Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Ag(I)-Catalyzed Cyclization of *o*-Alkynylacetophenones Facilitated Through Acetal Formation: Synthesis of C3-Naphthyl Indole Derivatives

Golla Ramesh, Valmuri Srivardhan and Rengarajan Balamurugan*

School of Chemistry, University of Hyderabad, Gachibowli, Hyderabad-500046, India

bala@uohyd.ac.in

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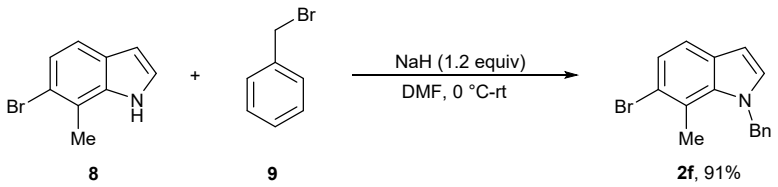
1. General information

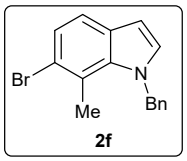
Unless otherwise mentioned, chemicals obtained from commercial suppliers were used without further purification. AgOTf and TMOF were purchased from Sigma-Aldrich, and Avra synthesis respectively, and were used without further purification. All the reactions were performed in oven-dried glassware with magnetic stirring. Dichloromethane (DCM) was dried in the presence of calcium hydride and distilled before use. Reactions were monitored using silica gel plates 60 F_{254} and were visualized with UV light (254 nm), with Seebach stain followed by heating. Column chromatography was carried out using silica gel (100-200 mesh) packed in glass columns. NMR spectra were recorded at 400, 500 MHz (^{1}H) and at 100, 125 MHz (^{13}C), respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $CDCl_3$ (H: δ = 7.26 and C: δ = 77.0 ppm) as internal standard, and coupling constants (J) are indicated in Hz. HRMS were recorded using ESI-TOF techniques.

2. Synthesis of *N*-protected indoles

N-protected indoles **2a-2e**, **2g**, **2h**, and **2o-2q** were synthesized according to the previous reports.[1] The other indole derivative **2f** was synthesized by the following procedure.

Procedure for the synthesis of 1-benzyl-6-bromo-7-methyl-1H-indole 2f





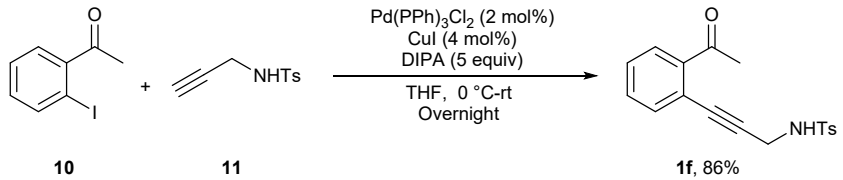
To a stirred solution of 6-bromo-7-methyl-1*H*-indole **8** (120 mg, 0.4 mmol) in DMF (3 mL) was added NaH (22 mg, 0.48 mmol) at 0 ˚C under nitrogen atmosphere. The reaction mixture was brought to room temperature and stirred for 30 minutes before adding benzyl bromide **9** (53 µL, 0.44 mmol) at 0 ˚C. Then, the reaction mixture was allowed to stir overnight at room temperature. After completion of the reaction, the reaction mixture was quenched with saturated aqueous NH_4Cl

solution and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with saturated brine solution, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/EtOAc mixture as eluent) to afford the pure product **2f** as a white solid (137 mg, 91%). mp 98-100 ˚C. R_f = 0.51 (in 5% EtOAc/Hex). IR (neat, cm^{-1}): 1514, 1492, 1447, 1371, 1384, 1353, 1315, 1177, 1101, 1027, 972, 798, 721, 693. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.33 (m, 1H), 7.31-7.26 (m, 4H), 7.06 (d, *J* = 3.2 Hz, 1H), 6.91-6.89 (m, 2H), 6.53 (d, *J* = 3.2 Hz, 1H), 5.57 (s, 2H), 2.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.1, 135.5, 131.3, 129.1, 128.9, 127.4, 125.3, 124.7, 120.7, 119.9, 119.8, 102.1, 52.8, 18.4. HRMS (ESI): calcd. for $[C_{16}H_{15}BrN]$ $[M+H]^+$: 300.0382; found: 300.0381.

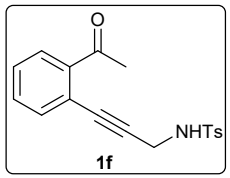
3. Synthesis of *o*-alkynylacetophenones 1

o-Alkynylacetophenones **1a-1e**, **1g**, **1h-1j**, **1l-1m** were synthesized according to the previous reports.[2] Other *o*-alkynylacetophenone derivatives **1f** and **1k** were synthesized by the following procedures.

Procedure for the synthesis of *N*-(3-(2-Acetylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide 1f[3]



10 **11** **1f**, 86%

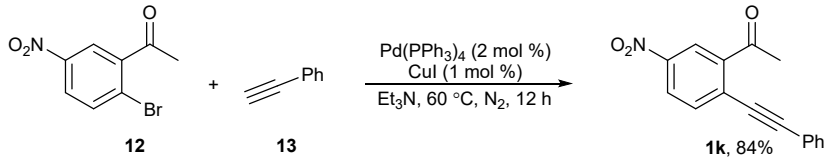


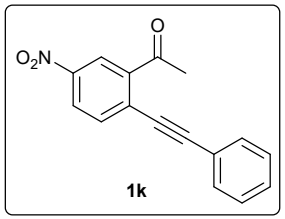
1f

2-Iodoacetophenone **10** (400 mg, 1.62 mmol), and 4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide **11** (405 mg, 1.94 mmol), were dissolved in dry THF (17 mL). Then diisopropylamine (DIPA) (1.2 mL, 8.1 mmol) was added to the above solution under stirring before cooling down to the 0 ˚C. Later, $Pd(PPh)_3Cl_2$ (12 mg, 0.064 mmol), and CuI (22 mg, 0.03 mmol) were added and the reaction mixture was allowed to warm to room temperature and stirred for overnight. After completion of the reaction, the reaction mixture was quenched with saturated aqueous NH_4Cl solution and

extracted with ethyl acetate (3 x 20 mL). The combined organic layers were washed with saturated brine solution, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc mixture as eluent) to afford the pure product **1f** as a yellow solid (461 mg, 86%). mp 103-105 ˚C. R_f = 0.33 (in 40% EtOAc/Hex). IR (neat, cm^{-1}): 3282, 1682, 1594, 1478, 1426, 1322, 1246, 1157, 1067, 964, 812, 767, 662, 608. ^1H NMR (500 MHz, $CDCl_3$): δ 7.79 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.67-7.65 (m, 1H), 7.40-7.34 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.22-7.20 (m, 1H), 4.90 (t, *J* = 5.5 Hz, 1H), 4.10 (d, *J* = 6.0 Hz, 2H), 2.55 (s, 3H), 2.33 (s, 3H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 199.7, 143.6, 140.3, 136.7, 134.1, 131.1, 129.6, 128.5, 128.4, 127.3, 126.3, 120.5, 88.8, 83.6, 33.8, 29.4, 21.3. HRMS (ESI): calcd. for [$C_{18}H_{17}NNaO_3S$] $[M+Na]^+$: 350.0821; found: 350.0827.

Procedure for the synthesis of 1-(5-nitro-2-(phenylethynyl)phenyl)ethan-1-one 1k

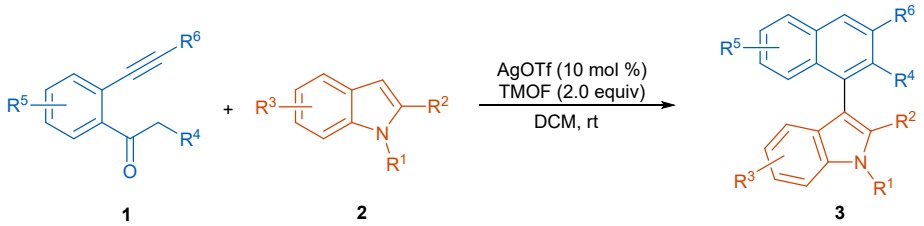




To a stirred solution of 1-(2-bromo-5-nitrophenyl)ethan-1-one **12** (500 mg, 2.05 mmol) in triethylamine (10 mL), $Pd(PPh_3)_4$ (47 mg, 0.041 mmol) was added under nitrogen atmosphere. The resulting solution was stirred for 5 min before adding CuI (4 mg, 0.021 mmol). Then, phenylacetylene **13** (0.27 mL, 2.46 mmol) was added, and the reaction mixture was stirred at 60 ℃ for 12 h. It was then diluted with EtOAc, filtered through a celite pad, and evaporated under reduced pressure. The crude reaction mixture was purified by column chromatography to obtain pure 1-(5-nitro-2-(phenylethynyl)phenyl)ethan-1-one **1k** as a yellow solid (461 mg, 84%). mp = 111-113˚C, R_f = 0.46 (in 10% EtOAc/Hex). IR (neat, cm^{-1}): 3103, 2214, 1686, 1599, 1574, 1509, 1490, 1340, 1294, 1259, 1109, 1061, 910, 890, 845, 743, 685. ^1H NMR (500 MHz, $CDCl_3$): *δ* 8.61 (d, *J* = 2.0 Hz, 1H), 8.31 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.59-7.57 (m, 2H), 7.45-7.39 (m, 3H), 2.83

(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6, 146.7, 141.3, 134.9, 131.8, 129.8, 128.6, 128.0, 125.5, 123.9, 121.8, 100.5, 87.1, 29.7. HRMS (ESI): calcd. for $[C_{16}H_{12}NO_3]$ $[M+H]^+$: 266.0812; found: 266.0813.

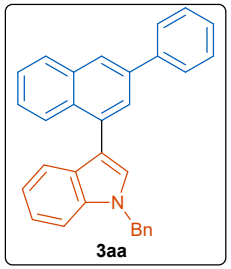
4. General procedure for the synthesis of C3-naphthyl indole derivatives 3



To a stirred solution of *o*-alkynylacetophenone **1** (1.2 equiv), *N*-protected indole **2** (0.4 mmol, 1.0 equiv) and TMOF (2.0 equiv) in DCM (4 mL) was added AgOTf (10 mol %) at room temperature. The reaction mixture was stirred at the same temperature. After completion of the reaction, the reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/EtOAc mixture as eluent) to afford the pure product **3**.

5. Characterization data of compounds 3, 4aa, 5aa, 5ak, 6k, and 7

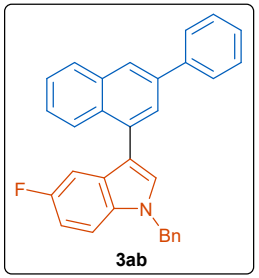
1-Benzyl-3-(3-phenylnaphthalene-1-yl)-1*H*-indole 3aa



3aa

White solid (140 mg, 85%). mp 88-90 ˚C. R_f = 0.5 (in 5% EtOAc/Hex). IR (neat, cm^{-1}): 1549, 1493, 1451, 1383, 1337, 1257, 1167, 1074, 1014, 883, 763, 736, 693. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (d, J = 8.5 Hz, 1H), 8.08 (s, 1H), 8.49 (d, J = 8.0 Hz, 1H), 7.94-7.93 (m, 1H), 7.81-7.79 (m, 2H), 7.61 (dd, J = 8.0, 0.5 Hz, 1H), 7.55 (d, J = 7.5 Hz, 1H), 7.52-7.49 (m, 2H), 7.45-7.40 (m, 3H), 7.38-7.35 (m, 3H), 7.33-7.28 (m, 2H), 7.26 (d, J = 7.0 Hz, 2H), 7.18-7.15 (m, 1H), 5.46 (s, 2H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 141.1, 138.2, 137.3, 136.6, 134.4, 133.5, 131.7, 128.9, 128.8, 128.6, 128.4, 127.7, 127.5, 127.4, 127.3, 127.0, 126.4, 126.1, 125.8, 124.9, 122.2, 120.6, 119.9, 115.6, 110.0, 50.3. HRMS (ESI): calcd. for $[C_{31}H_{24}N]$ $[M+H]^+$: 410.1903; found: 410.1905.

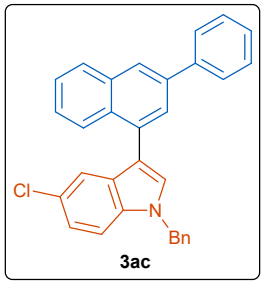
1-Benzyl-5-fluoro-3-(3-phenylnaphthalene-1-yl)-1*H*-indole 3ab



3ab

White solid (121 mg, 71%). mp 140-142 ˚C. R_f = 0.38 (in 5% EtOAc/Hex). IR (neat, cm^{-1}): 1542, 1480, 1447, 1246, 1181, 955, 895, 853, 790, 761, 693, 651. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.5 Hz, 2H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 2.0 Hz, 1H), 7.78 (dd, *J* = 8.5, 1.0 Hz, 2H), 7.55-7.52 (m, 1H), 7.51-7.48 (m, 2H), 7.45-7.42 (m, 1H), 7.42 (s, 1H), 7.39-7.38 (m, 1H), 7.37-7.35 (m, 2H), 7.33-7.28 (m, 2H), 7.26-7.20 (m, 3H), 7.00 (td, *J* = 9.5, 2.5 Hz, 1H), 5.43 (s, 2H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 159.1, 157.2, 141.0, 138.2, 136.9, 134.3, 133.1, 132.9, 131.5, 129.2, 128.9, 128.8, 128.6, 127.8, 127.4, 127.3, 127.2, 126.8, 126.1 (d, J_{CF} = 30 Hz), 125.9, 125.0, 115.5 (d, J_{CF} = 20 Hz), 110.7 (d, J_{CF} = 15 Hz), 110.6, 110.5, 105.4, 105.2, 50.5. ^{19}F NMR (470 MHz, $CDCl_3$), -124.0. HRMS (ESI): calcd. for $[C_{31}H_{23}FN]$ $[M+H]^+$: 428.1809; found: 428.1809.

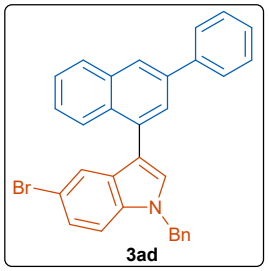
1-Benzyl-5-chloro-3-(3-phenylnaphthalene-1-yl)-1*H*-indole 3ac



3ac

White solid (130 mg, 73%). mp 158-160 ˚C. R_f = 0.41 (in 5% EtOAc/Hex). IR (neat, cm^{-1}): 1595, 1494, 1467, 1349, 1267, 1169, 1065, 1028, 884, 851, 747, 693, 642. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (s, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 1.5 Hz, 1H), 7.77 (d, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 7.0 Hz, 1H), 7.51-7.48 (m, 3H), 7.45-7.42 (m, 1H), 7.41-7.39 (m, 1H), 7.37 (s, 1H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.30-7.29 (m, 2H), 7.23-7.19 (m, 3H), 5.42 (s, 2H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 140.9, 138.2, 136.8, 134.9, 134.3, 132.7, 131.6, 129.3, 128.9, 128.8, 128.6, 127.9, 127.4(4), 127.4(0), 127.3, 126.8, 126.2, 126.0, 125.9, 125.8, 125.2, 122.5, 119.8, 115.2, 111.0, 50.4. HRMS (ESI): calcd. for $[C_{31}H_{23}ClN]$ $[M+H]^+$: 444.1514; found: 444.1514.

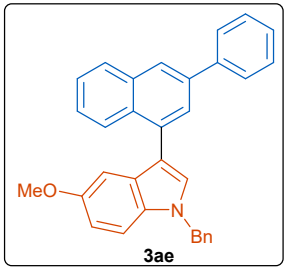
1-Benzyl-5-bromo-3-(3-phenylnaphthalene-1-yl)-1*H*-indole 3ad



3ad

White solid (156 mg, 80%). mp 64-66 ˚C. R_f = 0.48 (in 5% EtOAc/Hex). IR (neat, cm^{-1}): 1595, 1493, 1466, 1349, 1266, 1168, 1027, 884, 789, 749, 693. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 1.6 Hz, 1H), 7.99 (dd, *J* = 13.6, 8.4 Hz, 2H), 7.83 (d, *J* = 2.0 Hz, 1H), 7.78-7.75 (m, 2H), 7.65 (d, *J* = 2.0 Hz, 1H), 7.55-7.47 (m, 3H), 7.45-7.40 (m, 1H), 7.39-7.35 (m, 3H), 7.34-7.30 (m, 3H), 7.25 (d, *J* = 8.4 Hz, 1H), 7.21 (d, *J* = 6.8 Hz, 2H), 5.42 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 138.2, 136.8, 135.1, 134.3, 132.6, 131.6, 130.0, 128.9, 128.8, 128.7, 128.6, 127.9, 127.4, 127.3, 126.8, 126.2, 126.0(9), 126.0(0), 125.2, 125.1, 122.9, 115.1, 113.4, 111.4, 50.4. HRMS (ESI): calcd. for $[C_{31}H_{23}BrN]$ $[M+H]^+$: 488.1008; found: 488.1008.

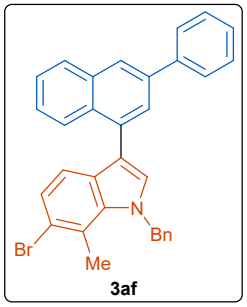
1-Benzyl-5-methoxy-3-(3-phenylnaphthalene-1-yl)-1*H*-indole 3ae



3ae

White solid (159 mg, 90%). mp 62-64 ˚C. R_f = 0.4 (in 5% EtOAc/Hex). IR (neat, cm^{-1}): 1482, 1448, 1338, 1282, 1213, 1175, 1040, 886, 790, 748, 694. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.5 Hz, 1H), 8.06 (d, *J* = 1.5 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 2.0 Hz, 1H), 7.79-7.77 (m, 2H), 7.54-7.51 (m, 1H), 7.50-7.47 (m, 2H), 7.44-7.40 (m, 1H), 7.39 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.36 (dt, *J* = 3.5, 1.0 Hz, 1H), 7.35-7.33 (m, 2H), 7.30-7.27 (m, 2H), 7.24-7.22 (m, 2H), 6.98 (d, *J* = 2.0 Hz, 1H), 6.91 (dd, *J* = 9.0, 2.5 Hz, 1H), 5.41 (s, 2H), 3.71 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.4, 141.0, 138.2, 137.3, 134.3, 133.6, 131.7, 131.6, 128.8, 128.6, 128.5, 128.3, 127.7, 127.4, 127.3, 127.2, 126.8, 126.5, 126.1, 125.7, 124.8, 115.1, 112.6, 110.8, 101.9, 55.8, 50.4. HRMS (ESI): calcd. for $[C_{32}H_{26}NO]$ $[M+H]^+$: 440.2009; found: 440.2009.

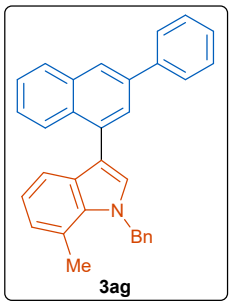
1-Benzyl-6-bromo-7-methyl-3-(3-phenylnaphthalen-1-yl)-1*H*-indole 3af



3af

White solid (156 mg, 77%). mp 164-166 ˚C. R_f = 0.58 (in 10% EtOAc/Hex). IR (neat, cm^{-1}): 1599, 1493, 1448, 1410, 1351, 1171, 1014, 963, 877, 820, 790, 757, 689. ^1H NMR (500 MHz, $CDCl_3$): δ 8.06 (d, J = 1.5 Hz, 1H), 8.01 (d, J = 8.5 Hz, 1H), 7.97 (d, J = 8.5 Hz, 1H), 7.85 (d, J = 2.0 Hz, 1H), 7.76 (dt, J = 8.0, 1.5 Hz, 2H), 7.53-7.47 (m, 3H), 7.42-7.41 (m, 1H), 7.39 (dt, J = 7.5, 1.0 Hz, 1H), 7.36-7.33 (m, 2H), 7.31-7.28 (m, 3H), 7.21 (dd, J = 8.5, 0.5 Hz, 1H), 7.05 (d, J = 7.0 Hz, 2H), 5.70 (s, 2H), 2.69 (s, 3H). ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 140.9, 138.9, 138.1, 135.7, 134.3, 132.7, 131.6, 130.6, 129.0, 128.8, 128.7, 128.6, 127.5, 127.49, 127.43, 127.3, 126.2, 126.1, 125.8, 125.4, 125.1, 124.9, 121.0, 120.3, 119.3, 115.6, 52.9, 18.4. HRMS (ESI): calcd. for $[C_{32}H_{25}BrN]$ $[M+H]^+$: 502.1165; found: 502.1164.

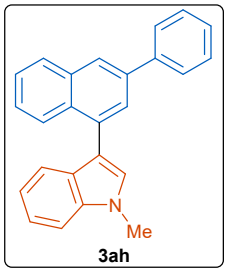
1-Benzyl-7-methyl-3-(3-phenylnaphthalen-1-yl)-1*H*-indole 3ag



3ag

White solid (136 mg, 80%). mp 102-104 ˚C. R_f = 0.57 (in 10% EtOAc/Hex). IR (neat, cm^{-1}): 1597, 1493, 1448, 1414, 1375, 1169, 1074, 1028, 883, 812, 745, 693. ^1H NMR (MHz, $CDCl_3$): δ 8.12 (d, J = 8.5 Hz, 1H), 8.08 (s, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 2.0 Hz, 1H), 7.79 (dt, J = 8.0, 1.0 Hz, 2H), 7.55-7.49 (m, 3H), 7.45-7.43 (m, 1H), 7.42 (dt, J = 7.0, 1.5 Hz, 1H), 7.39 (dt, J = 7.5, 1.5 Hz, 1H), 7.35 (tt, J = 7.0, 1.0 Hz, 2H), 7.31 (s, 1H), 7.30-7.27 (s, 1H), 7.08 (d, J = 7.5 Hz, 2H), 7.04 (t, J = 7.0 Hz, 1H), 6.99 (d, J = 7.0 Hz, 1H), 5.71 (s, 2H), 2.64 (s, 3H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 141.0, 139.4, 138.1, 135.2, 134.3, 133.4, 131.7, 129.6, 129.3, 128.9, 128.8, 128.5, 127.4, 127.3, 126.4, 126.1, 125.7, 125.5, 125.0, 124.8, 121.3, 120.1, 118.6, 115.5, 52.3, 19.6. HRMS (ESI): calcd. for $[C_{32}H_{26}N]$ $[M+H]^+$: 424.2060; found: 424.2060.

1-Methyl-3-(3-phenylnaphthalen-1-yl)-1*H*-indole 3ah

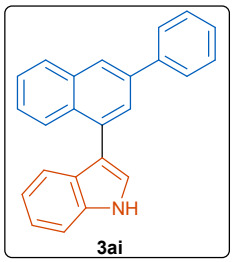


3ah

White solid (100 mg, 75%). mp 92-94 ˚C. R_f = 0.58 (in 5% EtOAc/Hex). IR (neat, cm^{-1}): 1594, 1472, 1355, 1227, 1154, 1114, 1064, 1012, 883, 735, 694. ^1H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 8.4 Hz, 1H), 8.06 (s, 1H), 7.98

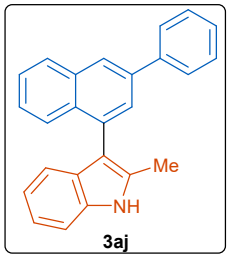
(d, J = 8.0 Hz, 1H), 7.90 (d, J = 1.6 Hz, 1H), 7.80-7.78 (m, 2H), 7.58 (d, J = 8.0 Hz, 1H), 7.55-7.49 (m, 3H), 7.48-7.43 (m, 2H), 7.42-7.39 (m, 1H), 7.37-7.33 (m, 1H), 7.31 (s, 1H), 7.17-7.13 (m, 1H), 3.93 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 141.1, 138.1, 136.9, 134.3, 133.6, 131.7, 128.8, 128.5, 128.3, 128.0, 127.4, 127.2(8), 127.2(4), 126.4, 126.1, 125.6, 124.7, 121.9, 120.4, 119.6, 114.9, 109.4, 32.8. HRMS (ESI): calcd. for $[C_{25}H_{20}N]$ $[M+H]^+$: 334.1590; found: 334.1593.

3-(3-Phenylnaphthalen-1-yl)-1*H*-indole 3ai



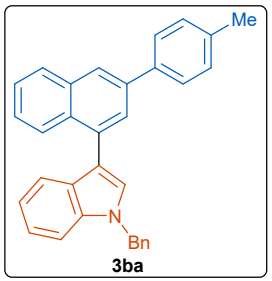
White solid (80 mg, 60%). mp 95-97 ˚C. R_f = 0.30 (in 10% EtOAc/Hex). IR (neat, cm^{-1}): 3412, 1594, 1492, 1452, 1418, 1243, 1092, 884, 739, 694. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (bs, 1H), 8.11-8.08 (m, 2H), 7.99 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 2.0 Hz, 1H), 7.80-7.78 (m, 2H), 7.57 (d, J = 8.0 Hz, 1H), 7.56-7.53 (m, 1H), 7.52-7.48 (m, 3H), 7.44-7.41 (m, 2H), 7.38 (dt, J = 7.2, 2.0 Hz, 1H), 7.32-7.28 (m, 1H), 7.18-7.14 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 141.0, 138.1, 136.0, 134.3, 133.5, 131.7, 128.8, 128.5, 127.6, 127.4, 127.3(4), 127.3(3), 126.3, 126.1, 125.7, 124.9, 123.6, 122.4, 120.3, 120.1, 116.4, 111.2. HRMS (ESI): calcd. for $[C_{24}H_{18}N]$ $[M+H]^+$: 320.1434; found: 320.1436.

2-Methyl-3-(3-phenylnaphthalen-1-yl)-1*H*-indole 3aj



Yellow liquid (87 mg, 65%). R_f = 0.33 (in 20% EtOAc/Hex). IR (neat, cm^{-1}): 3399, 1595, 1494, 1457, 1324, 1303, 1244, 1212, 1011, 883, 741, 694. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (bs, 1H), 8.09 (s, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.81-7.77 (m, 4H), 7.53-7.46 (m, 3H), 7.42-7.36 (m, 3H), 7.30 (d, J = 8.0 Hz, 1H), 7.20 (dt, J = 7.5, 1.5 Hz, 1H), 7.08-7.04 (m, 1H), 2.37 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 141.1, 138.1, 135.2, 134.2, 133.5, 132.7, 132.1, 129.3, 128.8, 128.5, 128.1, 127.4, 127.3, 126.6, 126.0, 125.6, 124.9, 121.4, 119.8, 119.3, 112.8, 110.2, 12.5. HRMS (ESI): calcd. for $[C_{25}H_{20}N]$ $[M+H]^+$: 334.1590; found: 334.1603.

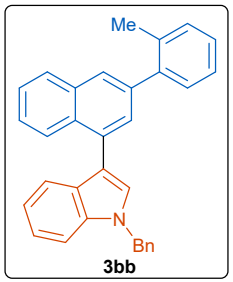
1-Benzyl-3-(3-(p-tolyl)naphthalen-1-yl)-1*H*-indole 3ba



3ba

White solid (140 mg, 82%). mp 66–68 °C. R_f = 0.59 (in 10% EtOAc/Hex). IR (neat, cm^{-1}): 1597, 1495, 1464, 1336, 1255, 1168, 1016, 887, 813, 731, 698. ^1H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 1.6 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 2.0 Hz, 1H), 7.68 (dt, *J* = 8.0, 2.4 Hz, 2H), 7.59 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.53-7.49 (m, 1H), 7.42-7.40 (m, 2H), 7.38-7.33 (m, 3H), 7.31-7.28 (m, 3H), 7.26-7.24 (m, 3H), 7.16-7.12 (m, 1H), 5.45 (s, 2H), 2.42 (s, 3H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 138.1, 138.0, 137.2, 137.0, 136.5, 134.3, 133.3, 131.5, 129.5, 128.8, 128.5, 128.3, 127.7, 127.6, 127.2, 126.8, 126.3, 126.0, 125.5, 124.4, 122.1, 120.5, 119.8, 115.5, 109.9, 50.1, 21.1. HRMS (ESI): calcd. for $[C_{32}H_{26}N]$ $[M+H]^+$: 424.2060; found: 424.2061.

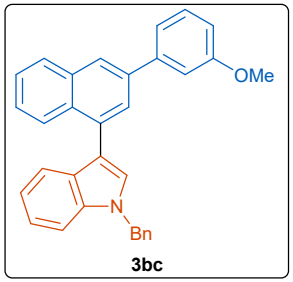
1-benzyl-3-(3-(*o*-tolyl)naphthalen-1-yl)-1*H*-indole 3bb



3bb

Yellow liquid (136 mg, 80%). R_f = 0.41 (in 5% EtOAc/Hex). IR (neat, cm^{-1}): 1595, 1492, 1463, 1336, 1168, 1015, 905, 889, 725, 647. ^1H NMR (500 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 1.5 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.54-7.51 (m, 1H), 7.45-7.41 (m, 1H), 7.40-7.39 (m, 2H), 7.36-7.30 (m, 6H), 7.29-7.27 (m, 2H), 7.24-7.23 (m, 2H), 7.15-7.12 (m, 1H), 5.44 (s, 2H), 2.39 (s, 3H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 141.8, 139.2, 137.2, 136.6, 135.5, 133.9, 132.6, 131.3, 130.3, 130.0, 129.4, 128.8, 128.3(7), 128.3(3), 127.7(5), 127.7(2), 127.3, 126.9, 126.8, 126.4, 125.9, 125.7, 125.6, 122.1, 120.5, 119.8, 115.5, 109.9, 50.2, 20.6. HRMS (ESI): calcd. for $[C_{32}H_{26}N]$ $[M+H]^+$: 424.2060; found: 424.2060.

1-benzyl-3-(3-(3-methoxyphenyl)naphthalen-1-yl)-1*H*-indole 3bc

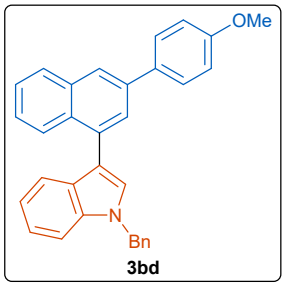


3bc

Yellow liquid (136 mg, 77%). R_f = 0.39 (in 5% EtOAc/Hex). IR (neat, cm^{-1}): 1595, 1490, 1383, 1247, 1169, 1041, 780, 730, 693, 618. ^1H NMR (500 MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.0 Hz, 1H), 8.04 (s, 1H), 7.96 (d, *J* =

8.5 Hz, 1H), 7.87 (d, J = 2.0 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.52-7.49 (m, 1H), 7.41-7.38 (m, 3H), 7.37-7.36 (m, 2H), 7.34-7.32 (m, 2H), 7.29-7.28 (m, 2H), 7.25-7.23 (m, 3H), 7.12 (t, J = 7.0 Hz, 1H), 6.93-6.91 (m, 1H), 5.44 (s, 2H), 3.88 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.9, 142.6, 138.0, 137.2, 136.5, 134.3, 133.4, 131.7, 129.7, 128.8, 128.5, 128.3, 127.7, 127.3, 126.9, 126.4, 126.1, 125.7, 124.9, 122.1, 120.5, 119.9(8), 119.9(2), 115.5, 113.1, 112.8, 109.9, 55.3, 50.2. HRMS (ESI): calcd. for $[C_{32}H_{26}NO]$ $[M+H]^+$: 440.2009; found: 440.2010.

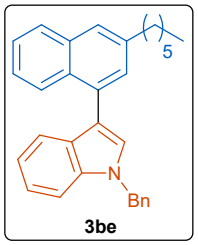
1-Benzyl-3-(3-(4-methoxyphenyl)naphthalen-1-yl)-1*H*-indole 3bd



3bd

Yellow liquid (152 mg, 86%). R_f = 0.31 (in 5% EtOAc/Hex). IR (neat, cm^{-1}): 1606, 1512, 1462, 1244, 1029, 827, 730, 698. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (d, J = 8.0 Hz, 1H), 8.00 (s, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.86 (s, 1H), 7.71 (d, J = 8.5 Hz, 2H), 7.58 (d, J = 7.5 Hz, 1H), 7.50 (t, J = 7.0 Hz, 1H), 7.40 (t, J = 8.0 Hz, 1H), 7.36 (s, 1H), 7.34 (d, J = 7.0 Hz, 1H), 7.29 (t, J = 7.0 Hz, 1H), 7.26-7.24 (m, 3H), 7.13 (t, J = 7.5 Hz, 1H), 7.02 (d, J = 8.5 Hz, 2H), 5.45 (s, 2H), 3.87 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.1, 137.7, 137.2, 136.5, 134.4, 133.5, 133.3, 131.3, 128.7, 128.4, 128.3, 127.7, 127.1, 126.8, 126.3, 126.0, 125.4, 124.0, 122.1, 120.5, 119.8, 115.5, 114.2, 109.9, 55.2, 50.1. HRMS (ESI): calcd. for $[C_{32}H_{26}NO]$ $[M+H]^+$: 440.2009; found: 440.2009.

1-Benzyl-3-(3-hexylnaphthalen-1-yl)-1*H*-indole 3be

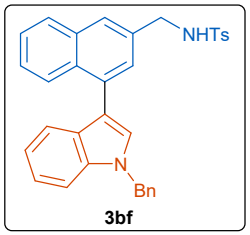


3be

Yellow liquid (122 mg, 73%). R_f = 0.7 (in 10% EtOAc/Hex). IR (neat, cm^{-1}): 1599, 1543, 1495, 1463, 1386, 1352, 1252, 1168, 1075, 1014, 955, 877, 783, 737, 694, 616. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (d, J = 8.5 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.63 (s, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 1.5 Hz, 1H), 7.47-7.44 (m, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.35 (tt, J = 7.0, 1.5 Hz, 3H), 7.33-7.26 (m, 3H), 7.25-7.23 (m, 3H), 7.14-7.11 (m, 1H), 5.44 (s, 2H), 2.81 (t, J = 7.5 Hz, 2H), 1.78-1.72 (m, 2H), 1.45-1.39 (m, 2H), 1.37-1.31 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 140.1, 137.4, 136.5, 134.3, 132.6, 130.9, 129.3, 128.8, 127.7, 127.6(9), 127.6(0), 126.9, 126.3, 125.6,

125.4, 124.8, 122.0, 120.5, 119.7, 115.7, 109.8, 50.2, 36.1, 31.7, 31.3, 29.1, 22.6. 14.0. HRMS (ESI): calcd. for $[C_{31}H_{32}N]$ $[M+H]^+$: 418.2529; found: 418.2529.

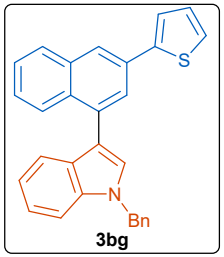
N-((4-(1-benzyl-1*H*-indol-3-yl)naphthalen-2-yl)methyl)-4-methylbenzenesulfonamide 3bf



3bf

Yellow liquid (143 mg, 69%). R_f = 0.28 (in 20% EtOAc/Hex). IR (neat, cm^{-1}): 3276, 3029, 2923, 1598, 1494, 1464, 1452, 1323, 1153, 1091, 880, 812, 739, 663, 547. ^1H NMR (500 MHz, $CDCl_3$): δ 8.03 (d, J = 8.5 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 2H), 7.61 (s, 1H), 7.47 (t, J = 7.0 Hz, 1H), 7.41-7.36 (m, 5H), 7.34 (d, J = 7.5 Hz, 2H), 7.31-7.28 (m, 2H), 7.22 (t, J = 7.5 Hz, 5H), 7.10 (t, J = 7.5 Hz, 1H), 5.42 (s, 2H), 4.73 (t, J = 6.0 Hz, 1H), 4.33 (d, J = 6.5 Hz, 2H), 2.32 (s, 3H). ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 143.4, 137.2, 136.9, 136.5, 133.8, 133.7, 133.2, 131.9, 129.6, 128.8, 128.1, 127.7, 127.6, 127.2, 127.1, 126.9, 126.5, 126.1, 125.9, 125.7, 122.2, 120.4, 119.9, 115.1, 109.9, 50.2, 47.4, 21.3. HRMS (ESI): calcd. for $[C_{33}H_{29}N_2O_2S]$ $[M+H]^+$: 517.1944; found: 517.1945.

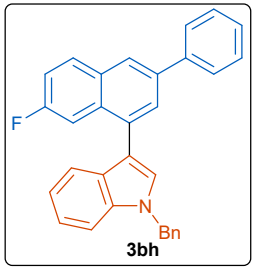
1-Benzyl-3-(3-(thiophen-2-yl)naphthalen-1-yl)-1*H*-indole 3bg



3bg

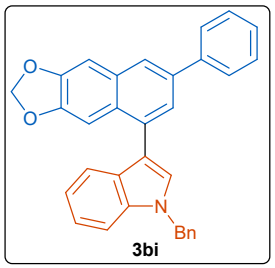
Yellow liquid (130 mg, 78%). R_f = 0.4 (in 5% EtOAc/Hex). IR (neat, cm^{-1}): 1596, 1542, 1494, 1463, 1385, 1352, 1234, 1167, 1028, 1012, 880, 853, 821, 729, 693. ^1H NMR (500 MHz, $CDCl_3$): δ 8.07-8.06 (m, 2H), 7.92 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 1.5 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.52-7.48 (m, 1H), 7.46 (dd, J = 3.5 1.0 Hz, 1H), 7.42-7.38 (m, 2H), 7.37 (s, 1H), 7.37-7.36 (m, 2H), 7.33-7.32 (m, 1H), 7.30-7.28 (m, 1H), 7.26-7.25 (m, 3H), 7.16-7.12 (m, 2H), 5.45 (s, 2H). ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 144.5, 137.2, 136.5, 134.3, 133.6, 131.8, 131.4, 128.8, 128.3, 128.2, 128.0, 127.7, 126.9, 126.4, 126.3, 126.0, 125.7, 124.9, 123.4, 123.3, 122.2, 120.4, 119.9, 115.2, 109.9, 50.2. HRMS (ESI): calcd. for $[C_{29}H_{22}NS]$ $[M+H]^+$: 416.1467; found: 416.1472.

1-Benzyl-3-(7-fluoro-3-phenylnaphthalen-1-yl)-1*H*-indole 3bh



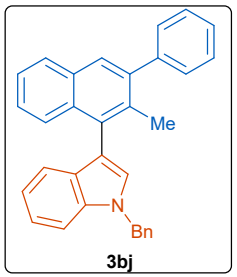
White solid (130 mg, 76%). mp 60–62 ˚C. R_f = 0.5 (in 10% EtOAc/Hex). IR (neat, cm^{-1}): 1598, 1543, 1497, 1451, 1386, 1328, 1241, 1173, 1075, 958, 915, 881, 805, 760, 725, 693. ^1H NMR (400 MHz, $CDCl_3$): δ. 8.04 (s, 1H), 7.98-7.93 (m, 2H), 7.77-7.74 (m, 3H), 7.58 (dt, J = 7.6, 1.2 Hz, 1H), 7.51-7.47 (m, 2H), 7.43-7.38 (m, 2H), 7.37-7.34 (m, 3H), 7.33-7.25 (m, 6H), 7.18-7.14 (m, 1H), 5.46 (s, 2H). ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 160.8 (d, J = 244.0 Hz), 140.8, 137.5 (d, J = 2.5 Hz), 137.1, 136.6, 132.8 (dd, J = 50, 5 Hz), 131.3, 130.9, 130.8, 128.8(7), 128.8(5), 128.1(9), 128.1(0), 127.7, 127.6, 127.3, 126.9, 124.6, 122.3, 120.2 (d, J = 21.2 Hz), 116.4 (d, J = 26.2 Hz), 115.0, 110.0, 109.8 (d, J = 21.2 Hz), 50.2. ^{19}F NMR (470 MHz, $CDCl_3$): δ -114.0. HRMS (ESI): calcd. for $[C_{31}H_{23}FN]$ $[M+H]^+$: 428.1809; found: 428.1809.

1-Benzyl-3-(7-phenylnaphtho[2,3-d][1,3]dioxol-5-yl)-1*H*-indole 3bi



Yellow liquid (146 mg, 80%). R_f = 0.27 (in 5% EtOAc/Hex). IR (neat, cm^{-1}): 2922, 1603, 1494, 1455, 1278, 1231, 1173, 1035, 951, 882, 737, 693. ^1H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 2.0 Hz, 1H), 7.74-7.72 (m, 3H), 7.56 (dt, J = 8.0, 1.0 Hz, 1H), 7.48-7.44 (m, 2H), 7.40 (d, J = 9.0 Hz, 2H), 7.37-7.33(7) (m, 3H), 7.33 (s, 1H), 7.31-7.27 (m, 1H), 7.25-7.23 (m, 3H), 7.15-7.12 (m, 1H), 6.02 (s, 2H), 5.44 (s, 2H). ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 147.7, 147.6, 141.1, 137.3, 136.8, 136.5, 132.6, 131.5, 128.9, 128.8, 128.7, 128.2, 127.7, 127.4, 127.2, 127.0, 126.9, 126.0, 124.1, 122.1, 120.5, 119.9, 115.9, 109.9, 104.3, 102.9, 101.0, 50.2. HRMS (ESI): calcd. for $[C_{32}H_{24}NO_2]$ $[M+H]^+$: 454.1802; found: 458.1802.

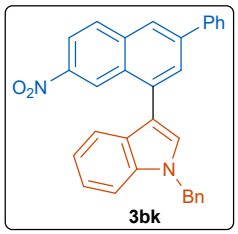
1-Benzyl-3-(2-methyl-3-phenylnaphthalen-1-yl)-1*H*-indole 3bj



3bj

White solid (105 mg, 62%). mp 62–64 ˚C. R_f = 0.35 (in 5% EtOAc/Hex). IR (neat, cm^{-1}): 1595, 1493, 1464, 1451, 1422, 1385, 1349, 1259, 1212, 1171, 1149, 908, 886, 734, 693. ^1H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.78 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.49-7.46 (m, 4H), 7.44-7.36 (m, 4H), 7.35-7.30 (m, 3H), 7.29-7.26 (m, 1H), 7.25-7.22 (m, 3H), 7.18 (s, 1H), 7.10-7.06 (m, 1H), 5.47 (s, 2H), 2.18 (s, 3H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 142.7, 141.2, 137.6, 136.5, 133.9, 133.5, 131.8, 131.4, 129.4, 128.9, 128.8, 128.0(9), 128.0(4), 127.9, 127.7, 127.6, 126.8, 126.7, 126.6, 125.6, 125.1, 121.9, 120.5, 119.6, 114.2, 109.8, 50.1, 19.4. HRMS (ESI): calcd. for $[C_{32}H_{26}N]$ $[M+H]^+$: 424.2060; found: 424.2061.

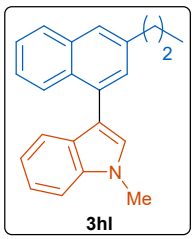
1-Benzyl-3-(7-nitro-3-phenylnaphthalen-1-yl)-1*H*-indole derivative 3bk



3bk

Yellow solid (132 mg, 73%). mp 160-162 ˚C. R_f = 0.40 (in 10% EtOAc/Hex). IR (neat, cm^{-1}): 2919, 2850, 1615, 1520, 1487, 1461, 1334, 1157, 1078, 886, 828, 735, 628. ^1H NMR (500 MHz, $CDCl_3$): δ 9.15 (d, *J* = 2.5 Hz, 1H), 8.26 (dd, *J* = 9.0, 2.5 Hz, 1H), 8.09-8.08 (m, 2H), 8.05 (d, *J* = 9.0 Hz, 1H), 7.94-7.77 (m, 2H), 7.62 (dt, *J* = 5.0, 1.0 Hz, 1H), 7.53-7.50 (m, 2H), 7.47-7.45 (m, 1H), 7.44 (tt, *J* = 7.5, 1.0 Hz, 1H), 7.40 (s, 1H), 7.39-7.37 (m, 1H), 7.33-7.29 (m, 4H), 7.20-7.16 (m, 1H), 5.49 (s, 2H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 145.4, 142.1, 140.0, 137.1, 136.8, 123.2, 130.3, 129.0(6), 129.0(0), 128.8, 128.2, 128.1, 127.9, 127.5, 127.1, 124.2, 123.5, 122.7, 120.6, 119.6, 113.8, 110.2, 50.3. HRMS (ESI): calcd. for $[C_{31}H_{23}N_2O_2]$ $[M+H]^+$: 455.1754; found: 455.1754.

1-Methyl-3-(3-propylnaphthalen-1-yl)-1*H*-indole 3hl

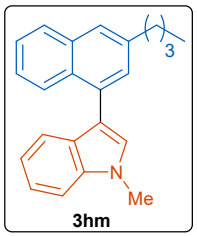


3hl

Yellow liquid (70 mg, 59%). R_f = 0.4 (in 10% EtOAc/Hex). IR (neat, cm^{-1}): 1613, 1597, 1574, 1540, 1498, 1476, 1372, 1333, 1244, 1225, 1149, 1130, 1113, 1056, 1011, 920, 850, 823, 807, 734, 647. ^1H NMR (500 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.67 (s, 1H), 7.58-7.57 (m, 1H), 7.51-7.48 (m, 2H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.40-7.33 (m, 2H), 7.28 (s, 1H), 7.19-7.16 (m, 1H), 3.92 (s, 3H), 2.84 (t, *J* = 7.0 Hz, 2H), 1.83 (sext, *J* = 7.5 Hz, 2H), 1.06 (t, *J* = 7.0 Hz, 3H). ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 139.8, 136.9, 134.2, 132.7, 130.9, 129.2,

128.1, 128.0, 127.7, 126.3, 125.6, 125.4, 124.7, 121.8, 120.4, 119.5, 115.0, 109.3, 38.1, 32.8, 24.4, 13.9. HRMS (ESI): calcd. for $[C_{22}H_{22}N]$ $[M+H]^+$: 300.1747; found: 300.1747.

