Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

The Baylis-Hillman acetates in organic synthesis: Unprecedented sodium nitrite induced intramolecular Friedel-Crafts cyclization of secondary nitro compounds

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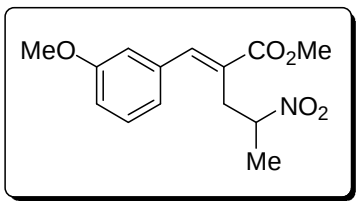
EXPERIMENTAL SECTION

General Remarks: Melting points were recorded on a Superfit (India) capillary melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO-FT-IR model 5300 spectrometer using solid samples as KBr plates and liquid sample as thin film between NaCl plates. For all the compounds ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in deuterochloroform ($CDCl_3$) on a Bruker-AVANCE-400 spectrometer using tetramethylsilane (TMS, $\delta = 0$) as an internal standard at room temperature. HRMS spectra were recorded on Bruker maXis ESI-TOF spectrometer. The X-ray diffraction measurements were carried out at 298 K on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo-Kα fine-focus sealed tube ($\lambda = 0.71073$ Å).

Methyl (*E*)-2-(3-methoxybenzylidene)-4-nitropentanoate (3a)

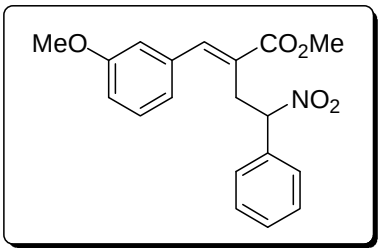
This compound was prepared following the literature [1] procedure known for similar compound with some modification.

To a stirred solution of methyl 3-acetoxy-3-(3-methoxyphenyl)-2-methylenepropanoate (**1a**) (3 mmol, 0.793 g) and nitroethane (**2a**) (9 mmol, 0.675 g) in DMF (12 mL) was added K_2CO_3 (9 mmol, 1.25 g) and reaction mixture was stirred at room temperature for 4 hours. The reaction mixture was diluted with brine (12 mL), extracted with diethyl ether (3x15 mL). The combined organic layer was washed with water (10 mL) and dried over anhydrous Na_2SO_4. Solvent was evaporated and the resulting crude product was purified by column chromatography (silica gel, 5% EtOAc in hexanes) to afford **3a** in 90% (0.76 g) yield as a pale brown viscous liquid.



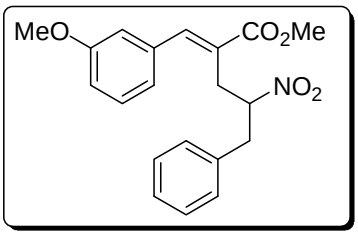
IR (Neat): ν 1709, 1632, 1556 cm^{-1}; ^{1}H NMR (400 MHz): δ 1.48 (d, 3H, J = 6.8 Hz), 2.95 & 3.25 [dABq, 2H, J = 14.0 & 6.0 (8.0) Hz], 3.84 (s, 3H), 3.85 (s, 3H), 4.87-4.97 (m, 1H), 6.82 (s, 1H), 6.84-6.94 (m, 2H), 7.30-7.37 (m, 1H), 7.86 (s, 1H); ^{13}C NMR (100 MHz) : δ 18.80, 32.97, 52.36, 55.33, 81.68, 113.98, 114.73, 121.13, 127.45, 129.82, 135.91, 143.46, 159.72, 167.62; HRMS (ESI) exact mass calc′d for $C_{14}H_{17}O_5NH$ $(M+H)^+$: 280.1185; Found: 280.1180.

Methyl (*E*)-2-(3-methoxybenzylidene)-4-nitro-4-phenylbutanoate (3b)



Reaction time: 3 h; Yield: 89 %; IR (Neat): ν 1709, 1626, 1550 cm^{-1}; ^{1}H NMR (400 MHz): δ 3.41 & 3.69 [dABq, 2H, J = 14.4 & 6.4 (7.6) Hz], 3.81 (s, 3H), 3.83 (s, 3H), 5.85 (t, 1H, J = 7.2 Hz), 6.70 (s, 1H), 6.78 (d, 1H, J = 7.6 Hz), 6.91 (dd, 1H, J = 8.4 & 2.4 Hz), 7.24-7.38* (m, 6H), 7.79 (s, 1H); *It also contains $CHCl_3$ peak. ^{13}C NMR (100 MHz): δ 31.95, 52.36, 55.32, 89.10, 113.88, 114.68, 120.98, 126.96, 127.87, 128.82, 129.76, 133.91, 136.01, 143.86, 159.69, 167.57; HRMS (ESI) exact mass calc′d for $C_{19}H_{19}O_5NH$ $(M+H)^+$: 342.1341; Found: 342.1342.

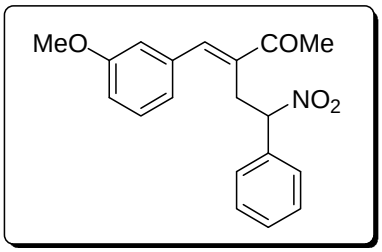
Methyl (*E*)-2-(3-methoxybenzylidene)-4-nitro-5-phenylpentanoate (3c)



Reaction time: 4 h; Yield: 92 %; IR (Neat): ν 1709, 1615, 1550 cm^{-1}; ^{1}H NMR (400 MHz): δ 2.94-3.07 (m, 2H), 3.21-3.35 (m, 2H), 3.83 (s, 3H), 3.84 (s, 3H), 5.05-5.14 (m, 1H), 6.78-6.87

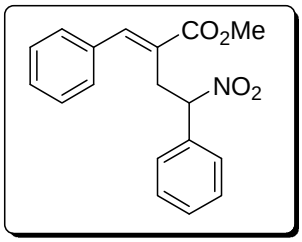
(m, 2H), 6.91 (dd, 1H, J = 8.0 & 2.4 Hz), 7.12* (d, 2H, J = 7.6 Hz), 7.22-7.36$^{\$}$ (m, 4H), 7.85 (s, 1H); *unresolved doublet of doublet. $ It also contains $CHCl_3$ peak. ^{13}C NMR (100 MHz): δ 31.77, 39.58, 52.38, 55.37, 88.02, 113.95, 114.83, 121.02, 127.29, 127.44, 128.82, 128.90, 129.83, 135.37, 135.85, 143.67, 159.73, 167.55; HRMS (ESI) exact mass calc′d for $C_{20}H_{21}O_5NH$ $(M+H)^+$: 356.1498; Found: 356.1498.

(*E*)-3-(3-Methoxybenzylidene)-5-nitro-5-phenylpentan-2-one (3d)



Reaction time: 3 h; Yield: 88 %; IR (Neat): ν 1665, 1626, 1544 cm^{-1}; ^1H NMR (400 MHz): δ 2.42 (s, 3H), 3.35 & 3.65 [dABq, 2H, J = 14.0 & 6.8 (8.4) Hz], 3.84 (s, 3H), 5.80 (t, 1H, J = 7.2 Hz), 6.75 (s, 1H), 6.82 (d, 1H, J = 7.6 Hz), 6.94 (dd, 1H, J = 8.4 & 2.0 Hz), 7.22-7.38* (m, 6H), 7.62 (s, 1H); * It also contains $CHCl_3$ peak. ^{13}C NMR (100 MHz): δ 25.95, 31.00, 55.38, 88.77, 113.87, 114.83, 120.96, 127.91, 128.79, 129.69, 129.89, 134.02, 135.97, 136.67, 144.30, 159.76, 199.71; HRMS (ESI) exact mass calc′d for $C_{19}H_{19}O_4NNa$ $(M+Na)^+$: 348.1212; Found: 348.1216.

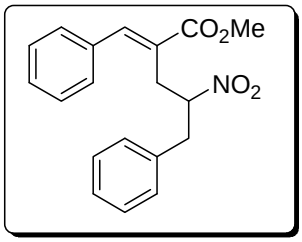
Methyl (*E*)-2-benzylidene-4-nitro-4-phenylbutanoate (3e)



Reaction time: 3 h; Yield: 90 %; IR (Neat): ν 1726, 1638, 1550 cm^{-1}; ^1H NMR (400 MHz): δ 3.40 & 3.69 [dABq, 2H, J = 14.0 & 7.2 (8.0) Hz], 3.82 (s, 3H), 5.84 (t, 1H, J = 7.6 Hz), 7.14-

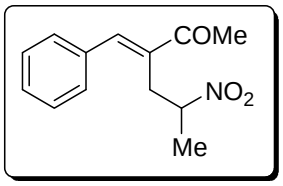
7.21 (m, 2H), 7.22-7.45* (m, 8 H), 7.81 (s, 1H); * It also contains $CHCl_3$ peak. ^{13}C NMR (100 MHz): δ 31.86, 52.34, 89.08, 126.74, 127.81, 128.69, 128.83, 129.74, 133.90, 134.70, 143.97, 167.60; HRMS (ESI) exact mass calc′d for $C_{18}H_{17}O_4NH$ $(M+H)^+$: 312.1236; Found: 312.1234.

Methyl (*E*)-2-benzylidene-4-nitro-5-phenylpentanoate (3f)



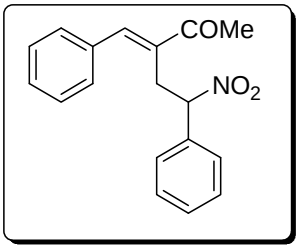
Reaction time: 4 h; Yield: 91 %; IR (Neat): ν 1709, 1626, 1544 cm^{-1}; ^1H NMR (400 MHz): δ 2.96-3.05 (m, 2H), 3.23 & 3.31 [dABq, 2H, J = 14.0 & 8.8 (9.6) Hz], 3.84 (s, 3H), 5.03-5.13 (m, 1H), 7.12 (d, 2H, J = 6.8 Hz), 7.22-7.33* (m, 5H), 7.34-7.43 (m, 3H), 7.89 (s, 1H); * It also contains $CHCl_3$ peak. ^{13}C NMR (100 MHz): δ 31.56, 39.59, 52.40, 88.03, 127.07, 127.47, 128.79, 128.84, 128.94, 129.00, 134.55, 135.36, 143.71, 167.63; HRMS (ESI) exact mass calc′d for $C_{19}H_{19}O_4NH$ $(M+H)^+$: 326.1392; Found: 326.1387.

(*E*)-3-Benzylidene-5-nitrohexan-2-one (3g)



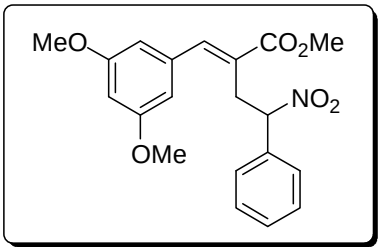
Reaction time: 4 h; Yield: 89 %; IR (Neat): ν 1665, 1626, 1550 cm^{-1}; ^1H NMR (400 MHz): δ 1.46 (d, 3H, J = 6.4 Hz), 2.49 (s, 3H), 2.93 & 3.15 [dABq, 2H, J = 14.0 & 5.2 (8.8) Hz], 4.77-4.90 (m, 1H), 7.29 (d, 2H, J = 7.6 Hz), 7.35-7.46 (m, 3H), 7.71 (s, 1H); ^{13}C NMR (100 MHz): δ 18.92, 25.97, 32.03, 81.55, 128.75, 128.83, 129.11, 134.57, 137.08, 143.98, 199.75; HRMS (ESI) exact mass calc′d for $C_{13}H_{15}O_3NH$ $(M+H)^+$: 234.1130; Found: 234.1129.

(*E*)-3-Benzylidene-5-nitro-5-phenylpentan-2-one (3h)



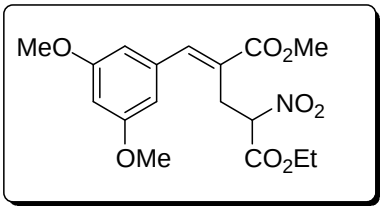
Reaction time: 3 h; Yield: 93 %; IR (Neat): ν 1665, 1621, 1544 cm^{-1}; ^{1}H NMR (400 MHz): δ 2.42 (s, 3H), 3.35 & 3.65 [dABq, 2H, J = 14.0 & 7.2 (8.4) Hz], 5.79 (t, 1H, J = 8.0 Hz), 7.20-7.46* (m, 10H), 7.65 (s, 1H); *It also contains $CHCl_3$ peak. ^{13}C NMR (100 MHz): δ 25.94, 30.88, 88.75, 127.85, 128.67, 128.80, 129.08, 129.68, 134.02, 134.67, 136.49, 144.44, 199.72; HRMS (ESI) exact mass calc′d for $C_{18}H_{17}O_3NH$ $(M+H)^+$: 296.1287; Found: 296.1284.

Methyl (*E*)-2-(3, 5-dimethoxybenzylidene)-4-nitro-4-phenylbutanoate (3i)



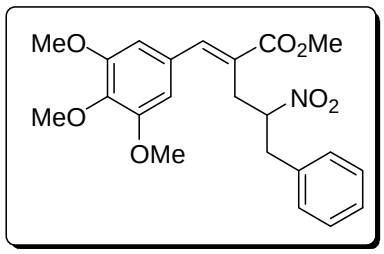
Reaction time: 3 h; Yield: 88 %; IR (Neat): ν 1704, 1610, 1550 cm^{-1}; ^{1}H NMR (400 MHz): δ 3.39 & 3.68 [dABq, 2H, J = 14.4 & 6.8 (8.0) Hz], 3.78 (s, 6H), 3.81 (s, 3H), 5.86 (t, 1H, J = 7.6 Hz), 6.32 (d, 2H, J = 1.6 Hz), 6.43-6.49 (m, 1H), 7.27-7.38 (m, 5H), 7.75 (s, 1H); ^{13}C NMR (100 MHz): δ 32.09, 52.40, 55.49, 89.16, 101.07, 106.49, 127.18, 127.95, 128.85, 129.79, 133.95, 136.54, 143.97, 160.92, 167.55; HRMS (ESI) exact mass calc′d for $C_{20}H_{21}O_6NNa$ $(M+Na)^+$: 394.1267; Found: 394.1266.

Ethyl (4*E*)-5-(3, 5-dimethoxyphenyl)-4-methoxycarbonyl-2-nitropent-4-enoate (3j)



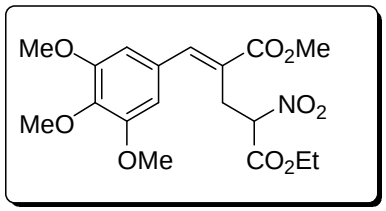
Reaction time: 3 h; Yield: 83 %; IR (Neat): *ν* 1753, 1709, 1620, 1572 cm^{-1}; ^{1}H NMR (400 MHz): δ 1.25 (t, 3H, *J* = 7.2 Hz), 3.39 & 3.53 [dABq, 2H, *J* = 14.8 & 6.4 (8.8) Hz], 3.81 (s, 6H), 3.85 (s, 3H), 4.17-4.29 (m, 2H), 5.62 (dd, 1H, *J* = 6.4 & 9.2 Hz), 6.42-6.49 (m, 3H), 7.85 (s, 1H); ^{13}C NMR (100 MHz): *δ* 13.82, 28.63, 52.48, 55.51, 63.14, 85.96, 101.38, 106.59, 125.74, 136.06, 144.57, 160.99, 164.15, 167.27; HRMS (ESI) exact mass calc′d for $C_{17}H_{21}O_8NNa$ $(M+Na)^+$: 390.1165; Found: 390.1174.

Methyl (*E*)-2-(3, 4, 5-trimethoxybenzylidene)-4-nitro-5-phenylpentanoate (3k)



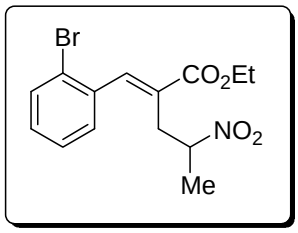
Reaction time: 4 h; Yield: 90 %; IR (Neat): ν 1703, 1632, 1544 cm^{-1}; ^{1}H NMR (400 MHz): δ 2.99 & 3.06 [dABq, 2H, *J* = 14.4 & 5.2 (4.8) Hz], 3.25-3.35 (m, 2H), 3.84 (s, 3H), 3.88 (s, 6H), 3.90 (s, 3H), 5.13-5.23 (m, 1H), 6.52 (s, 2H), 7.14 (d, 2H, *J* = 6.8 Hz), 7.22-7.34* (m, 3H), 7.81 (s, 1H); *It also contains $CHCl_3$ peak. ^{13}C NMR (100 MHz): *δ* 32.14, 39.67, 52.39, 56.27, 61.00, 87.92, 106.04, 126.39, 127.50, 128.85, 128.88, 129.90, 135.31, 138.71, 143.88, 153.36, 167.65; HRMS (ESI) exact mass calc′d for $C_{22}H_{25}O_7NH$ $(M+H)^+$: 416.1709; Found: 416.1712.

Ethyl (4*E*)-4-methoxycarbonyl-2-nitro-5-(3, 4, 5-trimethoxyphenyl)pent-4-enoate (3l)



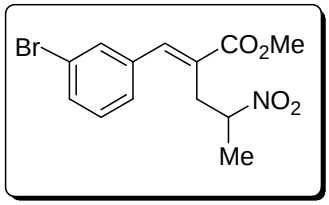
Reaction time: 3 h; Yield: 85 %; IR (Neat): *ν* 1742, 1704, 1630, 1561 cm^{-1}; ^{1}H NMR (400 MHz): *δ* 1.26 (t, 3H, *J* = 7.2 Hz), 3.44 & 3.56 [dABq, 2H, *J* = 14.8 & 6.8 (9.6) Hz], 3.86 (s, 3H), 3.88 (s, 6H), 3.89 (s, 3H), 4.24 (dq, 2H, *J* = 7.2 & 2.0 Hz), 5.68 (dd, 1H, *J* = 6.8 & 9.2 Hz), 6.59 (s, 2H), 7.84 (s, 1H); ^{13}C NMR (100 MHz): *δ* 13.87, 28.79, 52.49, 56.29, 61.00, 63.20, 85.93, 106.29, 124.51, 129.54, 138.94, 144.50, 153.41, 164.26, 167.44; HRMS (ESI) exact mass calc′d for $C_{18}H_{23}O_9NH$ $(M+H)^+$: 398.1451; Found: 398.1449.

Ethyl (*E*)-2-(2-bromobenzylidene)-4-nitropentanoate (3m)



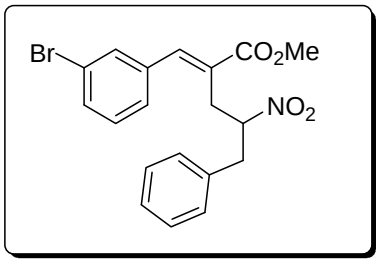
Reaction time: 4 h; Yield: 91 %; IR (Neat): *ν* 1704, 1620, 1550 cm^{-1}; ^{1}H NMR (400 MHz): *δ* 1.38 (t, 3H, *J* = 7.2 Hz), 1.41 (d, 3H, *J* = 6.8 Hz), 2.81 & 3.06 [dABq, 2H, *J* = 14.0 & 6.4 (8.0) Hz], 4.32 (q, 2H, *J* = 7.2 Hz), 4.83-4.94 (m, 1H), 7.16 (d, 1H, *J* = 7.2 Hz), 7.21-7.28 (m, 1H), 7.34-7.39 (m, 1H), 7.63* (d, 1H, *J* = 8.0 Hz), 7.83 (s, 1H); *Unresolved doublet of doublet. ^{13}C NMR (100 MHz): *δ* 14.26, 18.80, 32.99, 61.55, 81.55, 123.50, 127.52, 129.14, 129.82, 130.13, 132.89, 135.50, 142.75, 166.61; HRMS (ESI) exact mass calc′d for $C_{14}H_{16}O_4NBrH$ $(M+H)^+$: 342.0341; Found: 342.0337.

Methyl (*E*)-2-(3-bromobenzylidene)-4-nitropentanoate (3n)



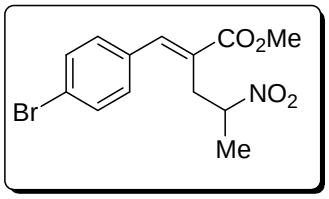
Reaction time: 4 h; Yield: 86 %; IR (Neat): ν 1709, 1627, 1550 cm^{-1}; ^{1}H NMR (400 MHz): δ 1.49 (d, 3H, J = 6.4 Hz), 2.89 & 3.20 [dABq, 2H, J = 14.4 & 5.6 (8.8) Hz], 3.86 (s, 3H), 4.85-4.96 (m, 1H), 7.20 (d, 1H, J = 7.6 Hz), 7.25-7.33 (m, 1H), 7.43 (s, 1H), 7.50 (d, 1H, J = 8.0 Hz), 7.81 (s, 1H); ^{13}C NMR (100 MHz) : δ 18.99, 32.93, 52.53, 81.67, 122.83, 127.21, 128.69, 130.34, 131.61, 131.90, 136.70, 141.89, 167.27; HRMS (ESI) exact mass calc′d for $C_{13}H_{14}O_4NBrH$ $(M+H)^+$: 328.0184; Found: 328.0185.

Methyl (*E*)-2-(3-bromobenzylidene)-4-nitro-5-phenylpentanoate (3o)



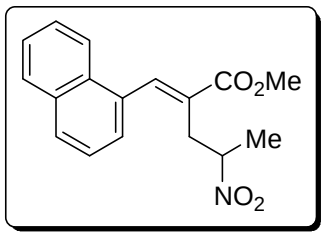
Reaction time: 4 h; Yield: 87 %; IR (Neat): ν 1709, 1620, 1550 cm^{-1}; ^{1}H NMR (400 MHz): δ 2.92 & 3.01 [dABq, 2H, J = 14.4 & 4.4 (6.0) Hz], 3.24 (ABq, 2H, J = 14.4 & 9.2 Hz), 3.83 (s, 3H), 5.03-5.13 (m, 1H), 7.11-7.35 (m, 7H), 7.40 (s, 1H), 7.50 (d, 1H, J = 8.0 Hz), 7.79 (s, 1H); ^{13}C NMR (100 MHz): δ 31.58, 39.69, 52.51, 87.94, 122.79, 127.14, 127.54, 128.48, 128.90, 130.31, 131.59, 131.88, 135.18, 136.59, 142.00, 167.15; HRMS (ESI) exact mass calc′d for $C_{19}H_{18}O_4NBrH$ $(M+H)^+$: 404.0497; Found: 404.0493.

Methyl (*E*)-2-(4-bromobenzylidene)-4-nitropentanoate (3p)



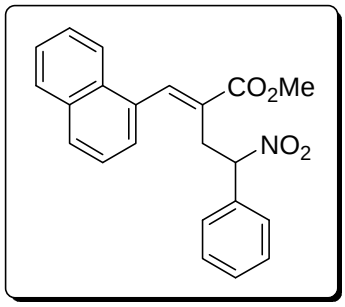
Reaction time: 4 h; Yield: 90 %; m.p. 73-74 ºC; IR (KBr): *ν* 1715, 1638, 1539 cm^{-1}; ^{1}H NMR (400 MHz): *δ* 1.48 (d, 3H, *J* = 6.4 Hz), 2.90 & 3.20 [dABq, 2H, *J* = 14.4 & 5.6 (8.4) Hz], 3.85 (s, 3H), 4.85-4.97 (m, 1H), 7.16 (d, 2H, *J* = 8.4 Hz), 7.54 (d, 2H, *J* = 8.4 Hz), 7.79 (s, 1H); ^{13}C NMR (100 MHz): *δ* 18.97, 32.93, 52.50, 81.66, 123.29, 128.00, 130.39, 132.06, 133.52, 142.32, 167.42; HRMS (ESI) exact mass calc′d for $C_{13}H_{14}O_4NBrH$ $(M+H)^+$: 328.0184; Found: 328.0184.

Methyl (*E*)-2-(naphthalen-1-yl)methylidene-4-nitropentanoate (3q)



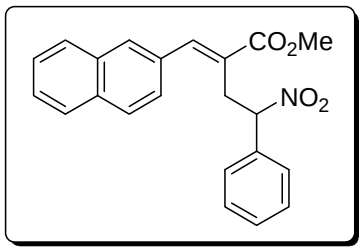
Reaction time: 4 h; Yield: 89 %; IR (Neat): *ν* 1715, 1632, 1550 cm^{-1}; ^{1}H NMR (400 MHz): *δ* 1.34 (d, 3H, *J* = 6.4 Hz), 2.84 & 3.09 [dABq, 2H, *J* = 14.4 & 6.0 (8.0) Hz], 3.92 (s, 3H), 4.82-4.94 (m, 1H), 7.26 (d, 1H, *J* = 6.8 Hz), 7.48-7.59 (m, 3H), 7.76-7.83 (m, 1H), 7.86-7.92 (m, 2H), 8.34 (s, 1H); ^{13}C NMR (100 MHz): *δ* 18.78, 33.42, 52.46, 81.67, 124.54, 125.29, 125.88, 126.44, 126.71, 128.66, 129.18, 129.57, 131.18, 132.05, 133.43, 142.69, 167.29; HRMS (ESI) exact mass calc′d for $C_{17}H_{17}O_4NNa$ $(M+Na)^+$: 322.1055; Found: 322.1064.

Methyl (*E*)-2-(naphthalen-1-yl)methylidene-4-nitro-4-phenylbutanoate (3r)



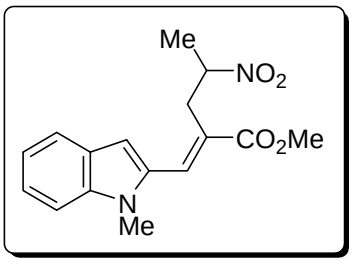
Reaction time: 3 h; Yield: 92 %; m.p. 66-67 ºC; IR (KBr): *v* 1709, 1632, 1545 cm^{-1}; ^{1}H NMR (400 MHz): δ 3.40 & 3.51 [dABq, 2H, *J* = 14.0 & 7.6 (7.2) Hz], 3.89 (s, 3H), 5.81 (t, 1H, *J* = 7.6 Hz), 7.01-7.11 (m, 4H), 7.12-7.19 (m, 2H), 7.38-7.54 (m, 4H), 7.87 (d, 2H, *J* = 8.0 Hz), 8.24 (s, 1H); ^{13}C NMR (100 MHz): δ 32.21, 52.46, 88.96, 124.56, 125.20, 125.91, 126.35, 126.57, 127.71, 128.48, 128.55, 128.63, 129.21, 129.55, 131.16, 132.04, 133.34, 133.56, 143.15, 167.30; HRMS (ESI) exact mass calc′d for $C_{22}H_{19}O_4NNa$ $(M+Na)^+$: 384.1212; Found: 384.1215.

Methyl (*E*)-2-(naphthalen-2-yl)methylidene-4-nitro-4-phenylbutanoate (3s)



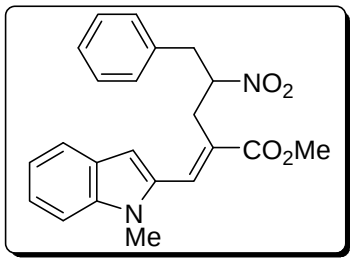
Reaction time: 3 h; Yield: 88 %; m.p. 97-98 ºC; IR (KBr): *v* 1704, 1632, 1545 cm^{-1}; ^{1}H NMR (400 MHz): δ 3.48 & 3.77 [dABq, 2H, *J* = 14.0 & 6.8 (8.0) Hz], 3.85 (s, 3H), 5.89 (t, 1H, *J* = 7.6 Hz), 7.21-7.27* (m, 4H), 7.28-7.35 (m, 2H), 7.50-7.57 (m, 2H), 7.61 (s, 1H), 7.77-7.82 (m, 1H), 7.83-7.89 (m, 2H), 7.97 (s, 1H); *It also contains $CHCl_3$ peak. ^{13}C NMR (100 MHz): δ 32.19, 52.44, 89.19, 125.99, 126.71, 126.90, 127.06, 127.80, 127.86, 128.44, 128.56, 128.87, 129.80, 132.17, 133.09, 133.18, 133.99, 144.05, 167.68; HRMS (ESI) exact mass calc′d for $C_{22}H_{19}O_4NNa$ $(M+Na)^+$: 384.1212; Found: 384.1212.

Methyl (*E*)-2-(1-methyl-1*H*-indol-2-yl)methylidene-4-nitropentanoate (3t)



Reaction time: 3 h; Yield: 93 %; m.p. 81-82 ºC; IR (KBr): *v* 1698, 1632, 1539 cm^{-1}; ^{1}H NMR (400 MHz): δ 1.58* (d, 3H, *J* = 6.8 Hz), 3.20 & 3.51 [dABq, 2H, *J* = 14.0 & 7.2 (8.0) Hz], 3.79 (s, 3H), 3.87 (s, 3H), 4.92-5.07 (m, 1H), 6.88 (s, 1H), 7.11-7.18 (m, 1H), 7.23-7.37$^{\$}$ (m, 2H), 7.66 (d, 1H, *J* = 8.0 Hz), 7.91 (s, 1H); *It also contains moisture peak. $ It also contains $CHCl_3$ peak. ^{13}C NMR (100 MHz) : δ 18.75, 30.08, 33.54, 52.47, 81.29, 105.51, 109.63, 120.49, 121.62, 123.86, 126.40, 127.64, 130.67, 132.93, 138.20, 167.62; HRMS (ESI) exact mass calc′d for $C_{16}H_{18}N_2O_4H$ $(M+H)^+$: 303.1345; Found: 303.1343.

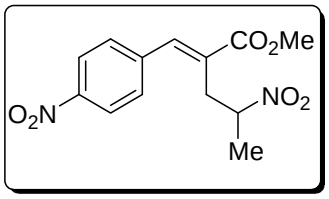
Methyl (*E*)-2-(1-methyl-1*H*-indol-2-yl)methylidene-4-nitro-5-phenylpentanoate (3u)



Reaction time: 4 h; Yield: 84 %; m.p. 116-117 ºC; IR (KBr): *v* 1693, 1621, 1545 cm^{-1}; ^{1}H NMR (400 MHz): δ 3.11 & 3.20 [dABq, 2H, *J* = 14.4 & 6.0 (4.8) Hz], 3.38 & 3.56 [dABq, 2H, *J* = 14.4 & 8.4 (9.2) Hz], 3.75 (s, 3H), 3.84 (s, 3H), 5.07-5.19 (m, 1H), 6.58 (s, 1H), 7.09-7.22 (m, 3H), 7.23-7.36 (m, 5H), 7.58 (d, 1H, *J* = 8.0 Hz), 7.87 (s, 1H); ^{13}C NMR (100 MHz): δ 30.10, 32.16, 39.70, 52.48, 87.51, 105.50, 109.64, 120.45, 121.68, 123.87, 126.25, 127.58, 127.64,

128.93, 129.14, 130.68, 132.86, 135.41, 138.23, 167.56; HRMS (ESI) exact mass calc′d for $C_{22}H_{22}N_2O_4H$ $(M+H)^+$: 379.1658; Found: 379.1661.

Methyl 2-(4-nitrobenzylidene)-4-nitropentanoate (3v)

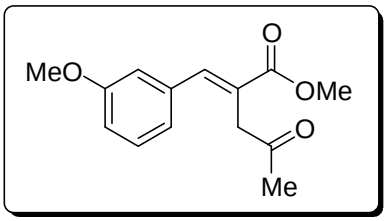


Reaction time: 2 h; Yield: 45 %; IR (Neat): *v* 1720, 1600, 1550 cm^{-1}; ^1H NMR (400 MHz): δ 1.49 (d, 3H, *J* = 6.4 Hz), 2.85 & 3.15 [dABq, 2H, *J* = 14.4 & 4.8 (5.2) Hz], 3.89 (s, 3H), 4.87-5.00 (m, 1H), 7.42 (d, 2H, *J* = 8.8 Hz), 7.89 (s, 1H), 8.27 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz): δ 19.17, 33.12, 52.72, 81.66, 124.00, 129.55, 130.35, 141.01, 141.27, 147.74, 166.80; HRMS (ESI) exact mass calc′d for $C_{13}H_{14}N_2O_6H$ $(M+H)^+$: 295.0930; Found: 295.0927.

Methyl (*E*)-2-(3-methoxybenzylidene)-4-oxopentanoate (5a)

This molecule was prepared following the Nef reaction procedure reported in the literature for similar compounds, with some modification[1]

To a stirred solution of methyl (*E*)-2-(3-methoxybenzylidene)-4-nitropentanoate (**3a**) (2 mmol, 0.558 g) in ethanol (4 mL) was added a solution of sodium ethoxide (2.2 mmol, 0.150 g) in ethanol (2 mL) at 0 °C. After stirring for 30 min at the same temperature, ethanolic H_2SO_4 solution was carefully added to the reaction mixture at 0 °C and continued stirring for 30 minutes. The reaction mixture was diluted with water and extracted with EtOAc (2x 15 mL). The combined organic layer was washed with aqueous saturated $NaHCO_3$ solution, water and dried over anhydrous Na_2SO_4. The residue, thus obtained, was purified by column chromatography (silica gel, 10 % EtOAc in hexanes) to afford the title compound (**5a**) in 52% (0.258 g) as pale yellow viscous liquid.

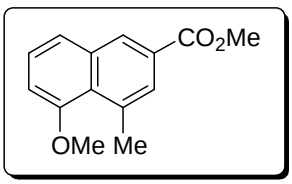


IR (Neat): ν 1720, 1704, 1632 cm^{-1}; ^{1}H NMR (400 MHz): δ 2.25 (s, 3H), 3.63 (s, 2H), 3.79 (s, 3H), 3.80 (s, 3H), 6.82-6.92 (m, 3H), 7.25-7.32* (m, 1H), 7.90 (s, 1H); *It also contains $CHCl_3$ peak. ^{13}C NMR (100 MHz): δ 30.15, 42.72, 52.33, 55.32, 114.06, 114.76, 121.16, 126.93, 129.71, 136.47, 142.29, 159.69, 167.92, 206.11. HRMS (ESI) exact mass calc′d for $C_{14}H_{16}O_4Na$ $(M+Na)^+$: 271.0946; Found: 271.0948.

