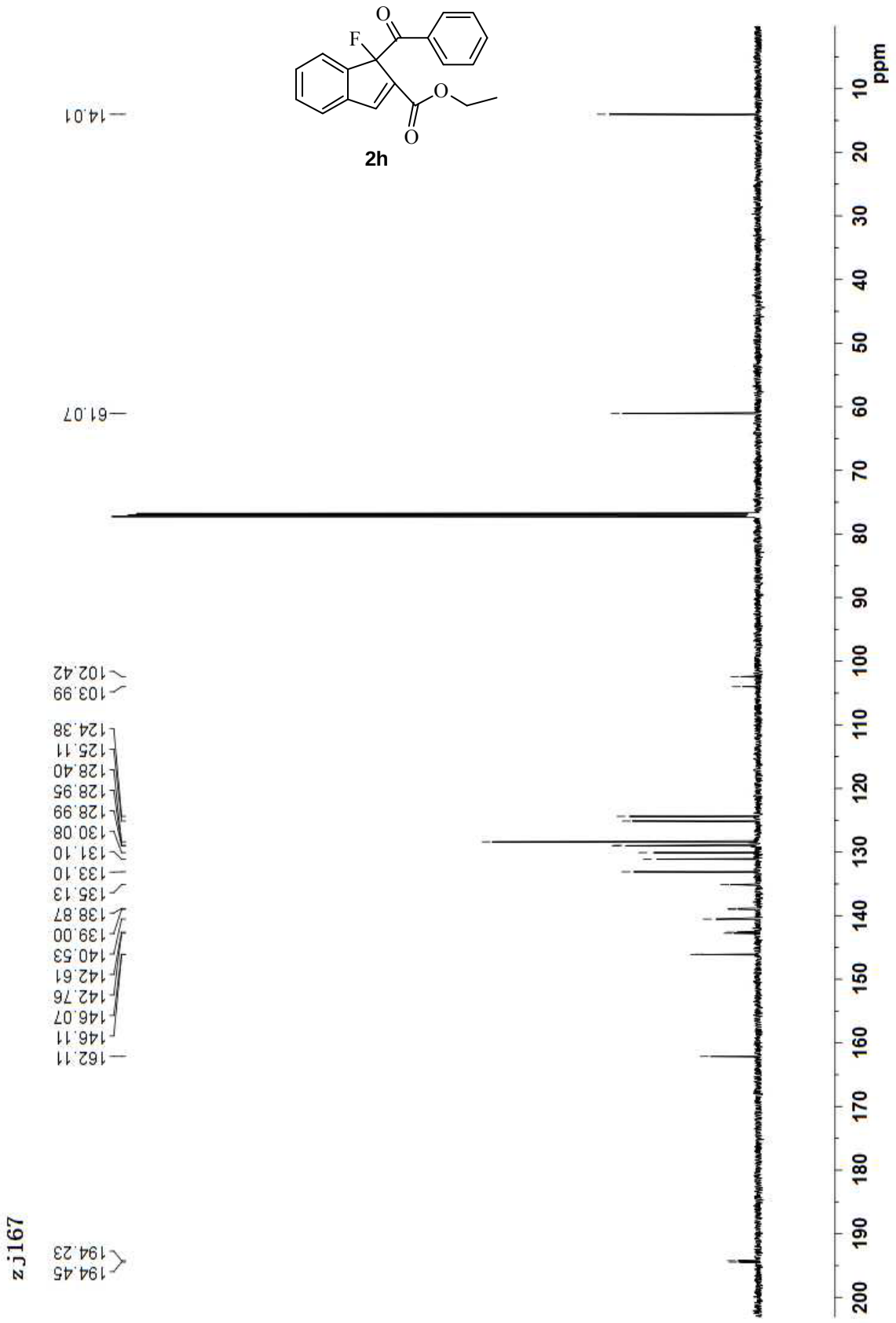

zj170
201.60
201.37
162.28
146.60
146.57
142.11
141.96
140.40
137.58
137.44
132.71
130.89
129.92
128.52
127.16
124.77
123.76
104.17
102.57
77.28
77.03
76.78
61.23
44.76
14.13
F
O
O
O
O
2g
ppm

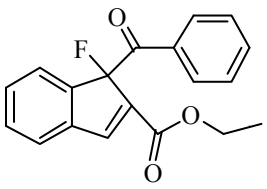

O
F
O
O

2g

-176.762
1.00
ppm
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
zj170 CDCl3 F19
Pulse Sequence: s2pul

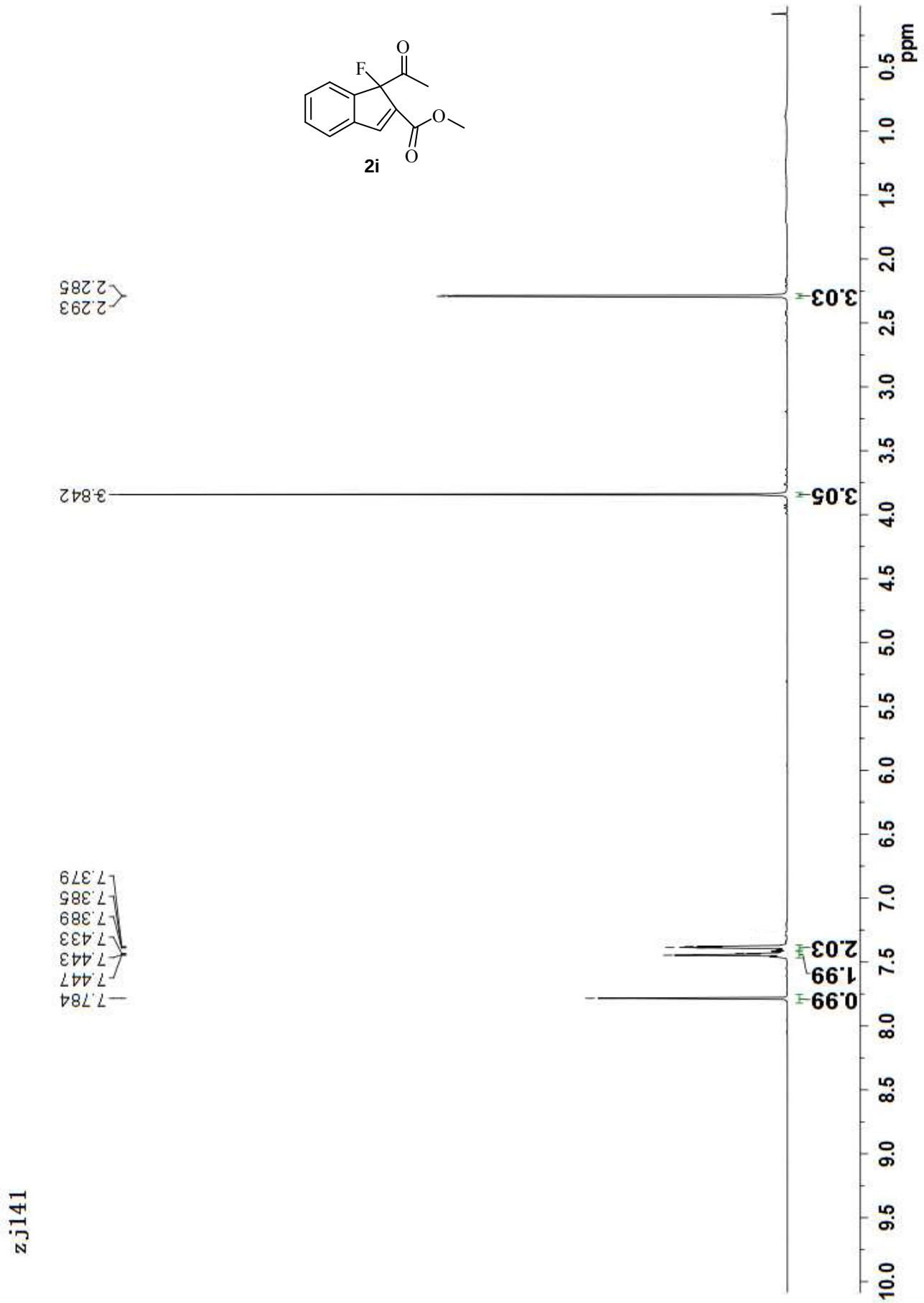

zj167
2h
F
O
O
O
1.207
1.221
1.235
4.166
4.173
4.180
4.187
4.201
4.215
4.229
4.243
4.251
4.257
4.265
7.341
7.356
7.371
7.380
7.396
7.410
7.420
7.437
7.452
7.466
7.492
7.506
7.529
7.543
7.558
7.809
7.837
7.853
3.07
2.04
7.09
2.95
ppm


O
F
O
O
O
2h
zj167
194.45
194.23
162.11
146.11
146.07
142.76
142.61
140.53
139.00
138.87
135.13
133.10
131.10
130.08
128.99
128.95
128.40
125.11
124.38
103.99
102.42
61.07
14.01
ppm

