

Supporting Information
for
Exploration of C–H and N–H-bond functionalization
towards 1-(1,2-diarylindol-3-yl)-
tetrahydroisoquinolines

Michael Ghobrial, Marko D. Mihovilovic and Michael Schnürch*

Address: Institute of Applied Synthetic Chemistry, Vienna University of Technology,
1060 Vienna, Austria

Email: Michael Schnürch - michael.schnuerch@tuwien.ac.at

* Corresponding author

Experimental procedures, analytical data, and copies of NMR
spectra of compounds unknown in the literature

Table of contents

1. General	S2
1.1. Caution.....	S2
1.2. Instrumentation	S2
2. Experimental	S2
3. Copies of ¹ H and ¹³ C NMR spectra of compounds.....	S18

1. General

Unless otherwise noted, chemicals were purchased from commercial suppliers and used without further purification. Flash column chromatography was performed on silica gel (40-63 μm). For thin layer chromatography (TLC) aluminum coated silica gel was used and signals were visualized with UV light (254 nm).

1.1. Caution

Mixing a metal salt and peroxide can cause explosion. See: Jones, A. K.; Wilson, T. E.; Nikam, S. S. In Encyclopedia of Reagents for Organic Synthesis, Paquette, L. A. Ed.; John Wiley & Sons, Inc. 1995, 2, 880.

1.2. Instrumentation

GC-MS runs were performed using a standard capillary column (30m x 0.32 mm ID), applying the following standardized temperature profile: 2 minutes at 80 $^{\circ}\text{C}$, 15 $^{\circ}\text{C}/\text{min}$ until 320 $^{\circ}\text{C}$, 7 minutes at 320 $^{\circ}\text{C}$. All samples subjected to HR-MS were analyzed by LC-IT-TOF-MS in only positive ion detection mode upon recording of MS and MS/MS spectra. For the evaluation in the following, only positive ionization spectra were used (where the quasi-molecular ion is the one of $[\text{M}+\text{H}]^{+}$), and further data or information were not taken into consideration. Microwave reactions were performed on a BIOTAGE InitiatorTM sixty microwave unit. Melting points were determined using a Kofler-type hot stage microscope and are uncorrected. ^1H -NMR and ^{13}C -NMR spectra were recorded either on 200 MHz or 400 MHz spectrometer. Chemical shifts are reported as ppm downfield from TMS (tetramethylsilane) as internal standard with multiplicity, number of protons, allocation, and coupling constant(s) in Hertz.

2. Experimental

General notes and instrumentation are provided in the supporting information as well as NMR-spectra of all new compounds. Compounds **3a-d** [1], **4a-d** [2,3], **9** [1] and N-arylated indoles **10a-q** [4,5] were synthesized according to literature procedures, and analytical data are in agreement with literature reports (see supporting info) [1-7].

General procedure A: N-Arylation of 6a towards 1a-d (see Table 8). Substrate **6a** (100 mg, 0.287 mmol, 1.0 equiv.), copper(I)-iodide (4.7 mg, 28.7 μmol , 0.10 equiv.), and K_3PO_4 (100 mg, 0.471 mmol, 2.0 equiv.) were placed in an oven-dried glass vial (2 mL), and aryl iodide (0.353 mmol, 1.5 equiv.) and DMEDA (4.6 μL , 47.1 μmol) were added under an argon atmosphere, followed by dry toluene (300 μL). The tube was sealed under argon, and the mixture was heated to 135 $^{\circ}\text{C}$ and stirred at this

temperature for 12 hours. In order to achieve full conversion, another batch of aryl iodide (0.353 mmol, 1.5 equiv.) and base (100 mg, 0.471 mmol, 2.0 equiv.) were added and the reaction mixture stirred 12 hours further. The reaction mixture was cooled down to room temperature, diluted with DCM and directly subjected to column chromatography using PE:EtOAc = 100:0 → 0:30 (90 minutes) to afford the desired product **1a-d**.

General procedure B: 1,2-diaryldindolation of N-Boc-THIQ **9 towards **1a,b,e-i** (see table 9):** Substrate **9** (100 mg, 0.429 mmol, 1.0 equiv.), copper(II)-nitrate trihydrate (5.2 mg, 21.5 μ mol), and 1,2-aryldindole derivative **8** (0.515 mmol, 1.2 equiv.) were placed into a 5 mL glass vial. Then, tert-butyl hydroperoxide (112 μ L, 0.558 mmol in decane, 1.3 equiv.) was added dropwise at 0 °C. The reaction mixture was capped and stirred for 10 minutes at 0 °C and then slowly heated to 50 °C and stirred for 2 days, unless stated differently. The reaction mixture was cooled to room temperature, diluted with DCM and directly subjected to column chromatography using PE:EtOAc = 100:0 → 0:30 (90 minutes) to afford the desired products **1a,b,e-i**.

1,1-Dimethylethyl 1-(1,2-diphenyl-1H-indol-3-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (1a**).**

General procedure A, table 8: Yield: 98 mg (68 %) *General procedure B*: Yield: 205 mg (48 %); white powder; M.p.: 78-81 °C; TLC: R_f (PE:Et₂O=3:1) = 0.43; GC/MS (EI⁺): m/z (rel. Intensity): 430 (M⁺-100, 69), 399 (100), 397 (19), 384 (14), 323 (32), 295 (26), 294 (20), 269 (25), 267 (17), 200 (28), 199 (10), 165 (16), 132 (12), 131 (12), 130 (32), 103 (12), 77 (20); HRMS (ESI⁺): exact mass calculated for C₃₄H₃₂N₂O₂: 523.2356. Found: 523.2363 [M+Na]⁺; ¹H NMR (200 MHz, CDCl₃): δ = 1.21 (s, 9H), 2.47 (ddd, ²J = 16.4 Hz, 3.7 Hz, 1.3 Hz, 1H), 2.89 (ddd, ²J = 16.6 Hz, ³J = 12.1 Hz, ³J = 6.0 Hz, 1H), 3.22 (ddd, ²J = 13.2 Hz, ³J = 12.3 Hz, ³J = 4.0 Hz, 1H), 4.00 (dd, ²J = 13.4 Hz, ³J = 5.8 Hz, 1H), 6.61 (s, 1H), 6.87-7.21 (m, 17H), 7.27 (dd, ³J = 7.3 Hz, ⁴J = 1.2 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃): δ = 28.2 (t), 28.3 (q, 3C), 38.6 (t), 51.2 (d), 79.5 (s), 110.4 (d), 116.2 (s), 120.0 (d), 120.3 (d), 122.1 (d), 125.9 (d), 126.4 (d), 127.0 (d), 127.5 (d, 3C overlapping), 127.8 (s), 128.20 (d), 128.24 (d, 2C), 128.72 (d), 128.76 (d, 2C), 131.3 (d, 2C), 131.8 (s), 134.8 (s), 137.16 (s), 137.23 (s), 137.8 (s), 139.4 (s), 154.3 (s)

1,1-Dimethylethyl 1-[1-(4-methoxyphenyl)-2-phenyl-1H-indol-3-yl]-3,4-dihydroisoquinoline-2(1H)-carboxylate (1b**).** *General procedure A*, table 8: Yield: 128 mg (84 %); colorless solid; M.p.: 88-92 °C; TLC: R_f (PE:Et₂O=3:1) = 0.22; GC/MS (EI⁺): m/z (rel. Intensity): 430 (M⁺-100, 78), 429 (100), 428 (25), 427 (70), 414 (18), 353 (36), 325 (21), 299 (16), 254 (17), 216 (24), 215 (24), 191 (20), 177 (22), 165 (18), 132 (32), 131 (31), 130 (64), 117 (10), 103 (18), 96 (11), 77 (25); HRMS (ESI⁺): exact mass calculated for C₃₅H₃₄N₂O₃: 553.2462. Found: 553.2465 [M+Na]⁺; ¹H NMR (200 MHz, CDCl₃): δ = 1.35 (s, 9H), 2.60 (ddd, ²J = 16.2 Hz, ³J = 3.6 Hz, ³J = 1.2 Hz, 1H), 3.03 (ddd, ²J = 16.2 Hz, ³J = 12.2 Hz, ³J = 6.0 Hz, 1H), 3.36 (dt, ²J = 13.0 Hz, ³J = 12.7 Hz, ³J = 3.7 Hz, 1H), 3.78 (s, 3H), 4.13 (dd, ²J = 13.3 Hz, ³J = 5.7 Hz, 1H), 6.73 (s, 1H), 6.82 (d, ³J = 8.9 Hz, 2H), 7.00-7.24 (m, 14H), 7.40 (d, ³J = 7.7 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃): δ = 28.2 (t), 28.3 (q, 3C), 38.5 (t), 51.2 (d), 55.2 (q), 79.4 (s), 110.4 (d), 114.0 (d, 2C), 115.8 (s), 119.9 (d), 120.2 (d), 121.9 (d), 125.9 (d), 126.3 (d), 127.45 (d), 127.52 (d, 2C), 127.6 (s), 128.2 (d), 128.7 (d), 129.4 (d, 2C), 130.5 (s), 131.3 (d, 2C), 131.9 (s), 134.8 (s), 137.3 (s), 137.5 (s), 139.7 (s), 154.3 (s), 158.3 (s)

1,1-Dimethylethyl 1-[2-phenyl-1-(thiophen-2-yl)-1H-indol-3-yl]-3,4-dihydroisoquinoline-2(1H)-carboxylate (1c**).** Prepared according to *general procedure A*, table 8: Yield: 86 mg (72 %); white powder; M.p.: 87-89 °C; TLC: R_f (PE:EtOAc=5:1) = 0.54; GC/MS (EI⁺): m/z (rel. Intensity): 406 (M⁺-100,

83), 405 (100), 404 (11), 403 (31), 329 (34), 301 (20), 275 (17), 241 (12), 216 (17), 203 (21), 186 (46), 178 (16), 171 (22), 165 (18), 164 (21), 151 (11), 132 (30), 131 (20), 130 (52), 117 (13), 115 (10), 105 (13), 103 (19), 77 (18); HRMS (ESI⁺): exact mass calculated for C₃₂H₃₀N₂O₂S: 529.1920. Found: 529.1926 [M+Na]⁺; ¹H NMR (200 MHz, CDCl₃): δ = 1.32 (s, 9H), 2.54 (ddd, ²J = 16.5 Hz, ³J = 3.9 Hz, ³J = 1.6 Hz, 1H), 2.97 (ddd, ²J = 16.6 Hz, ³J = 11.8 Hz, ³J = 6.1 Hz, 1H), 3.28 (ddd, ²J = 13.1 Hz, ³J = 12.3 Hz, ³J = 4.0 Hz, 1H), 4.08 (dd, ²J = 13.4 Hz, ³J = 5.7 Hz, 1H), 6.67 (s, 1H), 6.80 (dd, ³J = 3.7 Hz, ⁴J = 1.5 Hz, 1H), 6.85 (dd, ³J = 5.4 Hz, ³J = 3.7 Hz, 1H), 6.96-7.24 (m, 12H), 7.29 (dd, ³J = 7.7 Hz, ⁴J = 1.4 Hz, 1H), 7.41 (dd, ³J = 7.6 Hz, ⁴J = 1.1 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃): δ = 28.1 (t), 28.3 (q, 3C), 38.5 (t), 51.1 (d), 79.6 (s), 110.7 (d), 117.1 (s), 120.0 (d), 120.9 (d), 122.6 (d), 124.5 (d), 125.2 (d), 125.7 (d), 126.0 (d), 126.5 (d), 127.5 (d, 2C), 127.9 (d), 128.2 (d), 128.7 (d), 131.25 (d, 2C), 131.32 (s), 134.8 (s), 136.9 (s), 138.4 (s), 139.2 (s), 140.3 (s), 154.3 (s); (1 quaternary C missing due to potential overlap of signals)

1,1-Dimethylethyl 1-[1-(4-nitrophenyl)-2-phenyl-1H-indol-3-yl]-3,4-dihydroisoquinoline-2(1H)-carboxylate (1d). Prepared according to *general procedure A*, table 8: Yield: 70 mg (54 %); shining yellow powder; M.p.: 117-119 °C; TLC: R_f(PE:EtOAc=5:1) = 0.57; GC/MS (EI⁺): m/z (rel. Intensity): 445 (M⁺-100, 78), 444 (100), 443 (10), 442 (27), 429 (12), 398 (19), 368 (37), 340 (20), 339 (13), 293 (19), 292 (17), 267 (18), 223 (18), 217 (11), 199 (31), 191 (35), 184 (25), 177 (33), 165 (15), 146 (13), 132 (45), 131 (39), 130 (74), 117 (12), 105 (15), 103 (22), 77 (18); HRMS (ESI⁺): exact mass calculated for C₃₄H₃₁N₃O₄: 546.2387. Found: 546.2375 [M+H]⁺; ¹H NMR (200 MHz, CDCl₃): δ = 1.30 (s, 9H), 2.54 (ddd, ²J = 16.3 Hz, ³J = 3.6 Hz, ³J = 1.6 Hz, 1H), 2.95 (ddd, ²J = 16.4 Hz, ³J = 12.0 Hz, ³J = 5.9 Hz, 1H), 3.23 (ddd, ²J = 13.1 Hz, ³J = 12.3 Hz, ³J = 3.8 Hz, 1H), 4.05 (dd, ²J = 13.3 Hz, ³J = 5.5 Hz, 1H), 6.66 (s, 1H), 6.93-7.29 (m, 14H), 7.40 (dd, ³J = 7.5 Hz, ⁴J = 0.9 Hz, 1H), 8.12 (d, ³J = 8.9 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃): δ = 28.2 (t), 28.3 (q, 3C), 38.8 (t), 51.0 (d), 79.7 (s), 110.0 (d), 118.3 (s), 120.6 (d), 121.4 (d), 123.0 (d), 124.4 (d, 2C), 126.1 (d), 126.6 (d), 128.0 (d, 2C), 128.14 (d), 128.16 (d), 128.3 (d, 2C), 128.5 (s), 128.9 (d), 131.1 (s), 131.3 (d, 2C), 134.9 (s), 136.5 (s), 136.7 (s), 138.7 (s), 143.8 (s), 145.7 (s), 154.3 (s).

1,1-Dimethylethyl 1-[2-(4-methoxyphenyl)-1-phenyl-1H-indol-3-yl]-3,4-dihydroisoquinoline-2(1H)-carboxylate (1e). *General procedure B*, table 9: Yield: Cu: 143 mg (63 %), Fe: n.a.; colorless solid; M.p.: 93-95 °C; TLC: R_f(PE:EtOAc=5:1) = 0.43; GC/MS (EI⁺): m/z (rel. Intensity): 430 (M⁺-100, 76), 429 (100), 427 (44), 414 (19), 325 (16), 323 (24), 299 (19), 294 (17), 284 (14), 254 (18), 215 (50), 191 (23), 184 (20), 177 (22), 170 (16), 132 (26), 131 (26), 130 (59), 105 (12), 103 (16), 77 (30); HRMS (ESI⁺): exact mass calculated for C₃₅H₃₄N₂O₃: 553.2462. Found: 553.2470 [M+Na]⁺; ¹H NMR (200 MHz, CDCl₃): δ = 1.32 (s, 9H), 2.58 (ddd, ²J = 16.3 Hz, ³J = 3.8 Hz, ³J = 1.6 Hz, 1H), 2.99 (ddd, ²J = 16.5 Hz, ³J = 12.1 Hz, ³J = 6.0 Hz, 1H), 3.30 (ddd, ²J = 13.1 Hz, ³J = 12.1 Hz, ³J = 3.7 Hz, 1H), 3.72 (s, 3H), 4.08 (ddd, ²J = 13.4 Hz, ³J = 5.8 Hz, ³J = 1.2 Hz, 1H), 6.63 (d, ³J = 8.8 Hz, 2H), 6.66 (s, 1H), 6.93 (d, ³J = 8.7 Hz, 2H), 6.97-7.38 (m, 13H); ¹³C NMR (50 MHz, CDCl₃): δ = 28.2 (t), 28.3 (q, 3C), 38.6 (t), 51.3 (d), 55.1 (q), 79.5 (s), 110.3 (d), 113.1 (d, 2C), 116.1 (s), 119.9 (d), 120.3 (d), 121.9 (d), 124.1 (s), 126.0 (d), 126.3 (d), 126.9 (d), 127.8 (s), 128.2 (d), 128.3 (d, 2C), 128.7 (d), 128.8 (d, 2C), 132.5 (d, 2C), 134.8 (s), 137.1 (s), 137.4 (s), 137.9 (s), 139.3 (s), 154.4 (s), 158.8 (s).

1,1-Dimethylethyl 1-[2-(4-methylphenyl)-1-phenyl-1H-indol-3-yl]-3,4-dihydroisoquinoline-2(1H)-carboxylate (1f). Prepared according to *general procedure B*, table 9: Yield: Cu: 131 mg (59 %), Fe: n.a.; white powder; M.p.: 91-93 °C; TLC: R_f(PE:EtOAc=5:1) = 0.62; GC/MS (EI⁺): m/z (rel. Intensity): 414 (M⁺-100, 72), 413 (100), 398 (17), 323 (36), 309 (20), 294 (24), 283 (26), 191 (18), 177 (16), 165

(19), 132 (22), 131 (21), 130 (52), 103 (15), 77 (27); HRMS (ESI⁺): exact mass calculated for C₃₅H₃₄N₂O₂: 515.2693. Found: 515.2697 [M+Na]⁺; ¹H NMR (200 MHz, CDCl₃): δ = 1.29 (s, 9H), 2.25 (s, 3H), 2.60 (ddd, ²J = 16.3 Hz, ³J = 3.8 Hz, ³J = 1.7 Hz, 1H), 3.00 (ddd, ²J = 16.6 Hz, ³J = 12.0 Hz, ³J = 6.0 Hz, 1H), 3.33 (ddd, ²J = 13.2 Hz, ³J = 12.2 Hz, ³J = 4.0 Hz, 1H), 4.09 (ddd, ²J = 13.5 Hz, ³J = 4.7 Hz, ³J = 1.1 Hz, 1H), 6.65 (s, 1H), 6.87-7.37 (m, 17H); ¹³C NMR (50 MHz, CDCl₃): δ = 21.2 (q), 28.2 (q, 3C), 28.4 (t), 38.7 (t), 51.4 (d), 79.5 (s), 110.4 (d), 116.1 (s), 119.9 (d), 120.3 (d), 121.9 (d), 126.0 (d), 126.3 (d), 126.9 (d), 127.8 (s), 128.2 (d), 128.3 (d, 2C), 128.4 (d, 2C), 128.7 (d), 128.8 (d, 2C), 131.1 (d, 2C), 134.9 (s), 137.2 (s, 2C overlapping), 137.4 (s), 137.9 (s), 139.6 (s), 154.4 (s); (1 C missing due to potential overlap of signals); ¹H NMR (200 MHz, acetone-d₆): δ = 1.31 (s, 9H), 2.25 (s, 3H), 2.69 (ddd, ²J = 16.4 Hz, ³J = 4.0 Hz, ³J = 1.6 Hz, 1H), 2.97 (ddd, ²J = 16.6 Hz, ³J = 11.9 Hz, ³J = 6.1 Hz, 1H), 3.42 (ddd, ²J = 13.5 Hz, ³J = 12.0 Hz, ³J = 4.3 Hz, 1H), 4.10 (ddd, ²J = 13.3 Hz, ³J = 5.9 Hz, ³J = 1.1 Hz, 1H), 6.65 (s, 1H), 6.90-7.42 (m, 17H); ¹³C NMR (50 MHz, acetone-d₆): δ = 22.2 (q), 29.4 (q, 3C), 29.8 (t), 40.6 (t), 53.2 (d), 80.7 (s), 112.1 (d), 117.9 (s), 121.8 (d), 122.0 (d), 123.8 (d), 127.8 (d), 128.3 (d), 129.1 (d), 129.7 (s), 129.9 (d), 130.2 (d, 2C), 130.3 (d, 2C), 130.7 (d), 130.8 (s), 130.9 (d, 2C), 133.2 (d, 2C), 136.7 (s), 139.1 (s), 139.3 (s), 139.5 (s), 139.9 (s), 141.5 (s), 155.9 (s)

1,1-Dimethylethyl 1-[1-phenyl-2-[4-(trifluoromethyl)-phenyl]-1H-indol-3-yl]-3,4-

dihydroisoquinoline-2(1H)-carboxylate (1g). Prepared according to *general procedure B, table 9*: Yield: Cu: 111 mg (46 %), Fe: n.a.; white powder; M.p.: 88-89 °C; TLC: R_f (PE:EtOAc=5:1) = 0.58; GC/MS (EI⁺): m/z (rel. Intensity): 468 (M⁺-100, 60), 467 (81), 363 (18), 337 (14), 323 (31), 294 (23), 234 (39), 217 (12), 216 (13), 191 (18), 165 (22), 132 (49), 131 (52), 130 (100), 105 (18), 104 (18), 103 (35), 96 (22), 77 (52); HRMS (ESI⁺): exact mass calculated for C₃₅H₃₁F₃N₂O₂: 569.2410. Found: 569.2410 [M+H]⁺; ¹H NMR (200 MHz, acetone-d₆): δ = 1.34 (s, 9H), 2.66 (ddd, ²J = 16.5 Hz, ³J = 4.2 Hz, ³J = 1.3 Hz, 1H), 2.97 (ddd, ²J = 16.7 Hz, ³J = 12.0 Hz, ³J = 6.2 Hz, 1H), 3.43 (ddd, ²J = 13.5 Hz, ³J = 12.2 Hz, ³J = 4.3 Hz, 1H), 4.10 (ddd, ²J = 13.7 Hz, ³J = 6.1 Hz, ³J = 1.3 Hz, 1H), 6.71 (s, 1H), 6.94-7.55 (m, 17H); ¹³C NMR (50 MHz, acetone-d₆): δ = 29.5 (q, 3C), 29.7 (t), 40.4 (t), 52.9 (d), 80.8 (s), 112.2 (d), 118.7 (s), 122.2 (d), 122.3 (d), 124.4 (d), 126.17 (d, 2C, q, ³J_{CF} = 3.8 Hz), 126.22 (s, q, ¹J_{CF} = 271 Hz), 127.9 (d), 128.5 (d), 129.5 (d), 130.1 (d), 130.3 (d, 2C), 130.7 (d), 131.0 (d, 2C), 134.0 (d, 2C), 136.7 (s), 138.0 (s, q, ⁵J_{CF} = 1.3 Hz), 138.5 (s), 139.4 (s), 139.7 (s), 139.9 (s), 155.7 (s); (1 C missing due to potential overlap of signals)

1,1-Dimethylethyl 1-[2-(3-nitrophenyl)-1-phenyl-1H-indol-3-yl]-3,4-dihydroisoquinoline-2(1H)-

carboxylate (1h). Prepared according to *general procedure B, table 9*: Yield: Cu: 96 mg (41 %), Fe: n.a.; shining yellow powder; M.p.: 212-213 °C; TLC: R_f (PE:EtOAc=5:1) = 0.38; GC/MS (EI⁺): m/z (rel. Intensity): 445 (M⁺-100, 22), 444 (35), 443 (35), 442 (100), 428 (12), 396 (19), 323 (13), 294 (17), 267 (14), 253 (11), 197 (41), 191 (56), 190 (68), 177 (33), 132 (40), 131 (34), 130 (60), 103 (21), 96 (38), 77 (35), 73 (19); HRMS (ESI⁺): exact mass calculated for C₃₄H₃₁N₃O₄: 568.2207. Found: 568.2216 [M+Na]⁺; ¹H NMR (200 MHz, CDCl₃): δ = 1.40 (s, 9H), 2.54 (dd, ²J = 16.6, ³J = 3.2 Hz, 1H), 2.98 (ddd, ²J = 16.7 Hz, ³J = 12.4 Hz, ³J = 6.3 Hz, 1H), 3.35 (dt, ²J = 13.2 Hz, ³J = 13.0 Hz, ³J = 4.1 Hz, 1H), 4.12 (ddd, ²J = 13.6 Hz, ³J = 4.9 Hz, ³J = 1.1 Hz, 1H), 6.76 (s, 1H), 6.87-7.35 (m, 14H), 7.59 (dd, ³J = 7.4 Hz, ⁴J = 1.2 Hz, 1H), 7.78 (dd, ⁴J = 2.3 Hz, ⁴J = 1.5 Hz, 1H), 7.94 (ddd, ³J = 7.9 Hz, ⁴J = 2.0 Hz, ⁴J = 1.5 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃): δ = 28.0 (t), 28.4 (q, 3C), 38.4 (t), 51.0 (d), 79.8 (s), 110.5 (d), 117.3 (s), 120.5 (d), 120.8 (d), 122.4 (d), 123.0 (d), 126.1 (d), 126.3 (d), 126.6 (d), 127.5 (s), 127.6 (d), 128.2 (d), 128.3 (d), 128.4 (d, 2C), 128.7 (d), 129.2 (d, 2C), 133.7 (s), 134.6 (s, 2C overlapping), 136.0 (s), 136.6 (s), 137.1 (d), 137.5 (s), 147.1 (s), 154.2 (s)

1,1-Dimethylethyl 1-[2-(naphth-1-yl)-1-phenyl-1*H*-indol-3-yl]-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (1i). Prepared according to *general procedure B, table 9*: Yield: Cu: 70 mg (30 %); white powder; M.p.: 165-167 °C; TLC: R_f (PE:EtOAc=5:1) = 0.49; GC/MS (EI+): m/z (rel. Intensity): 450 (M^+ -100, 70), 449 (100), 433 (15), 345 (14), 330 (26), 321 (17), 294 (12), 253 (19), 225 (28), 217 (17), 191 (22), 177 (18), 165 (19), 133 (30), 132 (28), 131 (24), 130 (62), 105 (14), 103 (24), 96 (40), 77 (32); HRMS (ESI⁺): exact mass calculated for $C_{38}H_{34}N_2O_2$: 573.2513. Found: 573.2516 [$M+Na$]⁺; ¹H NMR (200 MHz, *acetone-d*₆): δ = 1.01 (s, 9H), 2.67 (ddd, ² J = 16.9 Hz, ³ J = 4.4 Hz, ³ J = 1.5 Hz, 1H), 2.83-3.00 (m, 1H), 3.48 (dt, ² J = 13.6 Hz, ³ J = 4.4 Hz, 1H), 4.04 (dd, ² J = 13.5 Hz, ³ J = 6.2 Hz, 1H), 6.64 (s, 1H), 6.86-7.51 (m, 17H), 7.66-7.83 (m, 3H); ¹³C NMR (50 MHz, *acetone-d*₆): δ = 29.4 (q, 3C), 29.5 (t), 40.4 (t), 53.2 (d), 80.4 (s), 112.2 (d), 119.6 (s), 121.8 (d), 122.2 (d), 123.9 (d), 126.8 (d), 127.55 (d), 127.61 (d), 127.8 (d), 128.3 (d), 128.4 (d), 129.2 (d), 129.8 (d, 3C overlapping), 130.1 (d), 130.6 (d, 2C), 130.67 (d), 130.74 (d), 133.1 (d), 135.1 (s), 135.2 (s), 136.7 (s), 139.2 (s), 139.4 (s), 139.5 (s), 139.7 (s), 154.6 (s); (2 quaternary C's missing due to potential overlap of signals)

1,1-Dimethylethyl 1-[2-(2-methylphenyl)-1-phenyl-1*H*-indol-3-yl]-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (1j). Prepared according to *general procedure B, table 9*: Yield: Cu: 81 mg (37 %); white powder; M.p.: 87-90 °C; TLC: R_f (PE:EtOAc=5:1)=0.57; GC/MS (EI+): m/z (rel. Intensity): 414 (M^+ -100, 79), 413 (100), 399 (49), 397 (48), 384 (12), 323 (26), 295 (31), 294 (45), 217 (17), 216 (14), 191 (17), 178 (20), 165 (18), 152 (12), 132 (39), 131 (27), 130 (64), 117 (11), 105 (16), 103 (20), 91 (11), 77 (31); HRMS (ESI⁺): exact mass calculated for $C_{35}H_{34}N_2O_2$: 515.2693. Found: 515.2692 [$M+H$]⁺; ¹H NMR (200 MHz, *CDCl*₃): δ = 1.30 (s, 9H), 2.00 (s, 3H), 2.46-2.70 (m, 1H), 2.78-3.12 (m, 2H), 3.91-4.09 (m, 1H), 6.48 (s, 1H), 6.85-7.33 (m, 17H); ¹³C NMR (50 MHz, *CDCl*₃): δ = 19.9 (q), 28.3 (q, 3C), 28.4 (t), 38.7 (t), 51.3 (d), 79.4 (s), 110.4 (d), 116.8 (s), 119.7 (d), 120.3 (d), 121.8 (d), 125.0 (d), 126.0 (d), 126.4 (d), 126.9 (d), 127.7 (d, 2C), 128.1 (d), 128.2 (s), 128.5 (d), 128.7 (d, 3C overlapping) 129.5 (d), 131.4 (s), 132.5 (d), 134.9 (s), 136.8 (s), 137.6 (s, 2C overlapping), 137.9 (s), 138.4 (s), 154.4 (s).

5-(1*H*-Indol-1-yl)-2-phenyloxazole (5m, see table 6). Indole (47 mg, 0.400 mmol, 1 equiv.), CuI (7.6 mg, 40 μ mol, 0.1 equiv.), and K_3PO_4 (171 mg, 0.800 mmol, 2 equiv.) were placed in an oven-dried tube, and 5-iodo-2-phenyloxazole (163 mg, 0.600 mmol, 1.5 equiv.) and DMEDA (9 μ L, 80 μ mol, 0.2 equiv.) were added under an argon atmosphere, followed by dry toluene (400 μ L). The tube was sealed under argon, and the mixture was heated up to 135 °C and stirred at this temperature for 12 hours. The reaction mixture was cooled to room temperature, diluted with DCM and directly subjected to column chromatography using PE:EtOAc =100:0 $\rightarrow$ 90:10 (20 minutes) to afford the desired product. Yield: 71 mg (68 %); colorless solid; M.p.: 131-133 °C; TLC: R_f (PE:EtOAc=10:1) = 0.38; GC/MS (EI+): m/z (rel. Intensity): 260 (M^+ , 57), 231 (10), 144 (53), 116 (100), 89 (48), 63 (14); ¹H NMR (200 MHz, *CDCl*₃) δ = 6.64 (dd, 3J = 3.4 Hz, 4J = 0.6 Hz, 1H), 7.02 (s, 1H), 7.09-7.25 (m, 2H), 7.28 (d, 3J = 3.5 Hz, 1H), 7.32-7.43 (m, 3H), 7.52 (d, 3J = 7.8 Hz, 1H), 7.58 (dd, 3J = 7.2 Hz, 4J = 1.2 Hz, 1H), 7.91-8.03 (m, 2H); ¹³C NMR (50 MHz, *CDCl*₃) δ = 106.0 (d), 111.0 (d), 114.8 (d), 121.3 (d), 121.7 (d), 123.6 (d), 126.0 (d, 2C), 126.3 (d), 127.0 (s), 128.9 (d, 2C), 129.1 (s), 130.4 (d), 135.6 (s), 145.4 (s), 157.5 (s).

General procedure C: C2-Arylation of 4a towards 6a-c (see table 2), 1-(Indol-3-yl)-N-Boc-THIQ 4a (200 mg, 0.574 mmol, 1.0 equiv.), aryl boronic acid (288 mg, 0.861 mmol, 1.5 equiv.), Cu(OAc)₂ (104 mg, 0.574 mmol) and Pd(OAc)₂ (6.4 mg, 28.7 μ mol, 0.05 equiv.) were placed in a 5 ml glass vial. After AcOH (2.0 mL) was added by syringe, the resulting solution was purged with oxygen for 30 seconds and stirred for 12 hours at room temperature in an oxygen atmosphere. Then, another 1.5 equiv. of

phenylboronic acid was added and the reaction stirred for another 12 hours. The black solution was poured onto ice-cold saturated sodium carbonate and extracted four times with EtOAc. The collected organic layers were washed twice with brine, dried over sodium sulfate, filtered and evaporated. The crude products **3a-c** were purified by flash chromatography, using gradient elution with PE:EtOAc=100:0 → 80:20 (45 minutes).

General procedure D: 2-Arylindolation of N-Boc-THIQ **9 towards **6a-c** (see table 1):** A mixture of *N*-Boc-THIQ **9** (200 mg, 0.858 mmol, 1.0 equiv.), catalyst (Cu(NO₃)₂ × 3H₂O: 10.4 mg, 42.9 μmol, 0.05 equiv.; FeCl₃: 7.0 mg, 42.9 μmol, 0.05 equiv.), and 2-arylindole **3** (1.03 mmol, 1.2 equiv.) were placed into a 5 mL glass vial. Then, *t*BHP (223 μL, 1.12 mmol in decane) was added dropwise at 0 °C. The reaction mixture was capped and stirred for 10 minutes, keeping the temperature constant using a cryostat. Then the reaction mixture was slowly heated to 50 °C and stirred for 48 hours. The reaction mixture was cooled to room temperature, diluted with DCM and directly subjected to column chromatography using PE:EtOAc =100:0 → 0:40 (60 minutes) to afford the desired products **6a-c**.

1,1-Dimethylethyl 1-(2-phenyl-1*H*-indol-3-yl)-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (6a**).** Yield: General procedure D: Fe: 205 mg (56 % table 1, Cu: 159 mg (44 %, table 1), General procedure C: 125 mg (51 %, table 2); colorless solid; M.p.: 89-92 °C; TLC: R_f(PE:EtOAc=5:1)=0.40; GC/MS (EI+): m/z (rel. Intensity): 324 (M⁺-100, 58), 323 (100), 321 (11), 308 (20), 294 (12), 247 (20), 219 (27), 218 (24), 217 (16), 204 (10), 193 (42), 165 (14), 147 (20), 139 (11), 132 (18), 131 (15), 130 (30), 103 (14), 77 (13); HRMS (ESI⁺): exact mass calculated for C₂₈H₂₈N₂O₂: 447.2043. Found: 447.2060 [M+Na]⁺; ¹H NMR (200 MHz, CDCl₃): δ = 1.15 (s, 9H), 2.54 (dd, ²J = 16.3 Hz, ³J = 2.2 Hz, 1H), 2.91 (ddd, ²J = 16.6 Hz, ³J = 12.1 Hz, ³J = 6.0 Hz, 1H), 3.26 (dt, ²J = 13.1 Hz, ³J = 12.8 Hz, ³J = 3.9 Hz, 1H), 4.02 (dd, ²J = 13.4 Hz, ³J = 5.5 Hz, 1H), 6.58 (s, 1H), 6.77-7.28 (m, 13H), 8.33 (s, 1H); ¹³C NMR (50 MHz, CDCl₃): δ = 28.2 (q, 3C), 28.3 (t), 38.8 (t), 51.1 (d), 79.6 (s), 110.7 (d), 114.2 (s), 119.7 (d), 120.1 (d), 121.7 (d), 126.0 (d), 126.4 (d), 127.9 (d), 128.1 (d), 128.2 (d, 2C), 128.7 (d), 129.3 (d, 2C), 133.2 (s), 134.8 (s), 135.4 (s), 137.0 (s), 137.3 (s), 154.5 (s); (1 C missing due to potential overlap of signals); ¹H NMR (200 MHz, acetone-D₆): δ = 1.31 (s, 9H), 2.79 (ddd, ²J = 16.4 Hz, ³J = 4.0 Hz, ³J = 1.4 Hz, 1H), 3.05 (ddd, ²J = 16.7 Hz, ³J = 12.0 Hz, ³J = 6.1 Hz, 1H), 3.50 (ddd, ²J = 13.4 Hz, ³J = 12.2 Hz, ³J = 4.2 Hz, 1H), 4.16 (ddd, ²J = 13.5 Hz, ³J = 4.7 Hz, ³J = 1.2 Hz, 1H), 6.72 (s, 1H), 6.90-6.78 (m, 1H), 6.95-7.66 (m, 12H), 10.44 (s, 1H); ¹³C NMR (50 MHz, acetone-D₆): δ = 29.4 (q, 3C), 30.0 (t, overlaps with acetone signal), 40.8 (t), 53.2 (d), 80.7 (s), 112.9 (d), 115.5 (s), 121.1 (d), 121.8 (d), 123.2 (d), 127.8 (d), 128.3 (d), 129.6 (d), 129.8 (d), 130.2 (d, 2C), 130.7 (d), 131.3 (d, 2C), 135.3 (s), 136.8 (s), 138.1 (s), 139.1 (s), 139.6 (s), 156.1 (s); (1 C missing due to potential overlap of signals)

1,1-Dimethylethyl 1-(2-(4-methylphenyl)-1*H*-indol-3-yl)-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (6b**).** Yield: General procedure D: Fe: 74 mg (20 %, table 1), Cu: n.a., General procedure C: 123 mg (49 %, table 2); white powder; M.p.: 79-82 °C; TLC: R_f (PE:EtOAc=5:1) = 0.41; GC/MS (EI+): m/z (rel. Intensity): 338 (M⁺-100, 62), 337 (100), 336 (11), 335 (29), 322 (26), 308 (11), 247 (25), 233 (24), 218 (33), 217 (21), 191 (10), 169 (34), 160 (21), 153 (22), 146 (26), 139 (17), 132 (25), 131 (24), 130 (48), 103 (23), 96 (11), 89 (11), 77 (15); HRMS (ESI⁺): exact mass calculated for C₂₉H₃₀N₂O₂: 461.2199. Found: 461.2206 [M+Na]⁺; ¹H NMR (200 MHz, CDCl₃): δ = 1.29 (s, 9H), 2.38 (s, 3H), 2.70 (ddd, ²J = 16.5 Hz, ³J = 3.9 Hz, ³J = 1.4 Hz, 1H), 3.06 (ddd, ²J = 17.0 Hz, ³J = 12.1 Hz, ³J = 6.1 Hz, 1H), 3.40 (ddd, ²J = 13.4 Hz, ³J = 12.3 Hz, ³J = 4.0 Hz, 1H), 4.07-4.23 (m, 1H), 6.67 (s, 1H), 6.89-6.99 (m, 1H), 7.03-7.21 (m, 8H), 7.27-7.34 (m, 3H), 8.13 (bs, 1H); ¹H NMR (200 MHz, acetone-D₆): δ = 1.30 (s, 9H), 2.38 (s, 3H),

2.74-2.89 (m, 1H), 3.05 (ddd, $^2J = 16.4$ Hz, $^3J = 12.0$ Hz, $^3J = 6.0$ Hz, 1H), 3.50 (ddd, $^2J = 13.5$ Hz, $^3J = 12.0$ Hz, $^3J = 4.3$ Hz, 1H), 4.15 (ddd, $^2J = 13.5$ Hz, $^3J = 4.6$ Hz, $^3J = 1.2$ Hz, 1H), 6.67 (s, 1H), 6.76-6.86 (m, 1H), 6.95-7.20 (m, 6H), 7.25 (d, $^3J = 8.0$ Hz, 2H), 7.37 (dd, $^3J = 7.6$ Hz, $^4J = 1.5$ Hz, 1H), 7.49 (d, $^3J = 8.1$ Hz, 2H), 10.38 (bs, 1H); ^{13}C NMR (50 MHz, CDCl_3): $\delta = 21.1$ (q), 28.2 (q, 3C), 28.4 (t), 38.9 (t), 51.2 (d), 79.5 (s), 110.7 (d), 114.0 (s), 119.6 (d), 120.0 (d), 121.6 (d), 126.1 (d), 126.3 (d), 128.1 (d), 128.4 (s), 128.7 (d), 129.0 (d, 2C), 129.2 (d, 2C), 130.3 (s), 134.9 (s), 135.4 (s), 137.1 (s), 137.4 (s), 137.7 (s), 154.6 (s)

1,1-Dimethylethyl 1-(2-(4-methoxyphenyl)-1H-indol-3-yl)-3,4-dihydroisoquinoline-2(1H)-

carboxylate (6c). Yield: General procedure D: Fe: 55 mg (14 %, table 1), Cu: n.a., General procedure C: 88 mg (34 %, table 2); Off colorless solid; M.p.: 76-78 °C; TLC: R_f (PE:EtOAc=5:1) = 0.32; GC/MS (EI^+): m/z (rel. Intensity): 354 ($\text{M}^+ - 100$, 37), 353 (62), 352 (35), 351 (100), 338 (20), 308 (12), 249 (15), 223 (34), 218 (20), 217 (17), 208 (42), 191 (18), 177 (28), 176 (35), 169 (19), 168 (22), 161 (18), 153 (31), 146 (28), 132 (28), 131 (25), 130 (42), 126 (13), 103 (18), 96 (31), 77 (20), 73 (12); HRMS (ESI^+): exact mass calculated for $\text{C}_{29}\text{H}_{30}\text{N}_2\text{O}_3$: 477.2149. Found: 477.2158 [$\text{M} + \text{Na}$] $^+$; ^1H NMR (200 MHz, CDCl_3): $\delta = 1.28$ (s, 9H), 2.64 (ddd, $^2J = 16.4$ Hz, $^3J = 3.8$ Hz, $^3J = 1.5$ Hz, 1H), 3.01 (ddd, $^2J = 16.6$ Hz, $^3J = 12.1$ Hz, $^3J = 6.0$ Hz, 1H), 3.35 (dt, $^2J = 13.2$ Hz, $^3J = 12.8$ Hz, $^3J = 3.9$ Hz, 1H), 3.76 (s, 3H), 4.03-4.18 (m, 1H), 6.64 (s, 1H), 6.80 (d, $^3J = 8.7$ Hz, 2H), 6.92 (ddd, $^3J = 7.9$ Hz, $^3J = 7.1$ Hz, $^4J = 0.9$ Hz, 1H), 7.19-6.98 (m, 6H), 7.29-7.19 (m, 3H), 8.28 (s, 1H); ^1H NMR (200 MHz, *acetone-D6*): $\delta = 1.32$ (s, 9H), 2.87-2.72 (m, 1H), 3.05 (ddd, $^2J = 16.2$ Hz, $^3J = 12.1$ Hz, $^3J = 6.0$ Hz, 1H), 3.49 (ddd, $^2J = 13.5$ Hz, $^3J = 12.0$ Hz, $^3J = 4.3$ Hz, 1H), 3.85 (s, 3H), 4.14 (ddd, $^2J = 13.5$ Hz, $^3J = 4.6$ Hz, $^3J = 1.3$ Hz, 1H), 6.81 (ddd, $^3J = 7.8$ Hz, $^3J = 7.0$ Hz, $^4J = 1.1$ Hz), 6.98 (d, $^3J = 8.9$ Hz, 2H), 7.01-7.29 (m, 6H), 7.32-7.40 (m, 1H), 7.50 (d, $^3J = 8.9$ Hz, 2H), 10.34 (bs, 1H); ^{13}C NMR (50 MHz, CDCl_3): $\delta = 28.2$ (q, 3C), 28.4 (t), 38.8 (t), 51.2 (d), 55.2 (q), 79.6 (s), 110.6 (d), 113.8 (d, 2C), 114.0 (s), 119.7 (d), 120.0 (d), 121.6 (d), 125.6 (s), 126.0 (d), 126.3 (d), 128.1 (d), 128.4 (s), 128.7 (d), 130.6 (d, 2C), 134.8 (s), 135.2 (s), 136.8 (s), 137.4 (s), 154.6 (s), 159.3 (s).

Phenylmethyl 1-(2-phenyl-1H-indol-3-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (6g, table 2).

1-(Indol-3-yl)-N-Cbz-THIQ **4b** (245 mg, 0.641 mmol, 1.0 equiv.), phenylboronic acid (117 mg, 0.961 mmol, 1.5 equiv.), $\text{Cu}(\text{OAc})_2$ (116 mg, 0.641 mmol) and $\text{Pd}(\text{OAc})_2$ (7.2 mg, 32.0 μmol , 0.05 equiv.) were placed in a 5 ml glass vial. After acetic acid (4.0 mL) was added by syringe, the resulting solution was degassed twice and refilled with O_2 (1.0 atm.). The mixture was stirred for 12 h at room temperature. Then, another 1.5 equiv. of phenylboronic acid was added and the reaction stirred for another 12 hours. The reaction mixture was poured onto saturated sodium carbonate and extracted four times with EtOAc. The collected organic layers were washed once with saturated sodium carbonate, dried over sodium sulfate, filtered and evaporated. Flash chromatography using PE:Et₂O=100:0 $\rightarrow$ 0:50 (1h 30 minutes) afforded the desired product **6g**. Yield: 151 mg (51 %); colorless solid; M.p.: 76-78 °C; TLC: R_f (PE:EtOAc=5:1)=0.28; GC/MS (EI^+): m/z (rel. Intensity): 458 (M^+ , 2), 367 (1), 324 (24), 323 (100), 218 (12), 217 (10), 193 (14), 165 (10), 130 (20), 103 (9), 91 (79), 77 (8), 65 (9); HRMS (ESI^+): exact mass calculated for $\text{C}_{31}\text{H}_{26}\text{N}_2\text{O}_2$: 481.1886. Found: 481.1891 [$\text{M} + \text{Na}$] $^+$; ^1H NMR (200 MHz, CDCl_3): $\delta = 2.69$ (dd, $^2J = 16.3$ Hz, $^3J = 1.8$ Hz, 1H), 2.96 (ddd, $^2J = 16.3$ Hz, $^3J = 12.3$ Hz, $^3J = 5.7$ Hz, 1H), 3.40 (dt, $^2J = 13.1$ Hz, $^3J = 12.9$ Hz, $^3J = 3.6$ Hz, 1H), 4.26 (dd, $^2J = 13.3$ Hz, $^3J = 5.0$ Hz, 1H), 4.49 (bs, 1H), 4.93 (d, $^2J = 12.4$ Hz, 1H), 6.71 (s, 1H), 6.88 (d, $^3J = 7.2$ Hz, 1H), 6.94-7.26 (m, 15H), 7.28-7.41 (m, 2H), 8.44 (s, 1H); ^{13}C NMR (50 MHz, CDCl_3): $\delta = 28.8$ (t), 39.2 (t), 51.1 (d), 66.6 (t), 110.8 (d), 113.7 (s), 119.8 (d), 120.1 (d), 121.8 (d), 126.3 (d), 126.5 (d), 127.6 (d), 127.7 (d, 2C), 127.85

(d), 127.90 (d), 128.1 (d, 2C), 128.3 (d, 2C), 128.7 (d), 128.9 (d, 2C), 133.2 (s), 134.6 (s), 135.6 (s), 136.6 (s), 136.8 (s), 137.4 (s), 155.3 (s); (1 C missing due to potential overlap of signals).

General procedure E: N-Arylation of 4 towards 7a-e,g (table 3). 1-(Indol-3-yl)-N-Boc-THIQ **4a** (100 mg, 0.287 mmol, 1.0 equiv.), iron(III)-chloride (4.7 mg, 28.7 μ mol, 0.1 equiv.), and K_3PO_4 (122 mg, 0.574 mmol, 2.0 equiv.) were placed in a 2 mL glass vial, and aryl iodide (0.431 mmol, 1.5 equiv.) and DMEDA (5.6 μ L, 57.4 μ mol, 0.20 equiv.) were added followed by dry toluene (300 μ L). The reaction mixture was purged with argon for 30 seconds, the vial sealed and heated to 135 °C and stirred at this temperature for 24 hours. The black slurry was cooled down to rt, diluted with DCM and filtered through a plug of celite. The solvent of the filtrate was evaporated and the crude product directly subjected to column chromatography using gradient elution with PE:EtOAc=100:0 $\rightarrow$ 0:40 (50 minutes) to afford the desired products **7a-e,g**.

General procedure F for N-arylation of N-Boc-THIQ 9 (table 5). To a mixture of N-Boc-THIQ **5** (200 mg, 0.858 mmol, 1.0 equiv.), catalyst ($Cu(NO_3)_2 \times 3H_2O$: 10.4 mg, 42.9 μ mol, 0.05 equiv.; $FeCl_3$: 7.0 mg, 42.9 μ mol, 0.05 equiv.), and N-Arylindole **5a** (1.03 mmol, 1.2 equiv.) placed into a 5 mL glass vial, tert-butyl hydroperoxide (223 μ L, 1.11 mmol in decane, 1.3 equiv.) was added dropwise at 0 °C. The reaction mixture was capped and stirred for 10 minutes at 0 °C and then slowly heated to 50 °C and stirred for 24 hours, unless stated differently. The dark brown slurry was cooled down to rt, diluted with DCM and directly subjected to column chromatography using gradient elution with PE:EtOAc=100:0 $\rightarrow$ 0:30 (75 minutes) to afford the desired product **7**.

