Photoinduced Intramolecular Cyclopentanation *vs* Photoprotolytic Oxametathesis in Policyclic Alkenes Outfitted with Conformationally Constrained Aroylmethyl Chromophores.‡

Roman A. Valiulin, Teresa M. Arisco, and Andrei G. Kutateladze*

Department of Chemistry & Biochemistry, University of Denver, Denver, CO 80208

akutatel@du.edu

SUPPORTING INFORMATION

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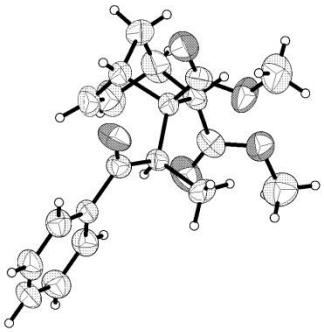
XRAY STRUCTURES

(cif file is included as a separate file)



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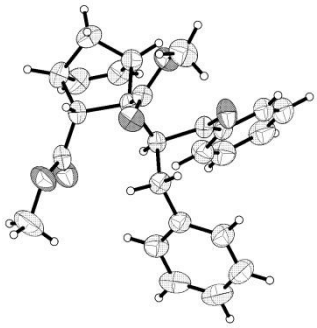

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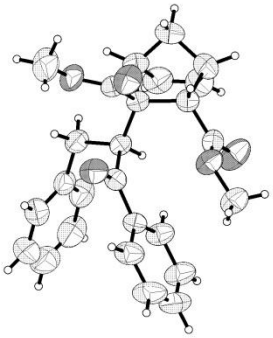

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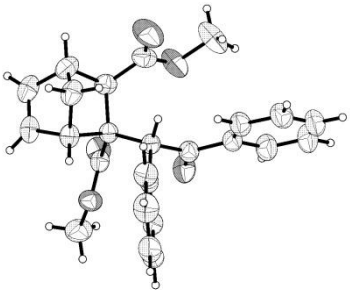

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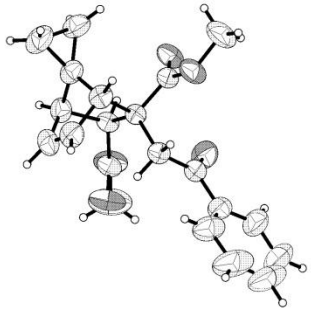

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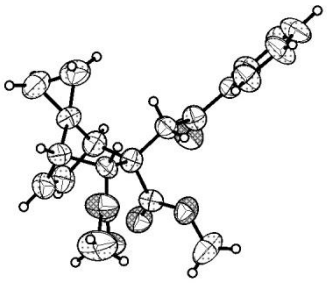

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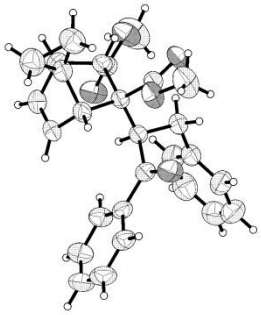

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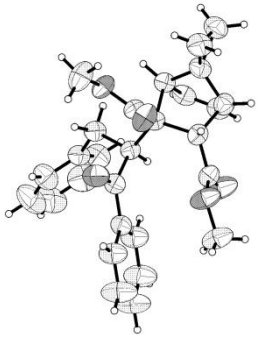

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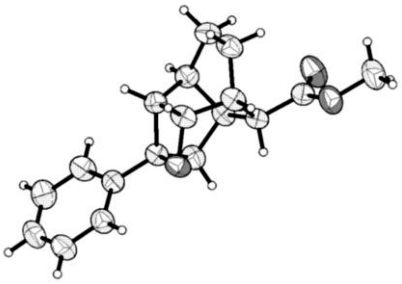

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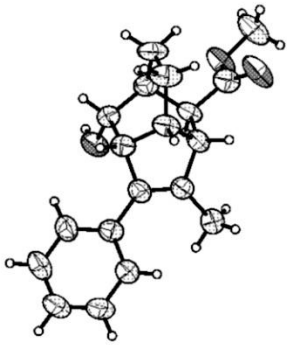

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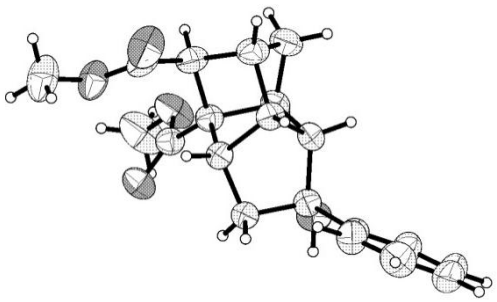

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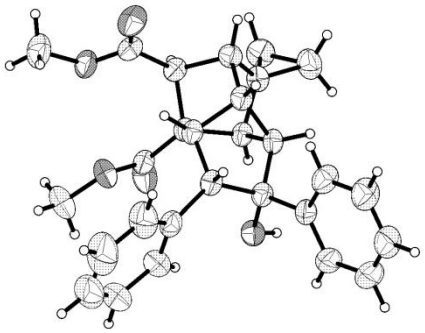

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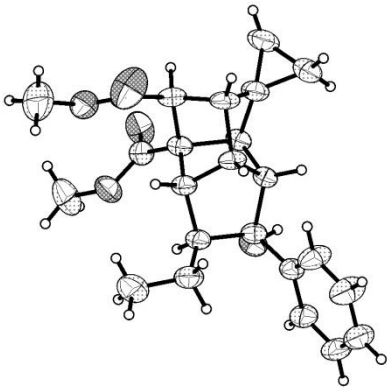

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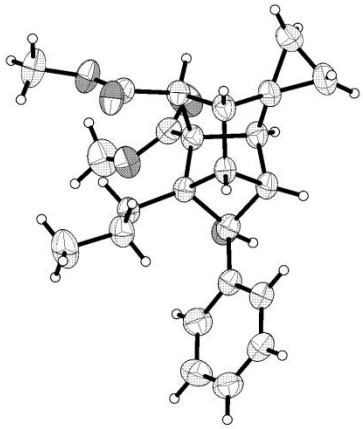

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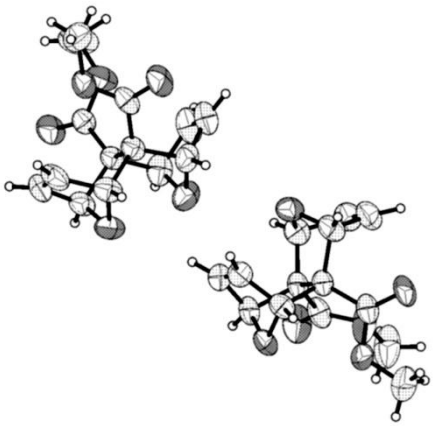

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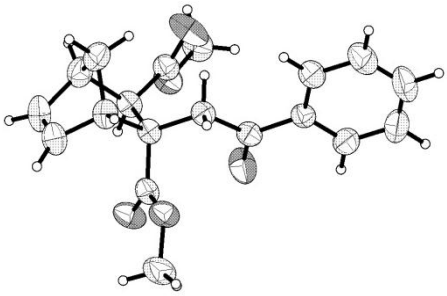

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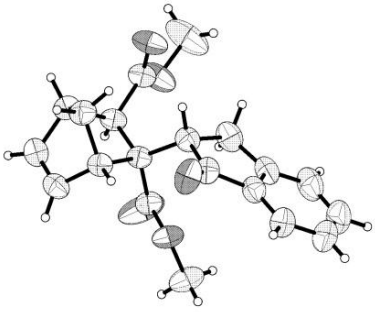

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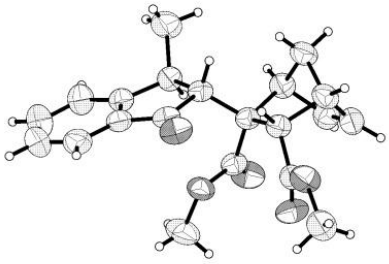

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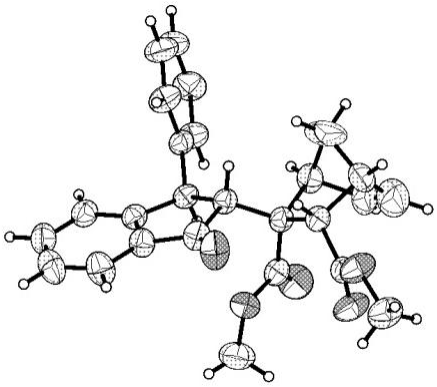

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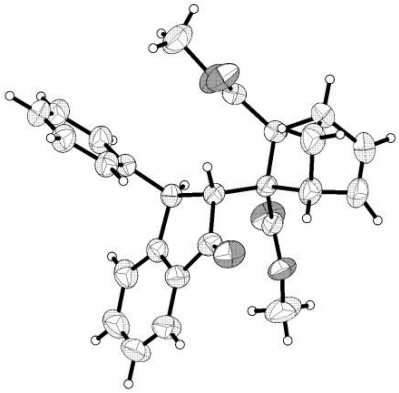

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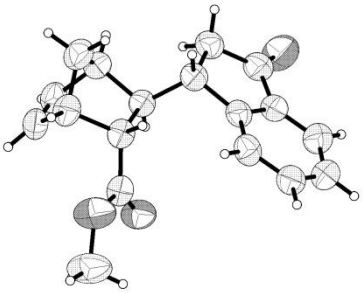

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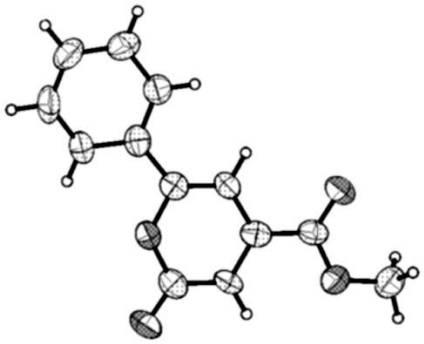

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COMPUTATIONAL DATA

Computations were carried out using Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr.,
J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand,
K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

Table S1. Computational comparison of the parent bicyclo[2.2.1]heptane system: gamma and delta oxetanes

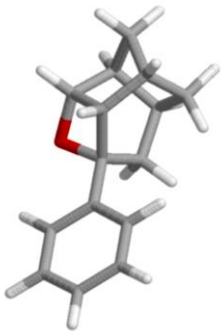
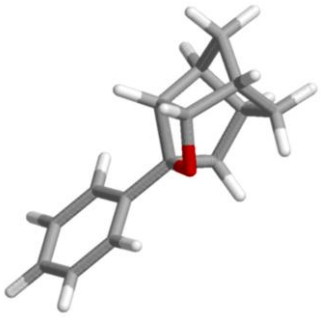
Gamma oxetane B3LYP/6-311+G(d,p) -656.563347295 Hartrees	Delta oxetane B3LYP/6-311+G(d,p) -656.587392075 Hartrees	ΔE = -15.1 kcal/mol (gamma oxetane is higher in energy)
		
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Table S2. Computational comparison of the parent bicyclo[2.2.2]octane system: gamma and delta oxetanes

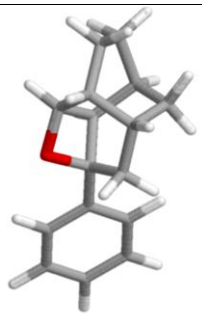
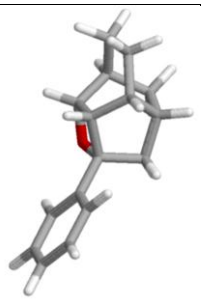
Gamma oxetane B3LYP/6-311+G(d,p) -695.907398932 Hartrees	Delta oxetane B3LYP/6-311+G(d,p) -695.922507038 Hartrees	ΔE = -9.5 kcal/mol (gamma oxetane is higher in energy)
		
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Table S3. Computational comparison in the bicyclo[2.2.2]octane system with vicinal exo-COOMe group: gamma and delta oxetanes

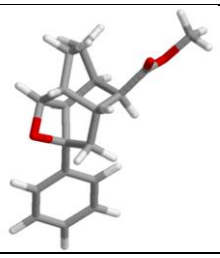
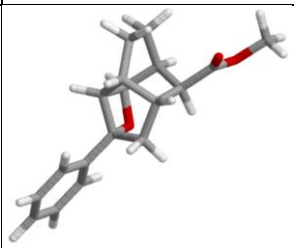
Gamma oxetane B3LYP/6-311+G(d,p) -923.847043399 Hartrees	Delta oxetane B3LYP/6-311+G(d,p) -923.864829830 Hartrees	ΔE = -11.2 kcal/mol (gamma oxetane is higher in energy)
		
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Table S4. Comparison of gamma and delta oxetanes in spirocyclopropano-norbornene series

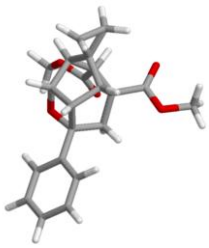
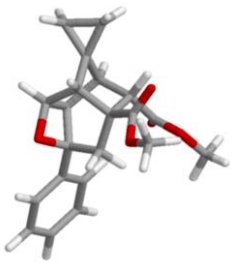
Gamma oxetane **10d** (not observed) B3LYP/6-311+G(d,p) -1189.87050995 Hartrees	Delta oxetane **8d** (observed) B3LYP/6-311+G(d,p) -1189.84528918 Hartrees	ΔE = -15.8 kcal/mol (gamma oxetane is higher in energy)
		
C -0.5247 -0.3786 1.5189 C -0.1055 1.1108 1.6036 C 0.7986 -1.0871 1.1633 O -0.9033 1.4445 0.4358 C 1.4280 1.0908 1.3634 C 1.6905 0.7858 -0.1287 C 1.3595 1.8657 -1.1354 C 1.7982 -0.2650 1.9696 C 1.0111 -0.6154 -0.3429 C 1.9393 -1.5581 -1.0971 C -1.2658 0.0385 0.2183 C -0.4259 -0.5592 -0.9136 C -2.7553 -0.1560 0.0977 C -3.6119 0.9373 -0.0506 C -4.9880 0.7448 -0.1743 C -5.5254 -0.5397 -0.1433 C -4.6767 -1.6360 0.0117 C -3.3028 -1.4448 0.1282 O 3.1099 -1.3602 -1.3200 O 1.3125 -2.6987 -1.4591 C 2.1199 -3.6683 -2.1533 O 1.0768 1.6825 -2.2956 O 1.5306 3.0951 -0.6036 C 1.2964 4.2007 -1.4940 C 3.1832 -0.6864 2.3534 C 2.1159 -0.5086 3.4186 H -1.1023 -0.8074 2.3346 H -0.4071 1.6997 2.4711 H 0.8127 -2.1684 1.2990 H 1.9657 1.9589 1.7398 H 2.7684 0.6302 -0.2462 H -0.7695 -1.5749 -1.1162 H -0.4988 0.0197 -1.8332 H -3.1915 1.9345 -0.0635 H -6.5955 -0.6874 -0.2363 H -5.6404 1.6030 -0.2931 H -2.6540 -2.3066 0.2495 H -5.0852 -2.6401 0.0420 H 1.4517 -4.4984 -2.3725 H 2.9485 -3.9966 -1.5242 H 2.5171 -3.2407 -3.0744 H 1.9667 4.1496 -2.3531 H 1.4938 5.0945 -0.9057 H 0.2630 4.1924 -1.8430 H 3.9758 0.0517 2.3006 H 3.5007 -1.6949 2.1142 H 2.1979 0.3474 4.0791 H 1.7174 -1.3998 3.8914	C -0.1417 -2.2974 0.5449 C 0.4717 -1.6141 -0.6918 C -1.4960 -1.5427 0.5610 O 0.8845 -1.8178 1.4179 C -0.7534 -1.1257 -1.5435 C -1.2129 0.2657 -1.0916 C -0.4487 1.4495 -1.6377 C -1.8939 -1.9133 -0.8724 C -1.2014 0.0490 0.4620 C -2.3902 -3.2720 -1.2794 C -3.2793 -2.0503 -1.4199 C -2.3274 0.8050 1.1481 C 1.1528 -0.7390 0.4580 C 0.2273 0.3901 0.9406 C 2.6147 -0.3932 0.3755 C 3.1227 0.3131 -0.7209 C 4.4736 0.6502 -0.7740 C 5.3314 0.2880 0.2643 C 4.8303 -0.4206 1.3543 C 3.4797 -0.7626 1.4097 O -3.4459 0.9089 0.7017 O -1.9638 1.3089 2.3427 C -2.9953 1.9948 3.0782 O 0.4351 1.3963 -2.4610 O -0.9217 2.6098 -1.1367 C -0.3096 3.8174 -1.6314 H -0.2661 -3.3786 0.6084 H 1.2095 -2.1906 -1.2452 H -2.1811 -1.8159 1.3631 H -0.6362 -1.2438 -2.6193 H -2.2492 0.4187 -1.4060 H -1.9903 -3.7162 -2.1842 H -2.6326 -3.9887 -0.5017 H -4.1145 -1.9394 -0.7388 H -3.4701 -1.6786 -2.4215 H 0.5256 1.3717 0.5691 H 0.3064 0.4204 2.0268 H 2.4654 0.5932 -1.5363 H 6.3826 0.5505 0.2201 H 4.8568 1.1928 -1.6313 H 3.0909 -1.3285 2.2468 H 5.4917 -0.7136 2.1624 H -3.3689 2.8438 2.5047 H -2.5206 2.3296 3.9979 H -3.8222 1.3176 3.2957 H -0.4378 3.8922 -2.7119 H 0.7549 3.8311 -1.3935 H -0.8258 4.6308 -1.1267	

Table S4. Comparison of gamma and delta initial Paternò-Büchi 1,4-diradicals in the parent bicyclo[2.2.1]heptane system

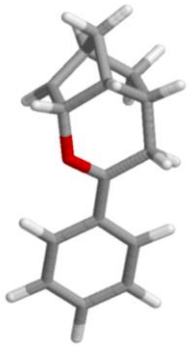
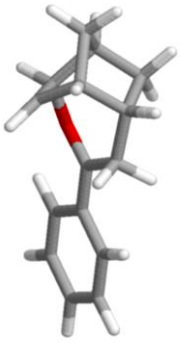
Gamma 1,4-diradical (triplet) B3LYP/6-311+G(d,p) -656.516623962 Hartrees	Delta 1,4-diradical (triplet) B3LYP/6-311+G(d,p) -656.500143424 Hartrees	ΔE = 10.3 kcal/mol (triplet gamma diradical is lower in energy)
		
C 1.6635 -1.2202 -0.5237 C 1.9155 -1.2831 0.9576 C 2.5781 -0.0452 -0.9487 O 0.2654 -1.0569 -0.8711 C 2.9232 -0.2281 1.2907 C 2.1993 1.1498 1.1452 C 3.7799 -0.2382 -0.0047 C 1.9313 1.2515 -0.3947 C -0.3365 0.1267 -0.5369 C 0.4505 1.3774 -0.7861 C -1.7204 0.0610 -0.2214 C -2.5062 1.2293 -0.0107 C -3.8507 1.1391 0.3134 C -4.4773 -0.1054 0.4338 C -3.7270 -1.2668 0.2177 C -2.3820 -1.1950 -0.1038 H 1.9346 -2.1455 -1.0432 H 1.2797 -1.8122 1.6555 H 2.7875 -0.0188 -2.0187 H 3.4505 -0.3549 2.2365 H 2.8514 1.9592 1.4877 H 1.2784 1.1899 1.7312 H 4.4936 0.5892 -0.0560 H 4.3135 -1.1795 -0.1594 H 2.4642 2.1151 -0.8019 H 0.0041 2.2202 -0.2555 H 0.3939 1.6228 -1.8599 H -2.0567 2.2101 -0.1039 H -4.4210 2.0483 0.4717 H -5.5291 -0.1685 0.6871 H -4.2023 -2.2385 0.3020 H -1.8126 -2.0992 -0.2716	C -1.9476 -0.4054 1.4729 C -1.6795 -1.3076 0.3098 C -2.8021 0.6828 0.9194 O -0.3160 -1.1236 -0.1866 C -2.7711 -0.8746 -0.7323 C -2.2430 0.3652 -1.4688 C -3.8343 -0.2007 0.1672 C -1.9626 1.3249 -0.2743 C 0.3100 0.0883 -0.0302 C -0.4523 1.4001 0.0137 C 1.7313 0.0343 -0.0164 C 2.4245 -1.2081 -0.0850 C 3.8082 -1.2555 -0.0696 C 4.5678 -0.0827 0.0162 C 3.9082 1.1478 0.0872 C 2.5232 1.2143 0.0706 H -1.3631 -0.3961 2.3834 H -1.7211 -2.3750 0.5354 H -3.1885 1.4116 1.6308 H -3.1114 -1.6865 -1.3750 H -3.0135 0.7586 -2.1364 H -1.3515 0.1722 -2.0658 H -4.5675 0.3647 -0.4152 H -4.3624 -0.8820 0.8379 H -2.3270 2.3360 -0.4722 H -0.0047 2.0658 -0.7358 H -0.2842 1.8960 0.9807 H 1.8490 -2.1214 -0.1516 H 4.3075 -2.2173 -0.1248 H 5.6506 -0.1276 0.0285 H 4.4830 2.0654 0.1575 H 2.0466 2.1846 0.1321	

Table S5. Comparison of gamma and delta initial Paternò-Büchi 1,4-diradicals in the parent bicyclo[2.2.2]octane system

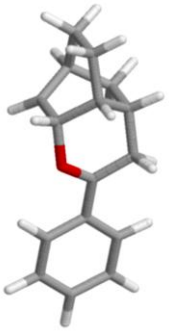
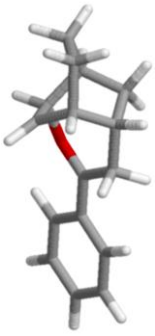
Gamma 1,4-diradical (triplet) B3LYP/6-311+G(d,p) -695.850204621	Delta 1,4-diradical (triplet) B3LYP/6-311+G(d,p) -695.839710157 Hartrees	ΔE = 6.6 kcal/mol (triplet gamma diradical is lower in energy)
		
C 1.4214 -1.1581 -0.5729 C 1.6796 -1.2713 0.8948 C 2.2130 0.0446 -1.1032 O -0.0088 -1.0294 -0.8591 C 2.5547 -0.2011 1.4666 C 1.9054 1.1727 1.1426 C 3.9306 -0.2527 0.7509 C 1.6433 1.2910 -0.3915 C -0.6197 0.1434 -0.5041 C 0.1448 1.4162 -0.7286 C -2.0059 0.0568 -0.1994 C -2.8076 1.2125 0.0188 C -4.1548 1.1021 0.3259 C -4.7682 -0.1510 0.4211 C -4.0014 -1.3004 0.1980 C -2.6537 -1.2082 -0.1064 C 3.7082 -0.1431 -0.7853 H 1.6846 -2.0750 -1.1112 H 1.1771 -2.0229 1.4913 H 2.0646 0.1312 -2.1837 H 2.6806 -0.3165 2.5453 H 2.5696 1.9735 1.4839 H 0.9678 1.2736 1.6959 H 4.5571 0.5676 1.1155 H 4.4449 -1.1830 1.0033 H 2.1502 2.1798 -0.7798 H -0.2945 2.2282 -0.1460 H 0.0497 1.7069 -1.7885 H -2.3689 2.1997 -0.0566 H -4.7377 2.0023 0.4896 H -5.8223 -0.2301 0.6603 H -4.4661 -2.2787 0.2632 H -2.0716 -2.1033 -0.2793 H 4.2681 0.7001 -1.2005 H 4.0785 -1.0390 -1.2937	C 1.6893 -0.3334 -1.4297 C 1.4126 -1.2706 -0.3077 C 2.3946 0.8971 -0.9646 O 0.0305 -1.1185 0.1777 C 2.4214 -0.9851 0.8308 C 2.0469 0.3571 1.4855 C 3.8574 0.4961 -0.6184 C 1.6707 1.3460 0.3510 C -0.6027 0.0924 0.0856 C 0.1416 1.4097 0.1712 C -2.0229 0.0287 0.0317 C -2.7052 -1.2199 -0.0303 C -4.0875 -1.2763 -0.0867 C -4.8565 -0.1064 -0.0839 C -4.2077 1.1304 -0.0223 C -2.8241 1.2055 0.0362 C 3.8216 -0.8267 0.1969 H 1.2592 -0.4693 -2.4141 H 1.4496 -2.3191 -0.6129 H 2.3729 1.6989 -1.7057 H 2.4069 -1.8003 1.5575 H 2.8954 0.7264 2.0688 H 1.2129 0.2399 2.1805 H 4.3285 1.3010 -0.0440 H 4.4415 0.3733 -1.5331 H 2.0146 2.3538 0.6044 H -0.2680 1.9704 1.0237 H -0.0940 2.0167 -0.7145 H -2.1224 -2.1311 -0.0323 H -4.5784 -2.2429 -0.1340 H -5.9381 -0.1582 -0.1280 H -4.7898 2.0460 -0.0192 H -2.3557 2.1806 0.0833 H 4.5862 -0.8231 0.9785 H 4.0374 -1.6813 -0.4527	

Table S6. Effect of the Me group in the tether on relative stability of the diradicals in the bicyclo[2.2.1]heptane parent system (Me is "in")

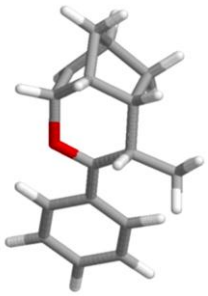
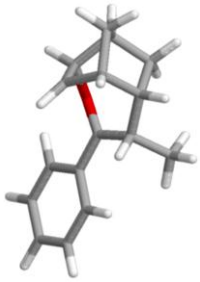
Gamma 1,4-diradical (triplet) Me is "in" B3LYP/6-311+G(d,p) -695.830712693 Hartrees	Delta 1,4-diradical (triplet) Me is "in" B3LYP/6-311+G(d,p) -695.819399207	ΔE = 7.1 kcal/mol (triplet gamma diradical is lower in energy)
		
C 1.5941 -1.3691 -0.6221 C 1.6935 -1.5717 0.8658 C 2.6288 -0.2447 -0.8545 O 0.2595 -1.0409 -1.0819 C 2.7250 -0.6176 1.3830 C 2.1073 0.8158 1.2799 C 3.7102 -0.5923 0.1846 C 2.0075 1.0473 -0.2668 C -0.3087 0.1197 -0.6018 C 0.5821 1.3280 -0.8105 C -1.6840 -0.0125 -0.2360 C -2.4961 1.0405 0.2751 C -3.8205 0.8266 0.6262 C -4.4112 -0.4319 0.4873 C -3.6374 -1.4842 -0.0117 C -2.3126 -1.2890 -0.3627 C 0.1021 2.7074 -0.3433 H 1.8358 -2.2694 -1.1970 H 0.9546 -2.1014 1.4529 H 2.9494 -0.1511 -1.8927 H 3.1393 -0.8511 2.3640 H 2.7694 1.5485 1.7513 H 1.1372 0.8729 1.7783 H 4.4770 0.1830 0.2723 H 4.1953 -1.5555 0.0075 H 2.6343 1.8981 -0.5518 H 0.6986 1.3957 -1.9061 H -2.0879 2.0269 0.4186 H -4.4011 1.6550 1.0183 H -5.4474 -0.5890 0.7630 H -4.0763 -2.4695 -0.1288 H -1.7322 -2.1135 -0.7508 H 0.8731 3.4449 -0.5850 H -0.0636 2.7499 0.7356 H -0.8124 3.0178 -0.8499	C -1.5455 -1.0260 1.3164 C -1.5421 -1.5218 -0.0923 C -2.5138 0.1065 1.3132 O -0.3456 -1.0060 -0.7927 C -2.8728 -0.9281 -0.6755 C -2.5628 0.5032 -1.1290 C -3.6900 -0.6196 0.6016 C -2.0207 1.1307 0.1934 C 0.2927 0.0771 -0.2345 C -0.4865 1.3317 0.1433 C 1.7050 -0.0498 -0.0868 C 2.3793 -1.2236 -0.5296 C 3.7481 -1.3659 -0.3756 C 4.5116 -0.3597 0.2271 C 3.8710 0.7983 0.6774 C 2.5021 0.9589 0.5249 C -0.1534 2.5138 -0.8019 H -0.7784 -1.2458 2.0466 H -1.4654 -2.6034 -0.2138 H -2.7216 0.5728 2.2756 H -3.3489 -1.5605 -1.4249 H -3.4773 0.9974 -1.4664 H -1.8420 0.5438 -1.9435 H -4.5517 0.0217 0.3938 H -4.0263 -1.4998 1.1538 H -2.4759 2.1065 0.3824 H -0.1612 1.6258 1.1512 H 1.7991 -2.0078 -0.9966 H 4.2316 -2.2712 -0.7275 H 5.5824 -0.4771 0.3457 H 4.4475 1.5828 1.1562 H 2.0402 1.8634 0.8989 H -0.6350 3.4300 -0.4447 H -0.5075 2.3193 -1.8169 H 0.9202 2.6948 -0.8599	

Table S7. Effect of the Me group in the tether on relative stability of the diradicals in the bicyclo[2.2.1]heptane parent system (continued – Me is "out")

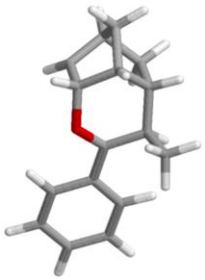
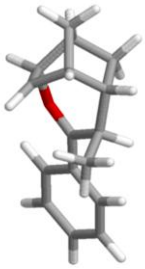
Gamma 1,4-diradical (triplet) Me is "out" B3LYP/6-311+G(d,p) -695.839769097 Hartrees	Delta 1,4-diradical (triplet) Me is "out" B3LYP/6-311+G(d,p) -695.820436164 Hartrees	ΔE = 12.1 kcal/mol (triplet gamma diradical is lower in energy)
		
C 1.6403 -1.0441 -0.9358 C 1.8595 -1.7880 0.3534 C 2.5717 0.1782 -0.7567 O 0.2512 -0.7104 -1.1868 C 2.8606 -1.0165 1.1555 C 2.1404 0.2827 1.6420 C 3.7486 -0.4428 0.0199 C 1.9159 1.0875 0.3169 C -0.3453 0.1935 -0.3483 C 0.4427 1.4265 0.0080 C -1.7298 -0.0059 -0.0957 C -2.5147 0.9445 0.6168 C -3.8605 0.7223 0.8620 C -4.4890 -0.4423 0.4093 C -3.7387 -1.3863 -0.3011 C -2.3929 -1.1805 -0.5538 C 0.3311 2.4905 -1.1113 H 1.9111 -1.6310 -1.8200 H 1.2087 -2.5731 0.7159 H 2.8161 0.6834 -1.6909 H 3.3630 -1.5698 1.9493 H 2.7807 0.8355 2.3365 H 1.2031 0.0589 2.1562 H 4.4653 0.3066 0.3681 H 4.2837 -1.2149 -0.5390 H 2.4714 2.0287 0.3666 H 0.0137 1.8568 0.9175 H -2.0626 1.8605 0.9765 H -4.4306 1.4653 1.4097 H -5.5420 -0.6091 0.6037 H -4.2148 -2.2925 -0.6607 H -1.8227 -1.9154 -1.1058 H 0.8910 3.3922 -0.8423 H 0.7267 2.1130 -2.0574 H -0.7111 2.7720 -1.2771	C 2.1174 -0.2893 -1.4378 C 1.6829 -1.3915 -0.5303 C 2.8993 0.6335 -0.5693 O 0.2711 -1.2591 -0.1884 C 2.6366 -1.2263 0.7086 C 2.0404 -0.1439 1.6186 C 3.8149 -0.4251 0.1076 C 1.9259 1.0510 0.6262 C -0.3252 -0.0291 -0.0426 C 0.4502 1.2610 0.2139 C -1.7507 -0.0919 0.0087 C -2.4411 -1.3018 -0.2901 C -3.8232 -1.3714 -0.2392 C -4.5879 -0.2537 0.1130 C -3.9328 0.9422 0.4194 C -2.5496 1.0295 0.3707 C 0.3072 2.3064 -0.9156 H 1.7061 -0.1074 -2.4208 H 1.7367 -2.3923 -0.9628 H 3.3883 1.4733 -1.0602 H 2.8788 -2.1671 1.2027 H 2.7277 0.0706 2.4407 H 1.0787 -0.4171 2.0537 H 4.4724 -0.0181 0.8813 H 4.4184 -0.9735 -0.6192 H 2.2861 1.9828 1.0707 H -0.0256 1.7036 1.1006 H -1.8646 -2.1750 -0.5626 H -4.3163 -2.3083 -0.4768 H -5.6693 -0.3143 0.1506 H -4.5090 1.8166 0.7035 H -2.0826 1.9713 0.6277 H 0.7711 3.2504 -0.6110 H -0.7405 2.5042 -1.1455 H 0.7890 1.9756 -1.8368	

Table S8. Effect of the Me group in the tether on relative stability of the diradicals in the bicyclo[2.2.2]octane parent system (Me is "in")

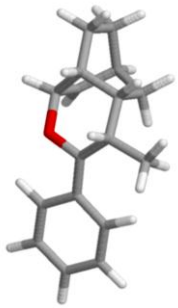
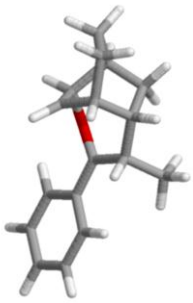
Gamma 1,4-diradical (triplet) Me is "in" B3LYP/6-311+G(d,p) -735.163731453 Hartrees	Delta 1,4-diradical (triplet) Me is "in" B3LYP/6-311+G(d,p) -735.159317186 Hartrees	ΔE =2.8 kcal/mol (triplet gamma diradical is lower in energy)
		
C 1.4021 -1.2435 -0.7253 C 1.5011 -1.5209 0.7402 C 2.3135 -0.0549 -1.0430 O 0.0232 -0.9632 -1.1306 C 2.3514 -0.5576 1.5077 C 1.8046 0.8756 1.2537 C 3.7958 -0.6170 0.9478 C 1.7224 1.1487 -0.2813 C -0.5737 0.1639 -0.6069 C 0.2709 1.4138 -0.7807 C -1.9413 -0.0251 -0.2333 C -2.7899 0.9884 0.2979 C -4.1032 0.7195 0.6534 C -4.6473 -0.5579 0.4991 C -3.8377 -1.5722 -0.0214 C -2.5236 -1.3215 -0.3772 C 3.7525 -0.3585 -0.5854 C -0.2435 2.7545 -0.2423 H 1.6529 -2.1190 -1.3337 H 0.8956 -2.2903 1.2036 H 2.2945 0.1420 -2.1190 H 2.3462 -0.7792 2.5772 H 2.4610 1.6019 1.7440 H 0.8182 0.9727 1.7148 H 4.4101 0.1341 1.4548 H 4.2389 -1.5916 1.1661 H 2.3122 2.0383 -0.5275 H 0.3613 1.5373 -1.8737 H -2.4198 1.9879 0.4523 H -4.7121 1.5199 1.0605 H -5.6751 -0.7580 0.7786 H -4.2398 -2.5716 -0.1514 H -1.9154 -2.1178 -0.7813 H 4.3977 0.4823 -0.8573 H 4.1312 -1.2270 -1.1338 H 0.5072 3.5227 -0.4506 H -1.1670 3.0650 -0.7319 H -0.4087 2.7427 0.8372	C -1.3936 -0.9499 1.2147 C -1.3420 -1.4301 -0.1902 C -2.1549 0.3292 1.3314 O -0.0890 -0.9590 -0.8417 C -2.5688 -0.8643 -0.9414 C -2.3242 0.6362 -1.1744 C -3.8069 -1.0073 -0.0295 C -1.7194 1.2341 0.1266 C 0.5673 0.1014 -0.2692 C -0.1773 1.3913 0.0400 C 1.9688 -0.0686 -0.0752 C 2.6137 -1.2799 -0.4570 C 3.9718 -1.4632 -0.2586 C 4.7536 -0.4620 0.3289 C 4.1422 0.7338 0.7173 C 2.7846 0.9352 0.5203 C 0.1925 2.5142 -0.9616 C -3.6629 -0.0249 1.1669 H -0.8010 -1.3941 2.0042 H -1.2788 -2.5172 -0.2743 H -1.9753 0.8408 2.2796 H -2.7115 -1.3936 -1.8863 H -3.2697 1.1252 -1.4266 H -1.6572 0.7892 -2.0222 H -4.7154 -0.7949 -0.5999 H -3.8931 -2.0380 0.3299 H -2.1303 2.2352 0.2935 H 0.1588 1.7283 1.0305 H 2.0191 -2.0600 -0.9126 H 4.4326 -2.3969 -0.5637 H 5.8160 -0.6113 0.4823 H 4.7331 1.5162 1.1818 H 2.3454 1.8704 0.8433 H -0.2833 3.4560 -0.6686 H 1.2704 2.6757 -0.9986 H -0.1339 2.2707 -1.9750 H -4.2364 0.8926 0.9962 H -4.0451 -0.4736 2.0865	

Table S9. Effect of the Me group in the tether on relative stability of the diradicals in the bicyclo[2.2.2]octane parent system (continued Me is "out")

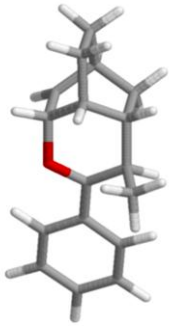
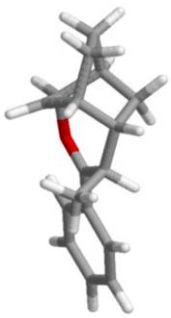
Gamma 1,4-diradical (triplet) Me is "out" B3LYP/6-311+G(d,p) -735.172668724 Hartrees	Delta 1,4-diradical (triplet) Me is "out" B3LYP/6-311+G(d,p) -735.160209632 Hartrees	ΔE = 7.8 kcal/mol (triplet gamma diradical is lower in energy)
		
C 1.4275 -0.8843 -1.0292 C 1.6373 -1.7233 0.1893 C 2.2410 0.4044 -0.8647 O 0.0077 -0.5928 -1.2434 C 2.4945 -1.0998 1.2451 C 1.8650 0.2665 1.6315 C 3.8946 -0.8162 0.6417 C 1.6468 1.1416 0.3566 C -0.6054 0.2336 -0.3392 C 0.1489 1.4591 0.1157 C -1.9836 -0.0200 -0.0972 C -2.7868 0.8487 0.6947 C -4.1258 0.5748 0.9256 C -4.7296 -0.5626 0.3799 C -3.9607 -1.4266 -0.4083 C -2.6213 -1.1689 -0.6472 C 3.7247 0.0557 -0.6354 C -0.0458 2.6318 -0.8756 H 1.6980 -1.4134 -1.9493 H 1.1190 -2.6664 0.3122 H 2.1424 1.0149 -1.7652 H 2.5799 -1.7405 2.1256 H 2.5252 0.7772 2.3403 H 0.9131 0.0982 2.1425 H 4.5112 -0.3039 1.3873 H 4.3958 -1.7582 0.4061 H 2.1710 2.0951 0.4788 H -0.2660 1.7755 1.0774 H -2.3544 1.7415 1.1293 H -4.7098 1.2558 1.5357 H -5.7774 -0.7700 0.5631 H -4.4172 -2.3113 -0.8398 H -2.0370 -1.8429 -1.2589 H 4.2980 0.9839 -0.5528 H 4.1132 -0.4685 -1.5144 H 0.4971 3.5186 -0.5322 H 0.3116 2.3780 -1.8759 H -1.1030 2.8919 -0.9619	C 1.9995 -0.1284 -1.4362 C 1.4598 -1.2749 -0.6574 C 2.6192 0.9004 -0.5543 O 0.0111 -1.1631 -0.4777 C 2.2006 -1.3378 0.7027 C 1.7472 -0.1522 1.5751 C 3.7091 -1.1551 0.4232 C 1.6366 1.0896 0.6547 C -0.5967 0.0079 -0.1048 C 0.1583 1.2892 0.2210 C -2.0174 -0.0916 -0.0118 C -2.6934 -1.2905 -0.3823 C -4.0713 -1.3961 -0.2907 C -4.8469 -0.3271 0.1717 C -4.2064 0.8581 0.5444 C -2.8280 0.9814 0.4568 C 0.0019 2.3708 -0.8725 C 3.9587 0.3128 -0.0212 H 1.8226 -0.0190 -2.4988 H 1.5535 -2.2235 -1.1911 H 2.7921 1.8476 -1.0670 H 2.0008 -2.2935 1.1921 H 2.4749 0.0066 2.3763 H 0.7884 -0.3541 2.0577 H 4.2847 -1.3939 1.3218 H 4.0350 -1.8523 -0.3557 H 1.9388 1.9908 1.1989 H -0.3364 1.6846 1.1176 H -2.1098 -2.1265 -0.7423 H -4.5525 -2.3234 -0.5838 H -5.9248 -0.4158 0.2399 H -4.7907 1.6964 0.9093 H -2.3742 1.9160 0.7604 H 0.4946 3.2989 -0.5629 H 0.4389 2.0522 -1.8207 H -1.0505 2.5923 -1.0555 H 4.3168 0.9231 0.8148 H 4.7239 0.3587 -0.7994	

Table S10. Effect of the Me group in the tether on relative stability of the diradicals in the bicyclo[2.2.1]heptane system with vicinal endo COOMe (Me is "in")

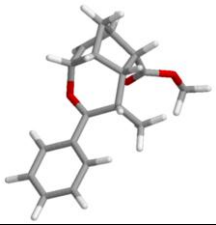
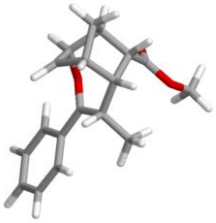
Gamma 1,4-diradical (triplet) Me is "in" B3LYP/6-311+G(d,p) -923.762636835 Hartrees	Delta 1,4-diradical (triplet) Me is "in" B3LYP/6-311+G(d,p) -923.747077507 Hartrees	ΔE = 9.8 kcal/mol (triplet gamma diradical is lower in energy)
		
C 0.3958 -2.0774 0.4847 C 1.6800 -1.8452 1.2229 C 0.8516 -2.0083 -0.9931 O -0.6178 -1.1020 0.8554 C 2.7425 -1.6185 0.1983 C 2.4727 -0.2418 -0.5148 C 2.2707 -2.5954 -0.9095 C 1.1121 -0.5164 -1.3080 C -1.1187 -0.2653 -0.0962 C -0.1895 0.3163 -1.1349 C -2.5039 0.0432 0.0137 C -3.2820 -0.4734 1.0894 C -4.6335 -0.1918 1.1950 C -5.2790 0.6061 0.2431 C -4.5372 1.1173 -0.8260 C -3.1817 0.8509 -0.9432 C 0.0413 1.8355 -0.9576 C 2.5853 0.9312 0.4346 O 2.1491 0.9962 1.5582 O 3.3125 1.9279 -0.1268 C 3.5101 3.0983 0.6879 H -0.0602 -3.0482 0.7179 H 1.7345 -1.6086 2.2745 H 0.1629 -2.4849 -1.6919 H 3.7710 -1.7193 0.5453 H 3.2484 -0.0911 -1.2676 H 2.8244 -2.4971 -1.8476 H 2.2963 -3.6385 -0.5870 H 1.3817 -0.4251 -2.3623 H -0.7020 0.2007 -2.0999 H -2.7943 -1.0906 1.8317 H -5.1968 -0.5970 2.0291 H -6.3372 0.8225 0.3314 H -5.0248 1.7287 -1.5781 H -2.6455 1.2531 -1.7934 H 0.7810 2.1999 -1.6770 H 0.3802 2.0718 0.0505 H -0.8856 2.3860 -1.1202 H 4.1230 3.7688 0.0895 H 4.0191 2.8360 1.6163 H 2.5524 3.5640 0.9256	C -0.5178 -2.5361 -0.1012 C -0.8297 -1.5826 -1.2083 C -1.5777 -2.2775 0.9182 O 0.0438 -0.3932 -1.0962 C -2.3345 -1.2285 -0.9414 C -2.3589 -0.0911 0.0902 C -2.8007 -2.3864 -0.0305 C -1.4941 -0.7136 1.2605 C 0.7315 -0.2197 0.0810 C -0.0167 -0.2608 1.4053 C 2.1417 -0.0382 -0.0484 C 2.7349 0.0985 -1.3352 C 4.1026 0.2608 -1.4804 C 4.9453 0.2836 -0.3636 C 4.3877 0.1338 0.9090 C 3.0187 -0.0207 1.0716 C 0.1059 1.0435 2.2312 C -2.1576 1.2865 -0.5175 O -2.1576 1.5208 -1.6999 O -2.1502 2.2629 0.4195 C -2.0961 3.6128 -0.0825 H 0.4267 -3.0457 0.0308 H -0.6496 -1.9493 -2.2193 H -1.5678 -2.9113 1.8043 H -2.9122 -1.0315 -1.8413 H -3.3831 -0.0214 0.4774 H -3.7657 -2.1836 0.4429 H -2.8485 -3.3589 -0.5242 H -1.9886 -0.5287 2.2162 H 0.4622 -1.0429 2.0158 H 2.0920 0.0831 -2.2048 H 4.5223 0.3709 -2.4748 H 6.0151 0.4093 -0.4834 H 5.0300 0.1308 1.7833 H 2.6271 -0.1586 2.0709 H -0.3334 0.8898 3.2225 H -0.4169 1.8693 1.7570 H 1.1473 1.3330 2.3684 H -2.0946 4.2504 0.7991 H -2.9661 3.8212 -0.7065 H -1.1898 3.7650 -0.6697	

Table S11. Effect of the Me group in the tether on relative stability of the diradicals in the bicyclo[2.2.1]octane system with vicinal endo COOMe (continued - Me is "out")

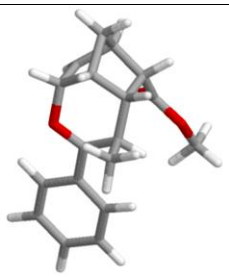
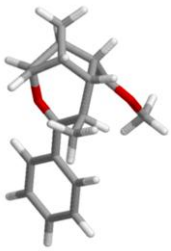
Gamma 1,4-diradical (triplet) Me is "out" B3LYP/6-311+G(d,p) -923.777367273 Hartrees	Delta 1,4-diradical (triplet) Me is "out" B3LYP/6-311+G(d,p) -923.755809161 Hartrees	ΔE =13.5 kcal/mol (triplet gamma diradical is lower in energy)
		
C -1.4628 -1.8855 -0.7056 C -1.7855 -0.8120 -1.7058 C -2.3839 -1.4995 0.4764 O -0.0551 -1.9693 -0.3745 C -2.8514 0.0558 -1.1123 C -2.2084 0.8972 0.0350 C -3.6294 -0.9873 -0.2687 C -1.7952 -0.2042 1.1022 C 0.4970 -0.9206 0.3102 C -0.2990 -0.3505 1.4538 C 1.8684 -0.6531 0.0458 C 2.5510 -1.3212 -1.0102 C 3.8833 -1.0570 -1.2796 C 4.5998 -0.1265 -0.5186 C 3.9517 0.5356 0.5289 C 2.6187 0.2821 0.8127 C -0.1244 -1.2208 2.7247 C -1.1711 1.8896 -0.4516 O -0.8679 2.0825 -1.6034 O -0.6708 2.6196 0.5730 C 0.2897 3.6336 0.2123 H -1.6854 -2.8941 -1.0709 H -1.1847 -0.5847 -2.5741 H -2.5410 -2.3051 1.1930 H -3.4207 0.6563 -1.8203 H -2.9897 1.5145 0.4939 H -4.3725 -0.5417 0.3990 H -4.1145 -1.7512 -0.8808 H -2.3262 0.0162 2.0315 H 0.0827 0.6437 1.6845 H 2.0074 -2.0424 -1.6054 H 4.3748 -1.5798 -2.0933 H 5.6423 0.0757 -0.7349 H 4.4967 1.2538 1.1326 H 2.1516 0.8058 1.6377 H 0.9277 -1.2687 3.0133 H -0.4691 -2.2444 2.5608 H -0.6895 -0.7980 3.5617 H 0.5588 4.1225 1.1462 H -0.1548 4.3482 -0.4813 H 1.1657 3.1775 -0.2502	C -2.0255 -2.0653 -0.4935 C -1.6329 -0.9903 -1.4515 C -2.8062 -1.3635 0.5628 O -0.2288 -0.6454 -1.2901 C -2.6228 0.1803 -1.0934 C -2.0700 0.9462 0.1198 C -3.7647 -0.5789 -0.3776 C -1.8461 -0.2202 1.1421 C 0.3903 -0.6796 -0.0647 C -0.3644 -0.6475 1.2588 C 1.8136 -0.5942 -0.1442 C 2.4791 -0.6591 -1.4020 C 3.8586 -0.5754 -1.4887 C 4.6439 -0.4191 -0.3411 C 4.0125 -0.3426 0.9035 C 2.6319 -0.4259 1.0082 C -0.2087 -1.9351 2.1015 C -0.9788 1.9590 -0.1773 O -0.7714 2.4427 -1.2620 O -0.3473 2.3626 0.9484 C 0.6613 3.3785 0.7725 H -1.6027 -3.0596 -0.4775 H -1.6994 -1.2637 -2.5058 H -3.2613 -1.9849 1.3322 H -2.8861 0.8089 -1.9409 H -2.8810 1.5770 0.5047 H -4.4565 0.0944 0.1363 H -4.3381 -1.2468 -1.0233 H -2.1874 0.0675 2.1391 H 0.1139 0.1505 1.8363 H 1.8858 -0.7730 -2.2986 H 4.3329 -0.6314 -2.4629 H 5.7232 -0.3565 -0.4156 H 4.6055 -0.2137 1.8030 H 2.1829 -0.3506 1.9902 H -0.6694 -1.7953 3.0853 H -0.6775 -2.7983 1.6277 H 0.8437 -2.1768 2.2554 H 1.0420 3.5844 1.7705 H 0.2246 4.2761 0.3332 H 1.4584 3.0085 0.1272	

Table S12. Effect of the Me group in the tether on relative stability of the diradicals in the bicyclo[2.2.2]octane system with vicinal endo COOMe (Me is "in")

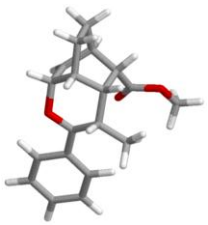
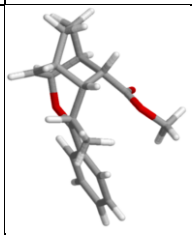
Gamma 1,4-diradical (triplet) Me is "in" B3LYP/6-311+G(d,p) -963.094593638 Hartrees	Delta 1,4-diradical (triplet) Me is "in" B3LYP/6-311+G(d,p) -963.084556125 Hartrees	ΔE = 6.3 kcal/mol (triplet gamma diradical is lower in energy)
		
C -1.0116 -2.1500 -0.2041 C -1.2790 -1.3302 -1.4234 C -1.9551 -1.6664 0.9043 O 0.3783 -2.0550 0.2159 C -2.3825 -0.3346 -1.2786 C -2.0597 0.6472 -0.0997 C -3.6745 -1.0897 -0.8762 C -1.5838 -0.1869 1.1579 C 0.8341 -0.8102 0.5980 C -0.0839 -0.1335 1.5984 C 2.1935 -0.5581 0.2314 C 2.9150 -1.5643 -0.4777 C 4.2308 -1.3770 -0.8664 C 4.9008 -0.1838 -0.5812 C 4.2141 0.8224 0.1023 C 2.8975 0.6485 0.5013 C 0.3067 1.2308 2.1826 C -1.1435 1.7567 -0.5765 O -0.2162 1.6395 -1.3385 O -1.5364 2.9558 -0.0757 C -0.7638 4.0960 -0.4939 H -1.1332 -3.2244 -0.3862 H -0.6208 -1.3720 -2.2808 H -1.7704 -2.2430 1.8150 H -2.5374 0.2291 -2.2000 H -2.9924 1.1391 0.1857 H -3.9410 -1.7934 -1.6683 H -2.1565 0.1758 2.0171 H -0.0710 -0.8201 2.4640 H 2.4158 -2.4947 -0.7066 H 4.7435 -2.1708 -1.3998 H 5.9298 -0.0393 -0.8892 H 4.7107 1.7620 0.3209 H 2.4084 1.4677 1.0008 H -0.4691 1.5467 2.8859 H 0.4084 2.0161 1.4353 H 1.2434 1.1651 2.7374 H -1.2277 4.9543 -0.0126 H -0.7938 4.1996 -1.5793 H 0.2754 3.9940 -0.1765 C -3.4213 -1.8318 0.4657 H -4.5043 -0.3820 -0.7852 H -3.6536 -2.8966 0.3691 H -4.0735 -1.4457 1.2551	C -2.4249 -1.8358 0.5331 C -1.6333 -1.5971 -0.7071 C -2.9155 -0.5562 1.1282 O -0.1872 -1.6455 -0.4663 C -2.0908 -0.2448 -1.3117 C -1.6062 0.9180 -0.4178 C -3.6360 -0.2120 -1.2589 C -1.6959 0.4371 1.0578 C 0.4516 -0.8150 0.4268 C -0.3974 -0.2932 1.5781 C 1.8710 -0.7846 0.2133 C 2.4344 -1.5900 -0.8215 C 3.7938 -1.5895 -1.0849 C 4.6703 -0.7919 -0.3440 C 4.1450 0.0131 0.6690 C 2.7851 0.0247 0.9447 C 0.2688 0.5283 2.6920 C -0.3215 1.5716 -0.9052 O 0.1231 1.4691 -2.0223 O 0.1859 2.4229 0.0160 C 1.3240 3.1987 -0.4126 H -2.5372 -2.8174 0.9754 H -1.7629 -2.3985 -1.4373 H -3.2430 -0.6710 2.1641 H -1.7112 -0.1350 -2.3266 H -2.3289 1.7374 -0.5307 H -4.0460 -1.1305 -1.6903 H -1.8912 1.2948 1.7050 H -0.7501 -1.2042 2.0829 H 1.7773 -2.2136 -1.4094 H 4.1777 -2.2193 -1.8806 H 5.7337 -0.7946 -0.5532 H 4.8046 0.6477 1.2519 H 2.4351 0.6823 1.7216 H -0.4794 0.7084 3.4699 H 0.6173 1.4998 2.3421 H 1.0948 -0.0103 3.1582 H 1.5911 3.8177 0.4417 H 1.0567 3.8213 -1.2675 H 2.1496 2.5415 -0.6853 C -4.0807 -0.0611 0.2253 H -4.0105 0.6172 -1.8658 H -4.9807 -0.6477 0.4229 H -4.3224 0.9800 0.4655	

Table S13. Effect of the Me group in the tether on relative stability of the diradicals in the bicyclo[2.2.2]octane system with vicinal endo COOMe (Me is "out")

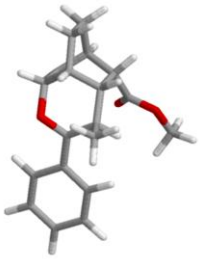
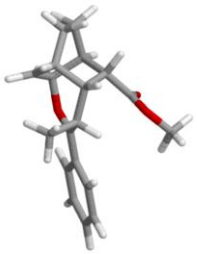
Gamma 1,4-diradical (triplet) Me is "out" B3LYP/6-311+G(d,p) -963.108676349 Hartrees	Delta 1,4-diradical (triplet) Me is "out" B3LYP/6-311+G(d,p) -963.097120510 Hartrees	ΔE = 7.3 kcal/mol (triplet gamma diradical is lower in energy)
		
C -1.2710 -1.9275 -0.4609 C -1.5613 -0.9974 -1.5919 C -2.0745 -1.4550 0.7582 O 0.1578 -1.9859 -0.1660 C -2.5432 0.0856 -1.2798 C -2.0151 0.9283 -0.0816 C -3.8678 -0.5697 -0.8127 C -1.5653 -0.0325 1.0921 C 0.7303 -0.8568 0.3552 C -0.0434 -0.0868 1.3961 C 2.1065 -0.6596 0.0551 C 2.7784 -1.5034 -0.8741 C 4.1169 -1.3136 -1.1741 C 4.8505 -0.2867 -0.5694 C 4.2125 0.5510 0.3506 C 2.8737 0.3737 0.6630 C 0.2108 -0.6672 2.8117 C -0.9923 1.9558 -0.5372 O -0.4884 2.0196 -1.6305 O -0.7486 2.8641 0.4391 C 0.1809 3.9139 0.1027 H -1.5033 -2.9703 -0.7059 H -1.0085 -1.0522 -2.5203 H -1.8818 -2.1228 1.6005 H -2.7103 0.7315 -2.1417 H -2.8508 1.5236 0.3029 H -4.2868 -1.1611 -1.6301 H -2.0573 0.3145 2.0047 H 0.3283 0.9379 1.4124 H 2.2213 -2.3005 -1.3474 H 4.6000 -1.9716 -1.8888 H 5.8978 -0.1435 -0.8086 H 4.7698 1.3484 0.8311 H 2.4151 1.0358 1.3872 H -0.3278 -0.0861 3.5673 H 1.2754 -0.6328 3.0513 H -0.1078 -1.7089 2.8876 H 0.2551 4.5326 0.9944 H -0.1944 4.4974 -0.7391 H 1.1530 3.4939 -0.1589 C -3.5787 -1.4617 0.4277 H -4.5999 0.2088 -0.5753 H -3.9069 -2.4904 0.2504 H -4.1344 -1.1083 1.3016	C -2.1158 -1.9684 -0.1750 C -1.5258 -1.1659 -1.2800 C -2.6814 -1.1005 0.8965 O -0.0701 -1.0998 -1.1682 C -2.1910 0.2353 -1.2750 C -1.7383 1.0367 -0.0348 C -3.7127 0.0158 -1.1158 C -1.6204 0.0335 1.1514 C 0.5578 -0.7595 -0.0004 C -0.1753 -0.5194 1.3072 C 1.9799 -0.6858 -0.1113 C 2.6309 -0.9544 -1.3491 C 4.0089 -0.8806 -1.4657 C 4.8074 -0.5389 -0.3688 C 4.1909 -0.2691 0.8563 C 2.8123 -0.3393 0.9903 C -0.1000 -1.7235 2.2759 C -0.5636 1.9682 -0.3039 O -0.1786 2.3019 -1.3971 O -0.0710 2.4882 0.8438 C 1.0003 3.4420 0.6920 H -2.0322 -3.0467 -0.1310 H -1.6594 -1.6376 -2.2560 H -2.8812 -1.6444 1.8205 H -1.9456 0.7722 -2.1904 H -2.5430 1.7418 0.2109 H -4.0629 -0.7192 -1.8472 H -1.8757 0.5411 2.0861 H 0.3751 0.2907 1.7912 H 2.0280 -1.2143 -2.2080 H 4.4718 -1.0901 -2.4244 H 5.8854 -0.4852 -0.4662 H 4.7943 -0.0031 1.7180 H 2.3766 -0.1250 1.9579 H -0.5908 -1.4813 3.2249 H -0.5738 -2.6152 1.8627 H 0.9402 -1.9745 2.4908 H 1.2489 3.7612 1.7019 H 0.6718 4.2902 0.0902 H 1.8601 2.9703 0.2155 C -3.9926 -0.4792 0.3317 H -4.2474 0.9470 -1.3225 H -4.7896 -1.2260 0.3403 H -4.3219 0.3424 0.9771	

Table S14. Comparison of triplet diradicals in the bicyclo[2.2.1]heptane system with vicinal endo COOMe (no Me substitution in the tether)

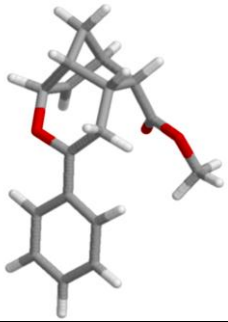
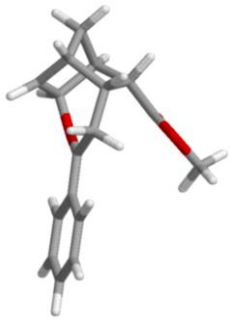
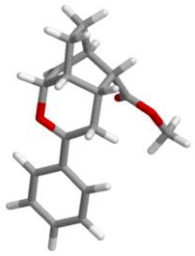
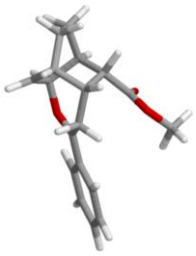
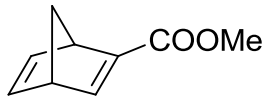
Gamma 1,4-diradical (triplet) B3LYP/6-311+G(d,p) -884.454817803 Hartrees	Delta 1,4-diradical (triplet) B3LYP/6-311+G(d,p) -884.435941011 Hartrees	ΔE = kcal/mol (triplet gamma diradical is lower in energy)
		
C -1.4469 -2.0135 -0.2907 C -1.8303 -1.0835 -1.4067 C -2.3449 -1.5036 0.8639 O -0.0272 -2.0253 -0.0039 C -2.9023 -0.1736 -0.8914 C -2.2479 0.8206 0.1186 C -3.6256 -1.1223 0.1002 C -1.7806 -0.1262 1.3028 C 0.5216 -0.9047 0.5567 C -0.2786 -0.2124 1.6163 C 1.8945 -0.6697 0.2708 C 2.5755 -1.4370 -0.7160 C 3.9099 -1.2058 -1.0049 C 4.6298 -0.2132 -0.3304 C 3.9835 0.5451 0.6508 C 2.6482 0.3264 0.9525 H 0.1172 0.7827 1.8096 C -1.2379 1.7557 -0.5158 O -0.9773 1.8165 -1.6924 O -0.7061 2.5972 0.4012 C 0.2330 3.5678 -0.1056 H -1.6548 -3.0647 -0.5186 H -1.2644 -0.9553 -2.3176 H -2.4495 -2.2133 1.6854 H -3.5091 0.3187 -1.6499 H -3.0281 1.4801 0.5166 H -4.1060 -1.9684 -0.3965 H -2.2887 0.1961 2.2144 H -0.1794 -0.7771 2.5590 H 2.0290 -2.2072 -1.2434 H 4.4004 -1.8039 -1.7657 H 5.6739 -0.0375 -0.5613 H 4.5318 1.3106 1.1896 H 2.1837 0.9219 1.7287 H 0.5244 4.1657 0.7554 H -0.2391 4.1919 -0.8651 H 1.0999 3.0662 -0.5368 H -4.3616 -0.6152 0.7309	C -1.6712 -2.3304 0.0216 C -1.4878 -1.3758 -1.1162 C -2.5572 -1.6088 0.9788 O -0.1639 -0.7635 -1.0659 C -2.6573 -0.3465 -0.9052 C -2.2143 0.6831 0.1491 C -3.6450 -1.1572 -0.0340 C -1.7890 -0.2509 1.3316 C 0.4839 -0.6262 0.1365 C -0.2666 -0.4562 1.4408 C 1.9016 -0.5500 0.0518 C 2.5736 -0.6737 -1.1978 C 3.9542 -0.6030 -1.2752 C 4.7304 -0.4086 -0.1265 C 4.0913 -0.2856 1.1109 C 2.7095 -0.3520 1.2071 H 0.1563 0.4119 1.9542 C -1.3036 1.7886 -0.3524 O -1.2547 2.1641 -1.4971 O -0.6406 2.3955 0.6567 C 0.1966 3.5075 0.2793 H -1.0323 -3.1817 0.2138 H -1.5197 -1.8275 -2.1092 H -2.8858 -2.1637 1.8566 H -3.0359 0.0883 -1.8273 H -3.1097 1.2345 0.4621 H -4.1050 -2.0056 -0.5444 H -2.1496 0.1401 2.2851 H -0.0767 -1.3166 2.0989 H 1.9845 -0.8202 -2.0929 H 4.4376 -0.6997 -2.2417 H 5.8108 -0.3563 -0.1946 H 4.6799 -0.1383 2.0103 H 2.2480 -0.2580 2.1822 H 0.6414 3.8630 1.2061 H -0.4005 4.2916 -0.1879 H 0.9694 3.1781 -0.4157 H -4.4347 -0.5329 0.3934	

Table S15. Comparison of triplet diradicals in the bicyclo[2.2.2]octane system with vicinal endo COOMe (no Me substitution in the tether)

Gamma 1,4-diradical (triplet) B3LYP/6-311+G(d,p) -923.786978746 Hartrees	Delta 1,4-diradical (triplet) B3LYP/6-311+G(d,p) -923.776963909 Hartrees	ΔE = 6.3 kcal/mol (triplet gamma diradical is lower in energy)
		
C 1.3016 -1.9386 0.2256 C 1.6237 -1.0643 1.3920 C 2.0774 -1.4088 -0.9896 O -0.1365 -1.9867 -0.0272 C 2.5854 0.0433 1.1032 C 2.0048 0.9353 -0.0329 C 3.9028 -0.5734 0.5665 C 1.5617 0.0262 -1.2471 C -0.7250 -0.8565 -0.5258 C 0.0480 -0.0617 -1.5355 C -2.1106 -0.6990 -0.2473 C -2.7701 -1.5570 0.6774 C -4.1182 -1.4056 0.9557 C -4.8730 -0.4060 0.3316 C -4.2477 0.4419 -0.5877 C -2.8992 0.3033 -0.8783 H -0.3746 0.9348 -1.6465 C 0.9571 1.8967 0.5056 O 0.5300 1.9181 1.6331 O 0.5941 2.8006 -0.4357 C -0.3719 3.7874 -0.0196 H 1.5403 -2.9914 0.4147 H 1.0992 -1.1688 2.3325 H 1.8569 -2.0311 -1.8619 H 2.7716 0.6494 1.9896 H 2.8106 1.5826 -0.3979 H 4.3609 -1.1826 1.3489 H 2.0377 0.4195 -2.1490 H -0.0557 -0.5481 -2.5207 H -2.1964 -2.3332 1.1654 H -4.5921 -2.0723 1.6685 H -5.9277 -0.2929 0.5539 H -4.8226 1.2149 -1.0868 H -2.4516 0.9659 -1.6086 H -0.5382 4.4160 -0.8918 H 0.0212 4.3773 0.8093 H -1.2990 3.3043 0.2915 C 3.5871 -1.4309 -0.6917 H 4.6125 0.2259 0.3295 H 3.9153 -2.4650 -0.5488 H 4.1266 -1.0551 -1.5663	C -2.0965 -2.0246 0.3660 C -1.5359 -1.4481 -0.8891 C -2.6768 -0.9705 1.2496 O -0.0791 -1.3493 -0.8268 C -2.2149 -0.0780 -1.1449 C -1.7538 0.9497 -0.0872 C -3.7331 -0.2742 -0.9289 C -1.6235 0.1953 1.2663 C 0.5516 -0.8011 0.2571 C -0.1965 -0.3652 1.4932 C 1.9729 -0.7533 0.1447 C 2.6224 -1.1399 -1.0624 C 4.0011 -1.0883 -1.1814 C 4.8004 -0.6604 -0.1155 C 4.1853 -0.2857 1.0825 C 2.8056 -0.3295 1.2182 H 0.3969 0.4157 1.9679 C -0.5733 1.8026 -0.5313 O -0.2141 1.9485 -1.6735 O -0.0415 2.4873 0.5063 C 1.0412 3.3822 0.1791 H -1.9454 -3.0601 0.6436 H -1.6858 -2.1033 -1.7503 H -2.8535 -1.3252 2.2672 H -1.9847 0.2751 -2.1494 H -2.5557 1.6919 0.0205 H -4.0831 -1.1367 -1.5046 H -1.8571 0.8734 2.0910 H -0.2552 -1.1879 2.2225 H 2.0177 -1.4672 -1.8967 H 4.4639 -1.3835 -2.1172 H 5.8790 -0.6244 -0.2150 H 4.7907 0.0382 1.9226 H 2.3695 -0.0475 2.1681 H 1.3186 3.8564 1.1181 H 0.7124 4.1269 -0.5467 H 1.8820 2.8220 -0.2309 C -3.9984 -0.4882 0.5889 H -4.2780 0.5971 -1.3025 H -4.7859 -1.2286 0.7455 H -4.3349 0.4376 1.0680	

^{1}H NMR (500 MHz, $CDCl_3$):



