Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Copper-Catalyzed [1,3]-Alkoxy Rearrangement for Selective Synthesis of Polycyclic *ortho*-Aminoarenol Derivatives

Itaru Nakamura,[1]* Satoru Nozawa,[2] Yasuhiro Ishida,[2] Ichiro Muranushi,[2] Alexandra Mayerweg,[2] and Masahiro Terada[2]

[1] Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

[2] Research and Analytical Center for Giant molecules, Graduate School of Science Tohoku University, Sendai 980-8578, Japan

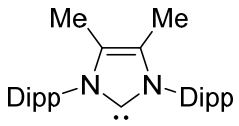
Supporting Information

1. General information.

^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM-ECS400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) or JEOL ECA-600 (600 MHz for ^{1}H and 151 MHz for ^{13}C) spectrometer. Chemical shifts are reported in ppm relative to $CHCl_3$ (for ^{1}H, δ 7.26), and $CDCl_3$ (for ^{13}C, δ 77.00). ^{1}H NMR data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet) and coupling constants (Hz). Infrared (IR) spectra were recorded on a JASCO FT/IR- 4100 spectrometer. High-resolution mass spectra analysis was performed on a Bruker Daltonics APEX III FT-ICR-MS spectrometer and Bruker Daltonics solariX FT-ICR-MS spectrometer at the Instrumental Analysis Center for Chemistry, Graduate School of Science, Tohoku University. Flash column chromatography was performed on silica gel 60N (Merck 40-63 μm or Kanto 40-50 μm). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 F254). All reactions were carried out under argon atmosphere.

Materials

Anhydrous acetonitrile, 1,4-dioxane, and toluene were purchased form Fujifilm WAKO and anhydrous PhCl, and DCE were purchased from Aldrich. These solvents were used as received. IPrCuBr,[1] SIPrCl,[2] and **L1**·HCl[3] were prepared in accordance with the literature method. Substrates **1** and **3** were synthesized in accordance with the literature method[1], except for **1l**. $AgSbF_6$ was purchased from Aldrich.



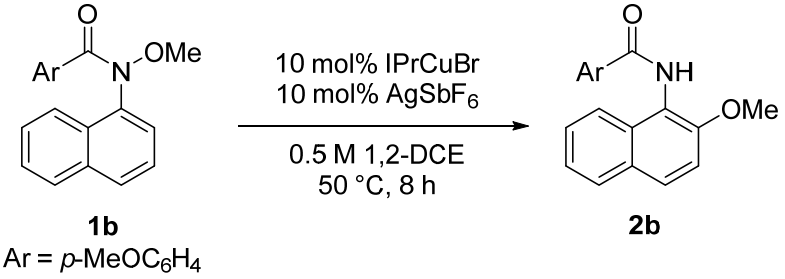
L1·HCl
(Dipp: 2,6-diisopropylphenyl)

[1] Nakamura, I.; Tashiro, H.; Ishida, Y.; Terada, M. *Org. Lett.* **2020**, *22*, 3794.

[2] Kuhn, K. M.; Grubbs, R. H. *Org. Lett.* **2008**, *10*, 2075.

[3] Gaillard, S.; Bantreil, X.; Slawin, A. M. Z.; Nolan, S. P. *Dalton Trans.* **2009**, 6967.