1,1-Dimethylethyl 1-(1-phenyl-1H-indol-3-yl)-3,4-dihydroisoquinoline-2(1H)-carboxylate (7a). Yield: General procedure F: Fe: 178 mg (49 %), Cu: 303 mg (83 %), General procedure E: 351 mg (72 %, table 3); colorless solid; M.p.: 123-125 °C; TLC: R_f (PE:EtOAc=5:1)=0.57; GC/MS (El^+): m/z (rel. Intensity): 324 (M^+ -100, 62), 323 (100), 295 (18), 294 (27), 232 (13), 219 (10), 217 (13), 216 (12), 193 (16), 165 (10), 162 (14), 132 (13), 131 (22), 130 (41), 103 (12), 77 (16); HRMS (ESI^+): exact mass calculated for $C_{23}H_{18}N_2$: 323.1543. Found: 323.1534. [$M-C_5H_{10}O_2+H$] $^+$; 1H NMR (200 MHz, $CDCl_3$): δ = 1.56 (s, 9H), 2.76 (dd, 2J = 16.5 Hz, 3J = 2.4 Hz, 1H), 2.94-3.35 (m, 2H), 4.08 (bs, 1H), 6.74 (s, 1H), 6.82 (bs, 1H), 7.12-7.24 (m, 6H), 7.27-7.51 (m, 5H), 7.55 (dd, 3J = 7.1 Hz, 4J = 1.5 Hz, 1H), 7.93 (bs, 1H); ^{13}C NMR (50 MHz, APT, $CDCl_3$): δ = 28.4 (t), 28.5 (q, 3C), 37.7 (t), 50.3 (d), 79.7 (s), 110.4 (d), 120.1 (s), 120.3 (d), 120.7 (d), 122.7 (d), 124.2 (d, 2C), 125.7 (d), 126.4 (d), 126.7 (d), 127.9 (s), 128.4 (d, 2C overlapping), 129.1 (d), 129.5 (d, 2C), 135.0 (s), 136.0 (s), 136.3 (s), 139.4 (s), 154.2 (s)

1,1-Dimethylethyl 1-[1-(4-methoxyphenyl)-1H-indol-3-yl]-3,4-dihydroisoquinoline-2(1H)-carboxylate (7b). Yield: General procedure F: Fe: 155 mg (40 %), Cu: 270 mg (69 %), General procedure E: 89 mg (68 %, table 3); colorless solid; M.p.: 71-72 °C; TLC: R_f (PE:EtOAc=5:1)=0.48; GC/MS (El^+): m/z (rel. Intensity): 354 (M^+ -100, 69), 353 (100), 325 (18), 324 (20), 232 (12), 216 (21), 177 (26), 133 (22), 132 (24), 131 (36), 130 (58), 77 (21); HRMS (ESI^+): exact mass calculated for $C_{29}H_{30}N_2O_3$: 455.2329. Found: 455.2340. [$M+H$] $^+$; 1H NMR (200 MHz, $CDCl_3$): δ = 1.54 (s, 9H), 2.74 (dd, 2J = 16.4 Hz, 3J = 2.3 Hz, 1H), 2.93-3.32 (m, 2H), 3.84 (s, 3H), 4.05 (bs, 1H), 6.66 (s, 1H, H1), 6.80 (bs, 1H), 6.96 (d, 3J = 8.9 Hz, 2H), 7.08-7.26 (m, 6H), 7.29 (d, 3J = 8.9 Hz, 2H), 7.42 (dd, 3J = 7.2 Hz, 4J = 1.4 Hz, 1H), 7.88 (bs, 1H); ^{13}C NMR (50 MHz, APT, $CDCl_3$): δ = 28.4 (t), 28.6 (q, 3C), 37.6 (t), 50.4 (d), 55.5 (q), 79.6 (s), 110.3 (d), 114.6 (d, 2C), 119.4 (s), 120.0 (d), 120.6 (d), 122.5 (d), 125.7 (d), 125.8 (d, 2C),

126.6 (d), 127.6 (s), 128.4 (d), 128.7 (d), 129.0 (d), 132.4 (s), 135.0 (s), 136.2 (s), 136.7 (s), 154.2 (s), 158.1 (s)

1,1-Dimethylethyl 1-[1-(thiophen-2-yl)-1H-indol-3-yl]-3,4-dihydroisoquinoline-2(1H)-carboxylate

(7c). Yield: General procedure F: Cu: 286 mg (78 %), General procedure E: 105 mg (85 %, table 3); colorless solid; M.p.: 69-71 °C; TLC: R_f (PE:EtOAc=5:1)=0.53; GC/MS (EI⁺): m/z (rel. Intensity): 330 (M⁺, 67), 329 (100), 301 (18), 300 (13), 232 (16), 217 (11), 216 (17), 199 (22), 198 (14), 165 (28), 148 (15), 133 (77), 132 (37), 131 (34), 130 (70), 103 (22), 77 (20); HRMS (ESI⁺): exact mass calculated for C₂₆H₂₆N₂O₂S: 453.1607. Found: 453.1624 [M+Na]⁺; ¹H NMR (200 MHz, acetone-D₆): δ = 1.53 (s, 9H), 2.78 (ddd, ²J = 16.3 Hz, ³J = 4.1 Hz, ³J = 2.2 Hz, 1H), 2.99 (ddd, ²J = 16.2 Hz, ³J = 11.8 Hz, ³J = 5.7 Hz, 1H), 3.23 (ddd, ²J = 13.1 Hz, ³J = 11.8 Hz, ³J = 4.3 Hz, 1H), 4.07 (d, ²J = 13.1 Hz, 1H), 6.73 (s, 1H), 6.79 (bs, 1H), 7.00-7.35 (m, 9H), 7.55 (dd, ³J = 7.8 Hz, ⁴J = 1.1 Hz, 1H), 7.86 (bs, 1H); ¹³C NMR (50 MHz, APT, acetone-D₆): δ = 29.7 (q, 3C), 30.0 (t), 39.2 (t), 52.3 (d), 81.1 (s), 112.3 (d), 122.3 (d, 2C overlapping), 122.6 (d), 122.7 (s), 123.7 (d), 125.1 (d), 127.6 (d), 128.1 (d), 128.7 (d), 129.7 (s), 130.0 (d), 131.0 (d), 131.1 (d), 136.9 (s), 137.6 (s), 139.3 (s), 142.7 (s), 155.8 (s)

1,1-Dimethylethyl 1-[1-(4-fluorophenyl)-1H-indol-3-yl]-3,4-dihydroisoquinoline-2(1H)-carboxylate

(7d). Yield: General procedure F: Cu: 245 mg (65 %), General procedure E: 107 mg (84 %, table 3); colorless solid; M.p.: 122-124 °C; TLC: R_f (PE:EtOAc=5:1)=0.54; GC/MS (EI⁺): m/z (rel. Intensity): 342 (M⁺-100, 69), 341 (100), 313 (21), 312 (28), 232 (814), 217 (16), 216 (17), 171 (31), 132 (32), 131 (48), 130 (82), 117 (10), 115 (11), 103 (22), 95 (14), 77 (16); HRMS (ESI⁺): exact mass calculated for C₂₈H₂₇FN₂O₂: 443.2129. Found: 443.2143 [M+H]⁺; ¹H NMR (200 MHz, CDCl₃): δ = 1.44 (s, 9H), 2.63 (dd, ²J = 16.4 Hz, ³J = 2.2 Hz, 1H), 2.81-3.22 (m, 2H), 3.97 (bs, 1H), 6.58 (s, 1H), 6.70 (bs, 1H), 6.94-7.18 (m, 8H), 7.23 (dd, ³J = 8.9 Hz, ⁴J = 4.8 Hz, 2H), 7.32 (dd, ³J = 7.1 Hz, ⁴J = 1.6 Hz, 1H), 7.81 (bs, 1H); ¹³C NMR (50 MHz, APT, CDCl₃): δ = 28.4 (t), 28.5 (q, 3C), 37.6 (t), 50.4 (d), 79.7 (s), 110.1 (d), 116.3 (d, 2C, d, ²J_{CF} = 22.8 Hz), 120.1 (s), 120.4 (d), 120.8 (d), 122.8 (d), 125.7 (d), 126.0 (d, 2C, d, ³J_{CF} = 8.4 Hz), 126.7 (d), 127.8 (s), 128.4 (d, 2C overlapping), 129.1 (d), 135.0 (s), 135.5 (s, d, ⁴J_{CF} = 3.0 Hz), 136.0 (s), 136.5 (s), 154.2 (s), 160.9 (s, d, ¹J_{CF} = 246 Hz)

1,1-Dimethylethyl 1-[1-(4-nitrophenyl)-1H-indol-3-yl]-3,4-dihydroisoquinoline-2(1H)-carboxylate

(7e). To a mixture of N-Boc-THIQ **9** (200 mg, 0.858 mmol, 1.0 equiv.), catalyst (10.4 mg, 42.9 μmol, 0.05 equiv.), and 1-(4-nitrophenyl)indole **5e** (245 mg, 1.03 mmol, 1.2 equiv.) placed into a 5 mL glass vial, tBHP (223 μL, 1.11 mmol in decane) was added dropwise at 0 °C. The reaction mixture was capped and stirred for 10 minutes, keeping the temperature constant using a cryostat. Then the reaction mixture was slowly heated up to 50 °C and stirred for 24 hours. No conversion could be detected by GC/MS. Thus, another 5 mol% catalyst and 1.3 equiv. of tBHP was added at 0 °C. The reaction mixture was slowly heated to 80 °C and stirred for another 24 hours under air. Workup and purification was carried out according to the general procedure (General procedure F). Yield: General procedure F Cu: 179 mg (45 %, table 5), General procedure E: 68 mg (50 %, table 3); shining yellow powder; M.p.: 97-99 °C; TLC: R_f (PE:EtOAc=5:1)=0.30; GC/MS (EI⁺): m/z (rel. Intensity): 369 (M⁺-100, 58), 368 (98), 340 (21), 339 (29), 336 (22), 322 (20), 293 (16), 232 (22), 217 (21), 216 (24), 191 (31), 145 (34), 132 (59), 131 (82), 130 (100), 117 (18), 103 (29), 96 (23), 77 (22); HRMS (ESI⁺): exact mass calculated for C₂₃H₁₉N₃O₂: 370.1556. Found: 370.1544. [M-C₅H₁₀O₂+H]⁺; ¹H NMR (200 MHz, CDCl₃): δ = 1.54 (s, 9H), 2.76 (d, ²J = 14.0 Hz, 1H), 2.95-3.29 (m, 2H), 4.10 (bs, 1H), 6.77 (bs, 2H), 7.14-7.36 (m, 6H), 7.56 (d, ³J = 9.0 Hz, 2H), 7.61 (dd, ³J = 7.6 Hz, ⁴J = 1.4 Hz, 1H), 7.92 (bs, 1H), 8.32 (d, ³J = 8.9 Hz,

2H); ^{13}C NMR (50 MHz, CDCl_3): δ = 28.4 (t), 28.5 (q, 3C), 37.8 (t), 50.3 (d), 80.0 (s), 110.4 (d), 121.2 (d), 121.6 (d), 122.7 (s), 123.2 (d, 2C), 123.7 (d), 125.4 (d, 2C), 125.9 (d), 126.9 (d), 127.3 (d), 128.3 (d), 128.8 (s), 129.2 (d), 135.0 (s), 135.5 (s), 135.7 (s), 144.9 (s, 2C overlapping), 154.2 (s)

Phenylmethyl 1-(1-phenyl-1*H*-indol-3-yl)-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (7g, table 3). N-Cbz-THIQ-Ind **4b** (110 mg, 0.287 mmol, 1.0 equiv.), iron(III)-chloride (4.7 mg, 28.7 μmol , 0.10 equiv.), and K_3PO_4 (122 mg, 0.574 mmol, 2.0 equiv.) were placed in an oven-dried tube, and 2-iodothiophene (90.5 mg, 0.431 mmol, 1.5 equiv.) and DMEDA (5.6 μL , 57.4 μmol , 0.20 equiv.) were added under an argon atmosphere, followed by dry toluene (300 μL). The tube was sealed under argon, and the mixture was heated up to 135 $^\circ\text{C}$ and stirred at this temperature for 48 hours. Yield: 102 mg (77 %); off colorless solid; M.p.: 58-60 $^\circ\text{C}$; TLC: R_f (PE:EtOAc=5:1)=0.43; GC/MS (EI+): m/z (rel. Intensity): 458 (M+, 3), 367 (5), 324 (24), 323 (100), 294 (10), 193 (10), 130 (23), 103 (12), 91 (68), 77 (12); HRMS (ESI⁺): exact mass calculated for $\text{C}_{31}\text{H}_{26}\text{N}_2\text{O}_2$: 481.1886. Found: 481.1892 [M+Na]⁺; ^1H NMR (200 MHz, CDCl_3): δ = 2.78 (dd, 2J = 16.3 Hz, 3J = 3.3 Hz, 1H), 3.06 (bs, 1H), 3.31 (dt, 2J = 12.6 Hz, 3J = 3.7 Hz, 1H), 4.17 (bs, 1H), 5.08-5.52 (m, 2H), 6.75 (s, 1H), 6.86 (bs, 1H), 7.08-7.62 (m, 17H), 7.88 (bs, 1H); ^{13}C NMR (50 MHz, APT, CDCl_3): δ = 28.6 (t), 37.6 (t), 51.3 (d), 67.1 (t), 110.4 (d), 119.6 (s), 120.5 (d), 120.7 (d), 122.7 (d), 124.2 (d, 2C), 125.9 (d), 126.4 (d), 126.8 (d), 128.0 (d, 2C overlapping), 128.5 (d, 3C overlapping), 129.0 (d), 129.5 (d, 2C), 134.6 (s), 135.7 (s, 2C overlapping), 136.2 (s), 136.7 (s), 139.4 (s), 154.9 (s); ^1H NMR (200 MHz, *acetone-D*₆): δ = 2.81 (dd, 2J = 16.0 Hz, 3J = 2.2 Hz, 1H), 3.02 (ddd, 2J = 16.6 Hz, 3J = 11.9 Hz, 3J = 5.9 Hz, 1H), 3.34 (ddd, 2J = 13.3 Hz, 3J = 11.8 Hz, 3J = 4.4 Hz, 1H), 4.14 (d, 2J = 13.3 Hz, 1H), 5.23 (s, 2H), 6.80 (bs, 1H), 6.88 (s, 1H), 6.97-7.95 (m, 18H); ^{13}C NMR (50 MHz, APT, *acetone-D*₆): δ = (CH₂-group at 28.6 ppm in CDCl_3 overlaps with acetone signal), 39.3 (t), 53.1 (d), 68.6 (t), 112.2 (d), 121.6 (s), 122.20 (d), 122.27 (d), 124.6 (d), 125.8 (d, 2C), 127.7 (d), 128.3 (d), 128.7 (d), 129.7 (d, 2C overlapping), 130.06 (d), 130.16 (d), 130.3 (d), 131.0 (d), 131.5 (d, 2C), 136.7 (s, 2C overlapping), 137.6 (s), 138.1 (s), 139.2 (s), 141.2 (s), 156.5 (s)

General procedure G: Regioselective N-arylation of 4d towards 7h-m (table 4). Substrate **4d** (100 mg, 0.805 mmol, 1.0 equiv.), copper(I)-iodide (3.9 mg, 20.1 μmol , 0.05 equiv.), and CsF (306 mg, 2.01 mmol, 2.5 equiv.) were placed in an oven-dried tube 2 mL glass vial, and aryl iodide (0.604 mmol, 1.5 equiv.) and dmeda (4 μL , 40.3 μmol , 0.30 equiv.) were added, followed by dry acetonitrile (1 mL). The tube was degassed with argon for 30 seconds and stirred for 4 hours at room temperature. Since no significant product formation was observed by TLC, the reaction was heated up to 70 $^\circ\text{C}$, and magnesium sulfate (49 mg, 0.403 mmol, 0.50 equiv.) was added to trap traces of water and stirred for another 20 hours. The reaction mixture was poured onto saturated sodium carbonate and extracted three times with EtOAc. The collected organic layer was washed twice with brine, dried over sodium sulfate, filtered and evaporated. The crude products **7h-m** were purified by flash chromatography, using gradient elution with PE:EtOAc=100:0 $\rightarrow$ 0:100 (90 minutes).

1-(1-Phenyl-1*H*-indol-3-yl)-1,2,3,4-tetrahydroisoquinoline (7h, table 4). Yield: 95 mg (73 %); white powder; M.p.: 51-53 $^\circ\text{C}$; TLC: R_f (EtOAc:MeOH=5:1) = 0.38; GC/MS (EI+): m/z (rel. Intensity): 324 (M+, 62), 323 (100), 295 (17), 294 (25), 232 (11), 217 (10), 193 (15), 162 (16), 132 (10), 131 (15), 130 (26), 77 (11); ^1H NMR (200 MHz, CDCl_3): δ = 2.39 (s, 1H), 2.77-3.37 (m, 4H), 5.55 (s, 1H), 7.00-7.36 (m, 8H), 7.41-7.49 (m, 4H), 7.52-7.60 (m, 2H); ^{13}C NMR (50 MHz, APT, CDCl_3): δ = 29.7 (t), 41.6 (t), 53.6 (d), 110.6 (d), 119.8 (d), 120.2 (d), 120.6 (s), 122.5 (d), 124.1 (d, 2C), 125.6 (d, 6C), 126.19 (d), 126.22 (d), 127.4 (d), 127.8 (s), 127.9 (d), 129.0 (d), 129.5 (d, 2C), 135.2 (s), 136.4 (s), 137.9 (s), 139.5 (s)

1-(1-(4-Methoxyphenyl)-1H-indol-3-yl)-1,2,3,4-tetrahydroisoquinoline (7i, table 4). Yield: 74 mg (52 %); off colorless solid; M.p.: 49-51 °C; TLC: R_f (EtOAc:MeOH=10:1) = 0.11; GC/MS (EI⁺): m/z (rel. Intensity): 354 (M⁺, 69), 353 (100), 337 (10), 325 (13), 324 (17), 232 (12), 216 (12), 177 (17), 133 (12), 132 (16), 131 (26); HRMS (ESI⁺): exact mass calculated for C₂₄H₂₂N₂O: 355.1805. Found: 355.1791 [M+H]⁺; ¹H NMR (200 MHz, CDCl₃): δ = 2.30 (bs, 1H), 2.78-3.41 (m, 4H), 3.86 (s, 3H), 5.56 (s, 1H), 6.94-7.24 (m, 9H), 7.37 (d, ³J = 8.9 Hz, 2H), 7.46 (dd, ³J = 8.0 Hz, ⁴J = 1.0 Hz, 1H), 7.56 (dd, ³J = 7.4 Hz, ⁴J = 1.1 Hz, 1H); ¹³C NMR (50 MHz, APT, CDCl₃): δ = 29.7 (t), 41.6 (t), 53.7 (d), 55.5 (q), 110.5 (d), 114.6 (d, 2C), 119.7 (d), 120.0 (d), 122.3 (d), 125.6 (d), 125.8 (d, 2C), 126.2 (d), 127.4 (s), 127.85 (d), 127.92 (d), 129.0 (d), 132.6 (s), 135.2 (s), 136.9 (s), 138.0 (s), 158.1 (s), (1 quaternary C missing due to potential overlap of signals)

1-(1-(Thiophen-2-yl)-1H-indol-3-yl)-1,2,3,4-tetrahydroisoquinoline (7j, table 4). Yield: 105 mg (79 %); colorless solid; M.p.: 46-47 °C; TLC: R_f (EtOAc:MeOH=10:1) = 0.44; GC/MS (EI⁺): m/z (rel. Intensity): 330 (M⁺, 88), 329 (100), 301 (17), 300 (11), 232 (14), 199 (12), 165 (12), 133 (28), 130 (30), 103 (10); HRMS (ESI⁺): exact mass calculated for C₂₁H₁₈N₂S: 331.1263. Found: 331.1254 [M+H]⁺; ¹H NMR (200 MHz, CDCl₃): δ = 2.05 (bs, 1H), 2.78-3.37 (m, 4H), 5.50 (s, 1H), 6.96-7.29 (m, 10H), 7.55 (t, ³J = 7.9 Hz, 2H); ¹³C NMR (50 MHz, APT, CDCl₃): δ = 29.7 (t), 41.8 (t), 53.7 (d), 110.8 (d), 119.9 (d), 120.1 (d), 120.7 (d), 121.3 (s), 121.4 (d), 123.0 (d), 125.6 (d), 125.9 (d), 126.2 (d), 127.6 (s), 127.8 (d), 128.6 (d), 129.0 (d), 135.2 (s), 137.7 (s), 137.8 (s), 141.5 (s)

1-(1-(4-Fluorophenyl)-1H-indol-3-yl)-1,2,3,4-tetrahydroisoquinoline (7k, table 4). Yield: 80 mg (58 %); off colorless solid; M.p.: 50-52 °C; TLC: R_f (EtOAc:EtOH=10:1) = 0.27; GC/MS (EI⁺): m/z (rel. Intensity): 342 (M⁺, 60), 341 (100), 313 (17), 312 (25), 232 (10), 211 (11), 171 (11), 132 (10), 131 (16), 130 (29); HRMS (ESI⁺): exact mass calculated for C₂₃H₁₉FN₂: 343.1605. Found: 343.1595 [M+H]⁺; ¹H NMR (200 MHz, CDCl₃): δ = 2.07 (bs, 1H), 2.79-3.39 (m, 4H), 5.56 (s, 1H), 7.00-7.24 (m, 9H), 7.36-7.51 (m, 3H), 7.59 (d, ³J = 7.6 Hz, 1H); ¹³C NMR (50 MHz, APT, CDCl₃): δ = 29.7 (t), 41.7 (t), 53.7 (d), 110.3 (d), 116.4 (d, ²J_{CF} = 22.8 Hz), 119.9 (d), 120.3 (d), 120.8 (s), 122.7 (d), 125.6 (d), 126.0 (d, ³J_{CF} = 8.4 Hz), 126.2 (d), 127.5 (d), 127.7 (s), 127.8 (d), 129.0 (d), 135.3 (s), 135.7 (s, d, ⁴J_{CF} = 3.0 Hz), 136.6 (s), 138.0 (s), 160.9 (s, d, ¹J_{CF} = 246 Hz)

1-(1-(3-Nitrophenyl)-1H-indol-3-yl)-1,2,3,4-tetrahydroisoquinoline (7l, table 4). Yield: 110 mg (74 %); pale yellow solid; M.p.: 59-61 °C; TLC: R_f (EtOAc:EtOH=5:1) = 0.54; GC/MS (EI⁺): m/z (rel. Intensity): 369 (M⁺, 57), 368 (100), 340 (24), 339 (30), 322 (23), 321 (14), 232 (25), 217 (21), 161 (21), 147 (29), 146 (38), 132 (46), 131 (59), 130 (78), 103 (20); HRMS (ESI⁺): exact mass calculated for C₂₃H₁₉N₃O₂: 370.1550. Found: 370.1542 [M+H]⁺; ¹H NMR (200 MHz, CDCl₃): δ = 2.09 (bs, 1H), 2.82-3.39 (m, 4H), 5.57 (s, 1H), 7.02-7.09 (m, 2H), 7.13 (s, 1H), 7.14-7.35 (m, 4H), 7.55-7.65 (m, 2H), 7.67 (t, ³J = 8.1 Hz, 1H), 7.83 (ddd, ³J = 8.0 Hz, ⁴J = 2.0 Hz, ⁴J = 1.1 Hz, 1H), 8.17 (ddd, ³J = 8.1 Hz, ⁴J = 2.1 Hz, ⁴J = 1.1 Hz, 1H), 8.36 (t, ⁴J = 2.1 Hz, 1H); ¹³C NMR (50 MHz, APT, CDCl₃): δ = 29.7 (t), 41.7 (t), 53.7 (d), 110.2 (d), 118.6 (d), 120.4 (d), 120.6 (d), 121.2 (d), 122.5 (s), 123.4 (d), 125.8 (d), 126.4 (d), 126.6 (d), 127.7 (d), 128.3 (s), 129.1 (d), 129.5 (d), 130.5 (d), 135.2 (s), 136.1 (s), 137.6 (s), 140.7 (s), 149.1 (s)

1-(1-(4-Ethoxycarbonylphenyl)-1H-indol-3-yl)-1,2,3,4-tetrahydroisoquinoline (7m, table 4). Yield: 101 mg (63 %); colorless solid; M.p.: 51-53 °C; TLC: R_f (EtOAc:EtOH=5:1) = 0.35; GC/MS (EI⁺): m/z (rel. Intensity): 396 (M⁺, 66), 395 (100), 367 (31), 366 (14), 232 (20), 175 (15), 160 (18), 132 (18), 131 (29), 130 (46), 103 (12); HRMS (ESI⁺): exact mass calculated for C₂₆H₂₄N₂O₂: 397.1911 Found: 397.1910

$[M+H]^+$; 1H NMR (200 MHz, $CDCl_3$): δ = 1.42 (t, 3J = 7.1 Hz, 3H, CH_3), 1.92 (bs, 1H, 2-NH), 2.81-3.40 (m, 4H, H3 & H4), 4.41 (q, 3J = 7.1 Hz, 2H, O- CH_2), 5.55 (s, 1H, H1), 7.02-7.31 (m, 7H), 7.55 (d, 3J = 8.6 Hz, 2H, H2''), 7.56-7.68 (m, 2H), 8.17 (d, 3J = 8.6 Hz, 2H, H3''); ^{13}C NMR (50 MHz, APT, $CDCl_3$): δ = 14.3 (q), 29.7 (t), 41.8 (t), 53.6 (d), 61.1 (t), 110.7 (d), 120.1 (d), 120.8 (d), 122.0 (s), 122.97 (d, 2C), 123.02 (d), 125.6 (d), 126.3 (d), 126.7 (d), 127.7 (d), 128.3 (s), 129.0 (d), 131.1 (d, 2C), 135.2 (s), 136.0 (s), 137.8 (s), 143.4 (s), 165.8 (s), one quaternary carbon overlapping.

General procedure H: Preparation of 2-aryl-1-phenylindoles 8a-q (table 6): 1-Arylindole **5** (1.50 mmol, 1.0 equiv.), arylboronic acid (2.25 mmol, 1.5 equiv.), and $Pd(OAc)_2$ (16.8 mg, 75 μ mol, 0.05 equiv.) were placed in a 25 mL glass vial. After AcOH (10 mL) was added by syringe, the resulting solution was purged with O_2 (1.0 atm.) for 1 minute. The mixture was stirred for 12 h at room temperature in an oxygen atmosphere. Another 1.5 equiv. of arylboronic acid were added and the reaction mixture stirred until full consumption of 1-phenylindole starting material was observed (monitored by GC/MS and TLC), unless stated differently. The reaction mixture was poured onto ice-cold, aqueous 2N NaOH and extracted three times with EtOAc. The collected organic layers were washed once with brine, dried over sodium sulfate, filtered and evaporated. Unless indicated differently, the crude product mixture was subjected to flash column chromatography using gradient elution with PE:EtOAc (100:0 to 90:10) to afford the desired products **8a-h,j,k,n-q**.

1,2-Diphenyl-1H-indole (8a, table 6). yield: 388 mg (96 %); colorless solid; M.p.: 80-82 °C; (Lit.: M.p.: 78-80 °C); TLC: R_f (PE:EtOAc=10:1) = 0.73; GC/MS (EI+): m/z (rel. Intensity): 269 (M^+ , 100), 268 (45), 267 (35), 266 (16), 165 (28), 133 (35), 132 (14), 127 (15), 121 (13); 1H NMR (200 MHz, $CDCl_3$): δ = 6.78 (s, 1H), 6.99-7.46 (m, 13H), 7.60-7.72 (m, 1H); ^{13}C NMR (50 MHz, APT, $CDCl_3$): δ = 103.7 (d), 110.6 (d), 120.5 (d), 120.7 (d), 122.3 (d), 127.1 (d), 127.2 (d), 128.0 (d, 2C), 128.1 (d, 2C), 128.2 (s), 128.8 (d, 2C), 129.2 (d, 2C), 132.5 (s), 138.5 (s), 139.0 (s), 140.7 (s)

2-(4-Chlorophenyl)-1-phenyl-1H-indole (8b, table 6). yield: 51 mg (11 %); colorless solid; M.p.: 170-172 °C; (Lit.: M.p.: 174-176 °C); TLC: R_f (PE) = 0.19; GC/MS (EI+): m/z (rel. Intensity): 305 (M^+ +2, 30), 303 (M^+ , 100), 267 (26), 266 (11), 165 (22), 134 (61), 132 (25), 121 (10); 1H NMR (200 MHz, $CDCl_3$): δ = 6.80 (bs, 1H), 7.11-7.53 (m, 12H), 7.62-7.74 (m, 1H); ^{13}C NMR (50 MHz, APT, $CDCl_3$): δ = 104.0 (d), 110.6 (d), 120.6 (d), 120.8 (d), 122.6 (d), 127.4 (d), 128.0 (d, 2C), 128.1 (s), 128.4 (d, 2C), 129.4 (d, 2C), 130.0 (d, 2C), 131.0 (s), 133.3 (s), 138.2 (s), 139.1 (s), 139.4 (s)

2-(4-Methoxyphenyl)-1-phenyl-1H-indole (8c, table 6). yield: 424 mg (94 %); colorless solid; M.p.: 109-117 °C; (Lit.: M.p.: 119-121 °C); TLC: R_f (PE:EtOAc=10:1) = 0.54; GC/MS (EI+): m/z (rel. Intensity): 299 (M^+ , 100), 284 (43), 256 (11), 255 (12), 254 (29), 150 (8), 127 (14); HRMS (ESI $^+$): exact mass calculated for $C_{21}H_{17}NO$: 300.1383. Found: 300.1384. $[M+H]^+$, 1H NMR (200 MHz, $CDCl_3$): δ = 3.73 (s, 3H), 6.72 (bs, 1H), 6.75 (d, 3J = 8.9 Hz, 2H), 7.10-7.45 (m, 10H), 7.59-7.71 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.1 (q), 102.7 (d), 110.5 (d), 113.6 (d, 2C), 120.2 (d), 120.6 (d), 122.0 (d), 125.0 (s), 127.1 (d), 128.0 (d, 2C), 128.3 (s), 129.2 (d, 2C), 130.1 (d, 2C), 138.5 (s), 138.8 (s), 140.6 (s), 158.9 (s)

2-(4-Methylphenyl)-1-phenyl-1H-indole (8d, table 6). yield: 371 mg (87 %); colorless needles; M.p.: 131-133 °C; TLC: R_f (PE:EtOAc=20:1) = 0.55; GC/MS (EI+): m/z (rel. Intensity): 283 (M^+ , 100), 277 (18), 165 (12), 140 (11), 133 (24), 132 (10); HRMS (ESI $^+$): exact mass calculated for $C_{21}H_{17}N$: 284.1434. Found: 284.1433 $[M+H]^+$; 1H NMR (200 MHz, $CDCl_3$): δ = 2.28 (s, 3H), 6.76 (bs, 1H), 7.02 (d, 3J = 7.8 Hz, 2H), 7.07-7.45 (m, 10H), 7.57-7.72 (m, 1H); ^{13}C NMR (50 MHz $CDCl_3$): δ = 21.2 (q), 103.2 (d), 110.5 (d),

120.4 (d), 120.6 (d), 122.1 (d), 127.1 (d), 128.0 (d, 2C), 128.3 (s), 128.7 (d, 2C), 128.8 (d, 2C), 129.2 (d, 2C), 129.6 (s), 137.1 (s), 138.6 (s), 138.9 (s), 140.8 (s)

1-Phenyl-2-[4-(trifluoromethyl)phenyl]-1H-indole (8e, table 6). yield: 462 mg (91 %); pale yellow solid; TLC: R_f (PE:EtOAc=10:1) = 0.65; GC/MS (EI+): m/z (rel. Intensity): 337 (M^+ , 100), 336 (23), 335 (12), 267 (18), 165 (34), 134 (19), 133 (42), 132 (17); HRMS (ESI⁺): exact mass calculated for $C_{21}H_{14}F_3N$: 338.1151. Found: 338.1156 [$M+H$]⁺; ¹H NMR (200 MHz, $CDCl_3$): δ = 6.87 (s, 1H), 7.03-7.97 (m, 13H); ¹³C NMR (50 MHz, $CDCl_3$): δ = 105.1 (d), 110.7 (d), 120.9 (d), 121.0 (d), 123.1 (d), 124.1 (s, q, ¹ $J_{C,F}$ = 272 Hz), 125.1 (d, 2C, q, ³ $J_{C,F}$ = 3.8 Hz), 127.5 (d), 127.9 (d, 2C), 128.1 (s), 128.7 (d, 2C), 128.9 (s, q, ² $J_{C,F}$ = 32.5 Hz), 129.4 (d, 2C), 136.0 (s, q, ⁵ $J_{C,F}$ = 1.2 Hz), 138.1 (s), 138.8 (s), 139.4 (s); mixture of C2:C3=11:1 also confirmed by ¹³C-NMR

2-(3-Nitrophenyl)-1-phenyl-1H-indole (8f, table 6). yield: 160 mg (34 %); shining yellow solid; M.p.: 134-135 °C; TLC: R_f (PE:EtOAc=10:1) = 0.44; GC/MS (EI+): m/z (rel. Intensity): 314 (M^+ , 100), 268 (34), 267 (44), 266 (22), 265 (16), 239 (6), 134 (10), 132 (18), 121 (9); HRMS (ESI⁺): exact mass calculated for $C_{20}H_{14}N_2O_2$: 315.1128. Found: 315.1131 [$M+H$]⁺; ¹H NMR (200 MHz, $CDCl_3$): δ = 6.93 (s, 1H), 7.13-7.54 (m, 10H), 7.65-7.75 (m, 1H), 8.04 (ddd, ³ J = 8.0 Hz, ⁴ J = 2.0 Hz, ⁴ J = 1.0 Hz, 1H), 8.16 (t, ⁴ J = 1.8 Hz, 1H); ¹³C NMR (50 MHz, $CDCl_3$): δ = 105.2 (d), 110.8 (d), 120.9 (d), 121.1 (d), 121.8 (d), 123.3 (d, 2C overlapping), 127.8 (d), 128.0 (d, 2C), 129.1 (d), 129.6 (d, 2C), 134.17 (s), 134.21 (d), 137.77 (s), 137.80 (s), 139.4 (s), 148.1 (s); (1 C missing due to potential overlap of signals); ¹³C NMR (50 MHz, *acetone-d*₆): δ = 107.0 (d), 112.4 (d), 122.8 (d, 2C overlapping), 123.6 (d), 124.8 (d), 125.0 (d), 129.7 (d), 129.9 (d, 2C), 130.0 (s), 131.4 (d), 131.6 (d, 2C), 136.0 (s), 136.4 (d), 139.79 (s), 139.84 (s), 141.5 (s), 150.0 (s)

2-(Naphth-1-yl)-1-phenyl-1H-indole (8g, table 6). yield: 161 mg (34); colorless solid; M.p.: 181-183 °C; TLC: R_f (PE:EtOAc=10:1) = 0.69 ; GC/MS (EI+): m/z (rel. Intensity): 319 (M^+ , 100), 318 (45), 317 (17), 242 (38), 241 (16), 215 (10), 159 (17), 158 (18), 157 (22), 152 (13); ¹H NMR (200 MHz, $CDCl_3$): δ = 6.83 (bs, 1H), 7.09-7.27 (m, 7H), 7.28-7.44 (m, 5H), 7.70-7.83 (m, 3H), 8.00-8.08 (m, 1H); ¹³C NMR (50 MHz, $CDCl_3$): δ = 105.9 (d), 110.7 (d), 120.5 (d), 120.7 (d), 122.3 (d), 124.8 (d), 125.8 (d), 126.16 (d), 126.22 (d), 126.8 (d), 127.3 (d, 2C), 128.1 (d), 128.2 (s), 128.4 (d), 128.9 (2C, d), 129.2 (d), 130.4 (s), 132.6 (s), 133.4 (s), 138.0 (s), 138.2 (s), 138.6 (s)

2-(2-Methylphenyl)-1-phenyl-1H-indole (8h, table 6). yield: 401 mg (94 %); colorless oil; TLC: R_f (PE:EtOAc=20:1) = 0.58; GC/MS (EI+): m/z (rel. Intensity): 283 (M^+ , 100), 282 (48), 280 (15), 267 (14), 206 (30), 204 (28), 178 (18), 165 (10), 140 (14), 139 (10), 133 (35), 132 (15); HRMS (ESI⁺): exact mass calculated for $C_{21}H_{17}N$: 284.1434. Found: 284.1421; ¹H NMR (200 MHz, $CDCl_3$): δ = 2.02 (s, 3H), 6.56 (bs, 1H), 6.94-7.48 (m, 12H), 7.54-7.66 (m, 1H); ¹³C NMR (50 MHz, $CDCl_3$): δ = 20.3 (q), 104.4 (d), 110.5 (d), 120.4 (d), 120.5 (d), 122.0 (d), 125.2 (d), 126.7 (d), 127.3 (d, 2C), 128.2 (d), 128.3 (s), 128.9 (d, 2C), 129.9 (d), 131.5 (d), 132.5 (s), 137.5 (s), 137.6 (s), 138.2 (s), 140.1 (s) - The desired product was isolated as mixture containing the 1,3-diaryldindole byproduct (GC/MS: C2:C3=45:55).

5-Methoxy-1,2-diphenyl-1H-indole (8j, table 6). yield: 103 mg (82 %); colorless solid; M.p.: 131-134 °C; TLC: R_f (PE:EtOAc=10:1)=0.62; GC/MS (EI+): m/z (rel. Intensity): 299 (M^+ , 100), 284 (28), 256 (37), 254 (24), 127 (13), 77 (11); ¹H NMR (200 MHz, $CDCl_3$): δ = 3.85 (s, 3H), 6.72 (s, 1H), 6.82 (dd, ³ J = 8.9 Hz, ⁴ J = 2.5 Hz, 1H), 7.08-7.43 (m, 12H); ¹³C NMR (50 MHz, $CDCl_3$): δ = 55.8 (q), 102.0 (d), 103.4 (d),

111.4 (d), 112.4 (d), 127.0 (d), 127.2 (d), 127.9 (d, 2C), 128.1 (d, 2C), 128.6 (s), 128.8 (d, 2C), 129.2 (d, 2C), 132.5 (s), 134.3 (s), 138.6 (s), 141.1 (s), 154.8 (s)

1-(4-Methoxyphenyl)-2-phenyl-1H-indole (8k, table 6). yield: 68 mg (54 %); pale yellow solid; M.p.: 138-140 °C; TLC: R_f (PE:EtOAc=10:1) = 0.59; GC/MS (EI+): m/z (rel. Intensity): 299 (M^+ , 100), 284 (25), 256 (12), 255 (13), 254 (23), 165 (14), 150 (11), 133 (12), 127 (15); 1H NMR (200 MHz, $CDCl_3$): δ = 3.73 (s, 3H), 6.70 (d, 4J = 0.5 Hz, 1H), 6.83 (d, 3J = 8.9 Hz, 2H), 7.01-7.26 (m, 10H), 7.53-7.66 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.4 (q), 103.1 (d), 110.6 (d), 114.4 (d, 2C), 120.4 (d), 120.5 (d), 122.1 (d), 127.2 (d), 128.0 (s), 128.1 (d, 2C), 128.9 (d, 2C), 129.1 (d, 2C), 131.3 (s), 132.6 (s), 139.3 (s), 140.8 (s), 158.5 (s)

5-Nitro-1,2-diphenyl-1H-indole (8n, table 6). yield: 59 mg (45 %); yellow solid; M.p.: 182-185 °C; TLC: R_f (PE:EtOAc=10:1) = 0.47; GC/MS (EI+): m/z (rel. Intensity): 314 (M^+ , 100), 268 (34), 267 (42), 266 (21), 133 (12), 77 (10); 1H NMR (200 MHz, $CDCl_3$): δ = 6.86 (s, 1H), 7.11-7.25 (m, 8H), 7.31-7.43 (m, 3H), 7.99 (dd, 3J = 9.1 Hz, 4J = 2.2 Hz, 1H), 8.55 (d, 4J = 2.2 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 105.0 (d), 110.6 (d), 117.5 (d), 117.8 (d), 127.4 (s), 127.8 (d, 2C), 128.20 (d), 128.25 (d), 128.4 (d, 2C), 128.9 (d, 2C), 129.6 (d, 2C), 131.2 (s), 137.3 (s), 141.6 (s), 142.4 (s), 144.0 (s)

1-(4-Nitrophenyl)-2-phenyl-1H-indole (8o, table 6). yield: 78 mg (59 %); yellow solid; M.p.: 139-141 °C; TLC: R_f (PE:EtOAc=10:1) = 0.57; GC/MS (EI+): m/z (rel. Intensity): 314 (M^+ , 100), 268 (39), 267 (36), 266 (28), 265 (15), 191 (10), 165 (10), 134 (17), 133 (12); 1H NMR (200 MHz, $CDCl_3$): δ = 6.74 (s, 1H), 7.05-7.22 (m, 8H), 7.27 (d, 3J = 8.9 Hz, 2H), 7.54-7.64 (m, 1H), 8.14 (d, 3J = 8.9 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 105.9 (d), 110.1 (d), 121.0 (d), 121.7 (d), 123.2 (d), 124.7 (d, 2C), 127.9 (d), 128.0 (d, 2C), 128.5 (d, 2C), 128.7 (s), 128.9 (d, 2C), 131.7 (s), 138.1 (s), 140.3 (s), 144.2 (s), 145.8 (s)

1-(4-Fluorophenyl)-2-phenyl-1H-indole (8p, table 6). yield: 93 mg (77 %); colorless solid; Mp.: 122-124 °C; TLC: R_f (PE:EtOAc=10:1) = 0.68; GC/MS (EI+): m/z (rel. Intensity): 287 (M^+ , 100), 286 (29), 285 (20), 183 (11), 165 (14); 1H NMR (200 MHz, $CDCl_3$): δ = 6.92 (s, 1H), 7.12-7.24 (m, 2H), 7.25-7.41 (m, 10H), 7.75-7.88 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 103.7 (d), 110.4 (d), 116.1 (d, d, $^3J_{CF}$ = 22.8 Hz), 120.7 (d, d, $^4J_{CF}$ = 10.6 Hz), 122.4 (d), 127.4 (d), 128.2 (d, 2C), 128.9 (d, 2C), 129.5 (d), 129.7 (d), 132.3 (s), 134.5 (s, d, $^4J_{CF}$ = 3.1 Hz), 139.1 (s), 140.7 (s), 161.4 (s, d, $^2J_{CF}$ = 247 Hz) - one quaternary carbon missing due to potential overlap

1-(Naphth-1-yl)-2-phenyl-1H-indole (8q, table 6). yield: 100 mg (75 %); pale yellow solid; M.p.: 48-52 °C (Lit. 73-74 °C); TLC: R_f (PE:EtOAc=10:1)=0.70; GC/MS (EI+): m/z (rel. Intensity): 319 (M^+ , 100), 318 (39), 317 (22), 241 (11), 165 (10), 158 (12), 152 (10); 1H NMR (200 MHz, $CDCl_3$): δ = 6.70 (dd, 3J = 8.1 Hz, 4J = 0.9 Hz, 1H), 6.83 (d, 4J = 0.7 Hz, 1H), 6.89-7.40 (m, 12H), 7.63 (d, 3J = 7.5 Hz, 1H), 7.69-7.84 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 103.2 (d), 111.2 (d), 120.5 (d), 120.6 (d), 122.2 (d), 123.5 (d), 125.5 (d), 126.5 (d), 127.0 (d), 127.1 (d), 127.3 (d), 128.07 (d, 2C), 128.13 (d, 2C), 128.2 (d), 128.5 (d), 131.3 (s), 132.5 (s), 134.3 (s), 135.2 (s), 140.2 (s), 142.1 (s); one quaternary carbon missing due to potential overlap.

N^1, N^2 -Bis(3-iodopyridin-2-yl)- N^1, N^2 -dimethylethane-1,2-diamine (11, Scheme 3). Formed as by-product in the attempted synthesis of **7h**. Yield: 42 mg (quant.); pale yellow needles, TLC: R_f (EtOAc:EtOAc=5:1) = 0.34, HRMS (ESI $^+$): exact mass calculated for $C_{14}H_{16}I_2N_4$: 494.9537 Found: 494.9550 [$M+H$] $^+$; 1H NMR (200 MHz, $CDCl_3$): δ = 2.90 (s, 6H), 3.49 (s, 4H), 6.50 (dd, 3J = 7.6 Hz, 3J = 4.7

Hz, 2H), 7.95 (dd, $^3J = 7.6$ Hz, $^4J = 1.6$ Hz, 2H), 8.14 (dd, $J = 4.7$, $^4J = 1.6$ Hz, 2H); ^{13}C NMR (50 MHz, APT , CDCl_3): $\delta = 40.4$ (q, 2C), 52.2 (t, 2C), 86.4 (s, 2C), 118.4 (d, 2C), 146.7 (d, 2C), 149.2 (d, 2C), 162.6 (s, 2C).

1-(1-Phenyl-1H-indol-3-yl)-3,4-dihydroisoquinoline (12, Scheme 4). Isolated as by-product. Yield: 23 mg (18 %); colorless solid; M.p.: 49-51 °C; GC/MS (EI+): m/z (rel. Intensity): 323 (M^+ , 10), 322 (52), 321 (100), 294 (15), 293 (10), 217 (10), 216 (10); HRMS (ESI+): exact mass calculated for $\text{C}_{23}\text{H}_{18}\text{N}_2$: 323.1543. Found: 323.1537 [$\text{M}+\text{H}$] $^+$; ^1H NMR (200 MHz, CDCl_3): $\delta = 2.68$ (dd, $^3J = 7.8$ Hz, $^3J = 6.4$ Hz, 1H), 3.75 (dd, $^3J = 7.8$ Hz, $^3J = 6.4$ Hz, 1H), 7.58-7.01 (m, 14H), 7.98-7.85 (m, 1H); ^{13}C NMR (50 MHz, APT , CDCl_3): $\delta = 26.3$ (t), 47.0 (t), 110.4 (d), 116.3 (s), 121.2 (d), 122.1 (d), 122.9 (d), 124.4 (d, 2C), 126.5 (d), 126.8 (d), 127.2 (d), 127.5 (d), 127.7 (s), 129.4 (s), 129.5 (d, 2C), 130.0 (d), 130.3 (d), 136.4 (s), 138.9 (s), 139.1 (s), 161.8 (s)

1,1-Dimethylethyl 2-[1-(4-nitrophenyl)-1H-indole-3-carbonyl]-phenethylcarbamate (13, Scheme 5). Procedure A: Isolated according to the general procedure for N-aryllindolation of BocNTHIQ, Procedure B: The starting material **7e** (20 mg, 0.0426 mmol) and $\text{Cu}(\text{NO}_3)_2 \times 3\text{H}_2\text{O}$ (1.0 mg, 4.2 μmol) were placed into a 5 mL glass vial and tBHP (26 μL , 0.128 mmol) added in one portion at room temperature. The mixture was heated to 80 °C under air for 17 hours. Another 3 equiv. of tBHP were added dropwise, and the reaction mixture stirred for another 11 hours. The reaction mixture was cooled down to room temperature, diluted with DCM and directly subjected to column chromatography to afford the desired product in good yield. Yield: Method A: 50 mg (12 %), Method B: 16 mg (77 %); shining yellow powder; M.p.: 78-82 °C; TLC: R_f (PE:EtOAc=5:1) = 0.11; HRMS (ESI $^+$): exact mass calculated for $\text{C}_{28}\text{H}_{27}\text{N}_3\text{O}_5$: 508.1843. Found: 508.1839 [$\text{M}+\text{Na}$] $^+$; ^1H NMR (200 MHz, CDCl_3): $\delta = 1.37$ (s, 9H), 2.93 (t, $^3J = 6.7$ Hz, 2H), 3.34-3.37 (m, 2H), 5.12 (bs, 1H), 7.28-7.68 (m, 8H), 7.74 (d, $^3J = 9.0$ Hz, 2H), 8.41 (d, $^3J = 9.0$ Hz, 2H), 8.45-8.54 (m, 1H); ^{13}C NMR (50 MHz, APT , CDCl_3): $\delta = 28.4$ (q, 3C), 33.2 (t), 42.1 (t), 78.9 (s), 110.6 (d), 120.3 (s), 123.3 (d), 124.1 (d), 124.8 (d, 2C), 125.1 (d), 125.5 (d, 2C), 125.8 (d), 127.5 (s), 128.2 (d), 130.1 (d), 131.0 (d), 136.5 (s), 137.0 (d), 137.8 (s), 140.4 (s), 143.6 (s), 146.4 (s), 156.0 (s), 193.0 (s)

3-(3-Nitrophenyl)-1-phenyl-1H-indole (14f, table 6). yield: 48 mg (10 %); shining yellow solid; M.p.: 126-127 °C; TLC: R_f (PE:EtOAc=10:1) = 0.42; GC/MS (EI+): m/z (rel. Intensity): 314 (M^+ , 100), 268 (34), 267 (30), 266 (14), 265 (9), 239 (5), 199 (11), 165 (20), 164 (13), 163 (10), 134 (10); ^1H NMR (200 MHz, CDCl_3): $\delta = 7.21$ -7.65 (m, 10H), 7.89-8.06 (m, 2H), 8.11 (dd, $^3J = 8.2$ Hz, $^4J = 1.8$ Hz, 1H), 8.53 (t, $^4J = 2.0$ Hz, 1H); ^{13}C NMR (50 MHz, CDCl_3): $\delta = 111.1$ (d), 116.7 (s), 119.5 (d), 120.7 (d), 121.5 (d), 121.8 (d), 123.3 (d), 124.5 (d, 2C), 126.4 (d), 127.1 (d), 129.6 (d), 129.8 (d, 2C), 133.0 (d), 136.8 (s), 137.0 (s), 139.0 (s), 148.8 (s) one quaternary C overlapping; ^{13}C NMR (50 MHz, $\text{acetone-}D_6$): $\delta = 112.9$ (d), 118.1 (s), 121.3 (d), 122.3 (d), 123.0 (d), 123.4 (d), 125.1 (d), 126.3 (d, 2C), 128.4 (s), 128.9 (d), 129.2 (d), 131.7 (d, 2C), 131.9 (d), 134.9 (d), 138.6 (s), 139.0 (s), 140.9 (s), 150.8 (s)

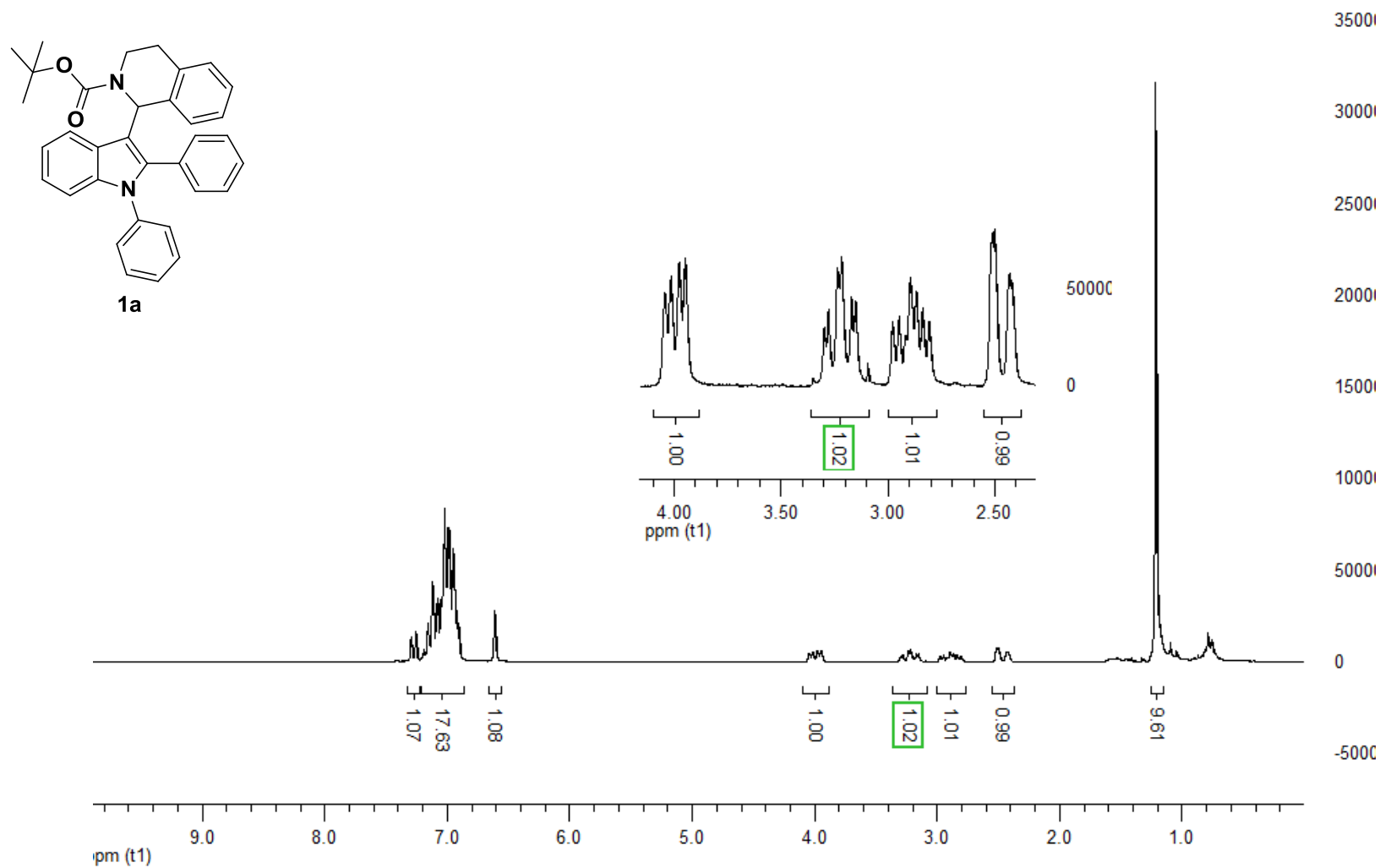
1-(1,2-Diphenyl-1H-indol-3-yl)-1,2,3,4-tetrahydroisoquinoline (15, table 9). TMSCI (204 mg, 1.88 mmol, 5.0 equiv.) was added dropwise to a solution of **1a** (188 mg, 0.375 mmol, 1.0 equiv.) in dry MeOH (3 mL) at room temperature. The reaction mixture was degassed with argon for 30 seconds and stirred for 2 hours in an argon atmosphere. Since the conversion was very low (TLC), the reaction mixture was heated to 40 °C and another 5 equiv. of TMSCI were added dropwise. After 10 hours another portion (5 equiv.) of TMSCI was added and the reaction mixture was stirred for additional 12

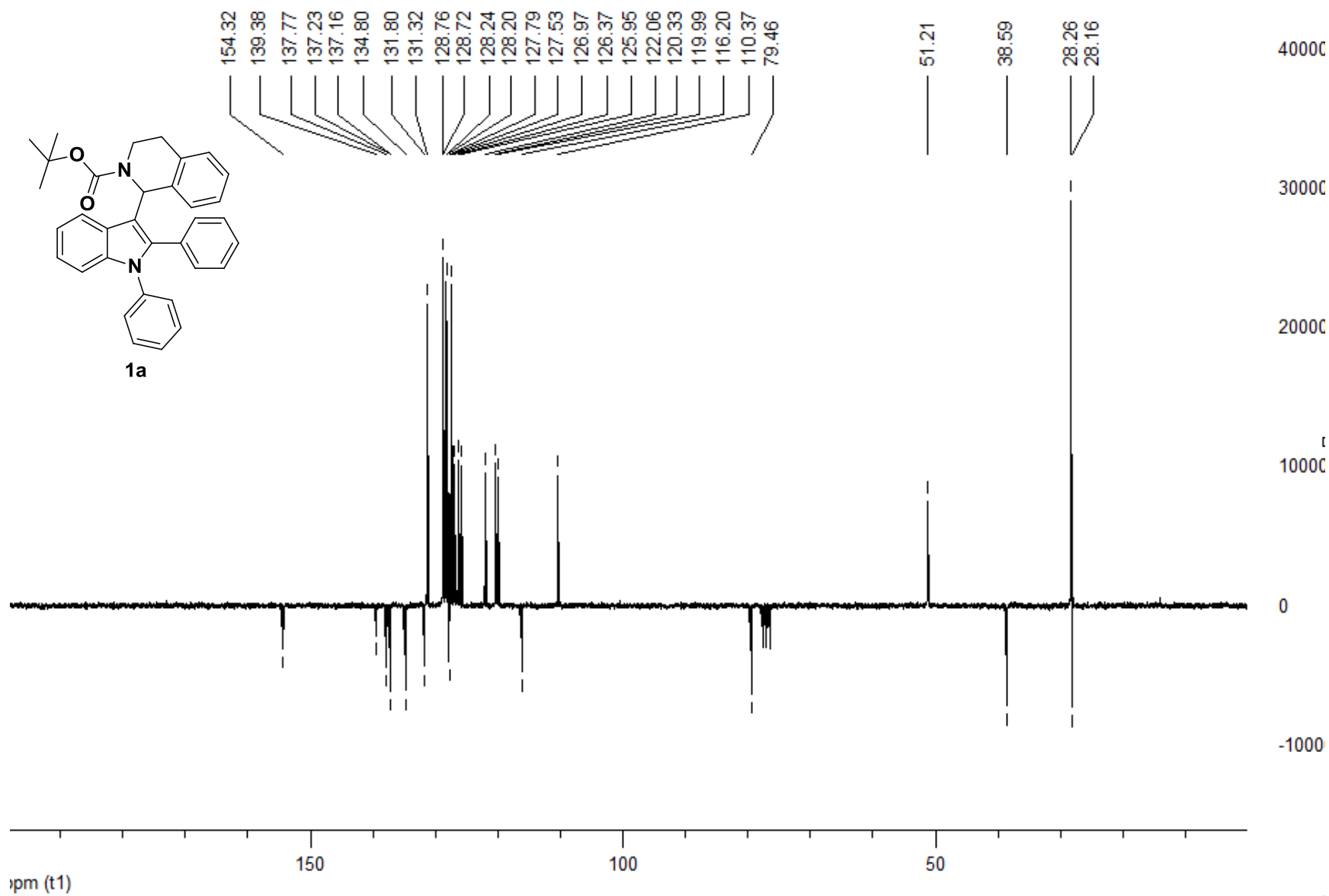
hours. The reaction mixture was poured onto ice-cold 2N aqueous sodium hydroxide solution and extracted three times with EtOAc. The collected organic layers were washed once with brine, dried over sodium sulfate, filtered and evaporated. Product **15** was obtained by flash chromatography using PE:EtOAc =100:0 → 0:100 (75 minutes). Yield: 122 mg (82 %); colorless solid; M.p.: 208-210 °C; TLC: Rf(EtOAc)=0.32; HRMS (ESI⁺): exact mass calculated for C₂₉H₂₄N₂: 401.2012. Found: 401.2013 [M+H]⁺; GC/MS (EI⁺): m/z (rel. Intensity): 400 (M⁺, 71), 399 (100), 398 (14), 397 (36), 384 (16), 323 (43), 295 (32), 294 (26), 269 (30), 268 (17), 267 (20), 217 (12), 216 (11), 200 (69), 199 (28), 191 (19), 177 (19), 165 (28), 132 (21), 131 (22), 130 (52), 103 (17), 77 (29); ¹H NMR (200 MHz, CDCl₃): δ = 1.90 (bs, 1H), 2.71-2.92 (m, 1H), 3.02-3.30 (m, 2H), 3.31-3.48 (m, 1H), 5.37 (s, 1H), 6.88-7.41 (m, 18H); ¹³C NMR (50 MHz, CDCl₃): δ = 30.2 (t), 44.1 (t), 54.5 (d), 110.4 (d), 117.2 (s), 120.2 (d), 120.9 (d), 122.3 (d), 125.93 (d), 125.95 (d), 126.3 (s), 126.8 (d), 127.4 (d), 127.7 (d), 128.0 (2C, d), 128.1 (2C, d), 128.9 (d), 129.0 (2C, d), 130.6 (2C, d), 131.5 (s), 135.2 (s), 138.16 (s), 138.24 (s), 139.1 (s), 139.2 (s)

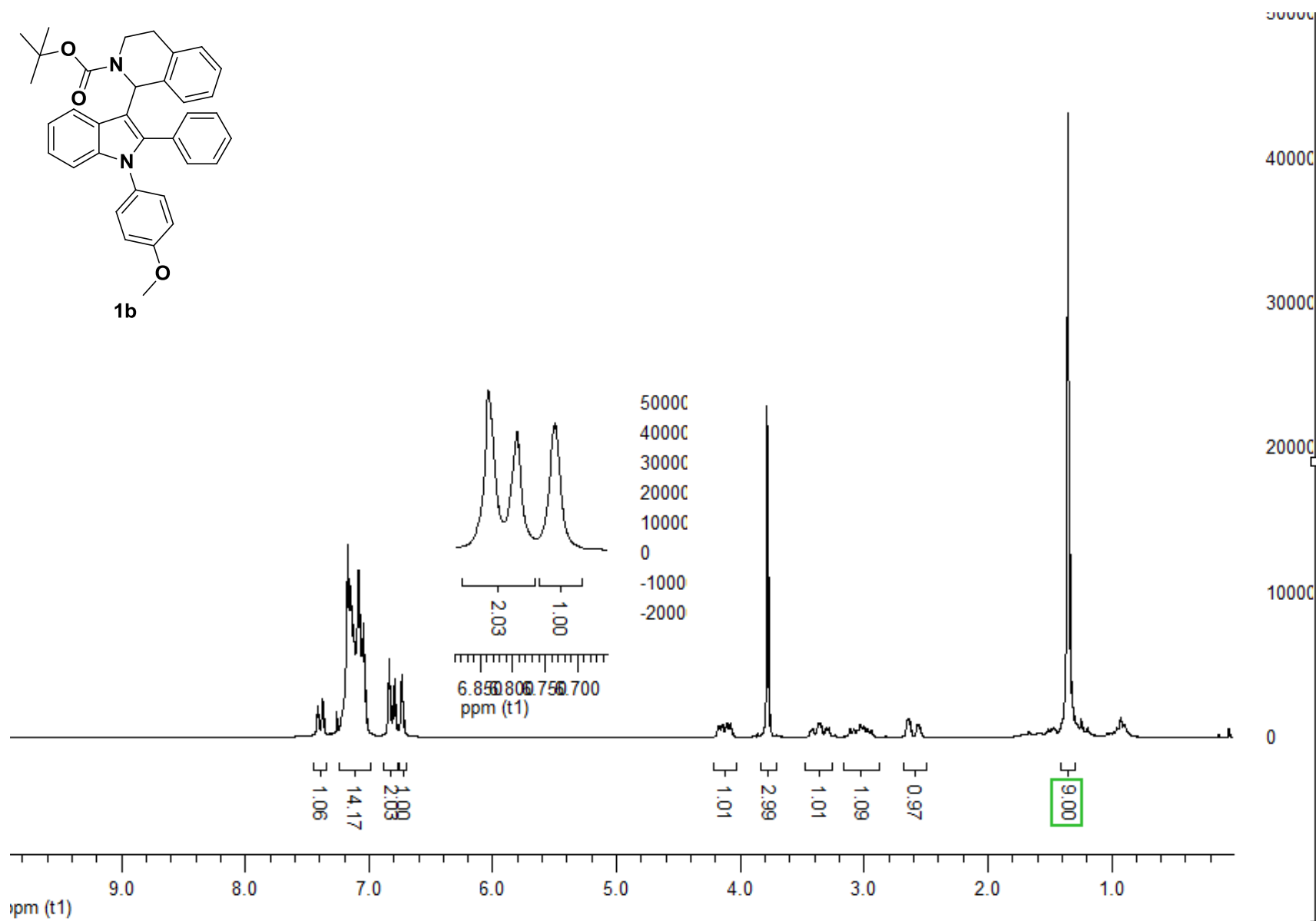
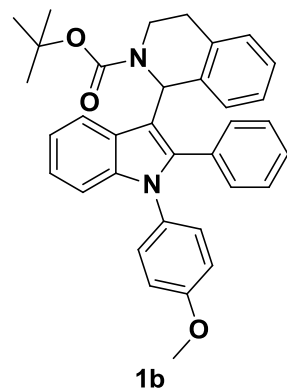
References:

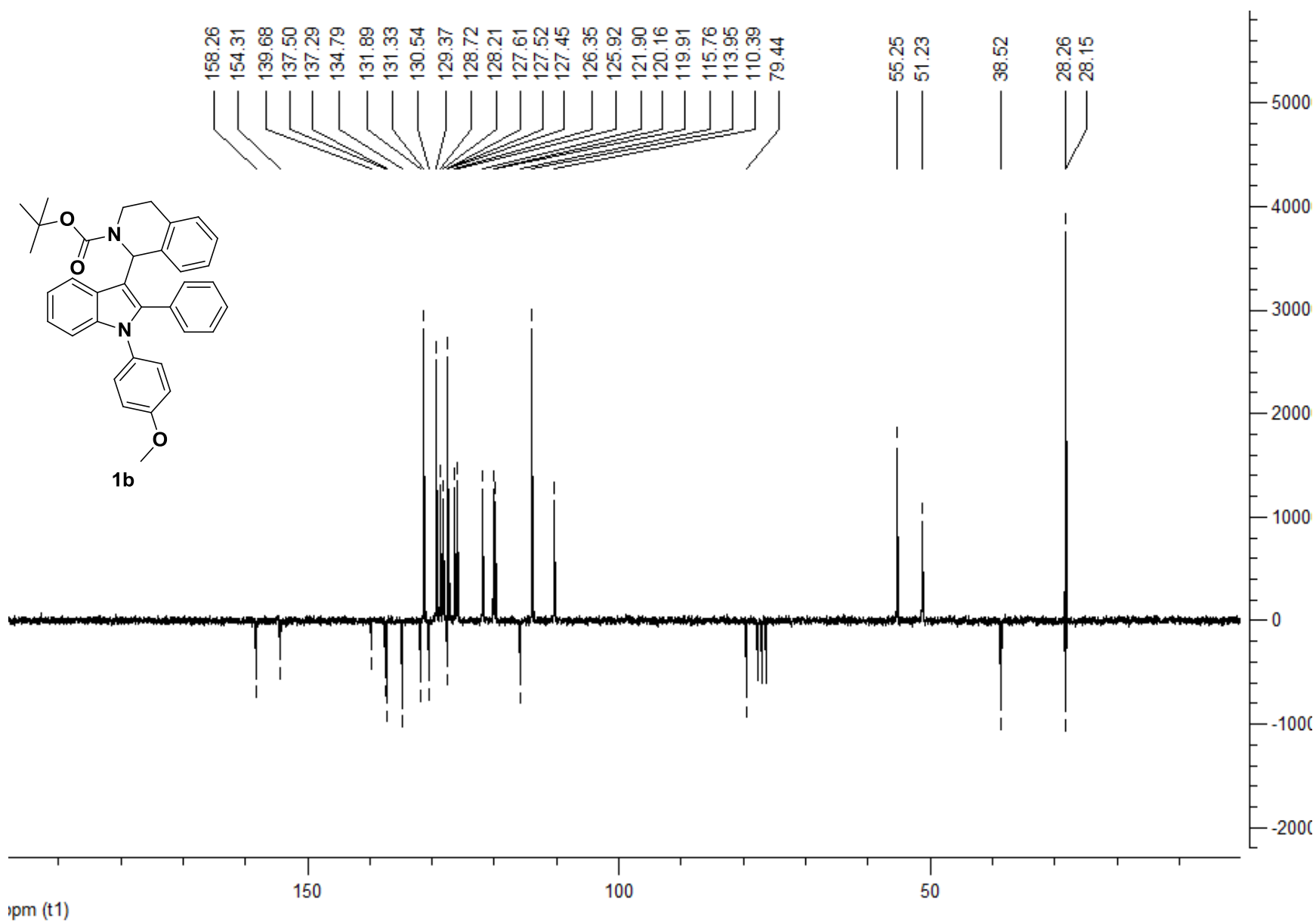
1. Yang, S.-D.; Sun, C.-L.; Fang, Z.; Li, B.-J.; Li, Y.-Z.; Shi, Z.-J. *Angew. Chem., Int. Ed.* **2008**, *47*, 1473-1476.
2. Ghobrial, M.; Harhammer, K.; Mihovilovic, M. D.; Schnürch, M. *Chem. Commun.* **2010**, *46*, 8836-8838.
3. Ghobrial, M.; Schnürch, M.; Mihovilovic, M. D. *J. Org.Chem.* **2011**, *76*, 8781-8793.
4. Kwong, F. Y.; Klapars, A.; Buchwald, S. L. *Org. Lett.* **2002**, *4*, 581-584.
5. Antilla, J. C.; Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 11684-11688.
6. Tang, B.-X.; Guo, S.-M.; Zhang, M.-B.; Li, J.-H. *Synthesis* **2008**, 1707-1716.
7. Rao, R. K.; Naidu, A. B.; Jaseer, E. A.; Sekar, G. *Tetrahedron* **2009**, *65*, 4619-4624.