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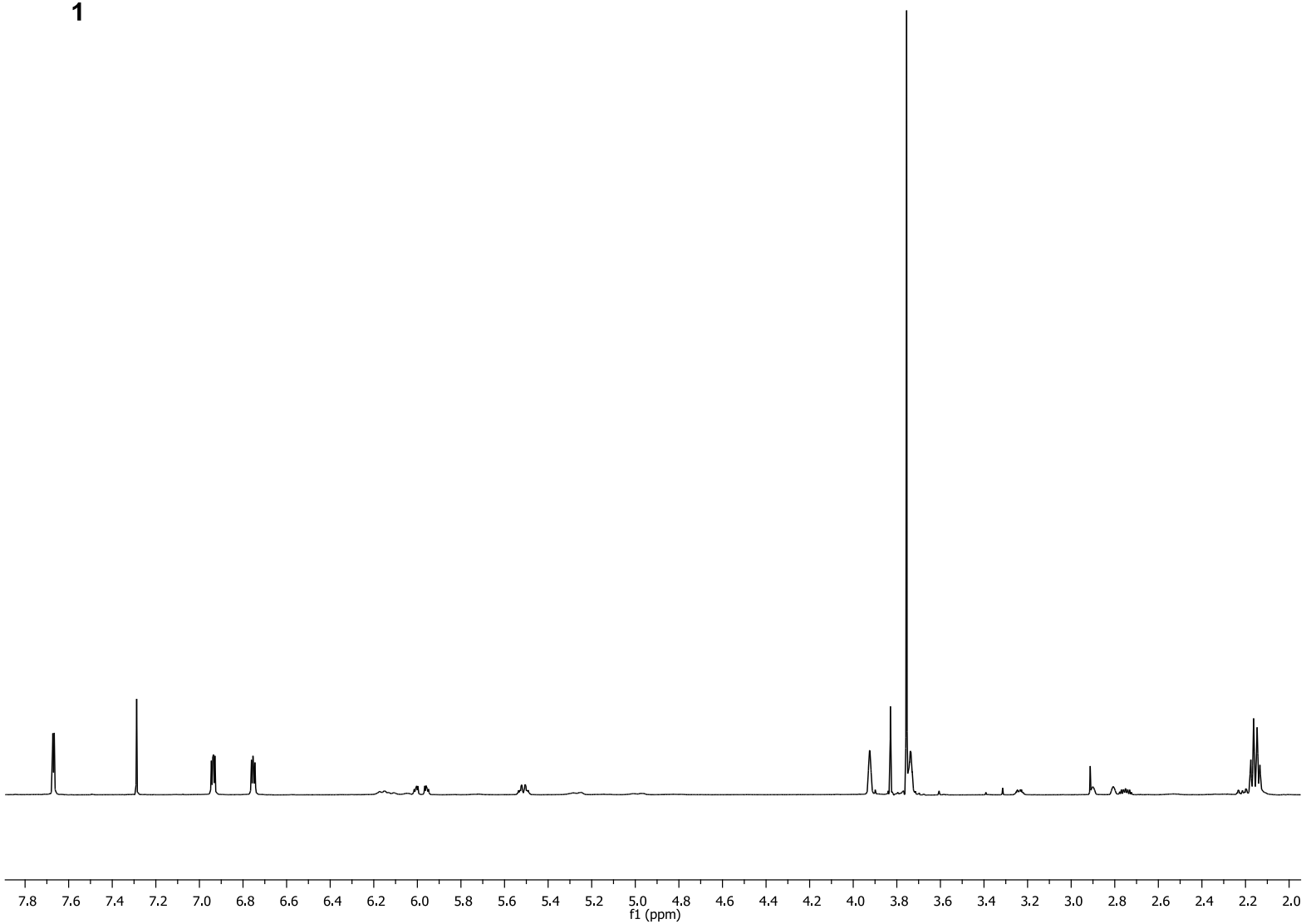
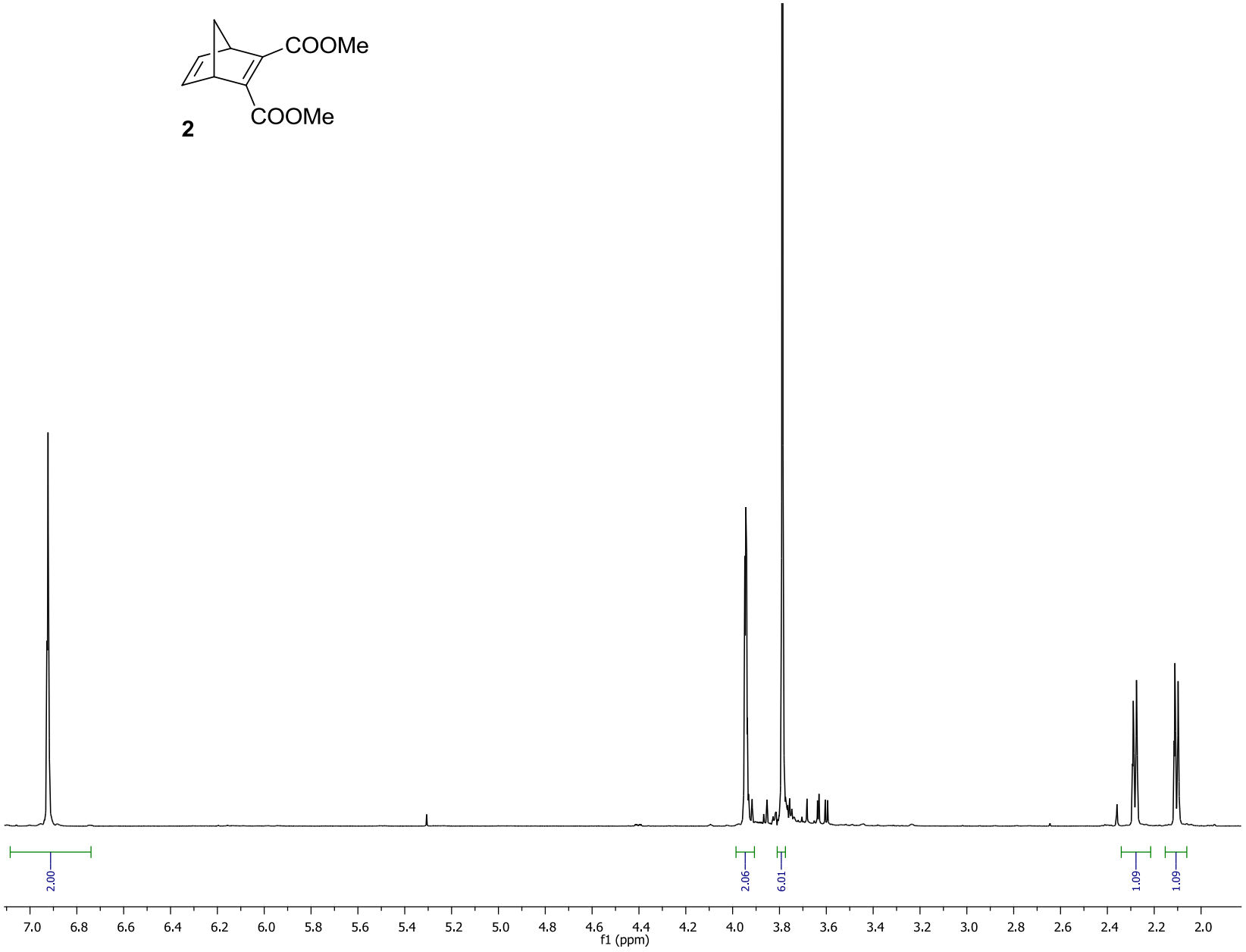
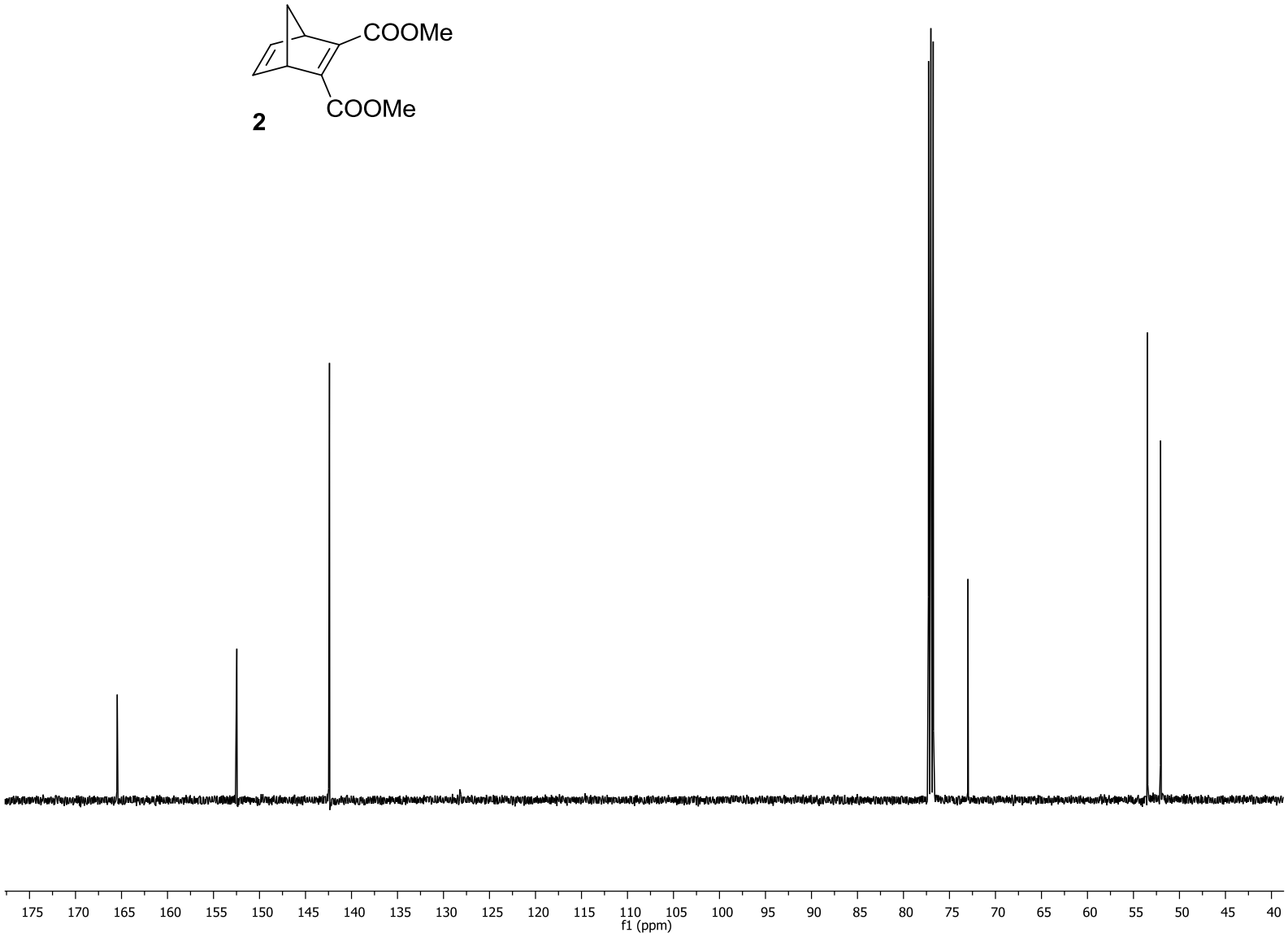


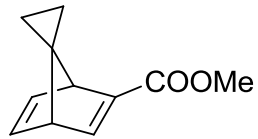
^{1}H NMR (500 MHz, $CDCl_3$):



^{13}C NMR (500 MHz, $CDCl_3$):



^{1}H NMR (500 MHz, $CDCl_3$):



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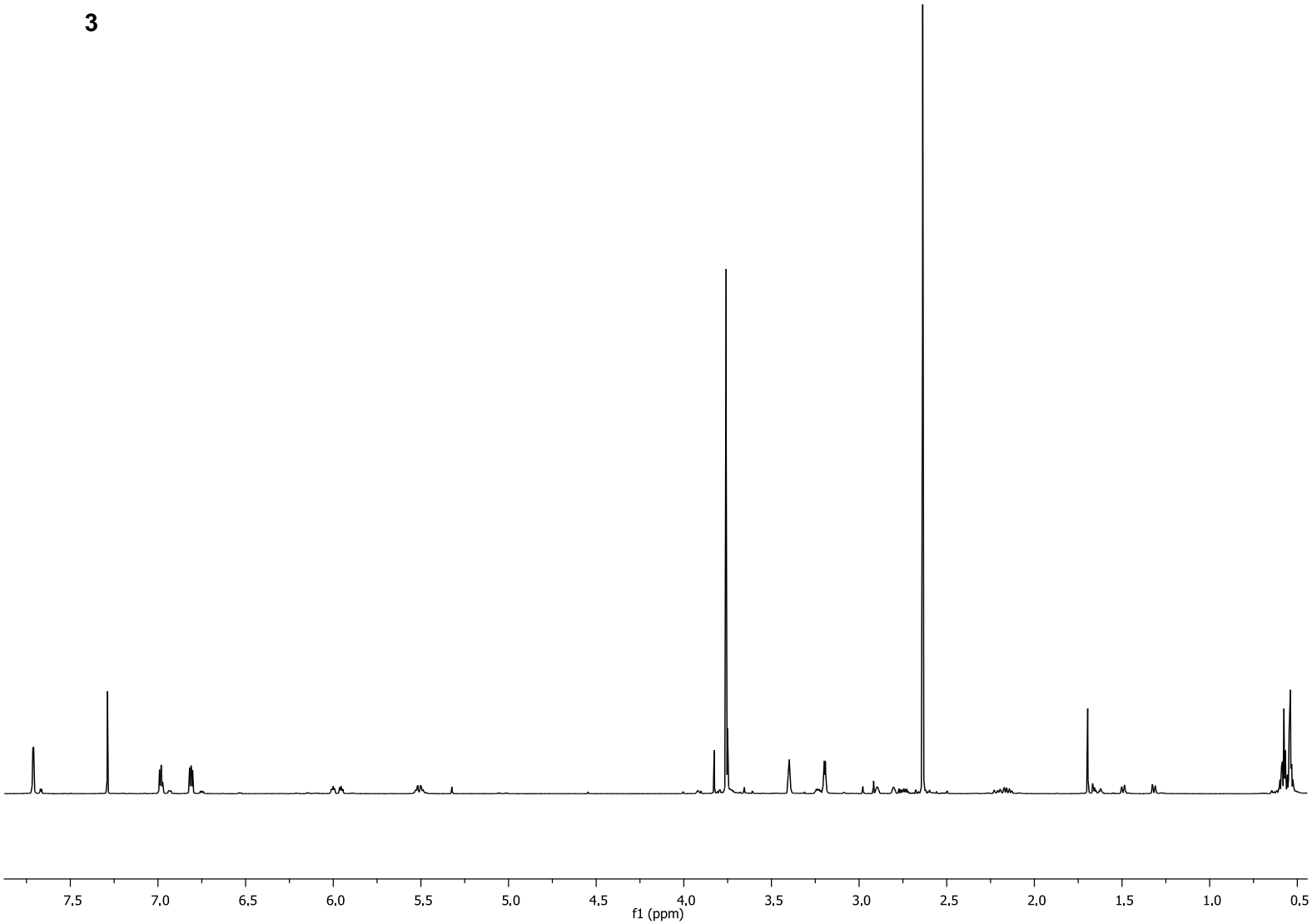
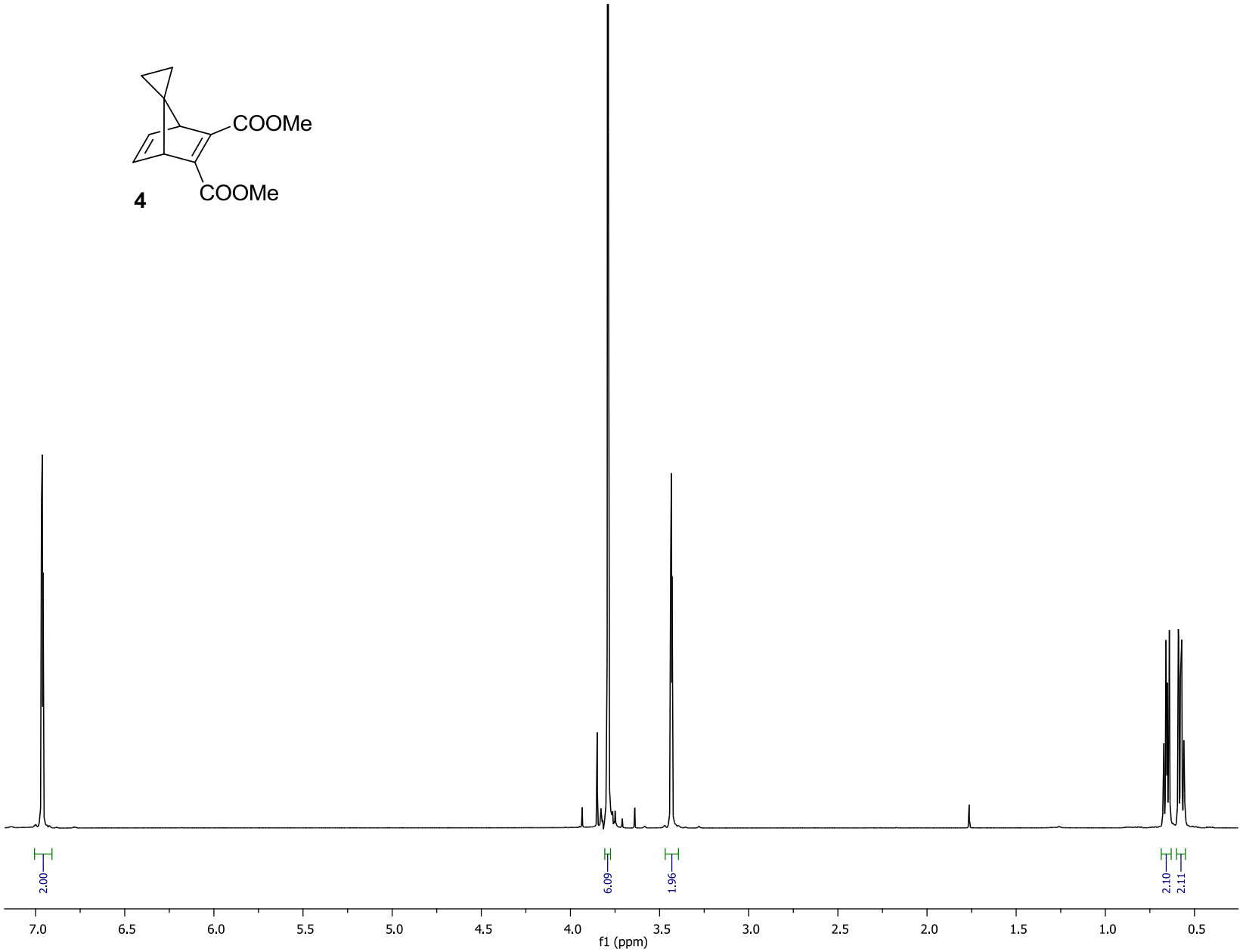
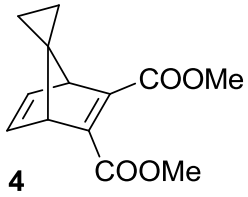


^{1}H NMR (500 MHz, $CDCl_3$):



^{13}C NMR (500 MHz, $CDCl_3$):



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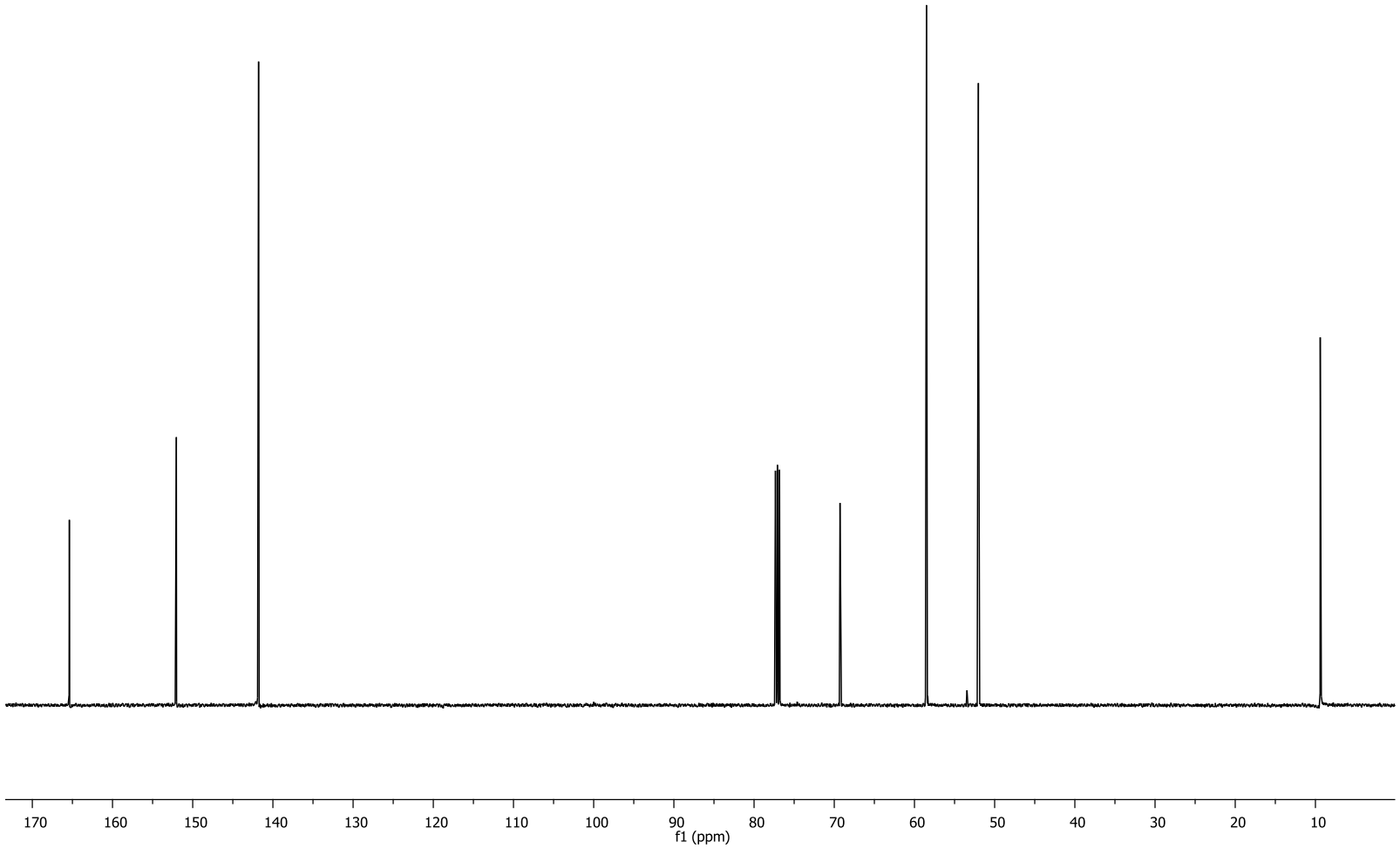
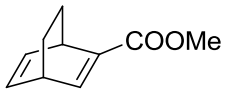
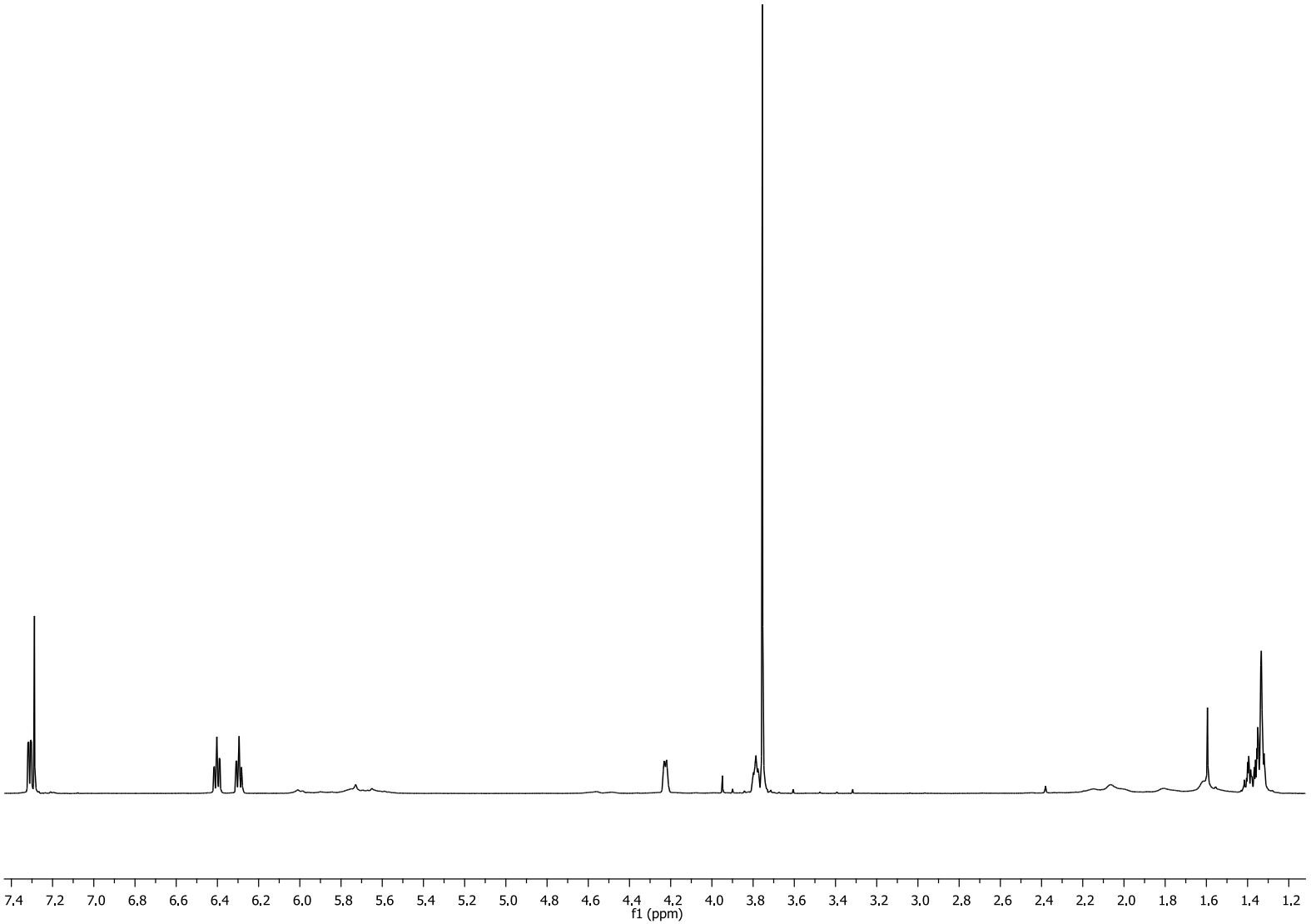


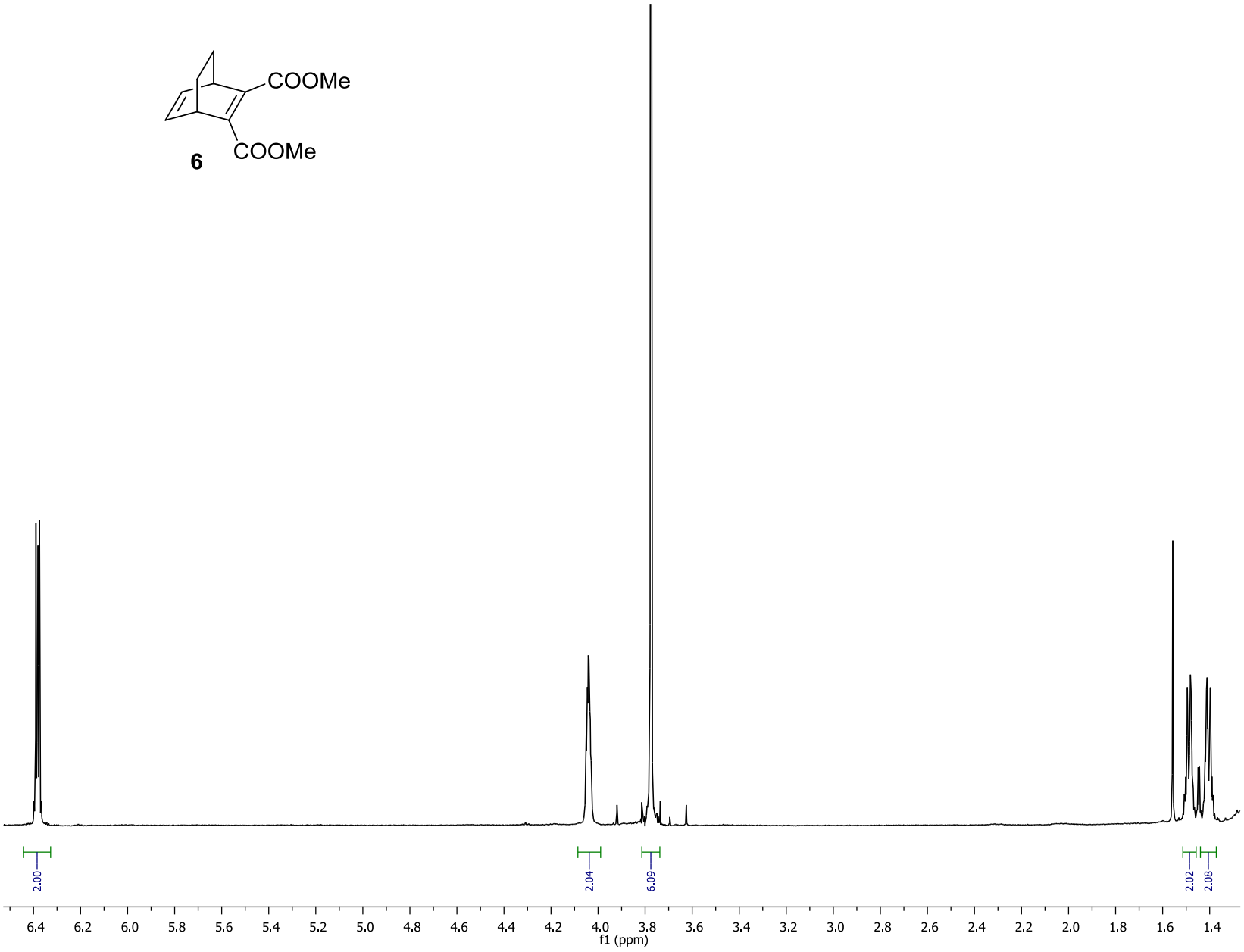
^{1}H NMR (500 MHz, $CDCl_3$):



5

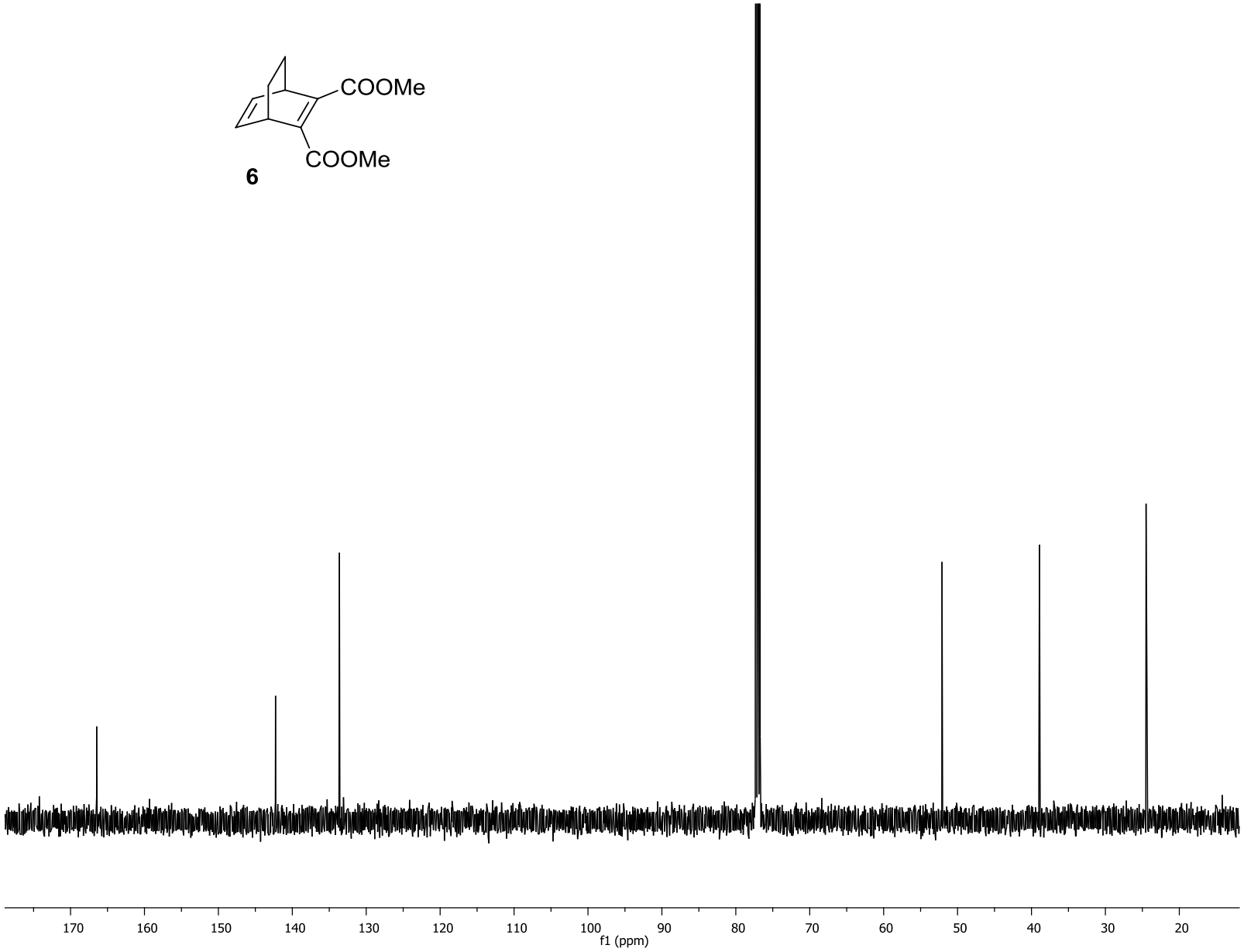


^{1}H NMR (500 MHz, $CDCl_3$):

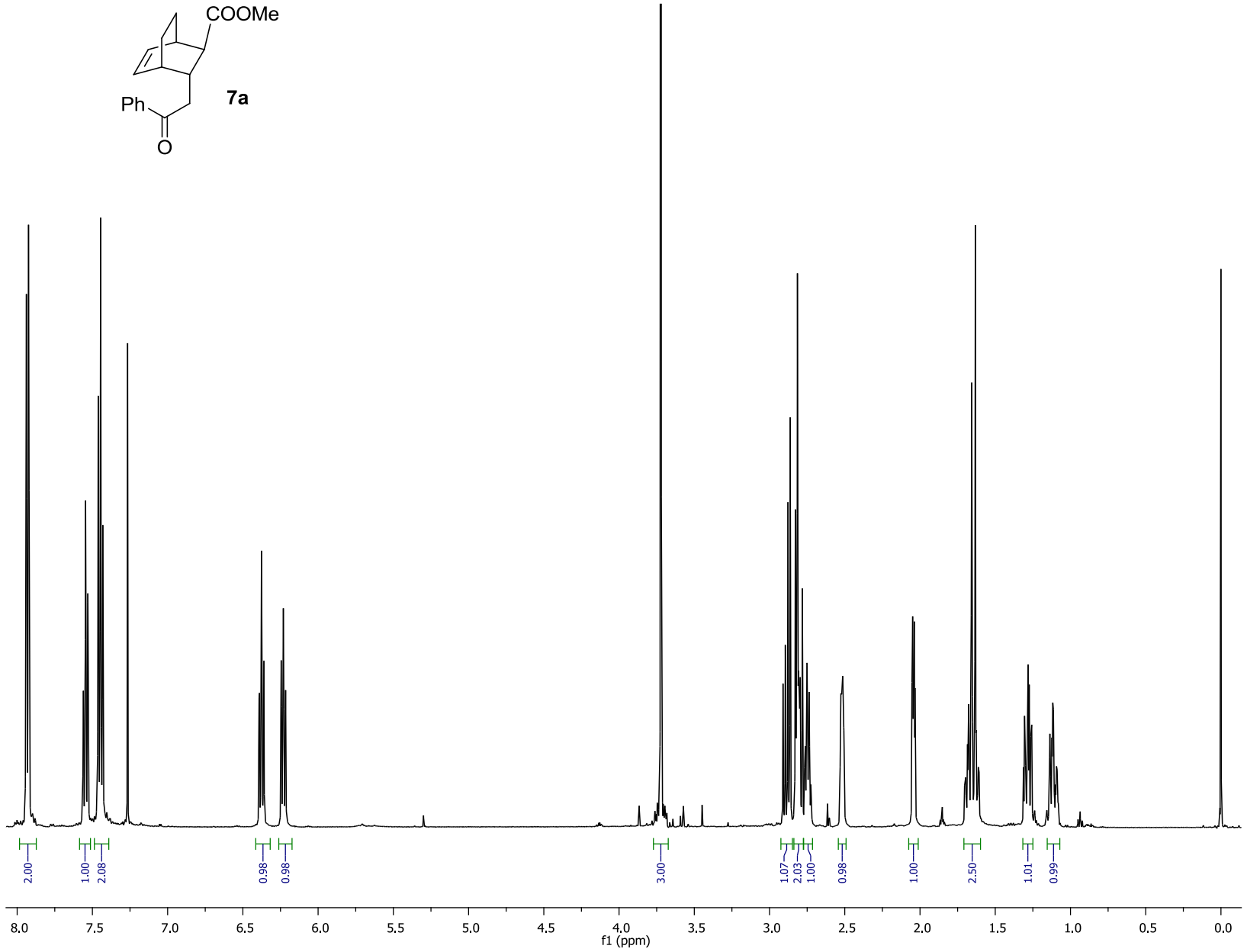


^{13}C NMR (500 MHz, $CDCl_3$):

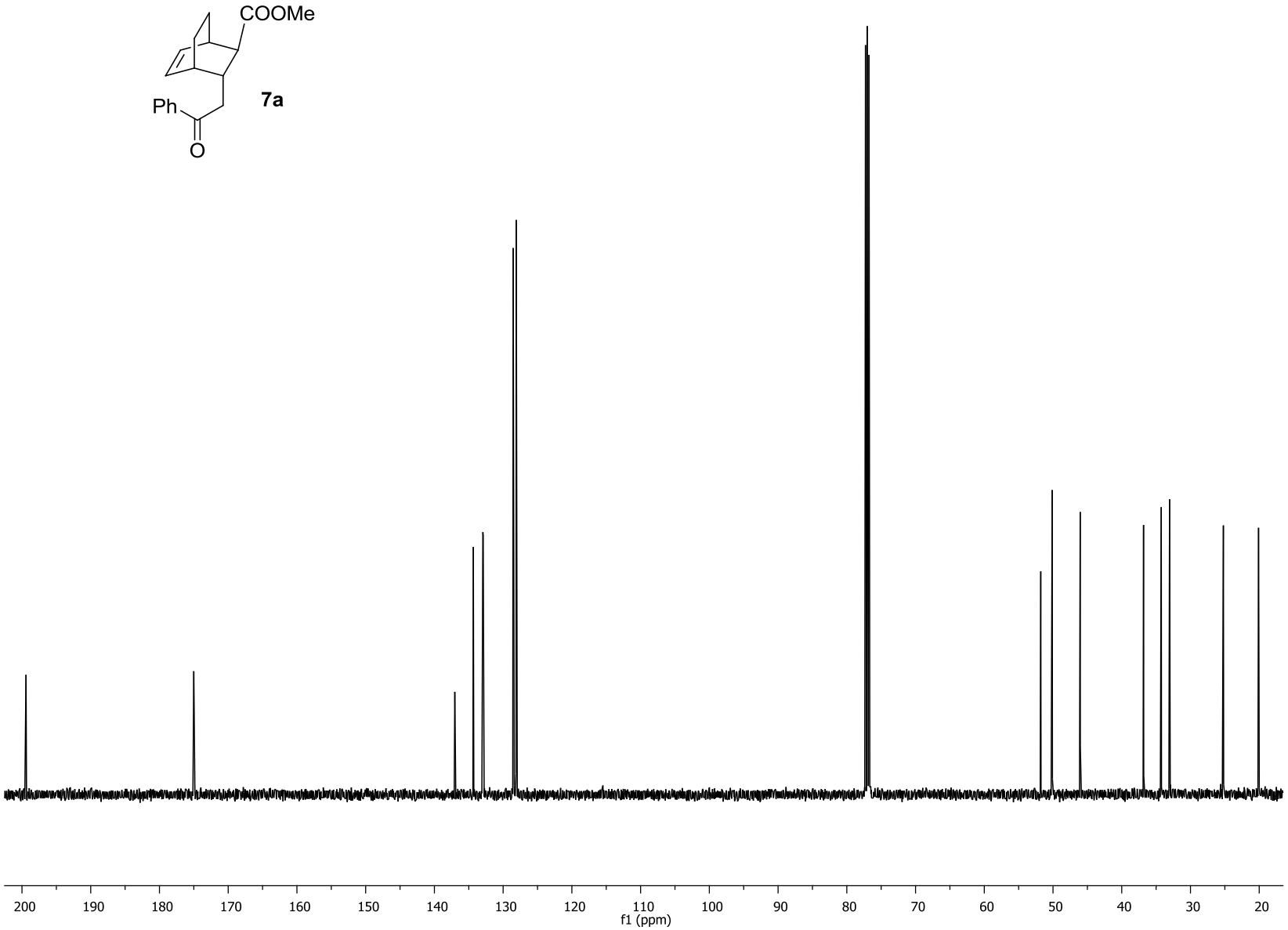
6



^{1}H NMR (500 MHz, $CDCl_3$):

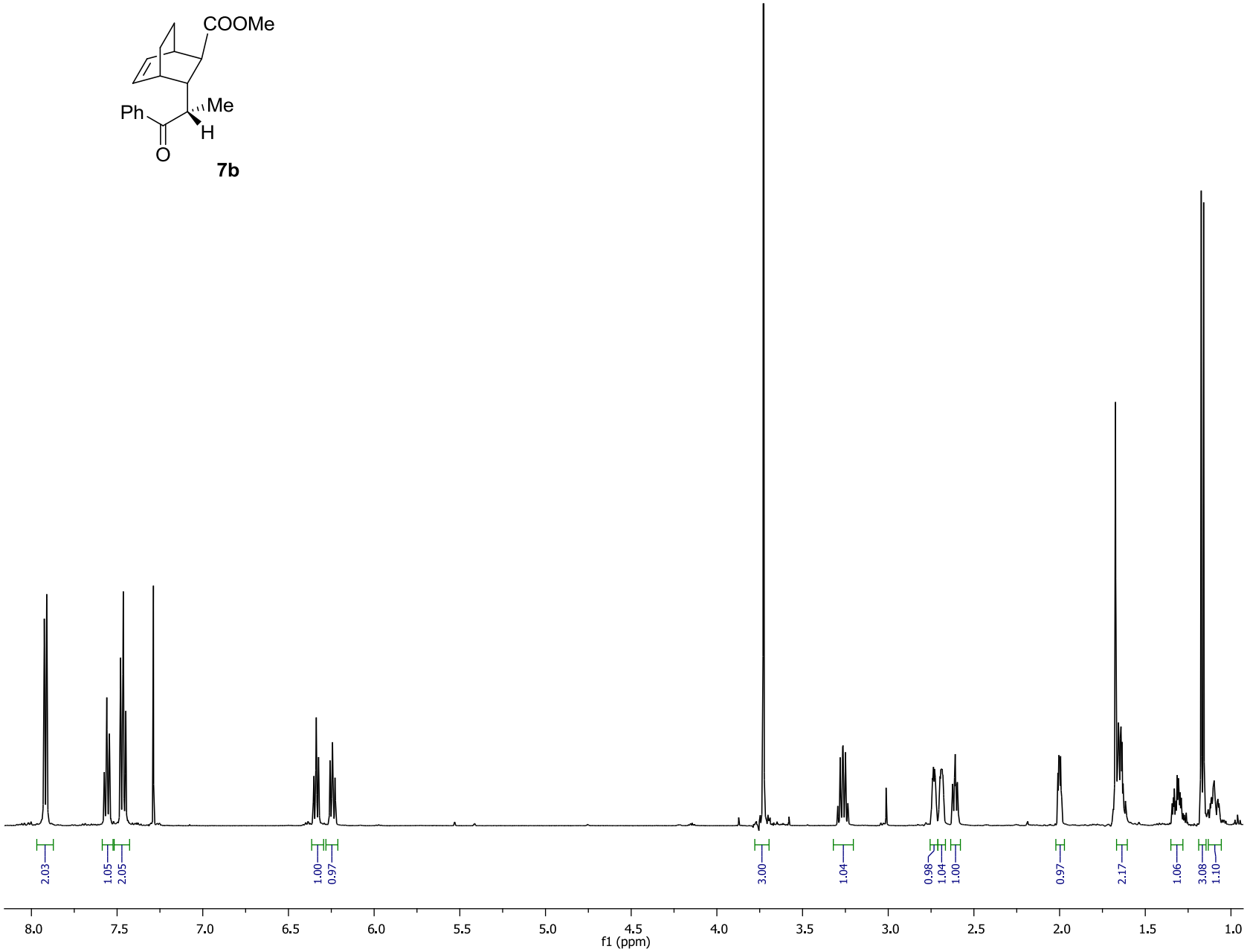


^{13}C NMR (500 MHz, $CDCl_3$):

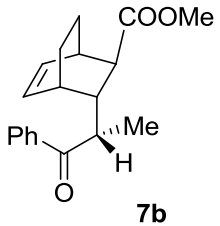


^{1}H NMR (500 MHz, $CDCl_3$):

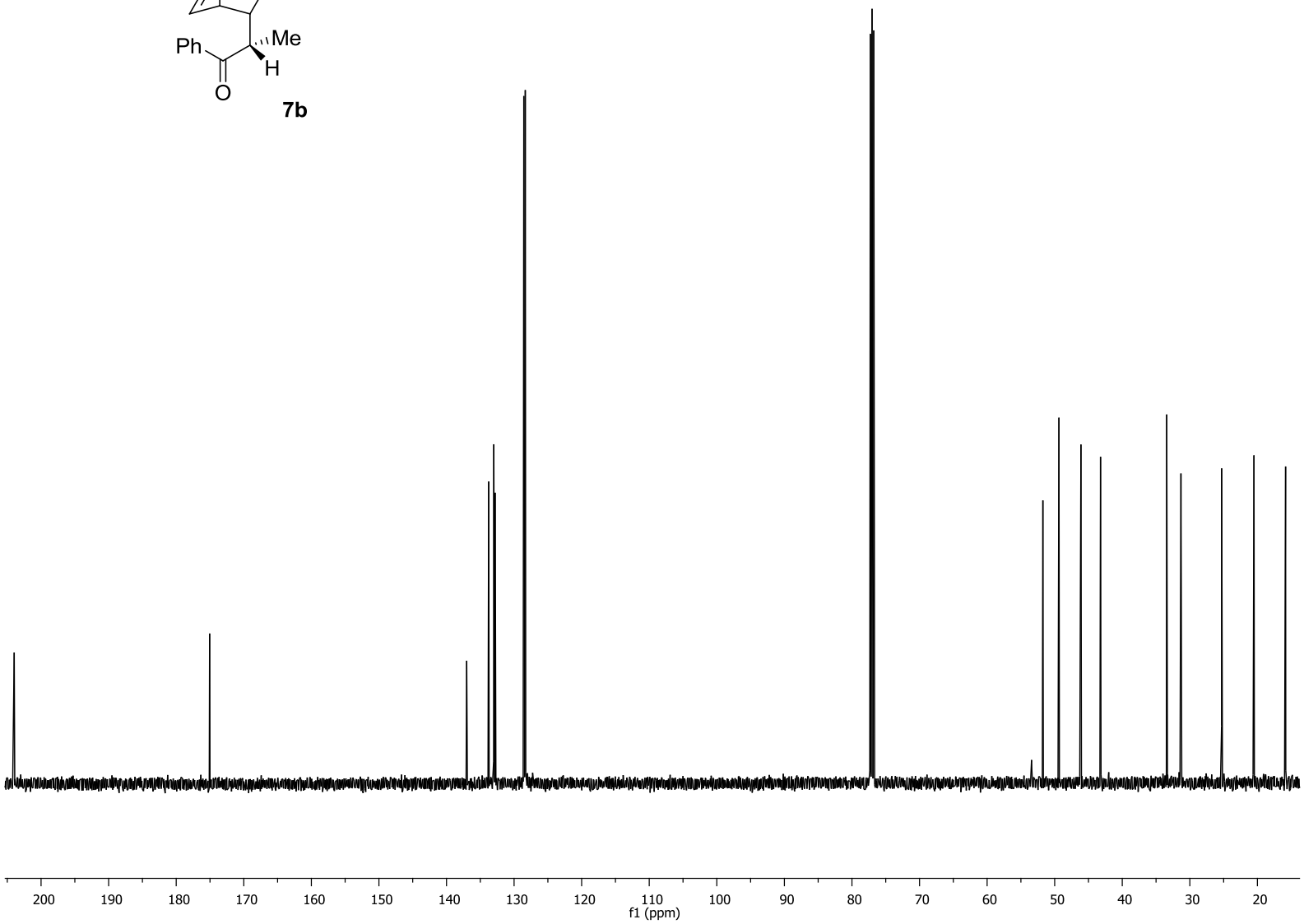
7b



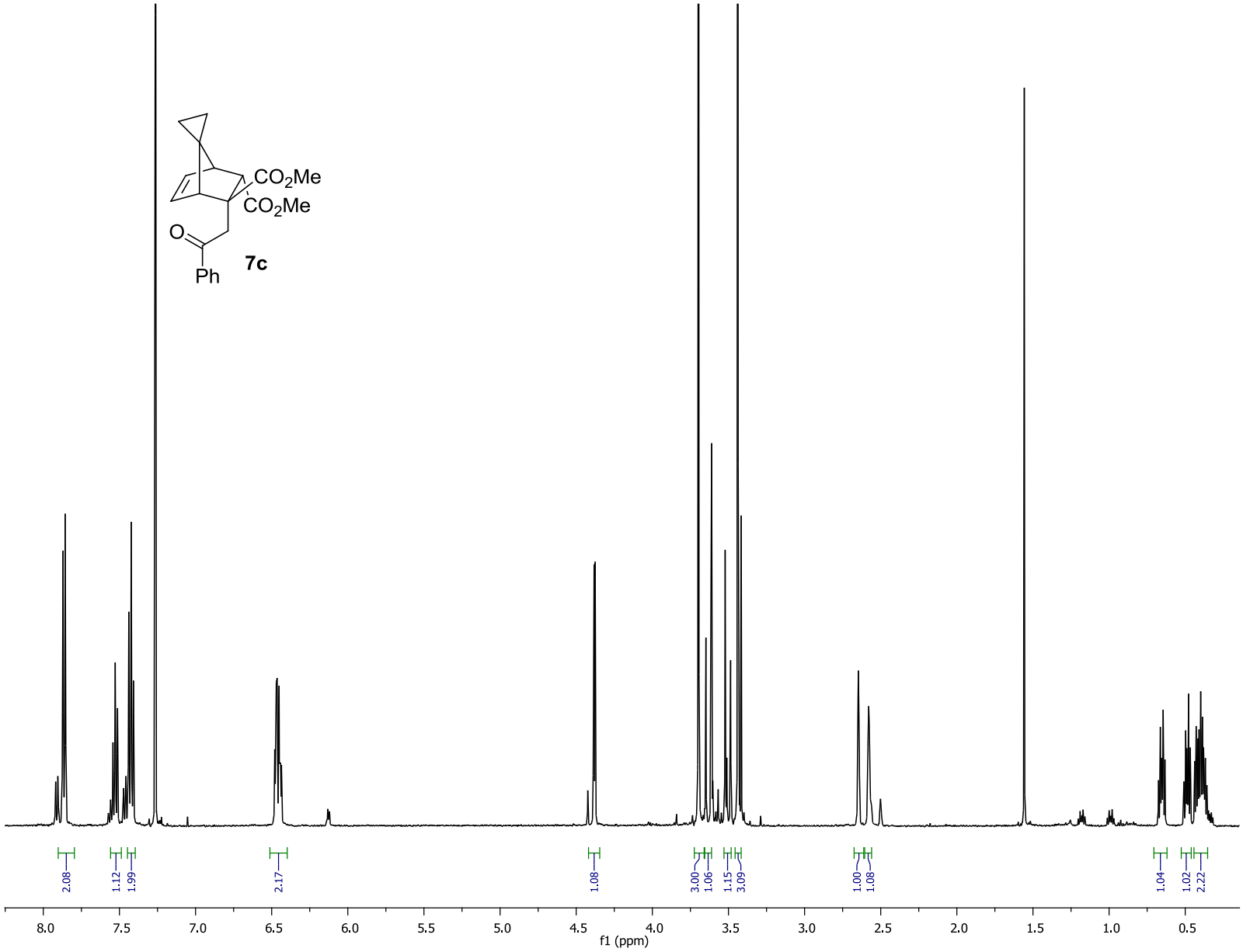
^{13}C NMR (500 MHz, $CDCl_3$):



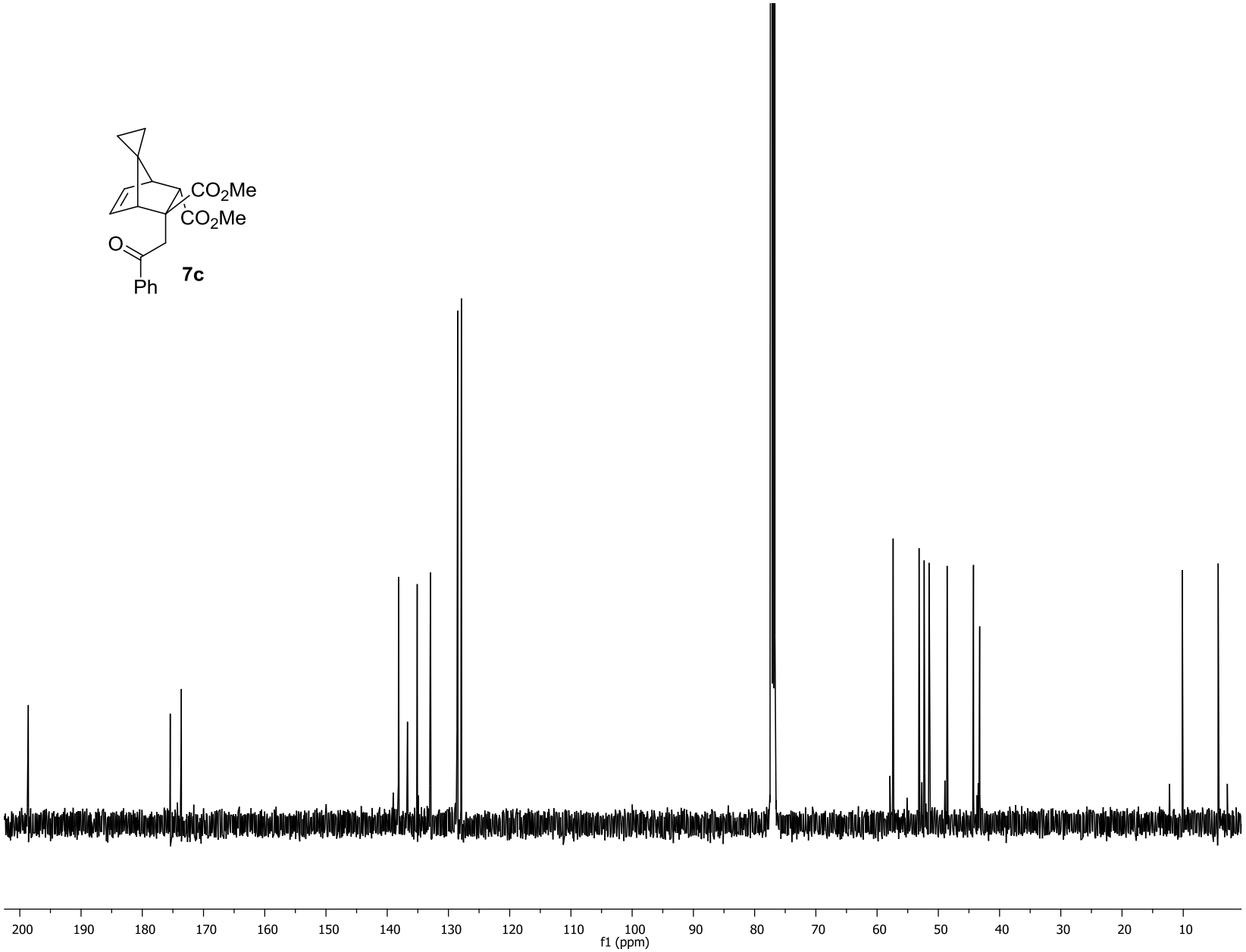
7b



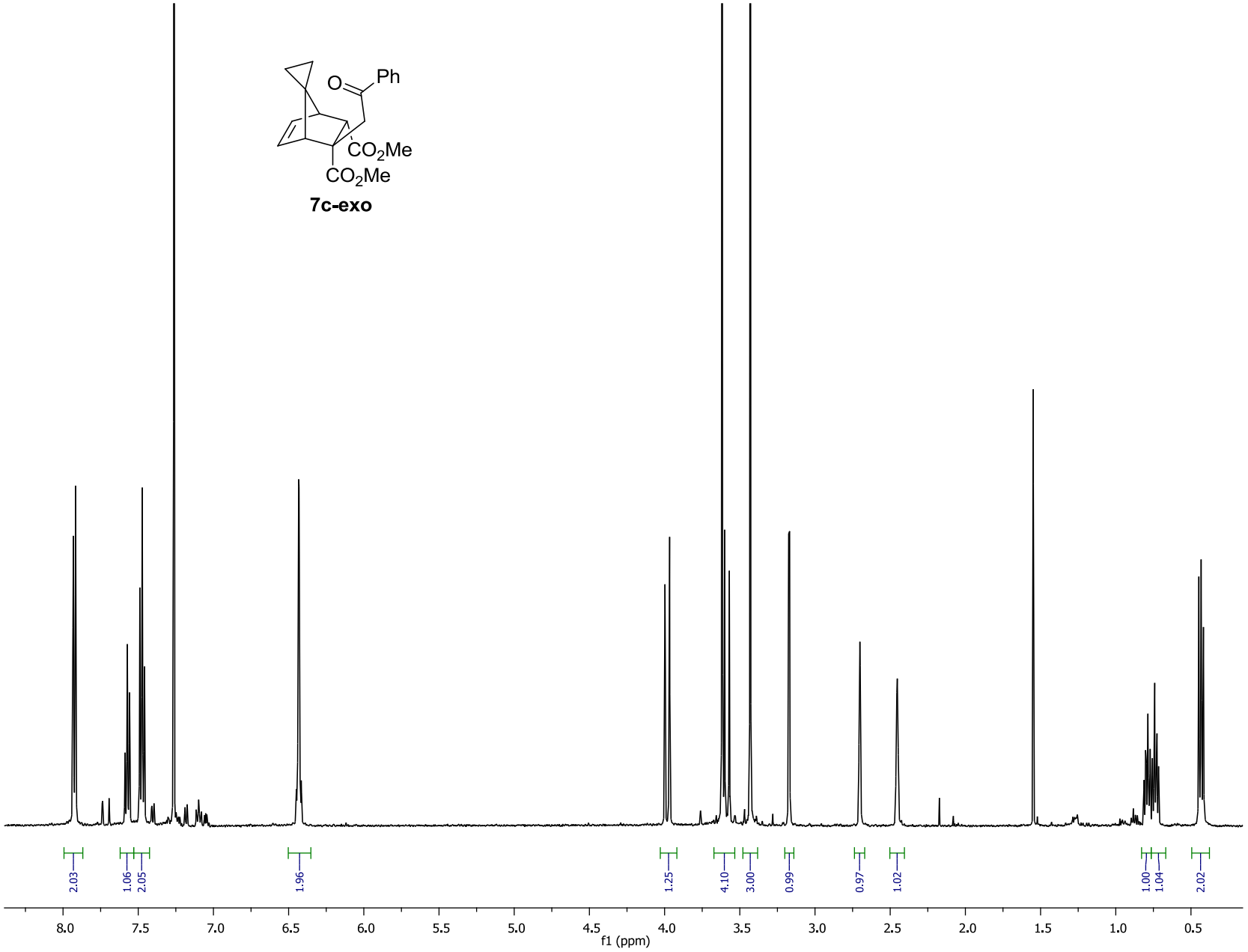
^{1}H NMR (500 MHz, $CDCl_3$):



^{13}C NMR (500 MHz, $CDCl_3$):

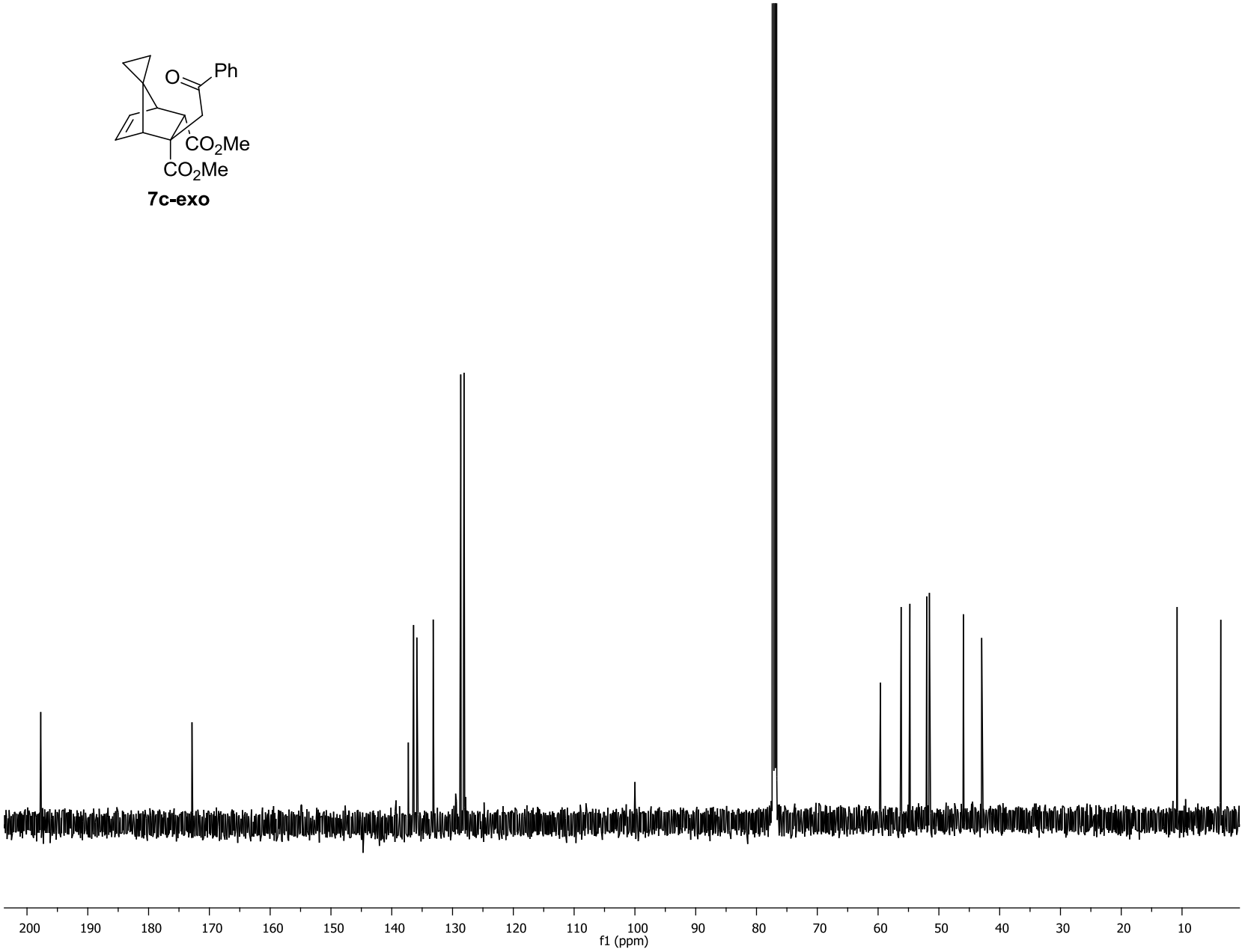


^{1}H NMR (500 MHz, $CDCl_3$):

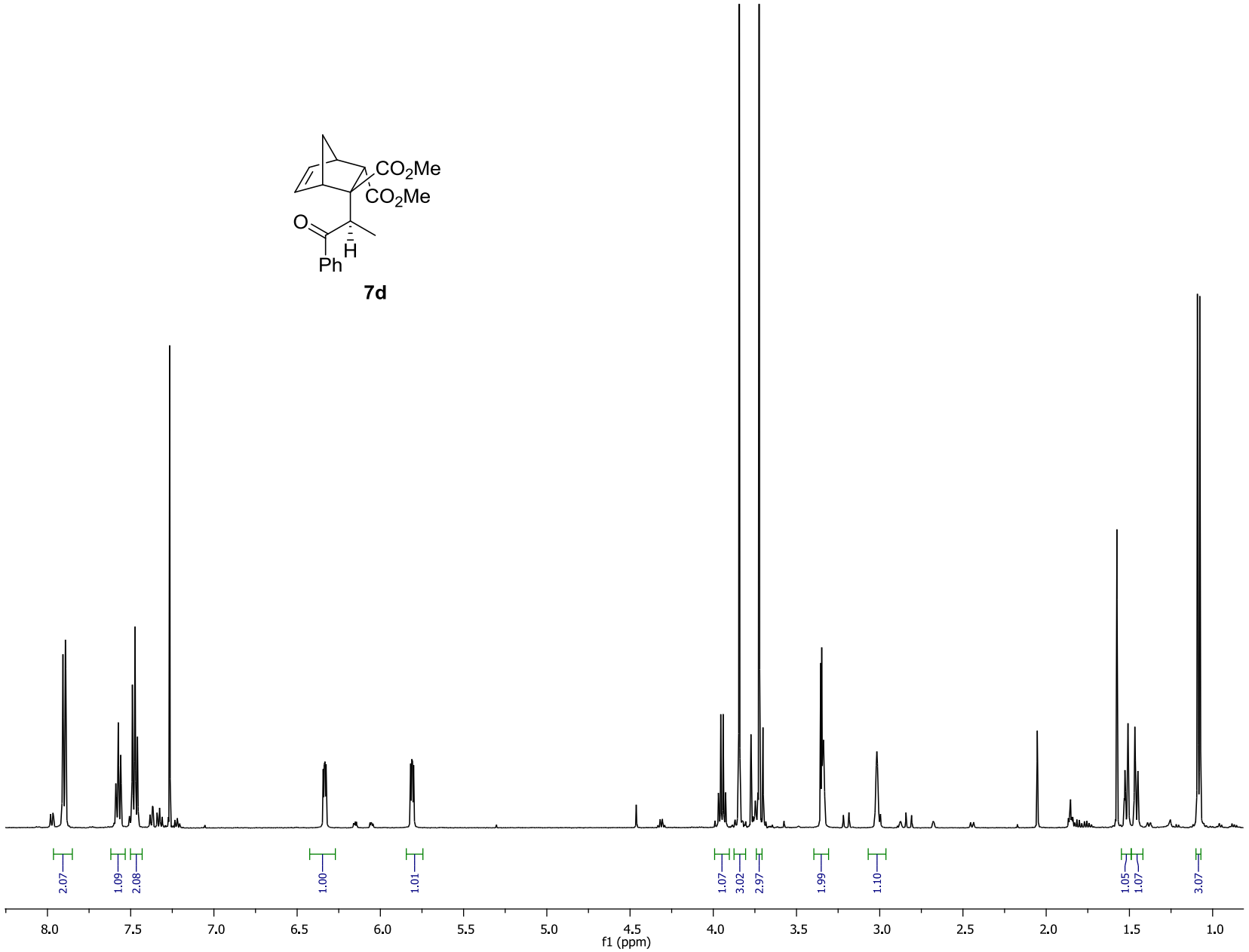


^{13}C NMR (500 MHz, $CDCl_3$):

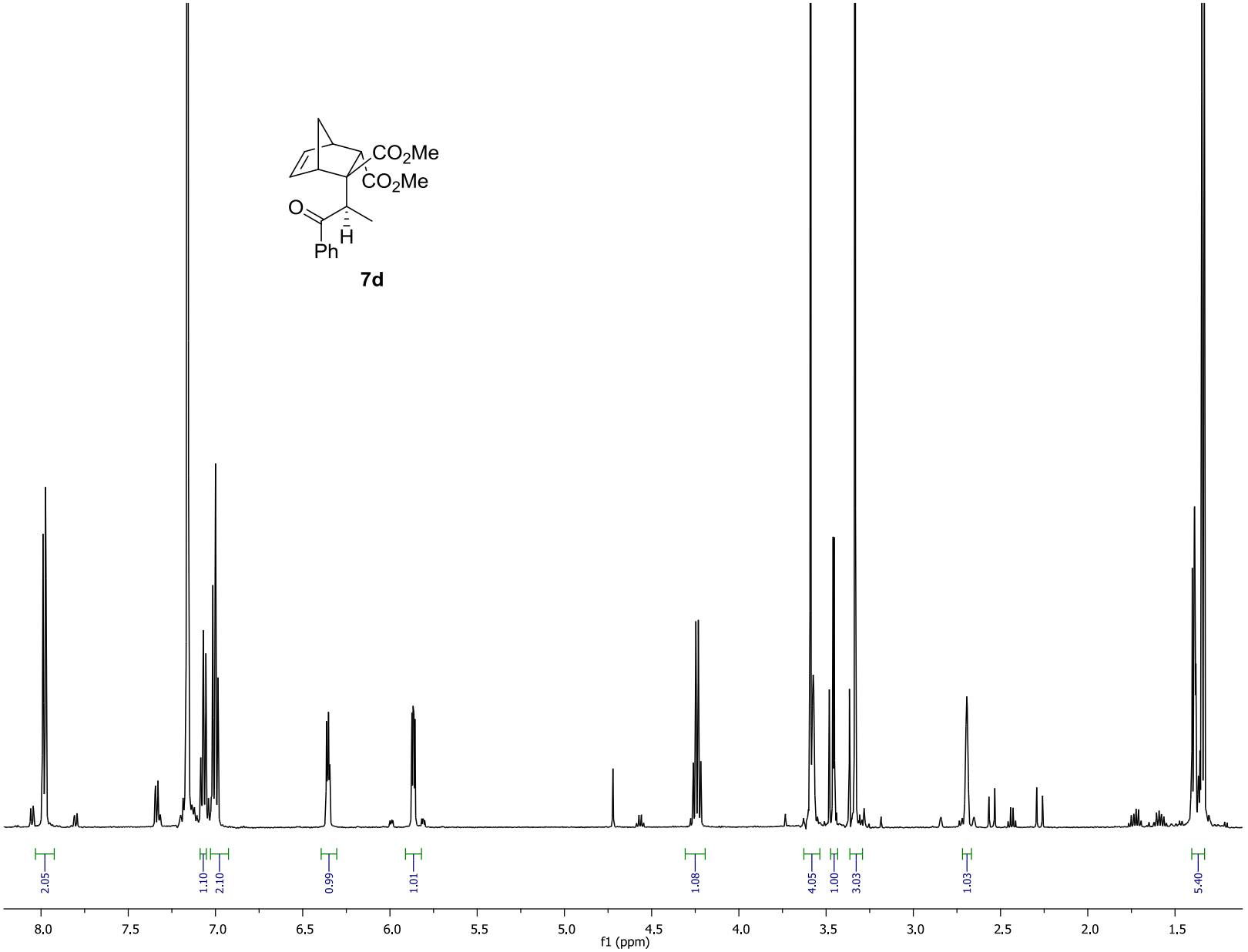
7c-exo



^{1}H NMR (500 MHz, $CDCl_3$):