Sodium nitrite induced intramolecular Friedel-Crafts reaction of methyl (*E*)-2-(3-methoxy-benzylidene)-4-nitropentanoate (3a):

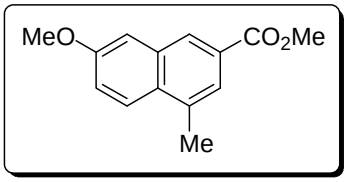
A solution of methyl (*E*)-2-(3-methoxybenzylidene)-4-nitropentanoate (**3a**) (1 mmol, 0.279 g) and sodium nitrite (1 mmol, 0.069 g) in DMF (4 mL) was heated with stirring at 100 ºC for 8 h. The reaction mixture was cooled to room temperature, diluted with brine (4 mL) and extracted with diethyl ether (3x10 mL). The combined organic layer was washed with water (10 mL), dried over anhydrous Na_2SO_4 and concentrated. The resulting crude product was purified by column chromatography (silica gel, 2 % EtOAc in hexanes) to afford methyl 5-methoxy-4-methylnaphthalene-2-carboxylate (*ortho*-**4a**) and methyl 7-methoxy-4-methylnaphthalene-2-carboxylate (*para*-**4a**) in 13 % (0.030 g) and 71 % (0.164 g) respectively. The compound *ortho*-**4a** (less polar and eluted first) is collected first and *para*-**4a** (more polar) is collected later**.**

Methyl 5-methoxy-4-methylnaphthalene-2-carboxylate (*ortho*-4a)



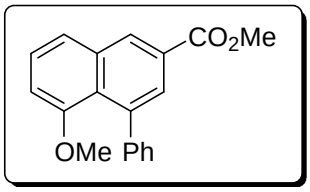
m.p. 51-52 ºC; IR (KBr): *v* 1714, 1604, 1582 cm^{-1}; ^{1}H NMR (400 MHz): δ 2.92 (s, 3H), 3.93 (s, 3H), 3.96 (s, 3H), 6.89 (d, 1H, *J* = 7.6 Hz), 7.36-7.42 (m, 1H), 7.49 (d, 1H, *J* = 8.0 Hz), 7.76 (s, 1H), 8.35 (s, 1H); ^{13}C NMR (100 MHz): δ 25.28, 52.23, 55.44, 107.43, 122.61, 126.42, 127.10, 127.21, 127.37, 129.20, 135.41, 136.13, 158.01, 167.41; HRMS (ESI) exact mass calc′d for $C_{14}H_{14}O_3H$ $(M+H)^+$: 231.1021; Found: 231.1015.

Methyl 7-methoxy-4-methylnaphthalene-2-carboxylate (*para*-4a)



m.p. 48-49 ºC; IR (KBr): *v* 1703, 1626, 1604 cm^{-1}; ^{1}H NMR (400 MHz): δ 2.66 (s, 3H), 3.91 (s, 3H), 3.95 (s, 3H), 7.20 (d, 1H, *J* = 2.4 Hz), 7.25* (dd, 1H, *J* = 9.2 & 2.4 Hz), 7.75 (s, 1H), 7.88 (d, 1H, *J* = 9.2 Hz), 8.34 (s, 1H); *It also contains $CHCl_3$ peak. ^{13}C NMR (100 MHz): δ 19.42, 52.18, 55.37, 107.64, 120.74, 123.71, 125.67, 127.50, 128.34, 130.28, 134.04, 134.75, 157.80, 167.56; HRMS (ESI) exact mass calc′d for $C_{14}H_{14}O_3H$ $(M+H)^+$: 231.1021; Found: 231.1018.

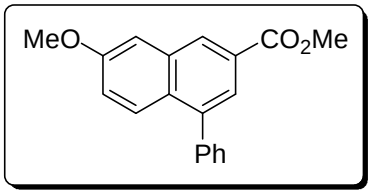
Methyl 5-methoxy-4-phenylnaphthalene-2-carboxylate (*ortho*-4b)



Reaction time: 6 h; Yield: 14 %; m.p. 98-99 ºC; IR (KBr): *v* 1714, 1625, 1572 cm^{-1}; ^{1}H NMR (400 MHz): δ 3.49 (s, 3H), 3.96 (s, 3H), 6.89 (d, 1H, *J* = 8.0 Hz), 7.29-7.40 (m, 5H), 7.44-7.50 (m, 1H), 7.61 (d, 1H, *J* = 8.0 Hz), 7.85 (d, 1H, *J* = 1.6 Hz), 8.55 (d, 1H, *J* = 1.6 Hz); ^{13}C NMR (100 MHz): δ 52.31, 55.34, 108.41, 122.55, 125.56, 126.12, 126.82, 126.93, 128.12, 128.70,

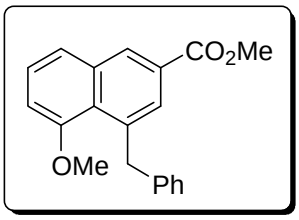
130.48, 135.12, 139.61, 144.69, 156.66, 167.16; HRMS (ESI) exact mass calc′d for $C_{19}H_{16}O_3Na$ $(M+Na)^+$: 315.0997; Found: 315.0993.

Methyl 7-methoxy-4-phenylnaphthalene-2-carboxylate (*para*-4b)



Reaction time: 6 h; Yield: 72 %; m.p. 89-90 ºC; IR (KBr): *v* 1714, 1626, 1599 cm^{-1}; ^1H NMR (400 MHz): δ 3.95 (s, 3H), 3.98 (s, 3H), 7.19 (dd, 1H, J = 9.2 & 2.4 Hz), 7.29 (d, 1H, J = 2.4 Hz), 7.41-7.55 (m, 5H), 7.82 (d, 1H, J = 9.2 Hz), 7.88 (d, 1H, J = 1.2 Hz), 8.51 (s, 1H); ^{13}C NMR (100 MHz): δ 52.29, 55.45, 107.32, 121.14, 124.15, 127.48, 127.60, 127.68, 128.41, 129.30, 129.99, 134.49, 140.16, 140.67, 157.98, 167.39; HRMS (ESI) exact mass calc′d for $C_{19}H_{16}O_3Na$ $(M+Na)^+$: 315.0997; Found: 315.0997.

Methyl 4-benzyl -5-methoxynaphthalene-2-carboxylate (*ortho*-4c)



Reaction time: 12 h; Yield: 17 %; m.p. 90-91 ºC; IR (KBr): *v* 1725, 1604, 1577 cm^{-1}; ^1H NMR (400 MHz): δ 3.68 (s, 3H), 3.95 (s, 3H), 4.71 (s, 2H), 6.83 (d, 1H, J = 8.0 Hz), 7.05 (d, 2H, J = 7.2 Hz), 7.08-7.15 (m, 1H), 7.17-7.25 (m, 2H), 7.33-7.41 (m, 1H), 7.52 (d, 1H, J = 8.0 Hz), 7.85 (s, 1H), 8.44 (d, 1H, J = 1.2 Hz); ^{13}C NMR (100 MHz): δ 43.24, 52.28, 55.18, 107.87, 122.74, 125.37, 126.56, 126.95, 127.15, 128.12, 128.14, 128.73, 130.22, 135.74, 137.30, 142.66, 157.24, 167.29; HRMS (ESI) exact mass calc′d for $C_{20}H_{18}O_3Na$ $(M+Na)^+$: 329.1154; Found: 329.1159.

Crystal data for *ortho*-**4c** Empirical formula, $C_{20}H_{18}O_3$; formula weight, 306.34; crystal color, habit: colorless, block; crystal dimensions, 0.40 X 0.35 X 0.30 mm^3; crystal system, triclinic; lattice type, primitive; lattice parameters, a = 8.1761(14) Å, b = 8.3698(19) Å, c =12.1493(14) Å; α = 76.098(15); β = 80.854(12); γ = 89.732(16); V = 796.3(2) $Å^3$; space group, P -1; Z = 2; D_{calcd} = 1.278 g / cm^3; F_{000} = 324; λ(Mo-Kα) = 0.71073 Å; R ($I \geq 2\sigma_1$) = 0.0535, wR^2 = 0.1369. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (**for compound** *ortho*-**4c CCDC # 982203).**

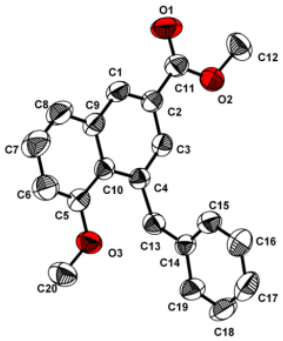
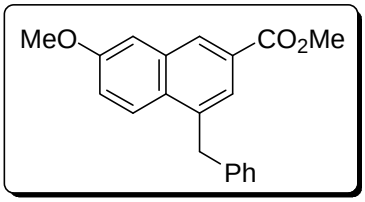


Figure 1 ORTEP diagram of compound *ortho*-**4c**

(Hydrogen atoms were omitted for clarity)

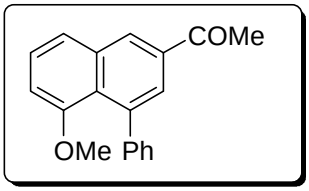
Methyl 4-benzyl -7-methoxynaphthalene-2-carboxylate (*para*-4c)



Reaction time: 12 h; Yield: 67 %; m.p. 87-88 ºC; IR (KBr): v 1714, 1621, 1610 cm^{-1}; ^{1}H NMR (400 MHz): δ 3.89 (s, 3H), 3.95 (s, 3H), 4.42 (s, 2H), 7.14-7.21 (m, 4H), 7.22-7.28 (m, 3H), 7.81 (d, 1H, J = 1.6 Hz), 7.87 (d, 1H, J = 9.2 Hz), 8.43 (s, 1H); ^{13}C NMR (100 MHz): δ 39.28, 52.27, 55.40, 107.82, 121.06, 124.69, 126.06, 126.24, 127.60, 128.56, 129.17, 129.85, 134.62, 137.10,

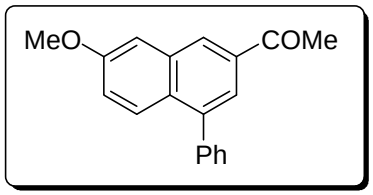
140.33, 157.79, 167.50; HRMS (ESI) exact mass calc′d for $C_{20}H_{18}O_3Na$ $(M+Na)^+$: 329.1154; Found: 329.1152.

2-Acetyl-5-methoxy-4-phenylnaphthalene (*ortho*-4d)



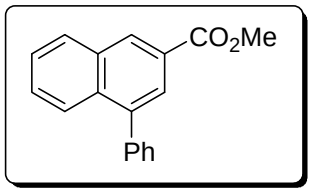
Reaction time: 6 h; Yield: 14 %; m.p. 74-75 ºC; IR (KBr): ν 1676, 1620, 1577 cm^{-1}; ^1H NMR (400 MHz): δ 2.71 (s, 3H), 3.49 (s, 3H), 6.90 (d, 1H, J = 7.6 Hz), 7.27-7.40 (m, 5H), 7.44-7.52 (m, 1H), 7.63 (d, 1H, J = 8.0 Hz), 7.79 (d, 1H, J = 1.2 Hz), 8.42 (d, 1H, J = 1.6 Hz); ^{13}C NMR (100 MHz): δ 26.88, 55.37, 108.66, 122.77, 125.62, 126.18, 126.86, 126.91, 127.08, 128.69, 129.44, 133.78, 135.18, 139.86, 144.69, 156.69, 198.18; HRMS (ESI) exact mass calc′d for $C_{19}H_{16}O_2Na$ $(M+Na)^+$: 299.1048; Found: 299.1047.

2-Acetyl-7-methoxy-4-phenylnaphthalene (*para*-4d)



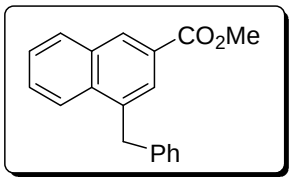
Reaction time: 6 h; Yield: 70 %; m.p. 86-87 ºC; IR (KBr): ν 1671, 1627, 1594 cm^{-1}; ^1H NMR (400 MHz): δ 2.73 (s, 3H), 3.96 (s, 3H), 7.19 (dd, 1H, J = 9.2 & 2.4 Hz), 7.31 (d, 1H, J = 2.4 Hz), 7.42-7.53 (m, 5H), 7.80-7.84 (m, 2H), 8.38 (s, 1H); ^{13}C NMR (100 MHz): δ 26.87, 55.48, 107.59, 127.31, 122.93, 127.66, 127.73, 128.34, 128.44, 129.41, 129.97, 134.51, 134.56, 140.16, 140.91, 158.09, 198.38; HRMS (ESI) exact mass calc′d for $C_{19}H_{16}O_2Na$ $(M+Na)^+$: 299.1048; Found: 299.1048.

Methyl 4-phenylnaphthalene-2-carboxylate (4e)



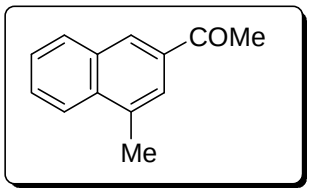
Reaction time: 9 h; Yield: 73 %; m.p. 93-94 ºC [lit.[2] m.p. 93.0-94.3 ºC]; IR (KBr): ν 1720, 1594 cm^{-1}; ^{1}H NMR (400 MHz): δ 3.98 (s, 3H), 7.41-7.58 (m, 7H), 7.90-7.95 (m, 1H), 7.99-8.04 (m, 2H), 8.61 (s, 1H); ^{13}C NMR (100 MHz): δ 52.35, 126.15, 126.19, 126.61, 126.95, 127.66, 128.45, 129.85, 130.08, 130.64, 133.10, 133.87, 140.02, 140.76, 167.31; HRMS (ESI) exact mass calc′d for $C_{18}H_{14}O_2Na$ $(M+Na)^+$: 285.0891; Found: 285.0885. This compound is known in the literature.[2] Melting point and ^{1}H and ^{13}C NMR spectral data are reported. Our data is in agreement with that of literature.

Methyl 4-benzylnaphthalene-2-carboxylate (4f)



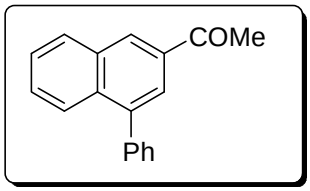
Reaction time: 20 h; Yield: 66 %; m.p. 43-44 ºC; IR (Neat): ν 1714, 1626, 1593 cm^{-1}; ^{1}H NMR (400 MHz): δ 3.98 (s, 3H), 4.49 (s, 2H), 7.16-7.30* (m, 5H), 7.49-7.59 (m, 2H), 7.94-8.04 (m, 3H), 8.54 (s, 1H); *It also contains $CHCl_3$ peak. ^{13}C NMR (100 MHz): δ 39.24, 52.32, 124.55, 126.30, 126.43, 126.68, 127.06, 128.46, 128.61, 130.28, 130.45, 133.23, 134.43, 137.21, 140.25, 167.42; HRMS (ESI) exact mass calc′d for $C_{19}H_{16}O_2Na$ $(M+Na)^+$: 299.1048; Found: 299.1048.

2-Acetyl-4-methylnaphthalene (4g)



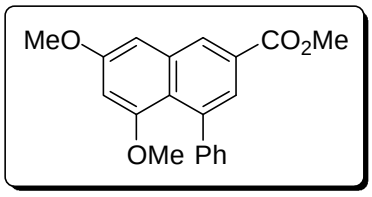
Reaction time: 12 h; Yield: 65 %; m.p. 37-38 ºC [lit.[3] m.p. 35-36 ºC]; IR (Neat): *v* 1676, 1621, 1599 cm^{-1}; ^1H NMR (400 MHz): δ 2.73 (s, 3H), 2.74 (s, 3H), 7.54-7.61 (m, 1H), 7.62-7.70 (m, 1H), 7.89 (s, 1H), 7.98 (d, 1H, *J* = 8.0 Hz), 8.03 (d, 1H, *J* = 8.4 Hz), 8.33 (s, 1H); ^{13}C NMR (100 MHz) : δ 19.51, 26.71, 124.26, 126.52, 128.47, 128.94, 130.29, 132.75, 134.15, 135.02, 135.17, 198.47; HRMS (ESI) exact mass calc′d for $C_{13}H_{12}OH$ $(M+H)^+$: 185.0966; Found: 185.0959.

2-Acetyl-4-phenylnaphthalene (4h)



Reaction time: 9 h; Yield: 73 %; m.p. 89-90 ºC; IR (KBr): *v* 1676, 1616 cm^{-1}; ^1H NMR (400 MHz): δ 2.75 (s, 3H), 7.43-7.61 (m, 7H), 7.90-7.96 (m, 1H), 7.98 (d, 1H, *J* = 1.6 Hz), 8.01-8.08 (m, 1H), 8.49 (s, 1H); ^{13}C NMR (100 MHz) : δ 26.82, 124.88, 126.19, 126.74, 127.70, 128.46, 128.67, 129.71, 130.04, 133.12, 133.97, 140.00, 140.99, 198.18; HRMS (ESI) exact mass calc′d for $C_{18}H_{14}OH$ $(M+H)^+$: 247.1123; Found: 247.1122.

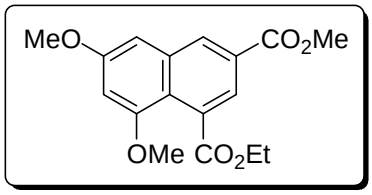
Methyl 5, 7-dimethoxy-4-phenylnaphthalene-2-carboxylate (4i)



Reaction time: 5 h; Yield: 91 %; m.p. 92-93 ºC; IR (KBr): *v* 1715, 1616, 1583 cm^{-1}; ^1H NMR (400 MHz): δ 3.46 (s, 3H), 3.93 (s, 3H), 3.94 (s, 3H), 6.53 (d, 1H, *J* = 2.4 Hz), 6.90 (d, 1H, *J* = 2.0 Hz), 7.26-7.38 (m, 5H), 7.69 (d, 1H, *J* = 1.6 Hz), 8.43 (d, 1H, *J* = 1.6 Hz); ^{13}C NMR (100 MHz): δ 52.22, 55.22, 55.43, 100.07, 101.24, 121.61, 126.07, 126.10, 126.77, 127.32, 128.67,

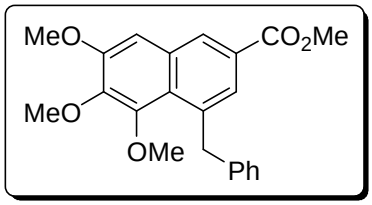
129.24, 135.90, 139.63, 144.58, 157.71, 158.46, 167.22; HRMS (ESI) exact mass calc′d for $C_{20}H_{18}O_4H$ $(M+H)^+$: 323.1283; Found: 323.1281.

Ethyl methyl 6, 8-dimethoxynaphthalene-1, 3-dicarboxylate (4j)



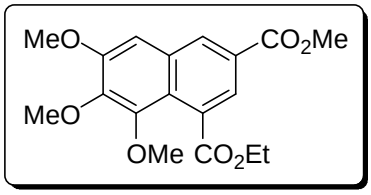
Reaction time: 4 h; Yield: 86 %; m.p. 112-113 ºC; IR (KBr): *v* 1715, 1627, 1589 cm^{-1}; ^1H NMR (400 MHz): *δ* 1.42 (t, 3H, *J* = 7.2 Hz), 3.93 (s, 6H), 3.97 (s, 3H), 4.44 (q, 2H, *J* = 7.2 Hz), 6.65 (d, 1H, *J* = 1.6 Hz), 6.87 (d, 1H, *J* = 1.6 Hz), 7.85 (d, 1H, *J* = 0.8 Hz), 8.47 (s, 1H); ^{13}C NMR (100 MHz): *δ* 14.42, 52.40, 55.56, 56.14, 61.56, 99.92, 101.51, 119.49, 121.93, 127.65, 130.55, 130.89, 135.13, 155.83, 159.12, 166.54, 170.82; HRMS (ESI) exact mass calc′d for $C_{17}H_{18}O_6H$ $(M+H)^+$: 319.1182; Found: 319.1178.

Methyl 5, 6, 7-trimethoxy-4-benzylnaphthalene-2-carboxylate (4k)



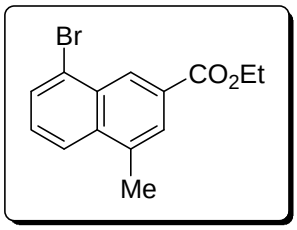
Reaction time: 8 h; Yield: 78 %; m.p. 62-63 ºC; IR (KBr): *v* 1709, 1600, 1572 cm^{-1}; ^1H NMR (400 MHz): *δ* 3.59 (s, 3H), 3.89 (s, 3H), 3.94 (s, 3H), 3.98 (s, 3H), 4.68 (s, 2H), 7.04-7.17 (m, 4H), 7.19-7.28* (m, 2H), 7.70 (s, 1H), 8.34 (d, 1H, *J* = 1.2 Hz); *It also contains $CHCl_3$ peak. ^{13}C NMR (100 MHz): *δ* 41.82, 52.19, 55.88, 60.91, 61.14, 104.76, 125.59, 125.70, 126.53, 127.39, 128.24, 128.35, 129.11, 131.58, 136.15, 142.25, 143.90, 150.44, 152.96, 167.32; HRMS (ESI) exact mass calc′d for $C_{22}H_{22}O_5H$ $(M+H)^+$: 367.1546; Found: 367.1543.

Ethyl methyl 6, 7, 8-trimethoxynaphthalene-1, 3-dicarboxylate (4l)



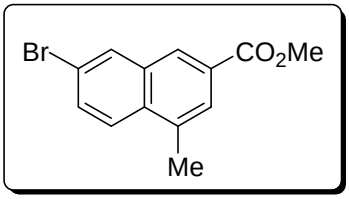
Reaction time: 5 h; Yield: 84 %; m.p. 84-85 ºC; IR (KBr): *v* 1715, 1700, 1605 cm^{-1}; ^{1}H NMR (400 MHz): *δ* 1.43 (t, 3H, *J* = 7.2 Hz), 3.95 (s, 3H), 3.96 (s, 3H), 3.98 (s, 3H), 3.99 (s, 3H), 4.45 (q, 2H, *J* = 7.2 Hz), 7.08 (s, 1H), 7.88 (d, 1H, *J* = 1.2 Hz), 8.47 (d, 1H, *J* = 1.2 Hz); ^{13}C NMR (100 MHz): *δ* 14.26, 52.31, 55.98, 61.02, 61.28, 61.56, 104.05, 122.34, 122.89, 126.40, 129.98, 130.31, 130.65, 143.66, 147.52, 153.96, 166.47, 170.63; HRMS (ESI) exact mass calc′d for $C_{18}H_{20}O_7H$ $(M+H)^+$: 349.1287; Found: 349.1285.

Ethyl 8-bromo-4-methylnaphthalene-2-carboxylate (4m):



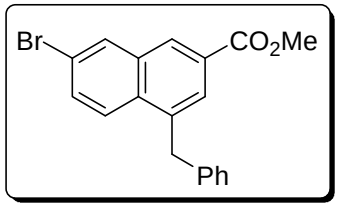
Reaction time: 12 h; Yield: 65 %; m.p. 63-64 ºC; IR (KBr): *v* 1714, 1615, 1500 cm^{-1}; ^{1}H NMR (400 MHz): *δ* 1.47 (t, 3H, *J* = 7.2 Hz), 2.73 (s, 3H), 4.46 (q, 2H, *J* = 7.2 Hz), 7.41-7.48 (m, 1H), 7.84 (d, 1H, *J* = 7.6 Hz), 7.97 (s, 1H), 7.98 (d, 1H, *J* = 8.8 Hz), 8.87 (s, 1H); ^{13}C NMR (100 MHz): δ 14.46, 19.68, 61.29, 123.98, 124.97, 126.69, 128.13, 128.49, 130.50, 131.51, 135.35, 135.98, 166.58; HRMS (ESI) exact mass calc′d for $C_{14}H_{13}BrO_2Na$ $(M+Na)^+$: 314.9997; Found: 315.0003.

Methyl 7-bromo-4-methylnaphthalene-2-carboxylate (4n):



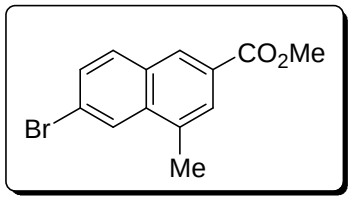
Reaction time: 15 h; Yield: 61 %; m.p. 73-74 ºC; IR (KBr): ν 1719, 1588 cm^{-1}; ^{1}H NMR (400 MHz): δ 2.71 (s, 3H), 3.98 (s, 3H), 7.69 (dd, 1H, J = 9.2 & 2.0 Hz), 7.89 (d, 1H, J = 9.2 Hz), 7.92 (s, 1H), 8.10 (d, 1H, J = 1.2 Hz), 8.36 (s, 1H); ^{13}C NMR (100 MHz): δ 19.38, 52.40, 120.50, 126.01, 126.19, 128.13, 128.52, 131.40, 131.86, 133.28, 133.98, 135.17, 167.08; HRMS (ESI) exact mass calc′d for $C_{13}H_{11}BrO_2Na$ $(M+Na)^+$: 300.9840; Found: 300.9836.

Methyl 4-benzyl-7-bromonaphthalene-2-carboxylate (4o):



Reaction time: 24 h; Yield: 63 %; m.p. 99-100 ºC; IR (KBr): ν 1726, 1594 cm^{-1}; ^{1}H NMR (400 MHz): δ 3.97 (s, 3H), 4.45 (s, 2H), 7.12-7.21 (m, 3H), 7.23-7.29* (m, 2H), 7.58 (dd, 1H, J = 8.8 & 2.0 Hz), 7.85 (d, 1H, J = 8.8 Hz), 7.96 (s, 1H), 8.10 (d, 1H, J = 1.6 Hz), 8.42 (s, 1H); *It also contains $CHCl_3$ peak. ^{13}C NMR (100 MHz): δ 39.20, 52.46, 120.56, 126.36, 126.45, 127.12, 128.20, 128.51, 128.68, 129.33, 131.66, 132.01, 132.83, 134.49, 137.51, 139.85, 166.97; HRMS (ESI) exact mass calc′d for $C_{19}H_{15}BrO_2Na$ $(M+Na)^+$: 377.0153; Found: 377.0156.

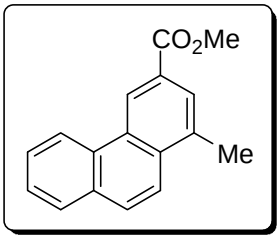
Methyl 6-bromo-4-methylnaphthalene-2-carboxylate (4p):



Reaction time: 10 h; Yield: 66 %; m.p. 79-80 ºC; IR (KBr): ν 1725, 1626 cm^{-1}; ^{1}H NMR (400 MHz): δ 2.69 (s, 3H), 3.98 (s, 3H), 7.62 (dd, 1H, J = 8.4 & 1.6 Hz), 7.81 (d, 1H, J = 8.8 Hz), 7.93 (s, 1H), 8.18 (s, 1H), 8.42 (s, 1H); ^{13}C NMR (100 MHz): δ 19.38, 52.37, 122.86, 126.76,

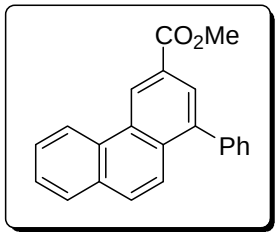
126.81, 127.44, 129.37, 129.87, 131.18, 131.60, 134.16, 135.93, 167.14; HRMS (ESI) exact mass calc′d for $C_{13}H_{11}BrO_2Na$ $(M+Na)^+$: 300.9840; Found: 300.9835.

Methyl 1-methylphenanthrene-3-carboxylate (4q):



Reaction time: 10 h; Yield: 75 %; m.p. 104-105 ºC; IR (KBr): *v* 1709, 1610 cm^{-1}; ^1H NMR (400 MHz): δ 2.79 (s, 3H), 4.02 (s, 3H), 7.61-7.67 (m, 1H), 7.68-7.75 (m, 1H), 7.86-7.98 (m, 3H), 8.06 (s, 1H), 8.81 (d, 1H, J = 8.4 Hz), 9.32 (s, 1H); ^{13}C NMR (100 MHz): δ 19.94, 52.25, 122.38, 123.13, 123.37, 126.94, 127.10, 127.18, 127.34, 128.61, 129.21, 129.80, 130.94, 131.70, 133.70, 135.18, 167.56; HRMS (ESI) exact mass calc′d for $C_{17}H_{14}O_2H$ $(M+H)^+$: 251.1072; Found: 251.1074.

Methyl 1-phenylphenanthrene-3-carboxylate (4r):



Reaction time: 8 h; Yield: 78 %; m.p. 133-134 ºC [lit.[4] m.p. 147-148 ºC]; IR (KBr): *v* 1709, 1605 cm^{-1}; ^1H NMR (400 MHz): δ 4.03 (s, 3H), 7.43-7.58 (m, 5H), 7.62-7.69 (m, 1H), 7.71-7.87 (m, 3H), 7.90 (d, 1H, J = 8.0 Hz), 8.17 (d, 1H, J = 1.2 Hz), 8.86 (d, 1H, J = 8.4 Hz), 9.48 (s, 1H); ^{13}C NMR (100 MHz): δ 52.40, 123.23, 124.24, 124.50, 127.17, 127.29, 127.36, 127.65, 127.68, 128.46, 128.65, 129.42, 130.20, 130.36, 130.74, 131.82, 132.88, 140.35, 141.28, 167.44; HRMS (ESI) exact mass calc′d for $C_{22}H_{16}O_2H$ $(M+H)^+$: 313.1229; Found: 313.1237. This compound is

known in the literature. ^{1}H NMR spectral data is reported. Our data is in agreement with that of literature.[4]

Crystal data for **4r:** Empirical formula, C_{22} H_{16} O_2; formula weight, 312.22; crystal color, habit: colorless, block; crystal dimensions, 0.60 X 0.40 X 0.28 mm^3; crystal system, monoclinic; lattice type, primitive; lattice parameters, a = 11.092(4) Å, b = 17.545(6) Å, c =17.517(5) Å; α = 90; β = 110.638(18); γ = 90; V = 3190.2(18) Å^3; space group, P 21/c; Z = 8; D_{calcd} = 1.300g / cm^3; F_{000} = 1312; λ(Mo-Kα) = 0.71073 Å; R (I≥2σ$_1$) = 0.0450, wR^2 = 0.1160. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (**for compound 4r CCDC # 982204).**

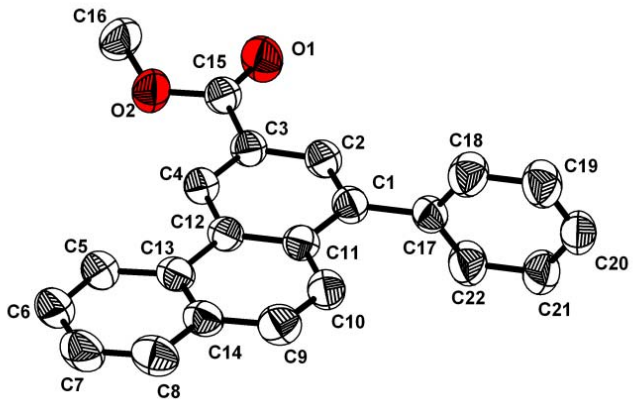
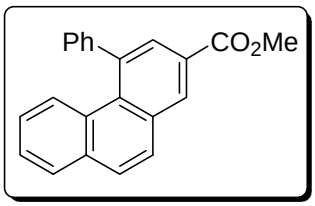


Figure 2 ORTEP diagram of compound **4r**

(Hydrogen atoms were omitted for clarity)

Methyl 4-phenylphenanthrene-2-carboxylate (4s):



Reaction time: 6 h; Yield: 77 %; m.p. 97-98 ºC; IR (KBr): ν 1715, 1600 cm^{-1}; ^{1}H NMR (400 MHz): δ 3.99 (s, 3H), 7.09-7.17 (m, 1H), 7.38-7.53 (m, 6H), 7.71-7.81 (m, 2H), 7.84 (d, 2H, J = 8.8 Hz), 8.07 (d, 1H, J = 1.6 Hz), 8.59 (d, 1H, J = 1.6 Hz); ^{13}C NMR (100 MHz): δ 52.34, 125.32, 126.92, 127.10, 127.49, 127.76, 128.46, 128.58, 128.62, 128.98, 129.16, 129.97, 130.41, 130.48, 131.74, 133.27, 134.34, 140.92, 144.61, 167.04; HRMS (ESI) exact mass calc′d for $C_{22}H_{16}O_2H$ $(M+H)^+$: 313.1229; Found: 313.1230.

Crystal data for 4**s**: Empirical formula, $C_{22}H_{16}O_2$; formula weight, 312.35; crystal color, habit: colorless, plate; crystal dimensions, 0.40 X 0.36 X 0.28 mm^3; crystal system, monoclinic; lattice type, primitive; lattice parameters, a = 9.057(2) Å, b = 7.6437(18) Å, c =23.756(5) Å; α = 90; β = 90.458(4); γ = 90; V = 1644.5(7) $Å^3$; space group, P 21/c; Z = 4; D_{calcd} = 1.262 g / cm^3; F_{000} = 656; λ(Mo-Kα) = 0.71073 Å; R ($I \geq 2\sigma_1$) = 0.0792, wR^2 = 0.2351. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (**for compound 4s CCDC # 982657).**

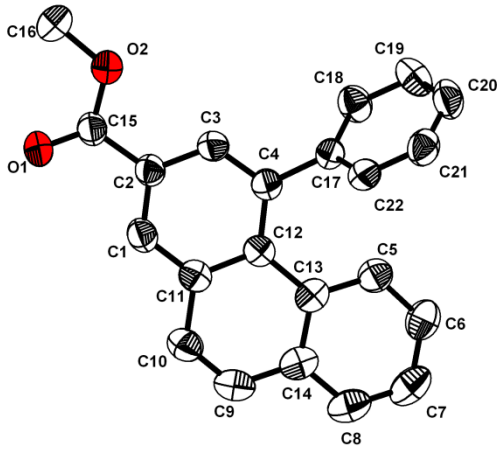
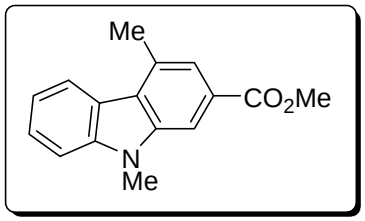


Figure 3 ORTEP diagram of compound 4**s**

(Hydrogen atoms were omitted for clarity)

Methyl 4, 9-dimethyl-9*H*-carbazole-2-carboxylate (4t)



Reaction time: 3 h; Yield: 92 %; m.p. 131-132 ºC; IR (KBr): *v* 1698, 1615, 1572 cm^{-1}; ^{1}H NMR (400 MHz): δ 2.93 (s, 3H), 3.91 (s, 3H), 3.99 (s, 3H), 7.25-7.32* (m, 1H), 7.46 (d, 1H, J = 8.0 Hz), 7.52-7.59 (m, 1H), 7.74 (s, 1H), 8.02 (s, 1H), 8.23 (d, 1H, J = 8.0 Hz); *It also contains $CHCl_3$ peak. ^{13}C NMR (100 MHz): δ 20.79, 29.23, 52.17, 108.03, 108.60, 119.34, 121.45, 122.69, 123.25, 125.05, 126.43, 126.69, 133.08, 140.47, 142.18, 168.06; HRMS (ESI) exact mass calc′d for $C_{16}H_{15}NO_2H$ $(M+H)^+$: 254.1181; Found: 254.1175.

