Supporting Information

$Yb(OTf)_3$ and Visible Light Relay Catalyzed [3+2] Cycloaddition /[3,3]-Rearrangement/[4+2] Cycloaddition in One Pot to Prepare Oxazonine-Fused Endoperoxides

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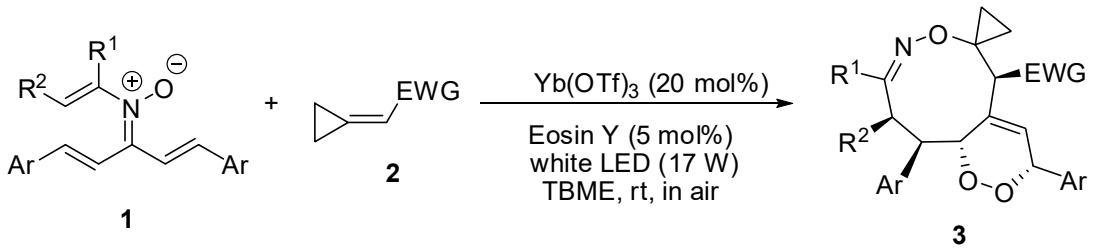
Contents

1. General experimental information

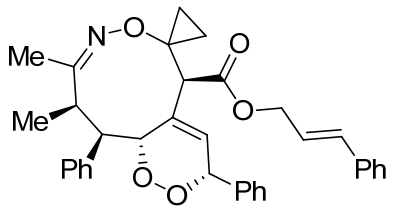
^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature using 400 MHz or 600 MHz spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. High resolution mass spectra were acquired on an LTQ FT spectrometer, and were obtained by peak matching. Melting points are reported uncorrected. Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. Chromatography was performed using with 300-400 mesh silica gel (SiO_2). Unless otherwise noted, all reactions were performed under air atmosphere. All reagents and solvents were obtained from commercial sources and, where appropriate, purified prior to use. The *N*-vinyl nitrones **1a-1o**[1] methylenecyclopropanes **2a-2l**[2], nine-membered heterocycles ***cis*-4aa**[3] **and *trans*-4aa**[3] and were prepared according the literature methods and their spectral data matched literature values.

2. General procedure for the synthesis of endoperoxides 3



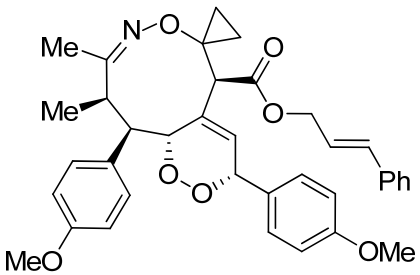
General procedure A: An oven-dried glass vial equipped with a magnetic stirrer was charged with the corresponding *N*-vinyl nitrone **1** (0.2 mmol), $Yb(OTf)_3$ (20 mol%, 0.04 mmol, 0.025 g), Eosin Y (5 mol%, 0.01 mmol, 0.006 g) and TBME (2 mL). Methylenecyclopropane **2** (0.4 mmol, 2.0 equiv.) was added to the mixture. The vial was closed with a plastic film. Then, the reaction mixture was stirred and irradiated (17 W white LED) at room temperature for 36−72 h (monitored by TLC). At this time, the solvent was removed under reduced pressure and the crude product was purified

by flash column chromatography (the crude residue was dry loaded with silica gel, 1/20 to 1/10, ethyl acetate/petroleum ether) to afford endoperoxide **3**.



3aa

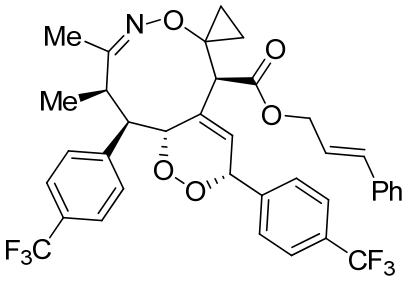
Oxazonine-fused endoperoxide 3aa, a light yellow solid, 0.090 g, 82% yield. Mp: 166–167 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, J = 7.2 Hz, 2H), 7.19–7.09 (m, 11H), 6.93 (d, J = 6.8 Hz, 2H), 6.56 (d, J = 15.6 Hz, 1H), 6.12 (dt, J = 15.6 Hz, 6.8 Hz, 1H), 5.80–5.76 (m, 1H), 5.62–5.58 (m, 1H), 5.46–5.42 (m, 1H), 4.70–4.58 (m, 2H), 3.95 (s, 1H), 3.29–3.28 (m, 1H), 2.69–2.64 (m, 1H), 1.87 (s, 3H), 1.44 (d, J = 7.2 Hz, 3H), 1.19–1.18 (m, 1H), 1.12–1.07 (m, 1H), 1.01–0.96 (m, 1H), 0.80–0.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4, 169.4, 142.8, 136.4, 135.8, 135.4, 135.3, 129.3, 128.5, 128.4, 128.2, 128.1, 127.9, 127.8, 126.6, 126.4, 124.9, 122.2, 79.8, 77.5, 65.4, 62.8, 50.8, 49.4, 46.0, 21.7, 12.4, 11.2, 9.3; IR (thin film) 3022, 2964, 1737, 1641, 1450, 1148, 1001, 695 cm^{-1}; HRMS (ESI) m/z calcd for $C_{35}H_{36}NO_5$ $[M + H]^+$: 550.2588, found: 550.2608.



3ba

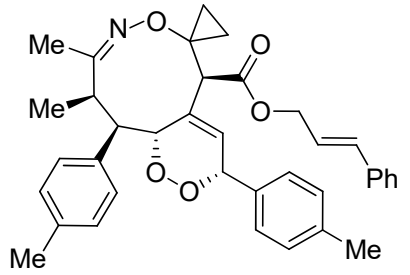
Oxazonine-fused endoperoxide 3ba, a light yellow solid, 0.096 g, 79% yield. Mp: 150–151 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27–7.25 (m, 7H), 6.98 (d, J = 8.4 Hz, 2H), 6.80 (d, J = 8.0 Hz, 2H), 6.72 (d, J = 8.4 Hz, 2H), 6.64 (d, J = 16.0 Hz, 1H), 6.21–6.14 (m, 1H), 5.80–5.76 (m, 1H), 5.70–5.62 (m, 1H), 5.50–5.41 (m, 1H), 4.80–4.64 (m, 2H), 4.01 (s, 1H), 3.72 (s, 6H), 3.34–3.29 (m, 1H), 2.77–2.72 (m, 1H),

1.94 (s, 3H), 1.47 (d, J = 7.2 Hz, 3H), 1.29–1.25 (m, 1H), 1.18–1.13 (m, 1H), 1.08–1.04 (m, 1H), 0.87–0.81 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.6, 169.5, 159.8, 158.0, 135.8, 135.6, 135.3, 135.0, 130.2, 129.6, 128.5, 128.3, 128.1, 126.5, 125.1, 122.2, 113.6, 113.2, 79.4, 77.6, 65.4, 62.8, 55.1, 55.0, 50.1, 49.4, 46.0, 21.7, 12.4, 11.3, 9.4; IR (thin film) 3003, 2938, 1739, 1610, 1512, 1147, 1028, 694 cm^{-1}; HRMS (ESI) m/z calcd for $C_{37}H_{40}NO_7$ $[M + H]^+$: 610.2799, found: 610.2794.



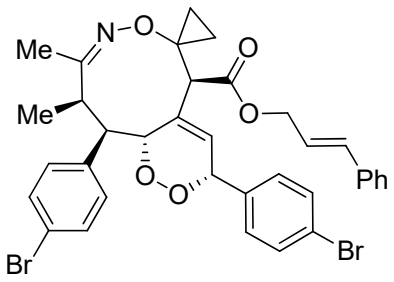
3ca

Oxazonine-fused endoperoxide 3ca, a light yellow solid, 0.110 g, 80% yield. Mp: 163–164 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 7.6 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.31–7.25 (m, 5H), 7.02 (d, J = 8.0 Hz, 2H), 6.66 (d, J = 16.0 Hz, 1H), 6.23–6.16 (m, 1H), 5.90–5.85 (m, 1H), 5.71–5.67 (m, 1H), 5.58–5.50 (m, 1H), 4.81–4.66 (m, 2H), 4.02 (s, 1H), 3.39–3.38 (m, 1H), 2.65–2.60 (m, 1H), 1.97 (s, 3H), 1.52 (d, J = 7.2 Hz, 3H), 1.31–1.17 (m, 2H), 1.10–1.04 (m, 1H), 0.87–0.82 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 169.2, 146.7, 140.3, 136.1, 135.8, 135.7, 131.2 (q, J = 32.0 Hz), 129.5, 129.0, 128.7, 128.5, 127.7, 126.6, 125.5 (d, J = 36.4 Hz), 125.3 (q, J = 3.6 Hz), 124.9 (q, J = 3.6 Hz), 124.0, 122.8, 122.0, 78.9, 77.3, 65.6, 62.9, 50.4, 49.3, 46.0, 21.8, 12.1, 11.2, 9.3; ^{19}F NMR (100 MHz, $CDCl_3$): δ -62.4, -62.6; IR (thin film) 3023, 2966, 1732, 1617, 1325, 1122, 692 cm^{-1}; HRMS (ESI) m/z calcd for $C_{37}H_{34}F_6NO_5$ $[M + H]^+$: 686.2336, found: 686.2331.



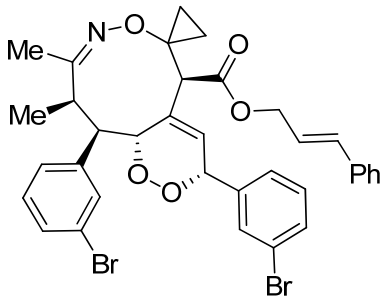
3da

Oxazonine-fused endoperoxide 3da, a light yellow solid, 0.090 g, 78% yield. Mp: 162–163 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19–7.16 (m, 7H), 6.99 (d, J = 7.6 Hz, 2H), 6.92 (d, J = 8.0 Hz, 2H), 6.85 (d, J = 7.6 Hz, 2H), 6.56 (d, J = 16.0 Hz, 1H), 6.12–6.05 (m, 1H), 5.74–5.70 (m, 1H), 5.59–5.55 (m, 1H), 5.40–5.35 (m, 1H), 4.70–4.56 (m, 2H), 3.95 (s, 1H), 3.27–3.26 (m, 1H), 2.67–2.62 (m, 1H), 2.18 (s, 6H), 3.14 (s, 3H), 1.41 (d, J = 7.2 Hz, 3H), 1.21–1.14 (m, 1H), 1.12–1.05 (m, 1H), 1.00–0.94 (m, 1H), 0.78–0.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 169.4, 139.8, 138.4, 135.9, 135.8, 135.4, 135.3, 133.3, 129.2, 128.9, 128.6, 128.5, 128.1, 128.0, 126.5, 125.1, 122.2, 79.6, 77.5, 65.4, 62.7, 50.5, 49.3, 46.1, 21.7, 21.1, 20.9, 12.4, 11.3, 9.3; IR (thin film) 3006, 2918, 1735, 1514, 1156, 1023, 725 cm^{-1}; HRMS (ESI) m/z calcd for $C_{37}H_{40}NO_5$ $[M + H]^+$: 578.2901, found: 578.2900.



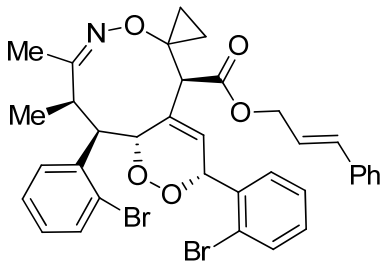
3ea

Oxazonine-fused endoperoxide 3ea, a light yellow solid, 0.093 g, 66% yield. Mp: 136–137 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J = 8.4 Hz, 2H), 7.33–7.24 (m, 7H), 7.21 (d, J = 8.0 Hz, 2H), 6.85 (d, J = 8.0 Hz, 2H), 6.64 (d, J = 15.6 Hz, 1H), 6.20–6.14 (m, 1H), 5.84–5.73 (m, 1H), 5.65–5.58 (m, 1H), 5.50–5.40 (m, 1H), 4.81–4.63 (m, 2H), 4.00 (s, 1H), 3.28–3.27 (m, 1H), 2.62–2.60 (m, 1H), 1.96 (s, 3H), 1.48 (d, J = 7.2 Hz, 3H), 1.27–1.23 (m, 1H), 1.19–1.13 (m, 1H), 1.07–1.03 (m, 1H), 0.86–0.81 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9, 169.2, 141.8, 135.9, 135.8, 135.7, 131.6, 131.5, 131.0, 130.9, 129.5, 128.6, 128.4, 126.5, 124.3, 122.8, 122.0, 120.5, 79.0, 77.2, 65.5, 62.7, 50.1, 49.1, 46.2, 21.8, 12.0, 11.2, 9.3; IR (thin film) 3024, 2948, 1736, 1488, 1155, 1009, 789 cm^{-1}; HRMS (ESI) m/z calcd for $C_{35}H_{34}Br_2NO_5$ $[M + H]^+$: 706.0798, found: 706.0796.



3fa

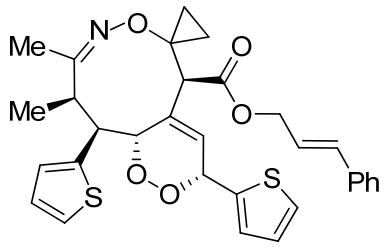
Oxazonine-fused endoperoxide 3fa, a light yellow solid, 0.106 g, 75% yield. Mp: 75–76 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (s, 1H), 7.27–7.18 (m, 8H), 7.12 (t, J = 7.6 Hz, 1H), 7.03 (s, 1H), 6.99 (t, J = 7.6 Hz, 1H), 6.85 (d, J = 7.6 Hz, 1H), 6.58 (d, J = 16.0 Hz, 1H), 6.15–6.07 (m, 1H), 5.80–5.71 (m, 1H), 5.58–5.53 (m, 1H), 5.37–5.32 (m, 1H), 4.73–4.59 (m, 2H), 3.93 (s, 1H), 3.20–3.18 (m, 1H), 2.61–2.56 (m, 1H), 1.90 (s, 3H), 1.46 (d, J = 7.2 Hz, 3H), 1.18–1.10 (m, 2H), 0.99–0.98 (m, 1H), 0.80–0.75 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9, 169.2, 144.9, 138.5, 135.7, 135.6, 132.2, 131.7, 130.6, 130.0, 129.6, 129.5, 128.6, 128.2, 127.7, 126.5, 126.4, 126.3, 124.1, 122.3, 122.0, 121.9, 78.9, 77.1, 65.6, 62.8, 50.0, 49.1, 46.2, 21.8, 12.2, 11.1, 9.2; IR (thin film) 3021, 2963, 1734, 1594, 1261, 1023, 803 cm^{-1}; HRMS (ESI) m/z calcd for $C_{35}H_{34}Br_2NO_5$ $[M + H]^+$: 706.0798, found: 706.0799.



3ga

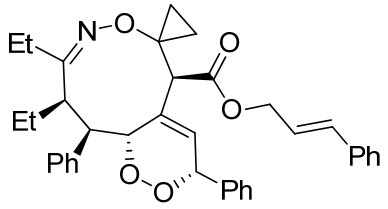
Oxazonine-fused endoperoxide 3ga, a light yellow solid, 0.073 g, 52% yield. Mp: 181–182 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 7.6 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.30 (d, J = 7.2 Hz, 1H), 7.20–7.18 (m, 6H), 7.01–6.91 (m, 4H), 6.55 (d, J = 16.0 Hz, 1H), 6.11–6.04 (m, 1H), 5.90–5.85 (m, 1H), 5.83–5.76 (m, 1H), 5.64–5.57 (m, 1H), 4.72–4.57 (m, 2H), 4.15–4.09 (m, 2H), 2.44–2.39 (m, 1H), 1.96 (s, 3H), 1.46 (d, J = 7.2 Hz, 3H), 1.26–1.11 (m, 2H), 0.98–0.94 (m, 1H), 0.82–0.78 (m, 1H); ^{13}C

NMR (100 MHz, $CDCl_3$): δ 171.8, 169.2, 142.2, 135.9, 135.6, 134.9, 132.5, 132.1, 131.0, 129.7, 129.4, 128.5, 128.4, 128.0, 127.9, 127.1, 127.0, 126.5, 126.4, 124.7, 123.4, 122.2, 78.3, 76.8, 65.2, 62.9, 49.0, 46.5, 46.3, 21.8, 11.7, 11.1, 9.4; IR (thin film) 3024, 2945, 1730, 1466, 1162, 1025, 747 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{35}H_{34}Br_2NO_5$ $[M + H]^+$: 706.0798, found: 706.0797.



3ha

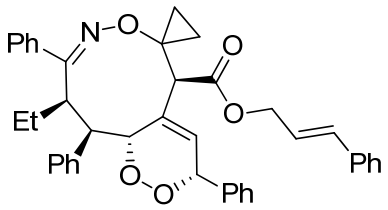
Oxazonine-fused endoperoxide 3ha, a light yellow solid, 0.064 g, 57% yield. Mp: 151–152 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.21–7.17 (m, 5H), 7.10–7.04 (m, 2H), 6.90–6.75 (m, 4H), 6.59 (d, *J* = 16.0 Hz, 1H), 6.17–6.10 (m, 1H), 5.72–5.70 (m, 3H), 4.76–4.58 (m, 2H), 3.92 (s, 1H), 3.70–3.69 (m, 1H), 2.73–2.68 (m, 1H), 1.89 (s, 3H), 1.42 (d, *J* = 7.2 Hz, 3H), 1.21–1.16 (m, 1H), 1.12–1.06 (m, 1H), 0.98–0.93 (m, 1H), 0.80–0.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 169.1, 143.8, 138.3, 135.8, 135.5, 135.4, 128.5, 128.1, 127.9, 126.7, 126.6, 126.4, 126.0, 125.9, 124.5, 123.7, 122.2, 77.6, 74.6, 65.5, 62.7, 48.9, 46.4, 46.0, 21.8, 12.3, 11.3, 9.4; IR (thin film) 3010, 2962, 1738, 1640, 1445, 1147, 1027, 692 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{31}H_{32}S_2NO_5$ $[M + H]^+$: 562.1716, found: 562.1716.



3ia

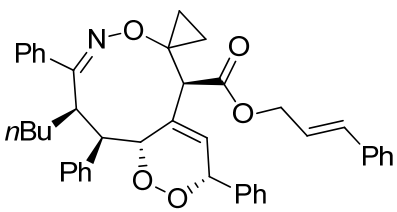
Oxazonine-fused endoperoxide 3ia, a light yellow solid, 0.076 g, 66% yield. Mp: 121–122 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.30–7.25 (m, 2H), 7.21–7.15 (m, 7H), 7.11–7.04 (m, 4H), 6.88 (d, *J* = 7.2 Hz, 2H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.11 (dt, *J* =

15.6 Hz, 6.8 Hz, 1H), 5.80–5.76 (m, 1H), 5.60–5.53 (m, 1H), 5.40–5.35 (m, 1H), 4.70–4.56 (m, 2H), 4.01 (s, 1H), 3.15–3.14 (m, 1H), 2.41–2.28 (m, 3H), 2.14–1.99 (m, 2H), 1.22–1.16 (m, 2H), 1.10 (t, J = 7.2 Hz, 3H), 0.97–0.91 (m, 1H), 0.87 (t, J = 7.2 Hz, 3H), 0.80–0.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.1, 169.3, 142.9, 136.5, 135.8, 135.4, 135.3, 129.3, 128.5, 128.4, 128.2, 128.1, 127.9, 127.8, 126.5, 126.4, 124.3, 122.2, 79.6, 77.5, 65.4, 62.6, 53.4, 51.2, 48.6, 30.8, 20.8, 13.2, 11.2, 11.1, 9.3; IR (thin film) 3028, 2970, 1737, 1599, 1453, 1154, 1023, 698 cm^{-1}; HRMS (ESI) m/z calcd for $C_{37}H_{40}NO_5$ $[M + H]^+$: 578.2901, found: 578.2901.



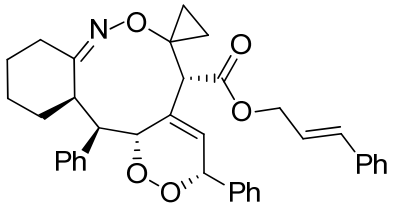
3ja

Oxazonine-fused endoperoxide 3ja, a light yellow solid, 0.084 g, 67% yield. Mp: 169–170 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 7.2 Hz, 2H), 7.35–7.34 (m, 2H), 7.26–7.01 (m, 14H), 6.86 (d, J = 6.8 Hz, 2H), 6.50 (d, J = 16.0 Hz, 1H), 6.04–5.97 (m, 1H), 5.90–5.86 (m, 1H), 5.58–5.54 (m, 1H), 5.39–5.35 (m, 1H), 4.65–4.50 (m, 2H), 4.09 (s, 1H), 3.42–3.41 (m, 1H), 3.09–3.06 (m, 1H), 2.48–2.40 (m, 1H), 2.14–2.09 (m, 1H), 1.28–1.17 (m, 2H), 1.04–1.01 (m, 1H), 0.82–0.81 (m, 1H), 0.78 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.0, 169.2, 143.0, 136.7, 136.4, 135.7, 135.3, 129.8, 129.3, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.8, 126.9, 126.5, 126.4, 126.3, 124.5, 122.0, 79.5, 77.6, 65.3, 63.4, 53.6, 51.6, 49.1, 21.3, 13.4, 11.1, 9.3; IR (thin film) 3027, 2951, 1735, 1493, 1155, 966, 694 cm^{-1}; HRMS (ESI) m/z calcd for $C_{41}H_{40}NO_5$ $[M + H]^+$: 626.2901, found: 626.2899.



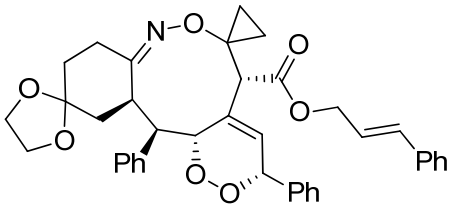
3ka

Oxazonine-fused endoperoxide 3ka, a light yellow solid, 0.097 g, 74% yield. Mp: 135–136 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 7.6 Hz, 2H), 7.35–7.19 (m, 8H), 7.17–7.03 (m, 8H), 6.88 (d, J = 7.2 Hz, 2H), 6.52 (d, J = 15.6 Hz, 1H), 6.07–5.99 (m, 1H), 5.95–5.89 (m, 1H), 5.60–5.55 (m, 1H), 5.40–5.35 (m, 1H), 4.67–4.52 (m, 2H), 4.10 (s, 1H), 3.41–3.40 (m, 1H), 3.15–3.13 (m, 1H), 2.45–2.38 (m, 1H), 2.10–2.04 (m, 1H), 1.23–1.16 (m, 4H), 1.05–1.00 (m, 2H), 0.82–0.79 (m, 2H), 0.72 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 169.2, 142.9, 136.6, 136.5, 135.7, 135.4, 129.8, 129.3, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 126.9, 126.6, 126.5, 124.5, 122.1, 79.6, 77.8, 65.4, 63.4, 51.8, 51.7, 49.2, 31.1, 28.1, 22.8, 13.7, 11.2, 9.4; IR (thin film) 3021, 2959, 1734, 1493, 1156, 694 cm^{-1}; HRMS (ESI) m/z calcd for $C_{43}H_{44}NO_5$ $[M + H]^+$: 654.3214, found: 654.3205.



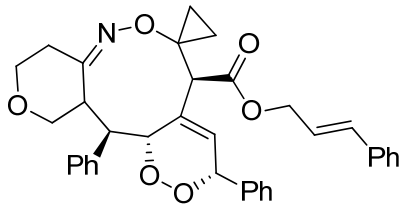
3la

Oxazonine-fused endoperoxide 3la, a light yellow oil, 0.037 g, 32% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.42 (m, 5H), 7.38–7.30 (m, 8H), 7.28–7.25 (m, 2H), 6.65 (d, J = 16.0 Hz, 1H), 6.50–6.47 (m, 1H), 6.26 (dt, J = 16.0 Hz, 6.0 Hz, 1H), 5.78–5.75 (m, 1H), 4.80–4.79 (m, 1H), 4.74 (d, J = 6.0 Hz, 2H), 4.34 (s, 1H), 3.92–3.85 (m, 2H), 2.22–2.18 (m, 1H), 1.92–1.90 (m, 2H), 1.78–1.75 (m, 1H), 1.59–1.57 (m, 2H), 1.28–1.20 (m, 2H), 1.15–1.10 (m, 2H), 0.86–0.82 (m, 2H); ^{13}C NMR (150MHz, $CDCl_3$): δ 176.6, 169.8, 142.8, 135.9, 135.4, 134.8, 134.3, 130.5, 129.5, 129.2, 128.9, 128.6, 128.5, 128.1, 128.0, 127.0, 126.6, 122.3, 87.9, 81.3, 65.5, 63.0, 60.6, 48.2, 37.3, 34.1, 31.5, 27.1, 22.0, 10.5, 10.4; IR (thin film) 3027, 2919, 1738, 1452, 1261, 1090, 697 cm^{-1}; HRMS (ESI) m/z calcd for $C_{37}H_{38}NO_5$ $[M + H]^+$: 576.2744, found: 576.2741.



3ma

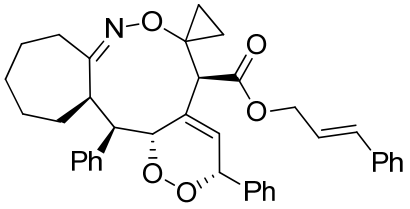
Oxazonine-fused endoperoxide 3ma, a light yellow oil, 0.062 g, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54–7.53 (m, 3H), 7.40–7.28 (m, 11H), 7.22–7.18 (m, 1H), 6.72 (d, J = 16.0 Hz, 1H), 6.34 (dt, J = 16.0 Hz, 6.0 Hz, 1H), 6.15–6.10 (m, 1H), 5.84–5.80 (m, 1H), 4.96–4.95 (m, 1H), 4.86–4.75 (m, 2H), 3.98–3.74 (m, 6H), 3.35 (s, 1H), 2.42–2.37 (m, 1H), 2.22–2.17 (m, 1H), 1.76–1.68 (m, 4H), 1.42–1.37 (m, 2H), 1.16–1.10 (m, 1H), 0.77–0.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.1, 171.3, 141.9, 136.1, 135.5, 134.1, 133.8, 129.9, 129.7, 129.6, 129.5, 128.8, 128.6, 128.2, 128.1, 126.6, 126.5, 122.9, 108.2, 86.8, 81.4, 65.8, 64.4, 64.3, 62.1, 57.0, 52.5, 39.9, 38.9, 33.7, 29.6, 13.0, 11.3; IR (thin film) 3023, 2930, 1731, 1457, 1263, 1091, 698 cm^{-1}; HRMS (ESI) m/z calcd for $C_{39}H_{40}NO_7$ $[M + H]^+$: 634.2799, found: 634.2787.



3na

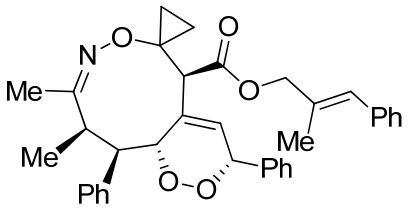
Oxazonine-fused endoperoxide 3na, a light yellow solid, 0.059 g, 51% yield. Mp: 165–166 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.35 (m, 5H), 7.31–7.22 (m, 10H), 6.67 (d, J = 16.0 Hz, 1H), 6.26 (dt, J = 16.0 Hz, 6.4 Hz, 1H), 5.83–5.78 (m, 2H), 5.20–5.18 (m, 1H), 4.77–4.69 (m, 2H), 4.06–4.02 (m, 2H), 3.88–3.83 (m, 1H), 3.74–3.72 (m, 1H), 3.50–3.43 (m, 1H), 3.27 (d, J = 7.2 Hz, 1H), 3.08–3.04 (m, 1H), 2.66–2.63 (m, 2H), 1.25–1.20 (m, 2H), 1.06–1.02 (m, 1H), 0.67–0.63 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 169.8, 140.9, 135.8, 135.6, 135.4, 134.9, 129.5, 129.4, 128.9, 128.6, 128.5, 128.4, 128.3, 126.9, 126.8, 126.6, 122.0, 85.3, 81.0, 71.4, 66.6, 65.7, 61.3, 52.0, 50.7, 43.7, 32.1, 10.0, 9.9; IR (thin film) 3025, 2963, 1735,

1618, 1260, 1018, 703 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{36}H_{36}NO_6$ $[M + H]^+$: 578.2537, found: 578.2536.



3oa

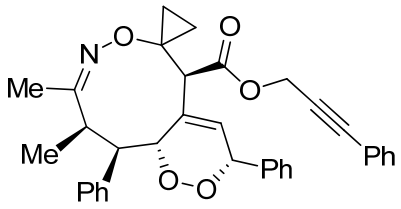
Oxazonine-fused endoperoxide 3oa, a light yellow solid, 0.053 g, 45% yield. Mp: 113–114 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.36–7.22 (m, 14H), 7.19 (d, J = 7.2 Hz, 1H), 6.71 (d, J = 15.6 Hz, 1H), 6.30–6.23 (m, 1H), 5.95–5.88 (m, 1H), 5.69–5.67 (m, 1H), 5.65–5.63 (m, 1H), 4.82 (d, J = 6.4 Hz, 2H), 3.76–3.74 (m, 1H), 3.53 (s, 1H), 3.45–3.43 (m, 1H), 2.29–2.26 (m, 1H), 1.98–1.60 (m, 7H), 1.35–1.14 (m, 5H), 0.74–0.71 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.9, 170.5, 141.1, 136.1, 136.0, 135.9, 134.5, 129.7, 129.1, 128.6, 128.5, 128.4, 128.2, 128.0, 127.9, 126.6, 126.5, 122.6, 82.2, 81.0, 65.5, 64.1, 56.1, 54.6, 45.8, 32.8, 31.1, 29.6, 28.7, 28.1, 10.9, 9.3; IR (thin film) 3028, 2930, 1733, 1494, 1148, 1022, 696 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{38}H_{40}NO_5$ $[M + H]^+$: 590.2901, found: 590.2901.



3ab

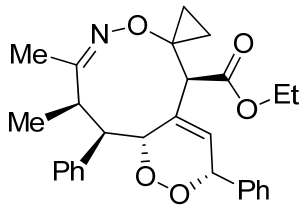
Oxazonine-fused endoperoxide 3ab, a light yellow solid, 0.077 g, 69% yield. Mp: 138–139 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 7.6 Hz, 2H), 7.32–7.14 (m, 11H), 7.00 (d, J = 7.2 Hz, 2H), 6.51 (s, 1H), 5.87–5.83 (m, 1H), 5.68–5.63 (m, 1H), 5.51–5.46 (m, 1H), 4.70 (d, J = 12.0 Hz, 1H), 4.57 (d, J = 12.0 Hz, 1H), 4.02 (s, 1H), 3.39–3.38 (m, 1H), 2.79–2.74 (m, 1H), 1.94 (s, 3H), 1.76 (s, 3H), 1.51 (d, J = 7.2 Hz, 3H), 1.30–1.25 (m, 1H), 1.19–1.15 (m, 1H), 1.10–1.06 (m, 1H), 0.85–0.81 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4, 169.5, 142.8, 136.6, 136.4, 135.5, 131.9, 129.6,

129.3, 128.8, 128.5, 128.2, 128.1, 127.9, 127.8, 126.8, 126.4, 125.0, 79.8, 77.6, 70.8, 62.8, 50.9, 49.8, 45.9, 21.6, 15.6, 12.5, 11.1, 9.3; IR (thin film) 3023, 2965, 1736, 1492, 1148, 1026, 699 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{36}H_{38}NO_5$ $[M + H]^+$: 564.2744, found: 564.2738.



3ac

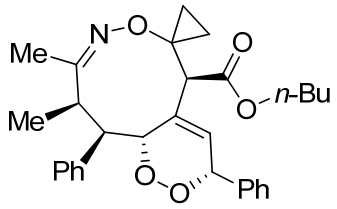
Oxazonine-fused endoperoxide 3ac, a light yellow solid, 0.084 g, 77% yield. Mp: 150–151 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 7.6 Hz, 2H), 7.30–7.24 (m, 7H), 7.18–7.13 (m, 4H), 7.00 (d, J = 6.4 Hz, 2H), 5.86–5.83 (m, 1H), 5.75–5.72 (m, 1H), 5.50–5.47 (m, 1H), 4.93–4.83 (m, 2H), 4.11 (s, 1H), 3.36–3.35 (m, 1H), 2.75–2.70 (m, 1H), 1.96 (s, 3H), 1.52 (d, J = 7.2 Hz, 3H), 1.26–1.16 (m, 2H), 1.09–1.04 (m, 1H), 0.89–0.85 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4, 168.9, 142.8, 136.3, 135.2, 131.7, 129.3, 128.7, 128.5, 128.3, 128.2, 127.9, 127.8, 126.4, 124.8, 121.7, 86.8, 82.1, 79.8, 77.3, 62.7, 53.0, 50.8, 48.9, 46.1, 21.7, 12.2, 11.2, 9.3; IR (thin film) 3021, 2954, 2217, 1735, 1490, 1145, 1026, 693 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{35}H_{34}NO_5$ $[M + H]^+$: 548.2431, found: 548.2432.



3ad

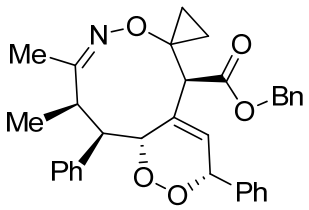
Oxazonine-fused endoperoxide 3ad, a light yellow solid, 0.070 g, 76% yield. Mp: 133–134 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 7.2 Hz, 2H), 7.29–7.16 (m, 6H), 7.03–7.02 (m, 2H), 5.85–5.80 (m, 1H), 5.65–5.62 (m, 1H), 5.54–5.48 (m, 1H), 4.14 (q, J = 6.8 Hz, 2H), 3.97 (s, 1H), 3.36–3.35 (m, 1H), 2.78–2.72 (m, 1H), 1.95 (s, 3H), 1.51 (d, J = 6.8 Hz, 3H), 1.28–1.25 (m, 1H), 1.23 (t, J = 7.2 Hz, 3H), 1.18–1.13

(m, 1H), 1.07–1.02 (m, 1H), 0.82–0.76 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4, 169.6, 142.9, 136.5, 135.4, 129.3, 128.5, 128.2, 127.9, 127.8, 126.4, 124.8, 79.8, 77.6, 62.8, 60.8, 50.8, 49.5, 45.9, 21.6, 14.0, 12.4, 11.2, 9.3; IR (thin film) 3023, 2968, 1725, 1651, 1452, 1248, 1035, 697 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{28}H_{32}NO_5$ $[M + H]^+$: 462.2275, found: 462.2272.



3ae

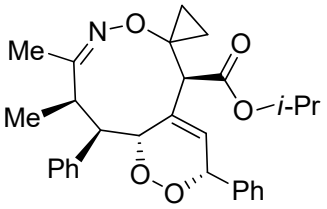
Oxazonine-fused endoperoxide, a light yellow solid, 0.059 g, 60% yield. Mp: 120–121 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 7.6 Hz, 2H), 7.29–7.16 (m, 6H), 7.02–7.01 (m, 2H), 5.85–5.80 (m, 1H), 5.63–5.60 (m, 1H), 5.50–5.47 (m, 1H), 4.12–3.99 (m, 2H), 3.96 (s, 1H), 3.37–3.36 (m, 1H), 2.79–2.73 (m, 1H), 1.95 (s, 3H), 1.60–1.54 (m, 3H), 1.51 (d, J = 7.2 Hz, 3H), 1.32–1.23 (m, 4H), 1.19–1.04 (m, 2H), 0.86 (t, J = 7.6 Hz, 3H), 0.80–0.76 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4, 169.7, 142.9, 136.5, 135.5, 129.3, 128.5, 128.2, 128.0, 127.9, 126.4, 124.9, 79.8, 77.6, 64.7, 62.8, 50.9, 49.8, 45.9, 30.4, 21.6, 19.0, 13.5, 12.5, 11.1, 9.3; IR (thin film) 3024, 2955, 1732, 1637, 1261, 1083, 698 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{30}H_{36}NO_5$ $[M + H]^+$: 490.2588, found: 490.2590.



3af

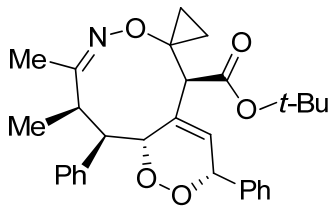
Oxazonine-fused endoperoxide 3af, a light yellow solid, 0.073 g, 70% yield. Mp: 88–89 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, J = 7.6 Hz, 2H), 7.27–7.16 (m, 11H), 6.98 (d, J = 6.8 Hz, 2H), 5.84–5.80 (m, 1H), 5.55–5.53 (m, 1H), 5.46–5.42 (m, 1H), 5.13 (d, J = 12.0 Hz, 1H), 5.03 (d, J = 12.0 Hz, 1H), 4.02 (s, 1H), 3.34–3.33 (m,

1H), 2.74–2.69 (m, 1H), 1.92 (s, 3H), 1.49 (d, J = 7.2 Hz, 3H), 1.27–1.15 (m, 1H), 1.13–1.10 (m, 1H), 1.06–1.01 (m, 1H), 0.80–0.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 169.5, 142.8, 136.4, 135.4, 135.0, 129.3, 128.6, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 126.4, 124.8, 79.7, 77.4, 66.7, 62.7, 50.8, 49.3, 45.9, 21.6, 12.3, 11.1, 9.3; IR (thin film) 3032, 2955, 1733, 1493, 1149, 1000, 699 cm^{-1}; HRMS (ESI) m/z calcd for $C_{33}H_{34}NO_5$ $[M + H]^+$: 524.2431, found: 524.2429.



3ag

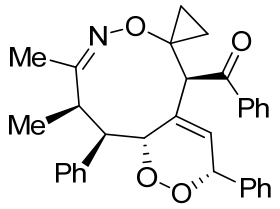
Oxazonine-fused endoperoxide 3ag, a light yellow solid, 0.061 g, 64% yield. Mp: 139–140 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 7.2 Hz, 2H), 7.28–7.15 (m, 6H), 7.03–7.02 (m, 2H), 5.85–5.80 (m, 1H), 5.65–5.63 (m, 1H), 5.53–5.48 (m, 1H), 5.01–4.95 (m, 1H), 3.92 (s, 1H), 3.37–3.36 (m, 1H), 2.78–2.73 (m, 1H), 1.95 (s, 3H), 1.51 (d, J = 7.2 Hz, 3H), 1.25 (d, J = 6.4 Hz, 3H), 1.23–1.24 (m, 1H), 1.17–1.16 (m, 1H), 1.13 (d, J = 6.4 Hz, 3H), 1.05–1.01 (m, 1H), 0.85–0.82 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 169.1, 142.9, 136.5, 135.7, 129.3, 128.5, 128.2, 127.9, 127.8, 126.4, 124.8, 79.8, 77.6, 68.4, 62.7, 50.8, 49.5, 45.9, 21.8, 21.7, 21.6, 12.4, 11.0, 9.3; IR (thin film) 3025, 2916, 1724, 1493, 1166, 1095, 699 cm^{-1}; HRMS (ESI) m/z calcd for $C_{29}H_{34}NO_5$ $[M + H]^+$: 476.2431, found: 476.2432.



3ah

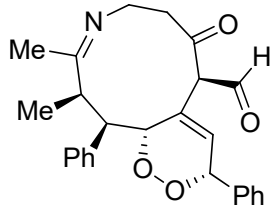
Oxazonine-fused endoperoxide 3ah, a light yellow solid, 0.055 g, 56% yield. Mp: 134–135 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 7.6 Hz, 2H), 7.28–7.15 (m, 6H), 7.04–7.03 (m, 2H), 5.83–5.78 (m, 1H), 5.70–5.68 (m, 1H), 5.52–5.50 (m, 1H), 3.82 (s, 1H), 3.36–3.35 (m, 1H), 2.79–2.73 (m, 1H), 1.94 (s, 3H), 1.50 (d, J = 7.2 Hz,

3H), 1.40 (s, 9H), 1.29–1.21 (m, 1H), 1.18–1.12 (m, 1H), 1.06–1.00 (m, 1H), 0.88–0.83 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 168.9, 142.9, 136.5, 136.1, 129.3, 128.5, 128.2, 127.9, 127.4, 126.3, 124.6, 81.7, 79.7, 77.7, 62.8, 50.8, 50.2, 45.8, 27.9, 21.6, 12.5, 10.9, 9.3; IR (thin film) 3022, 2968, 1725, 1491, 1142, 1072, 700 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{30}H_{36}NO_5$ $[M + H]^+$: 490.2588, found: 490.2587.



3ai

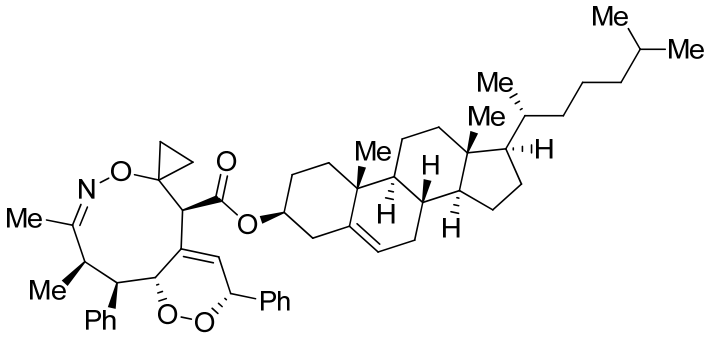
Oxazonine-fused endoperoxide 3ai, a light yellow oil, 0.073 g, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 7.6 Hz, 2H), 7.60 (t, J = 7.2 Hz, 1H), 7.51–7.47 (m, 2H), 7.38 (d, J = 7.6 Hz, 2H), 7.30–7.25 (m, 2H), 7.20–7.17 (m, 1H), 7.15–7.07 (m, 3H), 6.86 (d, J = 7.2 Hz, 2H), 5.95–5.91 (m, 1H), 5.64–5.60 (m, 1H), 5.50–5.45 (m, 1H), 5.11 (s, 1H), 3.44–3.43 (m, 1H), 2.77–2.72 (m, 1H), 2.05 (s, 3H), 1.61 (d, J = 7.2 Hz, 3H), 1.25–1.23 (m, 1H), 1.15–1.03 (m, 2H), 0.82–0.79 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2, 172.3, 142.8, 138.3, 136.5, 135.9, 133.3, 129.2, 128.8, 128.3, 128.2, 128.1, 127.9, 127.8, 126.5, 125.7, 79.8, 77.3, 63.0, 50.8, 47.0, 46.7, 22.0, 12.1, 11.4, 9.1; IR (thin film) 3022, 2963, 1683, 1449, 1251, 1019, 697 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{32}H_{32}NO_4$ $[M + H]^+$: 494.2326, found: 494.2341.



3aj

Oxazecine-fused endoperoxide 3aj, a light yellow oil, 0.033 g, 39% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.88 (s, 1H), 7.36–7.32 (m, 3H), 7.30–7.25 (m, 5H), 7.24–7.18 (m, 2H), 5.81–5.76 (m, 1H), 5.54–5.51 (m, 2H), 3.20–3.11 (m, 2H), 2.96–2.91 (m, 2H), 2.90–2.84 (m, 2H), 2.46–2.42 (m, 1H), 1.83 (s, 3H), 0.92 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.1, 200.0, 140.0, 139.1, 138.3, 133.3, 132.7, 128.4,

128.3, 128.2, 128.1, 126.7, 119.0, 80.7, 73.2, 46.4, 42.6, 36.9, 36.8, 36.0, 19.1, 14.1; IR (thin film) 3023, 2963, 2825, 2720, 1710, 1699, 1452, 1261, 698 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{26}H_{28}NO_4$ $[M + H]^+$: 418.2013, found: 418.1991.

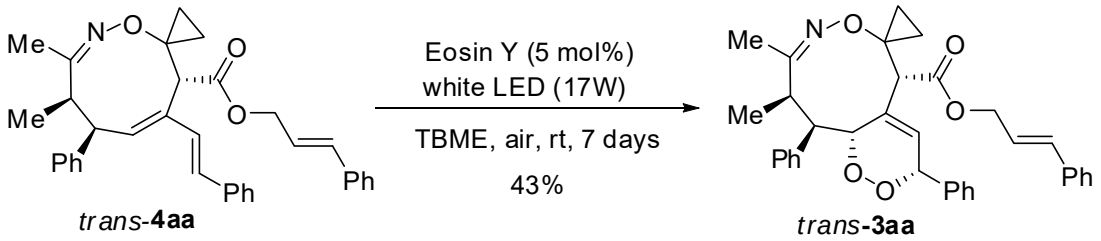


3ak (*dr* = 1:1)

Oxazonine-fused endoperoxide 3ak, *dr* = 1:1, a light yellow oil, 0.077 g, 48% yield. *one isomer*: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.28–7.18 (m, 7H), 7.03–7.02 (m, 2H), 5.85–5.80 (m, 1H), 5.65–5.62 (m, 1H), 5.54–5.48 (m, 1H), 4.58–4.57 (m, 1H), 3.93 (s, 1H), 3.36–3.35 (m, 1H), 2.76–2.74 (m, 1H), 2.32–2.25 (m, 3H), 2.10–2.00 (m, 2H), 1.96 (s, 3H), 1.86–1.78 (m, 3H), 1.65–1.54 (m, 6H), 1.51 (d, *J* = 7.2 Hz, 3H), 1.45–1.39 (m, 4H), 1.37–1.20 (m, 7H), 1.14–1.02 (m, 7H), 0.99 (s, 3H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.86 (d, *J* = 6.0 Hz, 6H), 0.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 169.0, 142.9, 139.2, 136.5, 135.6, 129.3, 128.6, 128.2, 127.9, 127.8, 126.4, 124.9, 122.9, 79.8, 77.7, 74.7, 62.8, 56.6, 56.1, 50.8, 49.9, 49.5, 46.0, 42.2, 39.6, 39.5, 37.9, 36.8, 36.5, 36.1, 35.7, 31.9, 31.8, 28.2, 28.0, 27.7, 24.2, 23.8, 22.8, 21.7, 20.9, 19.2, 18.6, 12.5, 11.8, 11.1, 9.4; *another isomer*: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.28–7.18 (m, 7H), 7.03–7.02 (m, 2H), 5.85–5.80 (m, 1H), 5.65–5.62 (m, 1H), 5.54–5.48 (m, 1H), 4.58–4.57 (m, 1H), 3.93 (s, 1H), 3.36–3.35 (m, 1H), 2.76–2.74 (m, 1H), 2.32–2.25 (m, 3H), 2.10–2.00 (m, 2H), 1.96 (s, 3H), 1.86–1.78 (m, 3H), 1.65–1.54 (m, 6H), 1.51 (d, *J* = 7.2 Hz, 3H), 1.45–1.39 (m, 4H), 1.37–1.20 (m, 7H), 1.14–1.02 (m, 7H), 0.99 (s, 3H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.86 (d, *J* = 6.0 Hz, 6H), 0.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 169.0, 142.9, 139.2, 136.5, 135.6, 129.3, 128.6, 128.2, 127.9, 127.8, 126.4, 124.9, 122.8, 79.8, 77.7, 74.7, 62.8, 56.6, 56.1, 50.8, 49.9, 49.5, 45.9, 42.2, 39.6, 39.5, 37.8, 36.8, 36.5, 36.1, 35.7, 31.9, 31.8, 28.2, 28.0, 27.5, 24.2, 23.8, 22.5, 21.7, 20.9, 19.2, 18.6,

12.4, 11.8, 11.1, 9.4; IR (thin film) 3021, 2959, 1732, 1454, 1261, 1026, 698 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{53}H_{72}NO_5$ $[M + H]^+$: 802.5405, found: 802.5410.

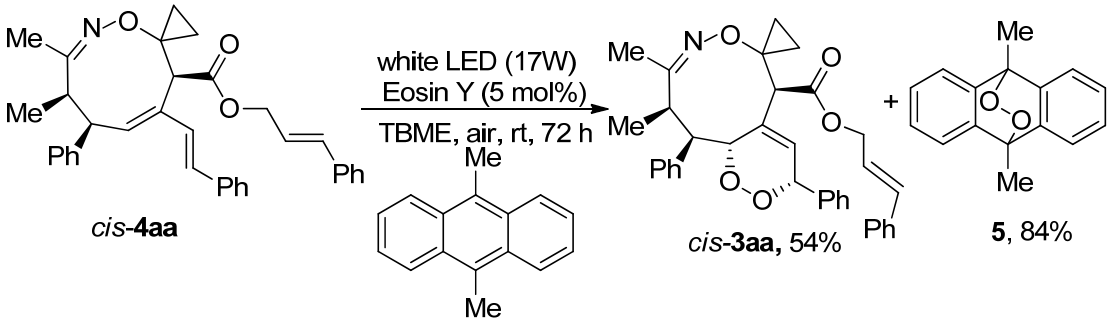
3. Synthesis of compound *trans*-3aa



trans-**4aa** *trans*-**3aa**

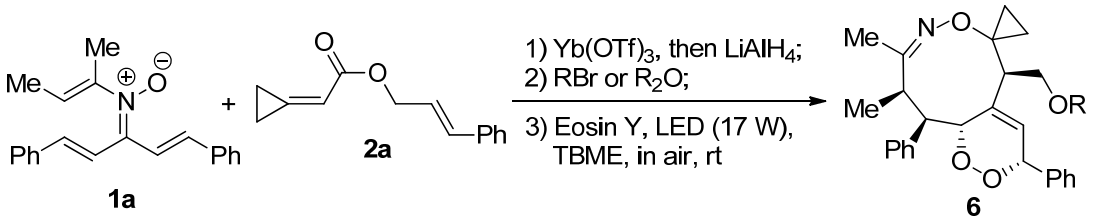
An oven-dried glass vial equipped with a magnetic stirrer was charged with the *trans*-**4aa** (0.2 mmol, 0.103 g), Eosin Y (5 mol%, 0.01 mmol, 0.006 g) and TBME (2 mL). The vial was closed with a plastic wrap. Afterwards, the reaction mixture was stirred and irradiated (17 W white LED) at room temperature for 7 days until *trans*-**4aa** was consumed completely (monitored by TLC). At this time, the solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (the crude residue was dry loaded with silica gel, 1/20, ethyl acetate/petroleum ether) to provide compound *trans*-**3aa** as a light yellow oil (0.047 g, 43%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.40–7.25 (m, 15H), 6.67 (d, J = 16.0 Hz, 1H), 6.52–6.50 (m, 1H), 6.28–6.21 (m, 1H), 5.75–5.74 (m, 1H), 5.03–5.01 (m, 1H), 4.76 (d, J = 6.0 Hz, 2H), 4.39 (s, 1H), 3.88–3.87 (m, 1H), 3.77–3.76 (m, 1H), 1.29 (s, 3H), 1.22–1.18 (m, 1H), 1.17 (d, J = 7.2 Hz, 3H), 1.12–1.08 (m, 1H), 0.88–0.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.5, 169.7, 140.7, 136.0, 135.6, 135.2, 134.4, 130.0, 129.4, 129.1, 128.8, 128.6, 128.5, 128.1, 127.8, 127.0, 126.6, 122.3, 85.7, 81.1, 65.5, 63.2, 59.1, 48.2, 35.7, 18.0, 17.3, 10.6, 10.1; IR (thin film) 3021, 2964, 1734, 1643, 1451, 1148, 1001, 697 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{35}H_{36}NO_5$ $[M + H]^+$: 550.2588, found: 550.2601.

4. Trapping experiment of *cis*-4aa to *cis*-3aa



An oven-dried glass vial equipped with a magnetic stirrer was charged with the *cis*-**4aa** (0.2 mmol, 0.103 g), 9,10-dimethylanthracene (2 equiv., 0.082 g), Eosin Y (5 mol%, 0.01 mmol, 0.006 g) and TBME (2 mL). The vial was closed with a plastic wrap. Afterwards, the reaction mixture was stirred and irradiated (17 W white LED) at room temperature for 72 h. At this time, the solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (the crude residue was dry loaded with silica gel, 1/30-1/20, ethyl acetate/petroleum ether) to provide compound *cis*-**3aa** (0.059 g, 54%) and compound **5** as a white solid (0.084 g, 84%). Compound **5**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.36 (m, 4H), 7.26–7.24 (m, 4H), 2.12 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 127.3, 120.6, 79.4, 13.6. The spectral data matched literature values.[4]

5. Synthesis of compounds 6

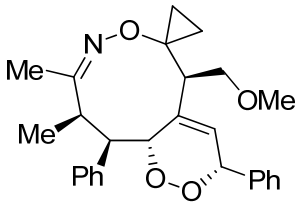


General procedure B: In a 25 mL round-bottom flask was charged with *N*-vinyl nitrone **1a** (0.2 mmol, 0.061 g), $Yb(OTf)_3$ (20 mol%, 0.04 mmol, 0.025 g) and TBME (2.0 mL) under an air atmosphere. And then, methylenecyclopropane **2a** (0.4 mmol, 2.0 equiv., 0.086 g) was added in one portion at room temperature. The mixture was stirred vigorously at room temperature for 36−48 h until nitrone **1a** was consumed completely (monitored by TLC). At this time, $LiAlH_4$ (0.4 mmol, 2.0 equiv. 0.030 g)

was added at 0 °C. Then, the reaction mixture was stirred vigorously at 0 °C for 0.5 h until substrate disappeared (monitored by TLC). At this time, the reaction was quenched with H_2O (10 mL) and exacted with Et_2O (20 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and filtered. The solvents were removed under the reduced pressure. The crude product was used directly in the next step.

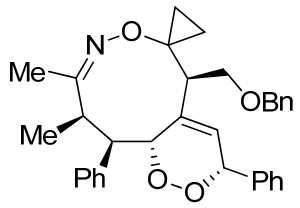
In a round-bottom flask was charged with the above alcohol and MeCN (2 mL). NaH (60% in mineral oil, 5 equiv., 1.0 mmol, 0.040 g) was added at 0 ℃ and allowed to stir for 30 min at 0 ℃, After adding MeI or RBr (5 equiv. 1 mmol), the solution was then allowed to stir at room temperature for 3-12 h minutes until the substrate disappeared (monitored by TLC). At this time, the reaction was quenched with H_2O (10 mL) and exacted with Et_2O (20 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and filtered. The solvents were removed under the reduced pressure and the crude product was used directly in the next step. [*Alternative method*: to a solution of the above alcohol in CH_2Cl_2 (2 mL) were added Et_3N (2.0 equiv., 0.4 mmol), 4-DMAP (1.0 equiv, 0.2 mmol) and anhydride R_2O (5 equiv, 1 mmol) at rt. The reaction mixture was stirred for 12-24 h until the mixture was consumed completely (monitored by TLC). At this time, the reaction was quenched with H_2O (10 mL) and exacted with CH_2Cl_2 (20 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and filtered. The solvents were removed under the reduced pressure and the crude product was used directly in the next step.]

An oven-dried glass vial equipped with a magnetic stirrer was charged with the above crude mixture, Eosin Y (5 mol%, 0.01 mmol, 0.006 g) and TBME (2 mL). The vial was closed with a plastic film. Then, the reaction mixture was stirred and irradiated (17 W white LED) at room temperature for 36−72 h until the mixture was consumed completely (monitored by TLC). At this time, the solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (the crude residue was dry loaded with silica gel, 1/20 to 1/10, ethyl acetate/petroleum ether) to provide compounds **6**.



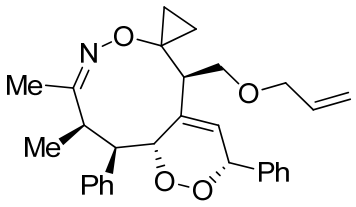
6aa

Oxazonine-fused endoperoxide 6aa, a light yellow solid, 0.056 g, 65% yield. Mp: 162–163 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, J = 7.2 Hz, 2H), 7.20–7.17 (m, 5H), 7.11–7.08 (m, 1H), 7.04–7.03 (m, 2H), 5.69–5.65 (m, 1H), 5.58–5.54 (m, 1H), 5.48–5.46 (m, 1H), 3.58 (dd, J = 9.6 Hz, 6.4 Hz, 1H), 3.40–3.38 (m, 2H), 3.19 (s, 3H), 2.98–2.97 (m, 1H), 2.86–2.84 (m, 1H), 1.79 (s, 3H), 1.36 (d, J = 7.2 Hz, 3H), 1.09–1.03 (m, 1H), 0.97–0.92 (m, 1H), 0.87–0.82 (m, 1H), 0.75–0.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.6, 142.6, 137.9, 136.9, 129.4, 128.5, 128.2, 128.1, 127.8, 126.4, 123.9, 80.2, 78.5, 71.2, 64.6, 58.7, 51.6, 43.9, 43.6, 20.9, 13.4, 11.4, 9.5; IR (thin film) 3023, 2935, 1732, 1601, 1452, 1116, 1019, 698 cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{32}NO_4$ $[M + H]^+$: 434.2326, found: 434.2327.



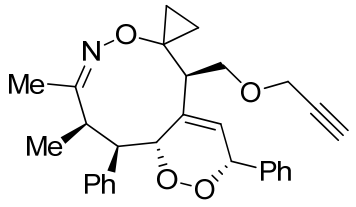
6ab

Oxazonine-fused endoperoxide 6ab, a light yellow oil, 0.066 g, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.25 (m, 12H), 7.18–7.15 (m, 1H), 7.12–7.10 (m, 2H), 5.81–5.78 (m, 1H), 5.58–5.55 (m, 2H), 4.49 (d, J = 12.0 Hz, 1H), 4.40 (d, J = 12.0 Hz, 1H), 3.72–3.60 (m, 2H), 3.48–3.47 (m, 1H), 3.08–3.06 (m, 1H), 2.97–2.92 (m, 1H), 1.83 (s, 3H), 1.40 (d, J = 7.2 Hz, 3H), 1.12–1.00 (m, 2H), 0.92–0.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.7, 142.6, 137.7, 137.5, 136.9, 129.4, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.6, 126.3, 124.5, 80.3, 78.5, 73.3, 68.8, 64.8, 51.7, 44.0, 43.6, 20.8, 13.5, 11.3, 9.7; IR (thin film) 3029, 2912, 1454, 1255, 1018, 698 cm^{-1}; HRMS (ESI) m/z calcd for $C_{33}H_{36}NO_4$ $[M + H]^+$: 510.2639, found: 510.2655.



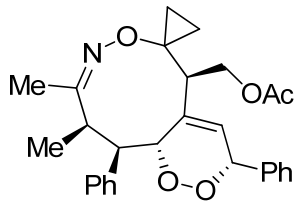
6ac

Oxazonine-fused endoperoxide 6ac, a light yellow solid, 0.062 g, 68% yield. Mp: 121–122 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.24 (m, 7H), 7.19–7.12 (m, 3H), 5.89–5.79 (m, 2H), 5.63–5.62 (m, 1H), 5.56–5.54 (m, 1H), 5.25 (d, J = 17.2 Hz, 1H), 5.17 (d, J = 10.0 Hz, 1H), 3.96–3.85 (m, 2H), 3.71–3.55 (m, 2H), 3.50–3.49 (m, 1H), 3.09–3.08 (m, 1H), 2.95–2.90 (m, 1H), 1.86 (s, 3H), 1.43 (d, J = 7.2 Hz, 3H), 1.14–1.10 (m, 1H), 1.06–1.01 (m, 1H), 0.95–0.90 (m, 1H), 0.84–0.79 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.7, 142.6, 137.8, 136.9, 134.2, 129.5, 128.5, 128.3, 128.2, 127.8, 126.4, 124.3, 117.3, 80.3, 78.6, 72.1, 68.8, 64.7, 51.7, 44.1, 43.7, 20.9, 13.6, 11.3, 9.5; IR (thin film) 3024, 2901, 1600, 1453, 1106, 1015, 704 cm^{-1}; HRMS (ESI) m/z calcd for $C_{29}H_{34}NO_4$ $[M + H]^+$: 460.2482, found: 460.2496.