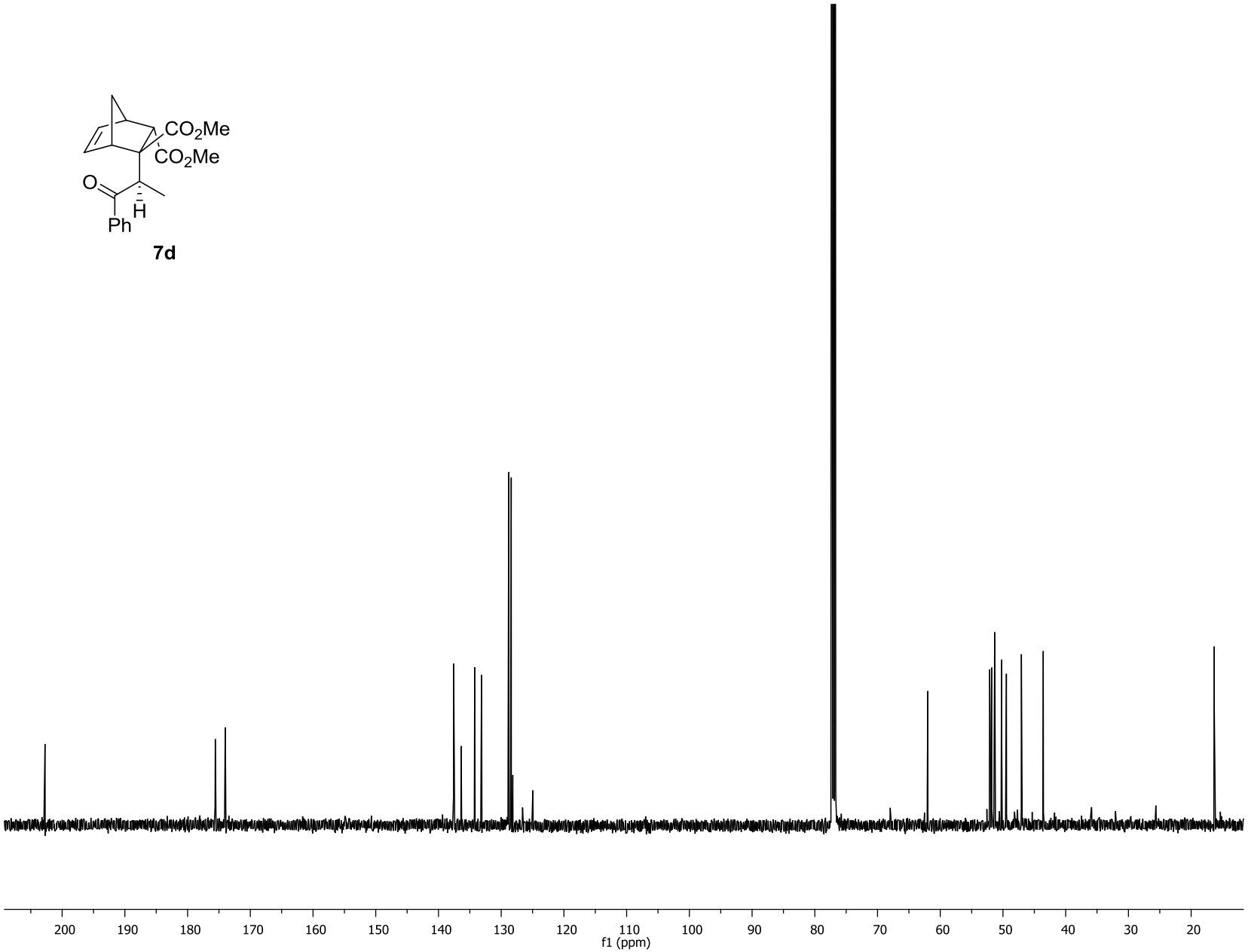


^{1}H NMR (500 MHz, C_6D_6):

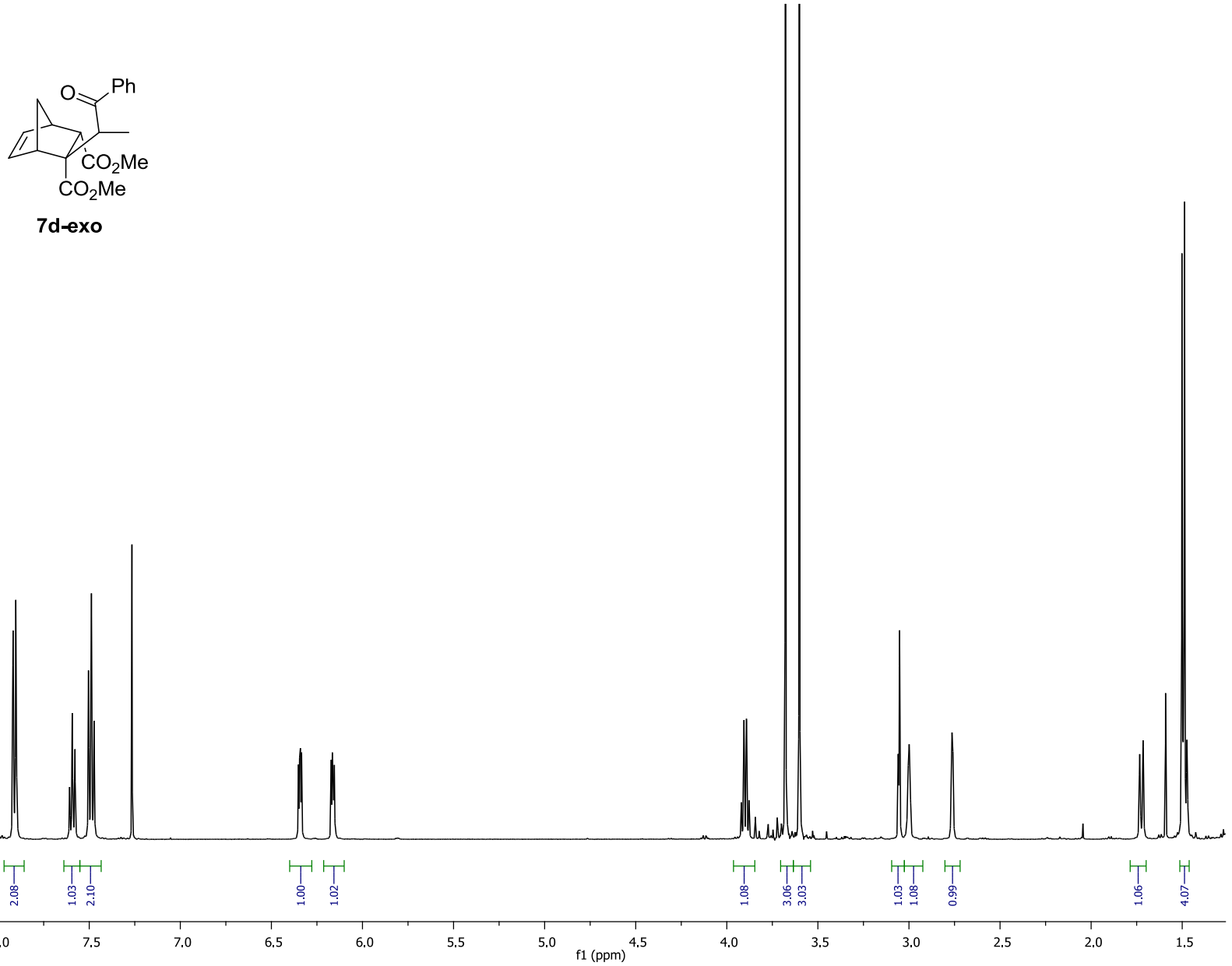


^{13}C NMR (500 MHz, $CDCl_3$):

7d

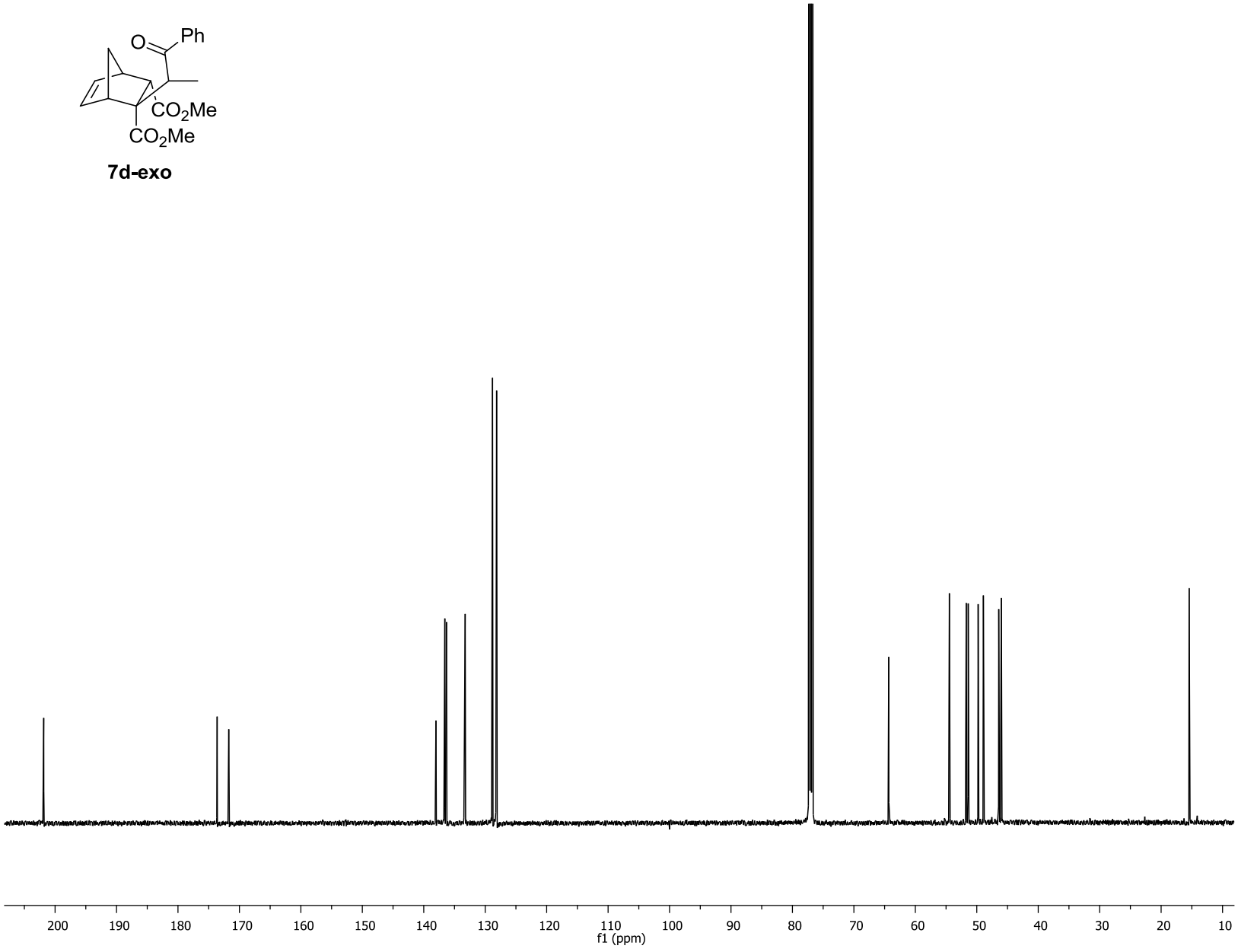


^{1}H NMR (500 MHz, $CDCl_3$):

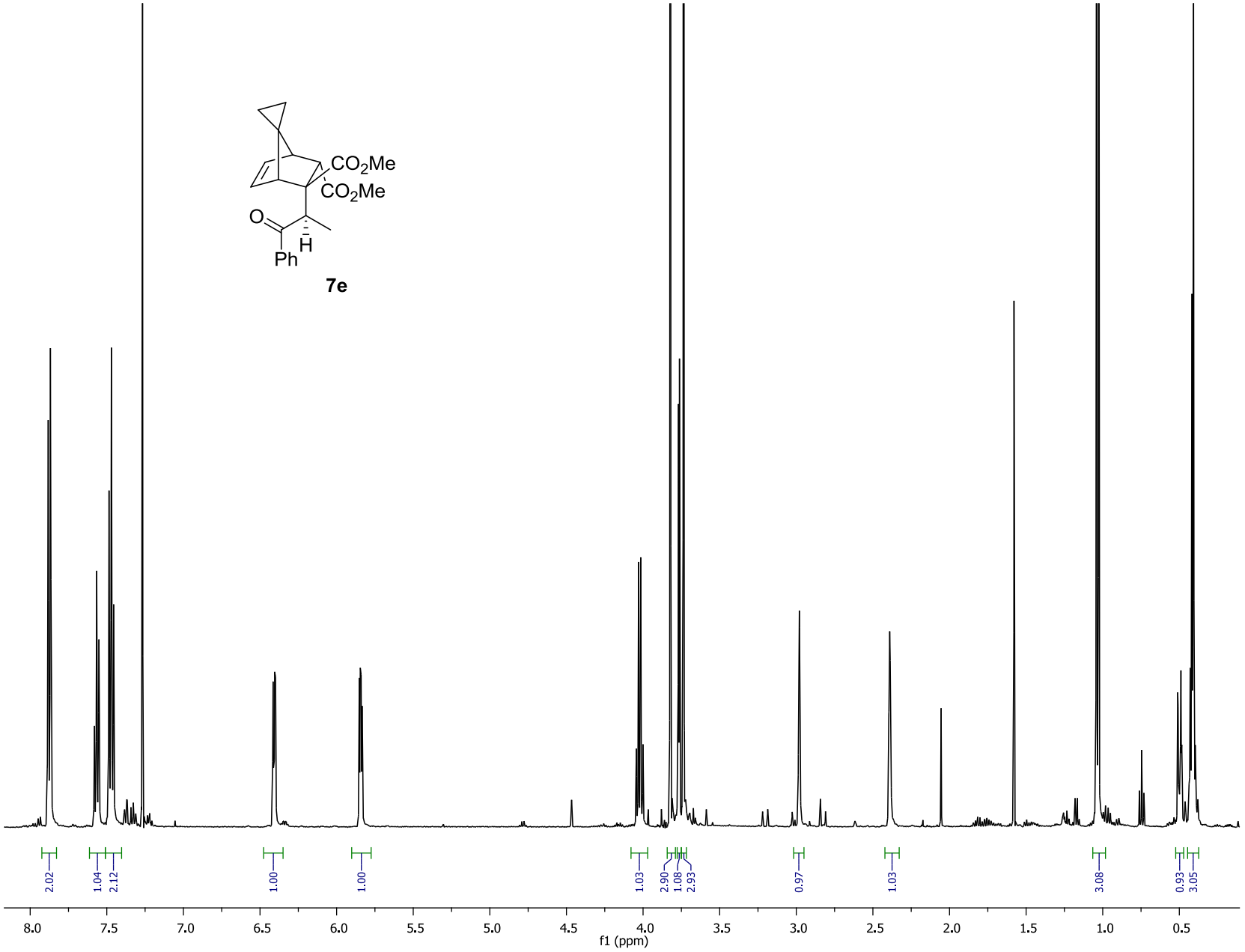


^{13}C NMR (500 MHz, $CDCl_3$):

7d-exo

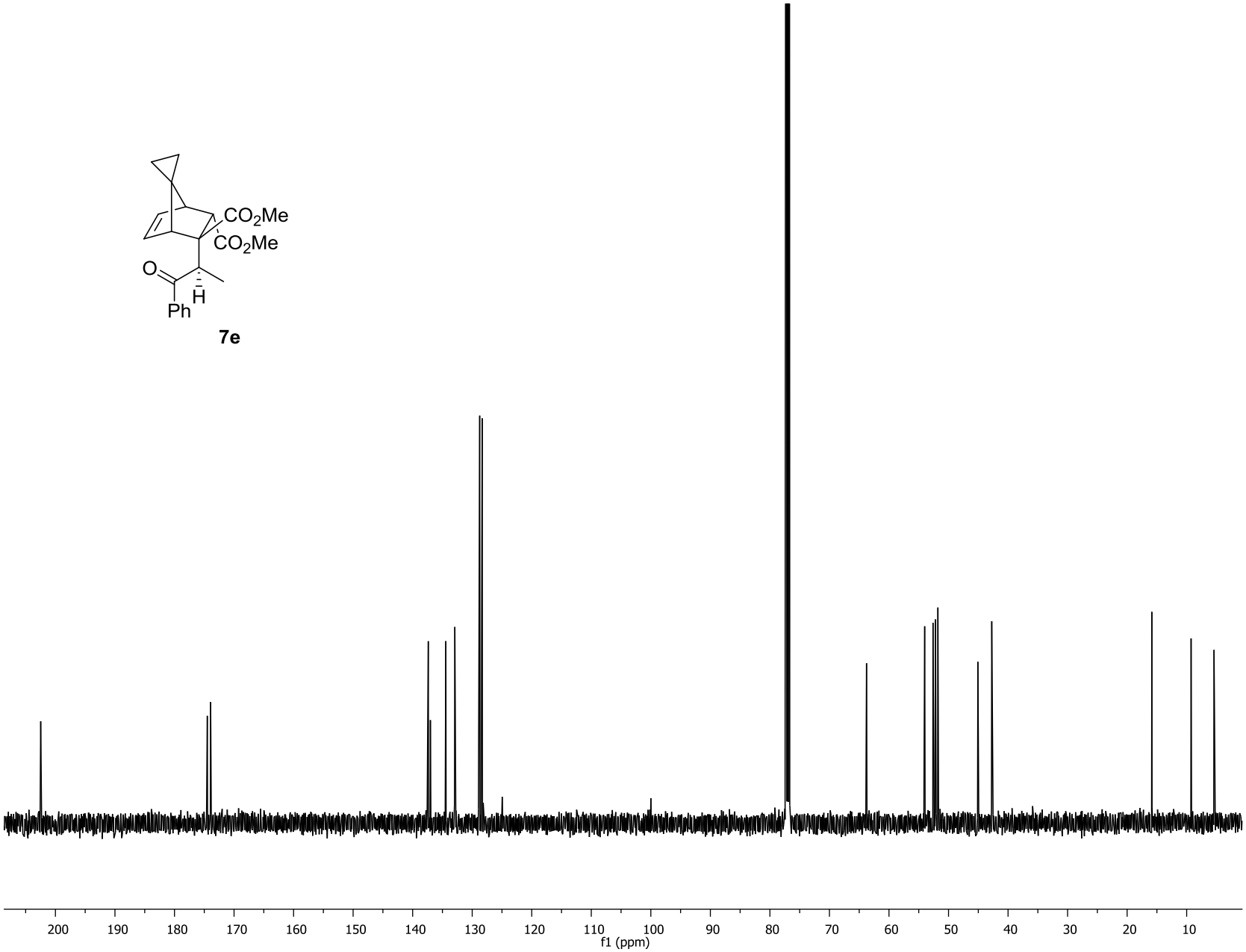


^{1}H NMR (500 MHz, $CDCl_3$):

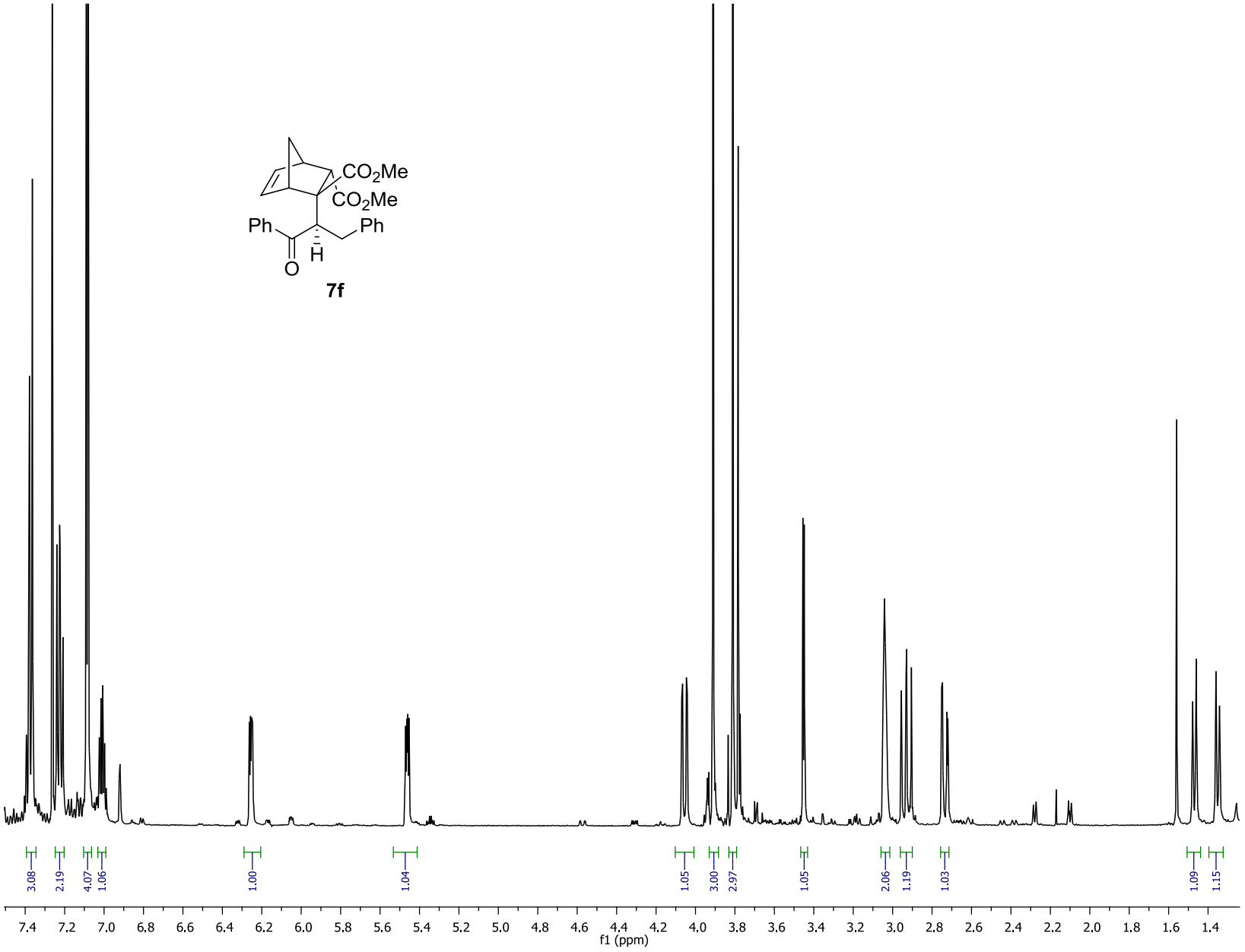


^{13}C NMR (500 MHz, $CDCl_3$):

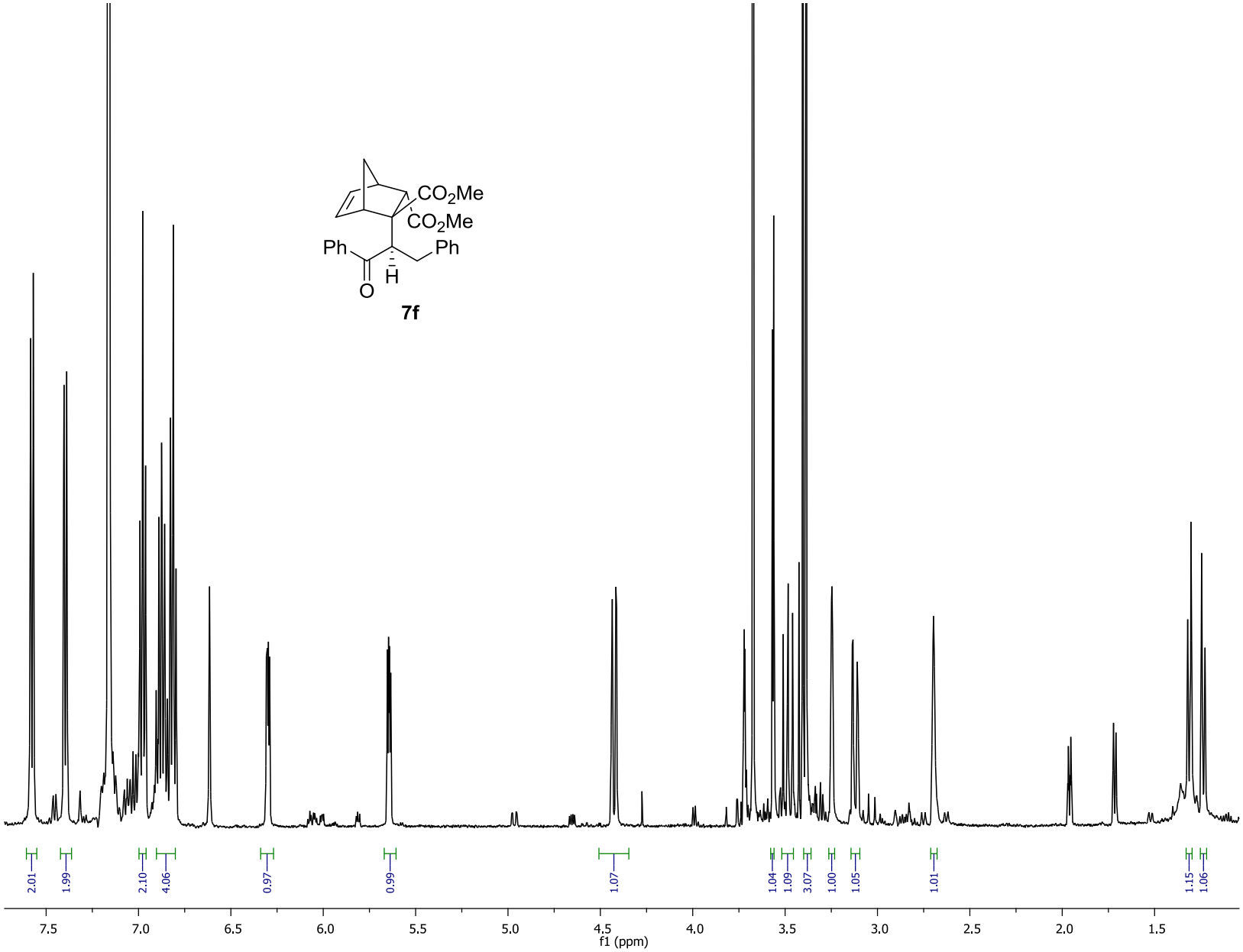
7e



^{1}H NMR (500 MHz, $CDCl_3$):

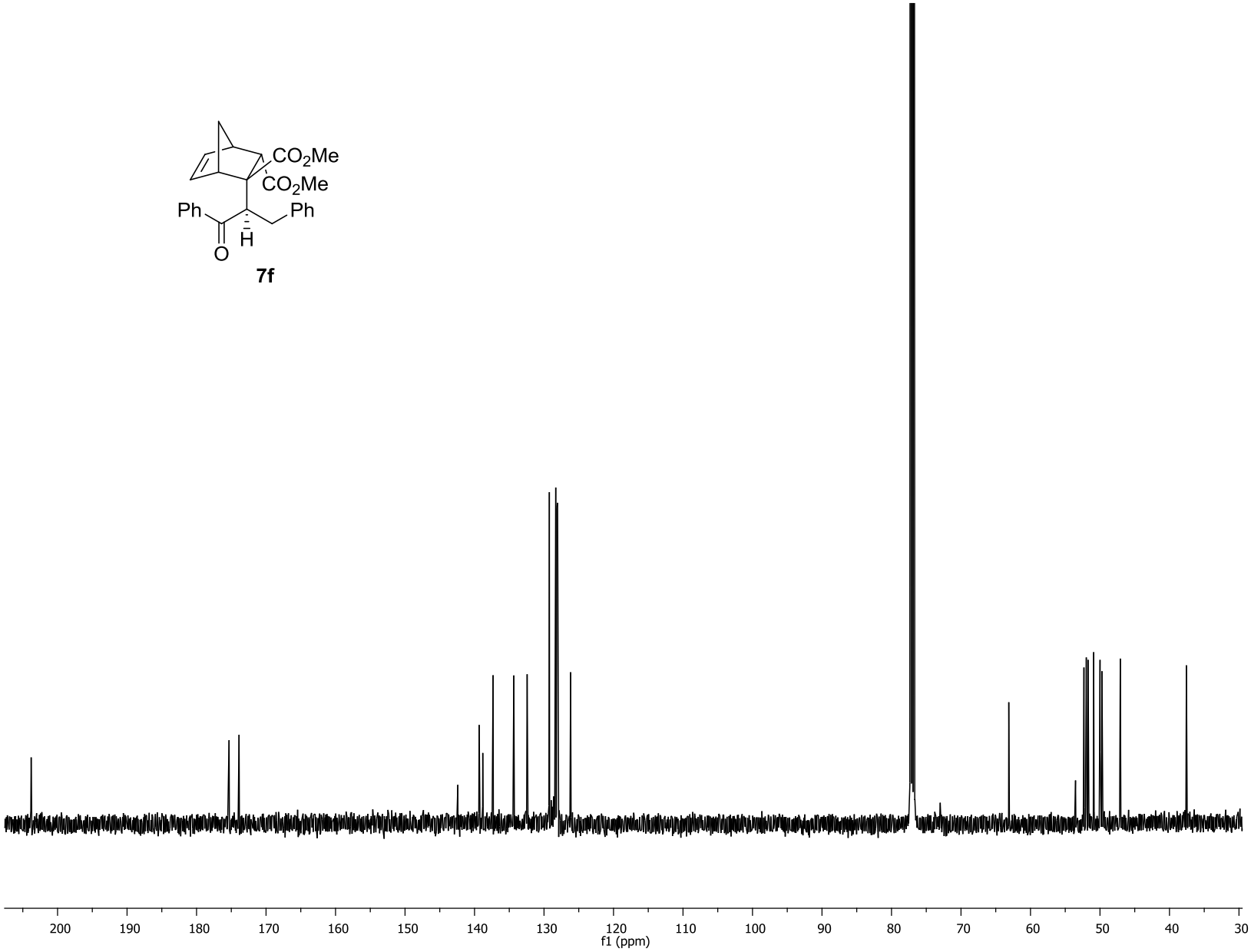


^{1}H NMR (500 MHz, C_6D_6):

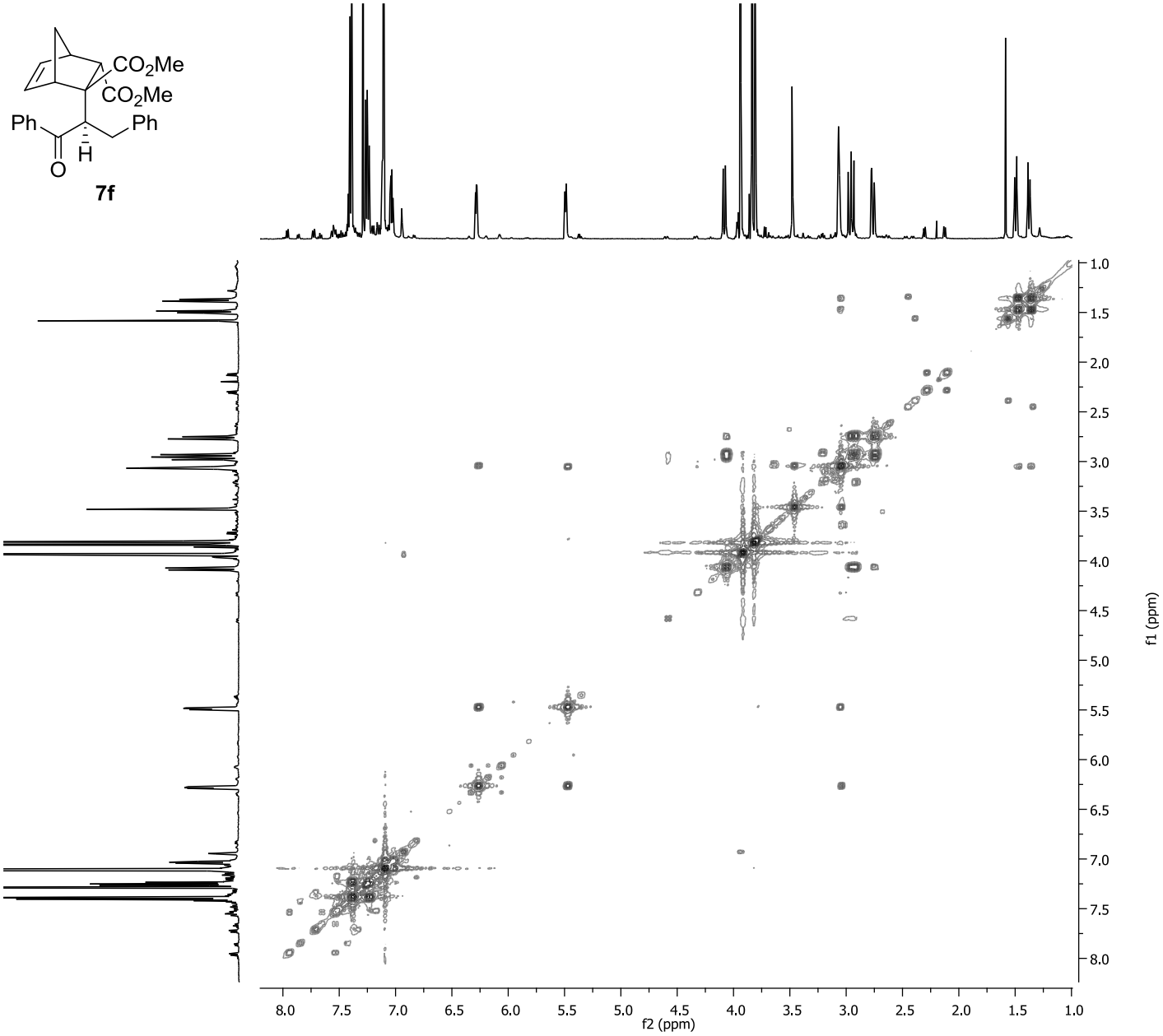


^{13}C NMR (500 MHz, $CDCl_3$):

7f



COSY (500 MHz, $CDCl_3$):



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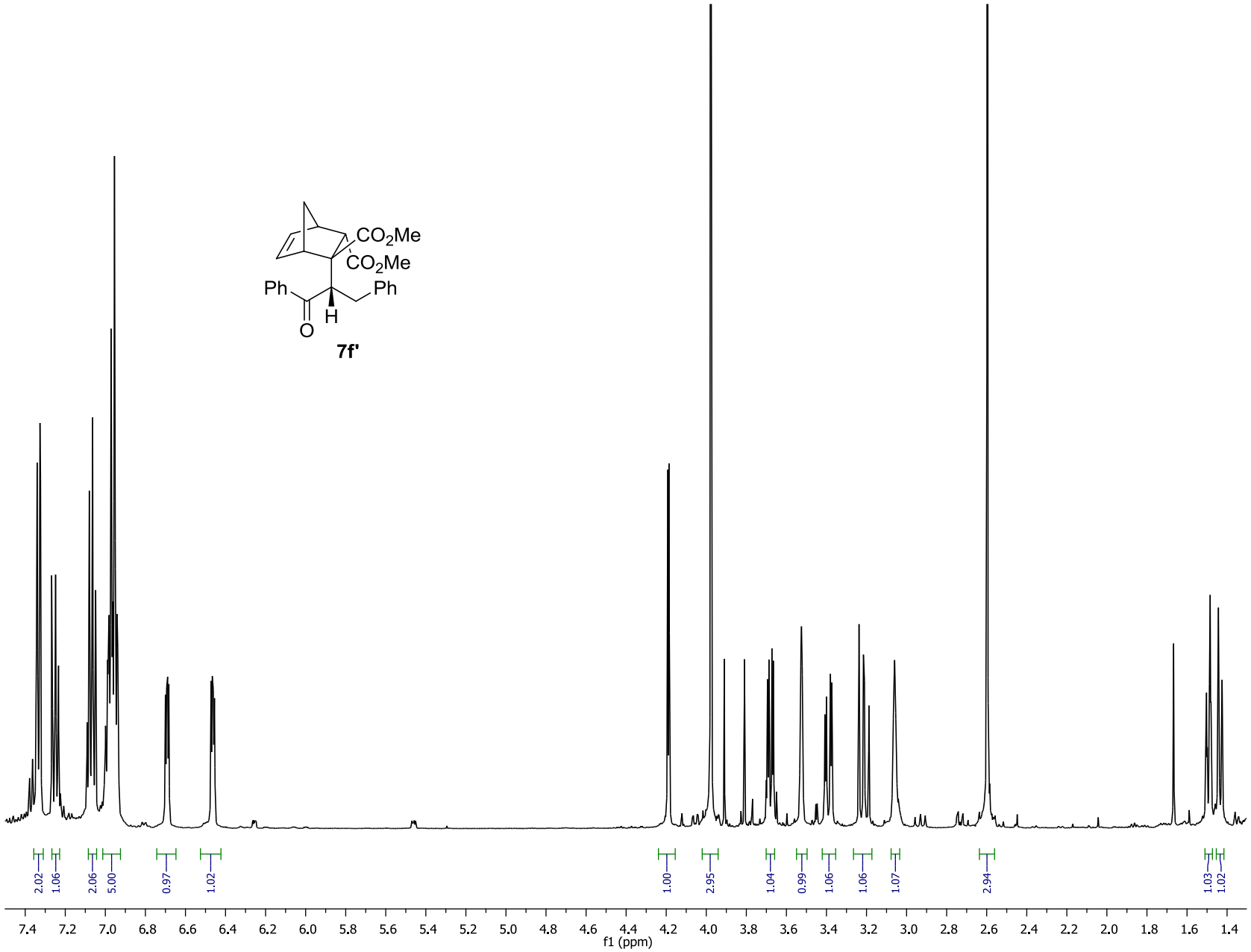
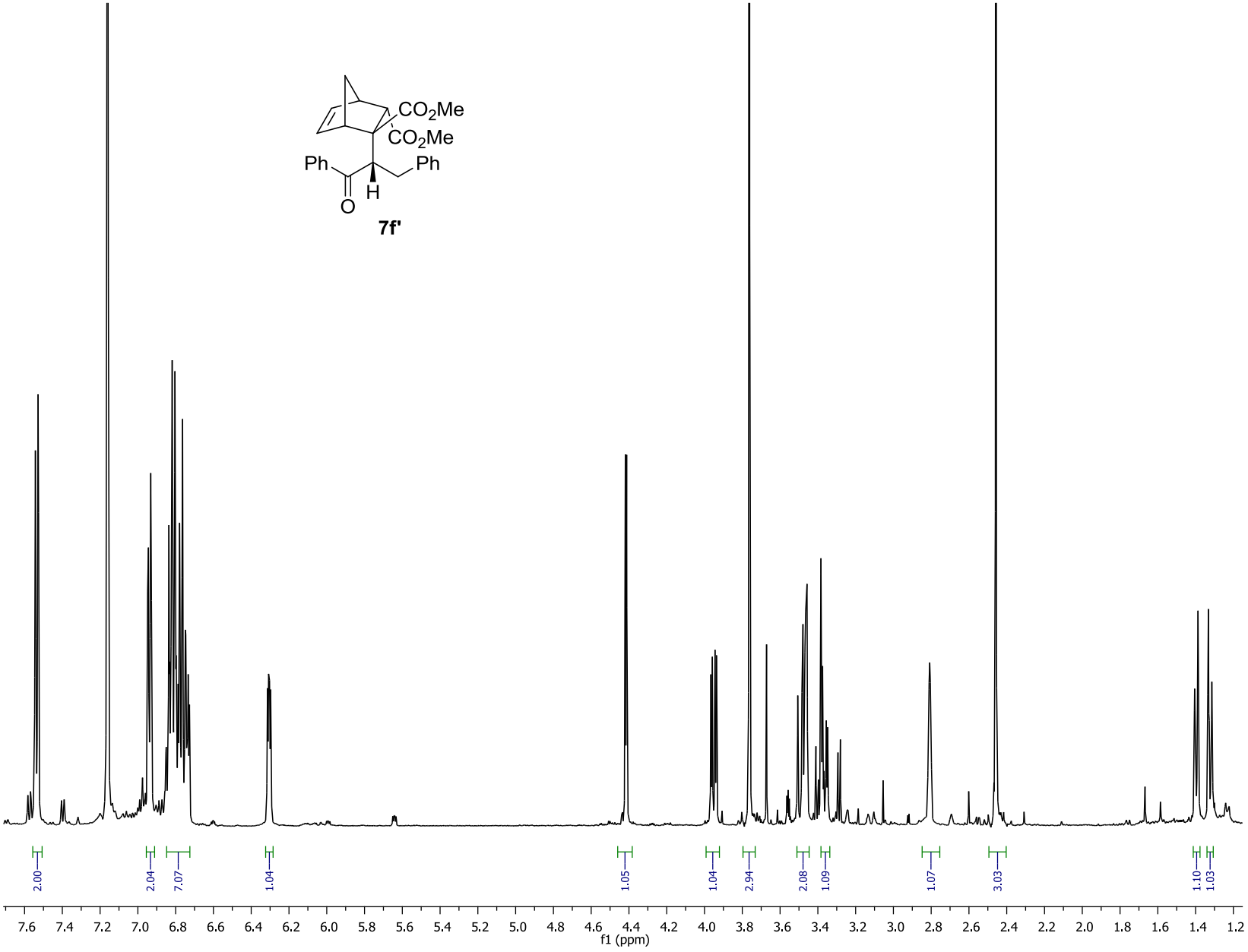
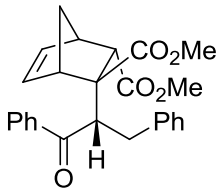


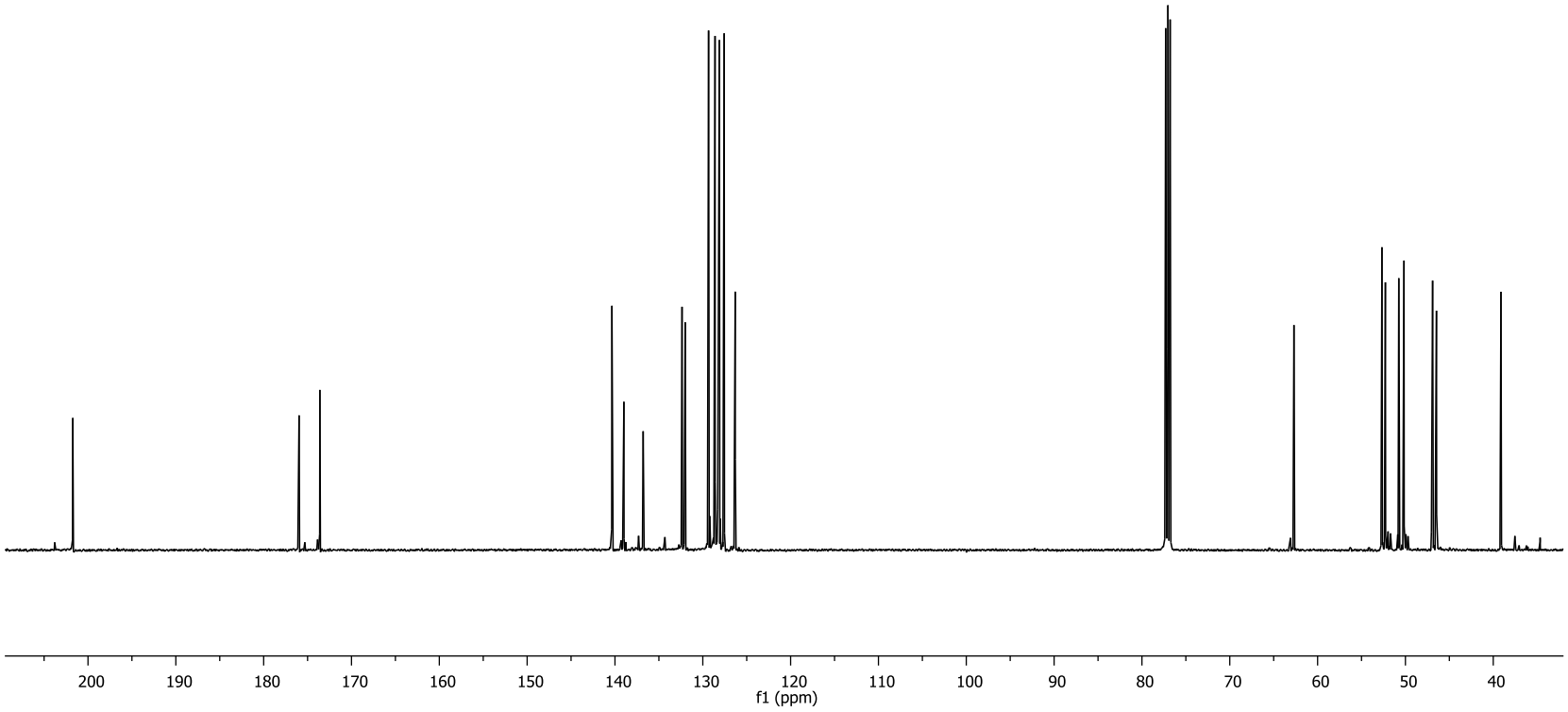
^{1}H NMR (500 MHz, C_6D_6):



^{13}C NMR (500 MHz, $CDCl_3$):



7f'



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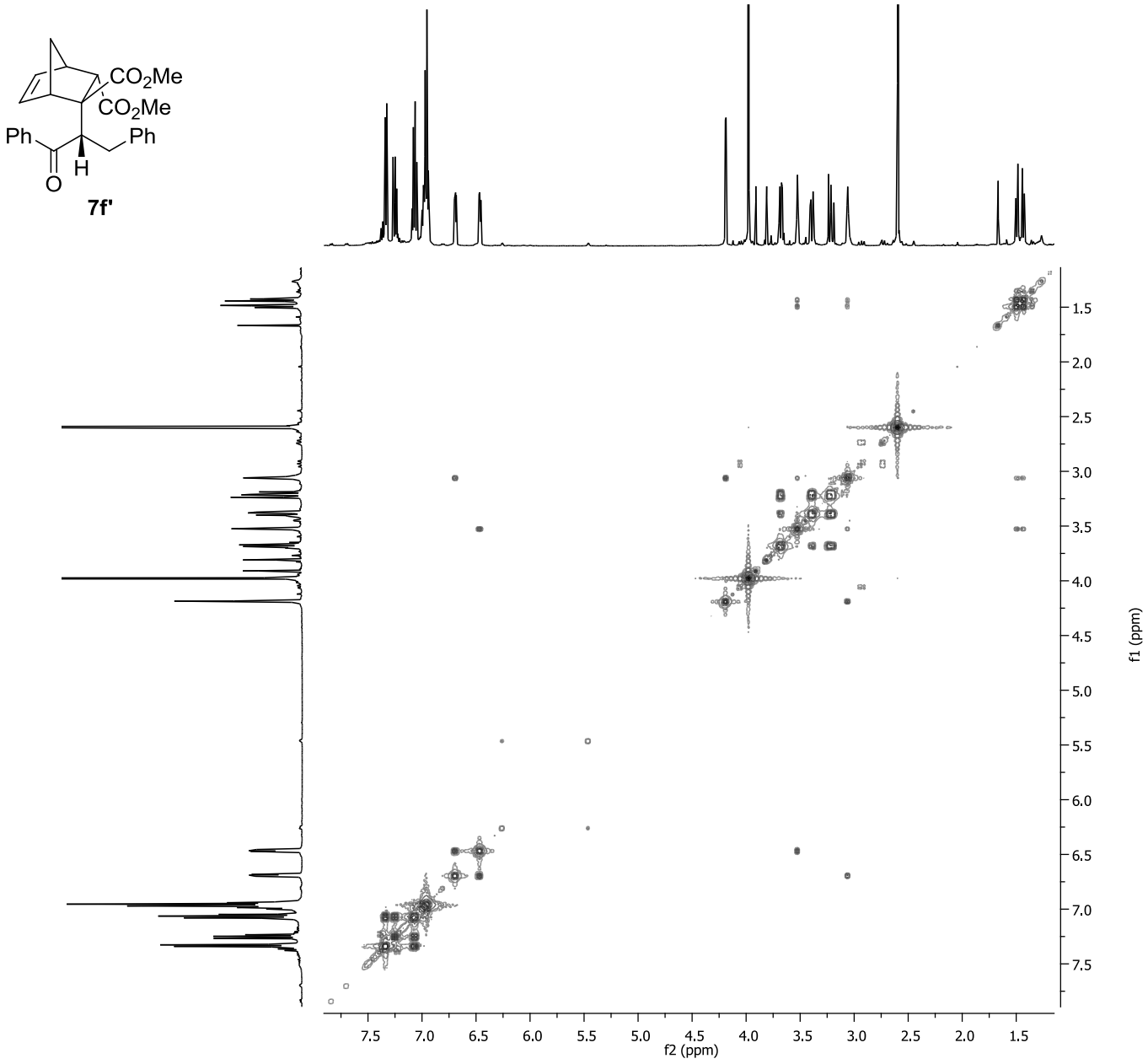
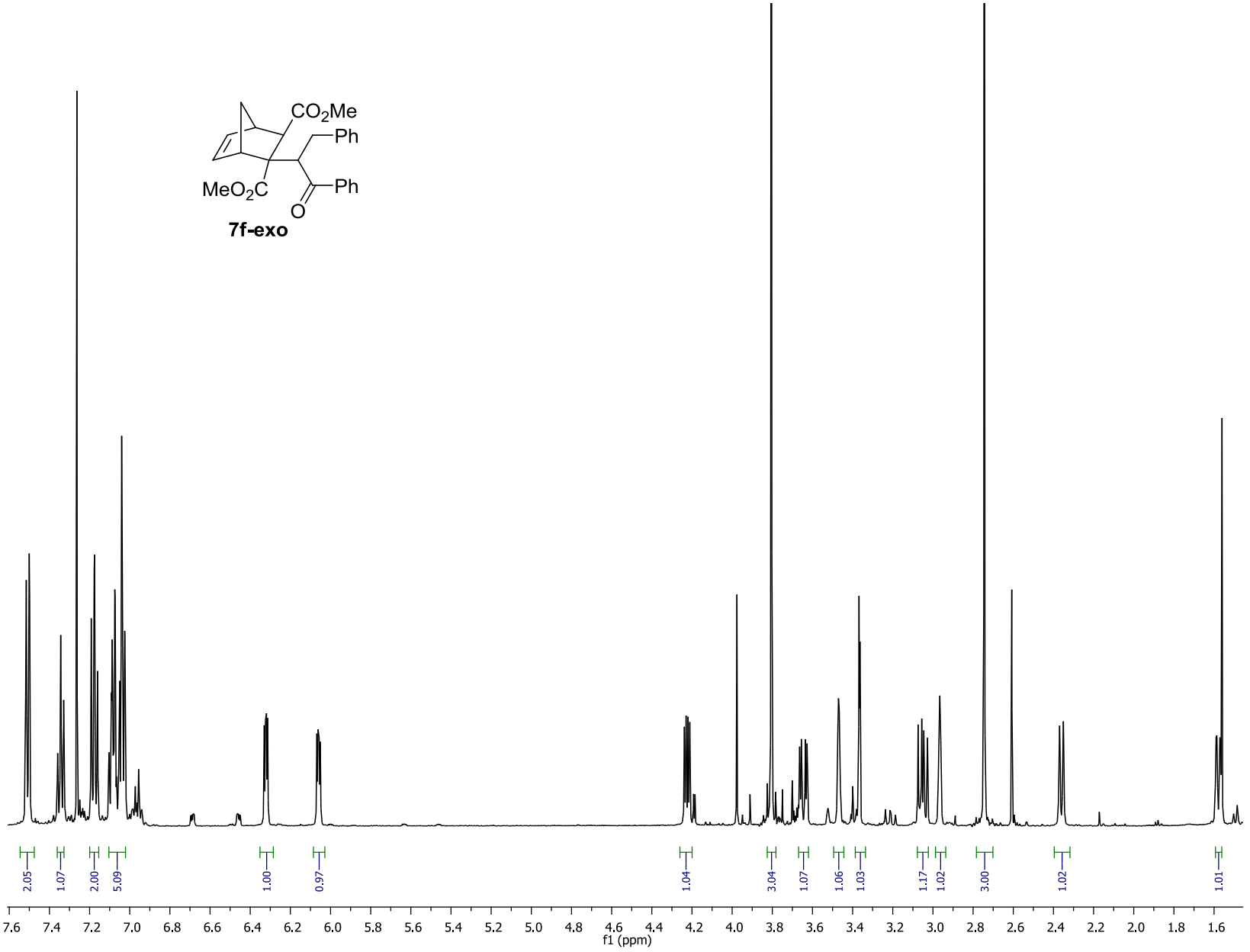
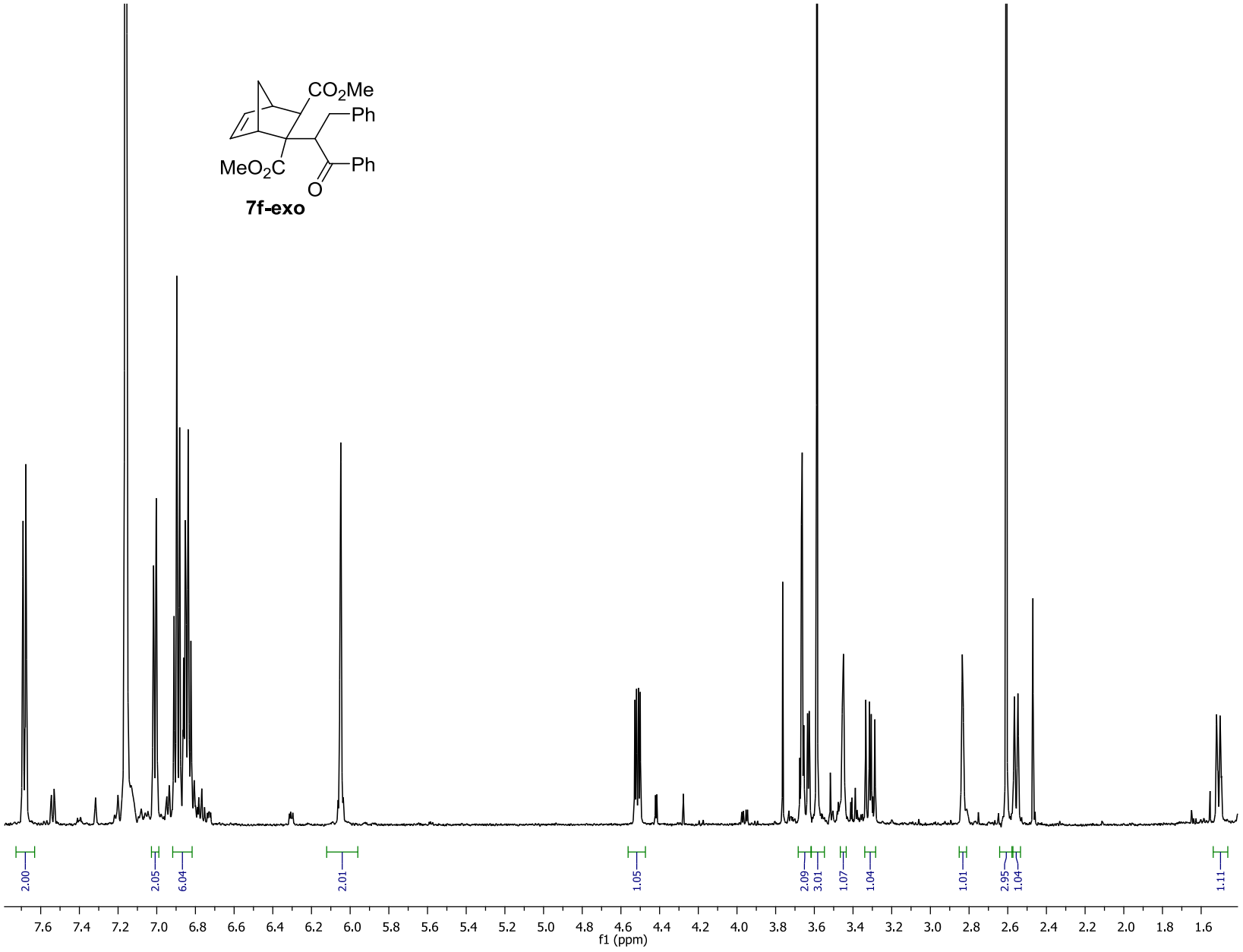


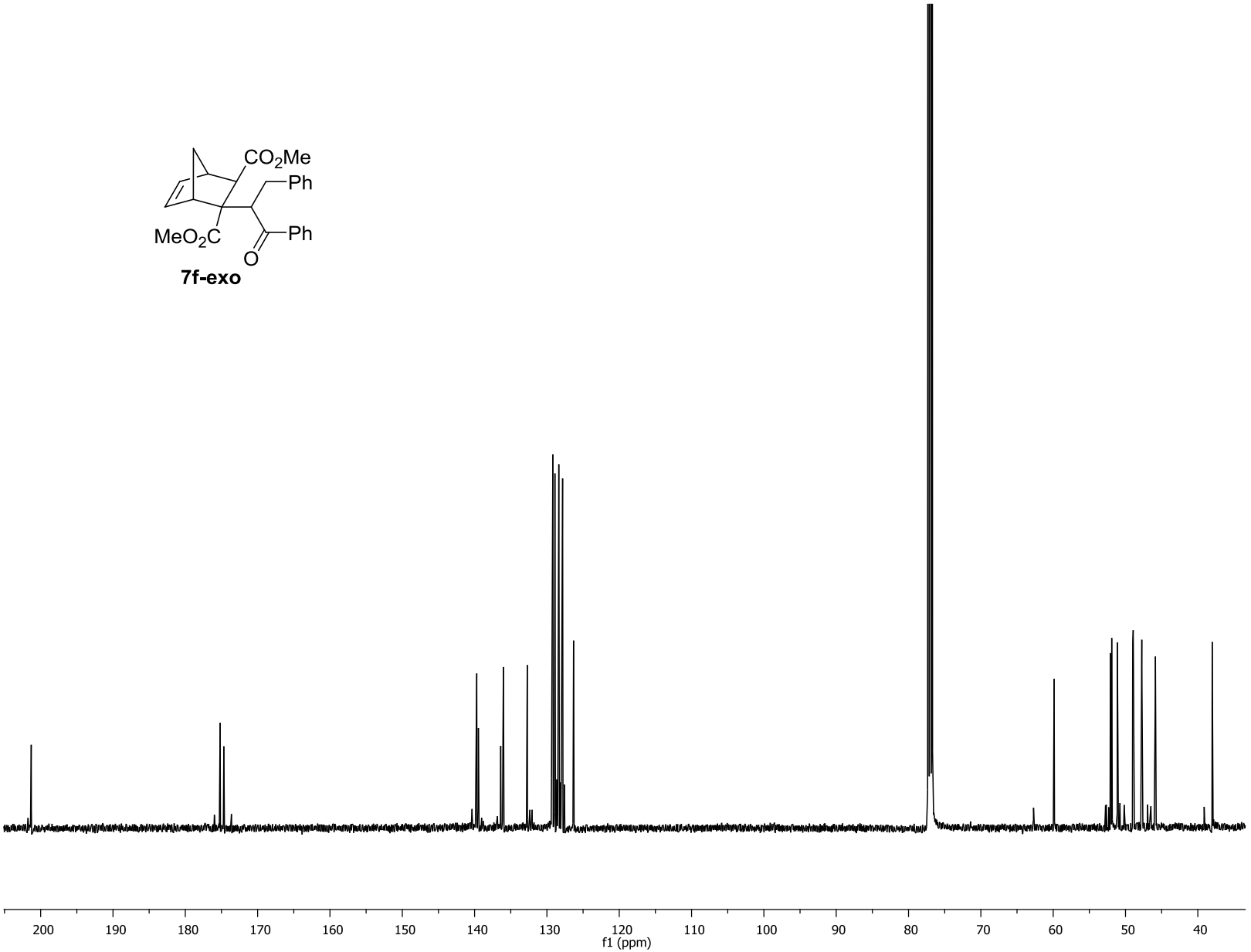
^{1}H NMR (500 MHz, $CDCl_3$):



^{1}H NMR (500 MHz, C_6D_6):



^{13}C NMR (500 MHz, $CDCl_3$):



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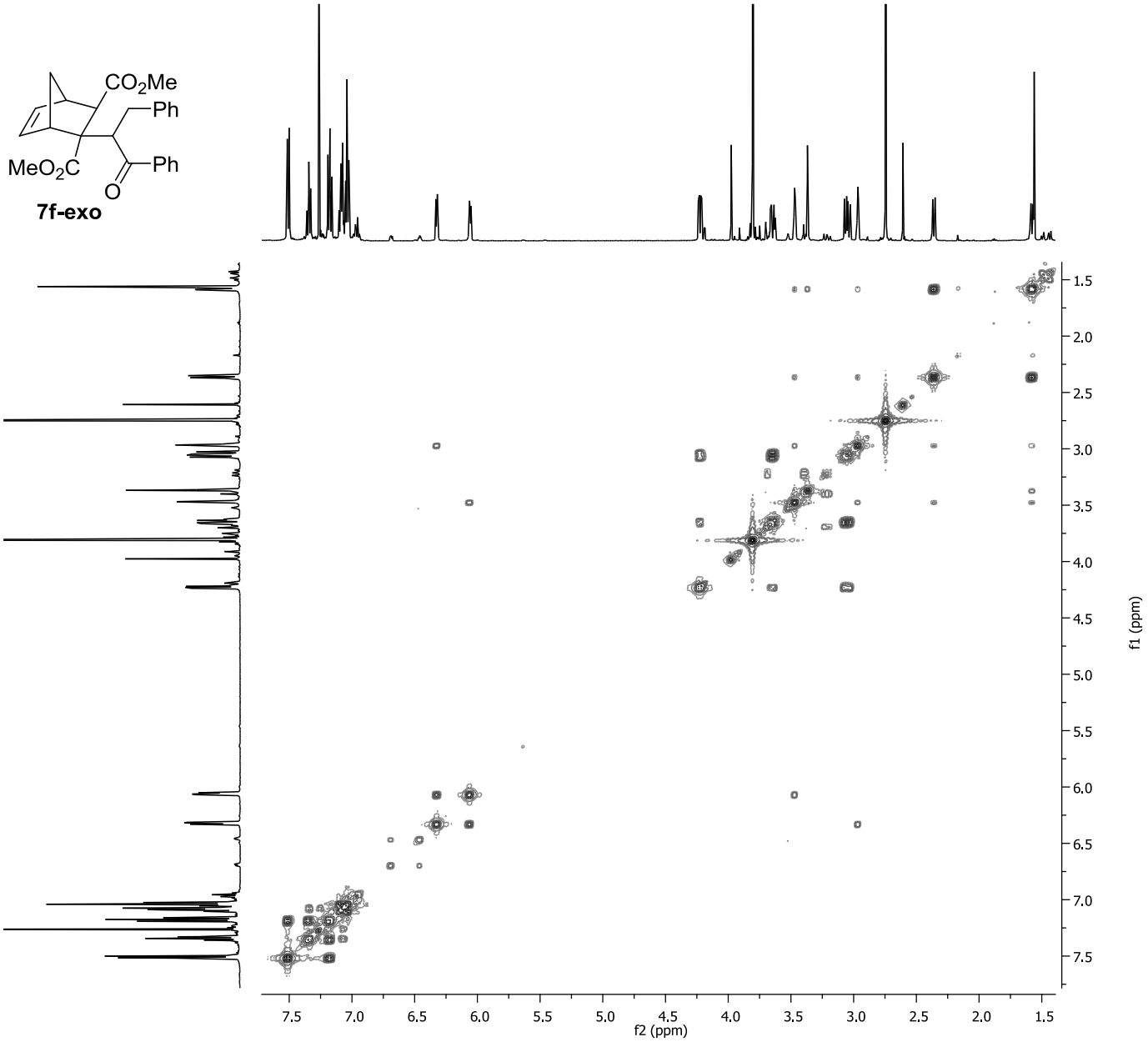

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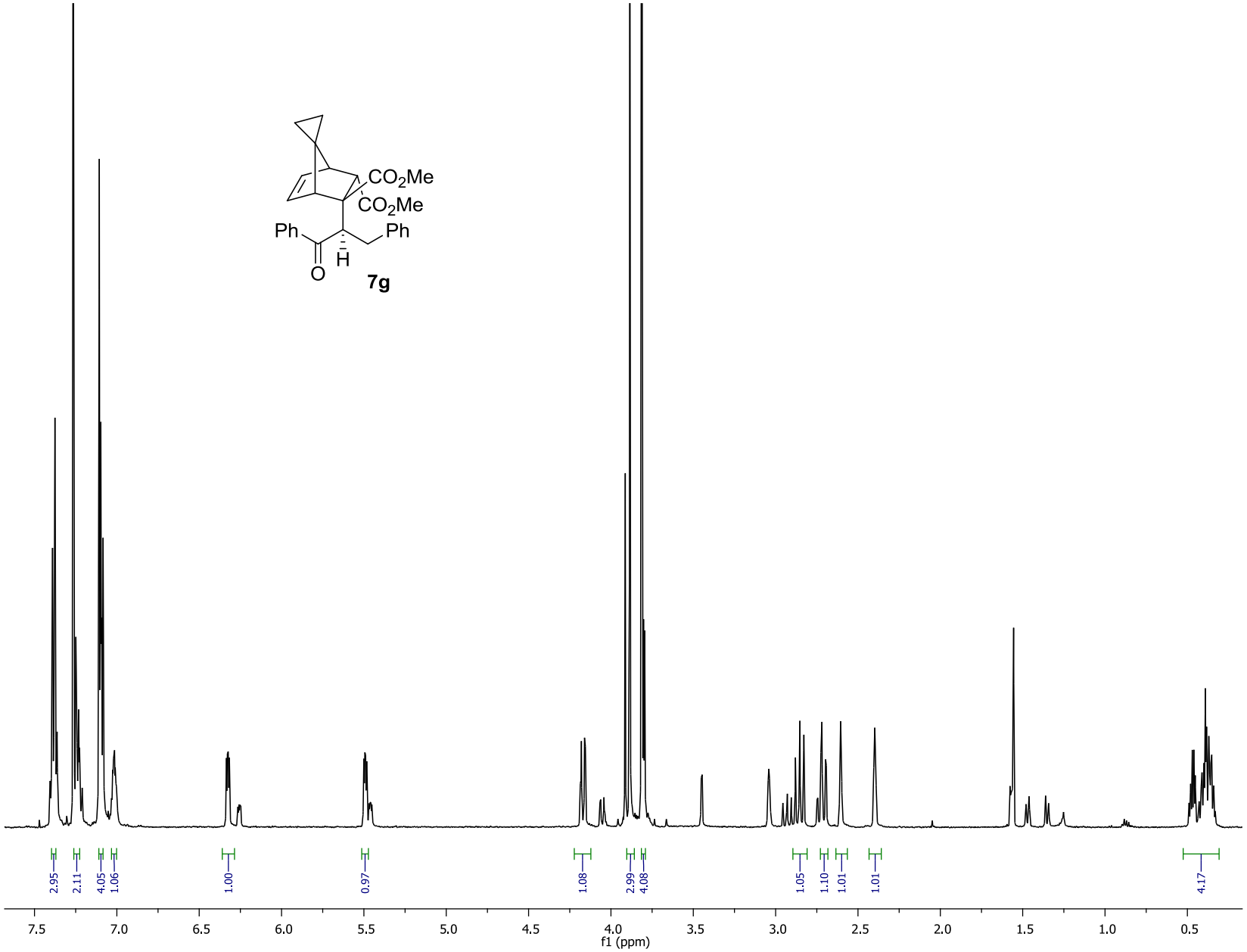