Crystal data for **4t:** Empirical formula, C_{16} H_{15} N O_2; formula weight, 253.29; crystal color, habit: colorless, block; crystal dimensions, 0.45 X 0.38 X 0.25 mm^3; crystal system, monoclinic; lattice type, primitive; lattice parameters, a = 8.526(6) Å, b = 38.83(3) Å, c =7.910(6) Å; α = 90; β = 94.242(14); γ = 90; V = 2612(3) $Å^3$; space group, P2 (1)/c; Z = 8; D_{calcd} = 1.288 g / cm^3; F_{000} = 1072; λ(Mo-Kα) = 0.71073 Å; R ($I \geq 2\sigma_1$) = 0.0707, wR^2 = 0.1665. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (**for compound 4t CCDC # 982658).**

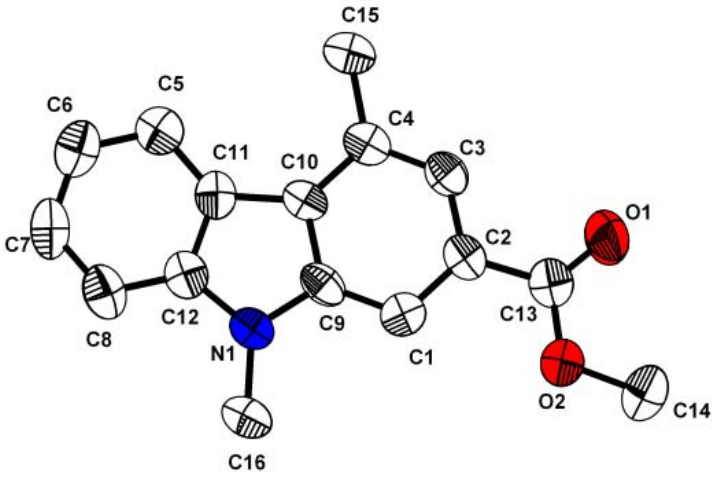
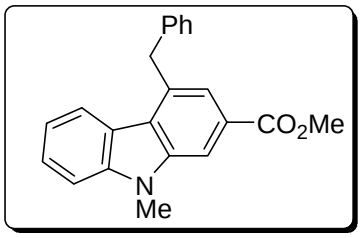


Figure 4 ORTEP diagram of compound **4t**

(Hydrogen atoms were omitted for clarity)

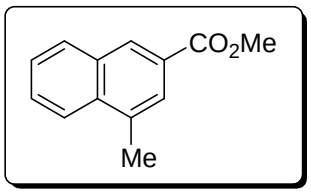
Methyl 4-benzyl-9-methyl -9*H*-carbazole-2-carboxylate (4u)



Reaction time: 10 h; Yield: 87 %; m.p. 147-148 ºC; IR (KBr): *v* 1704, 1621, 1572 cm^{-1}; ^{1}H NMR (400 MHz): δ 3.92 (s, 3H), 3.95 (s, 3H), 4.67 (s, 2H), 7.13-7.28* (m, 6H), 7.43 (d, 1H, J = 8.0 Hz), 7.47-7.53 (m, 1H), 7.71 (s, 1H), 8.03-8.10$^{\$}$ (m, 2H); *It also contains $CHCl_3$ peak. $^{\$}$It looks like a singlet at 8.08 (1H) and doublet at 8.06 (1H, J = 8.0 Hz). ^{13}C NMR (100 MHz): δ 29.27, 39.84, 52.18, 108.69, 119.47, 121.98, 123.45, 125.05, 126.27, 126.59, 126.95, 128.62, 128.66, 135.21, 139.50, 140.89, 142.30, 167.92; HRMS (ESI) exact mass calc′d for $C_{22}H_{19}NO_2Na$ $(M+Na)^+$: 352.1313; Found: 352.1318.

Methyl 4-methylnaphthalene-2-carboxylate (6):

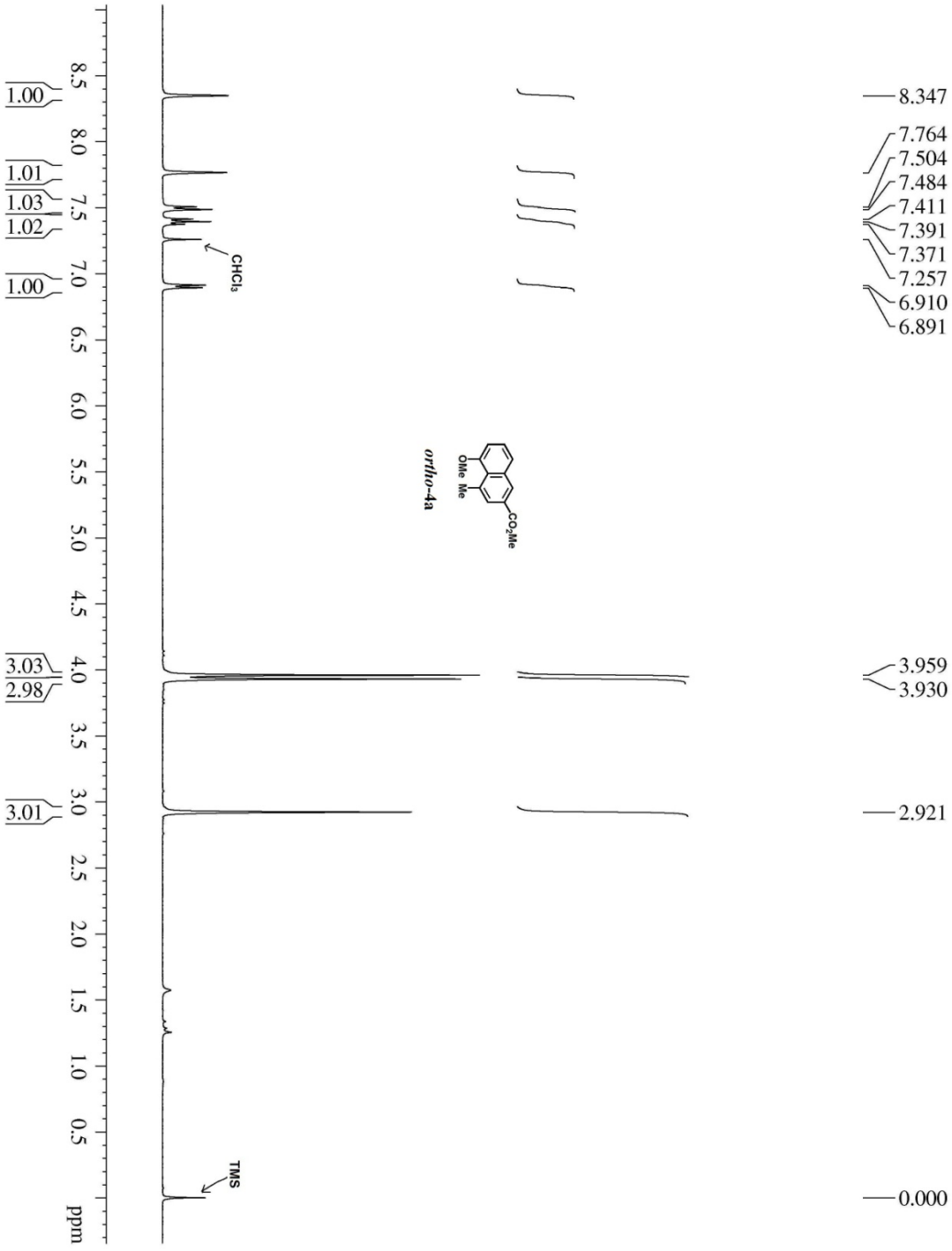
To a stirred solution of methyl 3-acetoxy-3-(2-nitrophenyl)-2-methylenepropanoate (**1m**) (3 mmol, 0.837 g) and nitroethane (**2a**) (9 mmol, 0.675 g) in DMF (12 mL) was added K_2CO_3 (9 mmol, 1.25 g) and reaction mixture was stirred at room temperature for 3 hours. The reaction mixture was diluted with brine (12 mL), extracted with diethyl ether (3x15 mL) and the combined organic layer was washed with water (10 mL), dried over anhydrous Na_2SO_4. Solvent was evaporated and the resulting crude product was purified by column chromatography (silica gel, 3% EtOAc in hexanes) to afford **6** in 57% (0.34g) yield as a colorless viscous liquid.



Reaction time: 3 h; Yield: 57 %; IR (Neat): *v* 1715, 1627 cm^{-1}; ^1H NMR (400 MHz): δ 2.72 (s, 3H), 3.97 (s, 3H), 7.51-7.58 (m, 1H), 7.59-7.66 (m, 1H), 7.91 (s, 1H), 7.95 (d, 1H, J = 8.0 Hz), 8.01 (d, 1H, J = 8.8 Hz), 8.47 (s, 1H); ^{13}C NMR (100 MHz): δ 19.41, 52.22, 124.15, 125.65, 126.34, 126.96, 128.16, 129.59, 130.09, 132.70, 134.85, 167.46; HRMS (ESI) exact mass calc′d for $C_{13}H_{12}O_2H$ $(M+H)^+$: 201.0916; Found: 201.0912.

