Gold-Catalyzed Rearrangement of *O*-Vinyl Oximes for the Synthesis of Highly Substituted Pyrroles

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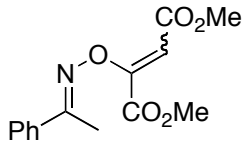
I. General Experimental Information

Unless otherwise indicated, all commercially available reagents and solvents were used directly from the supplier without further purification. THF, toluene and DCM were dried over sodium / benzophenone, sodium and calcium carbonate respectively and purified by distillation prior to use. Solvents used for column chromatography were of technical grade. Column chromatography was performed on silica gel (60-120) mesh. Visualization was accomplished with UV light and a potassium permanganate solution. ^{1}H NMR and ^{13}C NMR were recorded at ambient temperature using $CDCl_3$ (7.27 ppm) or toluene-d^8 (2.09). Chemical shift values are expressed as parts per million (ppm) and *J* values are in Hertz. Splitting patterns are indicated as s: singlet, d: doublet, t: triplet, q: quartet or combination, br.s broad singlet or m: multiplet. The melting points reported are uncorrected. Microwave reactions were run in a sealed reaction vessel in a Biotage Initiator 2.0 microwave and the temperature of the reaction was monitored by IR.

II. Preparation of vinyl oximes (4a-5e)

General Procedure A: To a stirred solution of DABCO (0.1 equiv) and oxime (1 equiv) in dichloromethane at -10 °C was added drop wise a solution of an alkyne (1 equiv) in dichloromethane over 15 minutes. The reaction mixture was allowed to warm to room temperature and stirred for 12 hours. The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel.

Preparation of vinyl oximes 4a-4i and 5a-5e



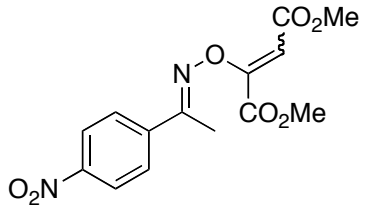
4a

Dimethyl 2-(((*E/Z*)-(1-Phenylethylidene)amino)oxy)maleate (4a).

Vinyl oxime **4a** was synthesized according to general procedure A. To a stirred solution of DABCO (45 mg, 0.37 mmol) and (*E*)-acetophenone oxime (500 mg, 3.7 mmol) in dichloromethane (32 mL) was added drop wise a mixture of dimethylacetylene dicarbonate (0.61 mL, 0.37 mmol) in dichloromethane (12 mL). The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (6:1 Petroleum/EtOAc) to afford dimethyl 2-(((*E/Z*)-(1-phenylethylidene)amino)oxy)maleate (**4a**, 762 mg, 79%) as a colourless oil that is an inseparable *E:Z* mixture (1:8), which had spectra identical to that reported in the literature.[i] IR ($CHCl_3$) ν (cm^{-1}), 3435, 3086, 2953, 2888, 2494, 1956, 1722, 1642, 1573, 1437, 1308, 1274, 1135, 1026, 946, 844, 637 cm^{-1}; HRMS (ESI) m/z Calcd for $C_{14}H_{15}NO_5Na$, 300.0848; found, 300.0849.

For (E)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.68-7.64 (m, 2H), 7.43-7.36 (m, 3H), 6.05 (s, 1H), 3.88 (s, 3H), 3.70 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C: 165.1, 163.0, 160.2, 153.5, 134.7, 129.9, 128.1, 126.5, 105.5, 52.7, 50.4, 13.8.

For (Z)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.70-7.68 (m, 2H), 7.49-7.44 (m, 3H), 5.94 (s, 1H), 3.96 (s, 3H), 3.47 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C; 13.8, 50.3, 52.7 , 96.1, 126.5, 128.0, 129.8, 134.6, 153.46, 160.1, 163.0, 165.1.

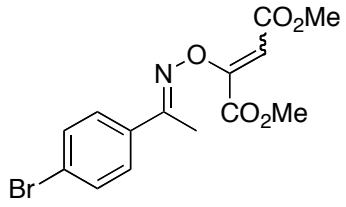


4b

Dimethyl 2-(((*E/Z*)-(1-(4-Nitrophenyl)ethylidene)amino)oxy)fumarate (4b). Vinyl oxime **4b** was synthesized according to general procedure A. To a stirred solution of DABCO (19 mg, 0.17 mmol) and (*E*)-1-(4-nitrophenyl)ethanone oxime (300 mg, 1.7 mmol) in dichloromethane (12 mL) was added drop wise a mixture of dimethylacetylene dicarbonate (0.27 mL, 1.7 mmol) in dichloromethane (4.5 mL). The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (6:1 Petroleum/EtOAc) to afford dimethyl 2-(((*E/Z*)-(1-(4-nitrophenyl)ethylidene)amino)oxy)fumarate (**4b**, 452 mg, 84%) as an orange solid that is an inseparable *E:Z* mixture (1:9). m.p. 58-60°C; IR ($CHCl_3$) ν (cm^{-1}) 3630, 3569, 3044, 2848, 2337, 1804, 1725, 1654, 1524, 1437, 1348, 1275, 1179, 901; HRMS (ESI) m/z Calcd for $C_{14}H_{14}N_2O_7Na$, 345.0693; found, 345.0699.

For (E)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.24 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 8.1 Hz, 2H), 3.88 (s, 3H), 6.14 (s, 1H), 3.71 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 164.6, 162.6, 158.3, 153.1, 148.8, 140.7, 127.6, 123.8, 107.4, 53.0, 51.9, 13.6.

For (Z)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.31 (d, J = 8.9 Hz, 2H), 7.86 (d, J = 9.1 Hz, 2H), 5.93 (s, 1H), 3.95 (s, 3H), 3.74 (s, 3H), 2.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 166.1, 162.8, 162.8, 159.7, 149.1, 140.2, 127.7, 123.9, 97.2, 53.1, 51.8, 13.9.

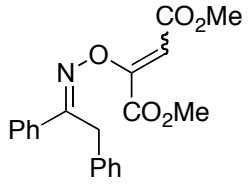


4c

Dimethyl 2-(((*E/Z*)-(1-(4-Bromophenyl)ethylidene)amino)oxy)fumarate (4c). Vinyl oxime **4c** was synthesized according to general procedure A. To a stirred solution of DABCO (13 mg, 0.11 mmol) and (*E*)-1-(4-bromophenyl)ethanone oxime (250 mg, 1.1 mmol) in dichloromethane (8 mL) was added drop wise a mixture of dimethylacetylene dicarbonate (0.19 mL, 1.1 mmol) in dichloromethane (3 mL). The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (7:1 Petroleum:EtOAc) to afford dimethyl 2-(((*E/Z*)-(1-(4-bromophenyl)-ethylidene)amino)oxy)fumarate (**4c**, 317 mg, 76 %) as a colourless oil that is an inseparable *E:Z* mixture (1:9). IR ($CHCl_3$) ν (cm^{-1}) 3630, 3569, 3044, 2954, 2848, 2337, 1804, 1725, 1654, 1524, 1348, 1275, 954, 855; HRMS (ESI) m/z Calcd for $C_{14}H_{14}BrNO_5Na$, 377.9953; found, 377.9951.

For (E)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.53-7.49 (m, 4H), 6.07 (s, 1H), 3.87 (s, 3H), 3.69 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 164.9, 162.8, 159.2, 153.3, 133.5, 131.7, 128.1, 124.7, 106.1, 52.8, 51.8, 13.5.

For (Z)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.55-7.53 (m, 4H), 5.91 (s, 1H) 3.94 (s, 1H), 3.73 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 166.4, 160.7, 152.2, 135.7, 133.0, 131.9, 128.2, 125.3, 96.3, 53.0, 51.7, 13.7.

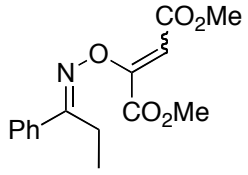


4d

Dimethyl 2-(((*E/Z*)-(1,2-Diphenylethylidene)amino)oxy)fumarate (4d). Vinyl oxime **4d** was synthesized according to general procedure A. To a stirred solution of DABCO (46 mg, 0.38 mmol) and (*E*)-1,2-diphenylethanone oxime (800 mg, 3.8 mmol) in dichloromethane (32 mL) was added drop wise a mixture of dimethylacetylene dicarbonate (0.62 mg, 3.8 mmol) in dichloromethane (12 mL). The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (6:1 Petrol:EtOAc) to afford dimethyl 2-(((*E/Z*)-(1,2-diphenylethylidene)amino)oxy)fumarate (**4d**, 1.06 g, 85 %) as a colourless oil that is an inseparable *E:Z* mixture (1:9). IR ($CHCl_3$) ν (cm^{-1}) 3630, 2412, 3011, 2954, 2848, 2412, 1724, 1652, 1447, 1365, 1272, 1109, 1025, 885; HRMS (ESI) m/z Calcd for $C_{20}H_{19}NO_5Na$, 376.1161; found, 376.1162.

For (E)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.66 (dd, J = 8.2, 1.4 Hz, 2H), 7.46-7.41 (m, 6H), 7.38-7.34 (m, 2H), 6.17 (s, 1H), 4.46 (s, 2H), 3.94 (s, 3H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 164.7, 162.6, 160.7, 152.7, 135.2, 133.4, 129.9, 128.41, 128.4, 128.3, 128.3, 128.21, 128.2, 126.8, 126.79, 126.3, 106.1, 52.5, 51.4, 33.1.

For (Z)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.73 (dd, J = 7.0, 1.36 Hz, 2H), 7.49-7.41 (m, 10H), 6.01 (s, 1H), 4.24-4.20 (m, 2H), 3.94, (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 161.7, 161.3, 158.5, 142.9, 134.6, 132.8, 130.5, 129.2, 129.1, 128.5, 128.33, 128.31, 128.1, 128.0, 127.0, 126.5, 96.2, 52.7, 51.3, 33.3.



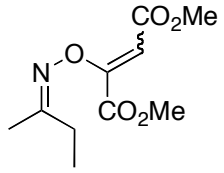
4e

Dimethyl 2-(((*E/Z*)-(1-Phenylpropylidene)amino)oxy)fumarate (4e). Vinyl oxime **4e** was synthesized according to general procedure A. To a stirred solution of DABCO (28 mg, 0.25 mmol) and (*E/Z*)-propiophenone oxime oxime (375 mg, 2.5

mmol) in dichloromethane (20 mL) was added drop wise a mixture of dimethylacetylene dicarbonate (0.41 mL, 2.5 mmol) in dichloromethane (9 mL). The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (7:1 Petroleum:EtOAc) to afford dimethyl 2-(((*E*/*Z*)-(1-phenylpropylidene)amino)oxy)-fumarate (**4e**, 507 mg, 74%) as a colourless oil that is an inseparable *E:Z* mixture (1:4). IR ($CHCl_3$) ν (cm^{-1}) 3645, 3007, 2876, 1723, 1634, 1436, 1366, 1274, 1274, 1273, 979, 908; HRMS (ESI) m/z Calcd for $C_{15}H_{17}NO_5Na$, 314.1004; found, 314.1001.

For (E)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.68-7.64 (m, 2H), 7.44-7.42 (m, 3H), 6.08 (s, 1 H), 3.95 (s, 3H), 3.78-3.75 (m, 3H), 2.94 (q, *J* = 7.6 Hz, 2H), 1.35 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 165.1, 164.7, 163.1, 153.7, 133.6, 130.2, 128.5, 126.8, 105.5, 52.8, 51.7, 21.2, 11.0.

For (Z)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.74-7.71 (m, 2H), 7.45-7.42 (m, 3H), 5.95 (s, 1H), 4.02 (s, 3H), 3.73 (s, 3H), 2.92 (d, *J* = 7.8 Hz, 2 H), 1.23 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 166.7, 166.5, 160.8, 133.2, 130.7, 128.7, 128.1, 127.0, 105.9, 53.0, 51.6, 28.7, 11.3.

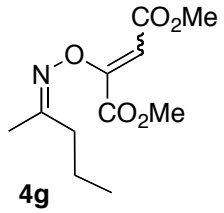


4f

Dimethyl 2-(((*E/Z*)-Butan-2-ylideneamino)oxy)fumarate (4f). Vinyl oxime **4f** was synthesized according to general procedure A. To a stirred solution of DABCO (56 mg, 0.46 mmol) and (*E/Z*)-butan-2-one oxime (400 mg, 4.6 mmol) in dichloromethane (32 mL) was added drop wise a mixture of dimethylacetylene dicarbonate (0.76 mL, 4.6 mmol) in dichloromethane (12 mL). The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (10:1 Petroleum:EtOAc) to afford dimethyl 2-(((*E/Z*)-butan-2-ylideneamino)oxy)fumarate (**4f**, 906 mg, 86%) as a colourless oil that is an inseparable *E:Z* mixture (1:9). IR ($CHCl_3$) ν (cm^{-1}) 3643, 3010, 2855, 2224, 1707, 1642, 1572, 1393, 1283, 1127, 1048, 869, 843, 633; HRMS (ESI) m/z Calcd for $C_{10}H_{15}NO_5Na$, 252.0848; found, 252.0841.

For (E)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 5.96 (s, 1H), 3.85 (s, 3H), 3.74 (s, 3H), 2.37 (q, *J* = 7.5 Hz, 2H), 2.04 (s, 3H), 1.15 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 165.1, 164.7, 163.3, 154.3, 104.4, 52.7, 51.6, 28.8, 14.8, 10.3.

For (Z)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 5.82 (s, 1H), 3.94 (s, 3H), 3.72 (s, 3H), 2.53 (q, *J* = 7.5 Hz, 2H), 1.94 (s, 3H), 1.22 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 166.5, 165.3, 165.0, 104.7, 95.1, 52.9, 51.5, 23.4, 18.9, 9.9.

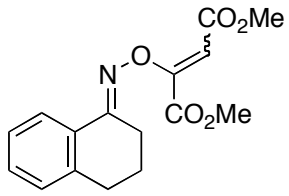


4g

Dimethyl 2-(((*E/Z*)-Pentan-2-ylideneamino)oxy)fumarate (4g). Vinyl oxime **4g** was synthesized according to general procedure A. To a stirred solution of DABCO (48 mg, 0.40 mmol) and (*E/Z*)-pentan-2-one oxime (400 mg, 4.0 mmol) in dichloromethane (32 mL) was added drop wise a mixture of dimethylacetylene dicarbonate (0.65 mL, 4.0 mmol) in dichloromethane (12 mL). The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (9:1 Petroleum:EtOAc) to afford dimethyl 2-(((*E/Z*)-pentan-2-ylideneamino)oxy)fumarate (**4g**, 568 mg, 59 %) as a colourless oil that is an inseparable *E:Z* mixture (1:9) as a colourless oil. IR ($CHCl_3$) ν (cm^{-1}) 3653, 3017, 2859, 2235, 1735, 1667, 1567, 1343, 1278, 1188, 1034, 835, 841, 623; HRMS (ESI) m/z Calcd for $C_{11}H_{17}NO_5Na$, 266.1004; found, 266.1009**.**

For (E)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 5.94 (s, 1H), 3.88 (s, 3H), 3.75 (s, 3H), 2.27 (t, *J* = 7.5 Hz, 2 H), 2.05 (s, 3H), 1.57 (q, *J* = 7.5 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 165.0, 163.6, 163.2, 154.4, 104.4, 52.6, 51.5, 37.2, 19.2, 14.9, 13.5.

For (Z)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 5.84 (s, 1H), 3.93 (s, 1H), 3.74 (s, 1H), 2.56 (t, *J* = 7.4 Hz, 2 H), 1.92 (s, 3H), 1.65 (q, *J* = 7.4 Hz, 2H), 1.06 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 165.0, 164.1, 163.2, 154.1, 104.5, 53.4, 51.5, 31.9, 19.4, 19.0, 14.0.

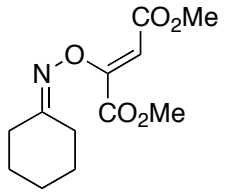


4h

Dimethyl 2-(((*E/Z*)-(3,4-Dihydronaphthalen-1(2H)-ylidene)amino)oxy)fumarate (4h). Vinyl oxime **4h** was synthesized according to general procedure A. To a stirred solution of DABCO (34mg, 0.28 mmol) and (*E*)-3,4-dihydronaphthalen-1(2H)-one oxime (400 mg, 2.8 mmol) in dichloromethane (24 mL) was added drop wise a mixture of dimethylacetylene dicarbonate (0.46 mL, 2.8 mmol) in dichloromethane (9 mL). The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (7:1 Petroleum:EtOAc) to afford dimethyl 2-(((*E/Z*)-(3,4-dihydronaphthalen-1(2H)-ylidene)amino)oxy)fumarate (**4h**, 696 mg, 82%) as a colourless oil that is an inseparable *E:Z* mixture (1:9). IR ($CHCl_3$) ν (cm^{-1}) 3667, 3445, 3023, 2956, 2878, 2446, 1746, 1612, 1568, 1479, 1275, 1142, 1123, 1058, 958, 613; HRMS (ESI) m/z Calcd for $C_{16}H_{17}NO_5Na$, 326.1004; found, 326.1005.

For (E)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.94 (dd, J = 7.9, 0.9 Hz, 1H), 7.44 (dd, J = 7.5, 1.5 Hz, 1H), 7.36-7.32 (m, 2 H), 6.16 (s, 1H), 4.03 (s, 3 H), 3.87 (s, 3 H), 3.15 (t, J = 6.6 Hz, 2H), 2.94-2.91 (m, 2H), 2.06 (q, J = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 165.1, 163.0, 159.1, 153.7, 140.6, 130.3, 128.7, 126.4, 124.9, 104.9, 52.7, 51.7, 29.5, 25.0, 21.1.

For (Z)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.13 (dd, J = 7.6, 0.9 Hz, 1H), 7.45 (dd, J = 7.6, 1.4 Hz, 1H), 7.37-7.34 (m, 2H), 6.05 (s, 1H), 4.07 (s, 3H), 3.84 (s, 3H), 3.06 (t, J = 6.5 Hz, 2H), 2.97 (s, 2H), 2.03 (q, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 166.5, 163.1, 160.8, 160.7, 140.9, 130.8, 128.8, 128.4, 126.5, 125.1, 95.7, 52.9, 51.5, 29.3, 25.1, 21.1.

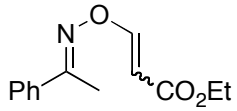


4i

Dimethyl 2-((Cyclohexylideneamino)oxy)but-2-enedioate (4i). Vinyl oxime **4i** was synthesized according to general procedure A. To a stirred solution of DABCO (37 mg, 0.31 mmol) and cyclohexanone oxime (350 mg, 3.1 mmol) in dichloromethane (24 mL) was added drop wise a mixture of dimethylacetylene dicarbonate (0.51 mL, 3.1 mmol) in dichloromethane (9 mL). The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (10:1 Petroleum:EtOAc) to afford dimethyl 2-((cyclohexylideneamino)oxy)but-2-enedioate (**4i**, 735 mg, 93%) as a colourless oil that is an inseparable *E:Z* mixture (1:9). IR ($CHCl_3$) ν (cm^{-1}) 3631, 3411, 3011, 2952, 2860, 2412, 1722, 1638, 1552, 1436, 1272, 1179, 1123, 1026, 928, 627; HRMS (ESI) m/z Calcd for $C_{12}H_{17}NO_5Na$, 278.1004; found, 278.1004.

For (E)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 5.88 (s, 1, H), 3.84 (s, 3H), 3.73 (s, 3H), 2.67-2.64 (m, 2H), 2.24-2.21 (m, 2H), 1.73-1.70 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 165.9, 165.1, 163.3, 154.3, 104.2, 52.7, 51.5, 31.5, 26.7, 26.2, 25.6, 25.4.

For (Z)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 5.77 (s, 1H), 3.91 (s, 3H), 3.70 (s, 3H), 2.54-2.51 (m, 2H), 2.28-2.25 (m, 2H), 1.64-1.62 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 165.6, 164.7, 162.3, 152.3, 104.7, 52.9, 51.4, 32.1, 27.0, 25.3, 23.4, 18.8.



5a

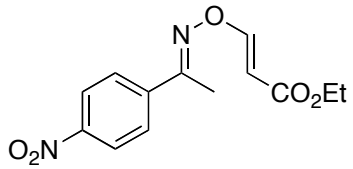
Ethyl 3-(((*E/Z*)-(1-Phenylethylidene)amino)oxy)acrylate (5a).

Vinyl oxime **5a** was synthesized according to general procedure A. To a stirred solution of DABCO (36 mg, 0.3 mmol) and (*E*)-acetophenone oxime (400 mg, 3.0 mmol) in dichloromethane (24 mL) was added drop wise a mixture of ethyl propiolate

(0.28 mL, 3.0 mmol) in dichloromethane (9 mL). The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (4:1 Petroleum/EtOAc) to afford ethyl 3-(((*E/Z*)-(1-phenylethylidene)amino)oxy)acrylate (**5a**, 503 mg, 72%) as a colourless oil that is an inseparable *E:Z* mixture (8:1). IR ($CHCl_3$) ν (cm^{-1}) 3180, 2961, 2872, 2728, 1701, 1615, 1573, 1465, 1312, 1129, 1048, 896, 840, 640; HRMS (ESI) m/z Calcd for $C_{13}H_{15}NO_3Na$, 256.0950; found, 256.0957.

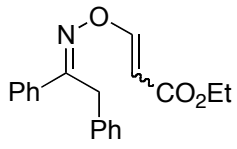
For (E)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.11 (d, *J* = 12.6 Hz, 1H), 7.67-7.74 (m, 2H), 7.37-7.46 (m, 3H), 5.71 (d, *J* = 12.6 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.31 (t, *J* = 7.1, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 167.6, 161.9, 160.3, 134.58, 130.4, 128.6, 126.9, 97.3, 59.8, 14.3, 13.6.

For (Z)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.68-7.77 (m, 2H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.45-7.49 (m, 3H), 4.94 (d, *J* = 7.5 Hz, 1H), 4.24 (q, *J* = 7.11 Hz, 2H), 1.31 (t, *J* = 7.1, 3H), 2.48 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ_C 165.2, 159.9, 159.2, 134.6, 130.2, 128.3, 125.9, 94.3, 59.7, 14.1, 13.6.



5b

Ethyl 3-(((*E*)-(1-(4-Nitrophenyl)ethylidene)amino)oxy)acrylate (5b). Vinyl oxime **5b** was synthesized according to general procedure A. To a stirred solution of DABCO (27 mg, 0.22 mmol) and (*E*)-1-(4-nitrophenyl)ethanone oxime (400 mg, 2.2 mmol) in dichloromethane (16 mL) was added drop wise a mixture of ethyl propiolate (0.21 mL, 2.2 mmol) in dichloromethane (6 mL). The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (4:1 Petroleum:EtOAc) to afford ethyl 3-(((*E*)-(1-(4-nitrophenyl)ethylidene)amino)oxy)acrylate (**5b**, 416 mg, 71 %) as an orange solid. m.p 52-53°C; IR ($CHCl_3$) ν (cm^{-1}) 3234, 2936, 2868, 2758, 1725, 1677, 1524, 1489, 1398, 1125, 1078, 801, 677; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.32 (d, *J* = 8.4 Hz, 2H), 8.13 (d, *J* = 13.0 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 5.73 (d, *J* = 13.0 Hz, 1H), 4.21 (q, *J* = 7.14, 1.53 Hz, 2H), 2.45 (s, 3H), 1.3 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 167.2, 161.4, 158.3, 148.8, 140.5, 127.4, 123.7, 98.2, 60.0, 14.3, 13.6; HRMS (ESI) m/z Calcd for $C_{13}H_{14}N_2O_3Na$, 301.0800; found, 301.0801.



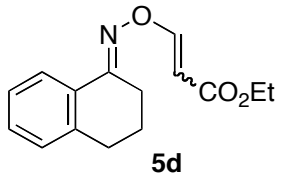
5c

Ethyl 3-(((*E/Z*)-(1,2-Diphenylethylidene)amino)oxy)acrylate (**5c**). Vinyl oxime **5c** was synthesized according to general procedure A. To a stirred solution of DABCO (300 mg, 0.14 mmol) and (*E*)-1,2-diphenylethanone oxime (300 mg, 1.4 mmol) in dichloromethane (12 mL) was added drop wise a mixture of ethyl propiolate (0.135 mL, 1.4 mmol) in dichloromethane (4 mL). The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica

gel (4:1 Petroleum:EtOAc) to afford ethyl 3-(((*E/Z*)-(1,2-diphenylethylidene)amino)oxy)acrylate (**5c**, 408 mg, 93 %) as a colourless oil that is an inseparable *E:Z* mixture (8:1). IR ($CHCl_3$) ν (cm^{-1}) 3146, 2924, 2846, 2732, 1777, 1624, 1576, 1447, 1325, 1125, 1057, 875, 647; HRMS (ESI) m/z Calcd for $C_{19}H_{19}NO_3Na$, 332.1263; found, 332.1265.

For (E)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.16 (d, *J* = 12.6 Hz, 1H), 7.74-7.71 (m, 2H), 7.49-7.45 (m, 3H), 7.33-7.29 (m, 2H), 7.25-7.21 (m, 3H), 5.76 (d, *J* = 12.6 Hz, 1H), 4.27 (q, *J* = 7.4 Hz, 2H), 1.33 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 167.5, 161.7, 157.2, 135.3, 133.7, 130.4, 128.8, 128.6, 128.3, 127.1, 126.7, 97.7, 59.9, 33.5, 14.3.

For (Z)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.41 (d, *J* = 7.1 Hz, 1H), 7.74-7.70 (m, 2H), 7.46-7.41 (m, 3H), 7.33-7.28 (m, 2H), 7.24-7.21 (m, 3H), 5.44 (d, *J* = 7.1Hz, 1H), 4.21 (q, *J* = 7.4 Hz, 2H), 1.32 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ_C 166.0, 160.4, 156.3, 135.4, 134.1, 131.3, 130.6, 129.6, 128.79, 128.72, 128.64, 12862, 121.5, 104.3, 98.5, 60.5, 58.0, 29.7, 14.2

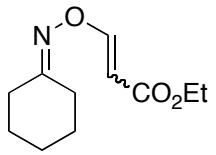


5d

Ethyl 3-(((*E*/*Z*)-(3,4-Dihydronaphthalen-1(2H)-ylidene)amino)oxy)acrylate (**5d**). Vinyl oxime **5d** was synthesized according to general procedure A. To a stirred solution of DABCO (42 mg, 0.34 mmol) and (*E*)-3,4-dihydronaphthalen-1(2H)-one oxime (500 mg, 3.4 mmol) in dichloromethane (24 mL) was added drop wise a mixture of ethyl propiolate (0.32 mL, 3.4 mmol) in dichloromethane (9 mL). The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (9:1 Petrol:EtOAc) to afford ethyl 3-(((*E*/*Z*)-(1,2-diphenylethylidene)amino)oxy)acrylate (**5d**, 886 mg, 77 %) as a colourless oil that is an inseparable *E:Z* mixture (9:1). IR ($CHCl_3$) ν (cm^{-1}) 3136, 2935, 2858, 2725, 1779, 1625, 1547, 1437, 1329, 1125, 1089, 899, 617; HRMS (ESI) m/z Calcd for $C_{15}H_{17}NO_3Na$, 282.1106; found, 282.1109.

For (E)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.12 (d, *J* = 12.6 Hz, 1 H), 7.33 (d, *J* = 7.5, 1.1 Hz, 1H), 7.38-7.31 (m, 1H), 7.27-7.21 (m, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 5.71 (d, *J* = 12.6 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 2.93 (t, *J* = 6.6 Hz, 2H), 2.86 (t, *J* = 6.0 Hz, 2H), 1.95 (q, *J* = 6.3 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 167.7, 162.1, 159.4, 140.6, 130.4, 128.89, 128.86, 126.5, 124.9, 97.1, 59.8, 29.5, 25.0, 21.2, 14.4.

For (Z)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.52 (d, *J* = 7.6 Hz, 1H), 7.3 (d, *J* = 7.5, 1.1 Hz, 1H), 7.36-7.30 (m, 1H), 7.26-7.22 (m, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 4.93 (d, *J* = 7.6 Hz, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 2.95 (t, *J* = 6.6 Hz, 2H), 2.84 (t, *J* = 6.0 Hz, 2H), 1.94 (q, *J* = 6.3 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 166.9, 150.5, 143.7, 137.6, 130.2, 127.6, 125.9, 124.7, 122.0, 94.0, 61.3, 25.4, 24.3, 19.3, 12.0.



