

Supplimentary Information

Palladium-Catalyzed Dearomative 1,4-Difunctionalization of Naphthalenes

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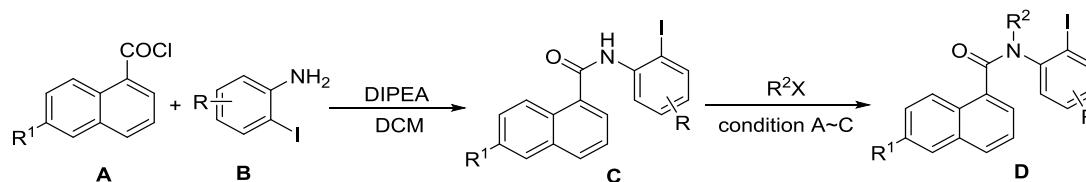
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General methods

Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use. ^1H and ^{19}F NMR spectra were recorded at room temperature unless otherwise noted on a Bruker, Varian or Agilent instrument (400 MHz and 377 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals, respectively. ^{13}C NMR spectra were recorded on a Bruker (101 MHz) or Varian instrument (101 MHz) and internally referenced to residual solvent signals. Data for ^1H NMR are recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant (s) in Hz, integration). Data for ^{13}C NMR and ^{19}F NMR are reported in terms of chemical shift (δ , ppm).

General procedure for the preparation of substrates



1-Naphthoyl chloride **A** (1.0 equiv) was dissolved in DCM (0.2 M), then DIPEA (1.3 equiv) and substituted 2-iodoaniline **B** (1.2 equiv) were added at room temperature. After completion (monitored by TLC), the reaction mixture was quenched with saturated aqueous NaHCO_3 and extracted with DCM ($50 \text{ mL} \times 3$). The combined DCM was dried over anhydrous Na_2SO_4 and filtrated. After the solvent was concentrated under reduced pressure, the crude product **C** was used without purification.

Conditions A:

To a solution of crude product **C** in THF (0.2 M), potassium tert-butoxide (1.2 equiv) was added carefully at room temperature. After 20 min, iodomethane (1.2 equiv) was added dropwise. Then the reaction mixture was stirred at room temperature. After completion (monitored by TLC), the reaction mixture was quenched with saturated aqueous NaHCO_3 and extracted with ethyl acetate ($50 \text{ mL} \times 3$). The combined ethyl acetate extract was dried over anhydrous Na_2SO_4 and filtrated. After the solvent was concentrated under reduced pressure, the crude product was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford the desired product (**1a**, **1d-1p**).

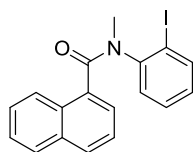
Conditions B:

Crude N-(2-iodophenyl)-1-naphthamide was dissolved in THF (0.4 M) in a sealed tube at 0°C . Sodium hydride (1.5 equiv) was added carefully. After 20 min, 2-bromopropane (3.0 equiv) was added dropwise. Then the reaction mixture was stirred at 80°C . After completion (monitored by TLC), the reaction mixture was quenched with H_2O and extracted with ethyl acetate ($50 \text{ mL} \times 3$). After the solvent

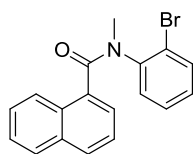
was concentrated under reduced pressure, the crude product was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford the desired product **1b**.

Conditions C:

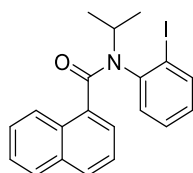
To a solution of crude N-(2-iodophenyl)-1-naphthamide in DMF (0.4 M) at 0 °C, sodium hydride (1.3 equiv) was added carefully. After 30 min, benzyl bromide (1.1 equiv) was added dropwise. Then the reaction mixture was stirred at room temperature. After completion (monitored by TLC), the reaction mixture was quenched with H₂O and extracted with ethyl acetate (50 mL × 3). The combined ethyl acetate extract was washed with H₂O (50 mL × 4), dried over anhydrous Na₂SO₄ and filtrated. After the solvent was concentrated under reduced pressure, the crude product was purified by silica gel column chromatography (PE/EtOAc = 20:1) to afford the desired product **1c**.



1a: white solid, 16.5 g, 85% yield (from **A** over 2 steps, 50 mmol scale), m.p. = 95-97 °C. Two sets of signals were observed due to the existence of rotamers. The peaks of the minor one are marked with asterisk. ¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, *J* = 8.4 Hz, 1H), 7.96* (d, *J* = 7.6 Hz, 1H), 7.91-7.88* (m, 2H), 7.73-7.68 (m, 2H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.58-7.51 (m, 1H), 7.49-7.43 (m, 2H), 7.17-7.13 (m, 1H), 7.10-7.06* (m, 1H), 6.93 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.87-6.83 (m, 1H), 6.71-6.67 (m, 1H), 3.51 (s, 3H), 3.06* (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 170.5, 146.3, 145.5, 140.2, 140.0, 134.1, 133.9, 133.6, 133.4, 130.4, 130.0, 129.6, 129.5, 129.4, 129.2, 129.14, 129.08, 129.0, 128.5, 128.3, 127.1, 126.8, 126.6, 126.1, 125.7, 125.2, 124.4, 124.33, 124.26, 98.7, 39.9, 36.9. IR (film): ν_{max} (cm⁻¹) = 3058, 1645, 1574, 1504, 1466, 1419, 1354, 1304, 1250, 1112, 1058, 1015, 977, 813, 796, 779, 747, 720, 657, 638, 587, 553, 511, 475, 446, 428. HRMS (ESI): Exact mass calcd. for C₁₈H₁₅NOI ([M+H]⁺): 388.01928. Found: 388.01886.

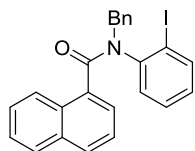


1a': white solid, 0.30 g, 40% yield (from **A** over 2 steps, 2.2 mmol scale), m.p. = 92-95 °C. Two sets of signals were observed due to the existence of rotamers. The peaks of the minor one are marked with asterisk. ^1H NMR (400 MHz, CDCl_3) δ 8.18 (d, J = 8.4 Hz, 1H), 7.91* (t, J = 7.6 Hz, 2H), 7.76-7.73 (m, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.57-7.53 (m, 1H), 7.48-7.44 (m, 2H), 7.38-7.37 (m, 1H), 7.19-7.15 (m, 1H), 6.95 (dd, J = 7.2, 1.6 Hz, 1H), 6.92-6.84 (m, 2H), 3.52 (s, 3H), 3.09* (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.7, 143.0, 134.0, 133.9, 133.7, 133.4, 130.4, 129.9, 129.63, 129.60, 129.5, 129.2, 129.1, 128.6, 128.3, 128.2, 127.3, 126.9, 126.6, 126.2, 125.7, 125.3, 124.44, 124.36, 124.3, 122.7, 39.8, 36.5. IR (film): ν_{max} (cm^{-1}) = 3064, 1643, 1575, 1470, 1420, 1353, 1305, 1247, 1116, 1060, 1022, 864, 795, 770, 724, 706, 660, 638, 587, 554, 511, 485, 454, 432. HRMS (ESI): Exact mass calcd. for $\text{C}_{18}\text{H}_{15}\text{NOBr}$ ($[\text{M}+\text{H}]^+$): 340.03315. Found: 340.03252.

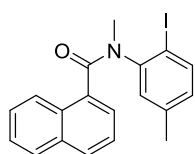


1b: white solid, 0.80 g, 19% yield (from **C** over 1 steps, 10 mmol scale), m.p. = 107-109 °C. Two sets of signals were observed due to the existence of rotamers. The peaks of the minor one are marked with asterisk. ^1H NMR (400 MHz, CDCl_3) δ 8.19 (d, J = 8.4 Hz, 1H), 8.01* (s, 2H), 7.91-7.88 (m, 1H), 7.70-7.63 (m, 2H), 7.60 (d, J = 8.4 Hz, 1H), 7.53 (d, J = 7.2 Hz, 1H), 7.43-7.40 (m, 1H), 7.15 (t, J = 7.6 Hz, 1H), 7.08 (d, J = 7.6 Hz, 1H), 6.91 (t, J = 7.6 Hz, 1H), 6.67 (t, J = 7.6 Hz, 1H), 4.79-4.73 (m, 1H), 4.24-4.21* (m, 1H), 1.68 (d, J = 6.4 Hz, 3H), 1.28 (d, J = 6.8 Hz, 3H), 1.08* (d, J = 6.4 Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.4, 143.5, 140.2, 134.8, 133.3, 130.8, 130.3, 129.2, 129.1, 128.4, 128.3, 127.0, 126.5, 126.0, 125.8, 125.1, 124.2, 103.1, 51.4, 22.3, 19.7. IR (film): ν_{max} (cm^{-1}) = 2967, 1631, 1504, 1463, 1421, 1403,

1373, 1346, 1318, 1259, 1217, 1109, 1018, 981, 811, 791, 776, 759, 742, 718, 701, 661, 637, 581, 559, 453. HRMS (ESI): Exact mass calcd. for $C_{20}H_{19}NOI$ ($[M+H]^+$): 416.05058. Found: 416.05014.

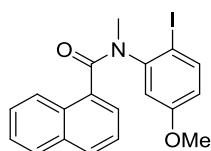


1c: white solid, 1.2 g, 26% yield (from **C** over 1 steps, 10 mmol scale), m.p. = 184-186 °C. Two sets of signals were observed due to the existence of rotamers. The peaks of the minor one are marked with asterisk. 1H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 1H), 7.96-7.91* (m, 4H), 7.73-7.69 (m, 2H), 7.62-7.56 (m, 1H), 7.51-7.24 (m, 8H), 7.15 (t, J = 7.6 Hz, 1H), 7.03-6.99* (m, 3H), 6.65-6.64 (m, 2H), 6.34 (d, J = 6.0 Hz, 1H), 6.08 (d, J = 14.0 Hz, 1H), 4.79* (br, 1H), 4.51* (d, J = 11.2 Hz, 1H), 4.29 (d, J = 14.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 143.6, 140.0, 137.0, 133.8, 133.3, 131.5, 130.4, 129.8, 129.3, 129.2, 128.6, 128.3, 127.9, 126.8, 126.1, 125.4, 124.4, 123.9, 99.6, 51.8. IR (film): ν_{max} (cm^{-1}) = 3060, 1645, 1576, 1503, 1467, 1440, 1403, 1374, 1323, 1292, 1252, 1203, 1152, 1081, 1007, 949, 801, 776, 752, 718, 702, 658, 634, 610, 582, 550, 496, 450, 434. HRMS (ESI): Exact mass calcd. for $C_{24}H_{19}NOI$ ($[M+H]^+$): 464.05058. Found: 464.04959.

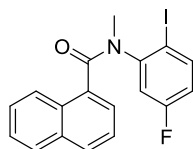


1d: white solid, 2.9 g, 72% yield (from **A** over 2 steps, 10 mmol scale), m.p. = 128-129 °C. Two sets of signals were observed due to the existence of rotamers. The peaks of the minor one are marked with asterisk. 1H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.4 Hz, 1H), 7.92-7.89* (m, 2H), 7.83* (d, J = 8.0 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.57-7.52 (m, 2H), 7.47-7.43 (m, 2H), 7.31* (s, 1H), 7.20-7.16 (m, 1H), 6.92* (dd, J = 8.0, 1.6 Hz, 1H), 6.80 (d, J = 1.6 Hz, 1H), 6.52 (dd, J = 8.0, 1.6 Hz, 1H), 3.49 (s, 3H), 3.06* (s, 3H), 2.40* (s, 3H), 1.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 146.0, 145.3, 140.4, 139.8, 139.6, 139.4, 134.3, 134.1,

133.7, 133.3, 130.8, 130.4, 130.22, 130.16, 129.8, 129.7, 129.5, 129.4, 128.5, 128.3, 127.2, 126.7, 126.6, 126.1, 125.8, 125.2, 124.4, 124.32, 124.30, 94.5, 40.0, 36.9, 21.1, 20.4. IR (film): $\nu_{\max}$ (cm⁻¹) = 1649, 1506, 1468, 1358, 1306, 1252, 1197, 1120, 1011, 858, 829, 797, 787, 775, 740, 718, 684, 645, 571, 494, 466, 432. HRMS (ESI): Exact mass calcd. for C₁₉H₁₇NOI ([M+H]⁺): 402.03493. Found: 402.03501.

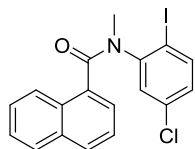


1e: white solid, 0.70 g, 42% yield (from **A** over 2 steps, 4 mmol scale), m.p. = 106-107 °C. Two sets of signals were observed due to the existence of rotamers. The peaks of the minor one are marked with asterisk. ¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, J = 8.4 Hz, 1H), 7.93-7.90* (m, 2H), 7.83* (d, J = 8.8 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.58-7.51 (m, 2H), 7.47-7.44 (m, 2H), 7.20 (dd, J = 8.0, 7.2 Hz, 1H), 7.04* (d, J = 2.8 Hz, 1H), 6.72* (dd, J = 8.8, 2.8 Hz, 1H), 6.47 (d, J = 2.8 Hz, 1H), 6.32 (dd, J = 8.8, 2.8 Hz, 1H), 3.86* (s, 3H), 3.51 (s, 3H), 3.20 (s, 3H), 3.07* (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 170.7, 161.3, 160.1, 147.0, 140.4, 140.0, 134.2, 133.3, 130.5, 129.6, 129.4, 128.6, 128.5, 127.2, 126.8, 126.6, 126.2, 125.6, 125.2, 124.6, 124.4, 124.1, 116.6, 115.2, 114.5, 86.7, 55.8, 55.2, 39.9, 36.8. IR (film): $\nu_{\max}$ (cm⁻¹) = 3002, 1650, 1568, 1506, 1461, 1440, 1401, 1359, 1320, 1253, 1230, 1183, 1108, 1038, 1007, 991, 919, 849, 832, 789, 774, 737, 711, 646, 599, 576, 500, 477, 430. HRMS (ESI): Exact mass calcd. for C₁₉H₁₇NO₂I ([M+H]⁺): 418.02985. Found: 418.02940.

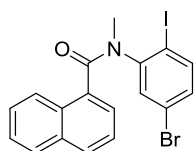


1f: white solid, 2.7 g, 67% yield (from **A** over 2 steps, 10 mmol scale), m.p. = 119-121 °C. Two sets of signals were observed due to the existence of rotamers. The peaks of the minor one are marked with asterisk. ¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, J = 8.4 Hz, 1H), 7.95-7.91 (m, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.69 (d, J = 8.0 Hz,

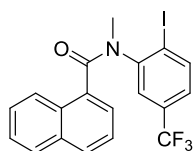
1H), 7.65 (dd, $J = 8.8, 6.0$ Hz, 1H), 7.59-7.54 (m, 1H), 7.49* (d, $J = 7.2$ Hz, 2H), 7.46-7.43 (m, 1H), 7.22-7.18 (m, 1H), 6.93-6.88* (m, 1H), 6.72 (dd, $J = 8.8, 2.8$ Hz, 1H), 6.56-6.51 (m, 1H), 3.50 (s, 3H), 3.08* (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.4, 162.6 (d, $J = 251.9$ Hz), 147.7 (d, $J = 9.4$ Hz), 140.8 (d, $J = 8.6$ Hz), 133.7, 133.5, 130.4, 129.8, 128.6, 128.5, 127.3, 127.1, 126.7, 126.4, 125.6, 125.2, 124.44, 124.40, 117.0 (d, $J = 22.7$ Hz), 116.9 (d, $J = 21.6$ Hz), 92.2 (d, $J = 3.8$ Hz), 39.8, 36.9; ^{19}F NMR (377 MHz, CDCl_3) δ -111.4 (s), -111.7 (m). IR (film): ν_{max} (cm^{-1}) = 3057, 1647, 1573, 1505, 1462, 1405, 1351, 1303, 1246, 1195, 1106, 1018, 994, 865, 825, 810, 784, 743, 714, 643, 578, 514, 471, 432. HRMS (ESI): Exact mass calcd. for $\text{C}_{18}\text{H}_{14}\text{NOFI}$ ($[\text{M}+\text{H}]^+$): 406.00986. Found: 406.00938.



1g: white solid, 2.4 g, 57% yield (from **A** over 2 steps, 10 mmol scale), m.p. = 109-111 °C. Two sets of signals were observed due to the existence of rotamers. The peaks of the minor one are marked with asterisk. ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 8.4$ Hz, 1H), 7.95-7.89 (m, 1H), 7.76 (d, $J = 8.4$ Hz, 1H), 7.69 (d, $J = 8.4$ Hz, 1H), 7.63-7.56 (m, 2H), 7.50-7.48 (m, 1H), 7.45* (s, 1H), 7.43* (s, 1H), 7.23-7.19 (m, 1H), 7.12* (dd, $J = 8.4, 2.4$ Hz, 1H), 7.00 (d, $J = 2.4$ Hz, 1H), 6.73 (dd, $J = 8.4, 2.4$ Hz, 1H), 3.49 (s, 3H), 3.08* (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.4, 147.4, 140.9, 140.7, 135.7, 134.7, 133.7, 133.5, 133.4, 130.3, 130.0, 129.84, 129.77, 129.7, 129.5, 128.6, 128.4, 127.4, 127.0, 126.7, 126.4, 125.6, 125.2, 124.45, 124.40, 124.38, 96.3, 39.8, 36.9. IR (film): ν_{max} (cm^{-1}) = 3055, 1647, 1567, 1505, 1458, 1389, 1347, 1294, 1247, 1168, 1118, 1093, 1015, 984, 896, 873, 826, 803, 781, 736, 715, 676, 642, 576, 525, 470, 455, 441, 424. HRMS (ESI): Exact mass calcd. for $\text{C}_{18}\text{H}_{14}\text{NOCII}$ ($[\text{M}+\text{H}]^+$): 421.98031. Found: 421.97919.

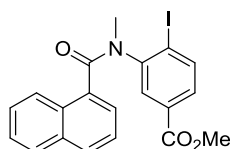


1h: white solid, 1.5 g, 32% yield (from **A** over 2 steps, 10 mmol scale), m.p. = 119-121 °C. Two sets of signals were observed due to the existence of rotamers. The peaks of the minor one are marked with asterisk. ^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, $J = 8.4$ Hz, 1H), 7.93 (t, $J = 8.4$ Hz, 1H), 7.84* (d, $J = 8.4$ Hz, 1H), 7.76 (d, $J = 8.4$ Hz, 1H), 7.70 (d, $J = 8.0$ Hz, 1H), 7.63* (d, $J = 2.0$ Hz, 1H), 7.61-7.60* (m, 1H), 7.58-7.56 (m, 1H), 7.53 (d, $J = 8.4$ Hz, 1H), 7.50-7.47 (m, 1H), 7.45* (s, 1H), 7.43* (s, 1H), 7.23-7.19 (m, 1H), 7.15 (d, $J = 2.0$ Hz, 1H), 6.86 (dd, $J = 8.4, 2.4$ Hz, 1H), 3.49 (s, 3H), 3.08* (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.5, 147.5, 141.2, 141.0, 133.5, 133.4, 132.9, 132.6, 132.4, 132.3, 130.2, 129.8, 128.7, 128.5, 127.4, 127.0, 126.7, 126.4, 125.6, 125.2, 124.41, 124.39, 123.3, 122.3, 97.2, 39.9, 36.9. IR (film): ν_{max} (cm^{-1}) = 3070, 1653, 1562, 1506, 1456, 1382, 1350, 1293, 1263, 1117, 1081, 1009, 983, 911, 894, 875, 859, 826, 796, 773, 755, 727, 712, 643, 569, 510, 465, 437. HRMS (ESI): Exact mass calcd. for $\text{C}_{18}\text{H}_{14}\text{NOBrI}$ ($[\text{M}+\text{H}]^+$): 465.92980. Found: 465.92904.

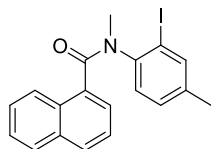


1i: white solid, 1.2 g, 75% yield (from **A** over 2 steps, 3.5 mmol scale), m.p. = 107-108 °C. Two sets of signals were observed due to the existence of rotamers. The peaks of the minor one are marked with asterisk. ^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, $J = 8.4$ Hz, 1H), 7.96-7.91 (m, 1H), 7.80 (d, $J = 8.4$ Hz, 1H), 7.74-7.72 (m, 1H), 7.66 (d, $J = 8.4$ Hz, 1H), 7.60-7.55 (m, 1H), 7.48-7.42 (m, 1H), 7.36* (d, $J = 7.2$ Hz, 1H), 7.21 (s, 1H), 7.20 -7.16 (m, 1H), 6.93 (dd, $J = 8.0, 1.2$ Hz, 1H), 3.53 (s, 3H), 3.11* (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.6, 146.9, 146.4, 141.0, 140.8, 133.7, 133.5, 133.3, 131.4 (q, $J = 33.6$ Hz), 130.1, 129.9, 129.8, 128.7, 128.4, 127.4, 127.1, 126.8, 126.5, 126.2 (q, $J = 3.4$ Hz), 126.0, 125.5 (q, $J = 3.7$ Hz), 125.3, 125.2, 124.5,

124.3, 124.2, 103.4, 103.3, 39.8, 36.7; ^{19}F NMR (377 MHz, CDCl_3) δ -62.7 (s), -63.6 (s). IR (film): ν_{max} (cm^{-1}) = 3067, 1656, 1594, 1469, 1406, 1330, 1285, 1258, 1174, 1115, 1078, 1013, 986, 915, 892, 860, 841, 798, 776, 744, 723, 708, 643, 578, 509, 475, 436. HRMS (ESI): Exact mass calcd. for $\text{C}_{19}\text{H}_{14}\text{NOF}_3\text{I}$ ($[\text{M}+\text{H}]^+$): 456.00667. Found: 456.00602.

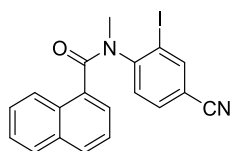


1j: white solid, 2.1 g, 47% yield (from **A** over 2 steps, 10 mmol scale), m.p. = 124-126 °C. Two sets of signals were observed due to the existence of rotamers. The peaks of the minor one are marked with asterisk. ^1H NMR (400 MHz, CDCl_3) δ 8.20 (d, J = 8.4 Hz, 1H), 8.12* (d, J = 2.0 Hz, 1H), 8.08* (d, J = 8.4 Hz, 1H), 7.92 (t, J = 8.4 Hz, 1H), 7.78-7.70 (m, 2H), 7.66-7.54 (m, 3H), 7.47-7.43 (m, 1H), 7.34 (dd, J = 8.0, 2.0 Hz, 1H), 7.19-7.15 (m, 1H), 3.96* (s, 3H), 3.68 (s, 3H), 3.52 (s, 3H), 3.10* (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.6, 166.0, 165.3, 146.6, 146.0, 140.5, 140.3, 133.8, 133.69, 133.65, 133.3, 132.3, 131.2, 130.2, 130.1, 130.0, 129.8, 129.7, 129.6, 128.6, 128.3, 127.3, 126.9, 126.7, 126.3, 125.8, 125.2, 124.4, 124.3, 105.3, 52.6, 52.3, 39.8, 36.8. IR (film): ν_{max} (cm^{-1}) = 2948, 1722, 1644, 1584, 1560, 1506, 1466, 1431, 1392, 1335, 1306, 1275, 1241, 1114, 1097, 1015, 993, 964, 897, 842, 804, 775, 755, 669, 647, 593, 551, 509, 475, 427. HRMS (ESI): Exact mass calcd. for $\text{C}_{20}\text{H}_{17}\text{NO}_3\text{I}$ ($[\text{M}+\text{H}]^+$): 446.02476. Found: 446.02361.

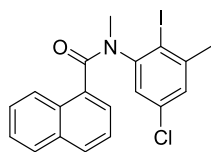


1k: white solid, 1.8 g, 45% yield (from **A** over 2 steps, 10 mmol scale), m.p. = 116-118 °C. Two sets of signals were observed due to the existence of rotamers. The peaks of the minor one are marked with asterisk. ^1H NMR (400 MHz, CDCl_3) δ 8.18 (d, J = 8.4 Hz, 1H), 7.92-7.88* (m, 2H), 7.81* (s, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.65

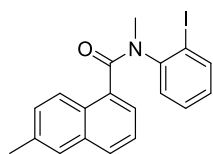
(d, $J = 8.4$ Hz, 1H), 7.58-7.52 (m, 2H), 7.47-7.43 (m, 2H), 7.36* (d, $J = 7.6$ Hz, 1H), 7.29* (dd, $J = 8.0, 1.2$ Hz, 1H), 7.20-7.16 (m, 1H), 6.82 (d, $J = 8.0$ Hz, 1H), 6.66 (dd, $J = 8.0, 1.2$ Hz, 1H), 3.49 (s, 3H), 3.06* (s, 3H), 2.36* (s, 3H), 2.07 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.7, 143.7, 140.6, 140.4, 140.0, 139.4, 134.1, 133.7, 133.4, 130.8, 130.4, 129.9, 129.5, 129.3, 128.7, 128.53, 128.46, 128.3, 127.1, 126.8, 126.6, 126.1, 125.8, 125.2, 124.5, 124.34, 124.28, 98.5, 40.0, 37.1, 20.7, 20.4. IR (film): ν_{max} (cm^{-1}) = 2919, 1638, 1484, 1415, 1351, 1300, 1257, 1122, 1057, 1034, 975, 901, 864, 826, 804, 775, 755, 664, 639, 613, 583, 561, 512, 492, 468, 445. HRMS (ESI): Exact mass calcd. for $\text{C}_{19}\text{H}_{17}\text{NOI}$ ($[\text{M}+\text{H}]^+$): 402.03493. Found: 402.03408.



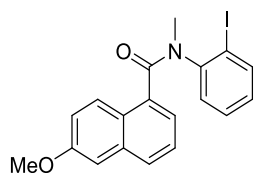
1I: white solid, 2.0 g, 49% yield (from **A** over 2 steps, 10 mmol scale), m.p. = 120-121 °C. Two sets of signals were observed due to the existence of rotamers. The peaks of the minor one are marked with asterisk. ^1H NMR (400 MHz, CDCl_3) δ 8.28* (s, 1H), 8.16 (d, $J = 8.4$ Hz, 1H), 8.02* (d, $J = 1.2$ Hz, 2H), 7.97-7.92* (m, 2H), 7.81-7.77 (m, 1H), 7.72 (d, $J = 8.0$ Hz, 1H), 7.58 (t, $J = 7.6$ Hz, 2H), 7.50 (t, $J = 7.6$ Hz, 1H), 7.37 (d, $J = 7.2$ Hz, 1H), 7.22-7.16 (m, 2H), 6.99 (d, $J = 8.4$ Hz, 1H), 3.51 (s, 3H), 3.10* (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.1, 150.8, 143.5, 133.6, 133.5, 133.2, 132.7, 130.3, 130.2, 130.1, 129.9, 129.7, 128.7, 128.6, 127.4, 127.3, 126.8, 126.6, 125.4, 125.2, 124.54, 124.47, 116.2, 113.0, 98.9, 39.6, 36.8. IR (film): ν_{max} (cm^{-1}) = 3054, 2231, 1643, 1583, 1478, 1416, 1355, 1305, 1260, 1118, 1052, 1033, 980, 890, 865, 845, 806, 777, 735, 671, 648, 603, 585, 503, 470, 443. HRMS (ESI): Exact mass calcd. for $\text{C}_{19}\text{H}_{14}\text{N}_2\text{OI}$ ($[\text{M}+\text{H}]^+$): 413.01453. Found: 413.01337.



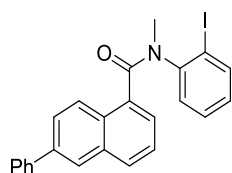
1m: white solid, 1.2 g, 75% yield (from **A** over 2 steps, 3.7 mmol scale), m.p. = 168-170 °C. Two sets of signals were observed due to the existence of rotamers. The peaks of the minor one are marked with asterisk. ¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.91 (t, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.61-7.52 (m, 2H), 7.46 (t, *J* = 6.8 Hz, 1H), 7.31* (d, *J* = 2.0 Hz, 1H), 7.26* (d, *J* = 2.4 Hz, 1H), 7.20-7.16 (m, 1H), 6.88-6.84 (m, 1H), 3.48 (s, 3H), 3.06* (s, 3H), 2.54* (s, 3H), 2.33 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 170.3, 147.6, 146.9, 145.6, 145.2, 135.0, 133.9, 133.8, 133.7, 133.6, 133.4, 130.3, 129.8, 129.7, 129.2, 128.62, 128.59, 128.4, 127.3, 126.9, 126.7, 126.6, 126.3, 126.2, 125.7, 125.2, 124.31, 124.28, 124.1, 103.8, 39.8, 37.0, 29.3, 29.2. IR (film): ν_{max} (cm⁻¹) = 2915, 1639, 1555, 1505, 1429, 1406, 1362, 1306, 1264, 1170, 1150, 1112, 1085, 1057, 1020, 906, 868, 803, 775, 721, 647, 574, 558, 488, 467, 452, 415. HRMS (ESI): Exact mass calcd. for C₁₉H₁₆NOCl ([M+H]⁺): 435.99596. Found: 435.99541.



1n: white solid, 1.0 g, 50% yield (from **A** over 2 steps, 5.0 mmol scale), m.p. = 125-127 °C. Two sets of signals were observed due to the existence of rotamers. The peaks of the minor one are marked with asterisk. ¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, *J* = 8.8 Hz, 1H), 7.98* (d, *J* = 7.6 Hz, 1H), 7.83* (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.50 (s, 1H), 7.44-7.34 (m, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.95-6.87 (m, 2H), 6.73 (t, *J* = 7.6 Hz, 1H), 3.51 (s, 3H), 3.08* (s, 3H), 2.54* (s, 3H), 2.49 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 170.8, 146.4, 140.2, 140.1, 136.4, 135.9, 134.0, 133.7, 133.6, 130.0, 129.7, 129.5, 129.3, 129.1, 128.9, 128.8, 128.7, 127.5, 127.3, 125.6, 125.3, 124.5, 123.6, 123.5, 98.8, 39.9, 37.0, 21.8, 21.7. IR (film): ν_{max} (cm⁻¹) = 2940, 1645, 1467, 1411, 1373, 1350, 1302, 1250, 1160, 1111, 1050, 1017, 981, 877, 823, 801, 772, 752, 722, 697, 647, 602, 558, 495, 457, 436. HRMS (ESI): Exact mass calcd. for C₁₉H₁₇NOI ([M+H]⁺): 402.03493. Found: 402.03517.



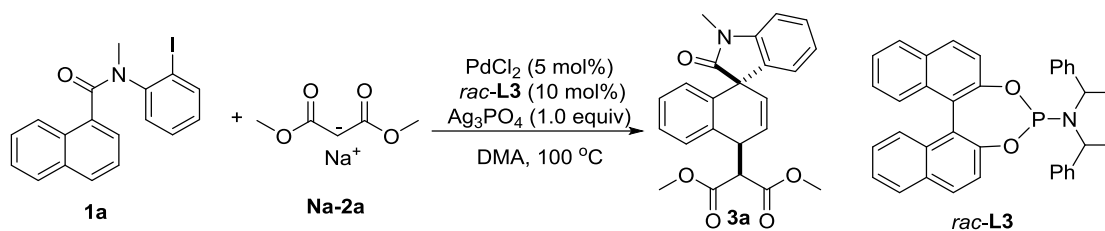
1o: white solid, 1.0 g, 48% yield (from **A** over 2 steps, 5.0 mmol scale), m.p. = 106-108 °C. Two sets of signals were observed due to the existence of rotamers. The peaks of the minor one are marked with asterisk. ^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, J = 9.2 Hz, 1H), 7.96* (d, J = 7.6 Hz, 1H), 7.79* (d, J = 8.0 Hz, 1H), 7.70 (d, J = 7.6 Hz, 1H), 7.55-7.51 (m, 1H), 7.28 (d, J = 6.8 Hz, 1H), 7.23-7.20 (m, 1H), 7.18* (d, J = 2.4 Hz, 1H), 7.13-7.09 (m, 1H), 7.01 (d, J = 2.4 Hz, 1H), 6.94-6.87 (m, 2H), 6.73-6.69 (m, 1H), 3.91* (s, 3H), 3.86 (s, 3H), 3.49 (s, 3H), 3.07* (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.6, 158.0, 157.6, 146.3, 140.1, 140.0, 135.1, 134.7, 133.7, 130.0, 129.6, 129.3, 129.10, 129.06, 129.02, 128.3, 128.2, 127.3, 125.82, 125.76, 125.0, 122.2, 121.9, 119.9, 119.5, 106.4, 106.1, 98.7, 55.4, 55.3, 39.9, 36.9. IR (film): ν_{max} (cm^{-1}) = 2931, 1628, 1511, 1467, 1430, 1376, 1356, 1302, 1267, 1249, 1217, 1170, 1112, 1059, 1021, 980, 937, 844, 820, 784, 772, 749, 723, 658, 618, 559, 509, 482, 456, 430. HRMS (ESI): Exact mass calcd. for $\text{C}_{19}\text{H}_{17}\text{NO}_2\text{I}$ ($[\text{M}+\text{H}]^+$): 418.02985. Found: 418.02983.



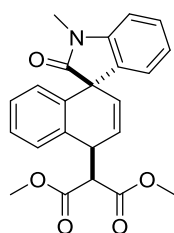
1p: white solid, 0.75 g, 32% yield (from **A** over 2 steps, 5.0 mmol scale), m.p. = 129-131 °C. Two sets of signals were observed due to the existence of rotamers. The peaks of the minor one are marked with asterisk. ^1H NMR (400 MHz, CDCl_3) δ 8.28 (d, J = 8.8 Hz, 1H), 8.09* (s, 1H), 7.97* (t, J = 7.6 Hz, 2H), 7.92 (s, 1H), 7.84-7.82 (m, 1H), 7.73-7.68 (m, 4H), 7.50-7.35 (m, 4H), 7.18 (t, J = 7.6 Hz, 1H), 7.10-7.08* (m, 1H), 6.98 (d, J = 7.6 Hz, 1H), 6.90 (t, J = 7.6 Hz, 1H), 6.72 (t, J = 7.6 Hz, 1H), 3.52 (s, 3H), 3.10* (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.5, 146.3, 140.7, 140.2,

140.1, 139.3, 138.7, 134.0, 133.7, 130.0, 129.8, 129.73, 129.66, 129.3, 129.20, 129.19, 129.02, 128.98, 127.7, 127.6, 127.5, 127.4, 126.9, 126.5, 126.4, 126.3, 126.1, 125.6, 124.9, 124.5, 124.3, 98.8, 40.0, 37.0. IR (film): ν_{max} (cm^{-1}) = 2975, 1637, 1473, 1441, 1370, 1348, 1308, 1251, 1132, 1020, 981, 886, 833, 809, 795, 772, 758, 721, 695, 659, 636, 620, 558, 500, 449, 420. HRMS (ESI): Exact mass calcd. for $\text{C}_{24}\text{H}_{19}\text{NOI}$ ($[\text{M}+\text{H}]^+$): 464.05058. Found: 464.05028.

General procedure for Pd-catalyzed dearomative reaction of naphthalenes with malonate diesters (sodium dimethyl malonate as an example)

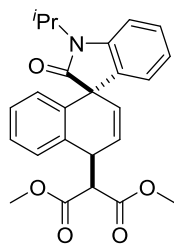


A flame-dried sealed tube was cooled to room temperature under argon. To this tube were added NaH (9.6 mg, 0.4 mmol), dimethyl malonate (52.8 mg, 0.4 mmol) and DMA (1.0 mL). Then the reaction mixture was stirred at room temperature for 0.5 h followed by the addition of **1a** (77.4 mg, 0.2 mmol), PdCl_2 (1.8 mg, 0.01 mmol), *rac*-**L3** (10.8 mg, 0.02 mmol) and Ag_3PO_4 (83.7 mg, 0.2 mmol). Then the reaction mixture was stirred at 100 °C. After completion (monitored by TLC), the reaction mixture was cooled to room temperature and diluted with ethyl acetate (3 mL). The mixture was filtered through celite, and the filtrate was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EtOAc = 20/1 – 10/1) to afford the desired product **3a**.

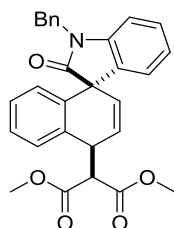


3a: white solid, 74.1 mg, 95% yield, m.p. = 150-152 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.34 (m, 1H), 7.27-7.25 (m, 1H), 7.19-7.15 (m, 1H), 7.09-7.02 (m, 2H), 6.97-6.94 (m, 2H), 6.56-6.50 (m, 2H), 5.71 (d, J = 9.6 Hz, 1H), 4.51 (d, J = 10.4 Hz, 1H), 4.39 (dd, J = 10.4, 5.2 Hz, 1H), 3.77 (s, 3H), 3.61 (s, 3H), 3.25 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.6, 169.5, 168.7, 144.1, 136.1, 135.6, 135.0, 130.9, 129.4, 128.9, 128.5, 127.5, 127.4, 127.3, 124.9, 123.6, 108.2, 62.5, 55.7, 52.6, 52.4, 40.4, 27.0. IR (film): ν_{max} (cm^{-1}) = 2956, 1749, 1712, 1611, 1490, 1469, 1434, 1371, 1337, 1314, 1262, 1156, 1125, 1073, 1019, 978, 960, 904, 826, 777, 745, 725, 690, 665, 637,

561, 542, 493, 477, 446. HRMS (ESI): Exact mass calcd. for $C_{23}H_{21}NO_5Na$ ($[M+Na]^+$): 414.13119. Found: 414.13112.

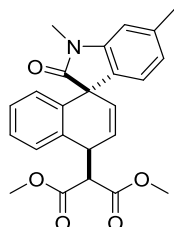


3b: white solid, 69.2 mg, 82% yield, m.p. = 160-162 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.29 (m, 1H), 7.26-7.24 (m, 1H), 7.19-7.12 (m, 2H), 7.07-7.01 (m, 2H), 6.93 (dd, J = 7.2, 0.8 Hz, 1H), 6.52 (dd, J = 9.6, 4.8 Hz, 1H), 6.49 (dd, J = 8.0, 0.8 Hz, 1H), 5.69 (d, J = 10.0 Hz, 1H), 4.74-4.64 (m, 1H), 4.43 (d, J = 10.4 Hz, 1H), 4.38 (dd, J = 10.4, 4.8 Hz, 1H), 3.77 (s, 3H), 3.62 (s, 3H), 1.50 (dd, J = 7.2, 3.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0, 169.6, 168.7, 142.6, 136.4, 135.7, 135.5, 130.5, 129.4, 128.46, 128.45, 127.4, 127.33, 127.29, 125.3, 122.9, 110.1, 62.5, 55.4, 52.7, 52.5, 44.1, 40.3, 19.5. IR (film): ν_{max} (cm^{-1}) = 2977, 1750, 1706, 1606, 1483, 1466, 1430, 1340, 1310, 1252, 1220, 1191, 1146, 1099, 1064, 963, 797, 774, 749, 720, 693, 572, 495, 451. HRMS (ESI): Exact mass calcd. for $C_{25}H_{25}NO_5Na$ ($[M+Na]^+$): 442.16249. Found: 442.16178.

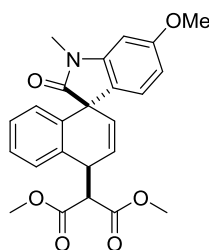


3c: white solid, 80.3 mg, 86% yield, m.p. = 148-149 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.25 (m, 6H), 7.23-7.18 (m, 2H), 7.09-7.05 (m, 1H), 7.04-7.00 (m, 1H), 6.96-6.94 (m, 1H), 6.79 (d, J = 8.0 Hz, 1H), 6.60-6.54 (m, 2H), 5.76 (d, J = 10.0 Hz, 1H), 5.00 (AB, J_{AB} = 15.6 Hz, 1H), 4.88 (BA, J_{BA} = 15.6 Hz, 1H), 4.50 (d, J = 10.4 Hz, 1H), 4.42 (dd, J = 10.4, 4.8 Hz, 1H), 3.77 (s, 3H), 3.62 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 169.5, 168.7, 143.1, 136.2, 135.8, 135.6, 135.1, 131.0, 129.3, 128.9, 128.7, 128.6, 127.7, 127.51, 127.47, 127.38, 127.2, 125.0, 123.5, 109.4, 62.5, 55.6,

52.7, 52.5, 44.3, 40.3. IR (film): $\nu_{\max}$ (cm⁻¹) = 2950, 1745, 1714, 1607, 1484, 1462, 1436, 1318, 1260, 1195, 1172, 1149, 1114, 961, 934, 905, 815, 776, 759, 731, 693, 664, 627, 573, 551, 497, 477, 456. HRMS (ESI): Exact mass calcd. for C₂₉H₂₅NO₅Na ([M+Na]⁺): 490.16249. Found: 490.16151.

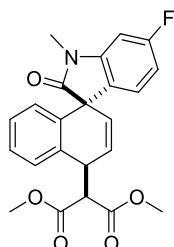


3d: white foam, 75.6 mg, 93% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.26-7.24 (m, 1H), 7.18-7.14 (m, 1H), 7.06-7.02 (m, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.77 (s, 1H), 6.54-6.50 (m, 2H), 5.69 (d, *J* = 10.0 Hz, 1H), 4.51 (d, *J* = 10.4 Hz, 1H), 4.38 (dd, *J* = 10.8, 5.2 Hz, 1H), 3.76 (s, 3H), 3.60 (s, 3H), 3.23 (s, 3H), 2.43 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 176.8, 169.5, 168.7, 144.1, 139.0, 136.3, 135.6, 132.1, 130.7, 129.7, 128.4, 127.5, 127.3, 127.2, 124.6, 124.0, 109.1, 62.5, 55.5, 52.6, 52.4, 40.5, 26.9, 21.9. IR (film): $\nu_{\max}$ (cm⁻¹) = 2957, 1751, 1712, 1617, 1440, 1364, 1311, 1260, 1152, 1076, 965, 901, 830, 809, 775, 747, 724, 698, 682, 650, 622, 592, 556, 541, 499, 479, 444. HRMS (ESI): Exact mass calcd. for C₂₄H₂₃NO₅Na ([M+Na]⁺): 428.14684. Found: 428.14697.

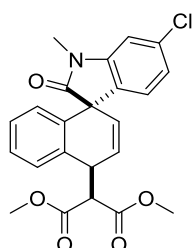


3e: white foam, 83.1 mg, 98% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.25 (d, *J* = 7.2 Hz, 1H), 7.19-7.15 (m, 1H), 7.07-7.03 (m, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.59-6.49 (m, 4H), 5.70 (d, *J* = 9.6 Hz, 1H), 4.49 (d, *J* = 10.8 Hz, 1H), 4.37 (dd, *J* = 10.4, 5.2 Hz, 1H), 3.86 (s, 3H), 3.76 (s, 3H), 3.60 (s, 3H), 3.22 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 177.1, 169.5, 168.7, 160.7, 145.3, 136.5, 135.6, 130.6, 129.9, 128.4, 127.5, 127.3, 127.2, 127.0, 125.5, 107.2, 96.2, 62.5, 55.6, 55.2, 52.6, 52.4, 40.4, 27.0. IR (film):

$\nu_{\max}$ (cm⁻¹) = 2931, 1747, 1712, 1622, 1503, 1436, 1366, 1319, 1258, 1148, 1079, 1032, 990, 965, 904, 857, 834, 775, 753, 722, 696, 651, 629, 582, 501, 476, 451, 420. HRMS (ESI): Exact mass calcd. for C₂₄H₂₃NO₆Na ([M+Na]⁺): 444.14176. Found: 444.14134.

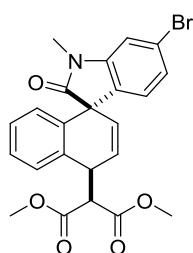


3f: white solid, 67.6 mg, 83% yield, m.p. = 148-150 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.27-7.25 (m, 1H), 7.21-7.17 (m, 1H), 7.09-7.05 (m, 1H), 6.92-6.89 (m, 1H), 6.78-6.73 (m, 1H), 6.69 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.56-6.49 (m, 2H), 5.68 (d, *J* = 10.0 Hz, 1H), 4.45 (d, *J* = 10.4 Hz, 1H), 4.38 (dd, *J* = 10.4, 5.2 Hz, 1H), 3.77 (s, 3H), 3.61 (s, 3H), 3.23 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 176.9, 169.5, 168.7, 163.5 (d, *J* = 246.9 Hz), 145.6 (d, *J* = 11.5 Hz), 135.9, 135.7, 131.2, 130.39 (d, *J* = 3.1 Hz), 129.2, 128.7, 127.6, 127.5, 127.4, 126.1 (d, *J* = 9.7 Hz), 109.7 (d, *J* = 22.4 Hz), 97.1 (d, *J* = 27.8 Hz), 62.5, 55.2, 52.7, 52.5, 40.4, 27.2; ¹⁹F NMR (377 MHz, CDCl₃) δ -111.2 (m). IR (film): $\nu_{\max}$ (cm⁻¹) = 3073, 1750, 1713, 1611, 1503, 1437, 1367, 1323, 1259, 1190, 1145, 1117, 1079, 974, 905, 867, 812, 768, 750, 719, 697, 652, 614, 542, 502, 479, 443. HRMS (ESI): Exact mass calcd. for C₂₃H₂₀NO₅FNa ([M+Na]⁺): 432.12177. Found: 432.12122.

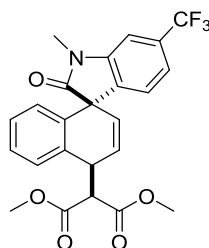


3g: white foam, 70.7 mg, 83% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.28-7.26 (m, 1H), 7.21-7.17 (m, 1H), 7.08-7.04 (m, 2H), 6.95 (d, *J* = 2.0 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.55 (dd, *J* = 9.6, 4.8 Hz, 1H), 6.50 (d, *J* = 7.6 Hz, 1H), 5.67 (d, *J* = 10.0 Hz, 1H),

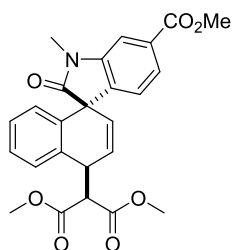
4.45 (d, $J = 10.4$ Hz, 1H), 4.38 (dd, $J = 10.4, 5.2$ Hz, 1H), 3.77 (s, 3H), 3.61 (s, 3H), 3.23 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.6, 169.5, 168.7, 145.3, 135.7, 135.6, 134.7, 133.4, 131.4, 128.9, 128.7, 127.7, 127.4, 125.9, 123.5, 109.0, 62.5, 55.3, 52.7, 52.5, 40.4, 27.1. IR (film): ν_{max} (cm^{-1}) = 2922, 1753, 1723, 1609, 1492, 1438, 1362, 1311, 1264, 1174, 1152, 1070, 981, 960, 902, 833, 811, 776, 742, 695, 678, 645, 621, 596, 556, 518, 499, 479, 449. HRMS (ESI): Exact mass calcd. for $\text{C}_{23}\text{H}_{20}\text{NO}_5\text{NaCl}$ ($[\text{M}+\text{Na}]^+$): 448.09222. Found: 448.09094.



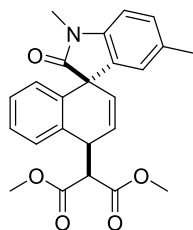
3h: white solid, 70.4 mg, 75% yield, m.p. = 180-182 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.28-7.25 (m, 1H), 7.23-7.17 (m, 2H), 7.10 (d, $J = 1.6$ Hz, 1H), 7.09-7.05 (m, 1H), 6.83 (d, $J = 7.6$ Hz, 1H), 6.55 (dd, $J = 9.6, 5.2$ Hz, 1H), 6.51 (dd, $J = 7.6, 0.8$ Hz, 1H), 5.67 (d, $J = 10.0$ Hz, 1H), 4.44 (d, $J = 10.4$ Hz, 1H), 4.38 (dd, $J = 10.4, 5.2$ Hz, 1H), 3.77 (s, 3H), 3.61 (s, 3H), 3.23 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.4, 169.5, 168.7, 145.5, 135.6, 135.5, 134.0, 131.4, 128.8, 128.7, 127.7, 127.5, 126.4, 126.3, 122.5, 111.8, 62.5, 55.4, 52.8, 52.5, 40.4, 27.2. IR (film): ν_{max} (cm^{-1}) = 2957, 1753, 1722, 1606, 1489, 1436, 1360, 1310, 1263, 1152, 1076, 1058, 981, 957, 902, 834, 810, 776, 738, 695, 676, 643, 620, 588, 573, 555, 499, 478, 448. HRMS (ESI): Exact mass calcd. for $\text{C}_{23}\text{H}_{20}\text{NO}_5\text{NaBr}$ ($[\text{M}+\text{Na}]^+$): 492.04171. Found: 492.04185.



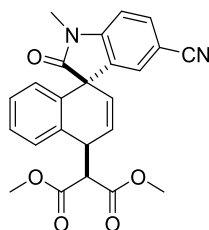
3i: white foam, 36.8 mg, 40% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.37 (d, J = 7.6 Hz, 1H), 7.28 (d, J = 7.6 Hz, 1H), 7.23-7.19 (m, 1H), 7.16 (s, 1H), 7.09-7.05 (m, 2H), 6.58 (dd, J = 9.6, 4.8 Hz, 1H), 6.47-6.45 (m, 1H), 5.67 (d, J = 9.6 Hz, 1H), 4.45 (d, J = 10.4 Hz, 1H), 4.40 (dd, J = 10.4, 4.8 Hz, 1H), 3.77 (s, 3H), 3.62 (s, 3H), 3.29 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.3, 169.4, 168.6, 144.8, 138.8, 135.6, 135.1, 131.7, 131.4 (q, J = 32.6 Hz), 128.8, 128.3, 127.8, 127.5, 127.4, 125.3, 124.0 (q, J = 273.4 Hz), 120.7 (q, J = 3.9 Hz), 105.1 (q, J = 3.7 Hz), 62.4, 55.5, 52.8, 52.6, 40.4, 27.2; ^{19}F NMR (377 MHz, CDCl_3) δ -62.4 (s). IR (film): ν_{max} (cm^{-1}) = 2954, 1743, 1713, 1623, 1454, 1317, 1257, 1158, 1120, 1058, 966, 906, 867, 830, 772, 747, 720, 672, 644, 601, 555, 508, 477, 451. HRMS (ESI): Exact mass calcd. for $\text{C}_{24}\text{H}_{20}\text{NO}_5\text{F}_3\text{Na}$ ($[\text{M}+\text{Na}]^+$): 482.11858. Found: 482.11826.



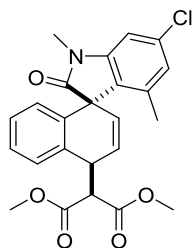
3j: white foam, 46.2 mg, 51% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.81 (dd, J = 7.6, 1.2 Hz, 1H), 7.61 (s, 1H), 7.29-7.27 (m, 1H), 7.22-7.18 (m, 1H), 7.07-7.03 (m, 2H), 6.57 (dd, J = 9.6, 5.2 Hz, 1H), 6.46 (d, J = 7.2 Hz, 1H), 5.68 (d, J = 9.6 Hz, 1H), 4.46 (d, J = 10.4 Hz, 1H), 4.40 (dd, J = 10.4, 5.2 Hz, 1H), 3.96 (s, 3H), 3.77 (s, 3H), 3.62 (s, 3H), 3.30 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.3, 169.5, 168.6, 166.7, 144.5, 140.0, 135.6, 135.3, 131.5, 131.1, 128.7, 128.4, 127.7, 127.5, 127.4, 125.4, 124.9, 109.0, 62.5, 55.7, 52.7, 52.5, 40.4, 27.2. IR (film): ν_{max} (cm^{-1}) = 2952, 1713, 1618, 1450, 1329, 1296, 1249, 1193, 1151, 1078, 980, 813, 762, 735, 579, 512. HRMS (ESI): Exact mass calcd. for $\text{C}_{25}\text{H}_{23}\text{NO}_7\text{Na}$ ($[\text{M}+\text{Na}]^+$): 472.13667. Found: 472.13564.



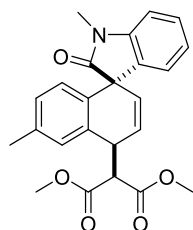
3k: white foam, 75.9 mg, 94% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.27-7.25 (m, 1H), 7.19-7.15 (m, 2H), 7.07-7.03 (m, 1H), 6.83 (d, J = 7.6 Hz, 1H), 6.79 (s, 1H), 6.54-6.51 (m, 2H), 5.71 (d, J = 10.0 Hz, 1H), 4.50 (d, J = 10.4 Hz, 1H), 4.38 (dd, J = 10.4, 5.2 Hz, 1H), 3.76 (s, 3H), 3.61 (s, 3H), 3.23 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.5, 169.5, 168.7, 141.7, 136.3, 135.6, 135.1, 133.2, 130.7, 129.6, 129.1, 128.4, 127.6, 127.33, 127.27, 125.6, 107.9, 62.5, 55.7, 52.6, 52.4, 40.4, 27.0, 21.1. IR (film): ν_{max} (cm^{-1}) = 2919, 1708, 1602, 1499, 1433, 1328, 1257, 1193, 1148, 1074, 959, 807, 770, 720, 702, 647, 622, 555, 495, 473, 439. HRMS (ESI): Exact mass calcd. for $\text{C}_{24}\text{H}_{23}\text{NO}_5\text{Na}$ ($[\text{M}+\text{Na}]^+$): 428.14684. Found: 428.14759.



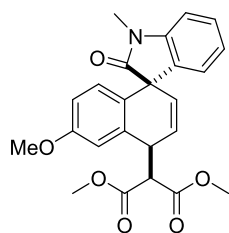
3l: white solid, 41.7 mg, 50% yield, m.p. = 186-188 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.70 (dd, J = 8.0, 1.6 Hz, 1H), 7.30-7.28 (m, 1H), 7.25-7.21 (m, 2H), 7.11-7.07 (m, 1H), 7.03 (d, J = 8.0 Hz, 1H), 6.60 (dd, J = 9.6, 4.4 Hz, 1H), 6.44 (dd, J = 8.0, 0.8 Hz, 1H), 5.65 (d, J = 9.6 Hz, 1H), 4.42 (dd, J = 10.4, 4.8 Hz, 1H), 4.38 (d, J = 10.4 Hz, 1H), 3.77 (s, 3H), 3.63 (s, 3H), 3.29 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.3, 169.3, 168.5, 147.9, 136.1, 135.6, 134.6, 134.2, 132.1, 128.9, 128.5, 128.1, 127.8, 127.7, 127.2, 118.9, 108.8, 106.8, 62.3, 55.2, 52.8, 52.6, 40.2, 27.3. IR (film): ν_{max} (cm^{-1}) = 2949, 2218, 1720, 1613, 1495, 1436, 1368, 1325, 1261, 1195, 1149, 1119, 1100, 1071, 957, 828, 789, 771, 744, 706, 644, 622, 584, 506, 481, 447. HRMS (ESI): Exact mass calcd. for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_5\text{Na}$ ($[\text{M}+\text{Na}]^+$): 439.12644. Found: 439.12583.



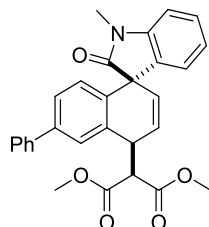
3m: white foam, 70.3 mg, 80% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.28-7.26 (m, 1H), 7.22-7.17 (m, 1H), 7.08-7.04 (m, 1H), 6.85 (d, J = 1.2 Hz, 1H), 6.79 (d, J = 1.6 Hz, 1H), 6.57-6.54 (m, 2H), 5.67 (d, J = 9.6 Hz, 1H), 4.49 (d, J = 10.4 Hz, 1H), 4.39 (dd, J = 10.4, 5.2 Hz, 1H), 3.77 (s, 3H), 3.61 (s, 3H), 3.22 (s, 3H), 1.70 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.4, 169.5, 168.7, 145.2, 137.0, 135.1, 134.5, 134.4, 131.3, 130.2, 128.9, 128.3, 127.7, 127.6, 126.6, 125.0, 106.7, 62.6, 55.2, 52.7, 52.5, 40.5, 27.2, 17.5. IR (film): ν_{max} (cm^{-1}) = 2952, 1742, 1709, 1596, 1436, 1322, 1262, 1195, 1160, 1062, 963, 908, 862, 842, 770, 743, 721, 679, 656, 627, 598, 561, 537, 509, 469. HRMS (ESI): Exact mass calcd. for $\text{C}_{24}\text{H}_{22}\text{NO}_5\text{NaCl}$ ($[\text{M}+\text{Na}]^+$): 462.10787. Found: 462.10661.



3n: white foam, 63.0 mg, 78% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.34 (m, 1H), 7.09-7.06 (m, 2H), 6.97-6.93 (m, 2H), 6.87 (dd, J = 8.0, 1.2 Hz, 1H), 6.53 (dd, J = 10.0, 5.2 Hz, 1H), 6.39 (d, J = 8.0 Hz, 1H), 5.70 (d, J = 9.6 Hz, 1H), 4.48 (d, J = 10.4 Hz, 1H), 4.33 (dd, J = 10.4, 5.2 Hz, 1H), 3.77 (s, 3H), 3.62 (s, 3H), 3.24 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.7, 169.6, 168.7, 144.1, 137.2, 135.4, 135.1, 133.1, 130.9, 129.5, 128.9, 128.8, 128.1, 127.3, 124.9, 123.5, 108.2, 62.5, 55.4, 52.6, 52.4, 40.4, 27.0, 21.1. IR (film): ν_{max} (cm^{-1}) = 2954, 1747, 1729, 1707, 1610, 1492, 1468, 1435, 1370, 1332, 1312, 1259, 1182, 1153, 1125, 1095, 1073, 963, 899, 847, 828, 748, 730, 688, 655, 633, 542, 515, 474, 434. HRMS (ESI): Exact mass calcd. for $\text{C}_{24}\text{H}_{23}\text{NO}_5\text{Na}$ ($[\text{M}+\text{Na}]^+$): 428.14684. Found: 428.14598.

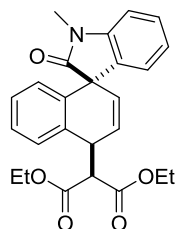


3o: white solid (purified by preparative TLC), 33.0 mg, 39% yield, m.p. = 167-169 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.36 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.97-6.92 (m, 2H), 6.82 (s, 1H), 6.61 (d, *J* = 6.8 Hz, 1H), 6.50 (dd, *J* = 9.6, 5.2 Hz, 1H), 6.41 (d, *J* = 8.4 Hz, 1H), 5.71 (d, *J* = 9.6 Hz, 1H), 4.51 (d, *J* = 10.4 Hz, 1H), 4.35 (dd, *J* = 10.4, 5.2 Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 3.64 (s, 3H), 3.24 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 176.9, 169.6, 168.7, 158.8, 144.1, 137.0, 135.1, 130.7, 129.8, 128.8, 128.6, 128.2, 124.9, 123.5, 113.8, 113.0, 108.2, 62.6, 55.4, 55.2, 52.7, 52.6, 40.7, 27.0. IR (film): ν_{max} (cm⁻¹) = 2952, 1745, 1708, 1607, 1492, 1468, 1370, 1330, 1258, 1155, 1124, 1093, 1074, 1045, 961, 902, 867, 829, 749, 731, 686, 636, 570, 541, 471, 427. HRMS (ESI): Exact mass calcd. for C₂₄H₂₃NO₆Na ([M+Na]⁺): 444.14176. Found: 444.14120.

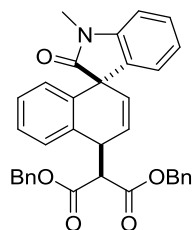


3p: white foam (purified by preparative TLC), 76.6 mg, 82% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.54-7.52 (m, 3H), 7.42-7.36 (m, 3H), 7.33-7.28 (m, 2H), 7.09 (t, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.59-6.56 (m, 2H), 5.74 (d, *J* = 10.0 Hz, 1H), 4.57 (d, *J* = 10.8 Hz, 1H), 4.46 (dd, *J* = 10.4, 5.2 Hz, 1H), 3.78 (s, 3H), 3.55 (s, 3H), 3.27 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 176.5, 169.6, 168.7, 144.1, 140.2, 136.1, 135.1, 134.9, 131.0, 129.5, 128.94, 128.91, 128.0, 127.5, 127.1, 126.9, 125.9, 125.0, 123.6, 108.3, 62.6, 55.6, 52.7, 52.6, 40.6, 27.0. IR (film): ν_{max} (cm⁻¹) = 2951, 1744, 1702, 1608, 1470, 1433, 1366, 1321, 1257, 1193, 1152,

1128, 1076, 1019, 963, 899, 825, 759, 728, 700, 632, 541, 513, 484, 460, 430. HRMS (ESI): Exact mass calcd. for $C_{29}H_{25}NO_5Na$ ($[M+Na]^+$): 490.16249. Found: 490.16171.

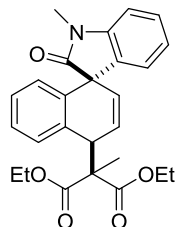


3q: white foam, 73.3 mg, 87% yield. 1H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, J = 7.6 Hz, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.16 (t, J = 7.2 Hz, 1H), 7.08-7.02 (m, 2H), 6.96-6.93 (m, 2H), 6.55 (dd, J = 10.0, 4.0 Hz, 1H), 6.50 (d, J = 8.0 Hz, 1H), 5.70 (d, J = 10.0 Hz, 1H), 4.43-4.37 (m, 2H), 4.31-4.03 (m, 4H), 3.25 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H), 1.13 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 169.1, 168.3, 144.1, 136.1, 135.8, 135.2, 131.1, 129.2, 128.80, 128.76, 127.5, 127.3, 127.1, 124.9, 123.5, 108.2, 62.8, 61.5, 61.4, 55.6, 40.2, 26.9, 14.1, 14.0. IR (film): ν_{max} (cm^{-1}) = 2980, 1729, 1709, 1609, 1490, 1465, 1348, 1298, 1228, 1180, 1127, 1094, 1076, 1036, 991, 939, 847, 789, 753, 724, 688, 664, 632, 540, 491, 474, 446. HRMS (ESI): Exact mass calcd. for $C_{25}H_{25}NO_5Na$ ($[M+Na]^+$): 442.16249. Found: 442.16243.



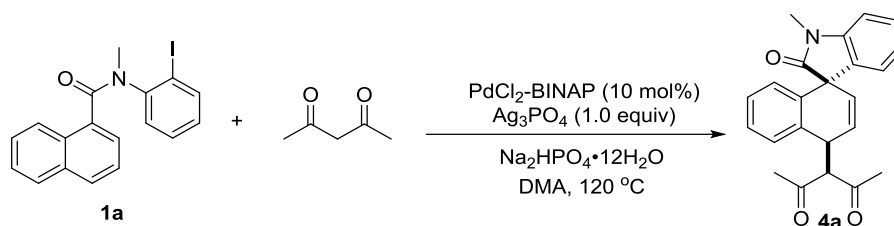
3r: colorless oil, 88.1 mg, 81% yield. 1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.33 (m, 1H), 7.31-7.27 (m, 5H), 7.26-7.20 (m, 4H), 7.17-7.14 (m, 2H), 7.07-6.97 (m, 3H), 6.95-6.92 (m, 2H), 6.52-6.48 (m, 2H), 5.68 (d, J = 10.0 Hz, 1H), 5.26 (AB, J_{AB} = 12.4 Hz, 1H), 5.16-5.12 (m, 2H), 4.98 (BA, J_{BA} = 12.4 Hz, 1H), 4.57 (d, J = 10.0 Hz, 1H), 4.42 (dd, J = 10.0, 5.2 Hz, 1H), 3.23 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 168.7, 168.0, 144.2, 136.1, 135.7, 135.6, 135.5, 135.2, 130.8, 129.3, 128.9, 128.7, 128.5, 128.4, 128.24, 128.21, 128.1, 127.53, 127.48, 127.3, 125.0, 123.5, 108.2, 67.2, 67.0, 62.7, 55.6, 40.2, 27.0. IR (film): ν_{max} (cm^{-1}) = 2932, 1712, 1610, 1491, 1469,

1368, 1343, 1253, 1153, 1074, 960, 907, 726, 694, 647, 541, 488. HRMS (ESI): Exact mass calcd. for $C_{35}H_{29}NO_5Na$ ($[M+Na]^+$): 566.19379. Found: 566.19338.

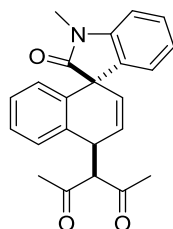


3s: white foam, 24.4 mg, 28% yield. 1H NMR (400 MHz, $CDCl_3$) δ 7.31-7.27 (m, 1H), 7.26-7.25 (m, 1H), 7.13-7.09 (m, 1H), 7.04-6.96 (m, 2H), 6.91 (d, J = 8.0 Hz, 1H), 6.78 (dd, J = 7.6, 0.8 Hz, 1H), 6.52 (dd, J = 7.6, 1.2 Hz, 1H), 6.18 (dd, J = 10.0, 4.0 Hz, 1H), 5.60 (dd, J = 10.0, 1.2 Hz, 1H), 4.88 (d, J = 3.6 Hz, 1H), 4.30-4.23 (m, 4H), 3.30 (s, 3H), 1.40 (s, 3H), 1.29 (q, J = 7.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.5, 172.0, 171.2, 143.2, 136.7, 135.6, 133.8, 128.6, 128.4, 128.1, 127.8, 127.6, 127.5, 127.3, 124.8, 123.5, 108.1, 61.8, 61.7, 59.6, 54.7, 42.5, 26.8, 15.6, 14.2, 14.1. IR (film): ν_{max} (cm^{-1}) = 2922, 1725, 1607, 1489, 1469, 1367, 1341, 1297, 1239, 1103, 1019, 960, 860, 749, 690, 540, 476. HRMS (ESI): Exact mass calcd. for $C_{26}H_{27}NO_5Na$ ($[M+Na]^+$): 456.17814. Found: 456.17784.

General procedure for Pd-catalyzed dearomative reaction of naphthalenes with 1,3-diketones (acetylacetone as an example)

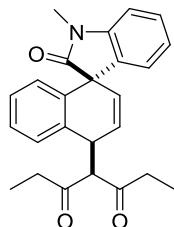


A flame-dried sealed tube was cooled to room temperature under argon. To this tube were added **1a** (0.2 mmol), pre-synthesized PdCl₂-BINAP (16.0 mg, 0.02 mmol), Na₂HPO₄·12H₂O (143.3 mg, 0.40 mmol), Ag₃PO₄ (83.7 mg, 0.2 mmol), acetylacetone (40.0 mg, 0.40 mmol) and DMA (1.0 mL). Then the reaction mixture was stirred at 120 °C. After completion (monitored by TLC), the reaction mixture was cooled to room temperature and diluted with ethyl acetate (3 mL). The mixture was filtered through celite, and the filtrate was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EtOAc = 10/1) to afford the desired product **4a**.

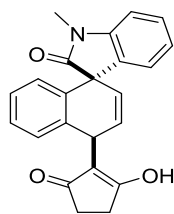


4a: white solid (purified by preparative TLC), 49.7 mg, 69% yield, m.p. = 133-135 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.36 (m, 1H), 7.17-7.13 (m, 2H), 7.11-7.03 (m, 2H), 6.98-6.95 (m, 2H), 6.52 (d, *J* = 7.6 Hz, 1H), 6.39 (dd, *J* = 9.6, 5.2 Hz, 1H), 5.65 (d, *J* = 9.6 Hz, 1H), 4.96 (d, *J* = 9.6 Hz, 1H), 4.44 (dd, *J* = 9.6, 5.2 Hz, 1H), 3.28 (s, 3H), 2.24 (s, 3H), 1.95 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 205.1, 202.4, 177.1, 144.0, 136.2, 136.1, 135.2, 131.7, 129.0, 128.9, 128.6, 127.8, 127.7, 127.1, 125.0, 123.8, 108.3, 76.9, 55.7, 40.5, 33.4, 31.6, 27.0. IR (film): ν_{max} (cm⁻¹) = 2919, 1713, 1610, 1489, 1469, 1418, 1343, 1275, 1239, 1147, 1125, 1090, 1067, 1019, 960, 813,

787, 773, 747, 716, 691, 642, 592, 541, 523, 491, 443. HRMS (ESI): Exact mass calcd. for $C_{23}H_{21}NO_3Na$ ($[M+Na]^+$): 382.14136. Found: 382.14155.

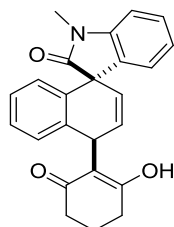


4b: white foam, 51.6 mg, 67% yield. 1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.36 (m, 1H), 7.16-7.06 (m, 3H), 7.05-7.01 (m, 1H), 6.98-6.94 (m, 2H), 6.51 (d, J = 7.6 Hz, 1H), 6.36 (dd, J = 9.6, 5.6 Hz, 1H), 5.62 (d, J = 10.0 Hz, 1H), 4.95 (d, J = 10.0 Hz, 1H), 4.47 (dd, J = 10.0, 5.2 Hz, 1H), 3.29 (s, 3H), 2.61-2.35 (m, 3H), 1.97-1.87 (m, 1H), 1.07 (t, J = 7.2 Hz, 3H), 0.84 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.1, 204.7, 177.1, 143.9, 136.2, 136.0, 135.2, 131.9, 128.9, 128.8, 128.3, 127.6, 127.5, 127.0, 124.9, 123.7, 108.3, 75.5, 55.7, 40.9, 39.8, 37.8, 27.0, 7.6, 7.2. IR (film): ν_{max} (cm^{-1}) = 2922, 1703, 1612, 1492, 1471, 1346, 1242, 1127, 1099, 1021, 982, 789, 766, 746, 714, 689, 541, 490, 443. HRMS (ESI): Exact mass calcd. for $C_{25}H_{25}NO_3Na$ ($[M+Na]^+$): 410.17266. Found: 410.17299.



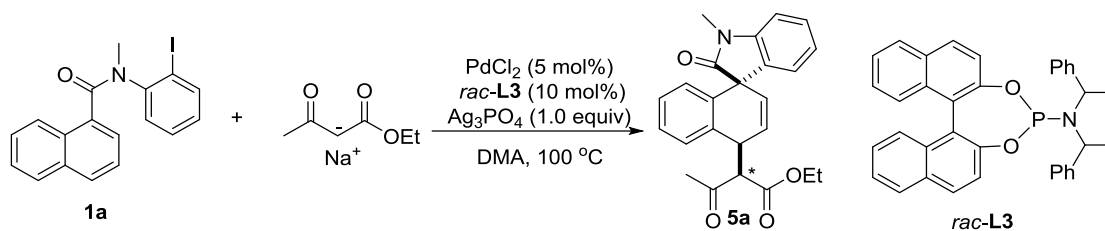
4c: white foam, 30.3 mg, 42% yield. 1H NMR (400 MHz, $CDCl_3$) δ 11.11 (s, 1H), 7.43-7.39 (m, 1H), 7.25-7.23 (m, 1H), 7.19 (d, J = 7.2 Hz, 1H), 7.17-7.15 (m, 2H), 7.05-6.98 (m, 2H), 6.40 (d, J = 8.0 Hz, 1H), 6.11 (dd, J = 10.0, 4.4 Hz, 1H), 5.57 (dd, J = 10.0, 2.0 Hz, 1H), 5.00 (d, J = 2.4 Hz, 1H), 3.31 (s, 3H), 2.57-2.51 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.6, 185.7, 180.6, 143.8, 136.6, 135.4, 132.3, 130.4, 129.6, 129.1, 128.5, 127.2, 126.4, 125.3, 124.6, 124.2, 118.6, 109.0, 54.9, 32.64, 32.60, 28.1, 27.2. IR (film): ν_{max} (cm^{-1}) = 2927, 1682, 1602, 1469, 1371, 1317, 1250, 1216, 1129, 1096, 1059, 998, 952, 812, 763, 742, 691, 655, 543, 494, 471, 454.

HRMS (ESI): Exact mass calcd. for $C_{23}H_{19}NO_3Na$ ($[M+Na]^+$): 380.12571. Found: 380.12554.

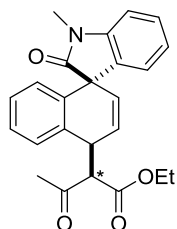


4d: white foam (purified by preparative TLC), 41.0 mg, 55% yield. 1H NMR (400 MHz, $CDCl_3$) δ 9.26 (s, 1H), 7.42-7.36 (m, 1H), 7.18 (d, J = 4.0 Hz, 2H), 7.13 (d, J = 4.4 Hz, 2H), 7.02-6.99 (m, 2H), 6.42 (d, J = 8.0 Hz, 1H), 6.10 (dd, J = 10.0, 4.0 Hz, 1H), 5.59-5.57 (m, 1H), 5.54 (dd, J = 10.0, 2.4 Hz, 1H), 3.28 (s, 3H), 2.55-2.46 (m, 4H), 2.03-1.96 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5, 180.3, 174.5, 144.1, 137.0, 135.4, 132.6, 131.3, 129.1, 129.0, 128.4, 127.2, 126.6, 125.2, 124.2, 123.9, 117.3, 108.8, 54.9, 36.9, 32.5, 30.7, 27.0, 20.7. IR (film): ν_{max} (cm^{-1}) = 2922, 1695, 1639, 1594, 1469, 1424, 1391, 1367, 1240, 1174, 1127, 1084, 958, 922, 790, 747, 691, 587, 540, 478, 447. HRMS (ESI): Exact mass calcd. for $C_{24}H_{21}NO_3Na$ ($[M+Na]^+$): 394.14136. Found: 394.14119.

General procedure for Pd-catalyzed dearomative reaction of naphthalenes with β -ketoesters (ethyl acetoacetate as an example)

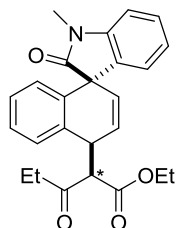


To this tube were added NaH (9.6 mg, 0.4 mmol), ethyl acetoacetate (52.1 mg, 0.4 mmol) and DMA (1.0 mL). Then the reaction mixture was stirred at room temperature for 0.5 h followed by the addition of **1a** (77.4 mg, 0.2 mmol), PdCl₂ (1.8 mg, 0.01 mmol), *rac*-**L3** (10.8 mg, 0.02 mmol) and Ag₃PO₄ (83.7 mg, 0.2 mmol). Then the reaction mixture was stirred at 100 °C. After completion (monitored by TLC), the reaction mixture was cooled to room temperature and diluted with ethyl acetate (3 mL). The mixture was filtered through celite, and the filtrate was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EtOAc = 20/1 – 10/1) to afford the desired product **5a**.

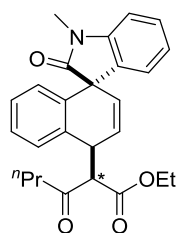


5a: white foam (purified by preparative TLC), 75.1 mg, 96% yield. Two sets of signals were observed due to the existence of diastereoisomers. ¹H NMR (400 MHz, CDCl₃) 7.39-7.35 (m, 1.5H), 7.18-7.14 (m, 1.5H), 7.11-7.02 (m, 2H), 6.97-6.94 (m, 2H), 6.58-6.49 (m, 1.5H), 6.41 (dd, *J* = 9.6, 5.2 Hz, 0.5H), 5.69-5.66 (m, 1H), 4.72 (d, *J* = 10.4 Hz, 0.5H), 4.65 (d, *J* = 10.0 Hz, 0.5H), 4.45 (dd, *J* = 10.0, 5.2 Hz, 0.5H), 4.39 (dd, *J* = 10.4, 5.2 Hz, 0.5H), 4.28-4.07 (m, 2H), 3.27 (s, 1.5H), 3.26 (s, 1.5H), 2.31 (s, 1.5H), 1.91 (s, 1.5H), 1.25 (t, *J* = 7.2 Hz, 1.5H), 1.17 (t, *J* = 7.2 Hz, 1.5H); ¹³C NMR (101 MHz, CDCl₃) δ 205.4, 203.0, 177.0, 176.7, 168.8, 168.4, 144.0, 136.6, 136.3, 135.8, 135.4, 135.2, 135.1, 132.1, 130.7, 129.4, 128.88, 128.86, 128.82, 128.7, 128.6,

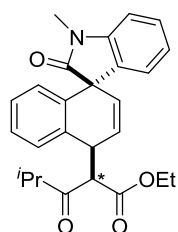
127.6, 127.5, 127.08, 127.06, 124.9, 123.7, 123.6, 108.3, 108.2, 69.8, 68.5, 61.45, 61.37, 55.8, 55.7, 40.4, 39.7, 33.2, 31.7, 26.94, 26.93, 14.12, 14.10. IR (film): $\nu_{\max}$ (cm^{-1}) = 2979, 1740, 1706, 1610, 1490, 1469, 1344, 1299, 1244, 1180, 1144, 1073, 1020, 960, 856, 748, 691, 540, 491, 445. HRMS (ESI): Exact mass calcd. for $\text{C}_{24}\text{H}_{23}\text{NO}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 412.15193. Found: 412.15120.



5b: white foam (purified by preparative TLC), 75.1 mg, 93% yield. Two sets of signals were observed due to the existence of diastereoisomers. ^1H NMR (400 MHz, CDCl_3) δ 7.42-7.37 (m, 1H), 7.20-7.04 (m, 4H), 6.99-6.96 (m, 2H), 6.60 (dd, J = 9.6, 5.2 Hz, 0.63H), 6.54-6.50 (m, 1H), 6.37 (dd, J = 9.6, 5.2 Hz, 0.37H), 5.70-5.66 (m, 1H), 4.71-4.64 (m, 1H), 4.50 (dd, J = 10.0, 5.2 Hz, 0.38H), 4.41 (dd, J = 10.8, 5.2 Hz, 0.58H), 4.28-4.08 (m, 2H), 3.30 (s, 1.73H), 3.29 (s, 1.13H), 2.73-2.60 (m, 0.76H), 2.50-2.40 (m, 0.63H), 1.92-1.82 (m, 0.59H), 1.27 (t, J = 7.2 Hz, 2H), 1.19 (t, J = 7.2 Hz, 1H), 1.09 (t, J = 7.2 Hz, 1H), 0.84 (t, J = 7.2 Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 207.9, 205.7, 177.1, 176.8, 168.9, 168.7, 144.0, 136.9, 136.3, 135.9, 135.5, 135.3, 135.2, 132.4, 130.8, 129.4, 128.9, 128.7, 128.6, 127.61, 127.57, 127.54, 127.46, 127.12, 127.08, 125.0, 123.73, 123.66, 108.3, 108.2, 69.1, 67.9, 61.5, 61.4, 55.8, 55.7, 40.6, 39.9, 39.6, 38.1, 27.0, 14.2, 7.5, 7.1. IR (film): $\nu_{\max}$ (cm^{-1}) = 2935, 1738, 1707, 1610, 1490, 1469, 1367, 1344, 1298, 1232, 1175, 1125, 1094, 959, 788, 749, 690, 541, 491, 445. HRMS (ESI): Exact mass calcd. for $\text{C}_{25}\text{H}_{25}\text{NO}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 426.16758. Found: 426.16690.

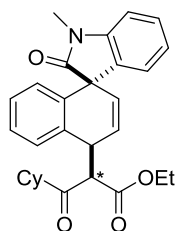


5c: white foam, 82.4 mg, 99% yield. Two sets of signals were observed due to the existence of diastereoisomers. ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.35 (m, 1.4H), 7.17-7.13 (m, 1.7H), 7.10-7.01 (m, 2H), 6.95 (d, J = 6.0 Hz, 2H), 6.57 (dd, J = 9.6, 5.2 Hz, 0.55H), 6.52-6.48 (m, 1H), 6.36 (dd, J = 9.6, 5.2 Hz, 0.42H), 5.67-5.64 (m, 1H), 4.68-4.62 (m, 1H), 4.47 (dd, J = 10.0, 5.2 Hz, 0.43H), 4.40 (dd, J = 10.4, 5.2 Hz, 0.57H), 4.28-4.05 (m, 2H), 3.28 (s, 1.55H), 3.27 (s, 1.33H), 2.65-2.53 (m, 0.85H), 2.45-2.37 (m, 0.62H), 1.87-1.79 (m, 0.63H), 1.68-1.59 (m, 0.89H), 1.50-1.30 (m, 1.32H), 1.25 (t, J = 7.2 Hz, 1.79H), 1.17 (t, J = 7.2 Hz, 1.3H), 0.90 (t, J = 7.2 Hz, 1.35H), 0.74 (t, J = 7.2 Hz, 1.75H); ^{13}C NMR (101 MHz, CDCl_3) δ 207.1, 205.0, 177.0, 176.8, 168.8, 168.5, 144.1, 144.0, 136.8, 136.3, 135.9, 135.6, 135.3, 135.2, 132.3, 130.9, 129.5, 128.89, 128.87, 128.85, 128.70, 128.67, 127.6, 127.52, 127.51, 127.48, 127.1, 125.0, 123.7, 123.6, 108.3, 108.2, 69.4, 68.1, 61.4, 61.3, 55.8, 55.7, 48.0, 46.4, 40.5, 39.9, 27.03, 27.01, 16.8, 16.4, 14.192, 14.186, 13.6, 13.5. IR (film): ν_{max} (cm^{-1}) = 2962, 2932, 2875, 1740, 1707, 1610, 1489, 1469, 1419, 1366, 1343, 1300, 1241, 1173, 1123, 1092, 1073, 1023, 989, 960, 748, 716, 690, 541, 491, 474, 445. HRMS (ESI): Exact mass calcd. for $\text{C}_{26}\text{H}_{27}\text{NO}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 440.18323. Found: 440.18355.



