Supplementary Information

Diversification Reactions of γ-Silyl Allenyl Esters: Selective Conversion to All-Carbon Quaternary Centers and γ-Allene Dicarbinols

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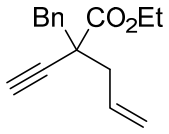
EXPERIMENTAL SECTION

General Information: All the reactions were performed in oven-dried glassware with magnetic stirring under an argon atmosphere (unless otherwise stated). Reaction products were purified using flash silica gel 40–63 μm. Extracts were concentrated in vacuo using both a rotary evaporator (bath temperatures up to 30 °C) at a pressure of either 15 mmHg (diaphragm pump) or 0.1 mmHg (oil pump), as appropriate, and a high vacuum line at room temperature. Analytical thin-layer chromatography was performed on 200 μm silica gel 60 F-254 plates. Visualization of TLC plates was accomplished with UV light (254 nm or 365 nm), followed by staining with vanillin or potassium permanganate and drying with a heat gun. ^{1}H NMR were acquired on a 400 MHz spectrometer and are reported in ppm (parts per million) using solvent as an internal standard ($CDCl_3$ at 7.26 ppm). Data are reported as br = broad, s = singlet, d = doublet, dd = doublet of doublet, ddd = doublet of doublet of doublet, t = triplet, q = quartet, m = multiplet; coupling constants in hertz (Hz). $^{13}C\{^1H\}$ NMR were measured on a 100 MHz spectrometer. Chemical shifts are reported in ppm, with solvent resonance employed as the internal standard ($CDCl_3$ at 77.0 ppm). High-resolution mass spectra were recorded by an ESI-TOF MS spectrometer (DART ion source). Reagents were purchased from commercially available sources and were used without further purification. Solvents were purified and dried on a solvent system or purchased anhydrous where required.

General Procedure for Synthesis of Ethynyl Substituted Quaternary Centers:

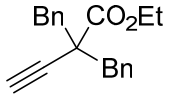
To the solution of Silylallenyl/alkynyl ester (1.0 eq.) in THF (0.10 M) and proper electrophile (2.0 eq.) at 0 °C was added 30 mol% LiO^iPr (3M in THF) followed by the addition of TBAF (2.0 eq.) dropwise over 15 min. Reaction was monitored for full consumption of allene using TLC. After stirring for 2 h, the reaction mixture was then quenched with sat. NH_4Cl, extracted with EtOAc. The organic layer was dried with anhydrous Na_2SO_4, concentrated, and purified by flash column chromatography to obtain pure product.

Ethyl 2-benzyl-2-ethynylpent-4-enoate (4a)



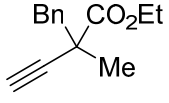
Following the general procedure, the product was obtained as a colorless oil (0.32 g, 78%) after flash column chromatography using 0-5% EtOAc/hexane as eluent.
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.19 (t, *J* = 7.1 Hz, 3H), 2.42 (s, 1H), 2.57 (ddd, *J* = 77,4, 13.5, 7.1, 2H), 3.07 (dd, *J* = 63.8, 13.2 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 5.14-5.19 (m, 2H), 5.87-5.98 (m, 1H), 7.23-7.28 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.1, 43.3, 44.3, 49.4, 61.6, 74.3, 83.0, 118.9, 127.0, 127.9(2C), 130.3(2C), 132.9, 136.1, 171.5. ESI-HRMS: m/z [M+H] calcd for $C_{16}H_{18}O_2$: 243.1380; found 243.1373.

Ethyl 2,2-dibenzylbut-3-ynoate (4b)



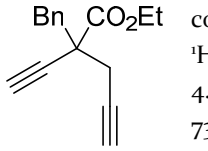
Following the general procedure, the product was obtained as a colorless oil (0.41 g, 85%) after flash column chromatography using 0-5% EtOAc/hexane as eluent.
^{1}H NMR (400 MHz, $CDCl_3$): 1.05 (t, *J* = 7.1 Hz, 3H), 2.43 (s, 1H), 3.15 (dd, *J* = 63.8, 13.2 Hz, 4H), 4.02 (q, *J* = 7.1 Hz, 2H), 7.22-7.32 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 13.9, 45.3, 51.3, 61.6, 75.7, 82.9, 127.0, 127.9(2C), 130.4(2C), 136.2, 171.6. ESI-HRMS: m/z [M+H] calcd for $C_{20}H_{20}O_2$: 293.1536; found 293.1535.

Ethyl 2-benzyl-2-methylbut-3-ynoate (4c)



Following the general procedure, the product was obtained as a colorless oil (0.25 g, 69%) after flash column chromatography using 0-5% EtOAc/hexane as eluent.
^{1}H NMR (400 MHz, $CDCl_3$): 1.23 (t, *J* = 7.1 Hz, 3H), 1.48 (s, 3H), 2.36 (s, 1H), 3.07 (dd, *J* = 63.8, 13.2 Hz, 4H), 4.17 (q, *J* = 7.1 Hz, 2H), 7.25-7.28 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.0, 25.2, 44.1, 45.4, 61.7, 72.5, 84.8, 127.0, 127.9(2C), 130.3(2C), 136.3, 172.6. ESI-HRMS: m/z [M+H] calcd for $C_{14}H_{16}O_2$: 217.1223; found 217.1225.

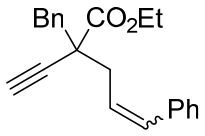
Ethyl 2-benzyl-2-ethynylpent-4-ynoate (4d)



Following the general procedure, the product was obtained as a colorless oil (0.18 g, 79%) after flash column chromatography using 0-5% EtOAc/hexane as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): 1.25 (t, *J* = 7.1 Hz, 3H), 2.17 (m, 1H), 2.43 (s, 1H), 2,67 (m, 2H), 3.21 (s, 2H), 4.15-4.26 (m, 2H), 7.24-7.32 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.0, 27.6, 42.3, 47.9, 62.0, 71.8, 73.8, 79.6, 82.5, 127.2, 128.1(2C), 130.3(2C), 135.5, 170.5. ESI-HRMS: m/z [M+H] calcd for $C_{16}H_{16}O_2$: 241.1223; found 241.1223.

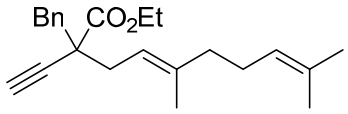
Ethyl 2-benzyl-2-ethynyl-5-phenylpent-4-enoate (4e)



Following the general procedure, the product was obtained as a colorless oil (0.34 g, 83%) after flash column chromatography using 0-5% EtOAc/hexane as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.18 (t, *J* = 7.1 Hz, 3H), 2.48 (s, 1H), 2.64-2.88 (m, 2H), 3.15 (dd, *J* = 63.8, 13.2 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 6.30-6.38 (m, 1H), 6.51-6.55 (m, 1H), 7.23-7.40 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.1, 42.7, 44.4, 49.8, 61.7, 74.5, 83.1, 124.6, 126.3(2C), 127.1, 127.4, 128.0(2C), 128.5(2C), 130.3(2C), 133.9, 136.2, 137.2, 171.6. ESI-HRMS: m/z [M+H] calcd for $C_{22}H_{22}O_2$: 319.1693; found 319.1708.

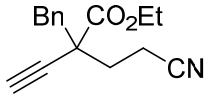
Ethyl (E)-2-benzyl-2-ethynyl-5,9-dimethyldeca-4,8-dienoate (4f)



Following the general procedure, the product was obtained as a colorless oil (0.15 g, 60%) after flash column chromatography using 0-5% EtOAc/hexane as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.18 (t, *J* = 7.1 Hz, 3H), 1.63 (s, 3H), 1.67 (s, 3H), 1.672 (s, 3H), 2.03-2.08 (m, 4H), 2.37 (s, 1H), 2.55 (ddd, *J* = 77,4, 13.5, 7.1, 2H), 3.07 (dd, *J* = 63.8, 13.2 Hz, 2H), 4.07-4.15 (m, 2H), 5.08-5.18 (m, 1H), 5.30 (t, *J* = 7.2 Hz, 3H), 7.24-7.28 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.0, 16.5, 17.7, 25.7, 26.5, 37.6, 39.9, 43.9, 49.6, 61.5, 73.8, 83.6, 118.6, 124.1, 126.8, 127.9(2C), 130.3(2C), 131.4, 136.4, 138.8, 171.9. ESI-HRMS: m/z [M+H] calcd for $C_{23}H_{30}O_2$: 339.2324; found 339.2324.

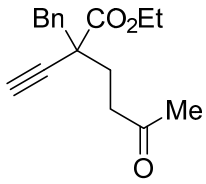
Ethyl 2-benzyl-2-(2-cyanoethyl)-but-3-ynoate (4g)



Following the general procedure, the product was obtained as a colorless oil (0.23 g, 72%) after flash column chromatography using 2-7% EtOAc/hexane as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): 1.21 (t, *J* = 7.1 Hz, 3H), 1.95 (ddd, *J* = 13.3, 10.7, 4.9 Hz, 1H), 2.30-2.47 (m, 2H), 2.48 (s, 1H), 2.57-2.65 (m, 1H), 3.08 (dd, *J* = 63.8, 13.2 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 7.22-7.32 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 13.7, 13.9, 33.6, 45.1, 48.6, 62.2, 75.6, 81.3, 119.0, 127.5, 128.2(2C), 130.2(2C), 134.9, 170.7. ESI-HRMS: m/z [M+H] calcd for $C_{16}H_{17}NO_2$: 256.1332; found 256.1324.

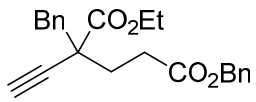
Ethyl 2-benzyl-2-ethynyl-5-oxohexanoate (4h)



Following the general procedure, the product was obtained as a colorless oil (0.21 g, 62%) after flash column chromatography using 2-7% EtOAc/hexane as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): 1.19 (t, *J* = 7.1 Hz, 3H), 1.98 (ddd, *J* = 13.6, 11.1, 4.7 Hz, 1H), 2.15 (s, 3H), 2.23 (ddd, *J* = 13.8, 10.9, 5.0 Hz, 1H), 2.41 (s, 1H), 2.51 (ddd, *J* = 17.5, 11.1, 5.0 Hz, 1H), 2.74 (ddd, *J* = 17.3, 10.8, 4.7 Hz, 1H), 3.07 (dd, *J* = 63.8, 13.2 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 7.22-7.29 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.0, 30.0, 32.5, 39.7, 45.2, 48.9, 61.7, 74.5, 82.8, 127.1, 128.0(2C), 130.2(2C), 135.8, 171.6, 207.4. ESI-HRMS: m/z [M+H] calcd for $C_{17}H_{20}O_3$: 273.1485; found 273.1486.

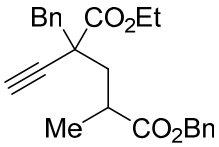
5-Benzyl 1-ethyl 2-benzyl-2-ethynylpentanedioate (4i)



Following the general procedure, the product was obtained as a colorless oil (0.17 g, 65%) after flash column chromatography using 2-10% EtOAc/hexane as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): 1.18 (t, *J* = 7.1 Hz, 3H), 2.06 (ddd, *J* = 13.4, 11.6, 4.9 Hz, 1H), 2.33 (ddd, *J* = 13.3, 11.4, 5.1 Hz, 1H), 2.40 (s, 1H), 2.46 (ddd, *J* = 16.4, 11.5, 5.1 Hz, 1H), 2.70 (ddd, *J* = 16.3, 11.3, 5.0 Hz, 1H), 3.08 (dd, *J* = 63.8, 13.2 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 5.12 (s, 2H), 7.27-7.39 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.0, 30.5, 33.6, 45.1, 49.0, 61.8, 66.4, 74.7, 82.5, 127.1, 128.0(2C), 128.2(2C), 128.5(2C), 130.2(2C), 135.7, 135.8, 171.4, 172,6. ESI-HRMS: m/z [M+H] calcd for $C_{23}H_{24}O_4$: 365.1753; found 365.1715.

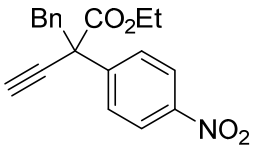
5-Benzyl 1-ethyl 2-benzyl-2-ethynyl-4-methylpentanedioate (4j)



Following the general procedure, the product was obtained as a colorless oil (0.15 g, 69%) after flash column chromatography using 2-10% EtOAc/hexane as eluent (1: 1.5 diastereomeric ratio).

^{1}H NMR (400 MHz, $CDCl_3$): 1.10-1.15 (m, 5H), 1.17-1.26 (m, 5H), 1.71 (dd, *J* = 14.0, 3.8 Hz, 1H), 2.08 (dd, *J* = 13.8, 5.5 Hz, 0.67H), 2.27 (s, 0.67H), 2.32 (dd, *J* = 13.8, 7.5 Hz, 1H), 2.36 (s, 1H), 2.59 (dd, *J* = 14.0, 8.3 Hz, 1H), 2.72-2.90 (m, 1.79H), 2.93-3.15 (m, 3.6H), 3.98-4.09 (m, 3.5H), 5.07-5.09 (m, 3.5H), 7.22-7.35 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 13.88, 13.9, 18.4, 19.3, 36.8, 37.3, 41.6, 42.0, 45.5, 46.1, 48.8, 48.9, 74.9, 75.0, 82.2, 82.8, 127.1, 127.12, 127.9, 127.92, 128.0, 128.08, 128.1, 128.2, 128.5, 130.2, 130.3, 135.7, 135.9, 136.0, 136.04, 171.4, 171.9, 175.8, 176.1. ESI-HRMS: m/z [M+H] calcd for $C_{24}H_{26}O_4$: 379.1865; found 379.1866.

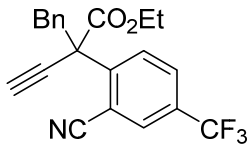
Ethyl 2-benzyl-2-(4-nitrophenyl)-but-3-ynoate (4k)



Following the general procedure, the product was obtained as a yellowish oil (0.22 g, 77%) after flash column chromatography using 3-10% EtOAc/hexane as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): 1.21 (t, *J* = 7.1 Hz, 3H), 2.72 (s, 1H), 3.46 (dd, *J* = 63.8, 13.2 Hz, 2H), 4.19-4.27 (m, 2H), 7.13-7.24 (m, 5H), 7.67 (d, *J* = 8.0 Hz, 2H), 8.16 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 13.9, 45.7, 54.0, 62.8, 77.8, 81.1, 123.6(2C), 127.2, 127.8(2C), 128.2(2C), 130.8(2C), 135.1, 145.7, 147.9, 170.2. ESI-HRMS: m/z [M+H] calcd for $C_{19}H_{17}NO_4$: 324.1236; found 324.1251.

Ethyl 2-benzyl-2-(2-cyano-4-(trifluoromethyl)-phenyl)-but-3-ynoate (4l)



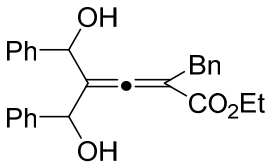
Following the general procedure, the product was obtained as a yellowish oil (0.25 g, 71%) after flash column chromatography using 5-10% EtOAc/hexane as eluent.

^{1}H NMR (400 MHz, $CDCl_3$): 1.32 (t, *J* = 7.1 Hz, 3H), 2.78 (s, 1H), 3.72 (dd, *J* = 63.8, 13.2 Hz, 2H), 4.32-4.43 (m, 2H), 6.85 (d, *J* = 4.0 Hz, 2H), 7.05-7.16 (m, 3H), 7.60 (d, *J* = 4.0 Hz, 2H), 7.96 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 13.7, 43.3, 54.1, 63.3, 78.0, 80.5, 112.0, 116.3, 121.4, 124.1, 127.2, 127.7(2C), 128.9-129.0 (q, 1C), 130.3(2C), 130.7-130.8(q, 1C), 131.1, 134.4, 145.2-145.3(q, 1C), 168.8. ESI-HRMS: m/z [M+H] calcd for $C_{21}H_{16}F_3NO_2$: 372.1206; found 372.1209.

General Procedure for the formation of γ-Disubstituted Allenoate:

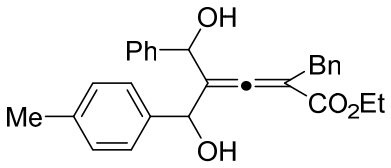
To the solution of Silylallenyl/alkynyl ester (1.0 eq.) in THF (0.20 M) and first aldehyde (1.0 eq.) at 0 °C was added 30 mol% LiO^iPr (3M in THF). The reaction was stirred for 2.5 h for the full consumption of allenoate. After all the allene was consumed, TBAF (3.5 eq.) was added followed by the addition of second aldehyde (1.0 eq.). Reaction was continued to stir for another 2.5 h after which the reaction mixture was then quenched with sat. NH_4Cl, extracted with EtOAc. The organic layers were collected, dried with anhydrous Na_2SO_4, concentrated, and purified by flash column chromatography to afford pure product.

Ethyl 2-benzyl-5-hydroxy-4-(hydroxy(phenyl)methyl)-5-phenylpenta-2,3-dienoate (5a)



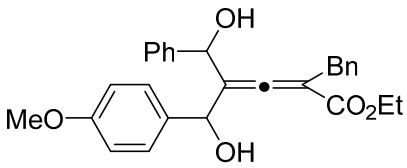
Following the general procedure, the product was obtained as a colorless oil (0.27 g, 74%) after flash column chromatography using 8-15% EtOAc/hexane as eluent.
^{1}H NMR (400 MHz, $CDCl_3$): 1.31 (t, *J* = 7.1 Hz, 3H), 3.00 (br. s, 2H), 3.43 (s, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 5.11 (s, 1H), 5.16 (s, 1H), 6.96-6.99 (m, 2H), 7.13-7.15 (m, 2H), 7.21-7.33 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.2, 34.9, 61.2, 72.7, 73.5, 105.4, 115.9, 126.3(2C), 126.4, 126.5(2C), 127.8, 127.9, 128.1(2C), 128.3(2C), 128.4(2C), 129.2(2C), 138.5, 140.78, 140.8, 166.3, 208.7. ESI-HRMS: m/z [M+Na] calcd for $C_{27}H_{26}O_4$: 437.1723; found 437.1728.

Ethyl 2-benzyl-5-hydroxy-4-(hydroxy(p-tolyl)methyl)-5-phenylpenta-2,3-dienoate (5b)



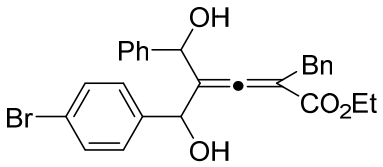
Following the general procedure, the product was obtained as a colorless oil (0.14 g, 60%) after flash column chromatography using 8-15% EtOAc/hexane as eluent (diastereomeric mixture).
^{1}H NMR (400 MHz, $CDCl_3$): 1.30-1.35 (m, 3H), 1.83-1.87 (m, 1H), 2.33-2.35 (m, 3H), 3.44-3.47 (m, 2H), 3.73-3.76 (m, 1H), 4.17-4.22 (m, 2H), 5.03-5.17 (m, 2H), 6.98-7.01 (m, 2H), 7.06-7.07 (m, 3H), 7.10-7.11 (m, 2H), 7.14-7.18 (m, 4H), 7.22-7.29 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.2, 14.25, 21.16, 21.2, 34.9, 34.93, 61.17, 61.2, 72.7, 72.72, 73.47, 73.5, 105.5, 105.53, 115.9, 116.0, 126.3, 126.32, 126.4, 126.44, 126.5, 126.6, 127.8, 127.9, 128.1, 128.3, 128.34, 128.4, 128.9, 129.0, 129.2, 129.22, 130.1, 130.2, 137.49, 137.5, 137.6, 137.7, 137.75, 137.9, 138.5, 138.55, 140.8, 140.83, 166.3, 166.4, 208.5, 208.8. ESI-HRMS: m/z [M+Na] calcd for $C_{28}H_{28}O_4$: 451.1880; found 451.1886.

Ethyl 2-benzyl-5-hydroxy-4-(hydroxy(4-methoxyphenyl)methyl)-5-phenylpenta-2,3-dienoate (5c)



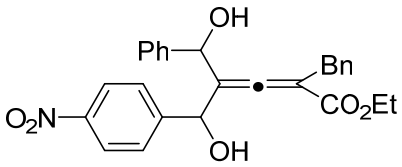
Following the general procedure, the product was obtained as a colorless oil (0.15 g, 63%) after flash column chromatography using 8-15% EtOAc/hexane as eluent (diastereomeric mixture).
^{1}H NMR (400 MHz, $CDCl_3$): 1.24-1.34 (m, 3H), 3.39-3.51 (m, 2H), 3.78-3.87 (m, 3H), 4.10-4.23 (m, 2H), 4.99-5.20 (m, 2H), 6.77-6.83 (m, 2H), 7.00-7.02 (m, 1H), 7.07-7.12 (m, 5H), 7.15-7.22 (m, 2H), 7.24-7.36 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.2, 14.3, 34.9, 35.0, 55.2, 55.3, 61.17, 61.2, 72.8, 73.0, 73.1, 73.5, 105.2, 105.7, 113.5, 113.7, 126.4, 126.43, 126.45, 126.5, 127.7, 127.8, 127.9, 128.0, 128.1, 128.15, 128.3, 128.4, 129.2, 129.25, 132.8, 132.9, 138.5, 138.6, 140.7, 140.8, 152.0, 152.1, 159.2, 159.4, 208.2, 208.3. ESI-HRMS: m/z [M+Na] calcd for $C_{28}H_{28}O_5$: 467.1829; found 467.1839.

Ethyl 2-benzyl-5-(4-bromophenyl)-5-hydroxy-4-(hydroxy(phenyl)methyl)penta-2,3-dienoate (5d)



Following the general procedure, the product was obtained as a yellowish oil (0.16 g, 65%) after flash column chromatography using 8-15% EtOAc/hexane as eluent (diastereomeric mixture).
^{1}H NMR (400 MHz, $CDCl_3$): 1.25-1.30 (m, 3H), 3.33-3.44 (m, 2H), 3.79 (br. s, 2H), 4.10-4.17 (m, 2H), 5.10-5.15 (m, 2H), 6.87-7.41 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 11.66, 11.7, 32.2, 32.24, 58.8, 58.9, 69.4, 69.5, 70.0, 70.1, 102.7, 102.8, 112.4, 112.7, 119.0, 119.2, 123.7, 123.9, 123.93, 124.0, 125.3, 125.4, 125.44, 125.45, 125.6, 125.63, 125.67, 125.7, 125.8, 125.9, 126.5, 126.54, 126.56, 126.6, 128.5, 128.6, 128.7, 128.73, 135.5, 135.7, 163.7, 163.8, 206.6, 206.61. ESI-HRMS: m/z [M+Na] calcd for $C_{27}H_{25}BrO_4$: 515.0828; found 515.0844.

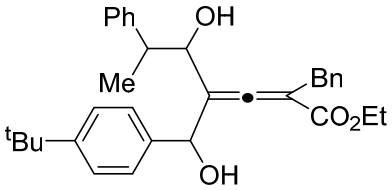
Ethyl 2-benzyl-5-hydroxy-4-(hydroxy(4-nitrophenyl)methyl)-5-phenylpenta-2,3-dienoate (5e)



Following the general procedure, the product was obtained as a yellow oil (0.19 g, 73%) after flash column chromatography using 8-15% EtOAc/hexane as eluent (diastereomeric mixture).

^{1}H NMR (400 MHz, $CDCl_3$): 1.29-1.33 (m, 3H), 3.34-3.44 (m, 2H), 4.16-4.23 (m, 2H), 4.83 (s, 1H), 5.18-5.32(m, 2H), 6.92-6.94 (m, 2H), 7.15-7.17 (m, 1H), 7.24-7.36 (m, 9H), 7.52-7.54 (m, 1H), 8.01-8.03(m, 1H), 8.20-8.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.3, 14.31, 34.6, 34.7, 61.4, 61.5, 63.3, 64.0, 71.6, 72.6, 72.8, 73.8, 105.7, 105.9, 114.1, 114.6, 123.1, 123.3, 123.7, 126.1, 126.2, 126.7, 126.71, 126.97, 127.0, 127.2, 128.1, 128.2, 128.3, 128.4, 128.42, 128.44, 129.1, 129.2, 138.1, 138.2, 140.1, 140.2, 147.2, 147.3, 148.1, 148.2, 165.8, 166.0, 209.2, 209.5. ESI-HRMS: m/z [M+Na] calcd for $C_{27}H_{25}NO_6$: 482.1574; found 482.1589.

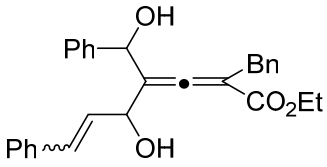
Ethyl 2-benzyl-4-((4-(tert-butyl)phenyl)(hydroxy)methyl)-5-hydroxy-6-phenylhepta-2,3-dienoate (5f)



Following the general procedure, the product was obtained as a yellowish oil (0.17 g, 64%) after flash column chromatography using 8-15% EtOAc/hexane as eluent (diastereomeric mixture).

^{1}H NMR (400 MHz, $CDCl_3$): 1.06-1.52 (m, 15H), 2.74-3.02 (m, 1H), 3.37-3.74 (m, 2H), 3.85-4.08 (m, 1H), 4.14-4.33 (m, 2.70H), 5.06-5.46 (m, 1H), 7.10-7.49 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 12.8, 14.1, 14.3, 14.33, 17.0, 17.6, 18.2, 18.4, 18.42, 18.7, 20.8, 21.0, 31.2, 31.3, 31.45, 31.5, 34.6, 34.61, 35.0, 35.2, 42.8, 44.8, 44.81, 44.9, 61.2, 61.23, 61.3, 72.3, 73.4, 73.7, 73.8, 74.4, 74.5, 74.9, 76.6, 104.9, 105.0, 105.4, 106.8, 113.4, 114.5, 115.4, 116.8, 125.0, 125.07, 125.1, 125.13, 125.15, 125.3, 126.2, 126.3, 126.5, 126.6, 126.7, 126.74, 126.8, 126.81, 127.3, 127.7, 127.8, 127.84, 128.0, 128.01, 128.1, 128.15, 128.2, 128.24, 128.3, 128.4, 128.43, 128.5, 128.51, 128.54, 128.6, 128.62, 128.7, 129.1, 129.15, 129.2, 129.3, 129.4, 137.8, 138.0, 138.05, 138.1, 139.0, 139.2, 139.5, 140.3, 141.9, 143.3, 144.6, 144.8, 150.7, 150.8, 150.9, 151.0, 166.4, 166.5, 166.6, 166.9, 208.7, 208.73, 209.2, 209.3 ESI-HRMS: m/z [M+Na] calcd for $C_{33}H_{38}O_4$: 521.2662; found 521.2654.

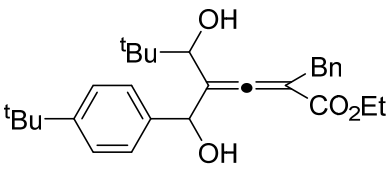
Ethyl 2-benzyl-5-hydroxy-4-(hydroxy(phenyl)methyl)-7-phenylhepta-2,3,6-trienoate (5g)



Following the general procedure, the product was obtained as a colorless oil (0.23 g, 77%) after flash column chromatography using 8-15% EtOAc/hexane as eluent (diastereomeric mixture).

^{1}H NMR (400 MHz, $CDCl_3$): 1.23-1.28 (m, 3H), 3.40-3.60 (m, 2H), 3.78-3.87 (m, 3H), 4.10-4.21 (m, 2H), 4.81-4.83 (m, 1H), 5.36-5.41 (m, 1H), 5.98-6.02 (m, 1H), 6.45-6.58 (m, 1H), 7.04-7.24 (m, 5H), 7.26-7.47 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.2, 14.22, 34.9, 35.1, 61.3, 61.4, 71.1, 71.3, 72.9, 73.4, 104.9, 105.6, 105.98, 106.0, 113.9, 114.1, 115.5, 115.6, 126.46, 126.5, 126.51, 126.52, 126.6, 126.62, 126.64, 126.7, 126.75, 126.86, 126.9, 128.1, 128.2, 128.24, 128.3, 128.35, 128.5, 128.54, 128.6, 128.8, 129.2, 129.25, 130.1, 130.9, 131.0, 131.5, 131.55, 133.4, 136.3, 136.4, 138.5, 138.6, 140.8, 141.0, 154.6, 155.0, 166.4, 166.6, 208.98, 209.0. ESI-HRMS: m/z [M+Na] calcd for $C_{29}H_{28}O_4$: 463.1880; found 463.1869.

Ethyl 2-benzyl-4-((4-(tert-butyl)phenyl)(hydroxy)methyl)-5-hydroxy-6,6-dimethylhepta-2,3-dienoate (5h)

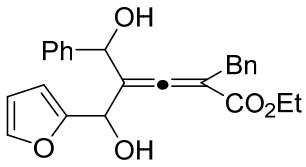


Following the general procedure, the product was obtained as a yellowish oil (0.17 g, 64%) after flash column chromatography using 8-15% EtOAc/hexane as eluent (diastereomeric mixture).

^{1}H NMR (400 MHz, $CDCl_3$): 0.81-0.97 (m, 9H), 1.22-1.38 (m, 12H), 3.43-3.71 (m, 3H), 4.13-4.29 (m, 2H), 5.12-5.32 (m, 1H), 7.12-7.38 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 13.7, 14.2, 14.3, 25.8, 25.9, 25.95, 31.1, 31.3, 31.4, 34.5, 34.51, 34.52, 35.1, 35.13, 35.2,

36.0, 36.2, 36.3, 61.0, 61.2, 61.3, 74.2, 74.8, 75.2, 77.7, 78.56, 78.6, 105.1, 105.3, 106.3, 114.1, 115.4, 115.5, 124.9, 125.1, 125.2, 126.3, 126.4, 126.5, 126.53, 126.6, 126.7, 128.4, 128.41, 128.5, 129.1, 129.4, 129.45, 137.6, 137.76, 138.78, 138.8, 138.81, 138.9, 150.8, 150.84, 150.9, 166.4, 166.64, 166.7, 209.1, 209.2, 209.24. ESI-HRMS: m/z [M+Na] calcd for $C_{29}H_{38}O_4$: 473.2662; found 473.2668.

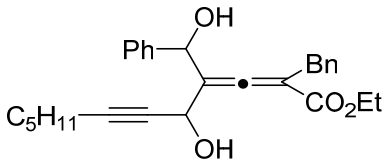
Ethyl 2-benzyl-5-(furan-2-yl)-5-hydroxy-4-(hydroxy(phenyl)methyl)penta-2,3-dienoate (5i)



Following the general procedure, the product was obtained as an orange oil (0.27 g, 74%) after flash column chromatography using 8-15% EtOAc/hexane as eluent (diastereomeric mixture)

^{1}H NMR (400 MHz, $CDCl_3$): 1.25-1.29 (m, 3H), 3.47-3.54 (m, 2H), 4.13-4.19 (m, 2H), 5.16-5.30 (m, 2H), 6.14-6.31 (m, 2H), 7.02-7.15 (m, 3H), 7.19-7.27 (m, 7H), 7.28-7.33 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.1, 14.16, 14.2, 34.9, 35.0, 35.1, 61.3, 61.33, 61.4, 66.7, 66.8, 66.84, 72.8, 72.85, 73.3, 105.8, 106.2, 106.7, 107.4, 107.5, 107.6, 110.27, 110.3, 110.32, 112.4, 113.8, 114.5, 126.4, 126.45, 126.5, 126.56, 126.6, 127.9, 127.92, 127.94, 128.1, 128.2, 128.25, 128.3, 128.33, 128.4, 129.1, 129.2, 129.3, 138.46, 138.48, 138.5, 140.5, 140.6, 140.64, 142.2, 142.3, 142.4, 153.3, 153.4, 153.5, 166.3, 166.4, 166.41, 208.3, 208.4, 208.7. ESI-HRMS: m/z [M+Na] calcd for $C_{25}H_{24}O_5$: 427.1516; found 427.1514.

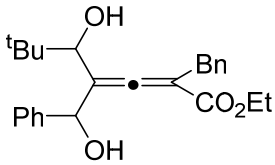
Ethyl 2-benzyl-5-hydroxy-4-(hydroxy(phenyl)methyl)dodeca-2,3-dien-6-ynoate (5j)



Following the general procedure, the product was obtained as a colorless oil (0.12 g, 52%) after flash column chromatography using 8-15% EtOAc/hexane as eluent (diastereomeric mixture)

^{1}H NMR (400 MHz, $CDCl_3$): 0.88-0.92 (m, 3H), 1.26-1.34 (m, 7H), 1.44-1.50 (m, 2H), 1.68 (br. s, 1H), 2.15-2.21 (m, 2H), 3.43-3.63 (m, 2H), 4.11-4.23 (m, 2H), 4.82-4.83 (m, 1H), 5.45-5.48 (m, 1H), 7.00-7.16 (m, 2H), 7.19-7.25 (m, 4H), 7.26-7.32(m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 13.89, 13.9, 13.92, 14.2, 14.23, 14.3, 18.6, 18.63, 18.7, 22.1, 22.15, 22.2, 28.1, 28.16, 28.2, 30.9, 30.97, 31.0, 34.9, 34.93, 35.0, 35.1, 61.2, 61.9, 62.1, 72.6, 72.7, 73.3, 77.6, 77.7, 77.8, 87.4, 87.6, 87.8, 105.3, 105.4, 106.2, 114.4, 114.49, 114.5, 126.3, 126.4, 126.44, 126.46, 126.5, 126.52, 127.8, 127.9, 128.0, 128.1, 128.2, 128.23, 128.3, 128.35, 128.4, 129.2, 129.24, 129.3, 138.4, 138.5, 138.6, 140.7, 140.8, 140.9, 165.8, 166.1, 166.2, 208.0, 208.16, 208.2. ESI-HRMS: m/z [M+Na] calcd for $C_{28}H_{32}O_4$: 455.2193; found 455.2195.

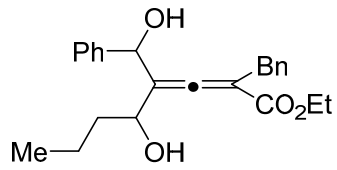
Ethyl 2-benzyl-5-hydroxy-4-(hydroxy(phenyl)methyl)-6,6-dimethylhepta-2,3-dienoate (5k)



Following the general procedure, the product was obtained as a colorless oil (0.32 g, 65%) after flash column chromatography using 8-15% EtOAc/hexane as eluent (4: 1 diastereomeric ratio).

^{1}H NMR (400 MHz, $CDCl_3$): 0.83 (s, 9H), 0.92 (s, 2.25H), 3.48-3.63(m, 4.28H), 4.14-4.27 (m, 2.70H), 5.26-5.31 (m, 1.28H), 7.16-7.32 (m, 15.25H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.1, 14.2, 25.8, 26.0, 35.0, 35.1, 35.9, 36.3, 61.2, 61.3, 74.2, 75.5, 77.7, 78.7, 104.9, 105.0, 113.4, 114.9, 126.5(2C), 126.6(2C), 126.67, 126.7, 127.8, 127.9, 128.1(2C), 128.2(2C), 128.4(2C), 128.45(2C), 129.2(2C), 129.4(2C), 138.7, 138.9, 140.7, 140.8, 166.5, 166.6, 209.2, 209.3. ESI-HRMS: m/z [M+Na] calcd for $C_{25}H_{30}O_4$: 417.2036; found 417.2047.