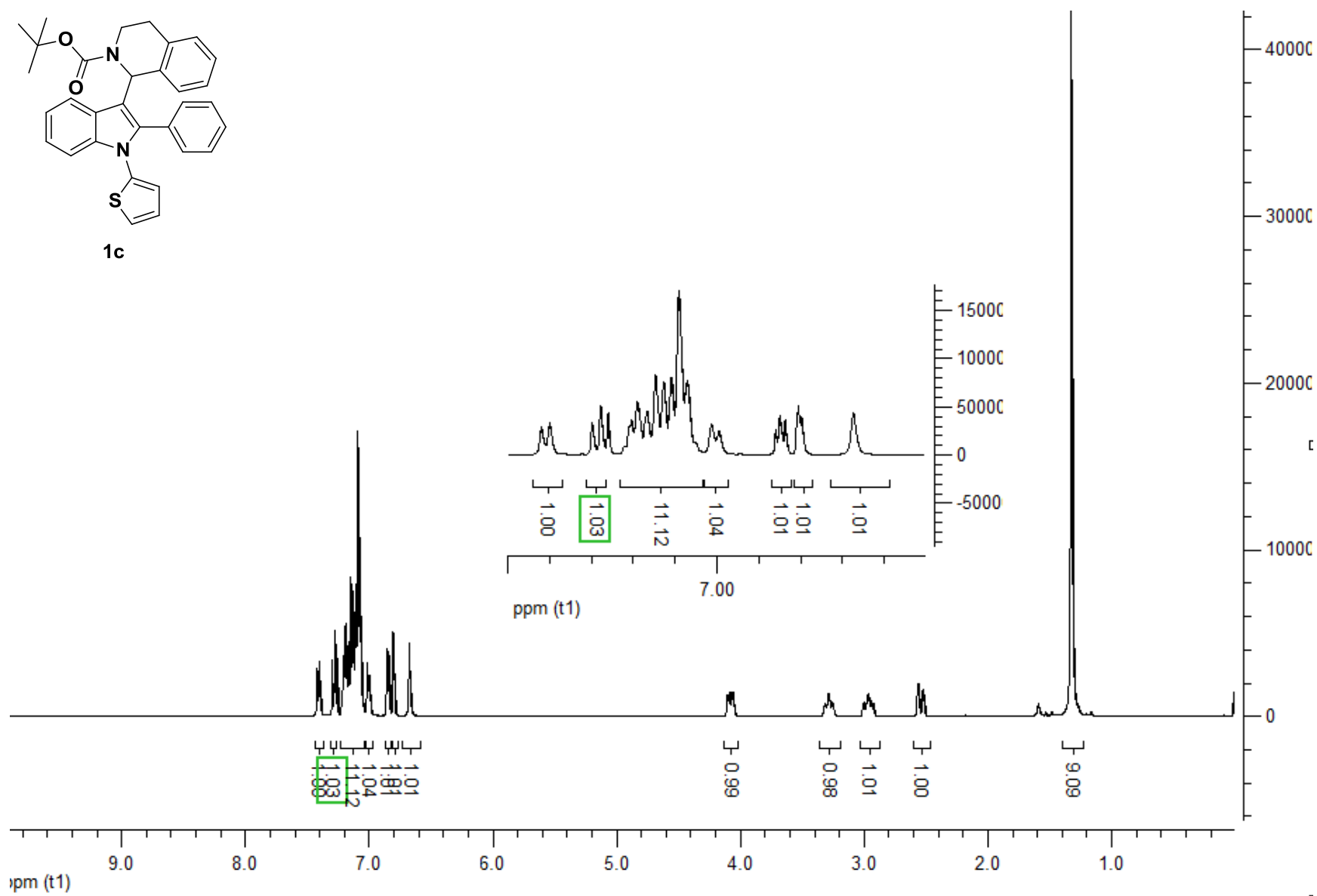
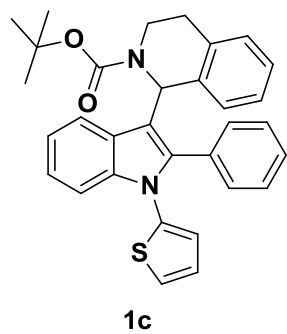
3. Copies of ^1H and ^{13}C -NMR spectra of compounds

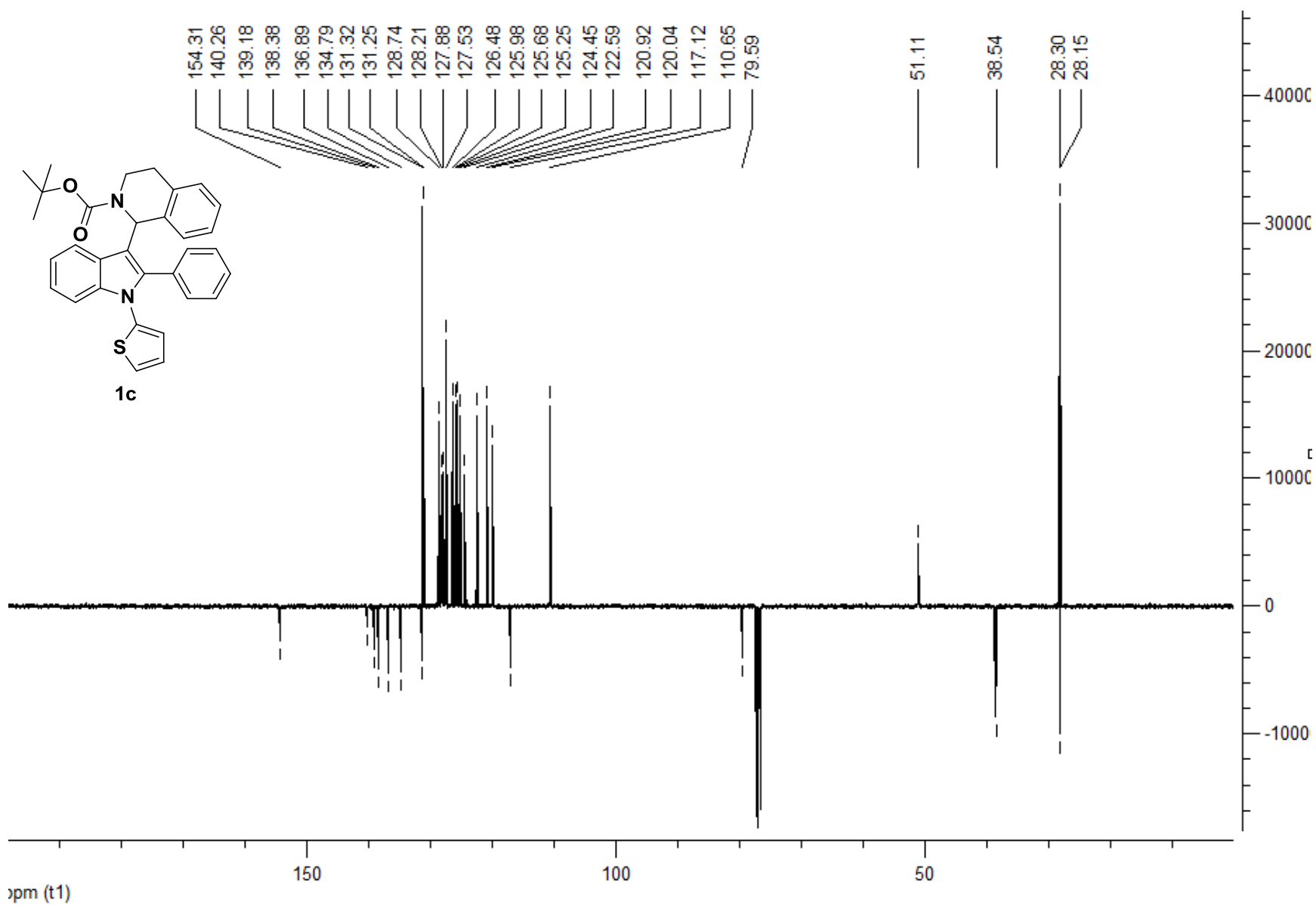


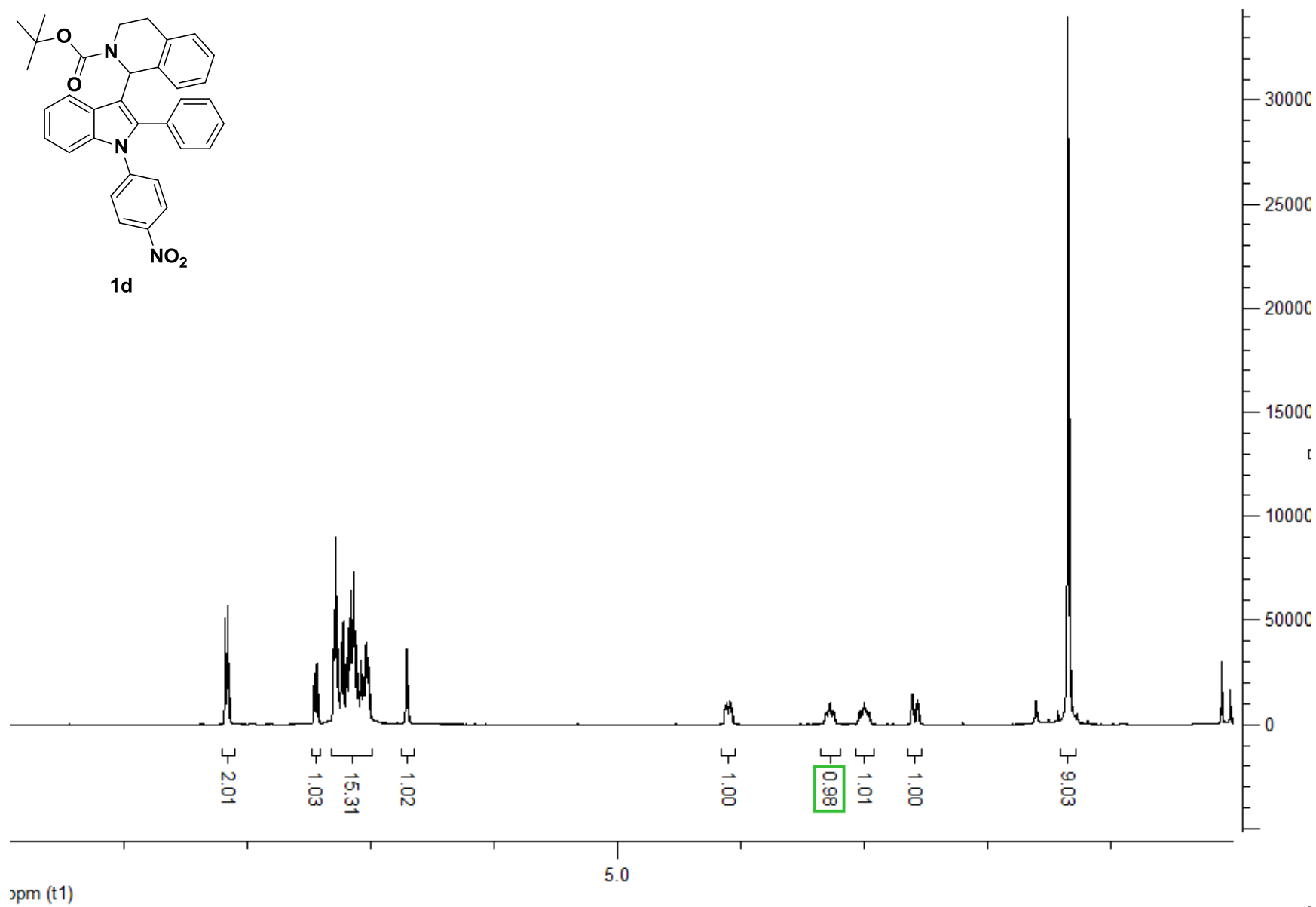
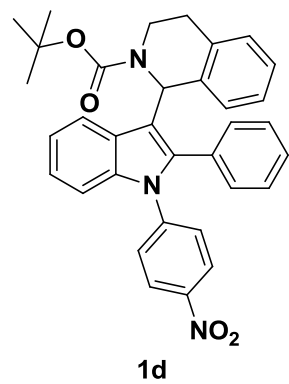


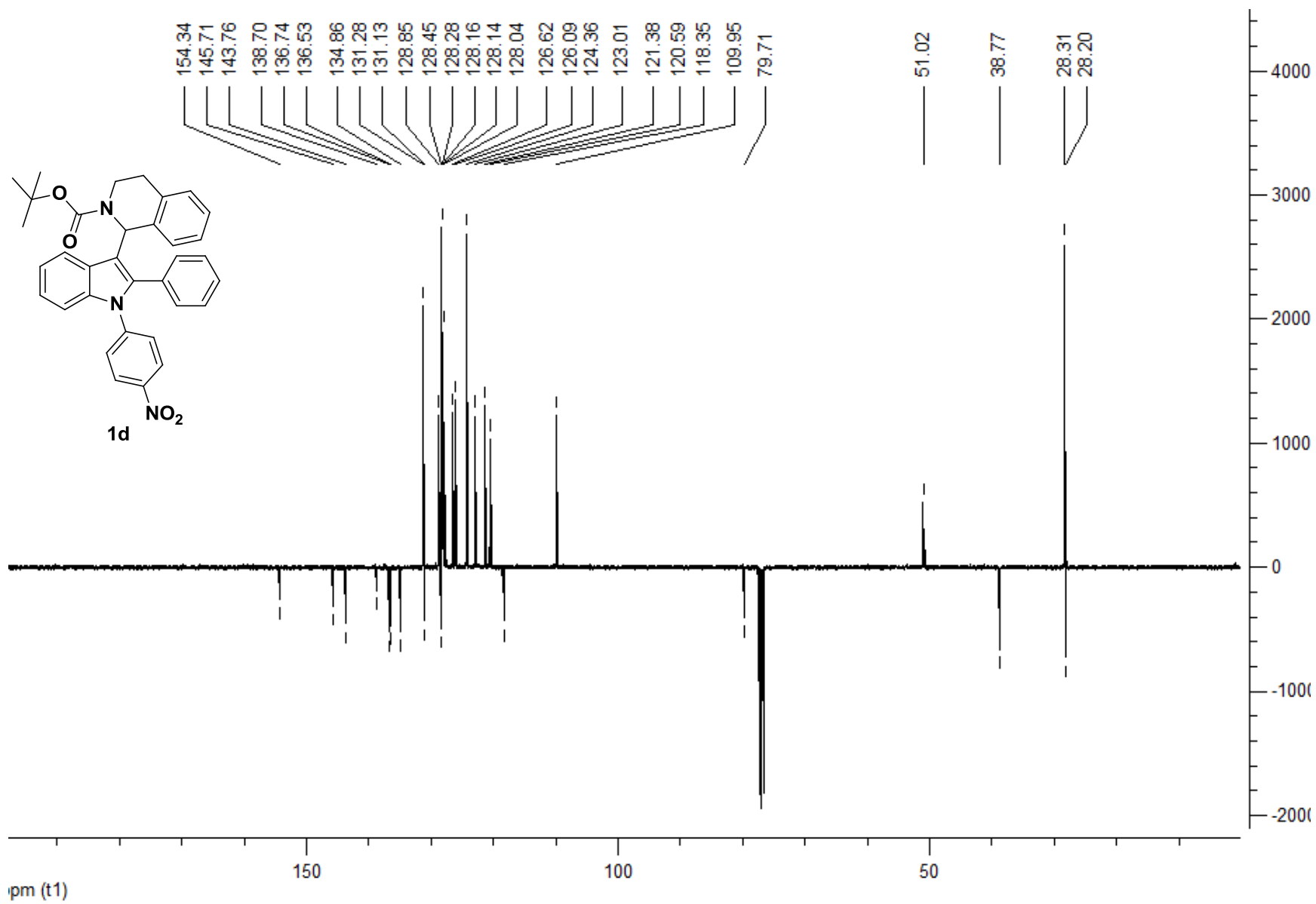


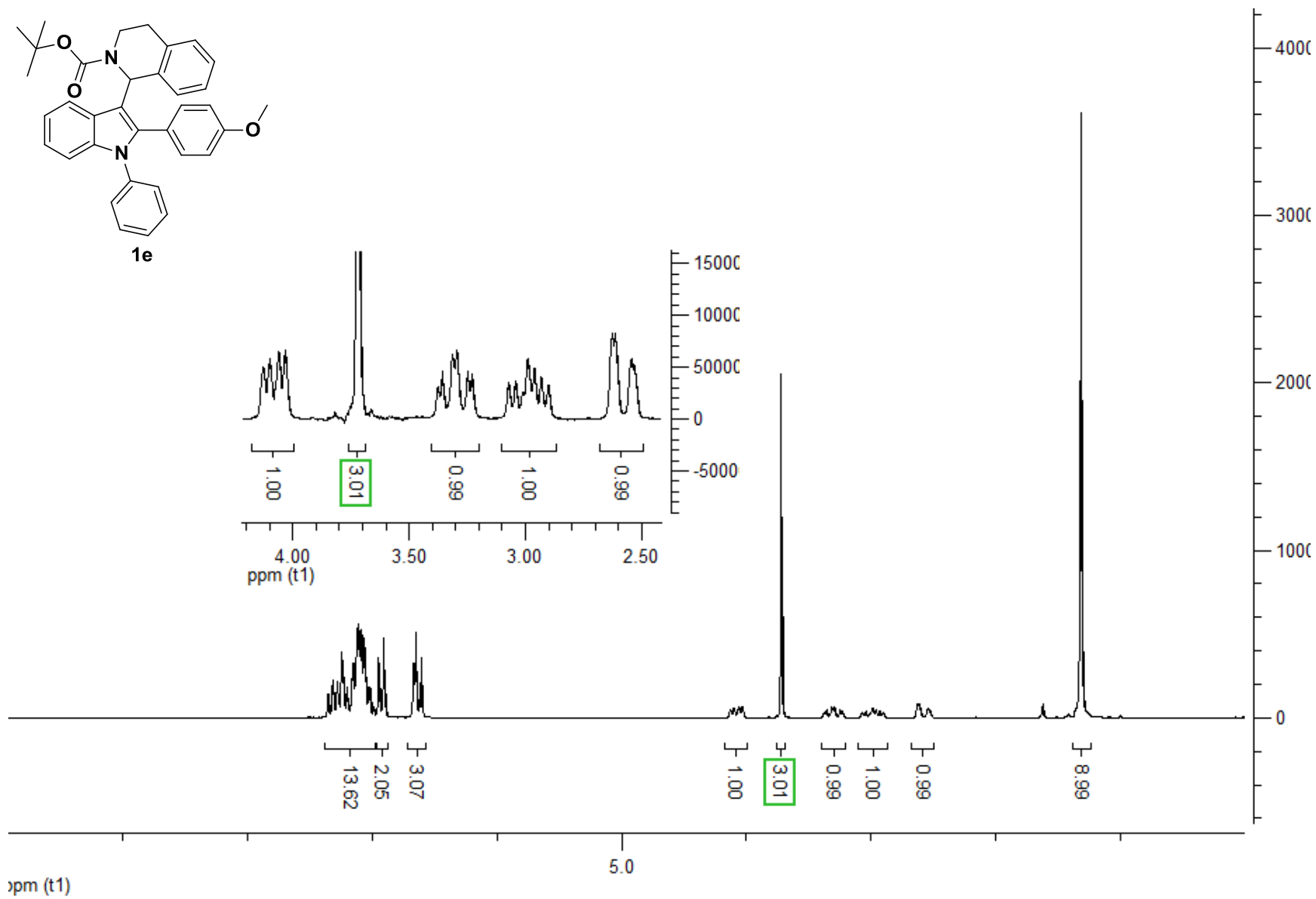


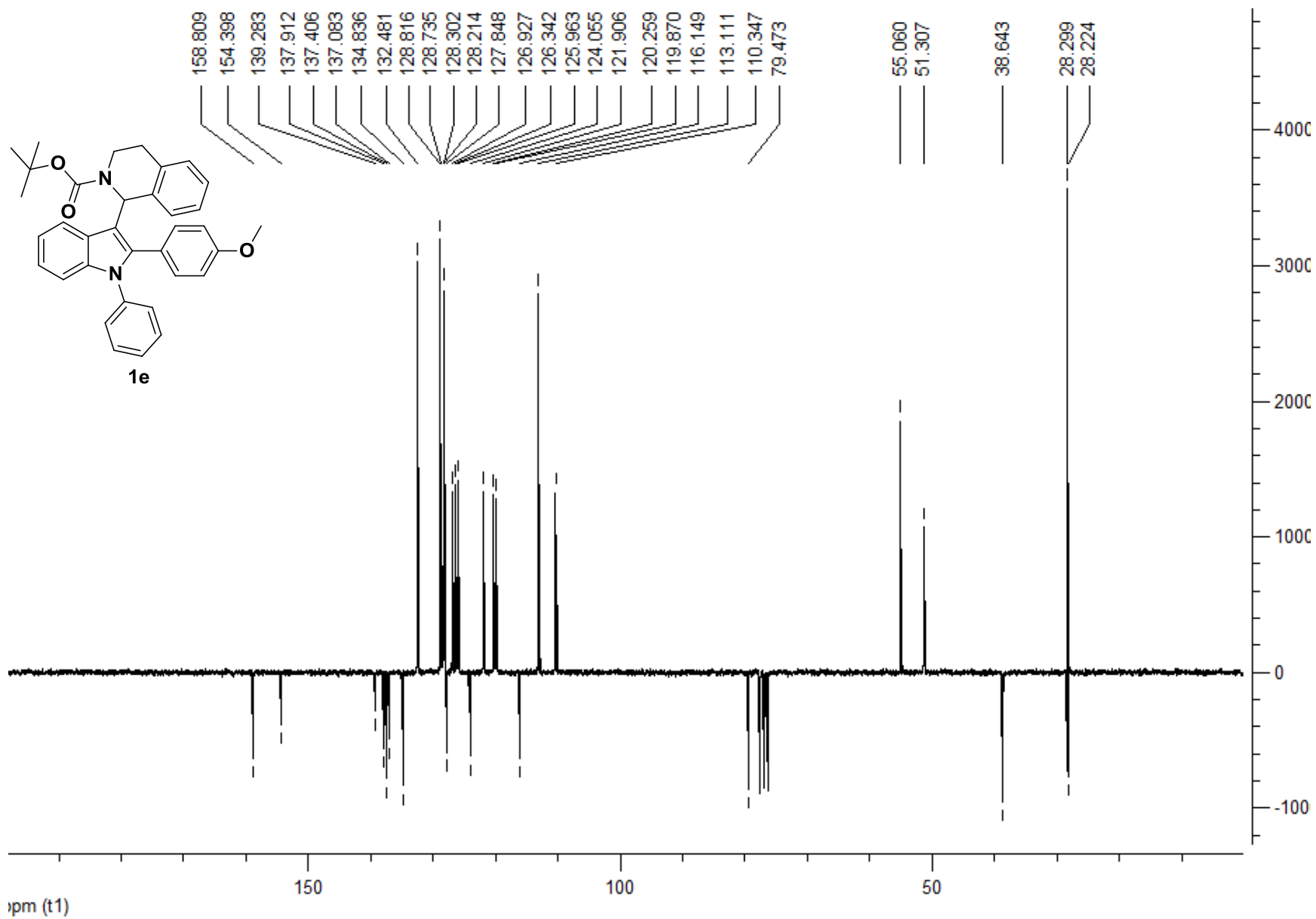


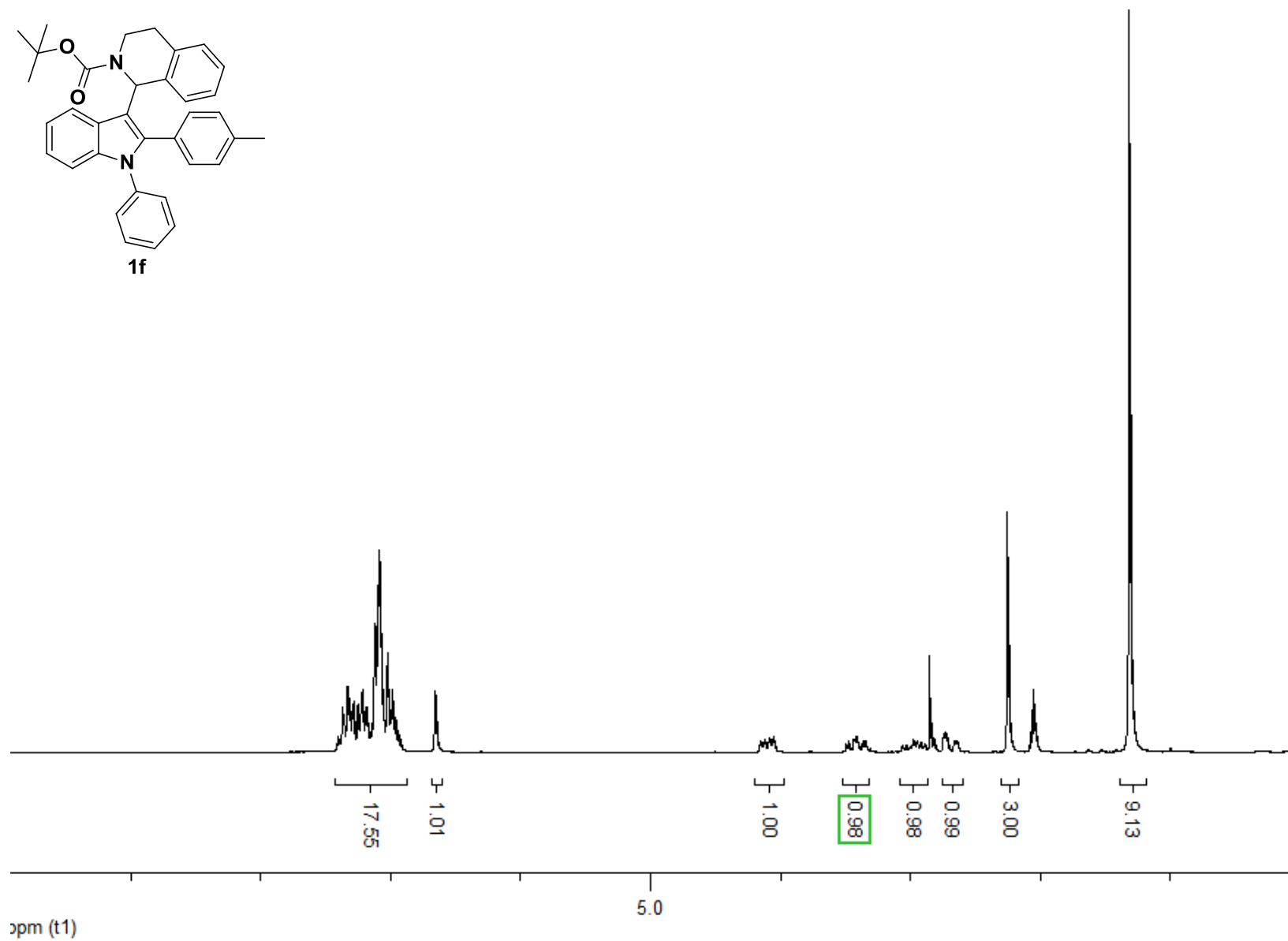
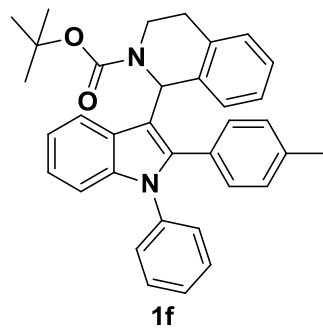


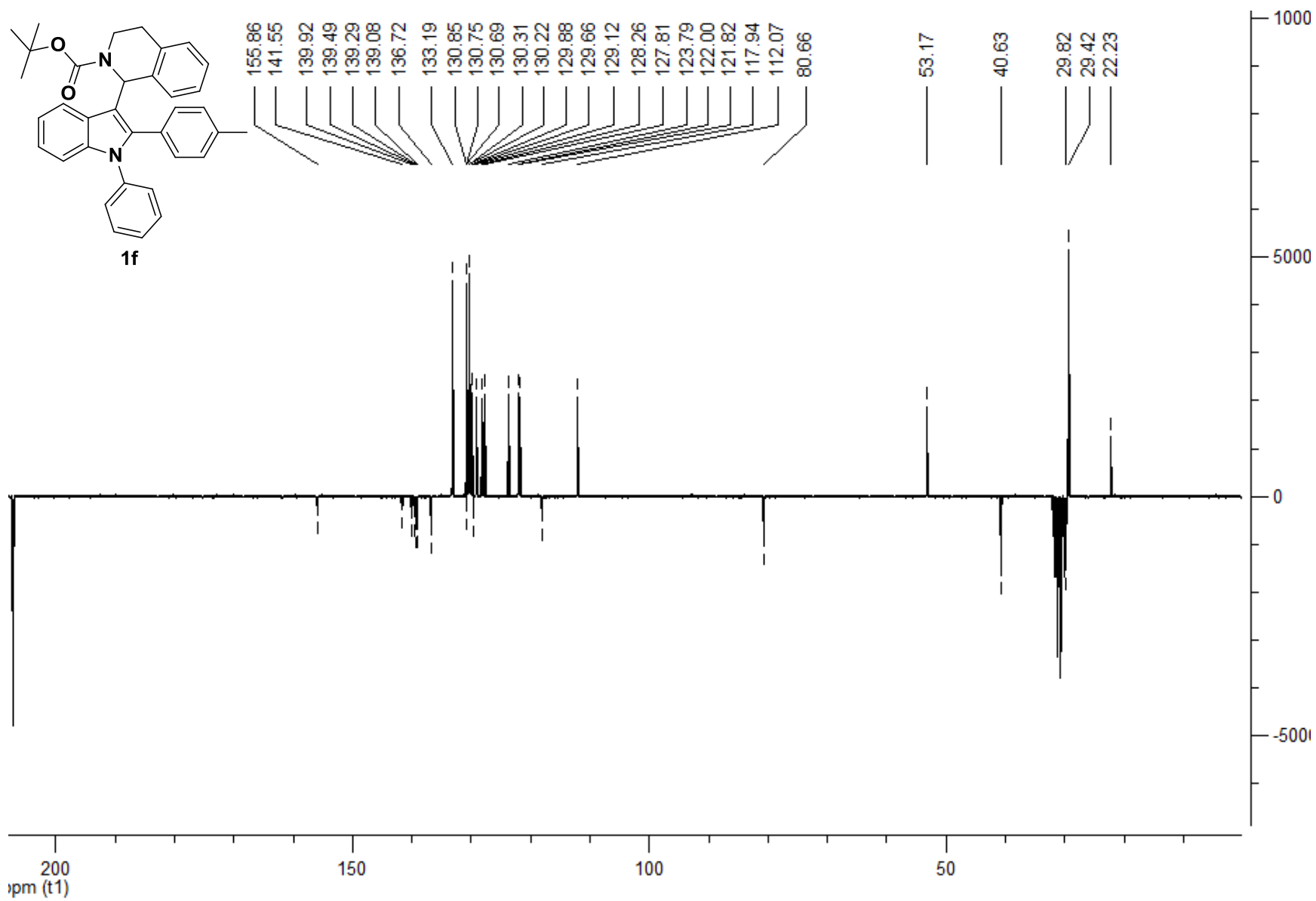


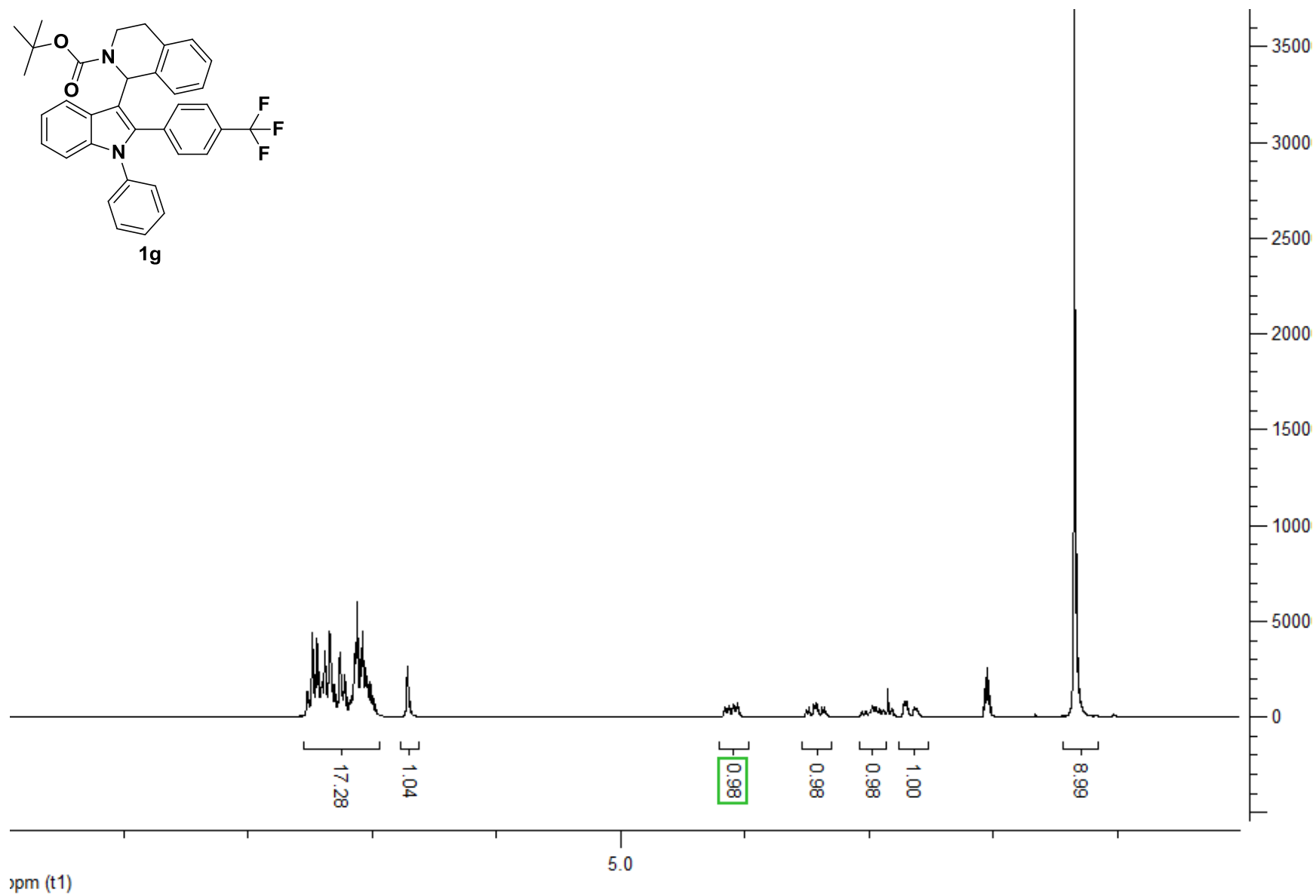
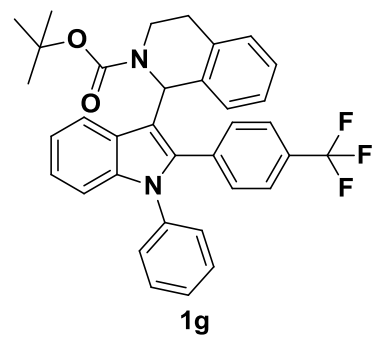


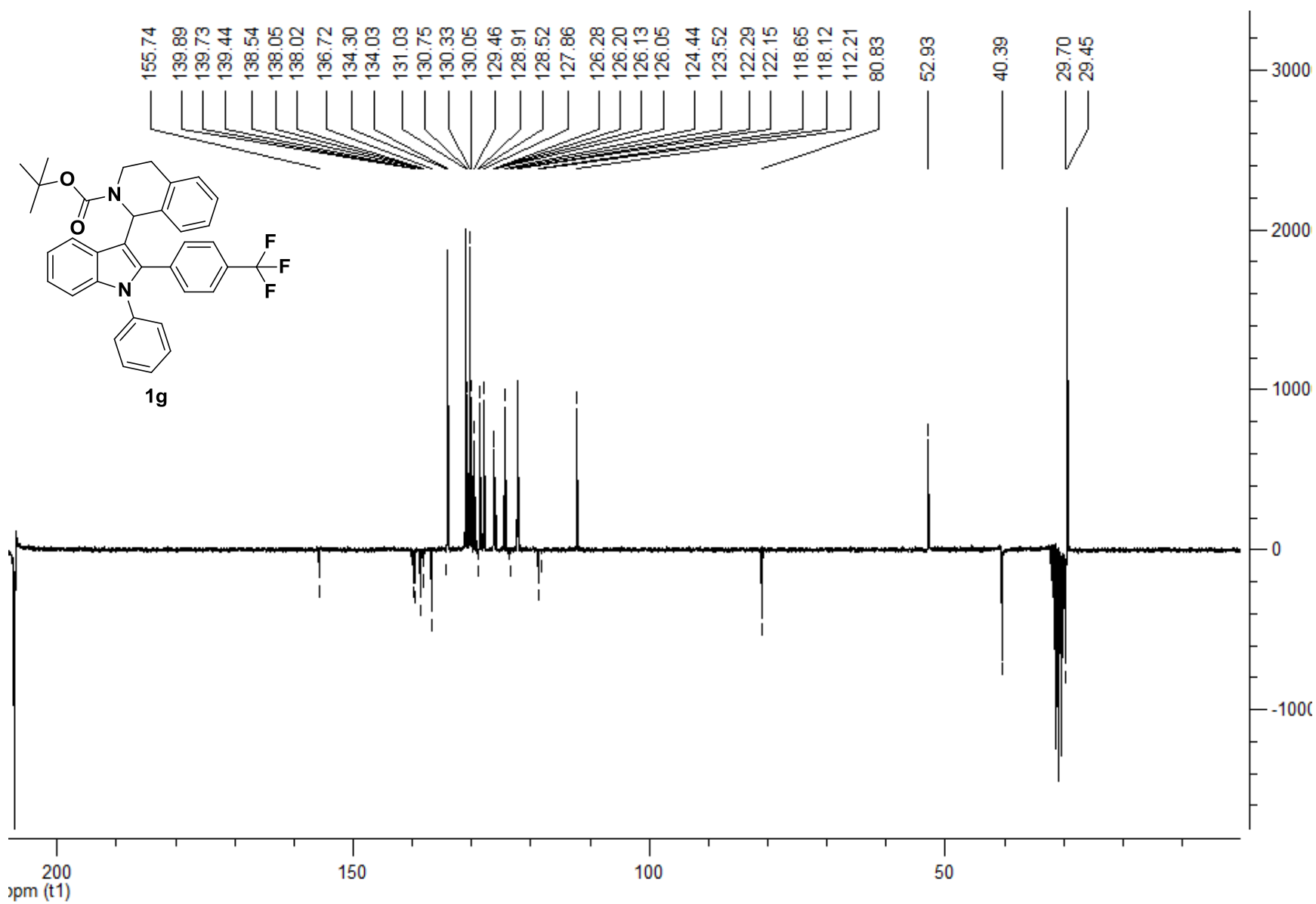


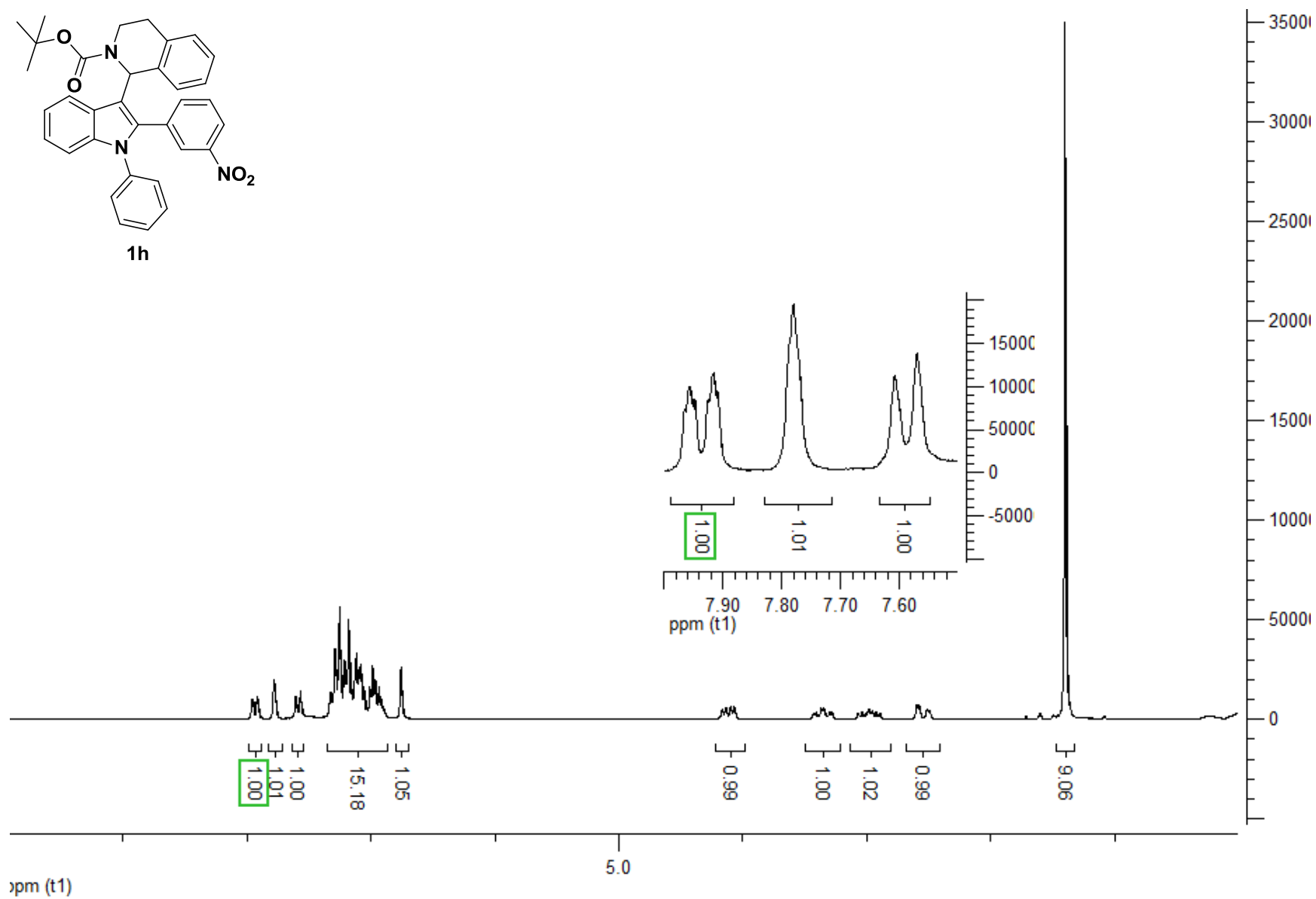
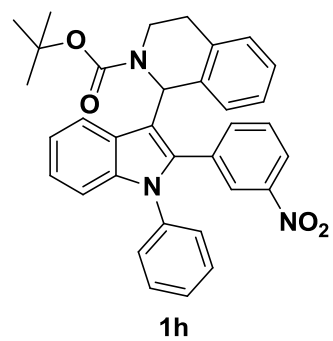


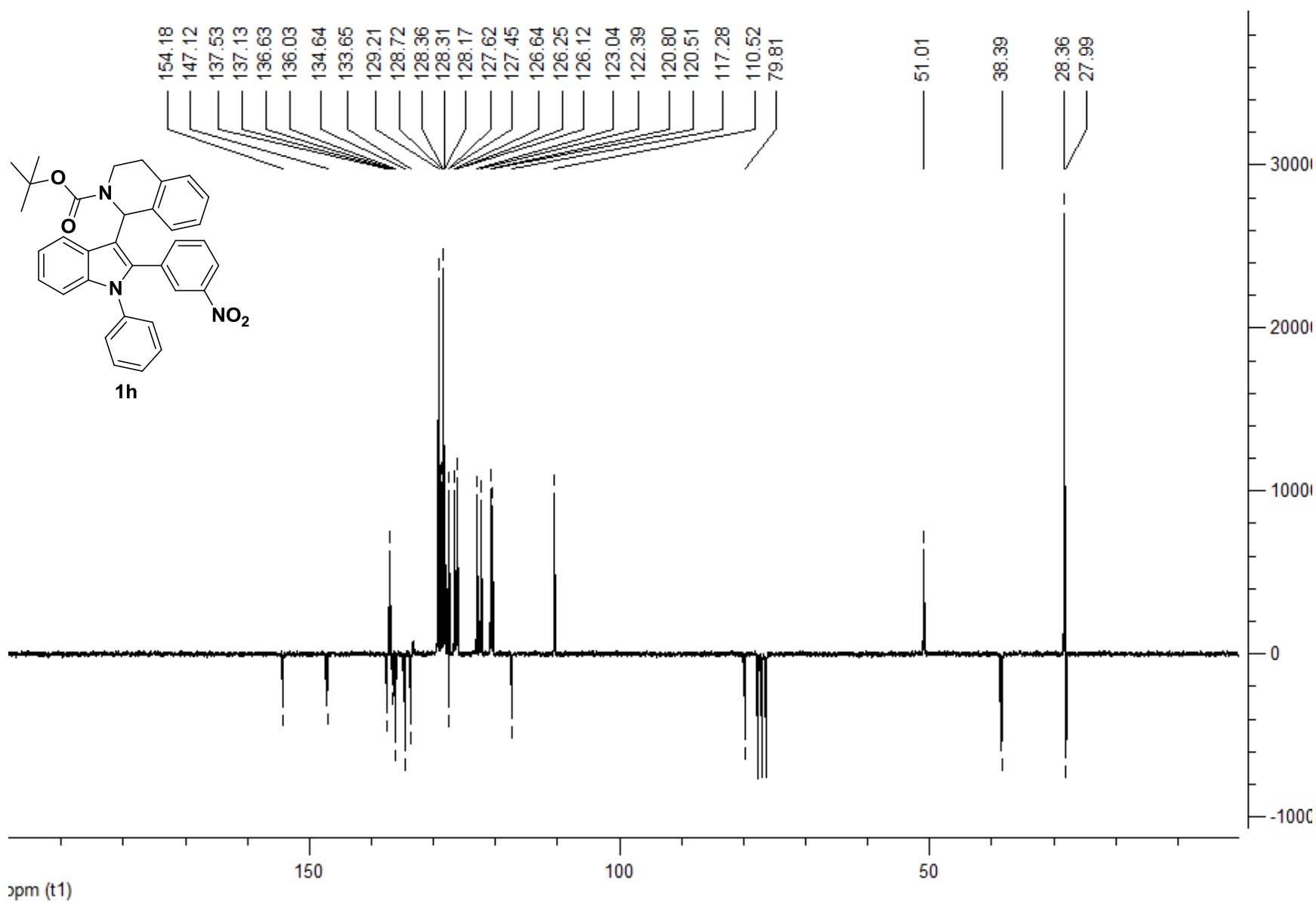


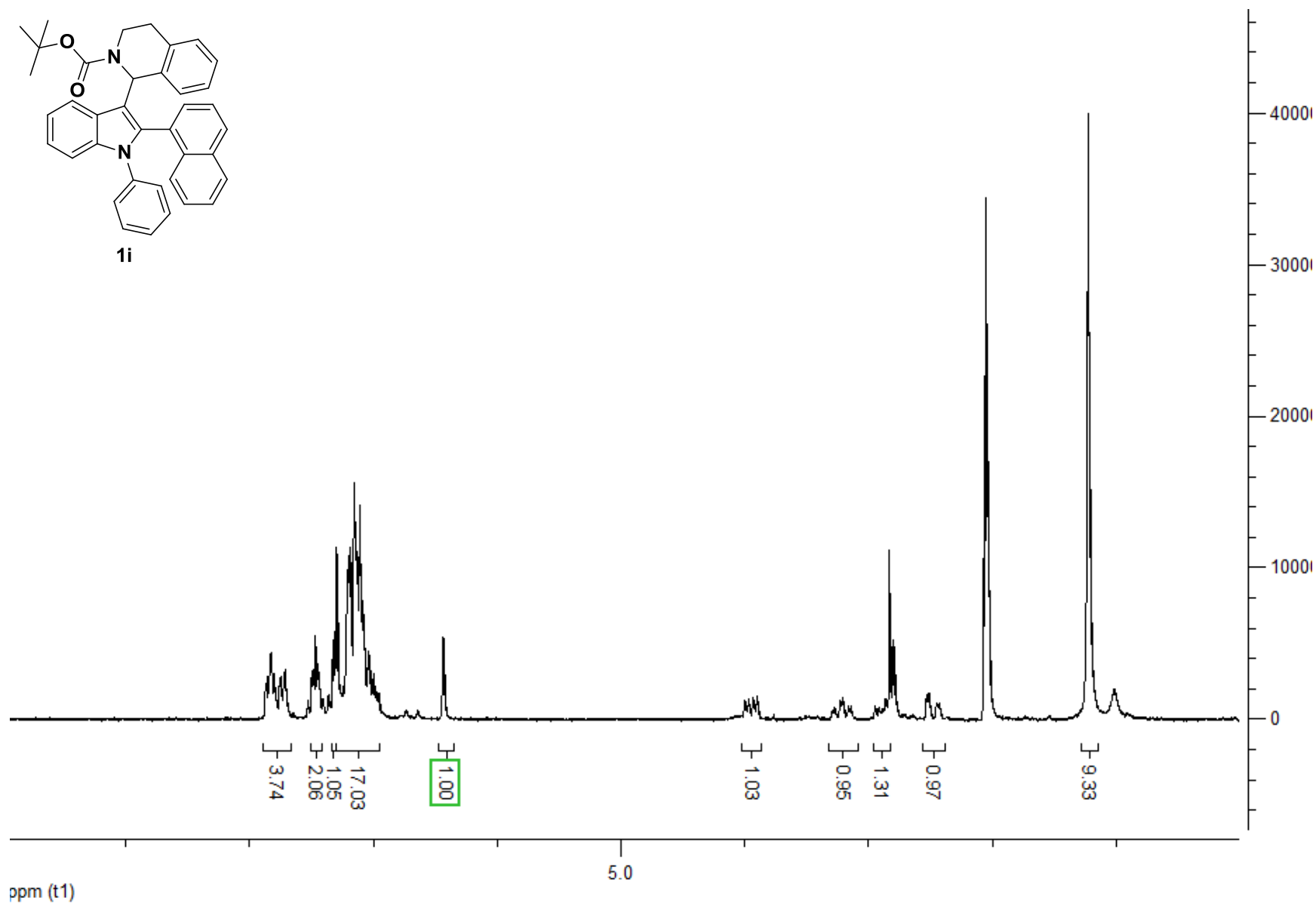
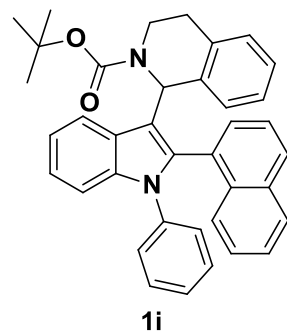