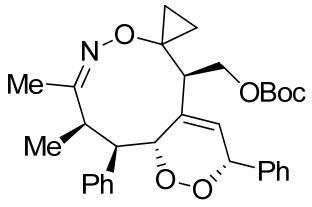
6ad

Oxazonine-fused endoperoxide 6ad, a light yellow solid, 0.056 g, 61% yield. Mp: 124–125 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, J = 7.2 Hz, 2H), 7.28–7.24 (m, 5H), 7.20–7.16 (m, 1H), 7.12–7.11 (m, 2H), 5.83–5.80 (m, 1H), 5.65–5.64 (m, 1H), 5.57–5.54 (m, 1H), 4.09 (s, 2H), 3.85–3.81 (m, 1H), 3.67–3.64 (m, 1H), 3.48–3.47 (m, 1H), 3.07–3.05 (m, 1H), 2.97–2.95 (m, 1H), 2.36 (s, 1H), 1.88 (s, 3H), 1.44 (d, J = 7.2 Hz, 3H), 1.14–1.12 (m, 1H), 1.04–1.01 (m, 2H), 0.84–0.81 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.6, 142.6, 137.6, 136.9, 129.5, 128.5, 128.2, 128.1, 127.8, 126.4, 124.3, 80.2, 79.1, 78.4, 74.9, 68.3, 64.7, 58.1, 51.6, 43.8, 43.4, 21.0, 13.4, 11.3, 9.6; IR (thin film) 3451, 3032, 2865, 2110, 1634, 1453, 1254, 1055, 700 cm^{-1}; HRMS (ESI) m/z calcd for $C_{29}H_{32}NO_4$ $[M + H]^+$: 458.2326, found: 458.2337.



6ae

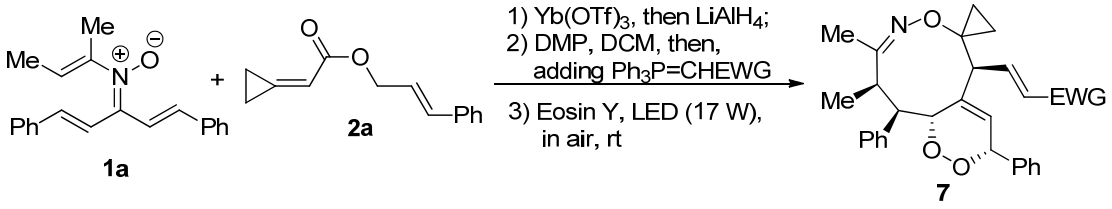
Oxazonine-fused endoperoxide 6ae, a light yellow solid, 0.074 g, 80% yield. Mp: 147–148 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, J = 7.2 Hz, 2H), 7.28–7.24 (m, 5H), 7.19–7.15 (m, 1H), 7.12–7.11 (m, 2H), 5.70–5.67 (m, 1H), 5.58–5.57 (m, 1H), 5.54–5.50 (m, 1H), 4.42–4.37 (m, 1H), 4.21–4.18 (m, 1H), 3.51–3.50 (m, 1H), 3.11–3.09 (m, 1H), 2.98–2.95 (m, 1H), 2.00 (s, 3H), 1.86 (s, 3H), 1.42 (d, J = 7.2 Hz, 3H), 1.18–1.08 (m, 2H), 0.86–0.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 170.6, 142.5, 137.1, 136.4, 129.4, 128.7, 128.3, 128.1, 127.8, 126.4, 125.0, 80.2, 78.6, 64.2, 63.0, 51.8, 44.0, 43.6, 20.8, 20.7, 13.8, 11.0, 8.8; IR (thin film) 3032, 2883, 1736, 1456, 1230, 1026, 698 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{32}NO_5$ $[M + H]^+$: 462.2275, found: 462.2284.



6af

Oxazonine-fused endoperoxide 6af, a light yellow solid, 0.065 g, 63% yield. Mp: 163–164 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, J = 7.6 Hz, 2H), 7.27–7.24 (m, 5H), 7.19–7.15 (m, 1H), 7.13–7.12 (m, 2H), 5.76–5.73 (m, 1H), 5.54–5.52 (m, 2H), 4.51 (dd, J = 11.2 Hz, 8.4 Hz, 1H), 4.18 (dd, J = 11.6 Hz, 4.4 Hz, 1H), 3.54–3.53 (m, 1H), 3.16–3.15 (m, 1H), 2.94–2.92 (m, 1H), 1.84 (s, 3H), 1.43 (s, 9H), 1.41 (d, J = 7.2 Hz, 3H), 1.14–1.12 (m, 2H), 0.85–0.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 153.2, 142.5, 136.9, 136.5, 129.5, 128.7, 128.3, 128.2, 127.8, 126.4, 125.4, 82.2, 80.3, 78.7, 65.5, 64.4, 52.1, 45.0, 43.2, 27.6, 20.5, 14.1, 11.1, 8.8; IR (thin film) 3011, 2922, 1737, 1454, 1279, 996, 759, 698 cm^{-1}; HRMS (ESI) m/z calcd for $C_{31}H_{38}NO_6$ $[M + H]^+$: 520.2694, found: 520.2713.

6. Synthesis of compounds 7

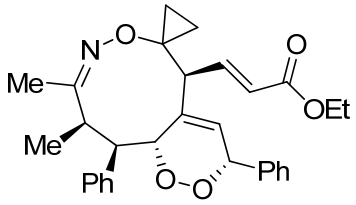


General procedure C: In a 25 mL round-bottom flask was charged with *N*-vinyl nitrone **1a** (0.2 mmol, 0.061 g), $Yb(OTf)_3$ (20 mol%, 0.04 mmol, 0.025 g) and TBME (2.0 mL) under an air atmosphere. And then, methylenecyclopropane **2a** (0.4 mmol, 2.0 equiv., 0.086 g) was added in one portion at room temperature. The mixture was stirred vigorously at room temperature for 36−48 h until nitrone **1a** was consumed completely (monitored by TLC). At this time, $LiAlH_4$ (0.4 mmol, 2.0 equiv. 0.030 g) was added at 0 °C. Then, the reaction mixture was stirred vigorously at 0 °C for 0.5 h until substrate disappeared (monitored by TLC). At this time, the reaction was quenched with H_2O (10 mL) and exacted with Et_2O (20 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and filtered. The solvents were removed under the reduced pressure. The crude product was used directly in the next step.

In a round-bottom flask was charged with the above alcohol and CH_2Cl_2 (2 mL). Dess-Martin Periodinane (DMP) (2.5 equiv., 0.5 mmol, 0.212 g) was added at room temperature. The resulting mixture was stirred at room temperature for 2 h until the substrate disappeared (monitored by TLC). Then Ph_3P=CHEWG (2 equiv., 0.4 mmol) was added at room temperature. The resulting mixture was stirred at room temperature for 1-2 h until the substrate disappeared (monitored by TLC). The solvents were removed under the reduced pressure and the crude product was used directly in the next step.

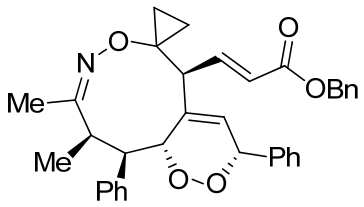
An oven-dried glass vial equipped with a magnetic stirrer was charged with the above crude olefin product, Eosin Y (5 mol%, 0.01 mmol, 0.006 g) and TBME (2 mL). The vial was closed with a plastic film. Then, the reaction mixture was stirred and irradiated (17 W white LED) at room temperature for 36−72 h until the olefin was

consumed completely (monitored by TLC). At this time, the solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (the crude residue was dry loaded with silica gel, 1/20 to 1/10, ethyl acetate/petroleum ether) to provide compounds **7**.



7aa

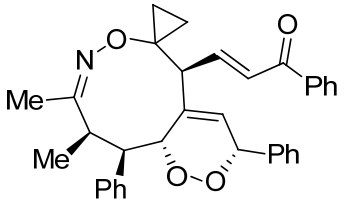
Oxazonine-fused endoperoxide 7aa, a light yellow solid, 0.051 g, 52% yield. Mp: 167–168 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, J = 7.6 Hz, 2H), 7.29–7.18 (m, 6H), 7.01–6.99 (m, 2H), 6.47 (dd, J = 15.6 Hz, 10.0 Hz, 1H), 6.03 (d, J = 15.6 Hz, 1H), 5.83–5.78 (m, 1H), 5.55–5.50 (m, 1H), 5.47–5.45 (m, 1H), 4.19 (q, J = 6.8 Hz, 2H), 3.79 (d, J = 9.6 Hz, 1H), 3.38–3.37 (m, 1H), 2.77–2.72 (m, 1H), 1.96 (s, 3H), 1.52 (d, J = 7.2 Hz, 3H), 1.28 (t, J = 6.8 Hz, 3H), 1.13–1.05 (m, 2H), 0.89–0.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.1, 165.6, 143.2, 142.9, 139.1, 136.7, 129.3, 128.5, 128.3, 128.0, 127.9, 126.5, 126.4, 124.7, 80.0, 77.9, 64.1, 60.5, 51.6, 46.0, 45.6, 21.6, 14.1, 12.5, 10.7, 8.4; IR (thin film) 3033, 2929, 1720, 1455, 1262, 1026, 700 cm^{-1}; HRMS (ESI) m/z calcd for $C_{30}H_{34}NO_5$ $[M + H]^+$: 488.2431, found: 488.2434.



7ab

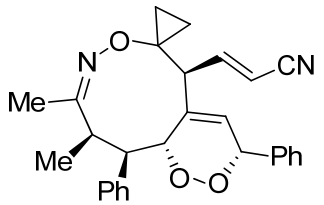
Oxazonine-fused endoperoxide 7ab, a light yellow solid, 0.078 g, 71% yield. Mp: 141–142 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.32 (m, 7H), 7.28–7.16 (m, 6H), 7.00–6.98 (m, 2H), 6.53 (dd, J = 15.6 Hz, 10.0 Hz, 1H), 6.09 (d, J = 15.6 Hz, 1H), 5.80–5.78 (m, 1H), 5.55–5.50 (m, 1H), 5.47–5.45 (m, 1H), 5.15 (s, 2H), 3.80–3.77 (m, 1H), 3.37–3.36 (m, 1H), 2.77–2.72 (m, 1H), 1.96 (s, 3H), 1.52 (d, J = 7.2 Hz, 3H),

1.14–1.05 (m, 2H), 0.79–0.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.1, 165.4, 143.9, 142.8, 139.0, 136.6, 135.6, 129.3, 128.6, 128.5, 128.3, 128.2, 128.0, 127.9, 127.8, 126.4, 126.1, 124.8, 80.0, 77.9, 66.3, 64.0, 51.5, 45.9, 45.7, 21.6, 12.5, 10.8, 8.4; IR (thin film) 3031, 2917, 1719, 1454, 1252, 1018, 697 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{35}H_{36}NO_5$ $[M + H]^+$: 550.2588, found: 550.2602.



7ac

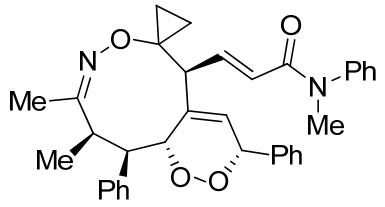
Oxazonine-fused endoperoxide 7ac, a light yellow solid, 0.073 g, 70% yield. Mp: 147–148 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 7.6 Hz, 2H), 7.59 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.37–7.35 (m, 2H), 7.30 (d, J = 7.2 Hz, 2H), 7.20–7.18 (m, 4H), 7.15 (d, J = 14.8 Hz, 1H), 6.99–6.98 (m, 2H), 6.61 (dd, J = 15.2 Hz, 10.0 Hz, 1H), 5.86–5.84 (m, 1H), 5.59–5.56 (m, 1H), 5.49–5.47 (m, 1H), 3.94 (d, J = 9.6 Hz, 1H), 3.41–3.40 (m, 1H), 2.79–2.74 (m, 1H), 2.00 (s, 3H), 1.55 (d, J = 7.2 Hz, 3H), 1.15–1.10 (m, 2H), 0.88–0.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.2, 172.1, 143.2, 142.9, 139.1, 137.2, 136.7, 133.1, 130.1, 129.3, 128.7, 128.6, 128.5, 128.2, 127.9, 127.7, 126.4, 125.0, 80.0, 77.9, 64.2, 51.5, 46.1, 46.0, 21.7, 12.4, 10.8, 8.6; IR (thin film) 3063, 2921, 1671, 1454, 1259, 1015, 699 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{34}H_{34}NO_4$ $[M + H]^+$: 520.2482, found: 520.2500.



7ad

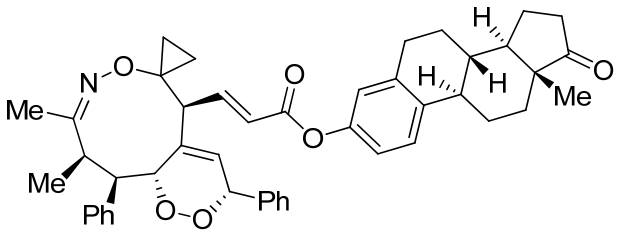
Oxazonine-fused endoperoxide 7ad, a light yellow solid, 0.051 g, 58% yield. Mp: 56–57 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.17 (m, 8H), 6.99–6.98 (m, 2H),

6.25 (dd, J = 16.4 Hz, 9.6 Hz, 1H), 5.76–5.73 (m, 1H), 5.58 (d, J = 16.0 Hz, 1H), 5.49–5.48 (m, 2H), 3.74 (d, J = 8.8 Hz, 1H), 3.34–3.33 (m, 1H), 2.76–2.71 (m, 1H), 1.94 (s, 3H), 1.50 (d, J = 7.2 Hz, 3H), 1.18–1.10 (m, 2H), 0.73–0.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 150.5, 142.6, 138.3, 136.2, 129.2, 128.7, 128.3, 127.9, 127.6, 126.5, 125.5, 116.4, 104.8, 79.8, 77.6, 63.6, 51.6, 47.2, 45.9, 21.5, 12.4, 10.6, 8.3; IR (thin film) 3012, 2925, 1736, 1454, 1261, 1019, 698 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{29}N_2O_3$ $[M + H]^+$: 441.2173, found: 441.2186.



7ae

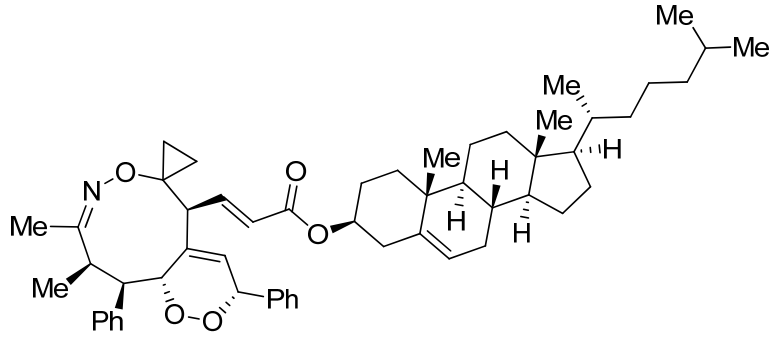
Oxazonine-fused endoperoxide 7ae, a white solid, 0.081 g, 74% yield. Mp: 75–76 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.35 (m, 3H), 7.31–7.15 (m, 8H), 7.11 (d, J = 6.8 Hz, 2H), 6.96–6.94 (m, 2H), 6.40 (dd, J = 15.2 Hz, 9.6 Hz, 1H), 5.90 (d, J = 15.2 Hz, 1H), 5.79–5.77 (m, 1H), 5.50–5.48 (m, 1H), 5.44–5.41 (m, 1H), 3.61–3.59 (m, 1H), 3.30 (s, 3H), 3.27–3.26 (m, 1H), 2.64–2.62 (m, 1H), 1.90 (s, 3H), 1.50 (d, J = 6.8 Hz, 3H), 1.06–1.00 (m, 2H), 0.83–0.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 164.9, 143.3, 143.1, 140.4, 139.1, 136.9, 129.6, 129.2, 128.4, 128.2, 127.8, 127.7, 127.5, 127.3, 126.3, 126.2, 124.9, 79.9, 77.8, 64.0, 51.2, 46.3, 45.0, 37.5, 21.7, 12.2, 10.6, 8.4; IR (thin film) 3032, 2911, 1658, 1454, 1276, 1008, 697 cm^{-1}; HRMS (ESI) m/z calcd for $C_{35}H_{37}N_2O_4$ $[M + H]^+$: 549.2748, found: 549.2754.



7af

Oxazonine-fused endoperoxide 7af, a light yellow solid, 0.082 g, 58% yield. Mp:

89–90 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 7.2 Hz, 2H), 7.30–7.17 (m, 7H), 7.04–7.03 (m, 2H), 6.87 (d, J = 7.6 Hz, 1H), 6.83 (s, 1H), 6.68 (dd, J = 15.2 Hz, 9.6 Hz, 1H), 6.24 (d, J = 15.2 Hz, 1H), 5.83–5.77 (m, 1H), 5.60–5.57 (m, 1H), 5.50–5.48 (m, 1H), 3.86–3.84 (m, 1H), 3.42–3.41 (m, 1H), 2.90–2.88 (m, 2H), 2.82–2.77 (m, 1H), 2.53–2.47 (m, 1H), 2.41–2.38 (m, 1H), 2.30–2.25 (m, 1H), 2.16–2.01 (m, 3H), 1.97 (s, 3H), 1.64–1.56 (m, 5H), 1.53 (d, J = 6.8 Hz, 3H), 1.48–1.44 (m, 2H), 1.19–1.09 (m, 2H), 0.90 (s, 3H), 0.82–0.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 220.7, 172.3, 164.2, 148.3, 145.4, 142.8, 138.9, 137.9, 137.4, 136.6, 129.3, 128.6, 128.3, 128.0, 127.9, 126.4, 126.3, 125.7, 125.0, 121.4, 118.6, 80.0, 78.0, 64.1, 51.7, 50.3, 47.8, 46.1, 45.8, 44.1, 37.9, 35.8, 31.5, 29.3, 26.2, 25.7, 21.5, 21.4, 13.7, 12.6, 10.8, 8.5; IR (thin film) 3028, 2928, 1737, 1649, 1492, 1153, 1015, 698 cm^{-1}; HRMS (ESI) m/z calcd for $C_{46}H_{50}NO_6$ $[M + H]^+$: 712.3633, found: 712.3650.

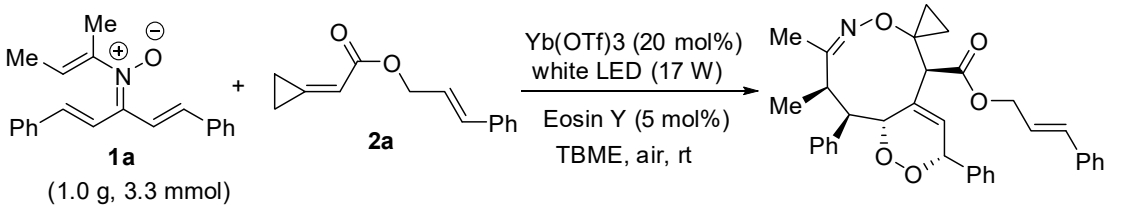


7ag

Oxazonine-fused endoperoxide 7ag, a light yellow solid, 0.052 g, 49% yield. Mp: 183–184 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, J = 7.2 Hz, 2H), 7.28–7.16 (m, 6H), 7.01–6.99 (m, 2H), 6.46 (dd, J = 15.2 Hz, 9.6 Hz, 1H), 6.02 (d, J = 15.6 Hz, 1H), 5.80–5.78 (m, 1H), 5.56–5.53 (m, 1H), 5.47–5.45 (m, 1H), 5.38–5.35 (m, 1H), 4.85–4.62 (m, 1H), 3.78–3.75 (m, 1H), 3.38–3.37 (m, 1H), 2.77–2.75 (m, 1H), 2.32–2.30 (m, 2H), 2.02–1.98 (m, 2H), 1.95 (s, 3H), 1.87–1.83 (m, 3H), 1.61–1.56 (m, 5H), 1.52 (d, J = 7.2 Hz, 3H), 1.46–1.32 (m, 7H), 1.12–1.08 (m, 11H), 1.01 (s, 3H), 0.92 (d, J = 6.0 Hz, 3H), 0.87 (d, J = 6.4 Hz, 6H), 0.78–0.75 (m, 2H), 0.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.1, 165.0, 143.0, 142.8, 139.5, 139.0, 136.7, 129.3,

128.5, 128.2, 128.0, 127.9, 126.9, 126.4, 124.7, 122.7, 80.0, 77.9, 74.2, 64.1, 56.6, 56.0, 51.5, 49.9, 45.9, 45.7, 42.2, 39.6, 39.4, 38.0, 36.9, 36.5, 36.1, 35.7, 31.9, 31.8, 28.1, 27.9, 27.7, 24.2, 23.7, 22.7, 22.5, 21.5, 20.9, 19.2, 18.6, 12.5, 11.8, 10.8, 8.4; IR (thin film) 3032, 2937, 1709, 1455, 1270, 1018, 699 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{55}H_{74}NO_5$ $[M + H]^+$: 828.5562, found: 828.5549.

7. Gram scale preparation of 3aa

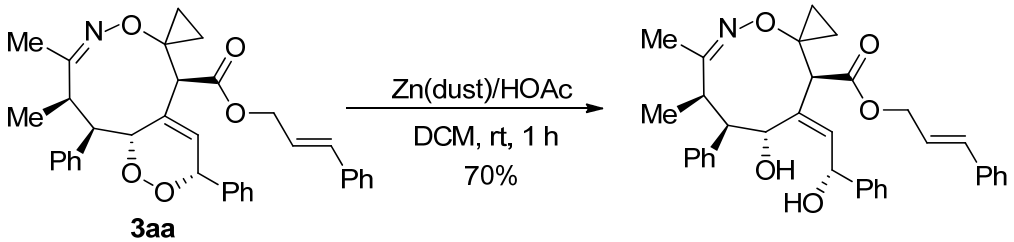


3aa (1.1 g, 62%, flash column chromatography
3aa (1.2 g, 65%, extraction and recrystallization

An oven-dried 100 mL round bottom flak equipped with a magnetic stirrer was charged with the corresponding *N*-vinyl nitrone **1a** (1.0 g, 3.3 mmol), $Yb(OTf)_3$ (20 mol%, 0.66 mmol, 0.409 g), Eosin Y (5 mol%, 0.165 mmol, 0.099 g) and TBME (40 mL). Methylenecyclopropane **2a** (1.42 g, 6.6 mmol, 2.0 equiv.) was added to the mixture. The flask was closed with a plastic film. Then, the reaction mixture was stirred and irradiated (17 W white LED) at room temperature for 72 h (monitored by TLC). At this time, the solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (the crude residue was dry loaded with silica gel, 1/20 to 1/10, ethyl acetate/petroleum ether) to afford endoperoxide **3aa** (1.1 g, 62% yield).

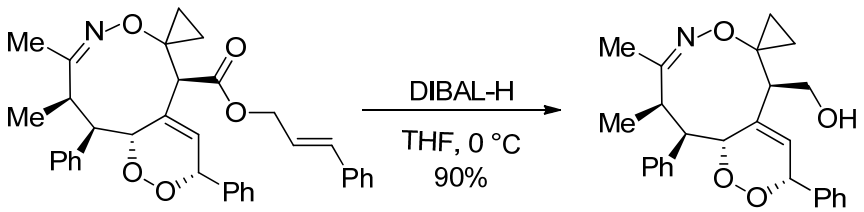
Alternatively, when the reaction was completed, the reaction was quenched with water (40 mL). Then, the water layer was extracted with Et_2O (3 × 30 mL). The organic layers were combined and dried with Na_2SO_4. The mixture was then filtered and the solvent was removed under reduced pressure. The crude product was recrystallized with petroleum ether to afford endoperoxide **3aa** (1.2 g, 65% yield).

8. Synthesis of compounds 8-10 from 3aa



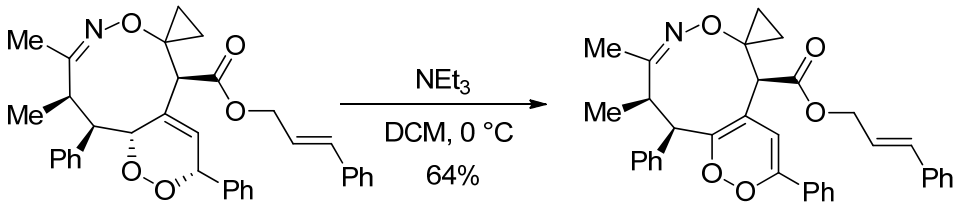
3aa **8**

In a 25 mL round-bottom flask was charged with **3aa** (0.2 mmol), Zn dust (10 equiv., 2 mmol) under an air atmosphere. And then, CH_2Cl_2 (2 mL) and HOAc (10 equiv., 2 mmol) was added at room temperature. The mixture was stirred vigorously at room temperature for 1 h until **3aa** was consumed completely (monitored by TLC). At this time, the reaction was diluted with H_2O (10 mL) and exacted with CH_2Cl_2 (20 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (the crude residue was dry loaded with silica gel, petroleum ether-EtOAc: 4/1) to provide compound **8** as a white solid (0.077 g, 70%). Mp: 146–147 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, J = 7.6 Hz, 2H), 7.27–7.15 (m, 12H), 6.57 (d, J = 15.6 Hz, 1H), 6.13–6.06 (m, 1H), 5.95 (d, J = 8.8 Hz, 1H), 5.75 (d, J = 8.8 Hz, 1H), 4.94 (d, J = 11.2 Hz, 1H), 4.67–4.51 (m, 2H), 4.03 (s, 1H), 3.87–3.86 (m, 1H), 3.54–3.50 (m, 1H), 3.26–3.23 (m, 1H), 2.95 (brs, 1H), 1.74–1.70 (m, 1H), 1.24 (s, 3H), 1.16–1.11 (m, 1H), 0.91–0.87 (m, 1H), 0.83 (d, J = 7.2 Hz, 3H), 0.70–0.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.0, 170.6, 143.7, 141.0, 138.8, 135.8, 135.7, 135.6, 129.2, 128.6, 128.4, 128.3, 128.1, 127.3, 127.0, 126.6, 125.7, 121.6, 71.0, 69.9, 65.9, 62.3, 59.7, 55.1, 34.1, 18.7, 15.7, 10.2, 9.9; IR (thin film) 3480, 3030, 2921, 1708, 1494, 1169, 1021, 699 cm^{-1}; HRMS (ESI) m/z calcd for $C_{35}H_{38}NO_5$ $[M + H]^+$: 552.2744, found: 552.2763.



3aa **9**

In a 25 mL round-bottom flask was charged with **3aa** (0.2 mmol) and THF (2 mL). DIBAL-H (0.4 mmol, 2.0 equiv., 1M) was added at 0 °C. Then, the reaction mixture was stirred vigorously at 0 °C for 0.5 h until **3aa** was consumed completely (monitored by TLC). At this time, the reaction was quenched with H_2O (10 mL) and exacted with Et_2O (20 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and filtered. The solvents were removed under the reduced pressure. The crude product was purified by flash chromatography (the crude residue was dry loaded with silica gel, petroleum ether-EtOAc: 4/1) to give alcohol **9** as a light yellow oil (0.075 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.24 (m, 7H), 7.20–7.12 (m, 3H), 5.81–5.79 (m, 1H), 5.58–5.57 (m, 2H), 3.99–3.83 (m, 2H), 3.56–3.55 (m, 1H), 3.14–3.12 (m, 1H), 2.66–2.64 (m, 1H), 1.81 (s, 3H), 1.42 (d, J = 7.2 Hz, 3H), 1.15–1.13 (m, 2H), 0.88–0.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.1, 142.6, 137.8, 136.5, 129.4, 128.7, 128.4, 128.2, 127.9, 126.5, 125.3, 80.4, 79.1, 64.6, 62.0, 52.2, 48.9, 43.5, 20.5, 14.4, 10.8, 8.6; IR (thin film) 3420, 3031, 2937, 1496, 1161, 1002, 697 cm^{-1}; HRMS (ESI) m/z calcd for $C_{26}H_{30}NO_4$ $[M + H]^+$: 420.2169, found: 420.2182.

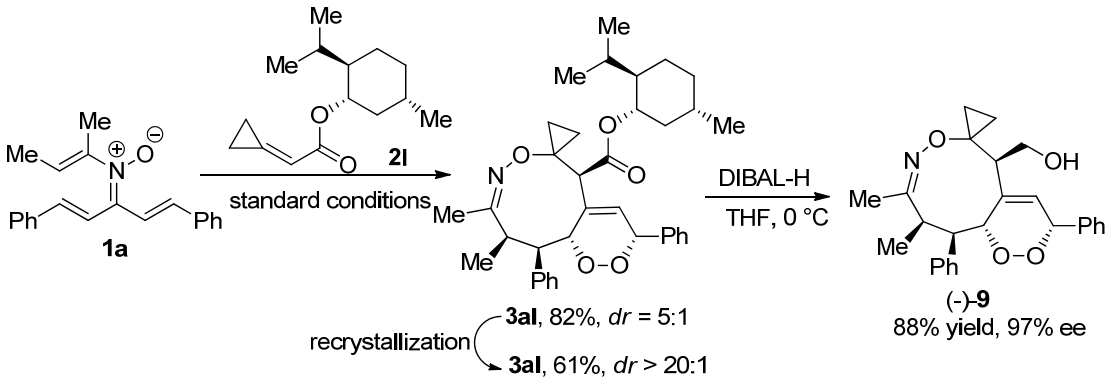


3aa **10**

To a solution of **3aa** (0.2 mmol) in CH_2Cl_2 (2 mL) at 0 °C was added NEt_3 (2 equiv., 0.4 mmol). Then, the reaction mixture was stirred vigorously at 0 °C for 10 h until **3aa** was consumed completely (monitored by TLC). The resulting mixture was allowed to warm to room temperature and SiO_2 was added stirring for 2 h. The solvents were removed under the reduced pressure. The crude product was purified by flash chromatography (the crude residue was dry loaded with silica gel, petroleum ether-EtOAc: 10/1) to give compound **10** as a white solid (0.070 g, 64%). Mp: 146–147 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57–7.52 (m, 4H), 7.41–7.37 (m, 4H),

7.33–7.23 (m, 5H), 7.22–7.16 (m, 2H), 7.02 (s, 1H), 6.70 (d, J = 16.0 Hz, 1H), 6.32 (dt, J = 15.6 Hz, 6.8 Hz, 1H), 4.81–4.70 (m, 2H), 4.26 (s, 1H), 4.23–4.22 (m, 1H), 3.00–2.95 (m, 1H), 1.98 (s, 3H), 1.38 (d, J = 7.2 Hz, 3H), 1.33–1.25 (m, 2H), 0.95–0.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 169.5, 151.9, 150.8, 141.9, 135.9, 135.1, 130.9, 128.6, 128.5, 128.4, 128.3, 128.2, 127.0, 126.9, 126.6, 123.4, 122.4, 119.7, 105.8, 65.5, 65.4, 47.3, 45.8, 43.7, 22.4, 14.6, 11.0, 9.9; IR (thin film) 3022, 2924, 1730, 1480, 1125, 697 cm^{-1}; HRMS (ESI) m/z calcd for $C_{35}H_{34}NO_5$ [M + H]$^+$: 548.2431, found: 548.2455.

9. Asymmetric synthesis of endoperoxide 9 by chiral auxiliary.

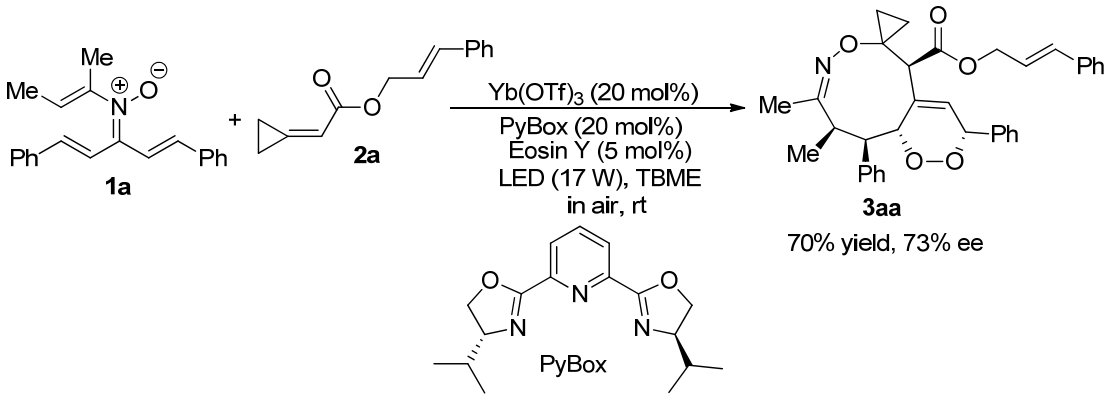


An oven-dried glass vial equipped with a magnetic stirrer was charged with the corresponding *N*-vinyl nitrone **1a** (0.2 mmol, 0.061 g), $Yb(OTf)_3$ (20 mol%, 0.04 mmol, 0.025 g), Eosin Y (5 mol%, 0.01 mmol, 0.006 g) and TBME (2 mL). Methylenecyclopropane **2l** (0.4 mmol, 2.0 equiv., 0.094 g) was added to the vial. The vial was closed with a plastic film. Then, the reaction mixture was stirred and irradiated (17 W white LED) at room temperature for 72 h until *N*-vinyl nitrone **1a** was consumed completely (monitored by TLC). At this time, the solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (the crude residue was dry loaded with silica gel, 1/20, ethyl acetate/petroleum ether) to afford endoperoxide **3al** (*dr* = 5:1). A light yellow solid, (0.094 g, 82% yield).

Then, **3al** (*dr* = 5:1) was further recrystallized with petroleum ether to afford **3al** (61% yield, *dr* >20:1). *Major isomer*: Mp: 131–132 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J = 7.6 Hz, 2H), 7.28–7.16 (m, 6H), 7.02–7.01 (m, 2H), 5.83–5.80 (m, 1H), 5.64–5.63 (m, 1H), 5.49–5.48 (m, 1H), 4.71–4.64 (m, 1H), 3.92 (s, 1H), 3.37–3.36 (m, 1H), 2.78–2.72 (m, 1H), 1.94 (s, 3H), 1.93–1.92 (m, 1H), 1.72–1.59 (m, 3H), 1.51 (d, J = 7.2 Hz, 3H), 1.41–1.28 (m, 3H), 1.17–1.12 (m, 1H), 1.05–0.98 (m, 2H), 0.90 (d, J = 7.2 Hz, 3H), 0.82–0.79 (m, 3H), 0.75 (d, J = 6.4 Hz, 3H), 0.71 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.2, 169.3, 143.0, 136.4, 135.6, 129.3, 128.5, 128.2, 127.9, 127.8, 126.4, 125.0, 79.8, 77.7, 74.9, 62.6, 50.7, 49.9, 46.7, 46.0, 40.6, 34.0, 31.2, 25.7, 22.9, 21.8, 21.7, 20.8, 15.7, 12.5, 10.9, 9.5; IR (thin film) 3021, 2981, 1730, 1451, 1222, 1054, 670 cm^{-1}; HRMS (ESI) m/z calcd for $C_{36}H_{46}NO_5$ $[M + H]^+$: 572.3371, found: 572.3388.

In a 25 mL round-bottom flask was charged with **3al** (*dr* >20:1) (0.2 mmol) and THF (2 mL). DIBAL-H (0.4 mmol, 2.0 equiv., 1M) was added at 0 °C. Then, the reaction mixture was stirred vigorously at 0 °C for 0.5 h until **3al** was consumed completely (monitored by TLC). At this time, the reaction was quenched with H_2O (10 mL) and exacted with Et_2O (20 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and filtered. The solvents were removed under the reduced pressure. The crude product was purified by flash chromatography (the crude residue was dry loaded with silica gel, petroleum ether-EtOAc: 4/1) to give alcohol **9** as a light yellow oil (0.074 g, 88%). The characteristic data matched with above racemic-**9**. The enantiomeric excess (ee) values of **9** were determined by chiral HPLC analysis. Ee = 97%, conditions: AD-H, hexane/*i*-PrOH = 65/35, flow rate 0.8 mL/min, λ = 254 nm, t (major) = 11.5 min, t (minor) = 6.4 min. $[\alpha]_D^{20}$ = –315.0 (*c* 0.125, CH_2Cl_2).

10. Asymmetric synthesis of 3aa by PyBox



An oven-dried glass vial equipped with a magnetic stirrer was charged with *N*-vinyl nitrone **1a** (0.2 mmol, 0.061 g), methylenecyclopropane **2a** (0.4 mmol, 2 equiv., 0.086 g) $Yb(OTf)_3$ (20 mol %, 0.025 g) and PyBox (20 mol %, 0.012 g), Eosin Y (5 mol%, 0.01 mmol, 0.006 g) and TBME (2 mL). The vial was closed with a plastic film. Then, the reaction mixture was stirred and irradiated (17 W white LED) at room temperature for 3 days until the mixture was consumed completely (monitored by TLC). At this time, the solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (the crude residue was dry loaded with silica gel, petroleum ether-EtOAc: 10/1) to provide endoperoxide **3aa** as a light yellow solid (0.078 g, 70%). The characteristic data matched with above racemic-**3aa**. The enantiomeric excess (ee) values of **3aa** were determined by chiral HPLC analysis. Ee = 73%, conditions: AD-H, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, t (major) = 20.6 min, t (minor) = 24.6 min.

11. Biological activity studies of endoperoxides 3, 4, 6

Cell Cuture: Murine monocyte-macrophage RAW264.7 cells maintained inDMEM (Gibco, USA) incubated at 37 °C in a humidified atmosphere containing 5% CO_2. Mouse peritoneal macrophages purchased from Procell Life Science&Technology Co., Ltd.

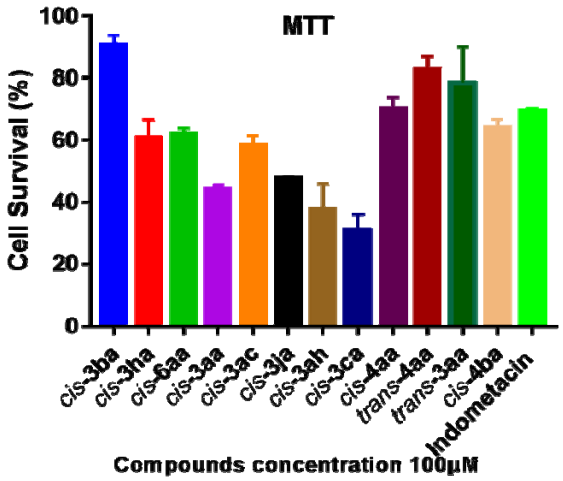
Cell viability assay: Cell cytotoxicity was evaluated by MTT. The MTT solution was added into each well and after incubation at 37 °C for 4 h, the culture media

containing MTT were removed, and then DMSO was added into each well and the absorbance at 570 nm was measured by a microplate reader[5].

Assay for NO production NO production was quantified by nitrite accumulation in the culture medium using the Griess reaction. Briefly, RAW264.7 cells were pretreated with compounds for 1 h, and then stimulated with or without LPS (1 mg/mL) for 24 h. The isolated supernatants were mixed with an equal volume of Griess reagent (Beyotime Biotechnology, China). $NaNO_2$ was used to generate a standard curve, and nitrite production was determined by measuring the optical density at 540 nm by a microplate reader [5].

Table S1. The effects of the target compounds on the cell viability of RAW 264.7 at the concentration of 100 μM (the MTT assay)

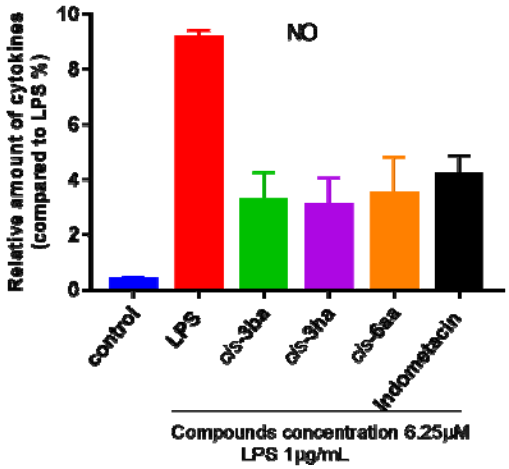
Compounds	Cell survival (% of normal)	Compounds	Cell survival (% of normal)）
cis-**3aa**	45±0.02	*cis*-**3ah**	39±0.08
cis-**3ba**	94±0.03	*cis*-**6aa**	64±0.04
cis-**3ca**	32±0.05	*cis*-**4aa**	91±0.42
cis-**3ha**	62±0.02	*trans*-**4aa**	86±0.35
cis-**3ja**	58±0.09	*trans*-**3aa**	75±0.25
cis-**3ac**	59±0.03	*cis*-**4ba**	74±0.18
		Indometacin	70±0.07



The Effect of the compounds ***cis*-3ba**、***cis*-3ha**、***cis*-6aa** on the inhibition of NO produced by RAW 264.7 cells induced by LPS. In the 6.25 μM compound concentration, LPS concentration (1 ug/mL).

Table S2 The effect of compounds ***cis*-3ba**、***cis*-3ha**、***cis*-6aa** on LPS-induced NO production.

Compounds	Concentration of NO (μmol/L)	Compounds	Concentration of NO (μmol/L)
con	0.38±0.07	***cis*-3ha**	3.07±0.99
LPS	9.16±0.26	***cis*-6aa**	8.27±0.69
***cis*-3ba**	3.25±1.03	**Indometacin**	3.51±1.30



12. References

[1] (a) N. Zou, J.-W. Jiao, Y. Feng, C.-H. Chen, C. Liang, G.-F. Su, D.-L. Mo, *Adv. Synth. Catal.* **2017**, *359*, 3545. (b) C.-H. Chen, Q.-Y. Wu, C. Wei, C. Liang, G.-F. Su, D.-L. Mo, *Green Chem.* **2018**, *20*, 2722.

[2] X.-P. Ma, J.-F. Zhu, S.-Y. Wu, C.-H. Chen, N. Zou, C. Liang, G.-F. Su, D.-L. Mo, *J. Org. Chem.* **2017**, *82*, 502.

[3] X. P. Ma, C.-M. Nong, J. Zhao, X. Lu, C. Liang, D.-L. Mo, *Adv. Synth. Catal.* **2020**, *362*, 478.

[4] G. Li, Q. Yan, X. Gong, X. Dou, D. Yang, *ACS Sustainable Chem. Eng.* **2019**, *7*, 14009.

[5] S. Y. Liu, P. Xu, X. L. Luo, J. F. Hu, X. H. Liu, *Neurochem. Res*. **2016**, *41*, 1570.

13. X-ray structure for compound *cis*-3aa.

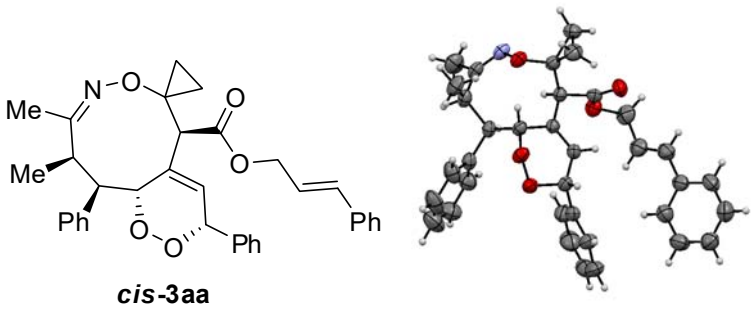
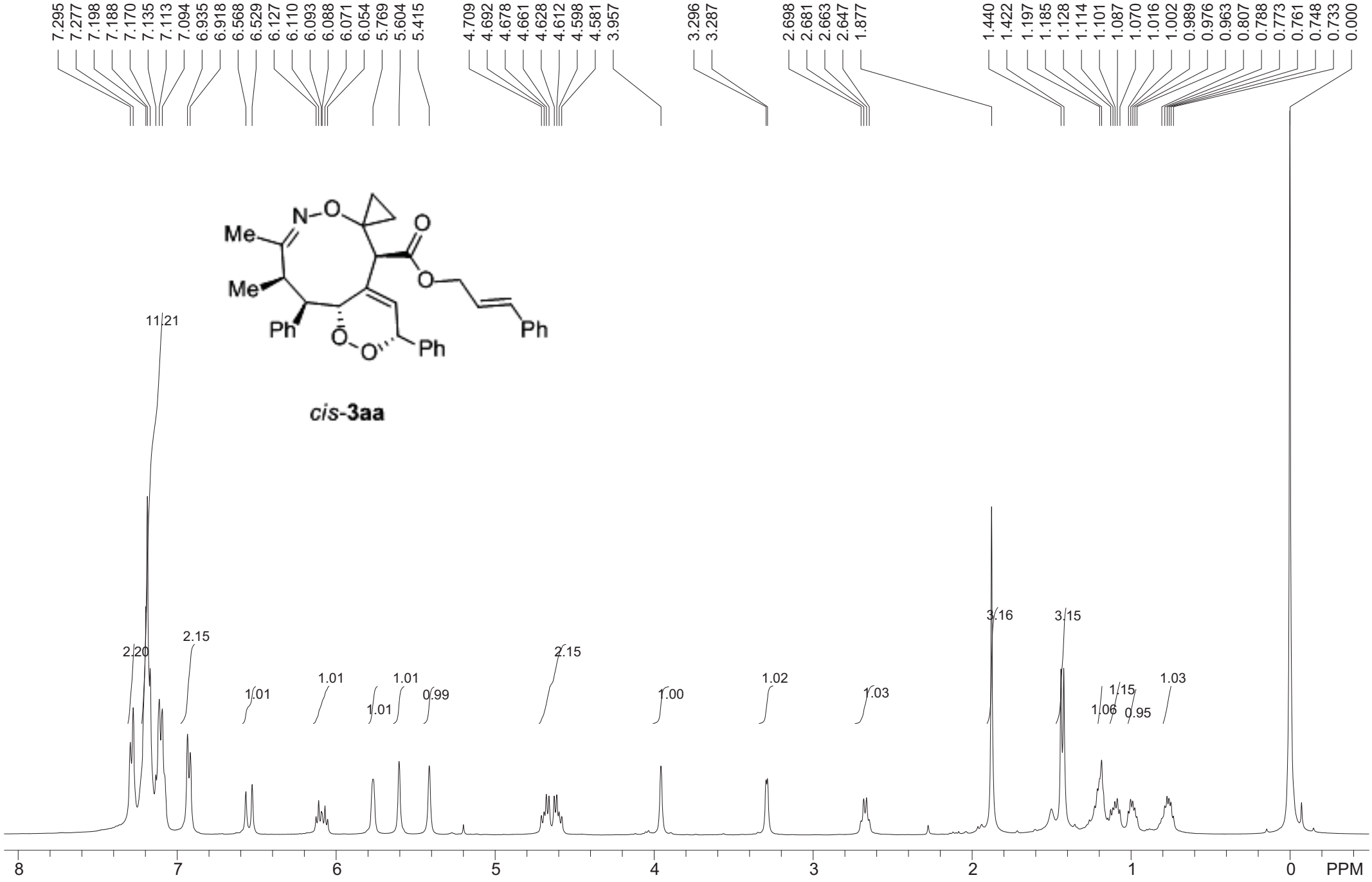


Figure S1: ORTEP diagram of ***cis*-3aa** at 50% ellipsoid probability

14. NMR spectra for compounds 3, 5-10 and HPLC for 9 and 3aa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6.110
6.093
6.088
6.071
6.054
5.769
5.604
5.415
4.709
4.692
4.678
4.661
4.628
4.612
4.598
4.581
3.957
3.296
3.287
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1.128
1.114
1.101
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1.070
1.016
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0.963
0.807
0.788
0.773
0.761
0.748
0.733
0.000
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Ph
Ph
Ph
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N
O
O
O
O
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2.20
2.15
1.01
1.01
1.01
1.01
0.99
2.15
1.00
1.02
1.03
3.16
3.15
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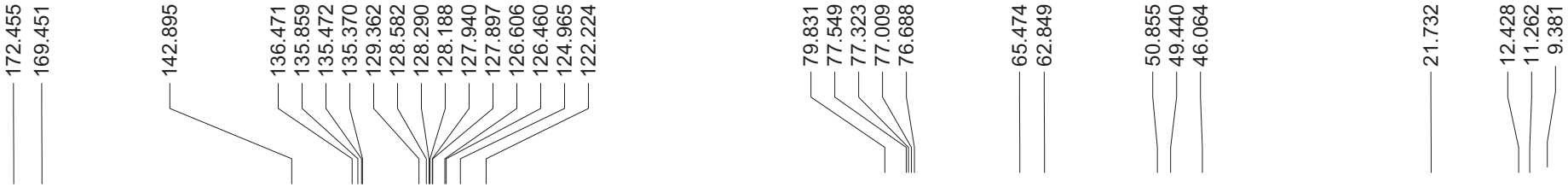
6
5
4
3
2
1
0
PPM

cis-**3aa**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122.224
79.831
77.549
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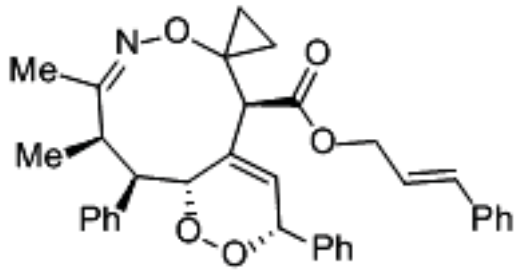
9.381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Me
O
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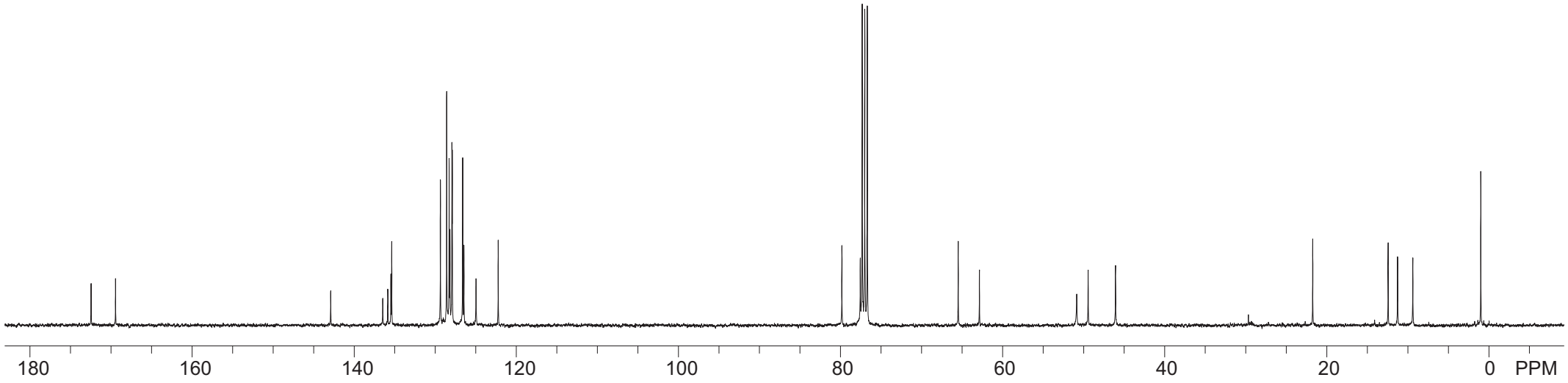
Ph
Ph
O
O
Ph

***cis*-3aa**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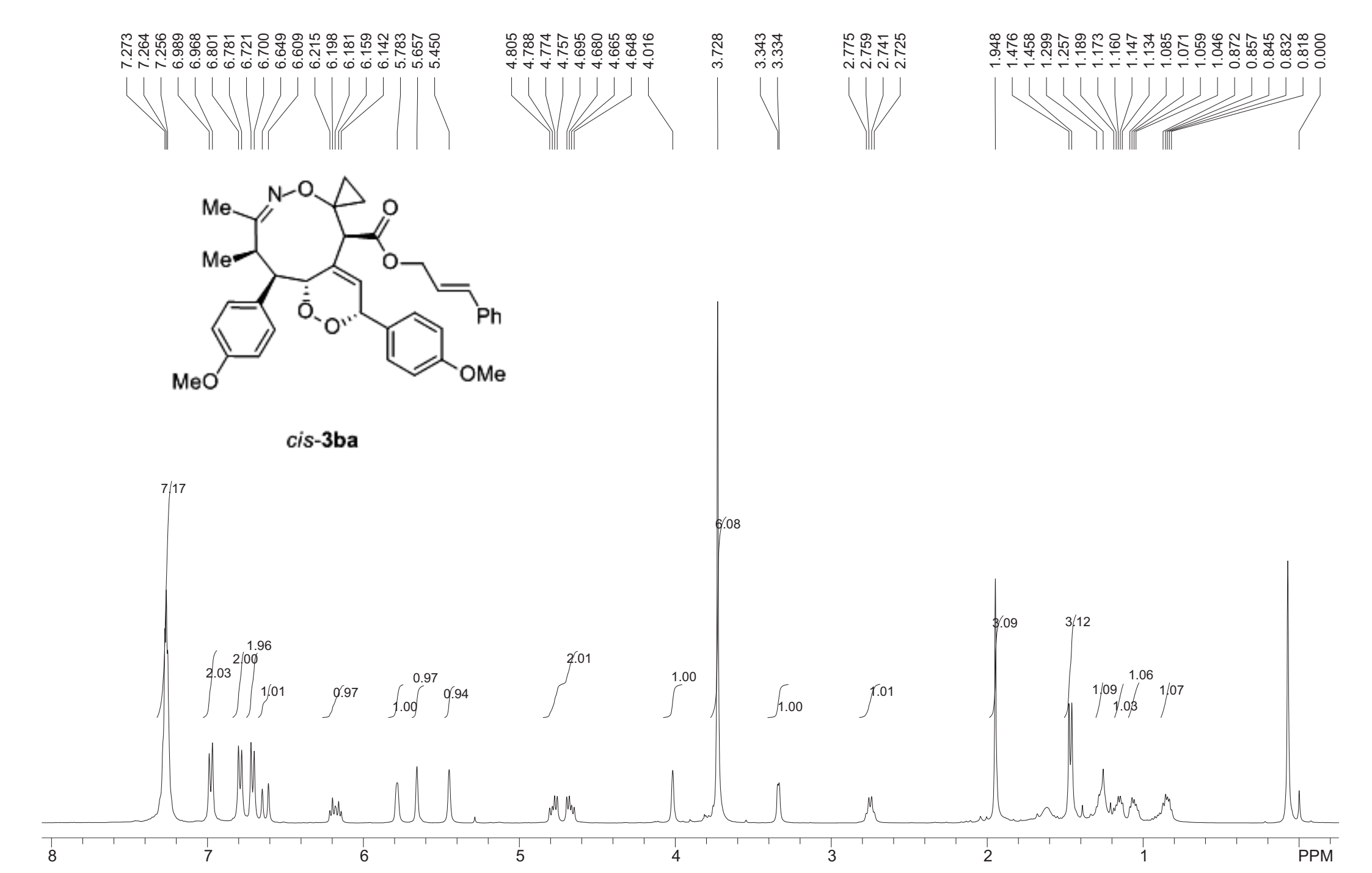
120
100
80
60
40
20
0
PPM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6.159
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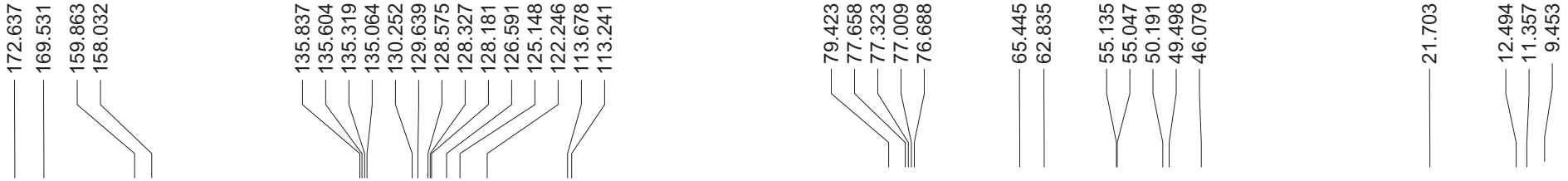
cis-**3ba**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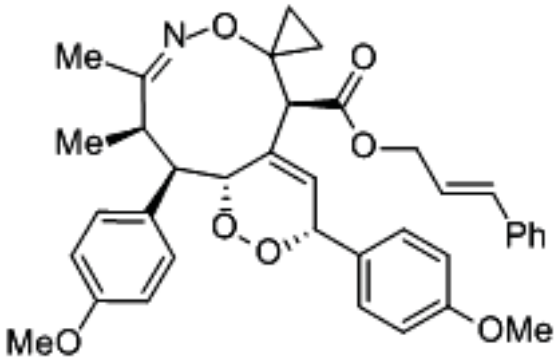
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Ph
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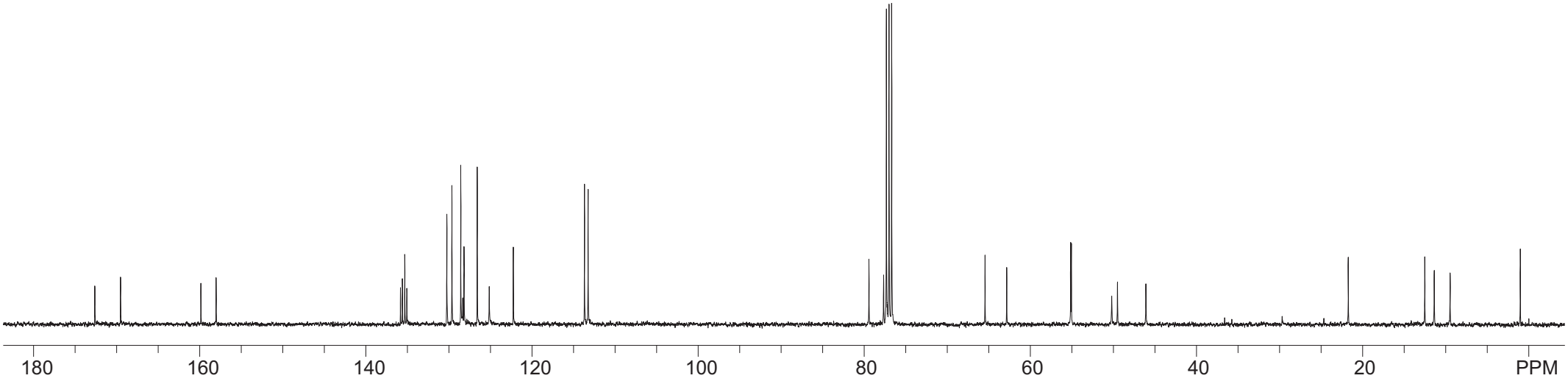
O
MeO
OMe