Ethyl 2-benzyl-5-hydroxy-4-(hydroxy(phenyl)methyl)octa-2,3-dienoate (5l)



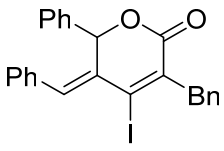
Following the general procedure, the product was obtained as a colorless oil (0.20 g, 78%) after flash column chromatography using 8-15% EtOAc/hexane as eluent (diastereomeric mixture)

^{1}H NMR (400 MHz, $CDCl_3$): 0.75-0.86 (m, 3H), 1.21-1.35 (m, 5H), 1.38-1.50 (m, 2H), 3.46-3.57 (m, 2H), 4.05-4.22 (m, 2H), 5.39-5.41 (m, 1H), 7.09-7.16 (m, 5H), 7.22-7.37 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 13.7, 13.8, 13.83, 14.1, 14.19, 18.5, 18.6, 35.0, 35.03, 37.6, 37.7, 37.74, 61.2, 61.26, 61.3, 69.97, 70.0, 70.5, 72.6, 73.5, 73.7, 104.4, 104.6, 104.62, 114.2, 114.21, 115.4, 126.3, 126.4, 126.44, 126.5, 126.9, 127.6, 128.1, 128.11, 128.3, 128.33, 128.35, 128.4, 129.1, 129.12, 129.2, 129.3, 138.78, 138.8, 138.84, 141.1, 141.11, 141.3, 166.6, 166.8, 166.82, 208.59, 208.6, 208.7. ESI-HRMS: m/z [M+Na] calcd for $C_{24}H_{28}O_4$: 403.1880; found 403.1869.

General Procedure for the Iododehydroxylation/Lactonization Reaction:

A round bottom flask containing allenoate dicarbinol **5a** or **7a** (1.0 eq.) was charged with hydroquinone (20 mol%) and LiI (5.0 eq.) in acetic acid (1.5 mL/mmol). The mixture was heated at 50 °C with stirring for 1 h (reaction was monitored by TLC). The reaction mixture was diluted with water and the aqueous phase was extracted with DCM. The organic layer was thoroughly washed with water, saturated $NaHCO_3$ and brine solution and was then dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product obtained was purified by flash chromatography using 2% EtOAc/Hexane eluent.

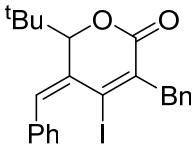
(E)-3-benzyl-5-benzylidene-4-iodo-6-phenyl-5,6-dihydro-2H-pyran-2-one (7a)



Following the general procedure, the product was obtained as a yellowish oil (0.14 g, 86%) after flash column chromatography using 2% EtOAc/hexane as eluent (single diastereomer).

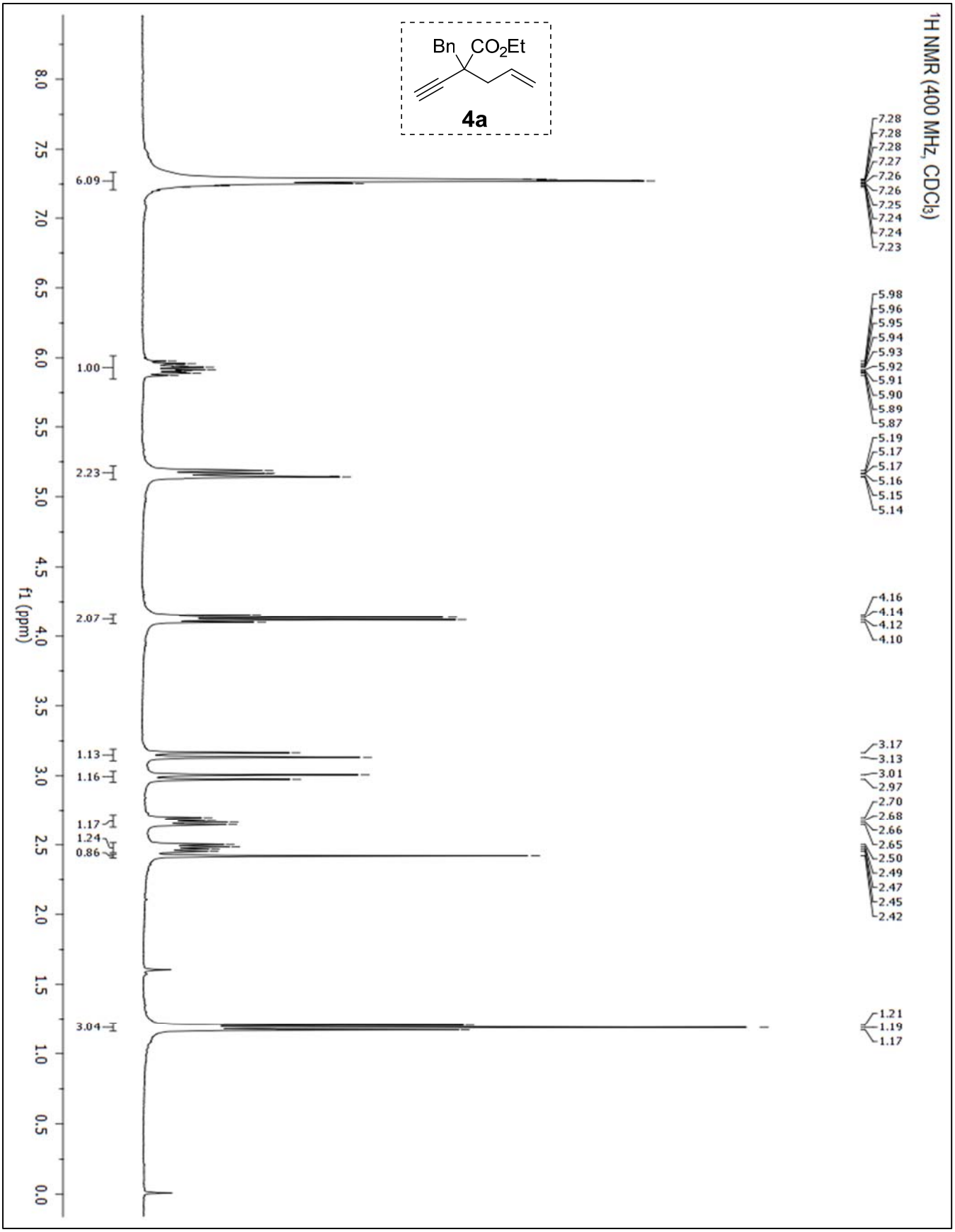
^{1}H NMR (400 MHz, $CDCl_3$): 4.03 (dd, *J* = 71.4, 14.8 Hz, 2H), 6.65 (s, 1H), 6.81-6.83 (m, 2H), 7.02-7.10 (m, 3H), 7.22-7.24 (m, 2H), 7.33-7.39 (m, 8H), 7.57 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 42.7, 76.8, 121.7, 126.3, 126.9, 128.3(2C), 128.4(2C), 128.8(2C), 128.84, 129.0(2C), 129.1(2C), 129.3, 133.5, 134.4, 137.3, 138.2, 142.7, 159.6. ESI-HRMS: m/z [M+H] calcd for $C_{25}H_{19}IO_2$: 479.0508; found 479.0502.

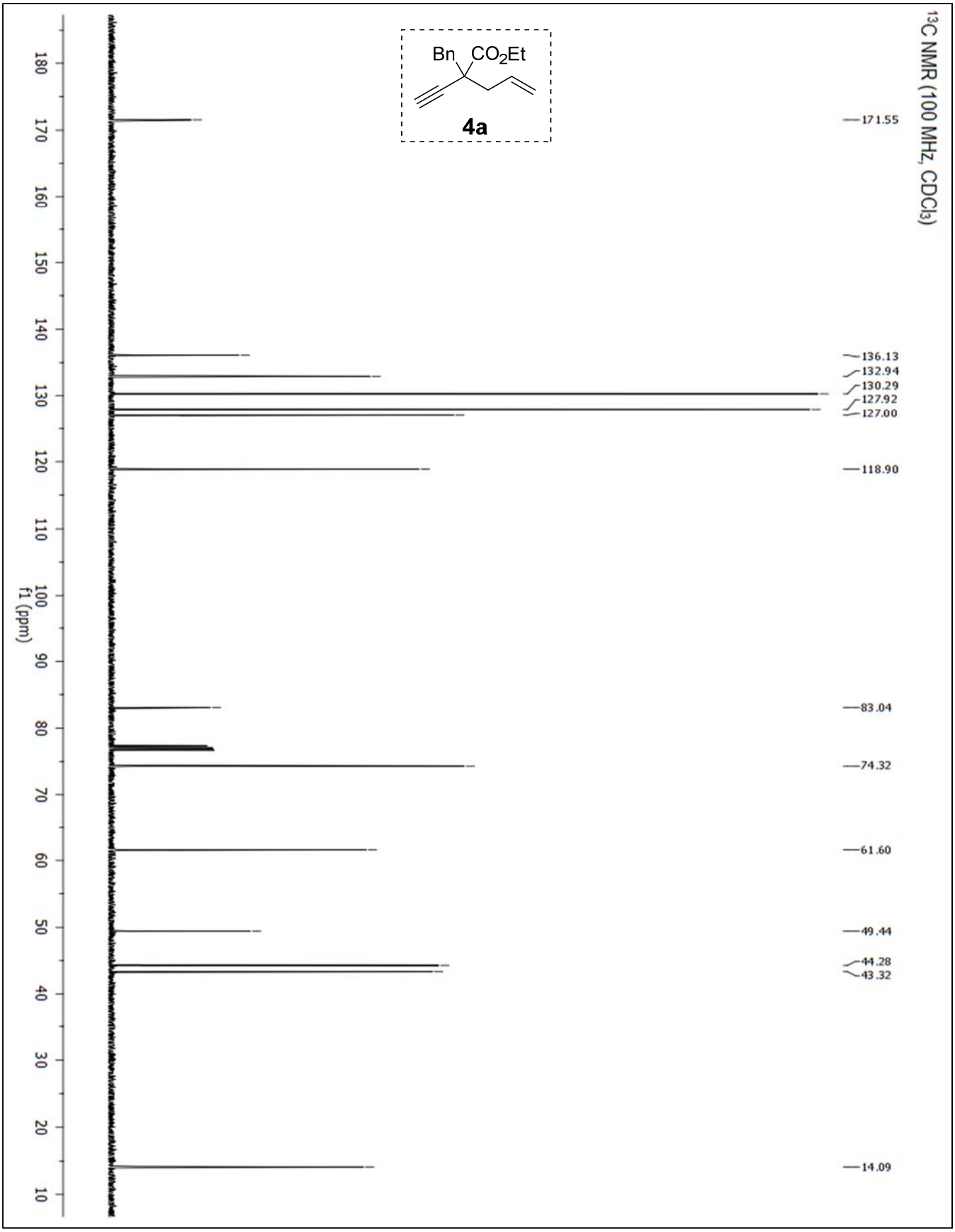
(Z)-3-benzyl-5-benzylidene-6-(tert-butyl)-4-iodo-5,6-dihydro-2H-pyran-2-one (7k)

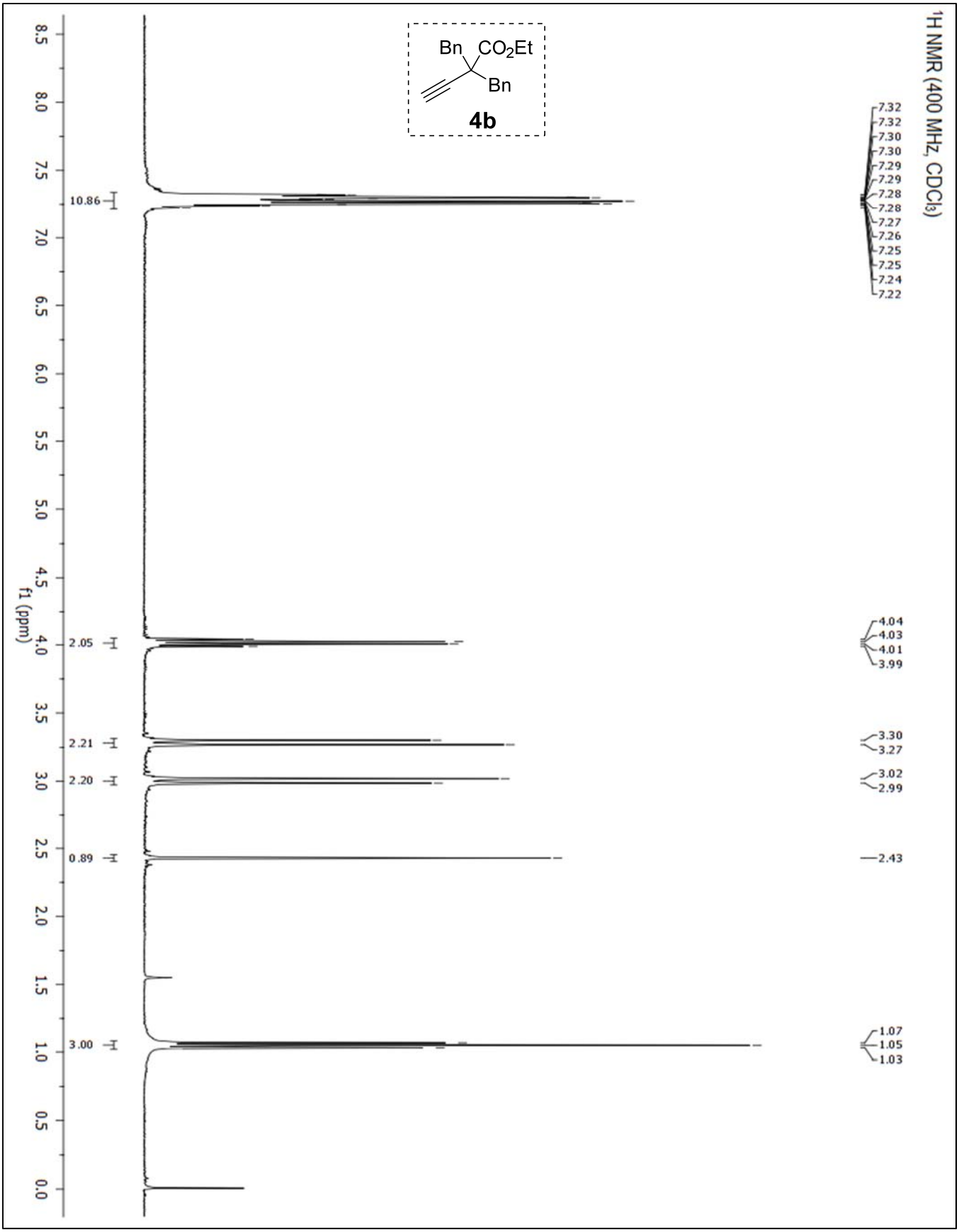


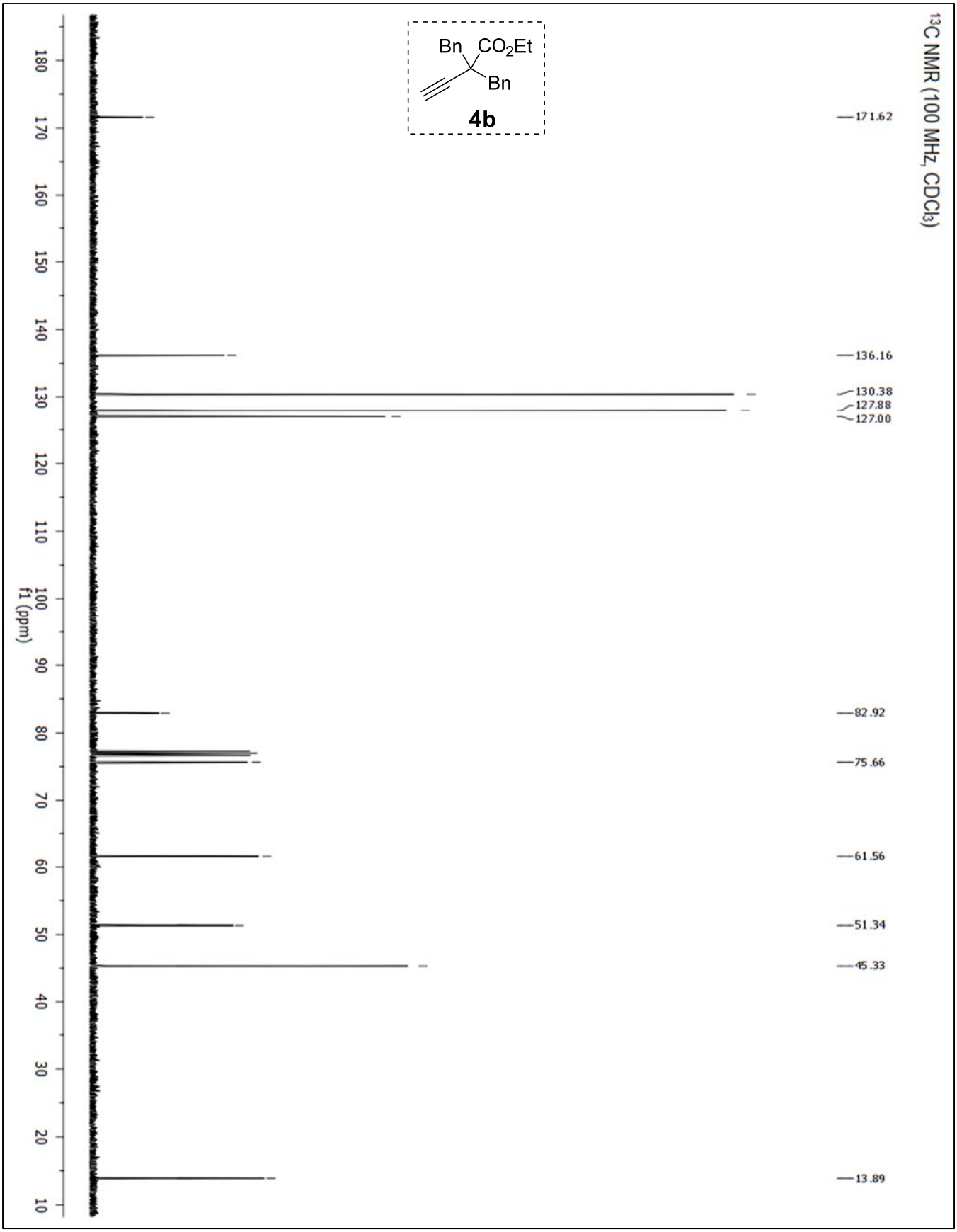
Following the general procedure, the product was obtained as a colorless oil (0.10 g, 84%) after flash column chromatography using 2% EtOAc/hexane as eluent (single diastereomer).

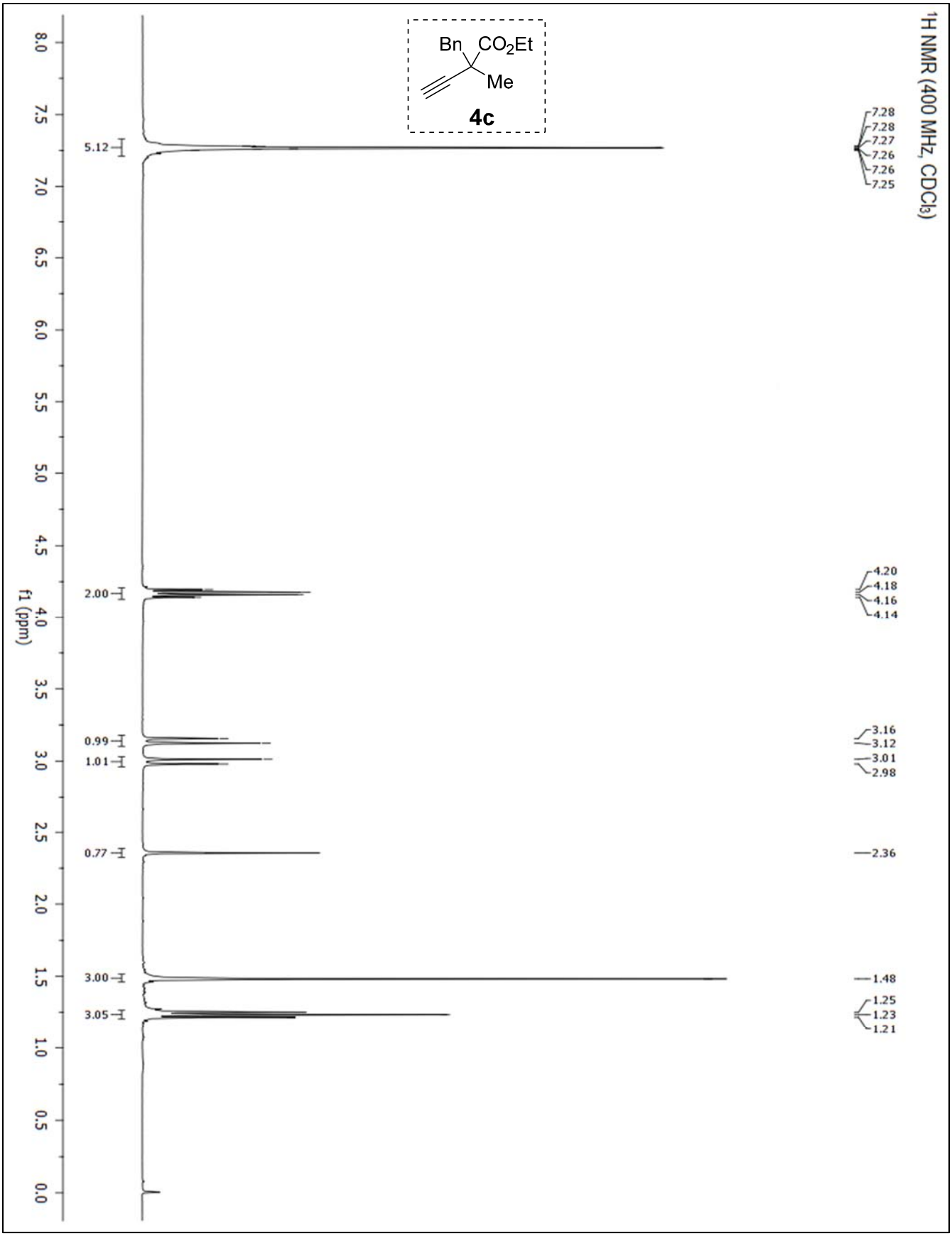
^{1}H NMR (400 MHz, $CDCl_3$): 0.80 (s, 9H), 3.90 (dd, *J* = 62.2, 13.7 Hz, 2H), 4.52 (s, 1H), 6.56 (s, 1H), 7.10-7.30 (m, 8H), 7.37 (d, *J* = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 26.8(3C), 36.6, 41.6, 92.6, 110.9, 126.7, 128.0(2C), 128.3(2C), 128.7, 129.5(2C), 130.7(2C), 131.7, 134.2, 136.9, 138.4, 139.8, 160.5. ESI-HRMS: m/z [M+Na] calcd for $C_{23}H_{23}IO_2$: 459.0821; found 459.0858.

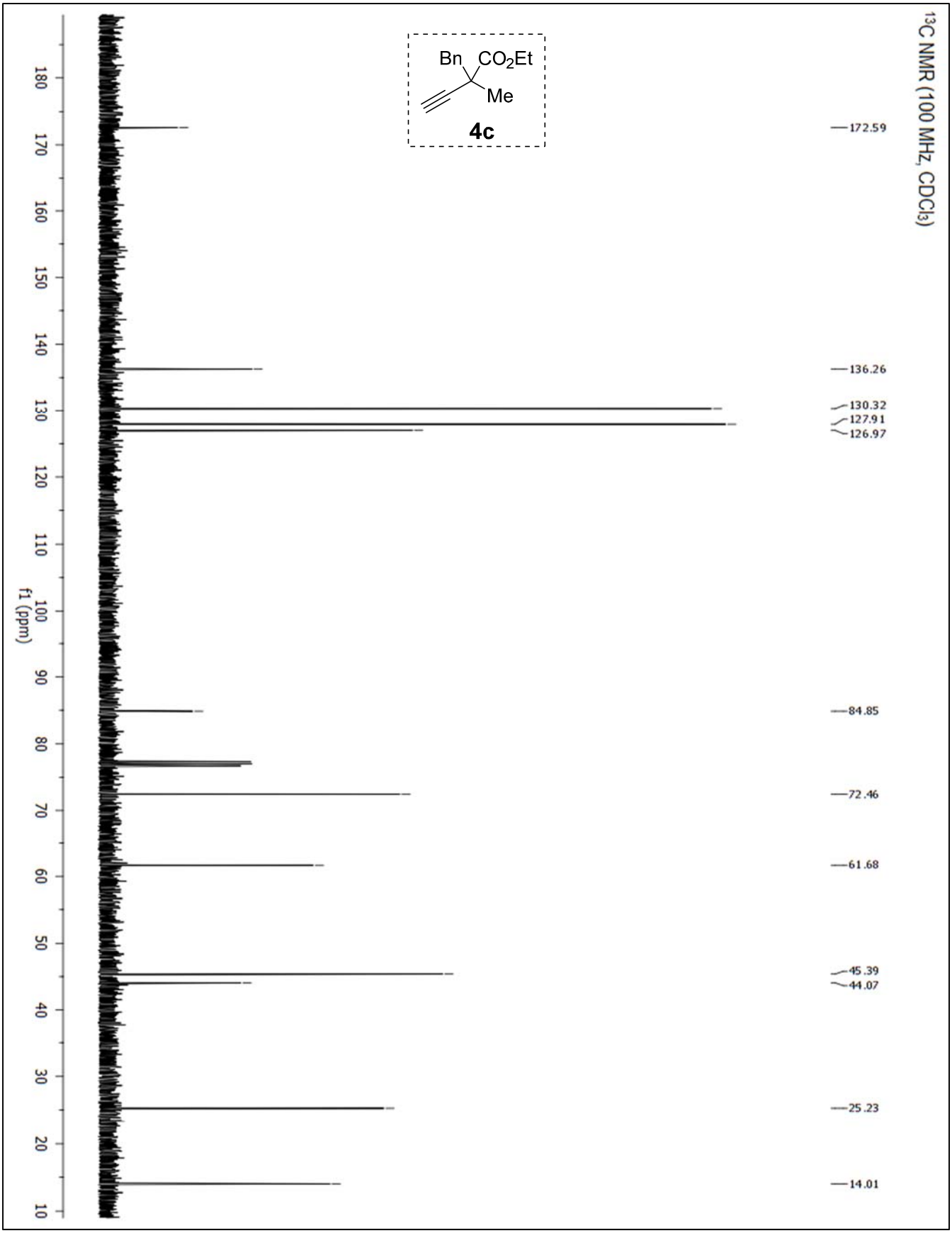

Bn
CO2Et
4a
1H NMR (400 MHz, CDCl3)
f1 (ppm)
6.09
1.00
2.23
2.07
1.13
1.16
1.17
1.24
0.86
3.04
7.28
7.28
7.28
7.27
7.26
7.26
7.25
7.24
7.24
7.23
5.98
5.96
5.95
5.94
5.93
5.92
5.91
5.90
5.89
5.87
5.19
5.17
5.17
5.16
5.15
5.14
4.16
4.14
4.12
4.10
3.17
3.13
3.01
2.97
2.70
2.68
2.66
2.65
2.50
2.49
2.47
2.45
2.42
1.21
1.19
1.17

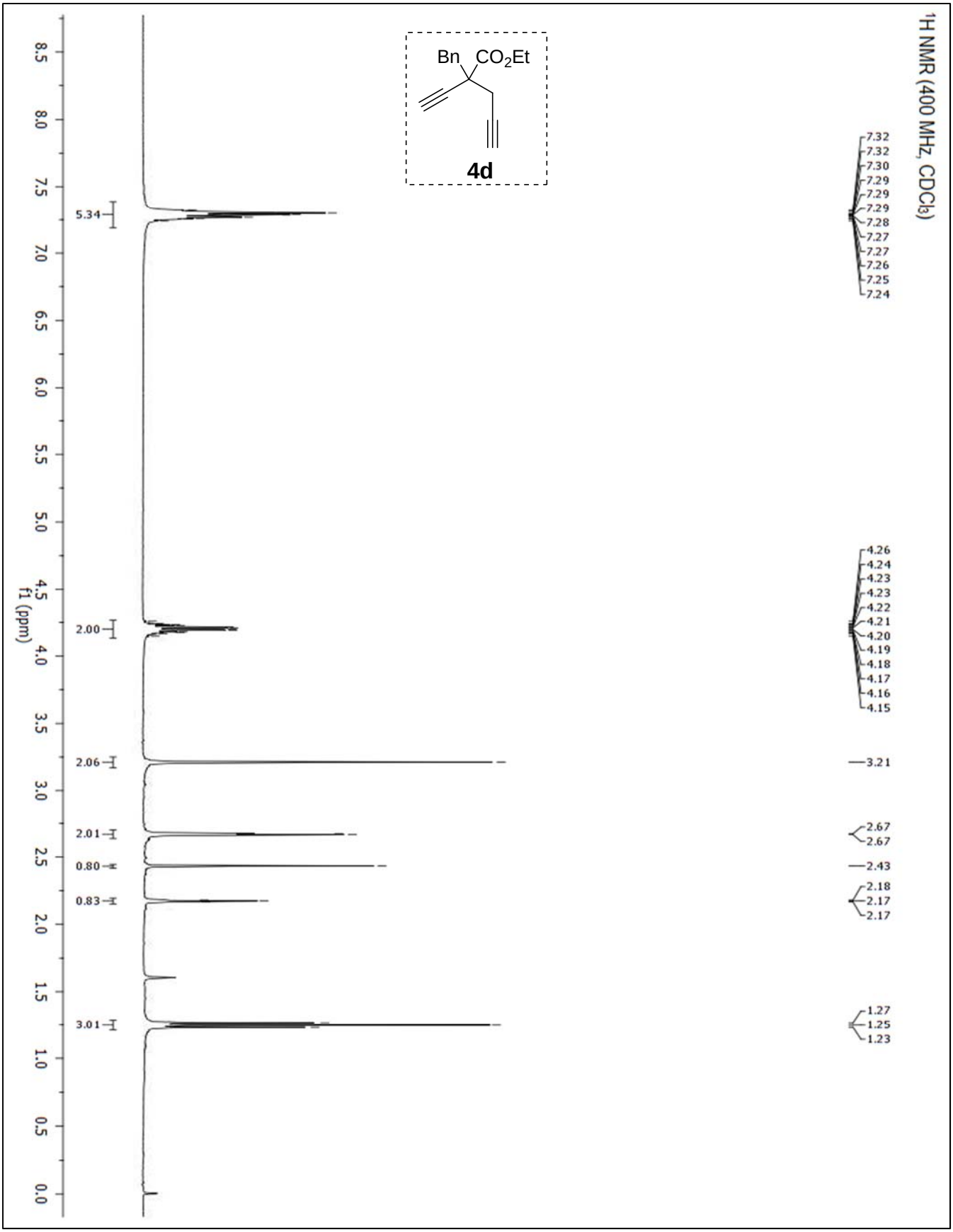

Bn
CO2Et
4a
13C NMR (100 MHz, CDCl3)
171.55
136.13
132.94
130.29
127.92
127.00
118.90
83.04
74.32
61.60
49.44
44.28
43.32
14.09
f1 (ppm)

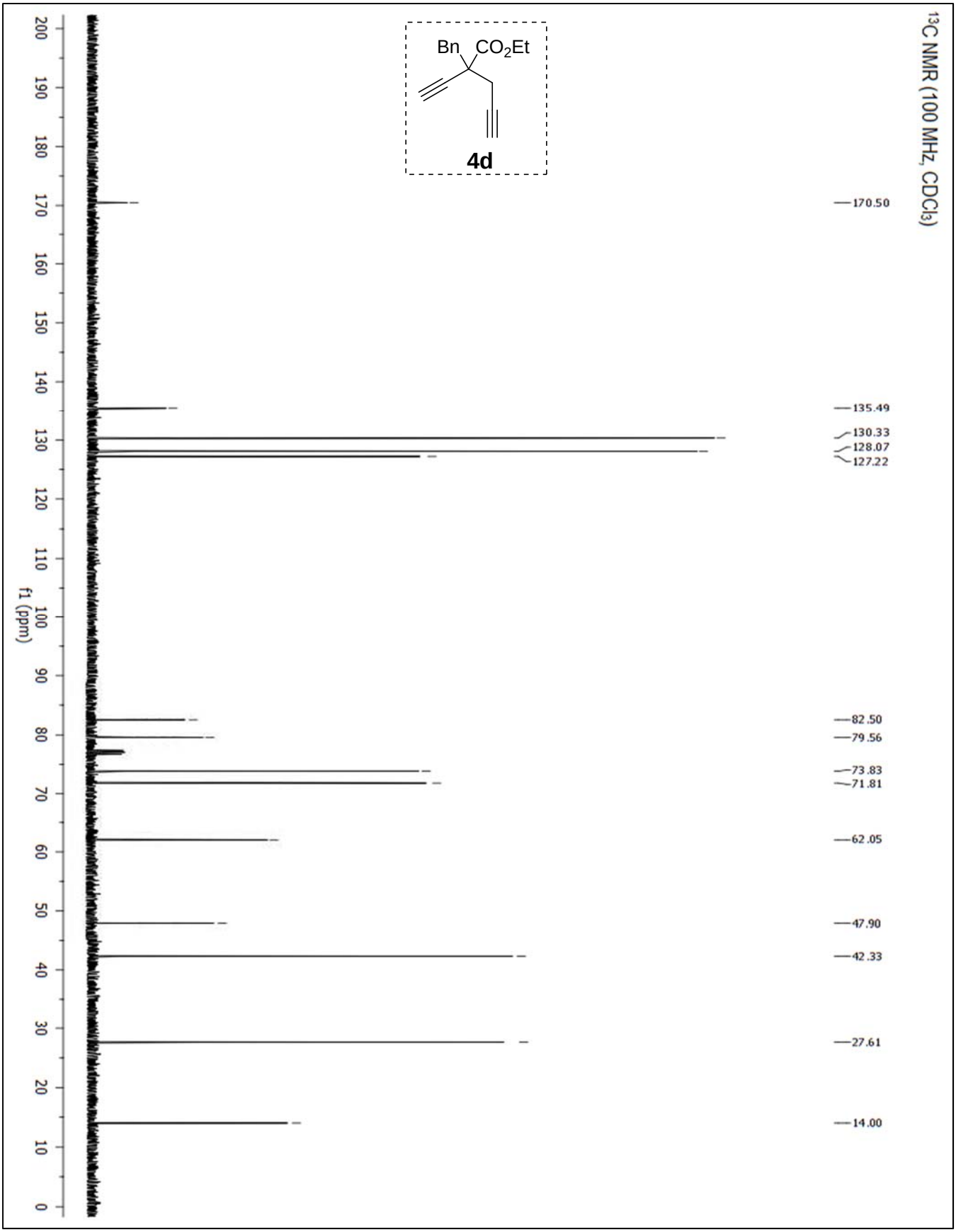

Bn CO2Et
Bn
4b
1H NMR (400 MHz, CDCl3)
f1 (ppm)
10.86
2.05
2.21
2.20
0.89
3.00
7.32
7.32
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.26
7.25
7.25
7.24
7.22
4.04
4.03
4.01
3.99
3.30
3.27
3.02
2.99
2.43
1.07
1.05
1.03