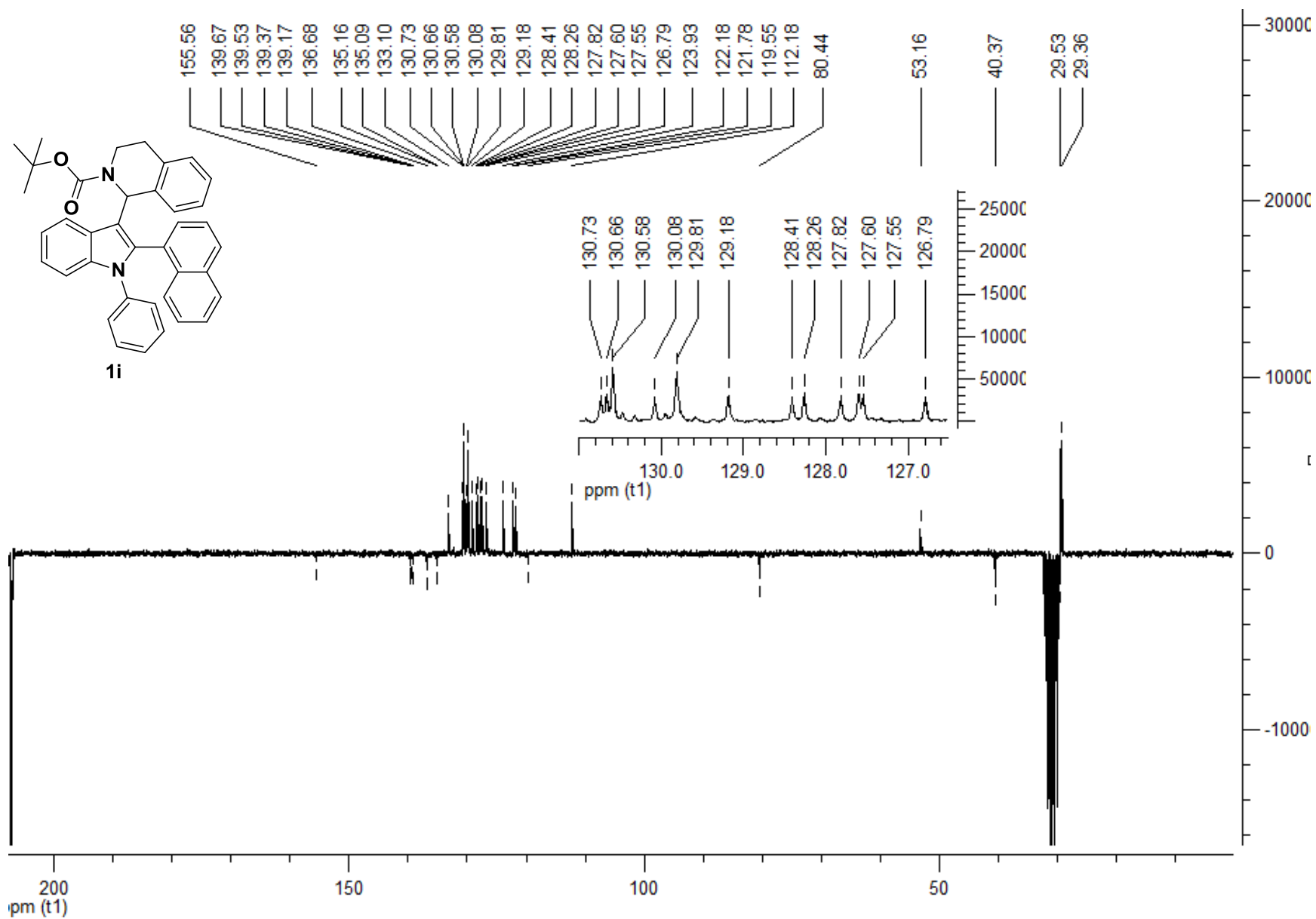


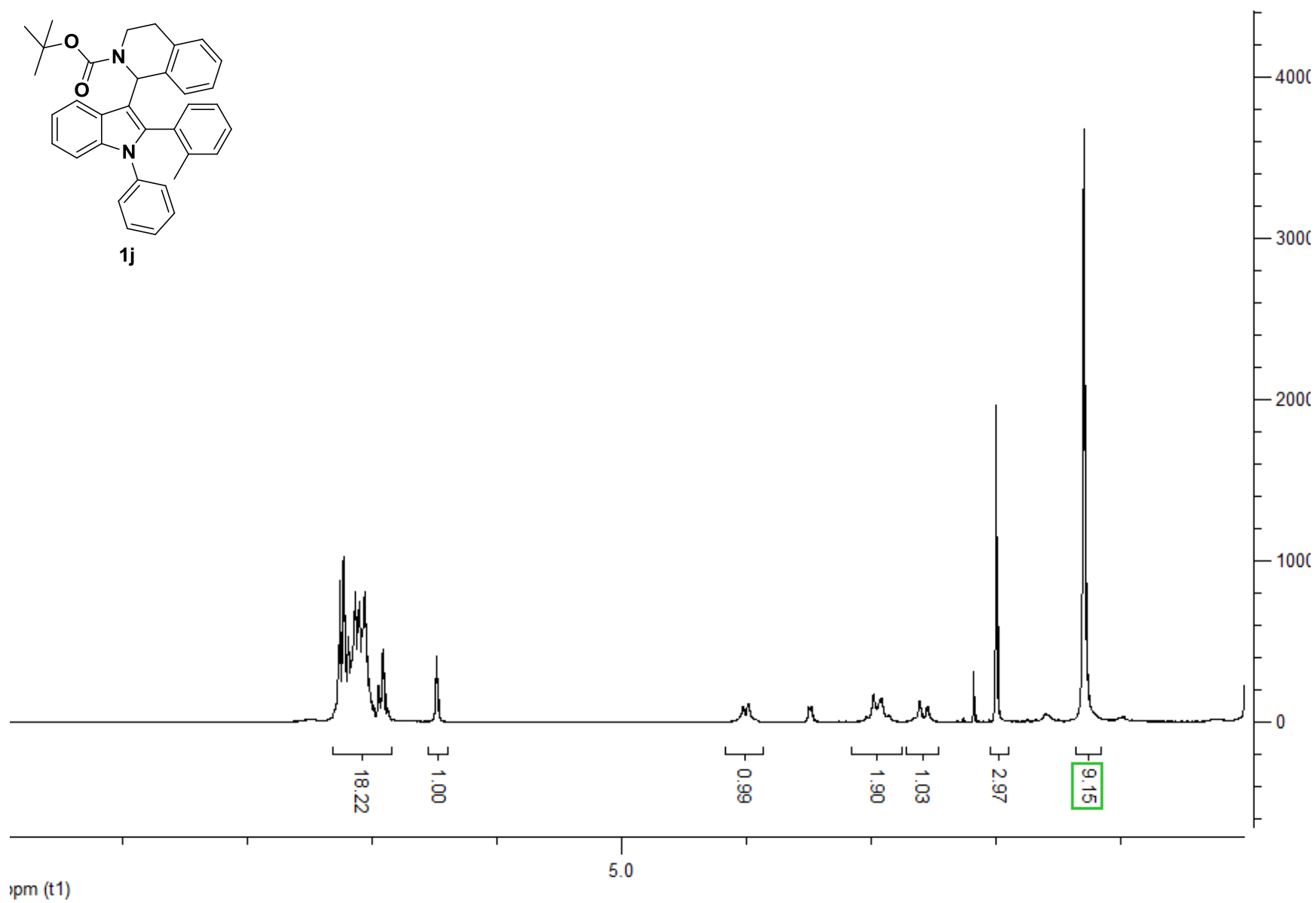
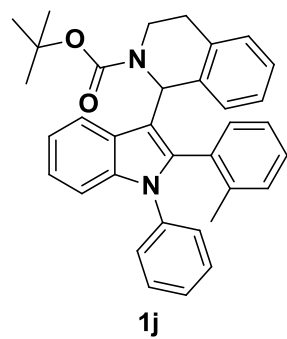


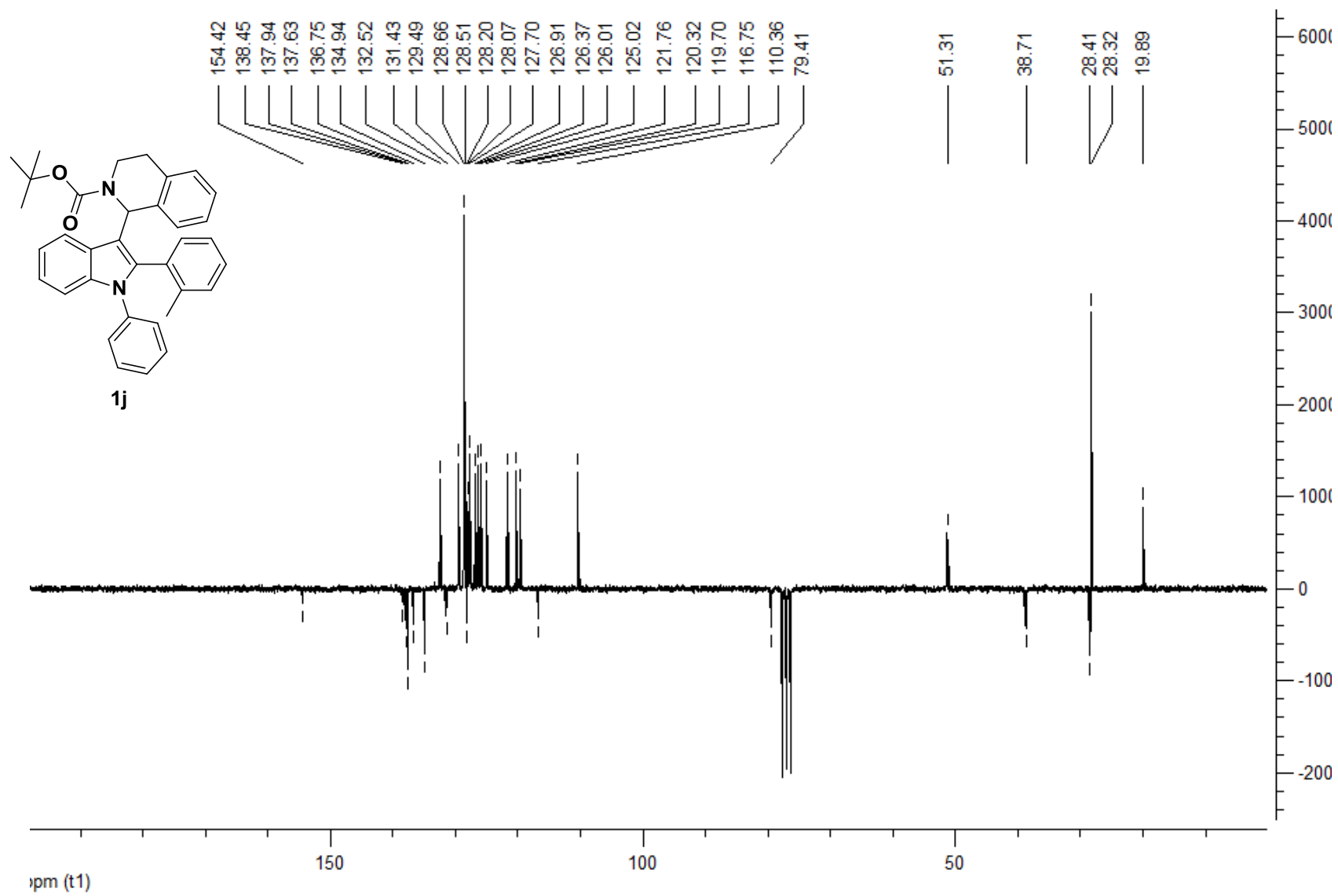


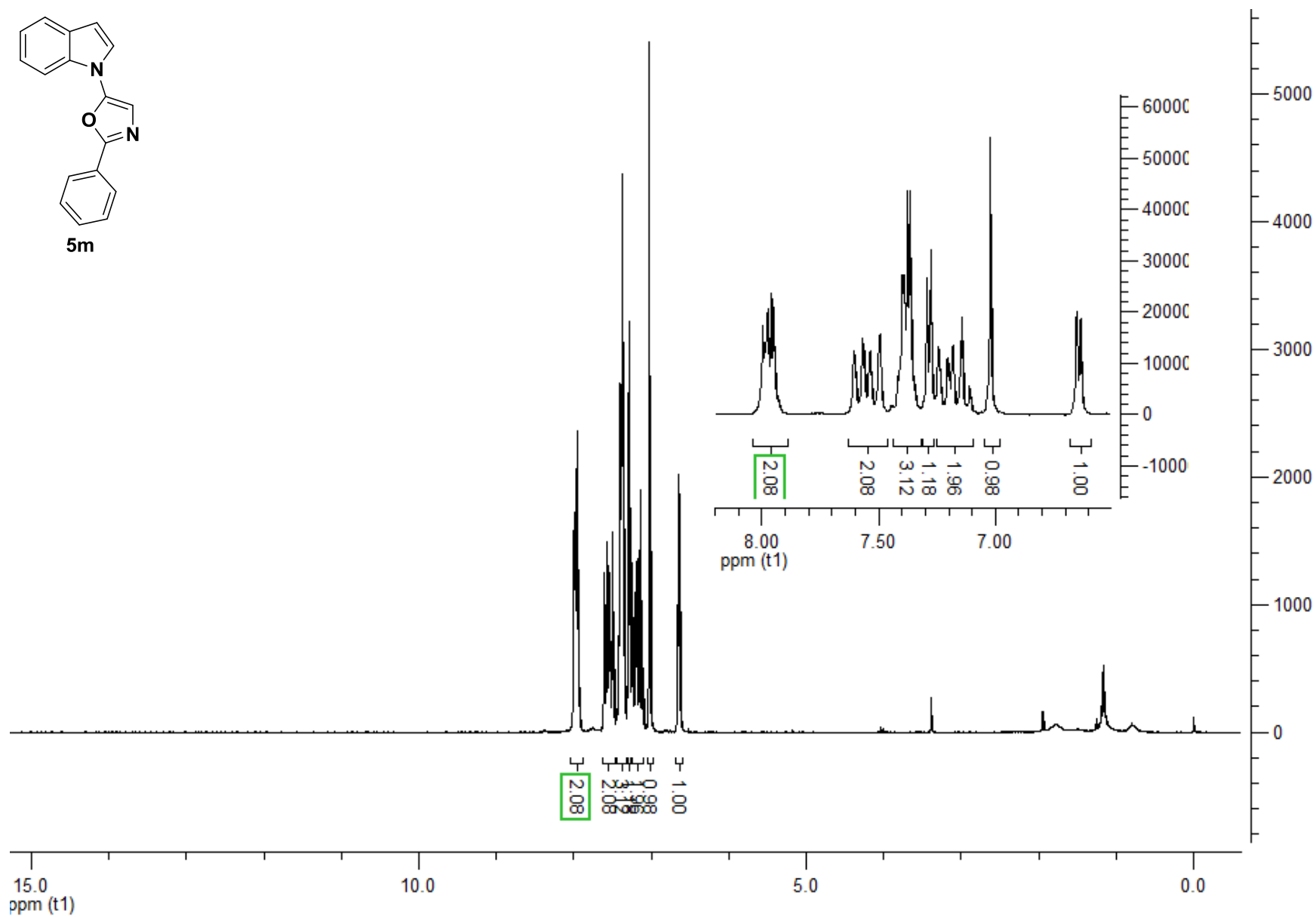
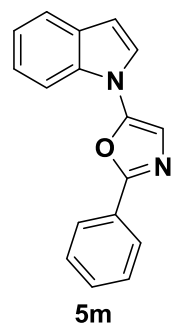


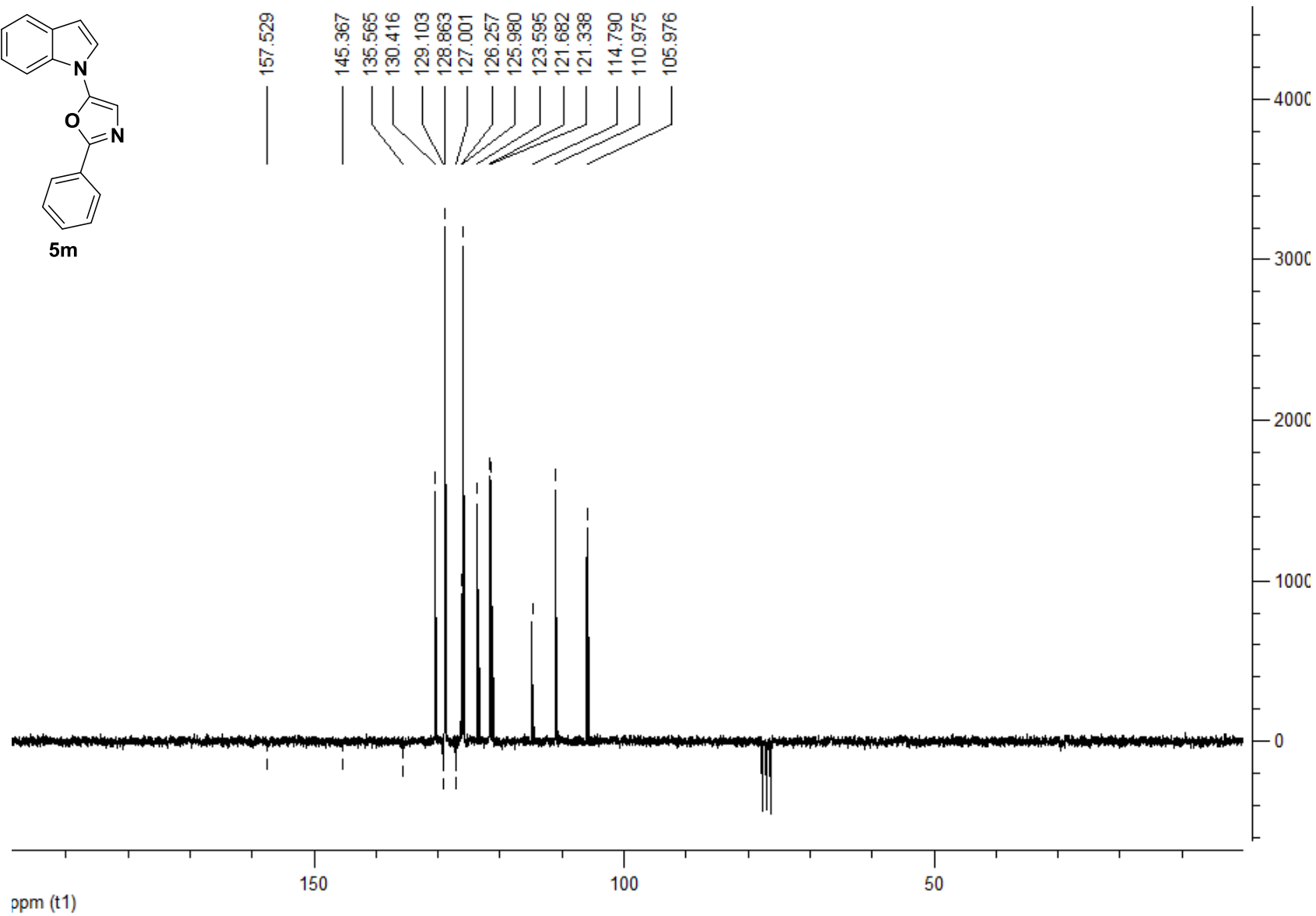
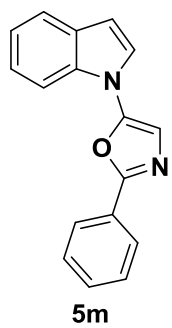


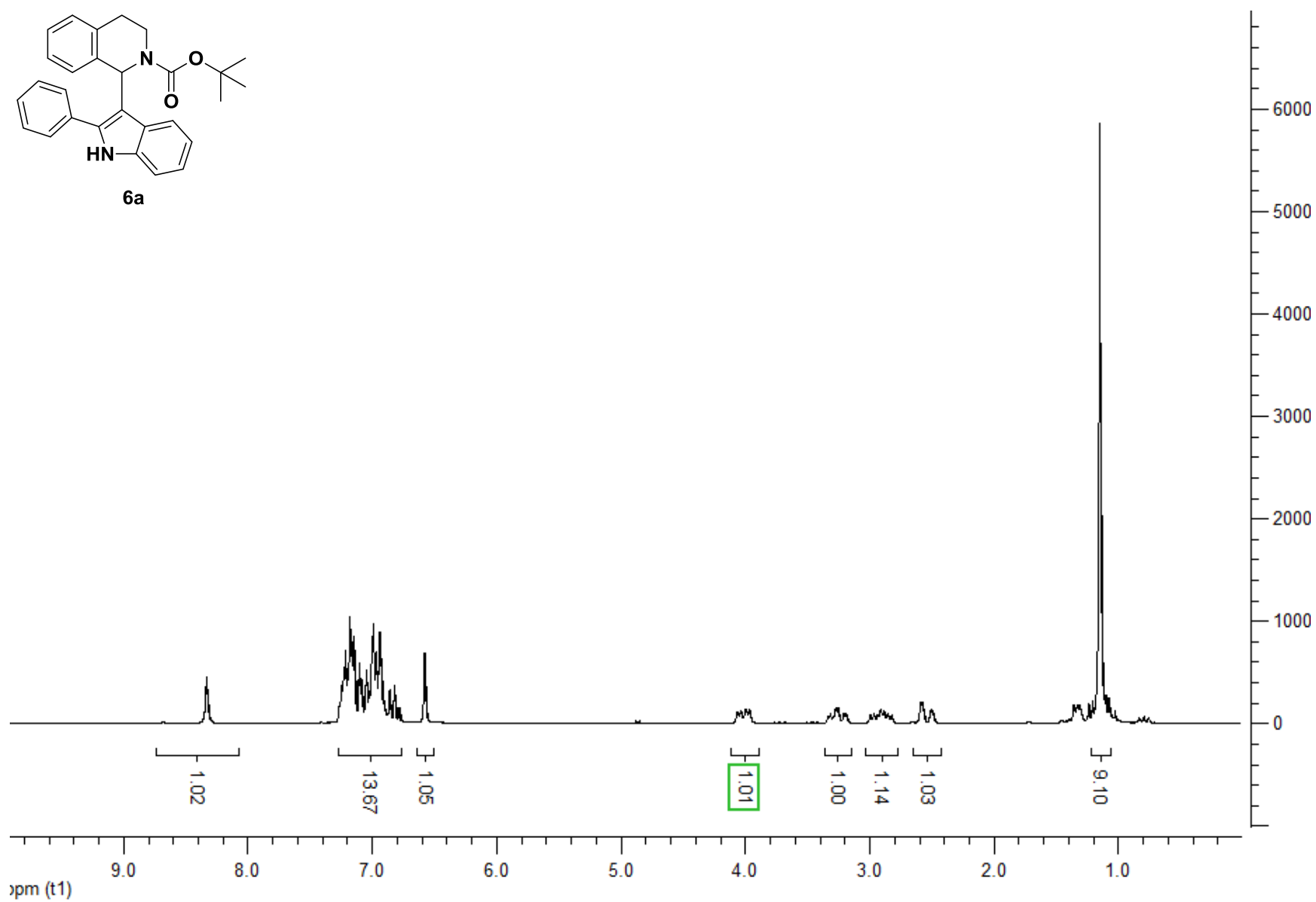
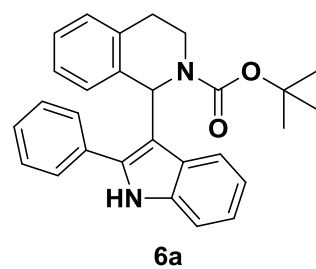


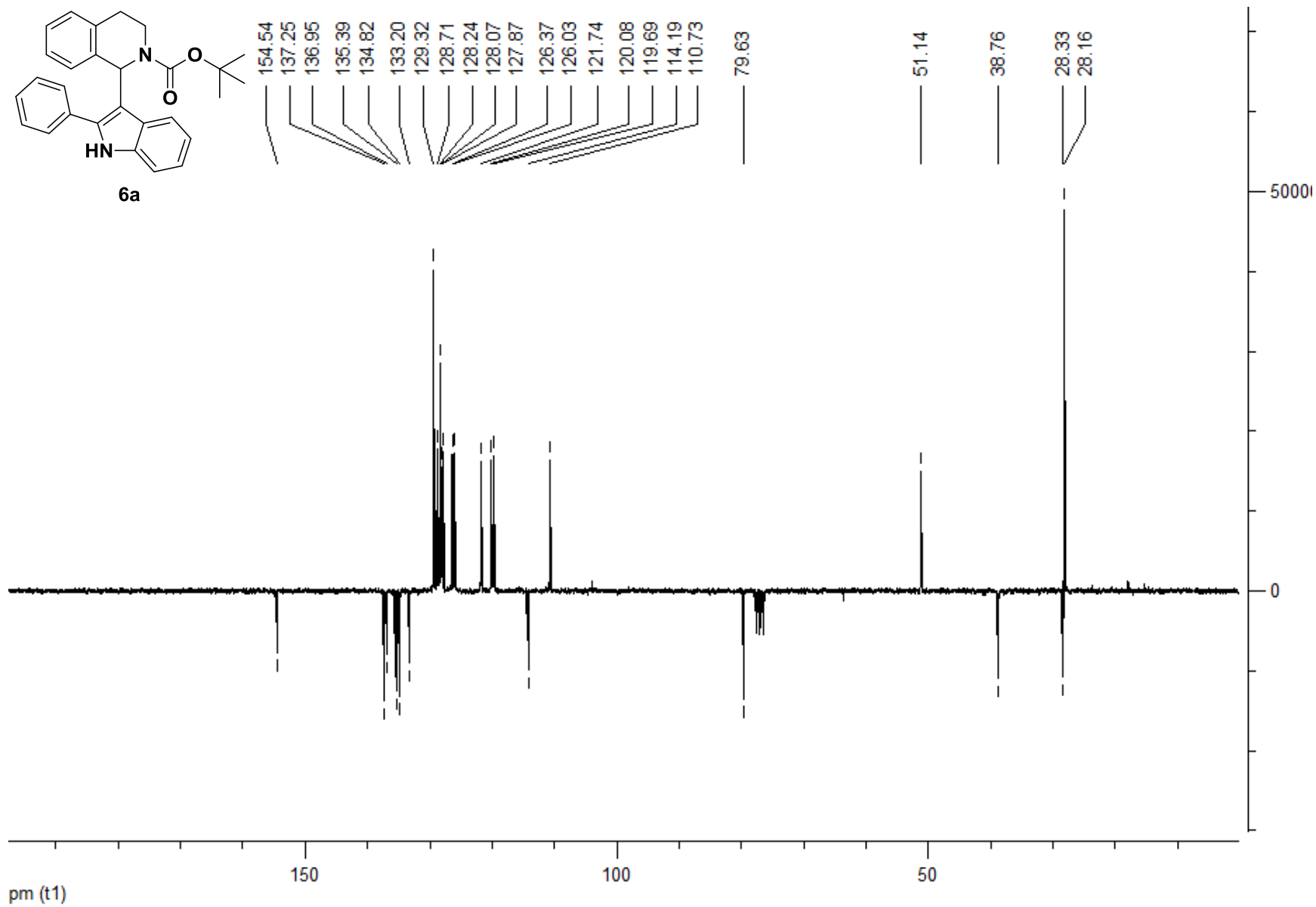


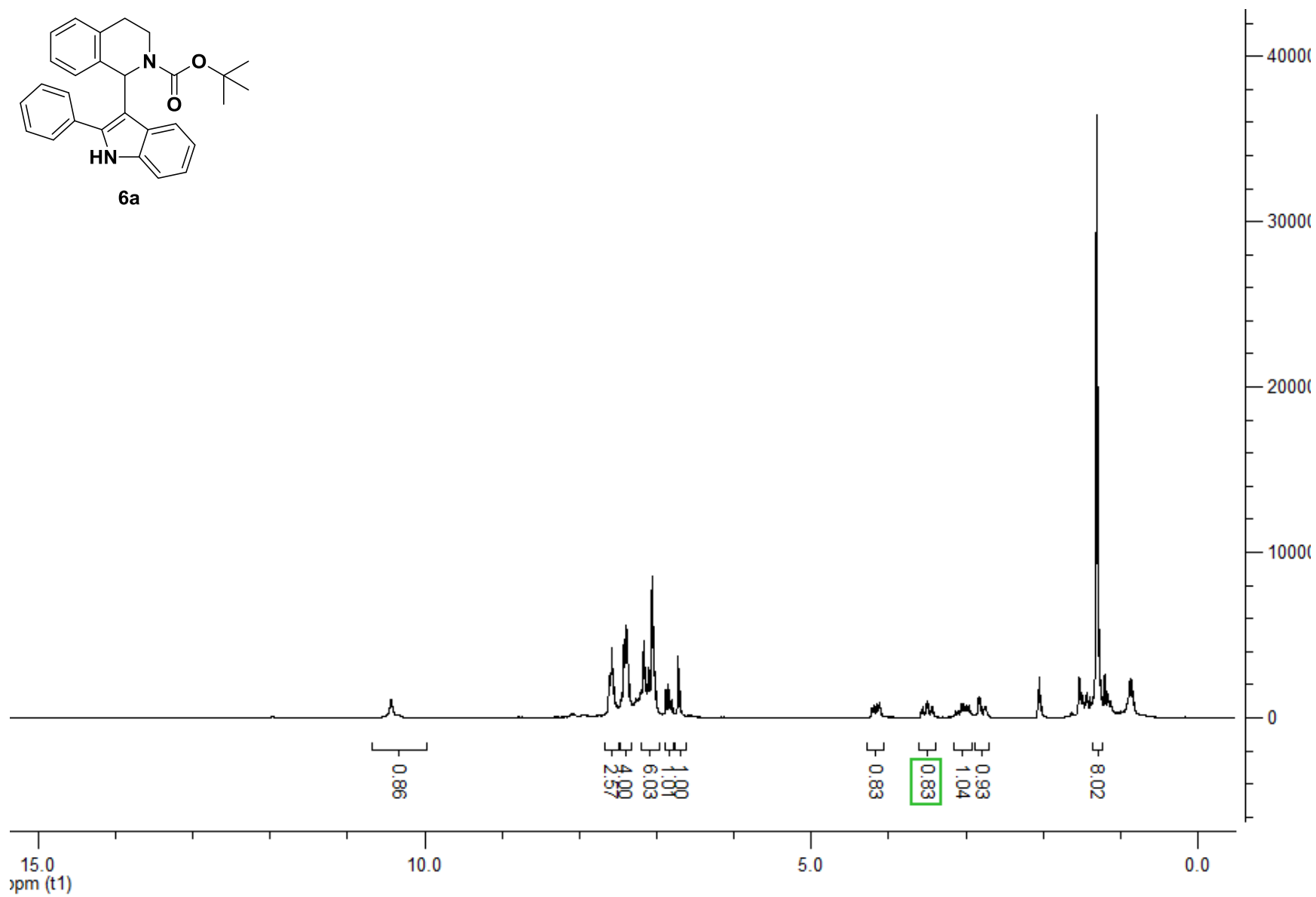
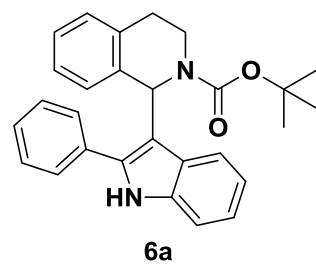


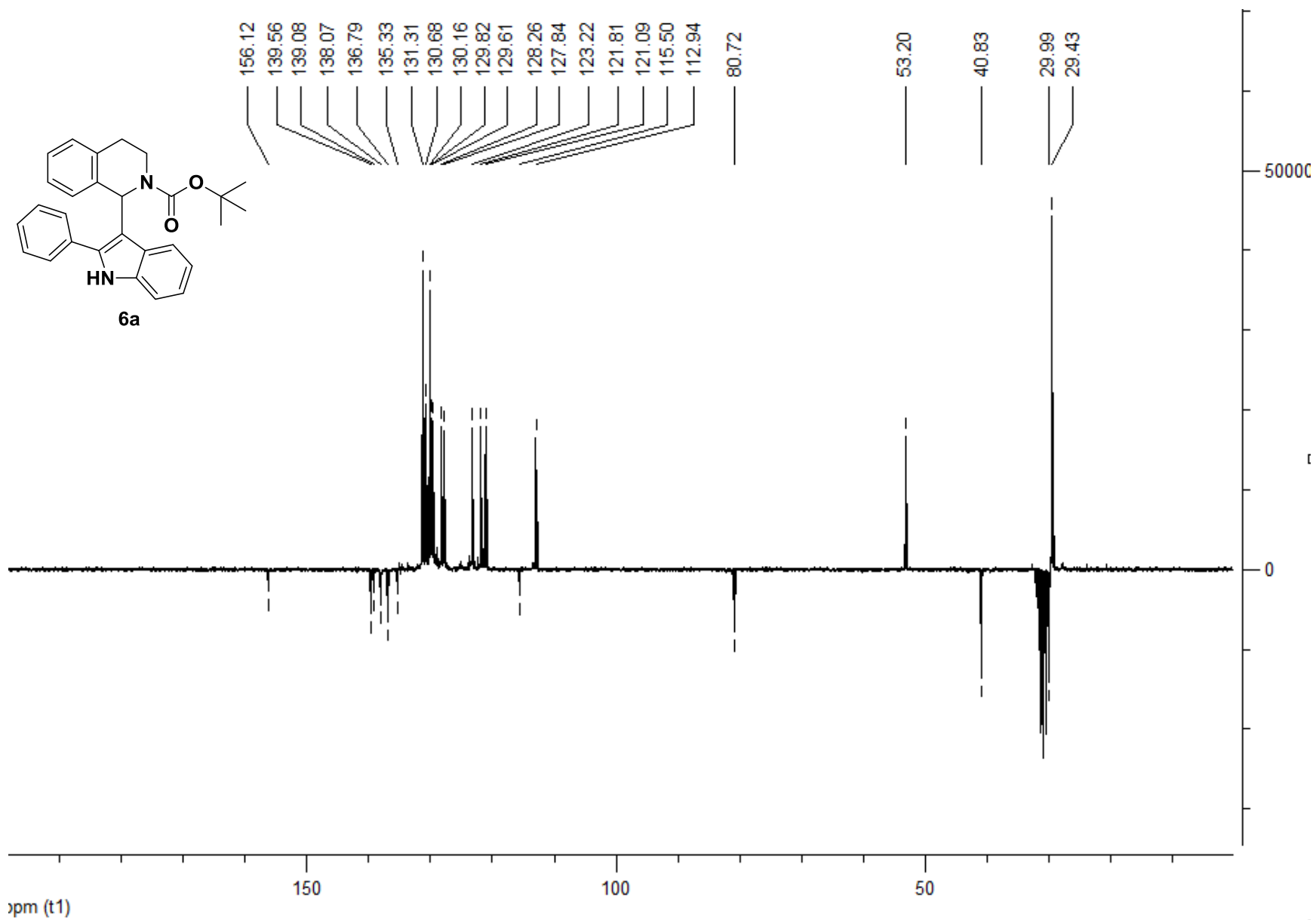


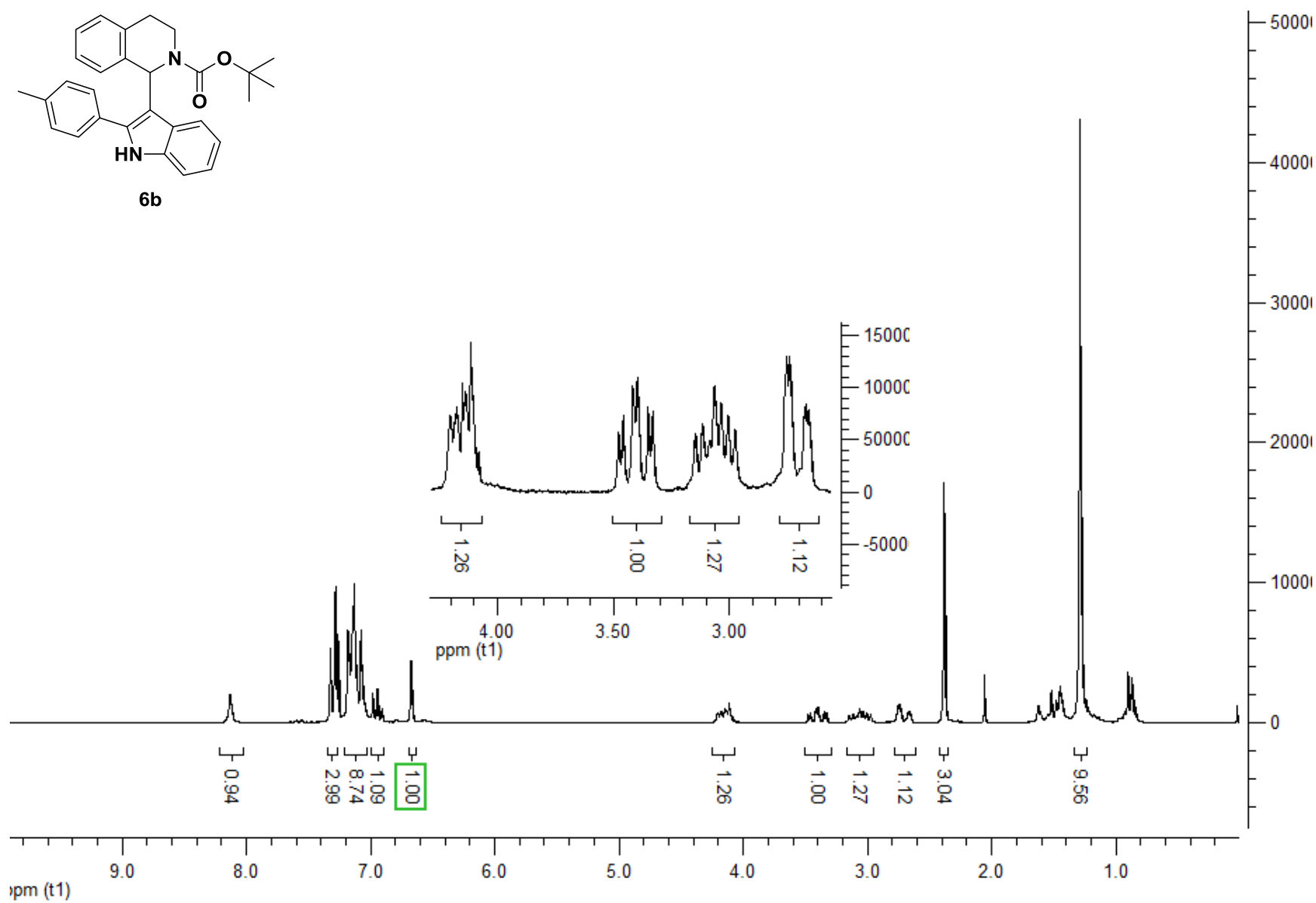
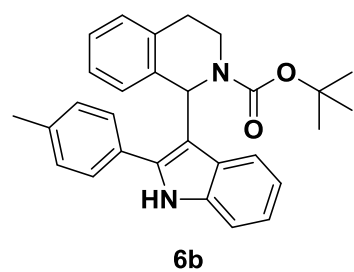


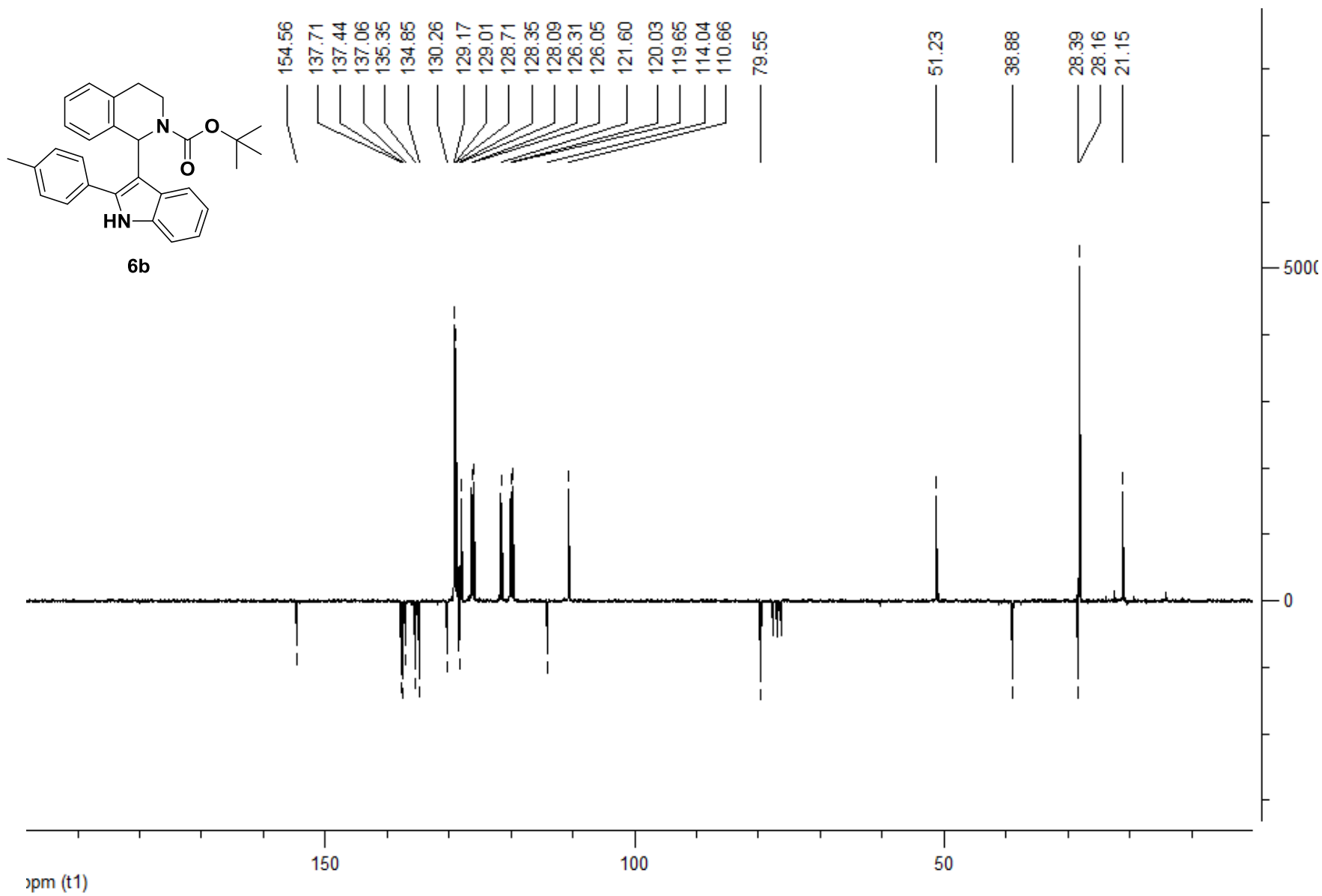


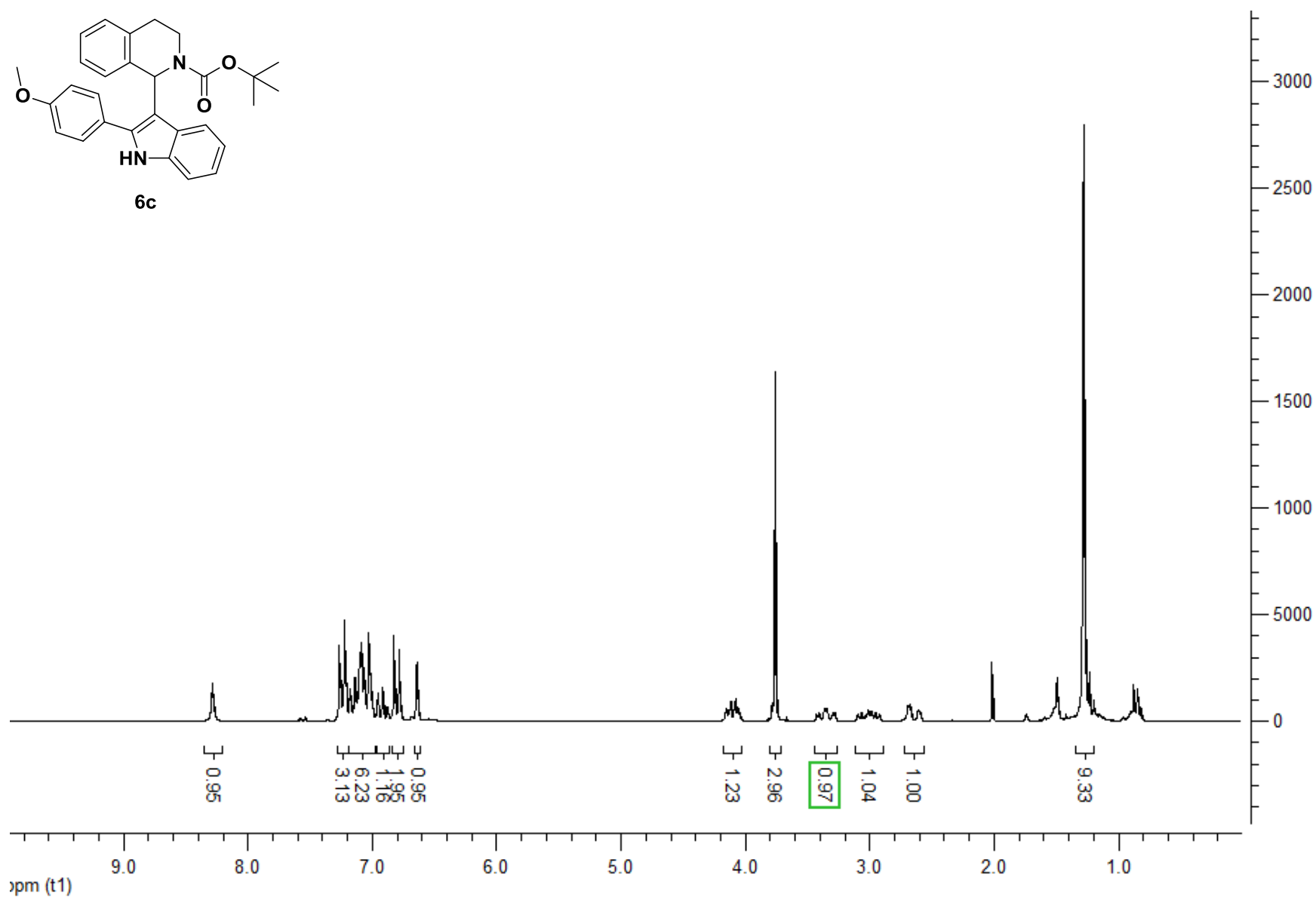
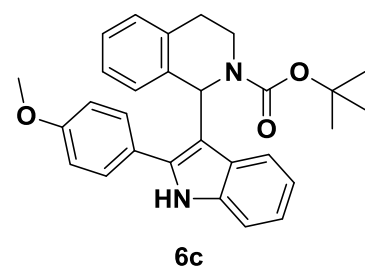


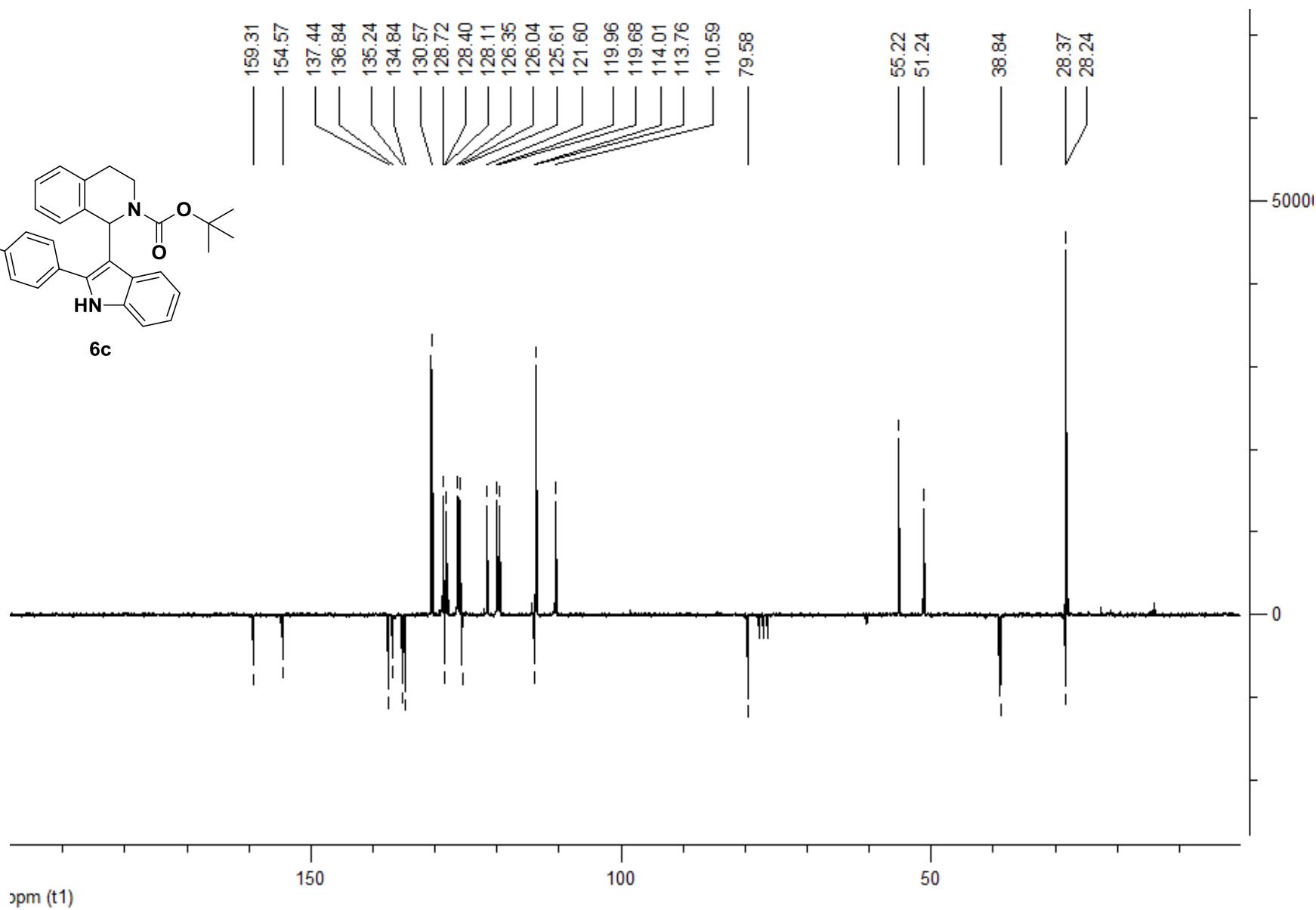
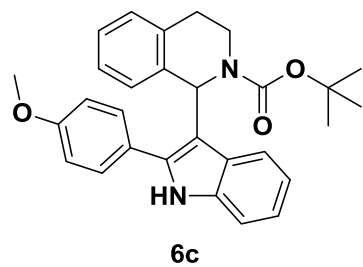