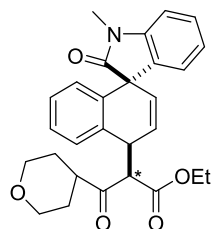
5d: white solid (purified by preparative TLC), 50.0 mg, 60% yield, m.p. = 114-116 °C. Two sets of signals were observed due to the existence of diastereoisomers. ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.33 (m, 1.43H), 7.17-7.00 (m, 3.86H), 6.96-6.93 (m, 2H), 6.58 (dd, J = 9.6, 5.2 Hz, 0.65H), 6.51-6.47 (m, 1H), 6.30 (dd, J = 9.6, 5.2 Hz, 0.35H),

5.68-5.62 (m, 1H), 4.84 (d, $J = 10.8$ Hz, 0.61H), 4.78 (d, $J = 10.4$ Hz, 0.35H), 4.48 (dd, $J = 10.4, 5.6$ Hz, 0.39H), 4.42 (dd, $J = 10.8, 5.6$ Hz, 0.59H), 4.29-4.03 (m, 2H), 3.28 (s, 1.74H), 3.26 (s, 1.08H), 2.88-2.77 (m, 0.38H), 2.22-2.12 (m, 0.61H), 1.24 (t, $J = 7.2$ Hz, 2H), 1.17-1.11 (m, 3H), 1.06 (d, $J = 7.2$ Hz, 2H), 0.66 (d, $J = 6.8$ Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 210.3, 208.5, 177.0, 176.7, 168.8, 168.6, 144.11, 144.05, 136.8, 136.3, 136.0, 135.8, 135.31, 135.29, 132.4, 131.0, 129.7, 128.87, 128.85, 128.84, 128.72, 128.69, 127.6, 127.51, 127.49, 127.4, 127.09, 127.06, 125.0, 123.7, 123.6, 108.2, 108.1, 68.0, 66.9, 61.4, 61.3, 55.9, 55.7, 43.5, 42.4, 40.8, 40.4, 27.1, 27.0, 17.9, 17.74, 17.70, 16.2, 14.2. IR (film): ν_{max} (cm^{-1}) = 2969, 2922, 1736, 1702, 1610, 1488, 1468, 1367, 1344, 1299, 1271, 1230, 1158, 1117, 1092, 1057, 1003, 961, 750, 725, 690, 666, 636, 541, 491, 474, 444. HRMS (ESI): Exact mass calcd. for $\text{C}_{26}\text{H}_{27}\text{NO}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 440.18323. Found: 440.18328.

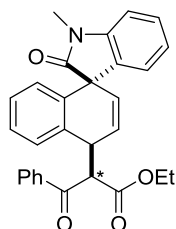


5e: yellow oil (purified by preparative TLC), 51.2 mg, 56% yield. Two sets of signals were observed due to the existence of diastereoisomers. ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.31 (m, 1H), 7.16-7.01 (m, 4H), 6.96-6.93 (m, 2H), 6.56 (dd, $J = 9.6, 5.2$ Hz, 0.65H), 6.51-6.48 (m, 1H), 6.32 (dd, $J = 9.6, 5.2$ Hz, 0.37H), 5.67-5.62 (m, 1H), 4.83 (d, $J = 10.8$ Hz, 0.65H), 4.76 (d, $J = 10.4$ Hz, 0.36H), 4.48-4.40 (m, 1H), 4.28-4.04 (m, 2H), 3.28-3.26 (m, 3H), 1.98-1.84 (m, 2H), 1.78-1.62 (m, 2H), 1.56-1.49 (m, 1H), 1.33-0.88 (m, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 209.6, 207.7, 176.8, 176.6, 168.8, 168.6, 144.11, 144.07, 136.7, 136.2, 136.1, 135.9, 135.2, 132.3, 131.2, 129.6, 128.83, 128.80, 128.7, 128.6, 127.5, 127.43, 127.40, 127.36, 127.0, 124.9, 123.6, 123.5, 108.2, 108.1, 68.1, 66.9, 61.3, 61.2, 55.8, 55.6, 52.9, 51.8, 40.7, 40.4, 28.1, 28.0, 27.8, 27.02, 26.98, 26.4, 25.9, 25.8, 25.6, 25.1, 14.19, 14.15. IR (film): ν_{max} (cm^{-1}) = 2928, 2853, 1738, 1706, 1610, 1469, 1448, 1367, 1343, 1244, 1165, 1125, 1093, 1072, 960, 748,

690, 541, 493, 474, 444. HRMS (ESI): Exact mass calcd. for $C_{29}H_{31}NO_4Na$ ($[M+Na]^+$): 480.21453. Found: 480.21385.

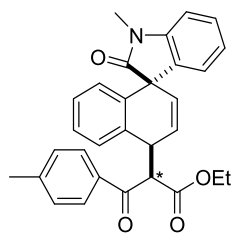


5f: white foam (purified by preparative TLC), 69.9 mg, 76% yield. Two sets of signals were observed due to the existence of diastereoisomers. 1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.34 (m, 1H), 7.18-7.02 (m, 4H), 6.98-6.93 (m, 2H), 6.59 (dd, J = 9.6, 5.6 Hz, 0.68H), 6.53-6.49 (m, 1H), 6.31 (dd, J = 9.6, 5.2 Hz, 0.31H), 5.69-5.64 (m, 1H), 4.86 (d, J = 10.8 Hz, 0.63H), 4.80 (d, J = 10.0 Hz, 0.30H), 4.51-4.40 (m, 1H), 4.27-3.73 (m, 4H), 3.45-3.39 (m, 1H), 3.31-3.26 (m, 4H), 3.12-3.06 (m, 0.71H), 2.81-2.74 (m, 0.34H), 2.09-1.52 (m, 4H), 1.24 (t, J = 7.2 Hz, 2H), 1.24 (t, J = 7.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.9, 205.9, 176.9, 176.6, 168.5, 168.4, 144.01, 143.97, 136.6, 136.4, 136.0, 135.7, 135.10, 135.06, 132.3, 130.8, 129.6, 129.0, 128.89, 128.86, 128.82, 128.6, 127.7, 127.5, 127.4, 127.12, 127.08, 124.9, 123.7, 123.6, 108.23, 108.16, 67.5, 67.32, 67.28, 67.23, 66.9, 66.5, 61.4, 61.3, 55.8, 55.7, 49.6, 48.7, 40.7, 40.3, 28.2, 27.8, 27.7, 27.4, 27.01, 26.97, 26.0, 14.1. IR (film): ν_{max} (cm^{-1}) = 2951, 2844, 1739, 1704, 1610, 1489, 1469, 1367, 1343, 1297, 1238, 1165, 1113, 1091, 1019, 960, 869, 826, 749, 690, 561, 541, 492, 474, 444. HRMS (ESI): Exact mass calcd. for $C_{28}H_{29}NO_5Na$ ($[M+Na]^+$): 482.19379. Found: 482.19481.



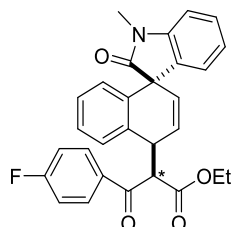
5g: white foam, 59.1 mg, 65% yield. Two sets of signals were observed due to the existence of diastereoisomers. 1H NMR (400 MHz, $CDCl_3$) δ 8.21-8.19 (m, 1H), 7.94-7.92 (m, 1H), 7.58-7.54 (m, 0.5H), 7.49-7.46 (m, 1H), 7.41-7.34 (m, 2H),

7.31-7.27 (m, 1H), 7.20-7.16 (m, 0.5H), 7.12-7.04 (m, 2H), 6.97-6.92 (m, 2H), 6.86-6.82 (m, 1H), 6.67 (dd, $J = 9.6, 5.2$ Hz, 0.5H), 6.54-6.42 (m, 1.5H), 5.73 (d, $J = 9.6$ Hz, 0.5H), 5.60-5.56 (m, 1H), 5.49 (d, $J = 10.8$ Hz, 0.5H), 4.69-4.61 (m, 1H), 4.25-3.95 (m, 2H), 3.31 (s, 1.5H), 3.27 (s, 1.5H), 1.17 (t, $J = 7.2$ Hz, 1.5H), 1.02 (t, $J = 7.2$ Hz, 1.5H); ^{13}C NMR (101 MHz, CDCl_3) δ 196.9, 194.3, 177.1, 176.8, 168.8, 168.6, 144.1, 144.0, 137.2, 136.62, 136.58, 136.3, 135.9, 135.7, 135.32, 135.30, 133.7, 133.2, 131.9, 131.6, 129.6, 129.43, 129.35, 129.1, 129.0, 128.82, 128.78, 128.4, 127.5, 127.4, 127.2, 127.1, 126.9, 125.0, 123.63, 123.59, 108.21, 108.16, 66.0, 63.7, 61.4, 55.8, 41.0, 40.7, 27.1, 27.0, 14.1, 14.0. IR (film): ν_{max} (cm^{-1}) = 2922, 1707, 1610, 1489, 1469, 1448, 1366, 1343, 1297, 1254, 1201, 1156, 1125, 1094, 1074, 1021, 1001, 960, 784, 749, 689, 613, 540, 492, 474, 445. HRMS (ESI): Exact mass calcd. for $\text{C}_{29}\text{H}_{25}\text{NO}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 474.16758. Found: 474.16693.

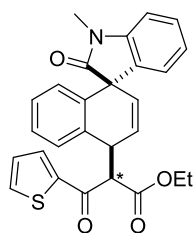


5h: white foam, 54.6 mg, 59% yield. Two sets of signals were observed due to the existence of diastereoisomers. ^1H NMR (400 MHz, CDCl_3) δ 8.13-8.11 (m, 1H), 7.86-7.84 (m, 1H), 7.40-7.33 (m, 2H), 7.28 (s, 0.5H), 7.20-7.16 (m, 0.5H), 7.13-7.05 (m, 3H), 6.96-6.92 (m, 2H), 6.85-6.83 (m, 1H), 6.67 (dd, $J = 9.6, 5.6$ Hz, 0.5H), 6.52 (d, $J = 7.6$ Hz, 0.5H), 6.48-6.42 (m, 1H), 5.72 (d, $J = 9.6$ Hz, 0.5H), 5.58-5.52 (m, 1H), 5.45 (d, $J = 10.8$ Hz, 0.5H), 4.69-4.61 (m, 1H), 4.22-4.09 (m, 1H), 4.07-3.97 (m, 1H), 3.31 (s, 1.5H), 3.26 (s, 1.5H), 2.39 (s, 1.5H), 2.29 (s, 1.5H), 1.16 (t, $J = 7.2$ Hz, 1.5H), 1.03 (t, $J = 7.2$ Hz, 1.5H); ^{13}C NMR (101 MHz, CDCl_3) δ 196.4, 193.8, 177.1, 176.8, 168.9, 168.7, 144.6, 144.11, 144.06, 144.0, 136.7, 136.3, 135.81, 135.78, 135.4, 134.8, 134.1, 131.9, 131.6, 129.7, 129.6, 129.5, 129.2, 128.9, 128.8, 127.5, 127.43, 127.38, 127.2, 127.0, 126.8, 125.0, 123.62, 123.57, 108.2, 108.1, 65.7, 63.6, 61.4, 55.8, 40.9, 40.7, 27.1, 27.0, 21.8, 21.7, 14.1, 14.0. IR (film): ν_{max} (cm^{-1}) = 2922, 1708, 1671, 1606, 1469, 1366, 1343, 1296, 1256, 1156, 1124, 1094, 1074, 1021, 959, 832,

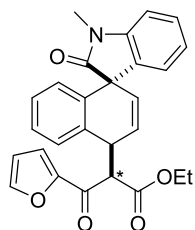
749, 692, 590, 540, 474, 445. HRMS (ESI): Exact mass calcd. for $C_{30}H_{27}NO_4Na$ ($[M+Na]^+$): 488.18323. Found: 488.18308.



5i: white foam, 71.6 mg, 76% yield. Two sets of signals were observed due to the existence of diastereoisomers. 1H NMR (400 MHz, $CDCl_3$) δ 8.27-8.24 (m, 1H), 7.99-7.96 (m, 1H), 7.40-7.34 (m, 1.54H), 7.21-7.12 (m, 1.65H), 7.09-7.05 (m, 2H), 6.98-6.91 (m, 3H), 6.87-6.80 (m, 1H), 6.68 (dd, J = 9.6, 5.2 Hz, 0.57H), 6.54-6.52 (m, 0.45H), 6.47-6.43 (m, 1H), 5.73 (d, J = 9.6 Hz, 0.55H), 5.59 (d, J = 10.0 Hz, 0.43H), 5.56 (d, J = 10.8 Hz, 0.44H), 5.45 (d, J = 10.8 Hz, 0.55H), 4.68-4.58 (m, 1H), 4.26-3.96 (m, 2H), 3.32 (s, 1.67H), 3.27 (s, 1.32H), 1.18 (t, J = 7.2 Hz, 1.69H), 1.04 (t, J = 7.2 Hz, 1.37H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.5, 192.8, 177.2, 176.8, 168.6, 168.5, 166.2 (d, J = 256.5 Hz), 165.9 (d, J = 256.3 Hz), 144.01, 143.97, 136.5, 136.3, 135.9, 135.5, 135.2, 133.7 (d, J = 2.7 Hz), 133.1 (d, J = 2.8 Hz), 132.3, 132.2, 132.1, 131.9, 131.4, 129.6, 129.1, 128.9, 128.85, 128.80, 127.6, 127.49, 127.47, 127.2, 127.1, 126.9, 125.0, 123.7, 123.6, 115.9 (d, J = 21.9 Hz), 115.5 (d, J = 21.9 Hz), 108.3, 108.2, 65.9, 63.6, 61.51, 61.48, 55.9, 41.1, 40.7, 27.1, 27.0, 14.1, 14.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ -104.4 (m), -105.0 (m). IR (film): ν_{max} (cm^{-1}) = 2979, 1737, 1706, 1676, 1595, 1489, 1469, 1412, 1366, 1344, 1298, 1255, 1235, 1200, 1156, 1125, 1094, 1074, 1020, 960, 845, 748, 690, 666, 635, 589, 540, 495, 475, 445. HRMS (ESI): Exact mass calcd. for $C_{29}H_{24}NO_4FNa$ ($[M+Na]^+$): 492.15816. Found: 492.15763.

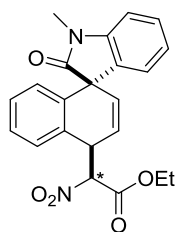


5j: colorless oil (purified by preparative TLC), 81.9 mg, 89% yield. Two sets of signals were observed due to the existence of diastereoisomers. ^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, $J = 4.0$ Hz, 0.39H), 7.74 (d, $J = 3.6$ Hz, 0.56H), 7.68 (d, $J = 4.8$ Hz, 0.36H), 7.52 (d, $J = 4.8$ Hz, 0.53H), 7.42-7.34 (m, 1H), 7.20-7.04 (m, 3H), 6.97-6.93 (m, 2H), 6.88-6.82 (m, 2H), 6.67 (dd, $J = 9.6, 5.2$ Hz, 0.59H), 6.52 (d, $J = 8.0$ Hz, 0.38H), 6.46-6.41 (m, 1H), 5.72 (d, $J = 9.6$ Hz, 0.55H), 5.60 (d, $J = 9.6$ Hz, 0.38H), 5.39 (d, $J = 10.4$ Hz, 0.39H), 5.28 (d, $J = 10.8$ Hz, 0.57H), 4.65 (dd, $J = 10.8, 5.2$ Hz, 0.39H), 4.56 (dd, $J = 10.8, 5.2$ Hz, 0.57H), 4.27-4.03 (m, 2H), 3.32 (s, 1.68H), 3.26 (s, 1.2H), 1.21 (t, $J = 7.2$ Hz, 1.76H), 1.08 (t, $J = 7.2$ Hz, 1.18H); ^{13}C NMR (101 MHz, CDCl_3) δ 189.2, 187.0, 177.2, 176.8, 168.6, 168.5, 145.2, 144.3, 144.1, 144.0, 136.5, 136.3, 135.7, 135.5, 135.42, 135.38, 135.31, 135.26, 135.21, 131.9, 131.2, 129.6, 129.1, 128.89, 128.87, 128.85, 128.7, 128.6, 127.6, 127.5, 127.4, 127.1, 126.9, 124.99, 124.98, 123.7, 123.6, 108.3, 108.2, 66.7, 65.0, 61.55, 61.53, 55.89, 55.87, 41.2, 40.7, 27.12, 27.05, 14.2, 14.1. IR (film): ν_{max} (cm^{-1}) = 2979, 1735, 1704, 1650, 1610, 1489, 1469, 1412, 1345, 1301, 1259, 1201, 1155, 1124, 1071, 960, 854, 819, 746, 692, 664, 631, 562, 540, 492, 445. HRMS (ESI): Exact mass calcd. for $\text{C}_{27}\text{H}_{23}\text{NO}_4\text{NaS}$ ($[\text{M}+\text{Na}]^+$): 480.12400. Found: 480.12359.

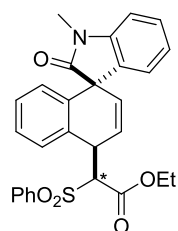


5k: white foam (purified by preparative TLC), 40.1 mg, 45% yield. Two sets of signals were observed due to the existence of diastereoisomers. ^1H NMR (400 MHz, CDCl_3) δ 7.66-7.65 (m, 0.72H), 7.51-7.50 (m, 0.67H), 7.41-7.34 (m, 1.45H), 7.30 (d, $J = 3.6$ Hz, 0.64H), 7.18 (t, $J = 7.6$ Hz, 0.48H), 7.10-7.04 (m, 2H), 6.98-6.92 (m, 2H), 6.90-6.85 (m, 1H), 6.66 (dd, $J = 9.6, 5.2$ Hz, 0.65H), 6.55-6.50 (m, 0.79H), 6.45-6.40 (m, 1H), 6.27 (dd, $J = 3.6, 1.6$ Hz, 0.6H), 5.71 (d, $J = 10.0$ Hz, 0.6H), 5.61 (d, $J = 9.6$ Hz, 0.36H), 5.19 (d, $J = 10.8$ Hz, 0.36H), 5.06 (d, $J = 10.8$ Hz, 0.61H), 4.65 (dd, $J = 10.8, 5.2$ Hz, 0.36H), 4.53 (dd, $J = 10.8, 5.2$ Hz, 0.60H), 4.28-4.04 (m, 2H), 3.32 (s,

1.76H), 3.27 (s, 1.06H), 1.22 (t, $J = 7.2$ Hz, 1.91H), 1.10 (t, $J = 7.2$ Hz, 1.18H); ^{13}C NMR (101 MHz, CDCl_3) δ 183.9, 182.1, 177.2, 176.8, 168.5, 168.4, 152.7, 152.0, 148.2, 148.0, 144.0, 143.9, 136.4, 136.2, 135.6, 135.5, 135.25, 135.23, 132.0, 131.0, 129.5, 129.12, 129.07, 128.89, 128.86, 127.53, 127.47, 127.18, 127.14, 126.9, 125.00, 124.98, 123.8, 123.7, 122.2, 121.9, 112.7, 112.6, 108.3, 108.2, 66.0, 64.5, 61.6, 55.87, 55.82, 41.0, 40.4, 27.1, 27.0, 14.2, 14.1. IR (film): ν_{max} (cm^{-1}) = 3017, 1735, 1705, 1664, 1611, 1562, 1489, 1464, 1393, 1367, 1345, 1263, 1218, 1160, 1125, 1075, 1019, 960, 883, 745, 691, 665, 592, 540, 491, 474, 445. HRMS (ESI): Exact mass calcd. for $\text{C}_{27}\text{H}_{23}\text{NO}_5\text{Na}$ ($[\text{M}+\text{Na}]^+$): 464.14684. Found: 464.14699.

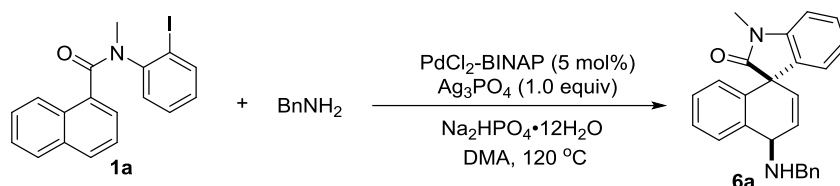


5l: white foam, 18.8 mg, 24% yield. Two sets of signals were observed due to the existence of diastereoisomers. ^1H NMR (400 MHz, CDCl_3) δ 7.42-7.38 (m, 1H), 7.31 (d, $J = 7.6$ Hz, 0.45H), 7.23-7.17 (m, 1.75H), 7.13-7.10 (m, 2H), 7.00-6.96 (m, 2H), 6.57-6.50 (m, 1.59H), 6.40 (dd, $J = 9.6, 5.2$ Hz, 0.43H), 6.26-6.20 (m, 1H), 5.90-5.87 (m, 1H), 4.70-4.59 (m, 1H), 4.37-4.10 (m, 2H), 3.26-3.25 (m, 3H), 1.32 (t, $J = 7.2$ Hz, 2H), 1.15 (t, $J = 7.2$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.3, 176.1, 164.7, 163.6, 144.2, 136.9, 136.3, 134.5, 134.3, 132.9, 132.4, 131.9, 129.3, 129.24, 129.22, 128.40, 128.38, 128.35, 128.2, 128.1, 127.9, 127.80, 127.78, 127.5, 125.02, 125.00, 123.84, 123.81, 108.5, 96.12, 96.05, 63.1, 62.9, 56.2, 56.0, 42.1, 41.7, 27.2, 27.1, 14.0, 13.9. IR (film): ν_{max} (cm^{-1}) = 2922, 1744, 1708, 1611, 1556, 1490, 1469, 1345, 1241, 1188, 1125, 1074, 1018, 961, 852, 748, 720, 690, 662, 632, 541, 492, 445. HRMS (ESI): Exact mass calcd. for $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_5\text{Na}$ ($[\text{M}+\text{Na}]^+$): 415.12644. Found: 415.12575.

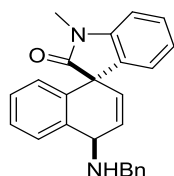


5m: white solid, 50.0 mg, 51% yield, m.p. = 145-147 °C. Two sets of signals were observed due to the existence of diastereoisomers. ^1H NMR (400 MHz, CDCl_3) δ 8.02-7.94 (m, 2H), 7.71 (d, J = 7.6 Hz, 0.24H), 7.63-7.59 (m, 1H), 7.54-7.48 (m, 2H), 7.39-7.34 (m, 1H), 7.24-7.22 (m, 0.71H), 7.15-7.01 (m, 3H), 6.95-6.90 (m, 2H), 6.81 (dd, J = 9.6, 5.6 Hz, 0.78H), 6.52-6.46 (m, 1H), 6.33 (dd, J = 9.6, 4.8 Hz, 0.24H), 5.76-5.72 (m, 1H), 5.46 (d, J = 10.8 Hz, 0.75H), 5.15 (d, J = 7.2 Hz, 0.22H), 4.79-4.78 (m, 0.24H), 4.62 (dd, J = 10.8, 5.6 Hz, 0.8H), 3.97 (q, J = 7.2 Hz, 0.46H), 3.80-3.72 (m, 1.6H), 3.24 (s, 3H), 0.94 (t, J = 7.2 Hz, 0.68H), 0.80 (t, J = 7.2 Hz, 2.33H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.3, 176.1, 166.5, 165.2, 144.1, 144.0, 139.1, 138.8, 137.1, 135.9, 135.0, 134.7, 134.4, 134.1, 134.0, 133.9, 130.6, 130.3, 130.2, 129.9, 129.4, 129.2, 129.02, 128.98, 128.90, 128.87, 128.5, 127.7, 127.55, 127.50, 127.2, 124.92, 124.88, 123.6, 123.5, 108.3, 108.2, 80.4, 77.9, 62.2, 61.8, 55.8, 55.4, 39.8, 38.7, 27.1, 27.0, 13.74, 13.67. IR (film): ν_{max} (cm^{-1}) = 2924, 1739, 1708, 1610, 1489, 1469, 1366, 1326, 1289, 1262, 1141, 1080, 1031, 986, 961, 832, 749, 714, 688, 633, 591, 555, 538, 493, 445. HRMS (ESI): Exact mass calcd. for $\text{C}_{28}\text{H}_{26}\text{NO}_5\text{S}$ ($[\text{M}+\text{H}]^+$): 488.15262. Found: 488.15190.

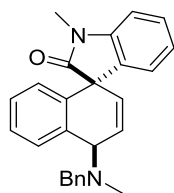
General procedure for Pd-catalyzed dearomative reaction of naphthalenes with amines (BnNH₂ as an example)



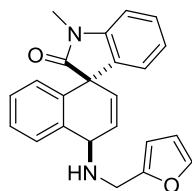
A flame-dried sealed tube was cooled to room temperature under argon. To this tube were added **1a** (77.4 mg, 0.2 mmol), pre-synthesized PdCl₂-BINAP (8.0 mg, 0.01 mmol), Na₂HPO₄·12H₂O (143.3 mg, 0.40 mmol), Ag₃PO₄ (83.7 mg, 0.2 mmol), BnNH₂ (42.9 mg, 0.40 mmol) and DMA (1.0 mL). Then the reaction mixture was stirred at 120 °C. After completion (monitored by TLC), the reaction mixture was cooled to room temperature and diluted with ethyl acetate (3 mL). The mixture was filtered through celite, and the filtrate was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EtOAc = 10/1) to afford the desired product **6a**.



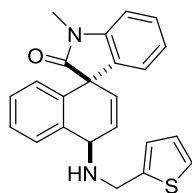
6a: white foam, 71.0 mg, 97% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.47-7.43 (m, 3H), 7.38-7.31 (m, 3H), 7.28-7.22 (m, 2H), 7.10-7.06 (m, 2H), 7.00 (d, *J* = 6.8 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.61 (dd, *J* = 9.6, 5.2 Hz, 1H), 6.54 (d, *J* = 7.6 Hz, 1H), 5.75 (d, *J* = 9.6 Hz, 1H), 4.39 (d, *J* = 4.8 Hz, 1H), 4.04-3.91 (m, 2H), 3.24 (s, 3H), 2.64 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 176.9, 144.2, 140.7, 137.4, 136.3, 134.6, 132.5, 129.5, 128.9, 128.6, 128.43, 128.41, 127.4, 127.2, 126.9, 126.8, 124.9, 123.6, 108.4, 55.6, 53.9, 50.5, 27.0. IR (film): ν_{max} (cm⁻¹) = 2927, 1705, 1609, 1489, 1468, 1343, 1258, 1124, 1072, 1021, 962, 837, 743, 692, 636, 576, 540, 483, 446. HRMS (ESI): Exact mass calcd. for C₂₅H₂₃N₂O ([M+H]⁺): 367.18049. Found: 367.18002.



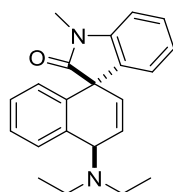
6b: yellow oil, 75.0 mg, 99% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, $J = 7.6$ Hz, 1H), 7.42-7.41 (m, 2H), 7.32 (t, $J = 7.2$ Hz, 2H), 7.28-7.21 (m, 3H), 7.05 (t, $J = 7.2$ Hz, 1H), 6.97 (t, $J = 7.6$ Hz, 1H), 6.91 (d, $J = 7.6$ Hz, 1H), 6.86 (d, $J = 7.2$ Hz, 1H), 6.53 (d, $J = 7.6$ Hz, 1H), 6.39 (dd, $J = 10.4, 3.2$ Hz, 1H), 5.75 (d, $J = 10.4$ Hz, 1H), 4.57 (s, 1H), 3.90 (AB, $J_{AB} = 13.2$ Hz, 1H), 3.65 (BA, $J_{BA} = 13.2$ Hz, 1H), 3.28 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 177.8, 143.6, 140.4, 136.6, 135.7, 135.1, 129.4, 128.9, 128.5, 128.3, 127.9, 127.6, 127.5, 126.9, 126.5, 125.2, 124.6, 123.3, 108.2, 58.03, 57.96, 54.4, 38.2, 26.8. IR (film): ν_{max} (cm^{-1}) = 3025, 2927, 1712, 1607, 1489, 1468, 1450, 1366, 1339, 1256, 1191, 1156, 1124, 1075, 1019, 991, 970, 875, 777, 733, 695, 632, 540, 482, 446. HRMS (ESI): Exact mass calcd. for $\text{C}_{26}\text{H}_{25}\text{N}_2\text{O}$ ($[\text{M}+\text{H}]^+$): 381.19614. Found: 381.19603.



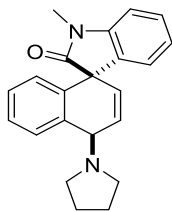
6c: yellow oil, 70.0 mg, 98% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.43 (d, $J = 7.6$ Hz, 1H), 7.38-7.35 (m, 2H), 7.26 (d, $J = 8.4$ Hz, 1H), 7.08-7.07 (m, 2H), 7.00 (d, $J = 7.2$ Hz, 1H), 6.95 (d, $J = 7.6$ Hz, 1H), 6.59-6.53 (m, 2H), 6.31-6.27 (m, 2H), 5.75 (d, $J = 9.6$ Hz, 1H), 4.42 (d, $J = 4.4$ Hz, 1H), 3.99 (AB, $J_{AB} = 14.4$ Hz, 1H), 3.90 (BA, $J_{BA} = 14.0$ Hz, 1H), 3.24 (s, 3H), 3.00 (s, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.8, 154.3, 144.1, 141.7, 137.1, 136.3, 134.5, 132.2, 129.4, 128.8, 127.4, 127.2, 127.0, 124.9, 123.6, 110.2, 108.3, 106.9, 55.6, 54.0, 43.3, 27.0. IR (film): ν_{max} (cm^{-1}) = 3287, 2886, 1705, 1610, 1489, 1468, 1365, 1343, 1300, 1256, 1218, 1188, 1146, 1124, 1093, 1071, 1009, 961, 917, 862, 836, 742, 690, 664, 636, 599, 563, 540, 478, 446. HRMS (ESI): Exact mass calcd. for $\text{C}_{23}\text{H}_{21}\text{N}_2\text{O}_2$ ($[\text{M}+\text{H}]^+$): 357.15975. Found: 357.16049.



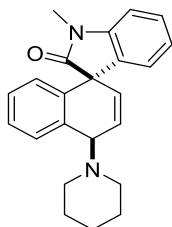
6d: yellow oil, 56.6 mg, 76% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.44 (d, $J = 7.6$ Hz, 1H), 7.36 (t, $J = 7.6$ Hz, 1H), 7.28 (t, $J = 7.2$ Hz, 1H), 7.24-7.22 (m, 1H), 7.10-7.05 (m, 2H), 7.01-6.99 (m, 2H), 6.97-6.94 (m, 2H), 6.60-6.52 (m, 2H), 5.75 (d, $J = 9.6$ Hz, 1H), 4.42 (d, $J = 4.8$ Hz, 1H), 4.21 (AB, $J_{AB} = 14.0$ Hz, 1H), 4.11 (BA, $J_{BA} = 14.0$ Hz, 1H), 3.23 (s, 3H), 2.66 (s, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.8, 145.3, 144.1, 137.4, 136.2, 134.6, 132.3, 129.4, 128.8, 128.7, 127.4, 127.2, 126.9, 126.6, 124.9, 124.6, 124.3, 123.6, 108.3, 55.6, 53.2, 45.3, 27.0. IR (film): ν_{max} (cm^{-1}) = 3285, 3011, 1704, 1610, 1489, 1468, 1365, 1344, 1299, 1257, 1216, 1159, 1125, 1093, 1072, 1020, 993, 961, 836, 743, 692, 665, 636, 563, 540, 472, 446. HRMS (ESI): Exact mass calcd. for $\text{C}_{23}\text{H}_{21}\text{N}_2\text{OS}$ ($[\text{M}+\text{H}]^+$): 373.13691. Found: 373.13723.



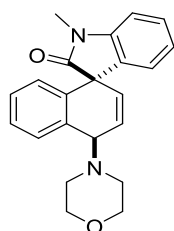
6e: white foam, 58.4 mg, 88% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, $J = 7.6$ Hz, 1H), 7.28 (t, $J = 7.2$ Hz, 1H), 7.24-7.21 (m, 1H), 7.05-6.97 (m, 2H), 6.92 (d, $J = 8.0$ Hz, 1H), 6.89 (d, $J = 7.2$ Hz, 1H), 6.53 (d, $J = 7.6$ Hz, 1H), 6.30 (d, $J = 10.0$ Hz, 1H), 5.66 (d, $J = 10.0$ Hz, 1H), 4.62 (s, 1H), 3.30 (s, 3H), 2.84-2.79 (m, 2H), 2.59-2.54 (m, 2H), 1.10 (t, $J = 6.8$ Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 178.1, 143.5, 137.6, 136.0, 135.0, 129.4, 128.4, 127.4, 127.3, 126.7, 126.5, 126.4, 124.6, 123.3, 108.2, 55.1, 54.4, 44.4, 26.7, 14.9. IR (film): ν_{max} (cm^{-1}) = 2967, 2800, 1710, 1606, 1488, 1470, 1367, 1342, 1297, 1255, 1193, 1121, 1078, 1048, 983, 950, 769, 741, 692, 607, 541, 479, 448. HRMS (ESI): Exact mass calcd. for $\text{C}_{22}\text{H}_{25}\text{N}_2\text{O}$ ($[\text{M}+\text{H}]^+$): 333.19614. Found: 333.19641.



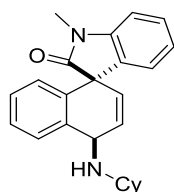
6f: white foam, 65.0 mg, 98% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, J = 8.0 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.25-7.21 (m, 1H), 7.03 (t, J = 7.6 Hz, 1H), 6.98 (t, J = 7.6 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 6.88 (d, J = 7.2 Hz, 1H), 6.54 (d, J = 7.6 Hz, 1H), 6.33 (dd, J = 10.0, 3.6 Hz, 1H), 5.74 (d, J = 10.0 Hz, 1H), 4.80 (s, 1H), 3.29 (s, 3H), 2.94-2.92 (m, 2H), 2.72-2.69 (m, 2H), 1.79-1.75 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 177.7, 143.5, 136.5, 135.8, 134.7, 129.5, 128.5, 128.1, 127.5, 127.3, 126.6, 125.6, 124.6, 123.3, 108.2, 55.2, 54.5, 48.1, 26.7, 24.1. IR (film): ν_{max} (cm^{-1}) = 2961, 2801, 1709, 1605, 1488, 1468, 1366, 1341, 1299, 1253, 1194, 1124, 1073, 1020, 989, 949, 930, 857, 772, 741, 688, 636, 543, 481, 449. HRMS (ESI): Exact mass calcd. for $\text{C}_{22}\text{H}_{23}\text{N}_2\text{O}$ ($[\text{M}+\text{H}]^+$): 331.18049. Found: 331.18115.



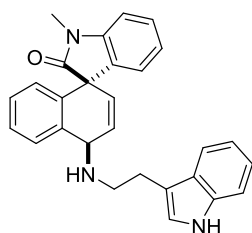
6g: yellow oil, 68.0 mg, 99% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.75 (d, J = 7.6 Hz, 1H), 7.31-7.21 (m, 2H), 7.04 (t, J = 7.6 Hz, 1H), 6.98 (t, J = 7.6 Hz, 1H), 6.92 (d, J = 7.6 Hz, 1H), 6.88 (d, J = 7.2 Hz, 1H), 6.53 (d, J = 7.6 Hz, 1H), 6.34 (dd, J = 10.0, 2.8 Hz, 1H), 5.68 (d, J = 10.0 Hz, 1H), 4.46 (s, 1H), 3.29 (s, 3H), 2.67 (s, 4H), 1.62-1.54 (m, 4H), 1.44-1.43 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 177.9, 143.5, 136.4, 135.9, 135.1, 129.3, 128.4, 127.4, 127.3, 127.1, 126.4, 124.6, 123.3, 108.2, 60.5, 54.4, 50.3, 26.9, 26.7, 24.9. IR (film): ν_{max} (cm^{-1}) = 2929, 2848, 2801, 1713, 1607, 1488, 1468, 1367, 1339, 1300, 1254, 1204, 1153, 1120, 1077, 1036, 1019, 988, 950, 863, 773, 739, 692, 634, 541, 481, 446. HRMS (ESI): Exact mass calcd. for $\text{C}_{23}\text{H}_{25}\text{N}_2\text{O}$ ($[\text{M}+\text{H}]^+$): 345.19614. Found: 345.19566.



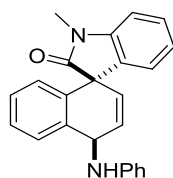
6h: white foam, 68.5 mg, 99% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, J = 7.6 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.25 (t, J = 7.6 Hz, 1H), 7.06 (t, J = 7.6 Hz, 1H), 7.00 (t, J = 7.6 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 6.89 (d, J = 7.2 Hz, 1H), 6.53 (d, J = 7.6 Hz, 1H), 6.31 (dd, J = 10.0, 2.8 Hz, 1H), 5.72 (d, J = 10.0 Hz, 1H), 4.48 (s, 1H), 3.77-3.68 (m, 4H), 3.29 (s, 3H), 2.75 (s, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 177.6, 143.5, 135.5, 135.4, 135.3, 129.4, 128.6, 128.0, 127.6, 127.5, 126.5, 125.5, 124.6, 123.4, 108.3, 67.9, 60.0, 54.3, 49.4, 26.7. IR (film): ν_{max} (cm^{-1}) = 2950, 2884, 2845, 1721, 1608, 1488, 1467, 1367, 1333, 1293, 1250, 1107, 1075, 1004, 986, 950, 928, 865, 851, 775, 742, 711, 689, 641, 584, 541, 487, 468, 445. HRMS (ESI): Exact mass calcd. for $\text{C}_{22}\text{H}_{23}\text{N}_2\text{O}_2$ ($[\text{M}+\text{H}]^+$): 347.17540. Found: 347.17422.



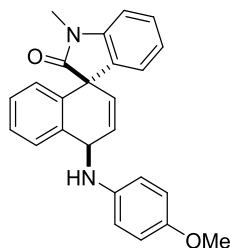
6i: white solid, 68.1 mg, 95% yield, m.p. = 148-150 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.35 (m, 2H), 7.27-7.24 (m, 1H), 7.10-7.00 (m, 3H), 6.94 (d, J = 7.6 Hz, 1H), 6.61 (dd, J = 9.6, 5.2 Hz, 1H), 6.51 (d, J = 7.6 Hz, 1H), 5.73 (d, J = 9.6 Hz, 1H), 4.49 (d, J = 4.0 Hz, 1H), 3.23 (s, 3H), 2.78 (s, 1H), 2.06 (d, J = 9.2 Hz, 1H), 1.85-1.65 (m, 4H), 1.33-1.26 (m, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.8, 144.2, 138.1, 136.2, 134.6, 133.0, 129.5, 128.8, 128.4, 127.3, 126.9, 124.9, 123.5, 108.3, 55.7, 53.0, 50.9, 33.8, 33.2, 27.0, 26.3, 25.1, 25.0. IR (film): ν_{max} (cm^{-1}) = 3283, 2922, 2849, 1700, 1611, 1491, 1468, 1365, 1344, 1258, 1097, 1075, 959, 888, 863, 837, 795, 777, 748, 723, 689, 635, 573, 542, 480, 448, 427. HRMS (ESI): Exact mass calcd. for $\text{C}_{24}\text{H}_{27}\text{N}_2\text{O}$ ($[\text{M}+\text{H}]^+$): 359.21179. Found: 359.21194.



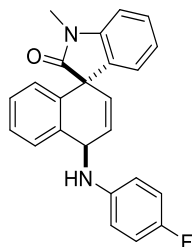
6j: white foam (purified by preparative TLC), 9.8 mg, 12% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.05 (s, 1H), 7.62 (d, $J = 7.6$ Hz, 1H), 7.40-7.34 (m, 3H), 7.24-7.15 (m, 2H), 7.10-7.05 (m, 4H), 7.01 (d, $J = 7.2$ Hz, 1H), 6.97 (d, $J = 8.0$ Hz, 1H), 6.61 (dd, $J = 9.6$, 4.8 Hz, 1H), 6.54 (d, $J = 7.6$ Hz, 1H), 5.78 (d, $J = 9.6$ Hz, 1H), 4.51 (d, $J = 3.2$ Hz, 1H), 3.25 (s, 3H), 3.13-3.11 (m, 3H), 3.04-2.97 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.9, 144.1, 136.4, 136.3, 134.5, 132.0, 129.7, 129.0, 127.7, 127.6, 127.4, 127.0, 125.0, 123.8, 122.1, 121.9, 119.3, 119.2, 114.2, 111.1, 108.5, 55.8, 55.0, 47.2, 27.1, 26.2. IR (film): ν_{max} (cm^{-1}) = 2917, 2852, 1700, 1610, 1489, 1467, 1365, 1344, 1300, 1259, 1125, 1092, 961, 907, 739, 690, 637, 541, 475, 447, 425. HRMS (ESI): Exact mass calcd. for $\text{C}_{28}\text{H}_{26}\text{N}_3\text{O}$ ($[\text{M}+\text{H}]^+$): 420.20704. Found: 420.20734.



6k: white solid, 68.4 mg, 97% yield, m.p. = 204-205 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, $J = 7.6$ Hz, 1H), 7.37 (t, $J = 7.2$ Hz, 1H), 7.22-7.18 (m, 3H), 7.12-7.06 (m, 3H), 6.95 (d, $J = 8.0$ Hz, 1H), 6.88 (d, $J = 7.6$ Hz, 2H), 6.73 (t, $J = 7.2$ Hz, 1H), 6.59 (dd, $J = 9.6$, 4.8 Hz, 1H), 6.53 (d, $J = 8.0$ Hz, 1H), 5.74 (d, $J = 9.6$ Hz, 1H), 5.35 (s, 1H), 4.94 (s, 1H), 3.24 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.9, 147.7, 144.2, 137.4, 136.0, 134.1, 131.2, 129.4, 129.1, 129.0, 128.8, 128.0, 127.5, 126.4, 124.9, 123.7, 118.0, 114.5, 108.5, 55.5, 50.7, 27.1. IR (film): ν_{max} (cm^{-1}) = 3336, 3045, 1705, 1598, 1500, 1365, 1342, 1297, 1260, 1173, 1122, 1094, 1057, 983, 955, 870, 742, 724, 690, 615, 541, 498, 470, 447. HRMS (ESI): Exact mass calcd. for $\text{C}_{24}\text{H}_{21}\text{N}_2\text{O}$ ($[\text{M}+\text{H}]^+$): 353.16484. Found: 353.16383.

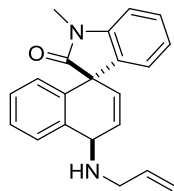


6l: white foam, 61.0 mg, 80% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.43 (d, J = 7.6 Hz, 1H), 7.39-7.35 (m, 1H), 7.18 (t, J = 7.2 Hz, 1H), 7.10 (t, J = 7.2 Hz, 1H), 7.06-7.03 (m, 2H), 6.95 (d, J = 7.6 Hz, 1H), 6.87-6.84 (m, 2H), 6.81-7.79 (m, 2H), 6.60 (dd, J = 9.6, 4.8 Hz, 1H), 6.52 (d, J = 7.6 Hz, 1H), 5.74 (d, J = 9.6 Hz, 1H), 5.20 (d, J = 4.8 Hz, 1H), 4.64 (s, 1H), 3.75 (s, 3H), 3.25 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.9, 152.7, 144.2, 141.8, 137.5, 136.0, 134.2, 131.7, 129.2, 129.0, 128.8, 127.9, 127.4, 126.5, 124.9, 123.7, 116.9, 114.9, 108.5, 55.8, 55.6, 52.5, 27.1. IR (film): ν_{max} (cm^{-1}) = 3300, 2929, 1701, 1610, 1506, 1467, 1365, 1344, 1229, 1178, 1124, 1093, 1035, 984, 960, 821, 746, 689, 637, 585, 540, 512, 488, 447. HRMS (ESI): Exact mass calcd. for $\text{C}_{25}\text{H}_{23}\text{N}_2\text{O}_2$ ($[\text{M}+\text{H}]^+$): 383.17540. Found: 383.17450.

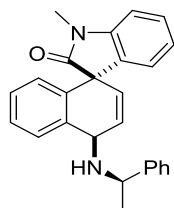


6m: white foam, 73.3 mg, 99% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.44-7.40 (m, 1H), 7.40-7.36 (m, 1H), 7.20 (t, J = 7.6 Hz, 1H), 7.11 (t, J = 7.6 Hz, 1H), 7.08-7.05 (m, 2H), 6.96 (d, J = 7.6 Hz, 1H), 6.93-6.88 (m, 2H), 6.84-6.81 (m, 2H), 6.59 (dd, J = 9.6, 4.8 Hz, 1H), 6.53 (d, J = 7.6 Hz, 1H), 5.77 (d, J = 9.6 Hz, 1H), 5.22 (d, J = 4.4 Hz, 1H), 4.85 (s, 1H), 3.25 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.9, 156.3 (d, J = 236.3 Hz), 144.2, 144.1 (d, J = 1.8 Hz), 137.3, 136.1, 134.1, 131.4, 129.3, 129.05, 129.03, 128.0, 127.5, 126.5, 124.9, 123.7, 116.2 (d, J = 7.5 Hz), 115.8 (d, J = 22.3 Hz), 108.5, 55.7, 52.1, 27.1; ^{19}F NMR (377 MHz, CDCl_3) δ -126.9 (s). IR (film): ν_{max} (cm^{-1}) = 3299, 3055, 1693, 1607, 1502, 1466, 1364, 1345, 1300, 1260, 1213, 1123, 1099, 1073, 1052, 963, 877, 820, 768, 749, 688, 640, 580, 541, 523, 499, 486, 468,

447, 413. HRMS (ESI): Exact mass calcd. for $C_{24}H_{20}N_2OF$ ($[M+H]^+$): 371.15542. Found: 371.15539.



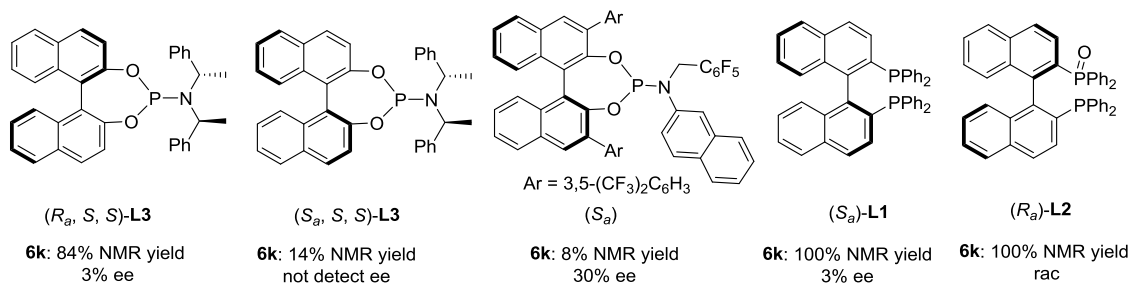
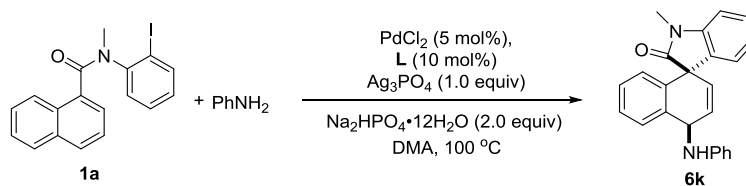
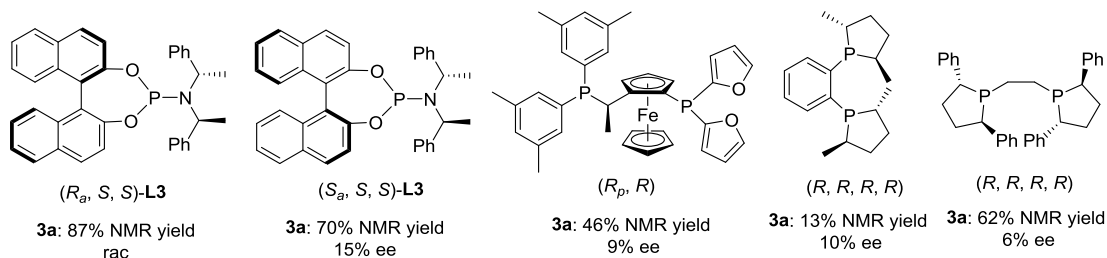
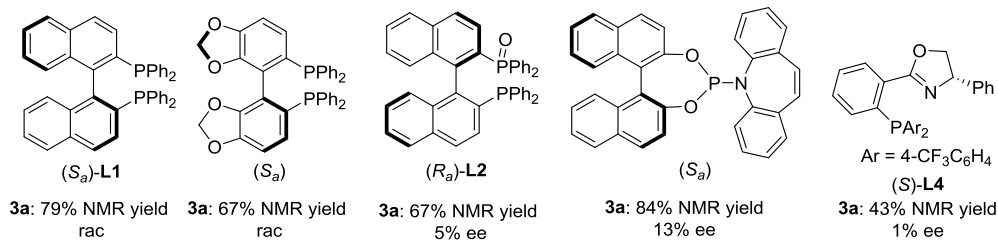
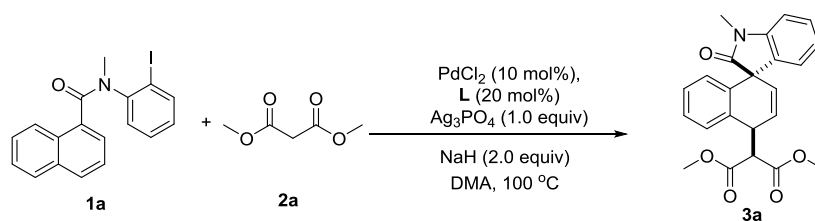
6n: white foam (purified by preparative TLC), 15.6 mg, 25% yield. 1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.6 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.29 (d, J = 7.2 Hz, 1H), 7.12-7.06 (m, 2H), 7.02 (d, J = 7.6 Hz, 1H), 6.96 (d, J = 7.6 Hz, 1H), 6.61 (dd, J = 9.6, 5.2 Hz, 1H), 6.53 (d, J = 7.6 Hz, 1H), 6.08-5.98 (m, 1H), 5.77 (d, J = 9.6 Hz, 1H), 5.29 (d, J = 17.2 Hz, 1H), 5.15 (d, J = 10.4 Hz, 1H), 4.41 (d, J = 5.2 Hz, 1H), 3.50-3.39 (m, 2H), 3.25 (s, 3H), 2.90 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.9, 144.2, 137.1, 137.0, 136.4, 134.5, 132.4, 129.6, 129.1, 128.9, 127.5, 127.3, 127.0, 125.0, 123.7, 116.4, 108.4, 55.7, 54.1, 49.3, 27.1. IR (film): ν_{max} (cm^{-1}) = 3290, 2925, 1706, 1609, 1489, 1468, 1417, 1366, 1342, 1300, 1257, 1124, 1093, 1072, 1020, 993, 961, 917, 858, 835, 745, 690, 636, 564, 540, 477, 446. HRMS (ESI): Exact mass calcd. for $C_{21}H_{21}N_2O$ ($[M+H]^+$): 317.16484. Found: 317.16568.



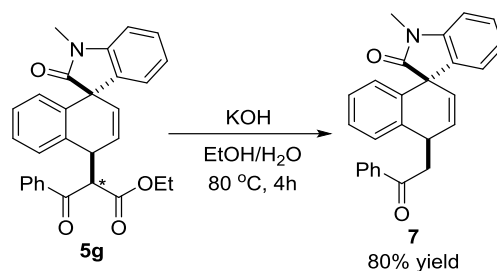
6o: white foam, 72.7 mg, 96% yield. Two sets of signals were observed due to the existence of diastereoisomers. 1H NMR (400 MHz, $CDCl_3$) δ 7.60-7.58 (m, 2H), 7.44-7.22 (m, 5H), 7.14-6.92 (m, 5H), 6.67 (dd, J = 9.6, 4.8 Hz, 0.5H), 6.55-6.50 (m, 1H), 6.45 (d, J = 7.6 Hz, 0.5H), 5.72 (dd, J = 9.6, 6.4 Hz, 1H), 4.29 (q, J = 6.4 Hz, 0.5H), 4.14-4.10 (m, 0.5H), 4.07-4.04 (m, 1H), 3.23 (s, 3H), 2.60 (s, 1H), 1.39 (d, J = 6.4 Hz, 1.5H), 1.32 (d, J = 6.4 Hz, 1.5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.9, 176.8, 146.2, 146.1, 144.24, 144.19, 138.8, 137.9, 136.7, 135.6, 134.6, 134.5, 133.5, 132.4,

129.9, 129.1, 128.82, 128.77, 128.67, 128.6, 128.30, 128.26, 127.8, 127.33, 127.30, 127.26, 127.1, 126.88, 126.82, 126.79, 126.2, 125.0, 124.9, 123.6, 123.5, 108.30, 108.26, 55.9, 55.5, 55.0, 54.6, 51.8, 51.5, 27.03, 27.01, 26.2, 25.8. IR (film): ν_{max} (cm^{-1}) = 3294, 2961, 1706, 1610, 1489, 1469, 1450, 1365, 1342, 1301, 1257, 1124, 1102, 1072, 1021, 968, 832, 746, 701, 637, 606, 539, 477, 445. HRMS (ESI): Exact mass calcd. for $\text{C}_{26}\text{H}_{25}\text{N}_2\text{O}$ ($[\text{M}+\text{H}]^+$): 381.19614. Found: 381.19607.

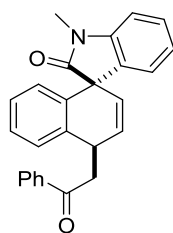
Preliminary asymmetric studies



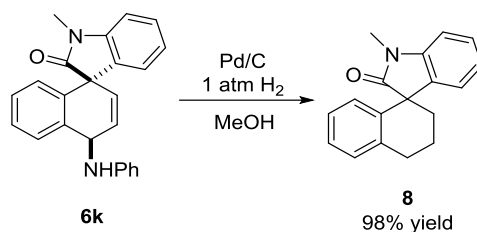
Transformations of products



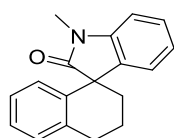
To a sealed tube were added **5g** (36.1 mg, 0.08 mmol), KOH (18 mg, 0.32 mmol, 4.0 equiv), H₂O (0.8 mL) and ethanol (0.8 mL). Then the reaction mixture was stirred at 80 °C for 4 h. After completion (monitored by TLC), the mixture was quenched with sat. NH₄Cl solution (10 mL) and extracted with EtOAc (3 x 10 mL). The combined organic layers were dried with anhydrous Na₂SO₄. The solvent was removed and the crude product was purified by flash chromatography on silica gel (PE/EtOAc = 20/1) to afford **7**.



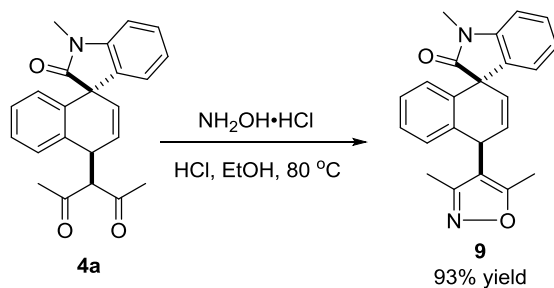
7: white foam, 24.2 mg, 80% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.38-7.34 (m, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.05-7.00 (m, 2H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.54-6.49 (m, 2H), 5.57 (d, *J* = 9.6 Hz, 1H), 4.40-4.36 (m, 1H), 3.91 (dd, *J* = 17.6, 9.2 Hz, 1H), 3.59 (dd, *J* = 17.6, 4.8 Hz, 1H), 3.26 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 199.5, 177.4, 144.1, 139.3, 137.2, 135.6, 135.1, 133.2, 132.9, 128.8, 128.7, 128.52, 128.47, 128.0, 127.1, 126.7, 126.3, 125.1, 123.6, 108.2, 55.4, 51.0, 36.3, 26.9. IR (film): ν_{max} (cm⁻¹) = 2930, 1711, 1684, 1607, 1489, 1467, 1343, 1263, 1206, 1154, 1128, 1092, 1072, 1023, 1001, 965, 756, 725, 692, 654, 628, 540, 489, 441. HRMS (ESI): Exact mass calcd. for C₂₆H₂₁NO₂Na ([M+Na]⁺): 402.14645. Found: 402.14677.



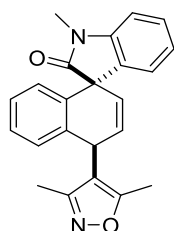
A flame-dried Schlenk tube was cooled down to room temperature under argon. To this tube were added **6k** (70.5 mg, 0.2 mmol), MeOH (2.0 mL) and Pd/C (5%, 30 mg). Then the reaction mixture was subjected to hydrogen (1 atm). The mixture was stirred at 30 °C for 24 h. After completion, the mixture was filtered and the filtrate was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EtOAc = 20/1) to afford **8**.



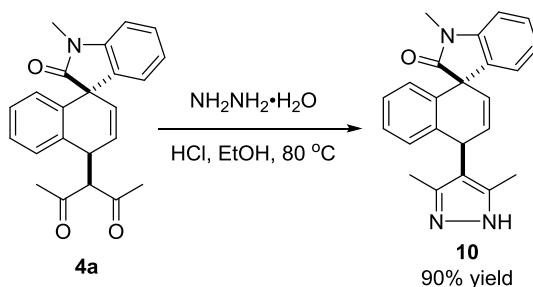
8: white solid, 52.0 mg, 98% yield, m.p. = 124-126 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.28 (t, J = 7.6 Hz, 1H), 7.16 (d, J = 7.2 Hz, 1H), 7.11 (t, J = 7.2 Hz, 1H), 7.05 (d, J = 7.2 Hz, 1H), 7.01-6.90 (m, 3H), 6.47 (d, J = 7.6 Hz, 1H), 3.28 (s, 3H), 3.04-2.92 (m, 2H), 2.36-2.34 (m, 1H), 2.22-2.16 (m, 1H), 2.03-1.93 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 180.5, 143.2, 137.9, 137.4, 135.2, 129.7, 128.0, 127.9, 127.1, 126.4, 124.1, 122.9, 108.1, 52.3, 34.1, 29.3, 26.6, 18.8. IR (film): ν_{max} (cm^{-1}) = 2931, 1710, 1606, 1488, 1466, 1370, 1341, 1301, 1252, 1154, 1130, 1093, 1063, 1022, 965, 771, 753, 689, 624, 588, 539, 494, 477, 439. HRMS (ESI): Exact mass calcd. for $\text{C}_{18}\text{H}_{18}\text{NO}$ ($[\text{M}+\text{H}]^+$): 264.13829. Found: 264.13825.



A solution of **4a** (35.9 mg, 0.1 mmol), hydroxylamine hydrochloride (13.9 mg, 0.2 mmol, 2.0 equiv) and con. HCl (20 μ L) in ethanol (1 mL) was heated to 80 $^{\circ}$ C for 7 h. After completion (monitored by TLC), the solvent of reaction mixture was removed under reduced pressure. The crude product was purified by silica gel column chromatography (PE/EtOAc = 20/1) to afford **9**.^[1]

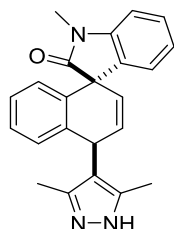


9: white solid, 33.1 mg, 93% yield, m.p. = 170-172 $^{\circ}$ C. ^1H NMR (400 MHz, CDCl_3) δ 7.34-7.30 (m, 1H), 7.17-7.13 (m, 1H), 7.08-7.04 (m, 1H), 7.02-7.01 (m, 2H), 6.97-6.95 (m, 2H), 6.65-6.63 (m, 1H), 6.01 (dd, J = 10.0, 3.2 Hz, 1H), 5.60 (dd, J = 10.0, 2.4 Hz, 1H), 4.78 (t, J = 2.8 Hz, 1H), 3.33 (s, 3H), 2.35 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 178.3, 166.2, 160.0, 143.4, 135.9, 135.1, 133.8, 129.0, 128.7, 128.6, 127.9, 127.7, 127.3, 124.7, 124.5, 123.5, 115.8, 108.5, 54.3, 33.5, 26.8, 11.3, 10.7. IR (film): ν_{max} (cm^{-1}) = 2925, 1716, 1639, 1605, 1489, 1469, 1370, 1342, 1256, 1202, 1129, 1078, 1016, 952, 888, 817, 774, 750, 690, 631, 541, 475, 449. HRMS (ESI): Exact mass calcd. for $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}_2\text{Na}$ ($[\text{M}+\text{Na}]^+$): 379.14170. Found: 379.14225.



A solution of **4a** (35.9 mg, 0.1 mmol), hydrazine monohydrate (10.0 mg, 0.2 mmol, 2.0 equiv) and con. HCl (20 μ L) in ethanol (1 mL) was heated to 80 $^{\circ}$ C for 7 h. After completion (monitored by TLC), the solvent of reaction mixture was removed under

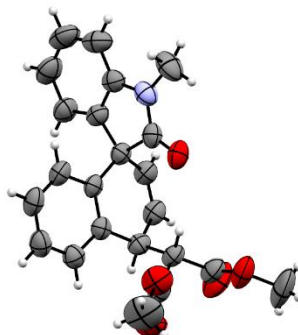
reduced pressure. The crude product was purified by silica gel column chromatography (DCM/MeOH= 20/1) to afford **10**.^[1]



10: white solid, 32.0 mg, 90% yield, m.p. = 129-131 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.12 (s, 1H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.13-7.10 (m, 1H), 7.05-7.00 (m, 4H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.62 (d, *J* = 7.6 Hz, 1H), 6.05 (dd, *J* = 10.0, 2.4 Hz, 1H), 5.56-5.53 (m, 1H), 4.85 (s, 1H), 3.34 (s, 3H), 2.23 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 178.7, 143.3, 136.8, 136.4, 133.6, 130.1, 129.3, 128.5, 127.7, 127.2, 127.0, 124.8, 123.5, 123.1, 118.0, 108.4, 54.4, 34.3, 26.8, 11.3. IR (film): ν_{max} (cm⁻¹) = 2921, 1712, 1607, 1488, 1468, 1368, 1342, 1299, 1253, 1126, 1080, 953, 909, 826, 728, 691, 541, 478, 447. HRMS (ESI): Exact mass calcd. for C₂₃H₂₂N₃O ([M+H]⁺): 356.17574. Found: 356.17563.

X-Ray crystal data

X-Ray crystal data of **3a** (CCDC 1982544)

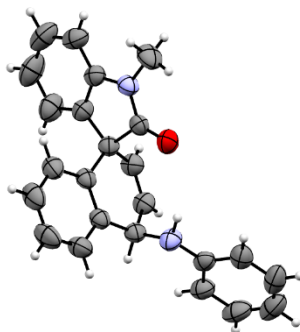


Crystal data and structure refinement for d8v19785.

Identification code	d8v19785	
Empirical formula	C ₂₃ H ₂₁ N O ₅	
Formula weight	391.41	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2 ₁ /c	
Unit cell dimensions	a = 16.6707(14) Å	$\alpha = 90^\circ$.
	b = 9.3051(9) Å	$\beta = 107.808(3)^\circ$.
	c = 13.8903(13) Å	$\gamma = 90^\circ$.
Volume	2051.5(3) Å ³	
Z	4	
Density (calculated)	1.267 Mg/m ³	
Absorption coefficient	0.090 mm ⁻¹	
F(000)	824	
Crystal size	0.190 x 0.150 x 0.100 mm ³	
Theta range for data collection	2.676 to 26.000°.	
Index ranges	-20 ≤ h ≤ 19, -11 ≤ k ≤ 11, -17 ≤ l ≤ 16	
Reflections collected	17265	
Independent reflections	4015 [R(int) = 0.0509]	
Completeness to theta = 25.242°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5563	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4015 / 0 / 266	

Goodness-of-fit on F^2	1.051
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0502$, $wR2 = 0.1150$
R indices (all data)	$R1 = 0.0854$, $wR2 = 0.1388$
Extinction coefficient	0.025(3)
Largest diff. peak and hole	0.157 and -0.145 e.Å ⁻³

X-Ray crystal data of **6k** (CCDC 1982545)



Crystal data and structure refinement for mo_d8v191162_0m.

Identification code	mo_d8v191162_0m	
Empirical formula	C ₂₄ H ₂₀ N ₂ O	
Formula weight	352.42	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	$a = 12.8388(4)$ Å	$\alpha = 90^\circ$.
	$b = 11.4187(4)$ Å	$\beta = 113.4690(10)^\circ$.
	$c = 13.7487(4)$ Å	$\gamma = 90^\circ$.
Volume	1848.85(10) Å ³	
Z	4	
Density (calculated)	1.266 Mg/m ³	
Absorption coefficient	0.078 mm ⁻¹	
F(000)	744	
Crystal size	0.200 x 0.160 x 0.130 mm ³	
Theta range for data collection	2.406 to 25.990°.	
Index ranges	$-15 \leq h \leq 14$, $-14 \leq k \leq 14$, $-16 \leq l \leq 16$	
Reflections collected	26778	
Independent reflections	3596 [$R(\text{int}) = 0.0307$]	

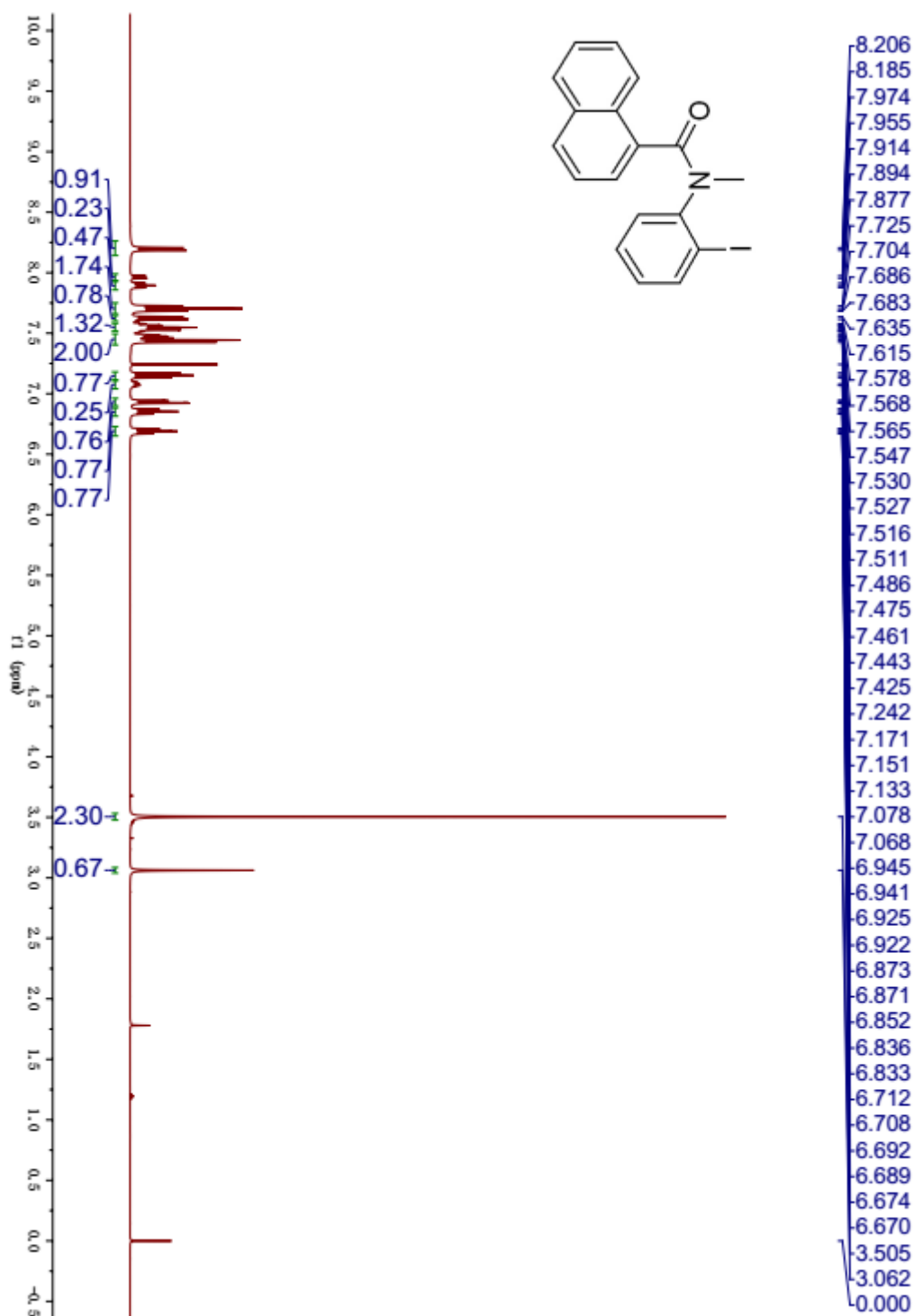
Completeness to theta = 25.242°	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6708
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3596 / 0 / 250
Goodness-of-fit on F ²	1.015
Final R indices [I>2sigma(I)]	R1 = 0.0415, wR2 = 0.1110
R indices (all data)	R1 = 0.0531, wR2 = 0.1220
Extinction coefficient	0.044(6)
Largest diff. peak and hole	0.182 and -0.145 e.Å ⁻³

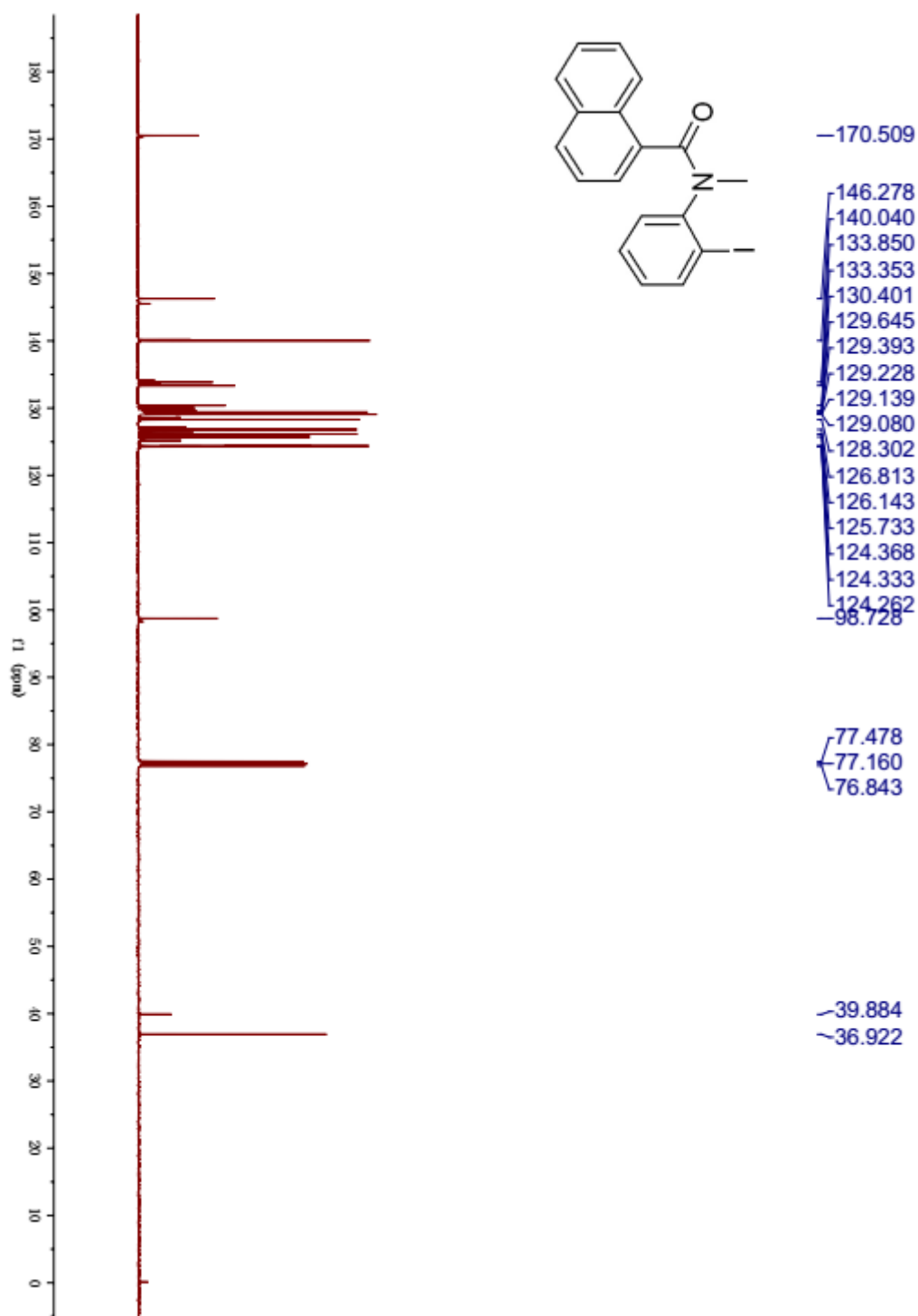
References

- [1] Tang, S.-B.; Zhang, X.; Tu, H.-F.; You, S.-L. *J. Am. Chem. Soc.* **2018**, *140*, 7737.