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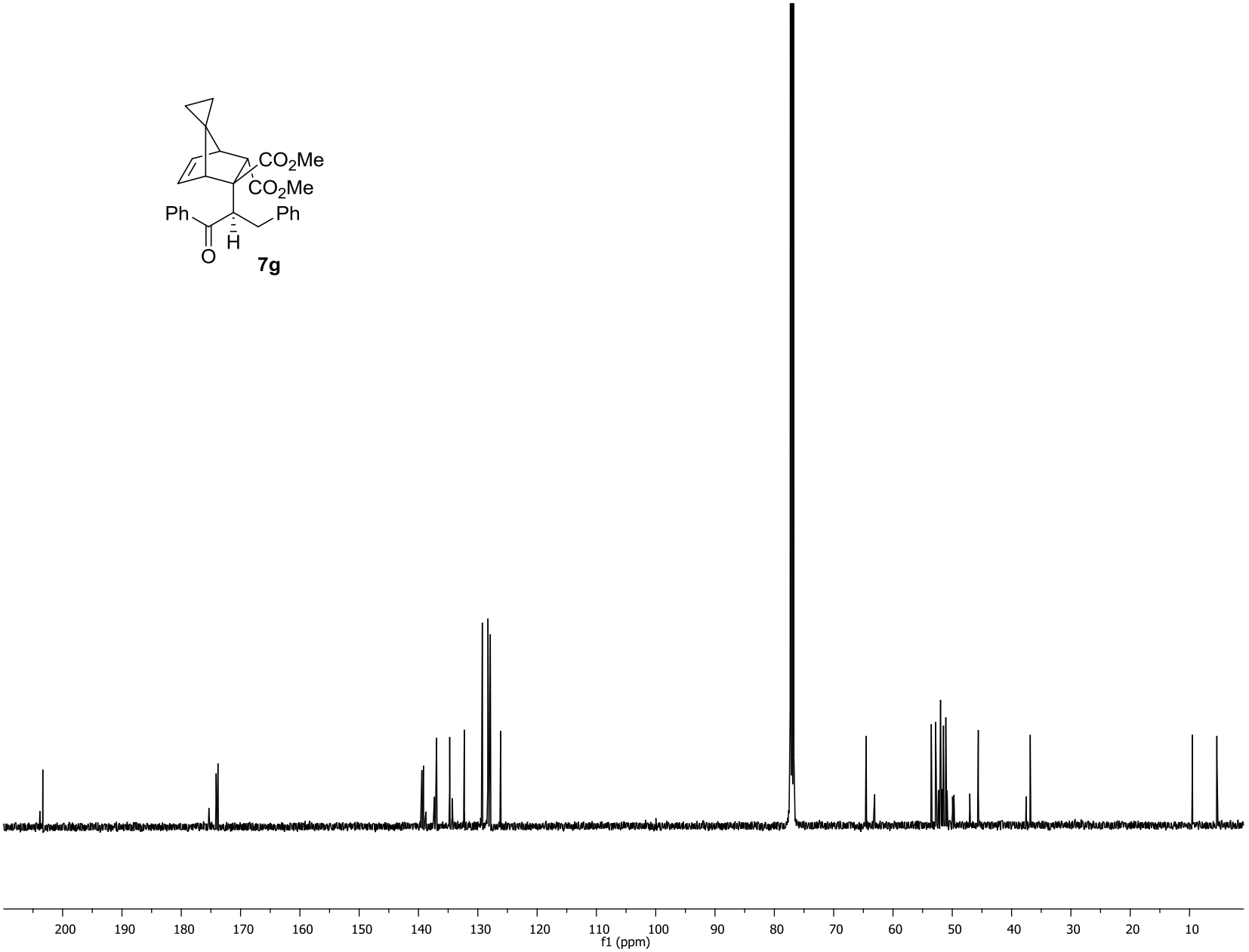
7g



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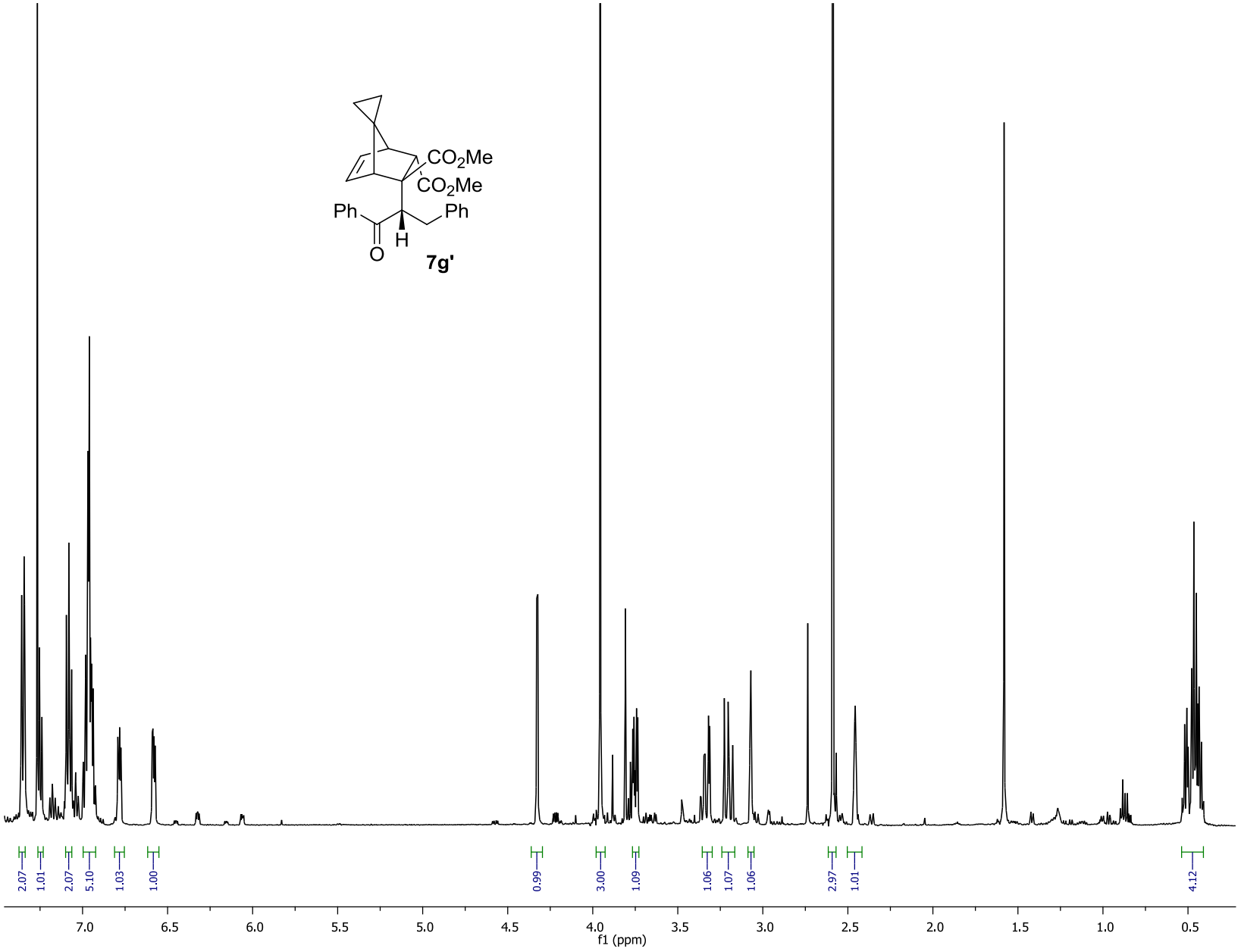

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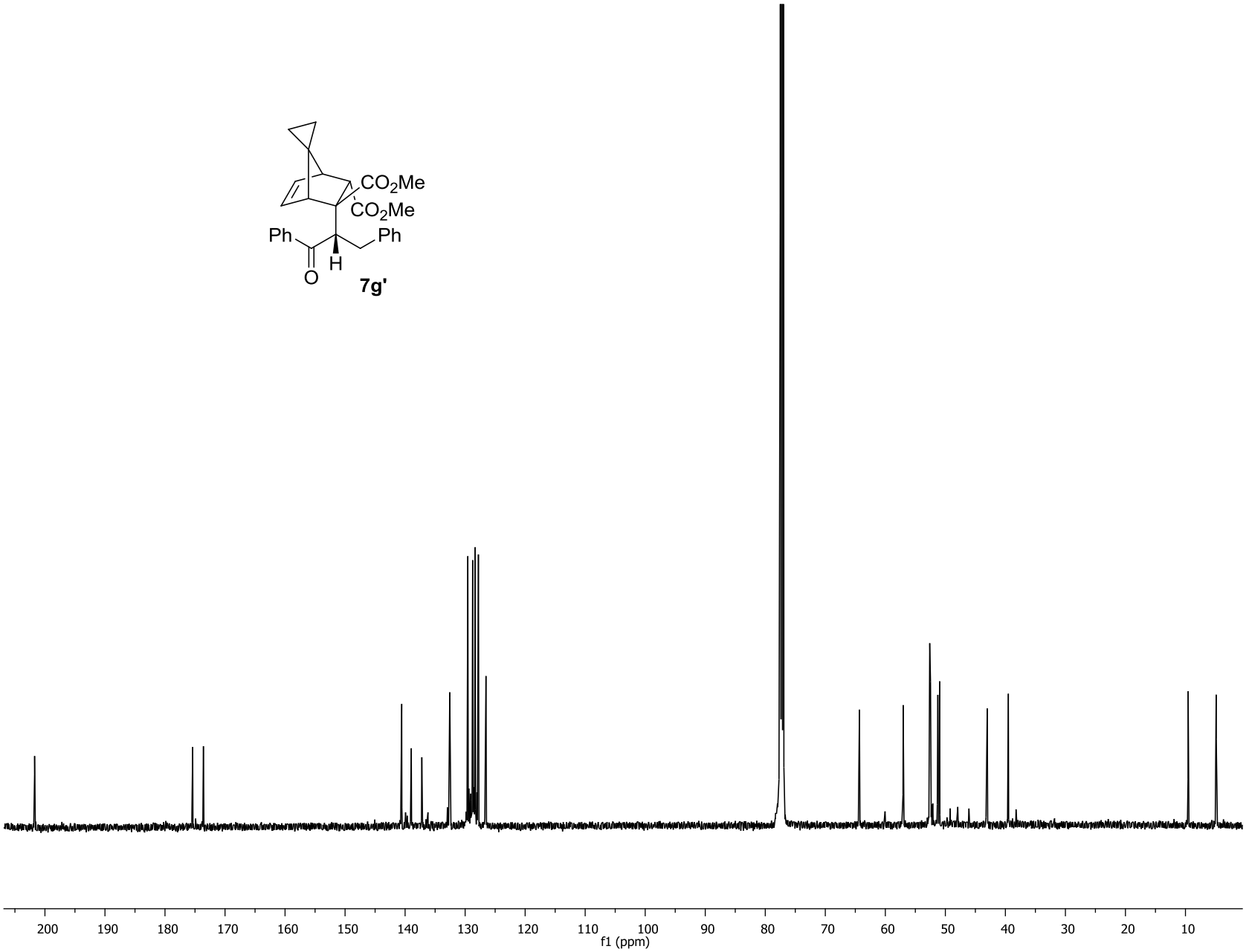

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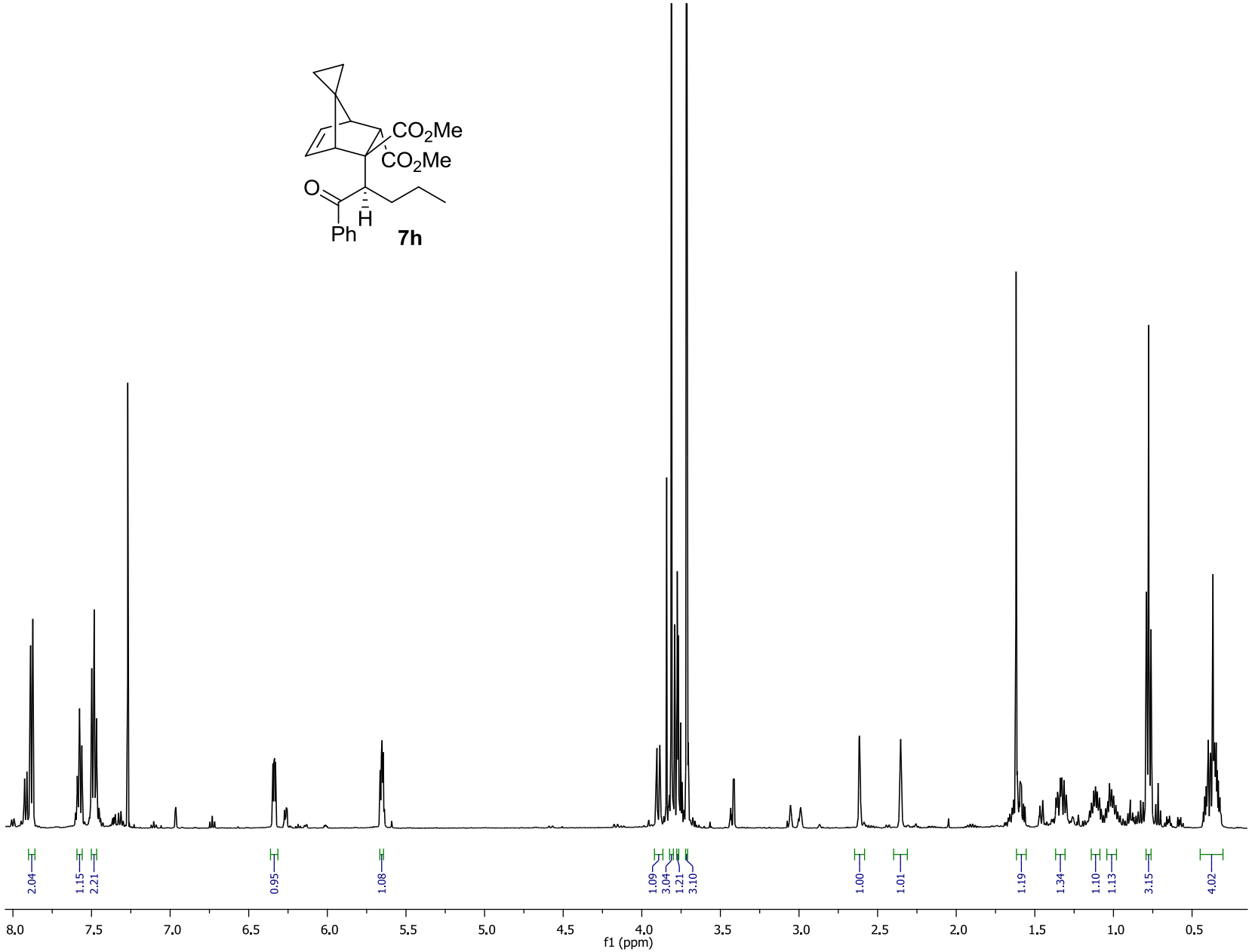
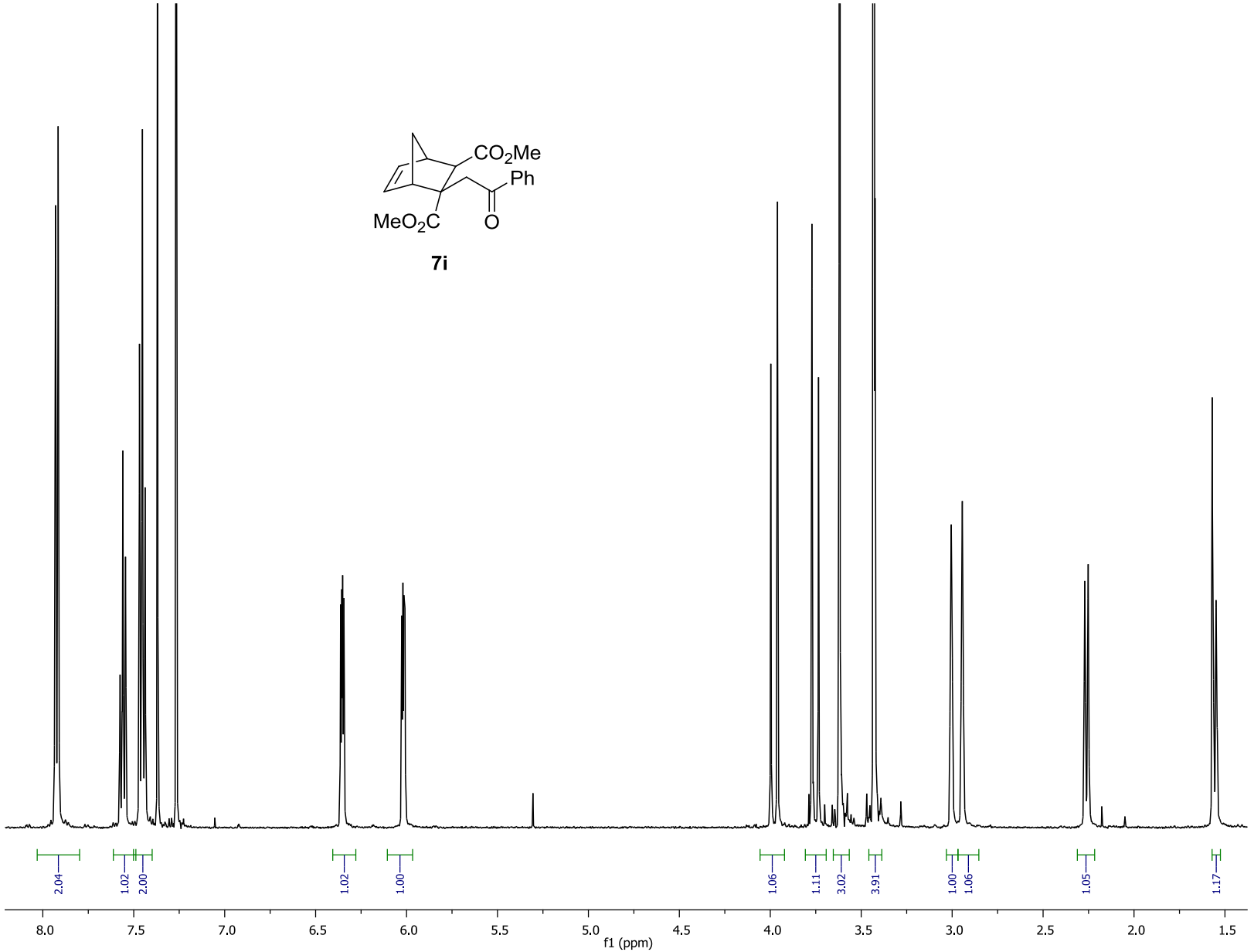
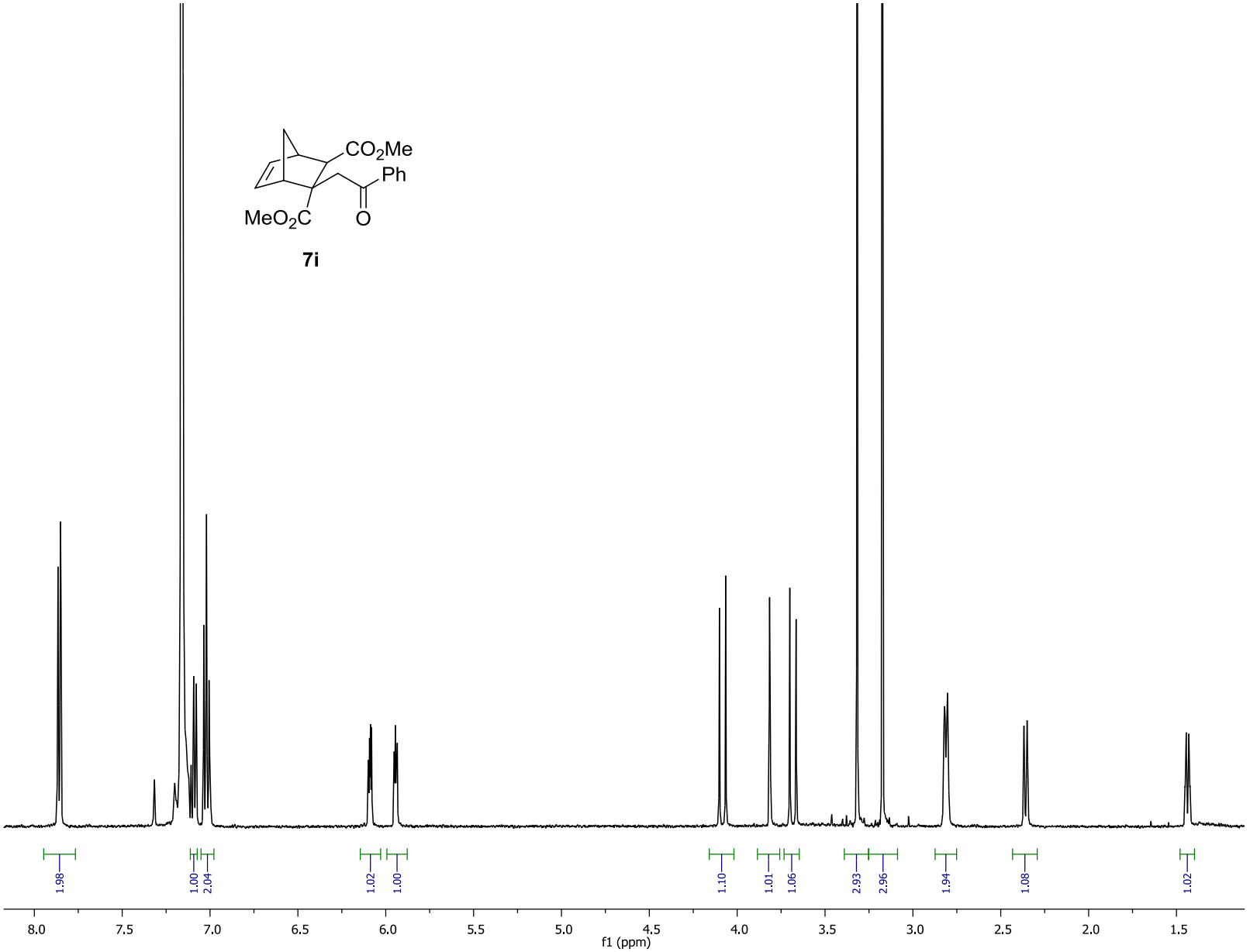


^{1}H NMR (500 MHz, $CDCl_3$):



^{1}H NMR (500 MHz, C_6D_6):



^{13}C NMR (500 MHz, $CDCl_3$):

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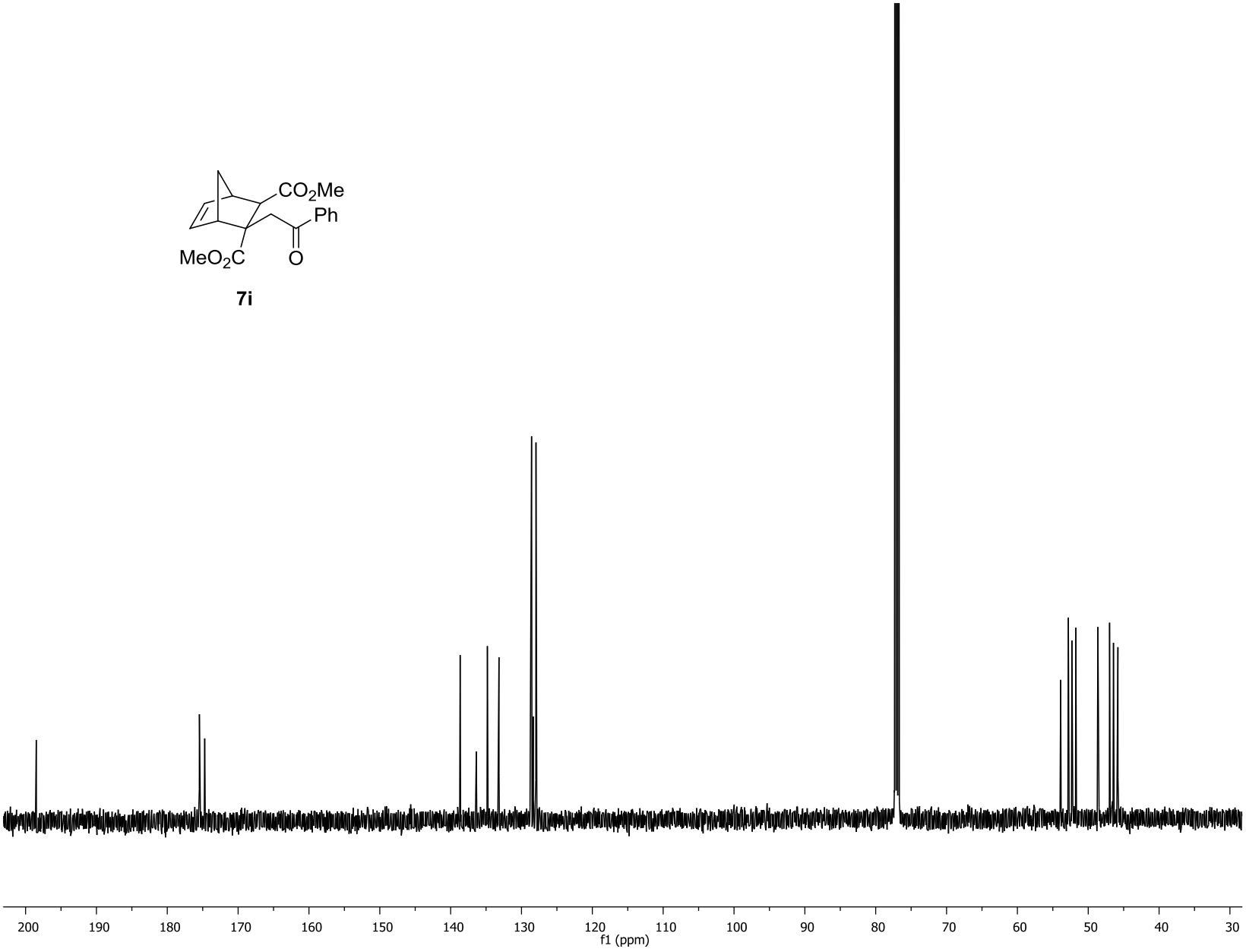

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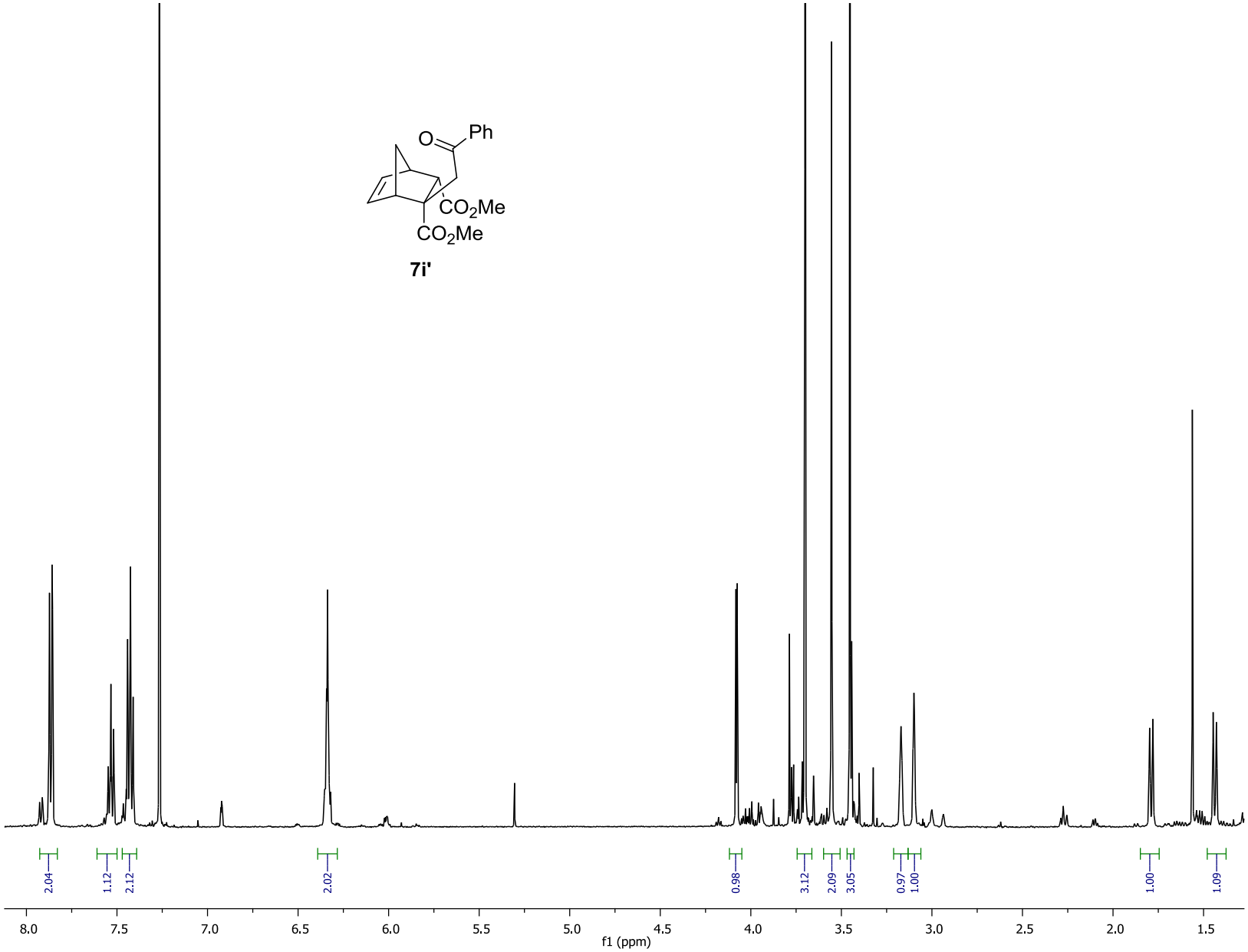

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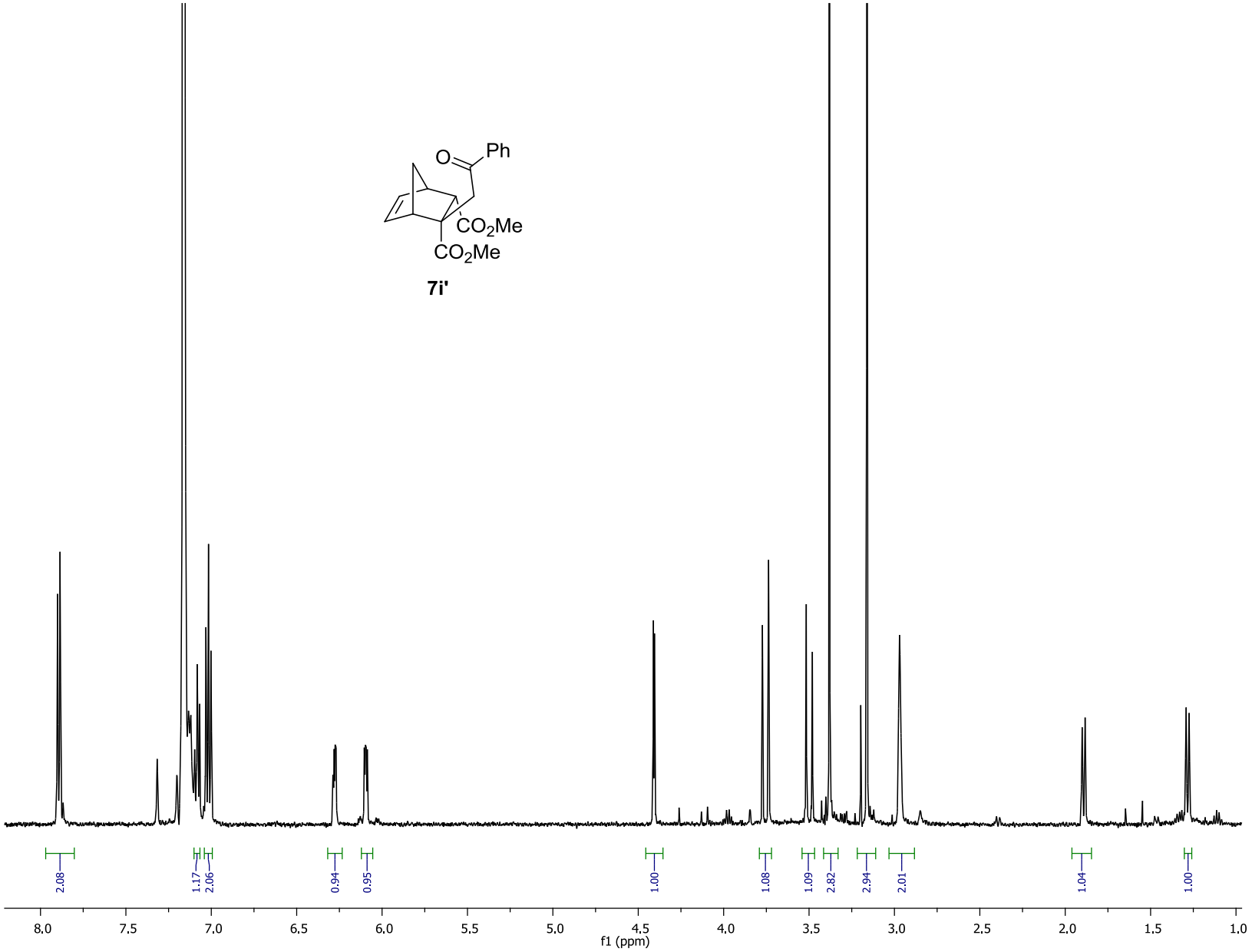
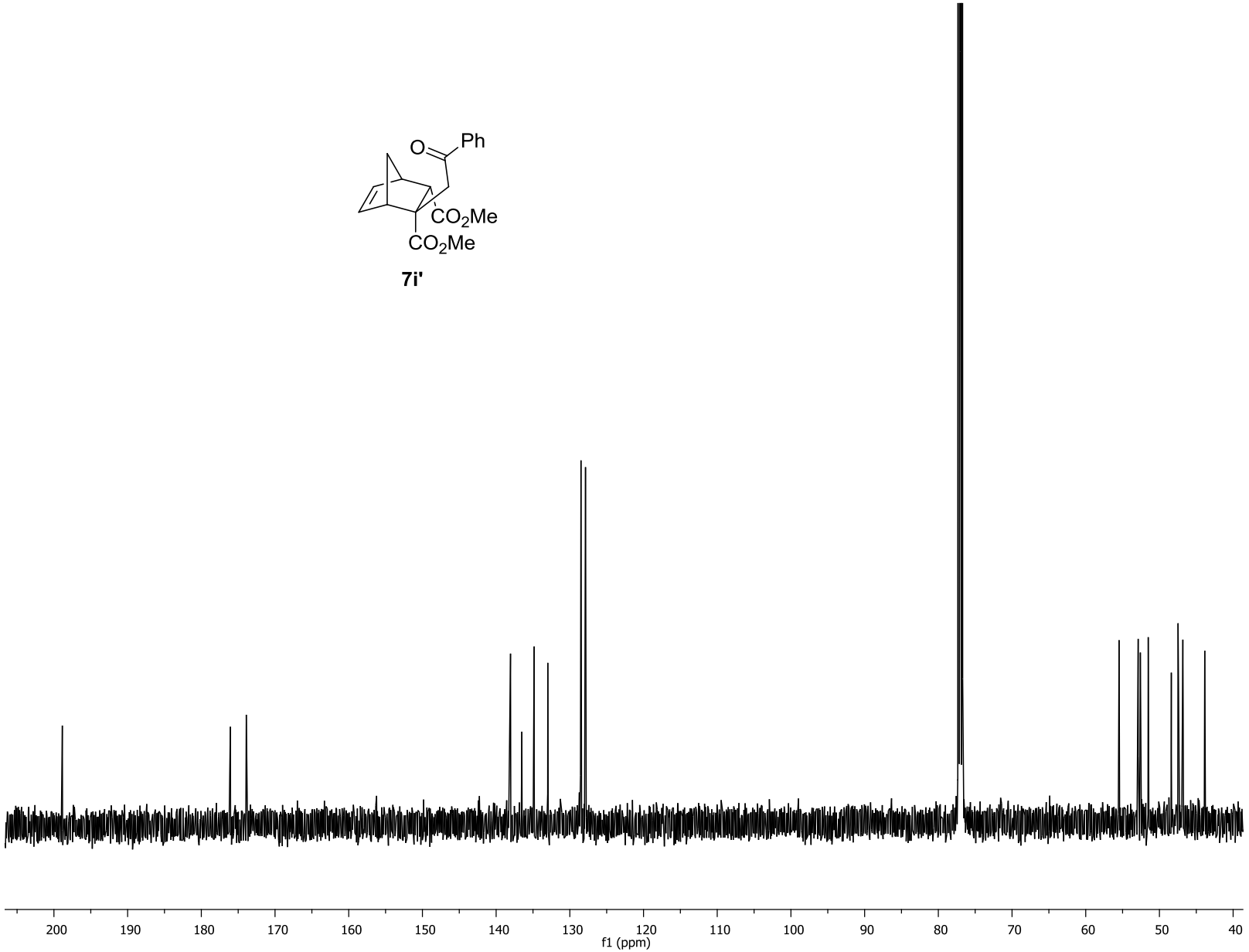


^{13}C NMR (500 MHz, $CDCl_3$):



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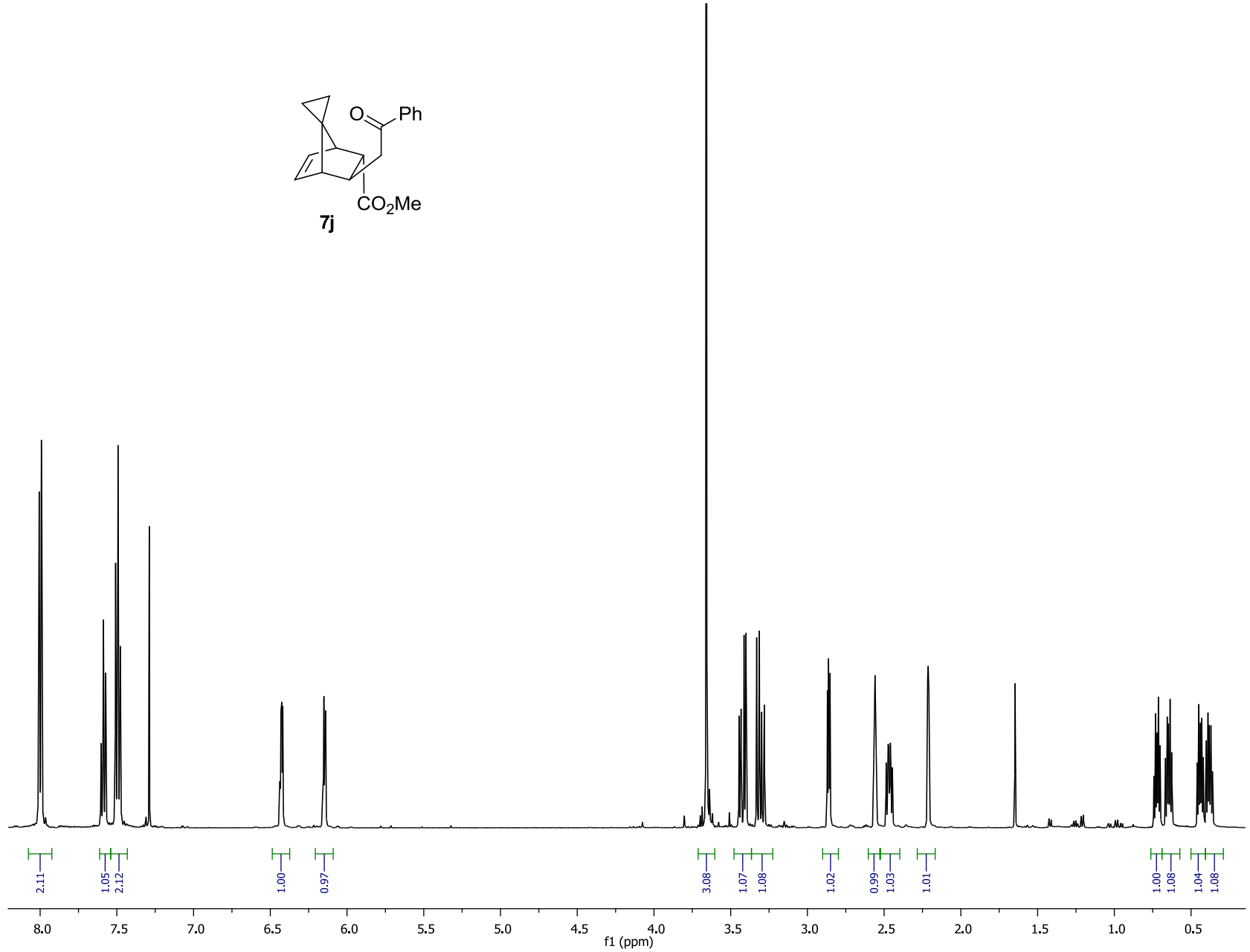

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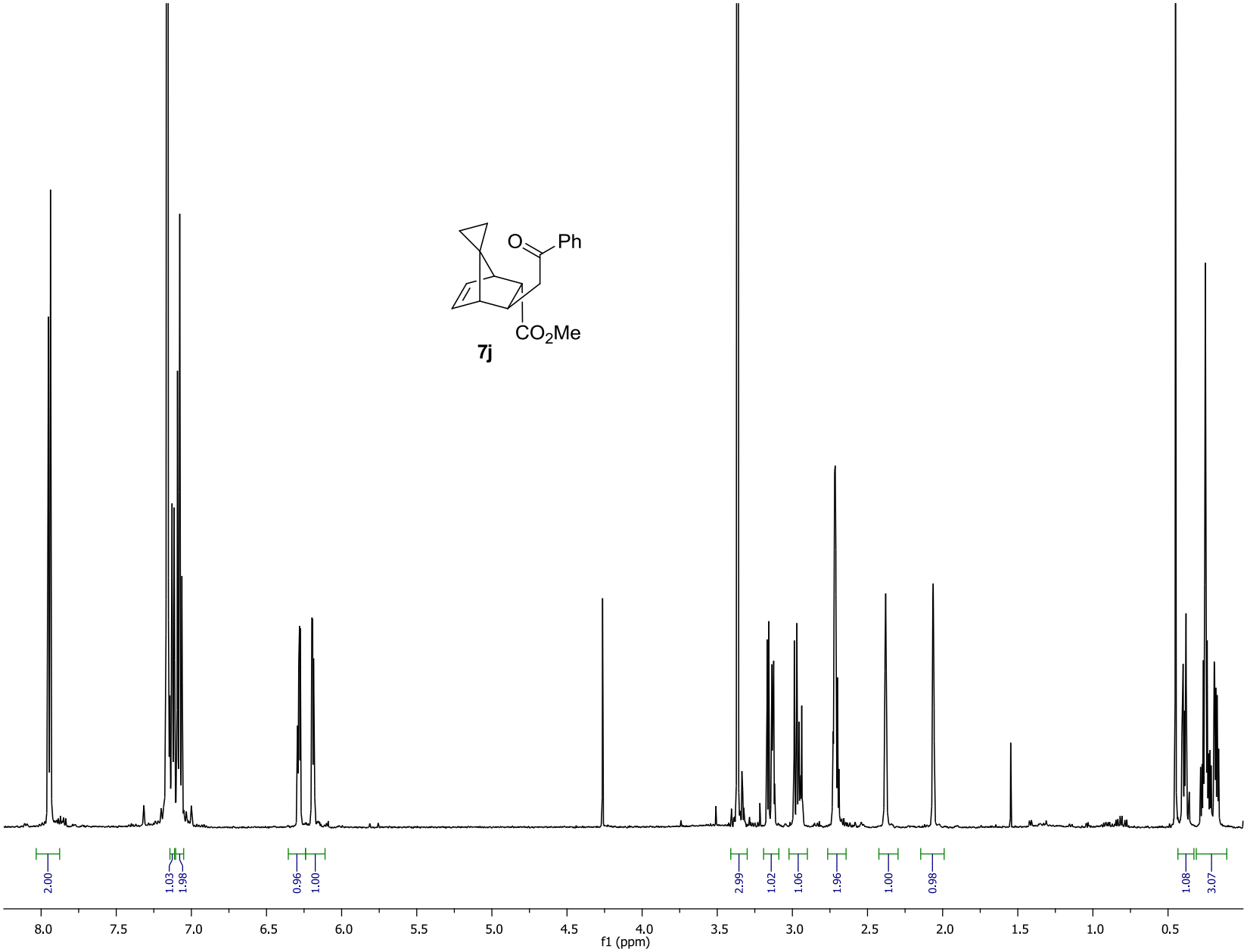
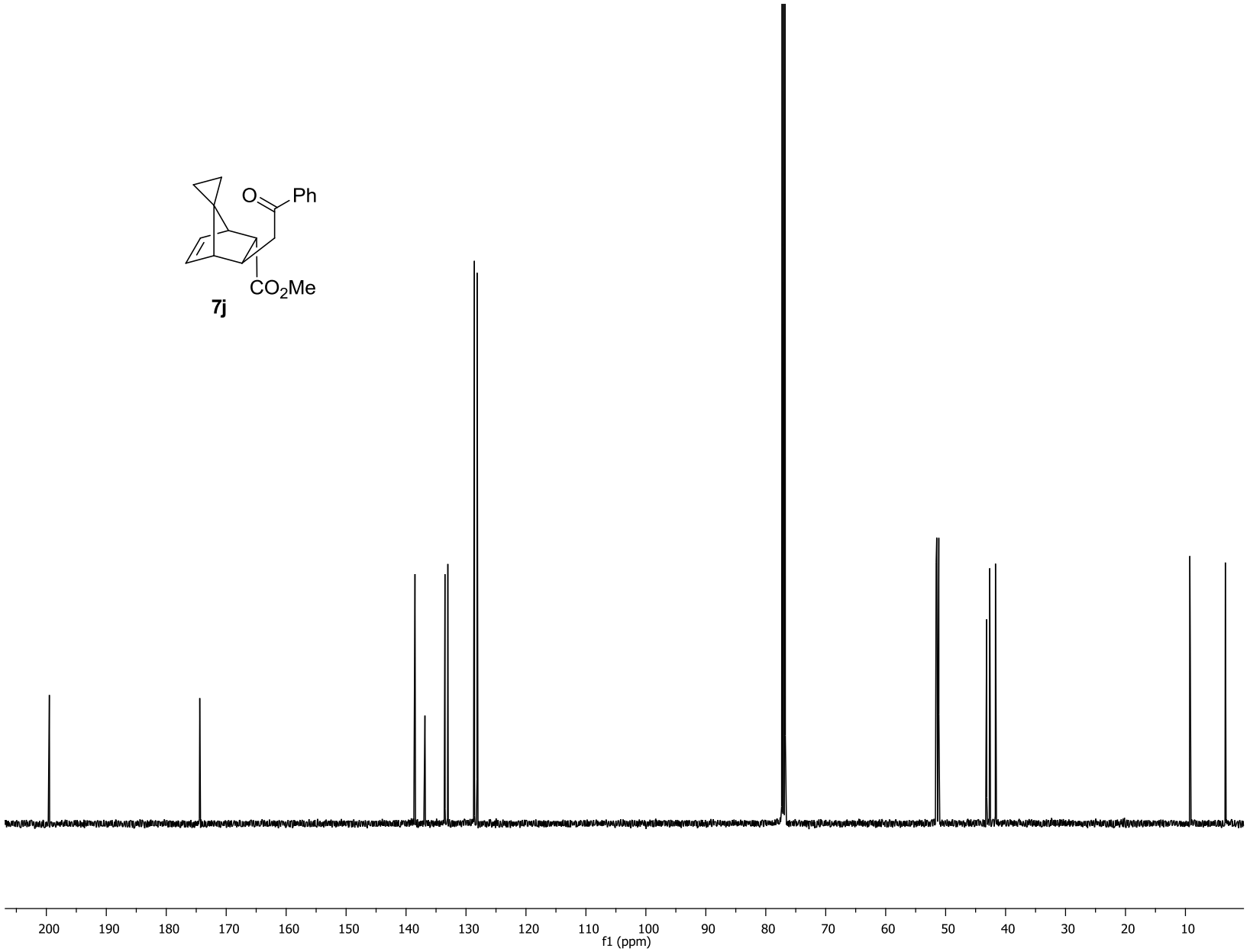
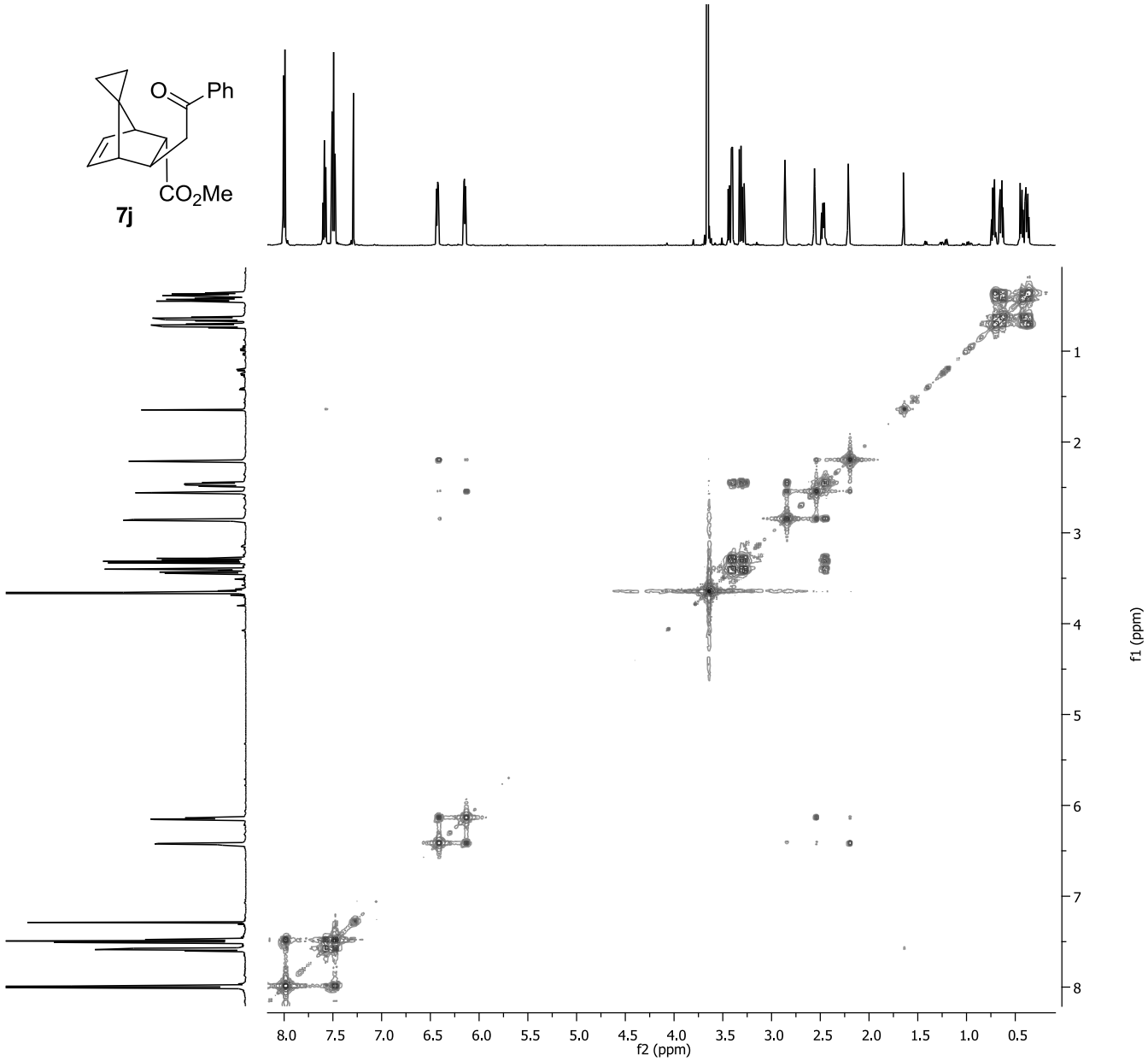


^{13}C NMR (500 MHz, $CDCl_3$):

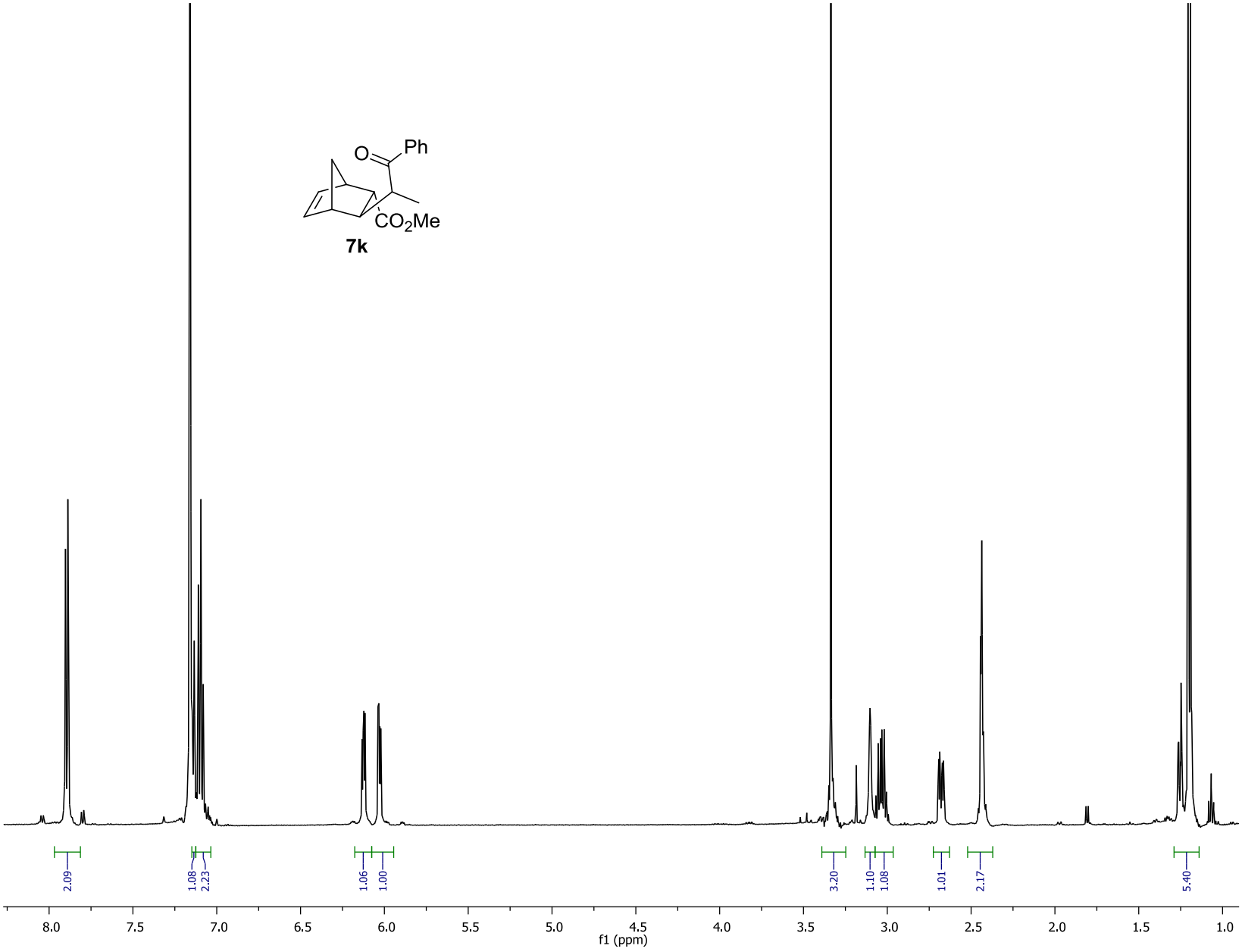
7j



COSY (500 MHz, $CDCl_3$):



^{1}H NMR (500 MHz, $CDCl_3$):



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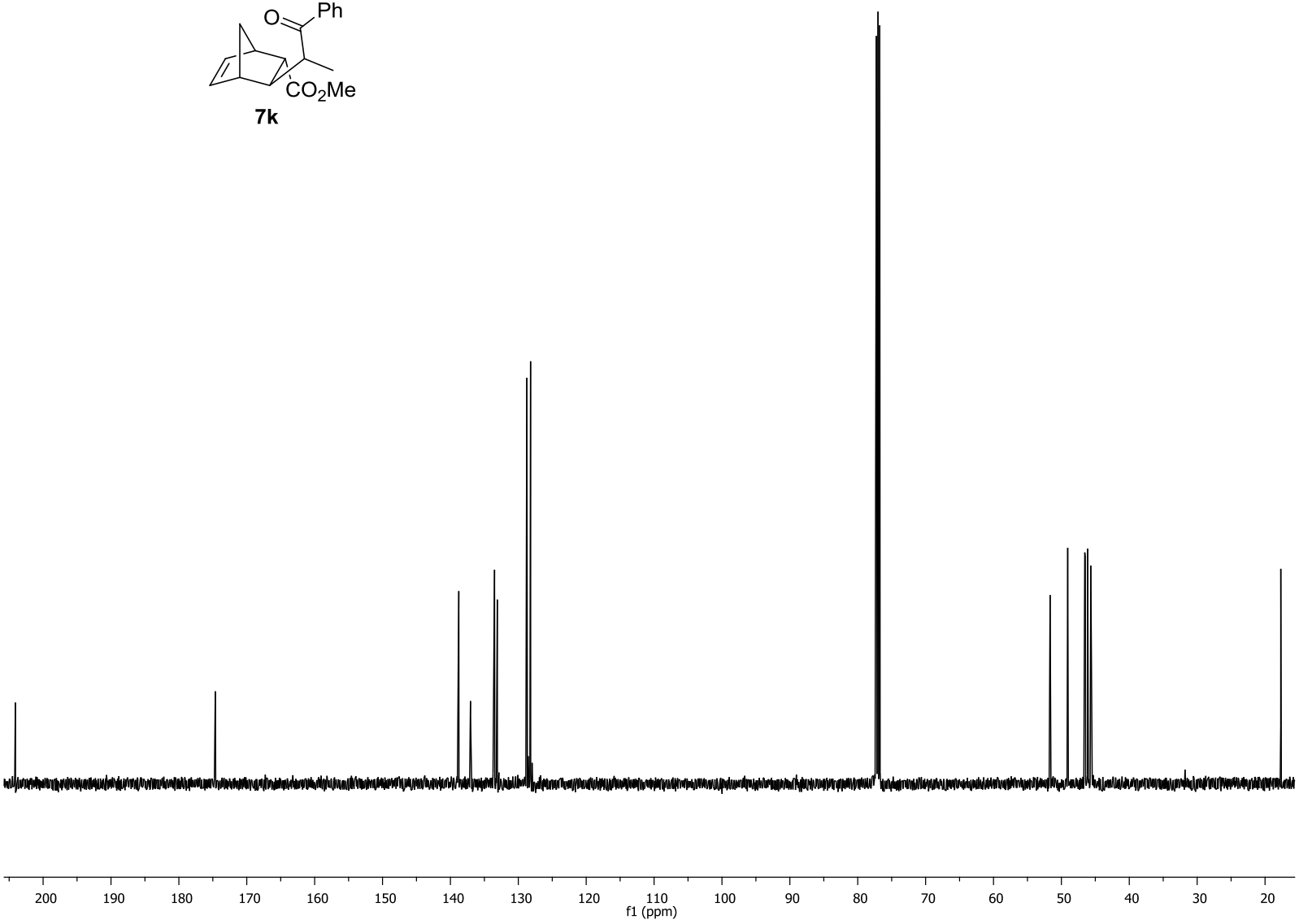

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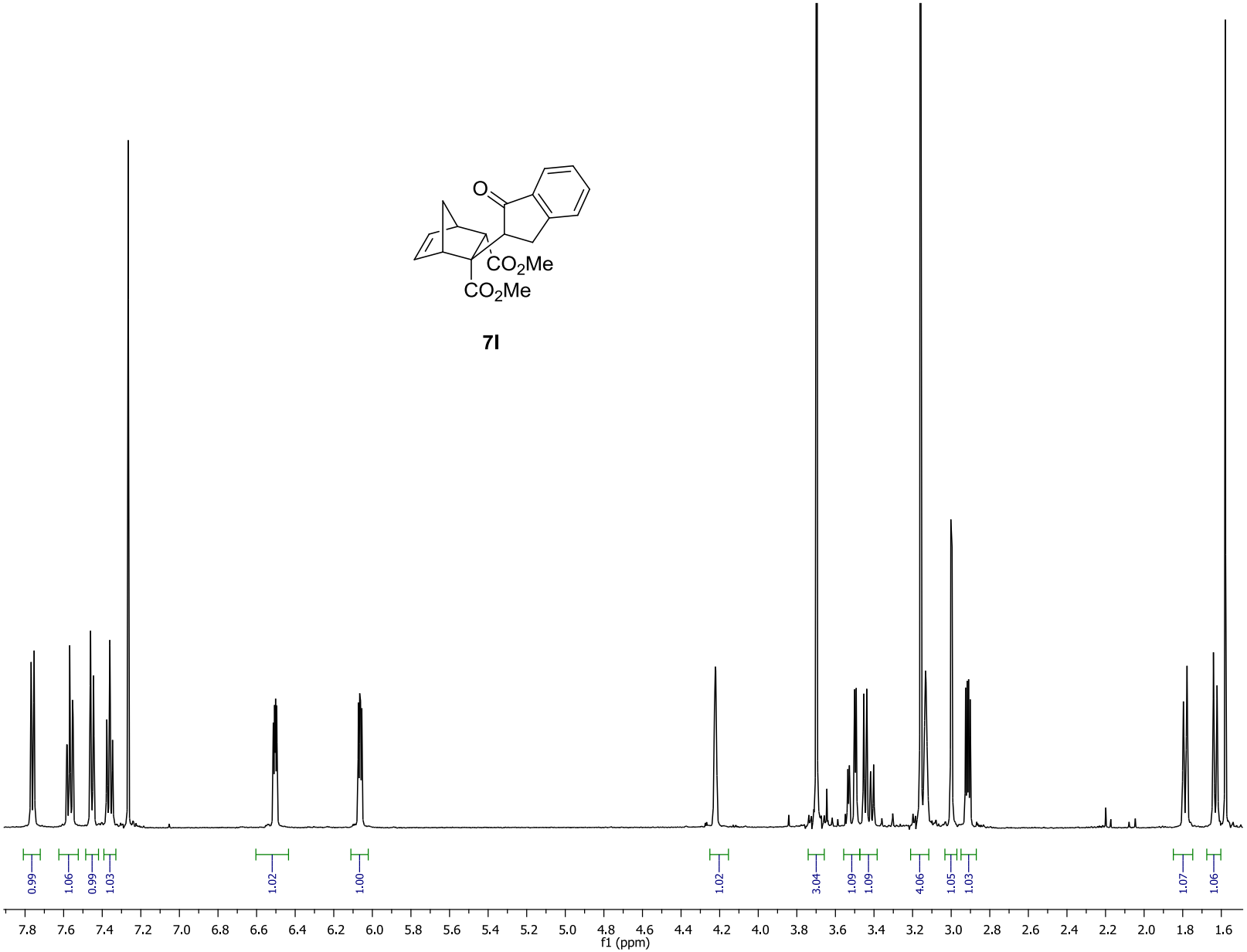
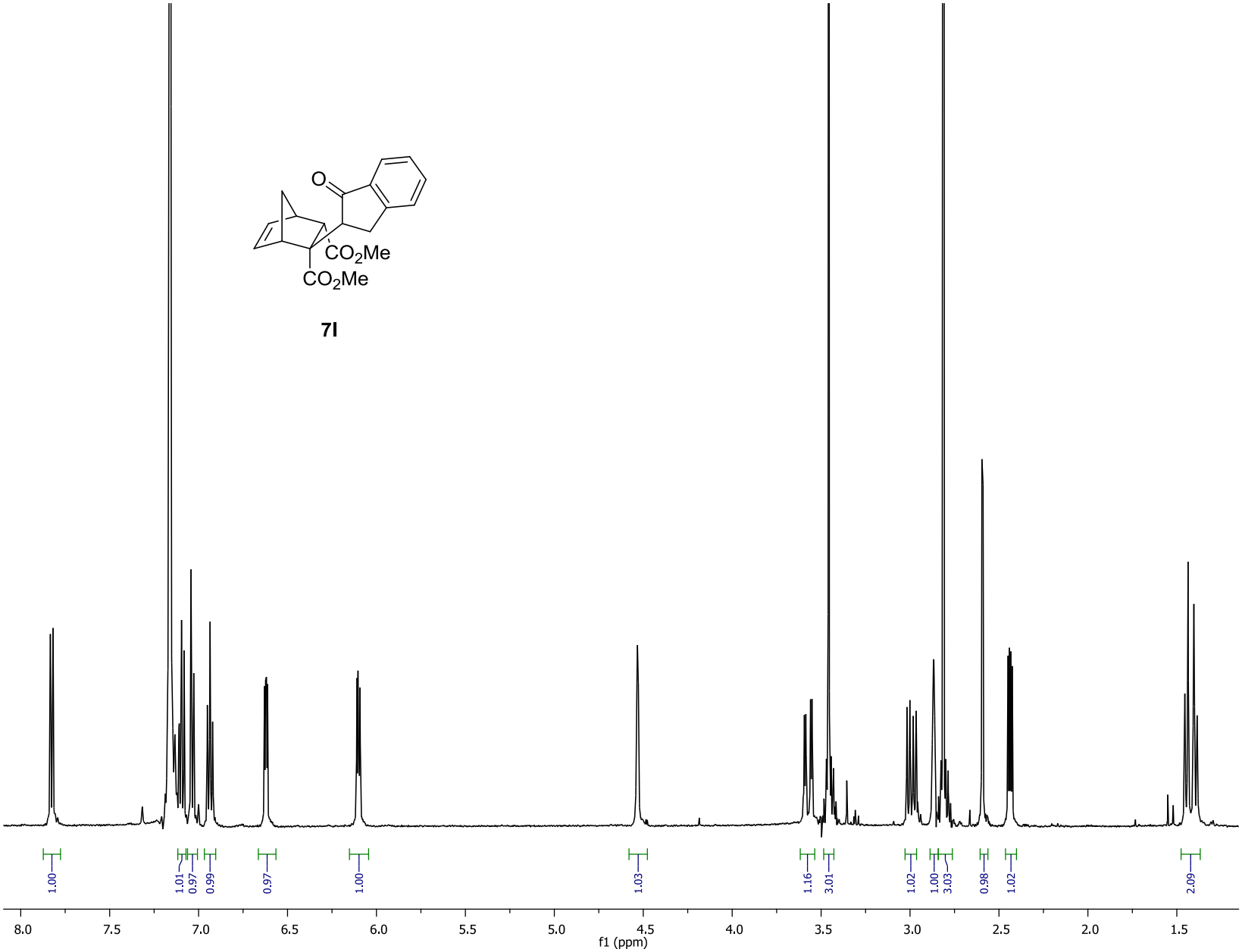


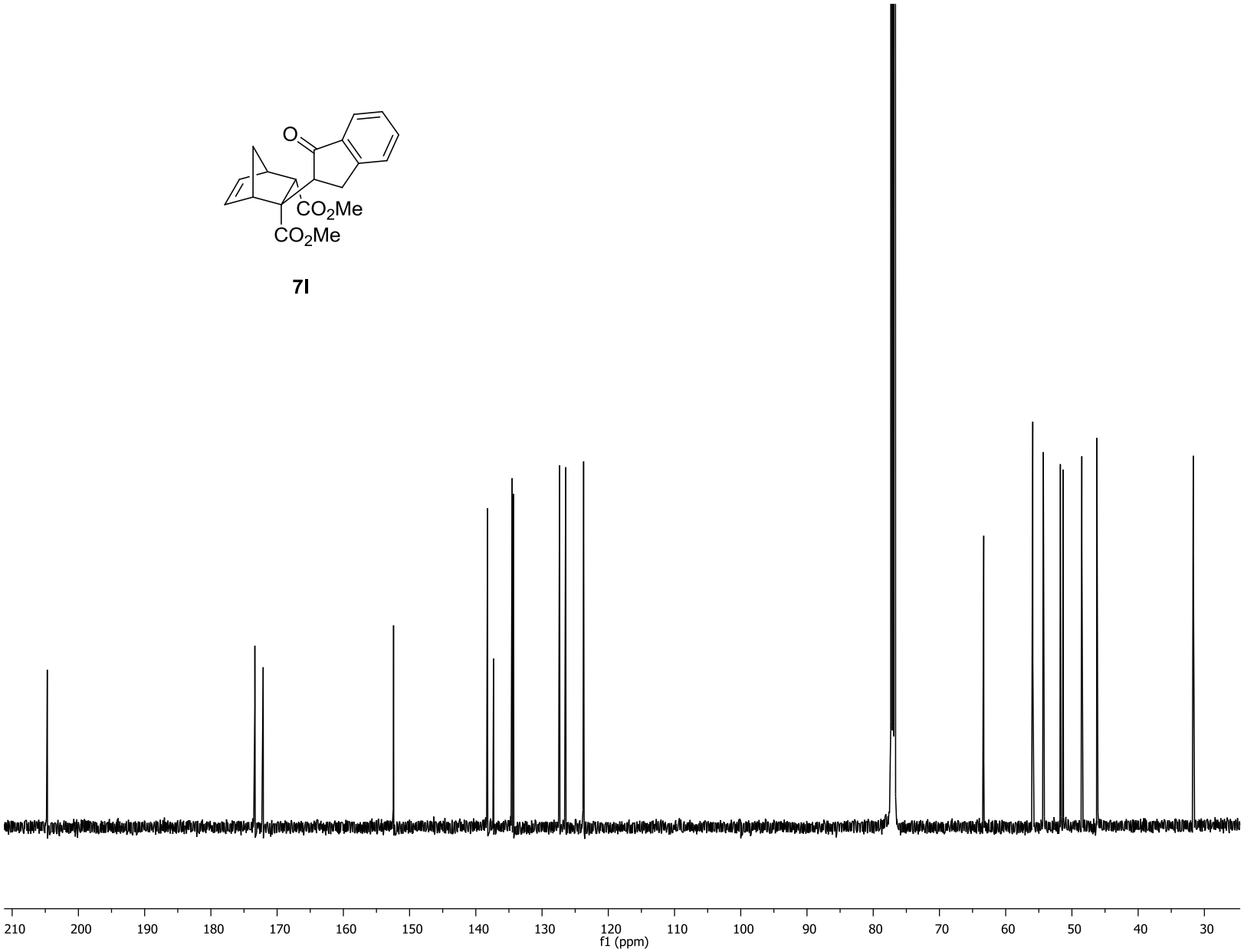
^{1}H NMR (500 MHz, C_6D_6):