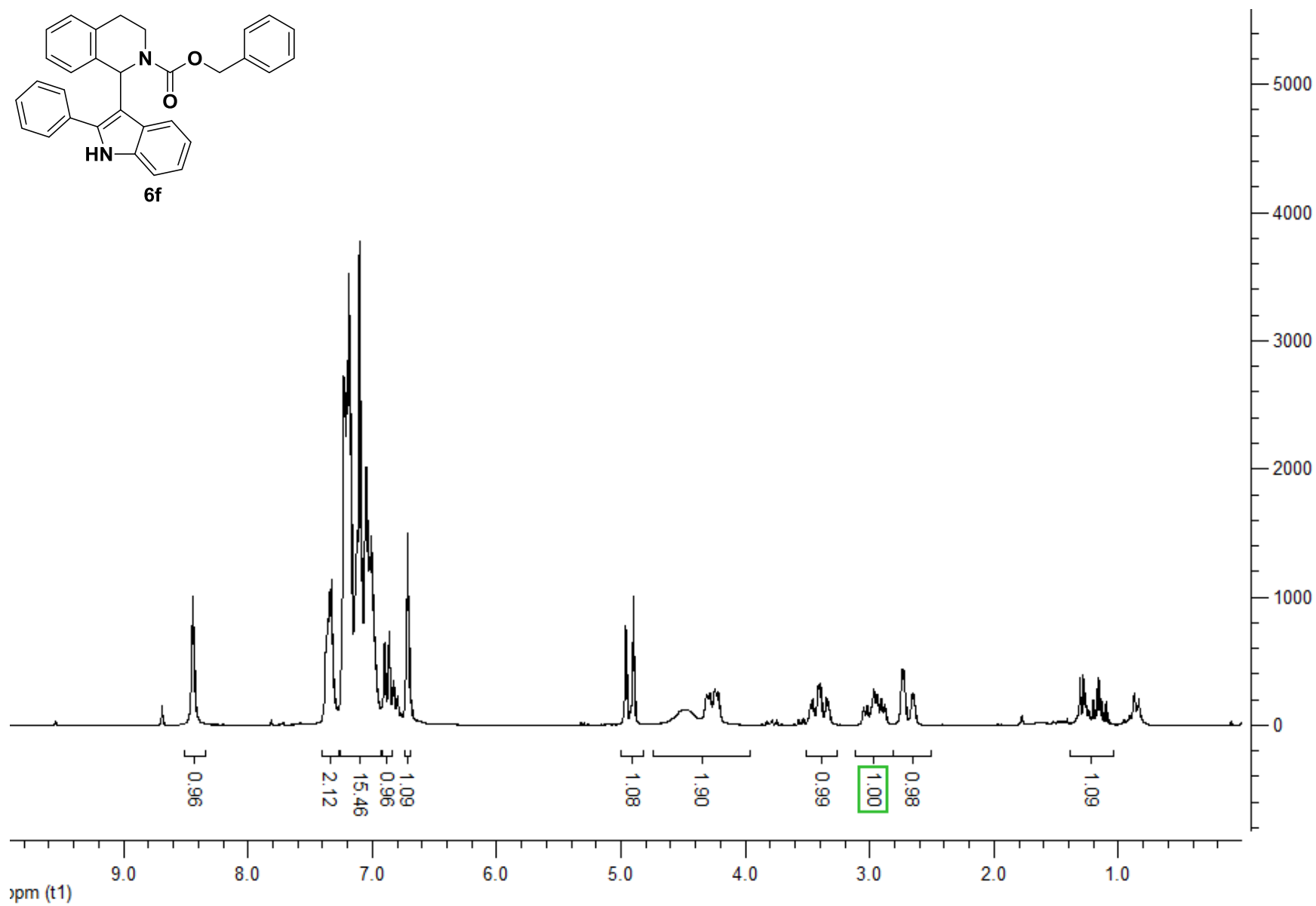
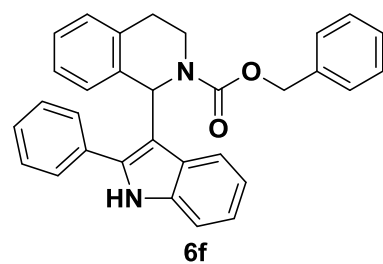


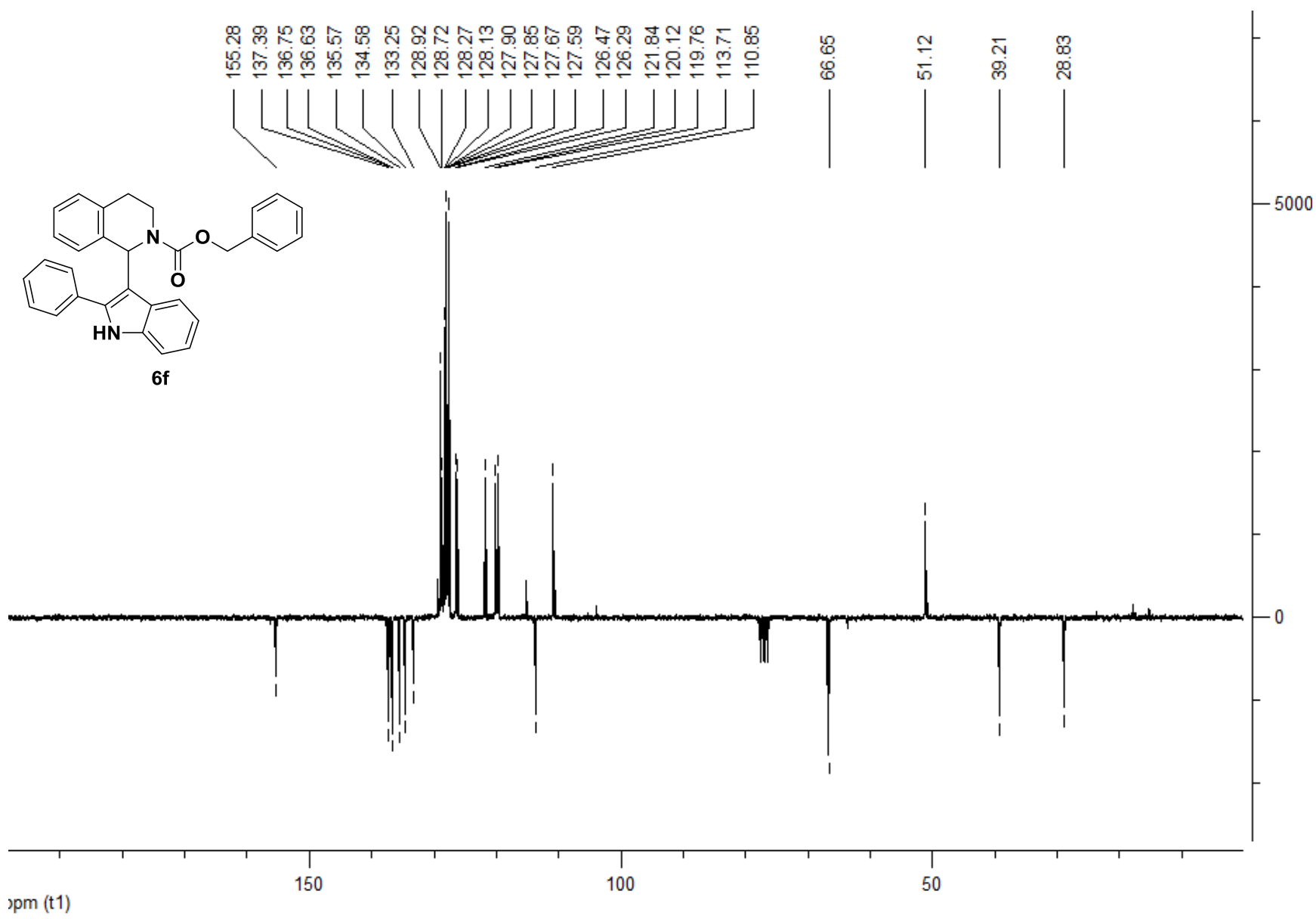


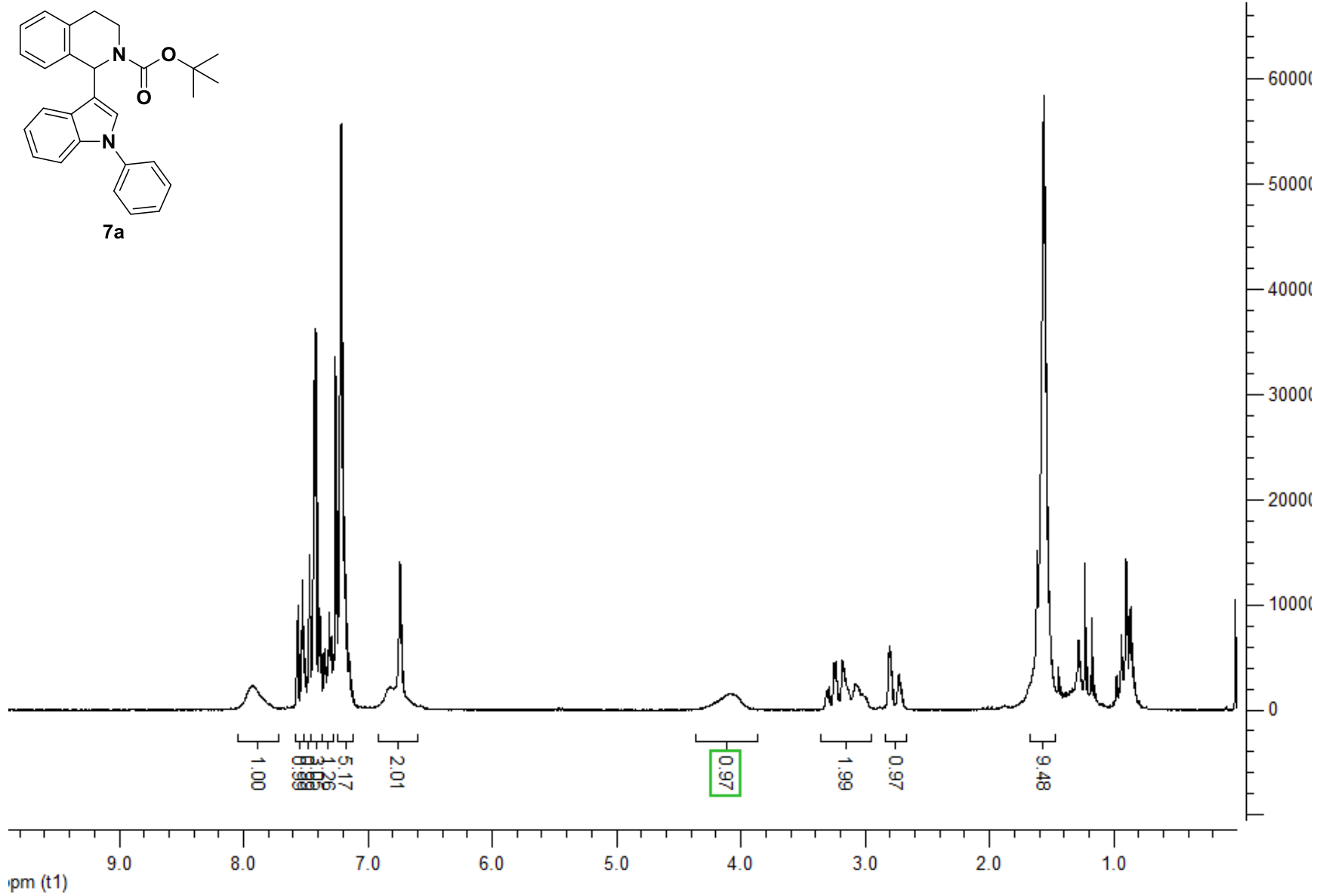


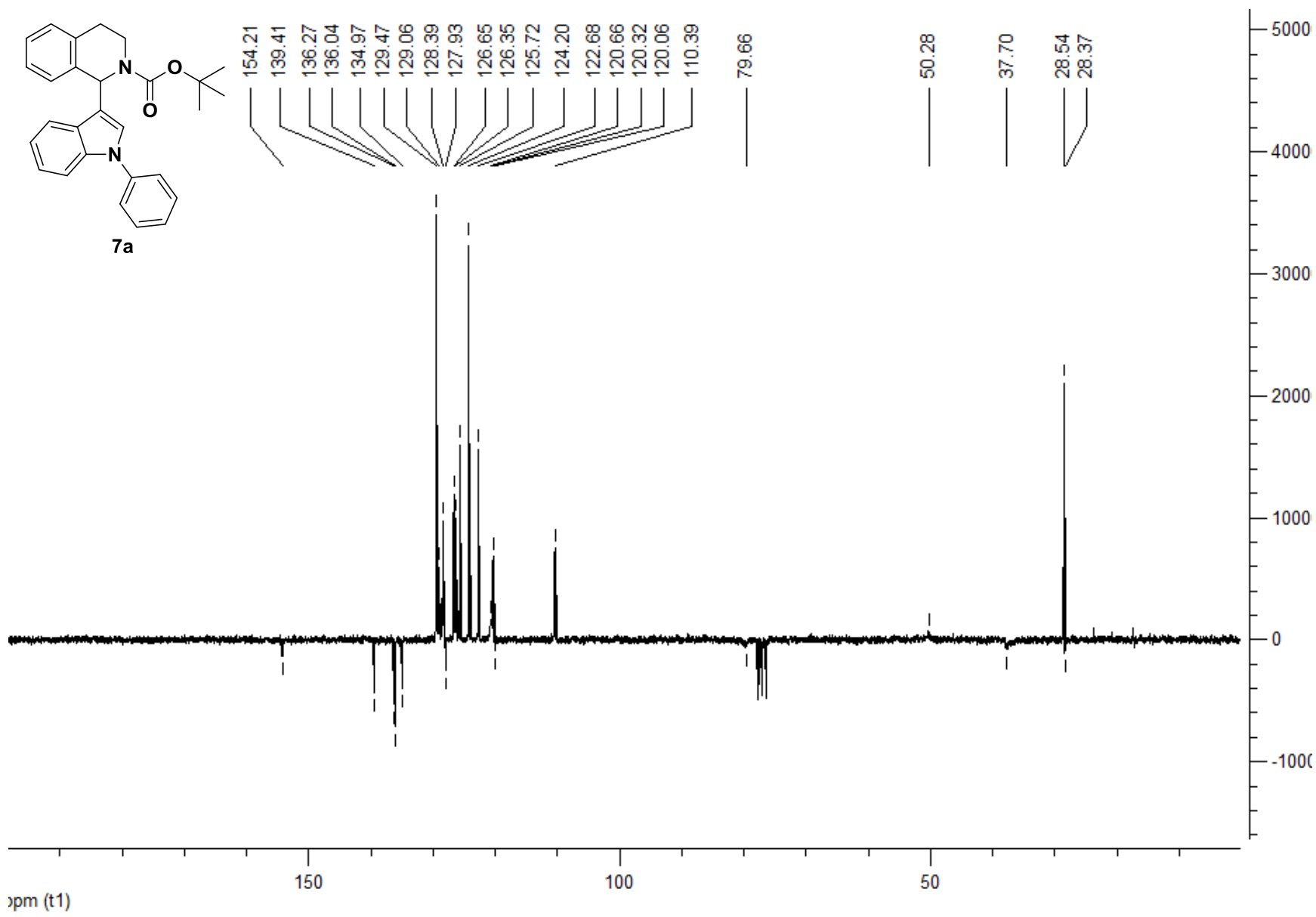


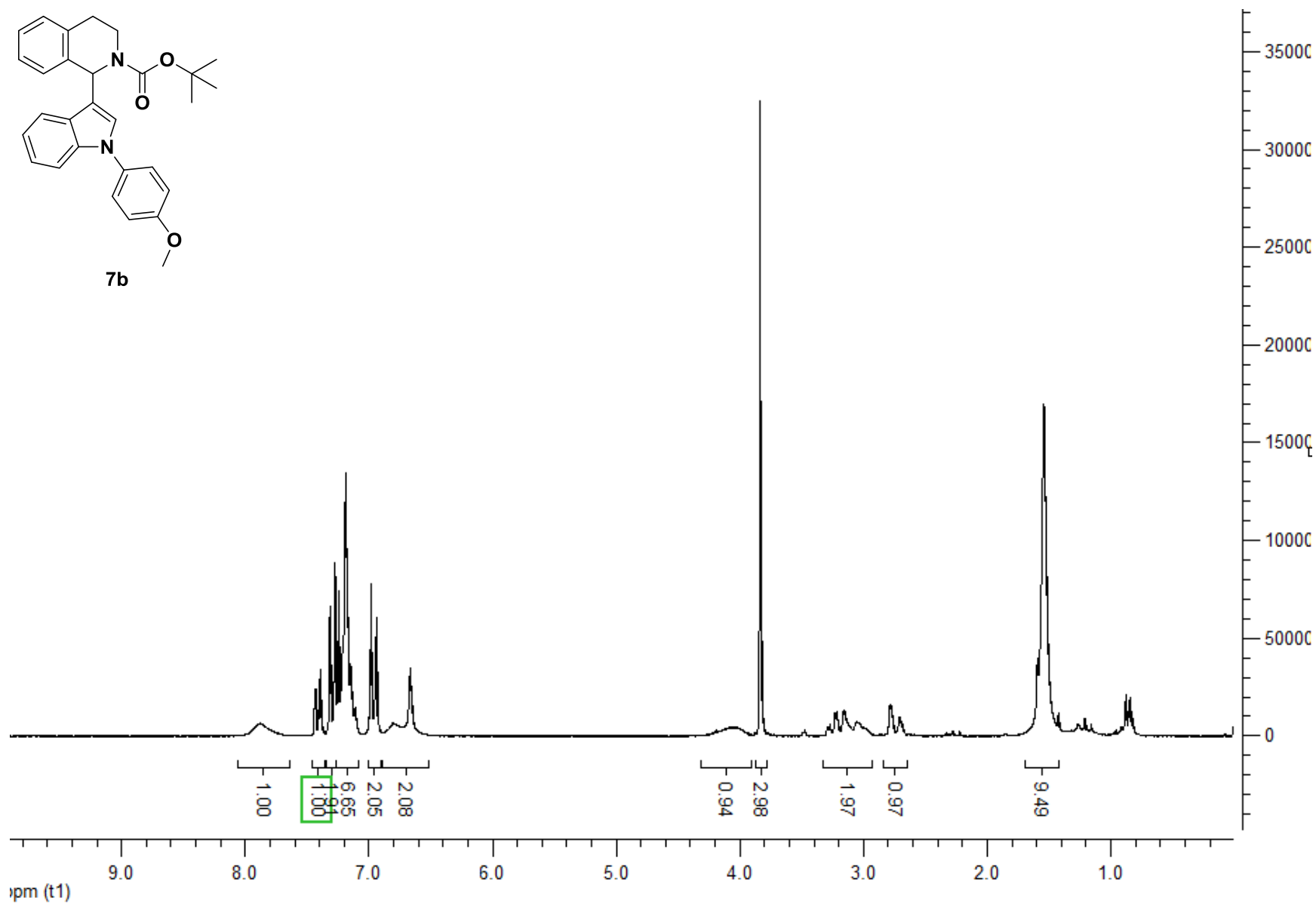
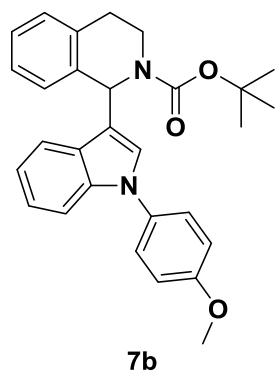


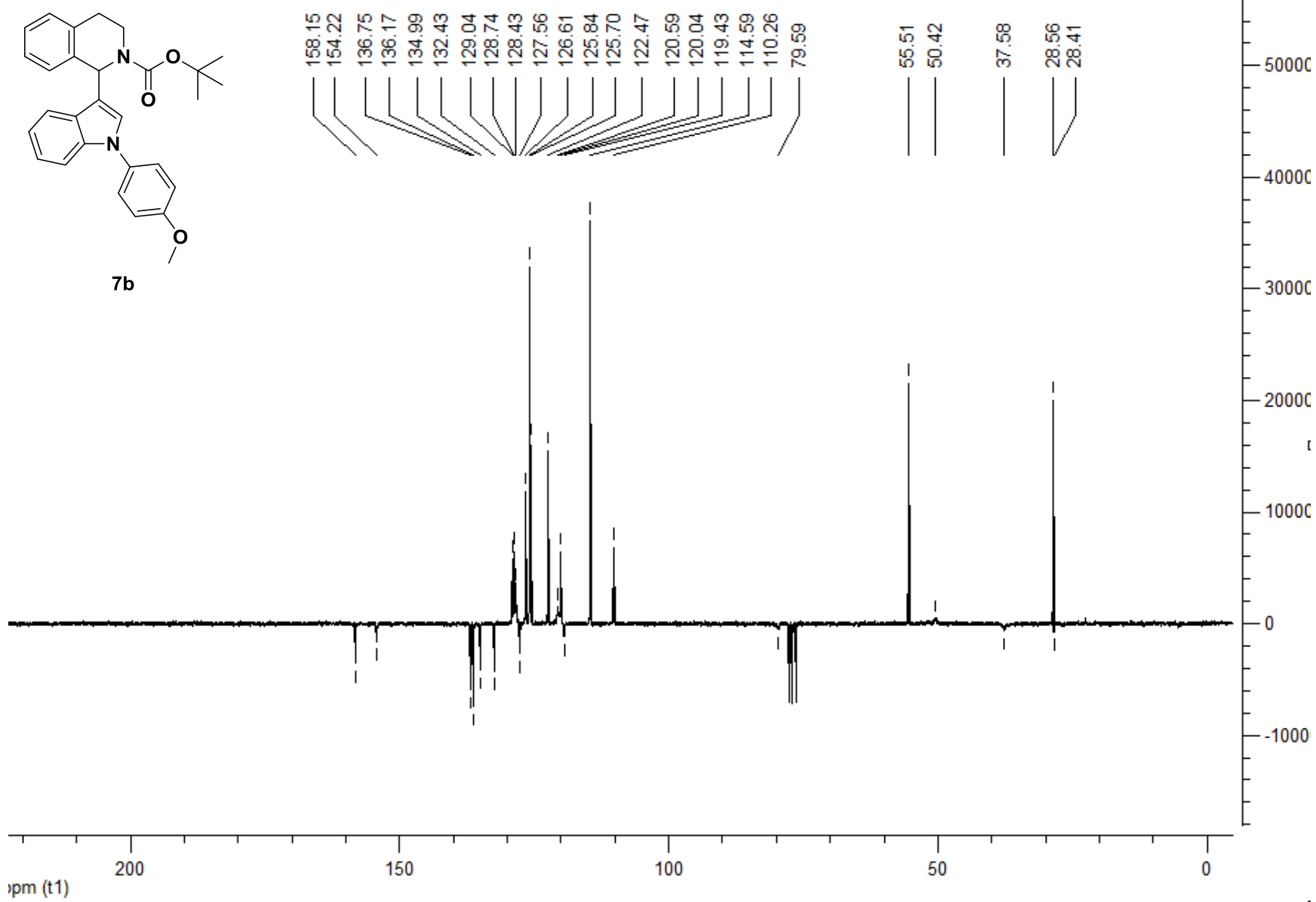


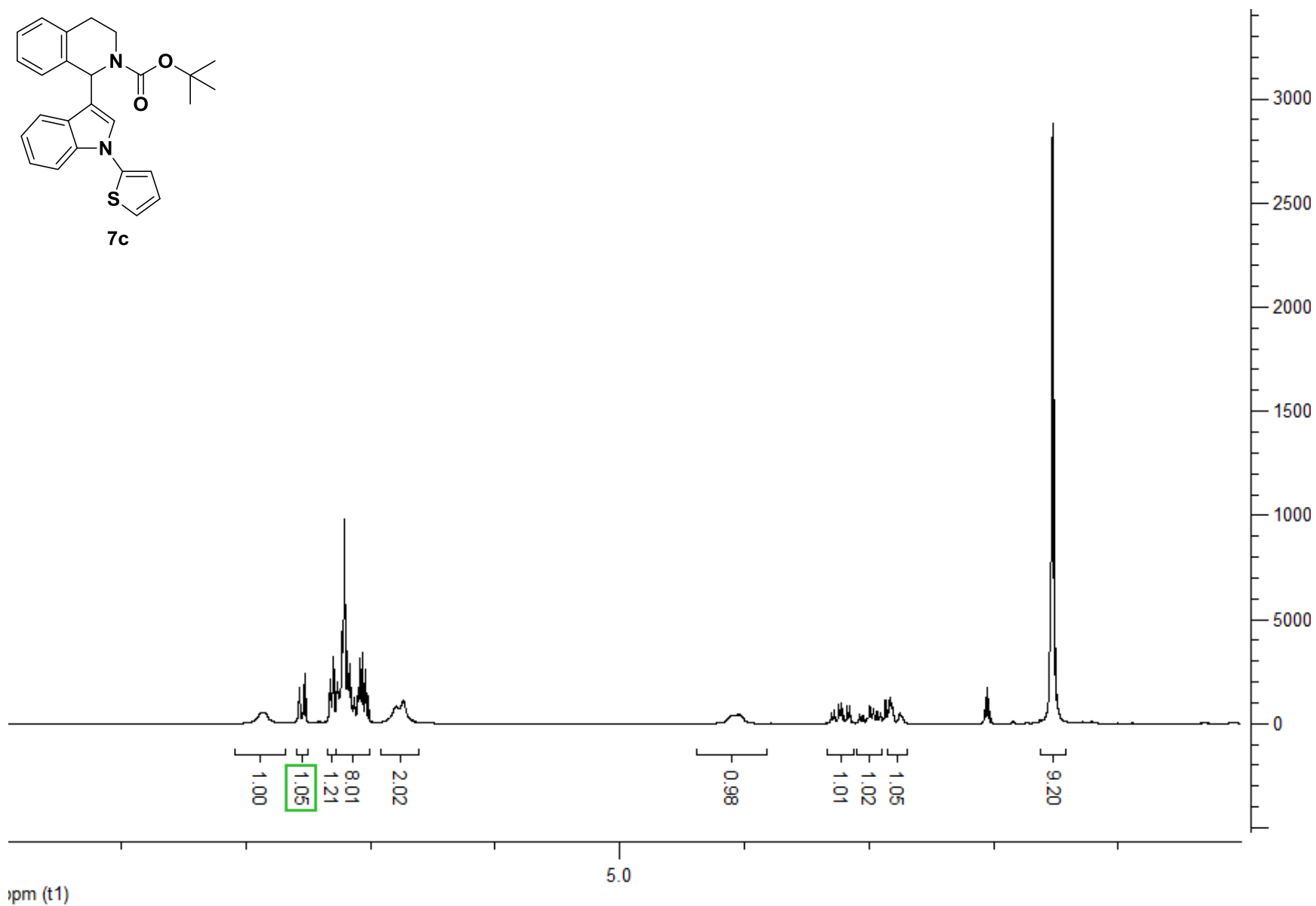
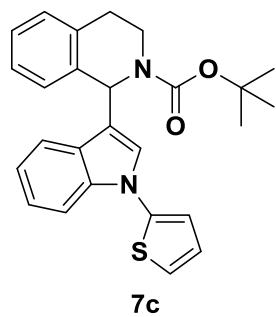


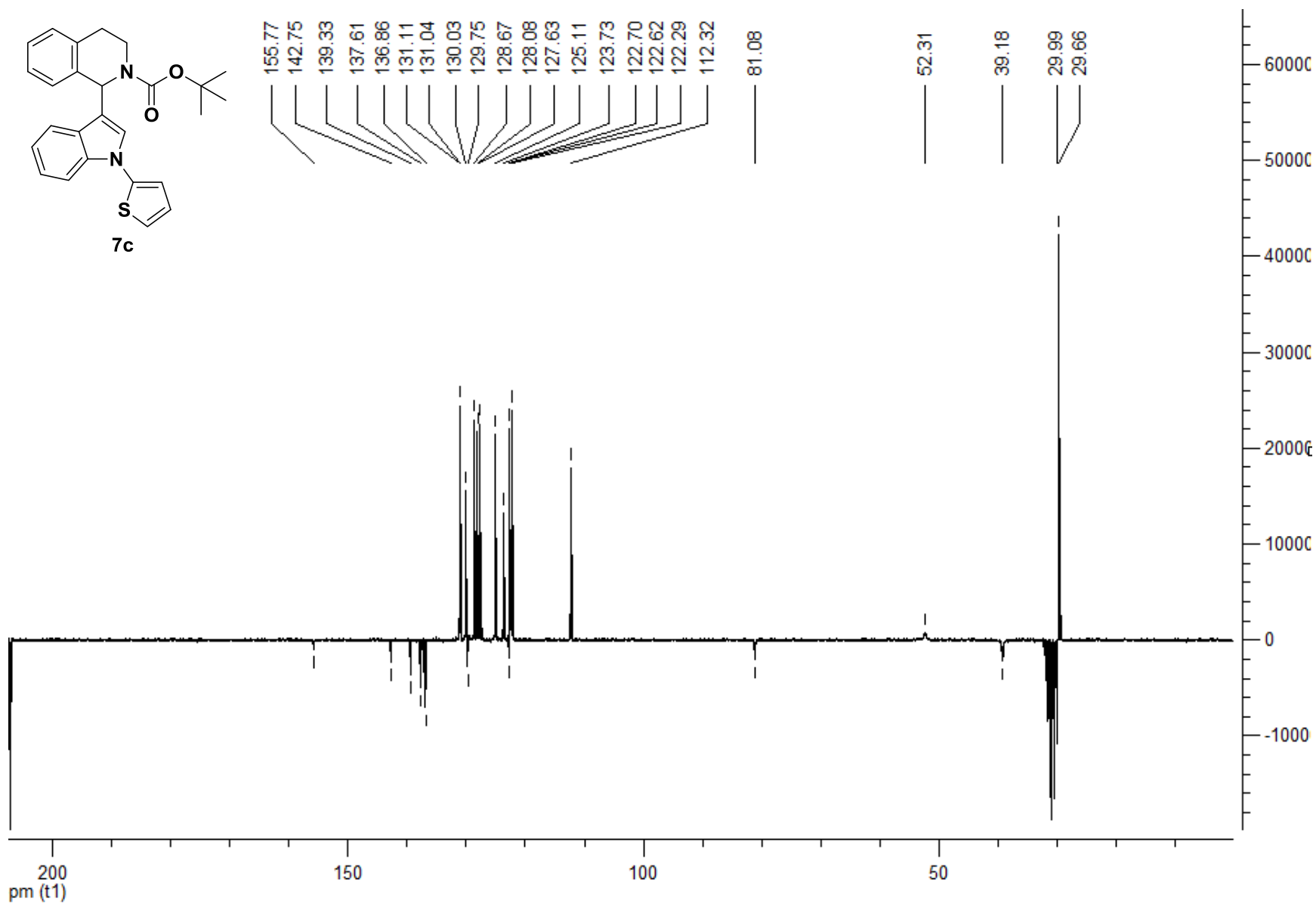


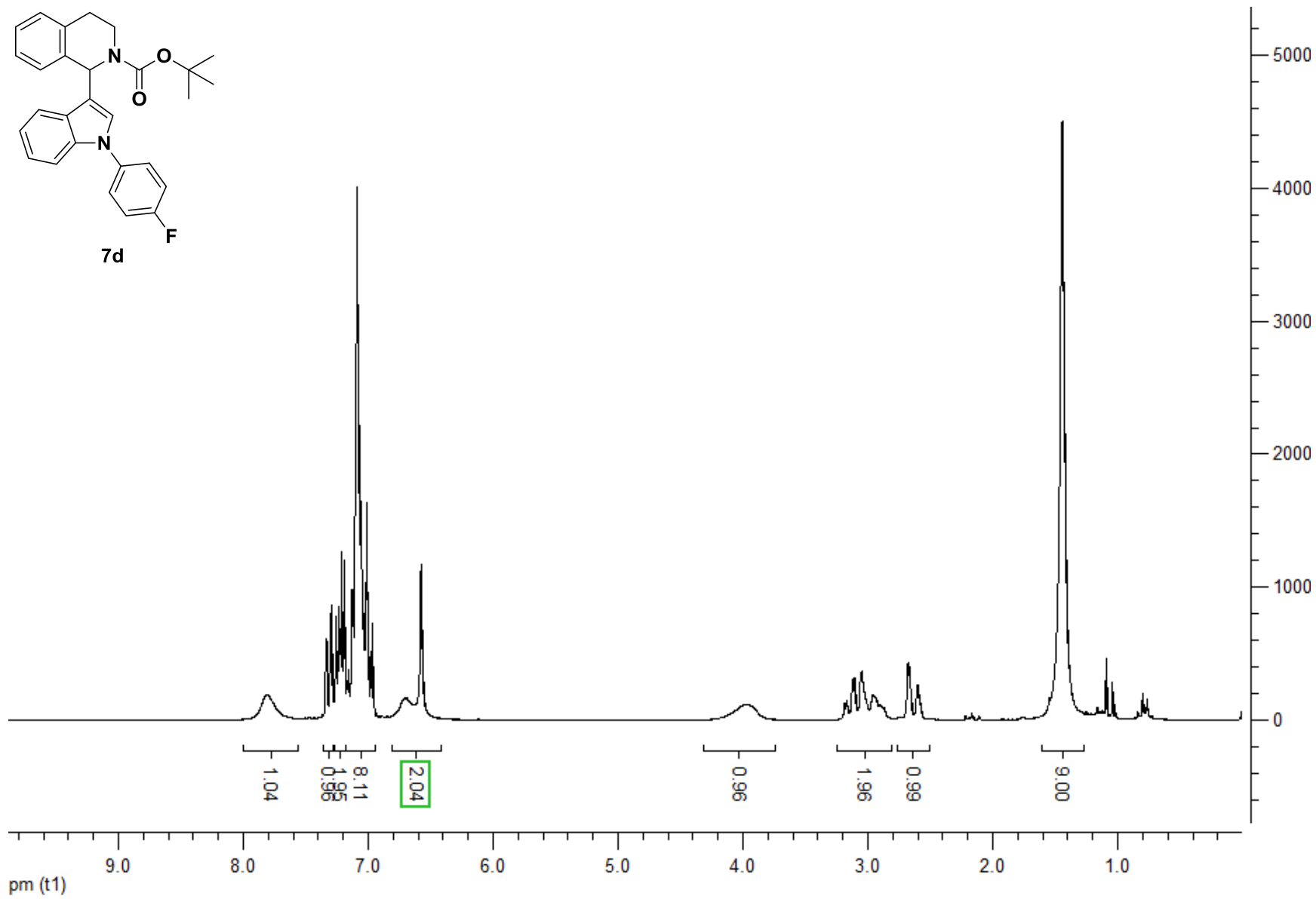


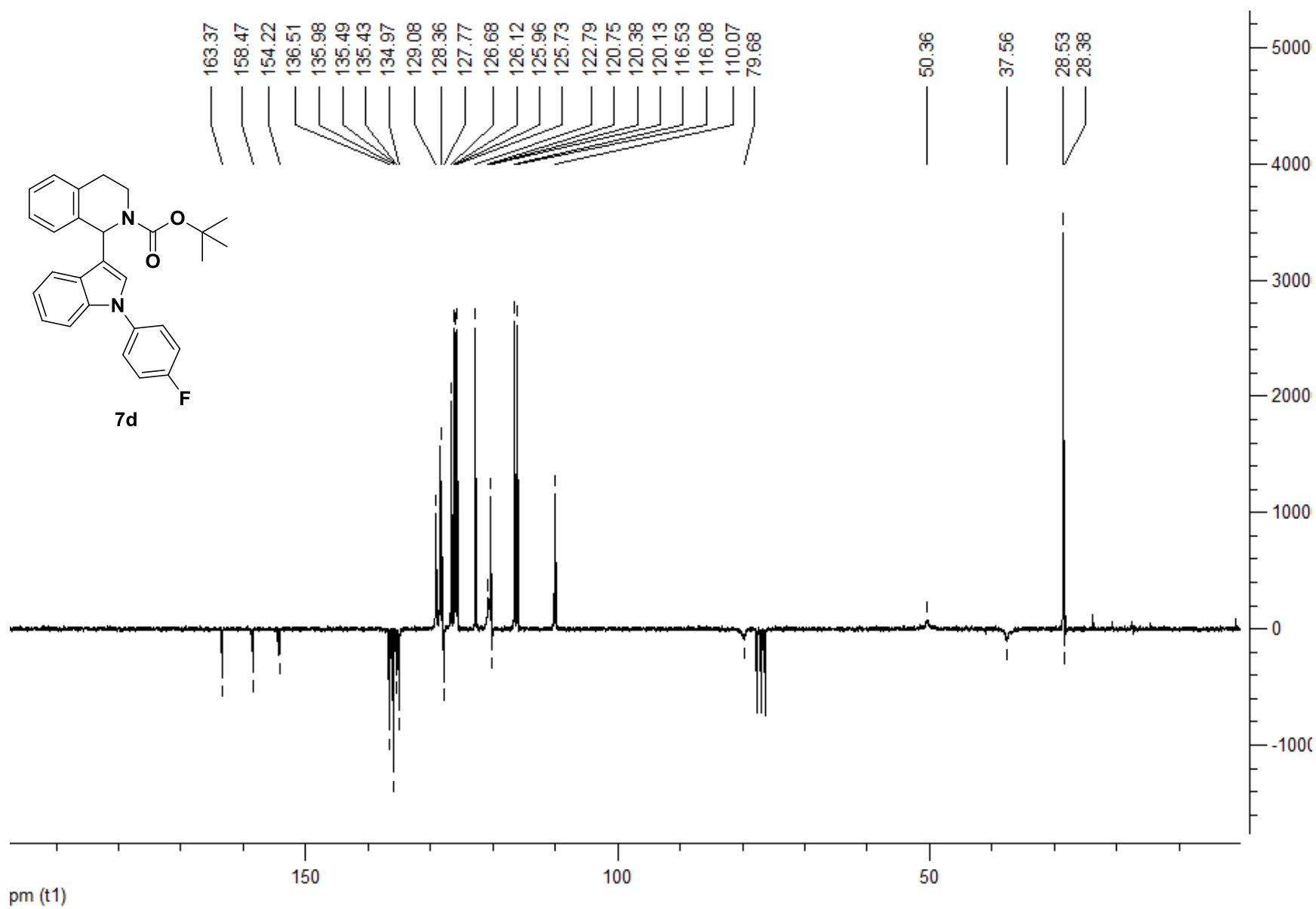


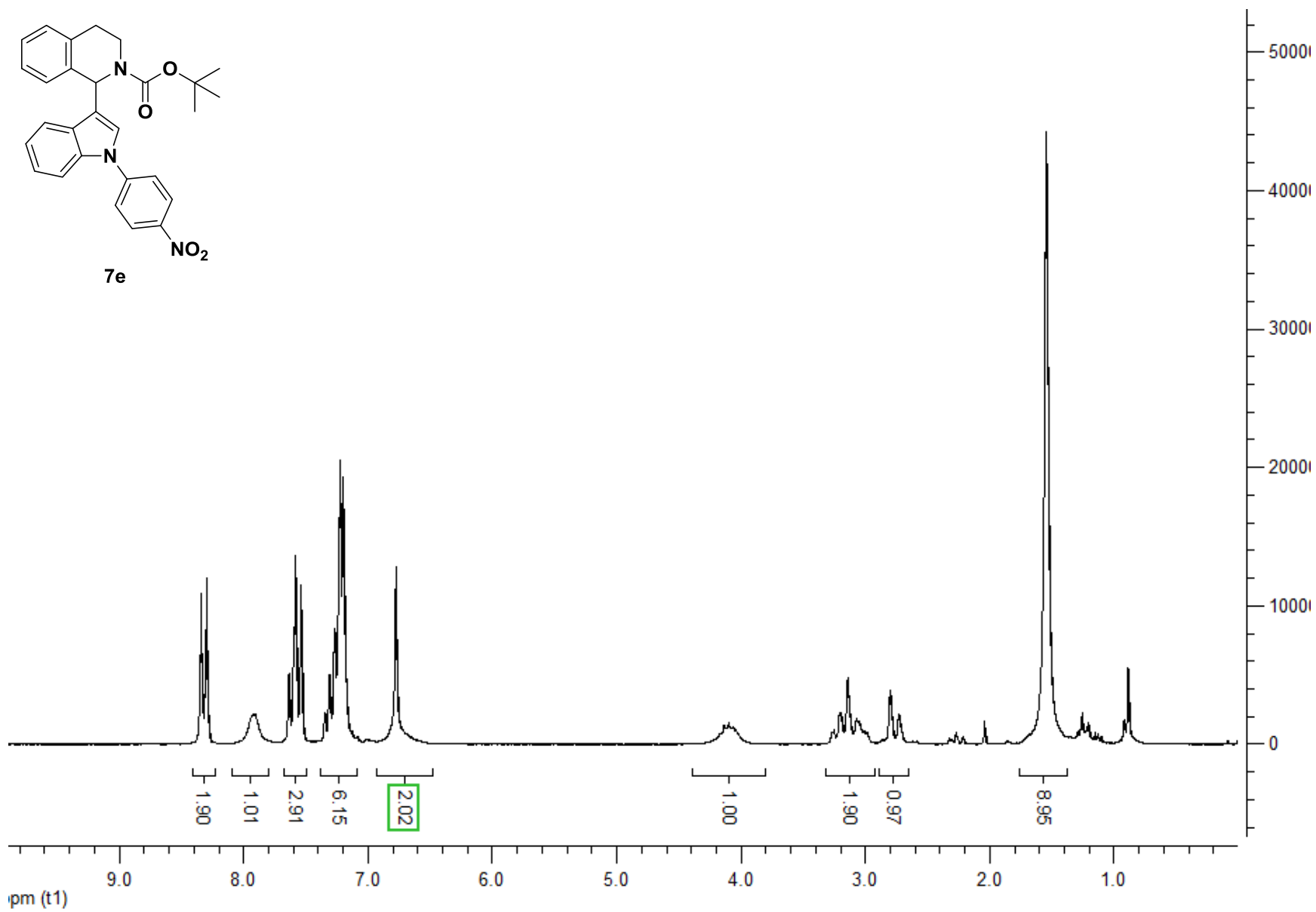


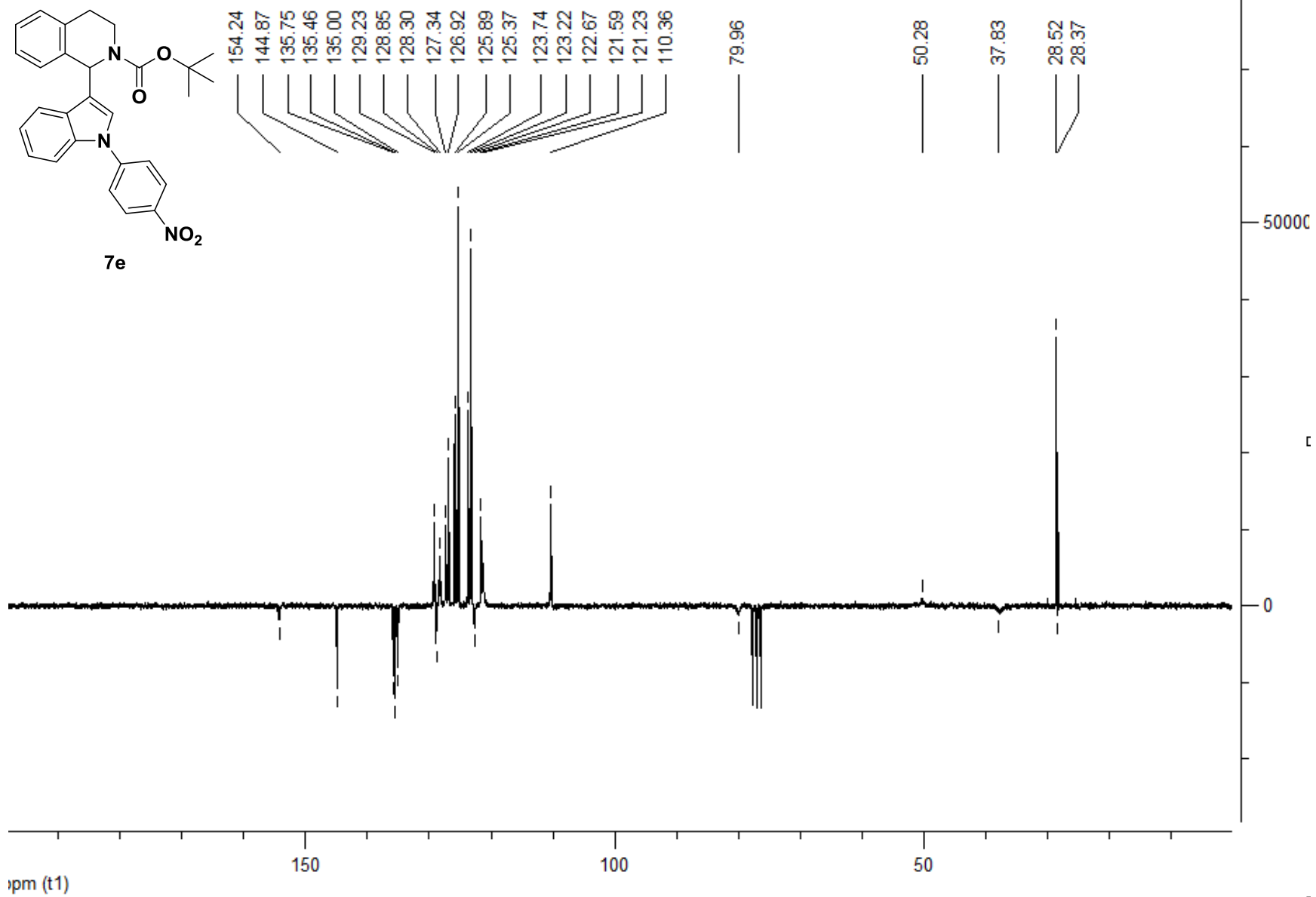


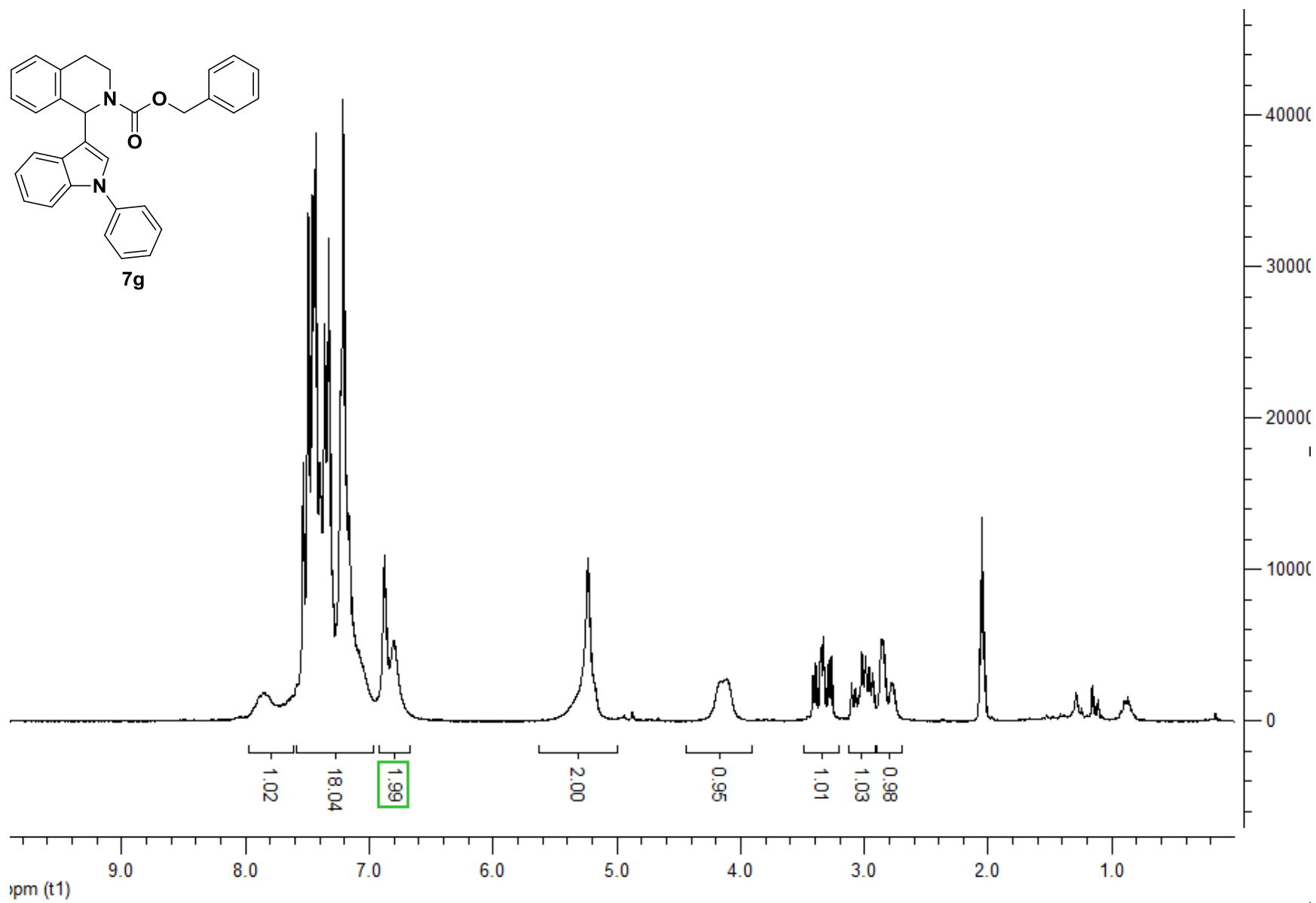
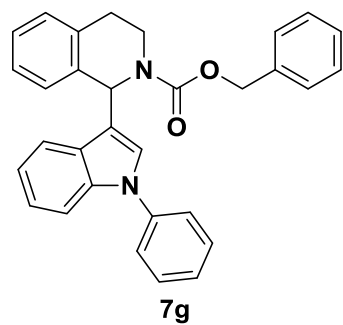


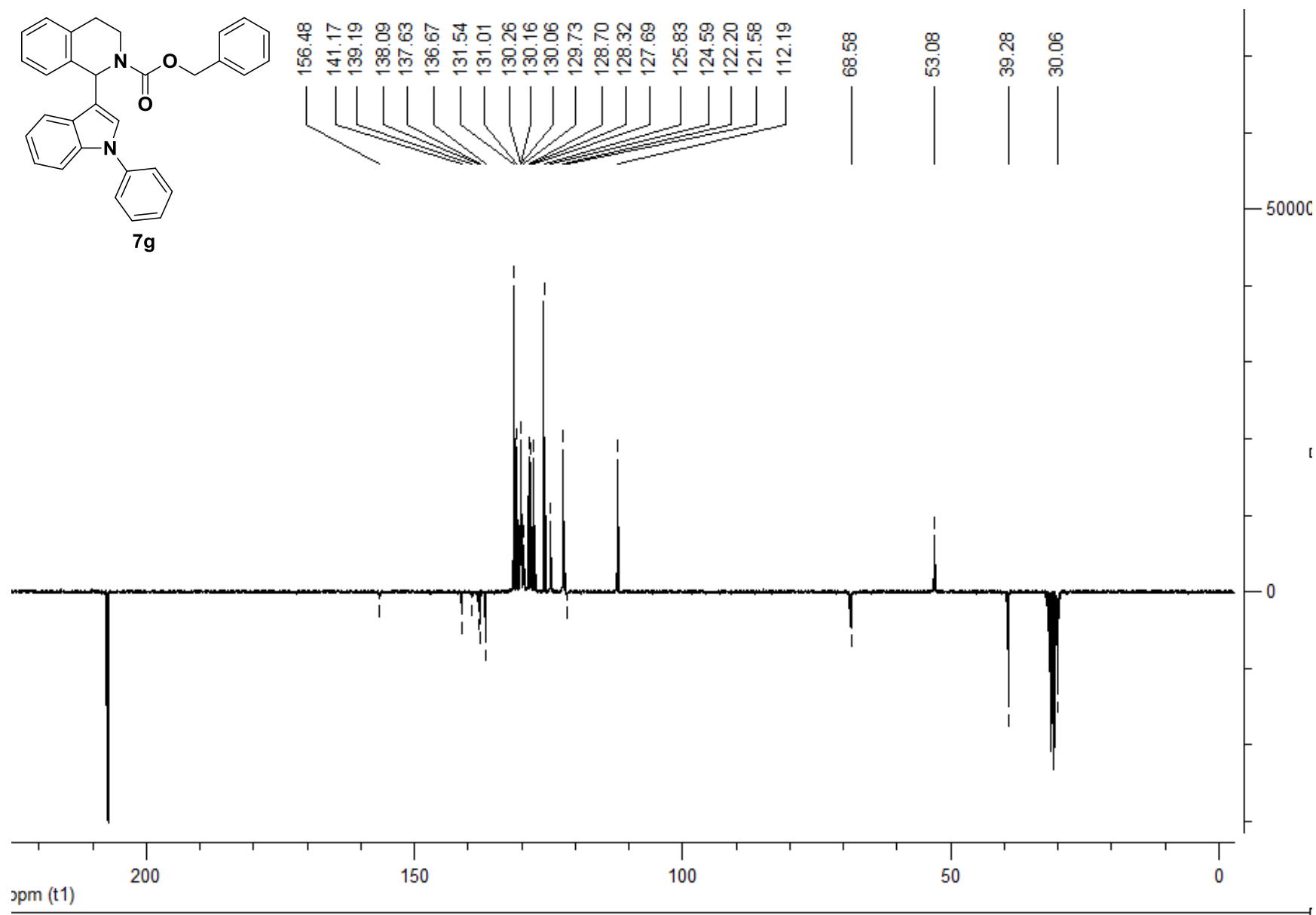
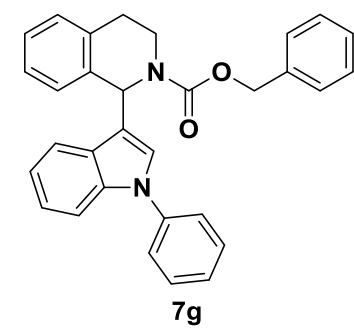