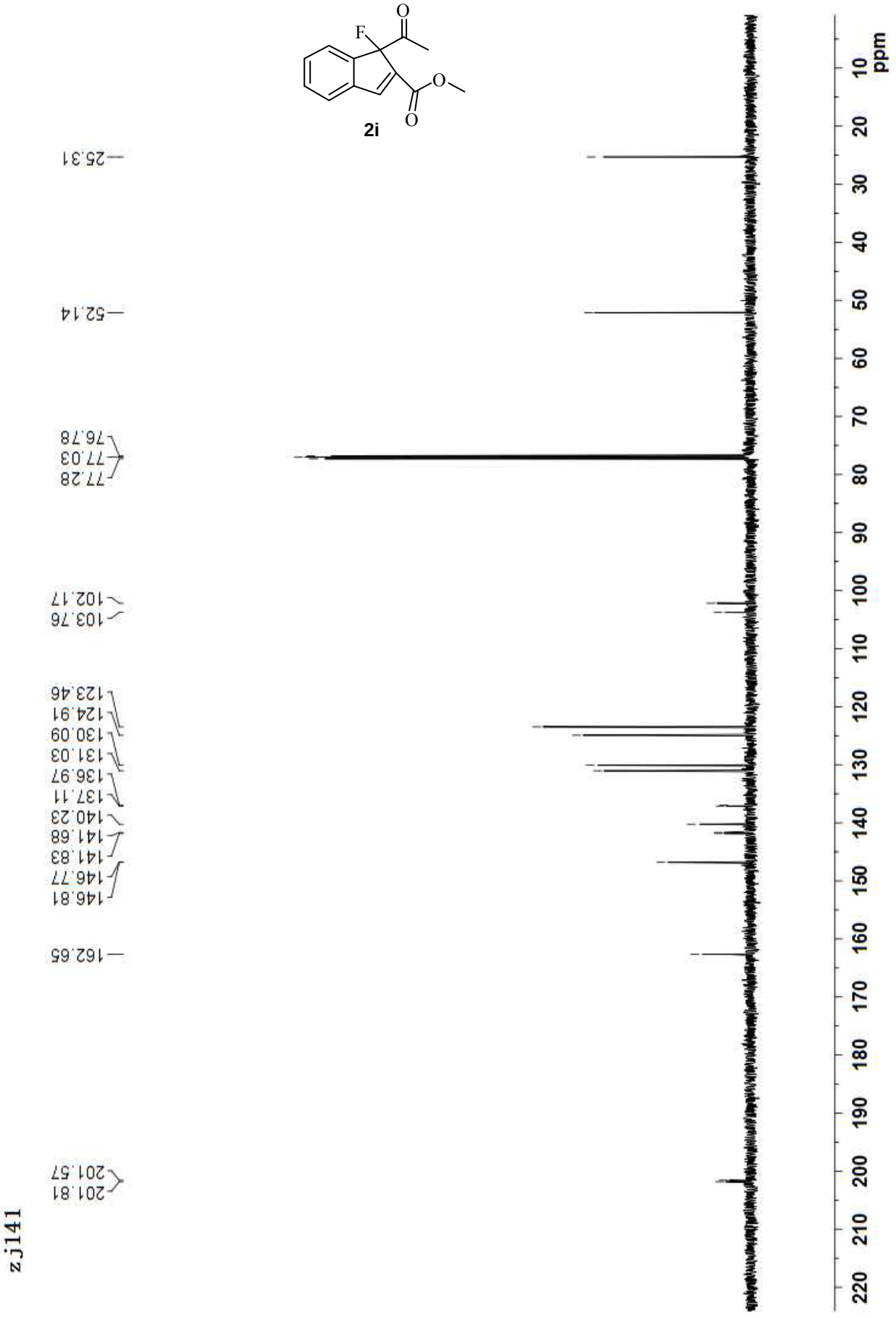


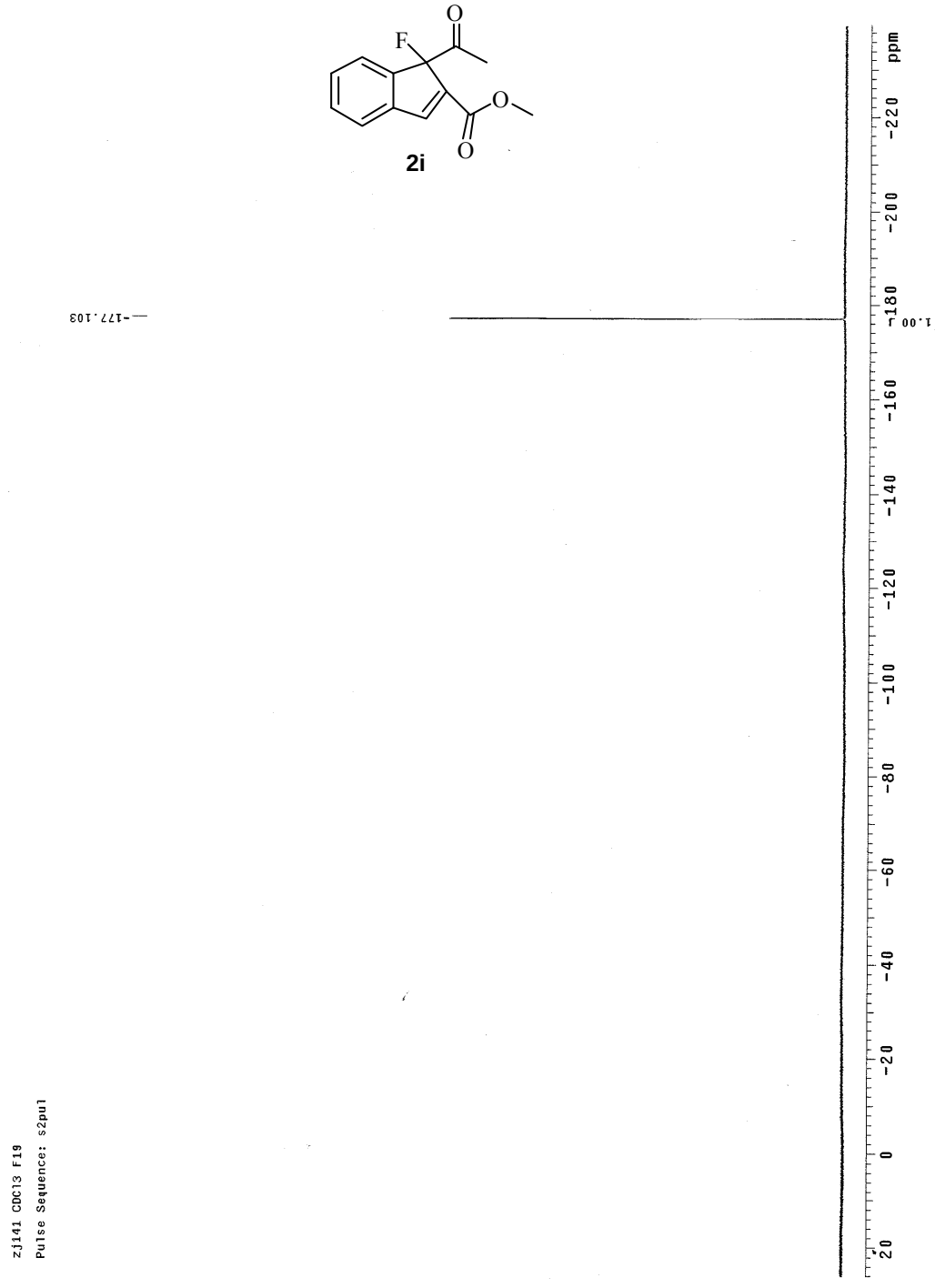
2h

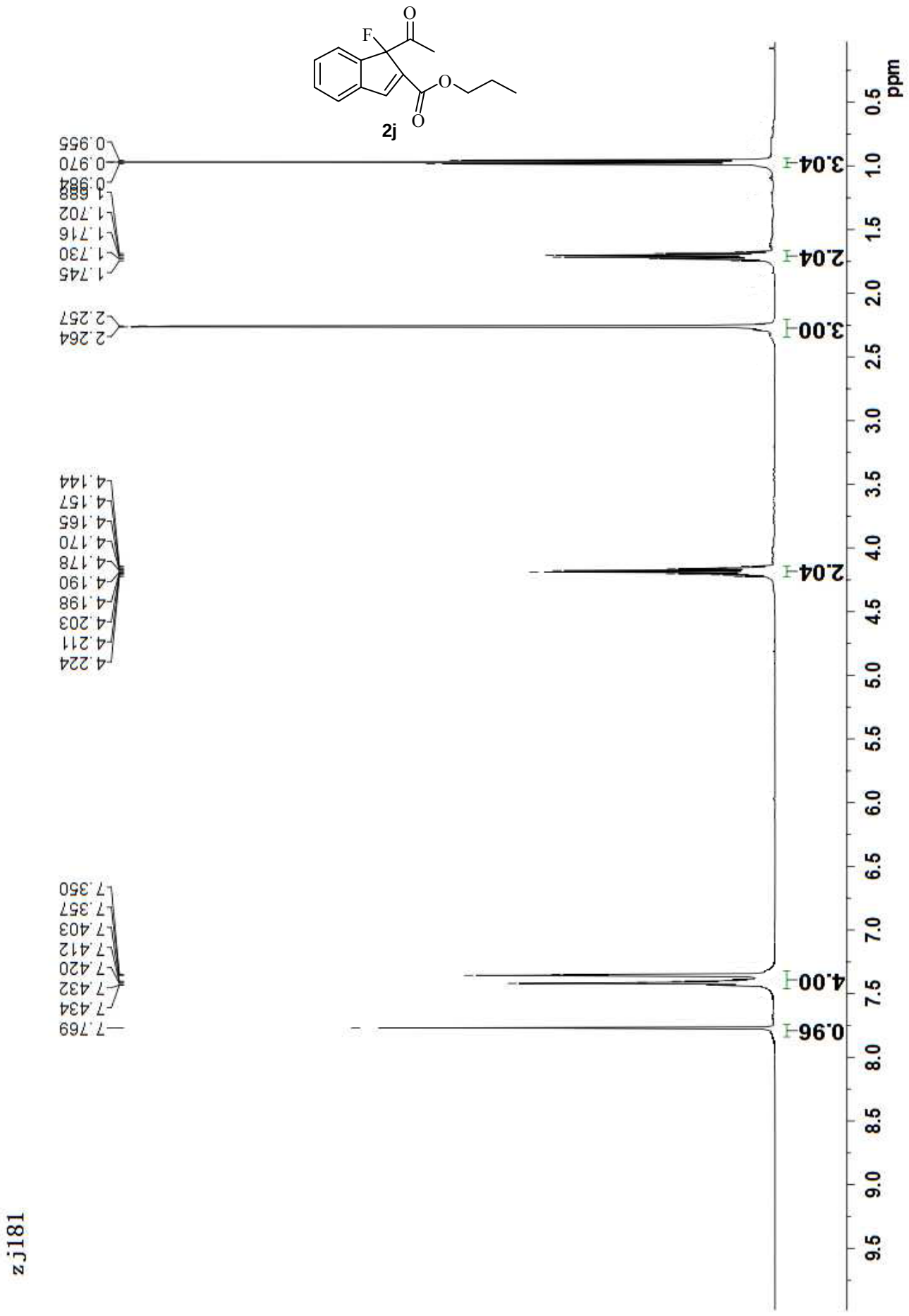
-168.404
1.00
ppm
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
zj167 CDCl3 F19
Pulse Sequence: s2pul

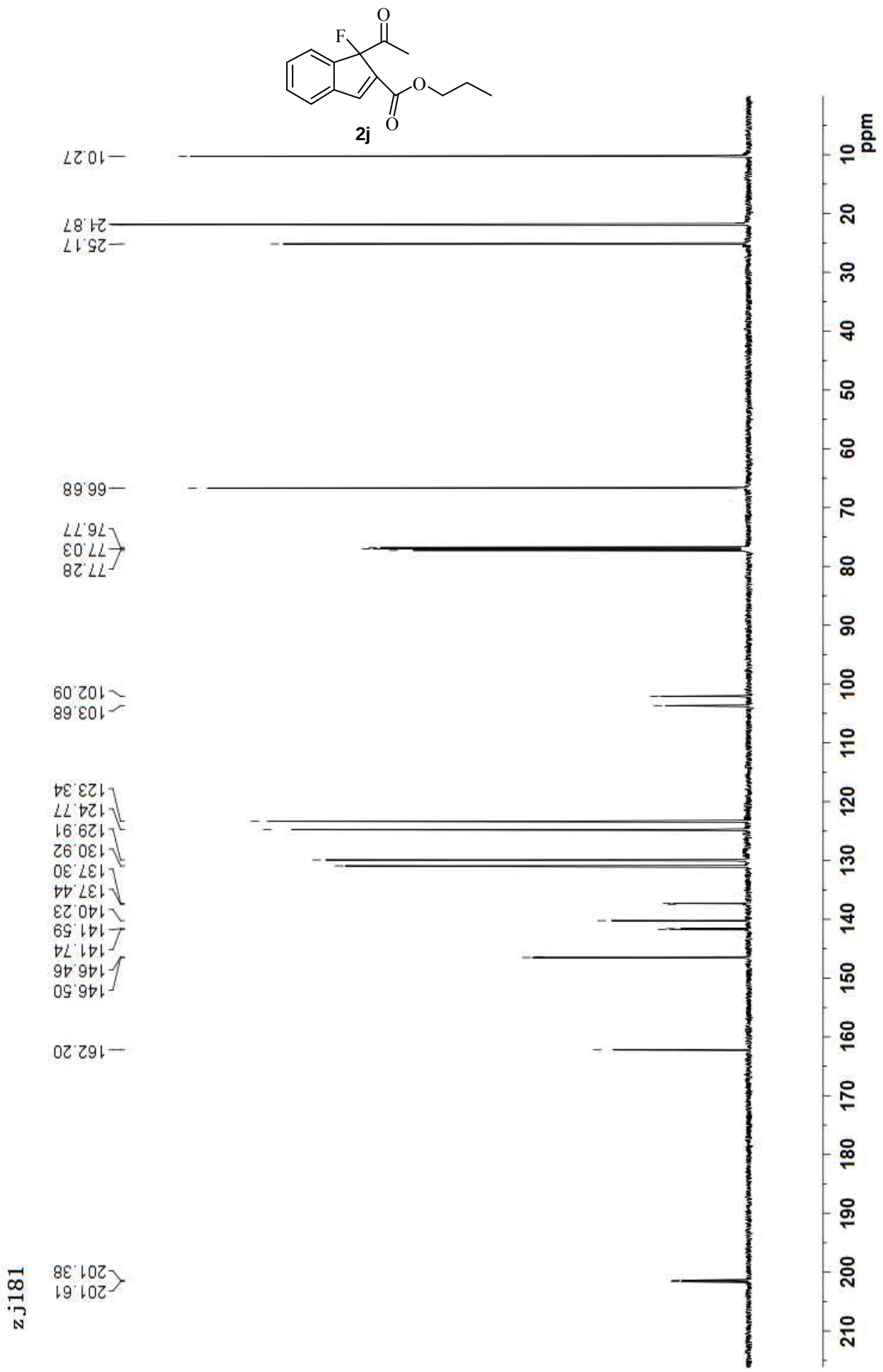

zj141
2.285
2.293
3.842
7.379
7.385
7.389
7.433
7.443
7.447
7.784
3.03
3.05
2.03
1.99
0.99
ppm
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

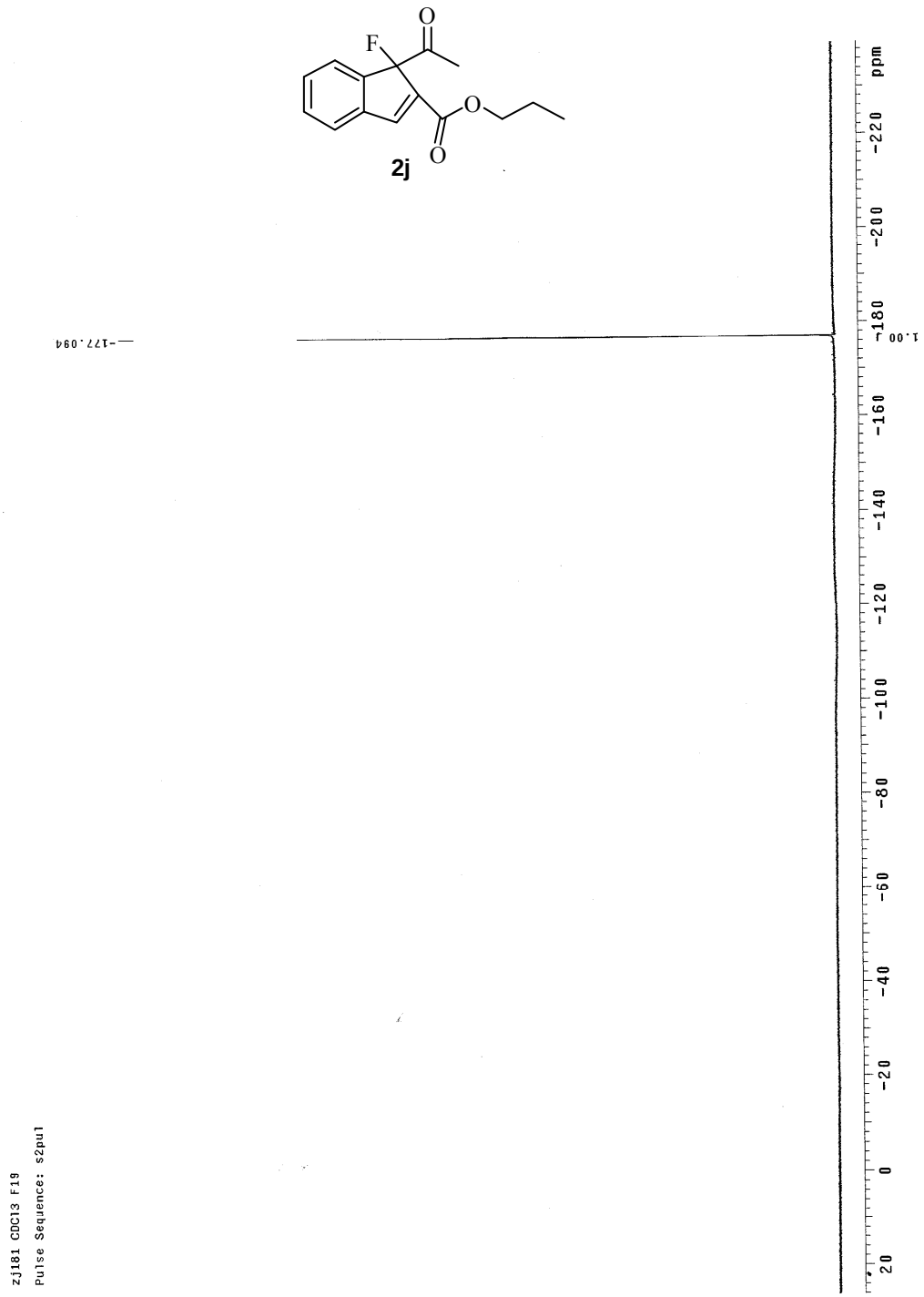
2i

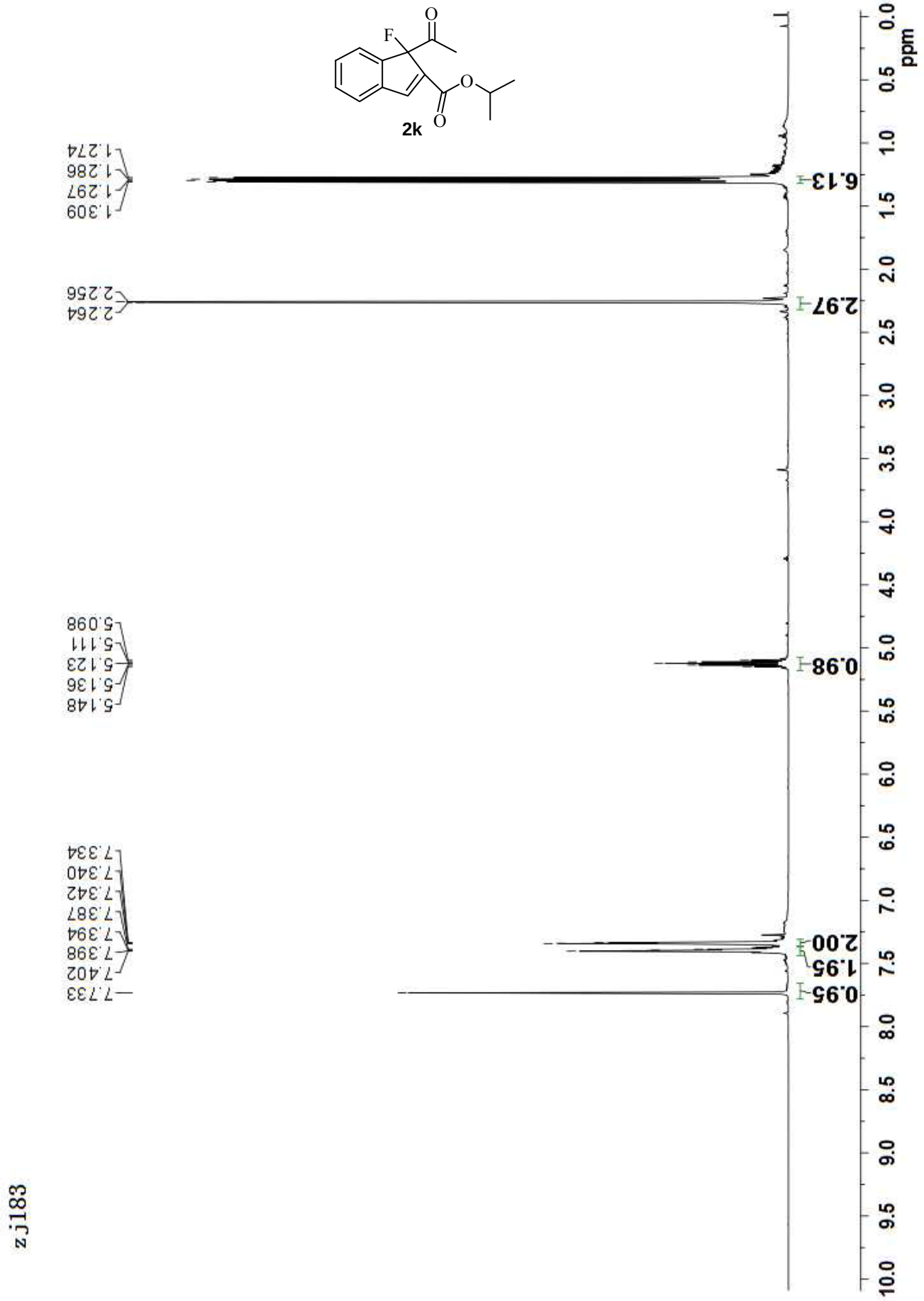

zj141
2i
F
O
O
O
201.81
201.57
162.65
146.81
146.77
141.83
141.68
140.23
137.11
136.97
131.03
130.09
124.91
123.46
103.76
102.17
77.28
77.03
76.78
52.14
25.31
ppm

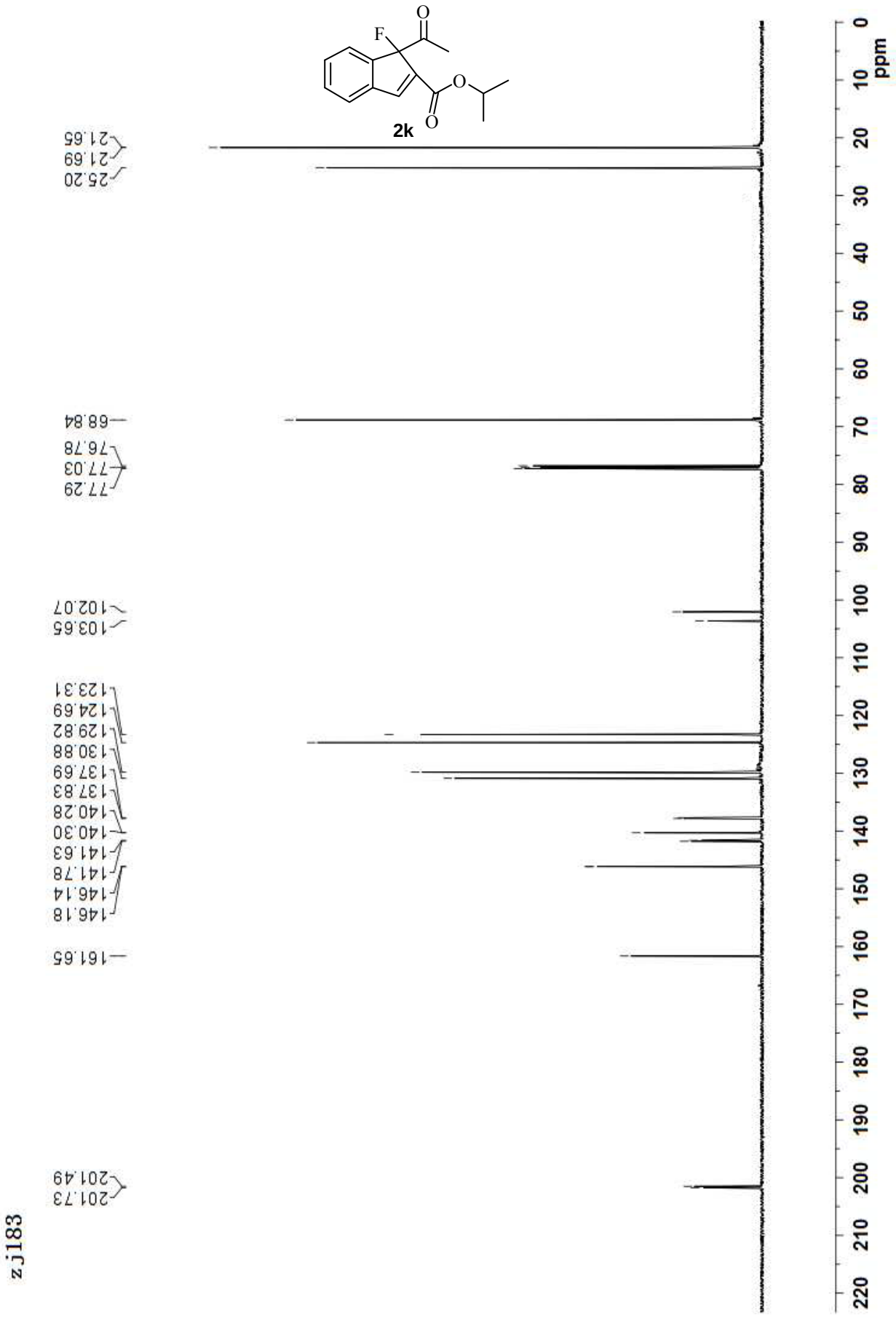

O
F
O
O
2i
-177.103
1.00
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
ppm
zj141 CDCl3 F19
Pulse Sequence: s2pul