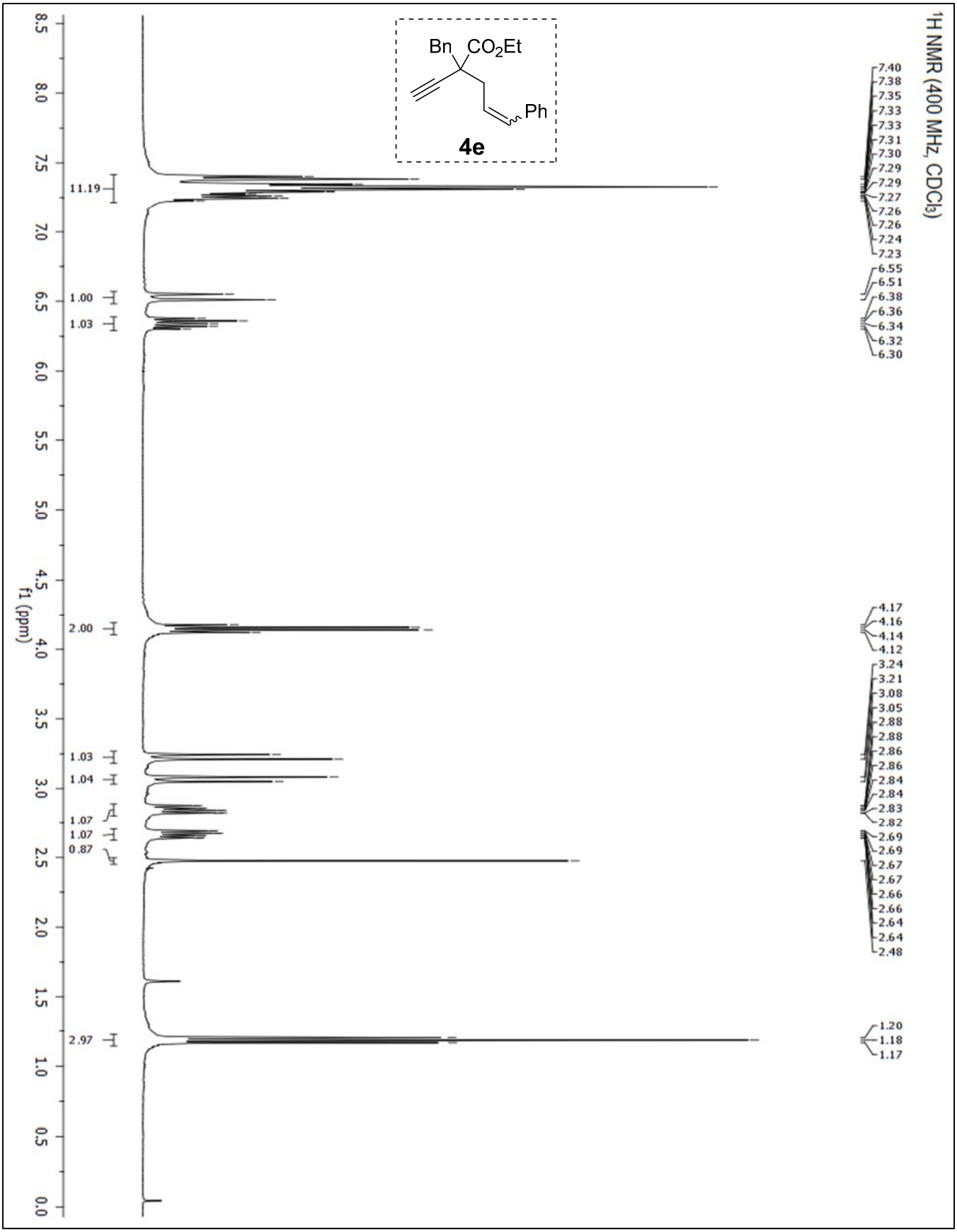

Bn
CO2Et
Bn
4b
13C NMR (100 MHz, CDCl3)
171.62
136.16
130.38
127.88
127.00
82.92
75.66
61.56
51.34
45.33
13.89
f1 (ppm)

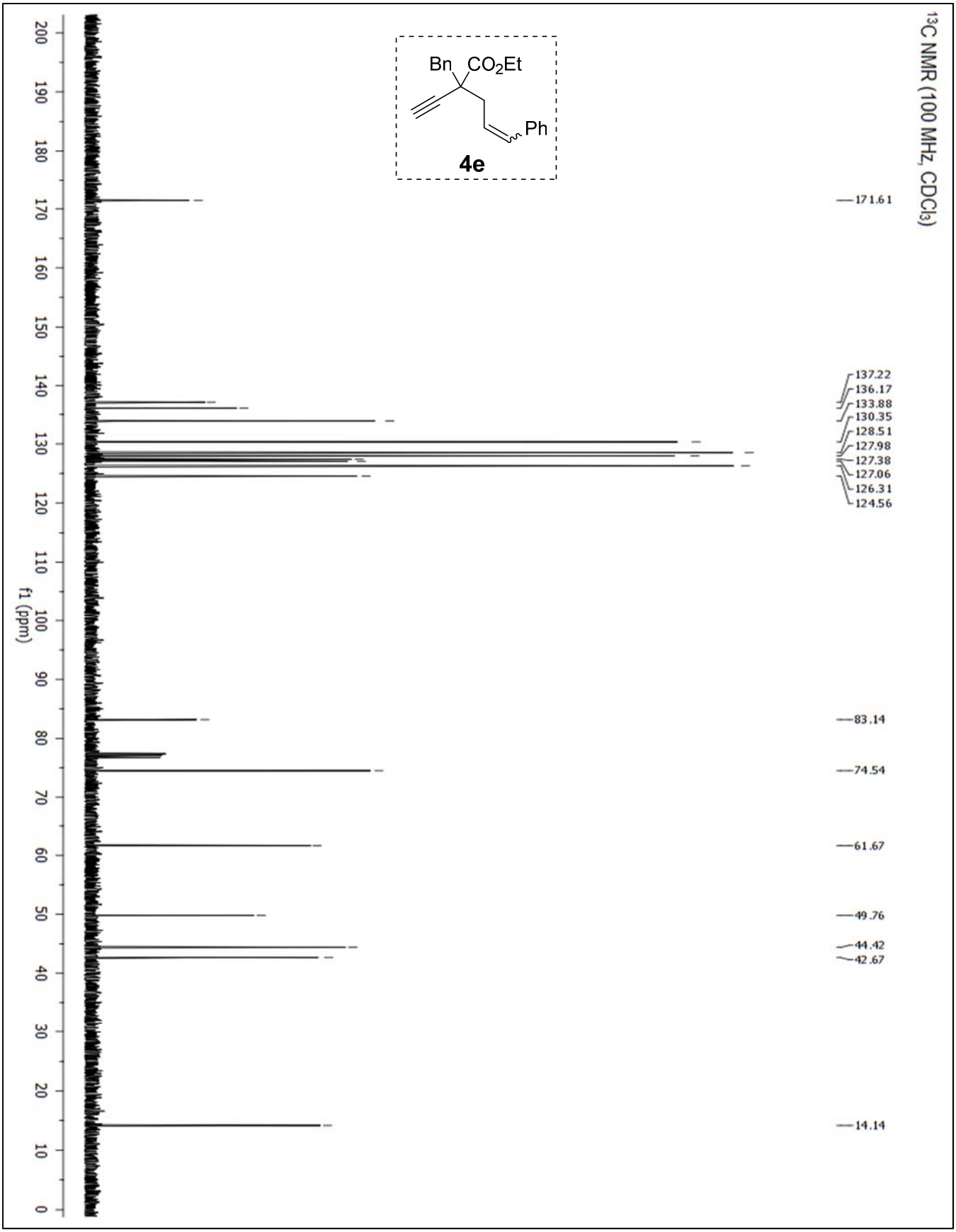

Bn
CO2Et
Me
4c
1H NMR (400 MHz, CDCl3)
f1 (ppm)
5.12
2.00
0.99
1.01
0.77
3.00
3.05
7.28
7.28
7.27
7.26
7.26
7.25
4.20
4.18
4.16
4.14
3.16
3.12
3.01
2.98
2.36
1.48
1.25
1.23
1.21

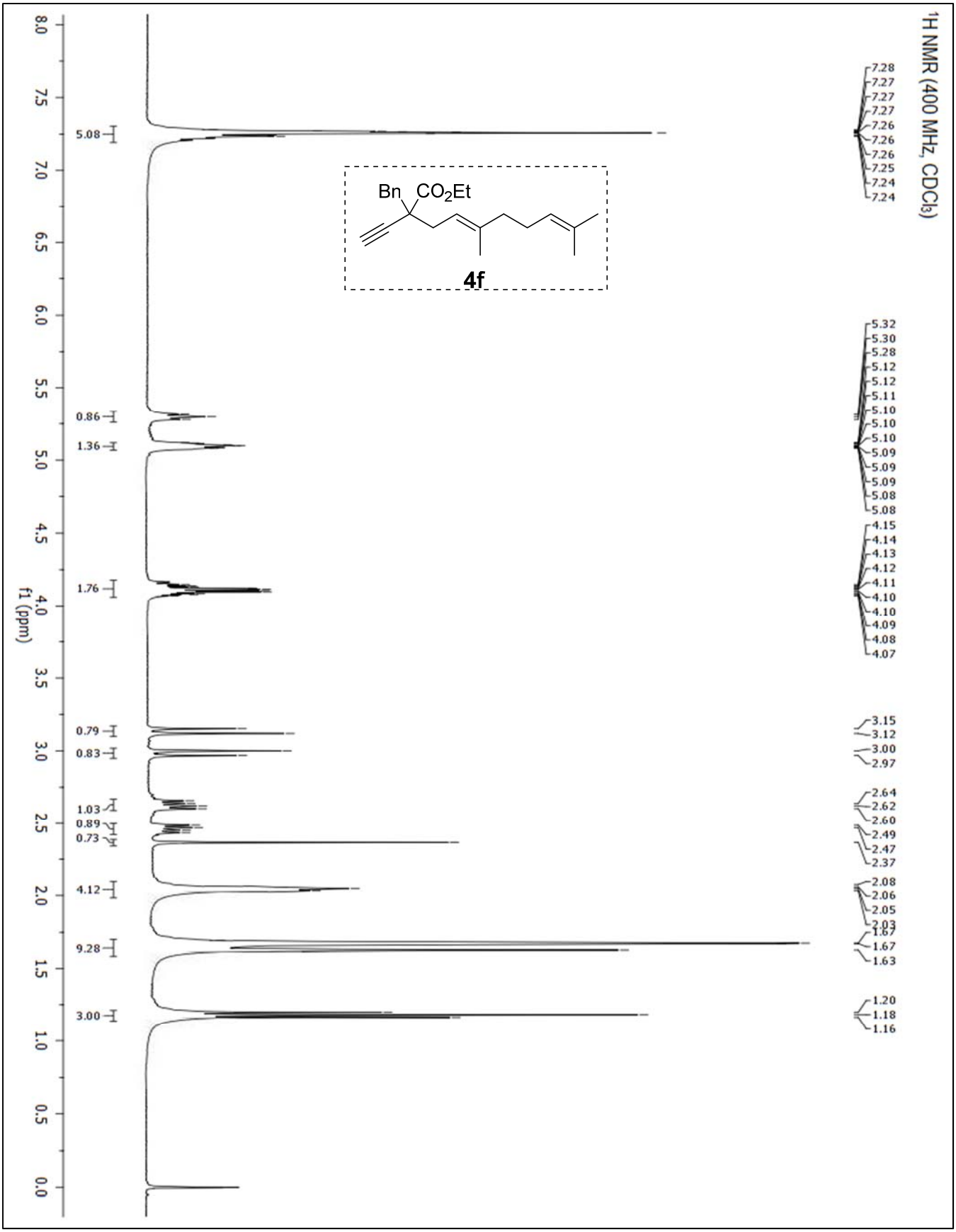

Bn
CO2Et
Me
4c
13C NMR (100 MHz, CDCl3)
172.59
136.26
130.32
127.91
126.97
84.85
72.46
61.68
45.39
44.07
25.23
14.01
f1 (ppm)

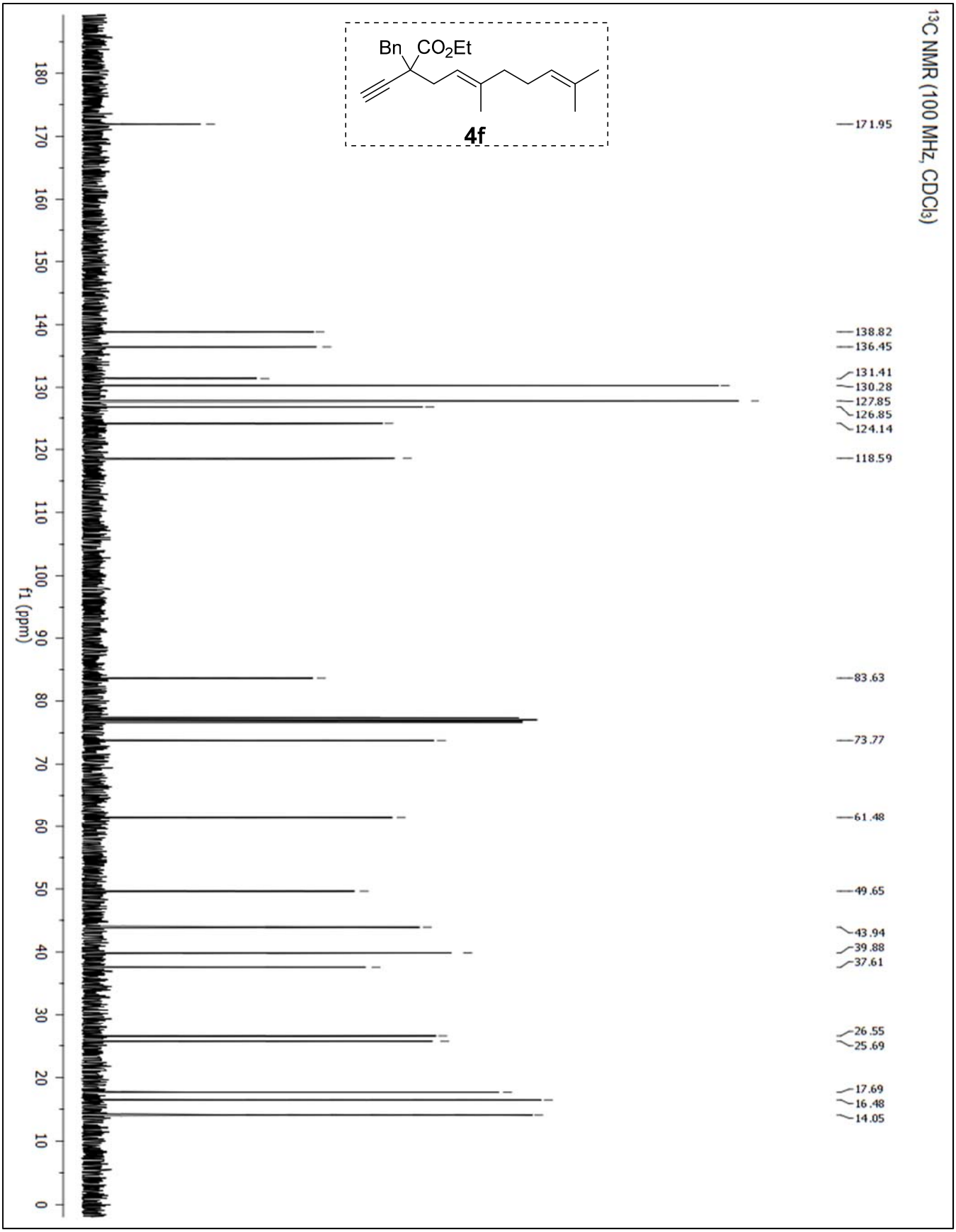

Bn
CO2Et
4d
1H NMR (400 MHz, CDCl3)
f1 (ppm)
5.34
2.00
2.06
2.01
0.80
0.83
3.01
7.32
7.32
7.30
7.29
7.29
7.29
7.28
7.27
7.27
7.26
7.25
7.24
4.26
4.24
4.23
4.23
4.22
4.21
4.20
4.19
4.18
4.17
4.16
4.15
3.21
2.67
2.67
2.43
2.18
2.17
2.17
1.27
1.25
1.23

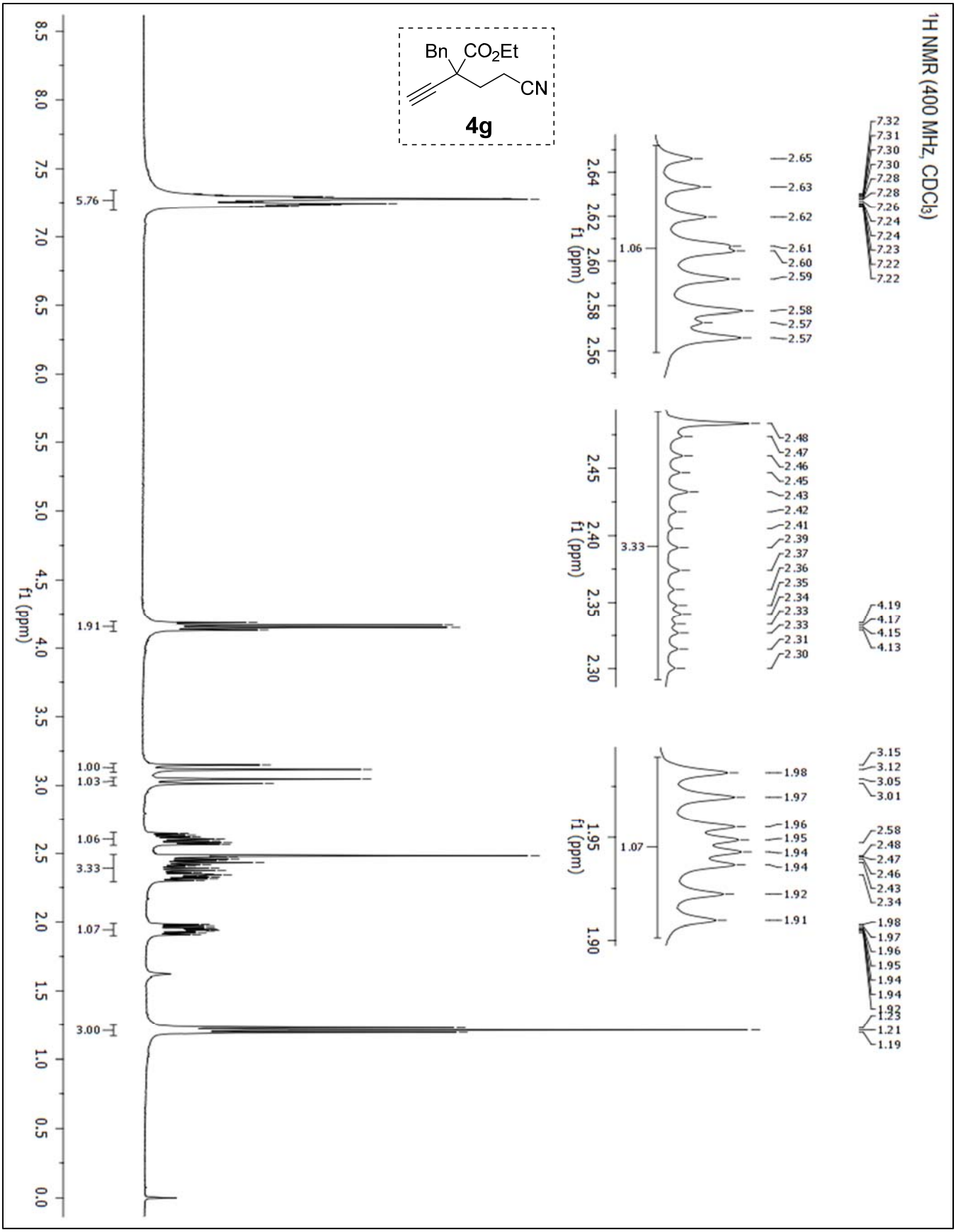

Bn
CO2Et
4d
13C NMR (100 MHz, CDCl3)
170.50
135.49
130.33
128.07
127.22
82.50
79.56
73.83
71.81
62.05
47.90
42.33
27.61
14.00
f1 (ppm)

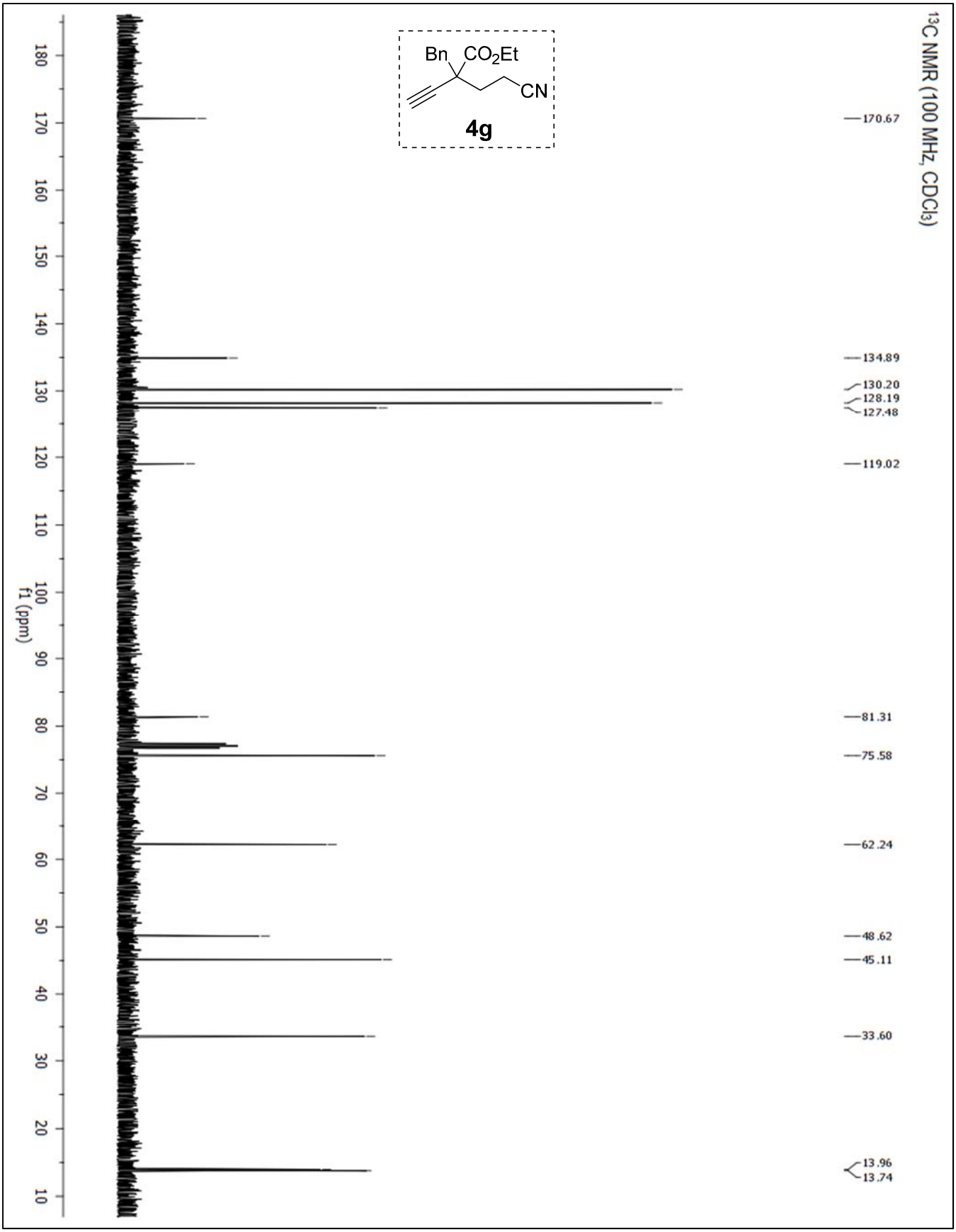

Bn
CO2Et
Ph
4e
1H NMR (400 MHz, CDCl3)
f1 (ppm)
11.19
1.00
1.03
2.00
1.03
1.04
1.07
1.07
0.87
2.97
7.40
7.38
7.35
7.33
7.33
7.31
7.30
7.29
7.29
7.27
7.26
7.26
7.24
7.23
6.55
6.51
6.38
6.36
6.34
6.32
6.30
4.17
4.16
4.14
4.12
3.24
3.21
3.08
3.05
2.88
2.88
2.86
2.86
2.84
2.84
2.83
2.82
2.69
2.69
2.67
2.67
2.66
2.66
2.64
2.64
2.48
1.20
1.18
1.17

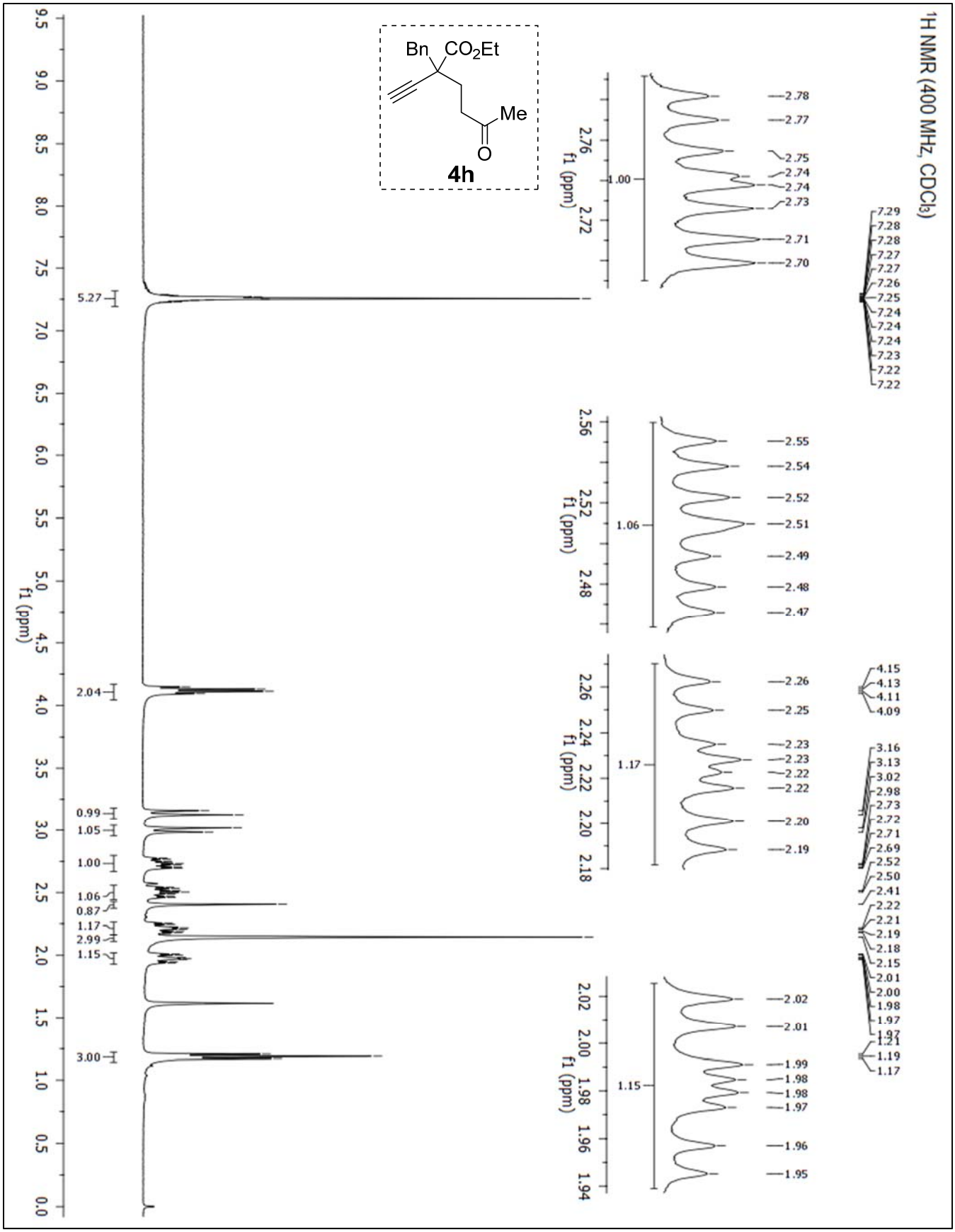

Bn
CO2Et
Ph
4e
13C NMR (100 MHz, CDCl3)
171.61
137.22
136.17
133.88
130.35
128.51
127.98
127.38
127.06
126.31
124.56
83.14
74.54
61.67
49.76
44.42
42.67
14.14
f1 (ppm)

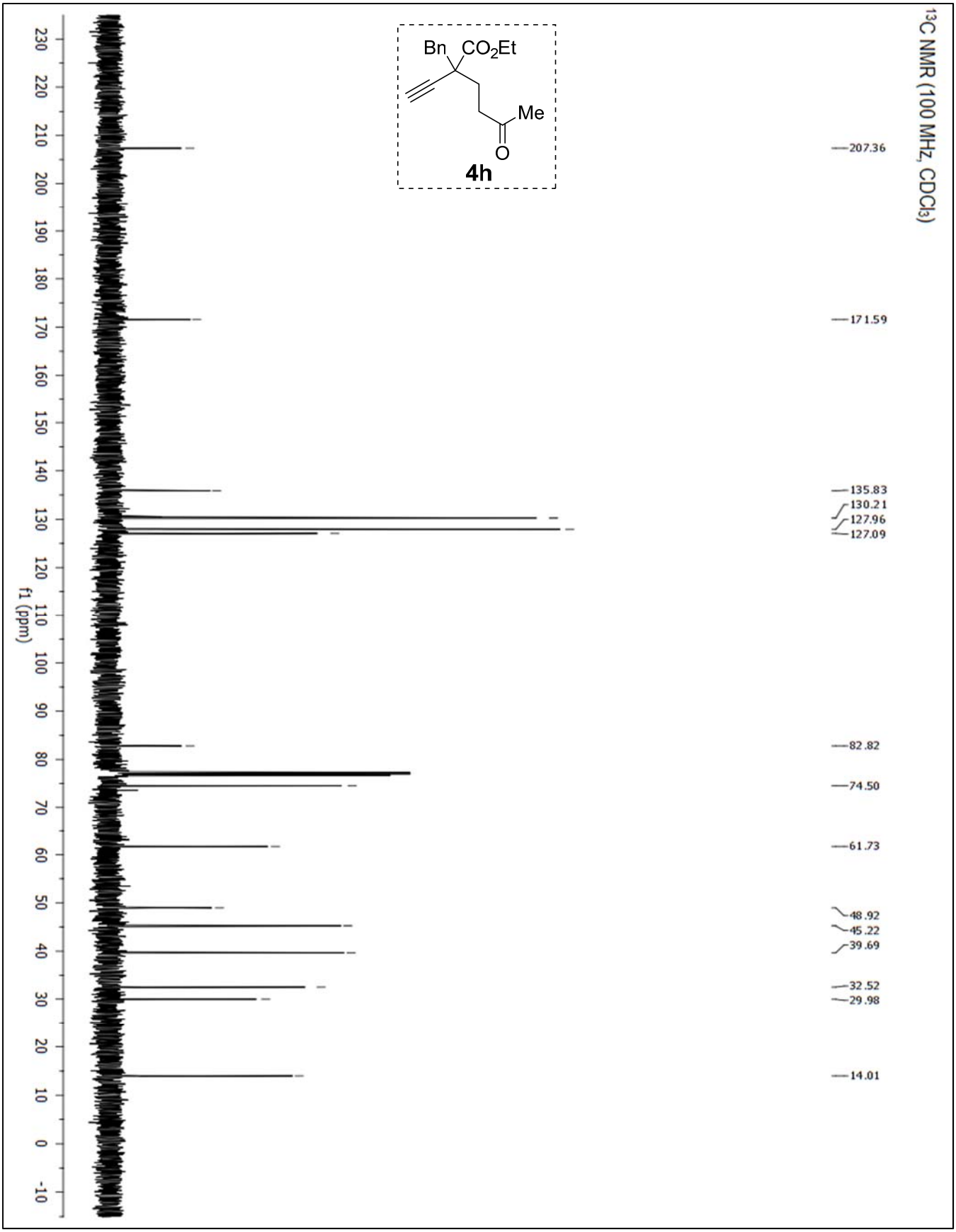

¹H NMR (400 MHz, CDCl₃)
Bn CO2Et
4f
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
5.08
0.86
1.36
1.76
0.79
0.83
1.03
0.89
0.73
4.12
9.28
3.00
7.28
7.27
7.27
7.27
7.26
7.26
7.26
7.25
7.24
7.24
5.32
5.30
5.28
5.12
5.12
5.11
5.10
5.10
5.10
5.09
5.09
5.09
5.08
5.08
4.15
4.14
4.13
4.12
4.11
4.10
4.10
4.09
4.08
4.07
3.15
3.12
3.00
2.97
2.64
2.62
2.60
2.49
2.47
2.37
2.08
2.06
2.05
2.03
1.67
1.67
1.63
1.20
1.18
1.16