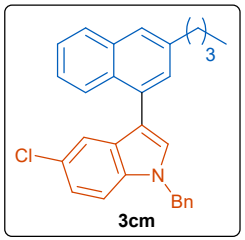
3-(3-Butylnaphthalen-1-yl)-1-methyl-1*H*-indole 3hm



3hm

Yellow liquid (78 mg, 62%). R_f = 0.5 (in 5% EtOAc/Hex). IR (neat, cm^{-1}): 1598, 1542, 1463, 1422, 1358, 1332, 1245, 1227, 1152, 1130, 1115, 1059, 1011, 875, 810, 735, 646. ^1H NMR (500 MHz, $CDCl_3$): δ 8.06 (d, J = 8.5 Hz, 1H), 7.84 (d, J = 8.5 Hz, 1H), 7.62 (s, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.47-7.45 (m, 2H), 7.43 (d, J = 8.5 Hz, 1H), 7.35-7.29 (m, 2H), 7.25(5)-7.25(2) (m, 1H), 7.14-7.11 (m, 1H), 3.92 (s, 3H), 2.81 (t, J = 8.0 Hz, 2H), 1.77-1.70 (m, 2H), 1.47-1.39 (m, 2H), 0.96 (t, J = 7.5 Hz, 3H). ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 140.0, 136.9, 134.2, 132.7, 130.9, 129.2, 128.1, 128.0, 127.7, 126.3, 125.6, 125.3, 124.7, 121.8, 120.4, 119.5, 115.0, 109.3, 35.8, 33.5, 32.8, 22.4, 14.0. HRMS (ESI): calcd. for $[C_{23}H_{24}N]$ $[M+H]^+$: 314.1903; found: 314.1904.

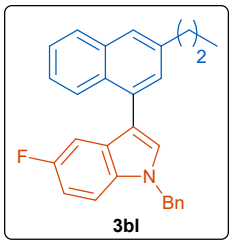
1-Benzyl-3-(3-butylnaphthalen-1-yl)-5-chloro-1*H*-indole 3cm



3cm

Yellow liquid (110 mg, 65%). R_f = 0.6 (in 10% EtOAc/Hex). IR (neat, cm^{-1}): 1600, 1495, 1468, 1386, 1352, 1261, 1169, 1065, 1025, 956, 872, 849, 789, 747, 729, 696. ^1H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, J = 8.5 Hz, 1H), 7.85 (d, J = 8.5 Hz, 1H), 7.64 (s, 1H), 7.48-7.43 (3H), 7.38-7.36 (m, 2H), 7.34-7.33 (m, 2H), 7.32 (d, J = 7.0 Hz, 1H), 7.28 (d, J = 9.0 Hz, 1H), 7.21 (d, J = 7.5 Hz, 2H), 7.19-7.17 (m, 1H), 5.41 (s, 2H), 2.82 (t, J = 8.0 Hz, 2H), 1.74 (quint, J = 7.5 Hz, 2H), 1.44 (sext, J = 7.5 Hz, 2H), 0.98 (t, J = 7.5 Hz, 3H). ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 140.0, 136.9, 134.8, 134.2, 131.8, 130.8, 129.4, 129.3, 128.9, 128.8, 127.8(5), 127.8(3), 126.7, 125.9, 125.8, 125.7(7), 125.7(1), 125.0, 122.4, 119.9, 115.3, 110.9, 50.3, 35.7, 33.5, 22.4, 14.0. HRMS (ESI): calcd. for $[C_{29}H_{27}ClN]$ $[M+H]^+$: 424.1827; found: 424.1827.

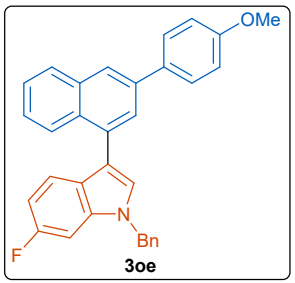
1-Benzyl-5-fluoro-3-(3-propylnaphthalen-1-yl)-1*H*-indole 3bl



3bl

Yellow liquid (108 mg, 68%). R_f = 0.51 (in 5% EtOAc/Hex). IR (neat, cm^{-1}): 1599, 1576, 1481, 1451, 1353, 1245, 1181, 1092, 1024, 928, 889, 850, 789, 748, 702, 651. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.65 (s, 1H), 7.50-7.45 (m, 2H), 7.39-7.36 (m, 3H), 7.35-7.30 (m, 2H), 7.29-7.26 (m, 1H), 7.24-7.22 (m, 2H), 7.18 (dd, *J* = 9.6, 2.4 Hz, 1H), 6.99 (td, *J* = 8.8, 2.4 Hz, 1H), 5.41 (s, 2H), 2.80 (t, *J* = 7.6 Hz, 2H), 1.8 (sext, *J* = 7.6 Hz, 2H), 1.03 (t, *J* = 7.2 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.1 (d, *J* = 233 Hz), 139.8, 137.0, 134.2, 133.1, 132.0, 130.8, 129.2 (d, *J* = 4.0 Hz), 128.9, 128.7 (d, *J* = 10 Hz), 127.8 (d, *J* = 2.0 Hz), 126.8, 126.0, 125.7 (d, *J* = 7.0 Hz), 125.0, 115.6 (d, *J* = 5.0 Hz), 110.6 (d, *J* = 3.0 Hz), 110.5, 110.4, 105.3 (d, *J* = 24 Hz), 50.5, 38.1, 24.4, 13.9. ^{19}F NMR (470 MHz, $CDCl_3$): *δ* -124.3. HRMS (ESI): calcd. for $[C_{28}H_{25}FN]$ $[M+H]^+$: 394.1966; found: 394.1966.

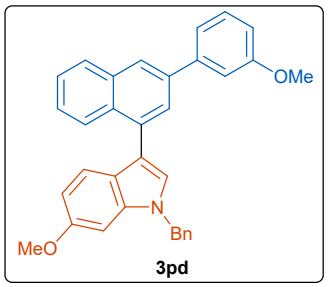
1-Benzyl-6-fluoro-3-(3-(4-methoxyphenyl)naphthalen-1-yl)-1H-indole 3oe



3oe

White solid (143 mg, 78%). mp 78-80 ˚C. R_f = 0.48 (in 5% EtOAc/Hex). IR (neat, cm^{-1}): 1606, 1579, 1545, 1512, 1466, 1452, 1332, 1281, 1244, 1170, 1112, 1089, 1029, 951, 907, 859, 826, 749, 701, 615. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.5 Hz, 1H), 8.00 (s, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 1.5 Hz, 1H), 7.70 (dt, *J* = 9.0, 3.0 Hz, 2H), 7.52-7.49 (m, 1H), 7.45 (dd, *J* = 8.5, 5.5 Hz, 1H), 7.41-7.39 (m, 1H), 7.38-7.35 (m, 2H), 7.34 (s, 1H), 7.32 (m, 1H), 7.24-7.23 (m, 2H), 7.05 (dd, *J* = 10.0, 5.0 Hz, 1H), 7.02 (dt, *J* = 9.0, 3.0 Hz, 2H), 6.88 (td, *J* = 9.0, 2.0 Hz, 1H), 5.38 (s, 2H), 3.87 (s, 3H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 160.0 (d, *J* = 236 Hz), 159.2, 137.7, 136.8, 136.5 (d, *J* = 11.2 Hz), 134.4, 133.4, 132.9, 131.2, 128.9, 128.4(8), 128.4(2), 127.9(3), 127.9(1), 127.8, 127.1, 126.9, 126.1 (d, *J* = 20 Hz), 125.5, 124.9, 124.3, 121.4 (d, *J* = 40 Hz), 115.8, 114.2, 108.6 (d, *J* = 25 Hz), 96.3 (d, *J* = 25 Hz), 55.3, 50.4. ^{19}F NMR (470 MHz, $CDCl_3$): δ -120.1. HRMS (ESI): calcd. for $[C_{32}H_{25}FNO]$ $[M+H]^+$: 458.1915; found: 458.1922.

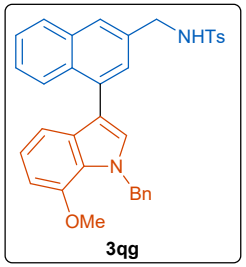
1-Benzyl-6-methoxy-3-(3-(3-methoxyphenyl)naphthalen-1-yl)-1*H*-indole 3pd



3pd

White solid (141 mg, 75%). mp 143–145 ˚C. R_f = 0.48 (in 5% EtOAc/Hex). IR (neat, cm^{-1}): 1595, 1571, 1488, 1453, 1331, 1257, 1212, 1168, 1094, 1040, 955, 879, 780, 748, 694. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.5 Hz, 1H), 8.03 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 2.0 Hz, 1H), 7.53-7.49 (m, 1H), 7.44-7.38 (m, 3H), 7.37-7.34 (m, 3H), 7.31-7.28 (m, 2H), 7.26-7.24 (m, 4H), 6.93 (ddd, *J* = 8.0, 2.5, 1.0 Hz, 1H), 6.84 (d, *J* = 2.0 Hz, 1H), 6.80 (dd, *J* = 9.0, 2.5 Hz, 1H), 5.39, (s, 2H), 3.89 (s, 3H), 3.84 (s, 3H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 159.9, 156.6, 142.6, 138.0, 137.3, 137.2, 134.2, 133.5, 131.7, 129.7, 128.8, 128.5, 127.7, 127.1, 126.9, 126.6, 126.4, 126.1, 125.7, 124.8, 122.7, 121.2, 119.9, 115.5, 113.0, 112.7, 93.5, 55.7, 55.3, 50.1. HRMS (ESI): calcd. for $[C_{33}H_{27}NNaO_2]$ $[M+Na]^+$: 492.1934; found: 492.1932.

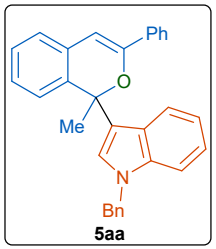
N-((4-(1-Benzyl-7-methoxy-1*H*-indol-3-yl)naphthalen-2-yl)methyl)-4-methylbenzenesulfonamide 3qg



3qg

White solid (156 mg, 71%). mp 90–92 ˚C. R_f = 0.41 (in 20% EtOAc/Hex). IR (neat, cm^{-1}): 1573, 1494, 1452, 1426, 1324, 1257, 1213, 1155, 1089, 1060, 811, 748, 695, 660. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.74 (dt, *J* = 8.0, 2.0 Hz, 2H), 7.58 (s, 1H), 7.47-7.44 (m, 1H), 7.37-7.34 (m, 1H), 7.33-7.29 (m, 3H), 7.26-7.23 (m, 1H), 7.21-7.19 (dd, *J* = 7.5, 1.5 Hz, 4H), 7.13 (s, 1H), 7.00-6.97 (m, 1H), 6.96-6.94 (m, 1H), 6.68 (dd, *J* = 7.0, 1.0 Hz, 1H), 5.72 (s, 2H), 4.75 (t, *J* = 6.0 Hz, 1H), 4.31 (d, *J* = 6.0 Hz, 2H), 3.88 (s, 3H), 2.31 (s, 3H). ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 147.6, 143.4, 139.3, 136.7, 133.8, 133.7, 133.1, 131.8, 130.1, 129.6, 128.5, 128.0, 127.2, 127.1, 126.8, 126.5, 126.1, 125.8, 125.7, 120.2, 115.3, 113.0, 103.0, 55.4, 52.5, 47.4, 21.3. HRMS (ESI): calcd. for $[C_{34}H_{31}N_2O_3S]$ $[M+H]^+$: 547.2050; found: 547.2049.

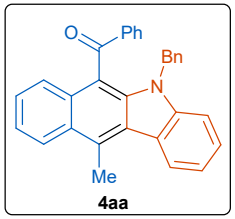
1-Benzyl-3-(1-methyl-3-phenyl-1H-isochromen-1-yl)-1*H*-indole 5aa



5aa

Yellow solid. mp 150-152 ˚C. R_f = 0.46 (in 10% EtOAc/Hex). IR (neat, cm^{-1}): 1594, 1494, 1450, 1384, 1167, 1027, 905, 733. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74-7.72 (m, 2H), 7.67 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.33-7.29 (m, 4H), 7.28-7.27 (m, 2H), 7.23 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.21 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.14 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.12-7.07 (m, 4H), 7.02-6.98 (m, 1H), 6.97 (dt, *J* = 7.5, 1.0 Hz, 1H), 6.89 (s, 1H), 6.44 (s, 1H), 5.26 (s, 2H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.4, 137.5, 137.4, 135.2, 135.0, 131.2, 128.8, 128.5, 128.2, 127.8, 127.6, 126.7, 126.6, 126.5, 125.3, 124.5, 123.9, 122.0, 121.8, 119.6, 119.4, 109.9, 100.2, 79.6, 50.1, 26.0. HRMS (ESI): calcd. for [$C_{31}H_{26}NO$] [M+H]$^+$: 428.2009; found: 428.2009.

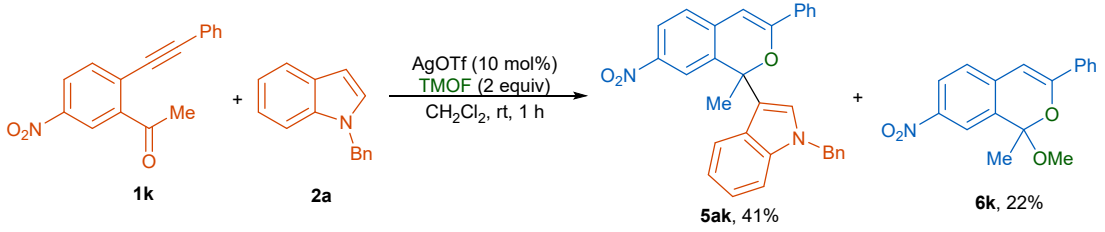
(5-Benzyl-11-methyl-5*H*-benzo[*b*]carbazol-6-yl)(phenyl)methanone 4aa



4aa

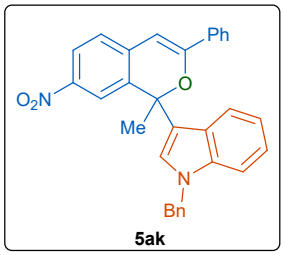
Yellow solid. mp 185-187 ˚C. R_f = 0.36 (in 5% EtOAc/Hex). IR (neat, cm^{-1}): 1663, 1594, 1470, 1398, 1316, 1228, 1157, 1026, 929, 731. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.49 (d, *J* = 7.5 Hz, 1H), 8.38 (dq, *J* = 1.0, 0.5 Hz, 1H), 7.57 (dq, *J* = 1.5, 1.0 Hz, 3H), 7.49-7.42 (m, 2H), 7.37 (dt, 7.0, 1.5 Hz, 1H), 7.35-7.31 (m, 2H), 7.24 (d, *J* = 8.5 Hz, 1H), 7.15 (t, *J* = 8.0 Hz, 2H), 6.98-6.92 (m, 3H), 6.73-6.71 (m, 2H), 5.39 (s, 2H), 3.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.3, 138.3, 136.6, 133.3, 131.1, 130.2, 129.9, 128.4, 128.2, 127.1, 126.8, 126.7, 125.8, 125.5, 124.9, 124.2, 124.0, 123.8, 123.4, 122.8, 119.8, 114.3, 108.9, 48.1, 15.9. HRMS (ESI): calcd. for [$C_{31}H_{24}NO$] [M+H]$^+$: 426.1852; found: 426.1857.

6. Procedure for the synthesis of 1-Benzyl-3-(1-methyl-7-nitro-3-phenyl-*1H*-isochromen-1-yl)-1*H*-indole 5ak and 1-Methoxy-1-methyl-7-nitro-3-phenyl-1*H*-isochromene 6k:



To a stirred solution of 1-(5-nitro-2-(phenylethynyl)phenyl)ethan-1-one **1k**[4] (127 mg, 0.48 mmol), 1-benzyl-1*H*-indole **2a** (83 mg, 0.48 mmol) and TMOF (88 µL, 0.8 mmol) in DCM (4 mL) was added AgOTf (10 mg, 0.04 mmol) at room temperature under nitrogen atmosphere. The reaction mixture was stirred at the same temperature. After completion of the reaction, reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/EtOAc mixture as eluent) to afford the pure products 1-benzyl-3-(1-methyl-7-nitro-3-phenyl-*1H*-isochromen-1-yl)-1*H*-indole **5ak** and 1-methoxy-1-methyl-7-nitro-3-phenyl-1*H*-isochromene **6k** in 41% and 22% respectively.

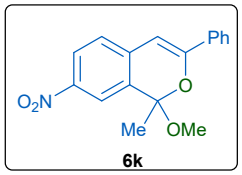
1-Benzyl-3-(1-methyl-7-nitro-3-phenyl-*1H*-isochromen-1-yl)-1*H*-indole 5ak



5ak

Yellow solid (78 mg, 41%). mp 142-144 ˚C. R_f = 0.15 (in 10% EtOAc/Hex). IR (neat, cm^{-1}): 1568, 1493, 1450, 1325, 1246, 1102, 1056, 899, 763, 718, 690. ^1H NMR (500 MHz, $CDCl_3$): δ 8.11 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.79-7.77 (m, 3H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.37-7.36 (m, 3H), 7.34 (d, *J* = 7.5 Hz, 2H), 7.30-7.27 (m, 2H), 7.23 (d, *J* = 8.5 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 2H), 7.01 (t, *J* = 7.0 Hz, 2H), 6.53 (s, 1H), 5.33 (s, 2H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5, 145.9, 137.9, 137.6, 137.1, 135.3, 134.0, 129.8, 128.9, 128.4, 127.7, 127.4, 126.7, 126.2, 125.8, 124.0, 123.7, 122.3, 121.5, 120.4, 119.8, 118.3, 110.1, 98.6, 80.3, 50.1, 26.0. HRMS (ESI): calcd. for $[C_{31}H_{25}N_2O_3]$ $[M+H]^+$: 473.1860; found: 473.1864.

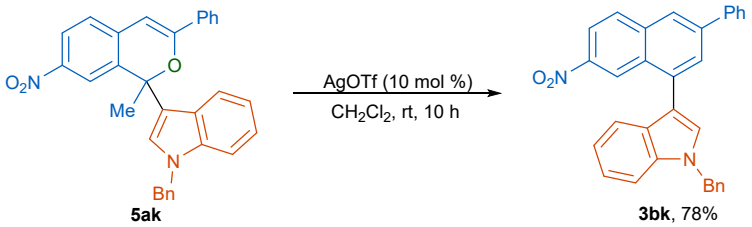
1-Methoxy-1-methyl-7-nitro-3-phenyl-1*H*-isochromene 6k



6k

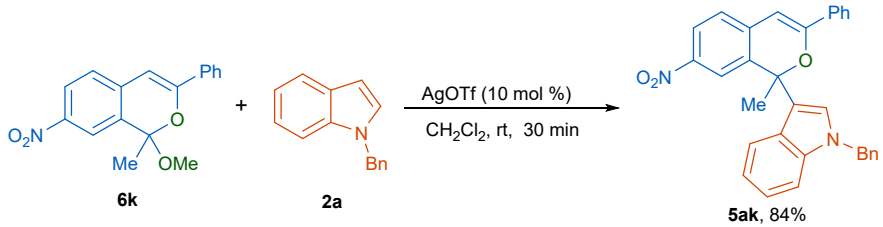
Yellow solid (30 mg, 22%). mp 86-88 ˚C. R_f = 0.35 (in 10% EtOAc/Hex). IR (neat, cm^{-1}): 1670, 1579, 1526, 1349, 1196, 911, 836, 735, 666. ^1H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, *J* = 2.4 Hz, 1H), 8.18 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.85-7.81 (m, 2H), 7.47-7.42 (m, 3H), 7.25 (d, *J* = 8.4 Hz, 1H), 6.51 (s, 1H), 3.32 (s, 3H), 1.97 (s, 3H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 154.4, 146.1, 137.8, 133.1, 130.5, 130.0, 128.6, 125.3, 124.6, 124.4, 120.6, 102.8, 97.9, 50.6, 25.7. HRMS (ESI): calcd. for $[C_{16}H_{12}NO_3]$ $[M-OMe]^+$: 266.0812; found: 266.0817.

7. Synthesis of 1-benzyl-3-(7-nitro-3-phenylnaphthalen-1-yl)-1*H*-indole 3bk from 5ak



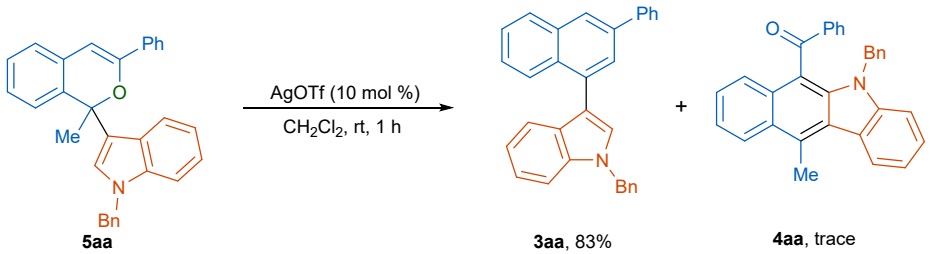
To a stirred solution of 1-benzyl-3-(1-methyl-3-phenyl-1*H*-isochromen-1-yl)-1*H*-indole **5ak** (12 mg, 0.028 mmol) in DCM (1 mL) was added AgOTf (0.7 mg, 0.0028 mmol) at room temperature under nitrogen atmosphere. The reaction mixture was stirred at the same temperature. After completion of the reaction, reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/EtOAc mixture as eluent) to afford the pure 1-benzyl-3-(7-nitro-3-phenylnaphthalen-1-yl)-1*H*-indole derivative **3bk** (10 mg, 78%).

8. Synthesis of 5ak from 1-methoxy-1-methyl-7-nitro-3-phenyl-1*H*-isochromene 6k and 1-benzyl-1*H*-indole 2a



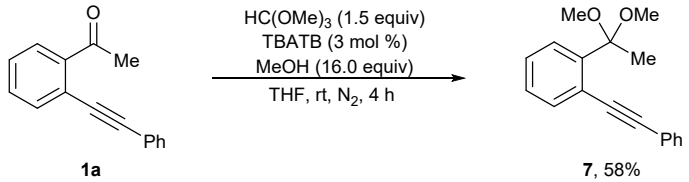
To a stirred solution of 1-methoxy-1-methyl-7-nitro-3-phenyl-1*H*-isochromene **6k** (15 mg, 0.06 mmol) and 1-benzyl-1*H*-indole **2a** (10 mg, 0.05 mmol) in DCM (1 mL) was added AgOTf (1.2 mg, 0.005 mmol) at room temperature under nitrogen atmosphere. The reaction mixture was stirred at the same temperature. After completion of the reaction, reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/EtOAc mixture as eluent) to afford the pure 1-benzyl-3-(1-methyl-7-nitro-3-phenyl-1*H*-isochromen-1-yl)-1*H*-indole **5ak** as a yellow solid (10 mg, 84%).

9. Synthesis of 1-benzyl-3-(3-phenylnaphthalen-1-yl)-1*H*-indole 3aa from 1-benzyl-3-(1-methyl-3-phenyl-1*H*-isochromen-1-yl)-1*H*-indole 5aa



To a stirred solution of 1-benzyl-3-(1-methyl-3-phenyl-1*H*-isochromen-1-yl)-1*H*-indole **5aa** (23 mg, 0.05 mmol) in DCM (1 mL) was added AgOTf (1.4 mg, 0.005 mmol) at room temperature under nitrogen atmosphere. The reaction mixture was stirred at the same temperature. After completion of the reaction, the reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/EtOAc mixture as eluent) to afford the pure 1-benzyl-3-(3-phenylnaphthalen-1-yl)-1*H*-indole **3aa** in 83% (17 mg) yield along with trace amount of (5-benzyl-11-methyl-5H-benzo[*b*]carbazol-6-yl)(phenyl)methanone **4aa**.

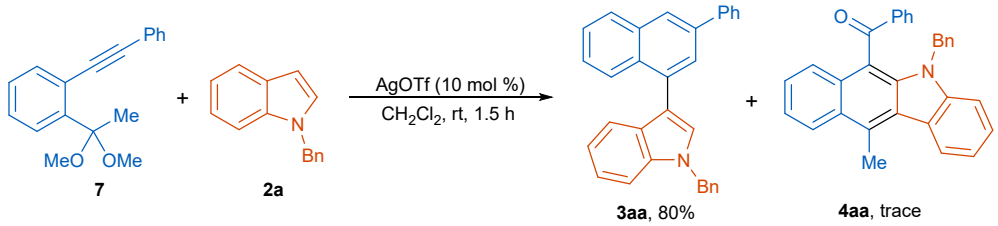
10. Procedure for the synthesis of 1-(1,1-dimethoxyethyl)-2-(phenylethynyl)benzene 7[5]



A solution of 1-(2-(phenylethynyl)phenyl)ethan-1-one **1a** (250 mg, 1.1 mmol), MeOH (712 µL, 17.6 mmol), TMOF (182 µL, 1.65 mmol), tetrabutylammonium tribromide (TBATB) (16 mg, 0.03 mmol) and THF (2 mL) were stirred for 4 h at room temperature. Then, the reaction mixture was diluted with EtOAc (15 mL), and washed with saturated aqueous solution of $NaHCO_3$. The resulting organic layer was concentrated under reduced pressure and purified by column chromatography (silica gel, hexane/EtOAc mixture as

eluent) to afford the pure product 1-(1,1-dimethoxyethyl)-2-(phenylethynyl)benzene **7** as a yellow liquid (170 mg, 58%). R_f = 0.43 (in 5% EtOAc/Hex). IR (neat, cm^{-1}): 1678, 1592, 1491, 1440, 1355, 1275, 1244, 1068, 956, 753, 688, 595. ^1H NMR (500 MHz, $CDCl_3$): δ 7.72 (dd, J = 8.0, 1.5 Hz, 1H), 7.57 (dd, J = 7.5, 1.5 Hz, 1H), 7.55-7.53 (m, 2H), 7.36-7.32 (m, 3H), 7.32-7.30 (m, 1H), 7.28 (dd, J = 7.5, 1.5 Hz, 1H), 3.25 (s, 6H), 1.75 (s, 3H). ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 144.0, 134.0, 131.4, 128.2, 128.04, 128.02, 127.5, 127.4, 123.9, 120.8, 101.5, 93.1, 89.1, 48.8, 23.7. HRMS (ESI): calcd. for $[C_{18}H_{18}NaO_2]$ $[M+Na]^+$: 289.1199; found: 289.1194.

11. Synthesis of 3aa from 1-(1,1-dimethoxyethyl)-2-(phenylethynyl)benzene 7 and 1-benzyl-1*H*-indole 2a



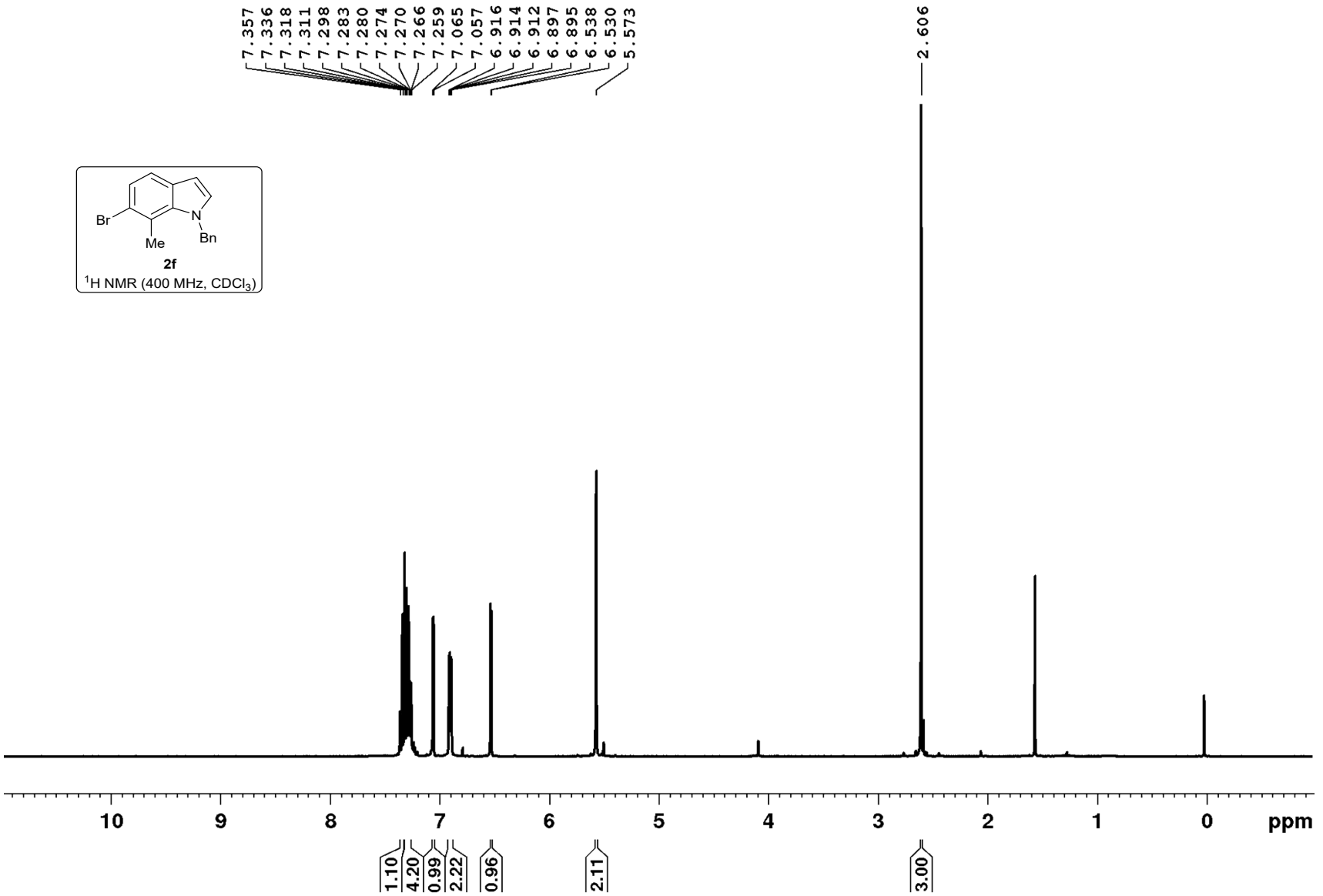
To a stirred solution of 1-(1,1-dimethoxyethyl)-2-(phenylethynyl)benzene **7** (64 mg, 0.24 mmol) and 1-benzyl-1*H*-indole **2a** (41 mg, 0.2 mmol) in DCM (2 mL) was added AgOTf (5 mg, 0.02 mmol) at room temperature under nitrogen atmosphere. The reaction mixture was stirred at the same temperature. After completion of the reaction, the reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/EtOAc mixture as eluent) to afford the pure 1-benzyl-3-(3-phenylnaphthalen-1-yl)-1*H*-indole **3aa** in 80% (66 mg) yield.

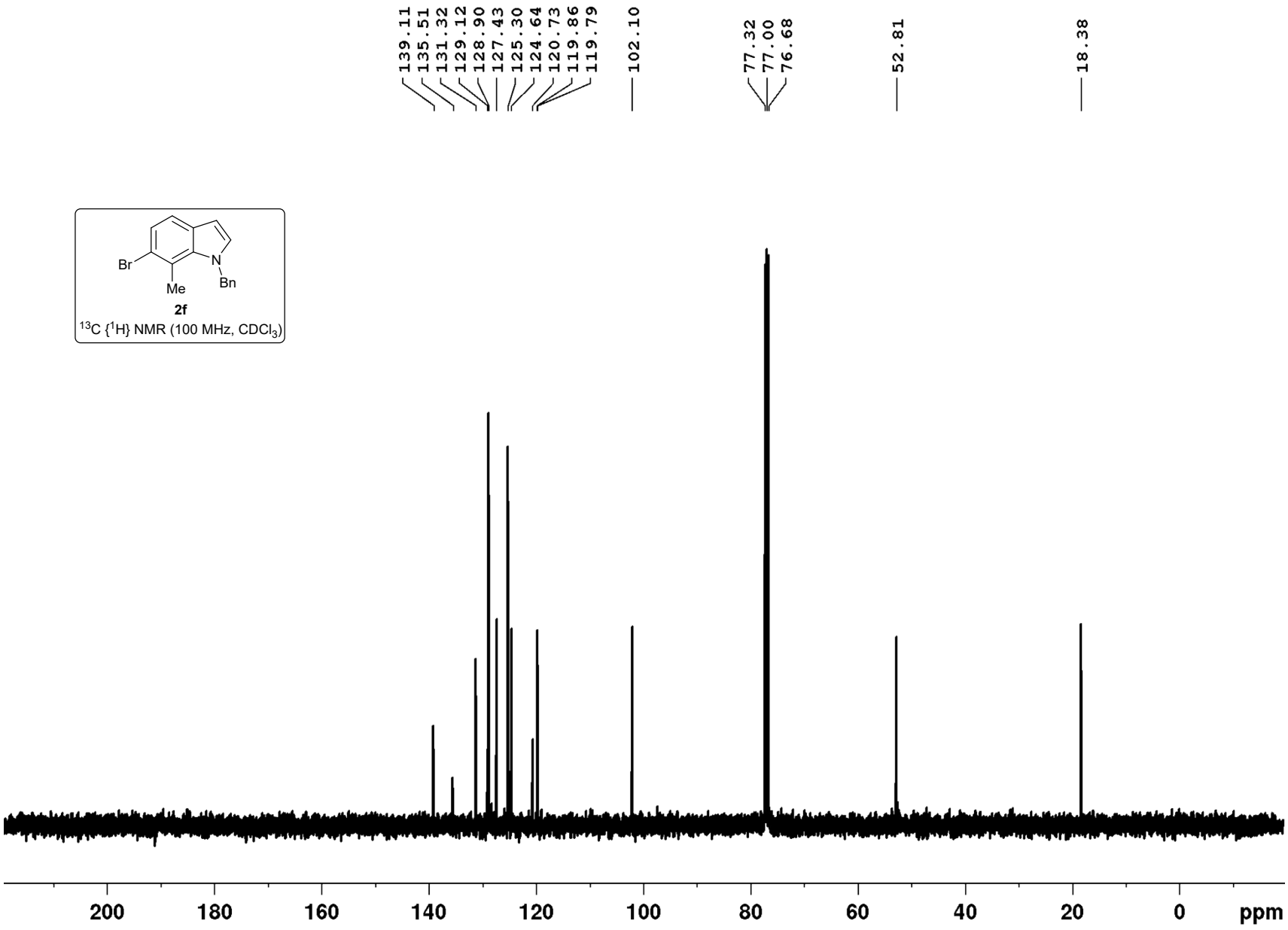
12. Procedure for scale-up reaction for the synthesis of 3aa

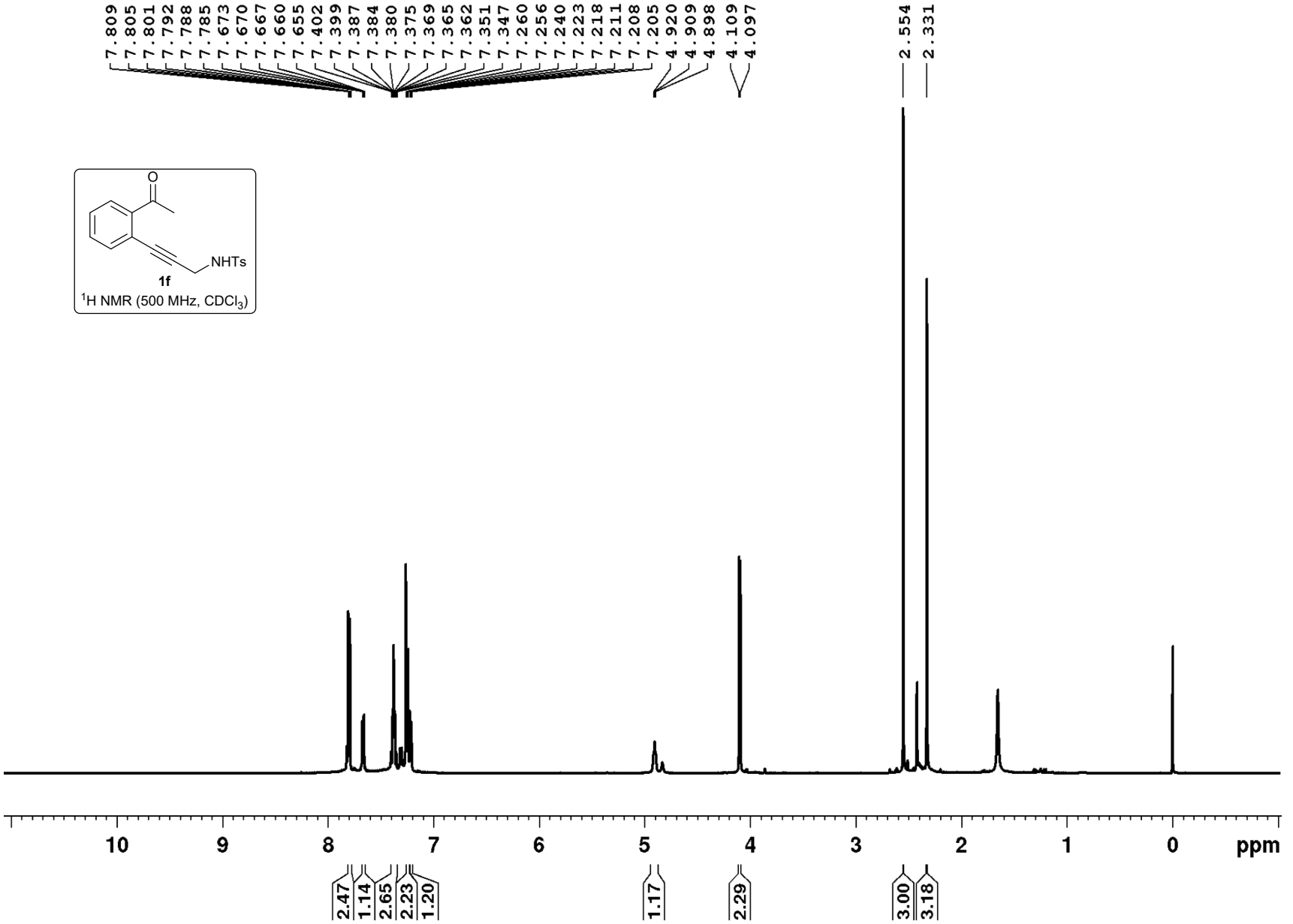
To a stirred solution of 1-(2-(phenylethynyl)phenyl)ethan-1-one **1a** (1.32 g, 6 mmol), 1-benzyl-1*H*-indole **2a** (1.03 g, 5 mmol) and TMOF (1.09 mL, 10 mmol) in DCM (40 mL) was added AgOTf (128 mg, 0.5 mmol) at room temperature under nitrogen atmosphere. The reaction mixture was stirred at the same temperature. After completion of the reaction, the reaction mixture was

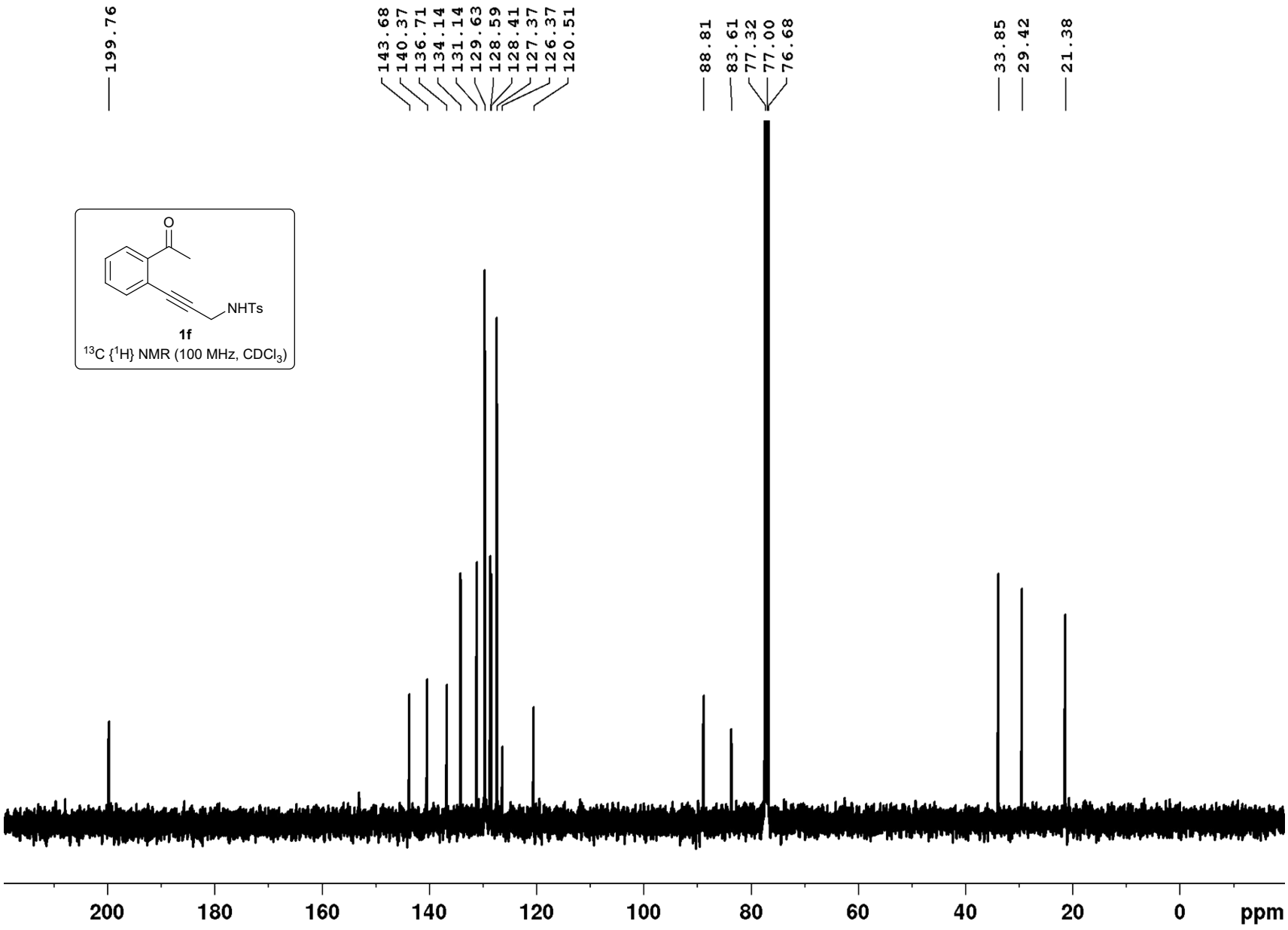
concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/EtOAc mixture as eluent) to afford the pure product **3aa** in 80% (1.65 g) yield along with 10% (212 mg) of the product **4aa**.