***cis*-3ba**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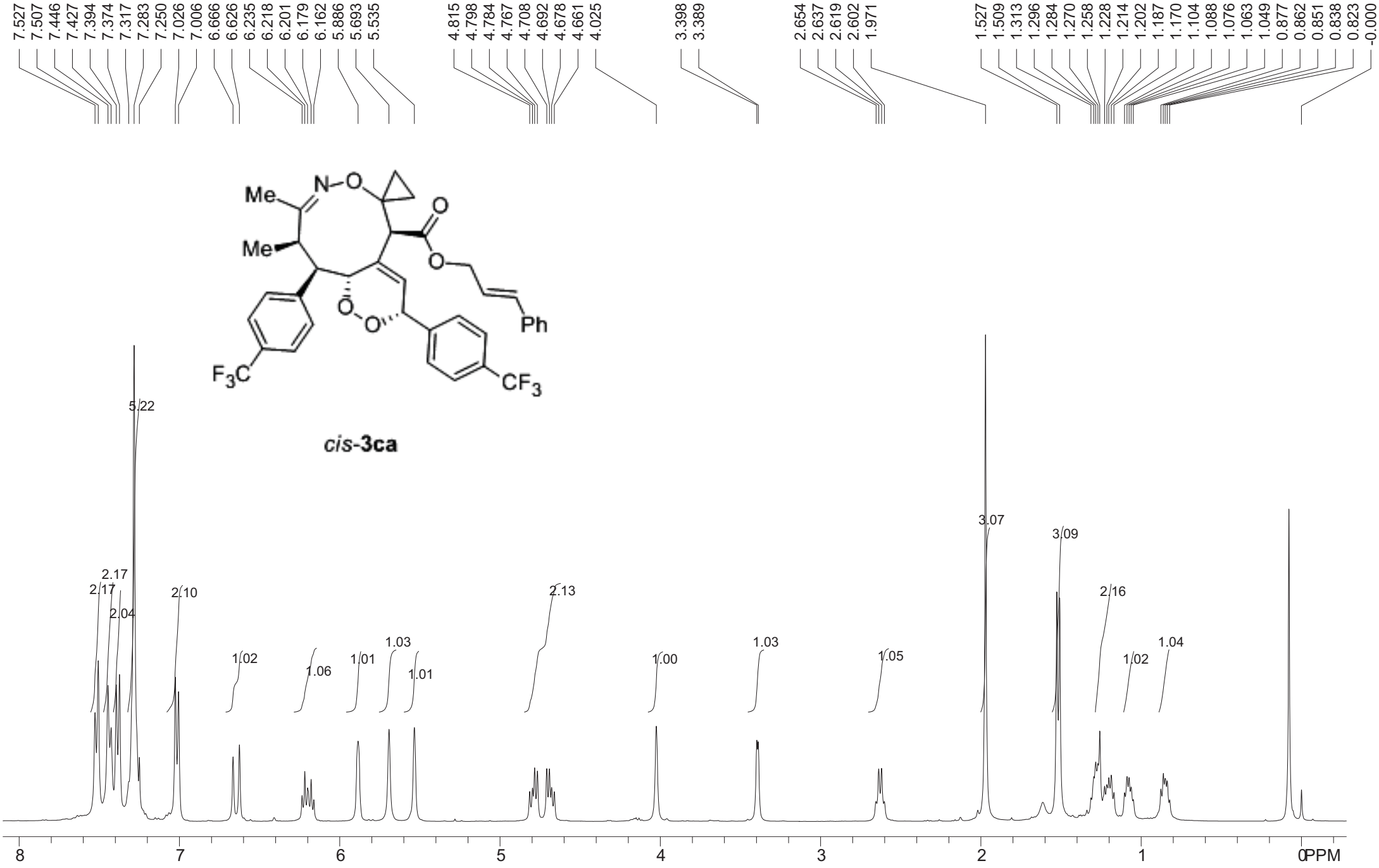
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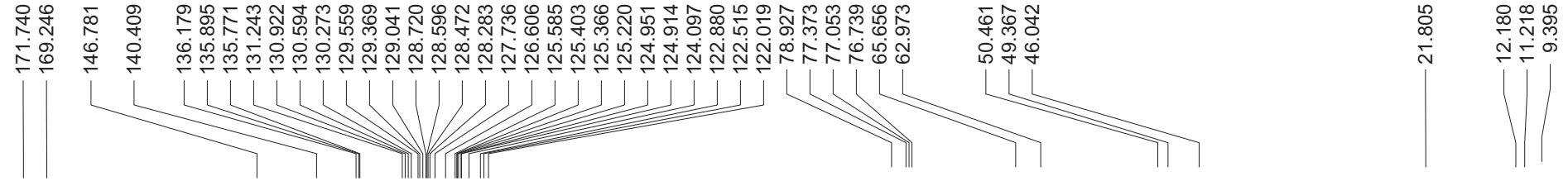
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128.596
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125.585
125.403
125.366
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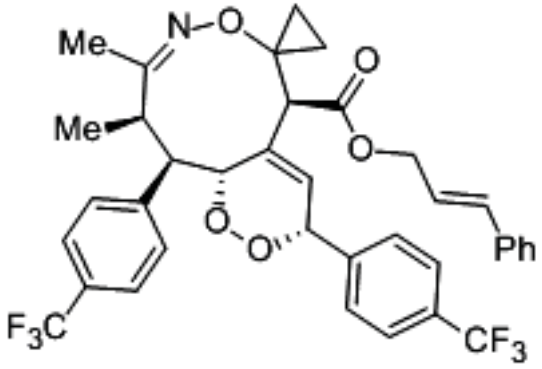
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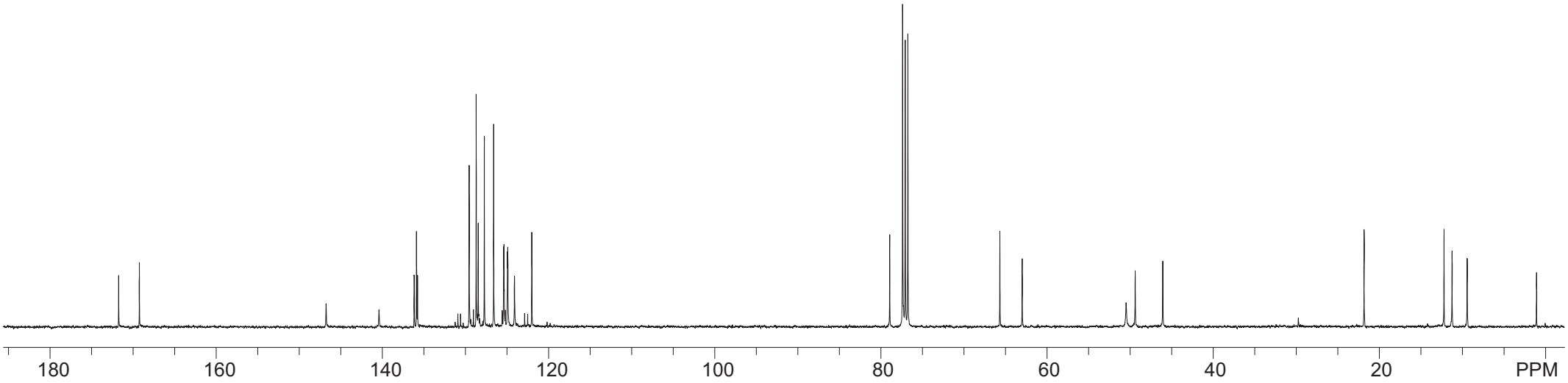
CF3

***cis*-3ca**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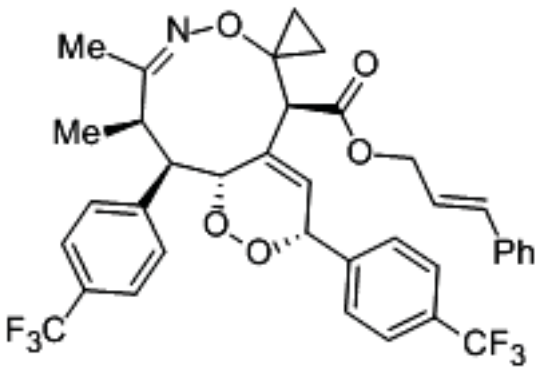

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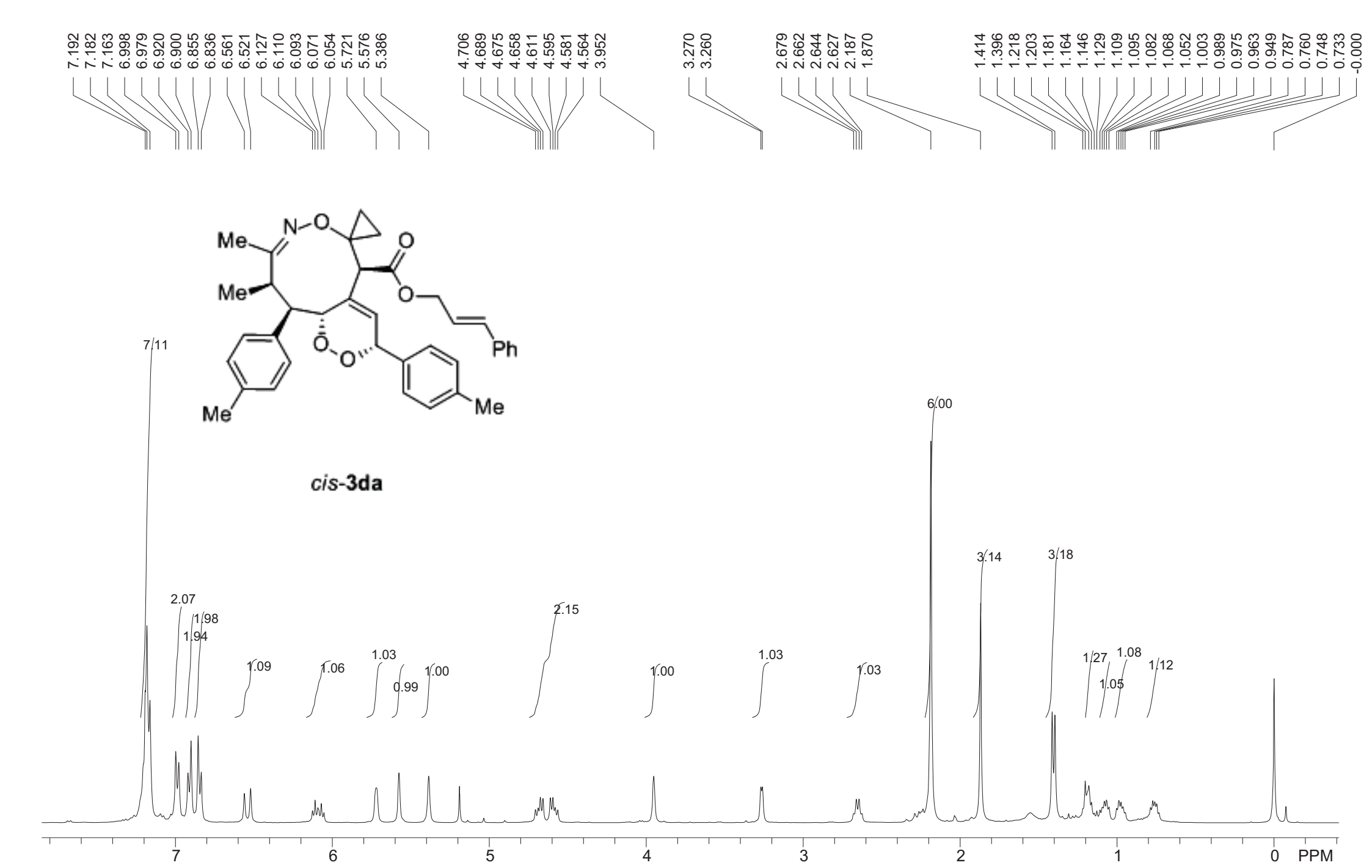
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Ph
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Me
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1.03
0.99
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1.03
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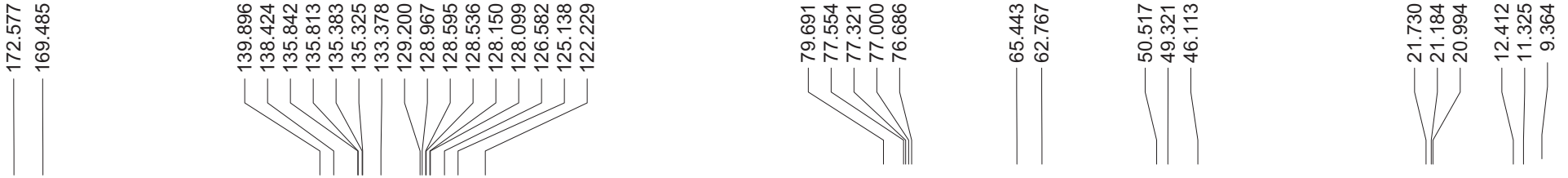
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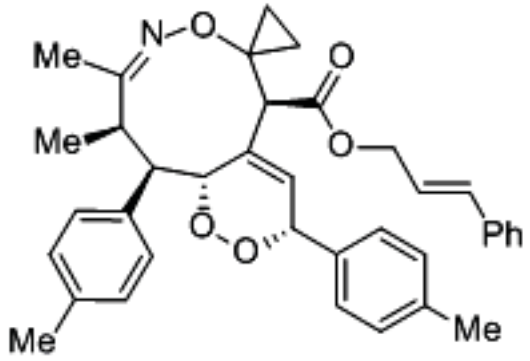
Me
N
O
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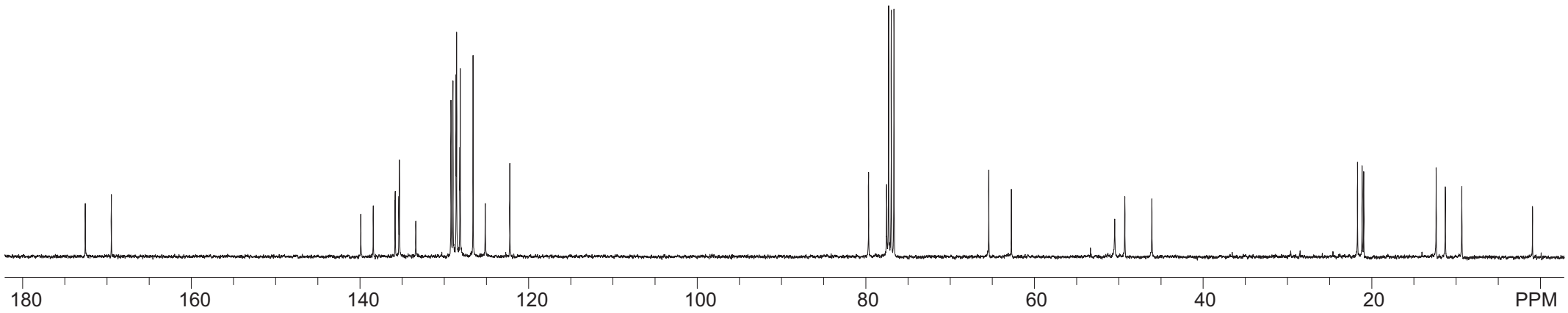
Me
O
Ph
O
O
Me
Me

cis-**3da**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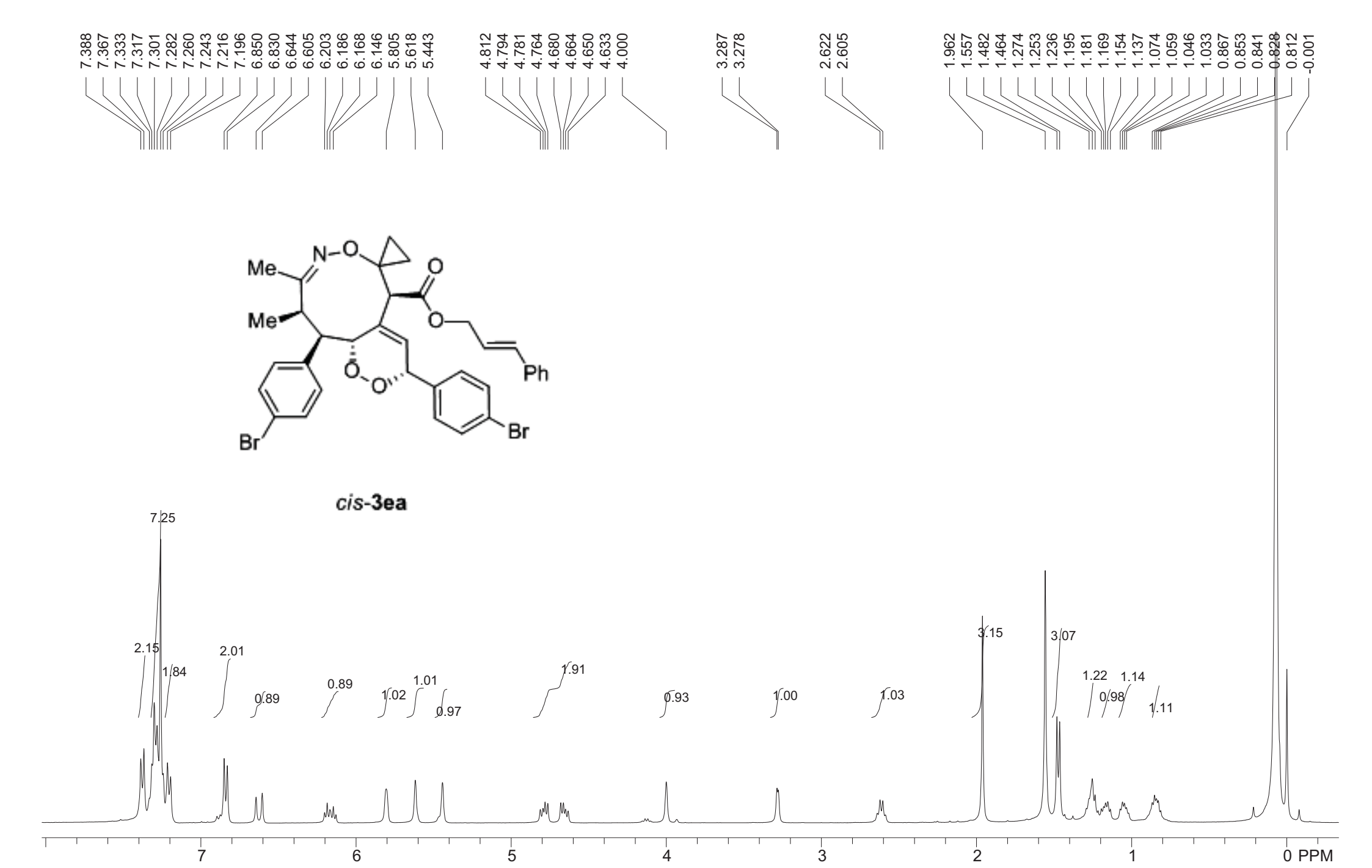
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4.000
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2.605
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-0.001
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Me
O
O
Ph
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O
Br
Br
cis-3ea
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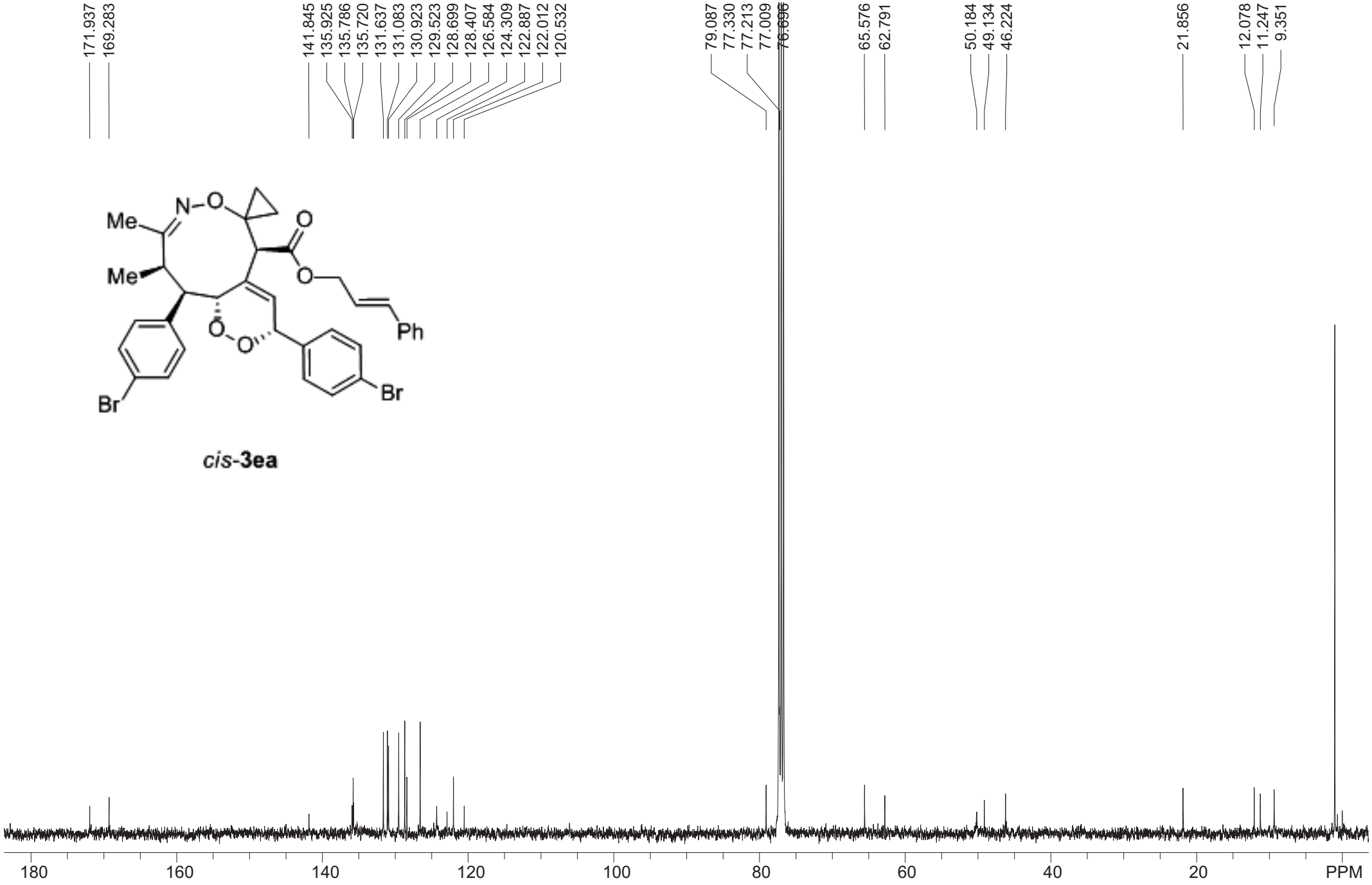
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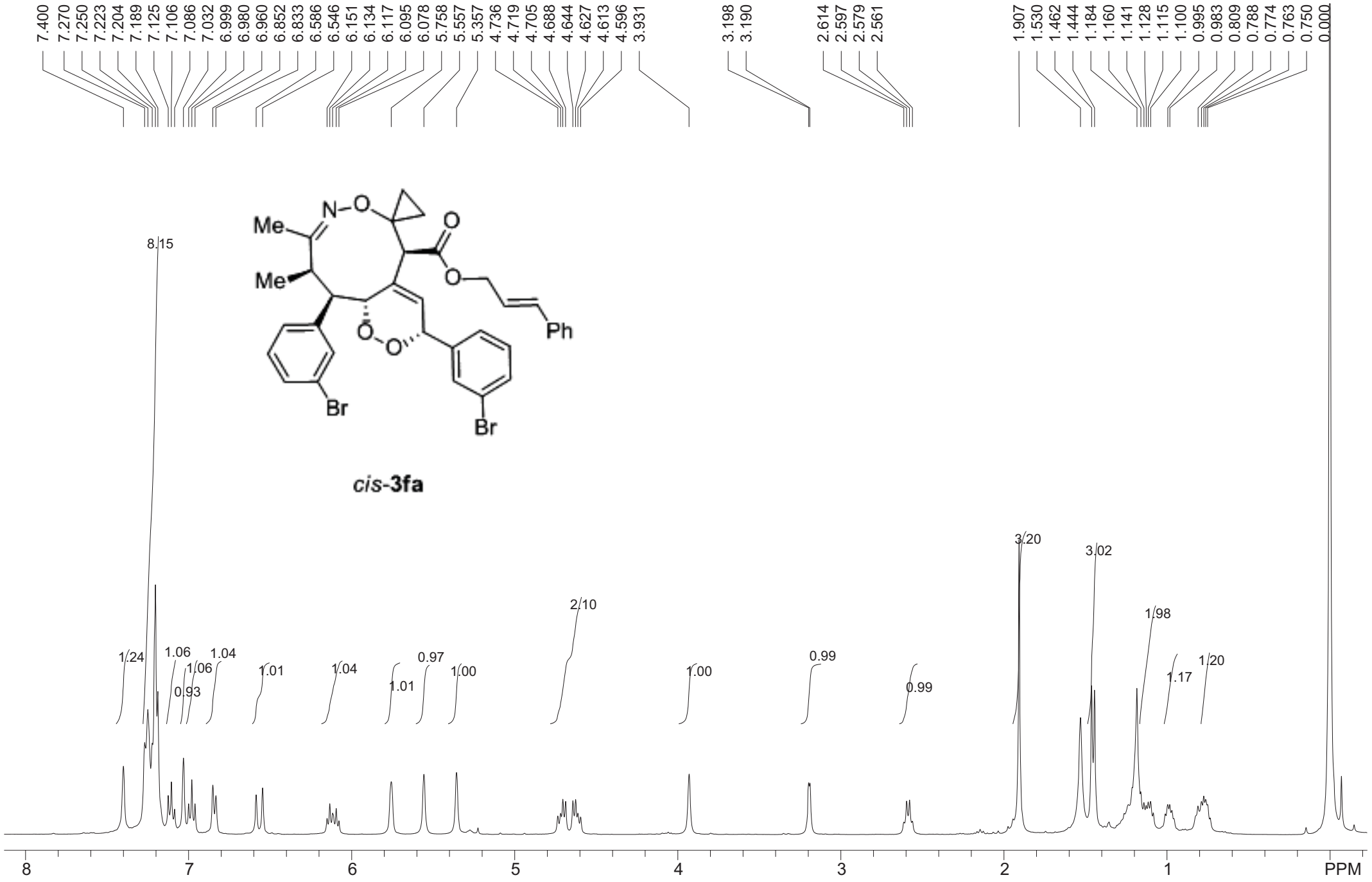
cis-**3ea**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Br
Br
cis-3fa
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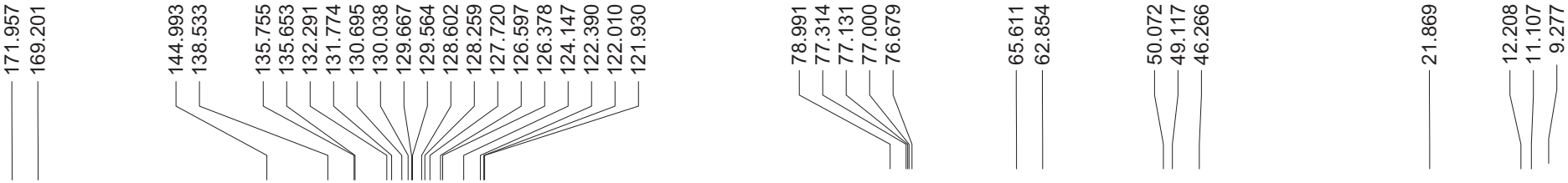
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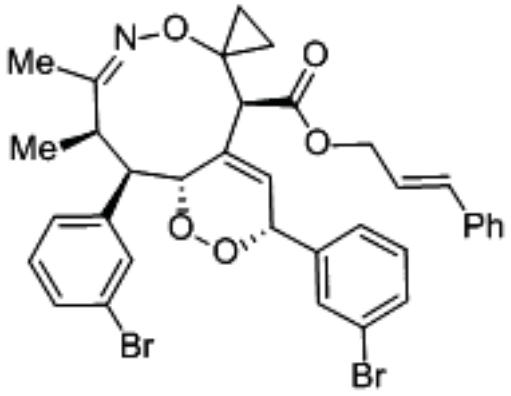
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***cis*-3fa**

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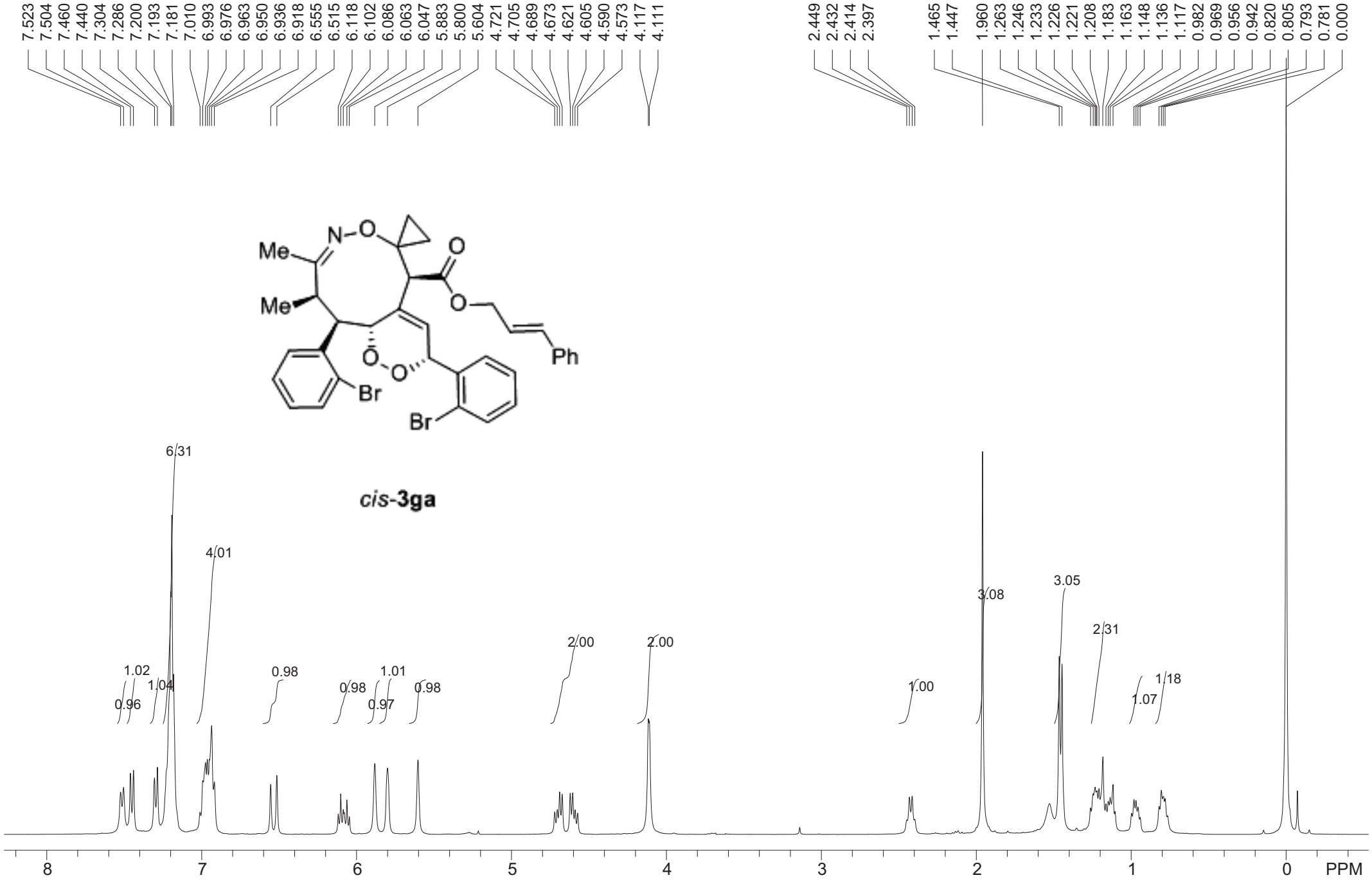
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Ph
Br
Br
cis-3ga
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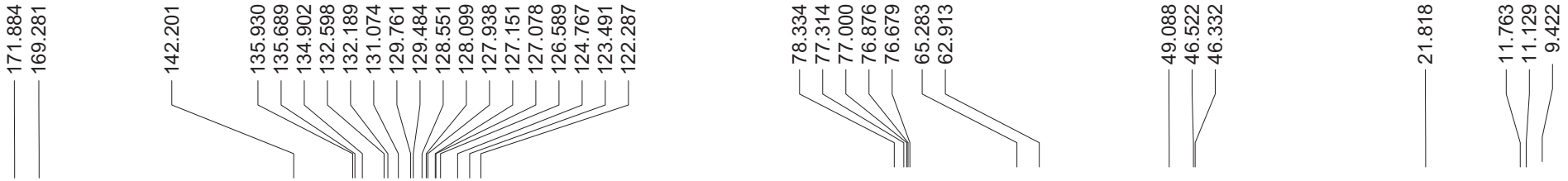
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127.078
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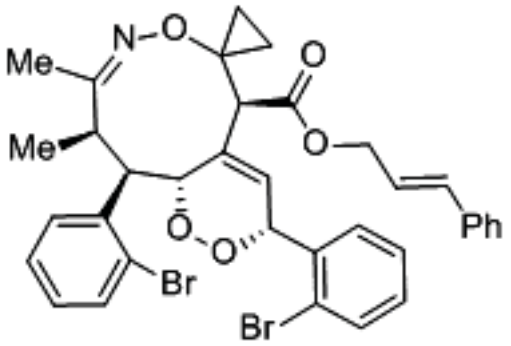
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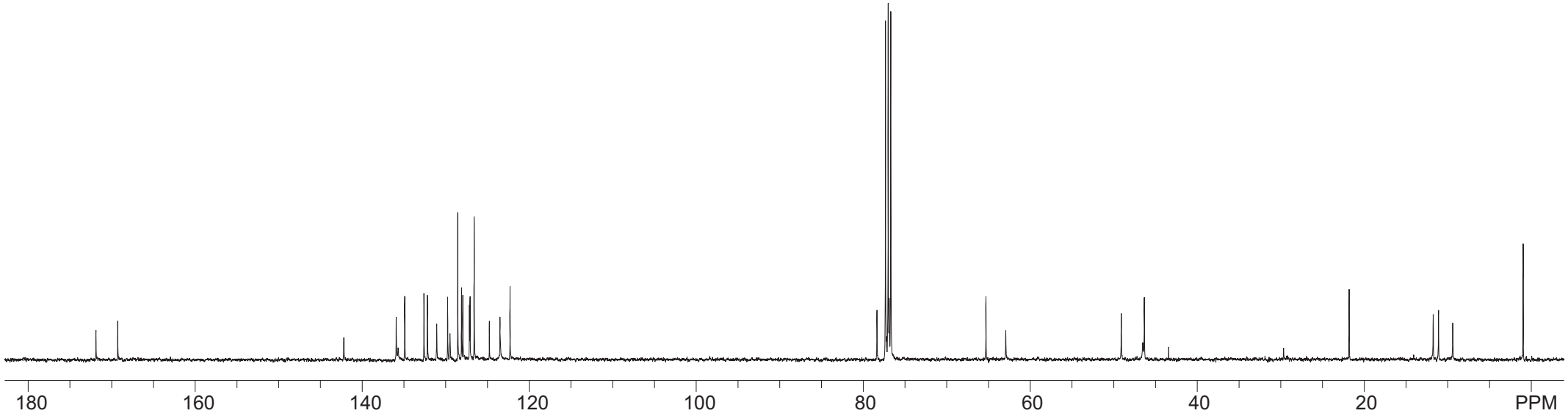
Br

cis-**3ga**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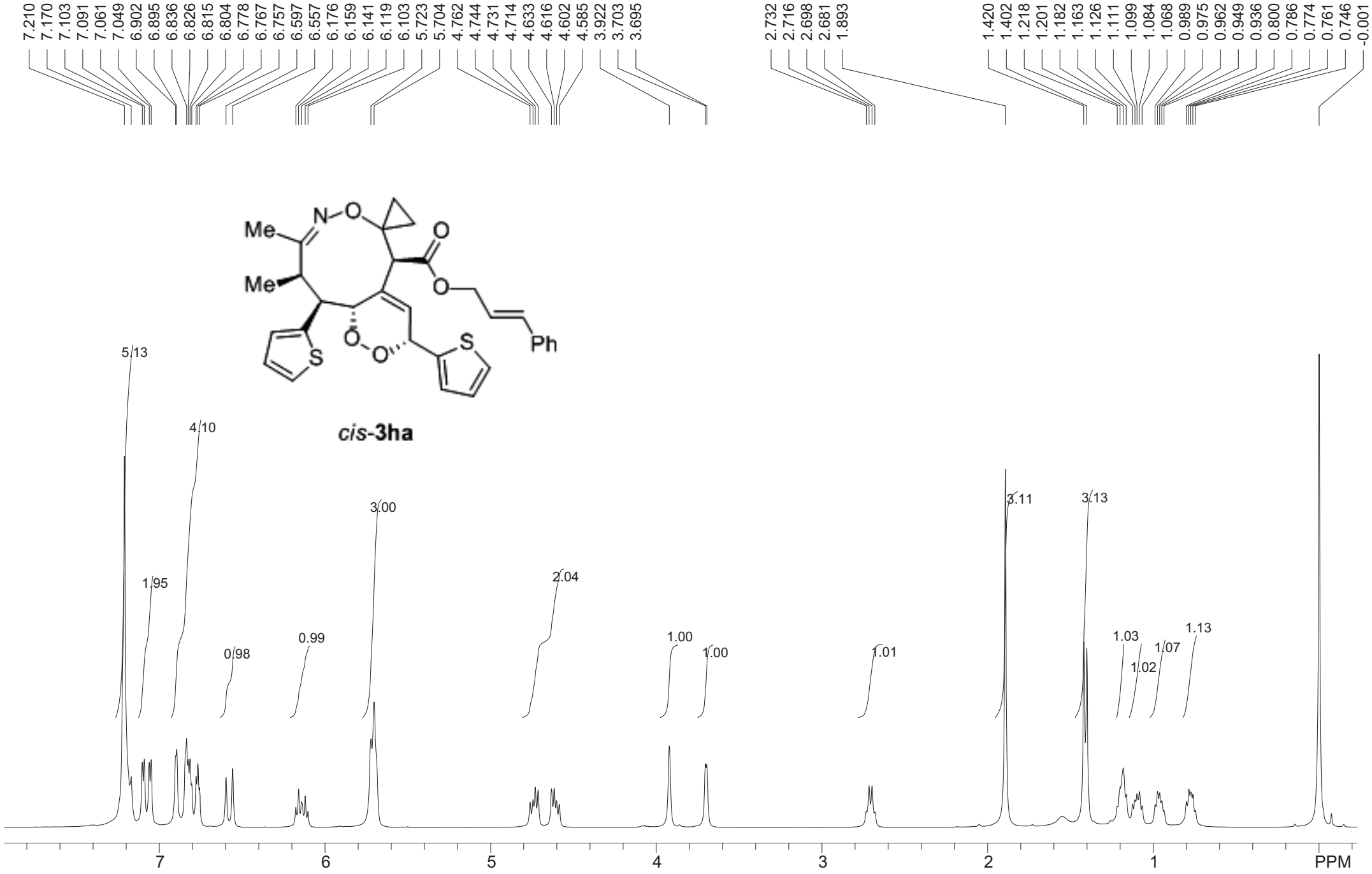
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cis-3ha
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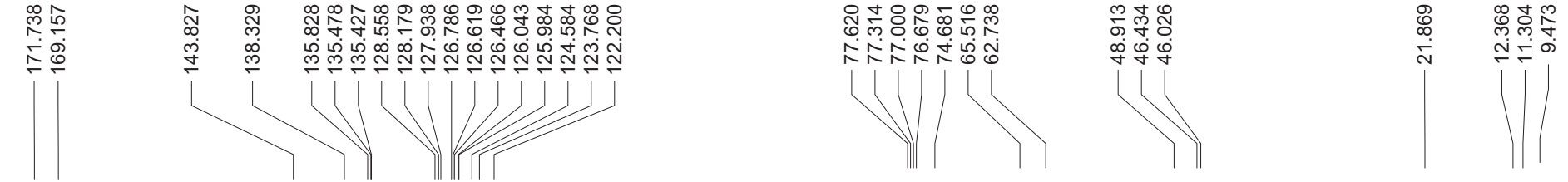
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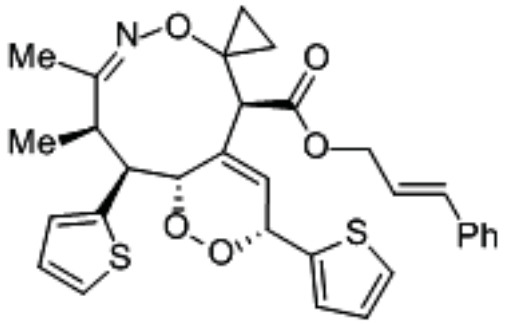
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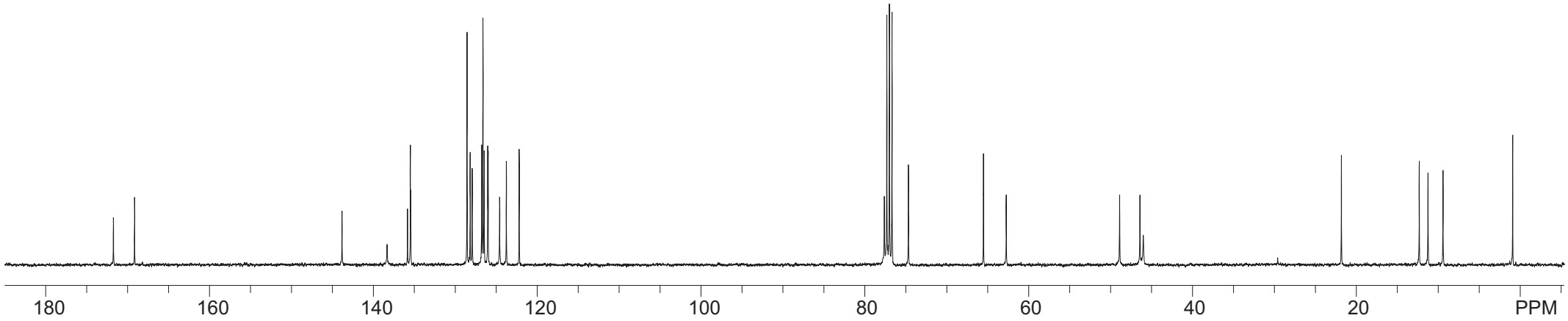
***cis*-3ha**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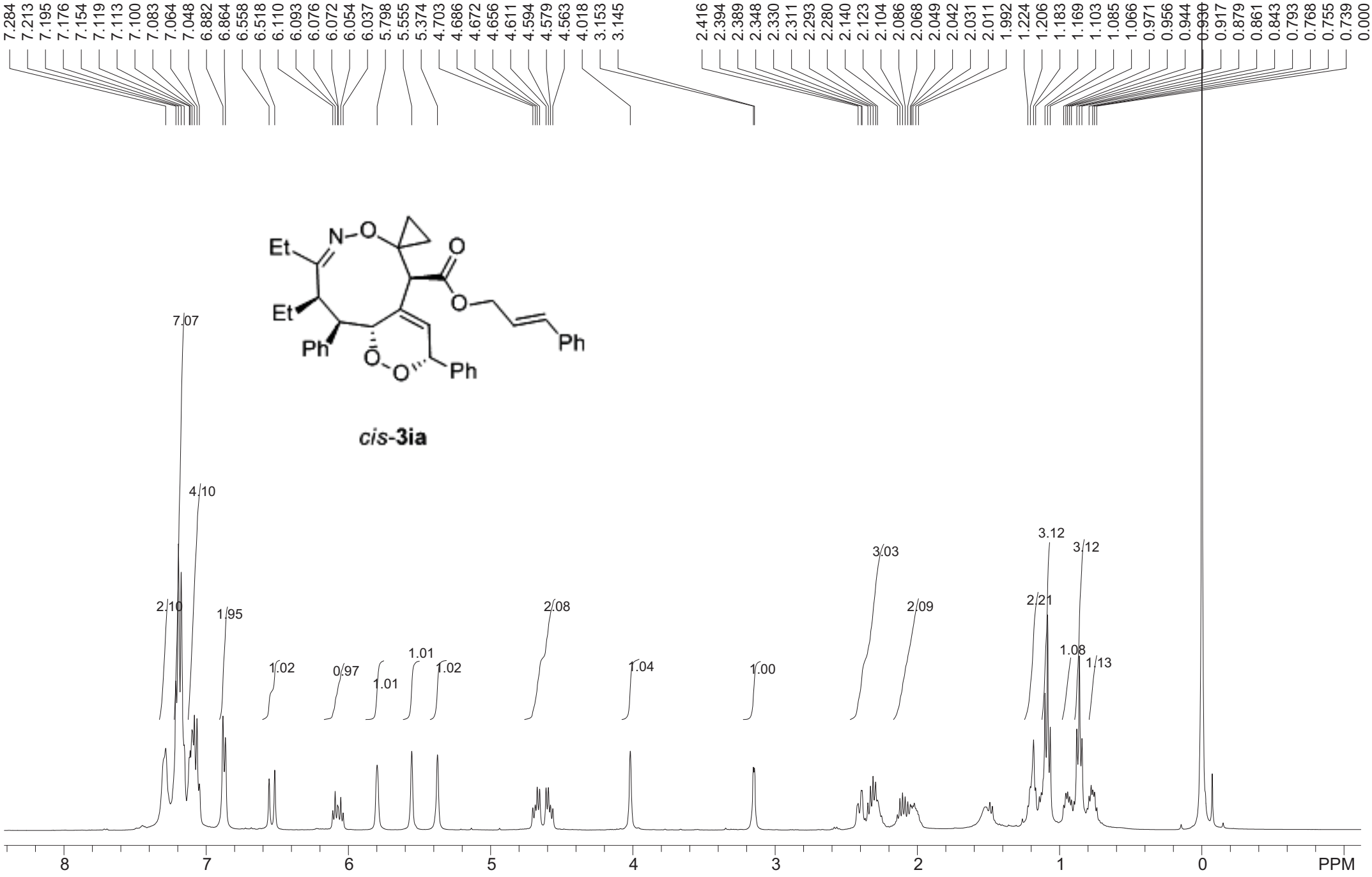
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Et
Ph
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Ph
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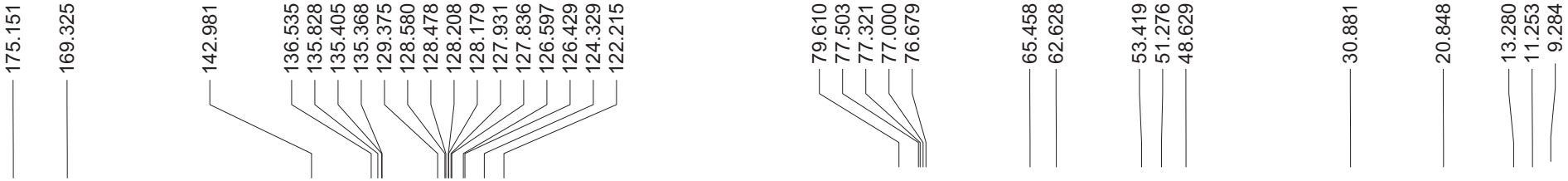
cis-**3ia**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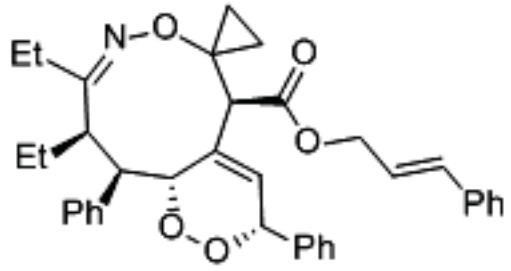
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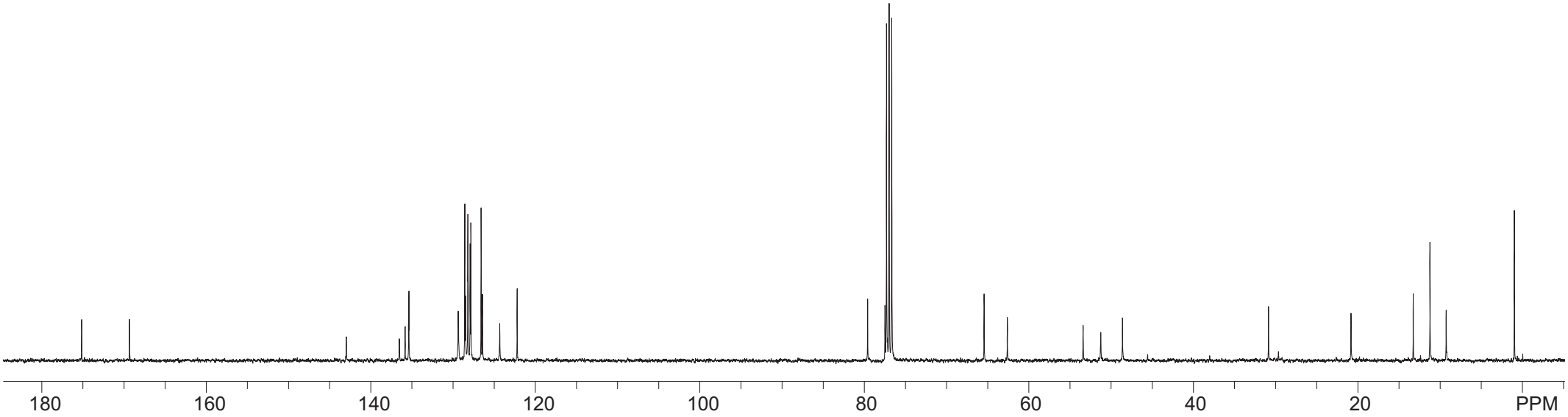
***cis*-3ia**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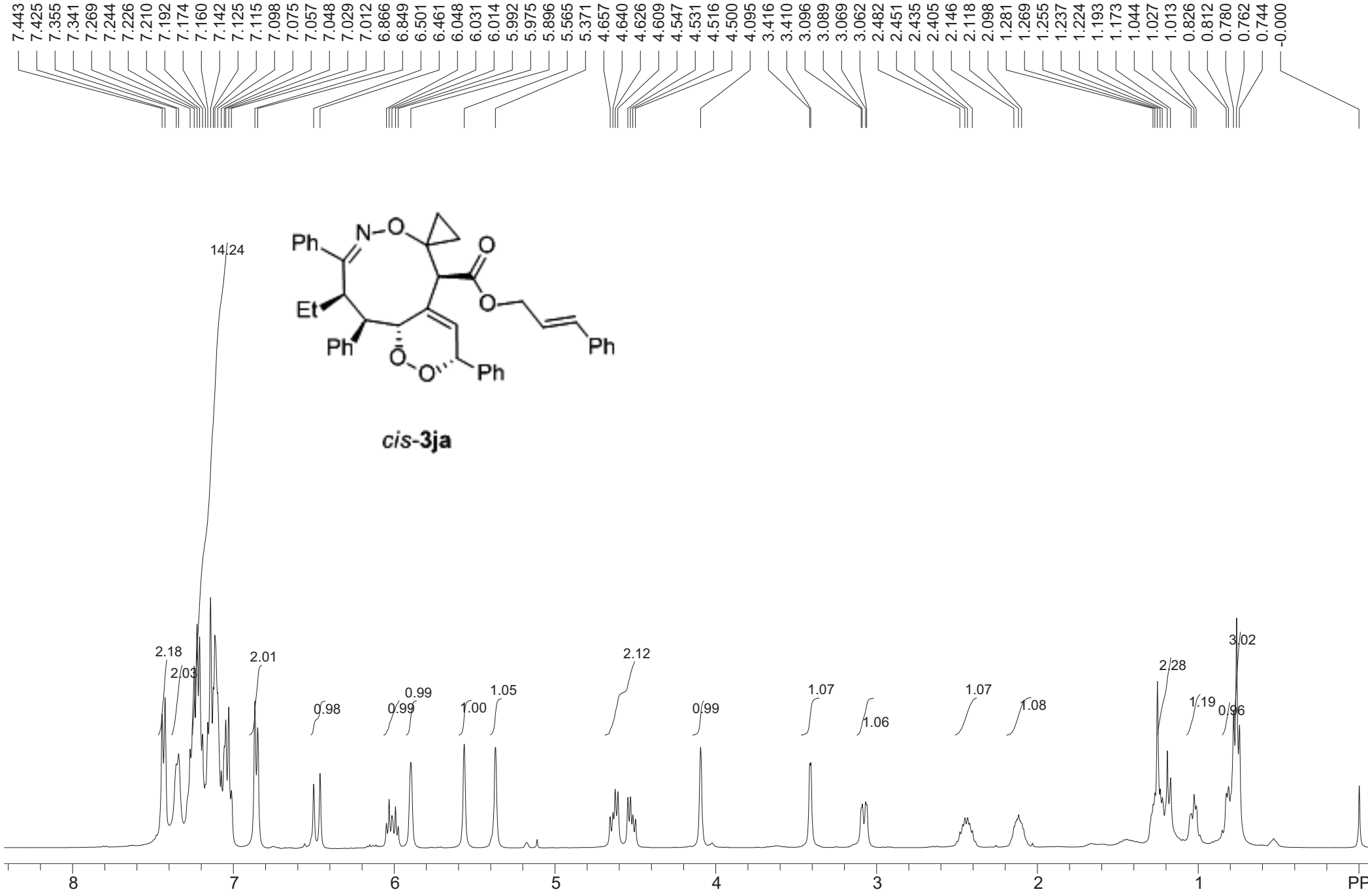
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cis-3ja
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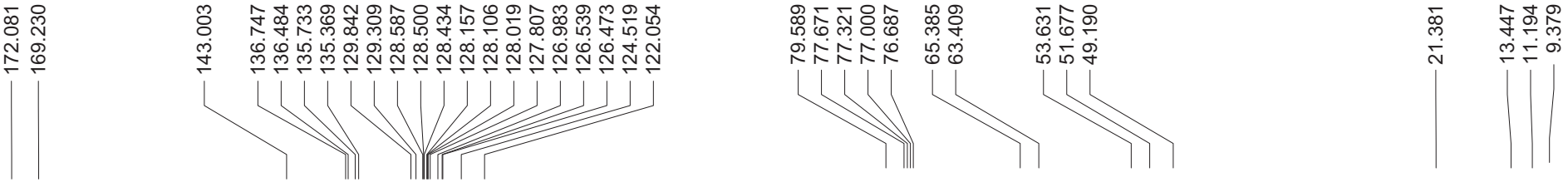
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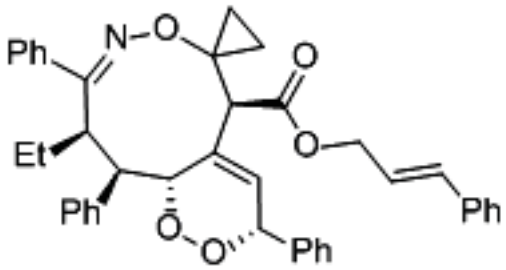
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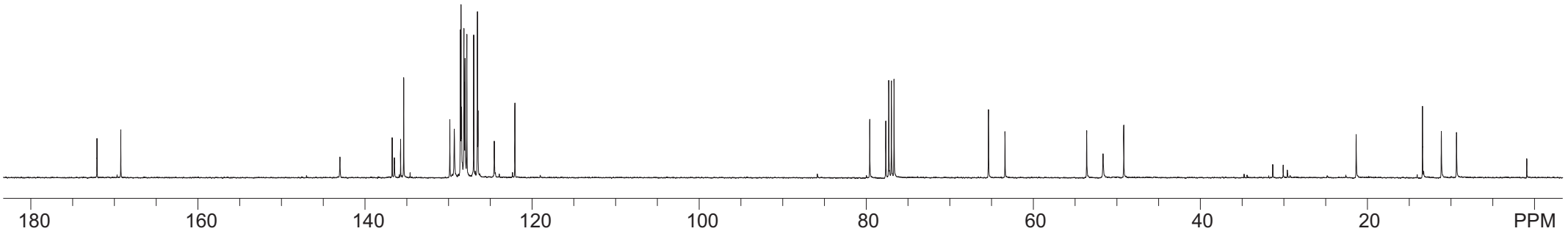
***cis*-3ja**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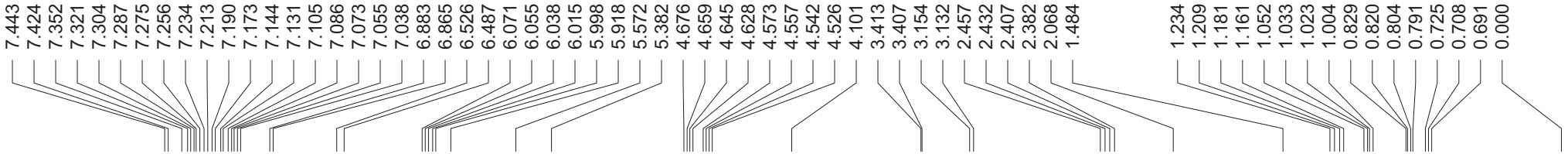
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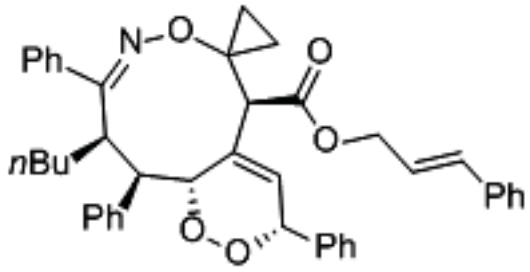
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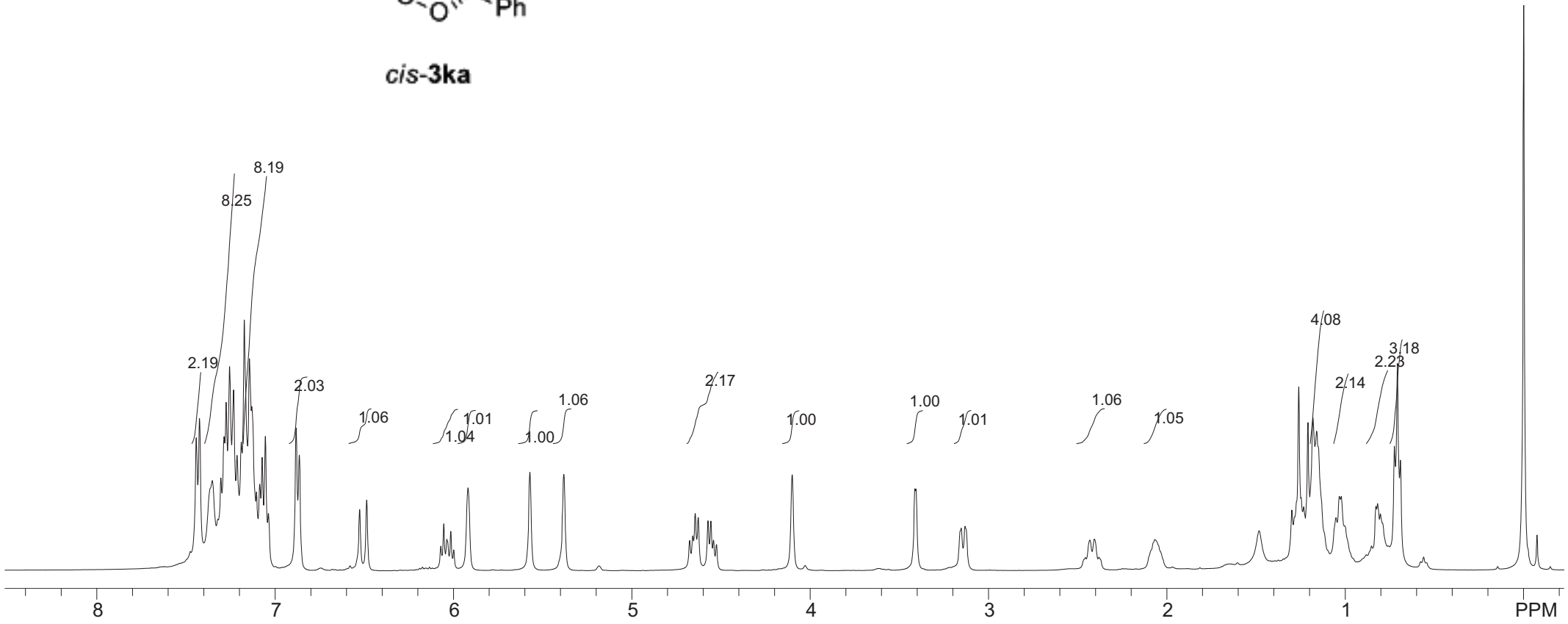
cis-**3ka**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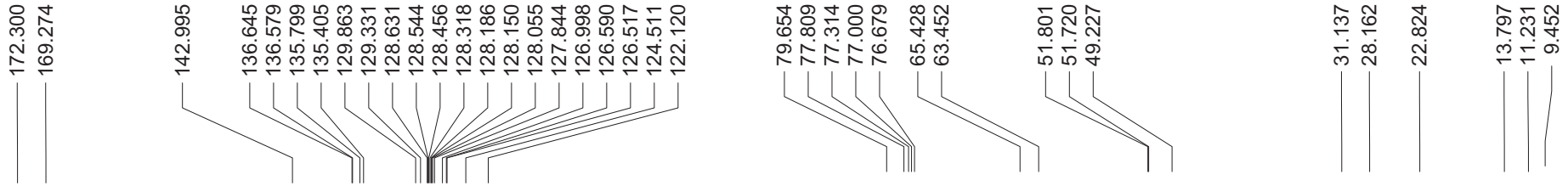
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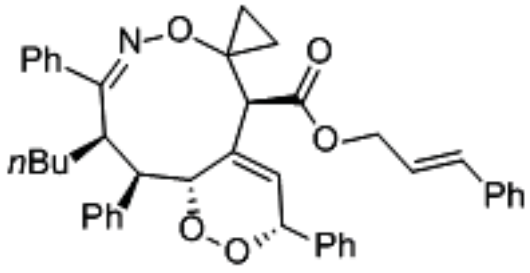
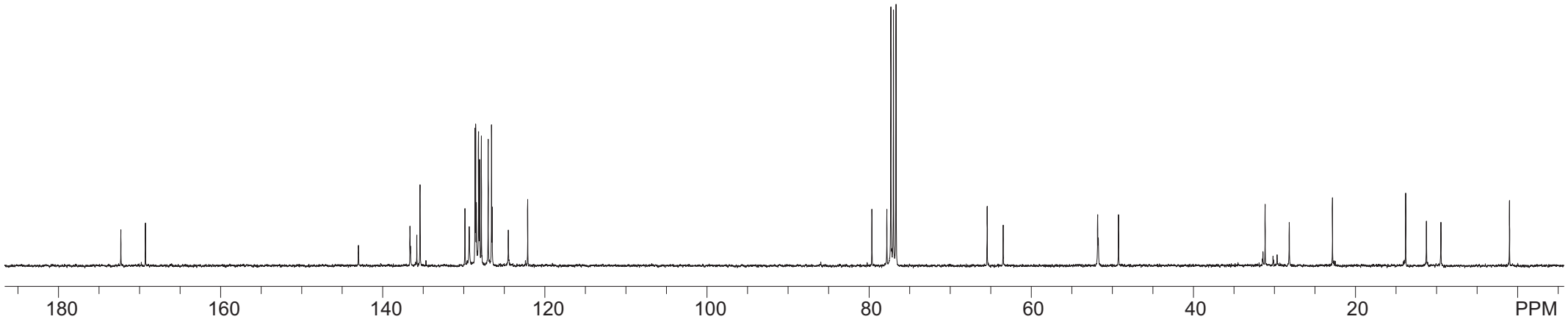
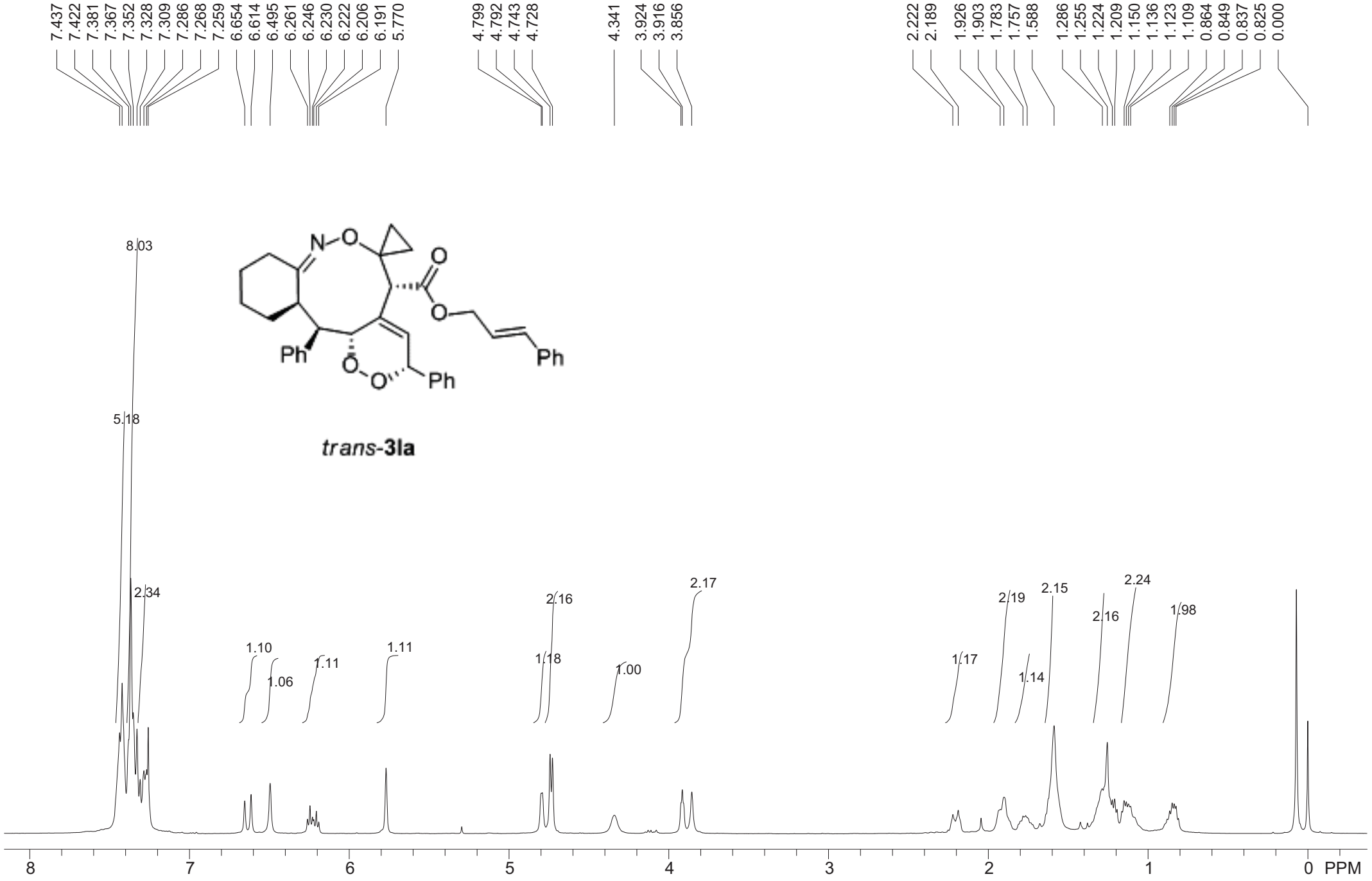
128.150
128.055
127.844
126.998
126.590
126.517
124.511
122.120
79.654
77.809
77.314
77.000
76.679
65.428
63.452
51.801
51.720
49.227
31.137
28.162
22.824
13.797
11.231
9.452