5e

Ethyl 3-((cyclohexylideneamino)oxy)acrylate (5e). Vinyl oxime **5e** was synthesized according to general procedure A. To a stirred solution of DABCO (40 mg, 0.35 mmol) and cyclohexanone oxime (400 mg, 3.5 mmol) in dichloromethane (24 mL) was added drop wise a mixture of ethyl propiolate (0.35 mL, 3.5 mmol) in dichloromethane (9 mL). The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (6:1 Petroleum:EtOAc) to afford ethyl 3-((cyclohexylideneamino)oxy)acrylate (**5e**, 747 mg, 80 %) as a colourless oil that is an inseparable *E:Z* mixture (9:1). IR ($CHCl_3$) ν (cm^{-1}) 3392, 3084, 2985, 2942, 2863, 2224, 1701, 1654, 1440, 1394, 1316, 1281, 1176, 1071, 960, 862, 641; HRMS (ESI) m/z Calcd for $C_{11}H_{17}NO_3Na$, 234.1106; found, 234.1108.

For (E)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.93 (d, *J* = 12.6 Hz, 1H), 5.54 (d, *J* = 12.6 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.54-2.51 (m, 2H), 2.34-2.30 (m, 2H), 1.65-1.62 (m, 6H), 1.37 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 167.8, 166.4, 162.1, 96.1, 59.7, 31.7, 26.8, 26.2, 25.7, 25.4, 14.3.

For (Z)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.34 (d, *J* = 7.5 Hz, 1H), 4.82 (d, *J* = 7.4 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.75-2.72 (m, 2H), 2.37-2.33 (m, 2H), 1.75-1.72 (m, 6H), 1.36 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 165.9, 165.5, 159.5, 93.2, 59.5, 31.4, 26.8, 26.6, 25.7, 25.4, 14.8.

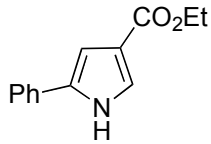
III. Preparation of Pyrroles (6a-7i)

General Procedure B: A mixture of vinyl oxime (1.0 equiv), PPh_3AuCl (0.1 equiv) and silver salt (0.1 equiv) in toluene was heated to 100 °C for 40 minutes under microwave irradiation. The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel.

General Procedure C: A mixture of vinyl oxime (1.0 equiv), PPh_3AuCl (0.1 equiv) and $AgBF_4$ (0.1 equiv) in toluene was heated to 100 °C for 12 h. The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel.

General Procedure D: To a stirred solution of oxime (1.0 equiv) and alkyne (1.0 eqv) in toluene were added PPh_3AuCl (0.1 equiv) and AgOTf (0.1 equiv) and the resultant mixture was heated to 100 °C for 12 h. The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel.

Preparation of pyrroles 6a-6c and 7a-7i



6a

Ethyl 5-Phenyl-1H-pyrrole-3-carboxylate (6a).

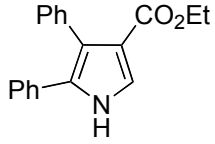
Method 1

Silver trifluoromethanesulfonate: Pyrrole **6a** was synthesized according to general procedure B. Vinyl oxime **5a** (100 mg, 0.43 mmol), PPh_3AuCl (24 mg, 0.043 mg, 0.043 mmol) and AgOTf (11 mg, 0.043 mmol) in toluene (2 mL) were heated to 100 °C for 40 minutes under microwave irradiation. The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (9:1 Petroleum/EtOAc) to afford ethyl 5-phenyl-1H-pyrrole-3-carboxylate (**6a**, 47 mg, 52%) as an orange oil, which had spectra identical to that reported in the literature.[ii]

Silver tetrafluoroborate: Pyrrole **6a** was synthesized according to general procedure B. Vinyl oxime **5a** (80 mg, 0.34 mmol), PPh_3AuCl (17 mg, 0.034 mmol) and $AgBF_4$ (6.7 mg, 0.034 mmol) in toluene (2 mL) were heated to 100 °C for 40 minutes under microwave irradiation. The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (7:1 Petroleum/EtOAc) to afford ethyl 5-phenyl-1H-pyrrole-3-carboxylate (**6a**, 50 mg, 68%) as an orange oil, which had spectra identical to that reported in the literature.[ii]

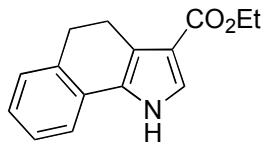
Method 2: Pyrrole **6a** was synthesized according to general procedure C. Vinyl oxime **5a** (80 mg, 0.34 mmol), PPh_3AuCl (17 mg, 0.034 mmol) and $AgBF_4$ (7 mg, 0.034 mmol) in toluene (2.5 mL) were heated to 100 °C for 12 h. The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (12:1 Petroleum/EtOAc) to afford ethyl 5-phenyl-1H-pyrrole-3-carboxylate (**6a**, 54 mg, 69%) as an orange oil, which had spectra identical to that reported in the literature.[ii]

Method 3: Pyrrole **6a** was synthesized according to general procedure D. To a stirred solution of acetophenone oxime (80 mg, 0.60 mmol) and ethyl propiolate (0.056 mL, 0.60 mmol) in toluene (2 mL) were added PPh_3AuCl (29 mg, 0.06 mmol) and AgOTf (15 mg, 0.06 mmol) and the resultant mixture was heated to 100 °C for 12 h. The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (9:1 Petroleum/EtOAc) to afford ethyl 5-phenyl-1H-pyrrole-3-carboxylate (**6a**, 37 mg, 22%) as an orange oil, which had spectra identical to that reported in the literature.[ii] IR ($CHCl_3$) ν (cm^{-1}) 3699, 3631, 2992, 2943 2838, 1708, 1626, 1486, 1392, 1217, 1073, 891, 838, 640 cm-1; ^{1}H NMR (400 MHz,$CDCl_3$) δ_H 8.77 (br.s, 1H), 7.52-7.50 (m, 1H), 7.50-7.47 (m, 2H), 7.43-7.36 (m, 2H), 7.30-723 (m, 1H), 6.92-6.93 (m, 1H), 4.32 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δc 164.9, 133.0, 131.7, 129.0, 127.0, 124.1, 118.1, 106.7, 59.9, 14.5; HRMS (ESI) m/z Calcd for $C_{13}H_{13}NO_2Na$, 238.0844; found, 238.0845.



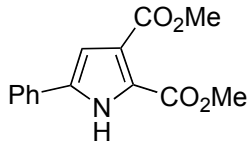
6b

Ethyl 4,5-Diphenyl-1H-pyrrole-3-carboxylate (6b). Pyrrole **6b** was synthesized according to general procedure C. Vinyl oxime **5b** (80 mg, 0.26 mmol), PPh_3AuCl (12 mg, 0.026 mmol) and $AgBF_4$ (5.0 mg, 0.026 mmol) in toluene (2.5 mL) were heated to 100 °C for 12 h. The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (10:1 Petroleum:EtOAc) to afford ethyl 4,5-diphenyl-1H-pyrrole-3-carboxylate (**6b**, 43 mg, 57 %) as an orange solid, which had spectra identical to that reported in the literature.[iii] m.p. 191-193 °C; IR ($CHCl_3$) ν (cm^{-1}) 3904, 3885, 3654, 3011, 2930, 2434, 2412, 2244, 1727, 1601, 1568, 1521, 1476, 1194, 1087, 1017, 928, 849, 662; ^{1}H NMR (400 MHz,$CDCl_3$) δ_H 9.09 (br.s, 1H), 7.39-7.35 (m, 3H), 7.37-7.31 (m, 6H), 7.26-7.22 (m, 1H), 7.08 (d, *J* = 2.8 Hz, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δc 161.2, 135.4, 133.1, 131.9, 128.7, 128.4, 128.4, 128.0, 127.9, 126.3, 124.0, 122.5, 116.7, 60.5, 14.5. HRMS (ESI) m/z Calcd for $C_{19}H_{17}NO_2Na$, 314.1157; found, 314.1156.



6c

Ethyl 4,5-Dihydro-1H-benzo[g]indole-3-carboxylate (6c). Pyrrole **6c** was synthesized according to general procedure C. Vinyl oxime **5c** (80 mg, 0.31 mmol), PPh_3AuCl (15 mg, 0.031 mmol) and $AgBF_4$ (6 mg, 0.031 mmol) in toluene (2.5 mL) were heated to 100 °C for 12 h. The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (8:1 Petroleum:EtOAc) to afford ethyl 4,5-dihydro-1H-benzo[g]indole-3-carboxylate (**6c**, 49 mg, 51 %) as an orange oil. IR ($CHCl_3$) ν (cm^{-1}) 3913, 3888, 3625, 3081, 2923, 24199, 2247, 17411, 1609, 1567, 1545, 1496, 1133, 1097, 965, 851, 669; ^{1}H NMR (400 MHz,$CDCl_3$) δ_H 9.22 (br.s, 1H), 7.42-7.38 (m, 1H), 7.28-7.23 (m, 2H), 7.25-7.21 (m, 1H), 6.83 (d, *J* = 2.3 Hz, 1H), 4.47 (q, *J* = 7.1 Hz, 2H), 3.05-3.01 (m, 2H), 2.84-2.81 (m, 2H), 1.44 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δc 160.0, 136.3, 128.7, 128.0, 127.5, 127.2, 127.0, 126.6, 121.7, 119.9, 114.2, 60.3, 29.7, 21.4. 14.2. HRMS (ESI) m/z Calcd for $C_{21}H_{15}NO_2Na$, 336.1000; found, 336.1001.

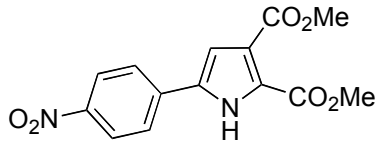


7a

Dimethyl 5-Phenyl-1H-pyrrole-2,3-dicarboxylate (7a).

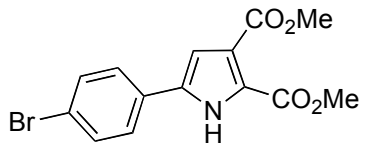
Method 1: Pyrrole **7a** was synthesized according to general procedure C. Vinyl oxime **4a** (80 mg, 0.30 mmol), PPh_3AuCl (15 mg, 0.03 mmol) and $AgBF_4$ (8 mg, 0.03 mmol) in toluene (2.5 mL) were heated to 100 °C for 12 h. The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (9:1 Petroleum:EtOAc) to afford dimethyl 5-phenyl-1H-pyrrole-2,3-dicarboxylate (**7a**, 63 mg, 85 %) as a white solid and which had spectra identical to that reported in the literature.[iv]

Method 2: Pyrrole **7a** was synthesized according to general procedure D*:* To a stirred solution of oxime (80 mg, 0.60 mmol) and dimethyacetylene dicarbonate (0.01 mL, 0.60 mmol) in toluene (2 mL) were added PPh_3AuCl (29 mg, 0.06 mmol) and $AgBF_4$ (15 mg, 0.06 mmol) and the resultant mixture was heated to 100 °C for 12 h. The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (9:1 Petroleum:EtOAc) to afford dimethyl 5-phenyl-1H-pyrrole-2,3-dicarboxylate (**7a**, 137 mg, 88%) as a white solid and which had spectra identical to that reported in the literature.[iv] m.p. 142-144 °C; IR ($CHCl_3$) ν (cm-[1]) 3667, 3689, 3479, 3045, 2889, 2098, 1781, 1621, 1589, 1459,1398, 1112, 987, 801, 687; ^{1}H NMR (400 MHz,$CDCl_3$) δ_H 9.63 (br.s, 1H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2 H), 7.36 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 3.1 Hz, 1H), 3.94 (s, 3H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δc 164.2, 160.6, 134.8, 130.2, 129.2, 129.1 128.4, 124.8, 124.7, 122.7, 121.5, 110.7, 52.3, 51.9. HRMS (ESI) m/z: Calcd for $C_{14}H_{13}NO_4Na$, 282.0742; found, 282.0741.



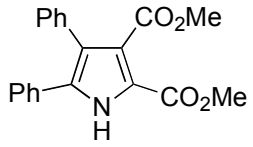
7b

Dimethyl 5-(4-Nitrophenyl)-1H-pyrrole-2,3-dicarboxylate (7b). Pyrrole **7b** was synthesized according to general procedure D. Vinyl oxime **4b** (80 mg, 0.25 mmol), PPh_3AuCl (12 mg, 0.025 mmol) and $AgBF_4$ (5 mg, 0.025) in toluene (2.5 mL) were heated to 100 °C for 12 h. The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (6:1 Petroleum:EtOAc) to afford dimethyl 5-(4-nitrophenyl)-1H-pyrrole-2,3-dicarboxylate (**7b**, 60 mg, 83 %) as an orange solid. m.p. 98-101 °C; IR ($CHCl_3$) ν (cm-1) 3697, 3634, 3411, 3067, 2856, 2078, 1791, 1611, 1578, 1490,1392, 1189, 985, 809, 612; ^{1}H NMR (400 MHz,$CDCl_3$) δ_H 9.81 (br.s, 1H), 8.34 (d, *J* = 8.9 Hz, 2H), 7.73 (d, *J* = 8.9 Hz, 2H), 7.13 (d, *J* = 3.1 Hz, 1H), 4.07 (s, 3H), 3.96-3.93 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δc 163.7, 160.4, 147.1, 136.1, 132.0, 125.1, 124.7, 124.6, 121.8, 113.0, 52.5, 52.0. HRMS (ESI) m/z Calcd for $C_{14}H_{12}NO_6Na$, 327.0593; found, 327.0591.



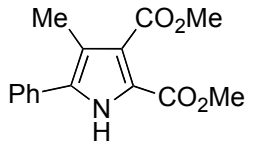
7c

(4-Bromophenyl)-1H-pyrrole-2,3-dicarboxylate (7c). Pyrrole **7c** was synthesized according to general procedure D. Vinyl oxime **4c** (80 mg, 0.22 mmol), PPh_3AuCl (11 mg, 0.022 mmol) and $AgBF_4$ (6 mg, 0.022 mmol) in toluene (2.5 mL) were heated to 100 °C for 12 h. The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (5:1 Petrol: EtOAc) to afford (4-bromophenyl)-1H-pyrrole-2,3-dicarboxylate (**7c**, 44 mg, 61 %) as a white solid. m.p. 132-134 °C; IR ($CHCl_3$) ν (cm^-1) 3689, 3634, 3423, 3087, 2887, 2087, 1721, 1653, 1565, 1489,1398, 1180, 998, 899, 634; ^1H NMR (400 MHz, $CDCl_3$) δ_H 9.86 (br.s, 1H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 6.91 (s, 1H), 3.92 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 164.1, 160.6, 133.7, 132.2, 131.0, 126.3, 122.9,122.2, 121.5, 110.9, 52.3, 51.9; HRMS (ESI) m/z Calcd for $C_{14}H_{12}BrNO_4Na$, 359.9847; found, 359.9841.



7d

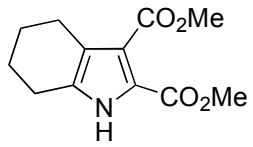
Dimethyl 4,5-Diphenyl-1H-pyrrole-2,3-dicarboxylate (7d). Pyrrole **7d** was synthesized according to general procedure D. Vinyl oxime **4d** (80 mg, 0.24 mmol), PPh_3AuCl (12 mg, 0.024 mmol) and $AgBF_4$ (6 mg, 0.024 mmol) in toluene (2.5 mL) were heated to 100 °C for 12 h. The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (5:1 Petroleum:EtOAc) to afford dimethyl 4,5-diphenyl-1H-pyrrole-2,3-dicarboxylate (**7d**, 63 mg, 79 %) as an orange solid and which had spectra identical to that reported in the literature.[iii] m.p. 190-192 °C; IR ($CHCl_3$) ν (cm^{-1}) 3621, 3433, 2997, 2886, 2542, 2011, 1732, 1604, 1476, 1350, 1296, 1165, 1096, 980, 908, 840, 640; ^1H NMR (400 MHz, $CDCl_3$) δ_H 9.53-9.47 (br.s, 1H), 7.33-7.22 (m, 10H), 3.83 (s, 3H), 3.76 (s,3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 166.3, 160.6, 133.3, 133.0, 130.8, 129.8, 128.8, 128.4, 127.8, 127.2, 123.2, 122.9, 119.9, 52.3, 52.2; HRMS (ESI) m/z Calcd for $C_{20}H_{17}NO_4Na$, 358.1055; found, 358.1059



7e

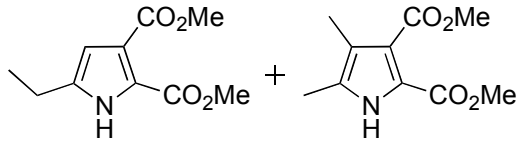
Dimethyl 4-Methyl-5-phenyl-1H-pyrrole-2,3-dicarboxylate (7e). Pyrrole **7e** was synthesized according to general procedure D. Vinyl oxime **4g** (80 mg, 0.29 mmol), PPh_3AuCl (14 mg, 0.029 mmol), $AgBF_4$ (7 mg, 0.029, mmol) and toluene (2.5 mL) were heated to 100 °C for 12 h. The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (7:1 Petroleum:EtOAc) to afford dimethyl 4-methyl-5-phenyl-1H-pyrrole-2,3-dicarboxylate (**7e**, mg 82 %) as a white solid and which had spectra identical to that reported in the literature.[iv] m.p. 148-150°C; IR ($CHCl_3$) ν (cm^{-1}) 3488, 3056, 2998, 2512, 1767, 1679, 1589, 1409, 1338, 1297, 1127, 1198, 1056, 1064, 945, 878, 649; ^1H NMR (400 MHz, $CDCl_3$) δ_H 9.36 (br.s, 1H), 7.52-7.56 (m, 5H), 3.96 (s, 3H), 3.94 (s, 3H) 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C ^{13}C 166.1, 160.7, 133.0, 128.9,

128.87, 128.67, 128.09, 127.6, 127.59, 122.1, 120.3, 118.8, 52.0, 51.9, 10.8. HRMS (ESI) m/z Calcd for $C_{15}H_{15}NO_4Na$, 296.0899; found, 296.0891.



7f

Dimethyl 4,5,6,7-Tetrahydro-1H-indole-2,3-dicarboxylate (**7f**). Pyrrole **7f** was synthesized according to general procedure D. Vinyl oxime **4f** (80 mg, 0.31 mmol), PPh_3AuCl (16 mg, 0.031 mmol) and $AgBF_4$ (6 mg, 0.031 mmol) and in (2.5 mL) were heated to 100 °C for 12 hours. The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (9:1 Petroleum:EtOAc) to afford dimethyl 4,5,6,7-tetrahydro-1H-indole-2,3-dicarboxylate (**7f**, 63 mg, 87 %) as an orange solid and which had spectra identical to that reported in the literature.[v] m.p. 138-140 °C; IR ($CHCl_3$) ν (cm^{-1}) 3435, 3903, 2979, 2562, 1769, 1658, 1597, 1480, 1379, 1269, 1179, 1098, 1047, 949, 898, 658; ^1H NMR (400 MHz, $CDCl_3$) δ_H 9.02 (br.s, 1H), 3.86 (s, 3H), 3.86 (s, 3H), 2.62 (t, J = 6.1 Hz, 1H), 2.59 (t, J = 6.1 Hz, 2 H), 1.79-1.77 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 165.6, 160.8, 132.1, 121.6, 119.8, 118.7, 51.8, 51.6, 22.9, 22.6, 22.4, 22.3. HRMS (ESI) m/z Calcd for $C_{12}H_{15}NO_4Na$, 260.0899; found, 260.0899.

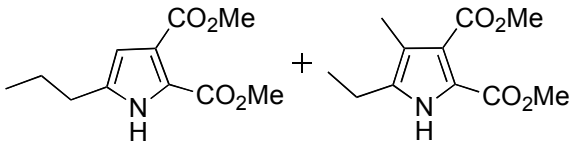


7g (1:4)

Dimethyl 5-Ethyl-1H-pyrrole-2,3-dicarboxylate/ Dimethyl 4,5-Dimethyl-1H-pyrrole-2,3-dicarboxylate (7g). Pyrroles **7g** was synthesized according to general procedure D. Vinyl oxime **4g** (80 mg, 0.44 mmol), PPh_3AuCl (22 mg, 0.044 mmol) and $AgBF_4$ (9 mg, 0.044 mmol) in toluene (2.5 mL) were heated to 100 °C for 12 h. The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (9:1 Petroleum:EtOAc) to afford an inseparable (*1:4*) mixture of dimethyl 5-ethyl-1H-pyrrole-2,3-dicarboxylate / dimethyl 4,5-dimethyl-1H-pyrrole-2,3-dicarboxylate (**7g**, 50 mg, 54 %) as an orange oil. IR ($CHCl_3$) ν (cm^{-1}); 3864, 3745, 3011, 3292, 2423, 2423, 1726, 1689, 1508, 1474, 1279, 1081, 929, 662; HRMS (ESI) m/z Calcd for $C_{10}H_{13}NO_4Na$, 234.0742; found, 234.0741

For dimethyl 4,5-dimethyl-1H-pyrrole-2,3-dicarboxylate: ^1H NMR (400 MHz, $CDCl_3$) δ_H 9.24 (br.s, 1H), 6.43-6.38 (m, 1H), 3.90 (s, 3H), 3.86 (s, 3H), 2.64 (q, J = 8.1 Hz, 2H), 1.27 (t, J = 8.1 Hz, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ_C 166.2, 160.5, 129.4, 121.0, 118.8, 118.4, 51.8, 51.7, 11.1, 9.7.

For dimethyl 5-ethyl-1H-pyrrole-2,3-dicarboxylate: ^1H NMR (400 MHz, $CDCl_3$) δ_H 9.03 (br.s, 1H), 3.89-3.86 (m, 3H), 3.84 (s, 3H), 2.21 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 166.0, 160.5, 137.8, 121.0, 118.7, 110.2, 53.3, 52.0, 20.5, 13.0.

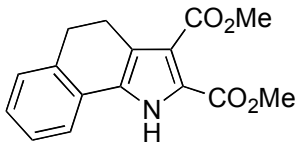


7h (2:3)

Dimethyl 5-Propyl-1H-pyrrole-2,3-dicarboxylate/ Dimethyl 5-Ethyl-4-methyl-1H-pyrrole-2,3-dicarboxylate (7h). Pyrrole **7h** was synthesized according to general procedure D. Vinyl oxime **4h** (80 mg, 0.33 mmol), PPh_3AuCl (16 mg, 0.033mmol) and $AgBF_4$ (6 mg, 0.033 mmol) in toluene (2.5 mL) were heated to 100 °C for 12 hours. The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (9:1 Petroleum:EtOAc) to afford an inseparable (*2:3)* mixture of dimethyl 5-propyl-1H-pyrrole-2,3-dicarboxylate / dimethyl 5-ethyl-4-methyl-1H-pyrrole-2,3-dicarboxylate (**7h**, 44 mg, 61 %) as an orange oil. IR ($CHCl_3$) ν (cm^{-1}); 3822, 3712, 3014, 3282, 2489, 2489, 1798, 1645, 1578, 1478, 1289, 1061, 997, 612; HRMS (ESI) m/z Calcd for $C_{11}H_{15}NO_4Na$, 248.0899; found, 248.0897.

For dimethyl 5-propyl-1H-pyrrole-2,3-dicarboxylate: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 9.36-9.33 (m, 1H), 6.43 (d, *J* = 3.1 Hz, 1H), 3.97 (s, 3H), 3.93 (s, 3H), 2.6 (t, *J* = 7.5 Hz, 2H), 1.73 (q, *J* = 7.5 Hz, 2H), 1.04 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 164.6, 160.8, 134.4, 120.7, 120.5, 111.1, 52.0, 51.9, 29.7, 22.3, 13.6.

For dimethyl 5-ethyl-4-methyl-1H-pyrrole-2,3-dicarboxylate: ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 9.07-9.04 (m, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 2.50 (q, *J* = 7.5 Hz, 2H), 2.22 (s, 3H), 1.09 (t, *J* = 7.5 Hz, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ_C 166.4, 160.5, 129.3, 128.6, 124.9, 118.4, 51.9, 51.7, 18.0, 15.5, 11.0.



7i

Dimethyl 4,5-Dihydro-1H-benzo[g]indole-2,3-dicarboxylate (7i). Pyrrole **7i** was synthesized according to general procedure D. Vinyl oxime **4i** (80 mg, 0.26 mmol), PPh_3AuCl (13 mg, 0.26 mmol) and $AgBF_4$ (5 mg, 0.26 mmol) in toluene (2.5 mL) were heated to 100 °C for 12 h. The mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel (8:1 Petroleum:EtOAc) to afford dimethyl 4,5-dihydro-1H-benzo[g]indole-2,3-dicarboxylate (**7i**, 66 mg, 89 %) as a white solid and which had spectra identical to that reported in the literature.[vi] m.p. 177-179 °C; IR ($CHCl_3$) ν (cm^{-1}) 3425, 3998, 2979, 2572, 1768, 1685, 1597, 1479, 1397, 1257, 1197, 1097, 1048, 997, 898, 696; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 9.75 (br.s, 1H), 7.43-.7.39 (m, 1H), 7.24-7.21 (m, 2H), 7.23-7.19 (m, 1H), 3.92 (s, 3H), 3.91-3.89 (m, 3H), 2.96 (d, *J* = 6.7 Hz, 2H), 2.94-2.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 165.2, 160.9, 136.3, 131.3, 128.6, 127.6, 127.59, 127.0, 126.7, 126.6, 123.2, 121.4, 120.2, 119.1, 52.1, 51.8. HRMS (ESI) m/z Calcd for $C_{16}H_{15}NO_4Na$, 308.0899; found, 308.0895.