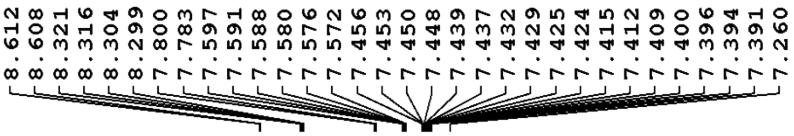
13. Copies of NMR Spectra

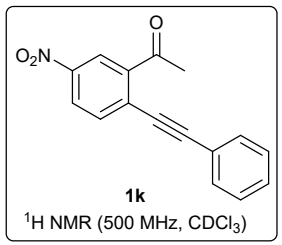



139.11
135.51
131.32
129.12
128.90
127.43
125.30
124.64
120.73
119.86
119.79
102.10
77.32
77.00
76.68
52.81
18.38
Br
N
Bn
Me
2f
13C {1H} NMR (100 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0
ppm


7.809
7.805
7.801
7.792
7.788
7.785
7.673
7.670
7.667
7.660
7.655
7.402
7.399
7.387
7.384
7.380
7.375
7.369
7.365
7.362
7.351
7.347
7.260
7.256
7.240
7.223
7.218
7.211
7.208
7.205
4.920
4.909
4.898
4.109
4.097
2.554
2.331
O
NHTs
1f
1H NMR (500 MHz, CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
2.47
1.14
2.65
2.23
1.20
1.17
2.29
3.00
3.18

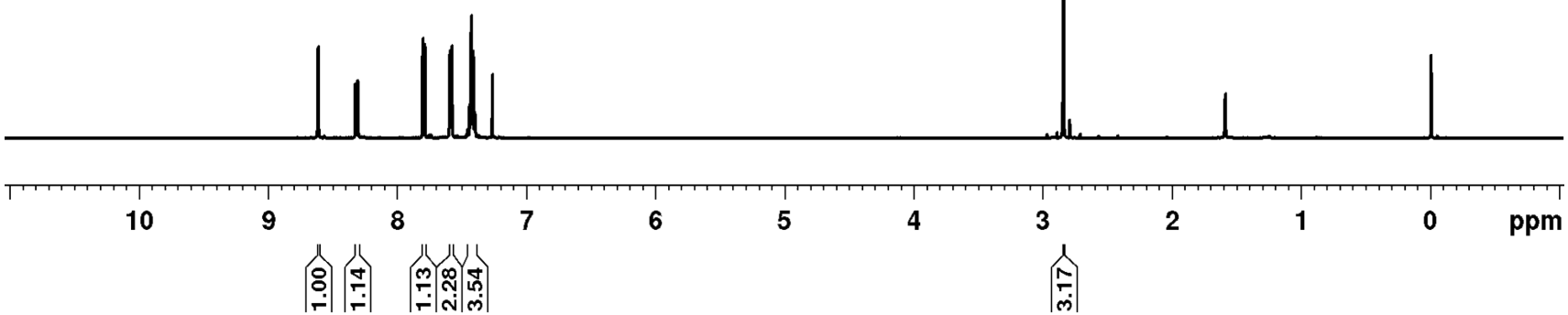

199.76
143.68
140.37
136.71
134.14
131.14
129.63
128.59
128.41
127.37
126.37
120.51
88.81
83.61
77.32
77.00
76.68
33.85
29.42
21.38
O
NHTs
1f
13C {1H} NMR (100 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0
ppm

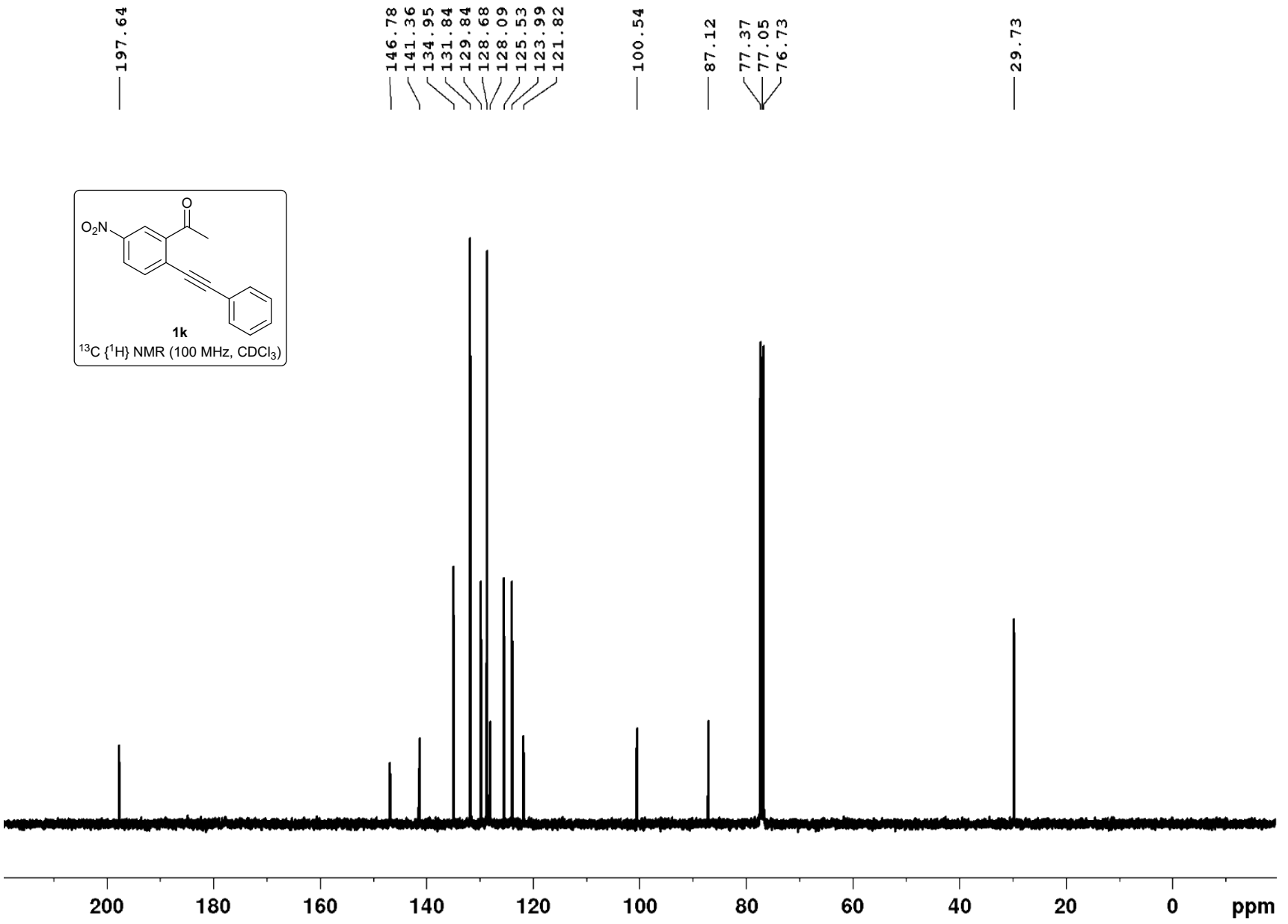


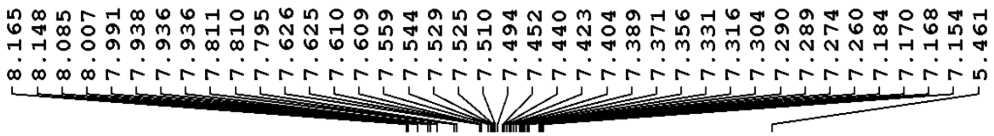


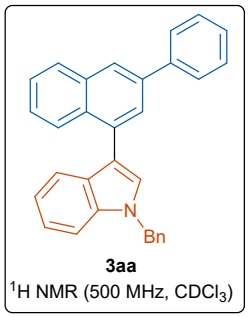
1k

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



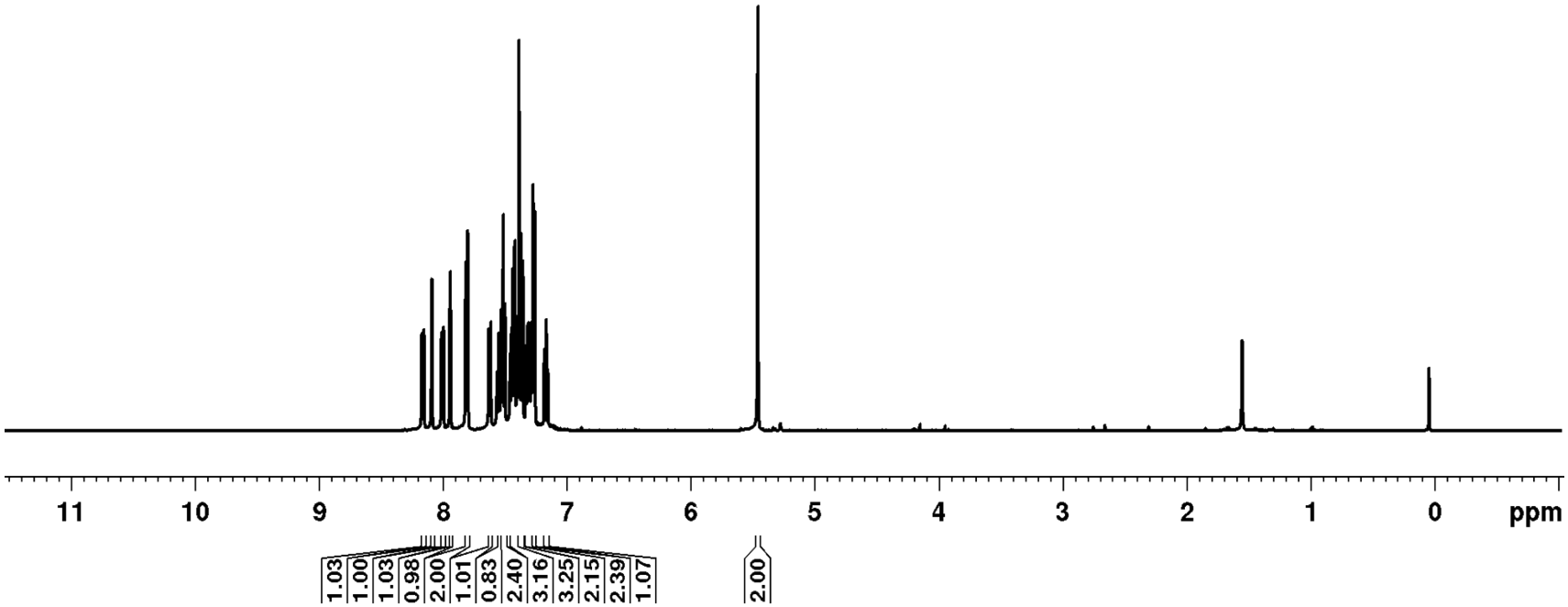

197.64
146.78
141.36
134.95
131.84
129.84
128.68
128.09
125.53
123.99
121.82
100.54
87.12
77.37
77.05
76.73
29.73
O2N
O
1k
13C {1H} NMR (100 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0
ppm

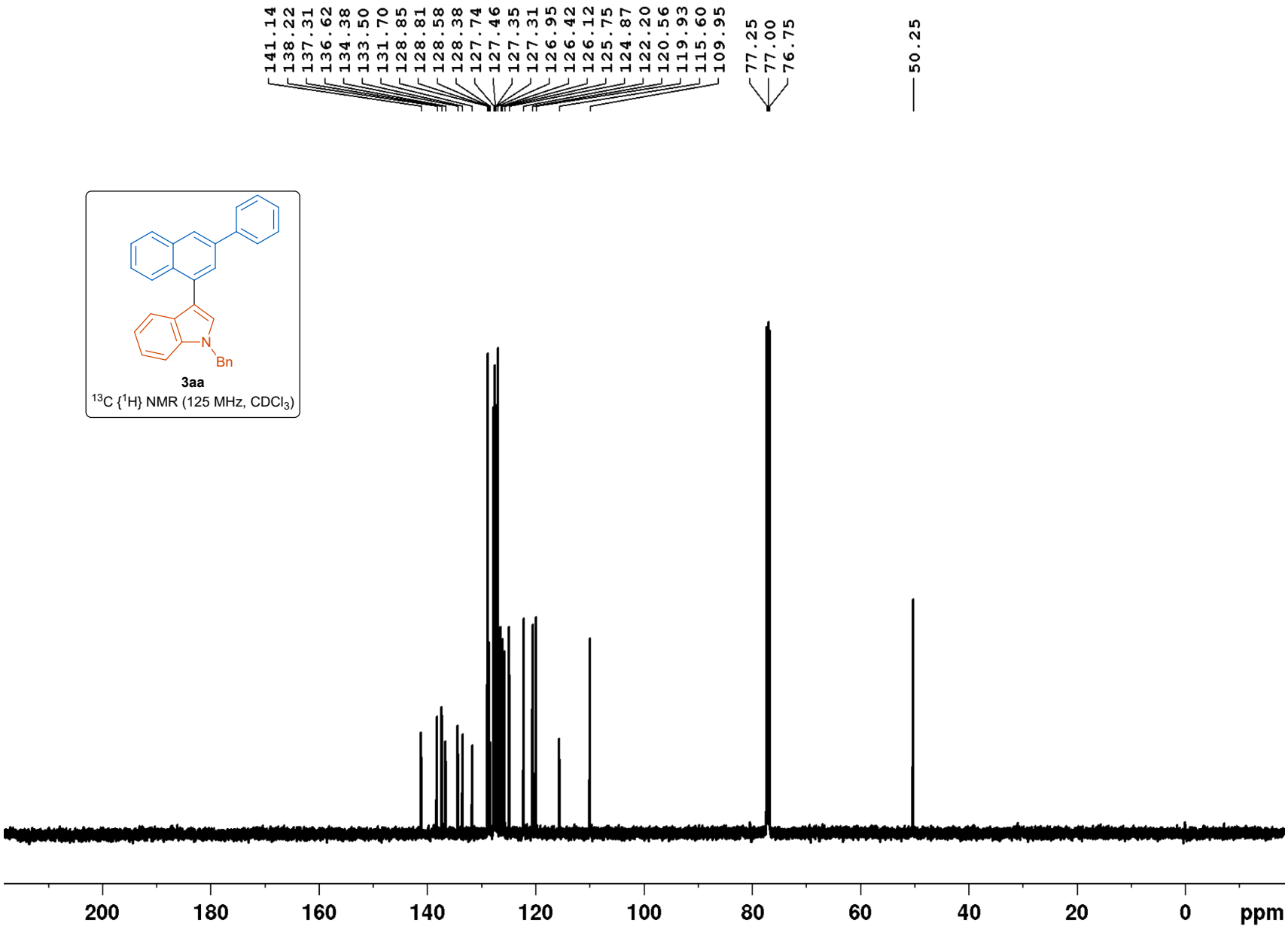


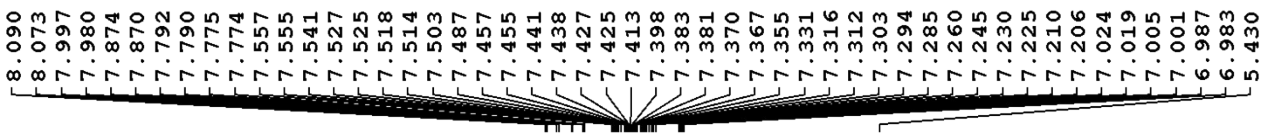


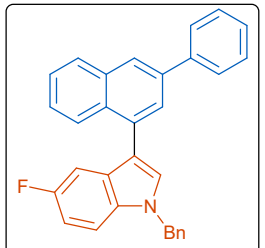
3aa

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



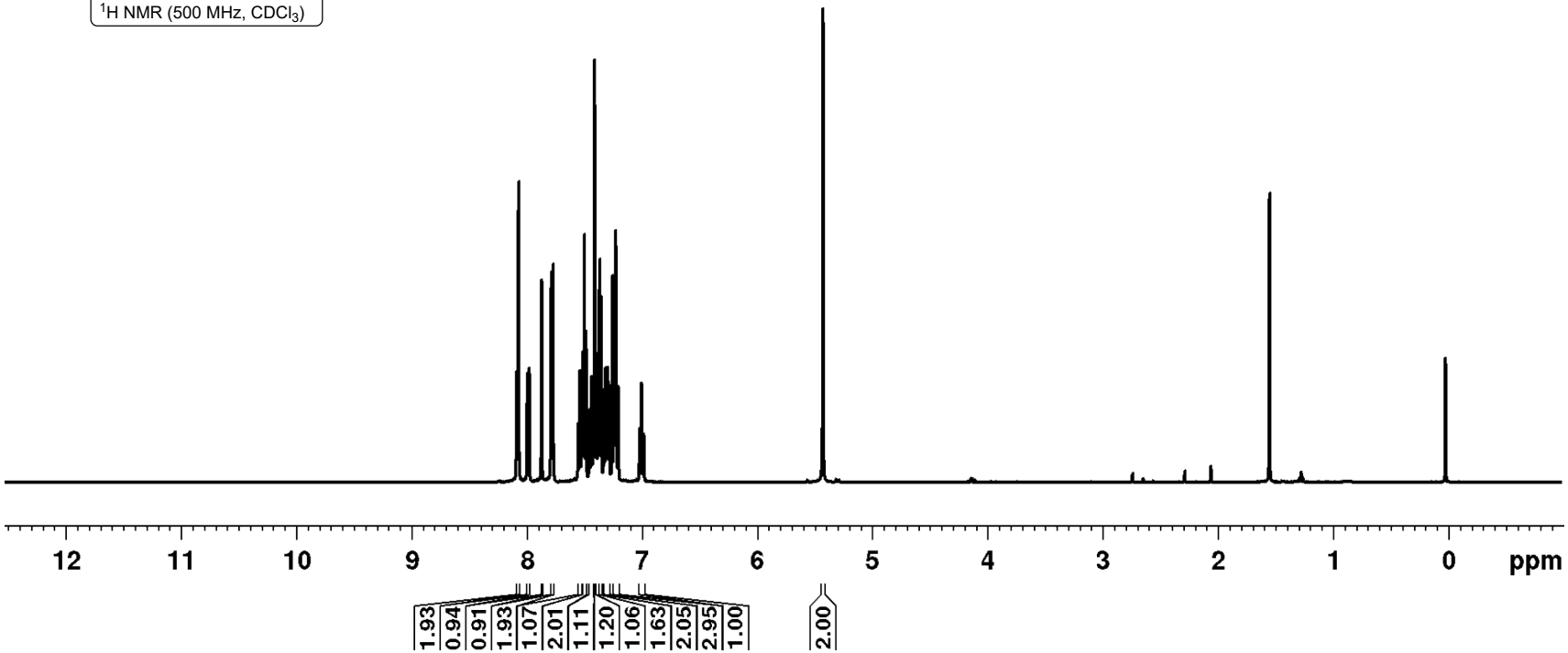

141.14
138.22
137.31
136.62
134.38
133.50
131.70
128.85
128.81
128.58
128.38
127.74
127.46
127.35
127.31
126.95
126.42
126.12
125.75
124.87
122.20
120.56
119.93
115.60
109.95
77.25
77.00
76.75
50.25
N
Bn
3aa
13C {1H} NMR (125 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0
ppm

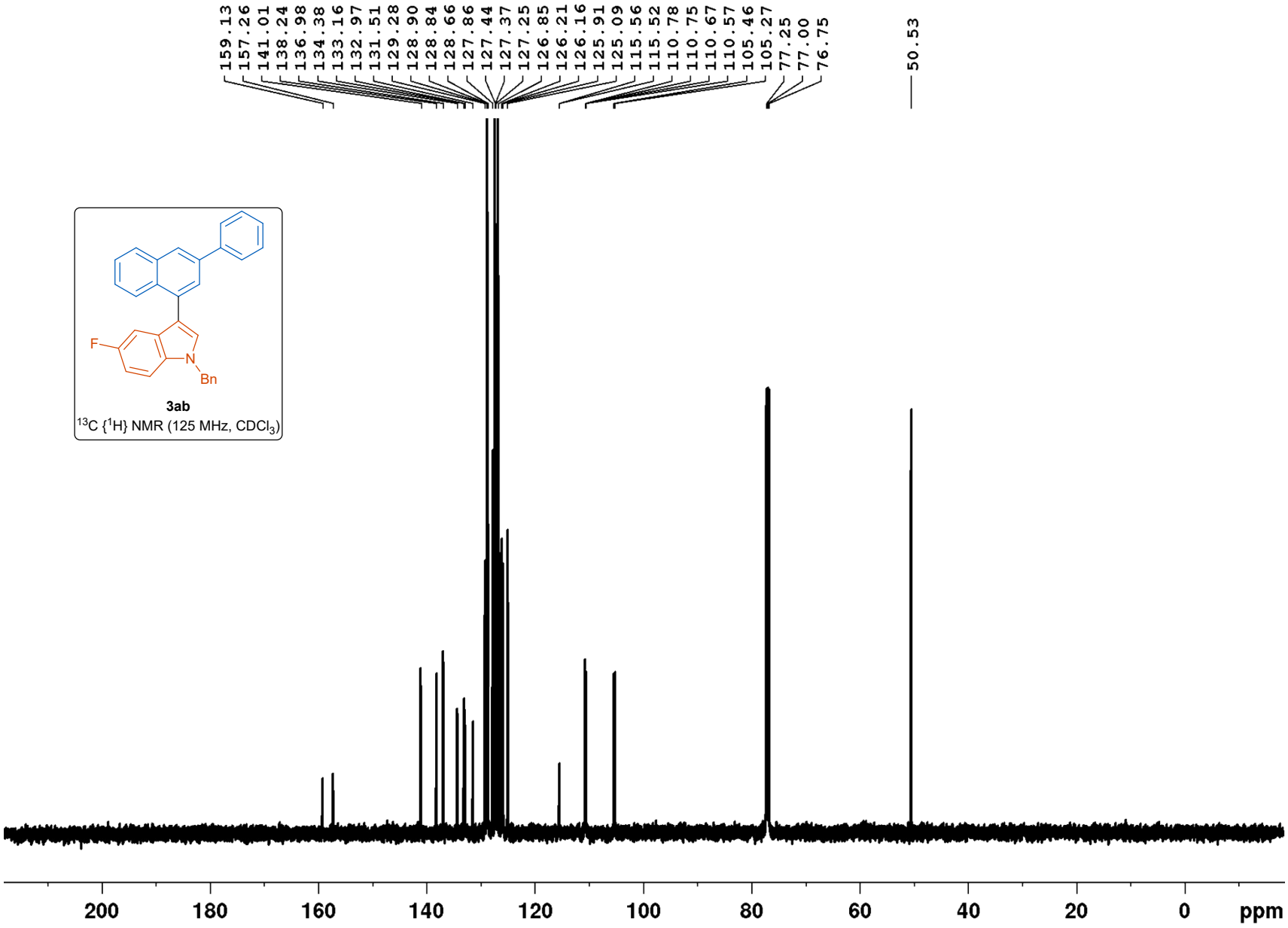




3ab

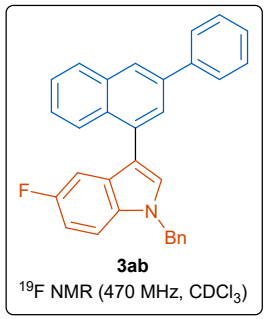
^{1}H NMR (500 MHz, $CDCl_3$)





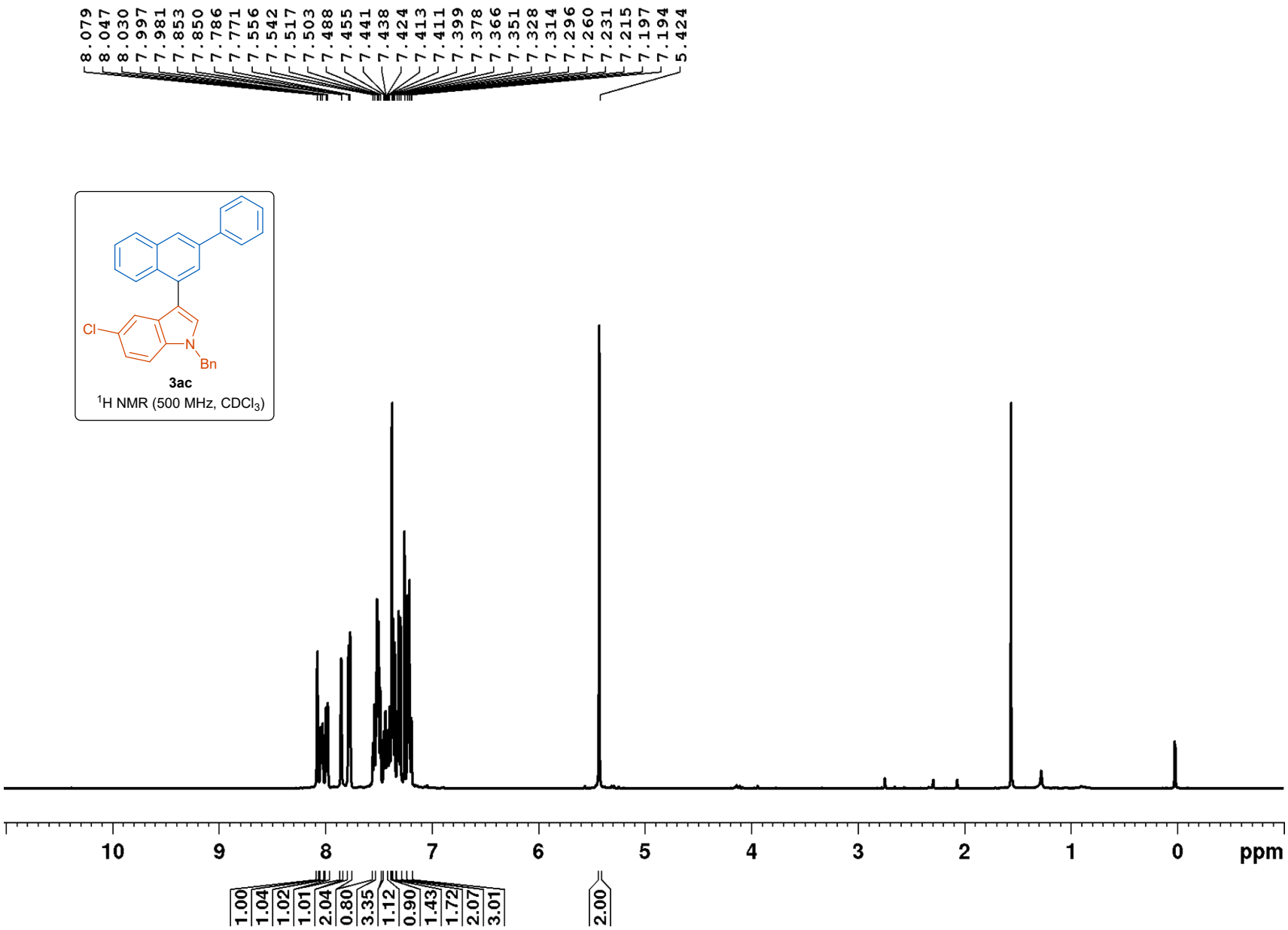
3ab

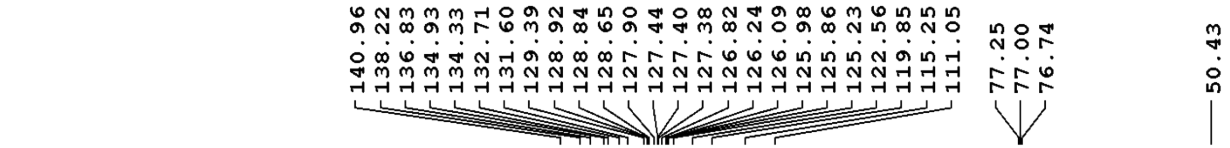
^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$)

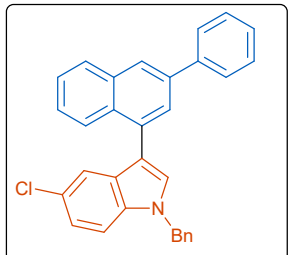


3ab

^{19}F NMR (470 MHz, $CDCl_3$)

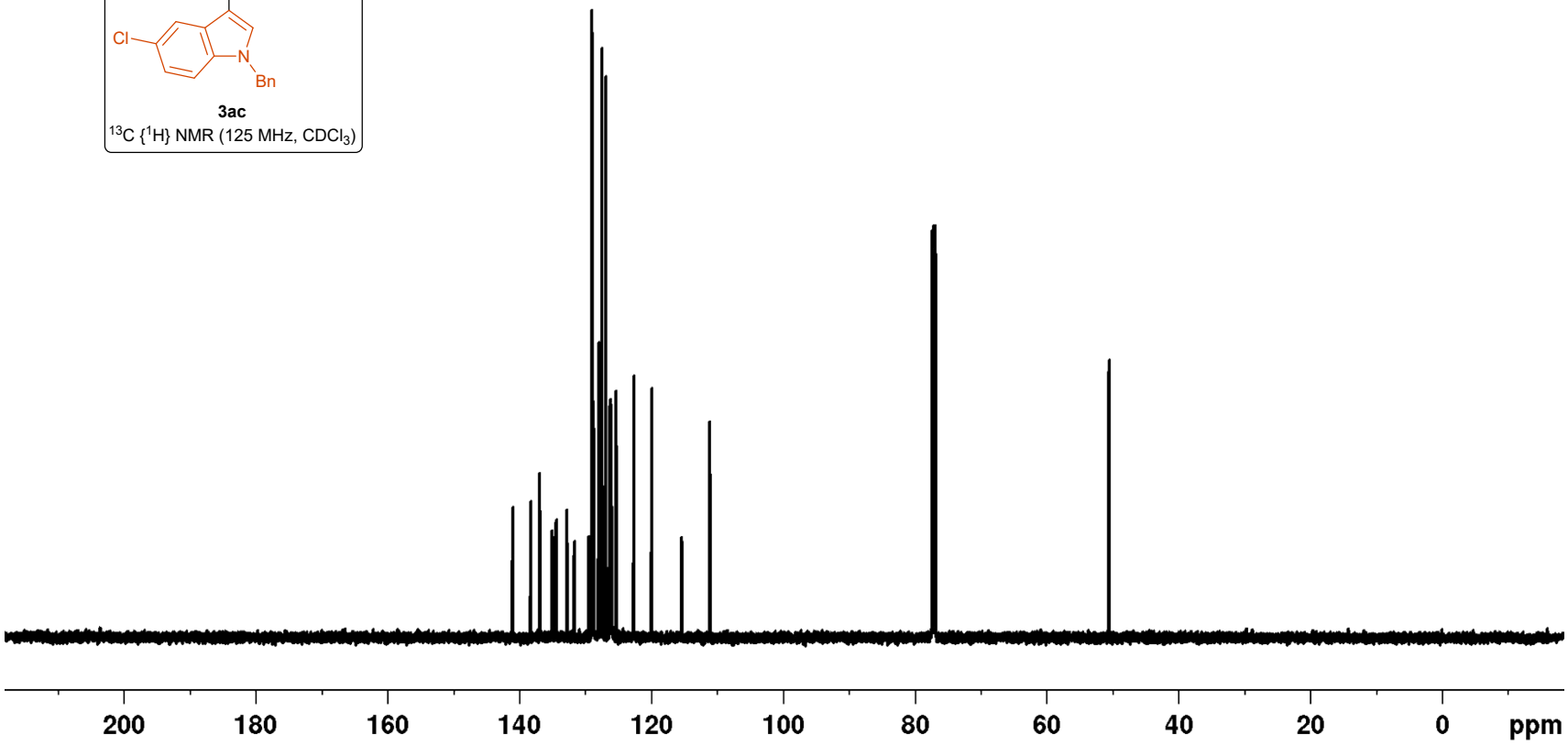

8.079
8.047
8.030
7.997
7.981
7.853
7.850
7.786
7.771
7.556
7.542
7.517
7.503
7.488
7.455
7.441
7.438
7.424
7.413
7.411
7.399
7.378
7.366
7.351
7.328
7.314
7.296
7.260
7.231
7.215
7.197
7.194
5.424
Cl
N
Bn
3ac
1H NMR (500 MHz, CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.04
1.02
1.01
2.04
0.80
3.35
1.12
0.90
1.43
1.72
2.07
3.01
2.00

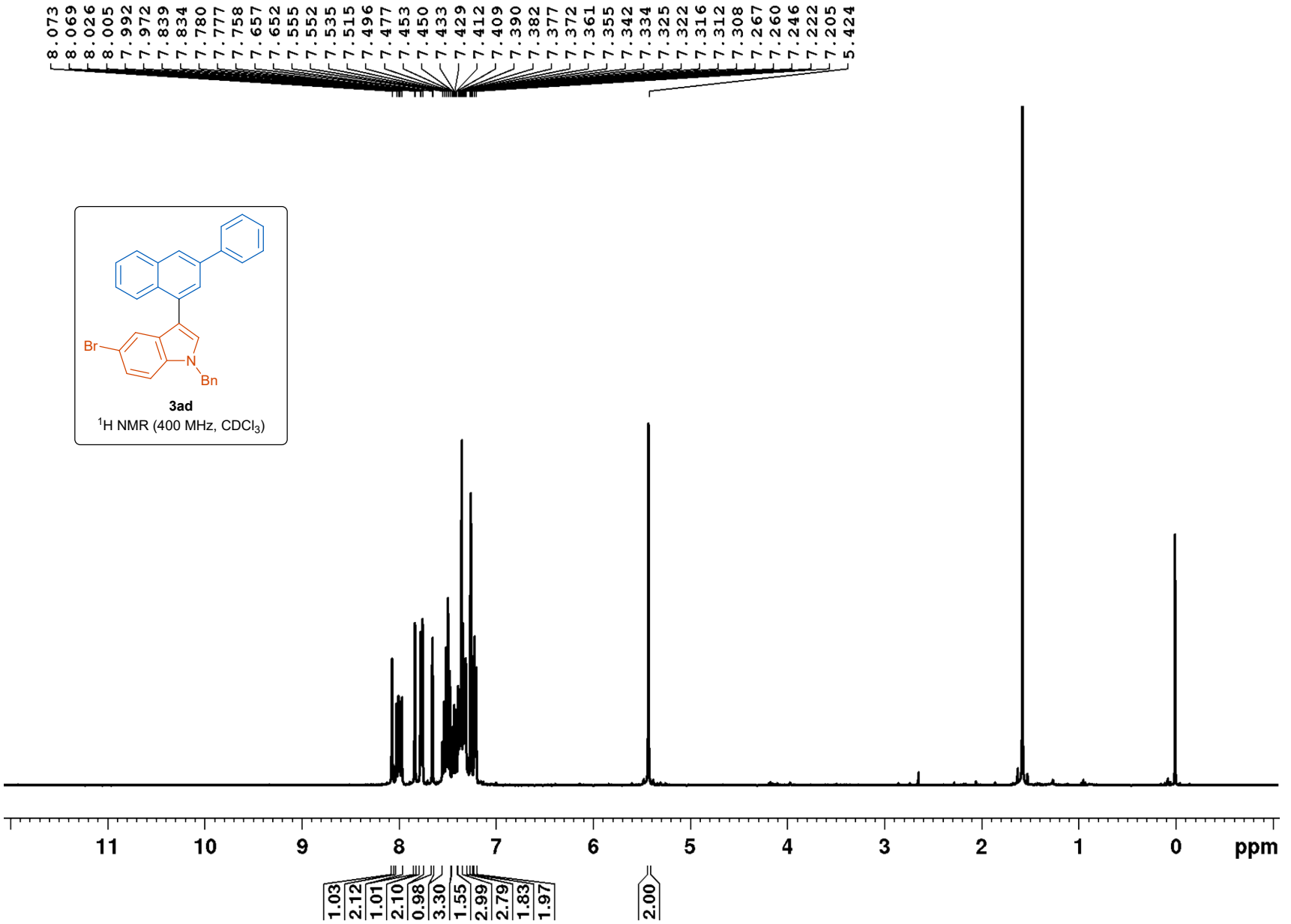


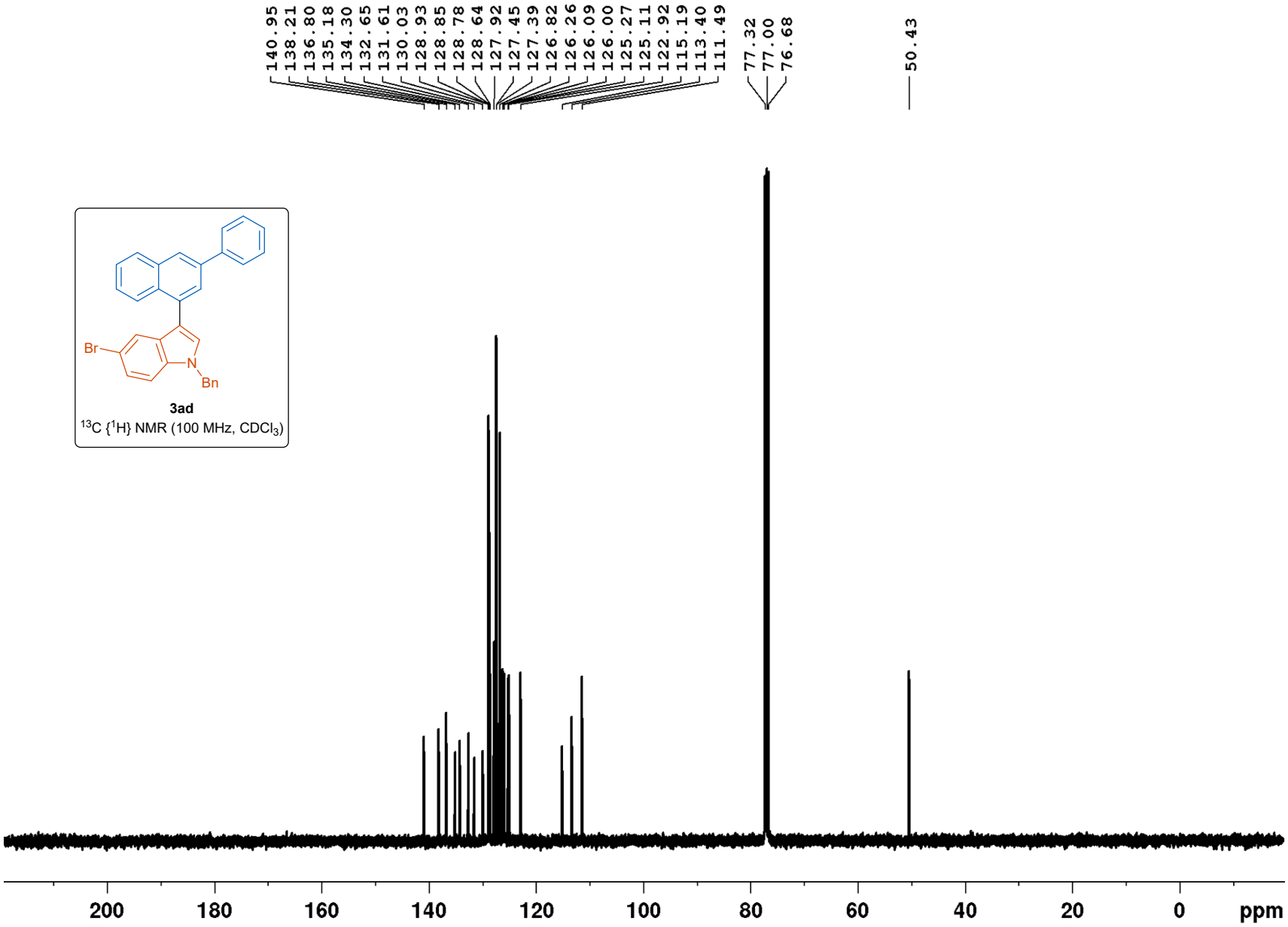


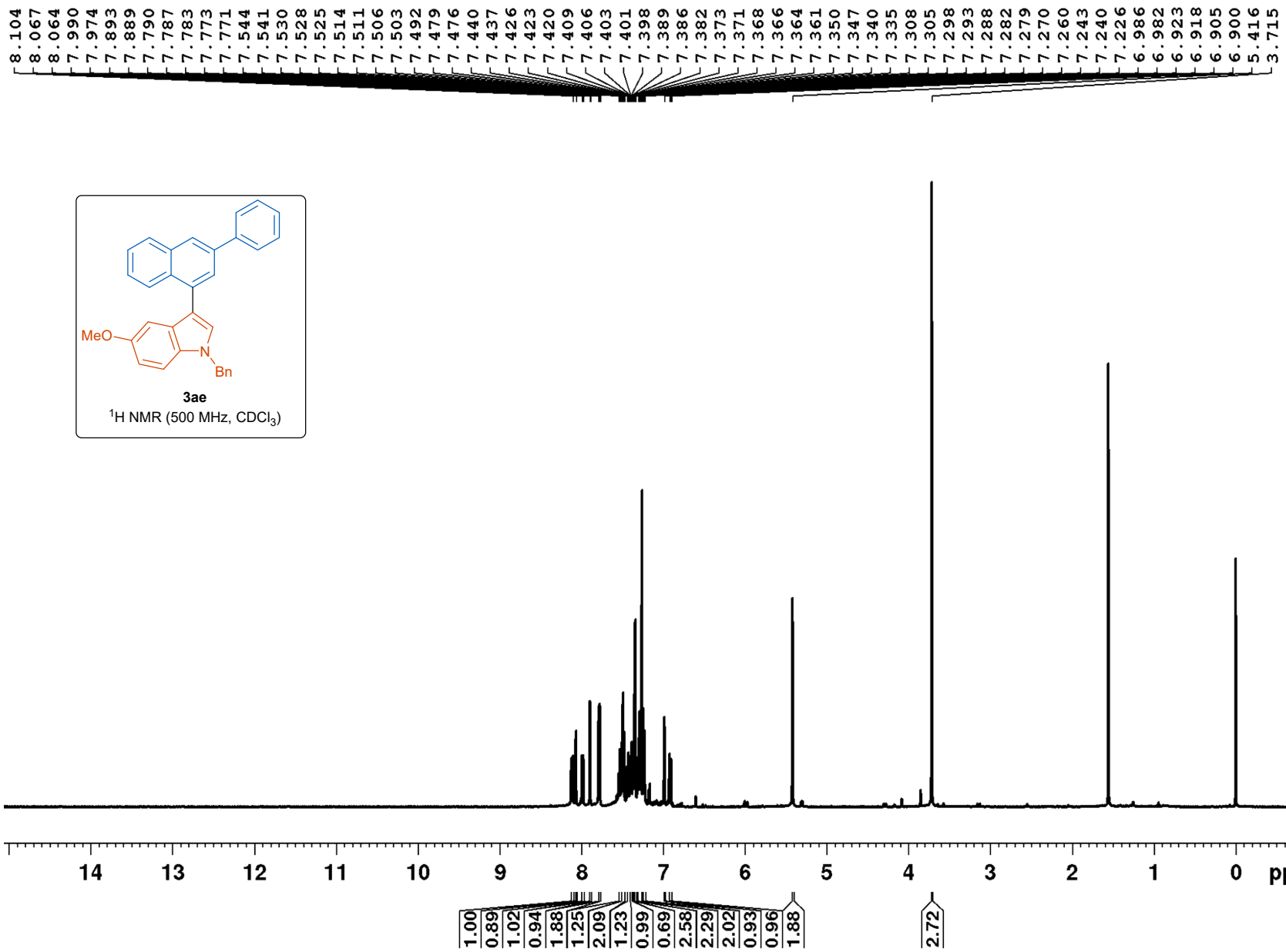
3ac

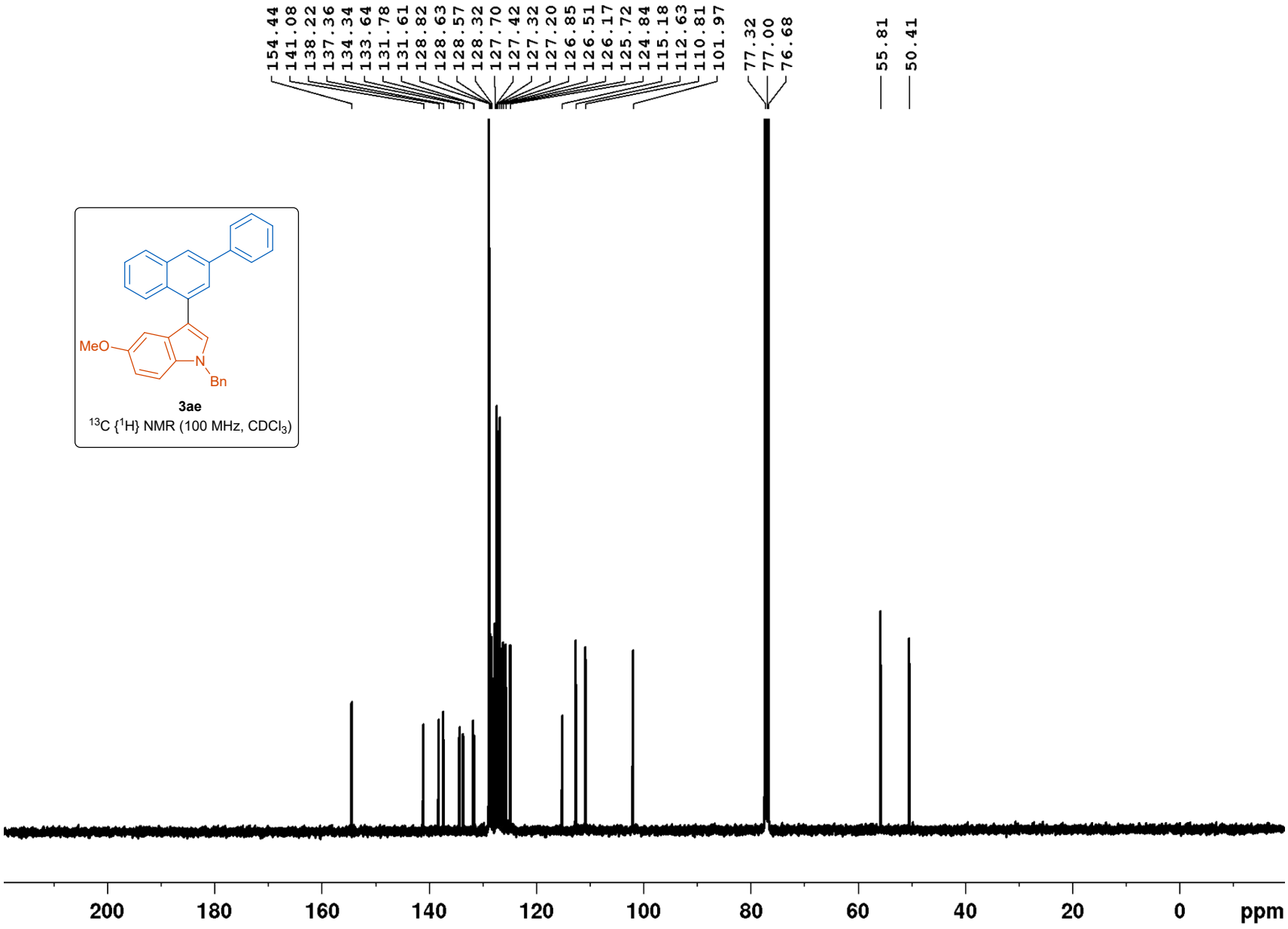
^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$)