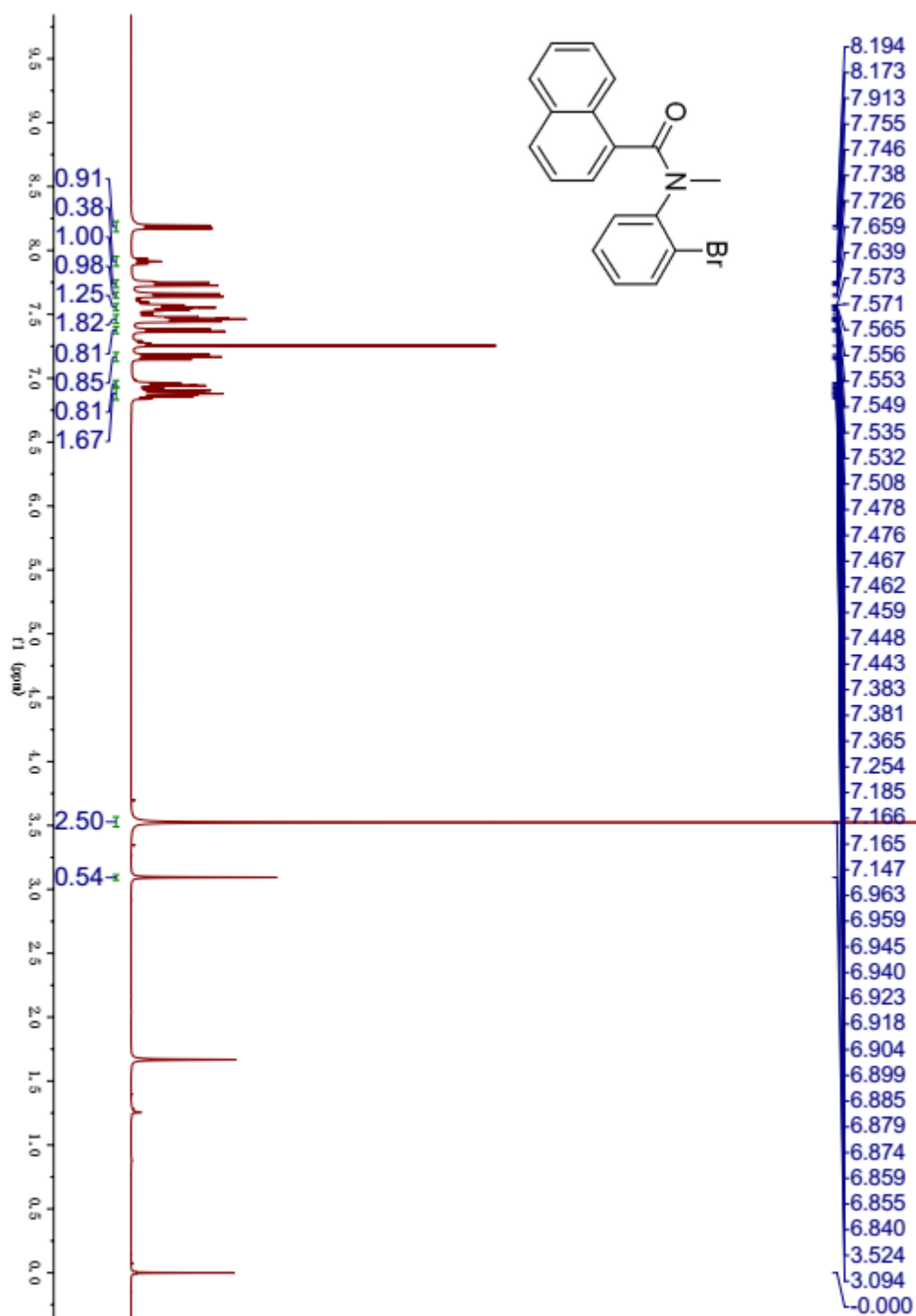
Copies of NMR spectra

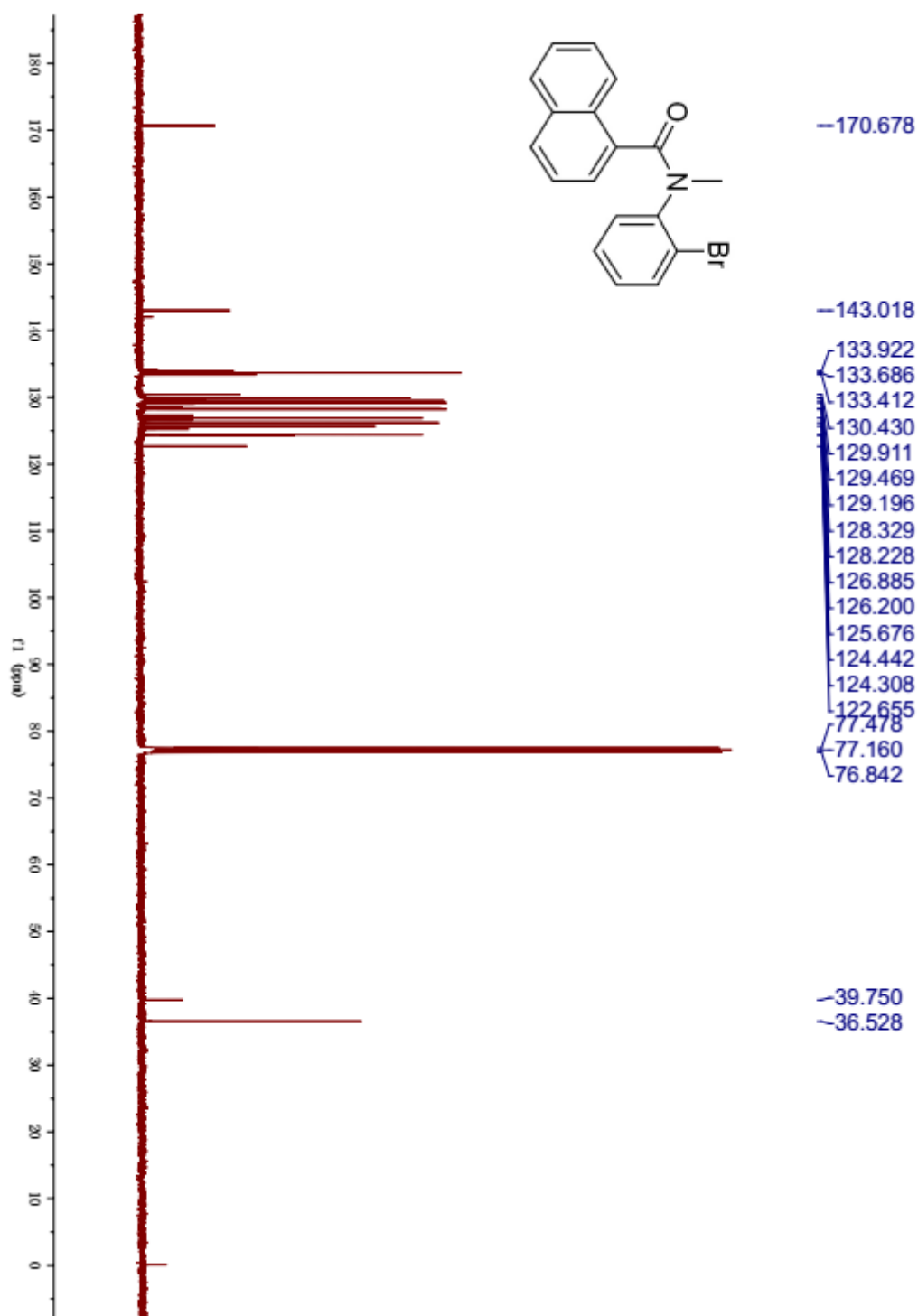
1a



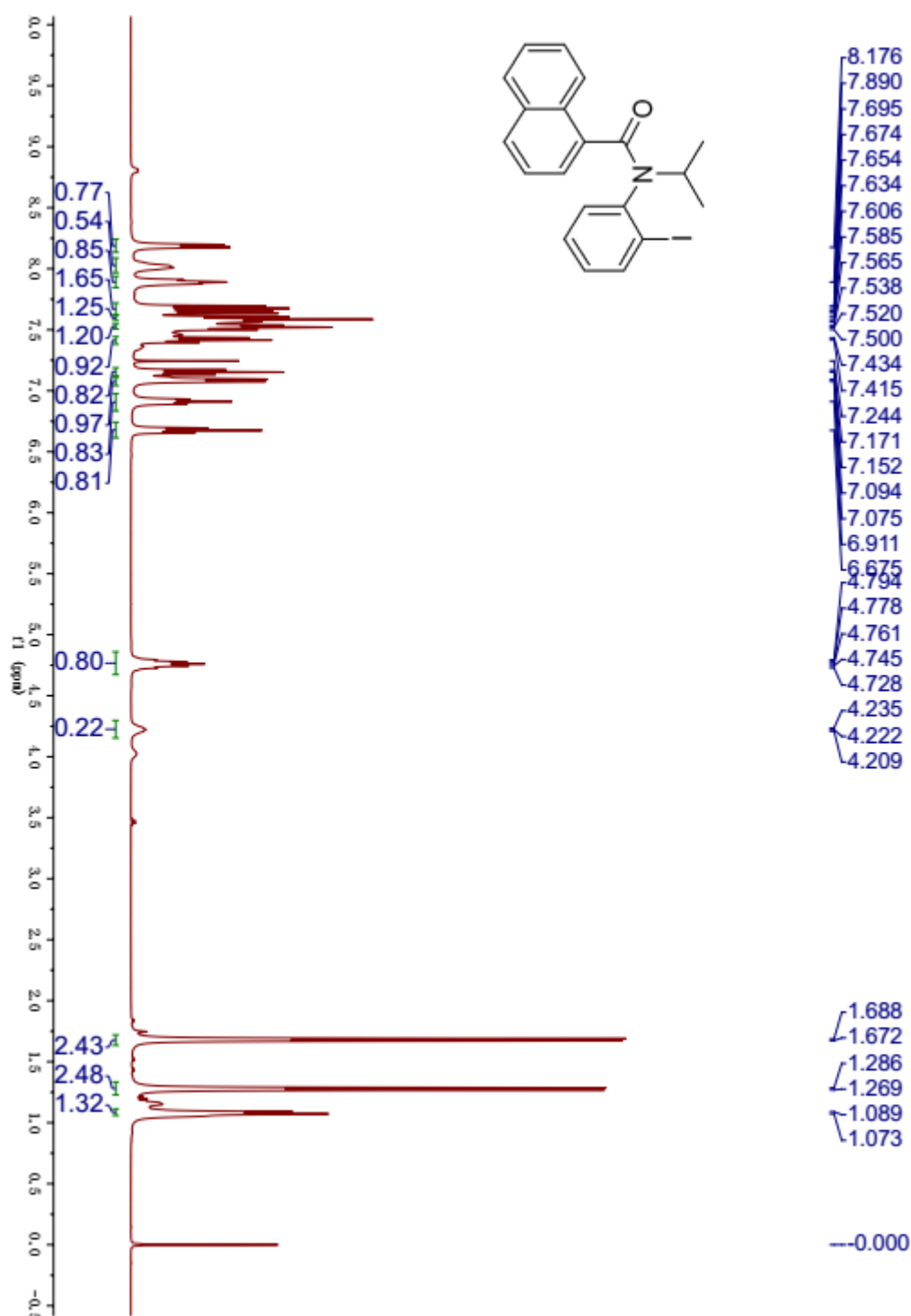


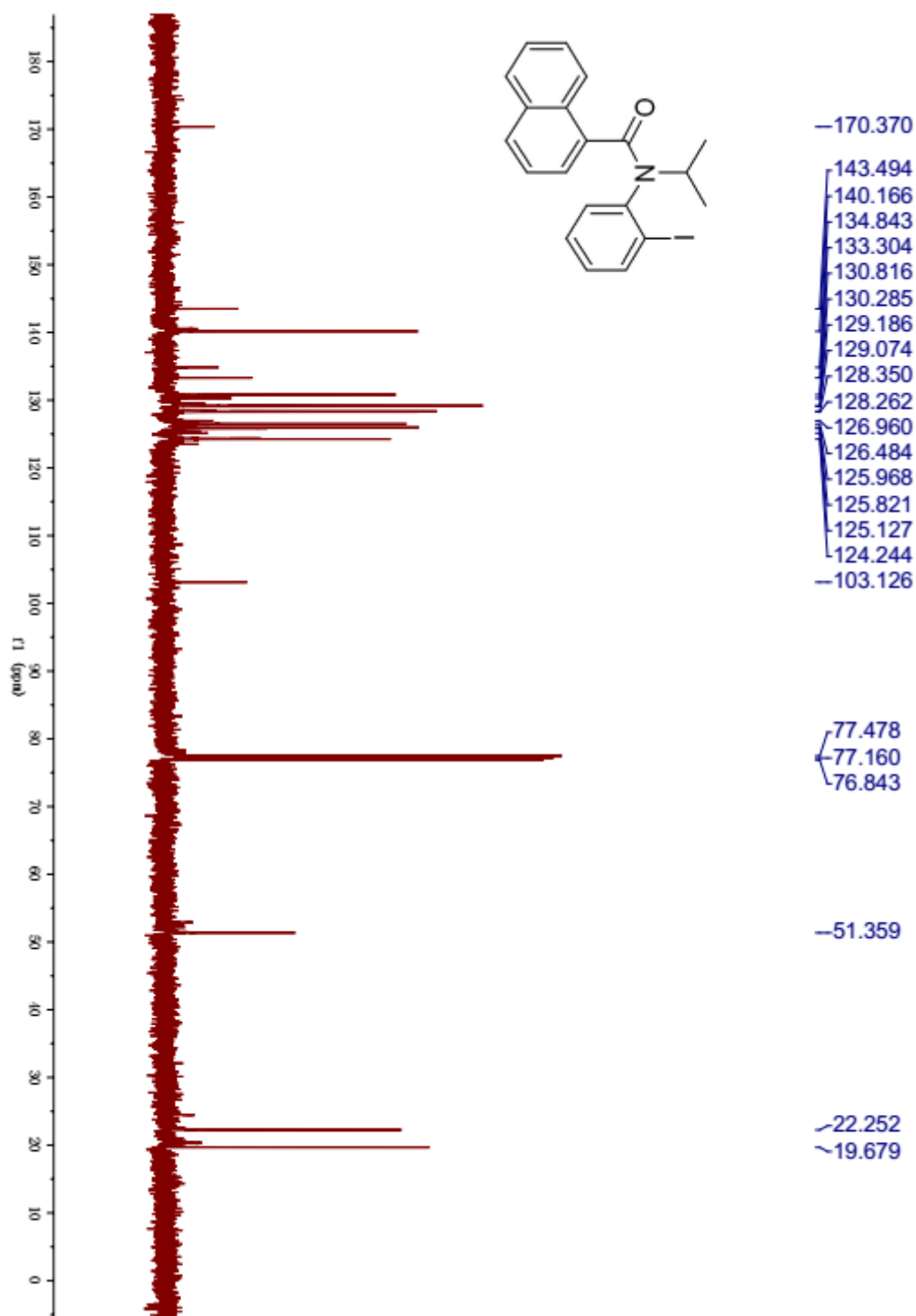
1a'



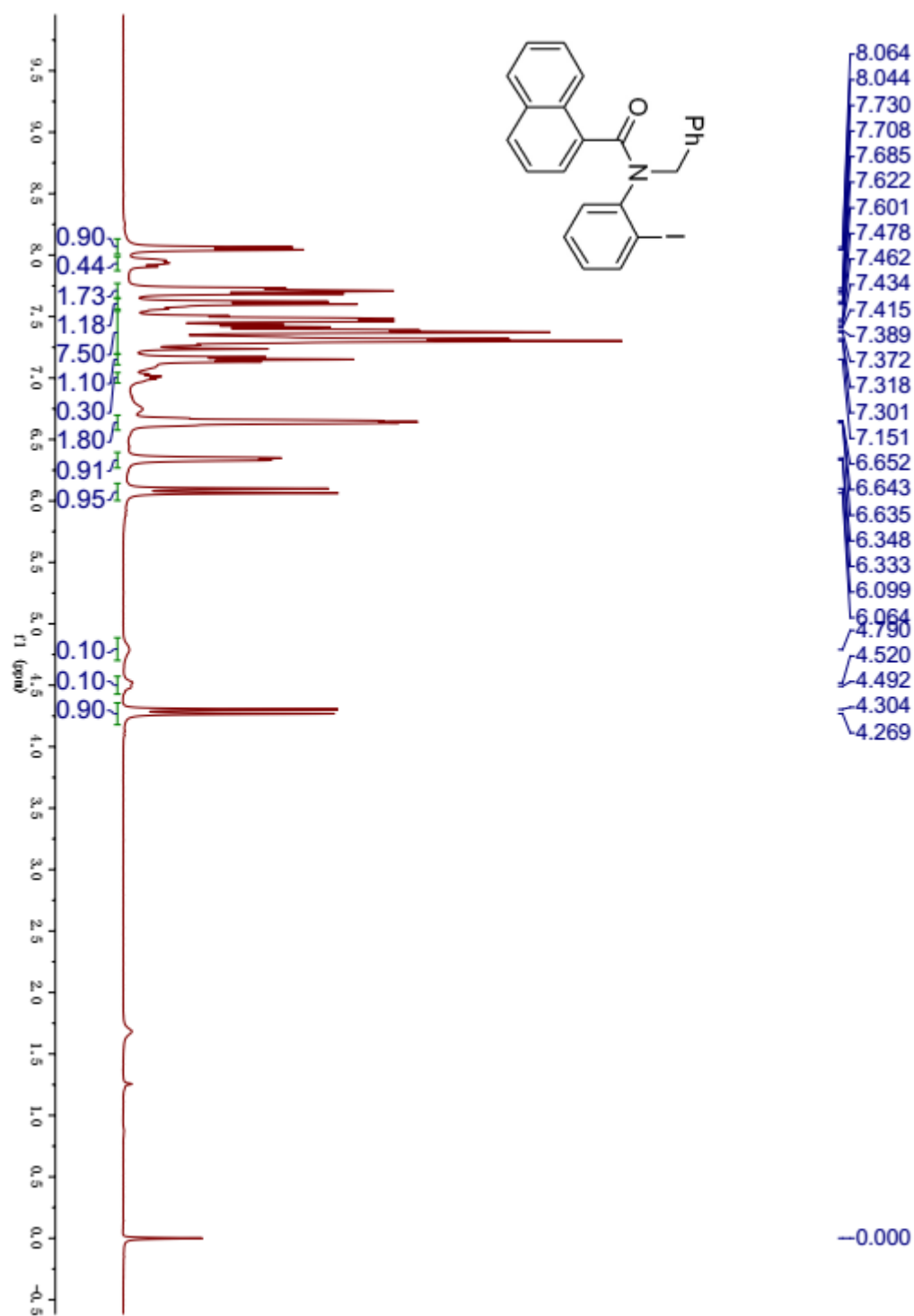


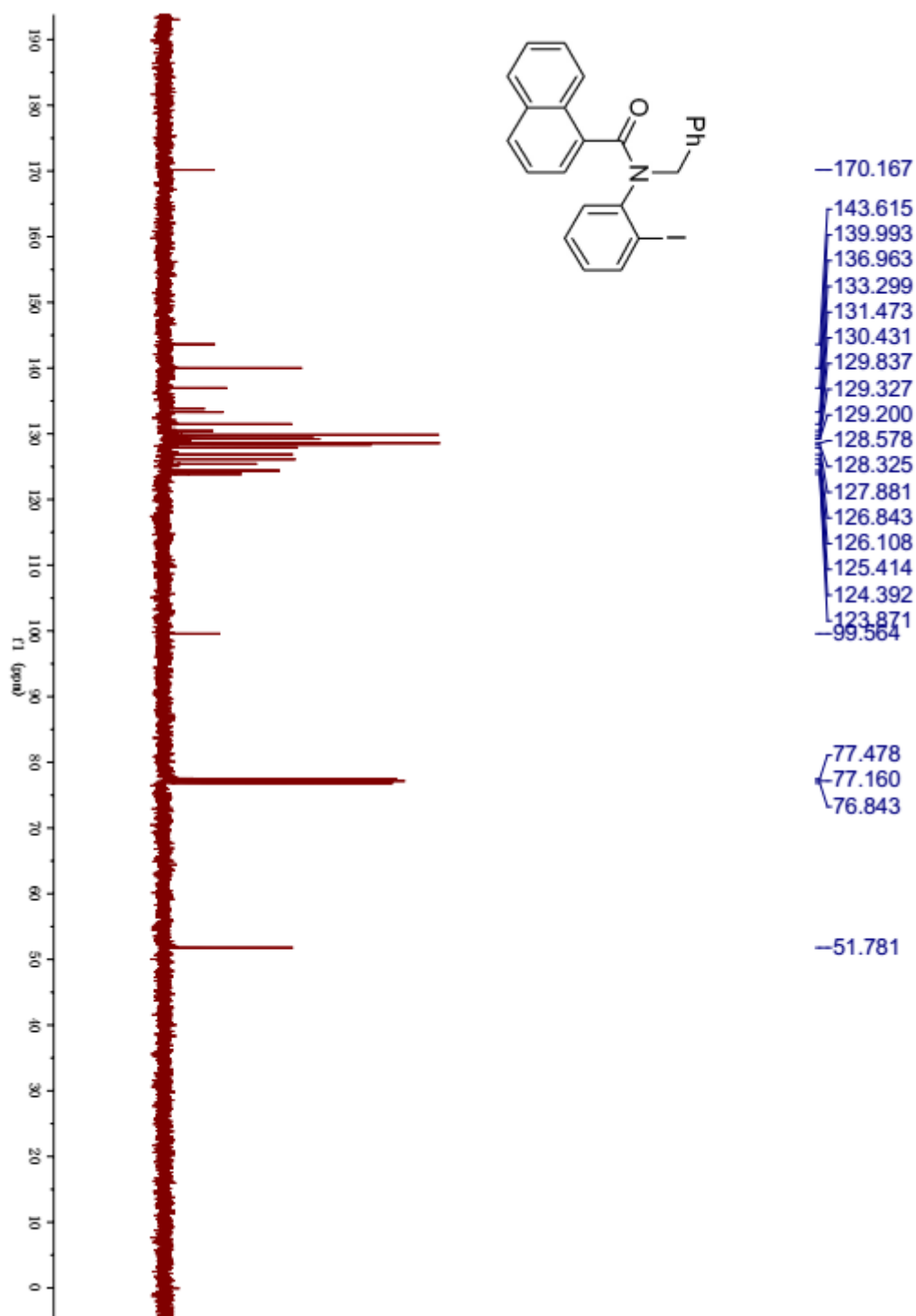
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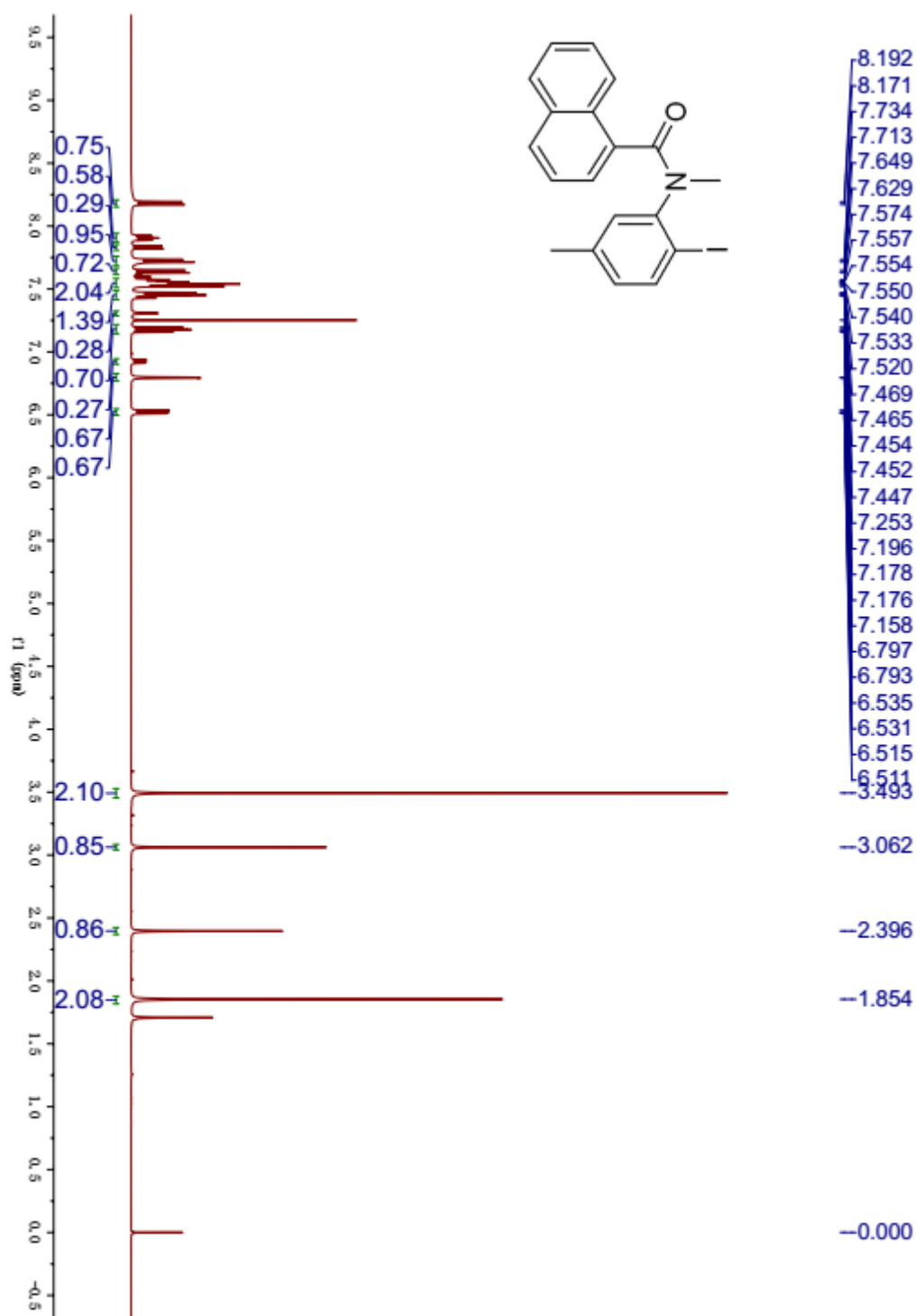


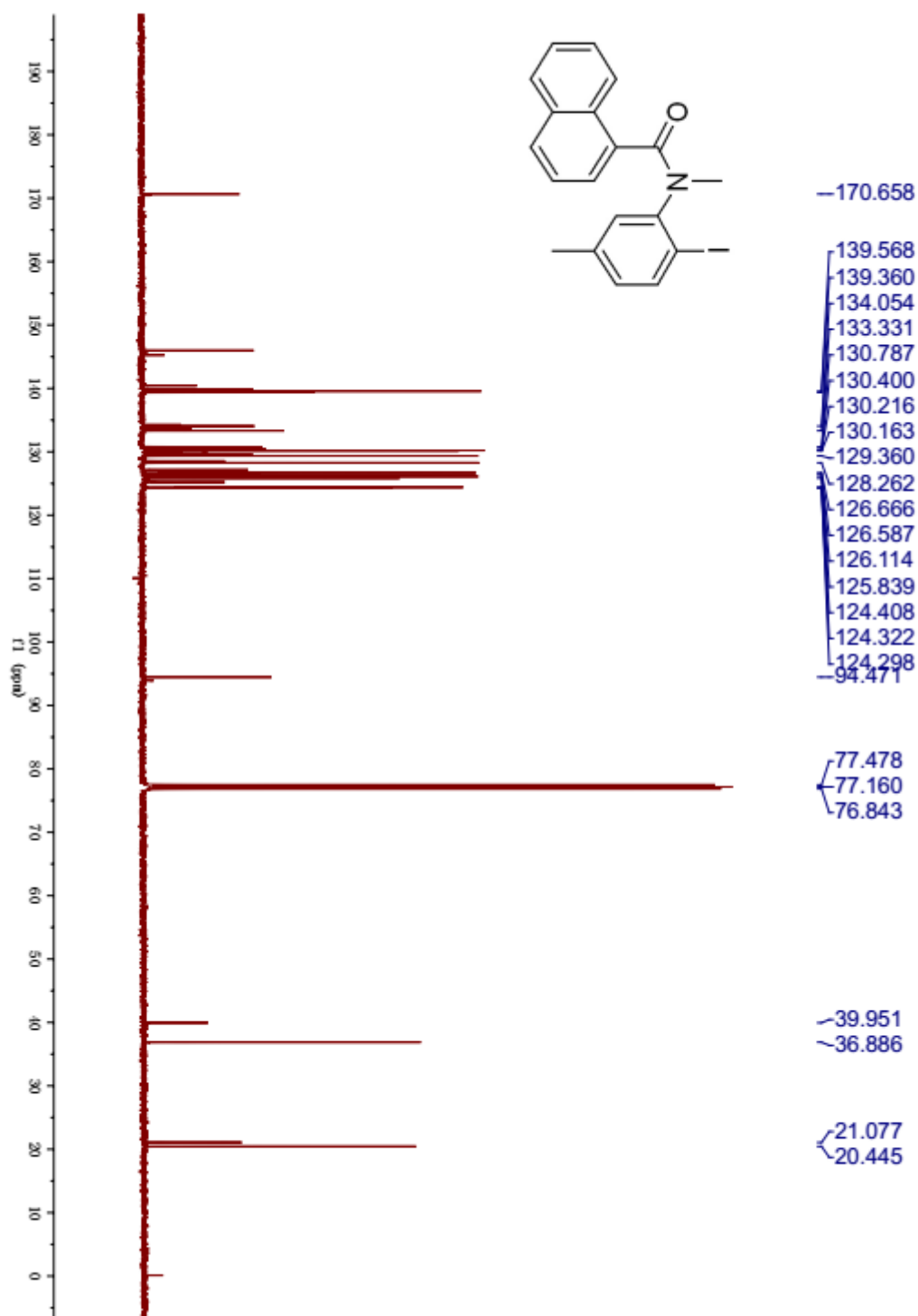
1c



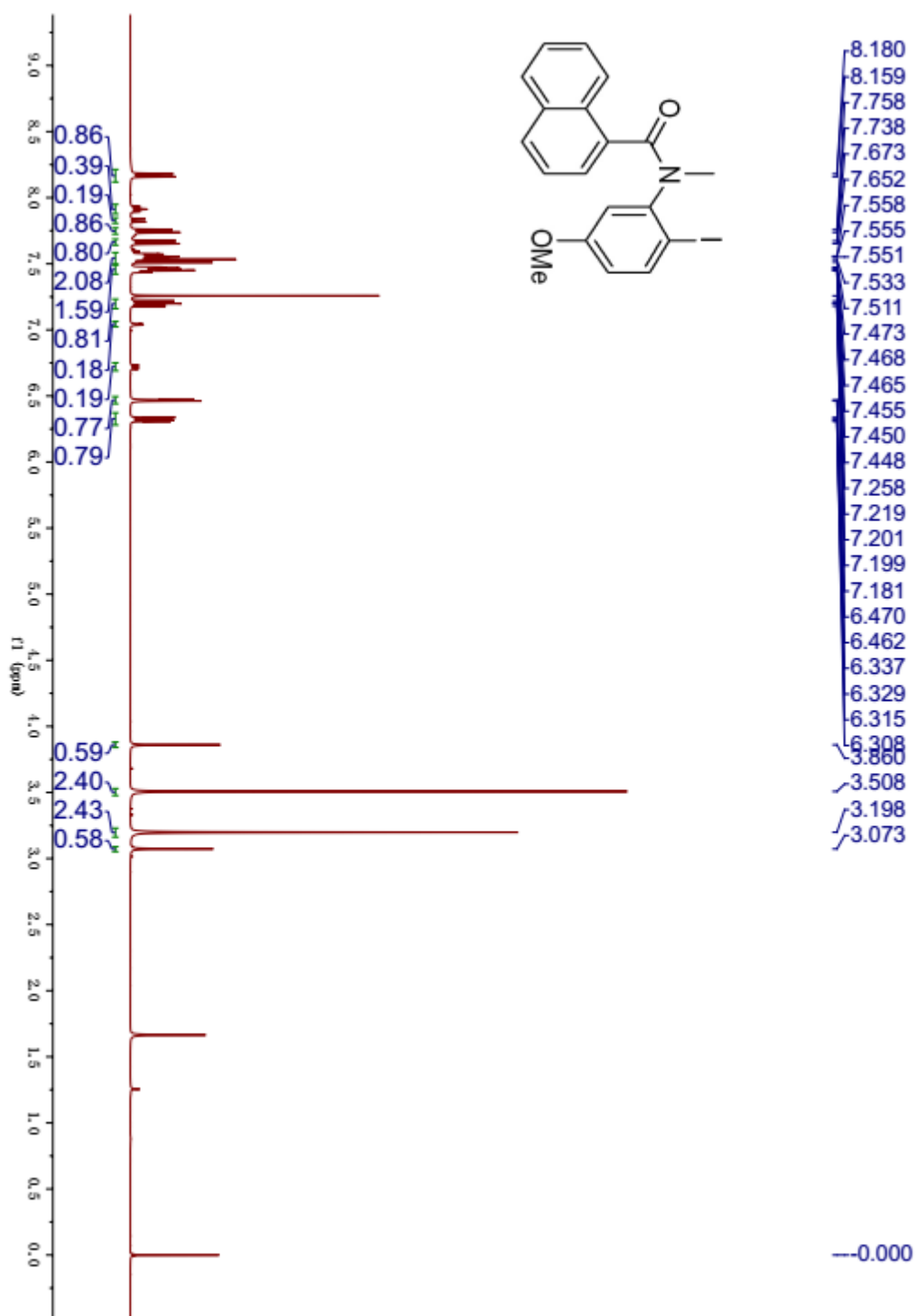


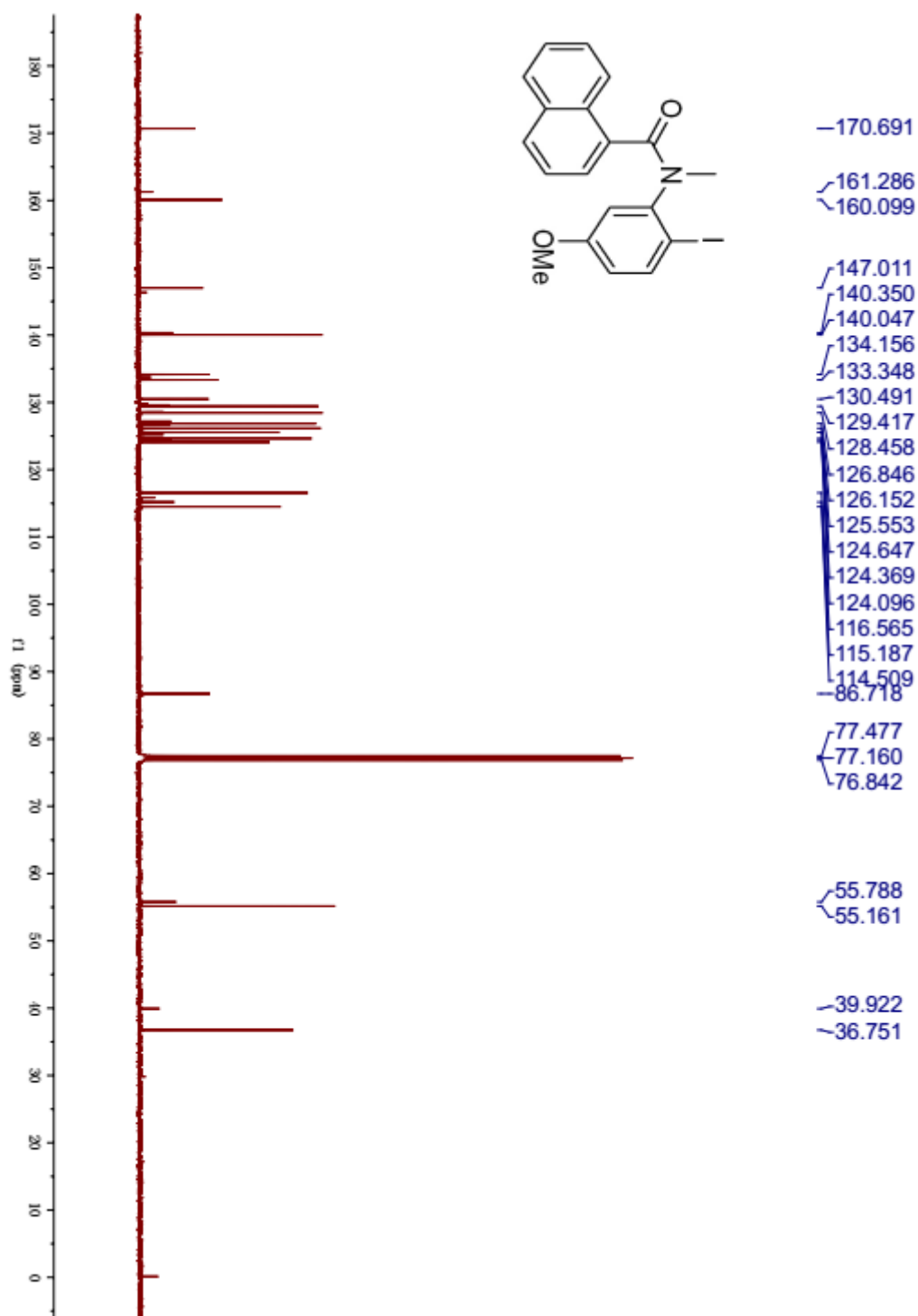
1d



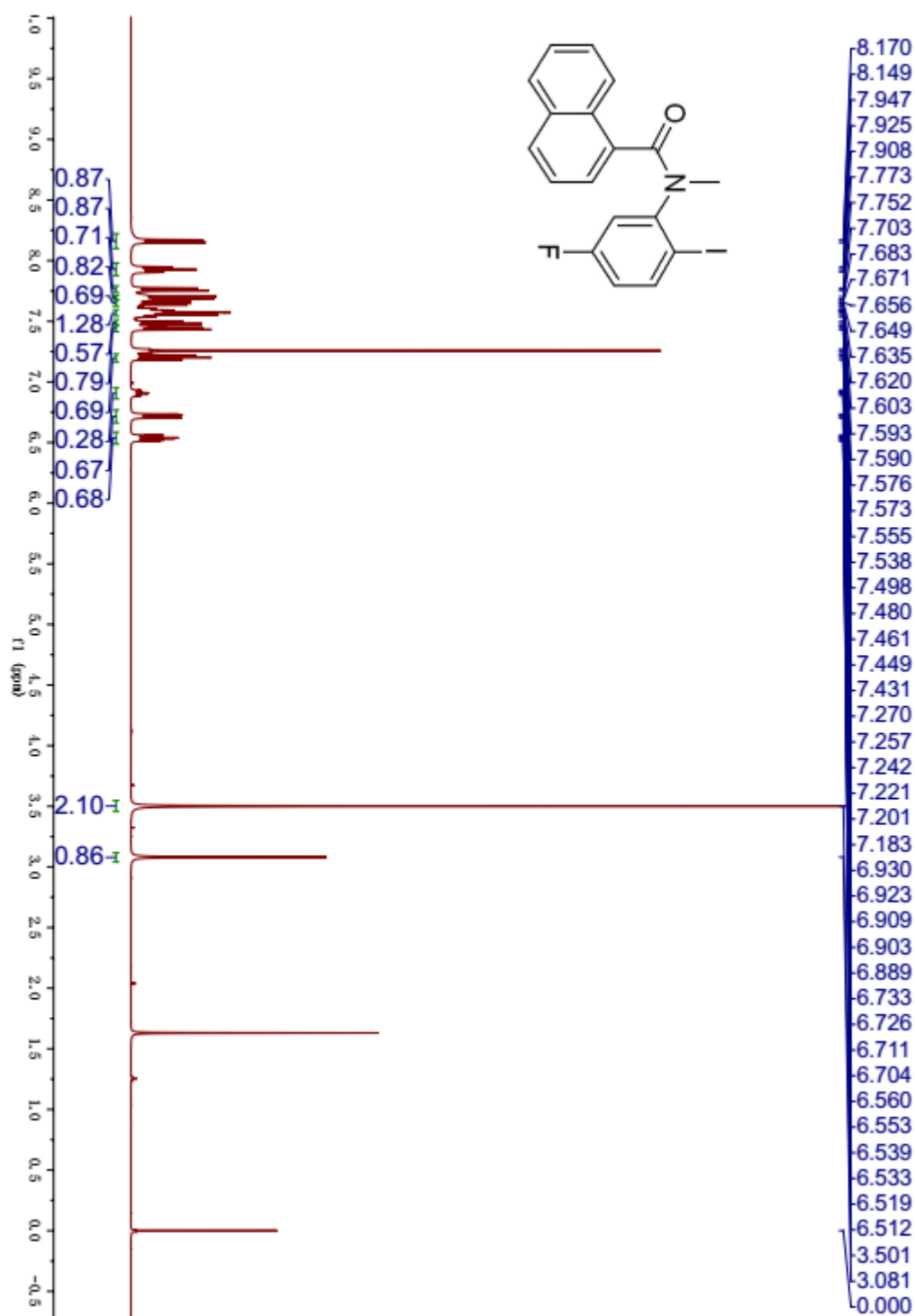


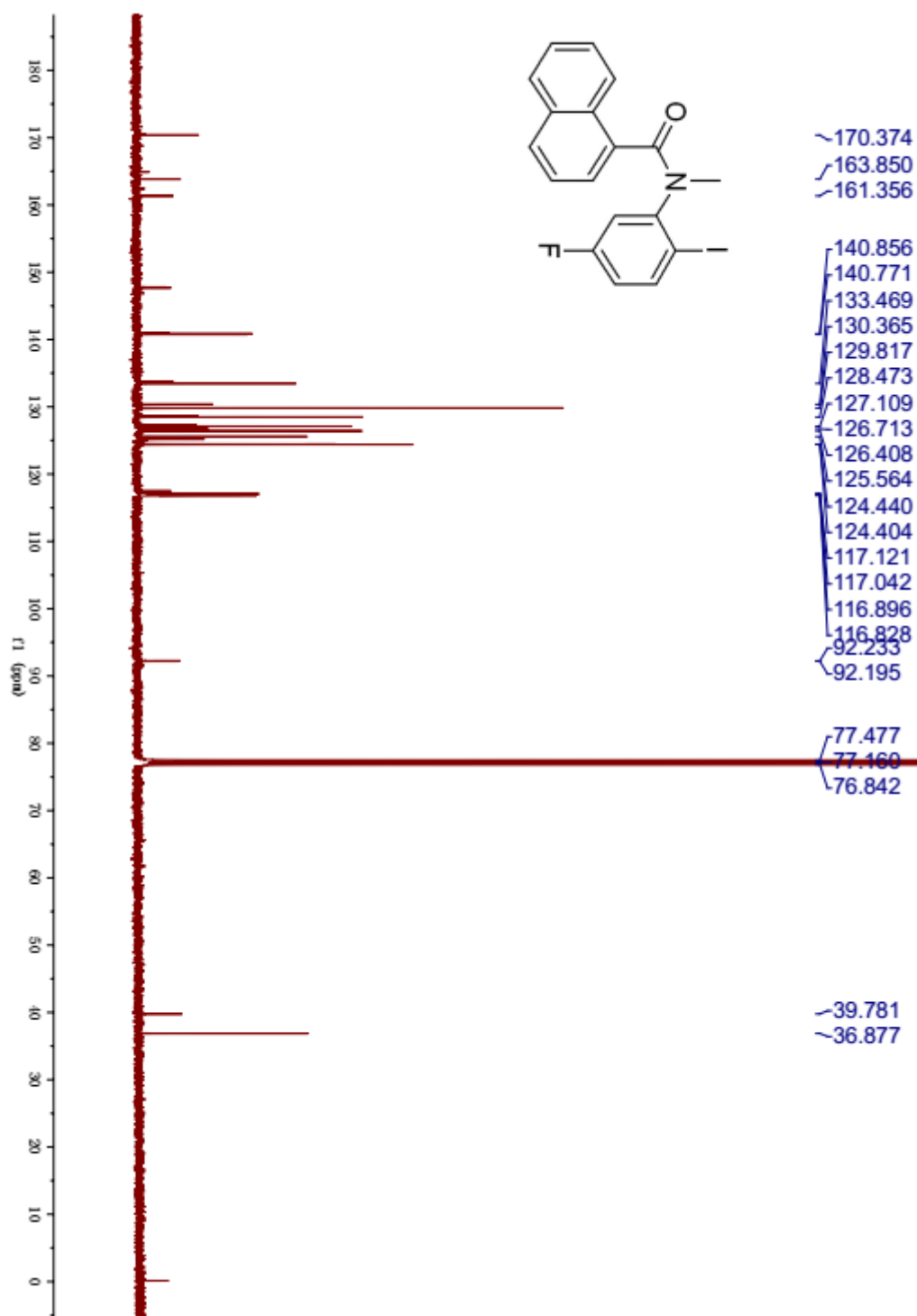
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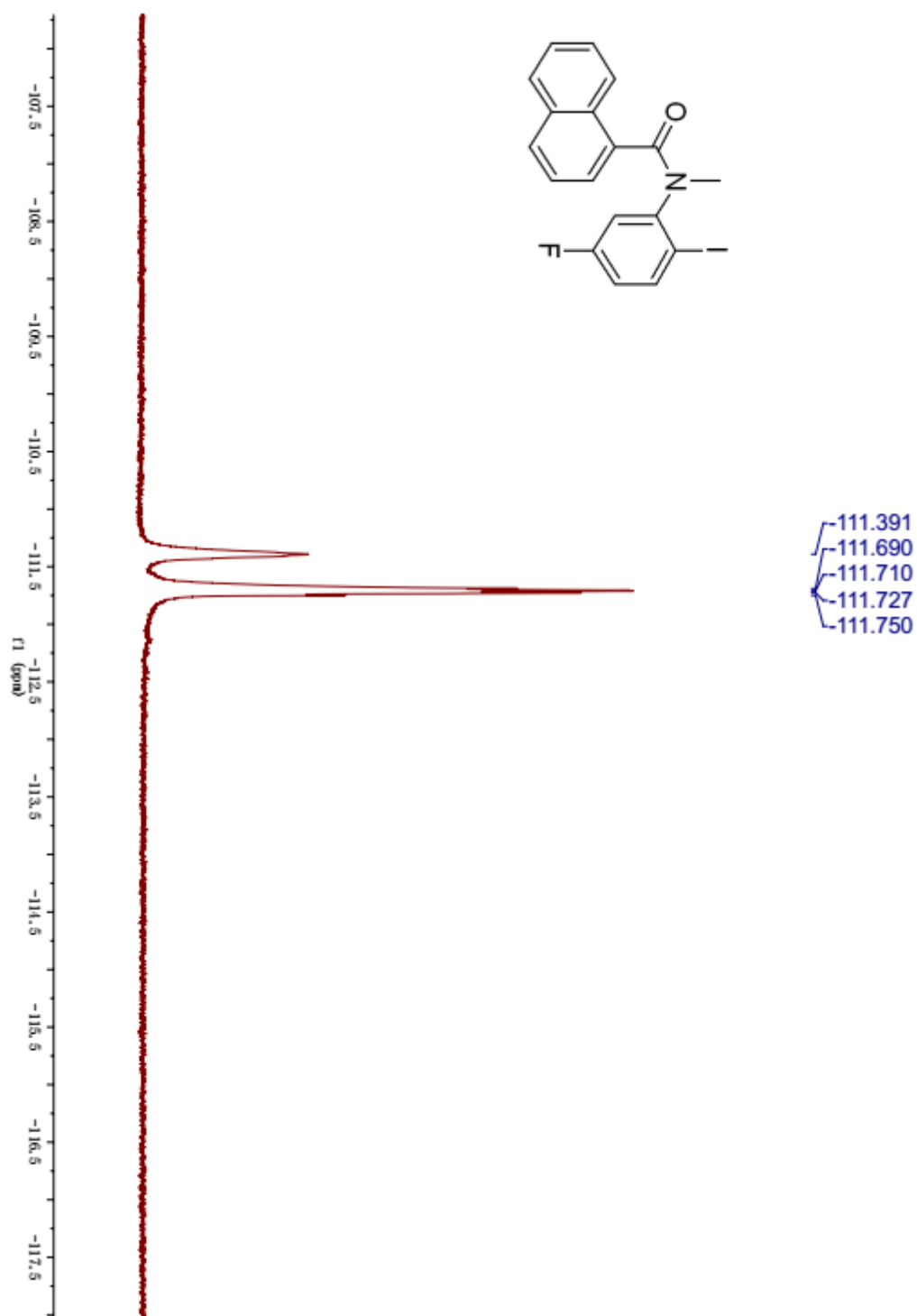




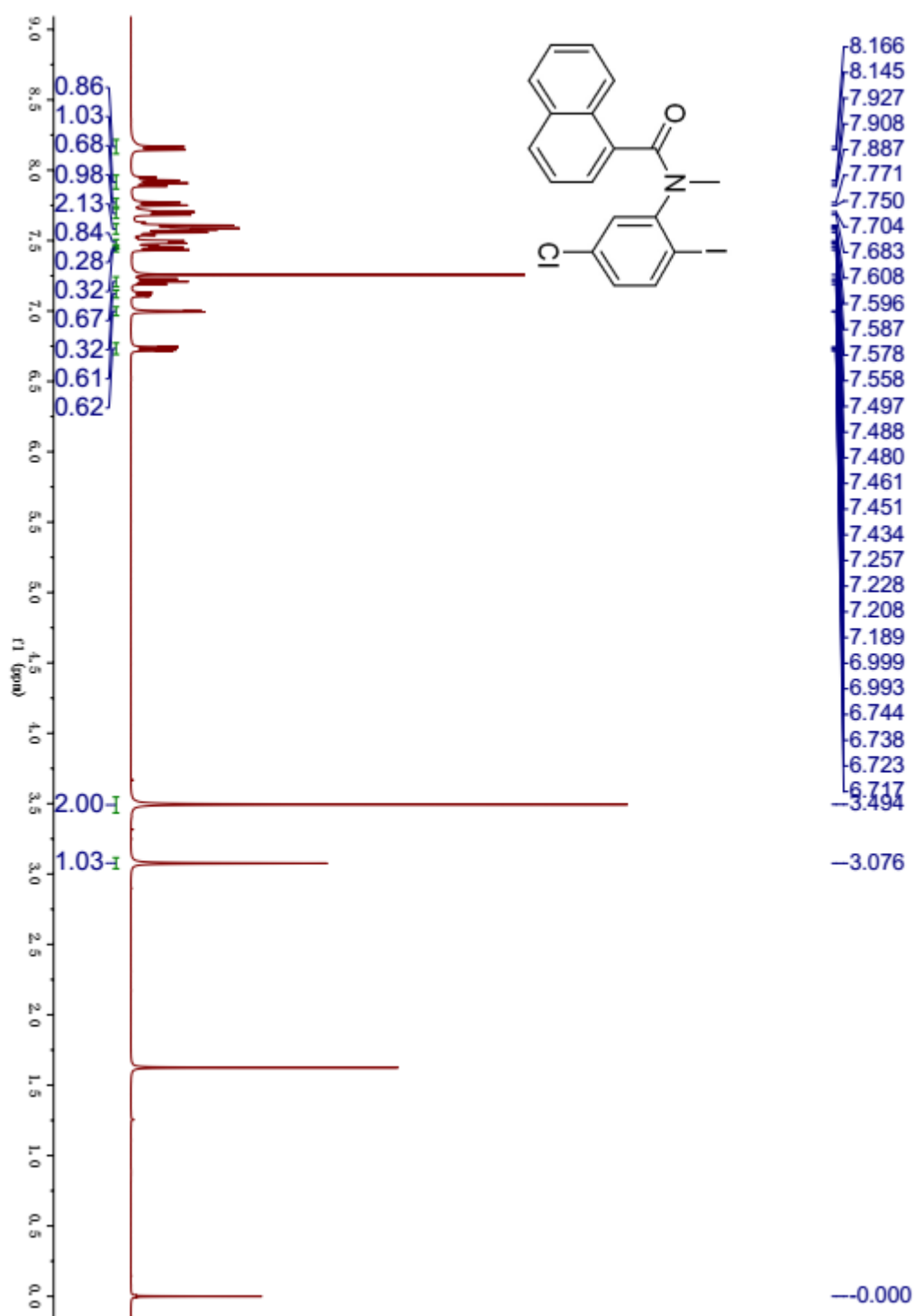
1f

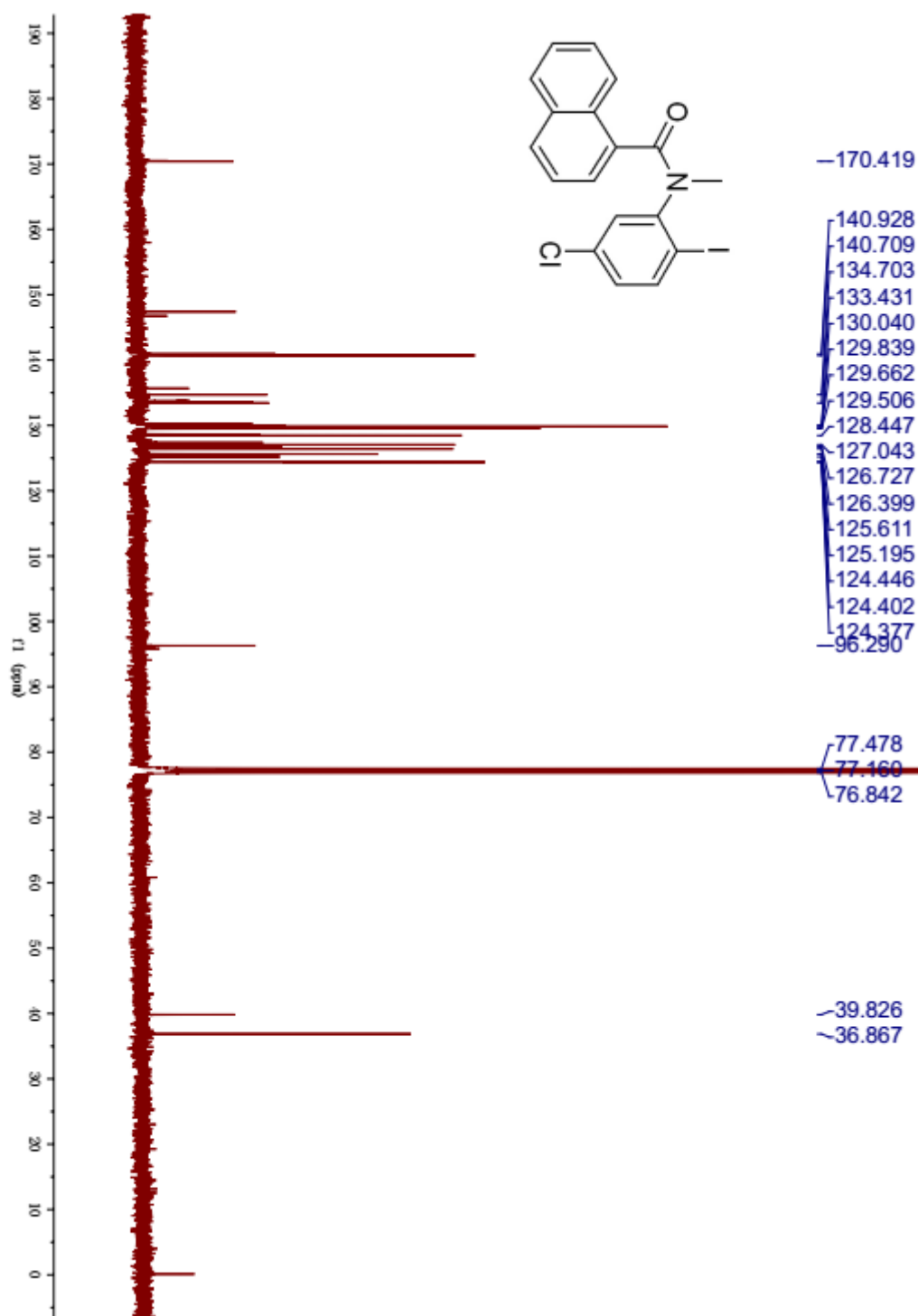




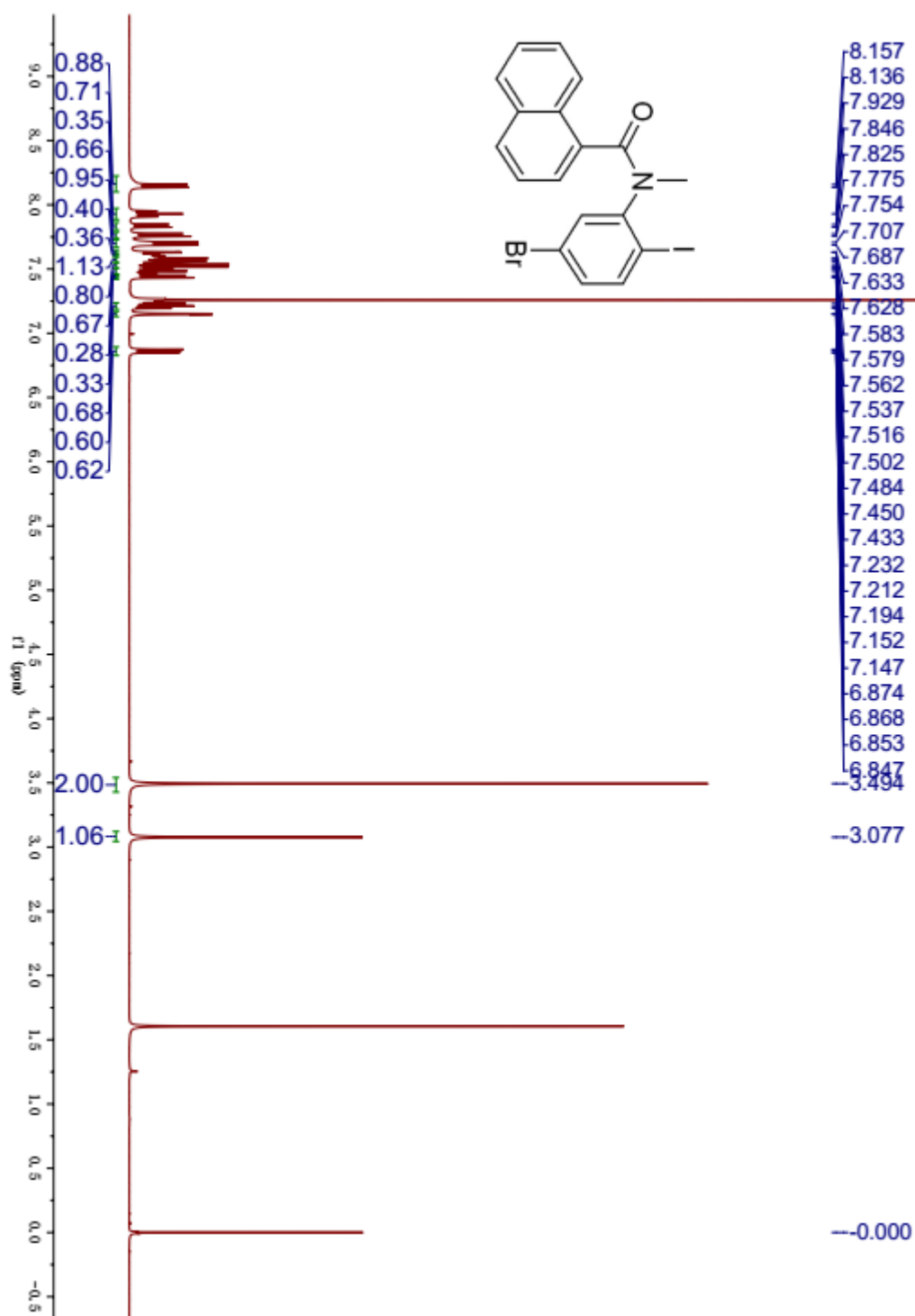


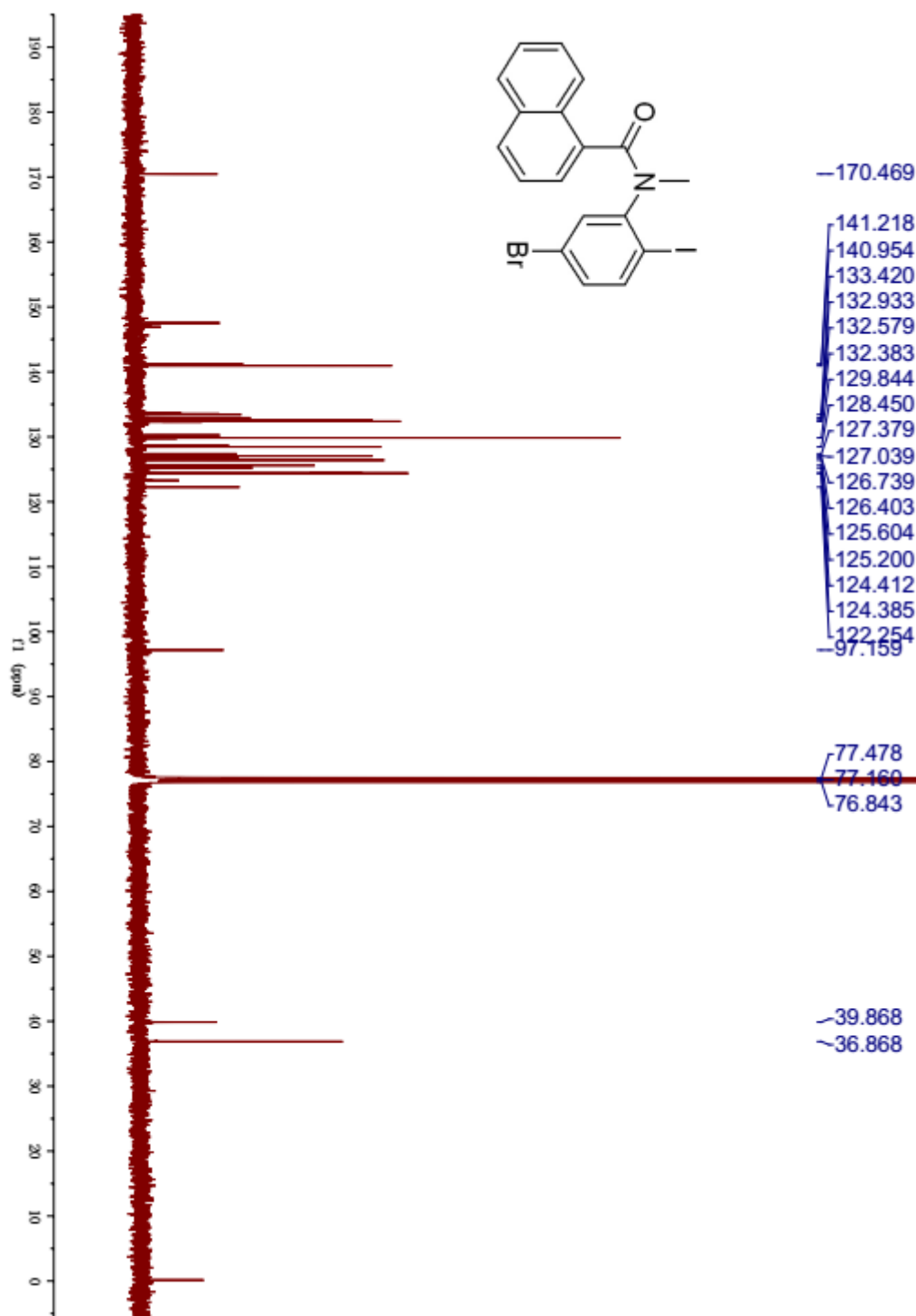
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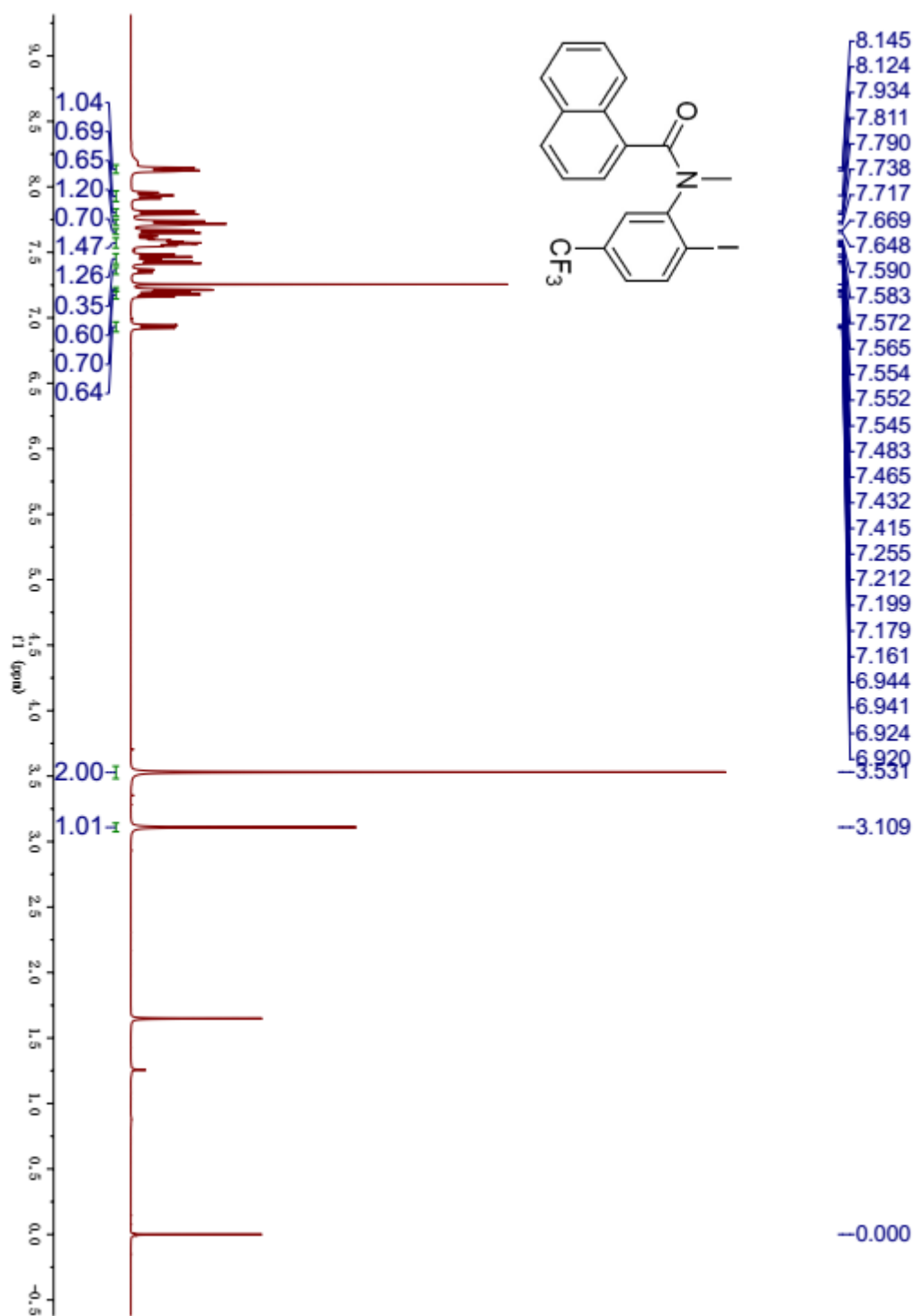


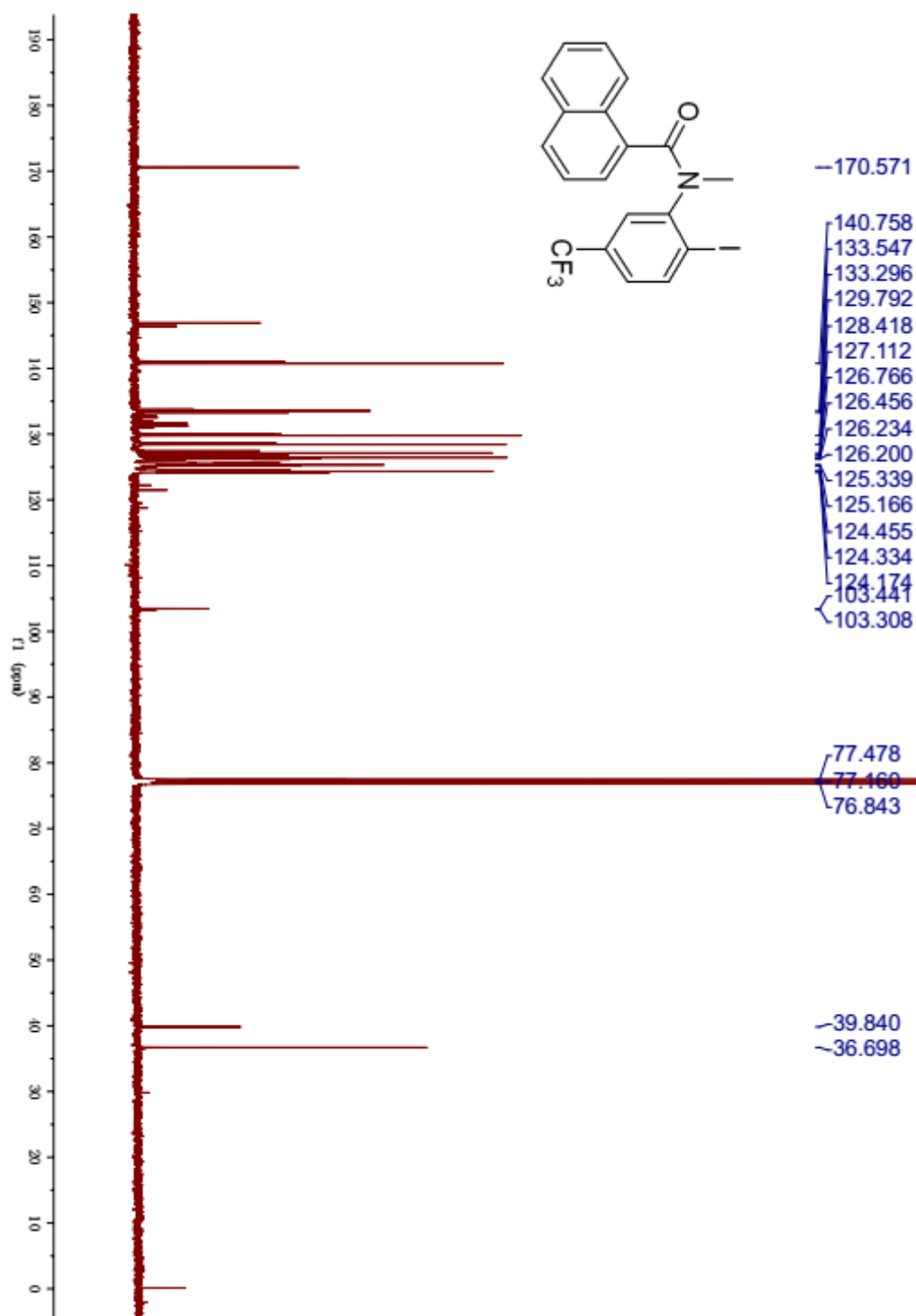
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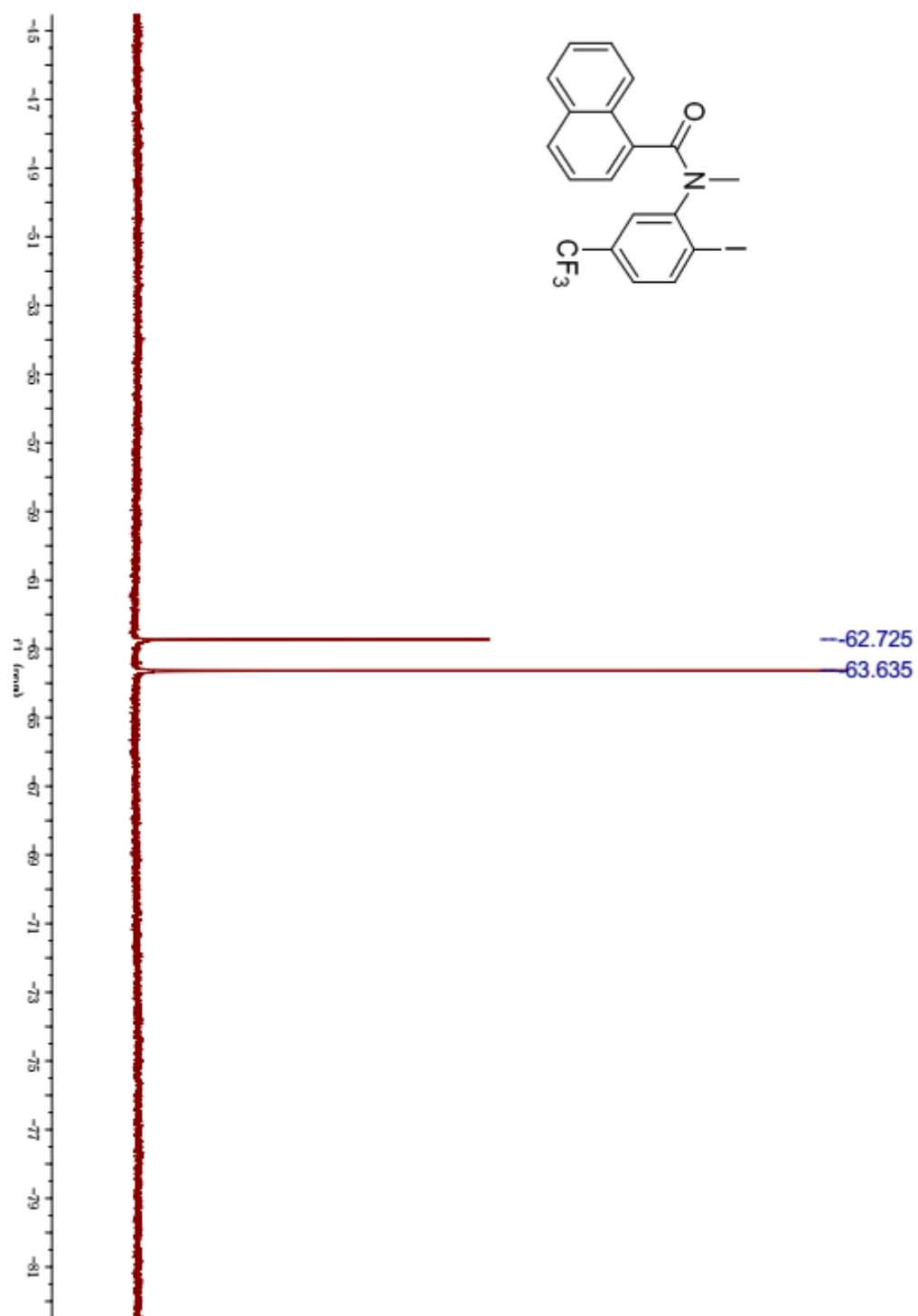




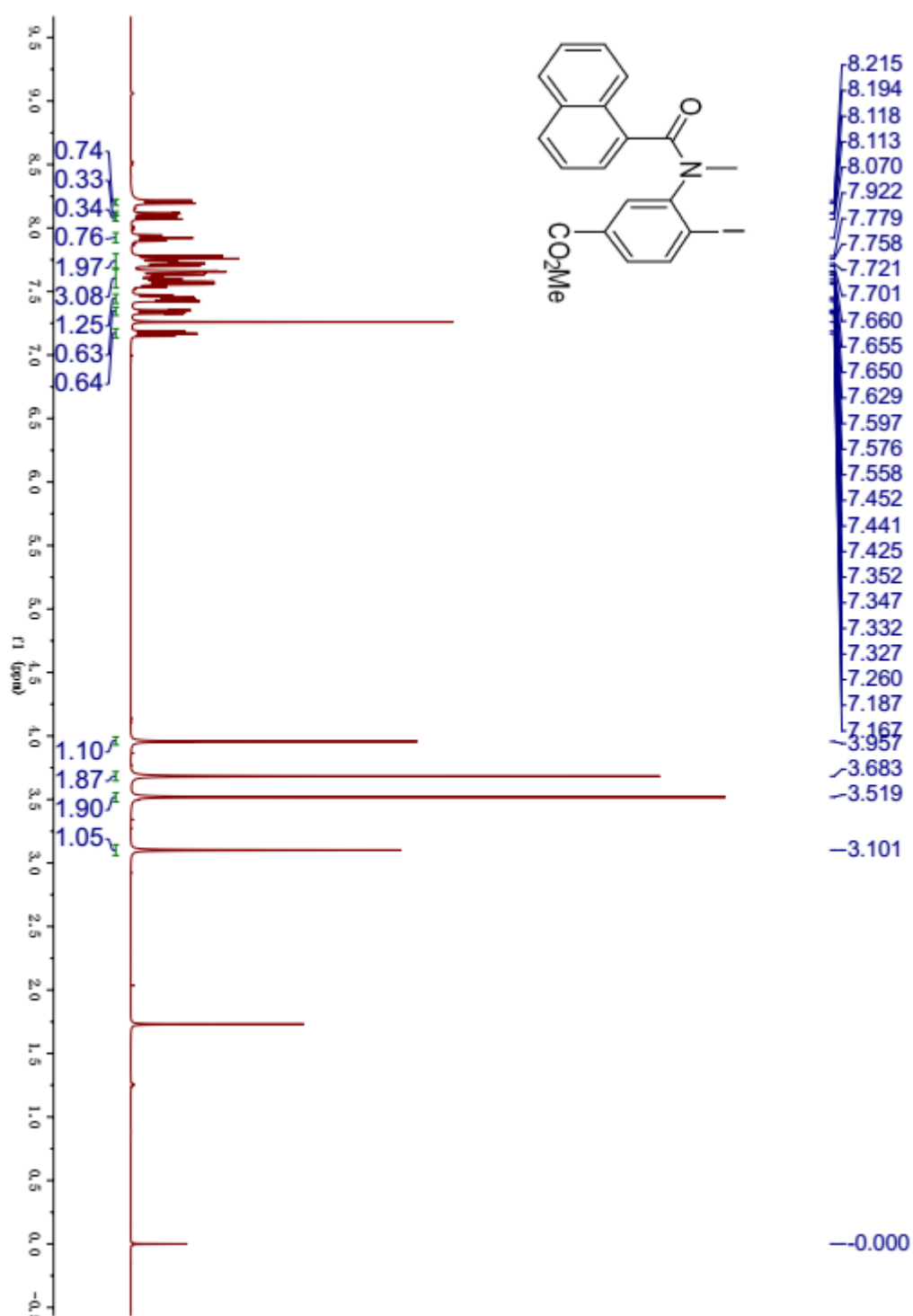
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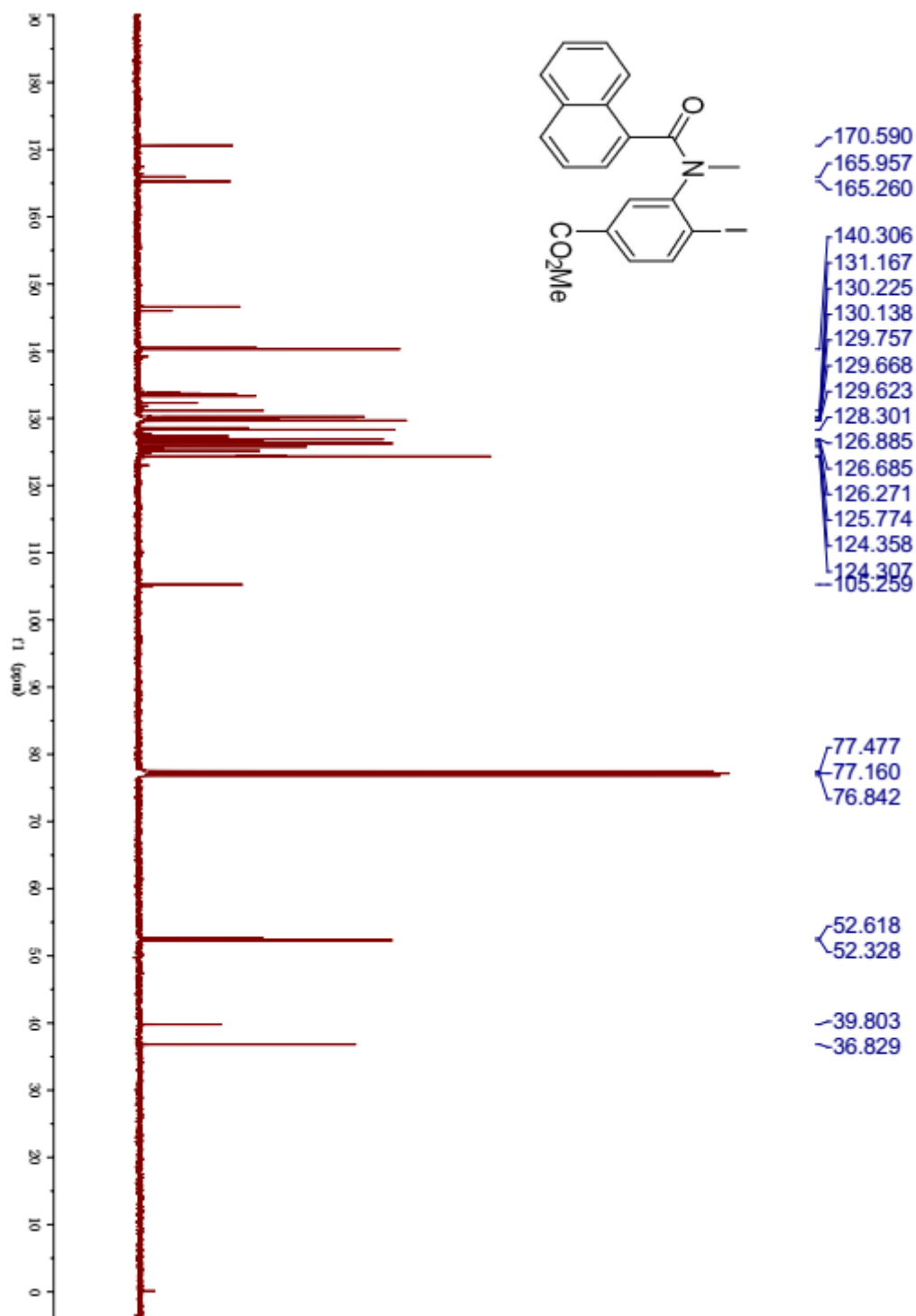




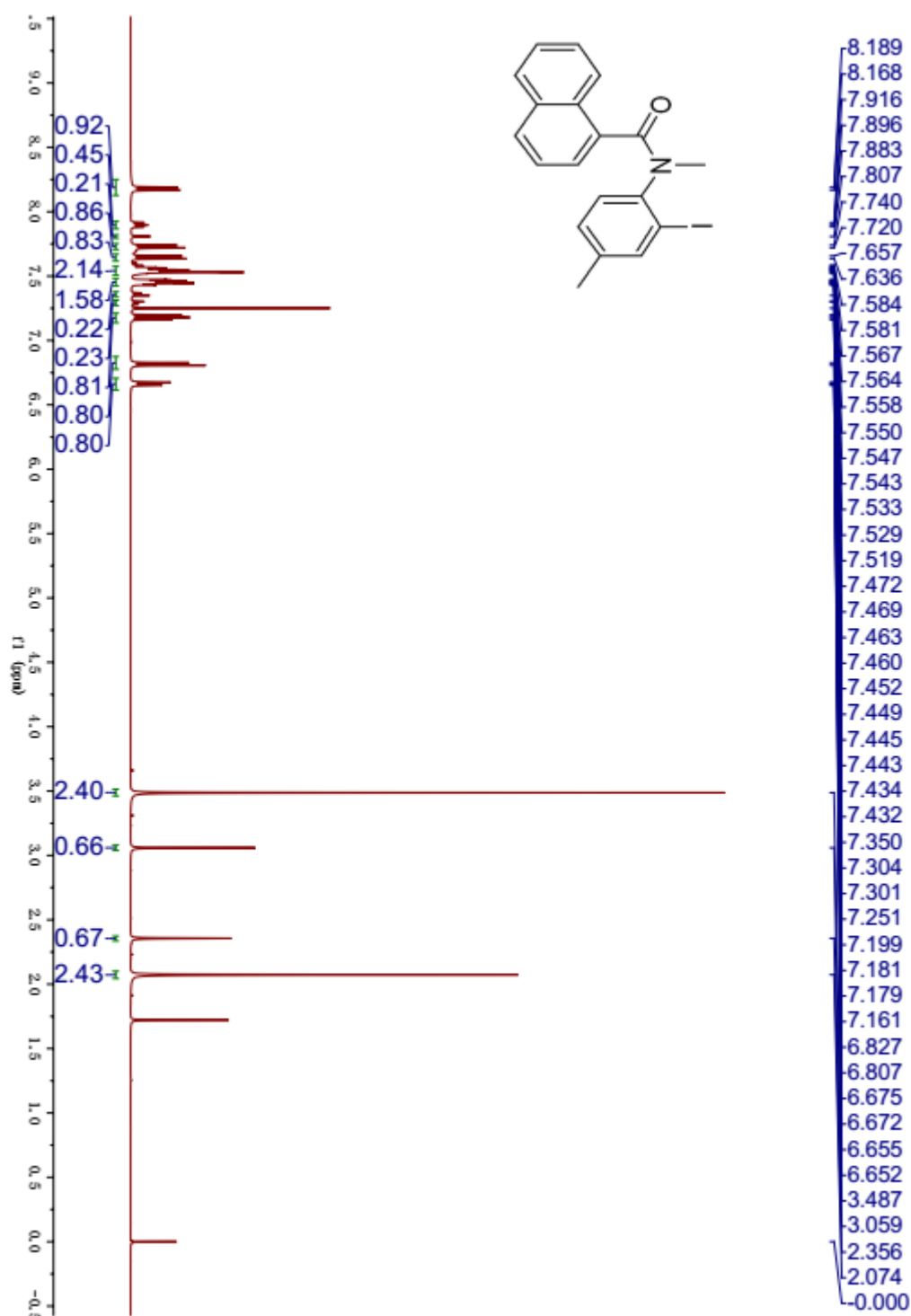


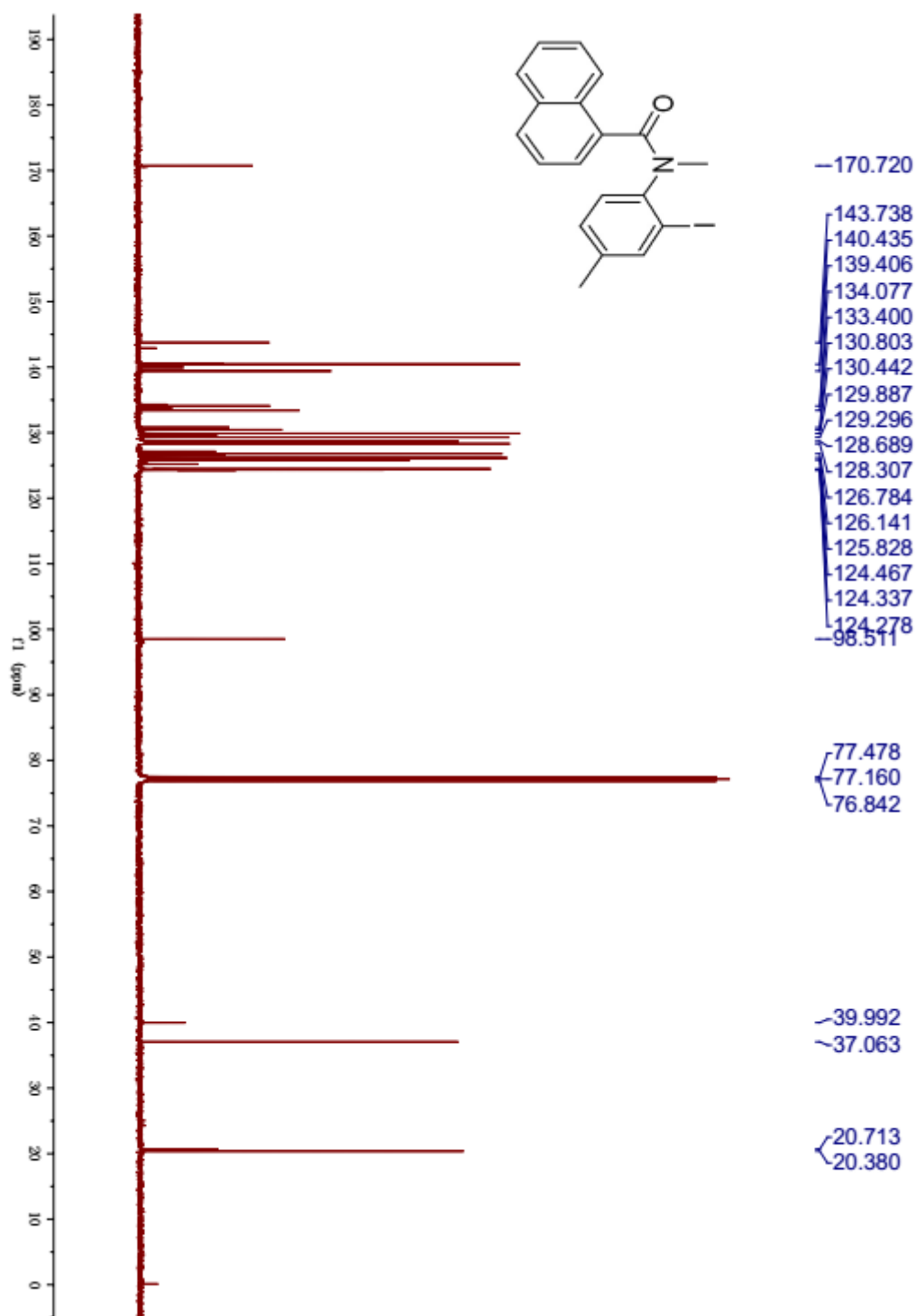
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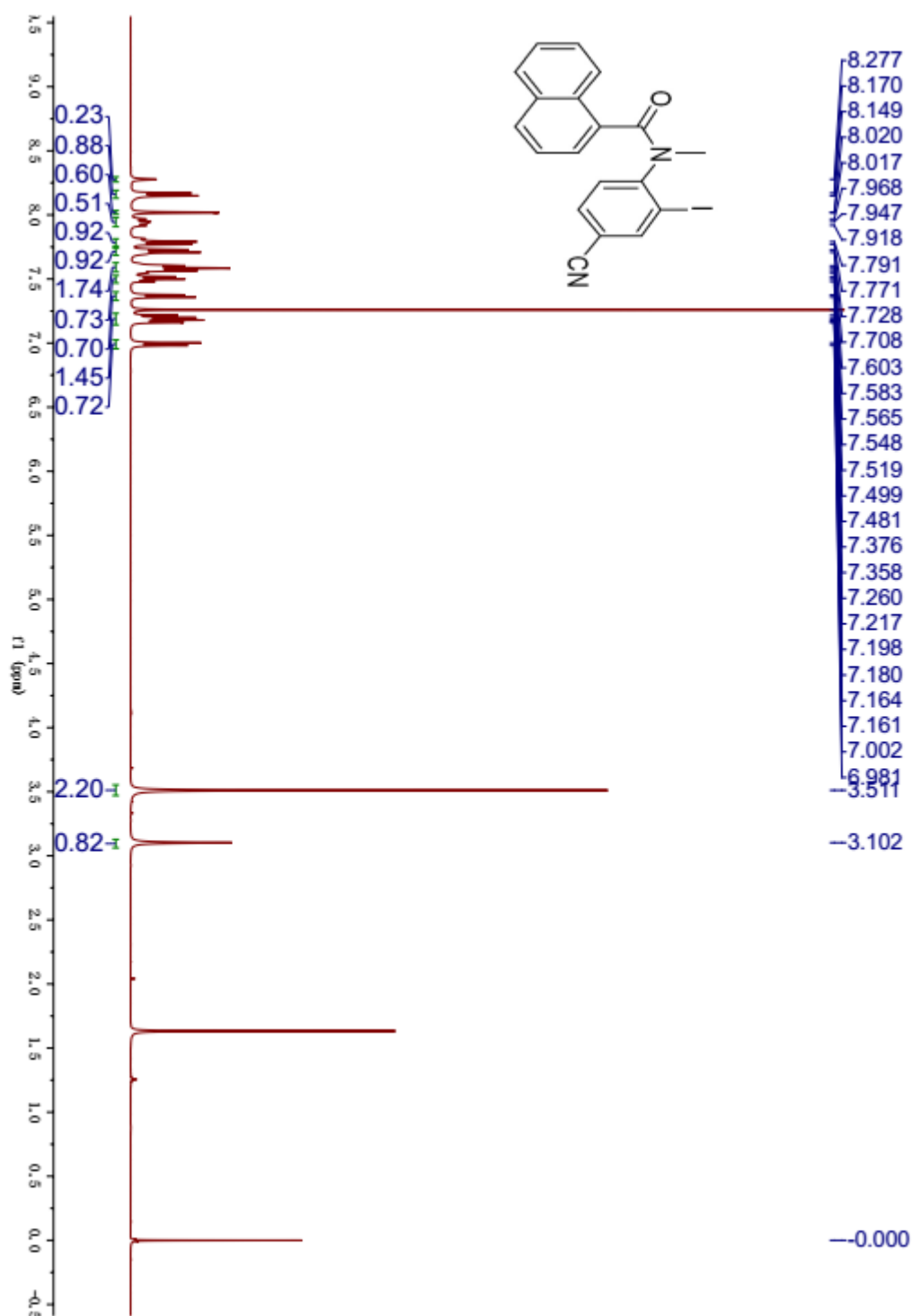