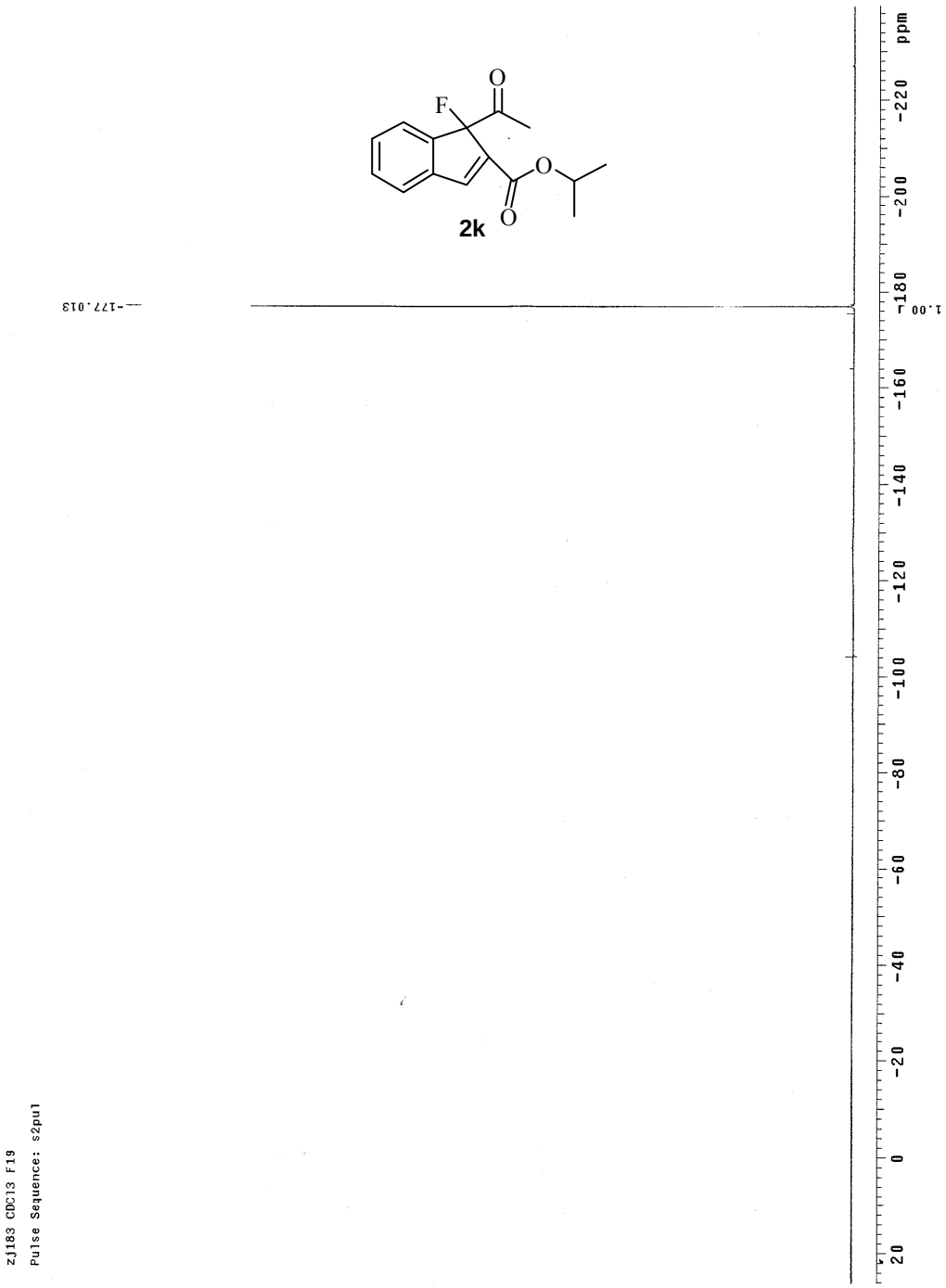

F
O
O
O
2j
0.955
0.970
0.984
1.688
1.702
1.716
1.730
1.745
2.257
2.264
4.144
4.157
4.165
4.170
4.178
4.190
4.198
4.203
4.211
4.224
7.350
7.357
7.403
7.412
7.420
7.432
7.434
7.769
3.04
2.04
3.00
2.04
4.00
0.96
ppm
zj181

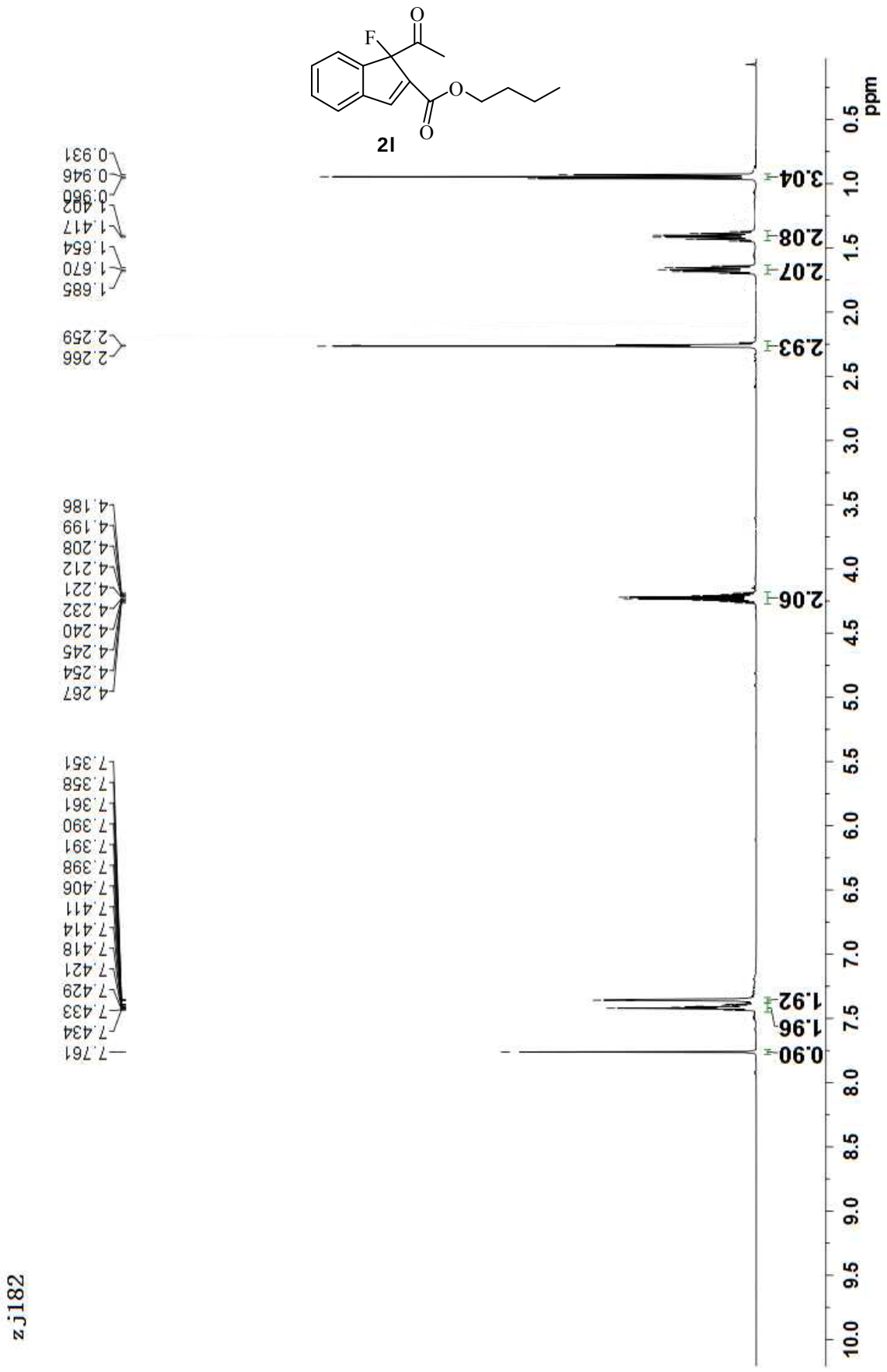

F
O
O
O
2j
zj181
10.27
21.87
25.17
66.68
76.77
77.03
77.28
102.09
103.68
123.34
124.77
129.91
130.92
137.30
137.44
140.23
141.59
141.74
146.46
146.50
162.20
201.38
201.61
ppm

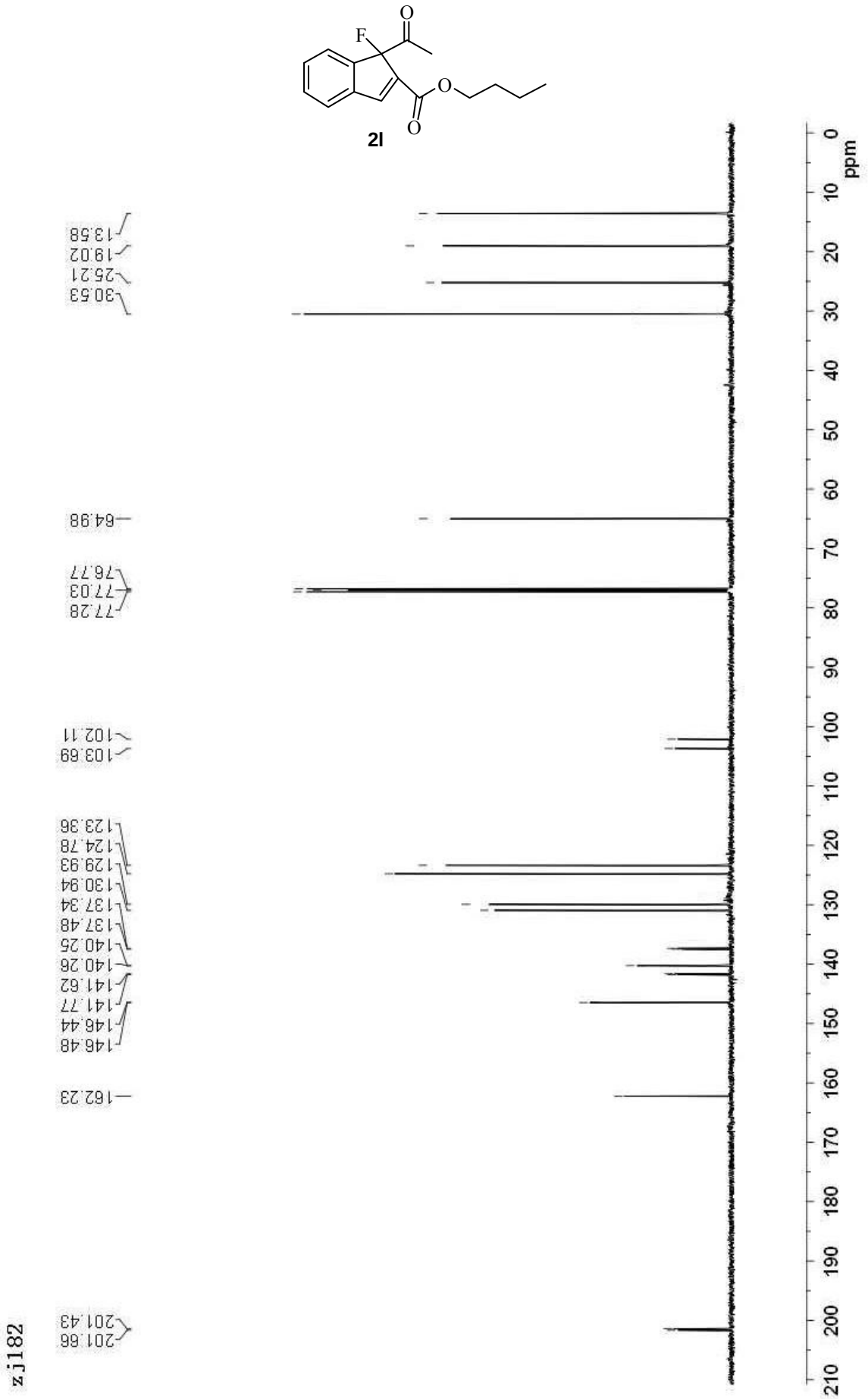

F
O
O
O
2j
-177.094
1.00
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
ppm
zj181 CDCl3 F19
Pulse Sequence: s2pul

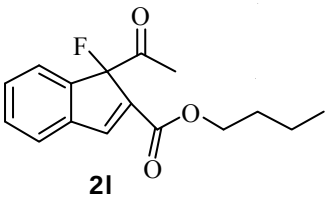

zj183
F
O
O
O
2k
1.274
1.286
1.297
1.309
2.256
2.264
5.098
5.111
5.123
5.136
5.148
7.334
7.340
7.342
7.387
7.394
7.398
7.402
7.733
6.13
2.97
0.98
2.00
1.95
0.95
ppm


2k
F
O
O
O
O
zj183
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
21.65
21.69
25.20
68.84
76.78
77.03
77.29
102.07
103.65
123.31
124.69
129.82
130.88
137.69
137.83
140.28
140.30
141.63
141.78
146.14
146.18
161.65
201.73
201.49


F
O
O
O
2k
-177.013
1.00
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
ppm
zj183 CDCl3 F19
Pulse Sequence: s2pul