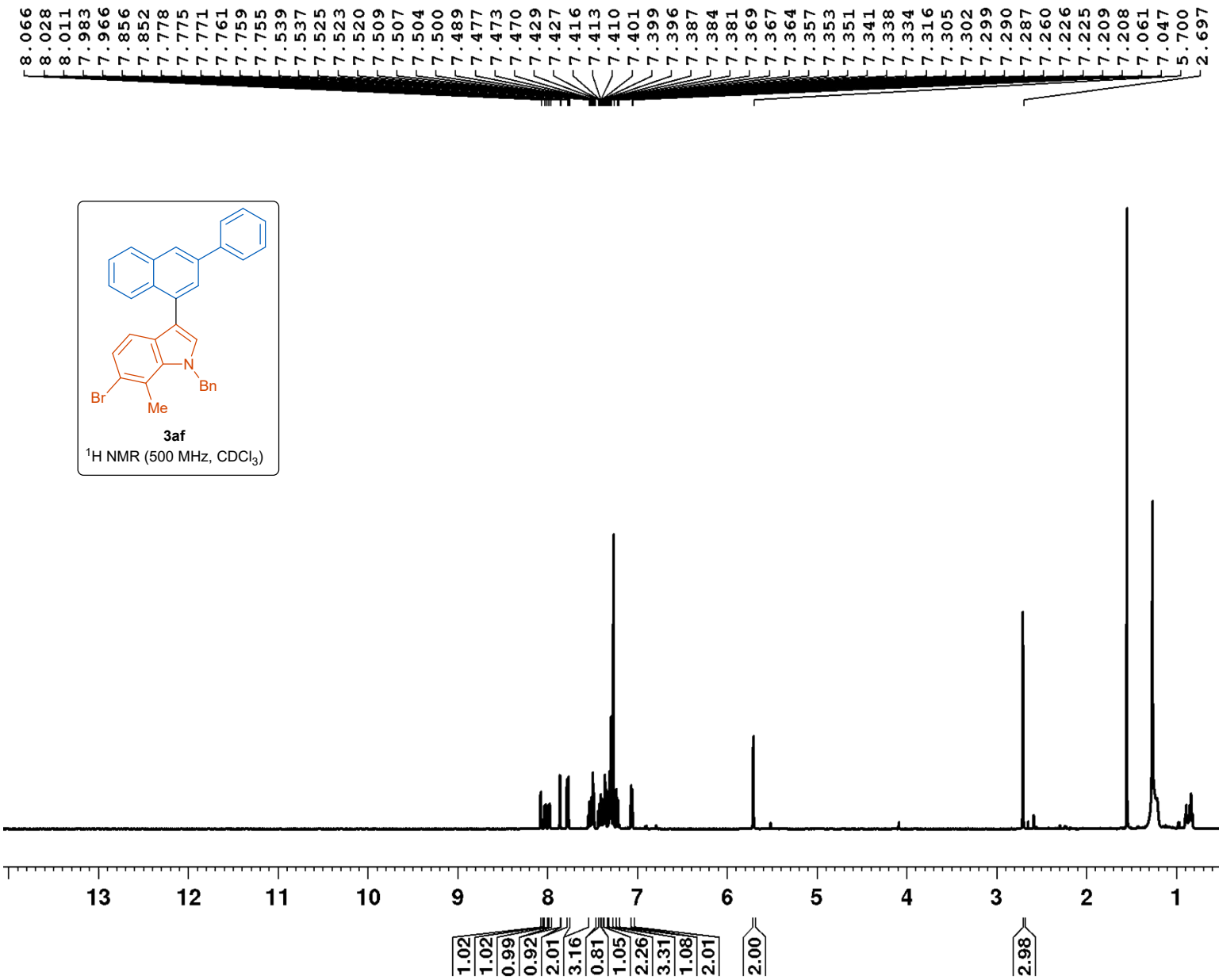


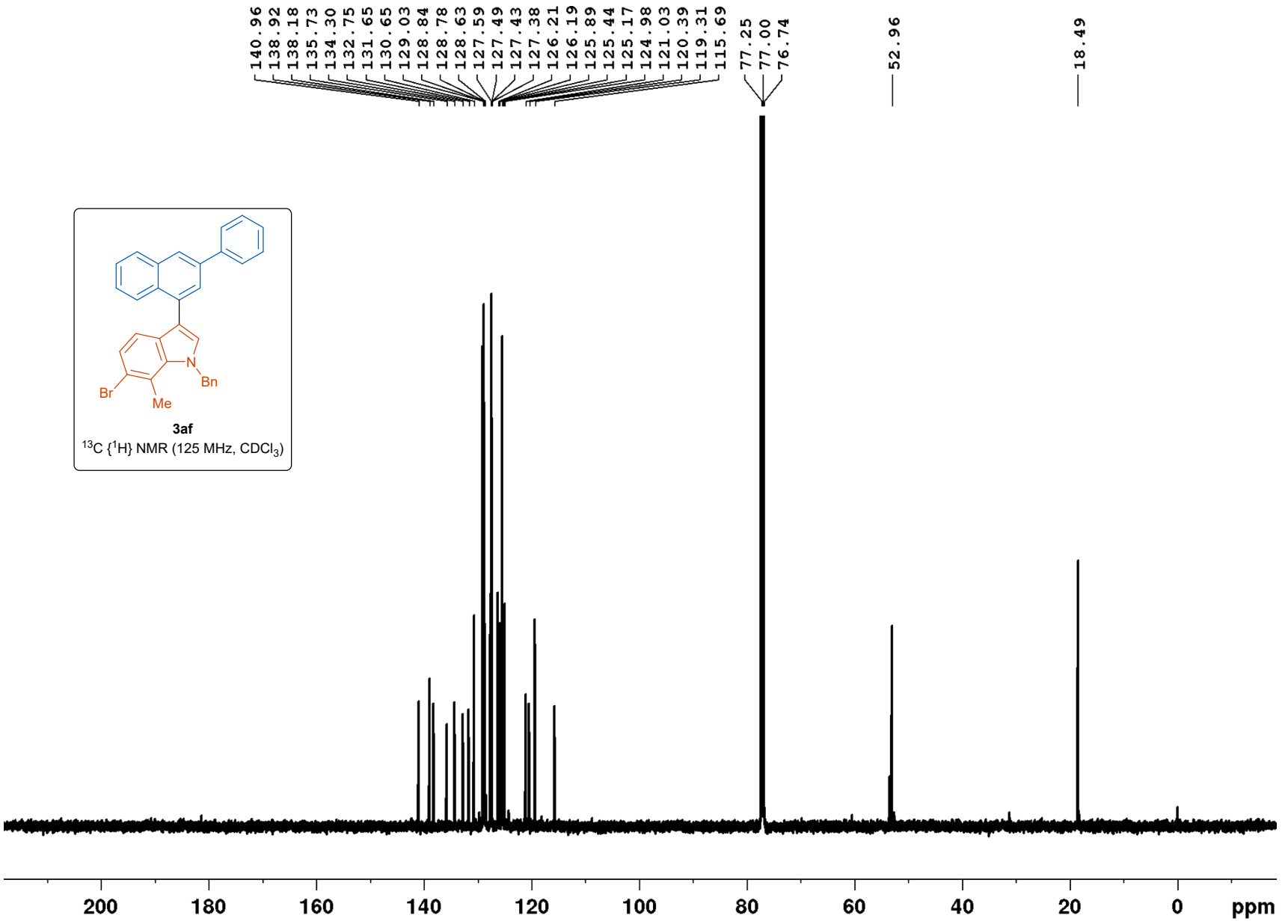

8.073
8.069
8.026
8.005
7.992
7.972
7.839
7.834
7.780
7.777
7.758
7.657
7.652
7.555
7.552
7.535
7.515
7.496
7.477
7.453
7.450
7.433
7.429
7.412
7.409
7.390
7.382
7.377
7.372
7.361
7.355
7.342
7.334
7.325
7.322
7.316
7.312
7.308
7.267
7.260
7.246
7.222
7.205
5.424
Br
N
Bn
3ad
1H NMR (400 MHz, CDCl3)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.03
2.12
1.01
2.10
0.98
3.30
1.55
2.99
2.79
1.83
1.97
2.00


140.95
138.21
136.80
135.18
134.30
132.65
131.61
130.03
128.93
128.85
128.78
128.64
127.92
127.45
127.39
126.82
126.26
126.09
126.00
125.27
125.11
122.92
115.19
113.40
111.49
77.32
77.00
76.68
50.43
Br
N
Bn
3ad
13C {1H} NMR (100 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0
ppm


8.104
8.067
8.064
7.990
7.974
7.893
7.889
7.790
7.787
7.783
7.773
7.771
7.544
7.541
7.530
7.528
7.525
7.514
7.511
7.506
7.503
7.492
7.479
7.476
7.440
7.437
7.426
7.423
7.420
7.409
7.406
7.403
7.401
7.398
7.389
7.386
7.382
7.373
7.371
7.368
7.366
7.364
7.361
7.350
7.347
7.340
7.335
7.308
7.305
7.298
7.293
7.288
7.282
7.279
7.270
7.260
7.243
7.240
7.226
6.986
6.982
6.923
6.918
6.905
6.900
5.416
3.715
MeO
N
Bn
3ae
1H NMR (500 MHz, CDCl3)
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.89
1.02
0.94
1.88
1.25
2.09
1.23
0.99
0.69
2.58
2.29
2.02
0.93
0.96
1.88
2.72

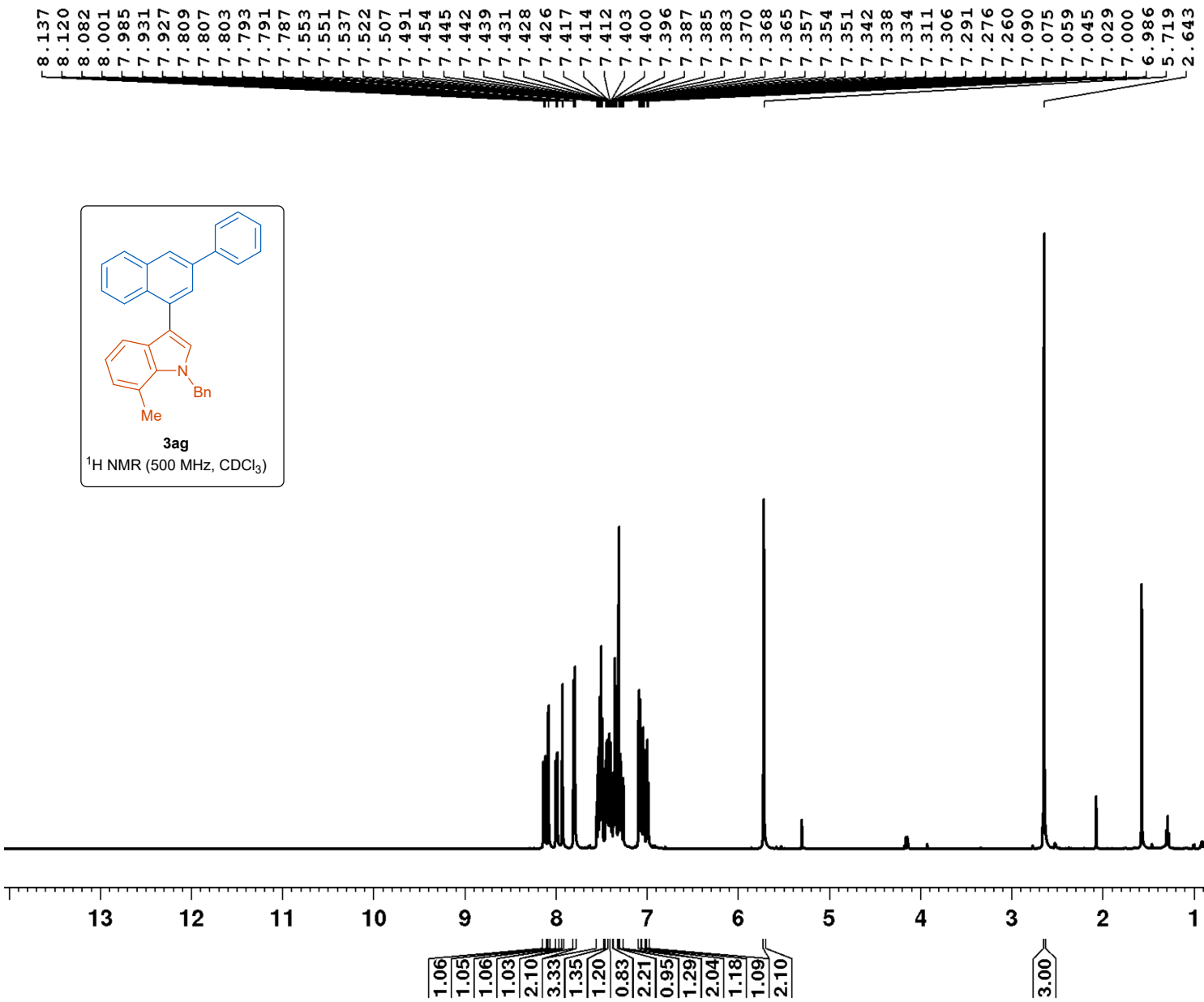

154.44
141.08
138.22
137.36
134.34
133.64
131.78
131.61
128.82
128.63
128.57
128.32
127.70
127.42
127.32
127.20
126.85
126.51
126.17
125.72
124.84
115.18
112.63
110.81
101.97
77.32
77.00
76.68
55.81
50.41
MeO
N
Bn
3ae
13C {1H} NMR (100 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0
ppm

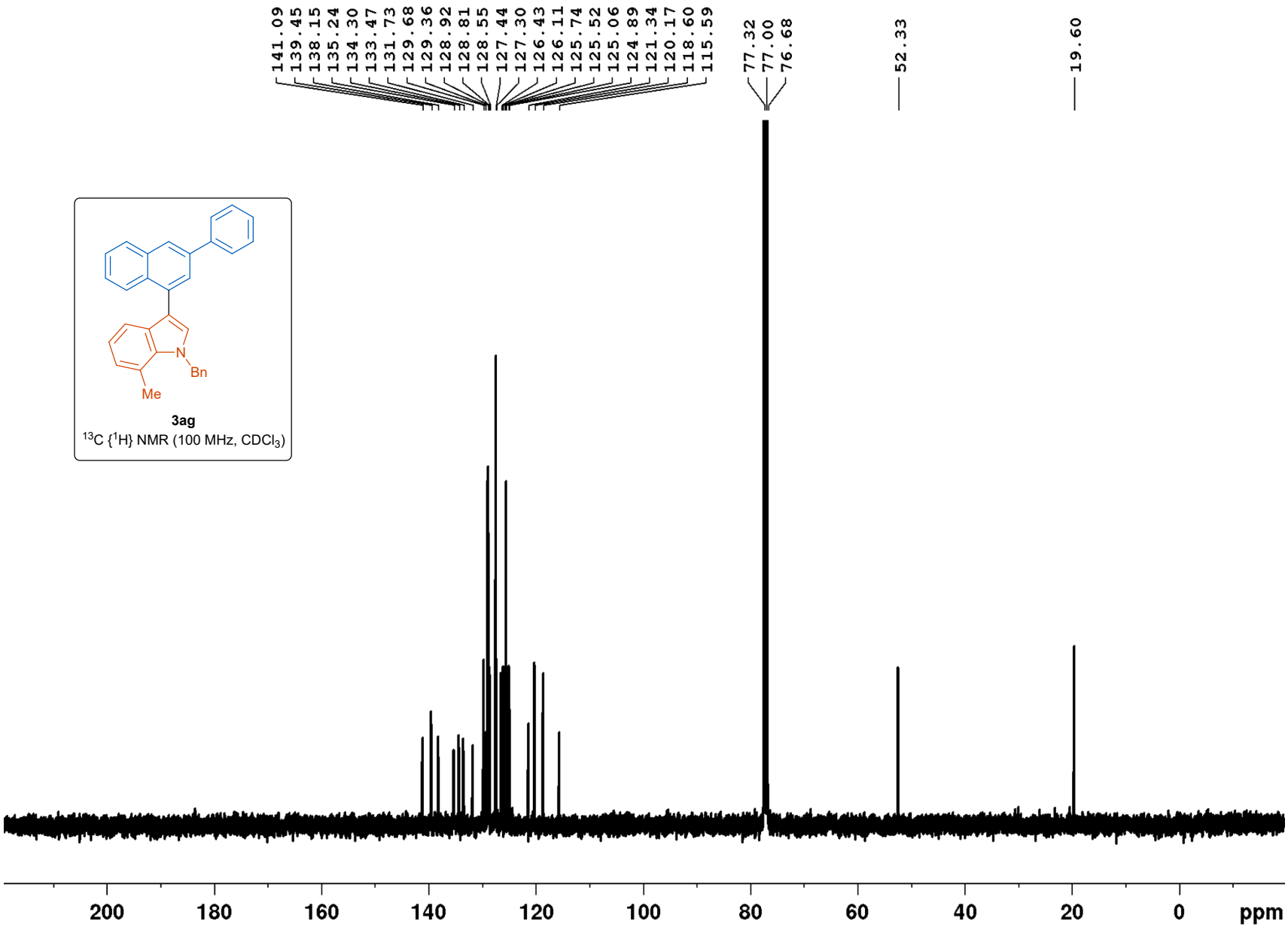

8.066
8.028
8.011
7.983
7.966
7.856
7.852
7.778
7.775
7.771
7.761
7.759
7.755
7.539
7.537
7.525
7.523
7.520
7.509
7.507
7.504
7.500
7.489
7.477
7.473
7.470
7.429
7.427
7.416
7.413
7.410
7.401
7.399
7.396
7.387
7.384
7.381
7.369
7.367
7.364
7.357
7.353
7.351
7.341
7.338
7.334
7.316
7.305
7.302
7.299
7.290
7.287
7.260
7.226
7.225
7.209
7.208
7.061
7.047
5.700
2.697
Br
Me
N
Bn
3af
1H NMR (500 MHz, CDCl3)
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.02
1.02
0.99
0.92
2.01
3.16
0.81
1.05
2.26
3.31
1.08
2.01
2.00
2.98

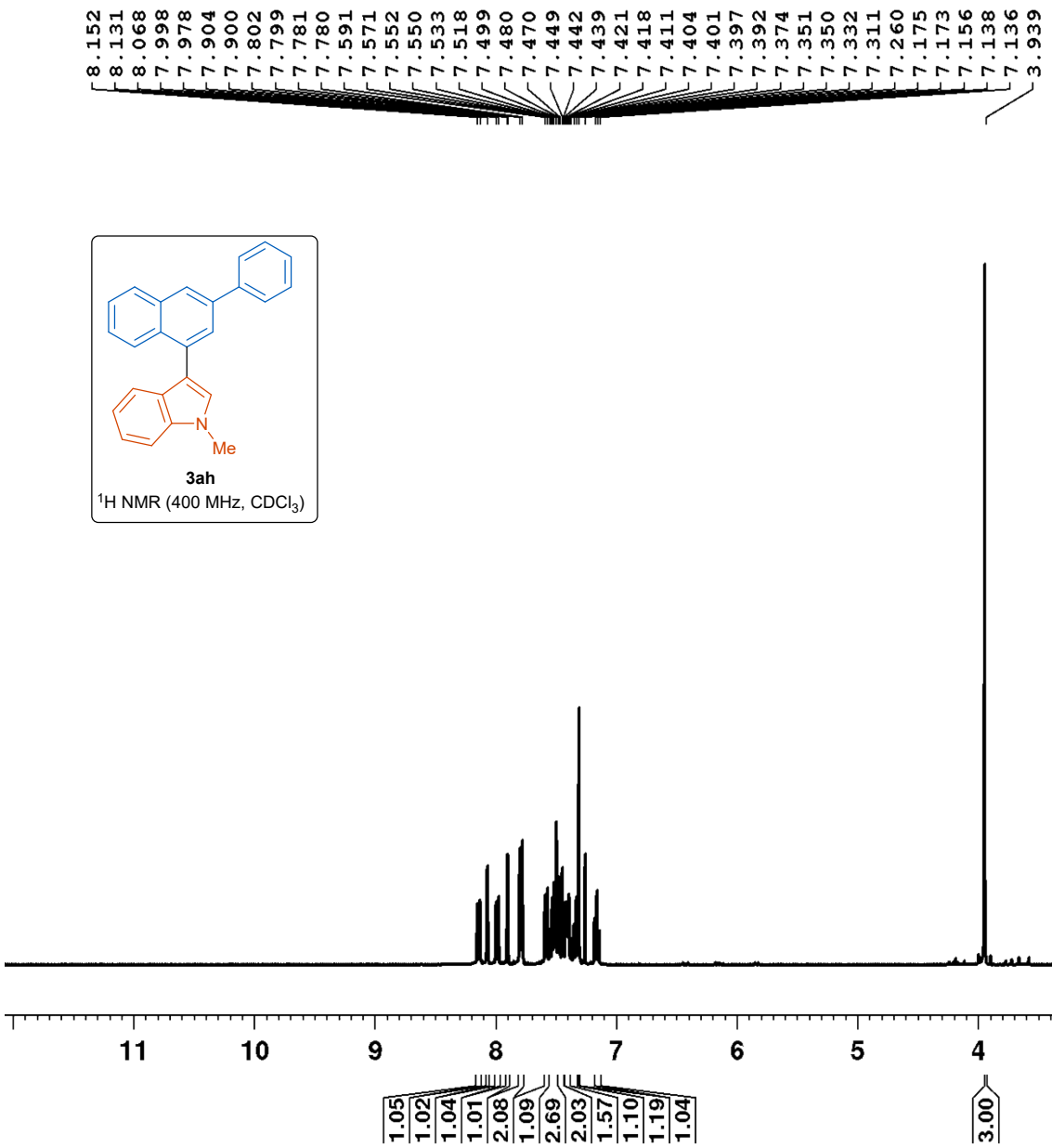


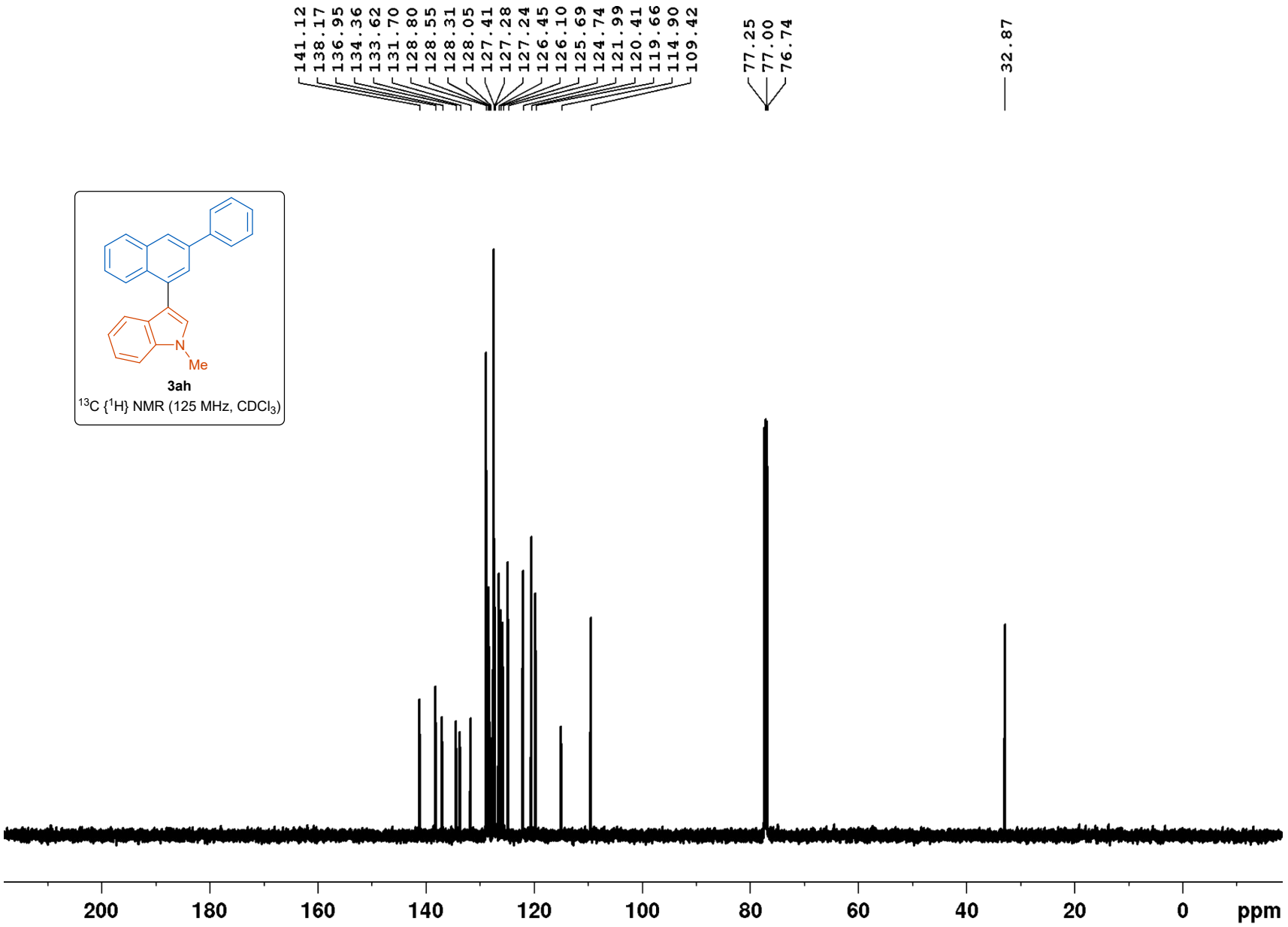
3af

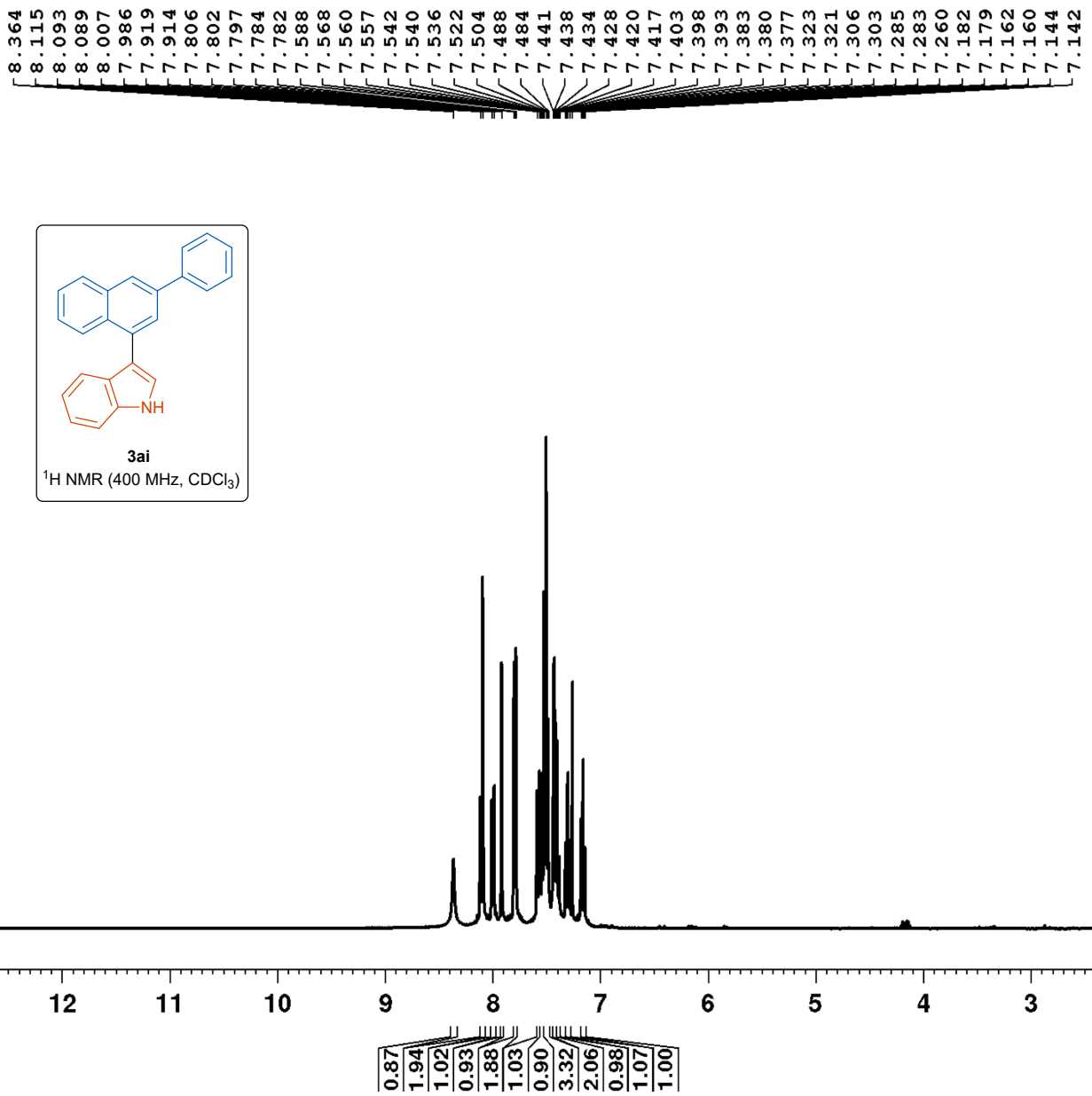
^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$)

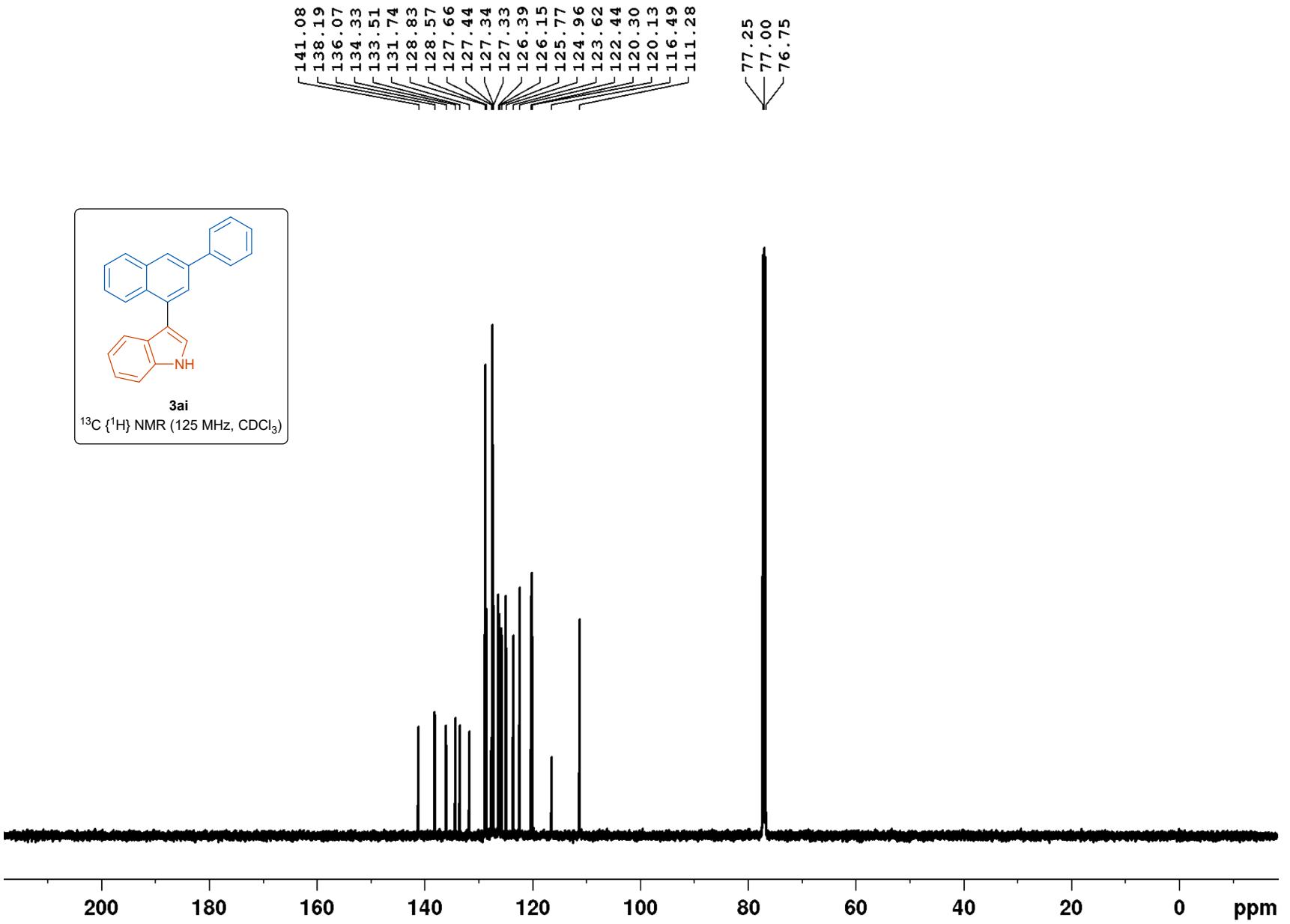

8.137
8.120
8.082
8.001
7.985
7.931
7.927
7.809
7.807
7.803
7.793
7.791
7.787
7.553
7.551
7.537
7.522
7.507
7.491
7.454
7.445
7.442
7.439
7.431
7.428
7.426
7.417
7.414
7.412
7.403
7.400
7.396
7.387
7.385
7.383
7.370
7.368
7.365
7.357
7.354
7.351
7.342
7.338
7.334
7.311
7.306
7.291
7.276
7.260
7.090
7.075
7.059
7.045
7.029
7.000
6.986
5.719
2.643
N
Bn
Me
3ag
1H NMR (500 MHz, CDCl3)
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.06
1.05
1.06
1.03
2.10
3.33
1.35
1.20
0.83
2.21
0.95
1.29
2.04
1.18
1.09
2.10
3.00

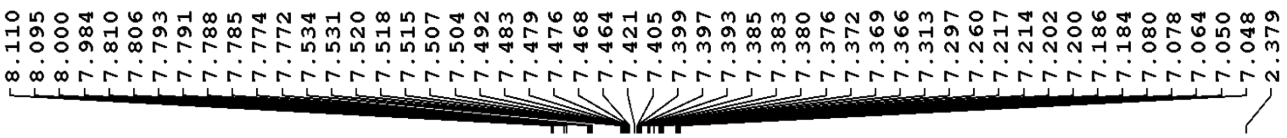

141.09
139.45
138.15
135.24
134.30
133.47
131.73
129.68
129.36
128.92
128.81
128.55
127.44
127.30
126.43
126.11
125.74
125.52
125.06
124.89
121.34
120.17
118.60
115.59
77.32
77.00
76.68
52.33
19.60
N
Bn
Me
3ag
13C {1H} NMR (100 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0
ppm

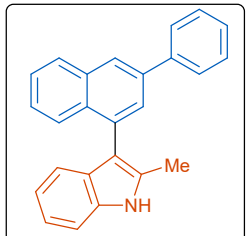

8.152
8.131
8.068
7.998
7.978
7.904
7.900
7.802
7.799
7.781
7.780
7.591
7.571
7.552
7.550
7.533
7.518
7.499
7.480
7.470
7.449
7.442
7.439
7.421
7.418
7.411
7.404
7.401
7.397
7.392
7.374
7.351
7.350
7.332
7.311
7.260
7.175
7.173
7.156
7.138
7.136
3.939
N
Me
3ah
1H NMR (400 MHz, CDCl3)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.05
1.02
1.04
1.01
2.08
1.09
2.69
2.03
1.57
1.10
1.19
1.04
3.00


141.12
138.17
136.95
134.36
133.62
131.70
128.80
128.55
128.31
128.05
127.41
127.28
127.24
126.45
126.10
125.69
124.74
121.99
120.41
119.66
114.90
109.42
77.25
77.00
76.74
32.87
N
Me
3ah
13C {1H} NMR (125 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0
ppm


8.364
8.115
8.093
8.089
8.007
7.986
7.919
7.914
7.806
7.802
7.797
7.784
7.782
7.588
7.568
7.560
7.557
7.542
7.540
7.536
7.522
7.504
7.488
7.484
7.441
7.438
7.434
7.428
7.420
7.417
7.403
7.398
7.393
7.383
7.380
7.377
7.323
7.321
7.306
7.303
7.285
7.283
7.260
7.182
7.179
7.162
7.160
7.144
7.142
NH
3ai
1H NMR (400 MHz, CDCl3)
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.87
1.94
1.02
0.93
1.88
1.03
0.90
3.32
2.06
0.98
1.07
1.00

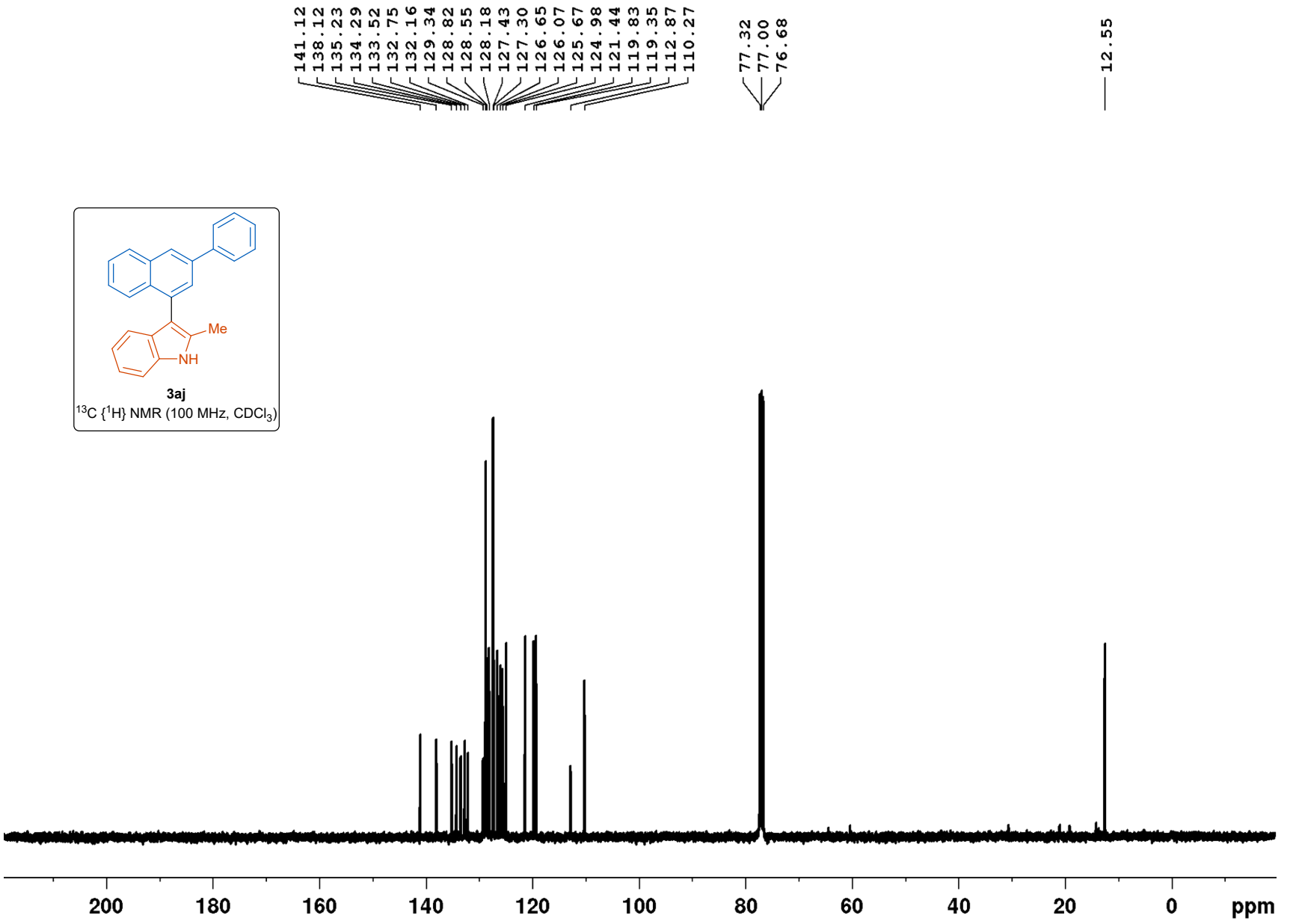

141.08
138.19
136.07
134.33
133.51
131.74
128.83
128.57
127.66
127.44
127.34
127.33
126.39
126.15
125.77
124.96
123.62
122.44
120.30
120.13
116.49
111.28
77.25
77.00
76.75
NH
3ai
13C {1H} NMR (125 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0
ppm

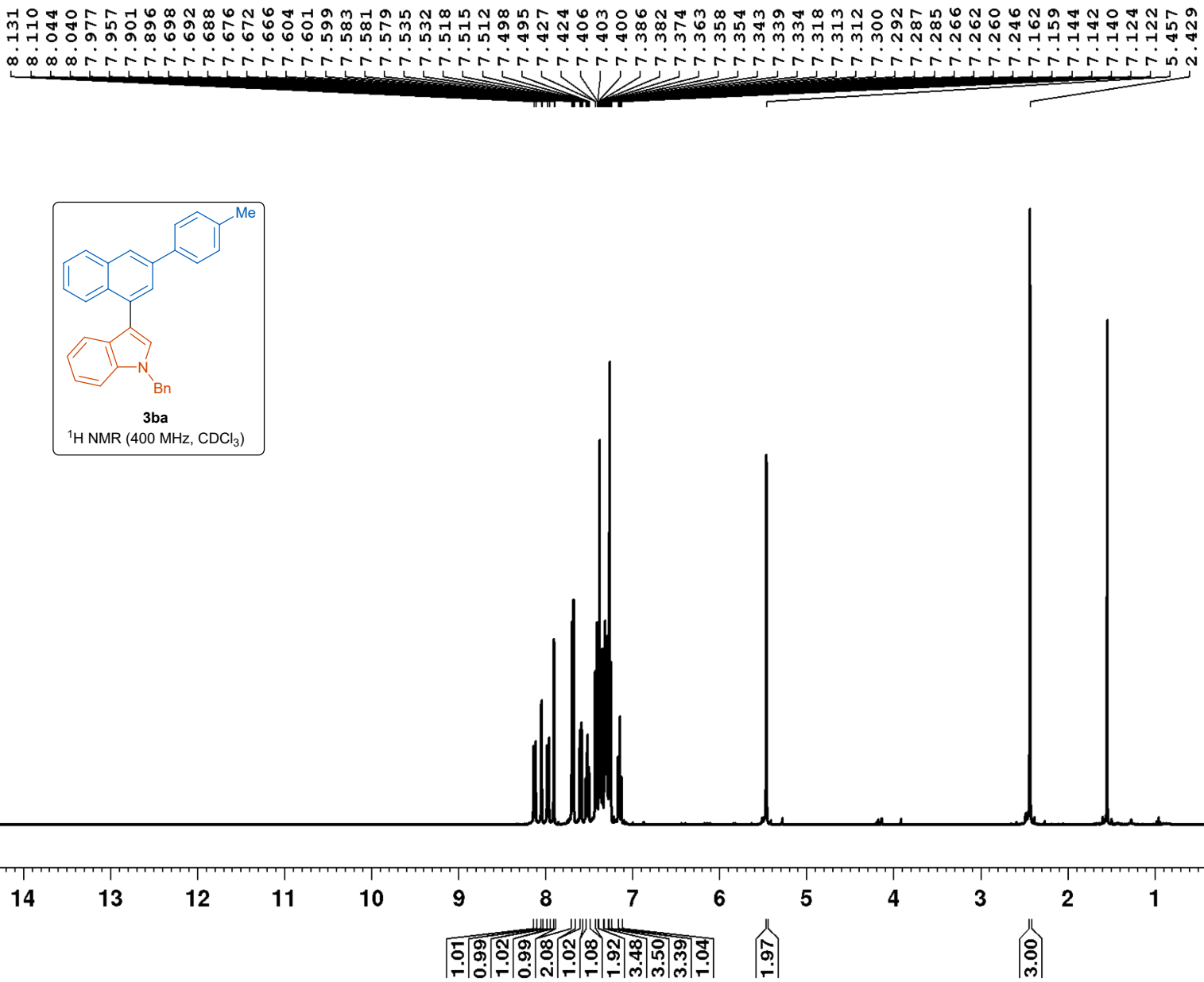


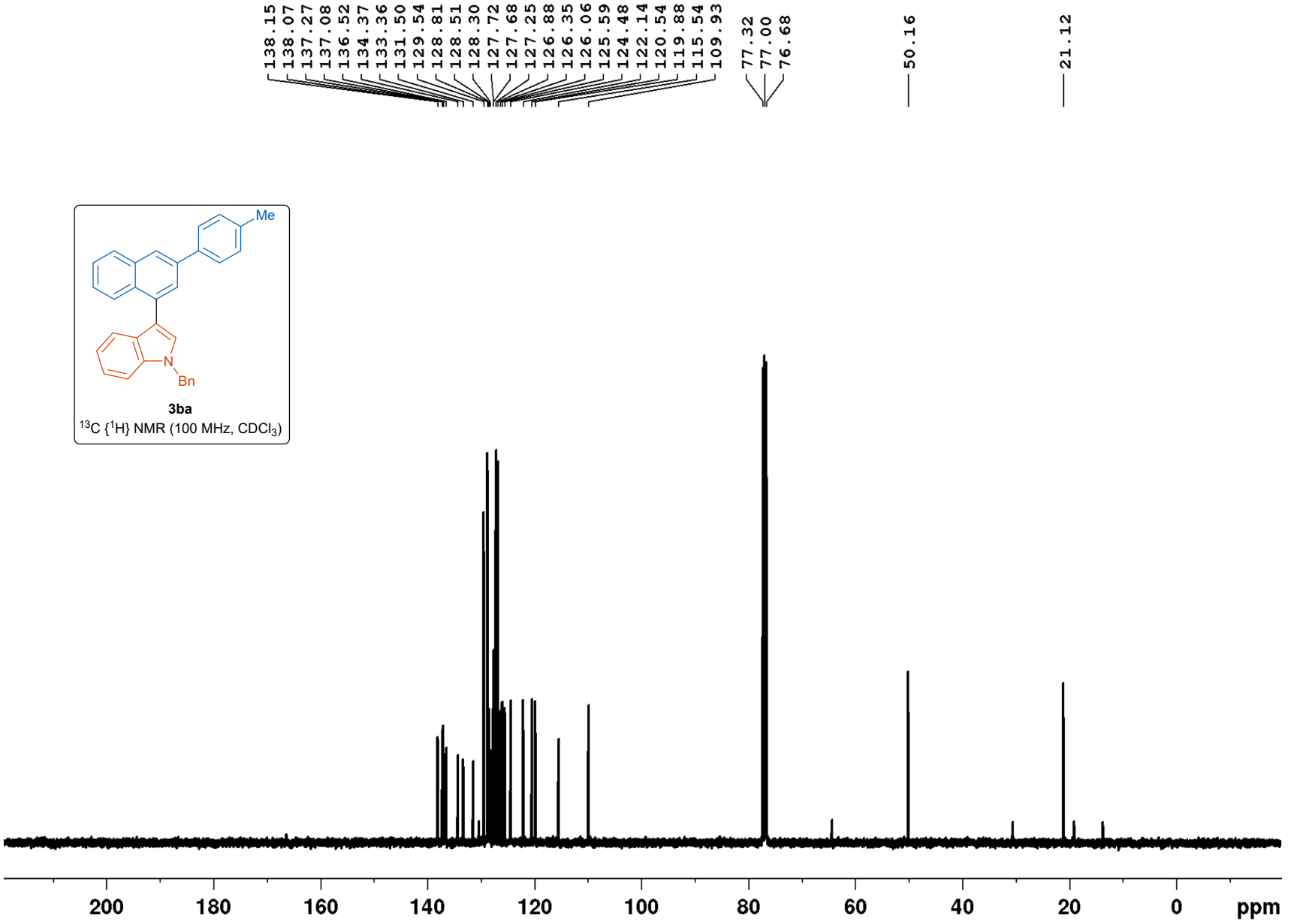


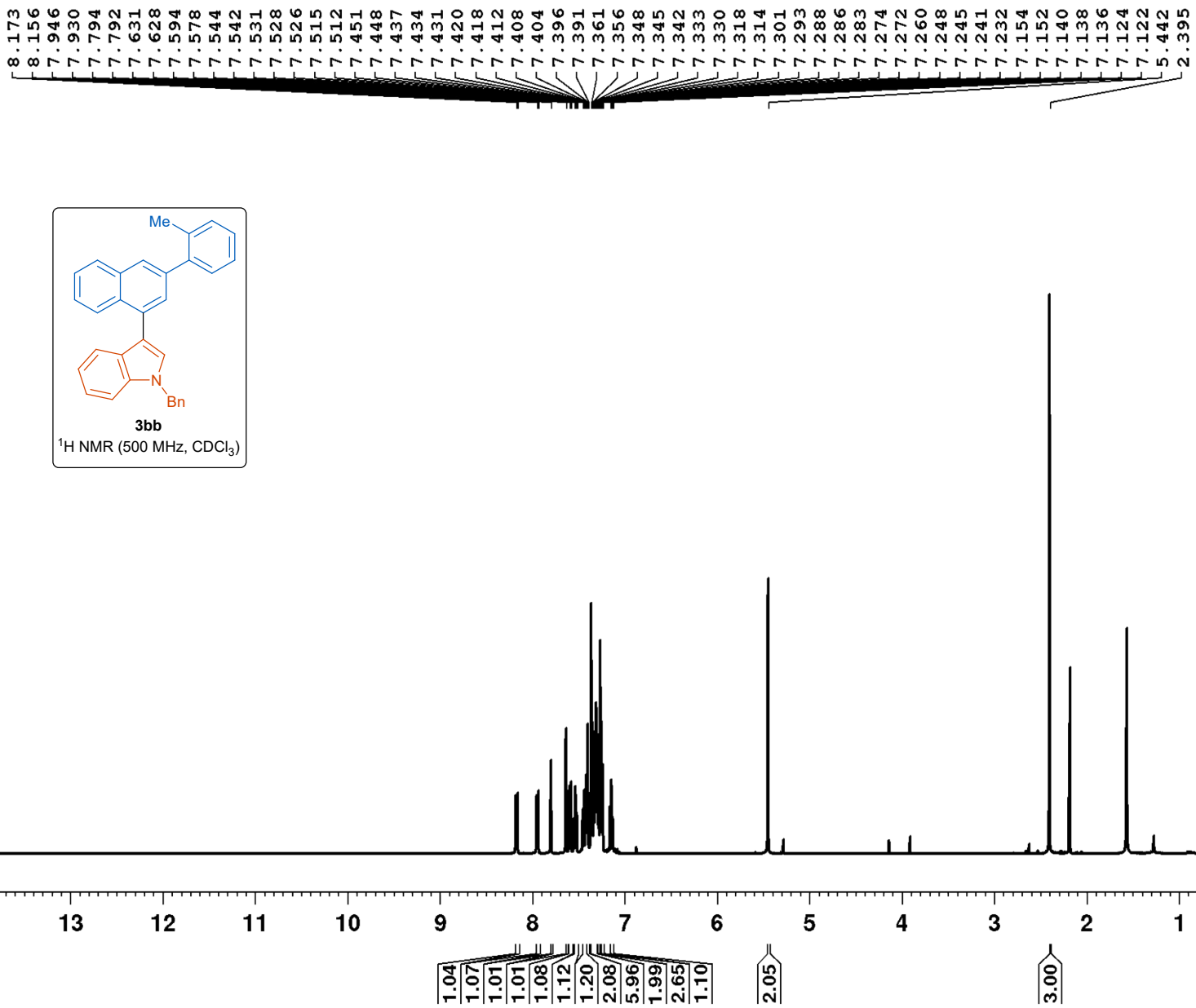
3aj

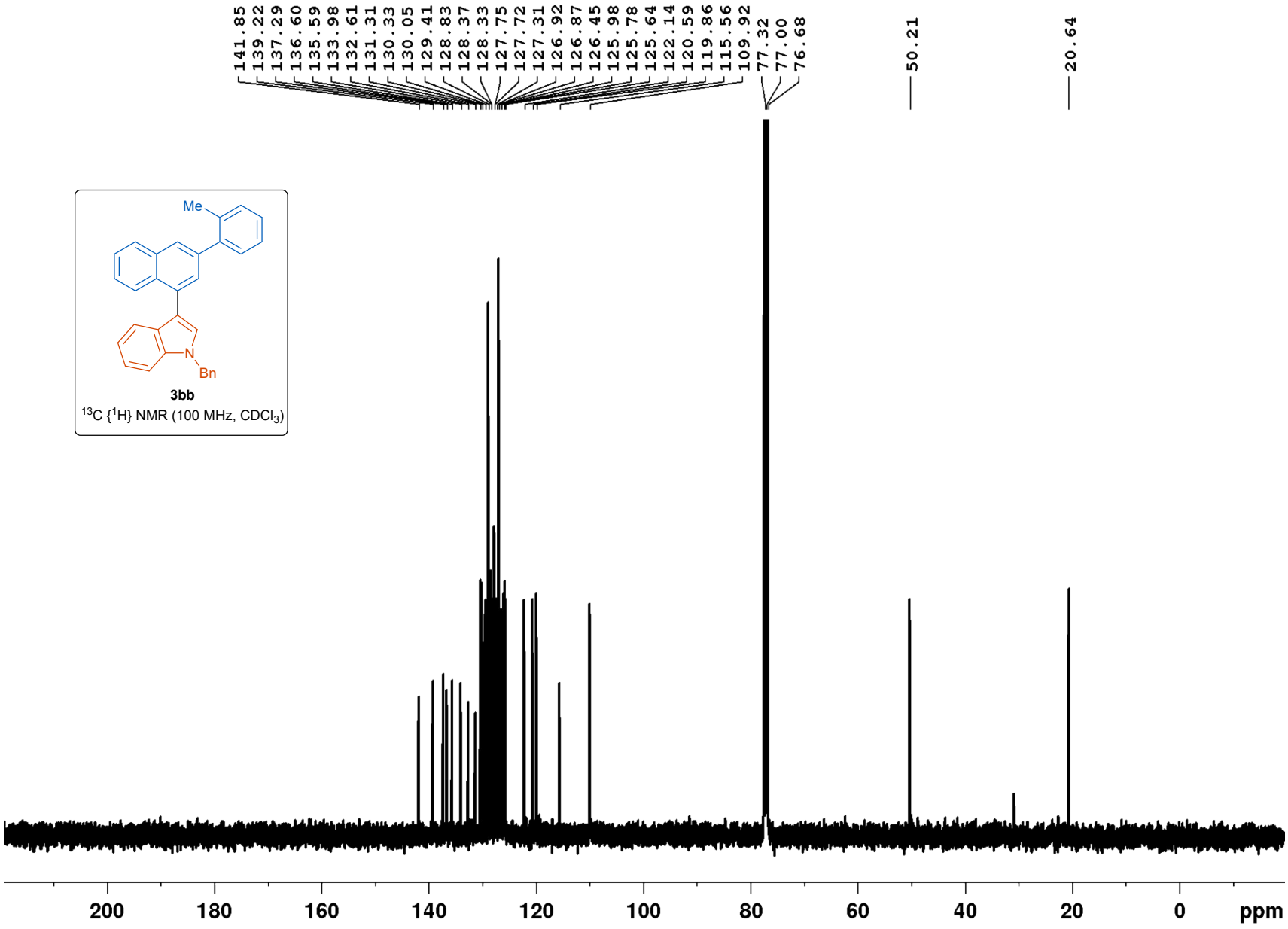
^{1}H NMR (500 MHz, $CDCl_3$)