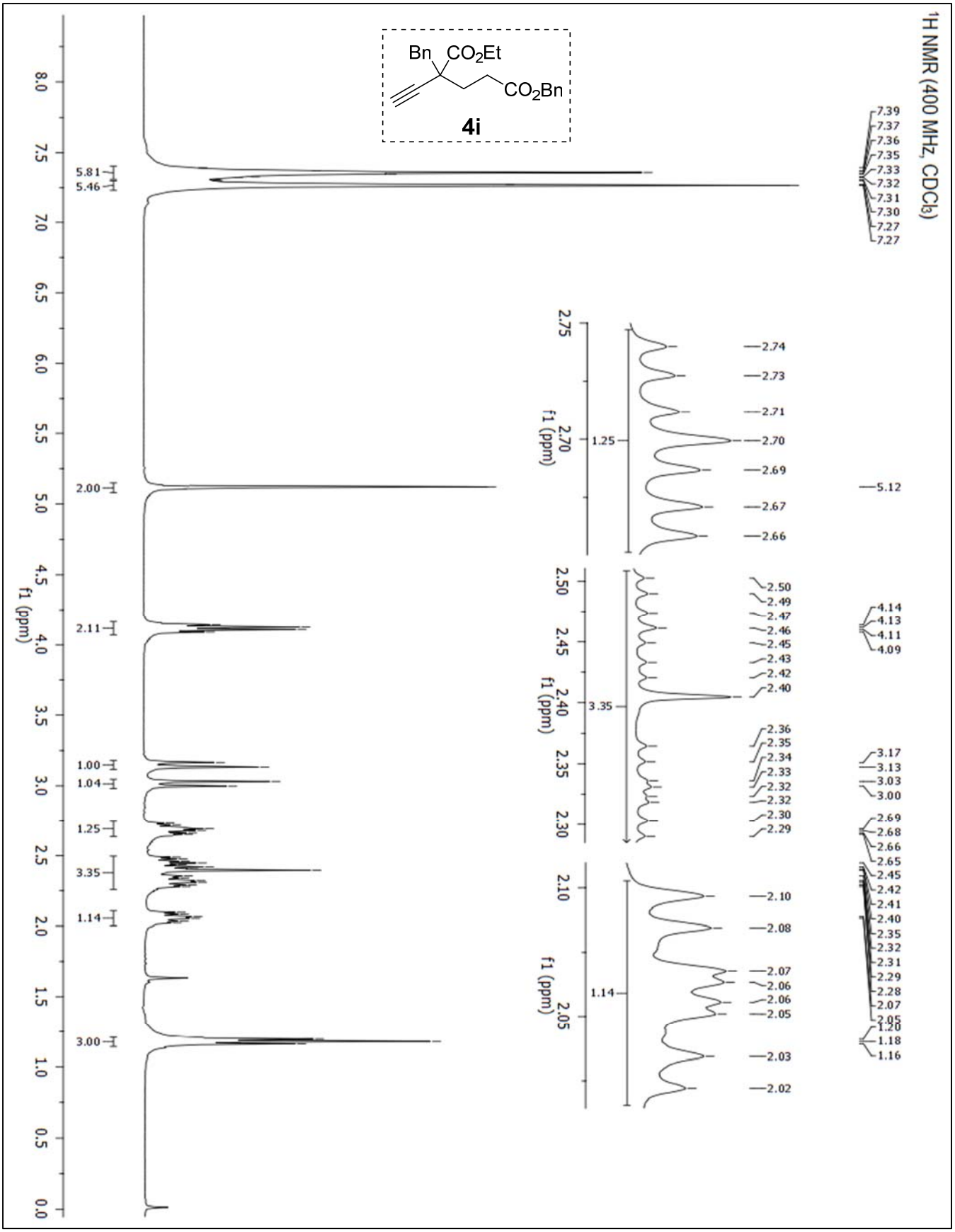

^{13}C NMR (100 MHz, CDCl$_3$)
Bn CO$_2$Et
4f
171.95
138.82
136.45
131.41
130.28
127.85
126.85
124.14
118.59
83.63
73.77
61.48
49.65
43.94
39.88
37.61
26.55
25.69
17.69
16.48
14.05
f1 (ppm)

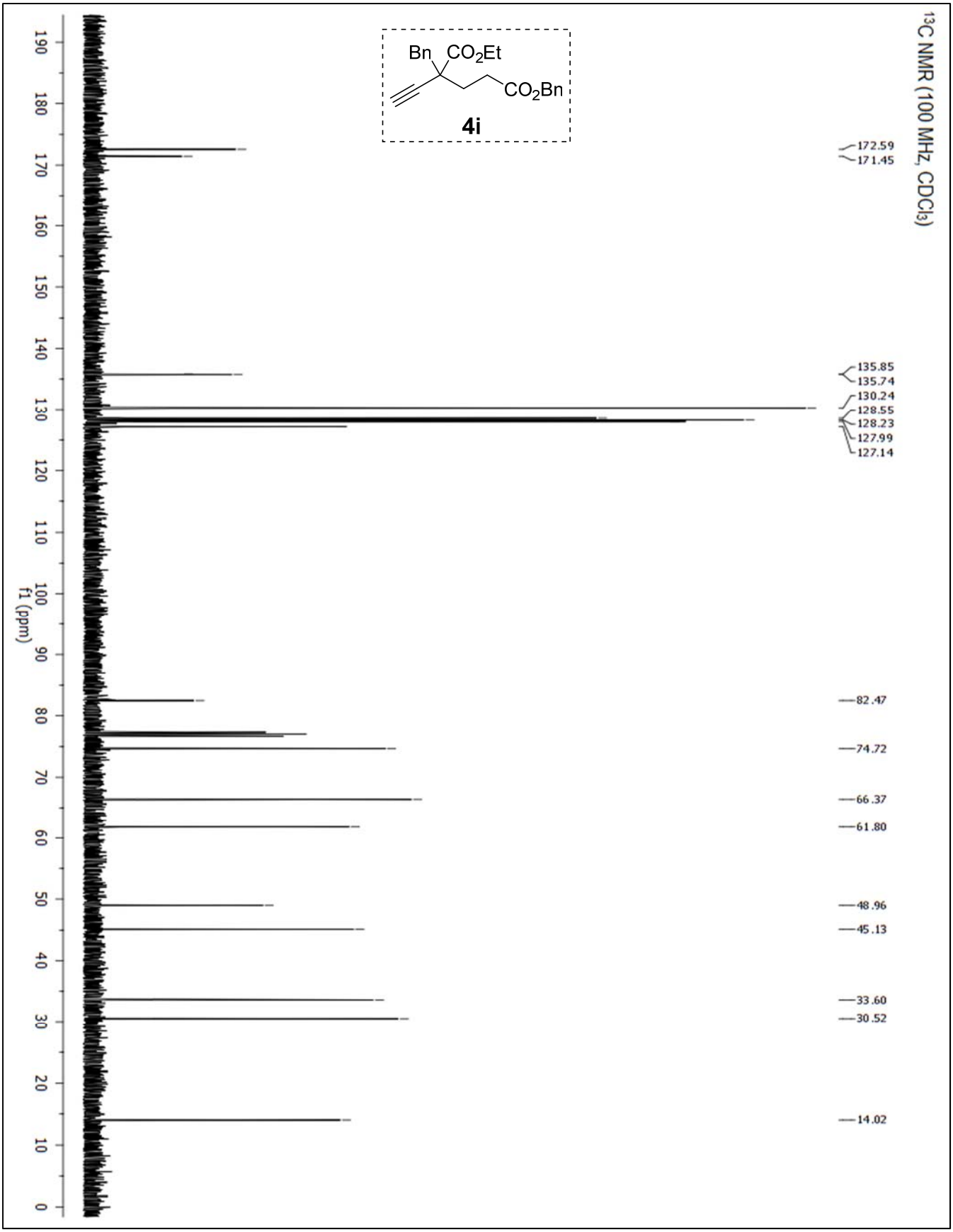

^{1}H NMR (400 MHz, CDCl$_3$)
Bn
CO_2Et
CN
4g
f1 (ppm)
5.76
1.91
1.00
1.03
1.06
3.33
1.07
3.00
1.06
3.33
1.07
7.32
7.31
7.30
7.30
7.28
7.28
7.26
7.24
7.24
7.23
7.22
7.22
2.65
2.63
2.62
2.61
2.60
2.59
2.58
2.57
2.57
4.19
4.17
4.15
4.13
3.15
3.12
3.05
3.01
2.58
2.48
2.47
2.46
2.43
2.34
1.98
1.97
1.96
1.95
1.94
1.94
1.92
1.91
1.23
1.21
1.19

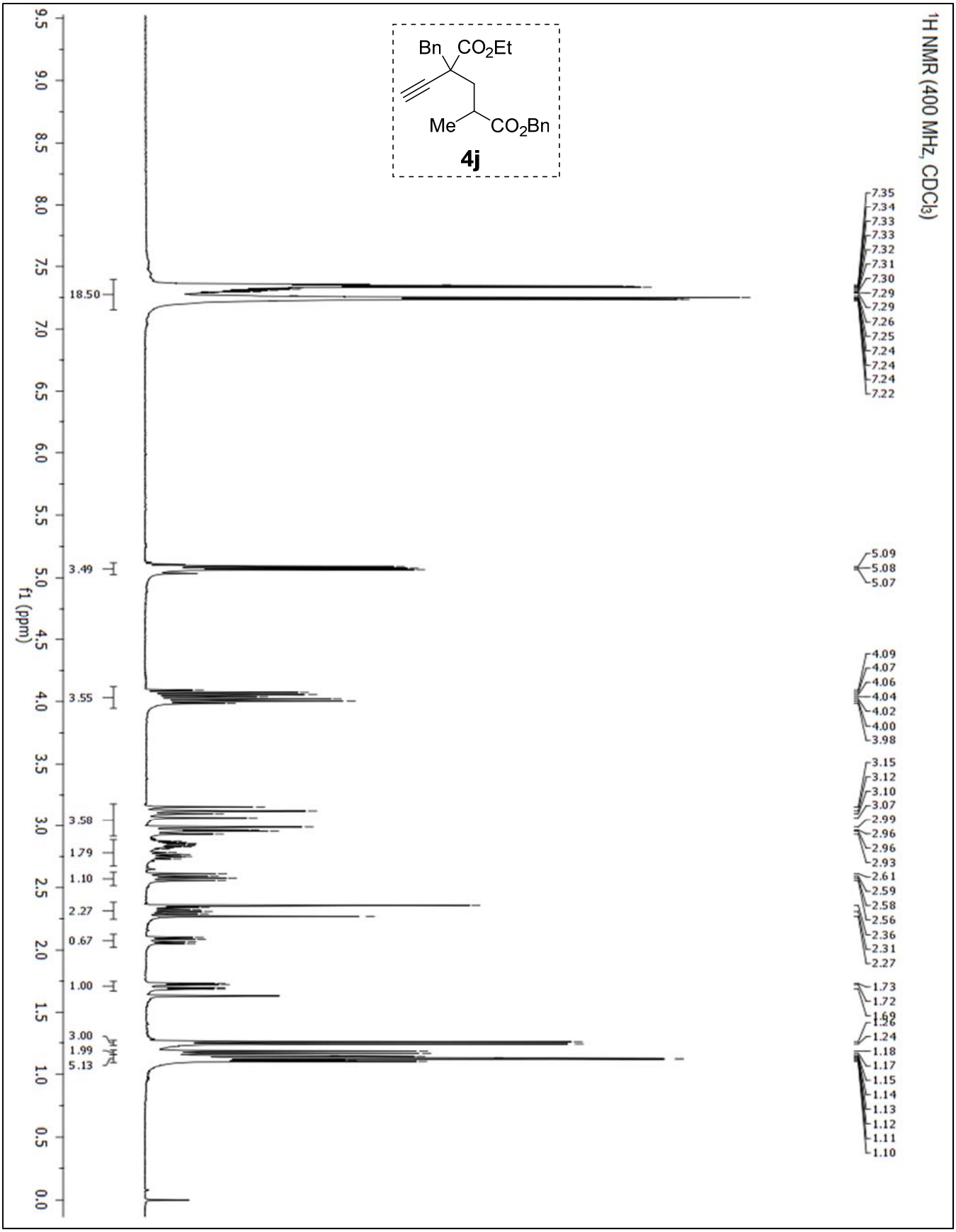

Bn
CO2Et
CN
4g
13C NMR (100 MHz, CDCl3)
170.67
134.89
130.20
128.19
127.48
119.02
81.31
75.58
62.24
48.62
45.11
33.60
13.96
13.74
f1 (ppm)

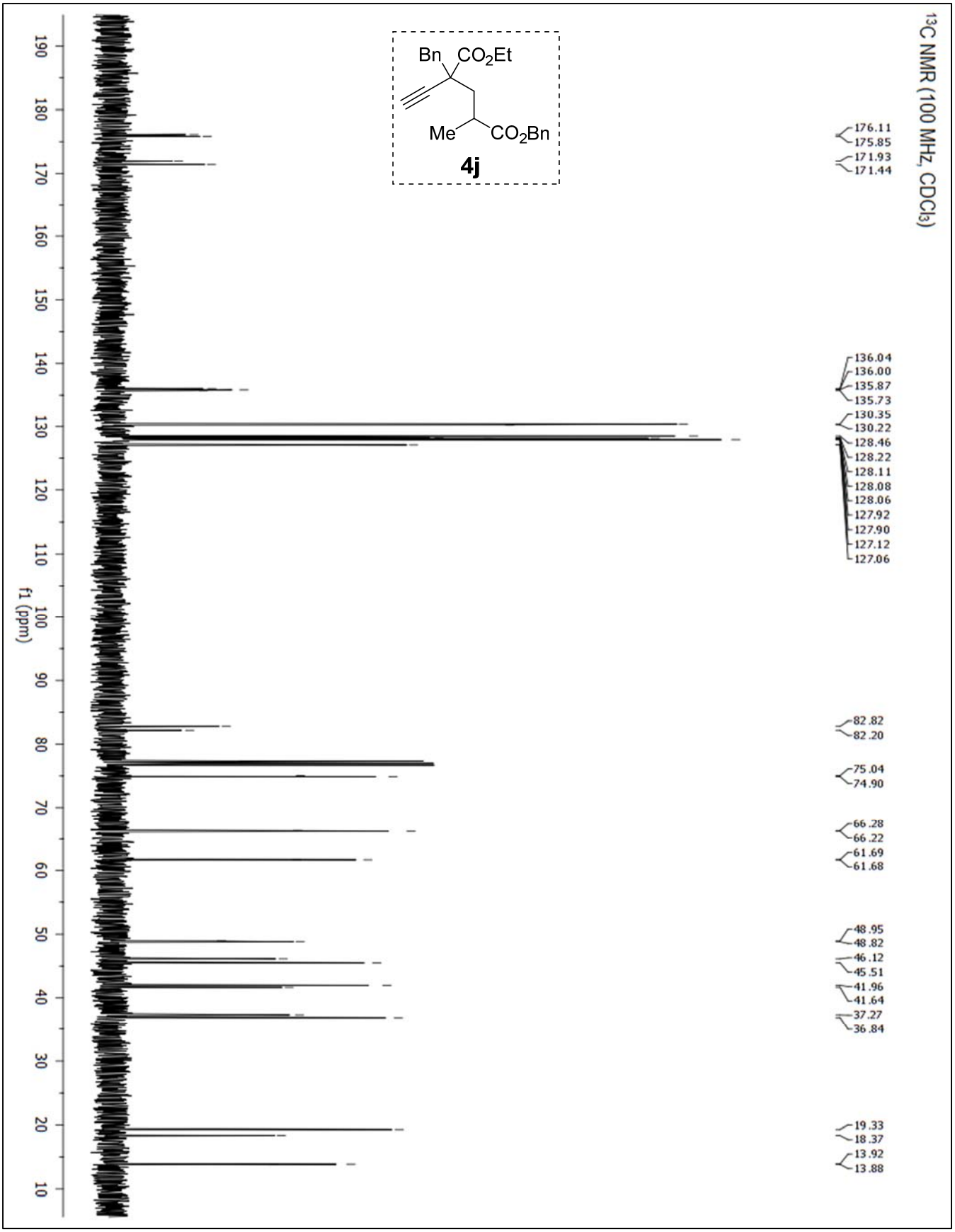

¹H NMR (400 MHz, CDCl₃)
Bn
CO₂Et
Me
O
4h
f1 (ppm)
5.27
2.04
0.99
1.05
1.00
1.06
0.87
1.17
2.99
1.15
3.00
1.00
1.06
1.17
1.15
2.78
2.77
2.75
2.74
2.74
2.73
2.71
2.70
2.55
2.54
2.52
2.51
2.49
2.48
2.47
2.26
2.25
2.23
2.23
2.22
2.22
2.20
2.19
2.02
2.01
1.99
1.98
1.98
1.97
1.96
1.95
7.29
7.28
7.28
7.27
7.27
7.26
7.25
7.24
7.24
7.24
7.23
7.22
7.22
4.15
4.13
4.11
4.09
3.16
3.13
3.02
2.98
2.73
2.72
2.71
2.69
2.52
2.50
2.41
2.22
2.21
2.19
2.18
2.15
2.01
2.00
1.98
1.97
1.21
1.19
1.17

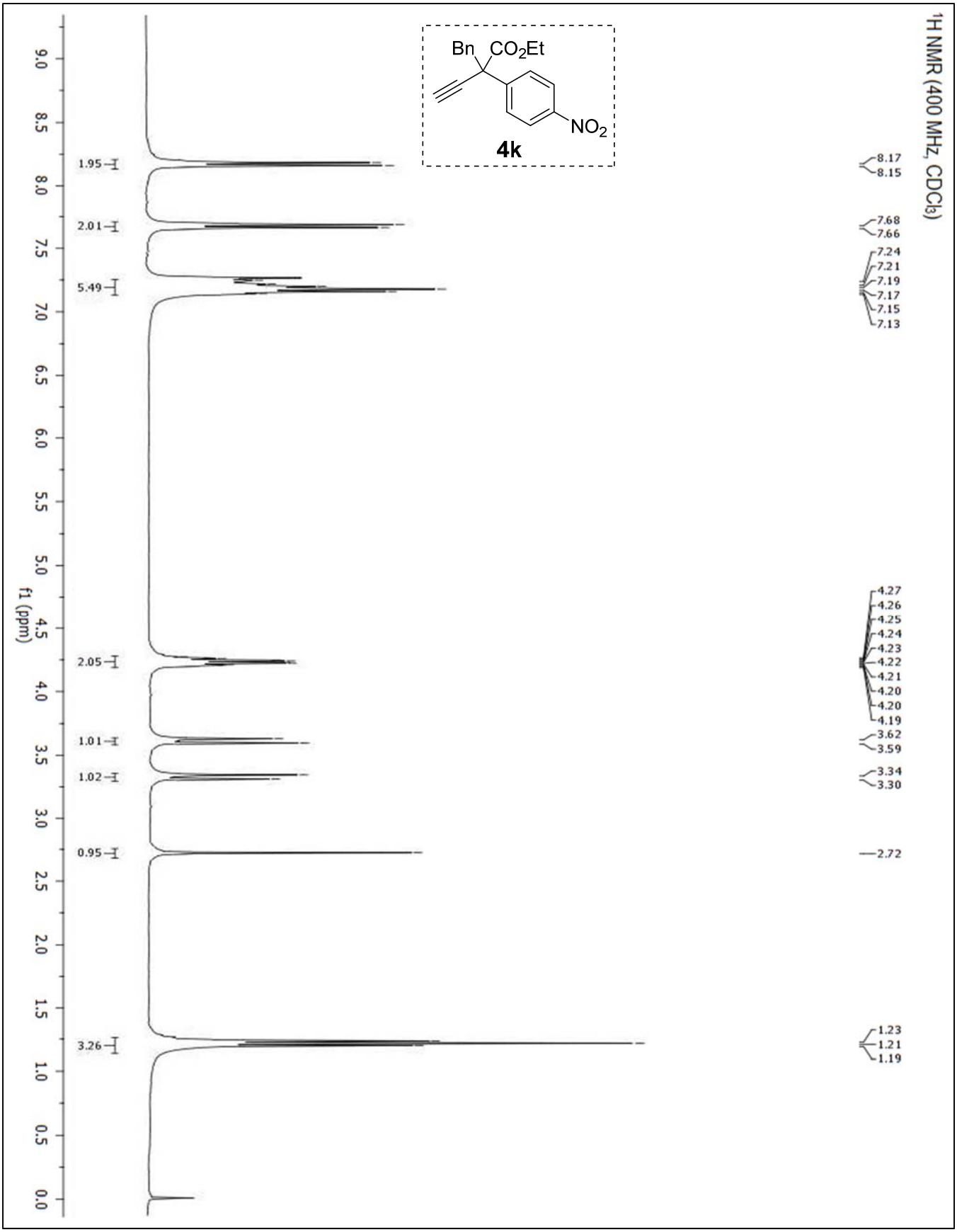

13C NMR (100 MHz, CDCl3)
Bn
CO2Et
Me
O
4h
207.36
171.59
135.83
130.21
127.96
127.09
82.82
74.50
61.73
48.92
45.22
39.69
32.52
29.98
14.01
f1 (ppm)

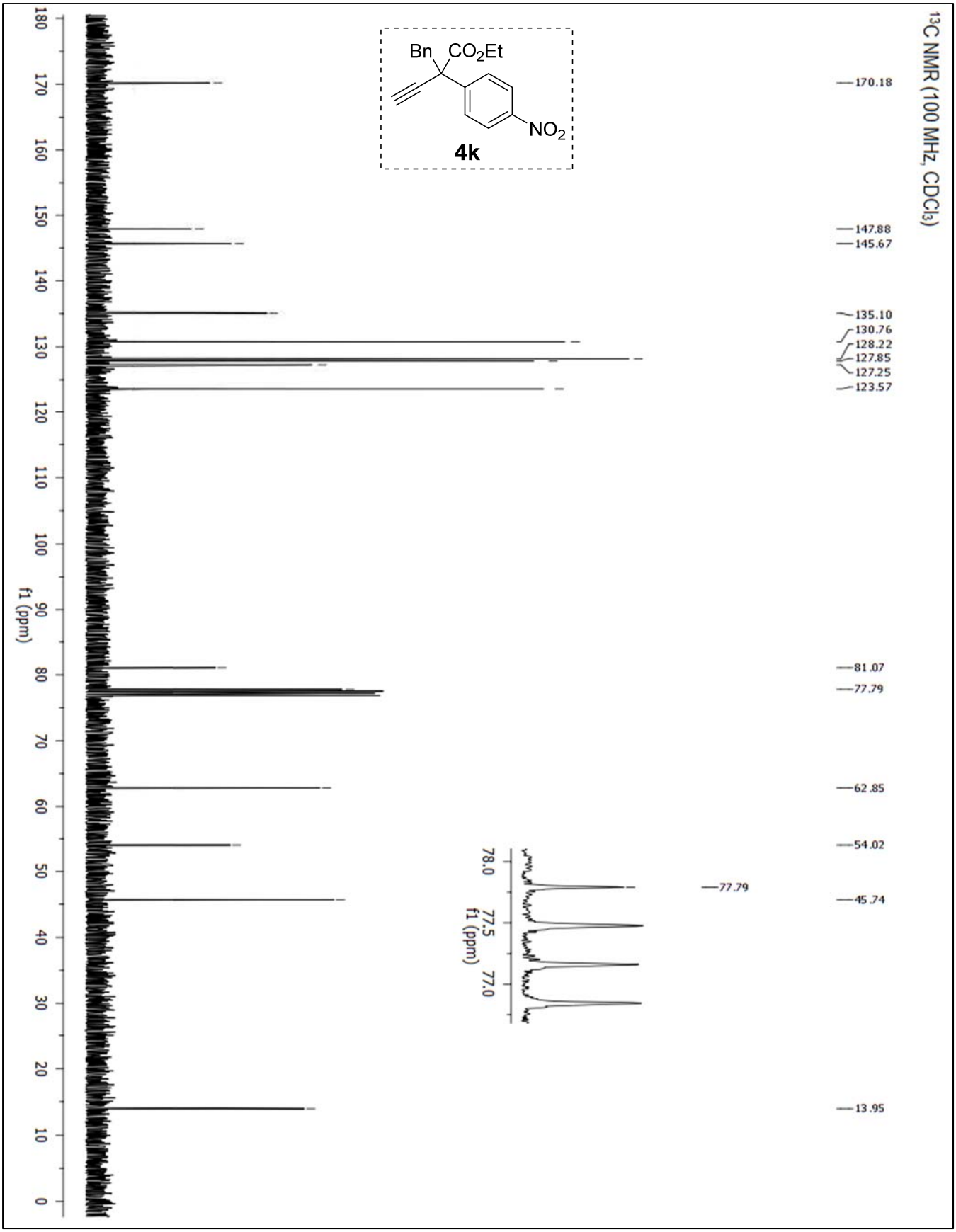

^{1}H NMR (400 MHz, CDCl$_3$)
Bn
CO_2Et
CO_2Bn
4i
f1 (ppm)
5.81
5.46
2.00
2.11
1.00
1.04
1.25
3.35
1.14
3.00
1.25
3.35
1.14
7.39
7.37
7.36
7.35
7.33
7.32
7.31
7.30
7.27
7.27
5.12
4.14
4.13
4.11
4.09
3.17
3.13
3.03
3.00
2.74
2.73
2.71
2.70
2.69
2.67
2.66
2.50
2.49
2.47
2.46
2.45
2.43
2.42
2.40
2.36
2.35
2.34
2.33
2.32
2.32
2.30
2.29
2.10
2.08
2.07
2.06
2.06
2.05
2.03
2.02
2.69
2.68
2.66
2.65
2.45
2.42
2.41
2.40
2.35
2.32
2.31
2.29
2.28
2.07
2.05
1.20
1.18
1.16

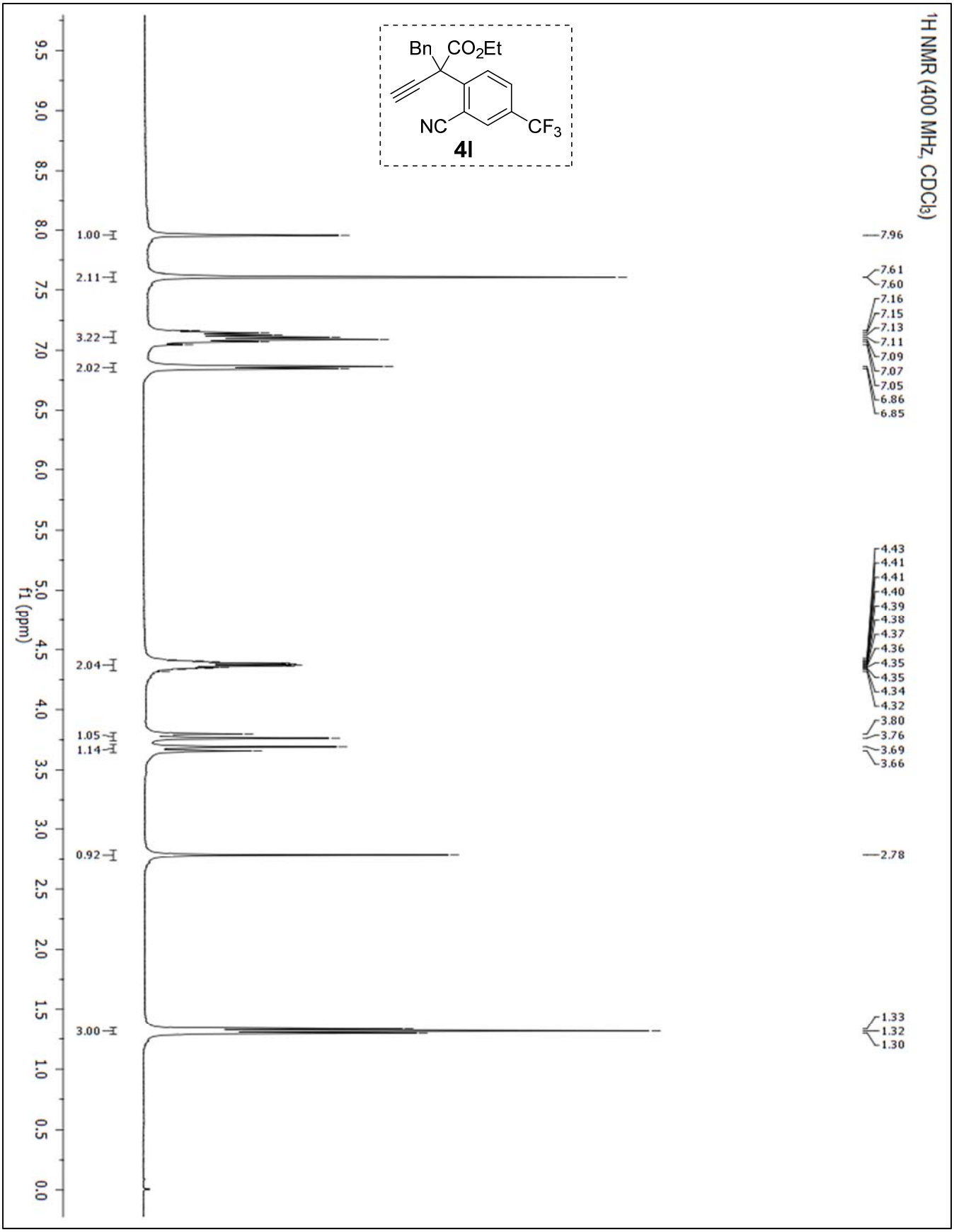

Bn
CO2Et
CO2Bn
4i
13C NMR (100 MHz, CDCl3)
172.59
171.45
135.85
135.74
130.24
128.55
128.23
127.99
127.14
82.47
74.72
66.37
61.80
48.96
45.13
33.60
30.52
14.02
f1 (ppm)

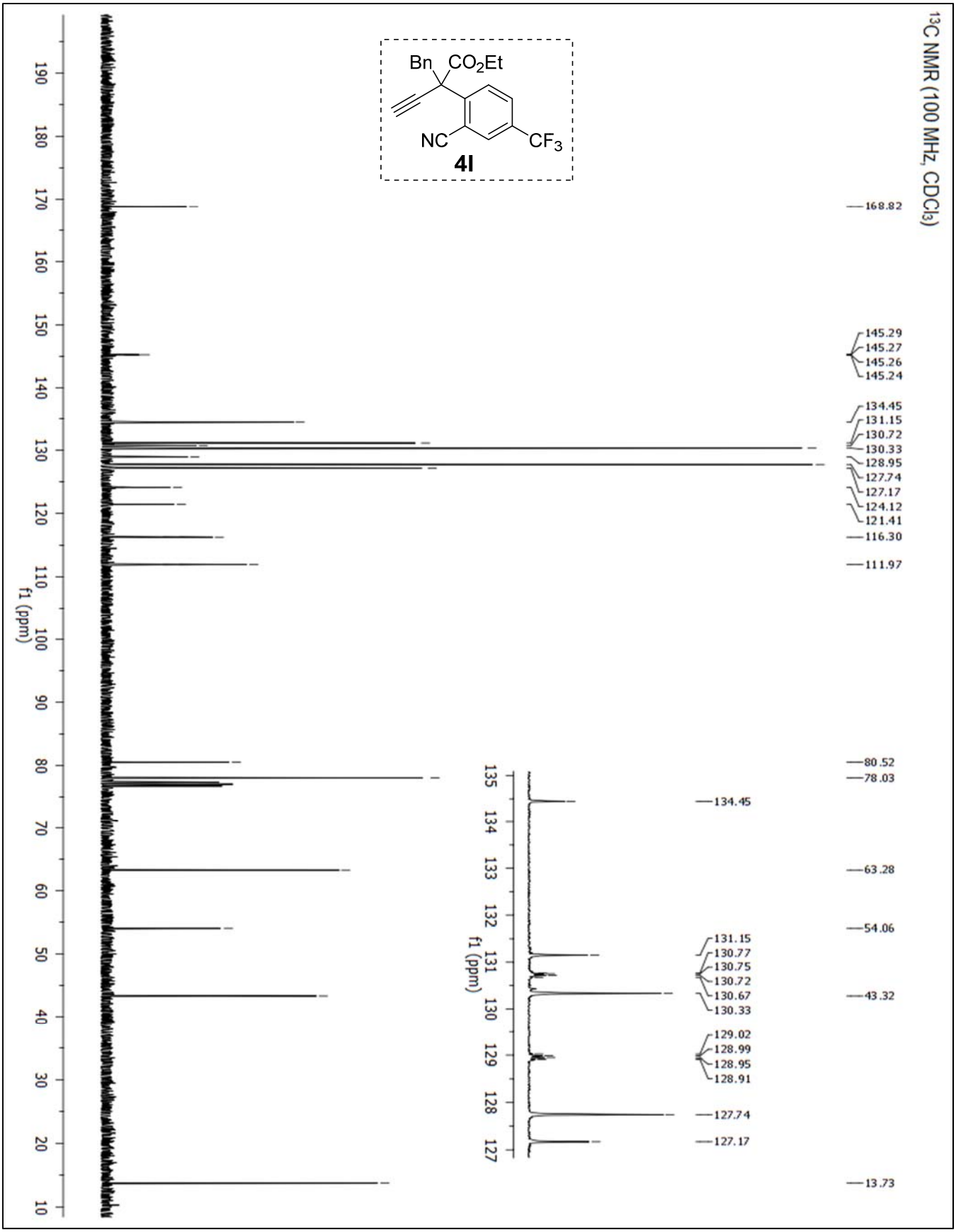

Bn
CO2Et
Me
CO2Bn
4j
1H NMR (400 MHz, CDCl3)
f1 (ppm)
18.50
3.49
3.55
3.58
1.79
1.10
2.27
0.67
1.00
3.00
1.99
5.13
7.35
7.34
7.33
7.33
7.32
7.31
7.30
7.29
7.29
7.26
7.25
7.24
7.24
7.24
7.22
5.09
5.08
5.07
4.09
4.07
4.06
4.04
4.02
4.00
3.98
3.15
3.12
3.10
3.07
2.99
2.96
2.96
2.93
2.61
2.59
2.58
2.56
2.36
2.31
2.27
1.73
1.72
1.69
1.24
1.18
1.17
1.15
1.14
1.13
1.12
1.11
1.10