2. Representative procedure for Cu-Catalyzed reaction of 1

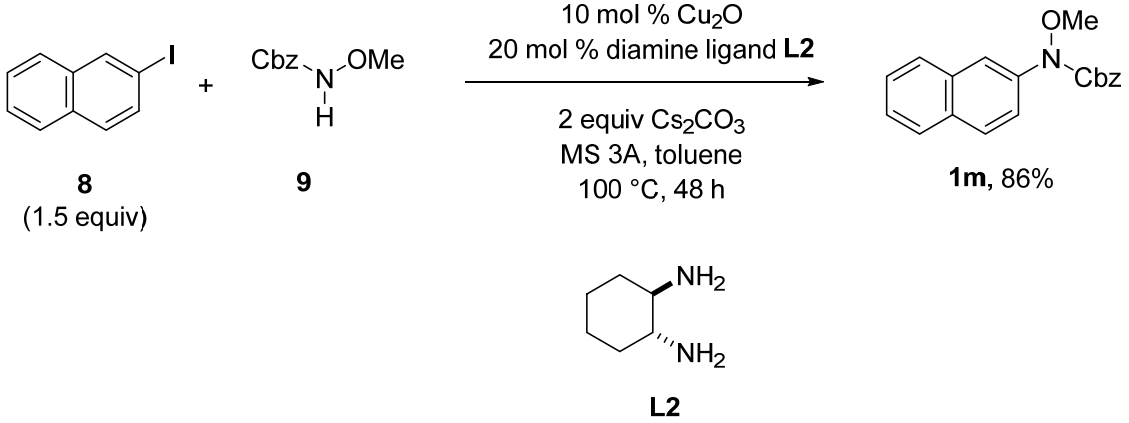


1b
Ar = *p*-$MeOC_6H_4$

2b

To a mixture of **1b** (122.9 mg, 0.4 mmol), IPrCuBr (21.3 mg, 0.04 mmol), and $AgSbF_6$ (7.79 mg, 0.04 mmol) in a pressure vial was added toluene (0.8 mL) under argon atmosphere. After stirring at 50 °C for 8 h, the reaction mixture was passed through a short pad of silica with EtOAc (50 mL), then the solvent was evaporated in vacuo. The crude product was purified by silica gel flash column chromatography using hexane/EtOAc (5/1) as eluent to give pure **2b** (0.388 mmol 119.3 mg, 97%) in an analytically pure form.

3. Preparation of 1m by Cu-catalyzed coupling reaction



8 (1.5 equiv) + **9** → **1m**, 86%

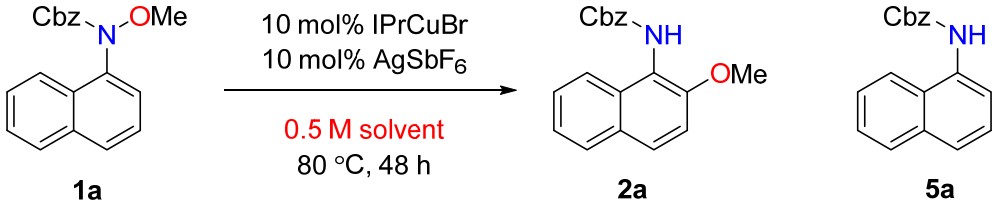
L2

To a mixture of **8**[4] (81.9 mg, 0.3 mmol), **9**[5] (36.0 mg, 0.2 mmol), Cu_2O (2.9 mg, 0.02 mmol), Cs_2CO_3 (130.3 mg, 0.4 mmol), and MS3A (18 mg) were added *trans*-1,2-diaminocyclohexane **L2** (4.6 mg, 0.04 mmol) and toluene (2 mL) under argon atmosphere. After stirring the solution at 100 °C for 48 h, the reaction mixture was passed through a short pad of celite with EtOAc (50 mL), then the solvent was evaporated in vacuo. The crude product was purified by silica gel column chromatography using hexane/EtOAc (5/1) as eluent to give pure **1m** (52.9 mg, 0.172 mmol, 86%).

[4] Yang, H.; Li, Y.; Jiang, M.; Wang, J.; Fu, H. *Chem. Eur. J.* **2011**, *17*, 5652.
[5] Quintard, A.; Alexakis, A. *Chem. Commun.* **2011**, *47*, 7212.