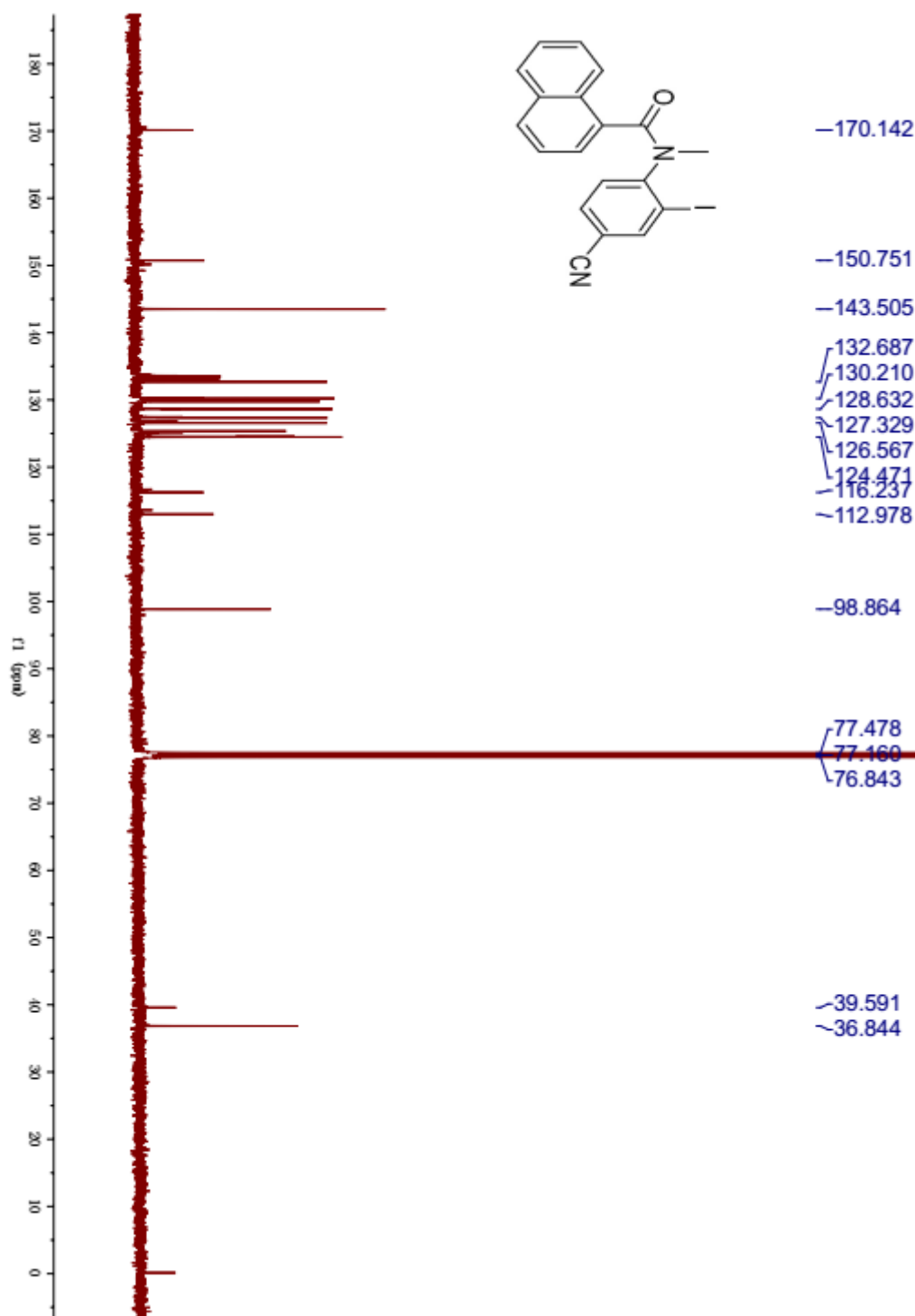


1k

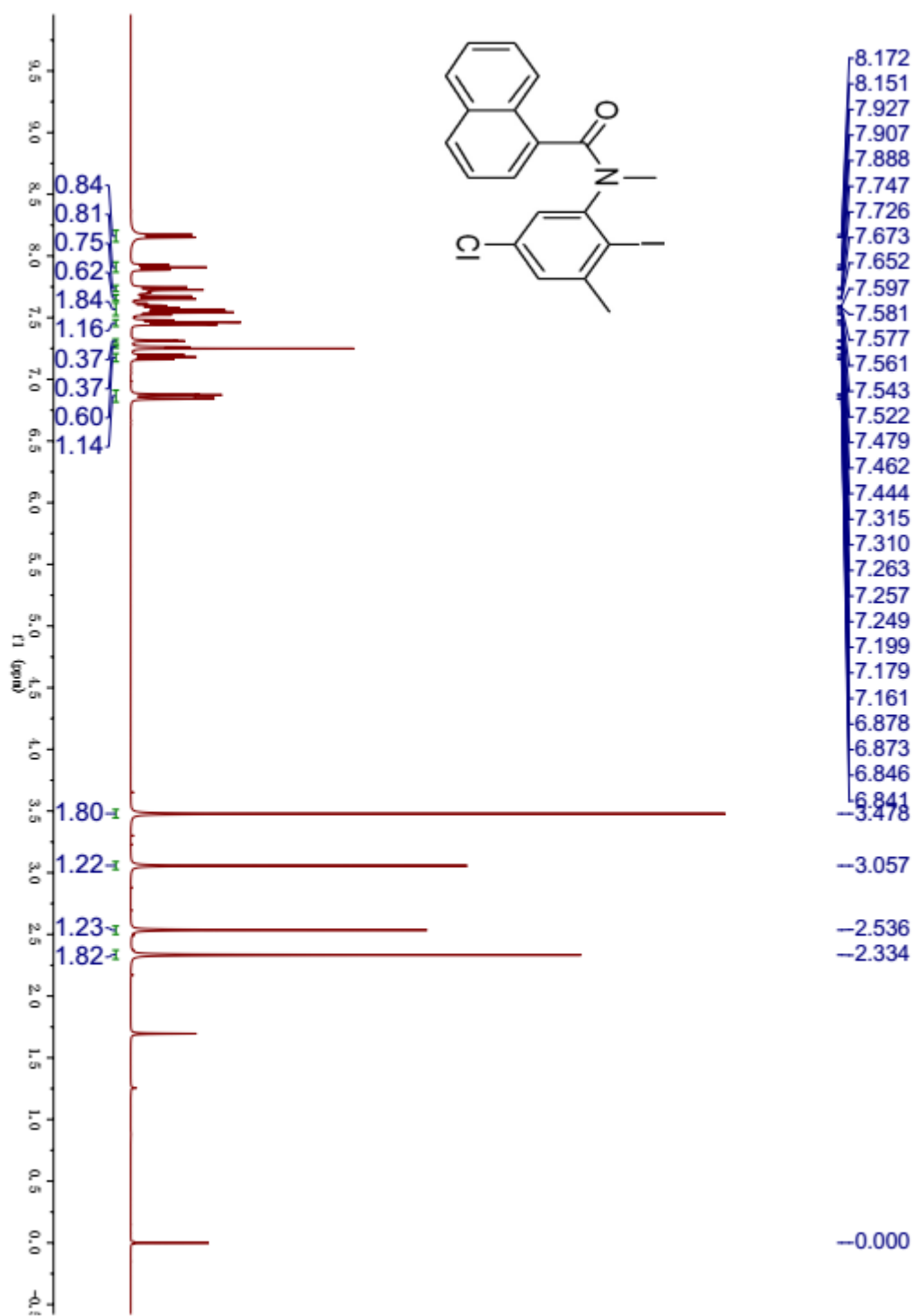


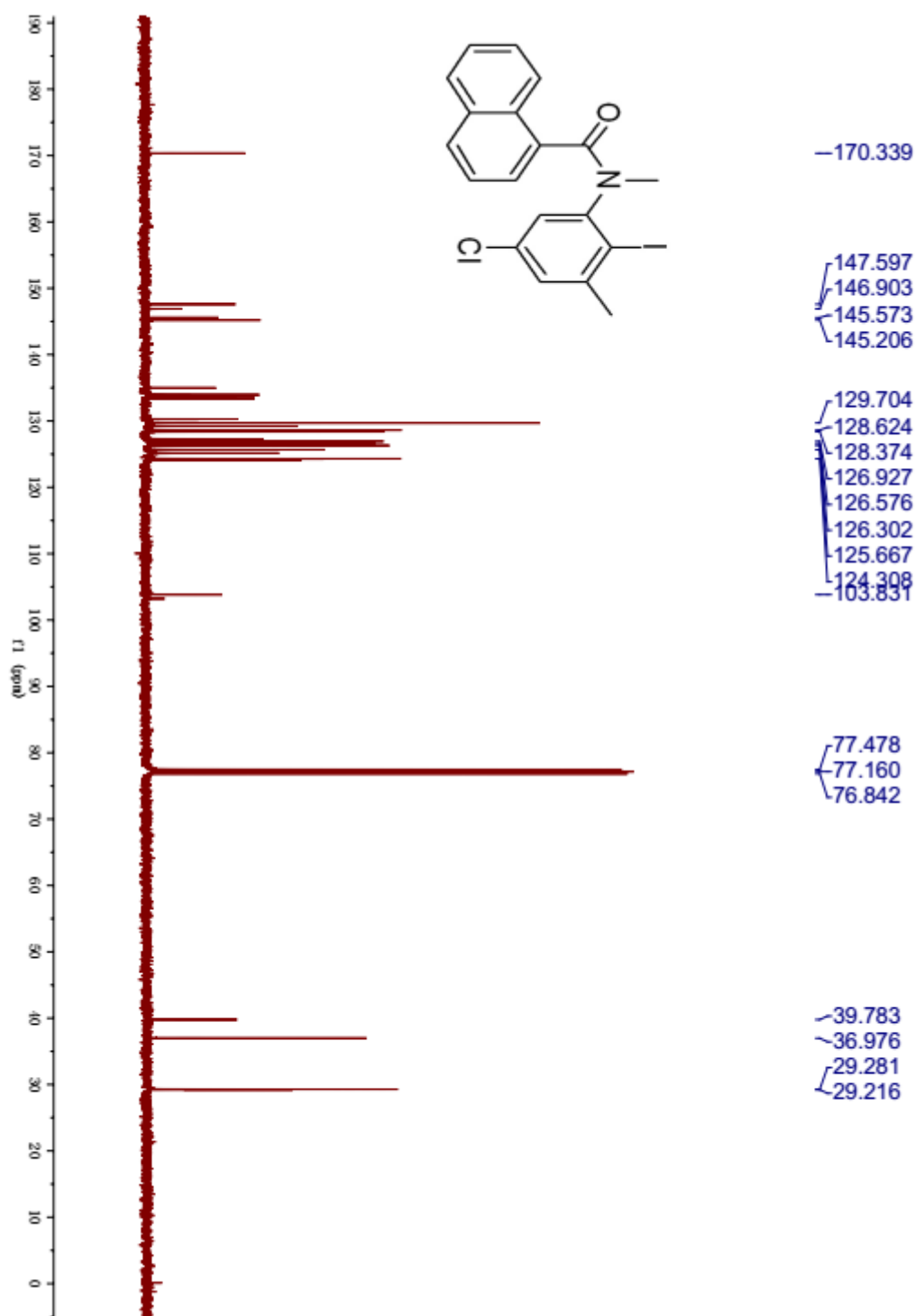




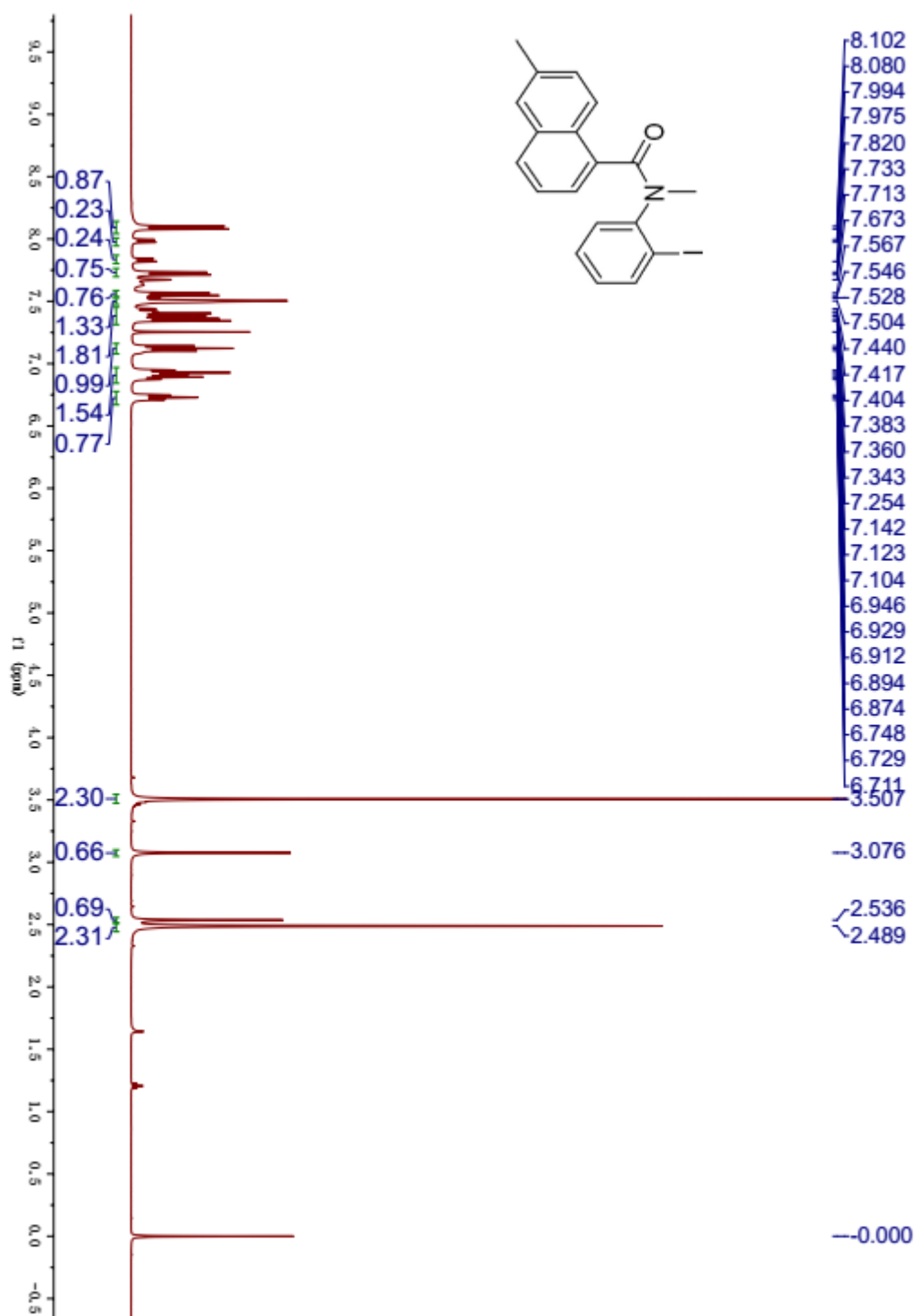


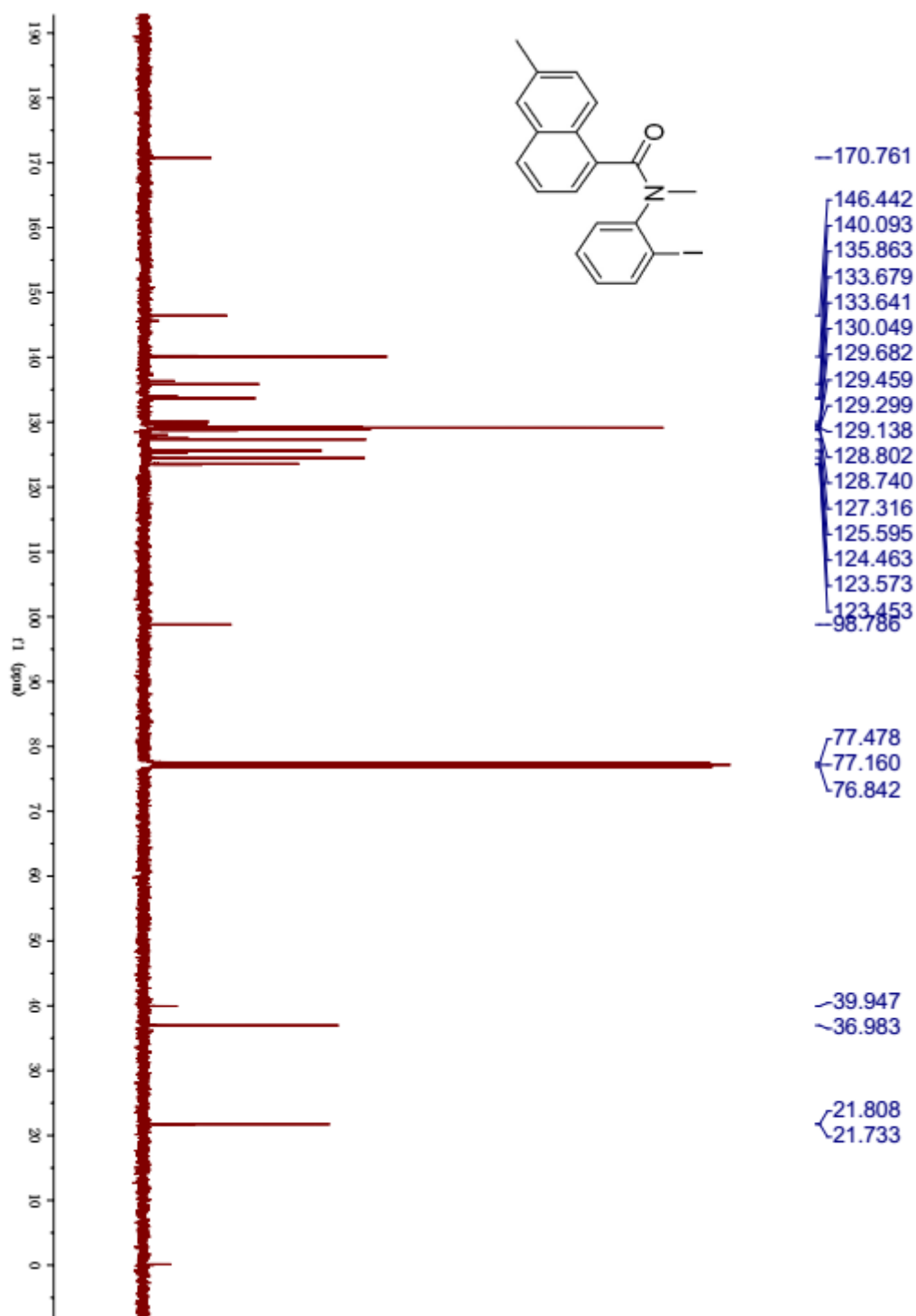
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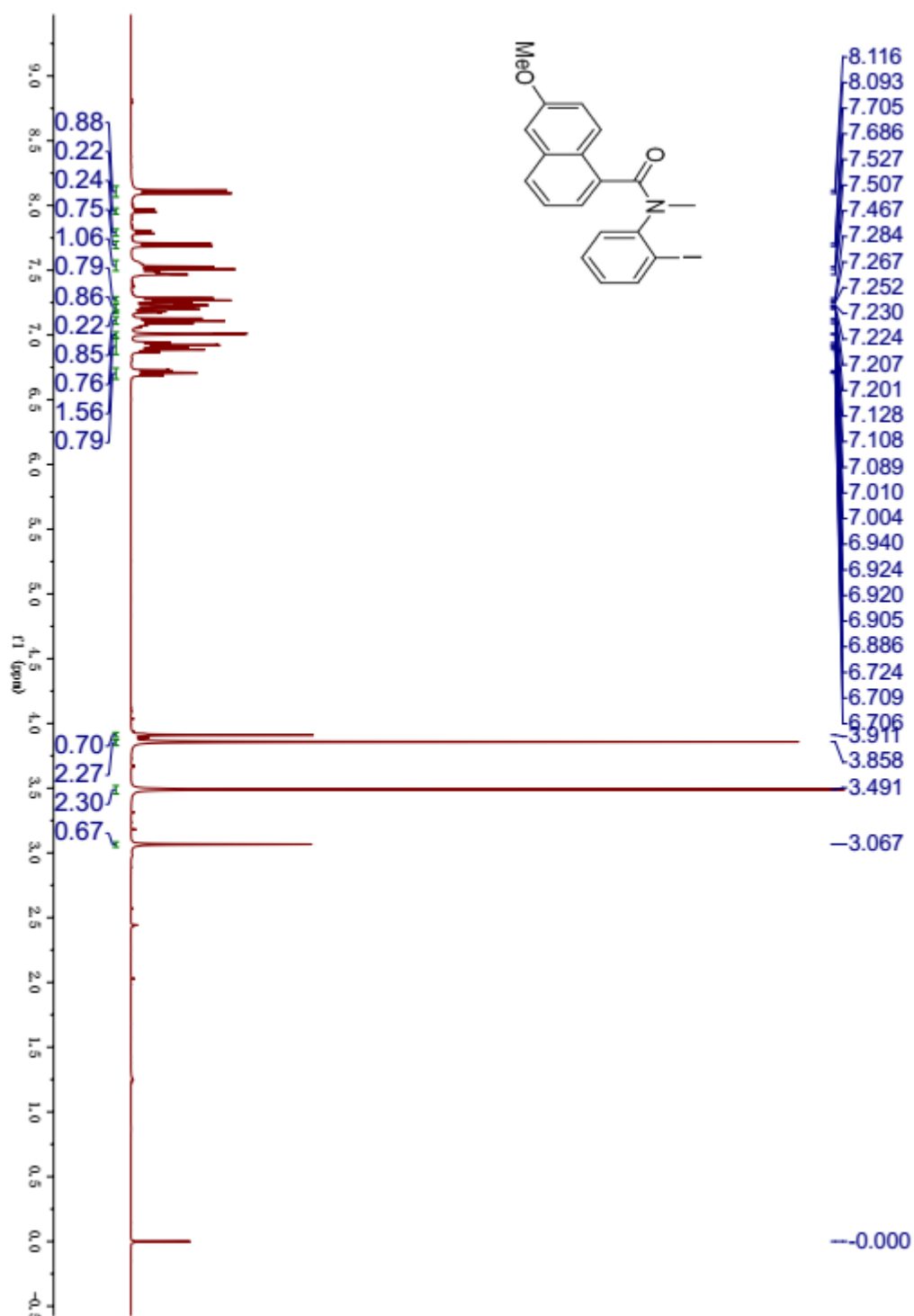


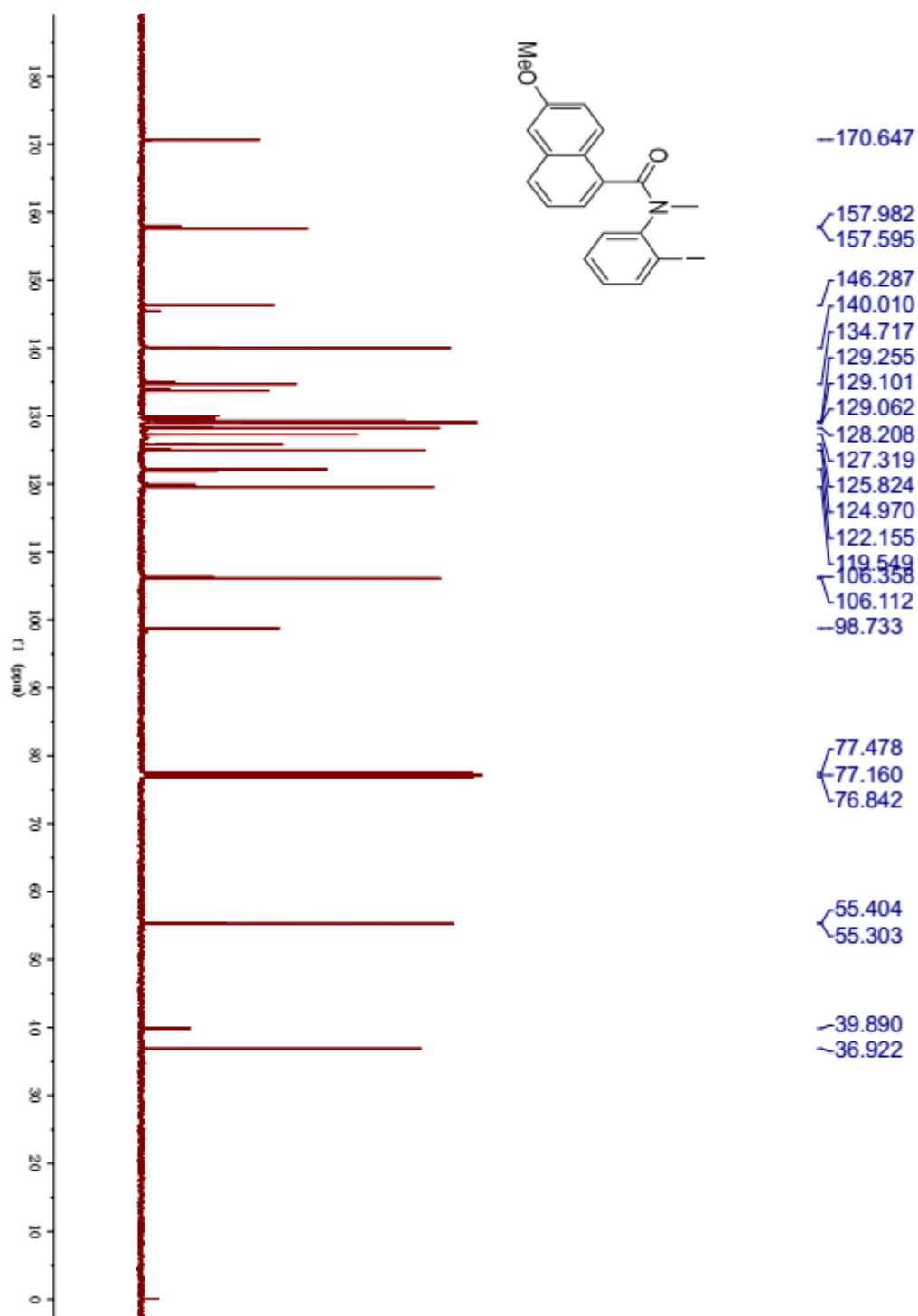
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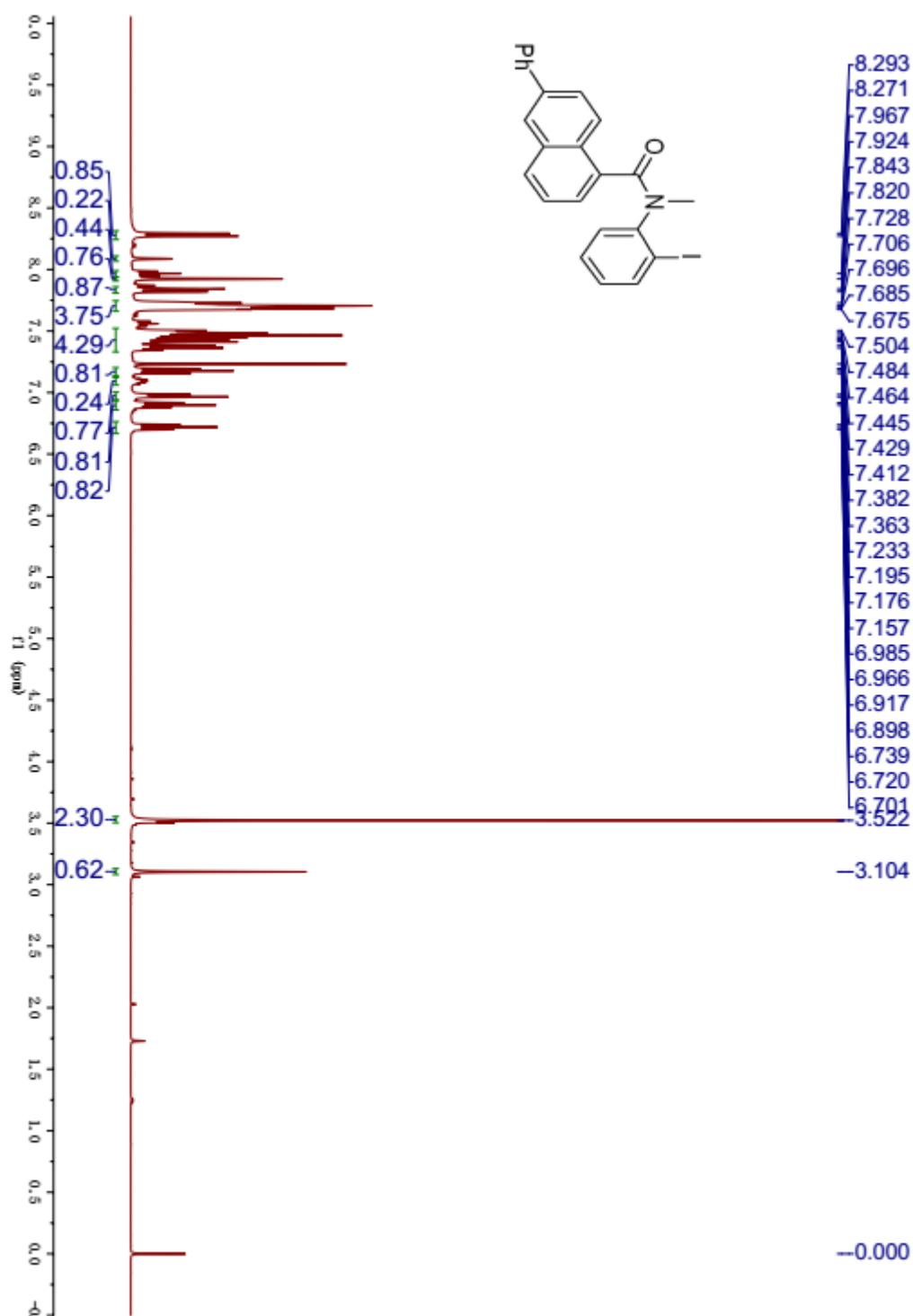


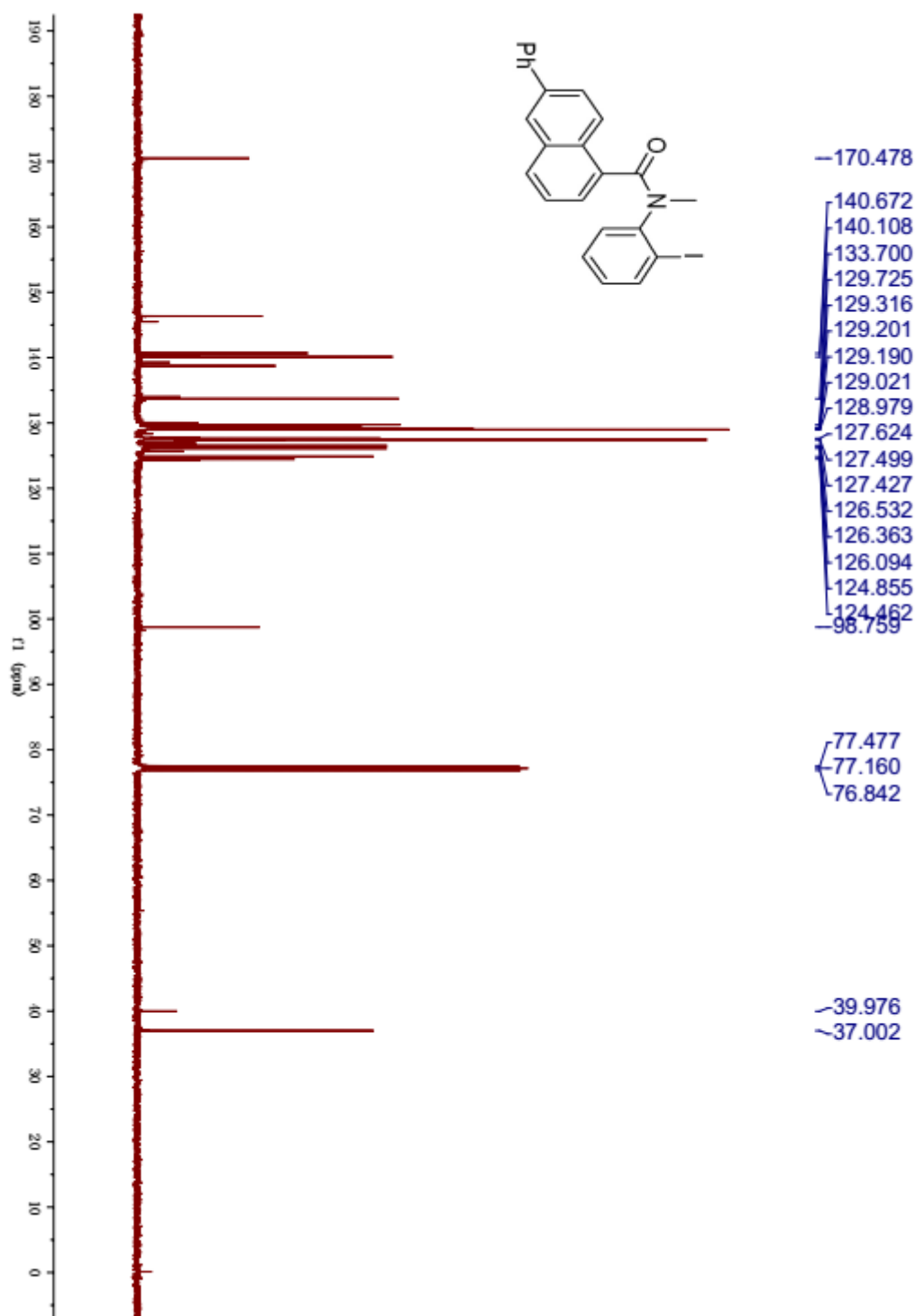
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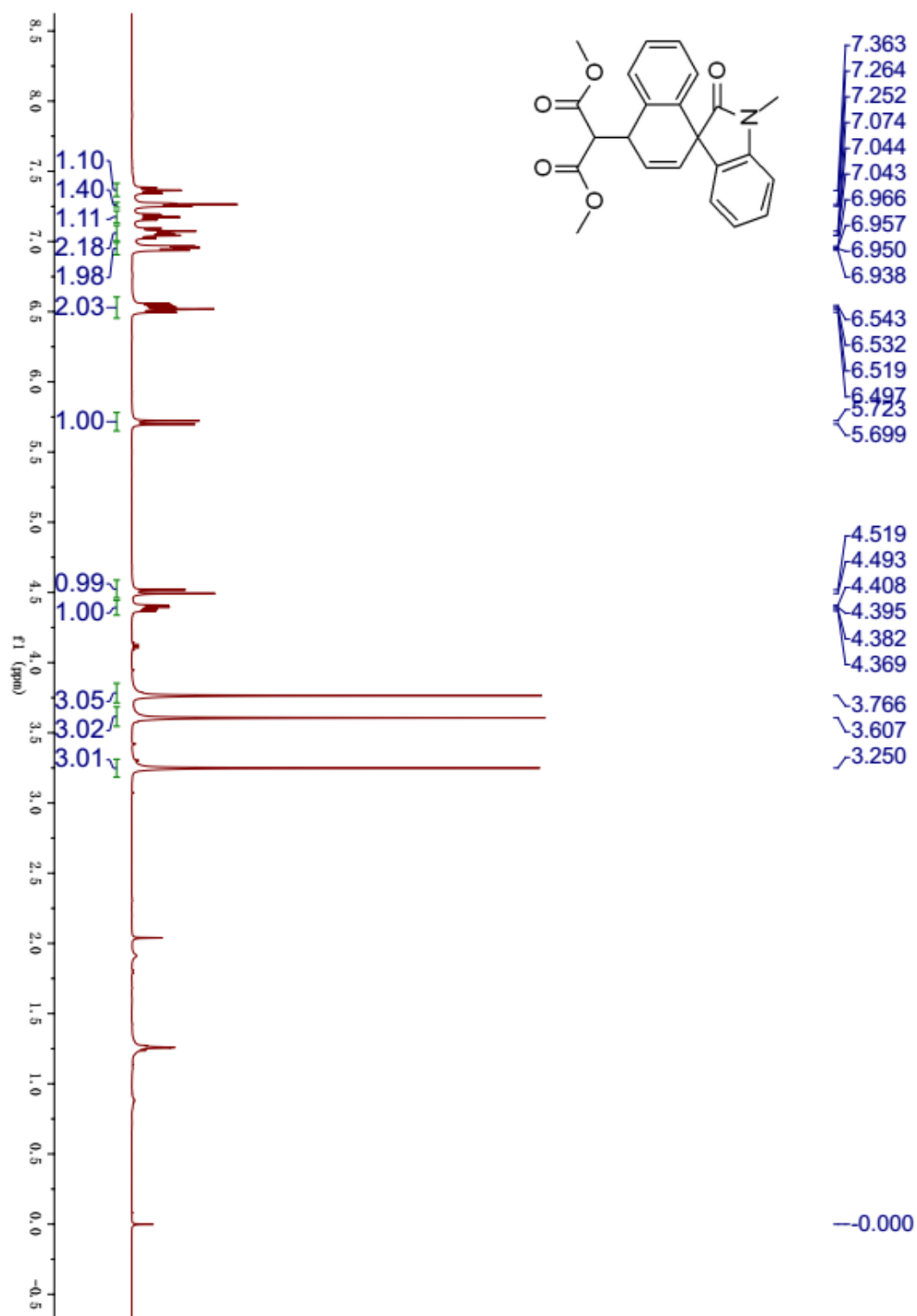


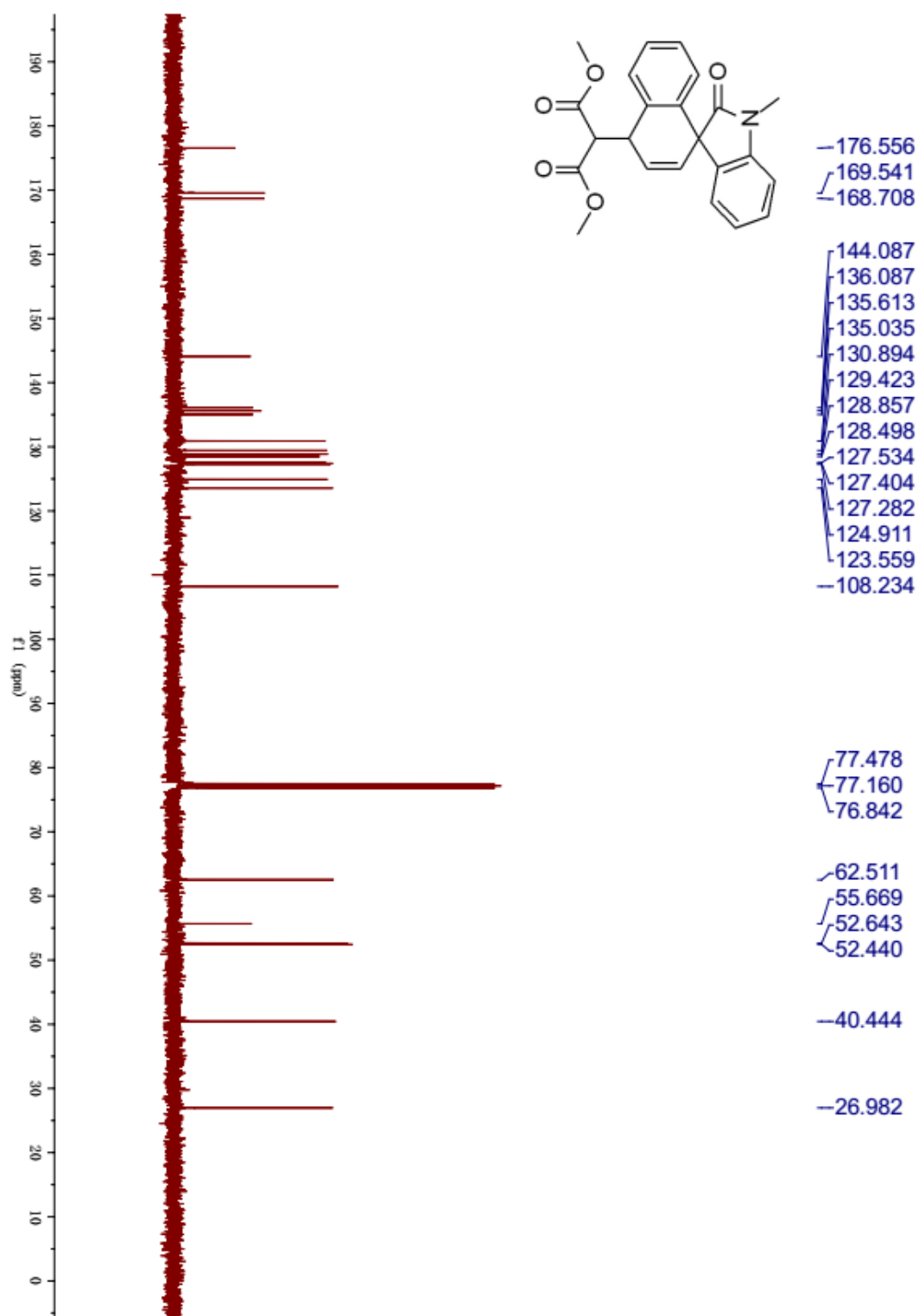
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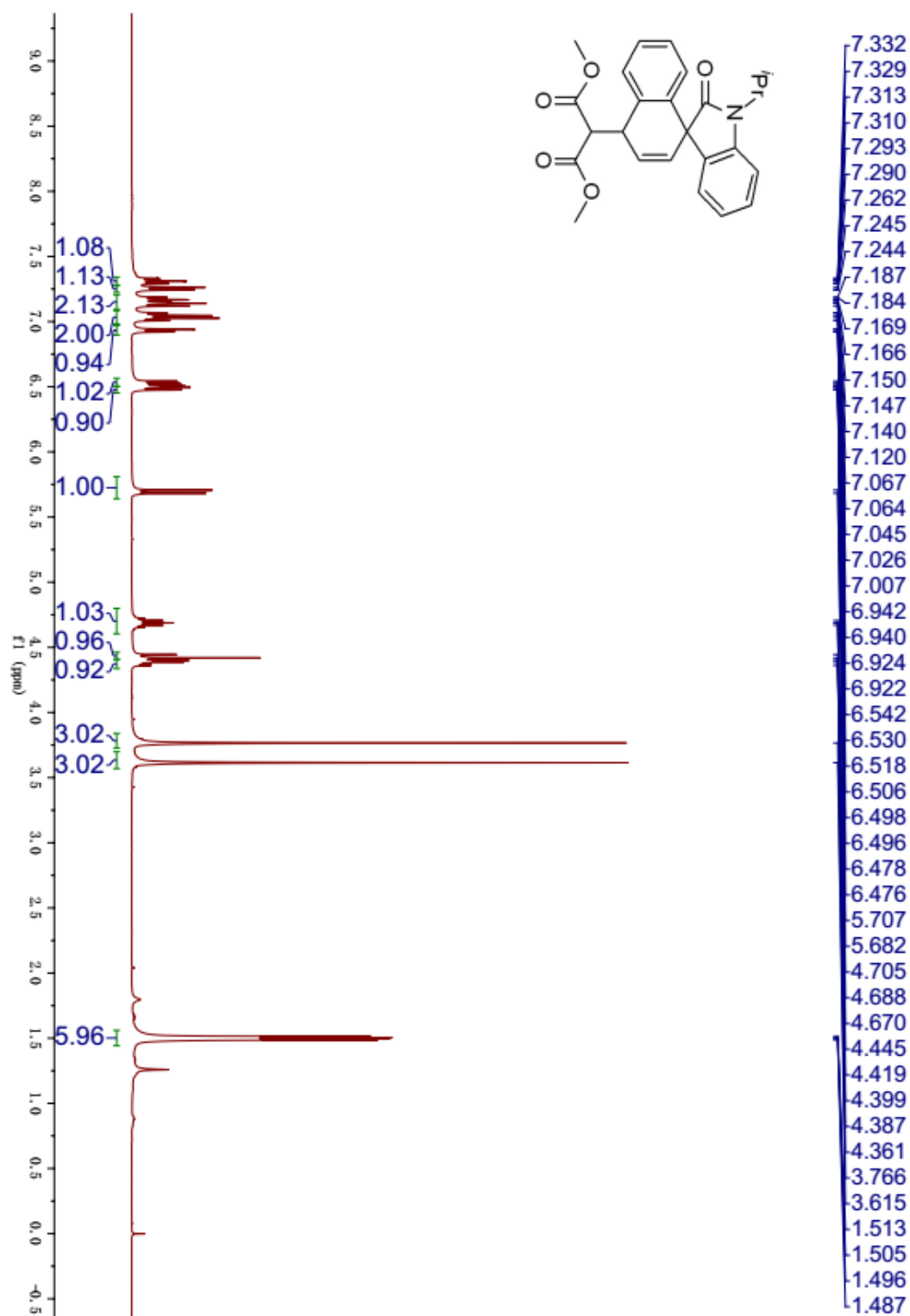


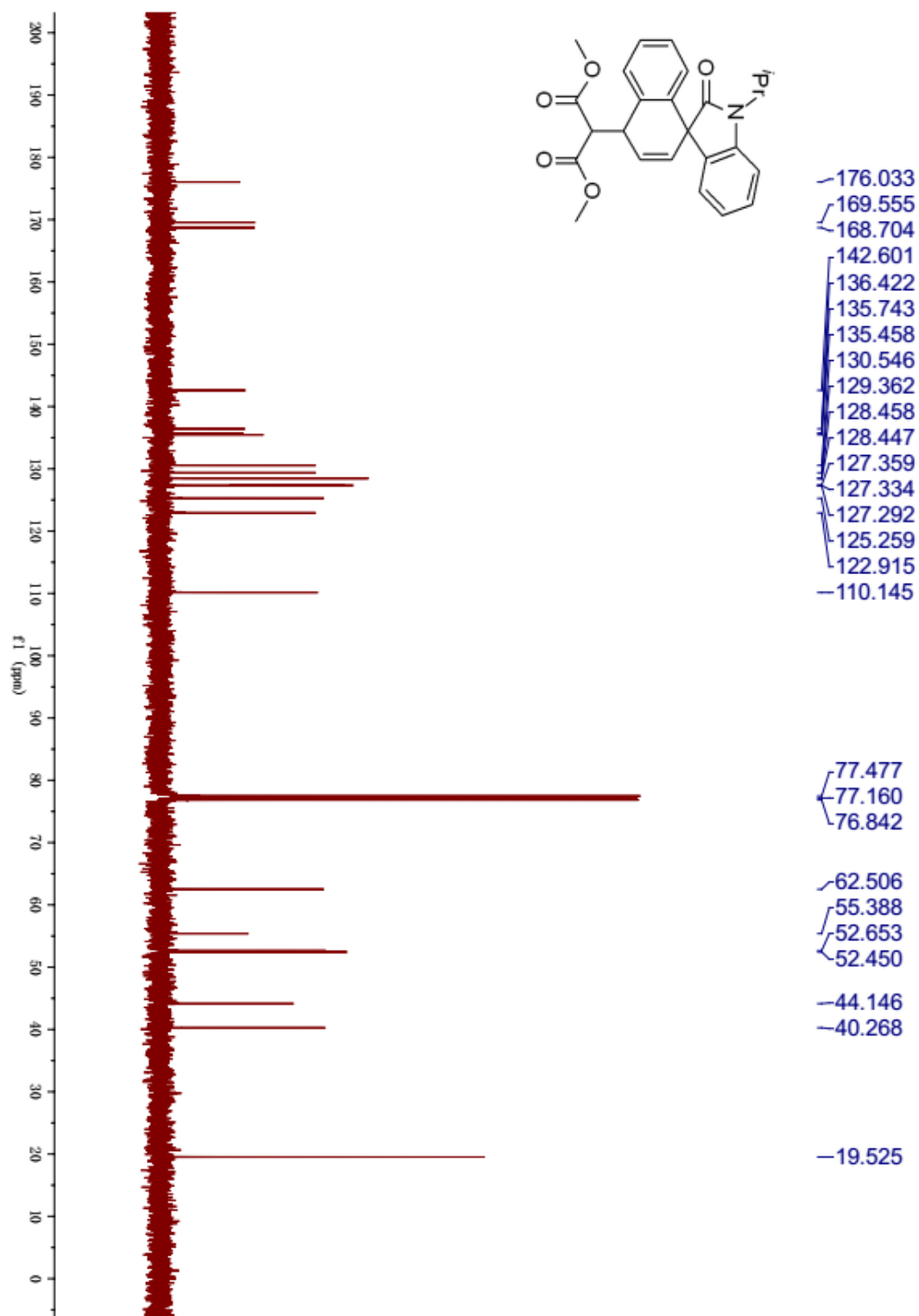
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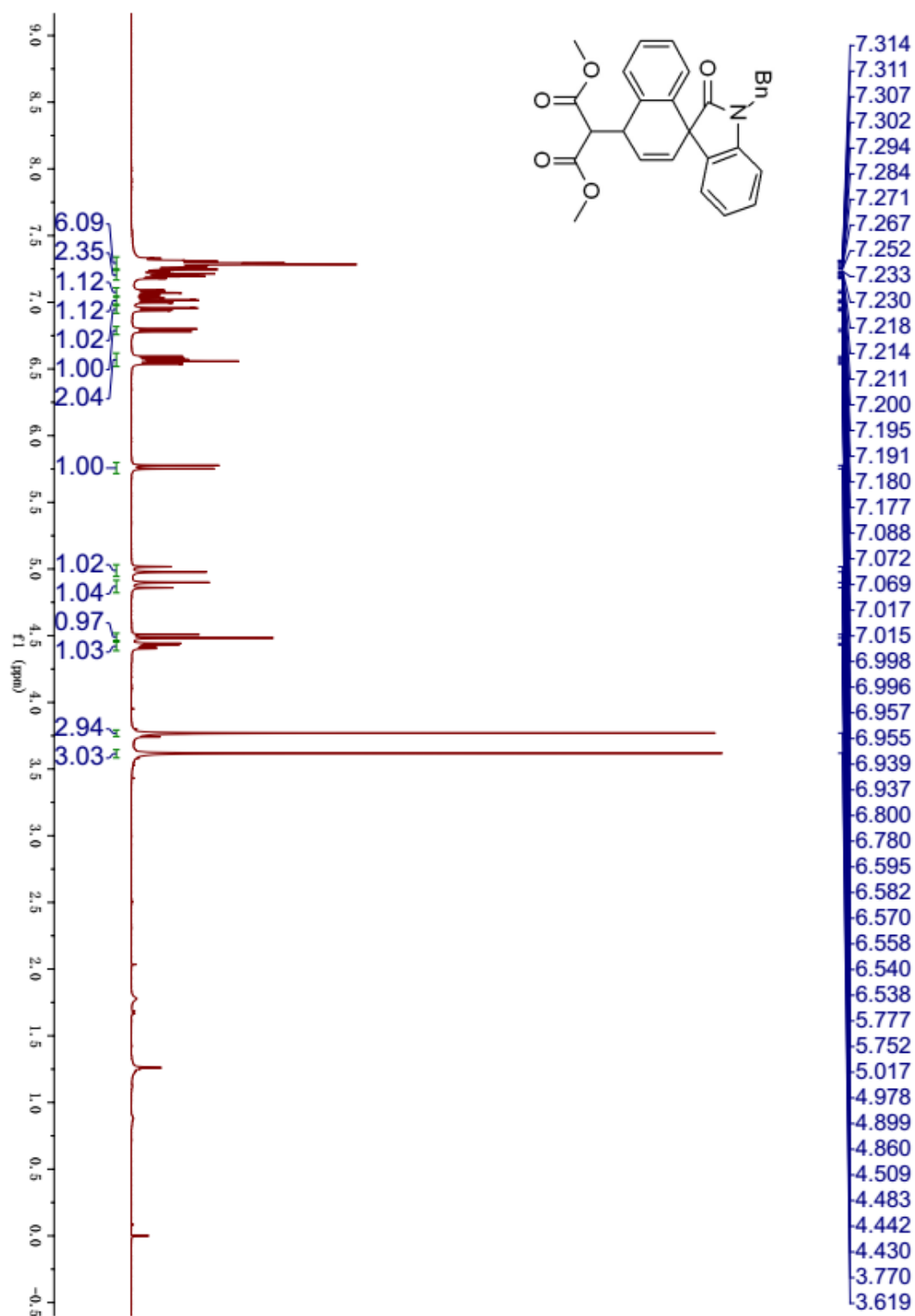


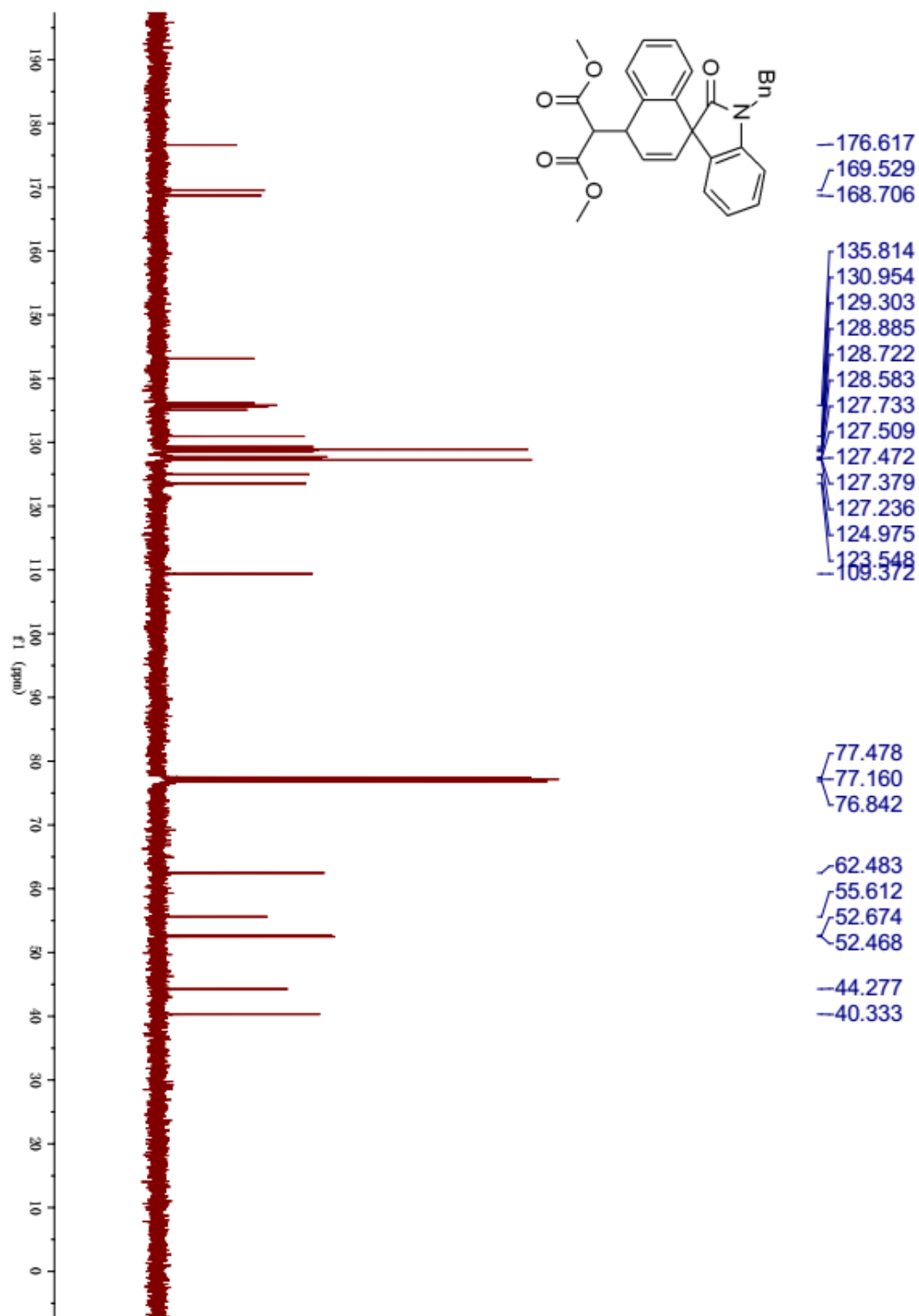
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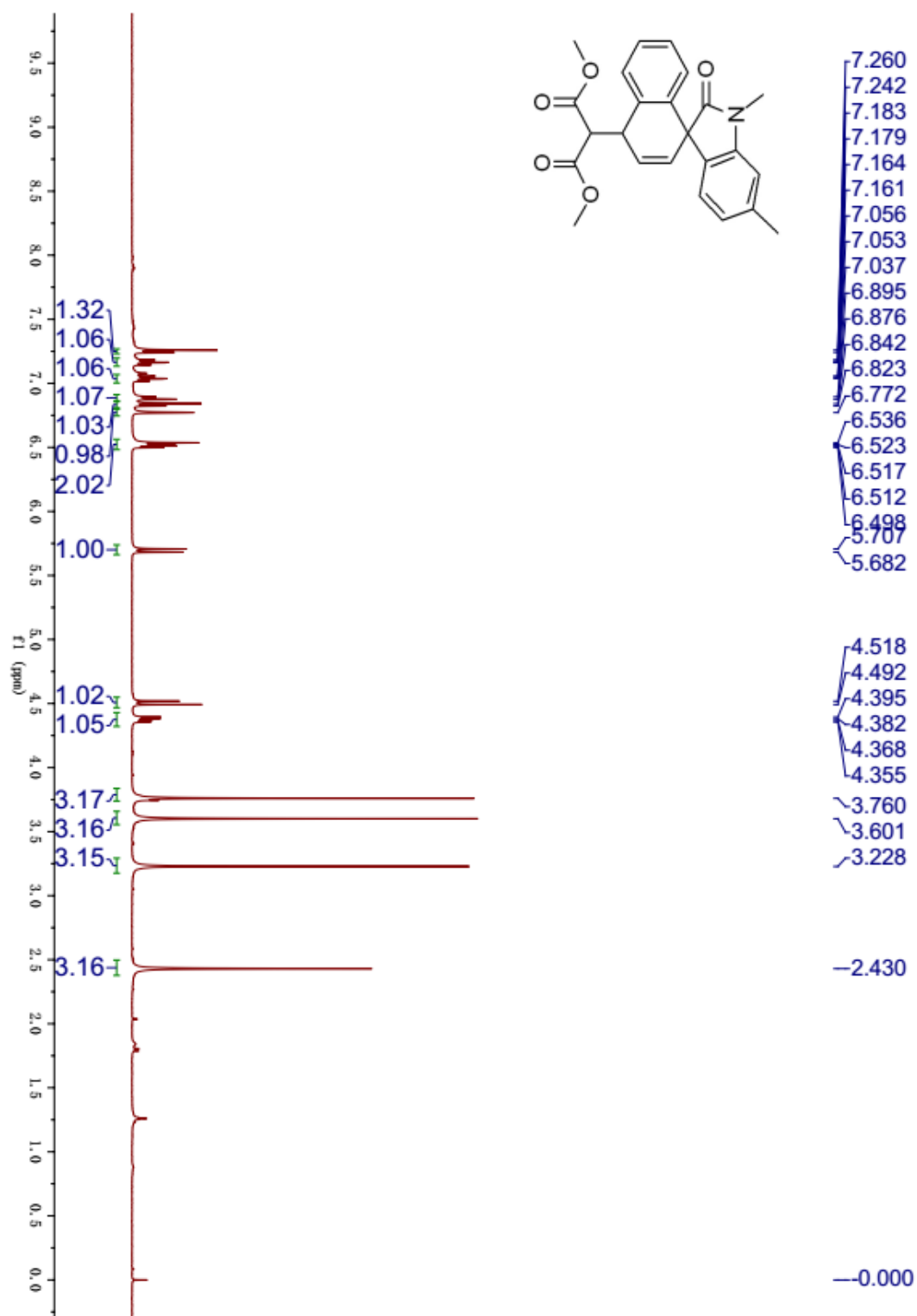


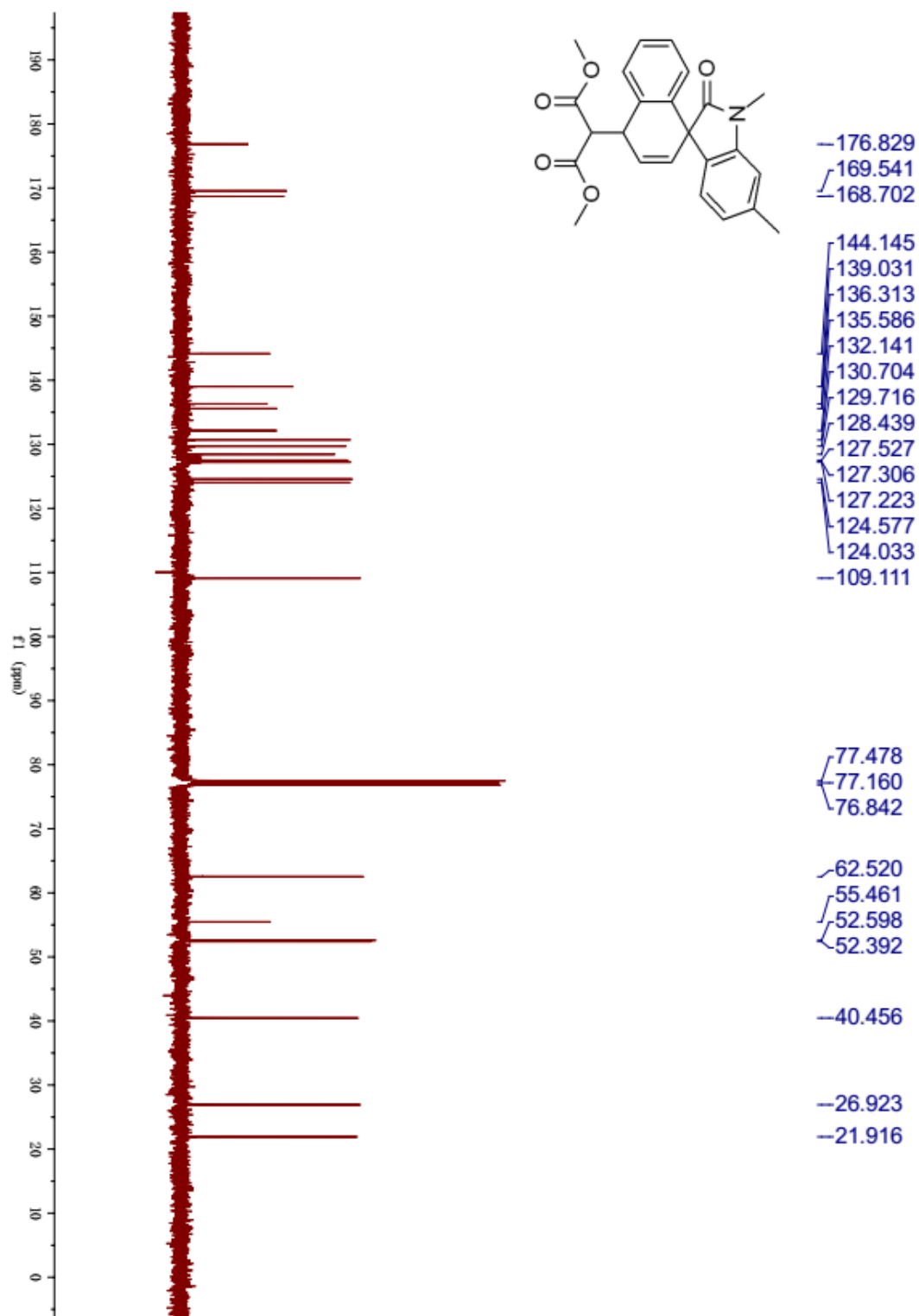
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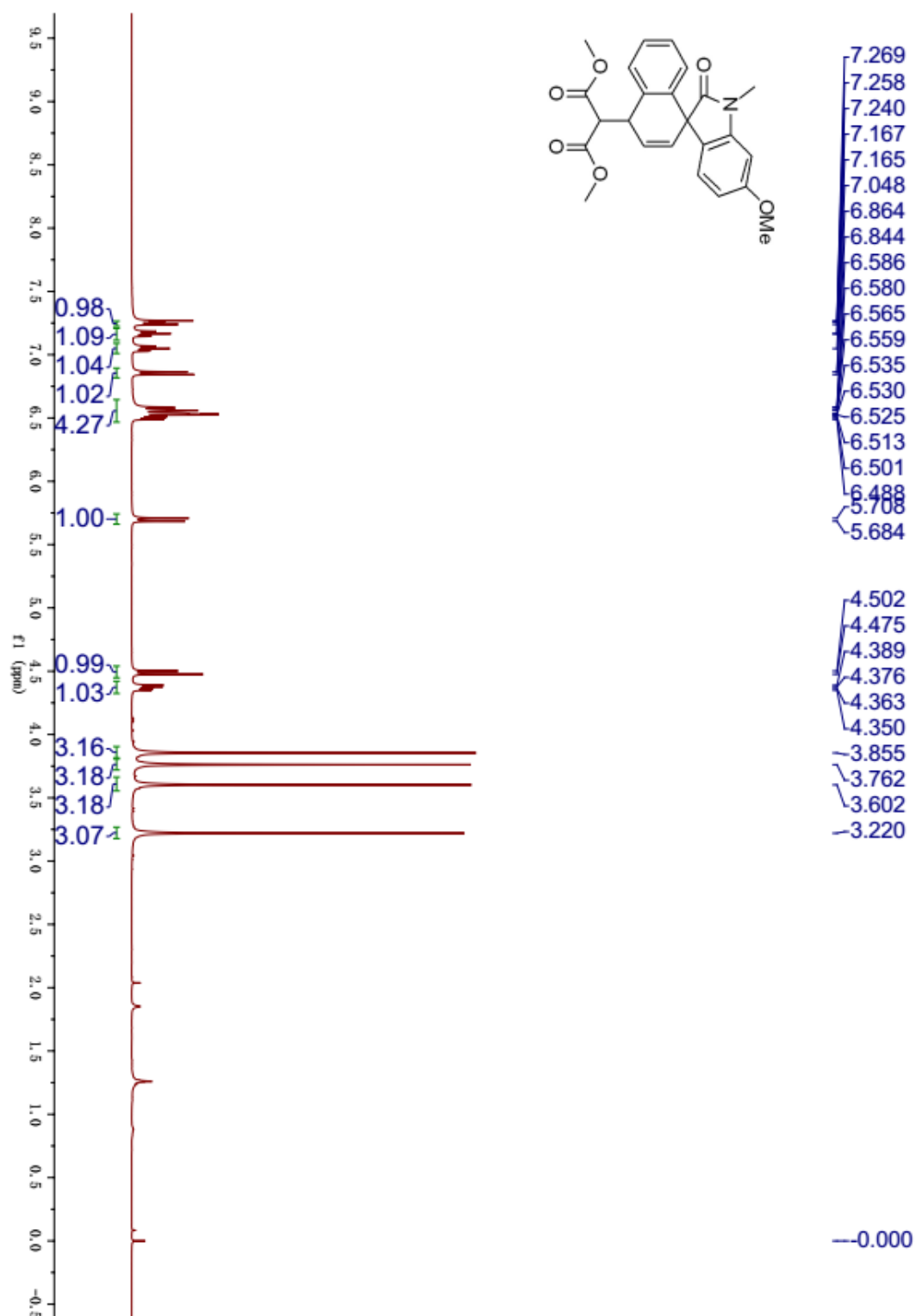


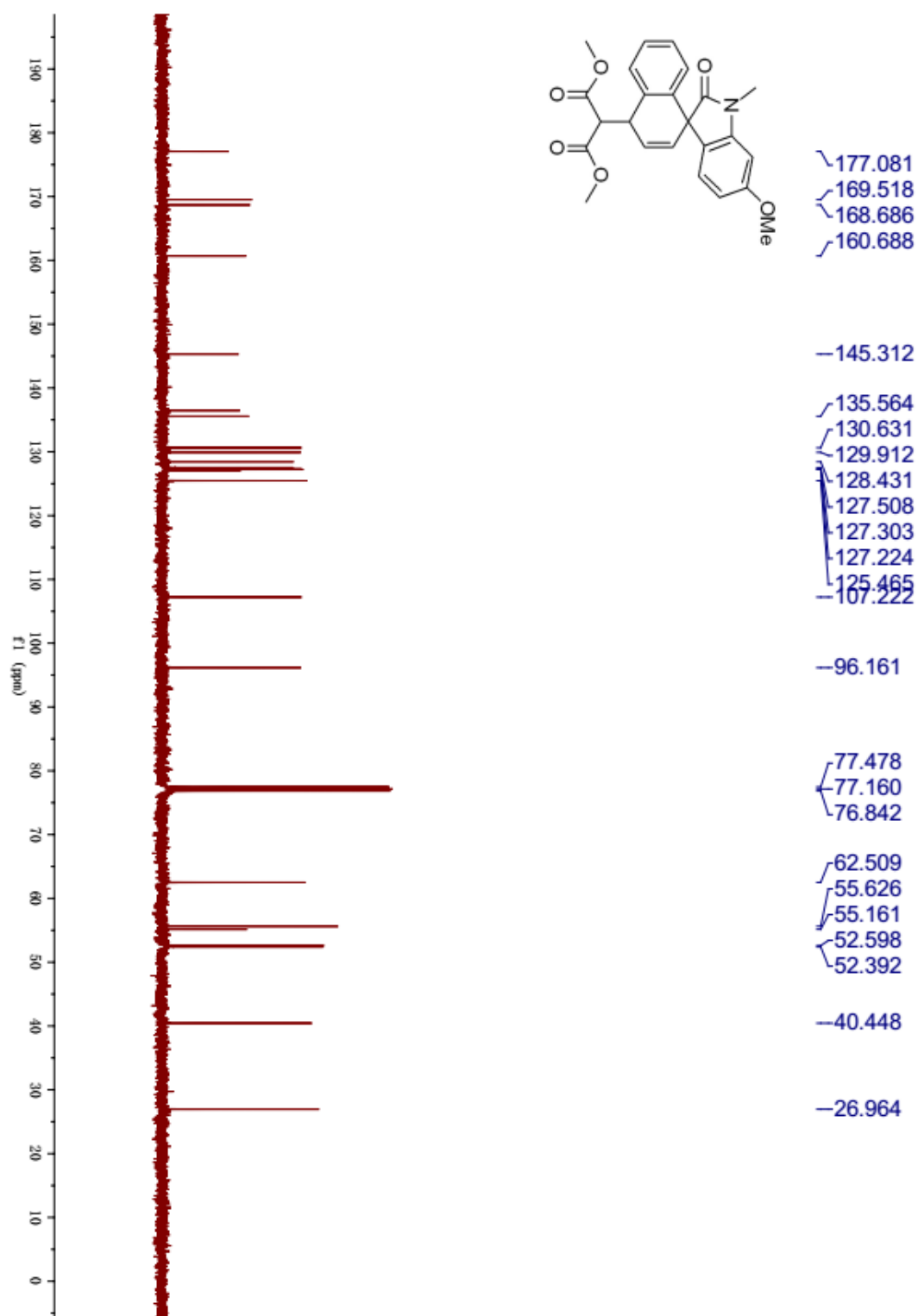
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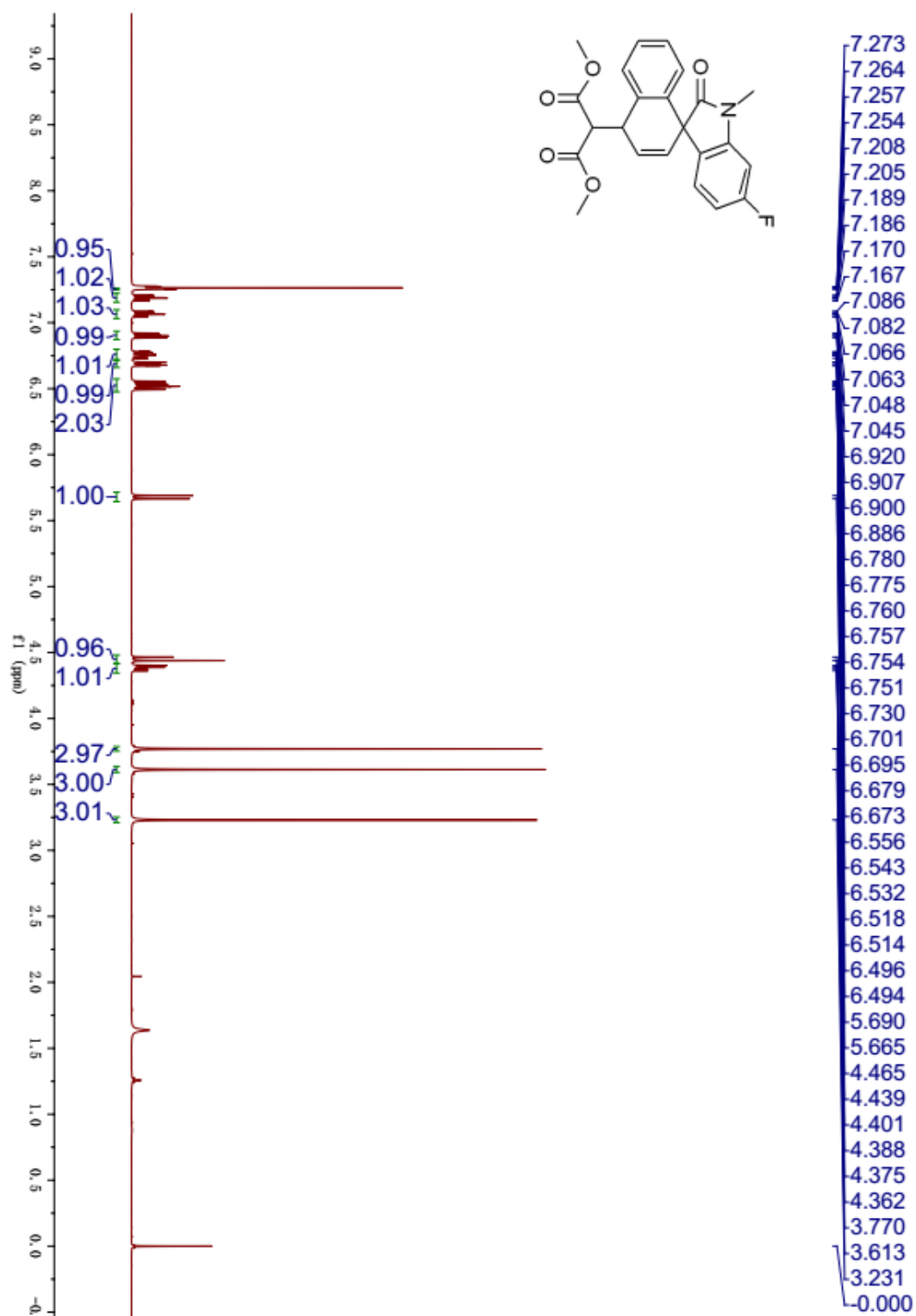