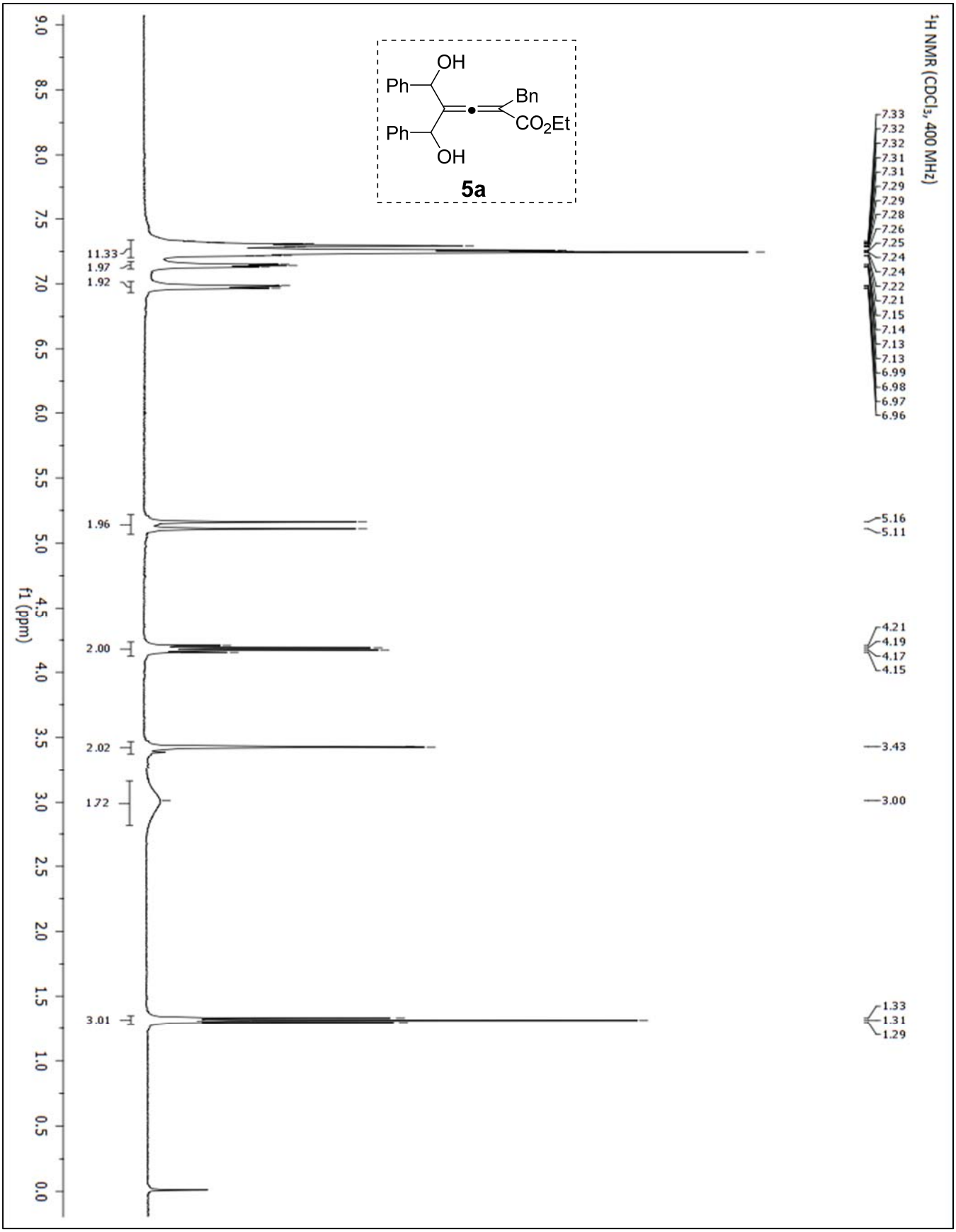

Bn
CO2Et
Me
CO2Bn
4j
13C NMR (100 MHz, CDCl3)
176.11
175.85
171.93
171.44
136.04
136.00
135.87
135.73
130.35
130.22
128.46
128.22
128.11
128.08
128.06
127.92
127.90
127.12
127.06
82.82
82.20
75.04
74.90
66.28
66.22
61.69
61.68
48.95
48.82
46.12
45.51
41.96
41.64
37.27
36.84
19.33
18.37
13.92
13.88
f1 (ppm)

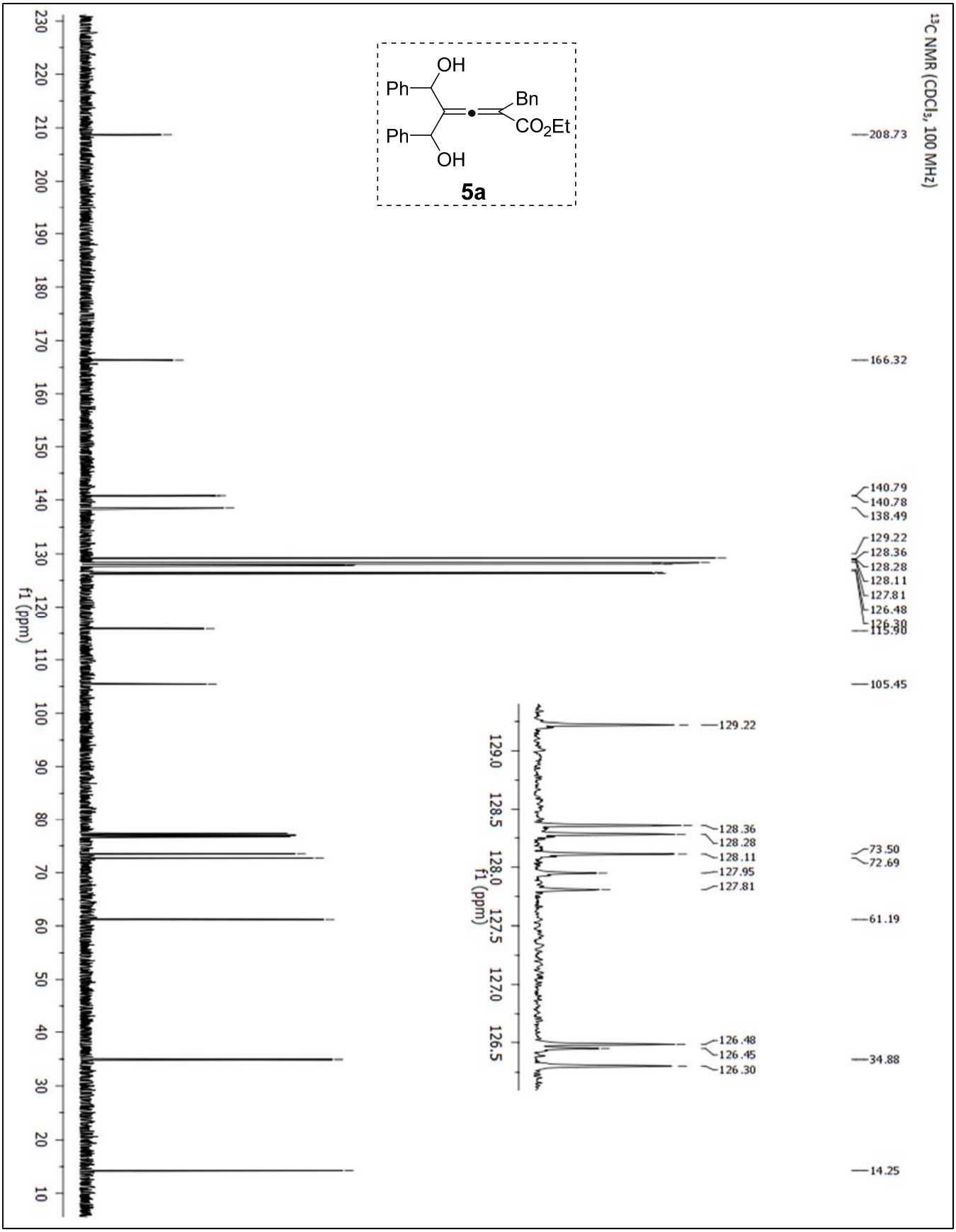

Bn
CO2Et
NO2
4k
1H NMR (400 MHz, CDCl3)
f1 (ppm)
1.95
2.01
5.49
2.05
1.01
1.02
0.95
3.26
8.17
8.15
7.68
7.66
7.24
7.21
7.19
7.17
7.15
7.13
4.27
4.26
4.25
4.24
4.23
4.22
4.21
4.20
4.20
4.19
3.62
3.59
3.34
3.30
2.72
1.23
1.21
1.19

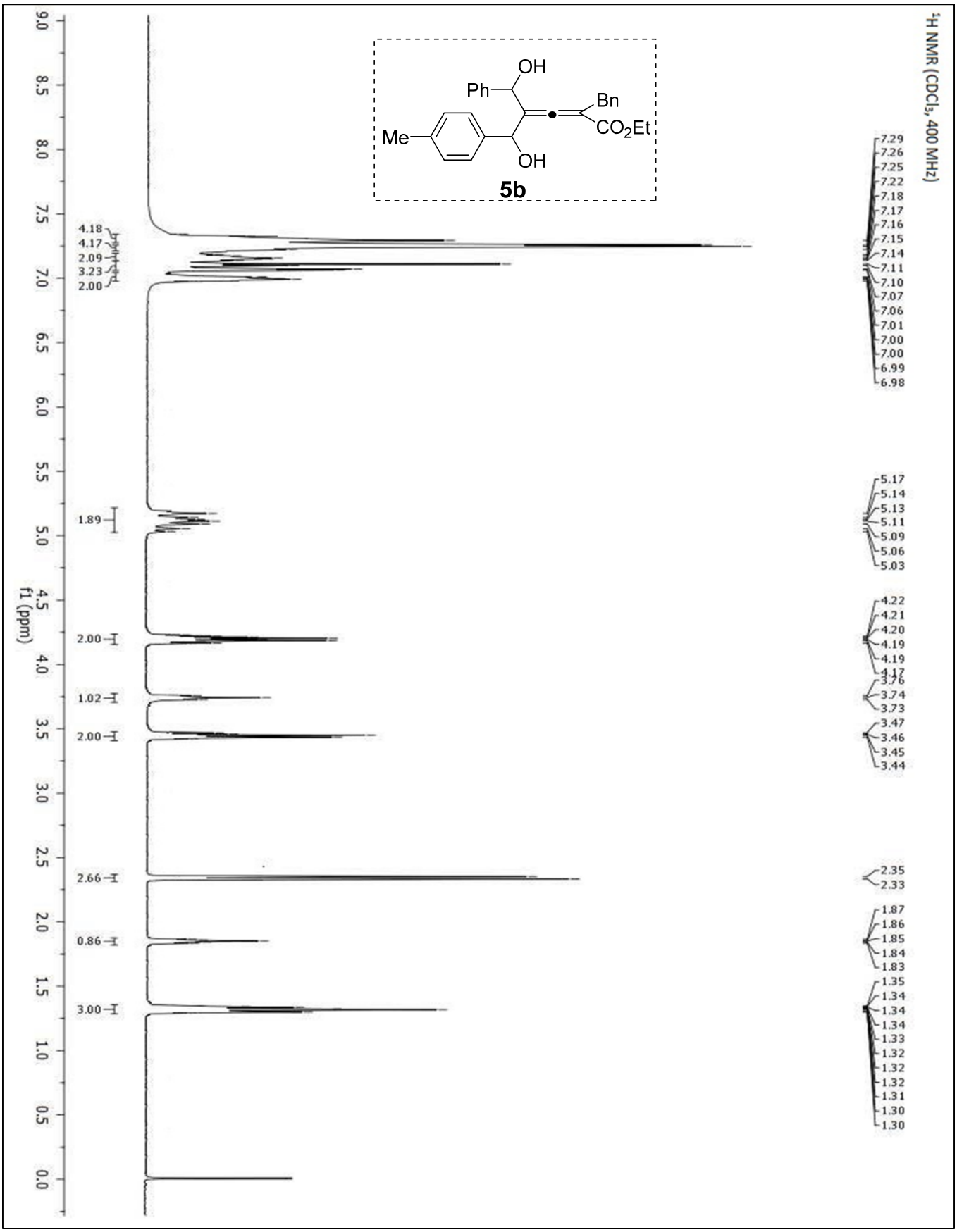

Bn
CO2Et
NO2
4k
13C NMR (100 MHz, CDCl3)
170.18
147.88
145.67
135.10
130.76
128.22
127.85
127.25
123.57
81.07
77.79
62.85
54.02
45.74
13.95
f1 (ppm)

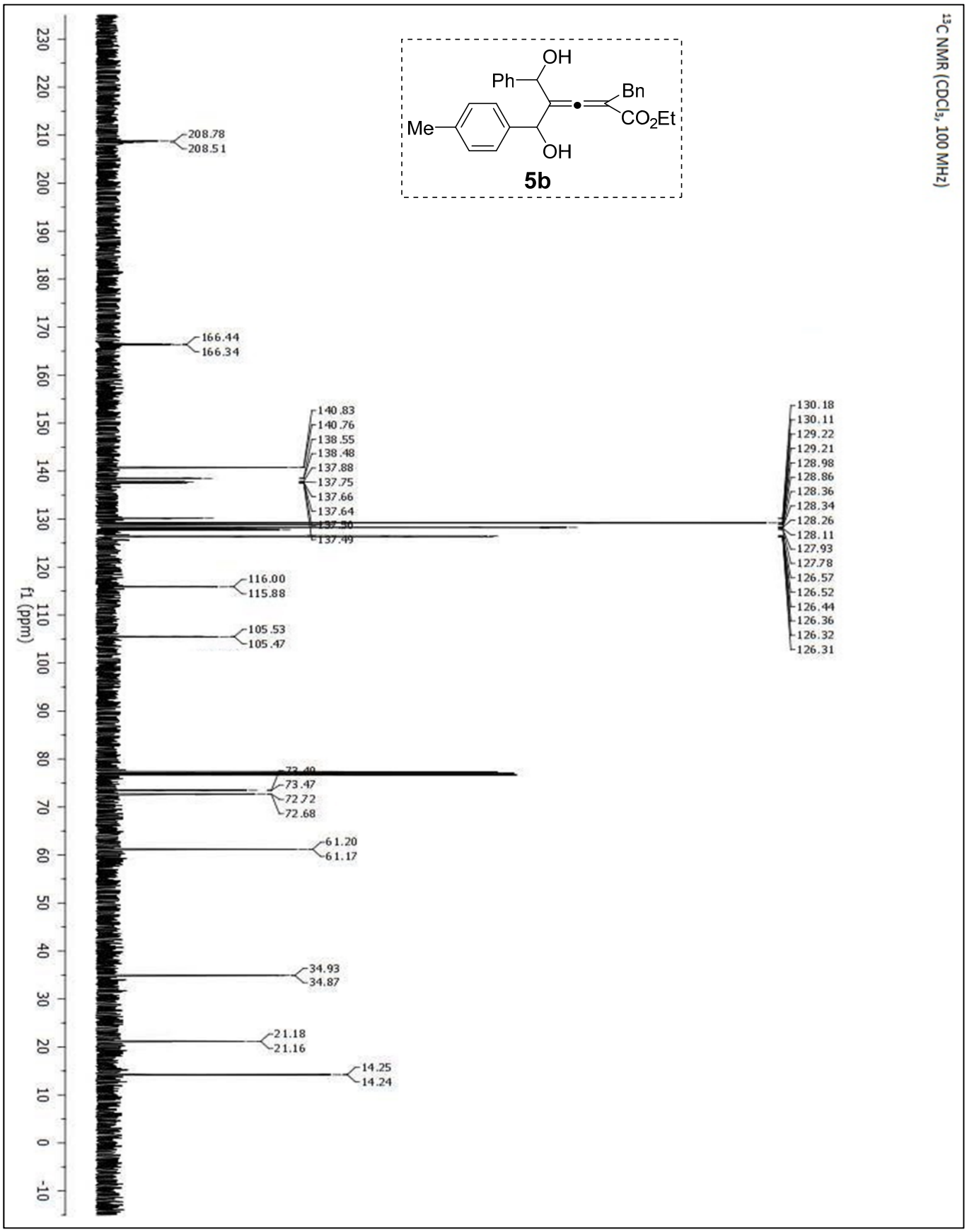

Bn
CO2Et
NC
CF3
4l
1H NMR (400 MHz, CDCl3)
f1 (ppm)
1.00
2.11
3.22
2.02
2.04
1.05
1.14
0.92
3.00
7.96
7.61
7.60
7.16
7.15
7.13
7.11
7.09
7.07
7.05
6.86
6.85
4.43
4.41
4.41
4.40
4.39
4.38
4.37
4.36
4.35
4.35
4.34
4.32
3.80
3.76
3.69
3.66
2.78
1.33
1.32
1.30

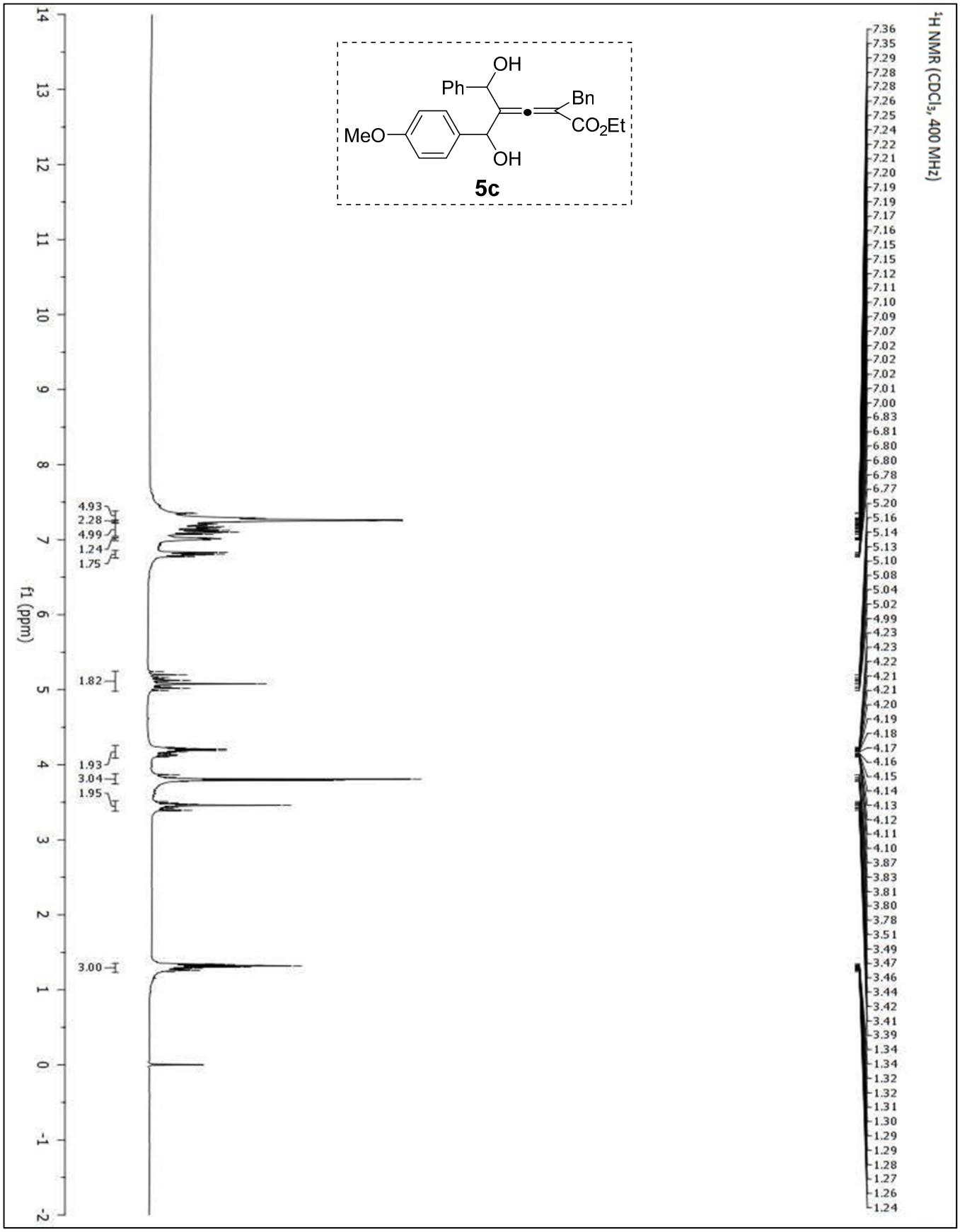

^{13}C NMR (100 MHz, CDCl$_3$)
Bn
CO$_2$Et
NC
CF$_3$
4l
168.82
145.29
145.27
145.26
145.24
134.45
131.15
130.72
130.33
128.95
127.74
127.17
124.12
121.41
116.30
111.97
80.52
78.03
63.28
54.06
43.32
13.73
131.15
130.77
130.75
130.72
130.67
130.33
129.02
128.99
128.95
128.91
f1 (ppm)

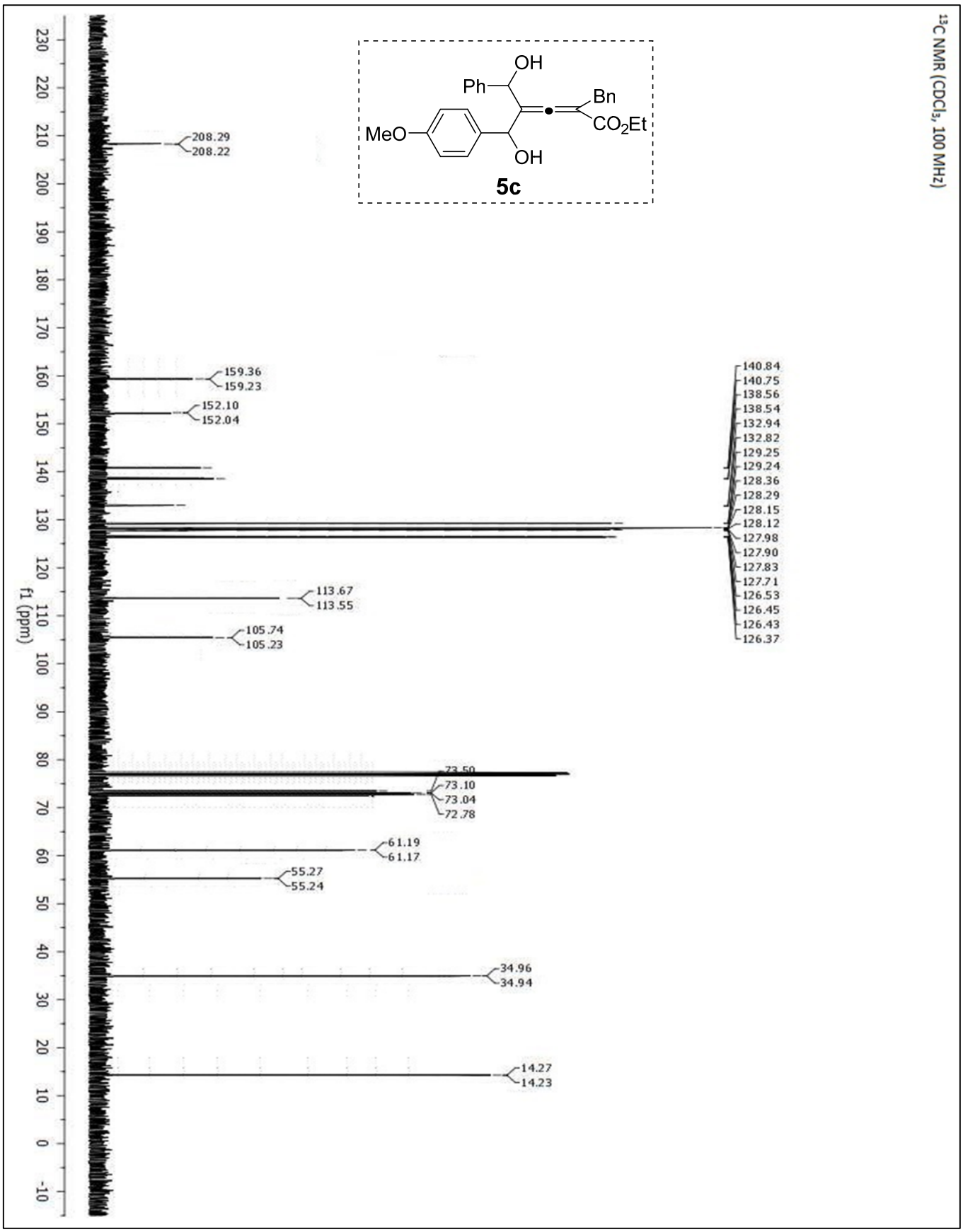

OH
Ph
Bn
CO2Et
Ph
OH
5a
1H NMR (CDCl3, 400 MHz)
f1 (ppm)
11.33
1.97
1.92
1.96
2.00
2.02
1.72
3.01
7.33
7.32
7.32
7.31
7.31
7.29
7.29
7.28
7.26
7.25
7.24
7.24
7.22
7.21
7.15
7.14
7.13
7.13
6.99
6.98
6.97
6.96
5.16
5.11
4.21
4.19
4.17
4.15
3.43
3.00
1.33
1.31
1.29

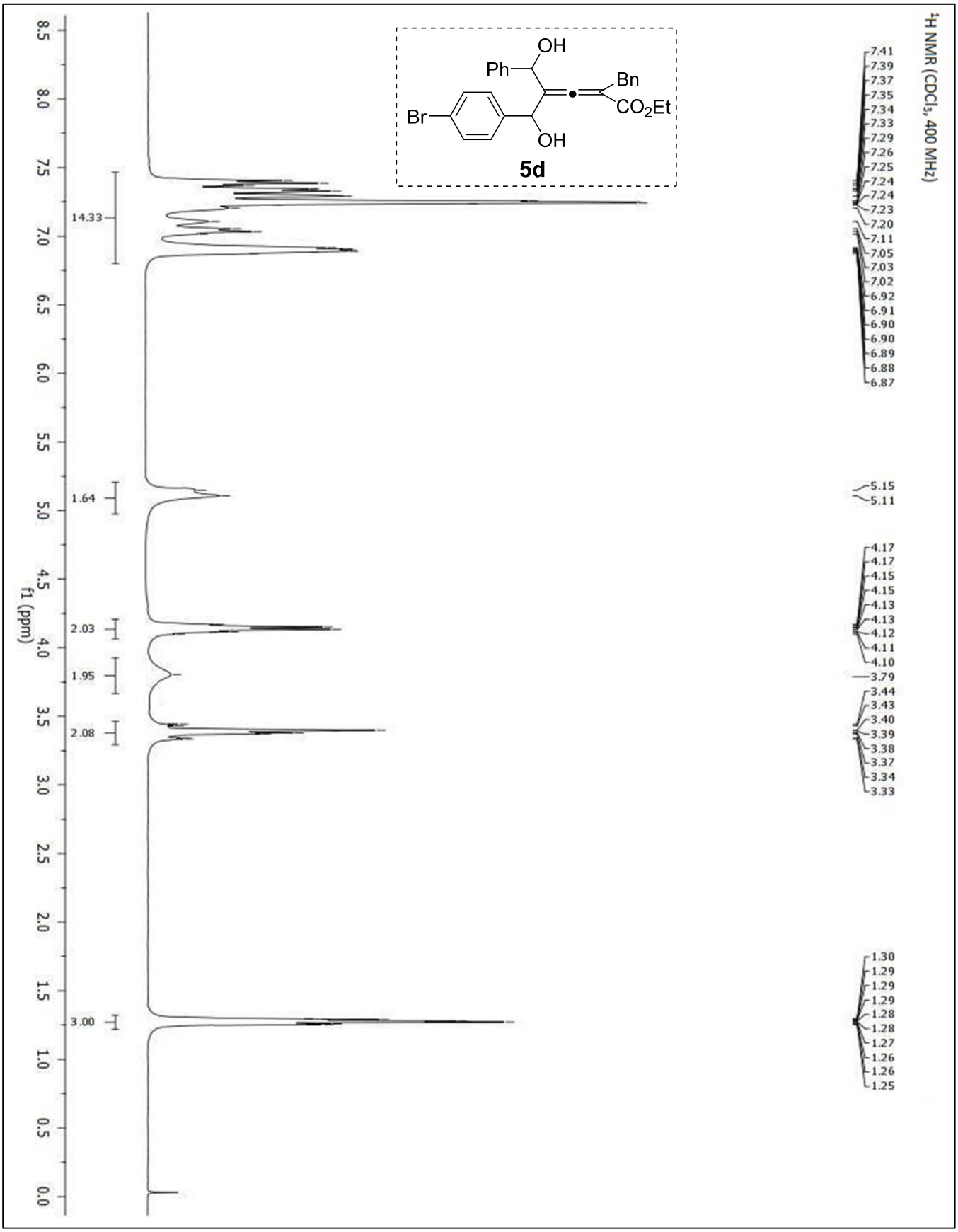

^{13}C NMR (CDCl$_3$, 100 MHz)
OH
Ph
Bn
CO$_2$Et
Ph
OH
5a
208.73
166.32
140.79
140.78
138.49
129.22
128.36
128.28
128.11
127.81
126.48
126.30
115.90
105.45
73.50
72.69
61.19
34.88
14.25
f1 (ppm)
129.22
128.36
128.28
128.11
127.95
127.81
126.48
126.45
126.30

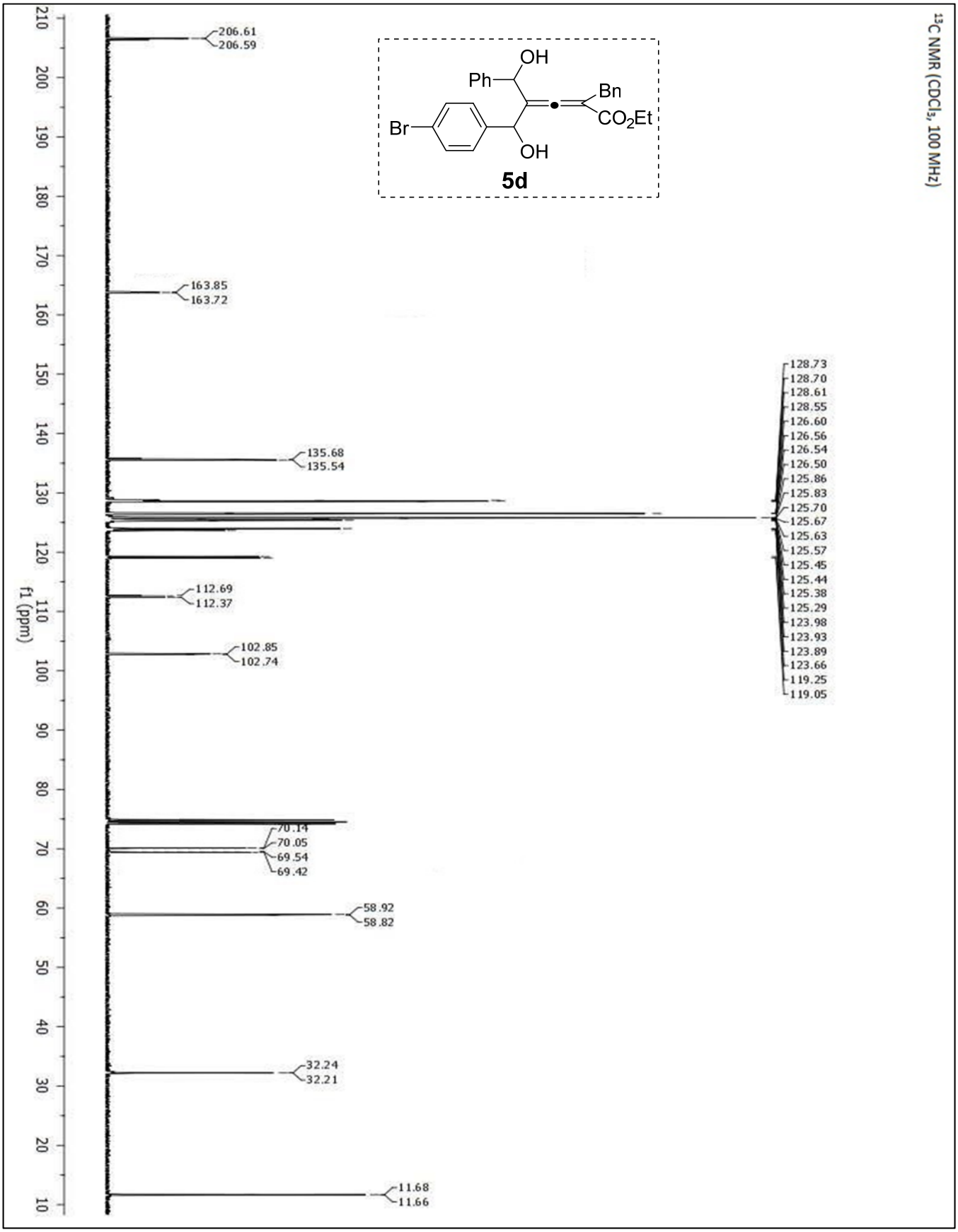

OH
Ph
Bn
CO2Et
Me
OH
5b
1H NMR (CDCl3, 400 MHz)
f1 (ppm)
4.18
4.17
2.09
3.23
2.00
1.89
2.00
1.02
2.00
2.66
0.86
3.00
7.29
7.26
7.25
7.22
7.18
7.17
7.16
7.15
7.14
7.11
7.10
7.07
7.06
7.01
7.00
7.00
6.99
6.98
5.17
5.14
5.13
5.11
5.09
5.06
5.03
4.22
4.21
4.20
4.19
4.19
3.76
3.74
3.73
3.47
3.46
3.45
3.44
2.35
2.33
1.87
1.86
1.85
1.84
1.83
1.35
1.34
1.34
1.34
1.33
1.32
1.32
1.32
1.31
1.30
1.30

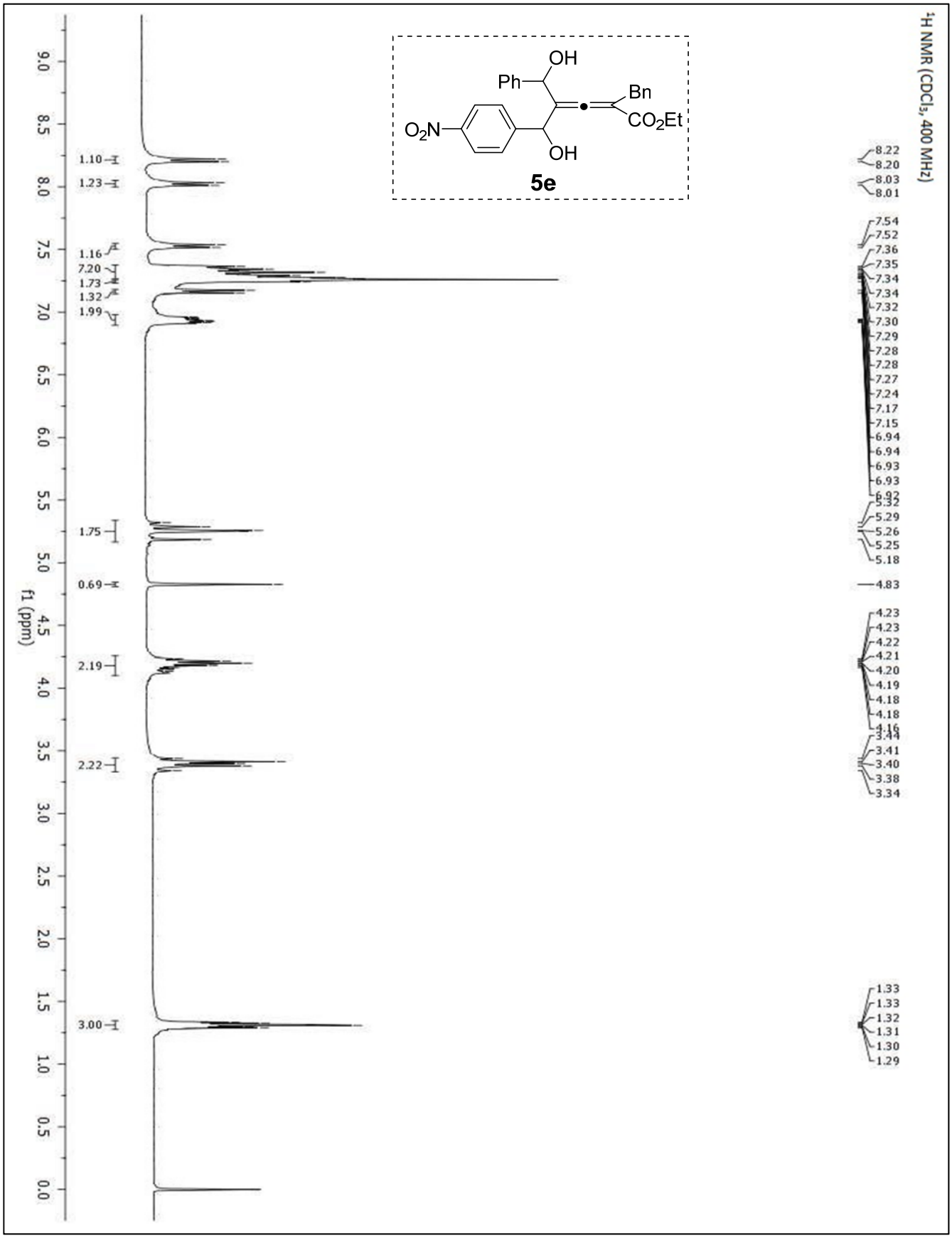

^{13}C NMR (CDCl$_3$, 100 MHz)
OH
Ph
Bn
CO$_2$Et
Me
OH
5b
208.78
208.51
166.44
166.34
140.83
140.76
138.55
138.48
137.88
137.75
137.66
137.64
137.50
137.49
130.18
130.11
129.22
129.21
128.98
128.86
128.36
128.34
128.26
128.11
127.93
127.78
126.57
126.52
126.44
126.36
126.32
126.31
116.00
115.88
105.53
105.47
73.49
73.47
72.72
72.68
61.20
61.17
34.93
34.87
21.18
21.16
14.25
14.24
f1 (ppm)