IV. References

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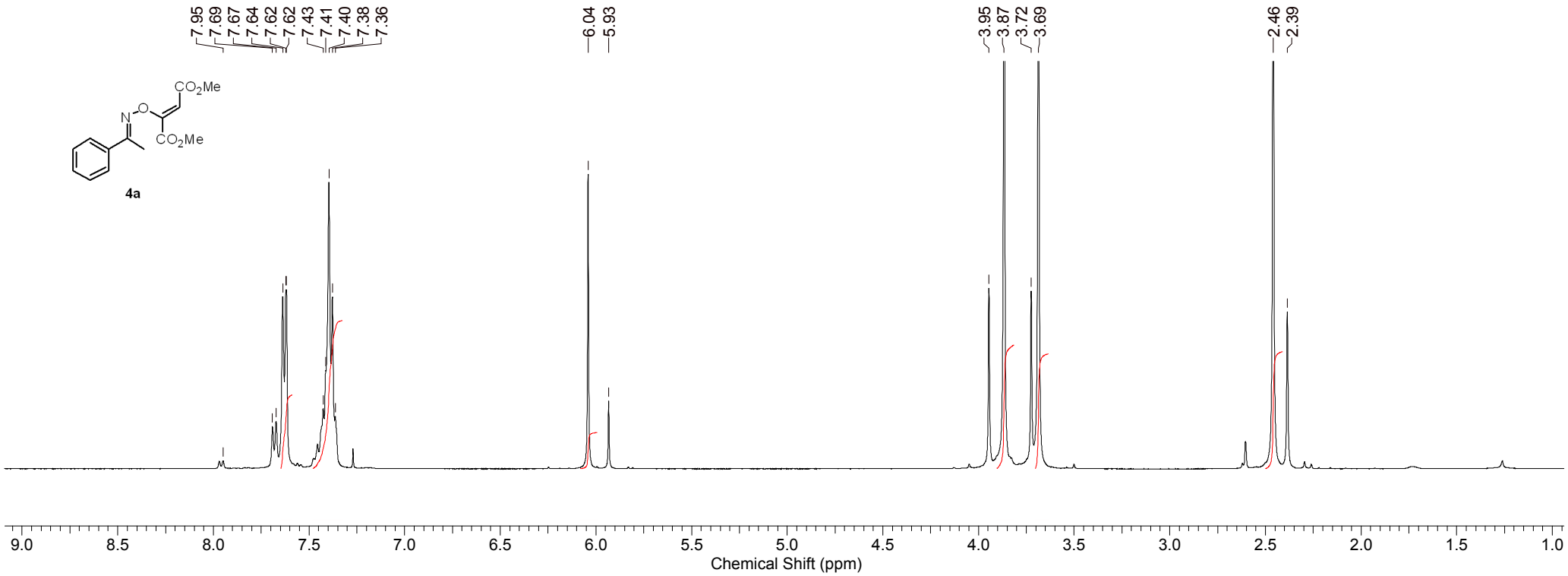
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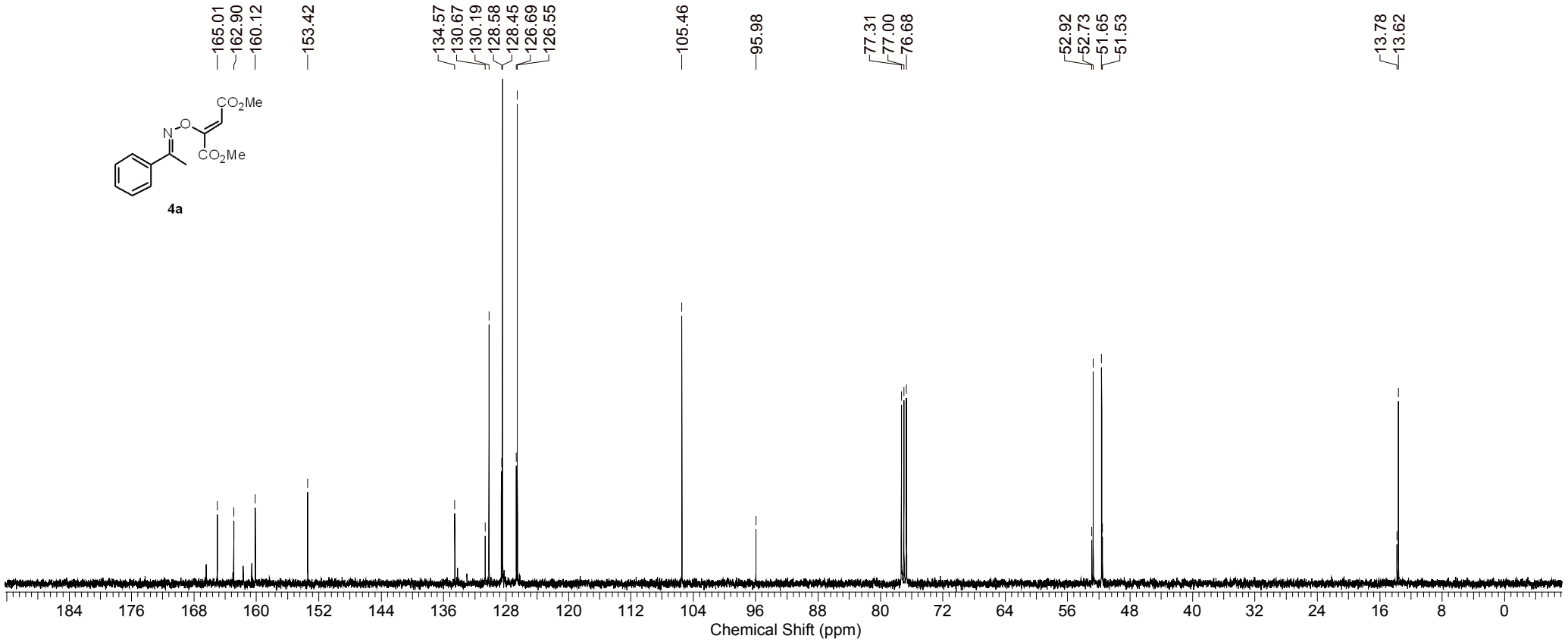
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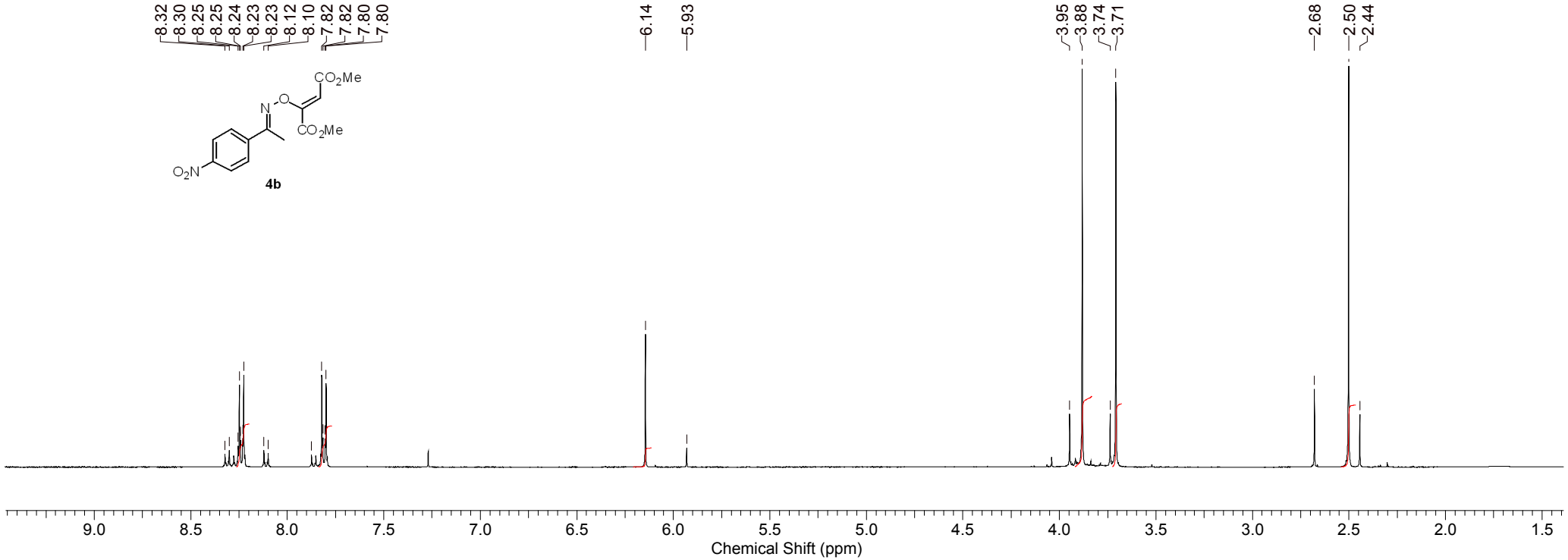
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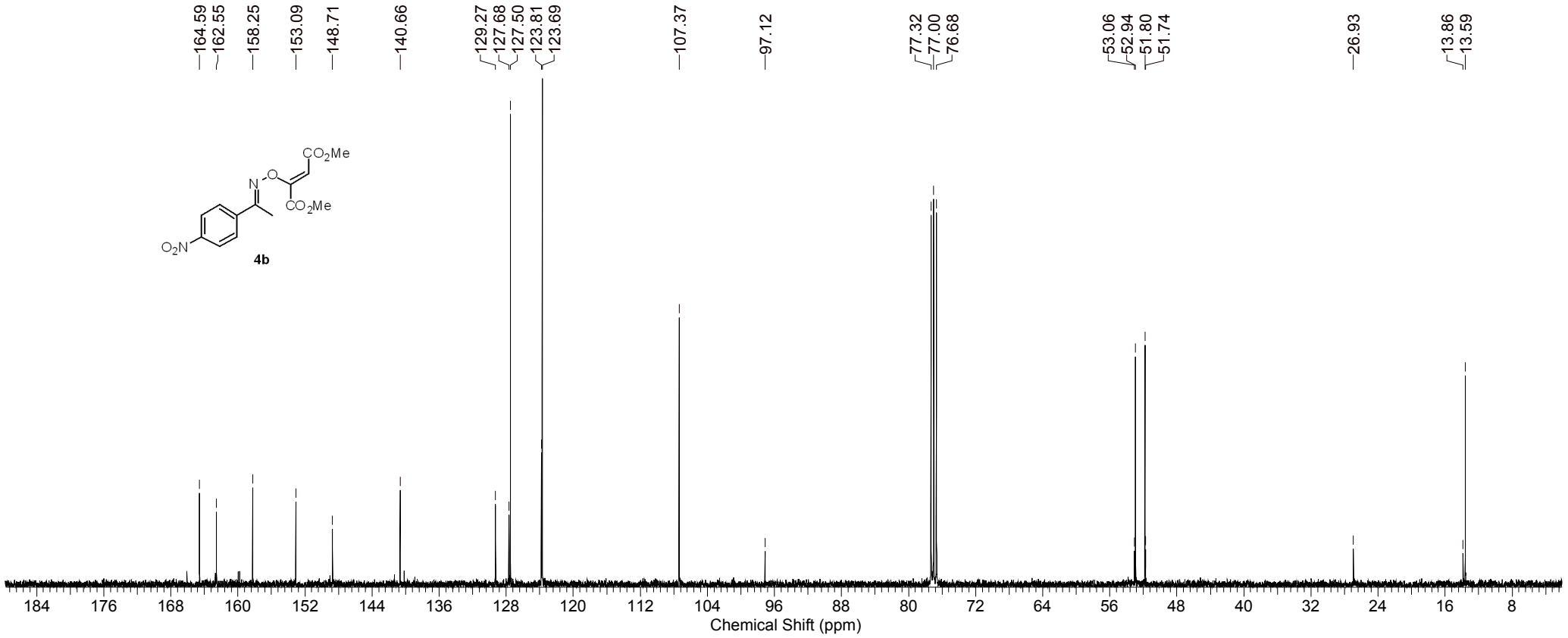
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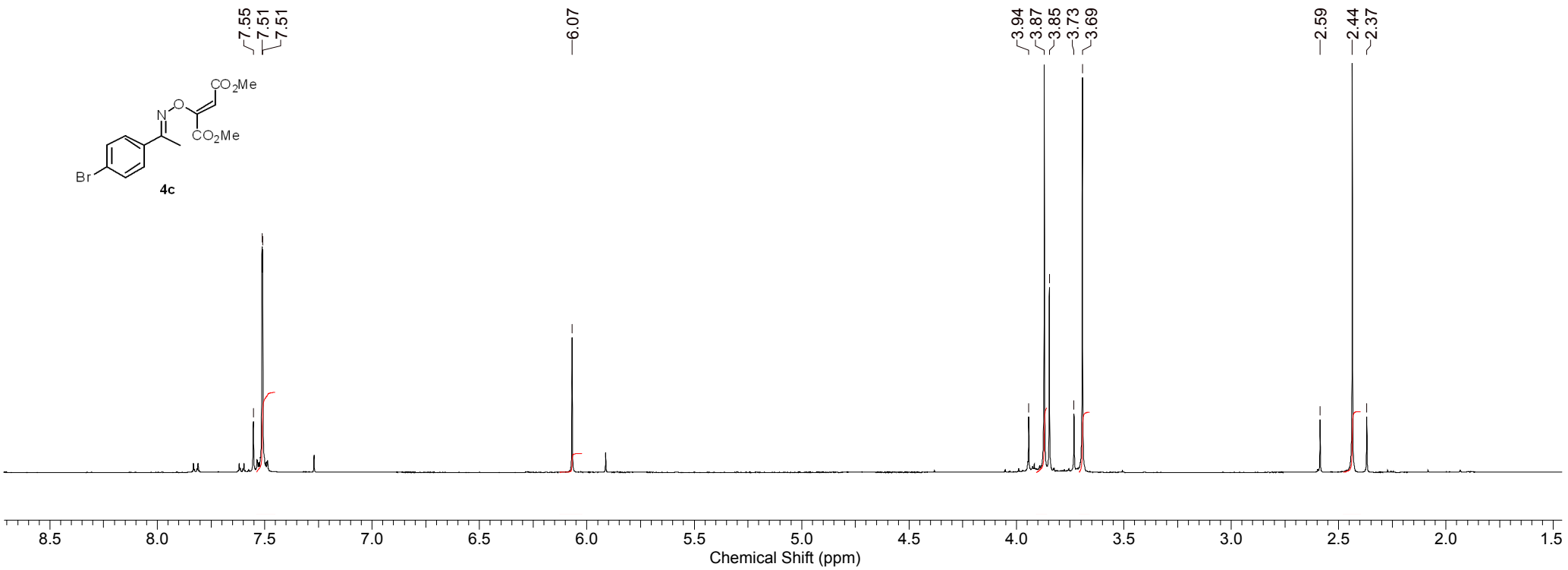
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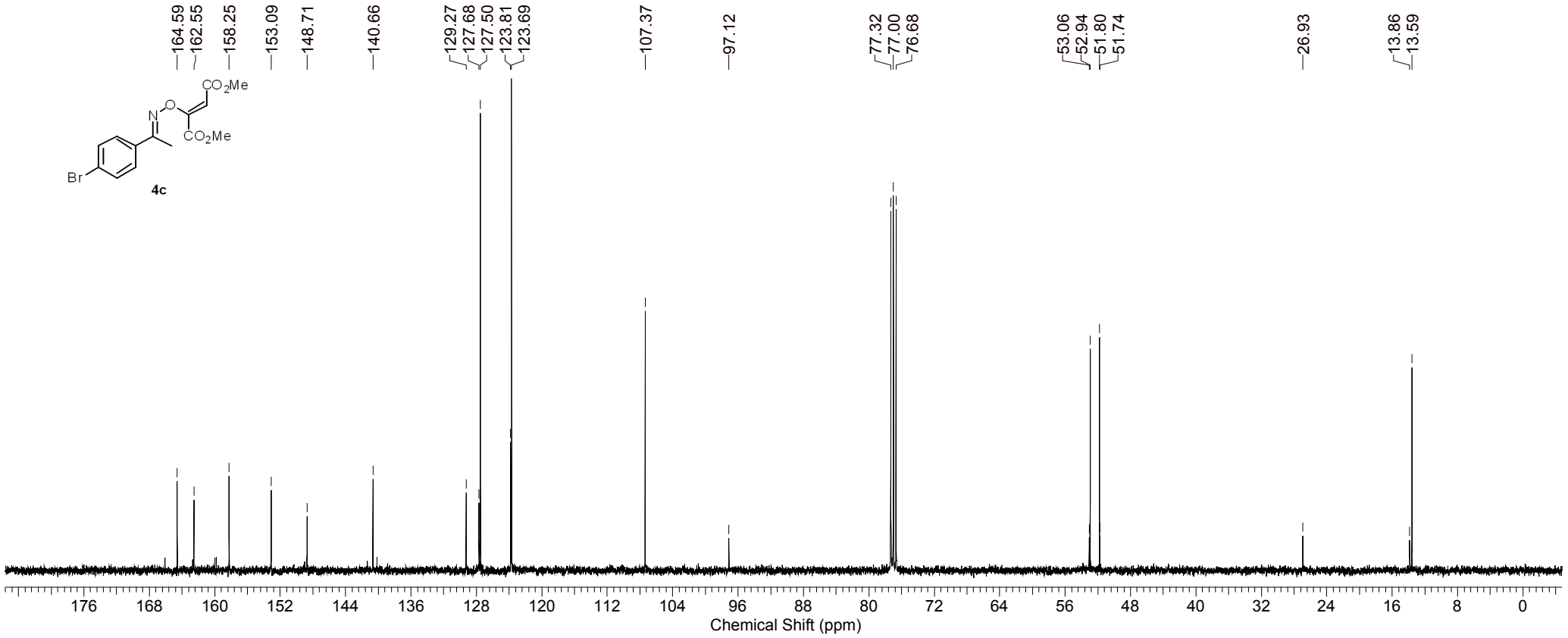
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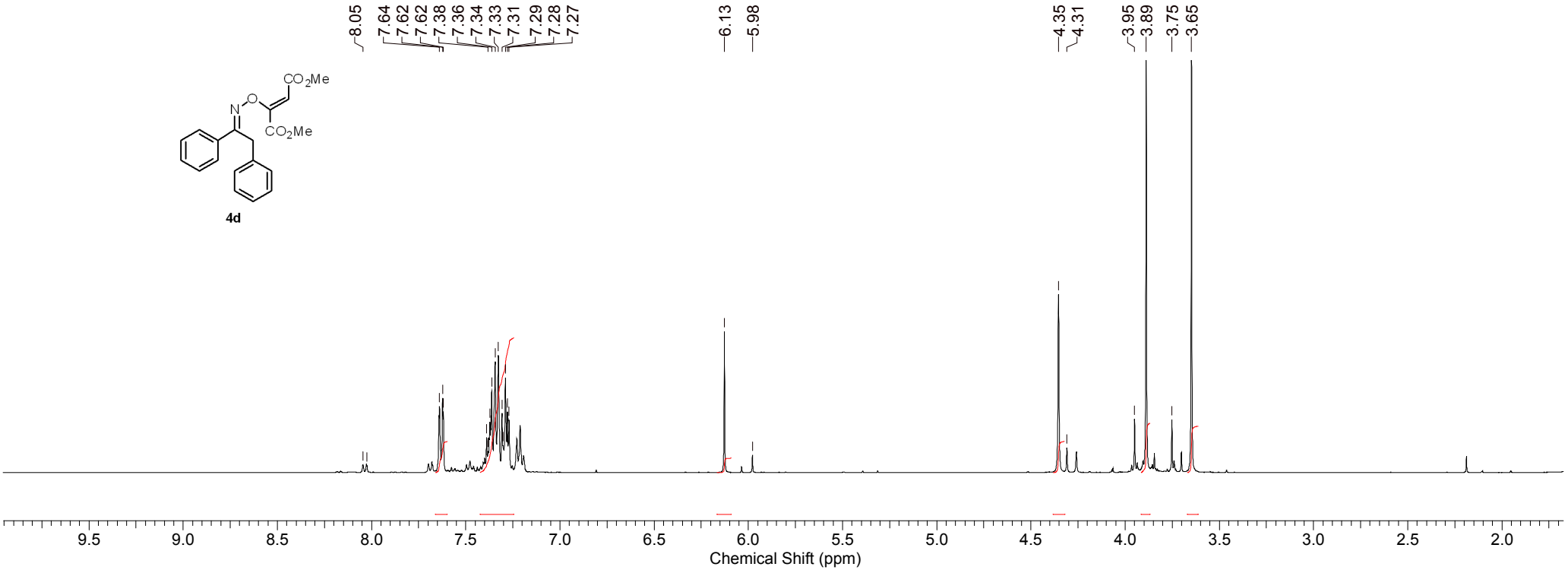
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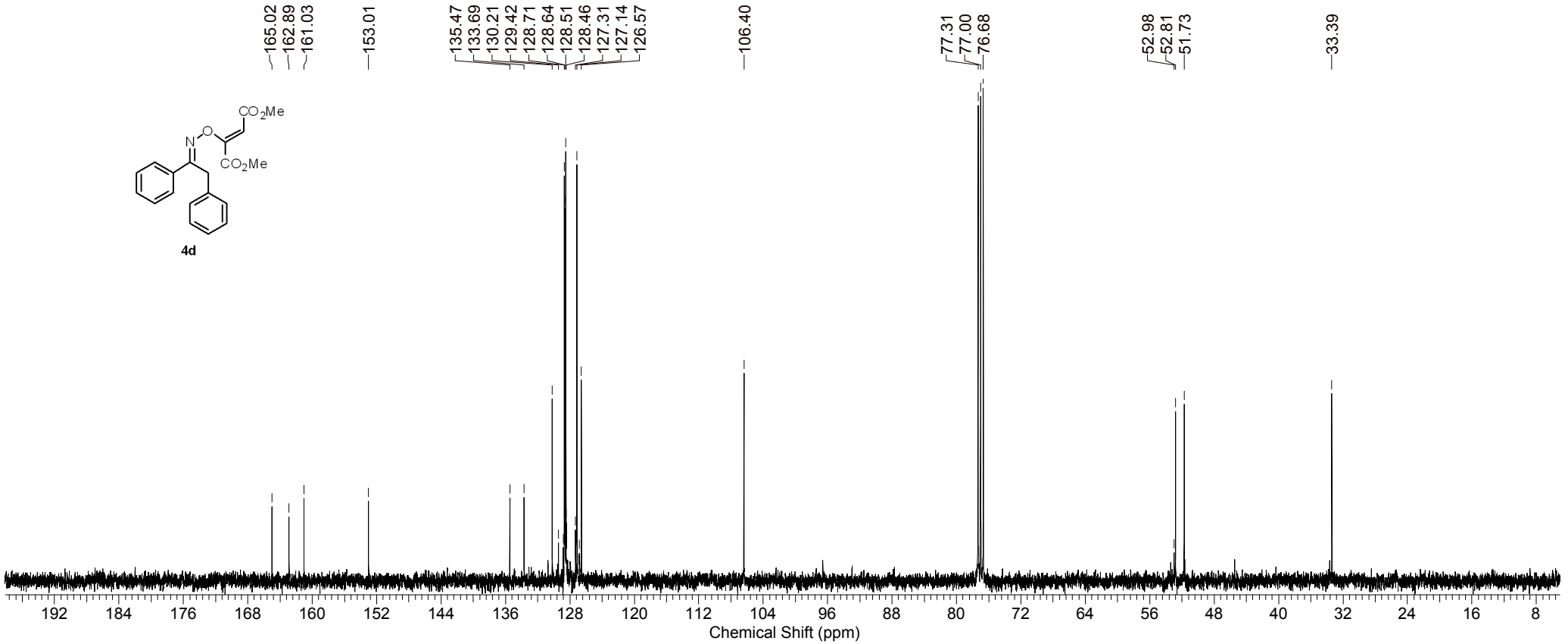
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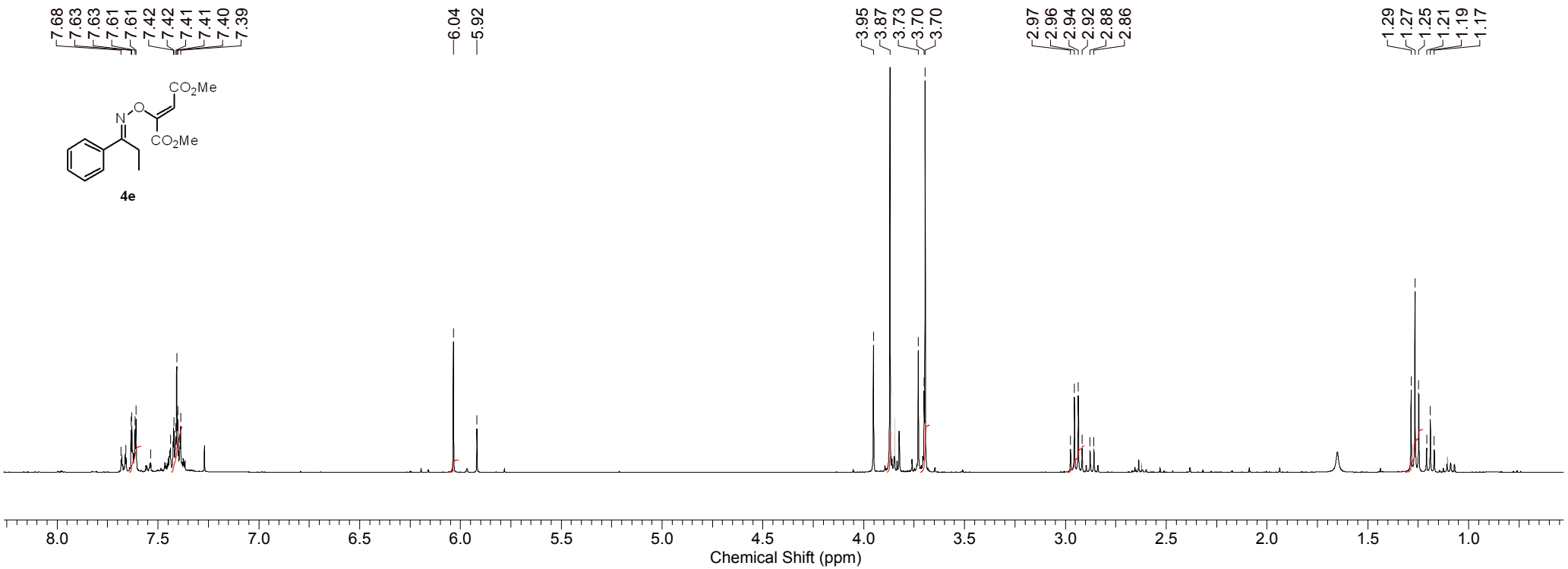
Chemical Shift (ppm)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7.63
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7.61
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7.41
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7.40
7.39
6.04
5.92
3.95
3.87
3.73
3.70
3.70
2.97
2.96
2.94
2.92
2.88
2.86
1.29
1.27
1.25
1.21
1.19
1.17
CO2Me
N
O
CO2Me
4e
8.0
7.5
7.0
6.5
6.0
5.5
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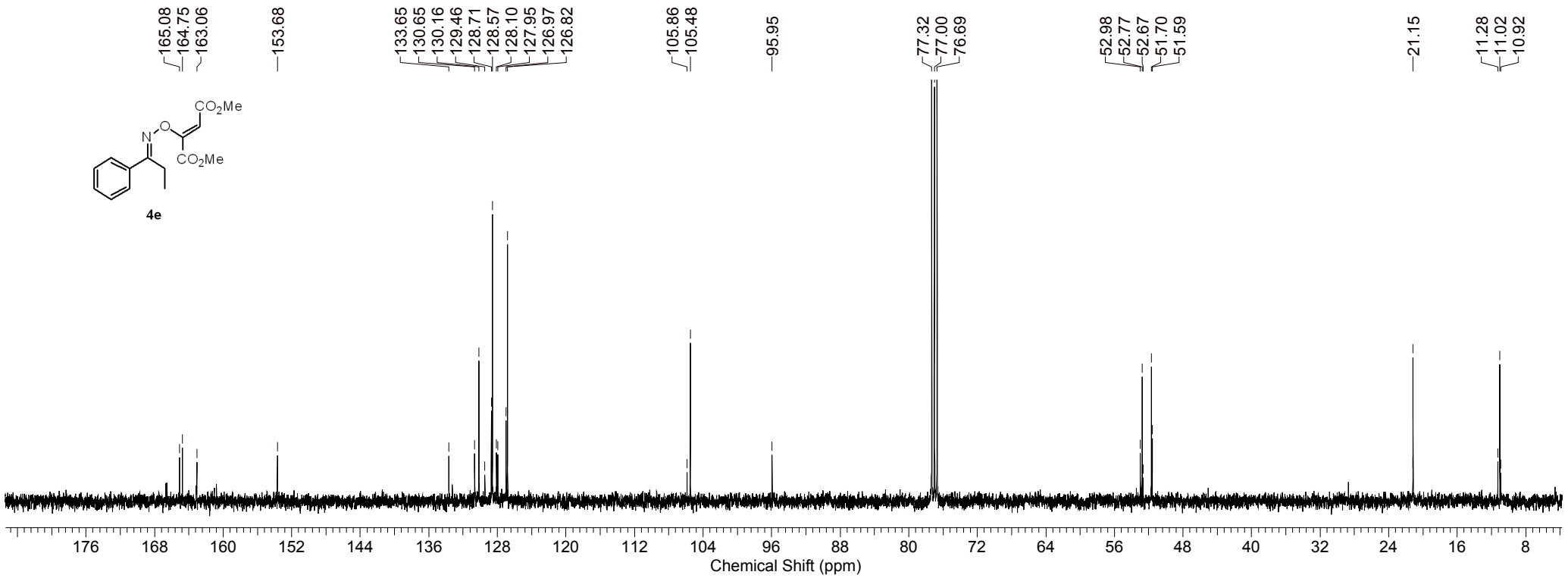
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)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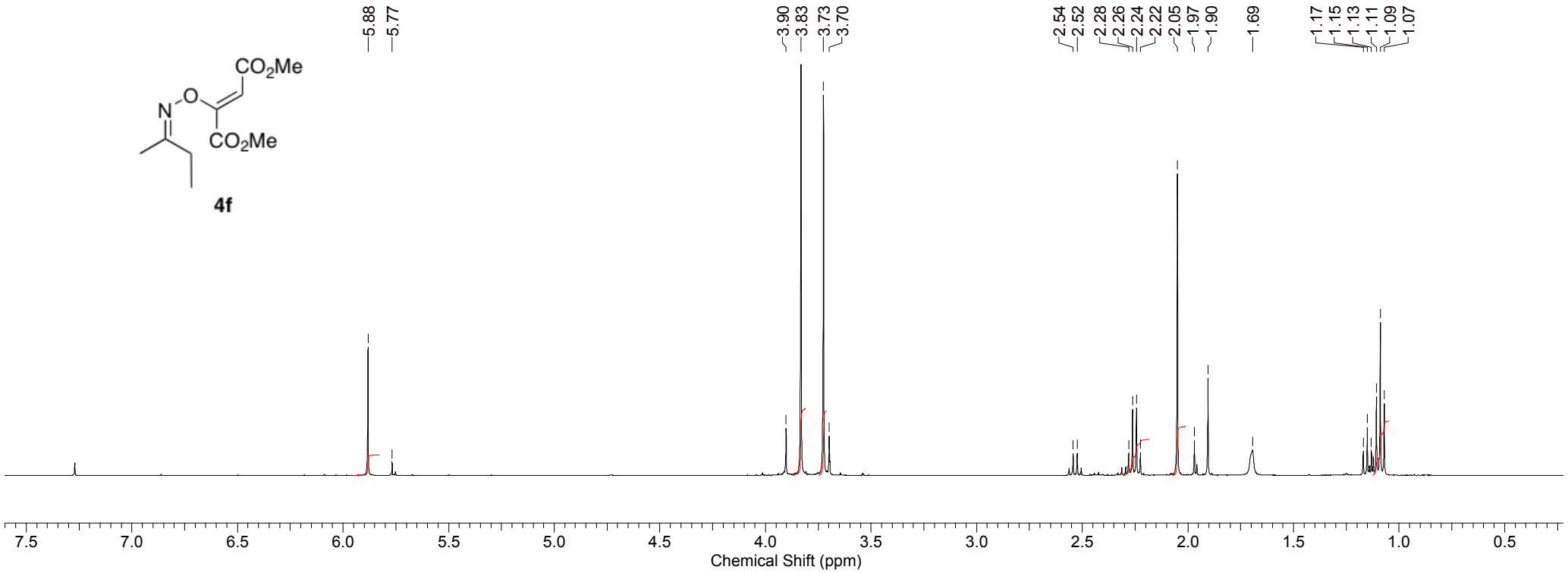
130.16
129.46
128.71
128.57
128.10
127.95
126.97
126.82
105.86
105.48
95.95
77.32
77.00
76.69
52.98
52.77
52.67
51.70
51.59
21.15
11.28
11.02
10.92
CO2Me
N
O
CO2Me
4e
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)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3.70
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2.52
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2.26
2.24
2.22
2.05
1.97
1.90
1.69
1.17
1.15
1.13
1.11
1.09
1.07
CO2Me
N
O
CO2Me
4f
7.5
7.0
6.5
6.0
5.5
5.0
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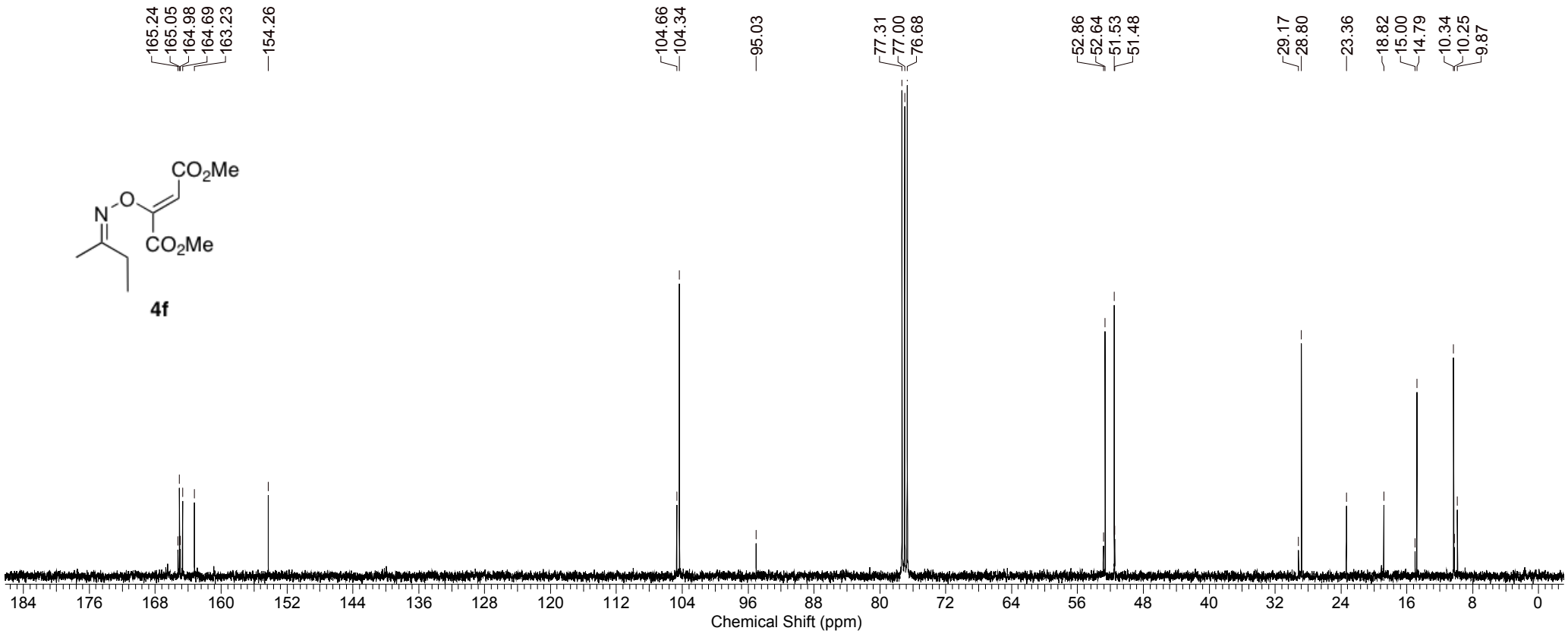
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)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165.05
164.98
164.69
163.23
154.26
104.66
104.34
95.03
77.31
77.00
76.68
52.86
52.64
51.53
51.48
29.17
28.80
23.36
18.82
15.00
14.79
10.34
10.25
9.87
CO2Me
CO2Me
N
O
4f
184
176
168
160
152
144
136
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120
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104
96
88
80
72
64
56
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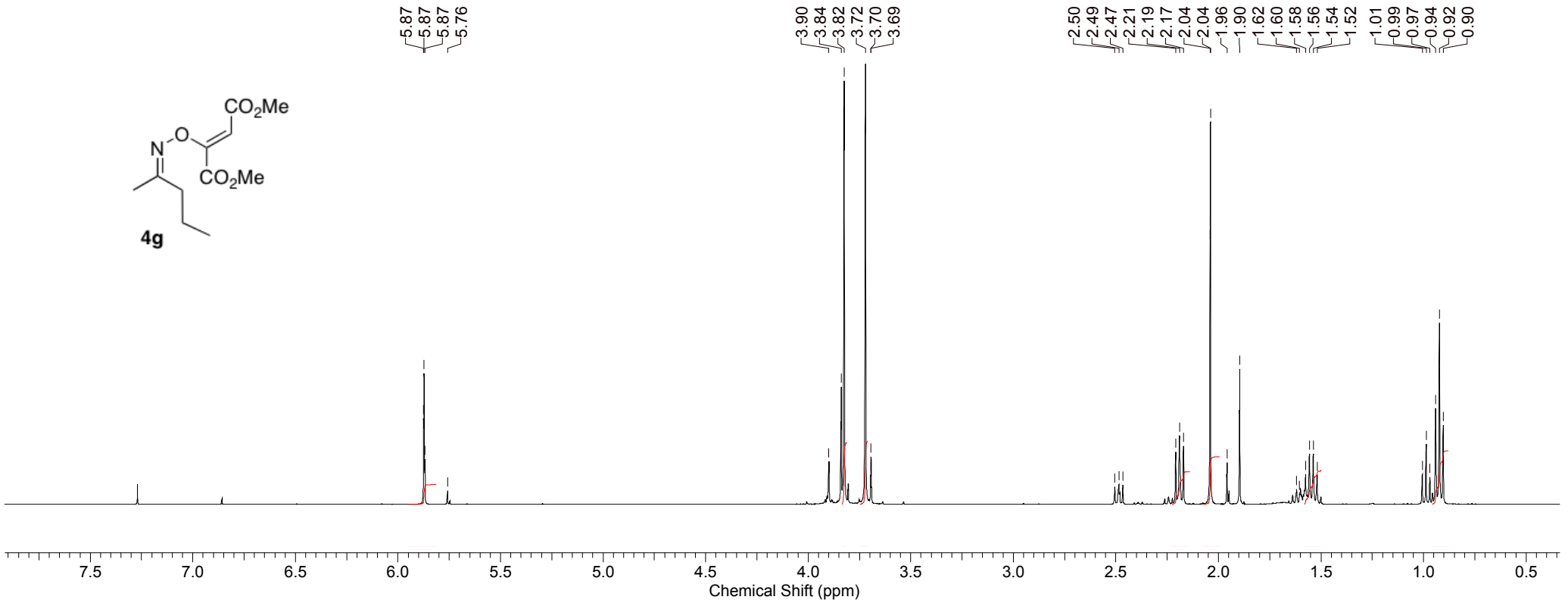
40
32
24
16
8
0
Chemical Shift (ppm)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5.87
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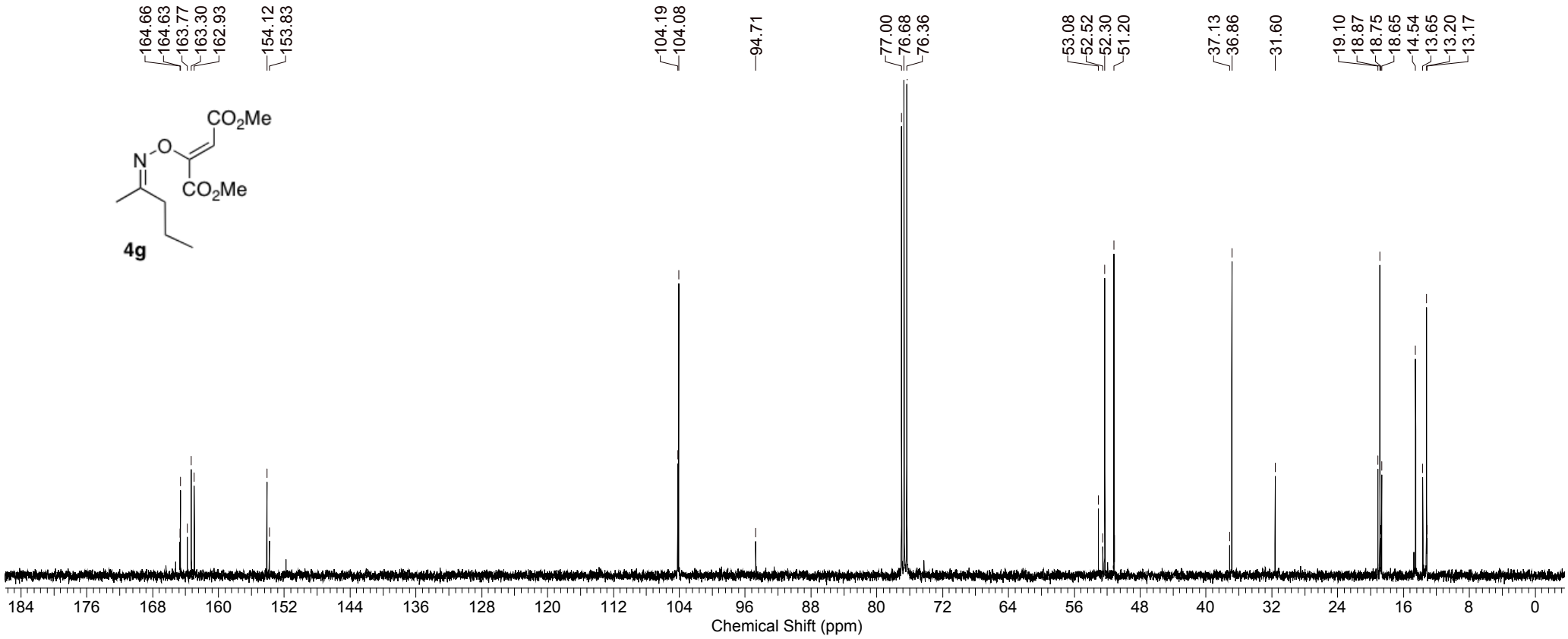
3.84
3.82
3.72
3.70
3.69
2.50
2.49
2.47
2.21
2.19
2.17
2.04
2.04
1.96
1.90
1.62
1.60
1.58
1.56
1.54
1.52
1.01
0.99
0.97
0.94
0.92
0.90
CO2Me
N
O
CO2Me
4g
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)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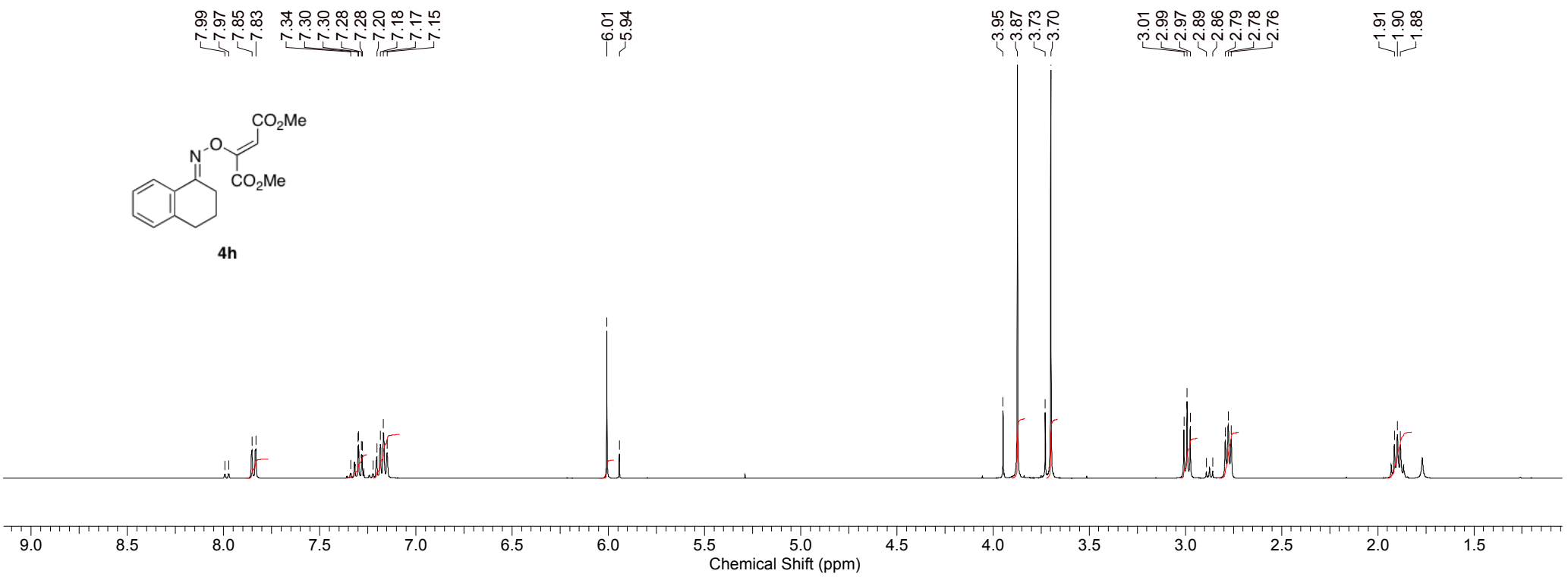
163.30
162.93
154.12
153.83
104.19
104.08
94.71
77.00
76.68
76.36
53.08
52.52
52.30
51.20
37.13
36.86
31.60
19.10
18.87
18.75
18.65
14.54
13.65
13.20
13.17
CO2Me
N
O
CO2Me
4g
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)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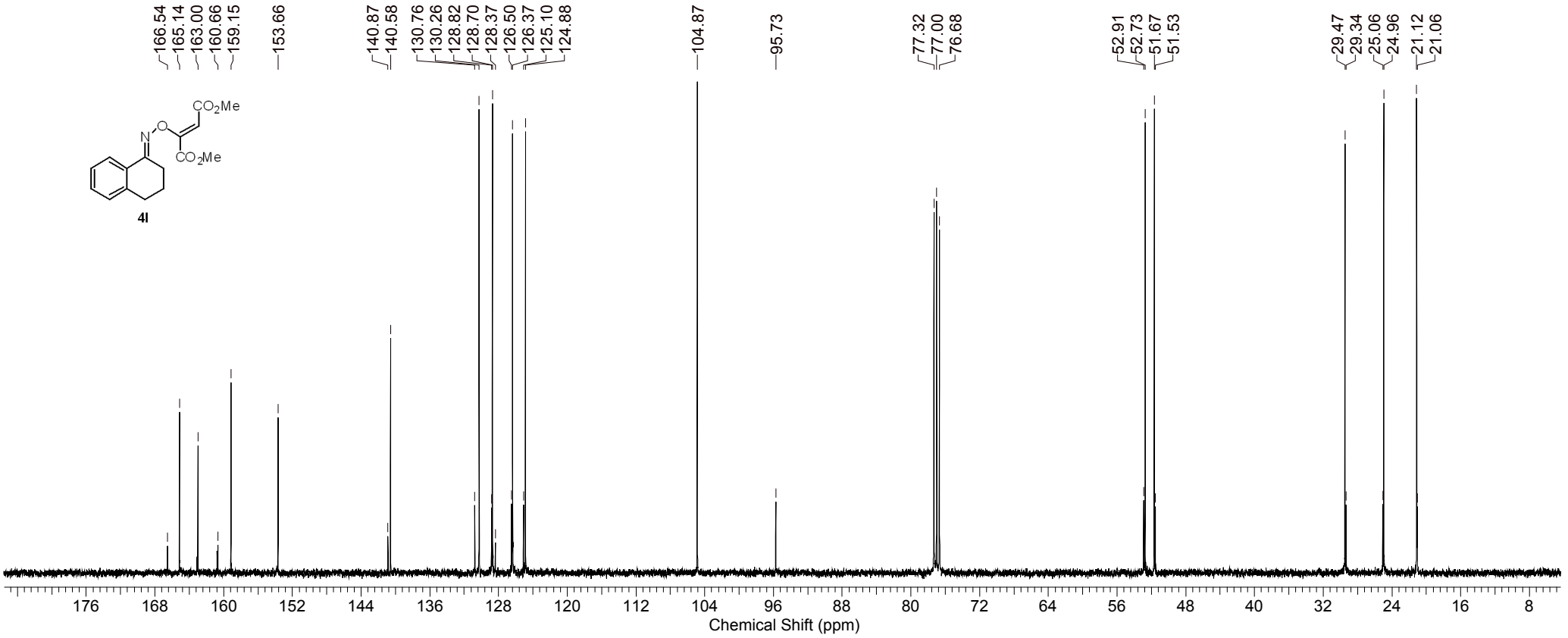
7.97
7.85
7.83
7.34
7.30
7.30
7.28
7.28
7.20
7.18
7.17
7.15
6.01
5.94
3.95
3.87
3.73
3.70
3.01
2.99
2.97
2.89
2.86
2.79
2.78
2.76
1.91
1.90
1.88
CO2Me
N
O
CO2Me
4h
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
Chemical Shift (ppm)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153.66
140.87
140.58
130.76
130.26
128.82
128.70
128.37
126.50
126.37
125.10
124.88
104.87
95.73
77.32
77.00
76.68
52.91
52.73
51.67
51.53
29.47
29.34
25.06
24.96
21.12
21.06
CO2Me
N
O
CO2Me
4l
176
168
160
152
144
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128
120
112
104
96
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80
72
64
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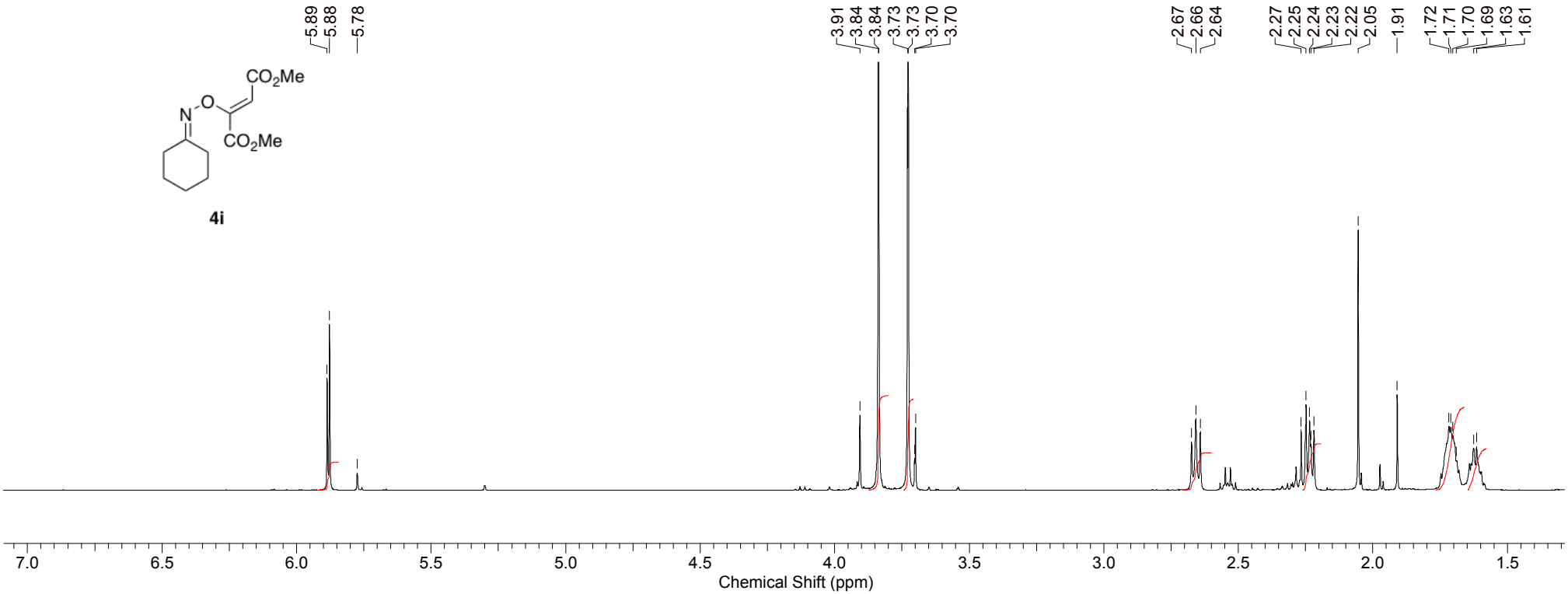
48
40
32
24
16
8
Chemical Shift (ppm)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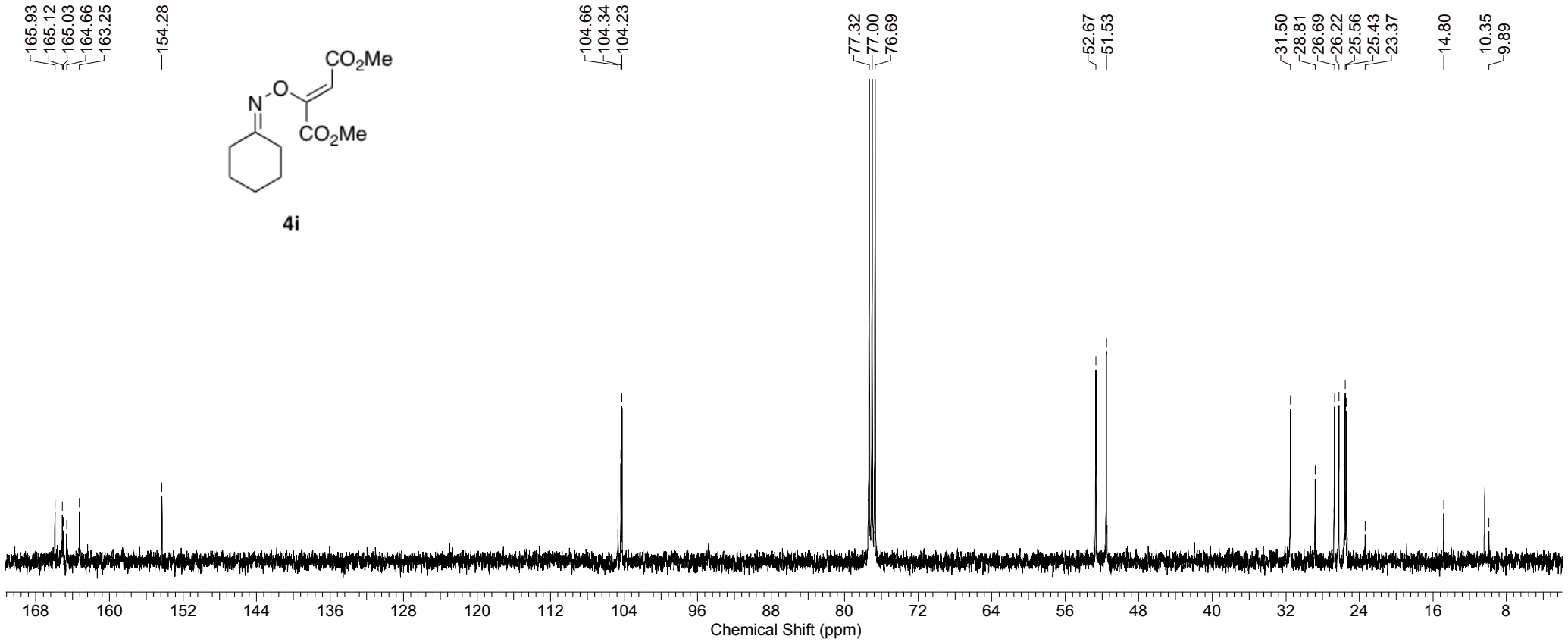
3.84
3.73
3.73
3.70
3.70
2.67
2.66
2.64
2.27
2.25
2.24
2.23
2.22
2.05
1.91
1.72
1.71
1.70
1.69
1.63
1.61
CO2Me
N
O
CO2Me
4i
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
Chemical Shift (ppm)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165.03
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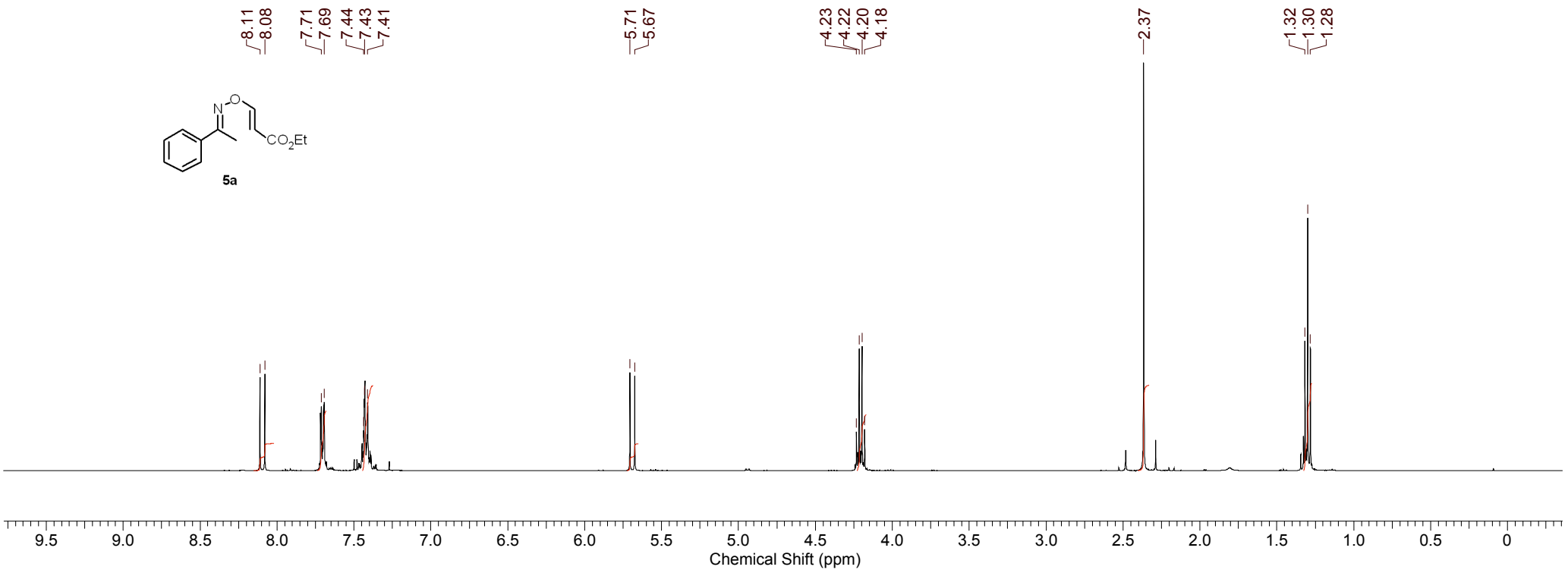
163.25
154.28
104.66
104.34
104.23
77.32
77.00
76.69
52.67
51.53
31.50
28.81
26.69
26.22
25.56
25.43
23.37
14.80
10.35
9.89
CO2Me
CO2Me
N
O
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