Ph
N
O
O
O
nBu
Ph
O
O
Ph
Ph

***cis*-3ka**


180
160
140
120
100
80
60
40
20
PPM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7.422
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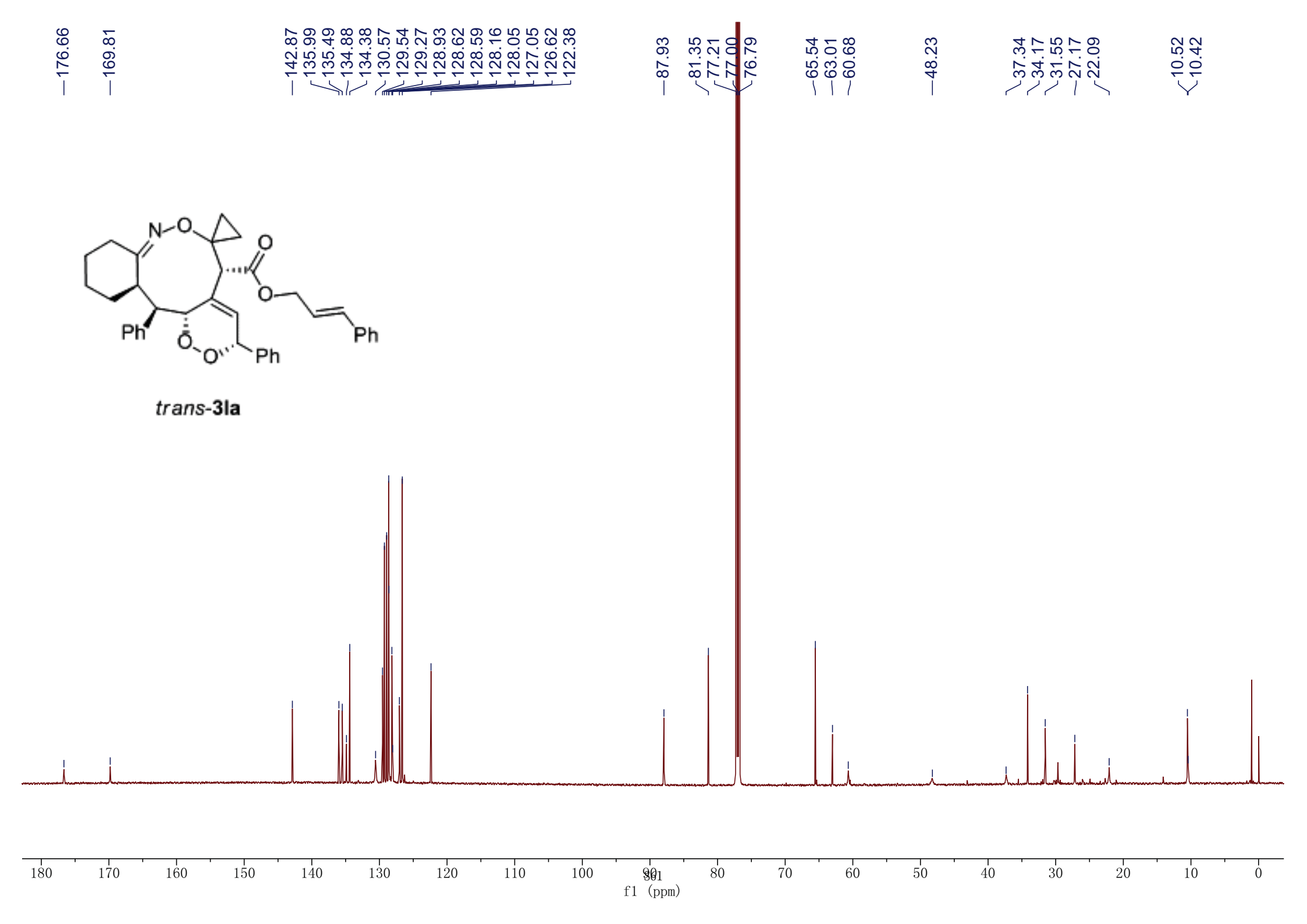
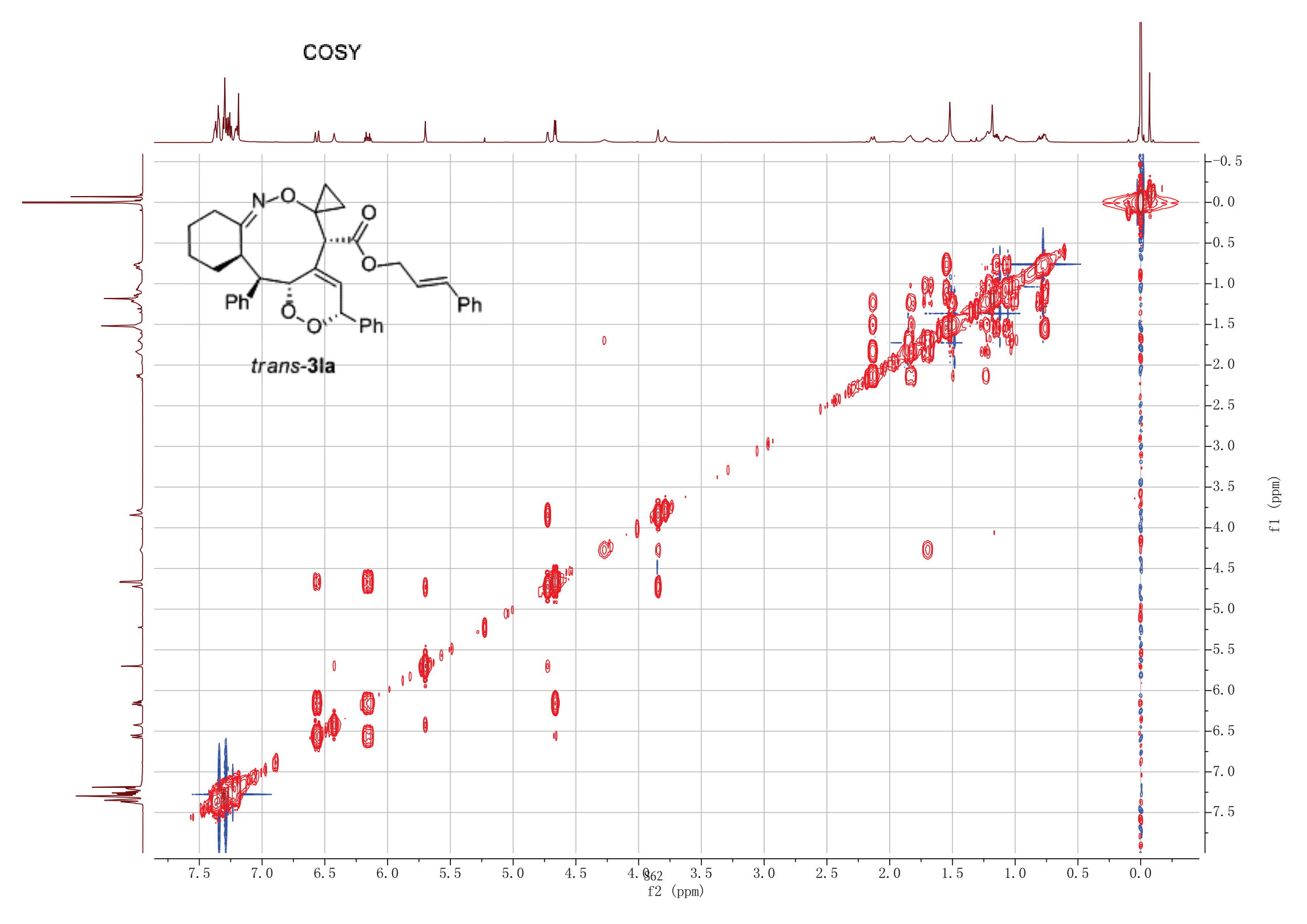
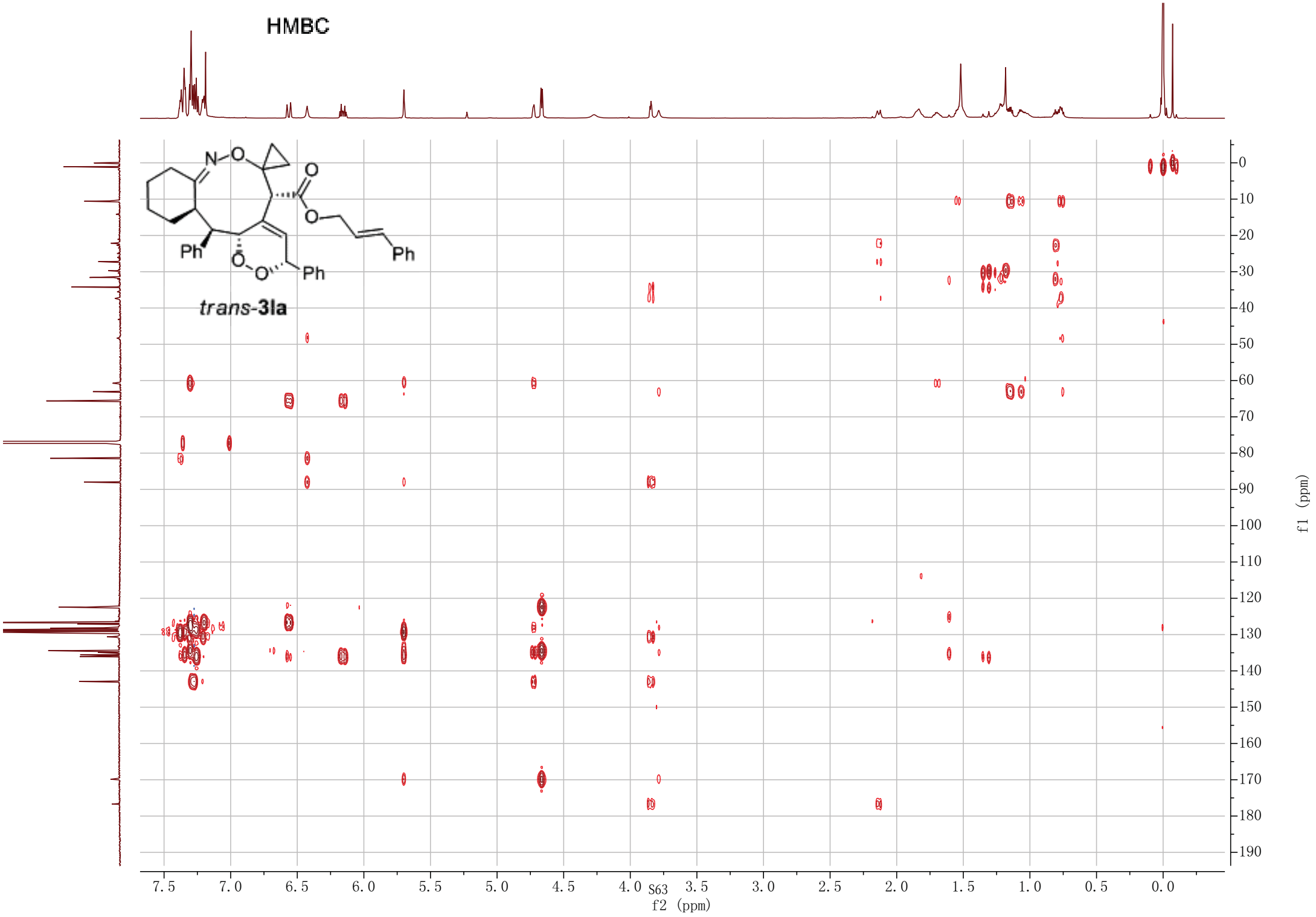
7.352
7.328
7.309
7.286
7.268
7.259
6.654
6.614
6.495
6.261
6.246
6.230
6.222
6.206
6.191
5.770
4.799
4.792
4.743
4.728
4.341
3.924
3.916
3.856
2.222
2.189
1.926
1.903
1.783
1.757
1.588
1.286
1.255
1.224
1.209
1.150
1.136
1.123
1.109
0.864
0.849
0.837
0.825
0.000
N
O
O
O
O
Ph
Ph
Ph
8.03
5.18
2.34
1.10
1.06
1.11
1.11
2.16
1.18
1.00
2.17
1.17
2.19
1.14
2.15
2.16
2.24
1.98
8
7
6
5
4
3
2
1
0
PPM

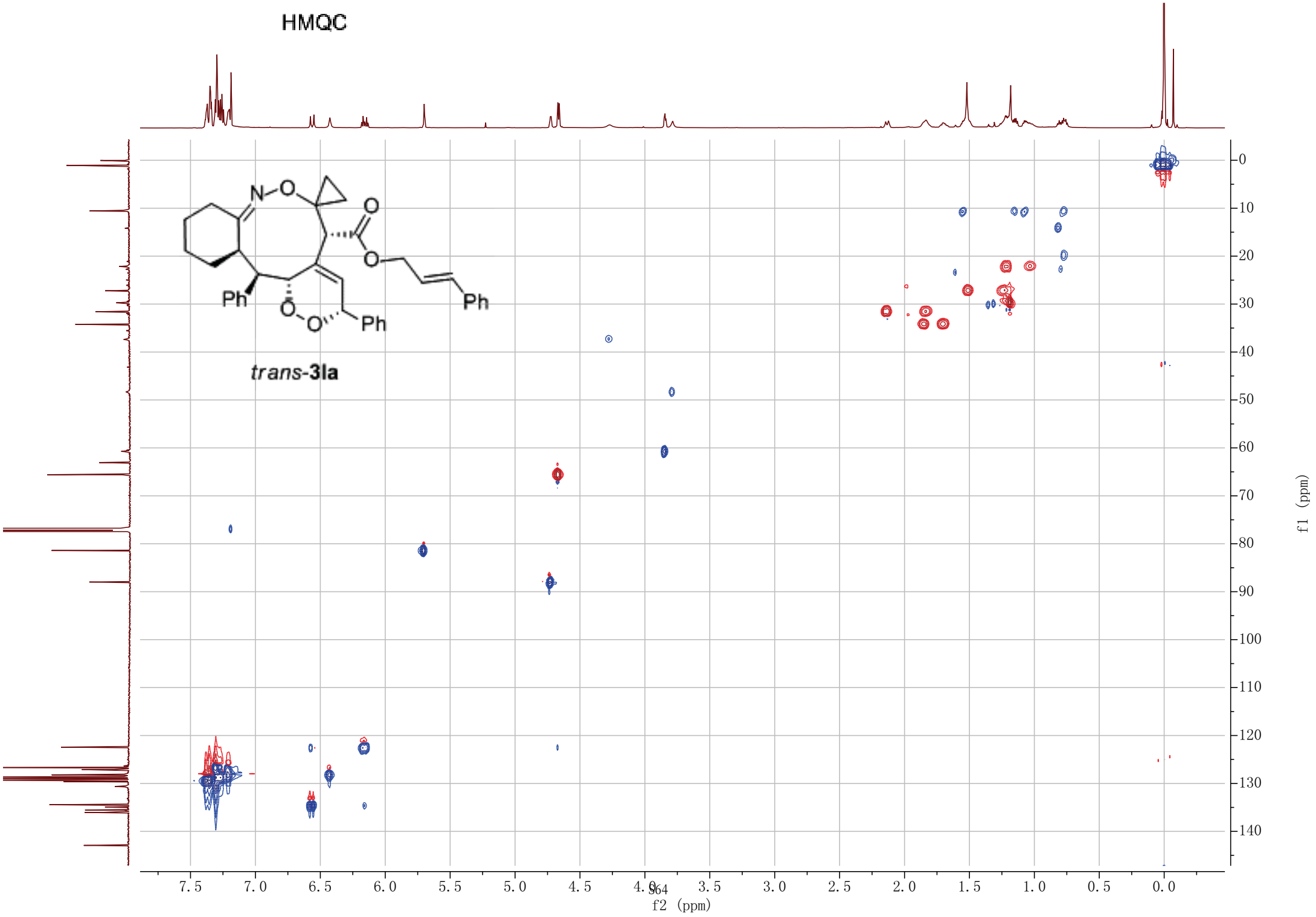
trans-**3la**

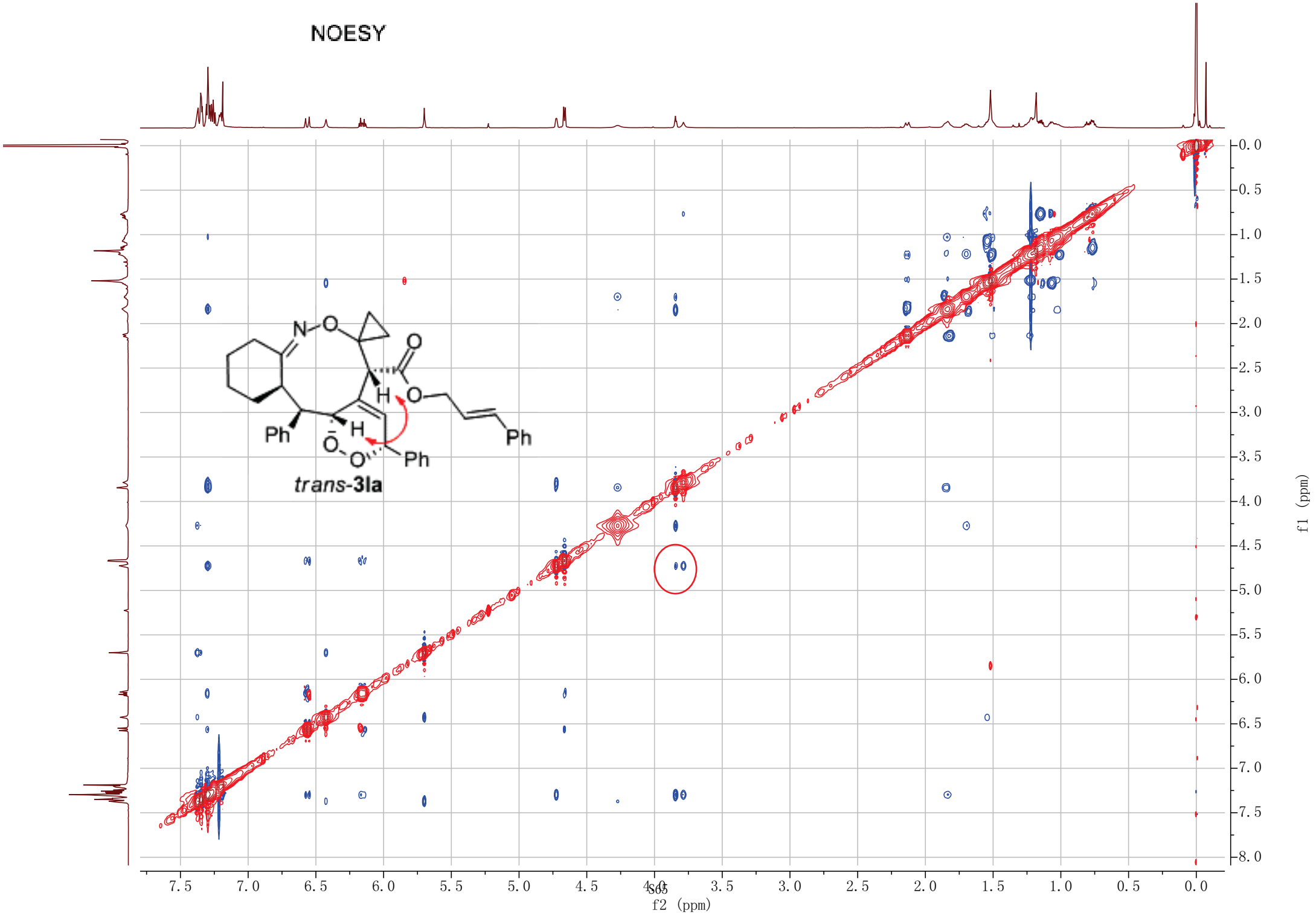

176.66
169.81
142.87
135.99
135.49
134.88
134.38
130.57
129.54
129.27
128.93
128.62
128.59
128.16
128.05
127.05
126.62
122.38
87.93
81.35
77.21
77.00
76.79
65.54
63.01
60.68
48.23
37.34
34.17
31.55
27.17
22.09
10.52
10.42
N
O
O
O
O
Ph
Ph
Ph
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

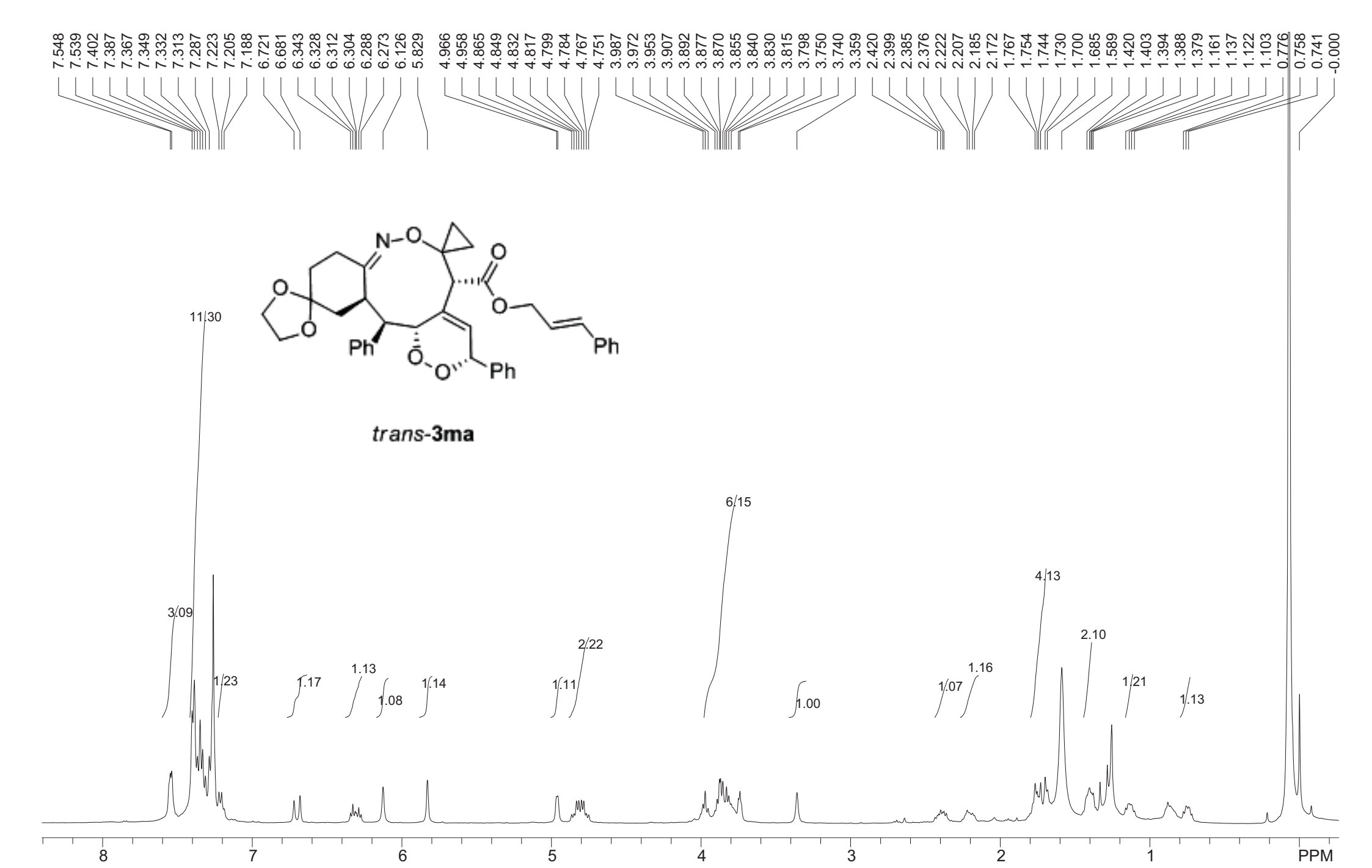
trans-**3la**


COSY
trans-3la
f2 (ppm)
f1 (ppm)

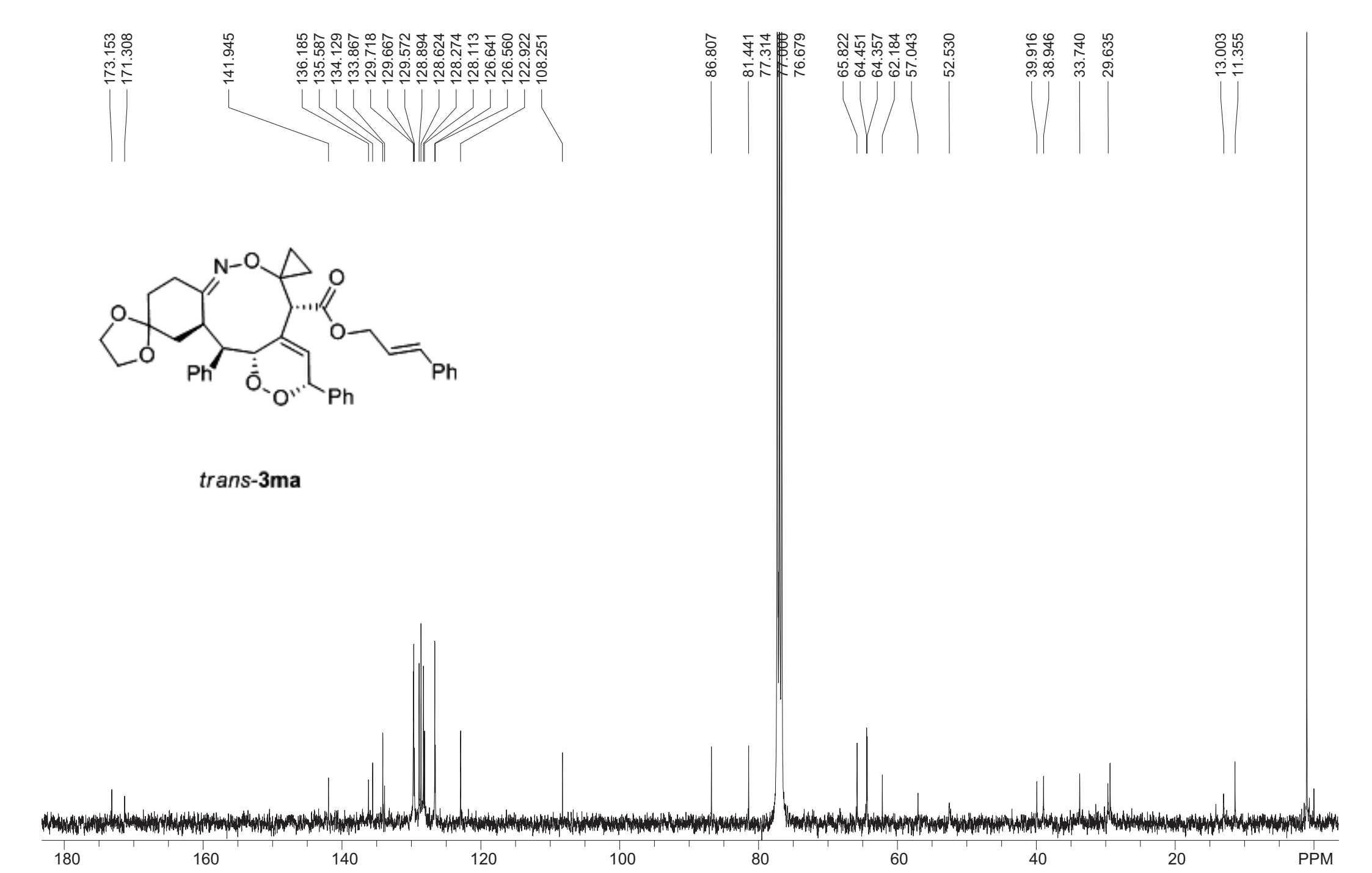

HMBC
trans-3la
f2 (ppm)
f1 (ppm)
S63


HMQC
N
O
O
O
O
Ph
Ph
Ph
trans-3la
f2 (ppm)
f1 (ppm)

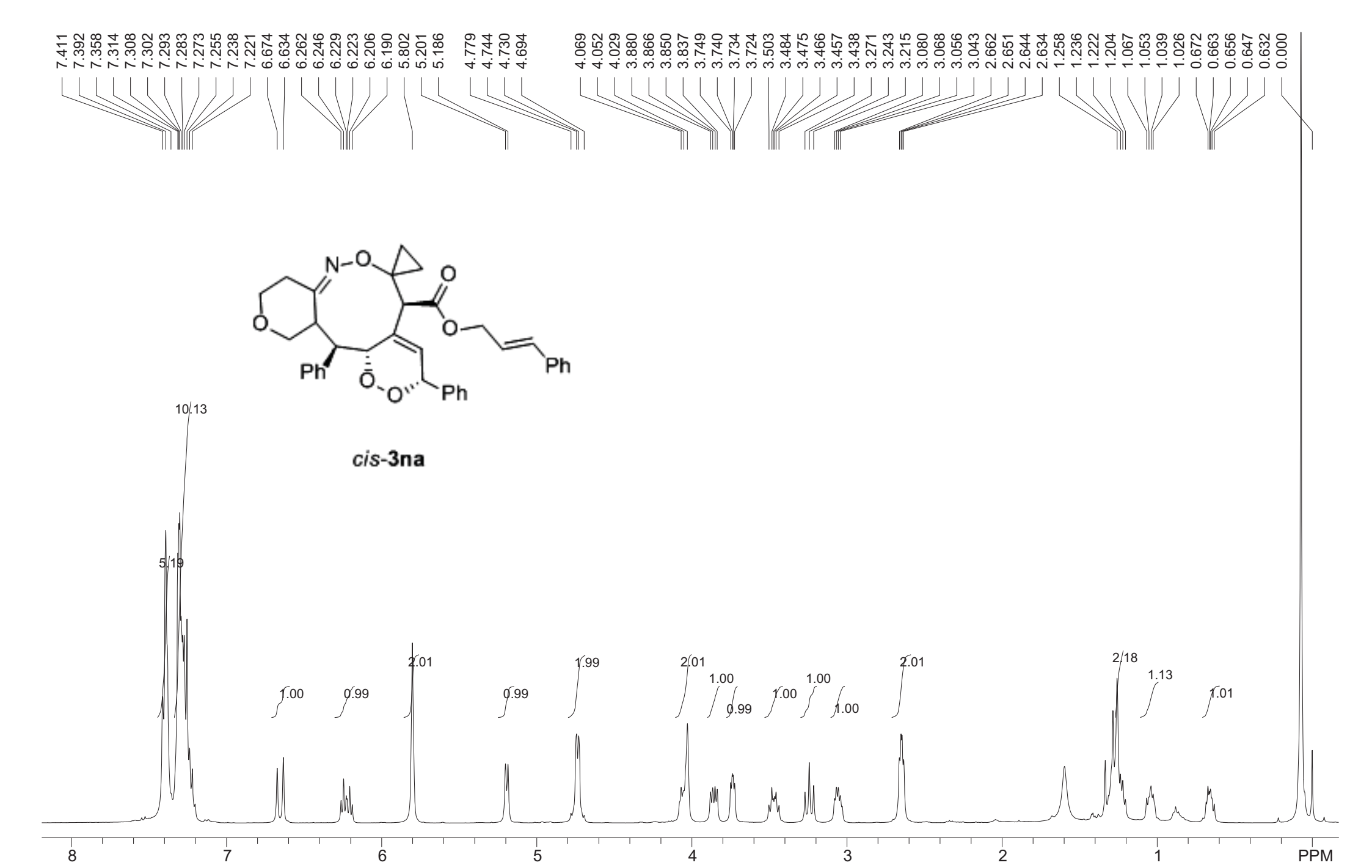

NOESY
N
O
O
H
O
Ph
H
Ph
O
O
Ph
trans-3la
f2 (ppm)
f1 (ppm)


7.548 7.539 7.402 7.387 7.367 7.349 7.332 7.313 7.287 7.223 7.205 7.188 6.721 6.681 6.343 6.328 6.312 6.304 6.288 6.273 6.126 5.829 4.966 4.958 4.865 4.849 4.832 4.817 4.799 4.784 4.767 4.751 3.987 3.972 3.953 3.907 3.892 3.877 3.870 3.855 3.840 3.830 3.815 3.798 3.750 3.740 3.359 2.420 2.399 2.385 2.376 2.222 2.207 2.185 2.172 1.767 1.754 1.744 1.730 1.700 1.685 1.589 1.420 1.403 1.394 1.388 1.379 1.161 1.137 1.122 1.103 0.776 0.758 0.741 -0.000
N
O
O
O
O
O
Ph
O
O
Ph
Ph
11.30
3.09
1.23
1.17
1.13
1.08
1.14
1.11
2.22
6.15
1.00
1.07
1.16
4.13
2.10
1.21
1.13
8
7
6
5
4
3
2
1
PPM

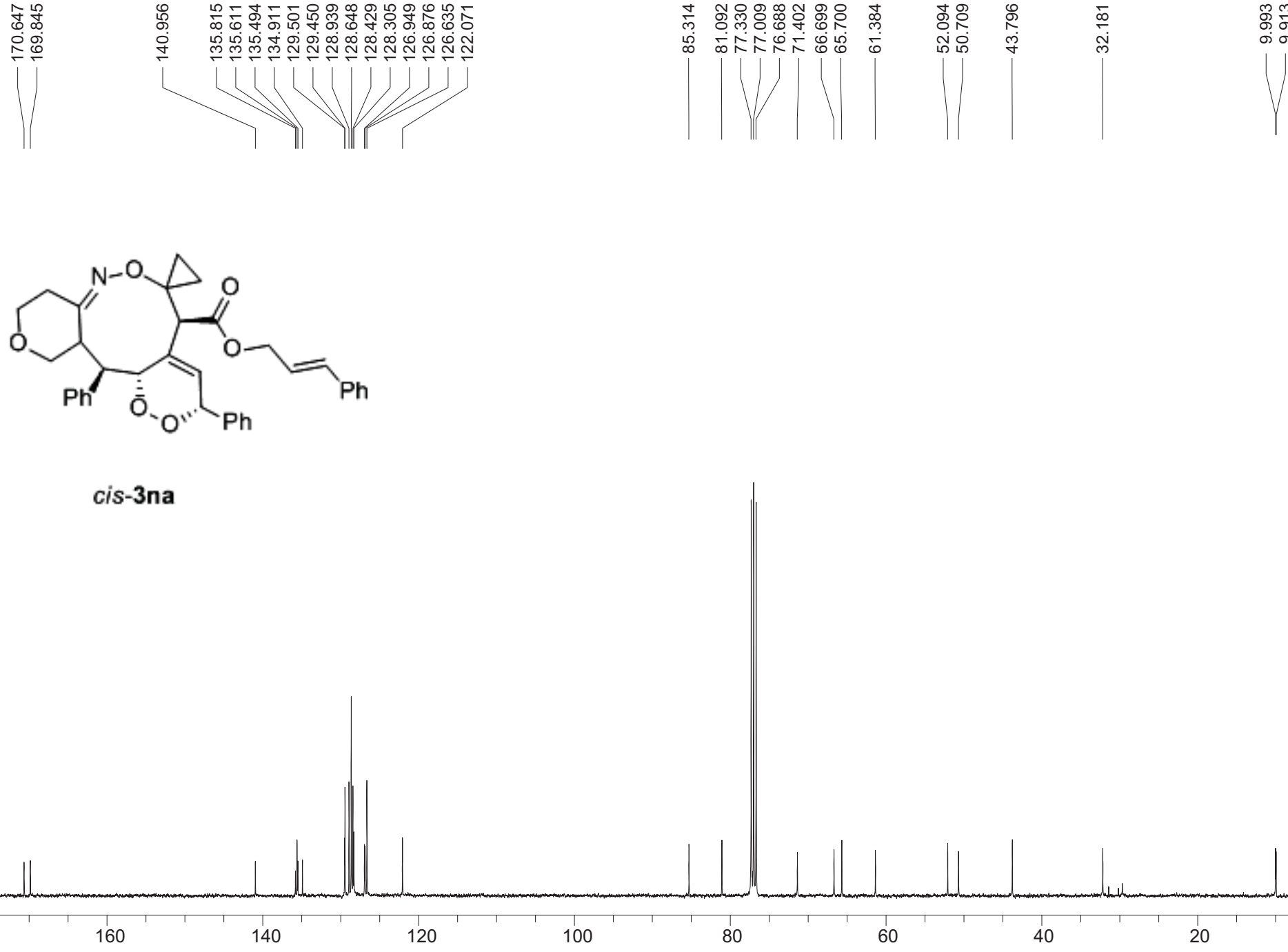
trans-**3ma**


173.153
171.308
141.945
136.185
135.587
134.129
133.867
129.718
129.667
129.572
128.894
128.624
128.274
128.113
126.641
126.560
122.922
108.251
86.807
81.441
77.314
77.000
76.679
65.822
64.451
64.357
62.184
57.043
52.530
39.916
38.946
33.740
29.635
13.003
11.355
N
O
O
O
O
O
O
Ph
Ph
Ph
180
160
140
120
100
80
60
40
20
PPM

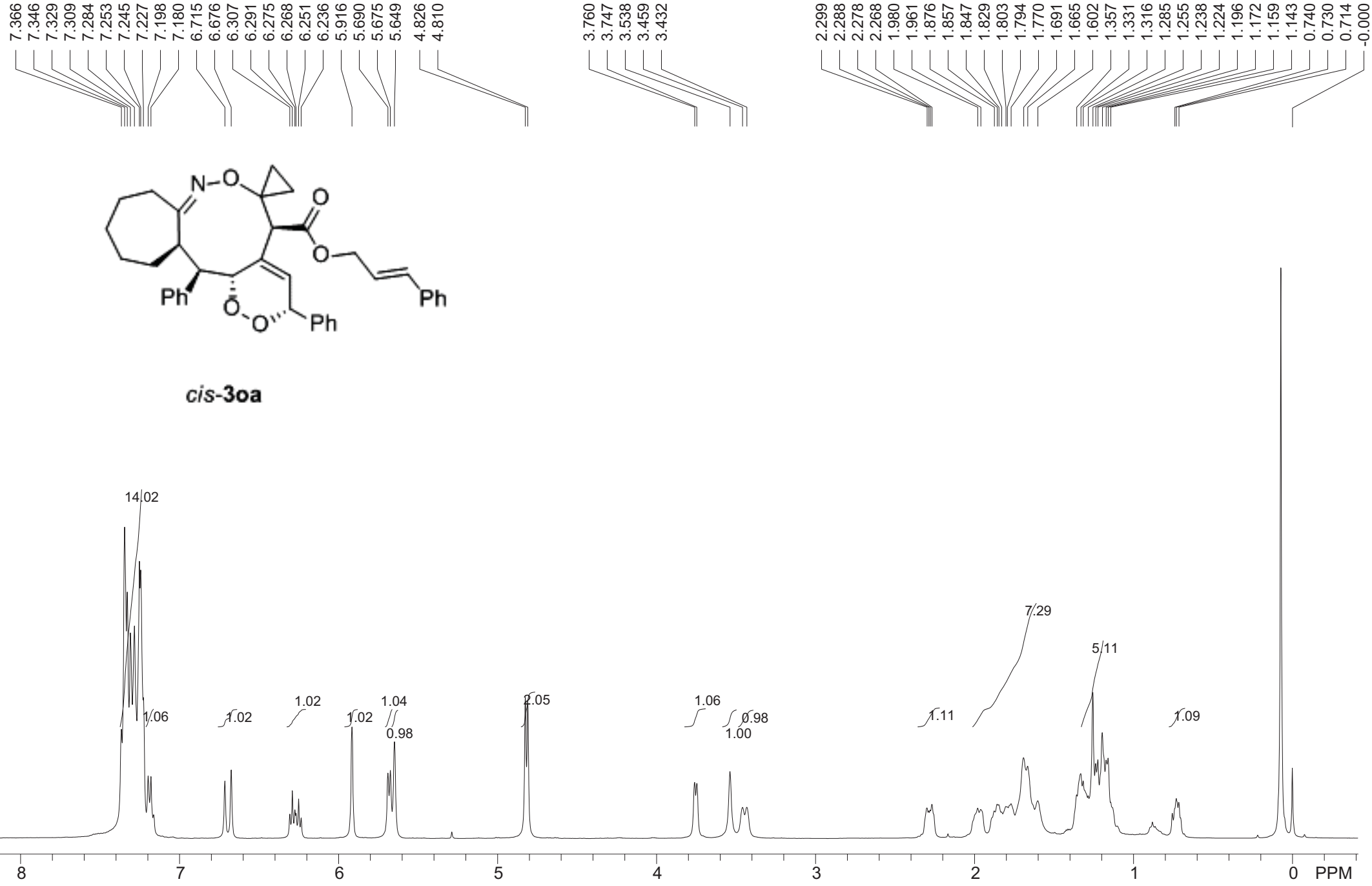
trans-**3ma**


7.411
7.392
7.358
7.314
7.308
7.302
7.293
7.283
7.273
7.255
7.238
7.221
6.674
6.634
6.262
6.246
6.229
6.223
6.206
6.190
5.802
5.201
5.186
4.779
4.744
4.730
4.694
4.069
4.052
4.029
3.880
3.866
3.850
3.837
3.749
3.740
3.734
3.724
3.503
3.484
3.475
3.466
3.457
3.438
3.271
3.243
3.215
3.080
3.068
3.056
3.043
2.662
2.651
2.644
2.634
1.258
1.236
1.222
1.204
1.067
1.053
1.039
1.026
0.672
0.663
0.656
0.647
0.632
0.000
N
O
O
O
O
Ph
Ph
Ph
10.13
5.19
1.00
0.99
2.01
0.99
1.99
2.01
1.00
0.99
1.00
1.00
1.00
2.01
2.18
1.13
1.01
8
7
6
5
4
3
2
1
PPM

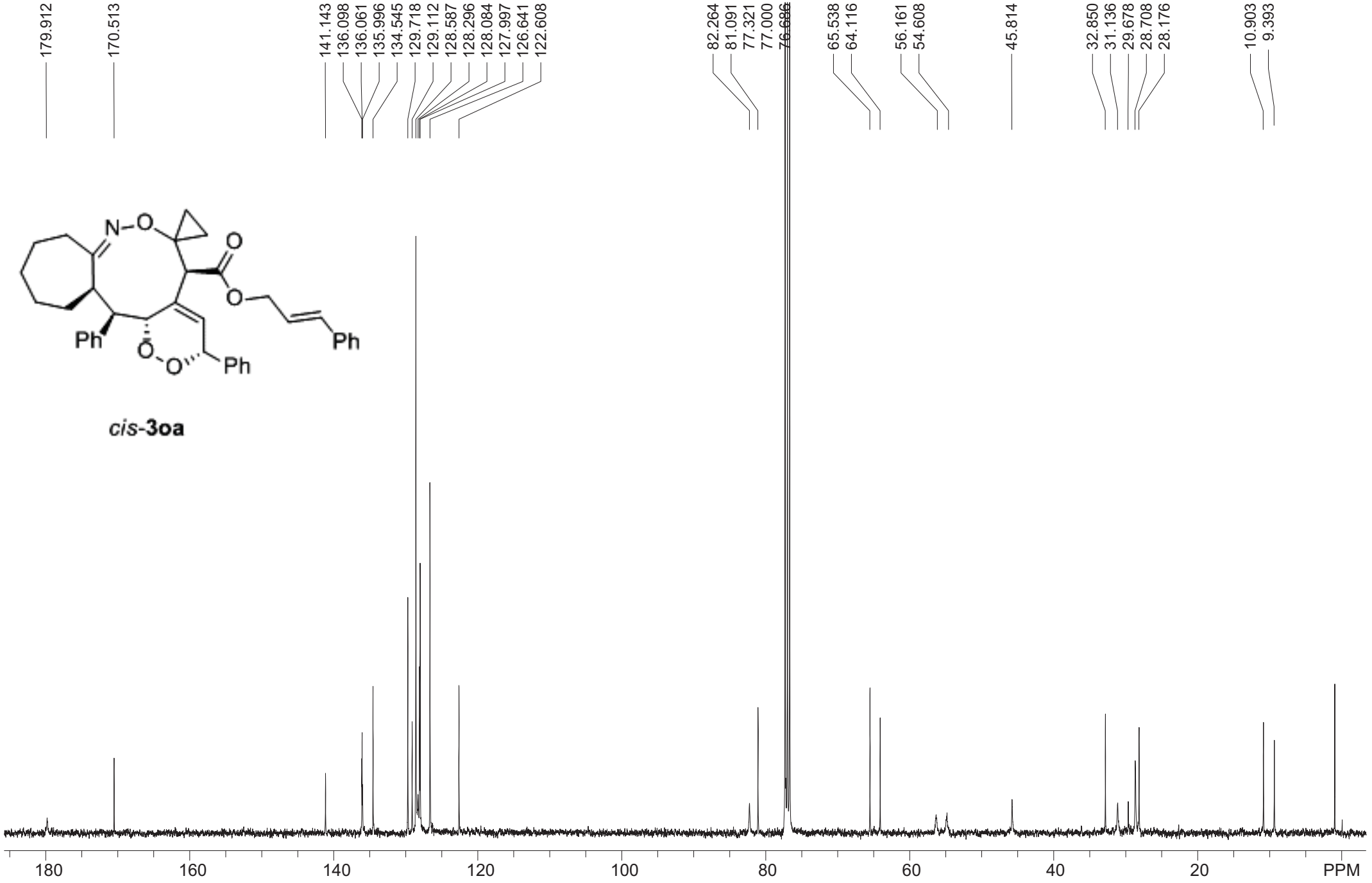
cis-**3na**


170.647
169.845
140.956
135.815
135.611
135.494
134.911
129.501
129.450
128.939
128.648
128.429
128.305
126.949
126.876
126.635
122.071
85.314
81.092
77.330
77.009
76.688
71.402
66.699
65.700
61.384
52.094
50.709
43.796
32.181
9.993
9.913
N
O
O
O
O
Ph
Ph
Ph
180
160
140
120
100
80
60
40
20
PPM

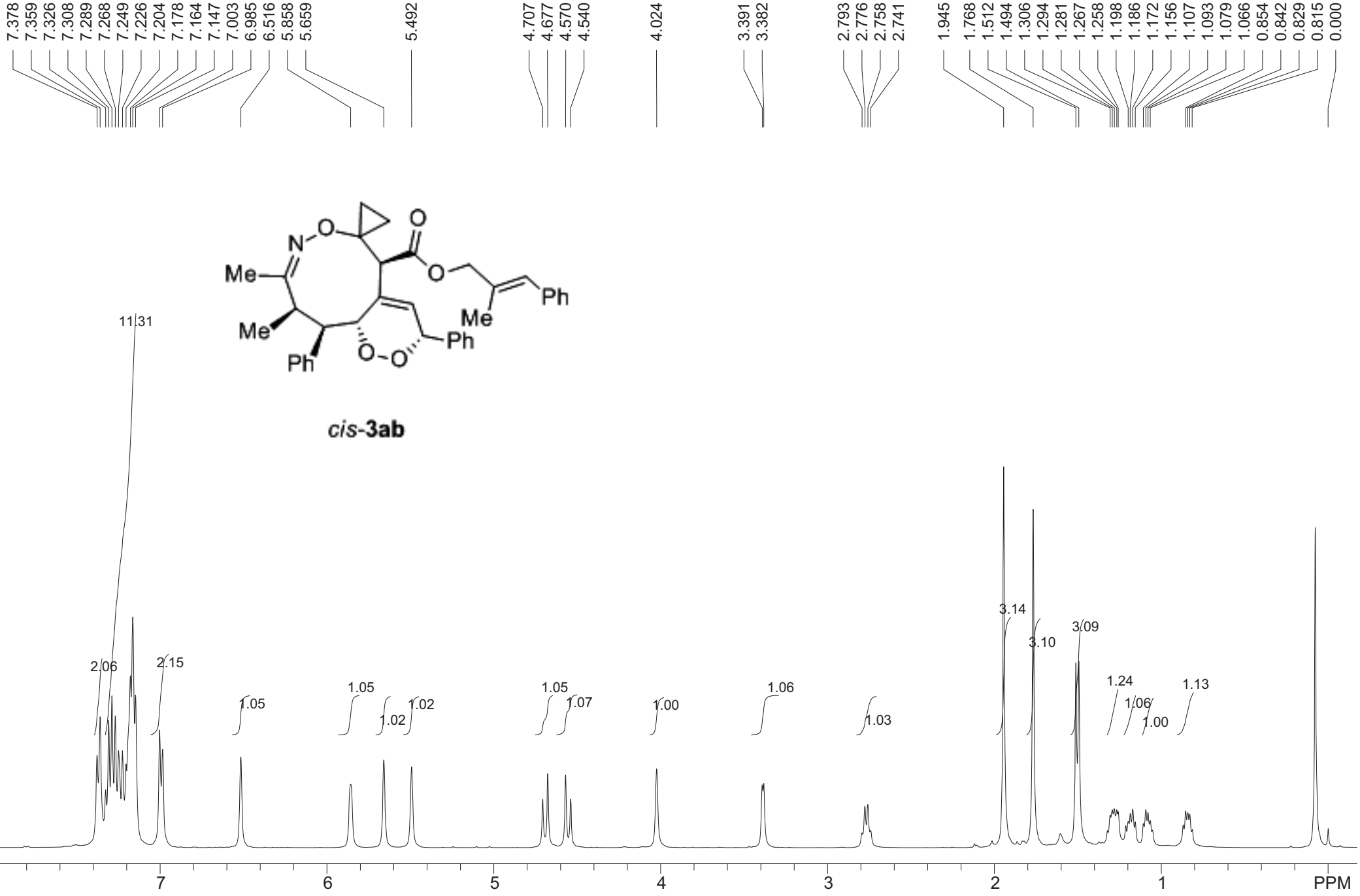
cis-**3na**


7.366
7.346
7.329
7.309
7.284
7.253
7.245
7.227
7.198
7.180
6.715
6.676
6.307
6.291
6.275
6.268
6.251
6.236
5.916
5.690
5.675
5.649
4.826
4.810
3.760
3.747
3.538
3.459
3.432
2.299
2.288
2.278
2.268
1.980
1.961
1.876
1.857
1.847
1.829
1.803
1.794
1.770
1.691
1.665
1.602
1.357
1.331
1.316
1.285
1.255
1.238
1.224
1.196
1.172
1.159
1.143
0.740
0.730
0.714
-0.000
N
O
O
O
Ph
O
O
Ph
Ph
14.02
1.06
1.02
1.02
1.02
1.04
0.98
2.05
1.06
0.98
1.00
1.11
7.29
5.11
1.09
8
7
6
5
4
3
2
1
0
PPM