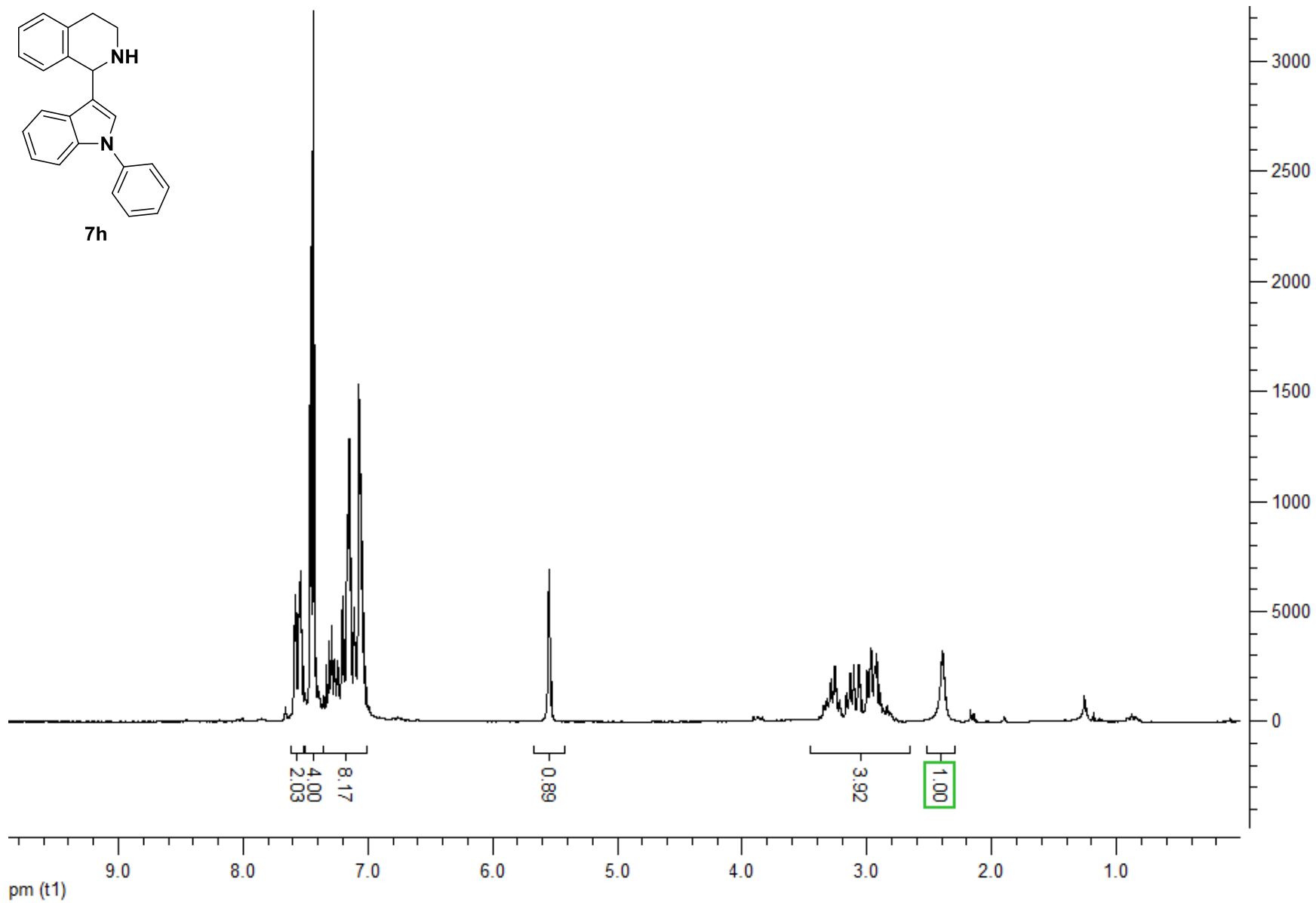


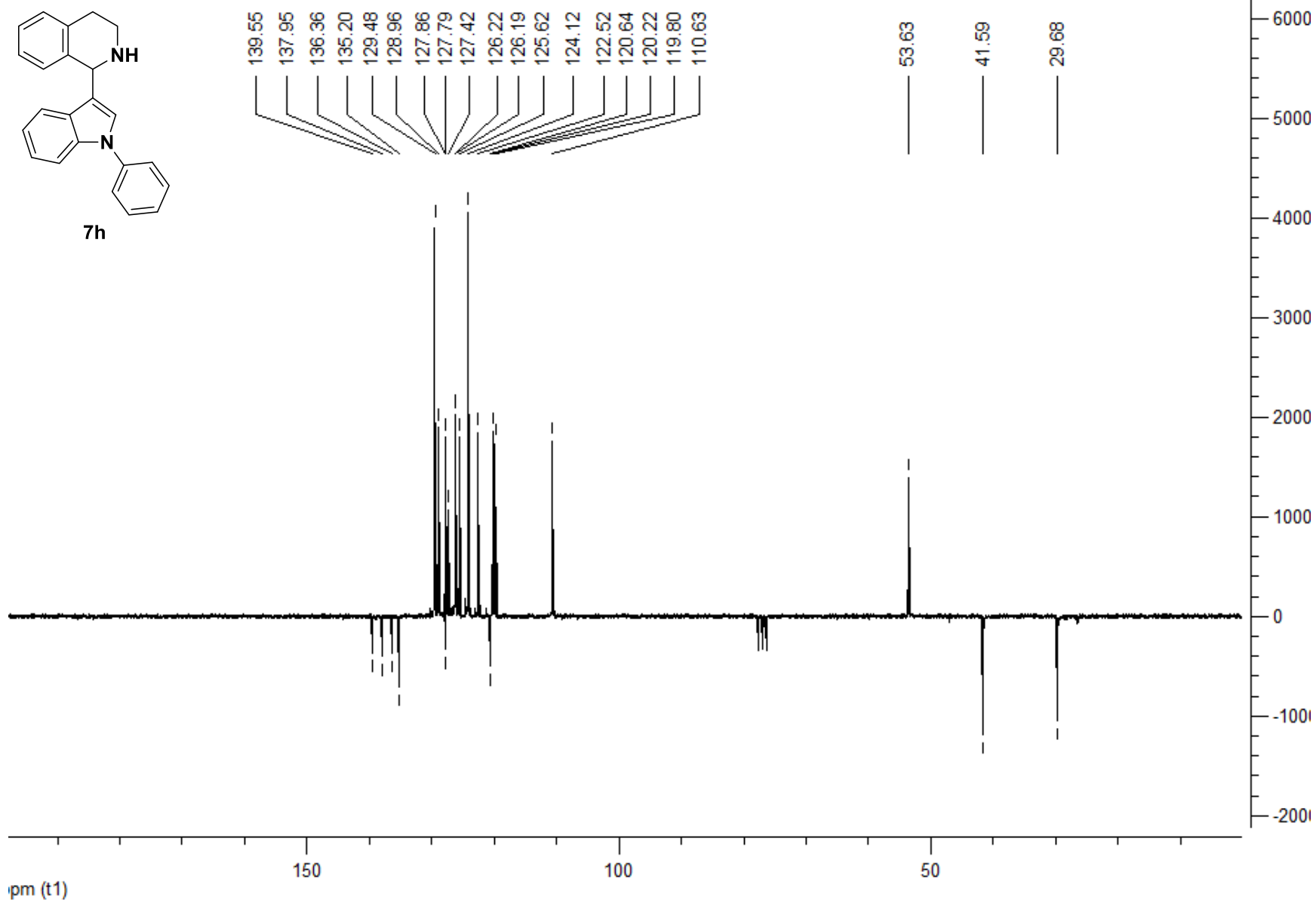


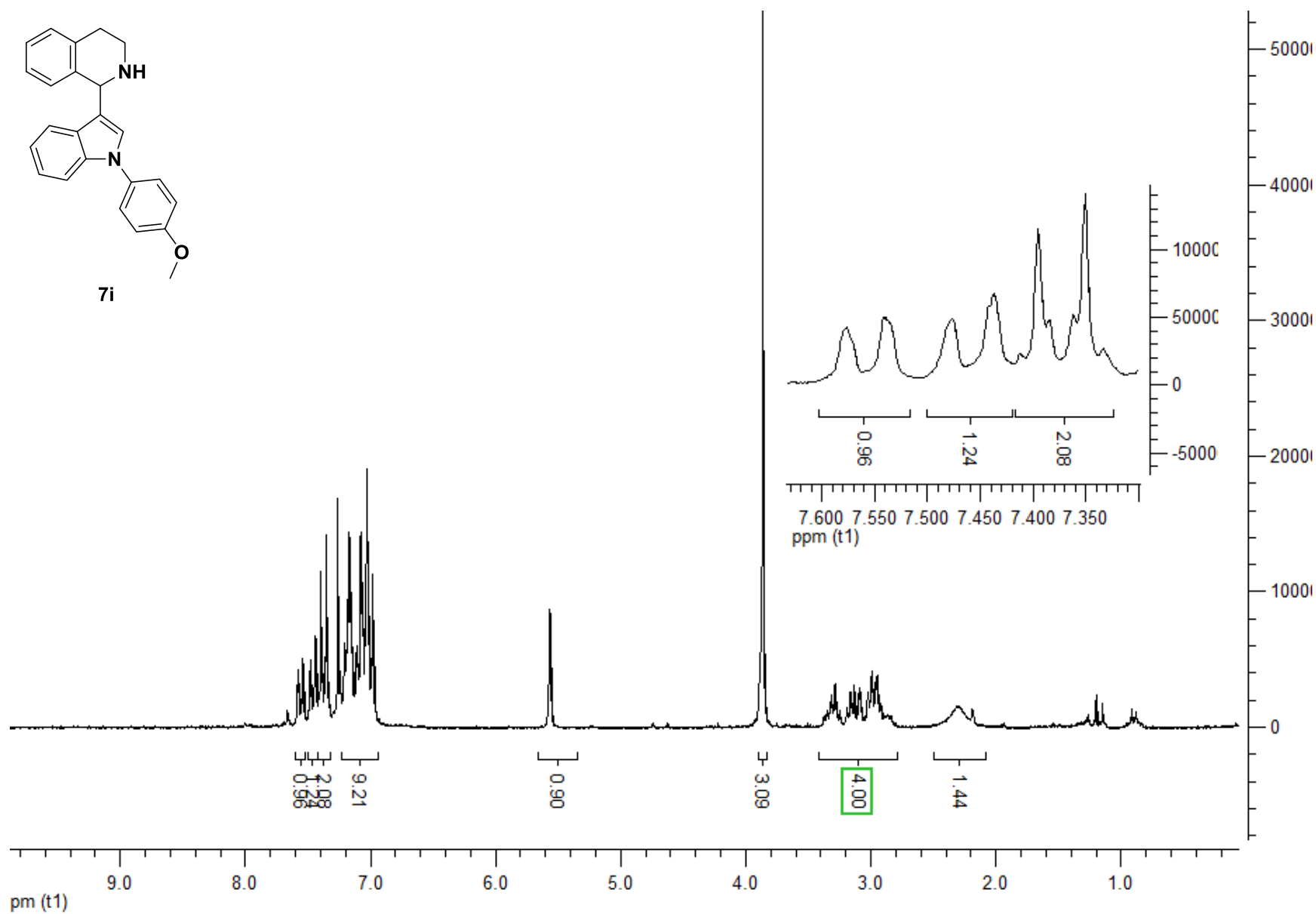
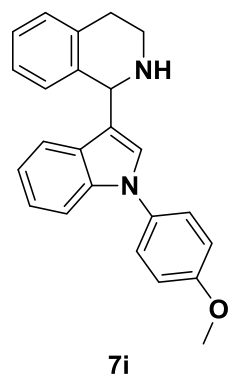


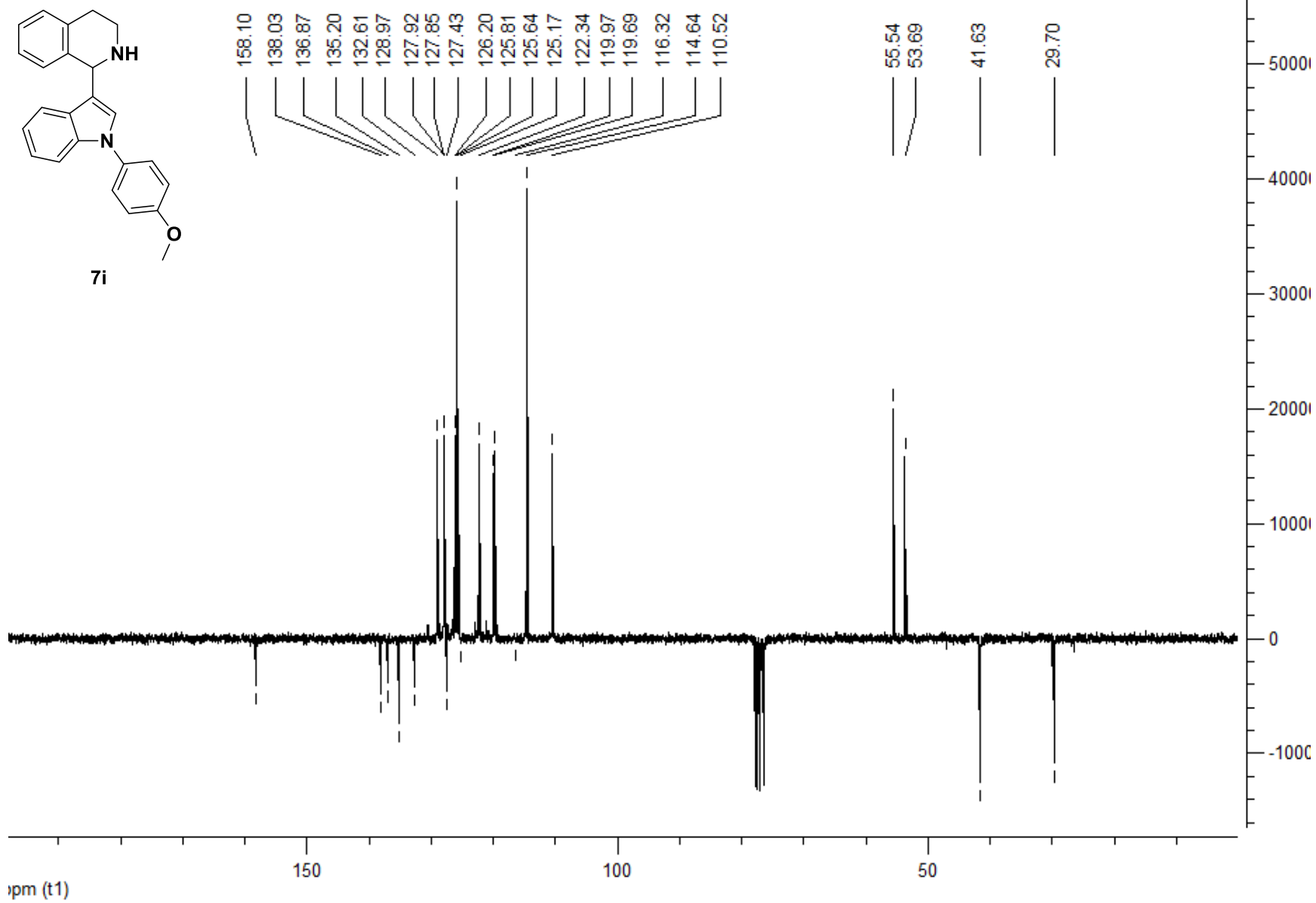


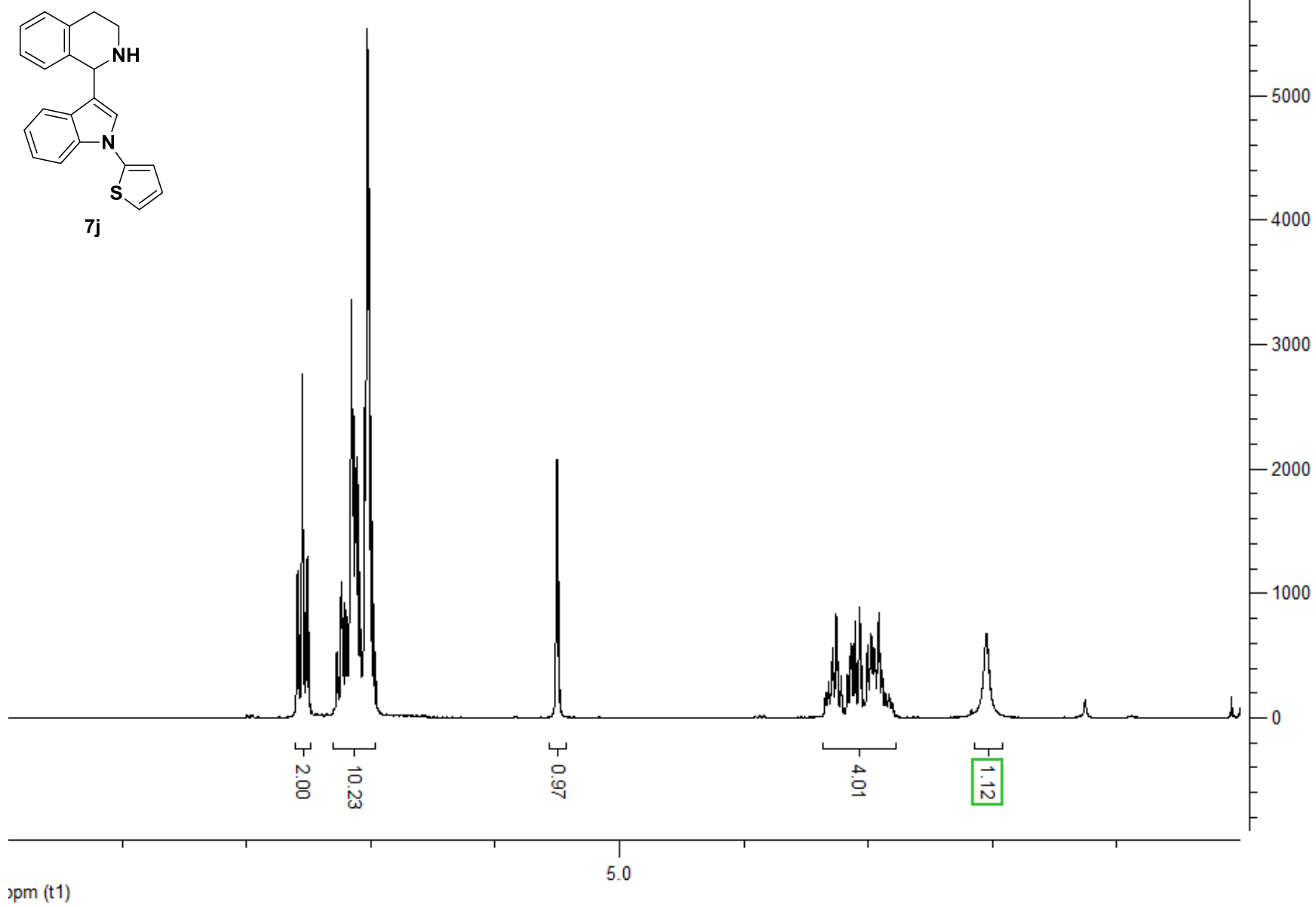


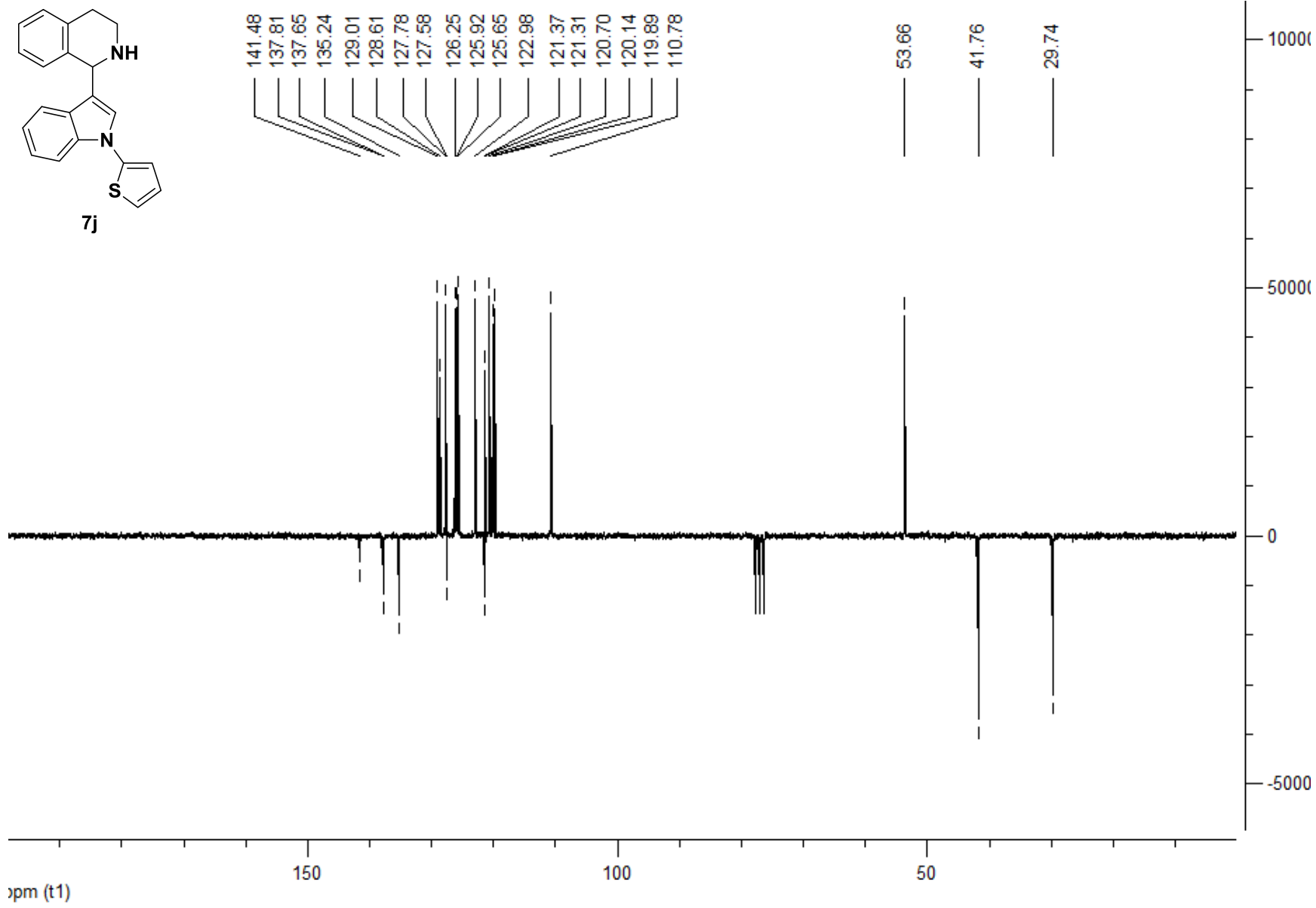


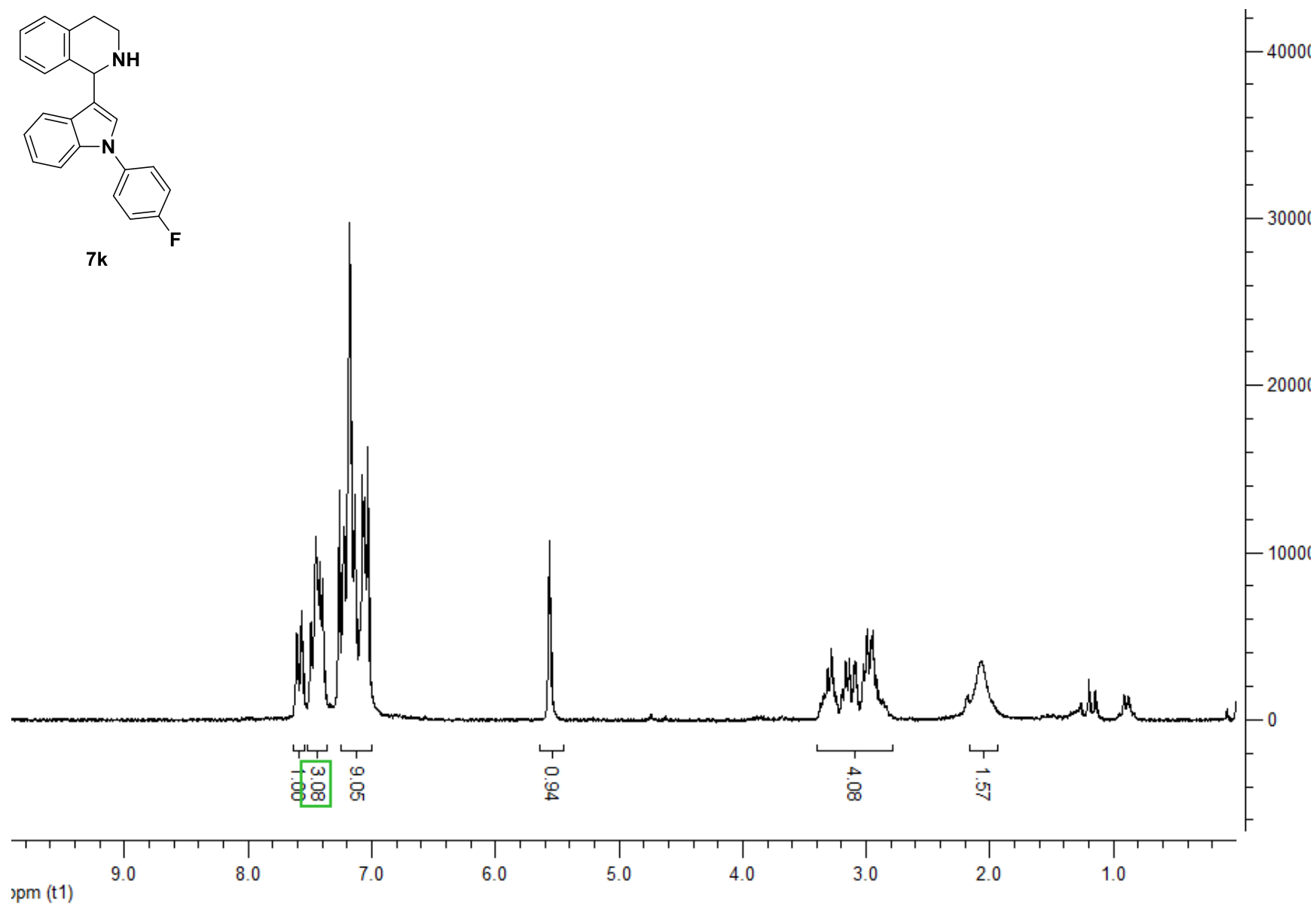


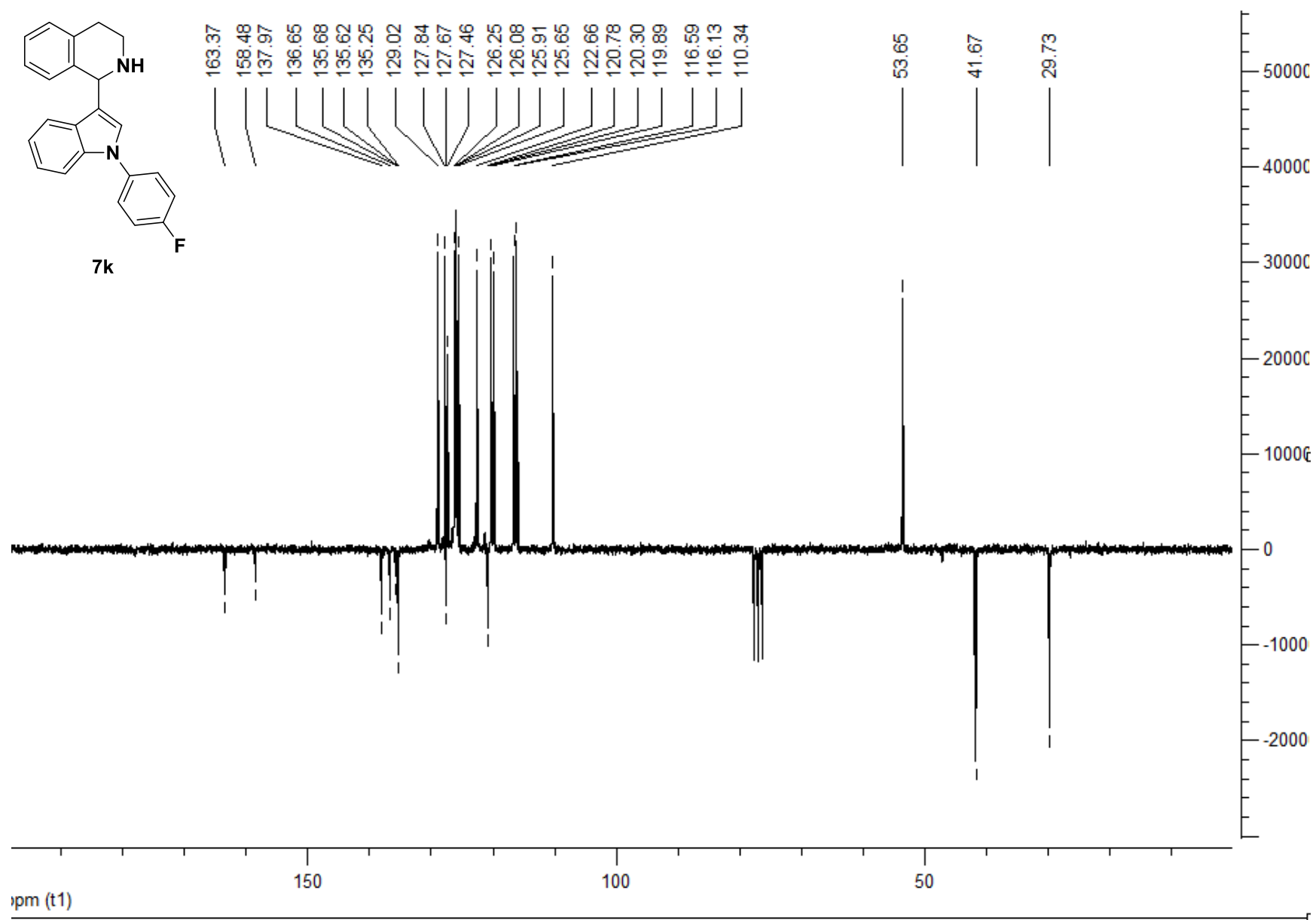


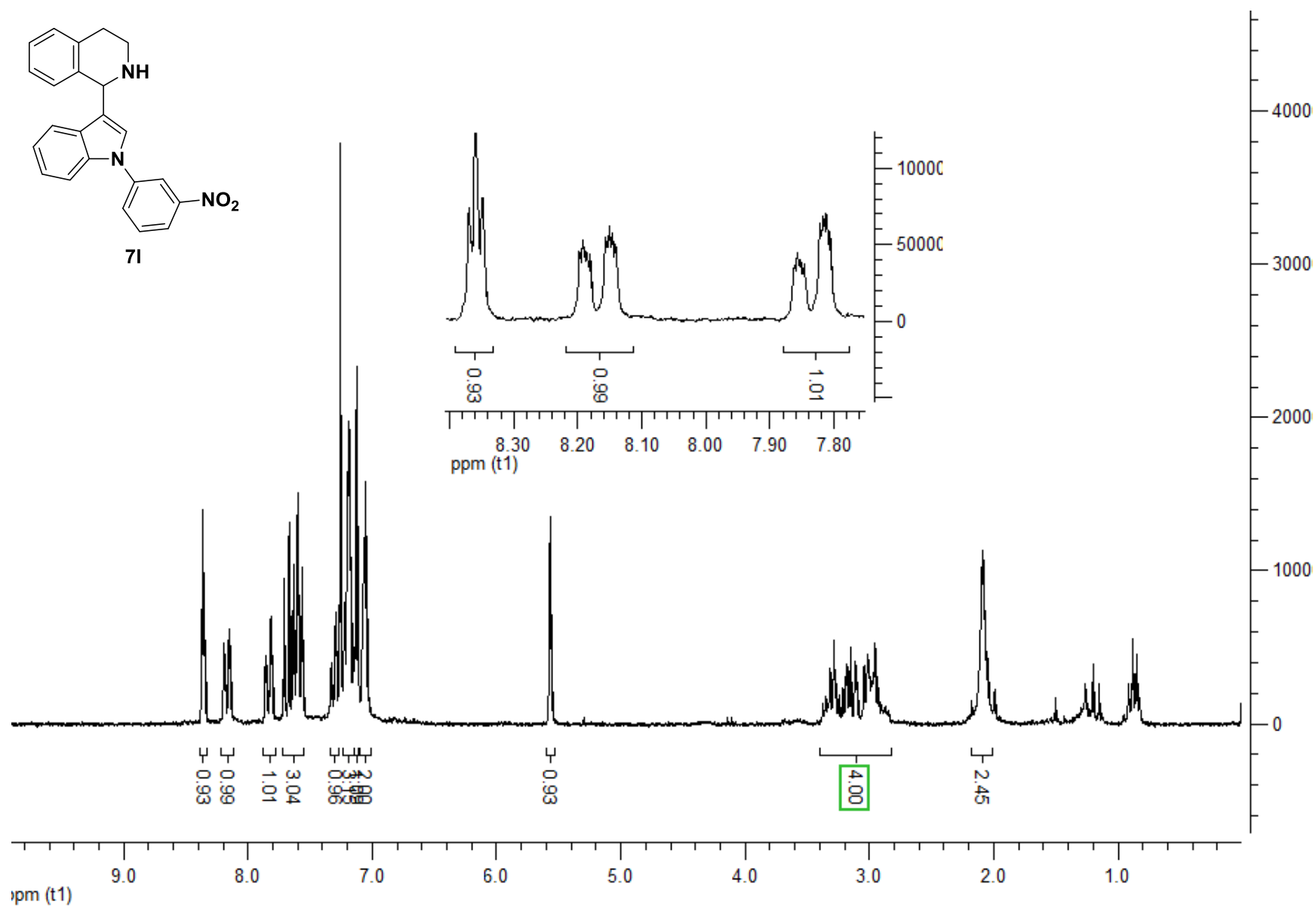


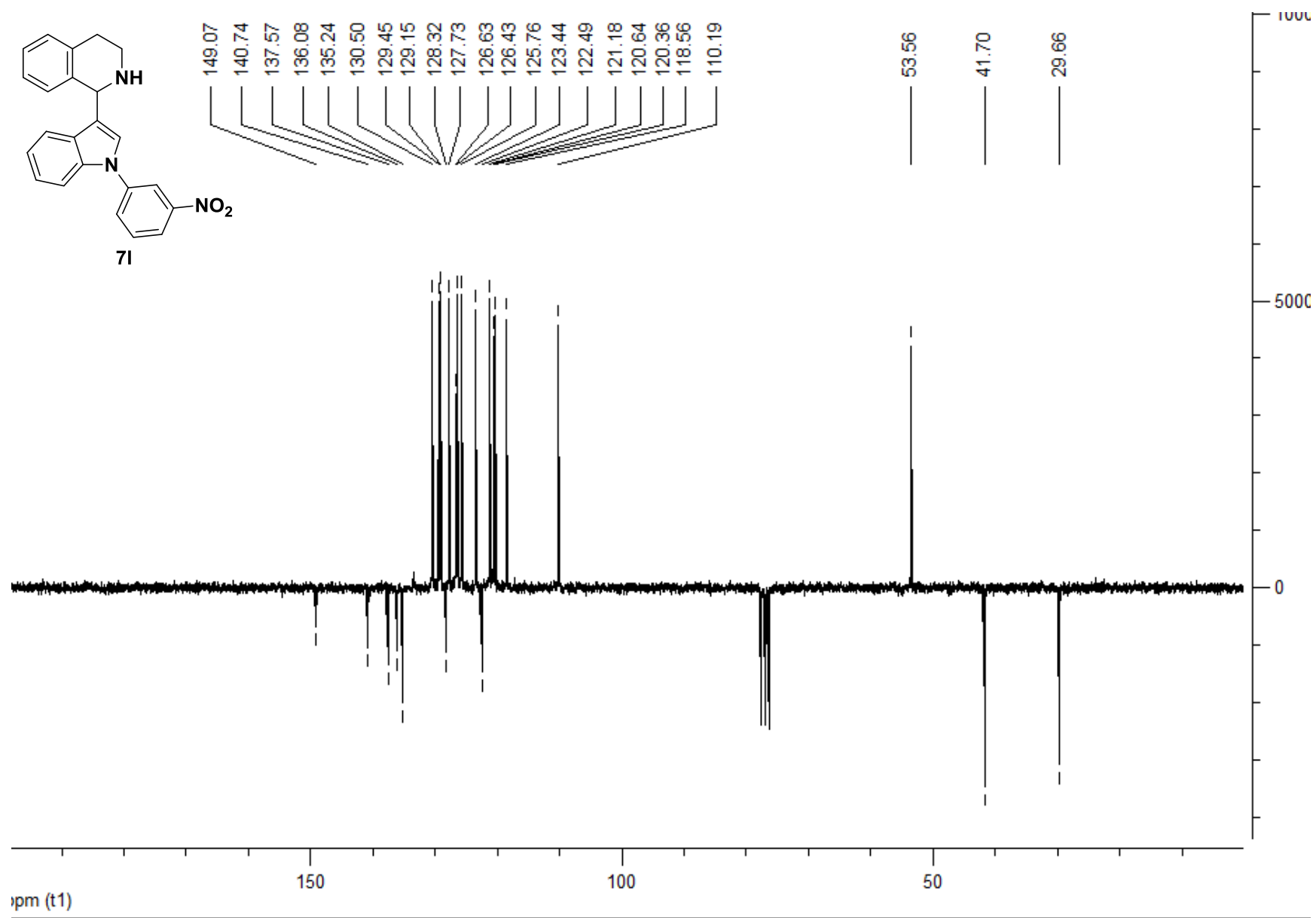


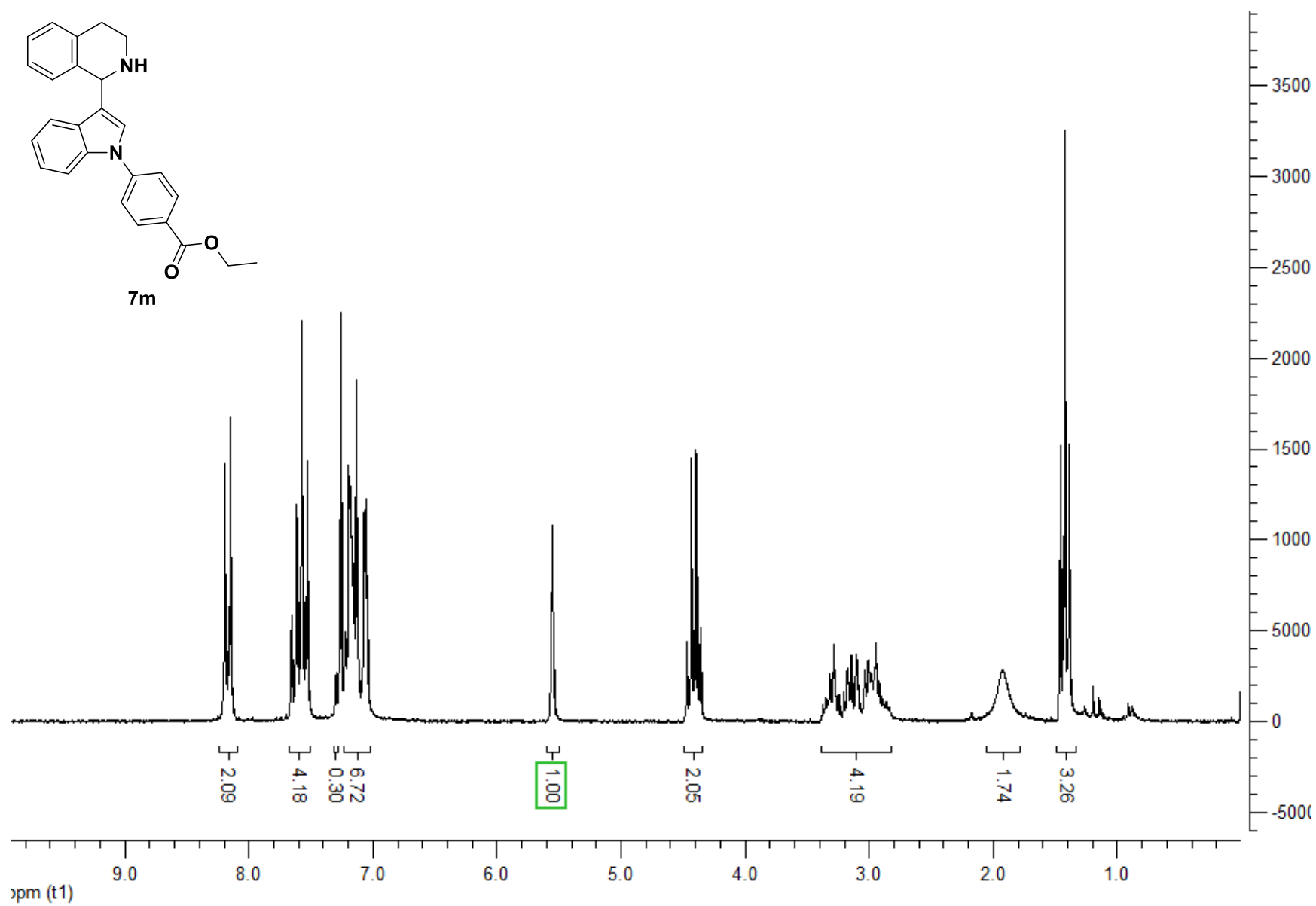


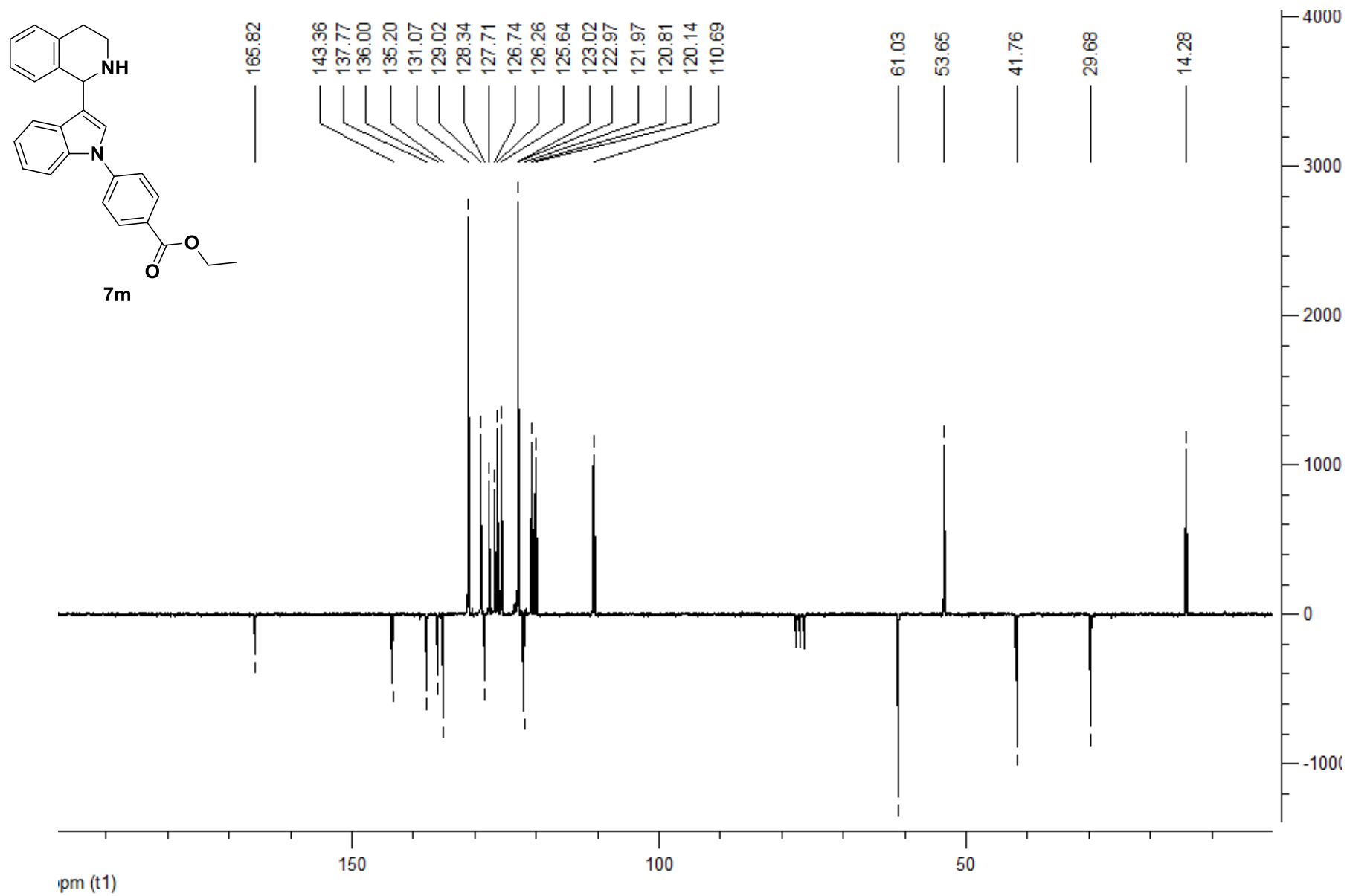


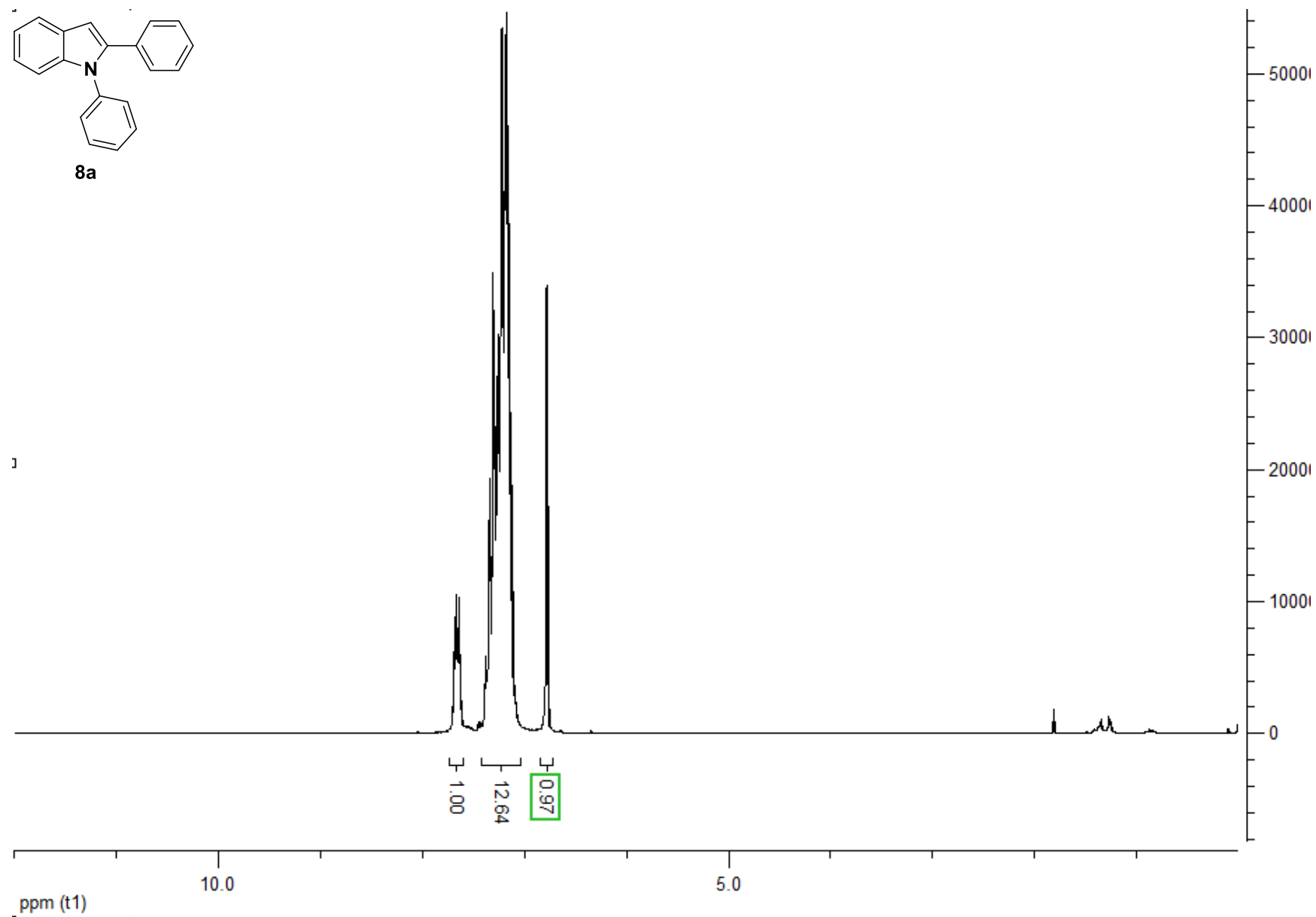
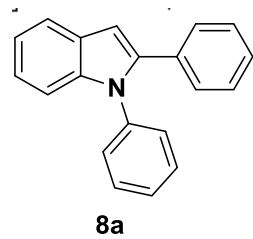


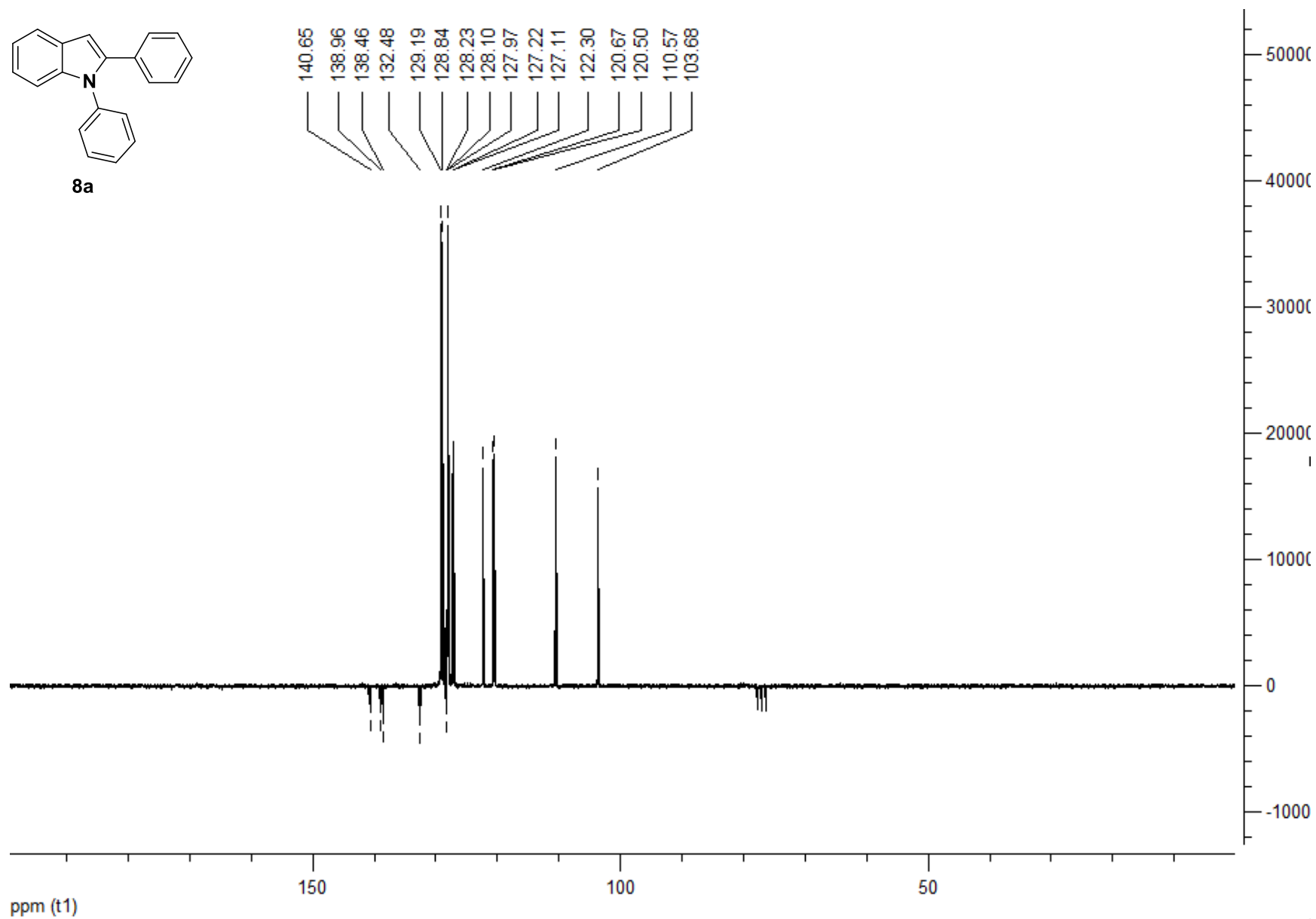
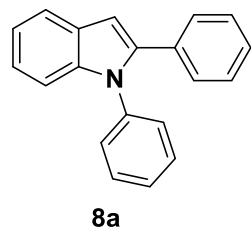


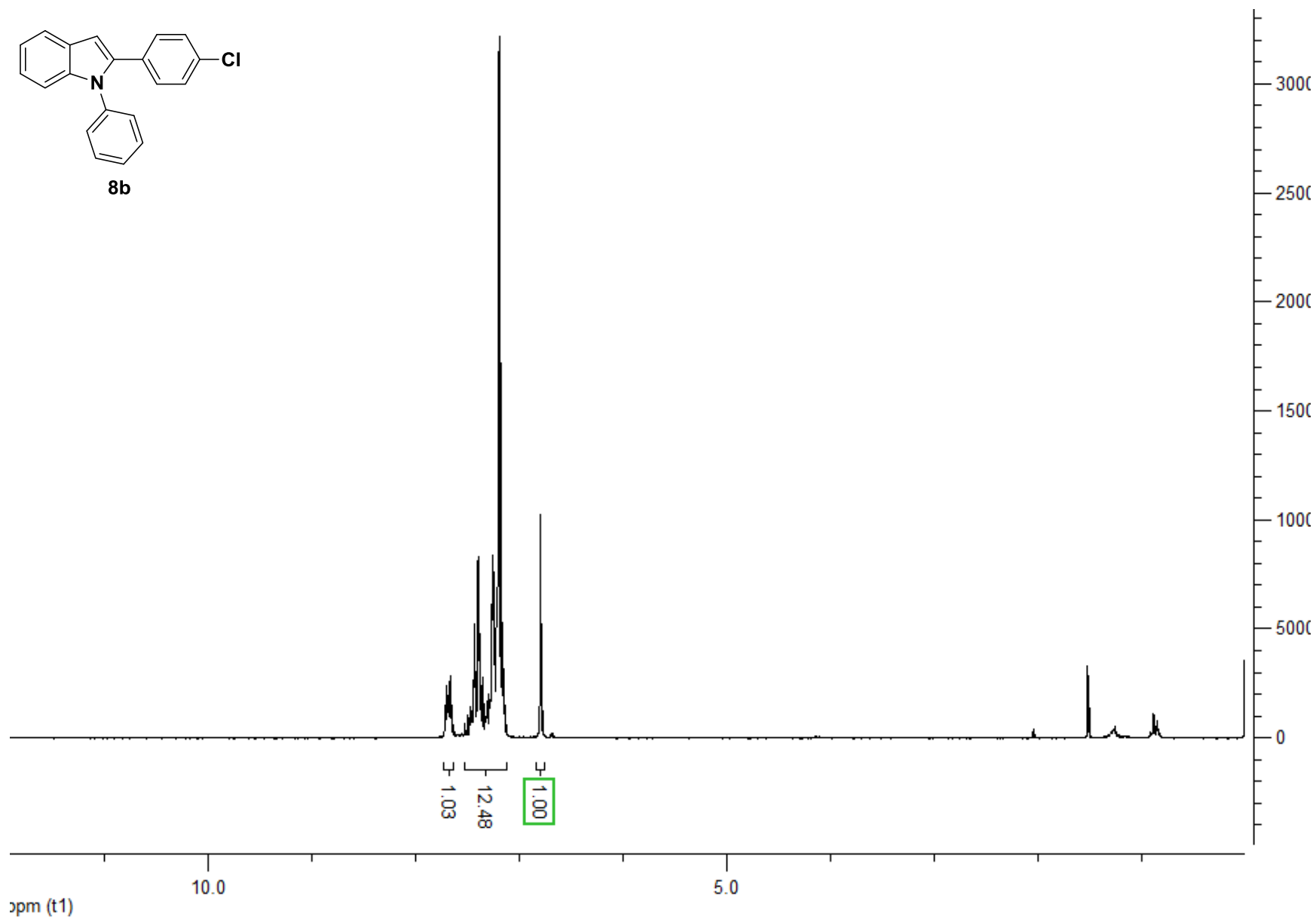
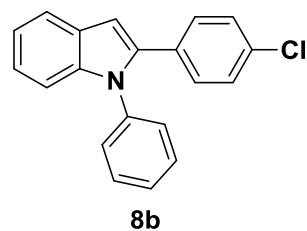