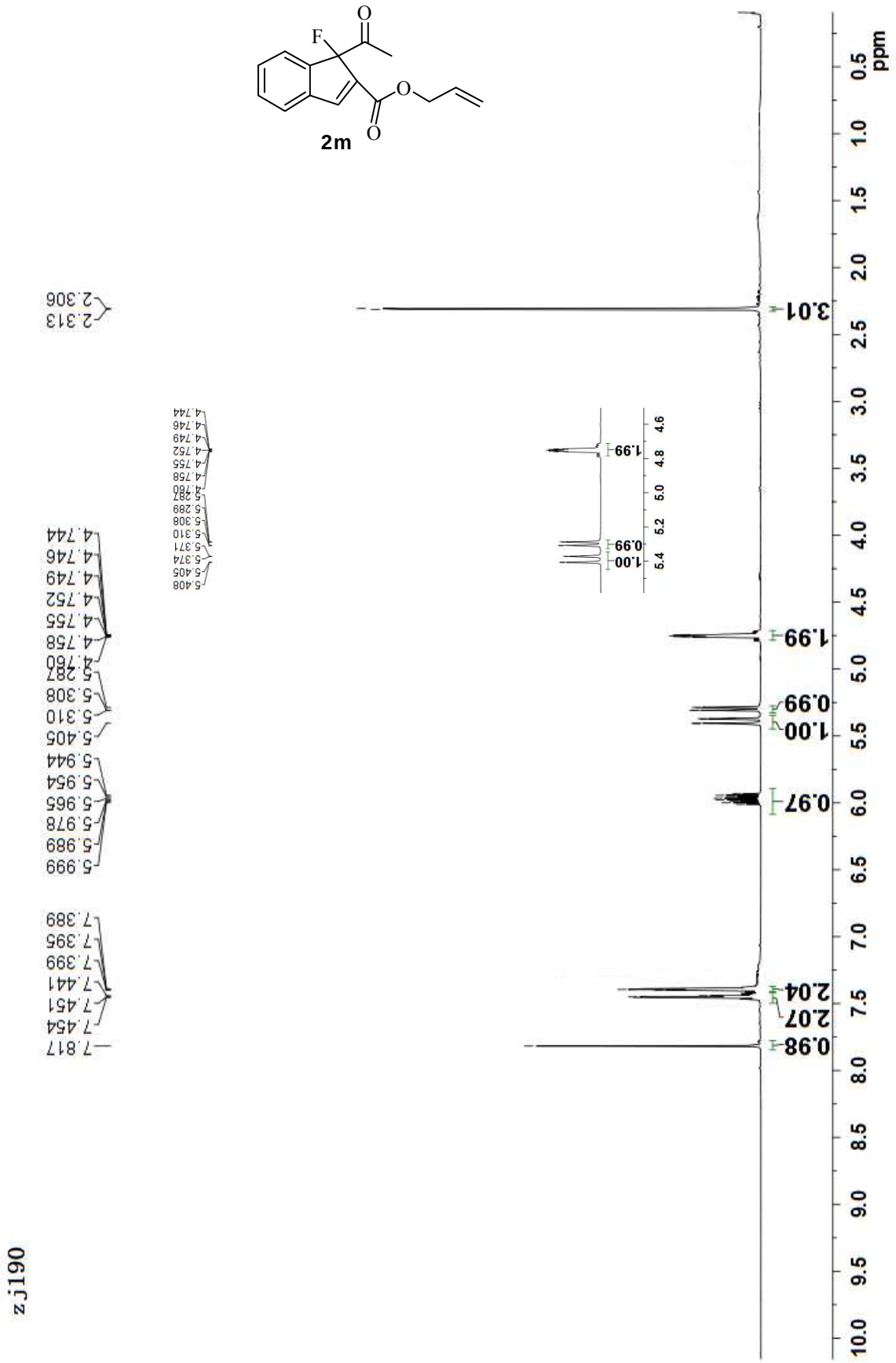

F
O
O
O
2l
zj182
ppm
3.04
2.08
2.07
2.93
2.06
1.92
1.96
0.90

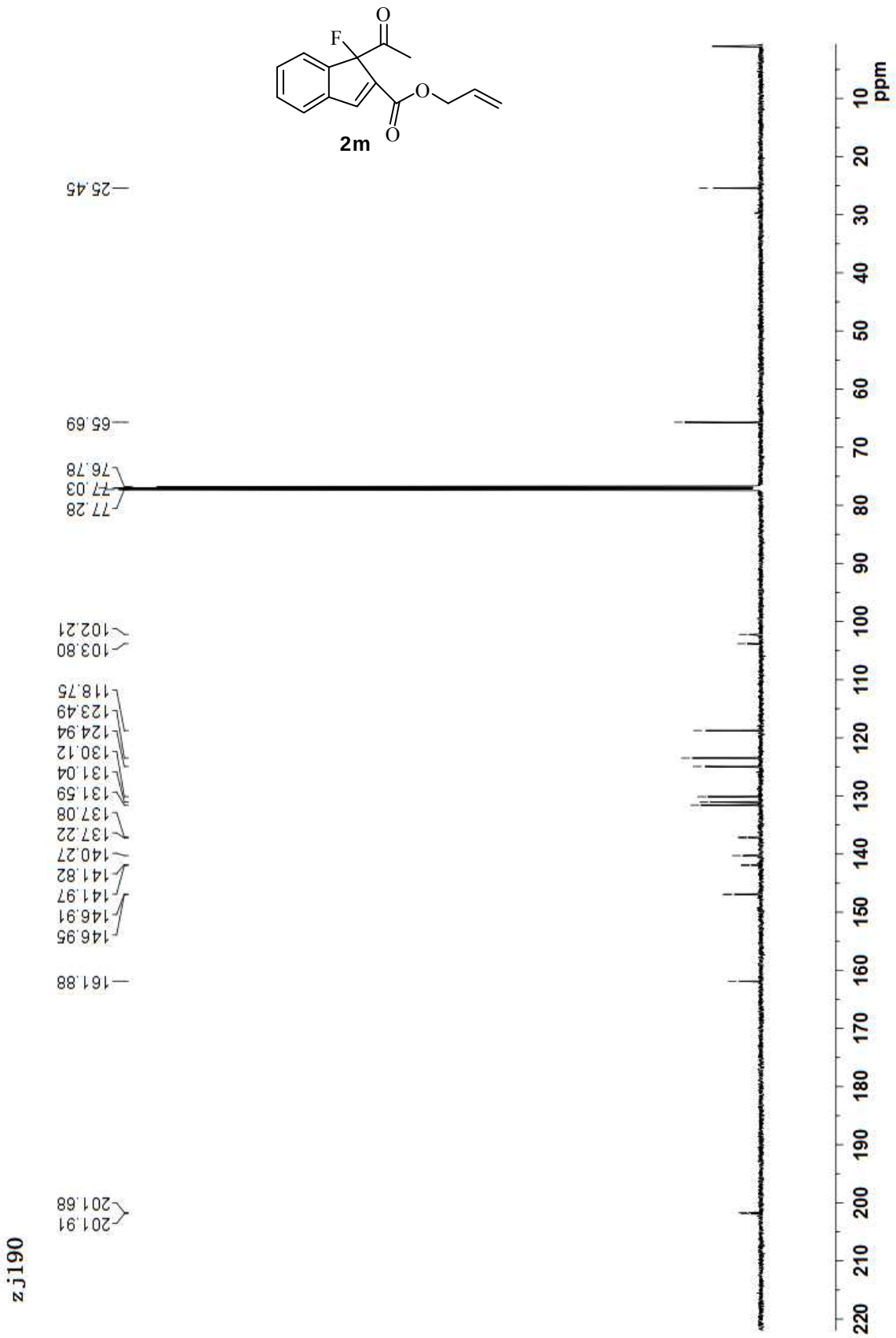

F
O
O
O
O
2l
zj182
13.58
19.02
25.21
30.53
64.98
76.77
77.03
77.28
102.11
103.69
123.36
124.78
129.93
130.94
137.34
137.48
140.25
140.26
141.62
141.77
146.44
146.48
162.23
201.43
201.86
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

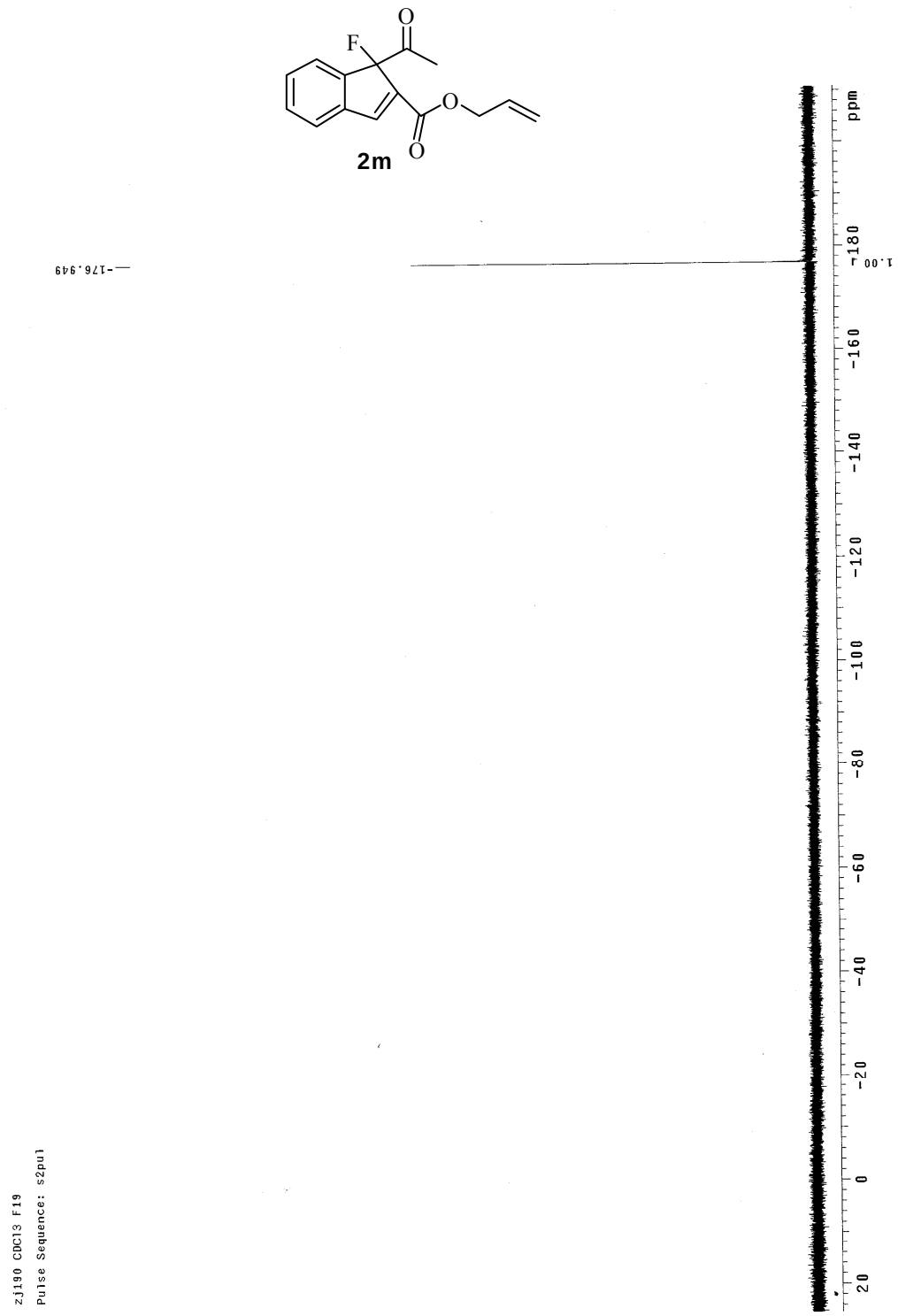


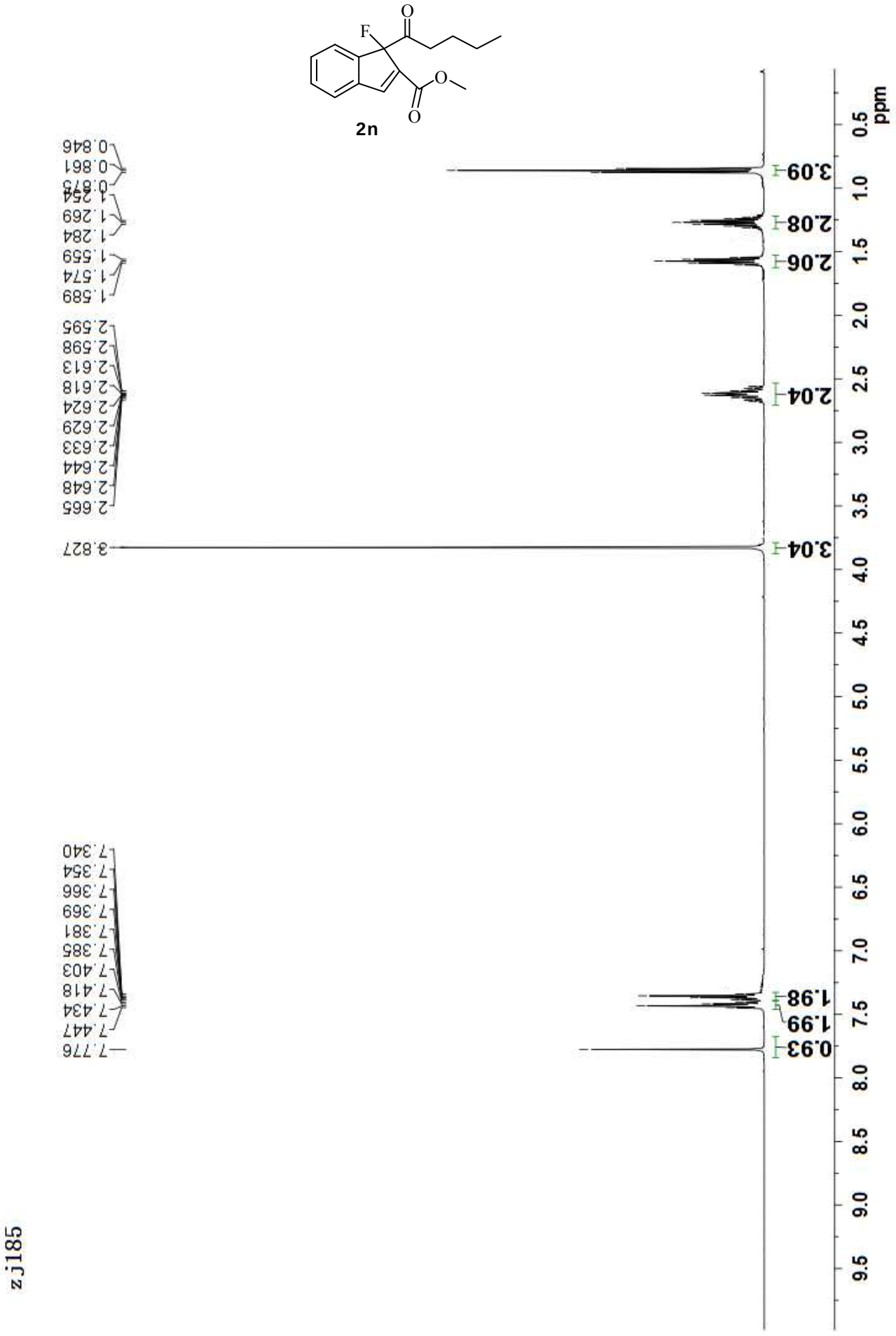
2l

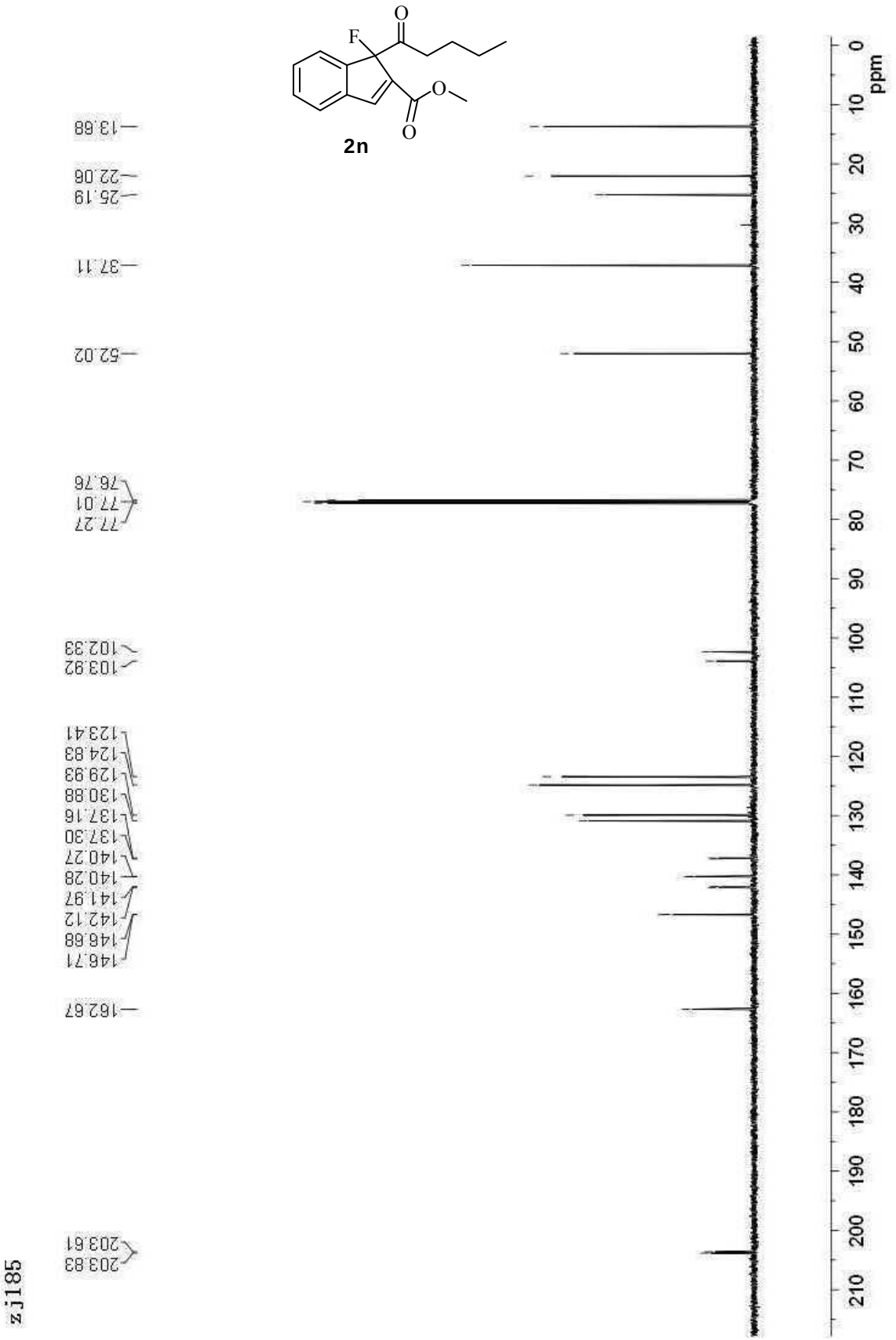
-177.074
1.00
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
ppm
zj182 CDCl3 F19
Pulse Sequence: s2pul


2m
zj190
ppm


F
O
O
O
2m
zj190
25.45
65.69
76.78
77.03
77.28
102.21
103.80
118.75
123.49
124.94
130.12
131.04
131.59
137.08
137.22
140.27
141.82
141.97
146.91
146.95
161.88
201.68
201.91
ppm


F
O
O
O
2m
-176.949
1.00
ppm
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
zj190 CDCl3 F19
Pulse Sequence: s2pul