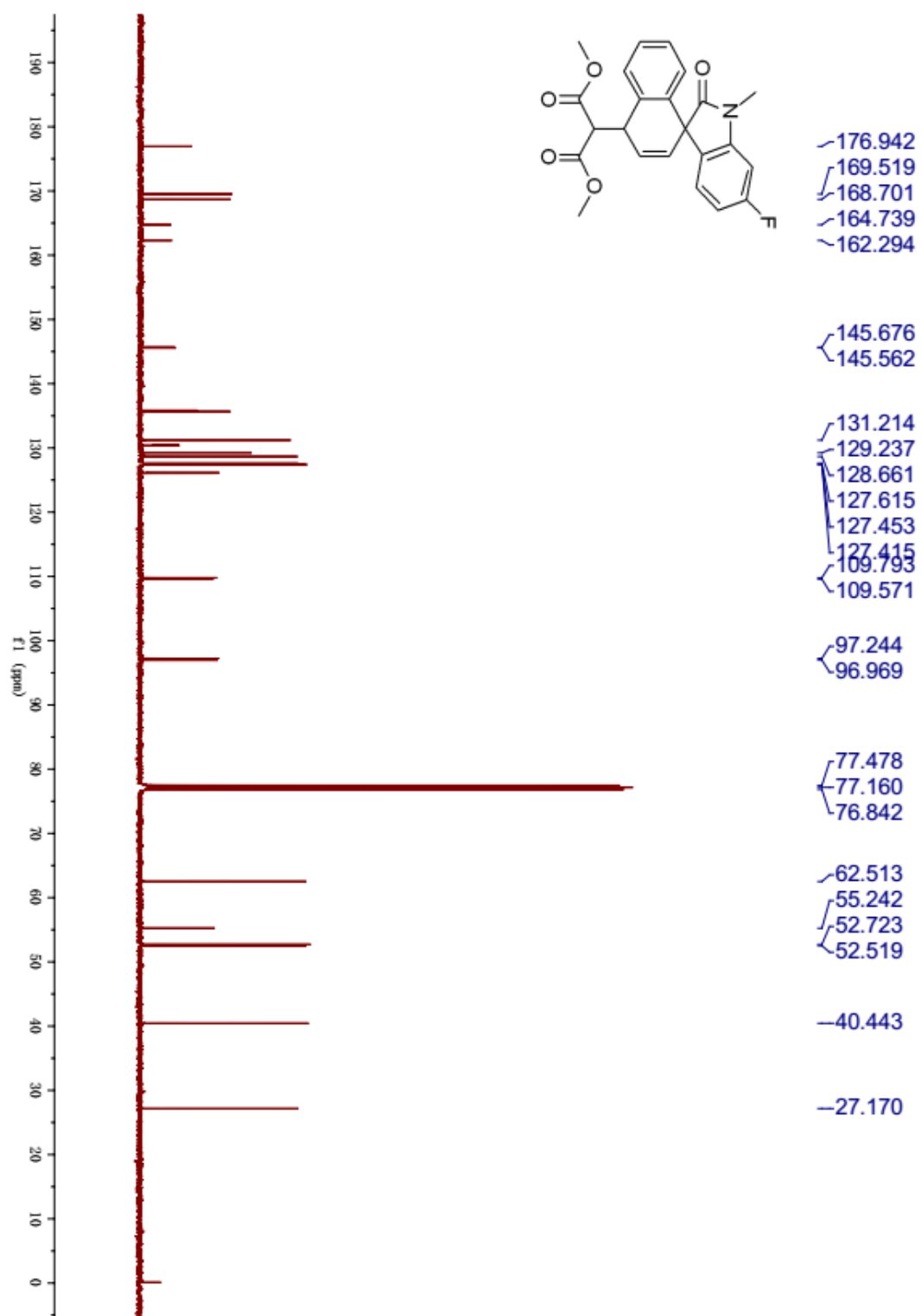
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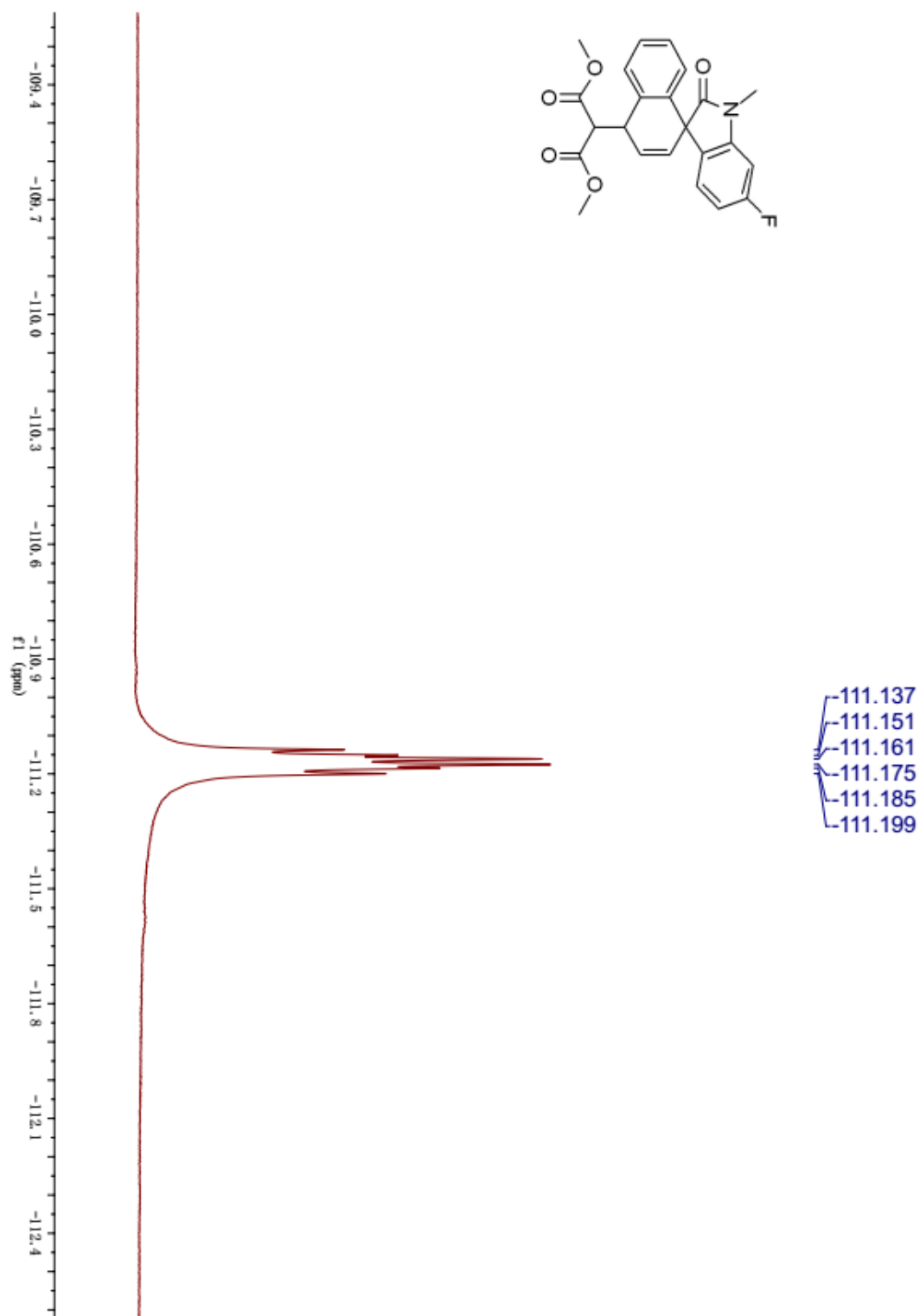
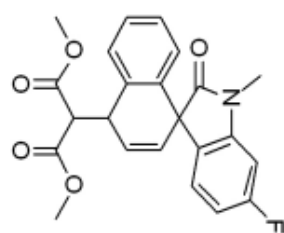




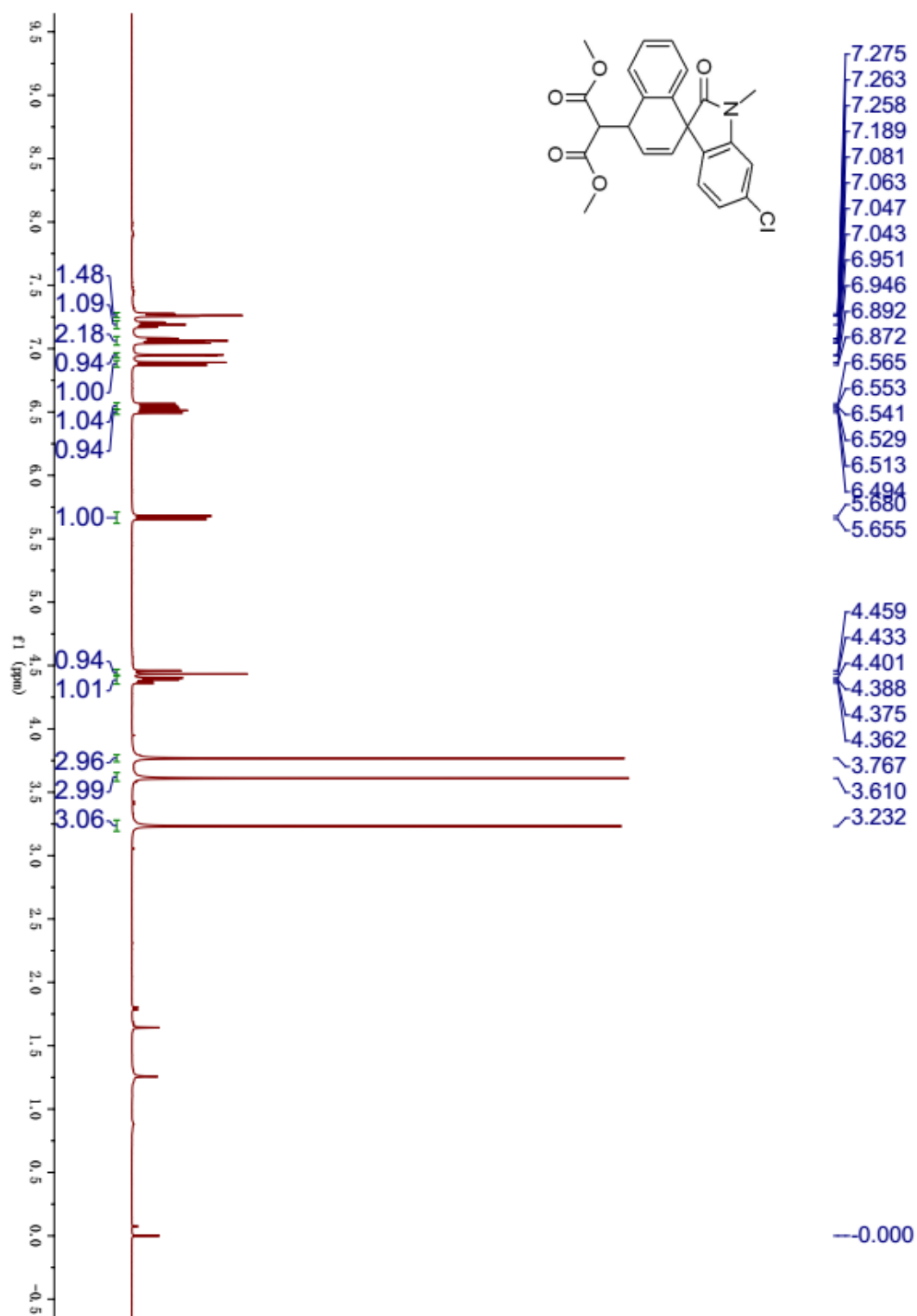
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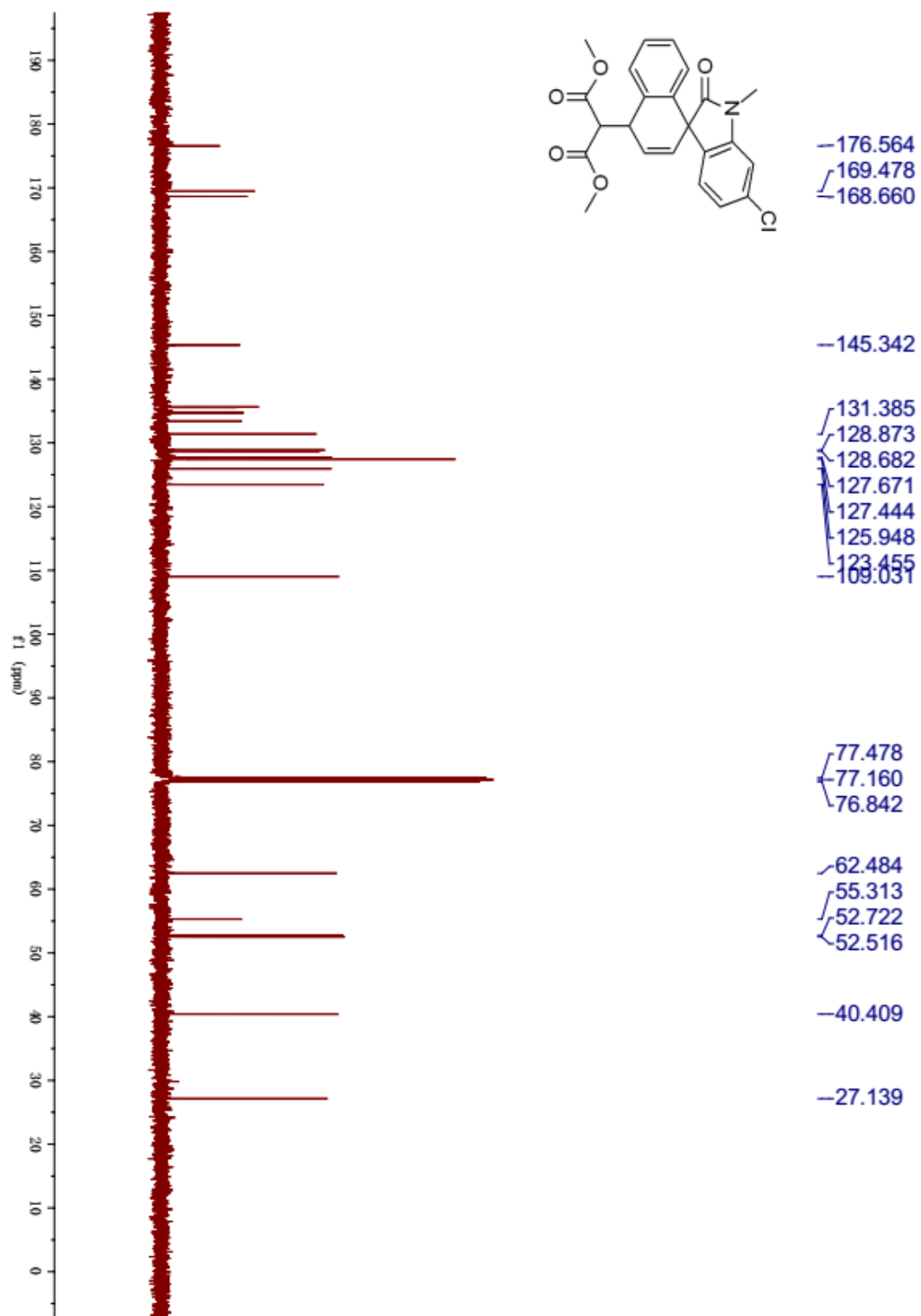




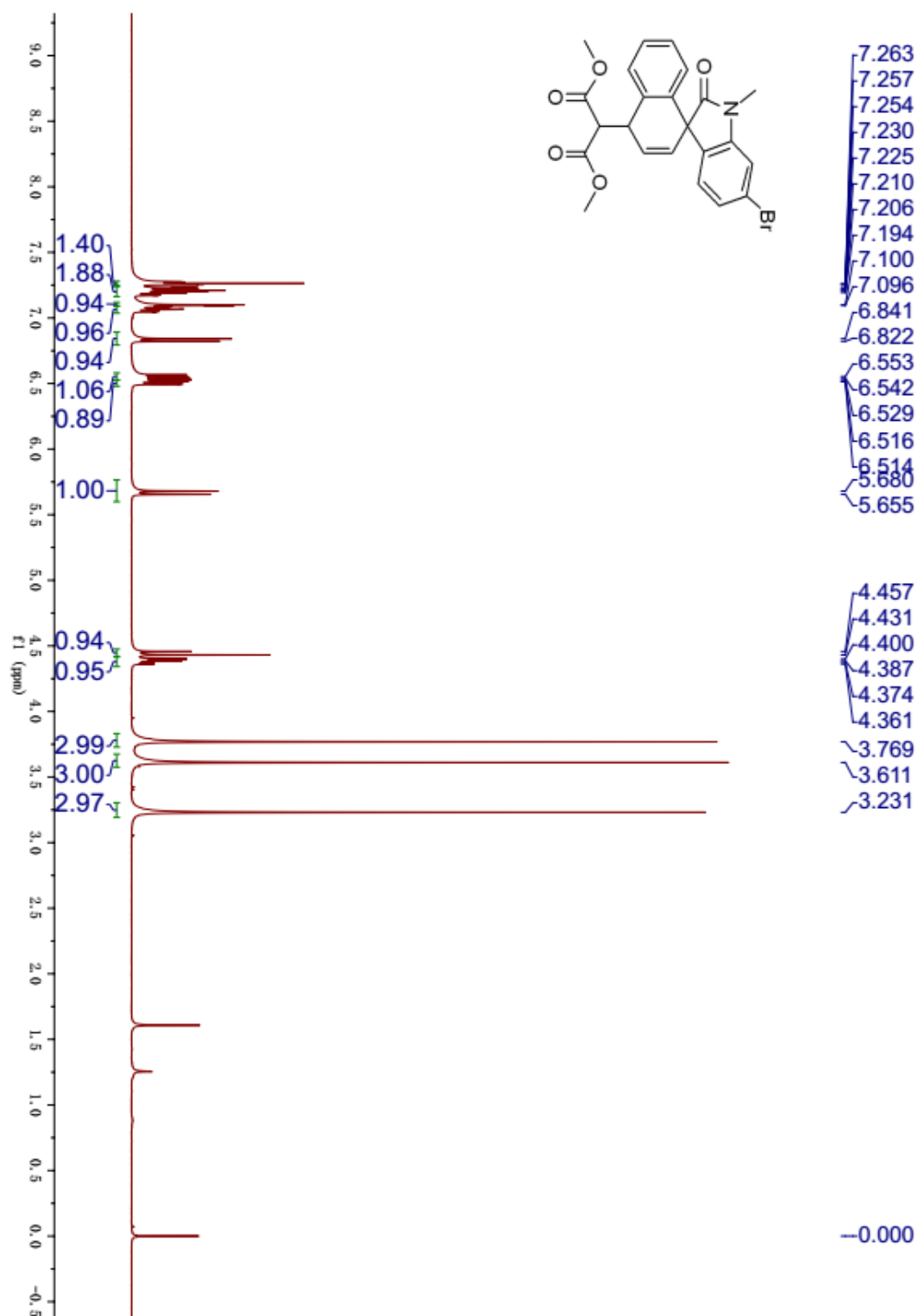


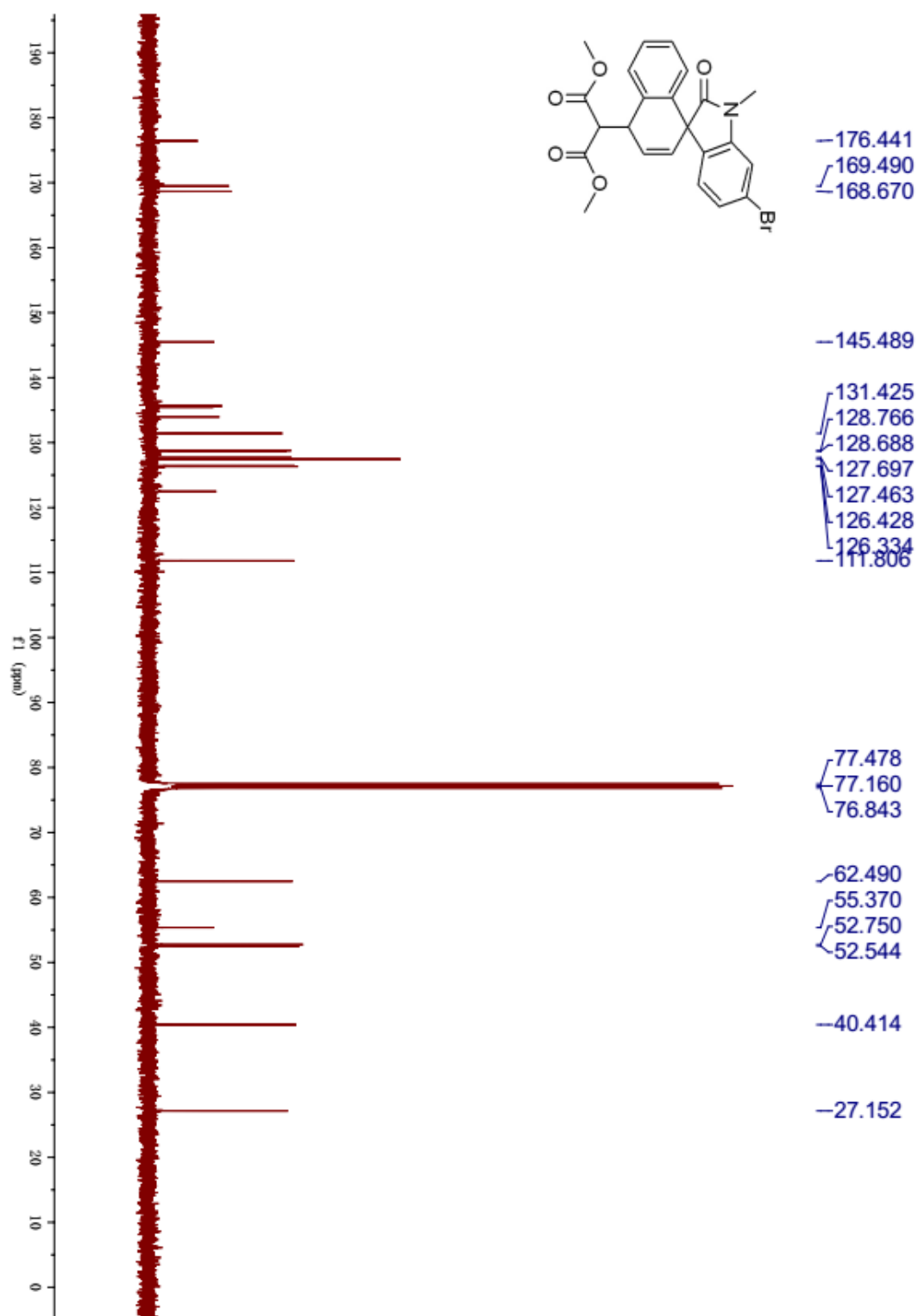
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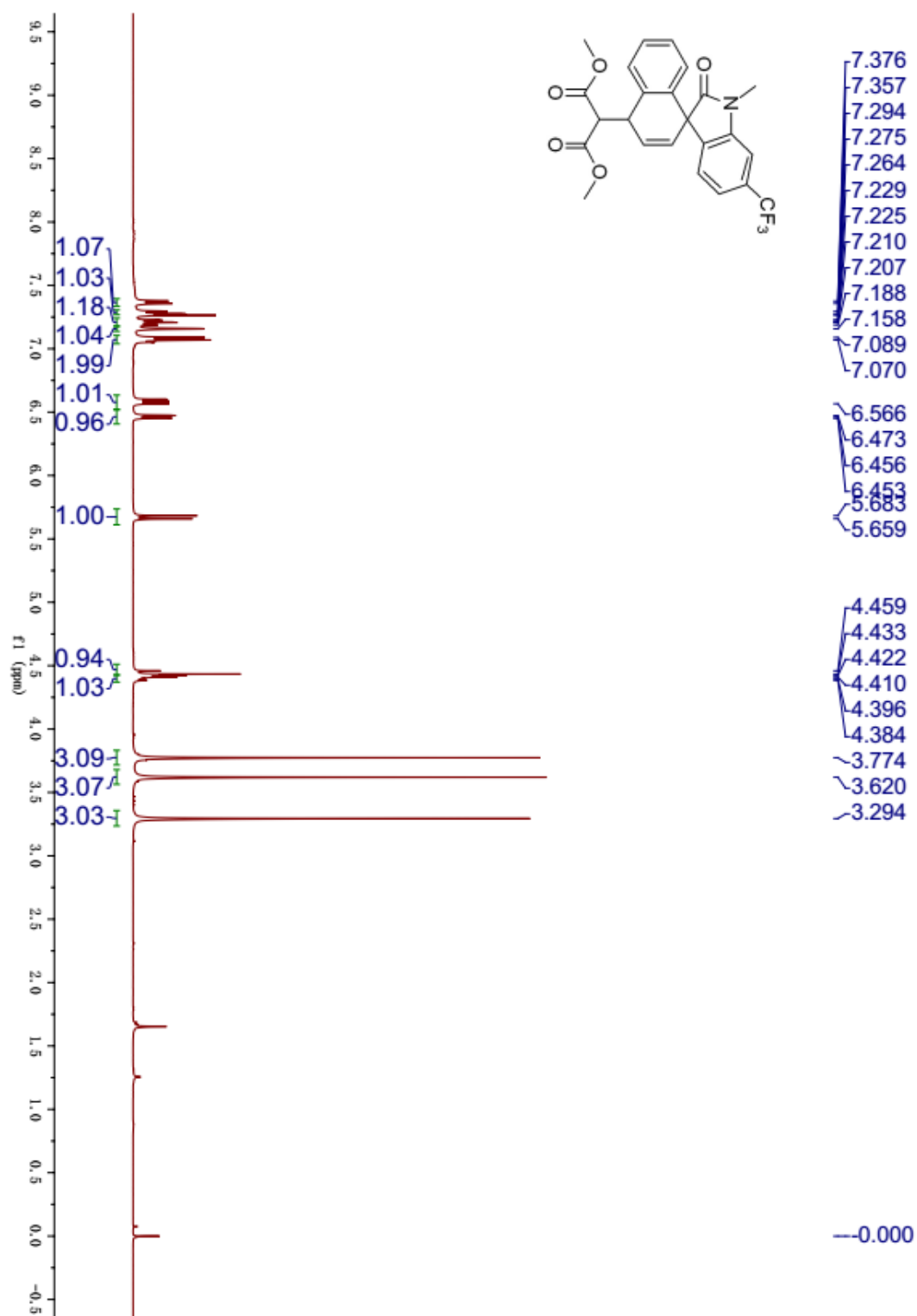


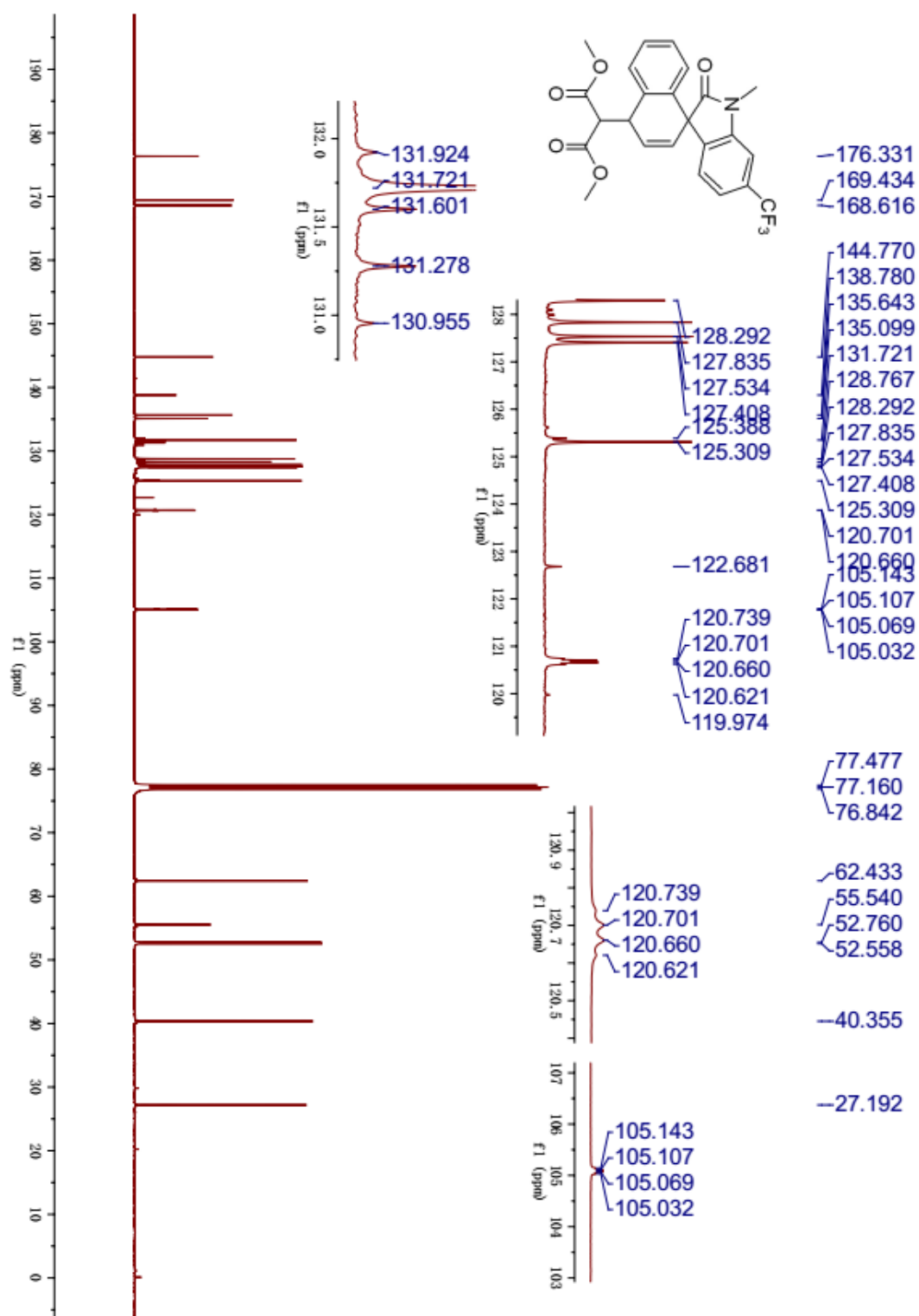
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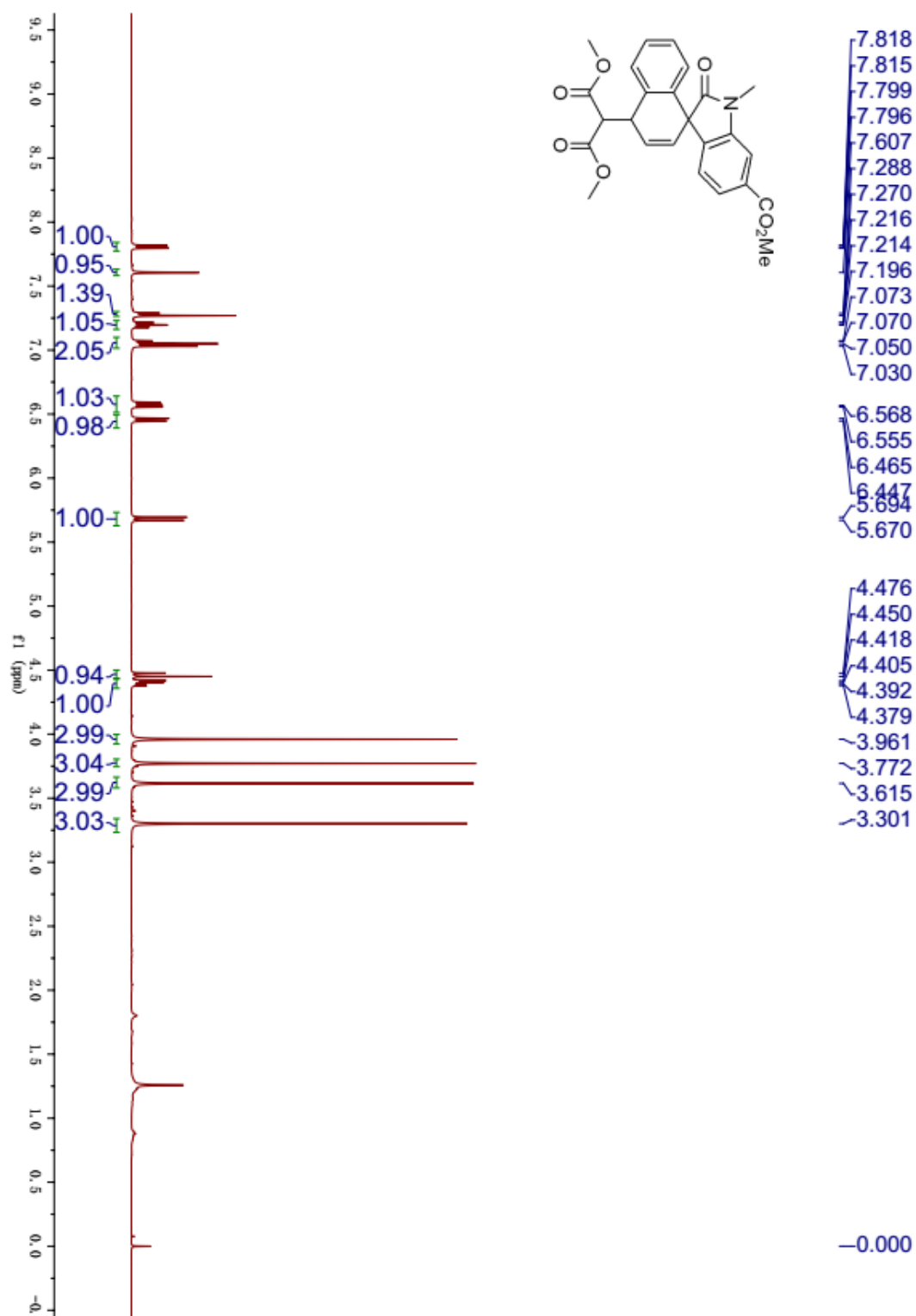
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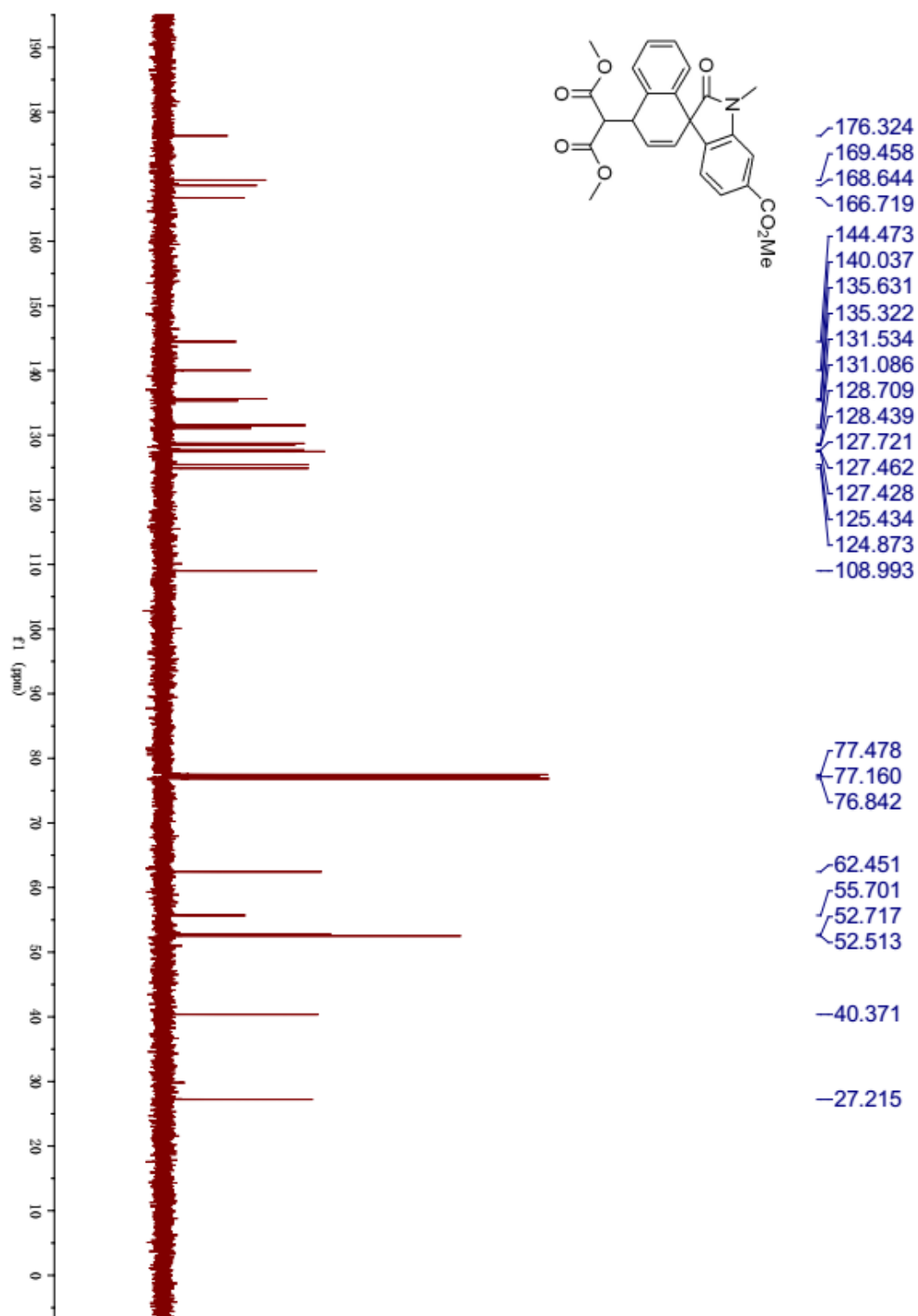




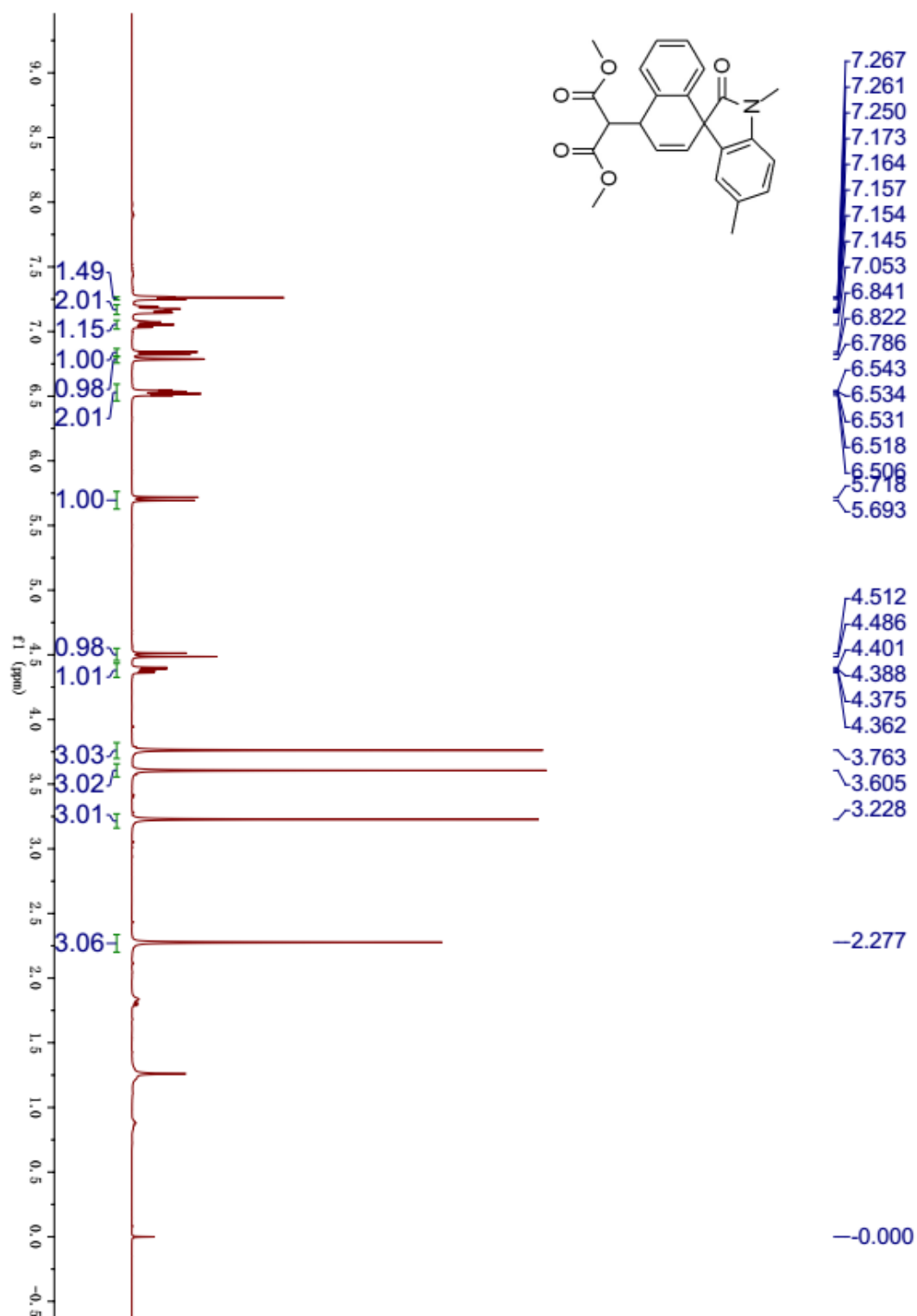


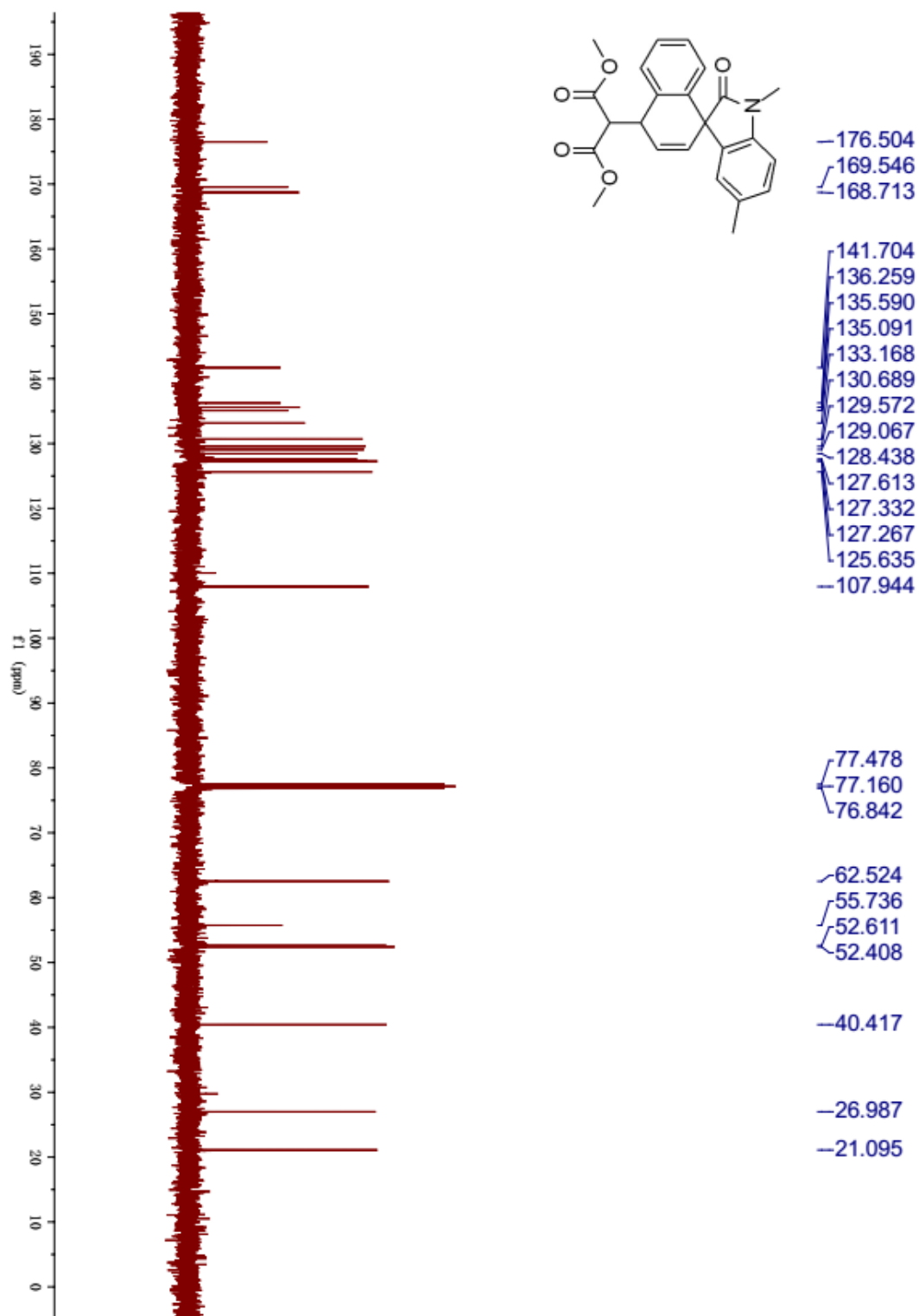
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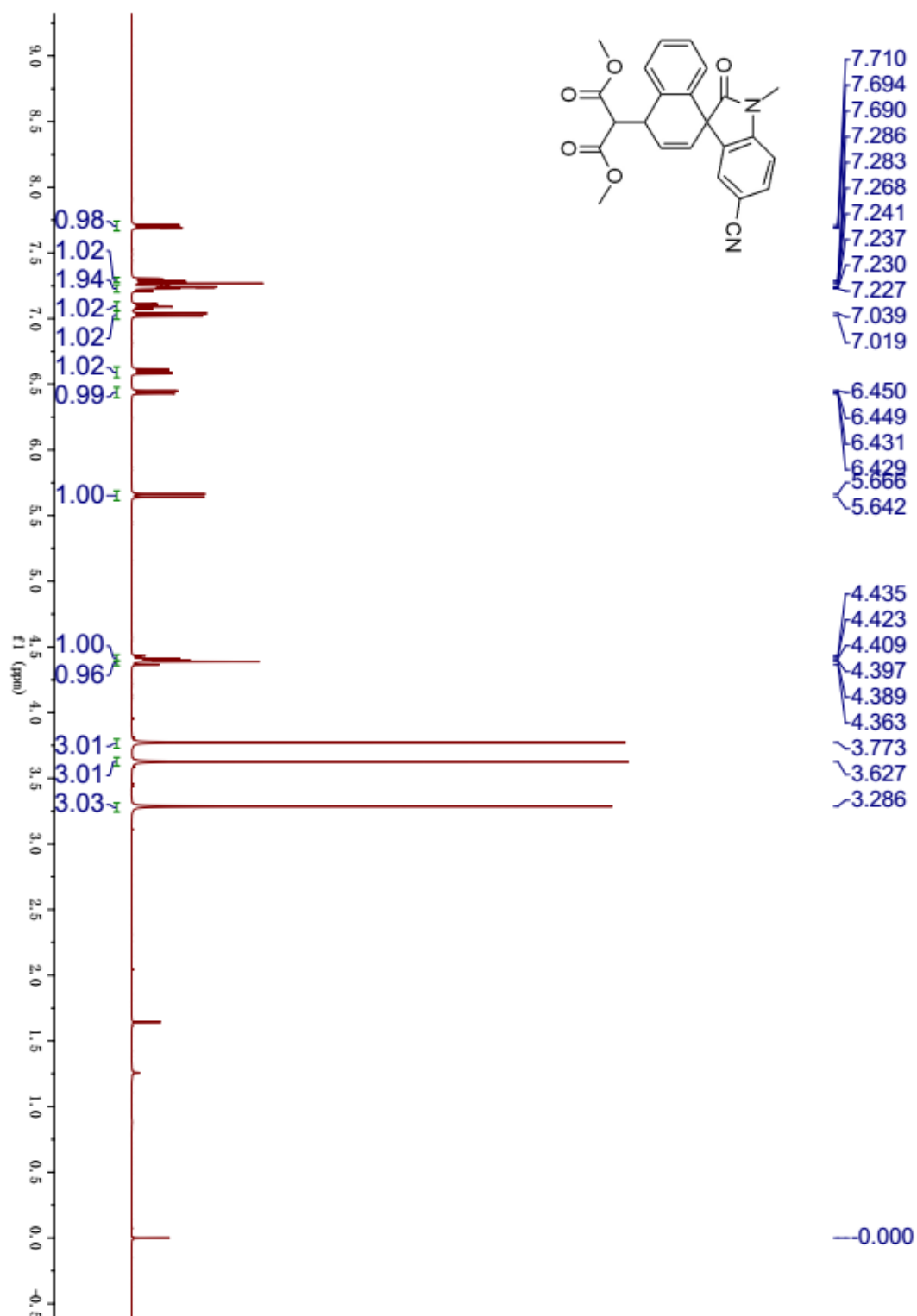


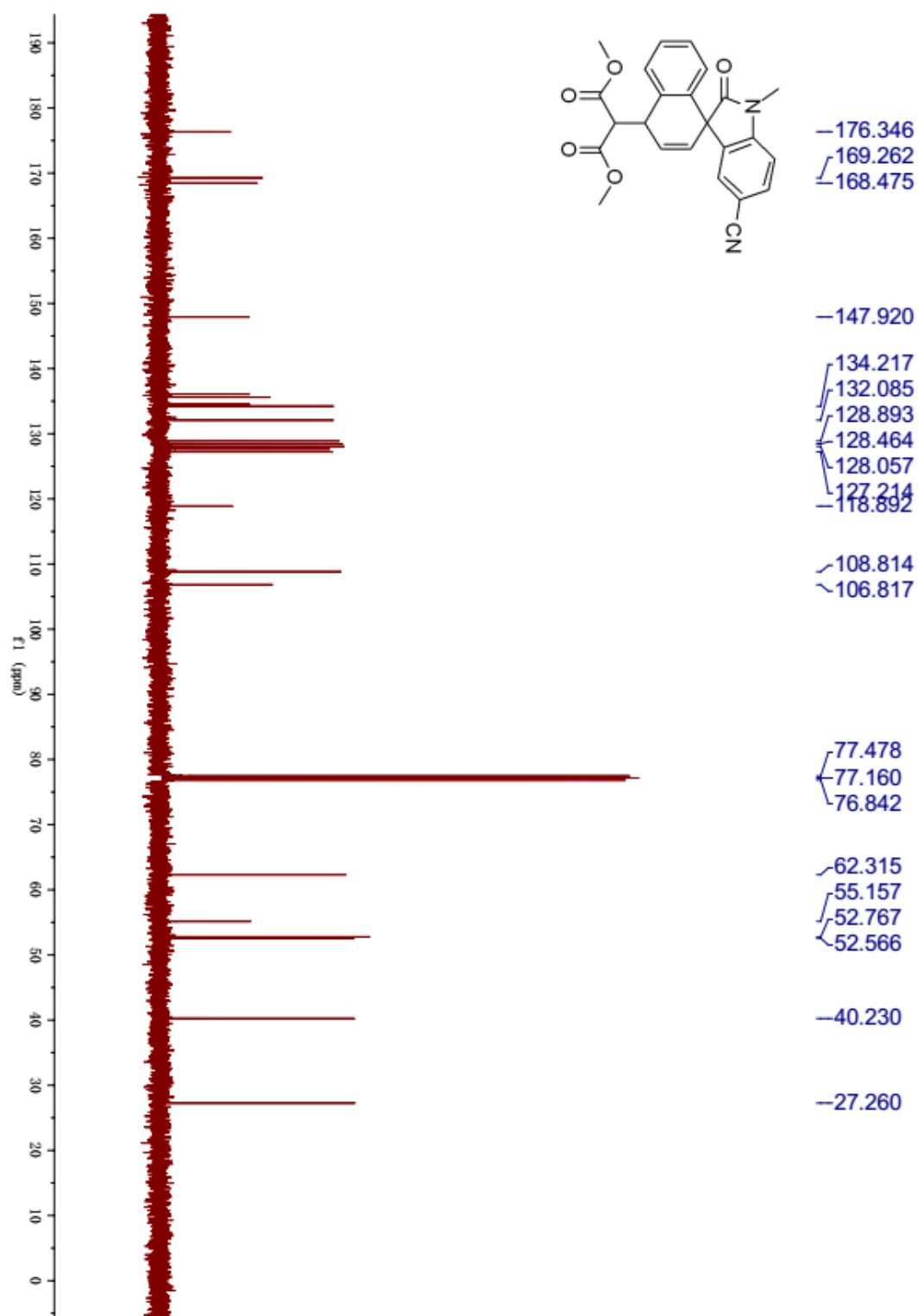


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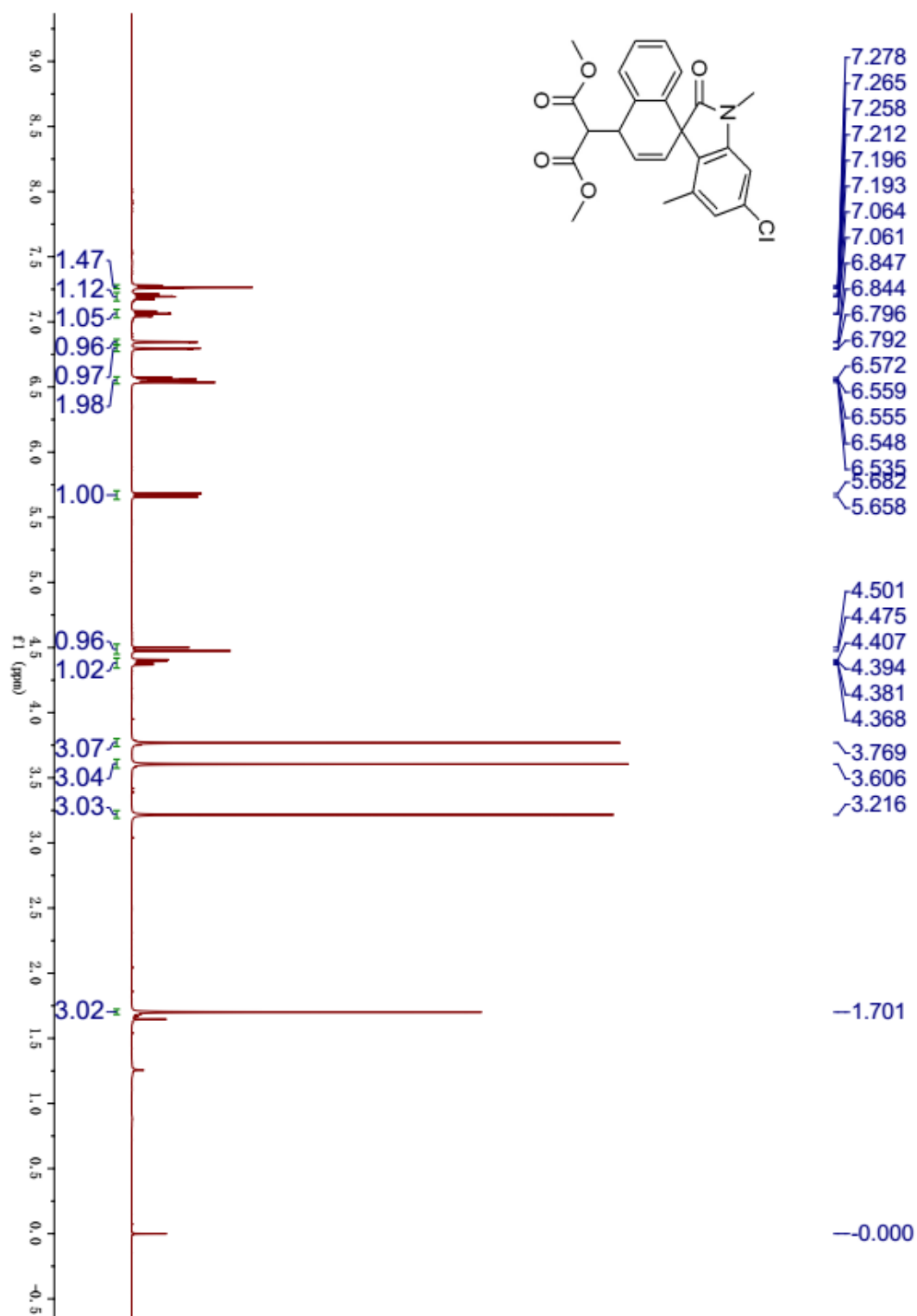


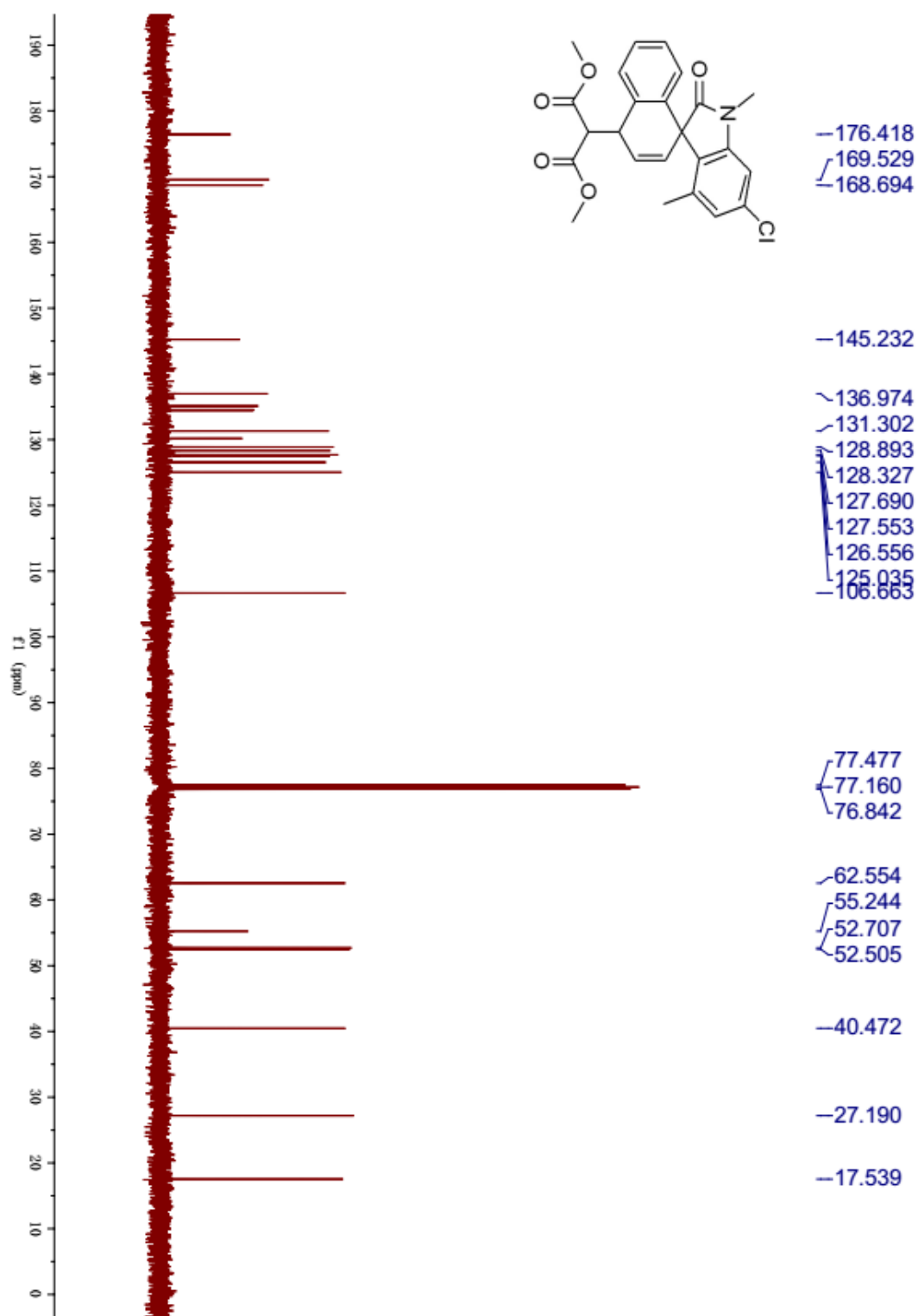




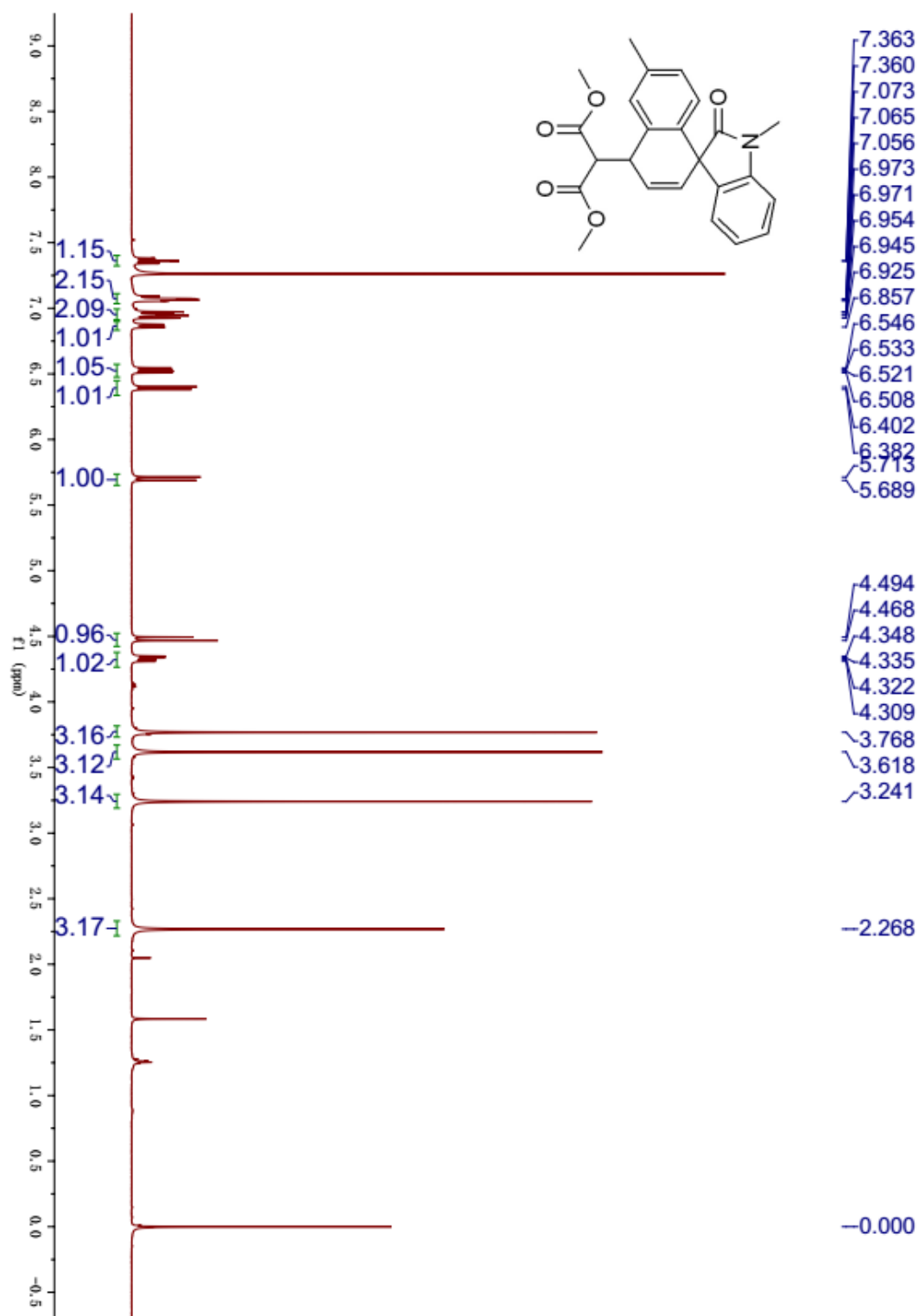


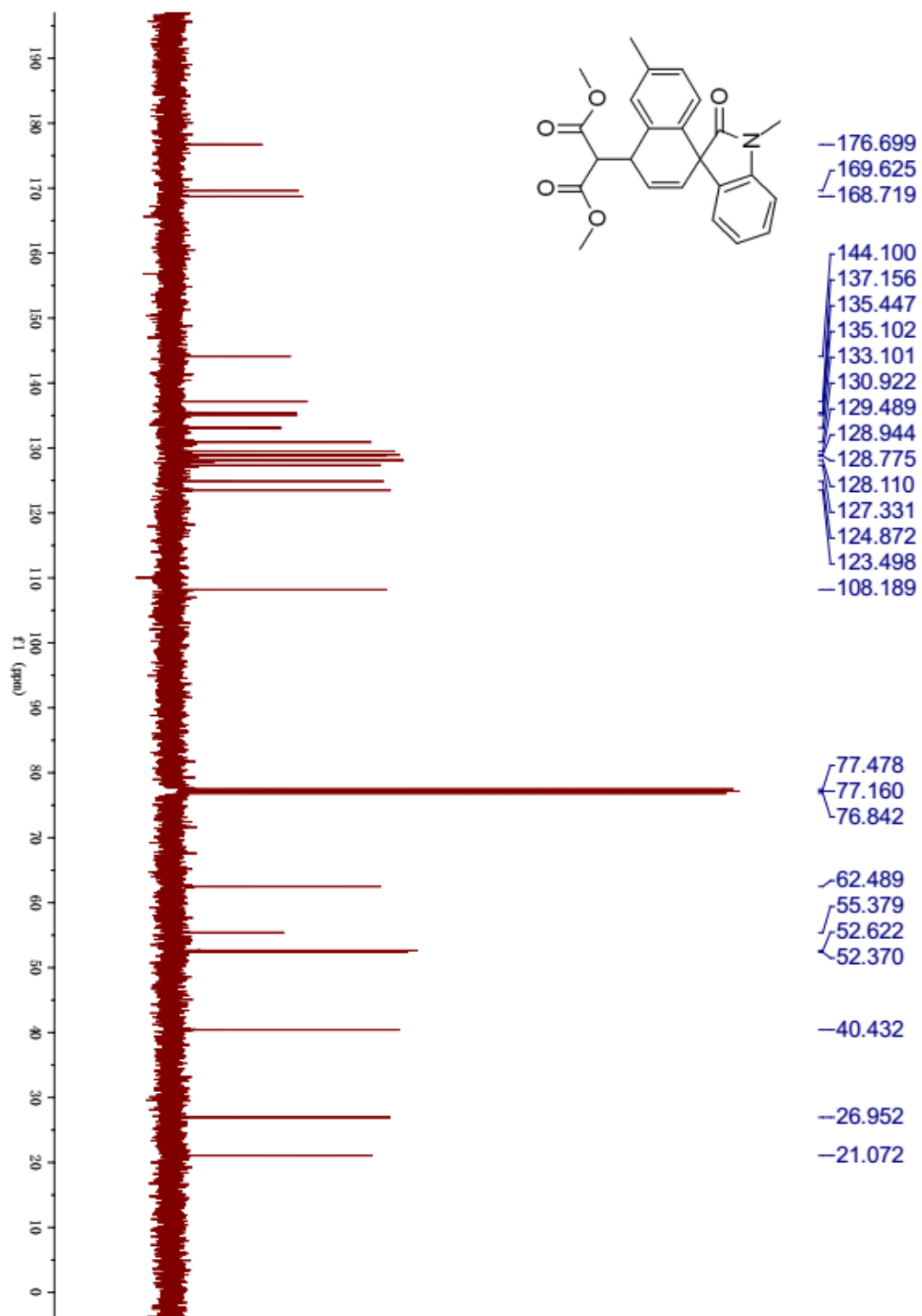
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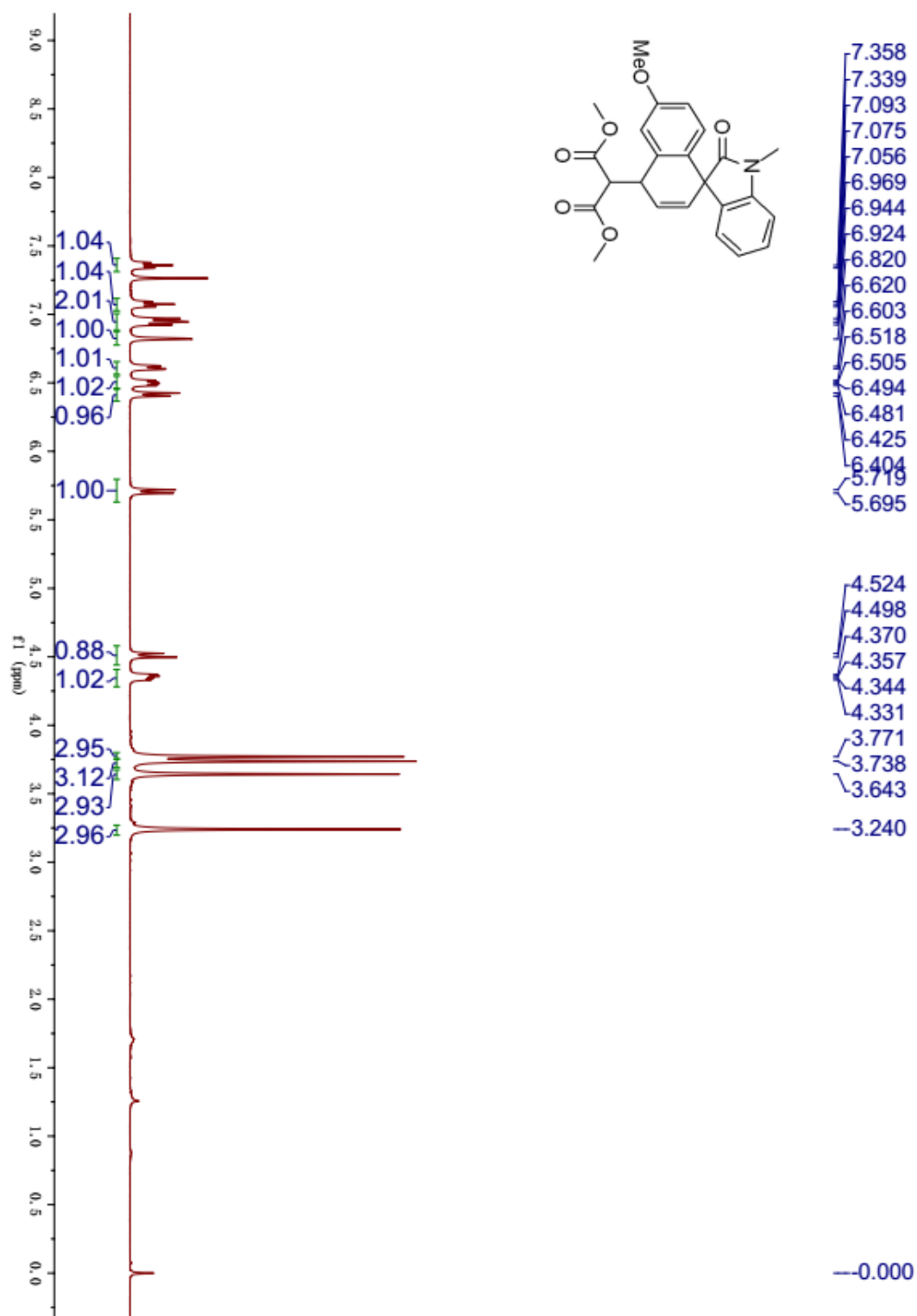


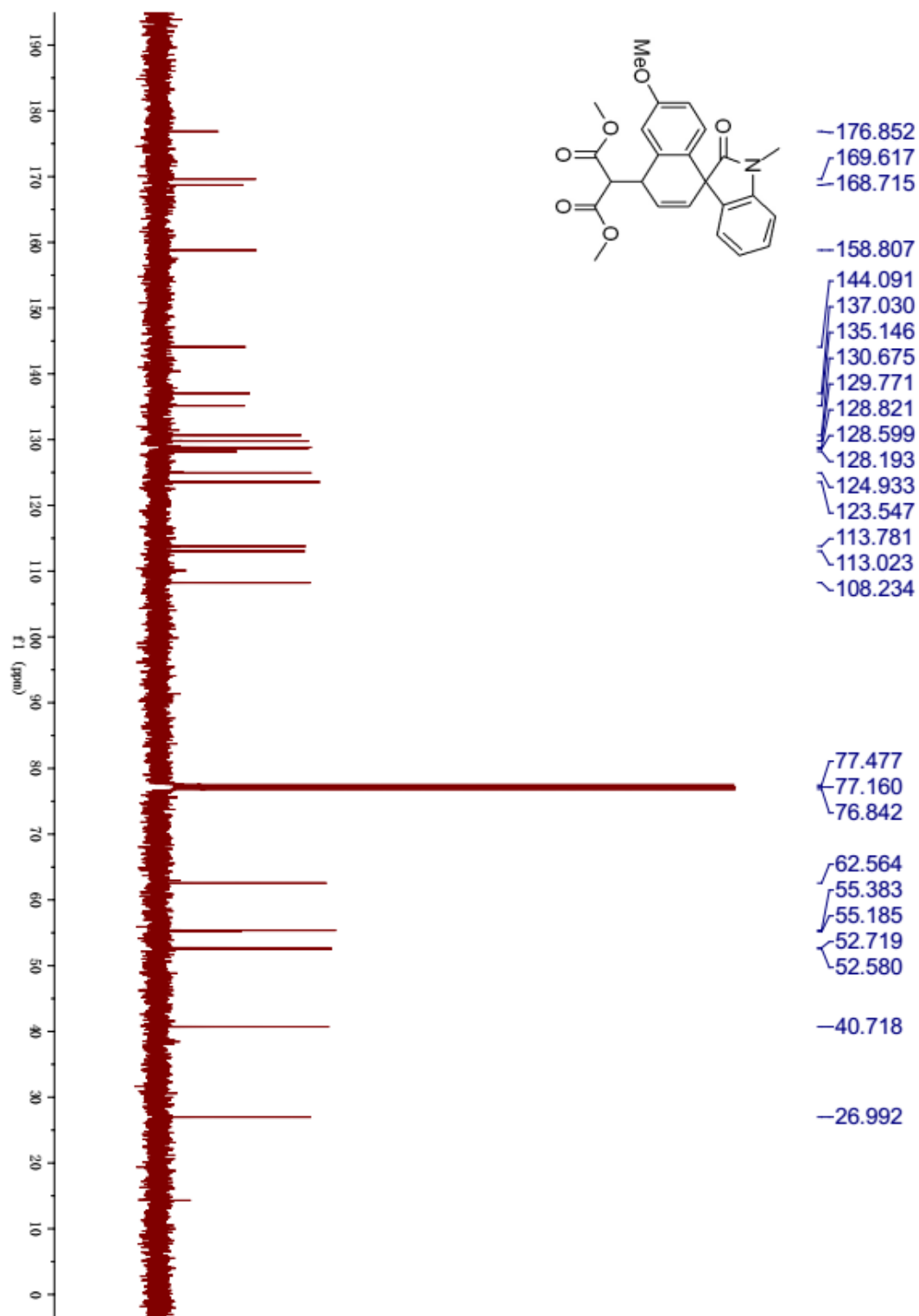


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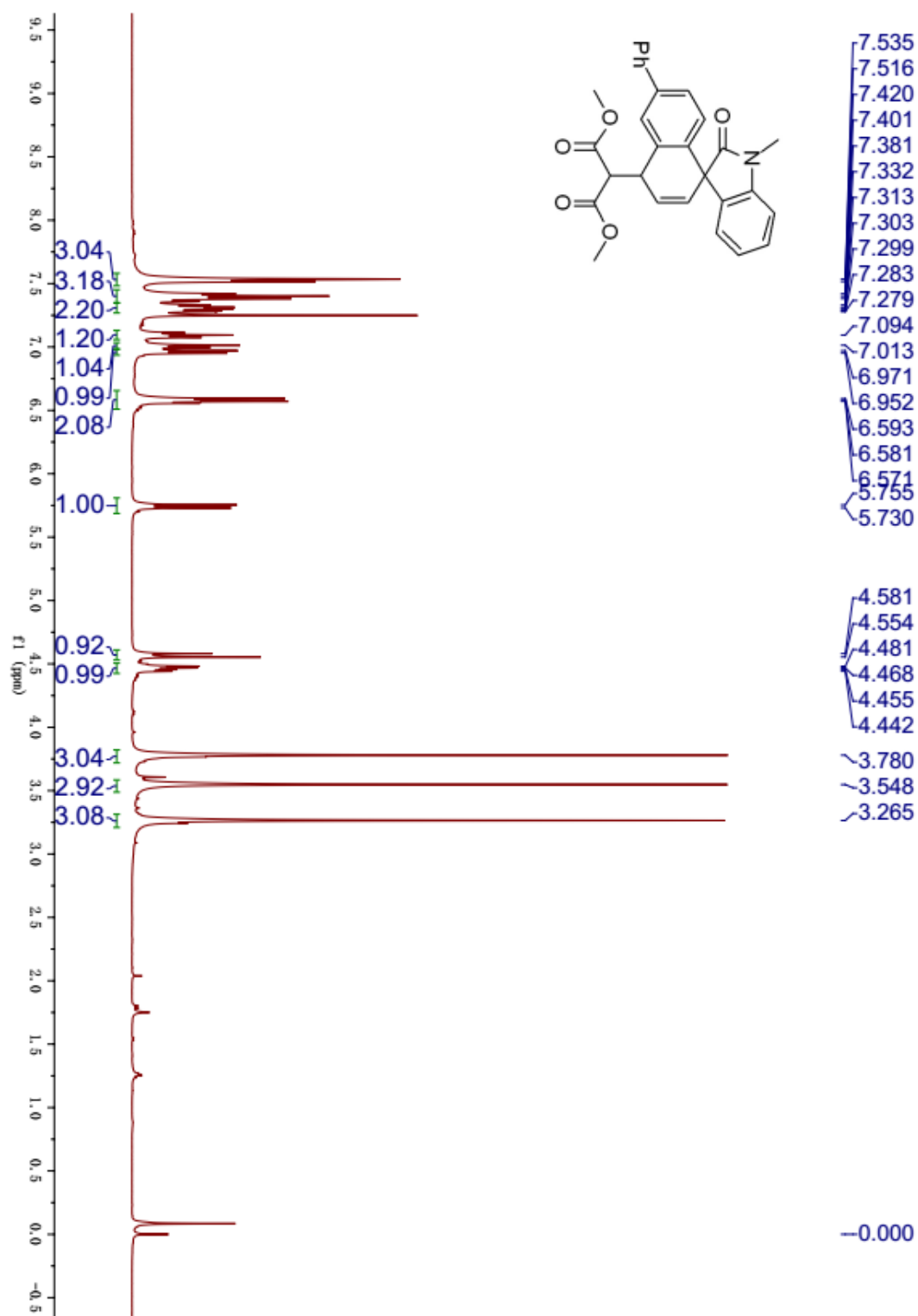