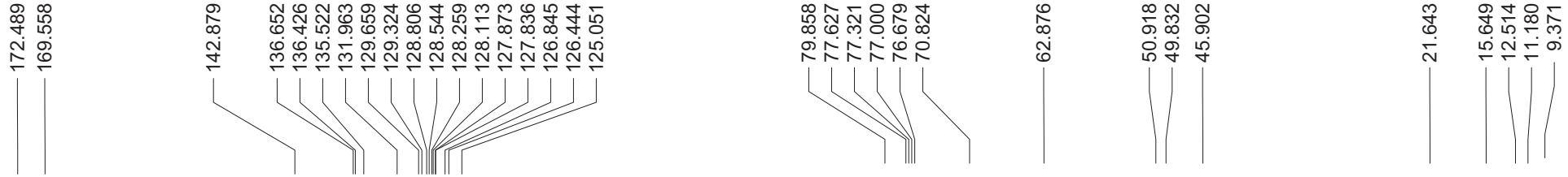
cis-**3oa**

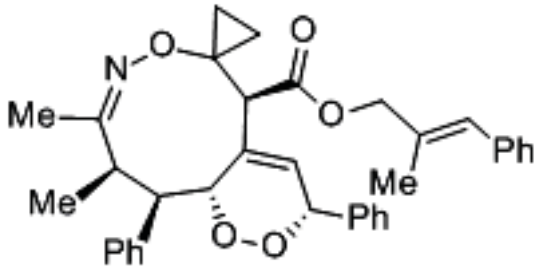

179.912
170.513
141.143
136.098
136.061
135.996
134.545
129.718
129.112
128.587
128.296
128.084
127.997
126.641
122.608
82.264
81.091
77.321
77.000
76.686
65.538
64.116
56.161
54.608
45.814
32.850
31.136
29.678
28.708
28.176
10.903
9.393
N
O
O
O
Ph
O
O
Ph
Ph
180
160
140
120
100
80
60
40
20
PPM

cis-**3oa**

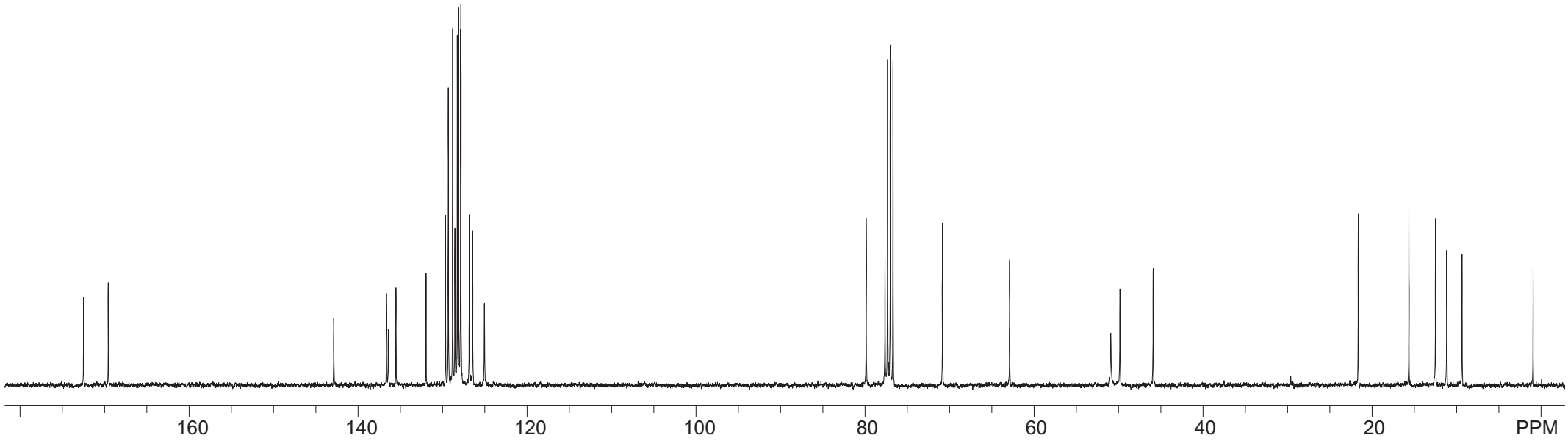

7.378
7.359
7.326
7.308
7.289
7.268
7.249
7.226
7.204
7.178
7.164
7.147
7.003
6.985
6.516
5.858
5.659
5.492
4.707
4.677
4.570
4.540
4.024
3.391
3.382
2.793
2.776
2.758
2.741
1.945
1.768
1.512
1.494
1.306
1.294
1.281
1.267
1.258
1.198
1.186
1.172
1.156
1.107
1.093
1.079
1.066
0.854
0.842
0.829
0.815
0.000
N
O
O
O
Me
Me
Ph
Me
Ph
Ph
O-O
11.31
2.06
2.15
1.05
1.05
1.02
1.02
1.05
1.07
1.00
1.06
1.03
3.14
3.10
3.09
1.24
1.06
1.00
1.13
8
7
6
5
4
3
2
1
PPM

cis-**3ab**

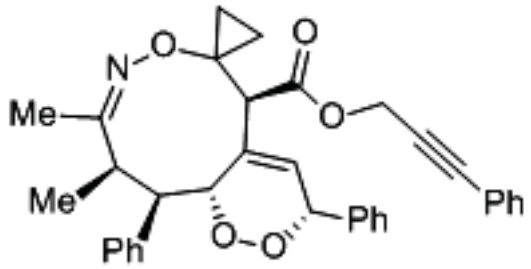

172.489
169.558
142.879
136.652
136.426
135.522
131.963
129.659
129.324
128.806
128.544
128.259
128.113
127.873
127.836
126.845
126.444
125.051
79.858
77.627
77.321
77.000
76.679
70.824
62.876
50.918
49.832
45.902
21.643
15.649
12.514
11.180
9.371


N
O
O
O
Me
Me
Ph
Ph
Me
Ph
O
O

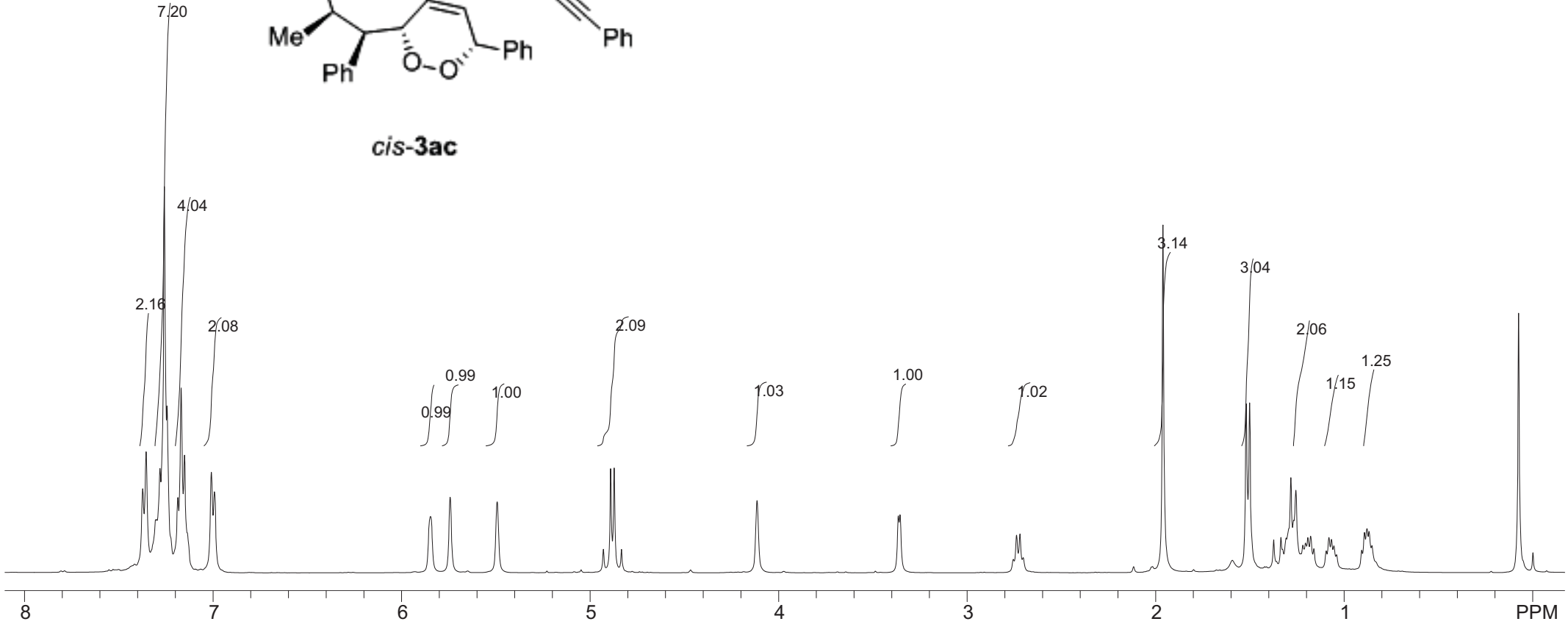
***cis*-3ab**

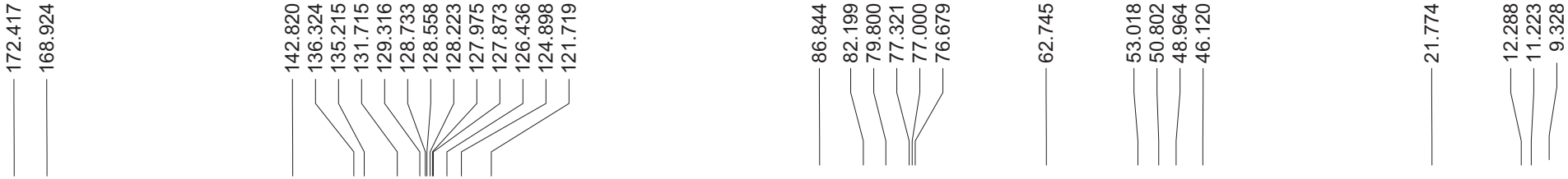

160
140
120
100
80
60
40
20
PPM

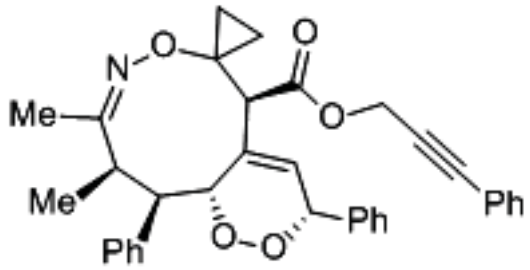

7.374
7.355
7.305
7.300
7.282
7.259
7.244
7.187
7.169
7.151
7.137
7.009
6.993
5.847
5.742
5.493
4.930
4.891
4.872
4.834
4.114
3.365
3.356
2.755
2.738
2.720
2.703
1.961
1.520
1.502
1.269
1.257
1.206
1.194
1.178
1.162
1.096
1.081
1.068
1.041
0.893
0.880
0.868
0.853
0.000


N
O
O
Me
Me
Ph
Ph
O
O
Ph
Ph

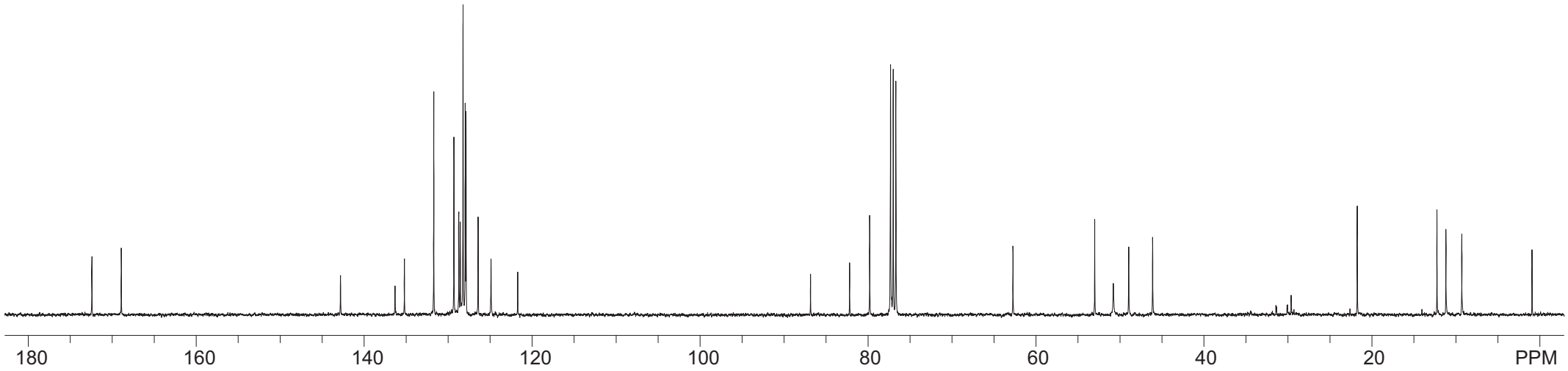
cis-**3ac**

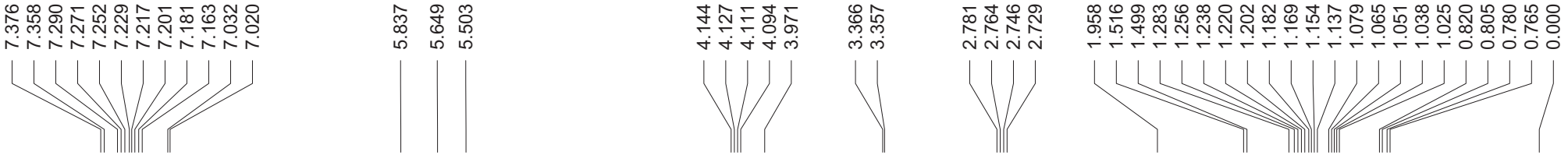

7.20
4.04
2.16
2.08
0.99
0.99
1.00
2.09
1.03
1.00
1.02
3.14
3.04
2.06
1.15
1.25
8
7
6
5
4
3
2
1
PPM

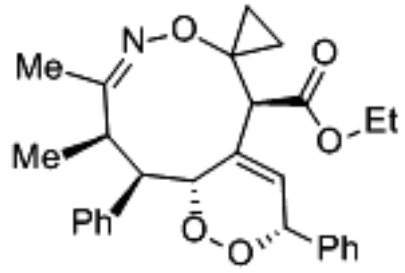

172.417
168.924
142.820
136.324
135.215
131.715
129.316
128.733
128.558
128.223
127.975
127.873
126.436
124.898
121.719
86.844
82.199
79.800
77.321
77.000
76.679
62.745
53.018
50.802
48.964
46.120
21.774
12.288
11.223
9.328


N
O
O
O
Me
Me
Ph
Ph
O
O
Ph
Ph

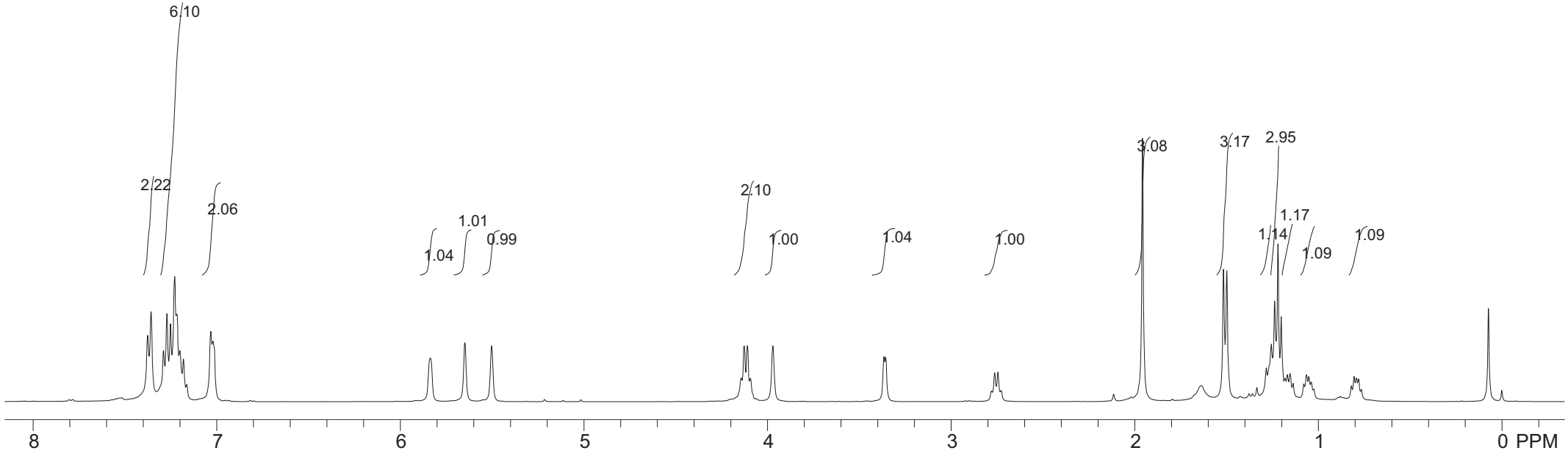
***cis*-3ac**

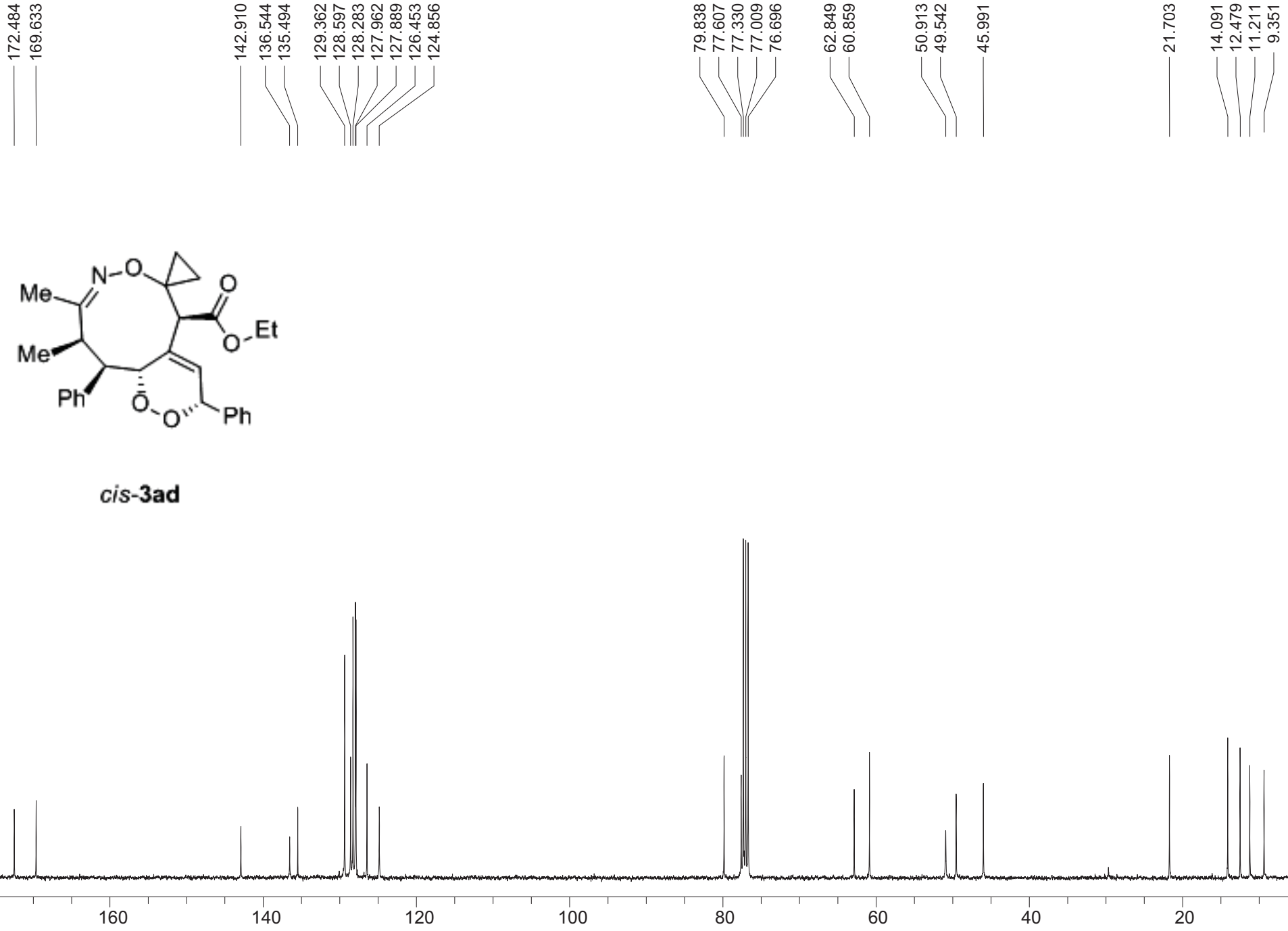

180
160
140
120
100
80
60
40
20
PPM


7.376
7.358
7.290
7.271
7.252
7.229
7.217
7.201
7.181
7.163
7.032
7.020
5.837
5.649
5.503
4.144
4.127
4.111
4.094
3.971
3.366
3.357
2.781
2.764
2.746
2.729
1.958
1.516
1.499
1.283
1.256
1.238
1.220
1.202
1.182
1.169
1.154
1.137
1.079
1.065
1.051
1.038
1.025
0.820
0.805
0.780
0.765
0.000


N
O
Me
Me
Ph
O
O
Et
O
Ph

***cis*-3ad**


6.10
2.22
2.06
1.04
1.01
0.99
2.10
1.00
1.04
1.00
3.08
3.17
2.95
1.14
1.17
1.09
1.09
8
7
6
5
4
3
2
1
0 PPM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79.838
77.607
77.330
77.009
76.696
62.849
60.859
50.913
49.542
45.991
21.703
14.091
12.479
11.211
9.351
N
O
Me
Me
Ph
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O
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Et
O
Ph
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160
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80
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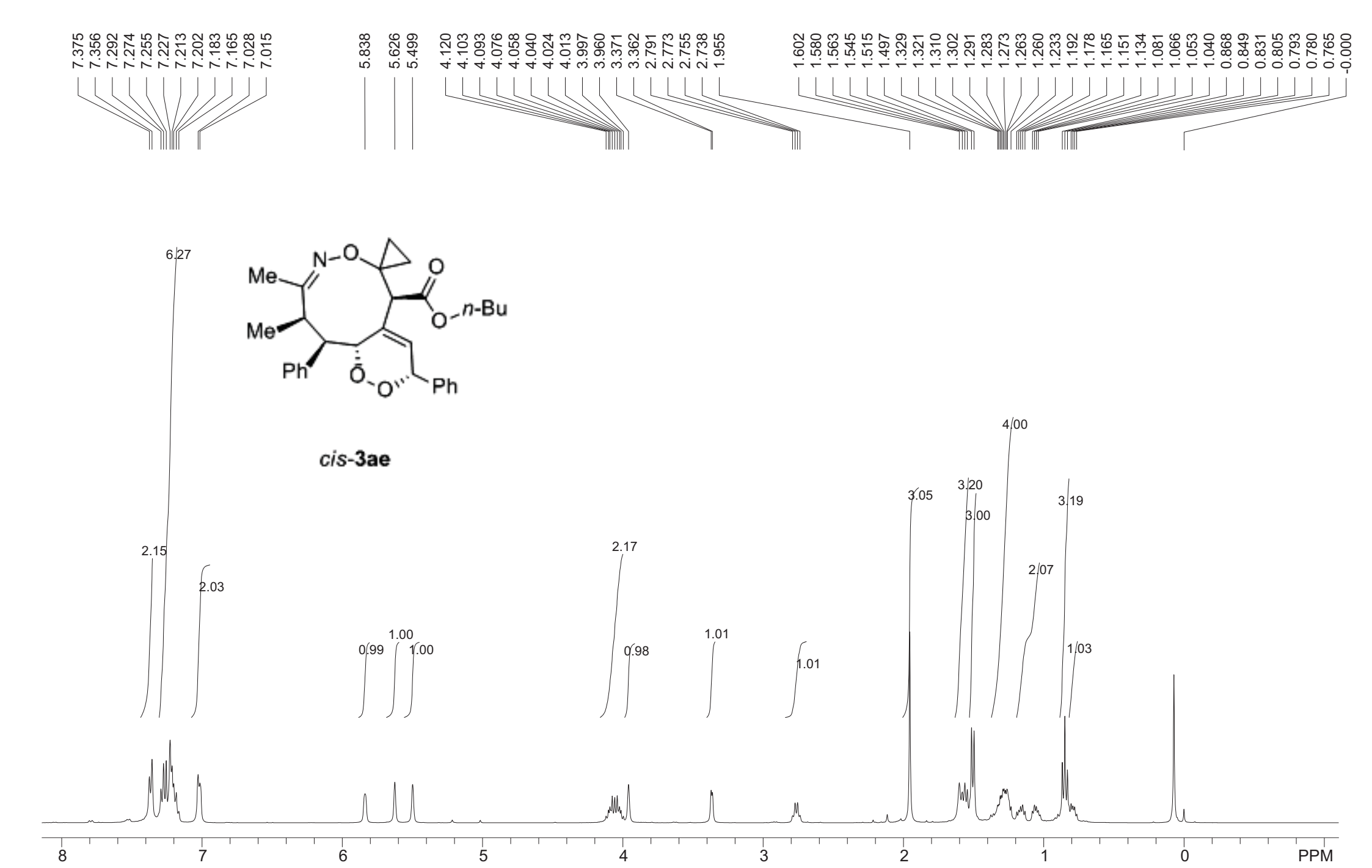
20
PPM

cis-**3ad**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7.202
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5.499
4.120
4.103
4.093
4.076
4.058
4.040
4.024
4.013
3.997
3.960
3.371
3.362
2.791
2.773
2.755
2.738
1.955
1.602
1.580
1.563
1.545
1.515
1.497
1.329
1.321
1.310
1.302
1.291
1.283
1.273
1.263
1.260
1.233
1.192
1.178
1.165
1.151
1.134
1.081
1.066
1.053
1.040
0.868
0.849
0.831
0.805
0.793
0.780
0.765
-0.000
Me
N
O
O
O
n-Bu
Me
Ph
O
O
Ph
cis-3ae
6.27
2.15
2.03
0.99
1.00
1.00
2.17
0.98
1.01
1.01
3.05
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1.03
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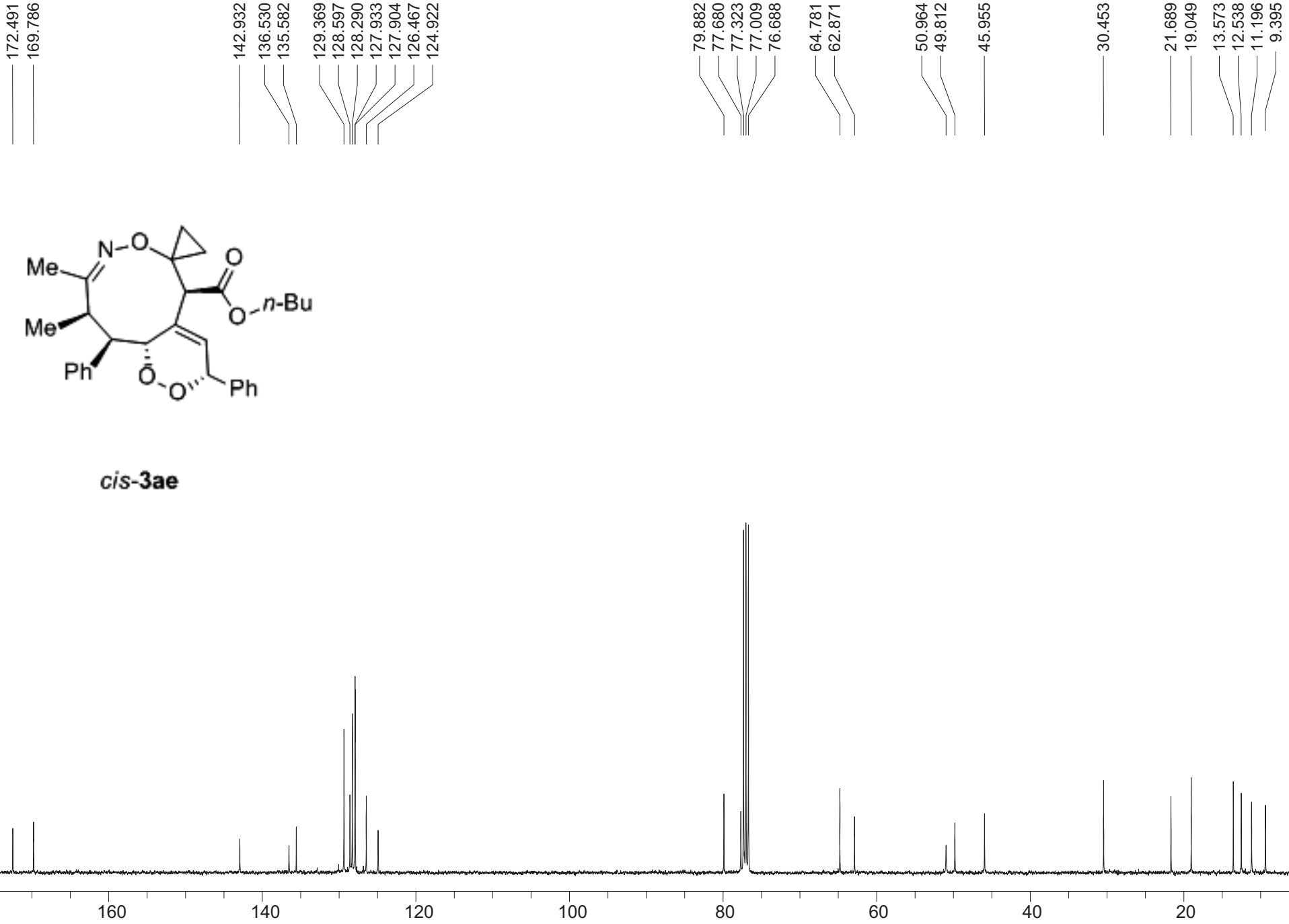
PPM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126.467
124.922
79.882
77.680
77.323
77.009
76.688
64.781
62.871
50.964
49.812
45.955
30.453
21.689
19.049
13.573
12.538
11.196
9.395
N
O
Me
Me
Ph
O
O
O
n-Bu
O
Ph
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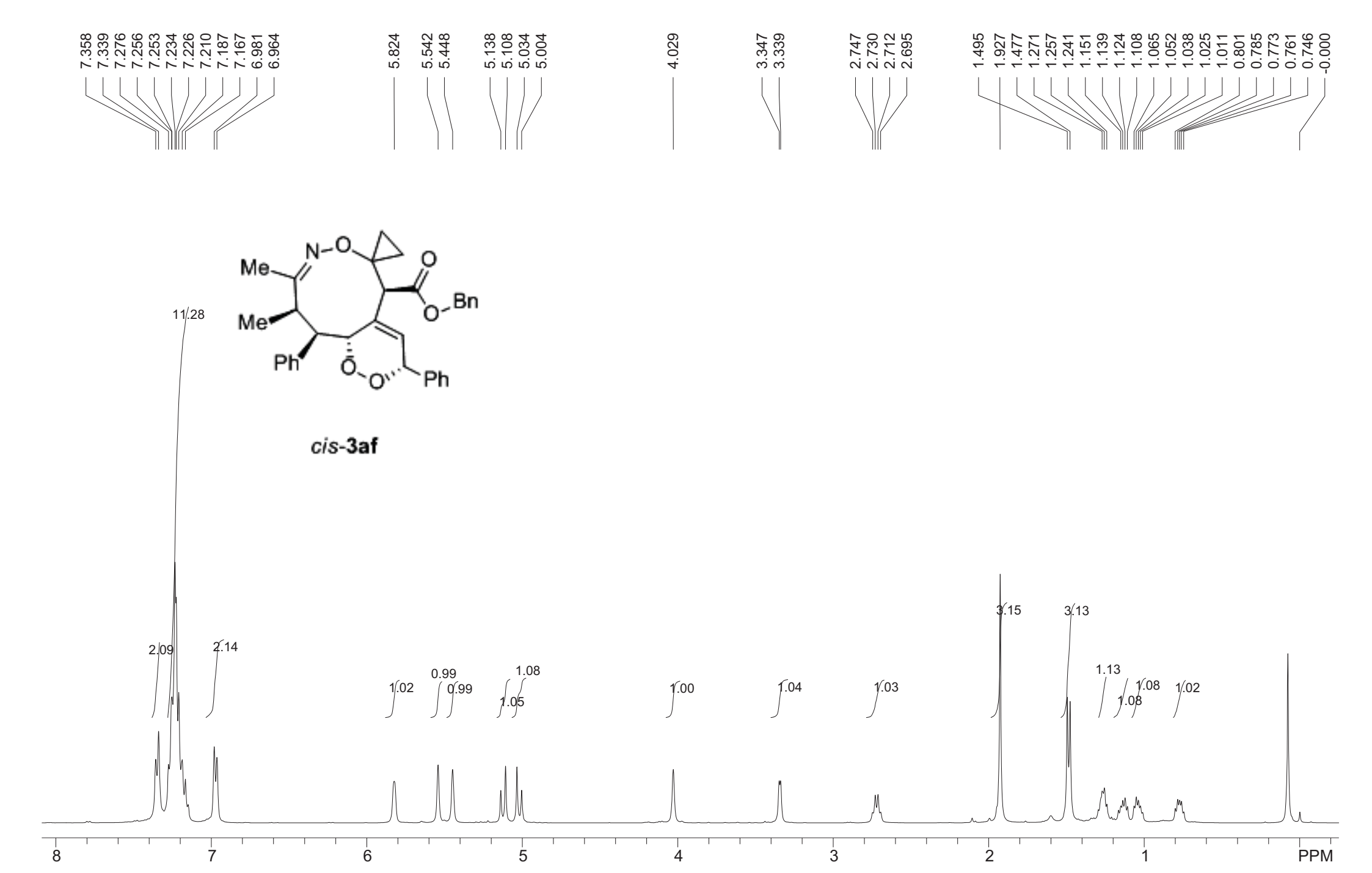
80
60
40
20
PPM

cis-**3ae**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7.210
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7.167
6.981
6.964
5.824
5.542
5.448
5.138
5.108
5.034
5.004
4.029
3.347
3.339
2.747
2.730
2.712
2.695
1.495
1.927
1.477
1.271
1.257
1.241
1.151
1.139
1.124
1.108
1.065
1.052
1.038
1.025
1.011
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0.785
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0.761
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-0.000
Me
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O
O
Me
O
Bn
Ph
O
O
Ph
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2.09
2.14
1.02
0.99
0.99
1.08
1.05
1.00
1.04
1.03
3.15
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1.08
1.02
8
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6
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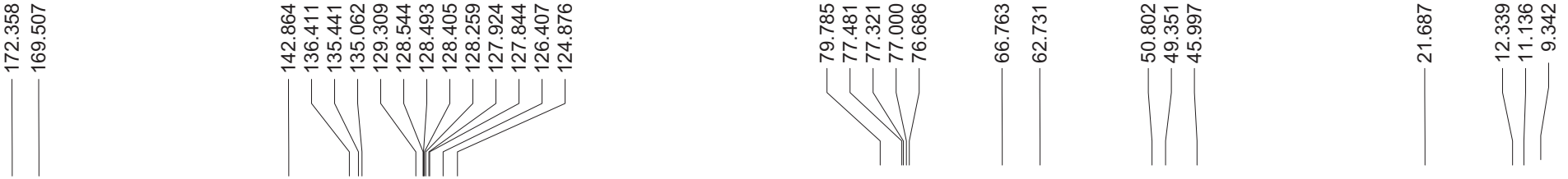
4
3
2
1
PPM

cis-**3af**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126.407
124.876
79.785
77.481
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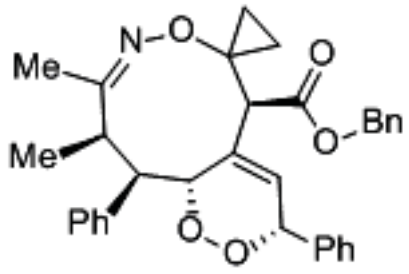
9.342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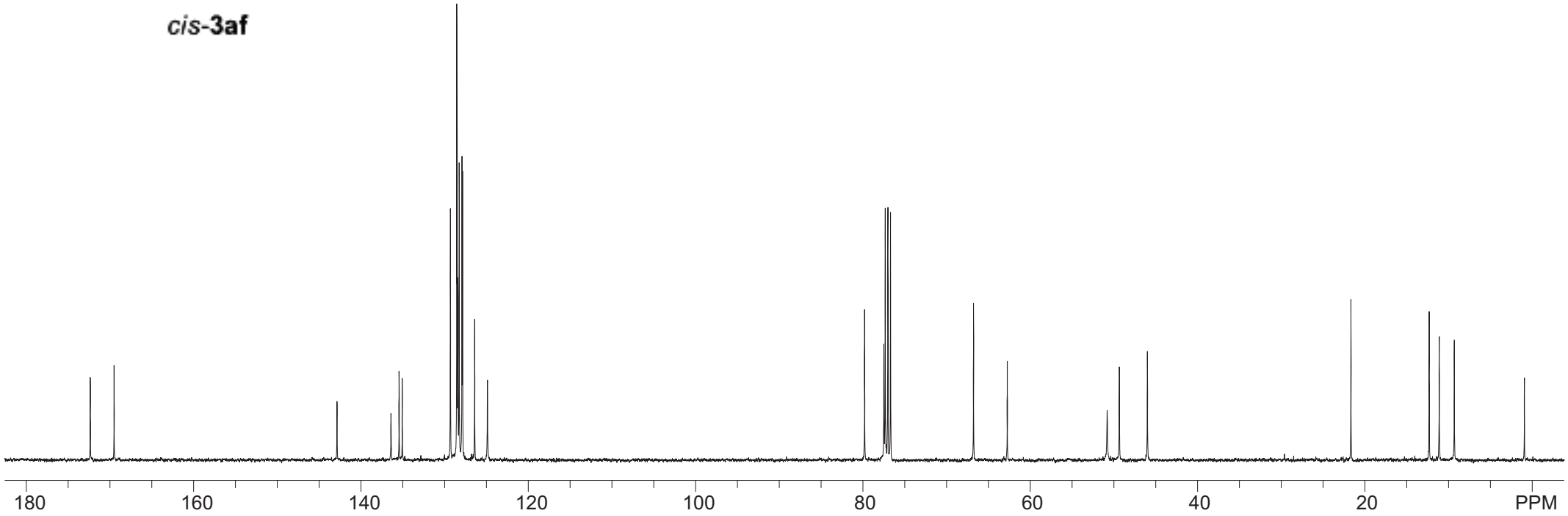
Bn
Me
Ph
O
O
Ph

cis-**3af**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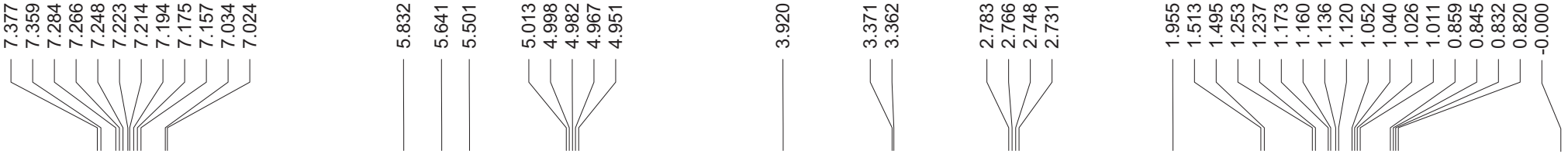
140
120
100
80
60
40
20
PPM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7.223
7.214
7.194
7.175
7.157
7.034
7.024
5.832
5.641
5.501
5.013
4.998
4.982
4.967
4.951
3.920
3.371
3.362
2.783
2.766
2.748
2.731
1.955
1.513
1.495
1.253
1.237
1.173
1.160
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1.026
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0.832
0.820
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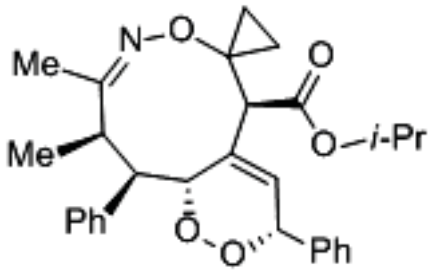
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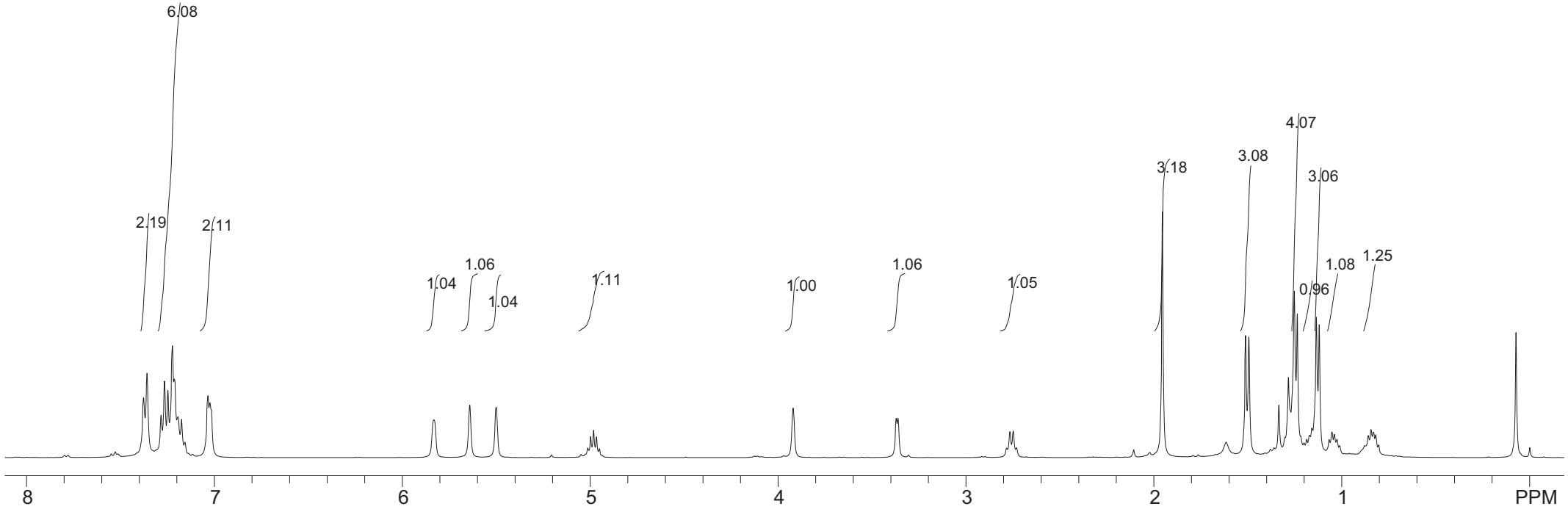
O–i-Pr
Me
Ph
O
O
Ph

***cis*-3ag**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1.04
1.06
1.04
1.11
1.00
1.06
1.05
3.18
3.08
4.07
3.06
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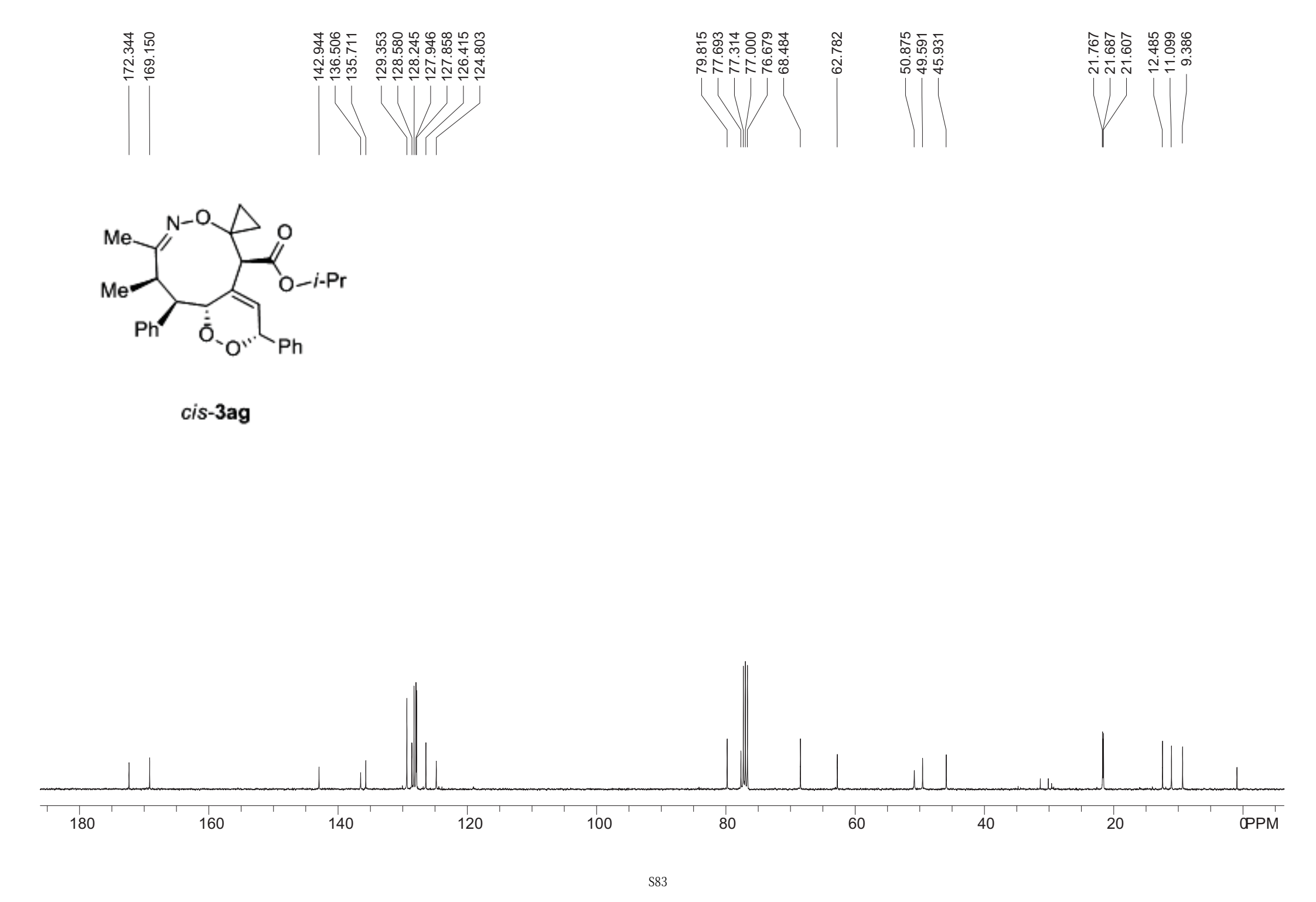
1.08
1.25
8
7
6
5
4
3
2
1
PPM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128.245
127.946
127.858
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124.803
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77.693
77.314
77.000
76.679
68.484
62.782
50.875
49.591
45.931
21.767
21.687
21.607
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11.099
9.386
Me
N
O
O
Me
O
i-Pr
Ph
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O
Ph
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140
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80
60
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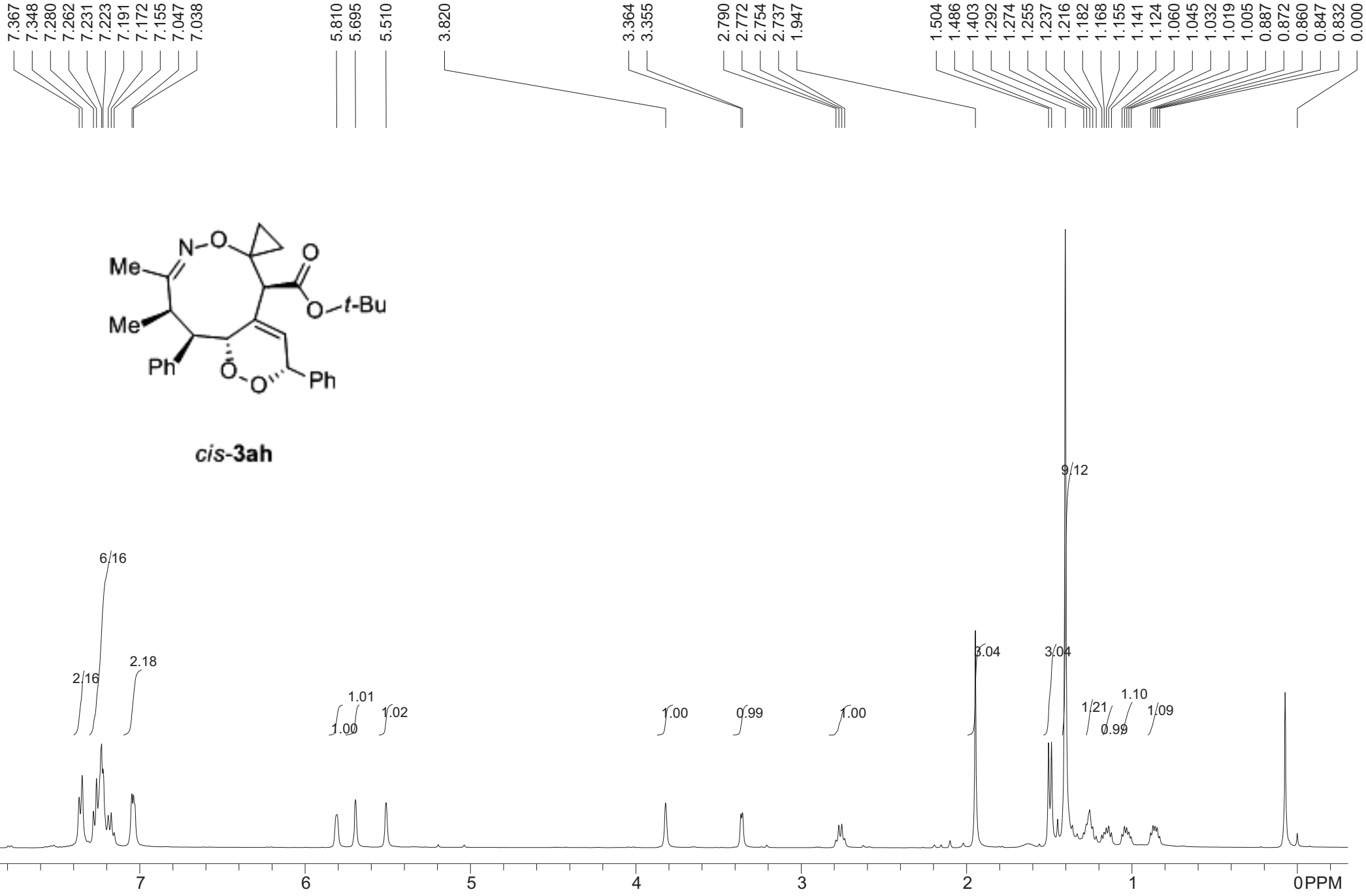
20
0
PPM

***cis*-3ag**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7.223
7.191
7.172
7.155
7.047
7.038
5.810
5.695
5.510
3.820
3.364
3.355
2.790
2.772
2.754
2.737
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1.504
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1.403
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1.255
1.237
1.216
1.182
1.168
1.155
1.141
1.124
1.060
1.045
1.032
1.019
1.005
0.887
0.872
0.860
0.847
0.832
0.000
N
O
O
Me
Me
O
t-Bu
Ph
O
O
Ph
cis-3ah
6.16
2.16
2.18
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1.00
1.02
1.00
0.99
1.00
3.04
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1.09
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6
5
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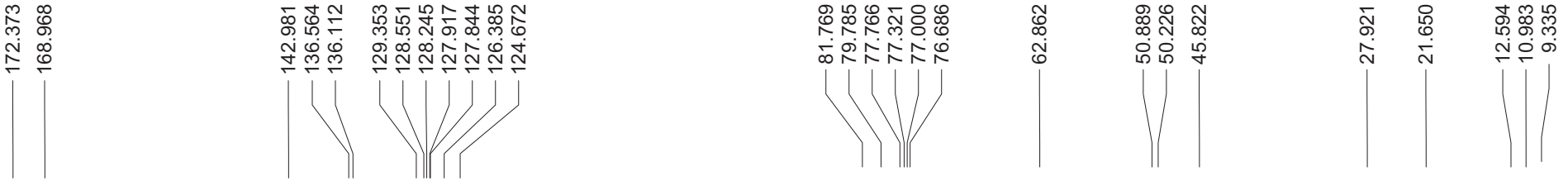
PPM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128.245
127.917
127.844
126.385
124.672
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79.785
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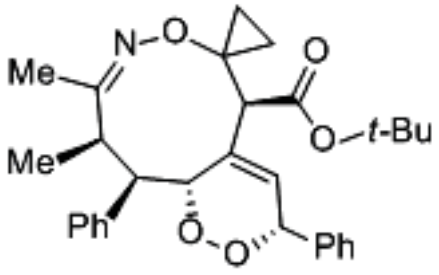
9.335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t-Bu
Ph
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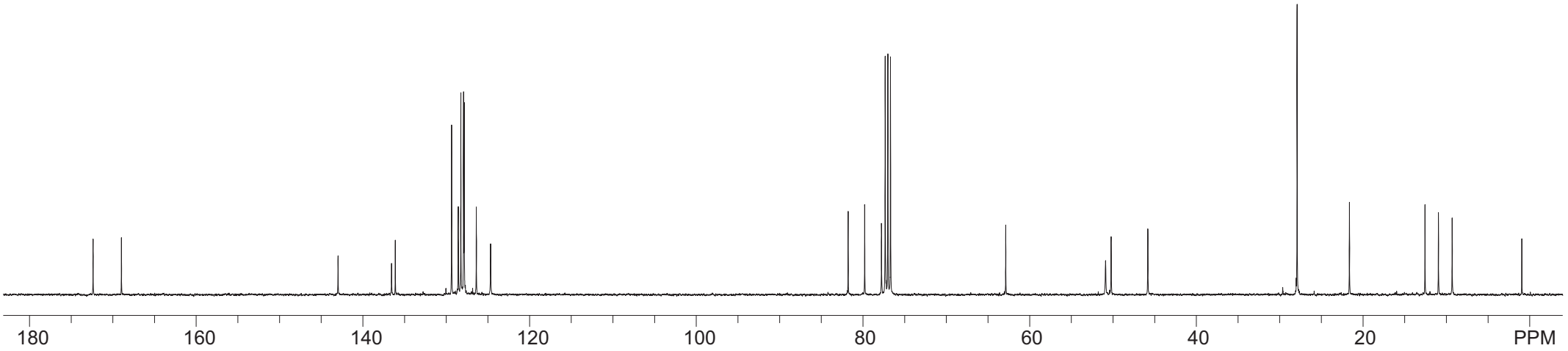
O
Ph

***cis*-3ah**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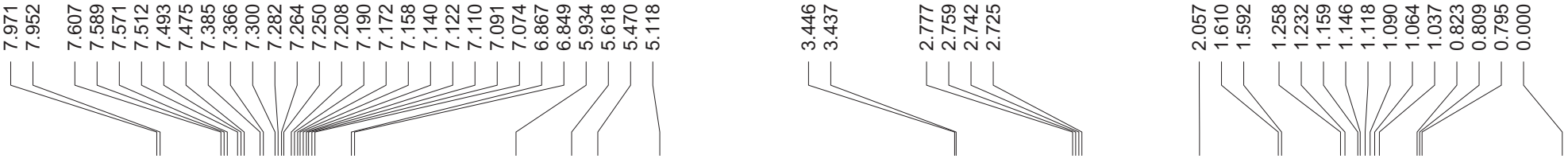
140
120
100
80
60
40
20
PPM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7.282
7.264
7.250
7.208
7.190
7.172
7.158
7.140
7.122
7.110
7.091
7.074
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6.849
5.934
5.618
5.470
5.118
3.446
3.437
2.777
2.759
2.742
2.725
2.057
1.610
1.592
1.258
1.232
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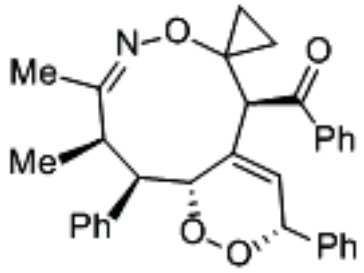
1.118
1.090
1.064
1.037
0.823
0.809
0.795
0.000


N
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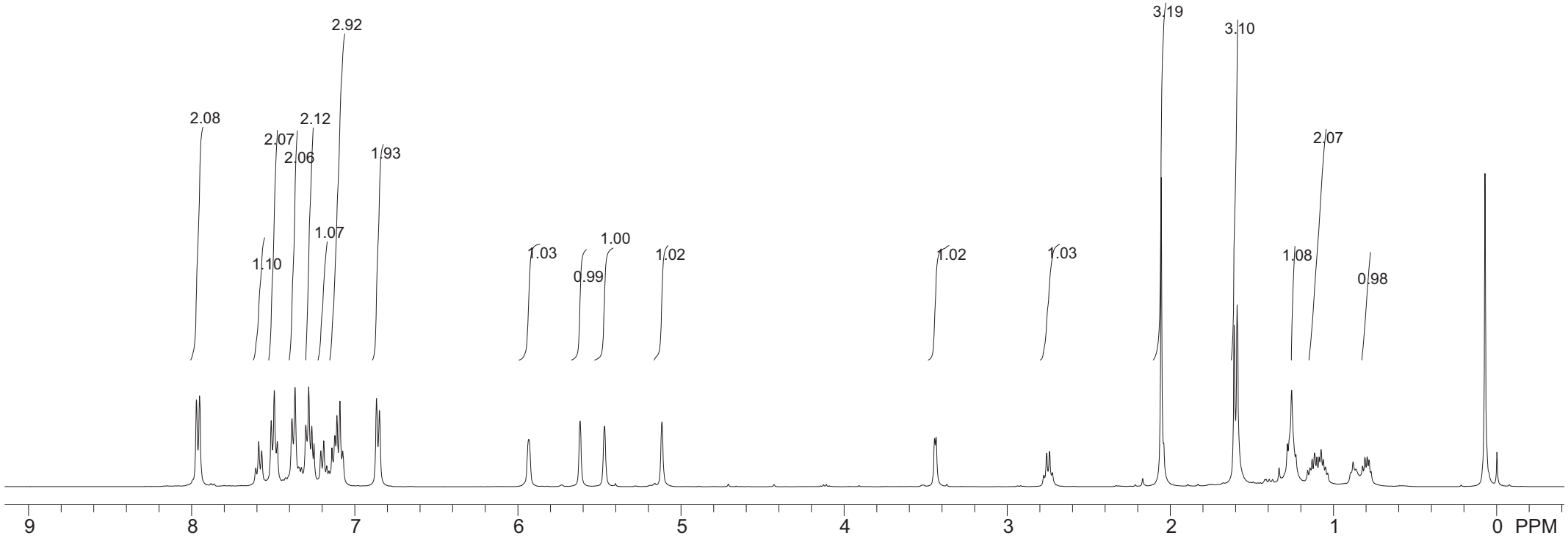
O
Me
Me
Ph
Ph
O
O
Ph