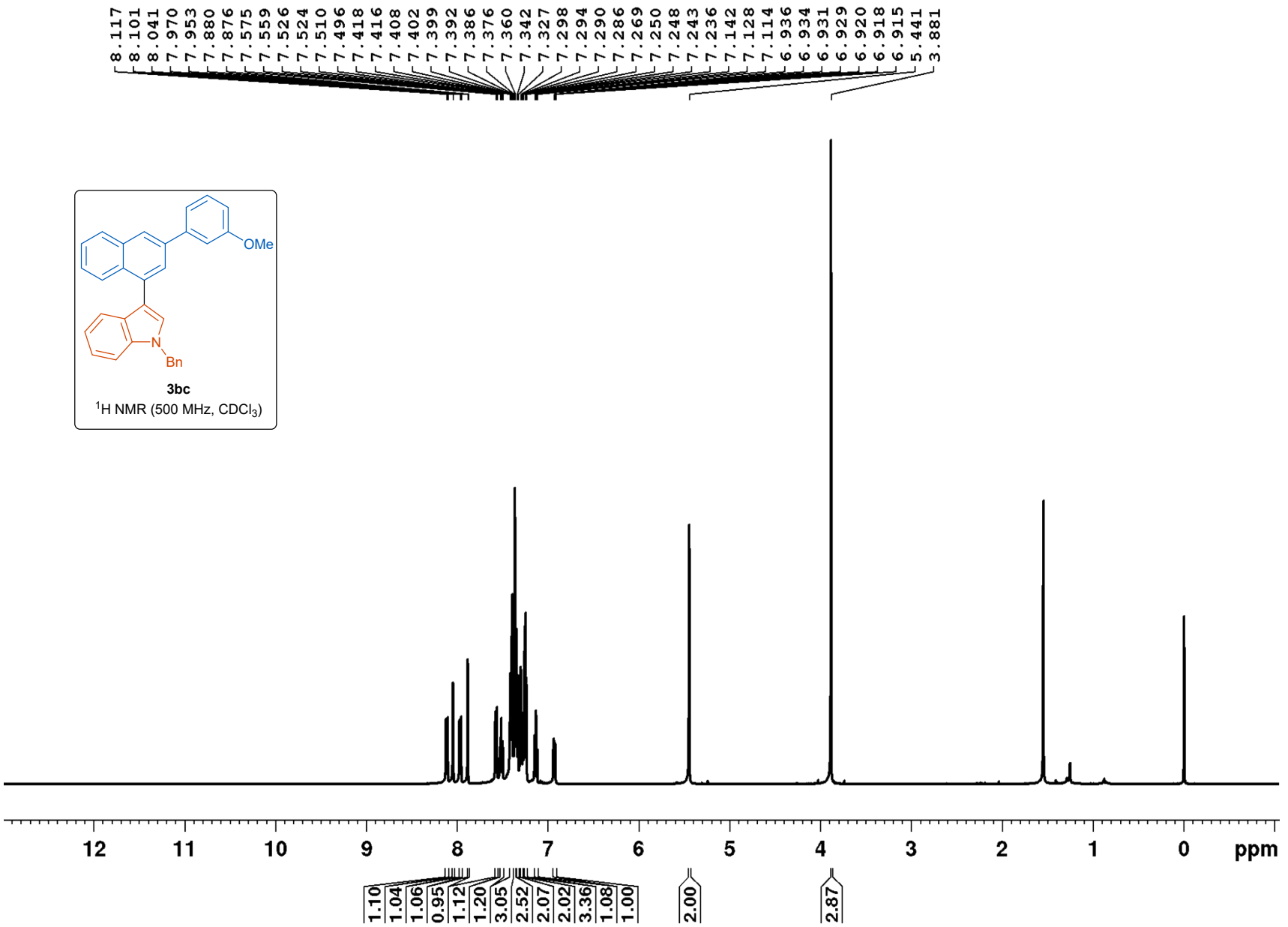

141.12
138.12
135.23
134.29
133.52
132.75
132.16
129.34
128.82
128.55
128.18
127.43
127.30
126.65
126.07
125.67
124.98
121.44
119.83
119.35
112.87
110.27
77.32
77.00
76.68
12.55
Me
NH
3aj
13C {1H} NMR (100 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0
ppm

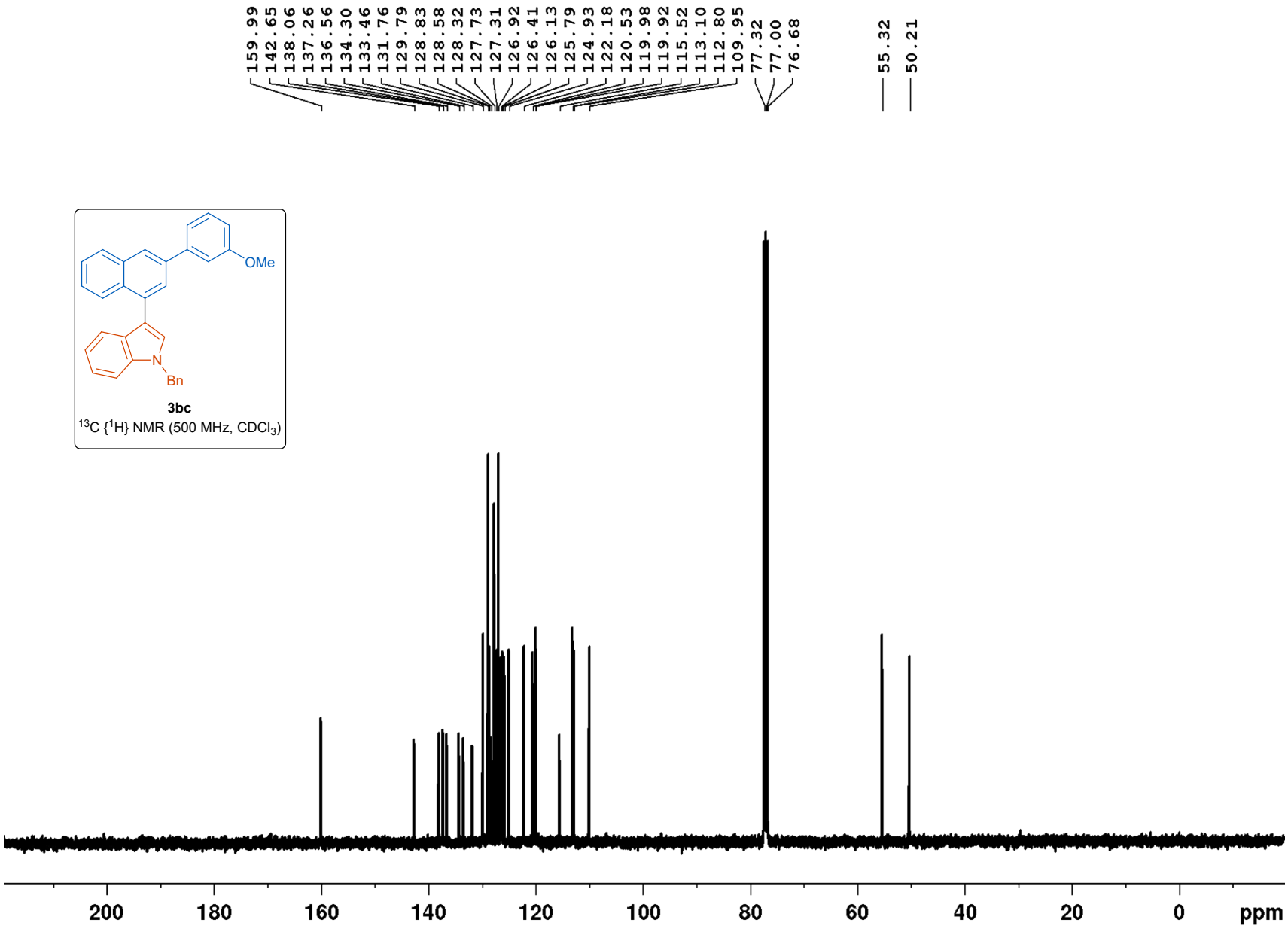

8.131
8.110
8.044
8.040
7.977
7.957
7.901
7.896
7.698
7.692
7.688
7.676
7.672
7.666
7.604
7.601
7.599
7.583
7.581
7.579
7.535
7.532
7.518
7.515
7.512
7.498
7.495
7.427
7.424
7.406
7.403
7.400
7.386
7.382
7.374
7.363
7.358
7.354
7.343
7.339
7.334
7.318
7.313
7.312
7.300
7.292
7.287
7.285
7.266
7.262
7.260
7.246
7.162
7.159
7.144
7.142
7.140
7.124
7.122
5.457
2.429
Me
N
Bn
3ba
1H NMR (400 MHz, CDCl3)
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
0.99
1.02
0.99
2.08
1.02
1.08
1.92
3.48
3.50
3.39
1.04
1.97
3.00

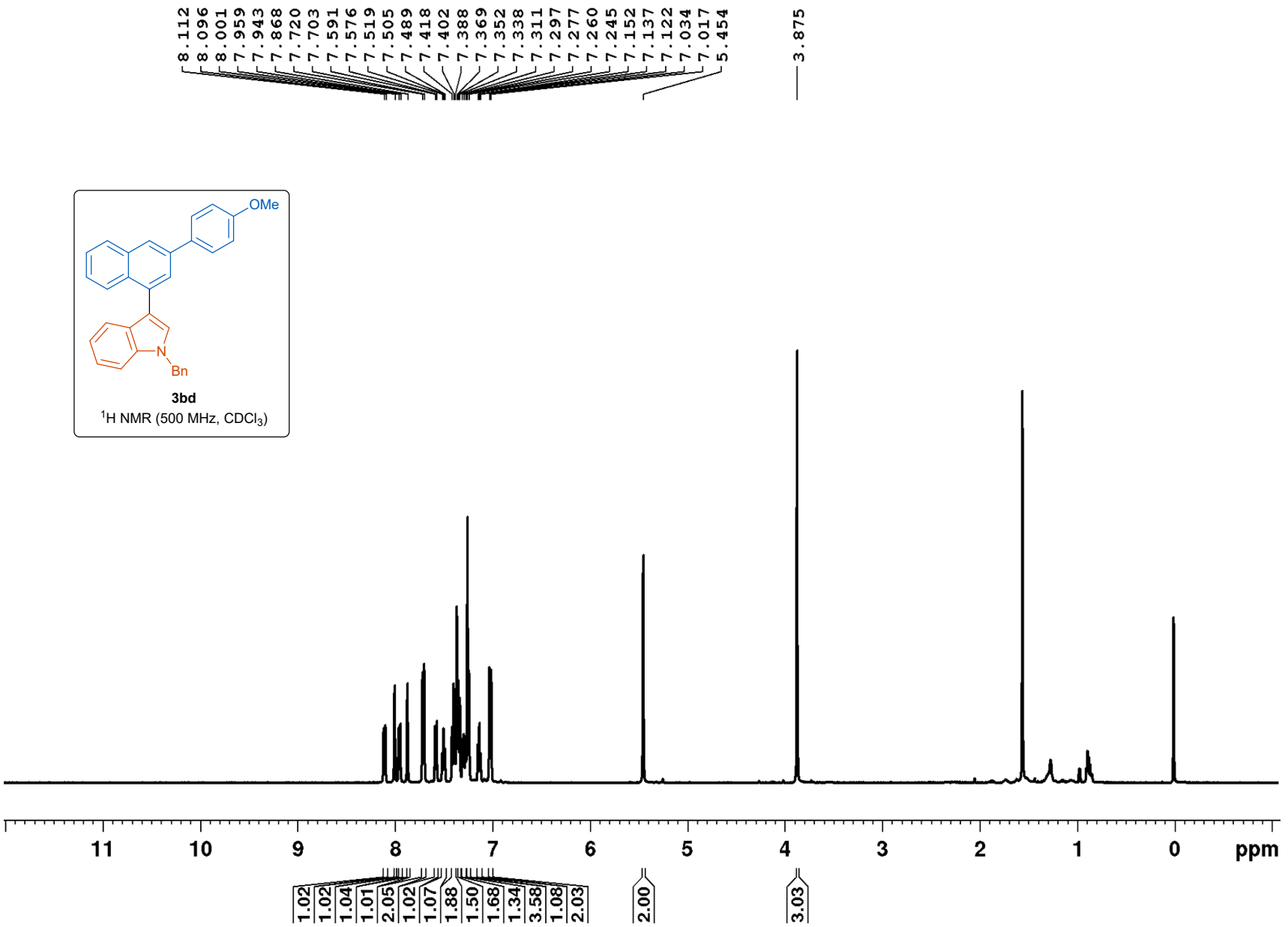

138.15
138.07
137.27
137.08
136.52
134.37
133.36
131.50
129.54
128.81
128.51
128.30
127.72
127.68
127.25
126.88
126.35
126.06
125.59
124.48
122.14
120.54
119.88
115.54
109.93
77.32
77.00
76.68
50.16
21.12
Me
N
Bn
3ba
13C {1H} NMR (100 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0
ppm

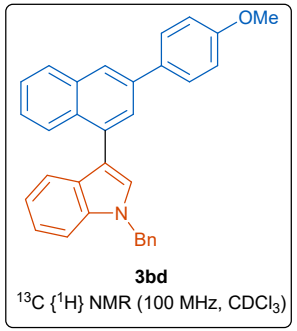

8.173
8.156
7.946
7.930
7.794
7.792
7.631
7.628
7.594
7.578
7.544
7.542
7.531
7.528
7.526
7.515
7.512
7.451
7.448
7.437
7.434
7.431
7.420
7.418
7.412
7.408
7.404
7.396
7.391
7.361
7.356
7.348
7.345
7.342
7.333
7.330
7.318
7.314
7.301
7.293
7.288
7.286
7.283
7.274
7.272
7.260
7.248
7.245
7.241
7.232
7.154
7.152
7.140
7.138
7.136
7.124
7.122
5.442
2.395
Me
N
Bn
3bb
1H NMR (500 MHz, CDCl3)
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.04
1.07
1.01
1.01
1.08
1.12
1.20
2.08
5.96
1.99
2.65
1.10
2.05
3.00


141.85
139.22
137.29
136.60
135.59
133.98
132.61
131.31
130.33
130.05
129.41
128.83
128.37
128.33
127.75
127.72
127.31
126.92
126.87
126.45
125.98
125.78
125.64
122.14
120.59
119.86
115.56
109.92
77.32
77.00
76.68
50.21
20.64
Me
N
Bn
3bb
13C {1H} NMR (100 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0
ppm


8.117
8.101
8.041
7.970
7.953
7.880
7.876
7.575
7.559
7.526
7.524
7.510
7.496
7.418
7.416
7.408
7.402
7.399
7.392
7.386
7.376
7.360
7.342
7.327
7.298
7.294
7.290
7.286
7.269
7.250
7.248
7.243
7.236
7.142
7.128
7.114
6.936
6.934
6.931
6.929
6.920
6.918
6.915
5.441
3.881
OMe
N
Bn
3bc
1H NMR (500 MHz, CDCl3)
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.10
1.04
1.06
0.95
1.12
1.20
3.05
2.52
2.07
2.02
3.36
1.08
1.00
2.00
2.87


159.99
142.65
138.06
137.26
136.56
134.30
133.46
131.76
129.79
128.83
128.58
128.32
127.73
127.31
126.92
126.41
126.13
125.79
124.93
122.18
120.53
119.98
119.92
115.52
113.10
112.80
109.95
77.32
77.00
76.68
55.32
50.21
OMe
N
Bn
3bc
13C {1H} NMR (500 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0
ppm

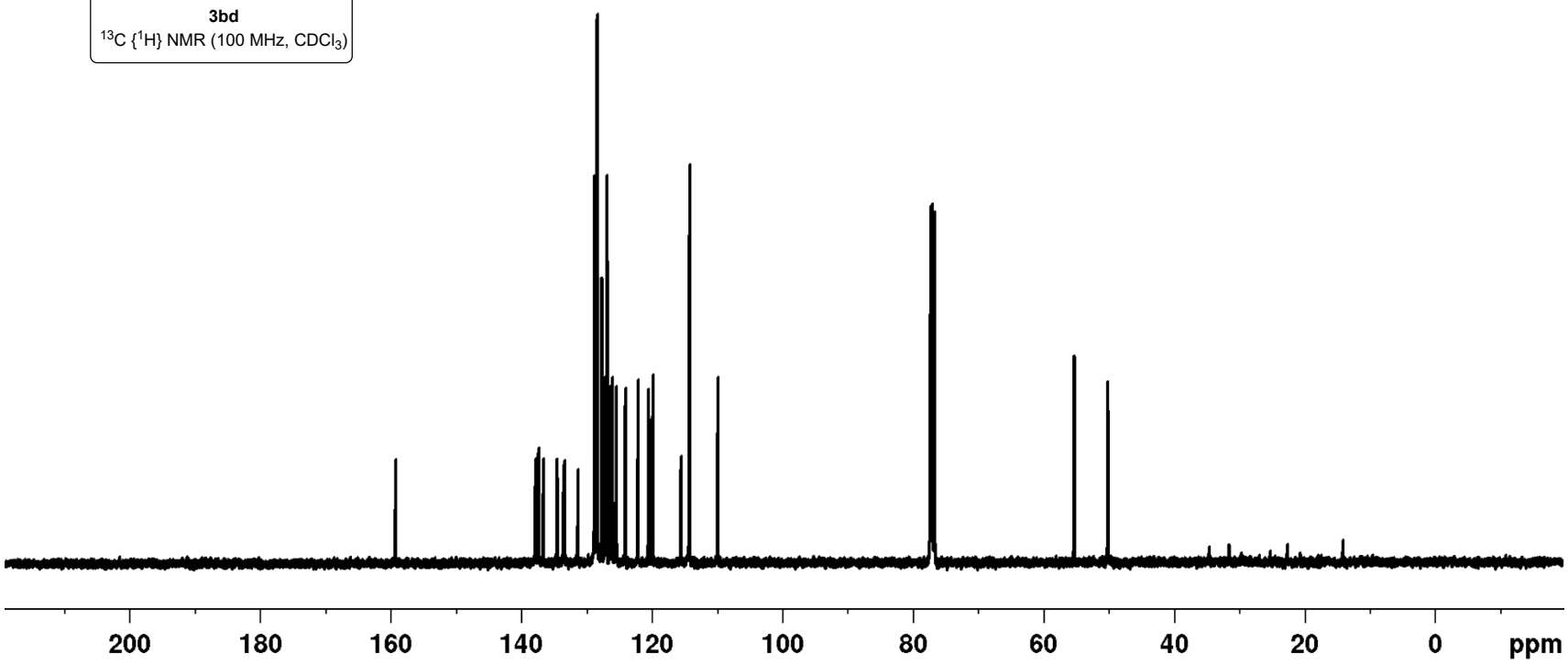

8.112
8.096
8.001
7.959
7.943
7.868
7.720
7.703
7.591
7.576
7.519
7.505
7.489
7.418
7.402
7.388
7.369
7.352
7.338
7.311
7.297
7.277
7.260
7.245
7.152
7.137
7.122
7.034
7.017
5.454
3.875
OMe
N
Bn
3bd
1H NMR (500 MHz, CDCl3)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.02
1.02
1.04
1.01
2.05
1.02
1.07
1.88
1.50
1.68
1.34
3.58
1.08
2.03
2.00
3.03

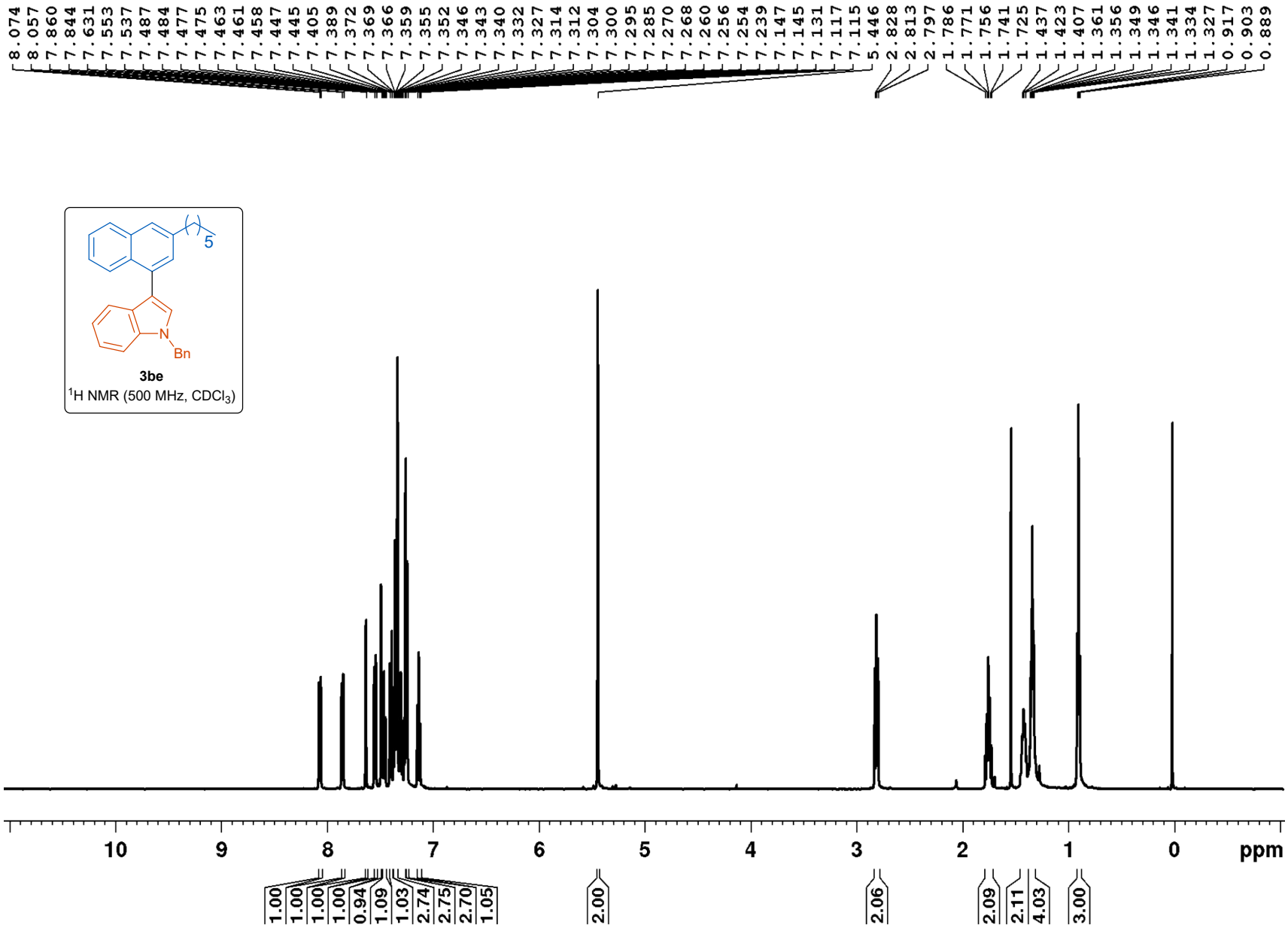


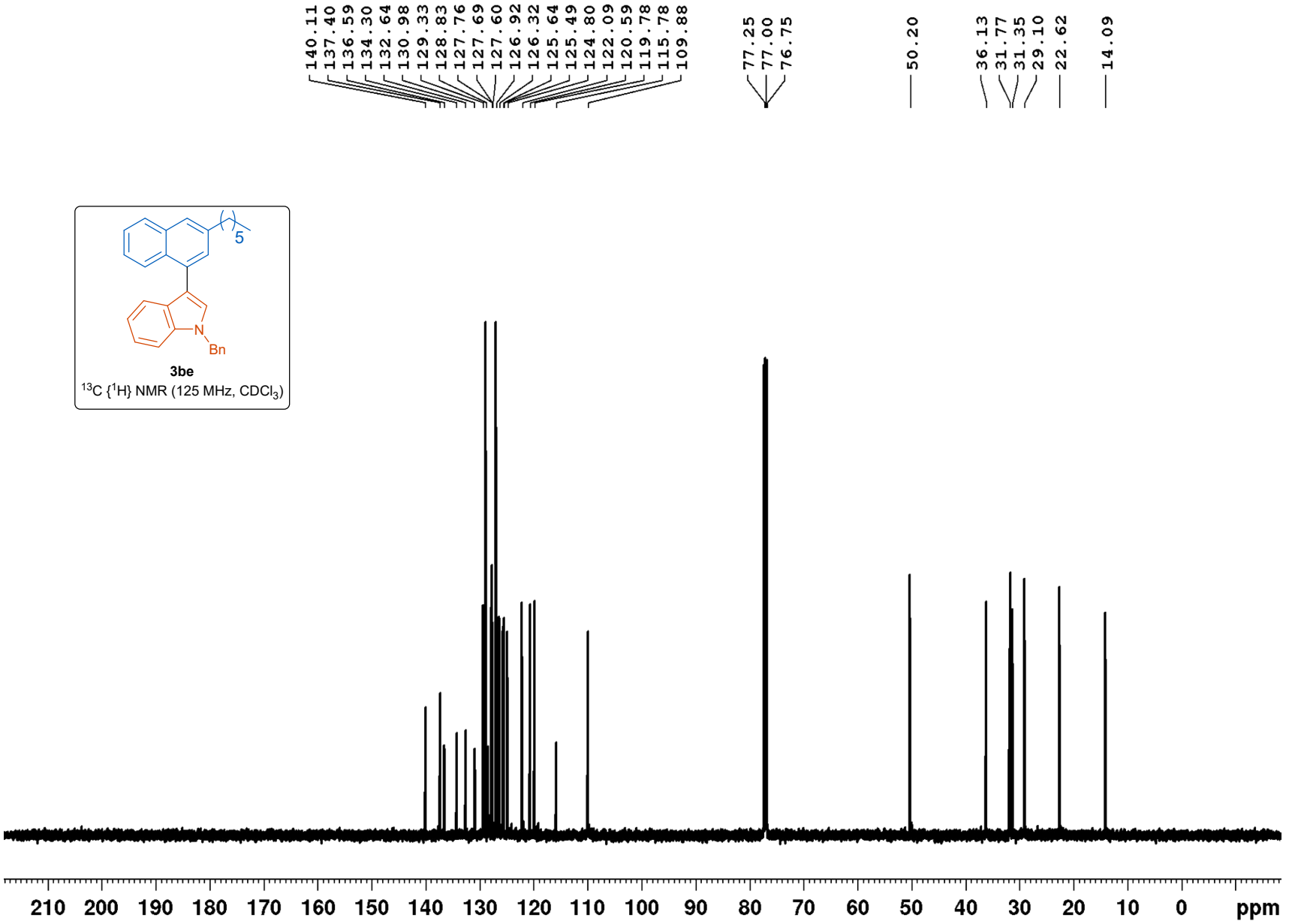
3bd

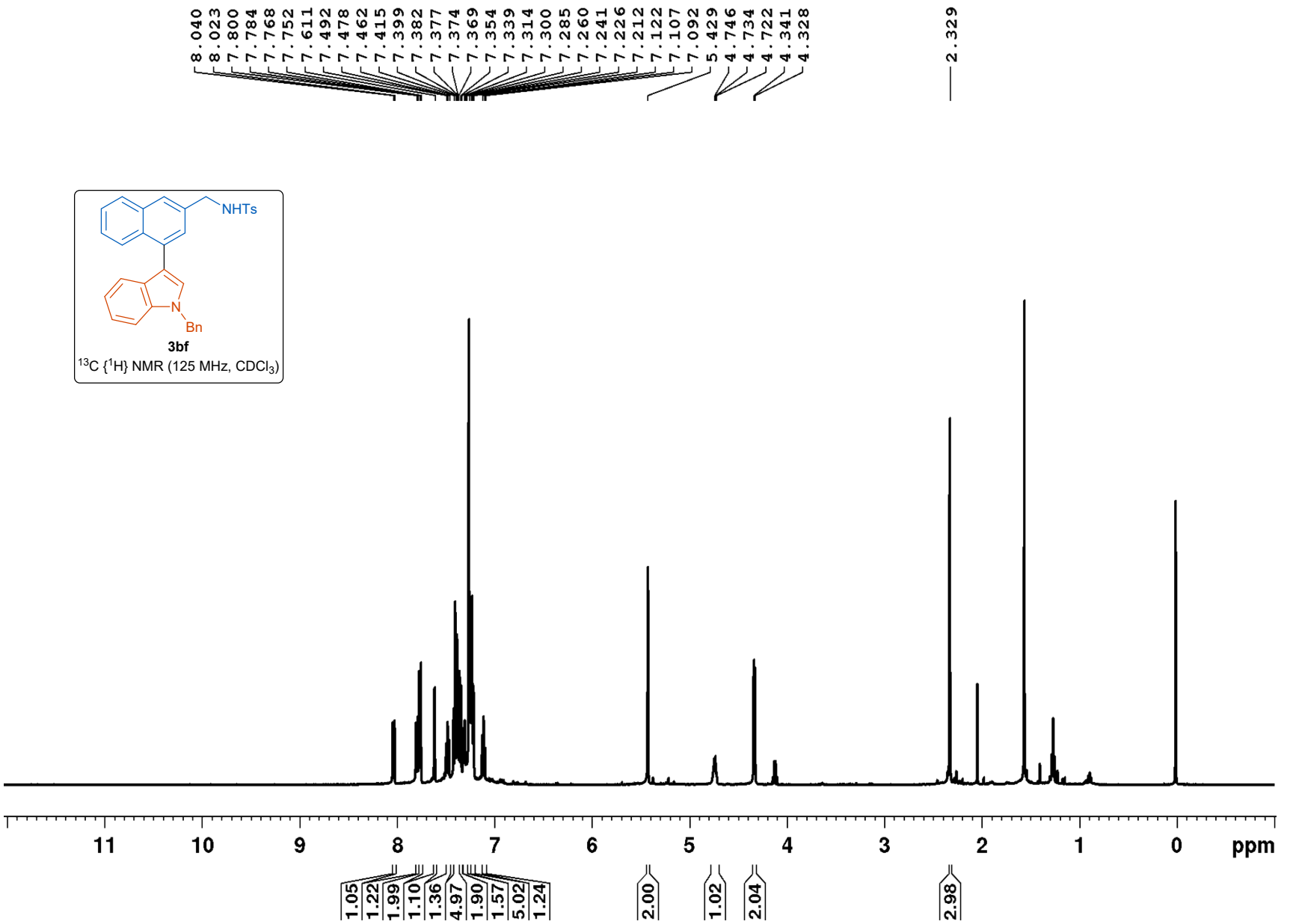
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)

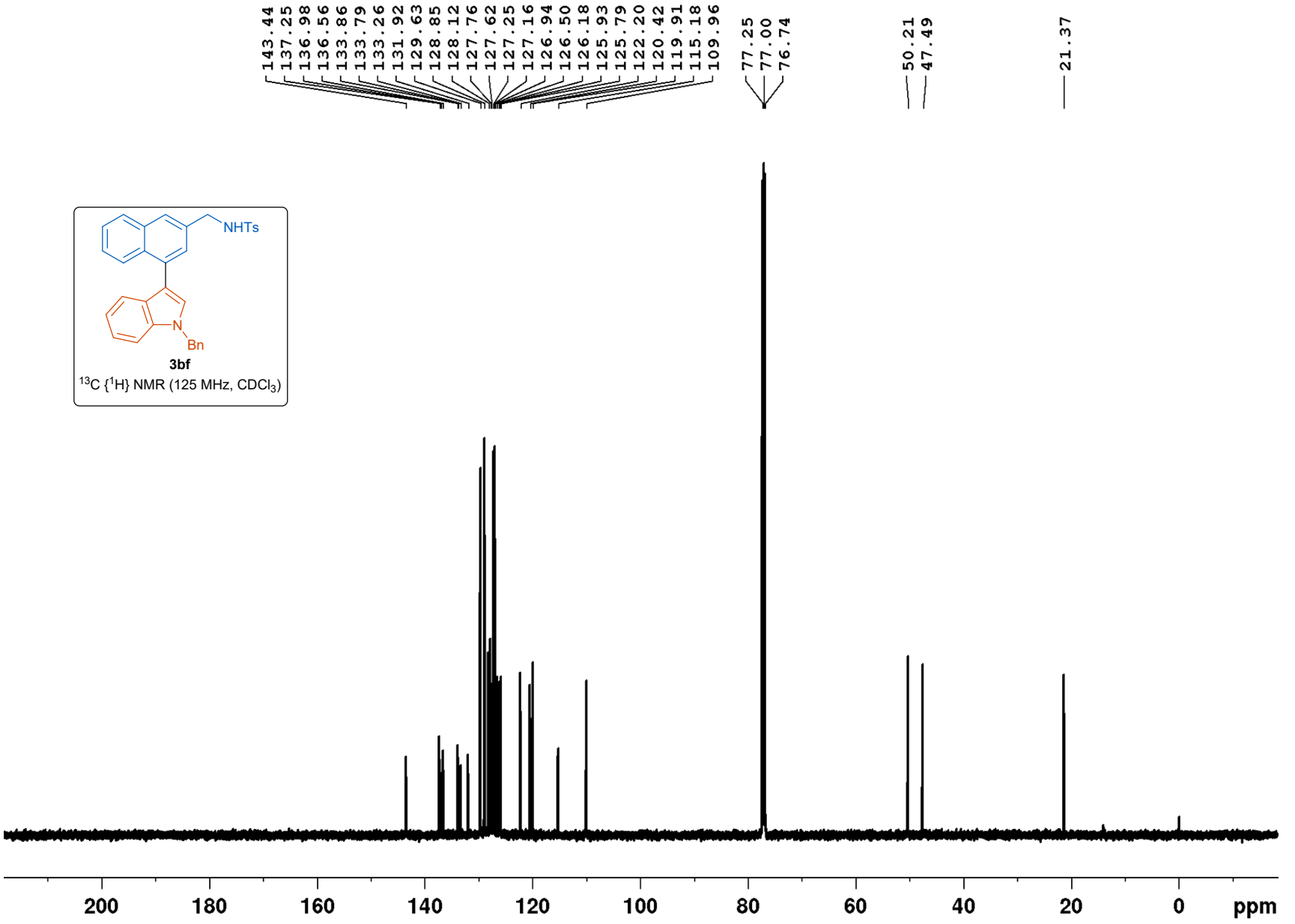
159.19
137.75
137.28
136.54
134.43
133.55
133.37
131.35
128.79
128.41
128.33
127.70
127.16
126.88
126.36
126.06
125.45
124.09
122.15
120.53
119.89
115.58
114.25
109.93
77.32
77.00
76.68
55.28
50.15

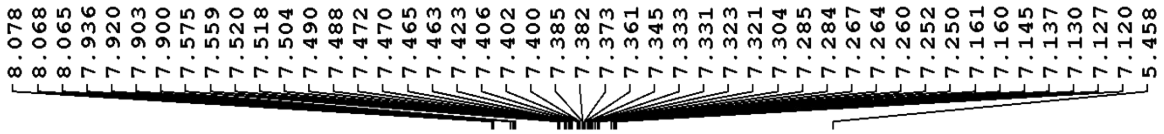


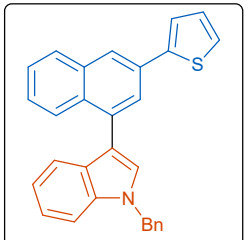

8.074
8.057
7.860
7.844
7.631
7.553
7.537
7.487
7.484
7.477
7.475
7.463
7.461
7.458
7.447
7.445
7.405
7.389
7.372
7.369
7.366
7.359
7.355
7.352
7.346
7.343
7.340
7.332
7.327
7.314
7.312
7.304
7.300
7.295
7.285
7.270
7.268
7.260
7.256
7.254
7.239
7.147
7.145
7.131
7.117
7.115
5.446
2.828
2.813
2.797
1.786
1.771
1.756
1.741
1.725
1.437
1.423
1.407
1.361
1.356
1.349
1.346
1.341
1.334
1.327
0.917
0.903
0.889
5
N
Bn
3be
1H NMR (500 MHz, CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.00
1.00
0.94
1.09
1.03
2.74
2.75
2.70
1.05
2.00
2.06
2.09
2.11
4.03
3.00


140.11
137.40
136.59
134.30
132.64
130.98
129.33
128.83
127.76
127.69
127.60
126.92
126.32
125.64
125.49
124.80
122.09
120.59
119.78
115.78
109.88
77.25
77.00
76.75
50.20
36.13
31.77
31.35
29.10
22.62
14.09
5
N
Bn
3be
13C {1H} NMR (125 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.040
8.023
7.800
7.784
7.768
7.752
7.611
7.492
7.478
7.462
7.415
7.399
7.382
7.377
7.374
7.369
7.354
7.339
7.314
7.300
7.285
7.260
7.241
7.226
7.212
7.122
7.107
7.092
5.429
4.746
4.734
4.722
4.341
4.328
2.329
NHTs
N
Bn
3bf
13C {1H} NMR (125 MHz, CDCl3)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.05
1.22
1.99
1.10
1.36
4.97
1.90
1.57
5.02
1.24
2.00
1.02
2.04
2.98

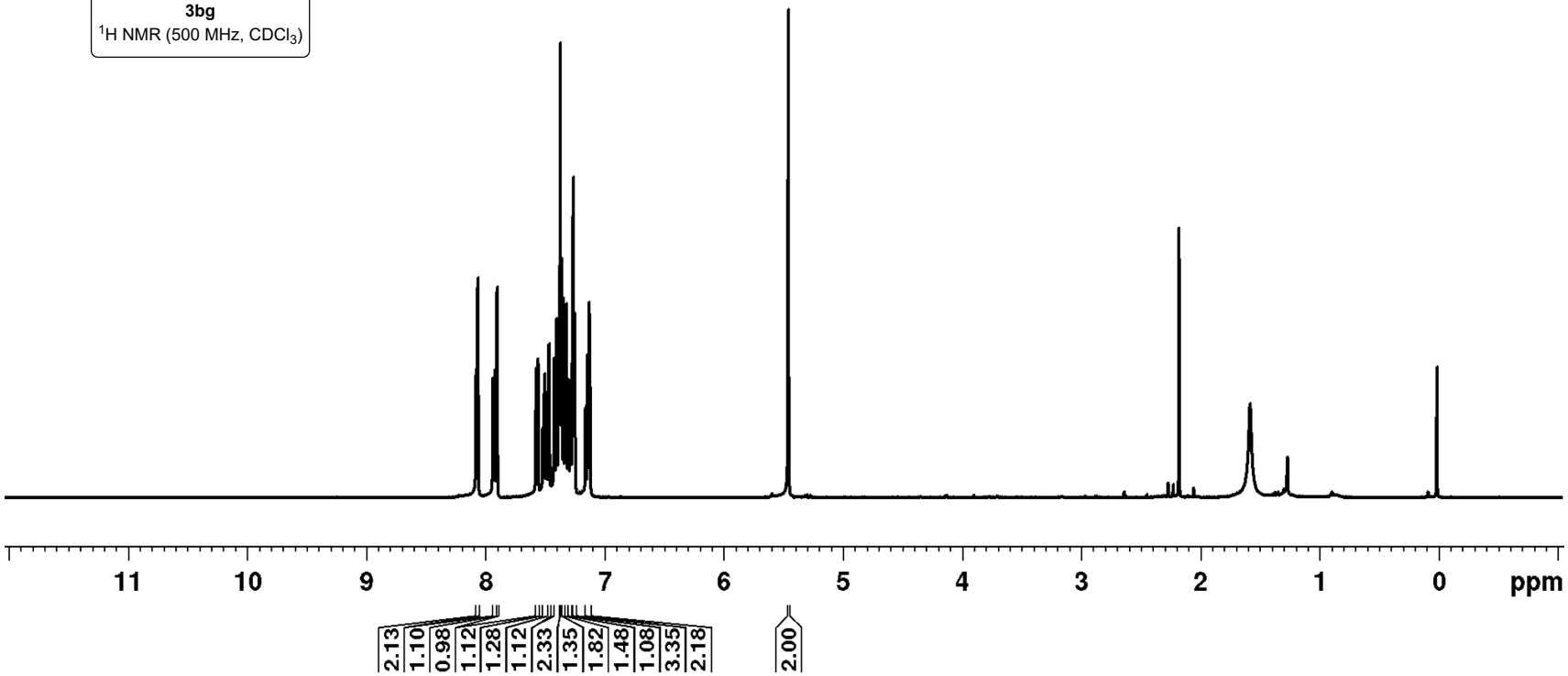

143.44
137.25
136.98
136.56
133.86
133.79
133.26
131.92
129.63
128.85
128.12
127.76
127.62
127.25
127.16
126.94
126.50
126.18
125.93
125.79
122.20
120.42
119.91
115.18
109.96
77.25
77.00
76.74
50.21
47.49
21.37
NHTs
N
Bn
3bf
13C {1H} NMR (125 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0
ppm