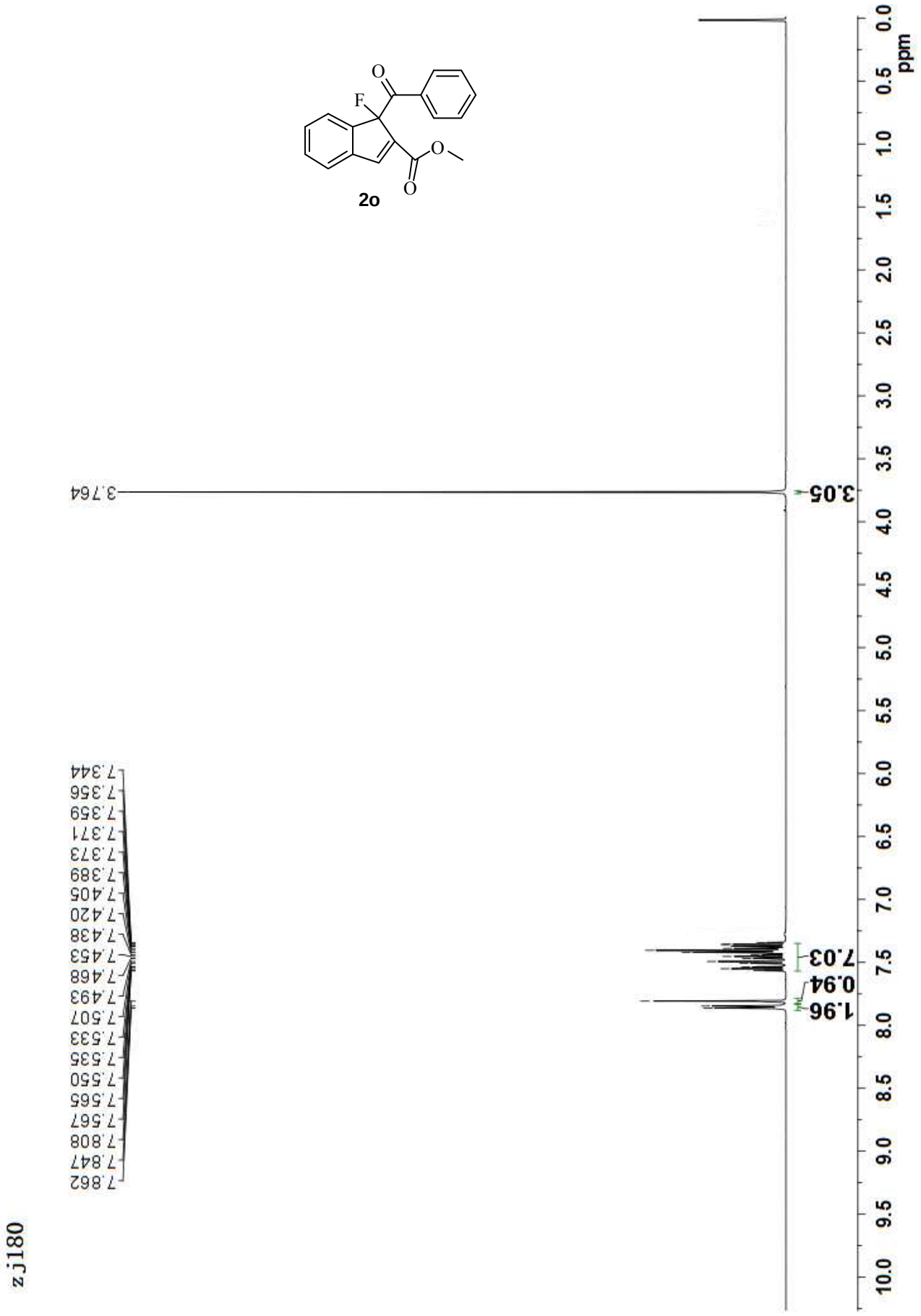

F
O
O
O
2n
zj185
0.846
0.861
0.873
1.254
1.269
1.284
1.559
1.574
1.589
2.595
2.598
2.613
2.618
2.624
2.629
2.633
2.644
2.648
2.665
3.827
7.340
7.354
7.366
7.369
7.381
7.385
7.403
7.418
7.434
7.447
7.776
3.09
2.08
2.06
2.04
3.04
1.98
1.99
0.93
ppm


F
O
O
O
2n
zj185
13.88
22.06
25.19
37.11
52.02
76.76
77.01
77.27
102.33
103.82
123.41
124.83
129.93
130.88
137.16
137.30
140.27
140.28
141.97
142.12
146.68
146.71
162.67
203.83
203.61
ppm

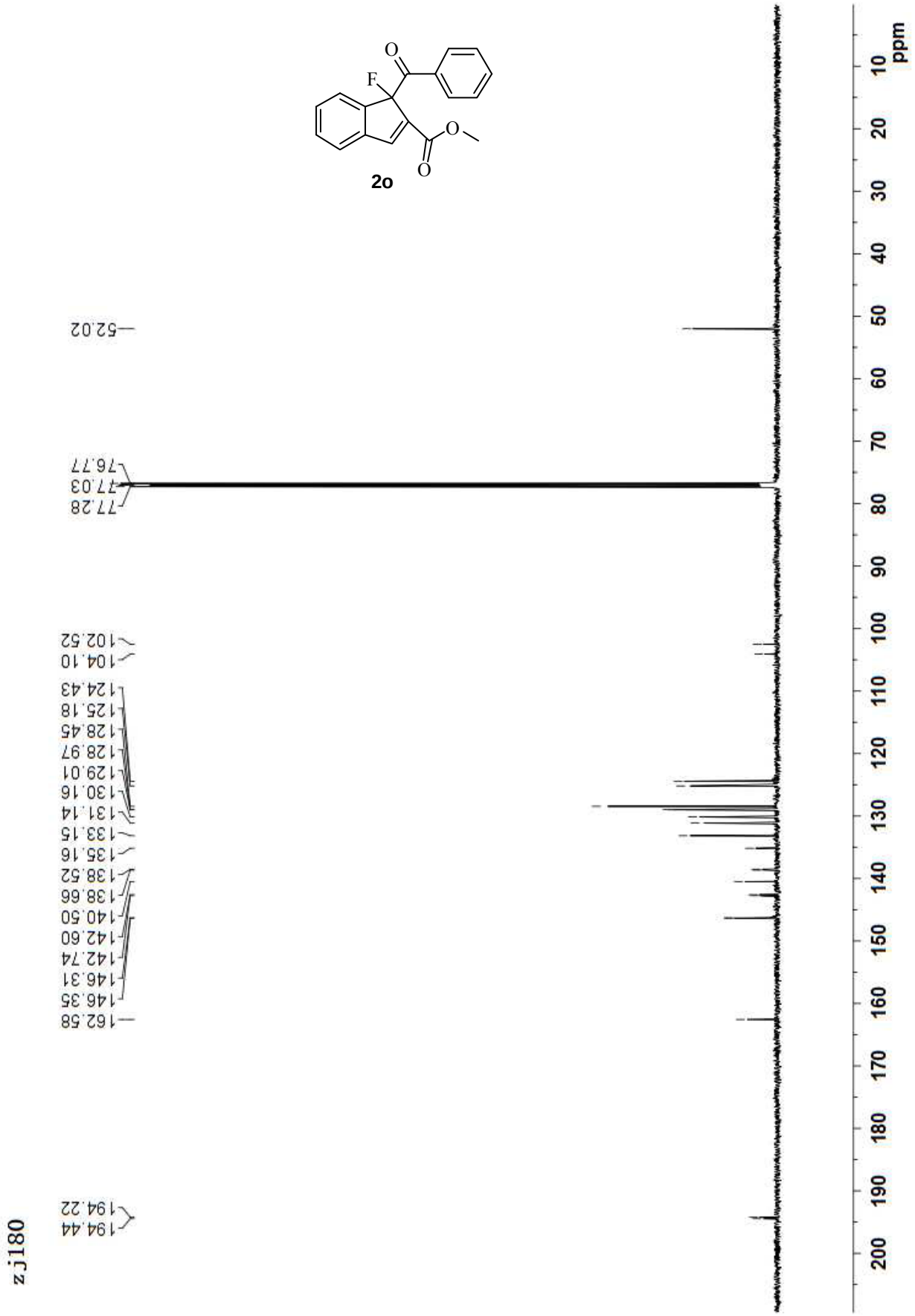
F
O
O
O

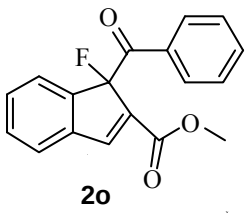
2n

-178.331
1.00
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
ppm
Pulse Sequence: s2pul


zj180
7.862
7.847
7.808
7.567
7.565
7.550
7.535
7.533
7.507
7.493
7.468
7.453
7.438
7.420
7.405
7.389
7.373
7.371
7.359
7.356
7.344
3.764
3.05
7.03
0.94
1.96
ppm
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0

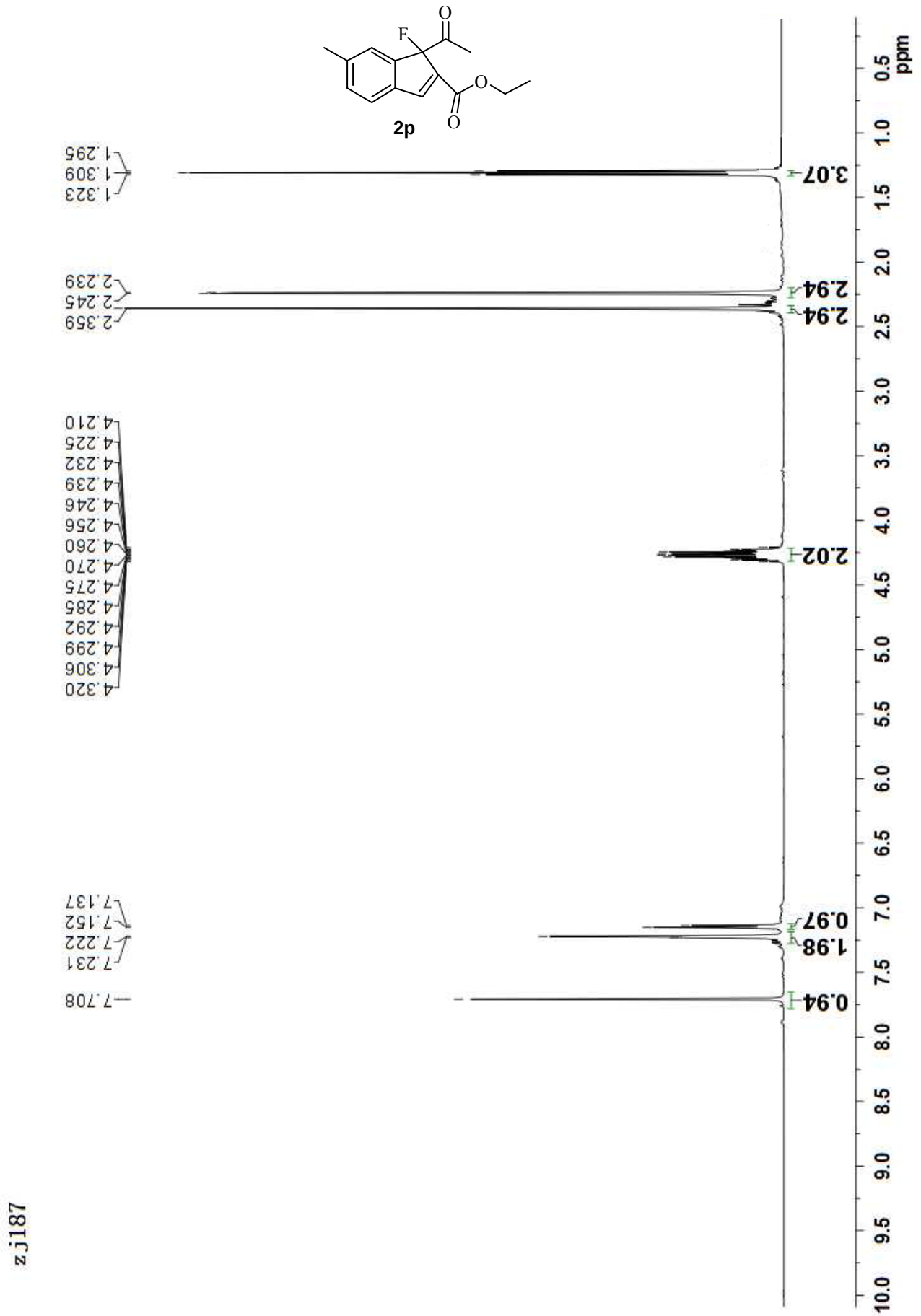
2o

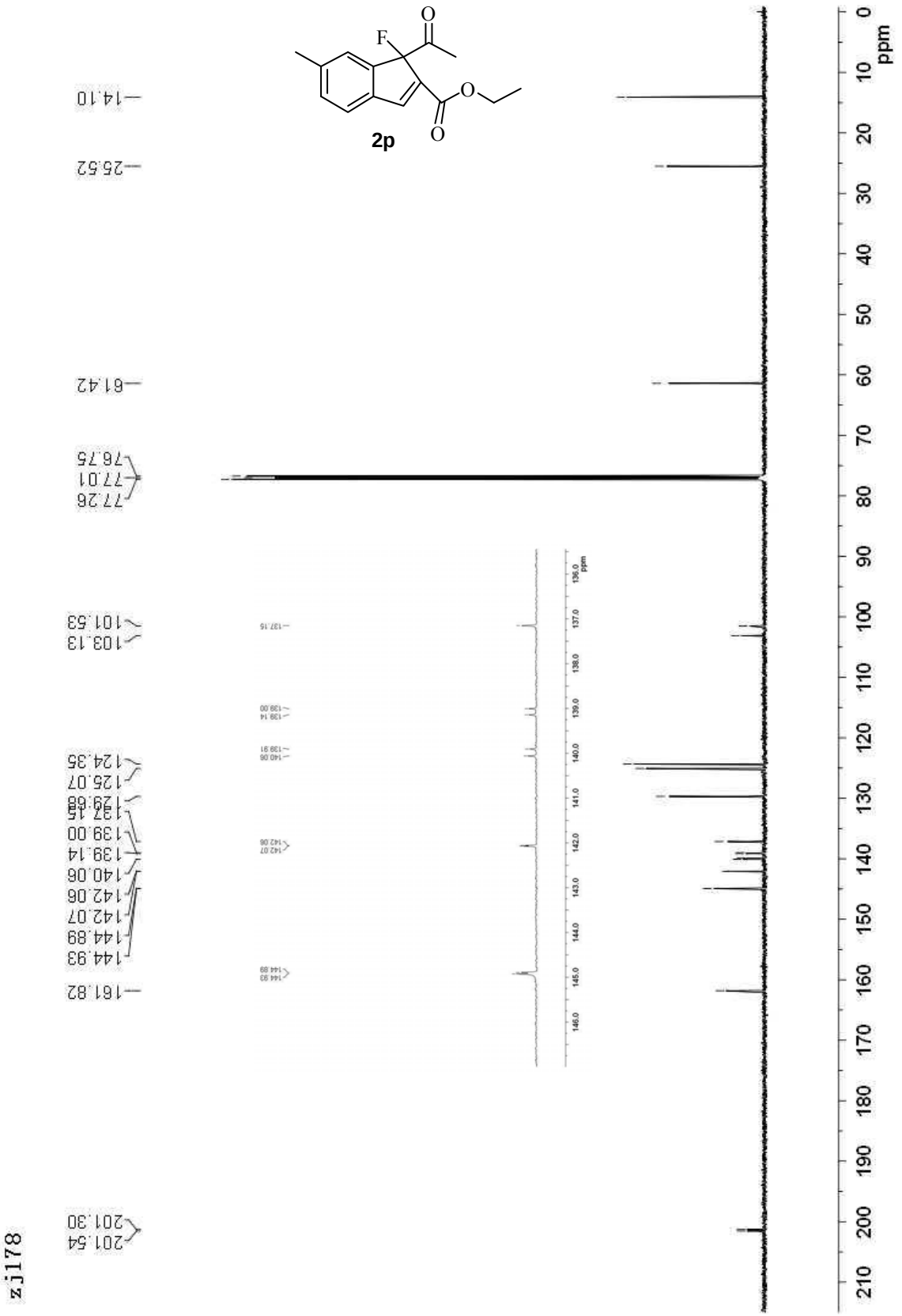

zj180
194.44
194.22
162.58
146.35
146.31
142.74
142.60
140.50
138.66
138.52
135.16
133.15
131.14
130.16
129.01
128.97
128.45
125.18
124.43
104.10
102.52
77.28
77.03
76.77
52.02
F
O
O
O
2o
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200

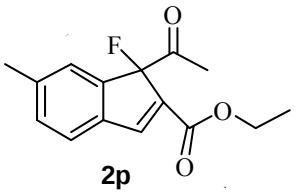

O
F
O
O
O

2o

-169.730
1.00
ppm
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
Pulse Sequence: s2pul