4. Optimization of reaction conditions

Table S1. Solvent Effect

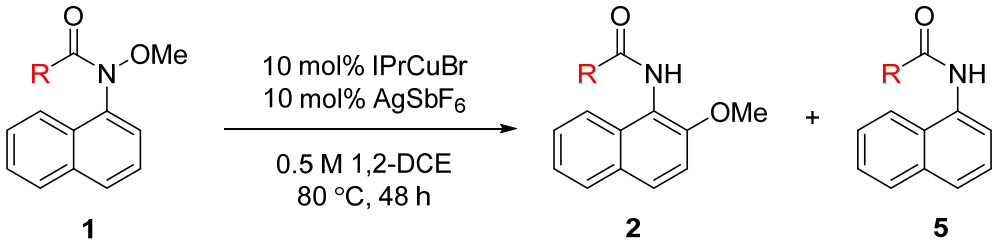


1a **2a** **5a**

Entry	Solvent	**2a** (%)[a]	**5a** (%)[a]	**1a** (%)[a]
1	**DCE**	**(84)**	**(9)**	**<1**
2	1,4-dioxane	72	15	<1
3	toluene	72	12	<1
4	DMF	<1	<1	96
5	MeCN	<1	<1	96

[a] ^{1}H NMR yields using CH_2Br_2 as the internal standard. Isolated yield in a parenthesis.

Table S2. Effect of the protective group

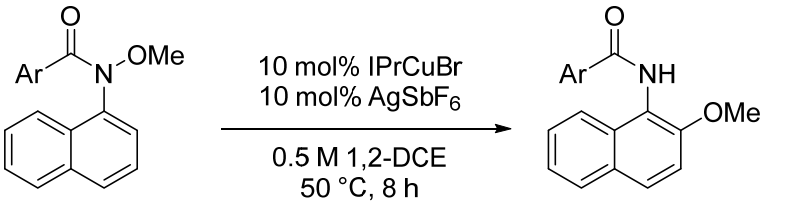


1 **2** **5**

Entry	R	Yield (%)[a]	**5** (%)[a]	**1** (%)[a]
1	3,4,5-$MeOC_6H_2$	(93)	(3)	<1
2	**4-$MeOC_6H_4$ (1b)**	**(2b, 93)**	**trace**	**<1**
3	Ph	85	trace	<1
4	4-$F_3CC_6H_4$	86	4	<1
5	BnO (**1a**)	(**2a**, 84)	(9)	<1

[a] ^1H NMR yields using CH_2Br_2 as the internal standard. Isolated yield in a parenthesis.

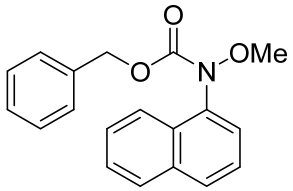
5. Gram-scale experiment



1b
Ar = *p*-$MeOC_6H_4$
1.00g (3.25 mmol)

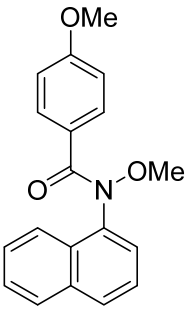
2b
0.72g (2.34 mmol, 72% yield)

6. Analytical data of substrates 1 and 3



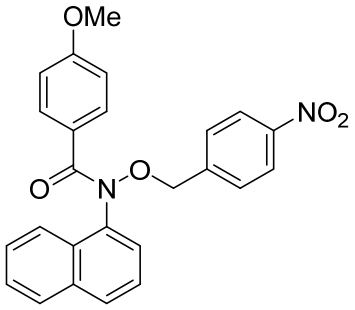
1a

Benzyl methoxy(naphthalen-1-yl)carbamate (1a). Dark red oil. Rf = 0.37 [hexane/EtOAc = 3:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 3H), 5.21 (s, 2H), 7.23 (, 2H), 7.28-7.29 (m, 3H), 7.48-7.52 (m, 4H), 7.88 (dd, 2H) 7.93 (dd, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 62.0, 67.6, 123.0, 125.0, 125.9, 126.2, 126.9, 127.7, 127.9, 128.0, 128.2, 129.5, 130.1, 134.3, 135.3, 135.8, 155.7. IR (neat) 3062, 2966, 2933, 2894, 2811, 1726, 1597, 1508, 1497, 1455, 1440, 1397, 1315, 1266, 1237, 1214, 1176, 1091, 1055, 1006, 934, 905, 864, 803 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{17}NO_3$ $(M+Na)^+$ 330.1101, found 330.1101.