***cis*-3ai**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1.93
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1.07
1.00
1.10
1.03
1.02
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1.08
0.99
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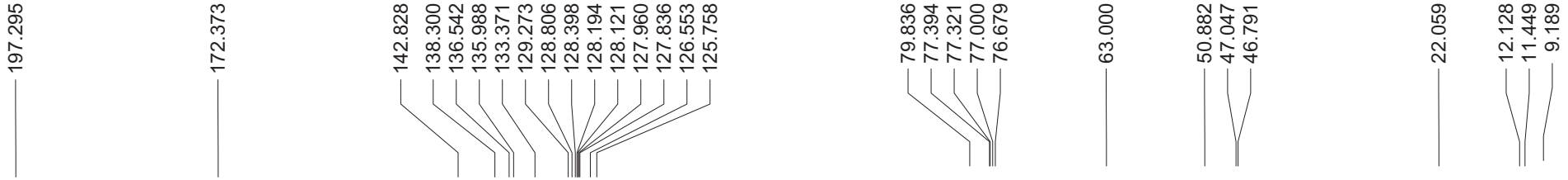
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129.273
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128.398
128.194
128.121
127.960
127.836
126.553
125.758
79.836
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77.321
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63.000
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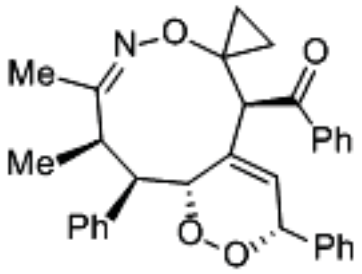
47.047
46.791
22.059
12.128
11.449
9.189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Me
Ph
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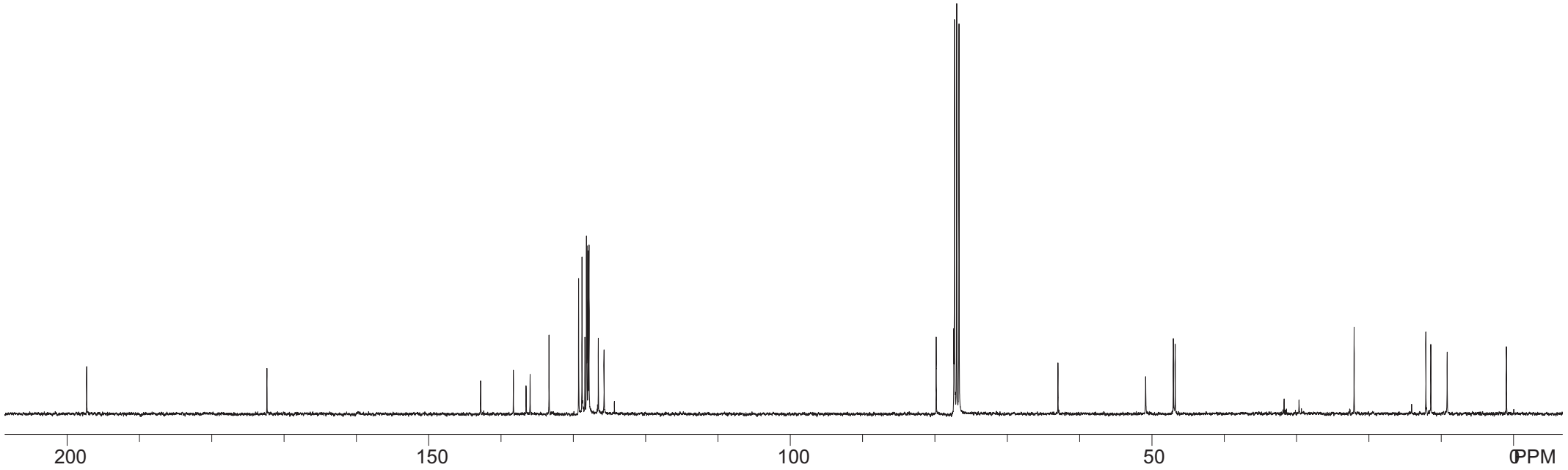
Ph

cis-**3ai**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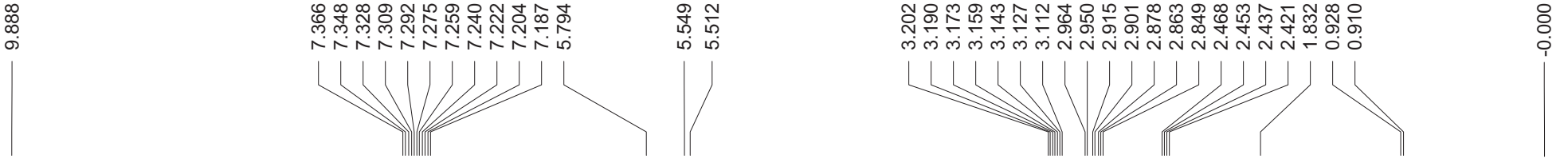
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5.512
3.202
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3.173
3.159
3.143
3.127
3.112
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2.950
2.915
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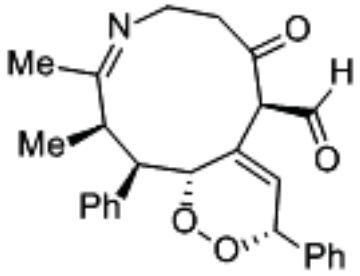
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Me
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Ph
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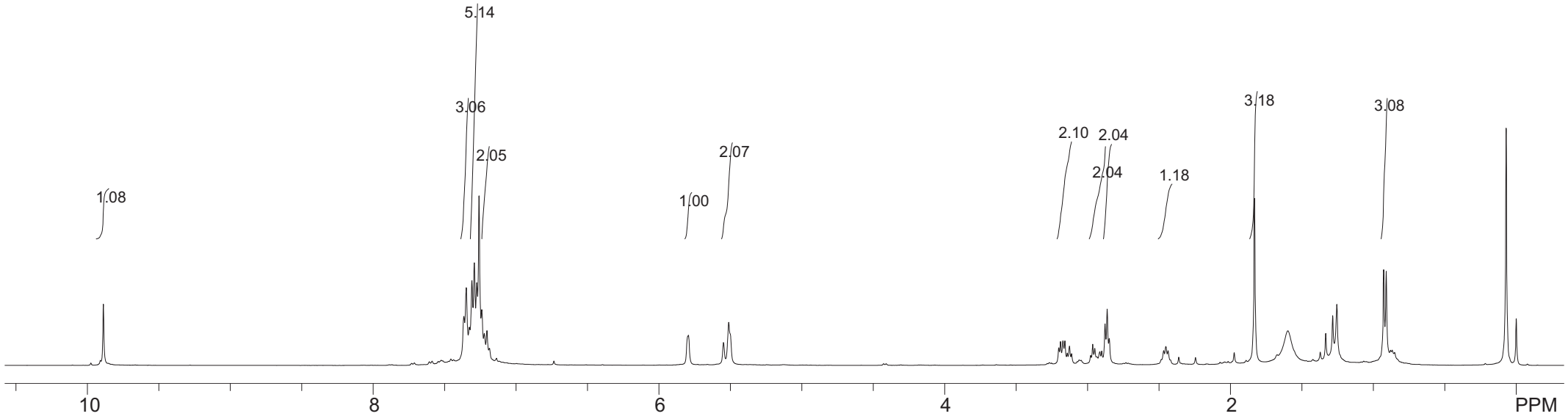
O
Ph

***cis*-3aj**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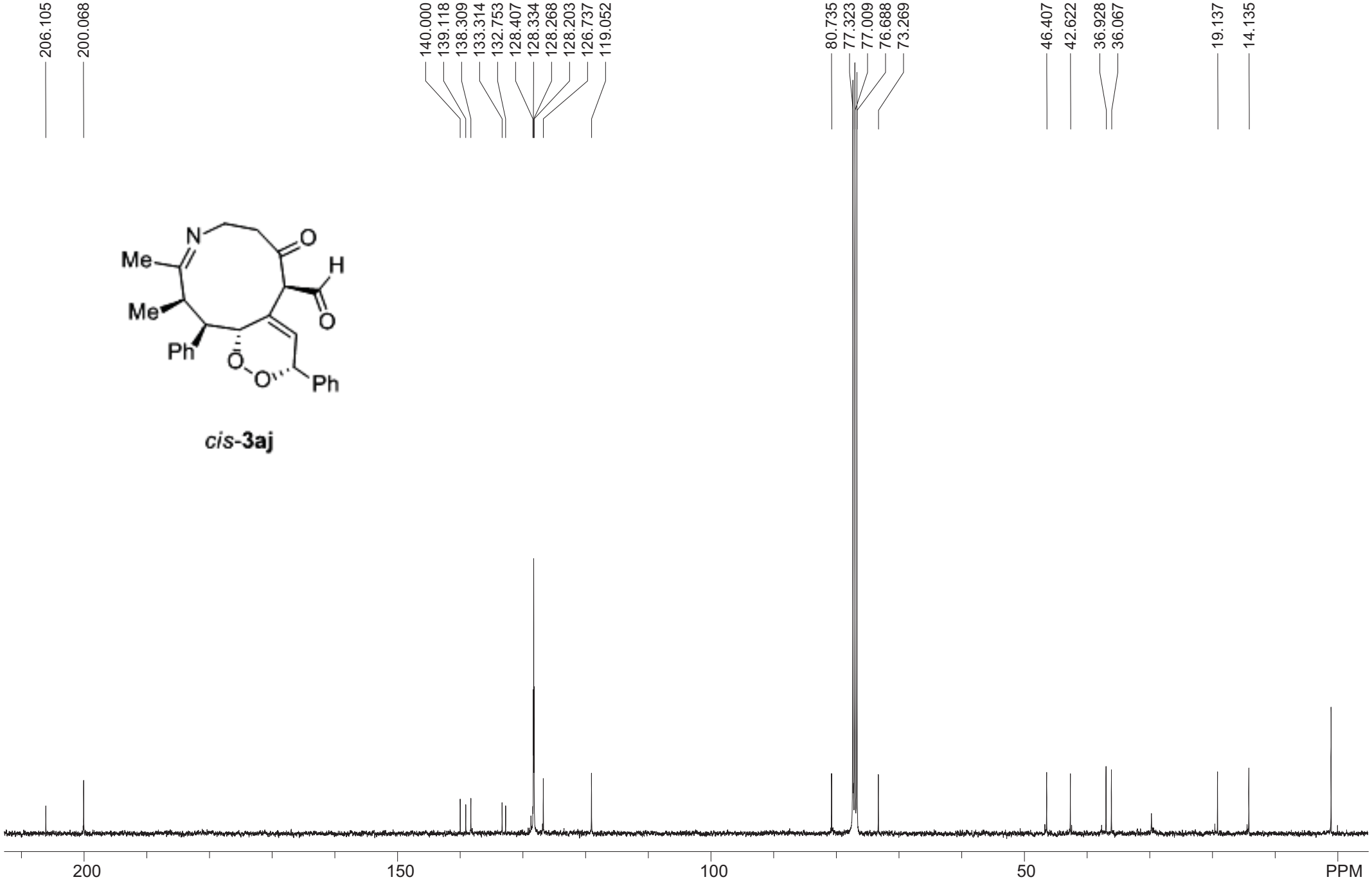
2.10
2.04
2.04
1.18
3.18
3.08
10
8
6
4
2
PPM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77.323
77.009
76.688
73.269
46.407
42.622
36.928
36.067
19.137
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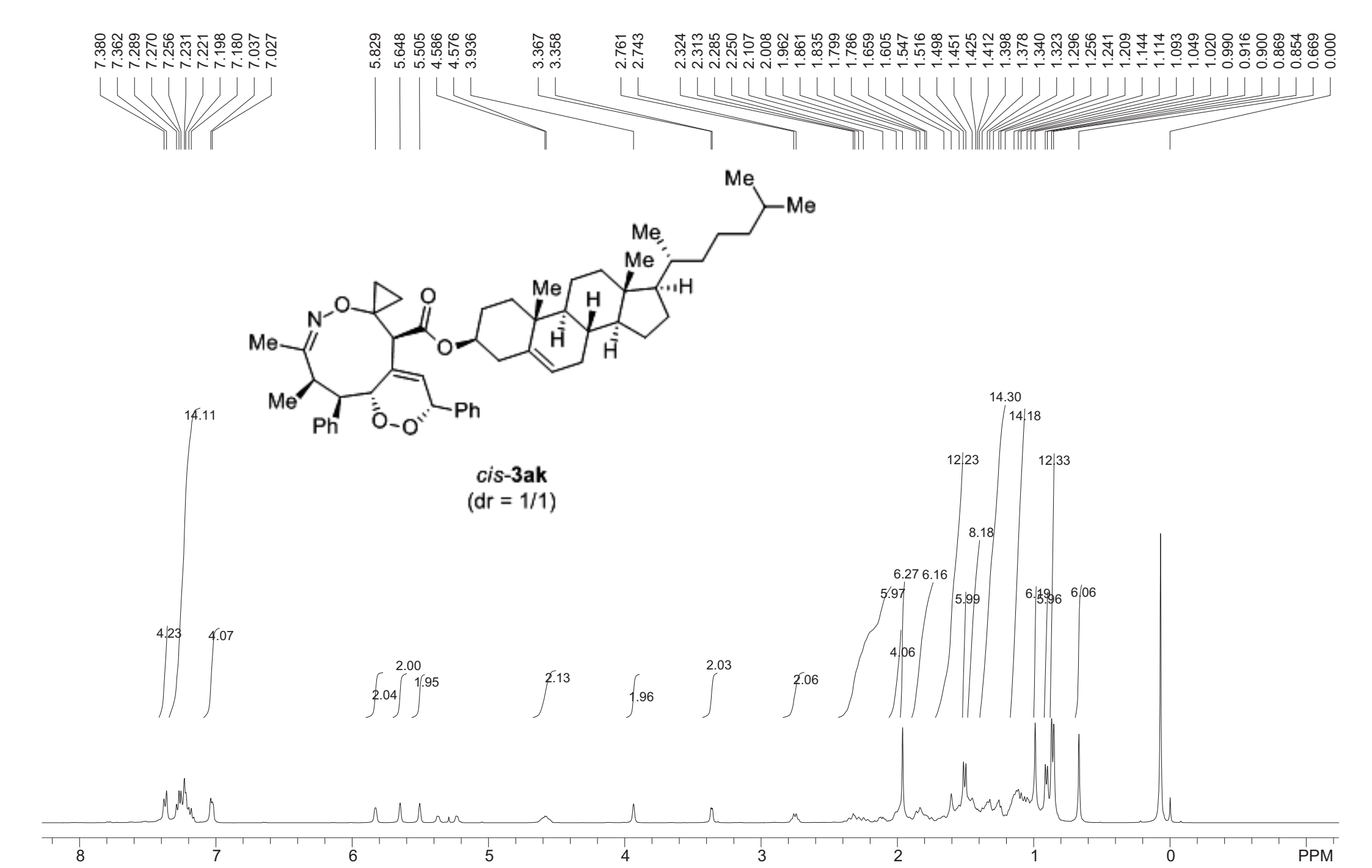
H
Me
Me
O
Ph
O
O
Ph
200
150
100
50
PPM

cis-**3aj**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5.829 5.648 5.505 4.586 4.576 3.936 3.367 3.358 2.761 2.743 2.324 2.313 2.285 2.250 2.107 2.008 1.962 1.861 1.835 1.799 1.786 1.659 1.605 1.547 1.516 1.498 1.451 1.425 1.412 1.398 1.378 1.340 1.323 1.296 1.256 1.241 1.209 1.144 1.114 1.093 1.049 1.020 0.990 0.916 0.900 0.869 0.854 0.669 0.000
Me
Me
Me
Me
Me
H
H
H
H
N
O
O
O
Me
Me
Ph
Ph
O-O
cis-3ak
(dr = 1/1)
14.11
4.23
4.07
2.00
2.04
1.95
2.13
1.96
2.03
2.06
6.27
6.16
5.97
4.06
14.30
14.18
12.23
12.33
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6.19
5.96
6.06
8
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6
5
4
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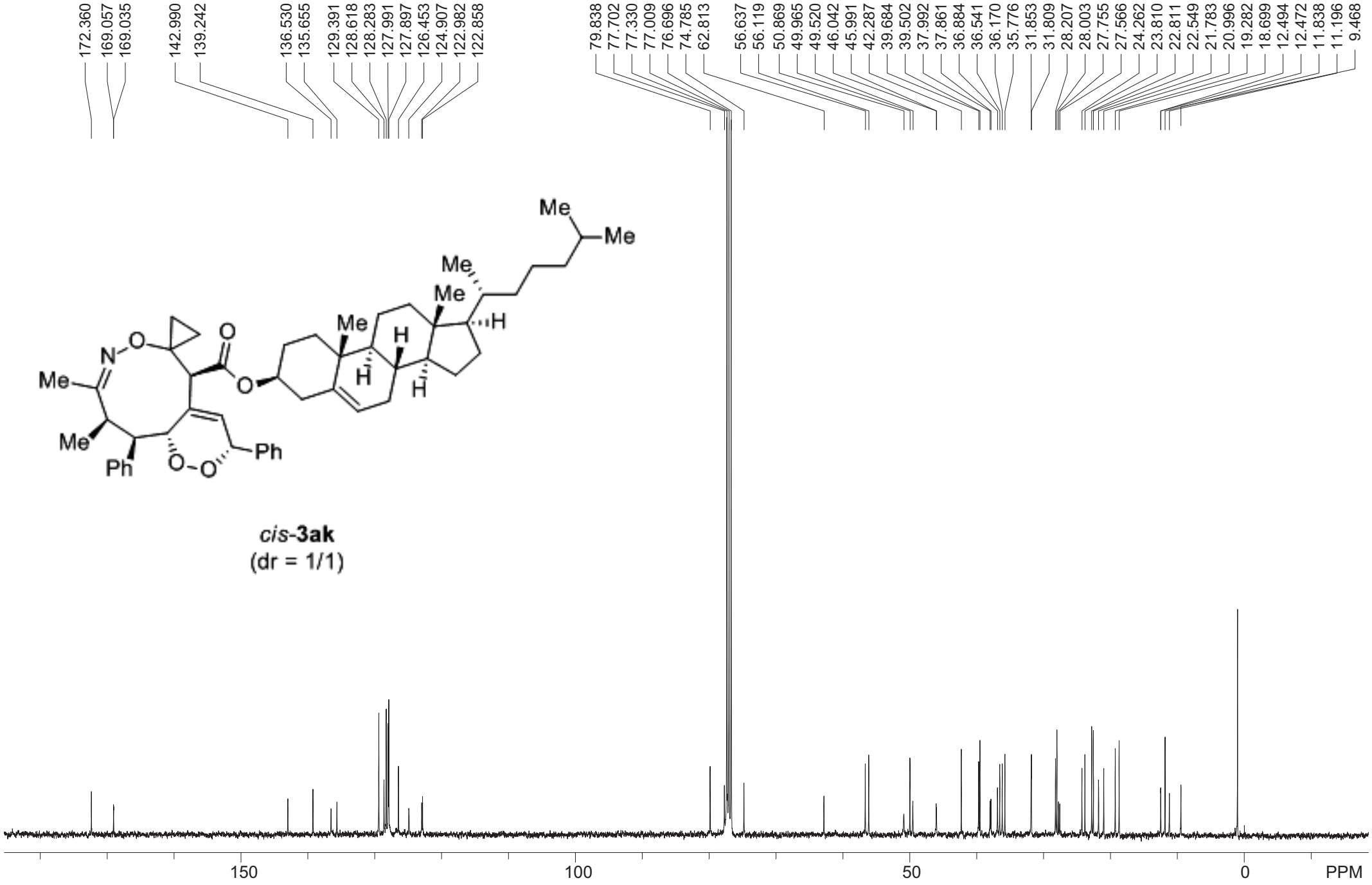
2
1
0
PPM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42.287
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37.861
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35.776
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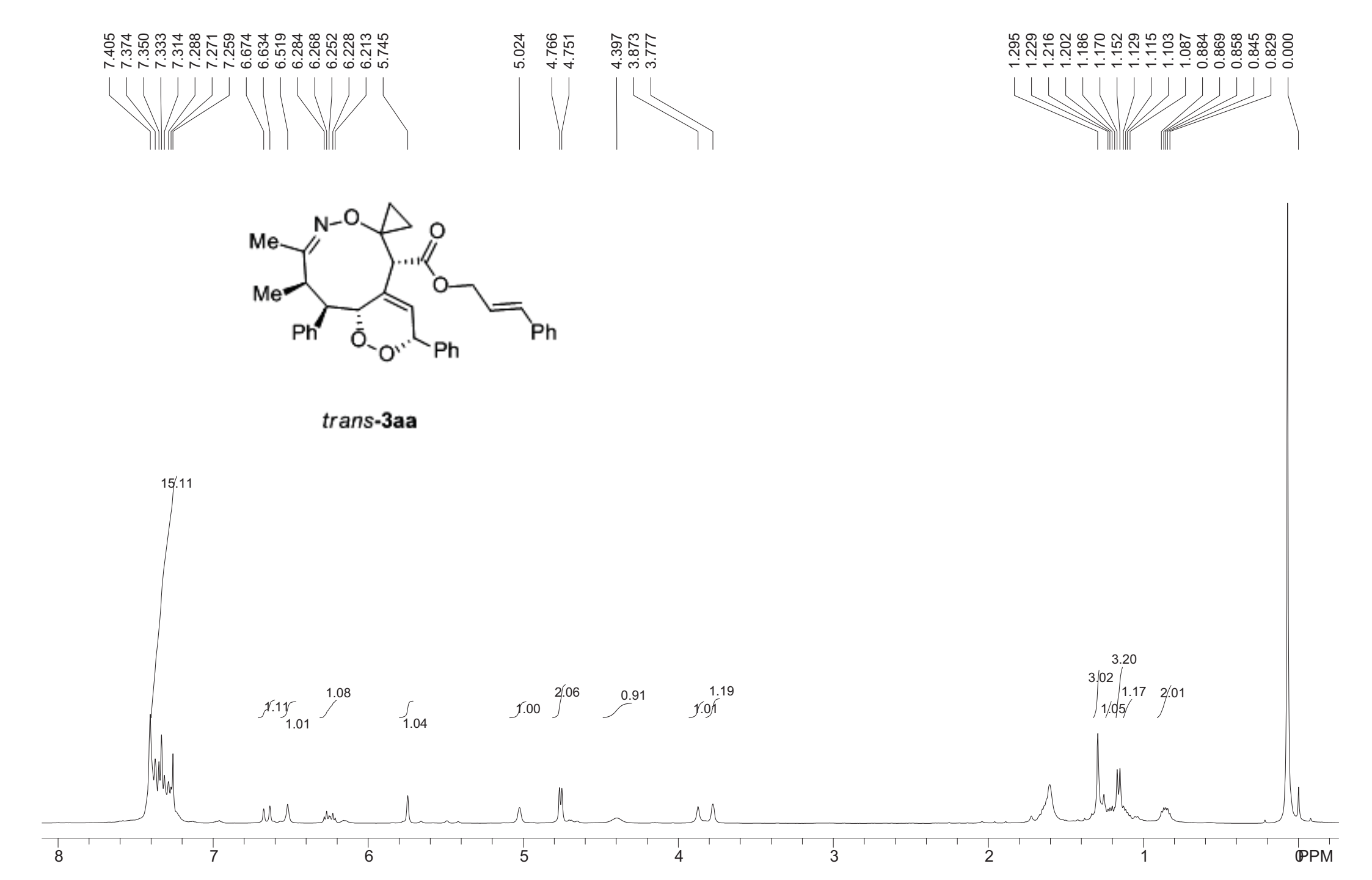
28.003
27.755
27.566
24.262
23.810
22.811
22.549
21.783
20.996
19.282
18.699
12.494
12.472
11.838
11.196
9.468
Me
Me
Me
Me
H
H
H
H
O
N
O
O
Me
Me
Ph
Ph
O
O
150
100
50
0
PPM

cis-**3ak**
(dr = 1/1)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6.268
6.252
6.228
6.213
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5.024
4.766
4.751
4.397
3.873
3.777
1.295
1.229
1.216
1.202
1.186
1.170
1.152
1.129
1.115
1.103
1.087
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0.858
0.845
0.829
0.000
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O
O
Me
Ph
O
O
Ph
O
Ph
trans-3aa
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1.11
1.01
1.08
1.04
1.00
2.06
0.91
1.01
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2.01
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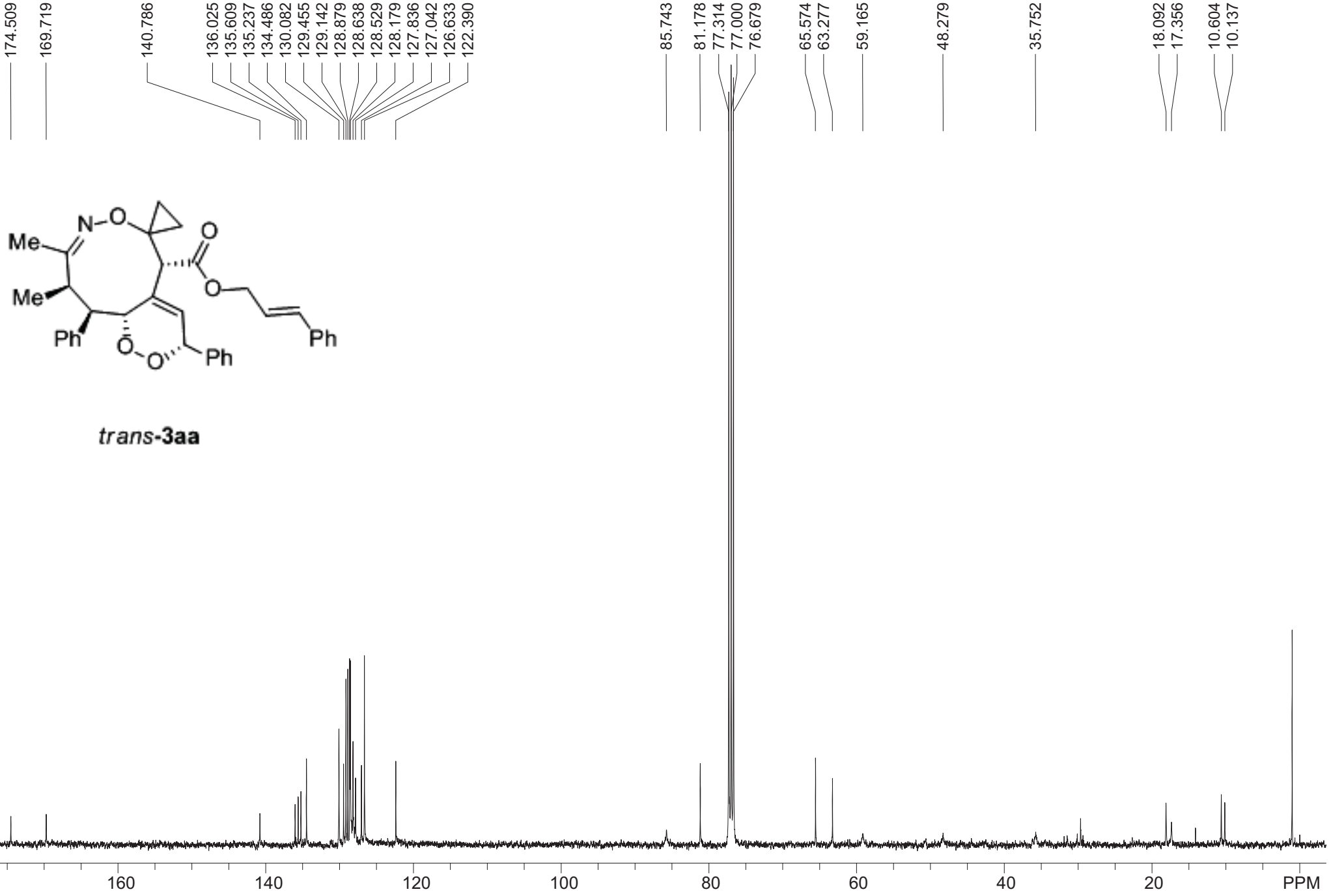
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129.142
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127.836
127.042
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85.743
81.178
77.314
77.000
76.679
65.574
63.277
59.165
48.279
35.752
18.092
17.356
10.604
10.137
Me
N
O
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Ph
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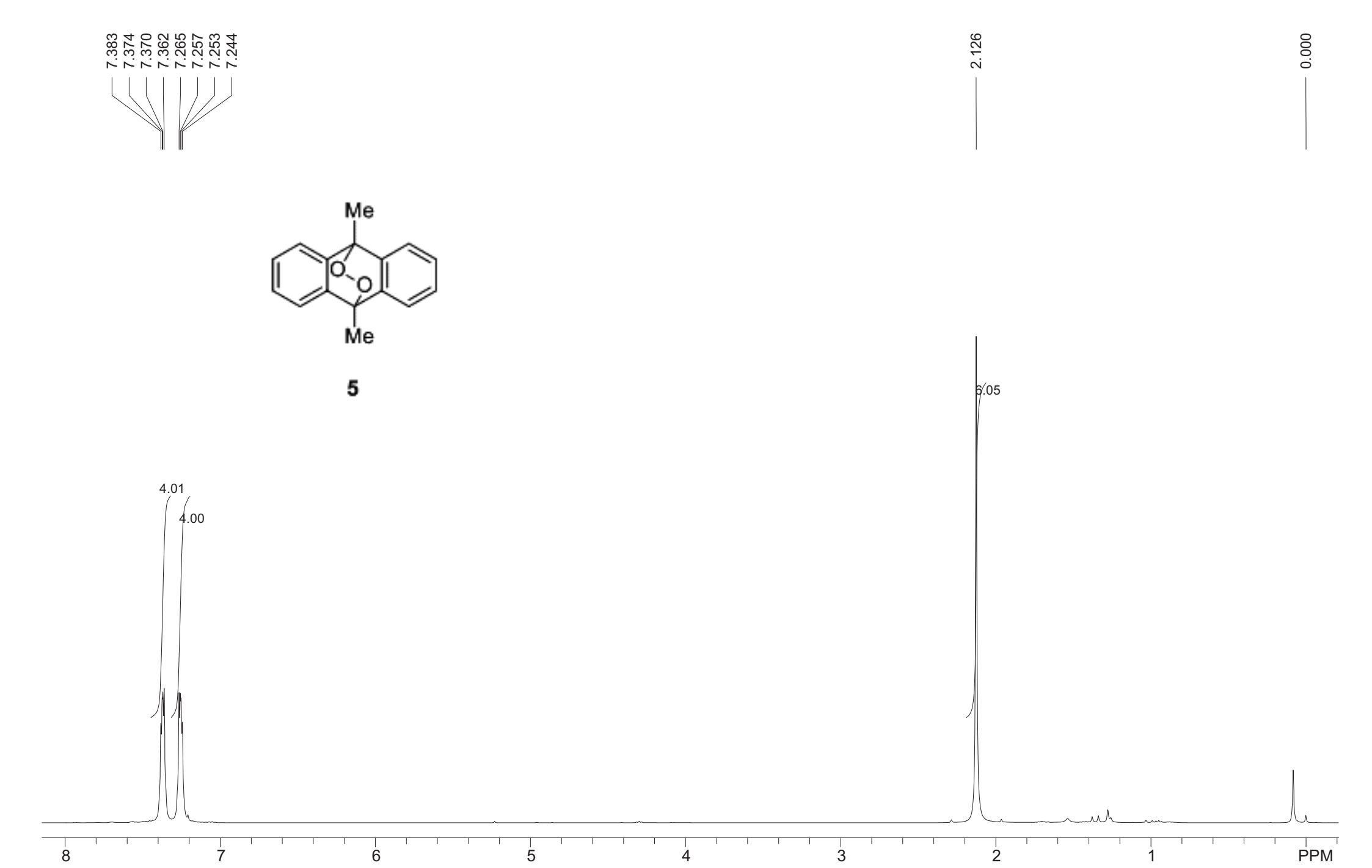
trans-**3aa**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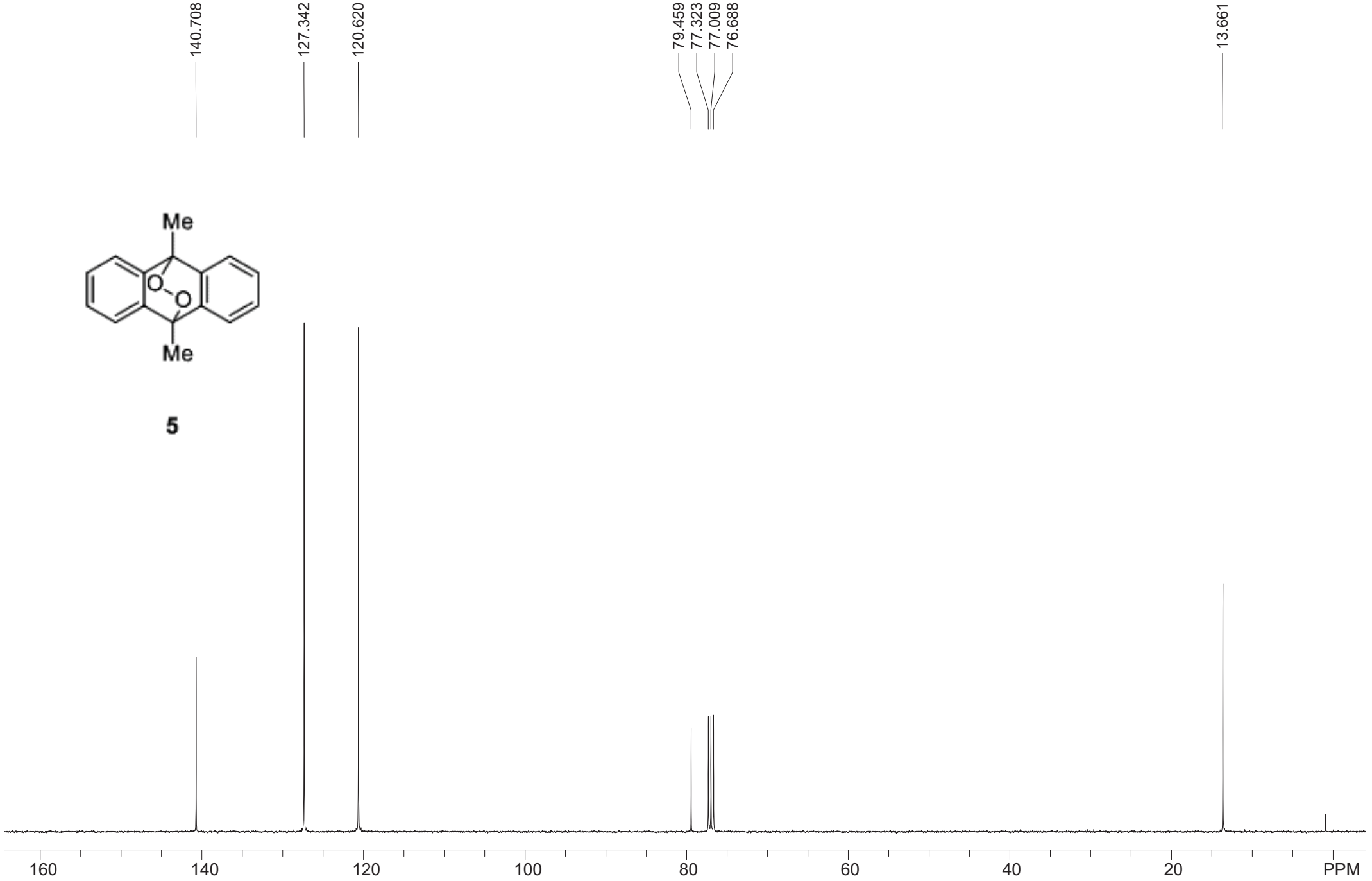
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13.661
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Me
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120
100
80
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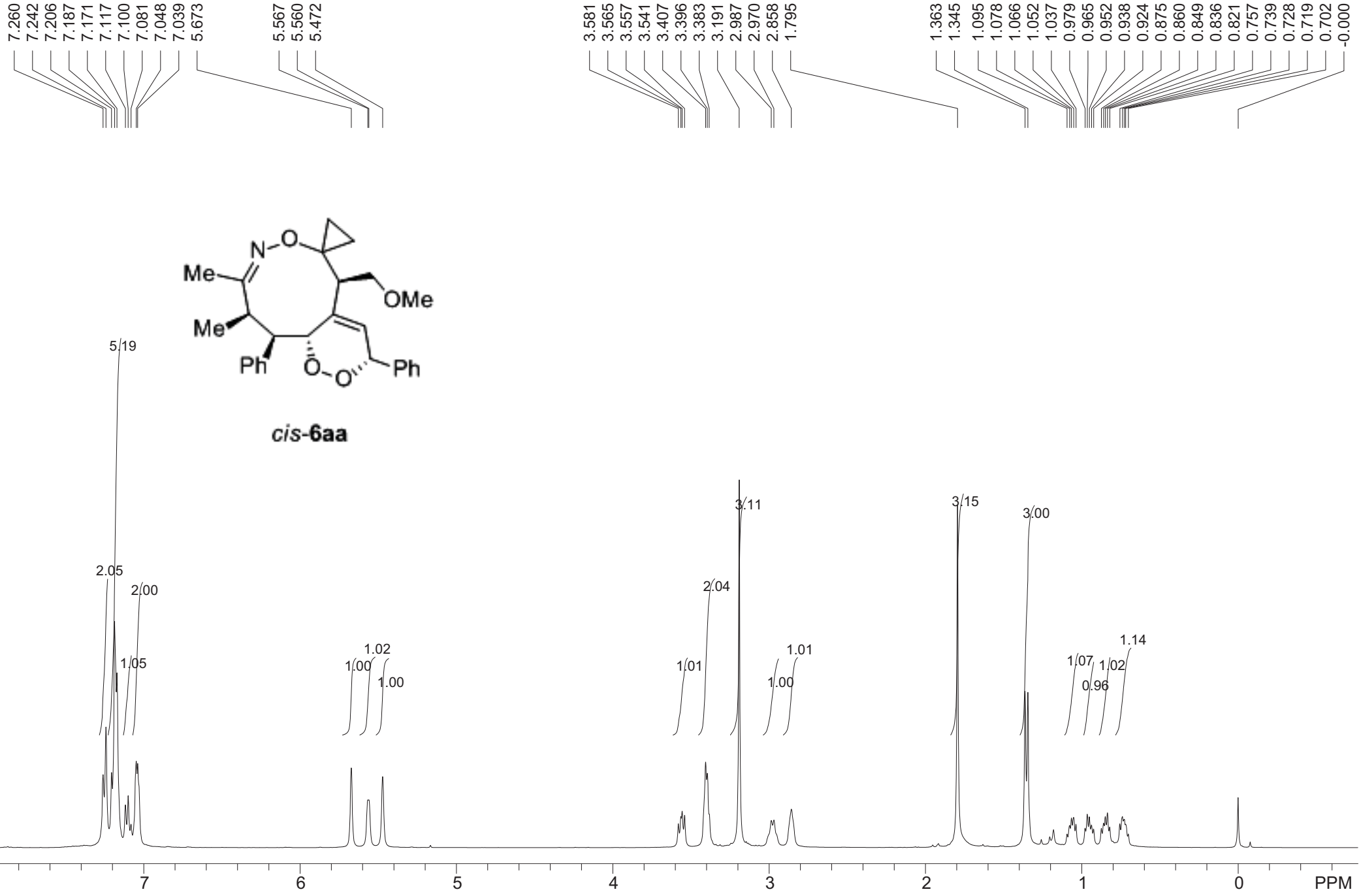
40
20
PPM

5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7.039
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5.560
5.472
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3.565
3.557
3.541
3.407
3.396
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2.970
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1.078
1.066
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0.924
0.875
0.860
0.849
0.836
0.821
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0.739
0.728
0.719
0.702
-0.000
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O
Me
OMe
Me
Ph
O
O
Ph
cis-6aa
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2.00
1.05
1.02
1.00
1.00
3.11
2.04
1.01
1.01
1.00
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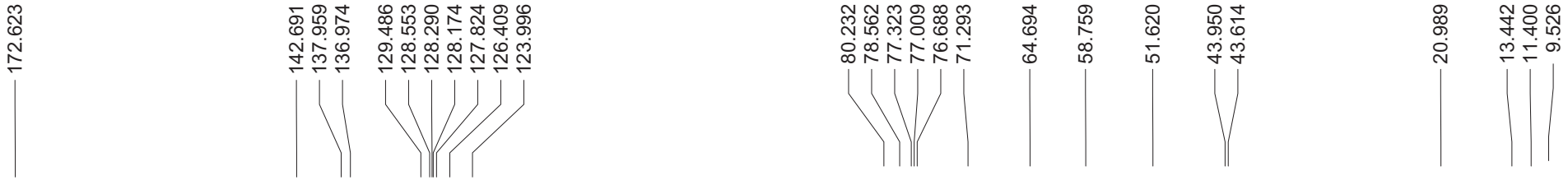
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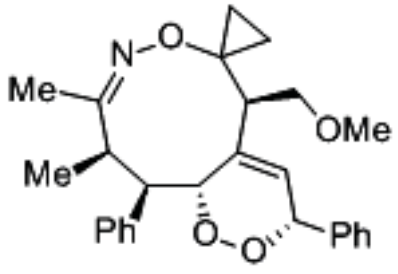
9.526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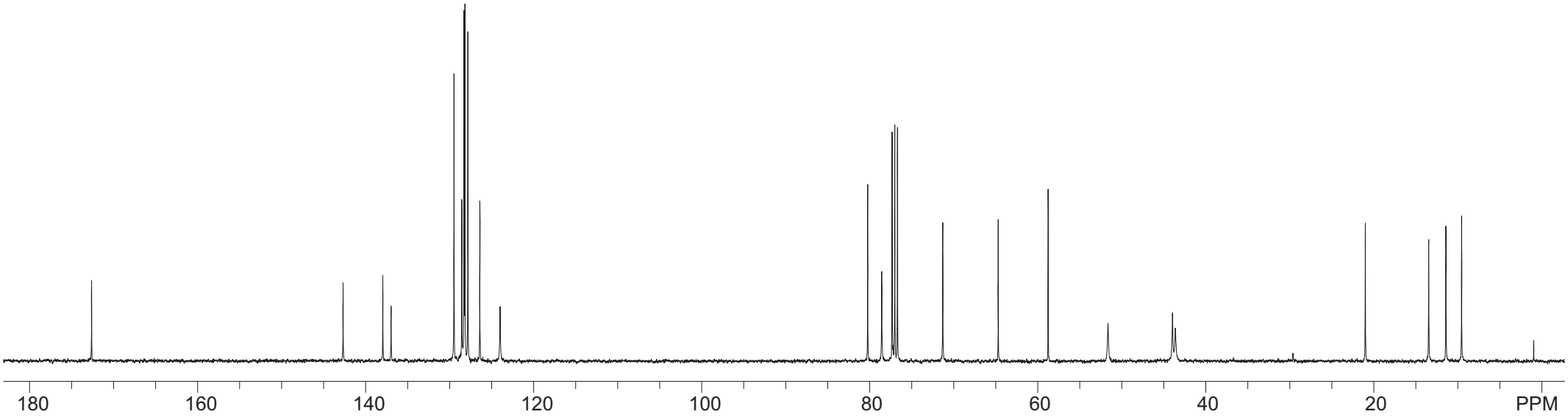
OMe
Me
Ph
O
O
Ph

cis-**6aa**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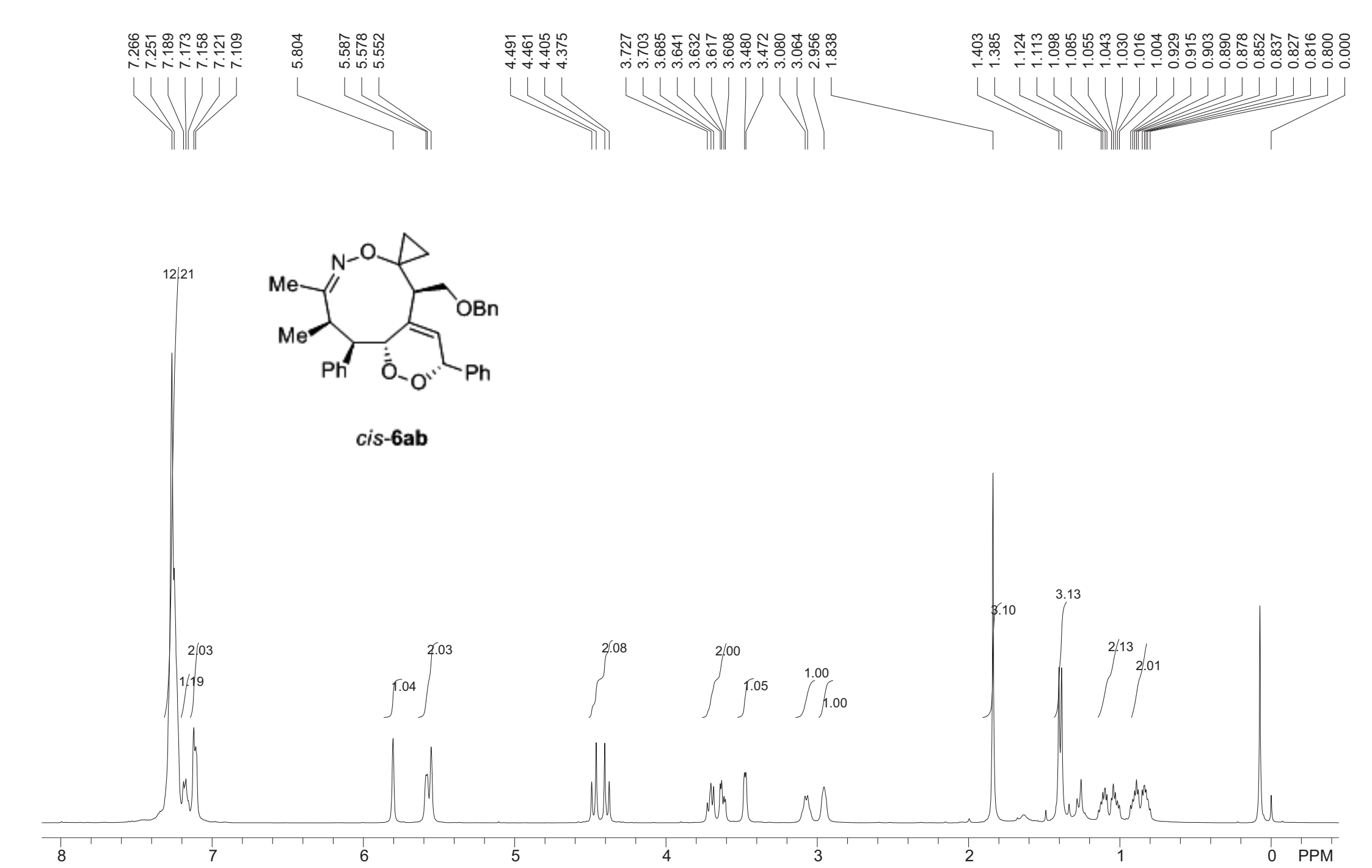
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4.405
4.375
3.727
3.703
3.685
3.641
3.632
3.617
3.608
3.480
3.472
3.080
3.064
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1.403
1.385
1.124
1.113
1.098
1.085
1.055
1.043
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1.016
1.004
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0.915
0.903
0.890
0.878
0.852
0.837
0.827
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0.800
0.000
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O
OBn
Me
Ph
O
O
Ph
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1.19
1.04
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2.08
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1.05
1.00
1.00
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2.01
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3
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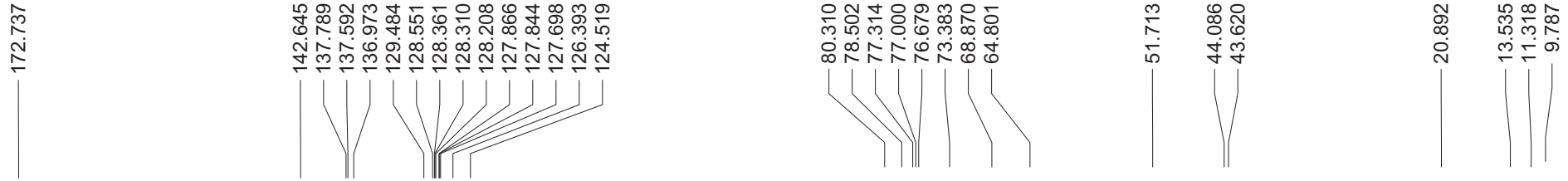
PPM

cis-**6ab**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126.393
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78.502
77.314
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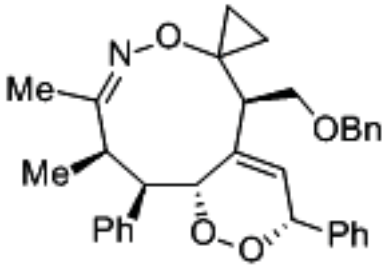
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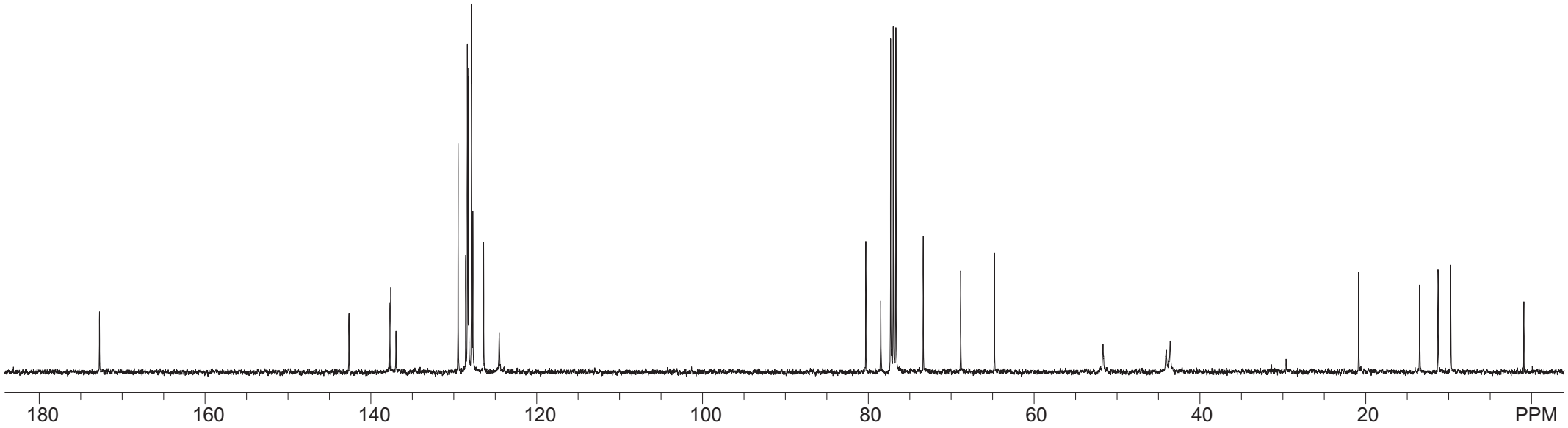
OBn
Me
Ph
O
O
Ph

cis-**6ab**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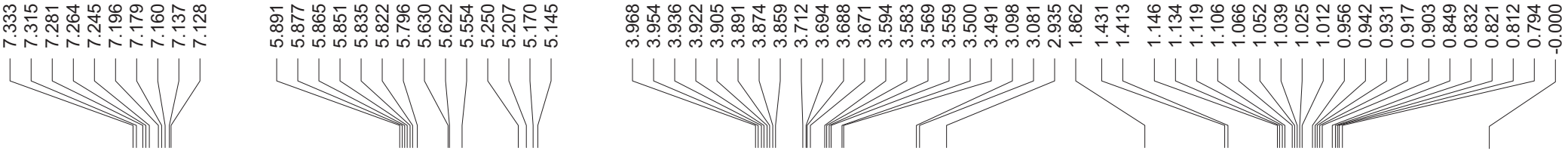
PPM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7.128
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5.851
5.835
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5.796
5.630
5.622
5.554
5.250
5.207
5.170
5.145
3.968
3.954
3.936
3.922
3.905
3.891
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1.052
1.039
1.025
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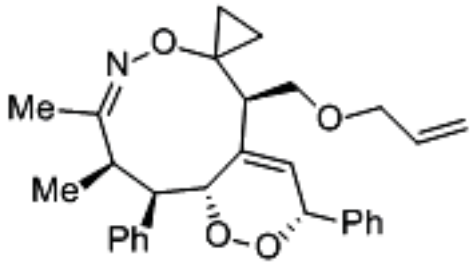
-0.000


N
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Me
Me
Ph
O
O
O
Ph

cis-**6ac**

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1.05
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1.00
1.03
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1.07
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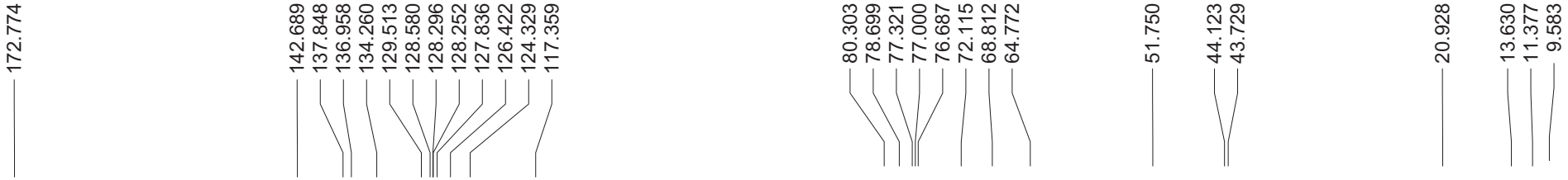
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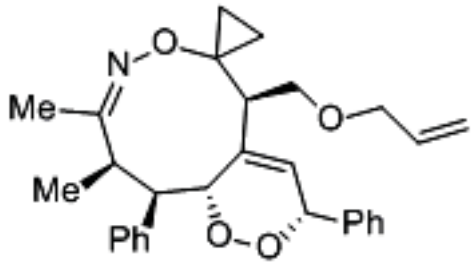
11.377
9.583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O
Me
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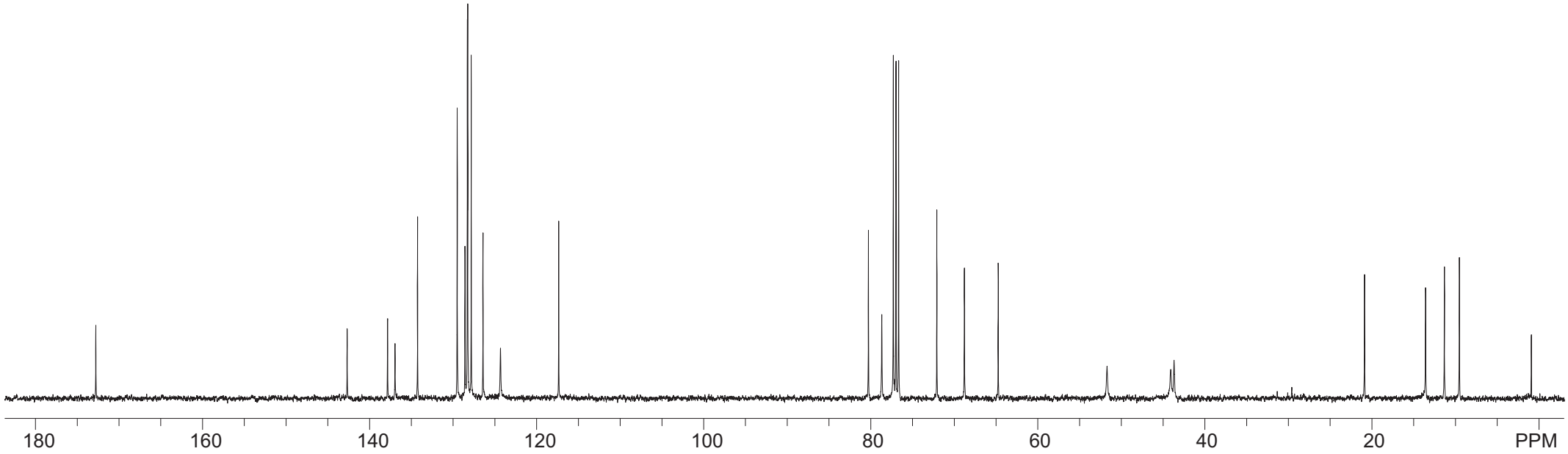
O
O
Ph