7l



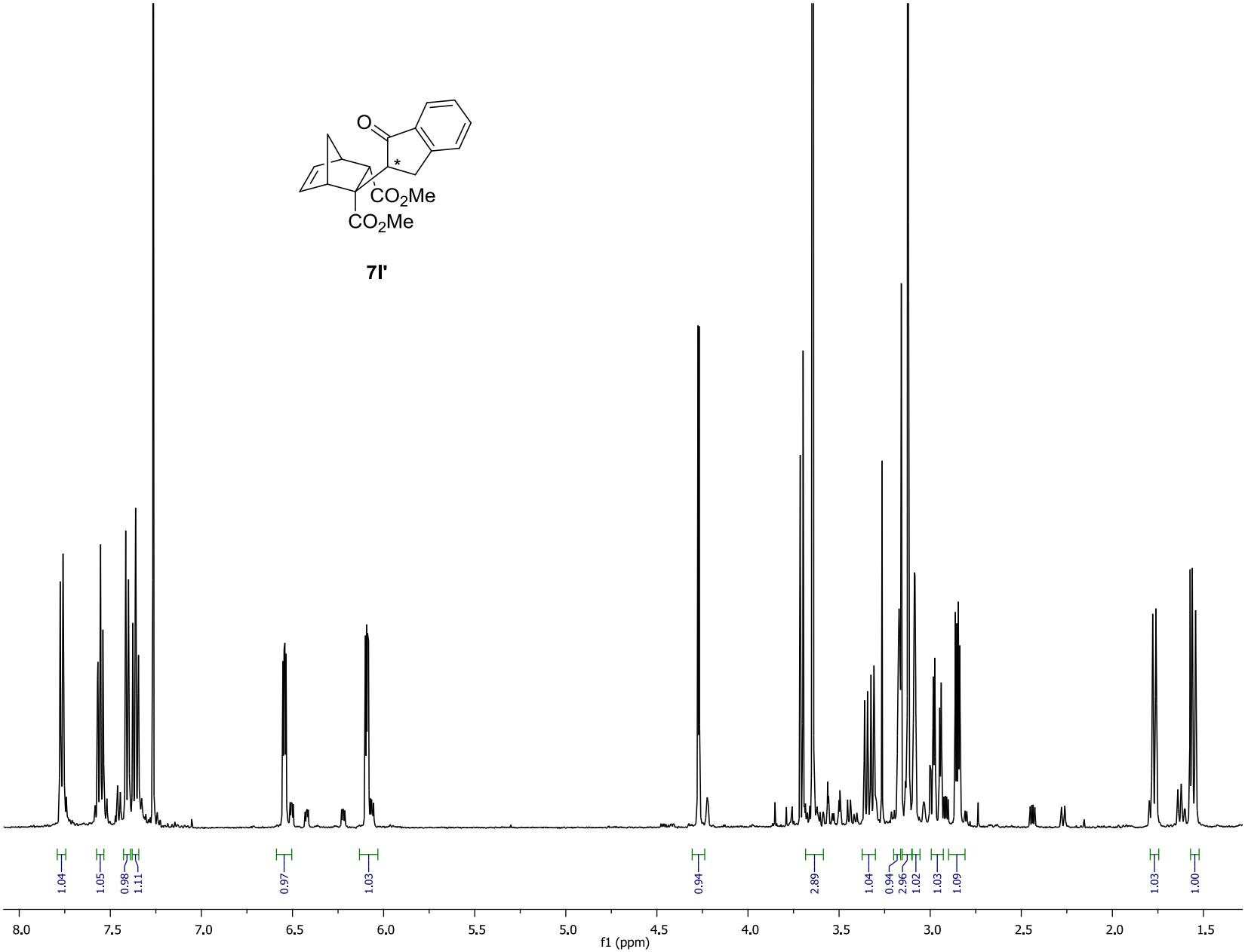
^{13}C NMR (500 MHz, $CDCl_3$):

7l



^{1}H NMR (500 MHz, $CDCl_3$):

7l'



^{13}C NMR (500 MHz, $CDCl_3$):

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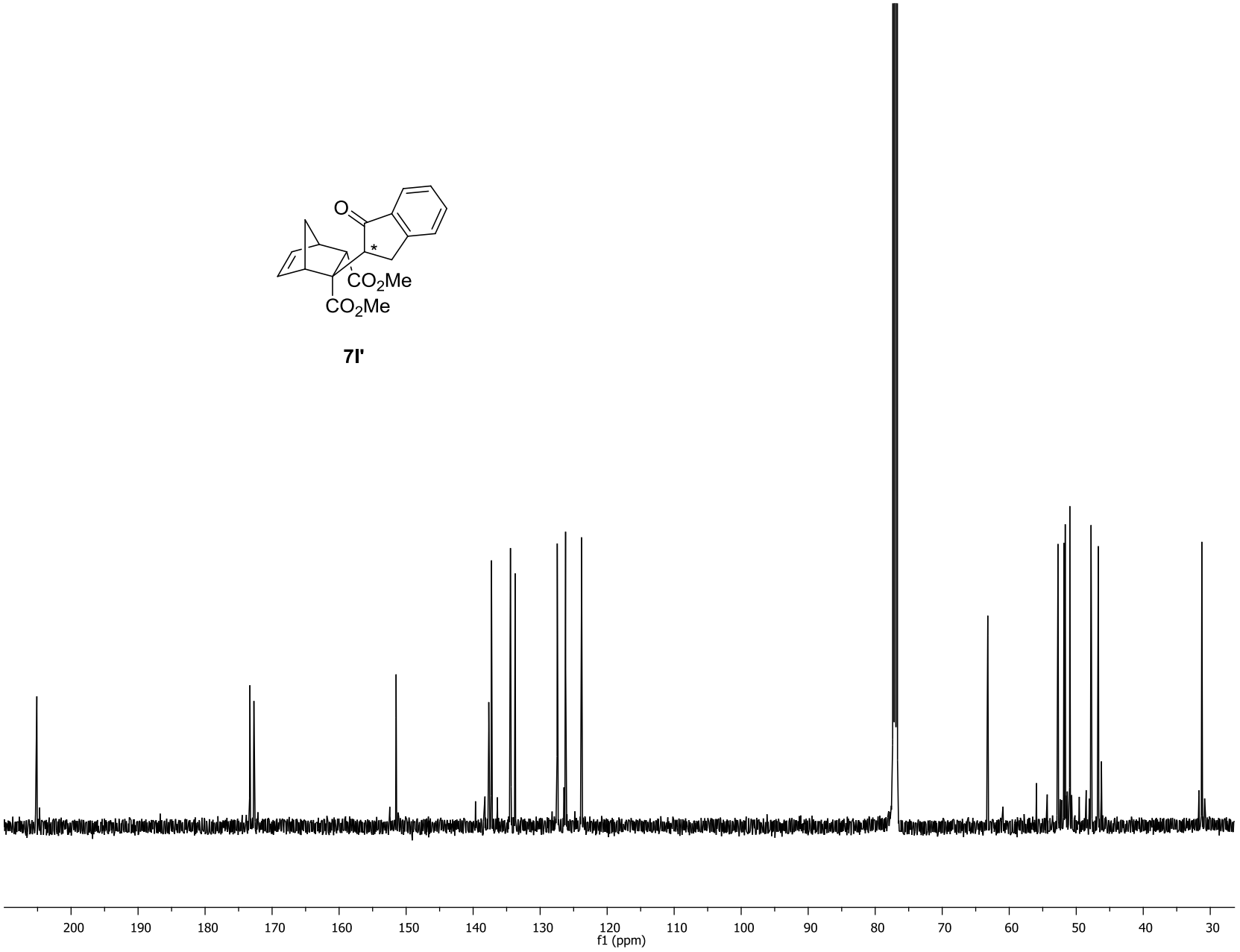
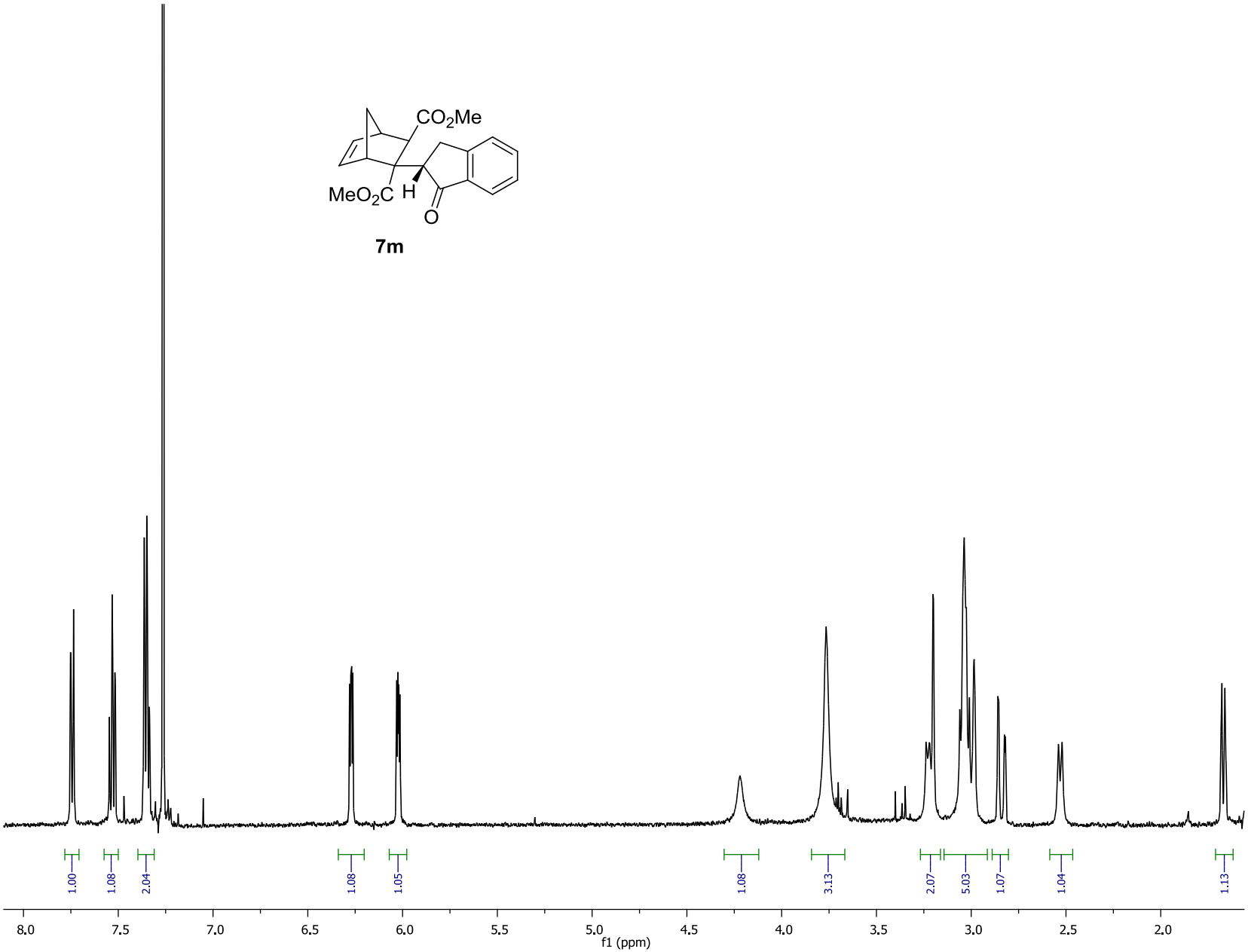
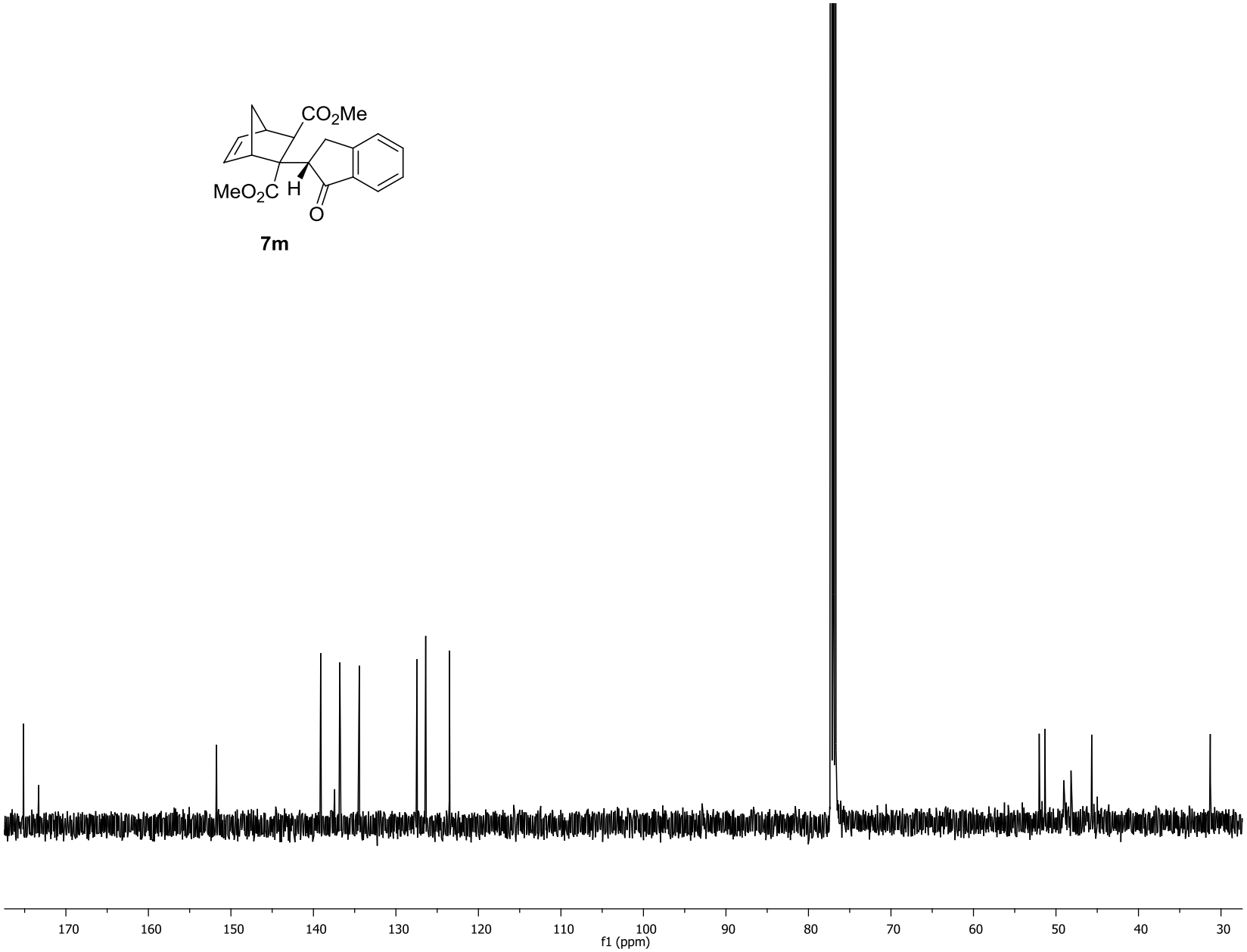


^{1}H NMR (500 MHz, $CDCl_3$):

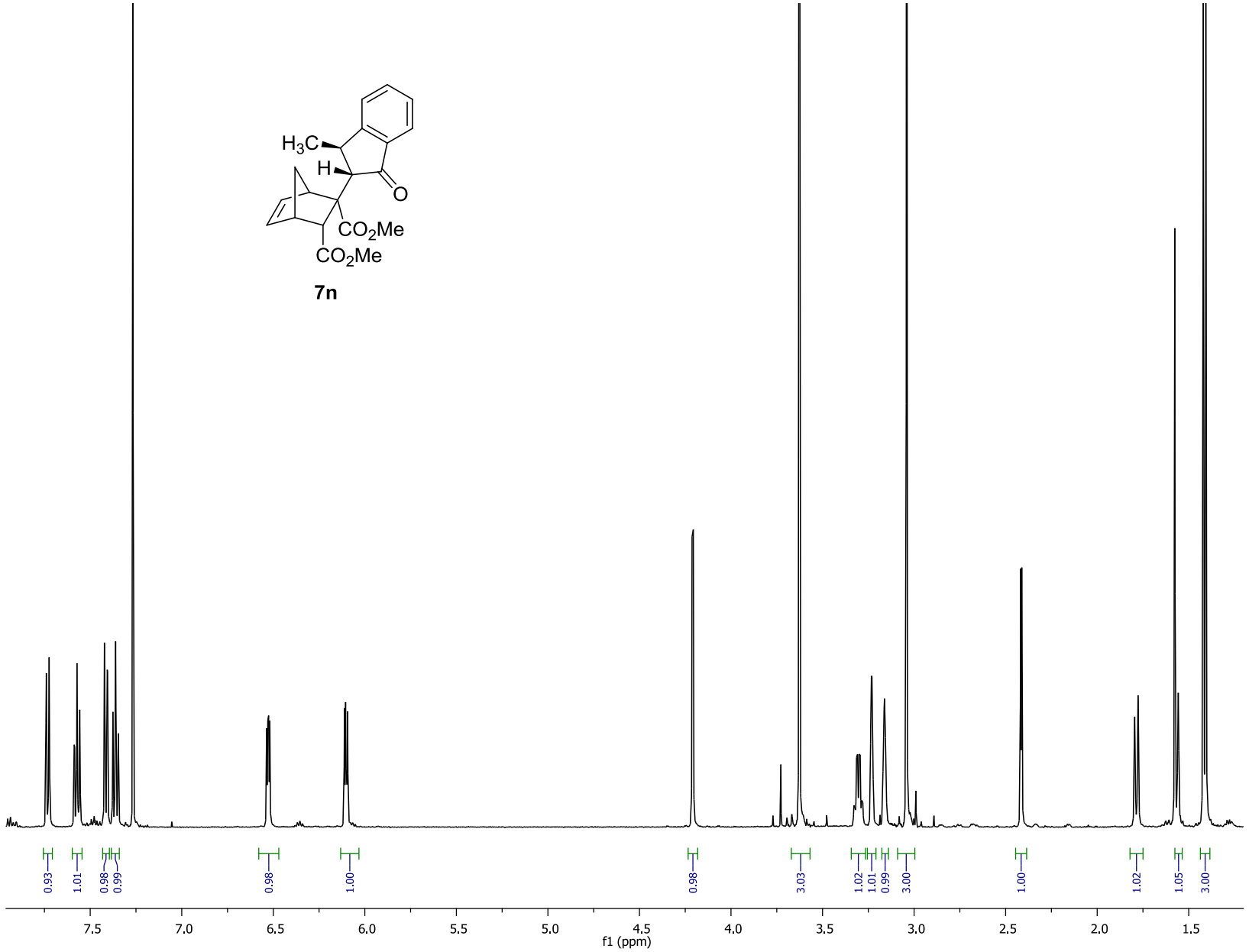


^{13}C NMR (500 MHz, $CDCl_3$):

7m

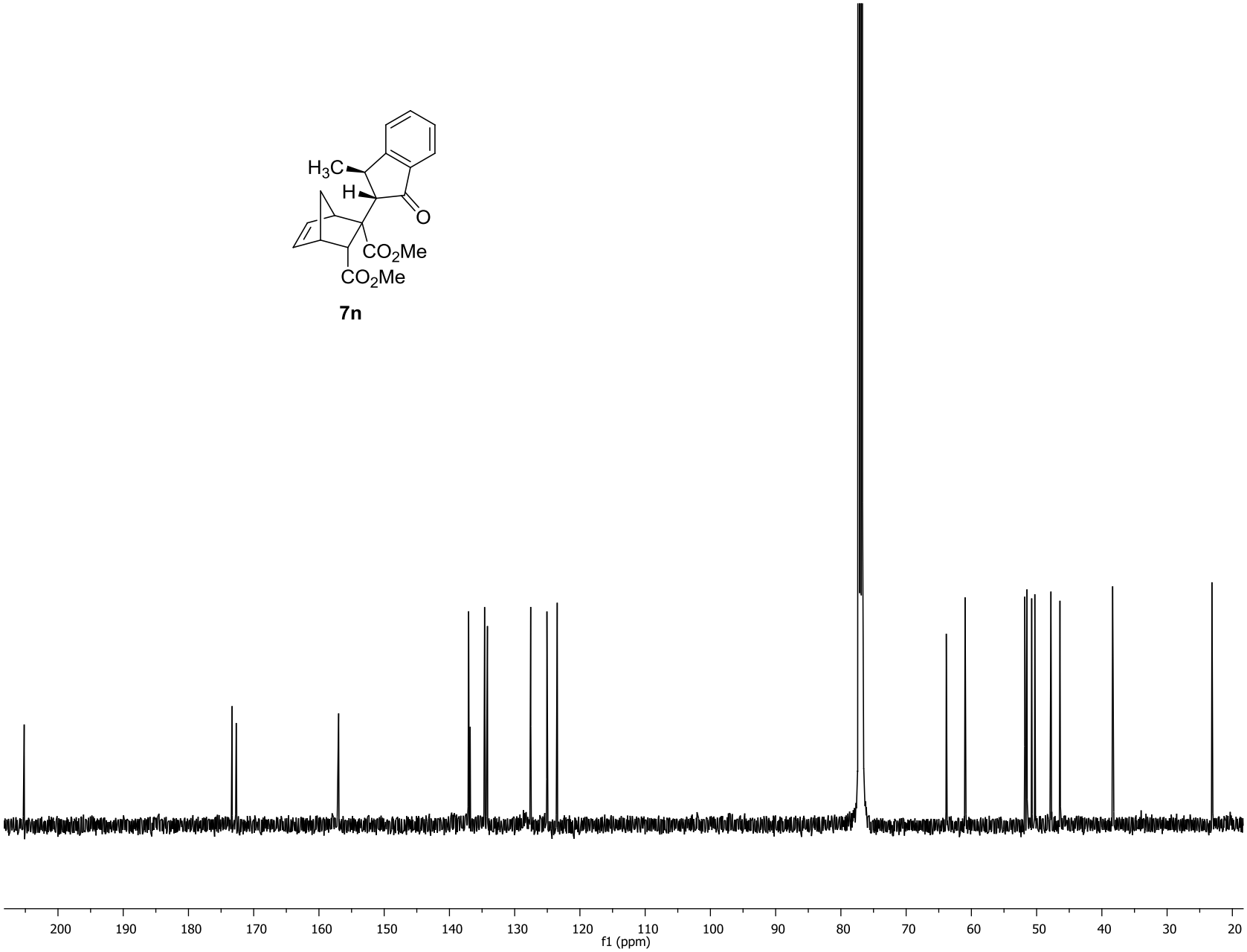


^{1}H NMR (500 MHz, $CDCl_3$):

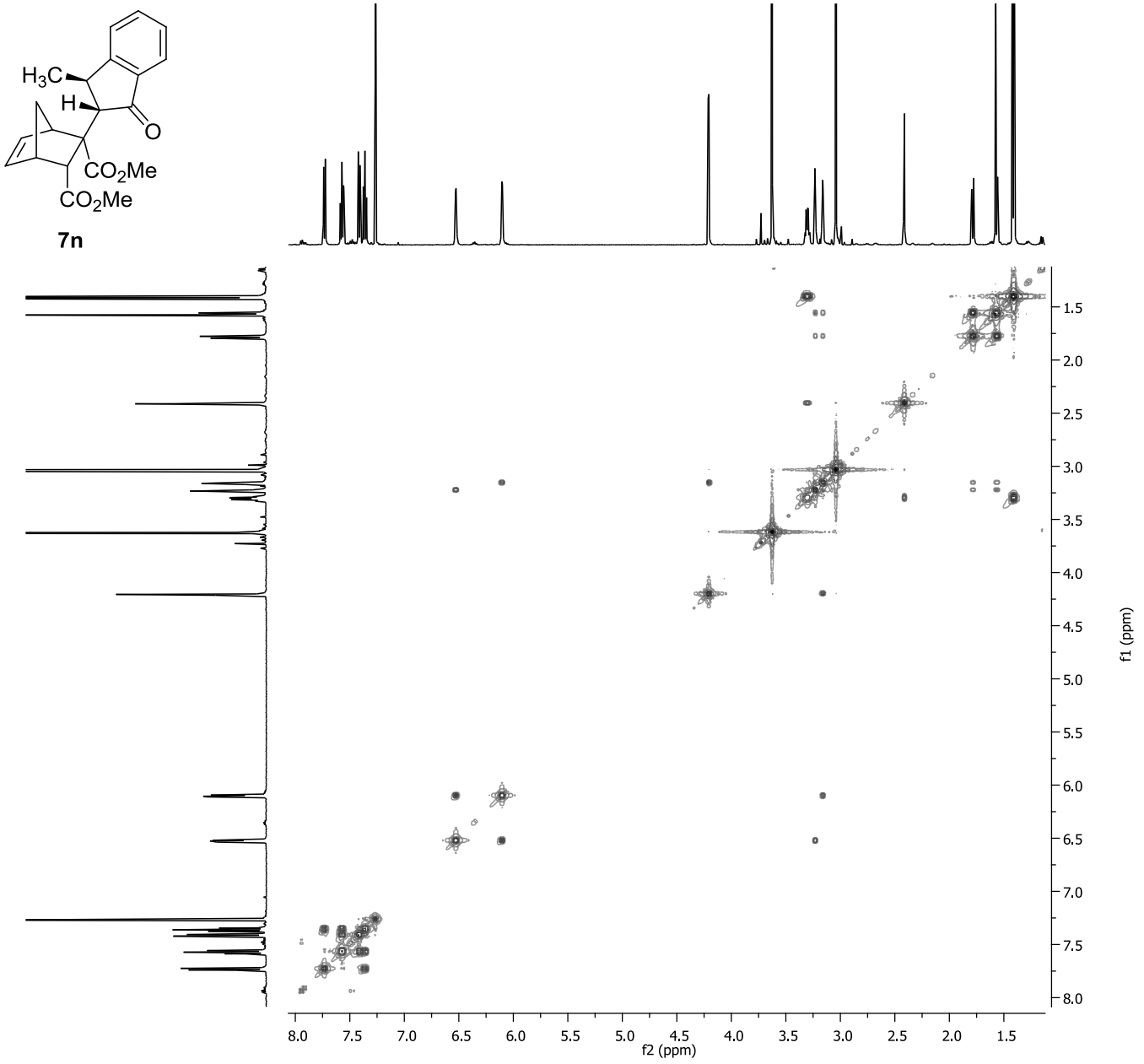


^{13}C NMR (500 MHz, $CDCl_3$):

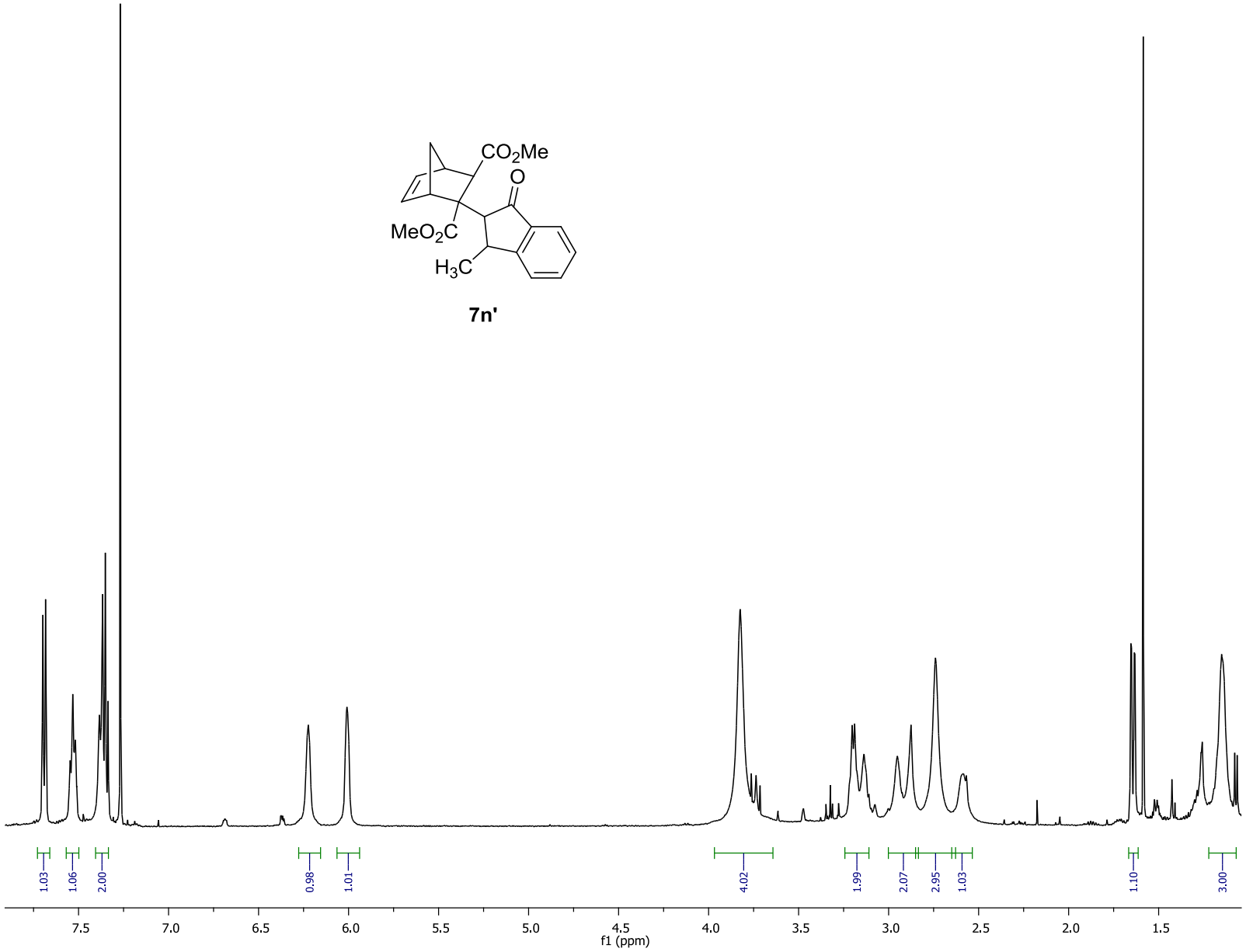
7n



COSY (500 MHz, $CDCl_3$):

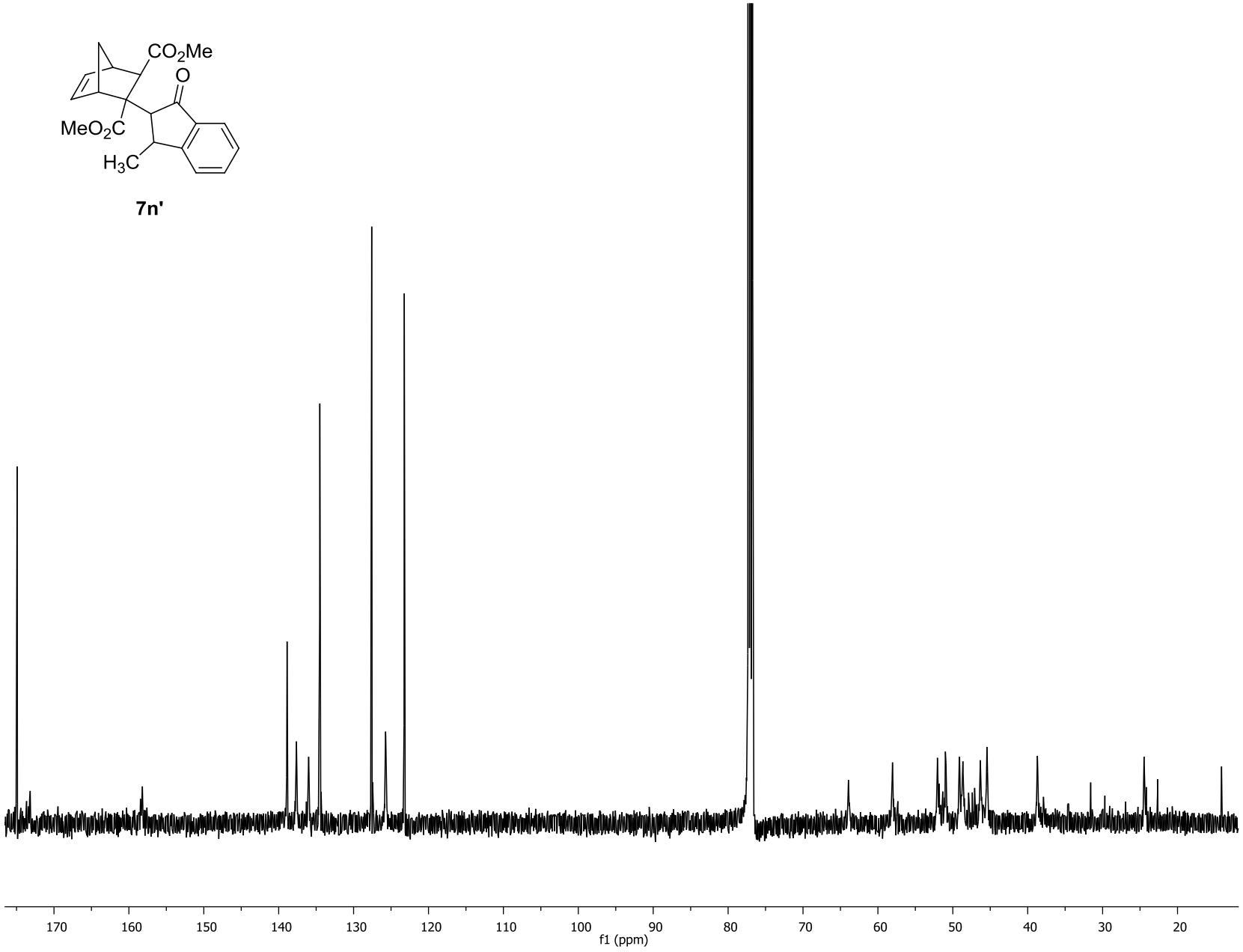


^{1}H NMR (500 MHz, $CDCl_3$):



^{13}C NMR (500 MHz, $CDCl_3$):

7n'



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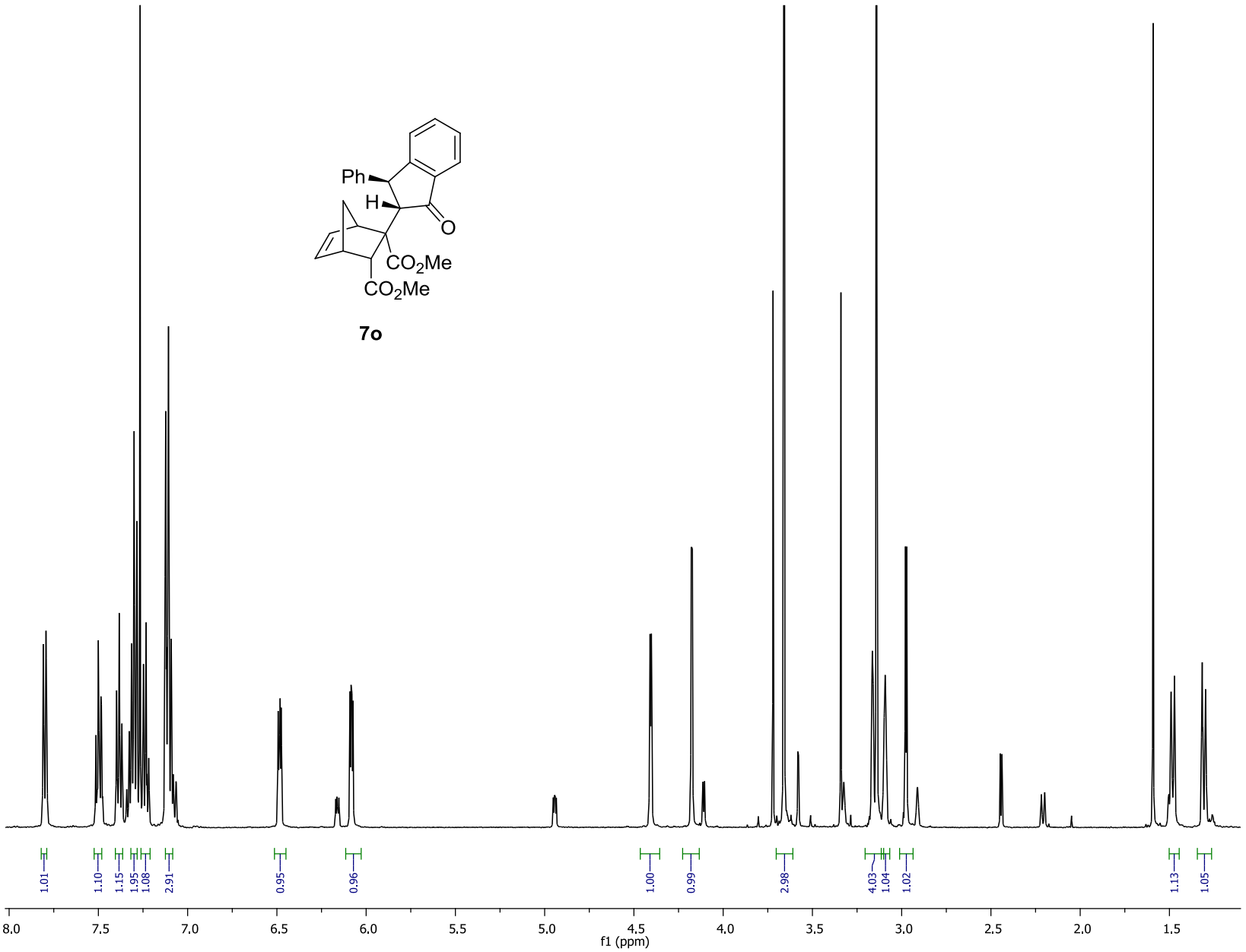
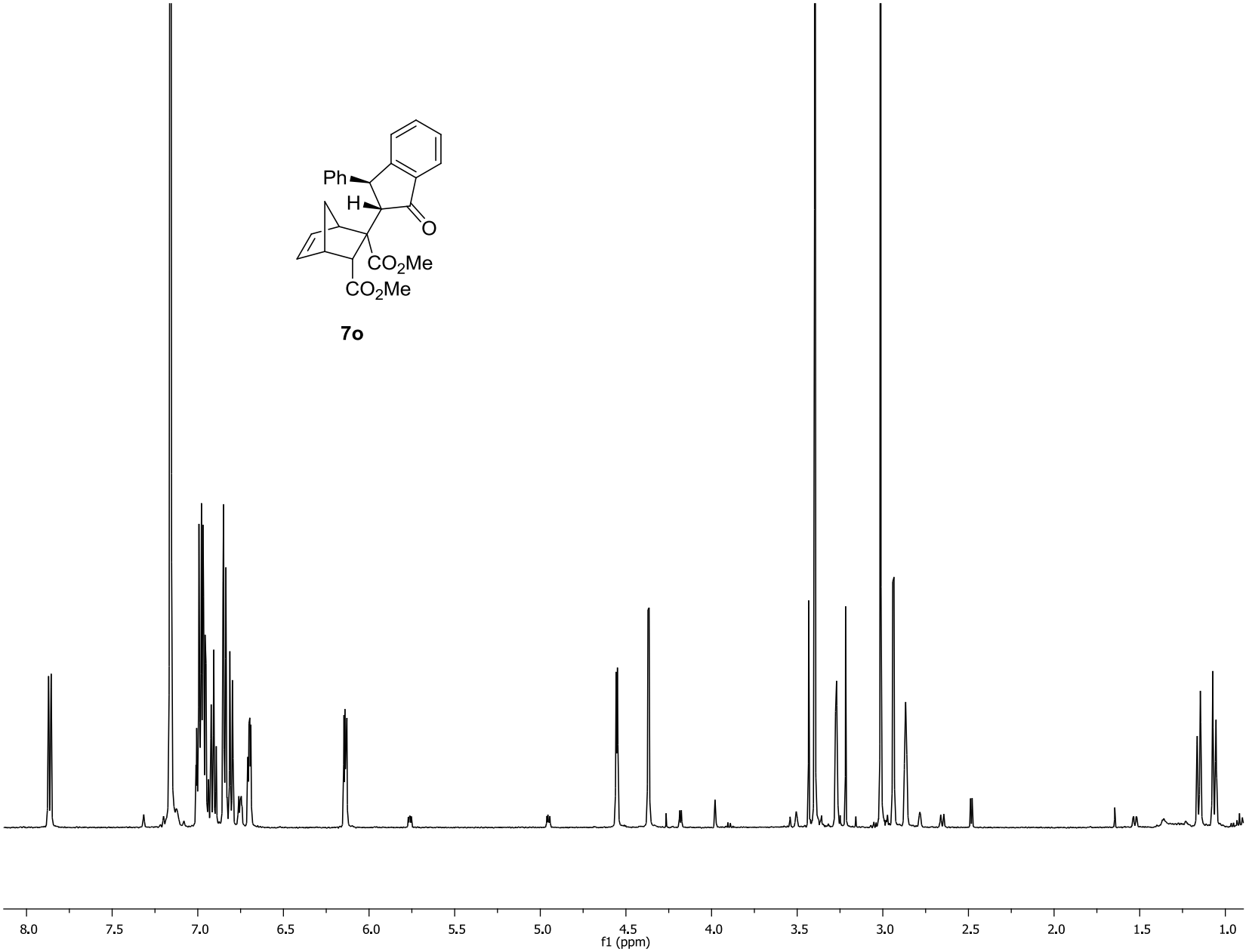


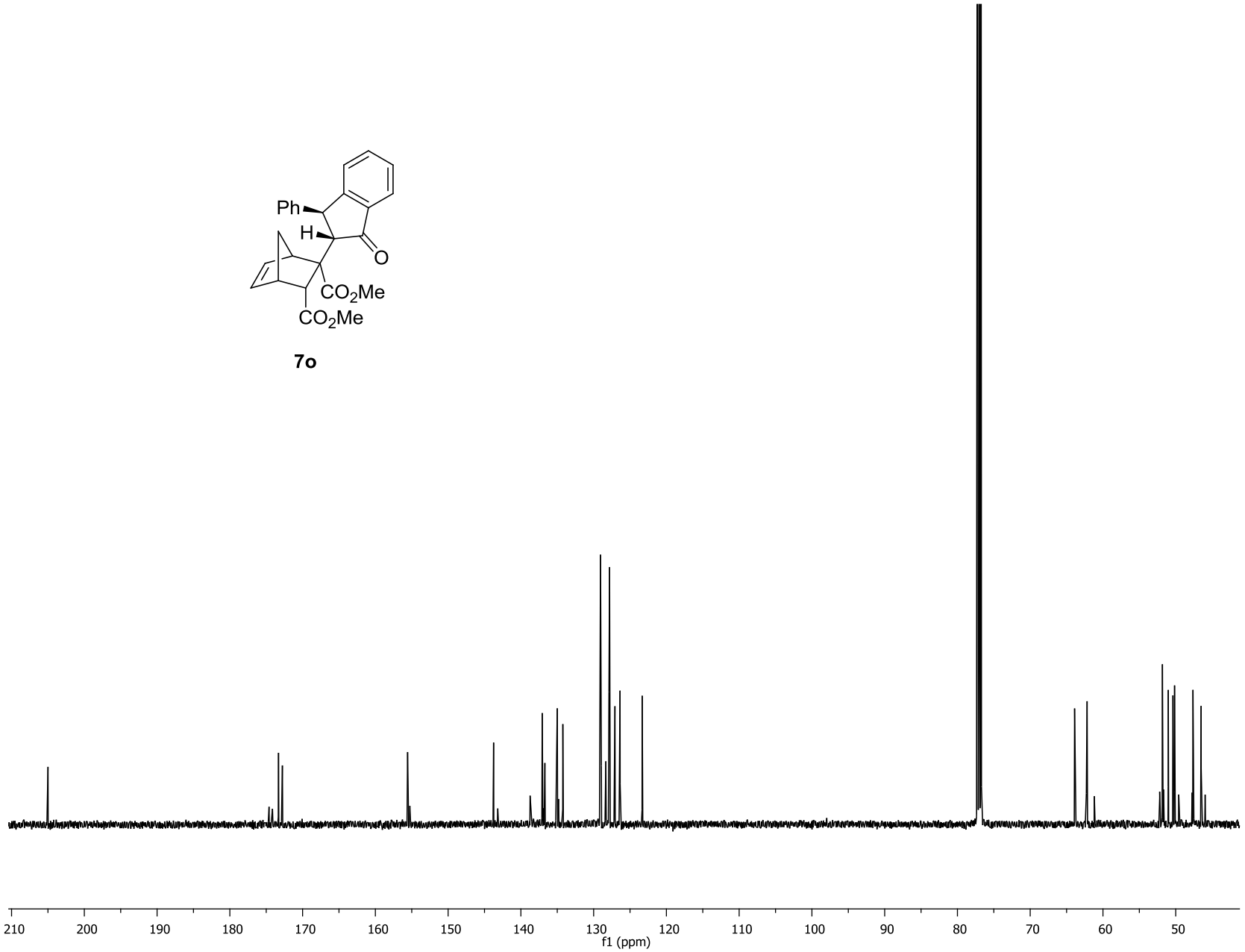
^{1}H NMR (500 MHz, C_6D_6):

7o



^{13}C NMR (500 MHz, $CDCl_3$):

7o



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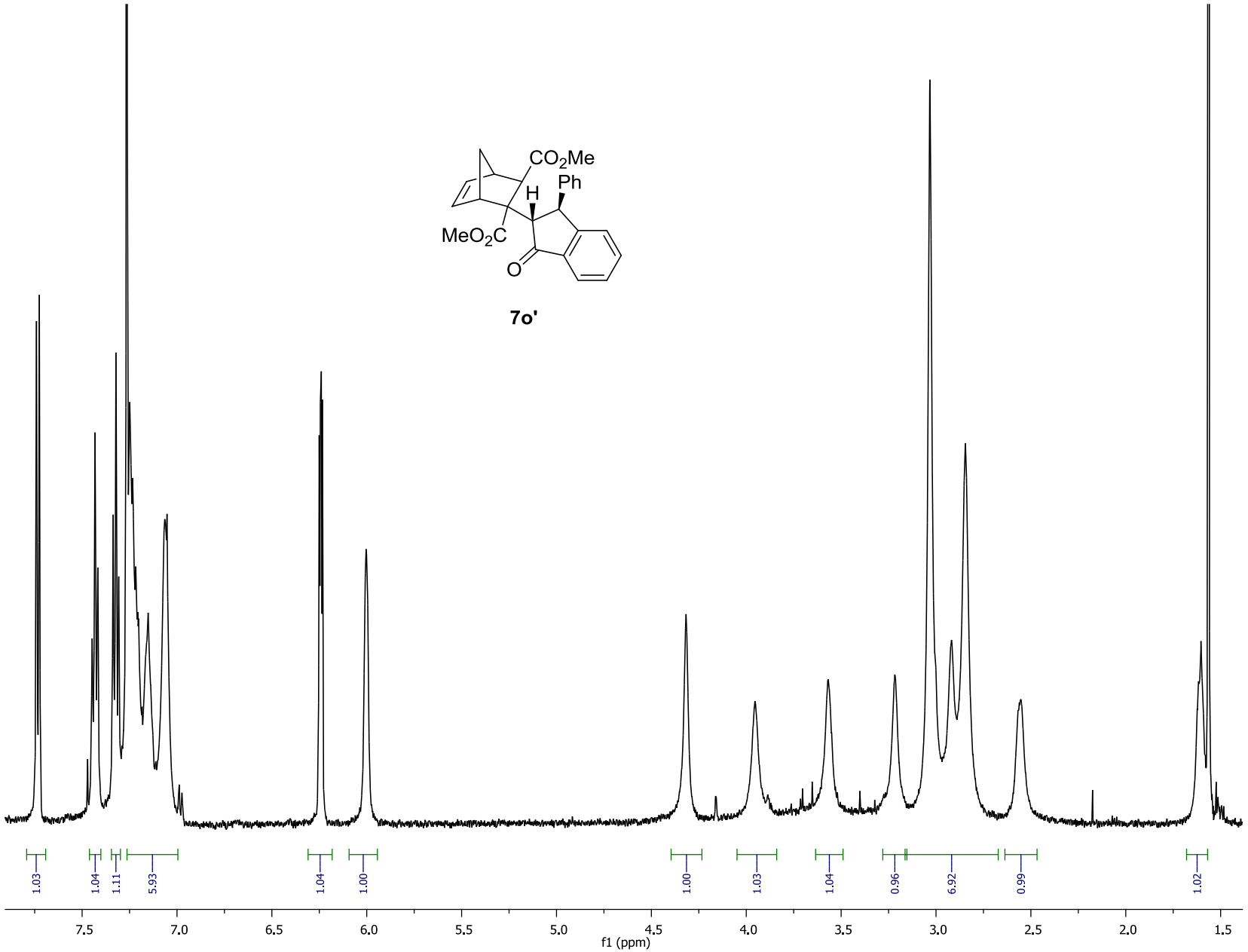
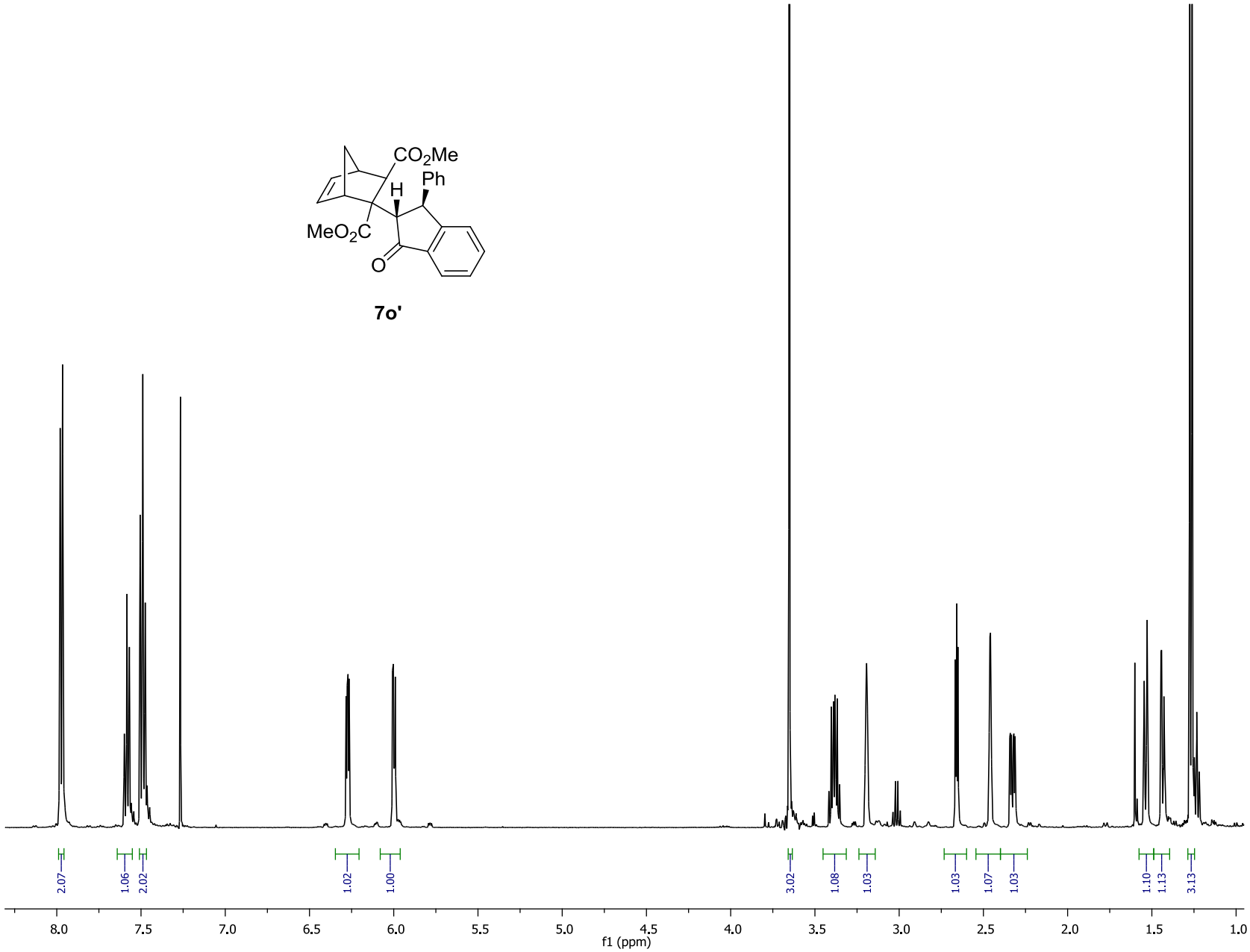
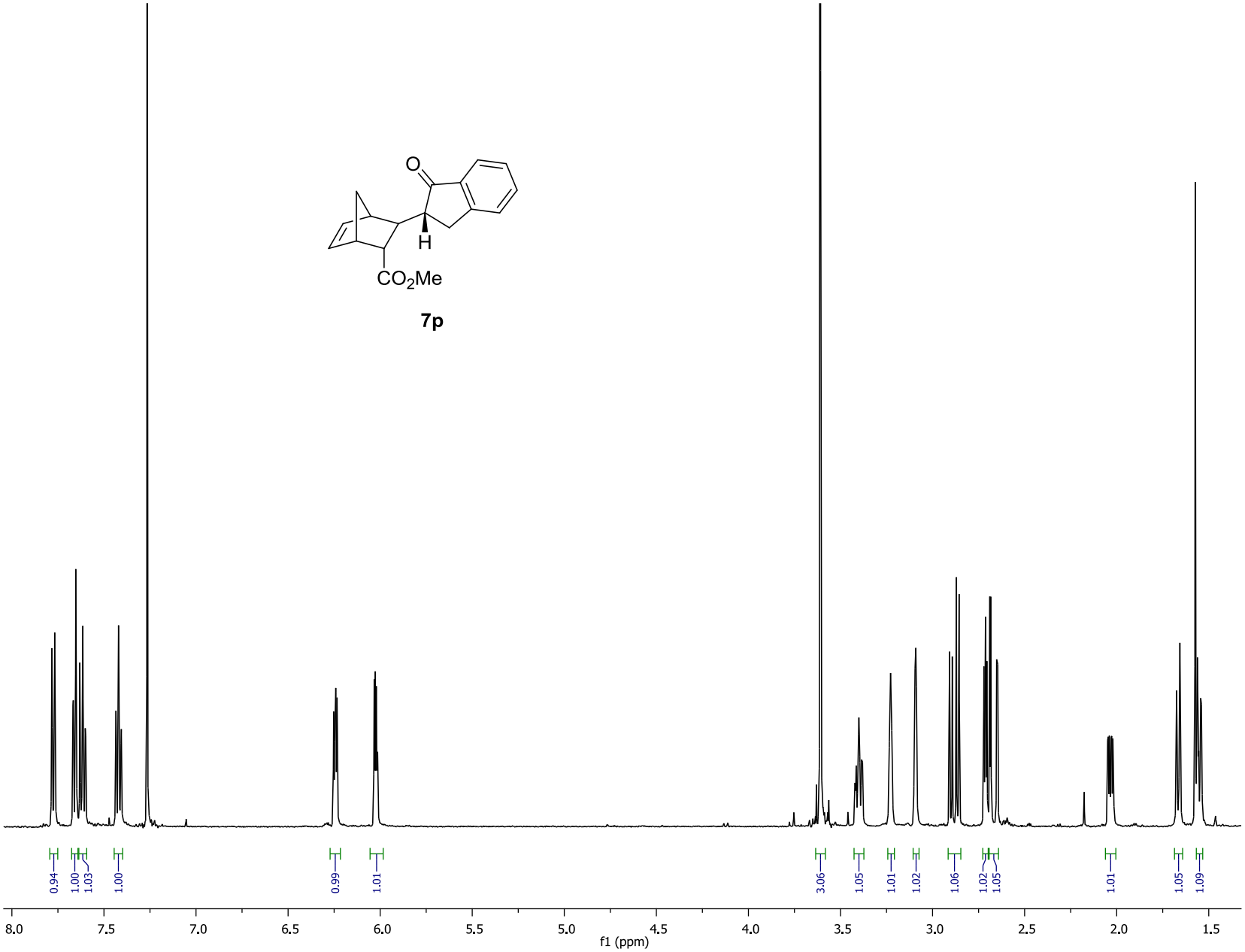


^{1}H NMR (500 MHz, $CDCl_3$):

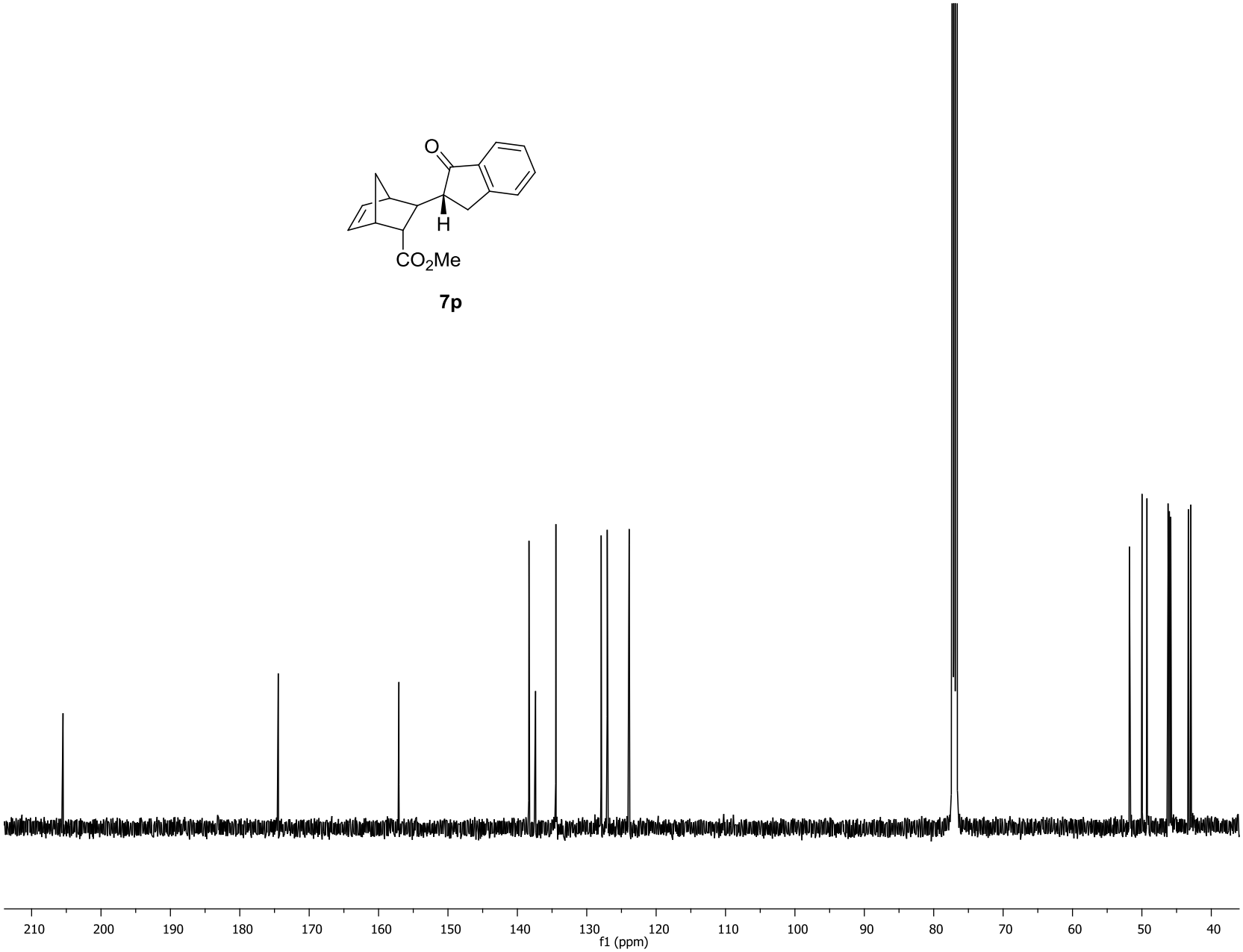


^{1}H NMR (500 MHz, $CDCl_3$):

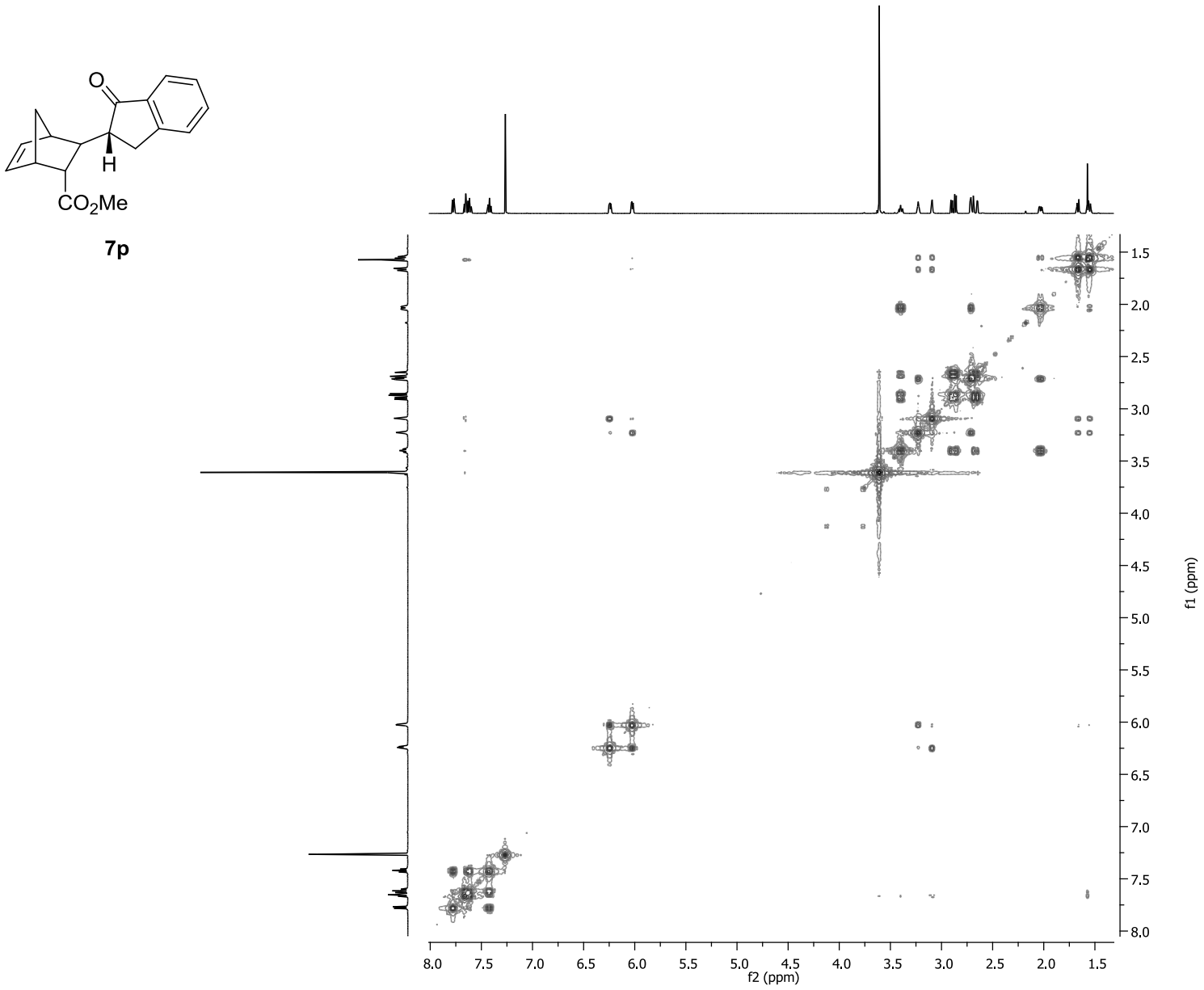


^{13}C NMR (500 MHz, $CDCl_3$):

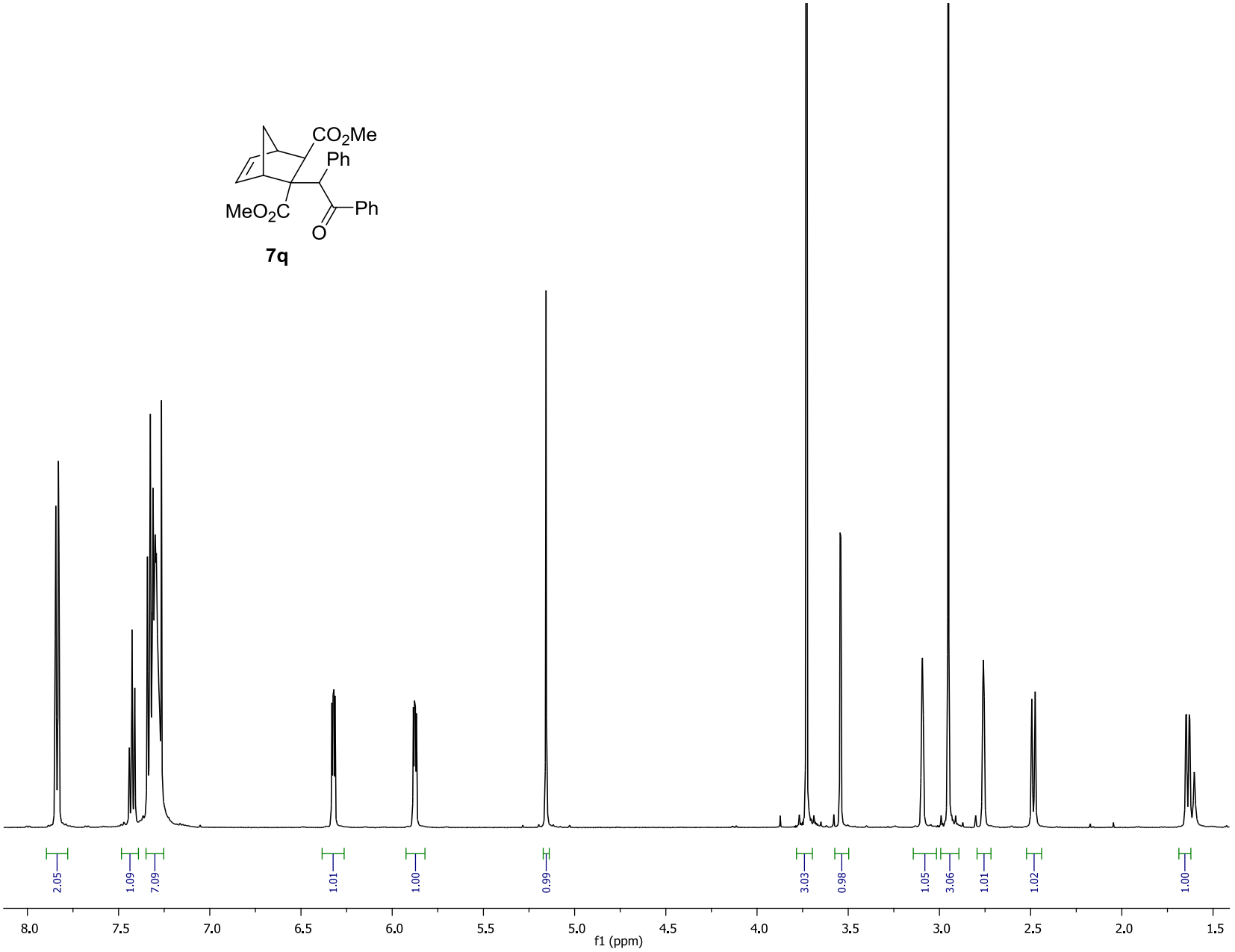
7p



COSY (500 MHz, $CDCl_3$):