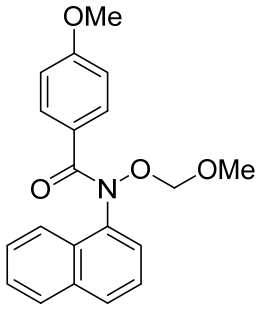
1b

***N*,4-Dimethoxy-*N*-(naphthalen-1-yl)benzamide (1b).** Brown solid. Mp: 141.8 °C. Rf = 0.21 [hexane/EtOAc = 2:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74 (s, 3H), 3.81 (s, 3H), 6.70 (d, 2H), 7.30 (br, 1H), 7.38 (t, 1H), 7.52 (d, 2H), 7.56 (t, 1H), 7.62 (t, 1H), 7.86 (d, 1H), 7.90 (d, 1H), 8.21 (d, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.2, 60.9, 113.2, 123.5, 125.0, 126.1, 126.7, 127.4, 128.3, 129.7, 130.3, 130.4, 134.6, 135.7, 161.5, 168.5. IR (neat)3040, 3004, 2977, 2936, 2841, 2360, 1653, 1604, 1576, 1510, 1458, 1435, 1417, 1392, 1380, 1350, 1338, 1306, 1255, 1180, 1158, 1140, 1111, 1030, 1015, 989, 947, 934, 909, 885, 867, 842, 816 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{17}NO_3$ $(M+Na)^+$ 330.1101, found 330.1101.



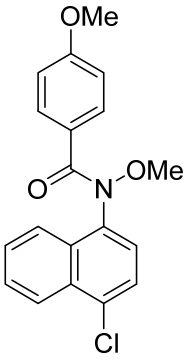
1c

4-Methoxy-*N*-(naphthalen-1-yl)-*N*-[(4-nitrobenzyl)oxy]benzamide (1c). Brown solid. Mp: 141.9°C. Rf = 0.19 [hexane/EtOAc = 3:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 3H), 5.17 (s, 2H), 6.67 (d, *J* = 8.2 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.46-7.48 (m, 4H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.64 (t, *J* = 6.9 Hz, 1H), 7.87 (d, *J* = 8.7 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 8.12 (d, *J* = 8.7 Hz, 2H), 8.25 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.2, 74.1, 113.3, 123.4, 123.5, 125.0, 125.8, 126.9, 127.5, 127.6, 128.5, 129.5, 130.0, 130.3, 130.4, 134.6, 136.3, 142.3, 147.8, 161.7, 169.0. IR (neat) 3062, 3011, 2935, 2840, 1663, 1605, 1521, 1346, 1256, 1174 cm^{-1}. HRMS (ESI) calcd. for $C_{25}H_{20}N_2O_5$ $(M+Na)^+$ 451.1264, found 451.1264.



1d

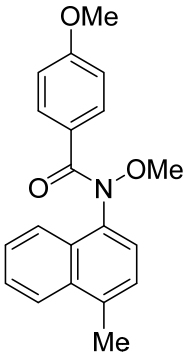
4-Methoxy-*N*-(methoxymethoxy)-*N*-(naphthalen-1-yl)benzamide (1d). Colorless liquid. Rf = 0.27 [hexane/EtOAc = 2:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.20 (s, 3H), 3.70(s, 3H), 5.06(s, 2H), 6.64(d, *J* = 8.4 Hz, 2H), 7.40(t, *J* = 8.0 Hz, 1H), 7.48-7.55(m, 4H), 7.60(dt, *J* = 0.8, 8.0 Hz, 1H), 7.85(t, *J* = 9.2 Hz, 2H), 8.24(d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.2, 57.0, 99.2, 113.1, 123.3, 125.1, 126.3, 126.6, 127.4, 128.2, 128.3, 129.8, 130.4, 130.6, 134.5, 137.3, 161.4, 169.8. IR (neat) 3055, 2934, 2837, 1661, 1604, 1576, 1509, 1462, 1441, 1416, 1395, 1304, 1253, 1212, 1173, 1155, 1110, 1084, 1028, 961, 922, 881, 839, 804, 774, 735, 703, 665, 607 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{19}NO_4$ $(M+Na)^+$ 360.1206, found 360.1206.



1e

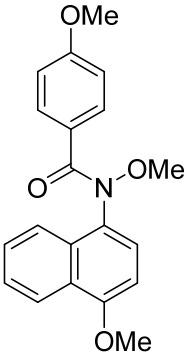
***N*-(4-Chloronaphthalen-1-yl)-*N*,4-dimethoxybenzamide (1e).** Orange oil. Rf = 0.57 [hexane/EtOAc = 1:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74 (s, 3H), 3.79 (s, 3H), 6.72 (s, 2H), 7.23 (s, 1H), 7.49-7.68 (m, 5H), 8.14-8.33 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.1, 60.9, 113.20, 113.23, 122.7, 124.0, 125.0, 125.3, 125.7, 126.0, 127.0, 127.8, 128.1, 130.4, 133.3, 161.6, 168.6. IR (neat) 3006, 2967, 2933, 2900, 2839, 1659, 1605, 1509, 1457, 1441, 1418, 1382, 1331, 1305, 1254, 1219, 1173, 1111, 1028, 1001, 962,

928, 892, 839 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{16}ClNO_3$ $(M+Na)^+$ 364.0711, found 364.0711.



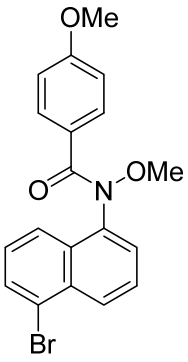
1f

***N*,4-Dimethoxy-*N*-(4-methylnaphthalen-1-yl)benzamide (1f).** Dark red oil. Rf = 0.28 [hexane/EtOAc = 2:1 (v/v)]. ^1H NMR (400 MHz, $CDCl_3$) δ 2.67 (s, 3H), 3.64 (s, 3H), 3.80 (s, 3H), 6.65 (m, 2H), 7.08-7.24 (m, 2H), 7.31-7.63 (m, 3H), 8.01 (d, *J* = 7.6 Hz, 1H), 8.24 (d, *J* = 6.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.4, 55.0, 60.5, 121.7, 123.9, 124.5, 125.6, 125.8, 126.1, 126.4, 126.9, 127.1, 130.1, 130.2. 133.5, 133.9, 136.5, 161.3, 168.4. IR (neat) 3003, 2970, 2933, 2899, 2839, 2349, 2309, 1658, 1605, 1577, 1510, 1462, 1441, 1419, 1391, 1338, 1305, 1220, 1173, 1111, 1078, 1027, 998, 973, 876, 840 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{19}NO_3$ $(M+Na)^+$ 344.1257, found 344.1257.



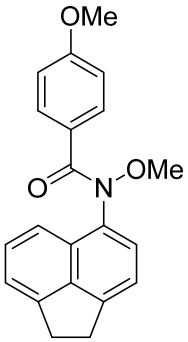
1g

***N*,4-Dimethoxy-*N*-(4-methoxynaphthalen-1-yl)benzamide (1g).** Dark red oil. Rf = 0.24 [hexane/EtOAc = 2:1 (v/v)]. ^1H NMR (400 MHz, $CDCl_3$) δ 3.71 (s, 3H), 3.80 (s, 3H), 3.98 (s, 3H), 6.66 (m, 3H), 7.18 (s, 1H), 7.46-7.55 (m, 3H), 7.63 (t, *J* = 6.9 Hz, 1H), 8.14 (d, *J* = 6.2 Hz, 1H), 8.29 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 55.8, 60.6, 102.7, 113.2, 122.6, 123.4, 126.1, 126.5, 127.4, 128.0, 128.3, 128.6, 130.4, 131.4, 156.5, 161.4. IR (neat) 3004, 2965, 2934, 2901, 2840, 1653, 1605, 1579, 1510, 1463, 1442, 1423, 1390, 1329, 1304, 1281, 1252, 1238, 1172, 1139, 1110, 1096, 1072, 1025, 998, 982, 961, 906, 876, 839, 817 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{19}NO_4$ $(M+Na)^+$ 360.1206, found 360.1206.



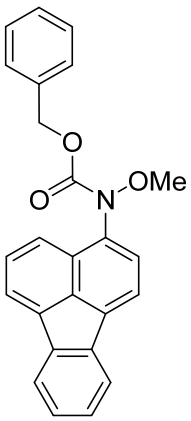
1h

***N*-(5-Bromonaphthalen-1-yl)-N,4-dimethoxybenzamide (1h).** Pink solid. Mp: 92.0 °C. Rf = 0.40 [hexane/EtOAc = 2:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 3H), 3.79 (s, 3H), 6.72 (s, 2H), 7.30-7.51 (m, 5H), 7.86 (d, *J* = 6.9 Hz, 1H), 8.19 (d, *J* = 7.6 Hz, 1H), 8.29 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.2, 60.9, 113.3, 123.2, 123.6, 125.8, 126.3, 127.6, 128.0, 128.9, 130.5, 130.9, 131.7, 133.1. 136.1. 161.7. 168.6. IR (neat) 3069, 3014, 2962, 2930, 2893, 2838, 1659, 1636, 1603, 1569, 1507, 1454, 1439, 1417, 1393, 1355, 1309, 1255, 1220, 1171, 1140, 1106, 1073, 1028, 1016, 1006, 973, 875, 844 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{16}BrNO_3$ $(M+Na)^+$ 330.1101, found 330.1101.



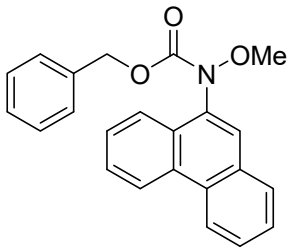
1i

***N*-(1,2-Dihydroacenaphthylen-5-yl)-*N*,4-dimethoxybenzamide (1i).** Brown oil. Rf = 0.30 [hexane/EtOAc = 2:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.37 (dd, 2H), 3.44 (dd, 2H), 3.73 (s, 3H), 3.81 (s, 3H), 6.68 (br, 2H), 7.16-7.26 (m, 2H), 7.35 (d, *J* = 6.9 Hz, 1H), 7.43-7.61 (m, 3H), 7.83 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.0, 30.6, 55.0, 60.6, 112.9, 118.4, 118.7, 120.0, 126.2, 128.4, 128.9, 129.1, 130.3, 131.7, 140.3, 146.2, 147.9, 161.2, 168.4. IR (neat) 3006, 2963, 2931, 2838, 2810, 1652, 1605, 1577, 1509, 1460, 1440, 1417, 1406, 1370, 1333, 1304, 1254, 1214, 1173, 1110, 1053, 1025, 973, 886, 837, 805 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{19}NO_3$ $(M+Na)^+$ 356.1257, found 356.1257.