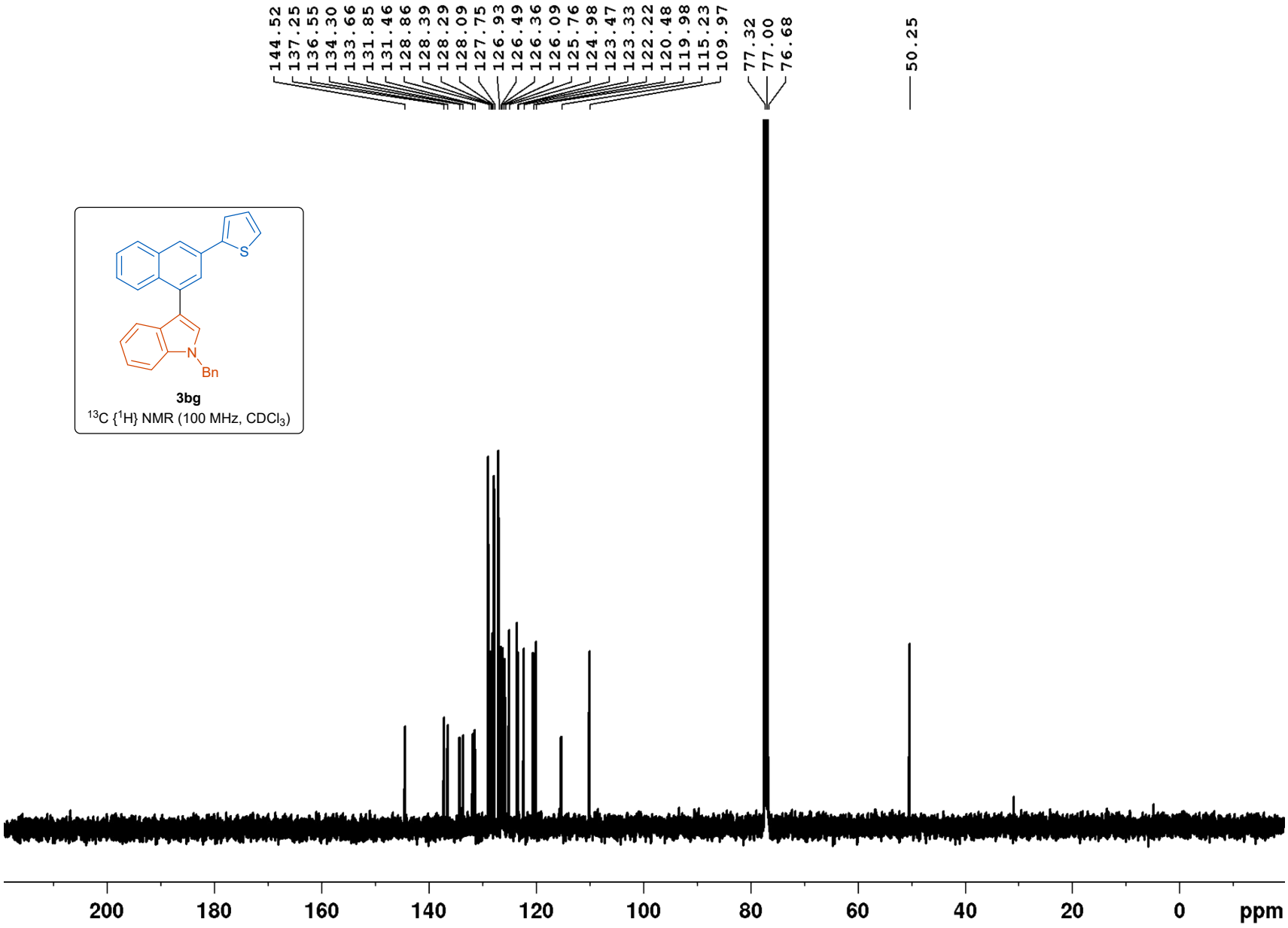


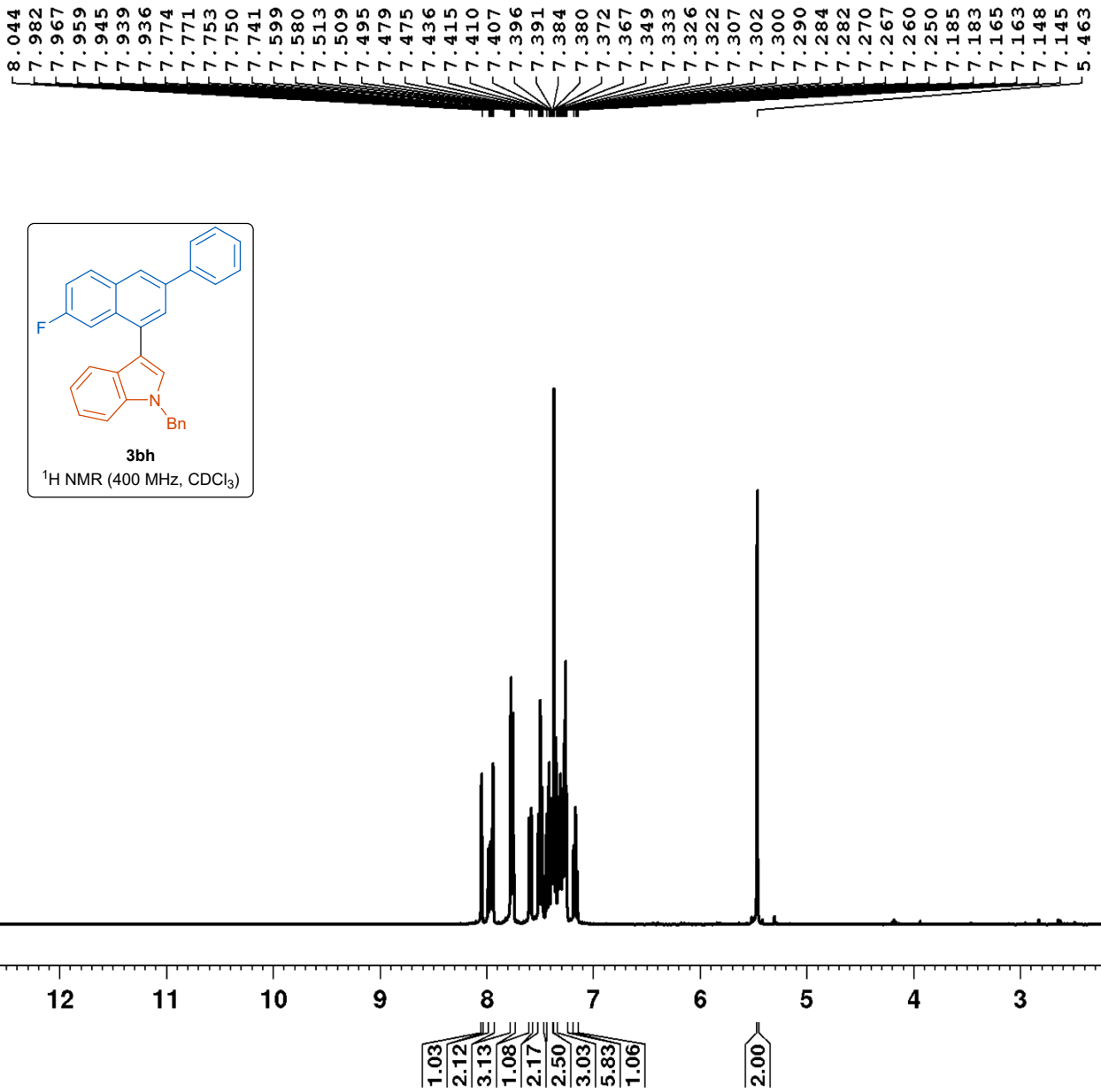


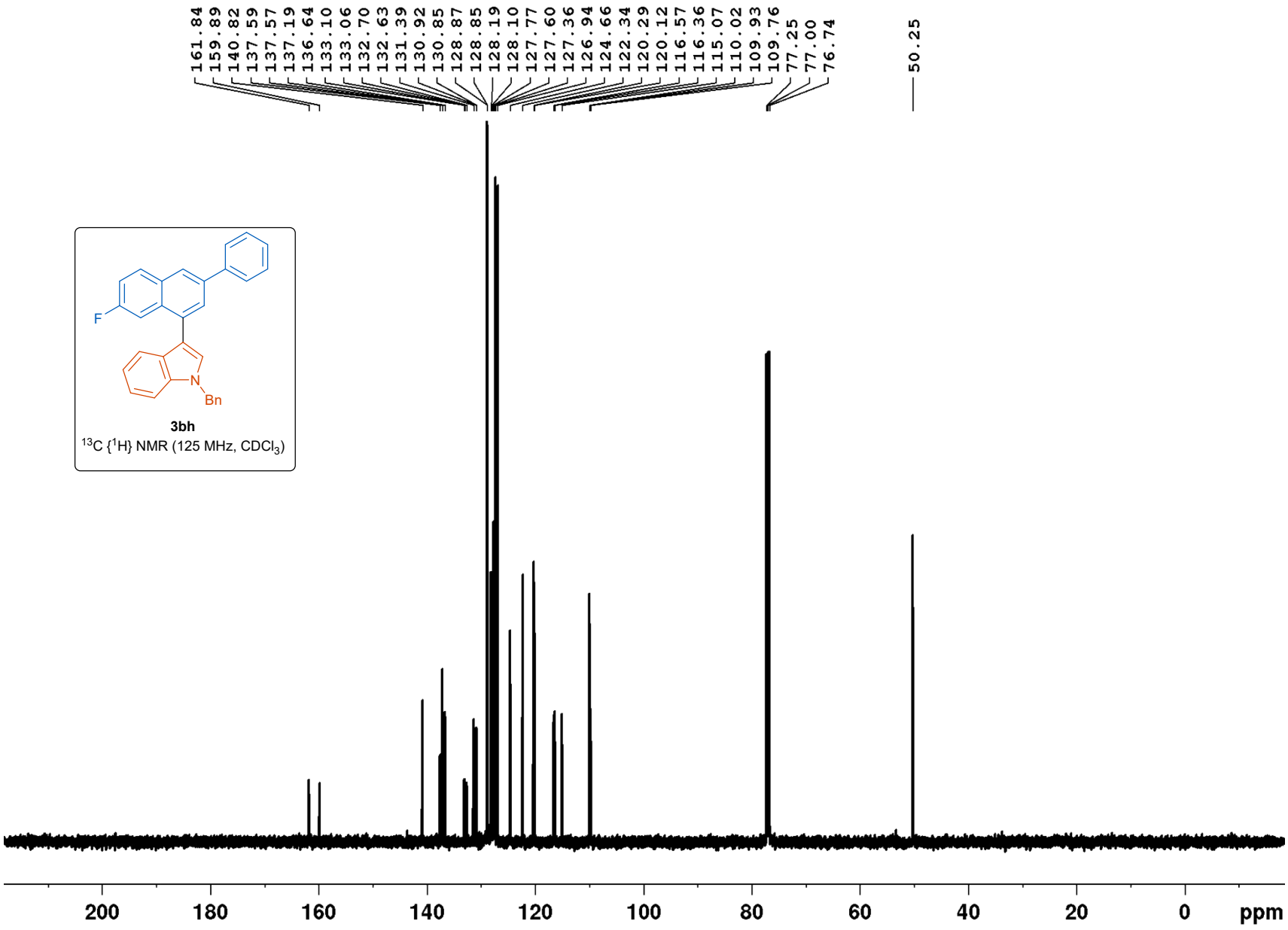
3bg

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



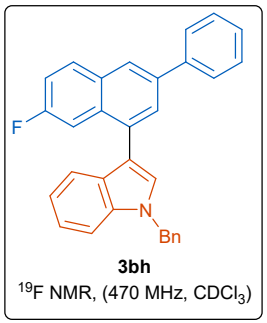

144.52
137.25
136.55
134.30
133.66
131.85
131.46
128.86
128.39
128.29
128.09
127.75
126.93
126.49
126.36
126.09
125.76
124.98
123.47
123.33
122.22
120.48
119.98
115.23
109.97
77.32
77.00
76.68
50.25
S
N
Bn
3bg
13C {1H} NMR (100 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0
ppm


8.044
7.982
7.967
7.959
7.945
7.939
7.936
7.774
7.771
7.753
7.750
7.741
7.599
7.580
7.513
7.509
7.495
7.479
7.475
7.436
7.415
7.410
7.407
7.396
7.391
7.384
7.380
7.372
7.367
7.349
7.333
7.326
7.322
7.307
7.302
7.300
7.290
7.284
7.282
7.270
7.267
7.260
7.250
7.185
7.183
7.165
7.163
7.148
7.145
5.463
F
N
Bn
3bh
^{1}H NMR (400 MHz, $CDCl_3$)
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.03
2.12
3.13
1.08
2.17
2.50
3.03
5.83
1.06
2.00



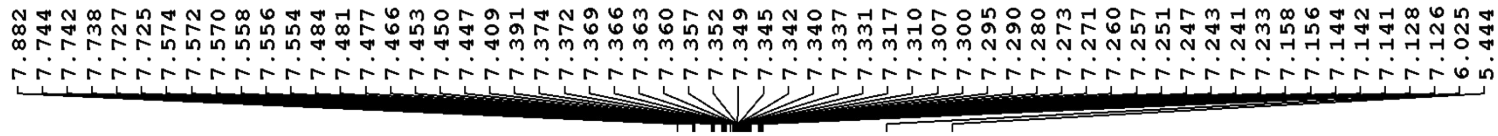
3bh

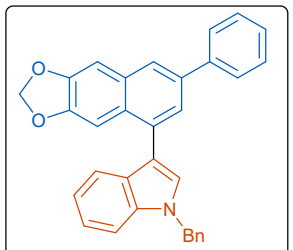
^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$)



3bh

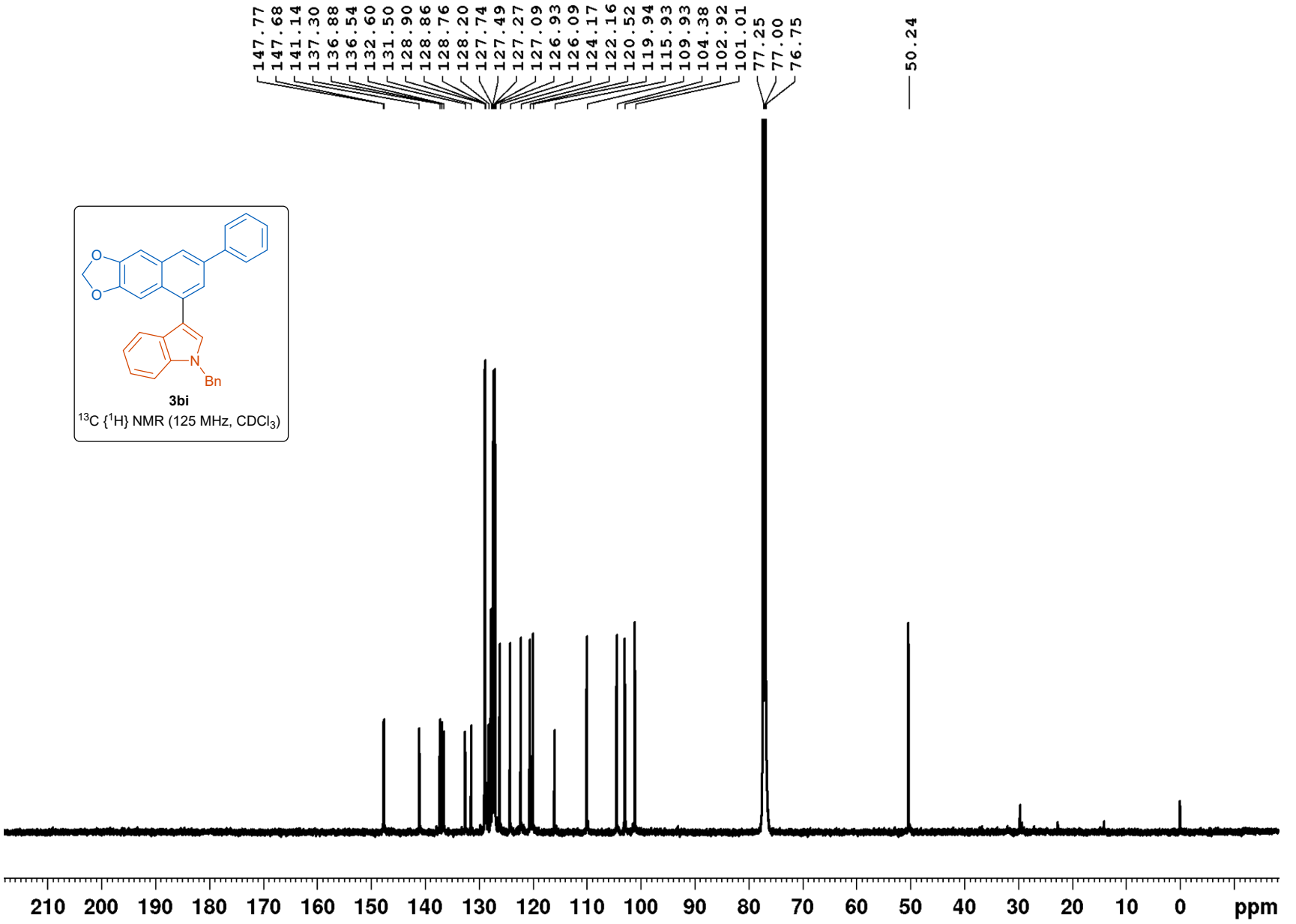
^{19}F NMR, (470 MHz, $CDCl_3$)





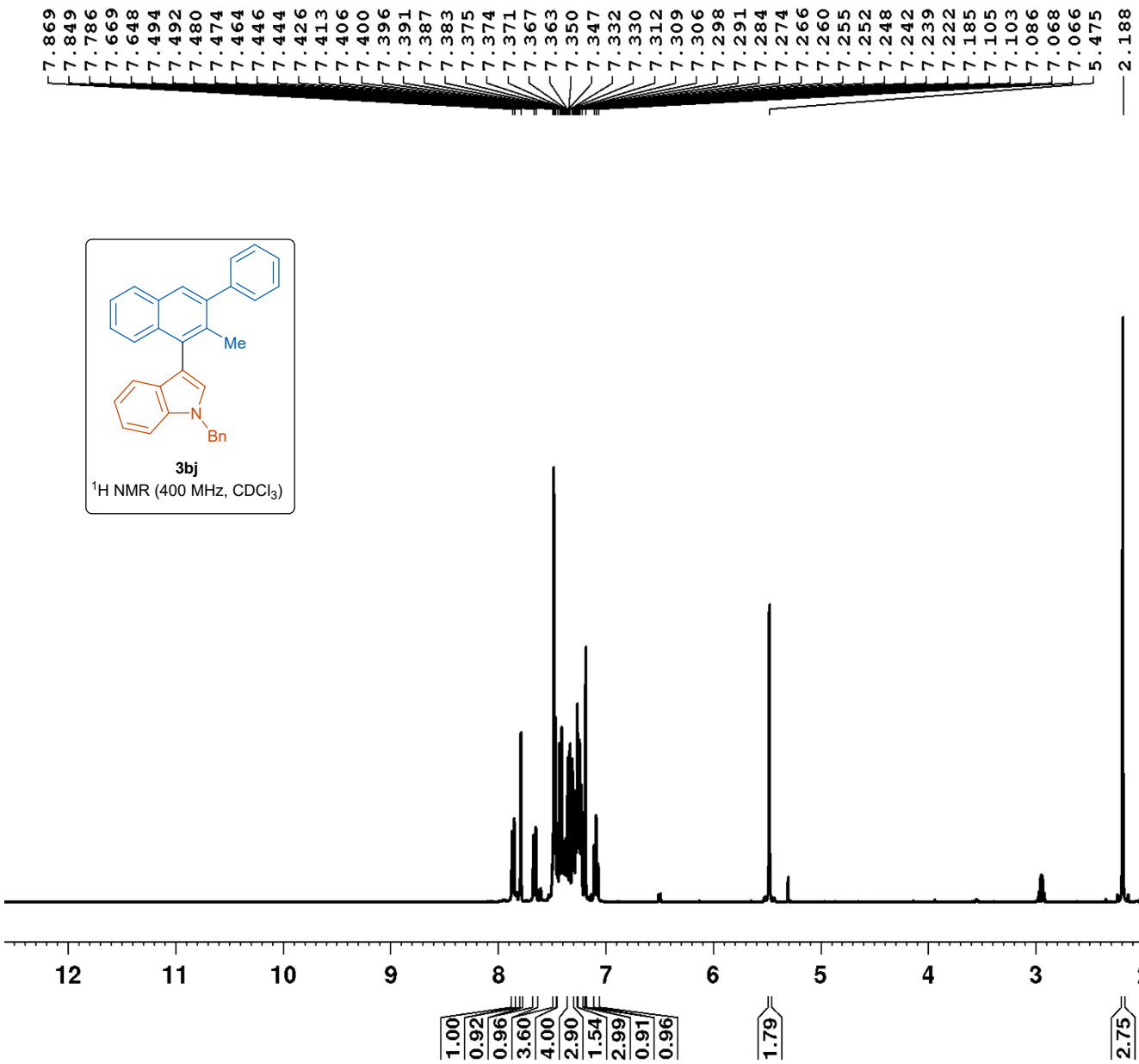
3bi

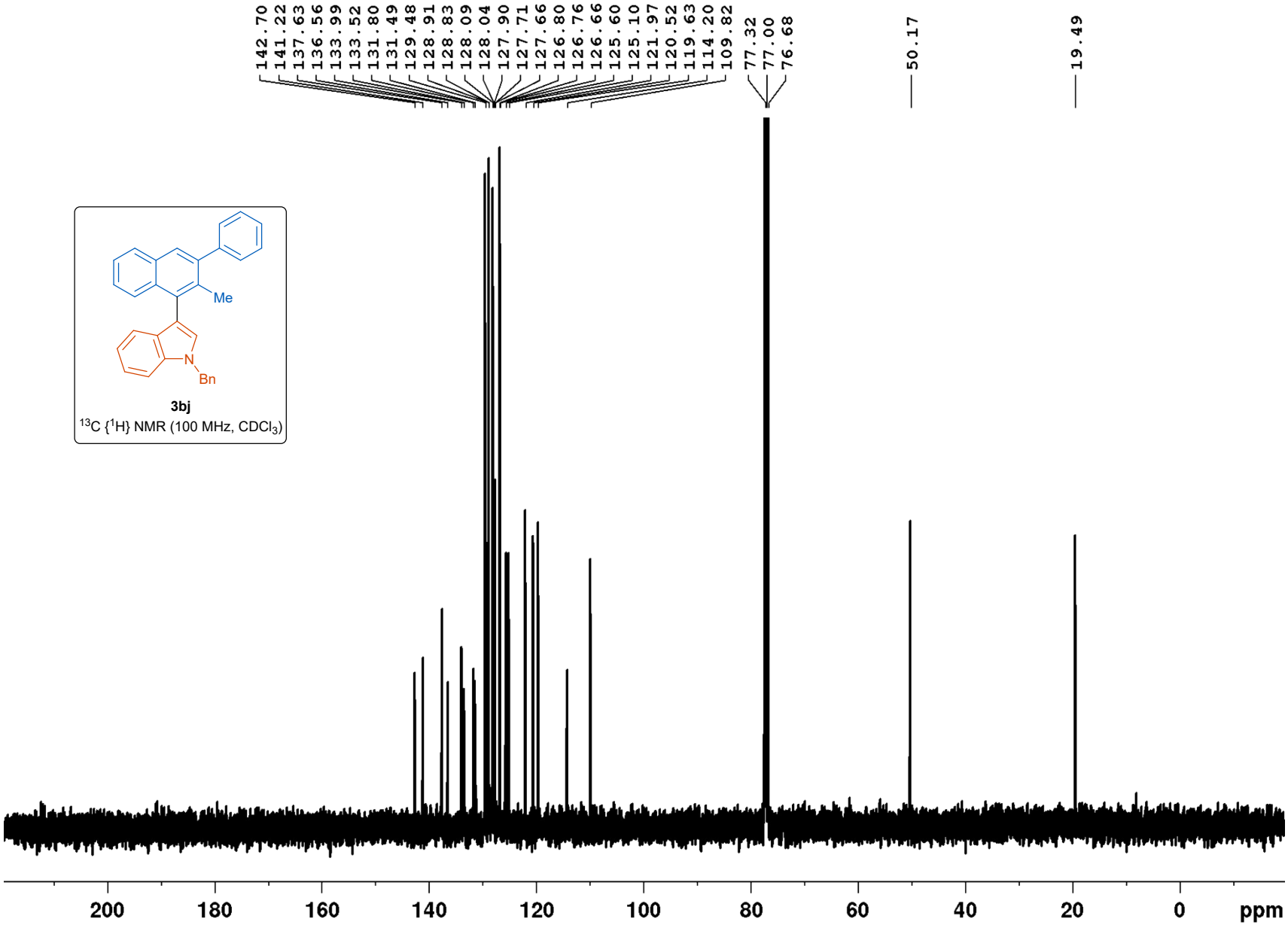
^{1}H NMR (500 MHz, $CDCl_3$)

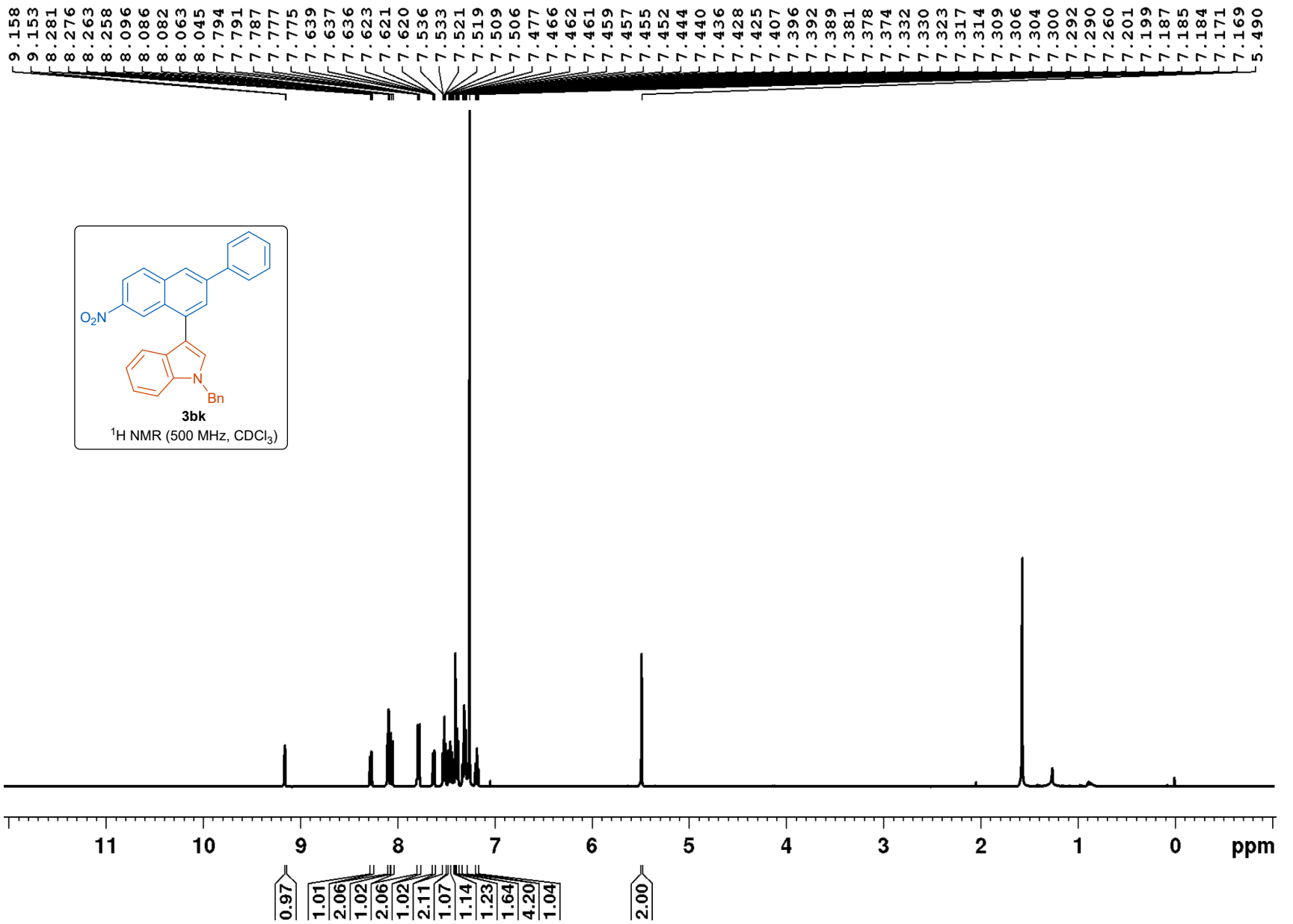


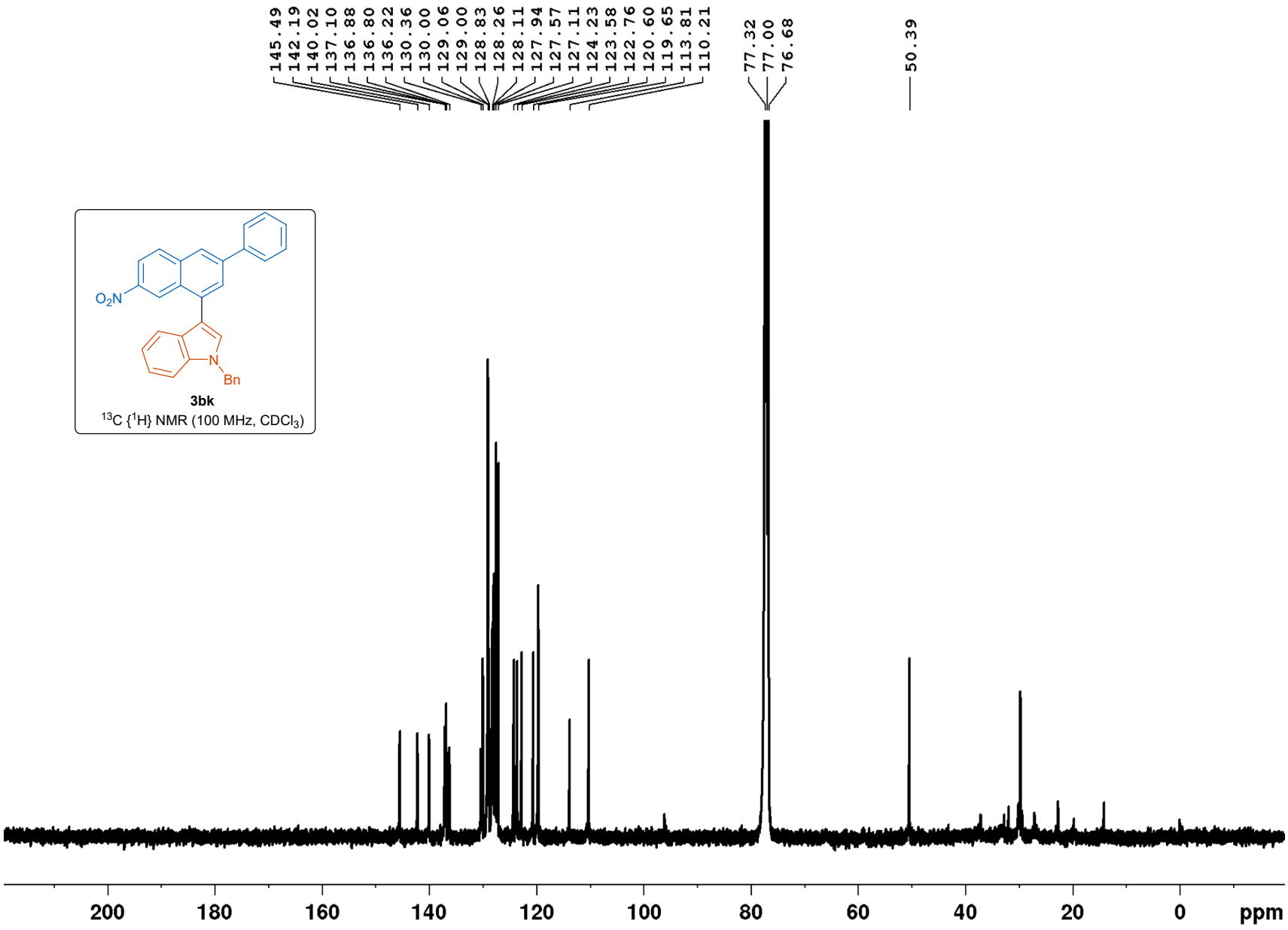
3bi

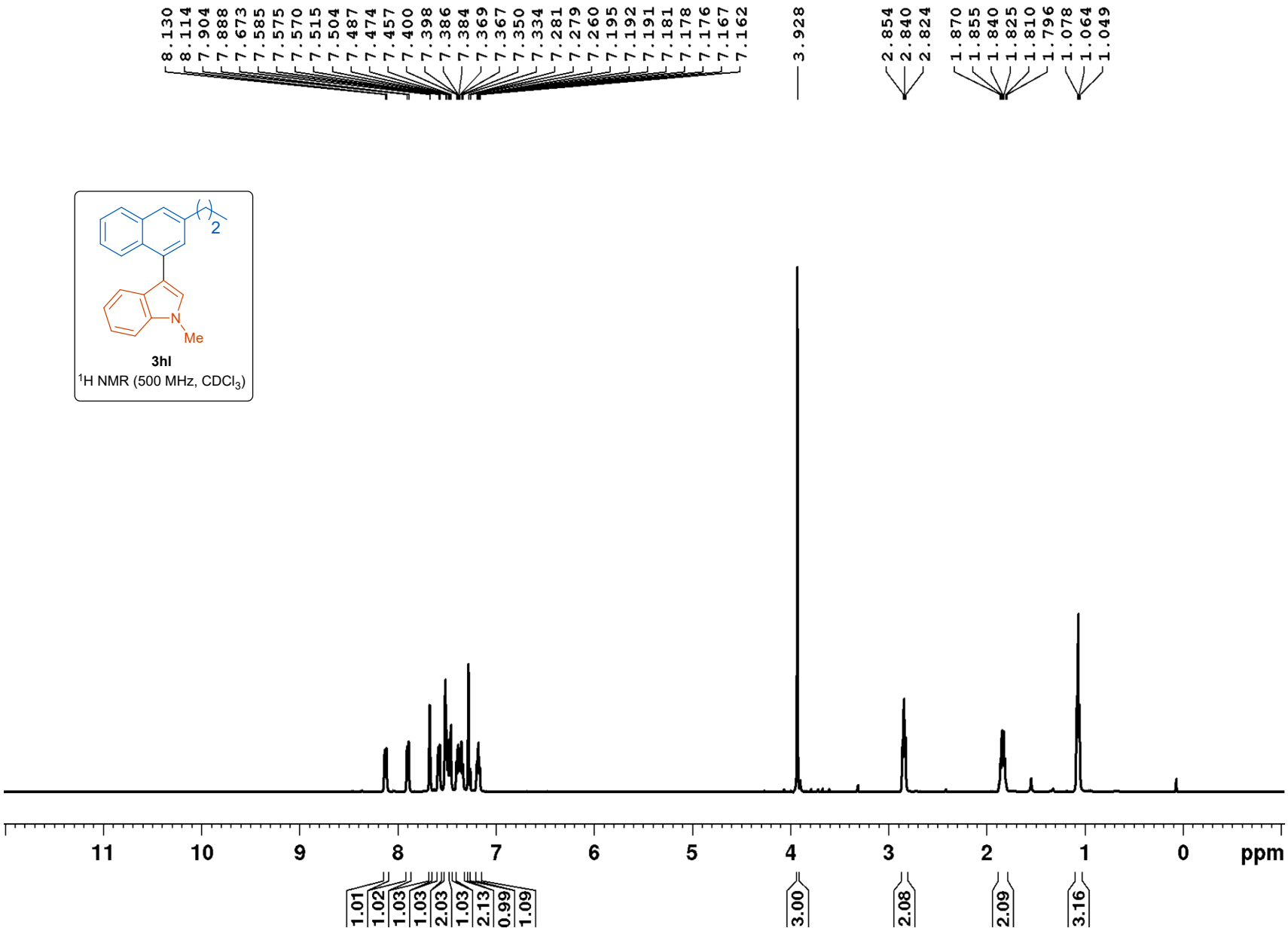
^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$)

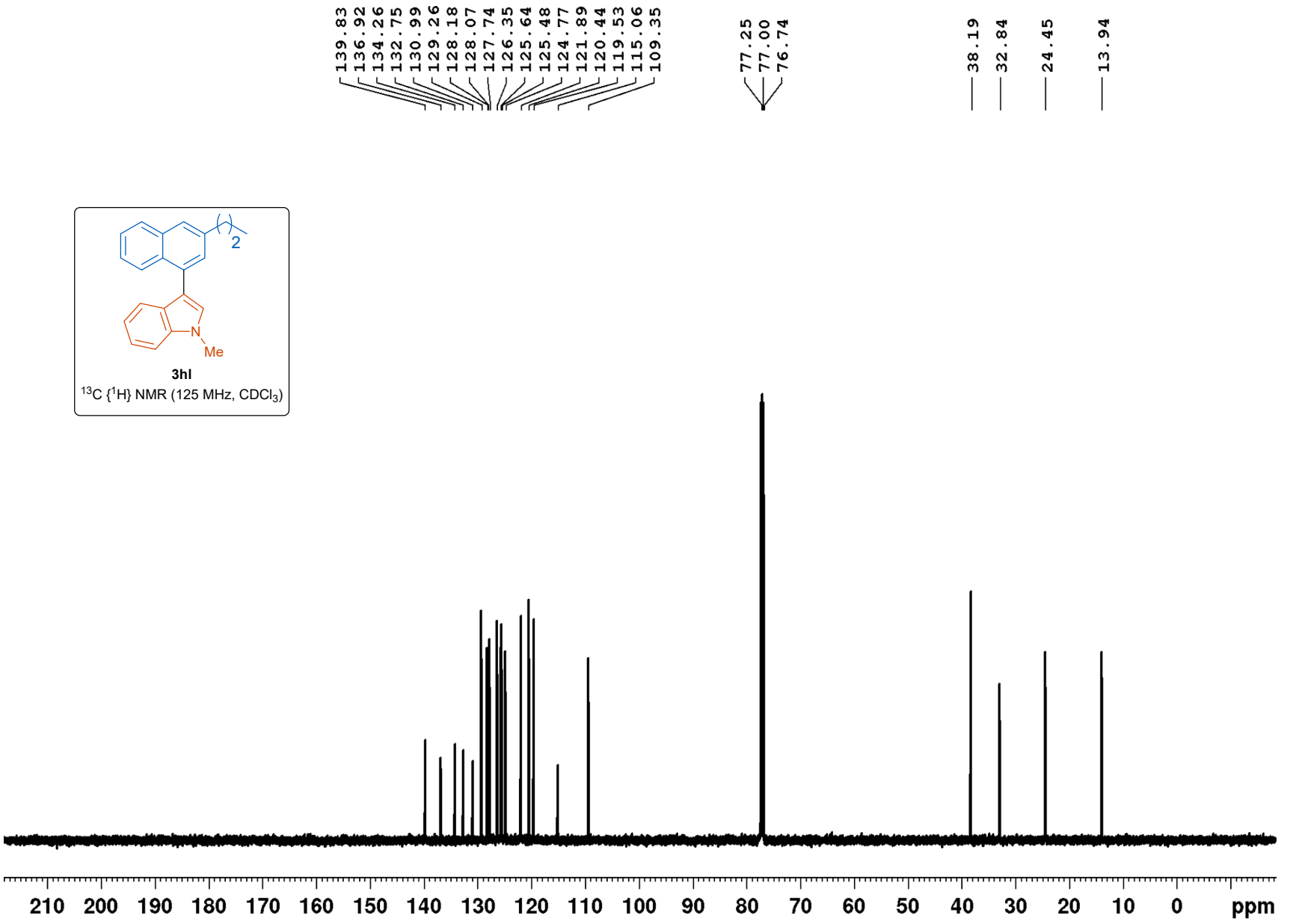

7.869
7.849
7.786
7.669
7.648
7.494
7.492
7.480
7.474
7.464
7.446
7.444
7.426
7.413
7.406
7.400
7.396
7.391
7.387
7.383
7.375
7.374
7.371
7.367
7.363
7.350
7.347
7.332
7.330
7.312
7.309
7.306
7.298
7.291
7.284
7.274
7.266
7.260
7.255
7.252
7.248
7.242
7.239
7.222
7.185
7.105
7.103
7.086
7.068
7.066
5.475
2.188
Me
N
Bn
3bj
1H NMR (400 MHz, CDCl3)
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.92
0.96
3.60
4.00
2.90
1.54
2.99
0.91
0.96
1.79
2.75

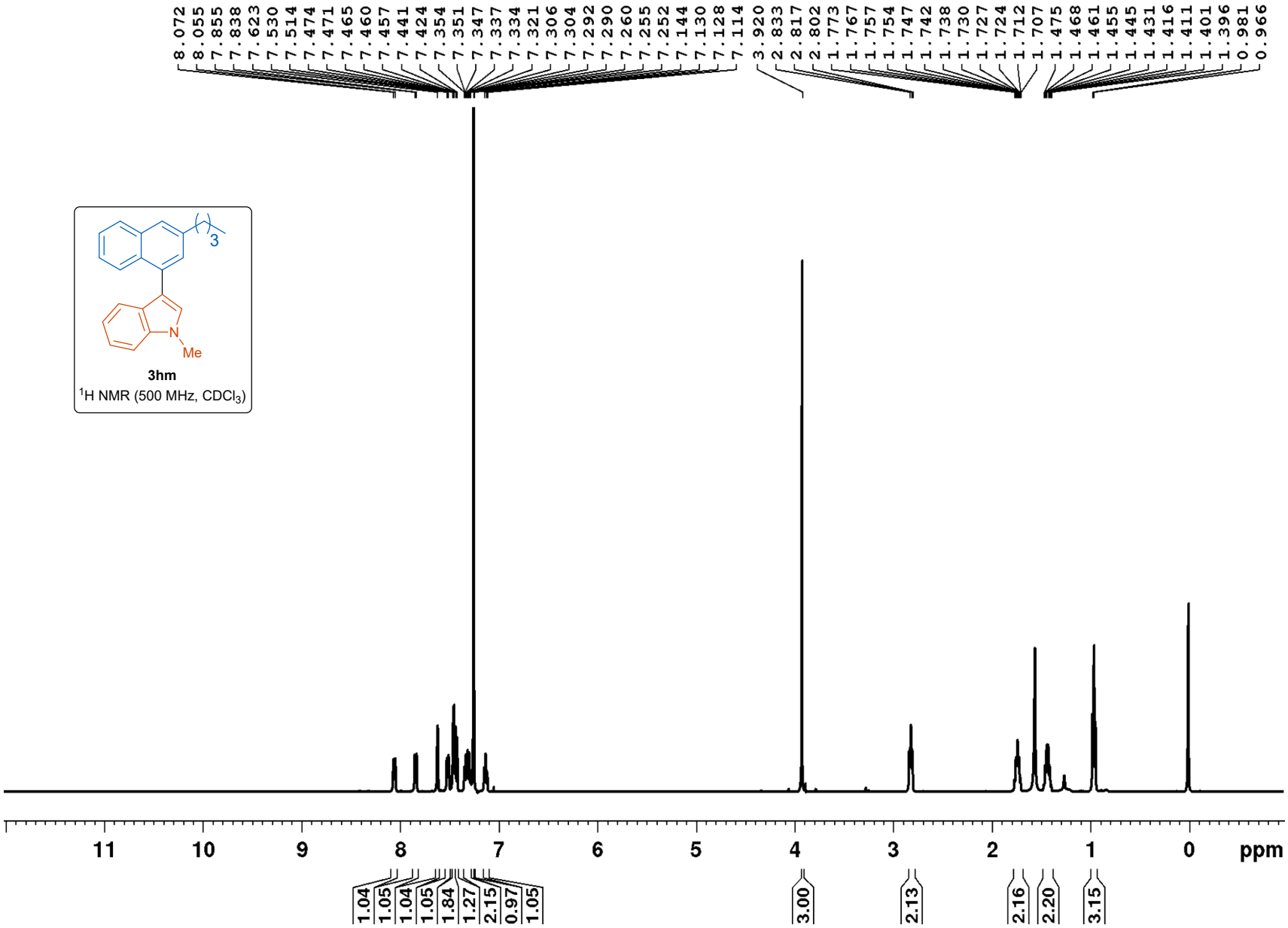

142.70
141.22
137.63
136.56
133.99
133.52
131.80
131.49
129.48
128.91
128.83
128.09
128.04
127.90
127.71
127.66
126.80
126.76
126.66
125.60
125.10
121.97
120.52
119.63
114.20
109.82
77.32
77.00
76.68
50.17
19.49
Me
N
Bn
3bj
13C {1H} NMR (100 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0
ppm