References

1. (*a*) J. M. Kim, Y. J. Im, T. H. Kim and J. N. Kim, *Bull. Korean Chem. Soc.,* 2002, **43**, 657. (*b*) A. Chamakh, M. M'hirsi, J. Villieras, J. Lebreton and H. Amri, *Synthesis*, 2000, 295.
2. P. Alvarez-Bercedo and R. Martin, *J. Am. Chem. Soc.*, 2010, **132**, 17352.
3. J. N. Kim, Y. J. Im, J. H. Gong and K. Y. Lee, *Tetrahedron Lett.,* 2001, **42**, 4195.
4. J. G. Smith, D. E. Fogg, I. J. Munday, R. E. Sandborn and P. W. Dibble, *J. Org. Chem.,* 1988, **53**, 2942.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ppm
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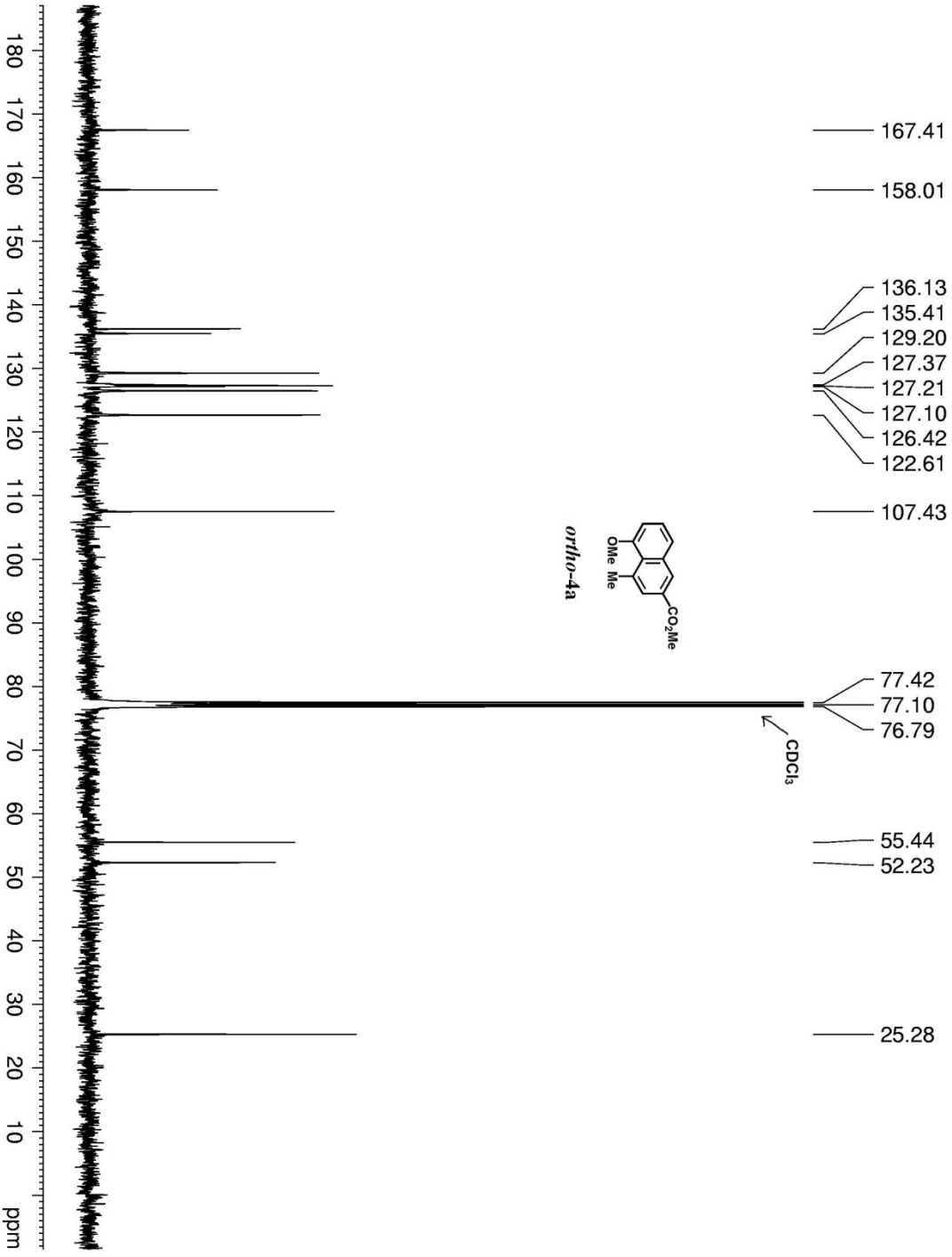
CO2Me
ortho-4a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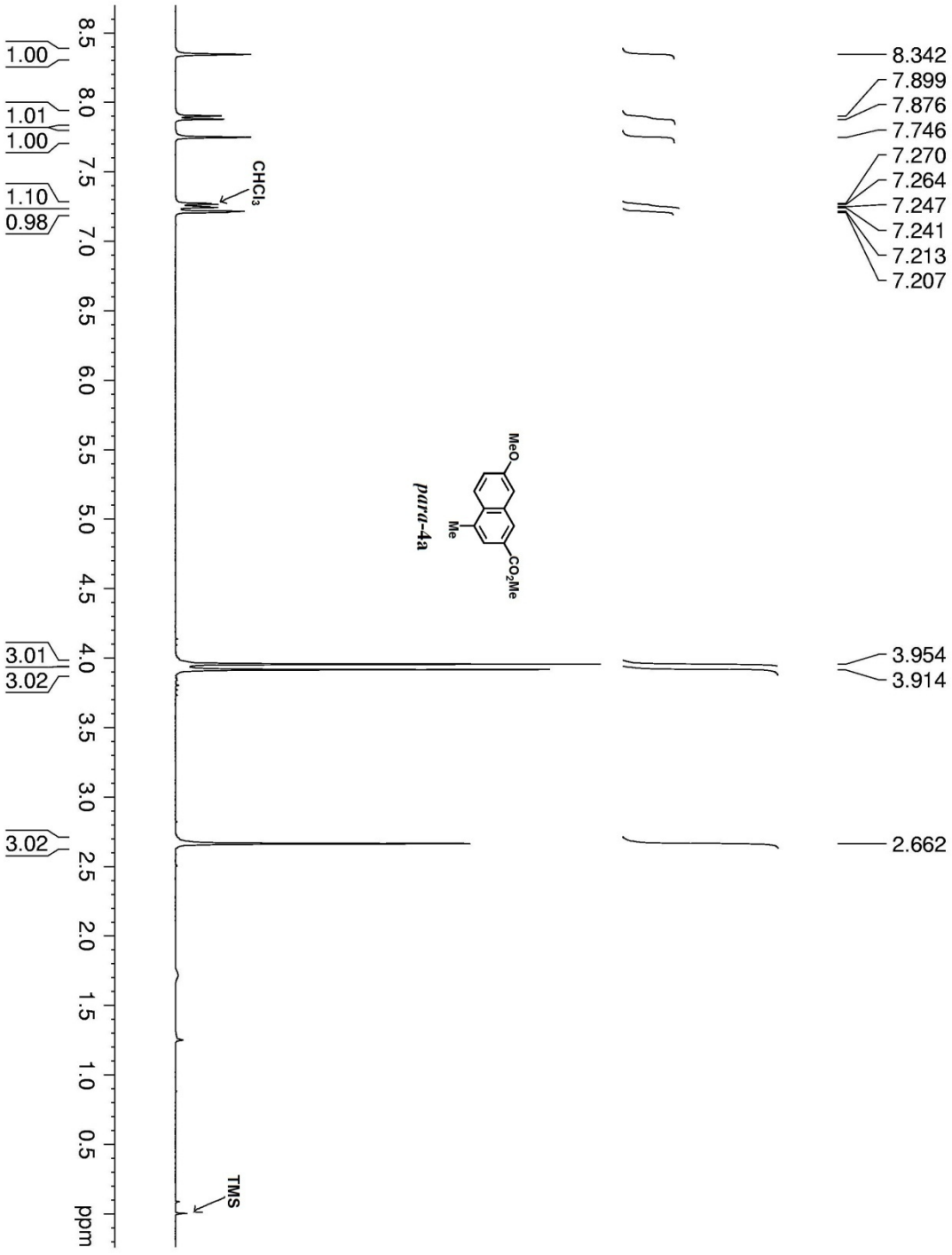
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3.02
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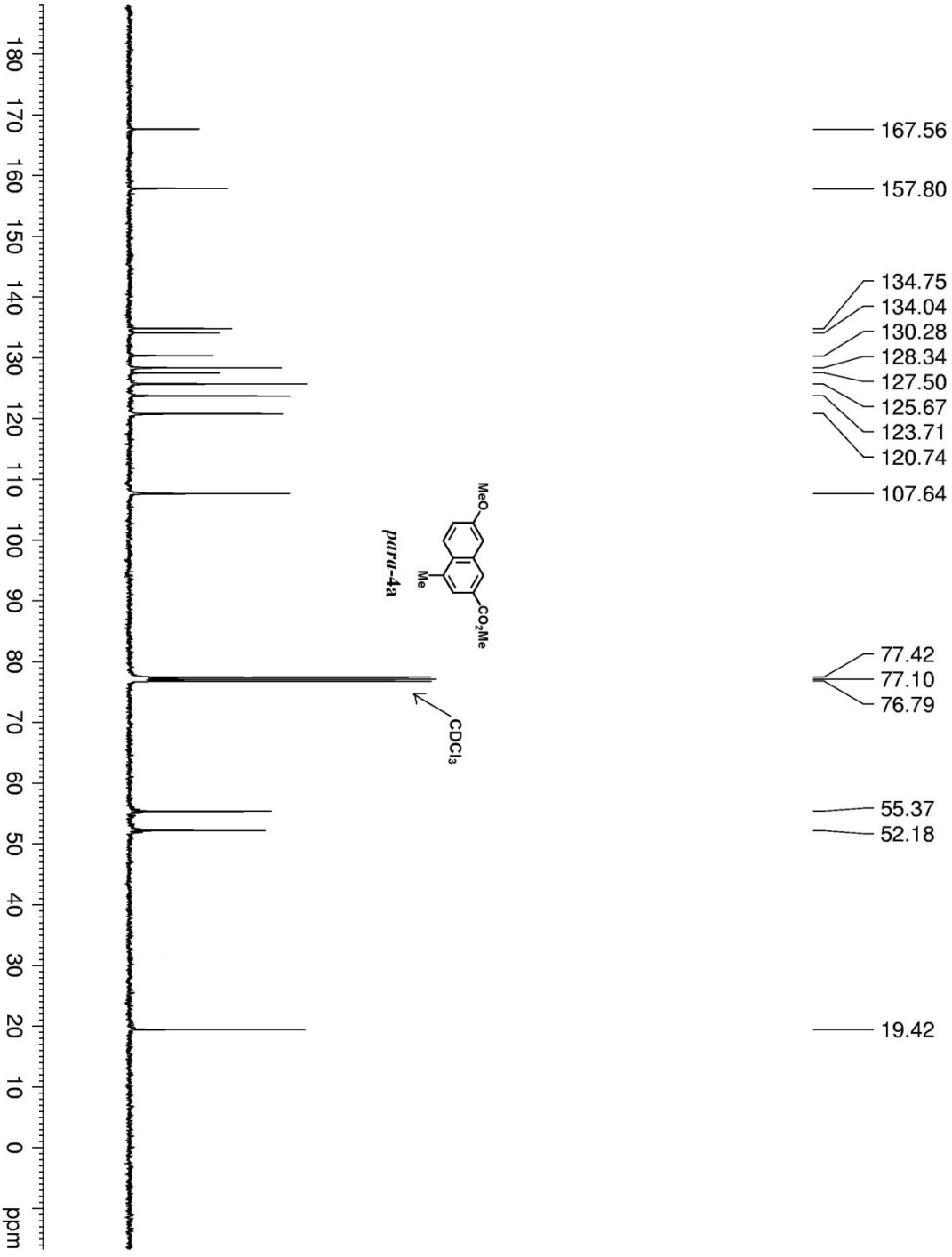
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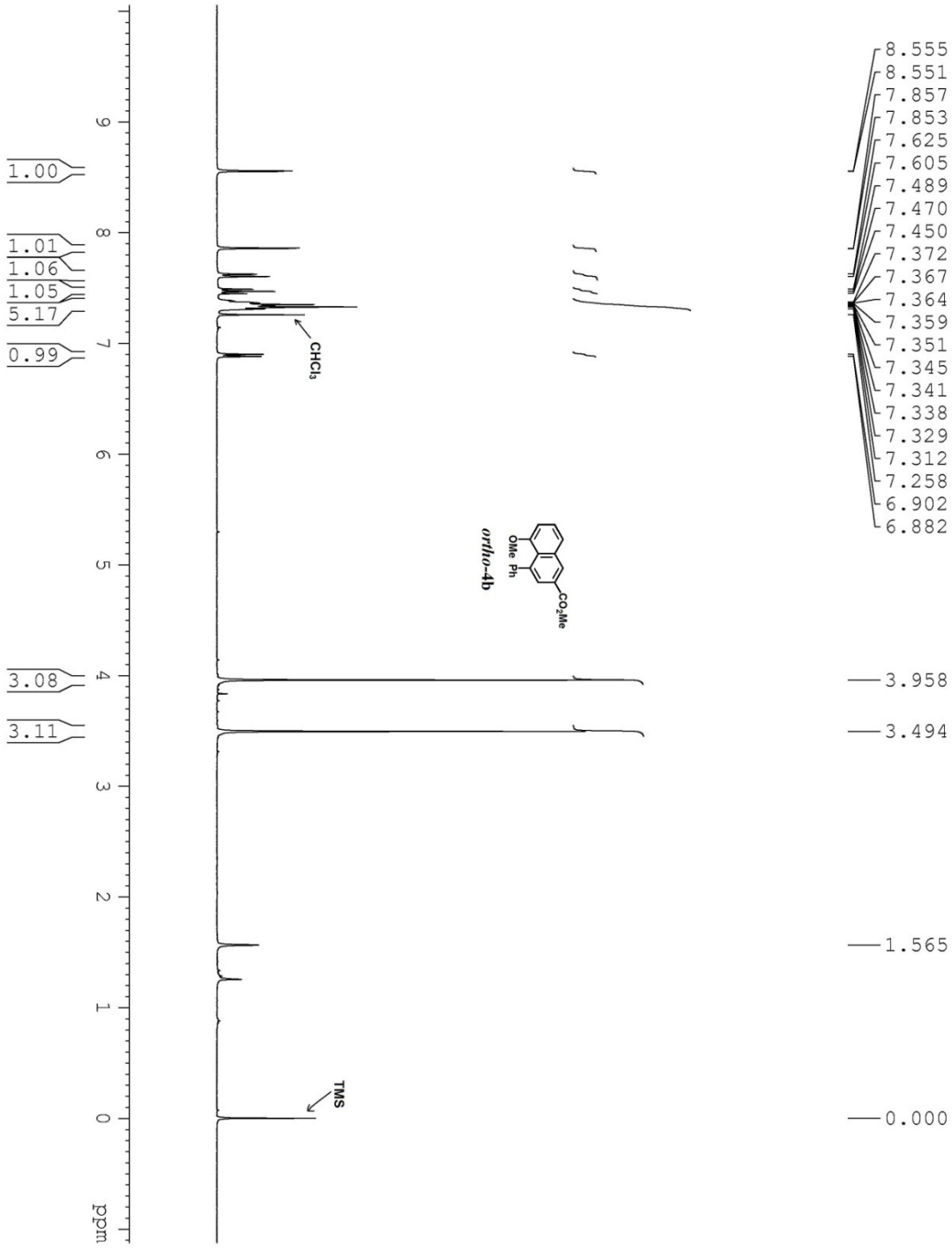
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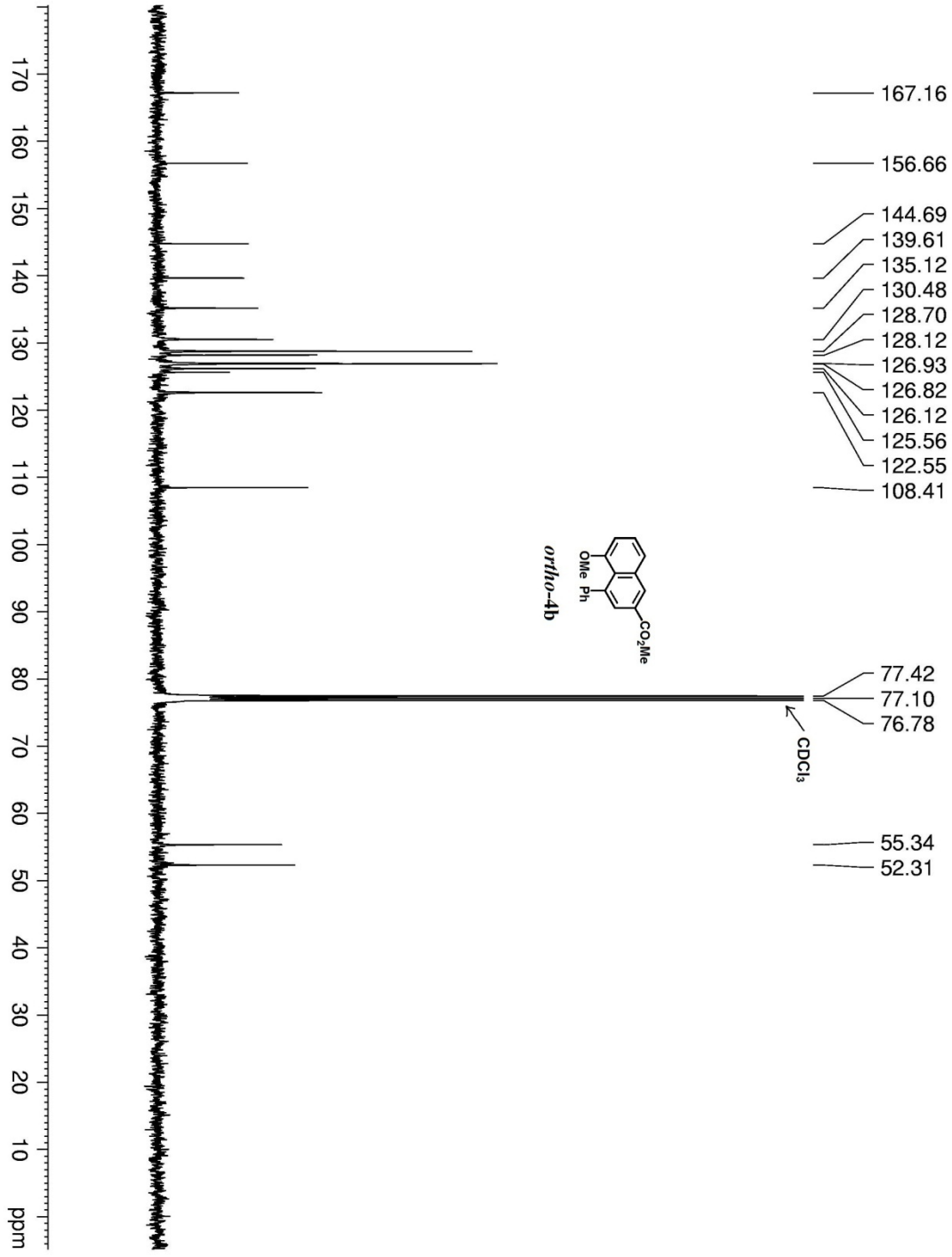
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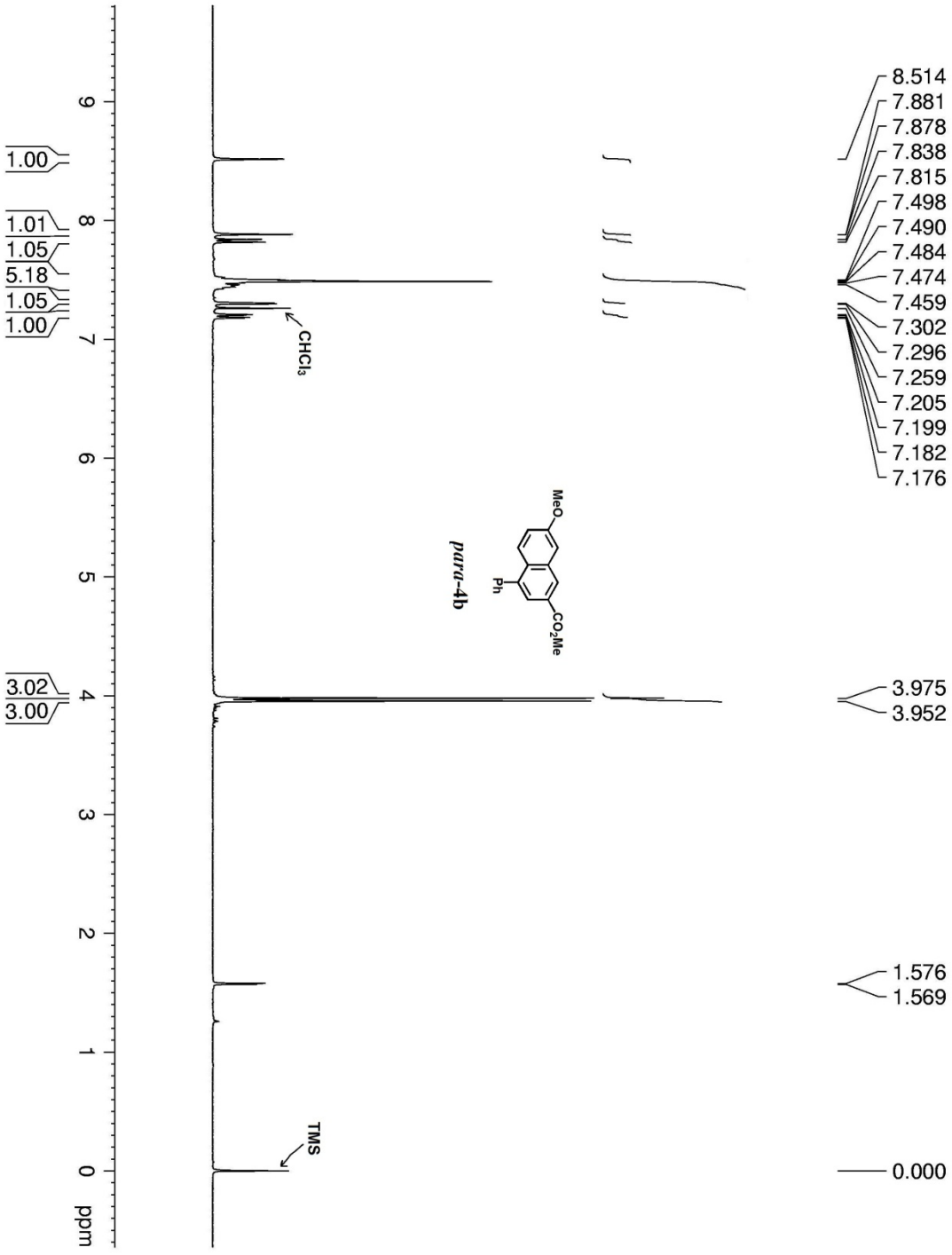
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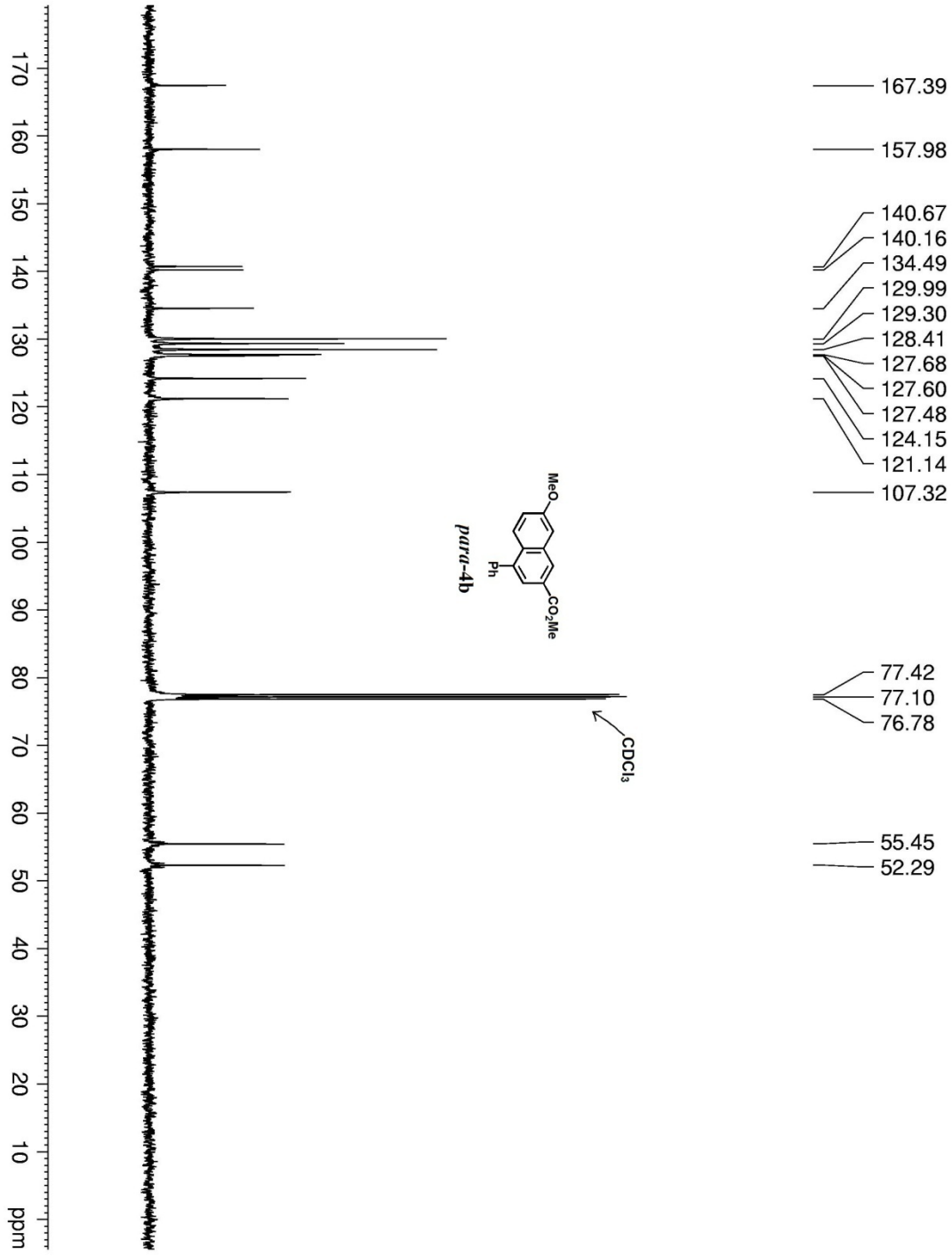
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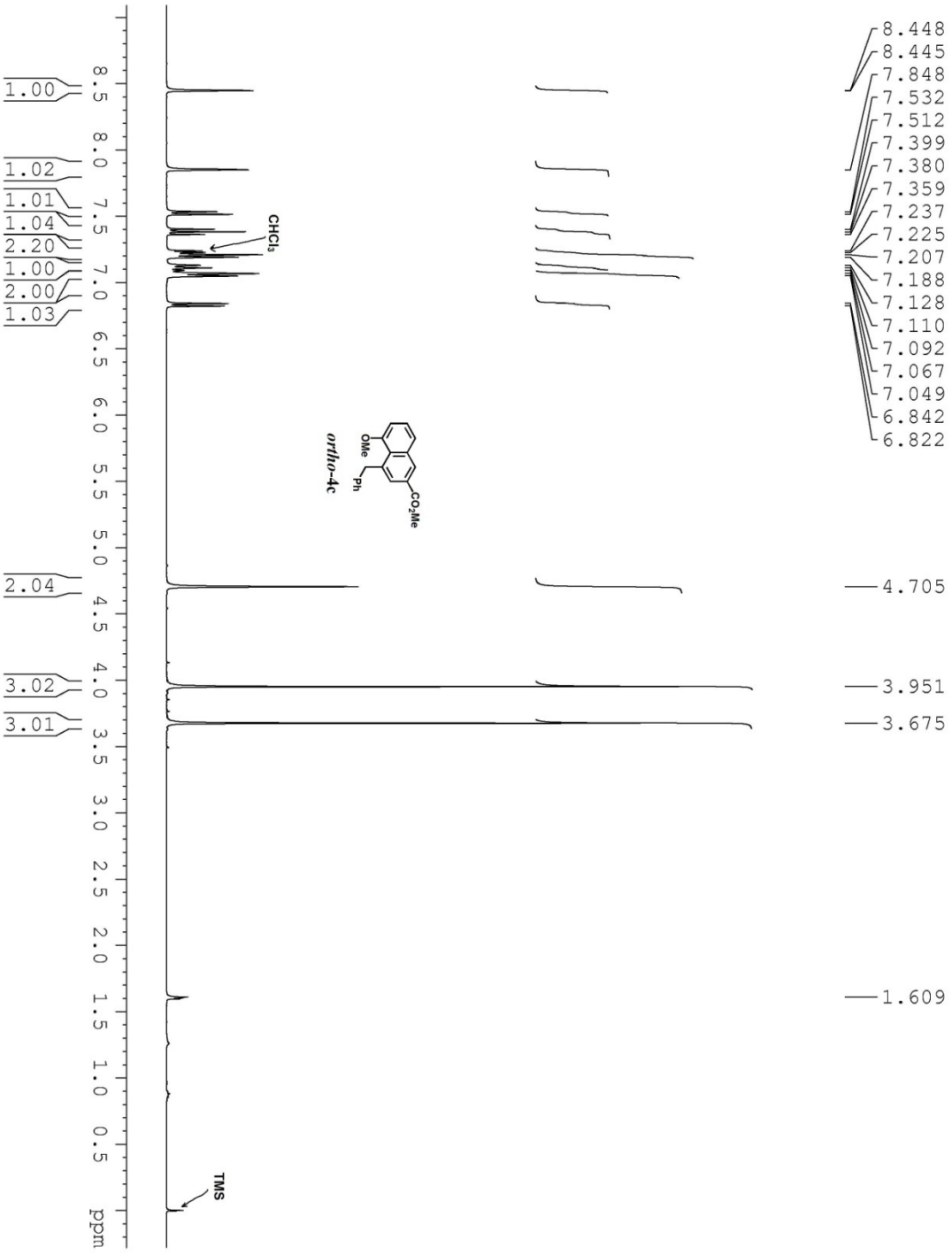
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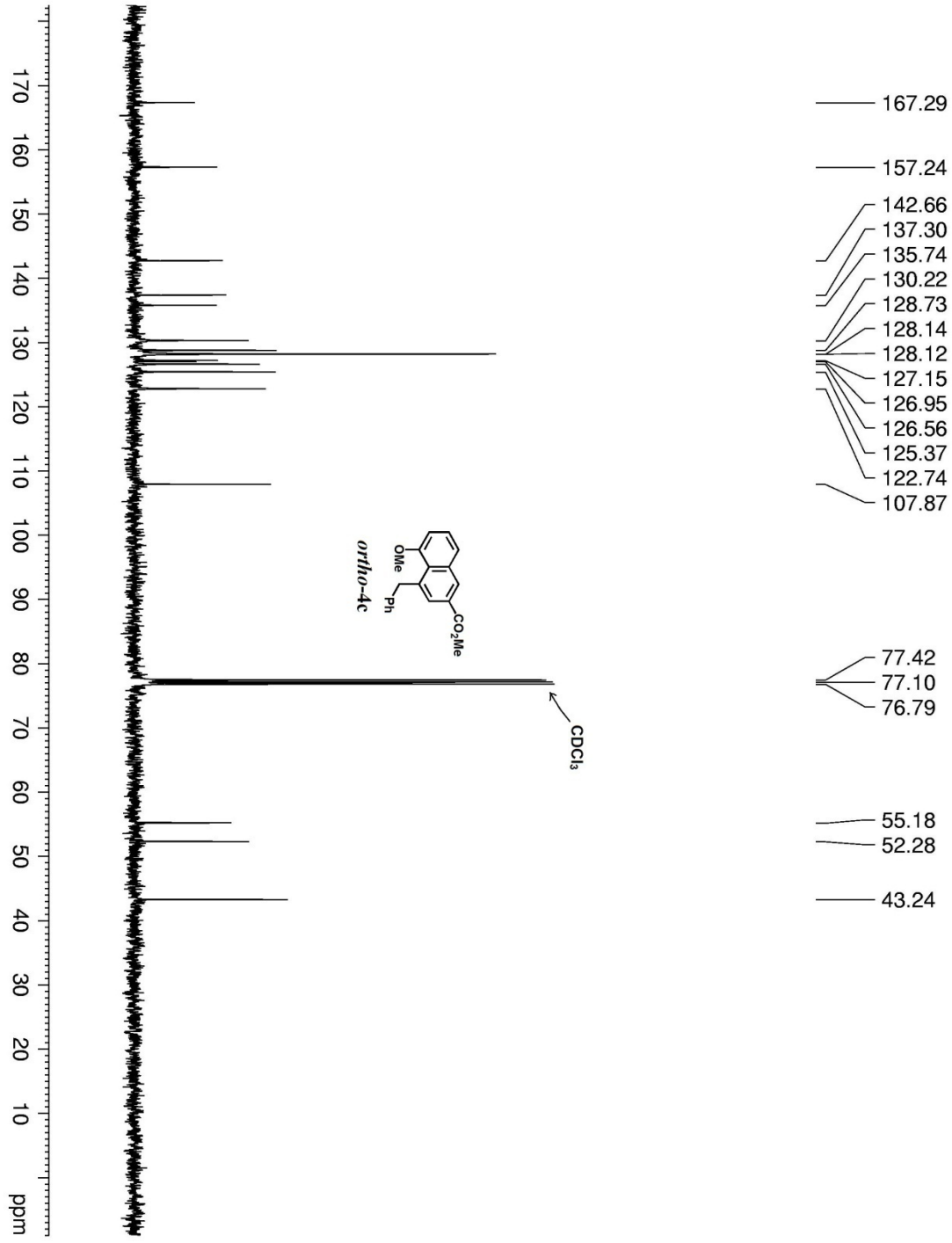
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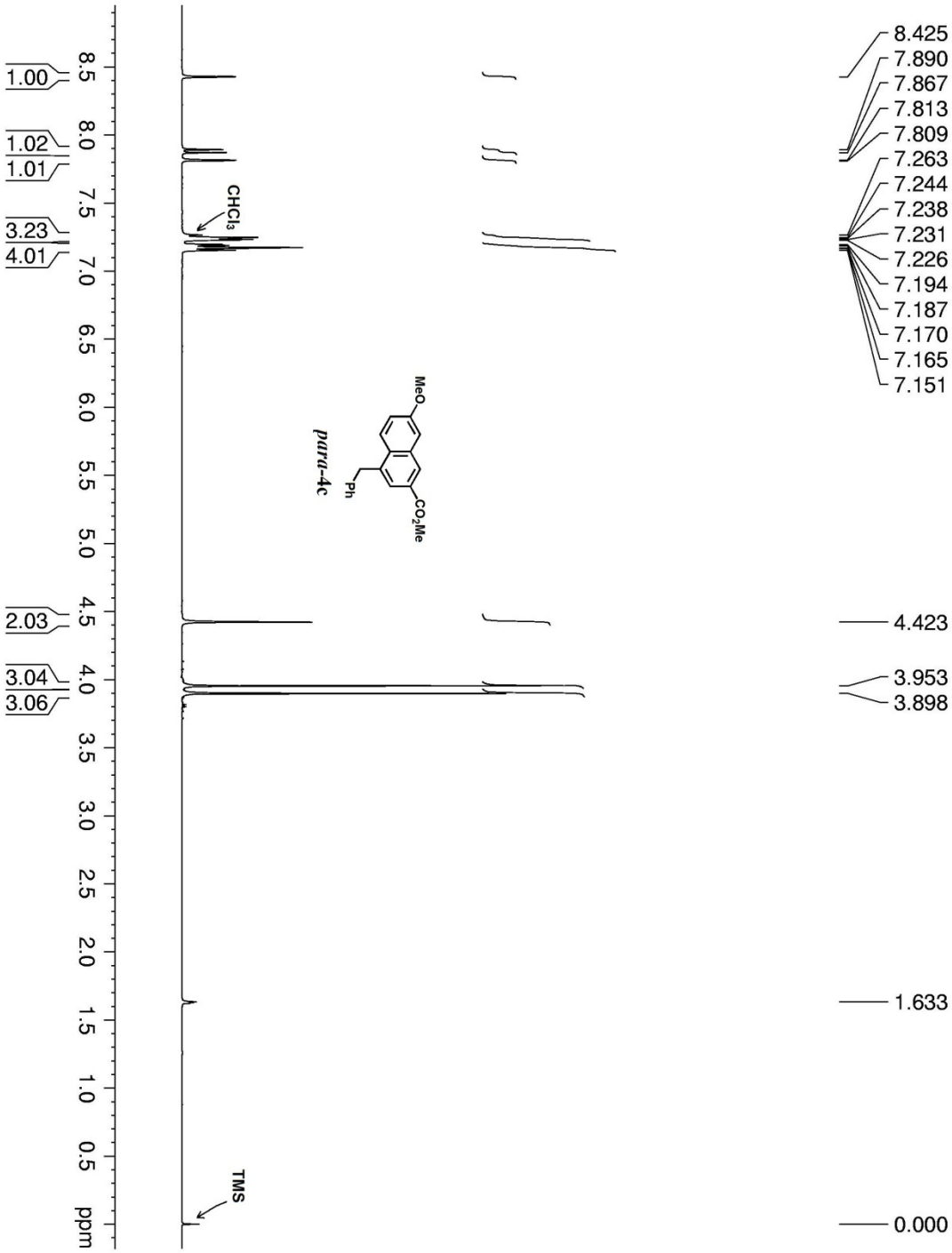
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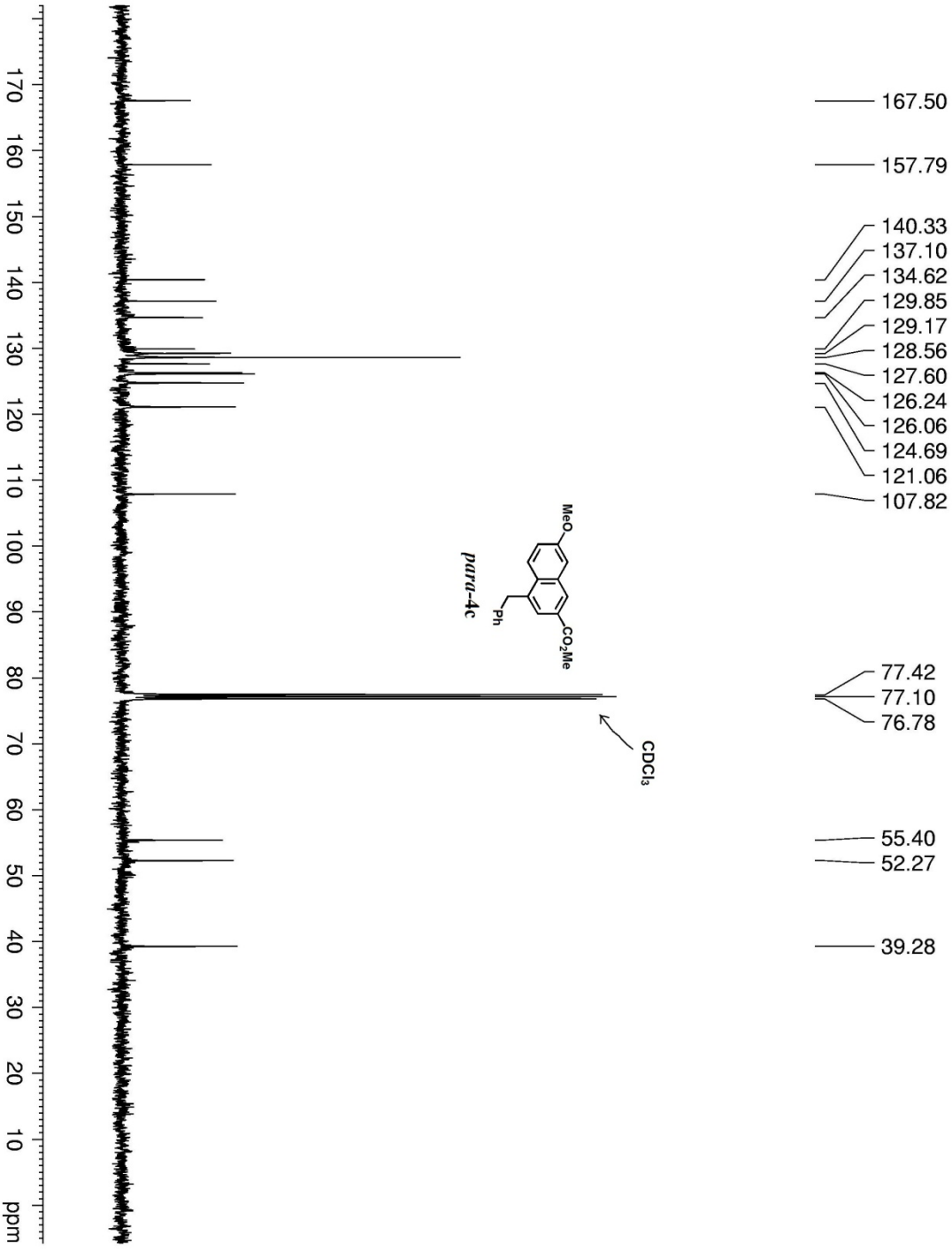
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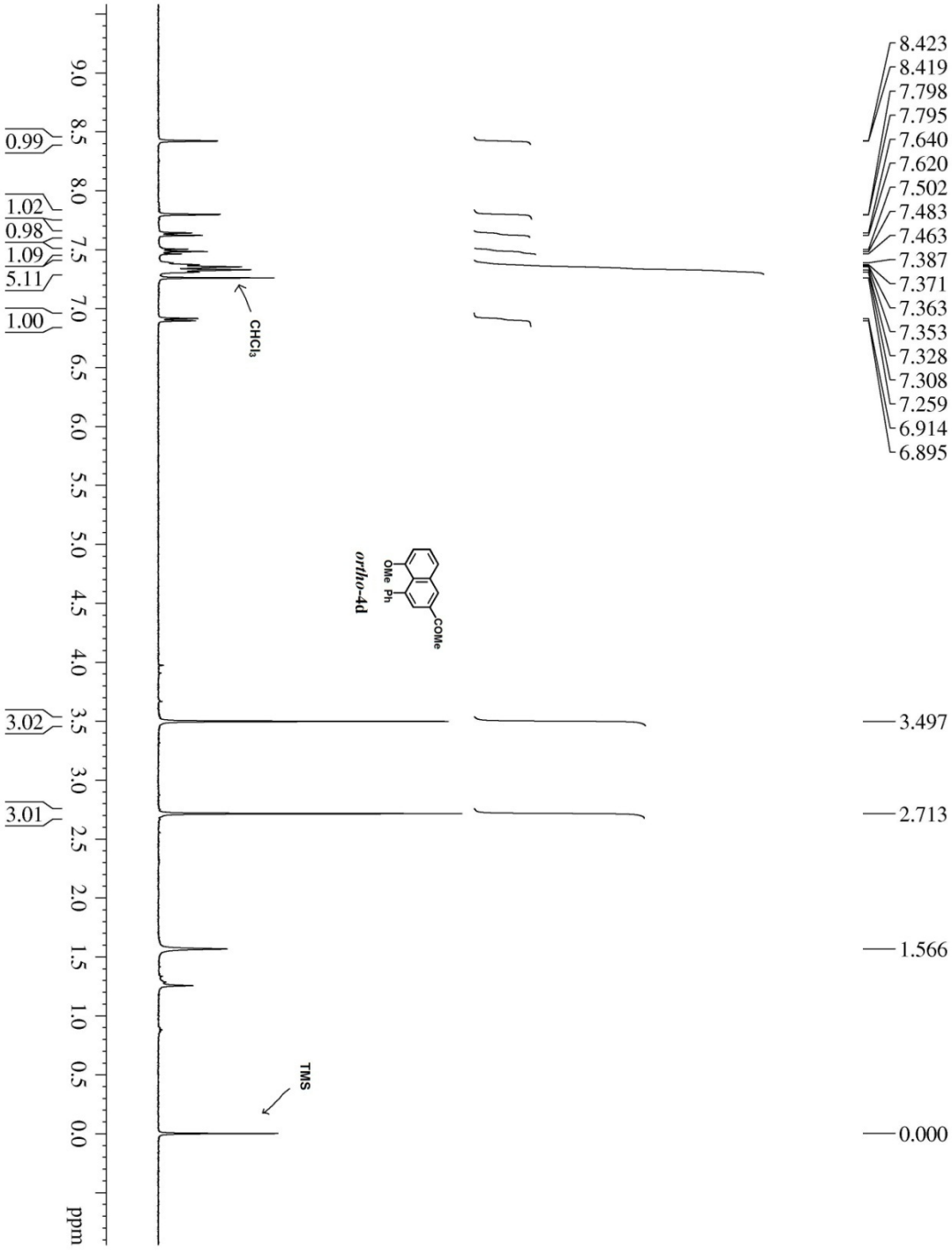
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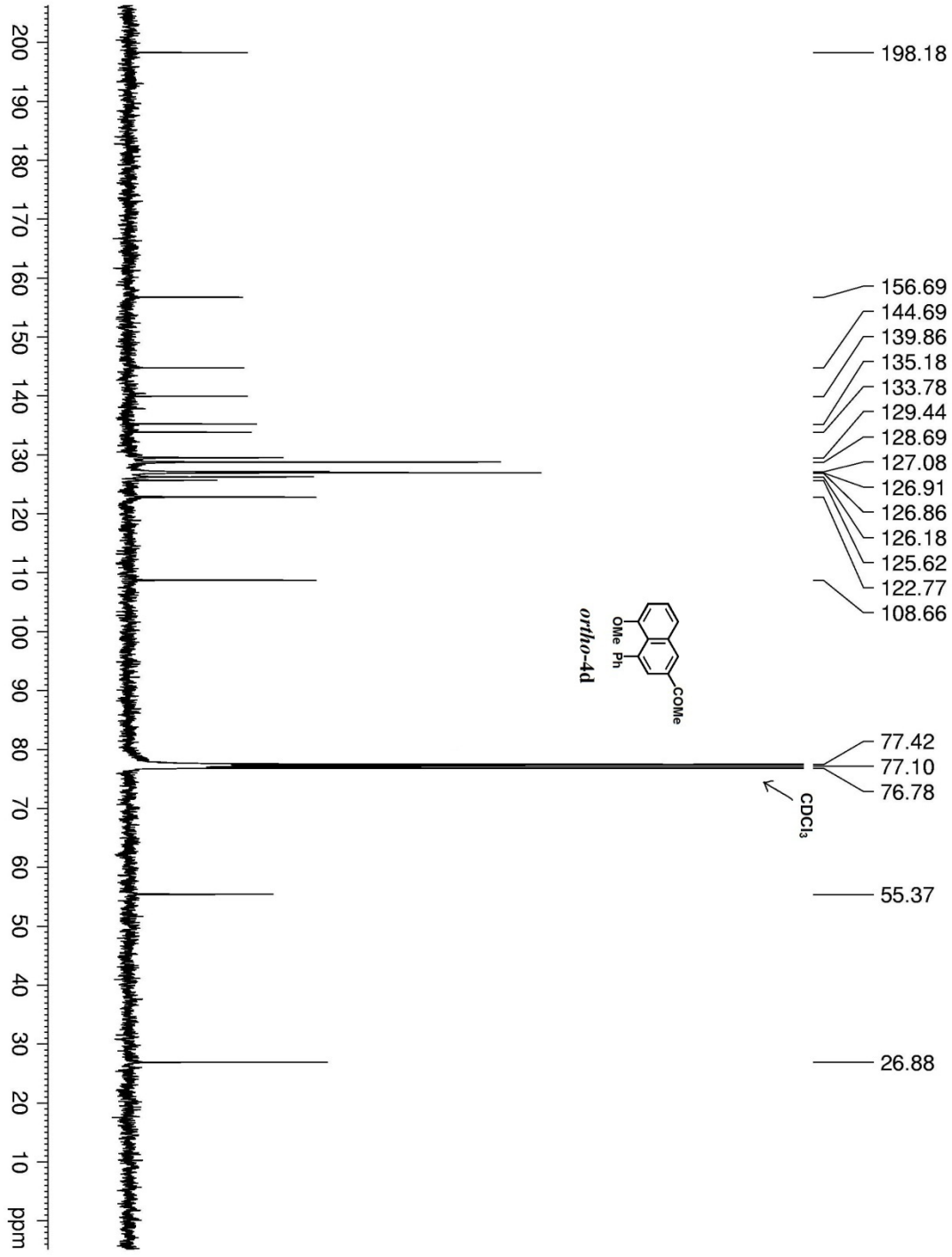
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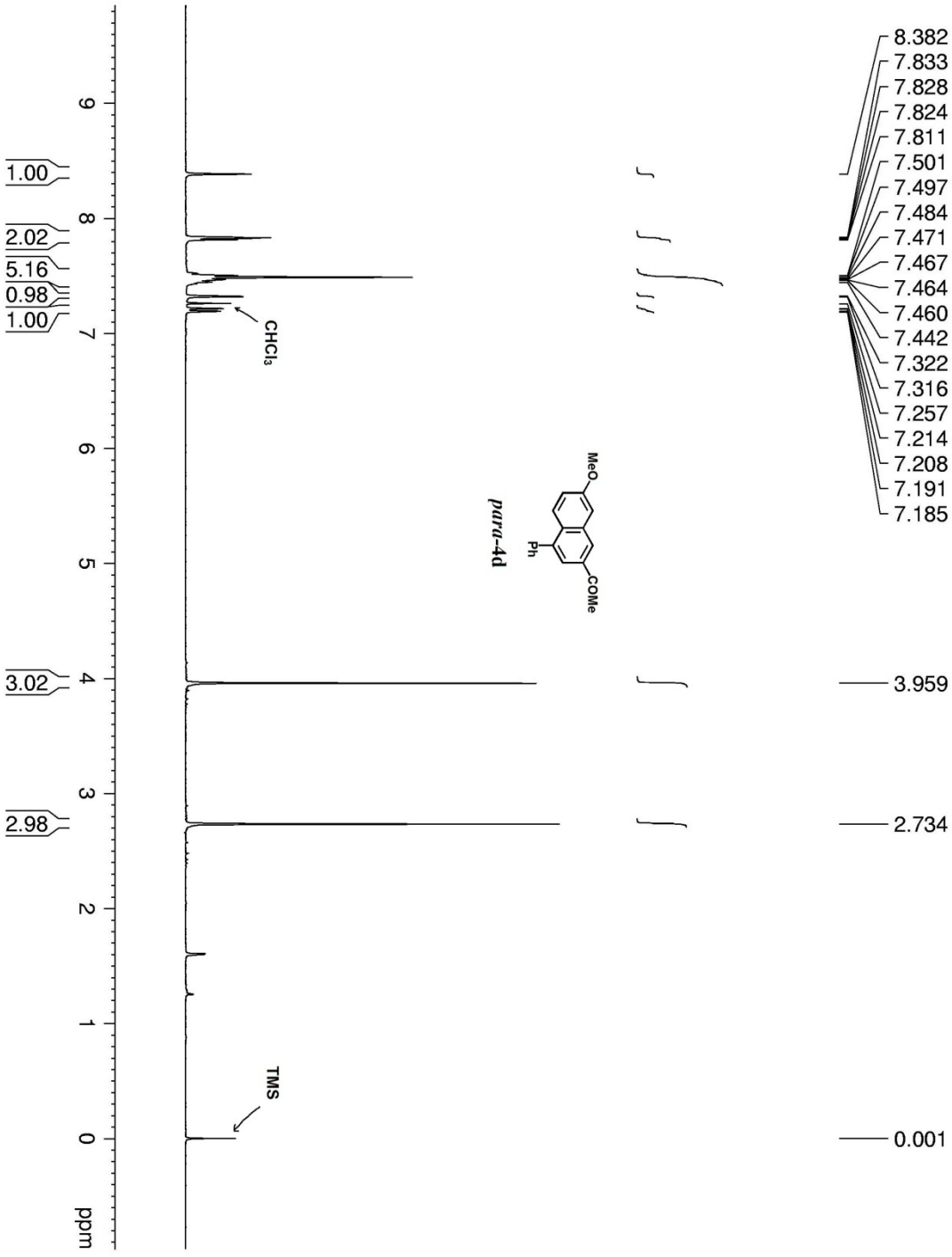
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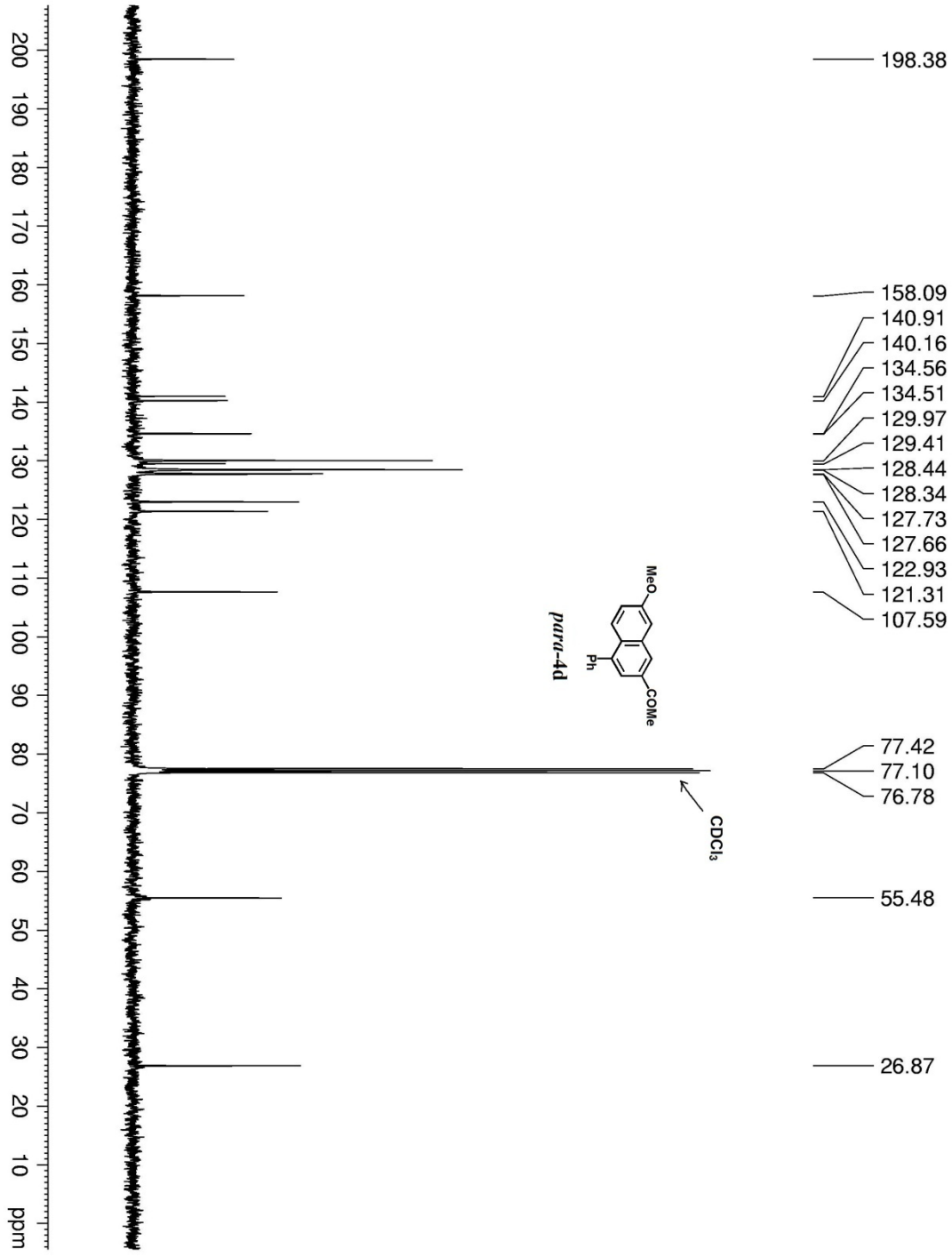
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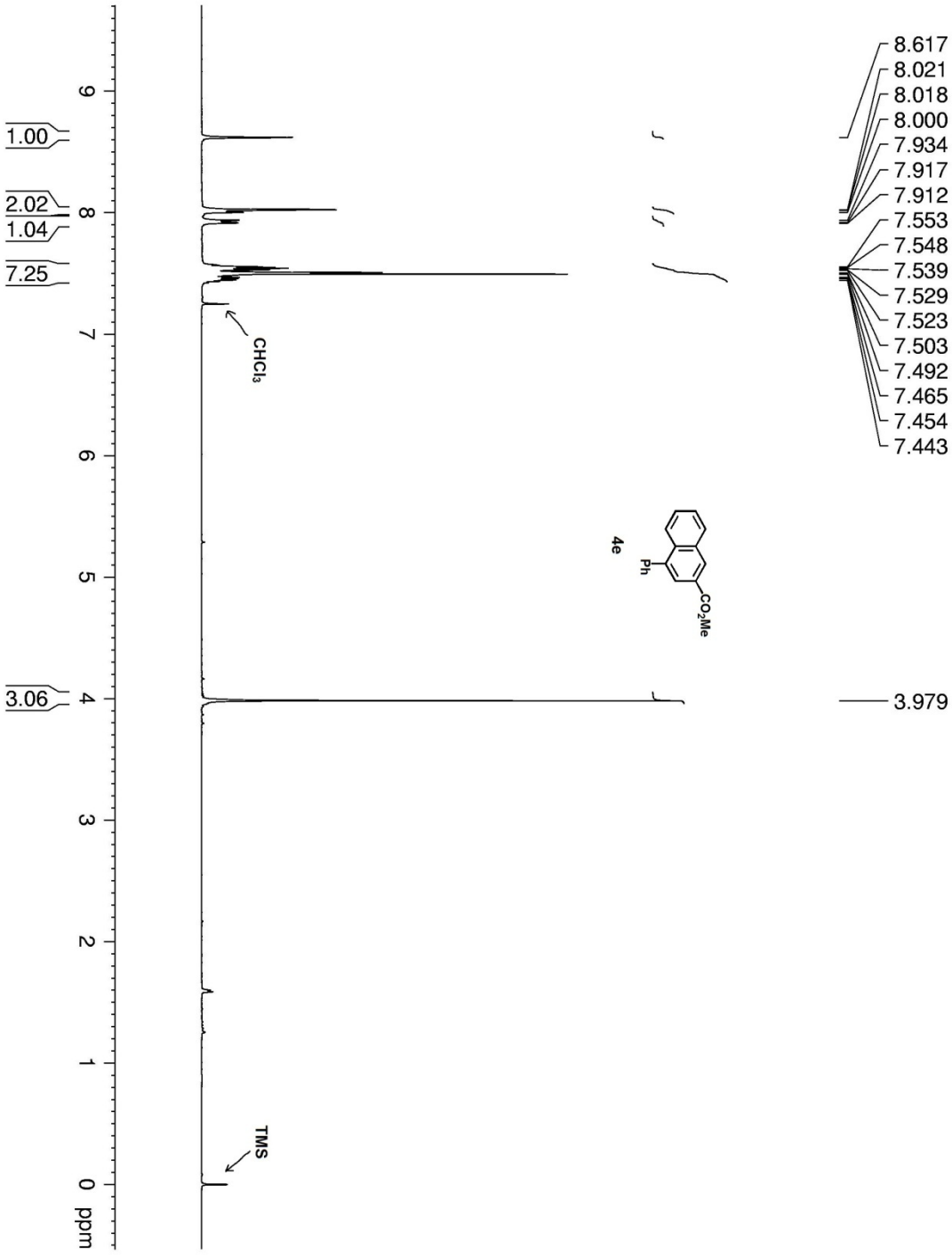
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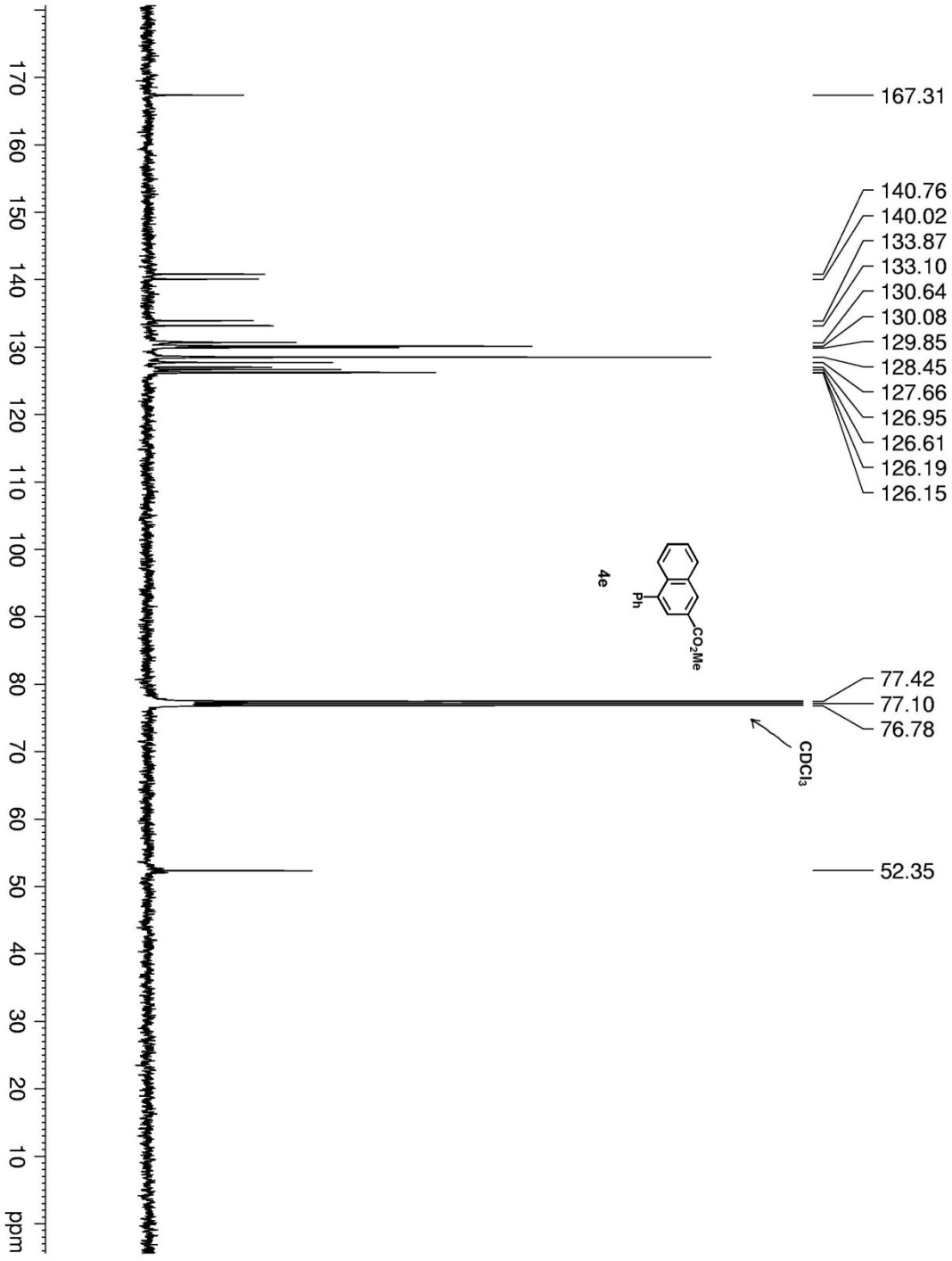
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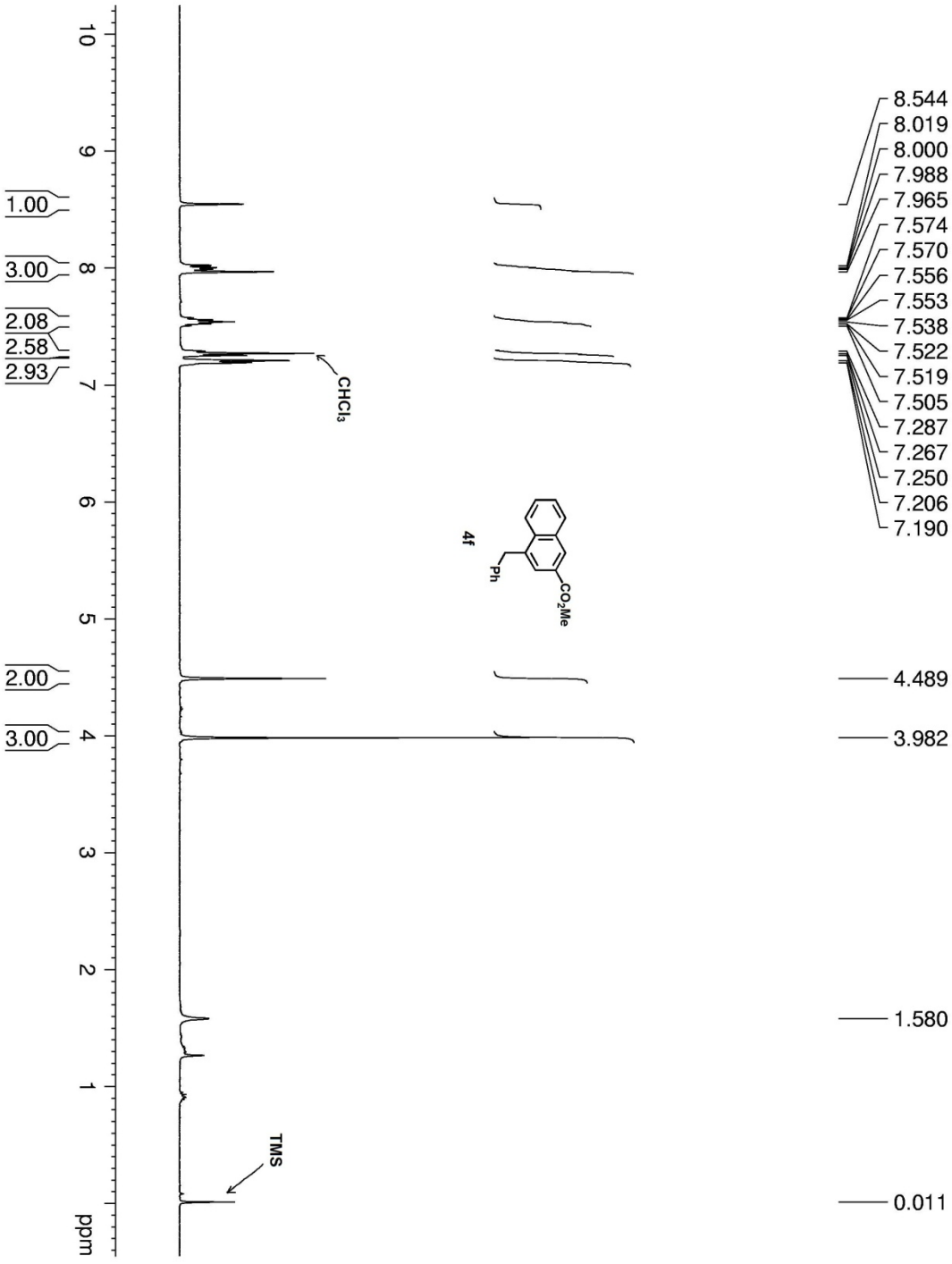
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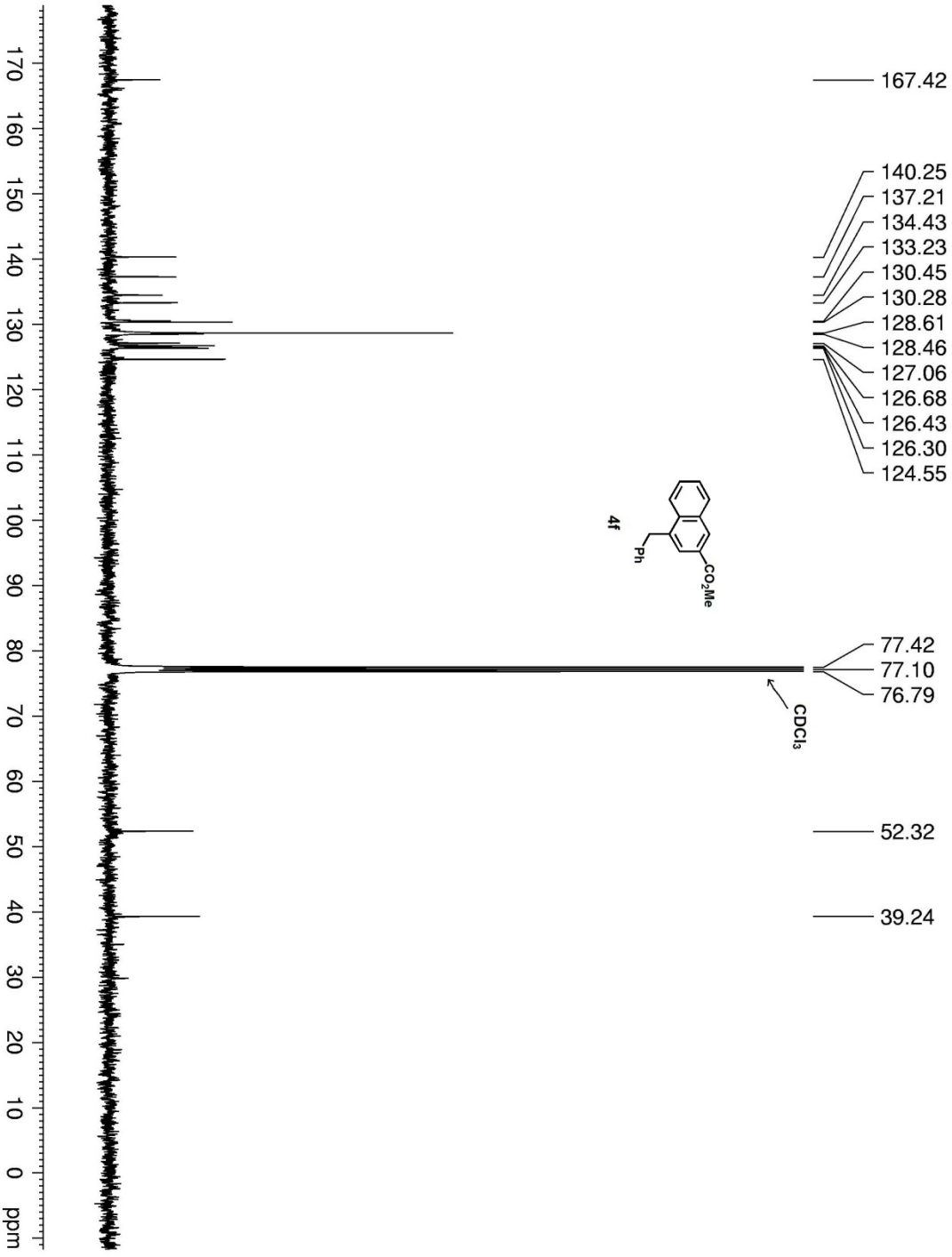
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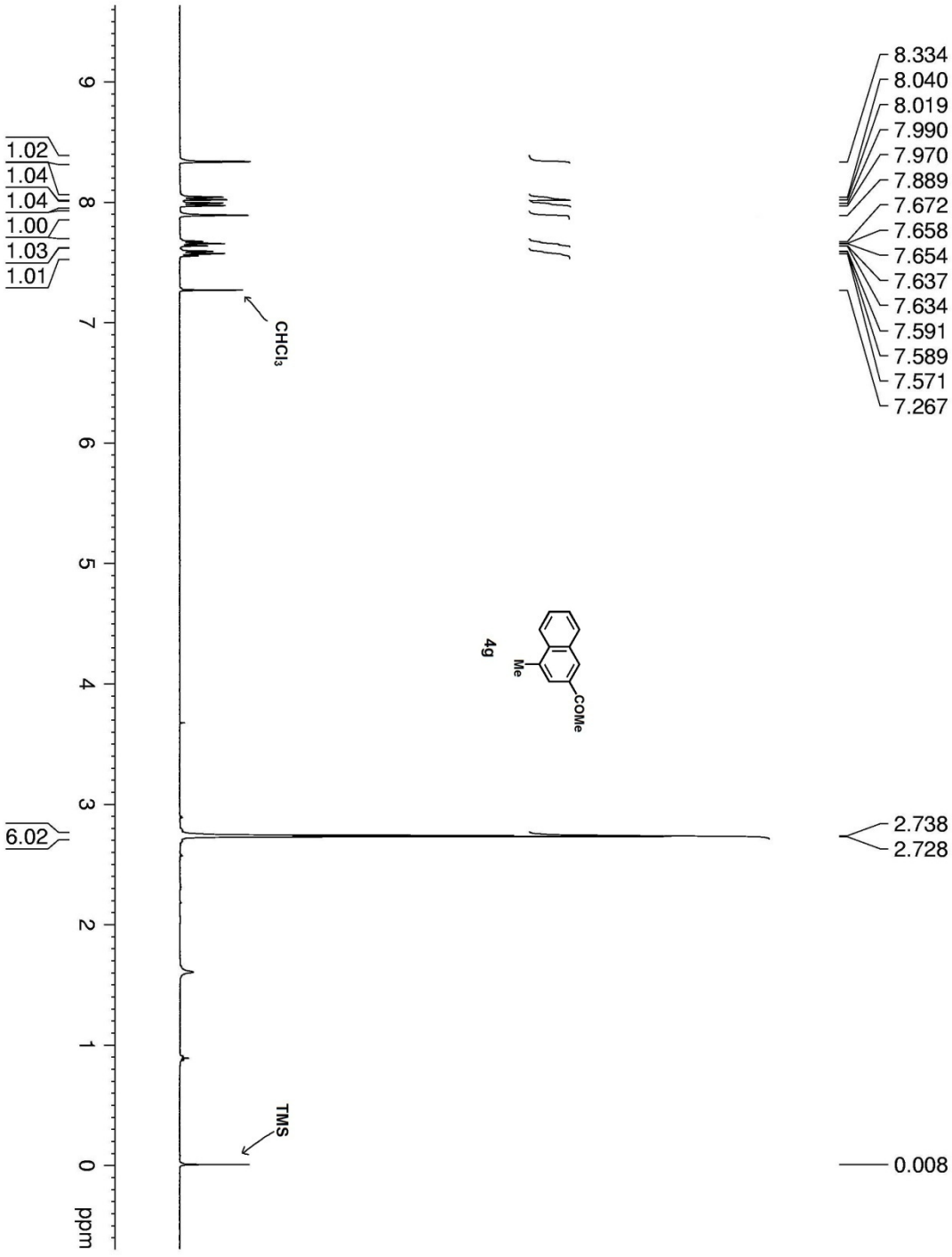
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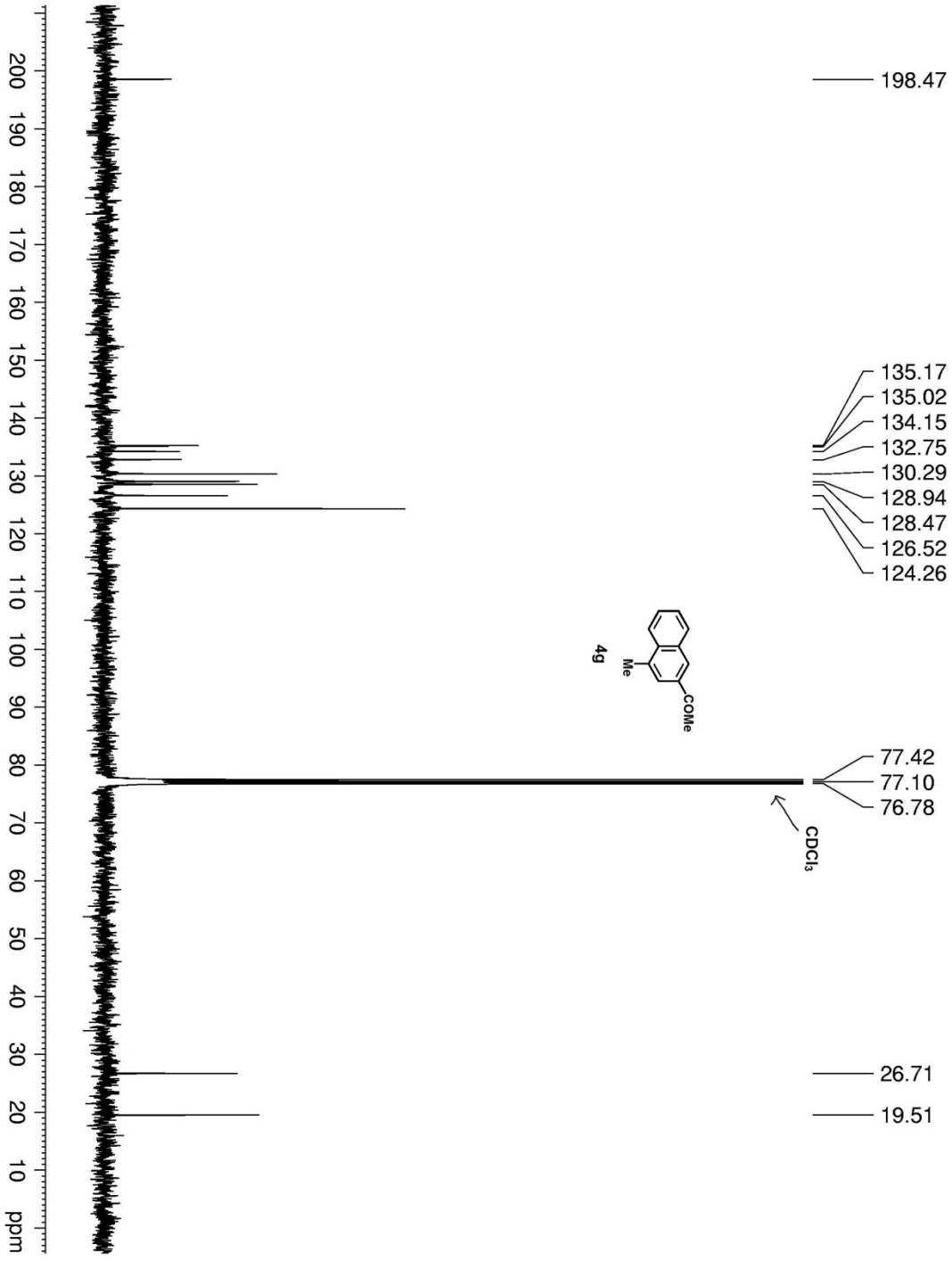
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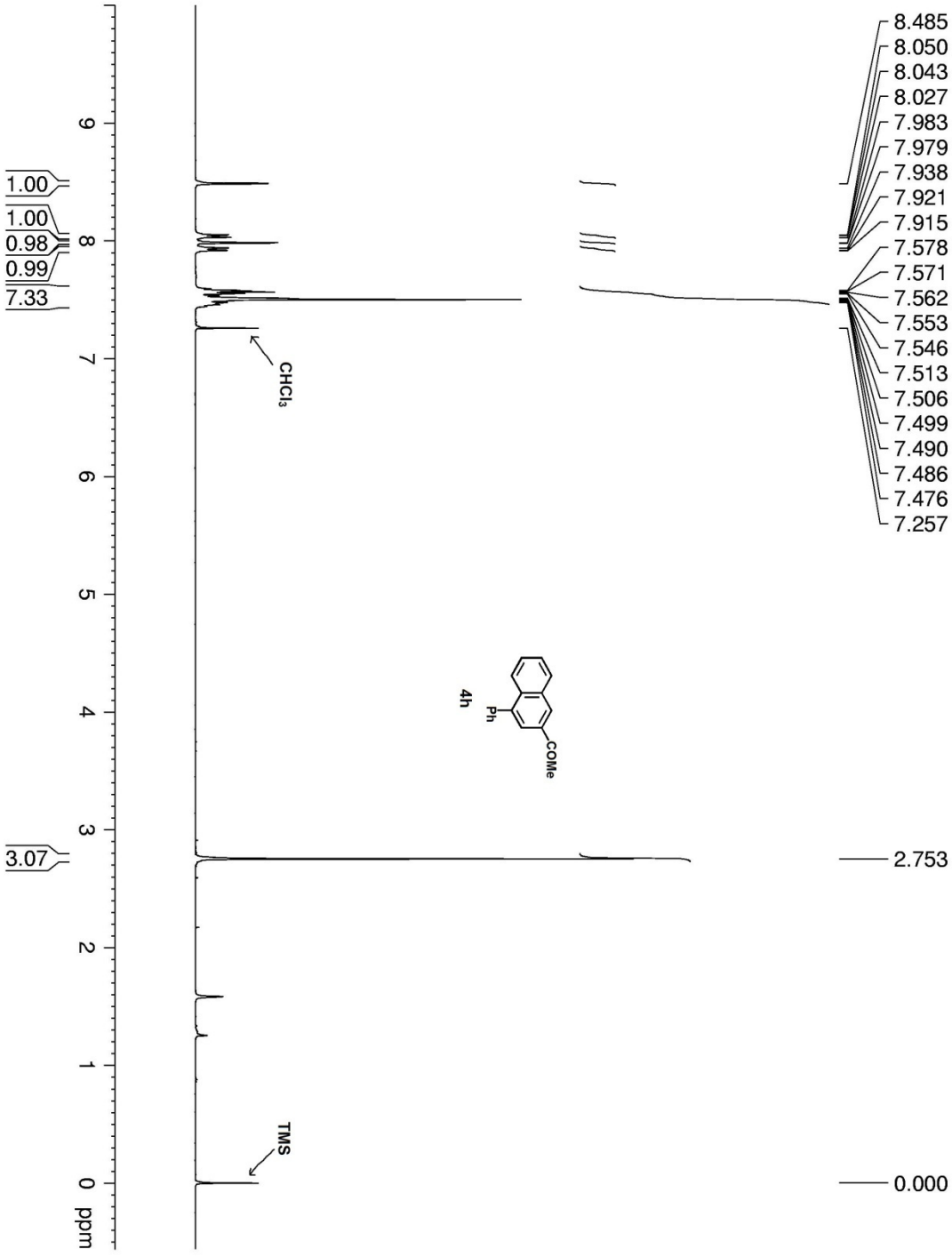
Me
COMe
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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8.050
8.043
8.027
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7.979
7.938
7.921
7.915
7.578
7.571