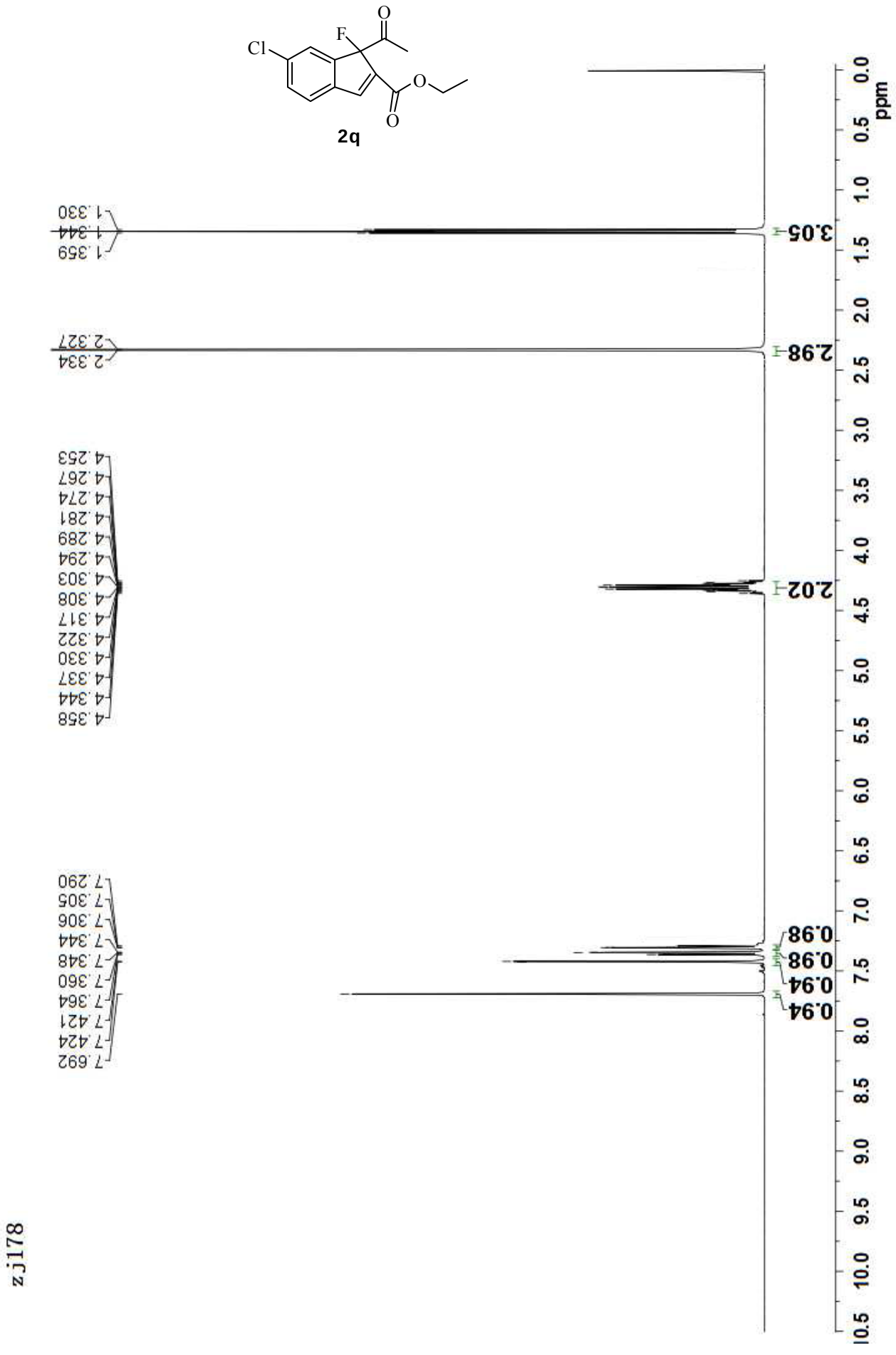

zj187
2p
F
O
O
O
1.295
1.309
1.323
2.239
2.245
2.359
4.210
4.225
4.232
4.239
4.246
4.256
4.260
4.270
4.275
4.285
4.292
4.299
4.306
4.320
7.137
7.152
7.222
7.231
7.708
3.07
2.94
2.94
2.02
0.97
1.98
0.94
ppm

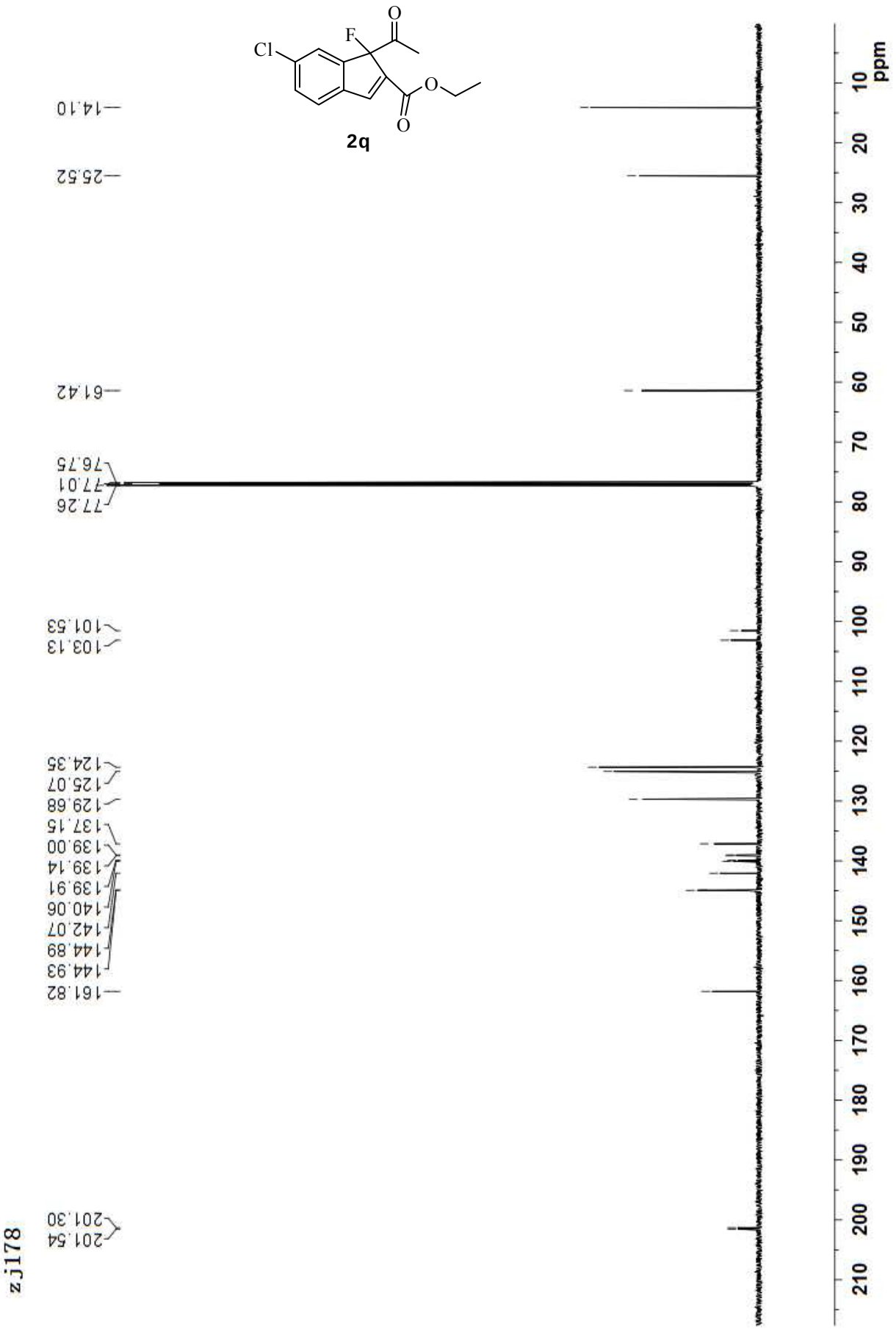

zj178
14.10
25.52
61.42
76.75
77.01
77.26
101.53
103.13
124.35
125.07
129.68
137.15
139.00
139.14
140.06
142.06
142.07
144.89
144.93
161.82
201.30
201.54
F
O
O
O
2p
ppm

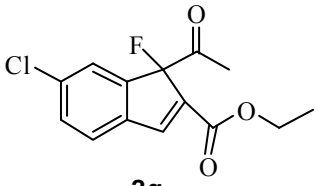

O
F
O
O
O

2p

-176.345
1.00
ppm
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
zj187 CDCl3 F19
Pulse Sequence: s2pul

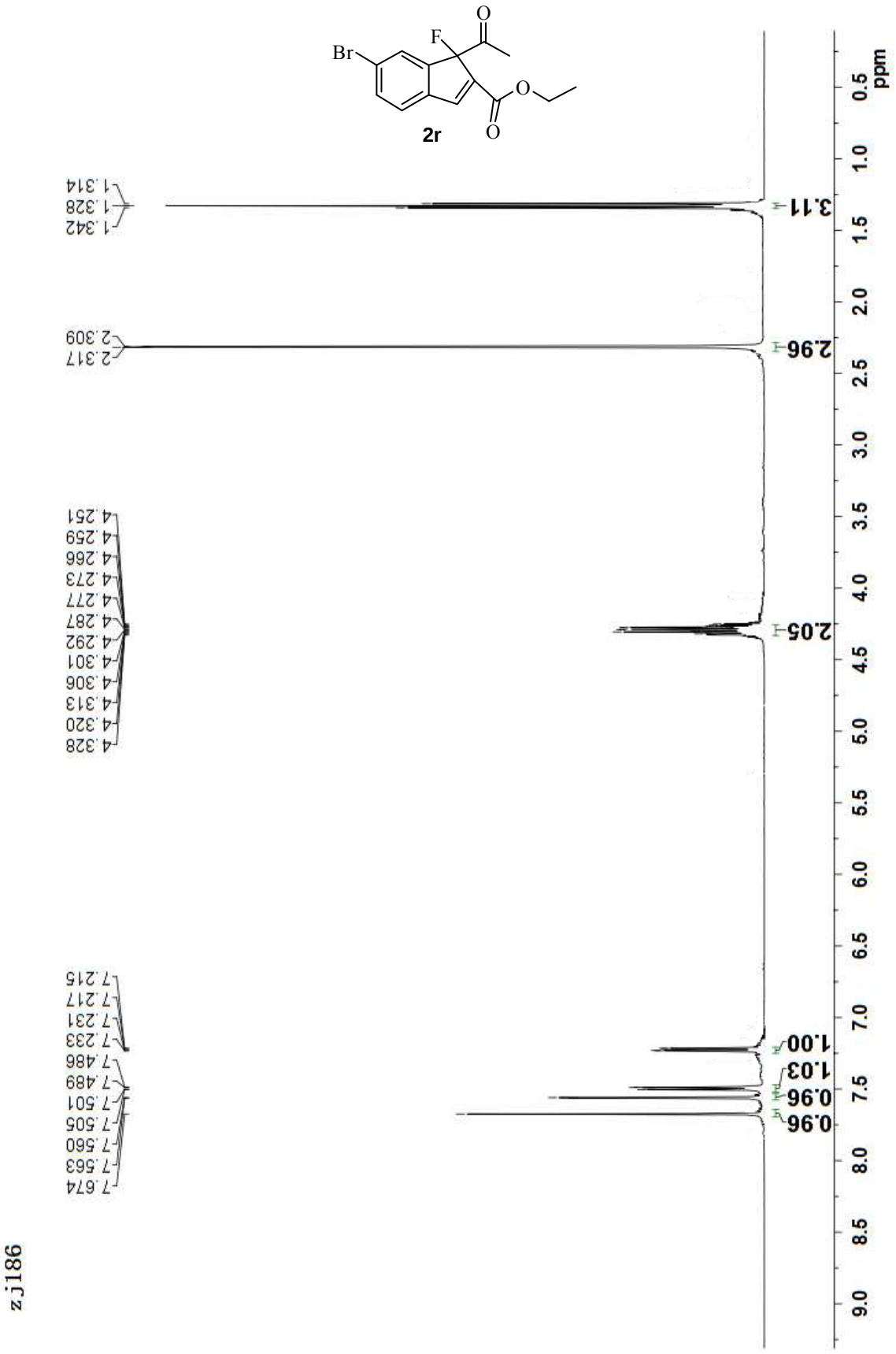

Cl
F
O
O
O
O
2q
zj178
ppm
3.05
2.98
2.02
0.98
0.98
0.94
0.94

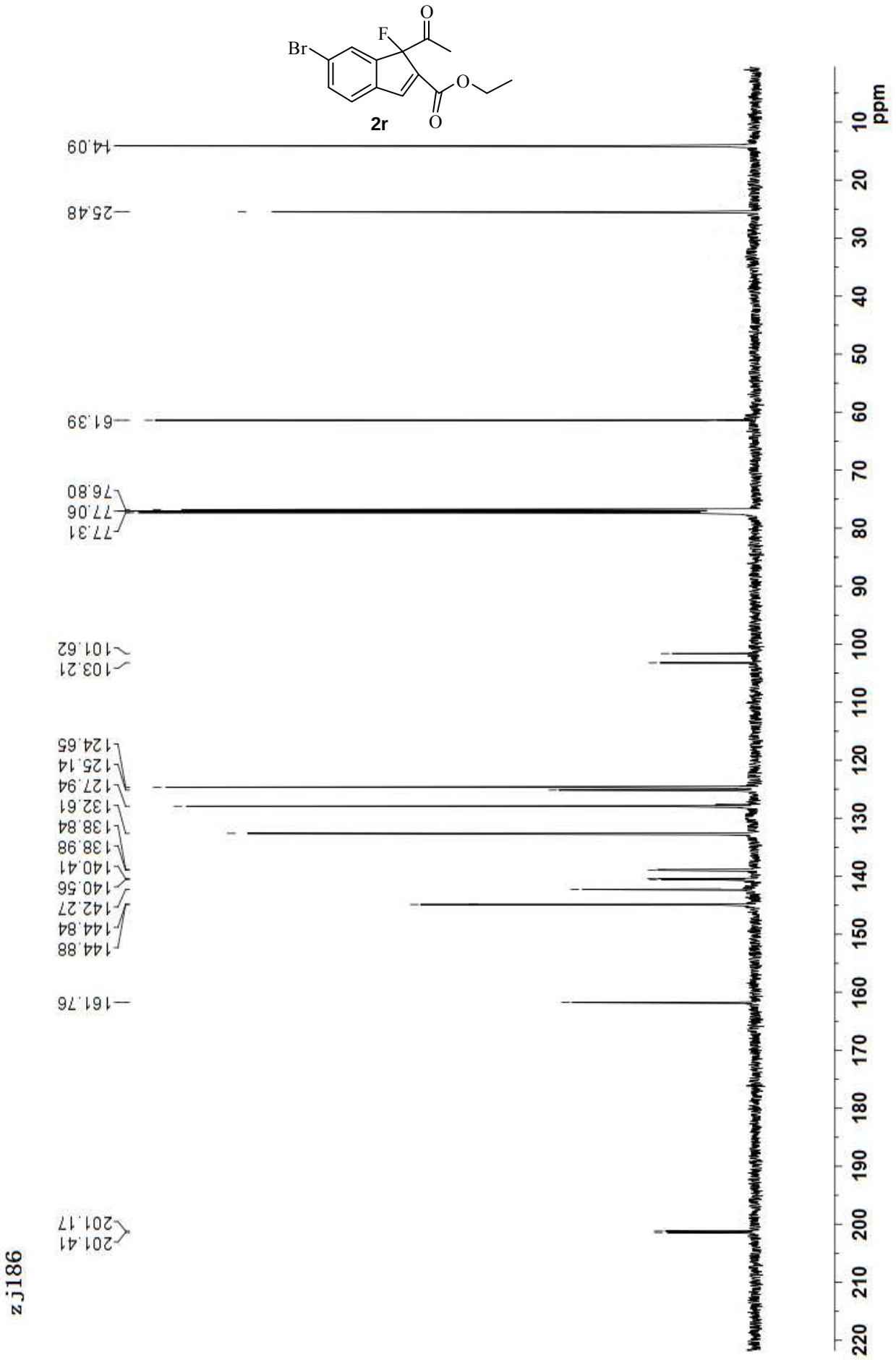

Cl
F
O
O
O
2q
14.10
25.52
61.42
76.75
77.01
77.26
101.53
103.13
124.35
125.07
129.68
137.15
139.00
139.14
139.91
140.06
142.07
144.89
144.93
161.82
201.30
201.54
zj178
ppm