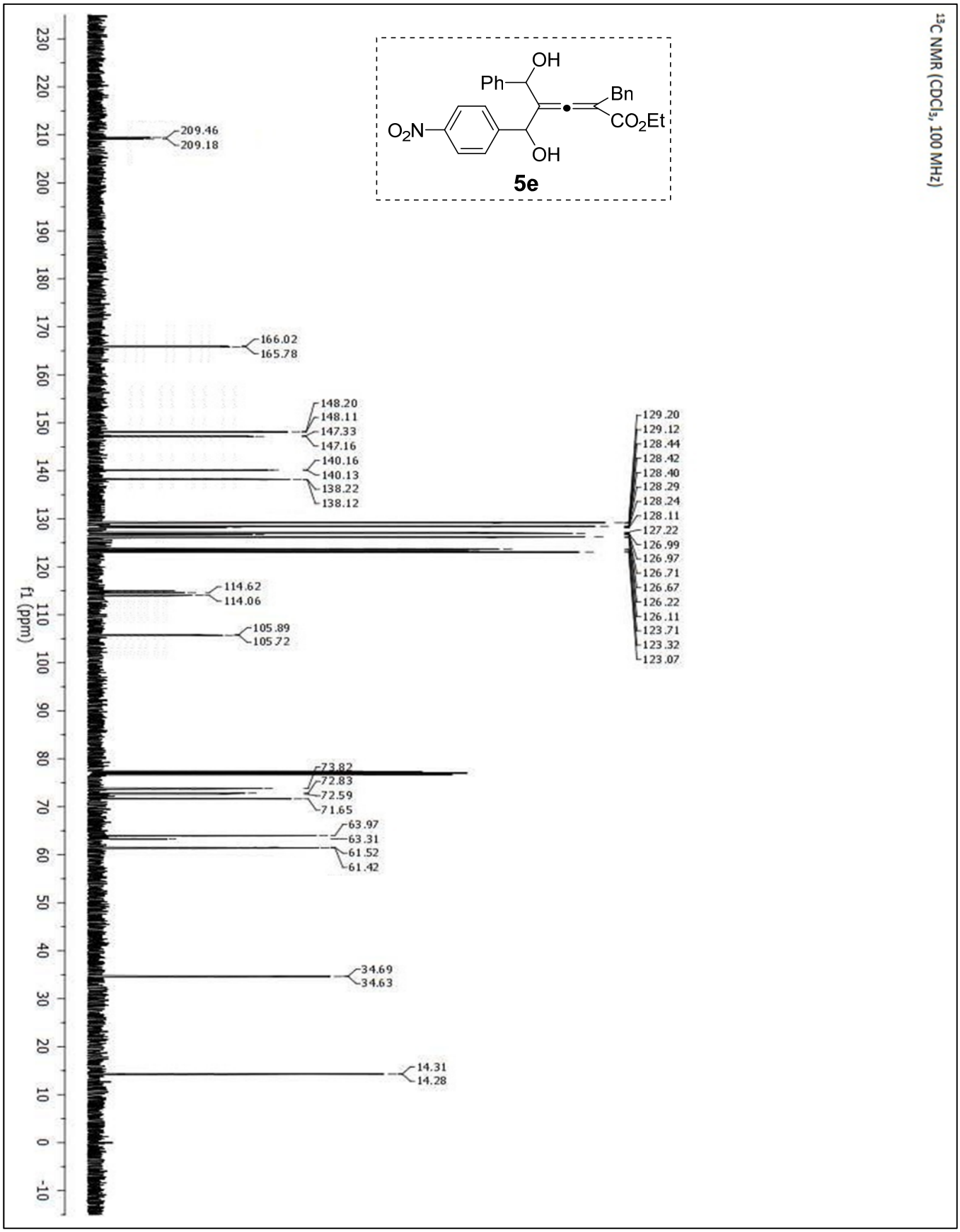

OH
Ph
Bn
MeO
CO2Et
OH
5c
1H NMR (CDCl3, 400 MHz)
f1 (ppm)
4.93
2.28
4.99
1.24
1.75
1.82
1.93
3.04
1.95
3.00

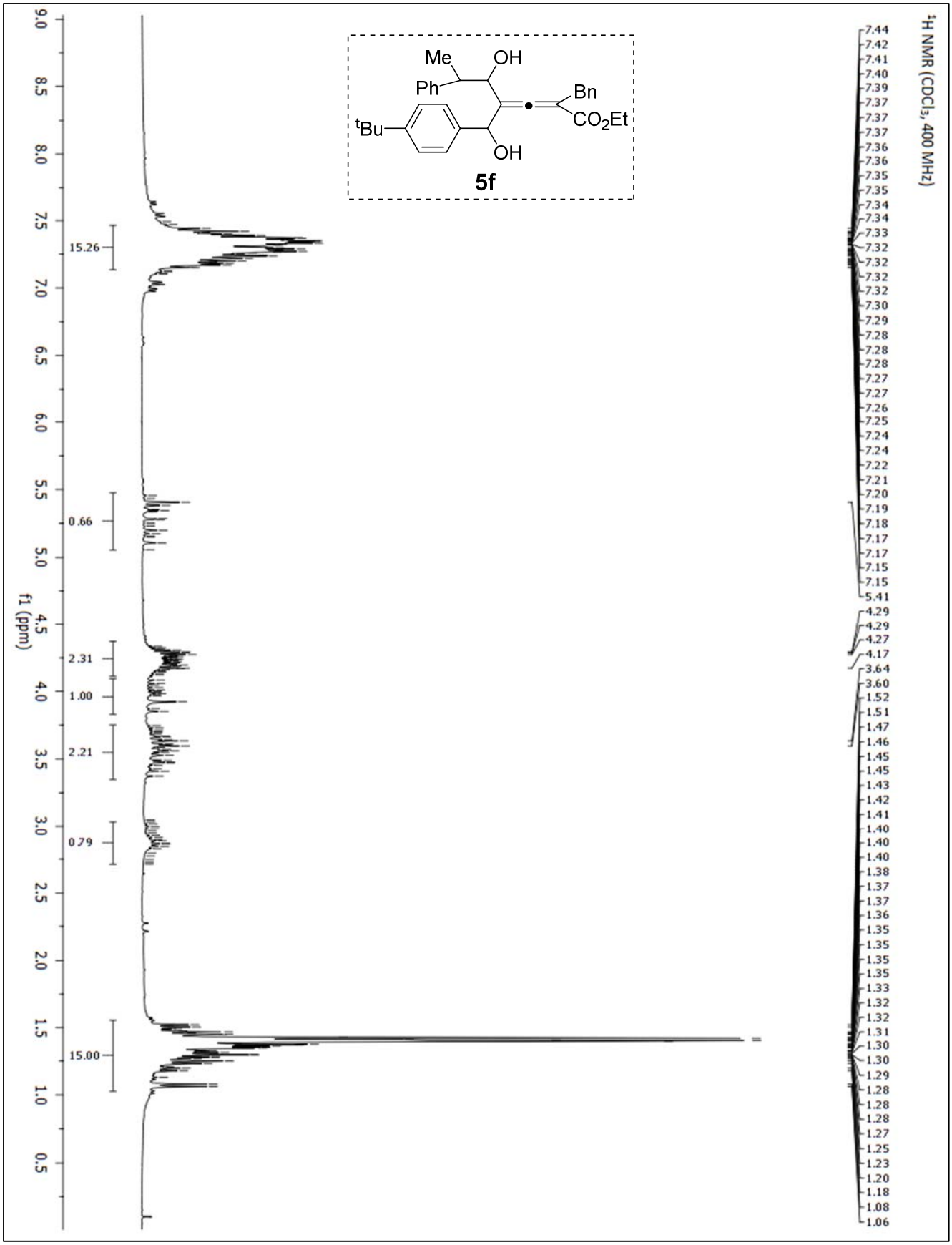

^{13}C NMR (CDCl$_3$, 100 MHz)
OH
Ph
Bn
MeO
CO$_2$Et
OH
5c
208.29
208.22
159.36
159.23
152.10
152.04
140.84
140.75
138.56
138.54
132.94
132.82
129.25
129.24
128.36
128.29
128.15
128.12
127.98
127.90
127.83
127.71
126.53
126.45
126.43
126.37
113.67
113.55
105.74
105.23
73.50
73.10
73.04
72.78
61.19
61.17
55.27
55.24
34.96
34.94
14.27
14.23
f1 (ppm)

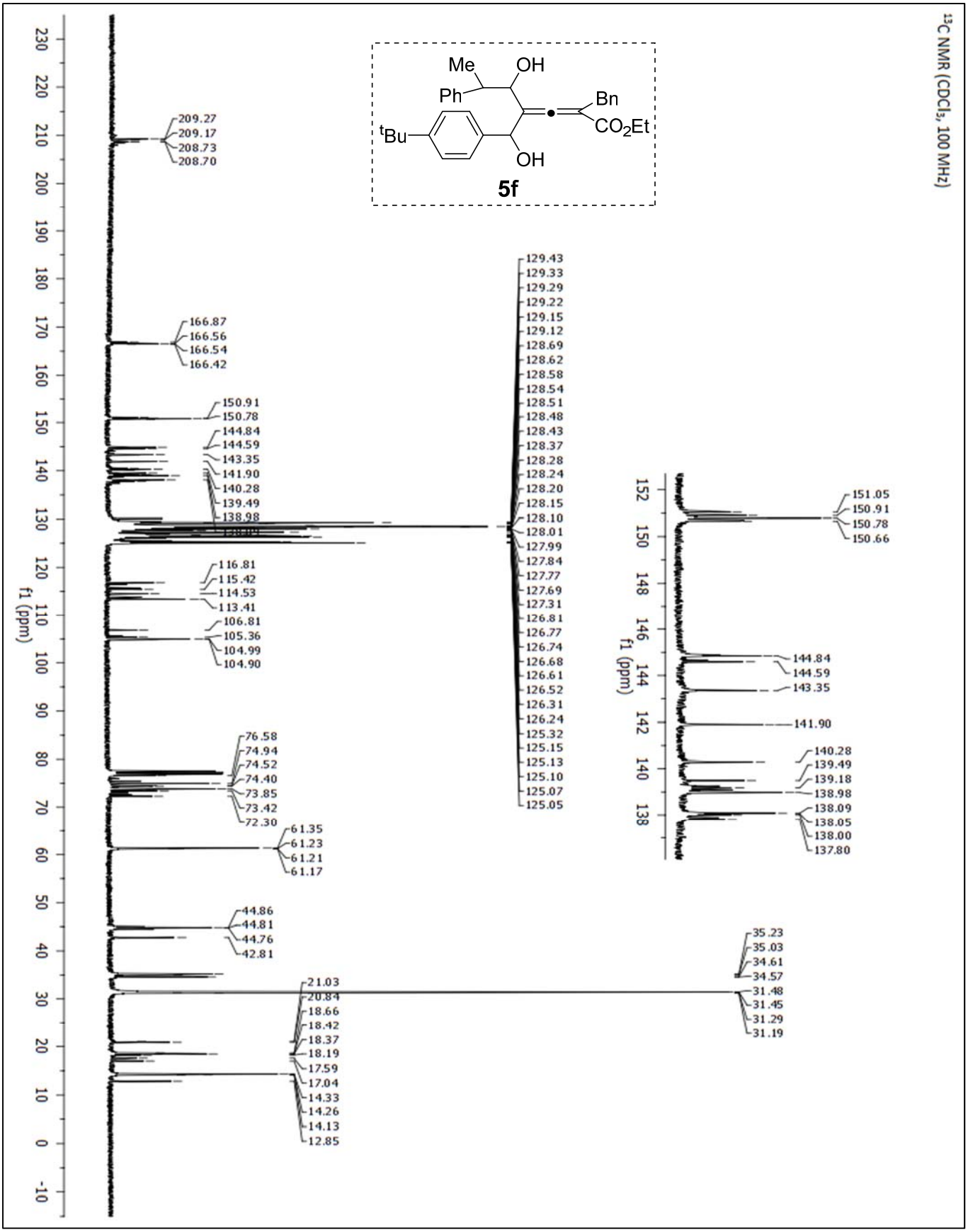

OH
Ph
Bn
Br
CO2Et
OH
5d
14.33
1.64
2.03
1.95
2.08
3.00
f1 (ppm)
1H NMR (CDCl3, 400 MHz)
7.41
7.39
7.37
7.35
7.34
7.33
7.29
7.26
7.25
7.24
7.24
7.23
7.20
7.11
7.05
7.03
7.02
6.92
6.91
6.90
6.90
6.89
6.88
6.87
5.15
5.11
4.17
4.17
4.15
4.15
4.13
4.13
4.12
4.11
4.10
3.79
3.44
3.43
3.40
3.39
3.38
3.37
3.34
3.33
1.30
1.29
1.29
1.29
1.28
1.28
1.27
1.26
1.26
1.25

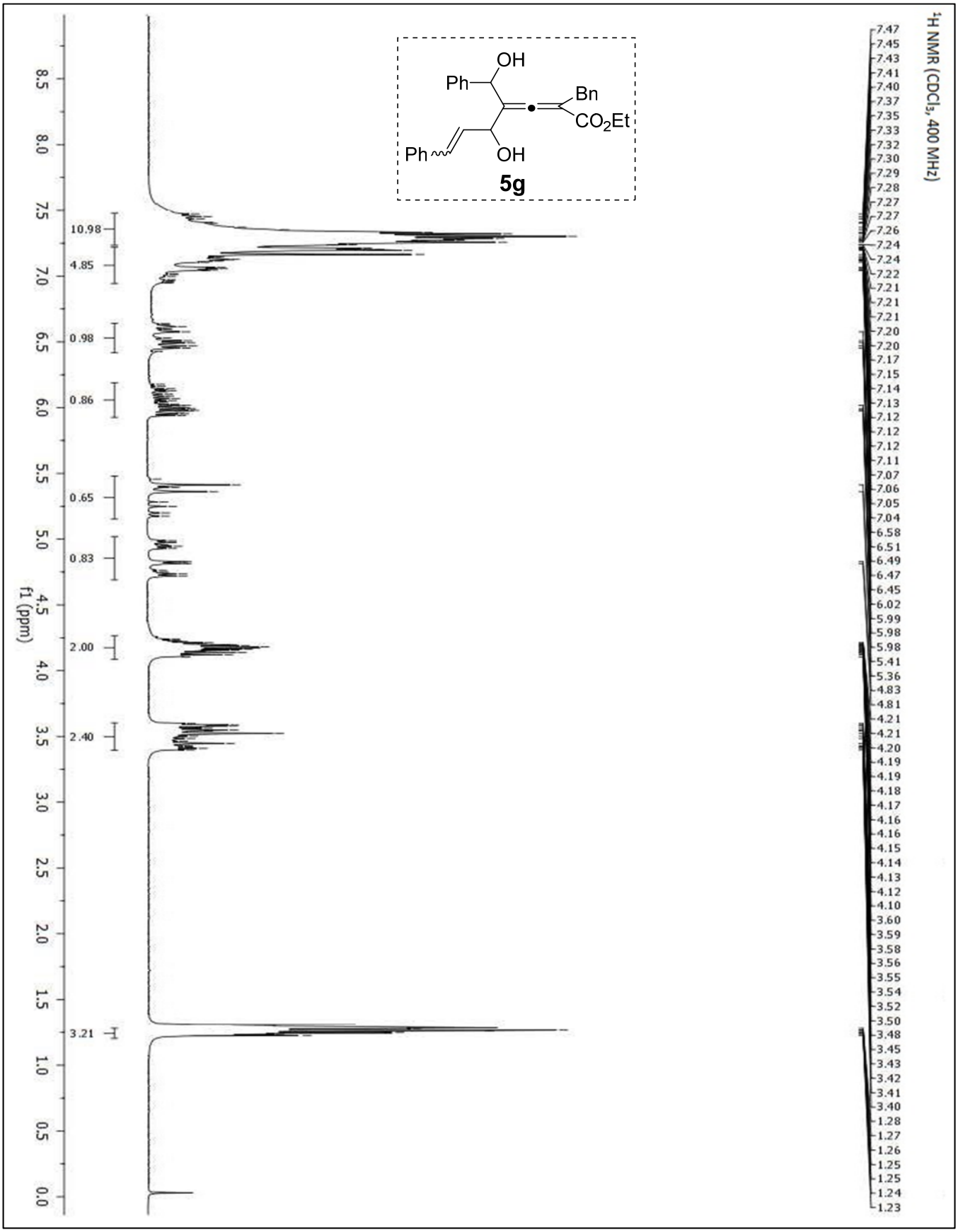

^{13}C NMR (CDCl$_3$, 100 MHz)
OH
Ph
Bn
CO$_2$Et
Br
OH
5d
206.61
206.59
163.85
163.72
135.68
135.54
128.73
128.70
128.61
128.55
126.60
126.56
126.54
126.50
125.86
125.83
125.70
125.67
125.63
125.57
125.45
125.44
125.38
125.29
123.98
123.93
123.89
123.66
119.25
119.05
112.69
112.37
102.85
102.74
70.14
70.05
69.54
69.42
58.92
58.82
32.24
32.21
11.68
11.66
f1 (ppm)

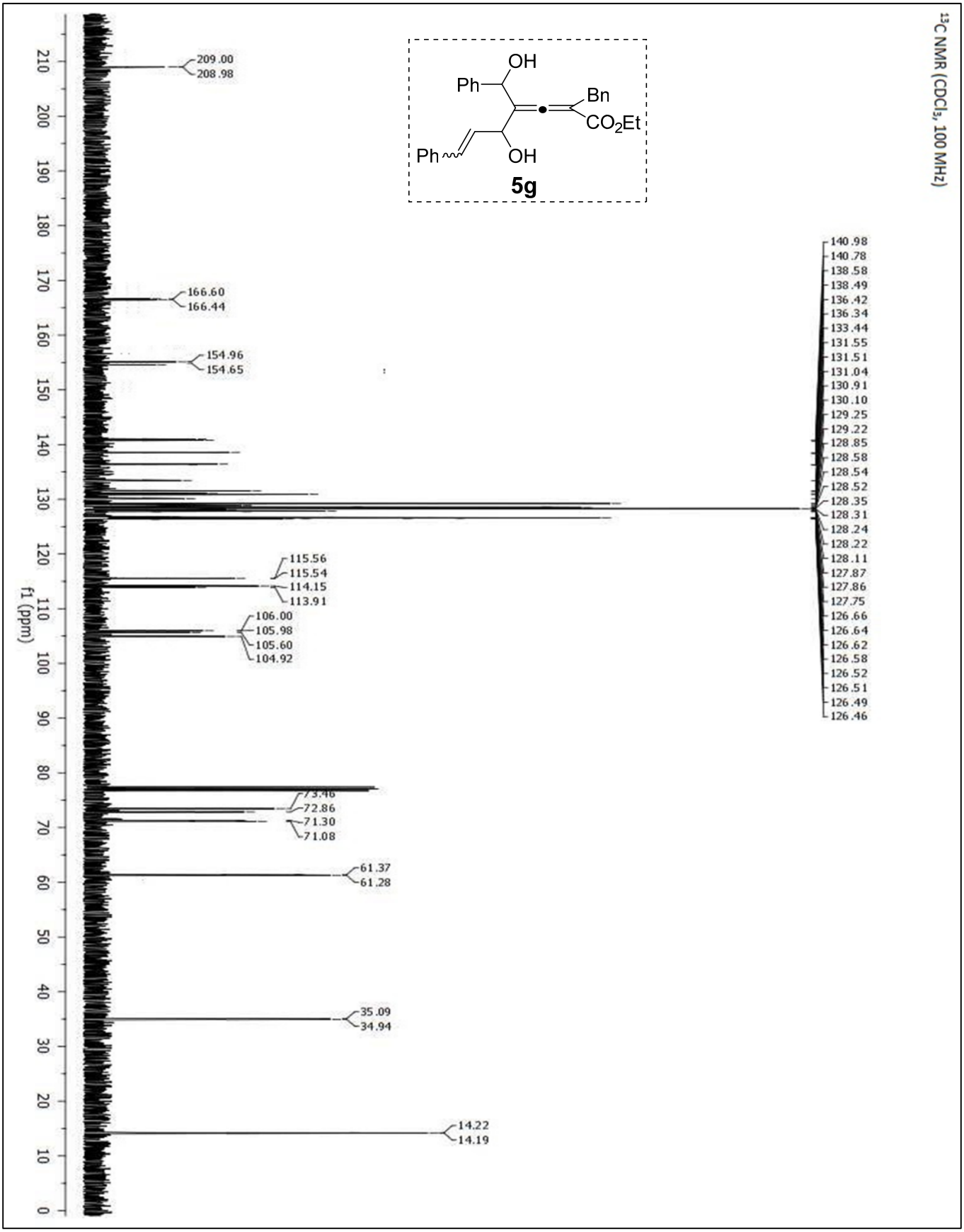

OH
Ph
Bn
O_2N
CO_2Et
OH
5e
^{1}H NMR ($CDCl_3$, 400 MHz)
f1 (ppm)
1.10
1.23
1.16
7.20
1.73
1.32
1.99
1.75
0.69
2.19
2.22
3.00
8.22
8.20
8.03
8.01
7.54
7.52
7.36
7.35
7.34
7.34
7.32
7.30
7.29
7.28
7.28
7.27
7.24
7.17
7.15
6.94
6.94
6.93
6.93
6.92
5.32
5.29
5.26
5.25
5.18
4.83
4.23
4.23
4.22
4.21
4.20
4.19
4.18
4.18
4.16
3.44
3.41
3.40
3.38
3.34
1.33
1.33
1.32
1.31
1.30
1.29

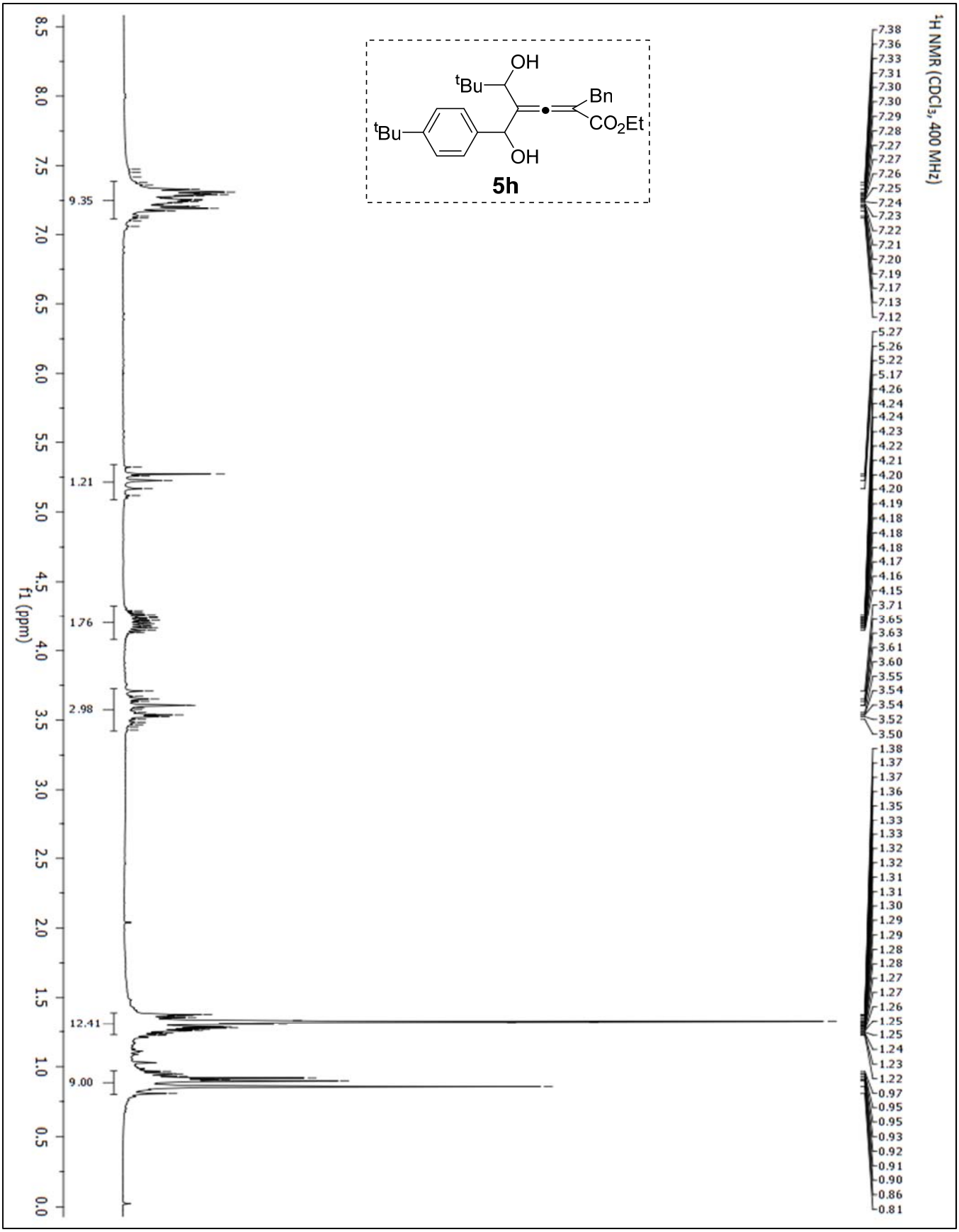

^{13}C NMR (CDCl$_3$, 100 MHz)
OH
Ph
Bn
CO_2Et
O_2N
OH
5e
209.46
209.18
166.02
165.78
148.20
148.11
147.33
147.16
140.16
140.13
138.22
138.12
129.20
129.12
128.44
128.42
128.40
128.29
128.24
128.11
127.22
126.99
126.97
126.71
126.67
126.22
126.11
123.71
123.32
123.07
114.62
114.06
105.89
105.72
73.82
72.83
72.59
71.65
63.97
63.31
61.52
61.42
34.69
34.63
14.31
14.28
f1 (ppm)

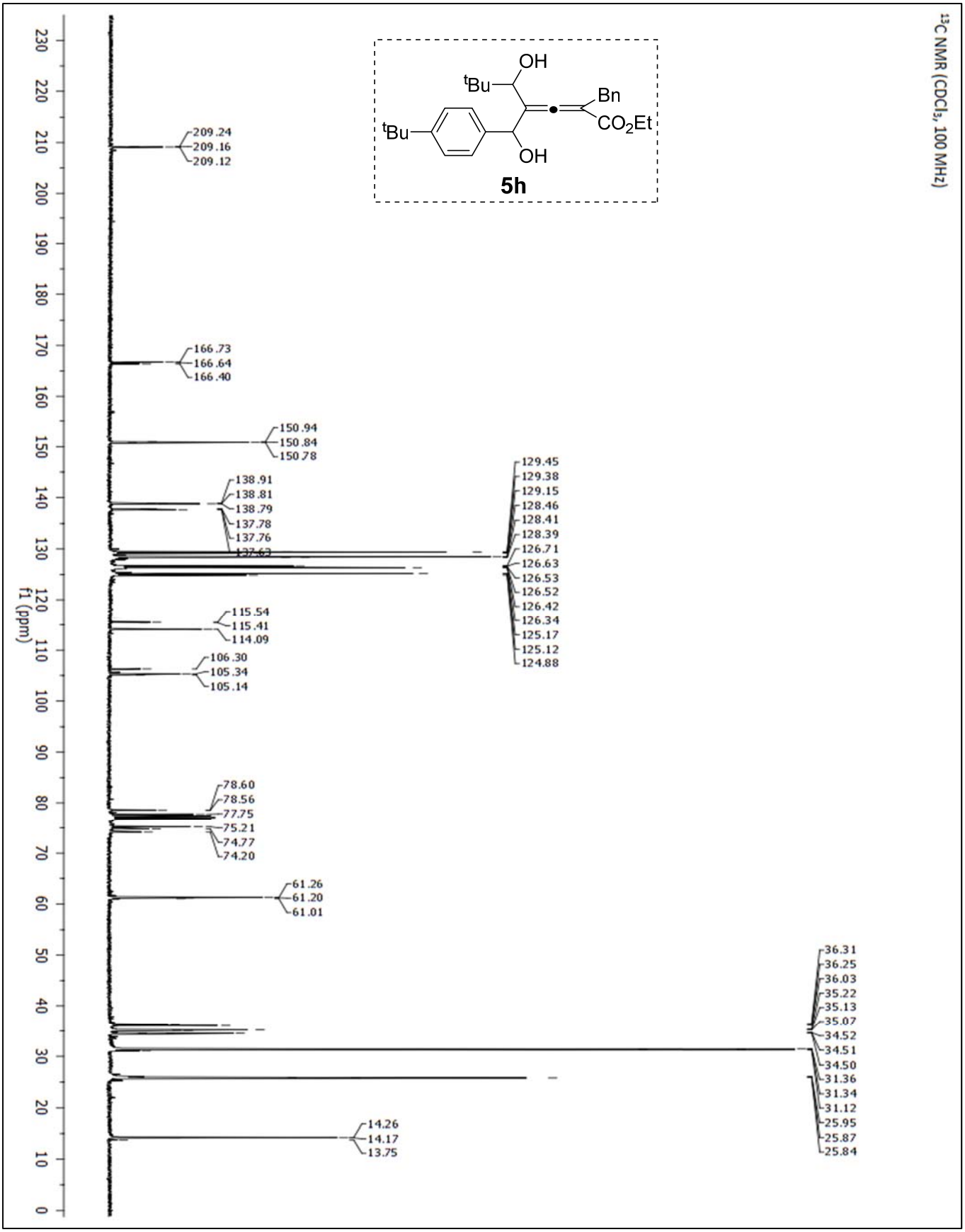

Me
OH
Ph
Bn
tBu
CO2Et
OH
5f
1H NMR (CDCl3, 400 MHz)
f1 (ppm)
15.26
0.66
2.31
1.00
2.21
0.79
15.00

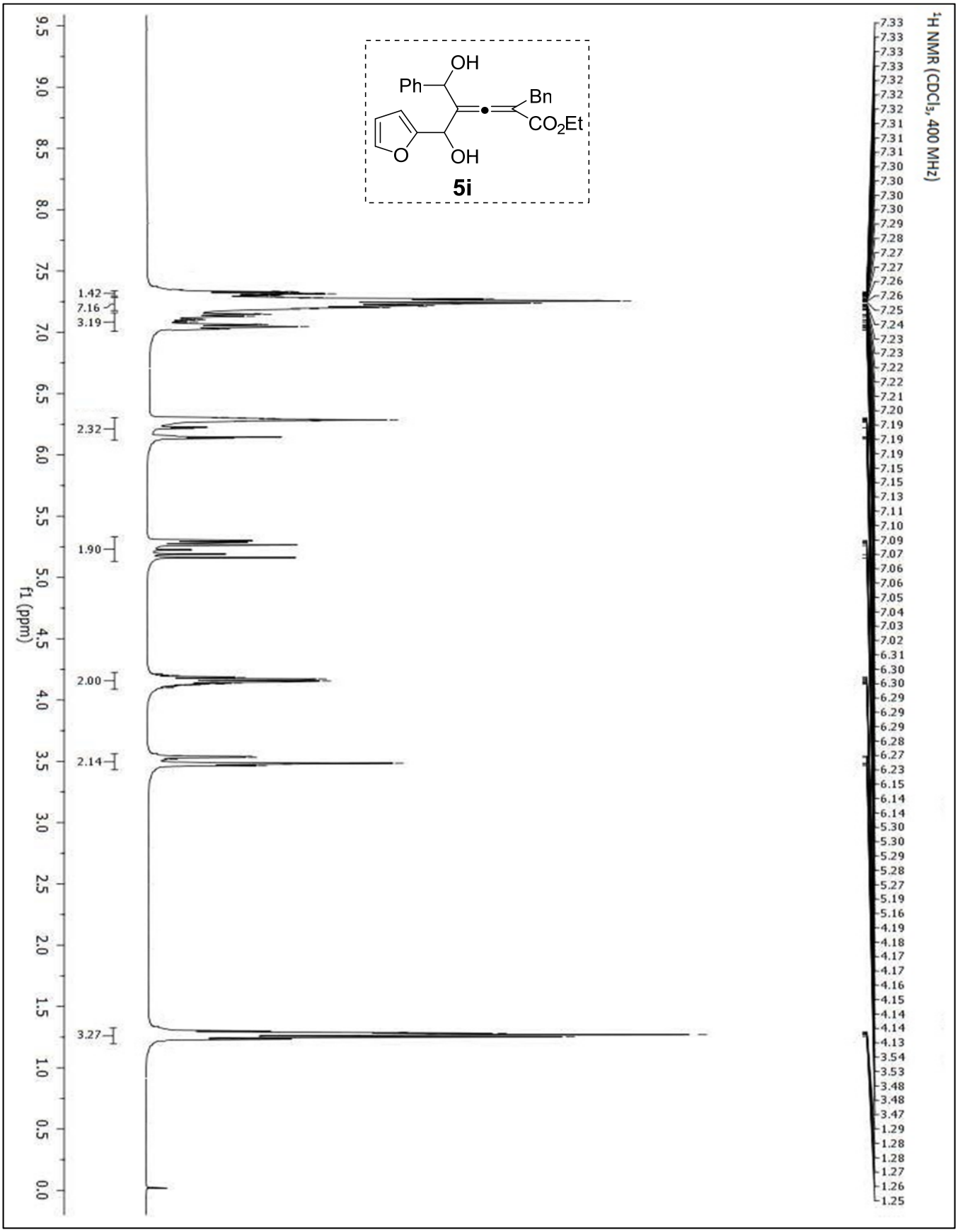

^{13}C NMR (CDCl$_3$, 100 MHz)
Me
OH
Ph
Bn
^{t}Bu
CO$_2$Et
OH
5f
209.27
209.17
208.73
208.70
166.87
166.56
166.54
166.42
150.91
150.78
144.84
144.59
143.35
141.90
140.28
139.49
138.98
129.43
129.33
129.29
129.22
129.15
129.12
128.69
128.62
128.58
128.54
128.51
128.48
128.43
128.37
128.28
128.24
128.20
128.15
128.10
128.01
127.99
127.84
127.77
127.69
127.31
126.81
126.77
126.74
126.68
126.61
126.52
126.31
126.24
125.32
125.15
125.13
125.10
125.07
125.05
116.81
115.42
114.53
113.41
106.81
105.36
104.99
104.90
76.58
74.94
74.52
74.40
73.85
73.42
72.30
61.35
61.23
61.21
61.17
44.86
44.81
44.76
42.81
35.23
35.03
34.61
34.57
31.48
31.45
31.29
31.19
21.03
20.84
18.66
18.42
18.37
18.19
17.59
17.04
14.33
14.26
14.13
12.85
f1 (ppm)
151.05
150.91
150.78
150.66
144.84
144.59
143.35
141.90
140.28
139.49
139.18
138.98
138.09
138.05
138.00
137.80
f1 (ppm)