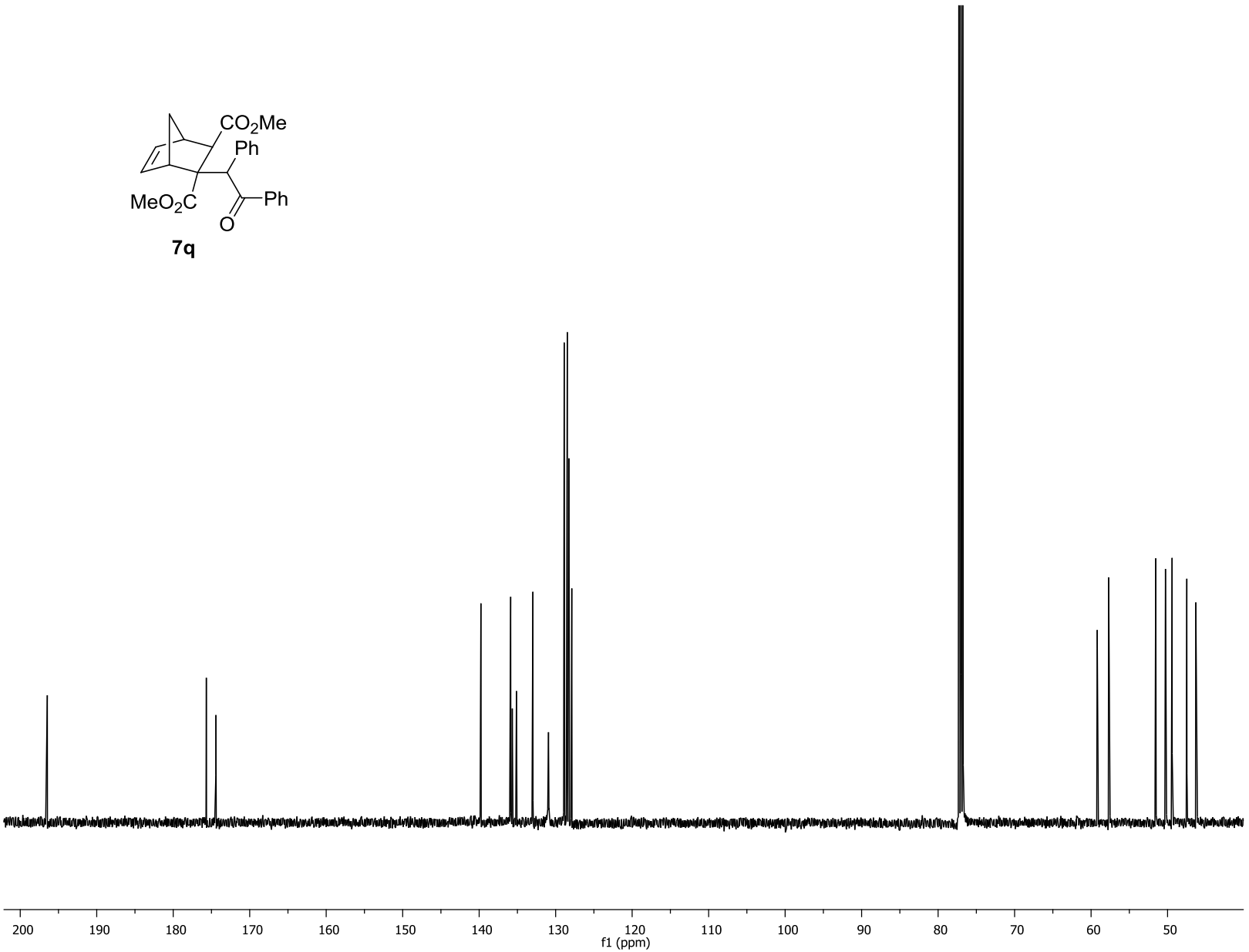


^{1}H NMR (500 MHz, $CDCl_3$):

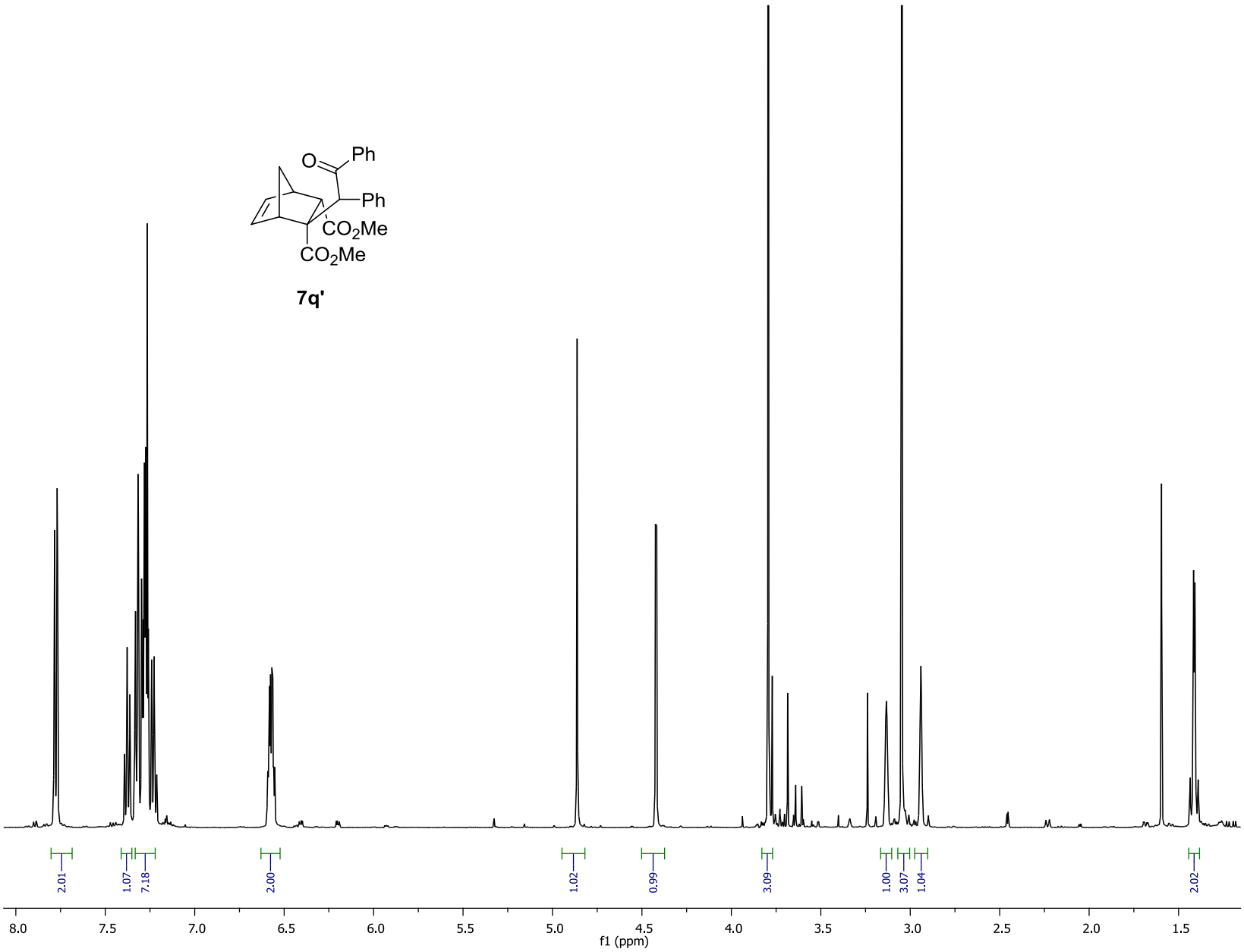


^{13}C NMR (500 MHz, $CDCl_3$):

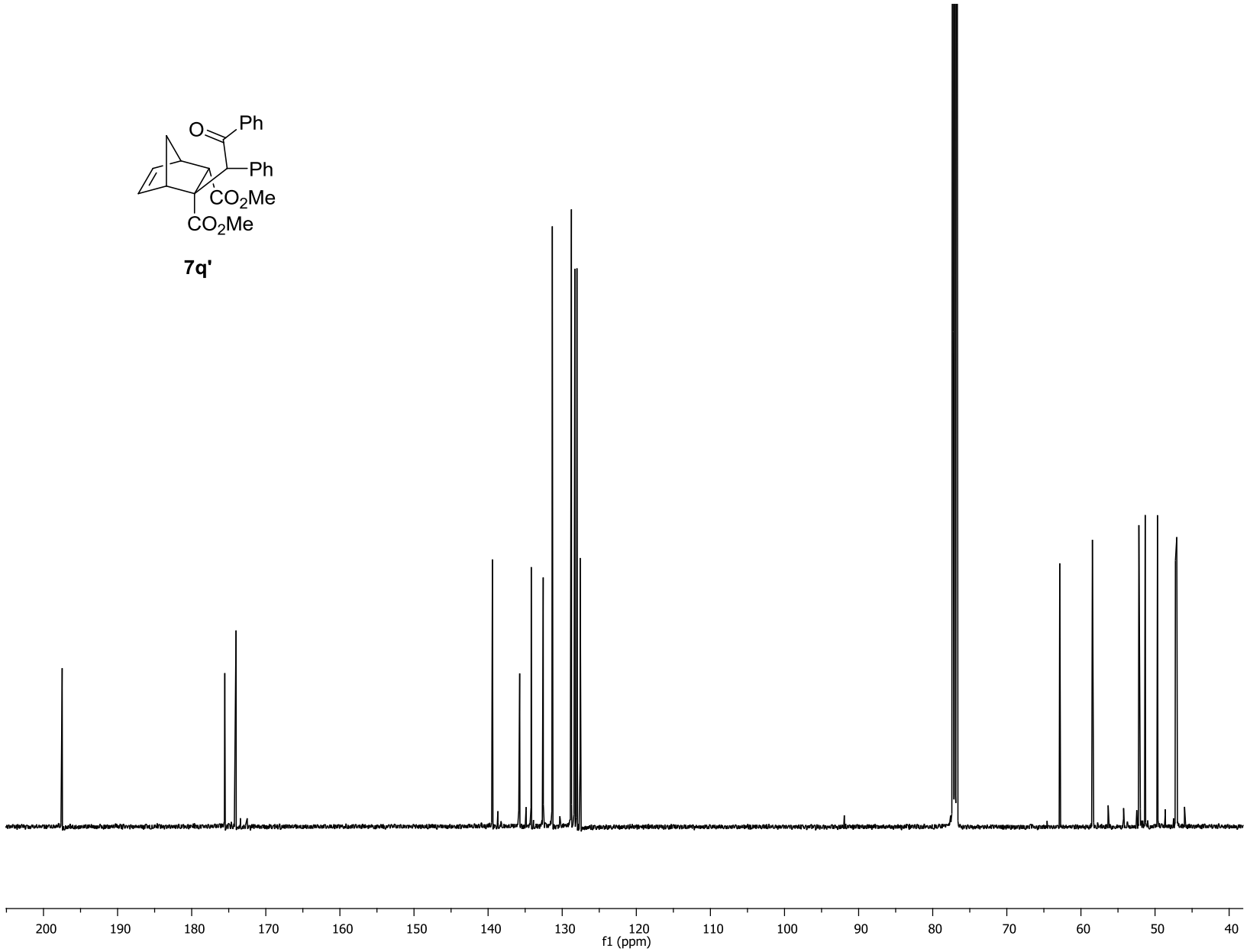
7q



^{1}H NMR (500 MHz, $CDCl_3$):



^{13}C NMR (500 MHz, $CDCl_3$):



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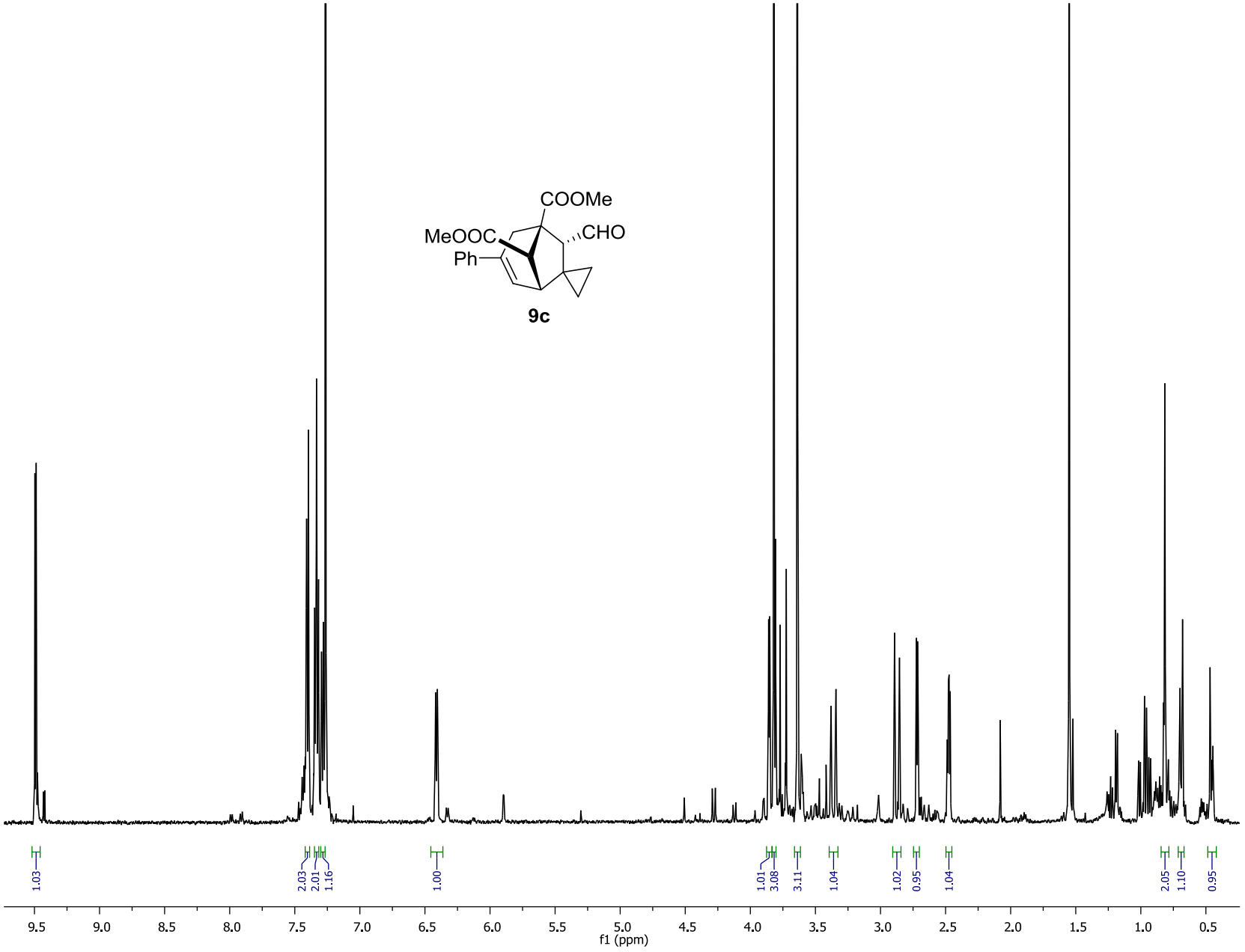
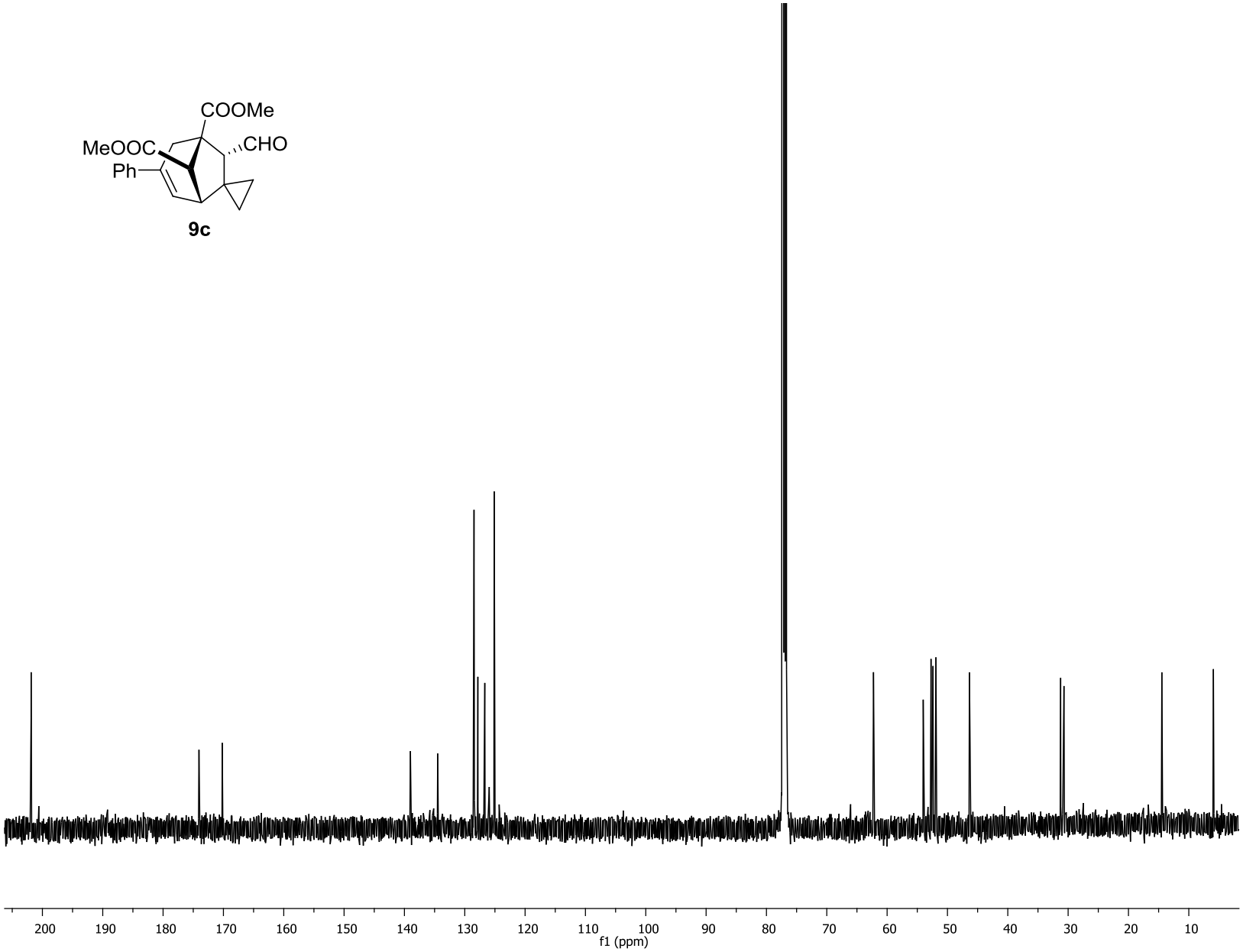
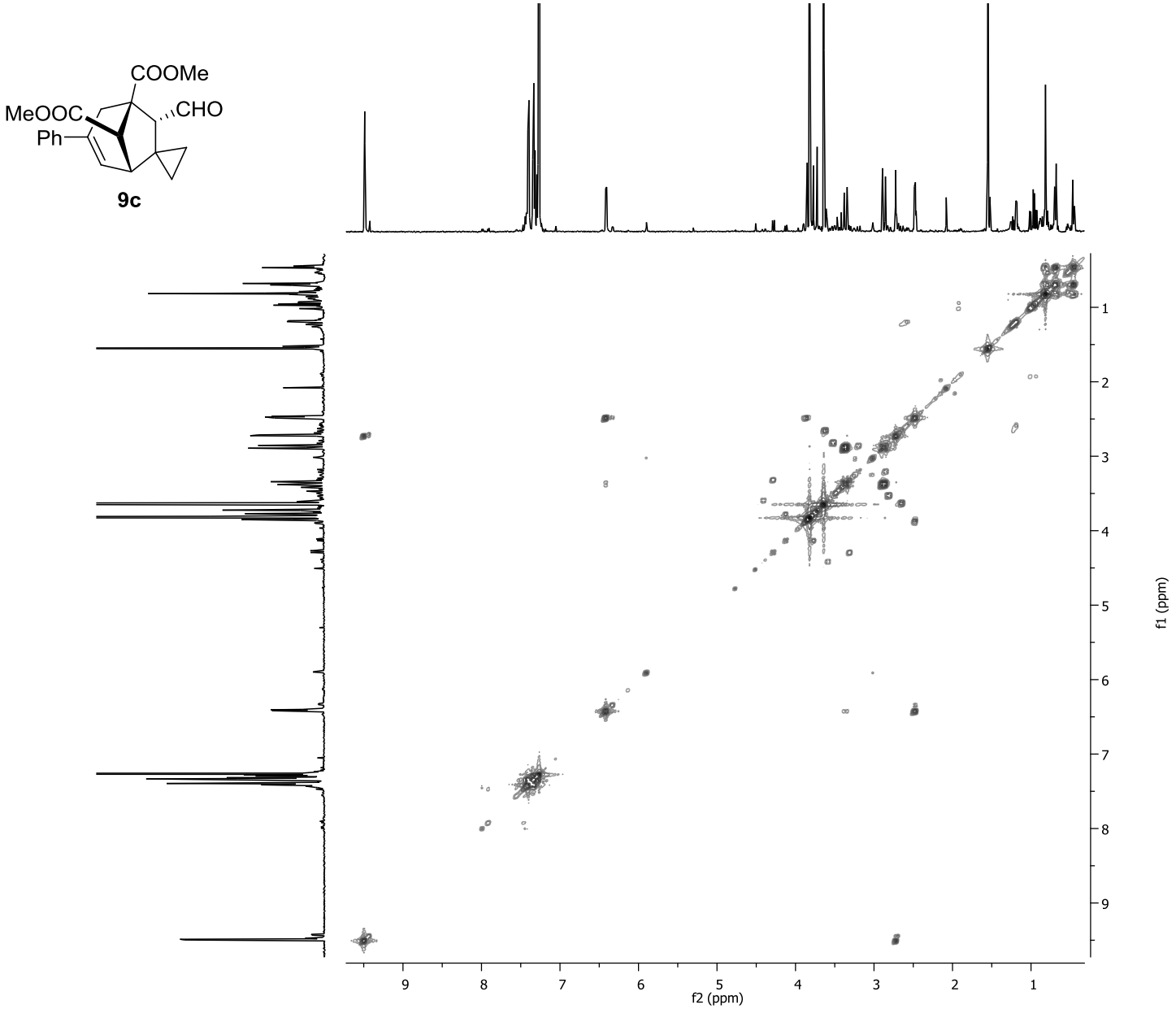


^{13}C NMR (500 MHz, $CDCl_3$):

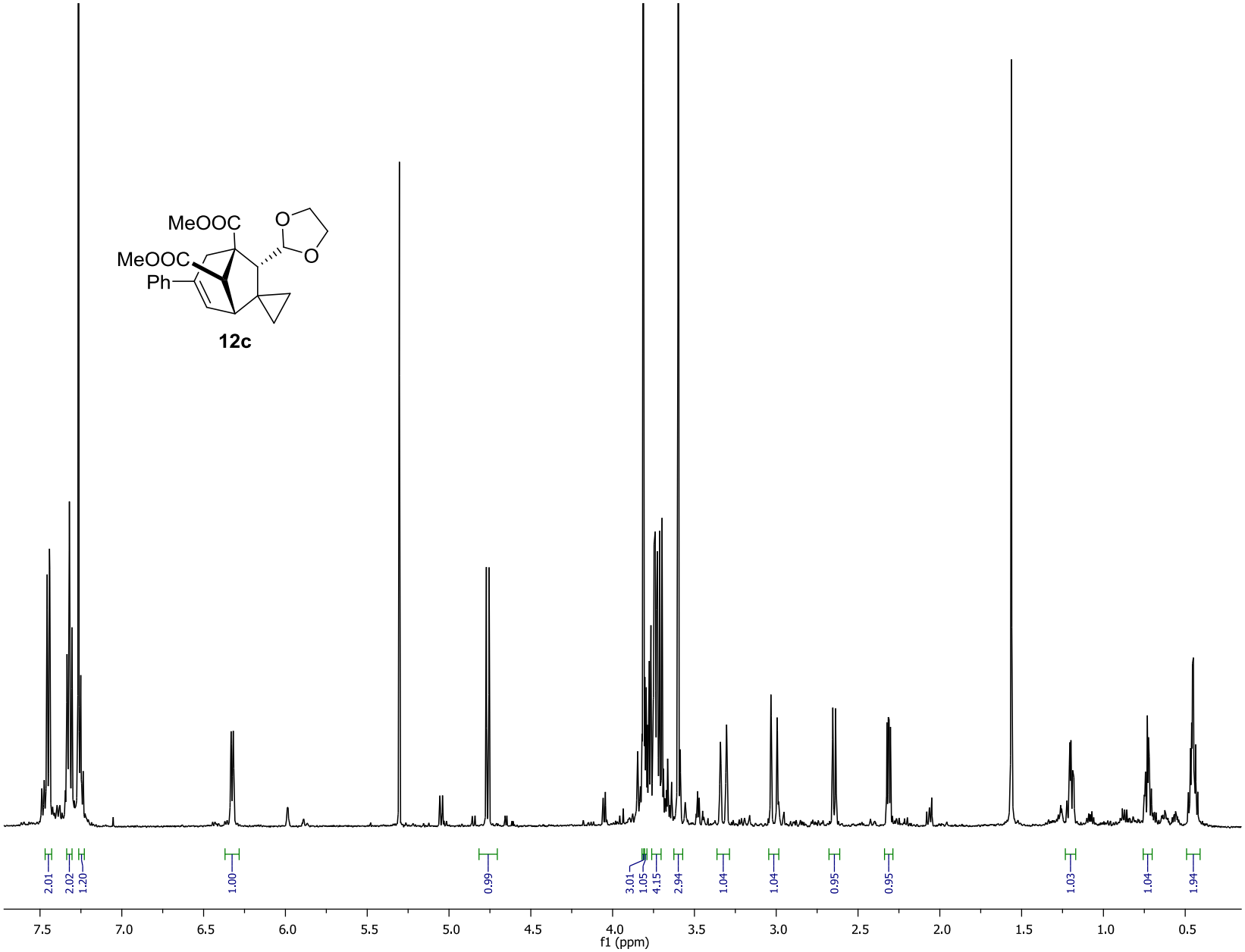
9c



COSY (500 MHz, $CDCl_3$):

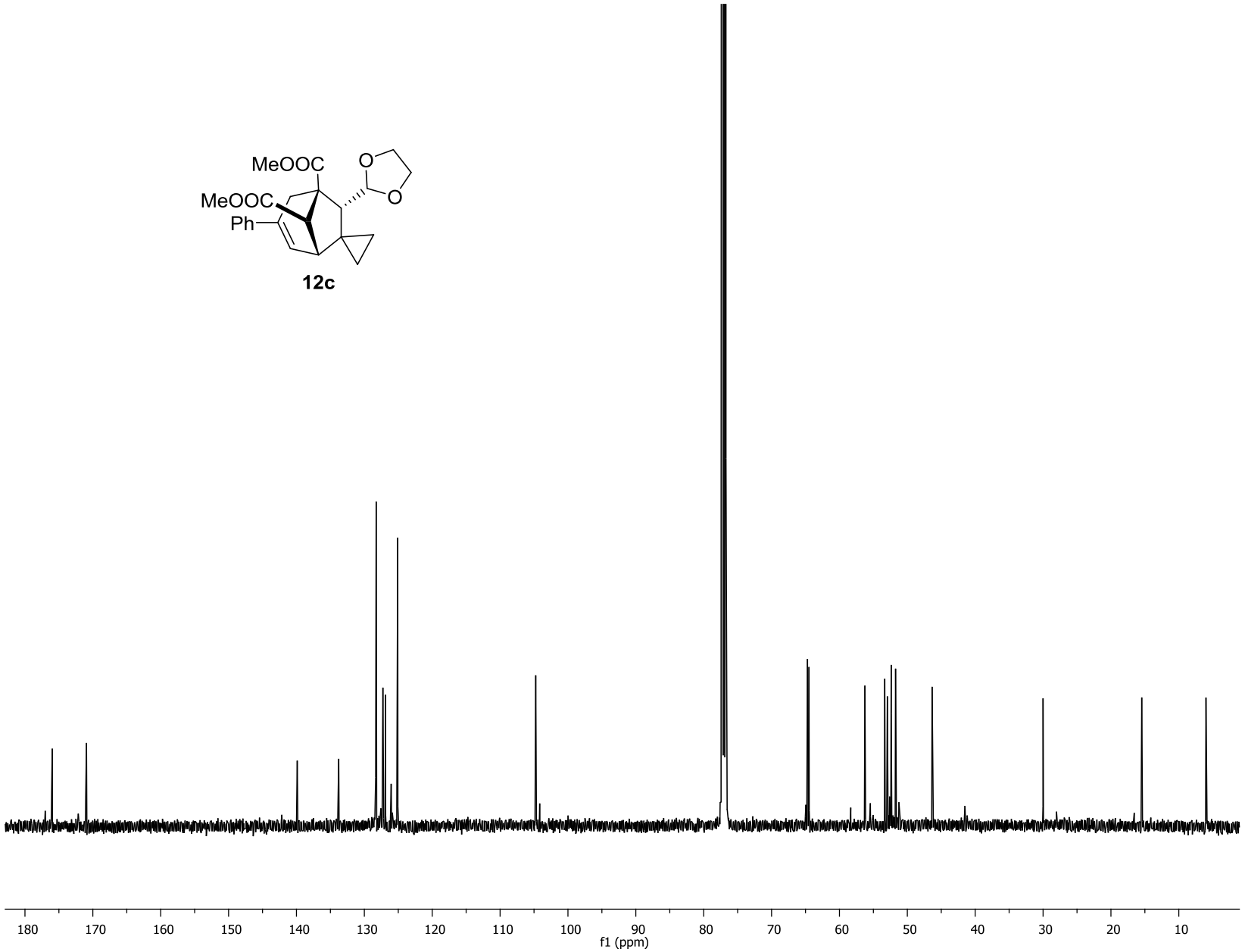


^{1}H NMR (500 MHz, $CDCl_3$):



^{13}C NMR (500 MHz, $CDCl_3$):

12c



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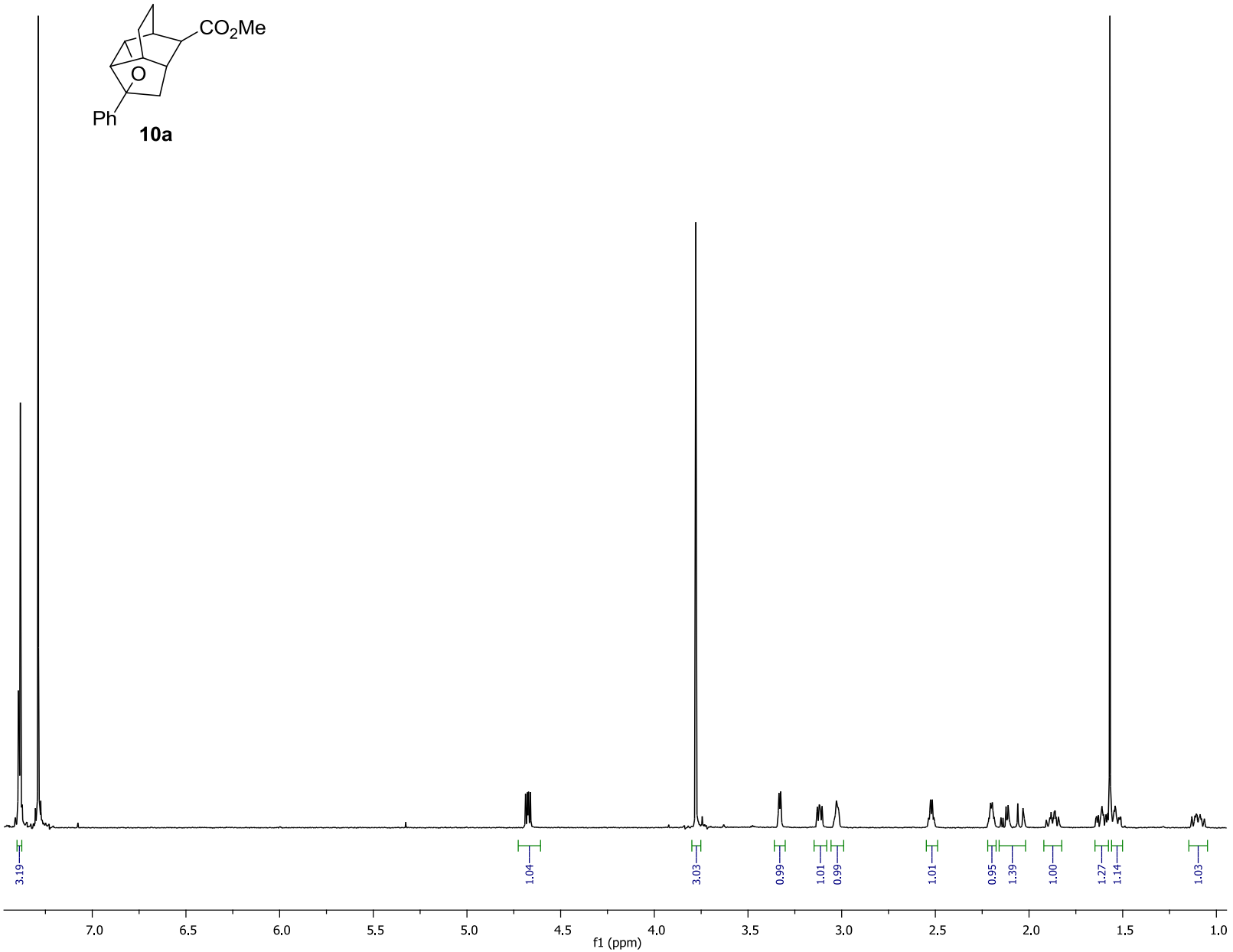
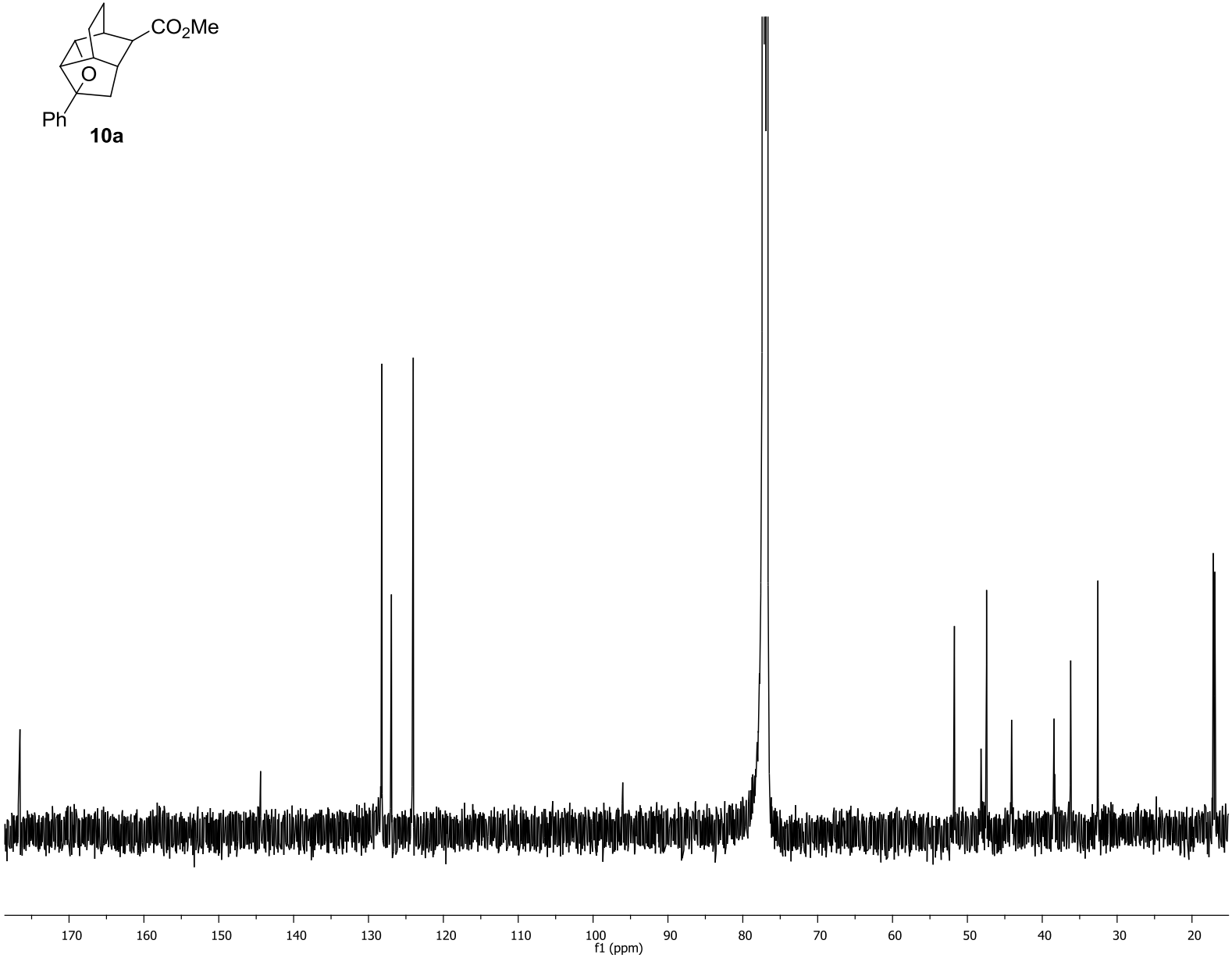
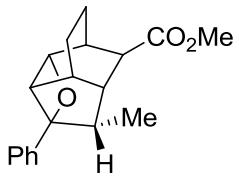


^{13}C NMR (500 MHz, $CDCl_3$):

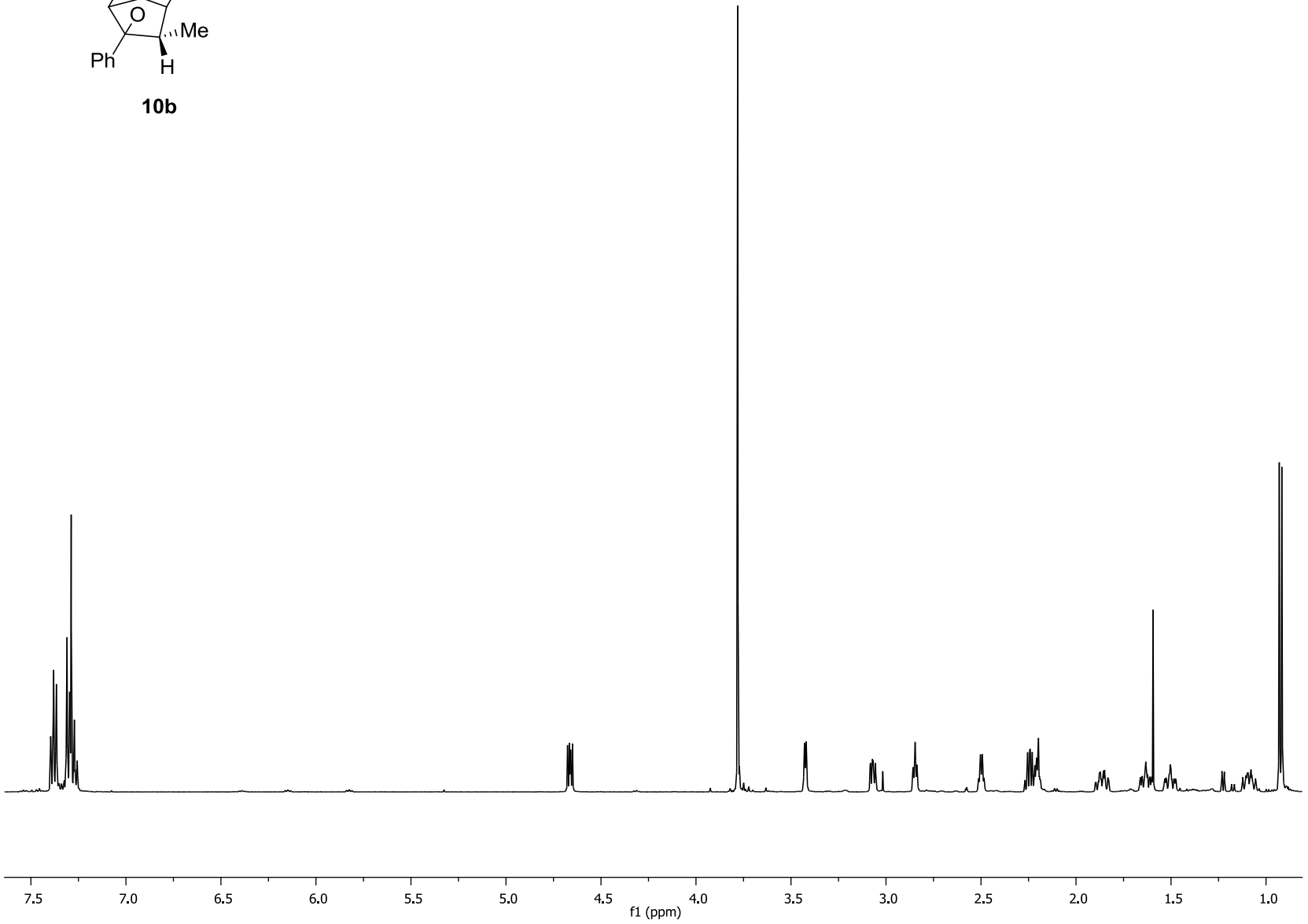
10a



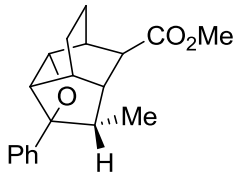
^{1}H NMR (500 MHz, $CDCl_3$):



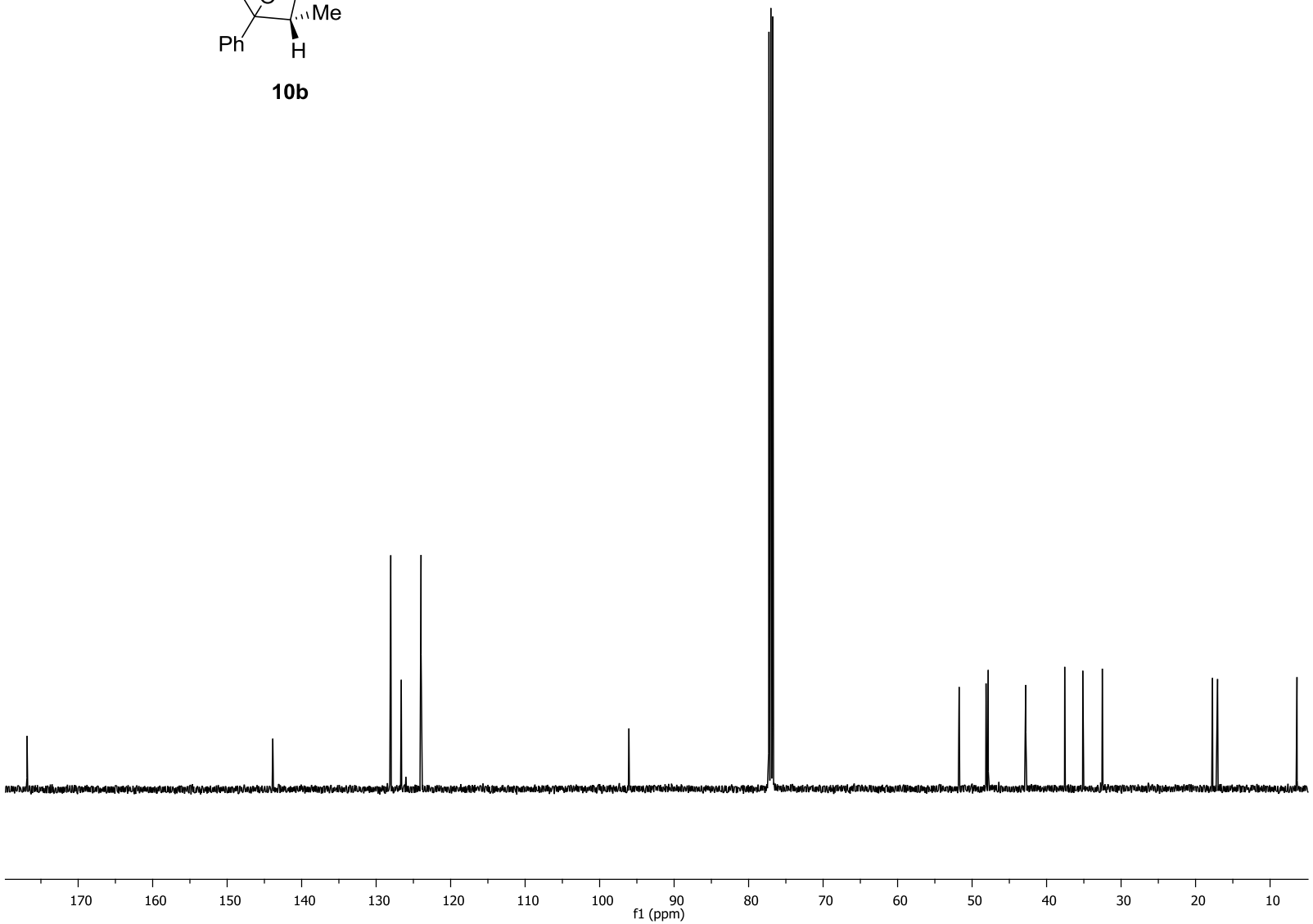
10b



^{13}C NMR (500 MHz, $CDCl_3$):



10b



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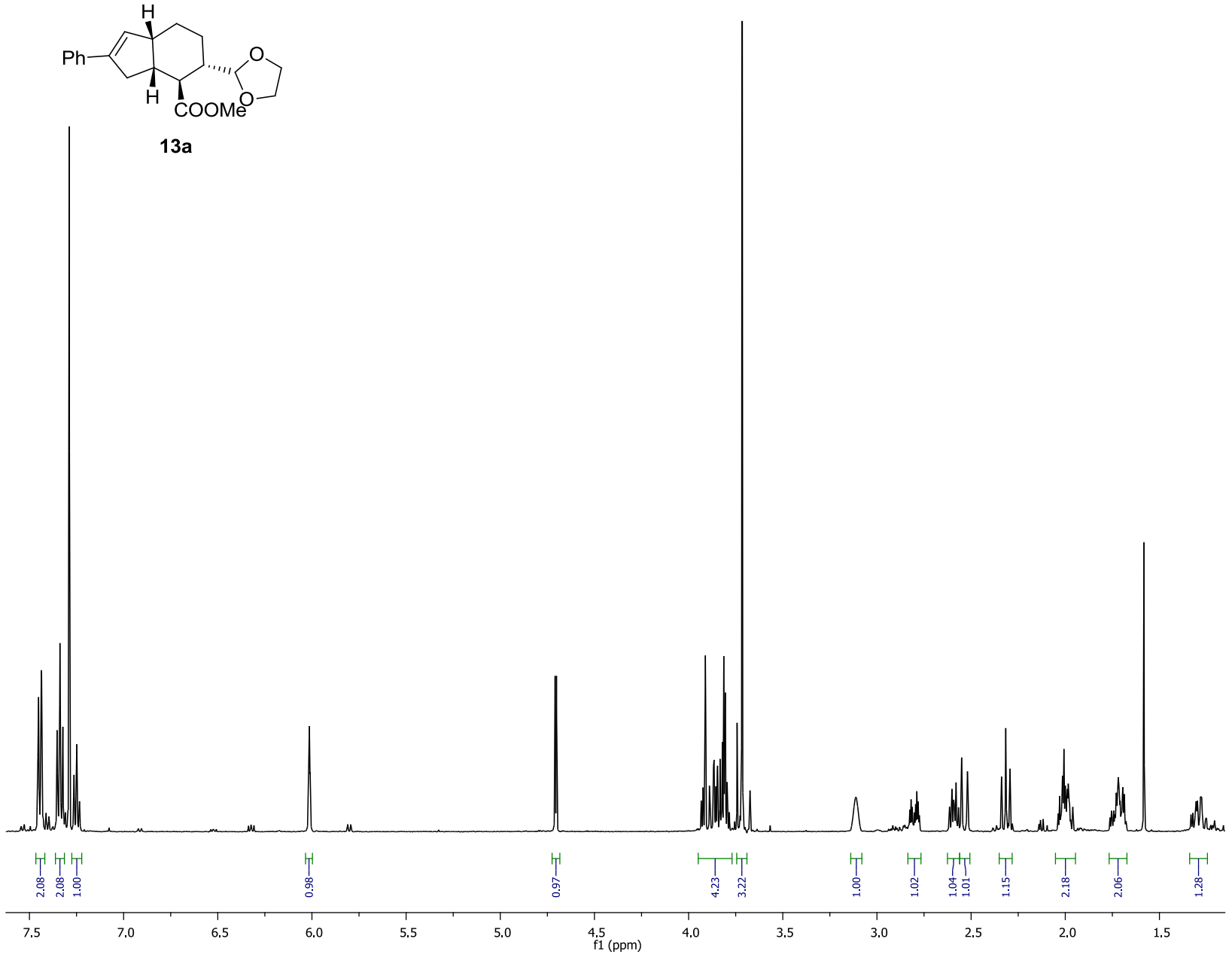
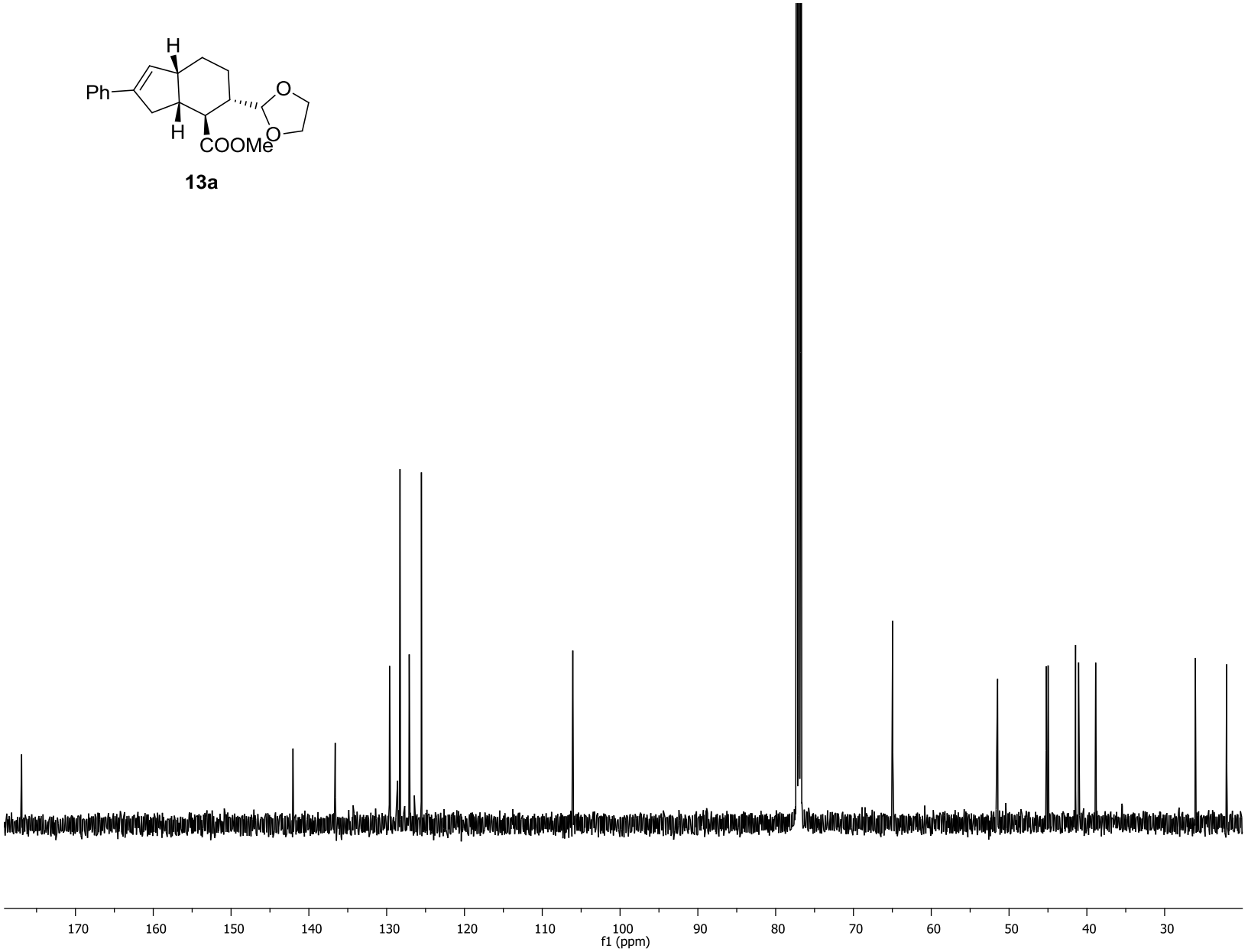
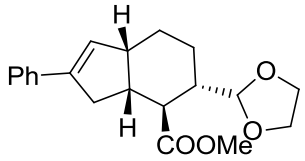


^{13}C NMR (500 MHz, $CDCl_3$):

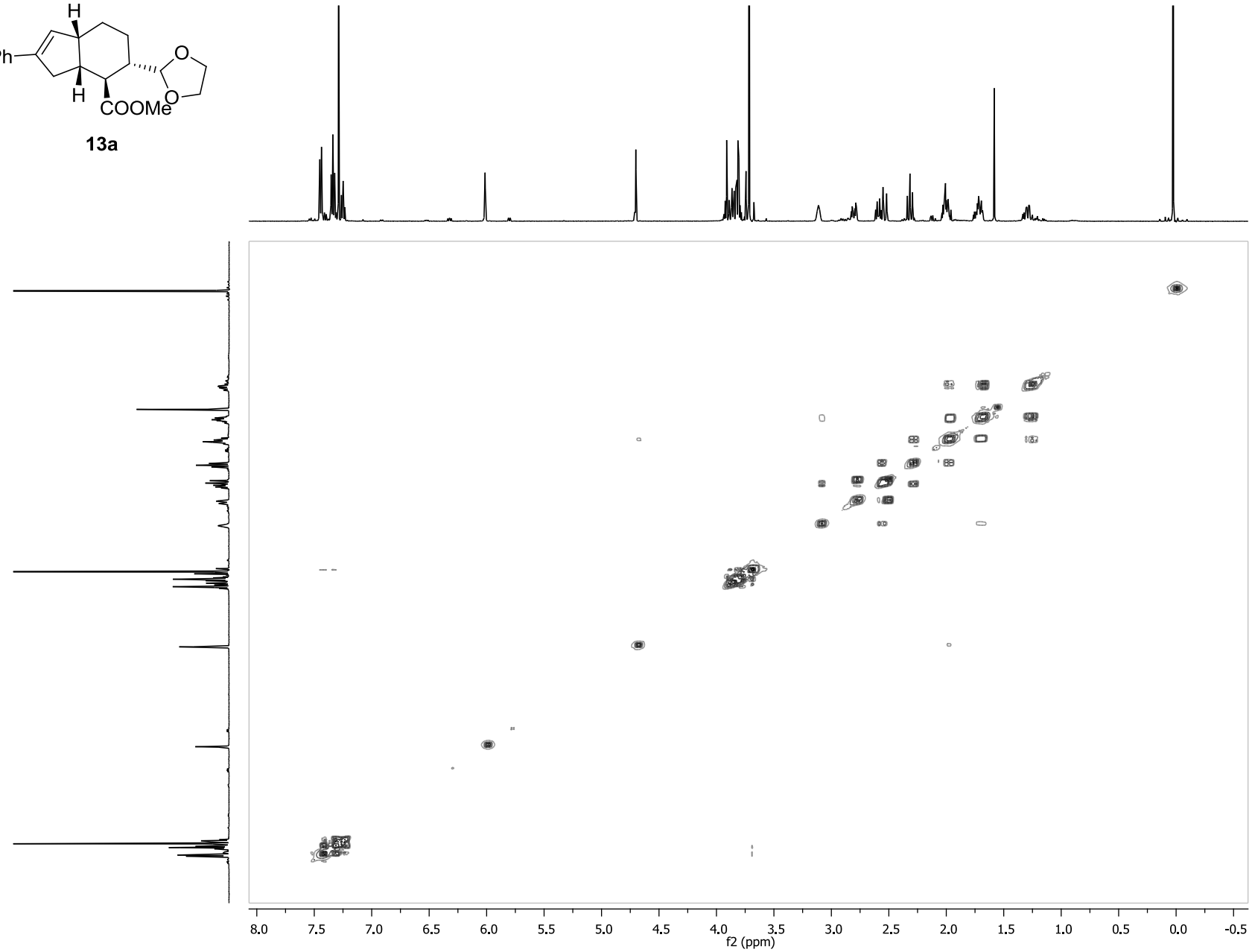
13a



COSY (500 MHz, $CDCl_3$):



13a



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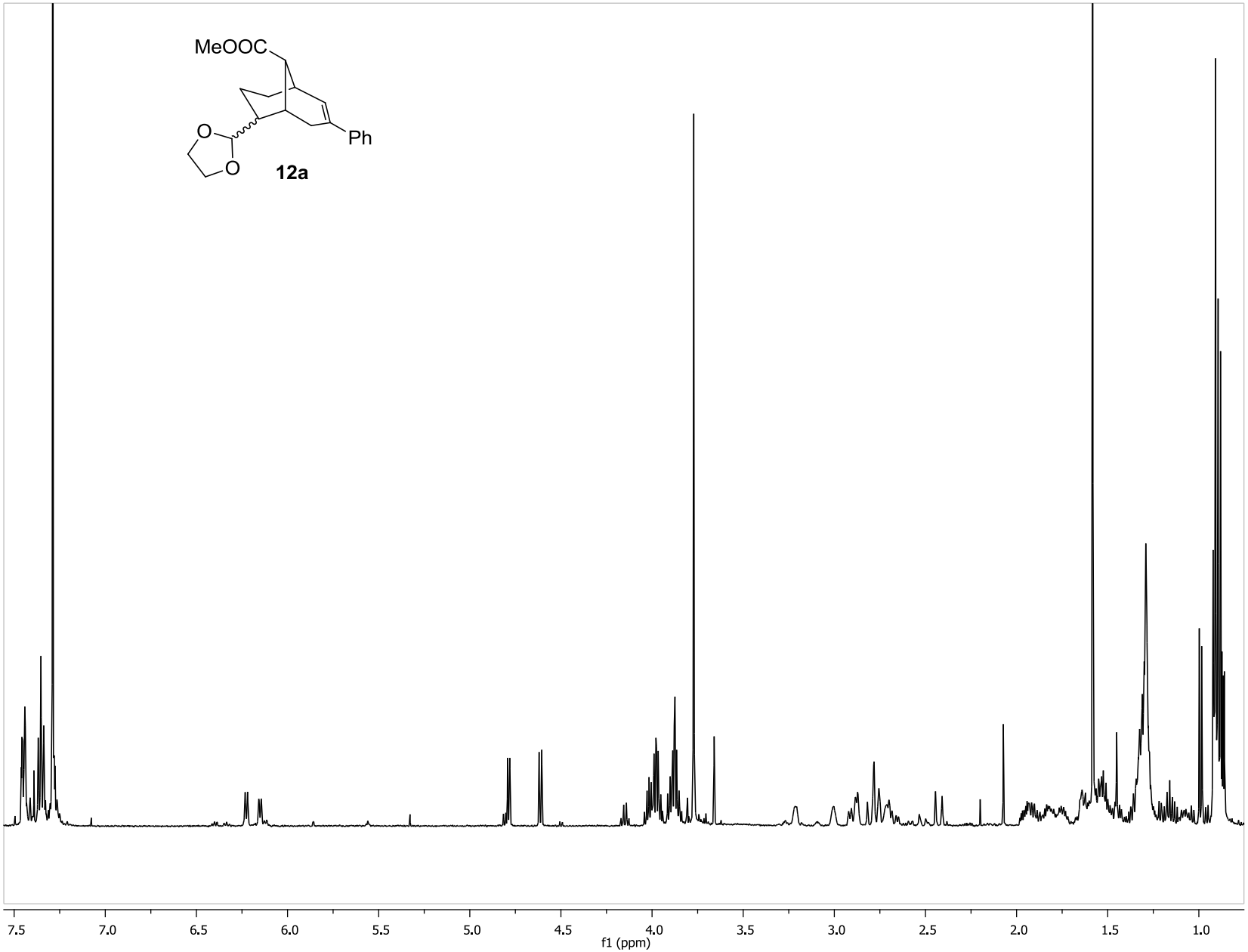
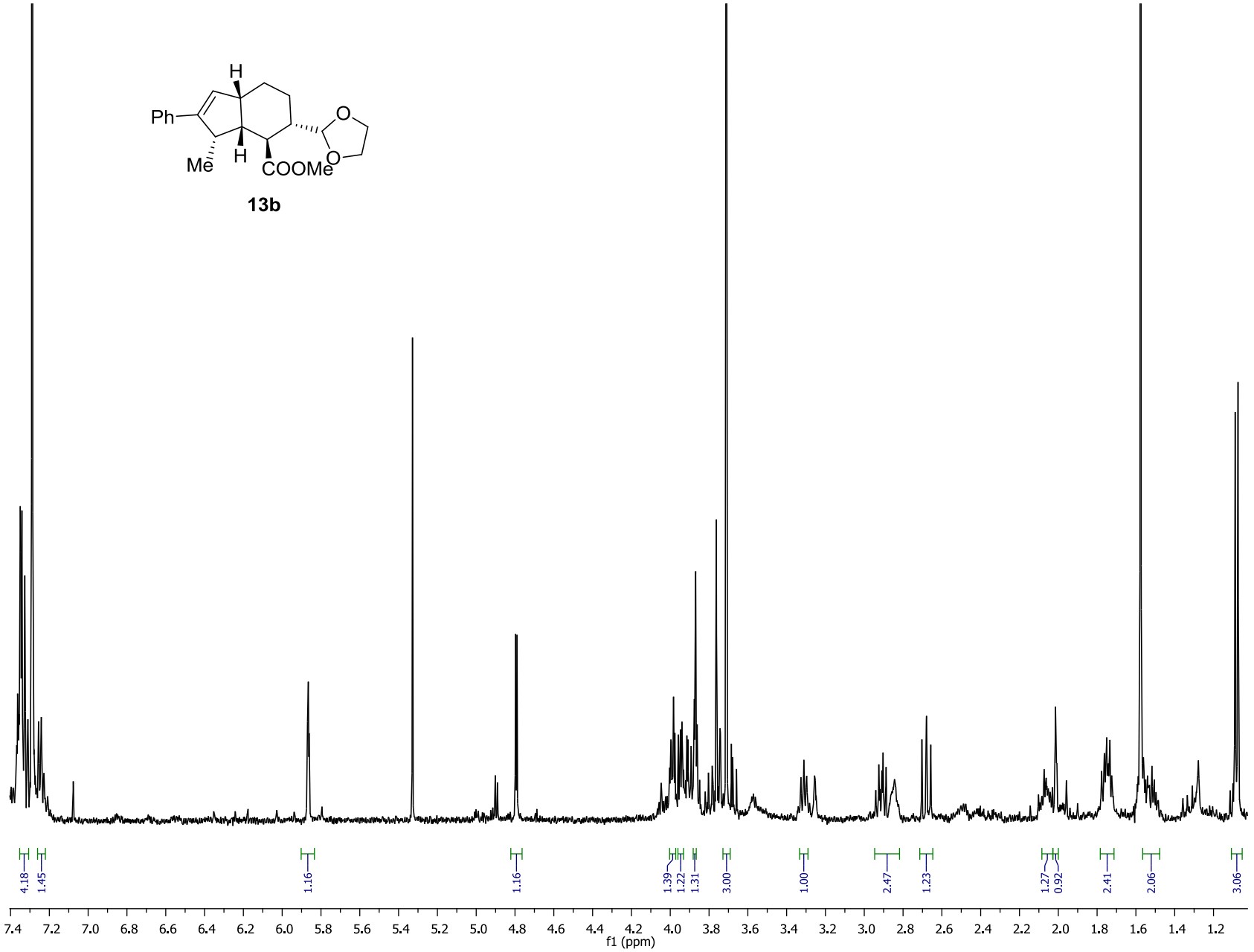


^{1}H NMR (500 MHz, $CDCl_3$):

13b



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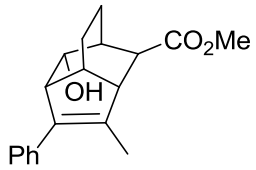
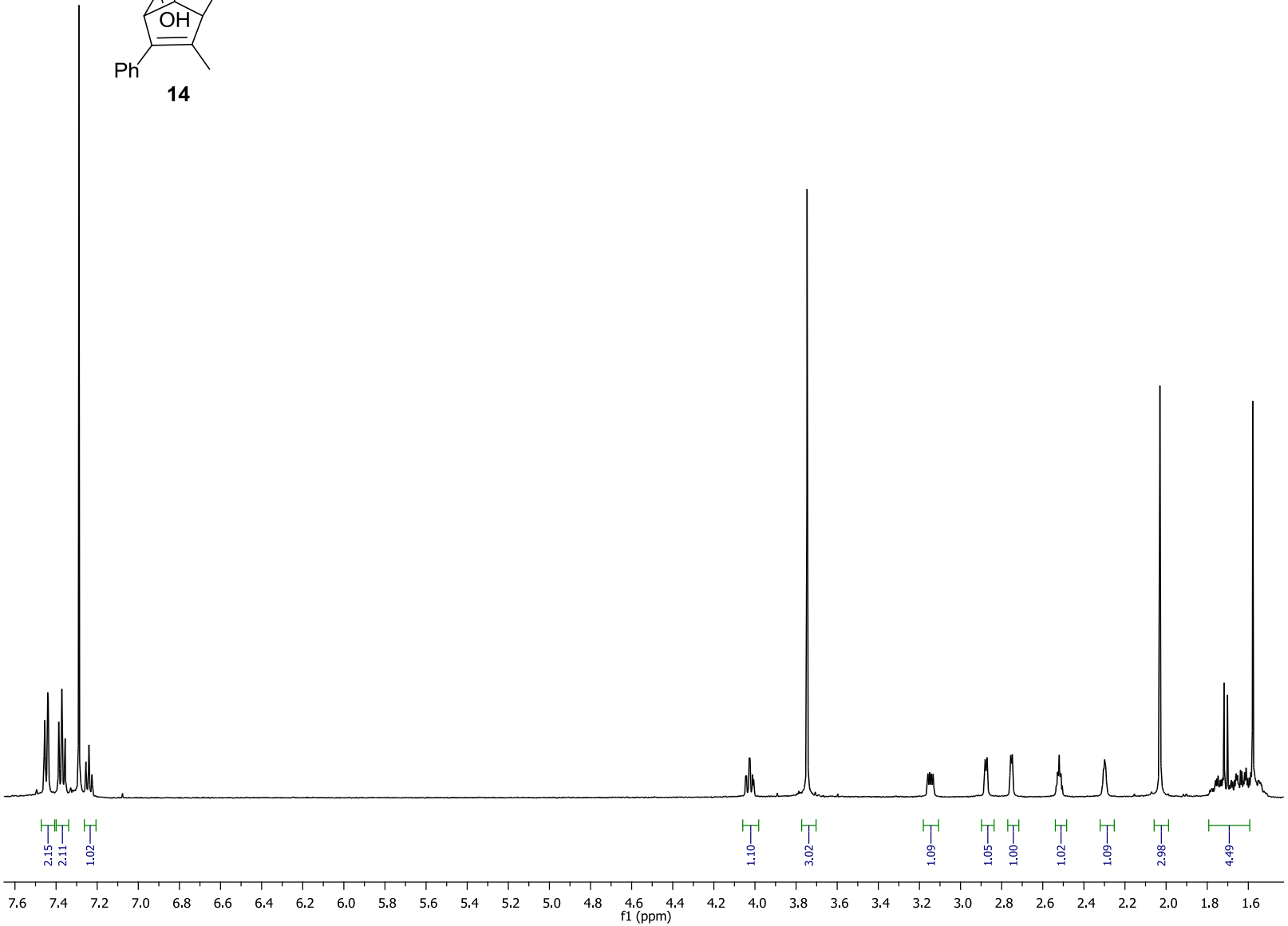
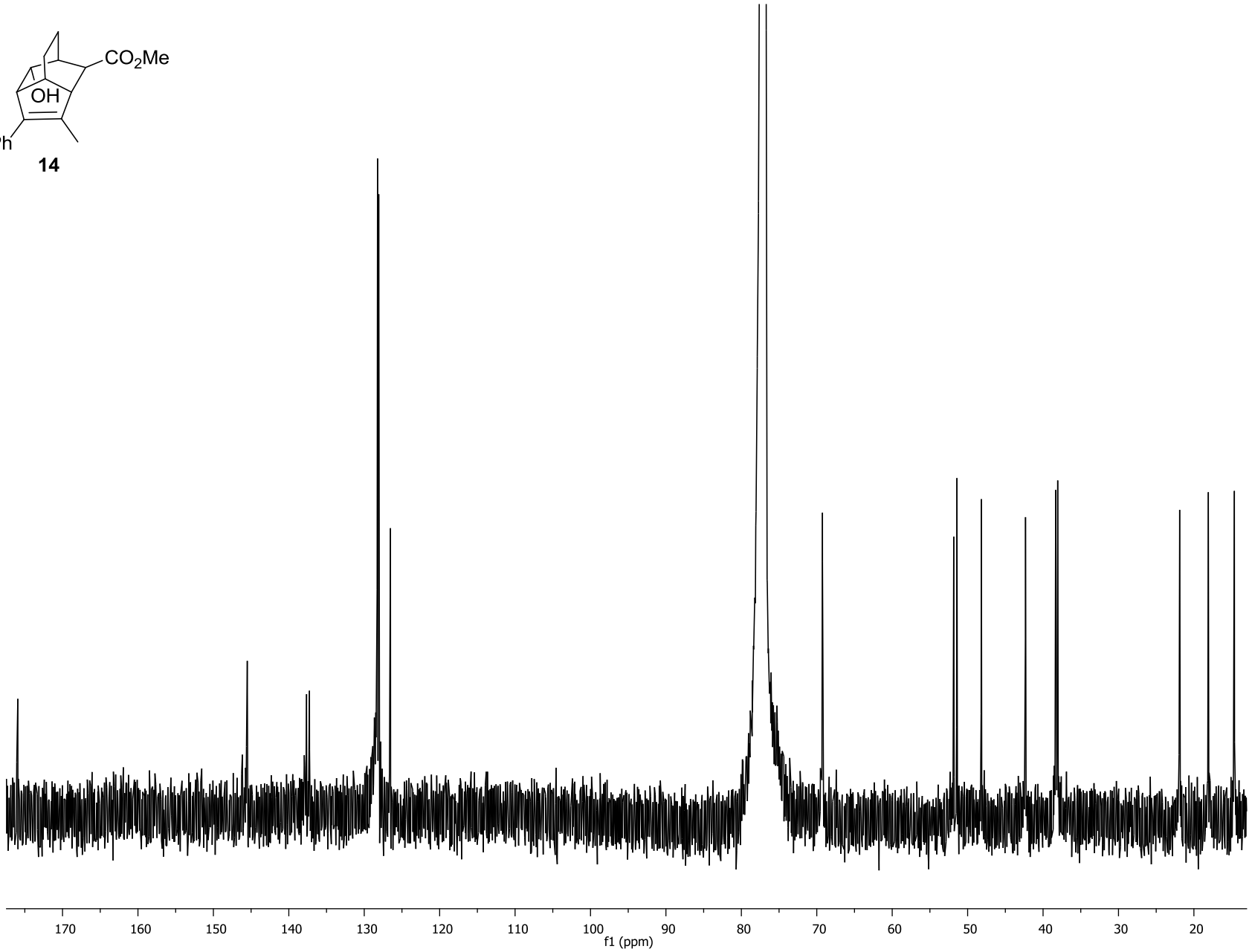