4i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7.43
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5.71
5.67
4.23
4.22
4.20
4.18
2.37
1.32
1.30
1.28
N
O
CO2Et
5a
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
4.0
3.5
3.0
2.5
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1.5
1.0
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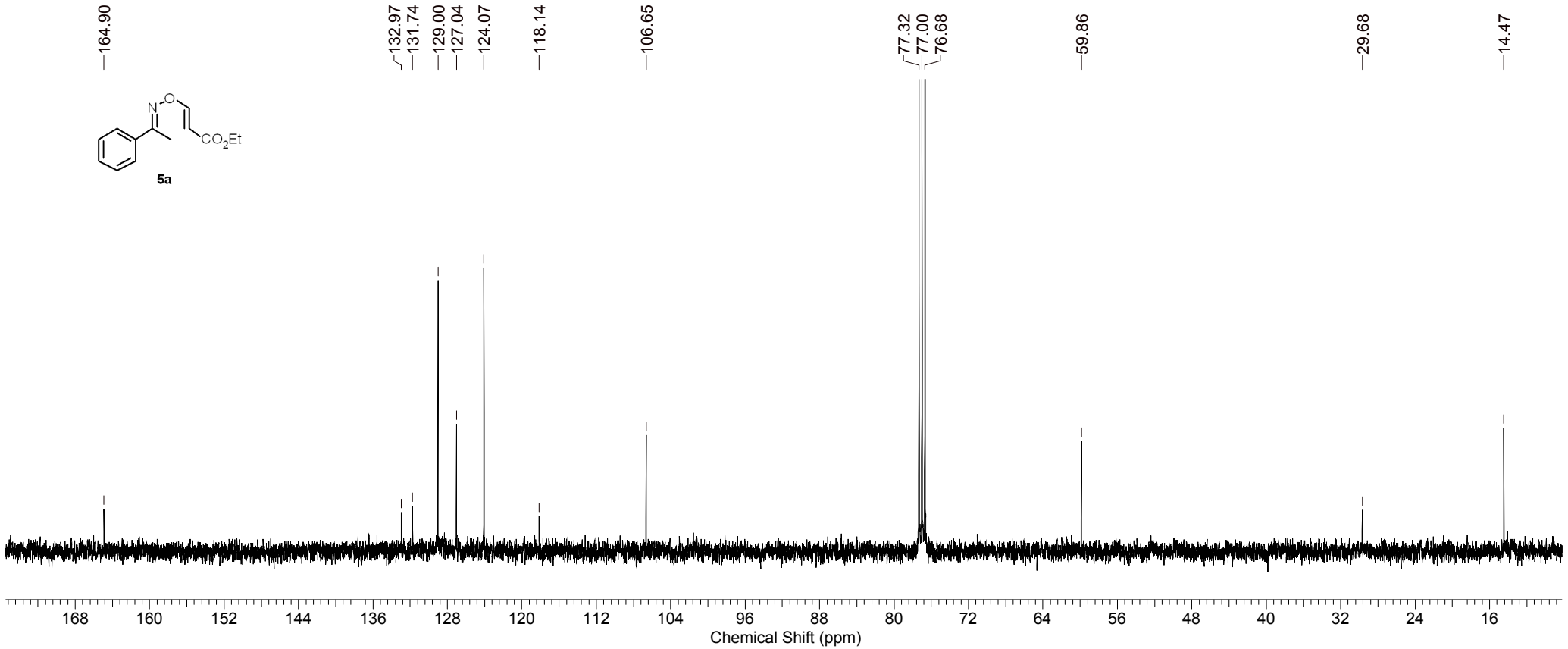
0
Chemical Shift (ppm)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129.00
127.04
124.07
118.14
106.65
77.32
77.00
76.68
59.86
29.68
14.47
N
O
CO2Et
5a
168
160
152
144
136
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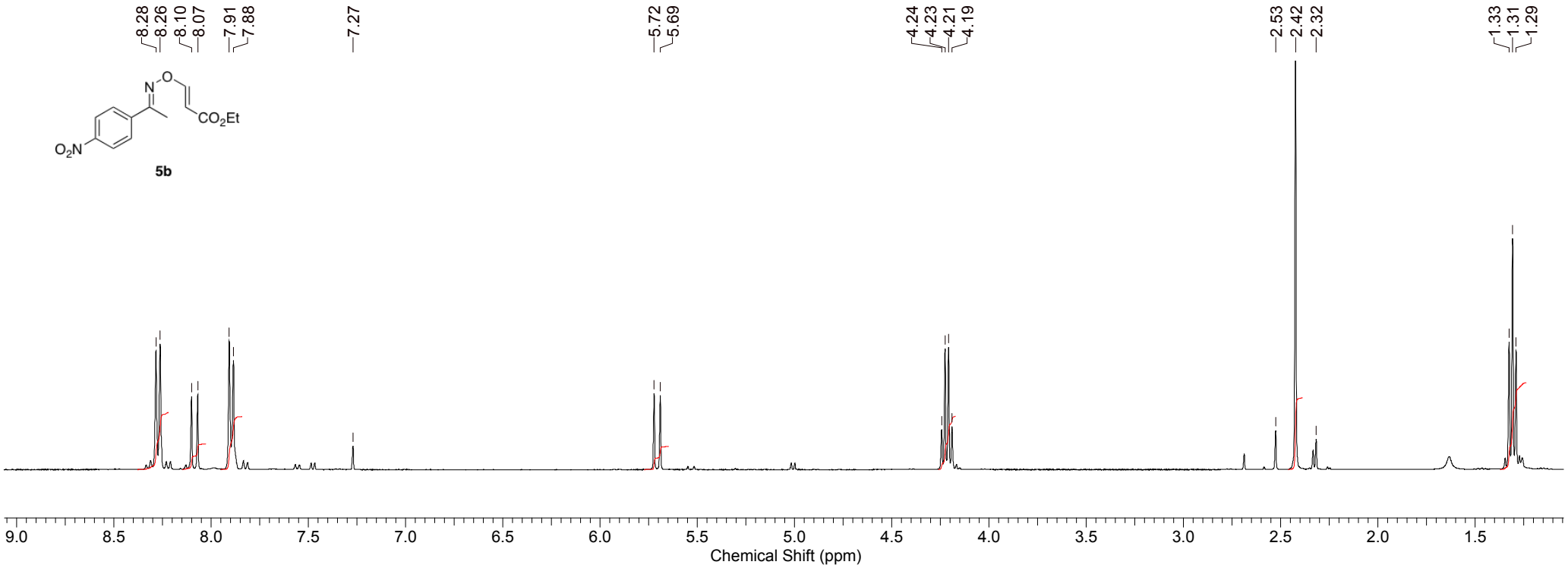
120
112
104
96
88
80
72
64
56
48
40
32
24
16
Chemical Shift (ppm)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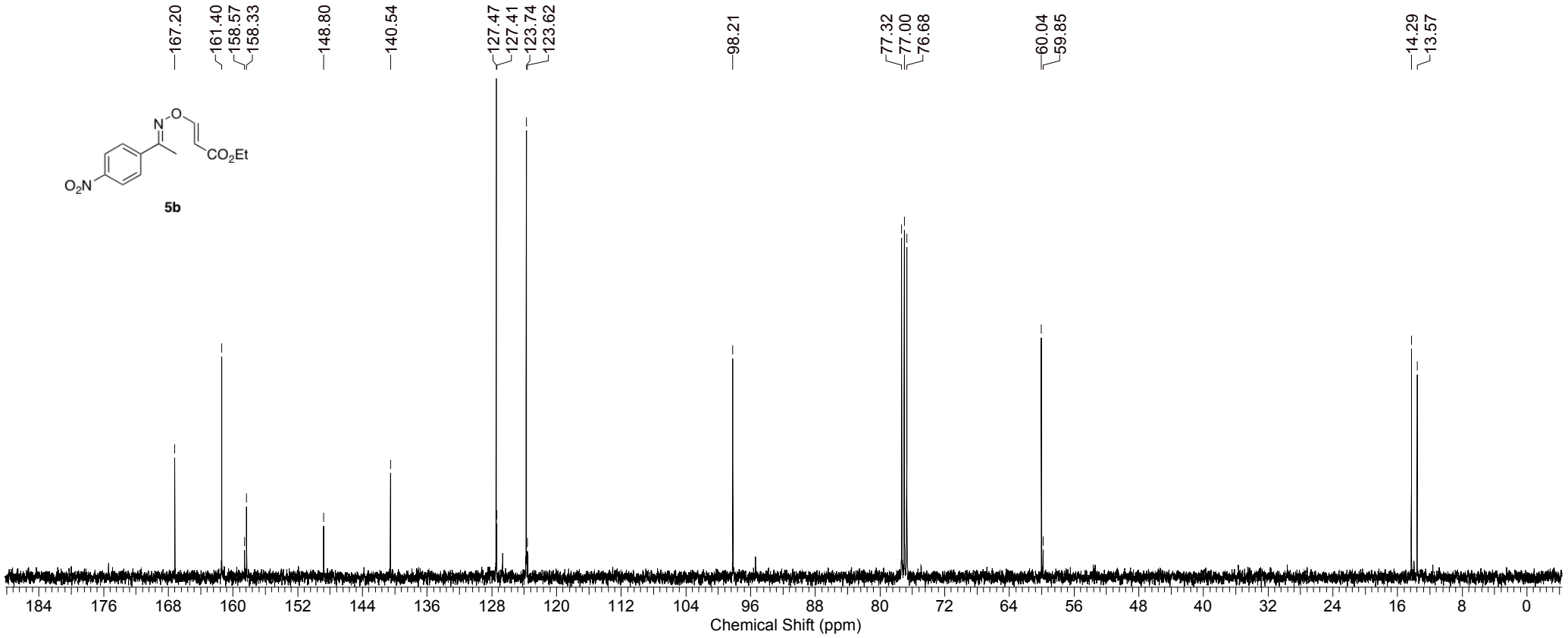
7.88
7.27
5.72
5.69
4.24
4.23
4.21
4.19
2.53
2.42
2.32
1.33
1.31
1.29
N
O
CO2Et
O2N
5b
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
Chemical Shift (ppm)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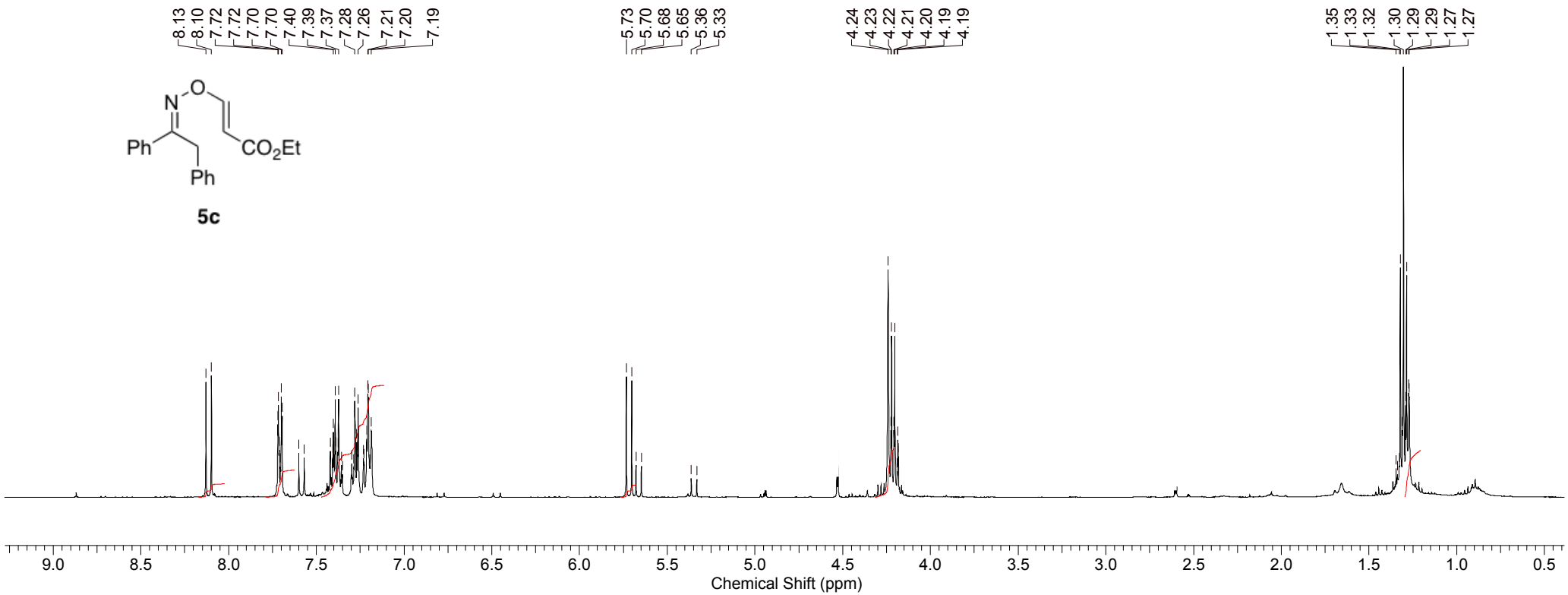
148.80
140.54
127.47
127.41
123.74
123.62
98.21
77.32
77.00
76.68
60.04
59.85
14.29
13.57
N
O
CO2Et
O2N
5b
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)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7.70
7.40
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7.28
7.26
7.21
7.20
7.19
5.73
5.70
5.68
5.65
5.36
5.33
4.24
4.23
4.22
4.21
4.20
4.19
4.19
1.35
1.33
1.32
1.30
1.29
1.29
1.27
1.27
N
O
Ph
CO2Et
Ph
5c
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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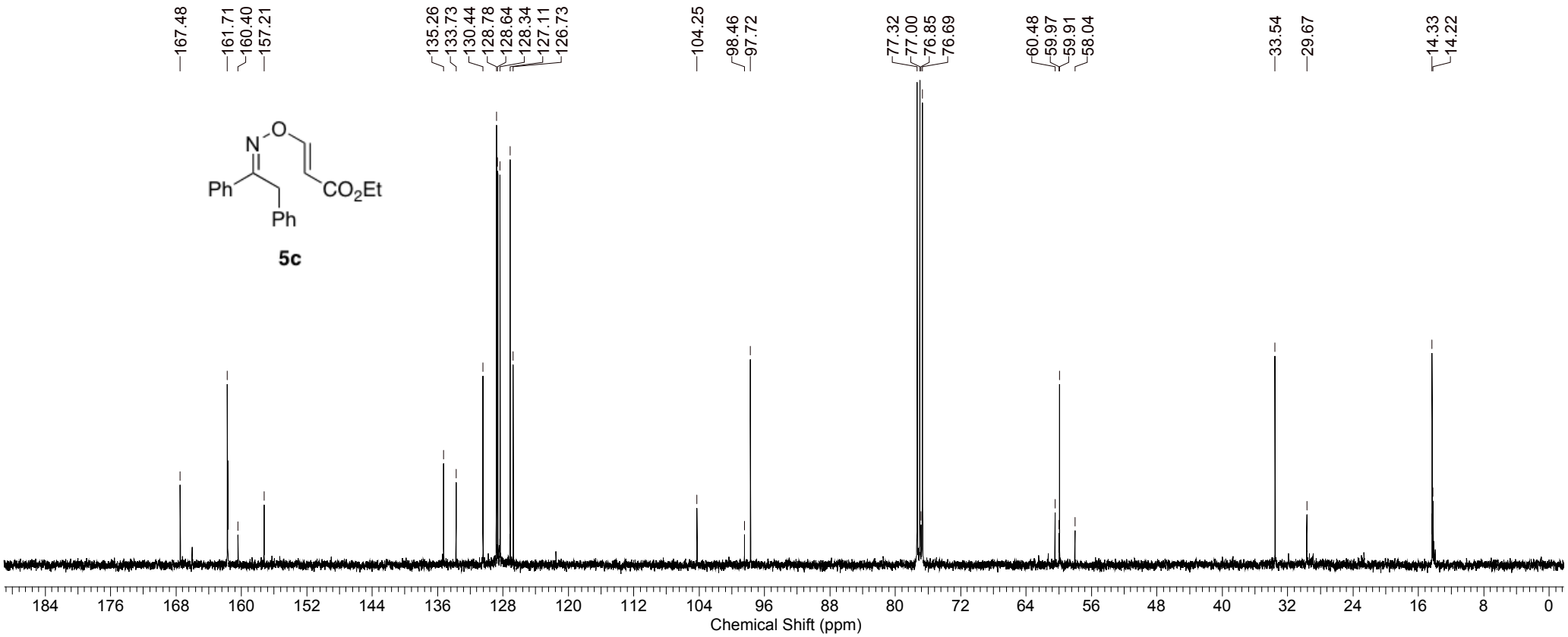
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)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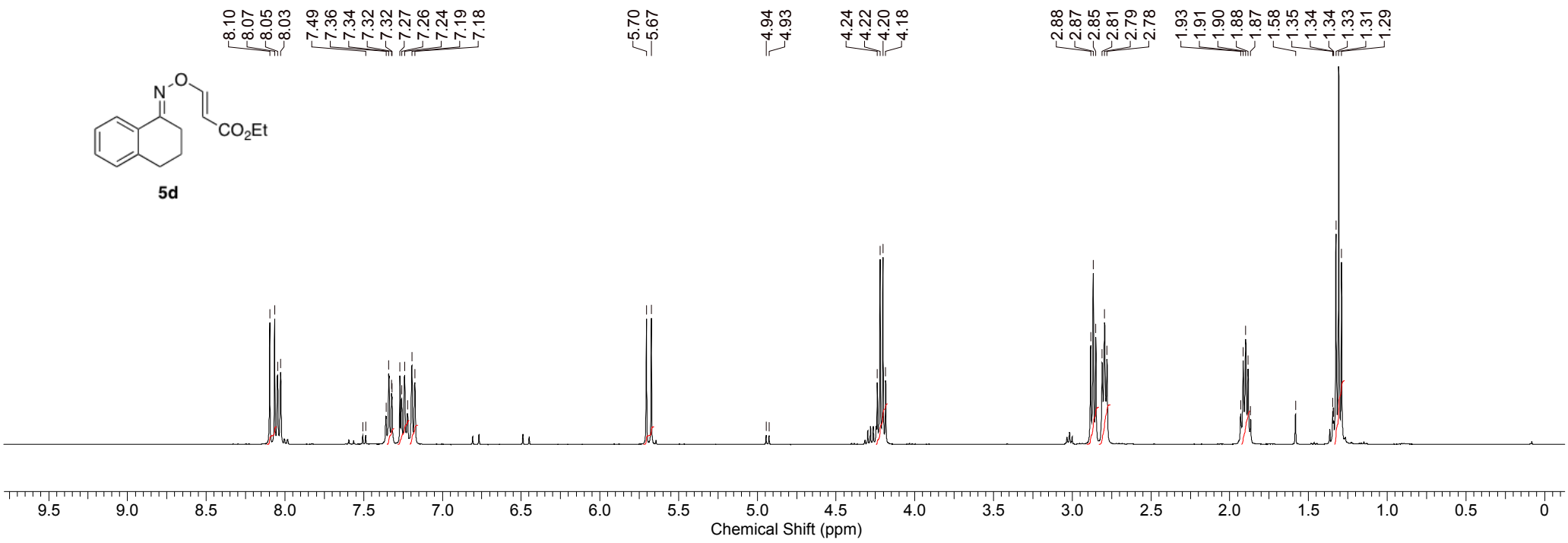
128.78
128.64
128.34
127.11
126.73
104.25
98.46
97.72
77.32
77.00
76.85
76.69
60.48
59.97
59.91
58.04
33.54
29.67
14.33
14.22
N
O
Ph
CO2Et
Ph
5c
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)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7.34
7.32
7.32
7.27
7.26
7.24
7.19
7.18
5.70
5.67
4.94
4.93
4.24
4.22
4.20
4.18
2.88
2.87
2.85
2.81
2.79
2.78
1.93
1.91
1.90
1.88
1.87
1.58
1.35
1.34
1.34
1.33
1.31
1.29
N
O
CO2Et
5d
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
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1.0
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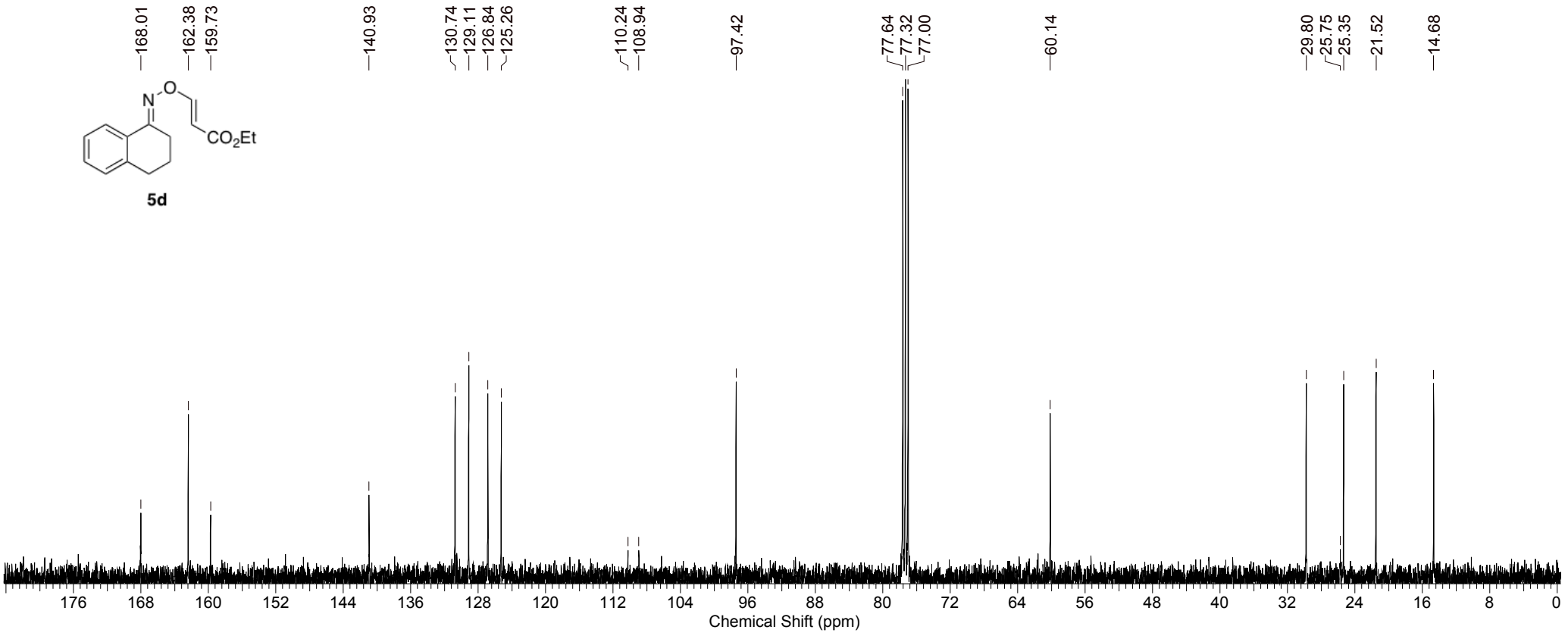
Chemical Shift (ppm)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125.26
110.24
108.94
97.42
77.64
77.32
77.00
60.14
29.80
25.75
25.35
21.52
14.68
N
O
CO2Et
5d
176
168
160
152
144
136
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120
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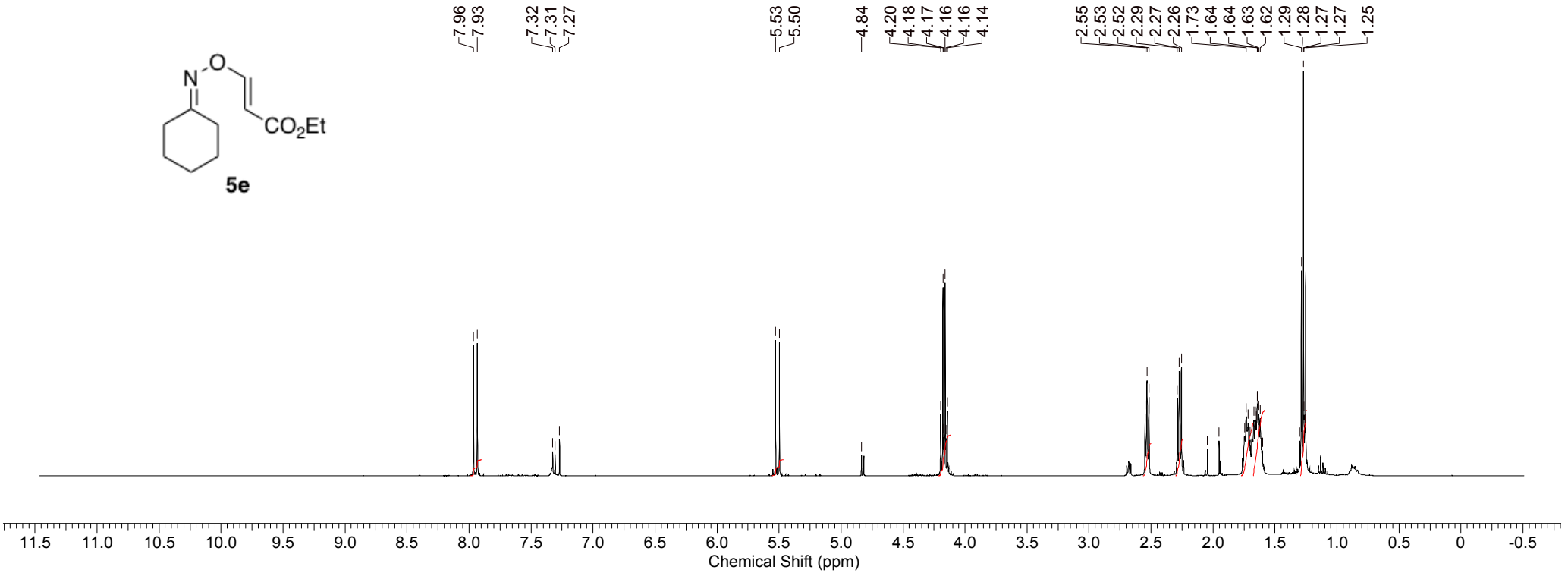
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)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4.16
4.16
4.14
2.55
2.53
2.52
2.29
2.27
2.26
1.73
1.64
1.64
1.63
1.62
1.29
1.28
1.27
1.27
1.25
N
O
CO2Et
5e
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
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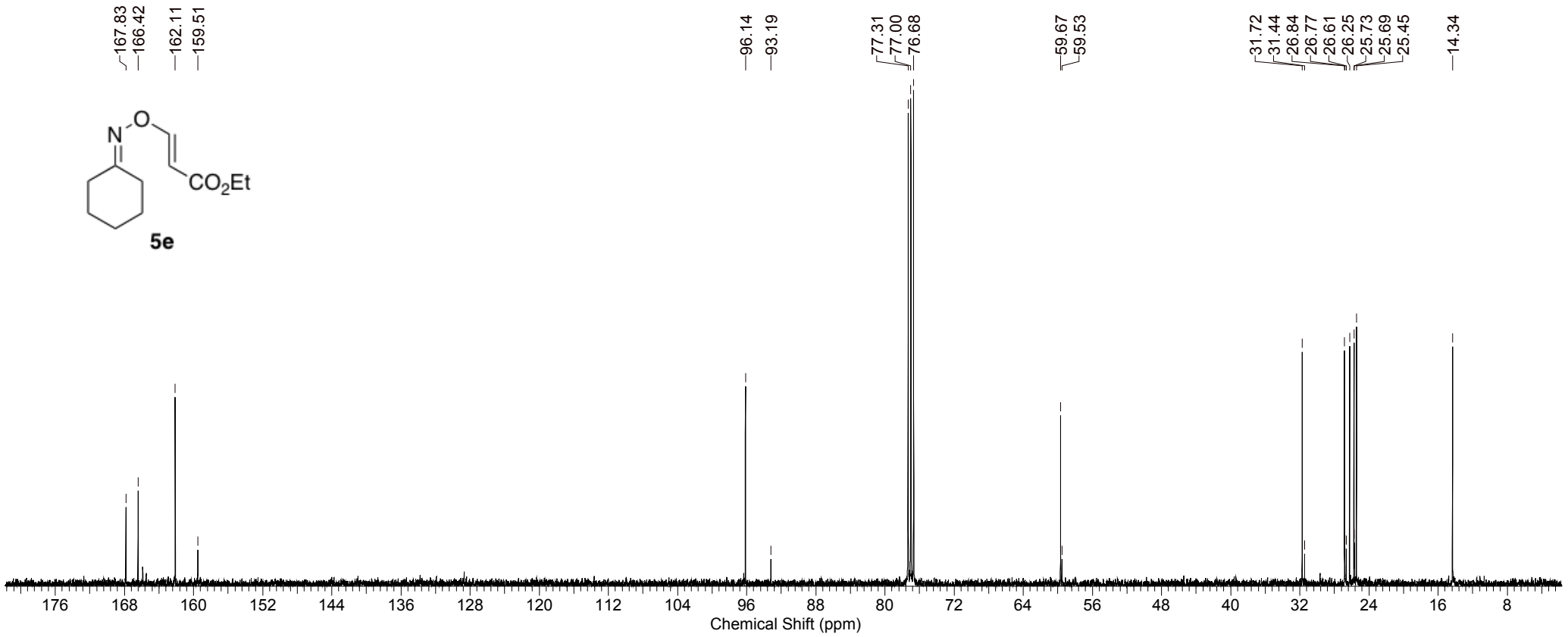
0.5
0
-0.5
Chemical Shift (ppm)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93.19
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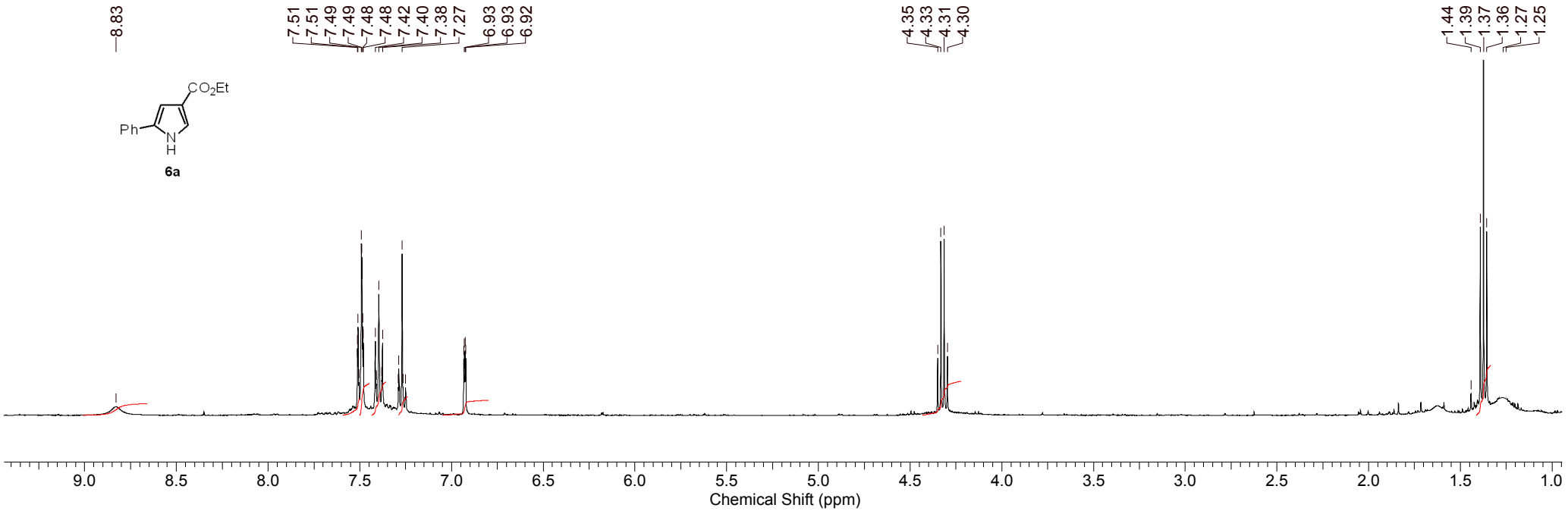
77.00
76.68
59.67
59.53
31.72
31.44
26.84
26.77
26.61
26.25
25.73
25.69
25.45
14.34
N
O
CO2Et
5e
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)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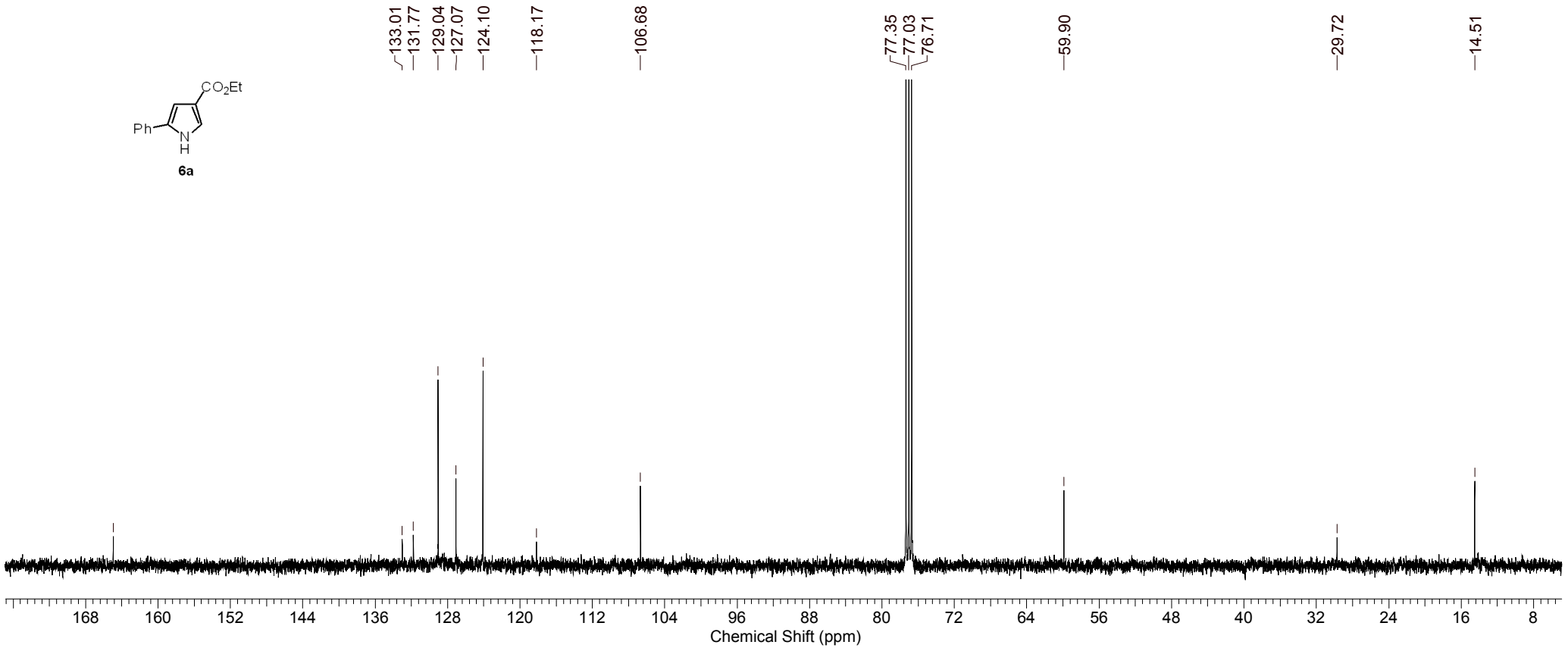
7.38
7.27
6.93
6.93
6.92
4.35
4.33
4.31
4.30
1.44
1.39
1.37
1.36
1.27
1.25
CO2Et
Ph
N
H
6a
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)