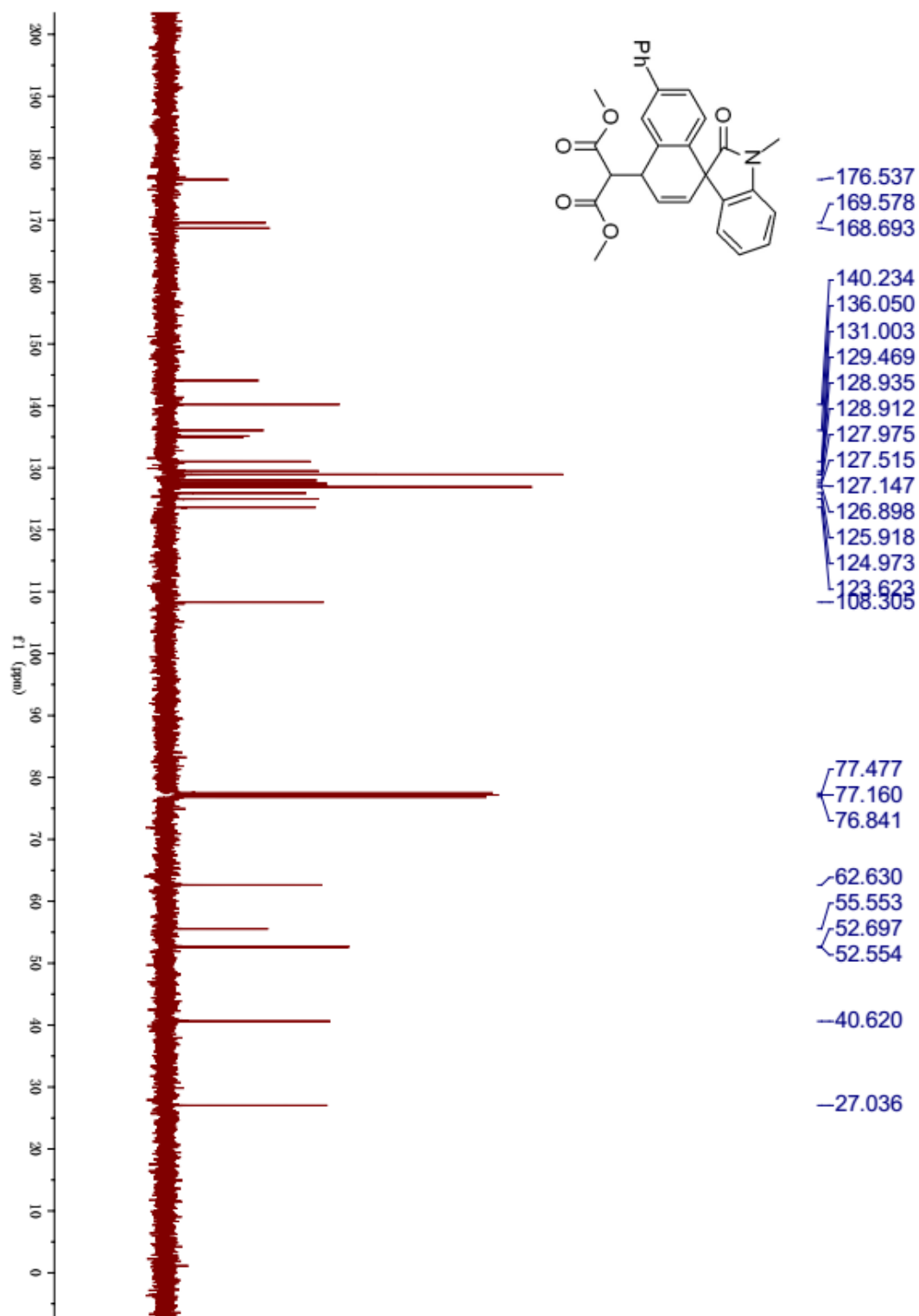




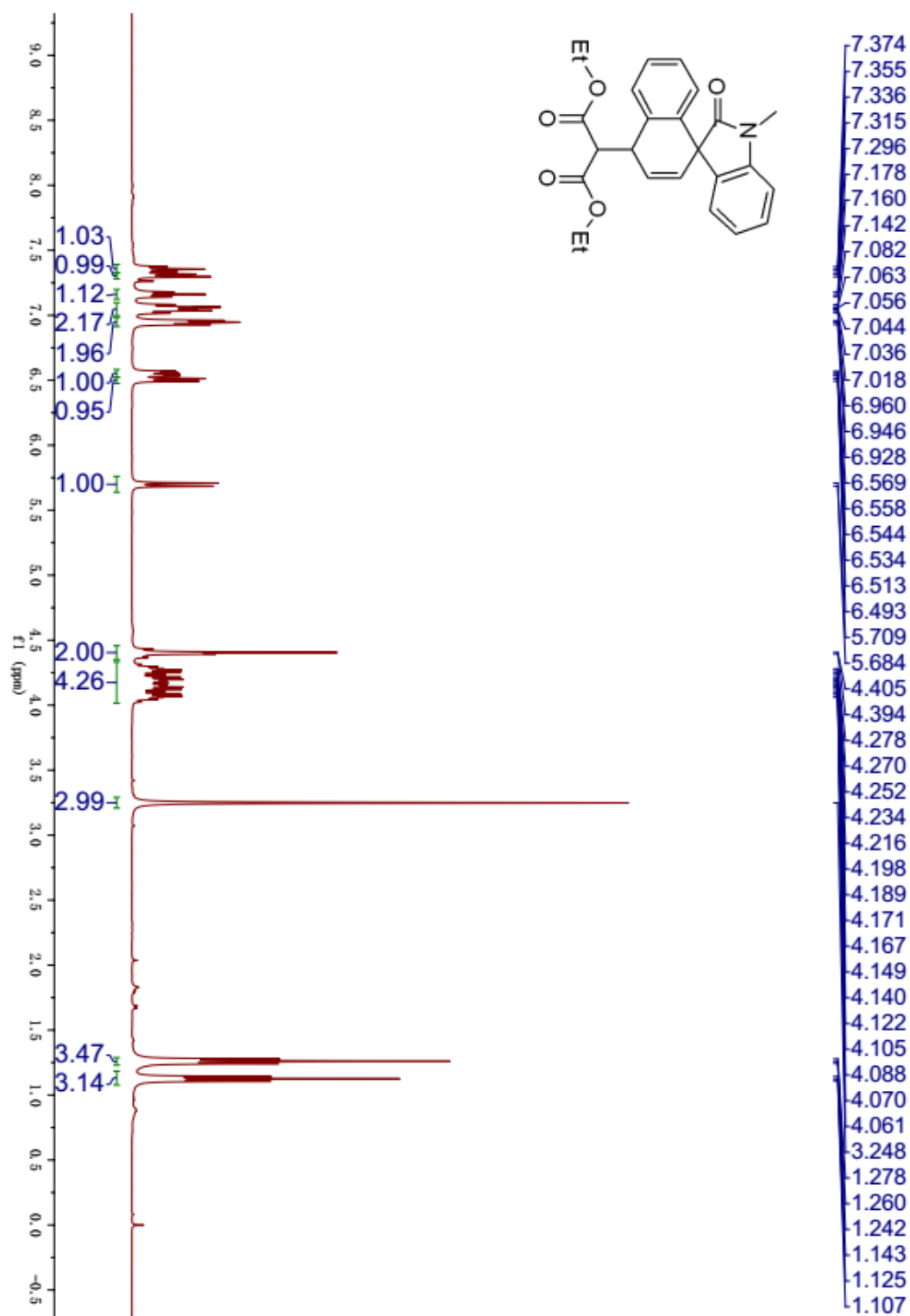


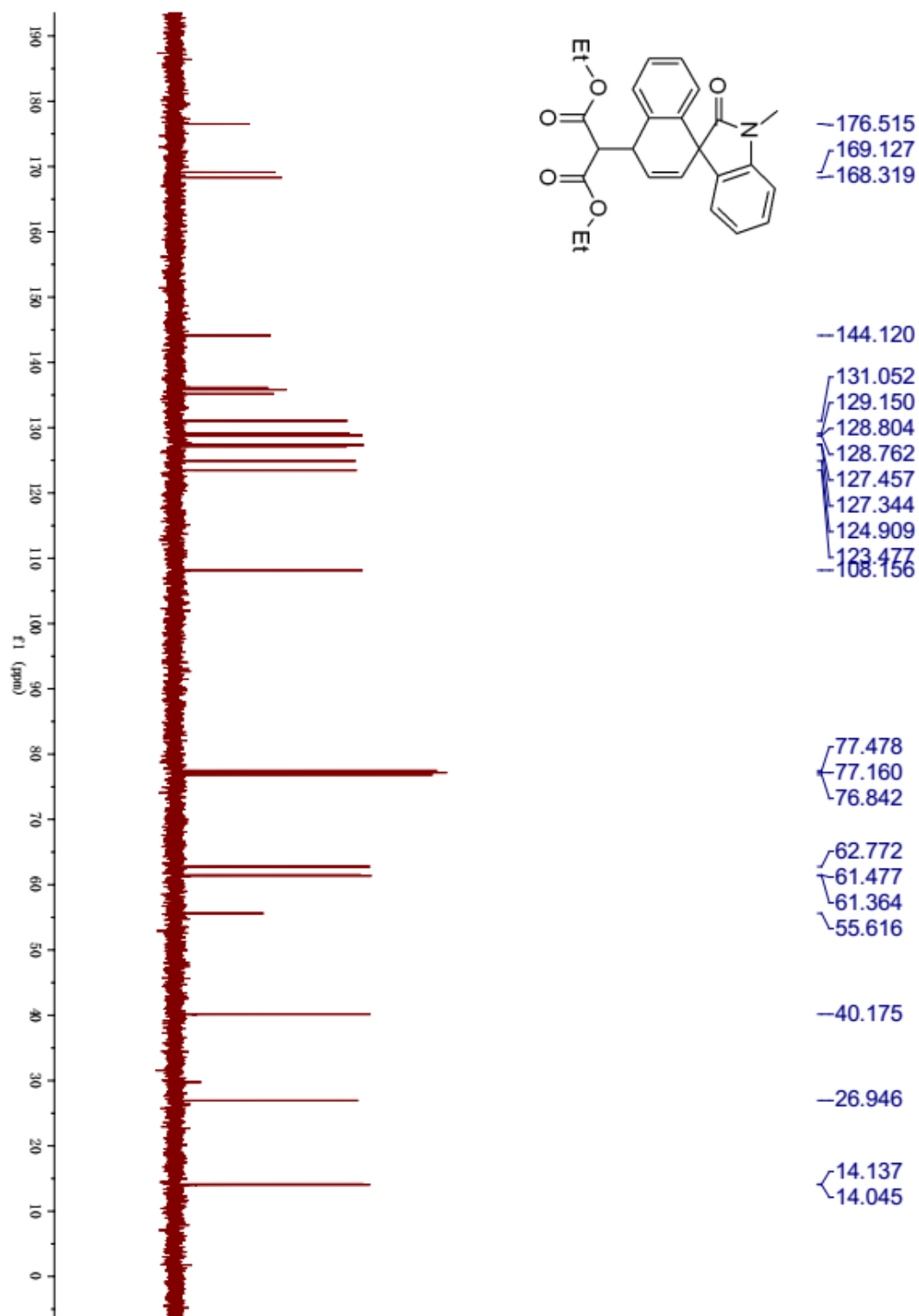
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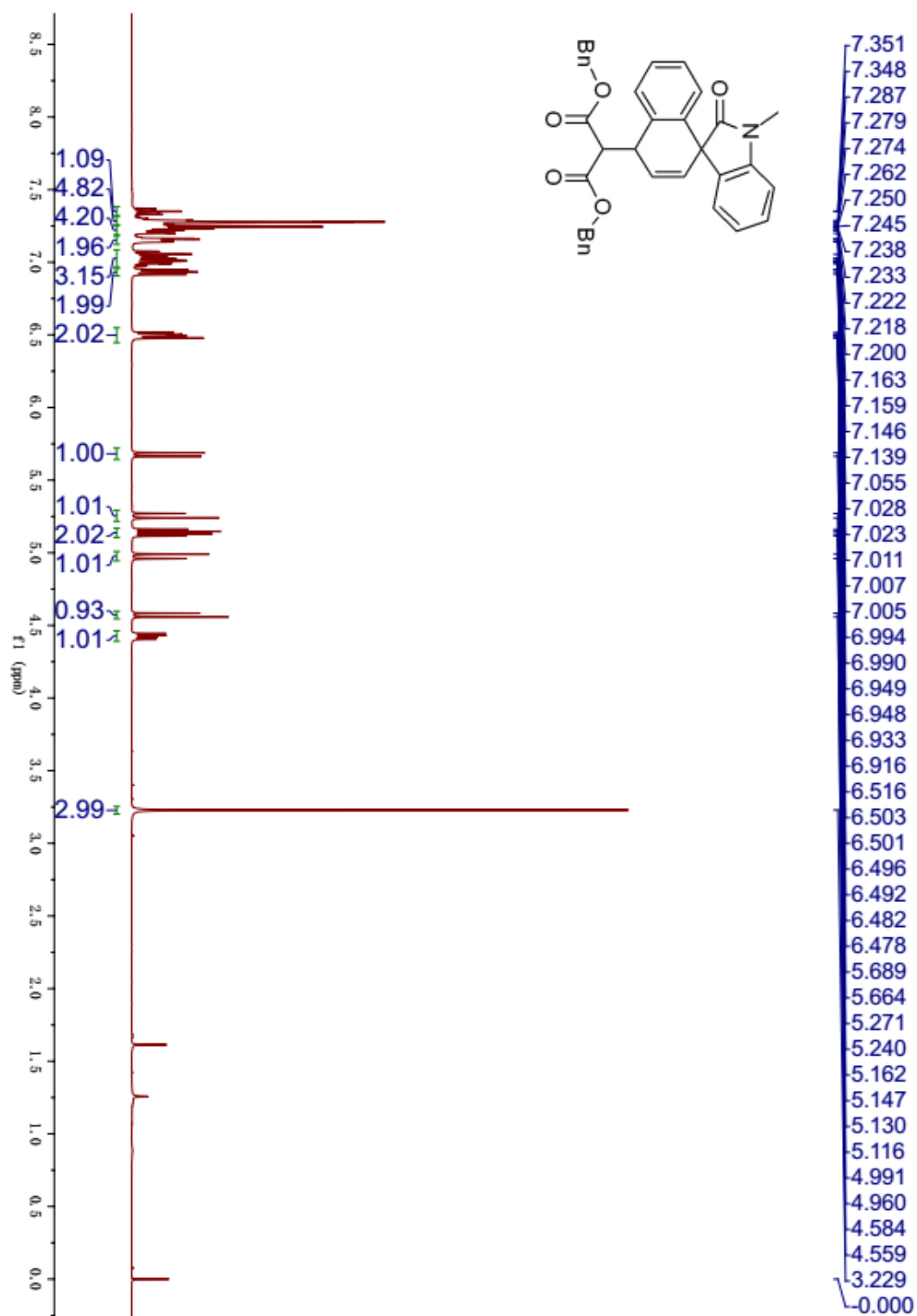


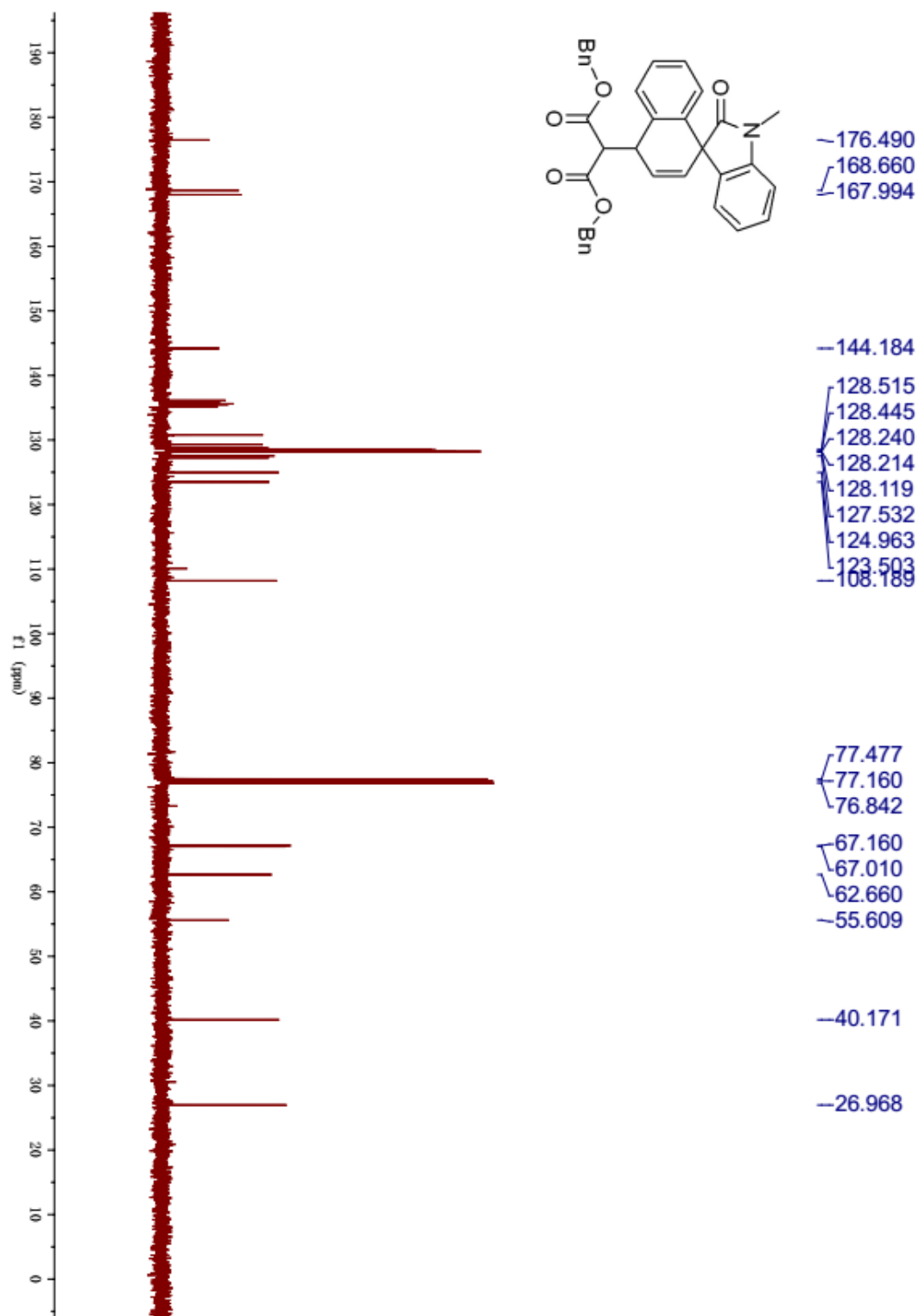
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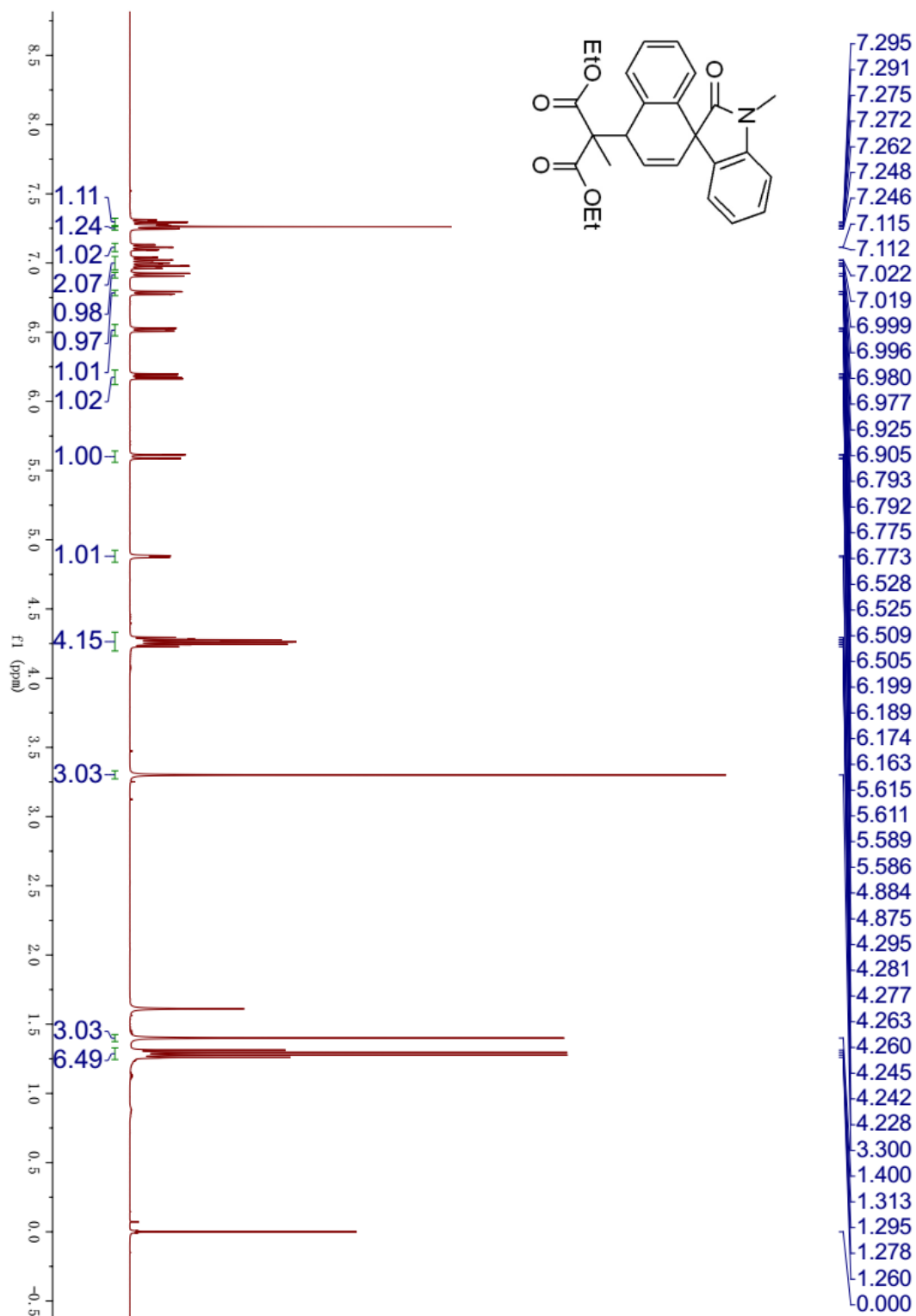


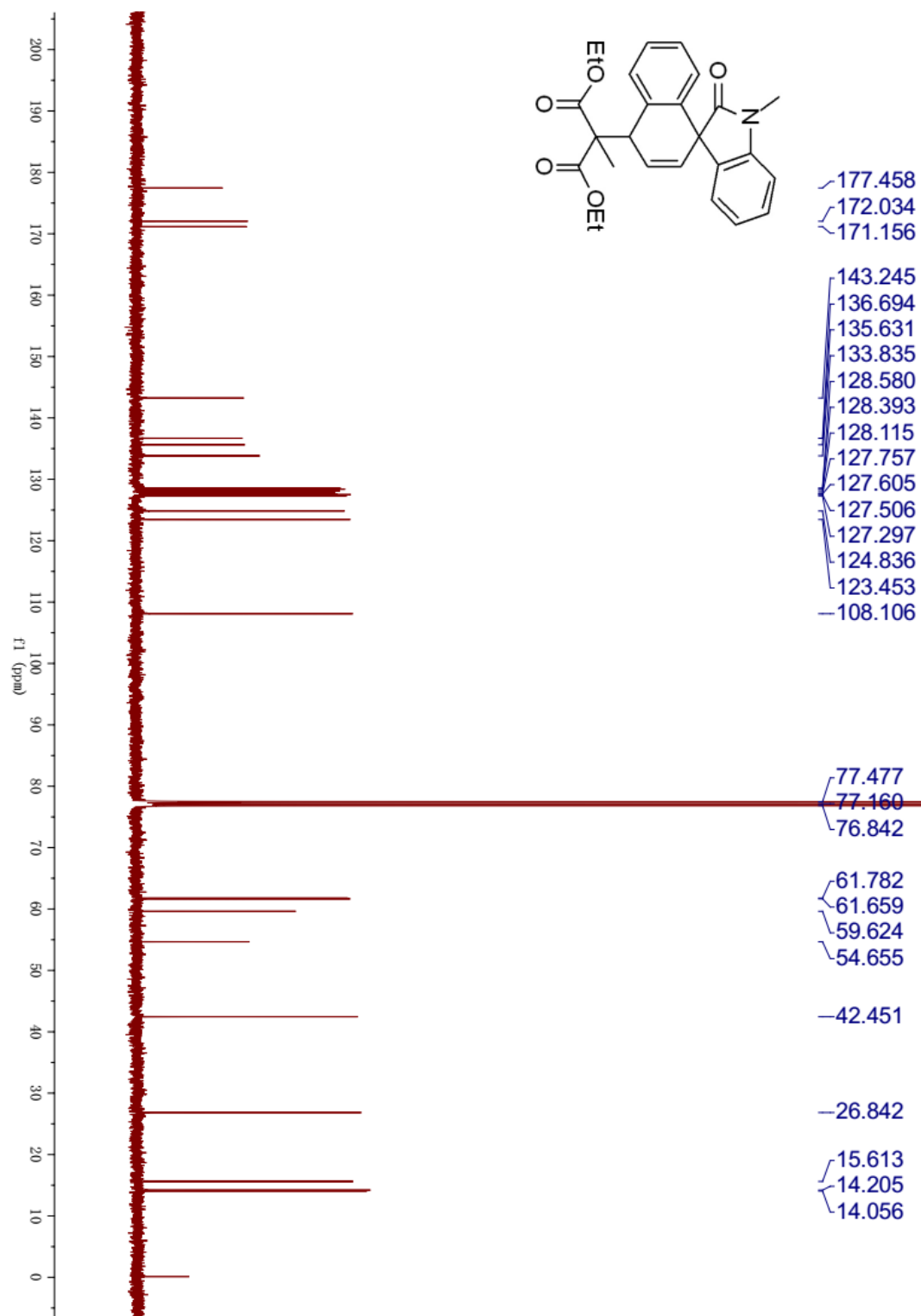
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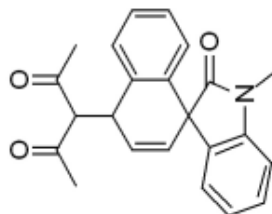


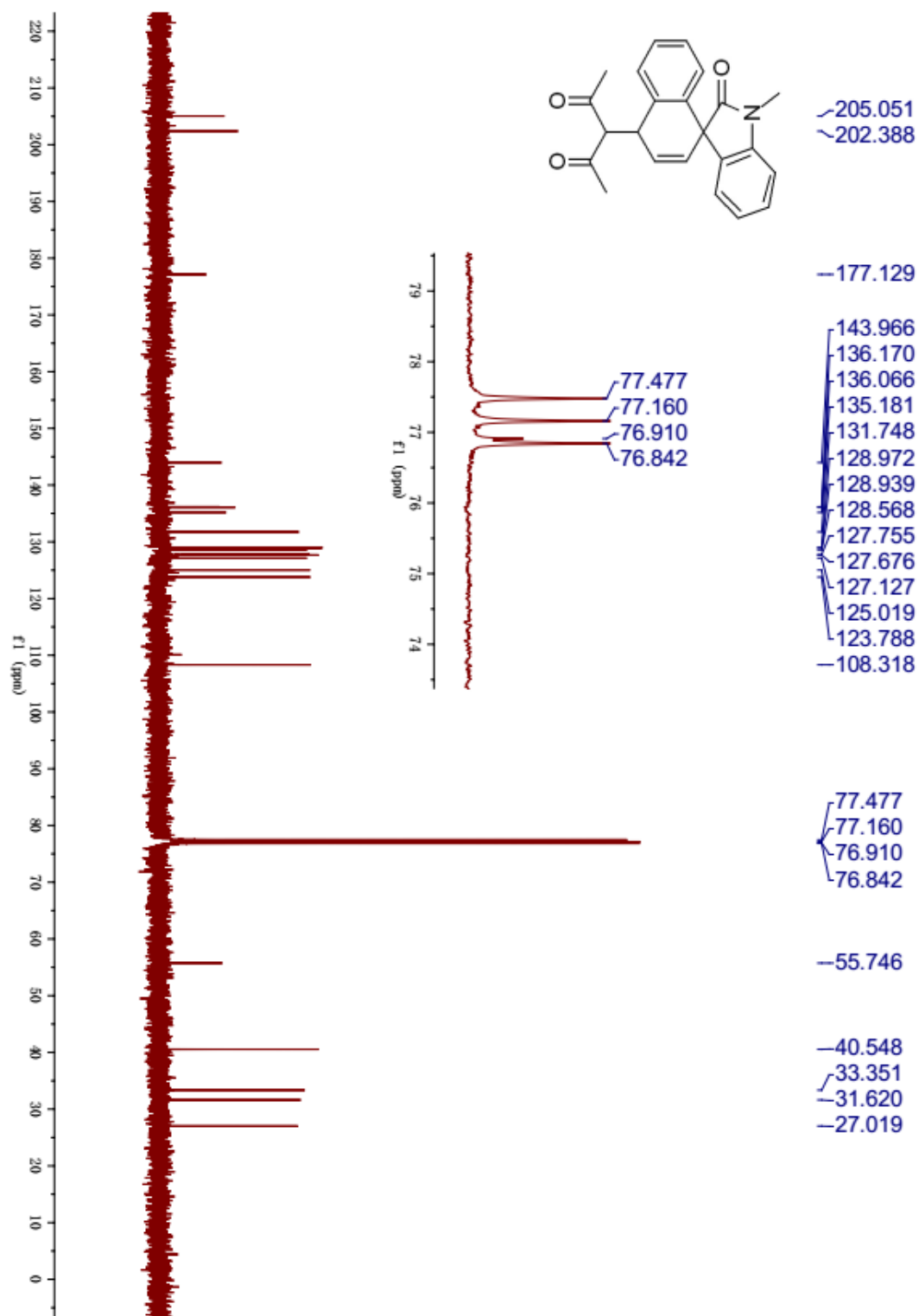
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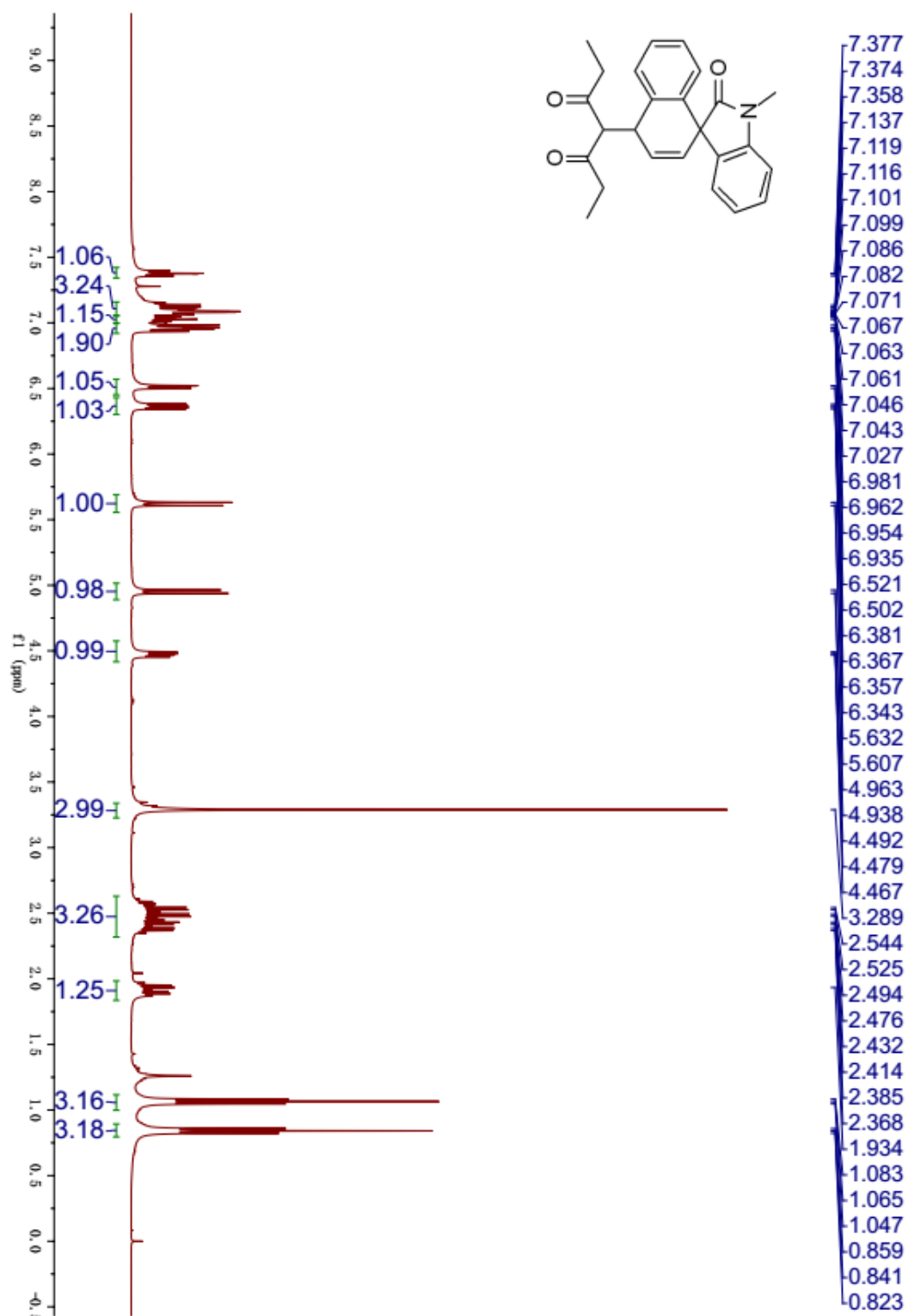


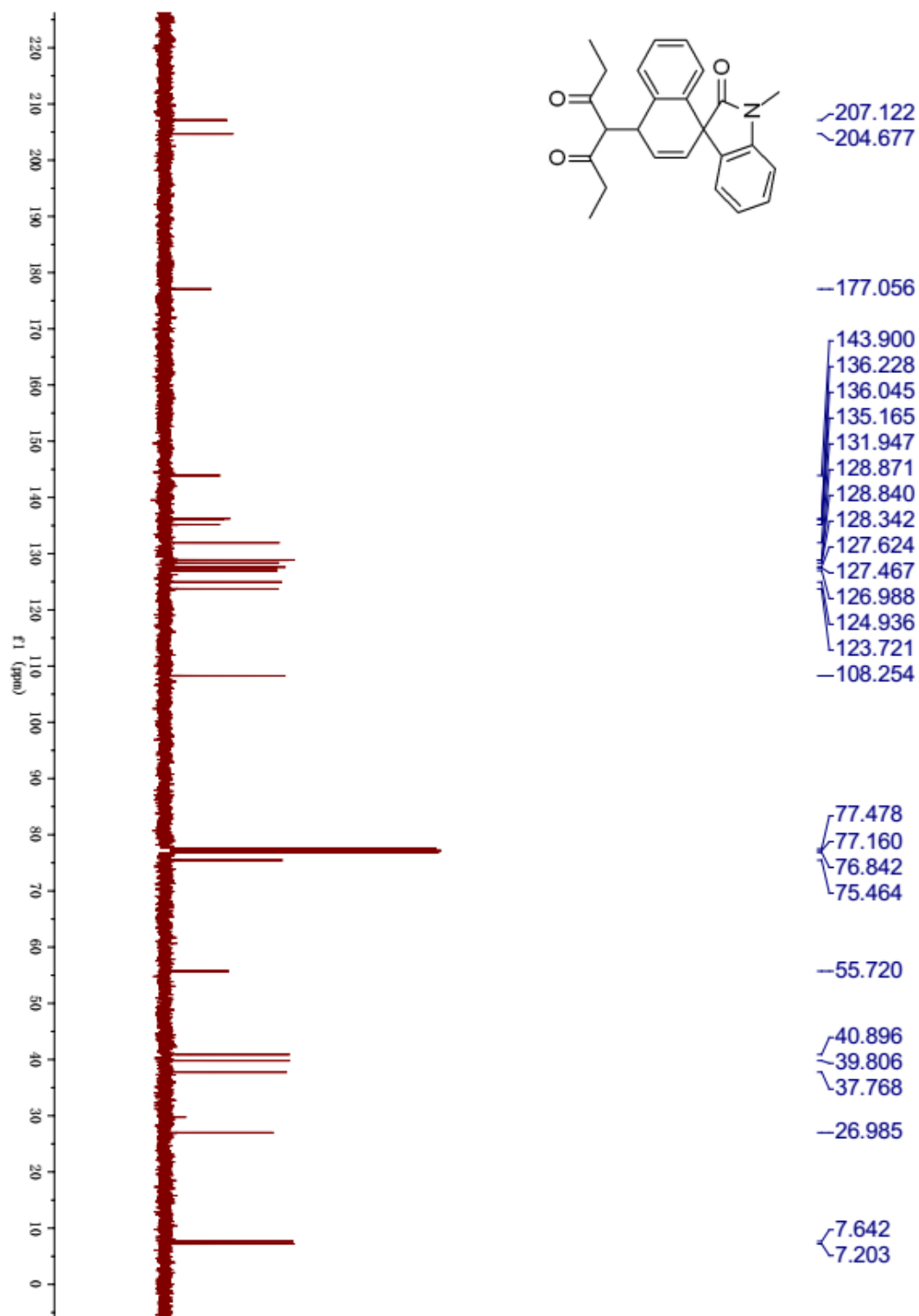
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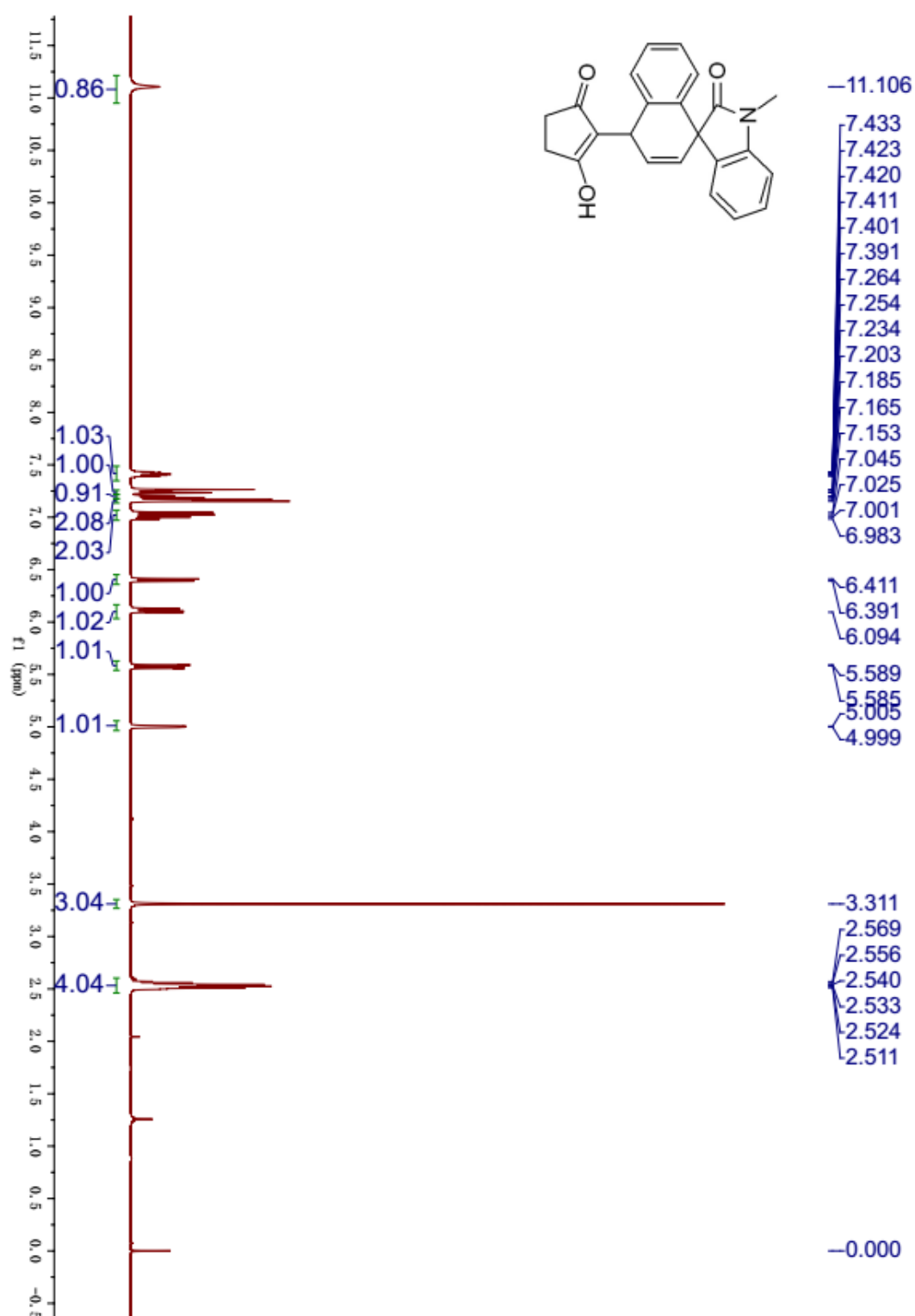


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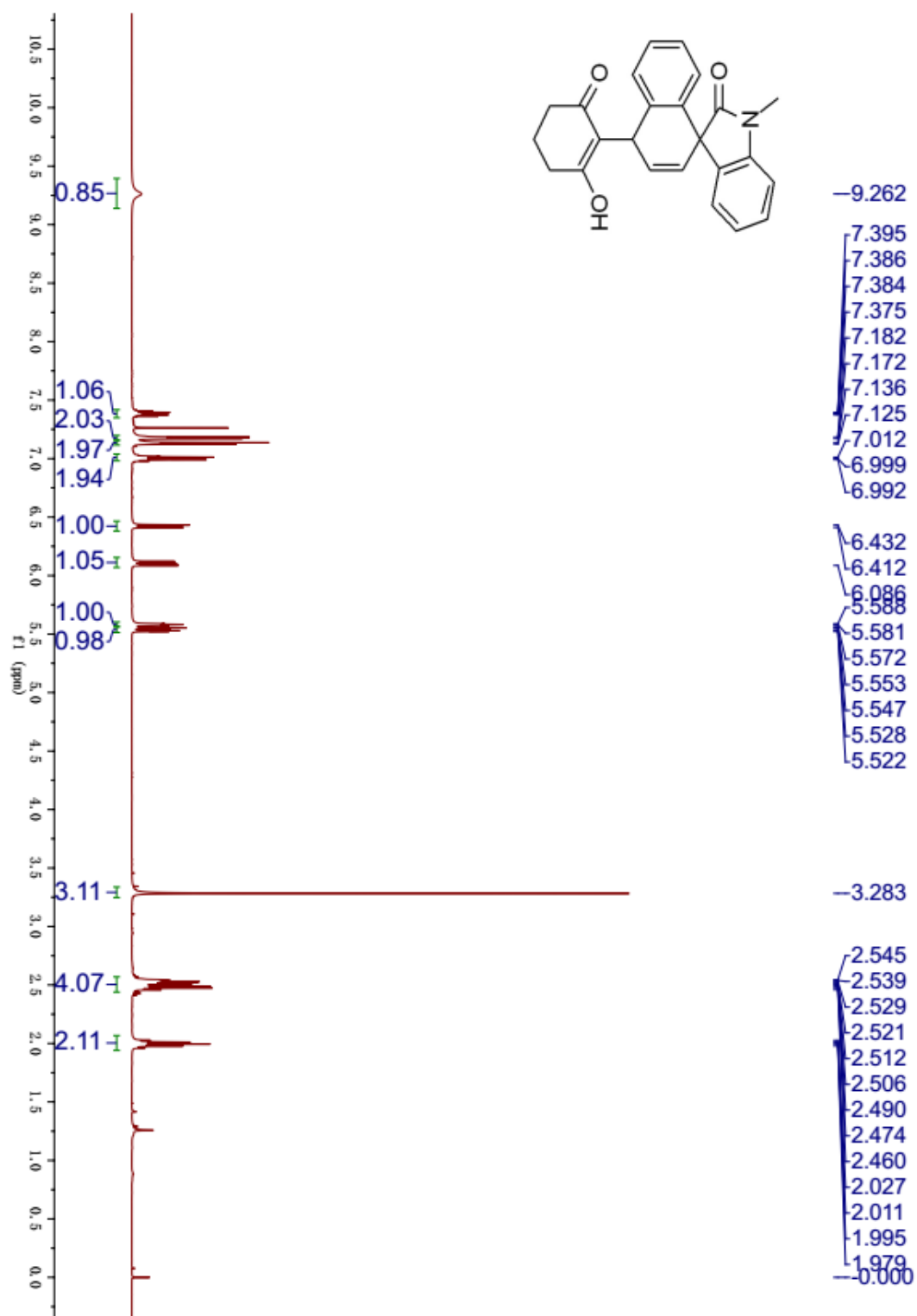


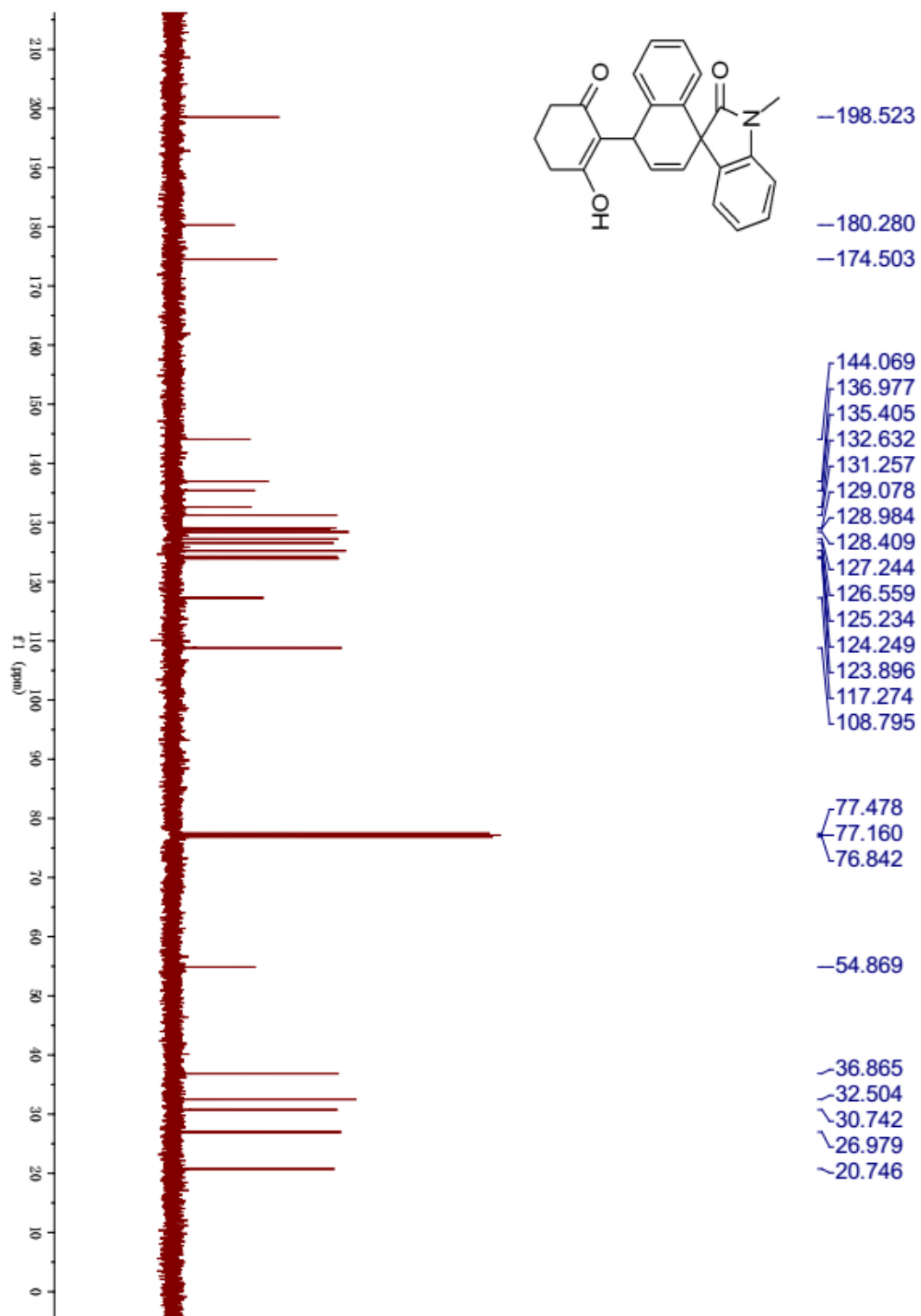


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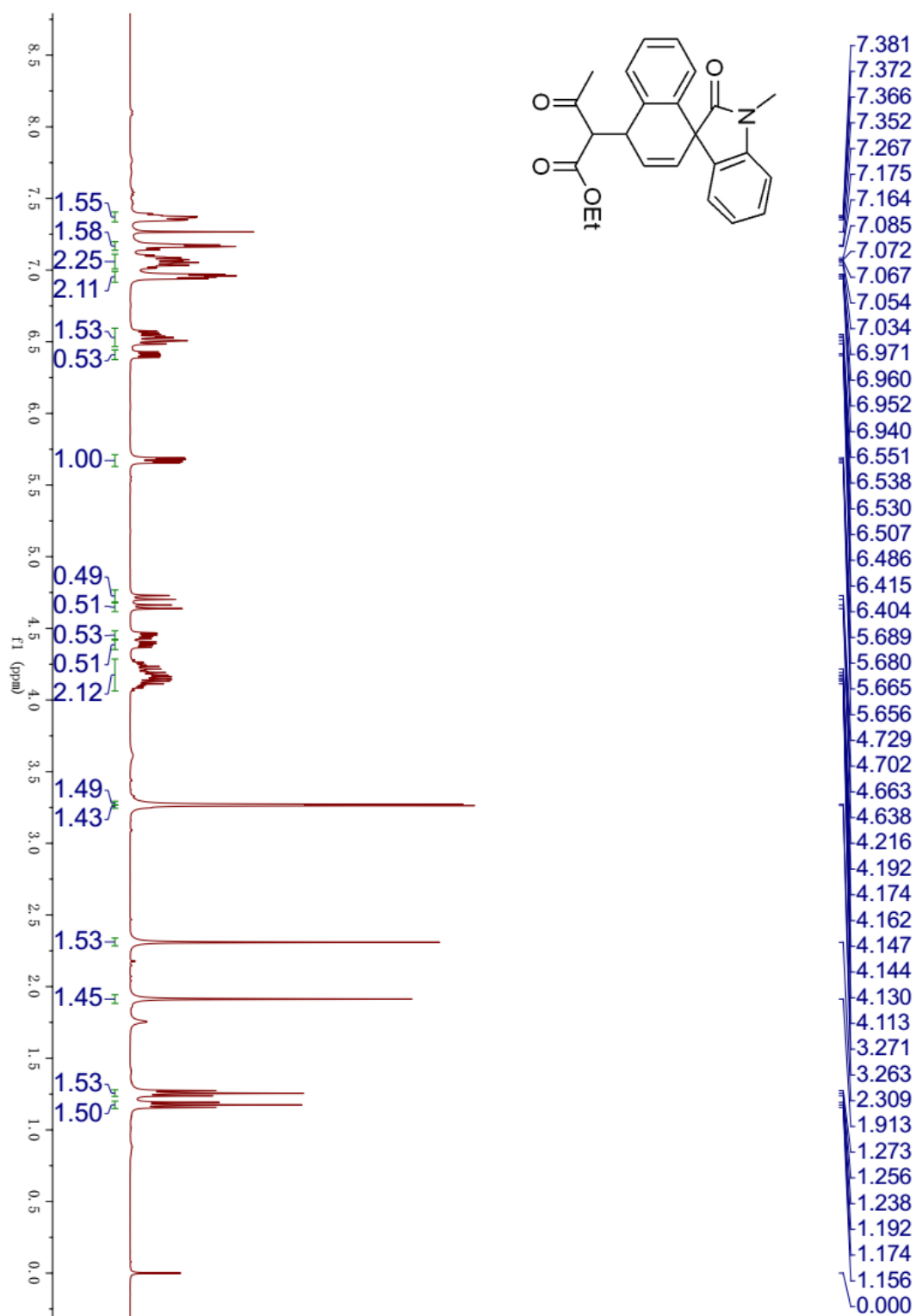


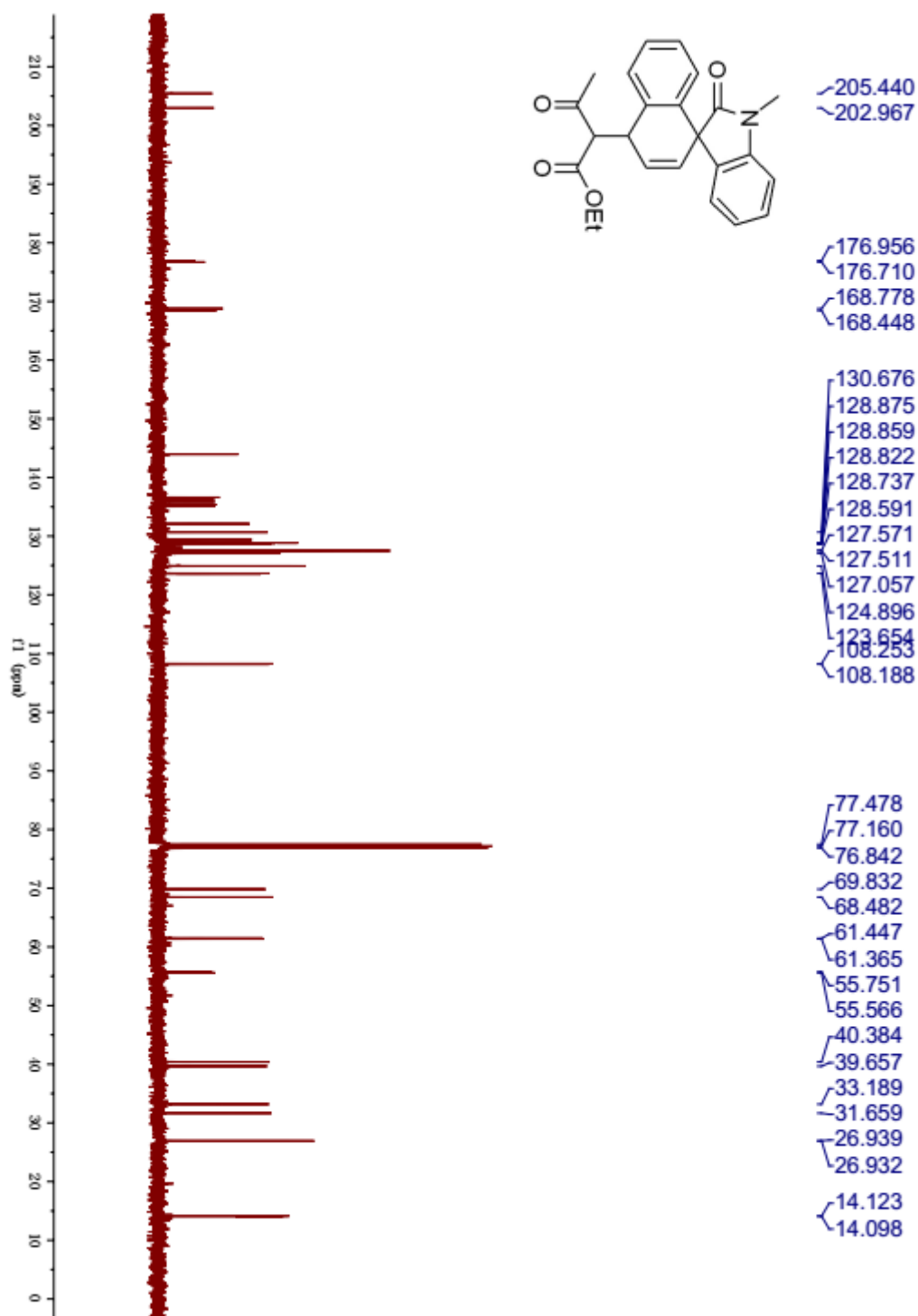
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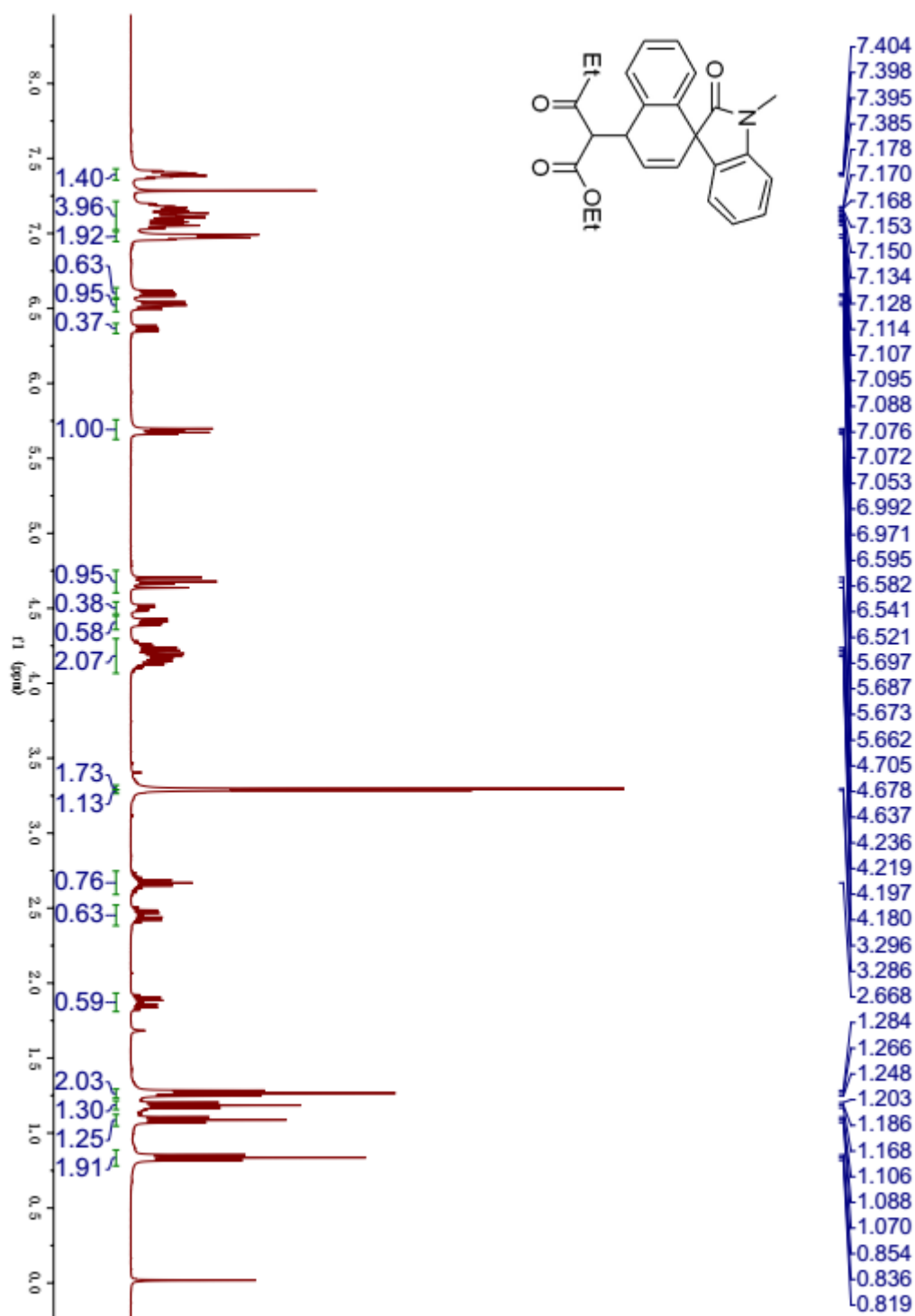


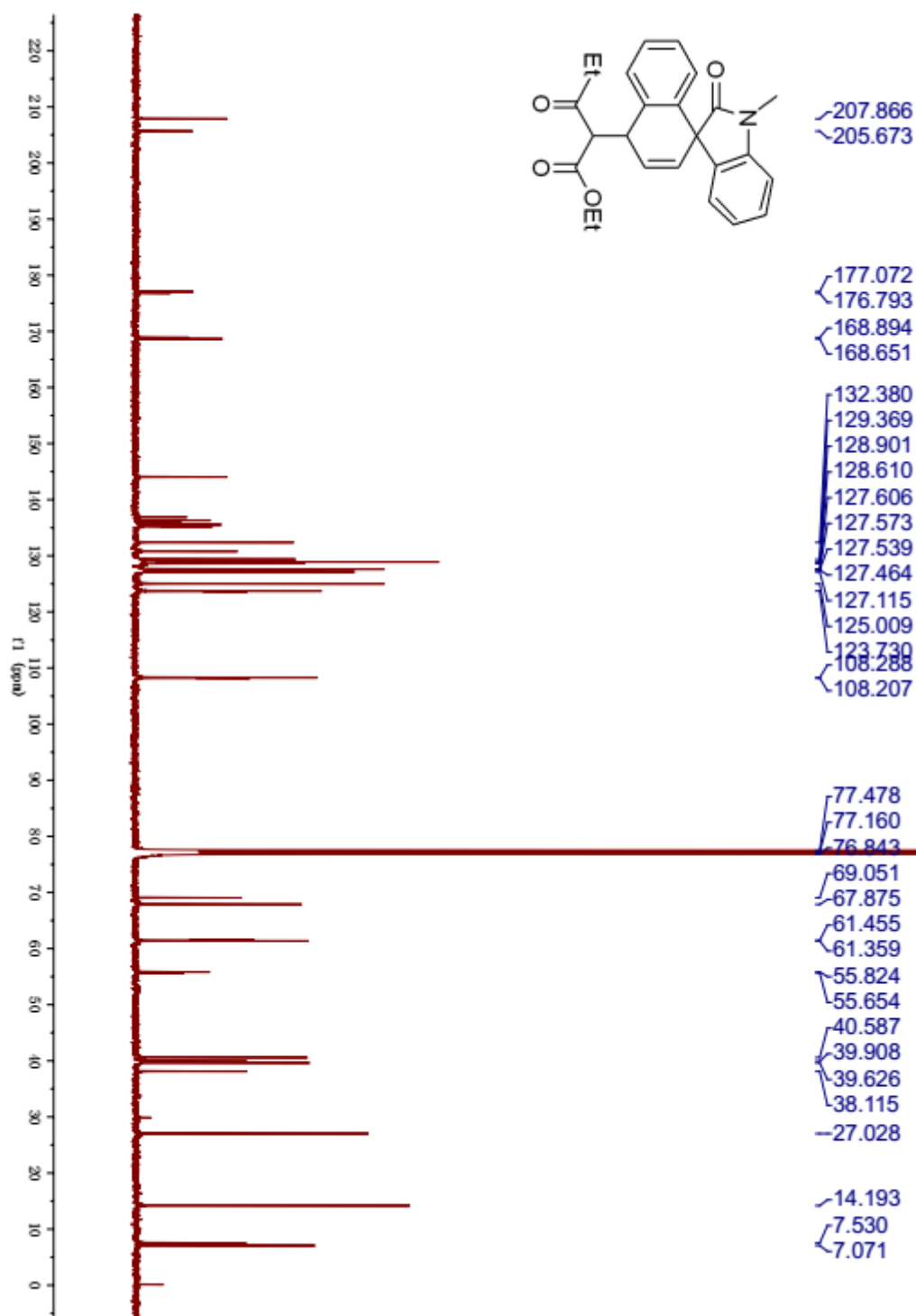
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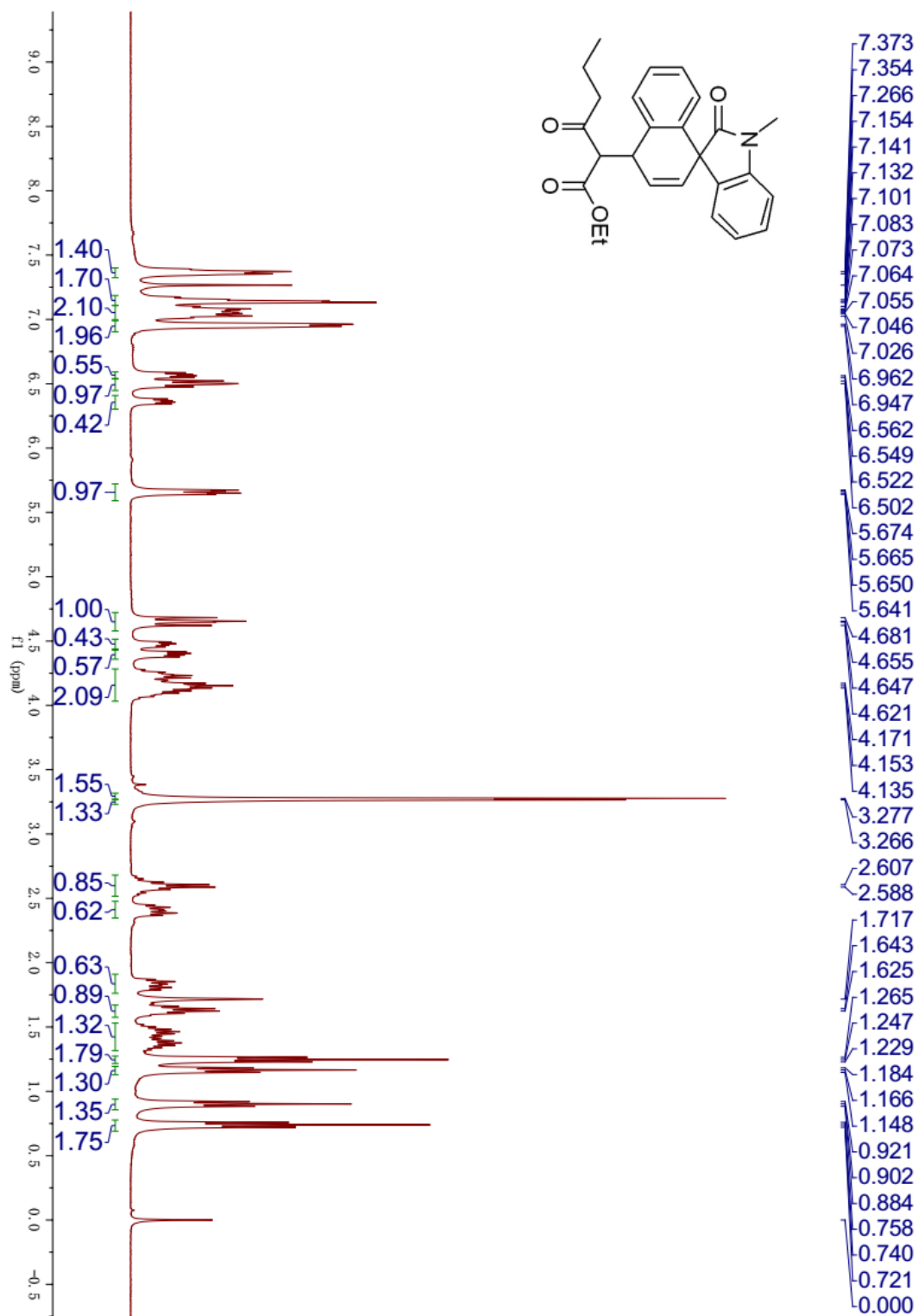


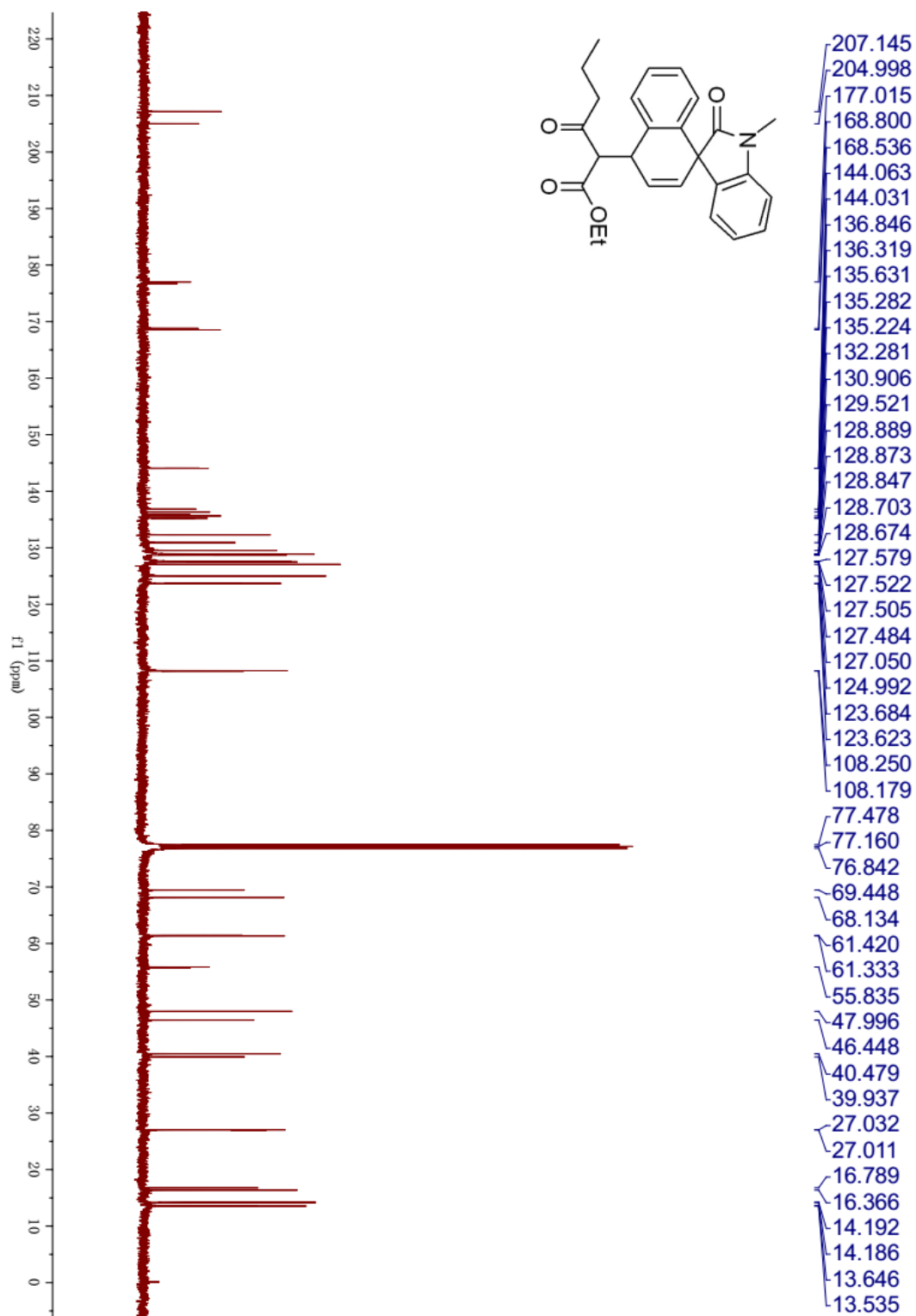
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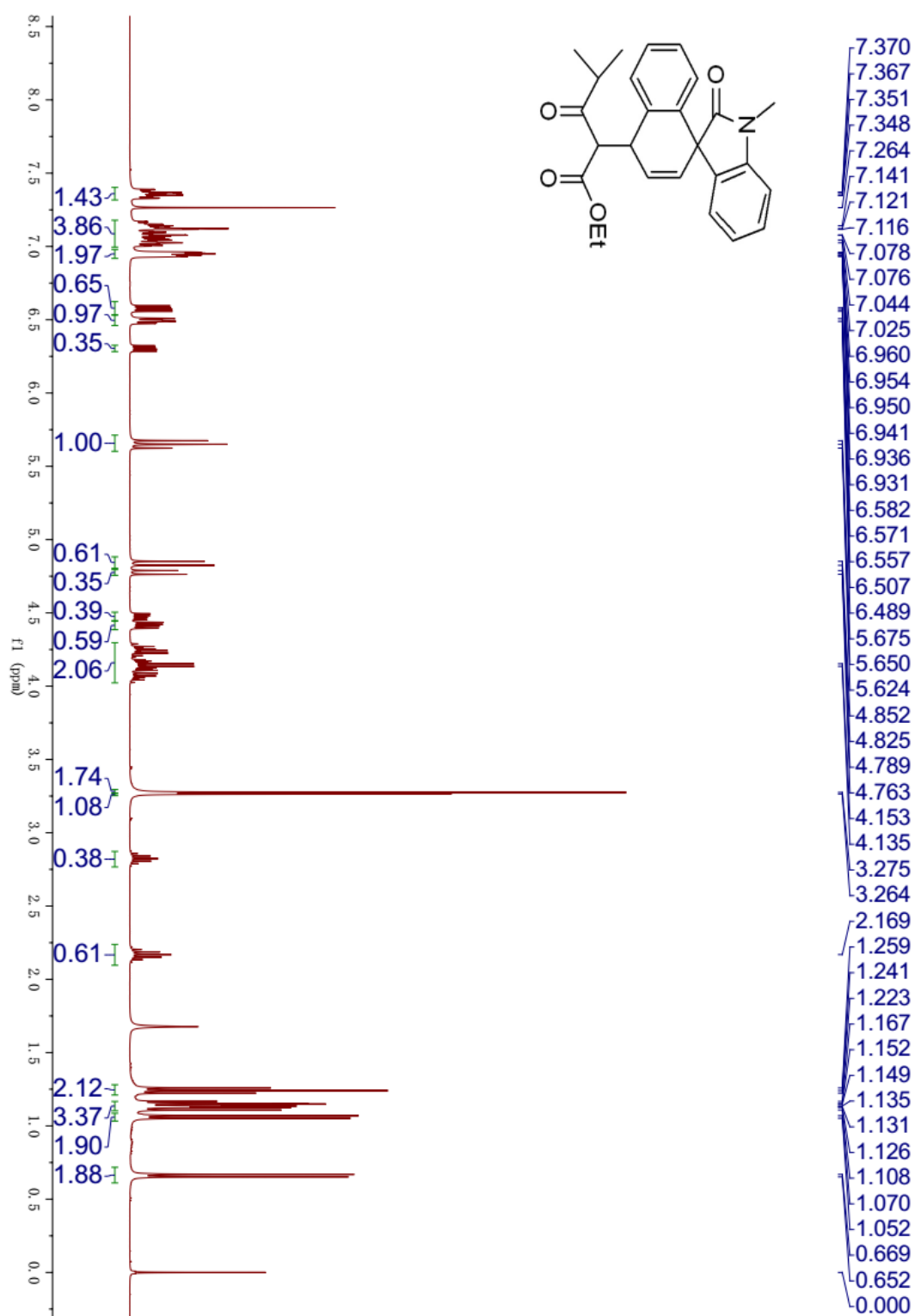


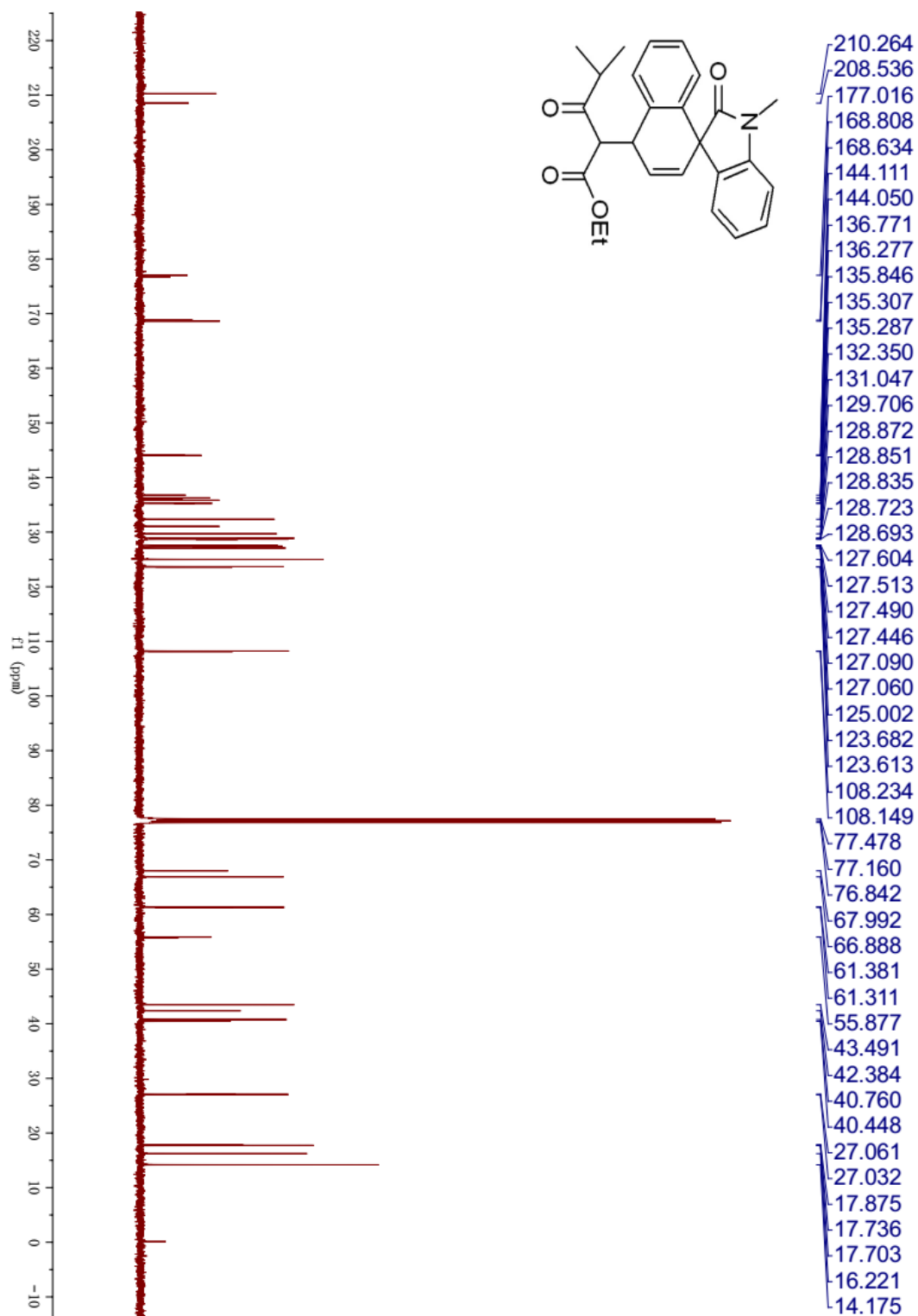
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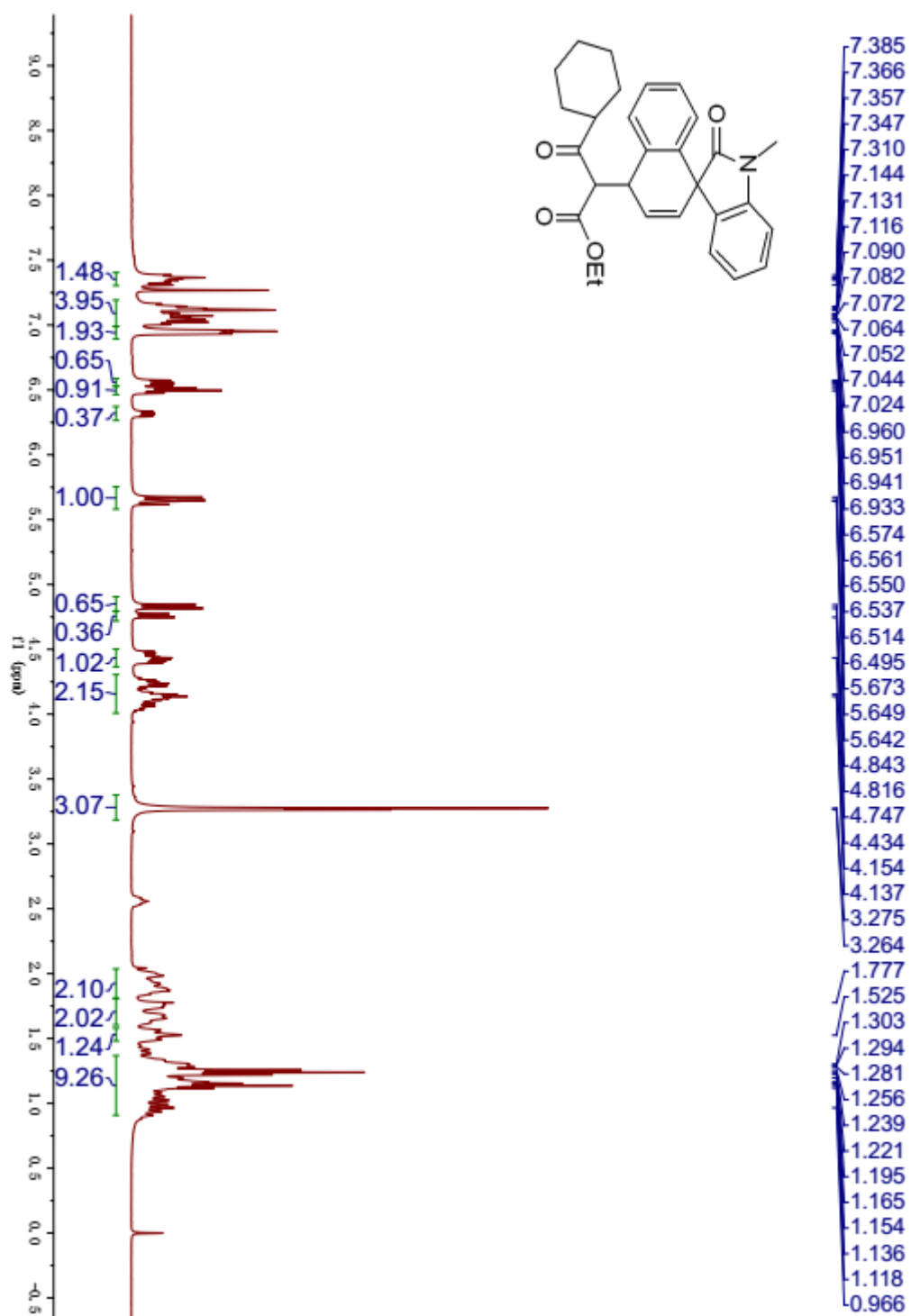