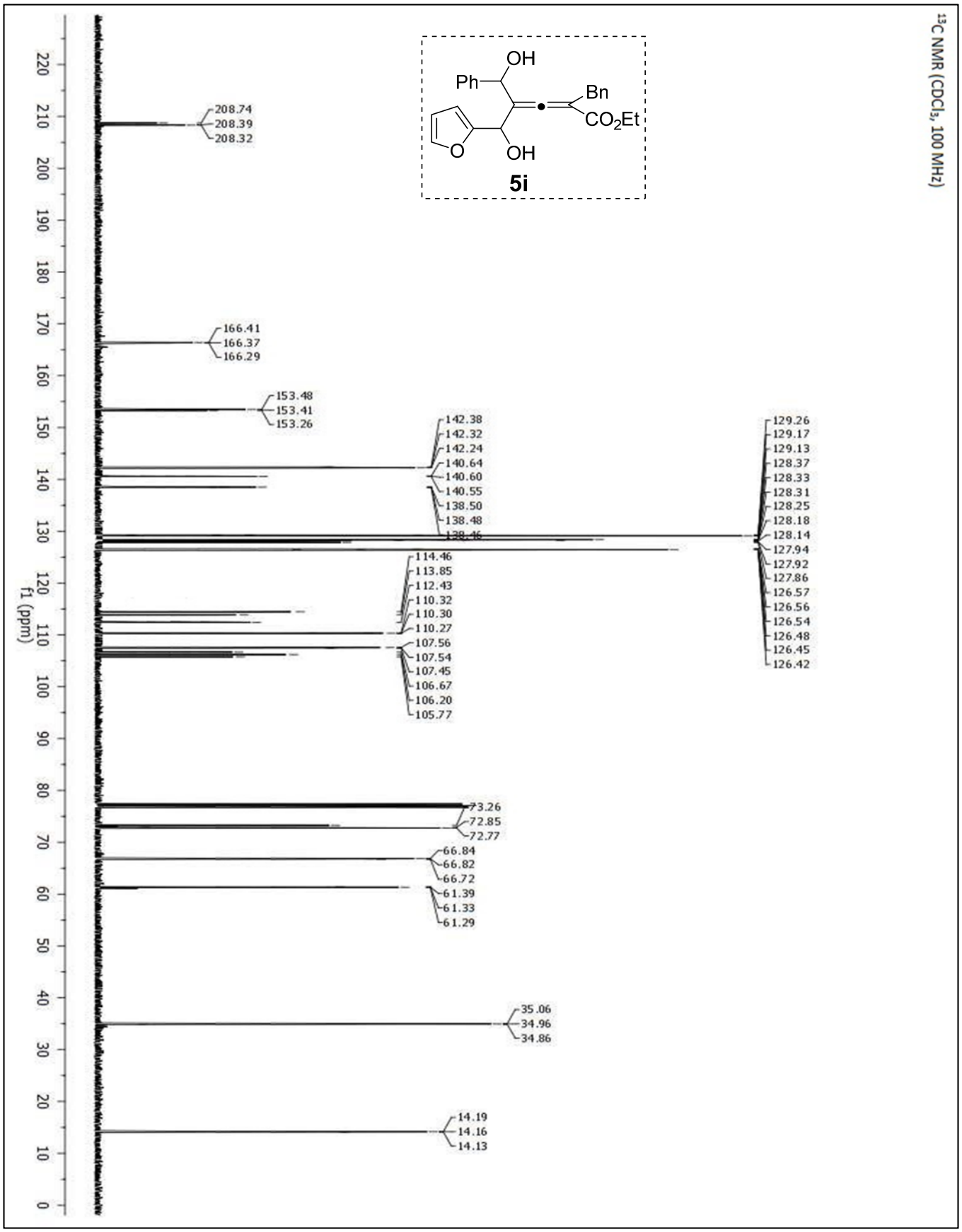

OH
Ph
Bn
CO2Et
Ph
OH
5g
10.98
4.85
0.98
0.86
0.65
0.83
2.00
2.40
3.21
f1 (ppm)
1H NMR (CDCl3, 400 MHz)

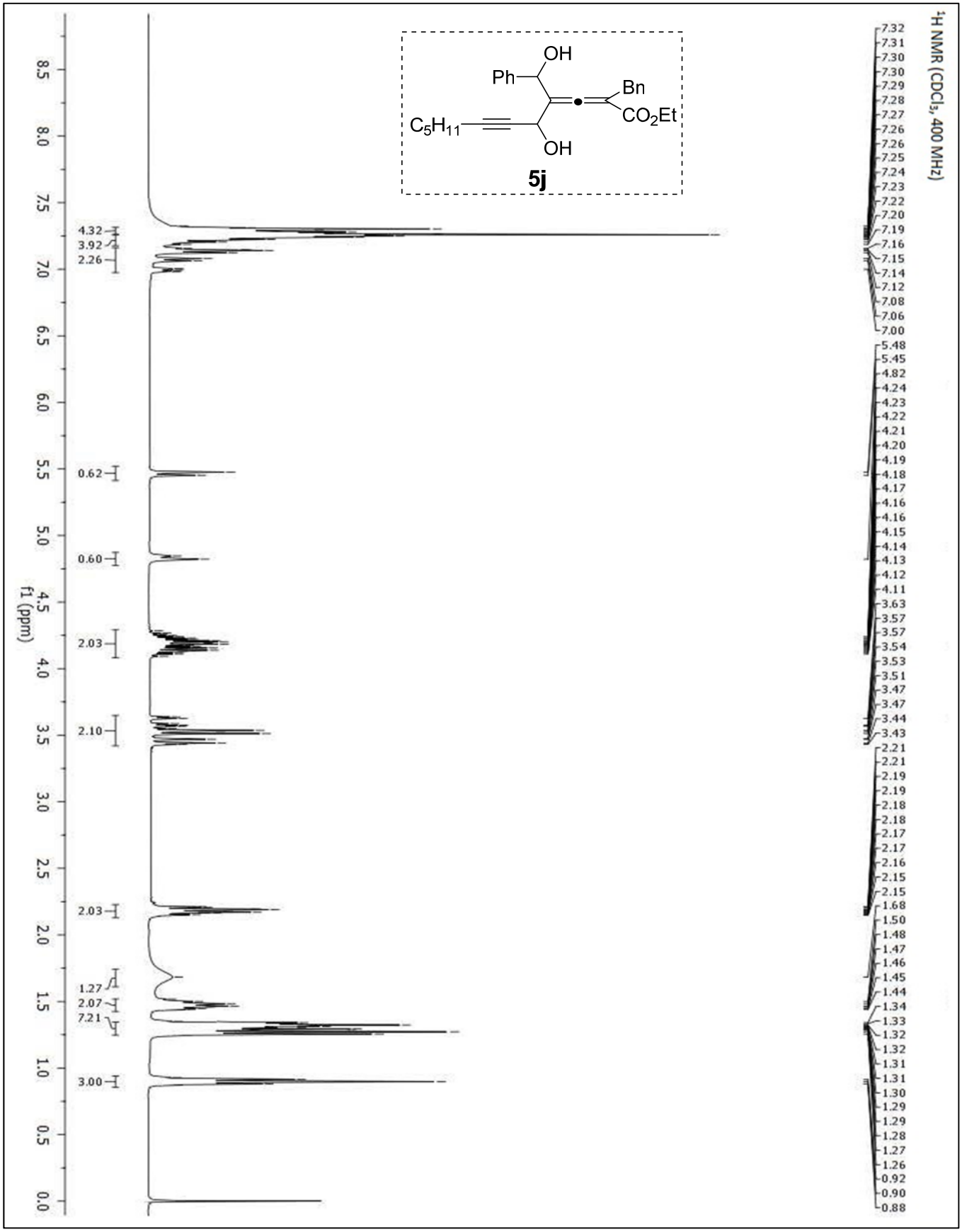

^{13}C NMR (CDCl$_3$, 100 MHz)
OH
Ph
Bn
CO$_2$Et
Ph
OH
5g
209.00
208.98
166.60
166.44
154.96
154.65
140.98
140.78
138.58
138.49
136.42
136.34
133.44
131.55
131.51
131.04
130.91
130.10
129.25
129.22
128.85
128.58
128.54
128.52
128.35
128.31
128.24
128.22
128.11
127.87
127.86
127.75
126.66
126.64
126.62
126.58
126.52
126.51
126.49
126.46
115.56
115.54
114.15
113.91
106.00
105.98
105.60
104.92
73.46
72.86
71.30
71.08
61.37
61.28
35.09
34.94
14.22
14.19
f1 (ppm)

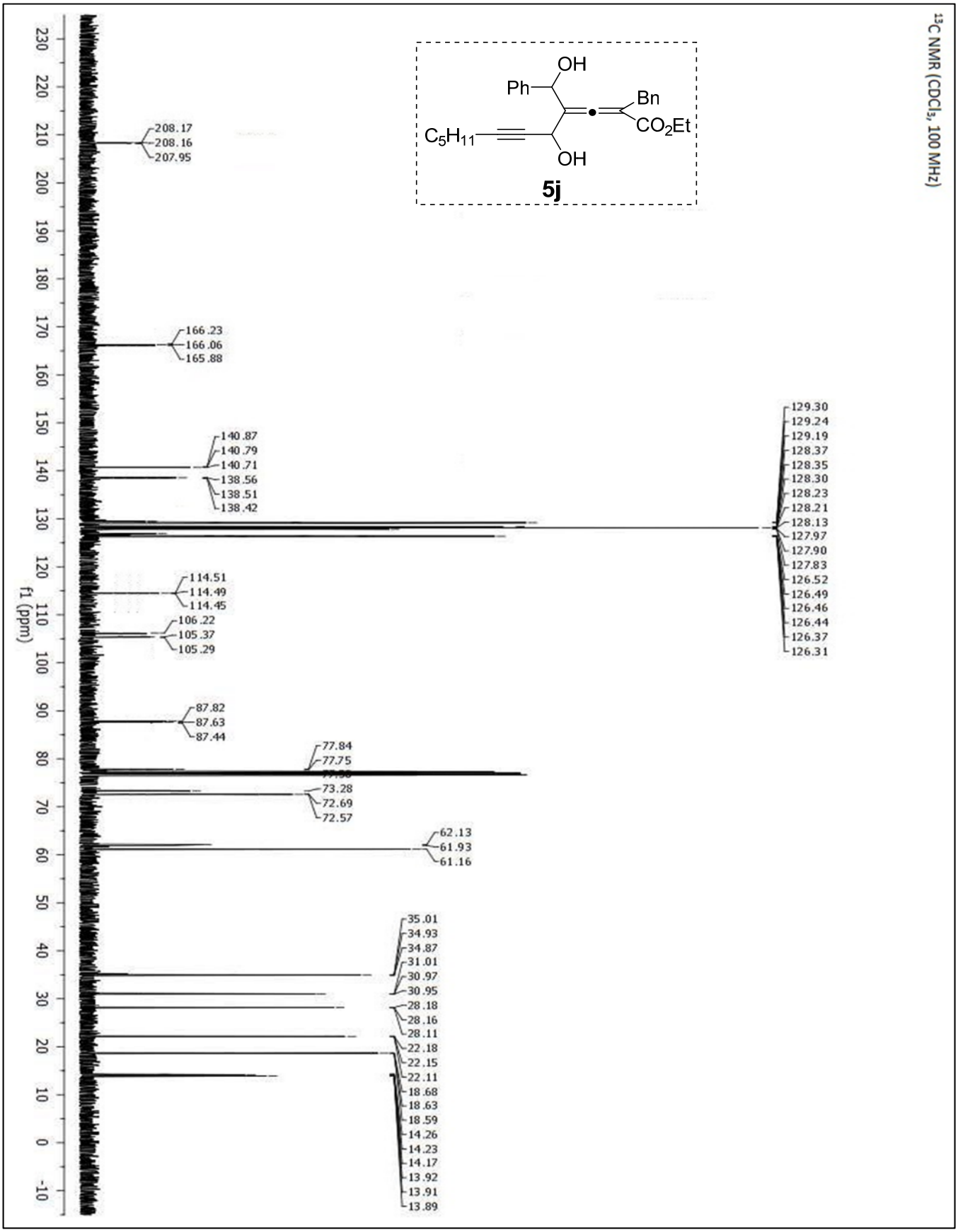

OH
tBu
Bn
CO2Et
tBu
OH
5h
1H NMR (CDCl3, 400 MHz)
f1 (ppm)
9.35
1.21
1.76
2.98
12.41
9.00

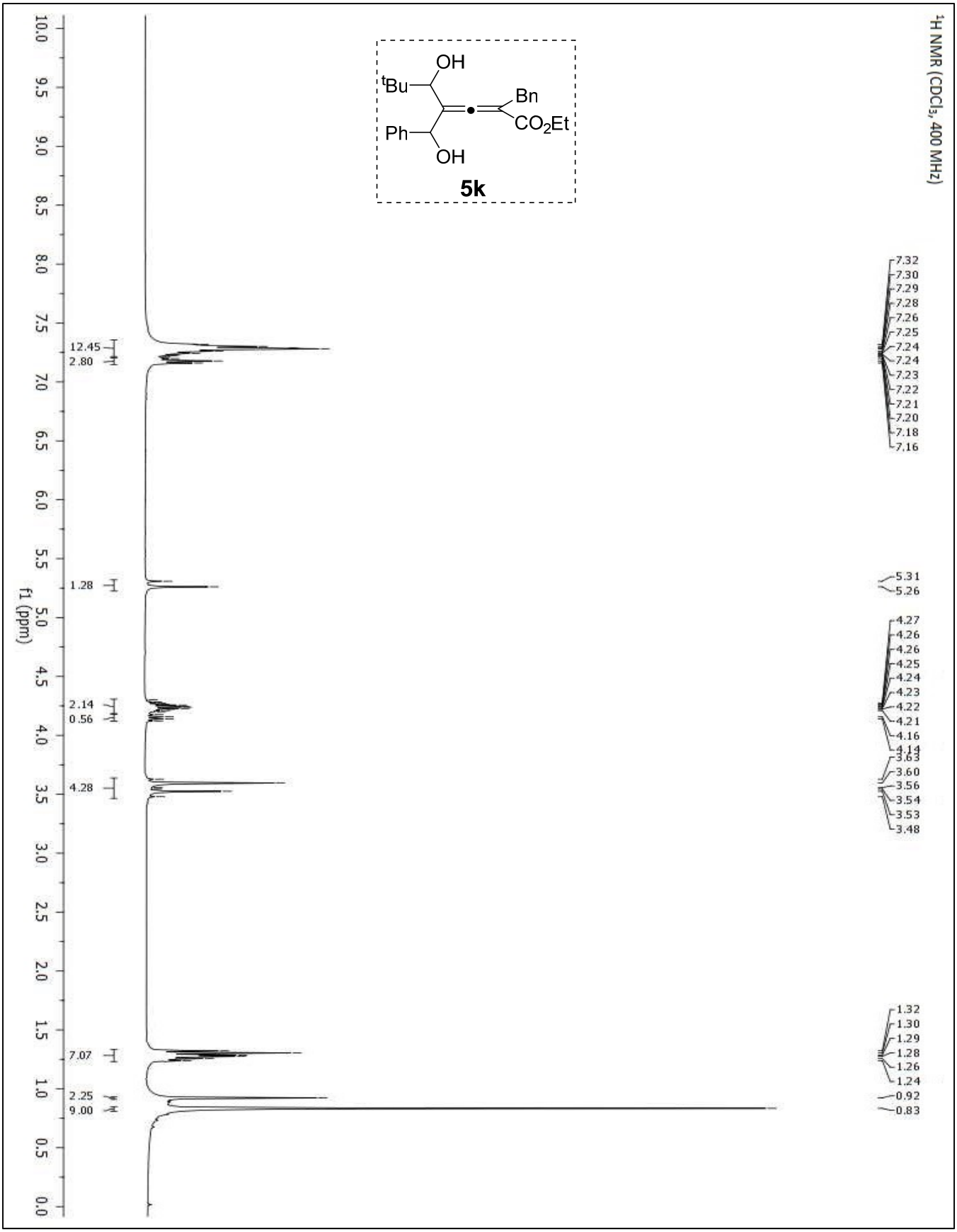

13C NMR (CDCl3, 100 MHz)
OH
tBu
Bn
CO2Et
tBu
OH
5h
209.24
209.16
209.12
166.73
166.64
166.40
150.94
150.84
150.78
138.91
138.81
138.79
137.78
137.76
137.63
129.45
129.38
129.15
128.46
128.41
128.39
126.71
126.63
126.53
126.52
126.42
126.34
125.17
125.12
124.88
115.54
115.41
114.09
106.30
105.34
105.14
78.60
78.56
77.75
75.21
74.77
74.20
61.26
61.20
61.01
36.31
36.25
36.03
35.22
35.13
35.07
34.52
34.51
34.50
31.36
31.34
31.12
25.95
25.87
25.84
14.26
14.17
13.75
f1 (ppm)

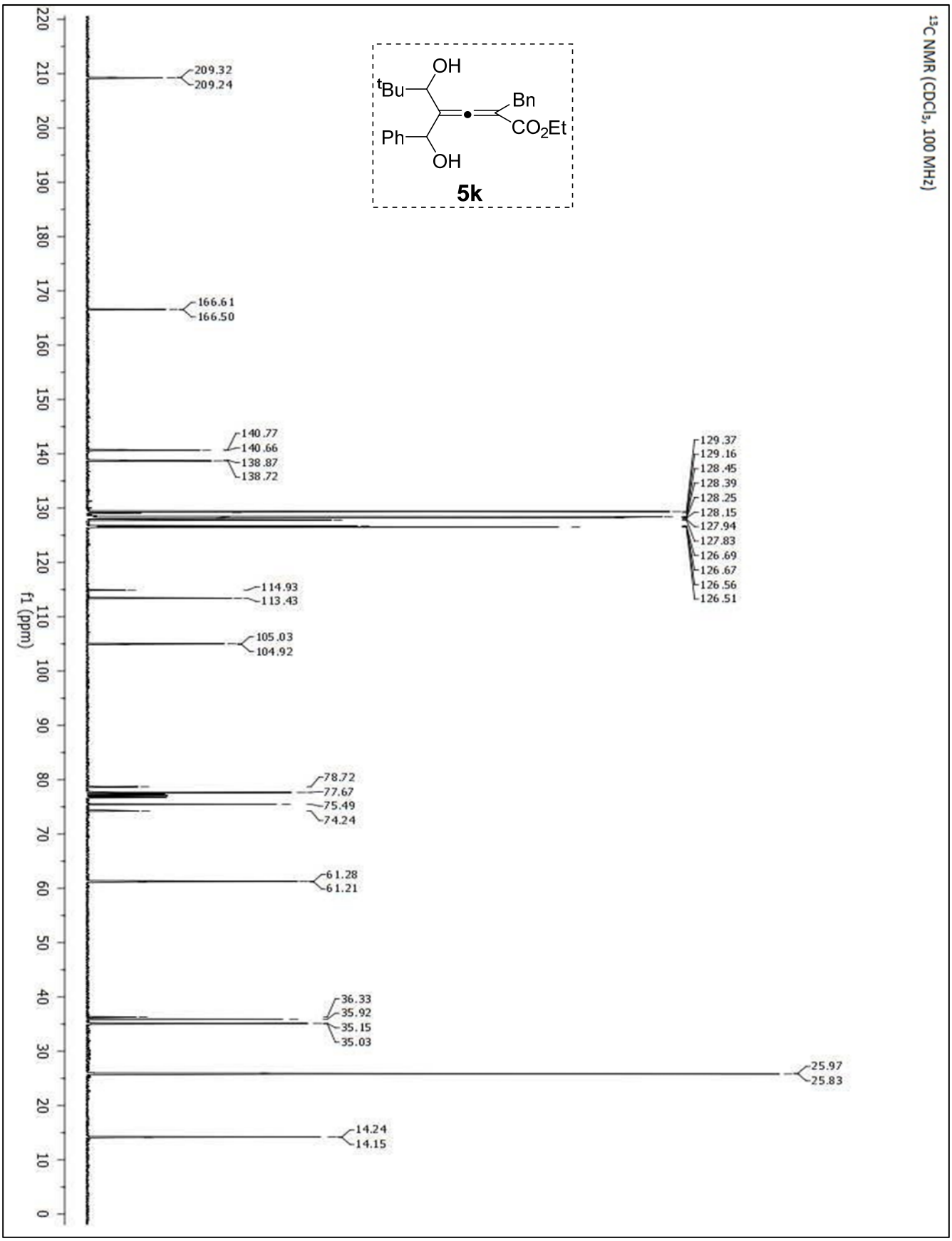

OH
Ph
Bn
CO2Et
O
OH
5i
1H NMR (CDCl3, 400 MHz)
f1 (ppm)
1.42
7.16
3.19
2.32
1.90
2.00
2.14
3.27

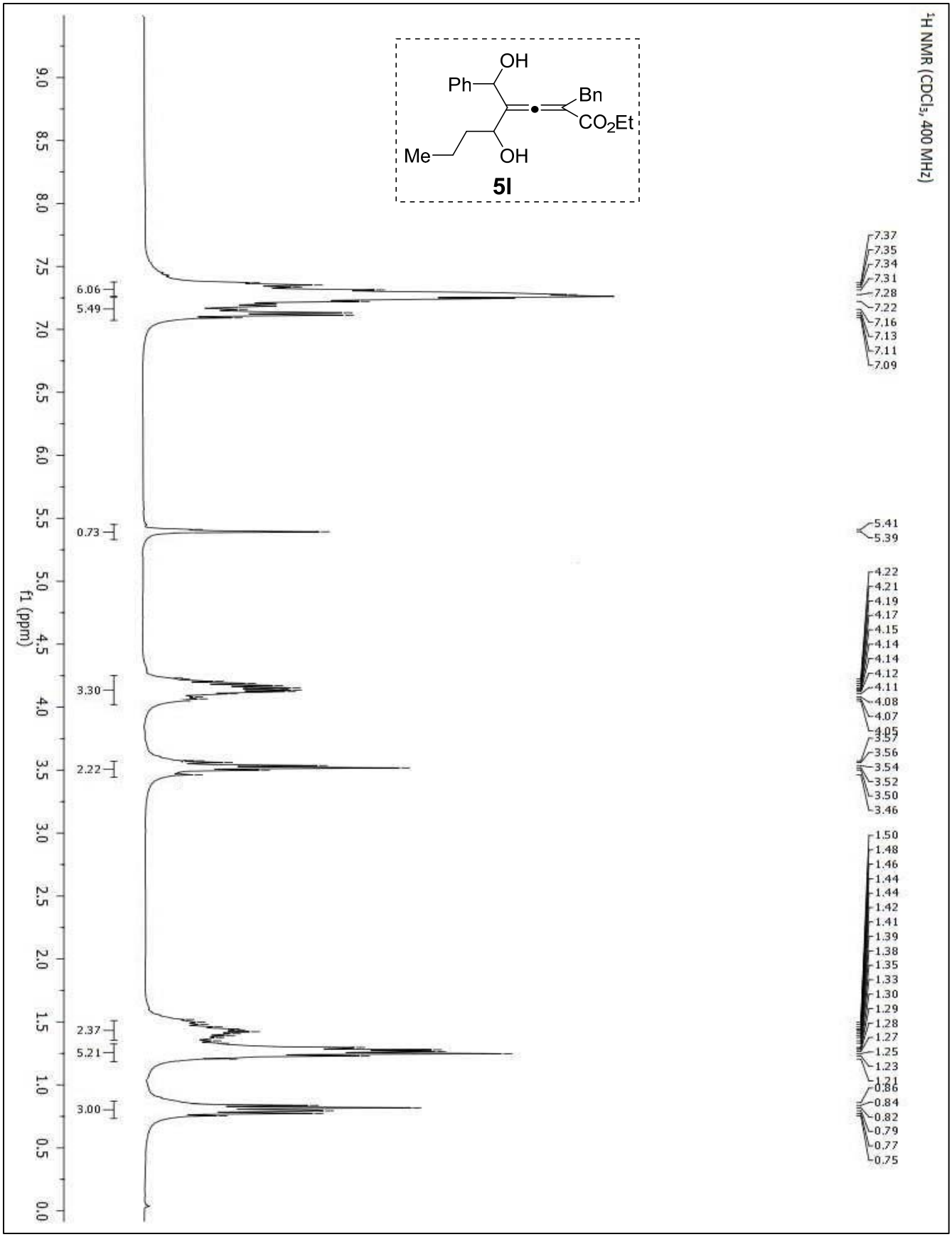

^{13}C NMR (CDCl$_3$, 100 MHz)
OH
Ph
Bn
CO$_2$Et
O
OH
5i
f1 (ppm)
208.74
208.39
208.32
166.41
166.37
166.29
153.48
153.41
153.26
142.38
142.32
142.24
140.64
140.60
140.55
138.50
138.48
138.46
129.26
129.17
129.13
128.37
128.33
128.31
128.25
128.18
128.14
127.94
127.92
127.86
126.57
126.56
126.54
126.48
126.45
126.42
114.46
113.85
112.43
110.32
110.30
110.27
107.56
107.54
107.45
106.67
106.20
105.77
73.26
72.85
72.77
66.84
66.82
66.72
61.39
61.33
61.29
35.06
34.96
34.86
14.19
14.16
14.13

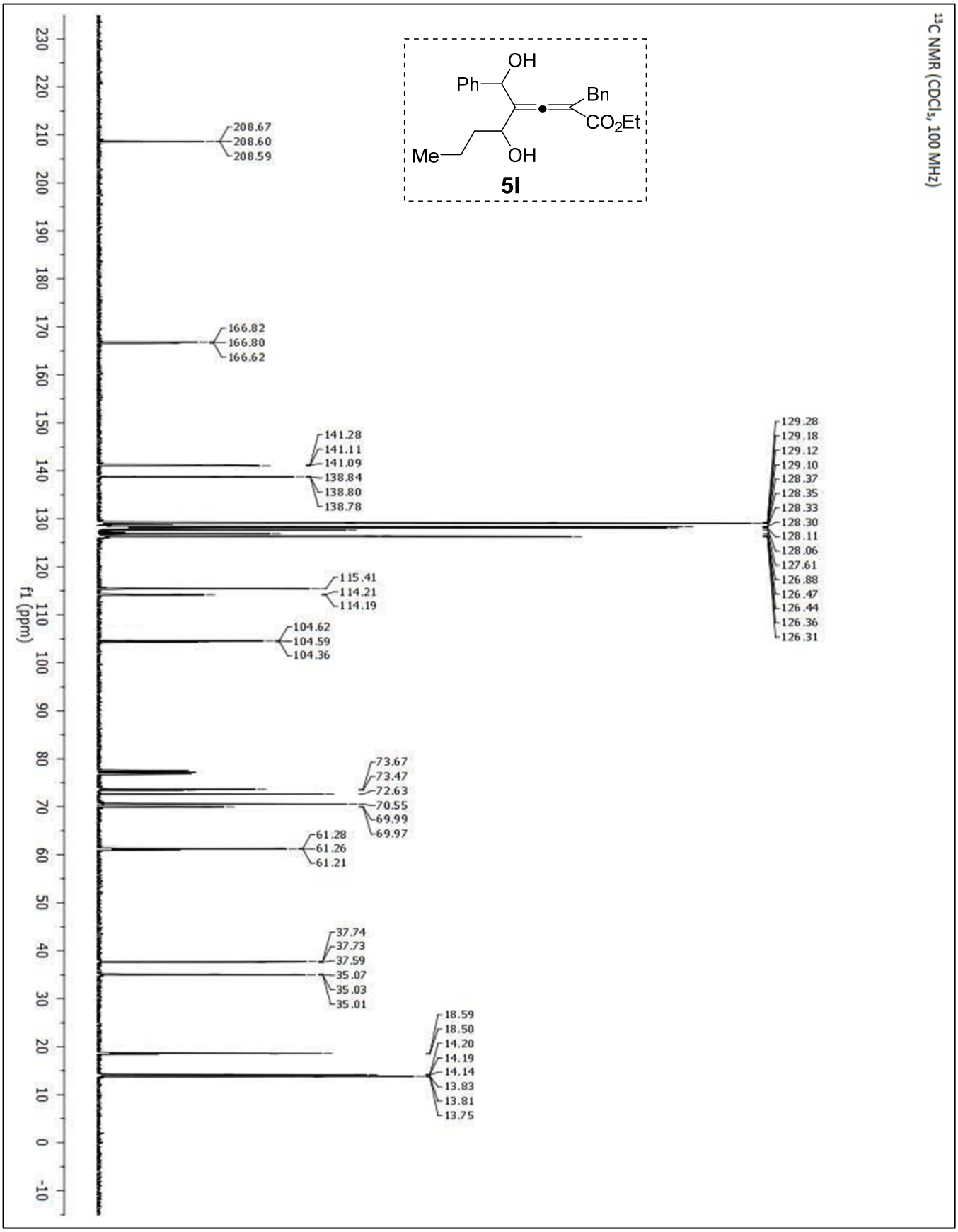

OH
Ph
Bn
CO_2Et
C_5H_{11}
OH
5j
^{1}H NMR ($CDCl_3$, 400 MHz)
f1 (ppm)
4.32
3.92
2.26
0.62
0.60
2.03
2.10
2.03
1.27
2.07
7.21
3.00

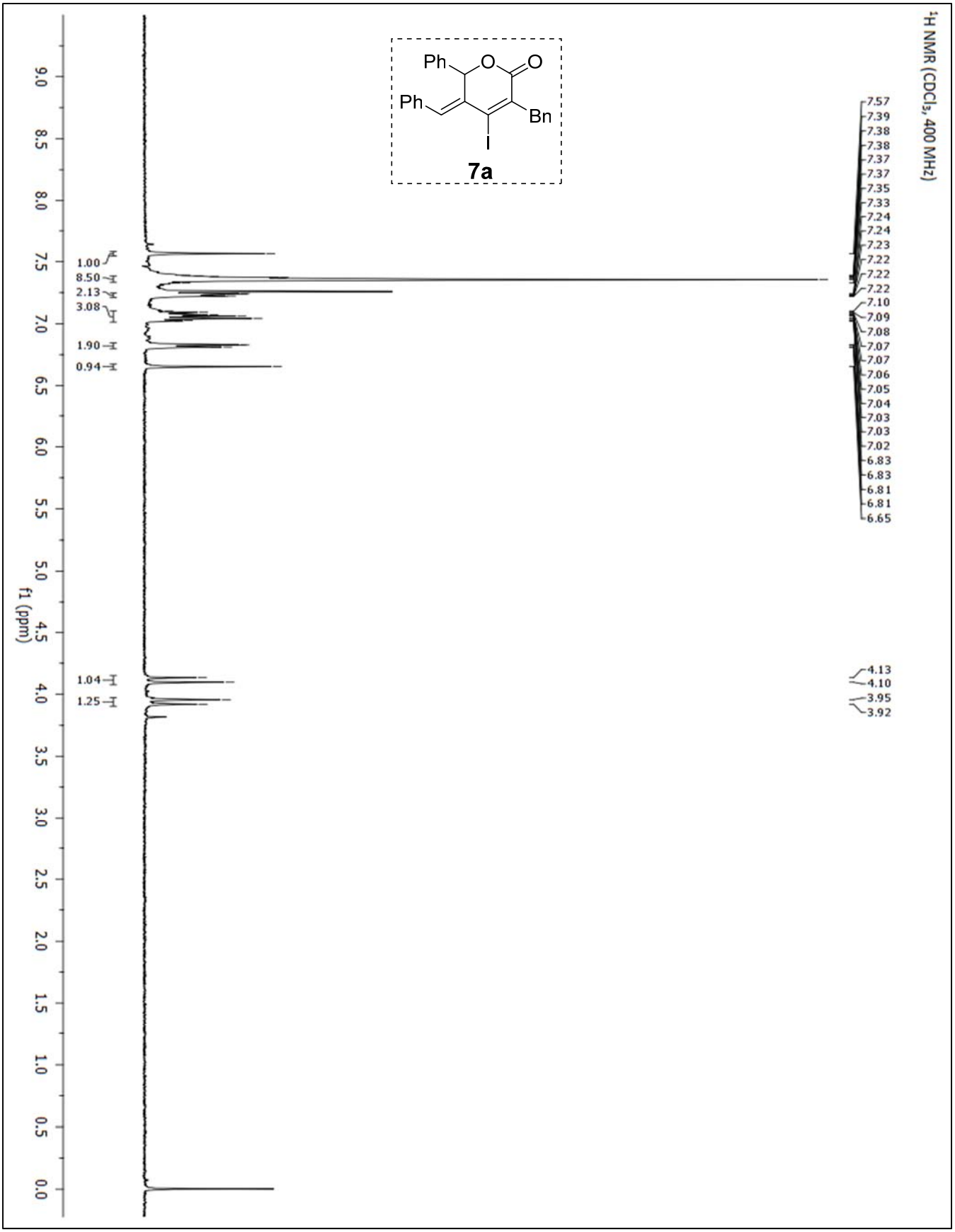

^{13}C NMR (CDCl$_3$, 100 MHz)
OH
Ph
Bn
CO_2Et
C_5H_{11}
OH
5j
f1 (ppm)
208.17
208.16
207.95
166.23
166.06
165.88
140.87
140.79
140.71
138.56
138.51
138.42
129.30
129.24
129.19
128.37
128.35
128.30
128.23
128.21
128.13
127.97
127.90
127.83
126.52
126.49
126.46
126.44
126.37
126.31
114.51
114.49
114.45
106.22
105.37
105.29
87.82
87.63
87.44
77.84
77.75
73.28
72.69
72.57
62.13
61.93
61.16
35.01
34.93
34.87
31.01
30.97
30.95
28.18
28.16
28.11
22.18
22.15
22.11
18.68
18.63
18.59
14.26
14.23
14.17
13.92
13.91
13.89