cis-**6ac**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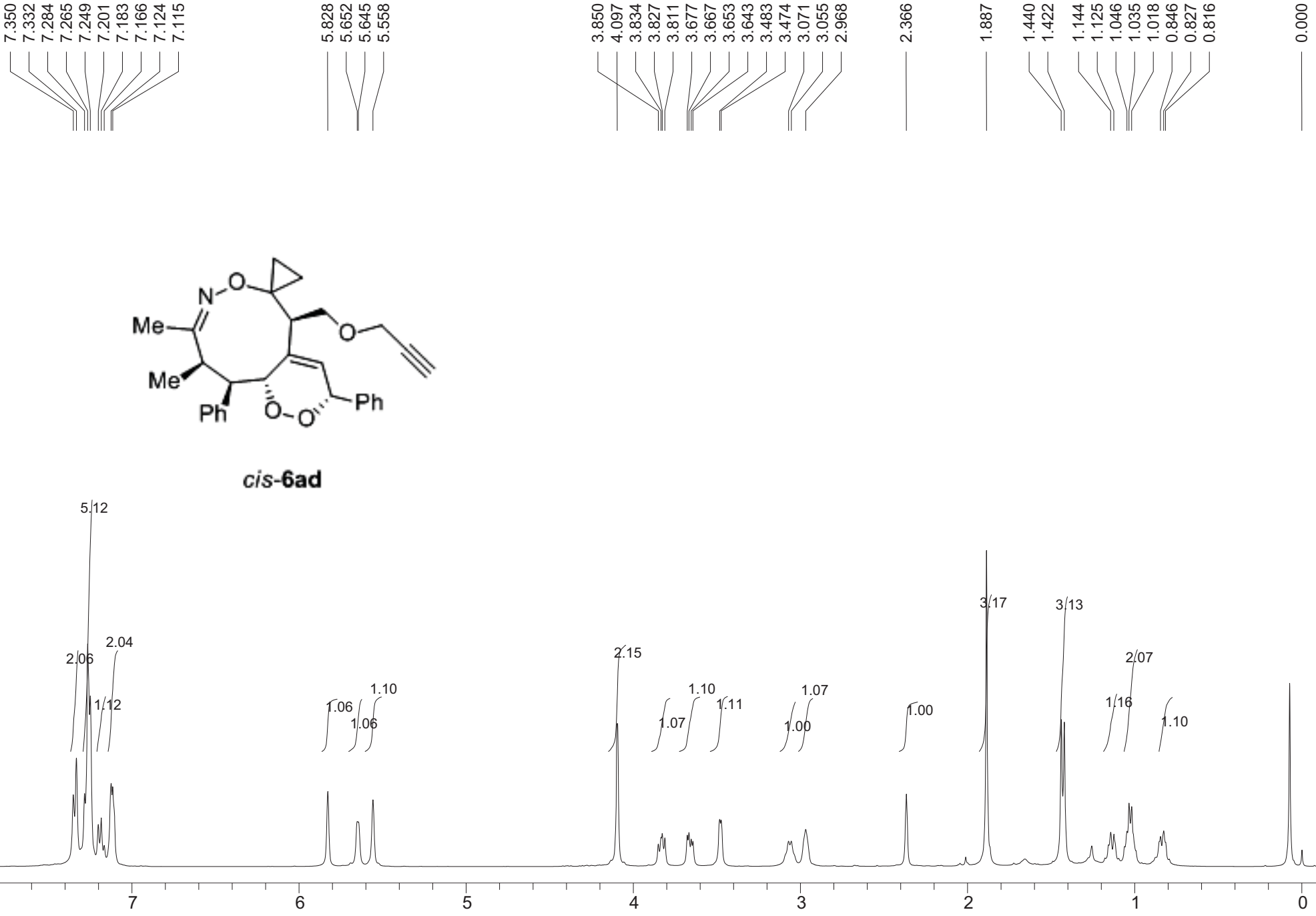
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Me
Ph
Ph
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O
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O
cis-6ad
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1.07
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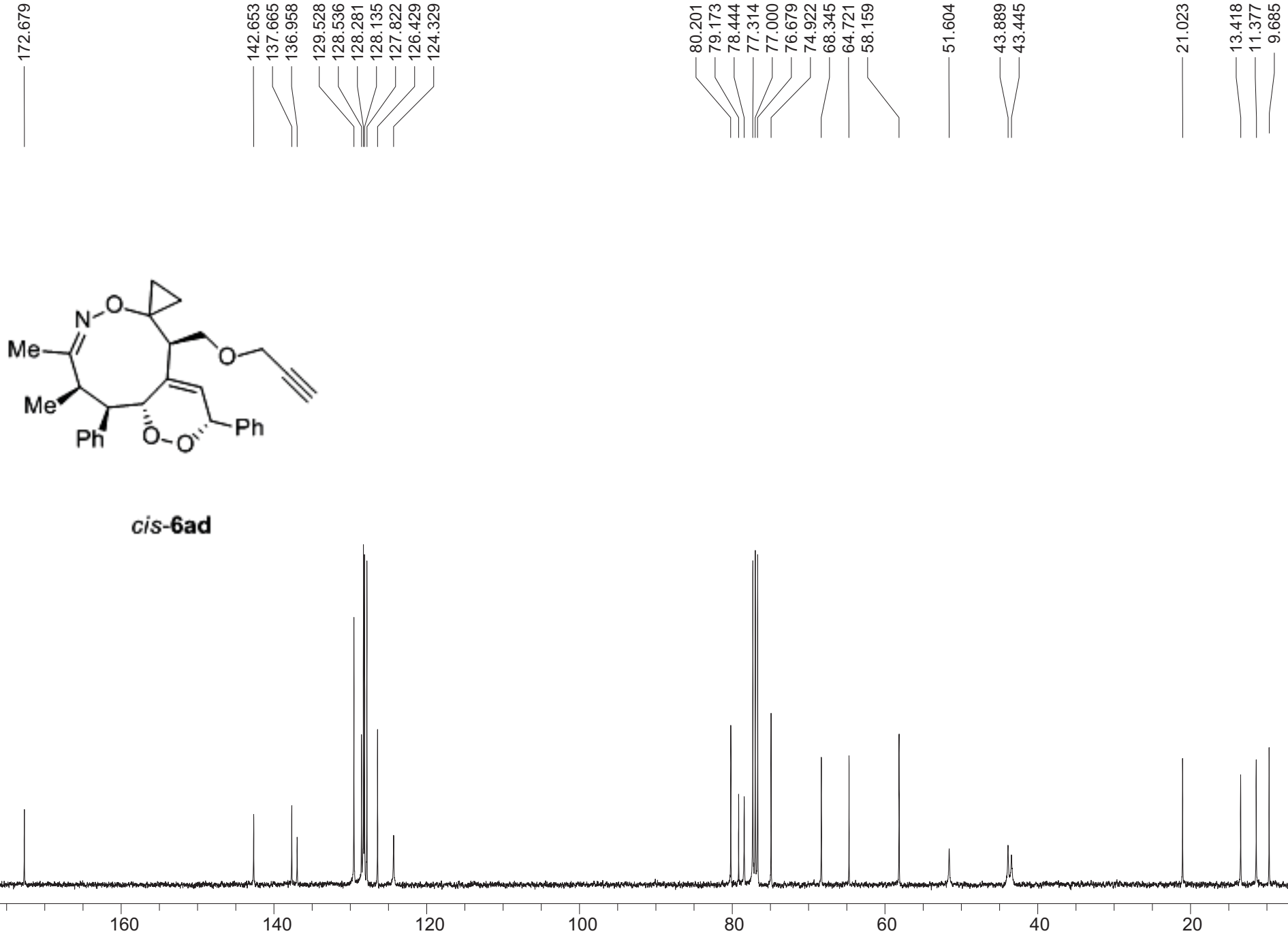
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58.159
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43.445
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9.685
N
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O
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Ph
O
O
Ph
cis-6ad
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140
120
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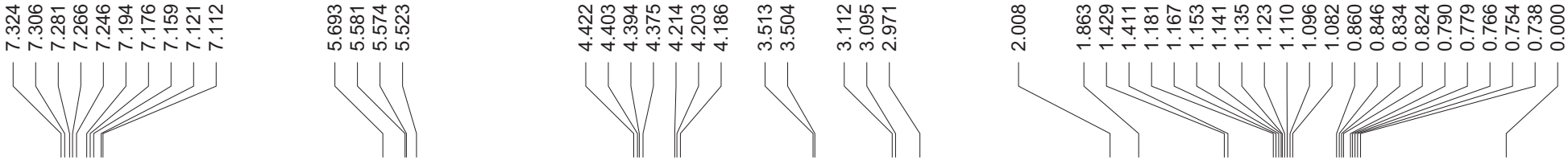
20
PPM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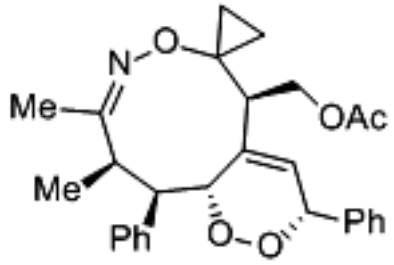
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OAc
Me
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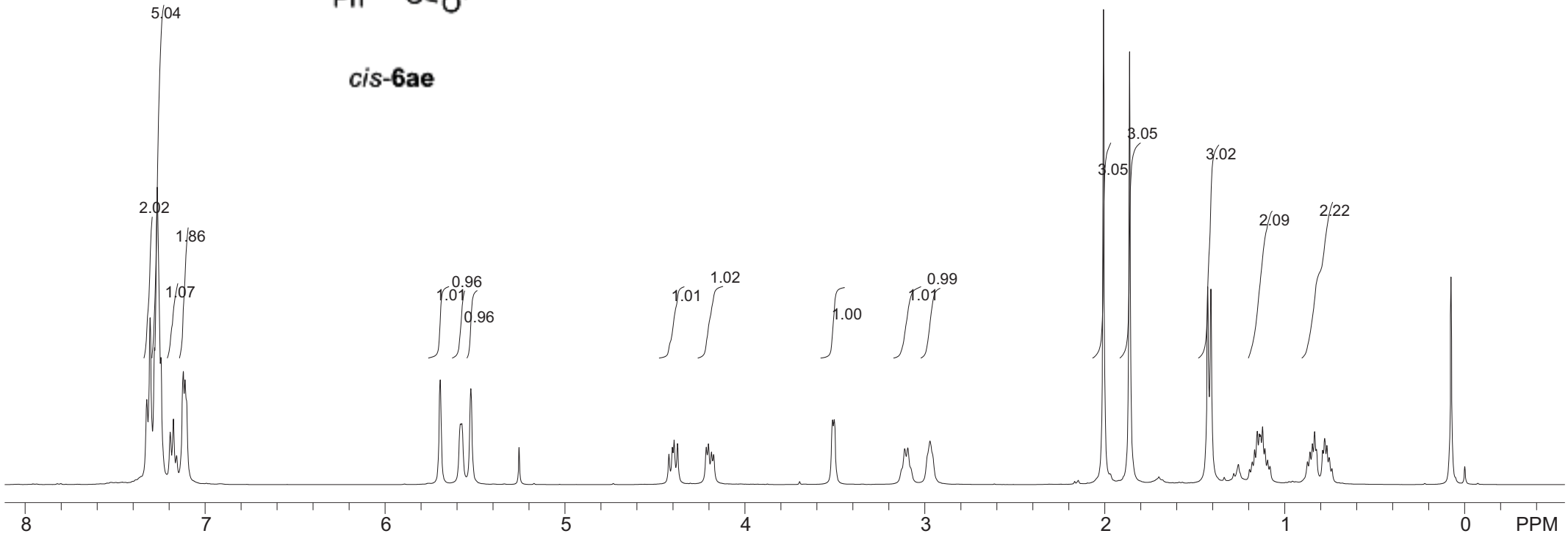
Ph

cis-**6ae**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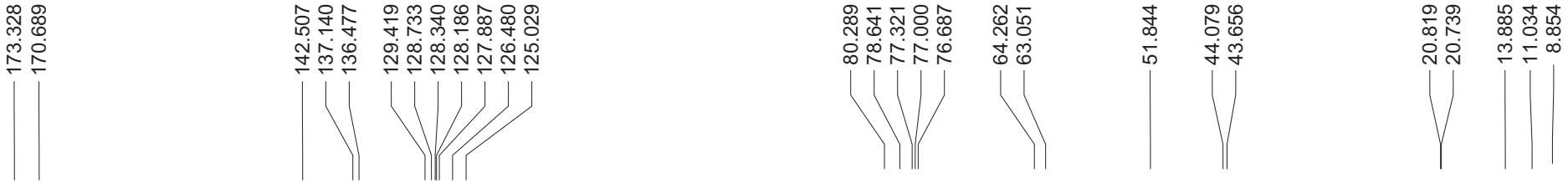
PPM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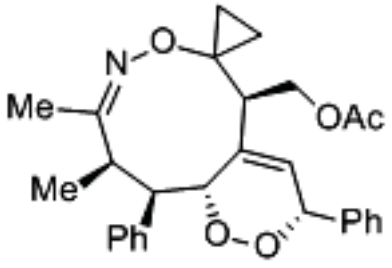
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OAc
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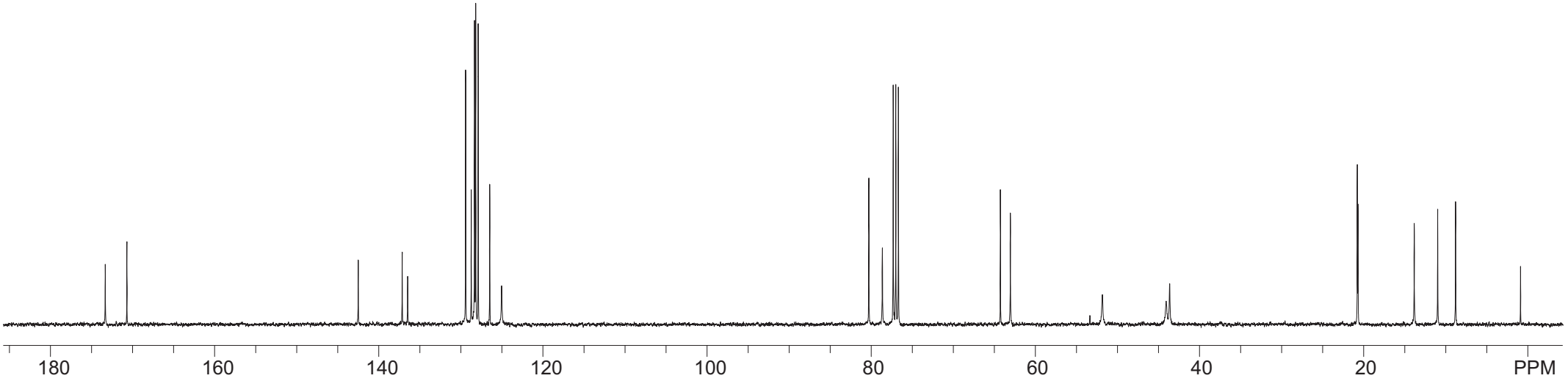
O
Ph

***cis*-6ae**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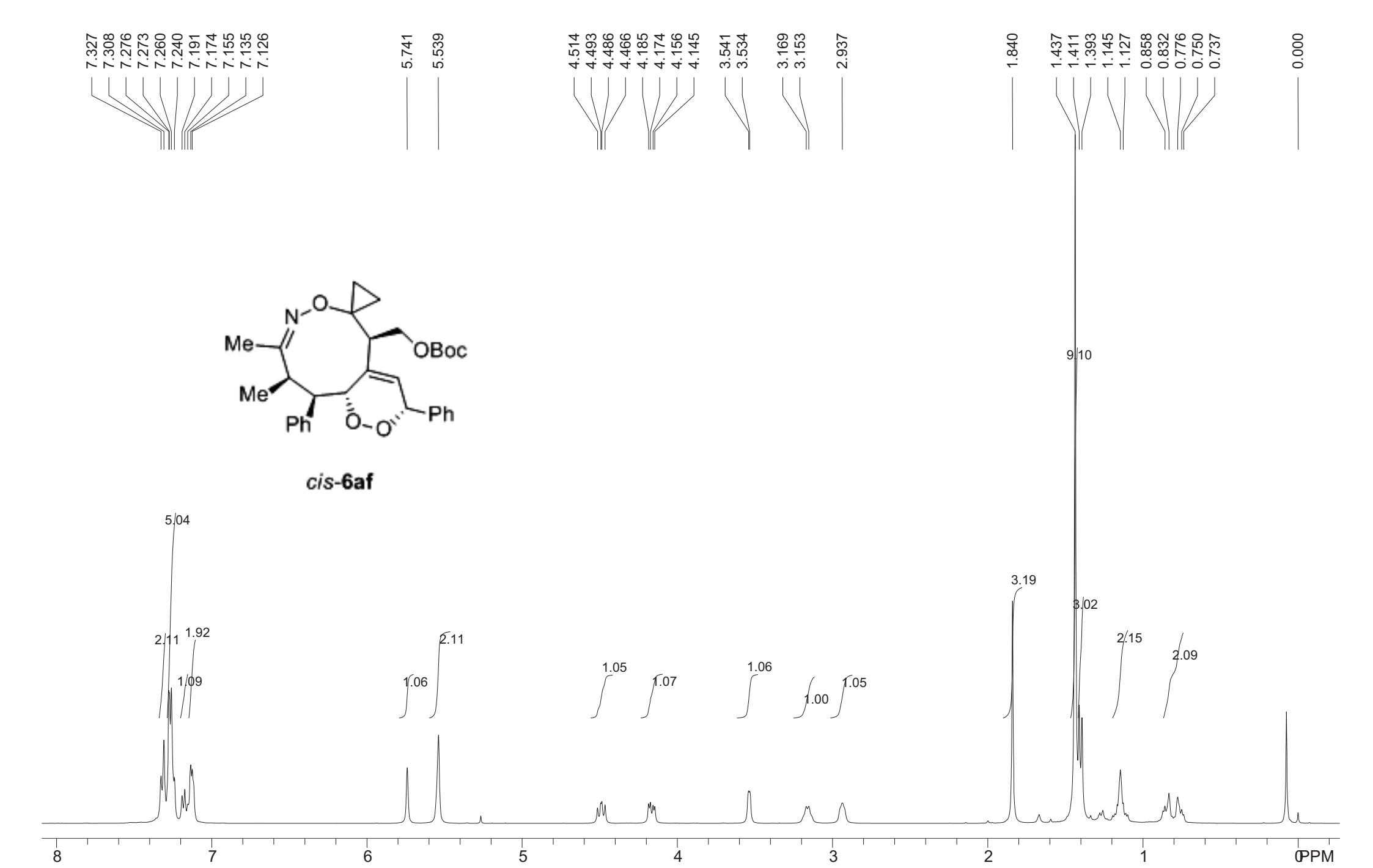
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Ph
cis-6af
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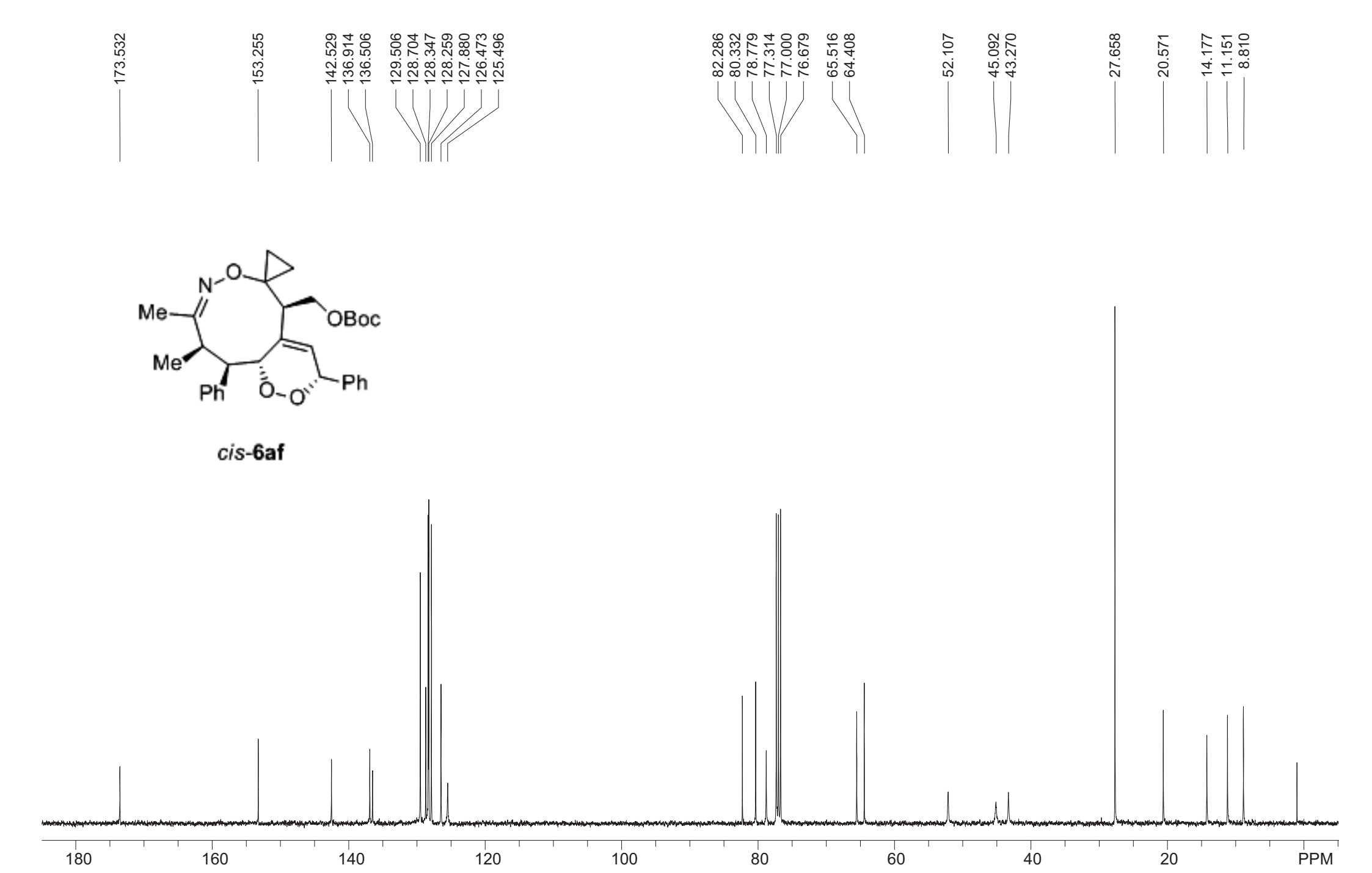
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11.151
8.810
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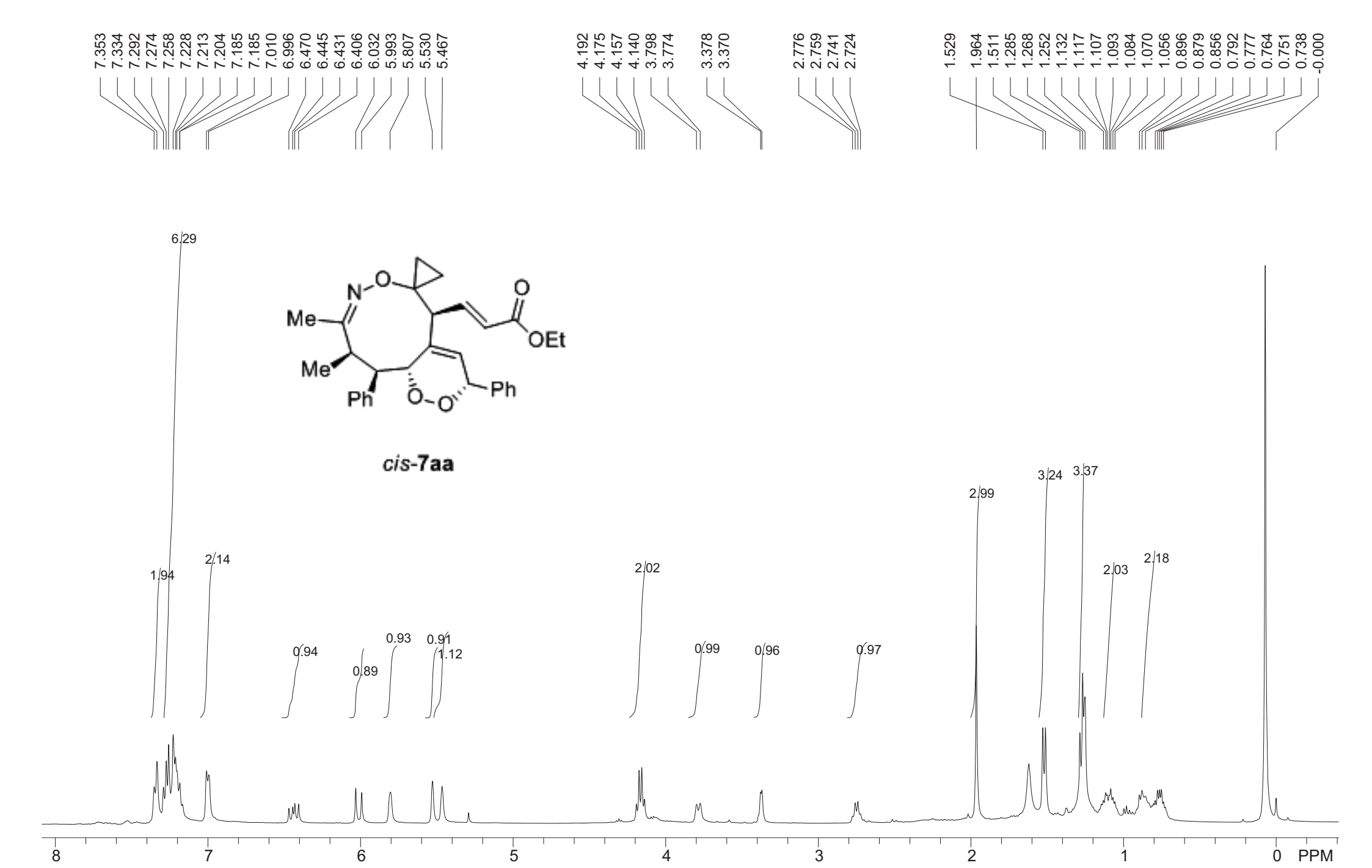
PPM

cis-**6af**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Me
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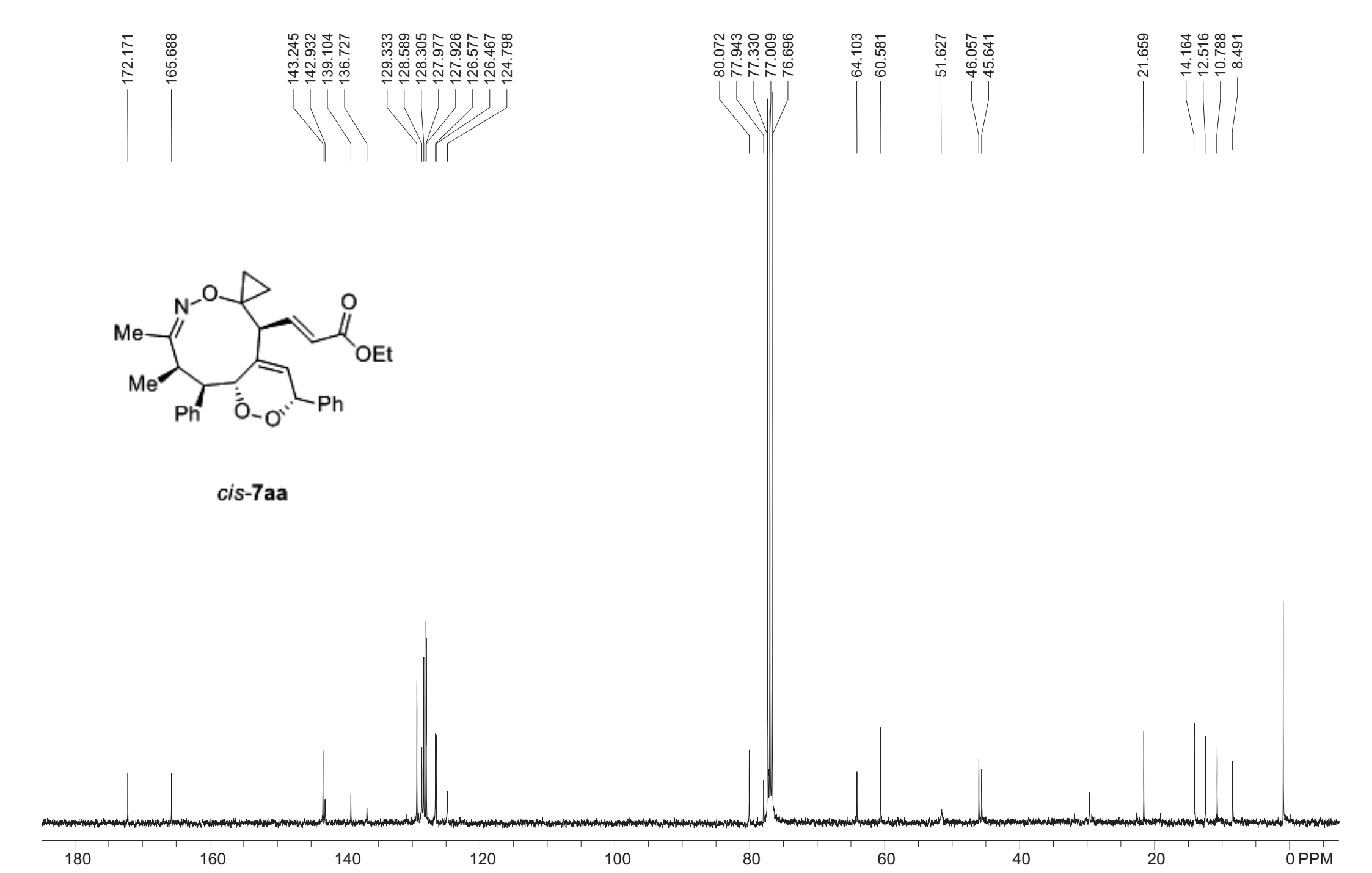
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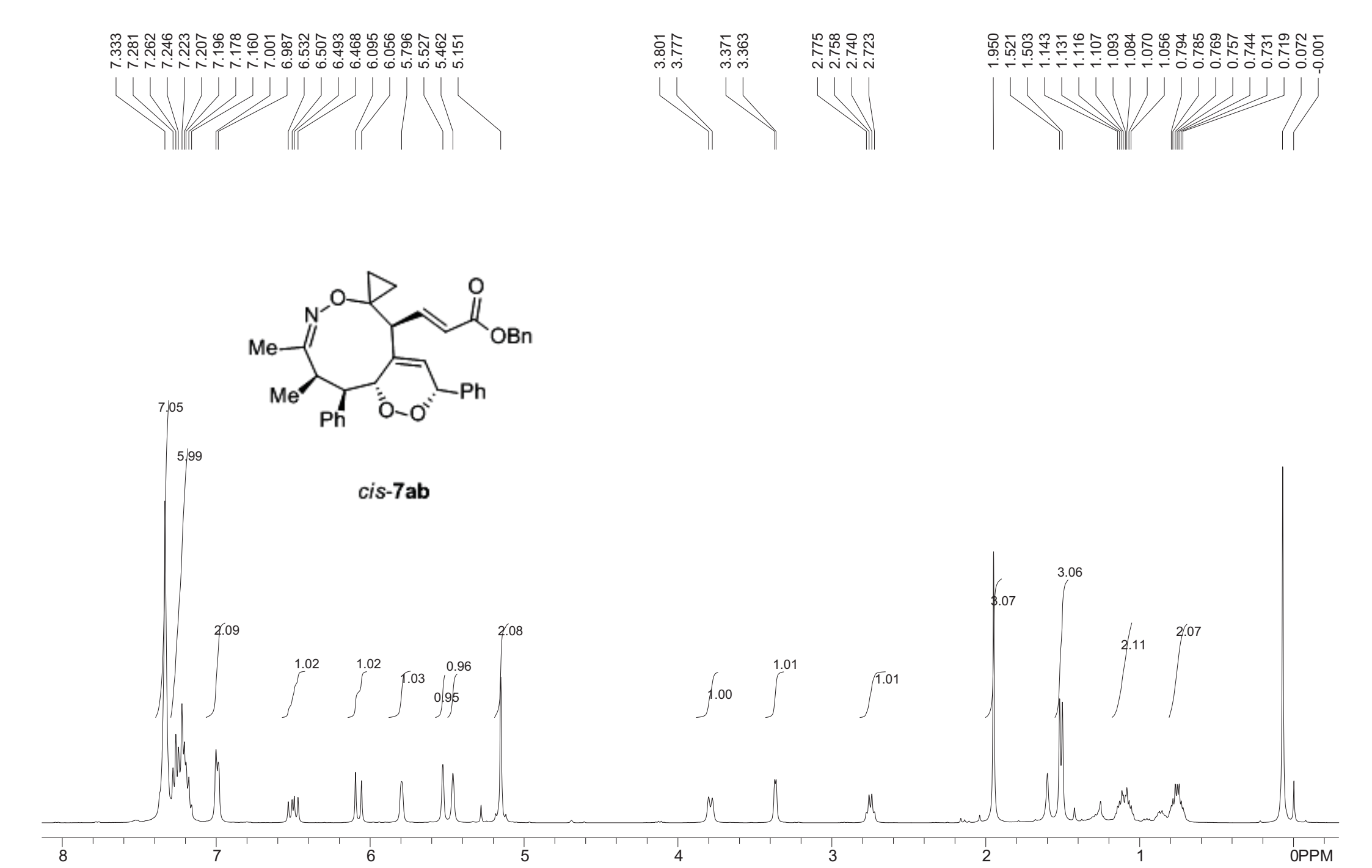
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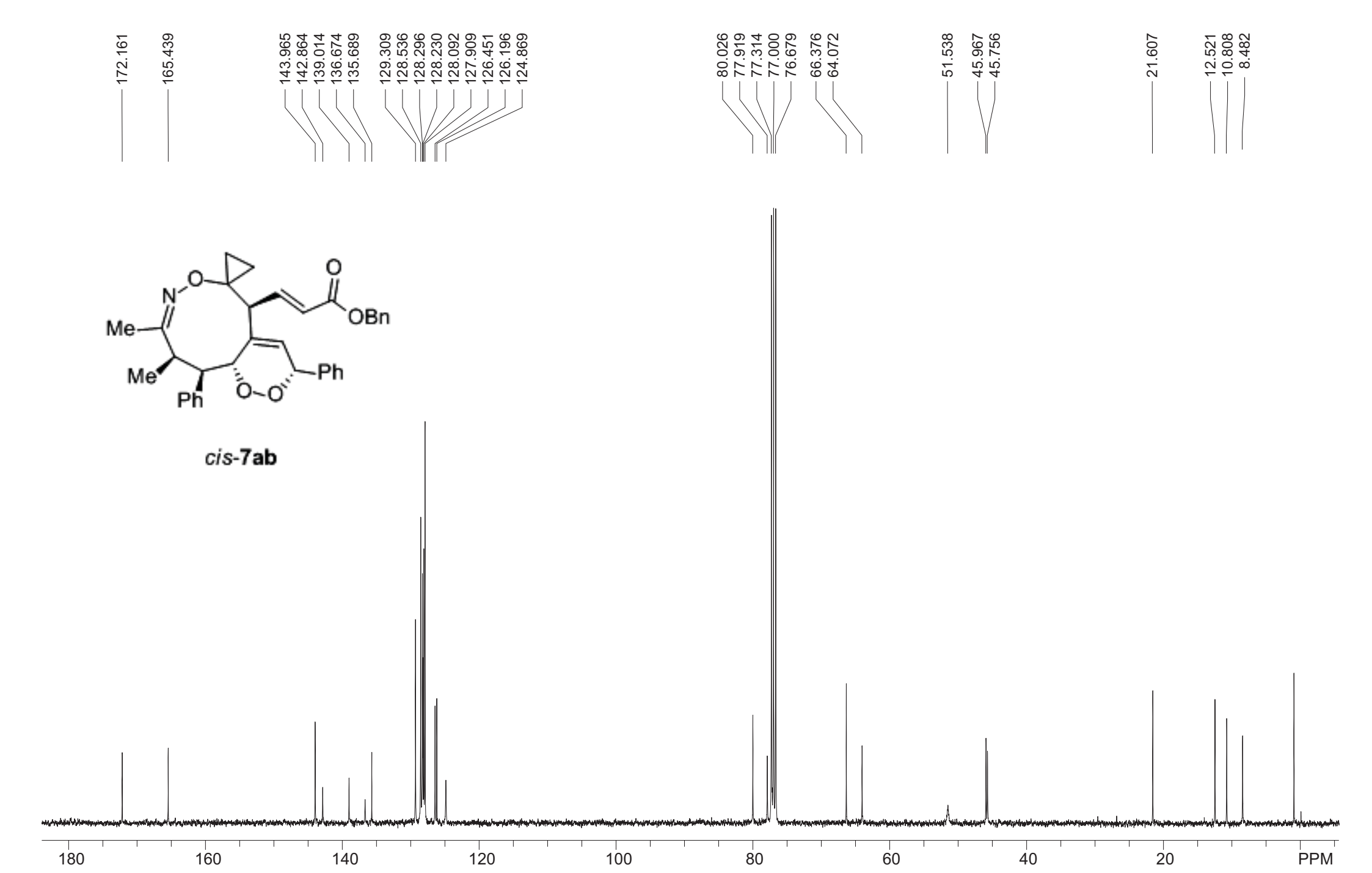
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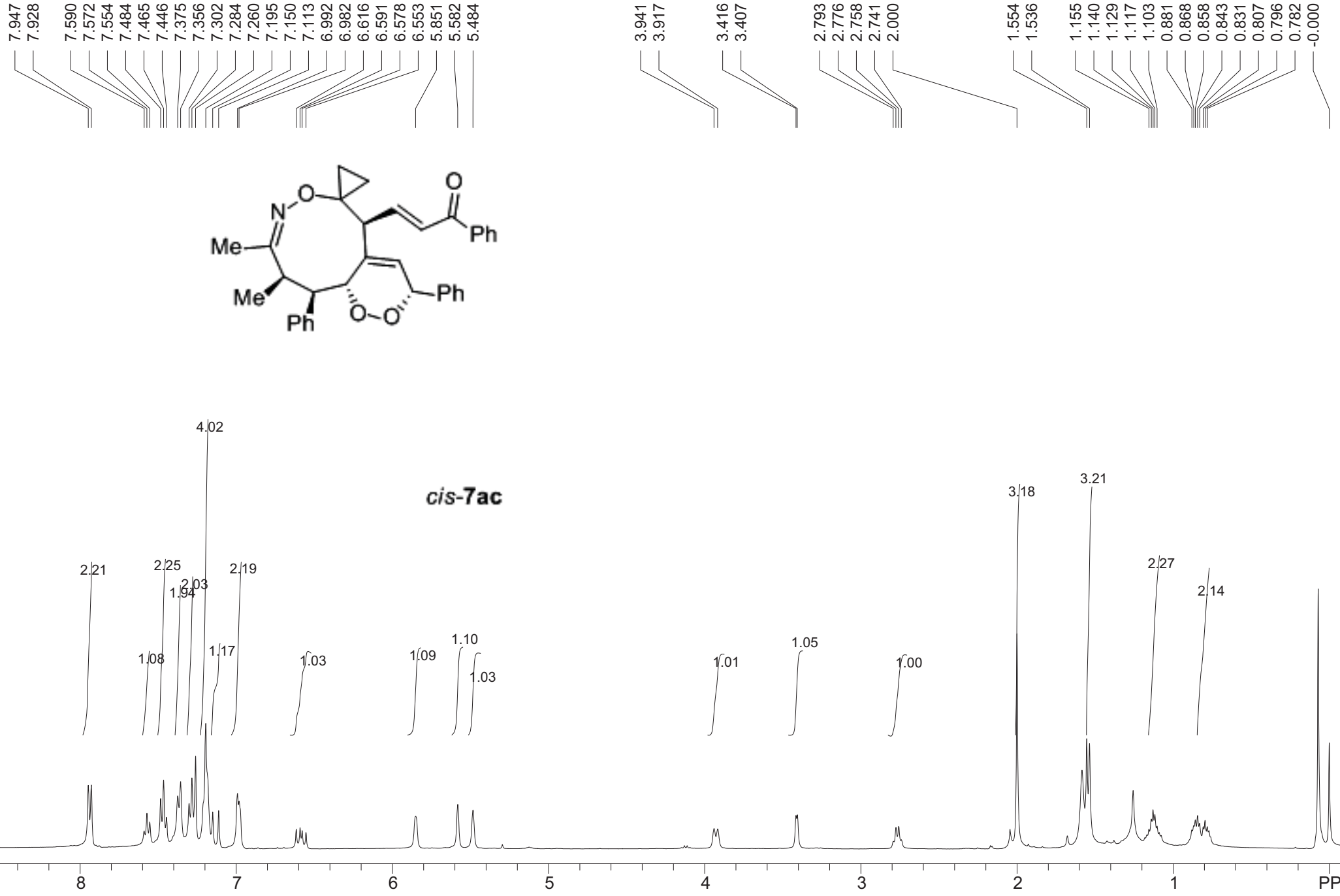
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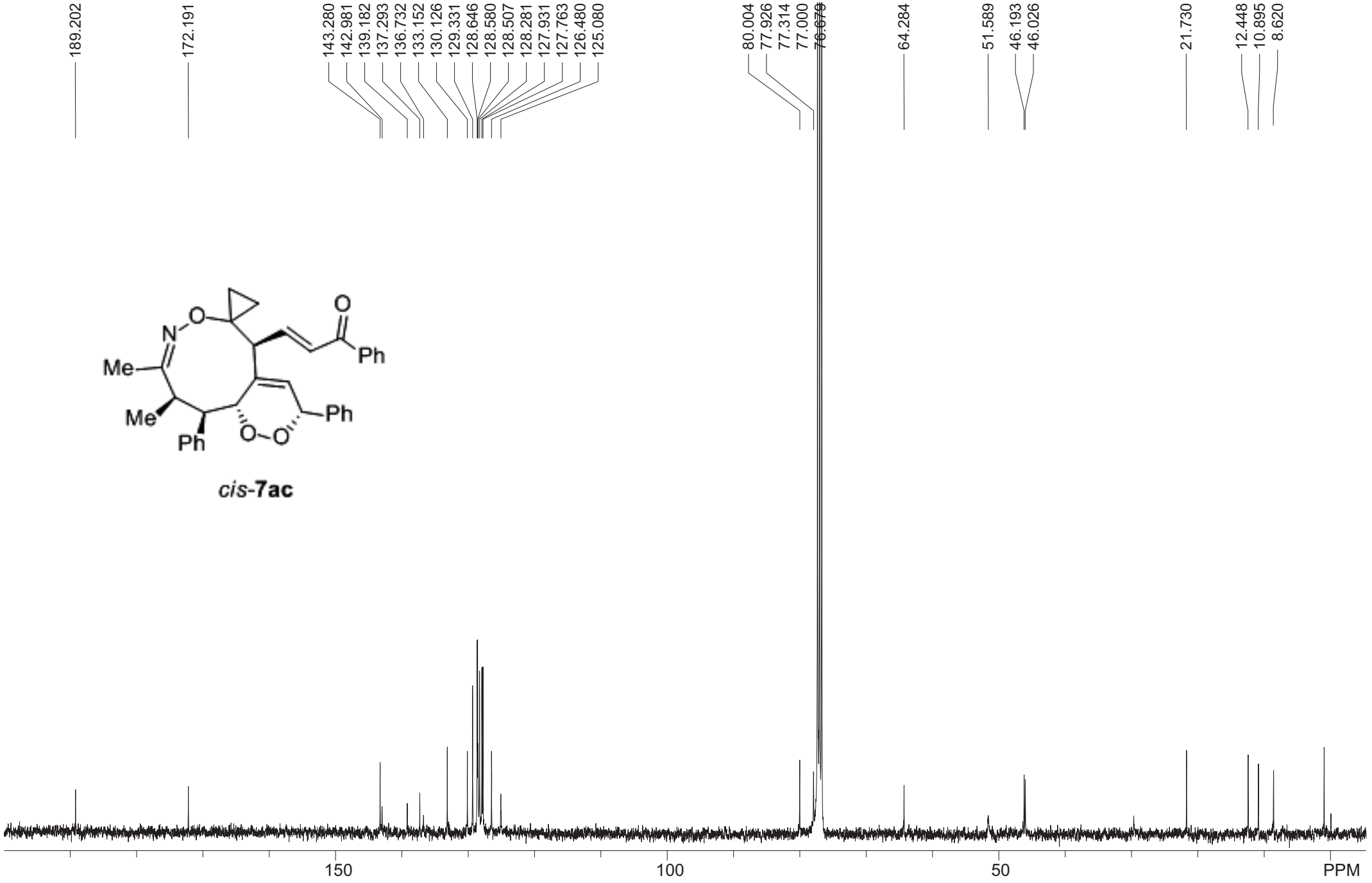
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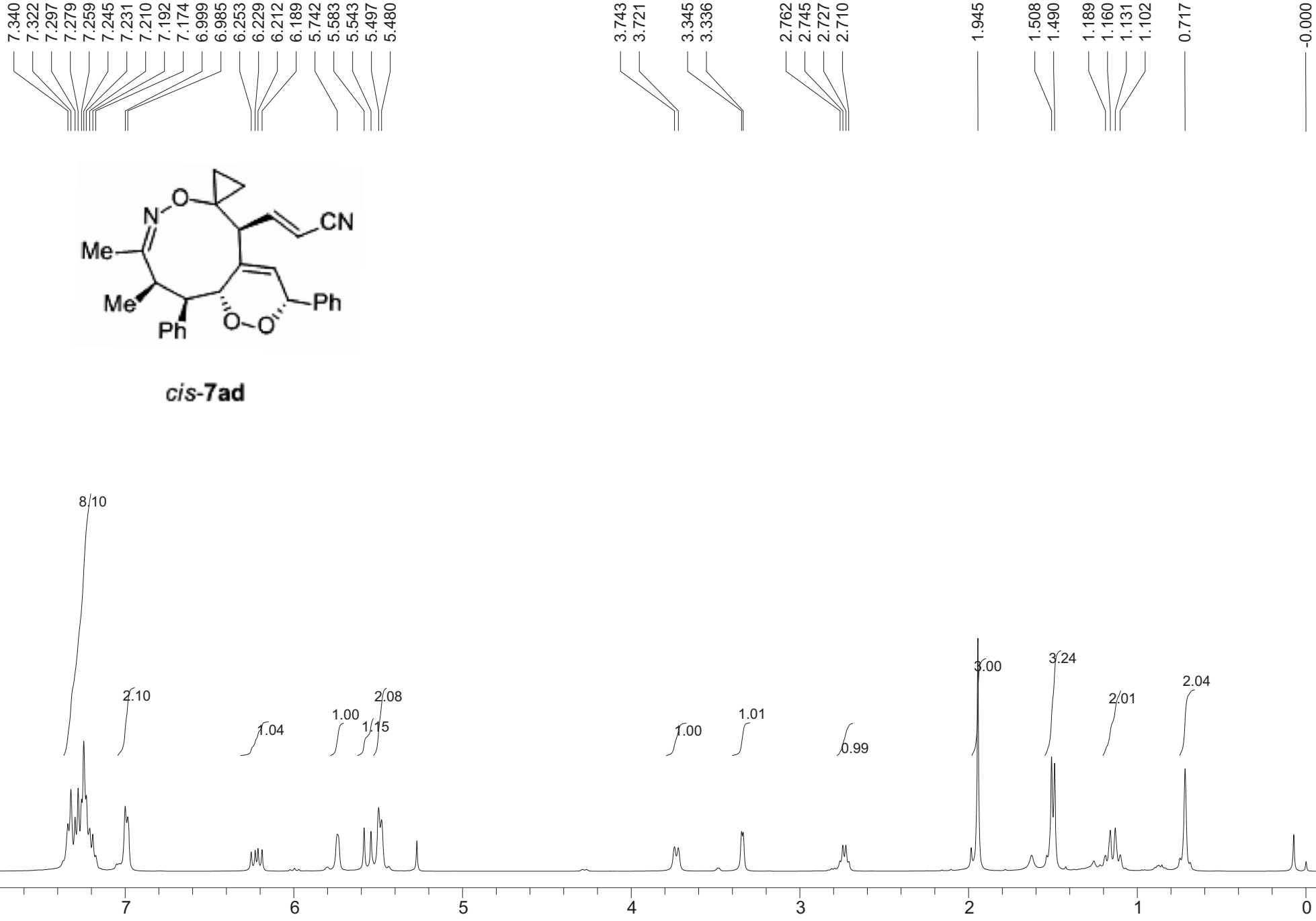
cis-**7ac**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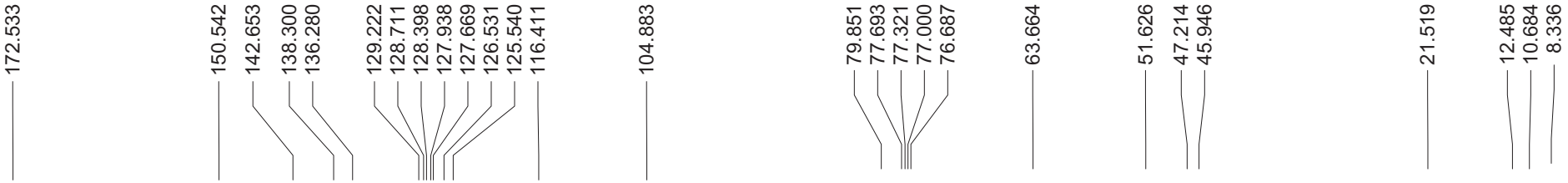
cis-**7ad**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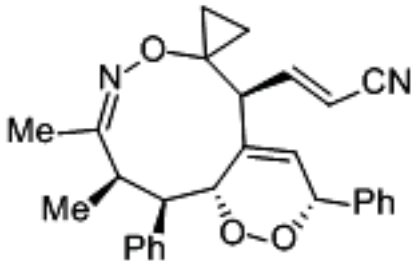
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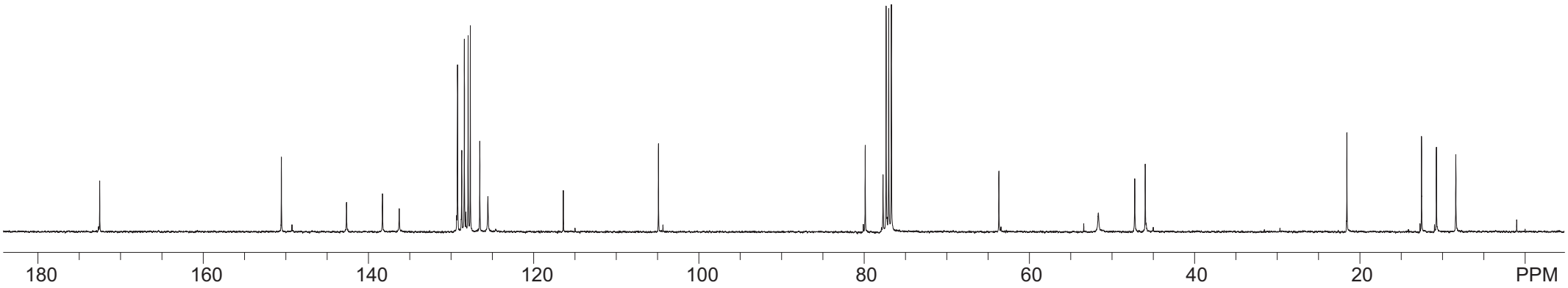
cis-**7ad**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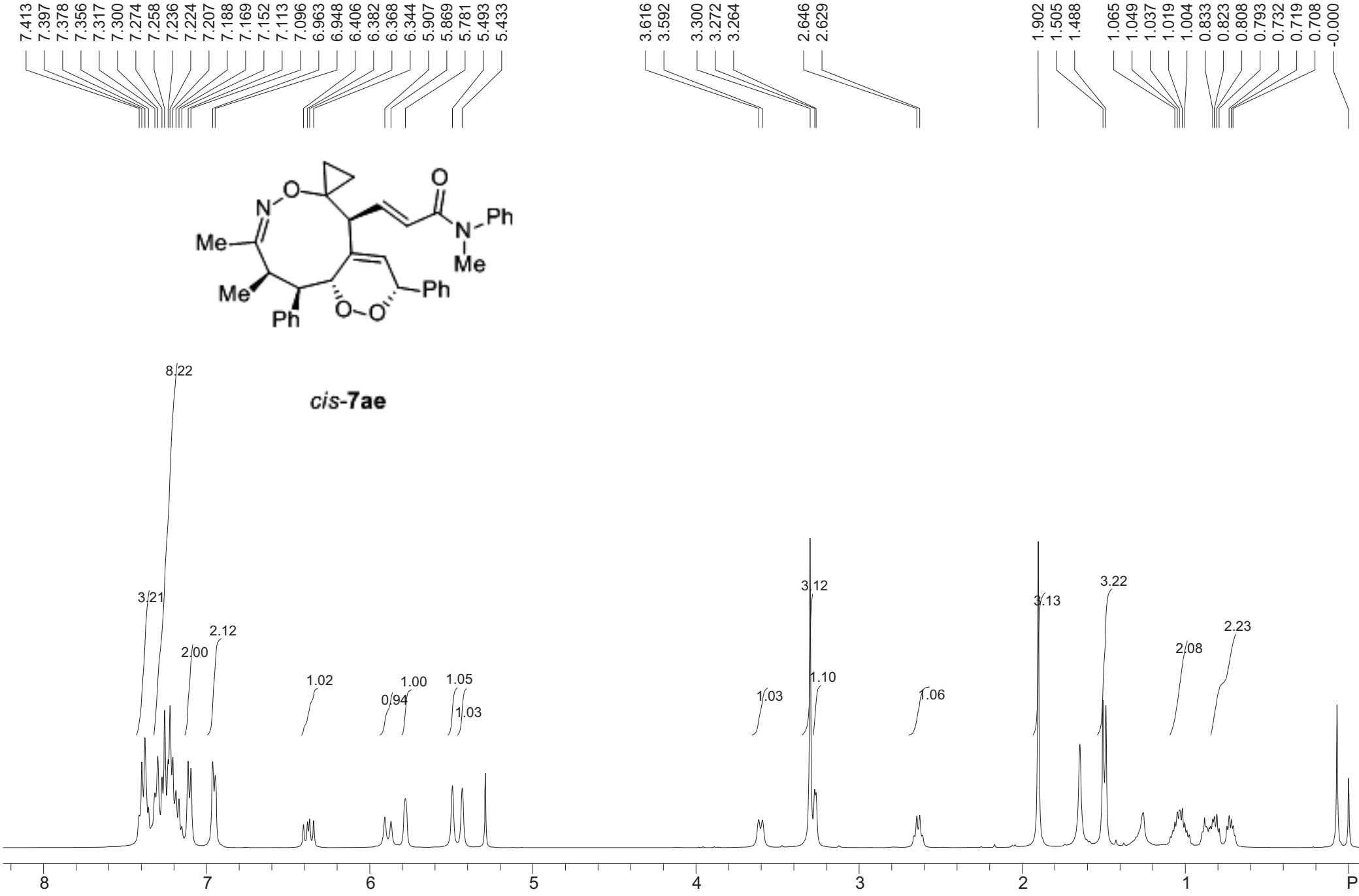
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cis-7ae
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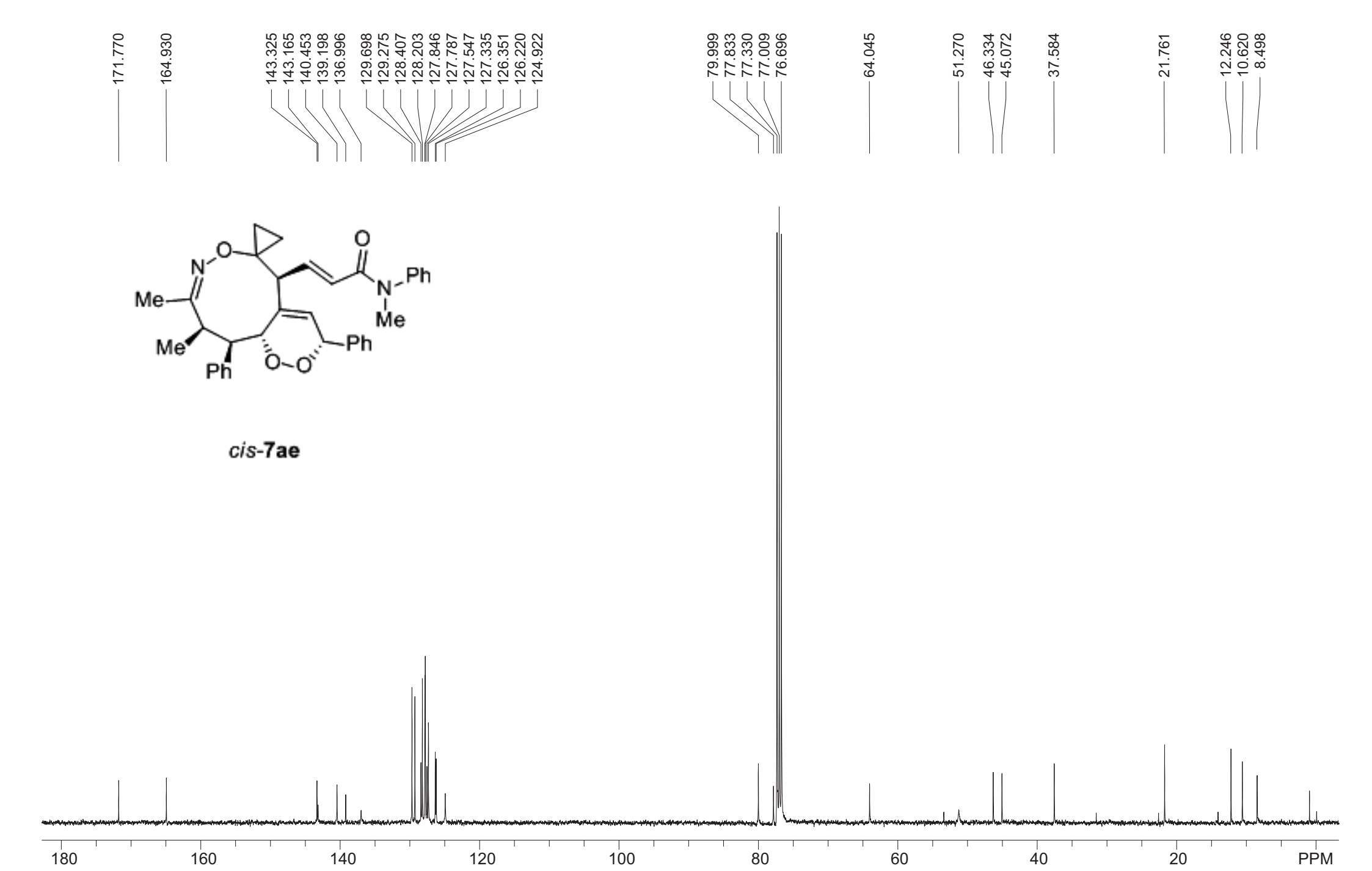
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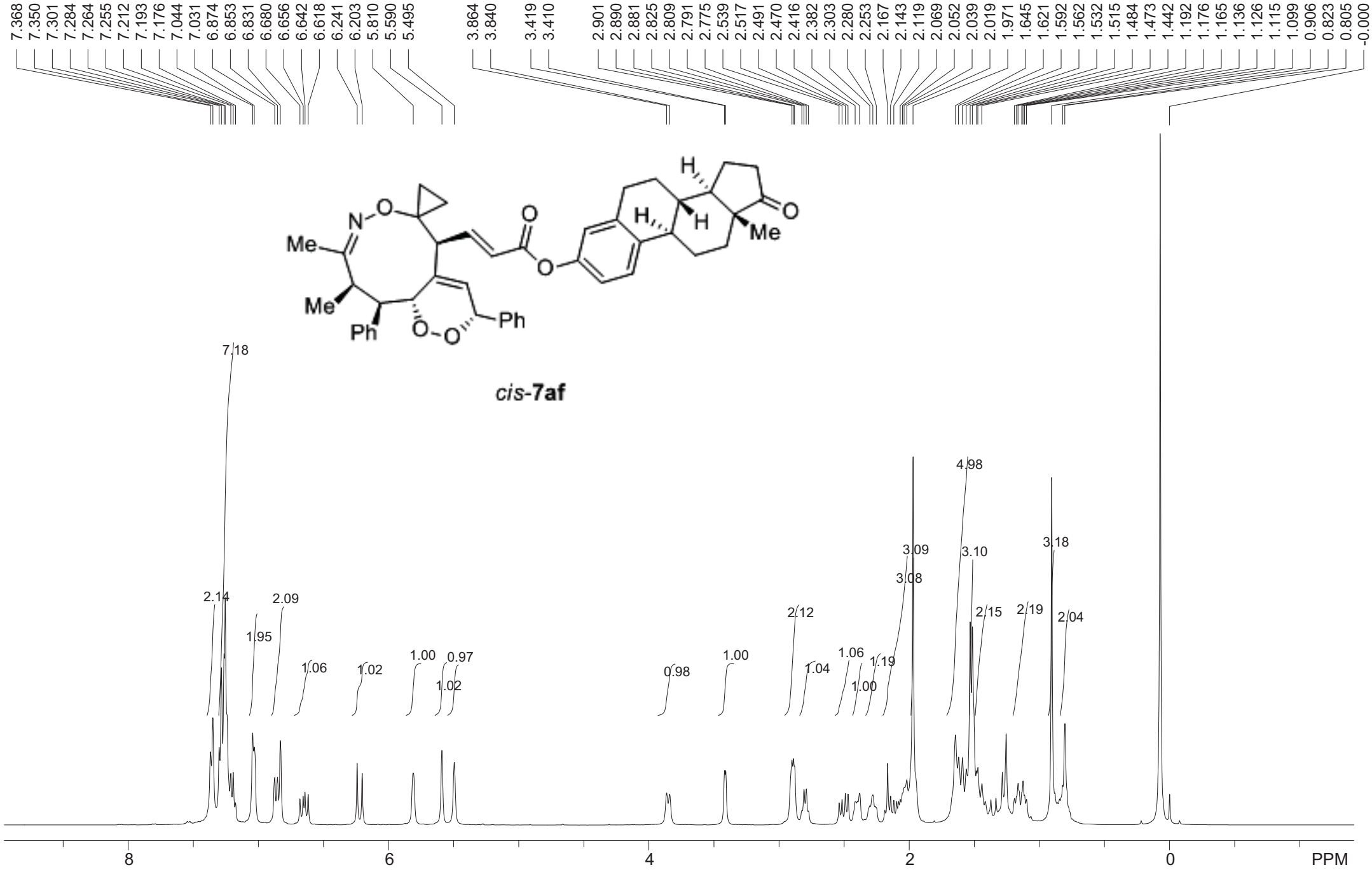
cis-**7ae**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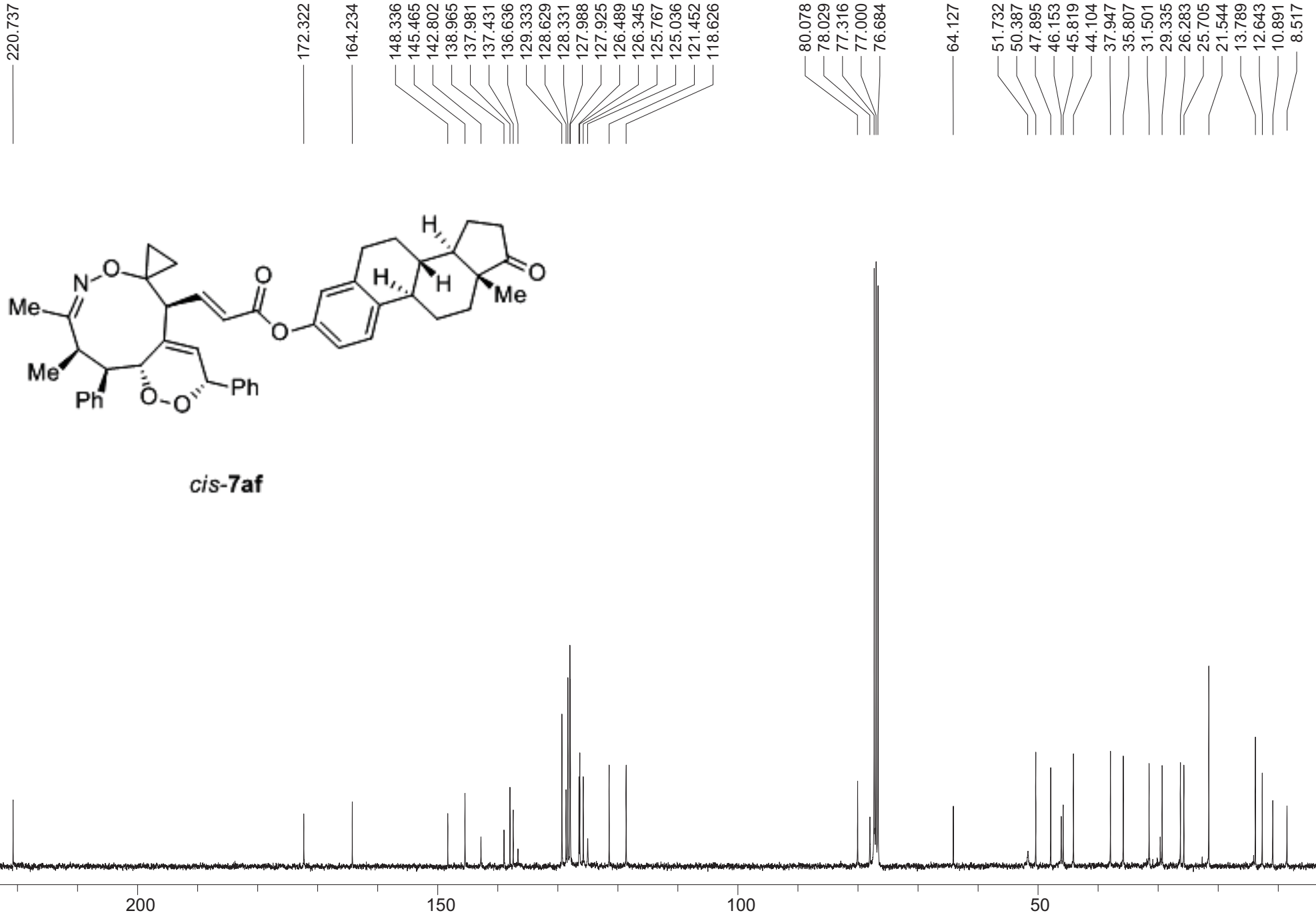
cis-**7af**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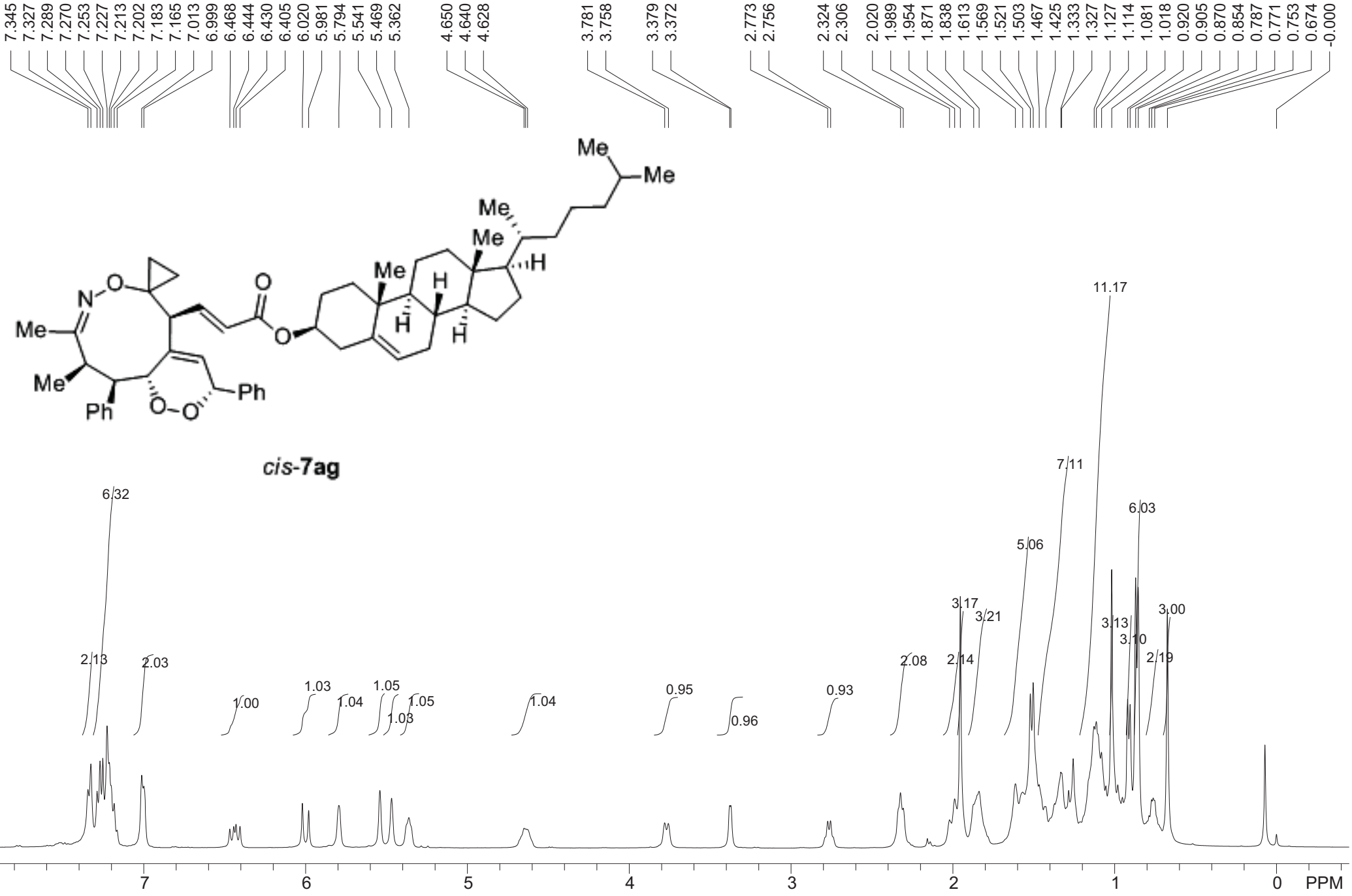
cis-**7af**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cis-7ag
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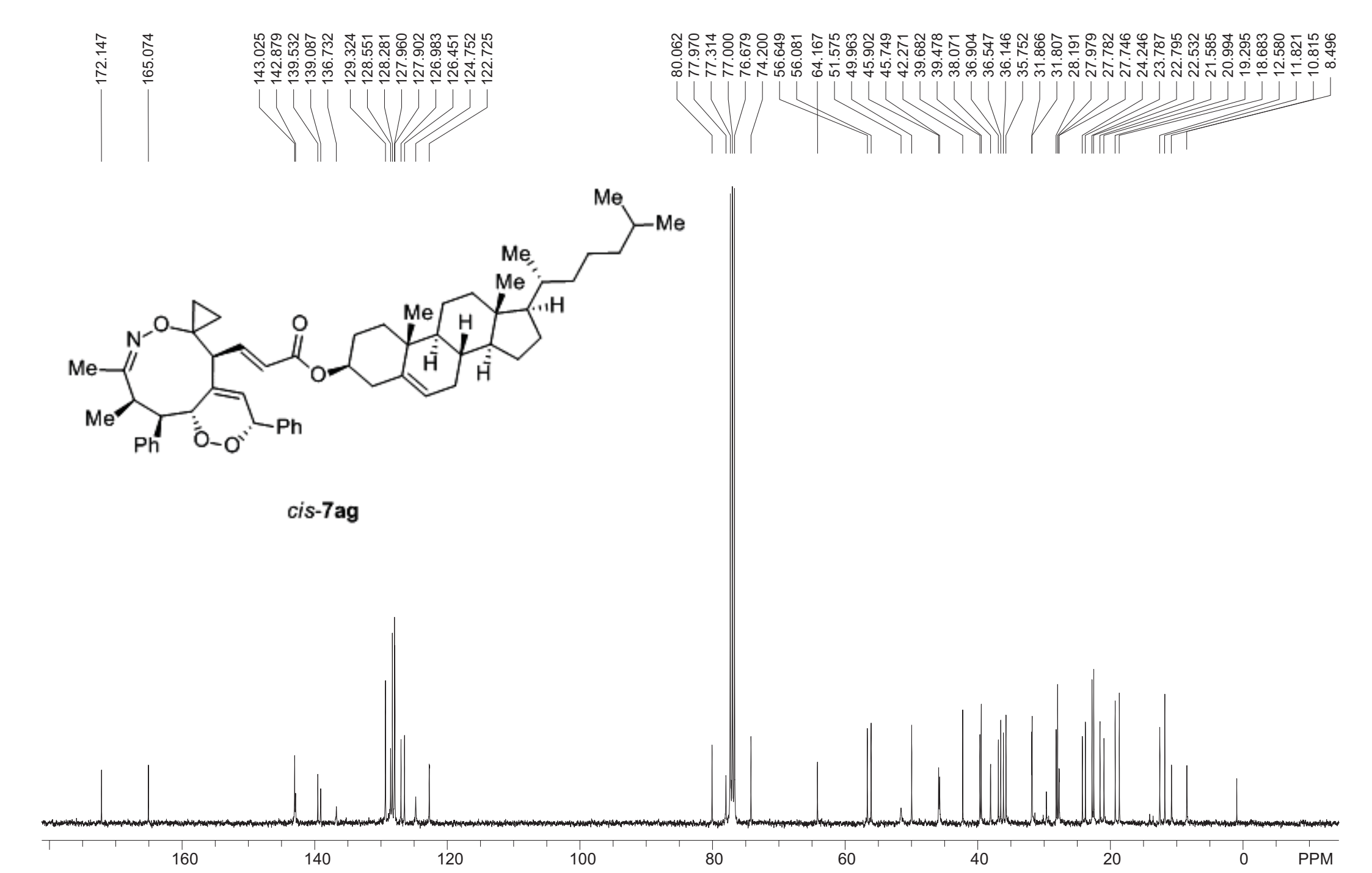
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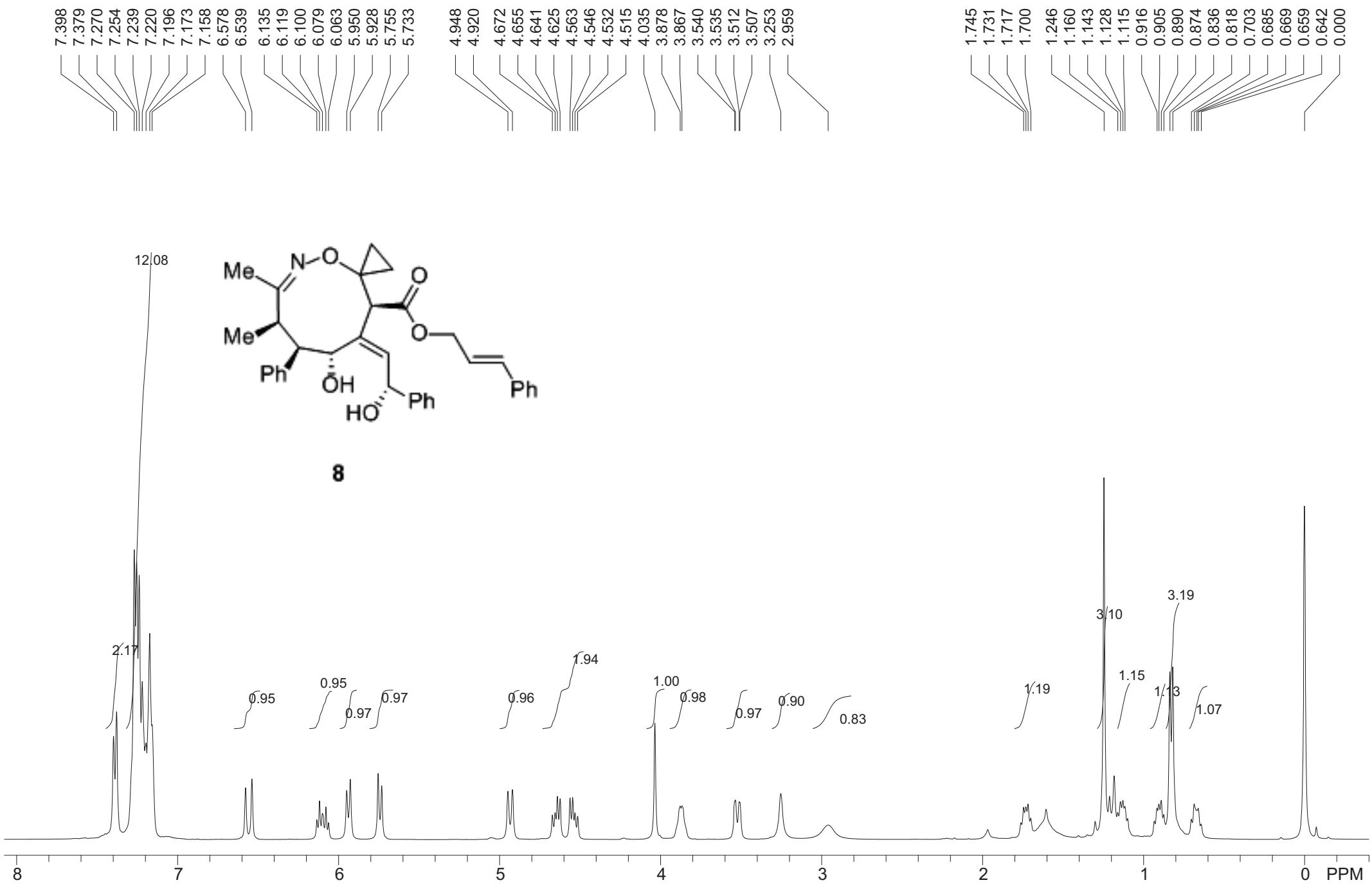
cis-**7ag**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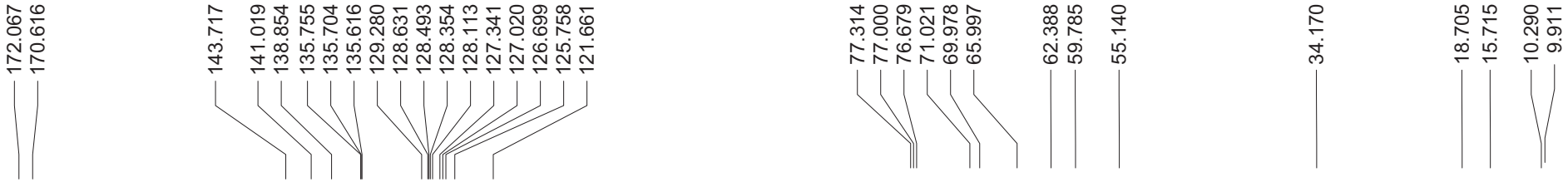
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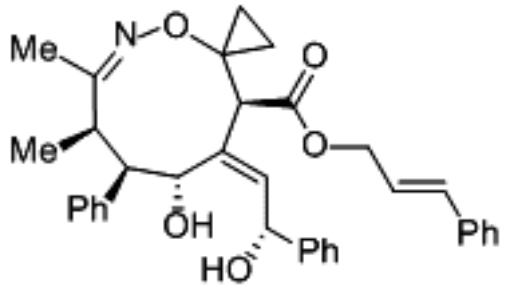
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HO
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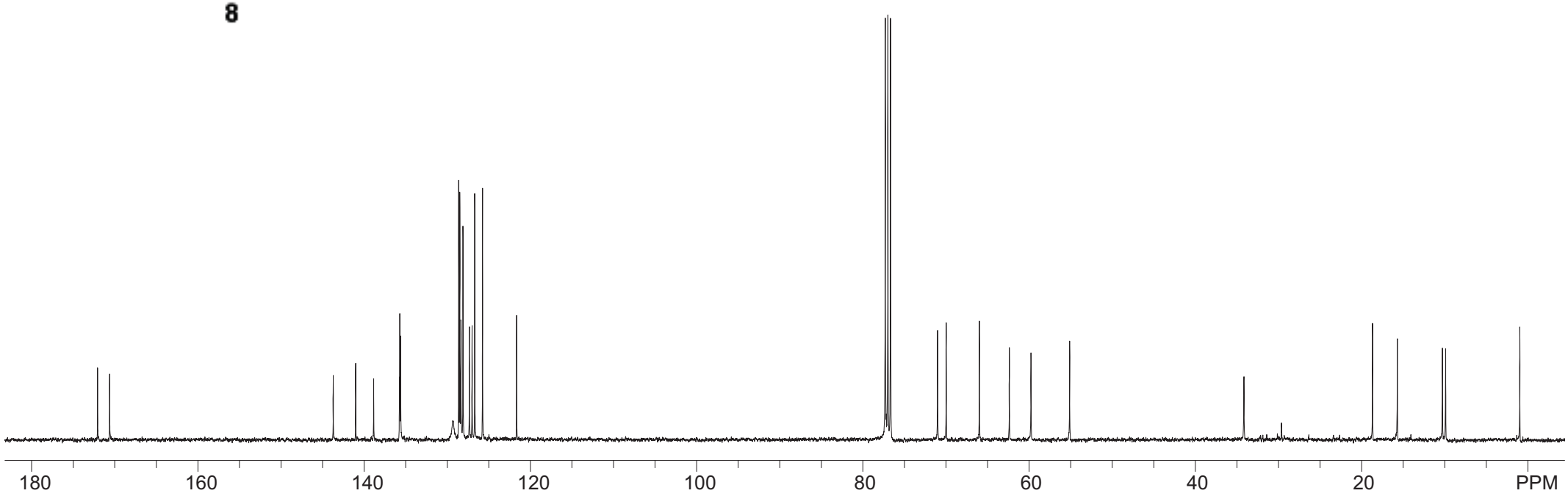
8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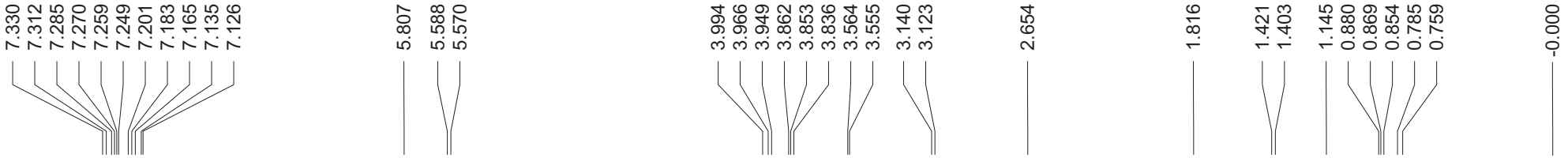
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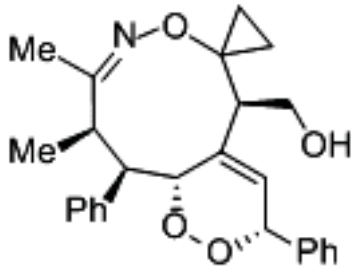
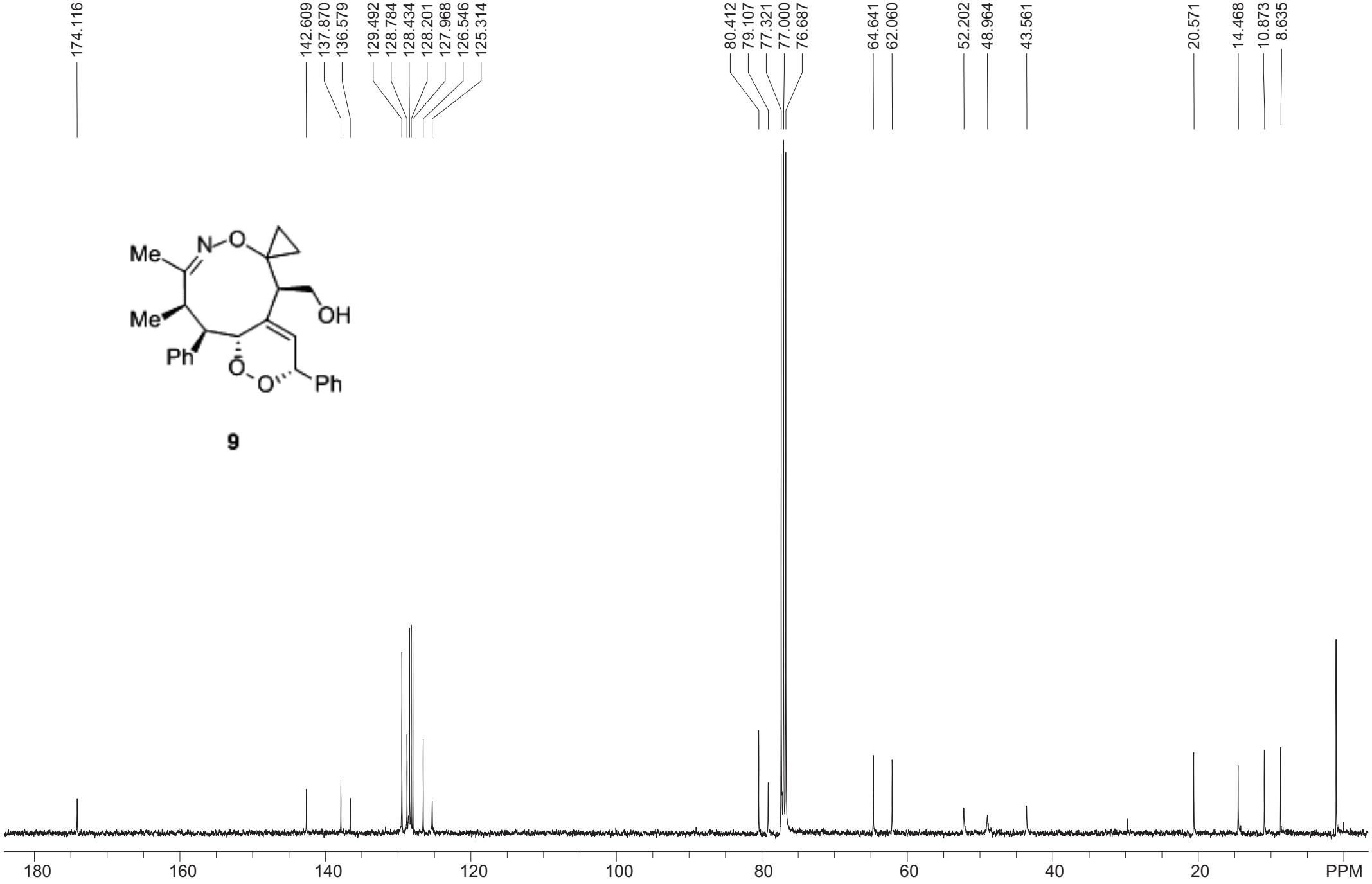