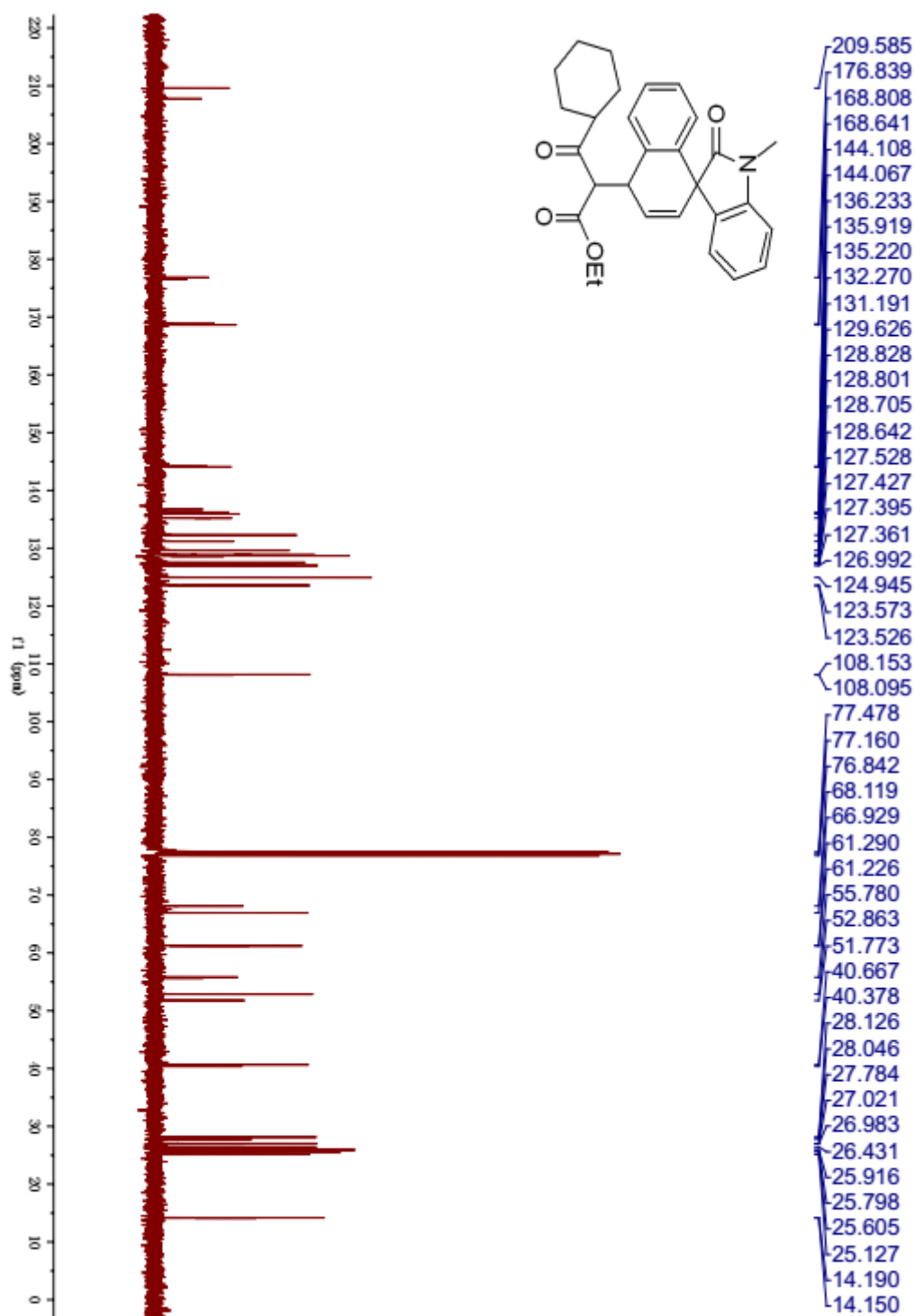
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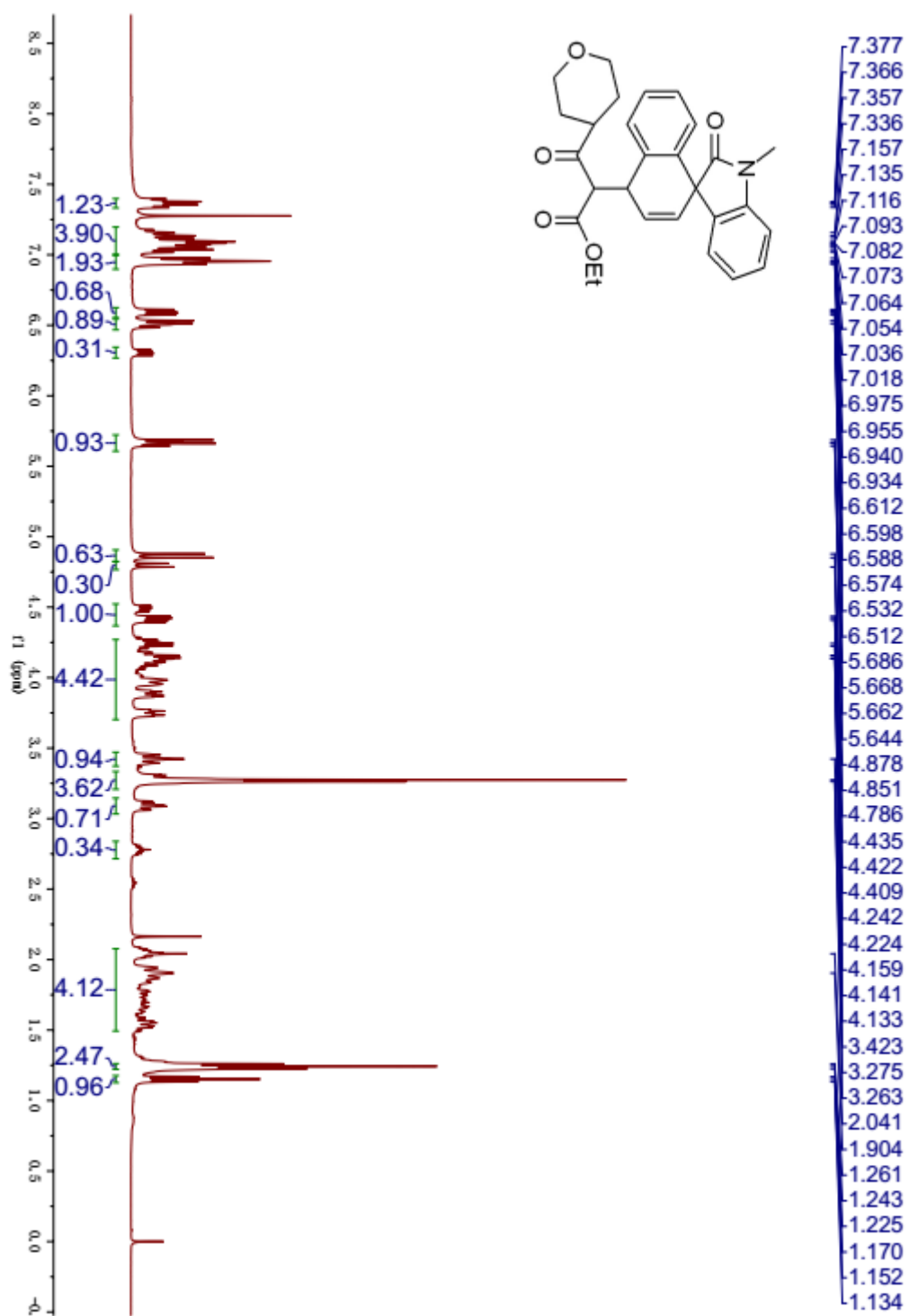


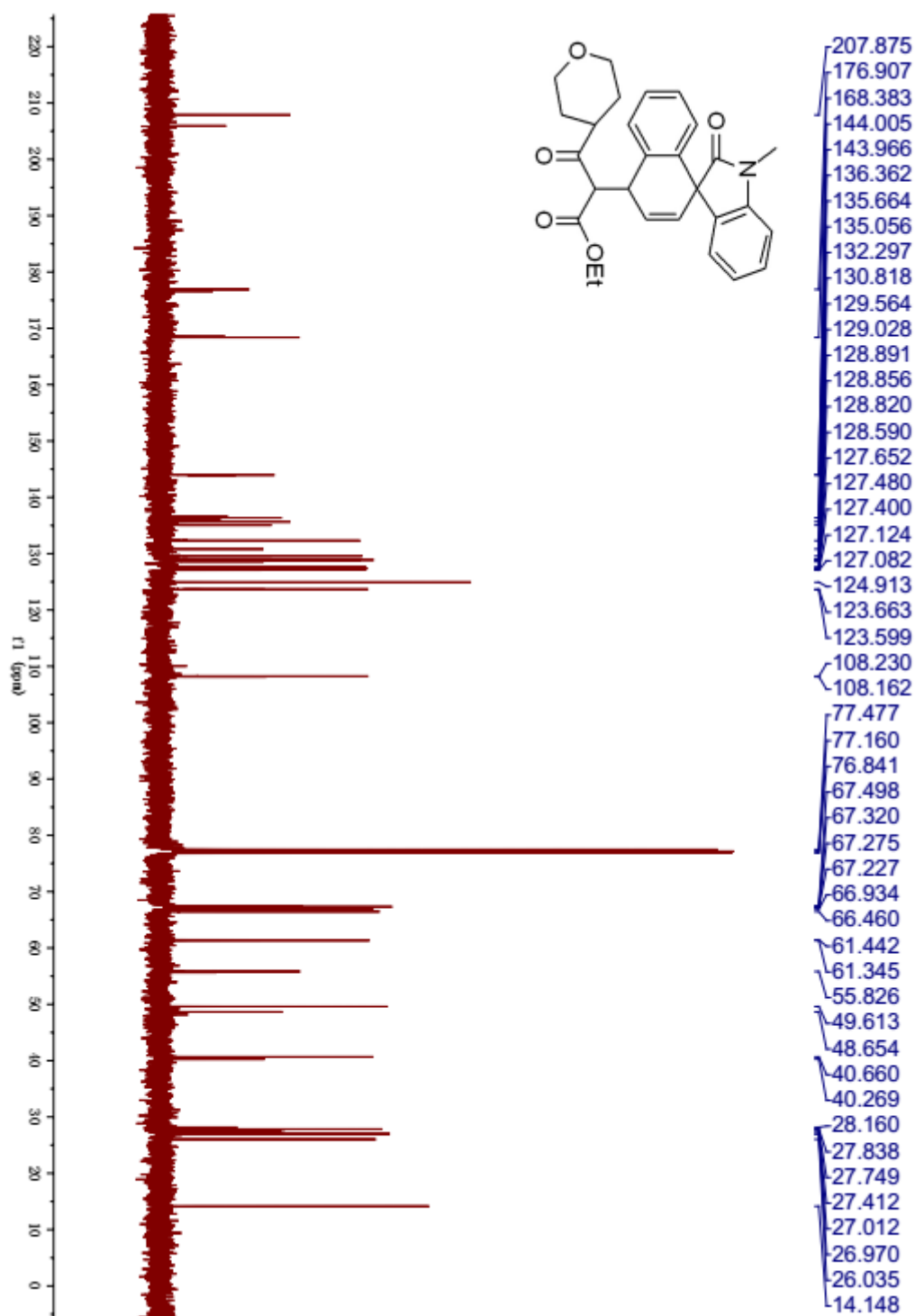
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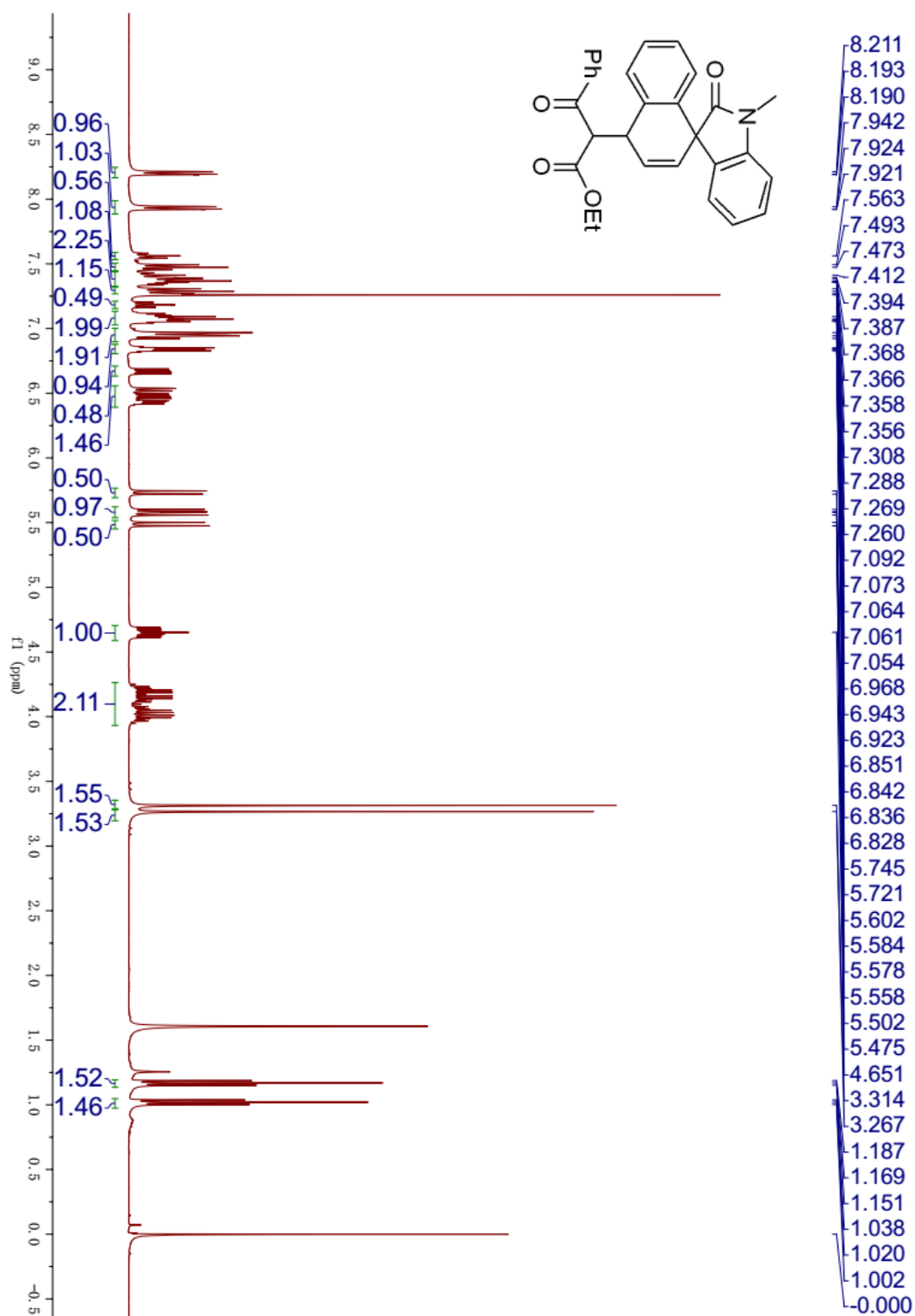


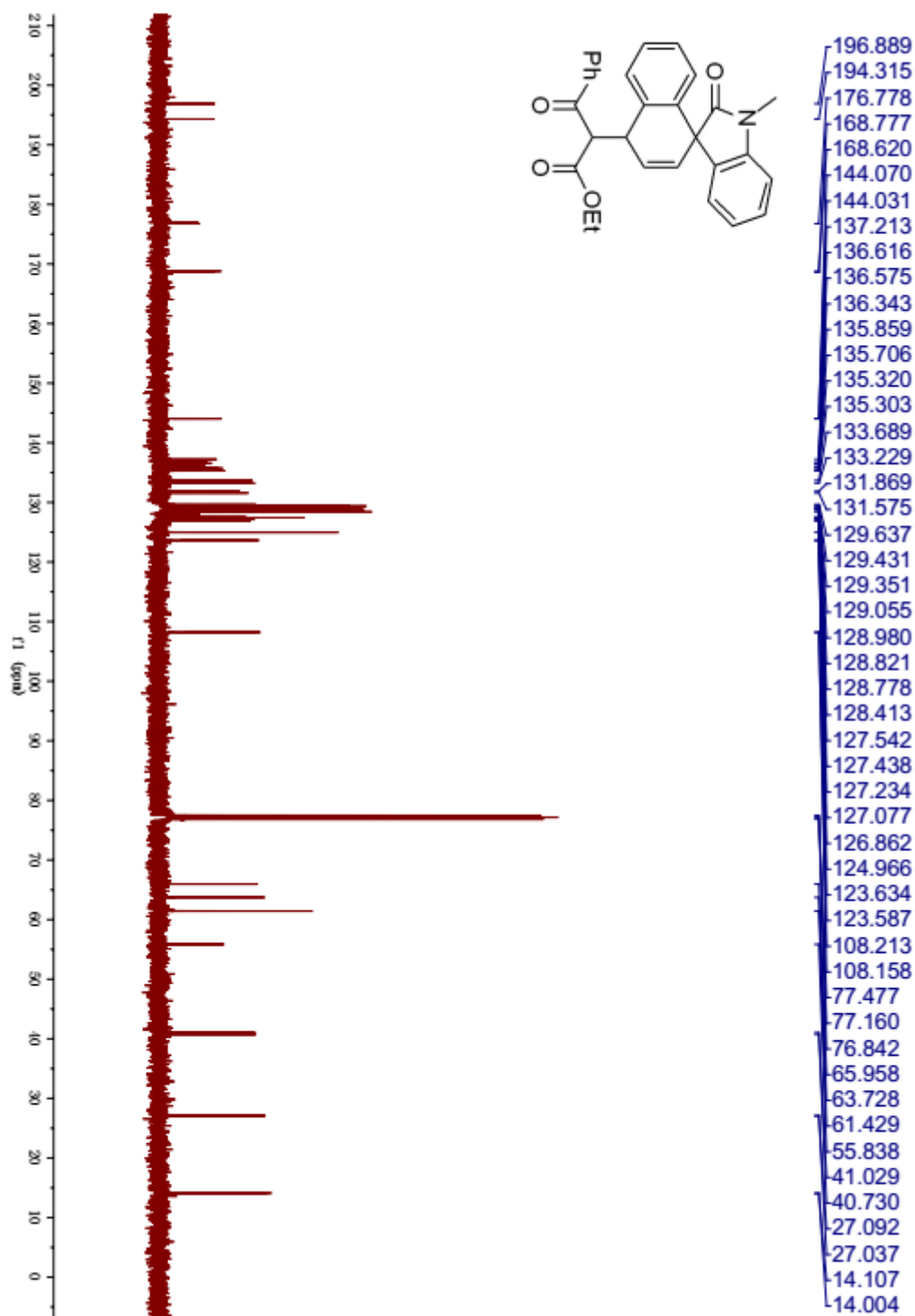
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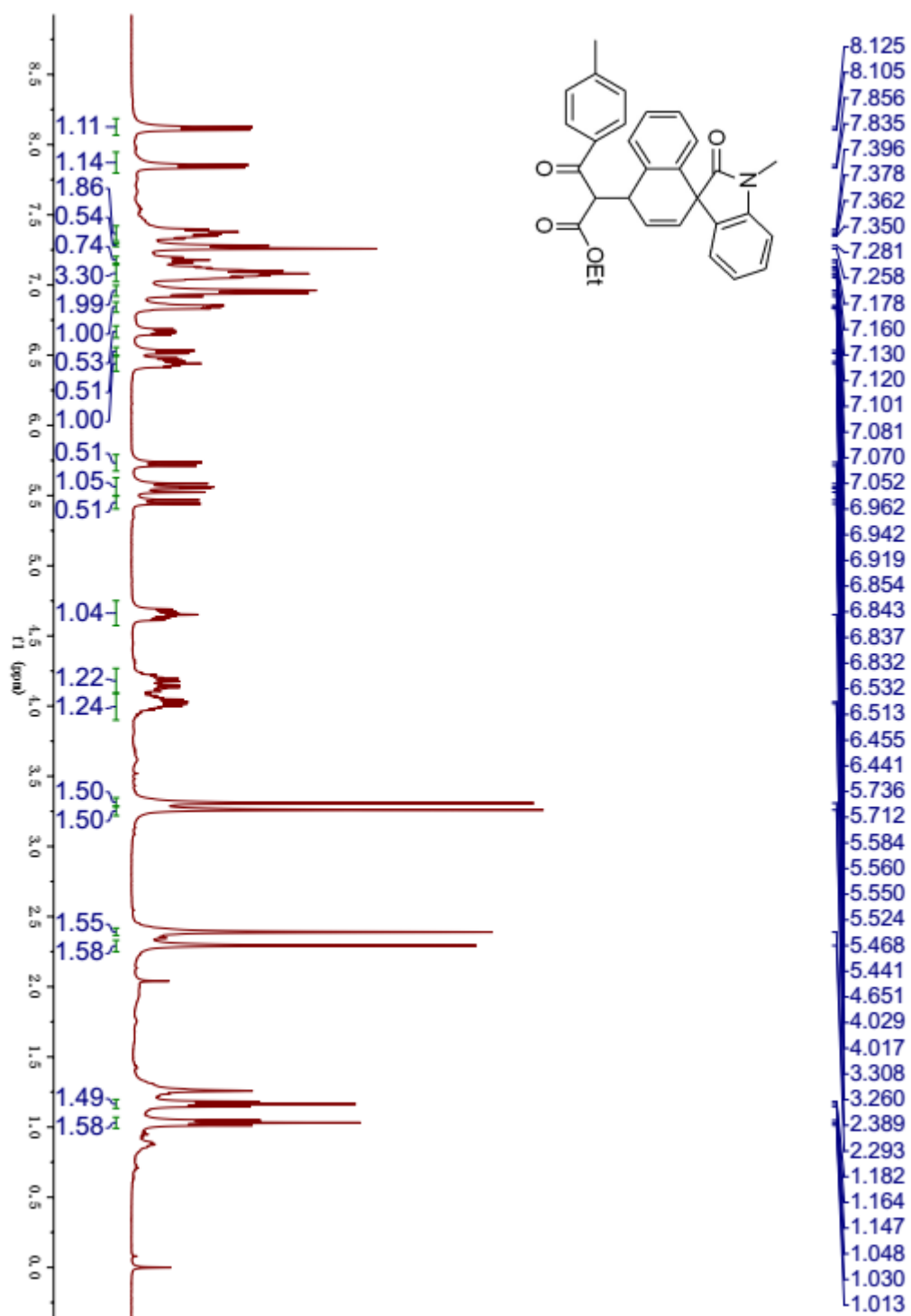


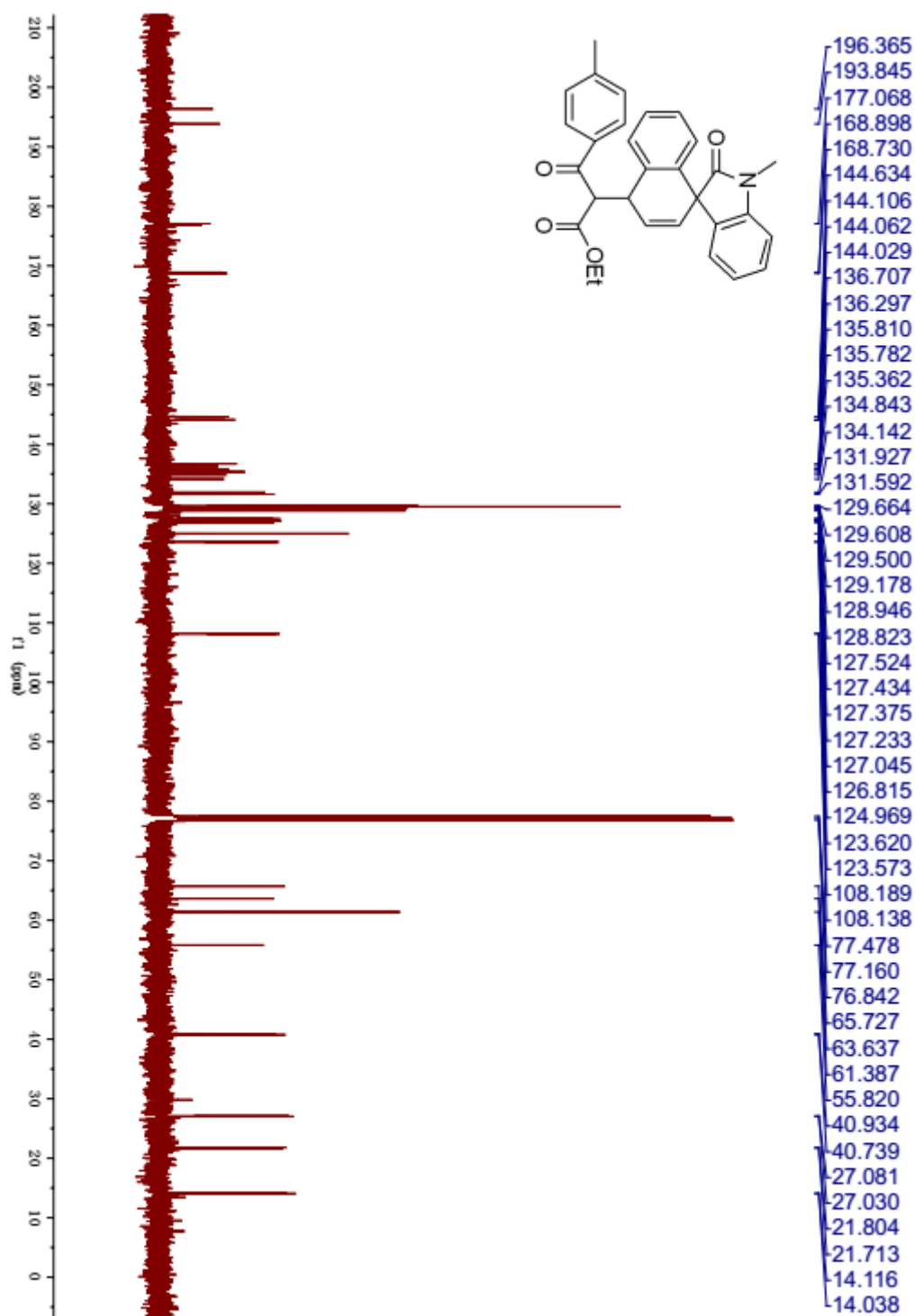
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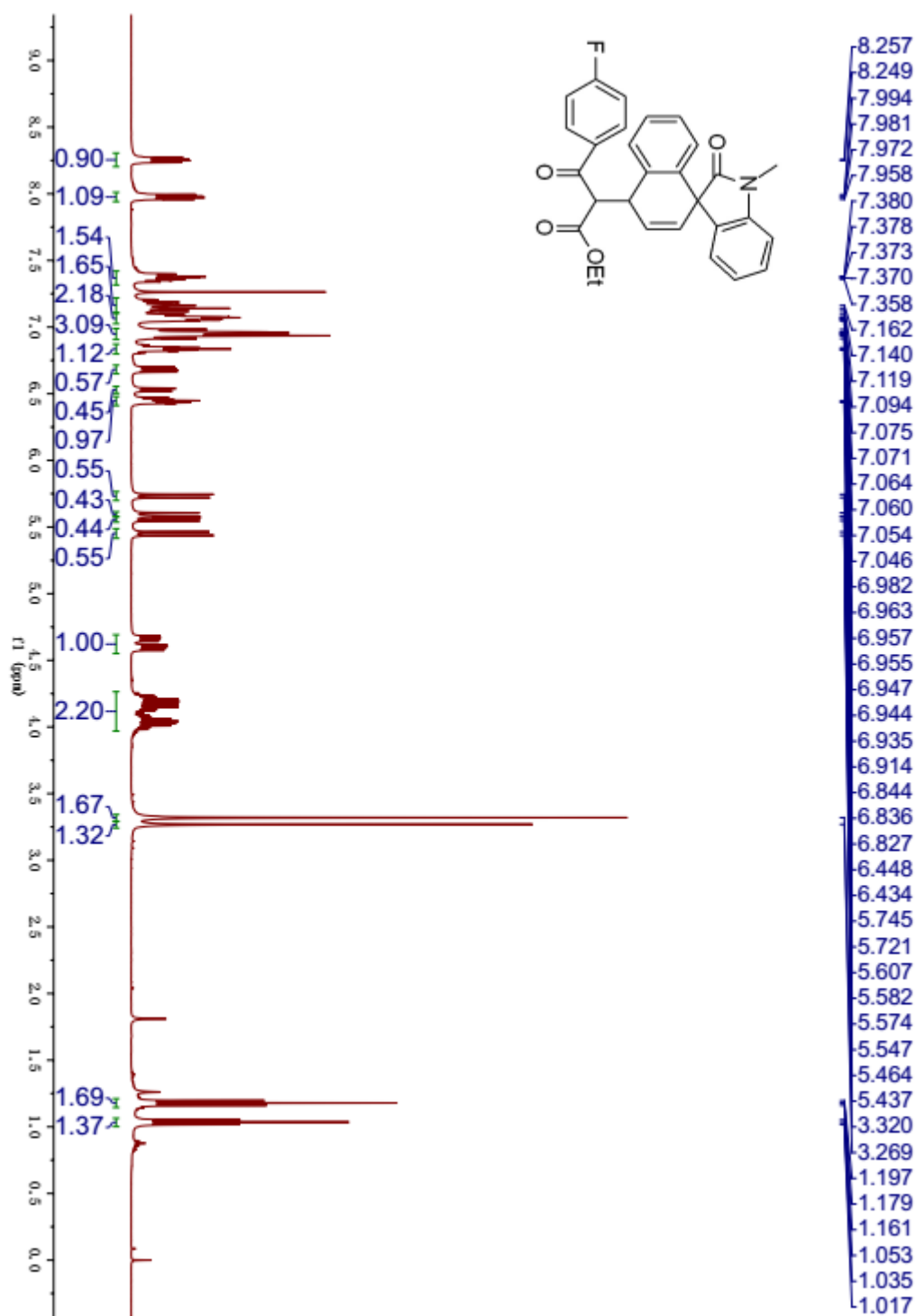


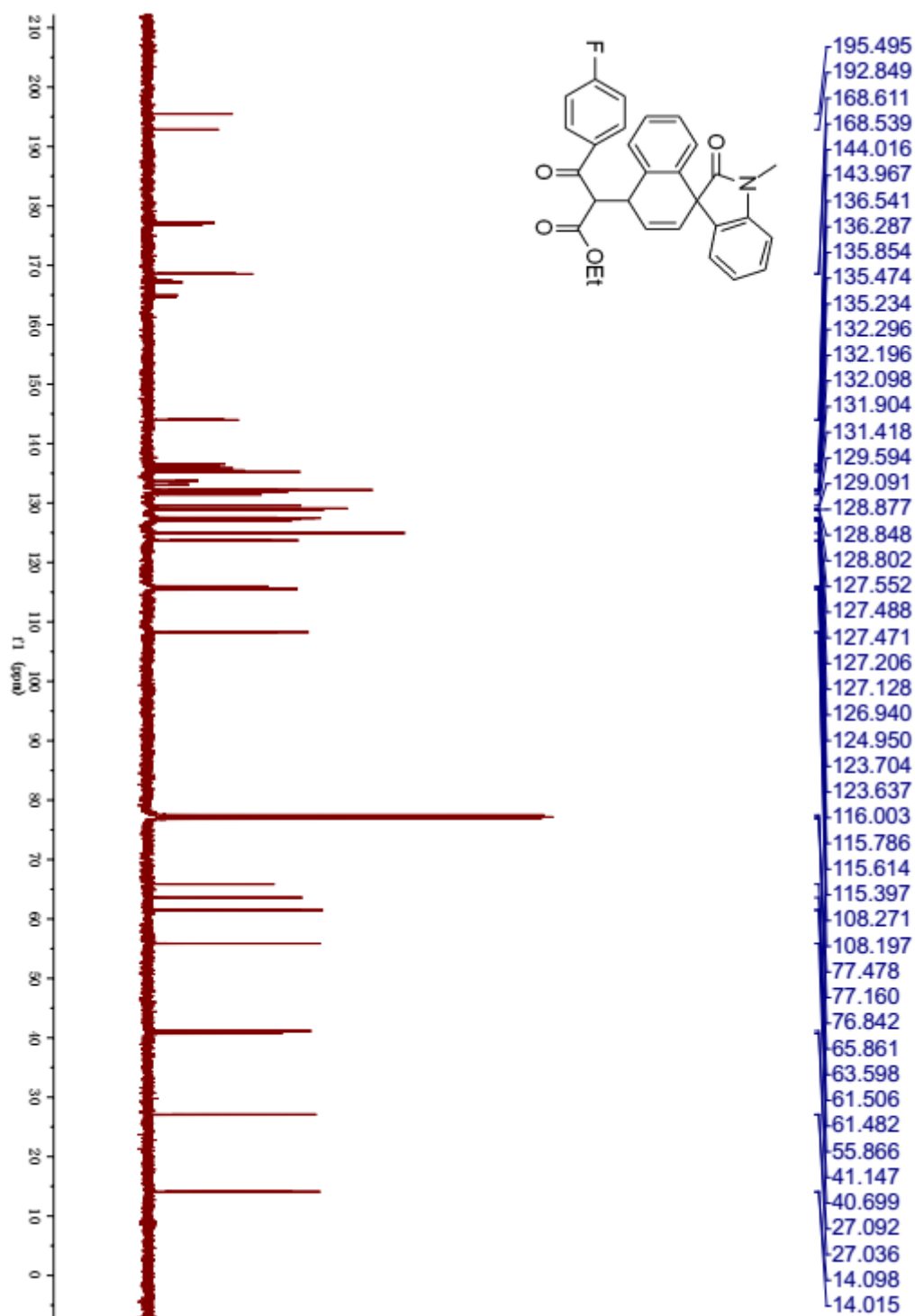


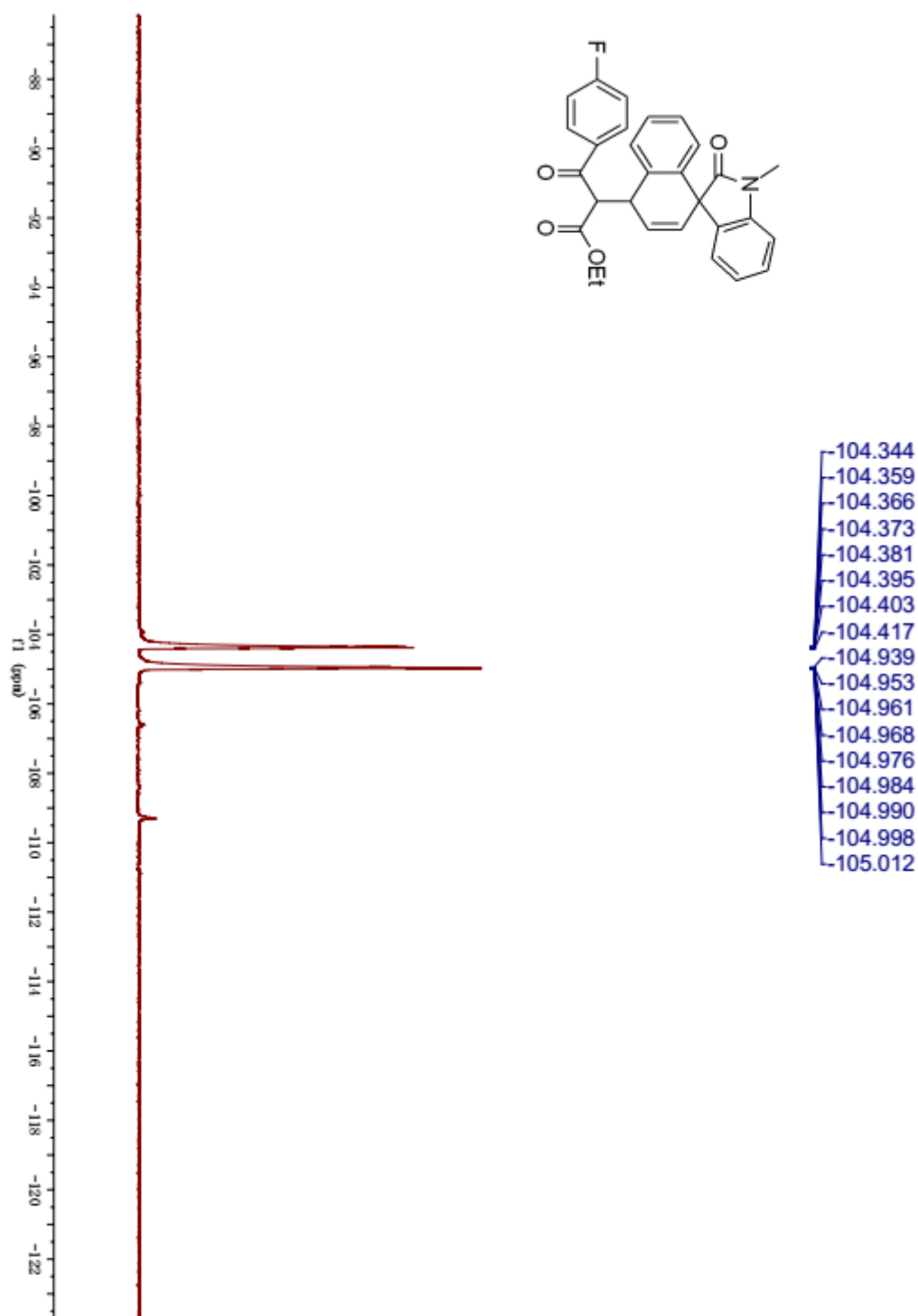
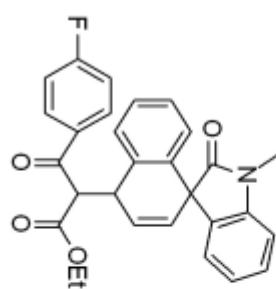
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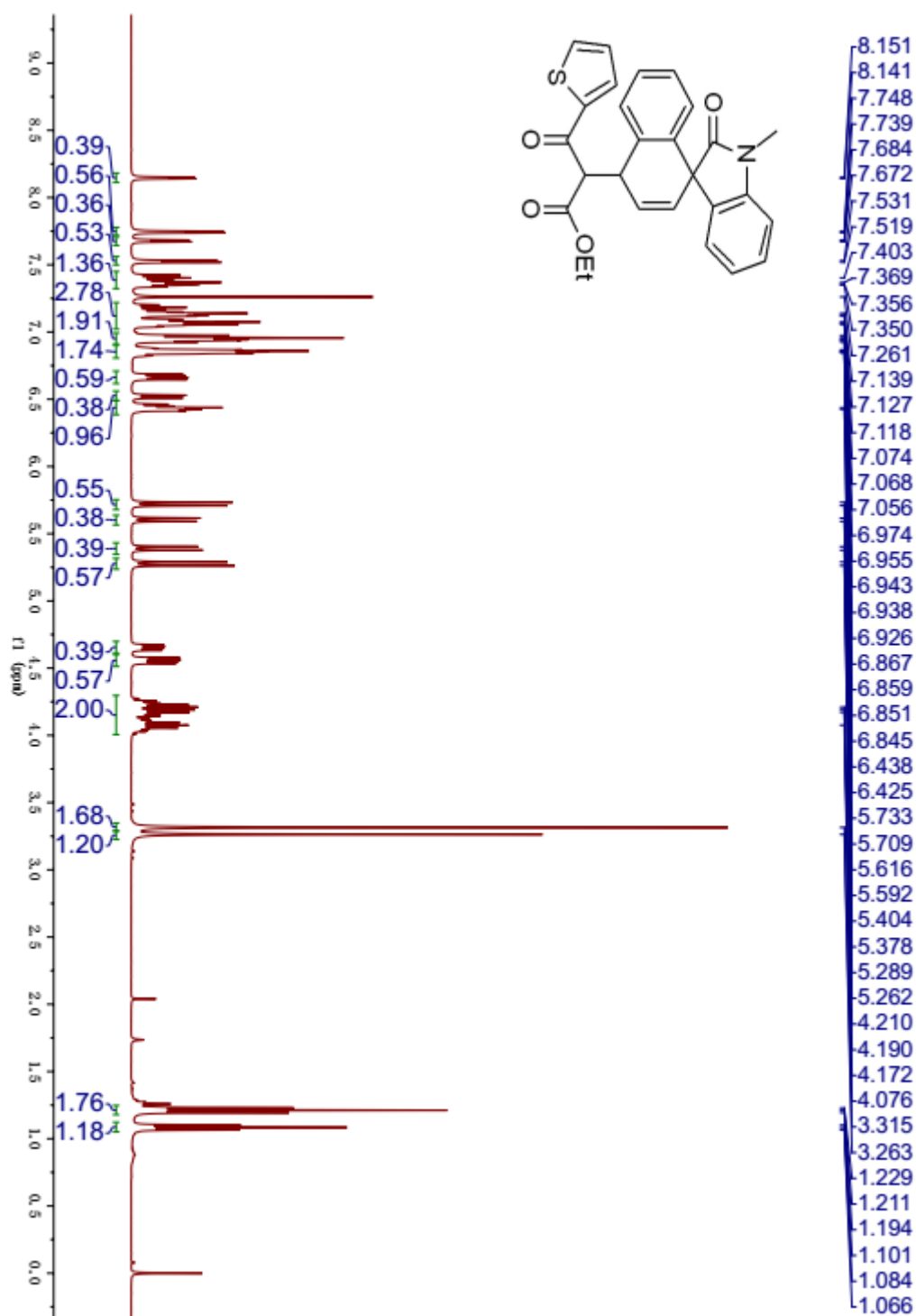


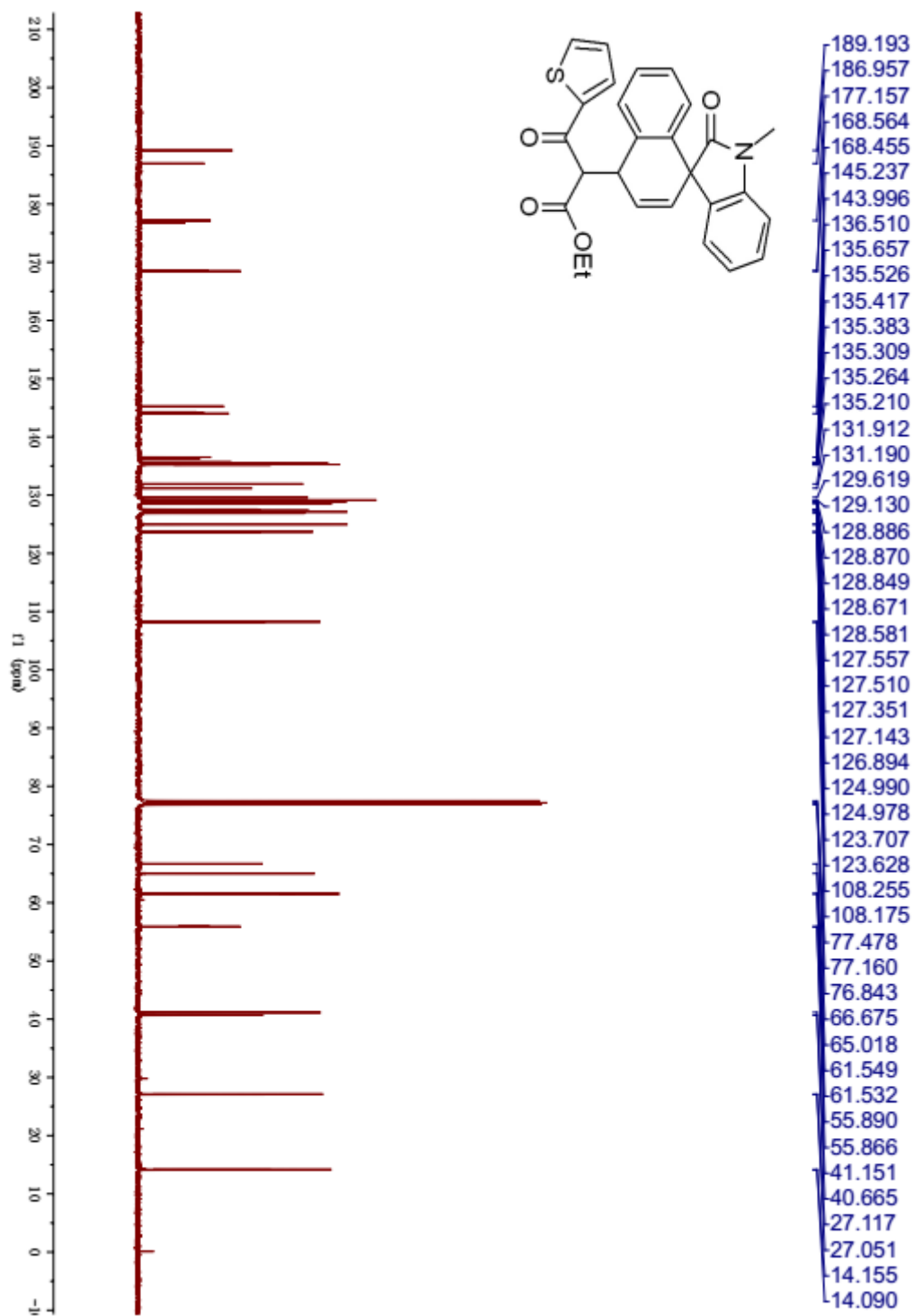




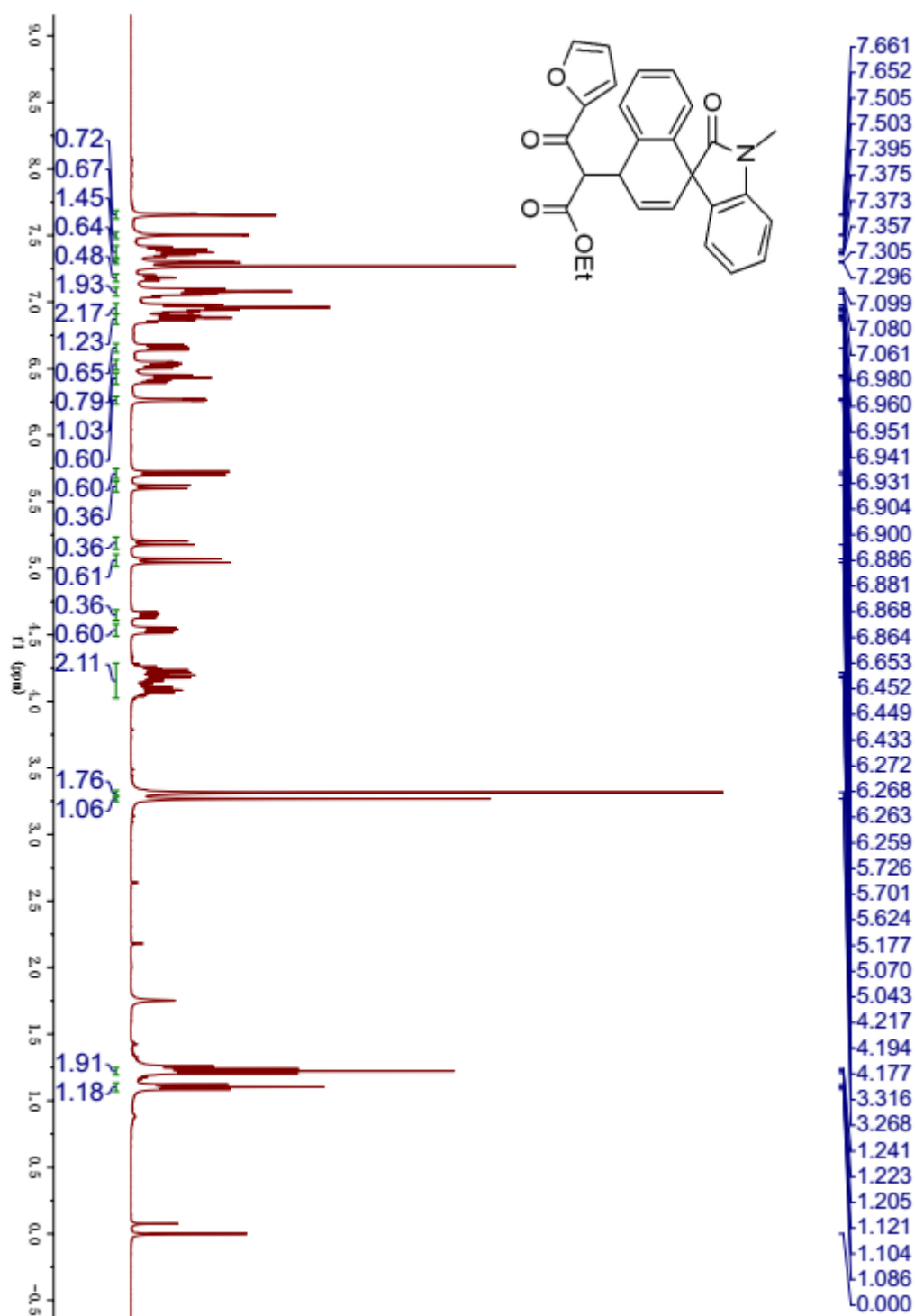


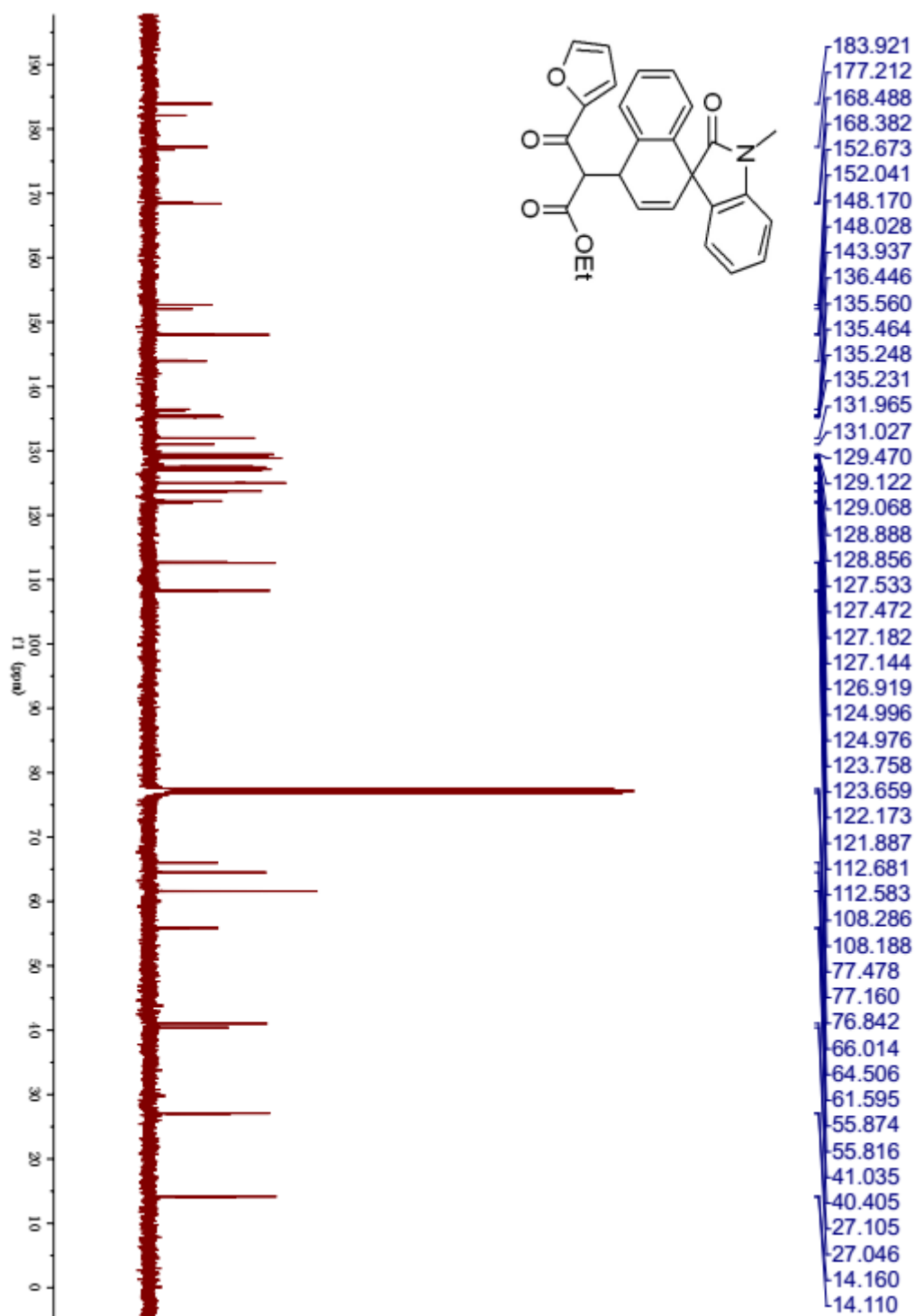
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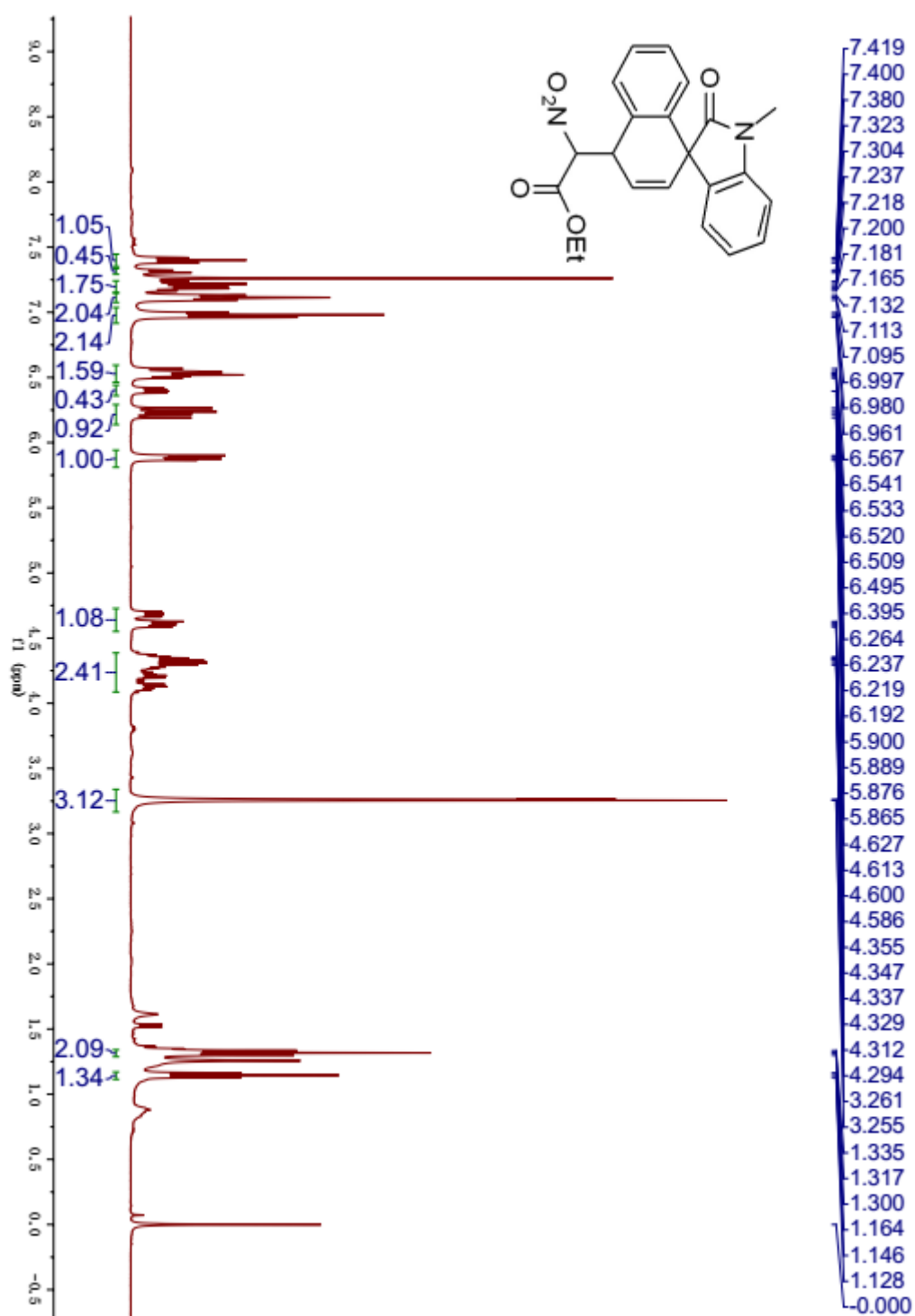


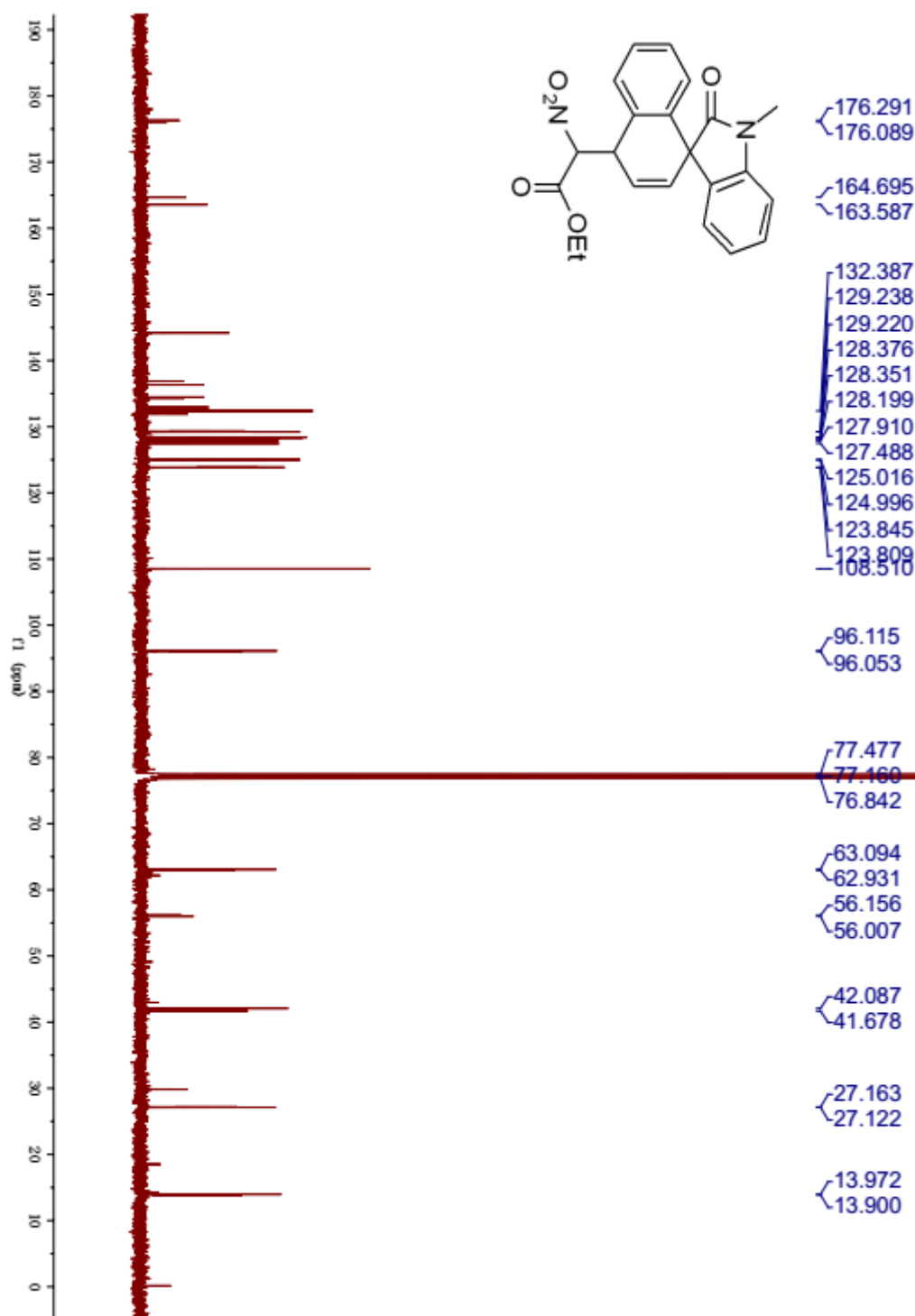


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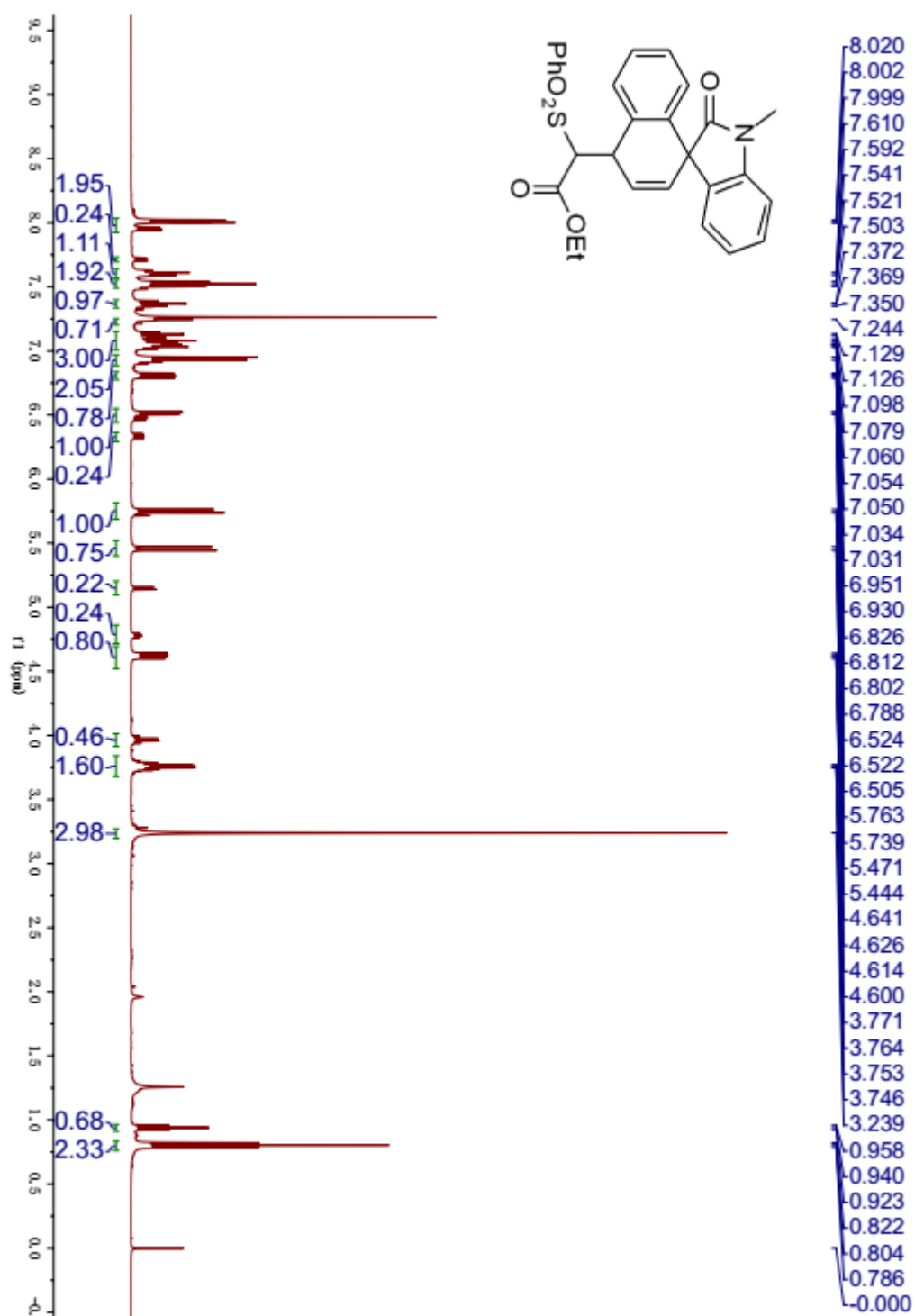


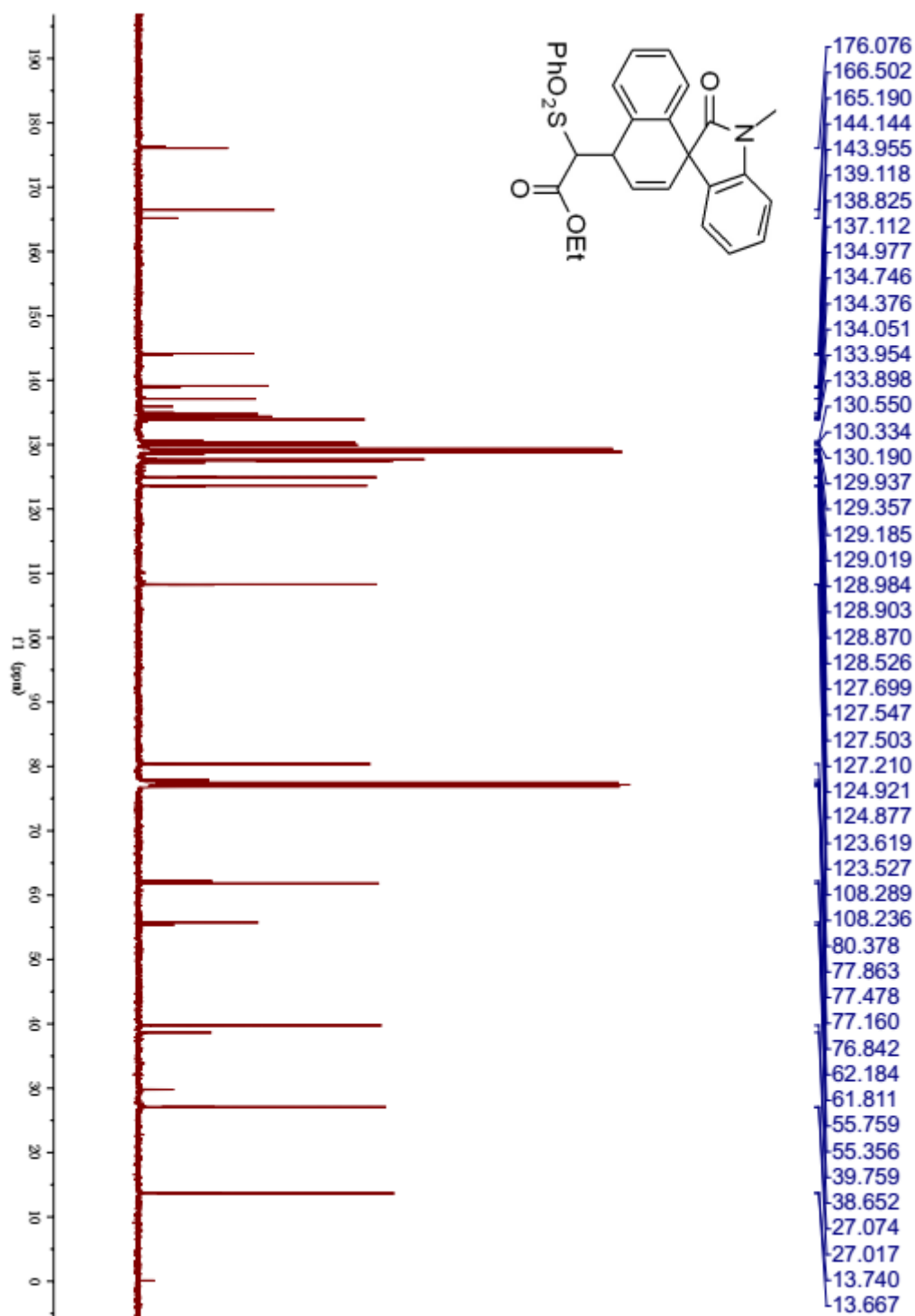




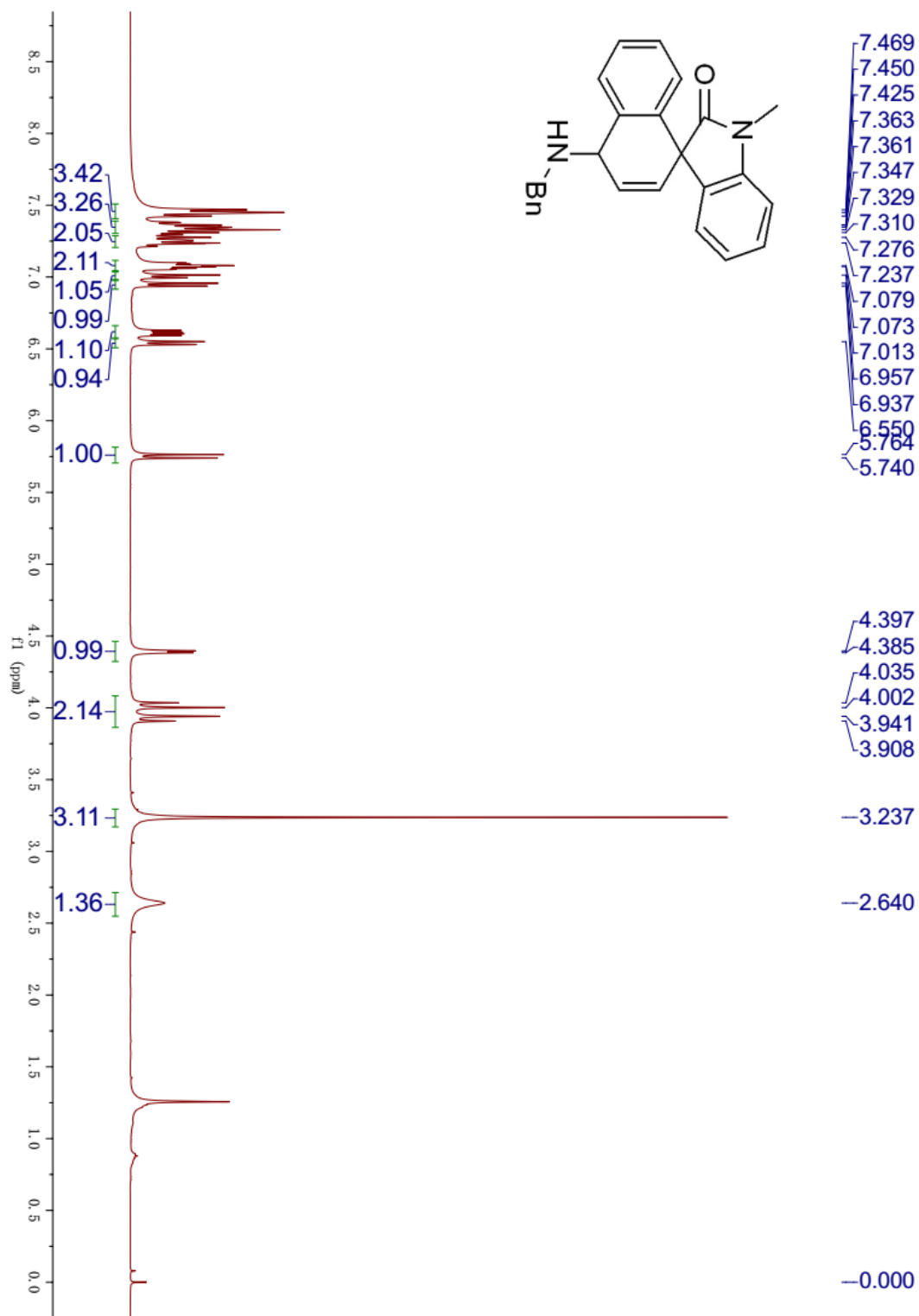


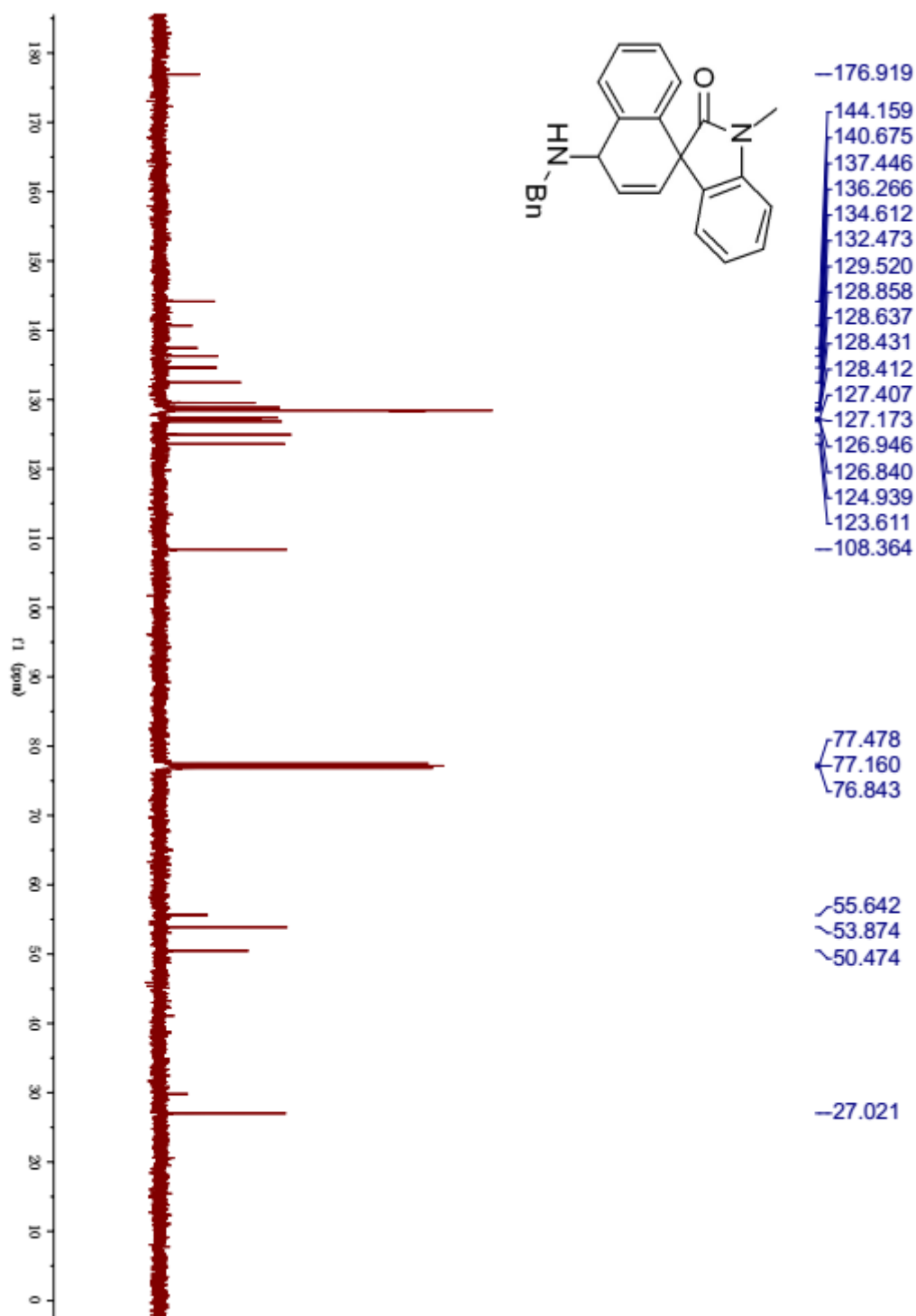
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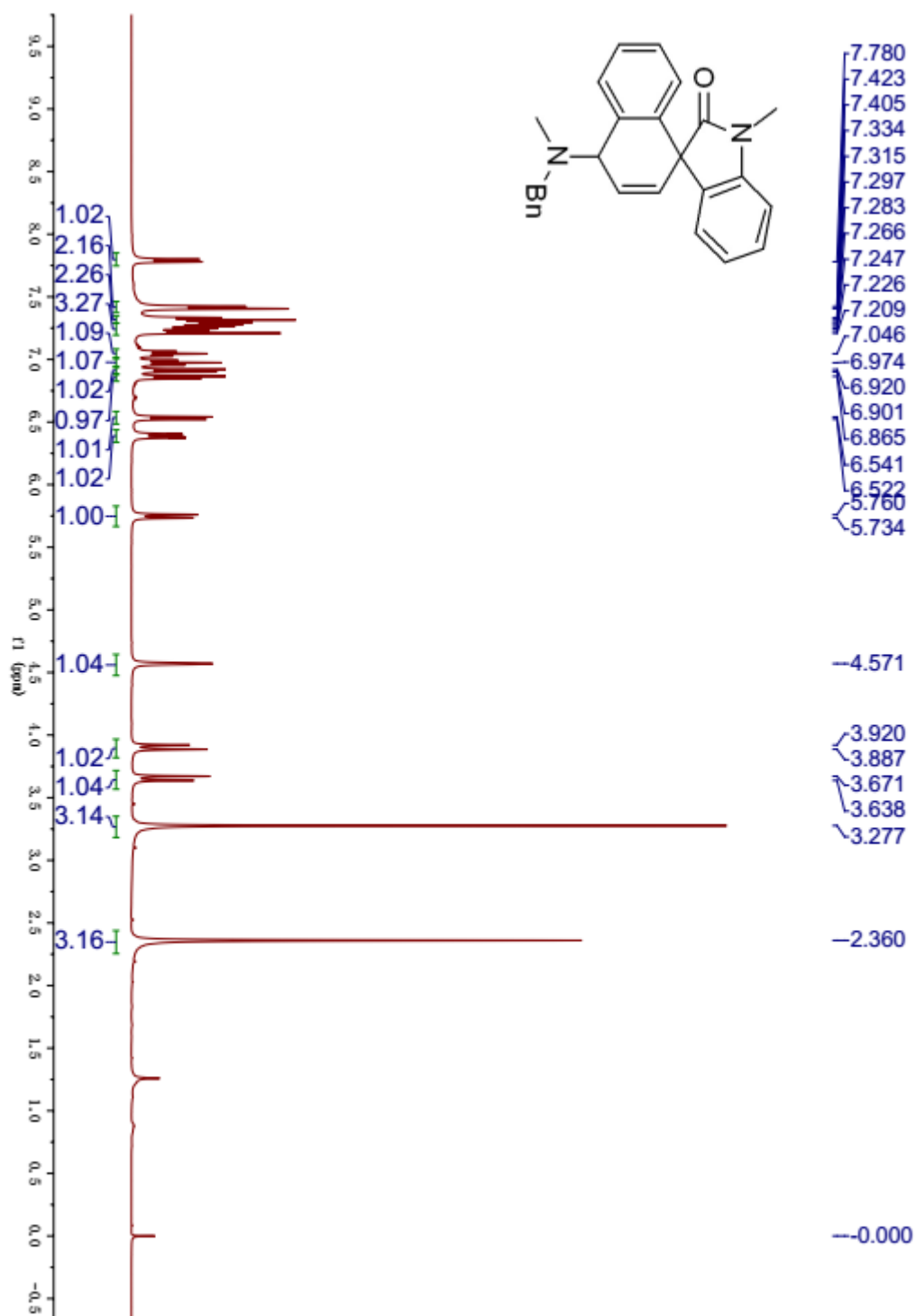


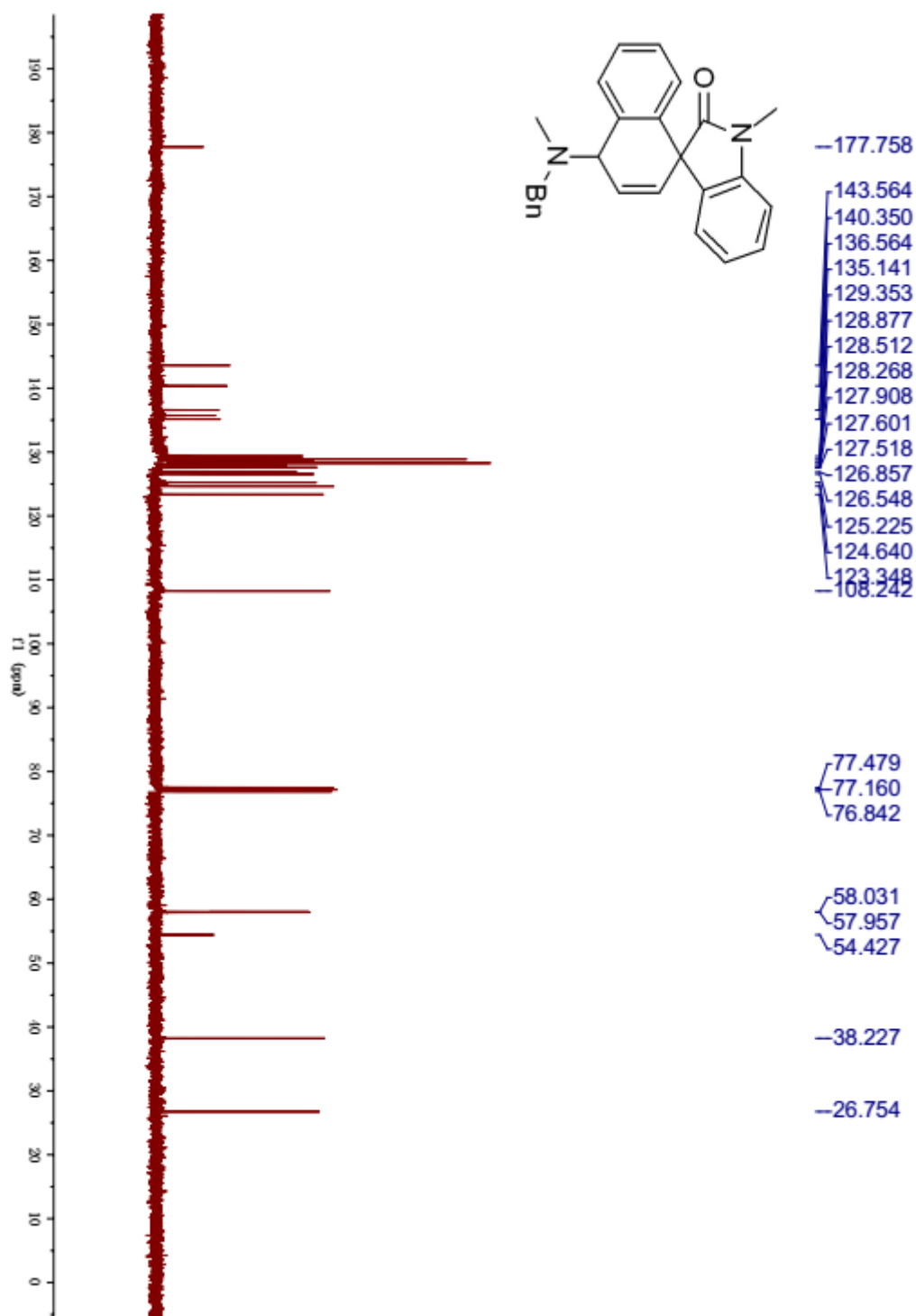
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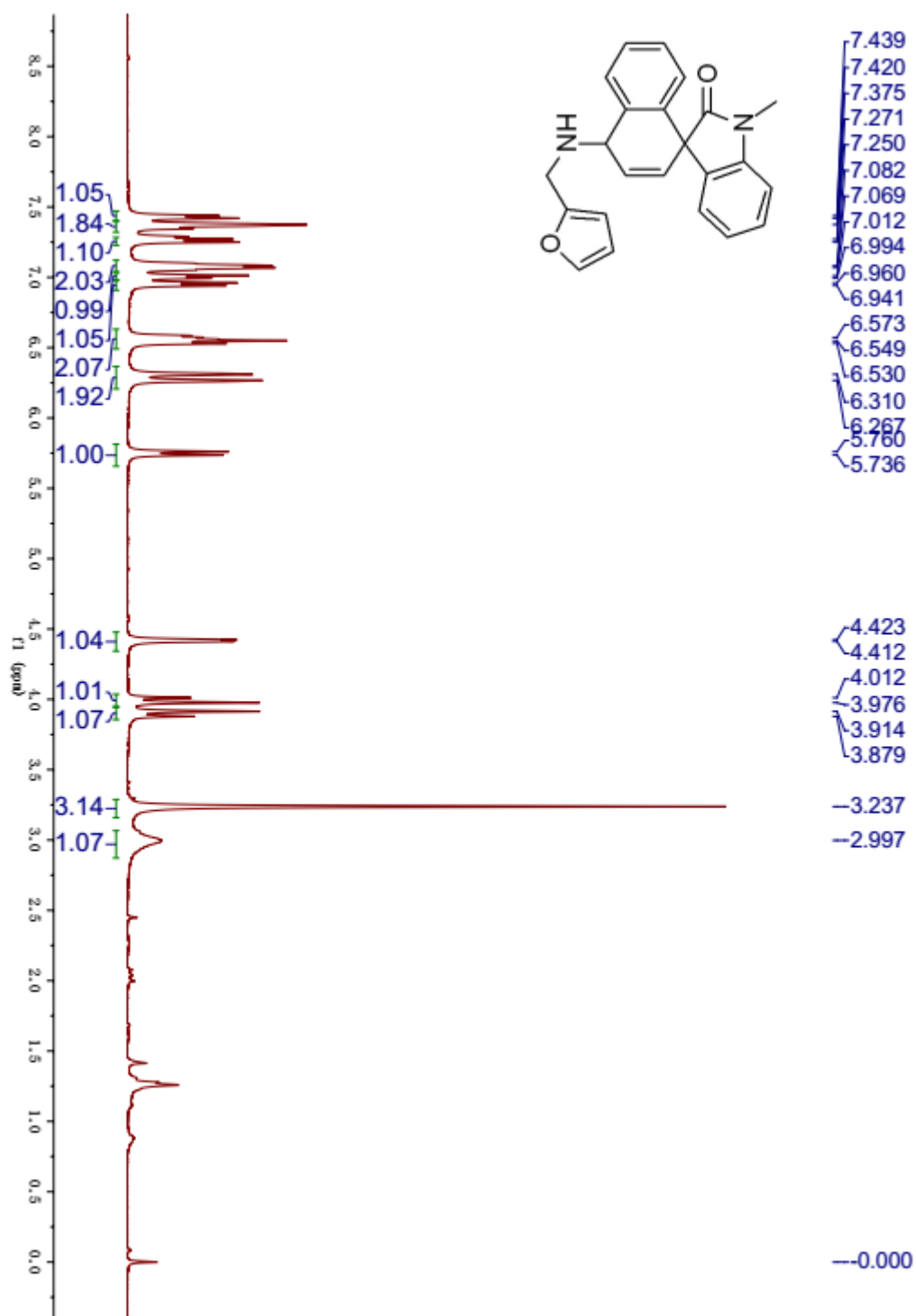