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7.553
7.546
7.513
7.506
7.499
7.490
7.486
7.476
7.257
2.753
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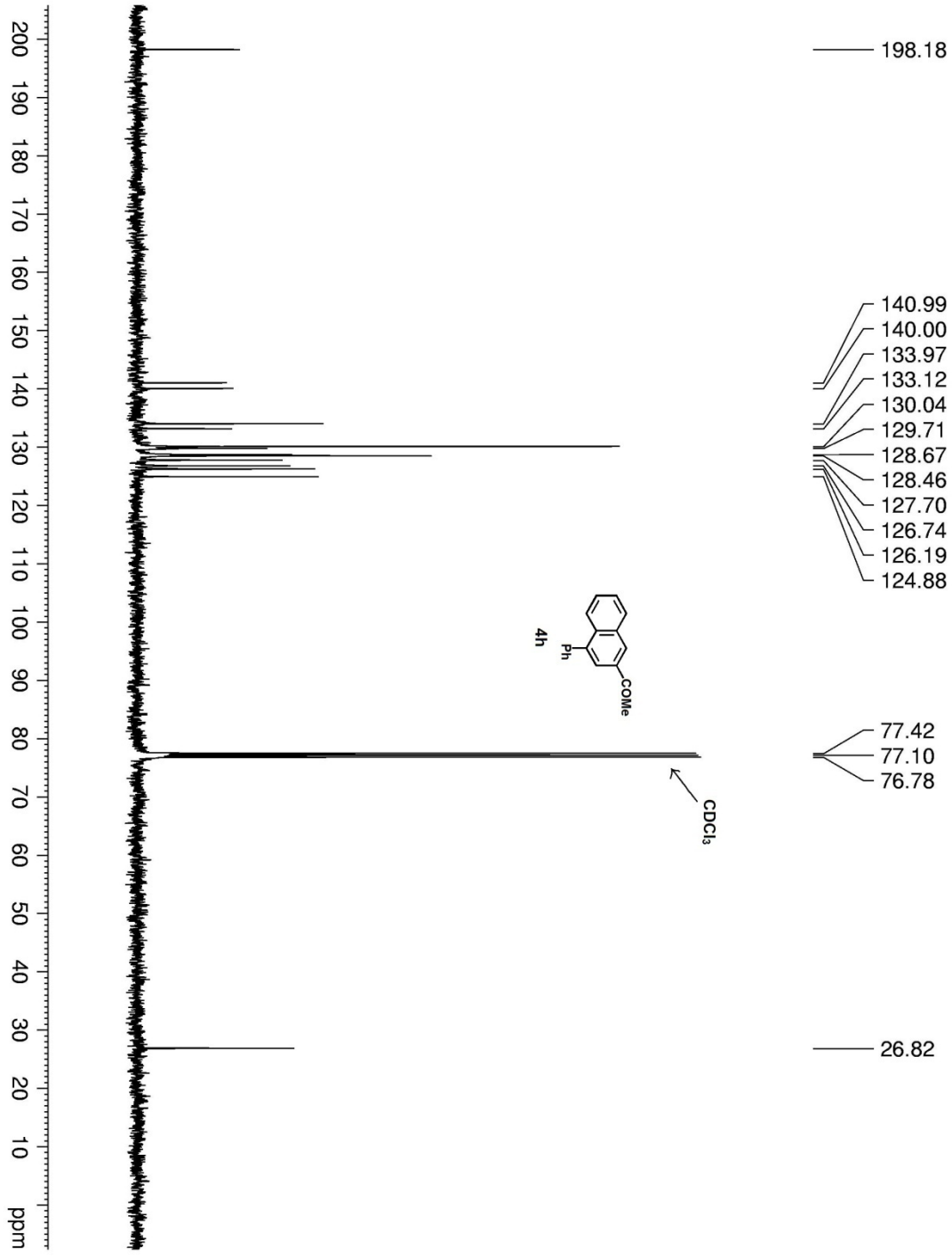
1.00
1.00
0.98
0.99
7.33
3.07
CHCl3
TMS
4h
Ph
COMe
ppm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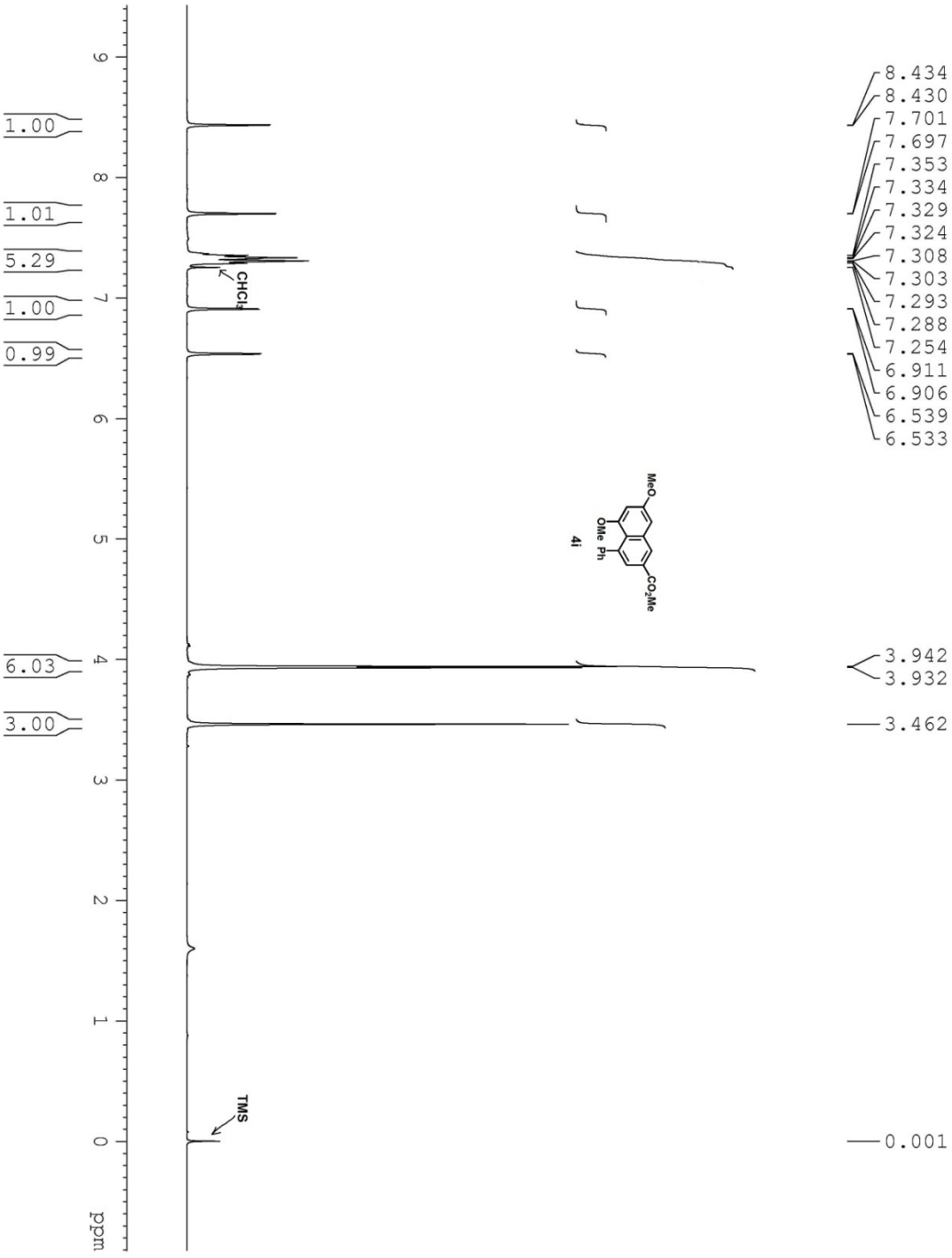
133.97
133.12
130.04
129.71
128.67
128.46
127.70
126.74
126.19
124.88
77.42
77.10
76.78
26.82
CDCl3
4h
Ph
COMe
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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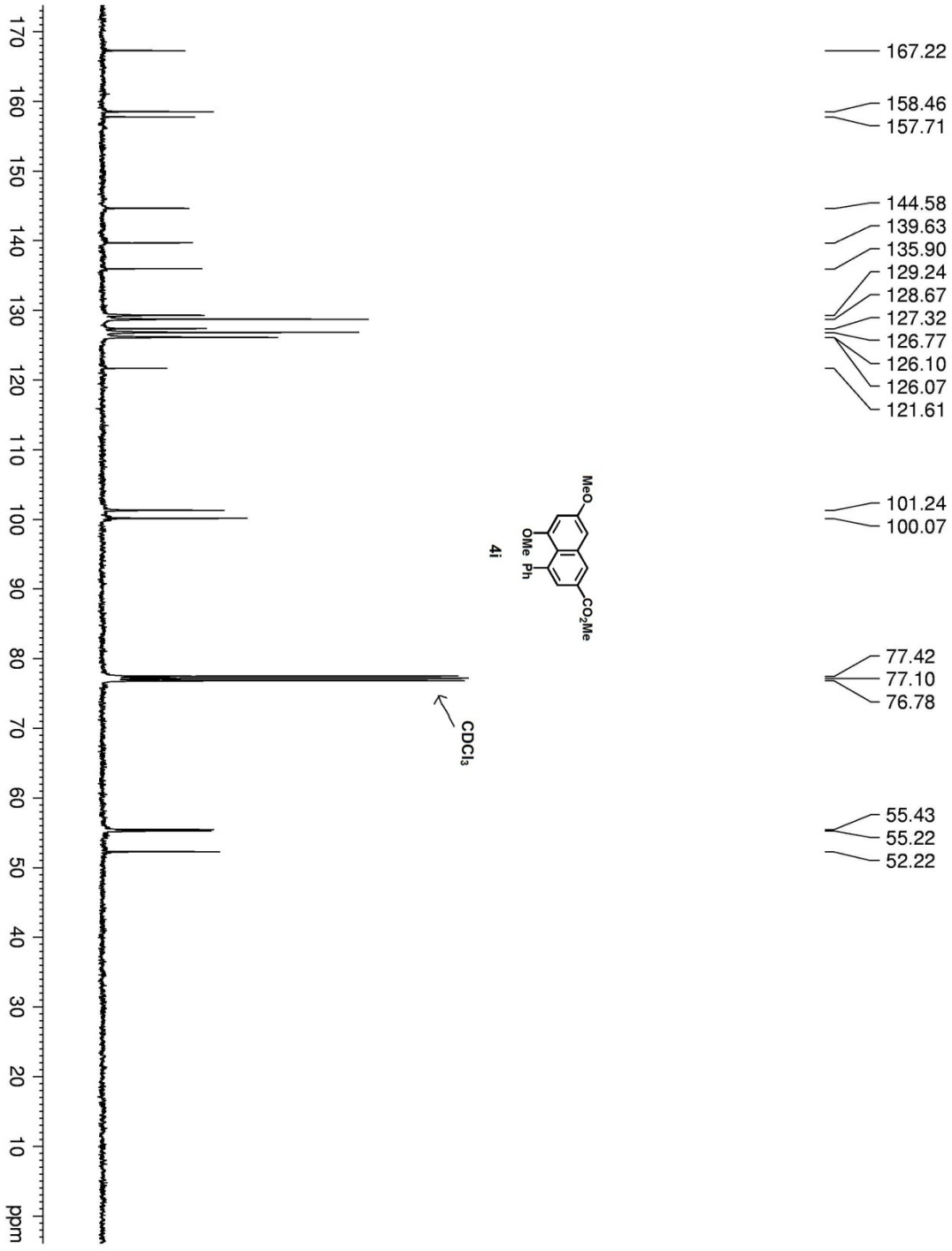
8.430
7.701
7.697
7.353
7.334
7.329
7.324
7.308
7.303
7.293
7.288
7.254
6.911
6.906
6.539
6.533
3.942
3.932
3.462
0.001
1.00
1.01
5.29
1.00
0.99
6.03
3.00
CHCl3
TMS
MeO
OMe Ph
CO2Me
4i
ppm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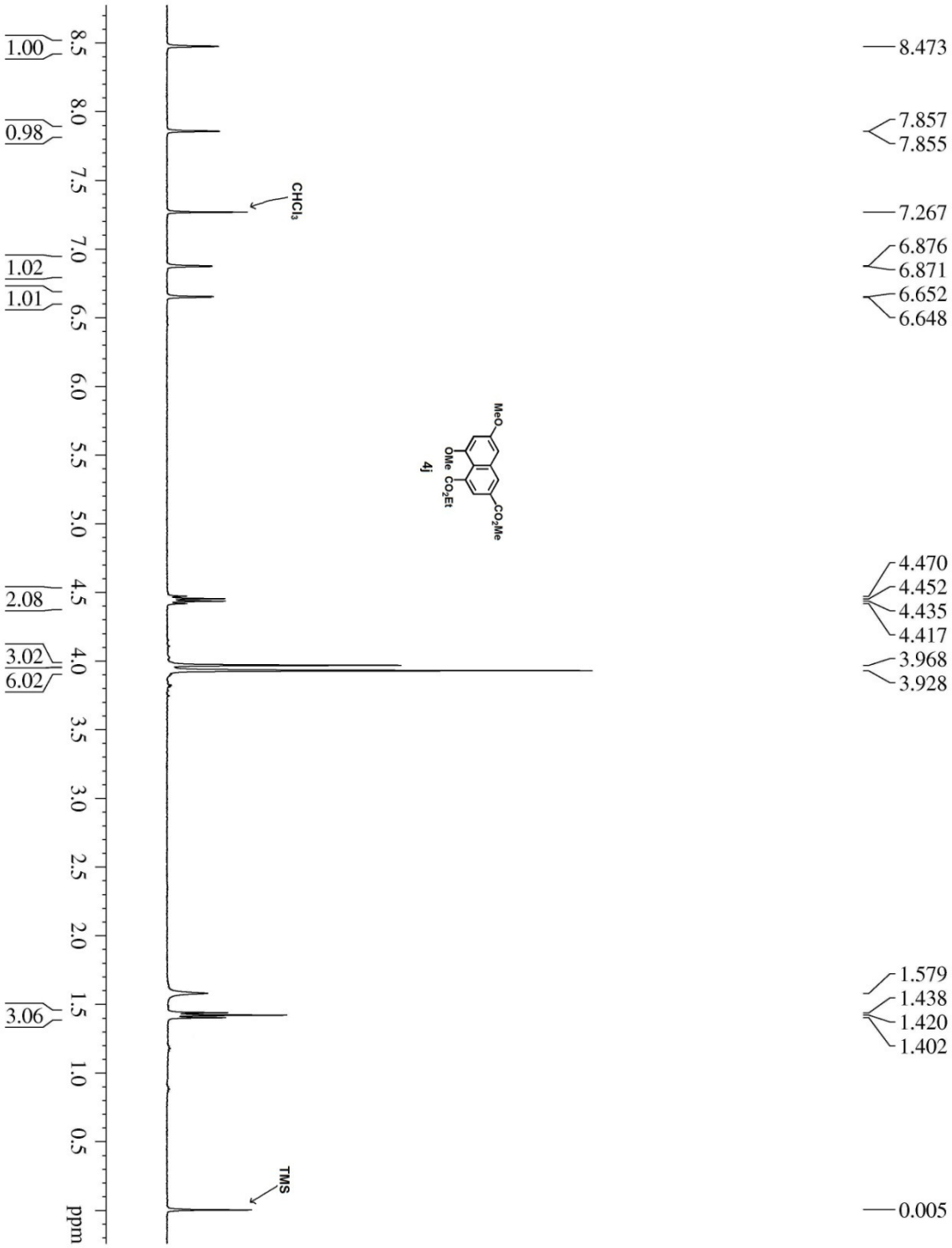
158.46
157.71
144.58
139.63
135.90
129.24
128.67
127.32
126.77
126.10
126.07
121.61
101.24
100.07
77.42
77.10
76.78
55.43
55.22
52.22
MeO
OMe Ph
CO2Me
4i
CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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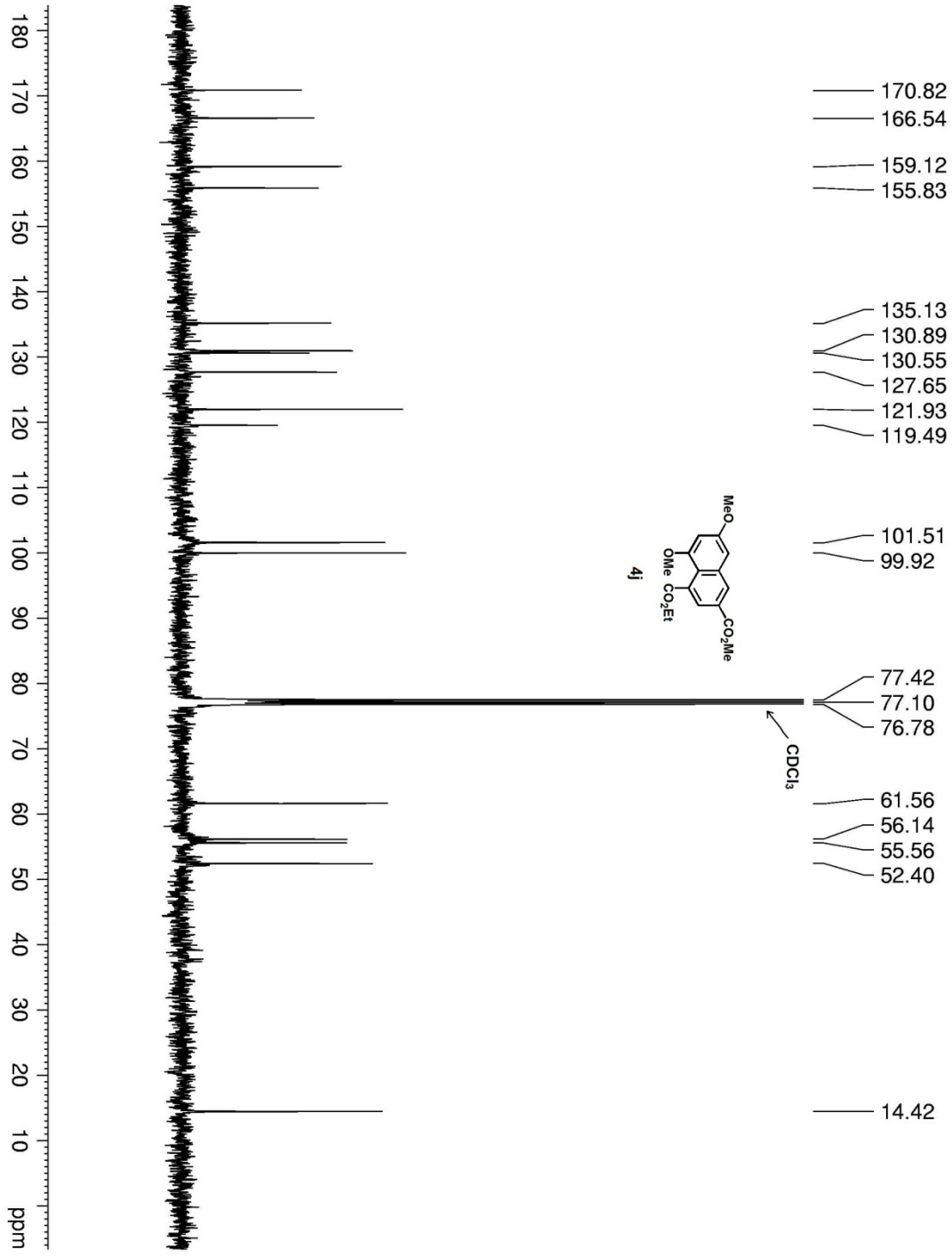
7.855
7.267
6.876
6.871
6.652
6.648
4.470
4.452
4.435
4.417
3.968
3.928
1.579
1.438
1.420
1.402
0.005
CHCl3
TMS
4j
MeO
OMe
CO2Et
CO2Me
1.00
0.98
1.02
1.01
2.08
3.02
6.02
3.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm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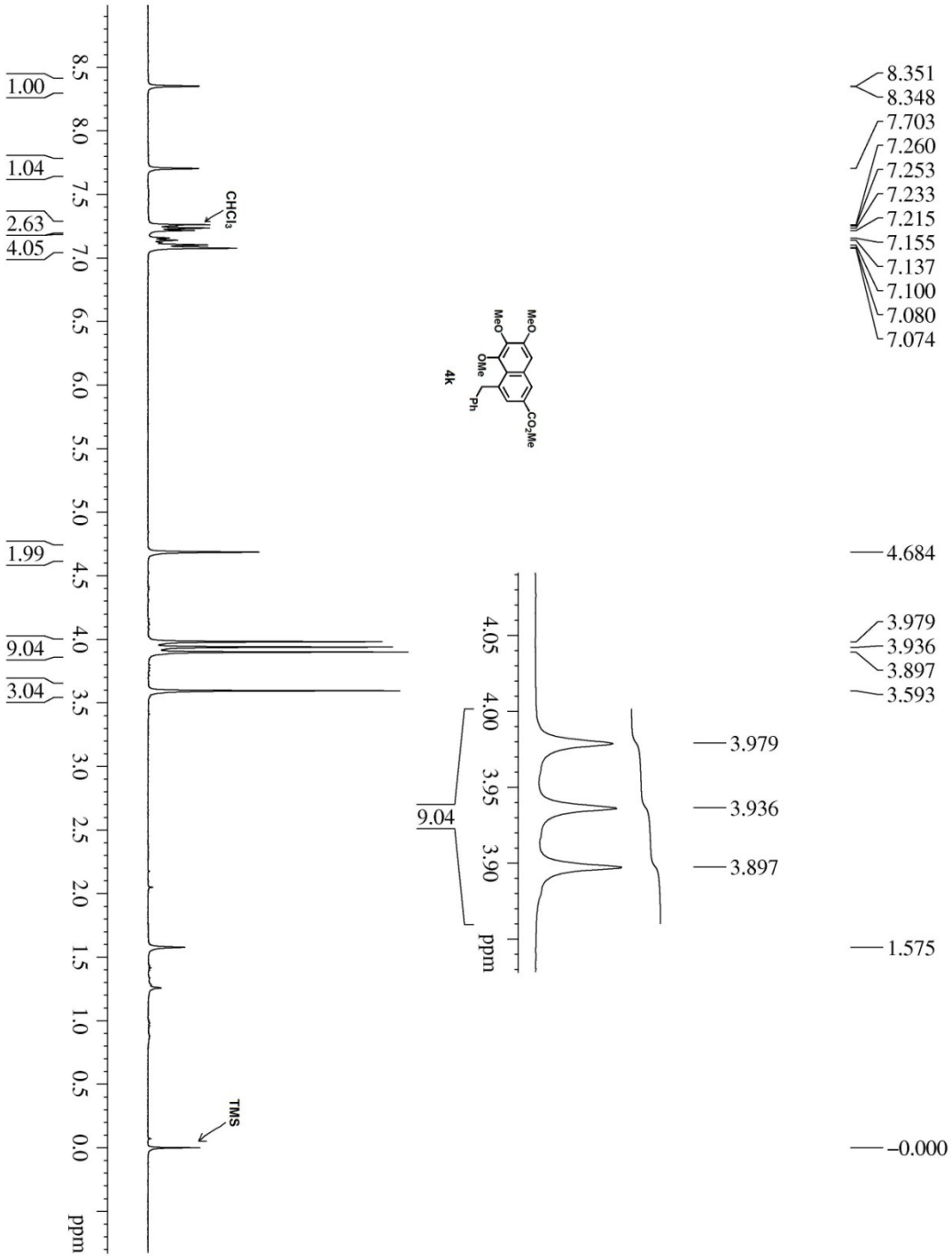
166.54
159.12
155.83
135.13
130.89
130.55
127.65
121.93
119.49
101.51
99.92
77.42
77.10
76.78
CDCl3
61.56
56.14
55.56
52.40
14.42
MeO
OMe
CO2Et
CO2Me
4j
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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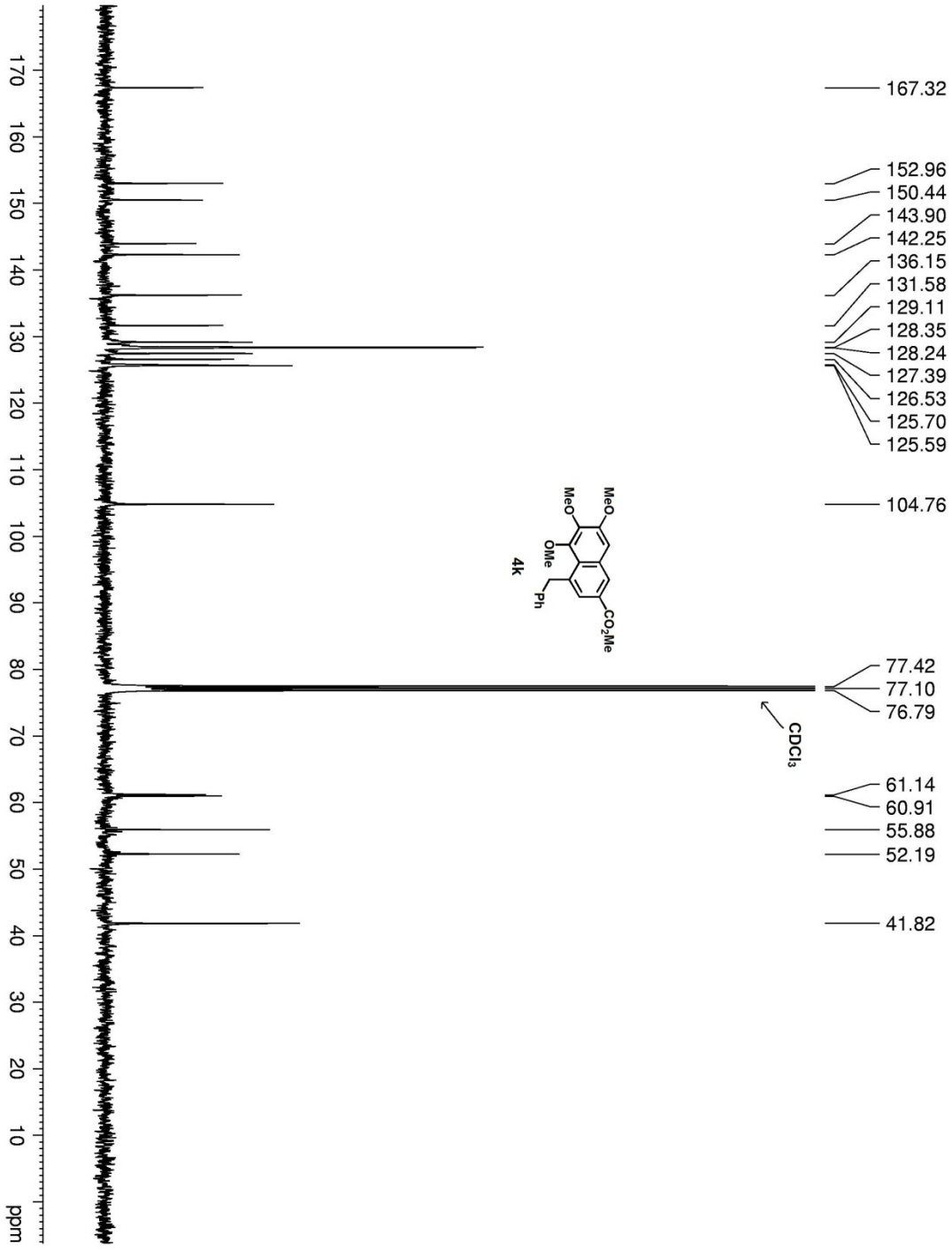
7.260
7.253
7.233
7.215
7.155
7.137
7.100
7.080
7.074
4.684
3.979
3.936
3.897
3.593
1.575
−0.000
CHCl3
TMS
1.00
1.04
2.63
4.05
1.99
9.04
3.04
MeO
MeO
OMe
Ph
CO2Me
4k
9.04
ppm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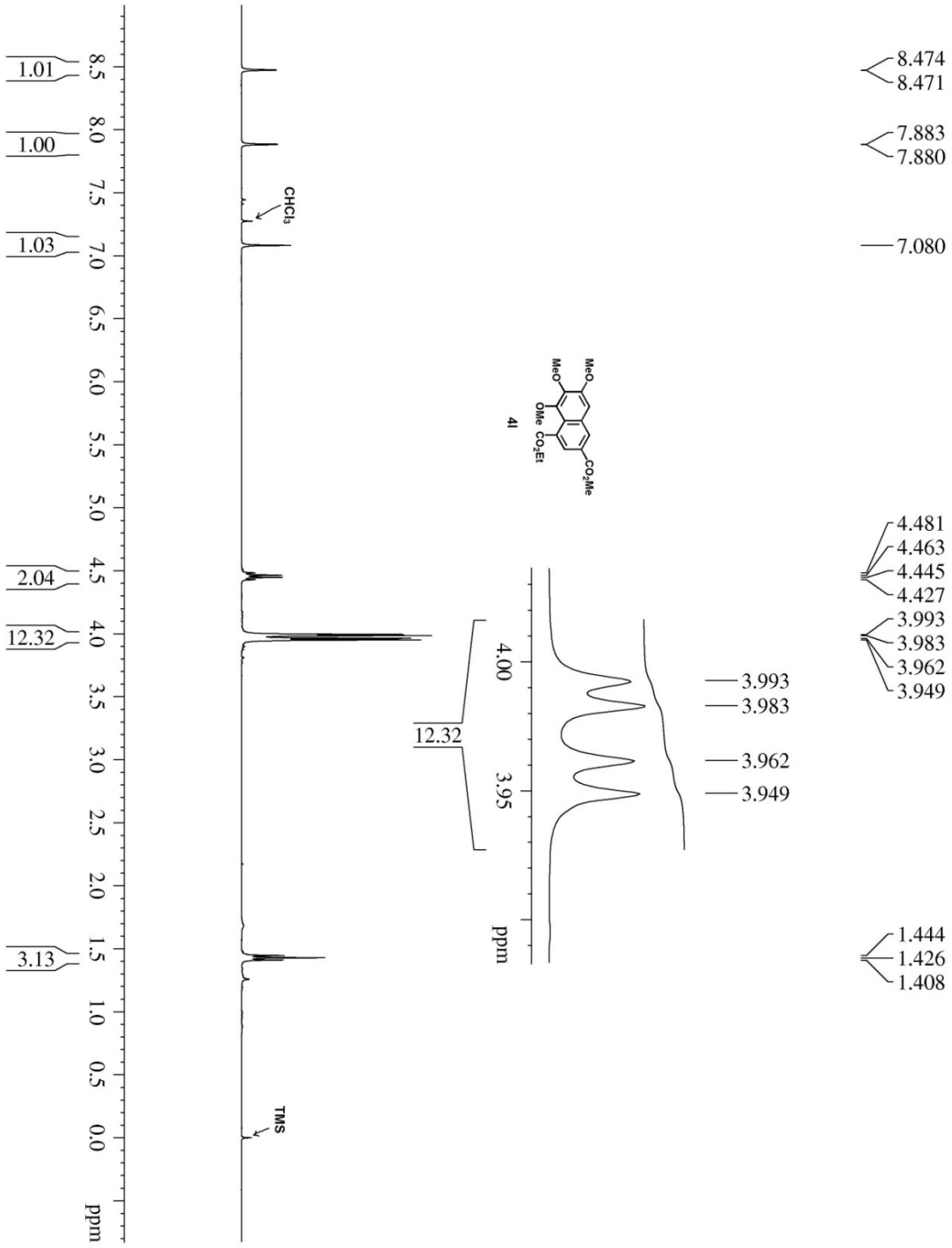
152.96
150.44
143.90
142.25
136.15
131.58
129.11
128.35
128.24
127.39
126.53
125.70
125.59
104.76
77.42
77.10
76.79
CDCl3
61.14
60.91
55.88
52.19
41.82
MeO
MeO
OMe
Ph
CO2Me
4k
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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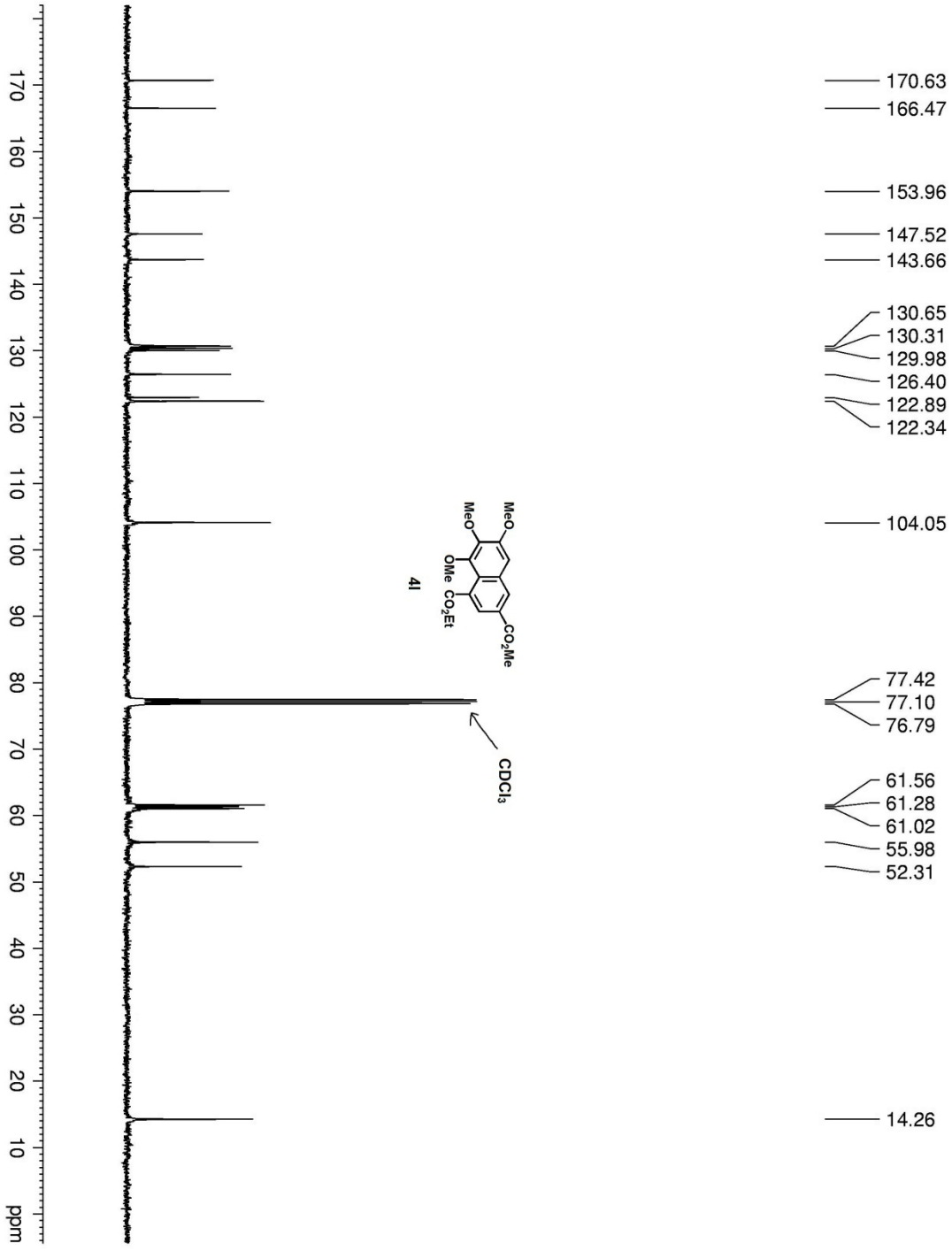
7.883
7.880
7.080
4.481
4.463
4.445
4.427
3.993
3.983
3.962
3.949
1.444
1.426
1.408
CHCl3
TMS
MeO
MeO
OMe
CO2Et
CO2Me
4l
1.01
1.00
1.03
2.04
12.32
3.13
4.00
12.32
3.95
ppm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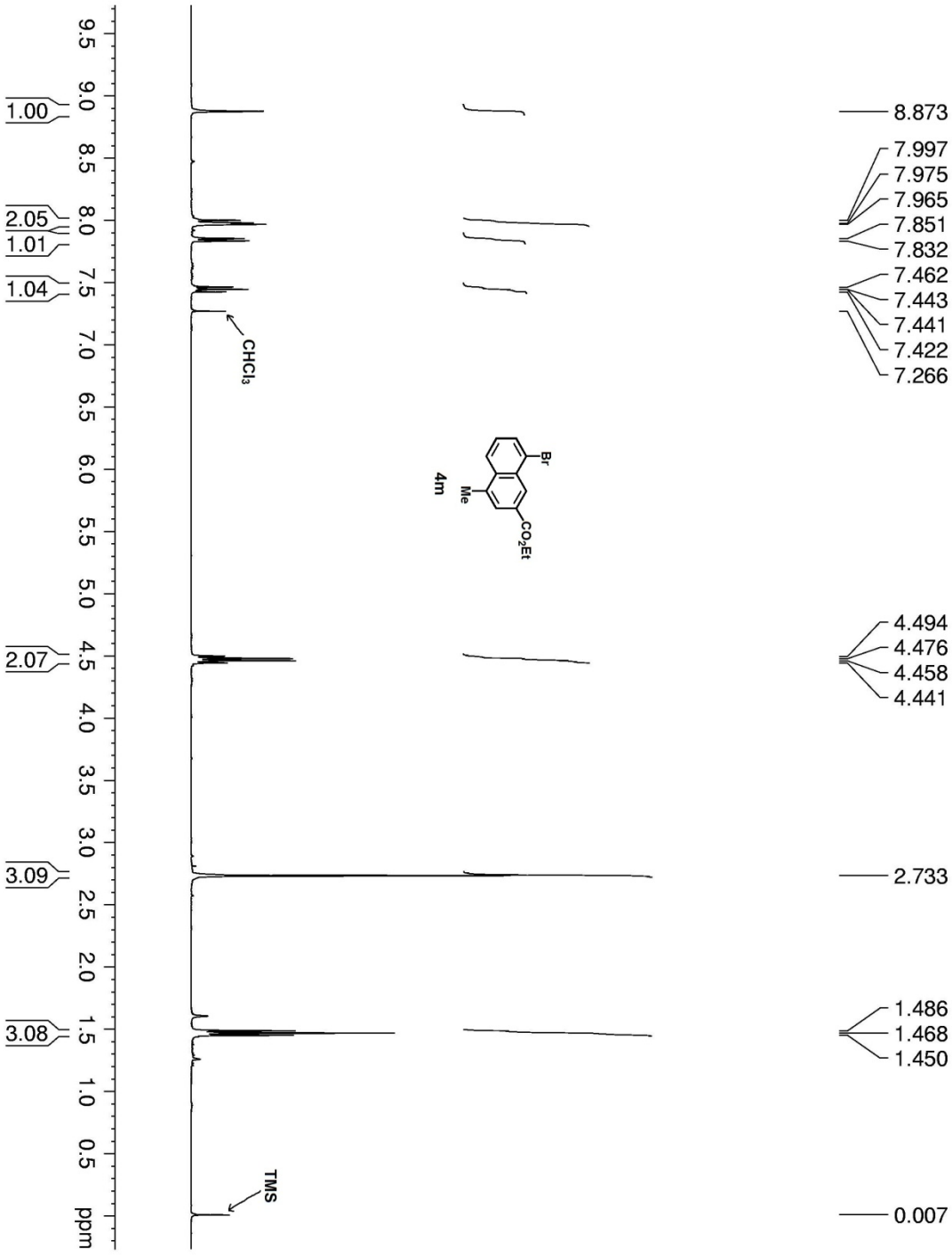
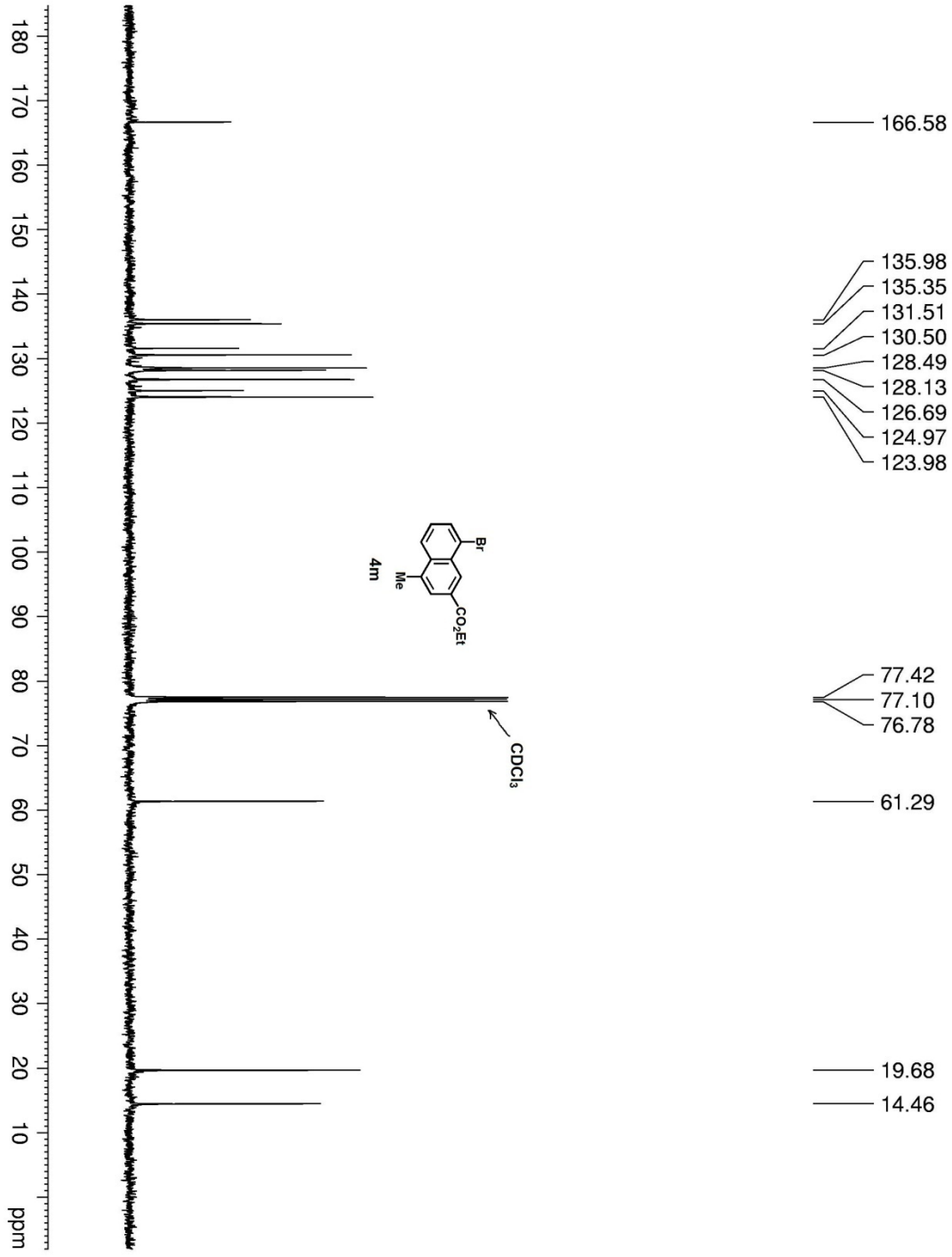
166.47
153.96
147.52
143.66
130.65
130.31
129.98
126.40
122.89
122.34
104.05
77.42
77.10
76.79
61.56
61.28
61.02
55.98
52.31
14.26
CDCl3
MeO
MeO
OMe
CO2Et
CO2Me
4l
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