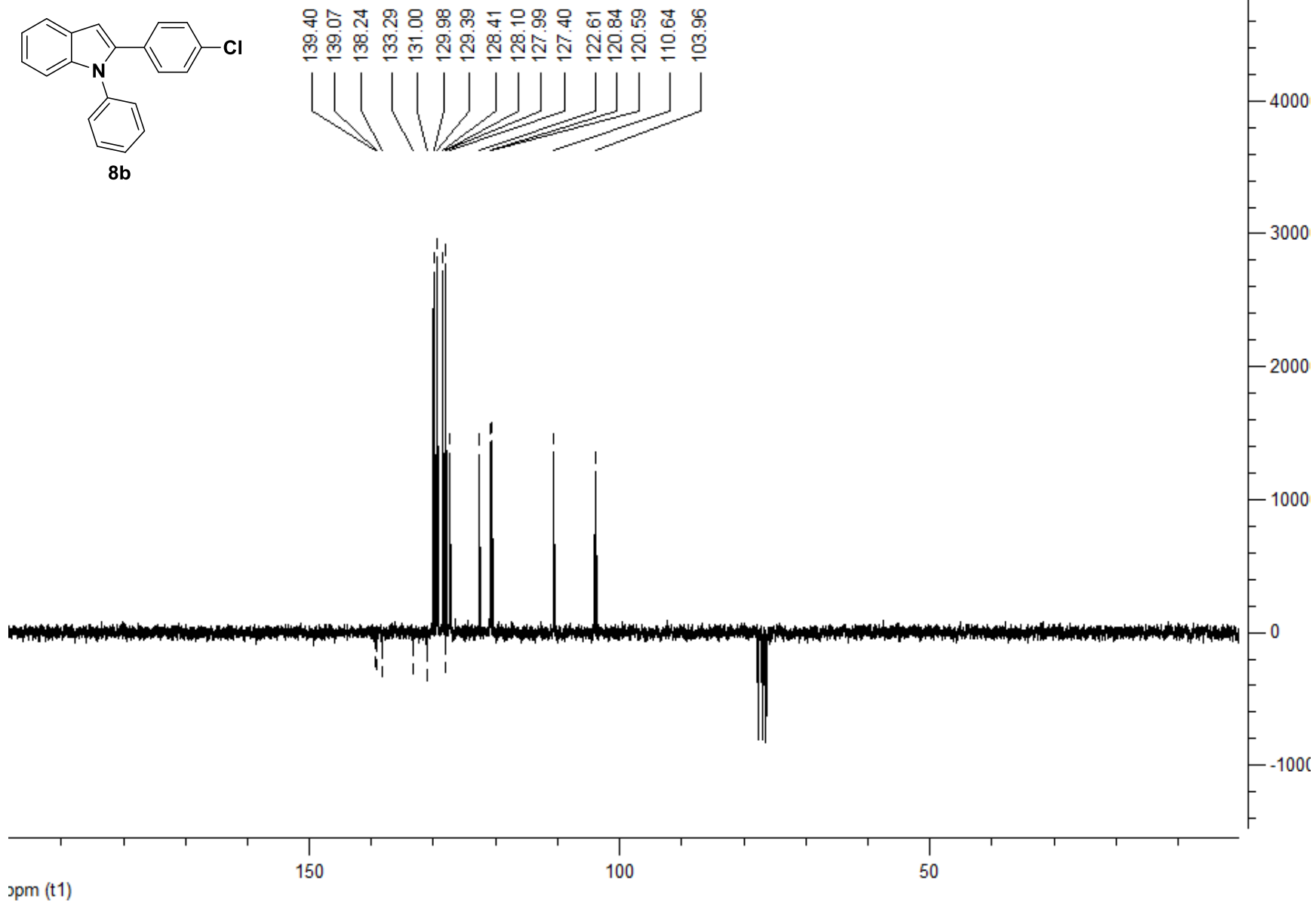


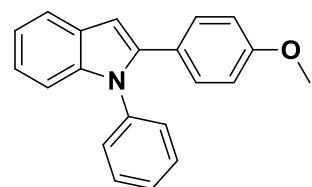




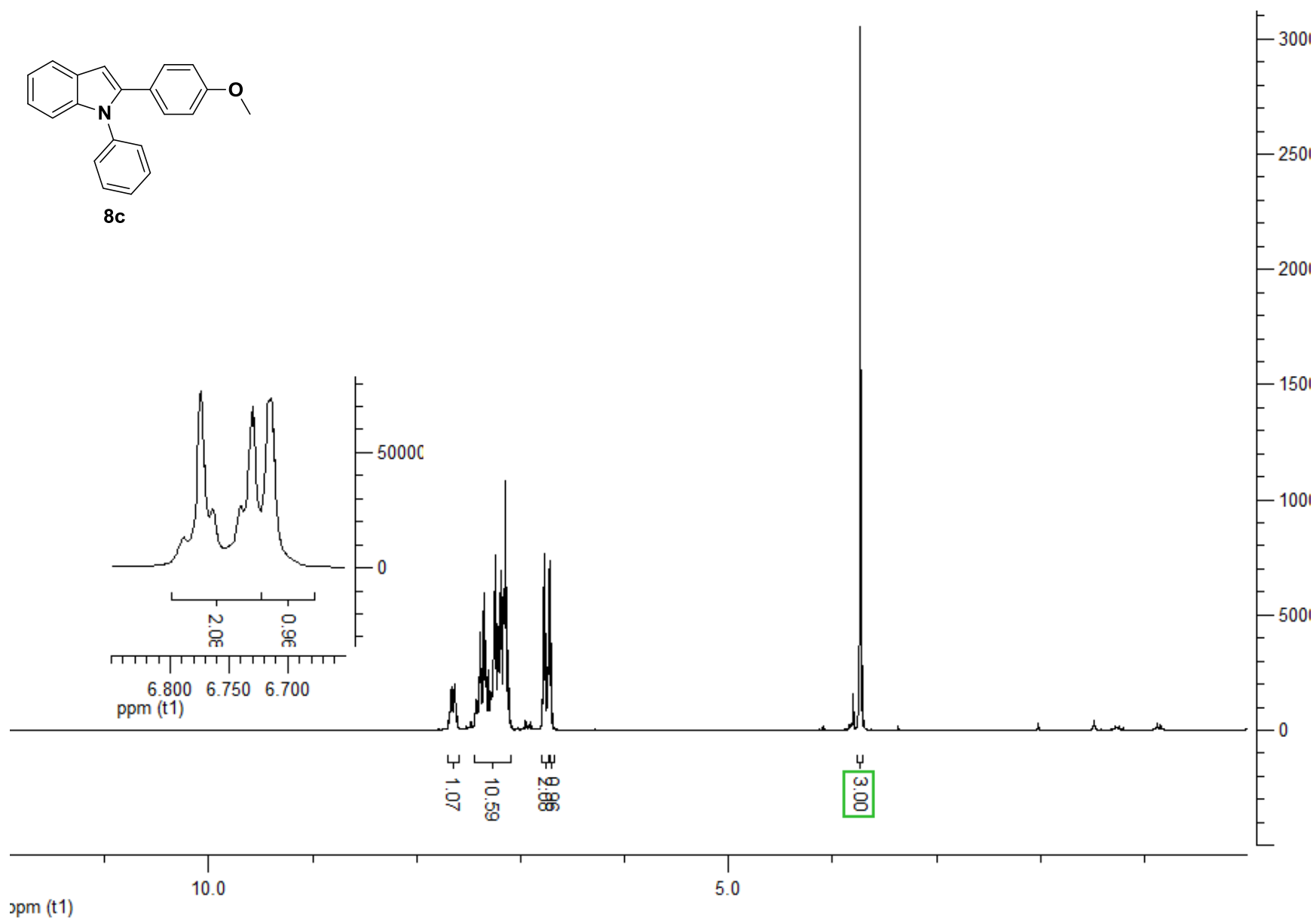


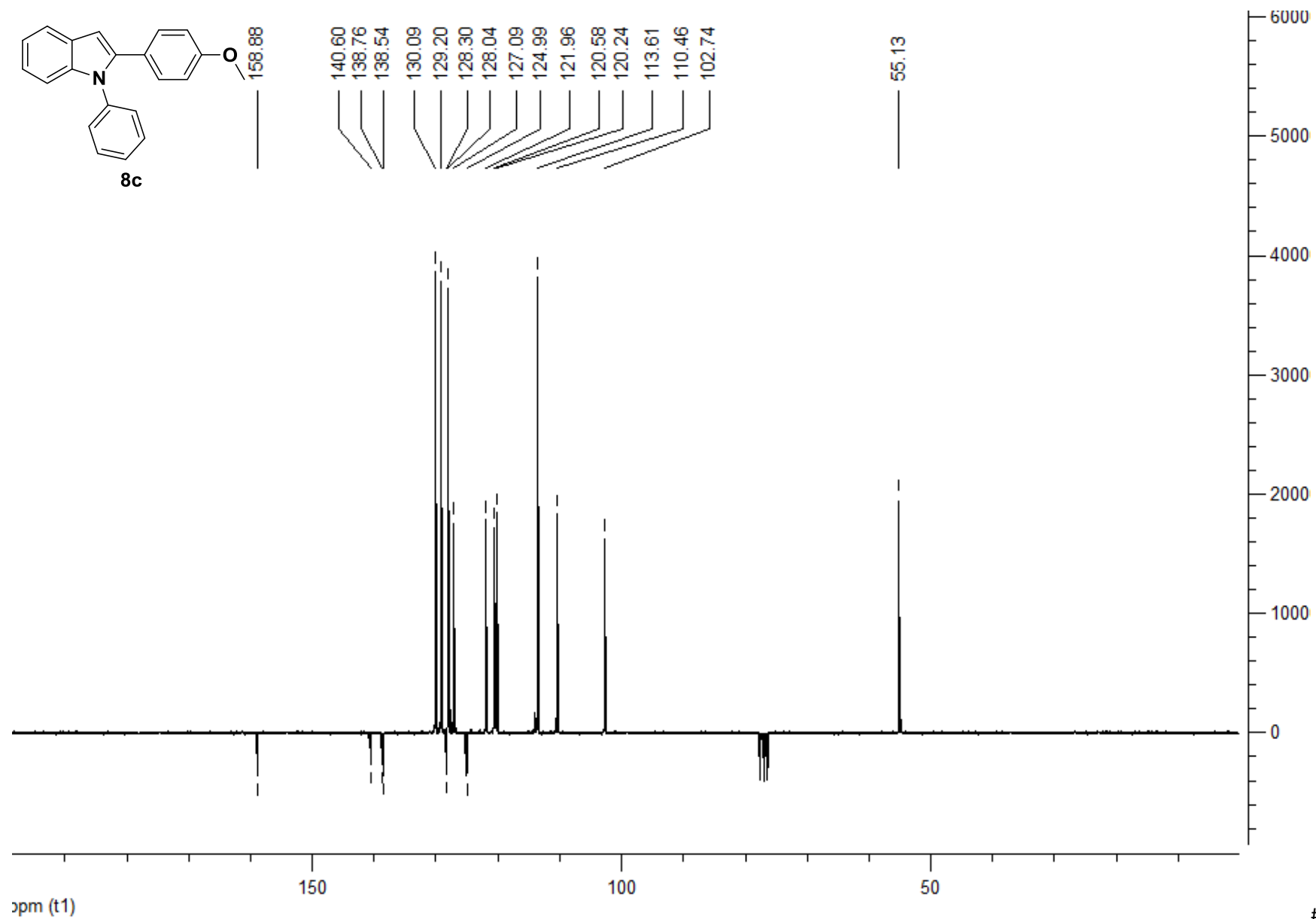
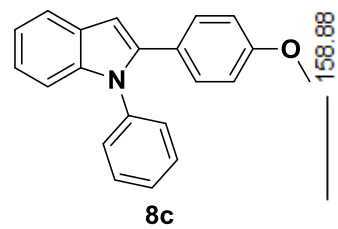


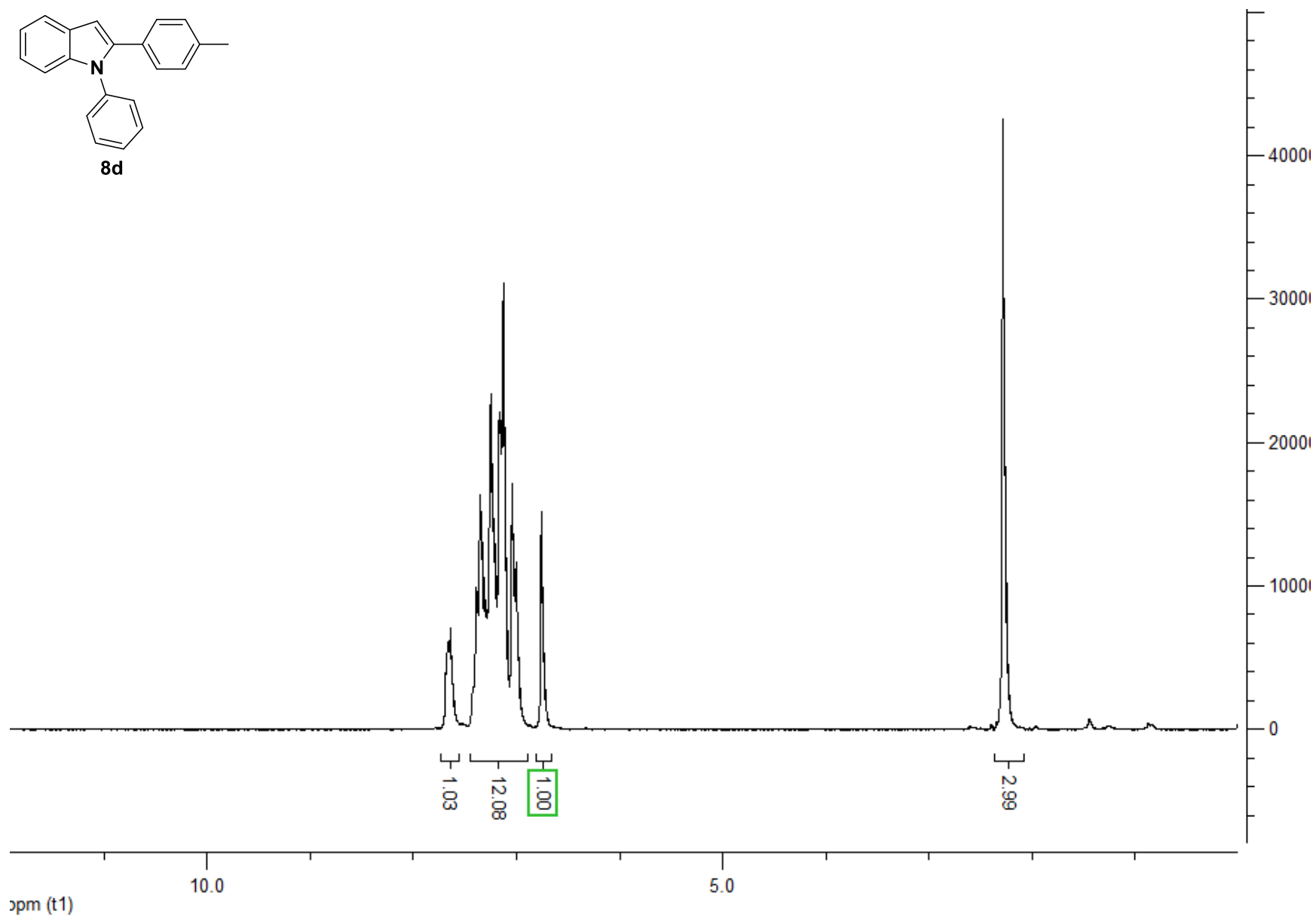
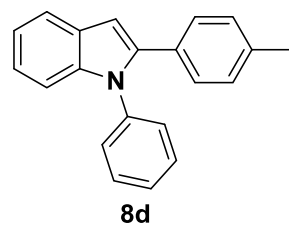


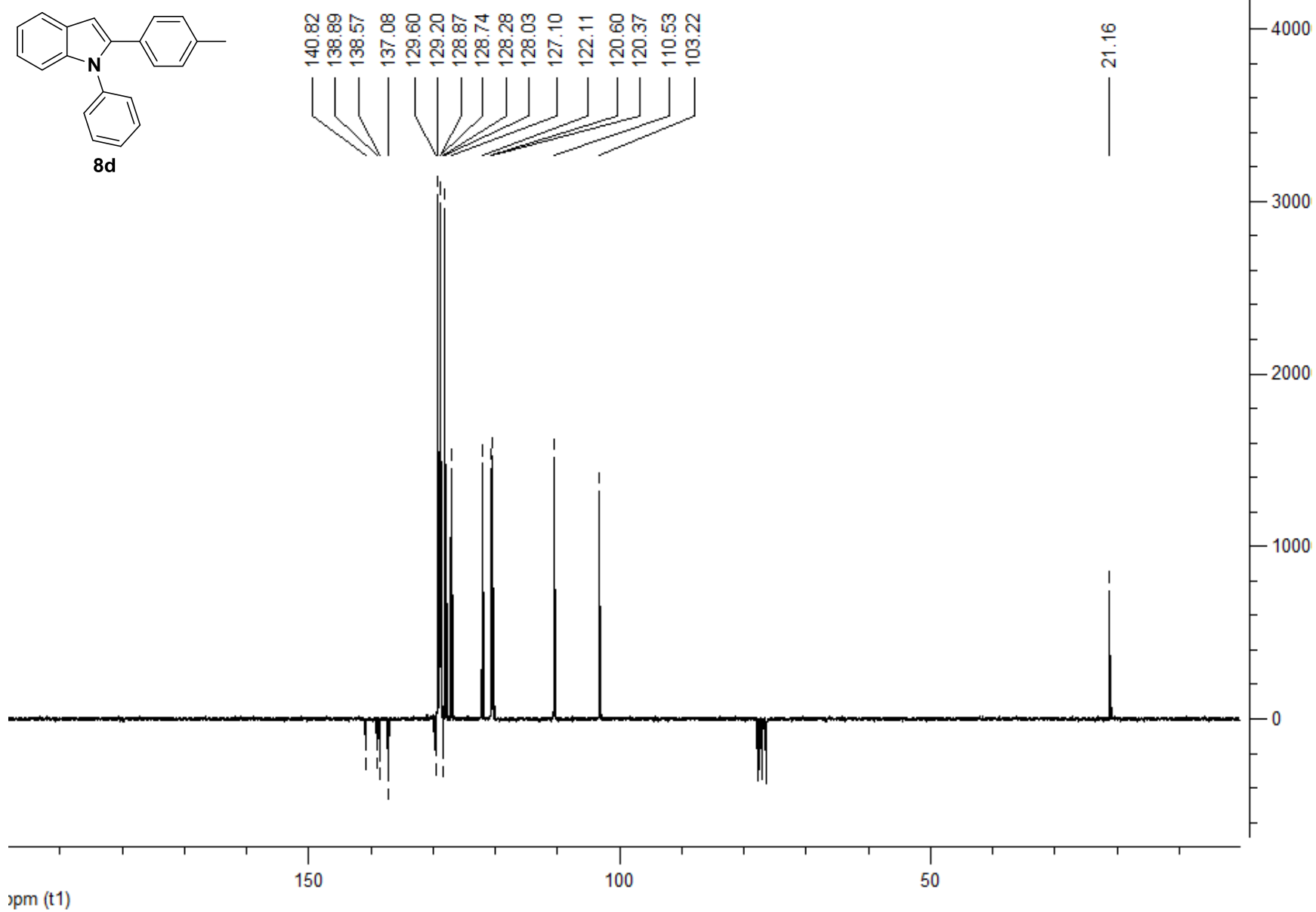


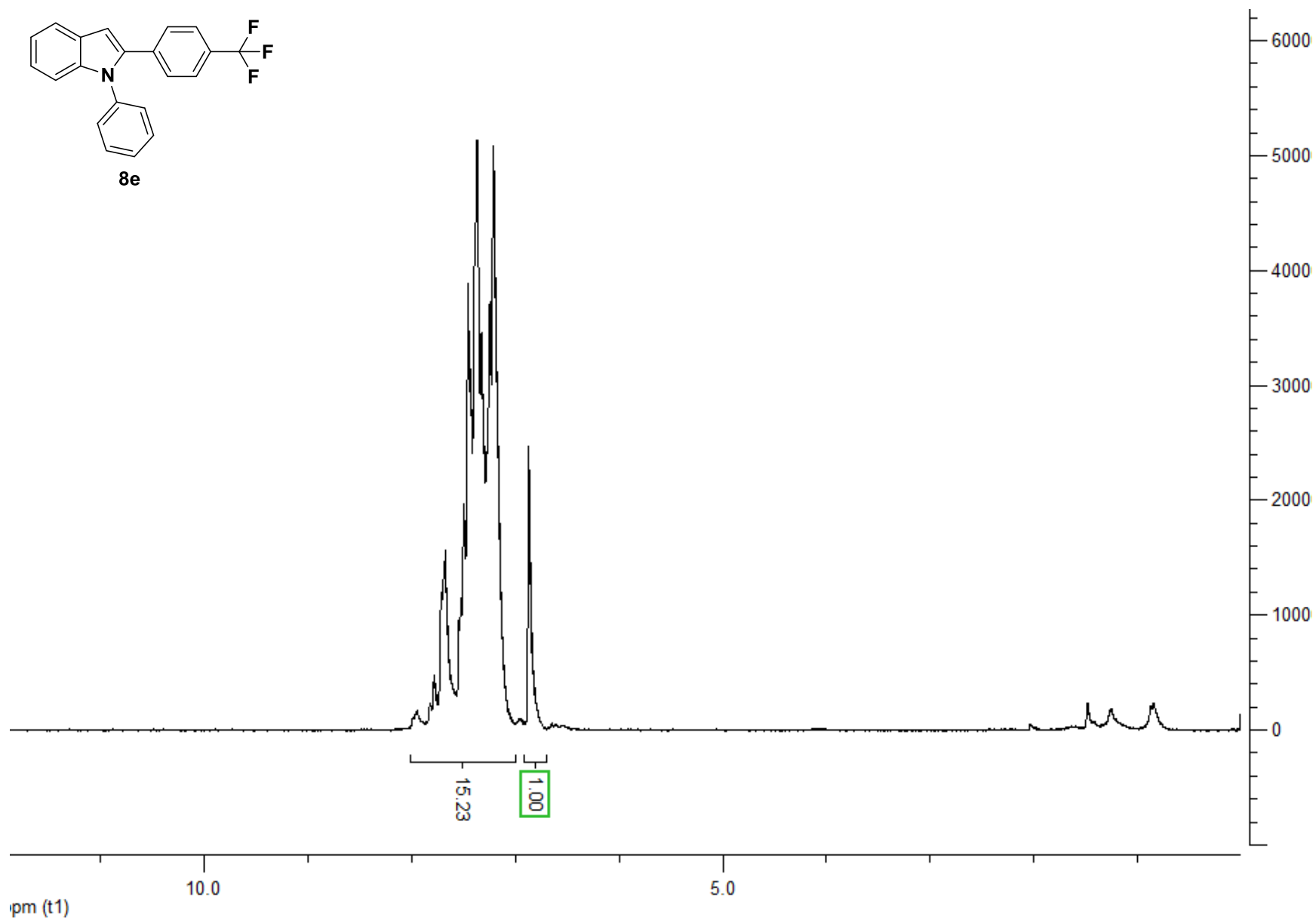
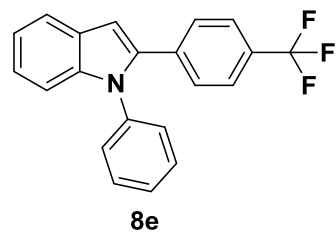
8c

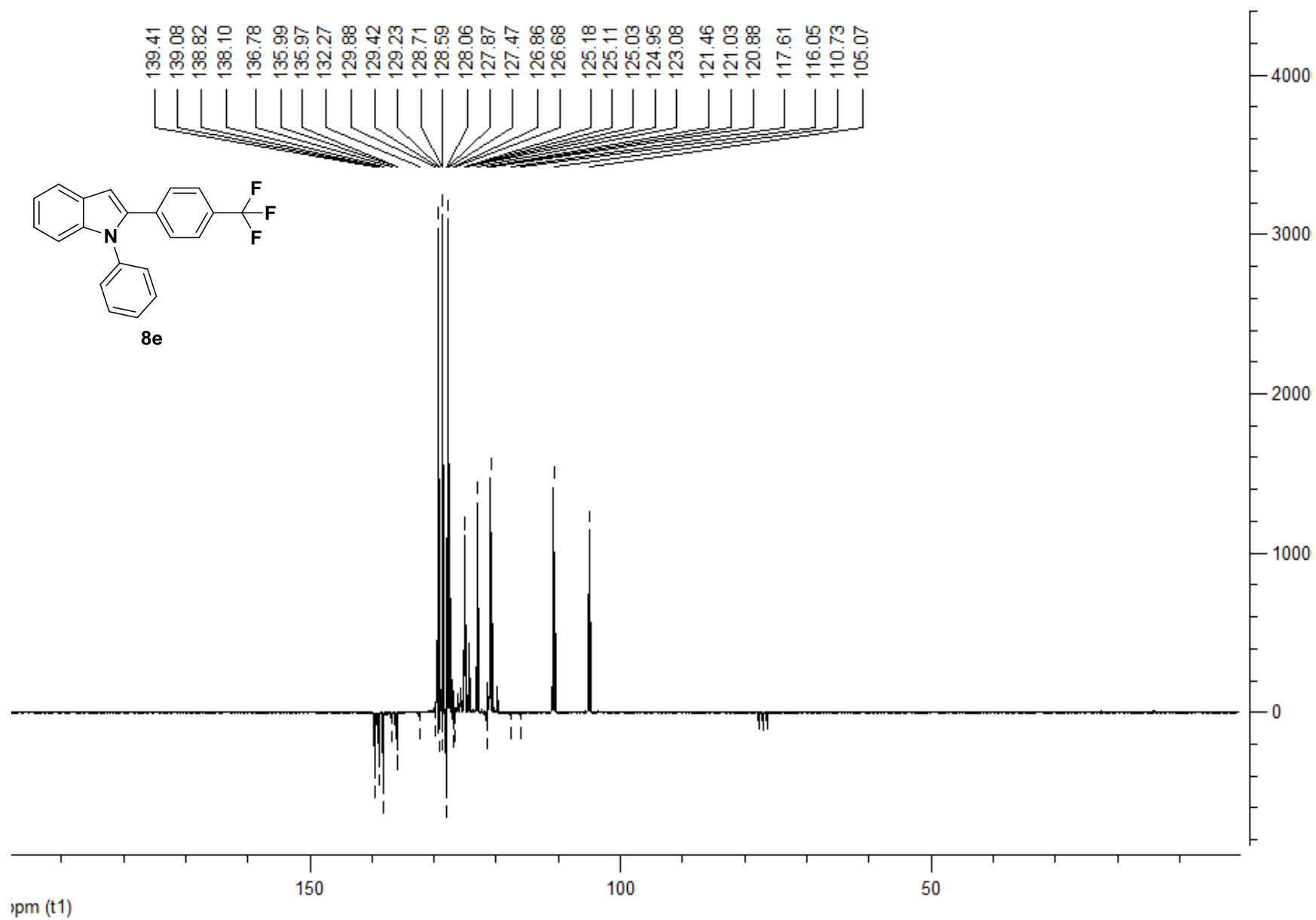


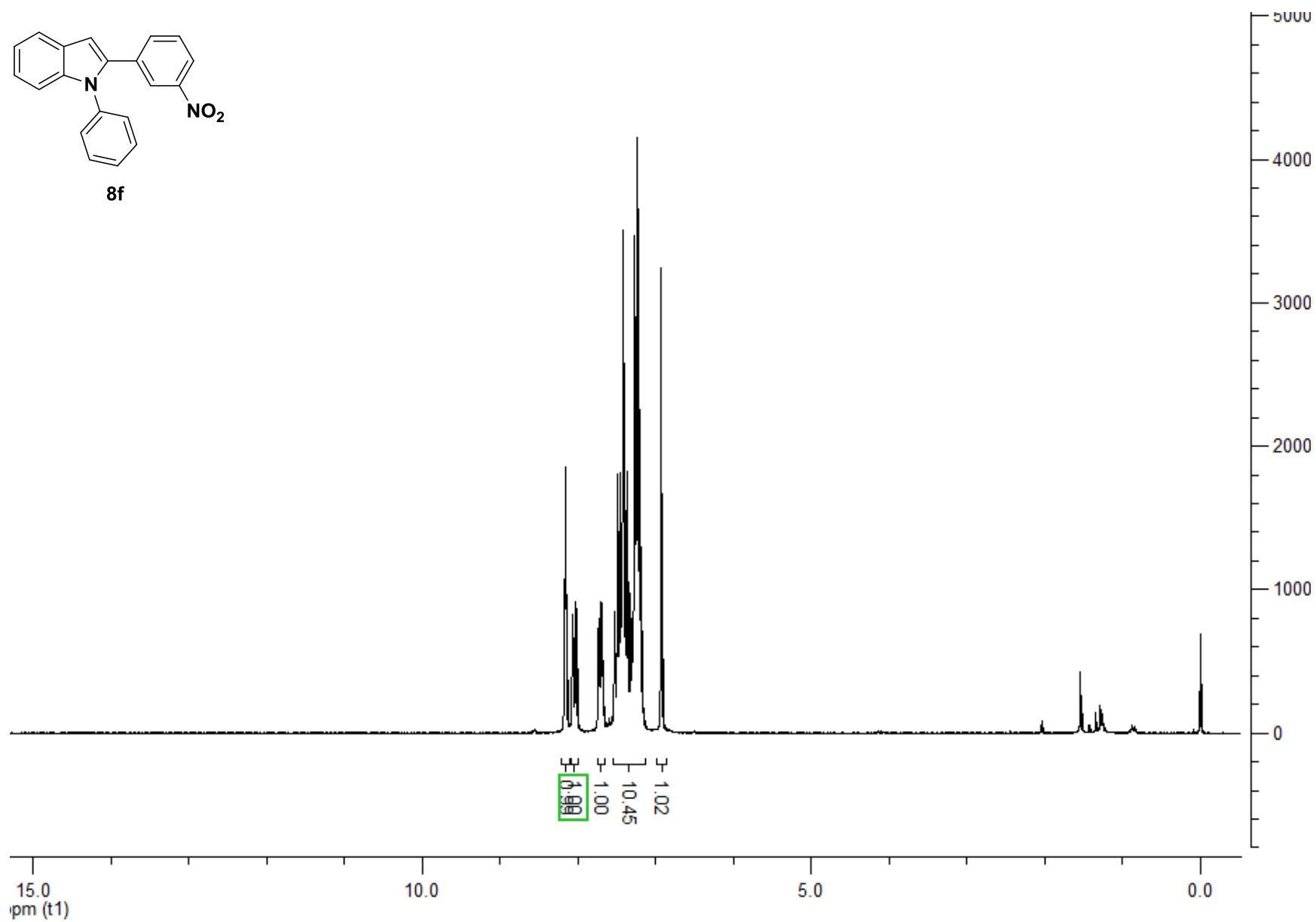
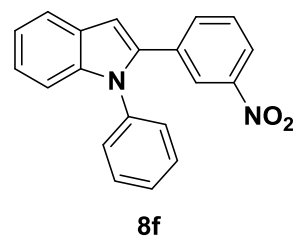


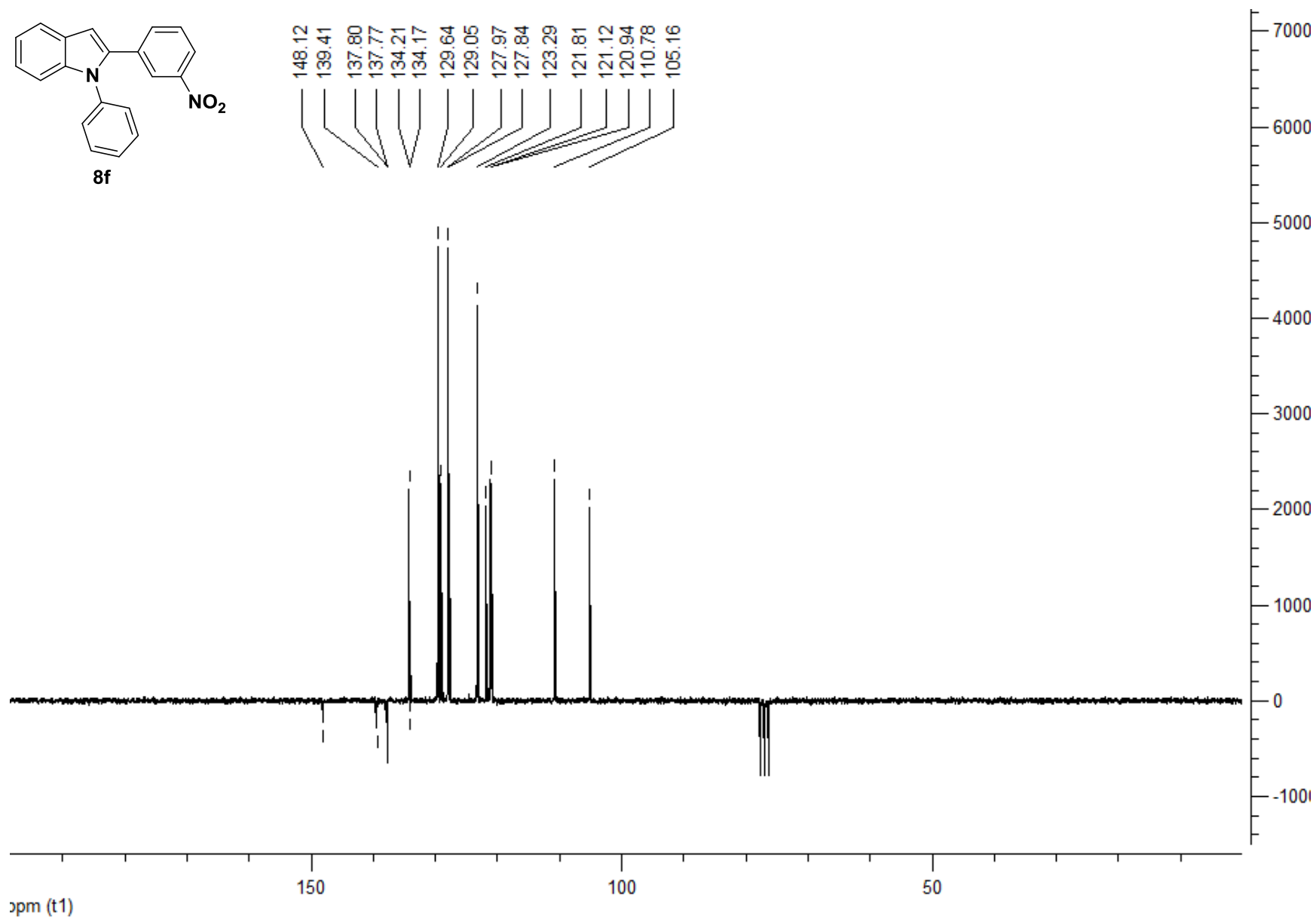
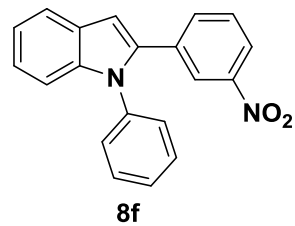


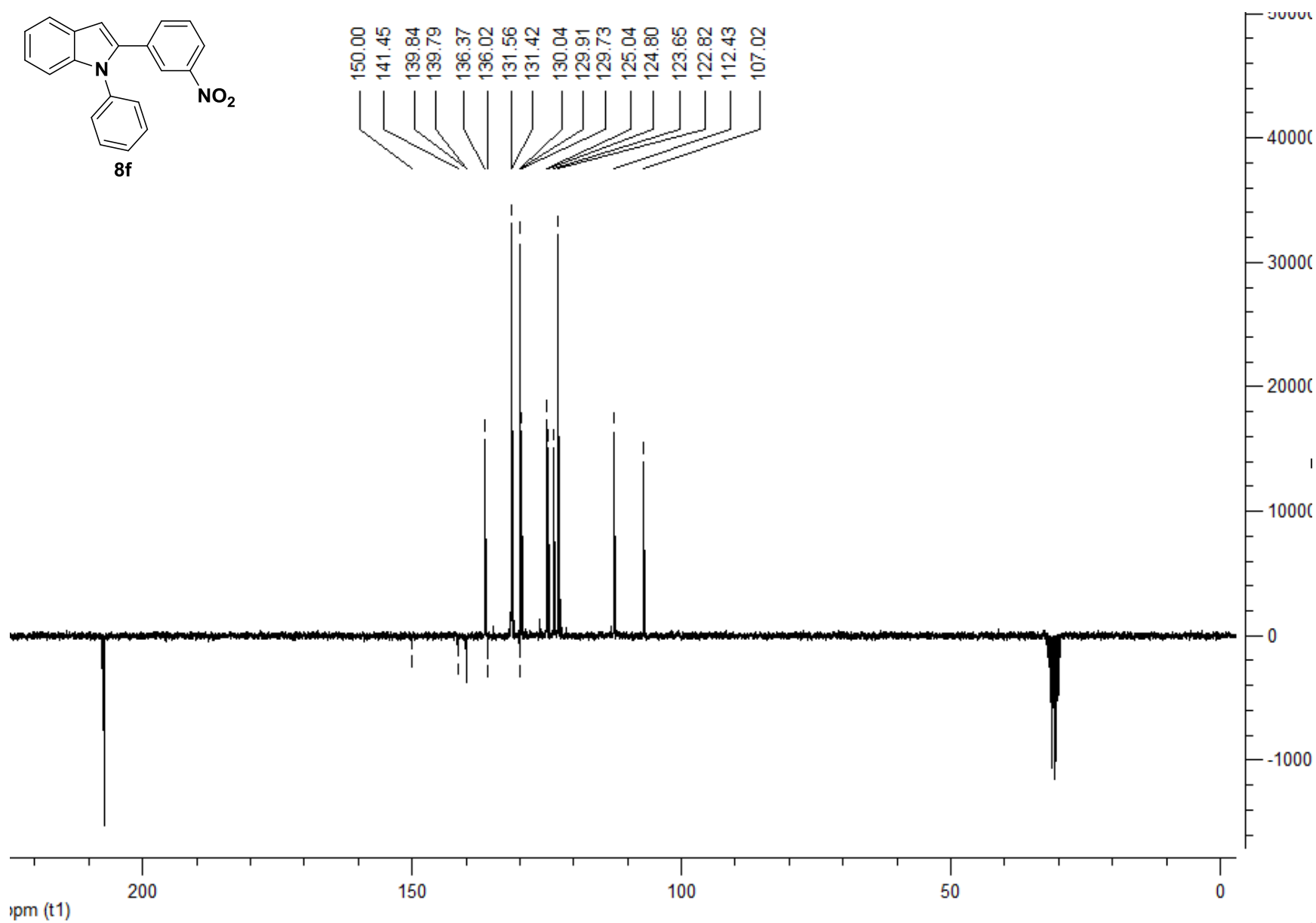
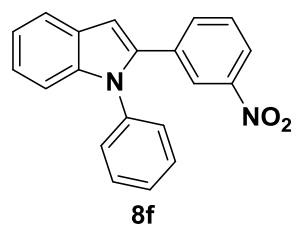


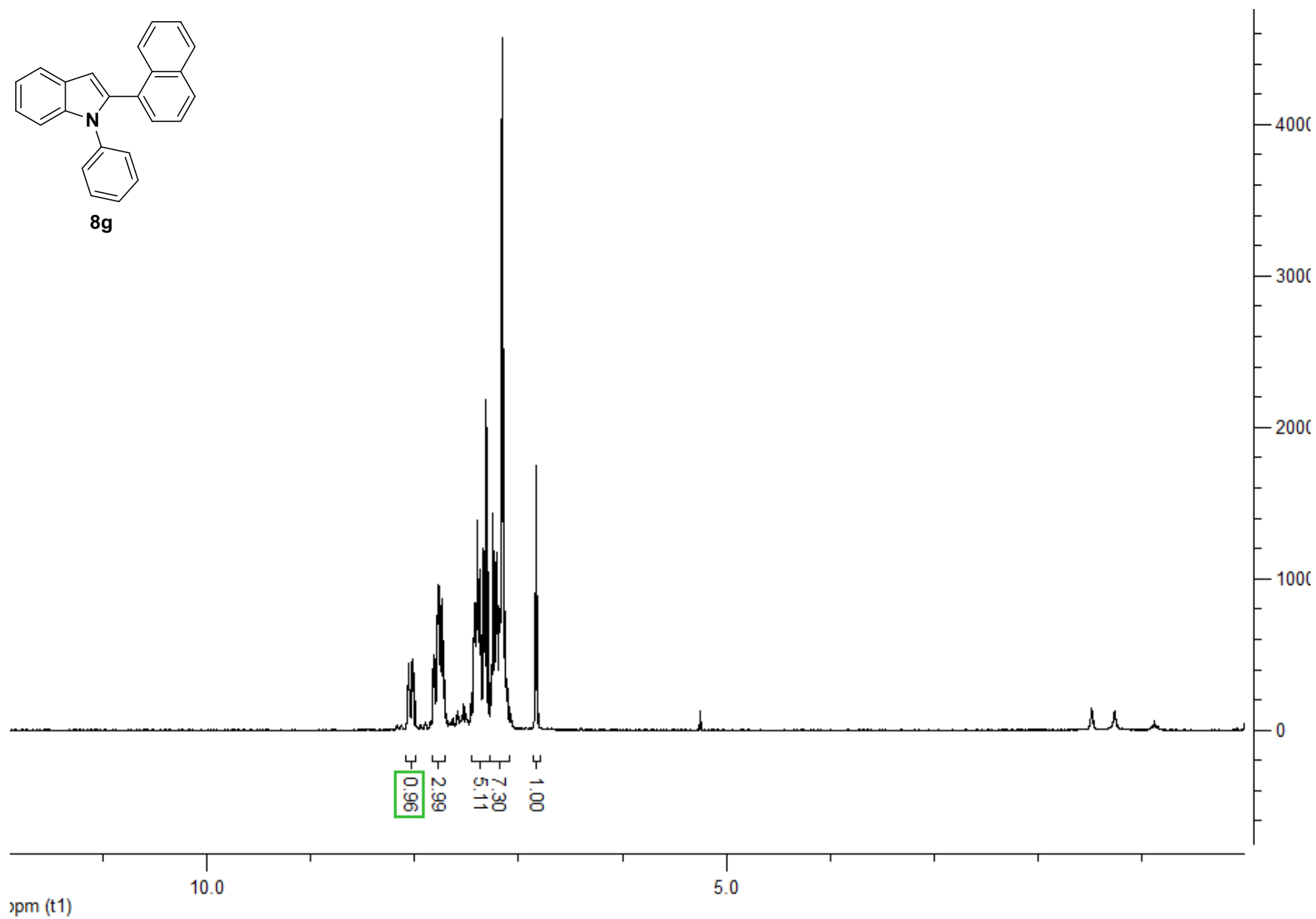
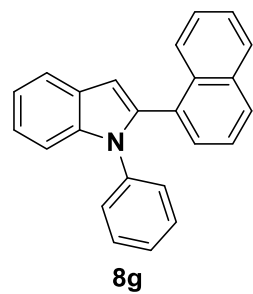


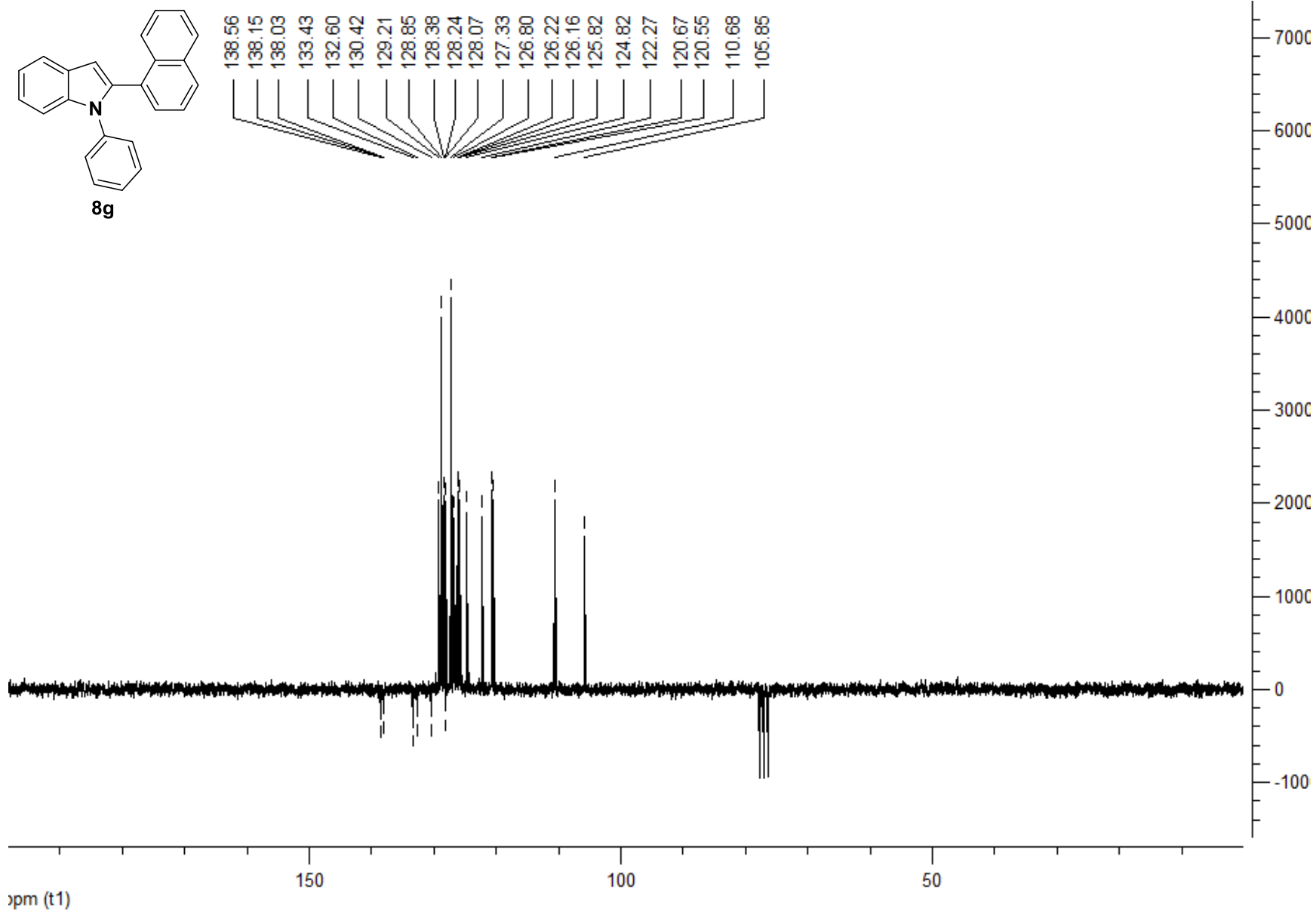


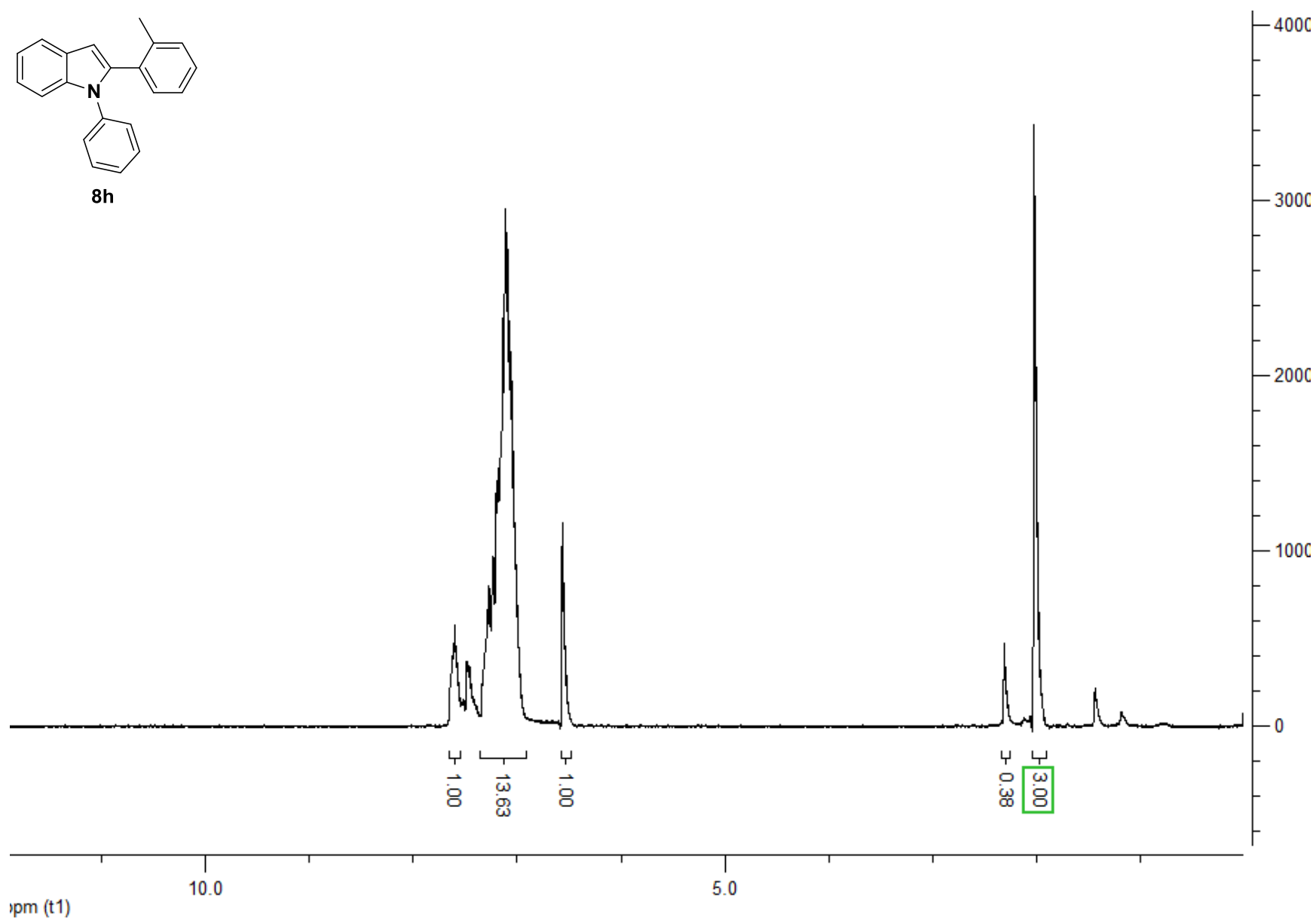
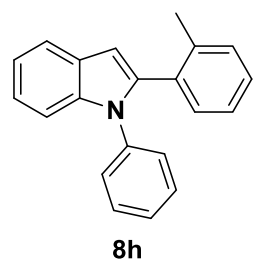