133.01
131.77
129.04
127.07
124.10
118.17
106.68
77.35
77.03
76.71
59.90
29.72
14.51
CO2Et
Ph
N
H
6a
168
160
152
144
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128
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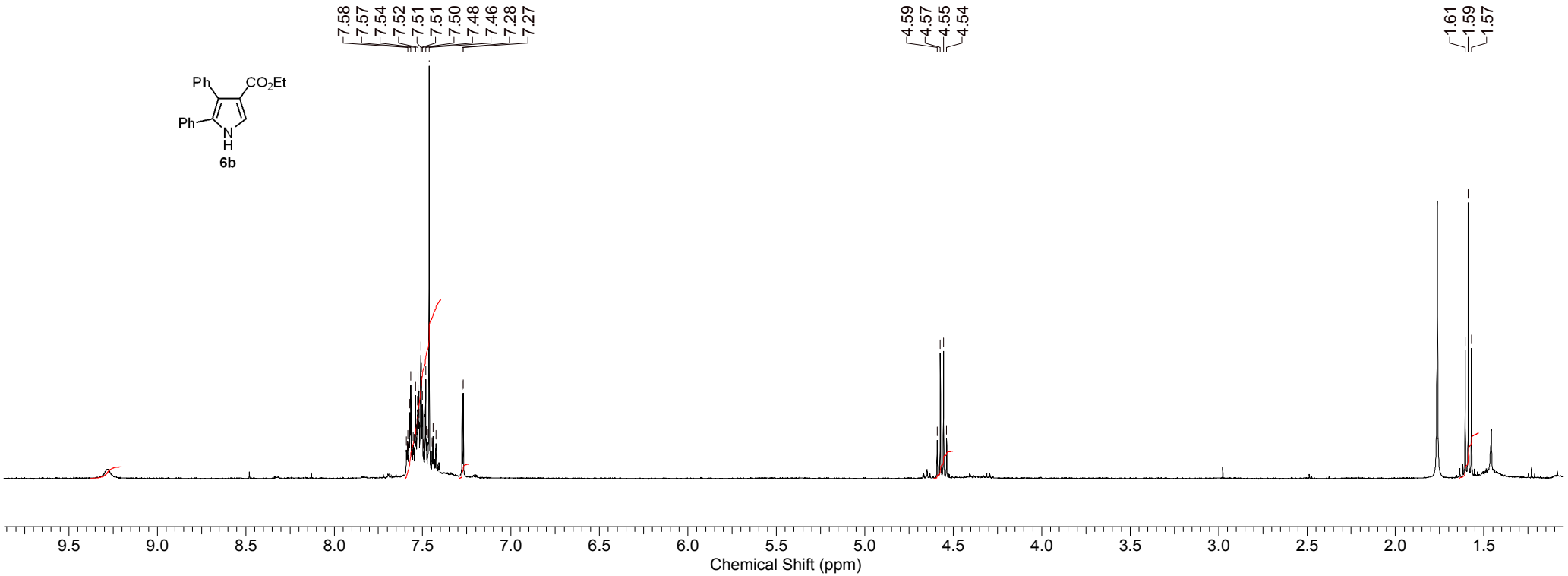
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