1.00
2.05
1.01
1.04
2.07
3.09
3.08
CHCl3
TMS
Br
Me
CO2Et
4m
8.873
7.997
7.975
7.965
7.851
7.832
7.462
7.443
7.441
7.422
7.266
4.494
4.476
4.458
4.441
2.733
1.486
1.468
1.450
0.007
ppm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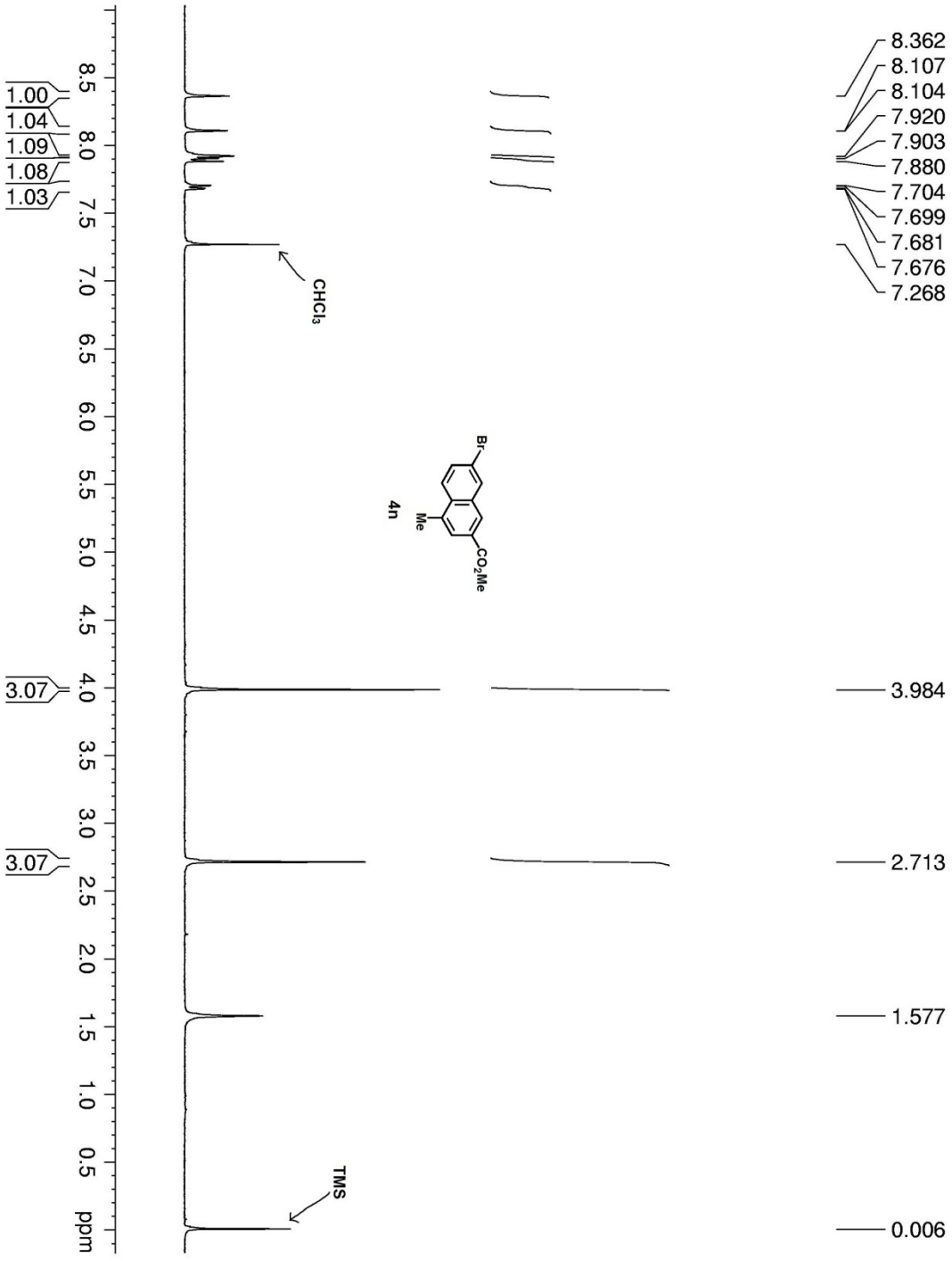
135.35
131.51
130.50
128.49
128.13
126.69
124.97
123.98
77.42
77.10
76.78
61.29
19.68
14.46
CDCl3
Br
Me
CO2Et
4m
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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8.104
7.920
7.903
7.880
7.704
7.699
7.681
7.676
7.268
1.00
1.04
1.09
1.08
1.03
CHCl3
Br
Me
CO2Me
4n
3.07
3.984
3.07
2.713
1.577
TMS
0.006
8.5
8.0
7.5
7.0
6.5
6.0
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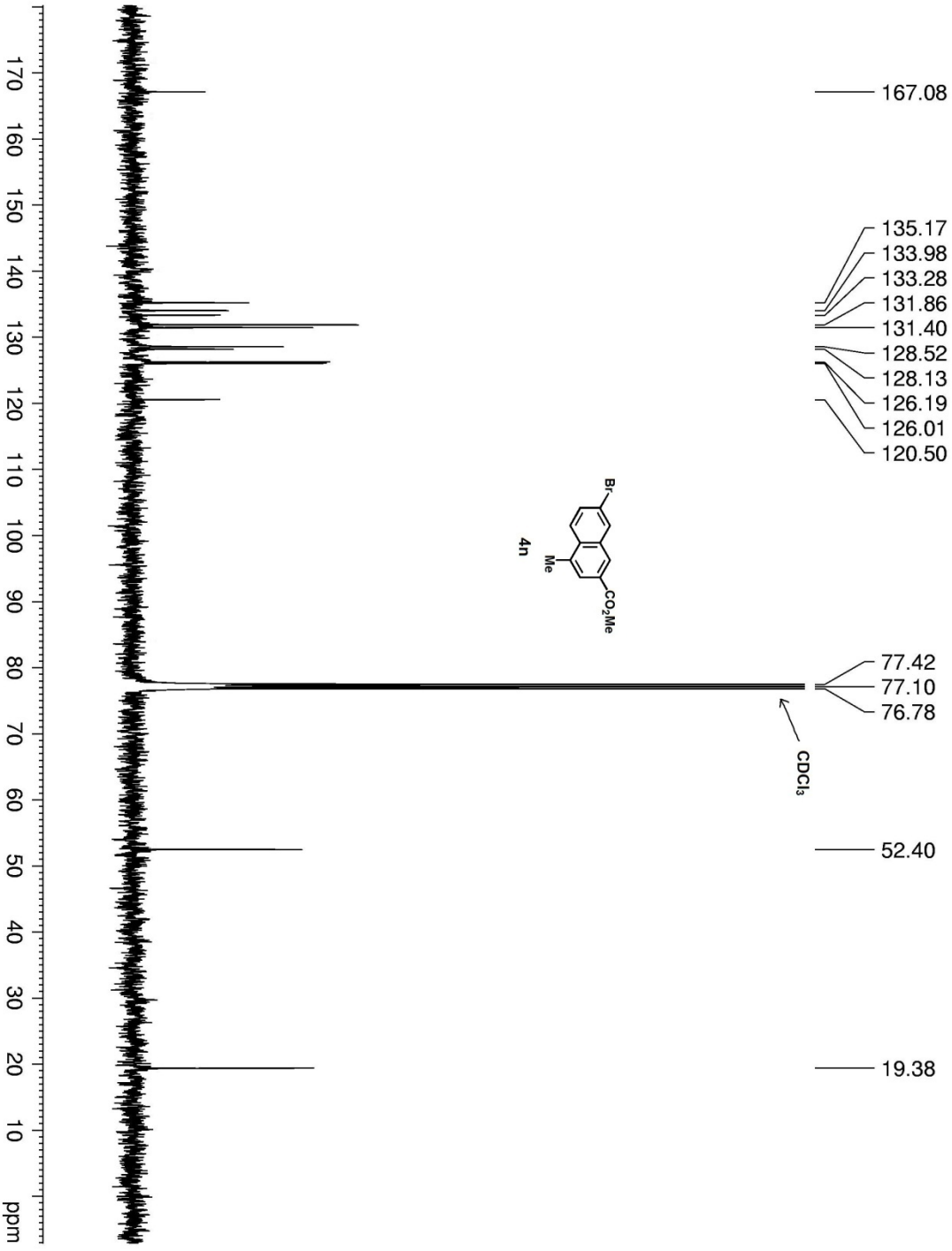
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm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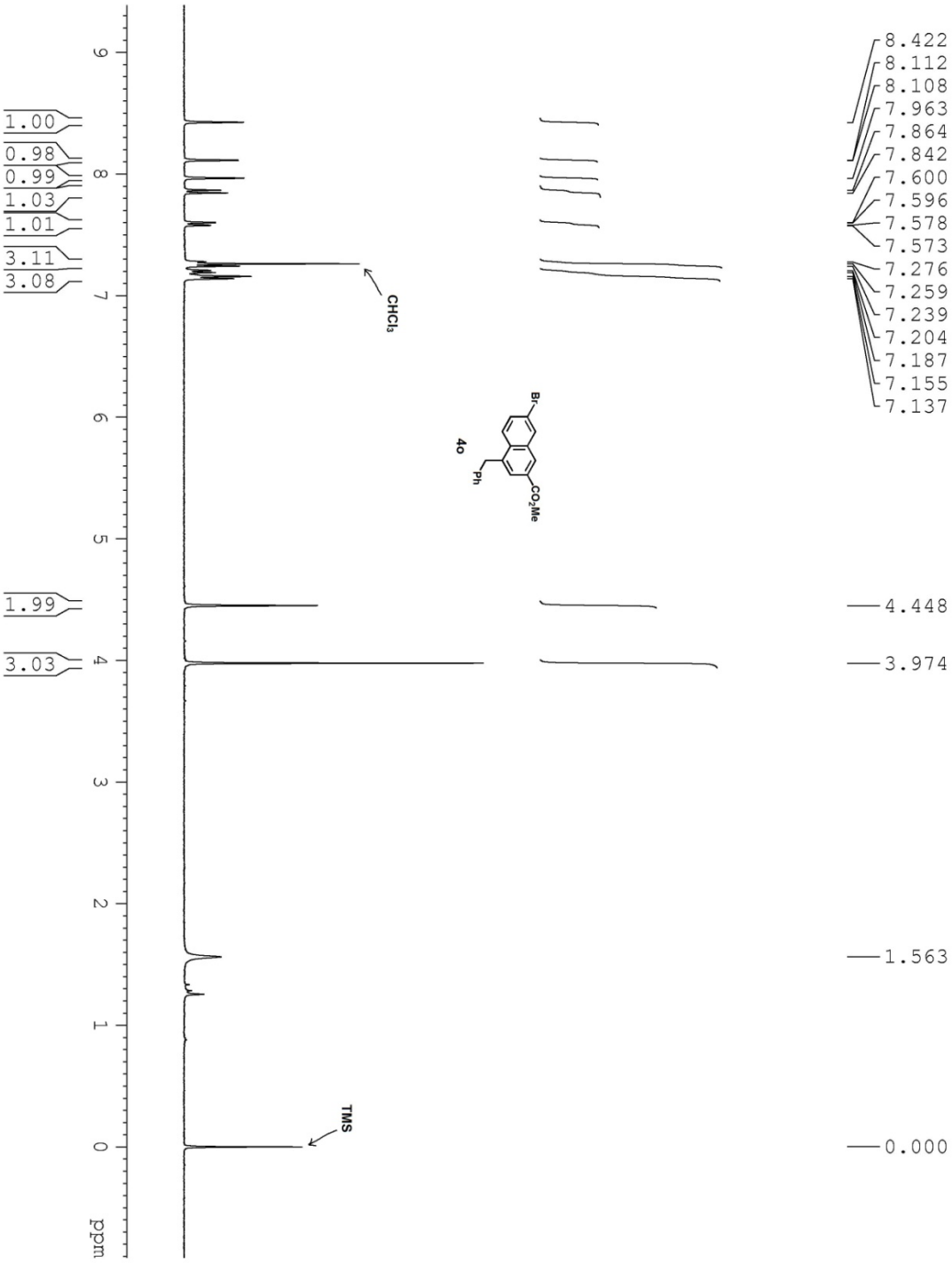
133.98
133.28
131.86
131.40
128.52
128.13
126.19
126.01
120.50
77.42
77.10
76.78
CDCl3
52.40
19.38
Br
Me
CO2Me
4n
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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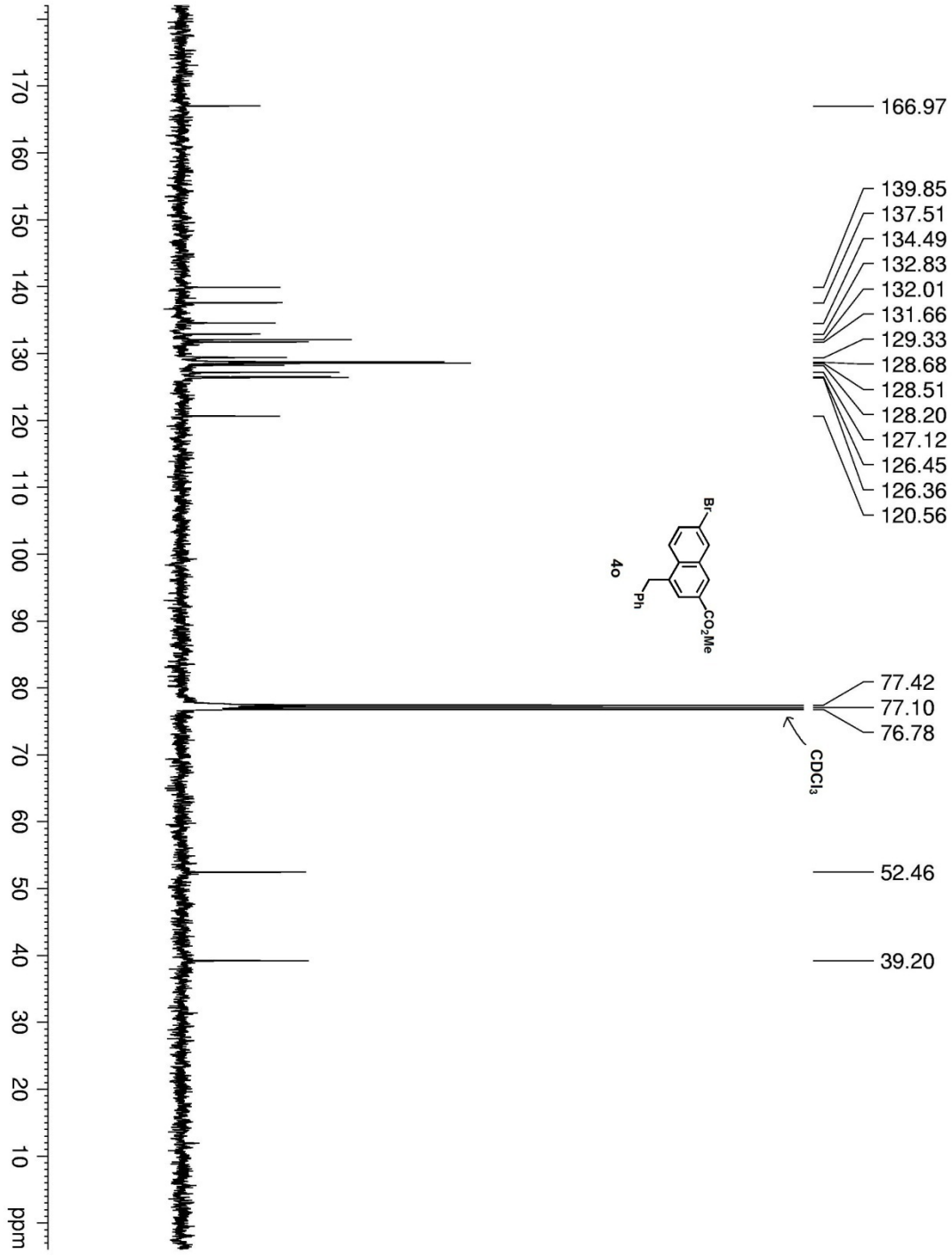
8.112
8.108
7.963
7.864
7.842
7.600
7.596
7.578
7.573
7.276
7.259
7.239
7.204
7.187
7.155
7.137
4.448
3.974
1.563
0.000
1.00
0.98
0.99
1.03
1.01
3.11
3.08
1.99
3.03
CHCl3
TMS
Br
4o
Ph
CO2Me
ppm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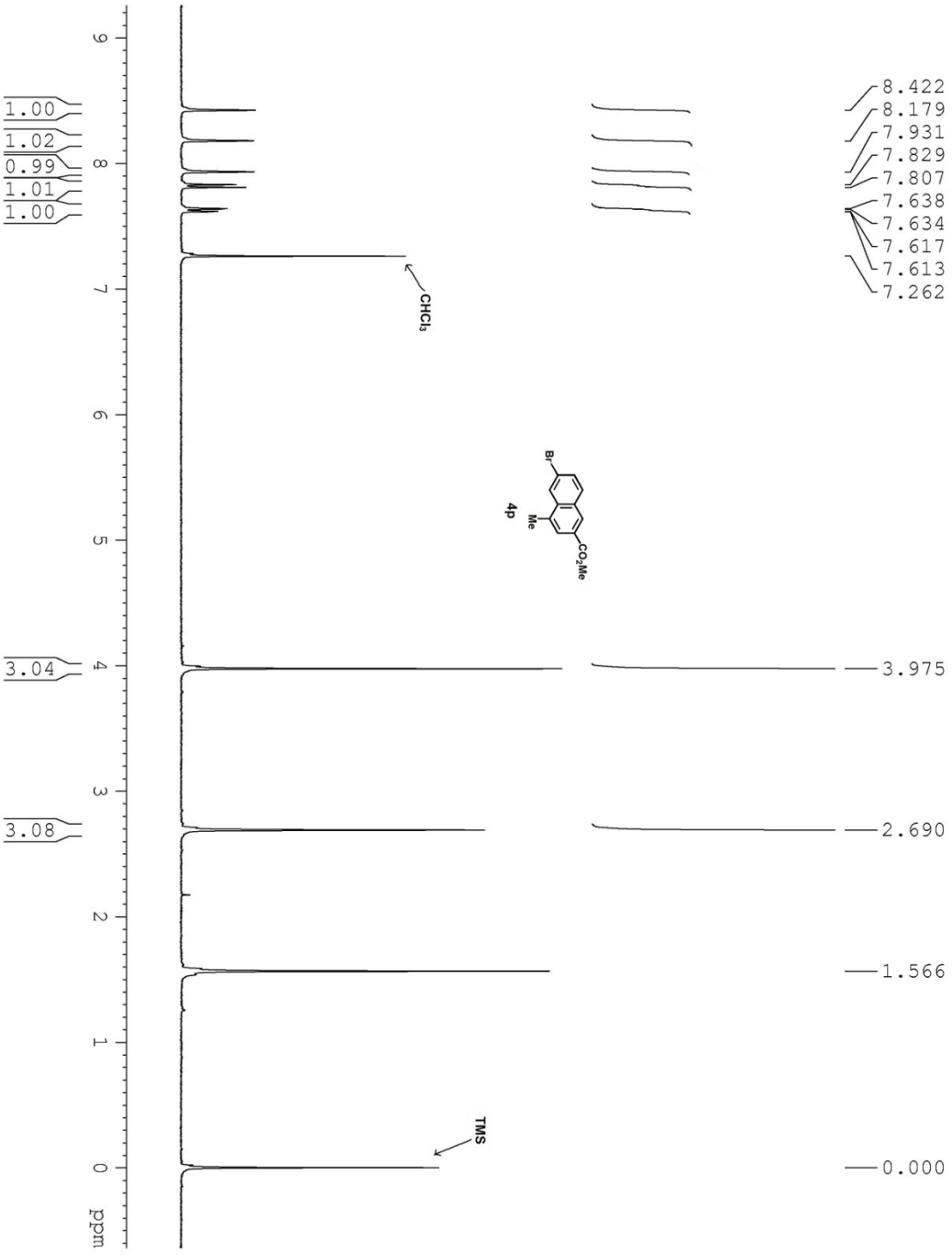
134.49
132.83
132.01
131.66
129.33
128.68
128.51
128.20
127.12
126.45
126.36
120.56
77.42
77.10
76.78
CDCl3
52.46
39.20
Br
Ph
CO2Me
4o
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.829
7.807
7.638
7.634
7.617
7.613
7.262
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1.02
0.99
1.01
1.00
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CHCl3
TMS
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Me
CO2Me
4p
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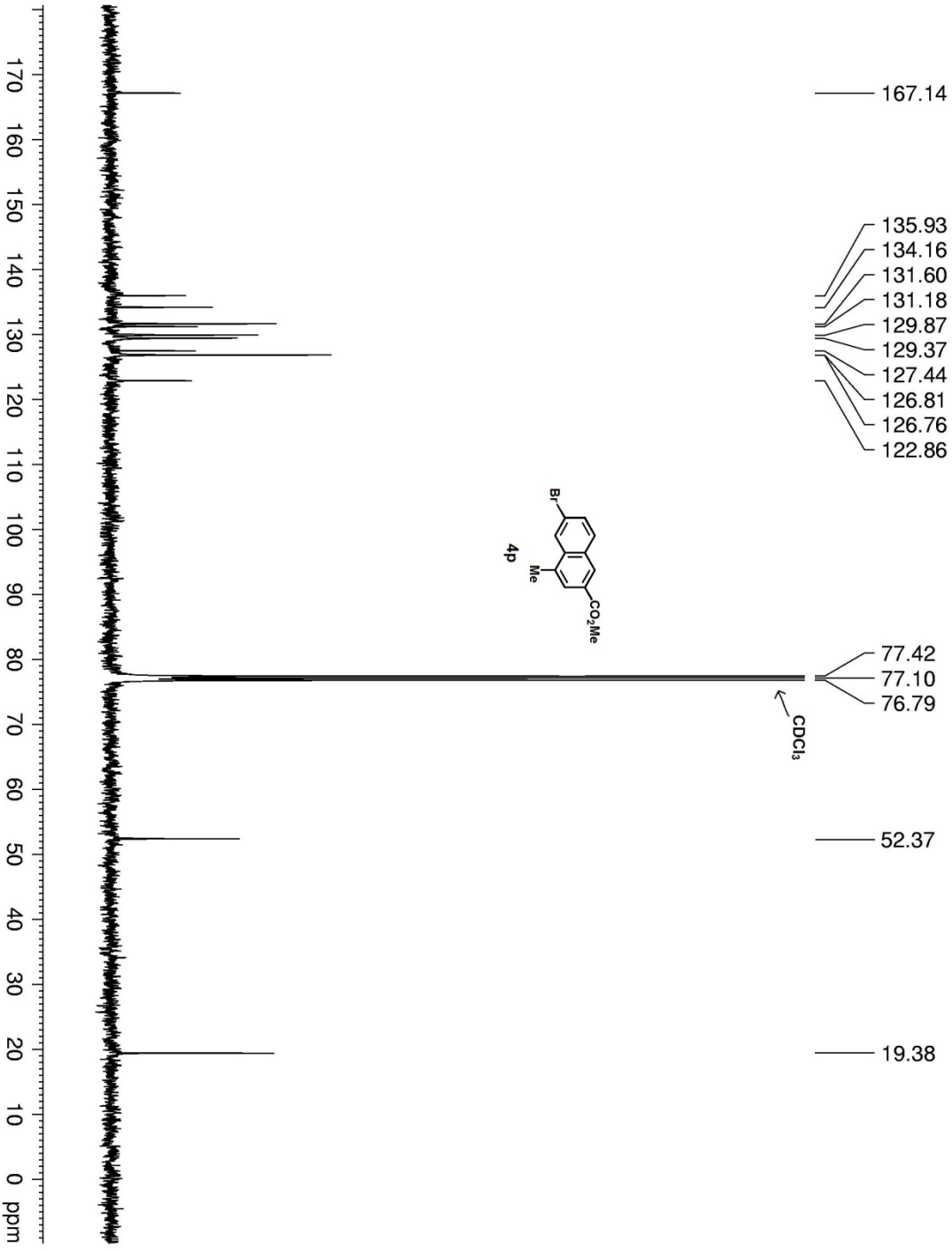
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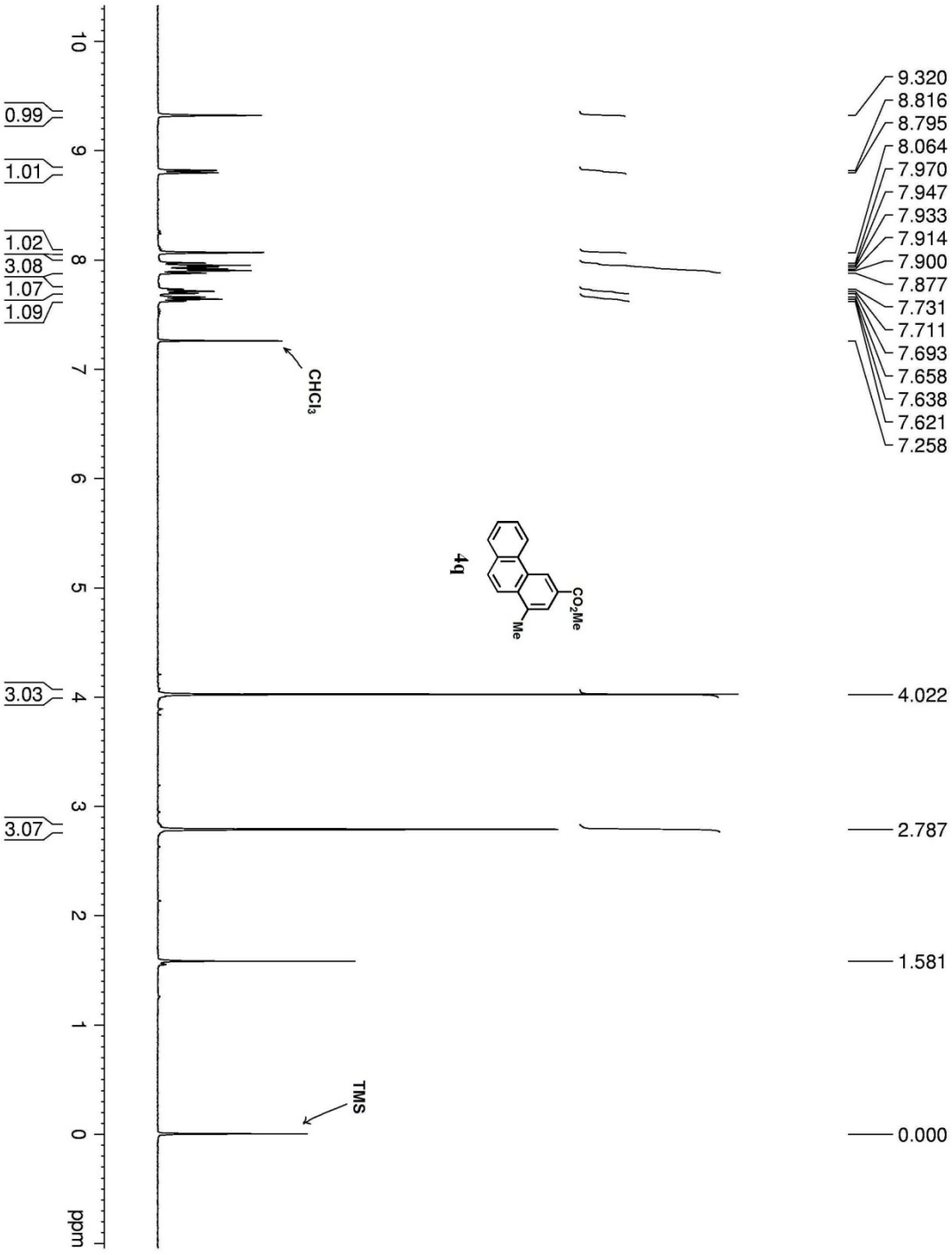
134.16
131.60
131.18
129.87
129.37
127.44
126.81
126.76
122.86
Br
Me
CO2Me
4p
77.42
77.10
76.79
CDCl3
52.37
19.38
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.947
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7.914
7.900
7.877
7.731
7.711
7.693
7.658
7.638
7.621
7.258
0.99
1.01
1.02
3.08
1.07
1.09
3.03
3.07
4.022
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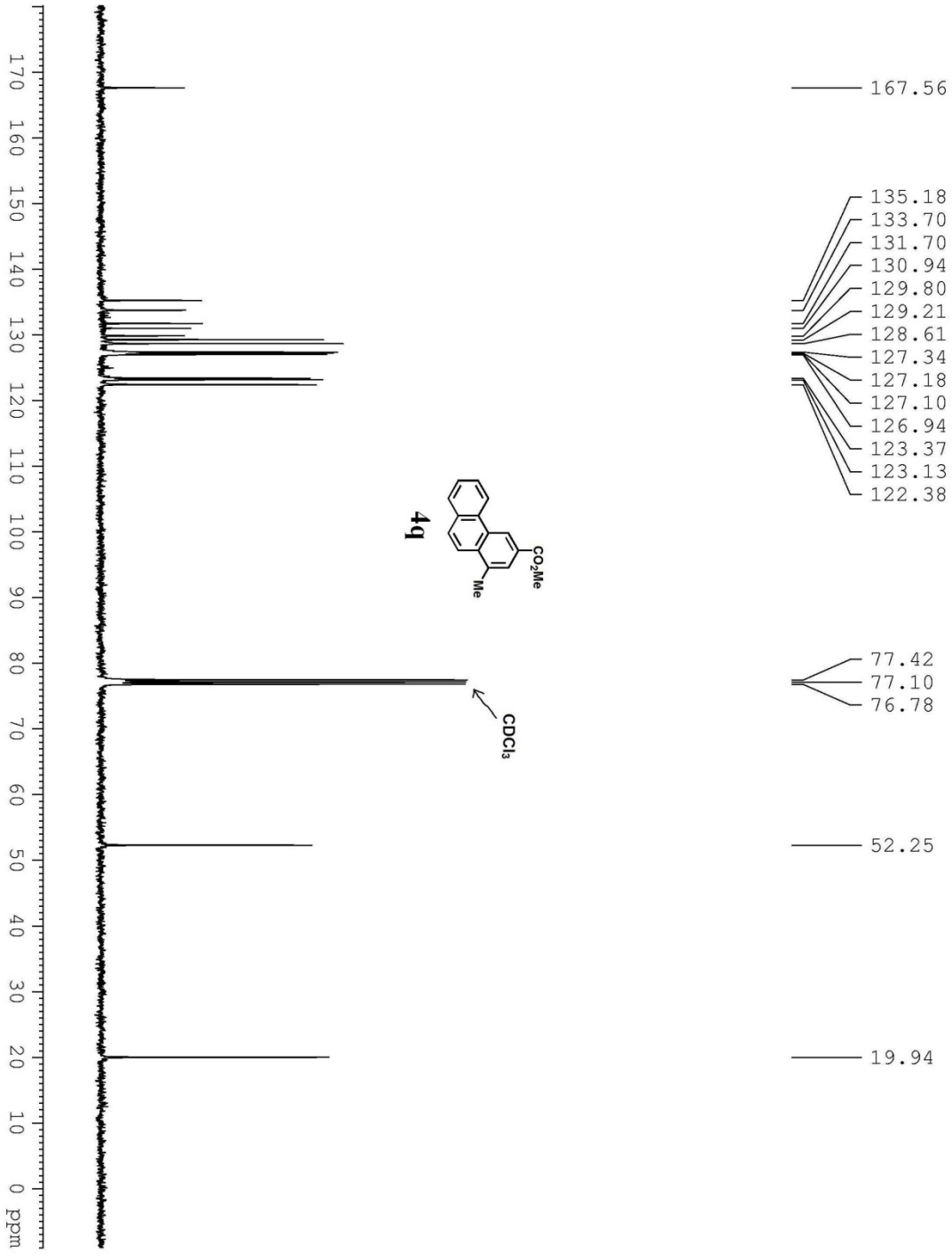
0.000
CHCl3
TMS
4q
CO2Me
Me
ppm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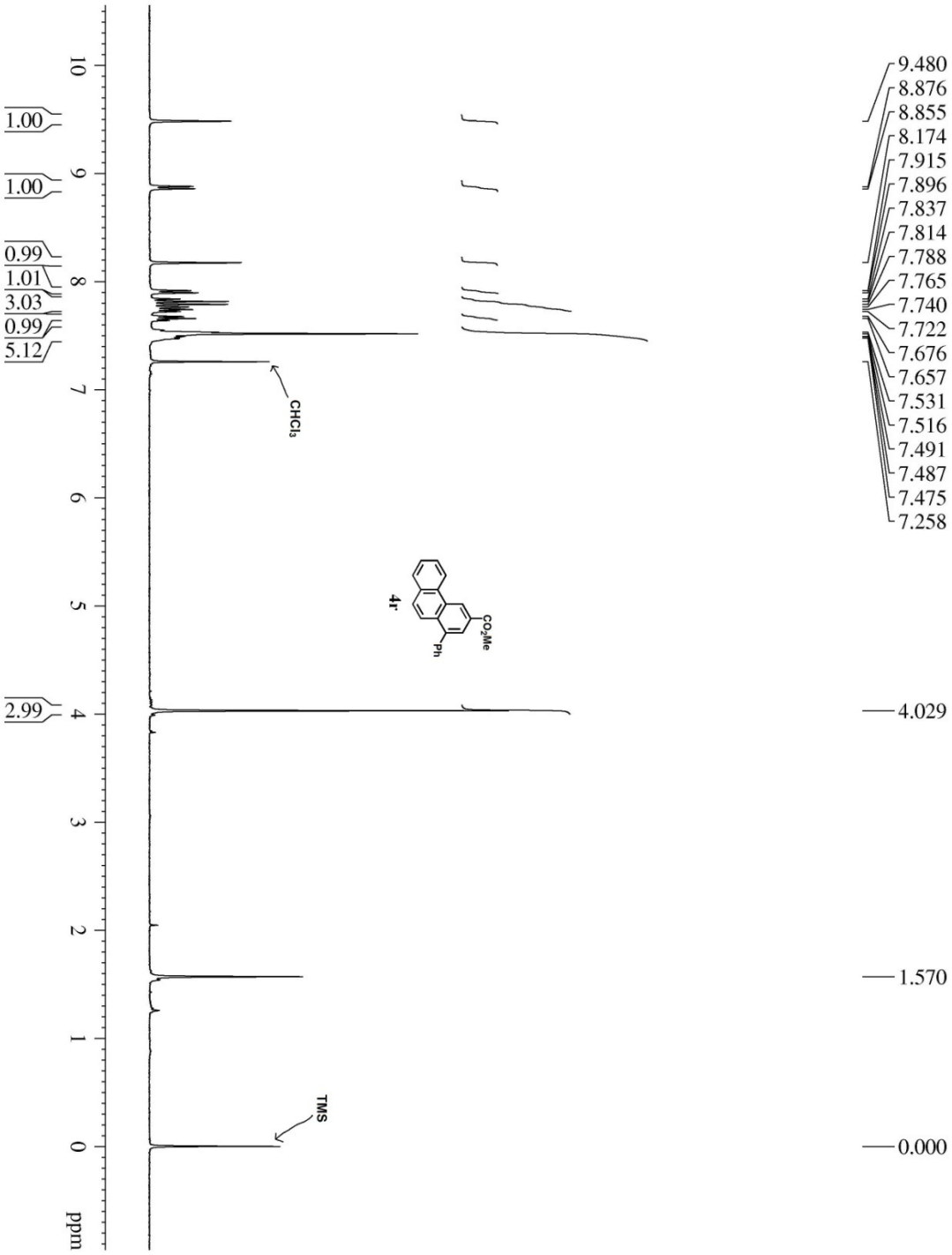
129.80
129.21
128.61
127.34
127.18
127.10
126.94
123.37
123.13
122.38
77.42
77.10
76.78
52.25
19.94
CDCl3
4q
CO2Me
Me
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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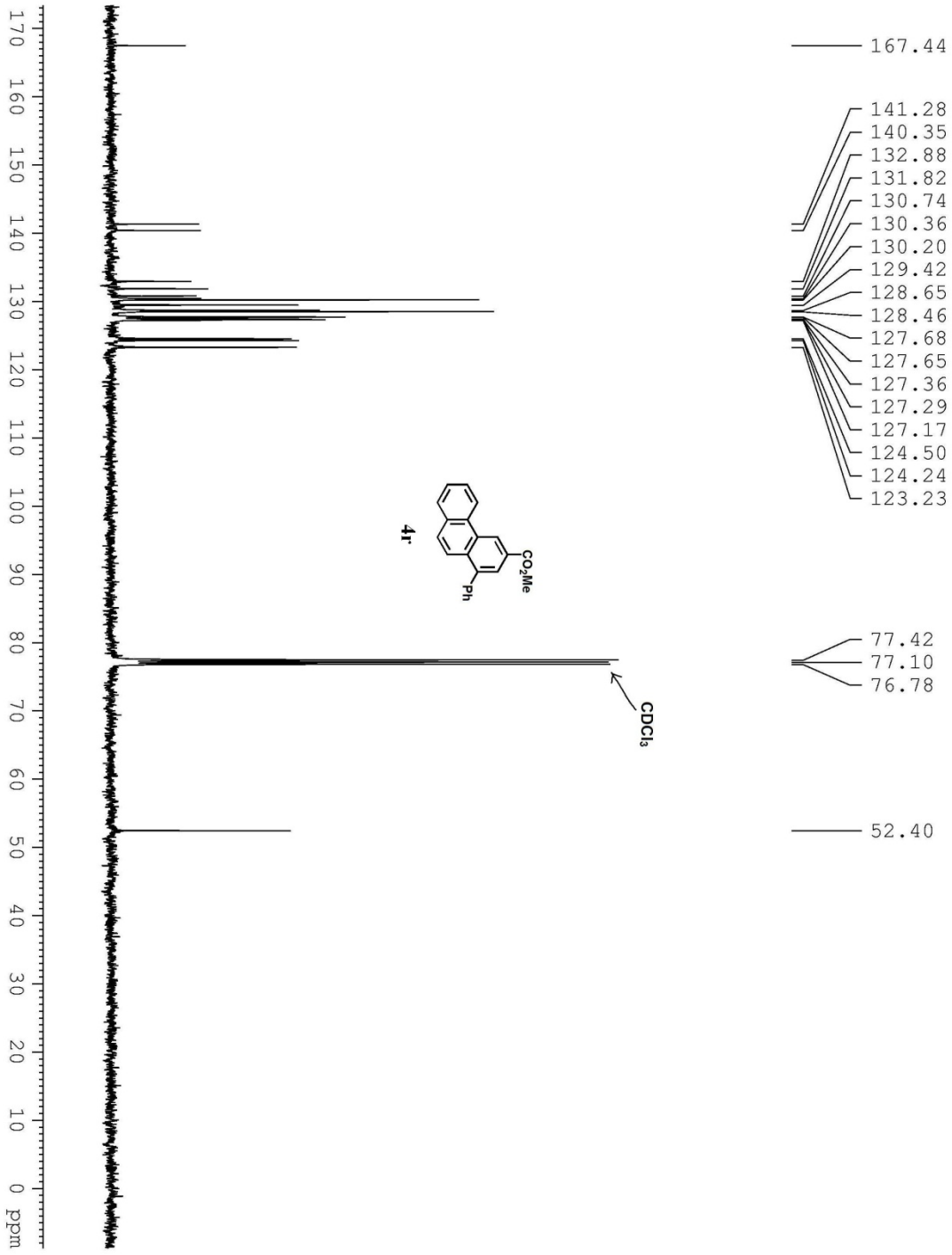
8.855
8.174
7.915
7.896
7.837
7.814
7.788
7.765
7.740
7.722
7.676
7.657
7.531
7.516
7.491
7.487
7.475
7.258
4.029
1.570
0.000
1.00
1.00
0.99
1.01
3.03
0.99
5.12
2.99
CHCl3
TMS
4r
CO2Me
Ph
ppm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130.74
130.36
130.20
129.42
128.65
128.46
127.68
127.65
127.36
127.29
127.17
124.50
124.24
123.23
77.42
77.10
76.78
52.40
CDCl3
4r
CO2Me
Ph
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