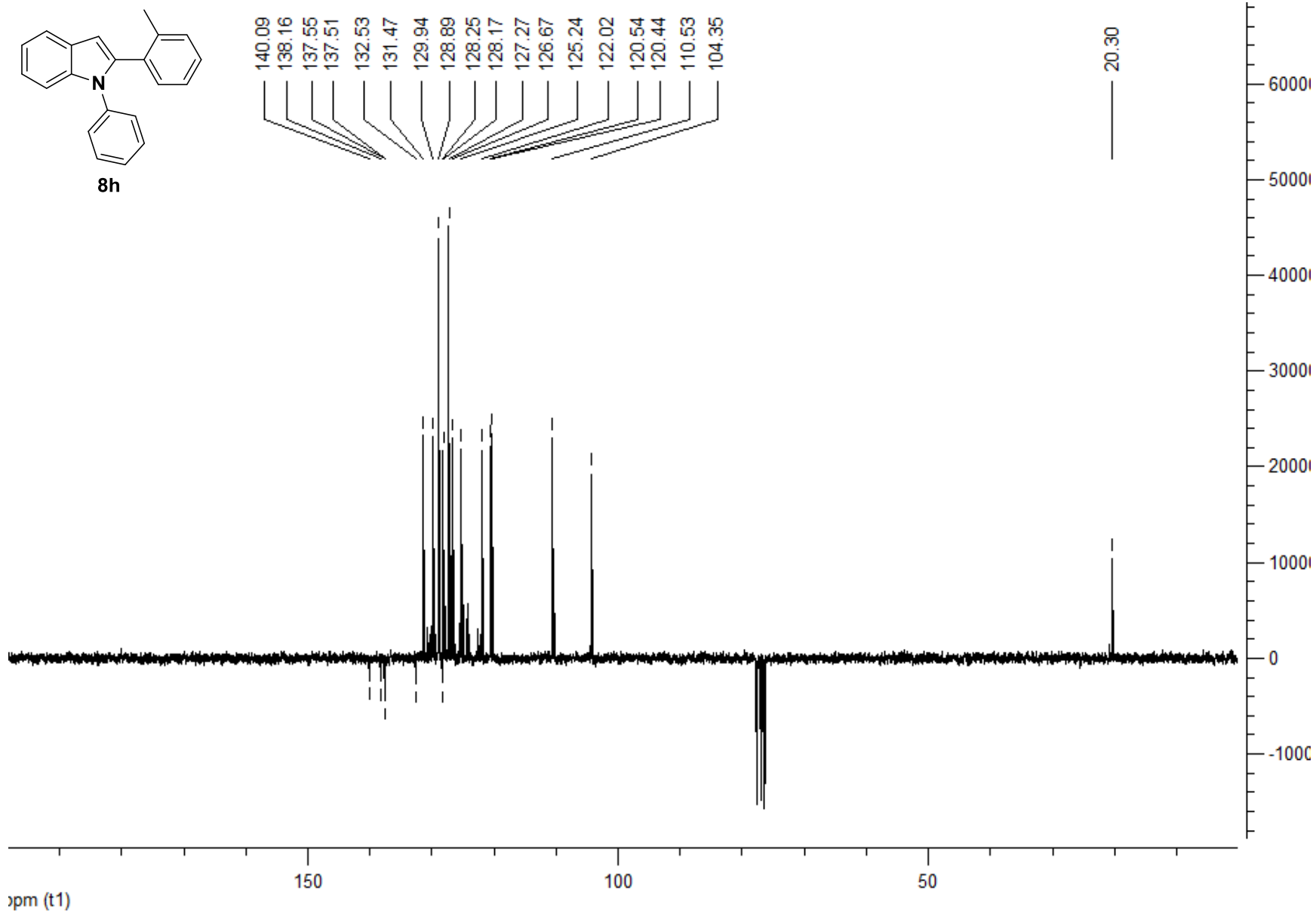


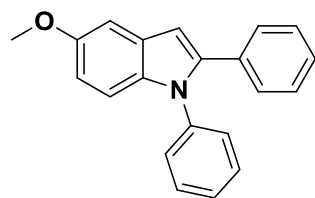




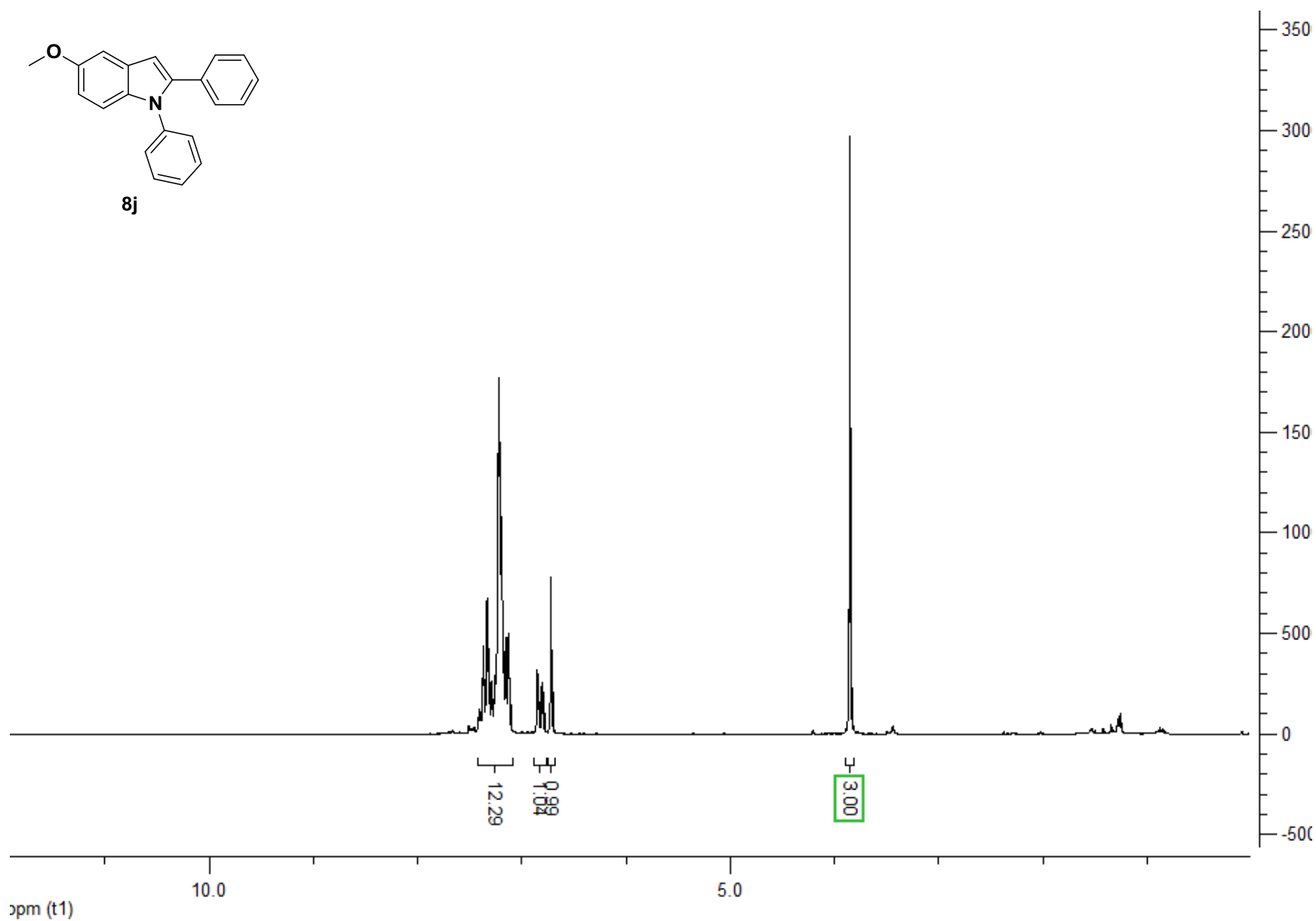


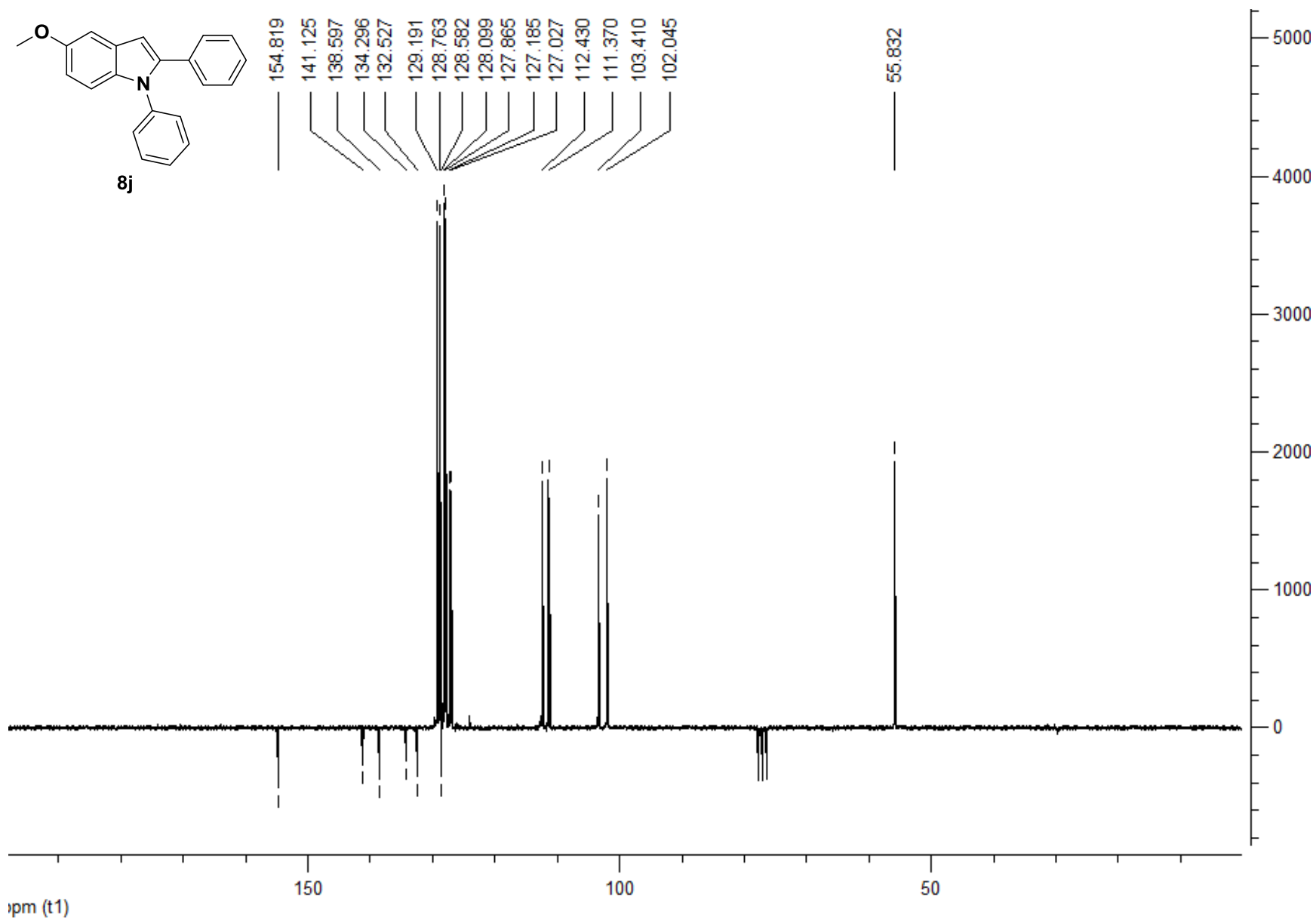


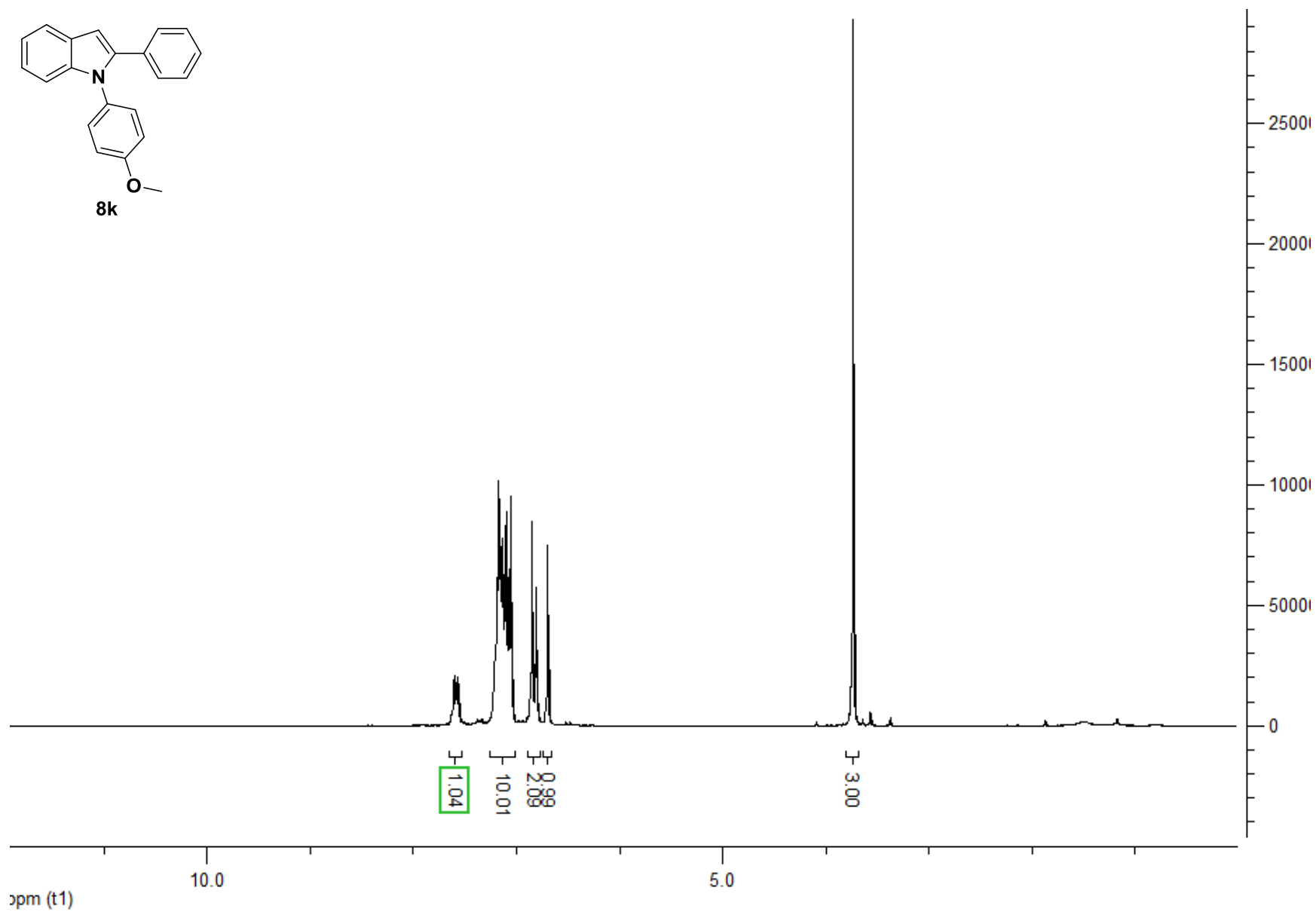
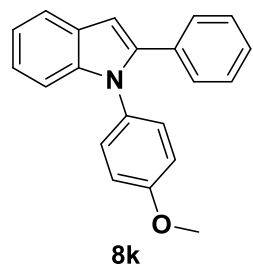


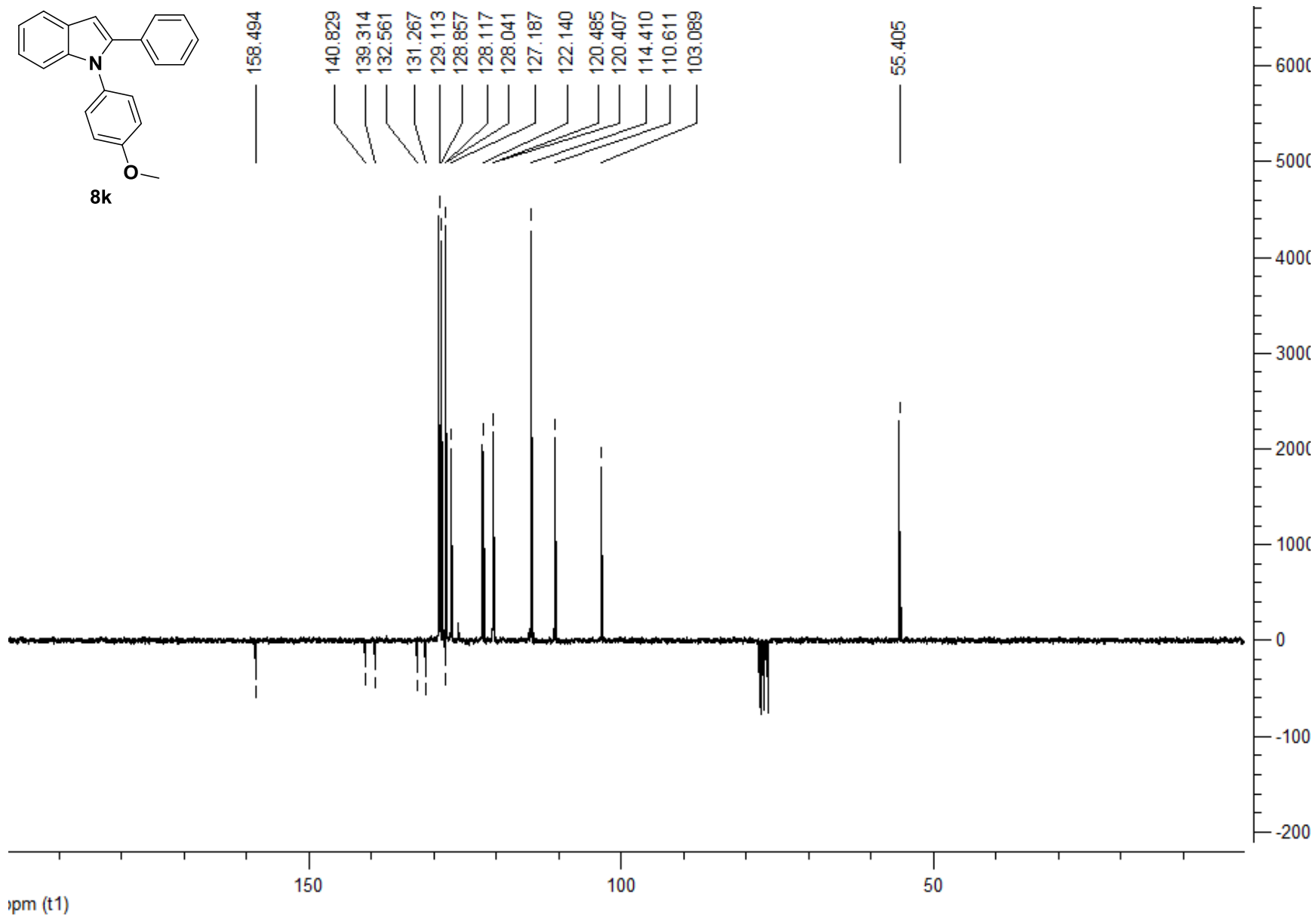


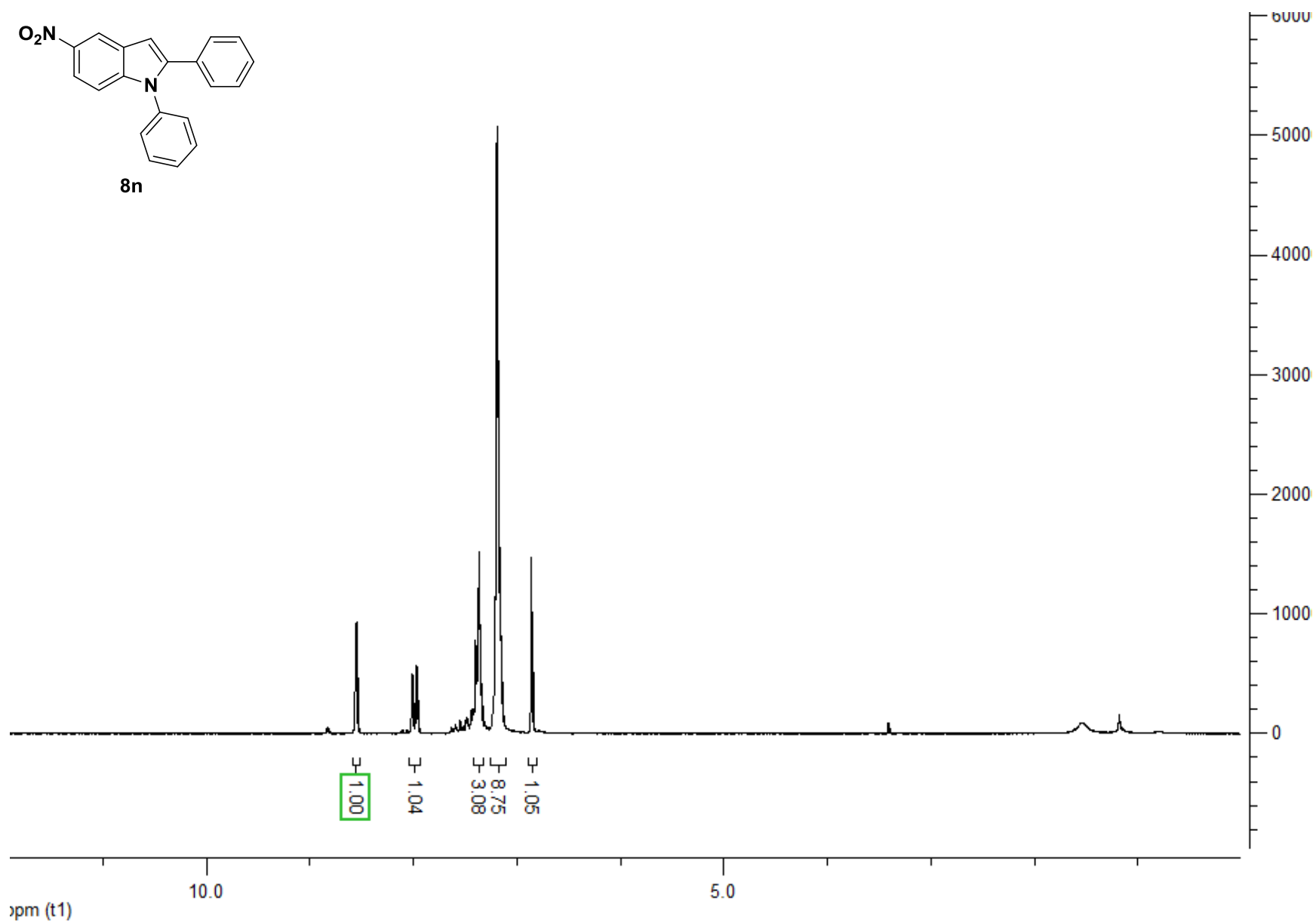
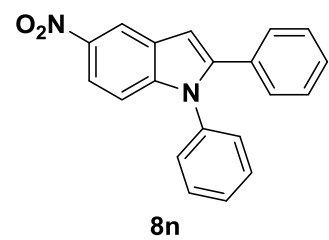
8j

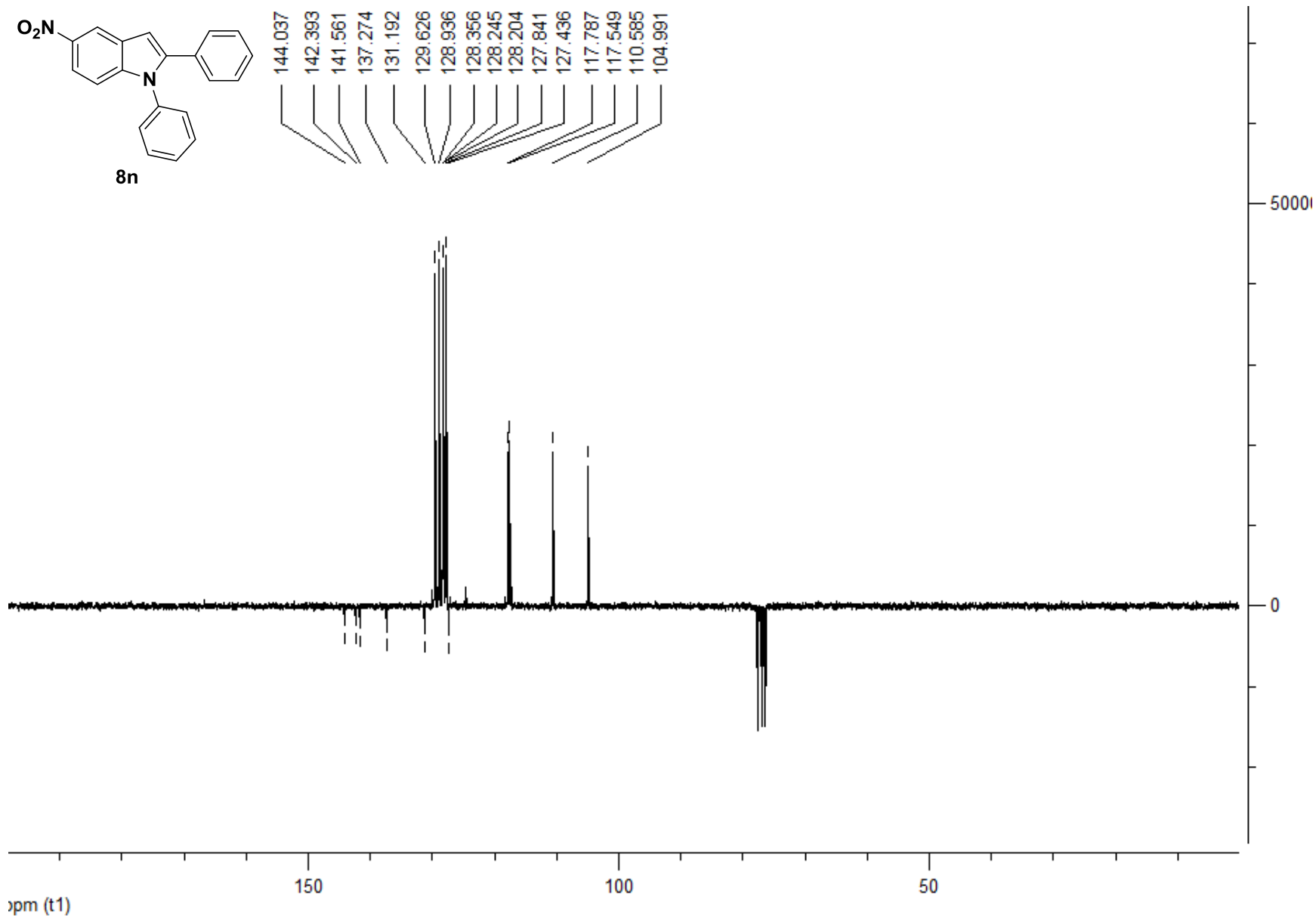


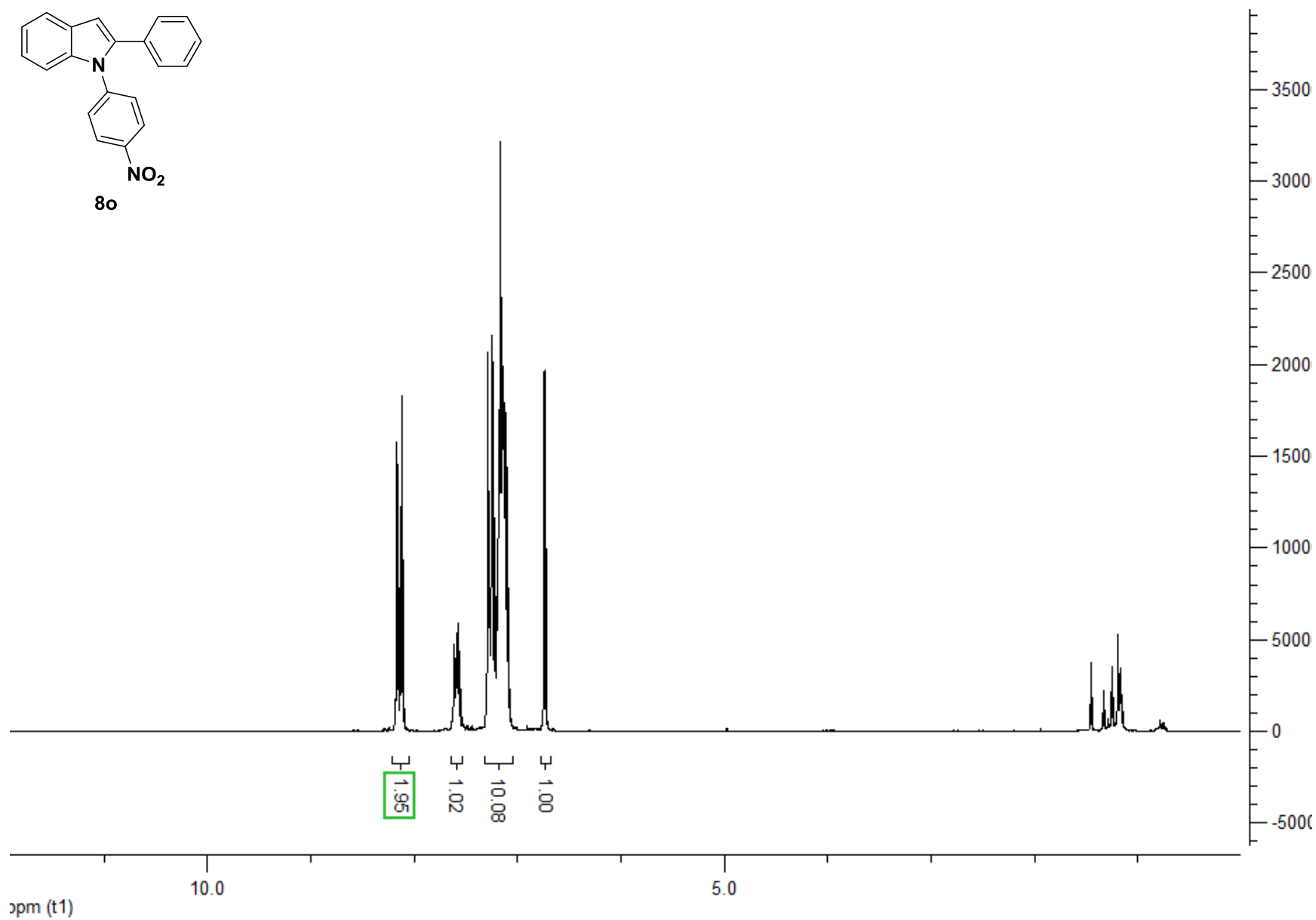
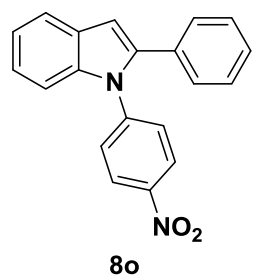


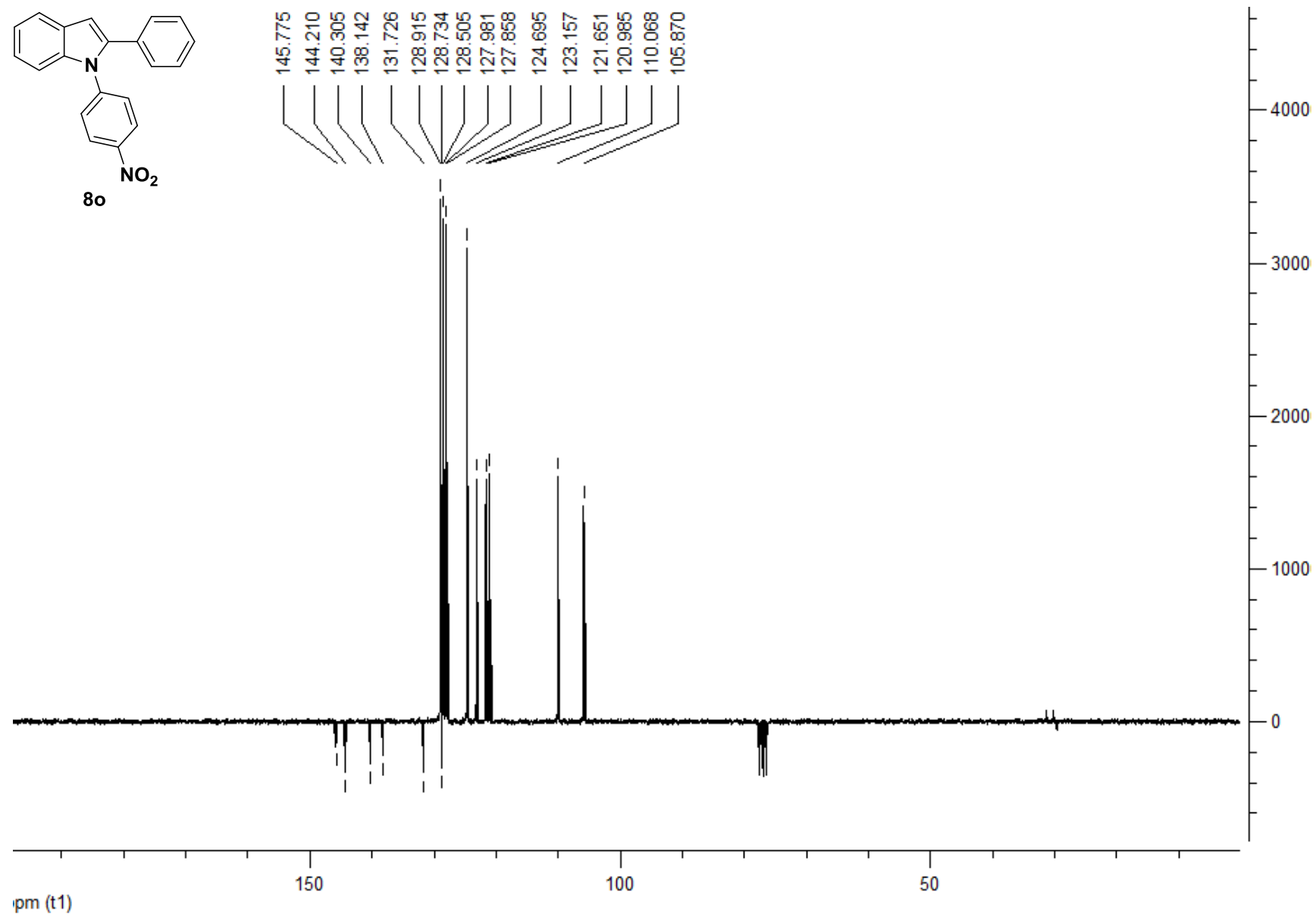
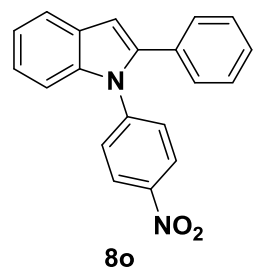


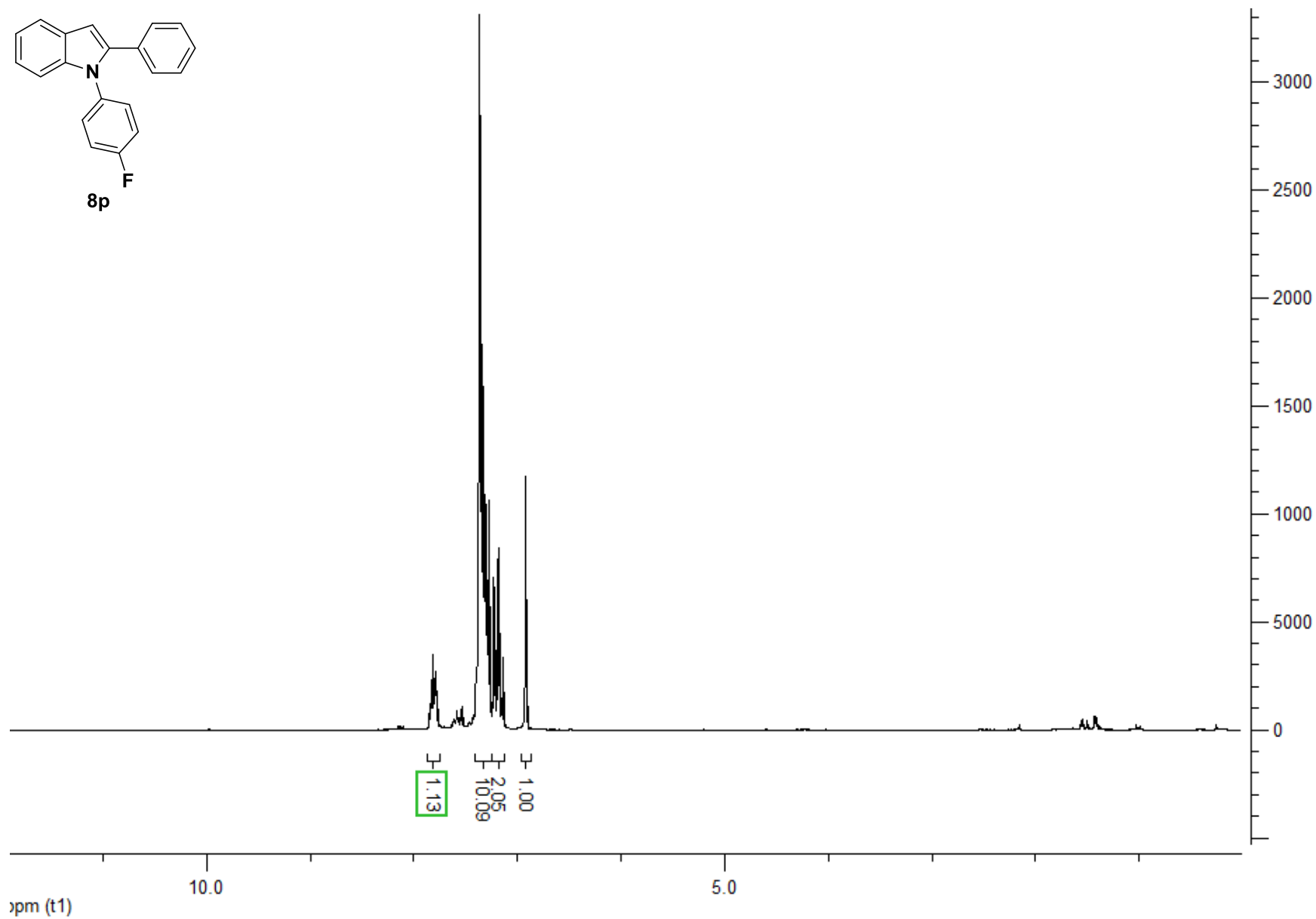
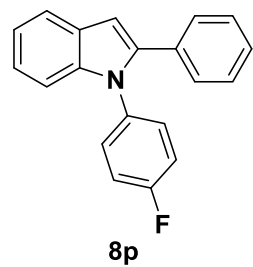


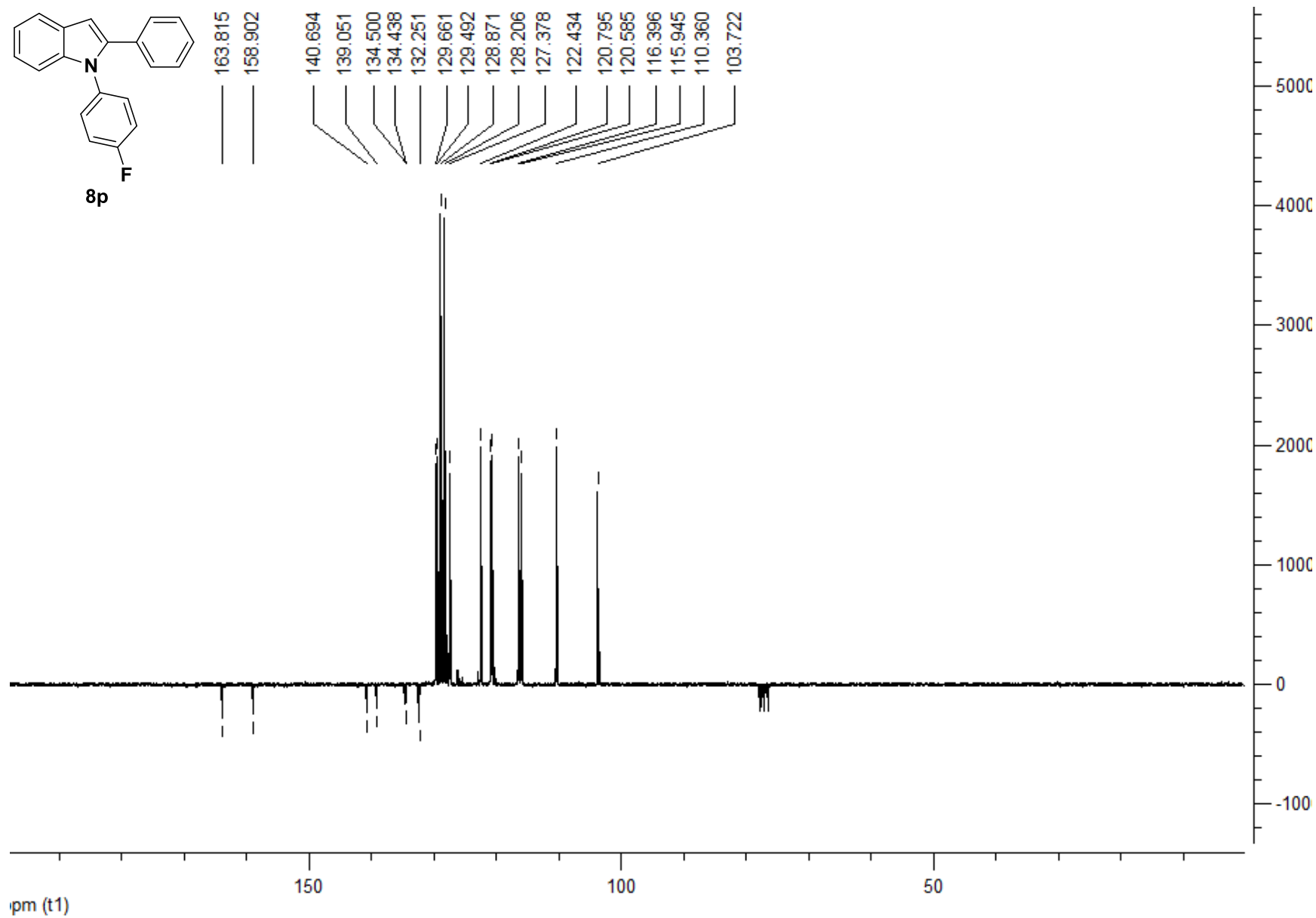
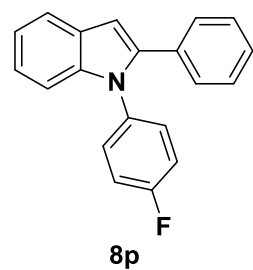


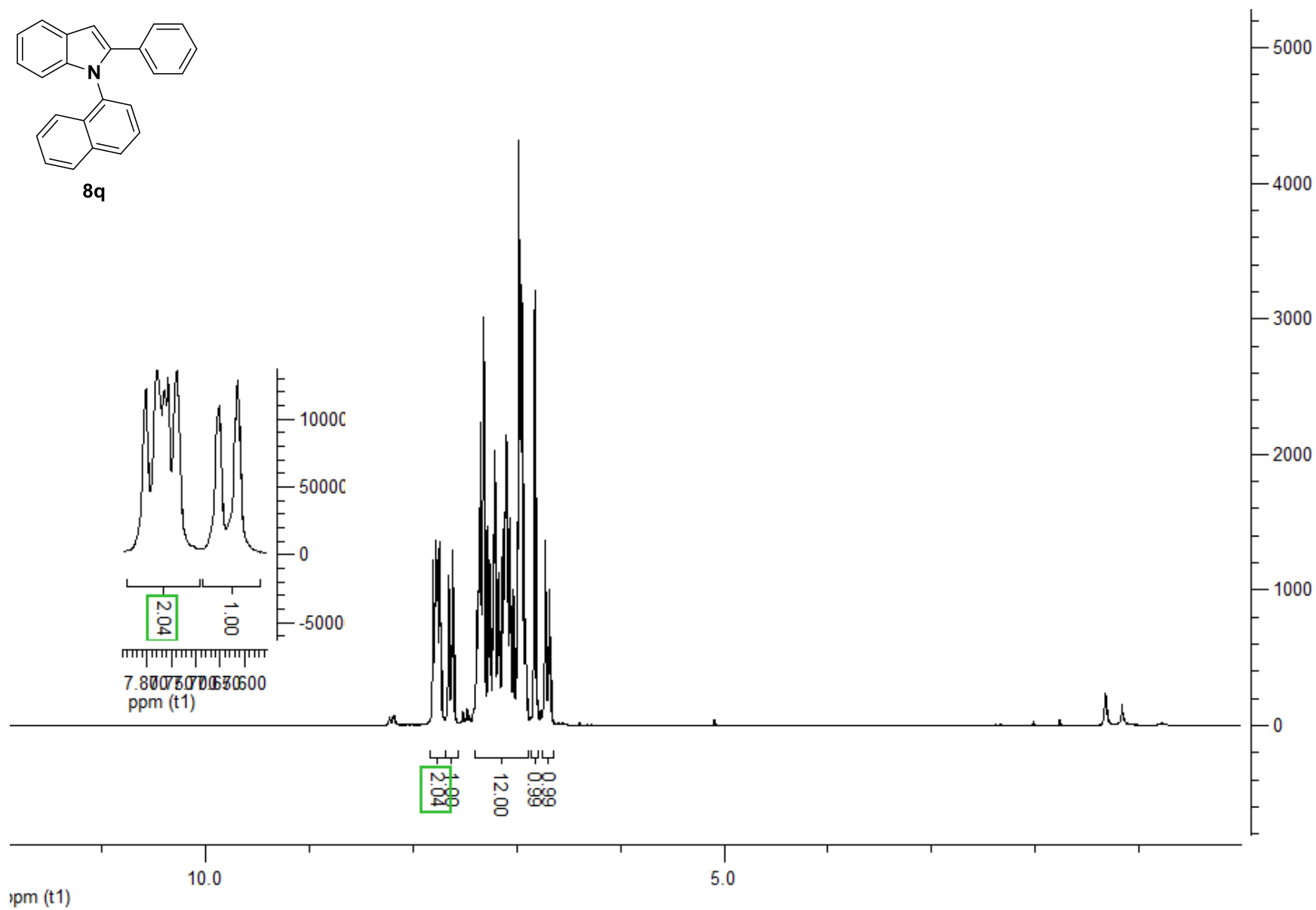
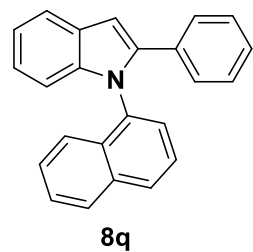


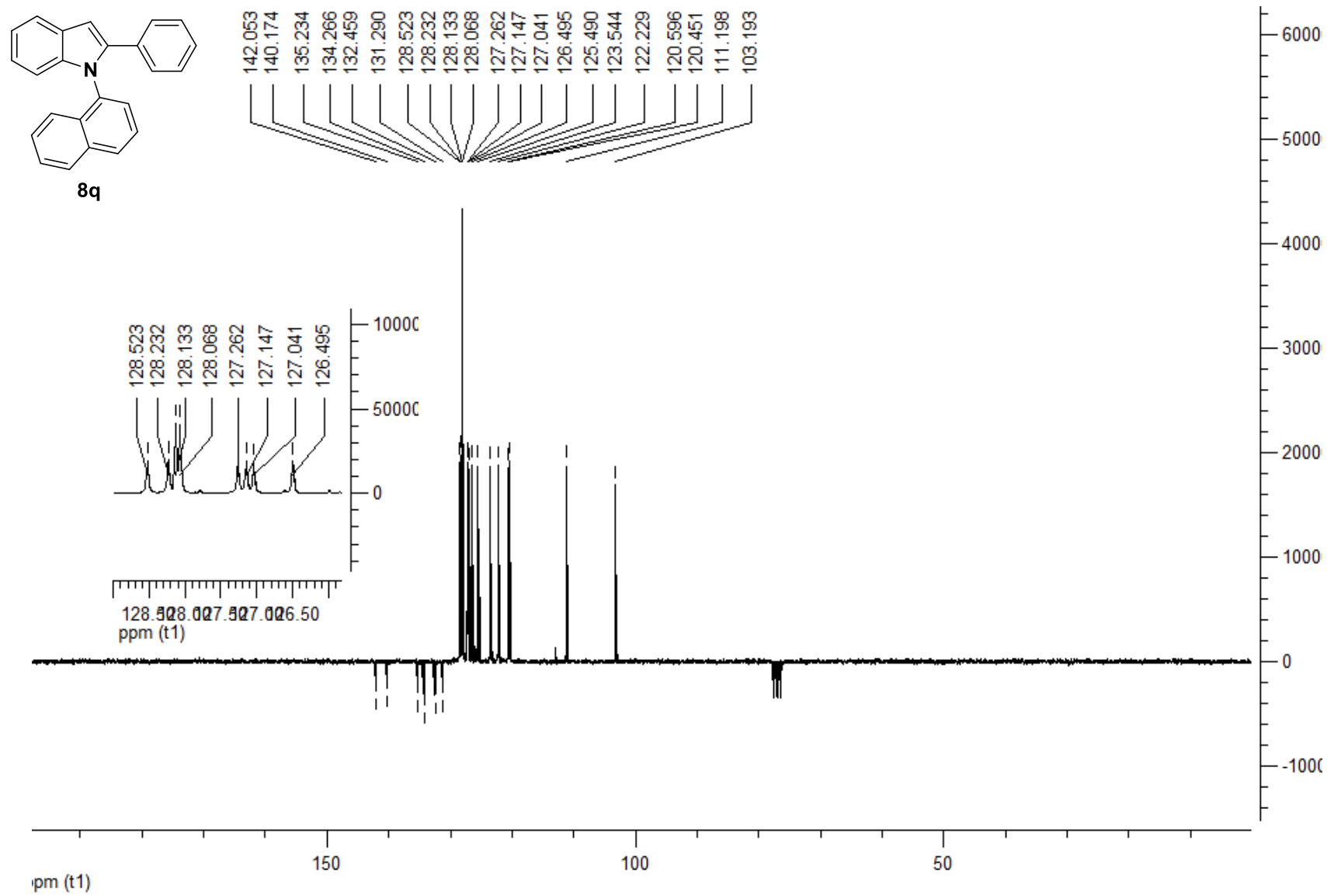


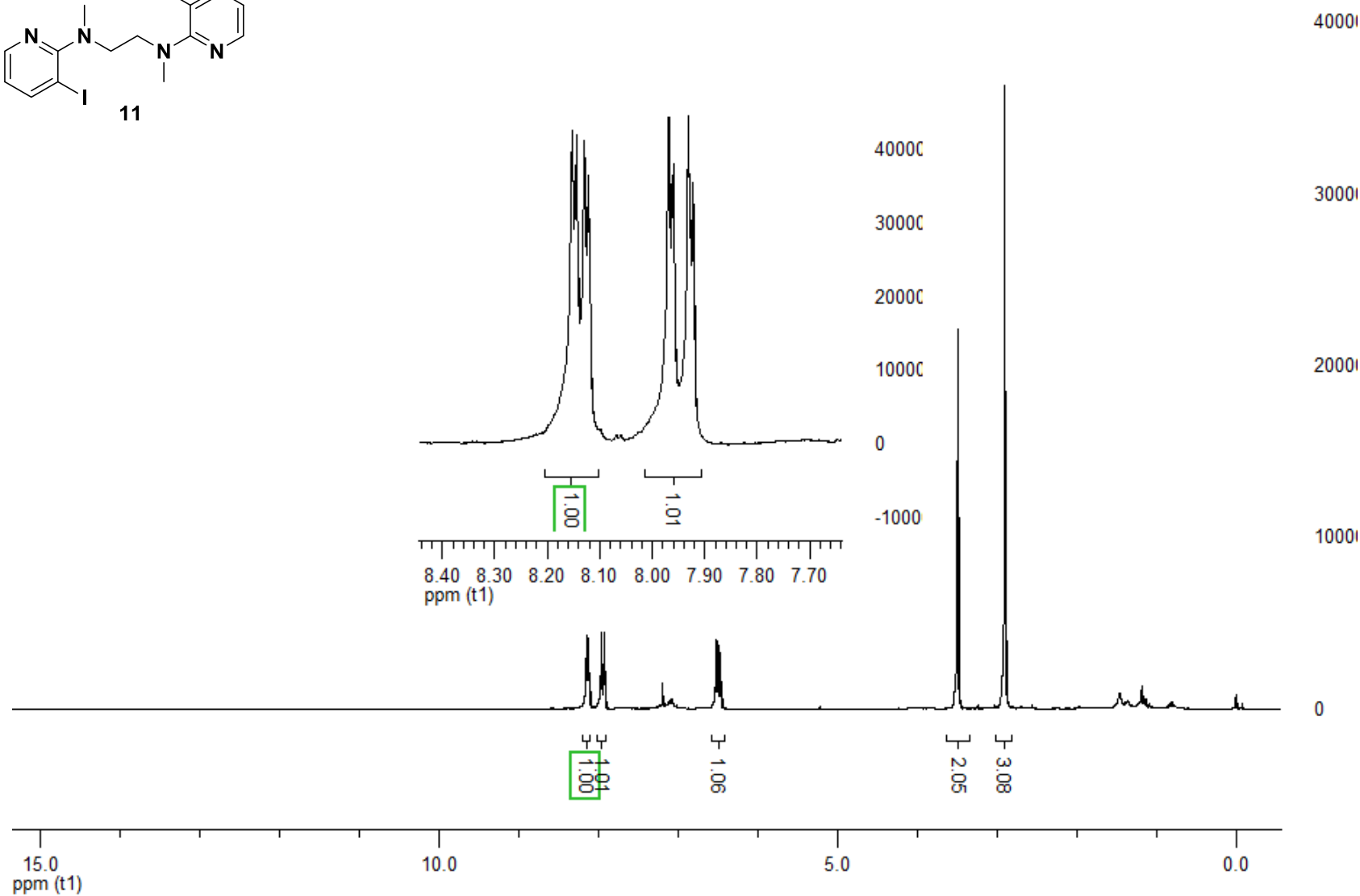
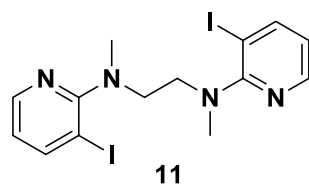


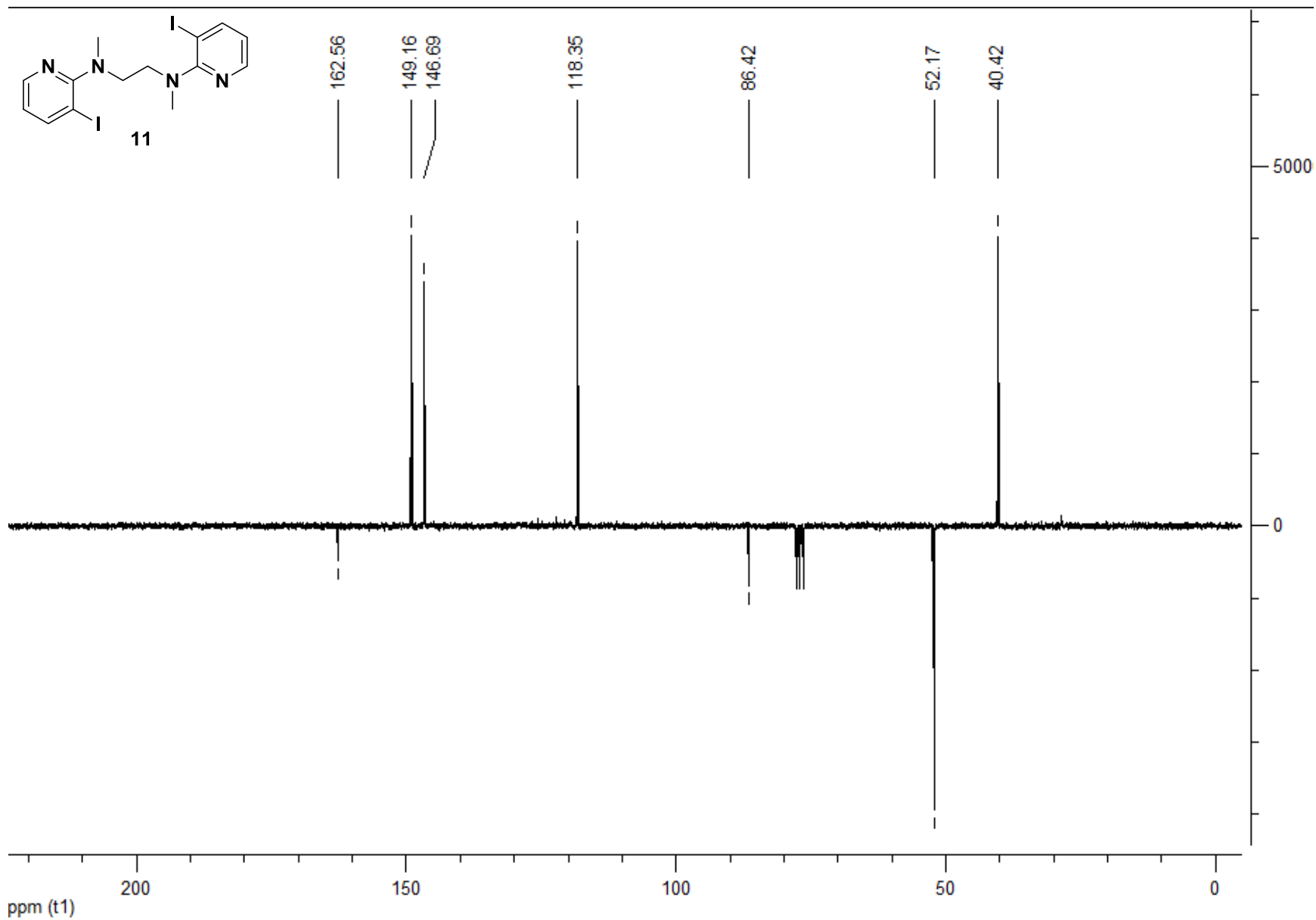


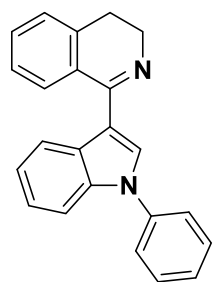












12