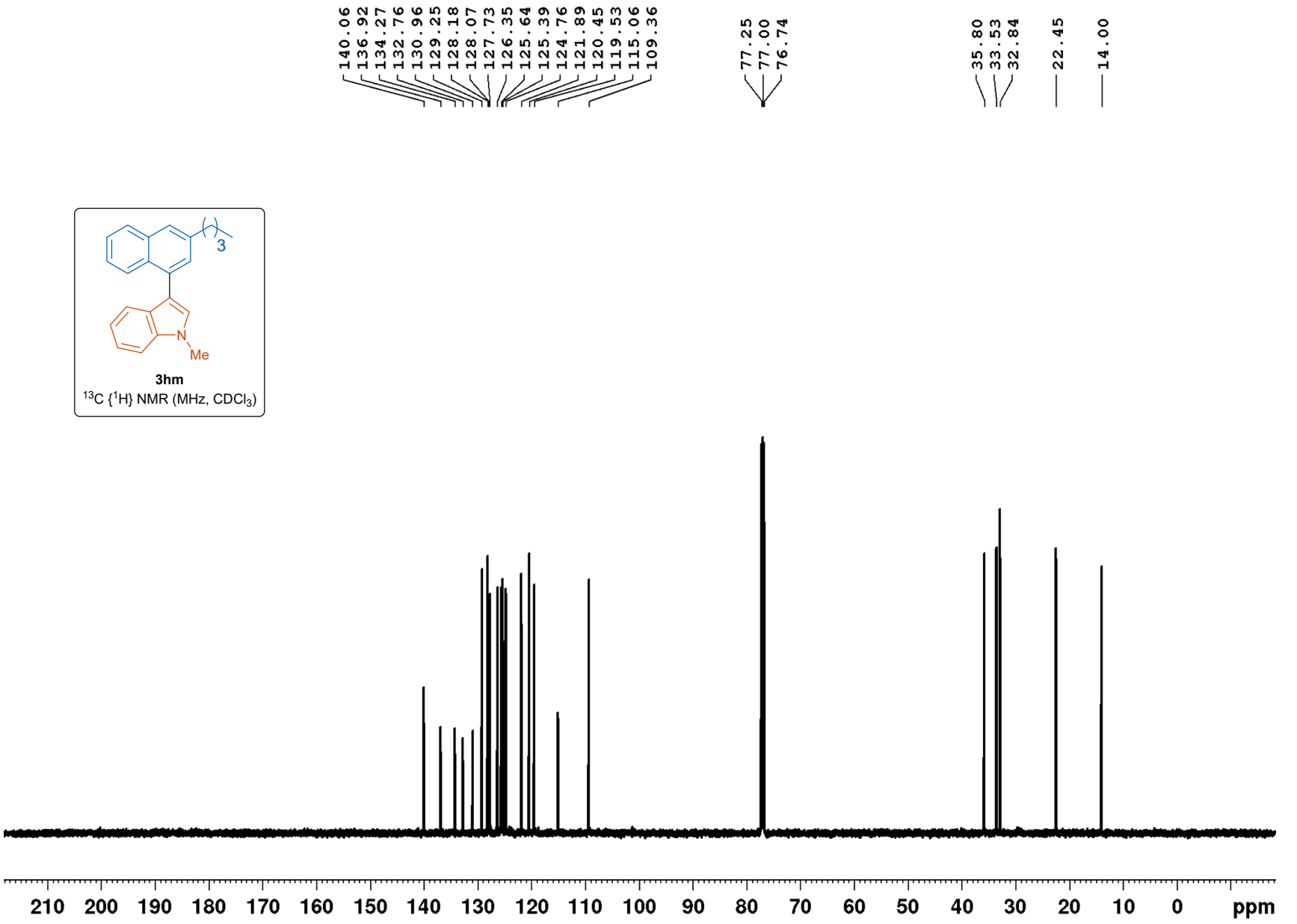

9.158
9.153
8.281
8.276
8.263
8.258
8.096
8.086
8.082
8.063
8.045
7.794
7.791
7.787
7.777
7.775
7.639
7.637
7.636
7.623
7.621
7.620
7.536
7.533
7.521
7.519
7.509
7.506
7.477
7.466
7.462
7.461
7.459
7.457
7.455
7.452
7.444
7.440
7.436
7.428
7.425
7.407
7.396
7.392
7.389
7.381
7.378
7.374
7.332
7.330
7.323
7.317
7.314
7.309
7.306
7.304
7.300
7.292
7.290
7.260
7.201
7.199
7.187
7.185
7.184
7.171
7.169
5.490
O2N
N
Bn
3bk
1H NMR (500 MHz, CDCl3)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.97
1.01
2.06
1.02
2.06
1.02
2.11
1.07
1.14
1.23
1.64
4.20
1.04
2.00

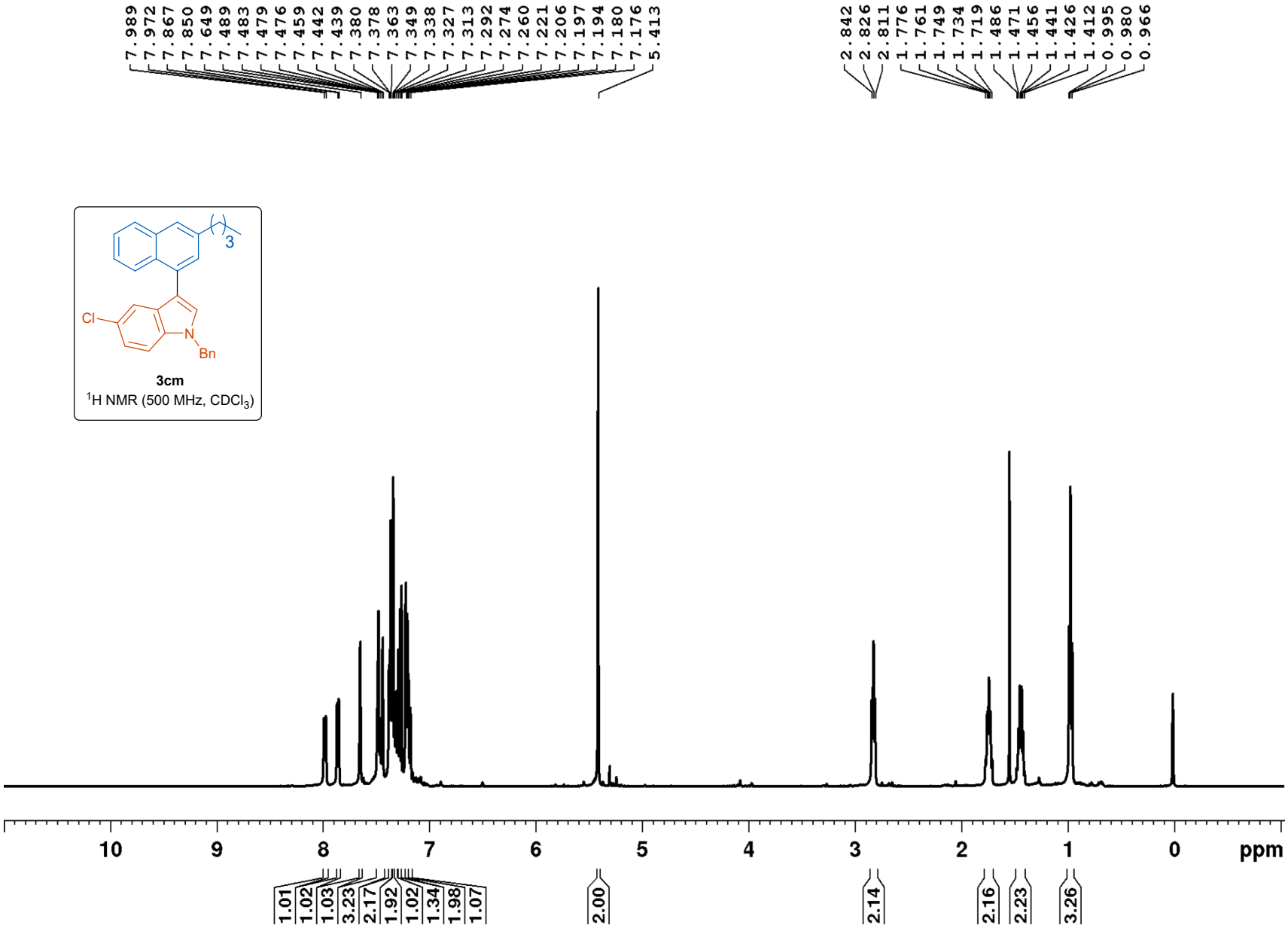

145.49
142.19
140.02
137.10
136.88
136.80
136.22
130.36
130.00
129.06
129.00
128.83
128.26
128.11
127.94
127.57
127.11
124.23
123.58
122.76
120.60
119.65
113.81
110.21
77.32
77.00
76.68
50.39
O2N
N
Bn
3bk
13C {1H} NMR (100 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0
ppm

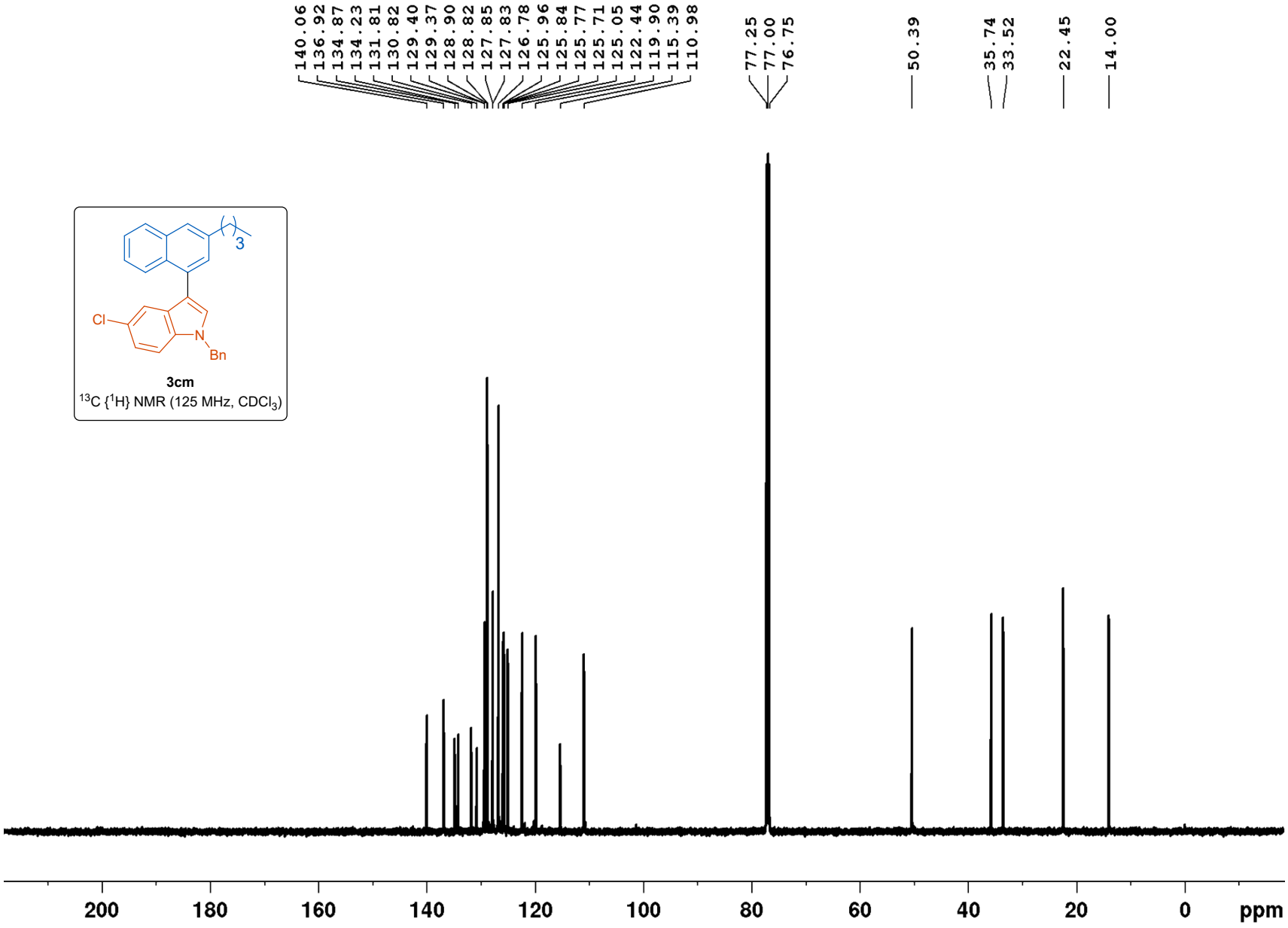

8.130
8.114
7.904
7.888
7.673
7.585
7.575
7.570
7.515
7.504
7.487
7.474
7.457
7.400
7.398
7.386
7.384
7.369
7.367
7.350
7.334
7.281
7.279
7.260
7.195
7.192
7.191
7.181
7.178
7.176
7.167
7.162
3.928
2.854
2.840
2.824
1.870
1.855
1.840
1.825
1.810
1.796
1.078
1.064
1.049
2
N
Me
3hl
1H NMR (500 MHz, CDCl3)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
1.02
1.03
1.03
2.03
1.03
2.13
0.99
1.09
3.00
2.08
2.09
3.16

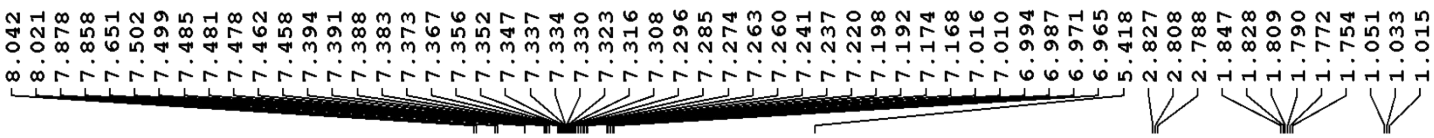

139.83
136.92
134.26
132.75
130.99
129.26
128.18
128.07
127.74
126.35
125.64
125.48
124.77
121.89
120.44
119.53
115.06
109.35
77.25
77.00
76.74
38.19
32.84
24.45
13.94
2
N
Me
3hl
13C {1H} NMR (125 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

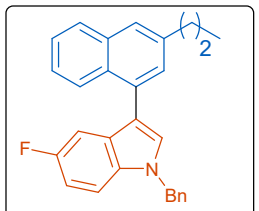

8.072
8.055
7.855
7.838
7.623
7.530
7.514
7.474
7.471
7.465
7.460
7.457
7.441
7.424
7.354
7.351
7.347
7.337
7.334
7.321
7.306
7.304
7.292
7.290
7.260
7.255
7.252
7.144
7.130
7.128
7.114
3.920
2.833
2.817
2.802
1.773
1.767
1.757
1.754
1.747
1.742
1.738
1.730
1.727
1.724
1.712
1.707
1.475
1.468
1.461
1.455
1.445
1.431
1.416
1.411
1.401
1.396
0.981
0.966
3
N
Me
3hm
1H NMR (500 MHz, CDCl3)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.04
1.05
1.04
1.05
1.84
1.27
2.15
0.97
1.05
3.00
2.13
2.16
2.20
3.15


140.06
136.92
134.27
132.76
130.96
129.25
128.18
128.07
127.73
126.35
125.64
125.39
124.76
121.89
120.45
119.53
115.06
109.36
77.25
77.00
76.74
35.80
33.53
32.84
22.45
14.00
3
N
Me
3hm
13C {1H} NMR (MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.989
7.972
7.867
7.850
7.649
7.489
7.483
7.479
7.476
7.459
7.442
7.439
7.380
7.378
7.363
7.349
7.338
7.327
7.313
7.292
7.274
7.260
7.221
7.206
7.197
7.194
7.180
7.176
5.413
2.842
2.826
2.811
1.776
1.761
1.749
1.734
1.719
1.486
1.471
1.456
1.441
1.426
1.412
0.995
0.980
0.966
3
Cl
N
Bn
3cm
1H NMR (500 MHz, CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
1.02
1.03
3.23
2.17
1.92
1.02
1.34
1.98
1.07
2.00
2.14
2.16
2.23
3.26

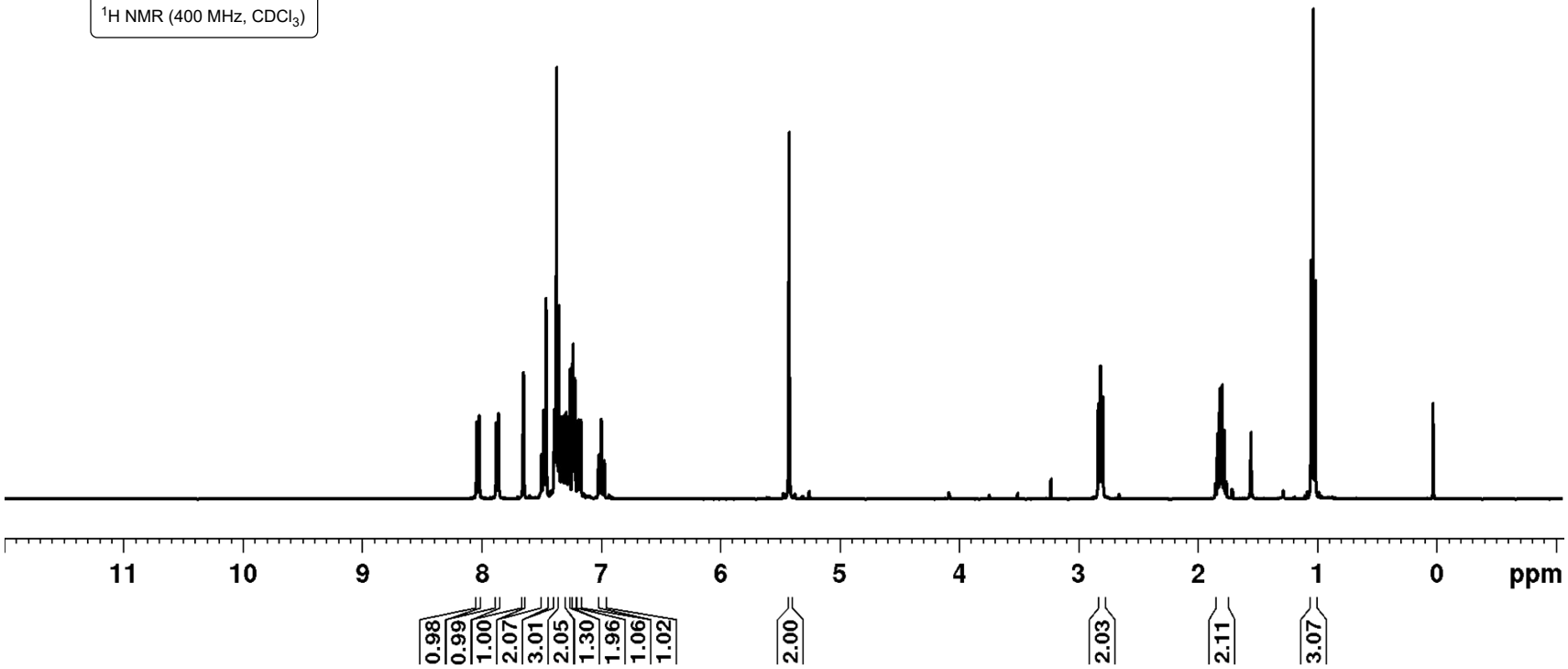

140.06
136.92
134.87
134.23
131.81
130.82
129.40
129.37
128.90
128.82
127.85
127.83
126.78
125.96
125.84
125.77
125.71
125.05
122.44
119.90
115.39
110.98
77.25
77.00
76.75
50.39
35.74
33.52
22.45
14.00
3
Cl
N
Bn
3cm
13C {1H} NMR (125 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0
ppm

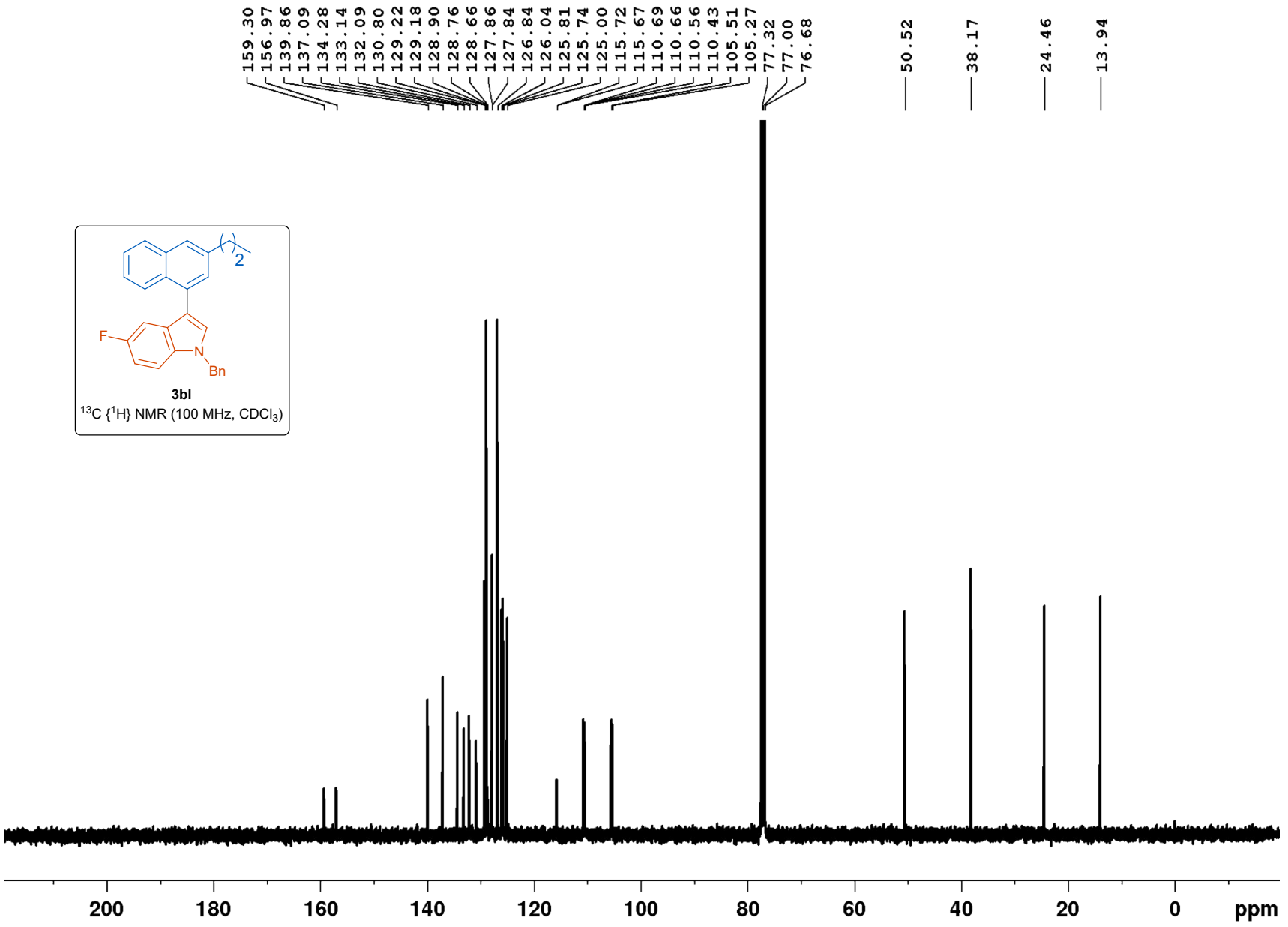




3bl

^{1}H NMR (400 MHz, $CDCl_3$)

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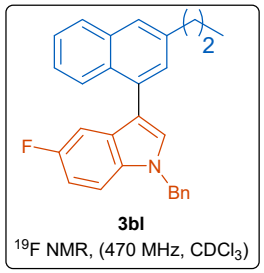
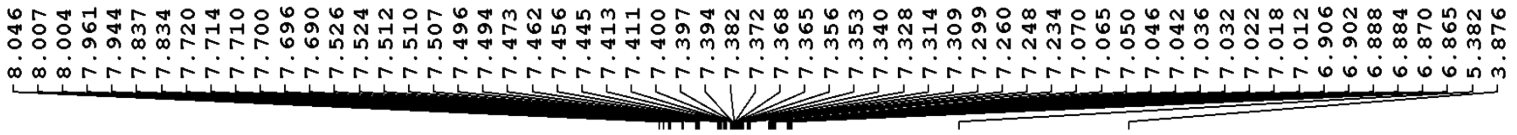
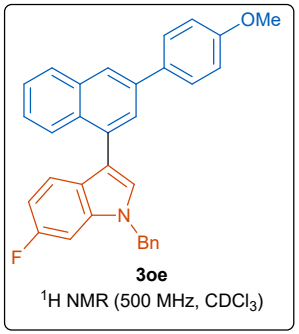
156.97
139.86
137.09
134.28
133.14
132.09
130.80
129.22
129.18
128.90
128.76
128.66
127.86
127.84
126.84
126.04
125.81
125.74
125.00
115.72
115.67
110.69
110.66
110.56
110.43
105.51
105.27
77.32
77.00
76.68
50.52
38.17
24.46
13.94
F
N
Bn
2
3bl
13C {1H} NMR (100 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0
ppm



3bl

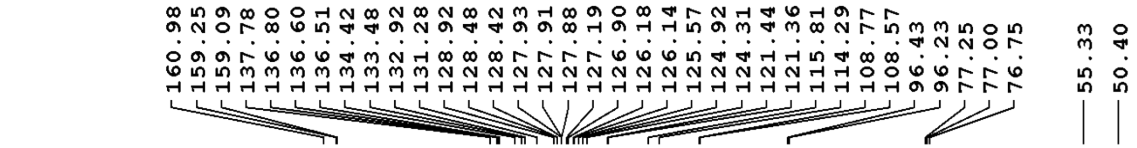
^{19}F NMR, (470 MHz, $CDCl_3$)

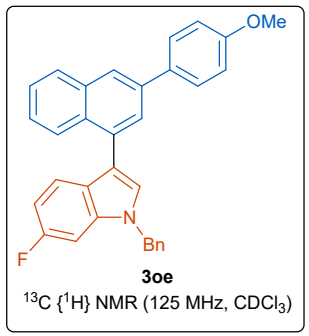




3oe

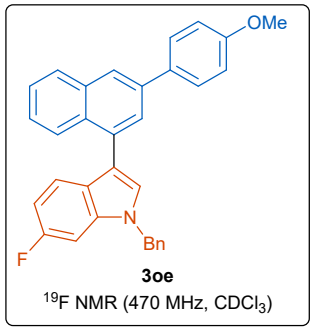
^{1}H NMR (500 MHz, $CDCl_3$)





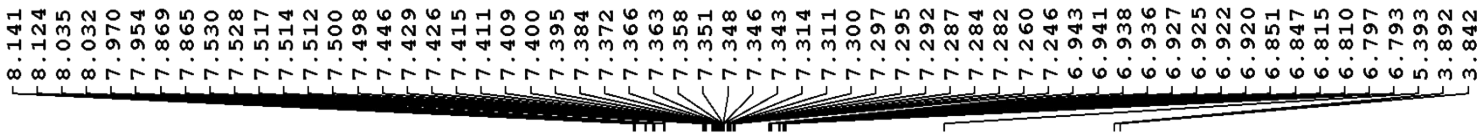
3oe

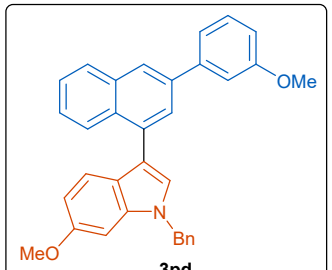
^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$)



3oe

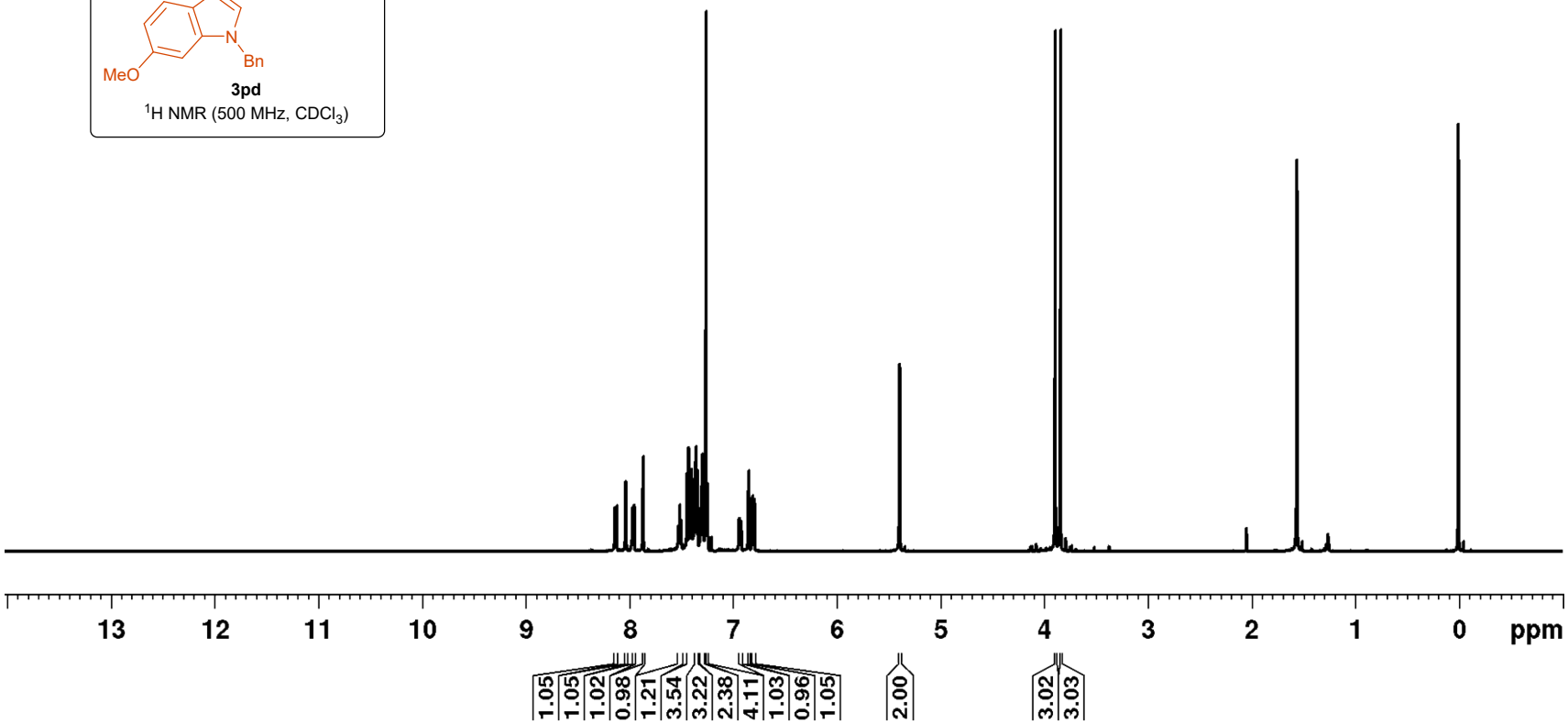
^{19}F NMR (470 MHz, $CDCl_3$)

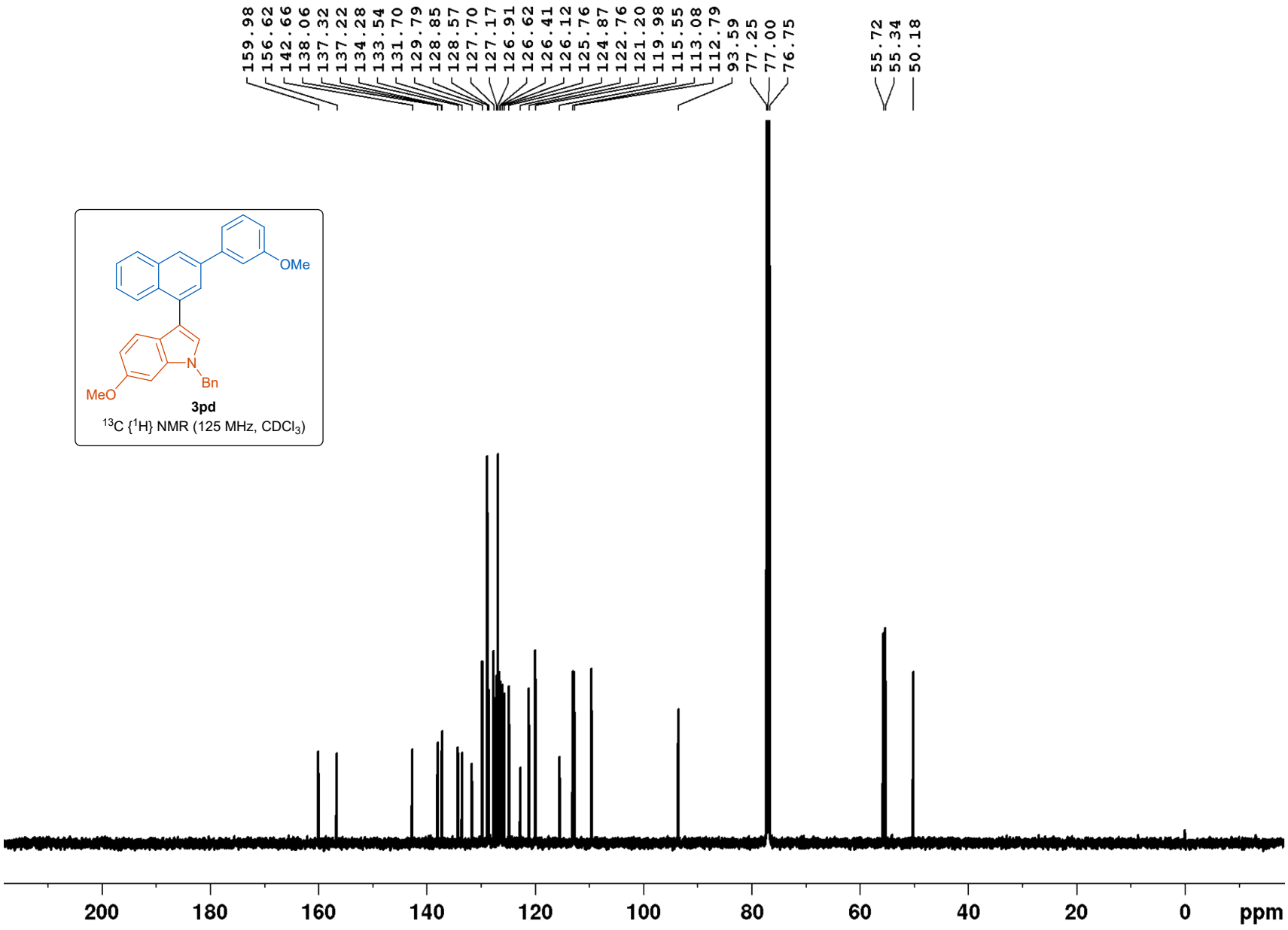


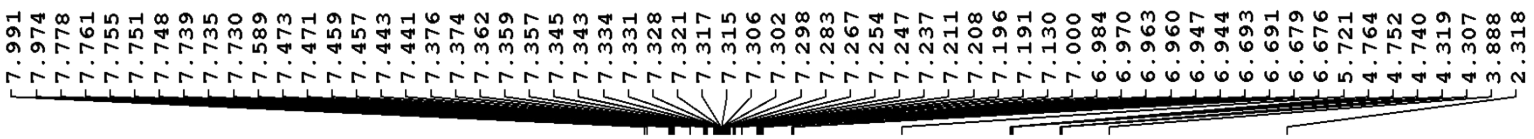


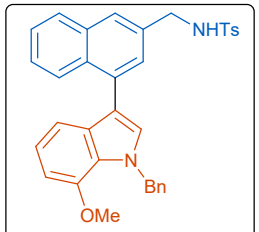
3pd

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



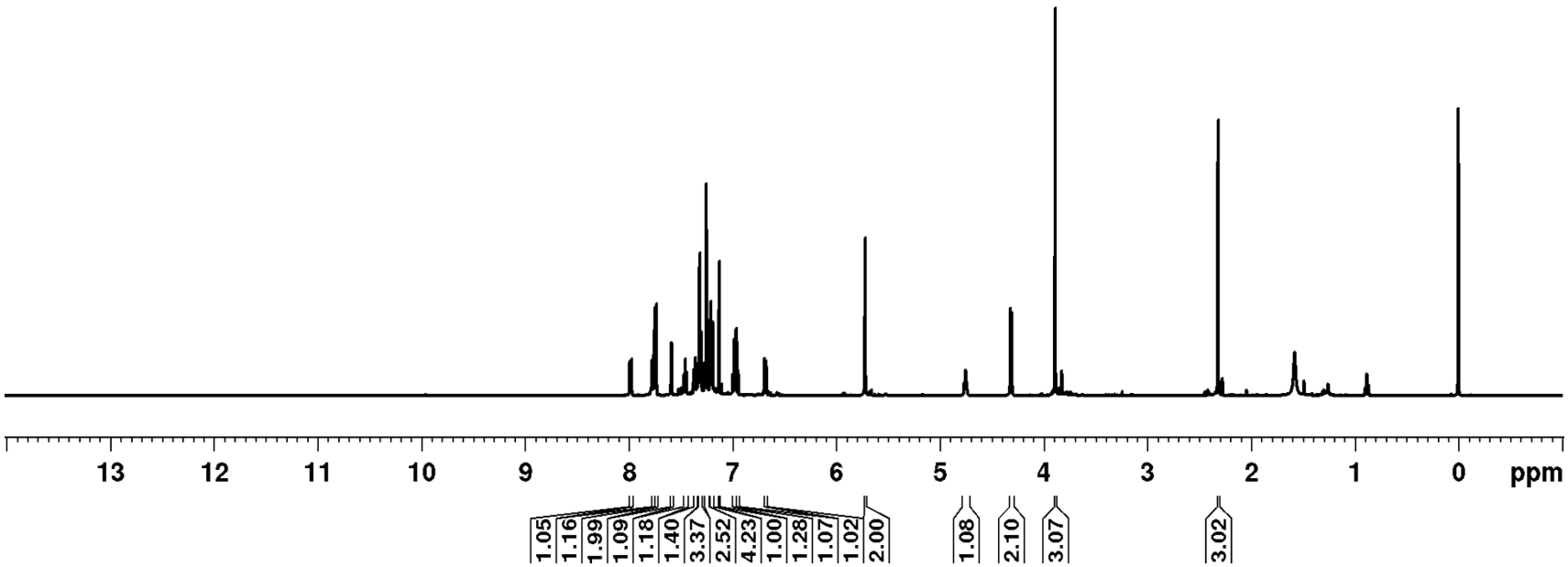

159.98
156.62
142.66
138.06
137.32
137.22
134.28
133.54
131.70
129.79
128.85
128.57
127.70
127.17
126.91
126.62
126.41
126.12
125.76
124.87
122.76
121.20
119.98
115.55
113.08
112.79
93.59
77.25
77.00
76.75
55.72
55.34
50.18
OMe
N
Bn
MeO
3pd
^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$)
200
180
160
140
120
100
80
60
40
20
0
ppm

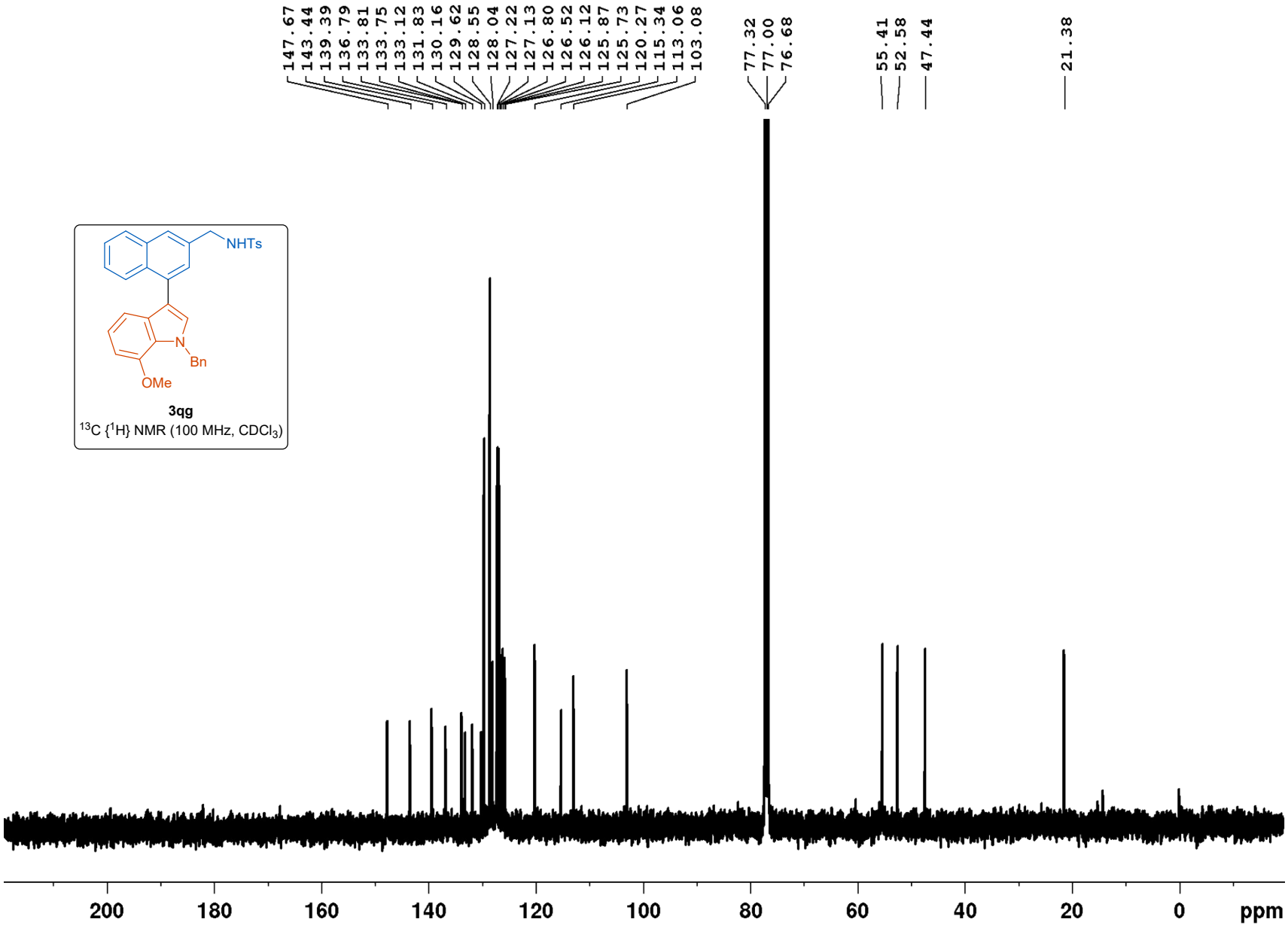


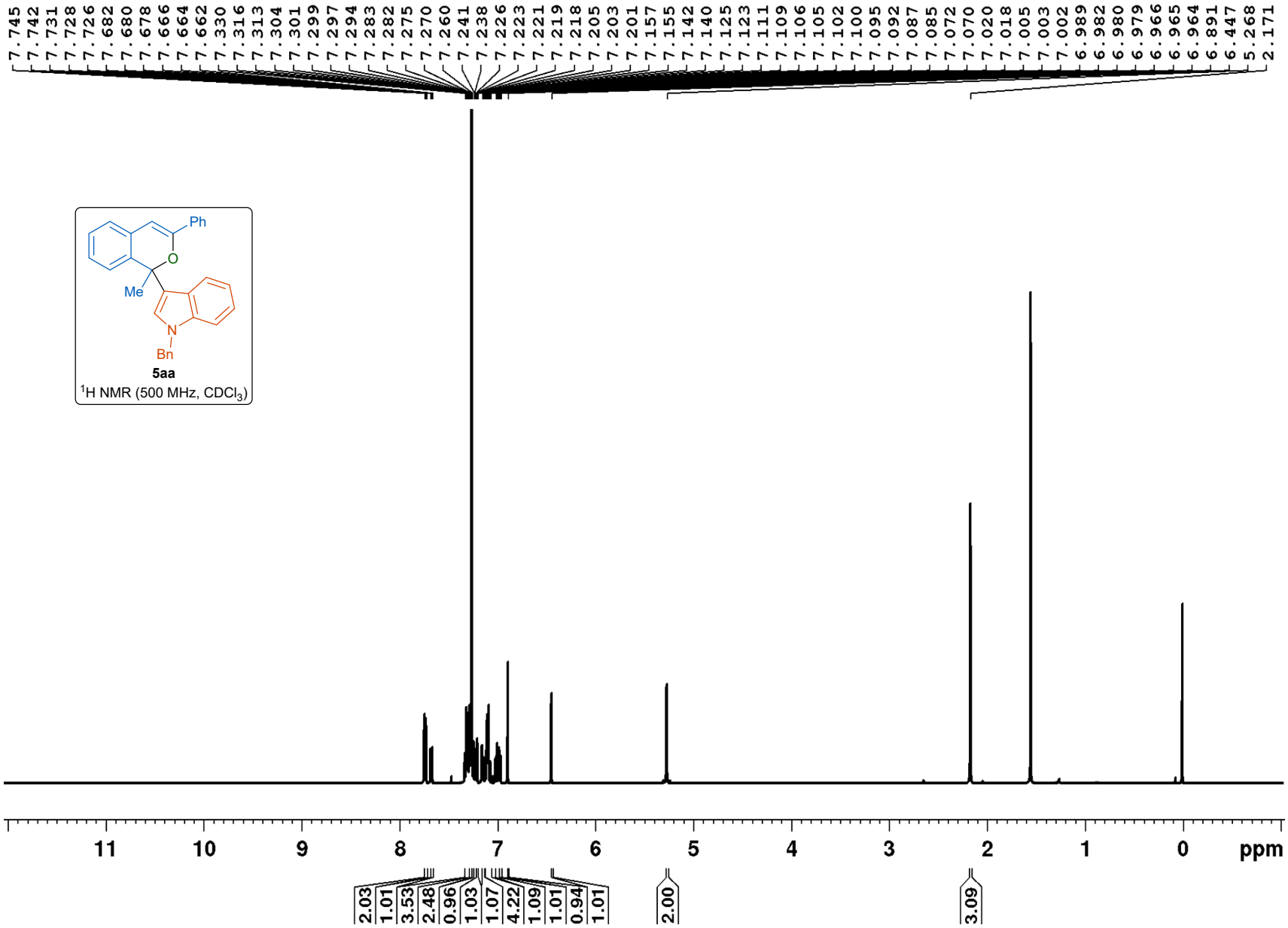


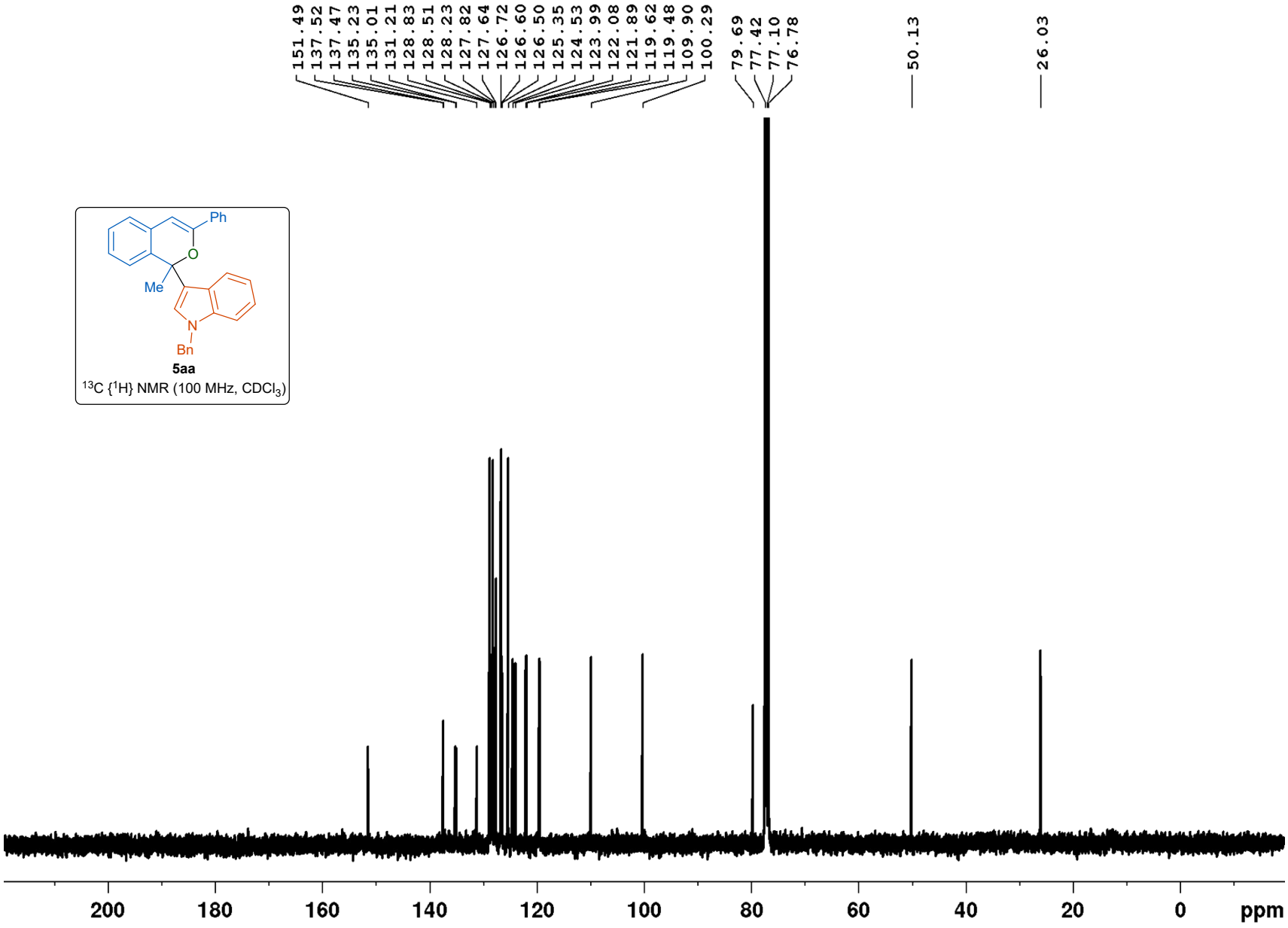
3qg

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




147.67
143.44
139.39
136.79
133.81
133.75
133.12
131.83
130.16
129.62
128.55
128.04
127.22
127.13
126.80
126.52
126.12
125.87
125.73
120.27
115.34
113.06
103.08
77.32
77.00
76.68
55.41
52.58
47.44
21.38
NHTs
N
Bn
OMe
3qg
13C {1H} NMR (100 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0
ppm


7.745
7.742
7.731
7.728
7.726
7.682
7.680
7.678
7.666
7.664
7.662
7.330
7.316
7.313
7.304
7.301
7.299
7.297
7.294
7.283
7.282
7.275
7.270
7.260
7.241
7.238
7.226
7.223
7.221
7.219
7.218
7.205
7.203
7.201
7.157
7.155
7.142
7.140
7.125
7.123
7.111
7.109
7.106
7.105
7.102
7.100
7.095
7.092
7.087
7.085
7.072
7.070
7.020
7.018
7.005
7.003
7.002
6.989
6.982
6.980
6.979
6.966
6.965
6.964
6.891
6.447
5.268
2.171
Ph
O
Me
N
Bn
5aa
1H NMR (500 MHz, CDCl3)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.03
1.01
3.53
2.48
0.96
1.03
1.07
4.22
1.09
1.01
0.94
1.01
2.00
3.09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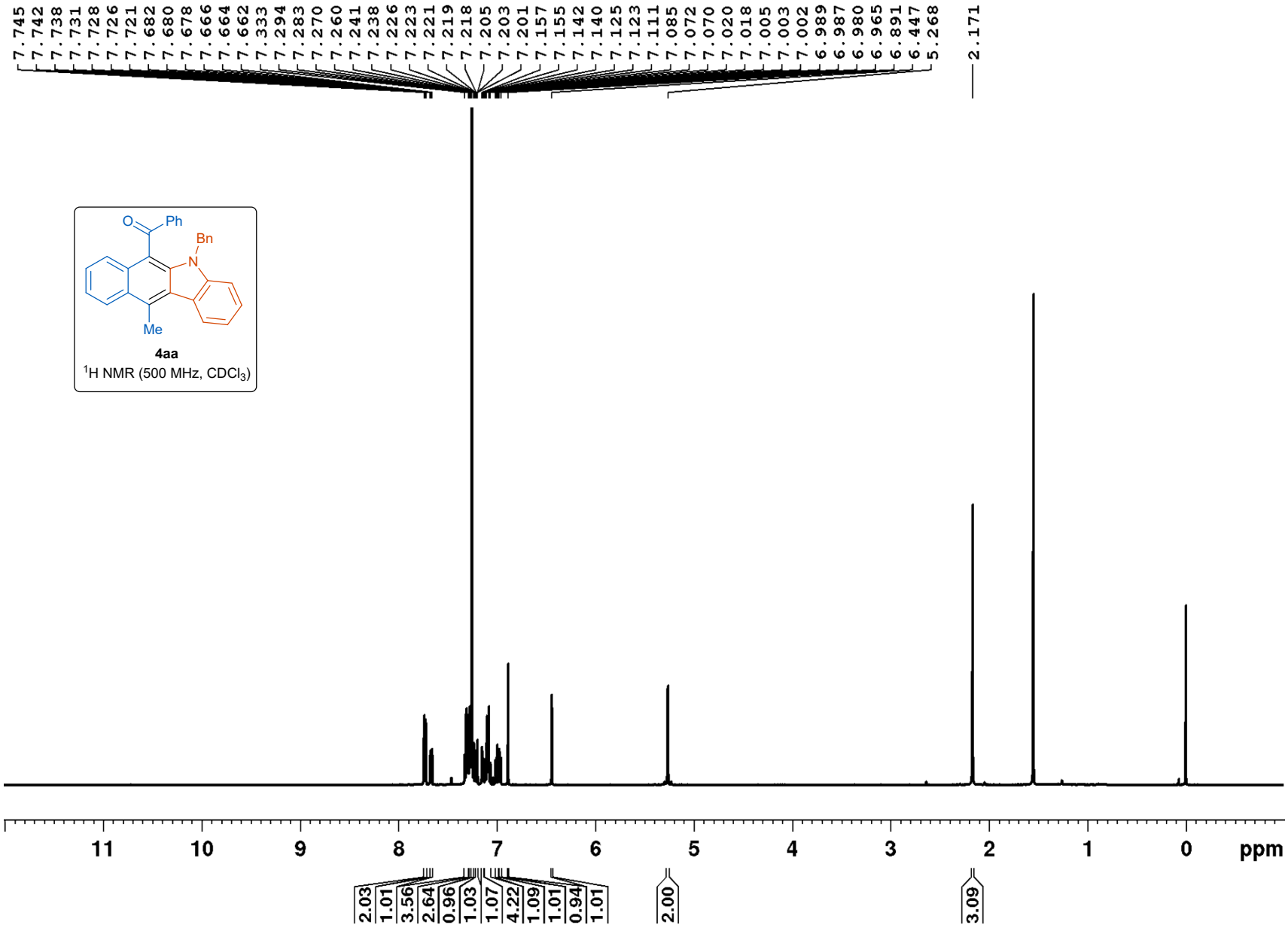
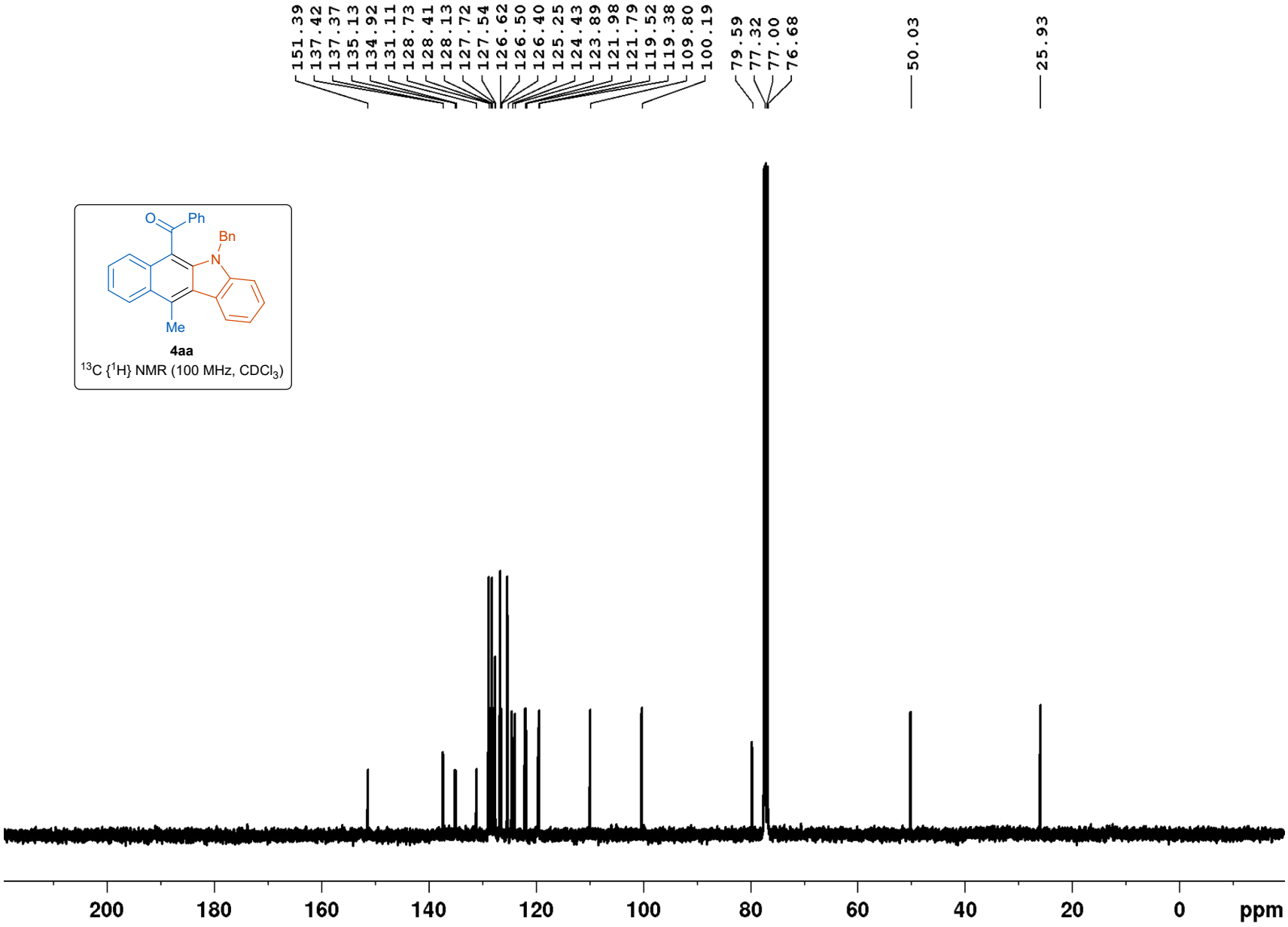
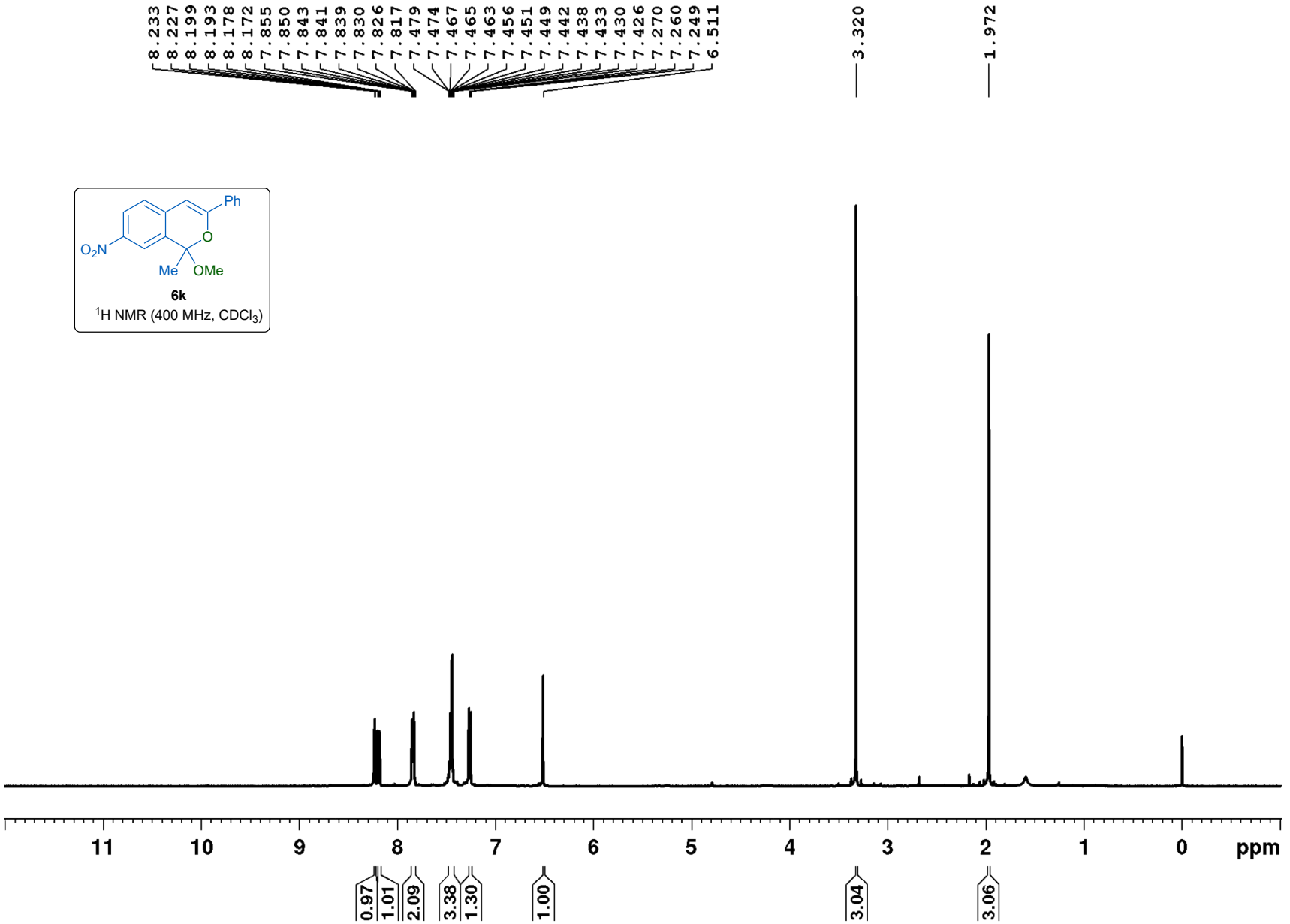
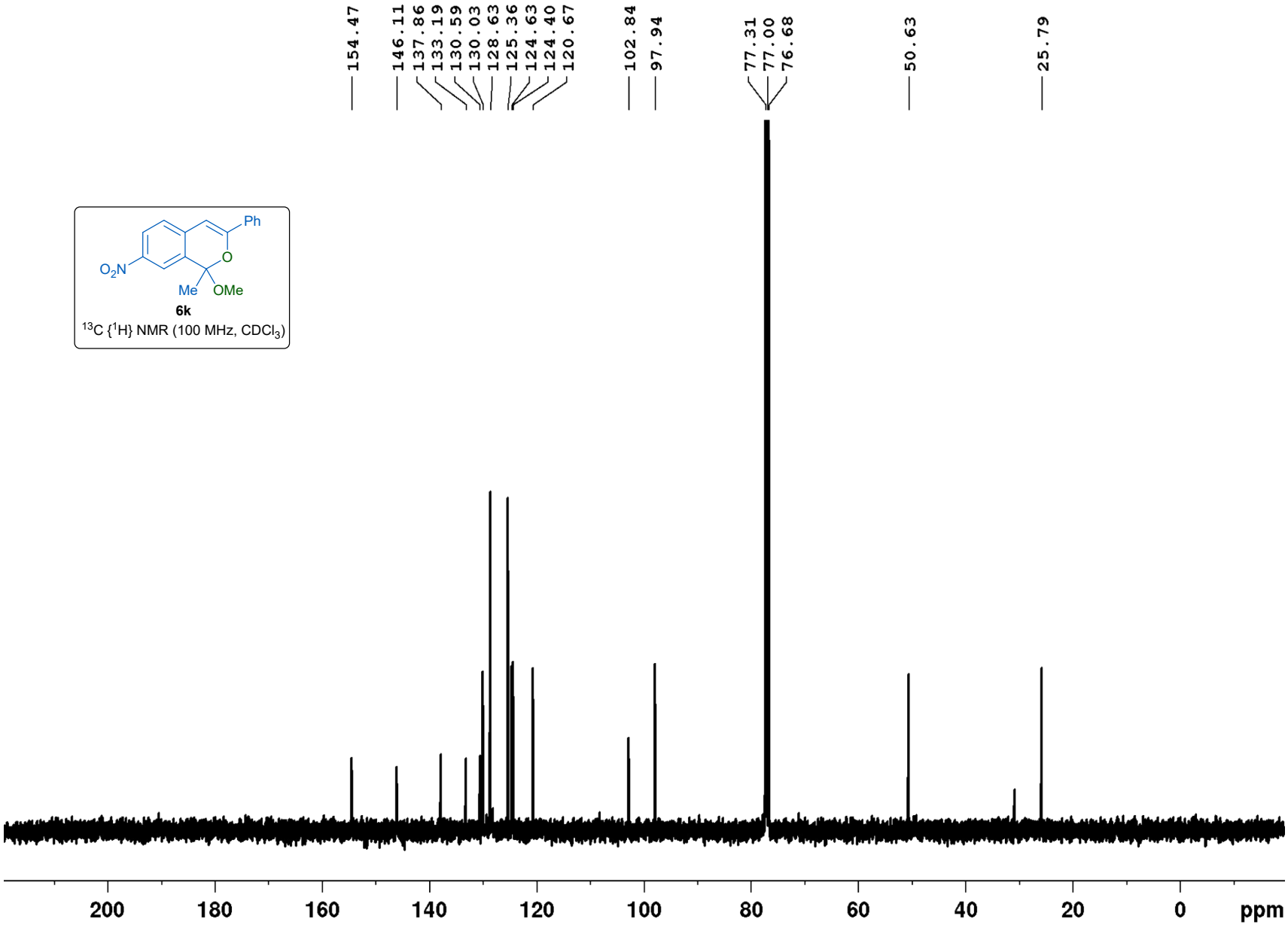
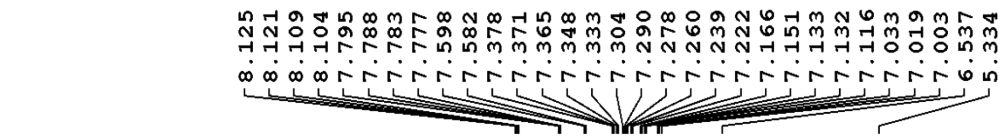
137.52
137.47
135.23
135.01
131.21
128.83
128.51
128.23
127.82
127.64
126.72
126.60
126.50
125.35
124.53
123.99
122.08
121.89
119.62
119.48
109.90
100.29
79.69
77.42
77.10
76.78
50.13
26.03
Ph
O
Me
N
Bn
5aa
13C {1H} NMR (100 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0
ppm

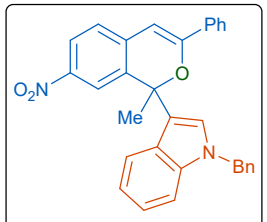

7.745
7.742
7.738
7.731
7.728
7.726
7.721
7.682
7.680
7.678
7.666
7.664
7.662
7.333
7.294
7.283
7.270
7.260
7.241
7.238
7.226
7.223
7.221
7.219
7.218
7.205
7.203
7.201
7.157
7.155
7.142
7.140
7.125
7.123
7.111
7.085
7.072
7.070
7.020
7.018
7.005
7.003
7.002
6.989
6.987
6.980
6.965
6.891
6.447
5.268
2.171
O
Ph
Bn
N
Me
4aa
1H NMR (500 MHz, CDCl3)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.03
1.01
3.56
2.64
0.96
1.03
1.07
4.22
1.09
1.01
0.94
1.01
2.00
3.09


151.39
137.42
137.37
135.13
134.92
131.11
128.73
128.41
128.13
127.72
127.54
126.62
126.50
126.40
125.25
124.43
123.89
121.98
121.79
119.52
119.38
109.80
100.19
79.59
77.32
77.00
76.68
50.03
25.93
O
Ph
Bn
N
Me
4aa
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)
200
180
160
140
120
100
80
60
40
20
0
ppm


8.233
8.227
8.199
8.193
8.178
8.172
7.855
7.850
7.843
7.841
7.839
7.830
7.826
7.817
7.479
7.474
7.467
7.465
7.463
7.456
7.451
7.449
7.442
7.438
7.433
7.430
7.426
7.270
7.260
7.249
6.511
3.320
1.972
Ph
O
O2N
Me
OMe
6k
1H NMR (400 MHz, CDCl3)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.97
1.01
2.09
3.38
1.30
1.00
3.04
3.06

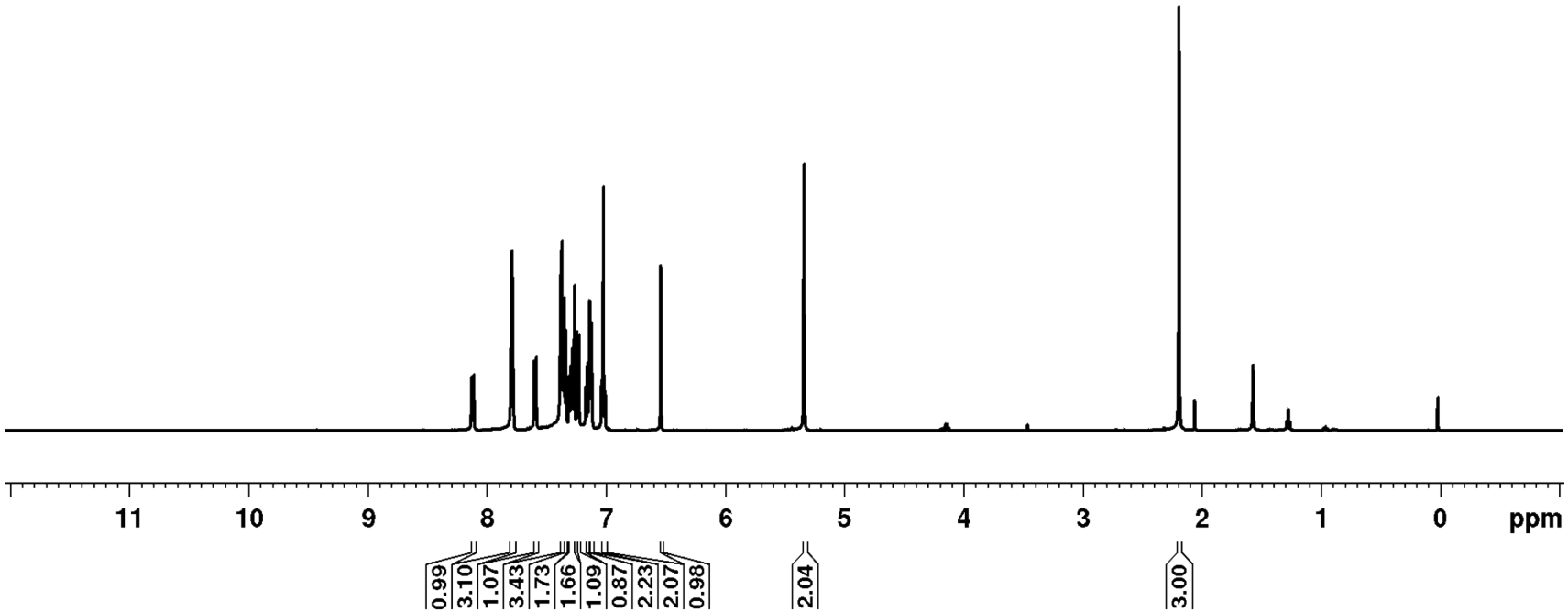

154.47
146.11
137.86
133.19
130.59
130.03
128.63
125.36
124.63
124.40
120.67
102.84
97.94
77.31
77.00
76.68
50.63
25.79
Ph
O
O2N
Me
OMe
6k
13C {1H} NMR (100 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0
ppm

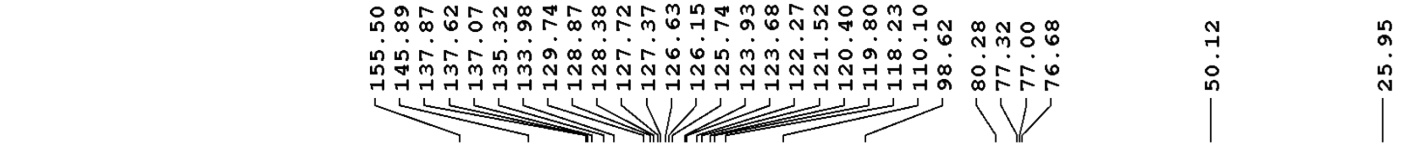


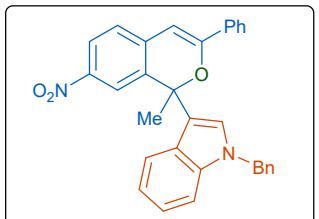


5ak

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

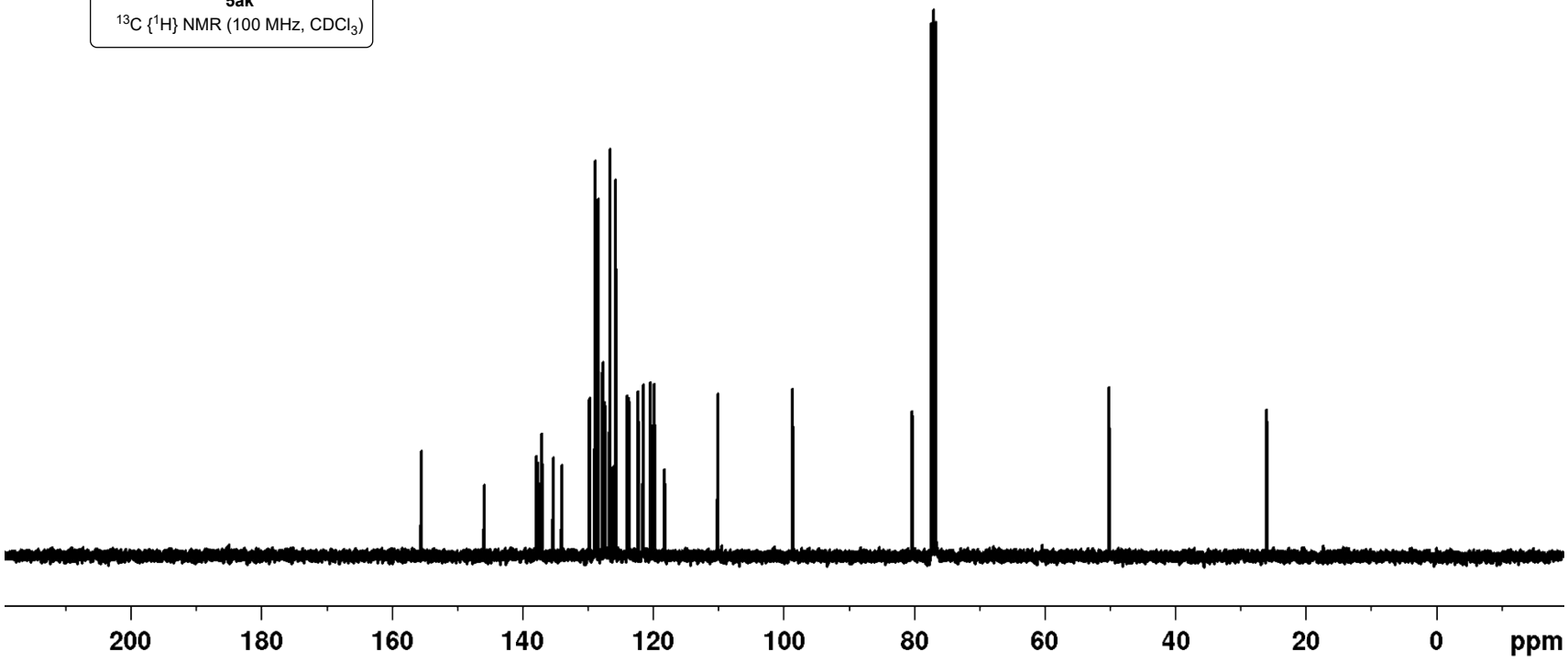


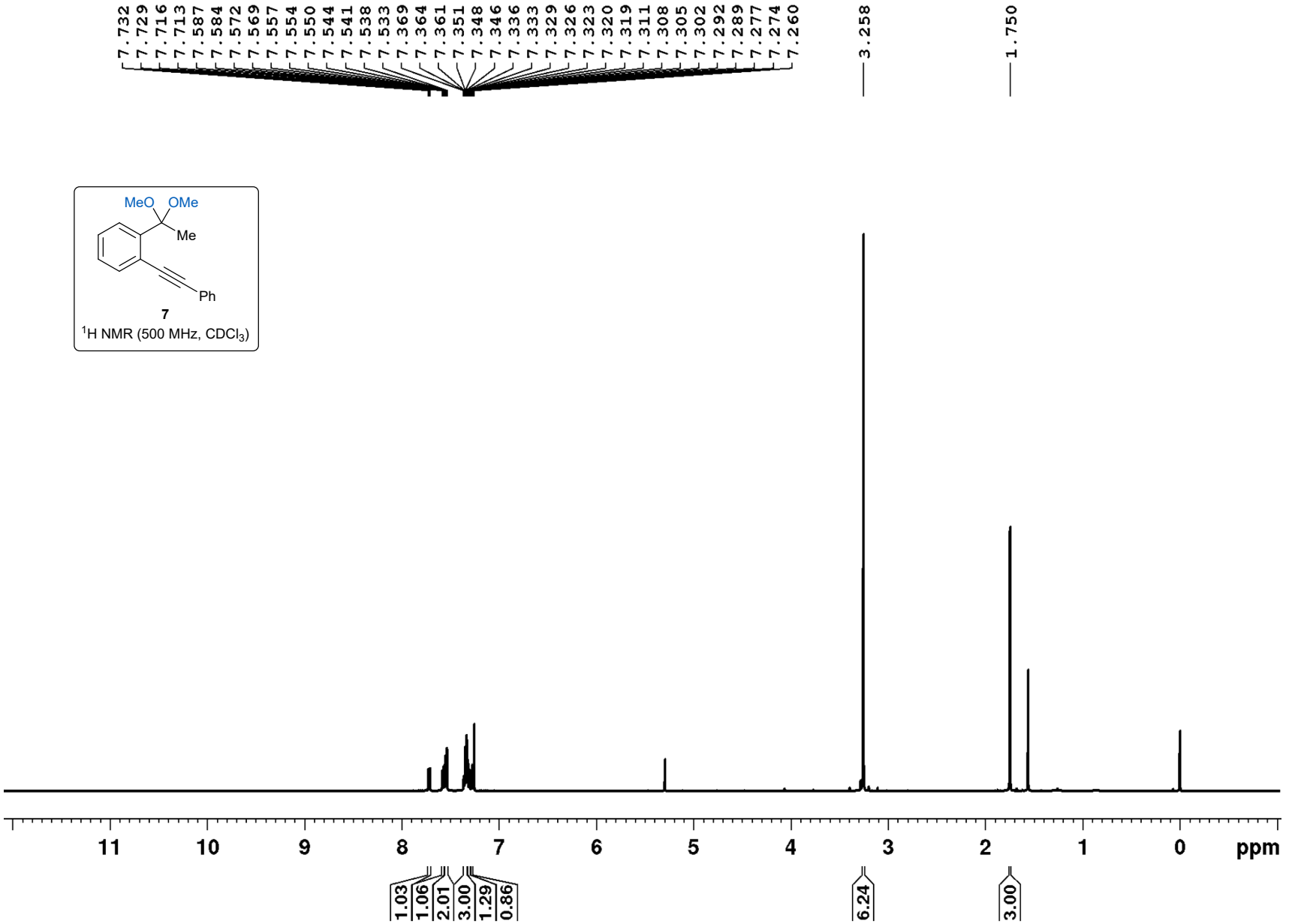


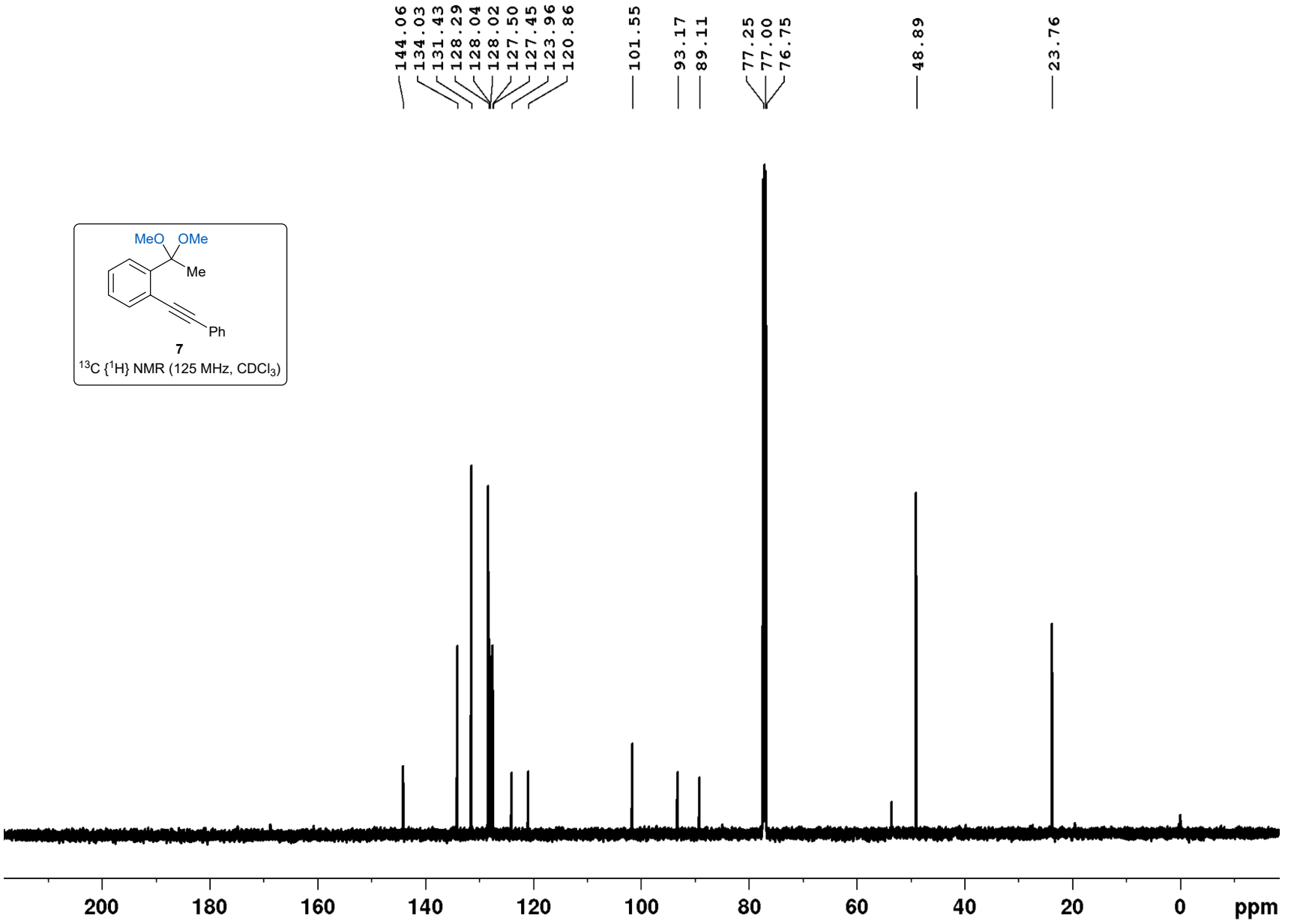


5ak

^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)




7.732
7.729
7.716
7.713
7.587
7.584
7.572
7.569
7.557
7.554
7.550
7.544
7.541
7.538
7.533
7.369
7.364
7.361
7.351
7.348
7.346
7.336
7.333
7.329
7.326
7.323
7.320
7.319
7.311
7.308
7.305
7.302
7.292
7.289
7.277
7.274
7.260
3.258
1.750
MeO
OMe
Me
Ph
7
1H NMR (500 MHz, CDCl3)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.03
1.06
2.01
3.00
1.29
0.86
6.24
3.00


144.06
134.03
131.43
128.29
128.04
128.02
127.50
127.45
123.96
120.86
101.55
93.17
89.11
77.25
77.00
76.75
48.89
23.76
MeO
OMe
Me
Ph
7
^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$)
200
180
160
140
120
100
80
60
40
20
0
ppm

14. ^{1}H NMR monitoring of the reaction of 1a with 2a in the presence of TMOF

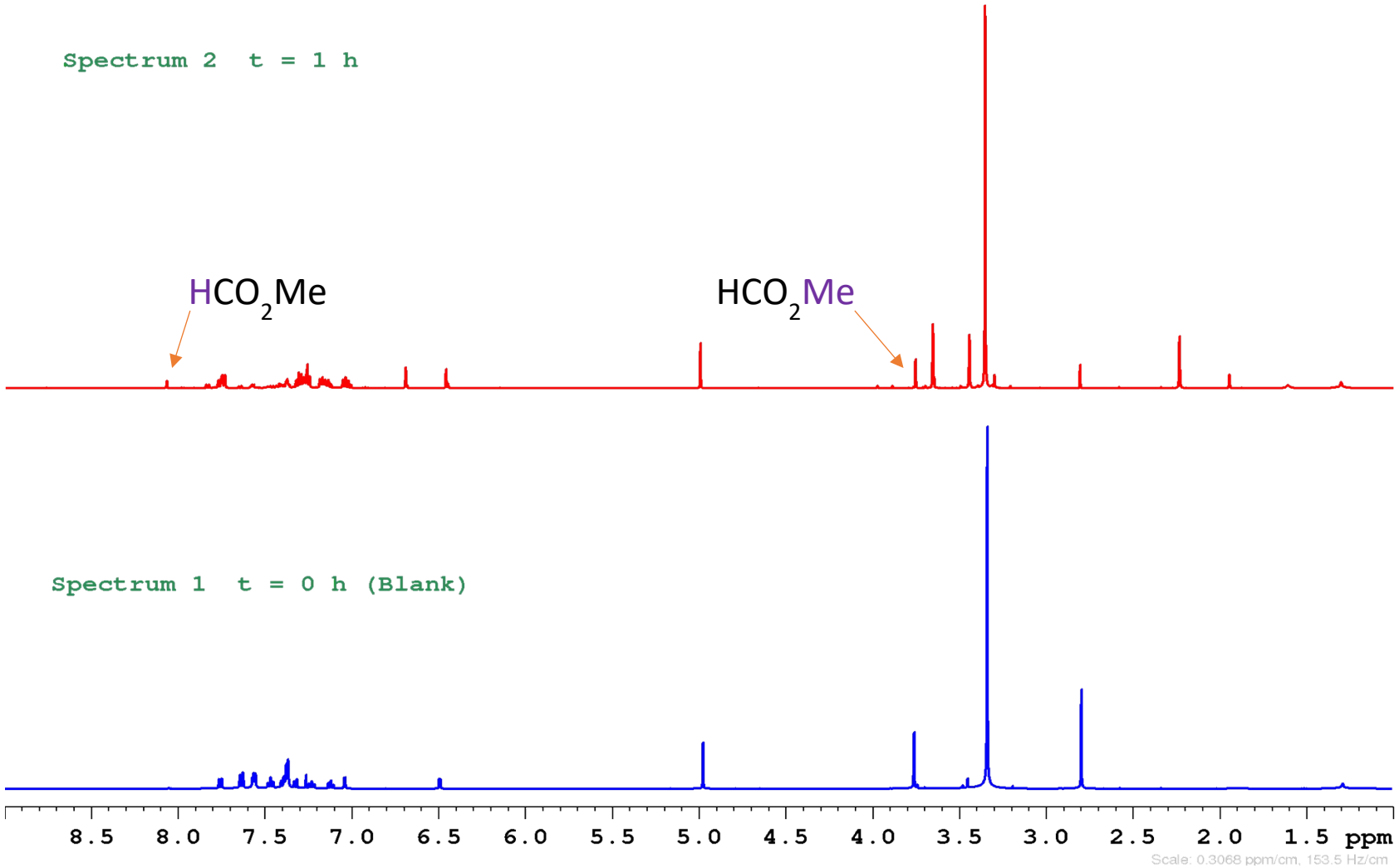


Figure S1: ^{1}H NMR monitoring of the reaction of **1a** with **2a** in the presence of TMOF (Spectrum 1: Reaction mixture before adding AgOTf, Spectrum 2: Reaction mixture after 1h of adding AgOTf).

15. X-ray data of 3af and 5ak

X-ray data of 3af

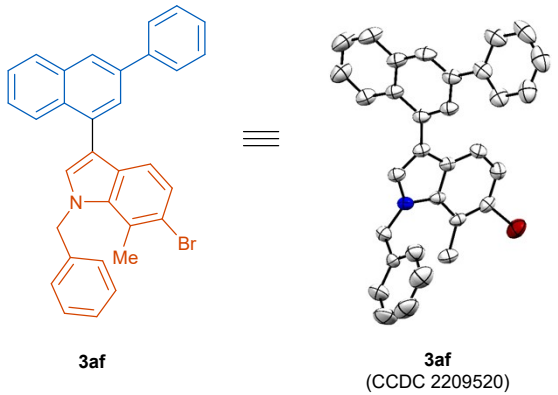


Figure 2: ORTEP representation of **3af**. Thermal ellipsoids are drawn with 50% probability.

Table S2. **Crystallographic data of compound 3af**

Compound	**3af**
Identification code	RB61
CCDC	**2209520**
Empirical formula	$C_{32}H_{24}BrN$
Formula weight	502.46
Temperature/K	300
Crystal system	Triclinic

Space group	P -1
a/Å	9.1848 (2)
b/ Å	9.7094 (2)
c/ Å	14.2815 (2)
$\alpha/^0$	95.361 (2)
$\beta/^0$	92.618 (1)
$\gamma/^0$	109.065 (2)
Volume/$Å^3$	1194.55 (4)
Z	2
Density(ρ)calc g/cm^3	1.397
Absorption Coefficient(μ) (mm^{-1})	1.742
F(000)	515.6
Crystal size/mm^3	0.02 x 0.02 x 0.01
Reflections collected	4208
Independent reflections	3396
Completeness to theta = 24.995	99.9%
R (reflections)	0.0385 (3396)

wR2 (reflections)	0.0823 (4208)

X-ray data of 5ak

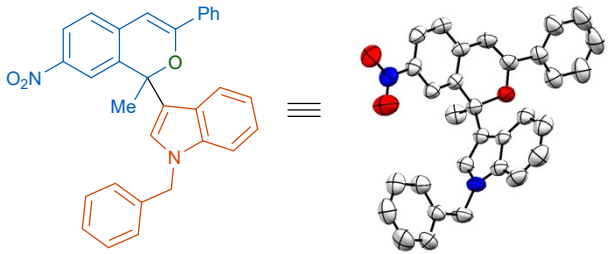


Figure 1: ORTEP representation of **5ak**. Thermal ellipsoids are drawn with 50% probability.

Table S1. **Crystallographic data of compound 5ak**

Compound	**5ak**
Identification code	rb005a
CCDC	**2204406**
Empirical formula	$C_{31}H_{24}N_2O_3$
Formula weight	472.52
Temperature/K	300
Crystal system	Monoclinic

Space group	C12/C1
a/Å	27.630(4)
b/ Å	9.6103(12)
c/ Å	22.543(3)
$\alpha/^0$	90
$\beta/^0$	123.585(4)
$\gamma/^0$	90
Volume/$Å^3$	4986.5(11)
Z	8
Density(ρ)calc g/cm^3	1.259
Absorption Coefficient(μ) (mm^{-1})	0.082
F(000)	1984.0
Crystal size/mm^3	0.02 x 0.02 x 0.01
Reflections collected	3602
Independent reflections	4385
Completeness to theta = 24.995	99.9%
R (reflections)	0.0553 (3602)

wR2 (reflections)	0.1521 (4385)

16. References

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