8.591
8.587
8.072
8.068
7.859
7.837
7.805
7.783
7.762
7.740
7.510
7.497
7.478
7.463
7.448
7.436
7.431
7.417
7.257
7.156
7.154
7.135
7.117
3.989
1.565
0.000
1.01
1.02
2.00
2.03
6.05
1.01
3.09
CHCl3
TMS
4s
Ph
CO2Me
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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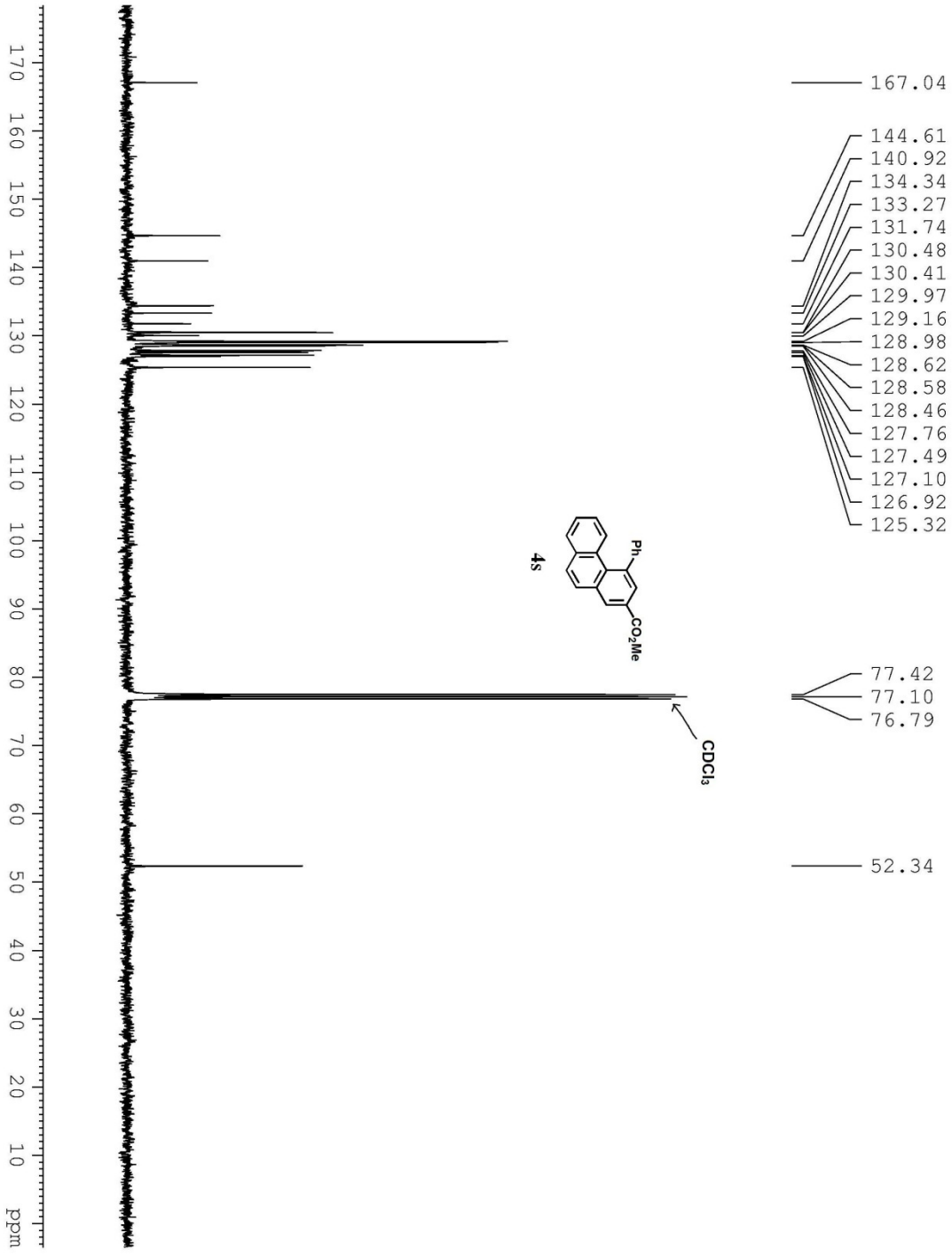
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm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130.48
130.41
129.97
129.16
128.98
128.62
128.58
128.46
127.76
127.49
127.10
126.92
125.32
77.42
77.10
76.79
52.34
CDCl3
4s
Ph
CO2Me
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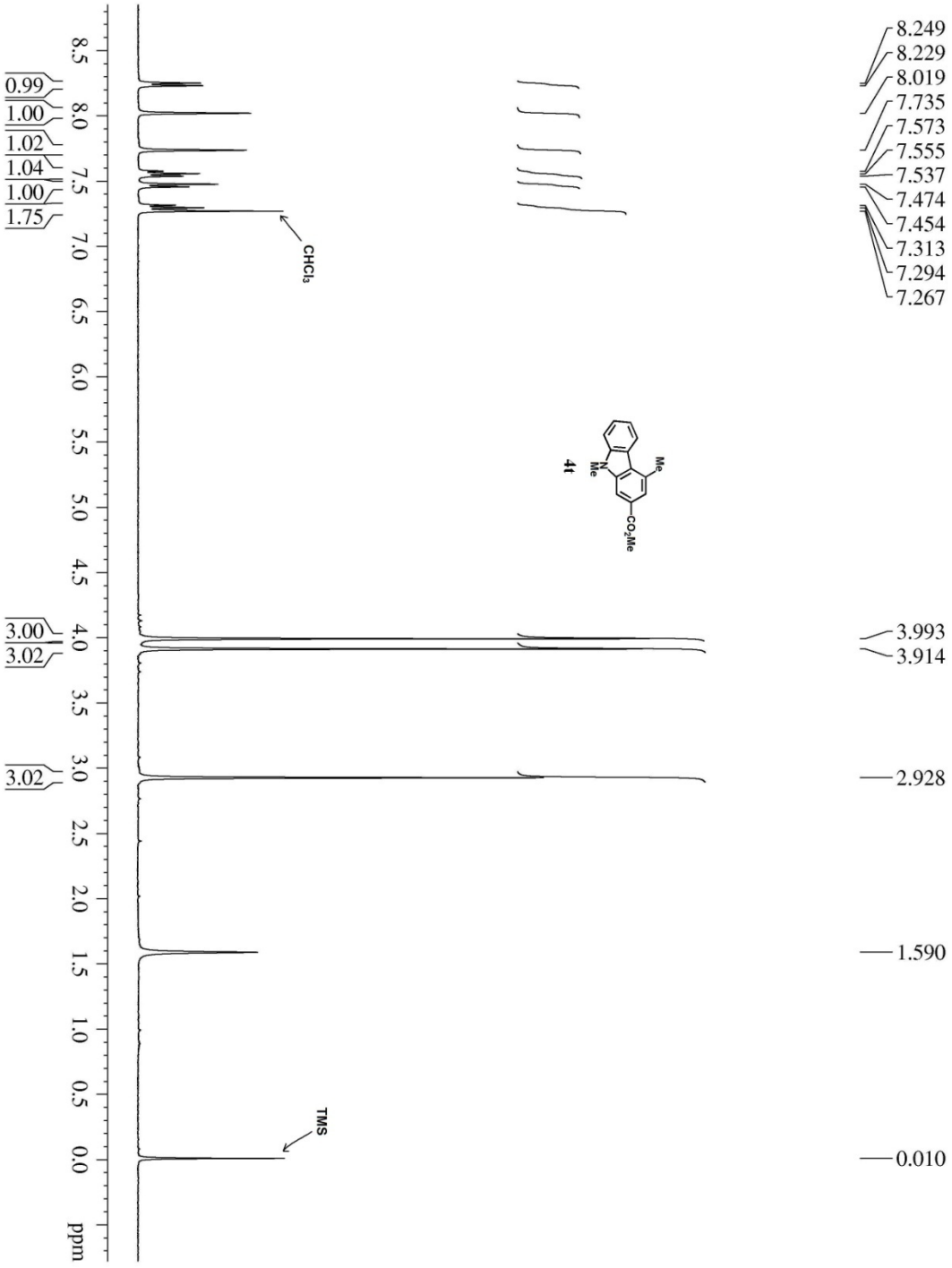
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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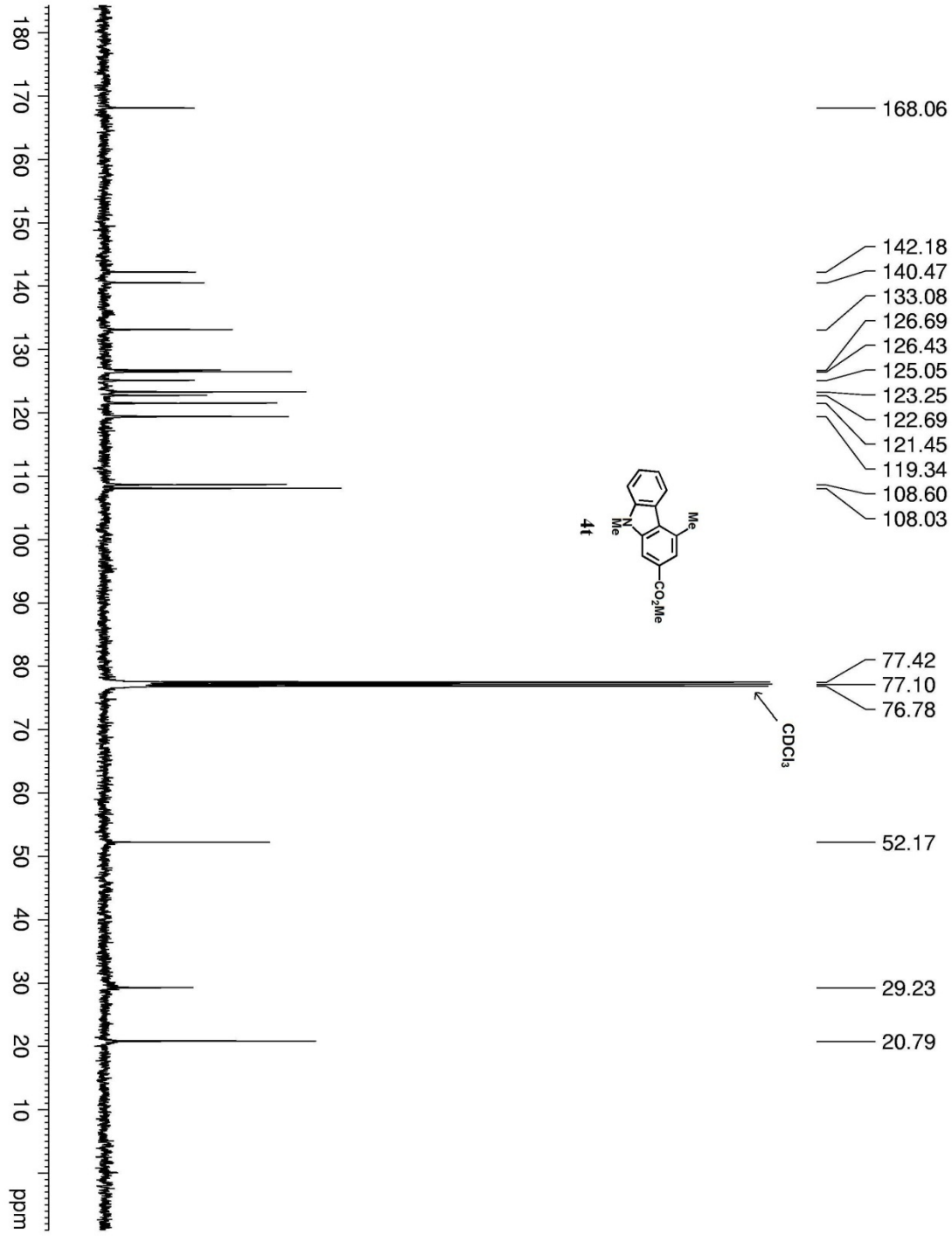
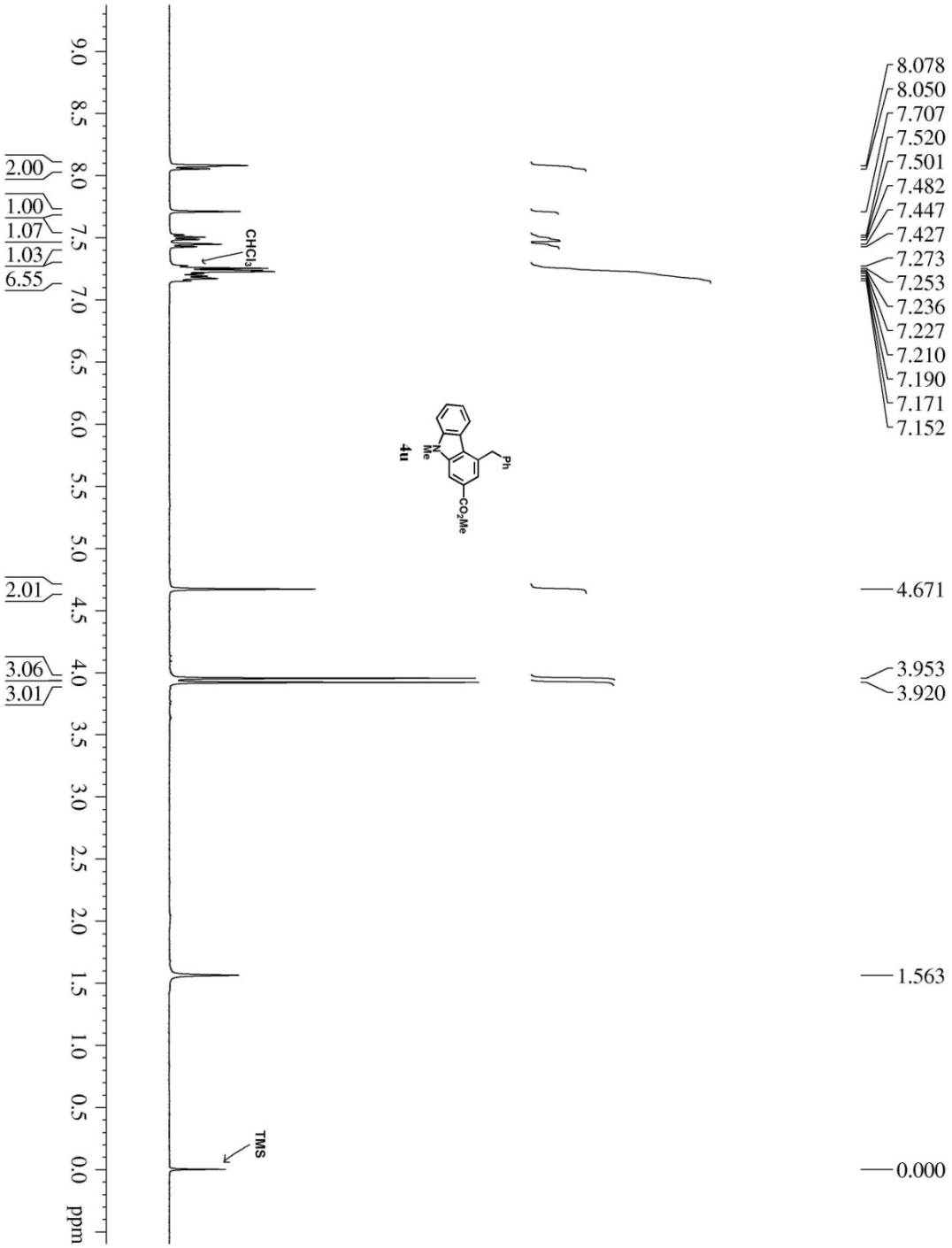
7.573
7.555
7.537
7.474
7.454
7.313
7.294
7.267
3.993
3.914
2.928
1.590
0.010
0.99
1.00
1.02
1.04
1.00
1.75
3.00
3.02
3.02
CHCl3
TMS
4t
Me
N
Me
CO2Me
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