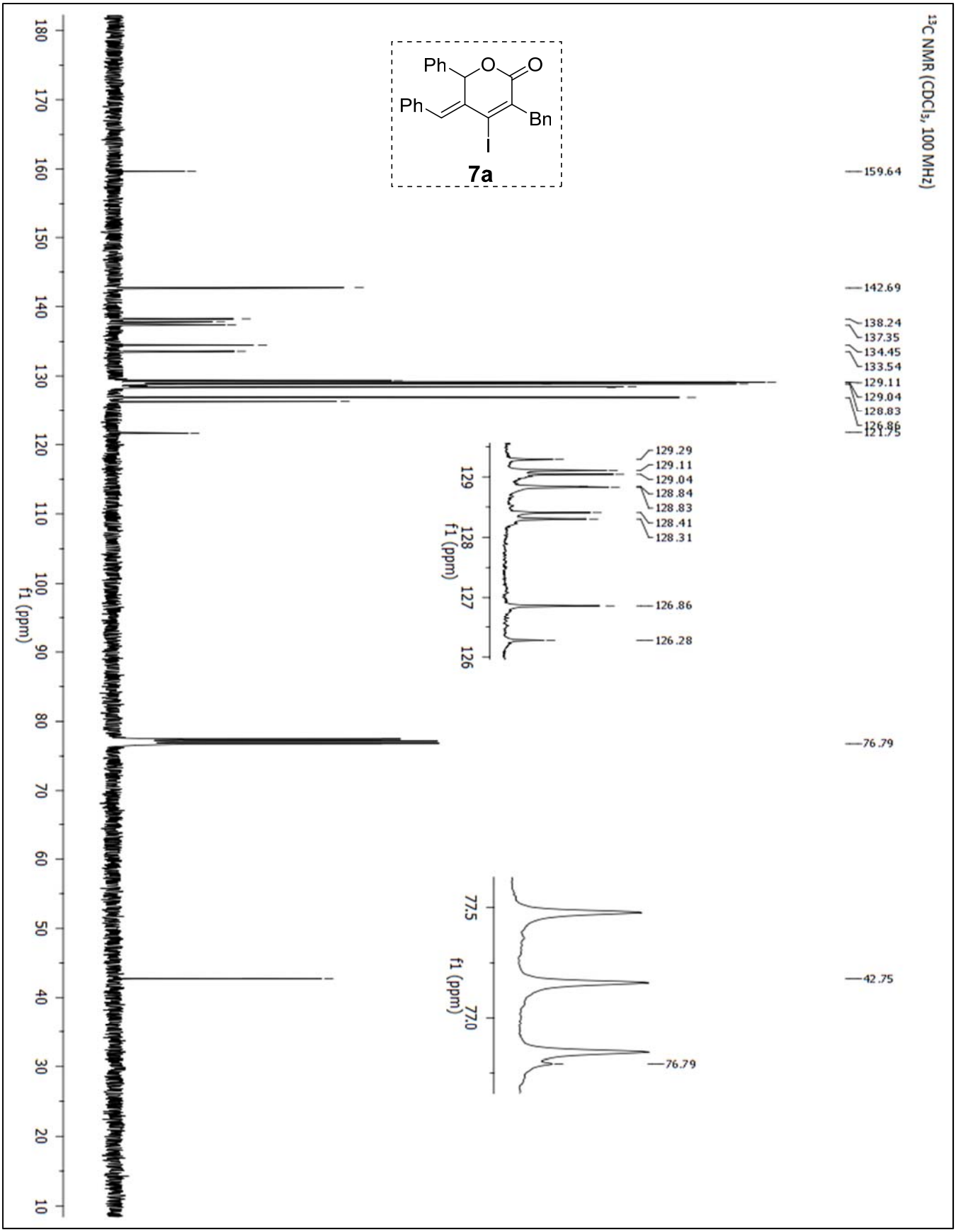

^{1}H NMR (CDCl$_3$, 400 MHz)
OH
^{t}Bu
Bn
CO$_2$Et
Ph
OH
5k
f1 (ppm)
12.45
2.80
1.28
2.14
0.56
4.28
7.07
2.25
9.00
7.32
7.30
7.29
7.28
7.26
7.25
7.24
7.24
7.23
7.22
7.21
7.20
7.18
7.16
5.31
5.26
4.27
4.26
4.26
4.25
4.24
4.23
4.22
4.21
4.16
3.63
3.60
3.56
3.54
3.53
3.48
1.32
1.30
1.29
1.28
1.26
1.24
0.92
0.83

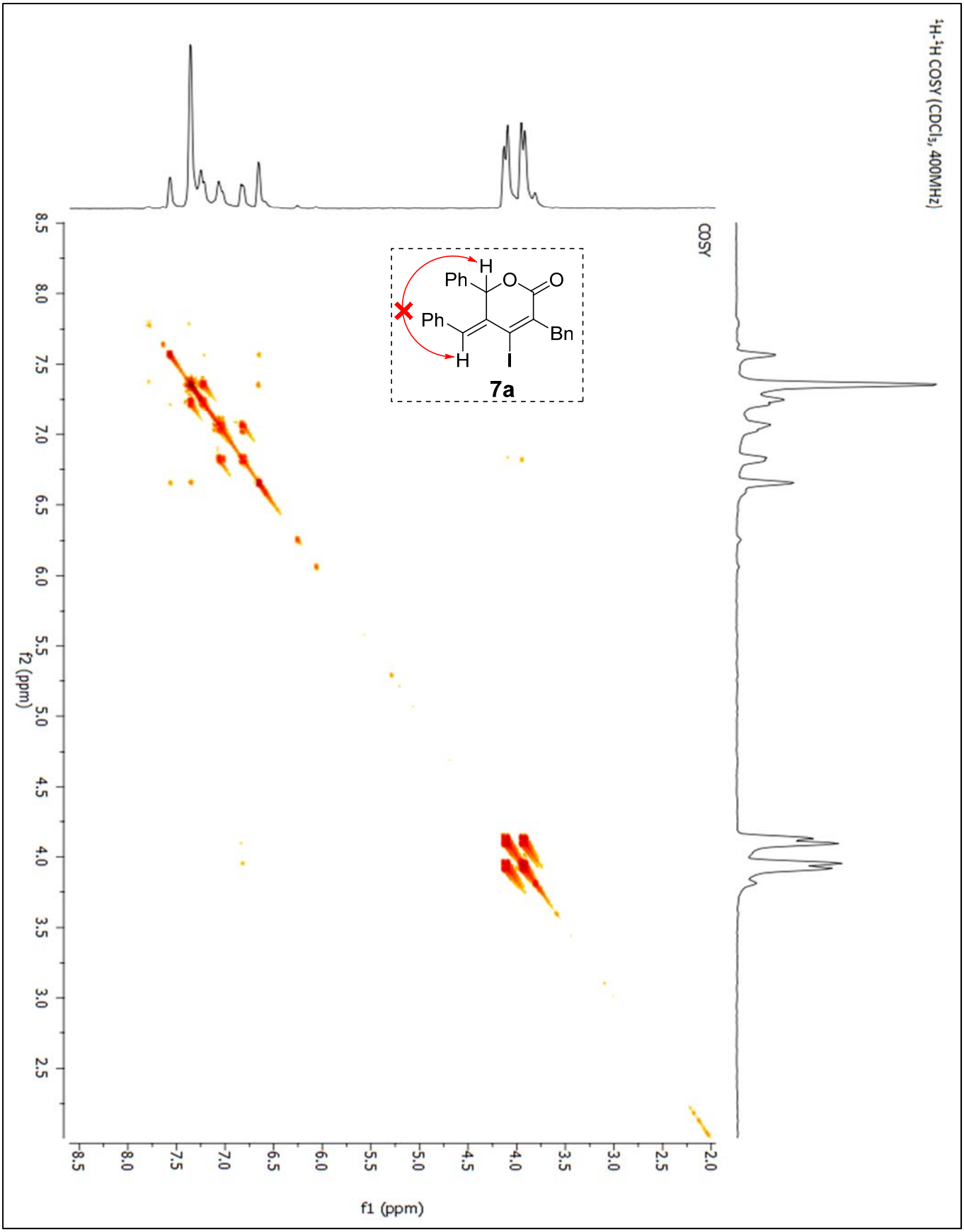

^{13}C NMR (CDCl$_3$, 100 MHz)
OH
^{t}Bu
Bn
CO$_2$Et
Ph
OH
5k
f1 (ppm)
209.32
209.24
166.61
166.50
140.77
140.66
138.87
138.72
129.37
129.16
128.45
128.39
128.25
128.15
127.94
127.83
126.69
126.67
126.56
126.51
114.93
113.43
105.03
104.92
78.72
77.67
75.49
74.24
61.28
61.21
36.33
35.92
35.15
35.03
25.97
25.83
14.24
14.15

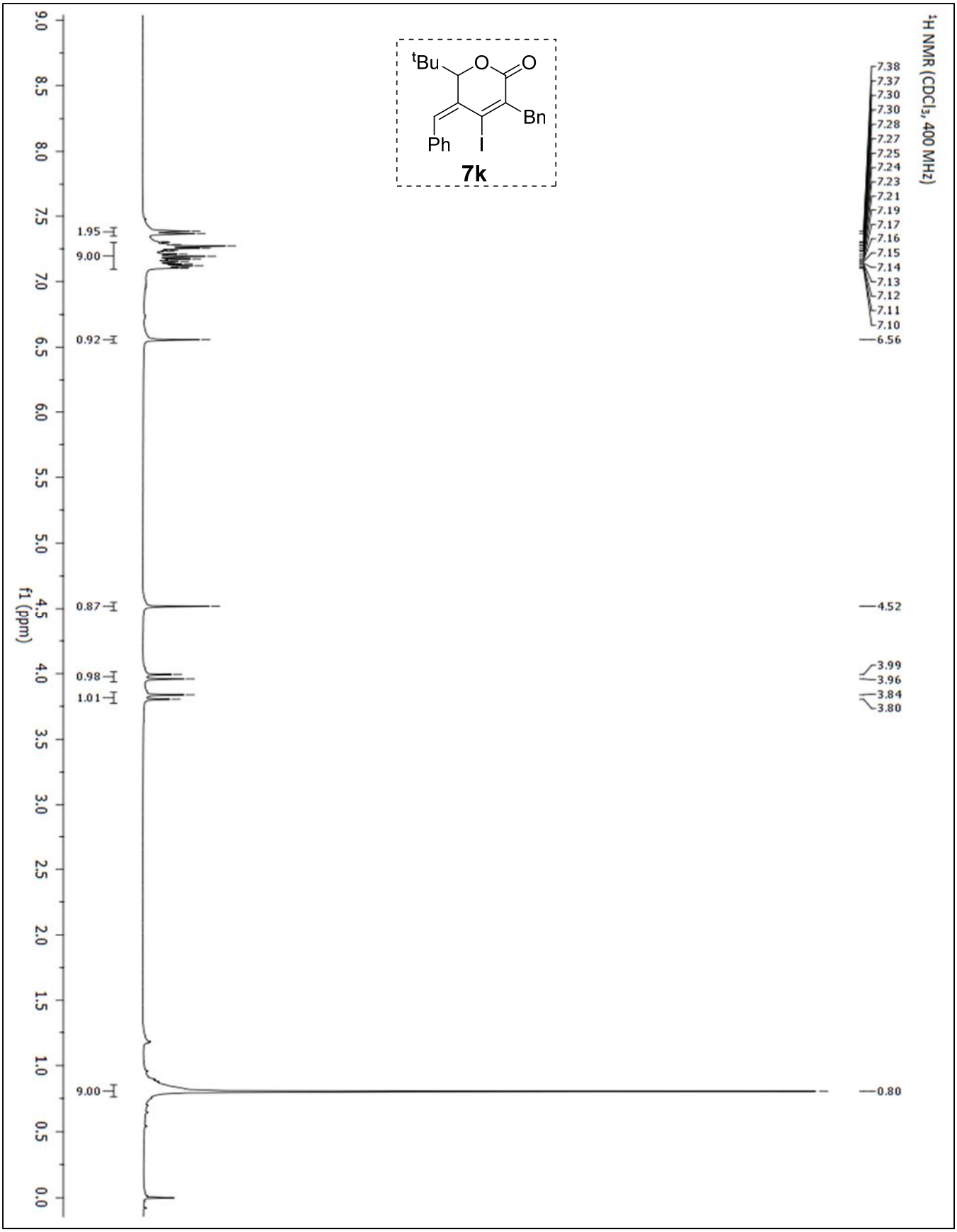

^{1}H NMR ($CDCl_3$, 400 MHz)
OH
Ph
Bn
CO_2Et
Me
OH
5l
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
6.06
5.49
0.73
3.30
2.22
2.37
5.21
3.00
7.37
7.35
7.34
7.31
7.28
7.22
7.16
7.13
7.11
7.09
5.41
5.39
4.22
4.21
4.19
4.17
4.15
4.14
4.14
4.12
4.11
4.08
4.07
4.05
3.57
3.56
3.54
3.52
3.50
3.46
1.50
1.48
1.46
1.44
1.44
1.42
1.41
1.39
1.38
1.35
1.33
1.30
1.29
1.28
1.27
1.25
1.23
1.21
0.86
0.84
0.82
0.79
0.77
0.75

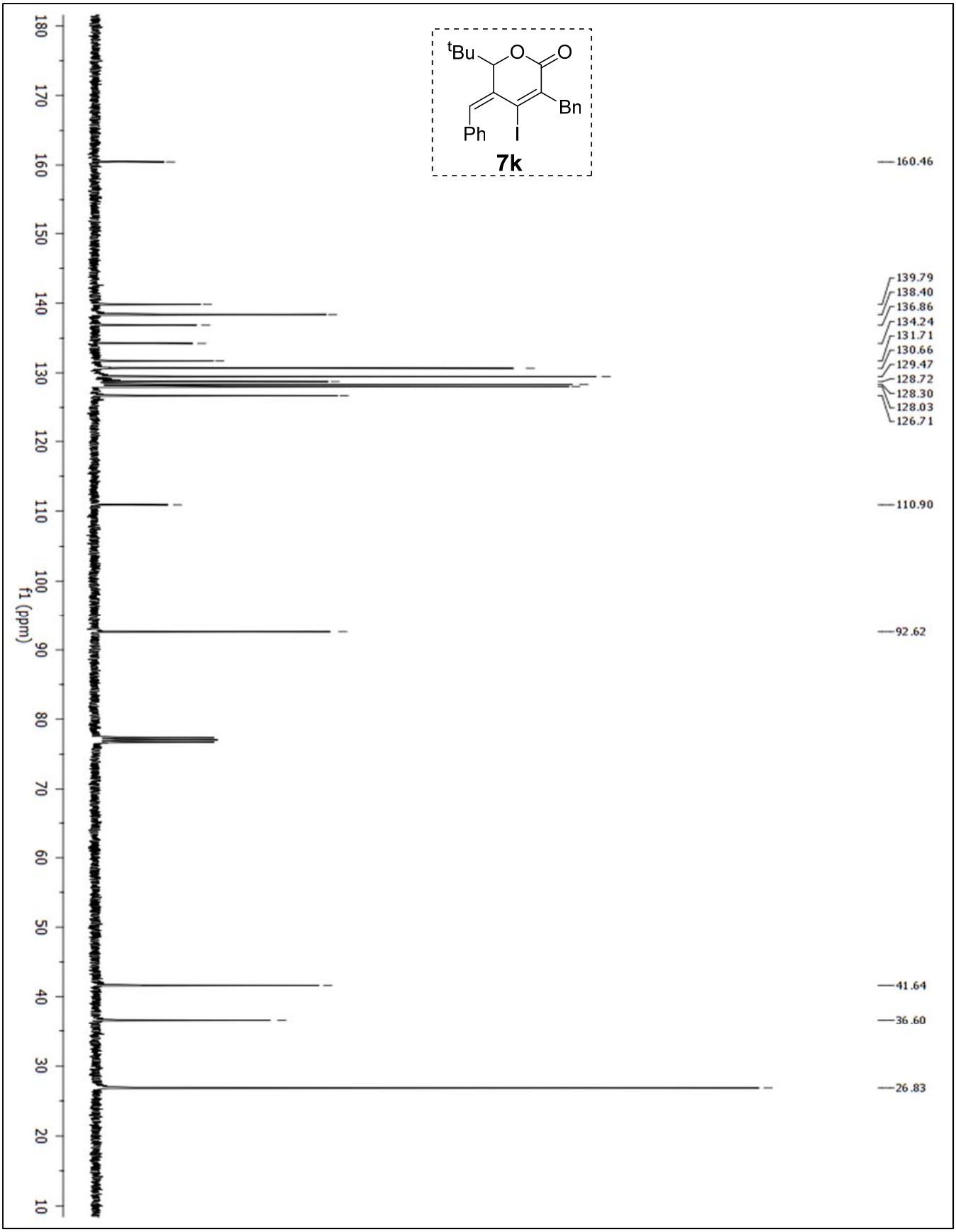

^{13}C NMR (CDCl$_3$, 100 MHz)
OH
Ph
Bn
CO$_2$Et
Me
OH
5l
208.67
208.60
208.59
166.82
166.80
166.62
141.28
141.11
141.09
138.84
138.80
138.78
129.28
129.18
129.12
129.10
128.37
128.35
128.33
128.30
128.11
128.06
127.61
126.88
126.47
126.44
126.36
126.31
115.41
114.21
114.19
104.62
104.59
104.36
73.67
73.47
72.63
70.55
69.99
69.97
61.28
61.26
61.21
37.74
37.73
37.59
35.07
35.03
35.01
18.59
18.50
14.20
14.19
14.14
13.83
13.81
13.75
f1 (ppm)

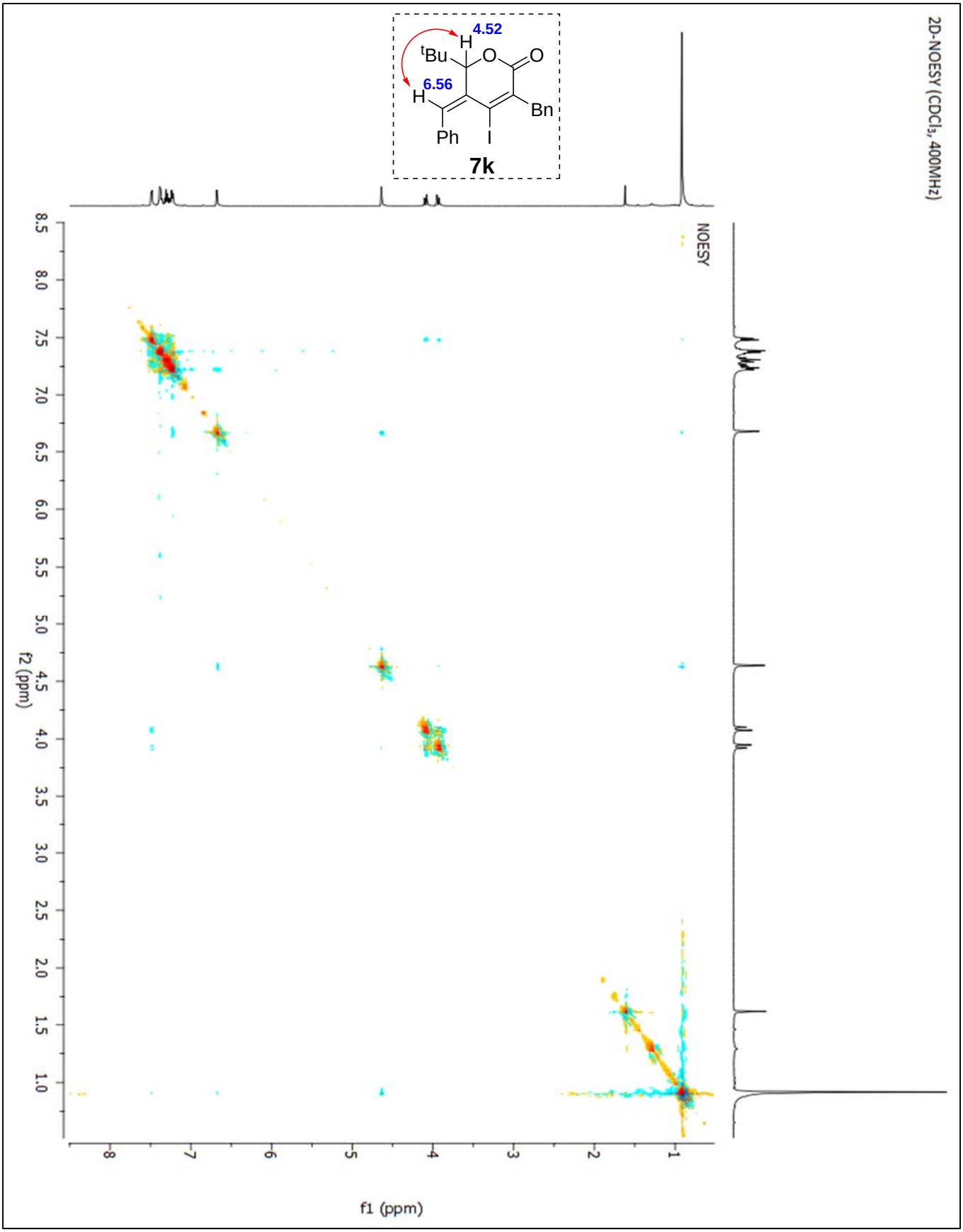

^{1}H NMR (CDCl$_3$, 400 MHz)
Ph
O
O
Ph
Bn
I
7a
7.57
7.39
7.38
7.38
7.37
7.37
7.35
7.33
7.24
7.24
7.23
7.22
7.22
7.22
7.10
7.09
7.08
7.07
7.07
7.06
7.05
7.04
7.03
7.03
7.02
6.83
6.83
6.81
6.81
6.65
4.13
4.10
3.95
3.92
1.00
8.50
2.13
3.08
1.90
0.94
1.04
1.25
f1 (ppm)

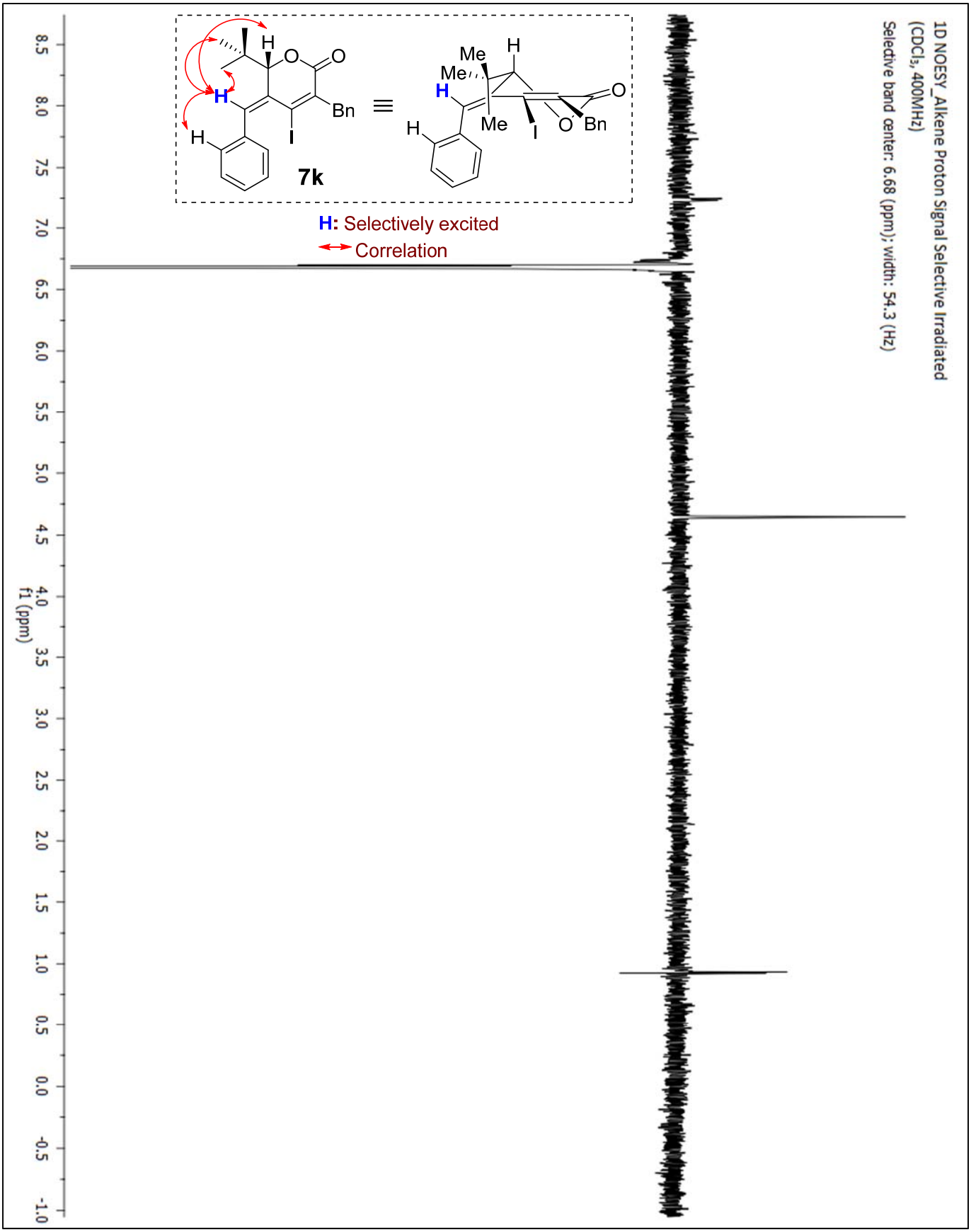

^{13}C NMR (CDCl$_3$, 100 MHz)
Ph
O
O
Ph
Bn
I
7a
159.64
142.69
138.24
137.35
134.45
133.54
129.11
129.04
128.83
126.86
121.75
129.29
129.11
129.04
128.84
128.83
128.41
128.31
126.86
126.28
76.79
42.75
77.5
77.0
76.79
f1 (ppm)

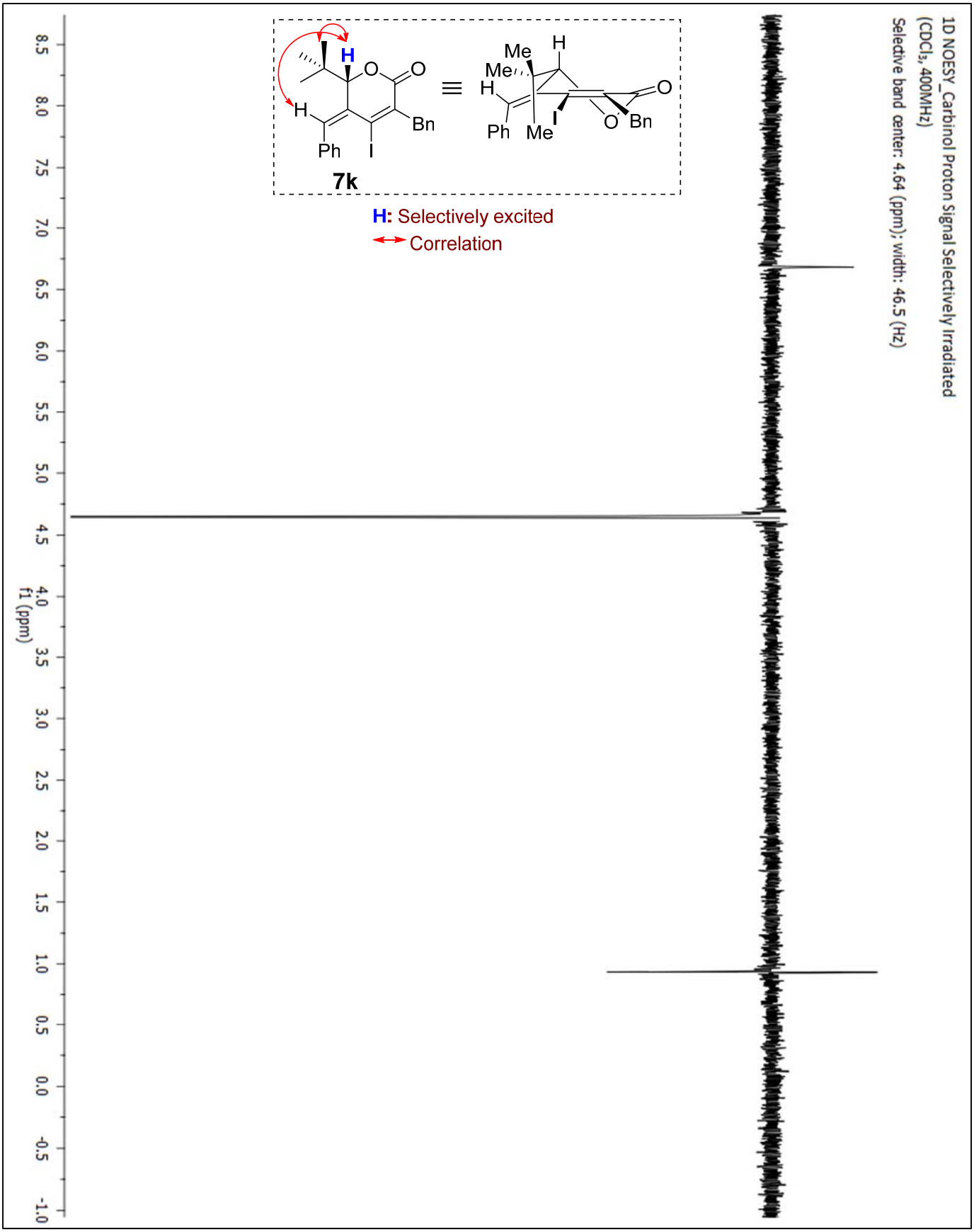

^{1}H-^{1}H COSY (CDCl$_3$, 400MHz)
COSY
Ph
H
O
O
Ph
Bn
H
I
7a
f2 (ppm)
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

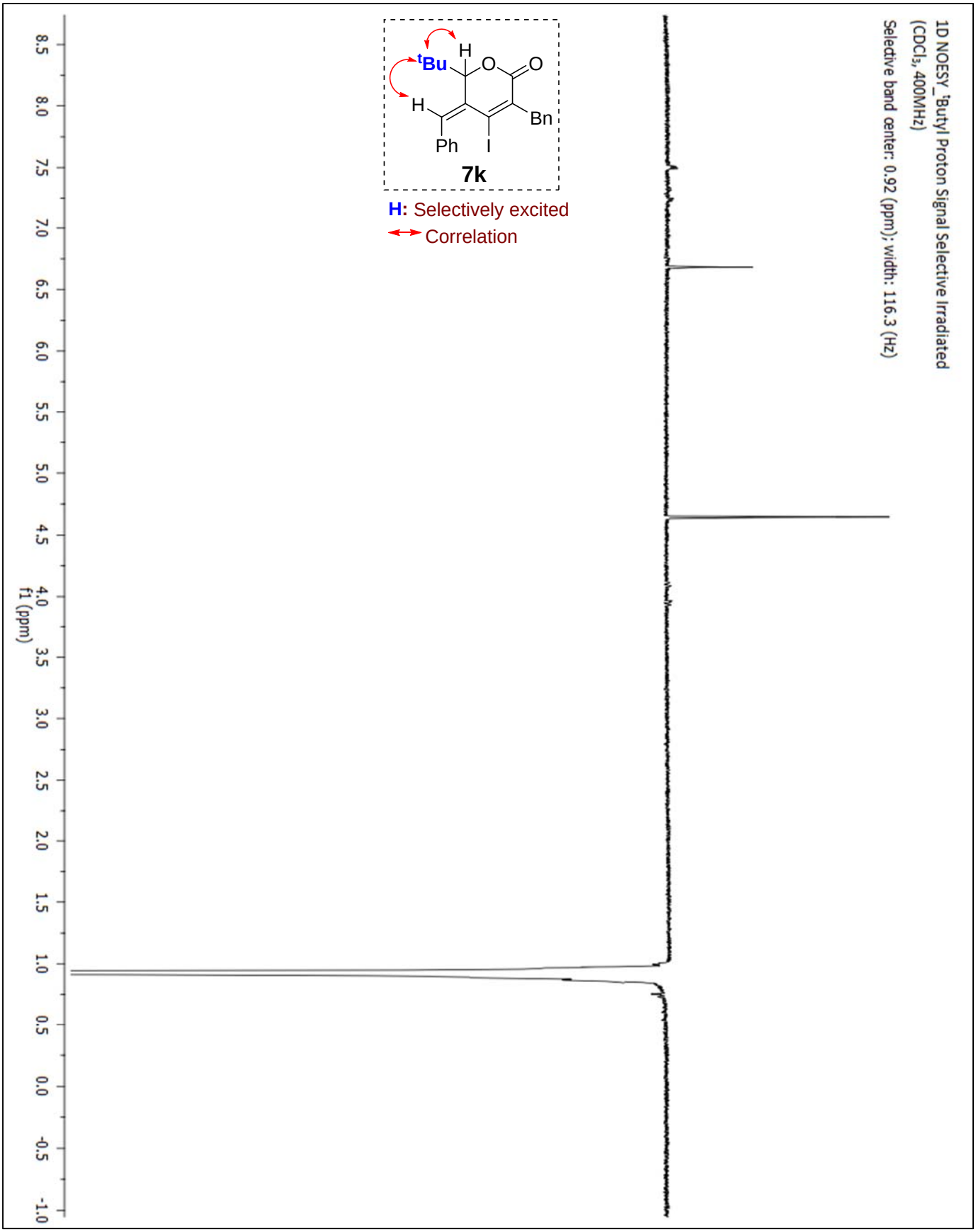

^{1}H NMR (CDCl$_3$, 400 MHz)
7.38
7.37
7.30
7.30
7.28
7.27
7.25
7.24
7.23
7.21
7.19
7.17
7.16
7.15
7.14
7.13
7.12
7.11
7.10
6.56
4.52
3.99
3.96
3.84
3.80
0.80
1.95
9.00
0.92
0.87
0.98
1.01
9.00
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
tBu
O
O
Bn
Ph
I
7k


tBu
O
O
Bn
Ph
I
7k
160.46
139.79
138.40
136.86
134.24
131.71
130.66
129.47
128.72
128.30
128.03
126.71
110.90
92.62
41.64
36.60
26.83
f1 (ppm)


2D-NOESY (CDCl3, 400MHz)
4.52
6.56
tBu
H
O
O
H
Bn
Ph
I
7k
NOESY
f2 (ppm)
f1 (ppm)


1D NOESY_Alkene Proton Signal Selective Irradiated
(CDCl3, 400MHz)
Selective band center: 6.68 (ppm); width: 54.3 (Hz)
H: Selectively excited
Correlation
7k
f1 (ppm)


1D NOESY_Carbinol Proton Signal Selectively Irradiated
(CDCl3, 400MHz)
Selective band center: 4.64 (ppm); width: 46.5 (Hz)
H
O
O
Bn
H
Ph
I
7k
≡
Me
Me
H
H
Ph
Me
I
O
O
Bn
H: Selectively excited
Correlation
f1 (ppm)
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
-0.5
-1.0


1D NOESY_tButyl Proton Signal Selective Irradiated
(CDCl3, 400MHz)
Selective band center: 0.92 (ppm); width: 116.3 (Hz)
tBu
H
O
O
H
Bn
Ph
I
7k
H: Selectively excited
Correlation
f1 (ppm)
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
-0.5
-1.0