7.58
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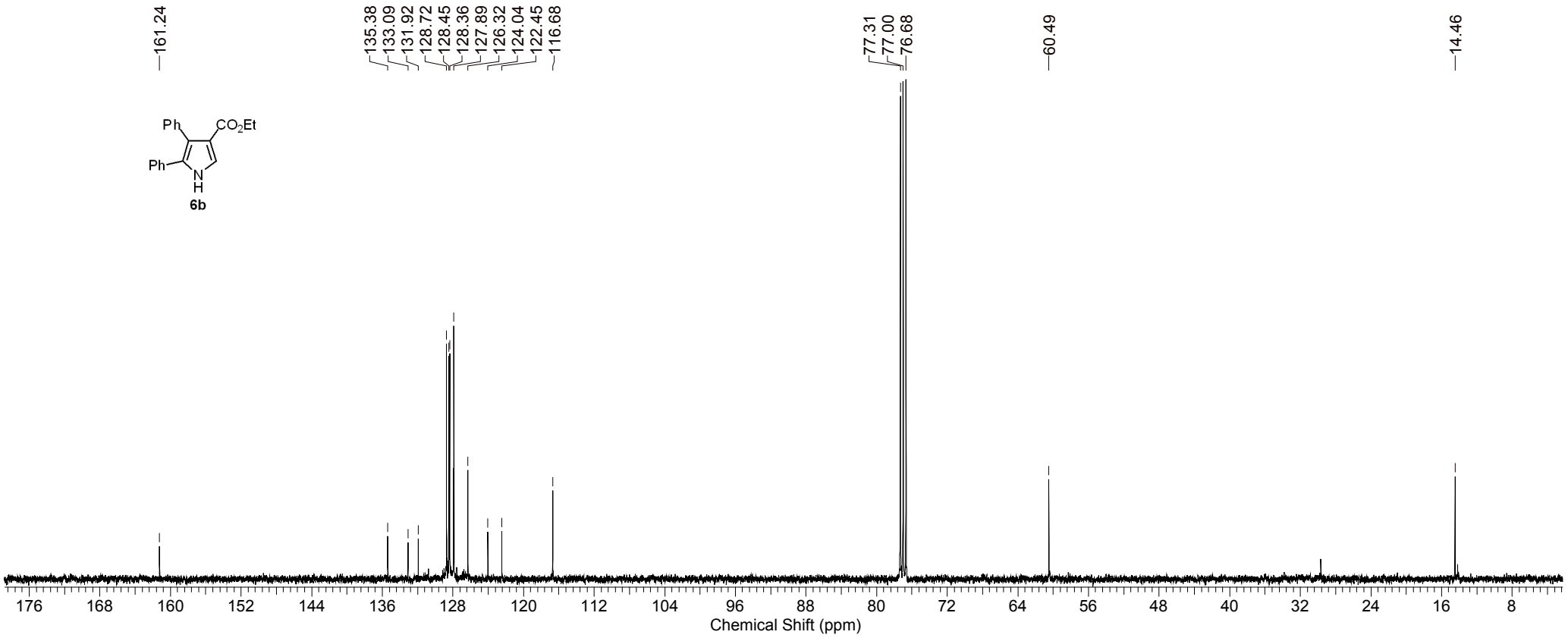
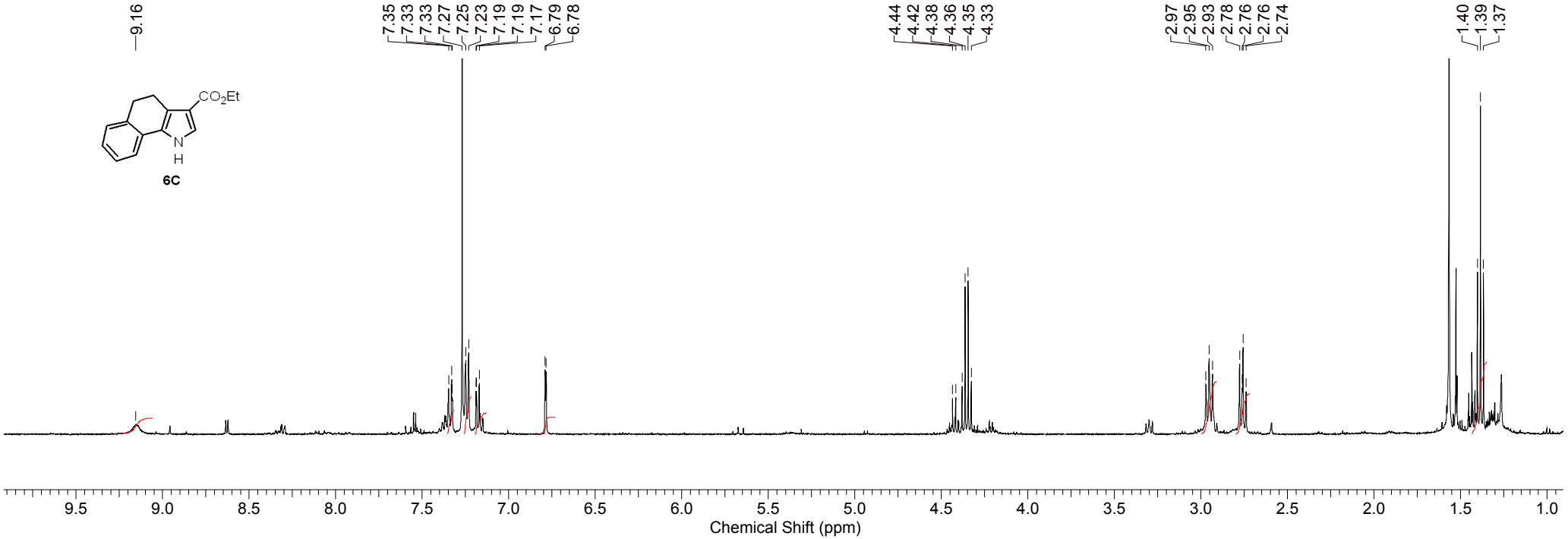
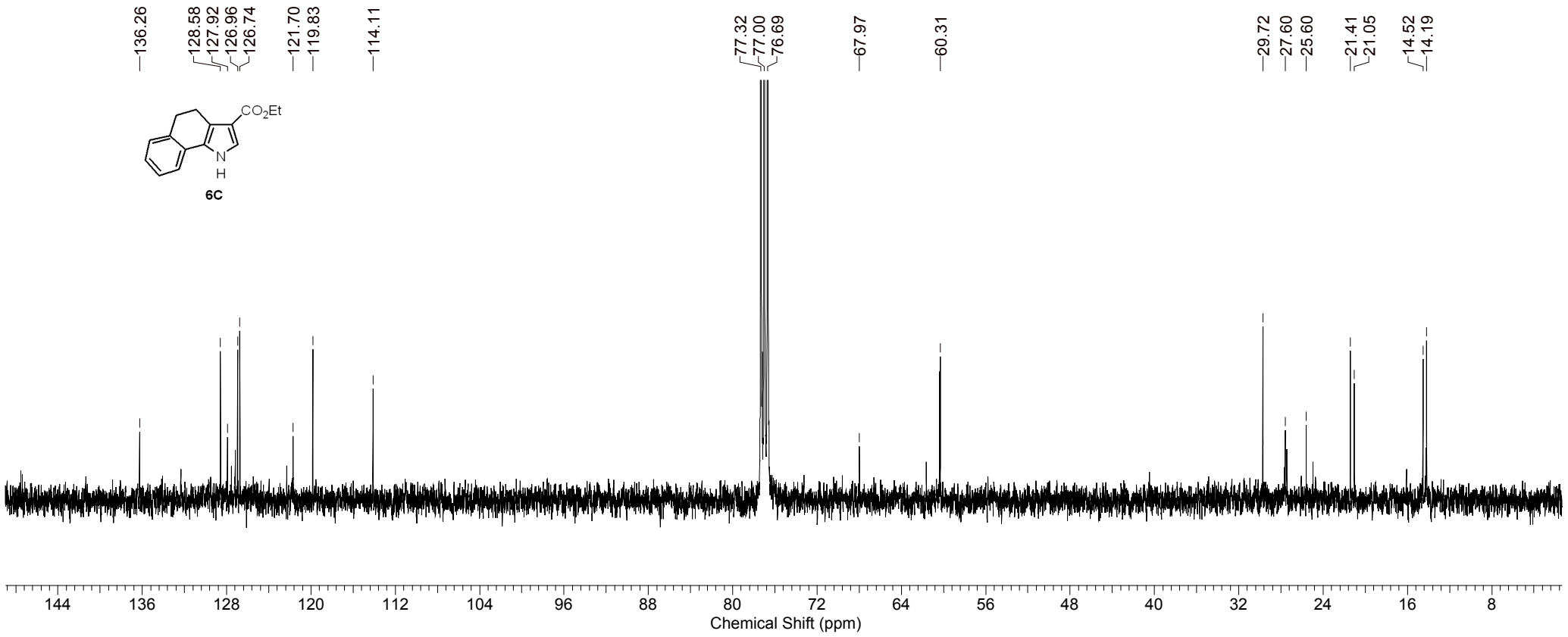
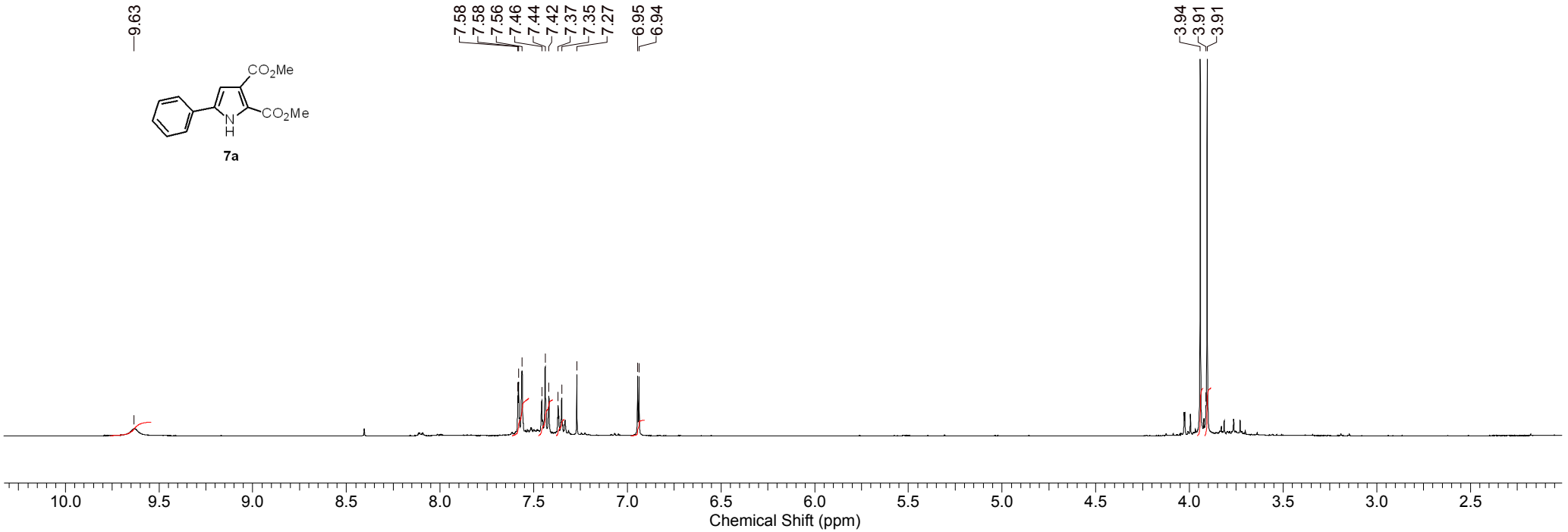
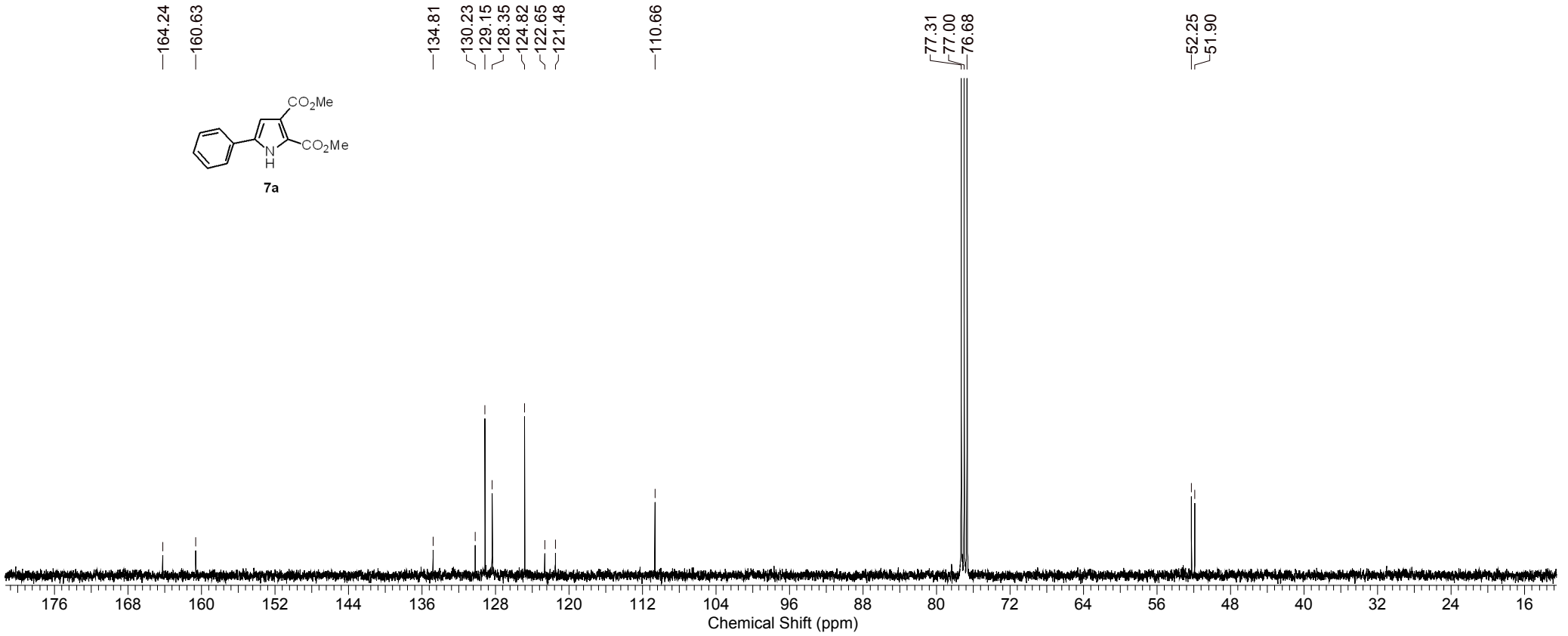
7.28
7.27
4.59
4.57
4.55
4.54
1.61
1.59
1.57
Ph
CO2Et
Ph
N
H
6b
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
Chemical Shift (ppm)