14

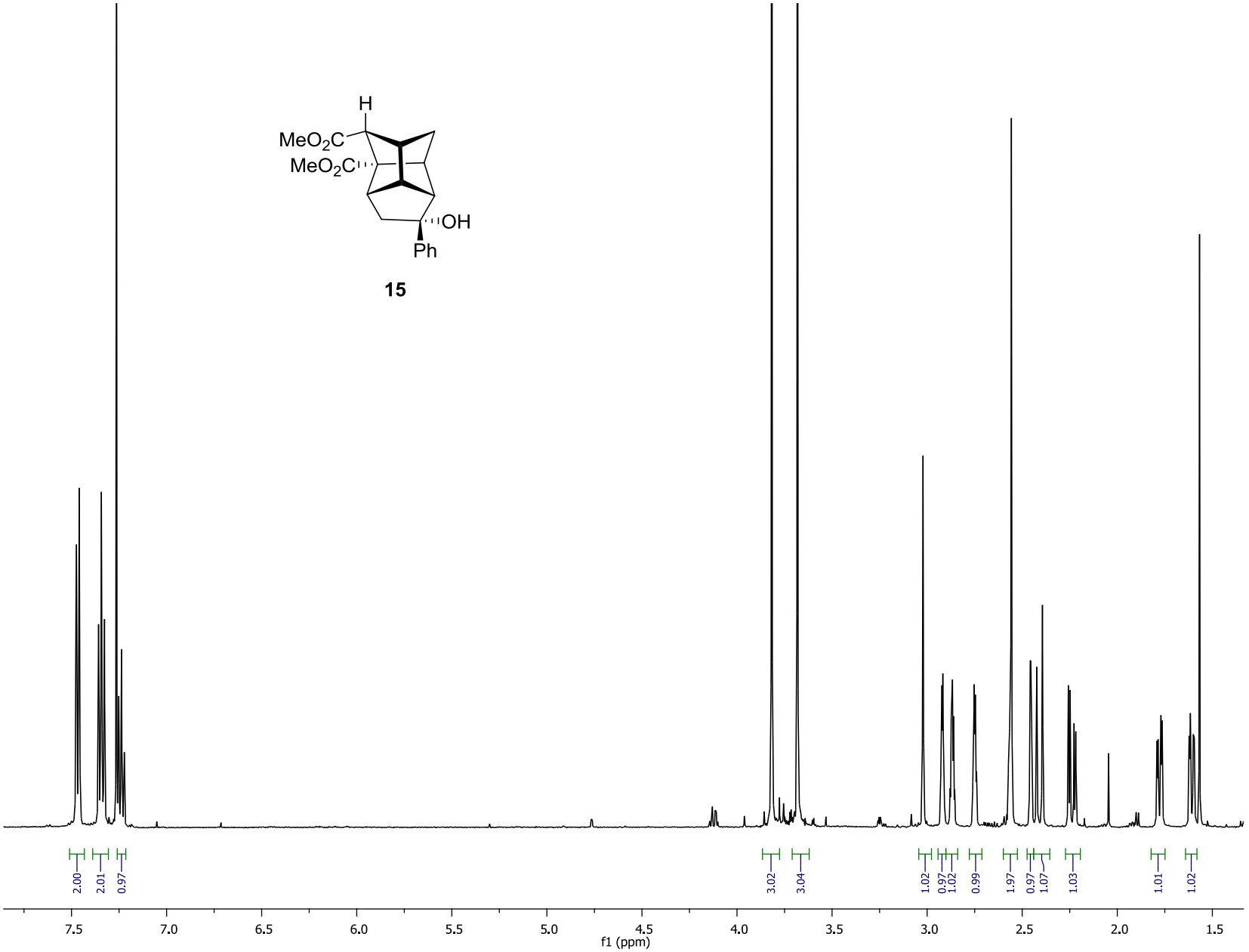


^{13}C NMR (500 MHz, $CDCl_3$):

14

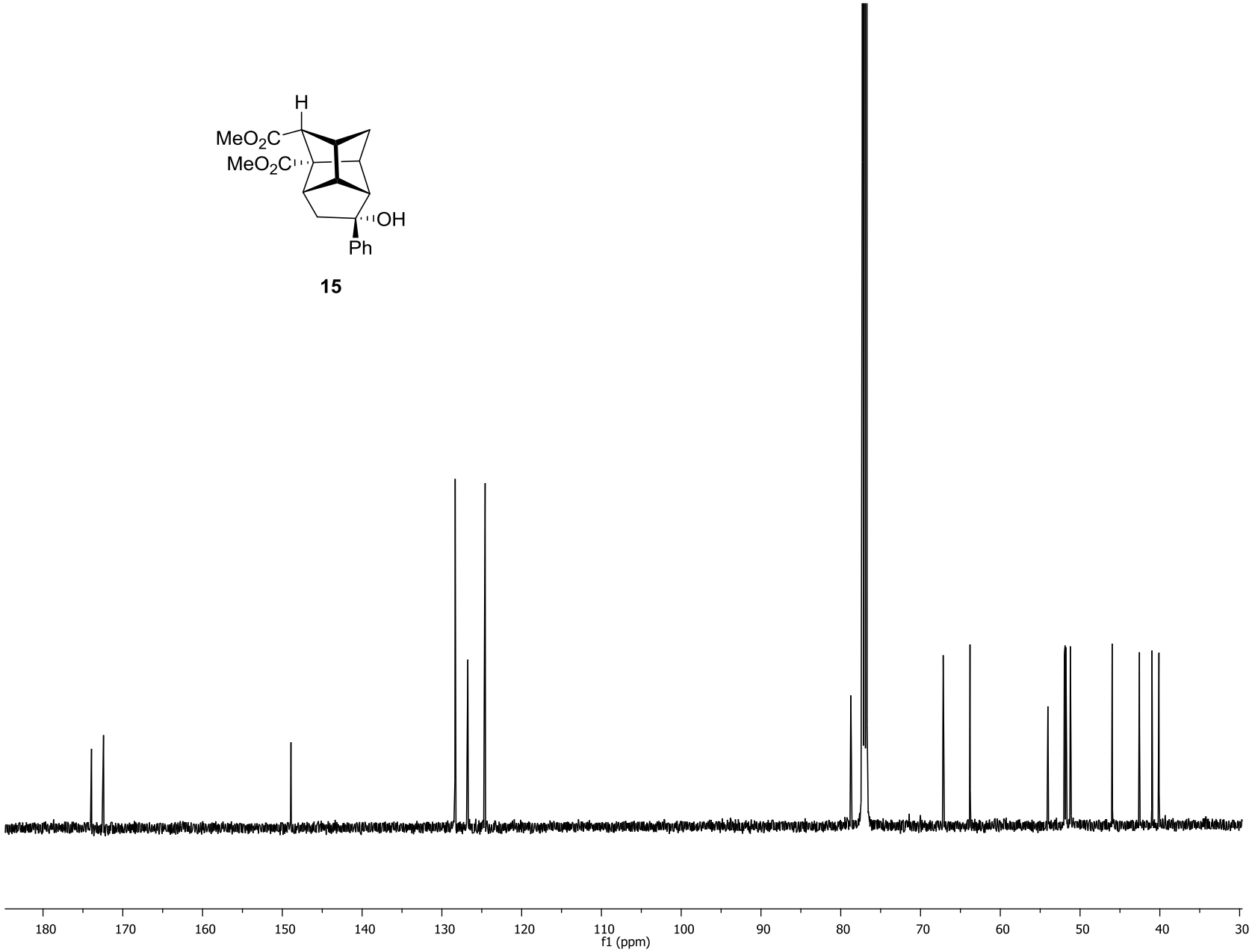


^{1}H NMR (500 MHz, $CDCl_3$):

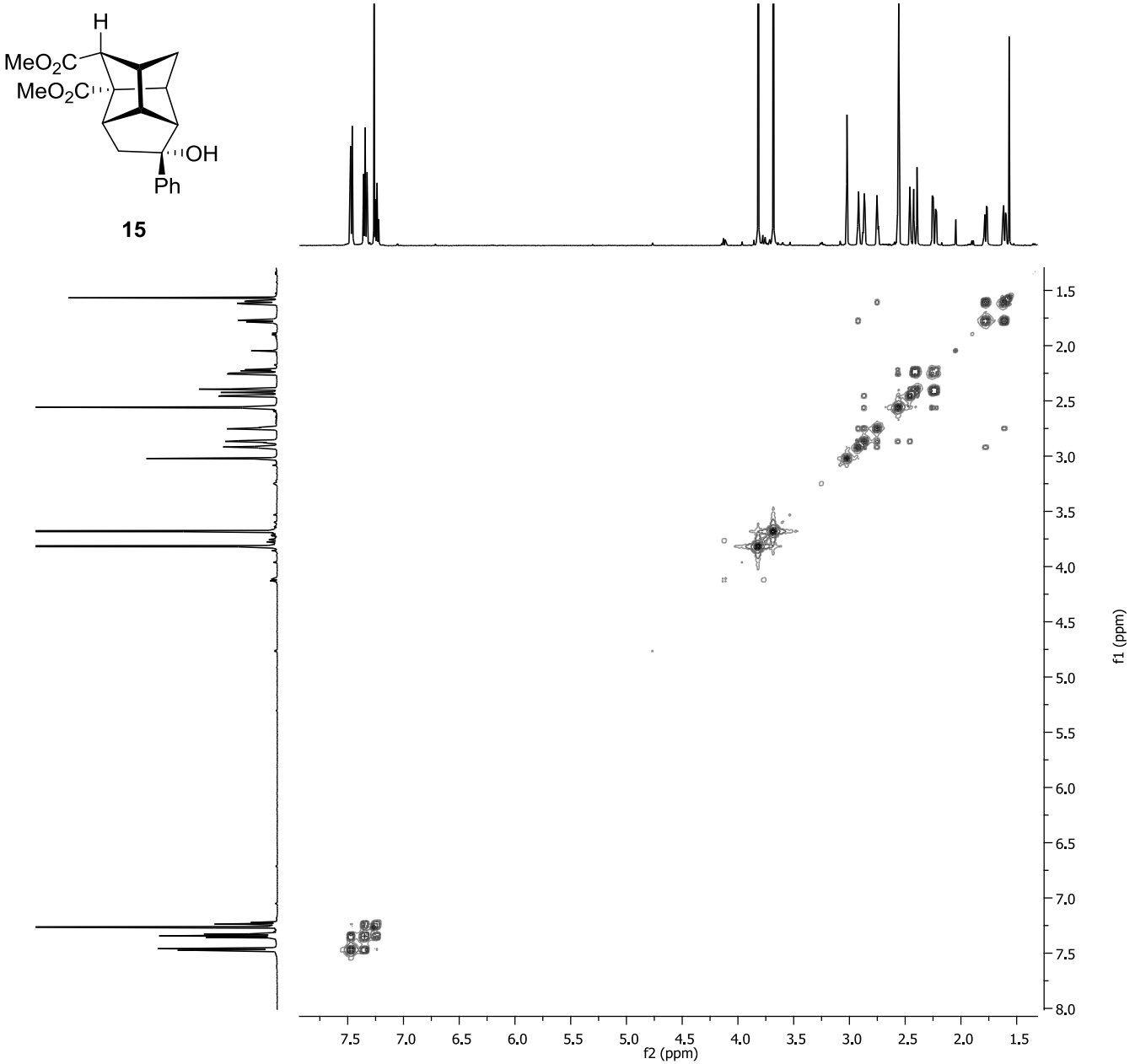


^{13}C NMR (500 MHz, $CDCl_3$):

15



COSY (500 MHz, $CDCl_3$):



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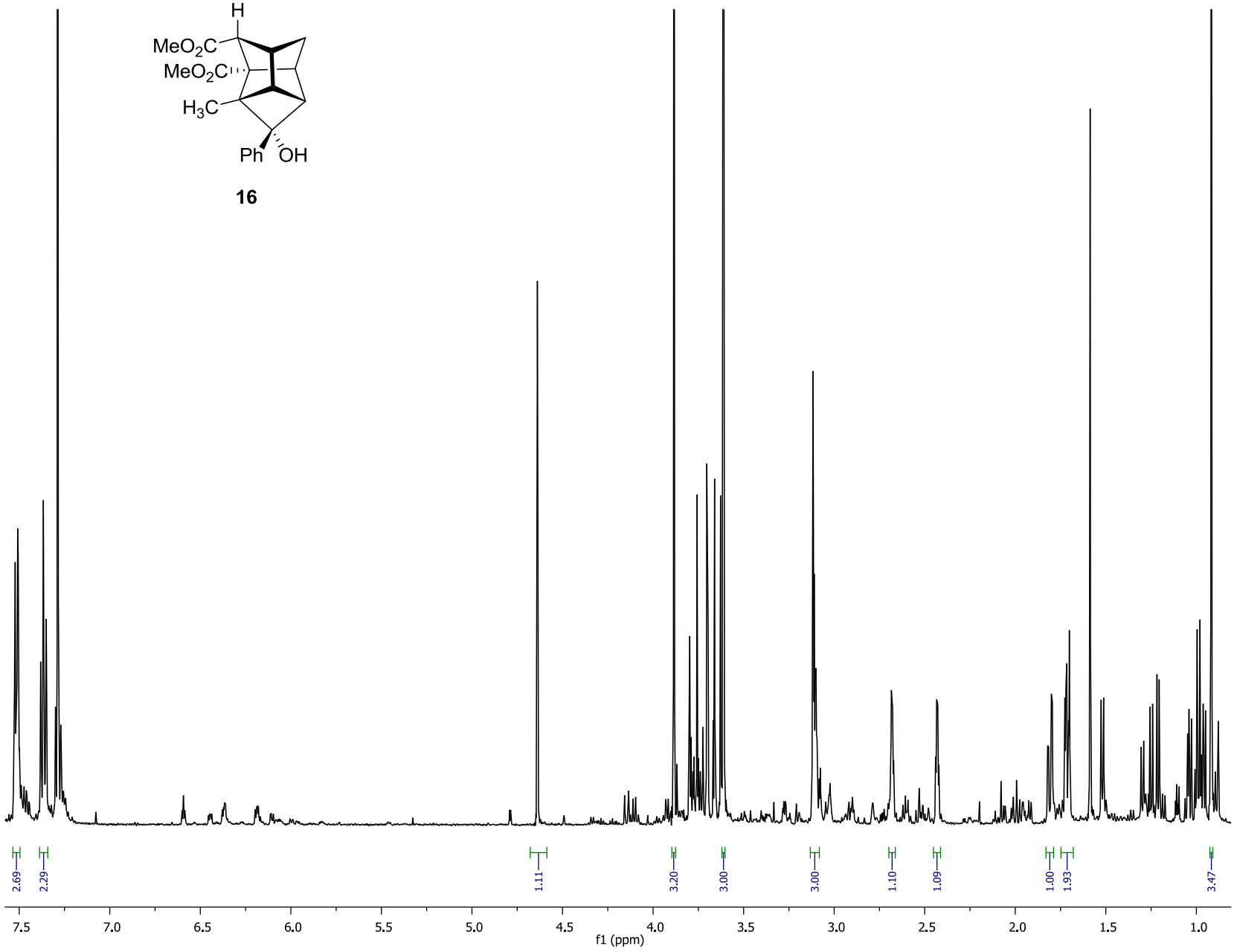

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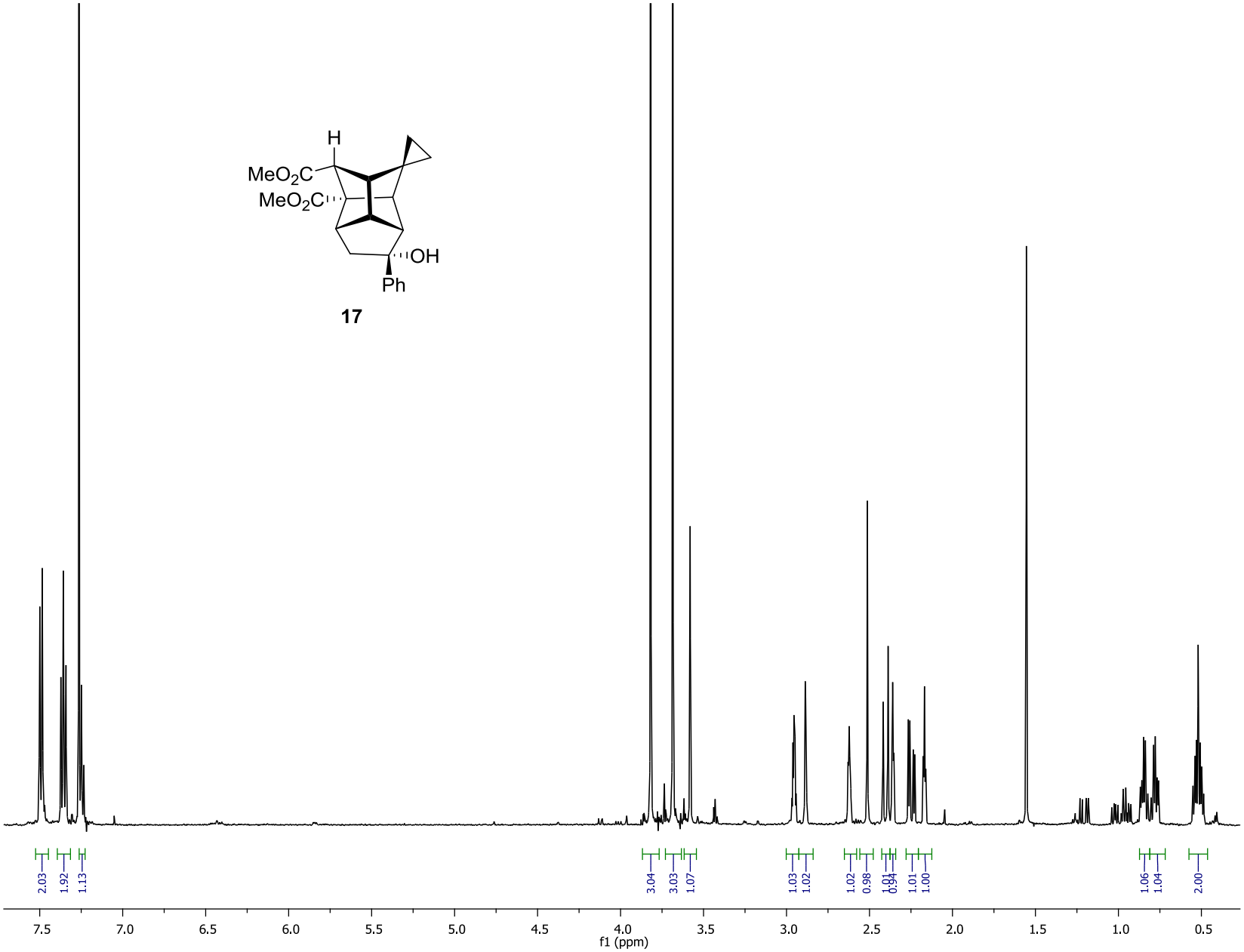
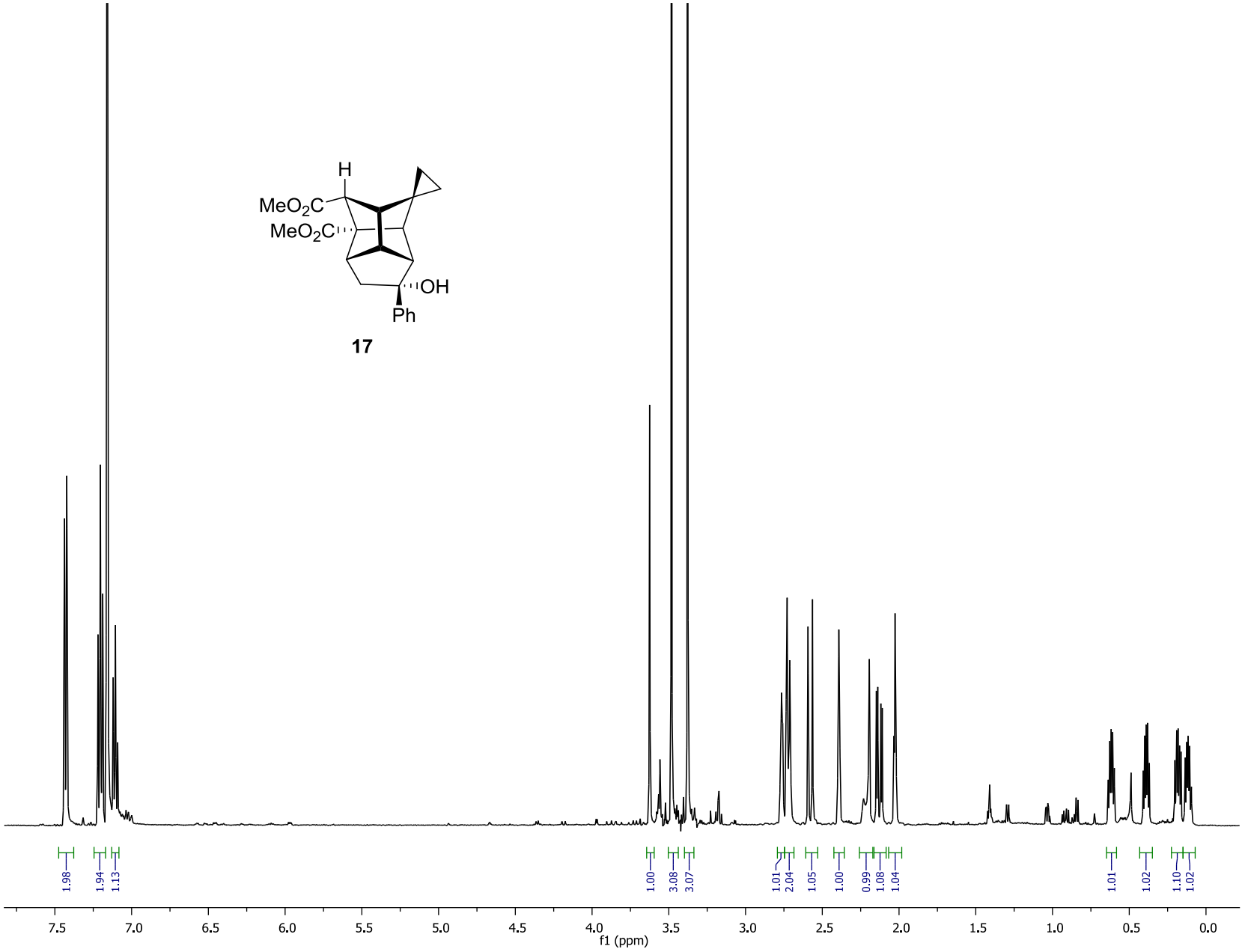


^{1}H NMR (500 MHz, C_6D_6):



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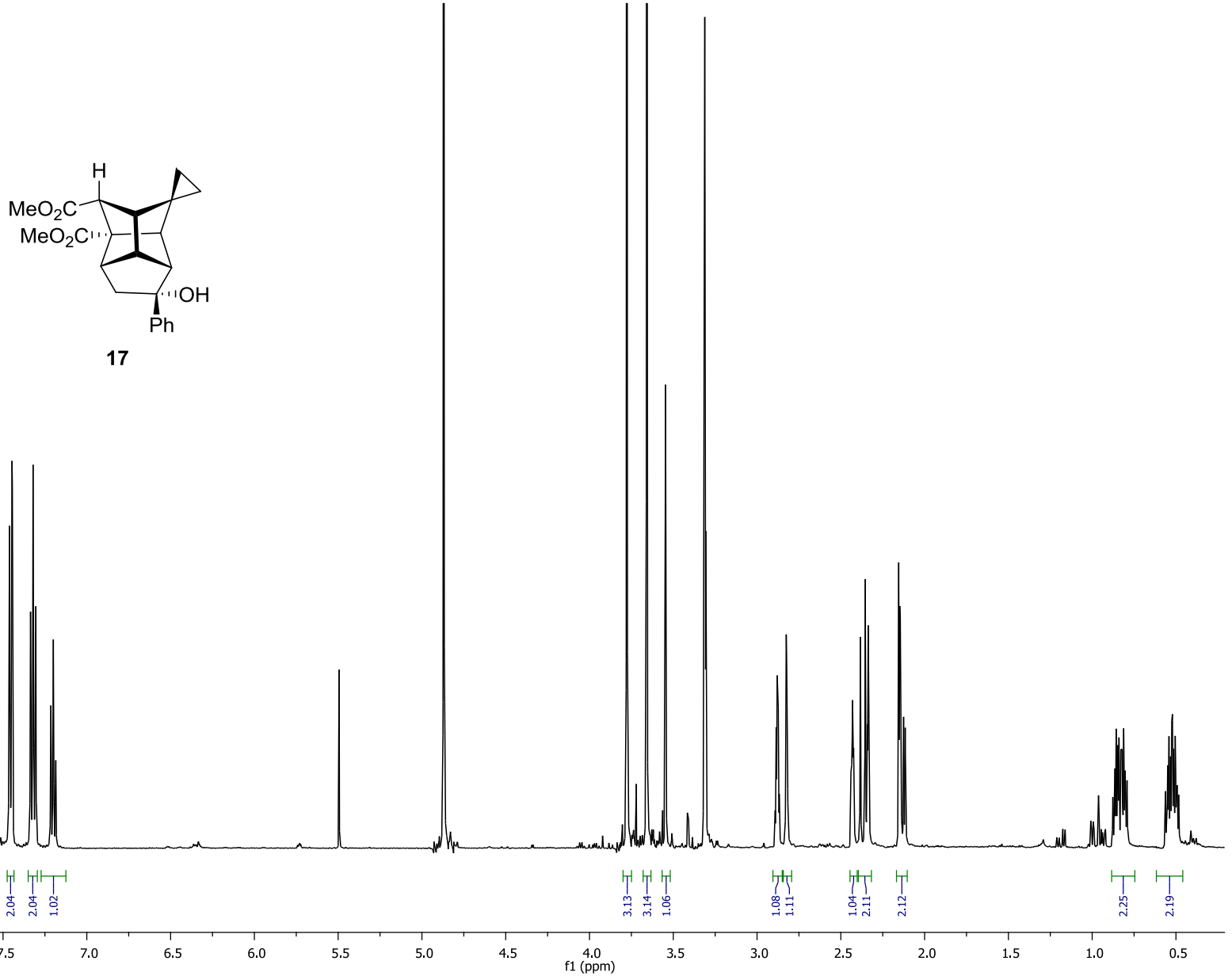
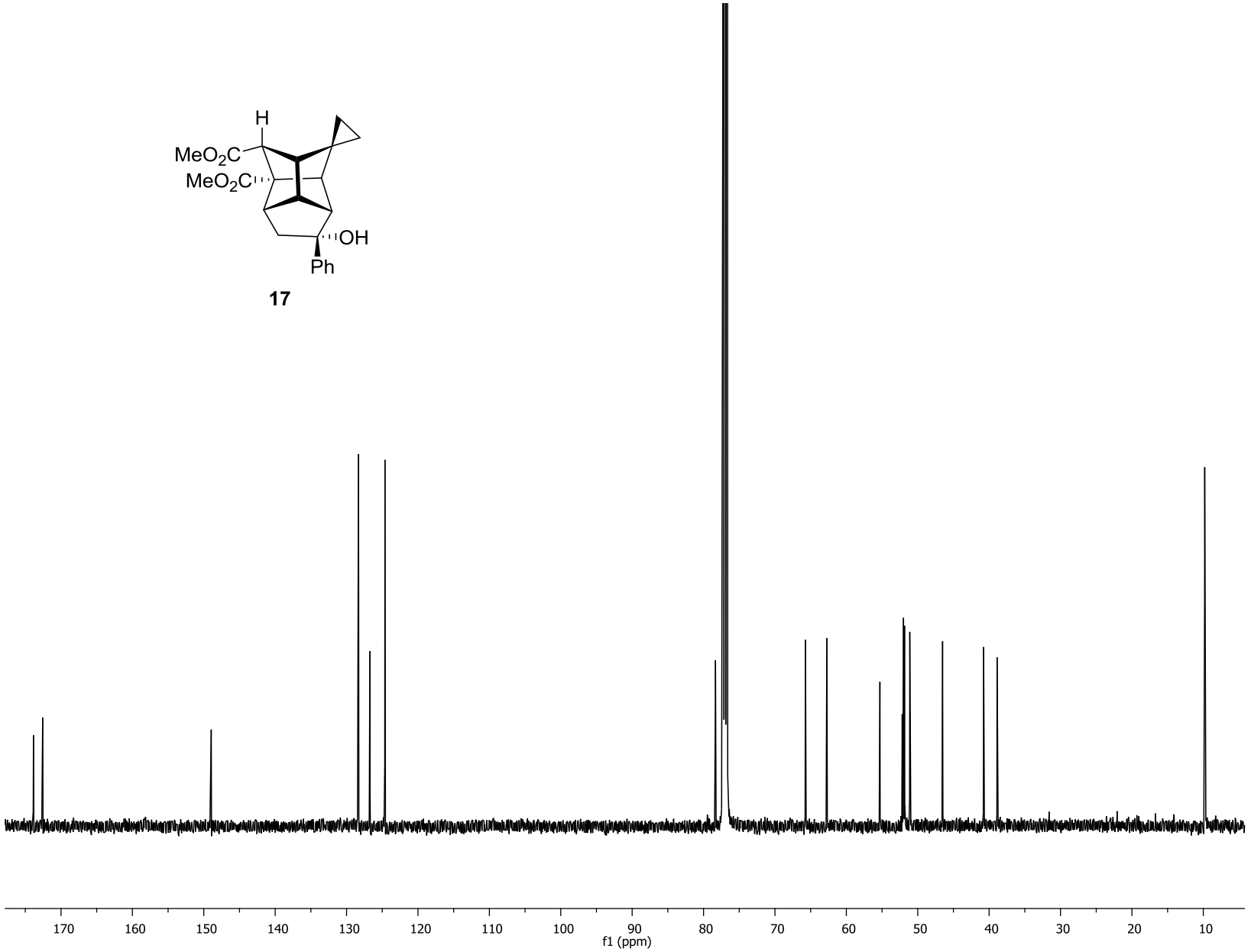


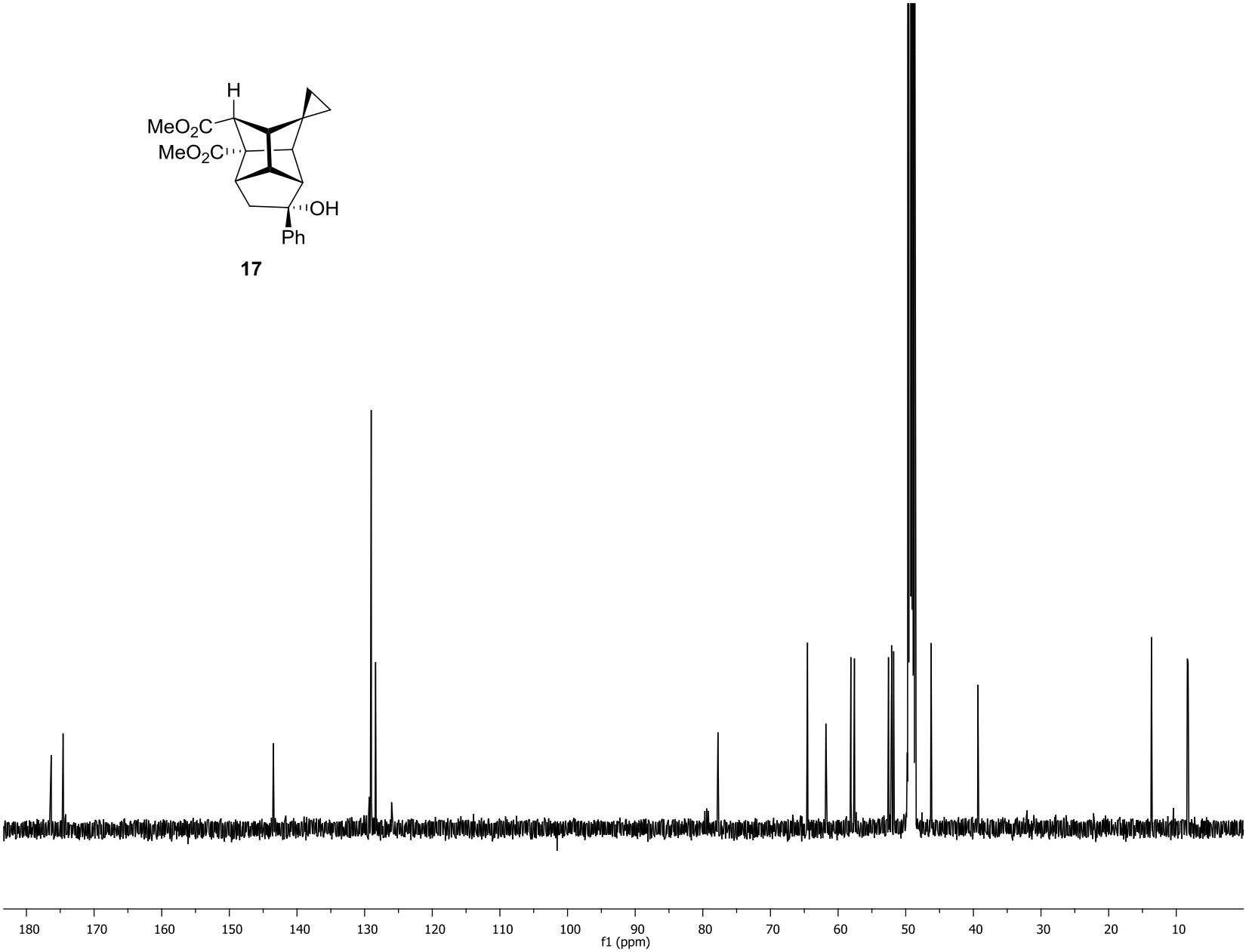
^{13}C NMR (500 MHz, $CDCl_3$):

17

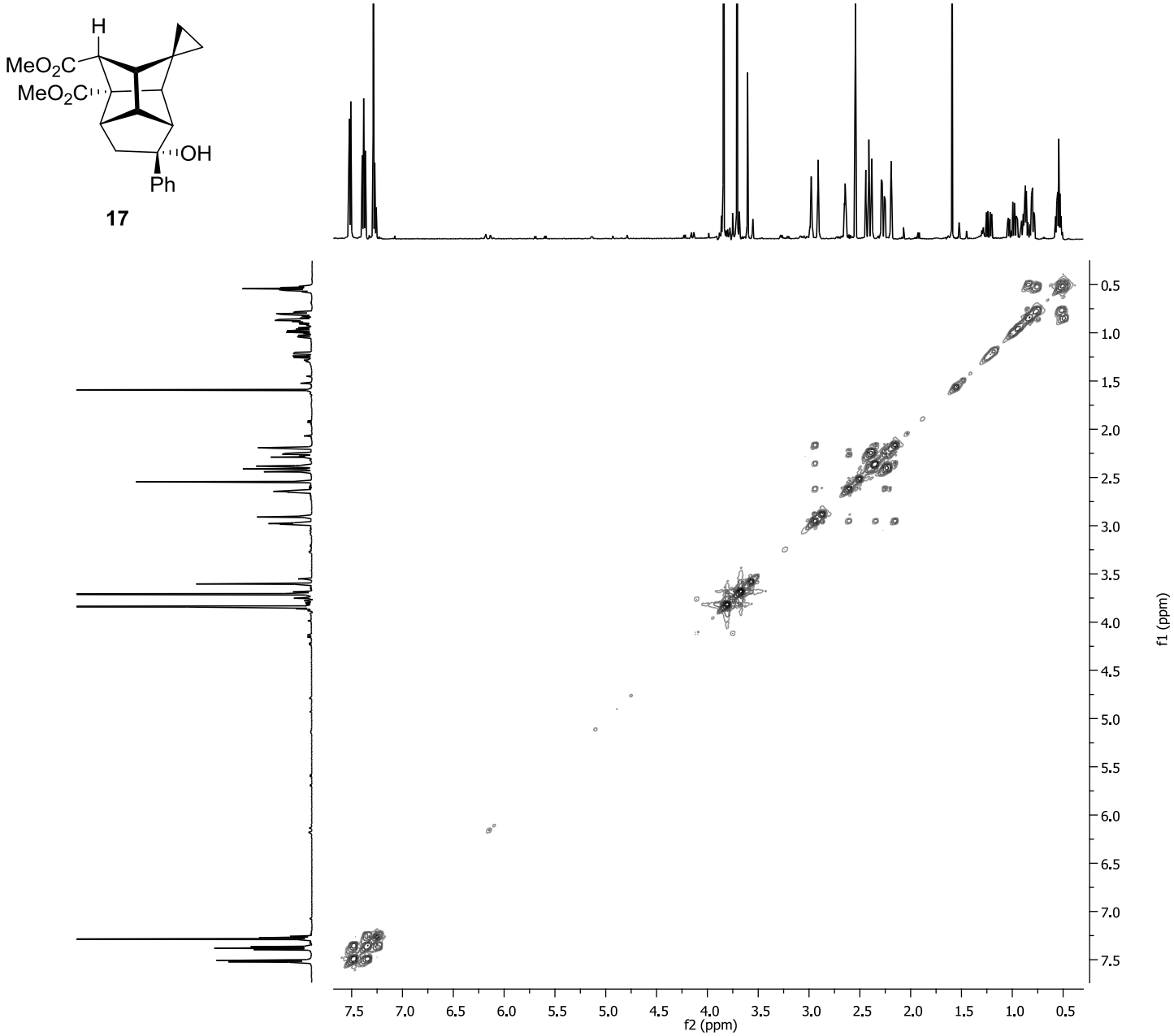


^{13}C NMR (500 MHz, $\underline{CD_3OD}$):

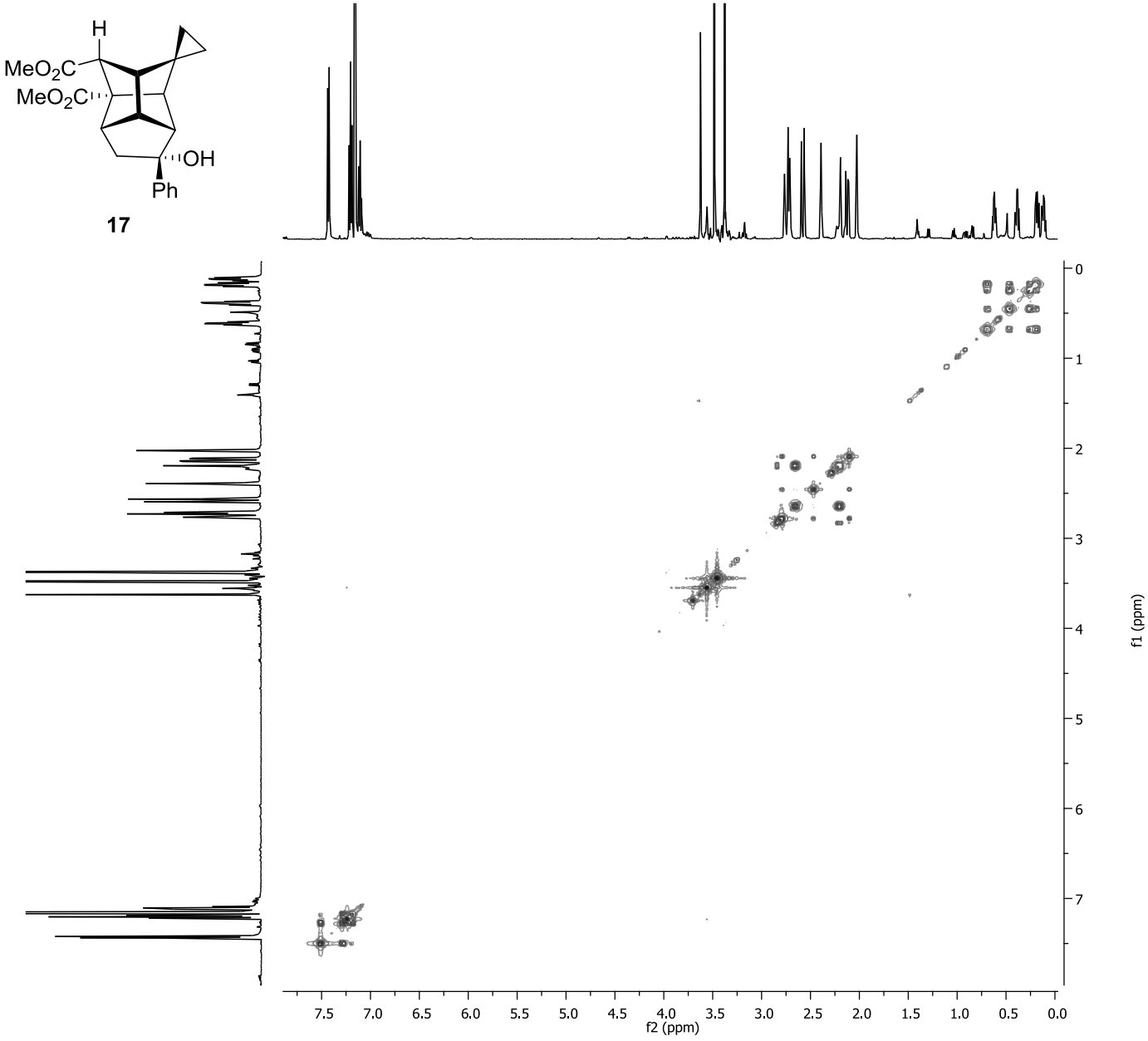
17



COSY (500 MHz, $CDCl_3$):



COSY (500 MHz, C_6D_6):



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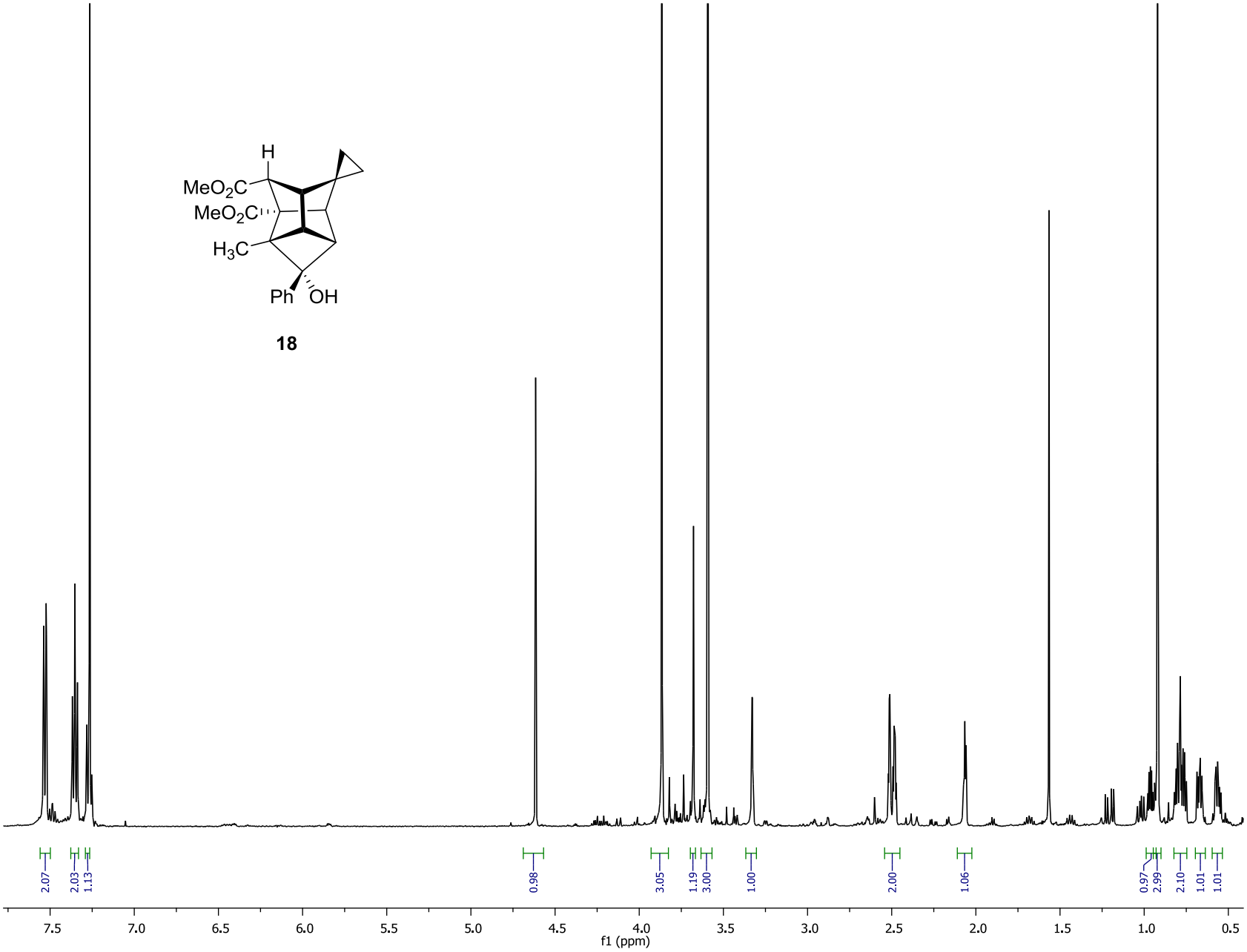
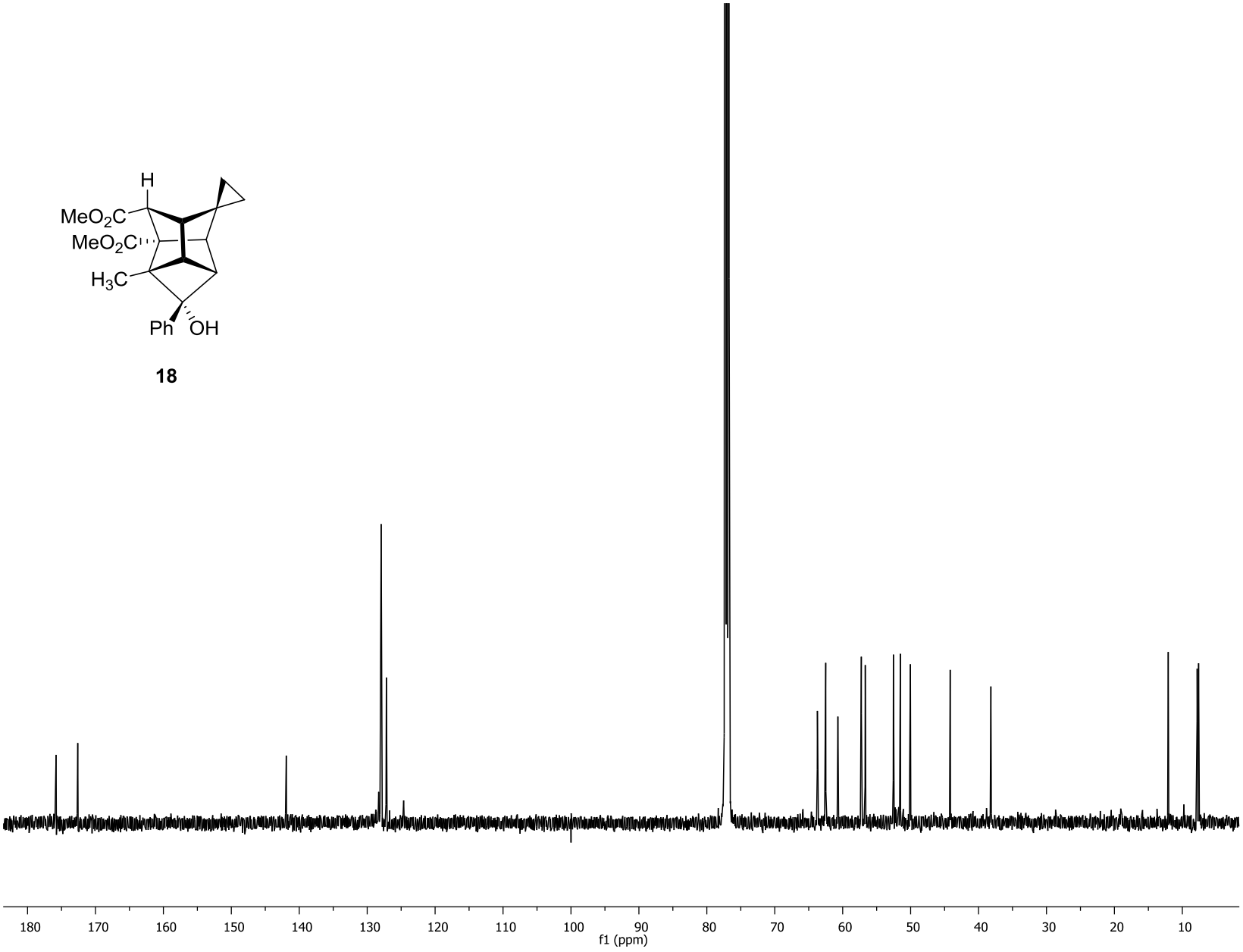
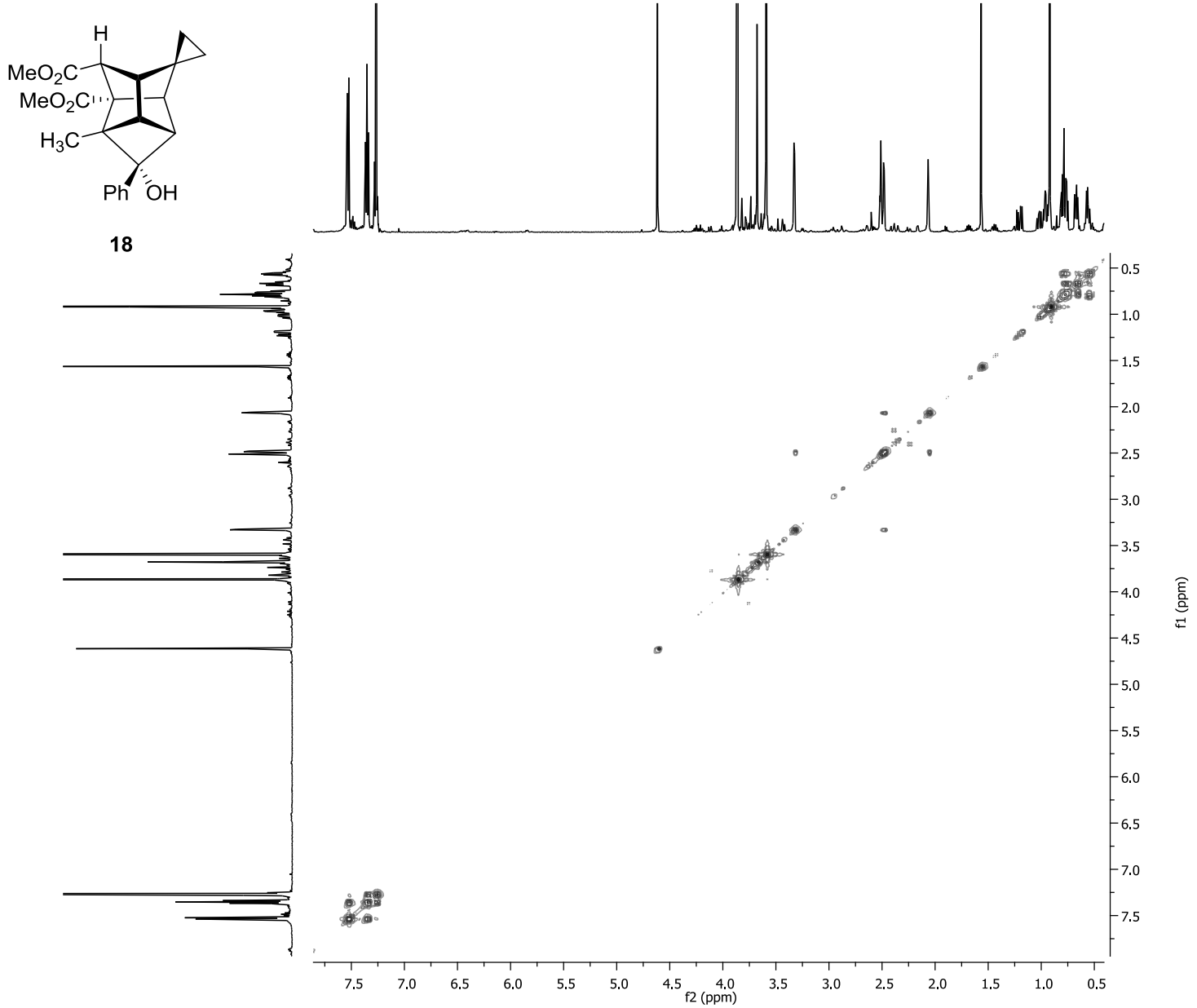


^{13}C NMR (500 MHz, $CDCl_3$):

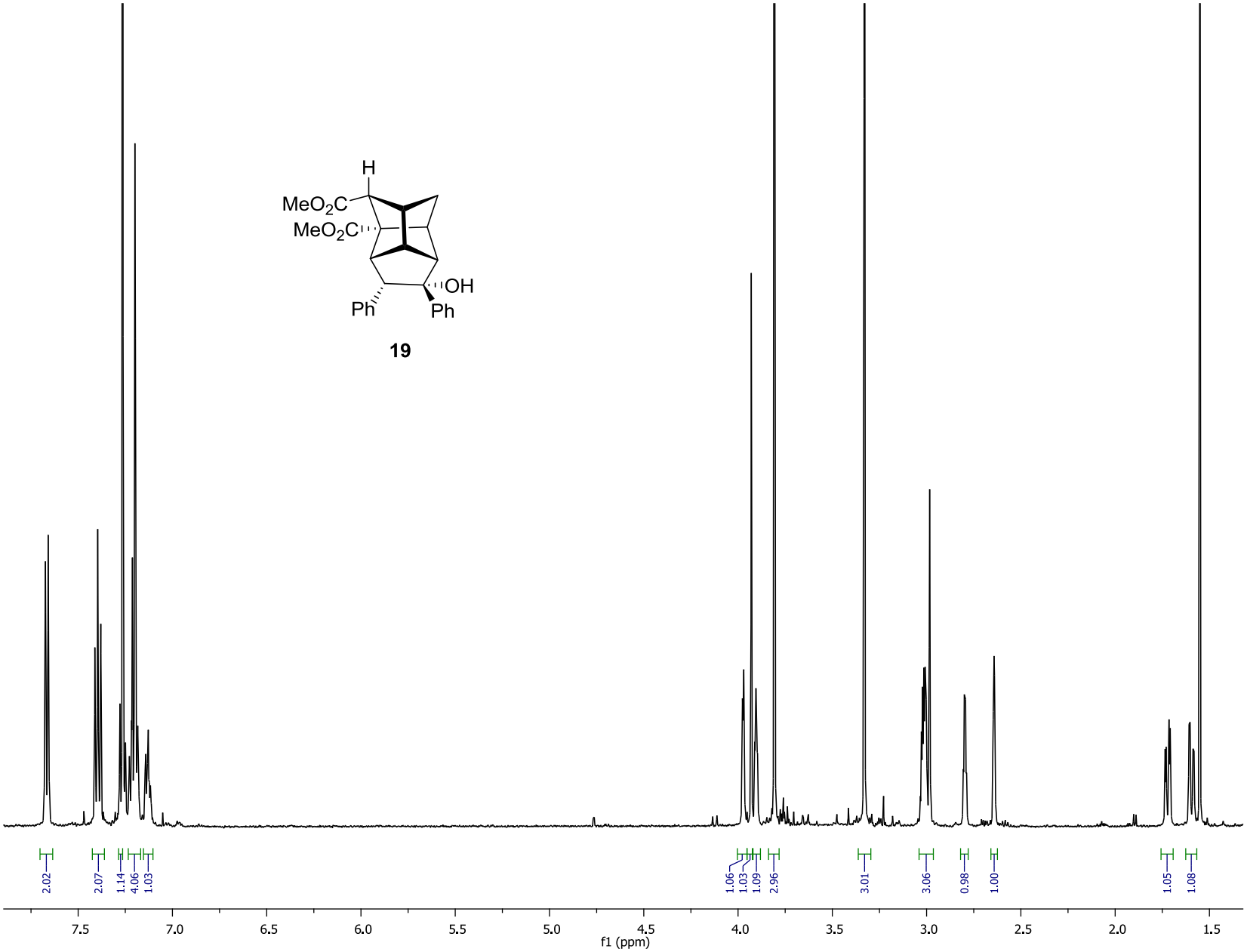
18



COSY (500 MHz, $CDCl_3$):

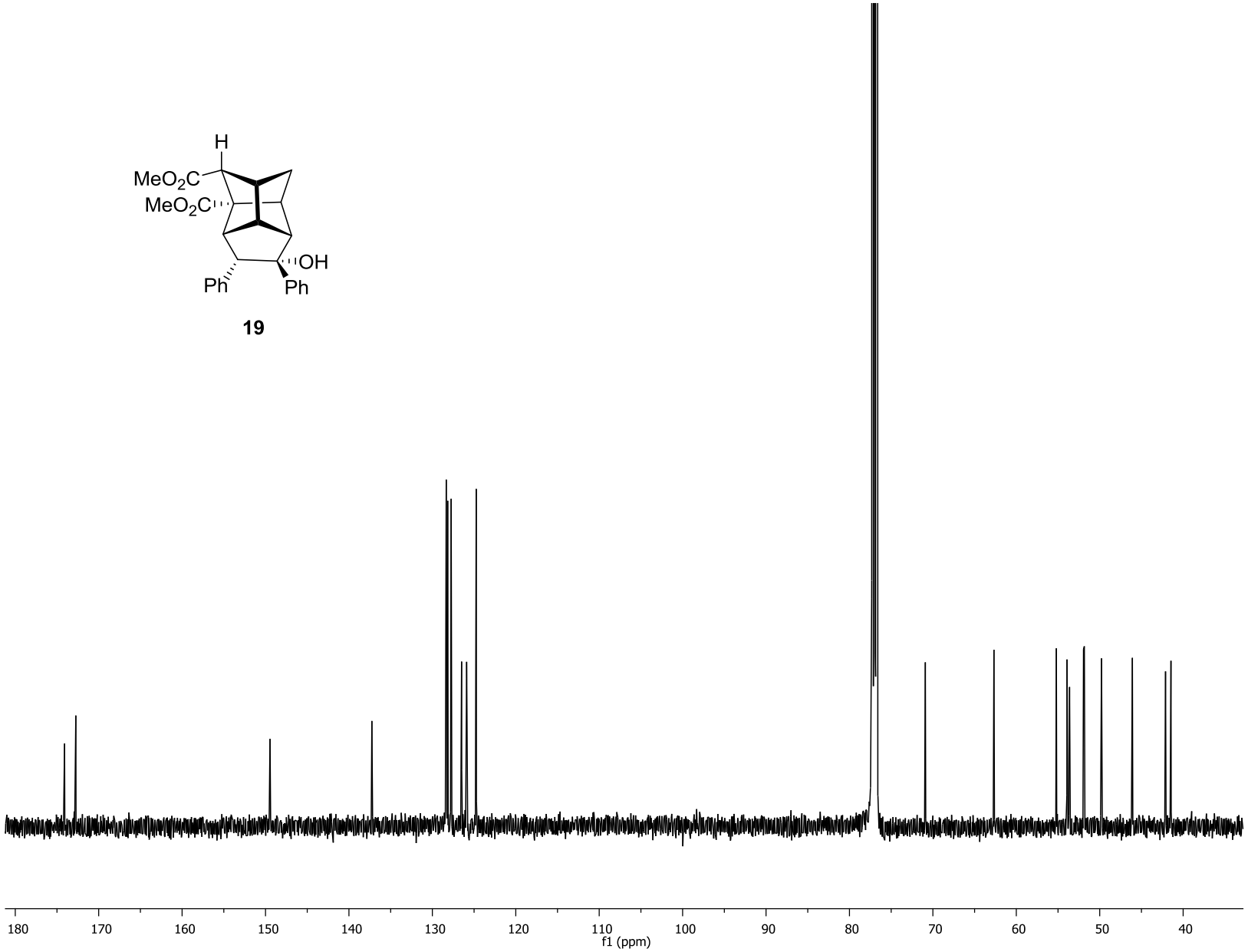


^{1}H NMR (500 MHz, $CDCl_3$):

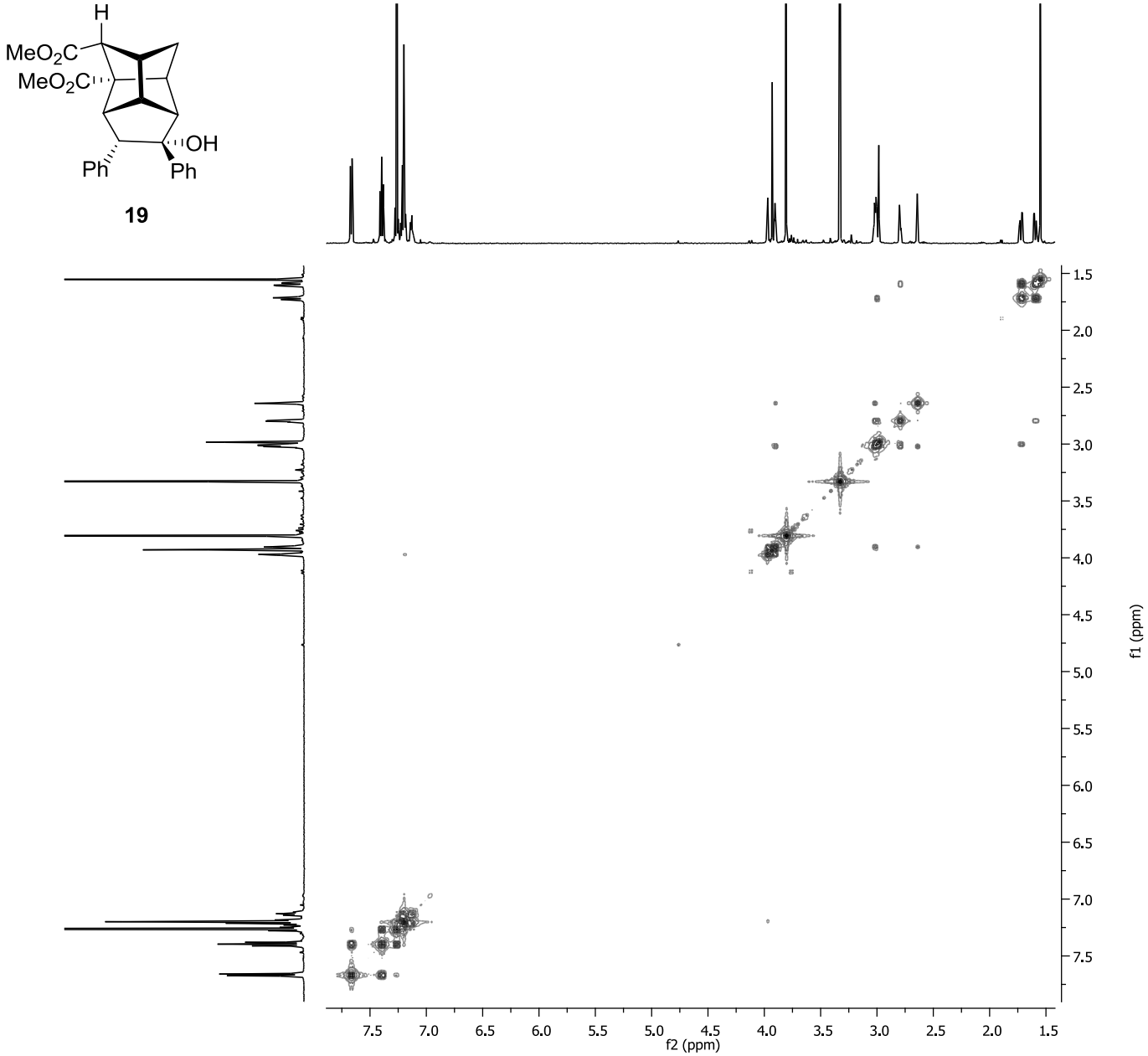


^{13}C NMR (500 MHz, $CDCl_3$):

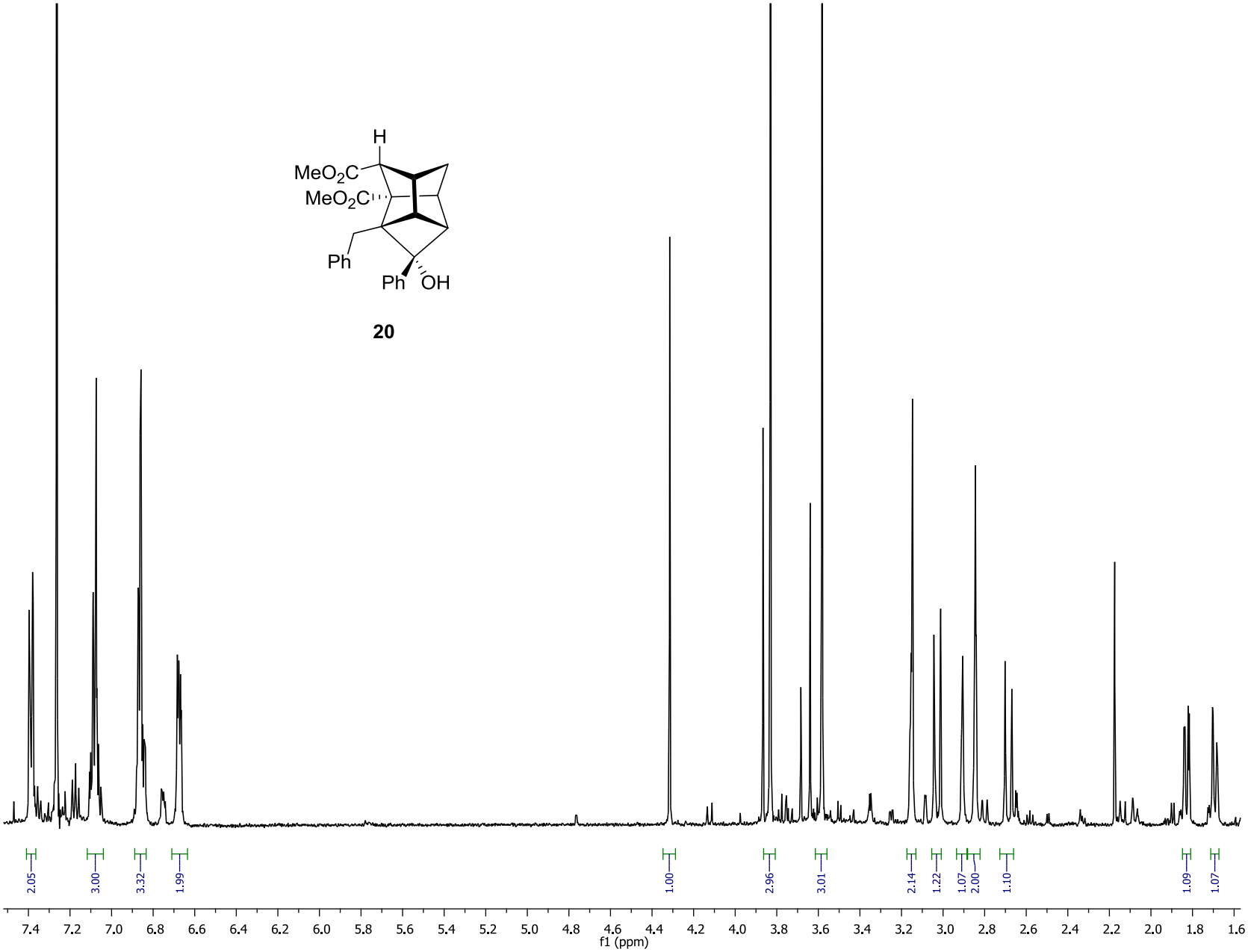
19



COSY (500 MHz, $CDCl_3$):