168.06
142.18
140.47
133.08
126.69
126.43
125.05
123.25
122.69
121.45
119.34
108.60
108.03
77.42
77.10
76.78
52.17
29.23
20.79
CDCl3
4t
Me
N
Me
CO2Me
ppm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7.253
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7.227
7.210
7.190
7.171
7.152
4.671
3.953
3.920
1.563
0.000
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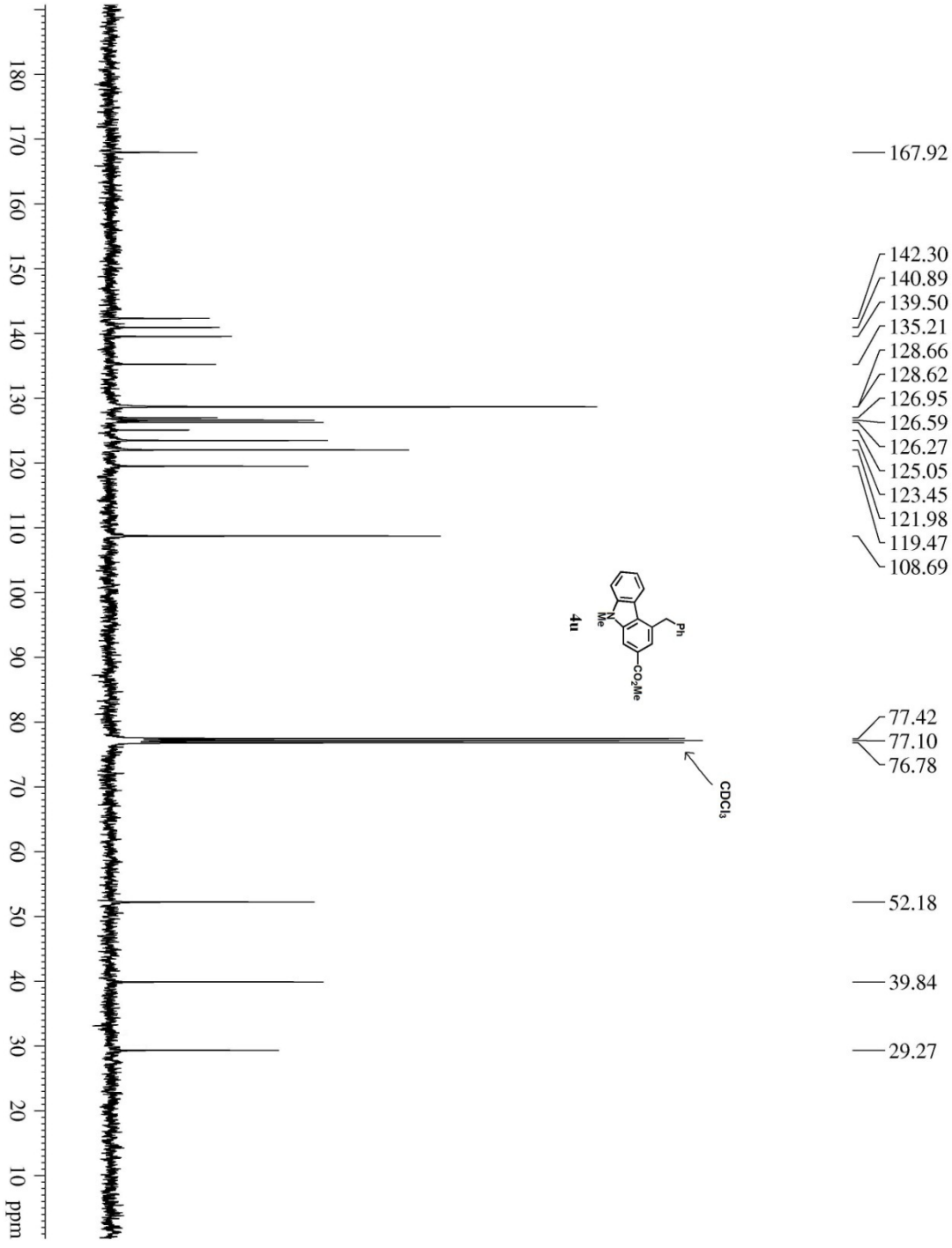
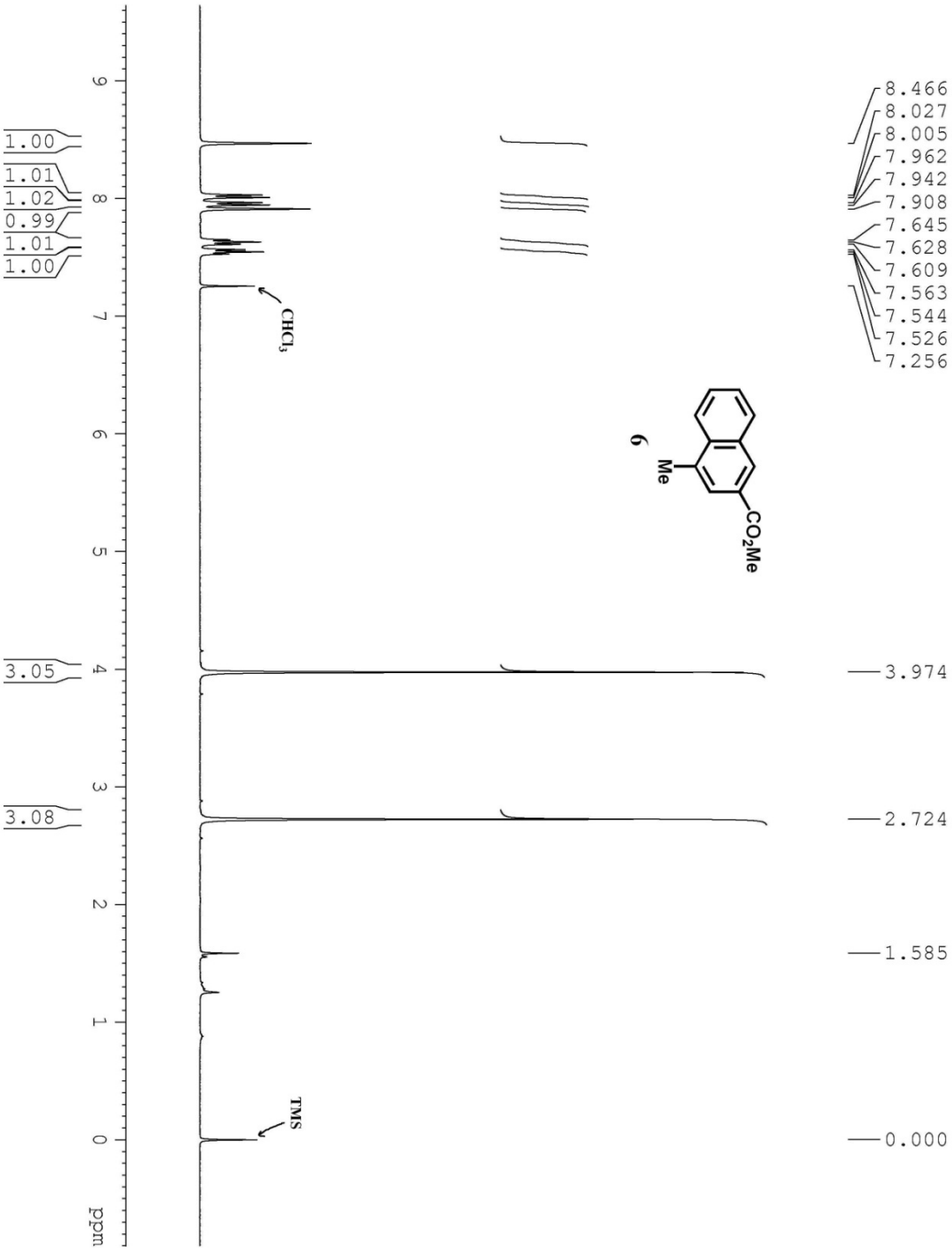
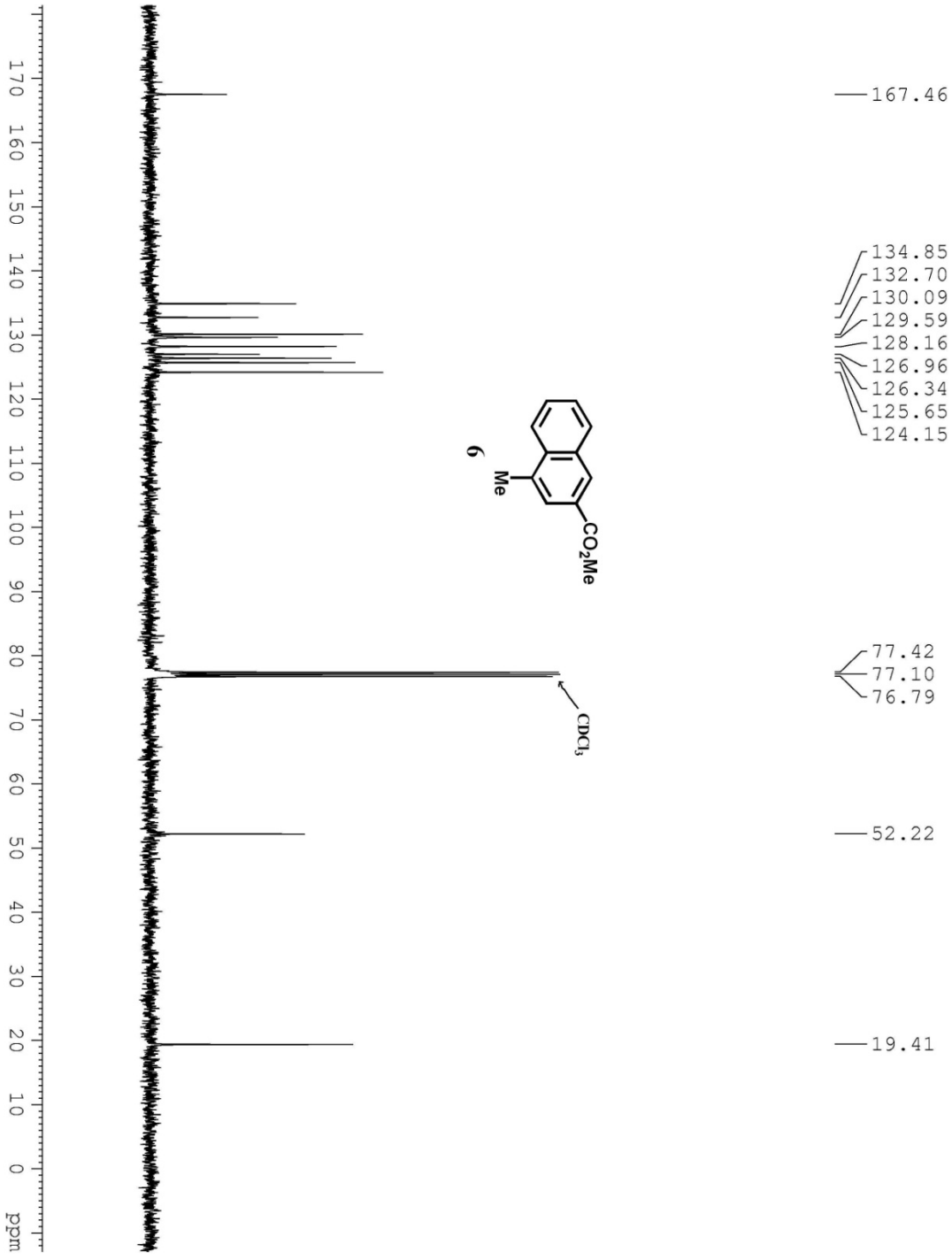
1.00
1.07
1.03
6.55
2.01
3.06
3.01
CHCl3
TMS
4u
Me
N
Ph
CO2Me
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


167.92
142.30
140.89
139.50
135.21
128.66
128.62
126.95
126.59
126.27
125.05
123.45
121.98
119.47
108.69
77.42
77.10
76.78
52.18
39.84
29.27
CDCl3
4lu
Me
N
Ph
CO2Me
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.466
8.027
8.005
7.962
7.942
7.908
7.645
7.628
7.609
7.563
7.544
7.526
7.256
1.00
1.01
1.02
0.99
1.01
1.00
3.05
3.08
CHCl3
TMS
3.974
2.724
1.585
0.000
ppm
Me
CO2Me
6


167.46
134.85
132.70
130.09
129.59
128.16
126.96
126.34
125.65
124.15
77.42
77.10
76.79
52.22
19.41
CDCl3
CO2Me
Me
6
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm