Supporting Information

Palladium-Catalyzed Aerobic Oxidative Cyclization of *N*-Aryl Imines: Indole Synthesis from Anilines and Ketones

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Contents

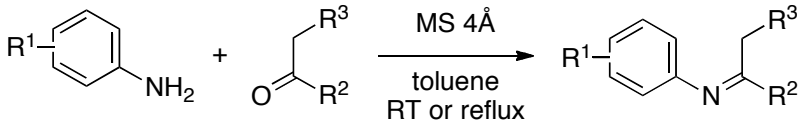
Materials and Methods

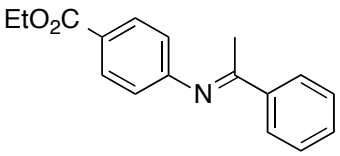
General. All reactions dealing with air- and moisture-sensitive compounds were carried out in dry reaction vessels under a nitrogen atmosphere. Analytical thin-layer chromatography (TLC) was performed on Merck 60 F254 silica gel plates. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV-400 (400 MHz) NMR spectrometers. ^{1}H and ^{13}C NMR spectra are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm) and $CHCl_3$ (77.0 ppm), respectively. Gas chromatographic (GC) analysis was performed on a Shimadzu GC-2010 system equipped with and FID detector and a capillary column, DB-5 (Agilent J&W, 0.25 mm i.d. x 30 m, 0.25 μm film thickness). High-resolution mass spectra (HRMS) were obtained with a Q-Tof Premier LC HR mass spectrometer. Melting points were determined using a capillary melting point apparatus and are uncorrected.

Materials. Unless otherwise noted, materials were purchased from Aldrich, Alfa Aesar, and other commercial suppliers and were used as received. Anhydrous DMSO was distilled over CaH_2 and stored under N_2 or purchased from Aldrich without further purification.

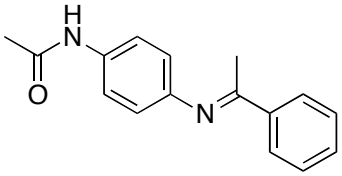
Preparation of Starting Materials

All imines were synthesized by condensation of the corresponding anilines and ketones according to the literature procedures,[1, 2] and purified by recrystallization from EtOAc/hexane or by flash chromatography on silica gel. Below are summarized characterization data for newly synthesized imines. ^{1}H and ^{13}C NMR spectral data for the rest of the imines (**1a**,[3] **1b**,[2] **1c**,[4] **1d**,[5] **1e**,[4] **1f**,[6] **1g**,[4] **1h**,[7] **1i**,[8] **1j**,[2] **1k**,[9] **1l**,[10] **1n**,[9] **1o**,[11] **1p**,[11] **1r**,[12] **1u**,[6] **1v**,[13] **1w**,[13] **1x**,[13] **1y**,[14] **1aa**,[1] **1ab**,[9] **1ae**,[15] **1aj**,[13] **1ak**,[16] and **1ar**[4]) showed good agreement with the literature data.



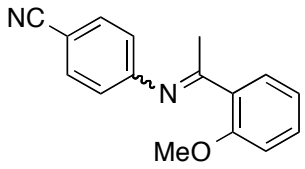


(*E*)-Ethyl 4-((1-phenylethylidene)amino)benzoate (1m): Yellow solid (60% yield); Mp = 89–90 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.07–8.04 (m, 2H), 7.98–7.96 (m, 2H), 7.49–7.43 (m, 3H), 6.85–6.82 (m, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.23 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.6, 165.7, 156.0, 138.9, 130.9, 130.8, 128.5, 127.3, 125.4, 119.1, 60.7, 17.6, 14.4; **HRMS** (ESI) Calcd for $C_{17}H_{17}NO_2$ $[M + H]^+$ 268.1338, found 268.1340.

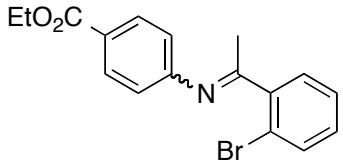


(*E*)-*N*-(4-((1-phenylethylidene)amino)phenyl)acetamide (1q): Yellow solid (71% yield); Mp = 164–165 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97–7.94 (m, 2H), 7.49–7.43 (m, 5H),

7.37 (brs, 1H), 6.76 (d, J = 8.5 Hz, 2H), 2.24 (s, 3H), 2.17 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 166.1, 148.1, 139.5, 133.5, 130.5, 128.4, 127.2, 120.9, 120.0, 24.5, 17.5; **HRMS** (ESI) Calcd for $C_{16}H_{16}N_2O$ $[M + H]^+$ 253.1341, found 253.1340.

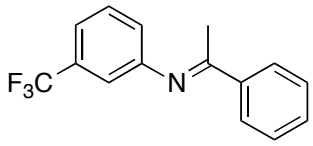


4-((1-(2-Methoxyphenyl)ethylidene)amino)benzonitrile (1s): Yellow solid (65% yield); Approx. 1.5:1 mixture of *E* and *Z* isomers; **^{1}H NMR** (400 MHz, $CDCl_3$): *Z* isomer: δ 7.35 (d, J = 8.0 Hz, 2H), 7.19 (t, J = 7.4 Hz, 1H), 6.84 (d, J = 7.0 Hz, 1H), 6.80 (d, J = 7.0 Hz, 1 H), 6.75 (d, J = 8.2 Hz, 1H), 6.71 (d, J = 8.2 Hz, 2H), 3.70 (s, 3H), 2.48 (s, 3H); *E* isomer: δ 7.62 (d, J = 6.0 Hz, 2H), 7.58 (t, J = 7.6 Hz, 1H), 7.40 (t, J = 8.0 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H), 6.96 (d, J = 8.02 Hz, 1H), 6.90 (d, J = 8.0 Hz, 2H), 3.88 (s, 3H), 2.19 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.2, 169.8, 157.4, 155.3, 155.2, 154.9, 133.1, 132.3, 131.2, 130.1, 130.0, 129.3, 127.5, 127.2, 120.8, 120.7, 120.3, 120.0 (x 2), 119.2, 111.2, 110.6, 106.4, 106.1, 55.3, 55.0, 28.3, 21.4; **HRMS** (ESI) Calcd for $C_{16}H_{15}N_2O$ $[M + H]^+$ 251.1184, found 251.1183.

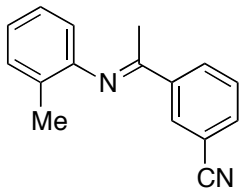


Ethyl 4-((1-(2-bromophenyl)ethylidene)amino)benzoate (1t): Approx. 1.2:1 mixture of *E* and *Z* isomers; Yellow solid (70% yield); **^{1}H NMR** (400 MHz, $CDCl_3$): *Z* isomer: δ 7.81–7.80 (m, 2 H), 7.41–7.38 (m, 1H), 7.28–7.24 (m, 2H), 7.05 (td, J = 7.6, 1.5 Hz, 1H), 6.80–6.78 (m, 2H), 4.27 (q, J = 7.1 Hz, 2H), 2.53 (s, 3H), 1.32 (t, J = 7.0 Hz, 3H); *E* isomer: δ 8.08–8.06 (m, 2H), 7.62 (d, J = 8.0 Hz, 1H), 7.45–7.41 (m, 2H), 7.14 (t, J = 7.4 Hz, 1H), 6.94–6.92 (m, 2H), 4.38 (q, J = 7.1 Hz, 2H), 2.19 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 169.9, 169.7, 154.7, 154.6, 142.5, 140.1, 133.2, 132.7, 130.9, 130.2, 130.1, 129.7, 128.7, 128.2, 127.6, 127.2, 126.0, 125.5, 119.8, 119.3, 118.9, 60.8, 60.7, 28.1,

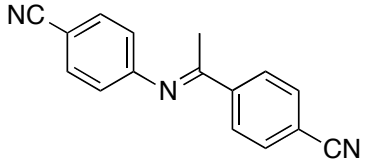
21.5, 14.4, 14.3; **HRMS** (ESI) Calcd for $C_{17}H_{16}BrNO_2$ $[M + H]^+$ 346.0443, found 346.0446.



(*E*)-*N*-(1-Phenylethylidene)-3-(trifluoromethyl)aniline (1z): Yellow oil (75% yield, eluent = hexane/EtOAc (95:5)); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.98 (dd, *J* = 7.7, 1.4 Hz, 2H), 7.50–7.45 (m, 4H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.01 (s, 1H), 6.98 (d, *J* = 7.9 Hz, 1H), 2.25 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.6, 152.1, 139.0, 131.3 (q, $^2J_{C\text{-}F}$ = 32 Hz), 130.9, 129.5, 128.5, 127.3, 128.4 (q, $^1J_{C\text{-}F}$ = 277 Hz), 122.8, 119.9 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 116.3 (q, $^3J_{C\text{-}F}$ = 3.9 Hz), 17.6; **HRMS** (ESI) Calcd for $C_{15}H_{12}F_3N$ $[M + H]^+$ 264.1000, found 264.1008.

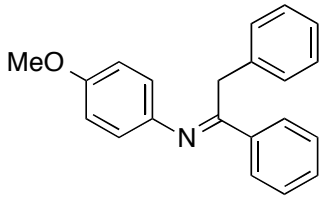


(*E*)-3-(1-(*o*-Tolylimino)ethyl)benzonitrile (1ac): Yellow solid (82% yield); Mp = 89–90 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.26 (s, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.24–7.18 (m, 2H), 7.04 (td, *J* = 7.5, 0.8 Hz, 1H), 6.62 (d, *J* = 7.6 Hz, 1H), 2.19 (s, 3H), 2.10 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.8, 149.4, 140.4, 133.5, 131.3, 131.0, 130.5, 129.3, 127.1, 126.5, 123.8, 118.6, 118.1, 112.8, 17.8, 17.3; **HRMS** (ESI) Calcd for $C_{16}H_{14}N_2$ $[M + H]^+$ 235.1235, found 235.1233.

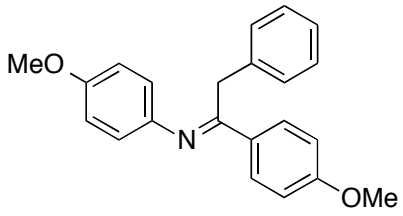


(*E*)-4-((1-(4-cyanophenyl)ethylidene)amino)benzonitrile (1ad): Yellow solid (75% yield); Mp = 176–177 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.6 Hz, 2H), 7.76 (d, *J* = 8.7

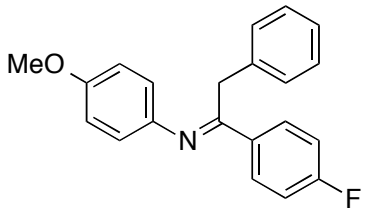
Hz, 2H), 7.67 (d, J = 8.2 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 2.26 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.7, 154.8, 142.1, 133.3, 132.2, 127.8, 119.6, 119.0, 118.2, 114.4, 107.2, 17.7; **HRMS** (ESI) Calcd for $C_{16}H_{11}N_3$ $[M + H]^+$ 246.1031, found 246.1026.



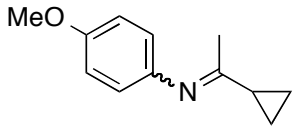
(*E*)-*N*-(1,2-Diphenylethylidene)-4-methoxyaniline (1af): Yellow solid (65% yield); Mp = 122–123 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95–7.93 (m, 2H), 7.40 –7.35 (m, 3H), 7.26–7.21 (m, 2H), 7.18–7.14 (m, 1H), 7.10 (d, J = 7.6 Hz, 2H), 6.89–6.86 (m, 2H), 6.82–6.80 (m, 2H), 4.13 (s, 2H), 3.80 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.5, 156.1, 144.3, 138.6, 137.3, 130.2, 128.7, 128.4, 128.3, 128.0, 126.2, 120.5, 114.3, 55.5, 36.1; **HRMS** (ESI) Calcd for $C_{21}H_{19}NO$ $[M + H]^+$ 302.1545, found 302.1548.



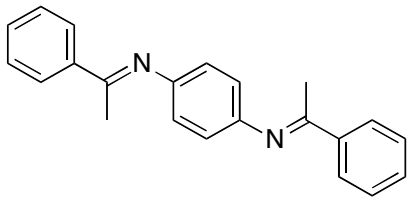
(*E*)-4-Methoxy-*N*-(1-(4-methoxyphenyl)-2-phenylethylidene)aniline (1ag): Yellow solid (50% yield); Mp = 114–115 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.88 (d, J = 8.0 Hz, 2H), 7.27–7.21 (com, 2H), 7.14 (d, J = 7.0 Hz, 1H), 7.08 (d, J = 7.0 Hz, 2H), 6.86–6.83 (com, 4H), 6.77–6.65 (com, 2H), 4.07 (s, 2H), 3.78 (s, 3H), 3.76 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.4, 161.2, 155.9, 144.4, 137.6, 131.1, 129.6, 128.6, 128.3, 126.1, 120.5, 114.2, 113.6, 55.4, 55.2, 35.8; **HRMS** (ESI) Calcd for $C_{22}H_{21}NO_2$ $[M + H]^+$ 332.1651, found 332.1649.



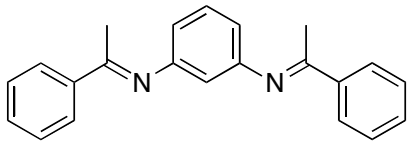
(*E*)-*N*-(1-(4-Fluorophenyl)-2-phenylethylidene)-4-methoxyaniline (1ah): The title compound contained small amounts of impurities (< 10%; see the attached ^{1}H spectrum) that could not be removed by chromatographic separation. Without further purification, it was used for the cyclization reaction; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.89 (dd, *J* = 9.0, 5.7 Hz, 2H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.16 (d, *J* = 7.0 Hz, 1H), 7.05–6.99 (com, 4 H), 6.86 (d, *J* = 9.0 Hz, 2H), 6.77 (d, *J* = 9 Hz, 2H), 5.08 (s, 2H), 3.78 (s, 3H).



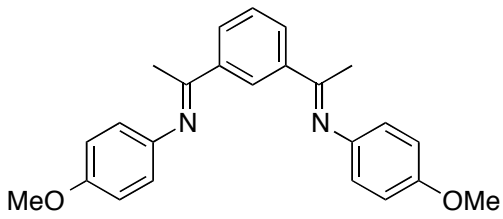
***N*-(1-cyclopropylethylidene)-4-methoxyaniline (1ai):** Yellow oil (76% yield); Approx. 3.1:1 mixture of *E* and *Z* isomers; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.86–6.59 (m, 4H for both isomers), 3.77 (s, 3H), 3.76 (s, 3H), 1.79 (s, 3H), 1.72 (s, 3H), 0.97–0.70 (m, 5H for both isomers); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 172.6, 172.5, 155.6, 155.5, 144.8, 144.3, 121.2, 120.8, 114.1, 114.1, 55.7, 55.4, 20.5, 20.2, 18.0, 14.8, 7.8, 6.8; **HRMS** (ESI) Calcd for $C_{12}H_{15}NO$ $[M + H]^+$ 190.1232, found 190.1237.



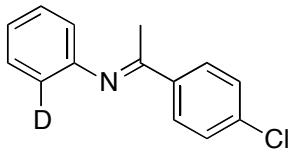
(*N*^{1}*E*,*N*^{4}*E*)-*N*^{1},*N*^{4}-Bis(1-phenylethylidene)benzene-1,4-diamine (1al): Yellow solid (80% yield); Mp = 213–214 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.99–7.97 (com, 4H), 7.45 - 7.42 (com, 6H), 6.81 (s, 4H), 2.28 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.6, 147.1, 139.5, 130.3, 128.3, 127.1, 120.1, 17.3; **HRMS** (ESI) Calcd for $C_{22}H_{20}N_2$ $[M + H]^+$ 313.1705, found 313.1702.



***(N*^{1}*E*,*N*^{3}*E*)-*N*^{1},*N*^{3}*-*bis(1-phenylethylidene)benzene-1,3-diamine (1am):** Pale yellow solid (70% yield); Mp = 113–114 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.97 (com, 4H), 7.45–7.41 (com, 6H), 7.32 (t, *J* = 7.6 Hz, 1H), 6.53 (dd, *J* = 5.9, 1.8 Hz, 2H), 6.24 (t, *J* = 1.8 Hz, 1H), 2.23, (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.6, 152.5, 139.4, 130.4, 129.5, 128.3, 127.1, 114.2, 109.9, 17.4; **HRMS** (ESI) Calcd for $C_{22}H_{20}N_2$ $[M + H]^+$ 313.1705, found 313.1702.



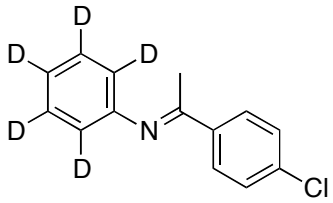
(*N*,*N*'*E*,*N*,*N*'*E*)-*N*,*N*'-(1,3-Phenylenebis(ethan-1-yl-1-ylidene))bis(4-methoxyaniline) (1an): Yellow solid (70% yield); Mp = 183–184 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.54 (t, *J* = 1.7 Hz, 1H), 8.04 (dd, *J* = 7.6, 2 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 1H), 6.93–6.90 (m, 4H), 6.79–6.75 (m, 4H), 3.82 (s, 6H), 2.30 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.6, 155.9, 144.6, 139.9, 128.9, 128.3, 125.8, 120.7, 114.2, 55.4; **HRMS** (ESI) Calcd for $C_{24}H_{24}N_2O_2$[M + H]$^+$ 373.1916, found 373.1916.



2-Deuterio-(*E*)-*N*-(1-(4-chlorophenyl)ethylidene)aniline: (1aq-*d*): Prepared from 2-deuterio-aniline (deuterium incorporation > 95%)[17] and 4'-chloroacetophenone; Yellow solid (70% yield); Mp = 93–94 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.38–7.34 (m, 2H), 7.10 (td, *J* = 7.5, 1.0 Hz, 1H), 6.78 (dd, *J* = 8.1,

0.8 Hz, 1H), 2.21 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.3, 151.3, 137.9 136.6, 129.0, 128.9, 128.6, 123.4, 119.3, 17.3 (two signals could not be observed because of ^{13}C-^{2}H coupling); **HRMS** (ESI) Calcd for $C_{14}H_{11}ClND$ $[M + H]^+$ 231.0799, found 231.0792.

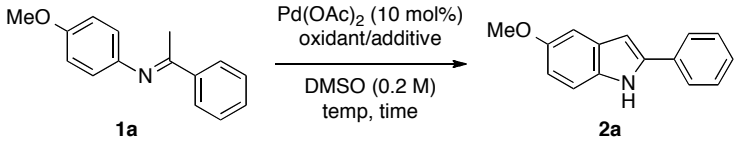
Pentadeuterio-aniline: Pentadeuterio-aniline was prepared by copper-catalyzed amination of bromobenzene-d_6 with aqueous ammonia according to the method reported by Wolf et al.[18] A 150 mL of Schlenk tube equipped with a stirrer bar was charged with bromobenzene-d_5 (20 mmol), Cu_2O (5 mol%), 15 mL of ammonium hydroxide solution (~25% NH_3 in H_2O, 10 equiv), and 15 mL of *N*-methyl pyrrolidinone (NMP). The tube was sealed with a Teflon screw cap, and then stirred at 80 °C for 15 h. Upon completion, the reaction mixture was cooled to room temperature and extracted with diethyl ethyl and dried over Na_2SO_4, filtered, concentrated under reduced pressure. The residue was directly used for the imine synthesis without further purification.



2,3,4,5,6-Pentadeuterio-(*E*)-*N*-(1-(4-chlorophenyl)ethylidene)aniline: (1aq-d_5): Prepared from pentadeuterio-aniline and 4'-chloroacetophenone; Yellow solid (58% yield); Mp = 92–93 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94–7.90 (m, 2H), 7.44–7.40 (m, 2H), 2.22 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.3, 151.2, 137.9, 136.6 128.6, 17.3 (except deuterated carbons); **HRMS** (ESI) Calcd for $C_{14}H_7D_5ClN$ $[M + H]^+$ 235.1050, found 235.1046.

Catalytic Oxidative Cyclization of *N*-Aryl Imines

Table S1. Screening of Reaction Conditions[a]

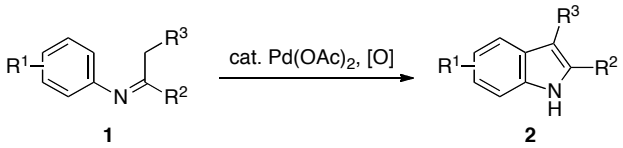


1a **2a**

Entry	Oxidant/additive/other changes	Temp (°C)	Time (h)	Yield (%)[b]
1	O_2 (1 atm)	40	16	27
2	O_2 (4 atm)	40	16	39
3	O_2 (1 atm)/Bu_4NCl (1 equiv)	40	16	24
4	O_2 (1 atm)/Bu_4NBr (1 equiv)	40	16	48
5	O_2 (1 atm)/Bu_4NI (1 equiv)	40	16	31
6	O_2 (1 atm)/Bu_4NOAc (1 equiv)	40	16	22
7	O_2 (1 atm)/LiBr (2 equiv)	40	16	45
8	O_2 (1 atm)/MS 4A	40	16	18
9	O_2 (1 atm)/HOAc (2 equiv)	40	16	17
10	O_2 (1 atm)/NaOAc (1 equiv)	40	16	15
11	O_2 (1 atm)/3-nitropyridine (20 mol %)	40	16	11
12	O_2 (1 atm)/Bu_4NBr (2 equiv)	25	16	76[c]
13	**O_2 (1 atm)/Bu_4NBr (2 equiv)**	**60**	**16**	**89[c]**
14	open air/Bu_4NBr (2 equiv)	60	16	67
15	**$Cu(OAc)_2$ (3 equiv)**	**40**	**12**	**93[c]**
16	$CuCl_2$ (3 equiv)	40	12	0
17	AgOAc (3 equiv)	40	12	0
18	BzO*t*Bu (3 equiv)	40	12	23
19	BQ (2 equiv)	40	12	8
20	*t*BuO*t*Bu (2 equiv)	40	12	5
21	$PhI(OAc)_2$ (3 equiv)	40	12	0
22	DDQ (2 equiv)	40	12	0
23	$Cu(OAc)_2$ (3 equiv)/DMF instead of DMSO	40	12	0
24	$Cu(OAc)_2$ (3 equiv)/dioxane instead of DMSO	40	12	0
25	$Cu(OAc)_2$ (3 equiv)/MeCN instead of DMSO	40	12	0
26[d]	$Pd(OAc)_2$ (10 mol%), $Cu(OAc)_2$ (3 equiv), K_2CO_3 (3 equiv) DMF (0.08 M), 80 °C			0
27[d]	CuI (5 mol%), phen (17.5 mol%), Li_2CO_3 (2 equiv) DMF, 100 °C, air			0
28[d]	$PhI(OAc)_2$ (1.3 equiv), DCE, 60 °C			0
29[d]	$FeCl_3$ (10 mol%), $Cu(OAc)_2$•$CuCl_2$ (3 equiv), K_2CO_3 (3 equiv) DMF, 120 °C			0

[a] Reaction was performed on a 0.2 mmol scale unless otherwise noted. [b] Determined by GC using *n*-tridecane as an internal standard. [c] Isolated yield. [d] Reaction conditions were adopted from the literature.[16,17,19,20]

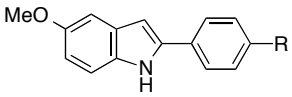
Scheme S1. Indole Synthesis from *N*-Aryl Imines: Comparison of Aerobic and Copper(II)-Mediated Systems[a]



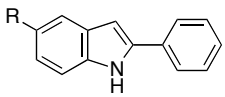
1 **2**

Conditions A: $Pd(OAc)_2$ (10 mol %), Bu_4NBr (2 equiv), O_2 (1 atm), DMSO, 60 °C, 24 h

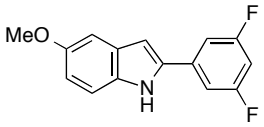
Conditions B: $Pd(OAc)_2$ (10 mol %), $Cu(OAc)_2$ (3 equiv), DMSO, 40 °C, 5–24 h



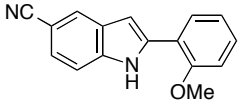
2a (R = H), 89%, 93%
2b (R = NO_2), 92%, 82%
2c (R = CN), 91%, 93%
2d (R = $CONR'_2$),[b] NA,[c] 81%
2e (R = CF_3), 86%, 86%
2f (R = Cl), 90%, 88%
2g (R = Br), 77%, 71%
2h (R = Me), 86%, 78%
2i (R = OMe), 82%, 75%



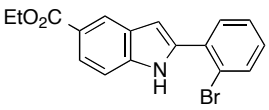
2j (R = H), 87%, 85%
2k (R = NO_2), 58%, 55%
2l (R = CF_3), 81%, 79%
2m (R = CO_2Et), 82%, 91%
2n (R = Cl), 88%, 83%
2o (R = Br), 93%, 91%
2p (R = Me), 92%, 92%
2q (R = NHAc), 64%, 64%



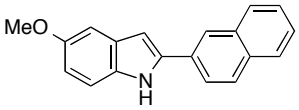
2r, 88%, 91%



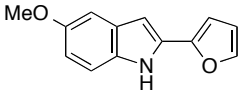
2s, 89%, 62%



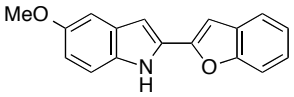
2t, 22%, 27%[d]



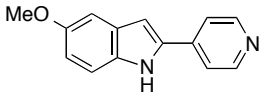
2u, 78%, 80%



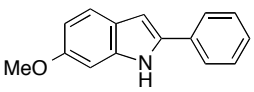
2v, 76%, 62%



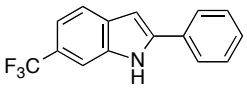
2w, 84%, 86%



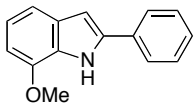
2x, 80%, 0%



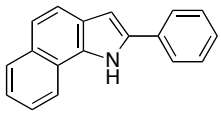
2y, 74%,[e] 73%[f]



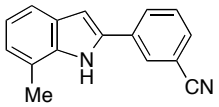
2z, 72%, NA



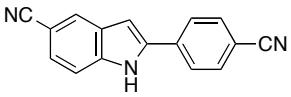
2aa, 67%, 50%



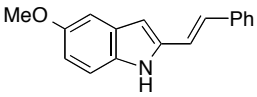
2ab, 88%, 71%[d]



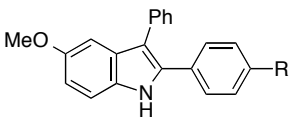
2ac, 87%, 84%



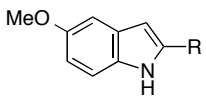
2ad, 74%, 84%



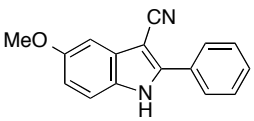
2ae, 78%, <10%[g]



2af (R = H), 40%, 86%
2ag (R = OMe), NA,[c] 82%
2ah (R = F), NA,[c] 74%



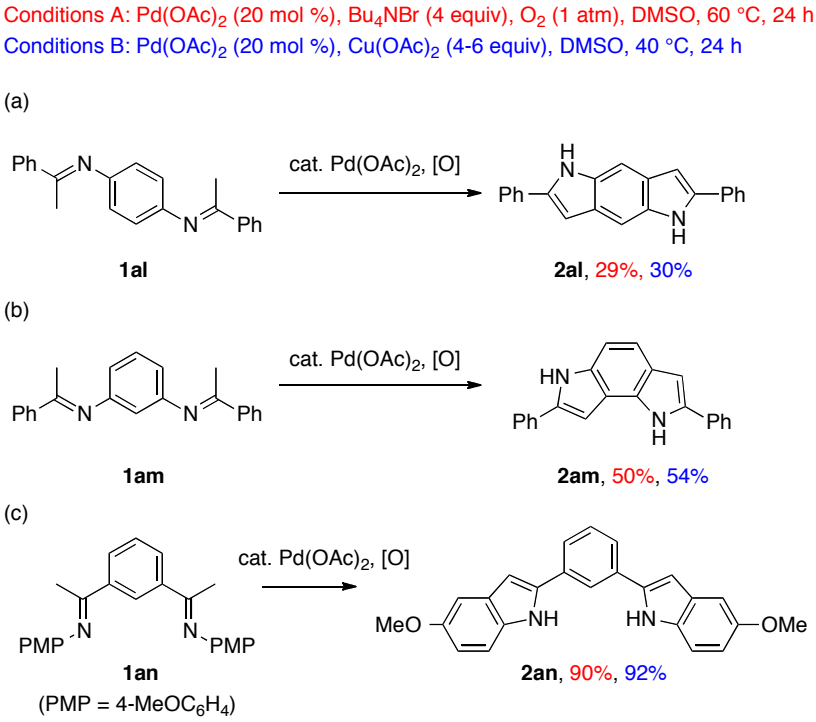
2ai (R = *c*-C_3H_5), 84%, <5%[g]
2aj (R = *t*Bu), 61%, 74%



2ak,[h] 85%, 63%

[a] Reaction was performed on a 0.2 mmol scale. Isolated yields obtained under conditions A and B are shown in red and blue, respectively. [b] NR_2' = morpholino. [c] NA = Not examined. [d] 20 mol % of $Pd(OAc)_2$ was used. [e] A regioisomeric product was obtained in 7% yield. [f] A regioisomeric product was obtained in 5% yield. [g] Estimated by GC analysis. [h] The starting material was in the form of enamine.

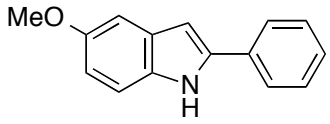
Scheme S2. Twofold Oxidative Cyclizations: Comparison of Aerobic and Copper(II)-Mediated Systems[a]



[a] Reaction was performed on a 0.2 mmol scale. Isolated yields obtained with conditions A and B are shown in red and blue, respectively.

General Procedure for Pd/Bu_4NBr/O_2 System: A Schlenk tube equipped with a stirrer bar was charged with *N*-aryl imine (0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%) and Bu_4NBr (129 mg, 0.4 mmol), followed by addition of DMSO (1 mL). The Schlenk tube was quickly evacuated, closed under vacuum, and then refilled with oxygen using an oxygen balloon. The resulting mixture was stirred at 60 °C for 24 h. Upon cooling to room temperature, the reaction mixture was diluted with 5 mL of ethyl acetate, followed by filtration through a pad of silica gel. The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel to afford the indole product.

General Procedure for Pd/Cu System: A Schlenk tube equipped with a stirrer bar was charged with *N*-aryl imine (0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%) and $Cu(OAc)_2$ (109 mg, 0.6 mmol, 3 equiv). The Schlenk tube was evacuated and refilled with N_2 for three times, followed by addition of DMSO (1 mL). The Schlenk tube was sealed with a Teflon screwcap and then the reaction mixture was stirred at 40 °C for 12 h. Upon cooling to room temperature, the reaction mixture was diluted with 5 mL of ethyl acetate, followed by filtration through a pad of silica gel. The filtrate was washed with water (10 mL), dried over Na_2SO_4, and then concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel was purified afforded the indole product.



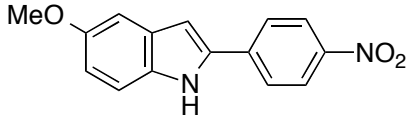
5-Methoxy-2-phenyl-1*H*-indole (2a)[21]

10 mmol-scale reaction (eq 1): A 100 mL round-bottom flask equipped with a stirrer bar was charged with (*E*)-4-methoxy-*N*-(1-phenylethylidene)aniline (10 mmol, 2.25 g), $Pd(OAc)_2$ (0.22 g, 1 mmol, 10 mol%) and Bu_4NBr (6.45 g, 20 mmol, 2 equiv), followed by addition of DMSO (50 mL). The flask was quickly evacuated, closed under vacuum, and then refilled with oxygen using an oxygen balloon. The resulting mixture was stirred at 60

°C for 24 h. Upon cooling to room temperature, the reaction mixture was diluted with 25 mL of ethyl acetate, followed by filtration through a pad of silica gel. The filtrate was concentrated under vacuum, and the residue was purified on silica gel to afford the title compound as an off-white solid (1.87 g, 84%).

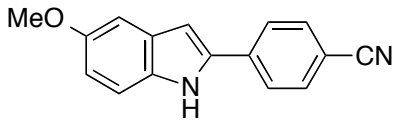
50 mmol-scale reaction (Table 1, entry 9): A 500 mL round-bottom flask equipped with a stirrer bar was charged with (*E*)-4-methoxy-*N*-(1-phenylethylidene)aniline (50 mmol, 11.3 g), $Pd(OAc)_2$ (0.56 g, 2.5 mmol, 5 mol%) and $Cu(OAc)_2$ (18.2 g, 100 mmol, 2 equiv). The flask was evacuated and refilled with N_2 for three times, followed by addition of DMSO (250 mL). The flask was sealed with a glass stopper and then the reaction mixture was stirred at 40 °C for 48 h. Upon cooling to room temperature, the reaction mixture was diluted with 150 mL of ethyl acetate and filtered through a pad of silica gel using 100 mL of ethyl acetate as additional eluent. The filtrate was washed with water (3 x 250 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by recrystallization (EtOAc/hexane) to afford the title compound as an off-white solid (9.7 g, 87%). The product showed the same degree of analytical purity compared with that obtained by a small-scale reaction.

Mp = 169–170 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.26 (brs, 1H), 7.66–7.64 (m, 2H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.27 (d, *J* = 8.6 Hz, 1H), 7.12 (d, *J* = 2.3 Hz, 1H), 6.90 (dd, *J* =8.7, 2.4 Hz, 1H), 6.77 (d, *J* = 1.9 Hz, 1H), 3.89 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.5, 138.6, 132.4, 132.0, 129.7, 129.0, 127.7, 125.1, 112.6, 111.6, 102.3, 99.8, 55.8; **HRMS** (ESI) Calcd for $C_{15}H_{13}ON$ $[M + H]^+$ 224.1075, found 224.1069. The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[22]

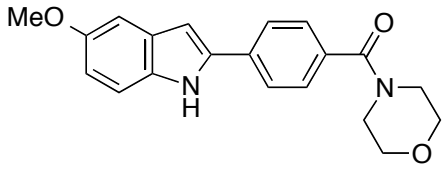


5-Methoxy-2-(4-nitrophenyl)-1*H*-indole (2b): Orange solid (92% yield, eluent = hexane/EtOAc (85:15)); Mp = 200–201 °C; **^{1}H NMR** (400 MHz, acetone-d_6): δ 10.8 (brs, 1H), 8.29 (d, *J* = 8.7 Hz, 2H), 8.06 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 9.0 Hz, 1H), 7.10 (d, *J* =

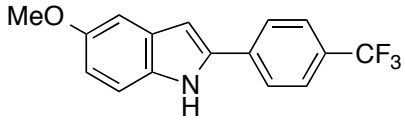
3.9 Hz, 2H), 6.86 (dd, *J* = 8.7, 1.9 Hz, 1H), 3.82 (s, 3H); **^{13}C NMR** (100 MHz, acetone-d_6): δ 154.7, 146.3, 138.9, 135.8, 133.5, 129.5, 125.2, 124.2, 114.2, 112.3, 102.5, 101.8, 55.9; **HRMS** (ESI) Calcd for $C_{15}H_{12}N_2O_3$ $[M + H]^+$ 269.0926, found 269.0923.



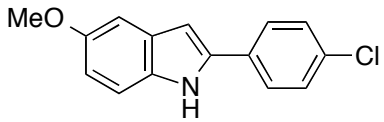
4-(5-Methoxy-1*H*-indol-2-yl)benzonitrile (2c): Pale yellow solid (91% yield, eluent = hexane/EtOAc (85:15)); Mp = 195-196 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.33 (brs, 1H), 7.73–7.68 (m, 4H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.09 (d, *J* = 2.2 Hz, 1H), 6.92 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.88 (*J* = 1.3 Hz, 1H), 3.87 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.8, 136.6, 136.1, 132.8, 132.7, 129.4, 125.1, 118.9, 114.4, 112.0, 110.5, 102.4, 102.3, 55.8; **HRMS** (ESI) Calcd for $C_{16}H_{12}N_2O$ $[M + H]^+$ 249.1028, found 249.1031.



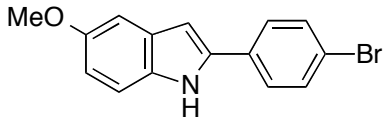
(4-(5-Methoxy-1*H*-indol-2-yl)phenyl)(morpholino)methanone (2d): The reaction was performed with the Pd/Cu system; Yellow solid (81% yield, eluent = hexane/acetone (60:40)); Mp = 223–224 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.79 (brs, 1H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.08 (d, *J* = 2.2 Hz, 1H), 6.87 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.77 (d, *J* = 1.4 Hz, 1H), 3.87 (s, 3H), 3.72–3.54 (m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.2, 154.6, 137.5, 134.2, 133.8, 132.4, 129.5, 128.0, 125.1, 113.2, 111.9, 102.2, 100.7, 66.9, 55.8 (signals of the carbon atoms bonded to the oxygen atom of the morpholine ring were not observed); **HRMS** (ESI) Calcd for $C_{20}H_{20}N_2O_3$ $[M + H]^+$ 337.1552, found 337.1549.



5-Methoxy-2-(4-(trifluoromethyl)phenyl)-1*H*-indole (2e): White solid (86% yield, eluent = hexane/EtOAc (92:8)); Mp = 196–197 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.26 (brs, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 1H), 7.08 (d, *J* = 2.3 Hz, 1H), 6.89 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.82 (d, *J* = 1.4 Hz, 1H), 3.86 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.7, 136.8, 135.7, 132.4, 129.5, 129.3 (q, $^2J_{C\text{-}F}$ = 32.3 Hz), 126.0 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.1 (q, $^1J_{C\text{-}F}$ = 271.9 Hz), 125.0, 113.7, 111.9, 102.4, 101.5, 55.8; **HRMS** (ESI) Calcd for $C_{16}H_{12}F_3ON$ $[M + H]^+$ 292.0949, found 292.0947. The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[22]

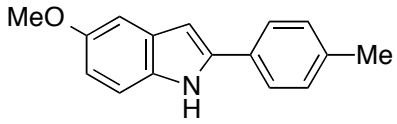


5-Methoxy-2-(4-chlorophenyl)-1*H*-indole (2f): White solid (90% yield, eluent = hexane/EtOAc (92:8)); Mp = 193-194 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.17 (brs, 1H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 1H), 7.07 (d, *J* = 2.1 Hz, 1H), 6.86 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.72 (d, *J* = 1.3 Hz, 1H), 3.85 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.6, 137.4, 133.4, 132.1, 130.9, 129.7, 129.2, 126.2, 113.0, 111.7, 102.3, 100.3, 55.8; **HRMS** (ESI) Calcd for $C_{15}H_{12}ONCl$ $[M + H]^+$ 258.0686, found 258.0683. The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[23]

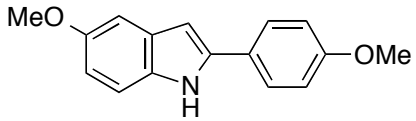


5-Methoxy-2-(4-bromophenyl)-1*H*-indole (2g): White solid (77% yield, eluent = hexane/EtOAc (92:8)); Mp = 201–202 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.18 (brs, 1H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 1H), 7.08 (d, *J* = 2.3 Hz, 1H), 6.87 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.75 (d, *J* = 1.5 Hz, 1H), 3.86 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.6, 137.4, 132.1, 131.4, 129.6, 126.5, 121.4, 113.1 (two signals are overlapped), 111.7, 102.3, 100.4, 55.8; **HRMS** (ESI) Calcd for $C_{15}H_{12}ONBr$ $[M + H]^+$

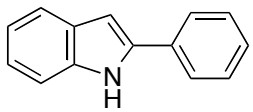
302.0181, found 302.0187.



5-Methoxy-2-(*p*-tolyl)-1*H*-indole (2h): White solid (86% yield, eluent = hexane/EtOAc (92:8)); Mp = 186–187 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.17 (brs, 1H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.23–7.20 (m, 3H), 7.07 (d, *J* = 2.3 Hz, 1H), 6.83 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.69 (d, *J* = 1.4 Hz, 1H), 3.84 (s, 3H), 2.37 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.5, 138.9, 137.6, 131.9, 129.8, 129.7, 129.6, 125.0, 112.4, 111.6, 102.2, 99.3, 55.9, 21.3; **HRMS** (ESI) Calcd for $C_{16}H_{15}ON$ $[M + H]^+$ 238.1232, found 238.1238. The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[23]

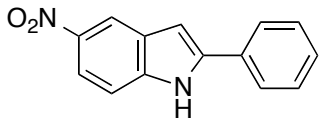


5-Methoxy-2-(4-methoxyphenyl)-1*H*-indole (2i): White solid (82% yield, eluent = hexane/EtOAc (90:10)); Mp = 218–219 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.14 (brs, 1H), 7.57 (d, *J* = 8.7 Hz, 2H), 7.26 (s, 1H), 7.07 (d, *J* = 1.8 Hz, 1H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.83 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.65 (s, 1H), 3.86 (s, 3H), 3.85 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.3, 154.5, 138.7, 131.8, 129.9, 126.4, 125.3, 114.5, 112.0, 111.4, 102.2, 98.7, 55.9, 55.4; **HRMS** (ESI) Calcd for $C_{16}H_{15}O_2N$ $[M + H]^+$ 254.1181, found 254.1188. The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[24]

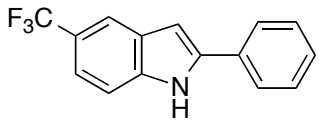


2-Phenyl-1*H*-indole (2j): White solid (87% yield, eluent = hexane/EtOAc (92:8)); Mp = 189–190 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.29 (brs, 1H), 7.63 (t, *J* = 6.6 Hz, 3H), 7.43 (t, *J* = 7.9 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.19 (td, *J* = 7.1, 1.0 Hz, 1H), 7.12 (td, *J* = 7.0, 0.7 Hz, 1H), 6.82 (d, *J* = 1.3 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ

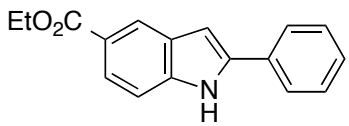
137.9, 136.8, 132.4, 129.3, 129.0, 127.7, 125.2, 122.3, 120.7, 120.3, 110.9, 100.0; **HRMS** (ESI) Calcd for $C_{14}H_{11}N$ $[M + H]^+$ 194.0970, found 194.1974. The ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[22]



5-Nitro-2-phenyl-1*H*-indole (2k): Yellow solid (58% yield, eluent = hexane/EtOAc (90:10)); Mp = 199–200 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.76 (brs, 1H), 8.59 (d, J = 2.1 Hz, 1H), 8.11 (dd, J = 9.0, 2.3 Hz, 1H), 7.70 (d, J = 8.1 Hz, 2H), 7.50 (t, J = 7.8 Hz, 2H), 7.45–7.39 (m, 2H), 6.97 (d, J = 1.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 142.3, 141.1, 139.7, 131.1, 129.3, 128.8, 128.6, 125.4, 118.0, 117.7, 110.8, 101.7; **HRMS** (ESI) Calcd for $C_{14}H_{10}N_2O_2$ $[M + H]^+$ 239.0821, found 239.0829. The ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[25]

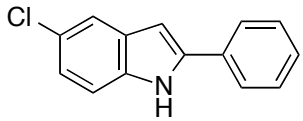


5-(Trifluoromethyl)-2-phenyl-1*H*-indole (2l): White solid (81% yield, eluent = hexane/EtOAc (92:8)); Mp = 153–154 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.46 (brs, 1H), 7.91 (s, 1H), 7.64 (d, J = 7.4 Hz, 2H), 7.47–7.42 (m, 4H), 7.36 (t, J = 7.3 Hz, 1H), 6.87 (d, J = 1.9 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 139.7, 138.1, 131.6, 129.2, 128.6, 128.4, 125.3 (q, $^1J_{C\text{-}F}$ = 272 Hz), 125.3, 122.7 (q, $^2J_{C\text{-}F}$ = 32.6 Hz), 119.0 (q, $^3J_{C\text{-}F}$ = 3.6 Hz), 118.3 (q, $^3J_{C\text{-}F}$ = 4.4 Hz), 111.1, 100.6; **HRMS** (ESI) Calcd for $C_{15}H_{10}NF_3$ $[M + H]^+$ 262.0844, found 262.0849. The ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[22]

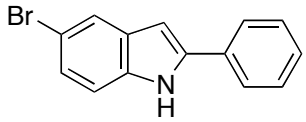


Ethyl 2-phenyl-1*H*-indole-5-carboxylate (2m): White solid (82% yield, eluent =

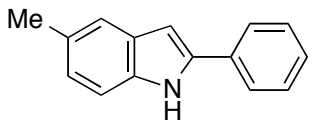
hexane/EtOAc (90:10)); Mp = 184–185 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.76 (brs, 1H), 8.41 (s, 1H), 7.93 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.68 (d, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 1.2 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.8, 139.4, 139.3, 131.8, 129.1, 128.8, 128.2, 125.3, 123.7, 123.5, 122.6, 110.6, 100.9, 60.7, 14.5; **HRMS** (ESI) Calcd for $C_{17}H_{15}NO_2$ $[M + H]^+$ 266.1181, found 266.1187.



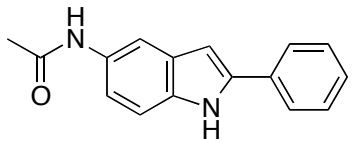
5-Chloro-2-phenyl-1*H*-indole (**2n**)**:** White solid (88% yield, eluent = hexane/EtOAc (92:8)); Mp = 196–197 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.33 (br s, 1H), 7.63 (d, *J* = 7.3 Hz, 2H), 7.57 (s, 1H), 7.43 (t, *J* = 7.31 Hz, 2H), 7.33 (t, *J* = 6.9 Hz, 1H), 7.27 (t, *J* = 8.6 Hz, 1H), 7.12 (d, *J* = 8.6 Hz, 1H), 6.75 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 139.3, 135.1, 131.8, 130.3, 129.1, 128.1, 125.8, 125.2, 122.5, 119.9, 111.8, 99.5; **HRMS** (ESI) Calcd for $C_{14}H_{10}ClN$ $[M + H]^+$ 228.0580, found 228.0578. The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[26]



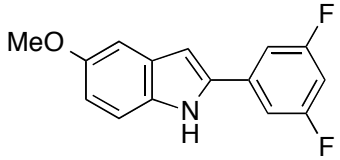
5-Bromo-2-phenyl-1*H*-indole (2o): White solid (93% yield, eluent = hexane/EtOAc (92:8)); Mp= 196–197 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.32 (brs, 1H), 7.73 (s, 1 H), 7.63–7.60 (com, 2 H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.33 (td, *J* = 7.4, 1.5 Hz, 1H), 7.25–7.24 (com, 2H), 6.73 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 139.0, 135.3, 131.7, 130.9, 129.0, 128.1, 125.2, 125.1, 123.0, 113.4, 112.2, 99.4; **HRMS** (ESI) Calcd for $C_{14}H_{10}NBr$ $[M + H]^+$ 272.0075, found 272.0085. The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[21]



5-Methyl-2-phenyl-1*H*-indole (2p): White solid (92% yield, eluent = hexane/EtOAc (92:8)); Mp = 216–218 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.13 (brs, 1H), 7.55 (d, *J* = 7.3 Hz, 2H), 7.33–7.31 (com, 3H), 7.23–7.14 (com, 2H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.65 (s, 1H), 2.34 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 137.9, 135.1, 132.5, 129.5, 129.4, 128.9, 127.5, 125.0, 123.9, 120.3, 110.5, 99.5, 21.5; **HRMS** (ESI) Calcd for $C_{15}H_{13}N$ $[M + H]^+$ 208.1126, found 208.1121. The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[22]

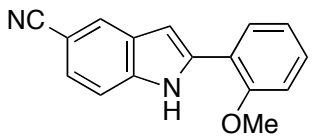


***N*-(2-Phenyl-1*H*-indol-5-yl)acetamide (2q):** Pale yellow solid (64% yield, eluent = hexane/EtOAc (20:80)); Mp = 218–219 °C; **^{1}H NMR** (400 MHz, acetone-d_6): δ 10.60 (brs, 1H), 9.01 (brs, 1H), 8.00 (s, 1H), 7.85 (d, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.33–7.27 (m, 3H), 6.85 (d, *J* = 1.8 Hz, 1H), 2.08 (s, 3H); **^{13}C NMR** (100 MHz, acetone-d_6): δ 167.4, 138.6, 134.3, 132.7, 132.4, 129.2, 128.9, 127.3, 125.0, 115.5, 110.9, 110.7, 99.1, 23.4; **HRMS** (ESI) Calcd for $C_{16}H_{14}N_2O$ $[M + H]^+$ 251.1184, found 251.1185.

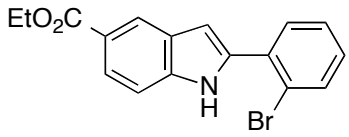


5-Methoxy-2-(3,5-difluorophenyl)-1*H*-indole (2r): White solid (86% yield, eluent = hexane/EtOAc (92:8)); Mp = 149–150 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.16 (brs, 1H), 7.26 (d, *J* = 8.9 Hz, 1H), 7.11–7.07 (m, 3H), 6.89 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.76–6.70 (m, 2H), 3.85 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 163.6 (dd, $^{1}J_{C\text{-}F}$ = 248.3 Hz, $^{3}J_{C\text{-}F}$ = 13.8 Hz), 154.7, 136.2 (t, $^{4}J_{C\text{-}F}$ = 2.9 Hz), 135.6 (t, $^{3}J_{C\text{-}F}$ = 10.4 Hz), 132.3, 129.4, 113.9, 120.0, 107.7 (dd, $^{2}J_{C\text{-}F}$ = 19.0 Hz, $^{4}J_{C\text{-}F}$ = 7.3 Hz), 102.7 (d, $^{2}J_{C\text{-}F}$ = 25.6 Hz), 102.4, 101.6, 55.8;

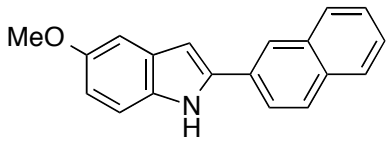
HRMS (ESI) Calcd for $C_{15}H_{11}ONF_2$ $[M + H]^+$ 260.0887, found 260.0891.



2-(2-Methoxyphenyl)-1*H*-indole-5-carbonitrile (2s): White solid (89% yield, eluent = hexane/EtOAc (70:30)); Mp = 145–146 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.99 (s, 1H), 7.94 (s, 1H), 7.81 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.45 (d, *J* = 8.6 Hz, 1H), 7.39–7.32 (com, 2H), 7.11–7.04 (com, 2H), 6.91 (d, *J* = 1.3 Hz, 1H), 4.03 (s, 3H); **^{13}C NMR** (100 MHz, acetone-d_6): δ 155.9, 138.5, 137.6, 129.6, 128.5, 127.8, 125.7, 124.6, 121.7, 121.1, 119.3, 120.0, 111.8, 102.7, 100.1, 55.9; **HRMS** (ESI) Calcd for $C_{16}H_{13}N_2O$ $[M + H]^+$ 249.1028, found 249.1018.

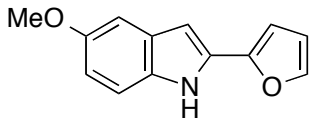


Ethyl 2-(2-bromophenyl)-1*H*-indole-5-carboxylate (2t): White solid (22% yield, eluent = hexane/EtOAc (90:10)); Mp = 157–158 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.84 (brs, 1H), 8.44 (s, 1H), 7.95 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.70 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.62 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.45–7.39 (m, 2H), 7.26–7.22 (m, 1H), 6.90 (d, *J* = 1.4, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.6, 138.7, 137.6, 134.1, 132.9, 131.5, 129.6, 127.8, 127.7, 124.0, 123.8, 122.7, 121.3, 110.7, 104.7, 60.6, 14.5; **HRMS** (ESI) Calcd for $C_{17}H_{14}BrNO_2$ $[M + H]^+$ 344.0286, found 344.0280.

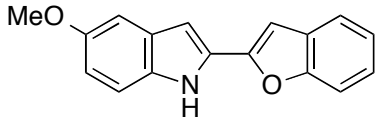


5-Methoxy-2-(naphthalen-2-yl)-1*H*-indole (2u): White solid (78% yield, eluent = hexane/EtOAc (92:8)); Mp = 213–214 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.37 (brs, 1H),

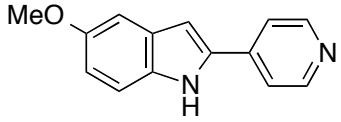
8.03 (s, 1H), 7.90–7.79 (m, 4H), 7.52–7.45 (m, 2H), 7.31 (d, J = 8.8 Hz, 1H), 7.11 (d, J = 2.2 Hz, 1H), 6.90–6.87 (m, 2H), 3.88 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.6, 138.6, 133.6, 132.8, 132.3, 129.9, 129.8, 128.8, 128.0, 127.8, 126.7, 126.1, 123.7, 122.9, 112.9, 111.7, 102.3, 100.5, 55.9; **HRMS** (ESI) Calcd for $C_{19}H_{15}NO$ $[M + H]^+$ 274.1232, found 274.1228.



2-(Furan-2-yl)-5-methoxy-1*H*-indole (2v): White solid (76% yield, eluent = hexane/EtOAc (92:8)); Mp = 185–186 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.33 (brs, 1H), 7.43 (d, J = 1.4 Hz, 1H), 7.23 (d, J = 8.8 Hz, 1H), 7.05 (d, J = 2.3 Hz, 1H), 6.84 (dd, J = 8.8, 2.5 Hz, 1H), 6.66 (d, J = 1.3 Hz, 1H), 6.59 (d, J = 3.4 Hz, 1H), 6.49–6.47 (m, 1H), 3.85 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.6, 147.8, 141.7, 131.3, 129.9, 129.3, 112.8, 111.8, 111.6, 105.3, 102.2, 98.7, 55.8; **HRMS** (ESI) Calcd for $C_{13}H_{11}NO_2$ $[M + H]^+$ 214.0868, found 214.0872.

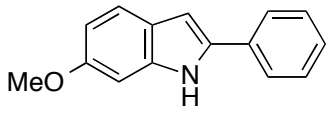


2-(Benzofuran-2-yl)-5-methoxy-1*H*-indole (2w): White solid (84% yield, eluent = hexane/EtOAc (92:8)); Mp = 185–186 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.54 (brs, 1H), 7.56 (d, J = 7.2 Hz, 1H), 7.50 (d, J = 7.7 Hz, 1H), 7.30–7.21 (m, 3H), 7.08 (d, J = 2.2 Hz, 1H), 6.93–6.88 (m, 3H), 3.86 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.7, 154.5, 149.4, 131.7, 129.2, 129.2, 129.1, 124.4, 123.3, 120.9, 113.7, 111.9, 111.0, 102.2, 101.3, 101.0, 55.8; **HRMS** (ESI) Calcd for $C_{17}H_{13}NO_2$ $[M + H]^+$ 264.1025, found 264.1025.

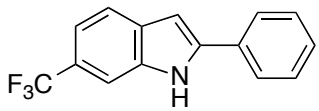


5-Methoxy-2-(pyridin-4-yl)-1*H*-indole (2x): Yellow solid (80% yield, eluent =

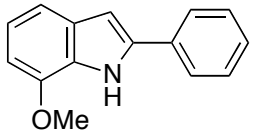
hexane/EtOAc (20:80)); Mp = 207–208 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.68 (brs, 1H), 8.64 (d, *J* = 4.7 Hz, 2H), 7.51 (d, *J* = 4.6 Hz, 2H), 7.32 (d, *J* = 8.9 Hz, 1H), 7.10 (d, *J* = 2.3 Hz, 1H), 6.96 (d, *J* = 1.5 Hz, 1H), 6.92 (dd, *J* =8.8, 2.4 Hz, 1H), 3.87 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.8, 150.4, 139.5, 135.2, 132.6, 129.3, 119.0, 114.5, 112.1, 102.6, 102.3, 55.8; **HRMS** (ESI) Calcd for $C_{14}H_{12}N_2O$ $[M + H]^+$ 225.1028, found 225.1031.



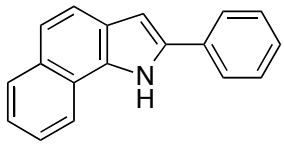
6-Methoxy-2-phenyl-1*H*-indole (2y): White solid (74% yield, eluent = hexane/EtOAc (92:8)); Mp = 177–178 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.22 (brs, 1H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.49 (d, *J* = 8.7 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 1H), 6.89 (s, 1H), 6.79 (dd, *J* = 8.6, 1.9 Hz, 1H), 6.75 (s, 1H), 3.85 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.7, 137.7, 136.8, 132.6, 129.0, 127.3, 124.7, 123.6, 121.3, 110.2, 99.9, 94.5, 55.7; **HRMS** (ESI) Calcd for $C_{15}H_{13}NO$ $[M + H]^+$ 224.1075, found 224.1085. The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[22]



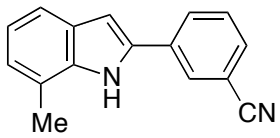
6-Trifluoromethyl-2-phenyl-1*H*-indole (2z): White solid (72% yield, eluent = hexane/EtOAc (95:5)); Mp = 171–172 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.52 (brs, 1H), 7.71–7.68 (m, 4H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.41–7.36 (m, 2H), 6.87 (d, *J* = 1.5 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 140.6, 135.6, 131.6, 129.2, 128.5, 125.2 (q, $^1J_{C\text{-}F}$ = 271.0 Hz), 125.4, 124.2 (q, $^2J_{C\text{-}F}$ = 31.9 Hz), 120.9, 117.1 (q, $^3J_{C\text{-}F}$ = 3.6 Hz), 117.0, 108.4 (q, $^3J_{C\text{-}F}$ = 4.0 Hz), 100.1; **HRMS** (ESI) Calcd for $C_{15}H_{10}F_3N$ $[M + H]^+$ 262.0844, found 262.0847. The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[22]



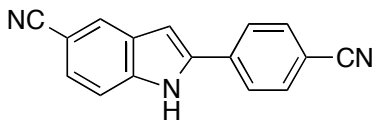
7-Methoxy-2-phenyl-1*H*-indole (2aa): White solid (67% yield, eluent = hexane/EtOAc (92:8)); Mp = 94–95 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.58 (brs, 1H), 7.64 (dd, *J* = 8.4, 1.0 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.31–7.27 (com, 1H), 7.23 (d, *J* = 8.1 Hz, 1H), 7.03 (t, *J* = 7.7 Hz, 1H), 6.77 (d, *J* = 2.3 Hz, 1H), 6.63 (d, *J* = 7.7 Hz, 1H), 3.95 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.9, 137.5, 132.4, 130.4, 128.9, 127.5, 127.2, 125.1, 120.5, 113.3, 102.1, 100.2, 55.3; **HRMS** (ESI) Calcd for $C_{15}H_{13}NO$ $[M + H]^+$ 224.1075, found 224.1085. The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[27]



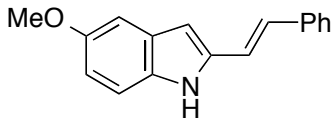
2-Phenylbenzo[*g*]indole (2ab): White solid (88% yield, eluent = hexane/EtOAc (92:8)); Mp = 171-172 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.98 (brs, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.71–7.68 (m, 3H), 7.54–7.50 (m, 2H), 7.47–7.40 (m, 3H), 7.31 (td, *J* = 7.4, 1.0 Hz, 1H), 6.93 (d, *J* = 2.3 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 136.3, 132.5, 131.4, 130.6, 129.2, 129.1, 127.5, 125.6, 125.3, 125.0, 124.0, 121.6, 121.2, 120.6, 119.4, 101.7; **HRMS** (ESI) Calcd for $C_{18}H_{13}N$ $[M + H]^+$ 244.1126, found 244.1122. The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[28]



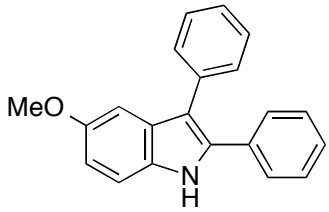
3-(7-Methyl-1*H*-indol-2-yl)benzonitrile (2ac): White solid (87% yield, eluent = hexane/EtOAc (92:8)); Mp = 193–194 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.37 (brs, 1H), 8.00 (s, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.60–7.50 (m, 3H), 7.10–7.05 (m, 2H), 6.91 (d, *J* = 1.9 Hz, 1H), 2.58 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 136.9, 135.1, 133.9, 130.6, 129.9, 129.4, 128.5, 128.4, 123.9, 120.9, 120.5, 118.8, 118.7, 113.2, 102.2, 16.8; **HRMS** (ESI) Calcd for $C_{16}H_{12}N_2$ $[M + H]^+$ 233.1079, found 233.1075.



2-(4-Cyanophenyl)-1*H*-indole-5-carbonitrile (2ad): White solid (74% yield, eluent = hexane/EtOAc (90:10)); Mp = 306–307 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ 12.38 (s, 1H), 8.17 (s, 1H), 8.12 (d, J = 8.1 Hz, 2H), 8.00 (d, J = 8.2 Hz, 2H), 7.63 (d, J = 8.7 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.31 (s, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ 138.7, 137.7, 135.0, 132.5, 127.5, 125.8, 125.3, 124.7, 120.0, 118.3, 112.3, 109.6, 101.5, 101.5; **HRMS** (ESI) Calcd for $C_{16}H_9N_3$ $[M + H]^+$ 244.0875, found 244.0882.

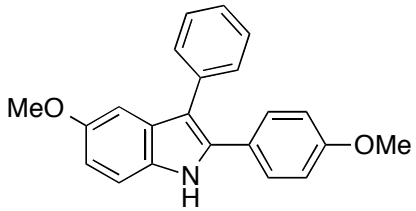


(*E*)-5-Methoxy-2-styryl-1*H*-indole (2ae): Light brown solid (78% yield, eluent = hexane/EtOAc (92:8)); Mp = 150–151 °C; **^{1}H NMR** (400 MHz, acetone-d_6): δ 10.37 (s, 1H), 7.55 (d, J = 8.4 Hz, 2H), 7.34 (t, J = 8.0 Hz, 2H), 7.22–7.29 (com, 3H), 7.15 (d, J = 16.8 Hz, 1H), 7.00 (d, J = 2.4 Hz, 1H), 6.77 (dd, J = 8.8, 2.4 Hz, 1H), 6.55 (d, J = 1.6 Hz, 1H), 3.78 (s, 3H); **^{13}C NMR** (100 MHz, acetone-d_6): δ 154.9, 138.1, 138.0, 133.4, 130.1, 129.3, 127.9, 127.3, 126.7, 120.1, 113.3, 112.1, 103.7, 102.2, 55.5; **HRMS** (ESI) Calcd for $C_{17}H_{15}NO$ $[M + H]^+$ 250.1232, found 250.1224.

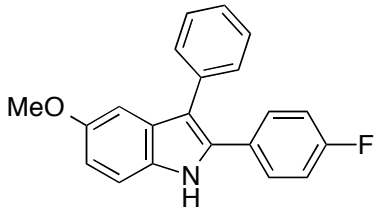


5-Methoxy-2,3-diphenyl-1*H*-indole (2af): The reaction was performed with the Pd/Cu system; White solid (86% yield, eluent = hexane/EtOAc (92:8)); Mp = 159–160 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.13 (brs, 1H), 7.45–7.38 (m, 6H), 7.34–7.28 (m, 5H), 7.12 (d, J = 2.1 Hz, 1H), 6.91 (dd, J = 8.7, 2.4 Hz, 1H), 3.83 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.8, 135.2, 135.0, 132.8, 131.1, 130.1, 129.2, 128.7, 128.6, 128.1, 127.6, 126.2, 115.0, 113.1, 111.7, 101.3, 56.0; **HRMS** (ESI) Calcd for $C_{21}H_{17}NO$ $[M + H]^+$ 300.1388, found

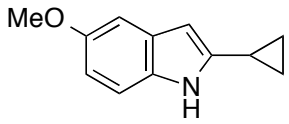
300.1386.



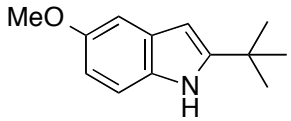
5-Methoxy-2-(4-methoxyphenyl)-3-phenyl-1*H*-indole (2ag): The reaction was performed with the Pd/Cu system; White solid (82% yield, eluent = hexane/EtOAc (92:8)); Mp = 58–59 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.46–7.38 (com, 4H), 7.34–7.29 (com, 4H), 7.14 (d, *J* = 1.8 Hz, 1H), 6.90 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H), 3.1 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.1, 154.7, 135.4, 135.0, 130.9, 130.0, 129.3, 129.1, 128.5, 126.0, 125.2, 114.1, 114.0, 112.5, 111.5, 101.1, 55.9, 55.2; **HRMS** (ESI) Calcd for $C_{22}H_{19}NO_2$ $[M + H]^+$ 330.1494, found 330.1491.



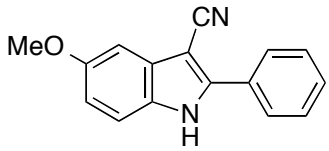
5-Methoxy-2-(4-fluorophenyl)-3-phenyl-1*H*-indole (2ah): The reaction was performed with the Pd/Cu system; White solid (74% yield, eluent = hexane/EtOAc (92:8)); Mp = 140-141 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.40–7.37 (com, 4H), 7.33–7.26 (com, 4H), 7.10 (d, *J* = 2.4 Hz, 1H), 6.97 (t, *J* = 8.8 Hz, 2H), 6.89 (dd, *J* = 8.7, 2.5 Hz, 1H), 3.80 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.3 (d, $^{1}J_{C\text{-}F}$ = 248 Hz), 154.9, 135.0, 134.1, 131.1, 130.1, 129.8 (d, $^{3}J_{C\text{-}F}$ = 7.9 Hz), 129.1, 128.8 (d, $^{4}J_{C\text{-}F}$ = 3.2 Hz), 128.7, 126.3, 115.7 (d, $^{2}J_{C\text{-}F}$ = 21.6 Hz), 115.0, 113.1, 111.8, 101.3, 56.0; **HRMS** (ESI) Calcd for $C_{21}H_{16}FNO$ $[M + H]^+$ 318.1294, found 318.1292.



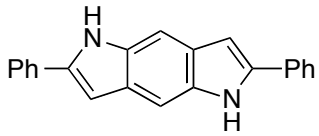
2-Cyclopropyl-5-methoxy-1*H*-indole (2ai): Yellow oil (84% yield, eluent = hexane/EtOAc (92:8)); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.85 (brs, 1H), 7.15 (d, *J* = 8.7 Hz, 1H), 7.00 (d, *J* = 2.4 Hz, 1H), 6.78 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.09 (d, *J* = 2.0 Hz, 1H), 3.85 (s, 3H), 1.97–1.90 (m, 1H), 0.99–0.94 (m, 2H), 0.80–0.75 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.2, 142.6, 130.9, 129.2, 110.9, 110.8, 101.9, 97.6, 55.9, 9.0, 7.4; **HRMS** (ESI) Calcd for $C_{12}H_{13}NO$ $[M + H]^+$ 188.1075, found 188.1082.



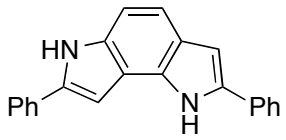
2-(*tert*-Butyl)-5-methoxy-1*H*-indole (2aj): White solid (61% yield, eluent = hexane/EtOAc (92:8)); Mp = 104–105 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.85 (brs, 1H), 7.18 (d, *J* = 8.8 Hz, 1H), 7.02 (d, *J* = 2.4 Hz, 1H), 6.78 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.19 (d, *J* = 1.9 Hz, 1H), 3.83 (s, 3H), 1.37 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.1, 149.7, 130.9, 129.0, 111.1, 111.0, 102.2, 96.9, 56.0, 31.9, 30.3; **HRMS** (ESI) Calcd for $C_{13}H_{17}NO$ $[M + H]^+$ 204.1388, found 204.1391. The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[29]



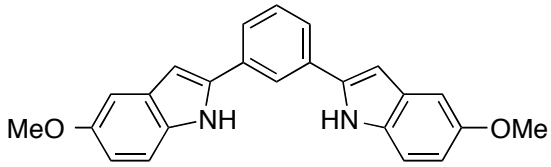
5-Methoxy-2-phenyl-1*H*-indole-3-carbonitrile (2ak): The reaction was performed according to the general procedure with enamine as the starting material; White solid (85% yield, eluent = hexane/EtOAc (90:10)); Mp = 251–252 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ 12.49 (s, 1H), 7.97 (d, *J* = 7.9 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.11 (d, *J* = 2.4 Hz, 1H), 6.96 (dd, *J* = 8.7, 1.3 Hz, 1H), 3.85 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ 156.0, 145.1, 130.9, 130.3, 130.0, 129.8, 129.7, 127.3, 117.7, 114.8, 114.1, 100.1, 81.7, 55.9; **HRMS** (ESI) Calcd for $C_{16}H_{12}ON_2$ $[M + H]^+$ 224.1075, found 224.1069.



2,6-Diphenyl-1,5-dihydropyrrolo[2,3-*f*]indole (2al): The reaction was performed using 20 mol% of $Pd(OAc)_2$ and 4 equiv of Bu_4NBr; Light brown solid (29% yield, eluent = hexane/EtOAc (90:10)); Mp = 242–243 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ 11.45 (s, 2H), 7.88 (d, J = 7.32 Hz, 4H), 7.47 (t, J = 7.7 Hz, 4H), 7.28 (t, J = 7.7 Hz, 2H), 7.22 (s, 2H), 7.11 (d, J = 2.0 Hz, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ 135.0, 132.5, 131.6, 128.6, 126.2, 124.1, 120.3, 106.9, 97.4; **HRMS** (ESI) Calcd for $C_{22}H_{16}N_2$ $[M + H]^+$ 309.1392, found 309.1397.

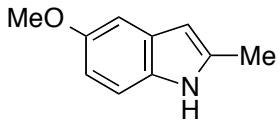


2,7-Diphenyl-1,6-dihydropyrrolo[2,3-*e*]indole (2am): The reaction was performed using 20 mol% of $Pd(OAc)_2$ and 4 equiv of Bu_4NBr; White solid (50% yield, eluent = hexane/EtOAc (90:10)); Mp = 226–227 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.62 (s, 1H), 8.48 (s, 1H), 7.70–7.67 (com, 4H), 7.44–7.42 (com, 5H), 7.32–7.19 (com, 3H), 6.99 (s, 1H), 6.92 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 136.0, 134.7, 134.2, 133.0, 132.6, 129.6, 129.1, 129.0, 127.3, 126.8, 124.8, 124.6, 122.5, 116.2, 114.6, 105.7, 101.3, 96.1; **HRMS** (ESI) Calcd for $C_{22}H_{16}N_2$ $[M + H]^+$ 309.1392, found 309.1390.

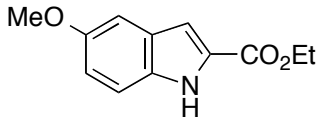


1,3-Bis(5-Methoxy-1*H*-indol-2-yl)benzene (2an): The reaction was performed using 20 mol % of $Pd(OAc)_2$ and 4 equiv of Bu_4NBr; Light brown solid (90% yield, eluent = hexane/EtOAc (90:10)); Mp = 223–224 °C; **^{1}H NMR** (400 MHz, acetone-d_6): δ 10.57 (s,

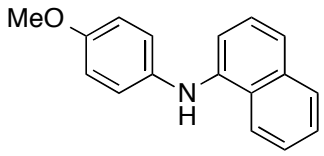
2H), 8.32 (s, 1H), 7.74 (dd, *J* = 7.8, 1.3 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.09 (d, *J* = 2.0 Hz, 2H), 6.92 (dd, *J* = 1.4 Hz, 2H), 6.80 (dd, *J* = 8.7, 2.3 Hz, 2H), 3.80 (s, 6H); **^{13}C NMR** (100 MHz, acetone-d_6): δ 155.1, 138.9, 134.1, 133.3, 130.4, 130.1, 124.4, 122.1, 113.0, 112.4, 102.4, 100.1, 55.5; **HRMS** (ESI) Calcd for $C_{24}H_{20}N_2O_2$ $[M + H]^+$ 369.1603, found 369.1604.



5-Methoxy-2-methyl-1*H*-indole (2ao): The reaction was performed using 5 equiv of acetone (HPLC grade), 20 mol % of $Pd(OAc)_2$ and 3 equiv of $Cu(OAc)_2$; Light yellow solid (55% yield, eluent = hexane/EtOAc (92:8)); Mp = 85–86 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (brs, 1H), 7.15 (dt, *J* = 8.7, 0.7 Hz, 1H), 6.99 (d, *J* = 2.4 Hz, 1H), 6.76 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.14–6.13 (m, 1H), 3.83 (s, 3H), 2.41 (d, *J* = 0.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.2, 136.0, 131.2, 129.6, 110.9, 110.7, 101.9, 100.4, 56.0, 13.9; **HRMS** (ESI) Calcd for $C_{10}H_{11}NO$ $[M + H]^+$ 162.0919, found 162.0923. The ^{1}H and ^{13}C NMR spectra showed good agreement with the literature data.[30]



Ethyl 5-methoxy-1*H*-indole-2-carboxylate (2ap): The reaction was performed using 5 equiv of ethyl pyruvate, 20 mol % of $Pd(OAc)_2$ and 3 equiv of $Cu(OAc)_2$; White solid (41% yield, eluent = hexane/EtOAc (90:10)); Mp = 156–157 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.86 (brs, 1H), 7.31 (d, *J* = 9.0 Hz, 1H), 7.15 (d, *J* = 1.9 Hz, 1H), 7.08 (d, *J* = 2.4 Hz, 1H), 7.00 (dd, *J* = 8.9, 2.4 Hz, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 3.85 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.9, 154.7, 132.1, 127.9, 127.8, 117.0, 112.7, 108.2, 102.6, 61.0, 55.7, 14.4; **HRMS** (ESI) Calcd for $C_{12}H_{13}NO_3$ $[M + H]^+$ 220.0974, found 220.0972.



***N*-(4-methoxyphenyl)naphthalen-1-amine (3, Scheme 4b):** Light brown solid (78% yield, eluent = hexane/EtOAc (98:2)); Mp = 111–112 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.02–8.00 (m, 1H), 7.87–7.83 (m, 1H), 7.52–7.47 (m, 2H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.11 (d, *J* = 7.0 Hz, 1H), 7.09–7.05 (m, 2H), 6.91–6.87 (m, 2H), 5.87 (brs, 1H), 3.82 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.1, 140.9, 136.9, 134.6, 128.6, 126.2, 126.0, 125.9, 125.4, 121.9, 121.1, 120.9, 114.8, 111.7, 55.6; **HRMS** (ESI) Calcd for $C_{17}H_{15}NO$ $[M + H]^+$ 250.1232, found 250.1233. The ^{1}H and ^{13}C NMR spectra showed good agreement with the literature data.[31]

Kinetic Isotope Effect Experiments

(A) Intramolecular Competition Reaction (Scheme 3a)

The reaction of 2-deuterio-(*E*)-*N*-(1-(4-chlorophenyl)ethylidene)aniline (**1aq**-*d*, 0.2 mmol) was performed under the standard conditions for 12 h, followed by the standard workup and purification to afford a mixture of **2aq**-*d* and **2aq** in 84% yield, respectively. ^{1}H NMR analysis of the mixture indicated a KIE value of 5.2 (see the attached spectrum).

(B) Intermolecular Competition (Scheme 3b)

A mixture of **1aq** and **1aq**-d_5 (0.2 mmol each) was subjected to the standard conditions for 3 h. Purification of the crude product on silica gel afforded a mixture of **2aq** and **2aq**-d_4 in 22% combined yield, the ratio of which was determined to be 1.7:1 by ^{1}H NMR analysis (see the attached spectrum).

(C) Individual Reactions of 1aq and 1aq-d_5 (Scheme 3c)

Parallel individual reactions of **1aq** and **1aq**-d_5 under the standard conditions were monitored by GC analysis of periodically taken aliquots (0–360 min, Figure S1a). Comparison of the reaction progress in the early stage (0–20 min) indicated a kinetic isotope effect of 1.6 ± 0.4 (Figure S1b).

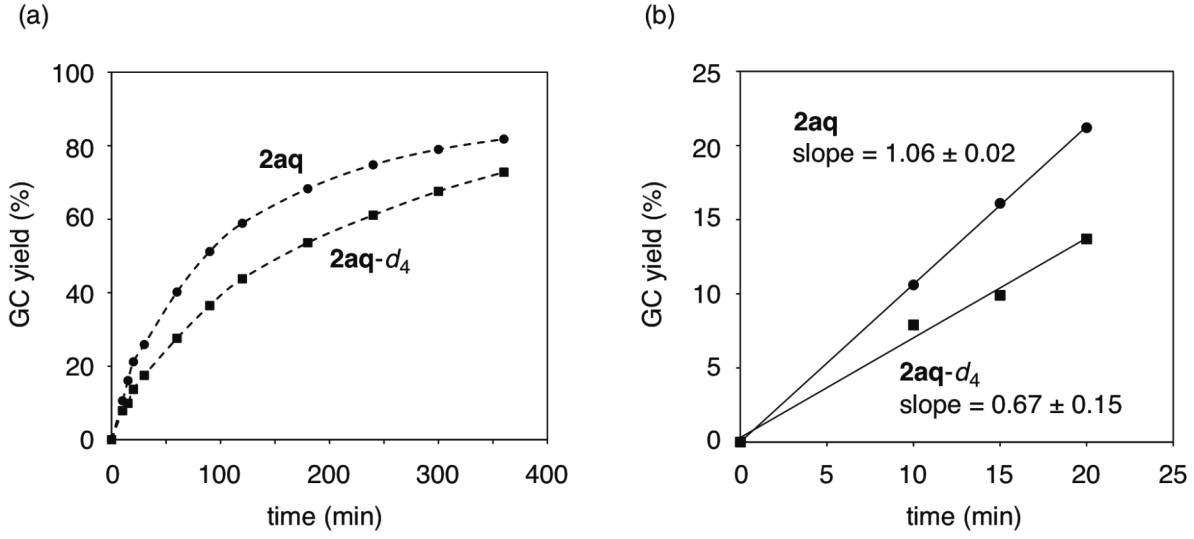


Figure S1. Progress of indiviual reactions of **1aq** and **1aq**-d_5 as monitored by GC analysis.

Complete Reference 17

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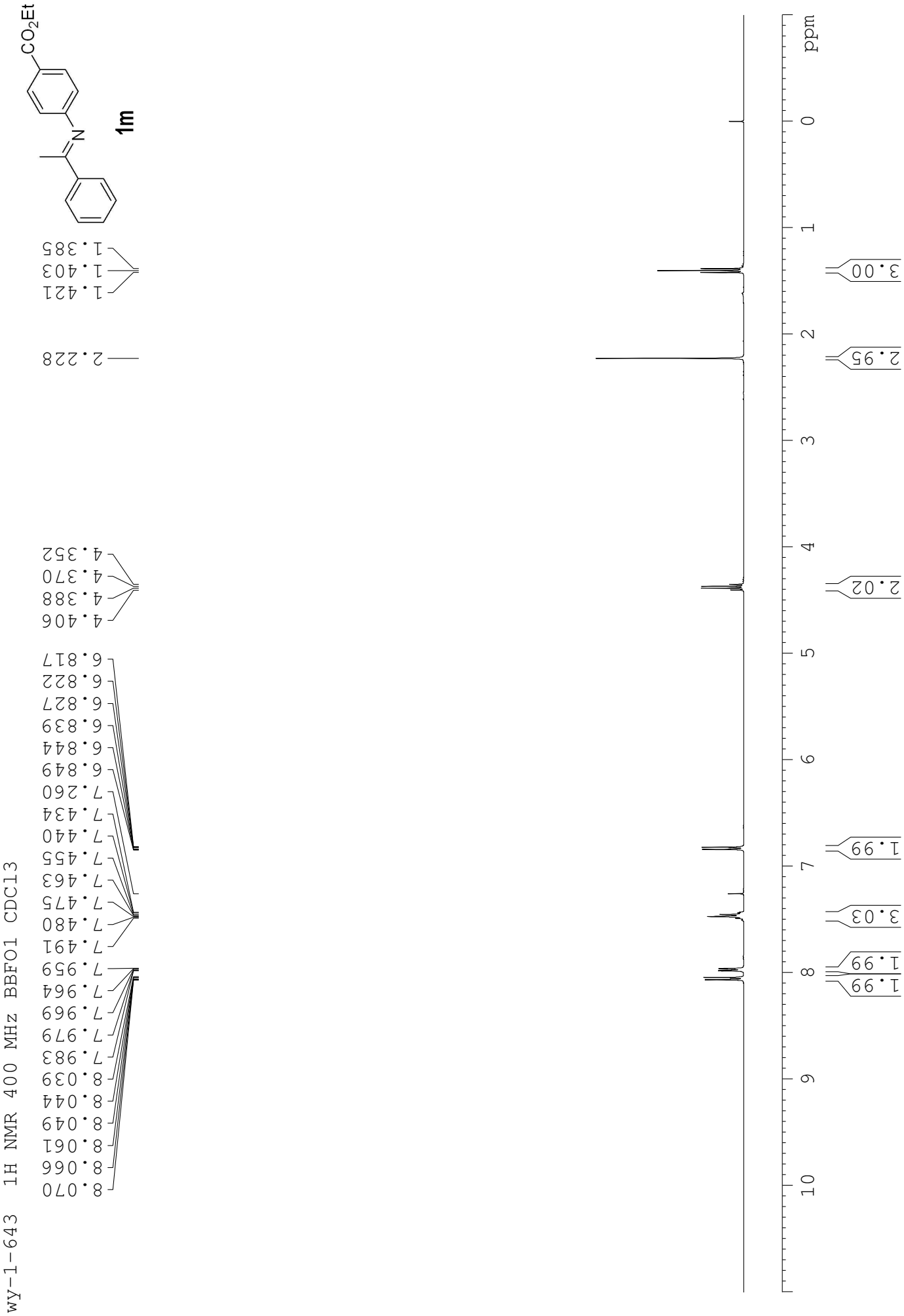
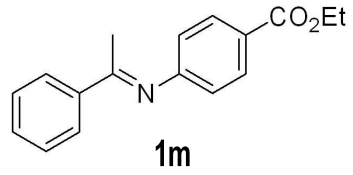
1H and 13C NMR Spectra of New Compounds

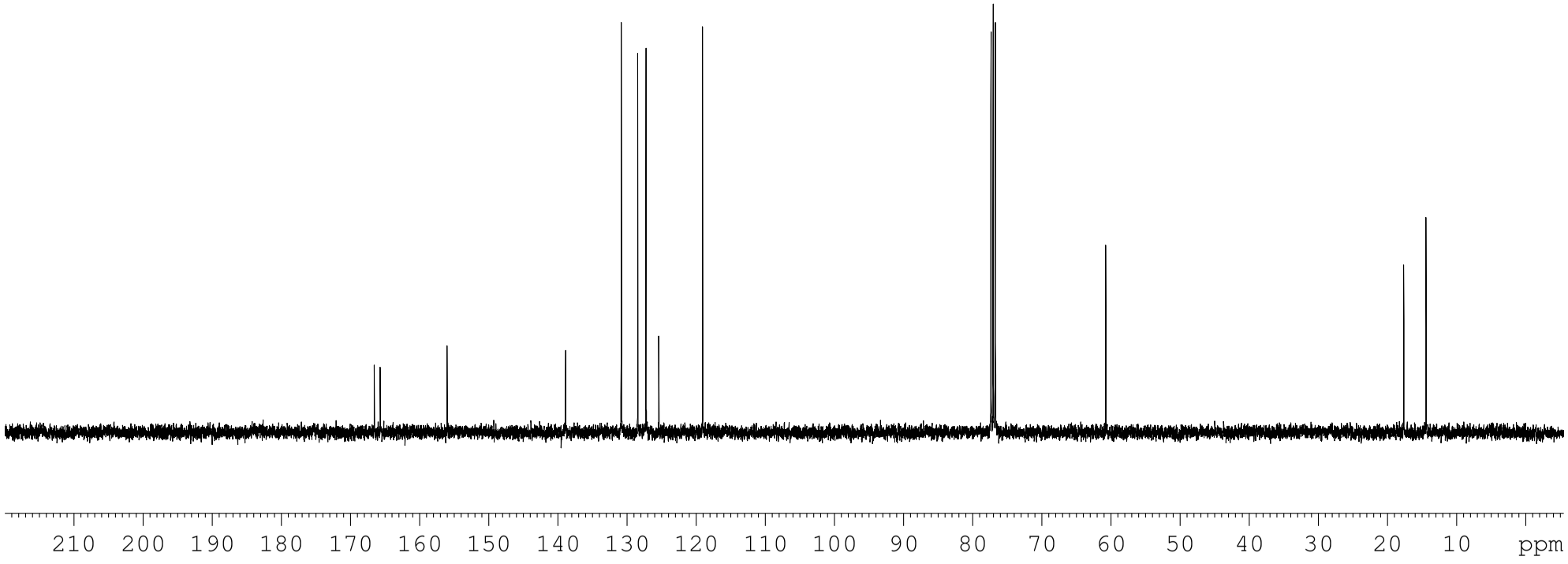


wy-1-643 13C NMR 400 MHz BBFO1 CDCl3

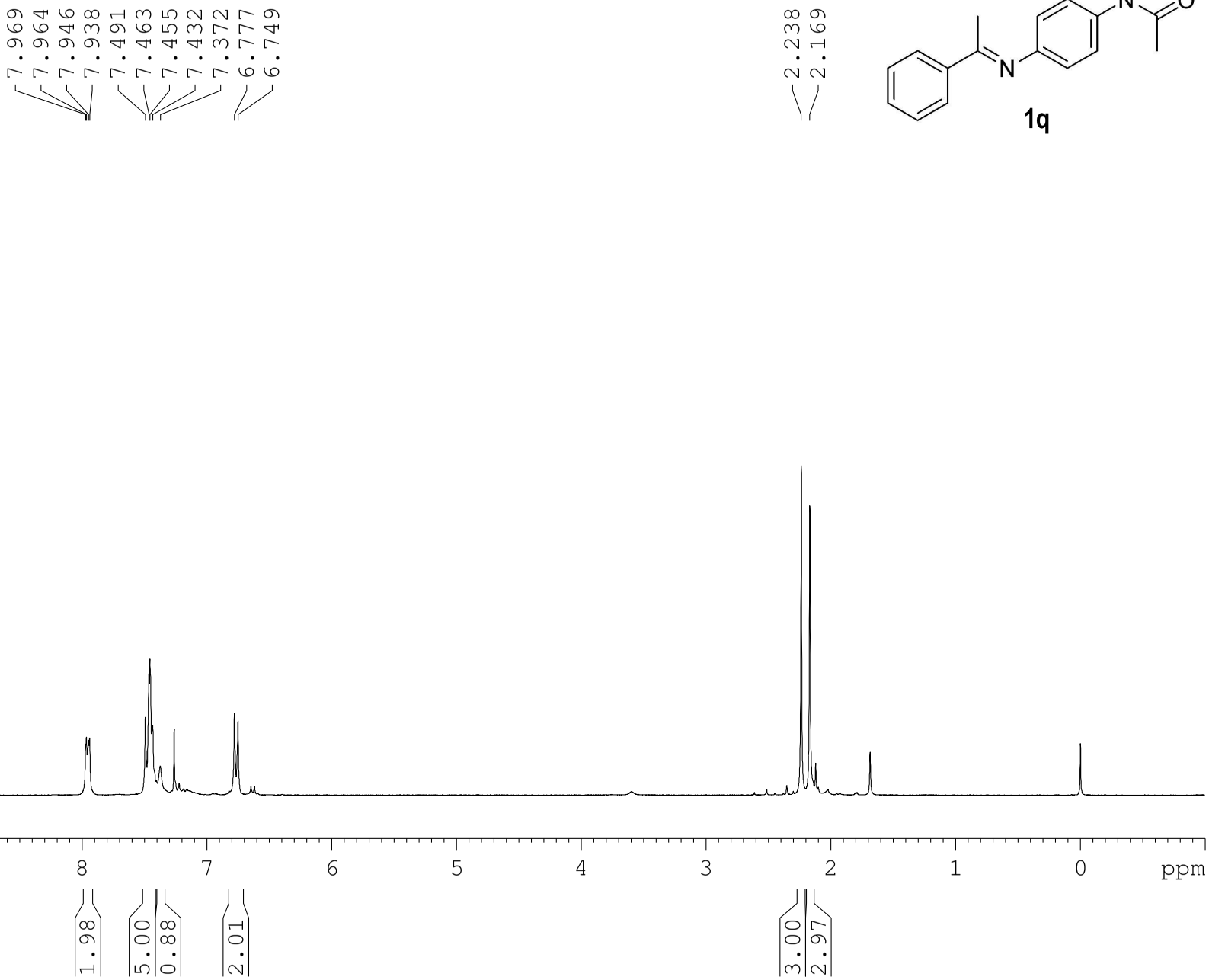


1m

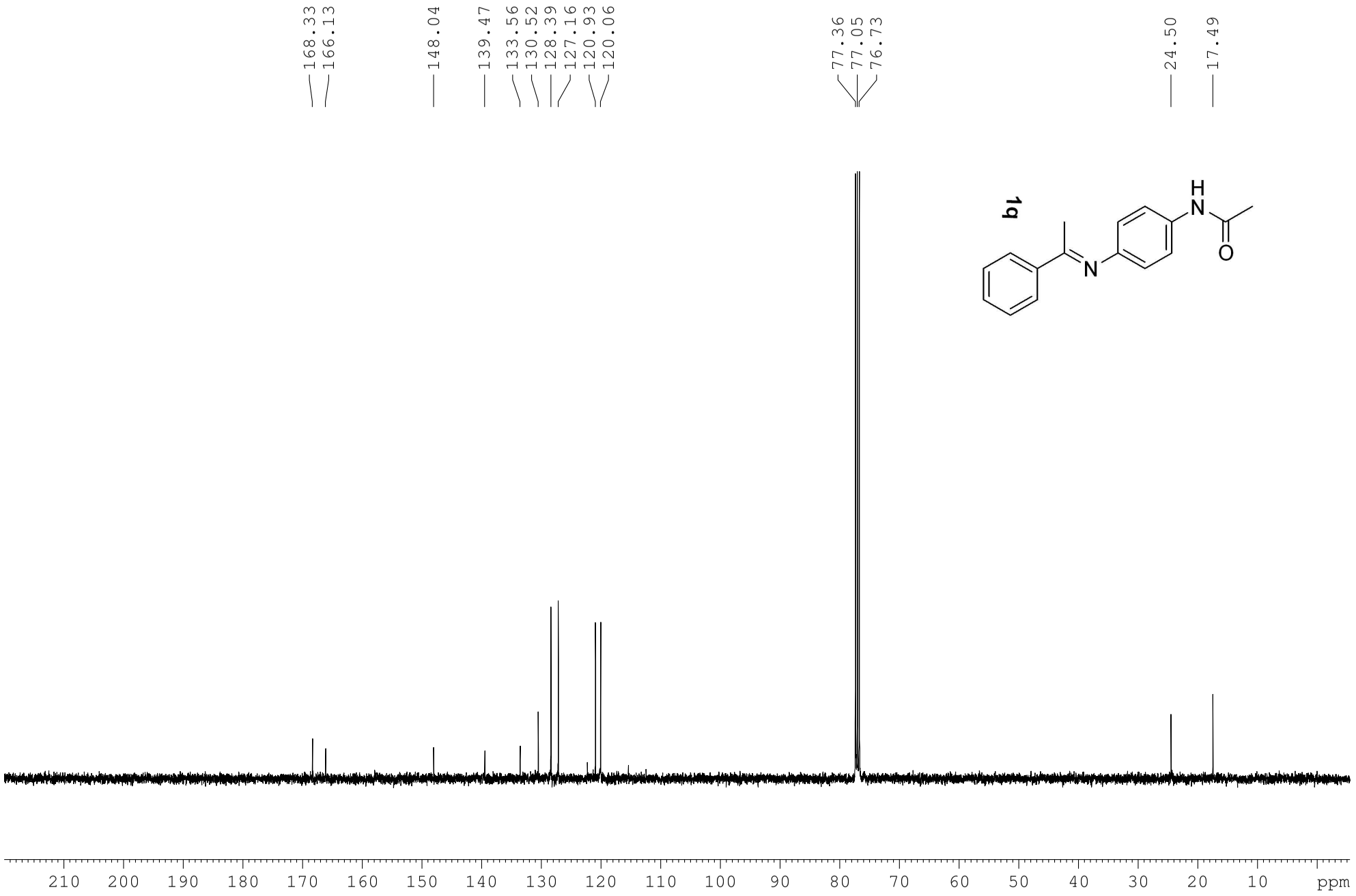
166.56
165.71
156.03
138.88
130.85
130.83
128.46
127.26
125.40
119.07
77.35
77.03
76.72
60.74
17.63
14.41



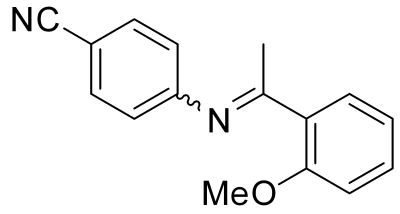
wy-2-76, 1HNMR, AV300, 1 cdcl3



wy-NHAc imine, 13C NMR BBFO1 400Hz in CDCl3



IBD-2-34, BBFO2 400MHz, 1H NMR, CDCl3

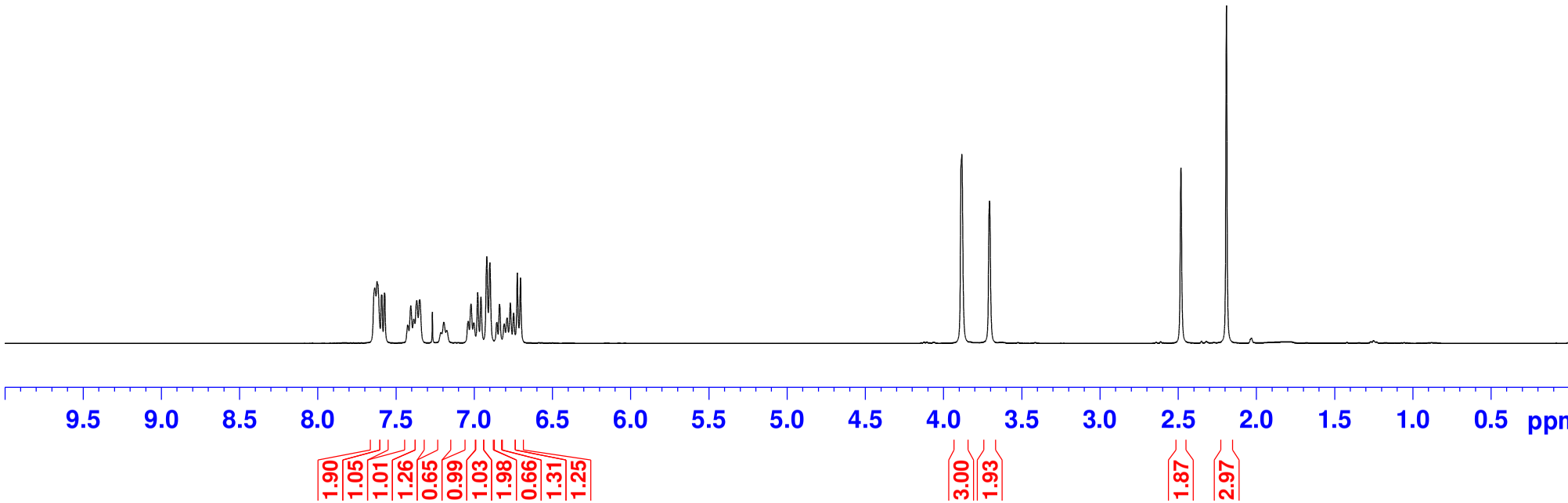


1s

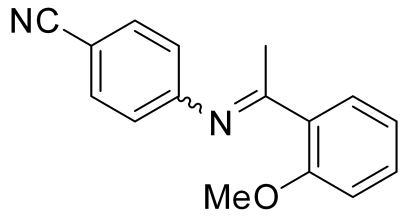
7.636
7.621
7.593
7.574
7.426
7.405
7.386
7.367
7.347
7.267
7.213
7.194
7.176
7.039
7.020
7.002
6.977
6.957
6.919
6.899
6.855
6.838
6.808
6.790
6.769
6.748
6.724
6.704

3.882
3.705

2.483
2.192



IBD-2-34-13C, BBFO2 400MHz, 1H NMR, CDCl3



1s

170.28
169.89
157.43
155.31
155.23
154.98
133.18
132.32
131.24
130.06
130.01
129.35
127.57
127.21
120.83
120.71
120.31
120.03
119.28
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110.61
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76.69
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55.03
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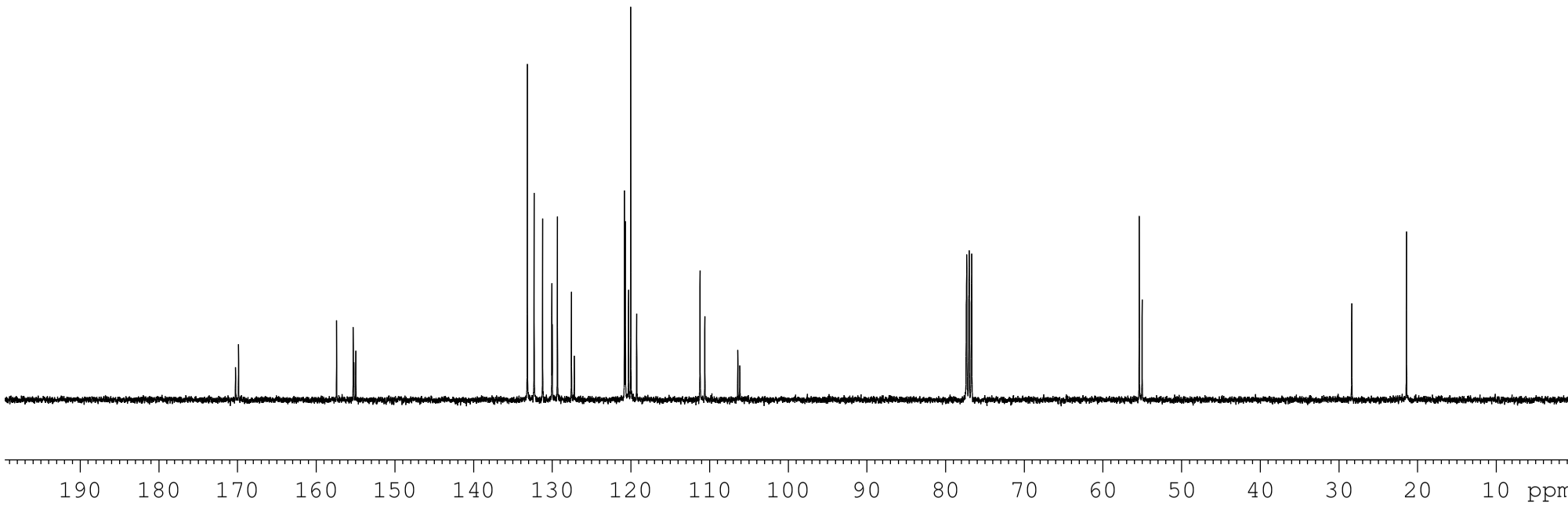
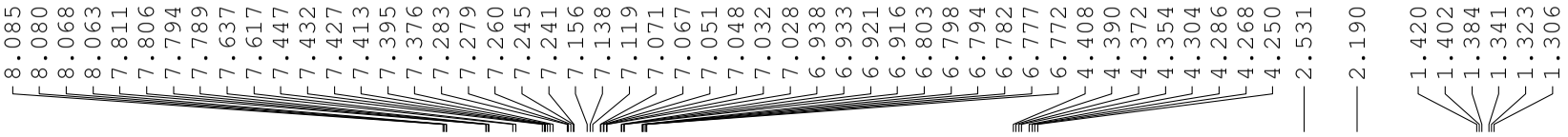
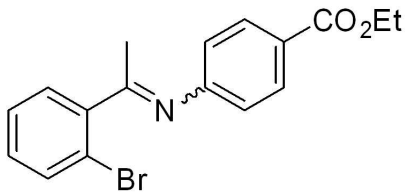
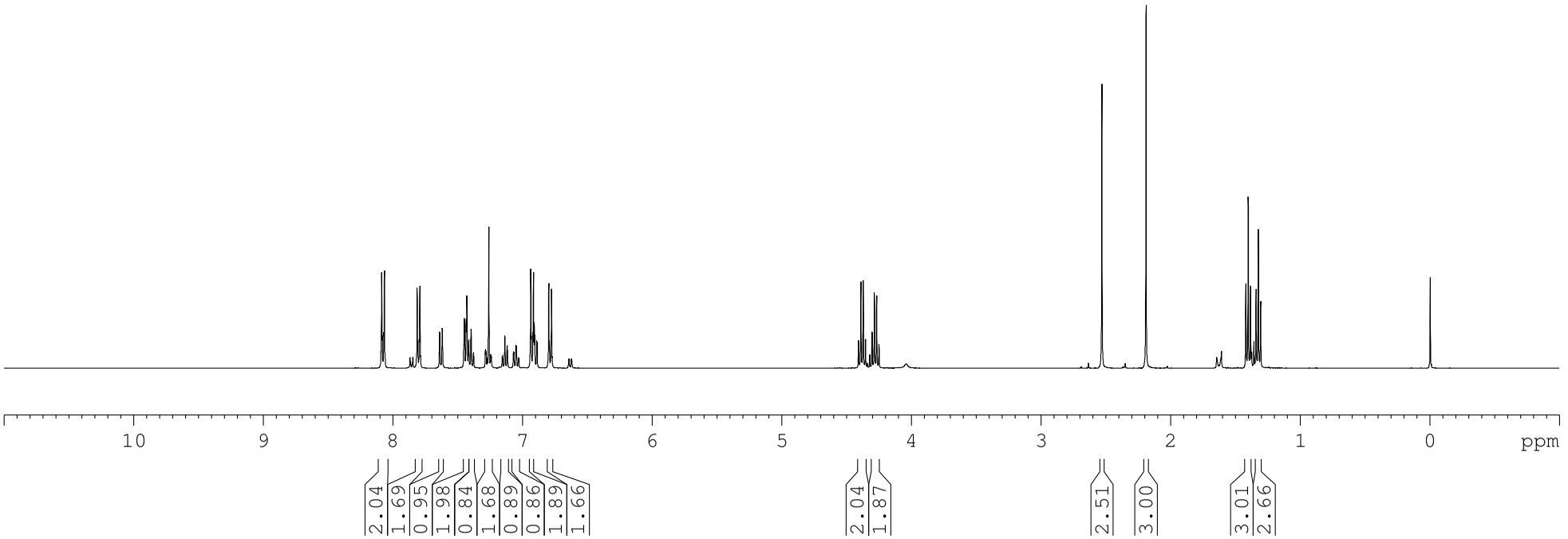
21.43



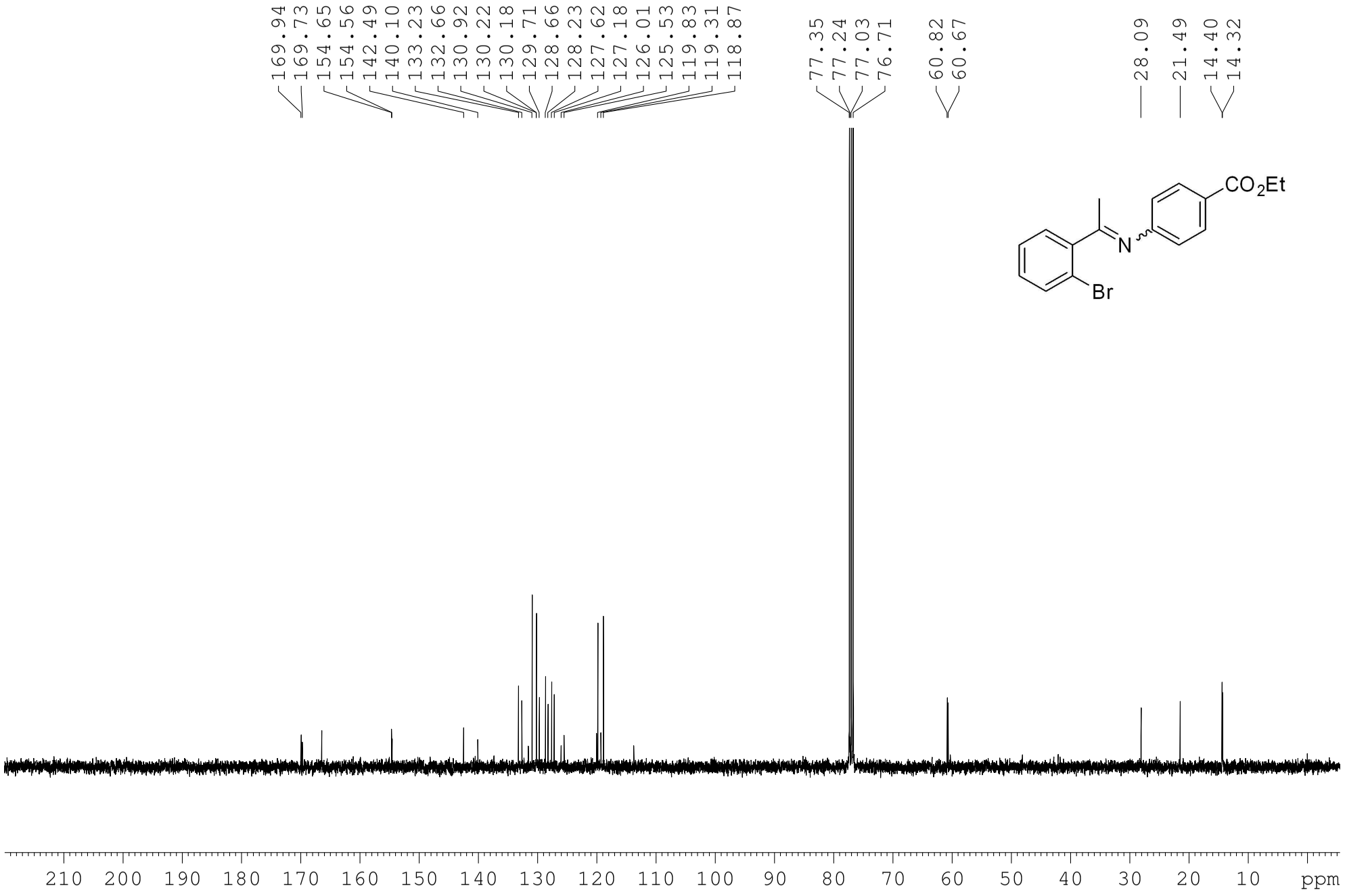
wy-2-27, 1H NMR BBOF01, 400Hz, CDCl3



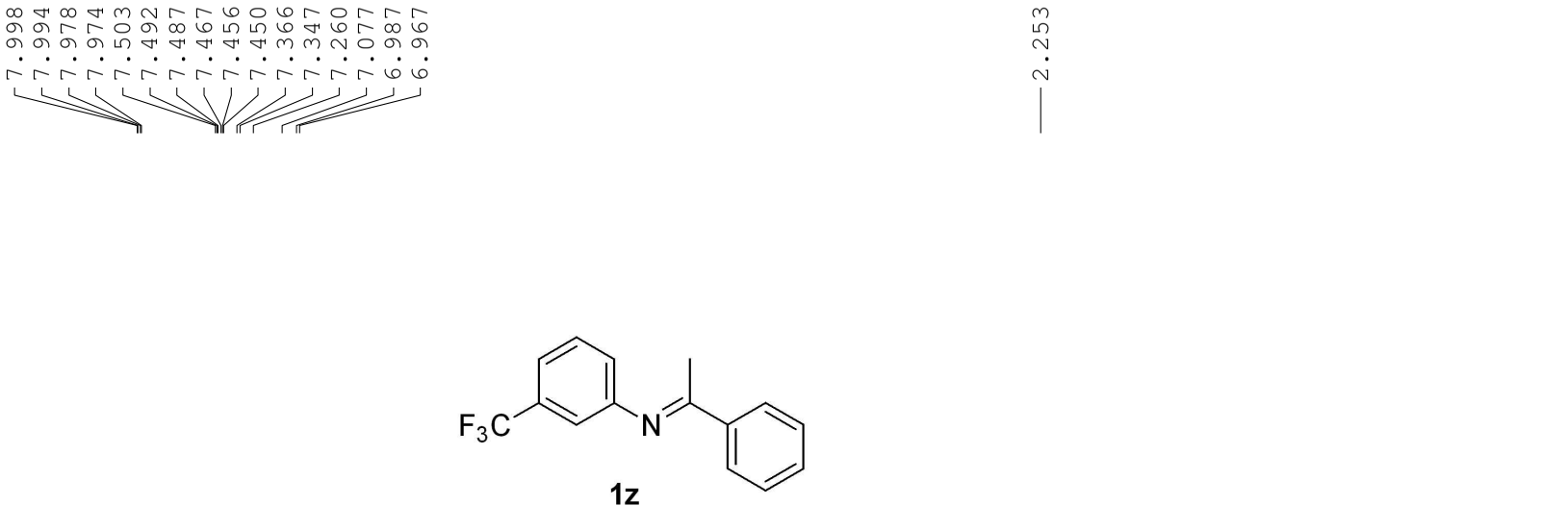




wy-2-27, 13C NMR BBOF01, 400Hz, CDCl3



meta-CF3 imine, 1H NMR BBFO2 400MHz CDCl3



meta-CF3 imine, 13C NMR BBFO2 400MHz CDCl3

166.64
152.09
138.96
131.62
131.30
130.90
129.54
128.49
127.26
125.49
122.76
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119.97
119.93
119.89
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116.35
116.31
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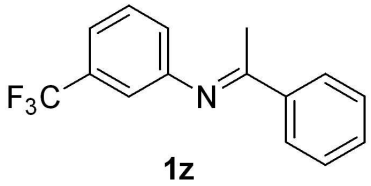
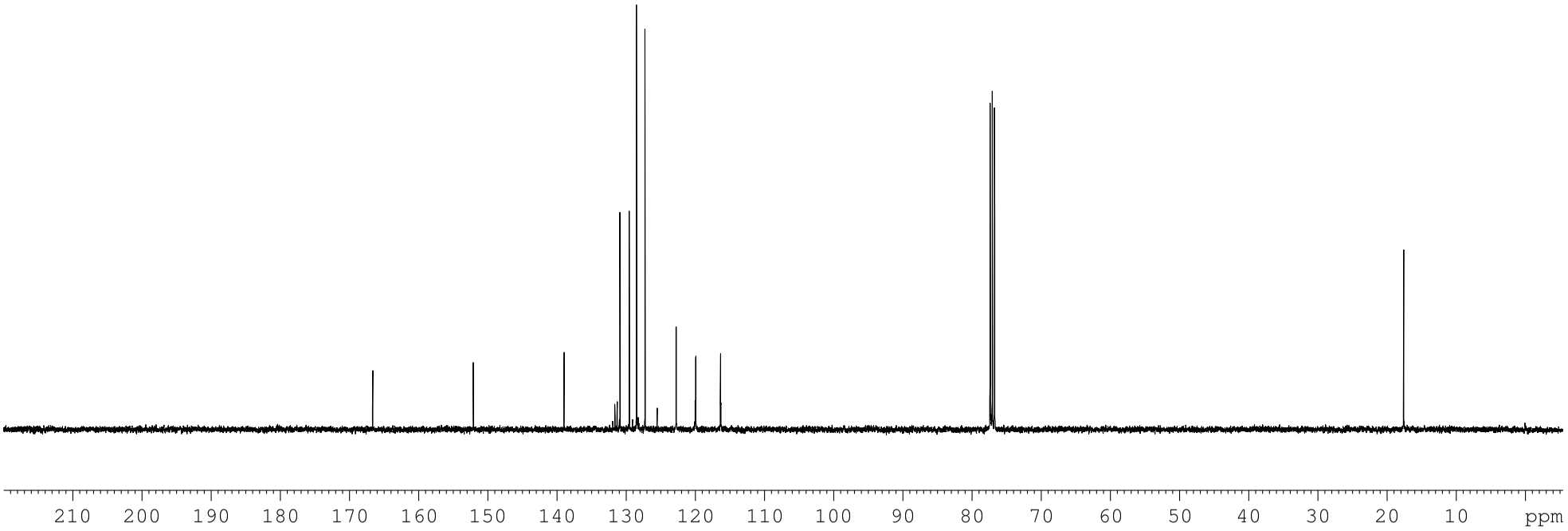
77.04
76.73
17.57



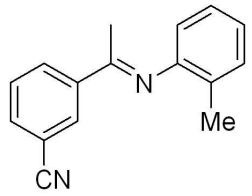
1z



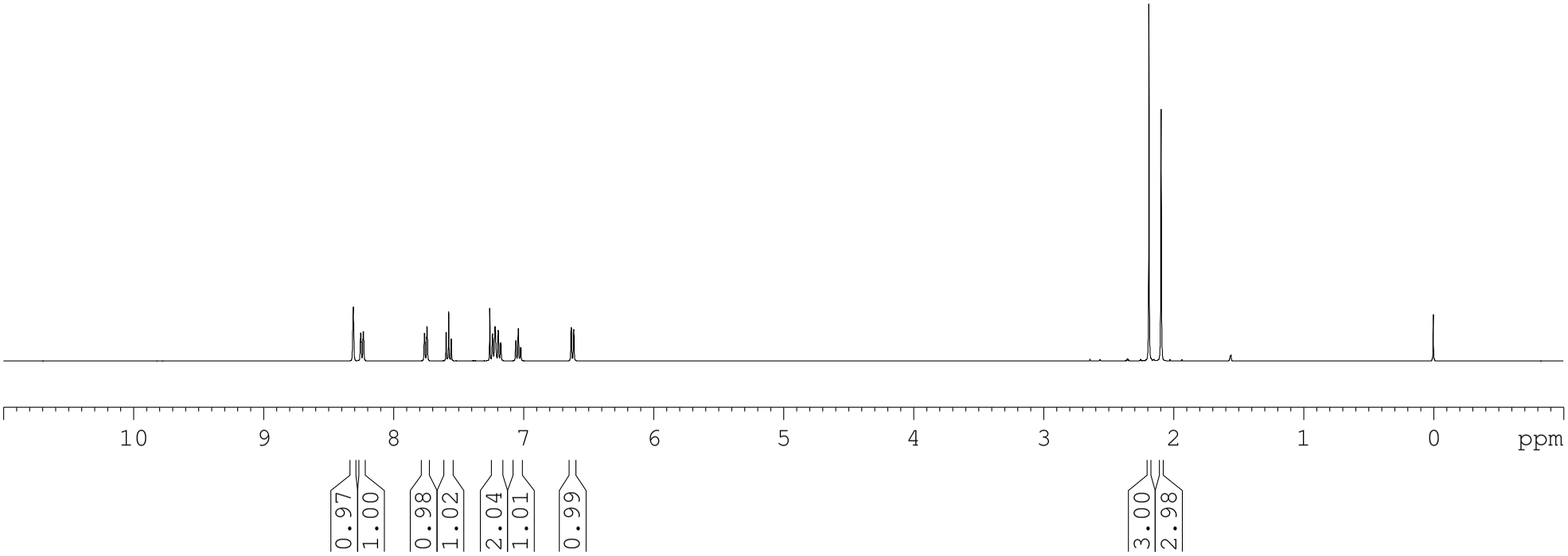
wy-2-14-2nd, 1H NMR 400 MHz, BBFO2, CDCl3

8.310
8.253
8.233
7.762
7.743
7.596
7.576
7.557
7.239
7.220
7.195
7.176
7.060
7.058
7.042
7.040
7.023
7.021
6.633
6.614

2.189
2.095

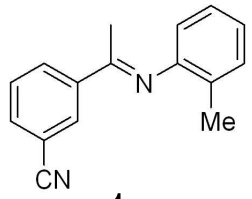


1ac

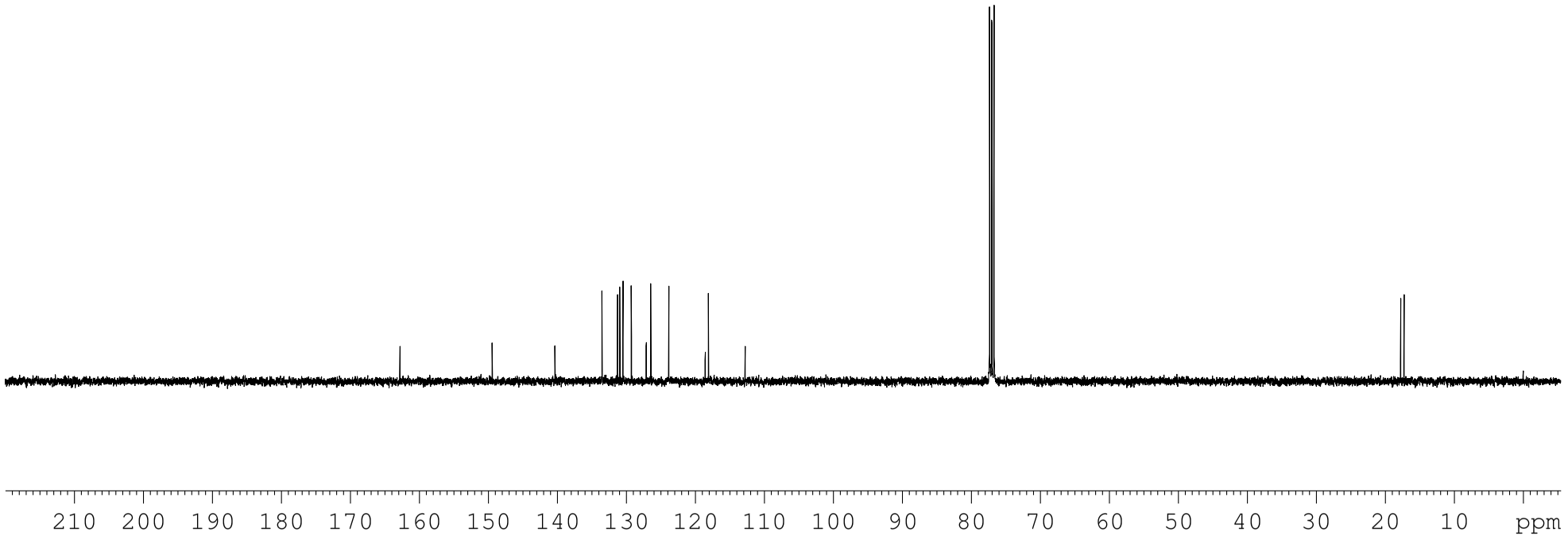


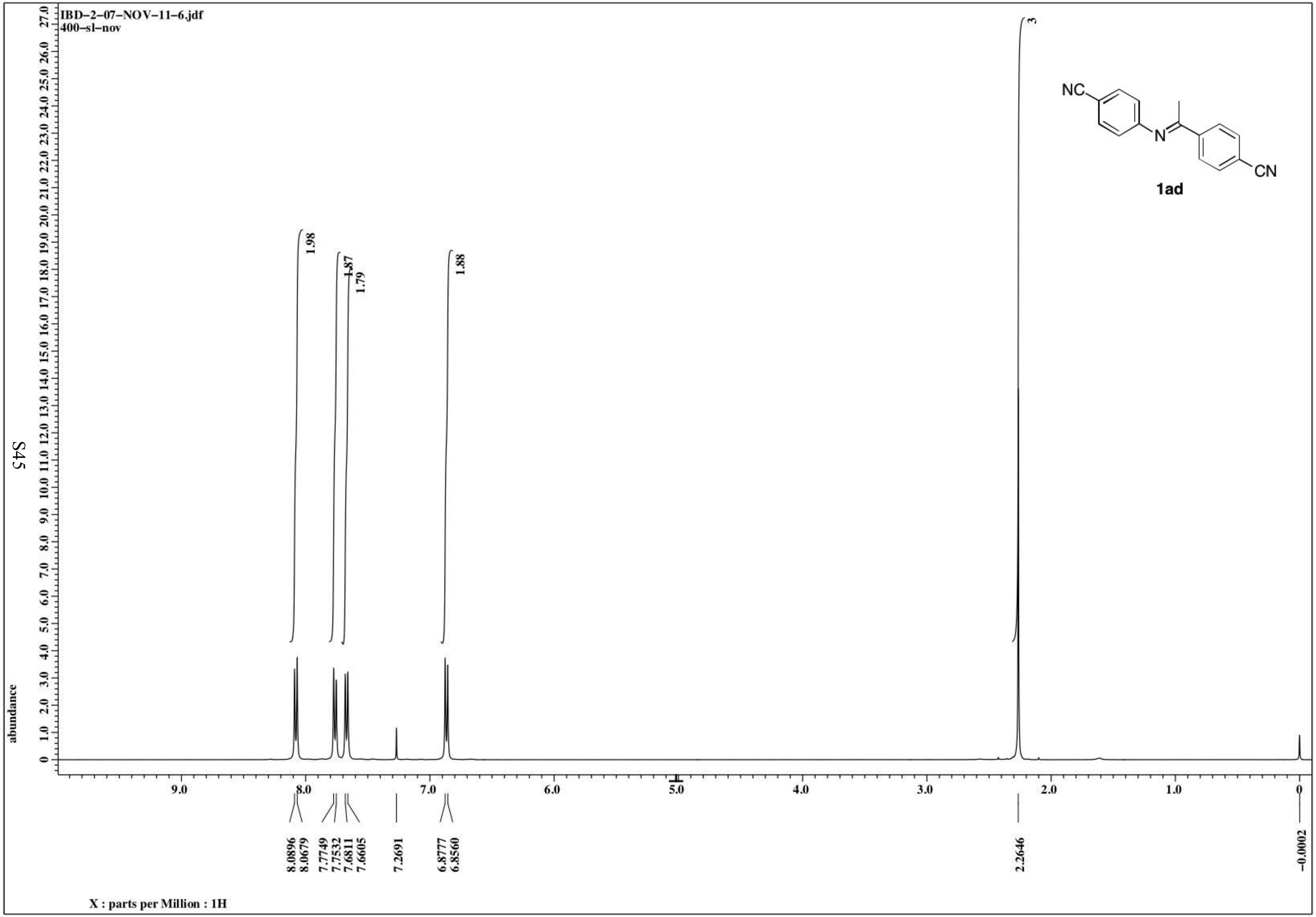
wy-2-14-2nd, 13C NMR 400 MHz, BBFO2, CDCl3

162.82
149.45
140.36
133.54
131.28
130.96
130.50
129.28
127.12
126.47
123.85
118.57
118.11
112.79
77.34
77.03
76.71
17.76
17.27



1ac

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400–sl–nov
1ad
NC
N
CN
3
1.98
1.87
1.79
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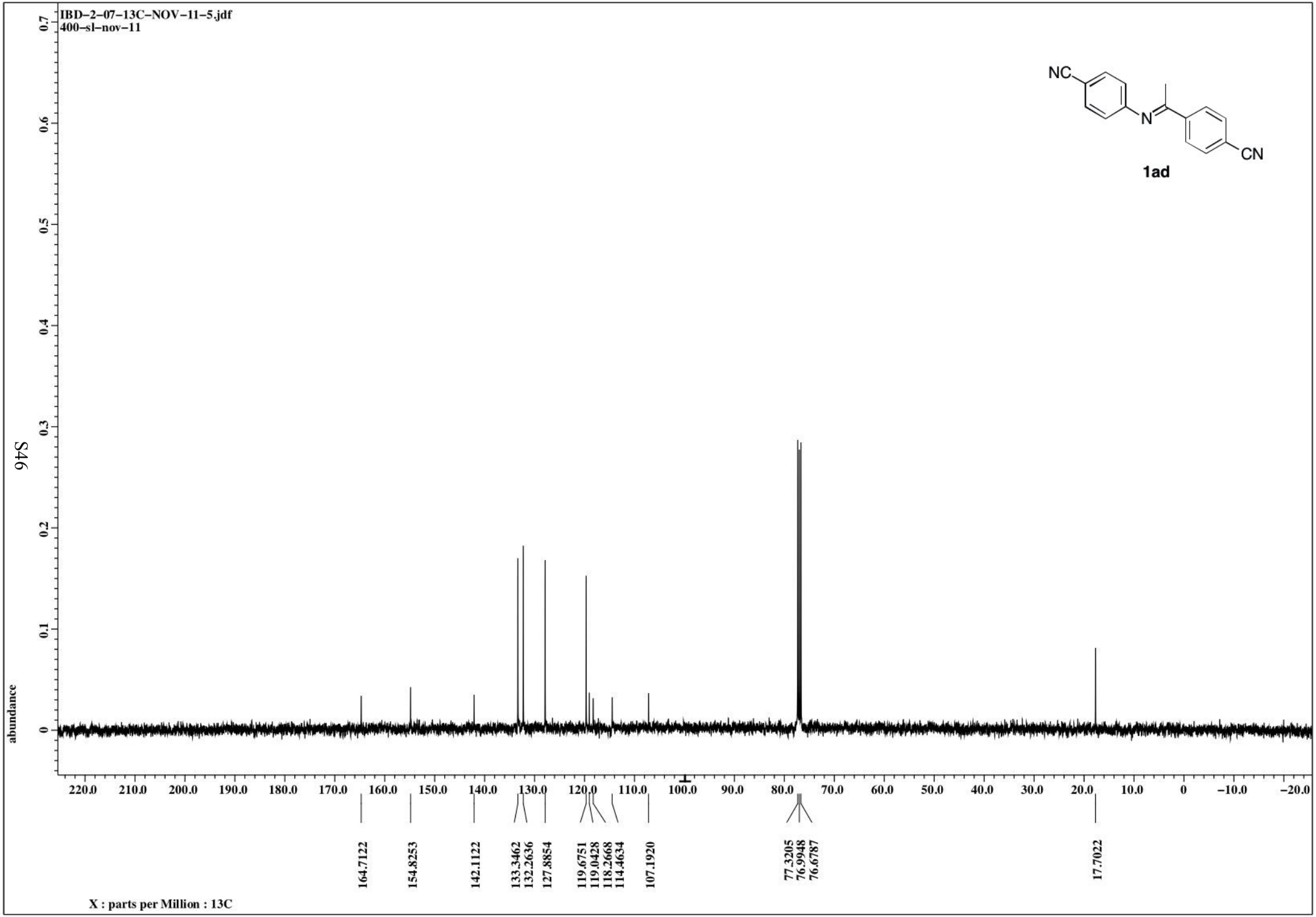
8.0896
8.0679
7.7749
7.7532
7.6811
7.6605
7.2691
6.8777
6.8560
2.2646
–0.0002
abundance
X : parts per Million : 1H


IBD-2-07-13C-NOV-11-5.jdf
400-sl-nov-11
NC
N
CN
1ad
abundance
X : parts per Million : 13C
164.7122
154.8253
142.1122
133.3462
132.2636
127.8854
119.6751
119.0428
118.2668
114.4634
107.1920
77.3205
76.9948
76.6787
17.7022

a-Ph-imine-PMP 1H NMR 400 MHz BBFO1 CDCL3

7.951
7.947
7.944
7.937
7.932
7.927
7.397
7.384
7.379
7.365
7.356
7.351
7.260
7.252
7.234
7.215
7.178
7.160
7.141
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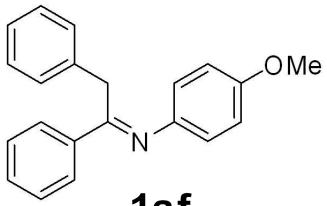
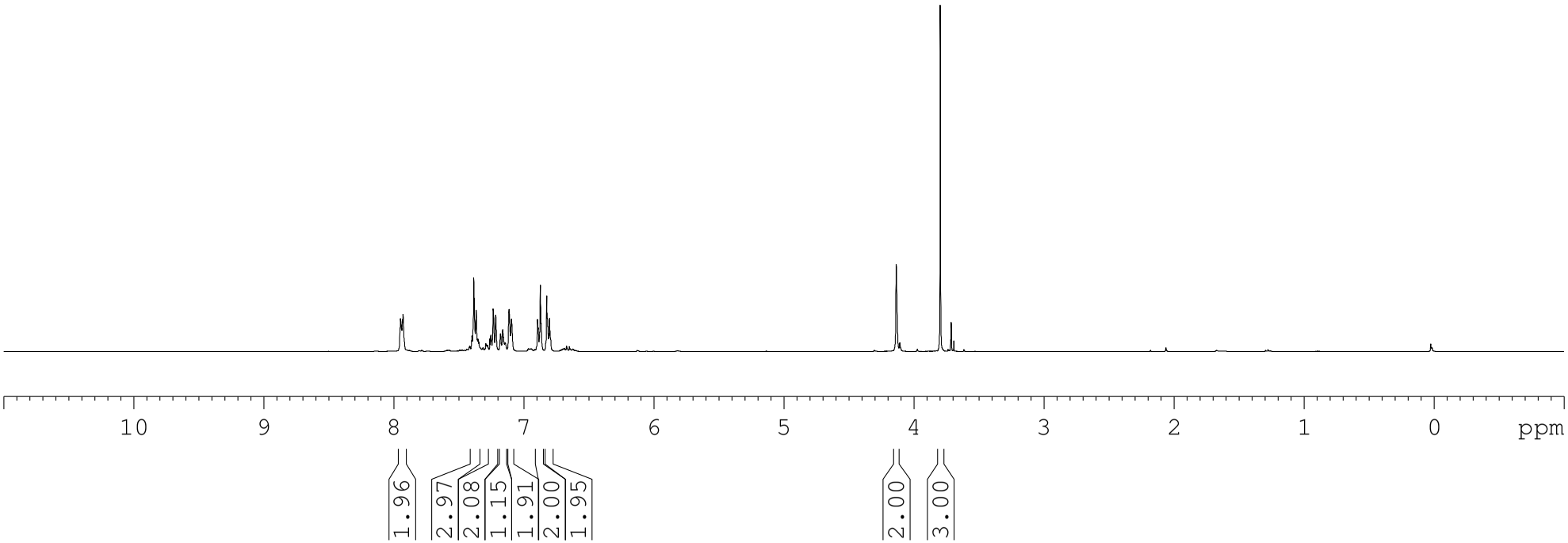
4.134
3.795

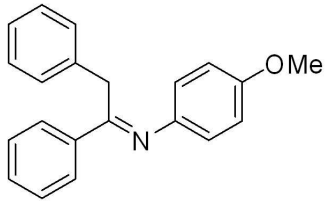


1af

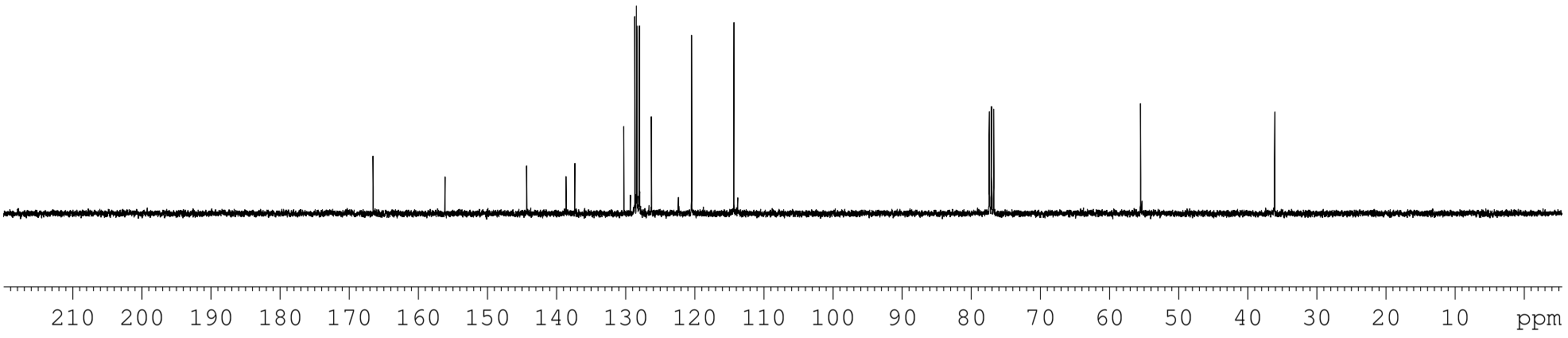


a-Ph-imine-PMP 13C NMR 400 MHz BBFO1 CDCL3

166.53
156.14
144.32
138.61
137.34
130.26
128.67
128.41
128.36
128.02
126.27
120.45
114.33
77.38
77.06
76.74
55.47
36.06



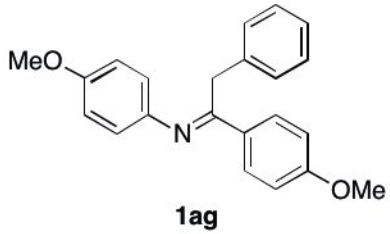
1af



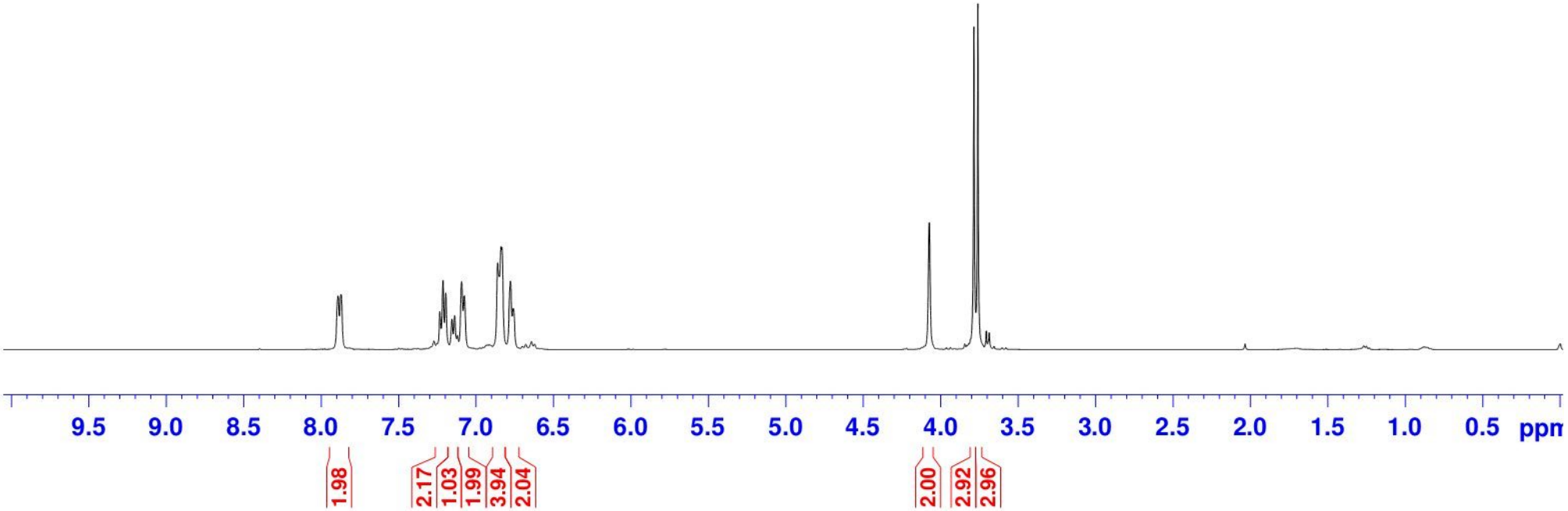
IBD-1-286-2ndtime-1H crude BBFO1-dec-1H NMR 20111201

7.891
7.871
7.271
7.234
7.213
7.195
7.155
7.138
7.120
7.093
7.075
6.860
6.849
6.838
6.832
6.777
6.759

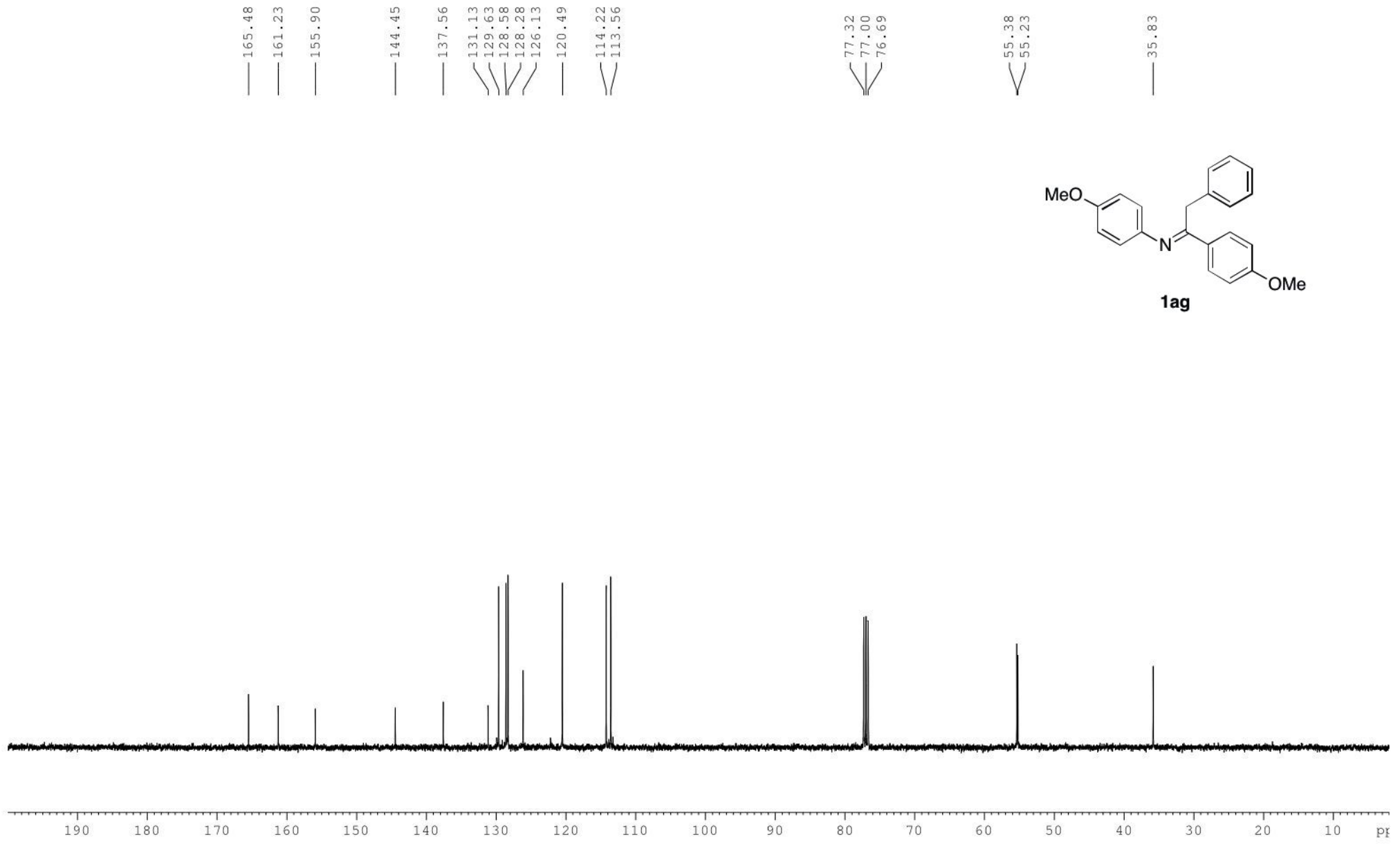
4.073
3.786
3.761



1ag



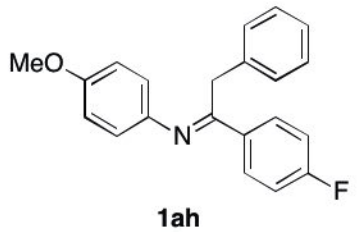
IBD-1-286-2ndtime-13C crude BBFO1-dec-1H NMR 20111201



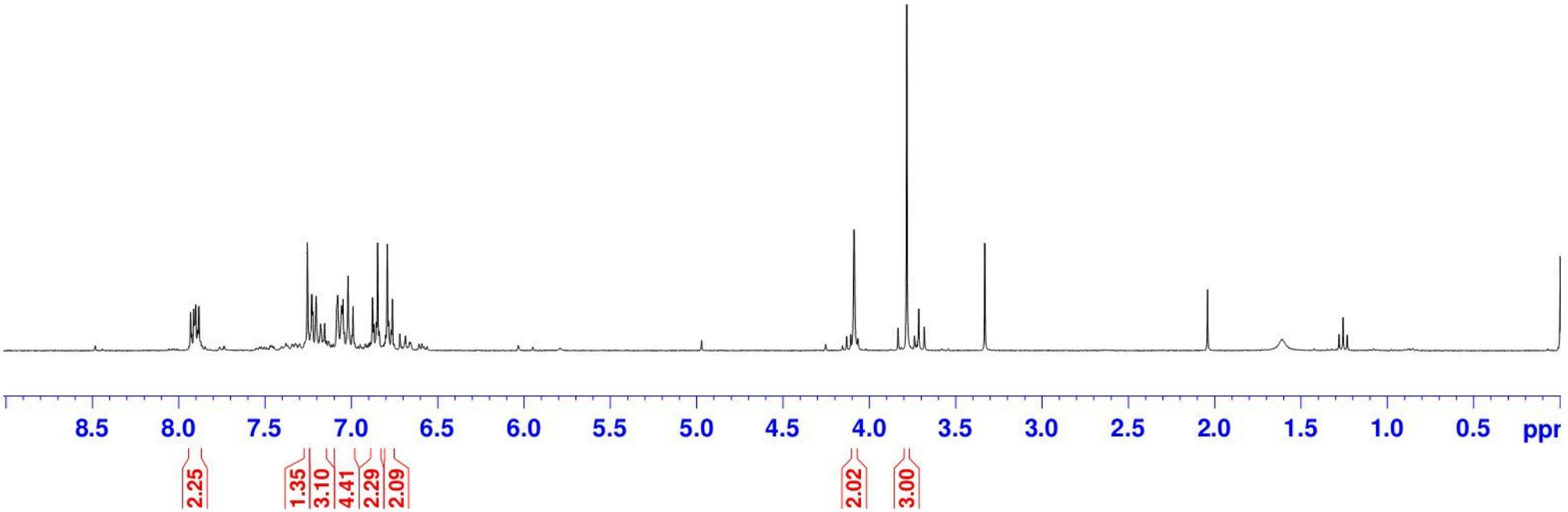
IBD-1-300-1

7.902
7.891
7.884
7.256
7.230
7.224
7.205
7.179
7.156
7.080
7.057
7.049
7.042
7.020
6.997
6.991
6.878
6.871
6.857
6.849
6.839
6.802
6.793
6.785
6.770
6.763

4.089
3.784
3.332



1ah

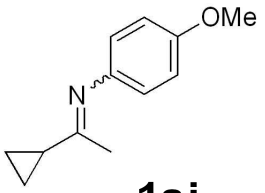


wy-cyclopropyl imine, 1H NMR BBFO1 400Hz in CDCl3

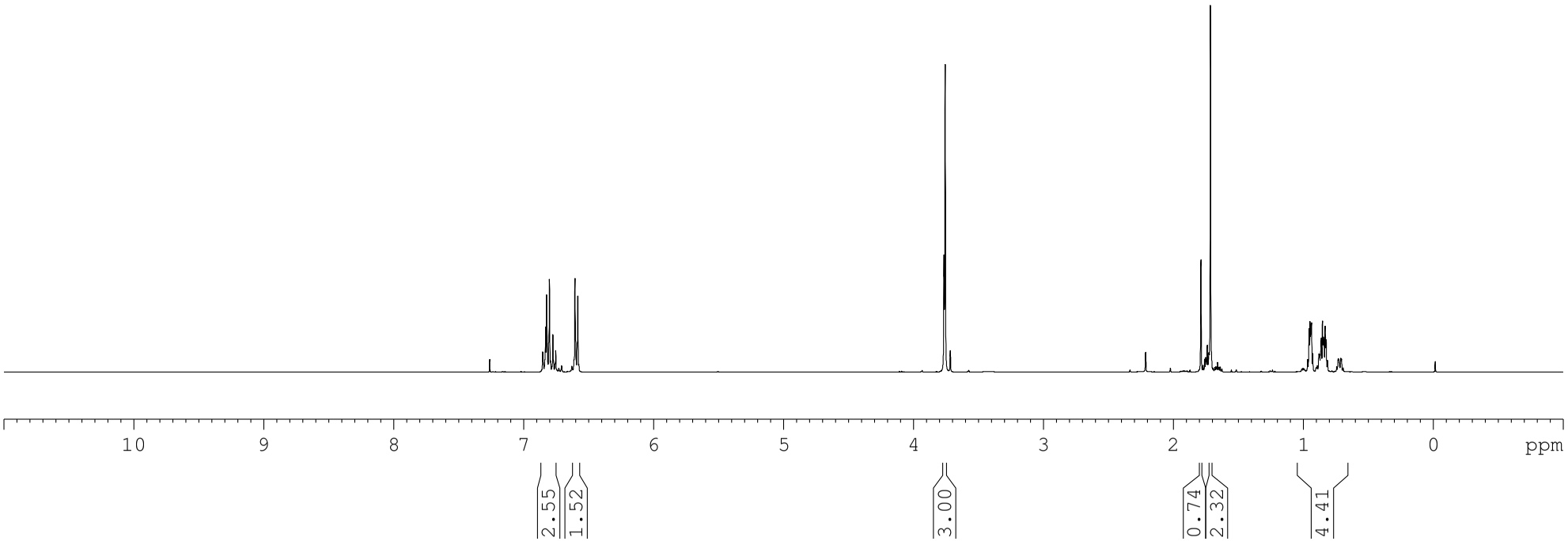
6.855
6.850
6.833
6.825
6.809
6.803
6.796
6.777
6.772
6.761
6.755
6.607
6.602
6.590
6.585

3.767
3.759

1.790
1.716
0.968
0.957
0.950
0.945
0.942
0.938
0.929
0.893
0.882
0.878
0.863
0.854
0.848
0.846
0.834
0.827
0.816
0.745
0.734
0.728
0.713

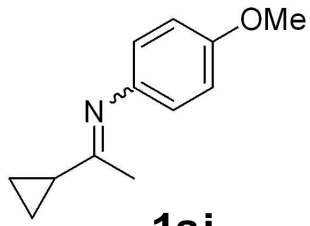


1ai

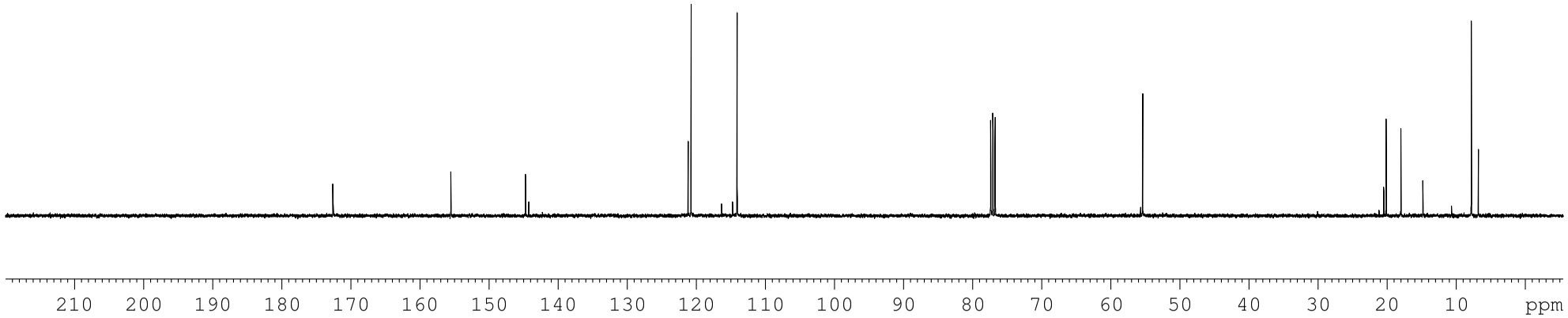


wy-cyclopropyl imine, 13C NMR BBFO1 400Hz in CDCl3

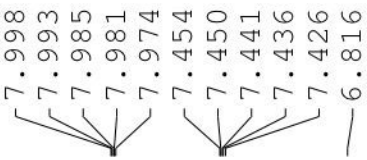
172.65
172.59
155.59
155.55
144.77
144.28
121.21
120.79
114.13
114.11
77.41
77.09
76.78
55.71
55.41
20.50
20.15
18.02
14.84
7.83
6.81

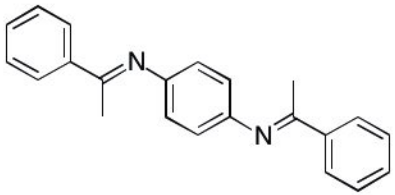


1ai

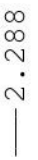


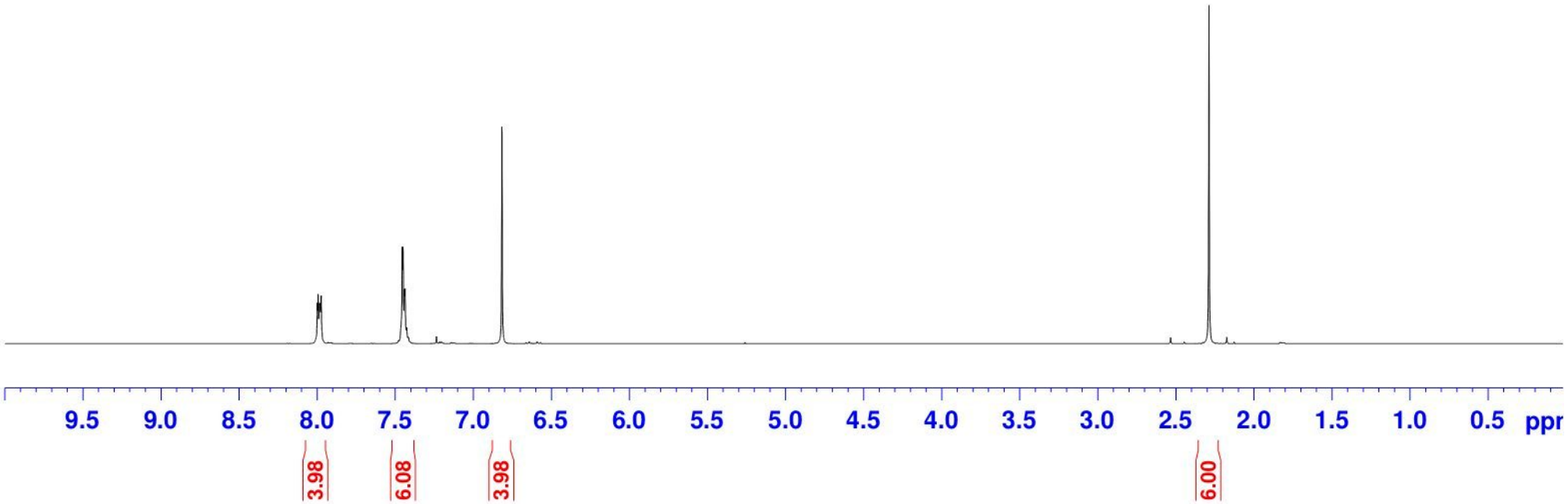
IBD-1-309-14dimine-1H- BBFO1-dec-1H NMR 20111201



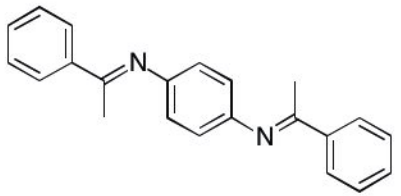


1al

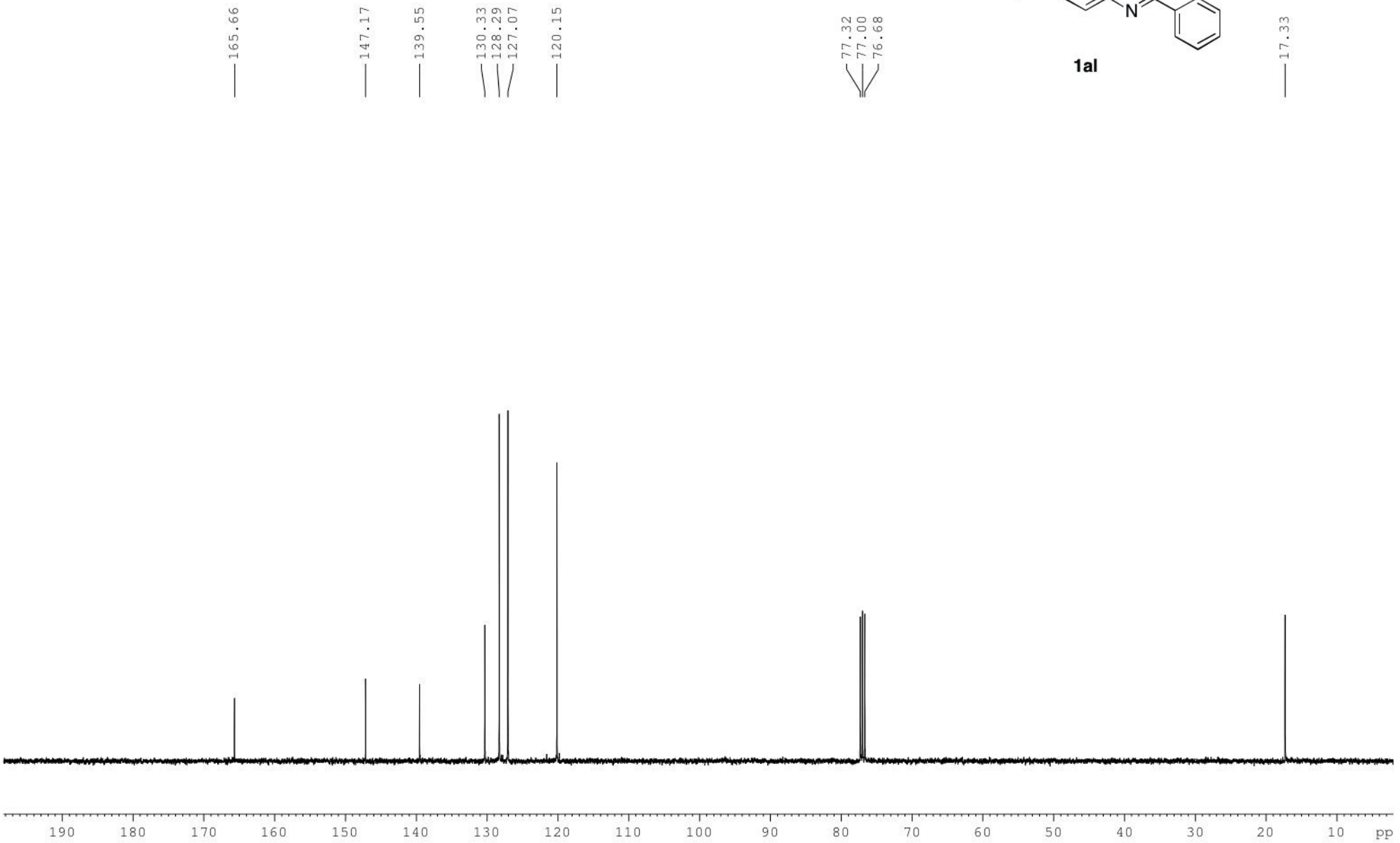


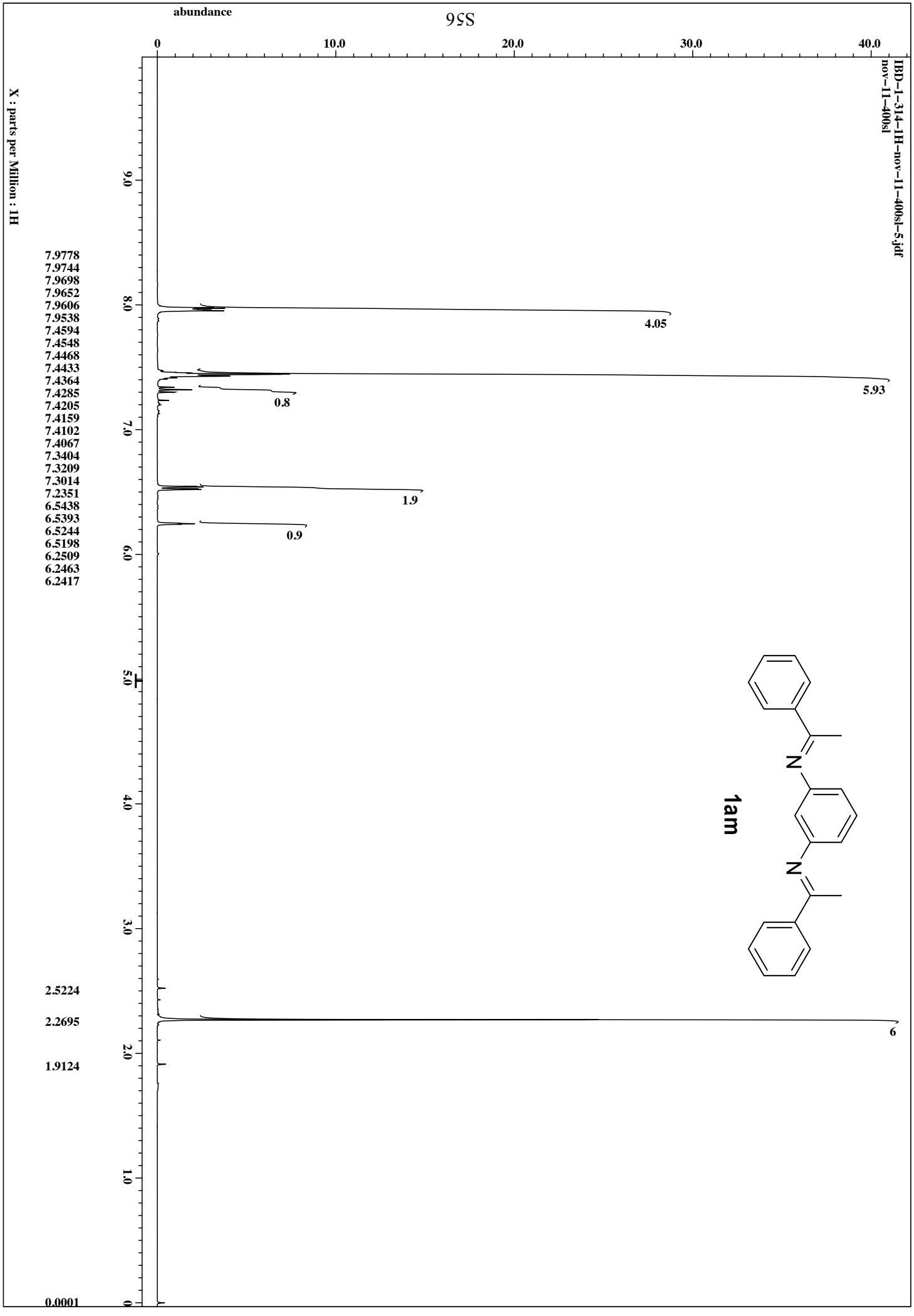


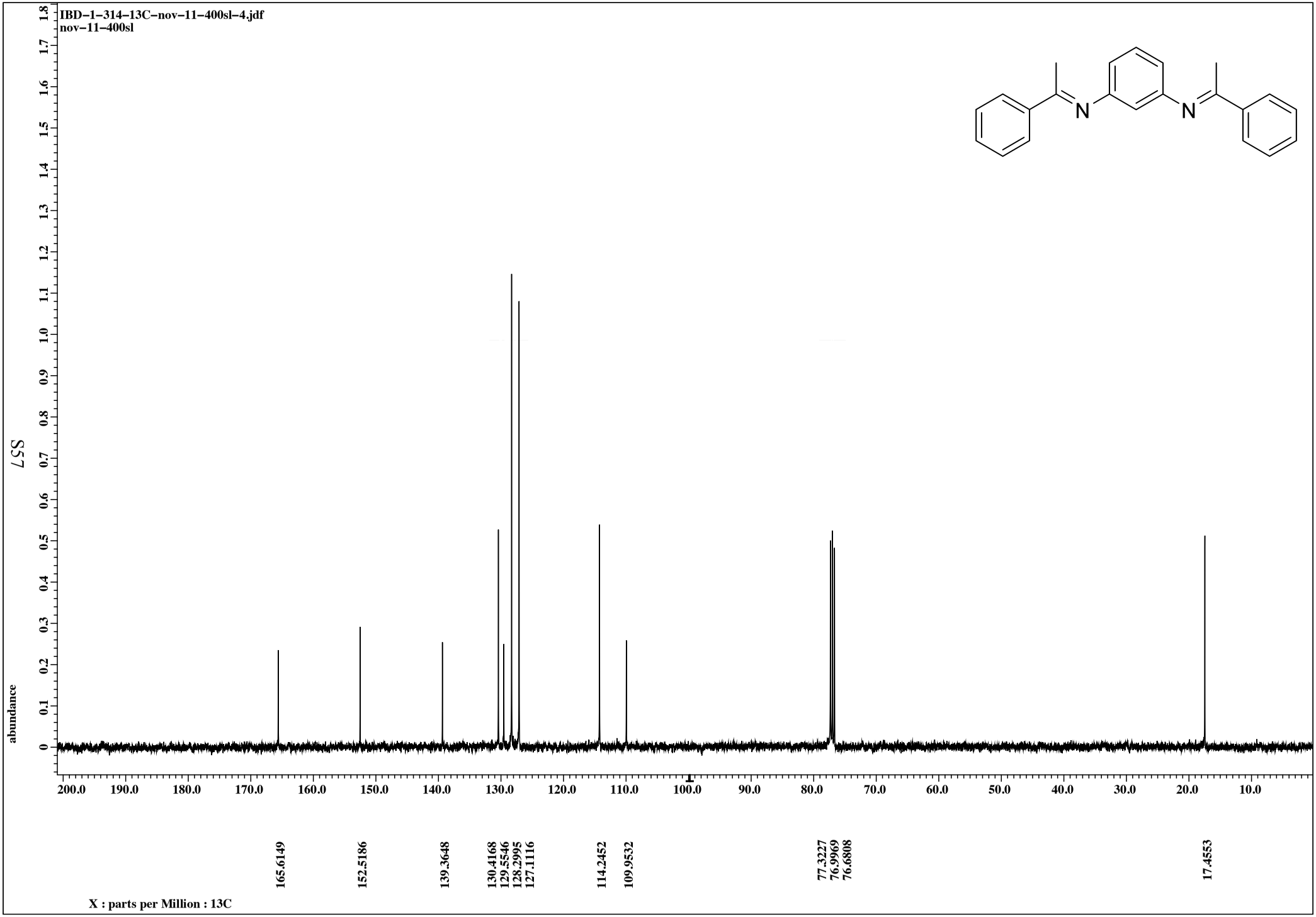
IBD-1-309-14dimine-13C- BBFO1-dec-1H NMR 20111201



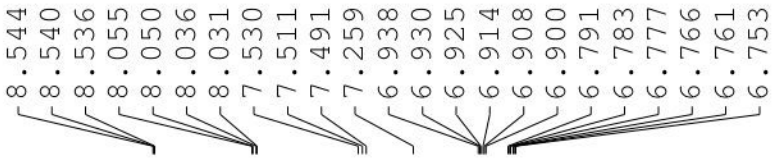
1al

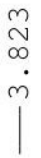


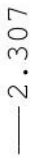

abundance
0
10.0
20.0
30.0
40.0
IBD-1-314-1H-nov-11-400sl-5.jdf
nov-11-400sl
X : parts per Million : 1H
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.9778
7.9744
7.9698
7.9652
7.9606
7.9538
7.4594
7.4548
7.4468
7.4433
7.4364
7.4285
7.4205
7.4159
7.4102
7.4067
7.3404
7.3209
7.3014
7.2351
6.5438
6.5393
6.5244
6.5198
6.2509
6.2463
6.2417
2.5224
2.2695
1.9124
0.0001
4.05
5.93
0.8
1.9
0.9
6
N
N
1am

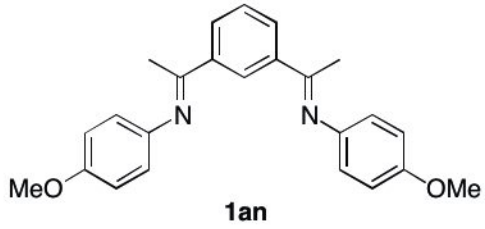

IBD-1-314-13C-nov-11-400sl-4.jdf
nov-11-400sl
N
N
S57
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
165.6149
152.5186
139.3648
130.4168
129.5546
128.2995
127.1116
114.2452
109.9532
77.3227
76.9969
76.6808
17.4553
X : parts per Million : 13C

IBD-1-321-1-3imine1H NMR 400 MHz BBFO1 CDCl3

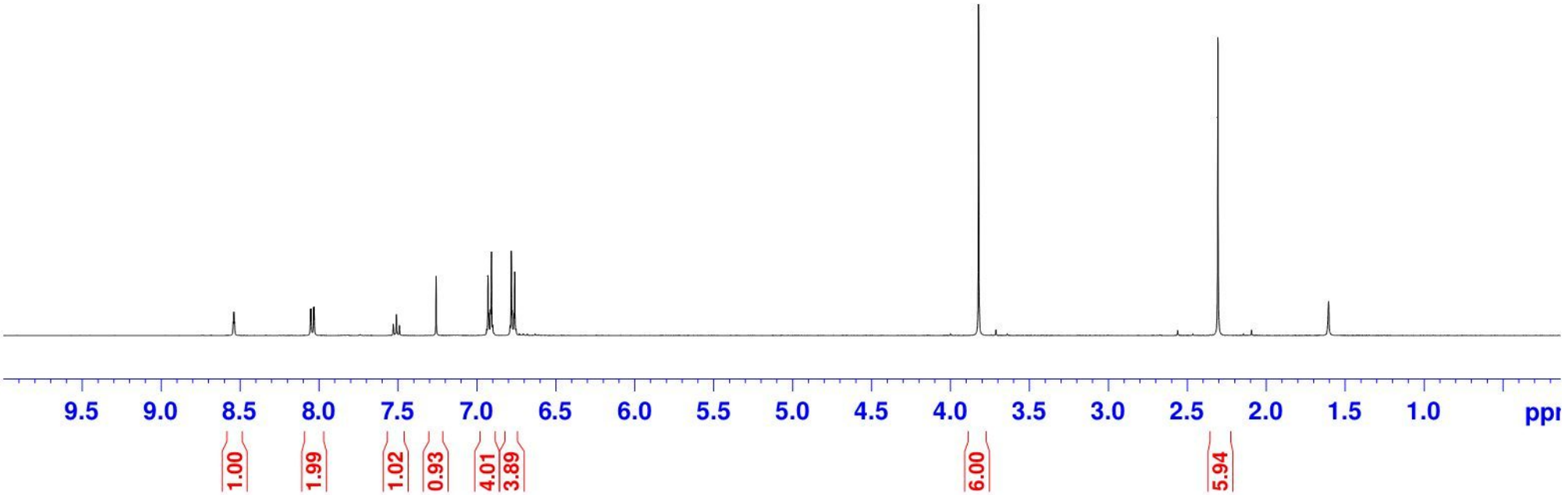




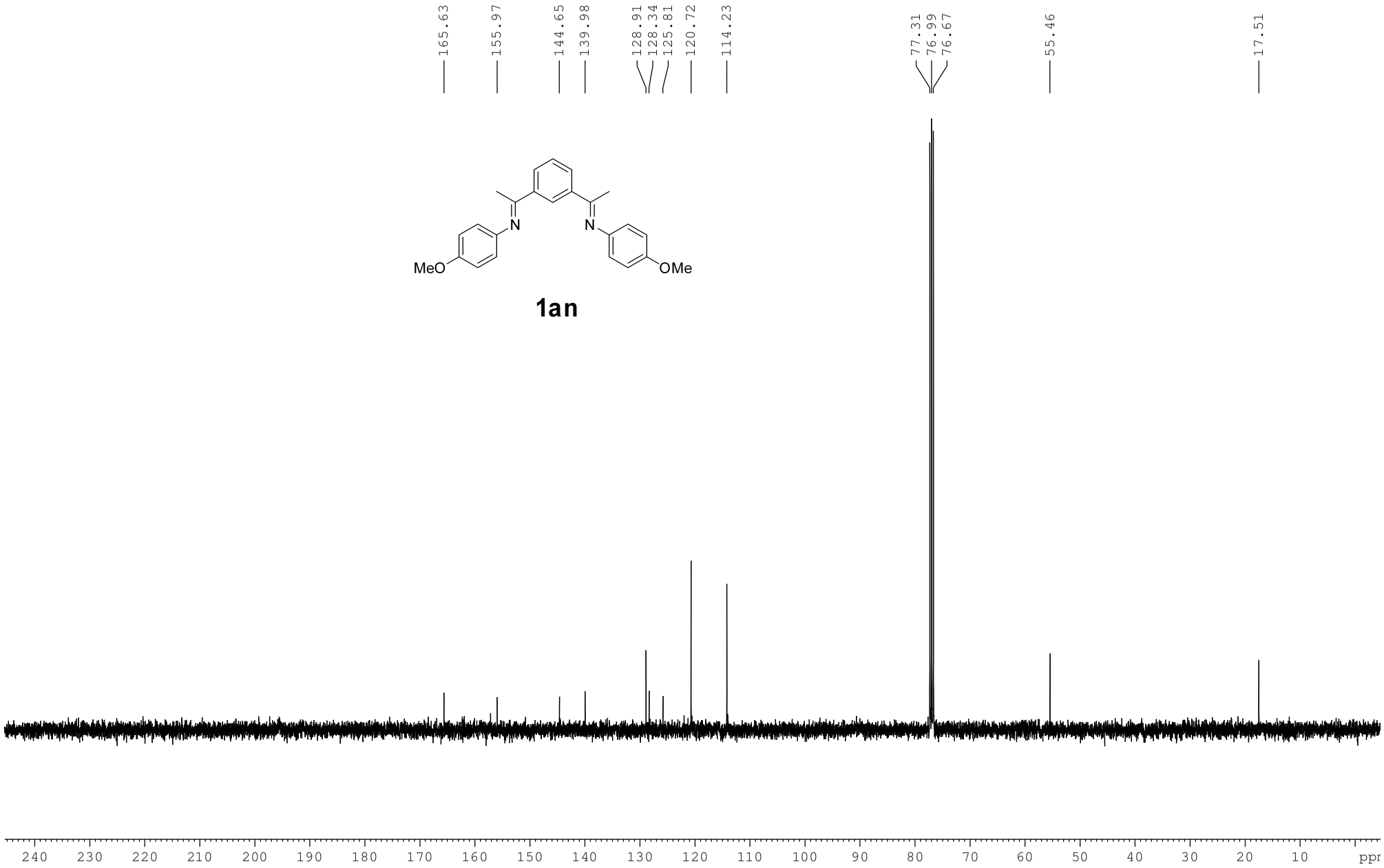




1an



IBD-1-321-1-3imine1H NMR 400 MHz BBFO1 CDCl3

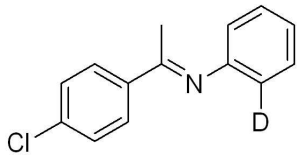


1an

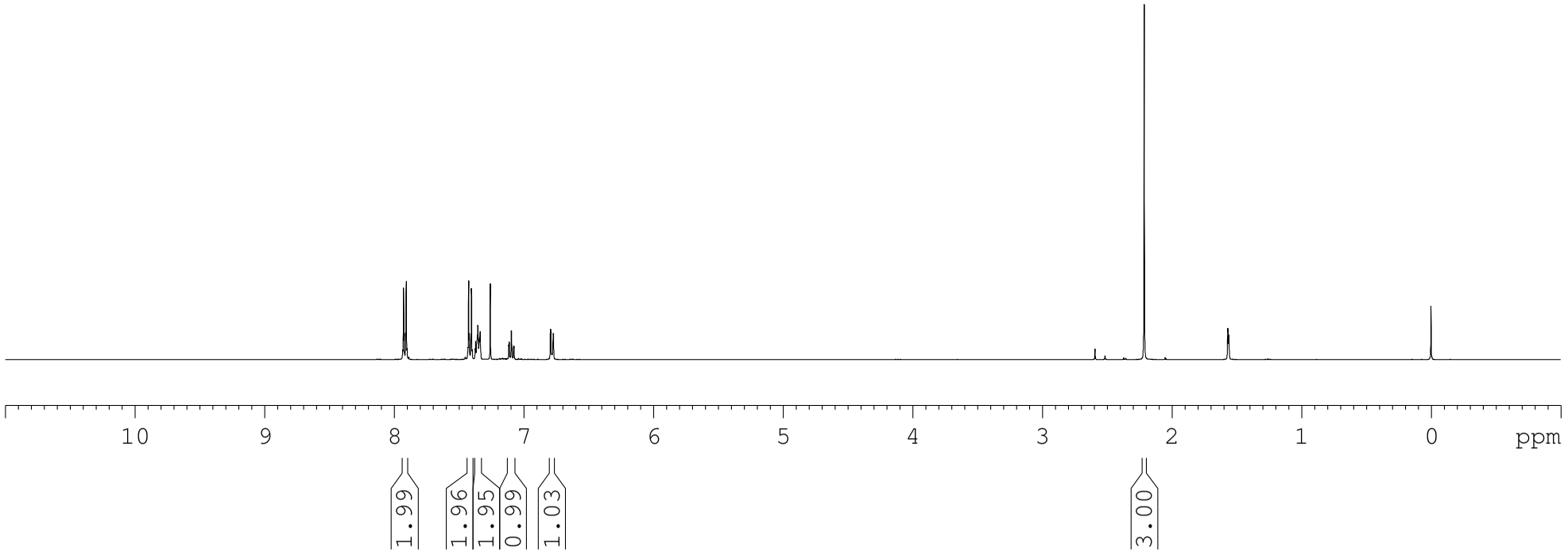
wy-2-64 1H NMR BBFO2 400 MHz CDCl3

7.936
7.929
7.924
7.912
7.908
7.901
7.433
7.427
7.422
7.410
7.405
7.399
7.376
7.373
7.356
7.354
7.342
7.337
7.116
7.114
7.098
7.095
7.079
7.077
6.795
6.793
6.784
6.775
6.772

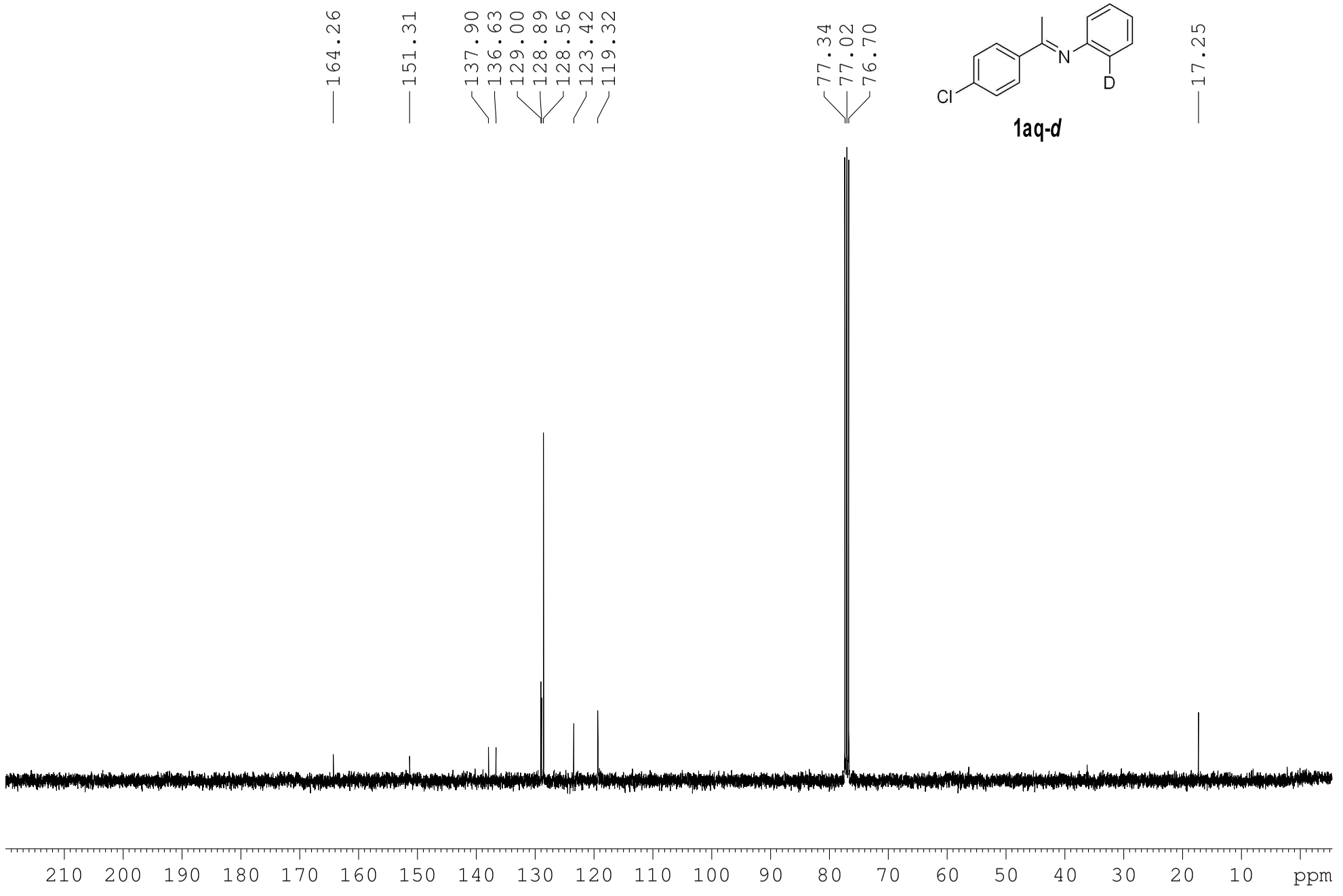
2.214



1aq-*d*



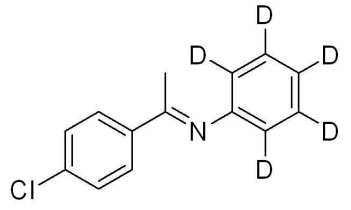
wy-2-64 13C NMR BBFO2 400 MHz CDCl3



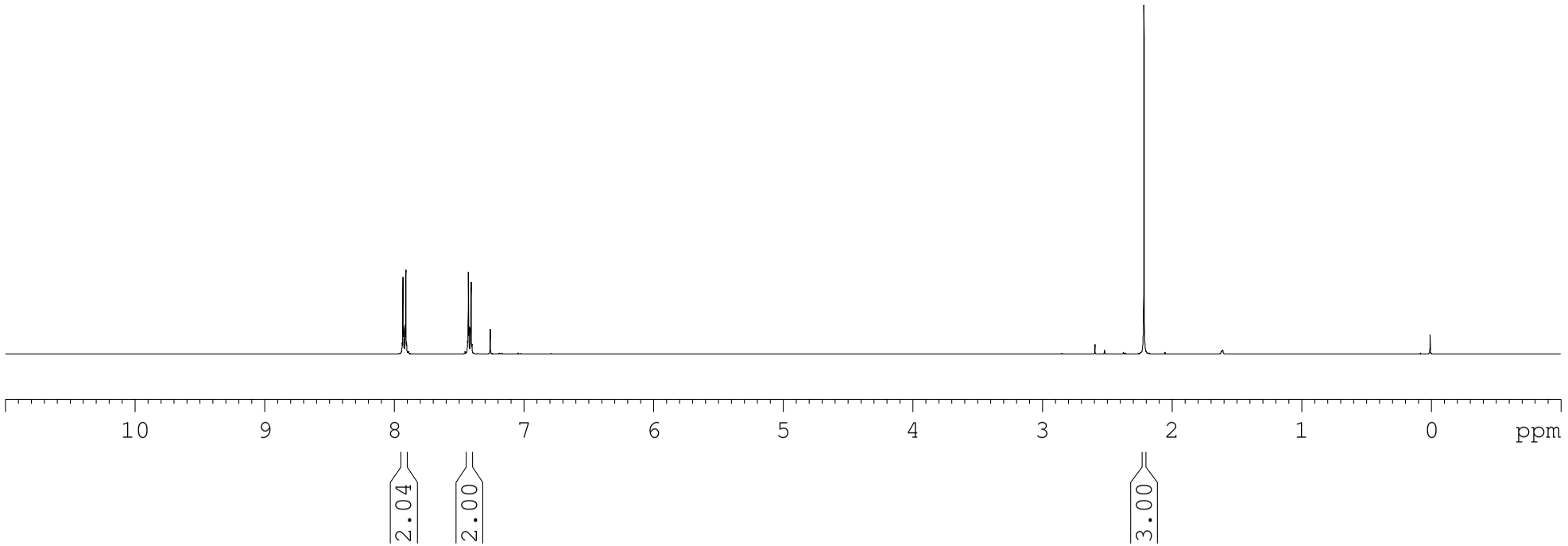
wy-2-7 1H NMR 400 MHz BBFO1 CDCL3

7.940
7.934
7.929
7.917
7.912
7.906
7.436
7.429
7.424
7.413
7.408
7.401

2.216

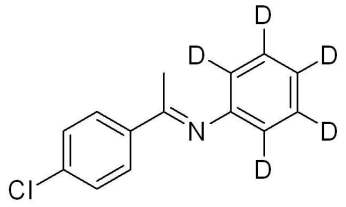


1aq-d_5



wy-2-7 13C NMR 400 MHz BBFO1 CDCL3

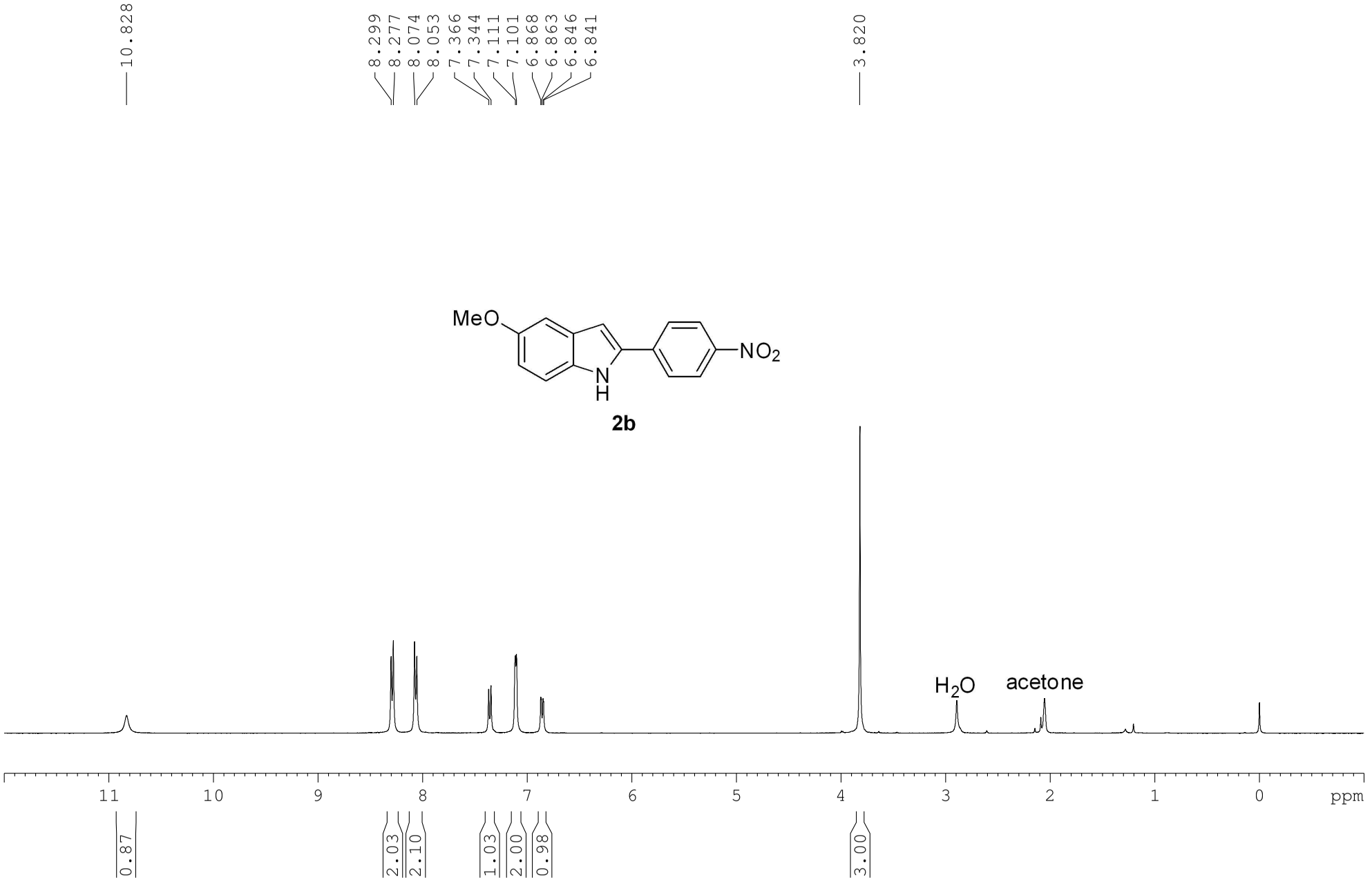
164.25
151.23
137.89
136.61
128.56
122.91
119.17
118.93
118.69
77.36
77.04
76.72
17.25



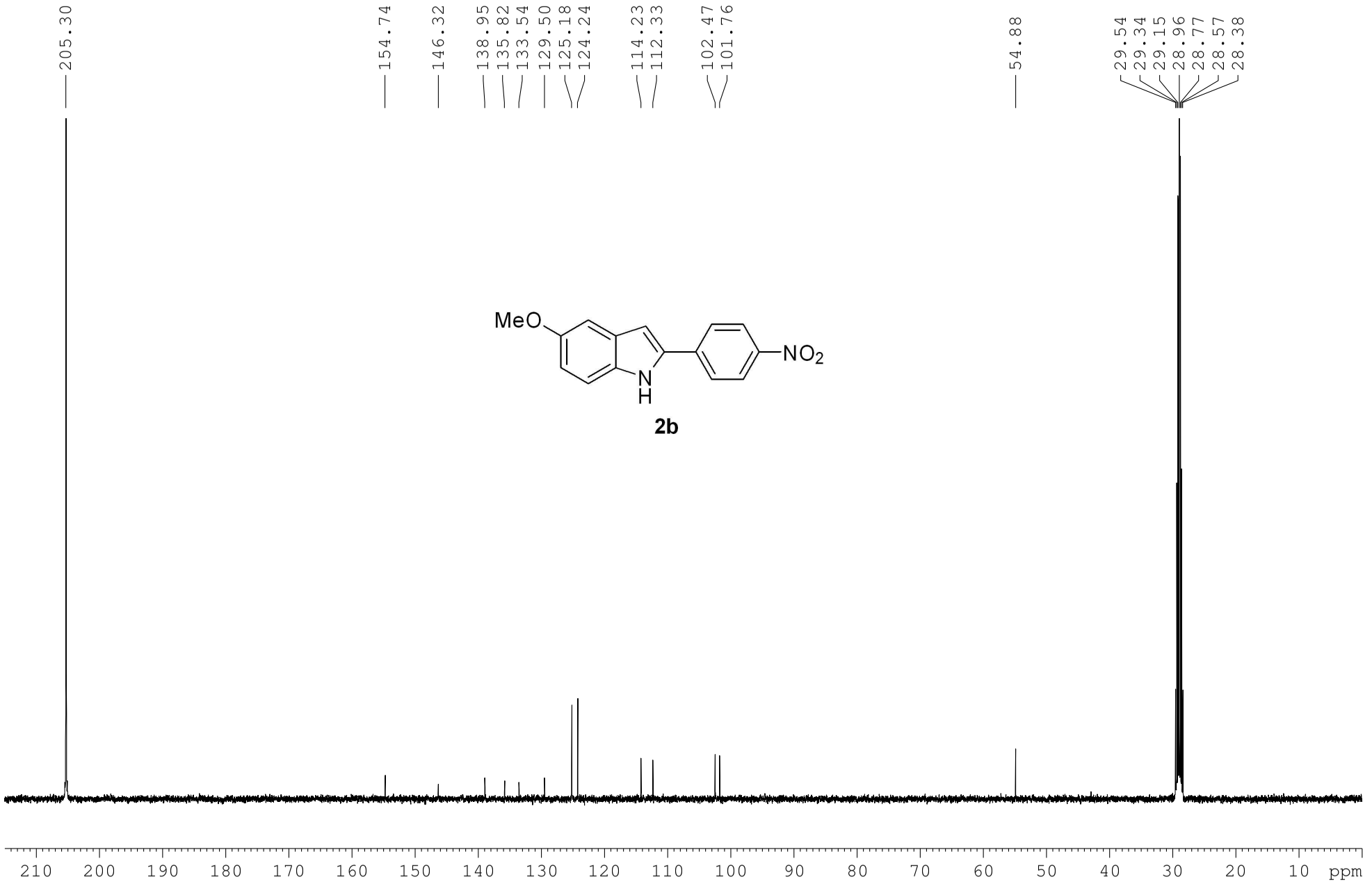
1aq-d_5

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

indole 2b, 1H NMR BBFO2 400MHz d6-acetone



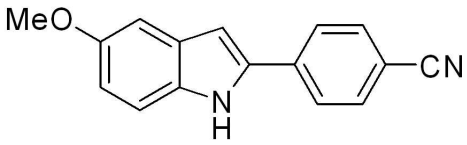
indole 2b, 13C NMR BBFO2 400MHz d6-acetone



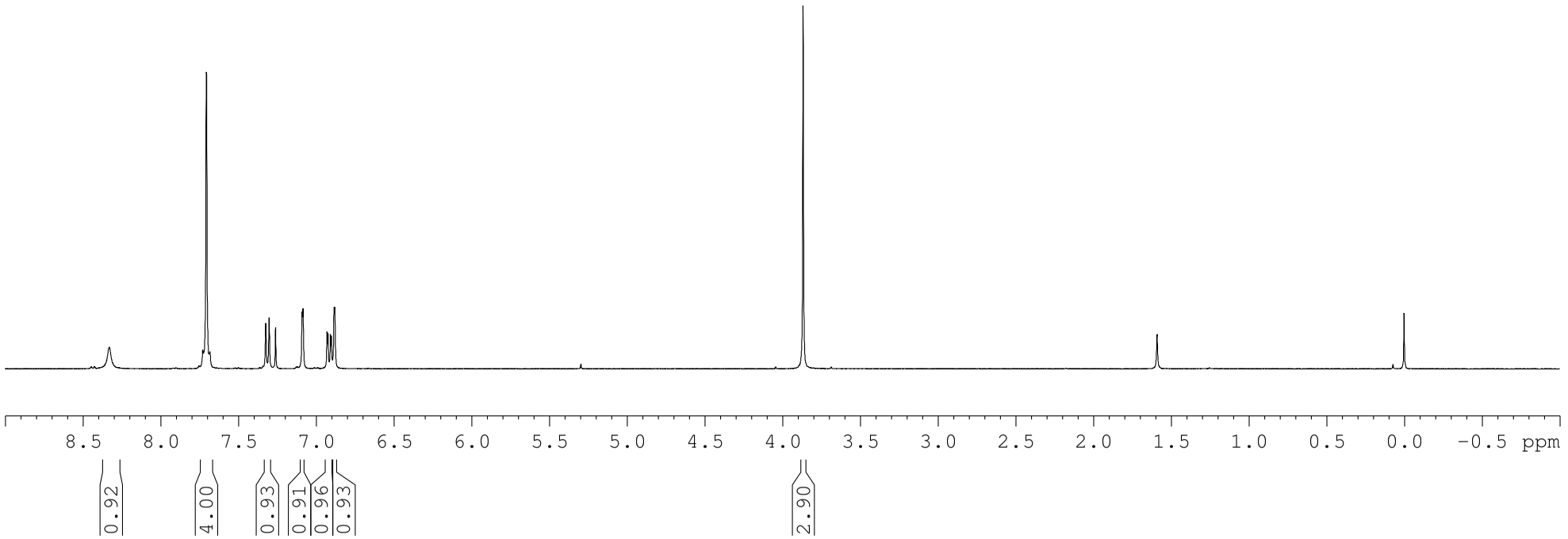
indole 2c, 1H NMR BBFO2 400MHz CDCl3

8.330
7.728
7.705
7.688
7.682
7.323
7.301
7.091
7.086
6.932
6.926
6.910
6.904
6.885
6.882

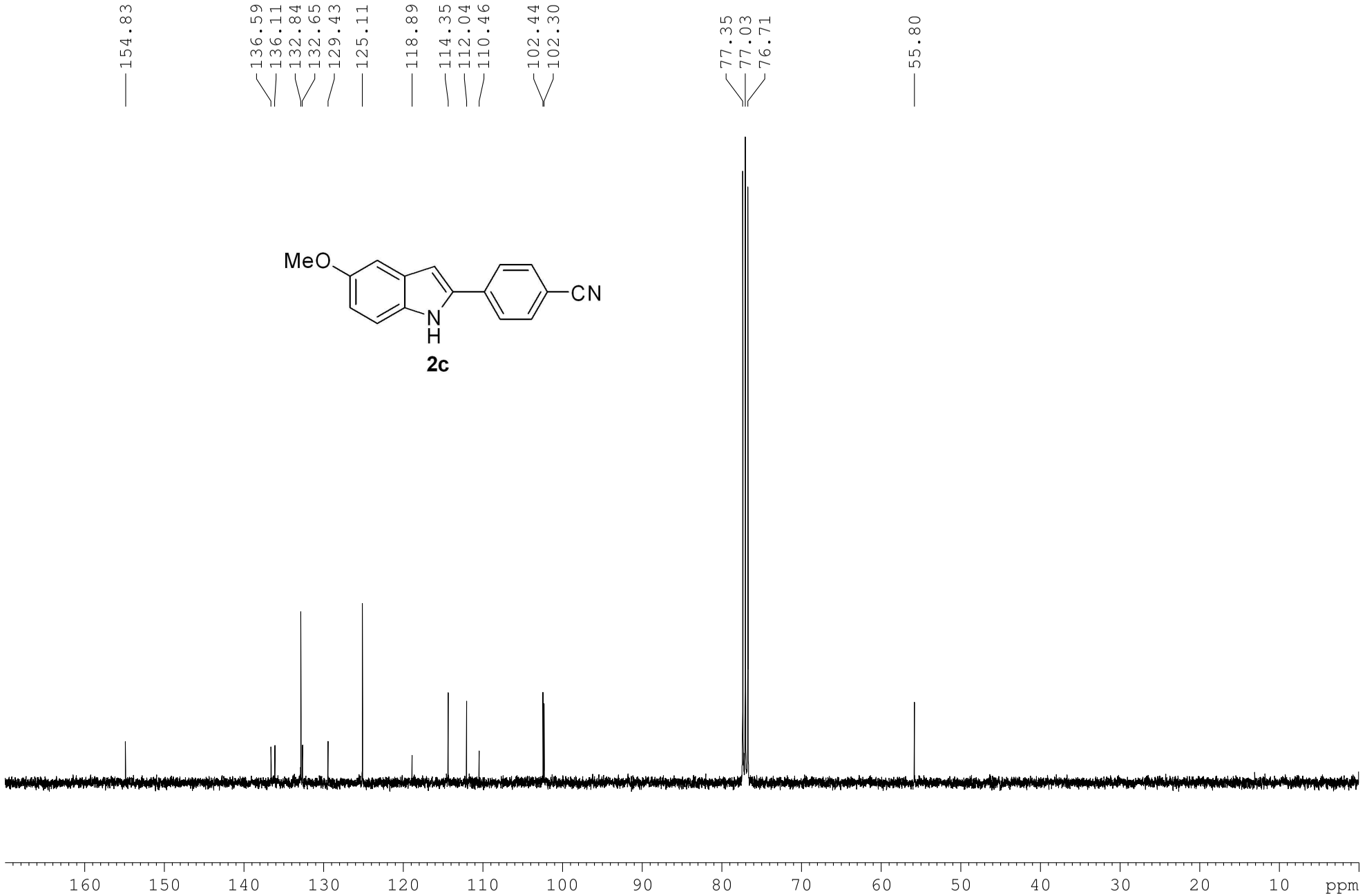
3.869



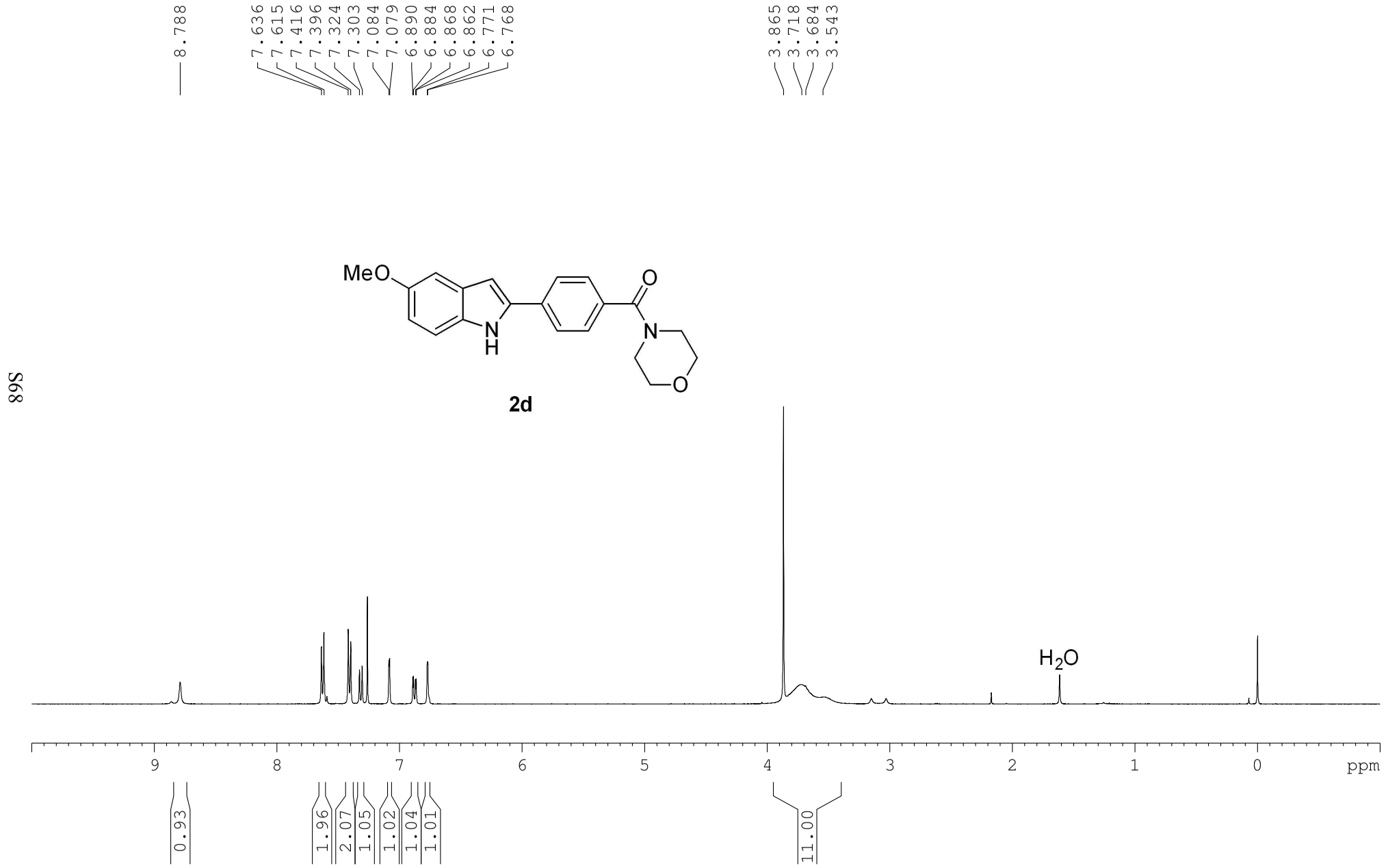
2c



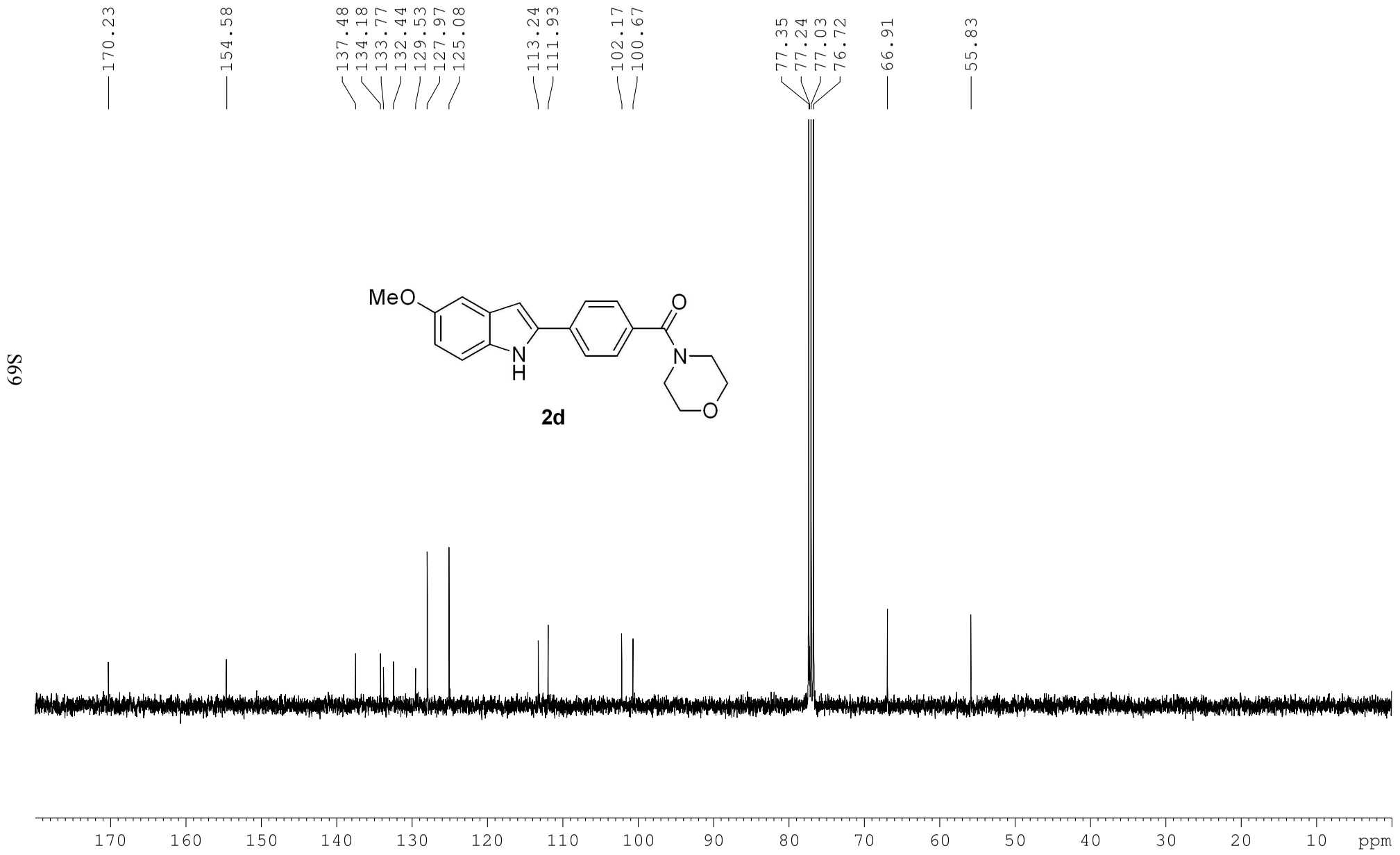
indole 2c, 13C NMR BBFO2 400MHz CDCl3



indole 2d, 1H NMR BBFO2 400MHz CDCl3



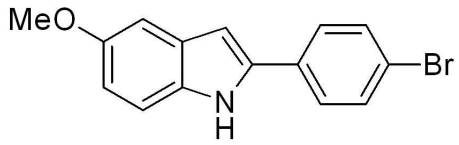
indole 2d, 13C NMR BBFO2 400MHz CDCl3



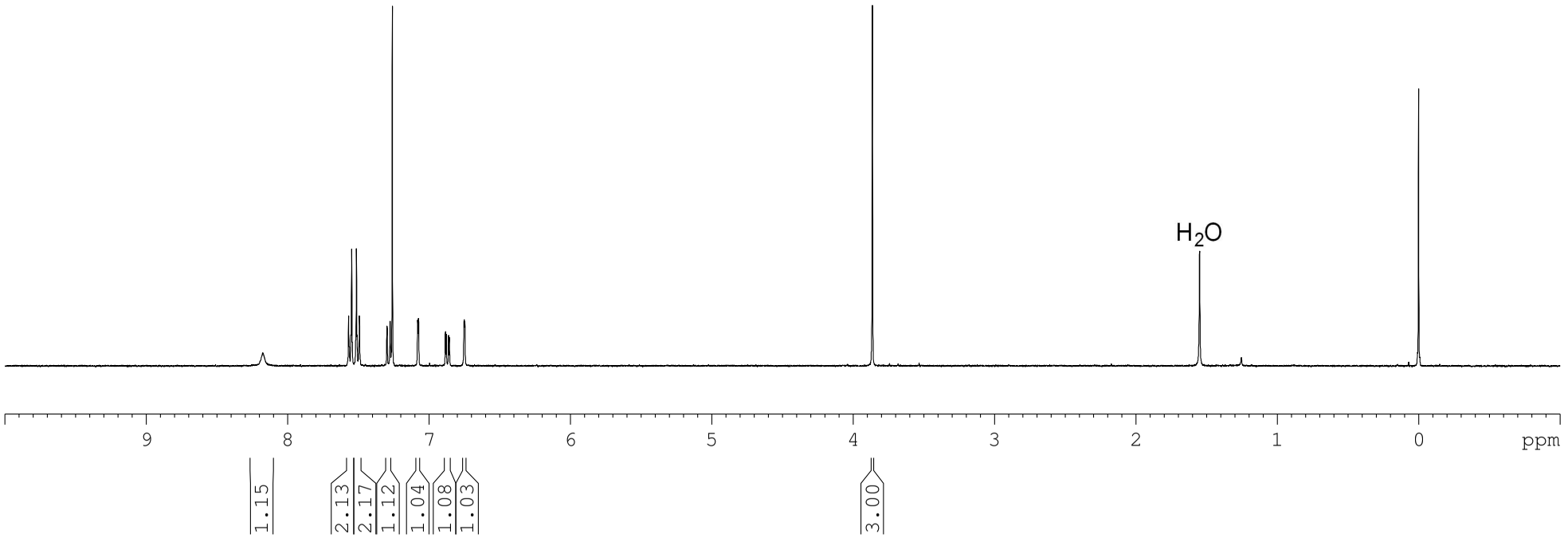
indole 2g, 1H NMR BBFO2 400MHz CDCl3

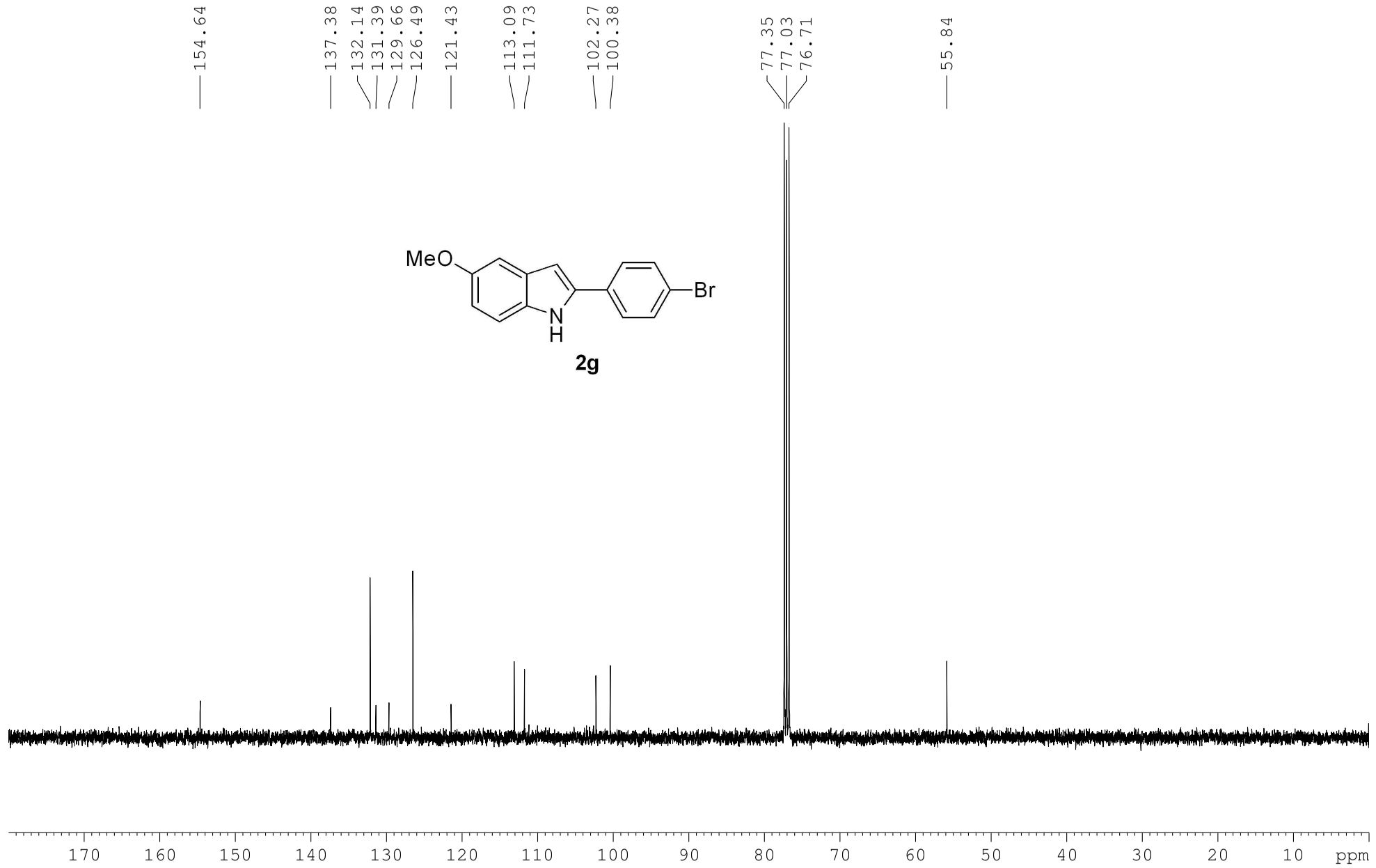
8.177
7.569
7.548
7.514
7.509
7.492
7.298
7.276
7.081
7.075
6.885
6.879
6.863
6.857
6.752
6.748

3.864



2g



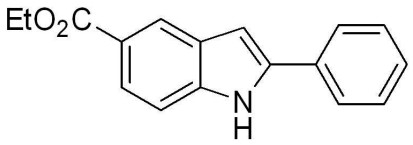

indole 2g 13C NMR BBFO2 400 MHz CDCl3
154.64
137.38
132.14
131.39
129.66
126.49
121.43
113.09
111.73
102.27
100.38
77.35
77.03
76.71
55.84
MeO
Br
N
H
2g
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

indole 2m, 1H NMR BBFO2 400MHz CDCl3

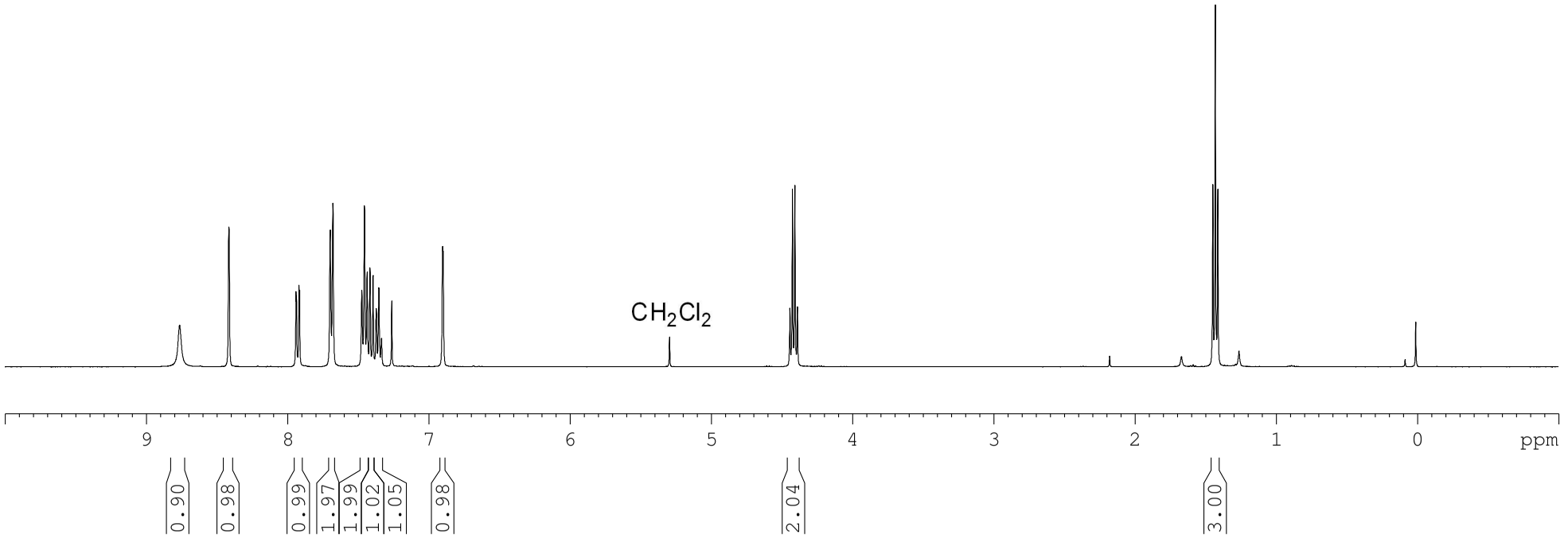
8.763
8.414
7.938
7.935
7.917
7.914
7.696
7.677
7.473
7.454
7.434
7.415
7.393
7.370
7.351
7.333
6.903
6.900

4.444
4.426
4.408
4.390

1.449
1.431
1.413

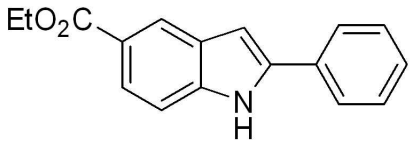


2m

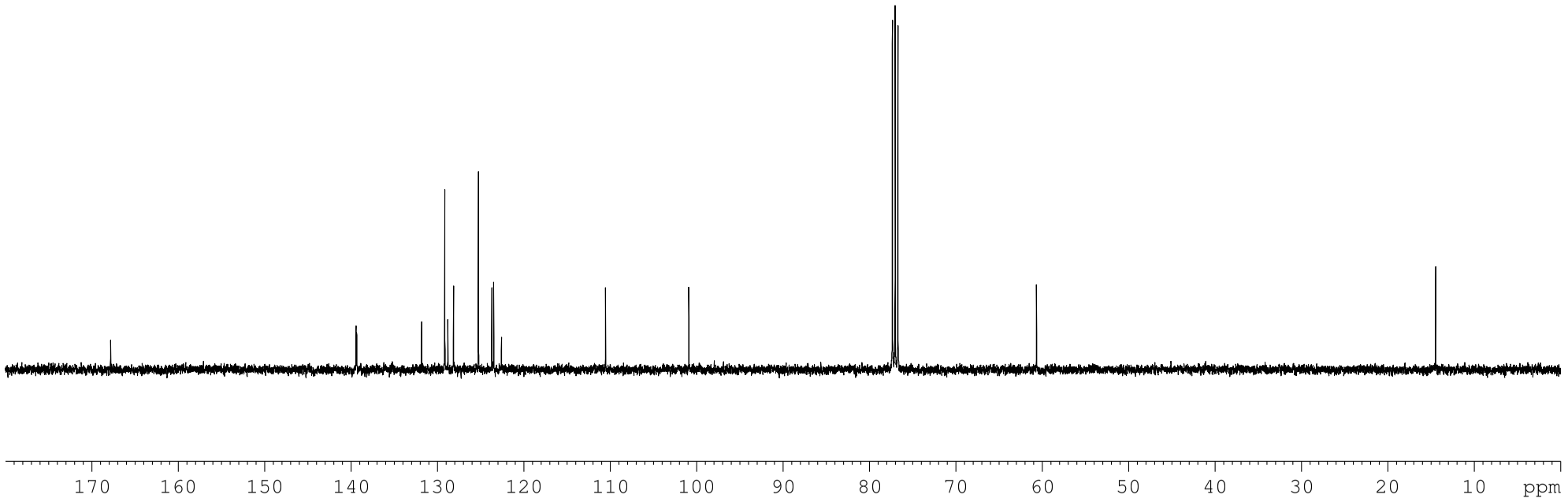


indole 2m, 13C NMR BBFO2 400MHz CDCl3

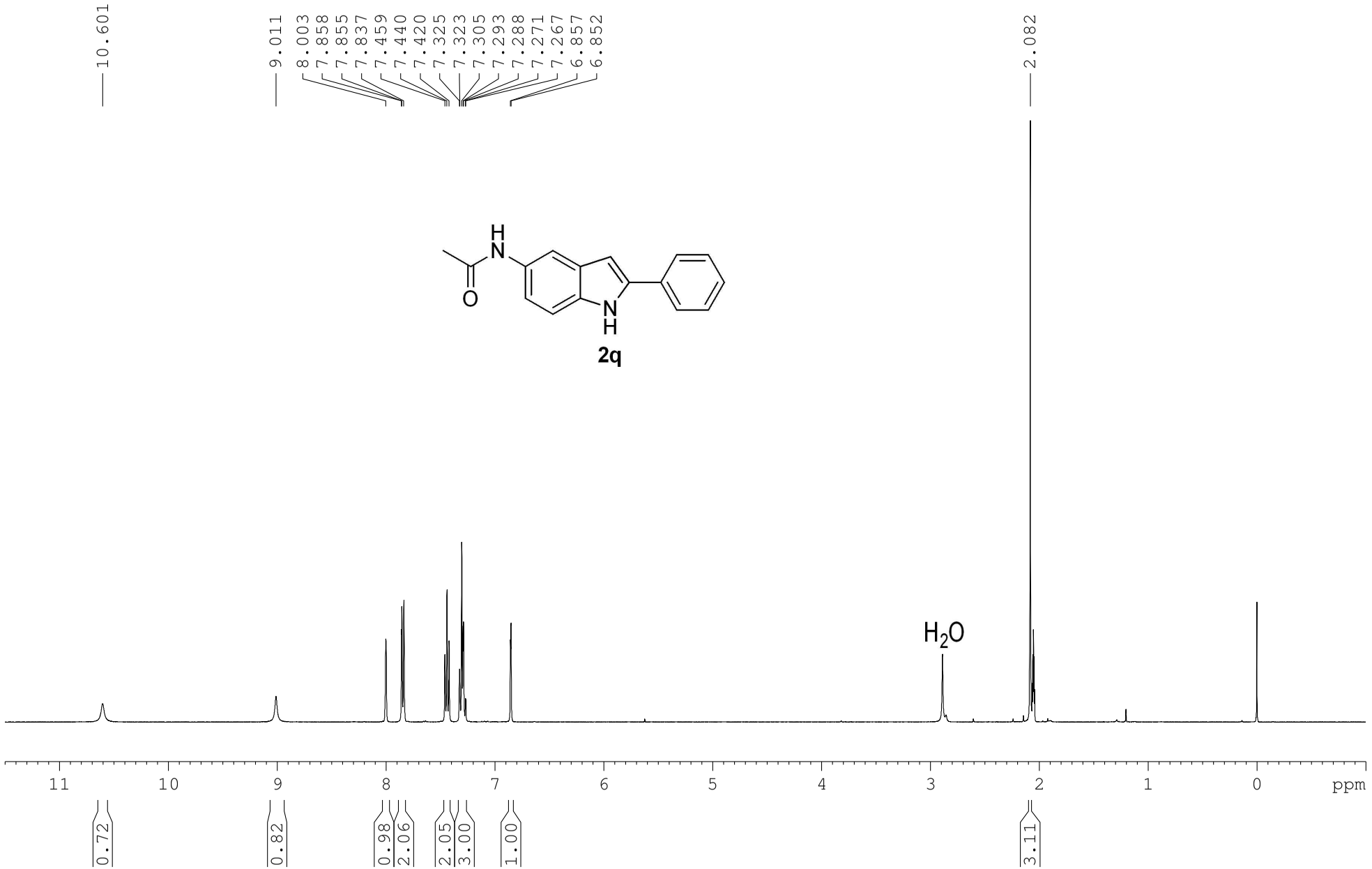
167.82
139.42
139.32
131.82
129.13
128.83
128.17
125.29
123.74
123.51
122.62
110.58
100.93
77.37
77.05
76.73
60.69
14.49



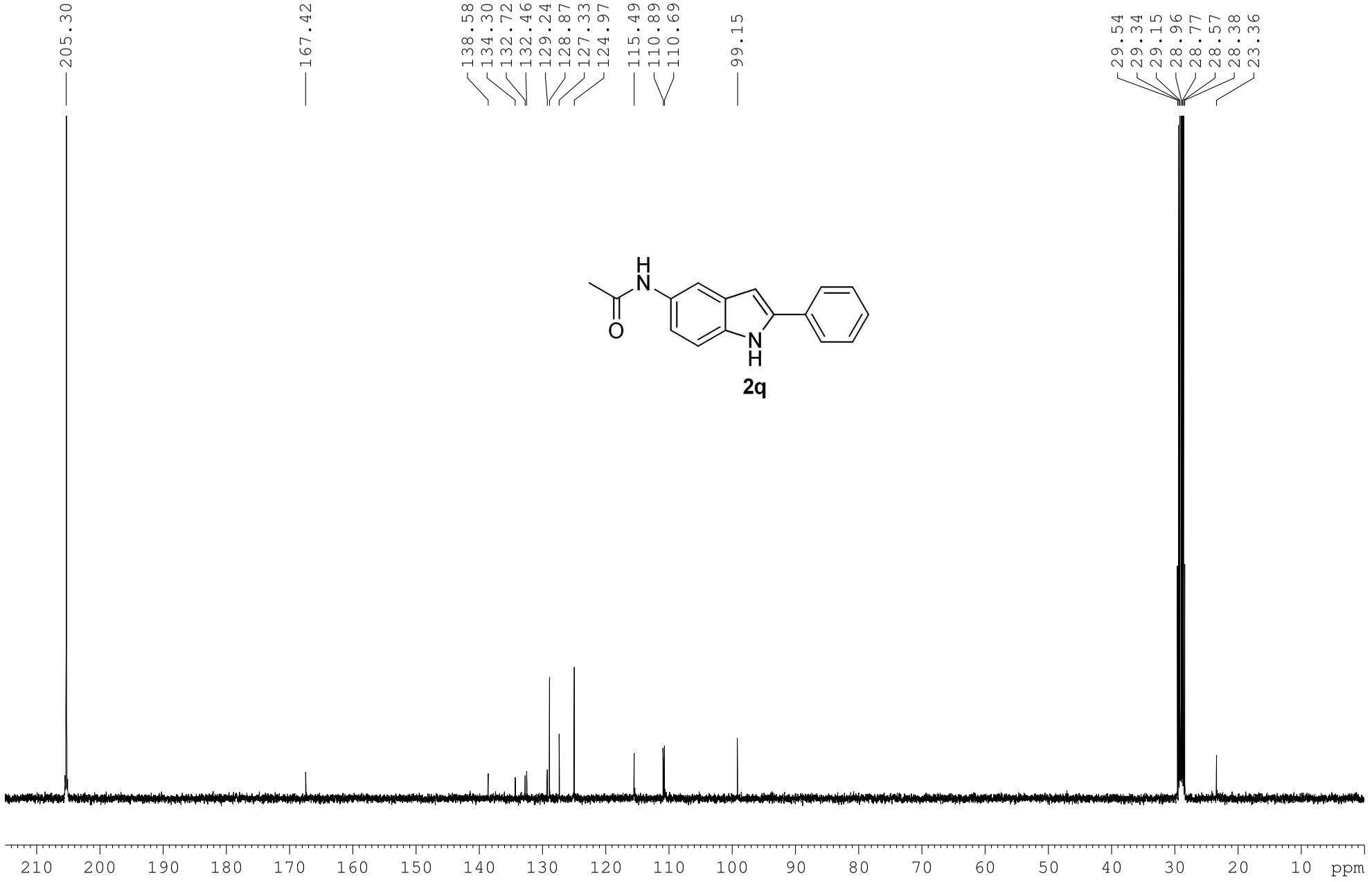
2m



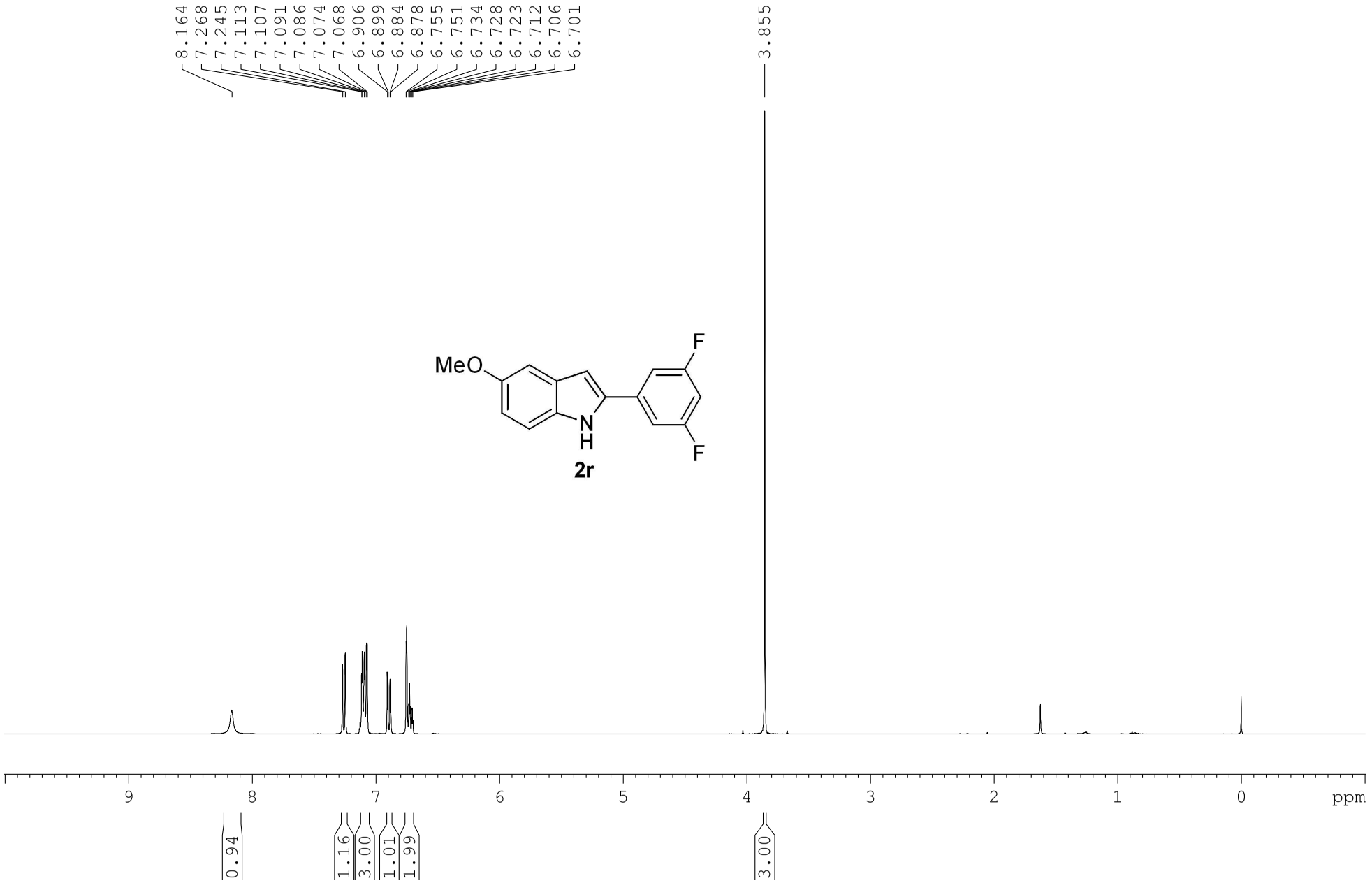
indole 2q, 1H NMR BBFO2 400MHz d6-acetone



indole 2q, 13C NMR BBFO2 400MHz d6-acetone

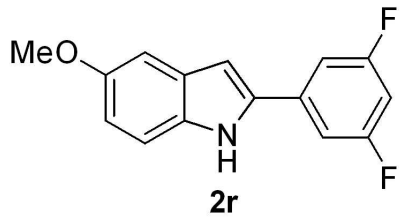


indole 2r 1H NMR BBFO2 400 MHz CDC3

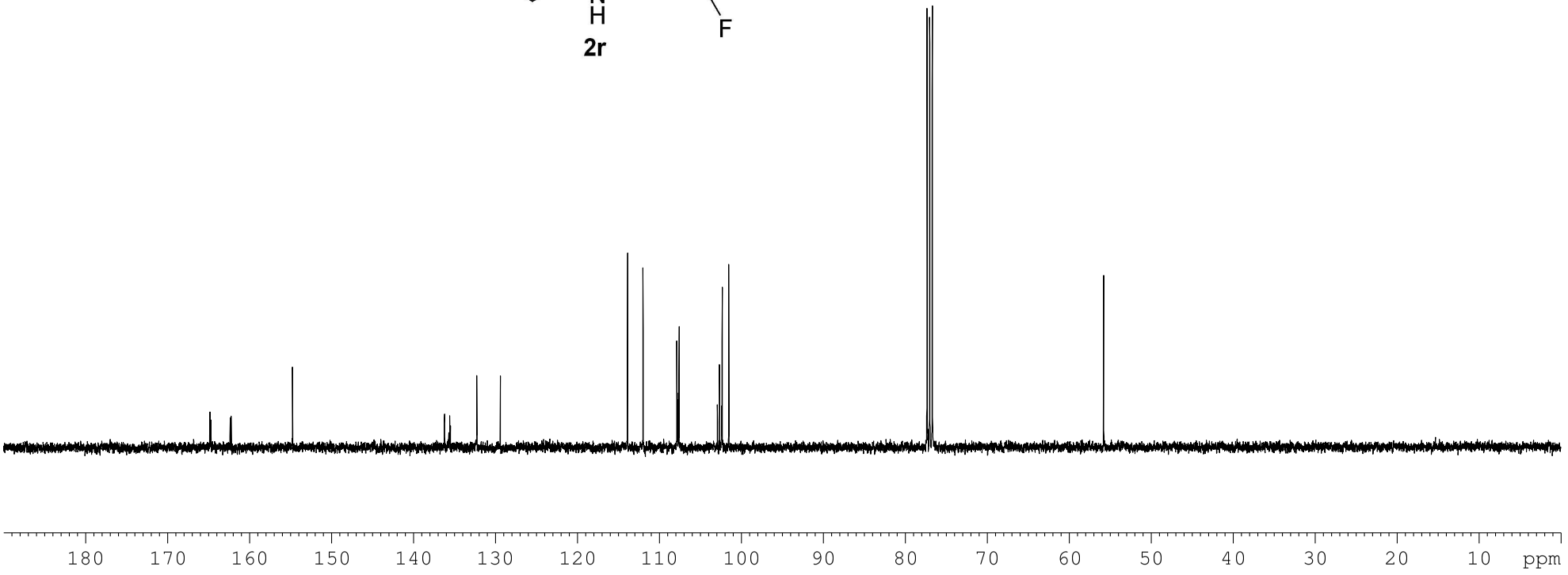


indole 2r 13C NMR BBFO2 400 MHz CDCl3

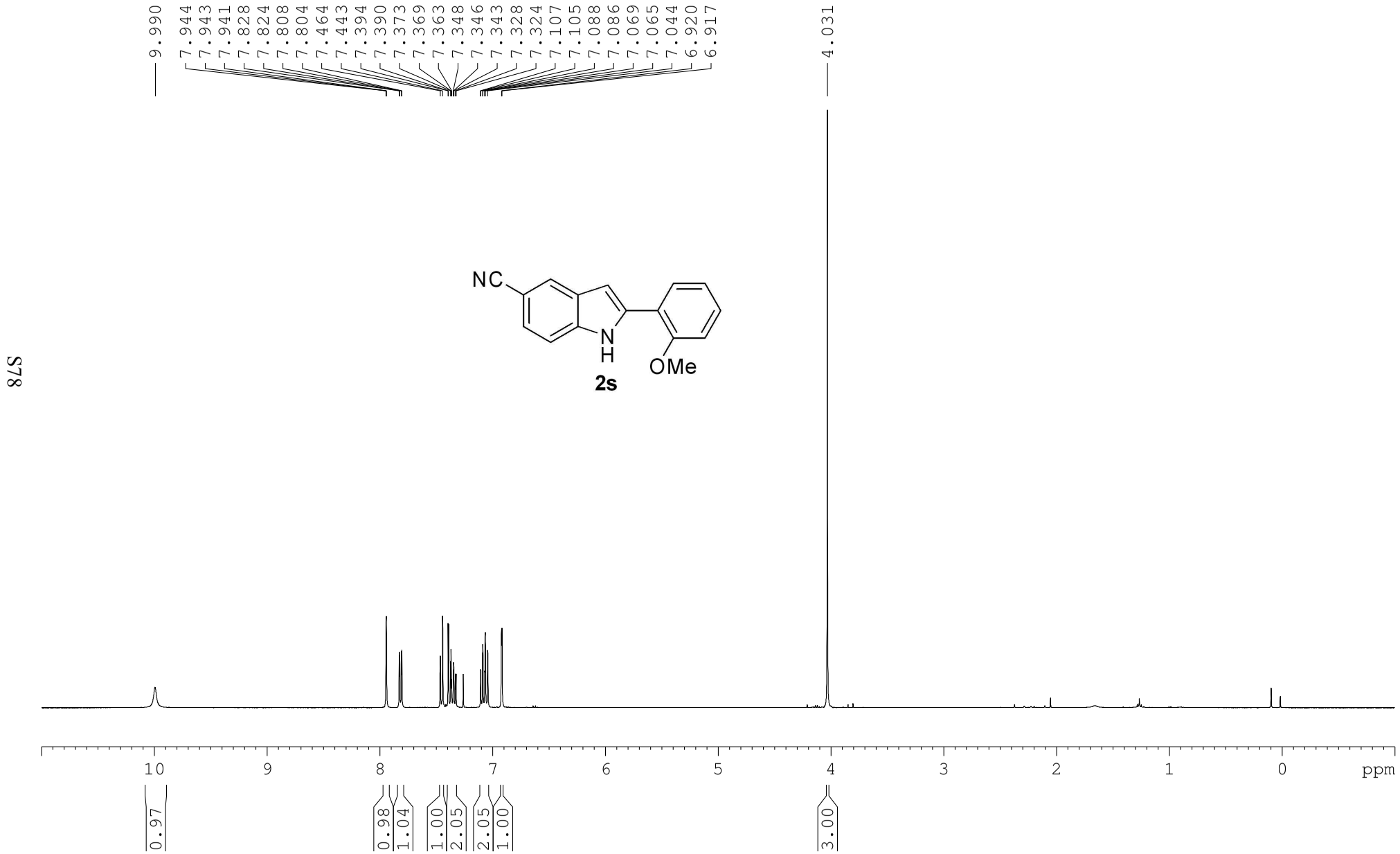
164.82
164.69
162.35
162.22
154.73
136.19
135.56
132.25
129.38
113.86
111.97
107.90
107.82
107.71
107.63
102.95
102.69
102.44
102.37
101.56
77.37
77.05
76.73
55.83

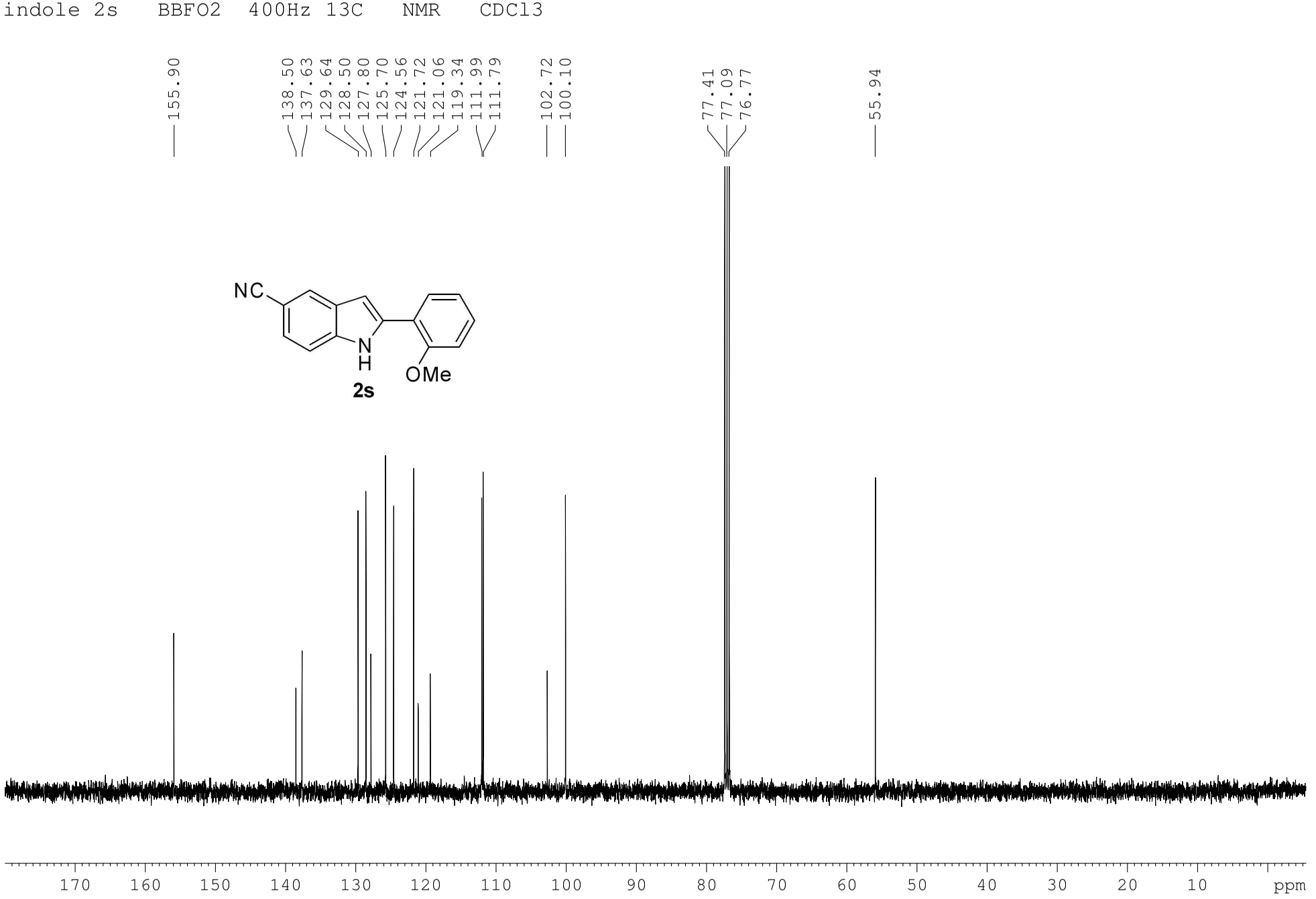


2r



indole 2s 1H NMR BBF02 400 MHz CDCl3



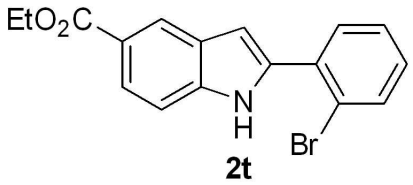

indole 2s BBFO2 400Hz 13C NMR CDCl3
155.90
138.50
137.63
129.64
128.50
127.80
125.70
124.56
121.72
121.06
119.34
111.99
111.79
102.72
100.10
77.41
77.09
76.77
55.94
NC
N
H
OMe
2s
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

indole 2t, 1H NMR BBFO2 400MHz CDCl3

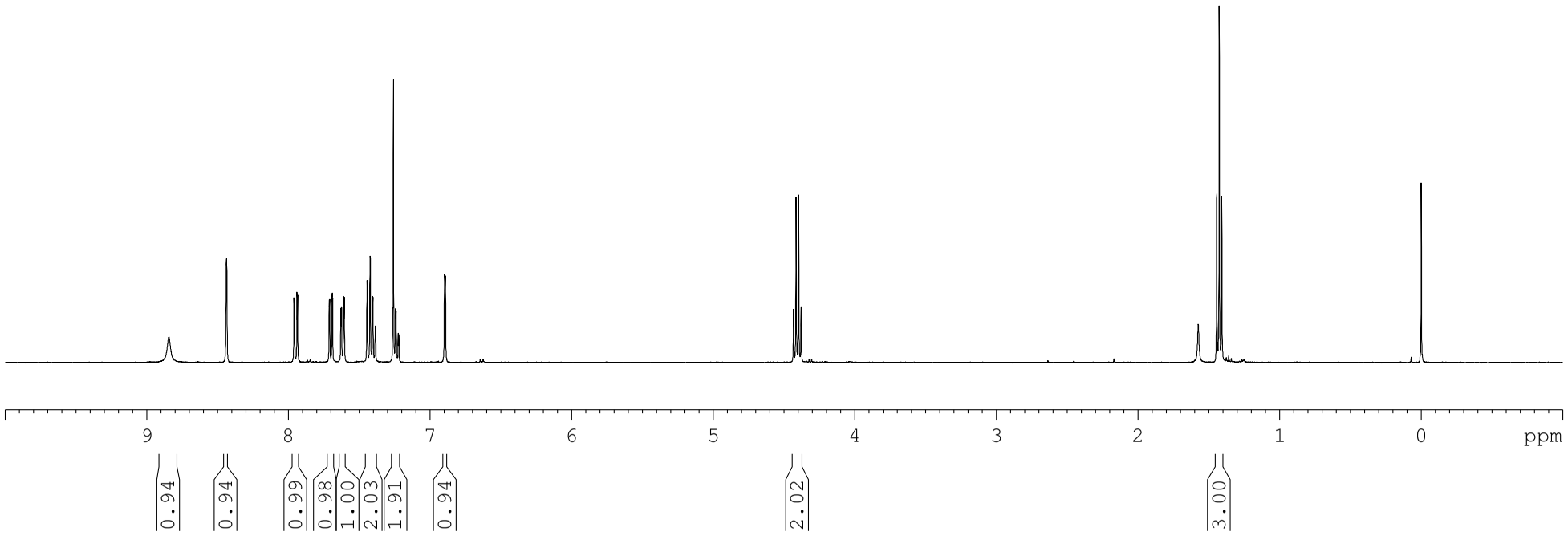
8.843
8.439
7.962
7.958
7.941
7.937
7.713
7.710
7.693
7.690
7.631
7.627
7.611
7.607
7.446
7.424
7.408
7.405
7.389
7.386
7.264
7.260
7.245
7.242
7.226
7.222
6.898
6.894

4.434
4.416
4.398
4.381

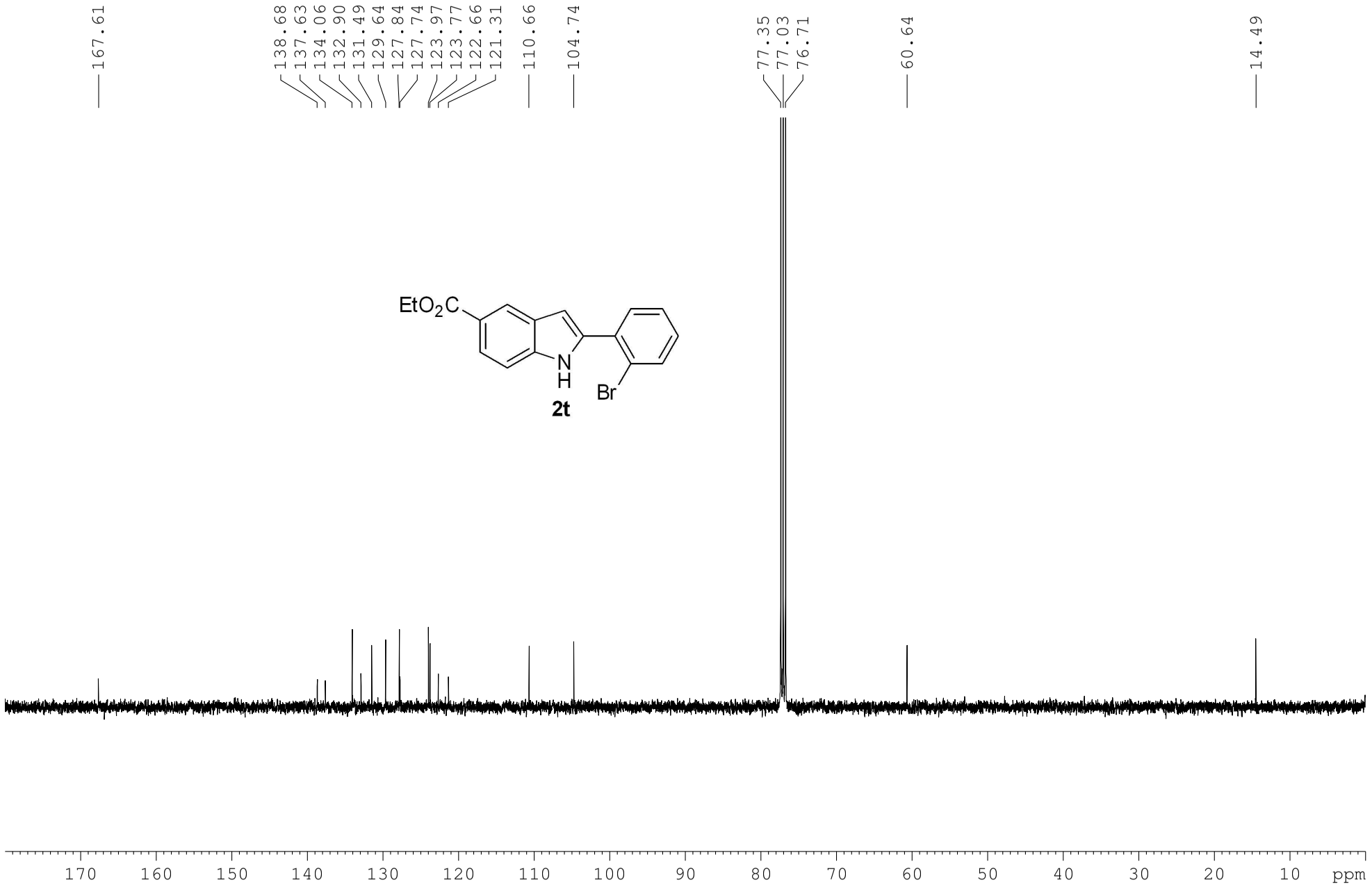
1.446
1.428
1.410



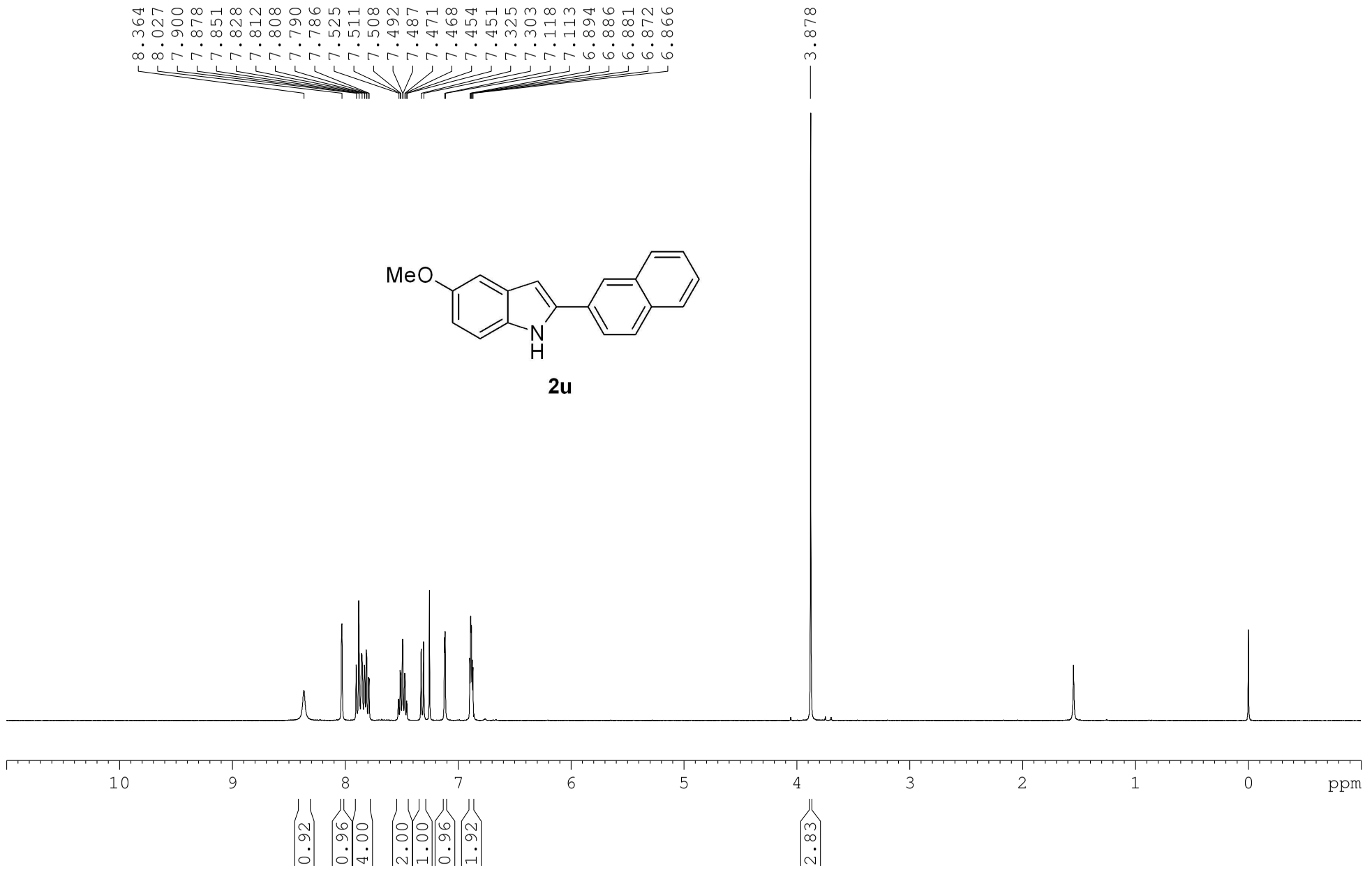
2t



indole 2t, 13C NMR BBFO2 400MHz CDCl3

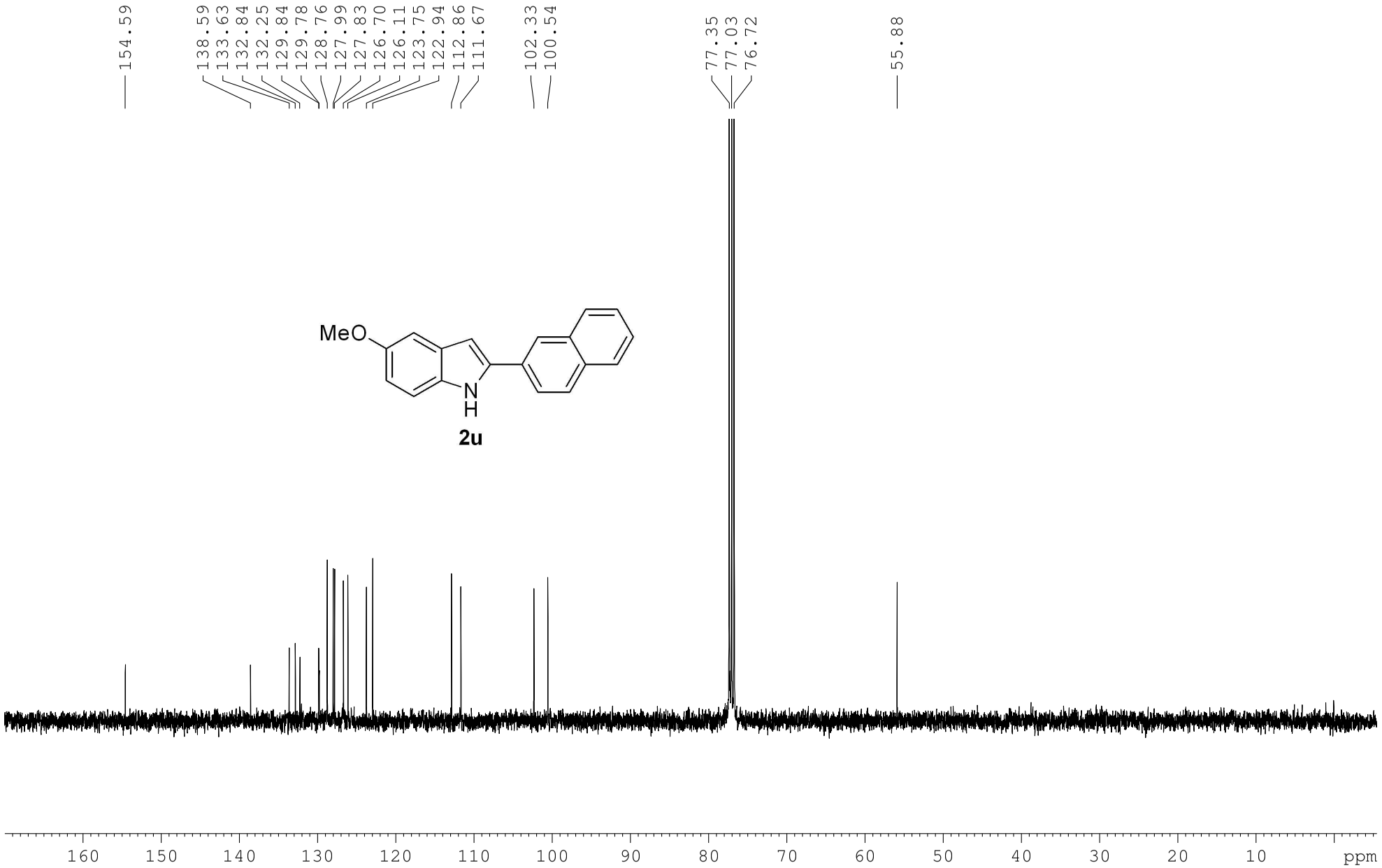


indole 2u 1H NMR BBFO2 400MHz CDCl3



2u

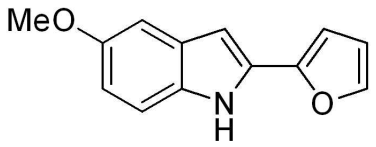
indole 2u 13C NMR BBFO2 400 MHz CDCL3



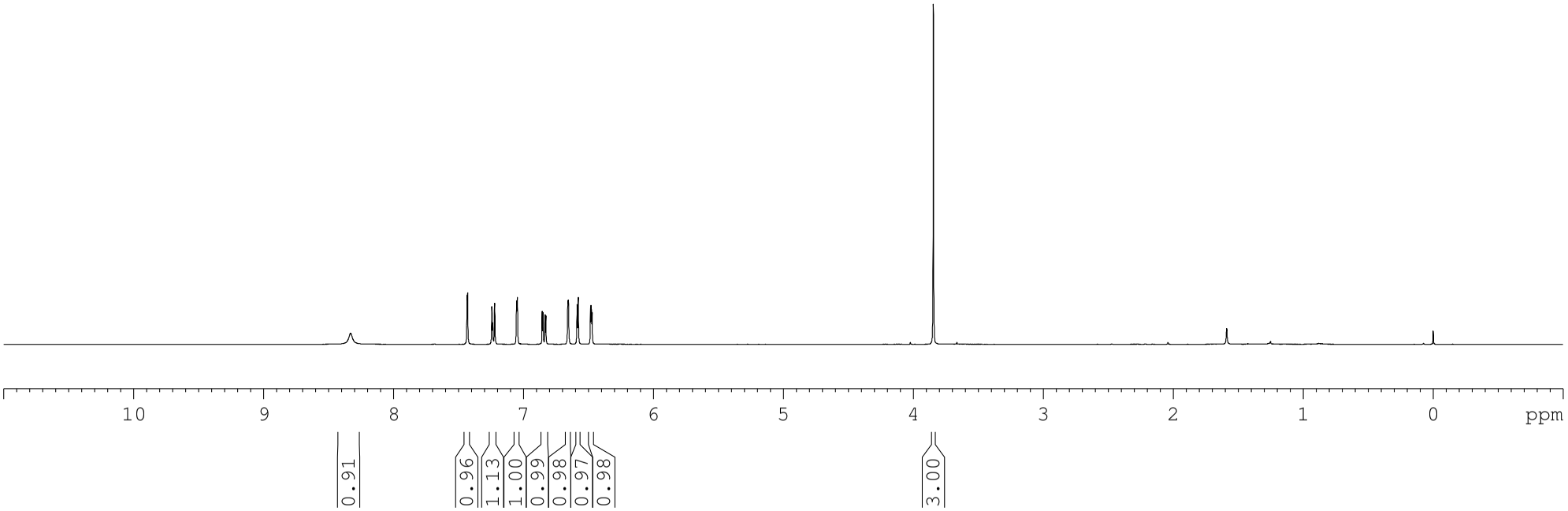
indole 2v 1H NMR BBFO2 400MHz CDCl3

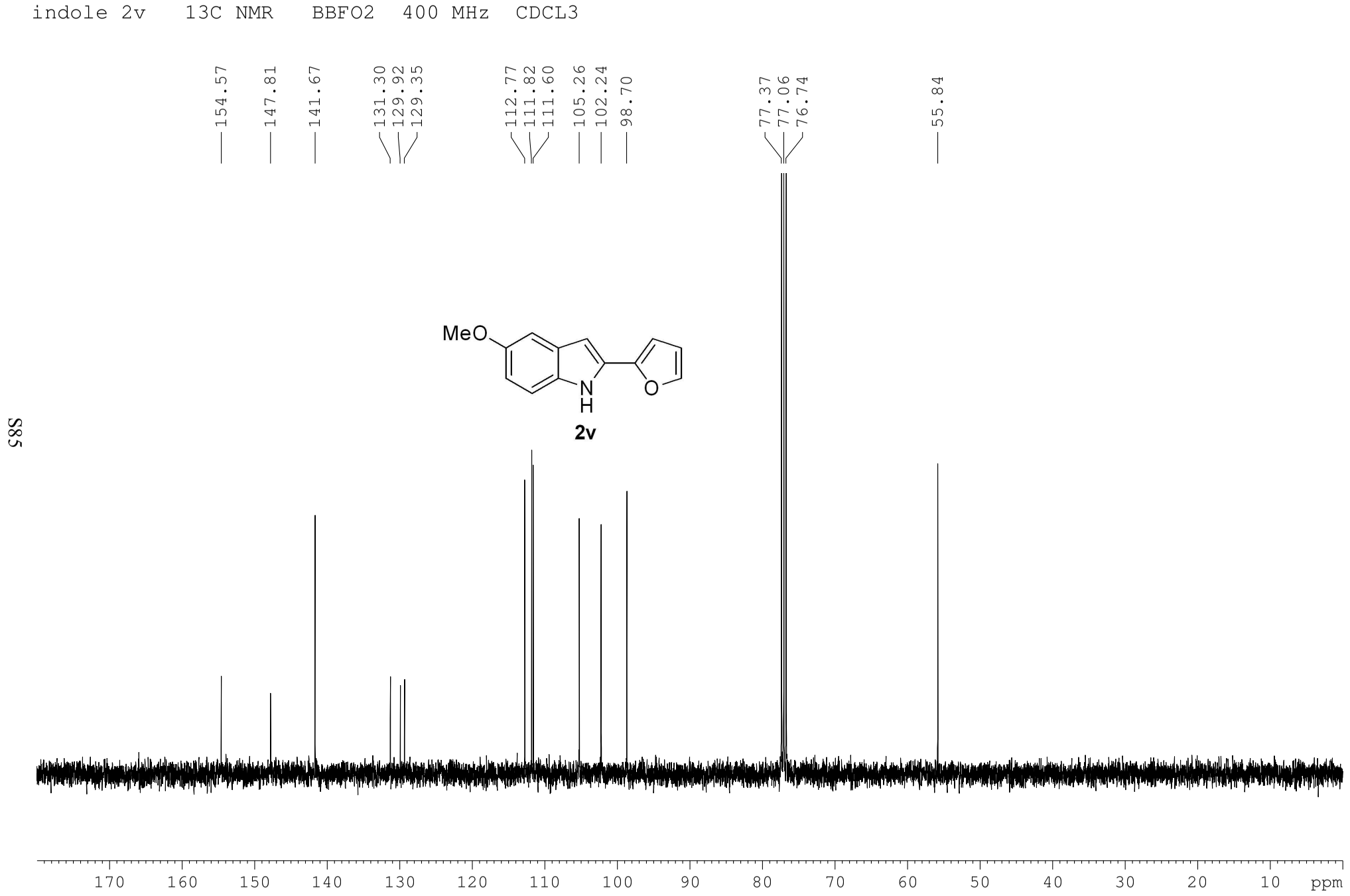
8.332
7.436
7.435
7.432
7.245
7.238
7.223
7.054
7.049
6.857
6.851
6.835
6.829
6.659
6.656
6.588
6.580
6.486
6.481
6.477
6.473

3.847

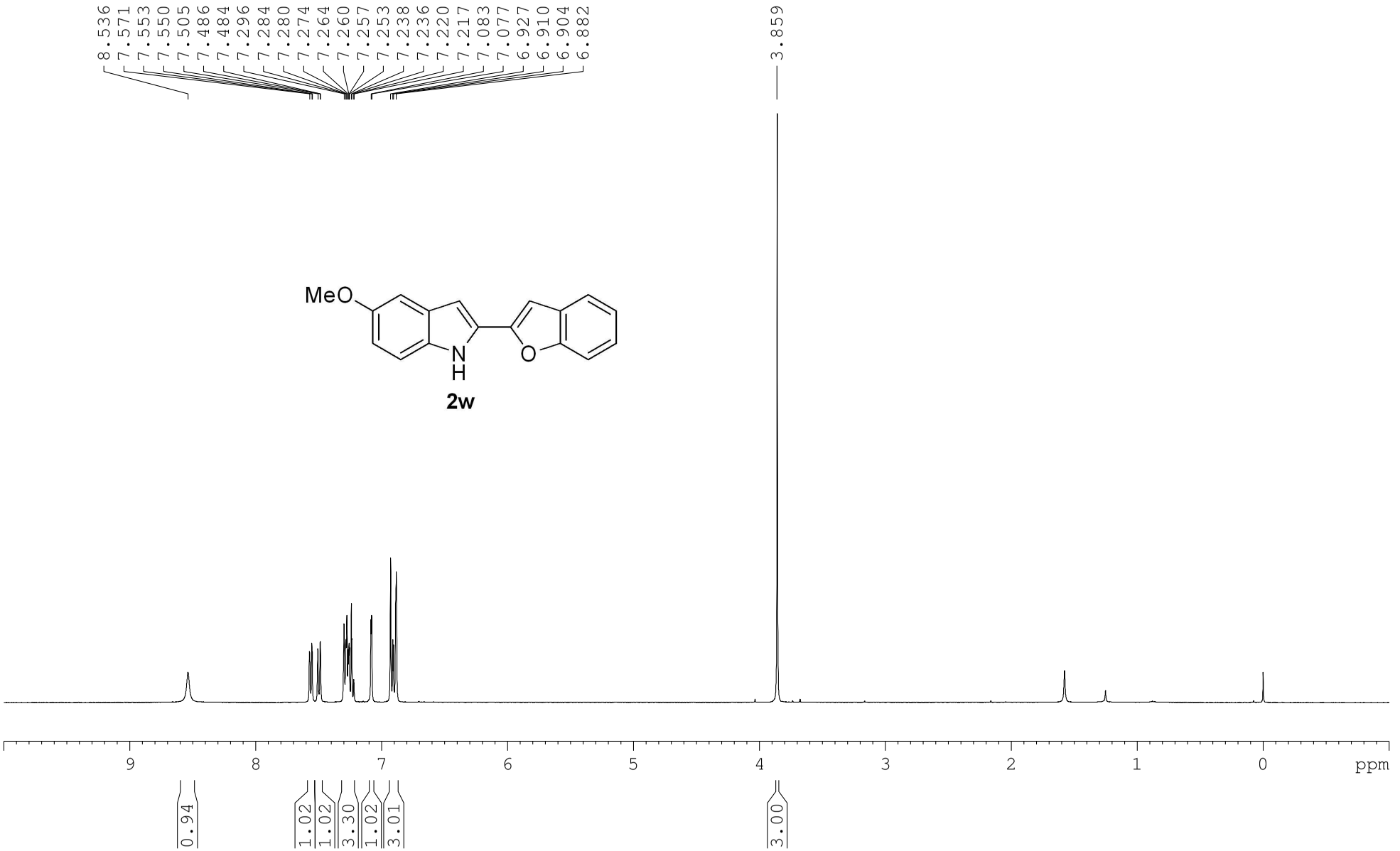


2v



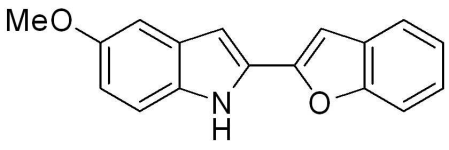

indole 2v 13C NMR BBFO2 400 MHz CDCL3
154.57
147.81
141.67
131.30
129.92
129.35
112.77
111.82
111.60
105.26
102.24
98.70
77.37
77.06
76.74
55.84
MeO
N
H
O
2v
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

indole 2w 1H NMR BBFO2 400 MHz CDCl3



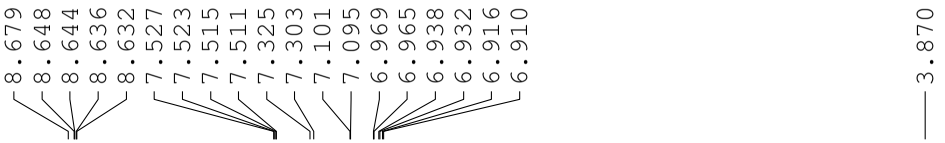
indole 2w 13C NMR BBFO2 400 MHz CDCl3

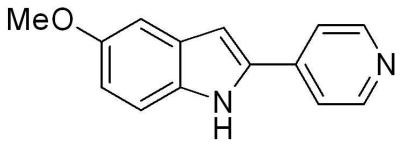
154.73
154.46
149.41
131.71
129.24
129.16
129.07
124.36
123.30
120.89
113.75
111.86
111.04
102.21
101.27
100.99
77.36
77.05
76.73
55.82



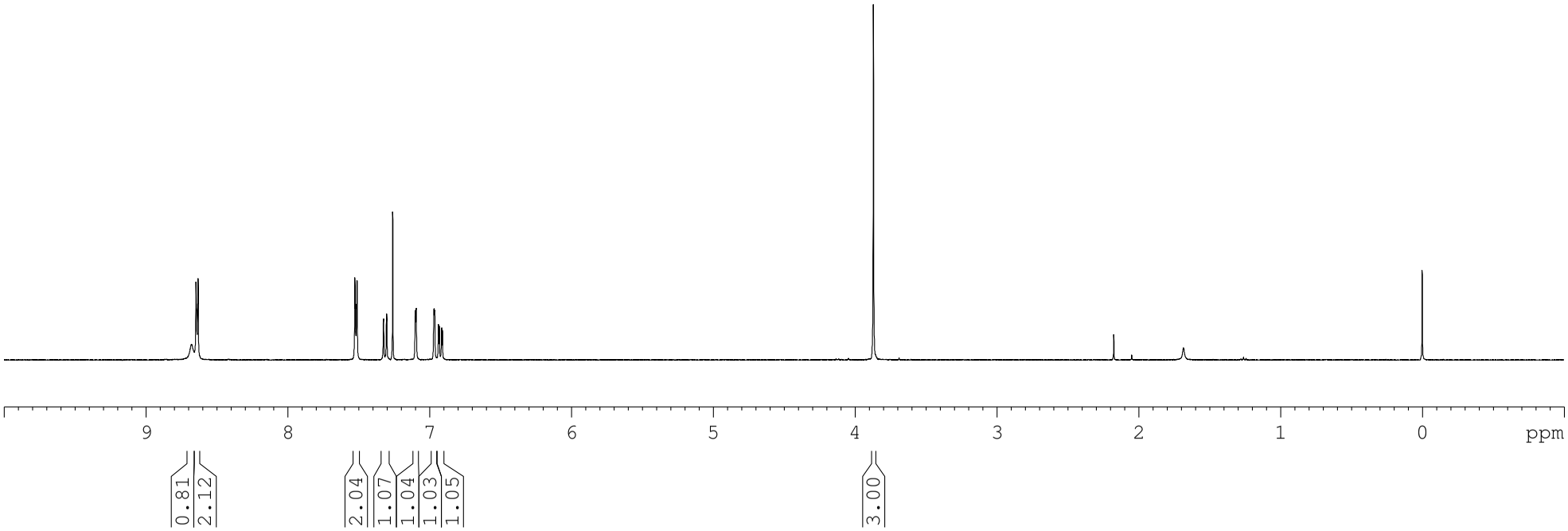
2w

indole 2x, 1H NMR BBFO2 400MHz CDCl3

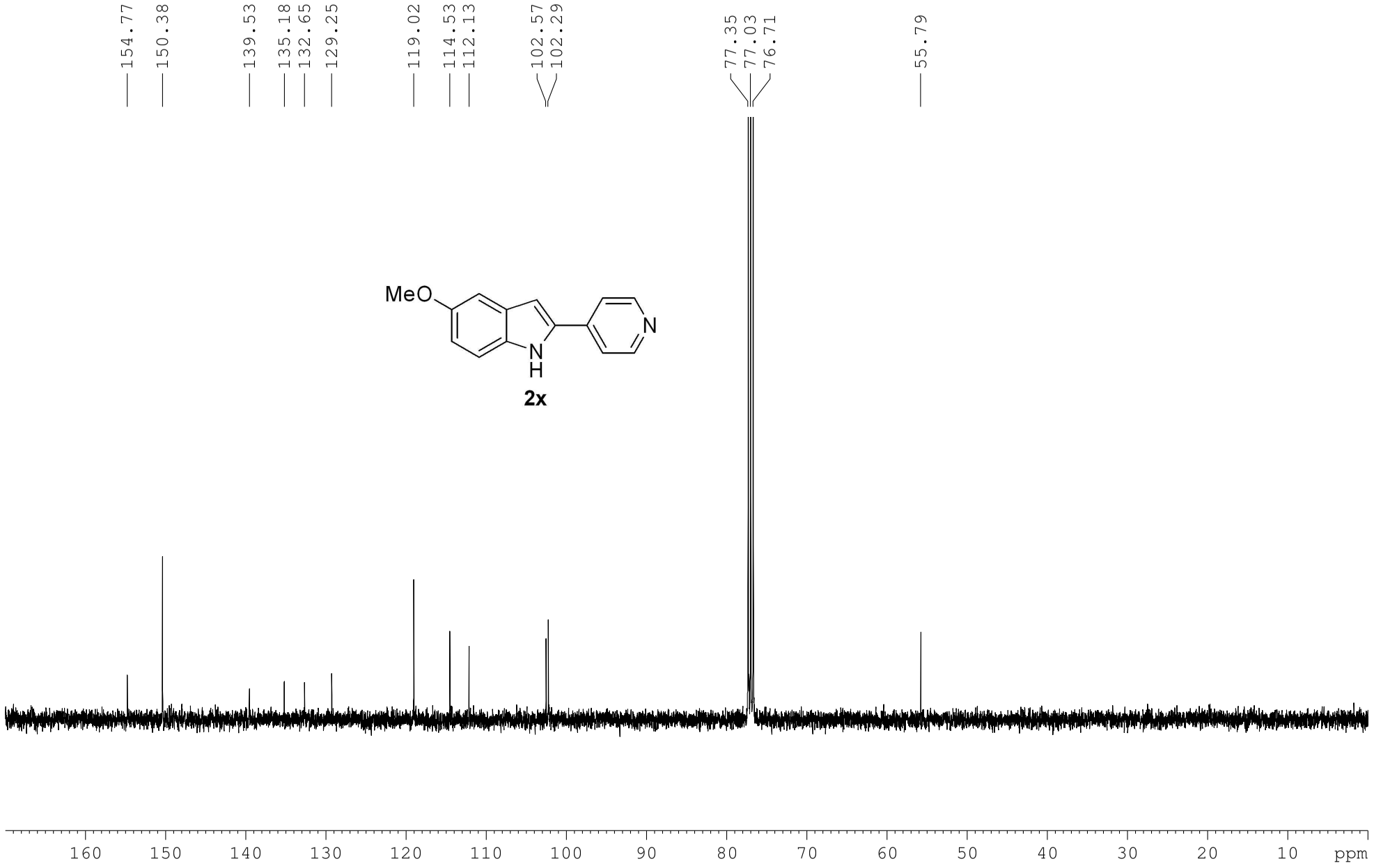




2x

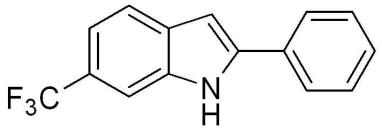


indole 2x, 13C NMR BBOF2 400 MHz CDCl3

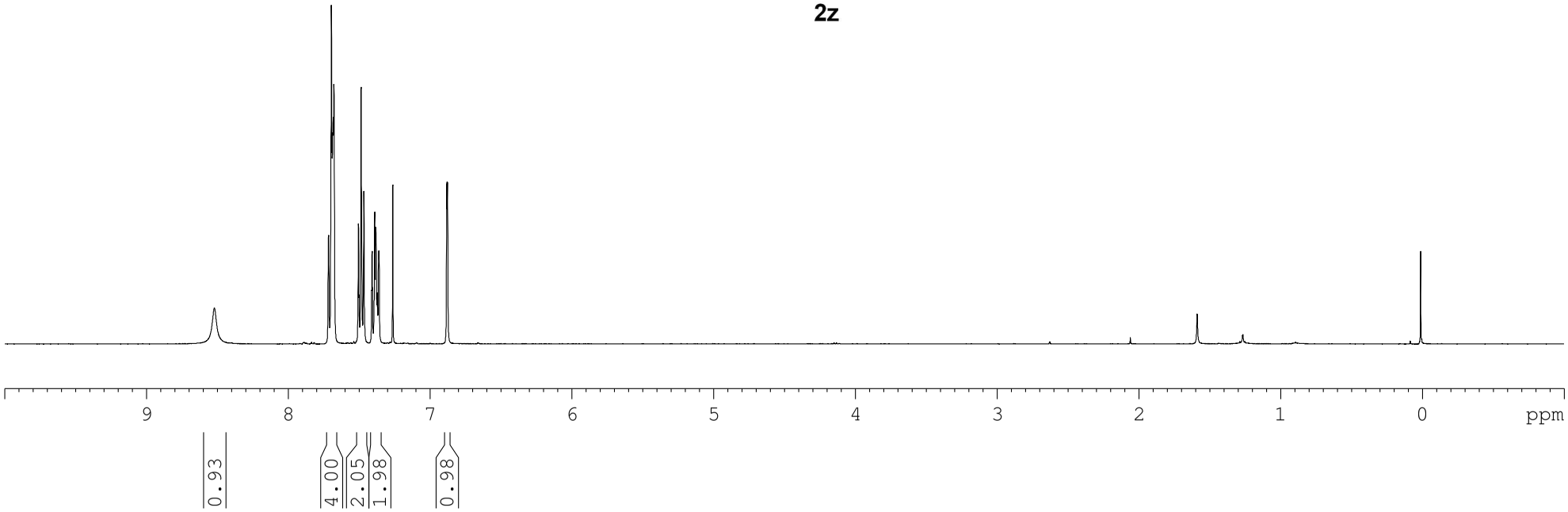


wy-2-348-indole 2z, 1H NMR BBFO2 400MHz CDCl3

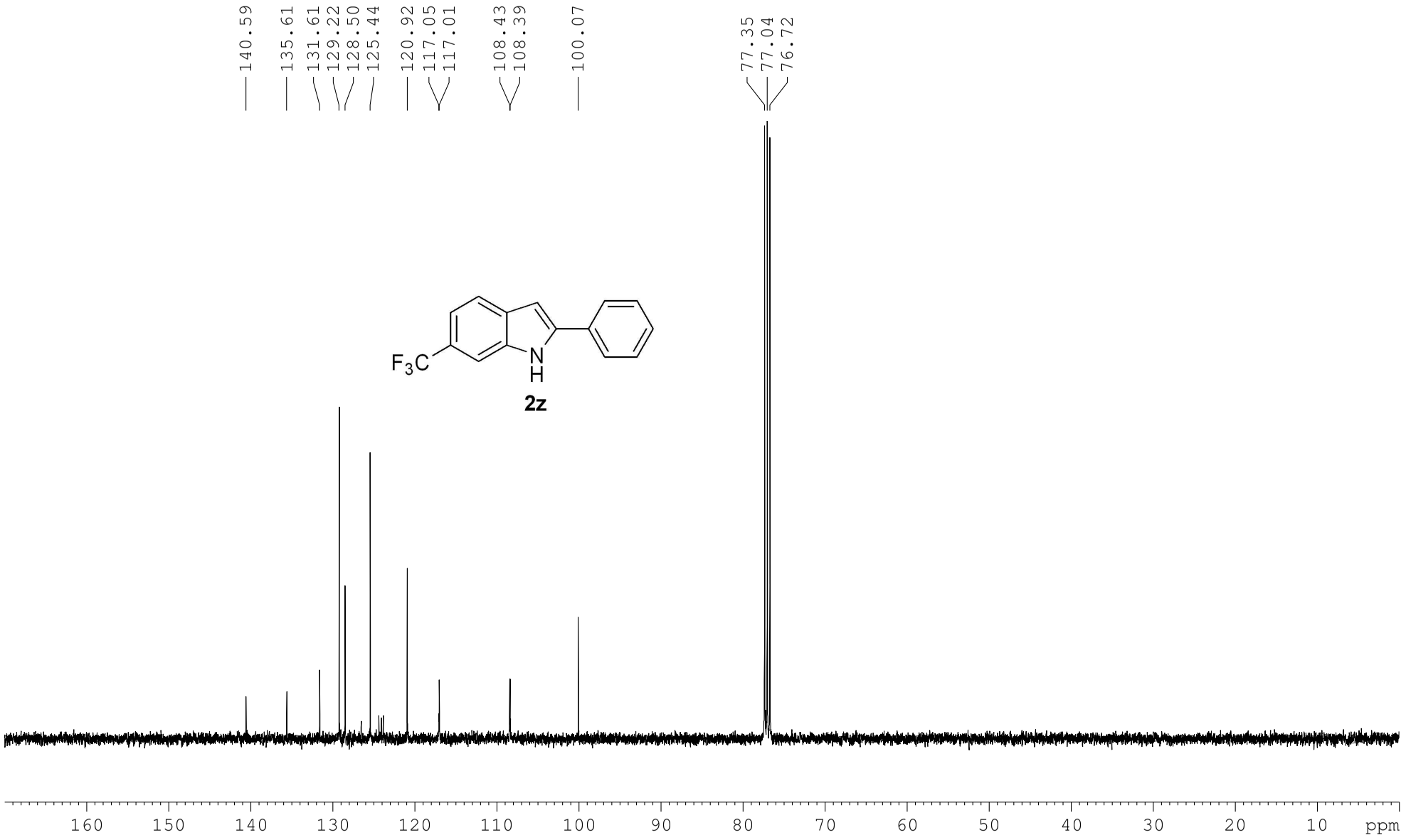
8.518
7.713
7.696
7.693
7.688
7.684
7.682
7.680
7.675
7.502
7.497
7.483
7.464
7.409
7.406
7.404
7.392
7.388
7.381
7.378
7.369
7.367
7.359
7.357
6.878
6.875
6.873



2z



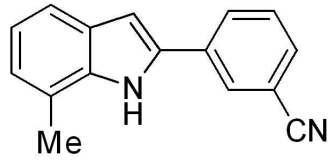
wy-2-348-indole 2z, 13C NMR BBFO2 400MHz CDCl3



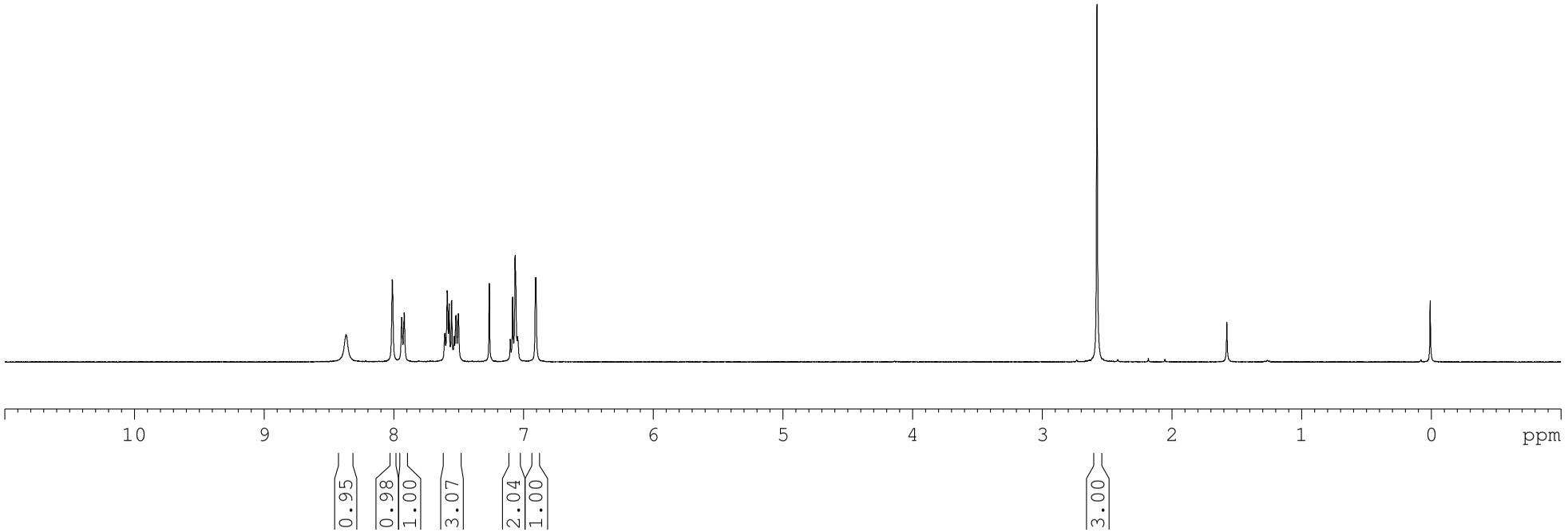
indole 2ac, 1H NMR BBFO2 400MHz CDCl3

8.365
8.008
7.936
7.917
7.603
7.584
7.570
7.551
7.532
7.517
7.499
7.101
7.083
7.065
7.045
6.908
6.903

2.577

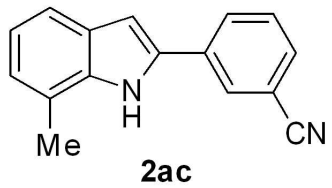


2ac



indole 2ac, 13C NMR BBFO2 400MHz CDCl3

136.92
135.05
133.94
130.62
129.86
129.37
128.50
128.47
123.88
120.94
120.52
118.77
113.18
102.24
77.36
77.04
76.72
16.85

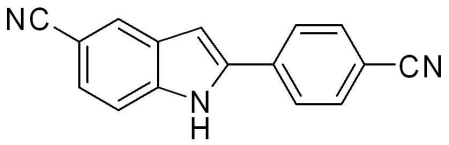


2ac

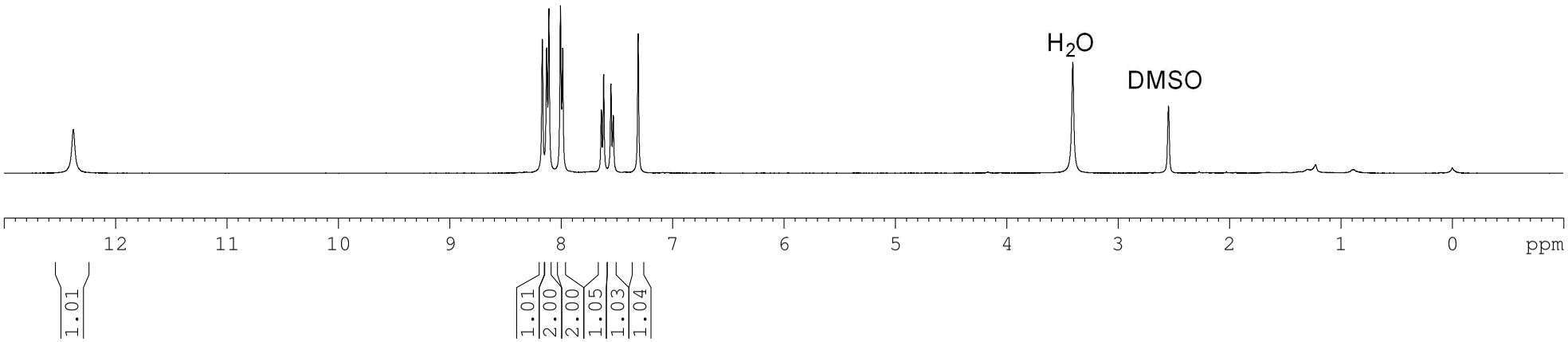
indole 2ad 1H NMR BBFO1 400 MHz DMSO-d6

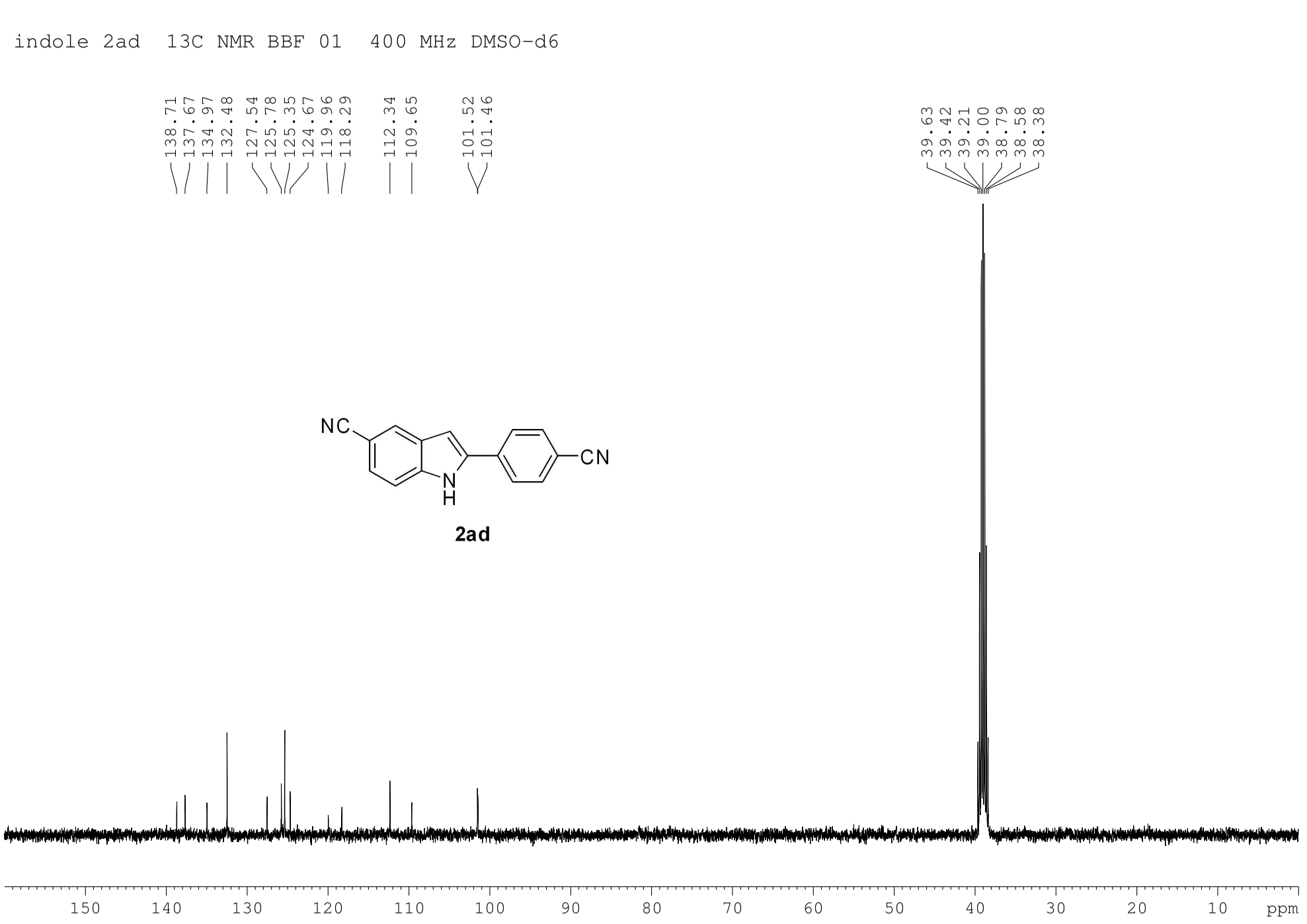
12.376

8.169
8.130
8.109
8.006
7.985
7.638
7.617
7.553
7.532
7.308

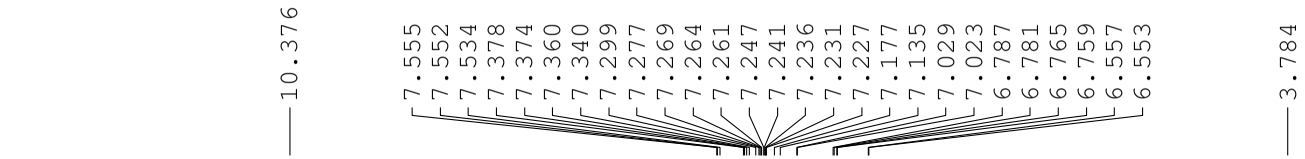


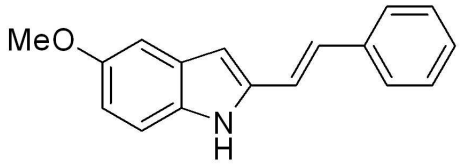
2ad



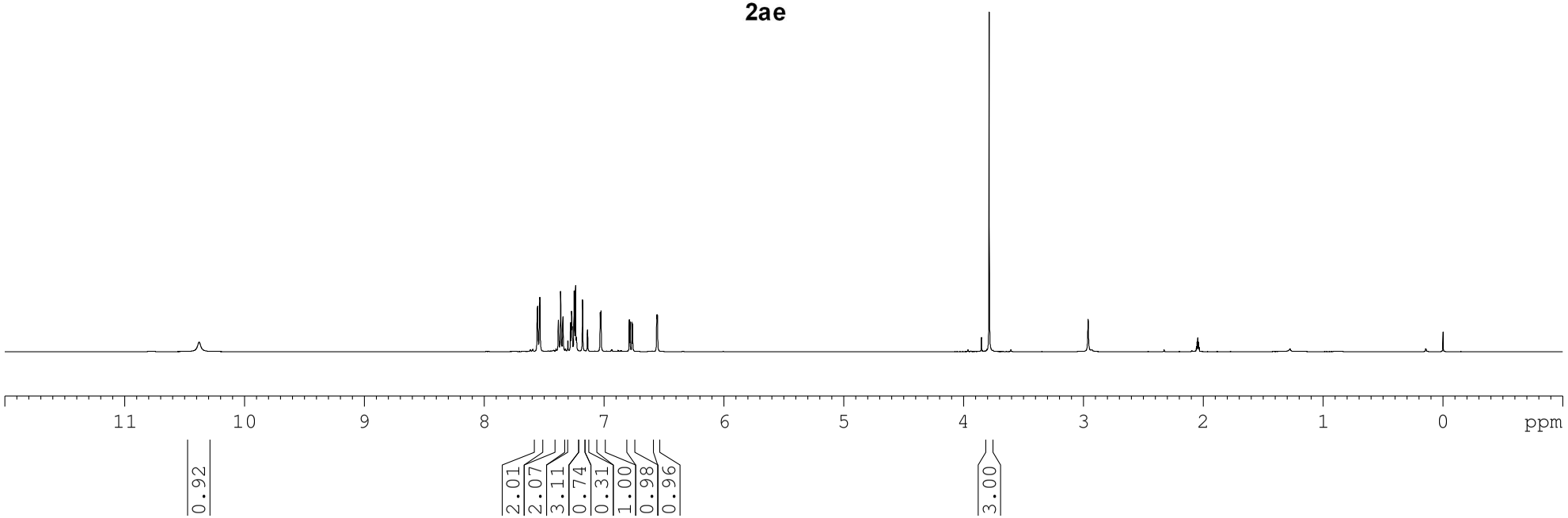

indole 2ad 13C NMR BBF 01 400 MHz DMSO-d6
138.71
137.67
134.97
132.48
127.54
125.78
125.35
124.67
119.96
118.29
112.34
109.65
101.52
101.46
39.63
39.42
39.21
39.00
38.79
38.58
38.38
NC
CN
N
H
2ad
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

indole 2ae 1H NMR BBFO1 400Hz acetone-d6



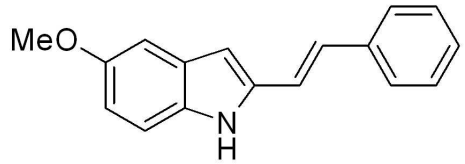


2ae

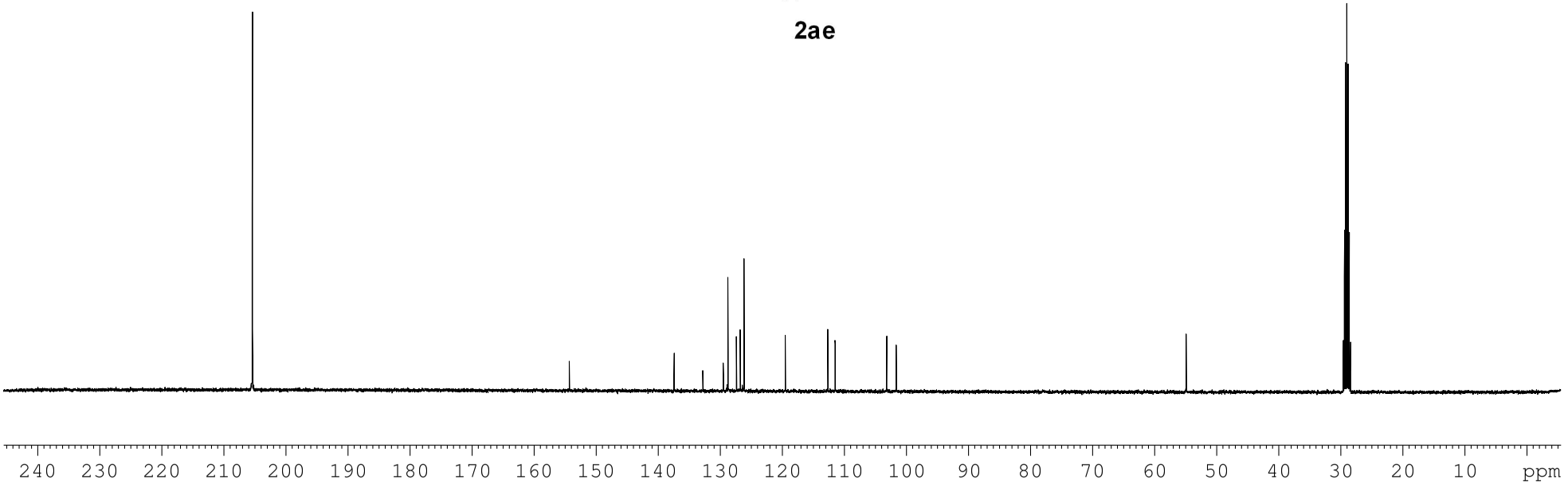


indole 2ae 13C NMR BBFO1 400Hz acetone-d6

205.39
154.32
137.43
137.42
132.79
129.49
128.74
127.38
126.78
126.15
119.50
112.67
111.47
103.15
101.63
54.88
29.56
29.37
29.18
28.99
28.79
28.60
28.41



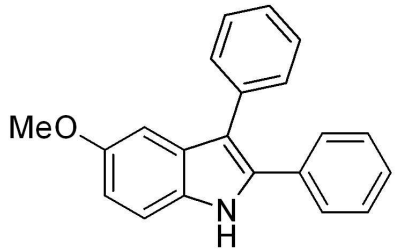
2ae



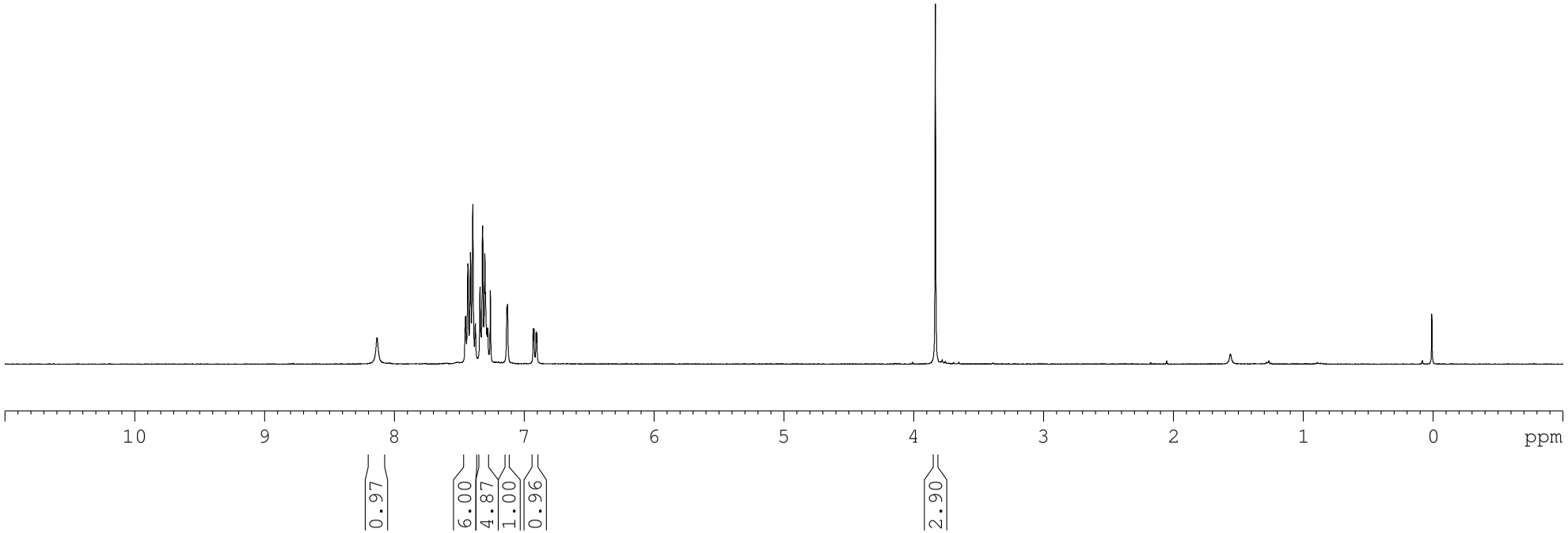
indole 2af, 1H NMR BBFO2 400MHz CDCl3

8.133
7.451
7.434
7.414
7.395
7.376
7.340
7.320
7.302
7.297
7.287
7.281
7.133
7.128
6.930
6.924
6.908
6.902

3.832

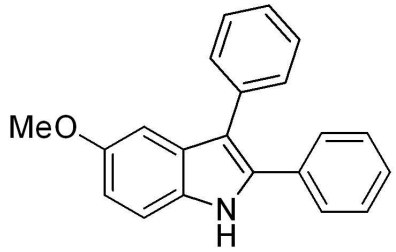


2af

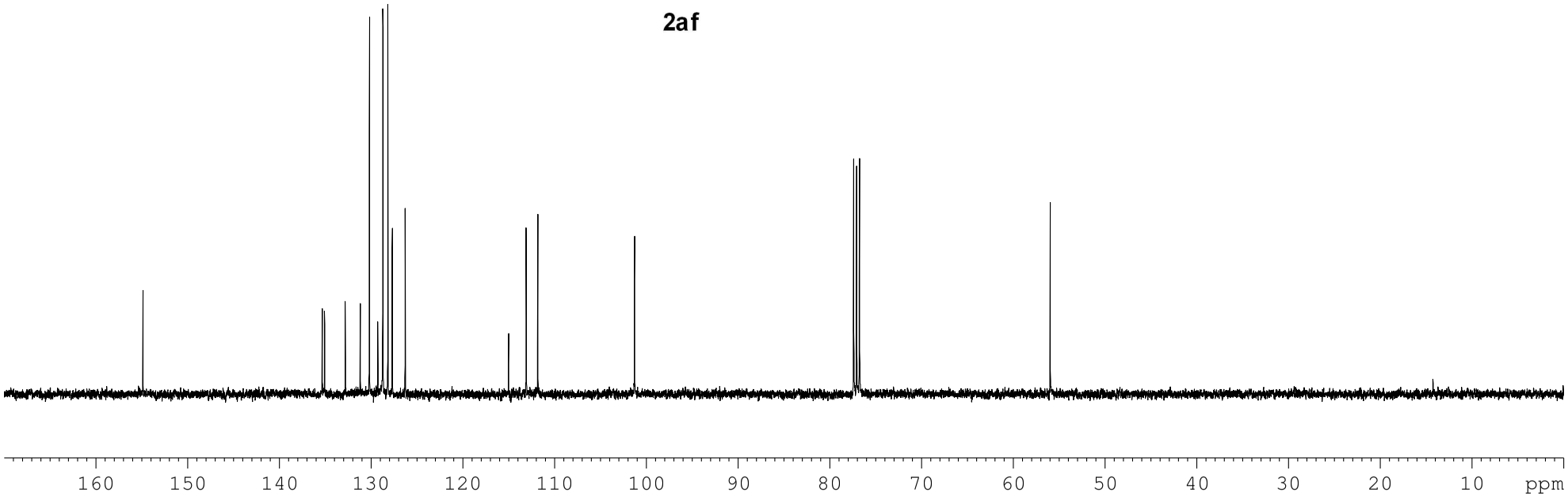


indole 2af 13C NMR BBOF01 CDCl3

154.82
135.28
135.02
132.77
131.13
130.14
129.22
128.68
128.66
128.12
127.65
126.24
114.97
113.05
111.78
101.28
77.40
77.08
76.77
55.98



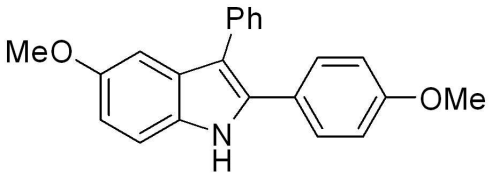
2af



ndole 2ag 1H NMR CDCl3, BBOF1 400MHz

8.088
7.460
7.442
7.422
7.404
7.384
7.338
7.333
7.321
7.316
7.309
7.287
7.144
7.140
6.917
6.911
6.895
6.889
6.866
6.862
6.844

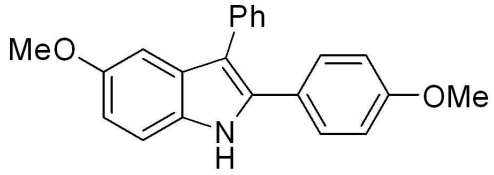
3.838
3.814



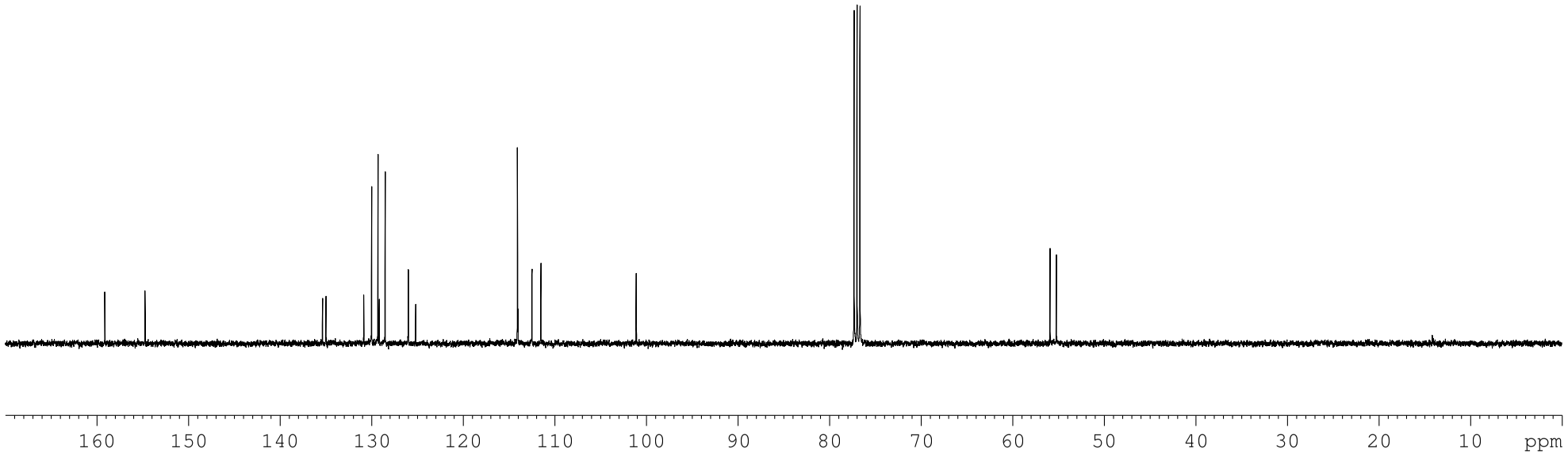
2ag

indole 2ag 13C NMR 400 MHz BBFO1 CDCl3

159.12
154.71
135.38
135.00
130.88
130.02
129.32
129.19
128.54
126.00
125.20
114.08
114.02
112.51
111.53
101.11
77.32
77.00
76.68
55.91
55.22



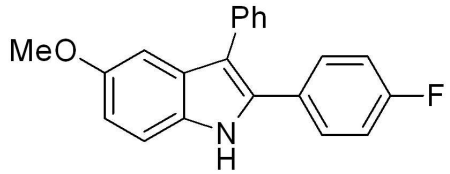
2ag



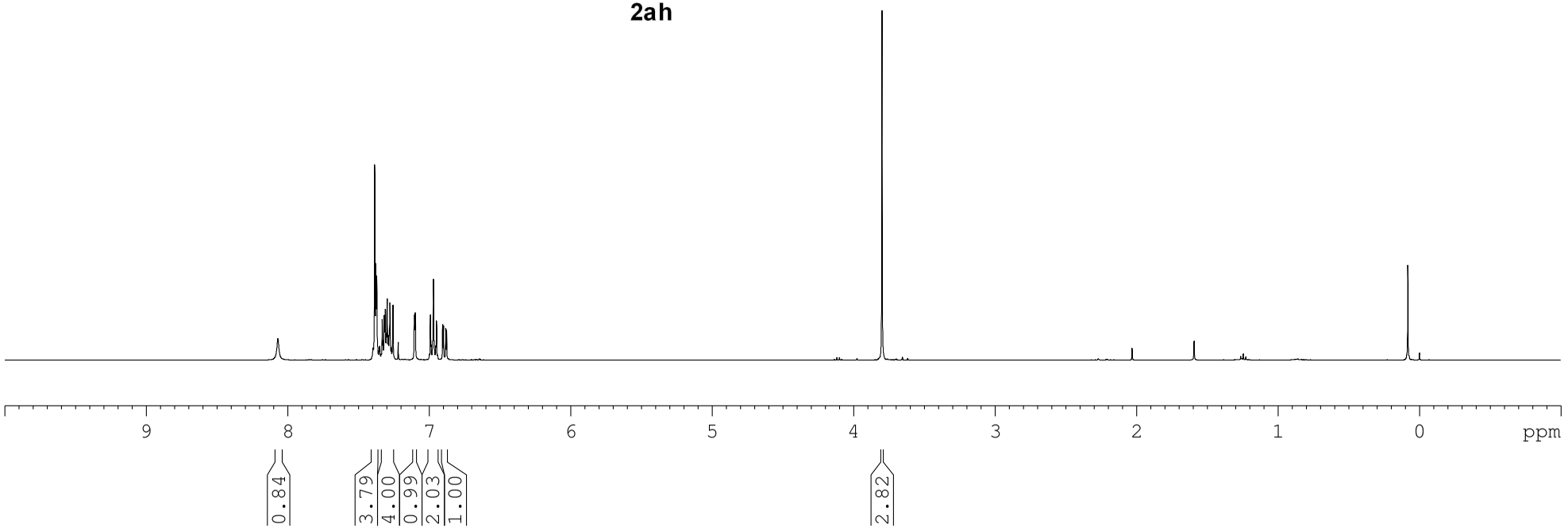
indole 2ah 1H NMR 400 MHz BBFO1 CDCl3

8.068
7.399
7.397
7.386
7.379
7.372
7.333
7.320
7.311
7.298
7.279
7.257
7.106
7.100
6.993
6.971
6.949
6.906
6.900
6.884
6.878

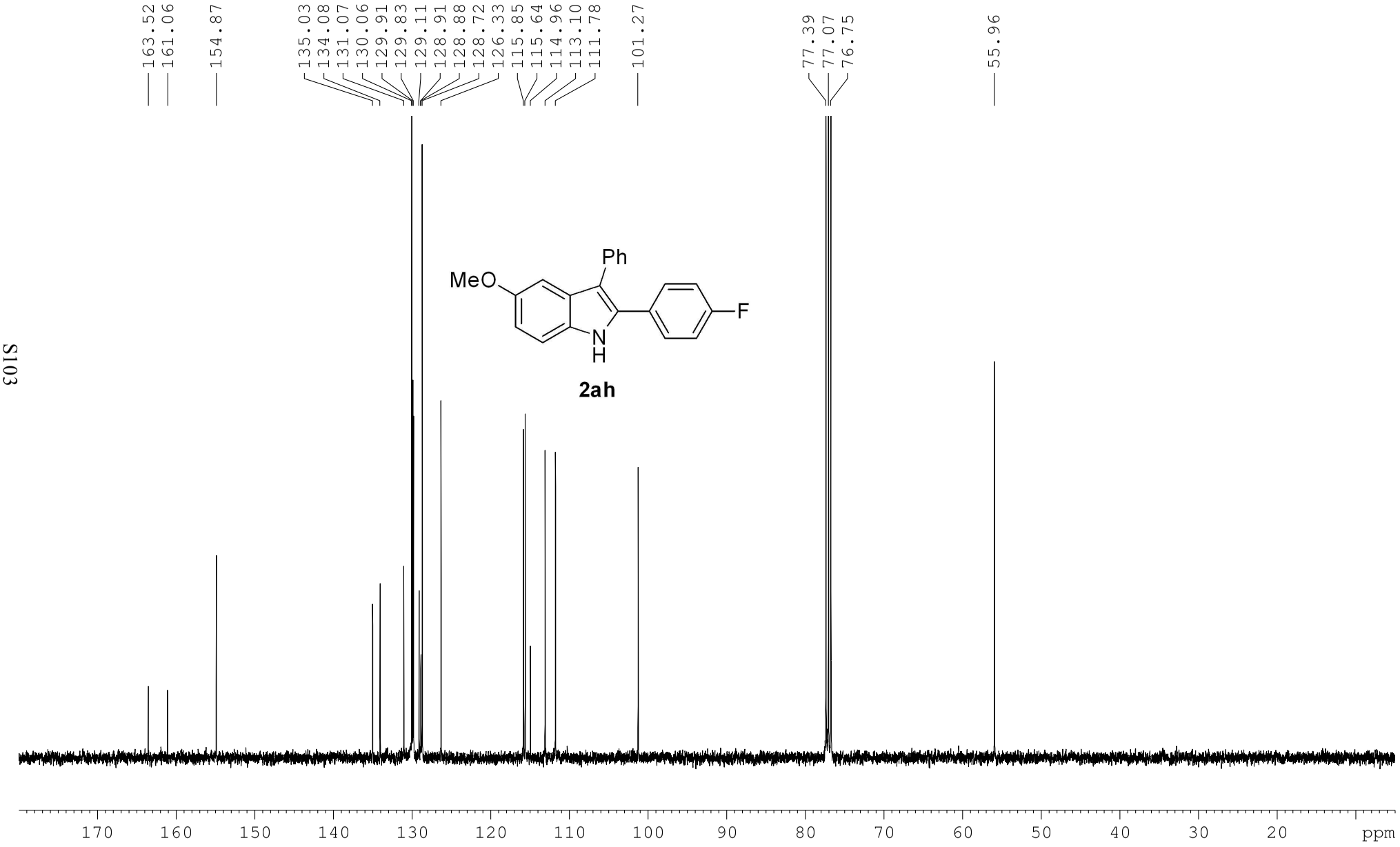
3.800



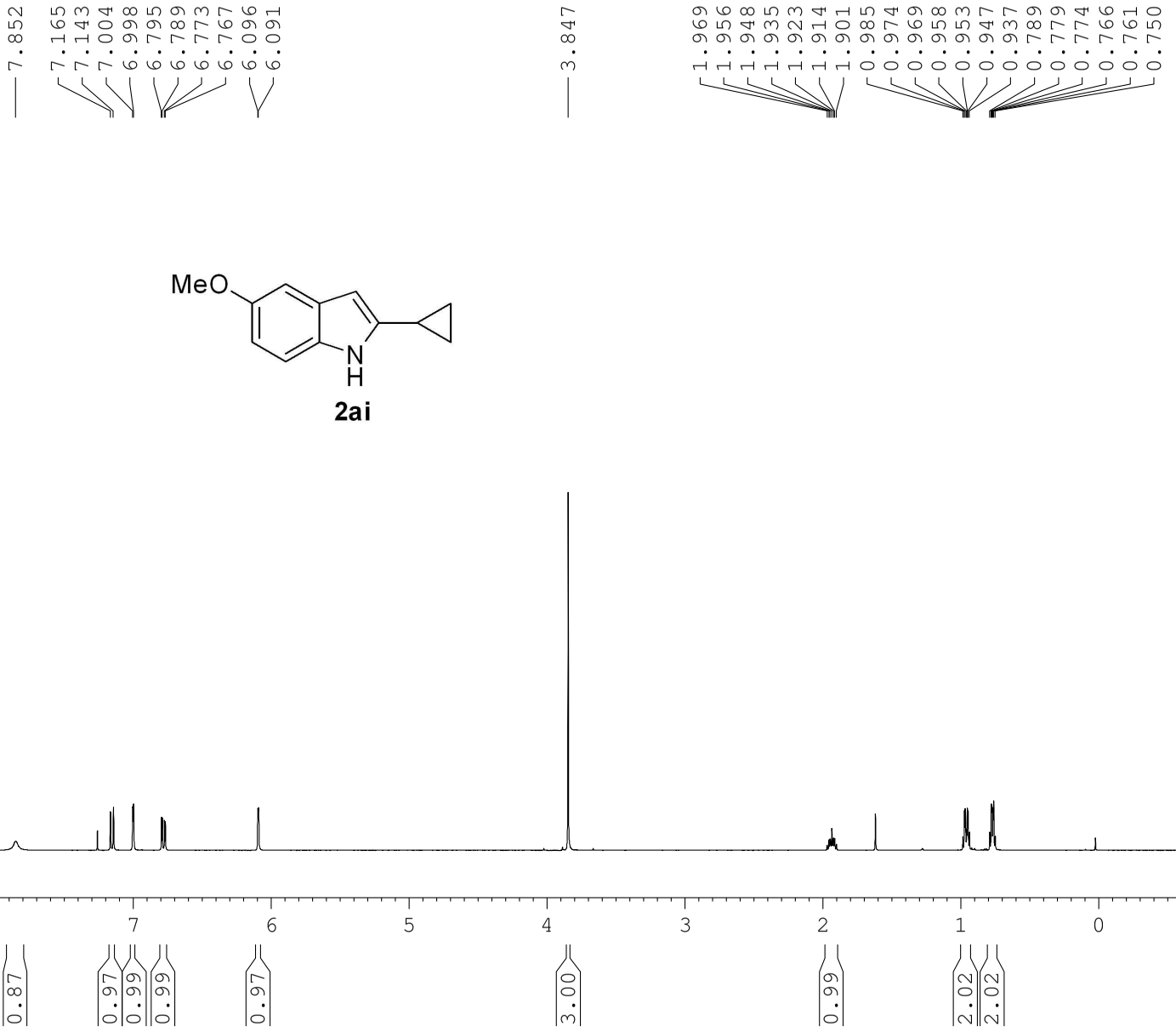
2ah



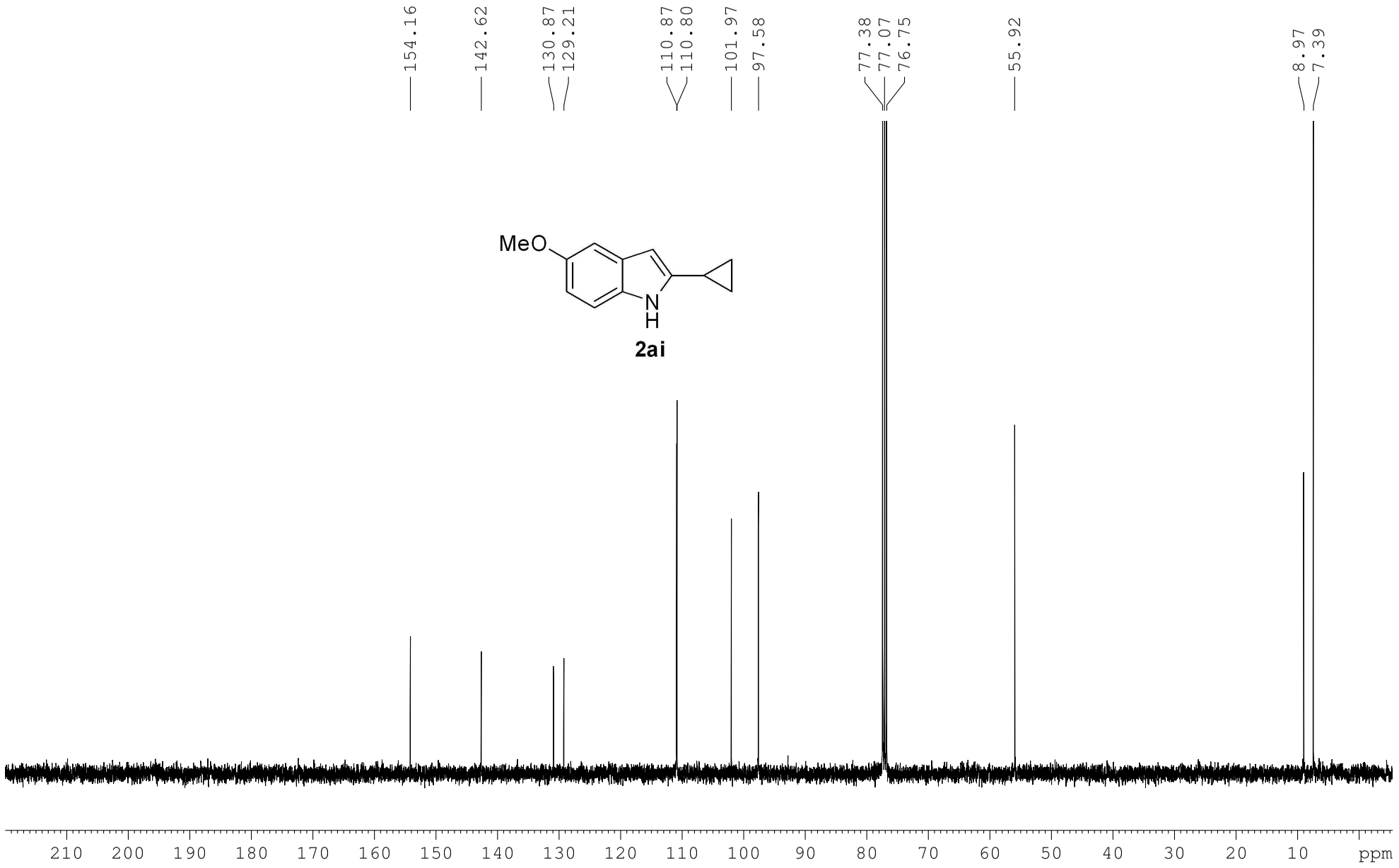
indole 2ah 13C NMR 400 MHz BBFO1 CDCl3



wy-2-236-indole 2ai, 1H NMR BBFO1 400Hz in CDCl3



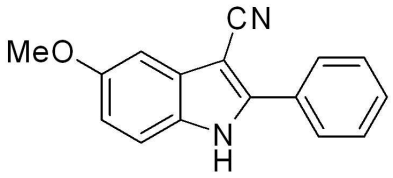
wy-2-236-indole 2ai, 13C NMR BBFO1 400Hz in CDCl3



indole-2ak 1H NMR DMSO-d6 BBOF1 400MHz

7.983
7.964
7.654
7.635
7.616
7.567
7.549
7.531
7.481
7.459
7.101
6.970
6.967
6.948
6.945

3.854



2ak

S106

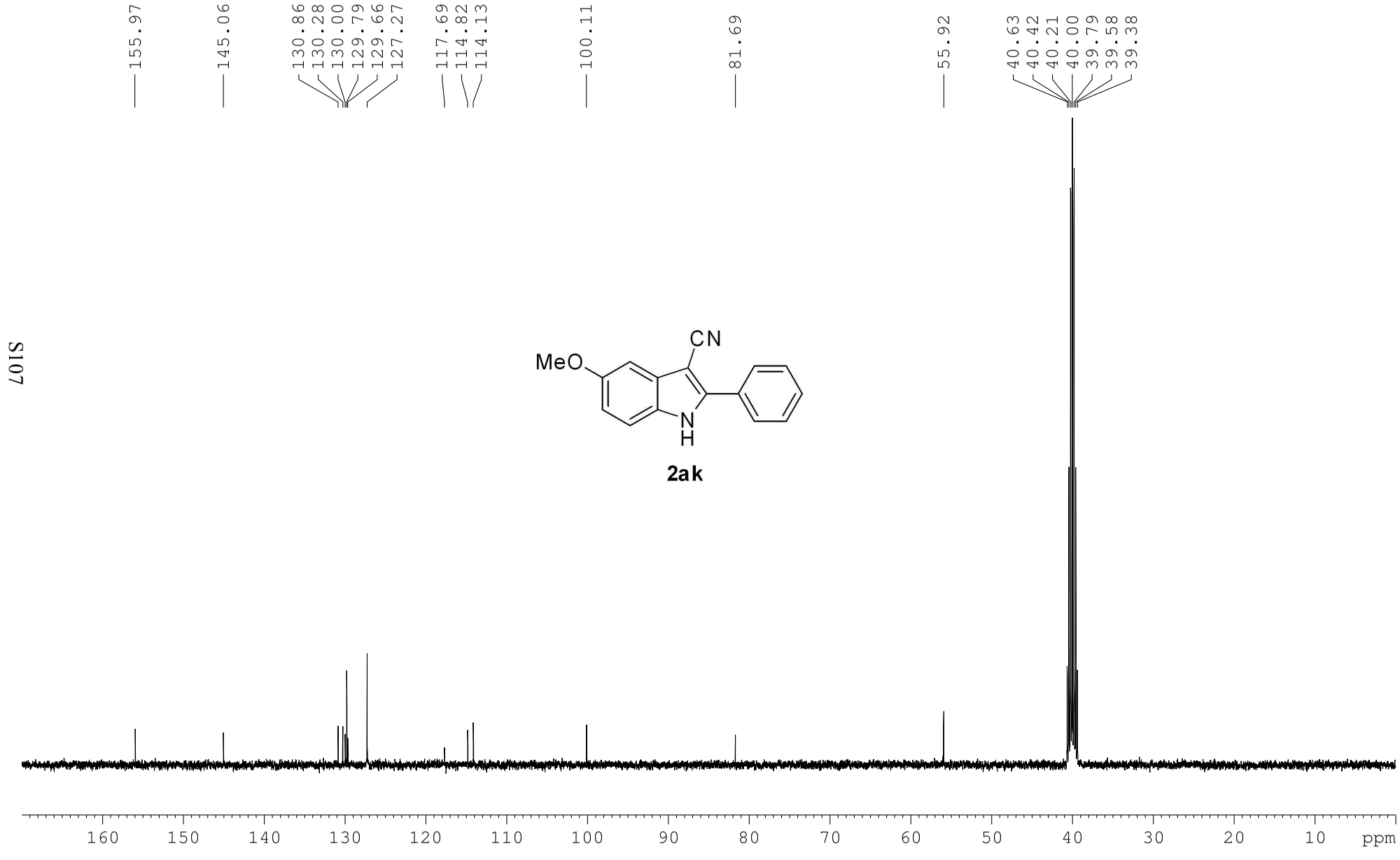
DMSO

H_2O

9 8 7 6 5 4 3 2 1 0 ppm

2.02 2.01 1.01 1.00 0.98 1.00 3.00

indole 2ak 13C NMR BBF 02 400 MHz DMSO-d6



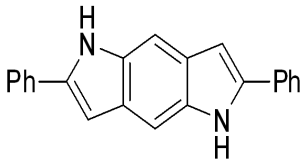
IBD-2al-7thmay-2012 1H NMR DMSO, BBOF1 400MHz

11.457
11.453

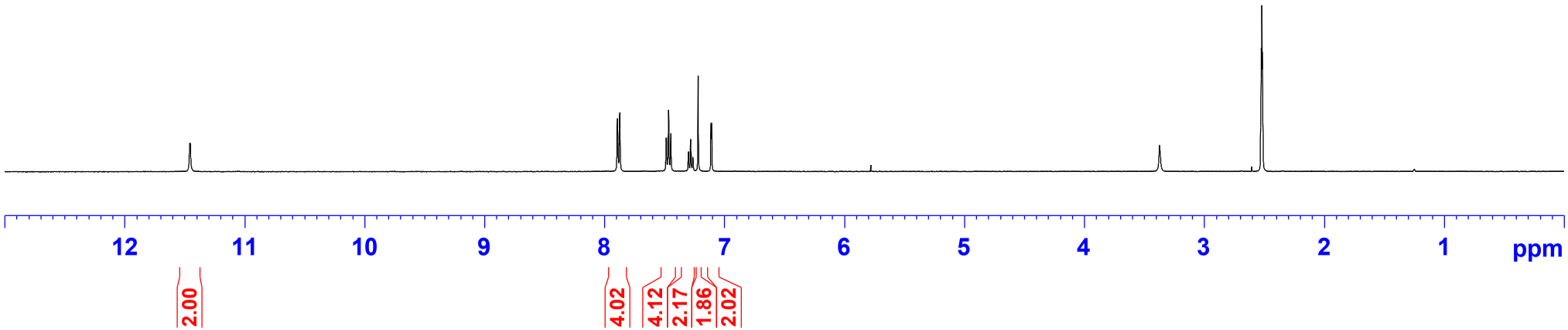
7.891
7.873
7.485
7.466
7.446
7.299
7.281
7.262
7.219
7.112
7.106

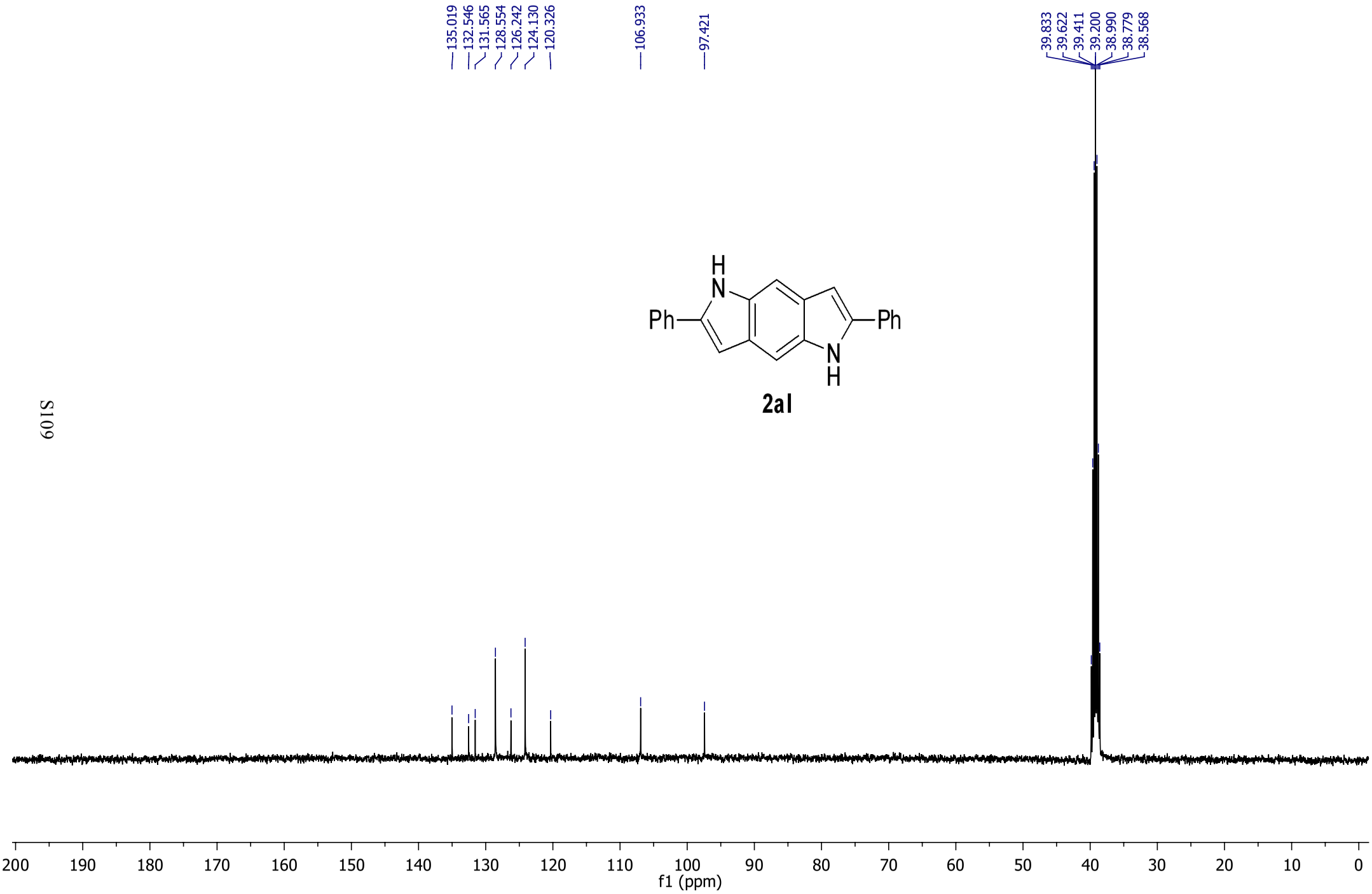
3.372

2.529
2.524
2.520
2.515
2.511



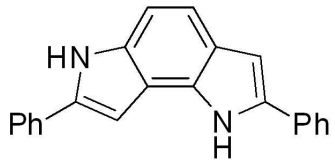
2al



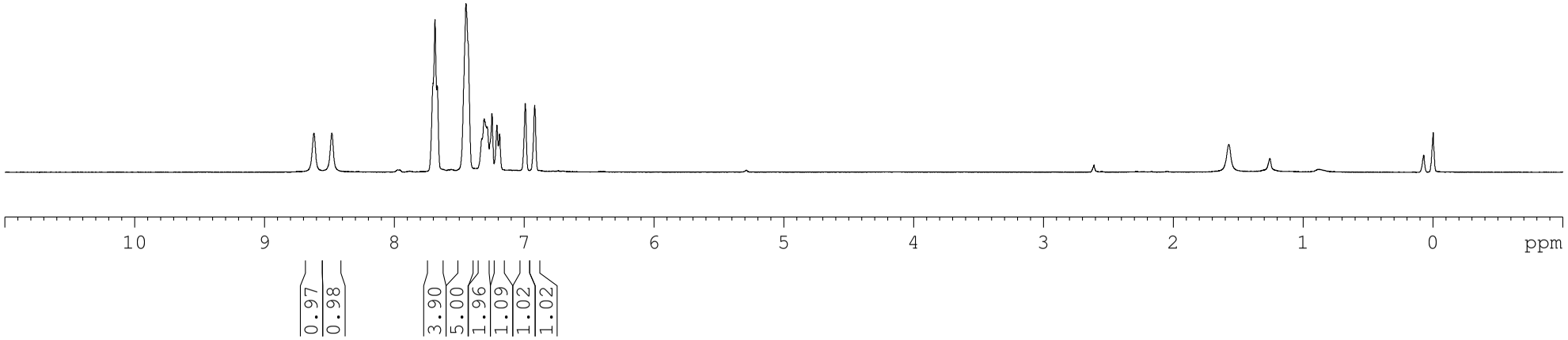

135.019
132.546
131.565
128.554
126.242
124.130
120.326
106.933
97.421
39.833
39.622
39.411
39.200
38.990
38.779
38.568
H
N
Ph
Ph
N
H
2al
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

indole 2am 1H NMR BBFO2 400MHz CDCl3

8.617
8.480
7.700
7.685
7.667
7.446
7.324
7.306
7.281
7.246
7.208
7.187
6.989
6.916

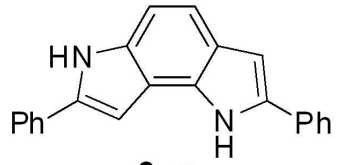


2am



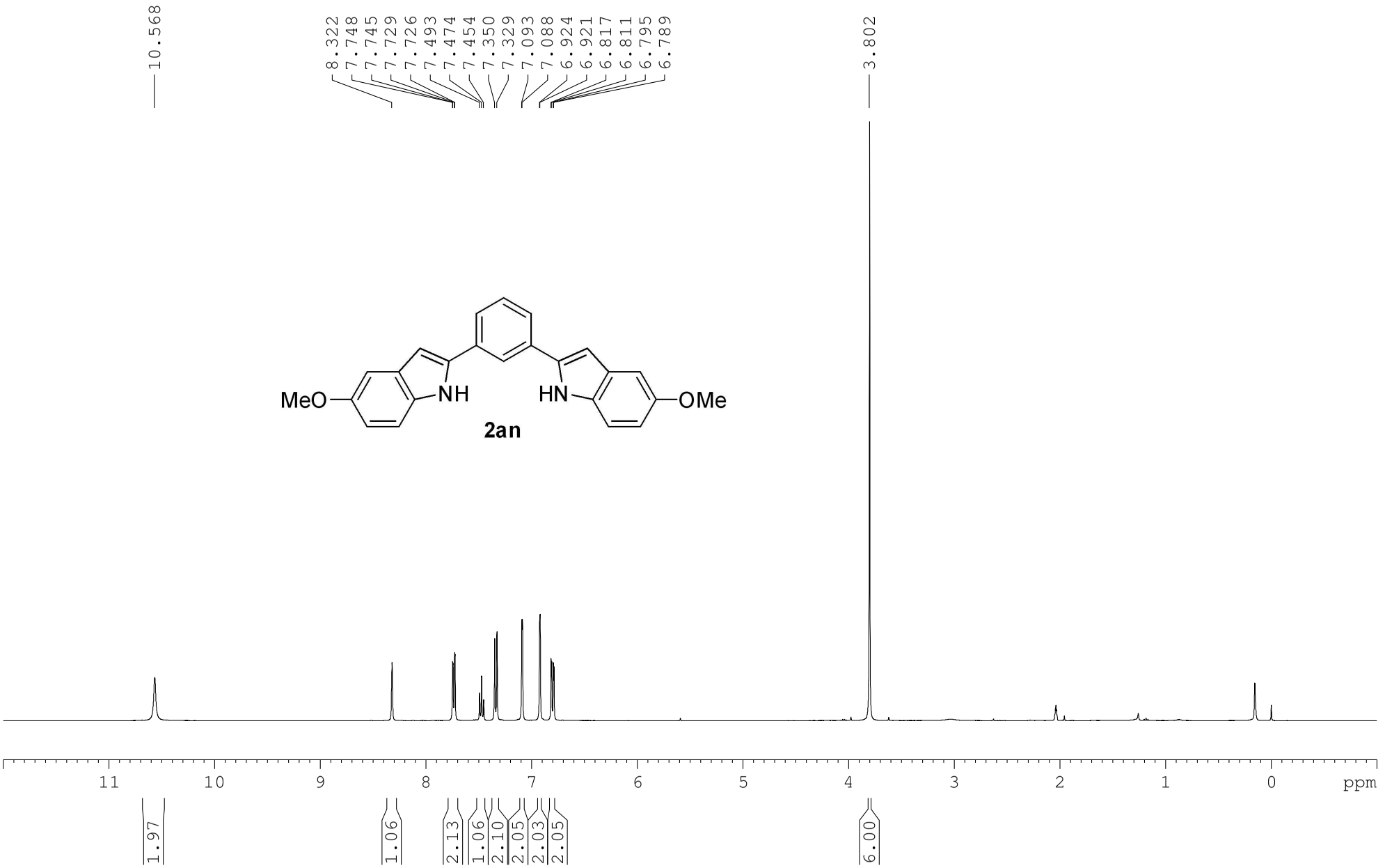
indole 2am 13C NMR 400 MHz BBFO1 CDCl3

136.02
134.66
134.20
132.97
132.55
129.63
129.05
128.97
127.30
126.81
124.83
124.60
122.47
116.19
114.65
105.65
101.30
96.09
77.32
77.01
76.69

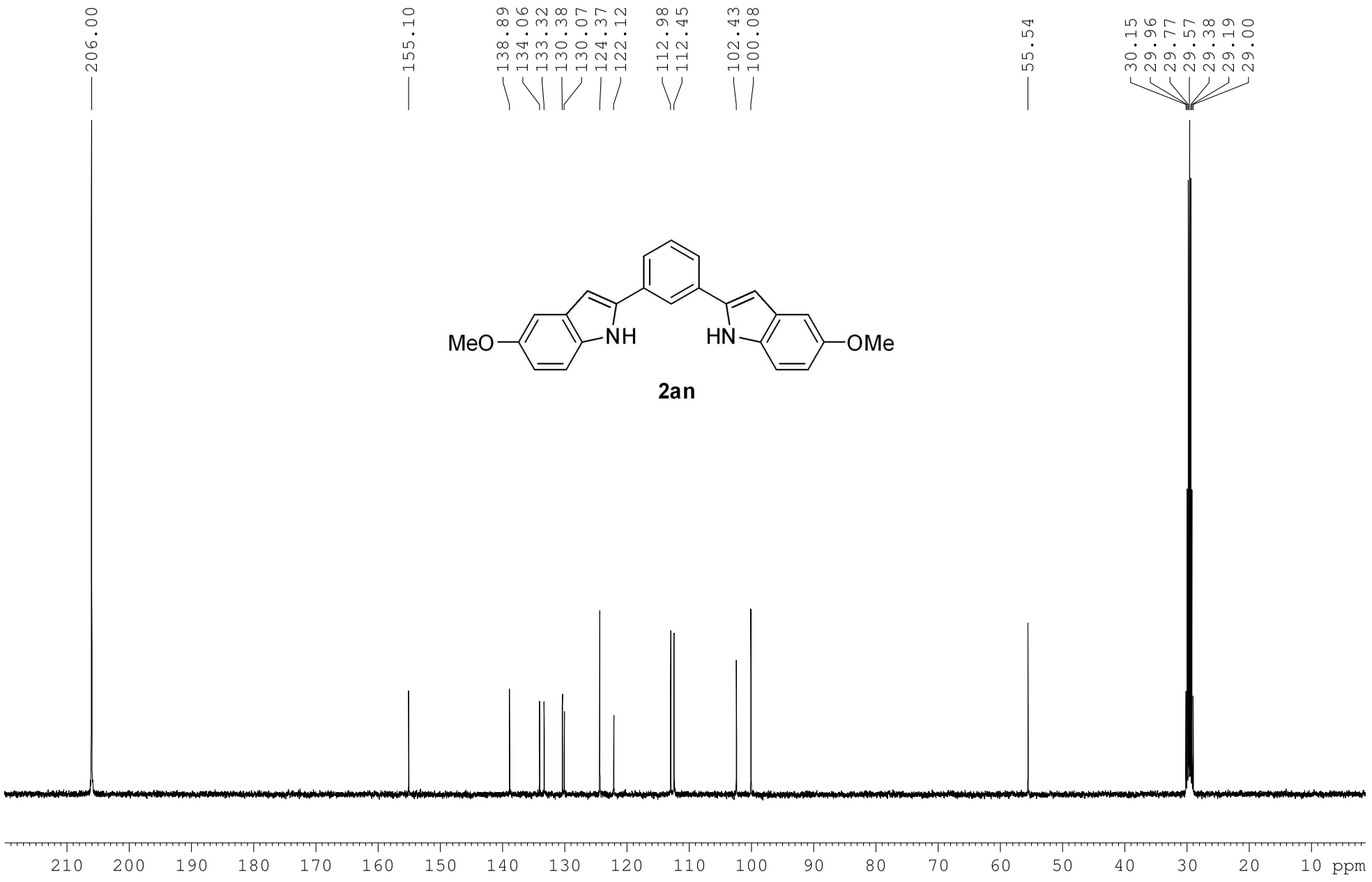


2am

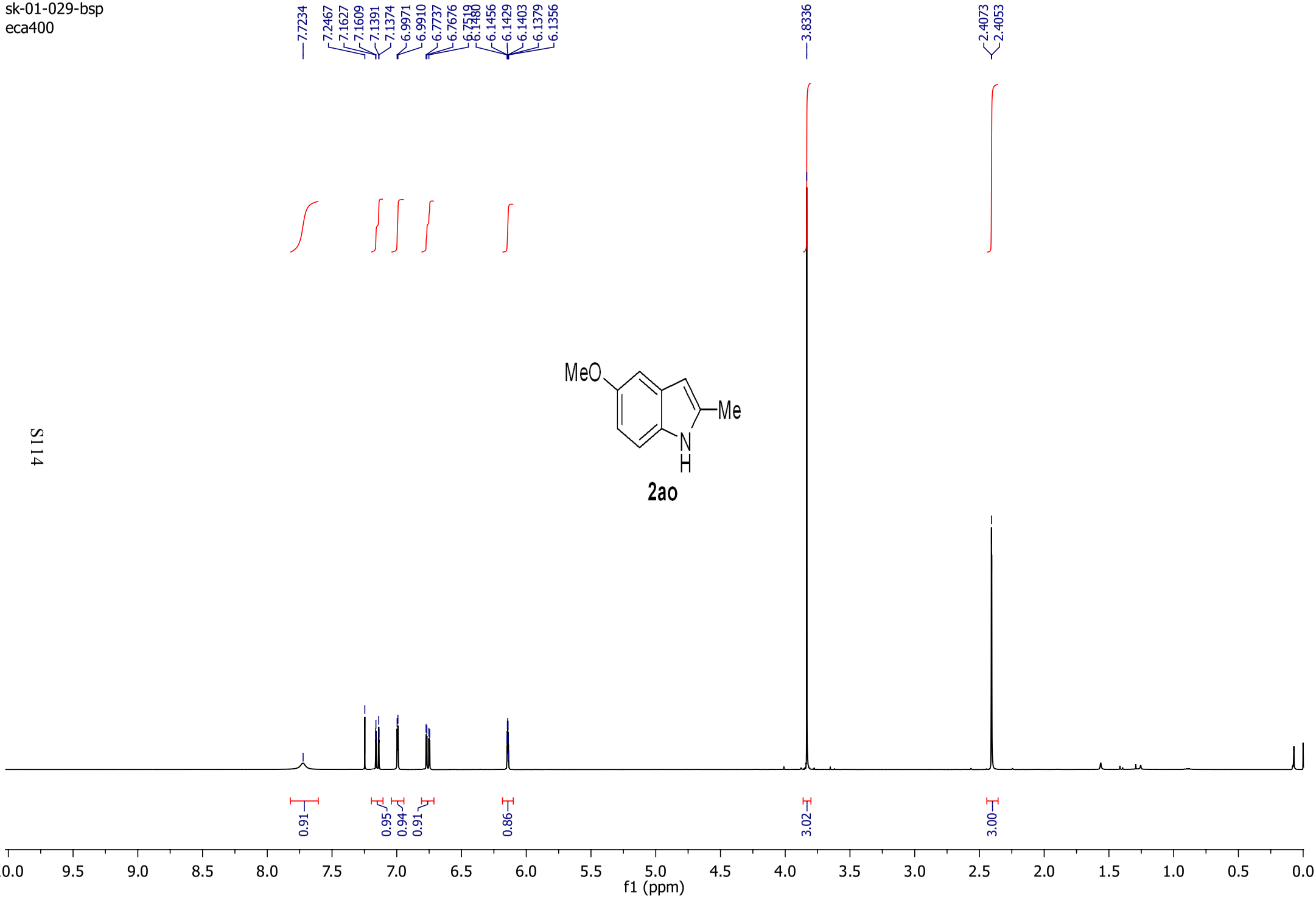
indole 2an 1H NMR 400 MHz, BBFO2, CDCl3

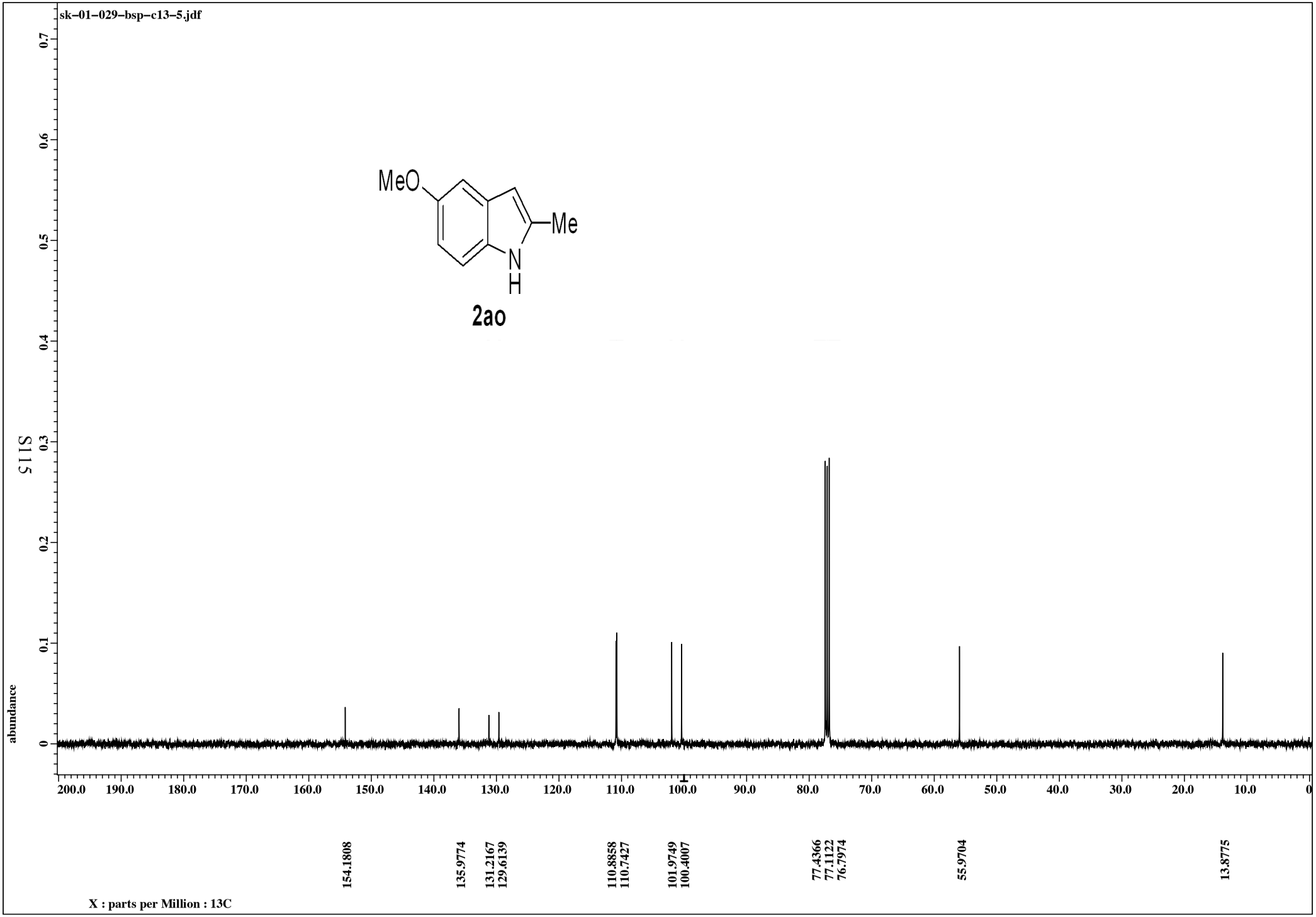


indole 2an 13C NMR 400 MHz BBFO2 acetone-d6



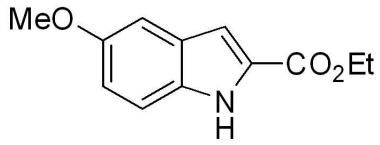
sk-01-029-bsp
eca400



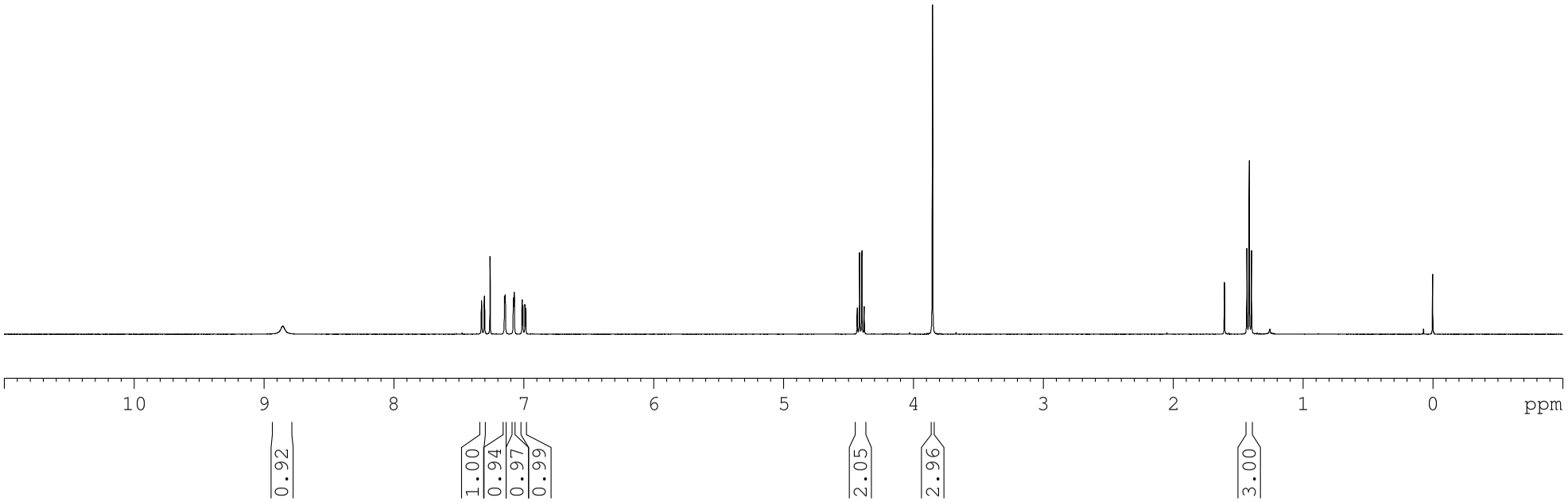

sk-01-029-bsp-c13-5.jdf
MeO
Me
N
H
2ao
S115
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
154.1808
135.9774
131.2167
129.6139
110.8858
110.7427
101.9749
100.4007
77.4366
77.1122
76.7974
55.9704
13.8775
X : parts per Million : 13C

indole 2ap 1H NMR CDCl3 BBOF1 400MHz

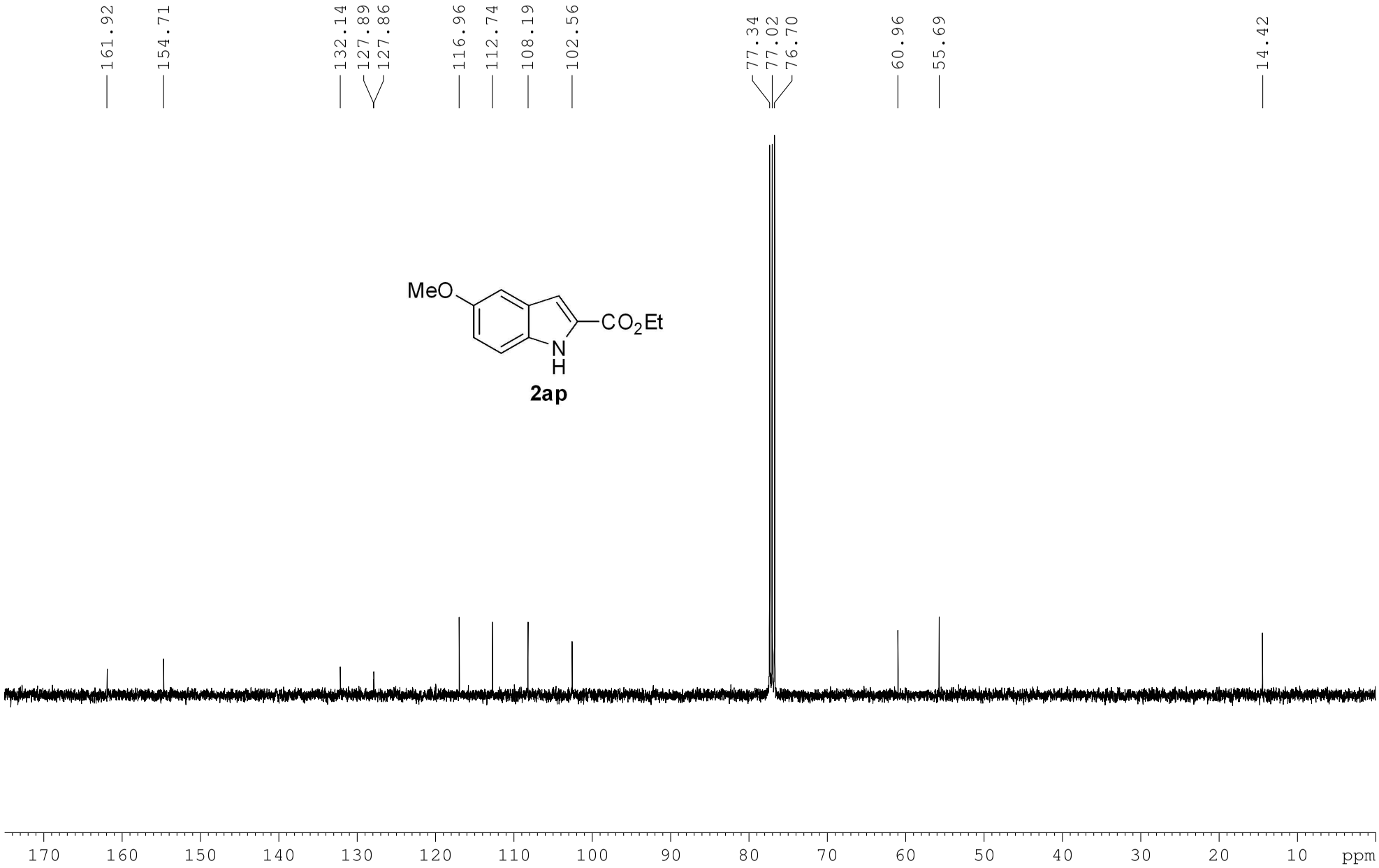
8.857
7.326
7.303
7.149
7.147
7.144
7.080
7.074
7.013
7.007
6.991
6.985
4.432
4.415
4.397
4.379
3.853
1.432
1.414
1.396



2ap

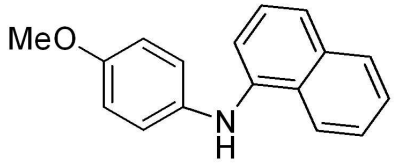


indole 2ap 13C NMR CDCl3, BBOF1 400MHz

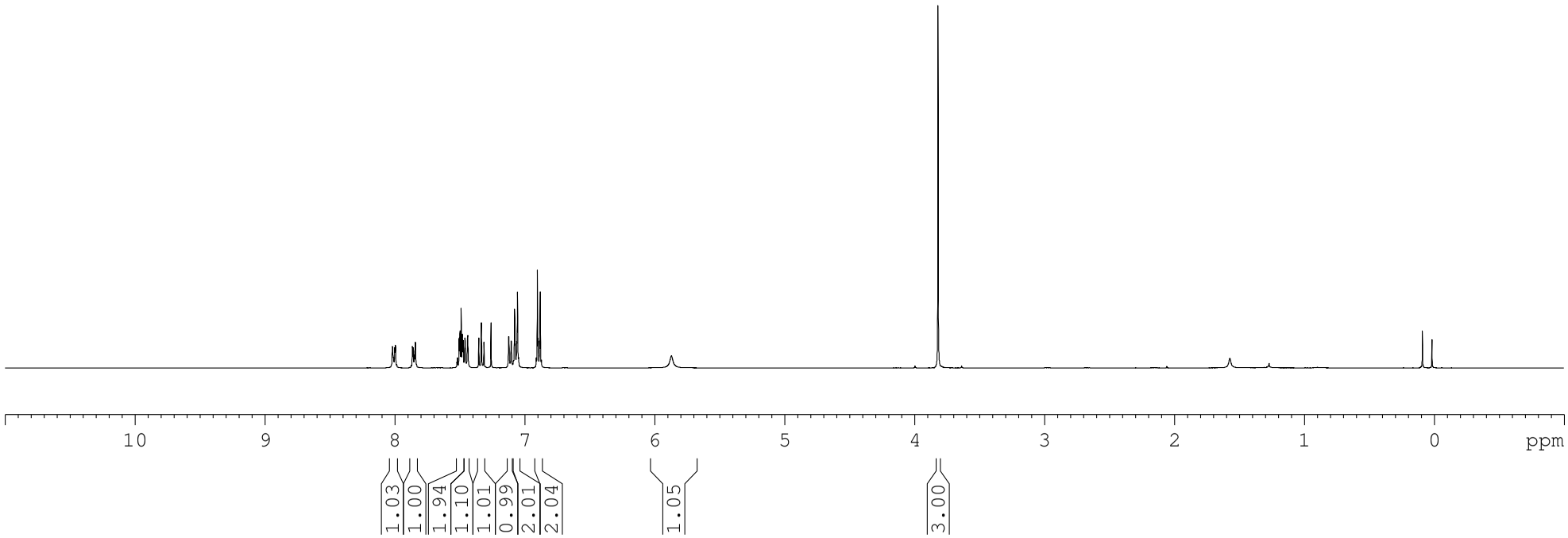


wy-2-140,1H NMR, 400MHz BBFO1 CDCl3

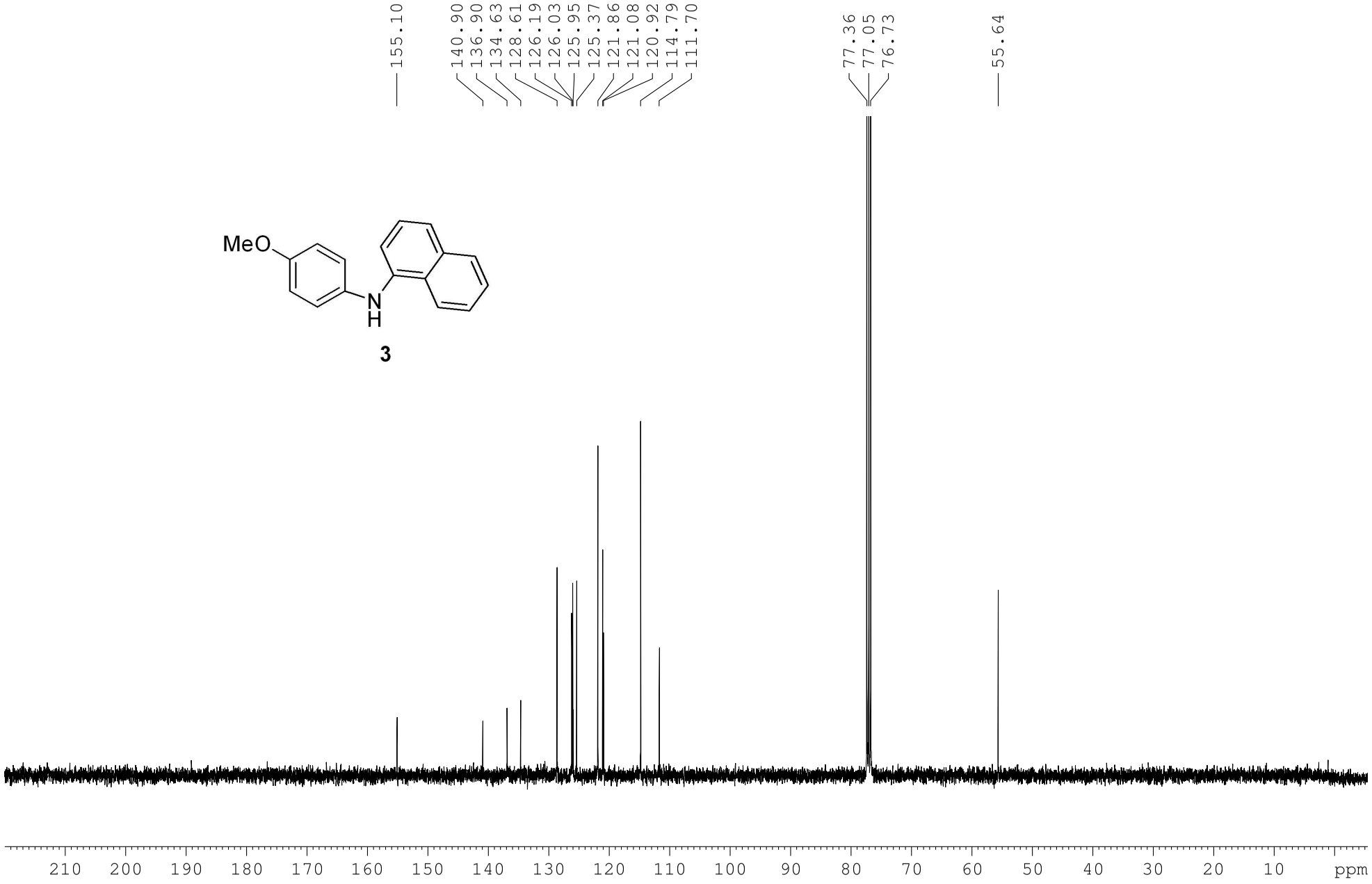
8.020
8.018
8.012
8.010
8.002
7.996
7.865
7.859
7.851
7.842
7.835
7.519
7.506
7.501
7.499
7.490
7.482
7.479
7.474
7.461
7.440
7.354
7.335
7.315
7.260
7.123
7.105
7.087
7.079
7.074
7.062
7.057
7.048
6.912
6.903
6.898
6.887
6.881
6.872
5.872
3.819



3



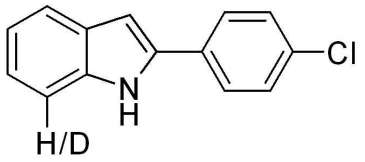
wy-2-140,13C NMR, 400MHz BBFO1 CDCl3



wy-2-224, 1H NMR BBFO1 400Hz in CDCl3

8.255 7.652 7.632 7.584 7.564 7.422 7.402 7.231 7.214 7.166 7.147 7.129 6.818 6.815

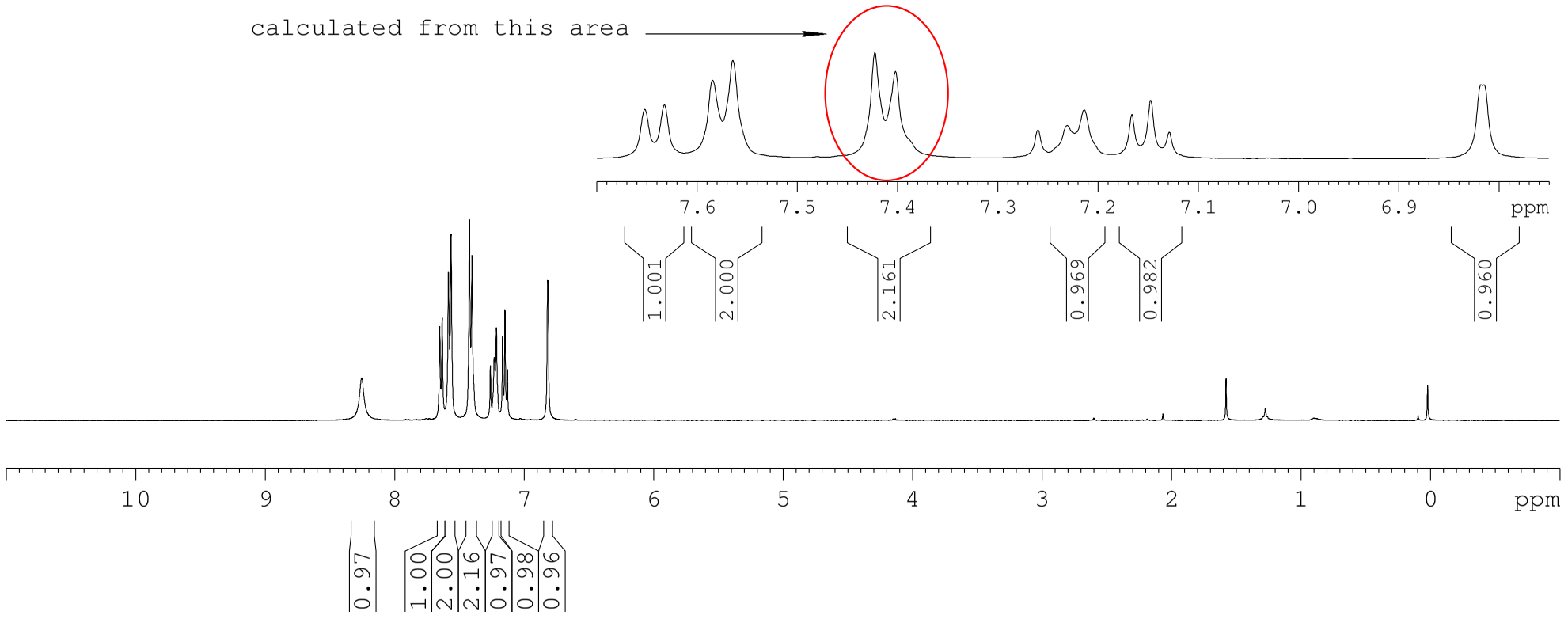
Intramolecular Competition



k_H/k_D = 0.839/0.161 = 5.2

7.652 7.632 7.584 7.564 7.422 7.402 7.231 7.214 7.166 7.147 7.129 6.818 6.815

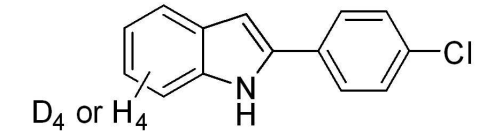
calculated from this area



wy-2-225, 1H NMR BBFO1 400Hz in CDCl3

8.272 7.646 7.627 7.601 7.594 7.590 7.578 7.573 7.567 7.431 7.425 7.420 7.408 7.403 7.397 7.392 7.390 7.237 7.234 7.219 7.217 7.199 7.196 7.159 7.157 7.139 7.122 7.120 6.821 6.815

Intermolecular Competition



k_H/k_D = 1/0.597 = 1.7

7.601 7.594 7.590 7.578 7.573 7.567 7.431 7.425 7.420 7.408 7.403 7.397 7.392 7.390 7.237 7.234 7.219 7.217 7.199 7.196 7.159 7.157 7.139 7.122 7.120 6.821 6.815