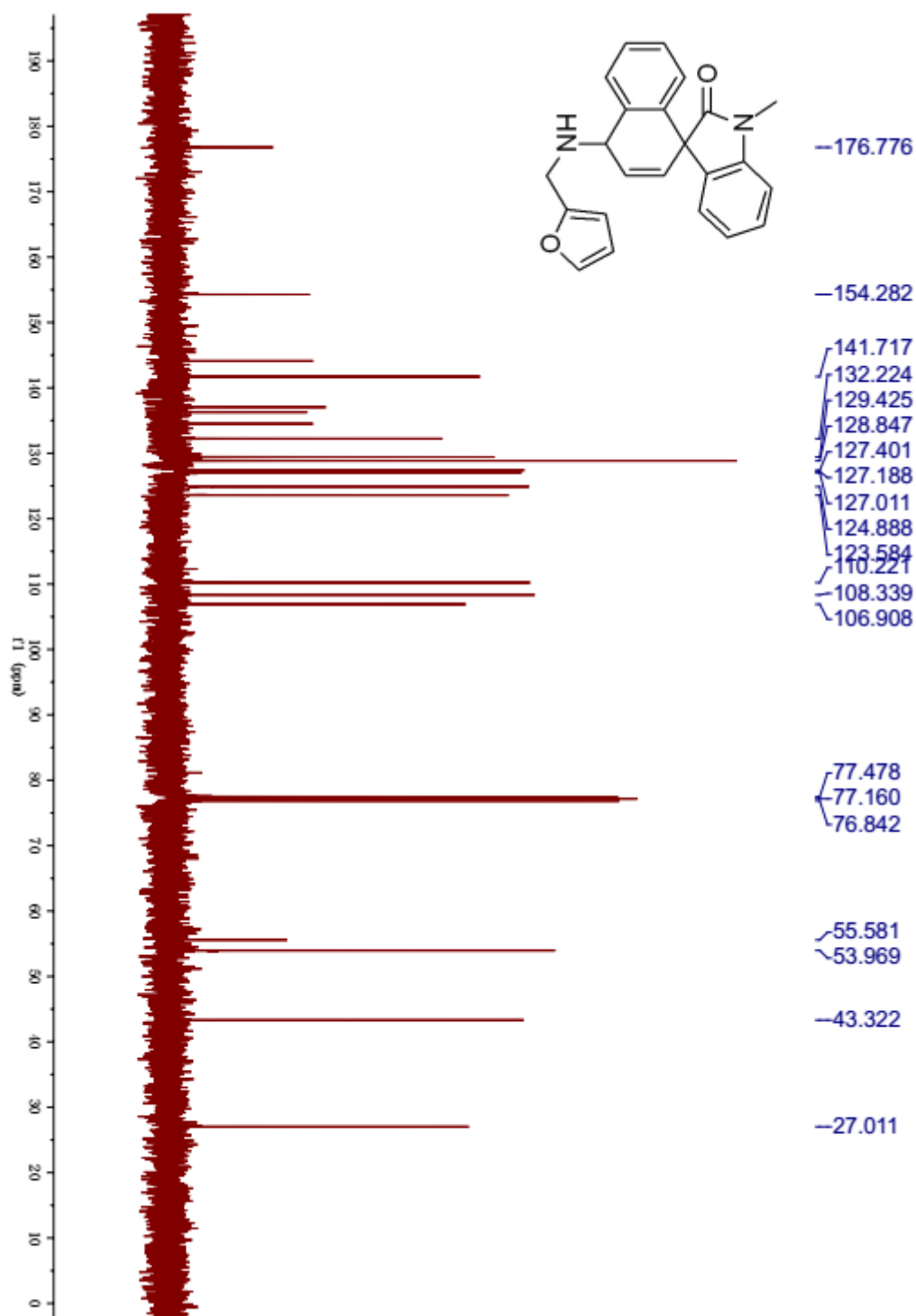
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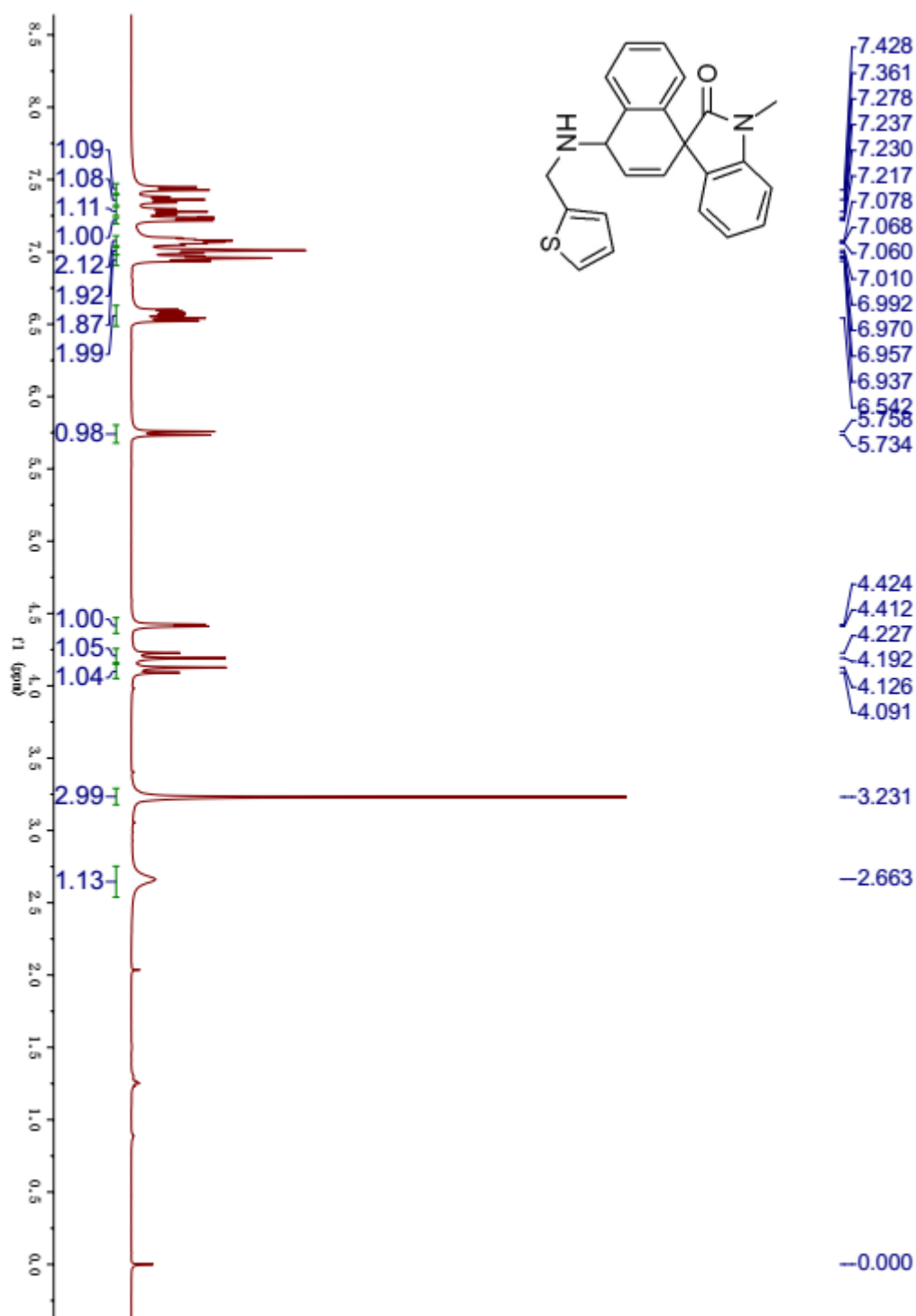


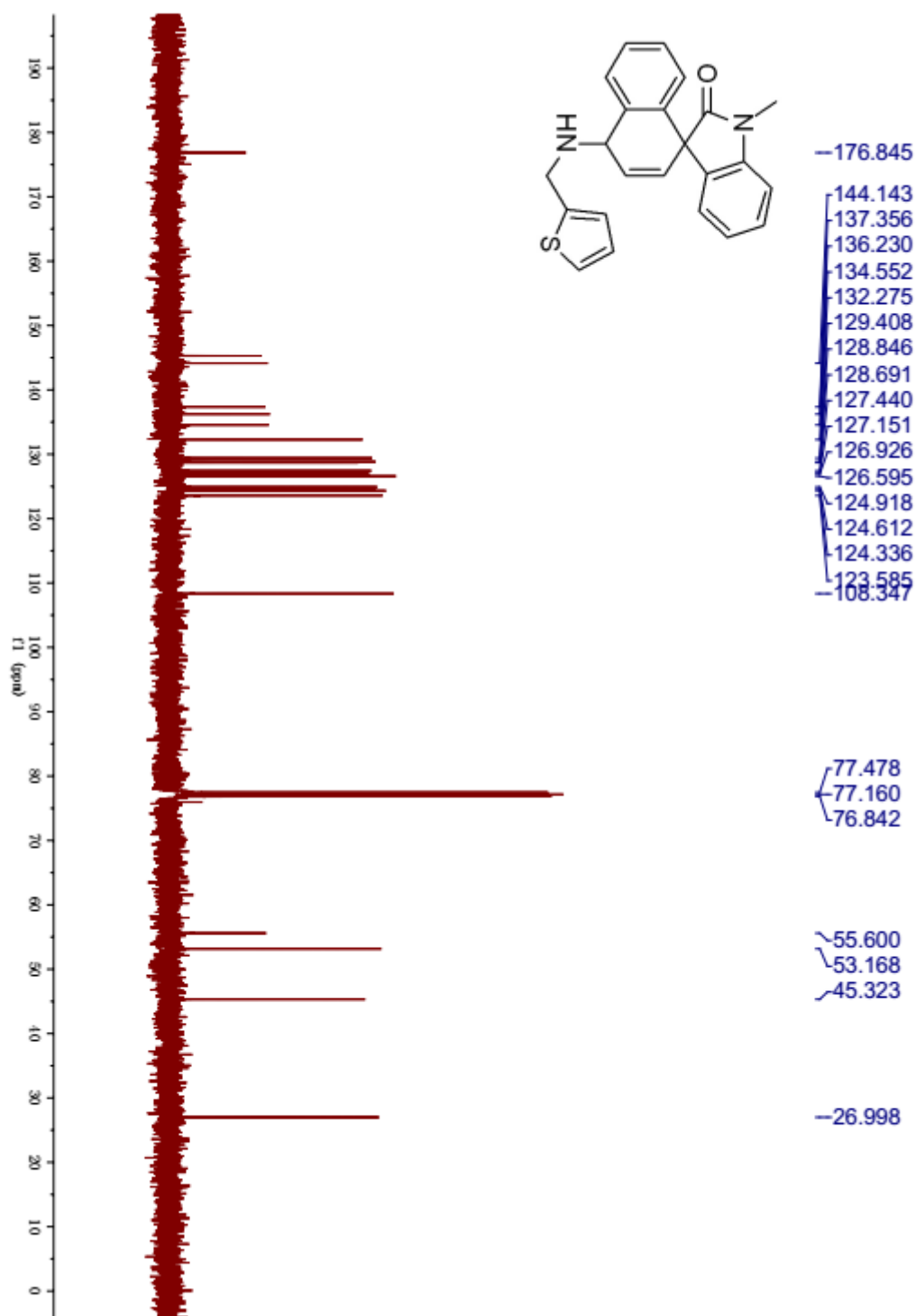
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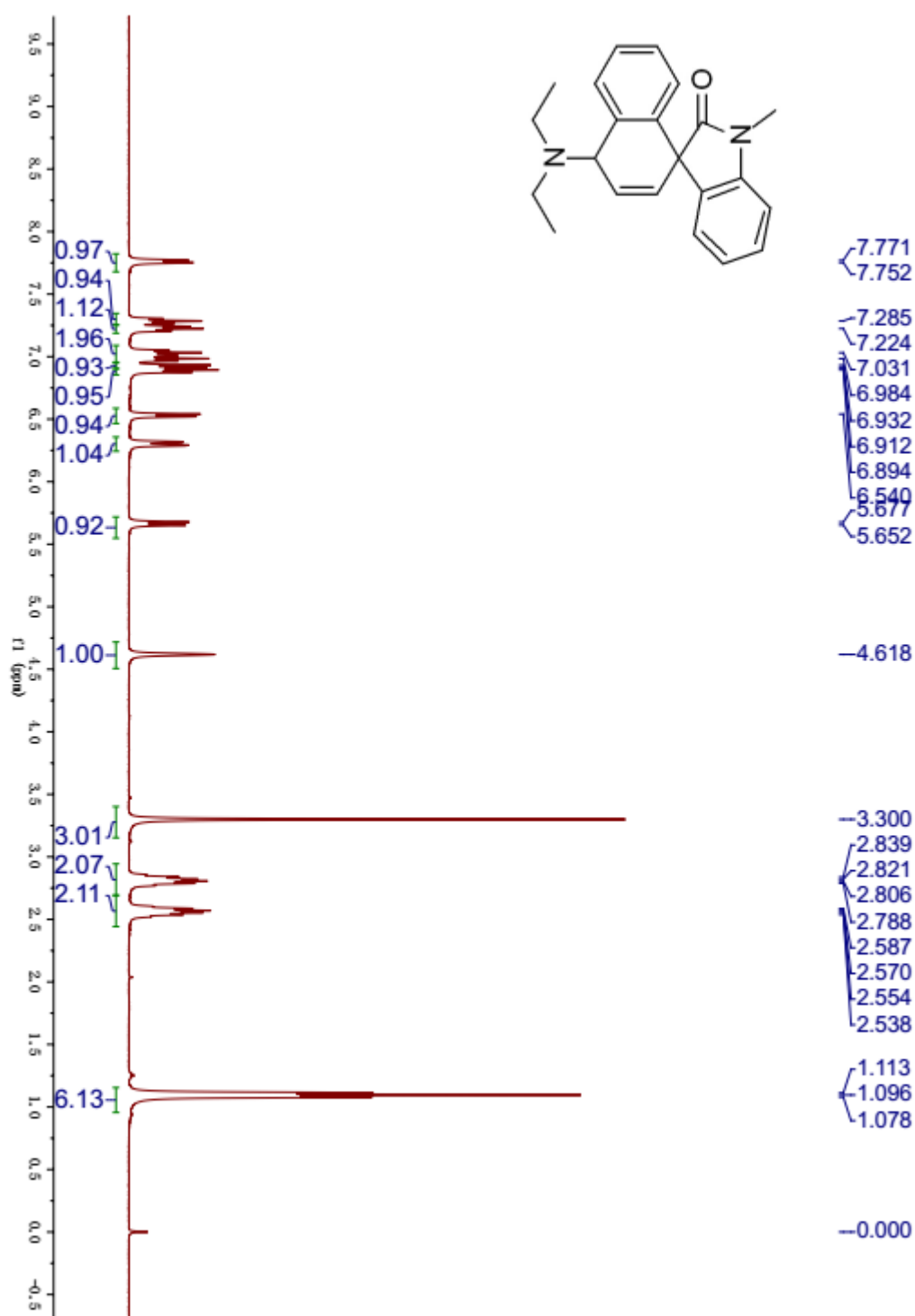


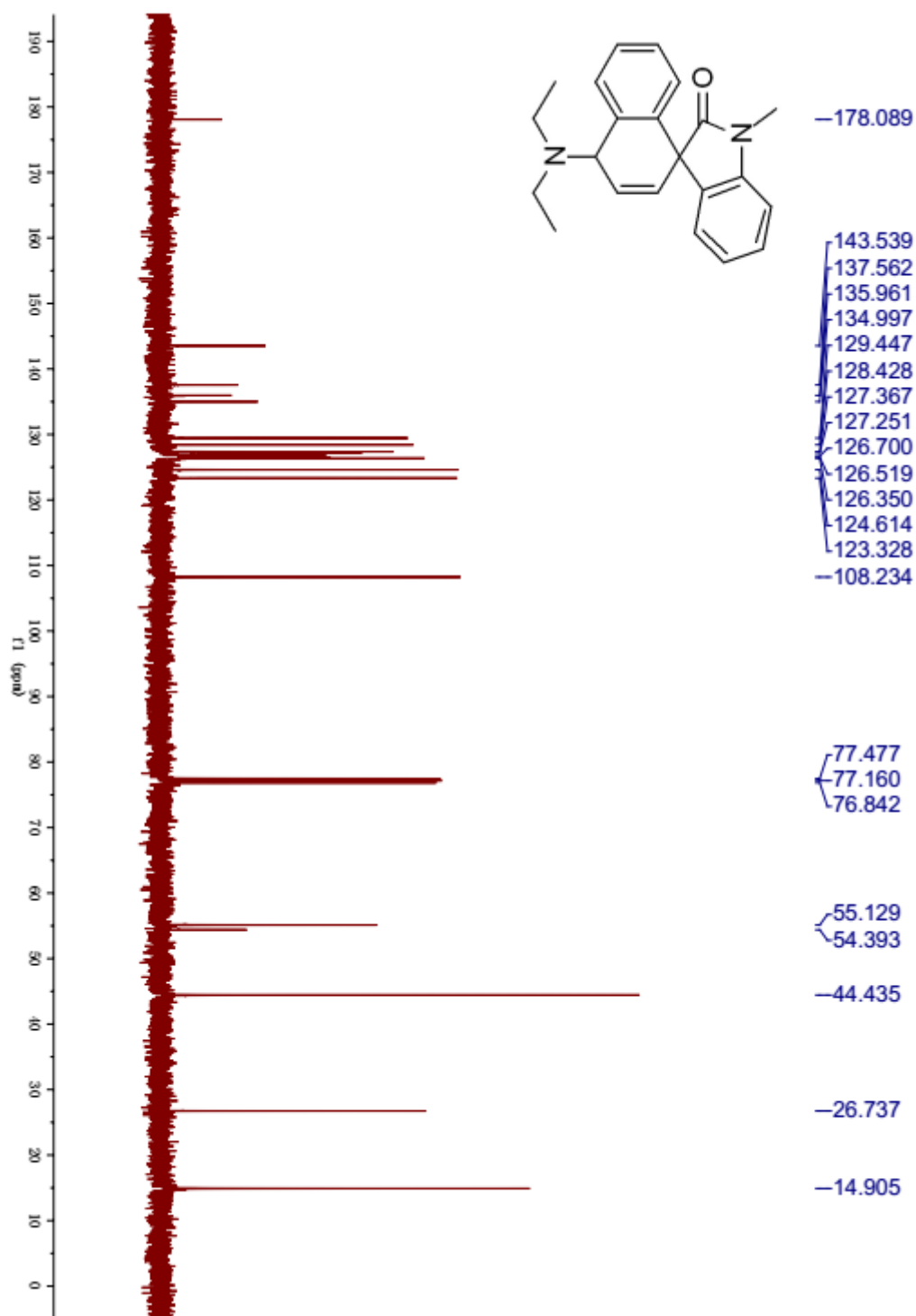
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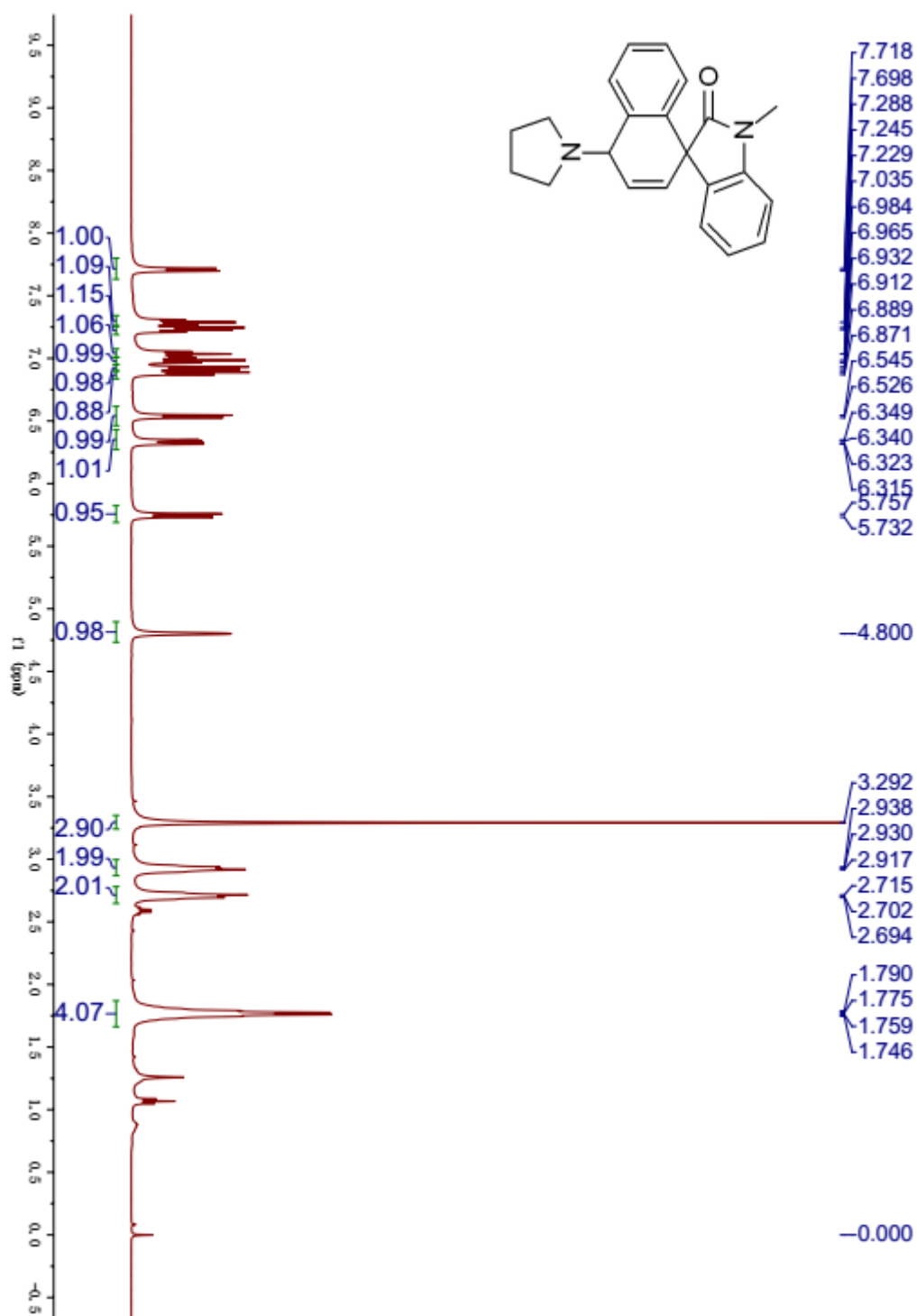


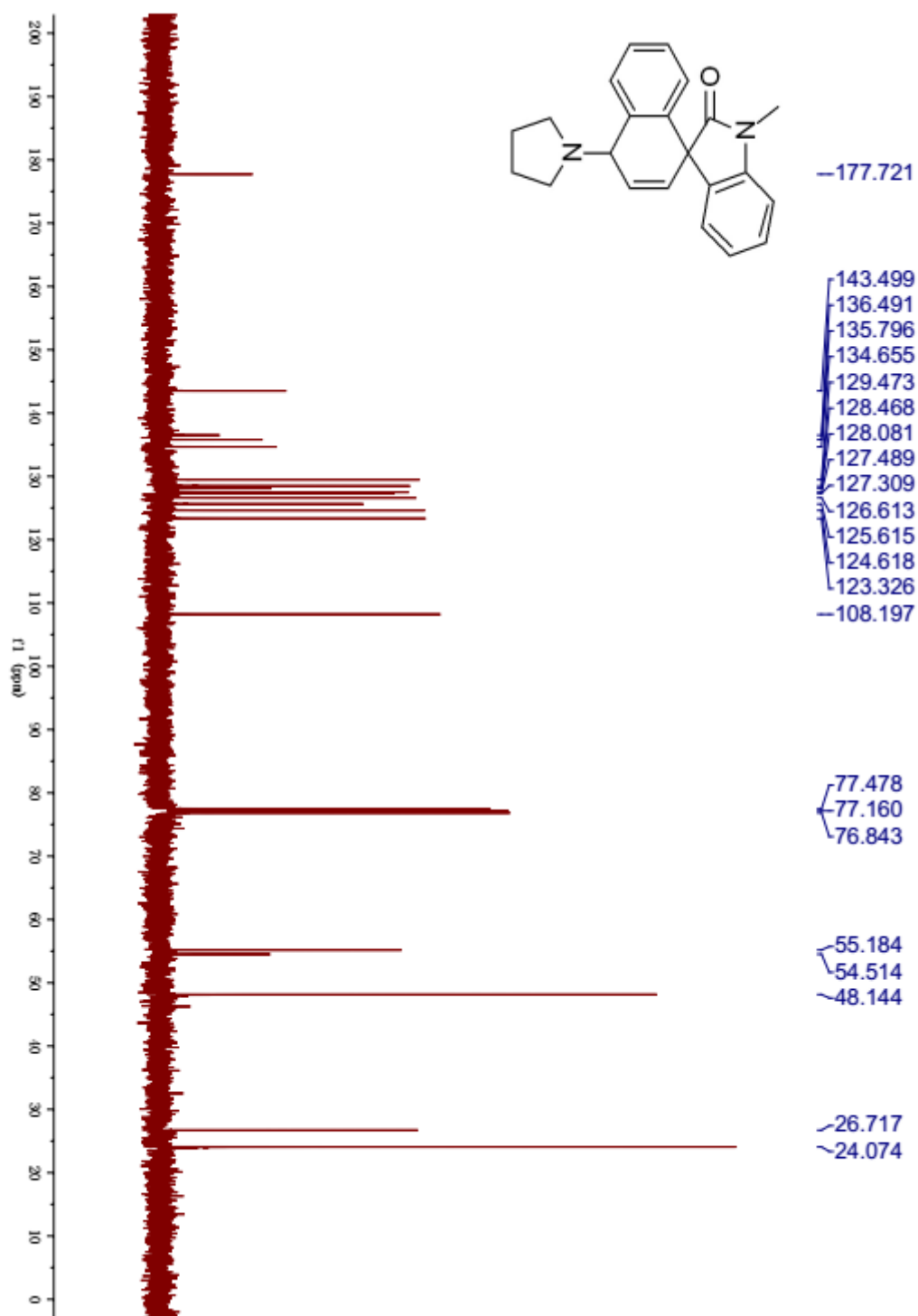
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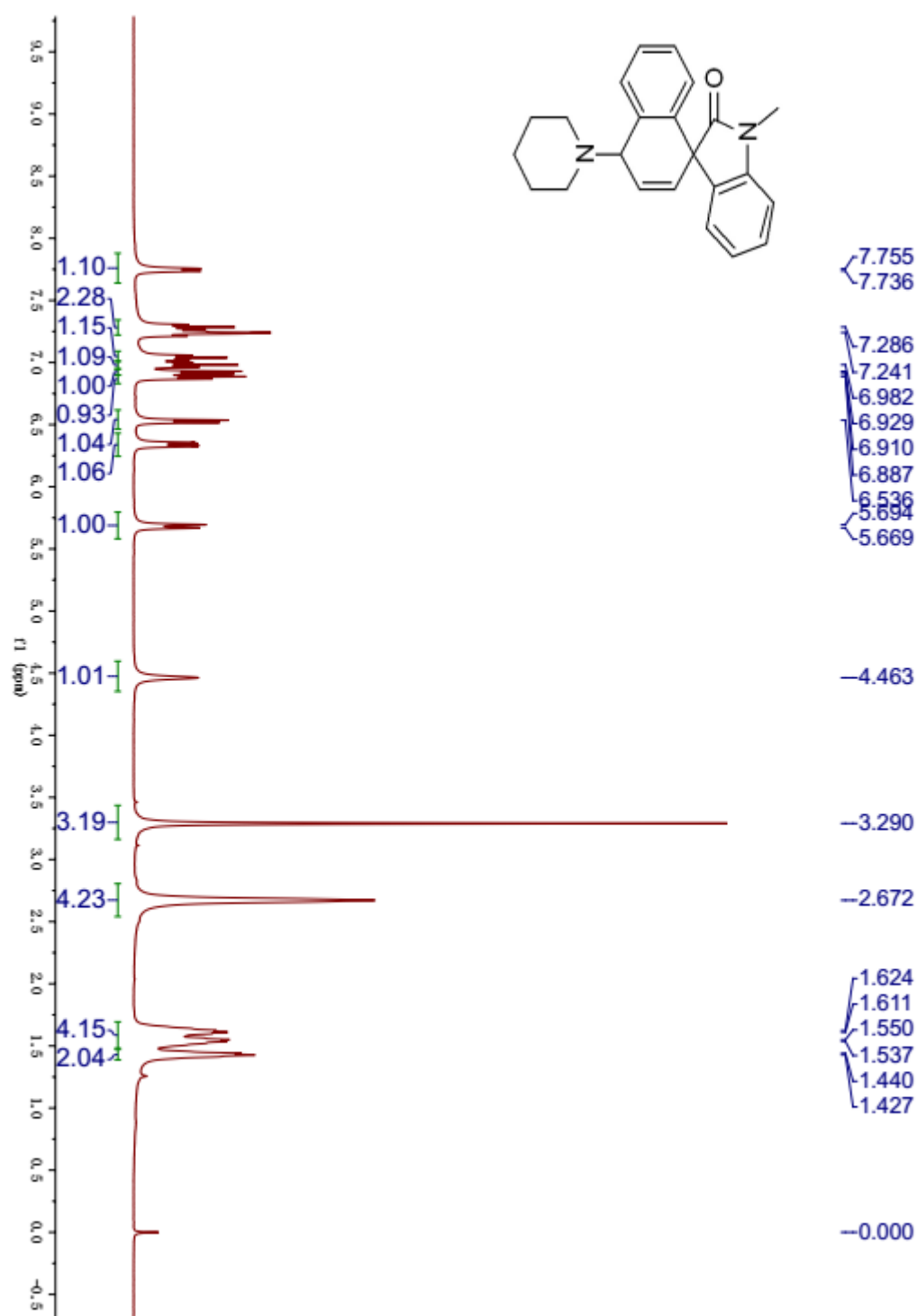


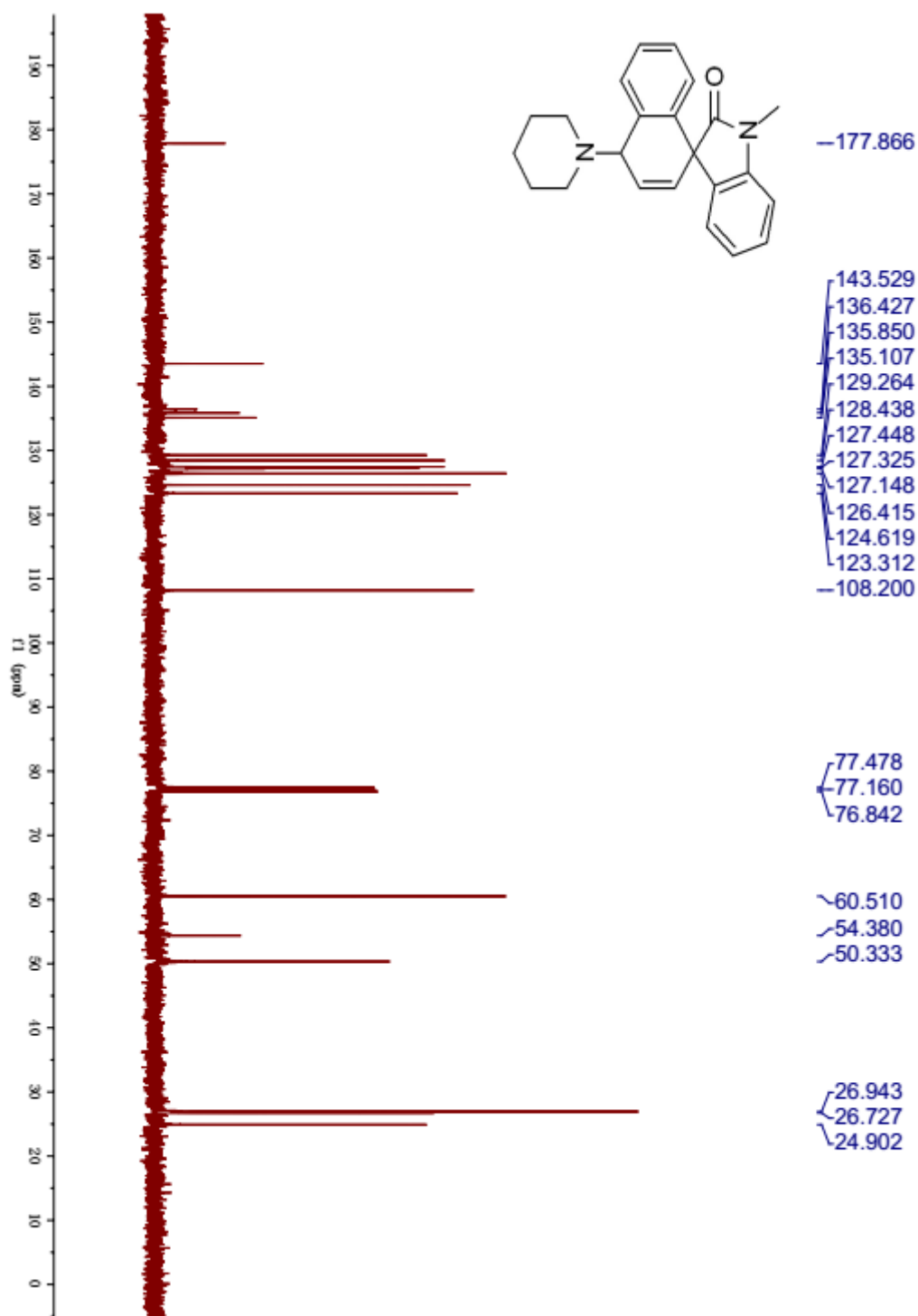
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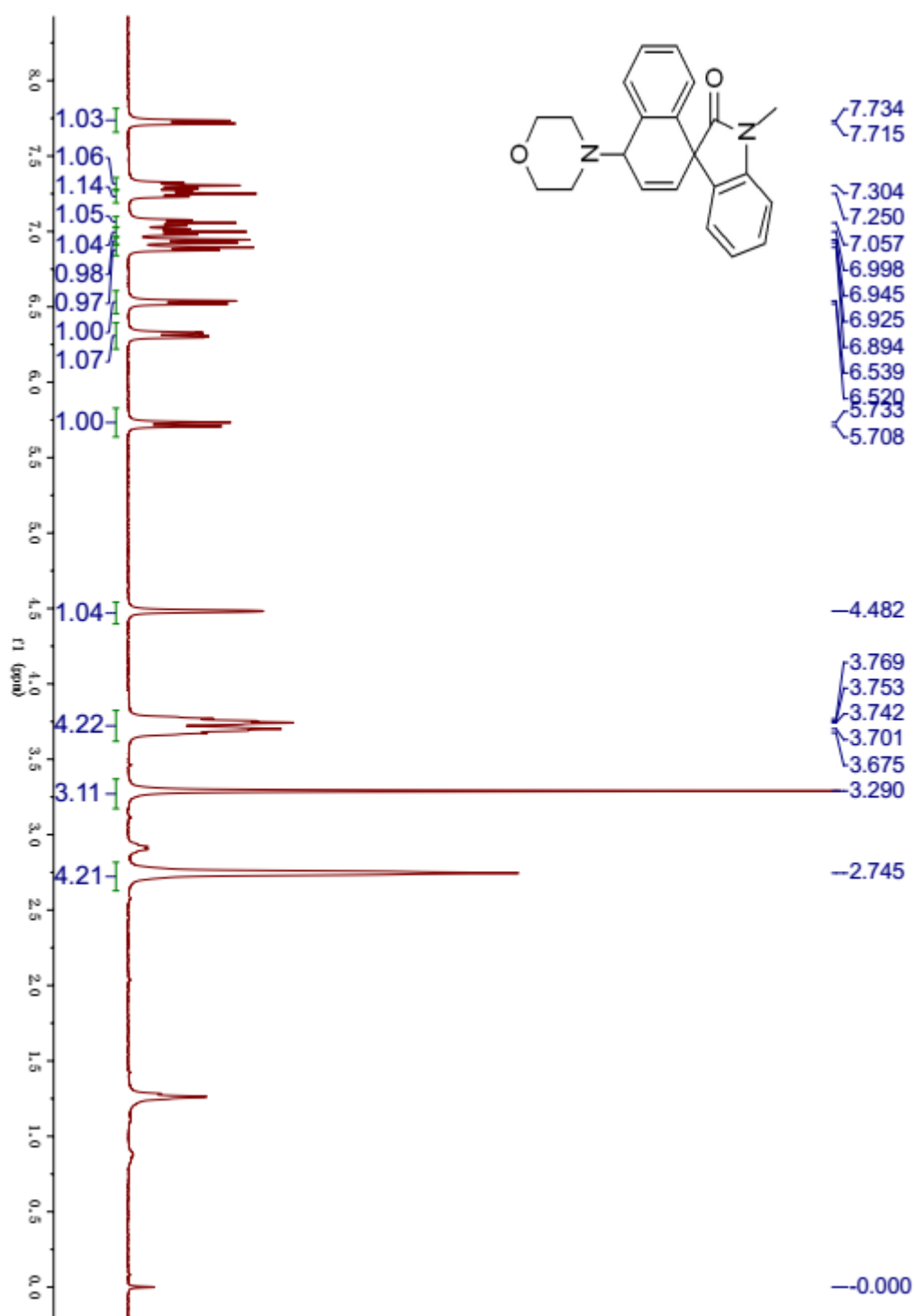


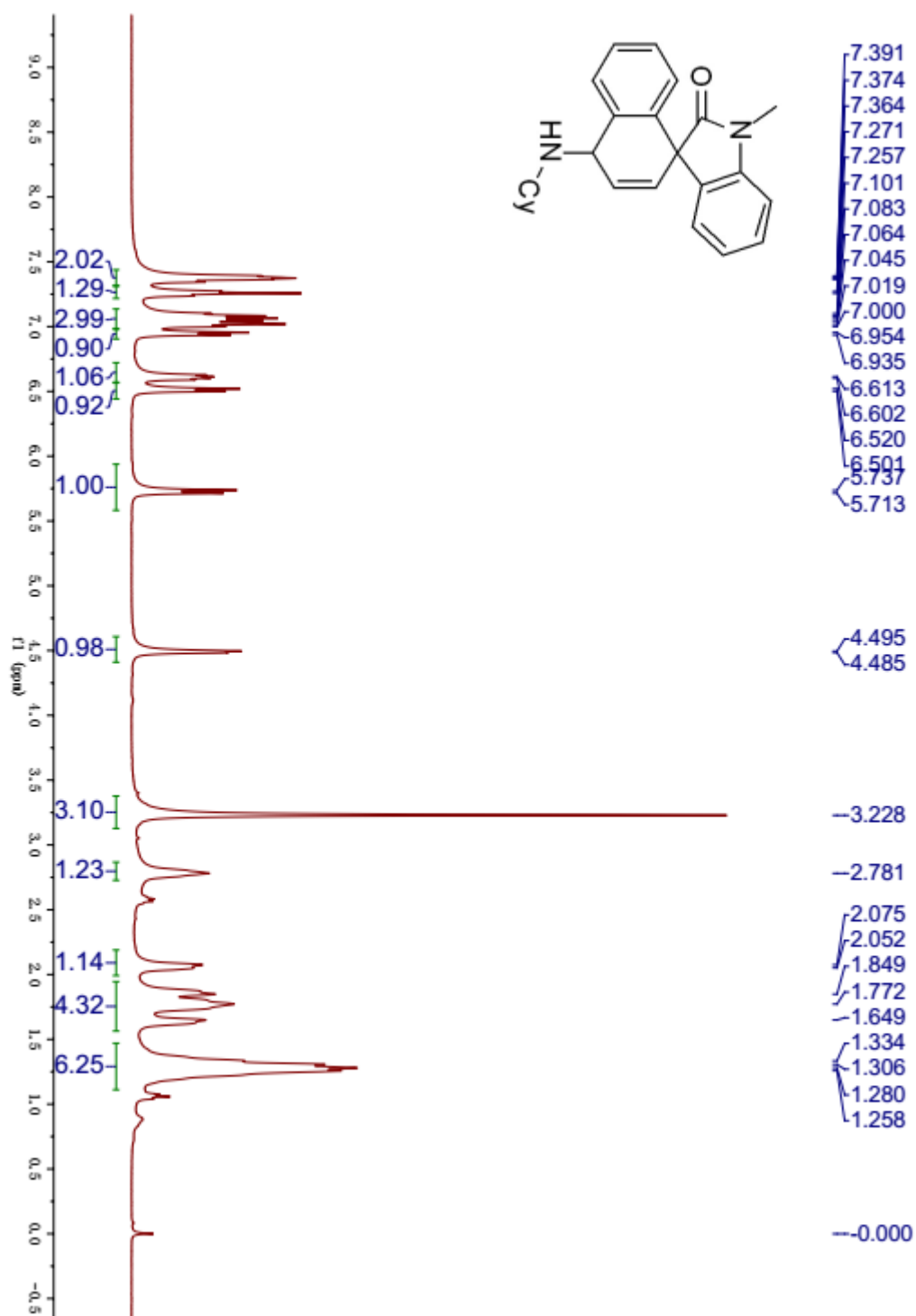
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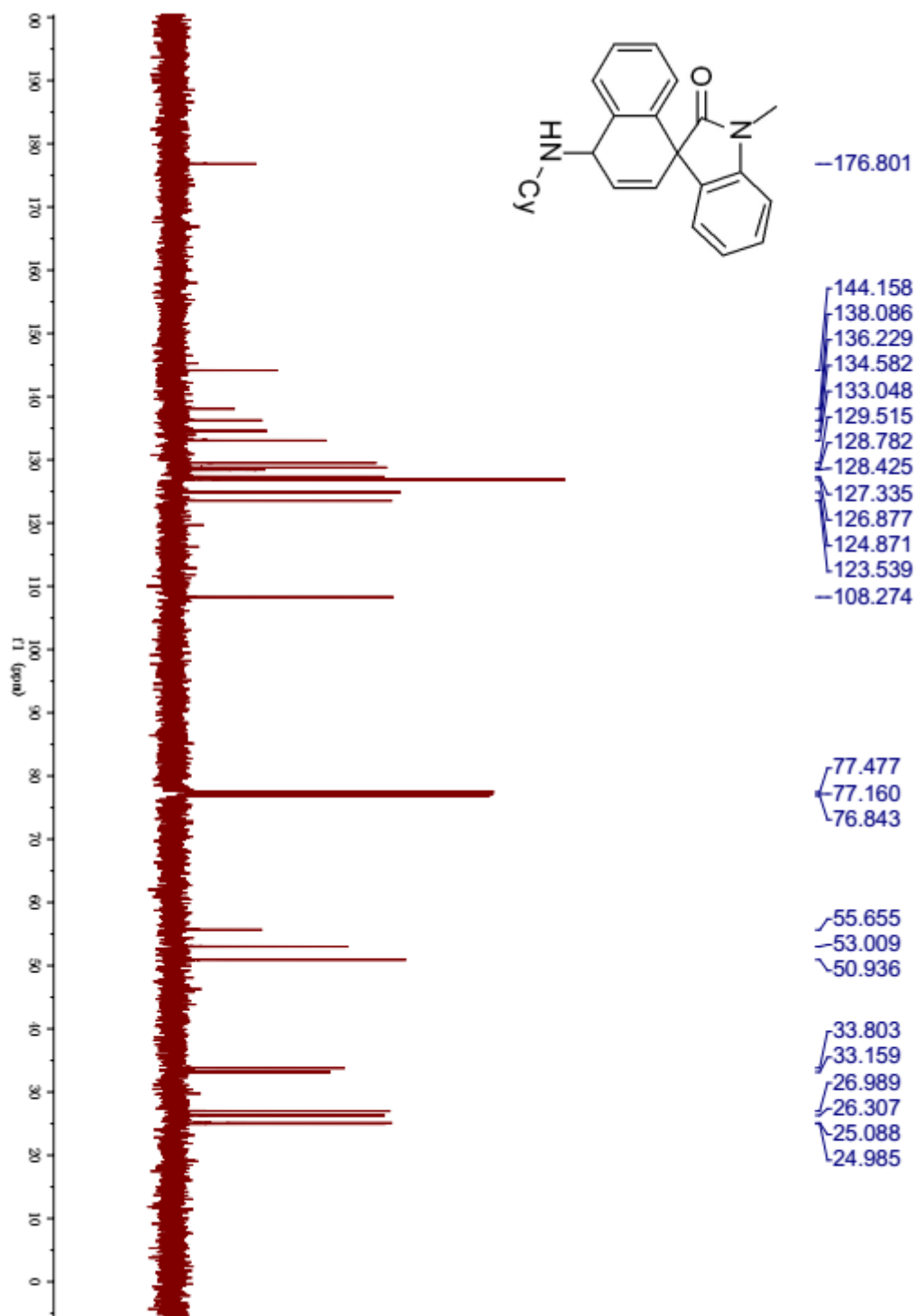




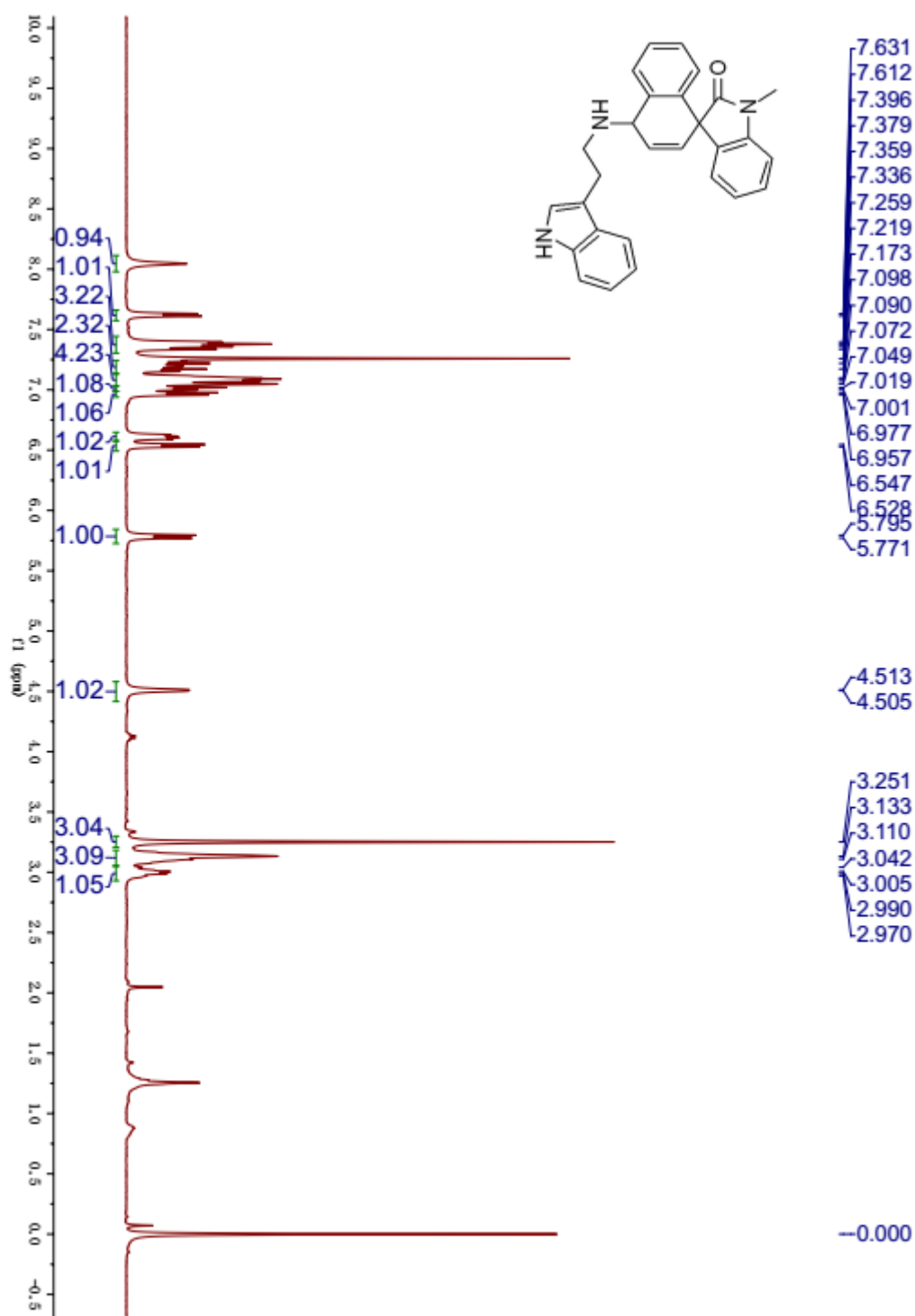
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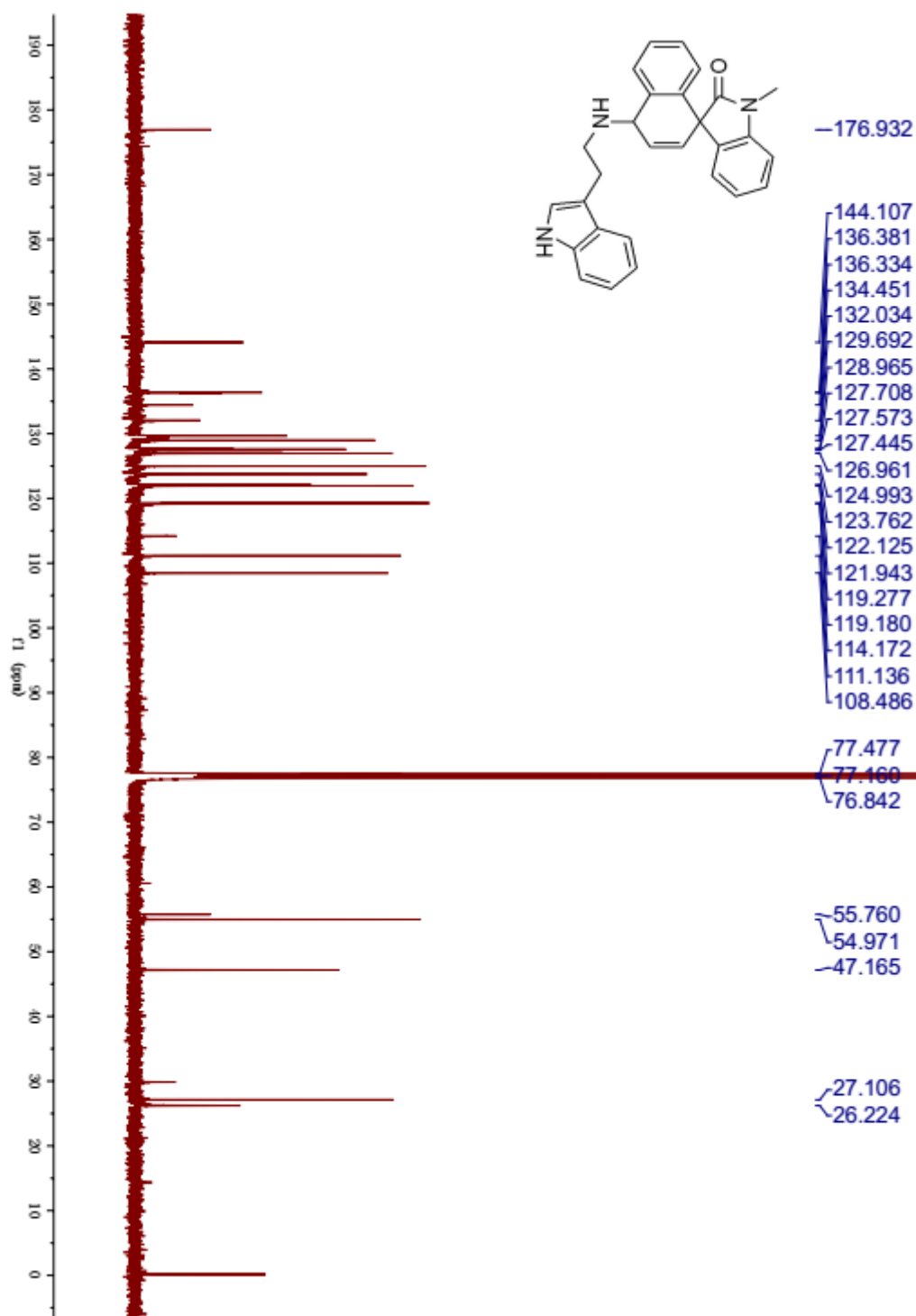




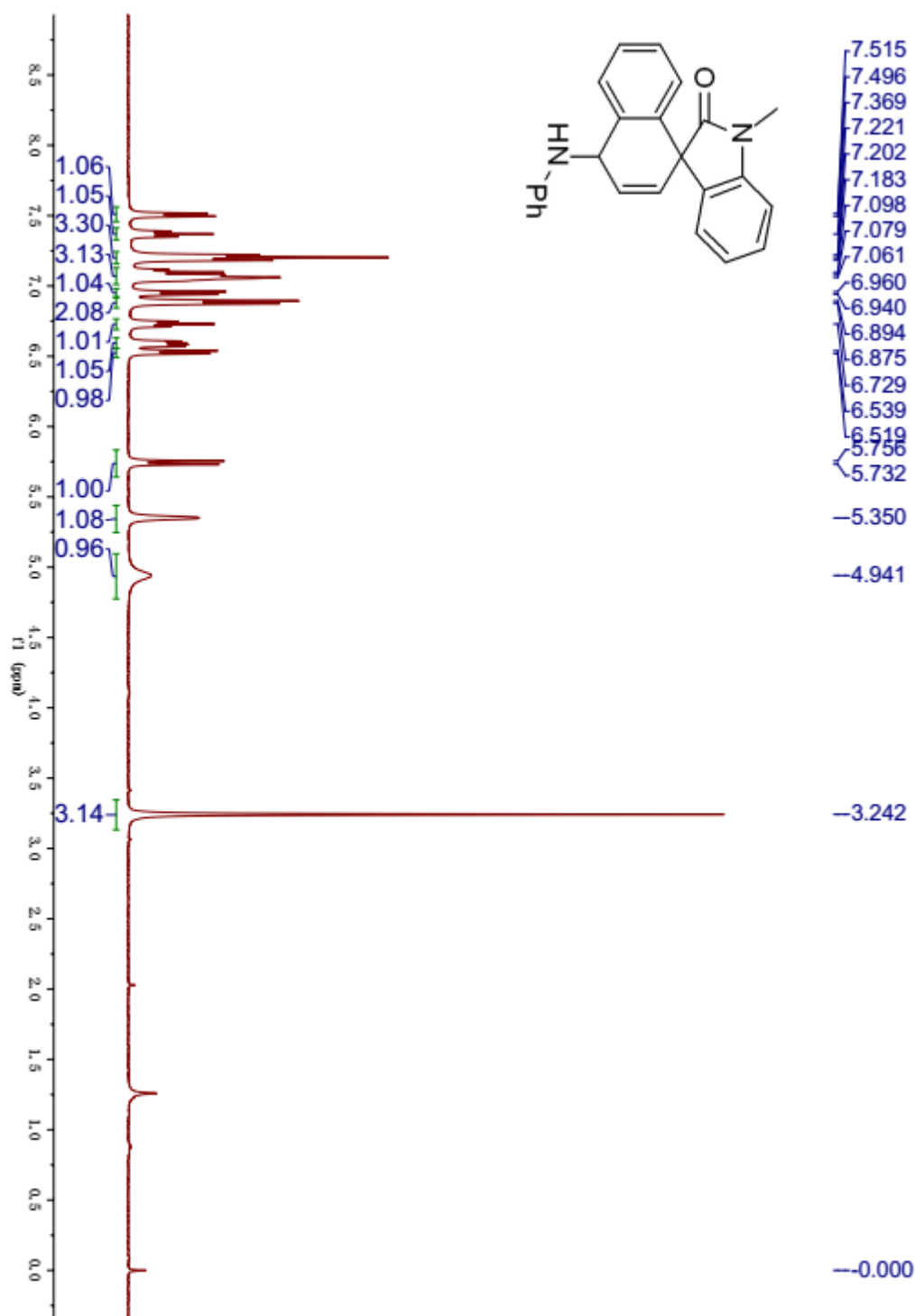


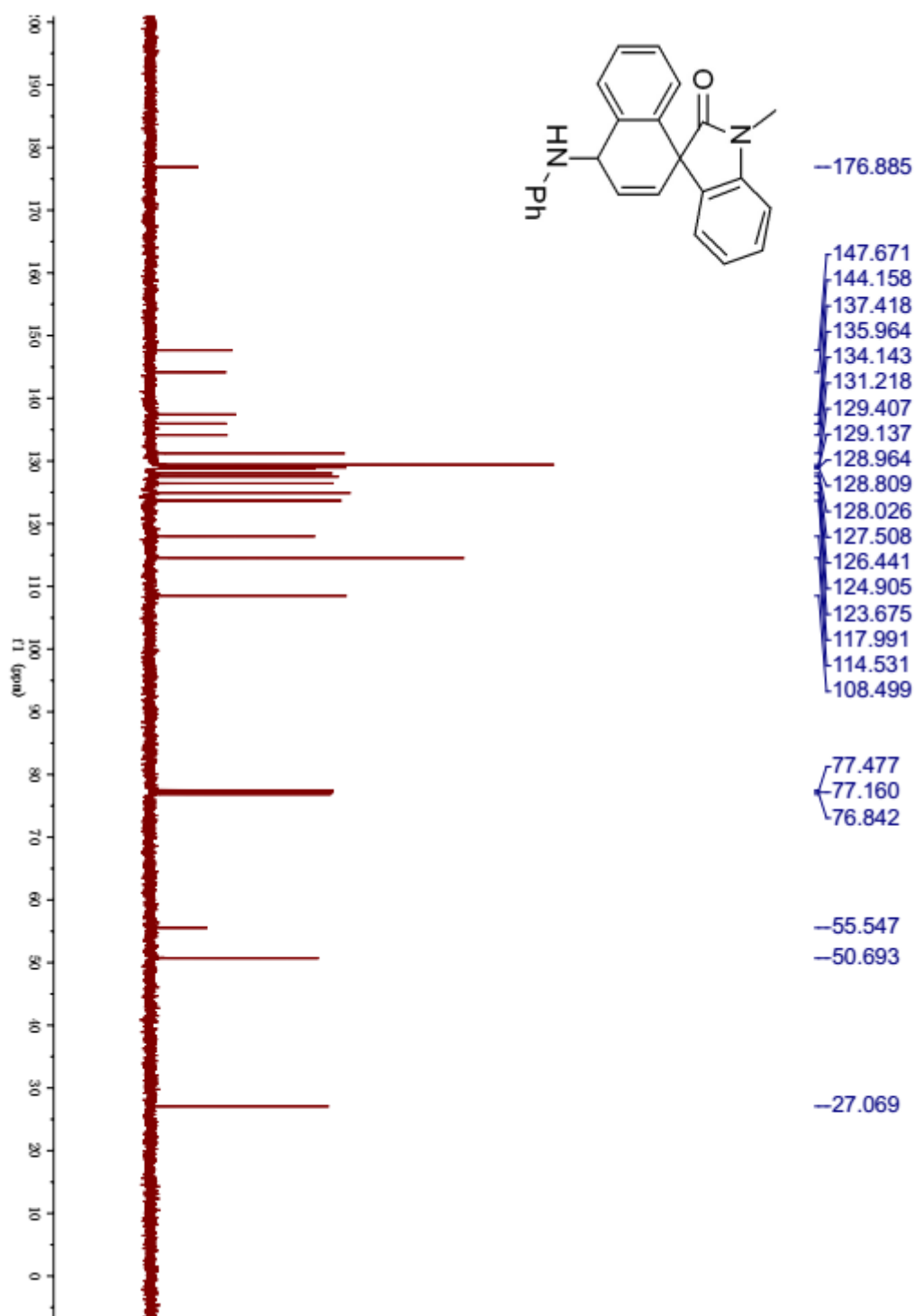
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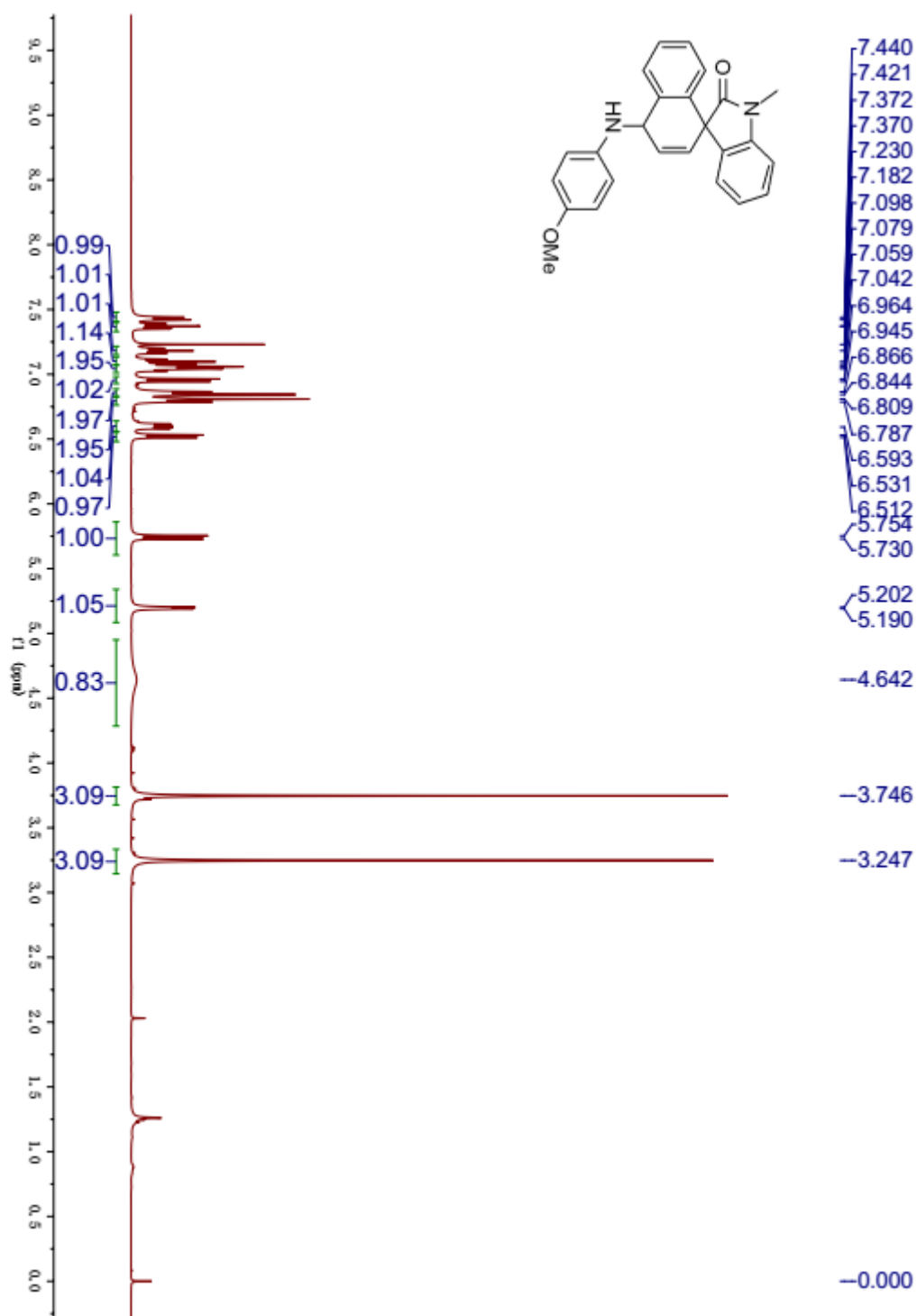


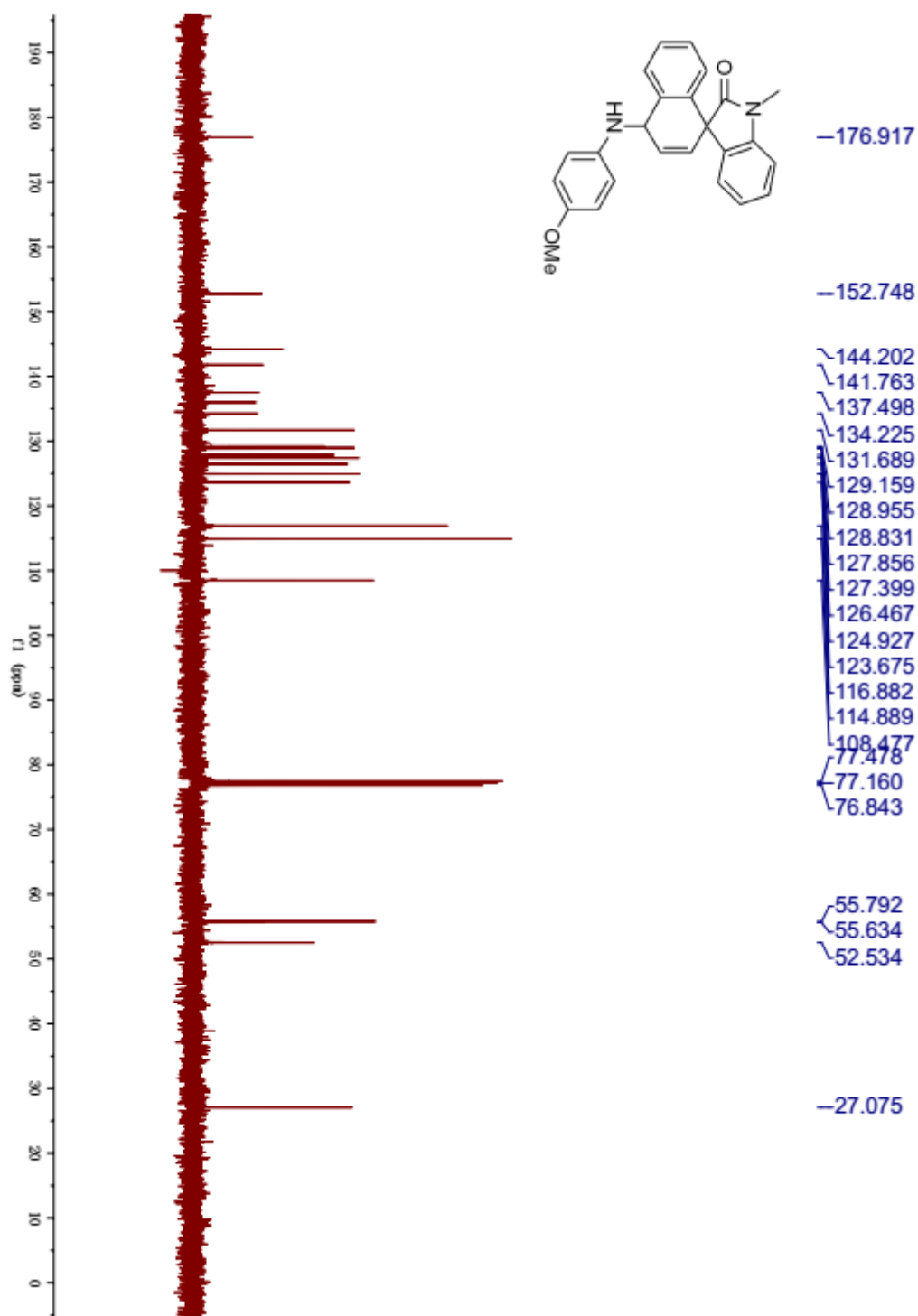


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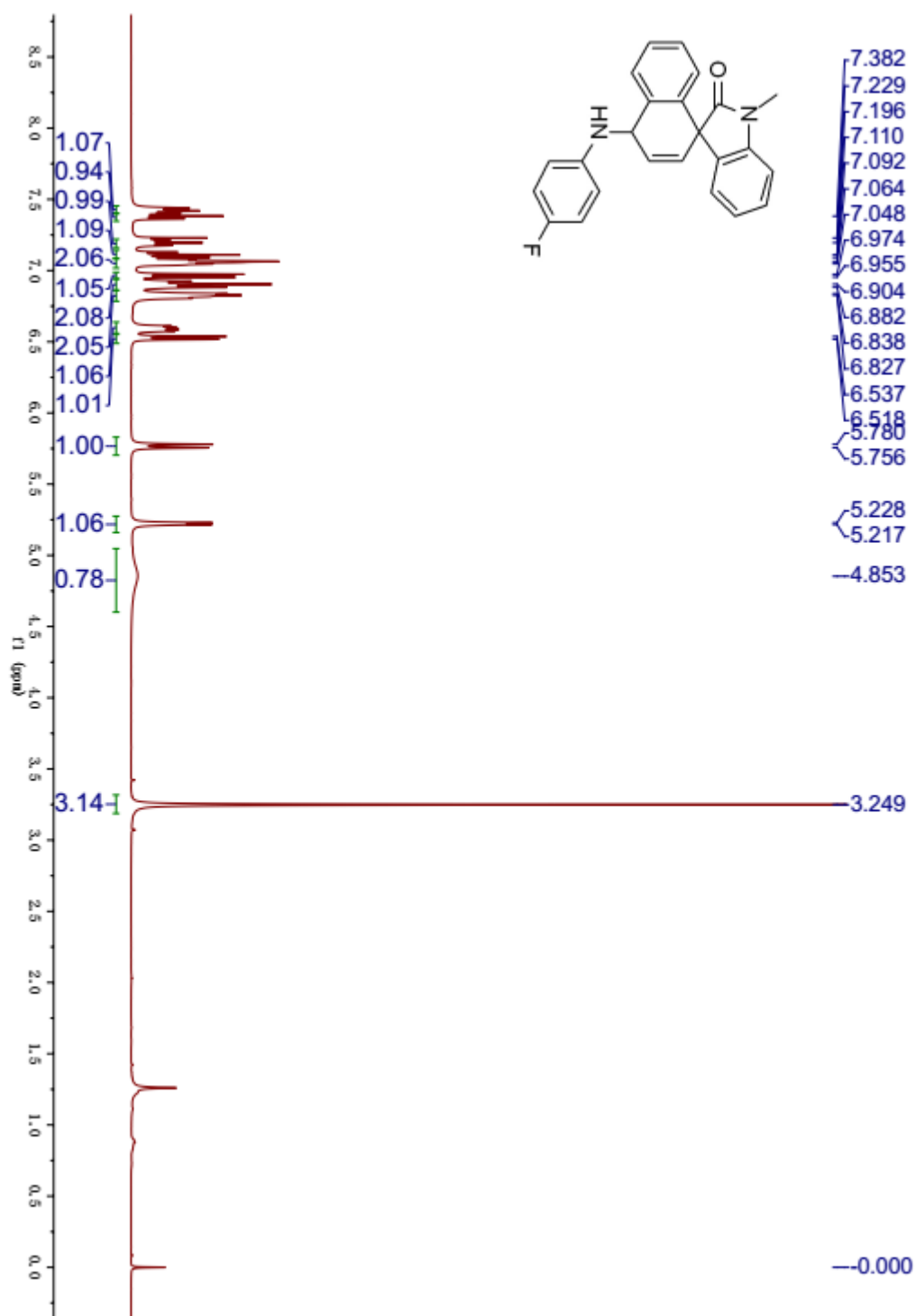


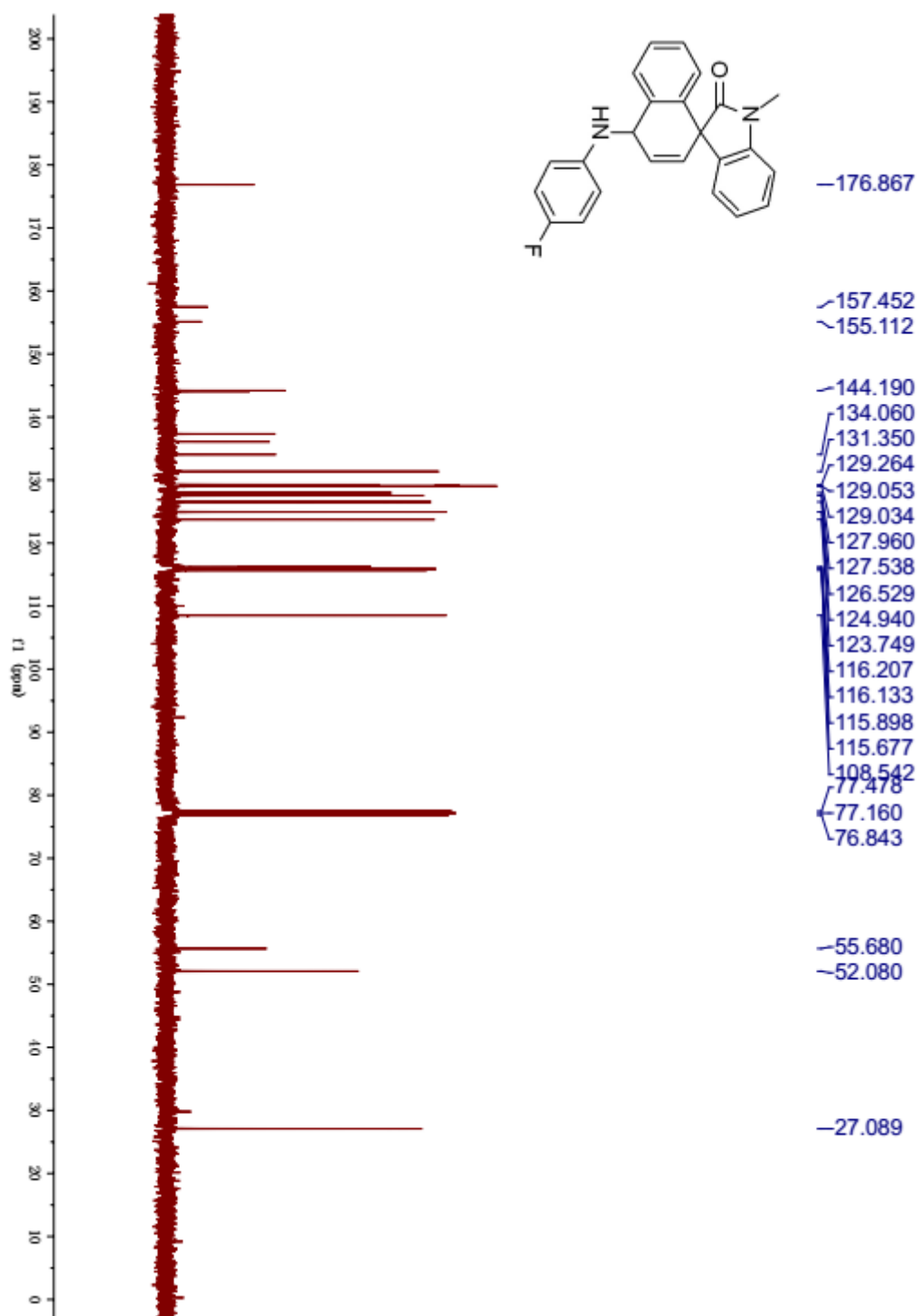


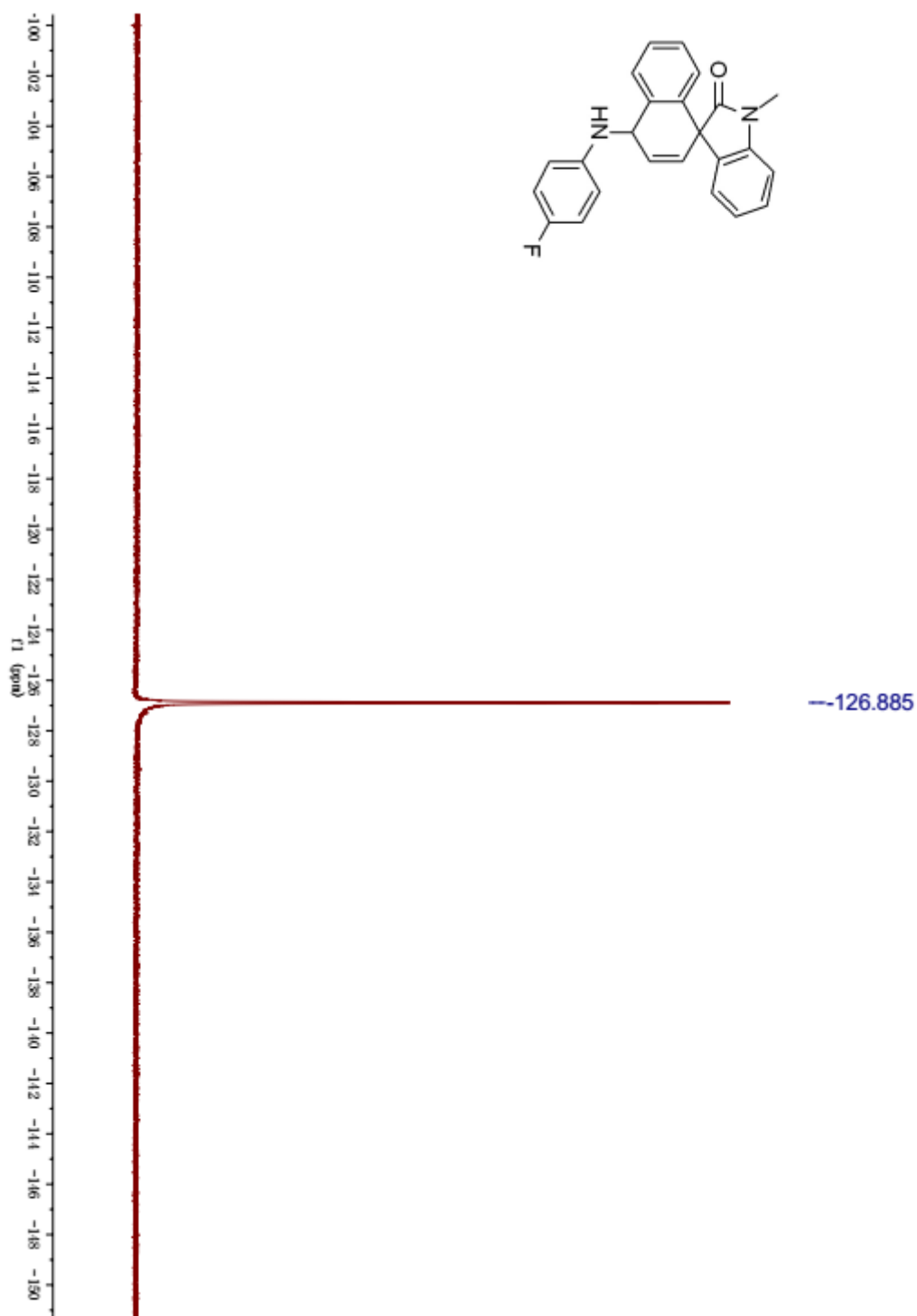
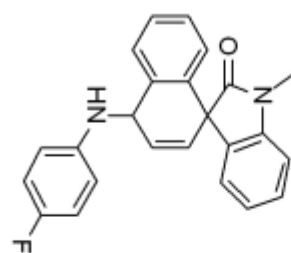




6m







6n