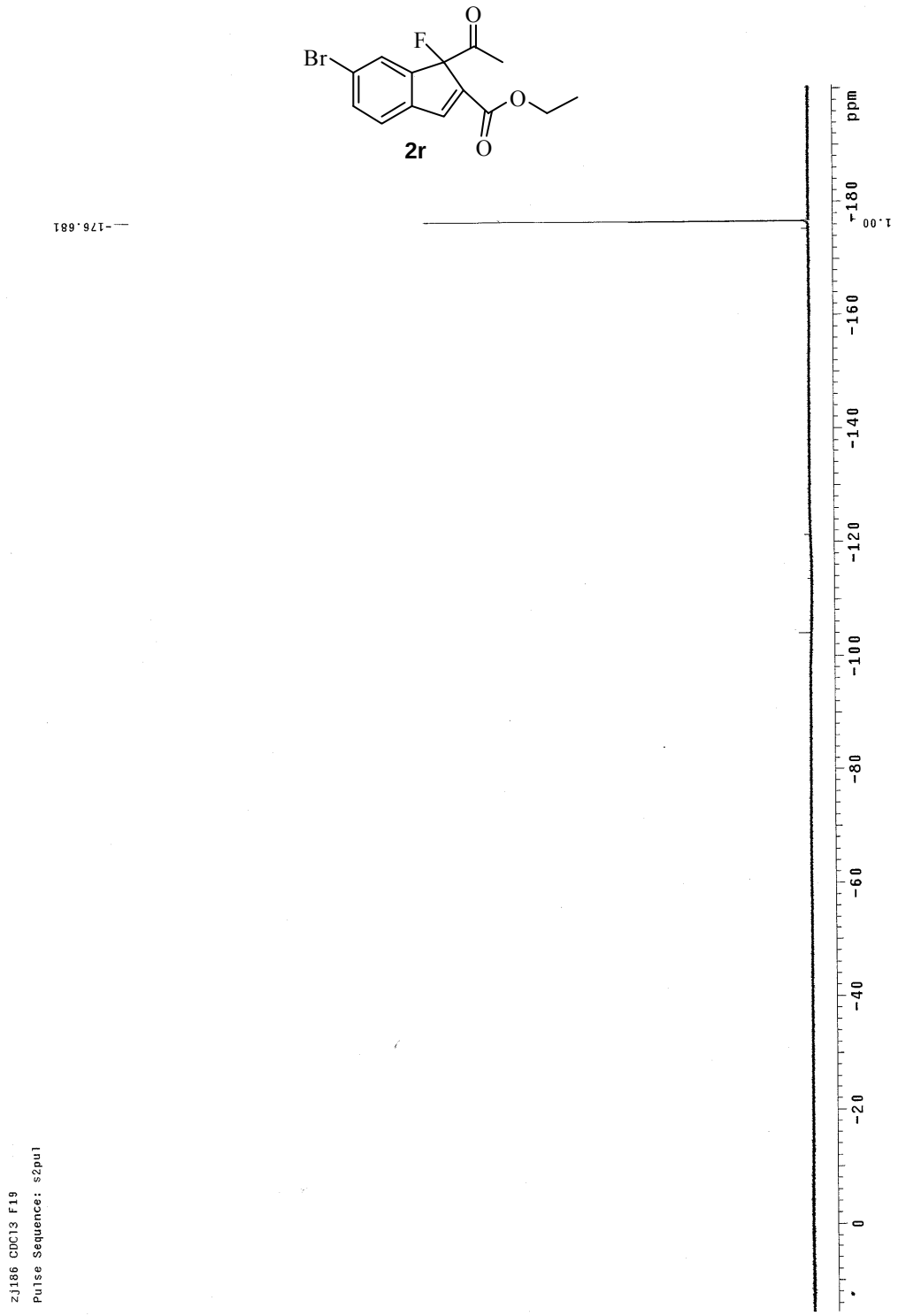

O
F
Cl
O
O

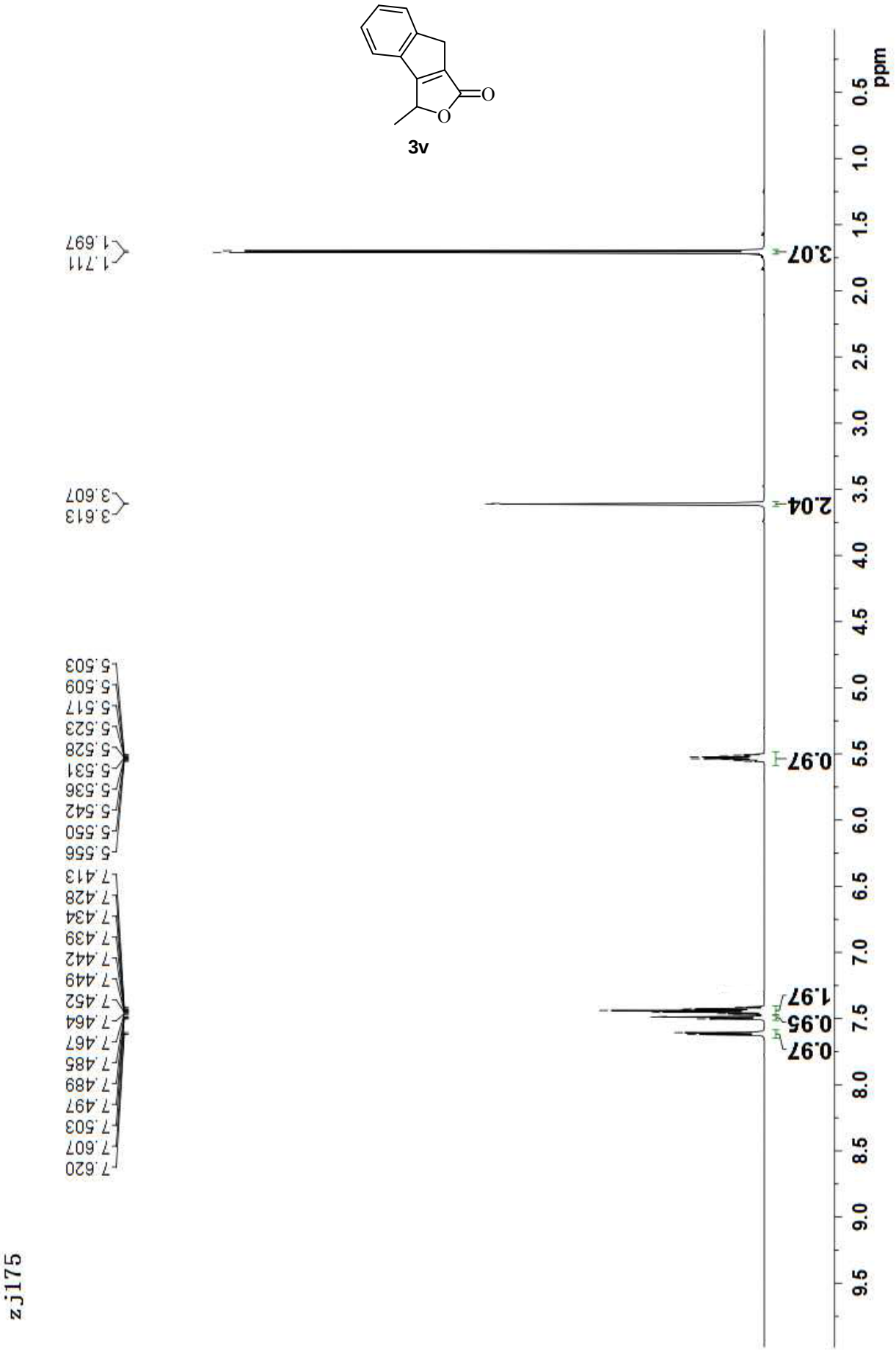
2q

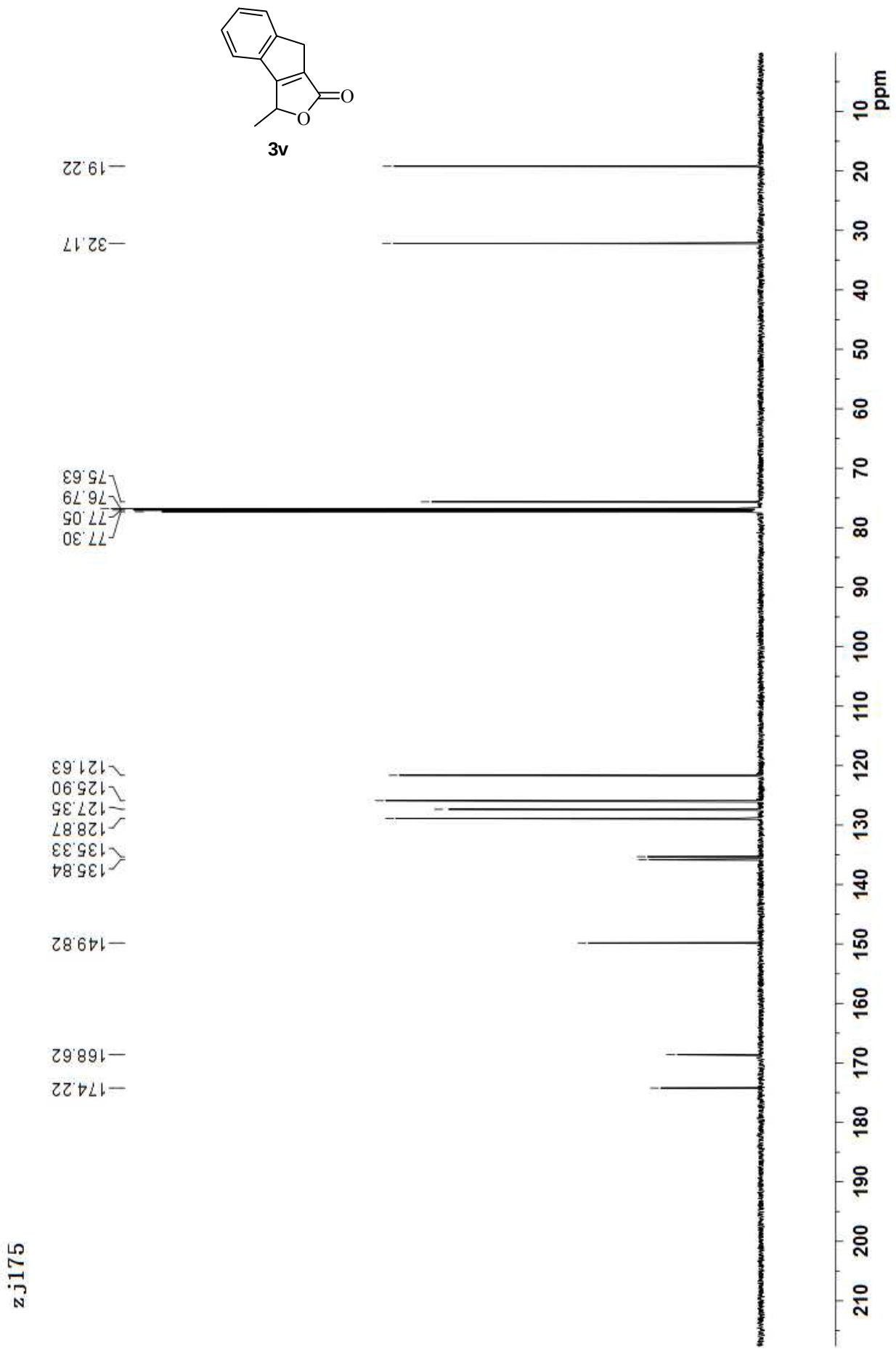
-176.523
1.00
ppm
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
zj178 CDCl3 F19
Pulse Sequence: s2pul

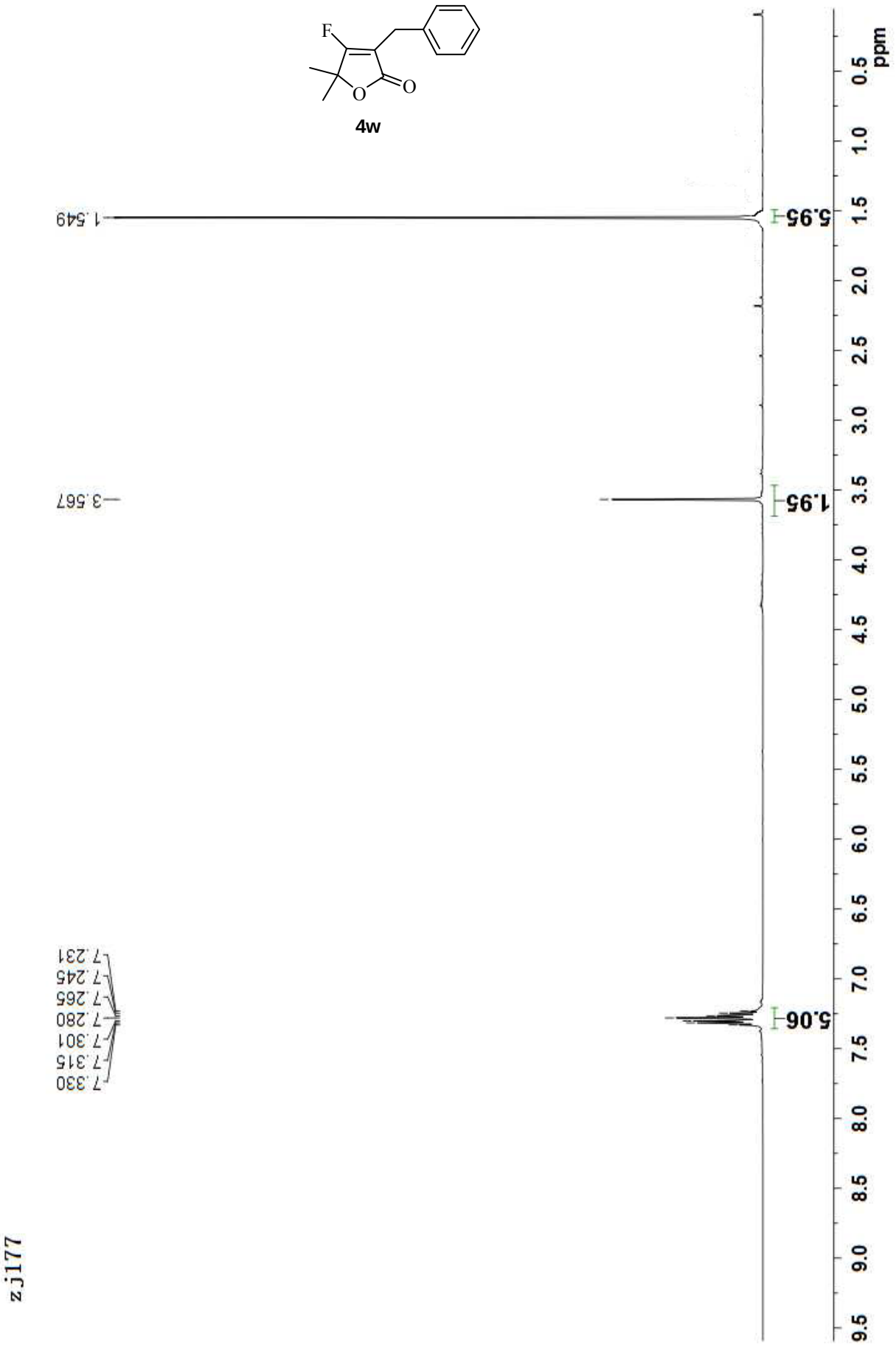

Br
F
O
O
O
2r
zj186
1.342
1.328
1.314
2.317
2.309
4.328
4.320
4.313
4.306
4.301
4.292
4.287
4.277
4.273
4.266
4.259
4.251
7.674
7.563
7.560
7.505
7.501
7.489
7.486
7.233
7.231
7.217
7.215
3.11
2.96
2.05
1.00
1.03
0.96
0.96
ppm

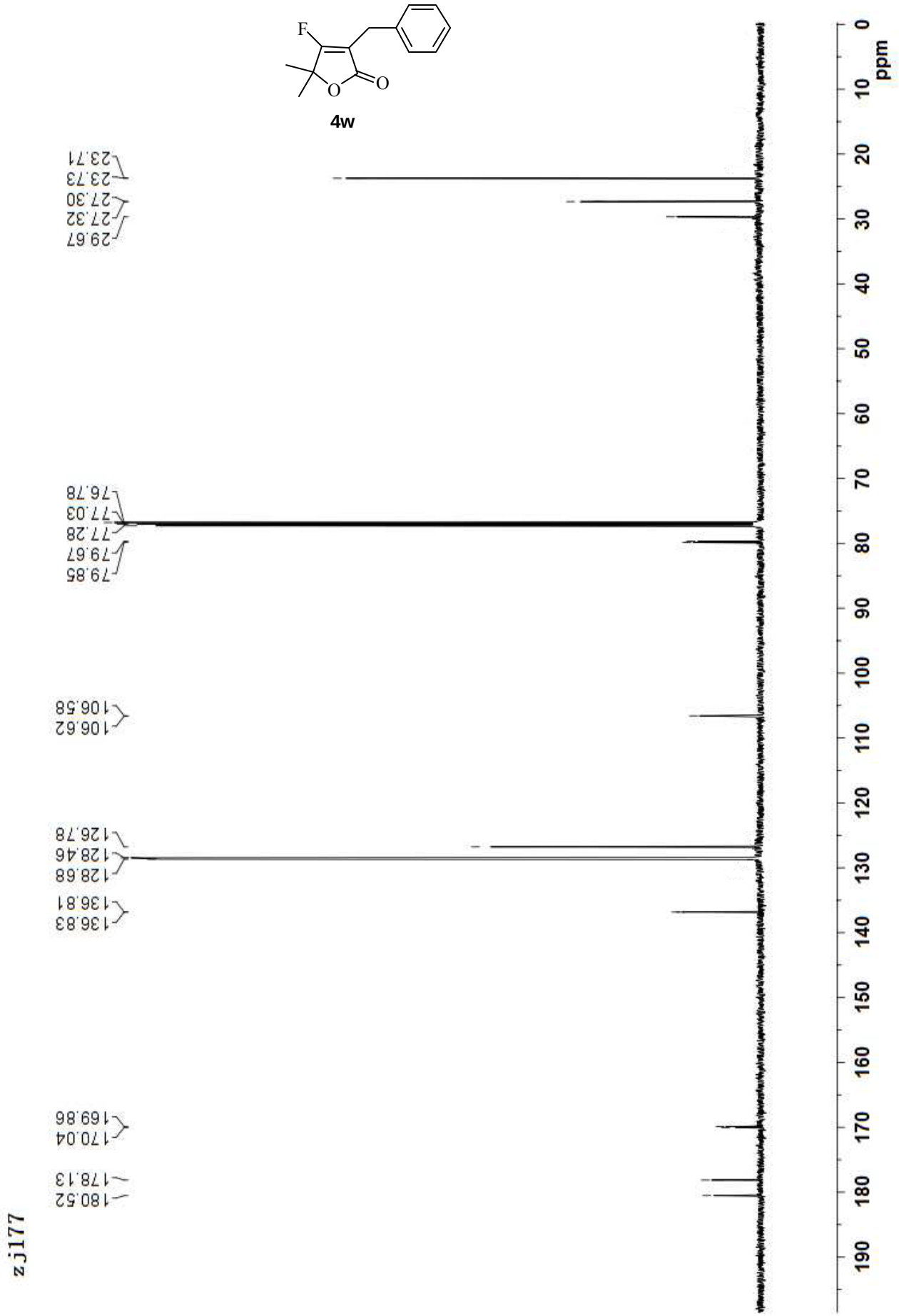

Br
F
O
O
O
2r
zj186
14.09
25.48
61.39
76.80
77.06
77.31
101.62
103.21
124.65
125.14
127.94
132.61
138.84
138.98
140.41
140.56
142.27
144.84
144.88
161.76
201.17
201.41
ppm