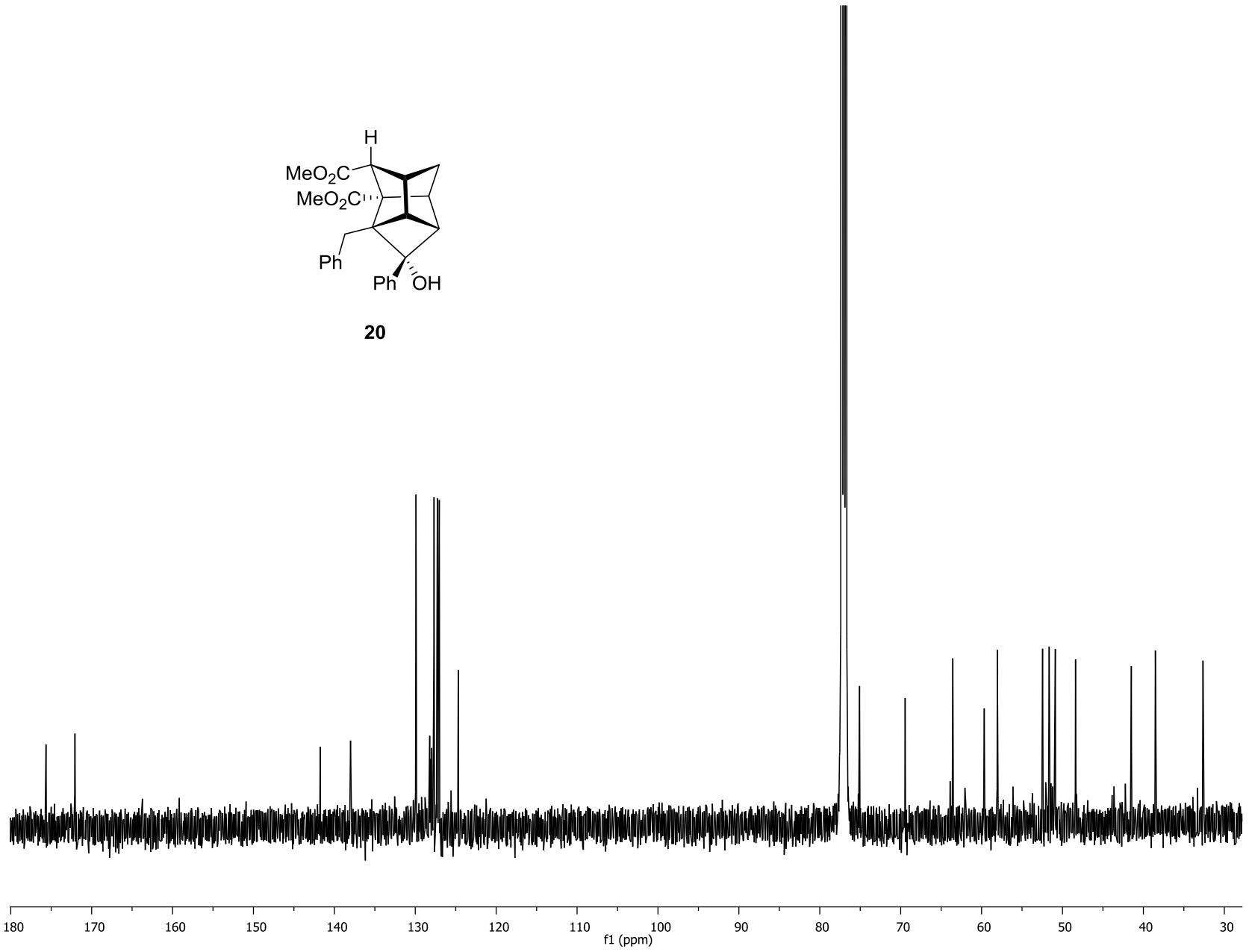


^{1}H NMR (500 MHz, $CDCl_3$):

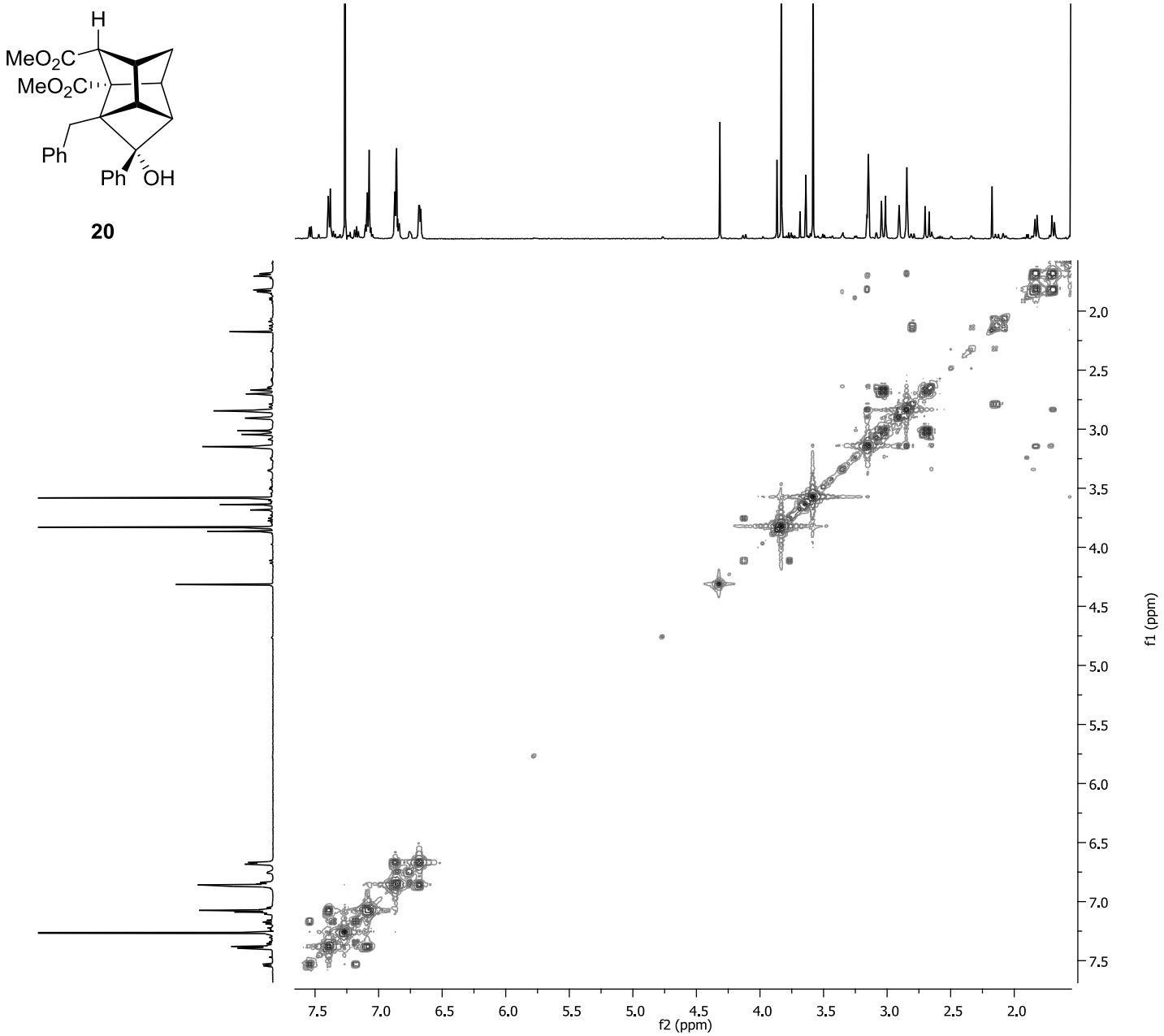


^{13}C NMR (500 MHz, $CDCl_3$):

20



COSY (500 MHz, $CDCl_3$):



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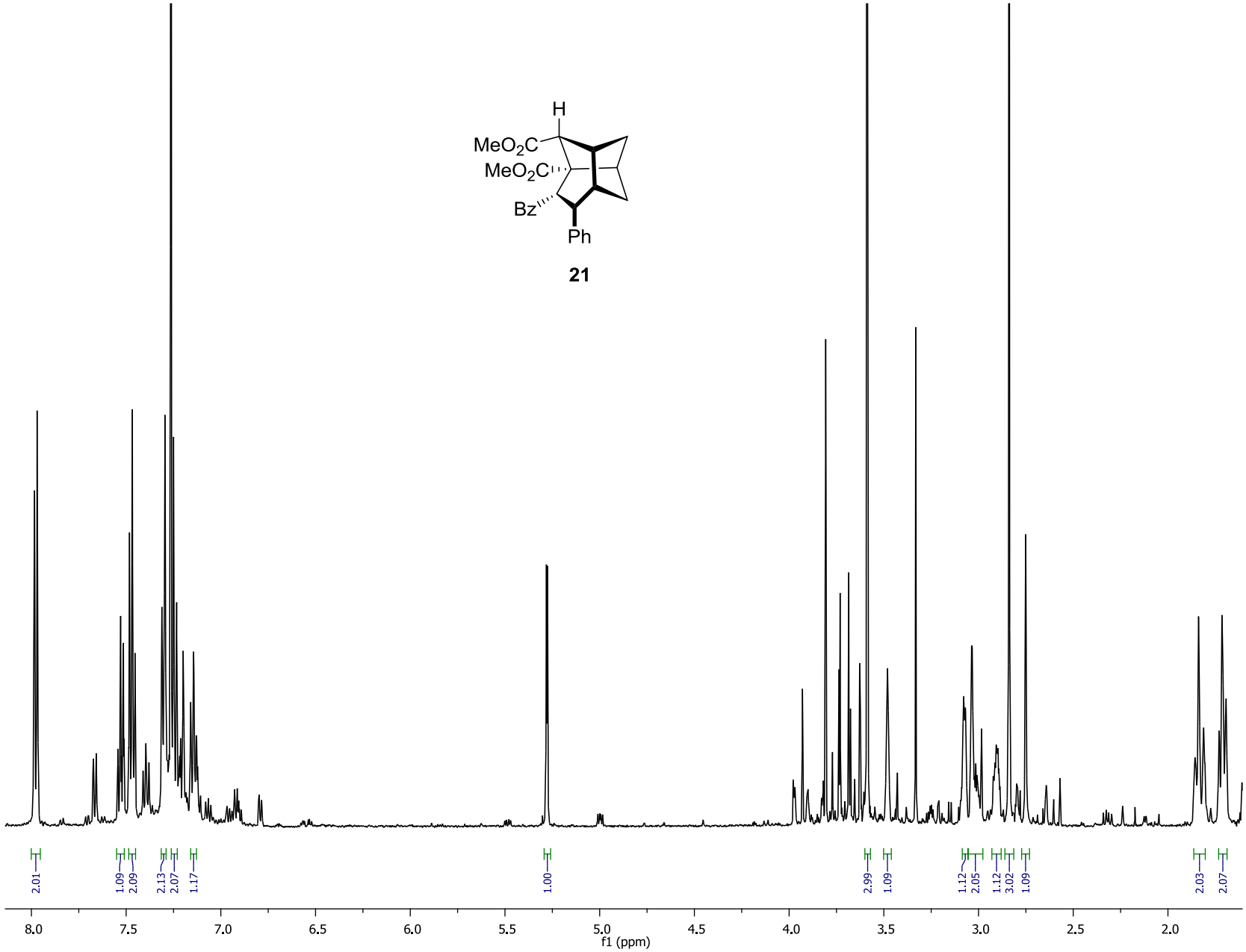

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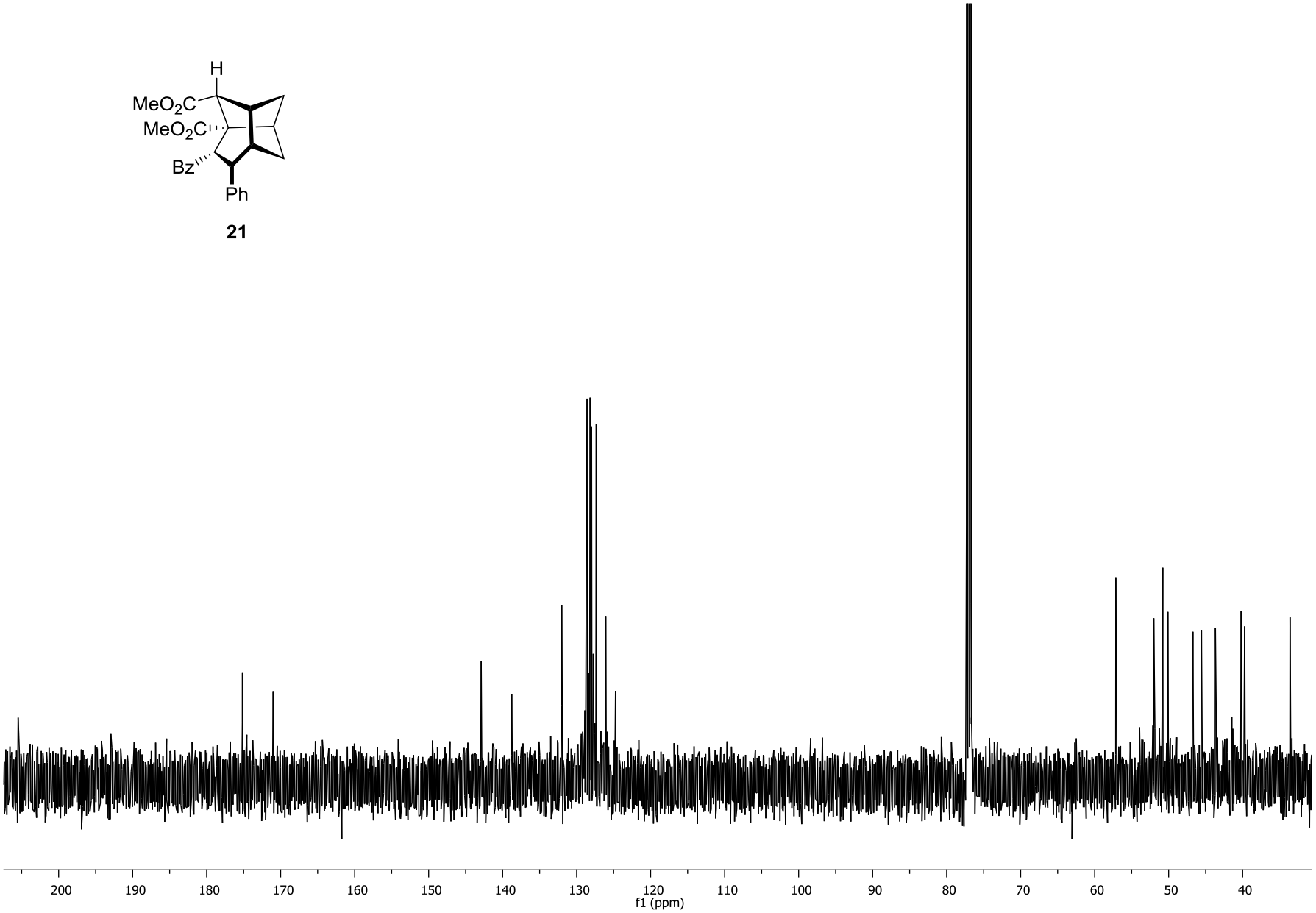
21



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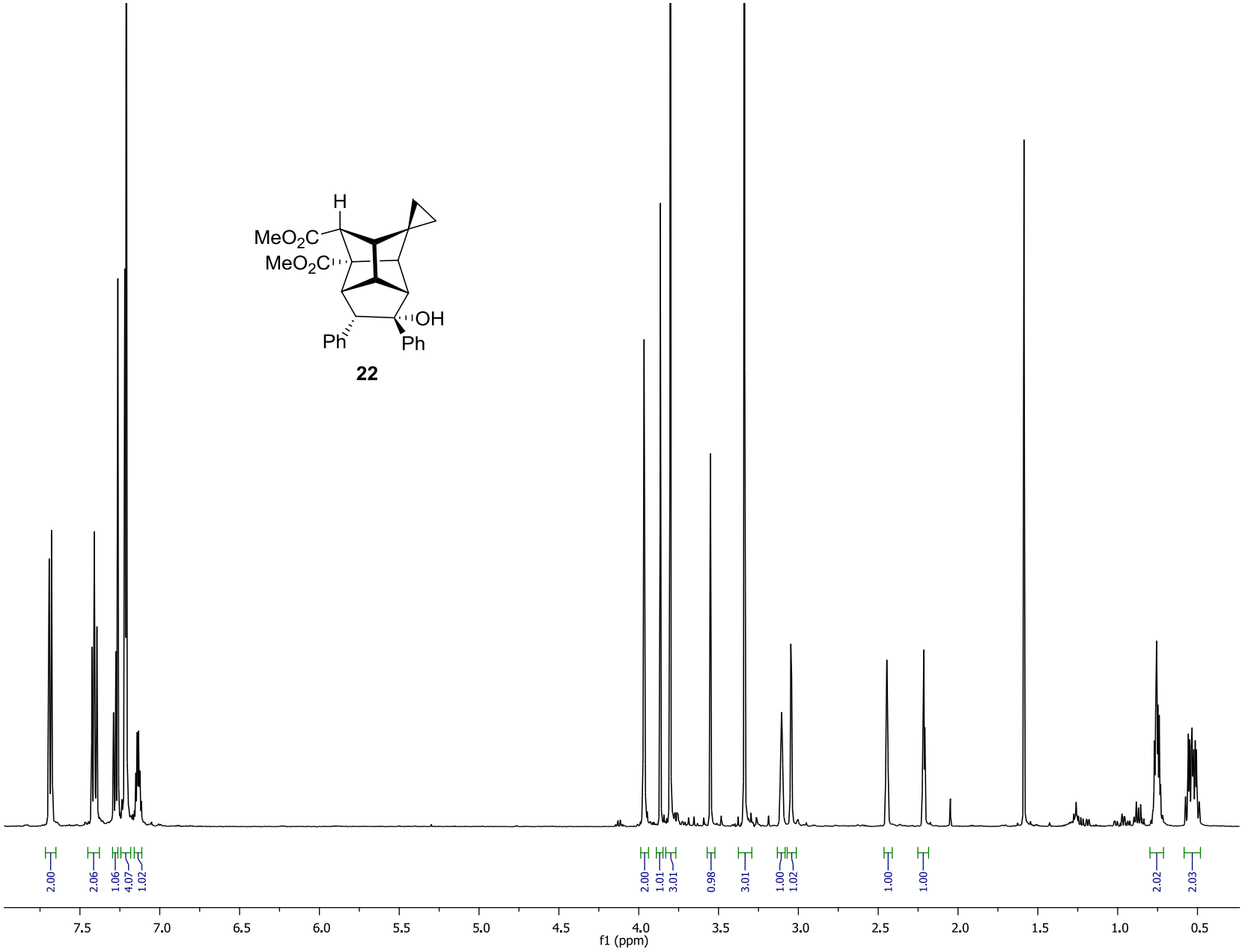

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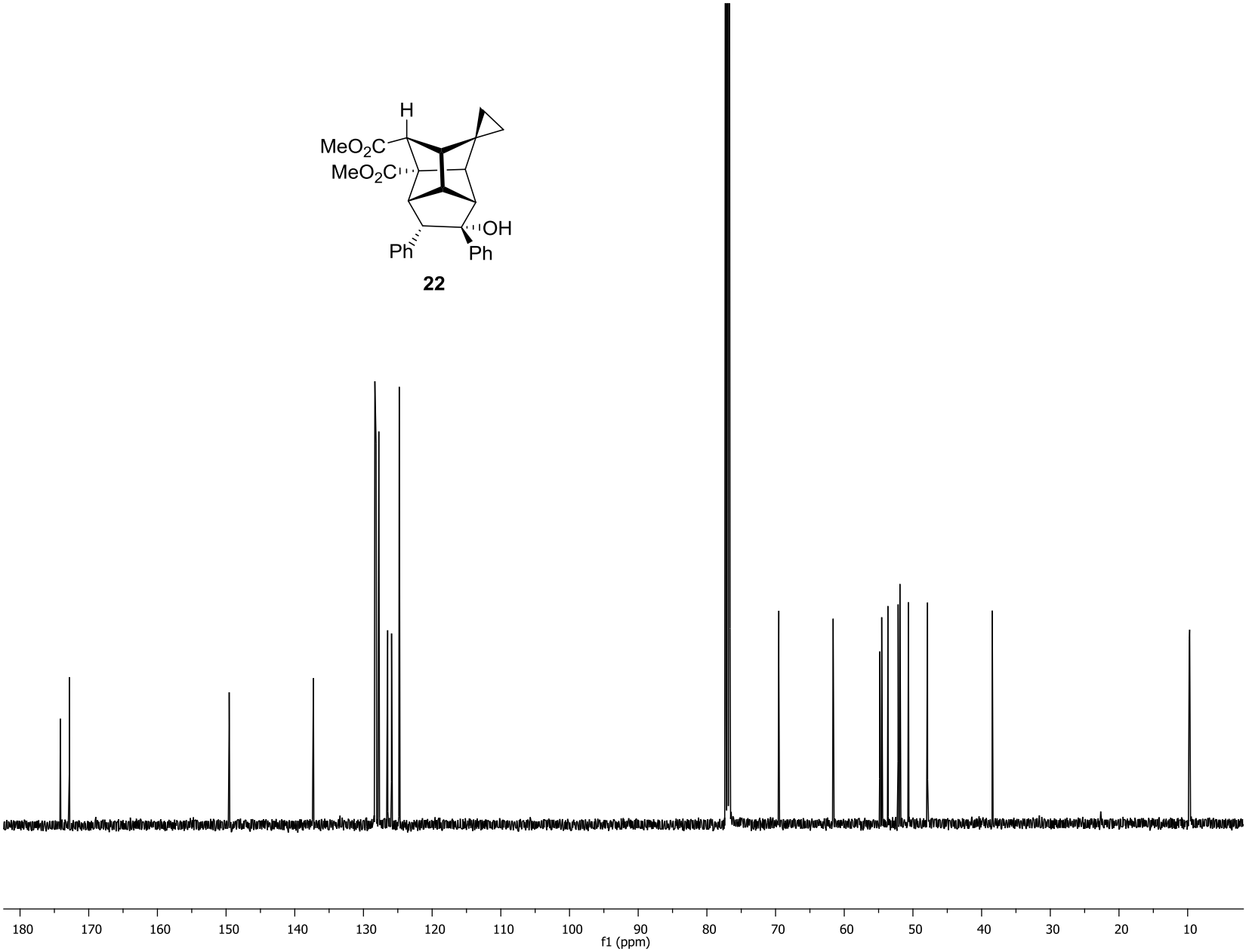
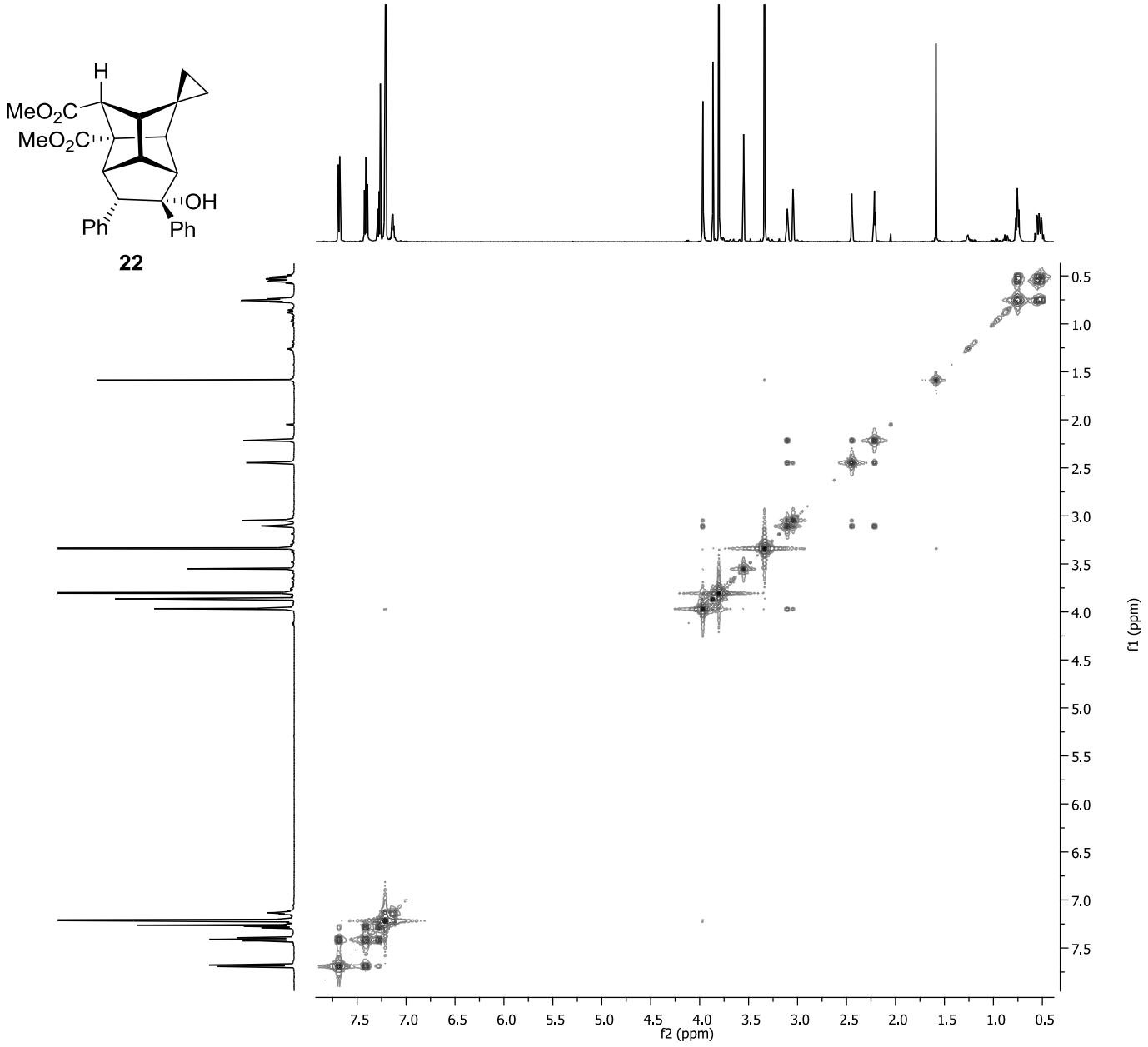
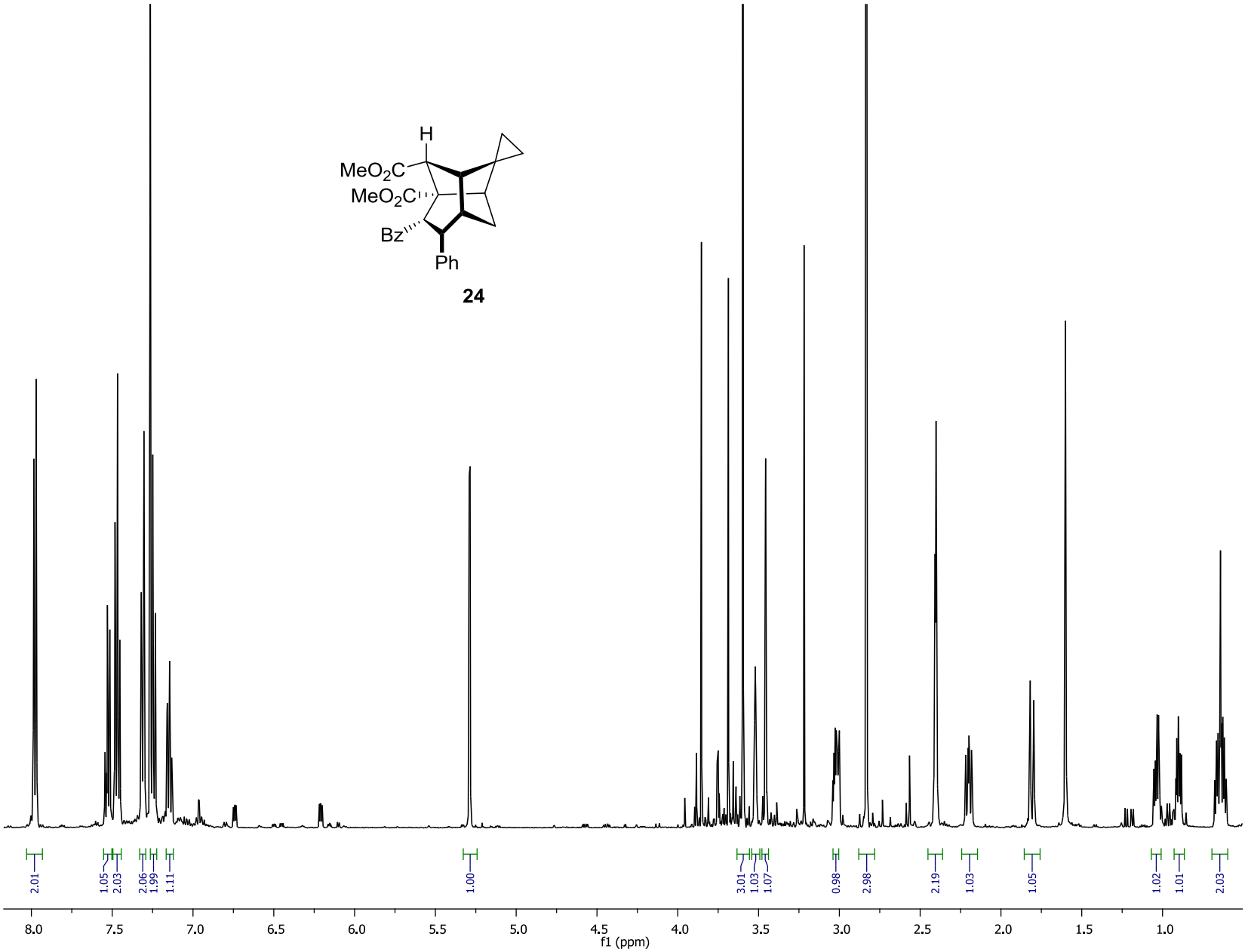
22



COSY (500 MHz, $CDCl_3$):

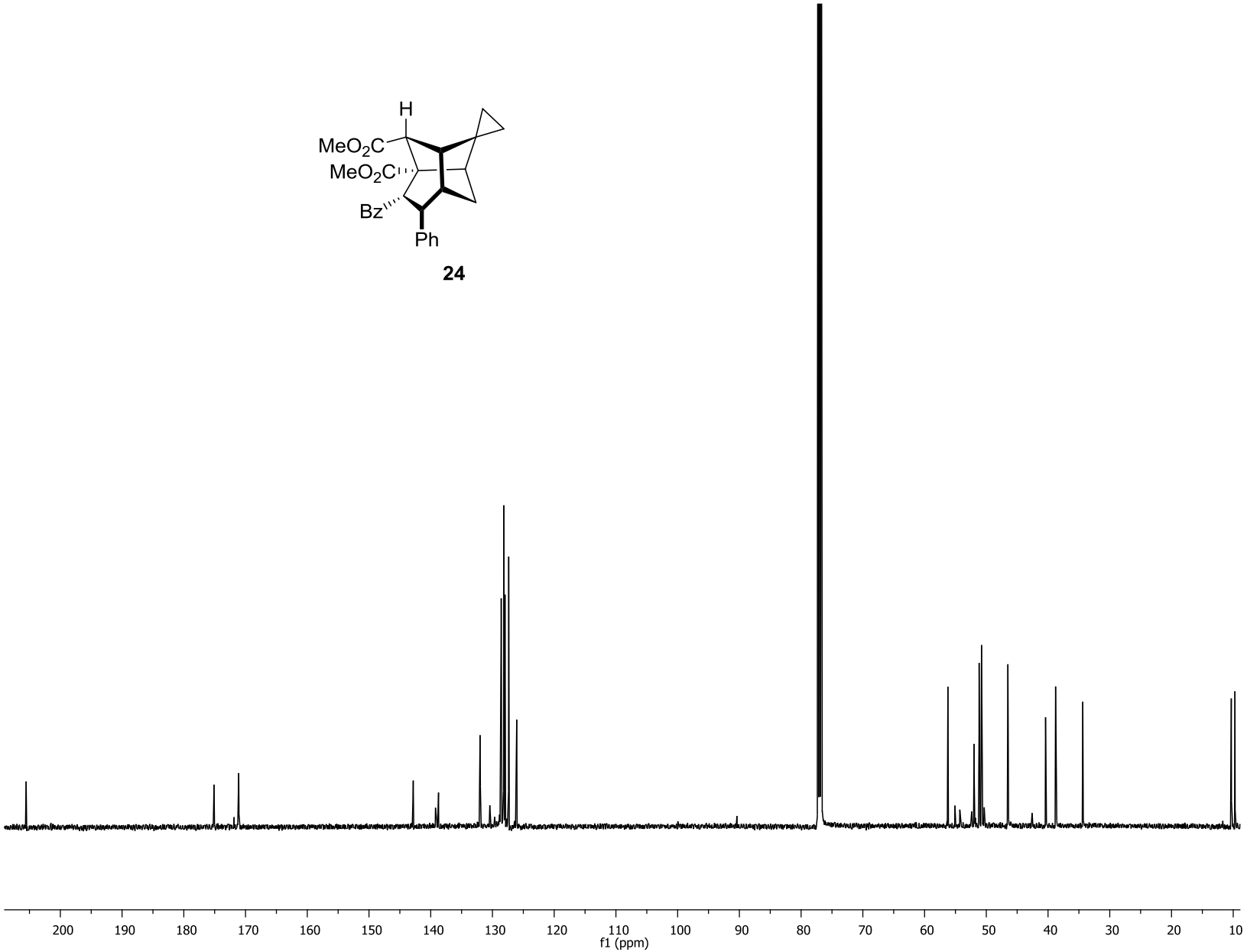


^{1}H NMR (500 MHz, $CDCl_3$):

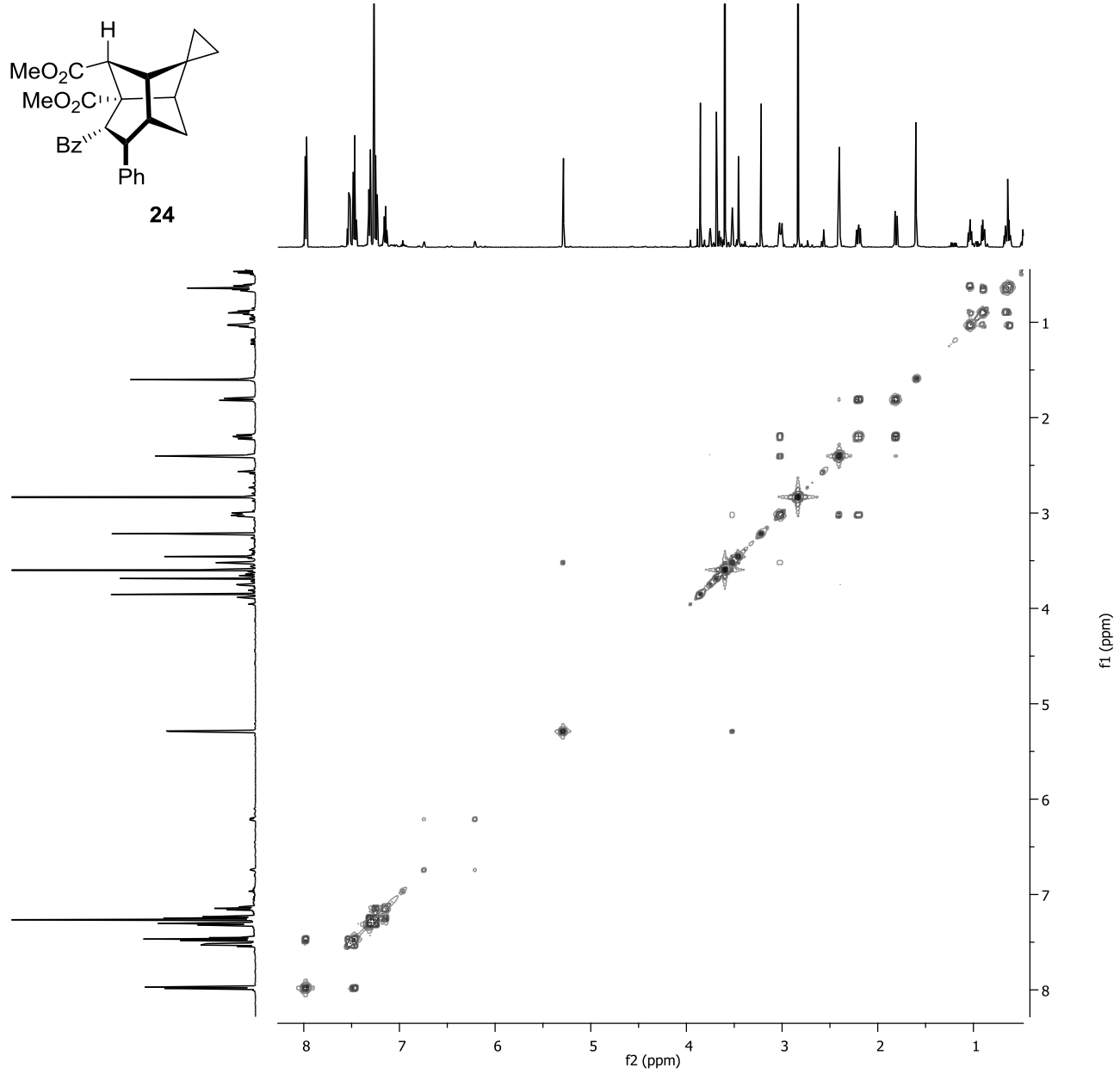


^{13}C NMR (500 MHz, $CDCl_3$):

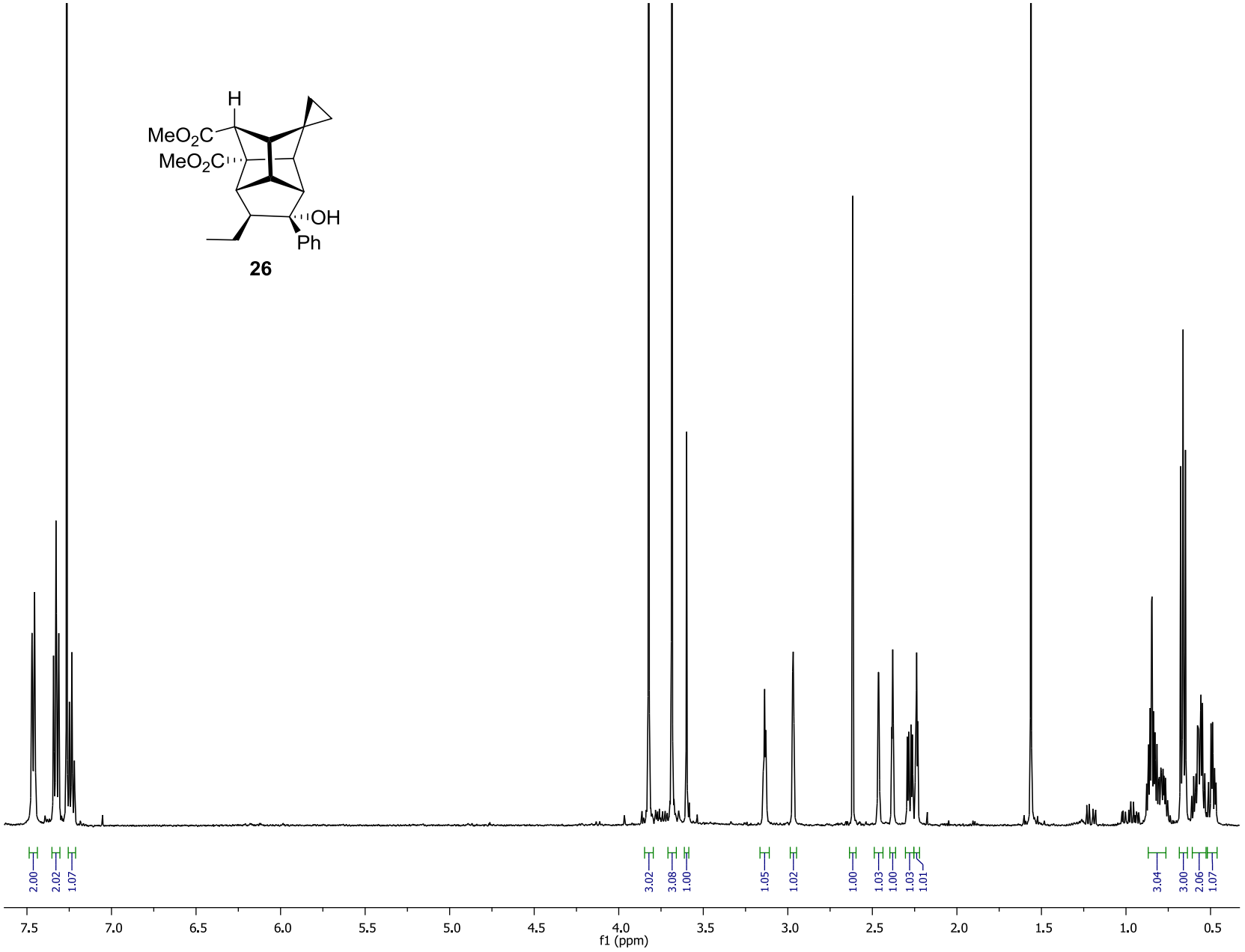
24



COSY (500 MHz, $CDCl_3$):

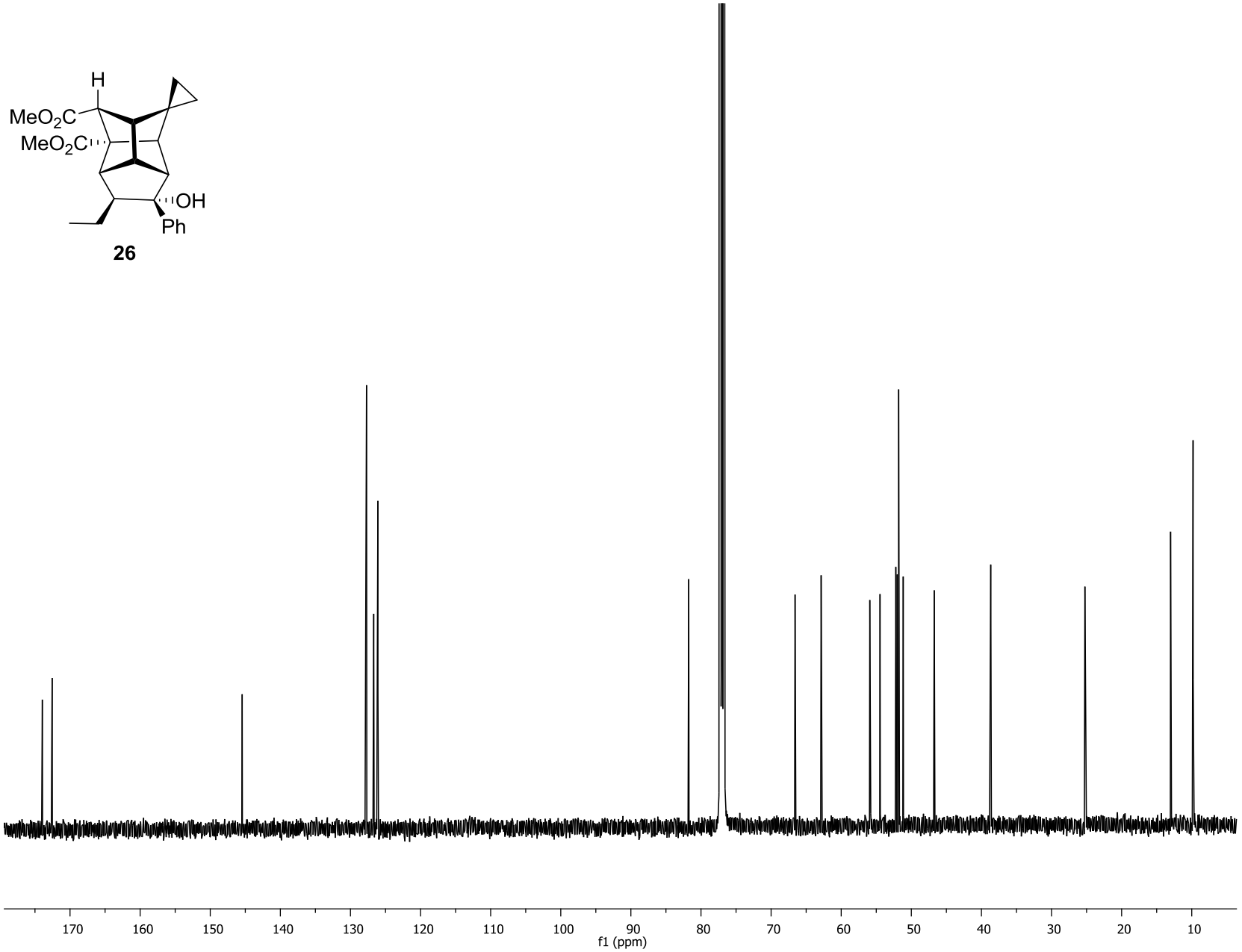


^{1}H NMR (500 MHz, $CDCl_3$):

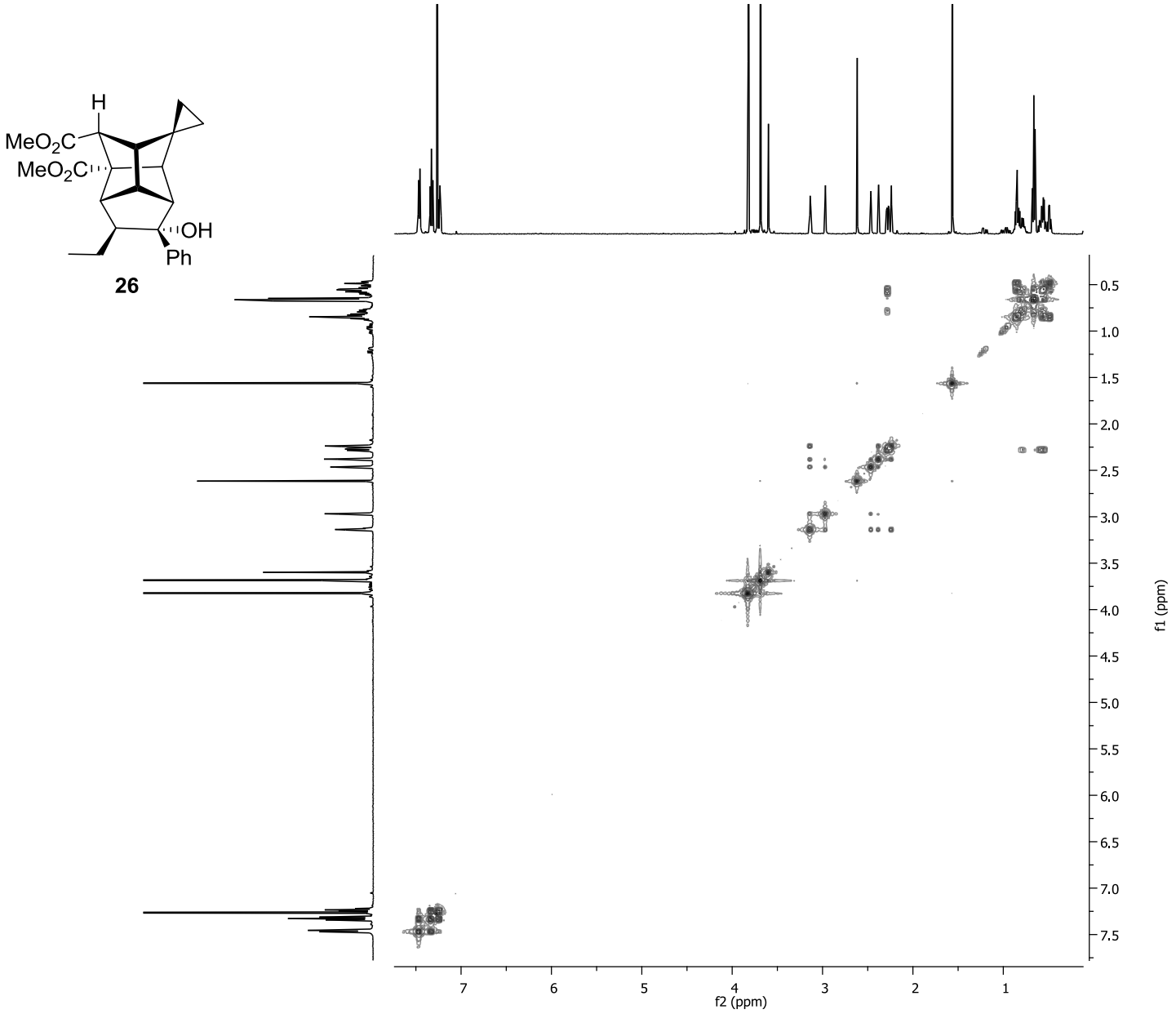


^{13}C NMR (500 MHz, $CDCl_3$):

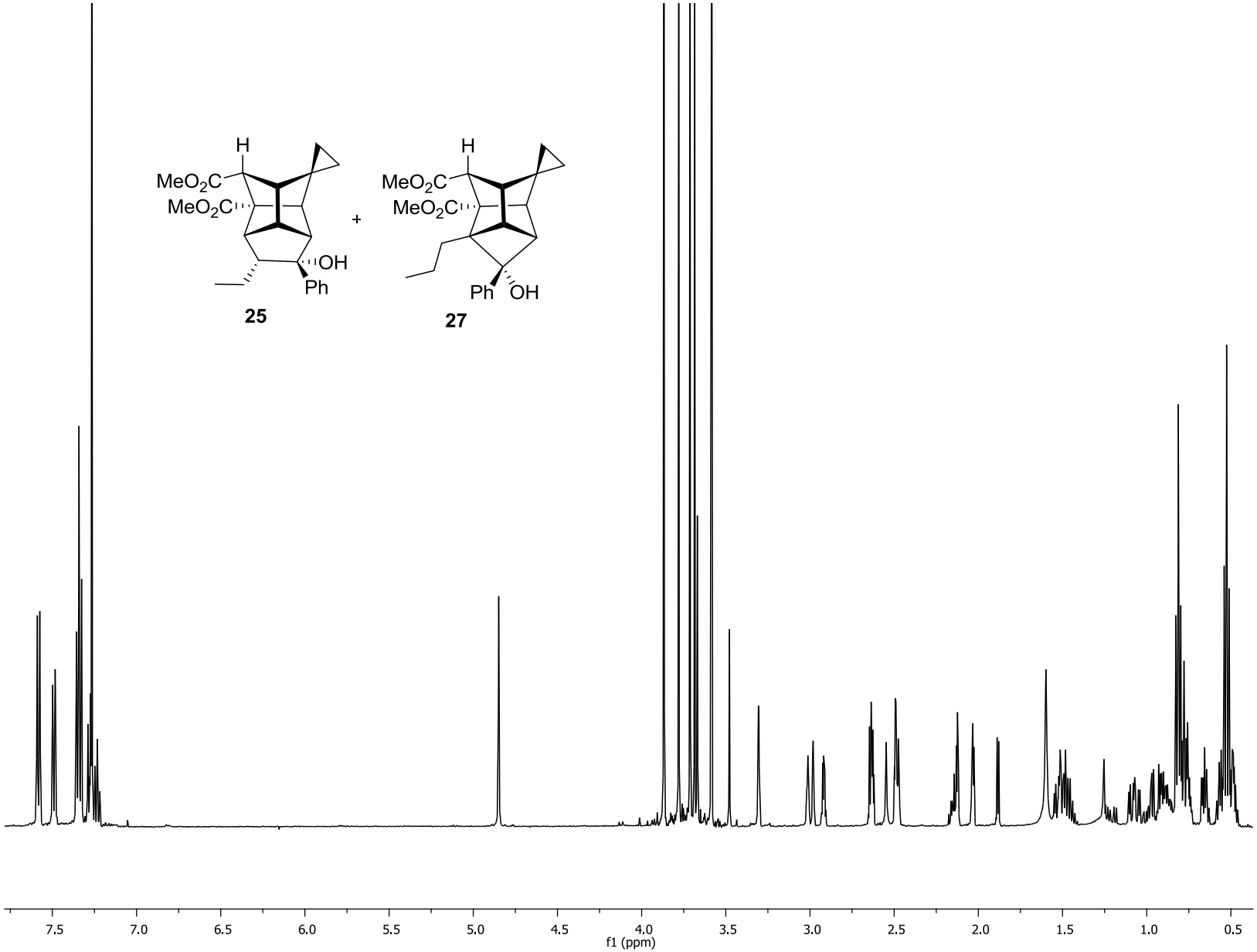
26



COSY (500 MHz, $CDCl_3$):

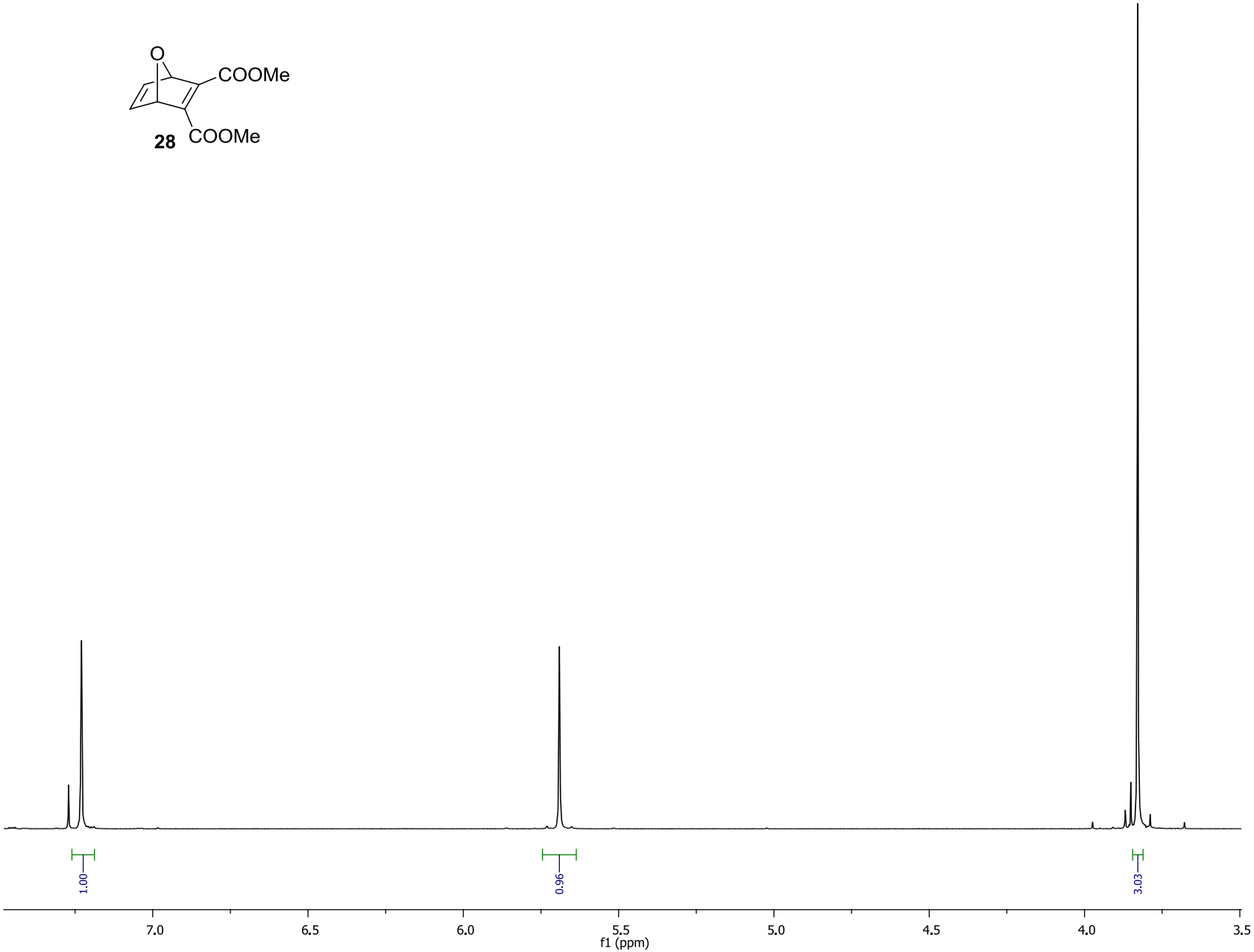


^{1}H NMR of the mixture of **9c-2** and **9c-3** (500 MHz, $CDCl_3$):

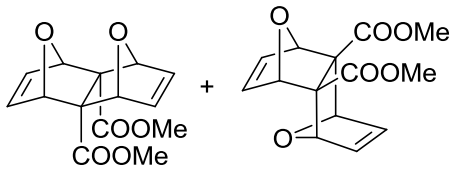


^{1}H NMR (500 MHz, $CDCl_3$):

28



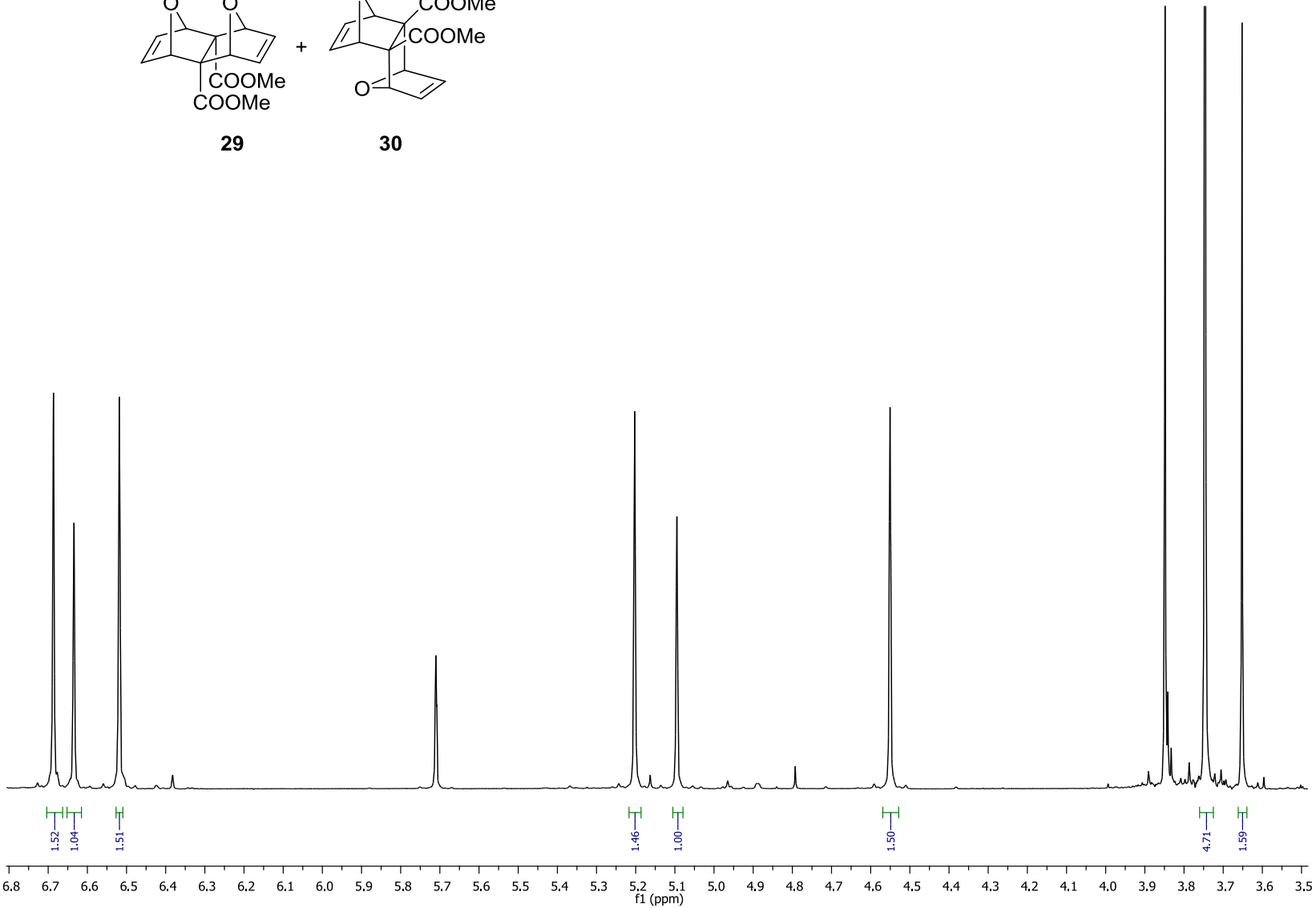
^{1}H NMR (500 MHz, $CDCl_3$):



29

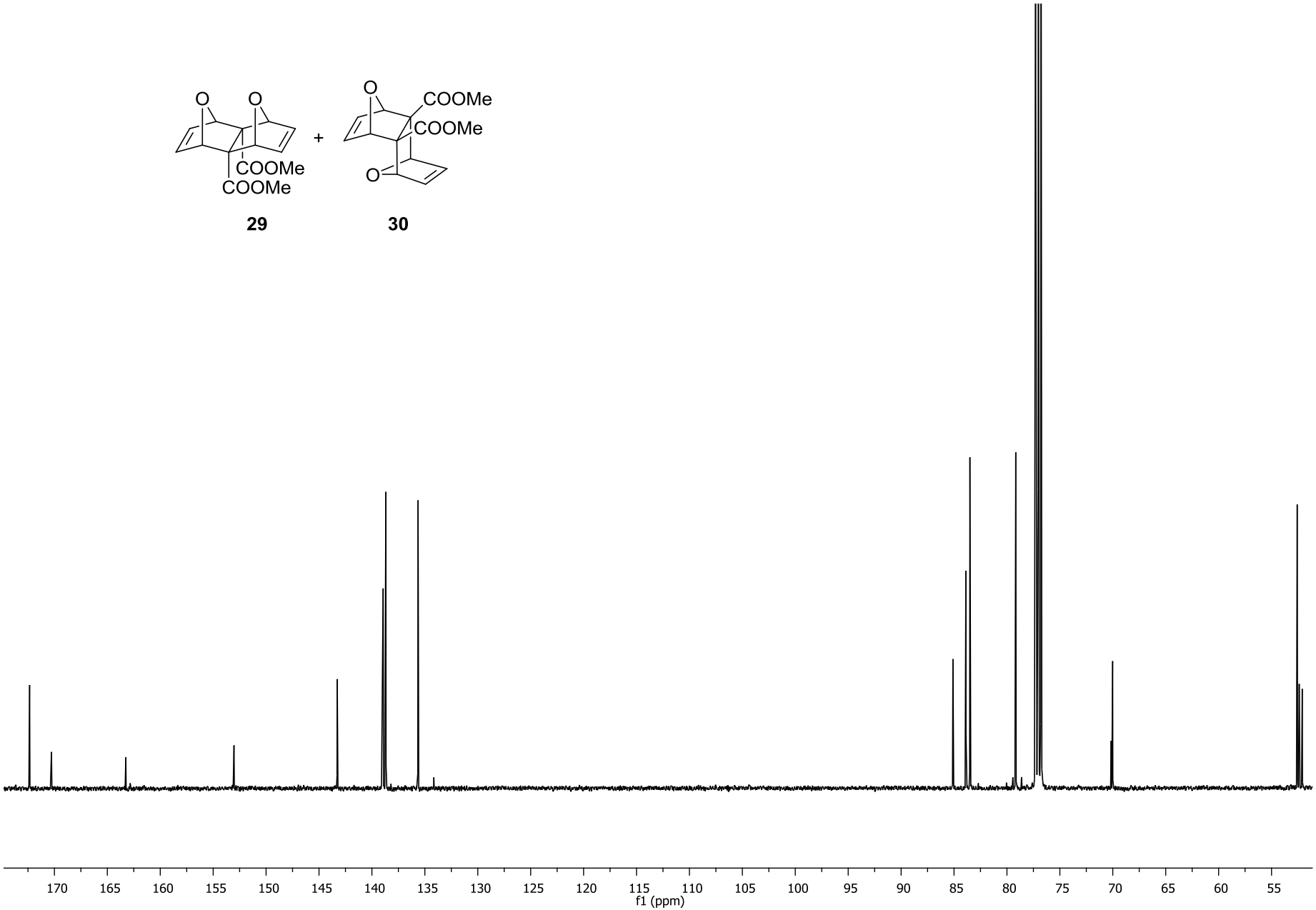
+

30



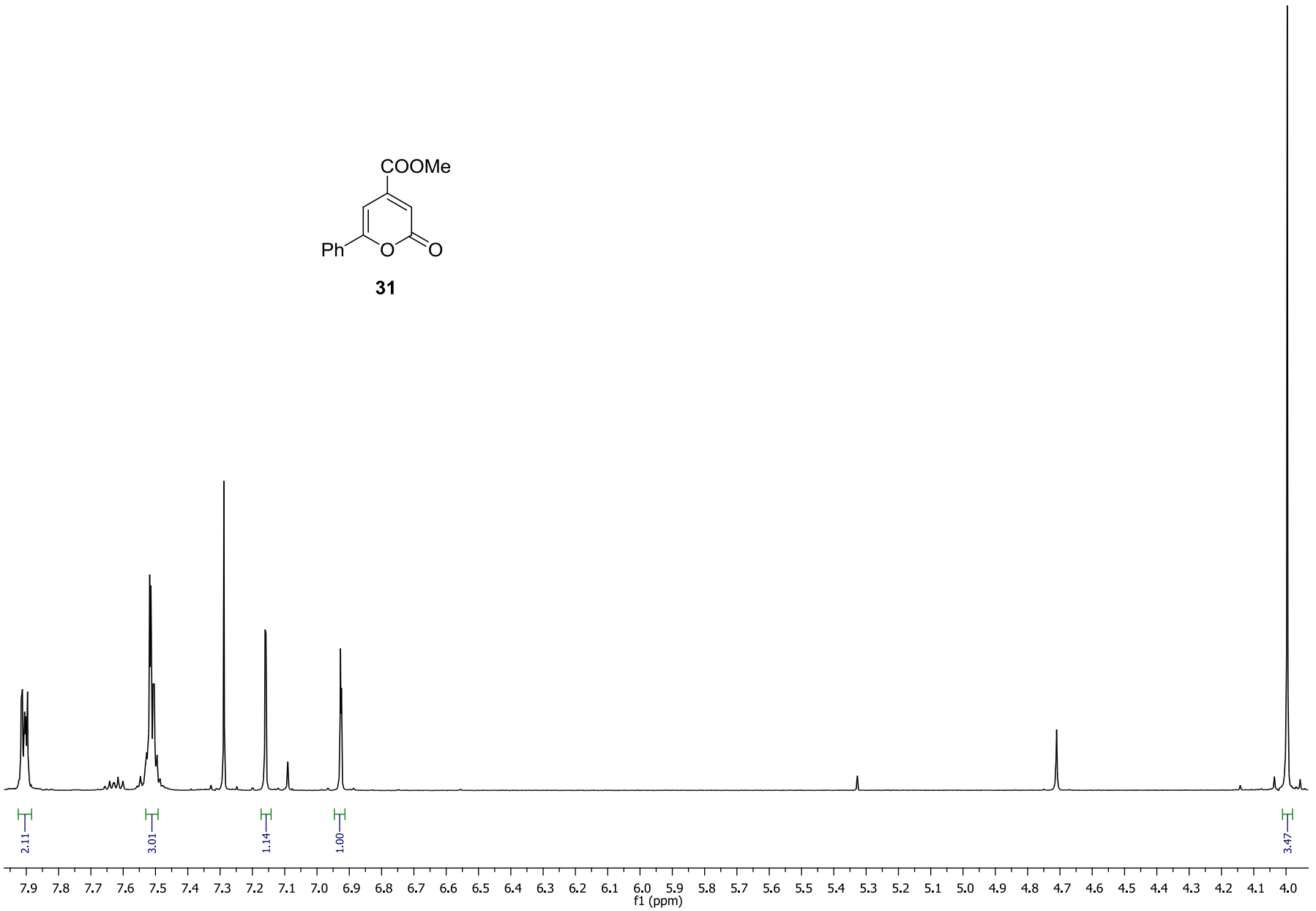
^{13}C NMR (500 MHz, $CDCl_3$):

29 **30**



^{1}H NMR (500 MHz, $CDCl_3$):

31



^{13}C NMR (500 MHz, $CDCl_3$):

31