Me
N
O
Me
OH
Ph
O
O
Ph

9

7.14
3.04
1.02
2.01
2.07
1.10
1.02
1.00
3.12
3.18
2.11
2.08
8
7
6
5
4
3
2
1
0 PPM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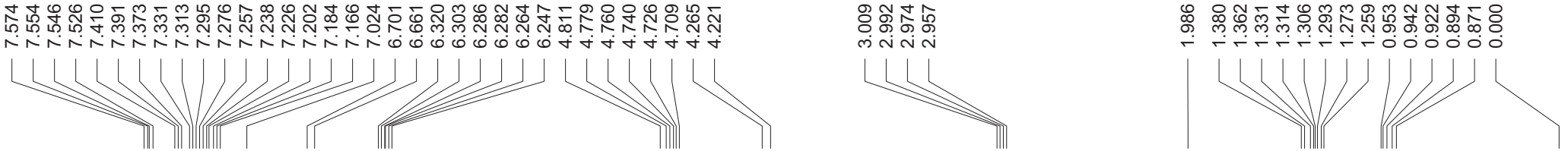
142.609
137.870
136.579
129.492
128.784
128.434
128.201
127.968
126.546
125.314
80.412
79.107
77.321
77.000
76.687
64.641
62.060
52.202
48.964
43.561
20.571
14.468
10.873
8.635
Me
N
O
Me
OH
Ph
O
O
Ph
180
160
140
120
100
80
60
40
20
PPM

9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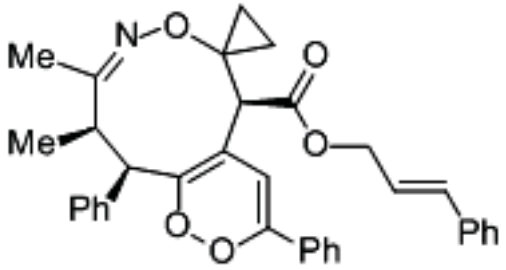
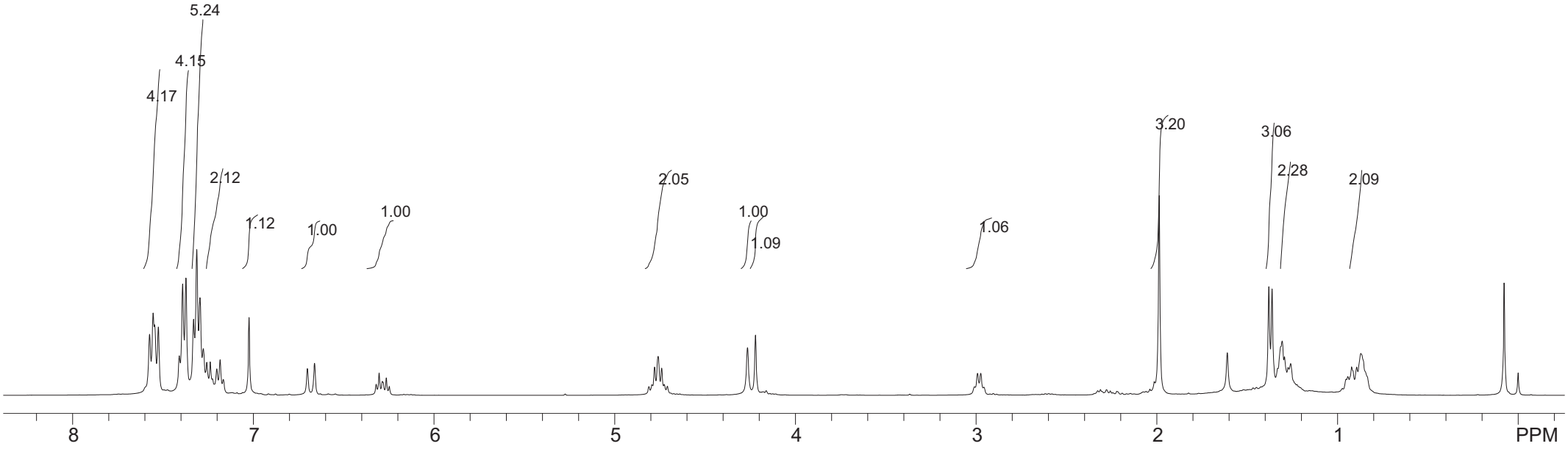
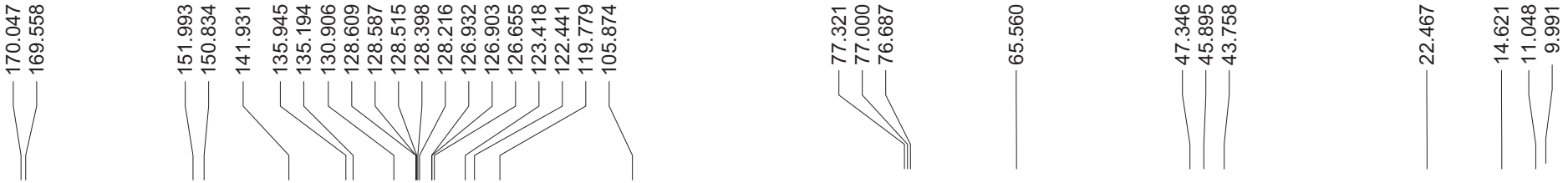
7.546
7.526
7.410
7.391
7.373
7.331
7.313
7.295
7.276
7.257
7.238
7.226
7.202
7.184
7.166
7.024
6.701
6.661
6.320
6.303
6.286
6.282
6.264
6.247
4.811
4.779
4.760
4.740
4.726
4.709
4.265
4.221
3.009
2.992
2.974
2.957
1.986
1.380
1.362
1.331
1.314
1.306
1.293
1.273
1.259
0.953
0.942
0.922
0.894
0.871
0.000


Me
N
O
O
Me
O
Ph
O
O
Ph
Ph

10


5.24
4.15
4.17
2.12
1.12
1.00
1.00
2.05
1.00
1.09
1.06
3.20
3.06
2.28
2.09
8
7
6
5
4
3
2
1
PPM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169.558
151.993
150.834
141.931
135.945
135.194
130.906
128.609
128.587
128.515
128.398
128.216
126.932
126.903
126.655
123.418
122.441
119.779
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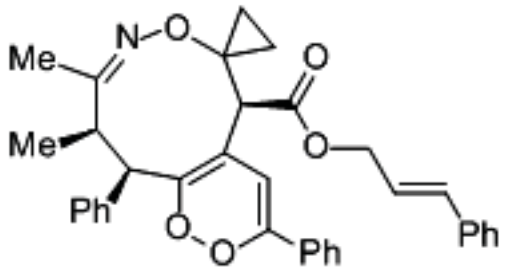
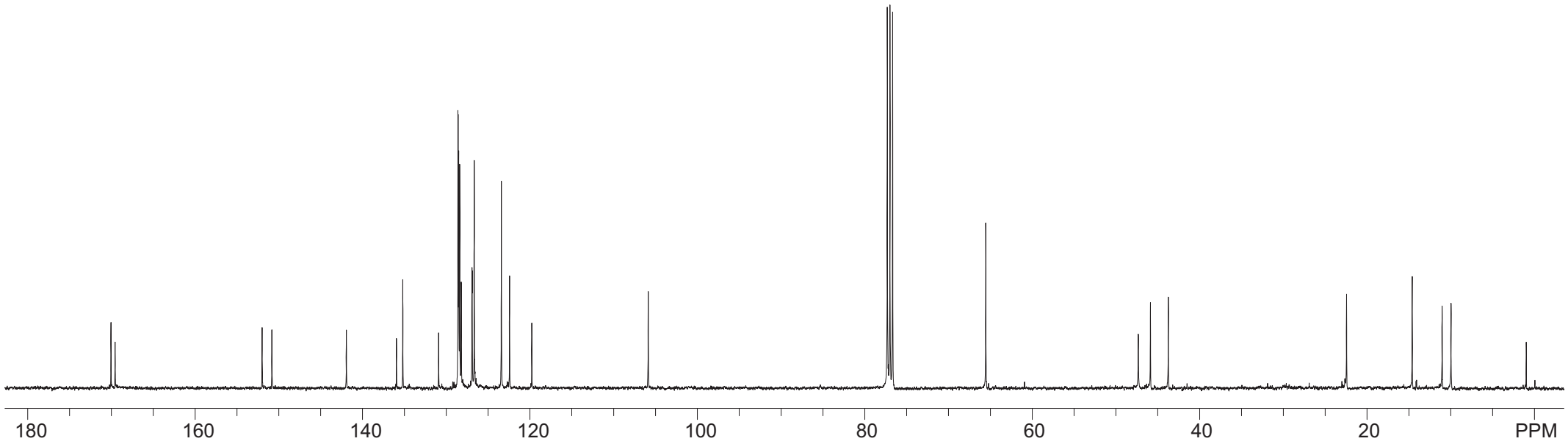
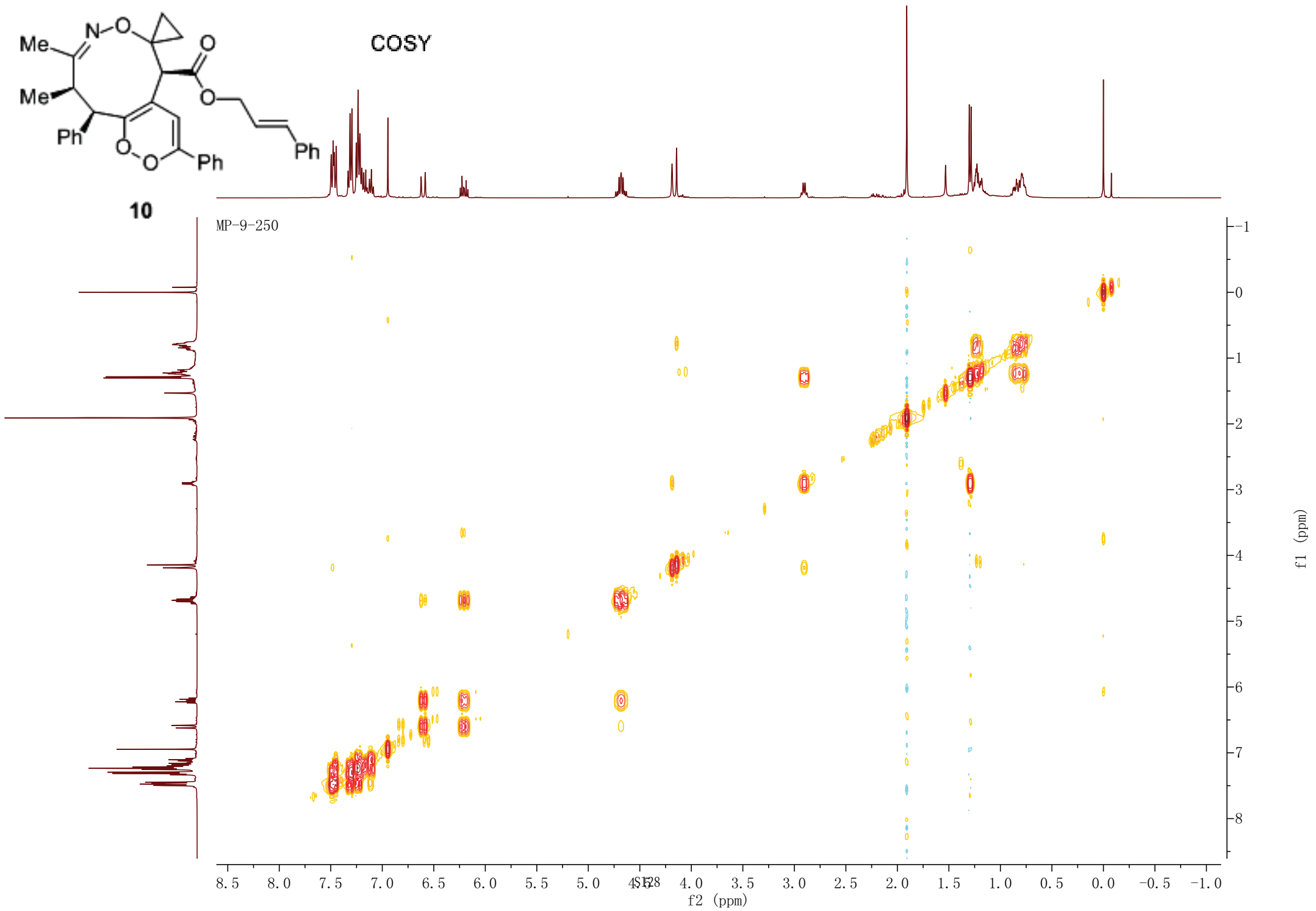
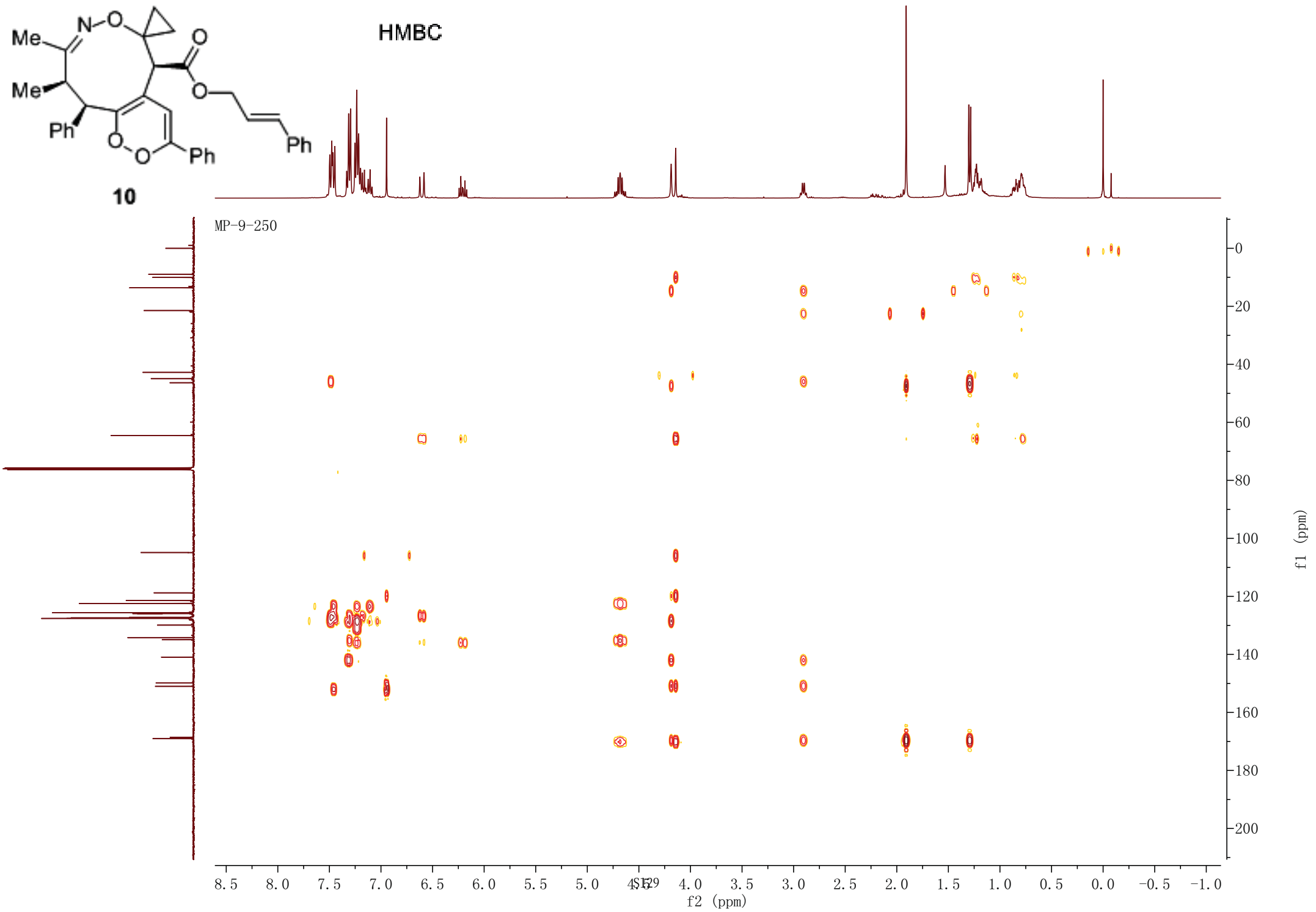
77.321
77.000
76.687
65.560
47.346
45.895
43.758
22.467
14.621
11.048
9.991

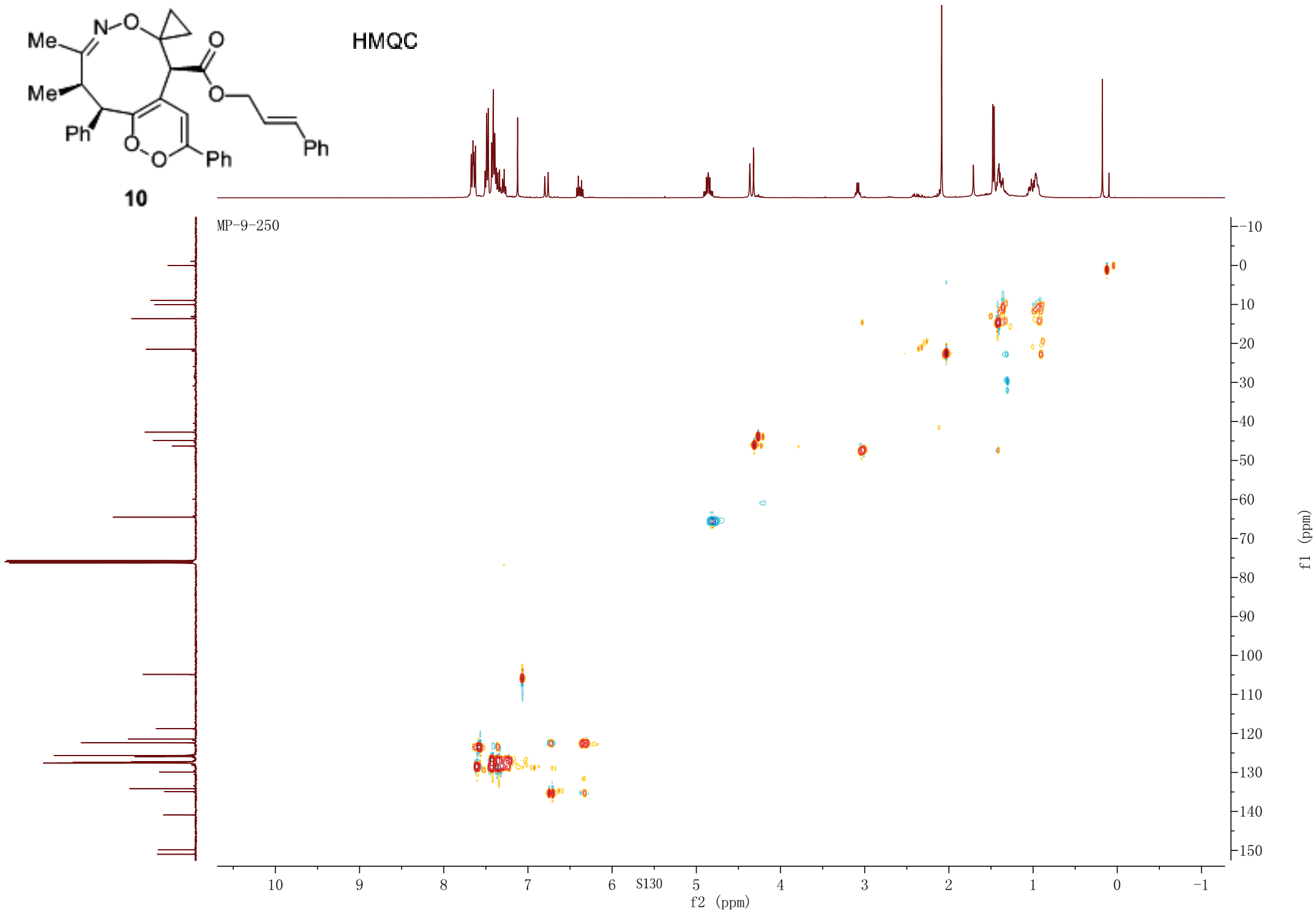

Me
N
O
O
Me
O
Ph
O
O
Ph
Ph

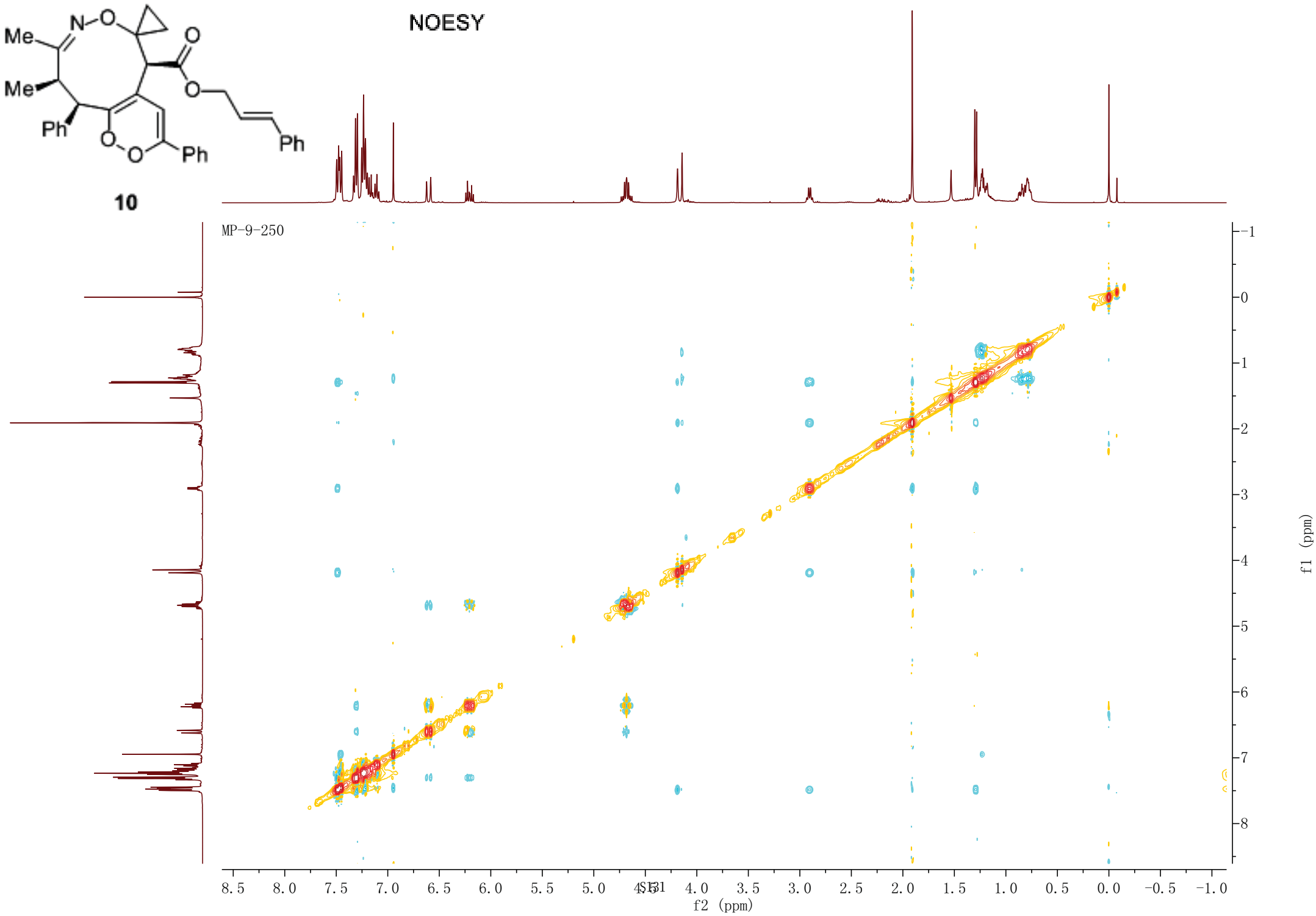
10

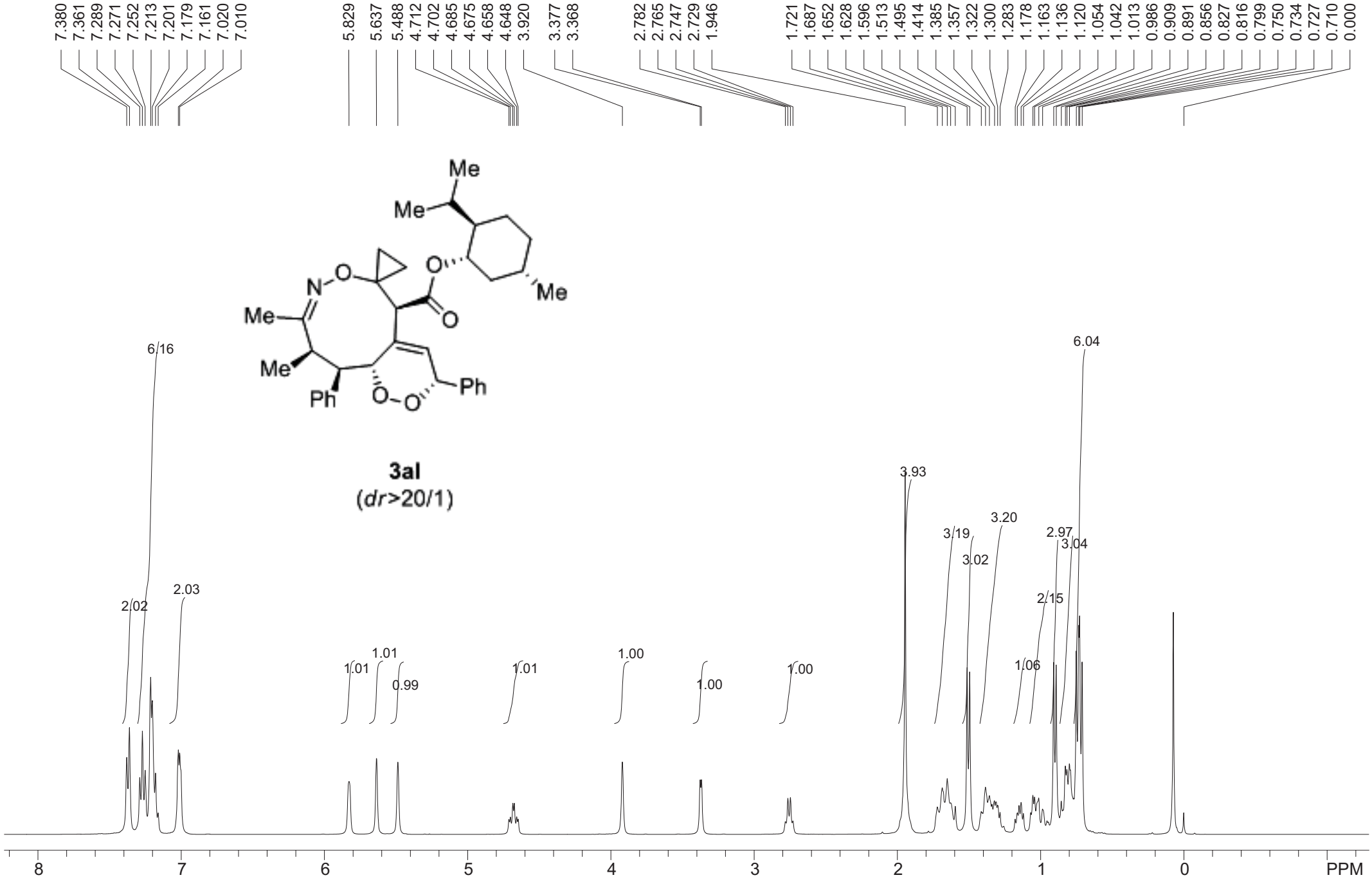

180
160
140
120
100
80
60
40
20
PPM

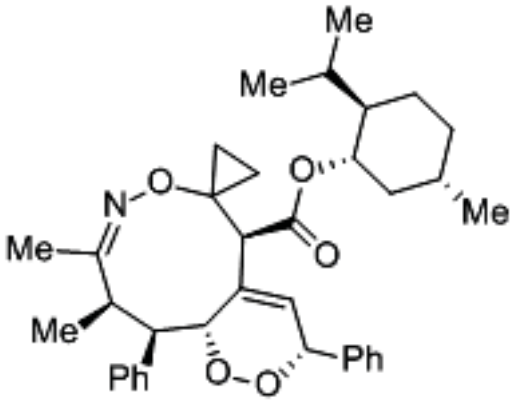

COSY
10
MP-9-250
f2 (ppm)
f1 (ppm)


HMBC
Me
N
O
O
Me
O
Ph
O
O
Ph
Ph
10
MP-9-250
f1 (ppm)
f2 (ppm)


HMQC
Me
N
O
Me
O
O
Ph
O
O
Ph
Ph
10
MP-9-250
f2 (ppm)
f1 (ppm)
S130

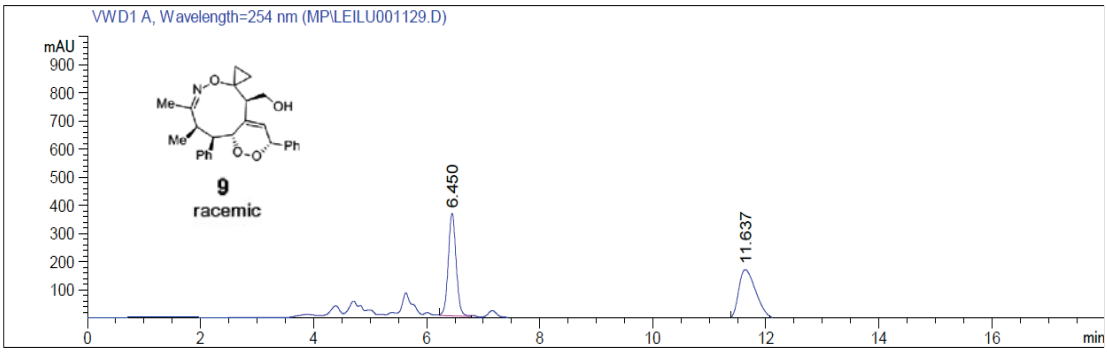

NOESY
Me
N
O
O
Me
O
Ph
O
O
Ph
Ph
10
MP-9-250
f2 (ppm)
f1 (ppm)


7.380
7.361
7.289
7.271
7.252
7.213
7.201
7.179
7.161
7.020
7.010
5.829
5.637
5.488
4.712
4.702
4.685
4.675
4.658
4.648
3.920
3.377
3.368
2.782
2.765
2.747
2.729
1.946
1.721
1.687
1.652
1.628
1.596
1.513
1.495
1.414
1.385
1.357
1.322
1.300
1.283
1.178
1.163
1.136
1.120
1.054
1.042
1.013
0.986
0.909
0.891
0.856
0.827
0.816
0.799
0.750
0.734
0.727
0.710
0.000
Me
Me
O
N
O
Me
O
Me
Me
Ph
O
O
Ph
3aI
(dr>20/1)
6.16
2.02
2.03
1.01
1.01
0.99
1.01
1.00
1.00
1.00
3.93
3.19
3.02
3.20
1.06
2.15
2.97
3.04
6.04
8
7
6
5
4
3
2
1
0
PPM

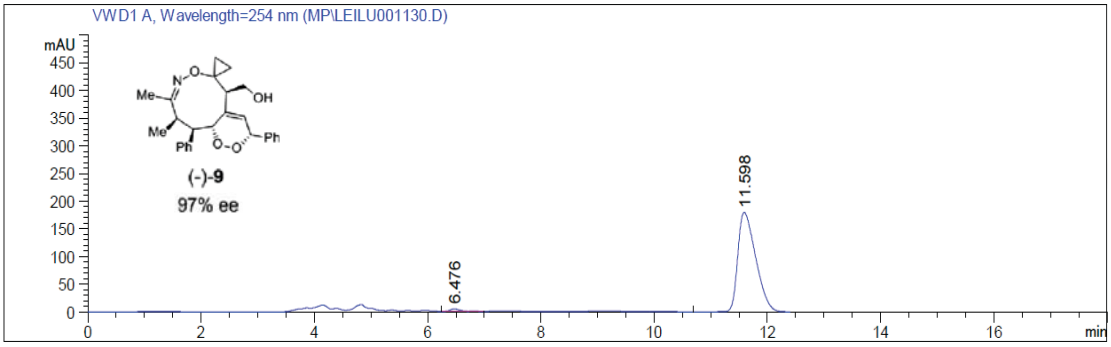

Me
Me
O
N
O
Me
O
Me
Me
Ph
O
O
Ph

3al
(*dr*>20/1)

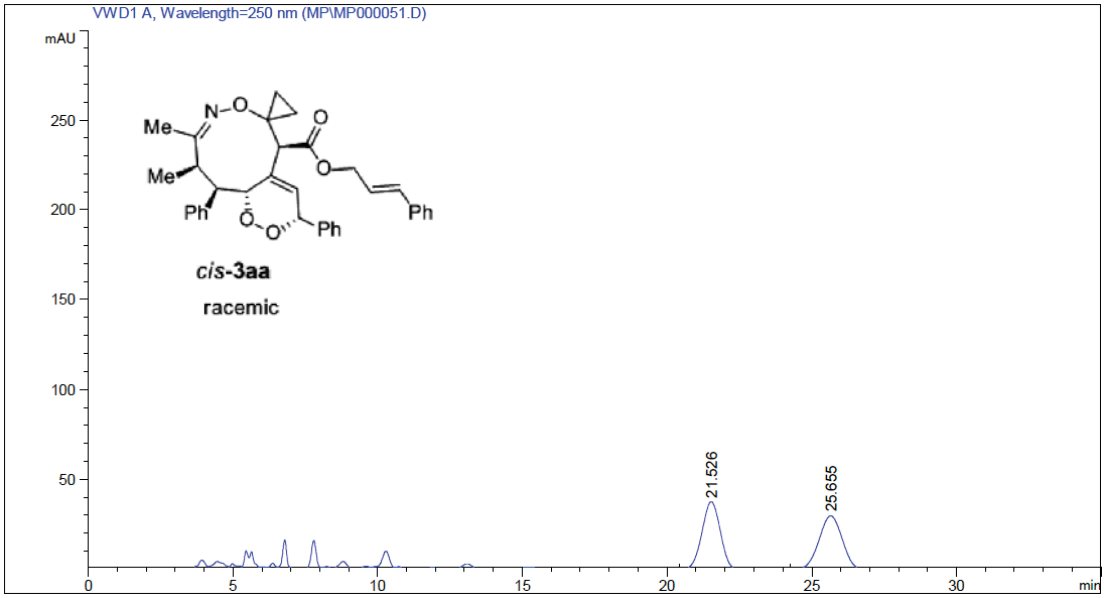
172.26
169.38
143.02
136.40
135.66
129.37
128.59
128.25
127.89
127.85
126.45
125.07
79.80
77.75
77.21
77.00
76.79
74.93
62.69
50.72
49.91
46.74
46.01
40.67
34.04
31.25
25.76
22.90
21.86
21.79
20.89
15.76
12.50
10.99
9.51
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



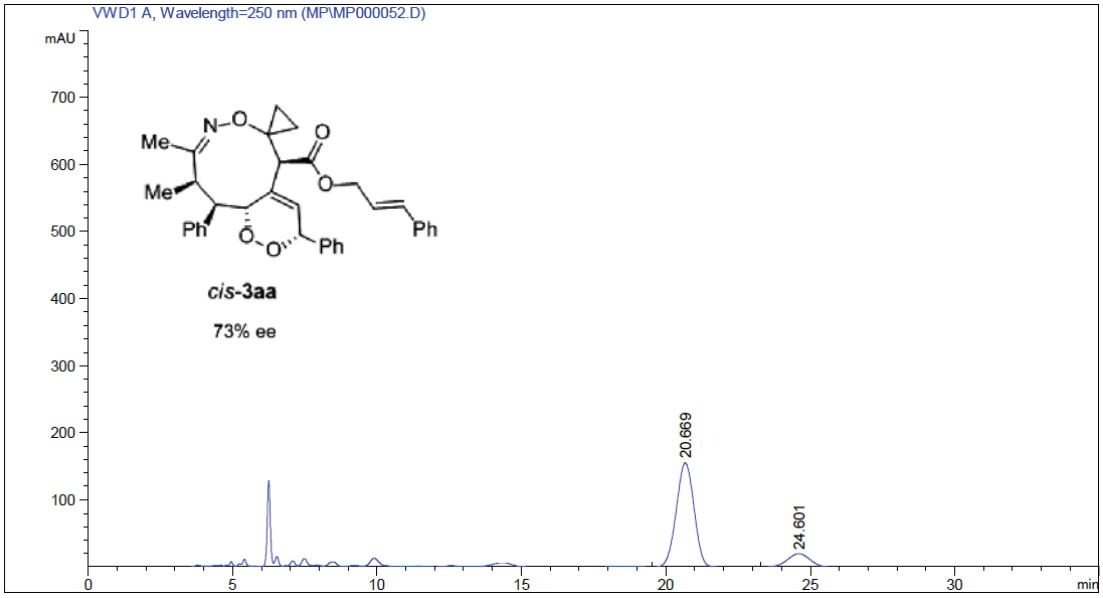
Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	6.450	MM	0.1608	3523.64258	365.31042	50.0481
2	11.637	MM	0.3410	3516.87134	171.90103	49.9519



Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	6.476	BV	0.2005	61.45310	4.65779	1.5311
2	11.598	BB	0.3381	3952.20190	179.73181	98.4689



Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	21.526	BB	0.6926	1646.56970	37.62419	50.0341
2	25.655	BB	0.8721	1644.32373	29.74473	49.9659



Peak	ReTime [min]	Type	Width [min]	Area [MAU*s]	Height [MAU]	Area %
1	20.669	BB	0.6651	6590.16113	154.96255	86.2521
2	24.601	BB	0.8345	1050.41870	19.65747	13.7479