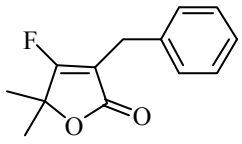

Br
F
O
O
O
2r
-176.681
1.00
ppm
-180
-160
-140
-120
-100
-80
-60
-40
-20
0
zj186 CDCl3 F19
Pulse Sequence: s2pul


3v
zj175
1.697
1.711
3.607
3.613
5.503
5.509
5.517
5.523
5.528
5.531
5.536
5.542
5.550
5.556
7.413
7.428
7.434
7.439
7.442
7.449
7.452
7.464
7.467
7.485
7.489
7.497
7.503
7.607
7.620
3.07
2.04
0.97
1.97
0.95
0.97
ppm


3v
zj175
19.22
32.17
75.63
76.79
77.05
77.30
121.63
125.90
127.35
128.87
135.33
135.84
149.82
168.62
174.22
ppm

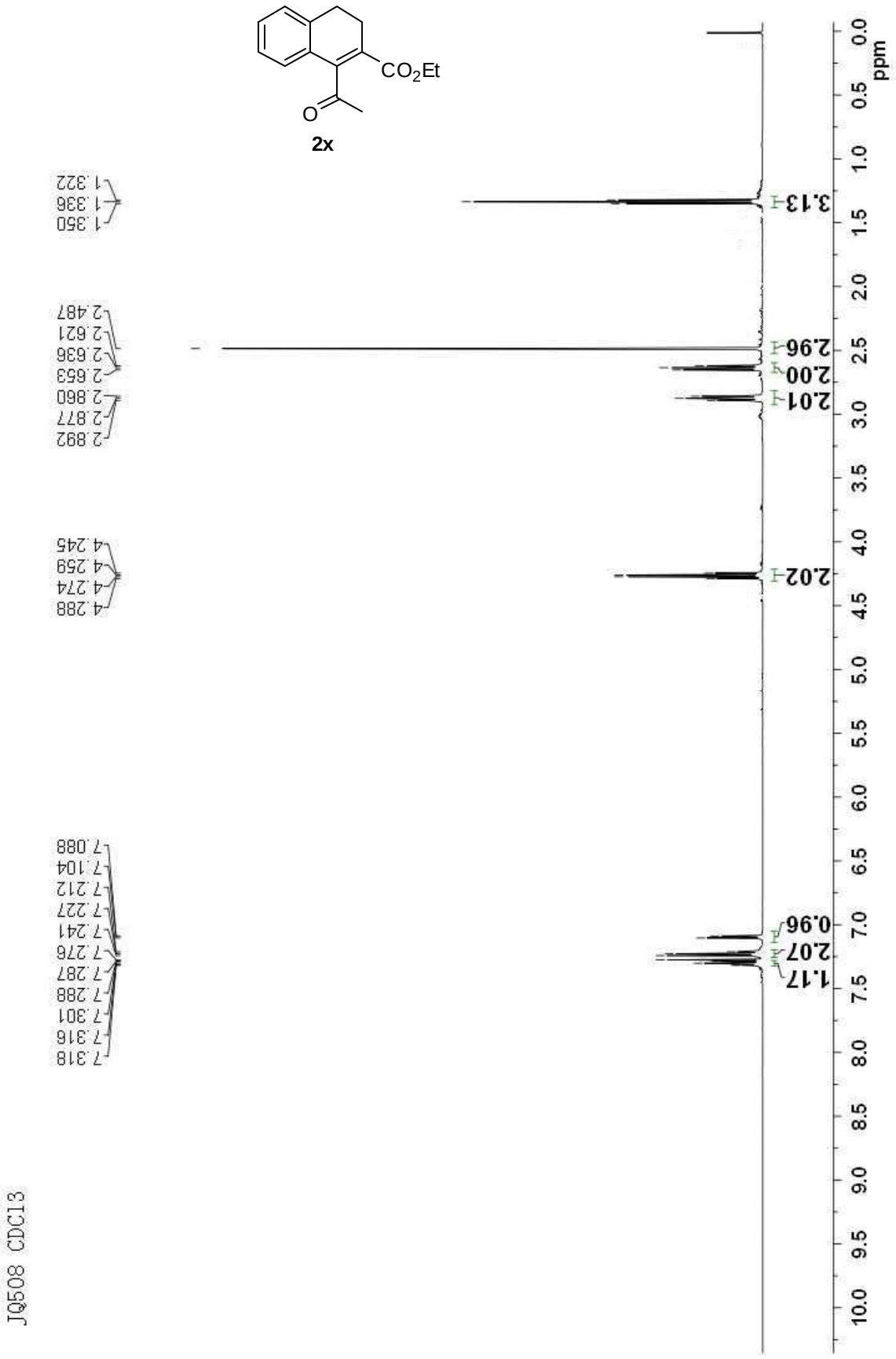

F
O
O
4w
1.549
3.567
7.231
7.245
7.265
7.280
7.301
7.315
7.330
5.95
1.95
5.06
ppm
zj177

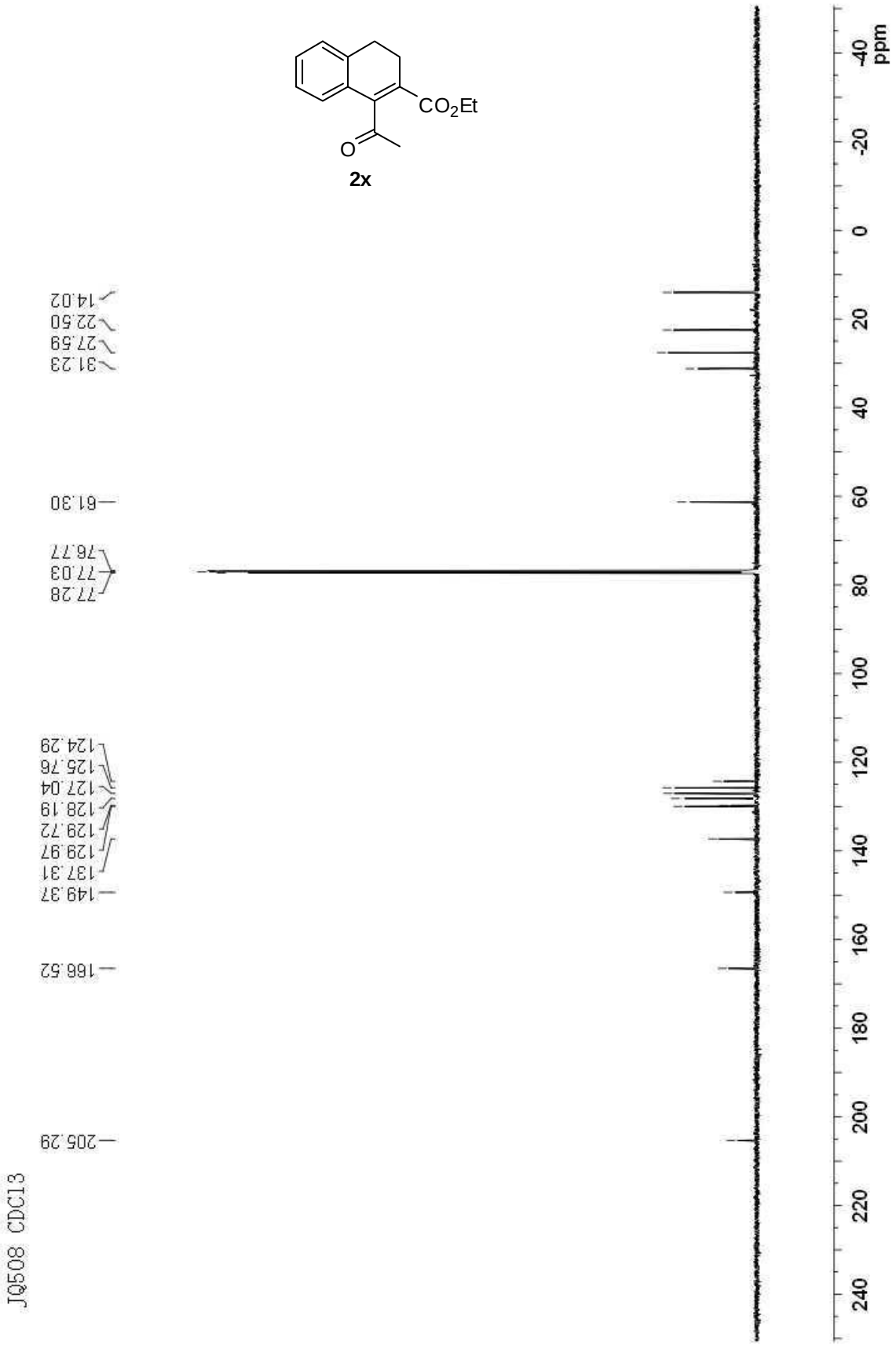

F
O
O
4w
zj177
180.52
178.13
170.04
169.86
136.83
136.81
128.68
128.46
126.78
106.62
106.58
79.85
79.67
77.28
77.03
76.78
29.67
27.32
27.30
23.73
23.71
ppm

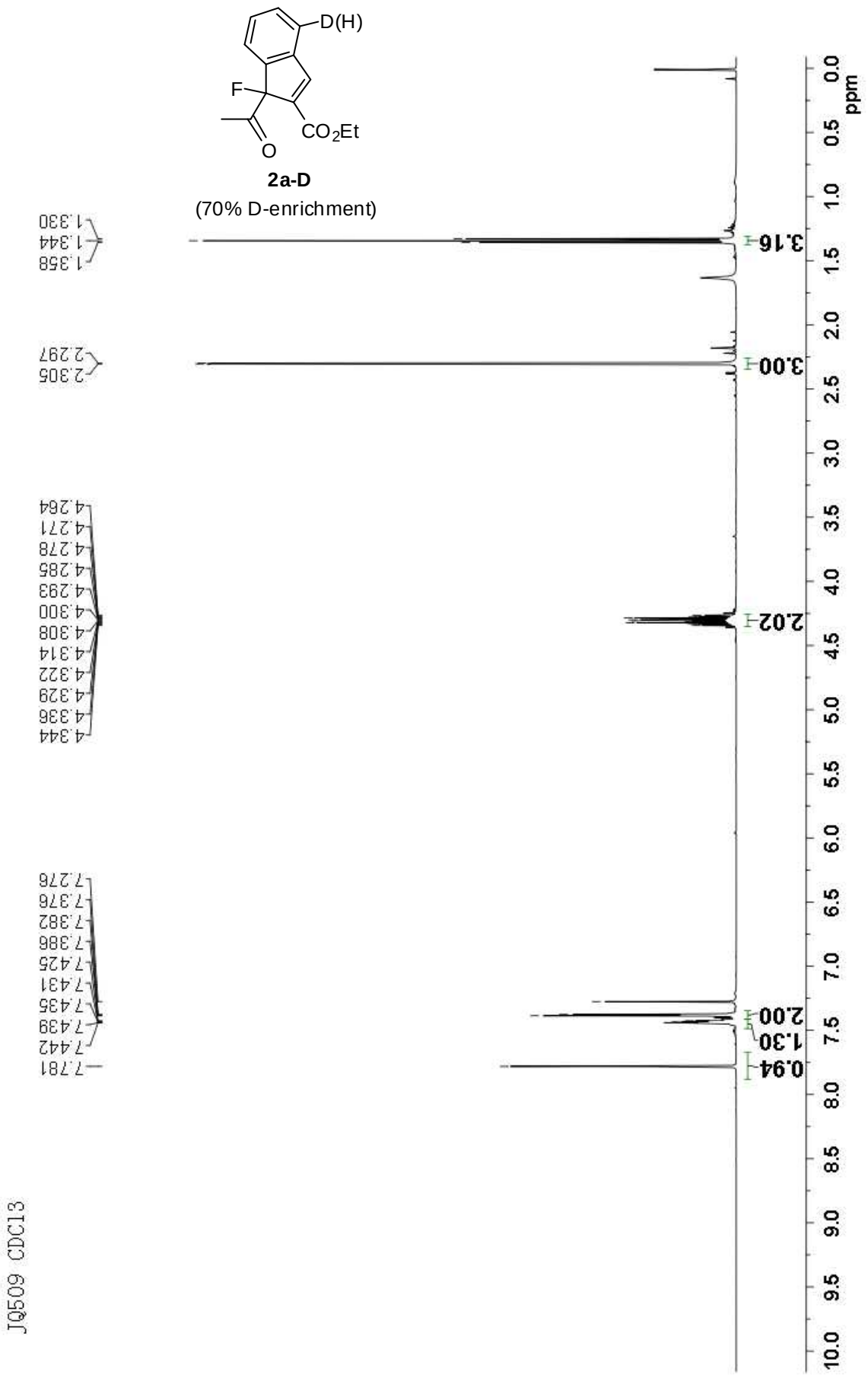

F
O
O

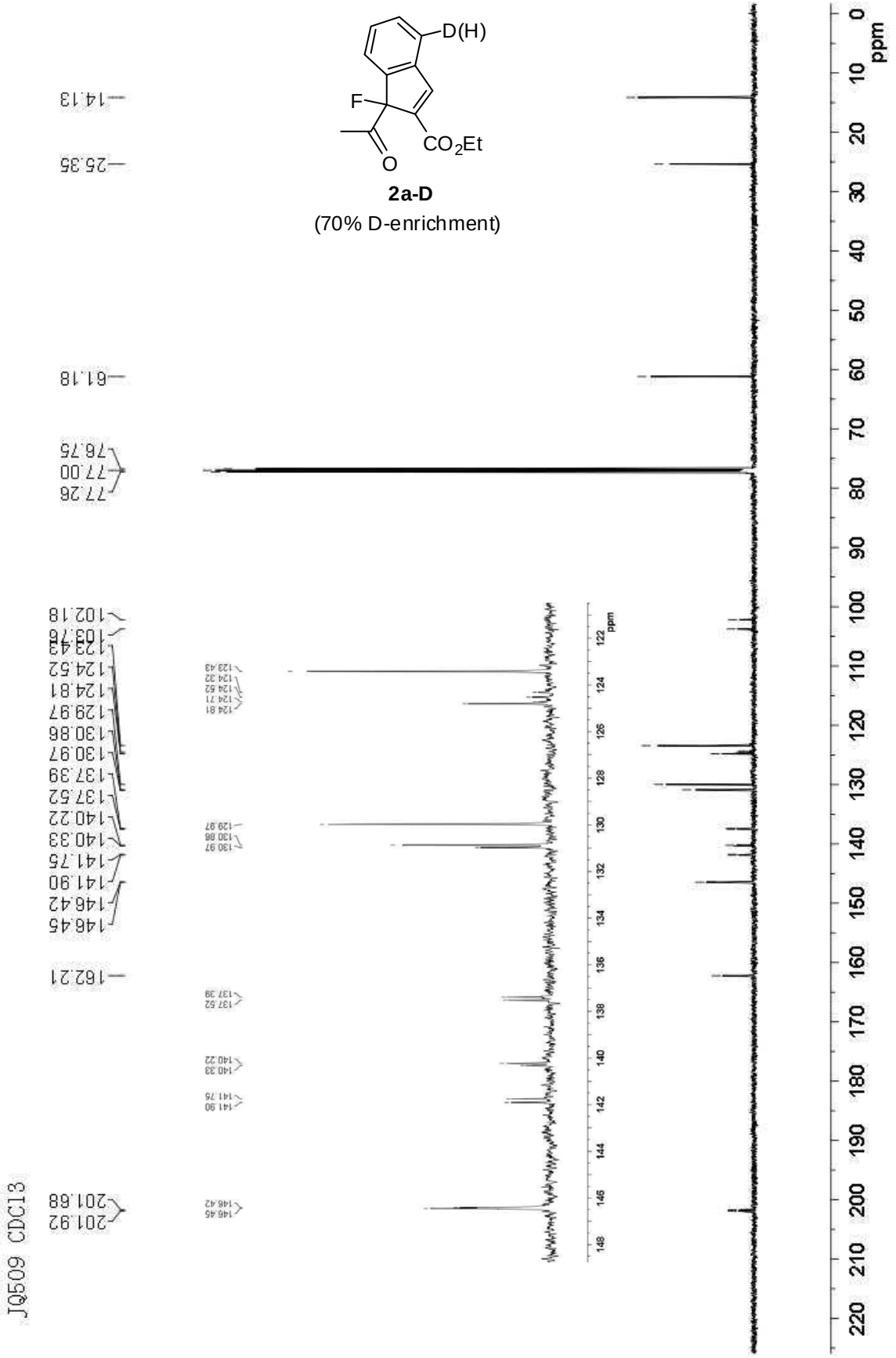
4w

-113.139
1.00
ppm
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
Pulse Sequence: s2pul


CO2Et
O
2x
JQ508 CDCl3
ppm
3.13
2.96
2.00
2.01
2.02
0.96
2.07
1.17


CO2Et
O
2x
JQ508 CDCl3
205.29
166.52
149.37
137.31
129.97
129.72
128.19
127.04
125.76
124.29
77.28
77.03
76.77
61.30
31.23
27.59
22.50
14.02
ppm


D(H)
F
CO2Et
O
2a-D
(70% D-enrichment)
1.330
1.344
1.358
2.297
2.305
4.264
4.271
4.278
4.285
4.293
4.300
4.308
4.314
4.322
4.329
4.336
4.344
7.276
7.376
7.382
7.386
7.425
7.431
7.435
7.439
7.442
7.781
3.16
3.00
2.02
2.00
1.30
0.94
ppm
JQ509 CDC13


D(H)
F
CO2Et
O
2a-D
(70% D-enrichment)
JQ509 CDCl3
ppm