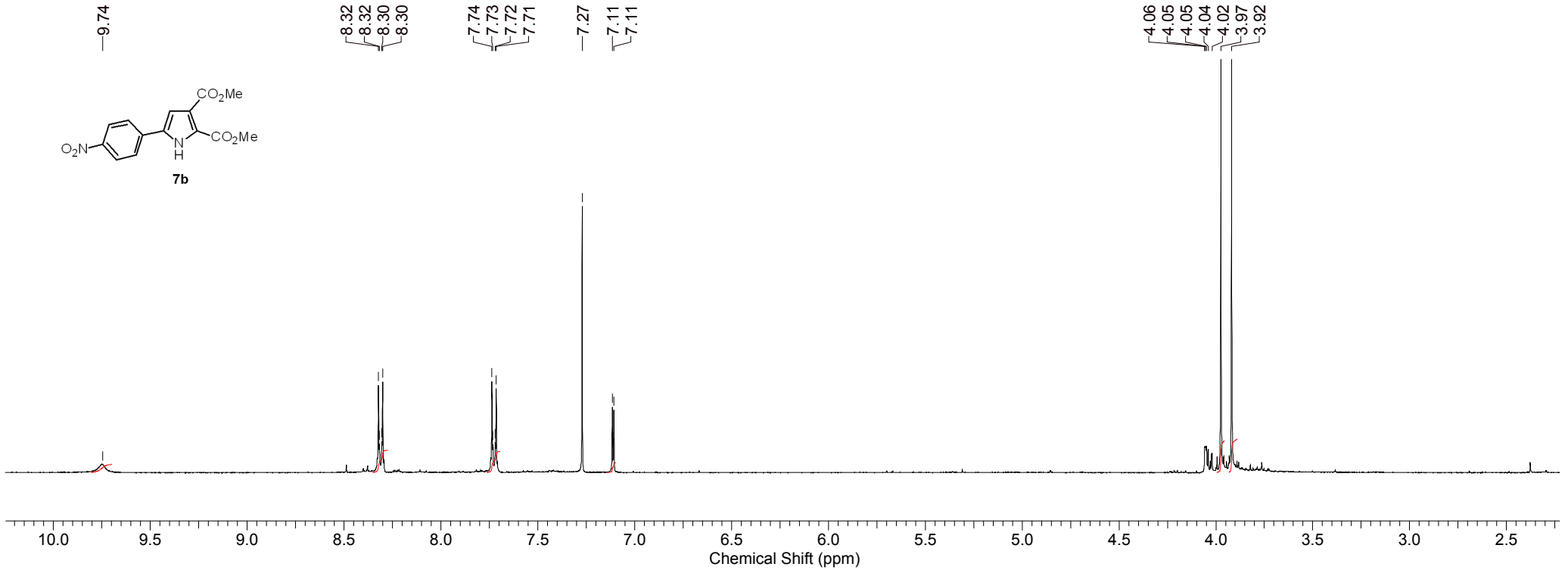

161.24
135.38
133.09
131.92
128.72
128.45
128.36
127.89
126.32
124.04
122.45
116.68
77.31
77.00
76.68
60.49
14.46
Ph
CO2Et
Ph
N
H
6b
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

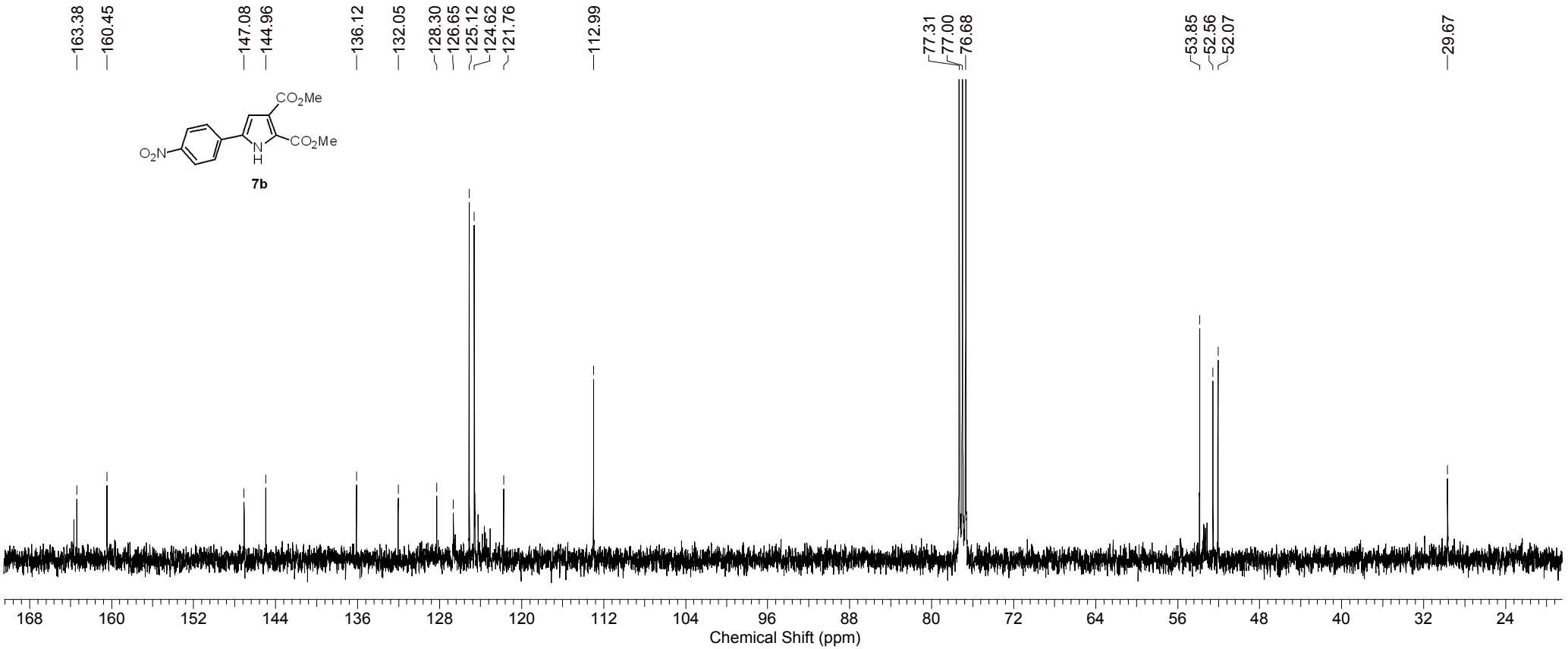

9.16
7.35
7.33
7.33
7.27
7.25
7.23
7.19
7.19
7.17
6.79
6.78
4.44
4.42
4.38
4.36
4.35
4.33
2.97
2.95
2.93
2.78
2.76
2.76
2.74
1.40
1.39
1.37
CO2Et
N
H
6C
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)

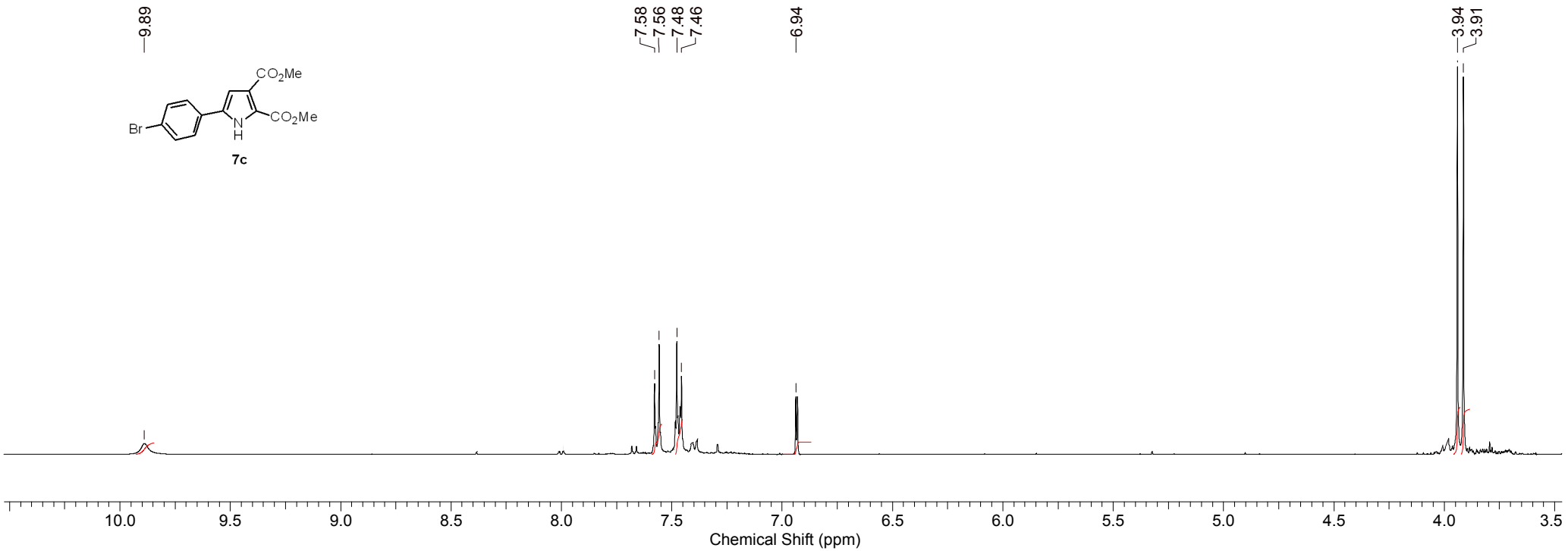

136.26
128.58
127.92
126.96
126.74
121.70
119.83
114.11
77.32
77.00
76.69
67.97
60.31
29.72
27.60
25.60
21.41
21.05
14.52
14.19
CO2Et
N
H
6C
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

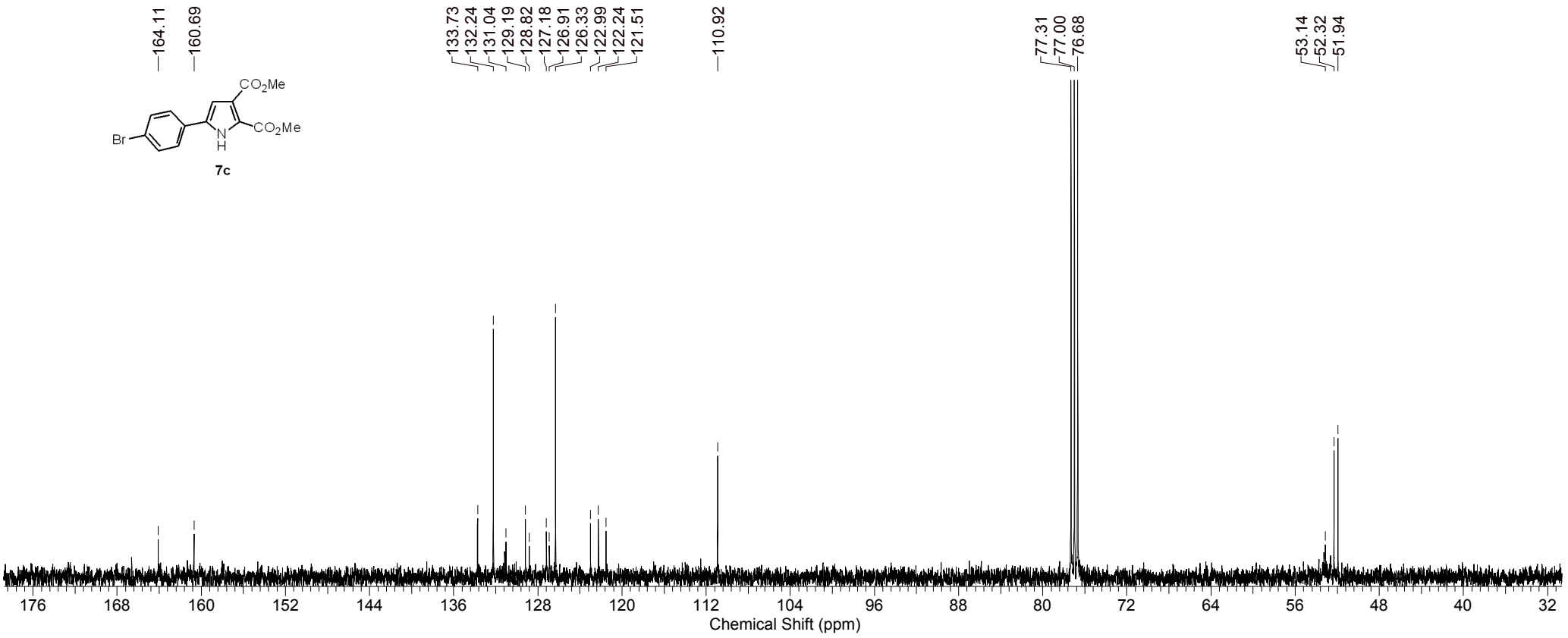

9.63
7.58
7.58
7.56
7.46
7.44
7.42
7.37
7.35
7.27
6.95
6.94
3.94
3.91
3.91
CO2Me
CO2Me
N
H
7a
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
Chemical Shift (ppm)

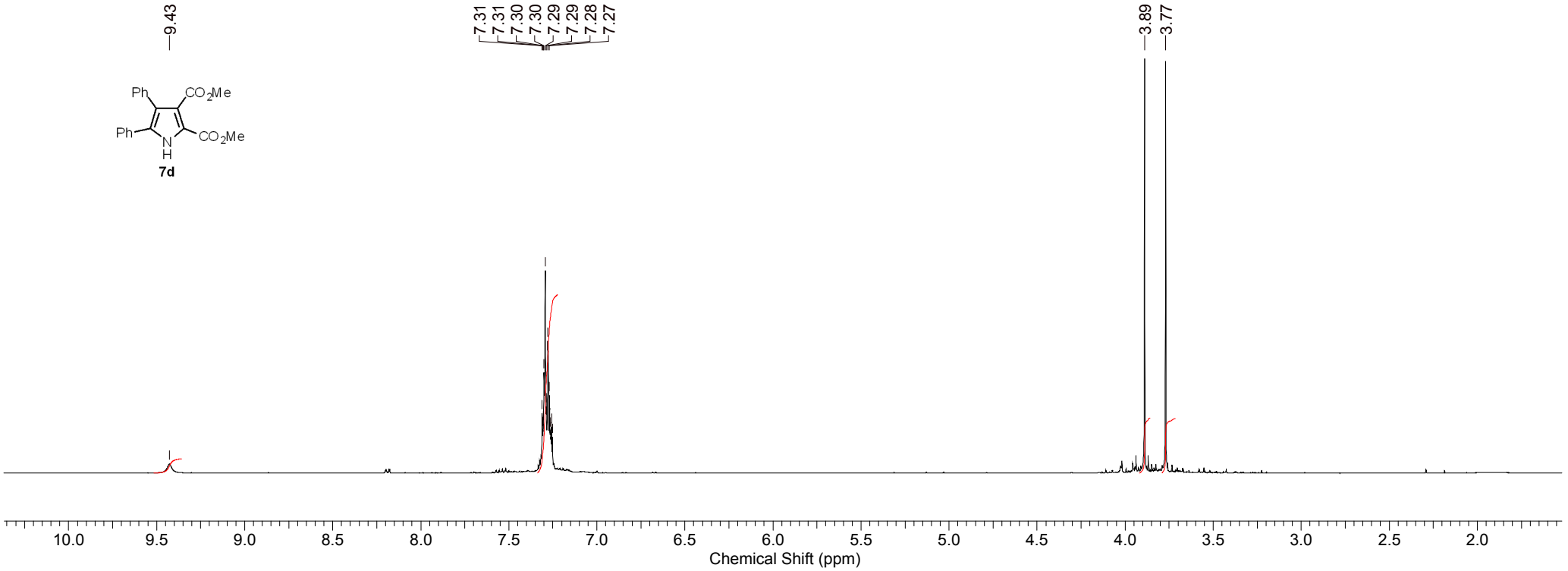

164.24
160.63
134.81
130.23
129.15
128.35
124.82
122.65
121.48
110.66
77.31
77.00
76.68
52.25
51.90
CO2Me
CO2Me
N
H
7a
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
Chemical Shift (ppm)

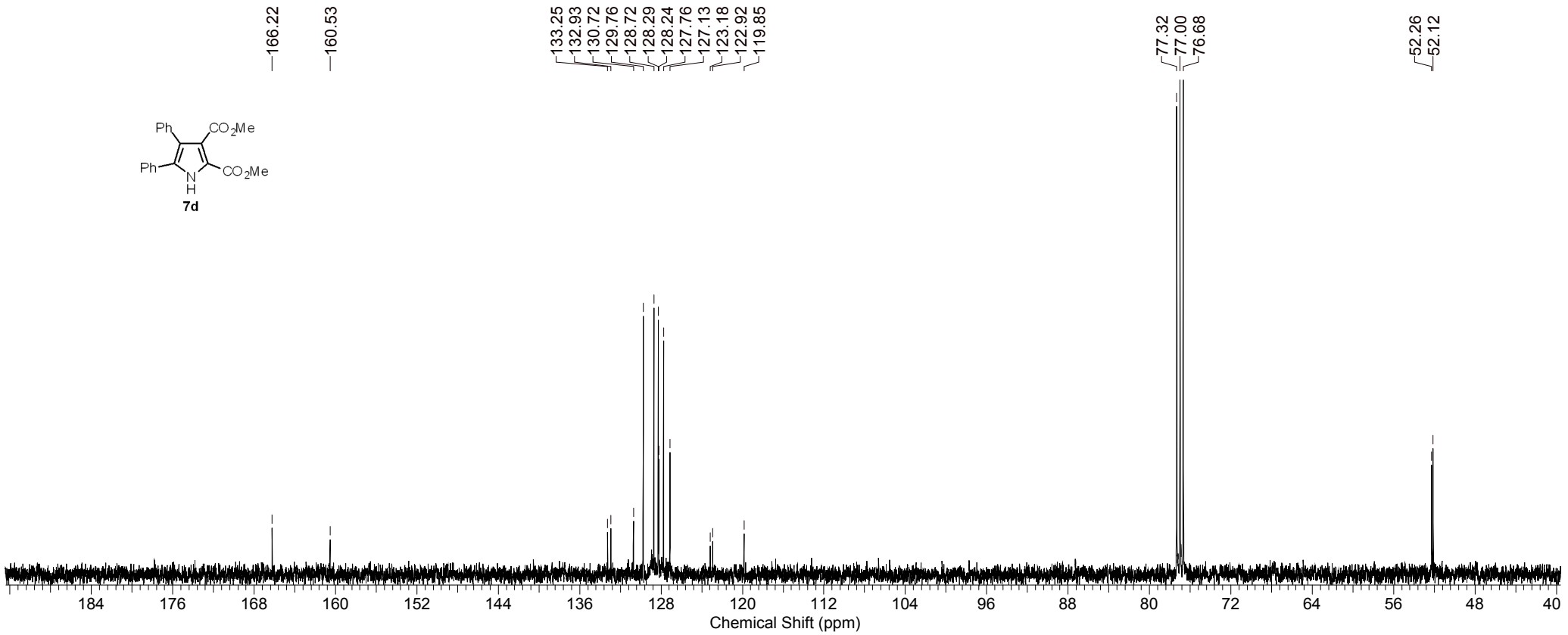

9.74
8.32
8.32
8.30
8.30
7.74
7.73
7.72
7.71
7.27
7.11
7.11
4.06
4.05
4.05
4.04
4.02
3.97
3.92
CO2Me
CO2Me
O2N
N
H
7b
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
Chemical Shift (ppm)

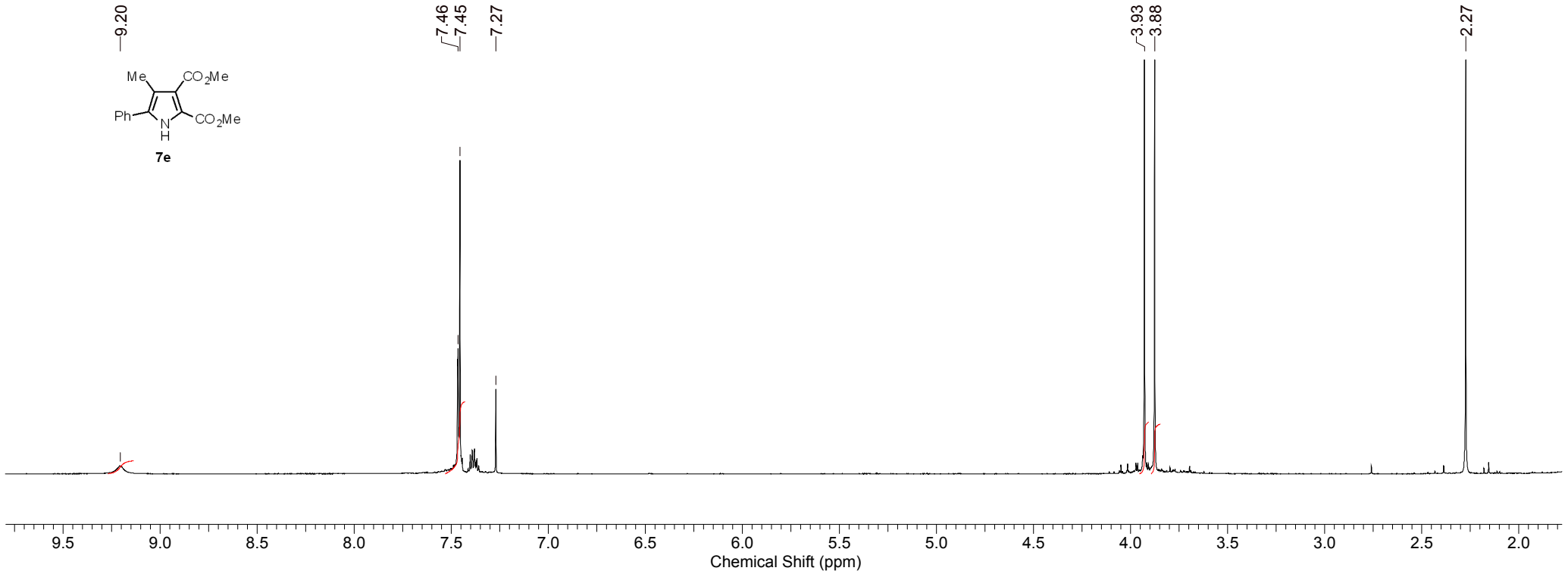

163.38
160.45
147.08
144.96
136.12
132.05
128.30
126.65
125.12
124.62
121.76
112.99
77.31
77.00
76.68
53.85
52.56
52.07
29.67
CO2Me
CO2Me
O2N
N
H
7b
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
Chemical Shift (ppm)

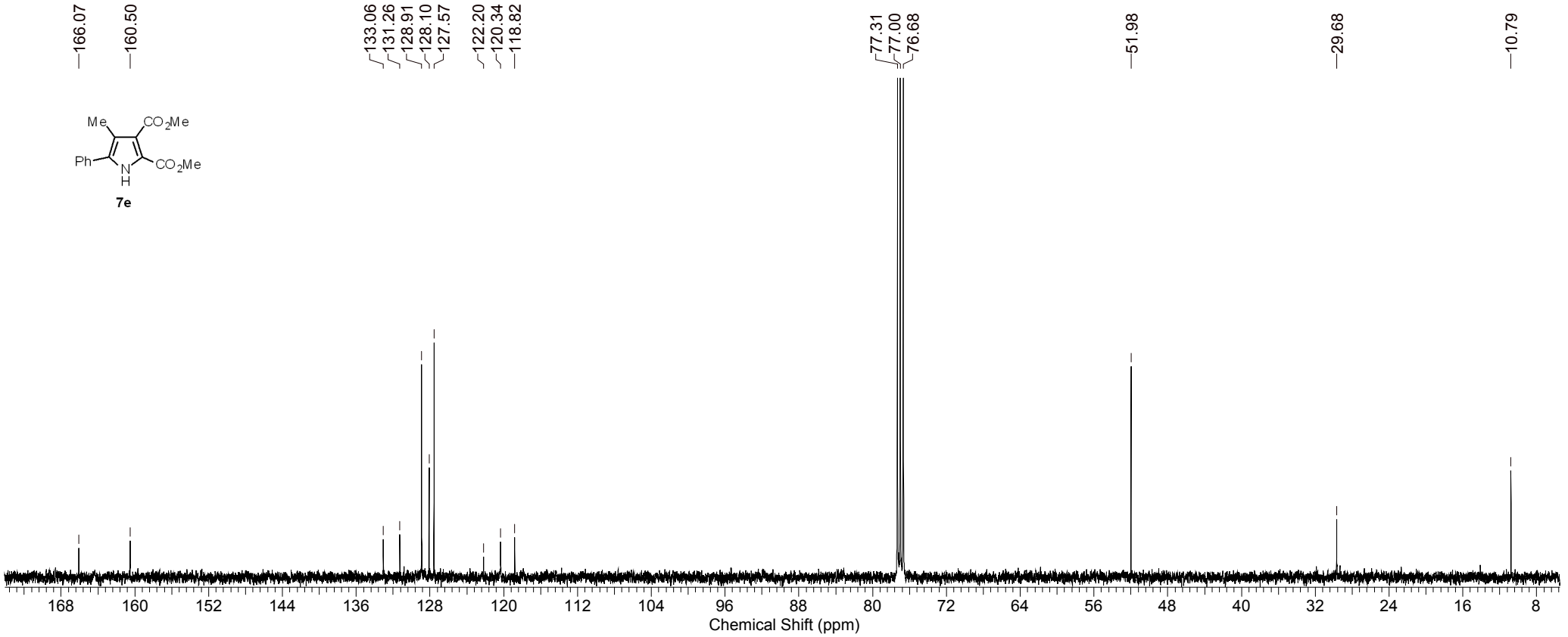

9.89
7.58
7.56
7.48
7.46
6.94
3.94
3.91
CO2Me
CO2Me
Br
N
H
7c
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
Chemical Shift (ppm)

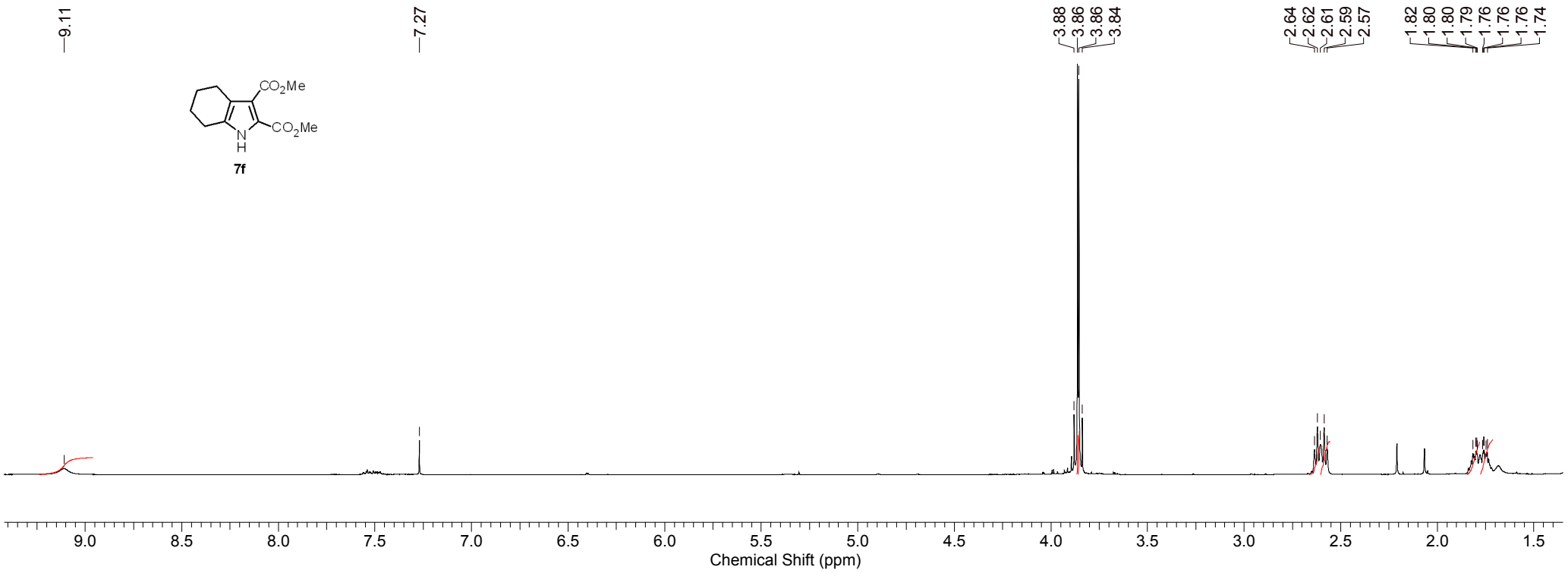

164.11
160.69
133.73
132.24
131.04
129.19
128.82
127.18
126.91
126.33
122.99
122.24
121.51
110.92
77.31
77.00
76.68
53.14
52.32
51.94
CO2Me
CO2Me
Br
N
H
7c
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
Chemical Shift (ppm)

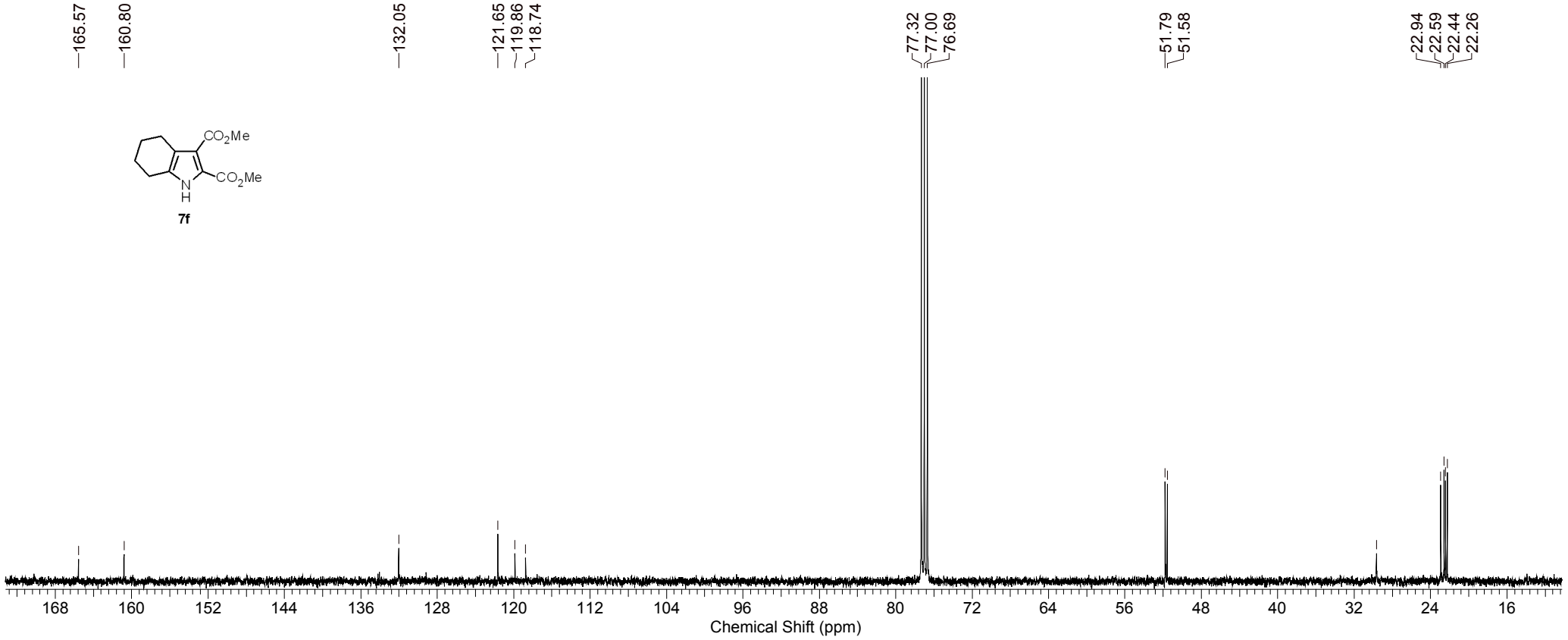

9.43
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.27
3.89
3.77
Ph
CO2Me
Ph
N
H
CO2Me
7d
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
Chemical Shift (ppm)

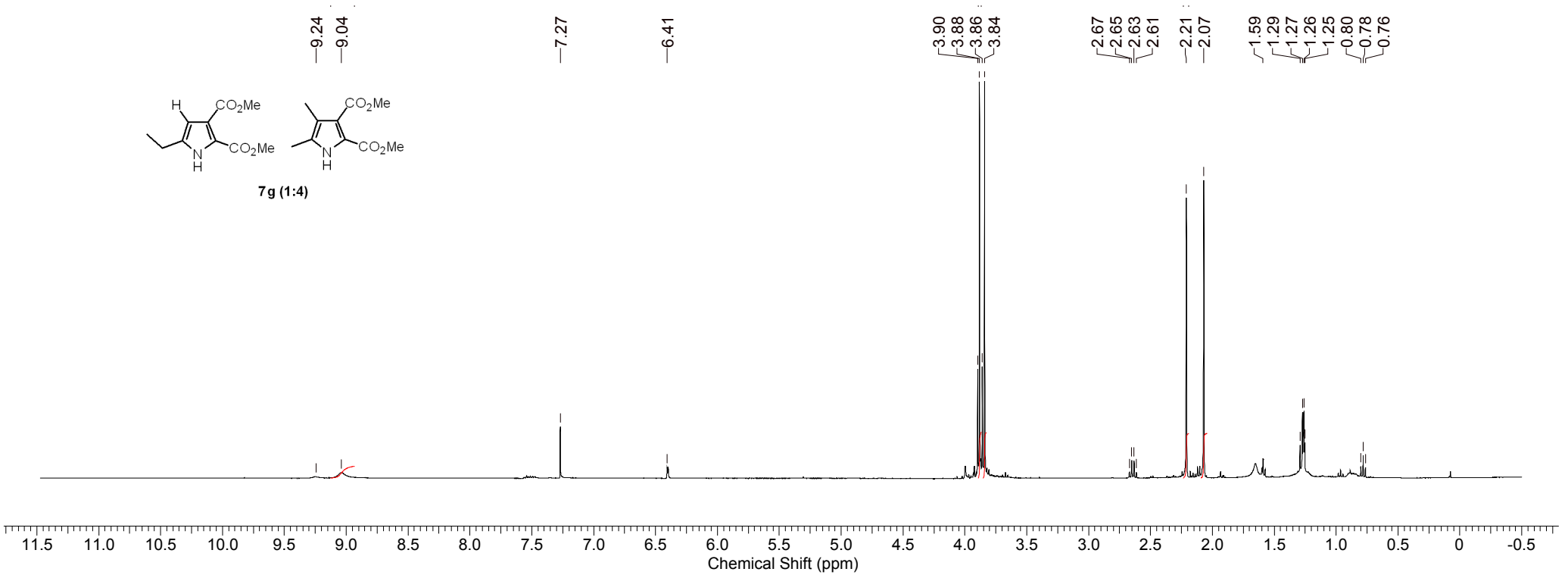

166.22
160.53
133.25
132.93
130.72
129.76
128.72
128.29
128.24
127.76
127.13
123.18
122.92
119.85
77.32
77.00
76.68
52.26
52.12
Ph
CO2Me
Ph
CO2Me
N
H
7d
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
Chemical Shift (ppm)

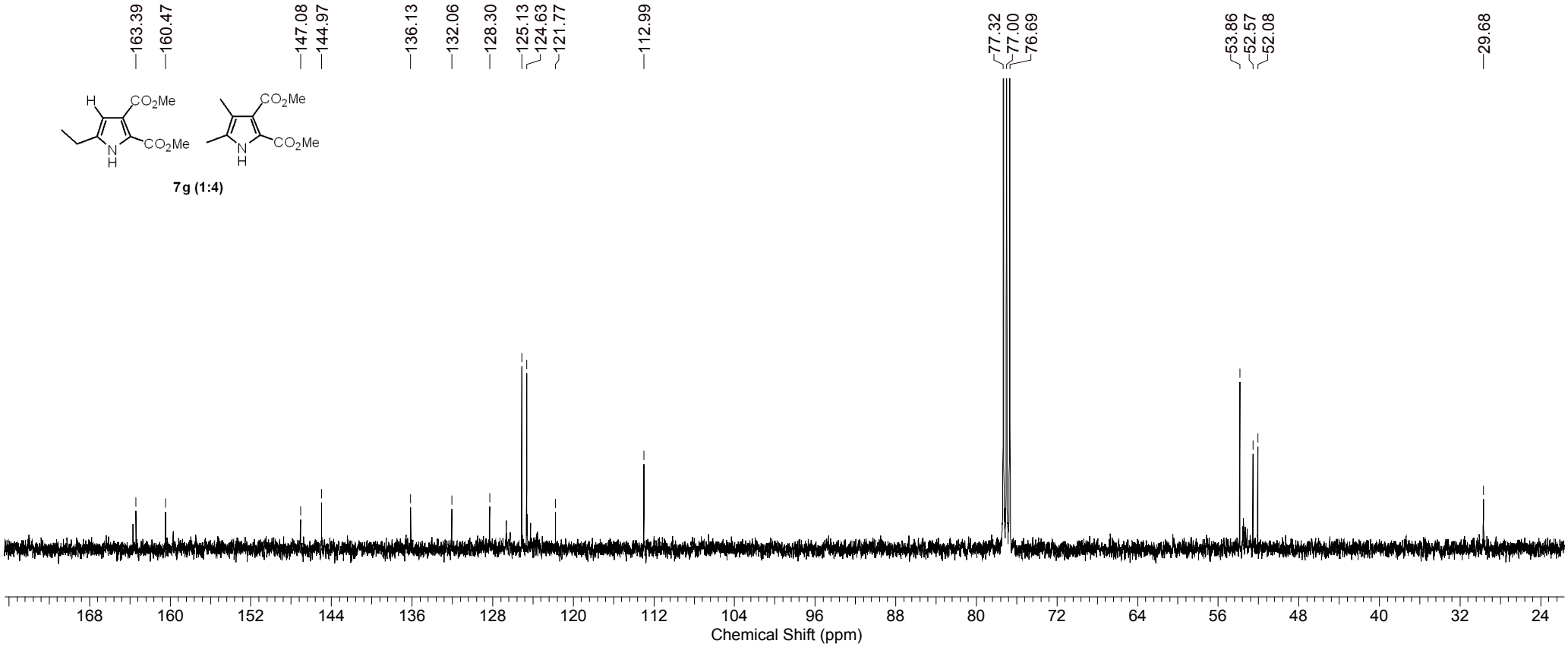

9.20
7.46
7.45
7.27
3.93
3.88
2.27
Me
CO2Me
Ph
N
H
CO2Me
7e
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
Chemical Shift (ppm)

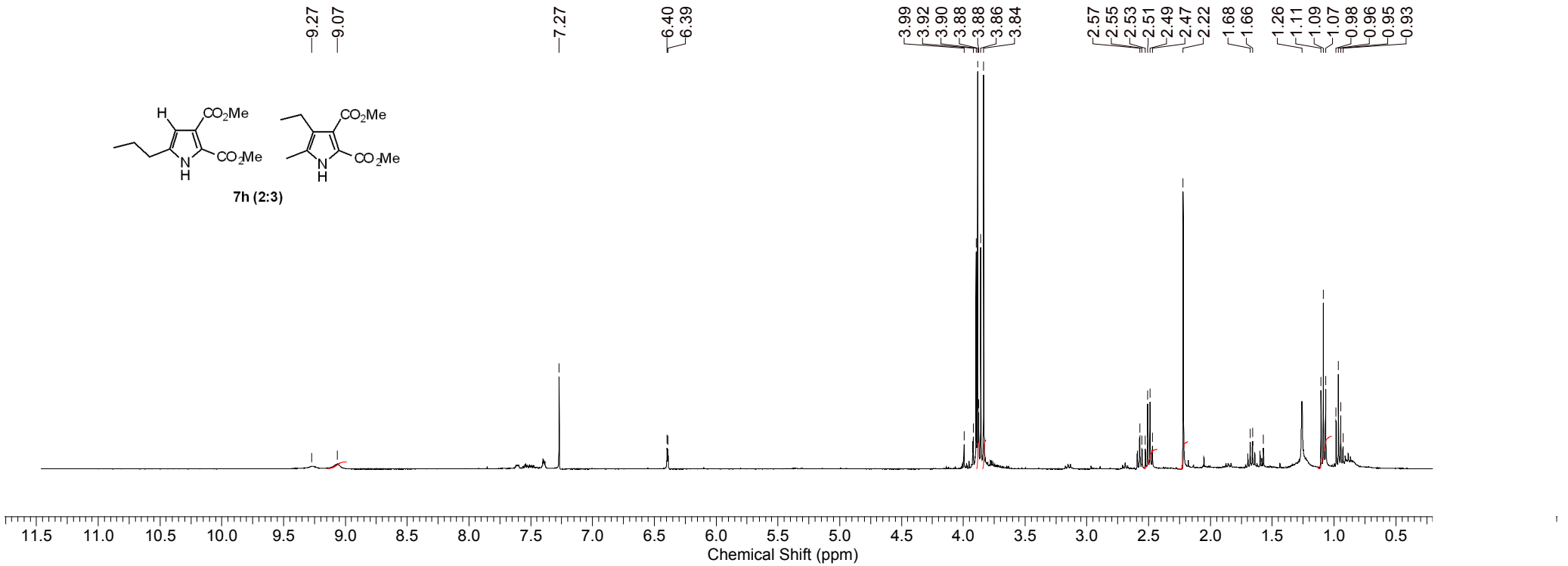

166.07
160.50
133.06
131.26
128.91
128.10
127.57
122.20
120.34
118.82
77.31
77.00
76.68
51.98
29.68
10.79
Me
CO2Me
Ph
N
H
CO2Me
7e
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


9.11
7.27
3.88
3.86
3.86
3.84
2.64
2.62
2.61
2.59
2.57
1.82
1.80
1.80
1.79
1.76
1.76
1.76
1.74
CO2Me
CO2Me
N
H
7f
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
Chemical Shift (ppm)

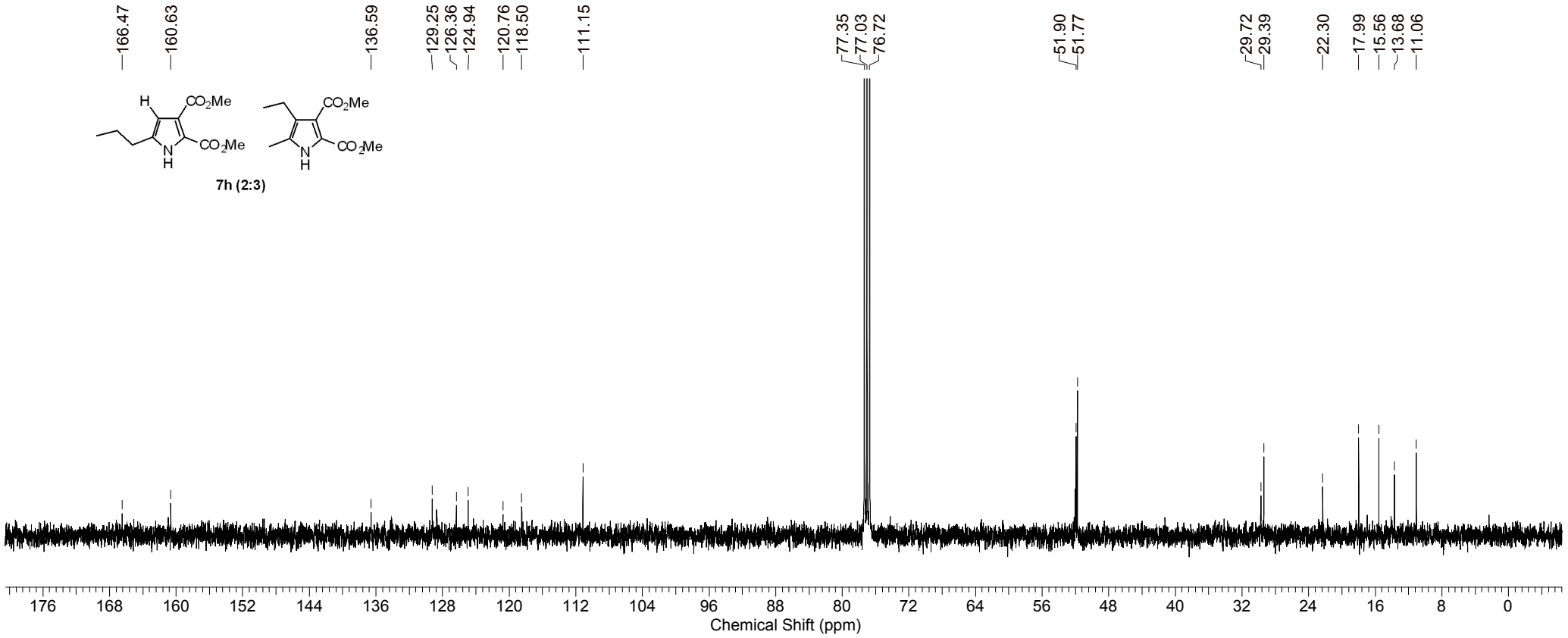

165.57
160.80
132.05
121.65
119.86
118.74
77.32
77.00
76.69
51.79
51.58
22.94
22.59
22.44
22.26
CO2Me
CO2Me
N
H
7f
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
Chemical Shift (ppm)


9.24
9.04
7.27
6.41
3.90
3.88
3.86
3.84
2.67
2.65
2.63
2.61
2.21
2.07
1.59
1.29
1.27
1.26
1.25
0.80
0.78
0.76
H
CO2Me
CO2Me
N
H
CO2Me
CO2Me
N
H
7g (1:4)
11.5 11.0 10.5 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 0 -0.5
Chemical Shift (ppm)

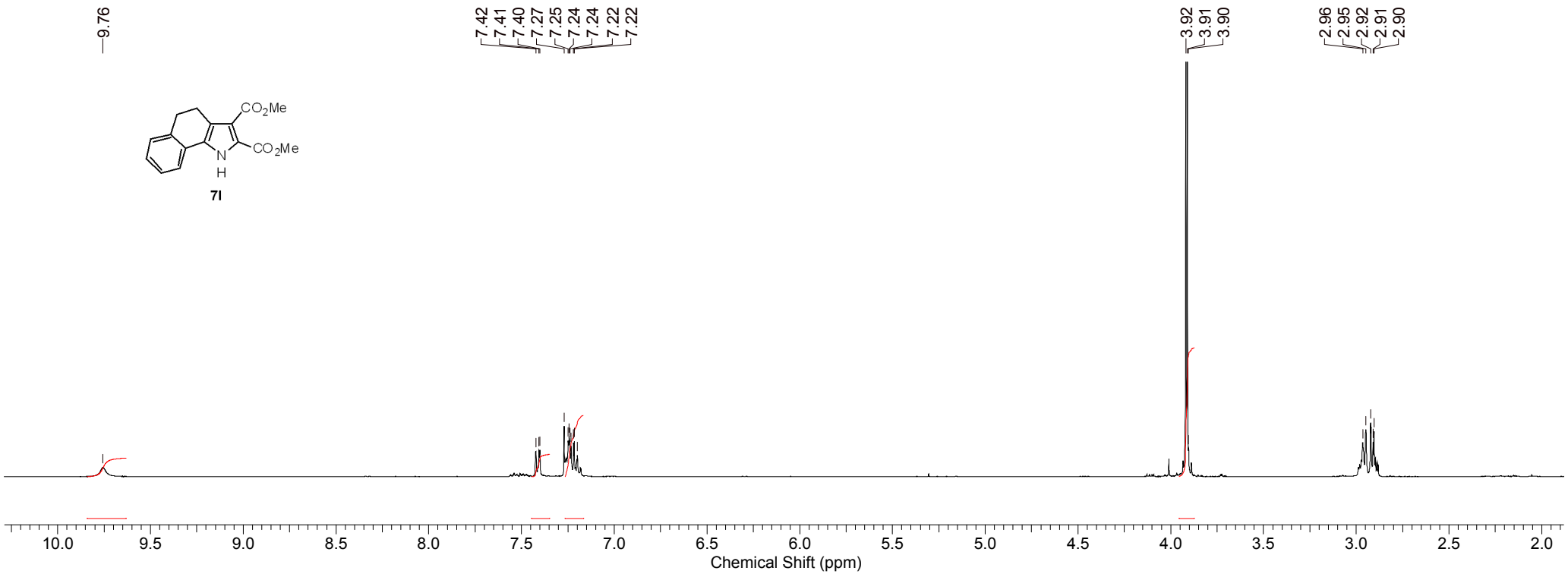

163.39
160.47
147.08
144.97
136.13
132.06
128.30
125.13
124.63
121.77
112.99
77.32
77.00
76.69
53.86
52.57
52.08
29.68
CO2Me
CO2Me
H
N
H
CO2Me
CO2Me
N
H
7g (1:4)
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
Chemical Shift (ppm)

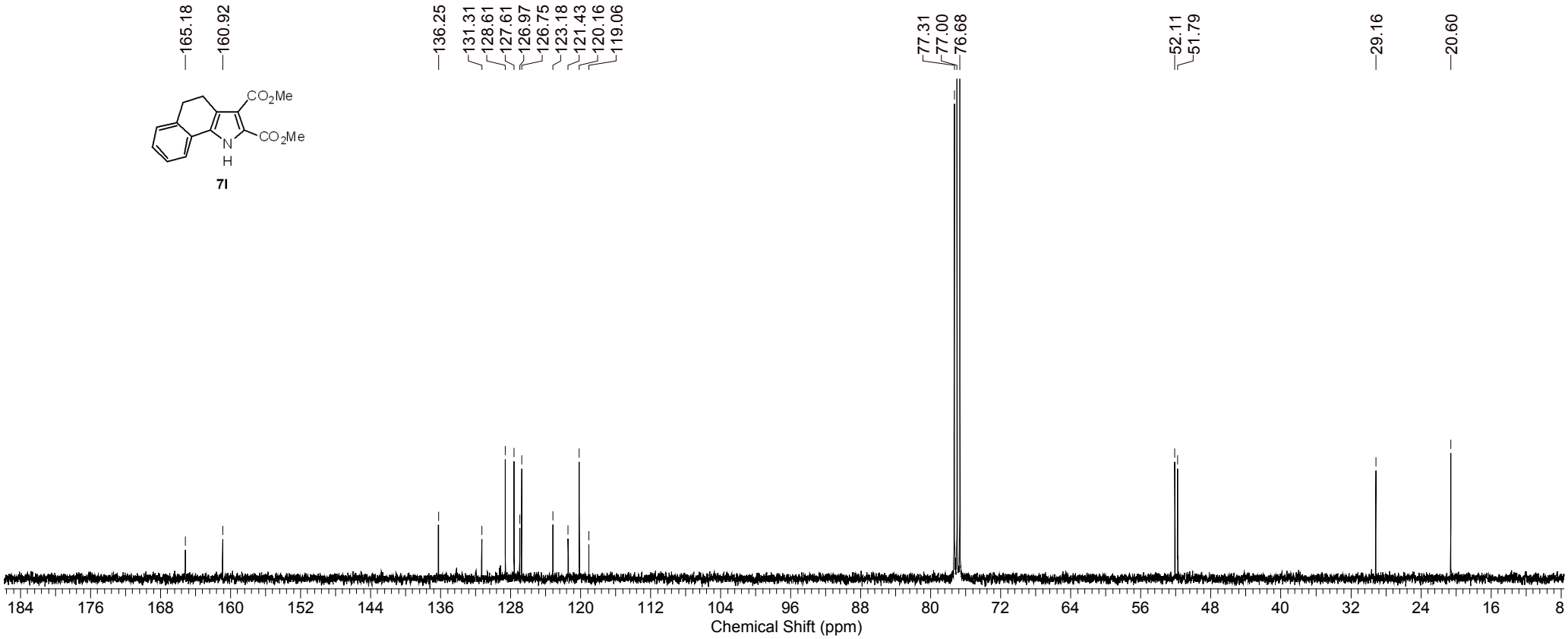

9.27
9.07
7.27
6.40
6.39
3.99
3.92
3.90
3.88
3.88
3.86
3.84
2.57
2.55
2.53
2.51
2.49
2.47
2.22
1.68
1.66
1.26
1.11
1.09
1.07
0.98
0.96
0.95
0.93
H
CO2Me
CO2Me
N
H
CO2Me
CO2Me
N
H
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

7h (2:3)

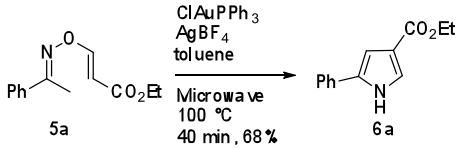

166.47
160.63
136.59
129.25
126.36
124.94
120.76
118.50
111.15
77.35
77.03
76.72
51.90
51.77
29.72
29.39
22.30
17.99
15.56
13.68
11.06
H
CO2Me
CO2Me
N
H
CO2Me
CO2Me
N
H
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

7h (2:3)


9.76
7.42
7.41
7.40
7.27
7.25
7.24
7.24
7.22
7.22
3.92
3.91
3.90
2.96
2.95
2.92
2.91
2.90
CO2Me
CO2Me
N
H
7l
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
Chemical Shift (ppm)


165.18
160.92
136.25
131.31
128.61
127.61
126.97
126.75
123.18
121.43
120.16
119.06
77.31
77.00
76.68
52.11
51.79
29.16
20.60
CO2Me
CO2Me
N
H
7l
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

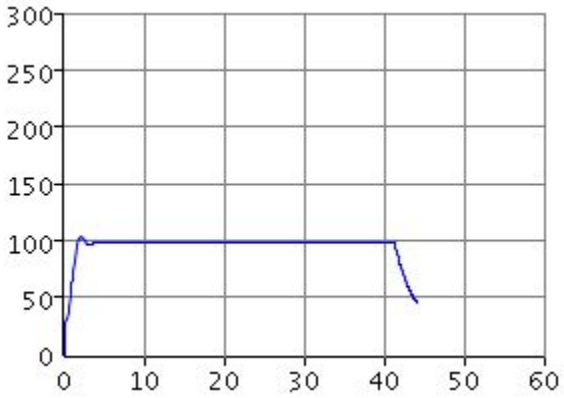
Microwave data



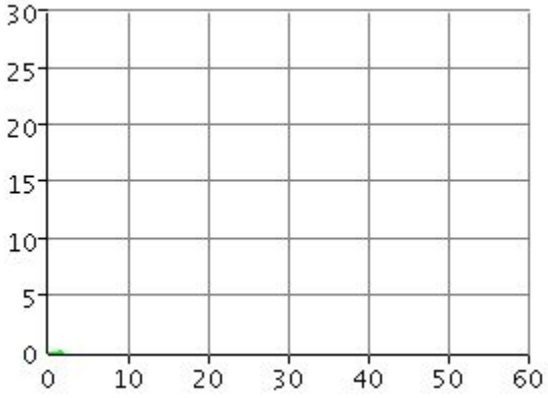
Status: OK
Absorption level: Normal
Vial type: 2.0-5.0 ml
Pre-stirring: 15
Initial power: 0
Dynamic deflector optimization: On

Step	Time	°C	bar	W	FHT	Cooling	Stir Rate
1	00:40:00	100	Off	Off	On	Off	600

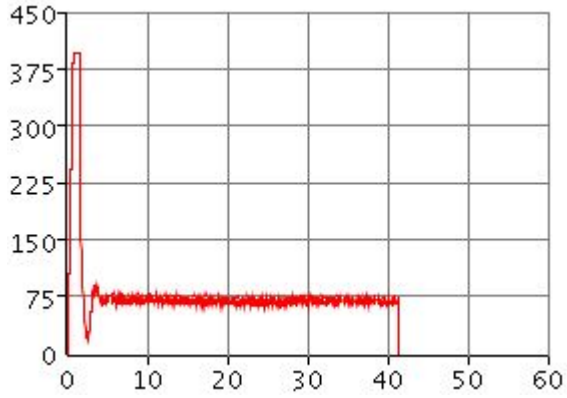
Temperature (C)

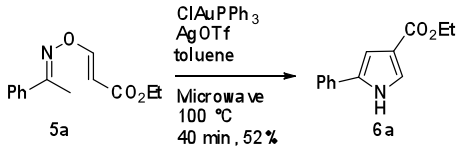


Pressure (bar)



Power (W)



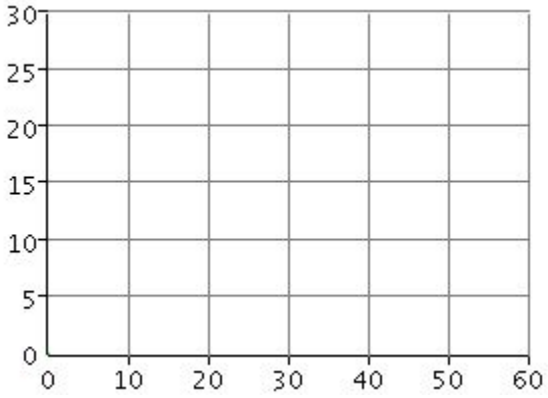


Status: OK
Absorption level: Normal
Vial type: 2.0-5.0 ml
Pre-stirring: 15
Initial power: 0
Dynamic deflector optimization: On

Step	Time	°C	bar	W	FHT	Cooling	Stir Rate
1	00:40:00	100	Off	Off	On	Off	600

Temperature (C)

Pressure (bar)



Power (W)