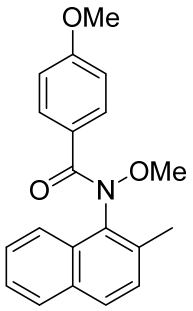
1j

Benzyl fluoranthen-3-yl(methoxy)carbamate (1j). Dark red oil. Rf = 0.62 [hexane/EtOAc = 3:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 3H), 5.25 (s, 2H), 7.28-7.31 (m, 5H), 7.37-7.40 (m, 2H), 7.59-7.61 (m, 2H), 7.85-7.92 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 62.3, 68.0, 119.6, 120.5, 121.65, 121.74, 123.3, 127.1, 127.2, 127.8, 127.95, 127.99, 128.1, 128.4, 128.8, 133.4, 135.4, 135.8, 137.1, 138.0, 138.7, 139.9, 155.7. IR (neat) 3320, 3060, 3034, 2964, 2933, 2894, 1725, 1610, 1537, 1492, 1475, 1452, 1403, 1388, 1322, 1270, 1236, 1213, 1153, 1094, 1022, 1007, 938, 909, 843, 822 cm^{-1}. HRMS (ESI) calcd. for $C_{25}H_{19}NO_3$ $(M+Na)^+$ 404.1257, found 404.1257.



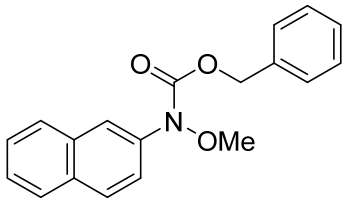
1k

Benzyl methoxy(phenanthren-9-yl)carbamate (1k). Dark red oil. Rf = 0.41 [hexane/EtOAc = 3:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H), 5.24 (s, 2H), 7.24-7.29 (m, 5H), 7.60-7.65 (m, 2H), 7.68-7.73 (m, 2H), 7.80 (s, 1H), 7.90 (d, *J* = 6.9 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 8.69 (d, *J* = 8.3 Hz, 1H), 8.72 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 62.2, 67.9, 122.7, 122.9, 124.0, 127.0, 127.1, 127.2, 127.4, 127.8, 127.9, 128.1, 128.4, 128.9, 129.1, 130.7, 131.0, 131.5, 133.9, 136.9, 156.1. IR (neat) 2934, 2369, 1730, 1603, 1527, 1496, 1453, 1396, 1453, 1396, 1332, 1297, 1226, 1151, 1095, 1009, 896 cm^{-1}. HRMS (ESI) calcd. for $C_{23}H_{19}NO_3$ $(M+Na)^+$ 380.1257, found 380.1257.



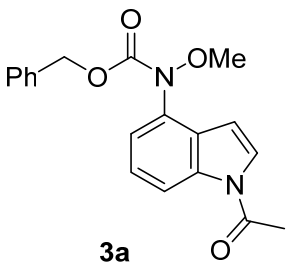
1l

***N*,4-Dimethoxy-*N*-(2-methylnaphthalen-1-yl)benzamide (1l).** Colorless solid. Mp: 92.0 °C. Rf = 0.35 [hexane/EtOAc = 2:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 (s, 3H), 3.63 (s, 3H), 3.91 (s, 3H), 6.52 (d, *J* = 8.3 Hz, 2H), 7.01 (br, 1H), 7.21 (d, *J* = 8.3 Hz, 1H), 7.42-7.50 (m, 3H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 2H), 8.03 (s, 1H), 8.20 (d, *J* = 8.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ18.7, 55.1, 60.9, 113.0, 123.5, 125.9, 126.0, 127.6, 128.1, 128.6, 129.7, 129.8, 130.9, 131.3, 133.1, 135.0, 161.3, 168.0. IR (neat) 3274, 3056, 3009, 2977, 2934, 2840, 1643, 1606, 1576, 1512, 1458, 1436, 1416, 1386, 1367, 1354, 1333, 1308, 1254, 1191, 1179, 1160, 1150, 1140, 1111, 1097, 1035, 1012, 990, 872, 843, 822 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{19}NO_3$ $(M+Na)^+$ 344.1257, found 344.1257.



1m

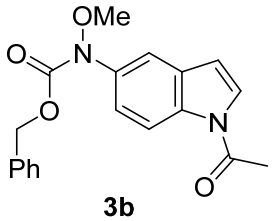
Benzyl methoxy(naphthalen-2-yl)carbamate (1m). Brown oil. Rf = 0.62 [hexane/EtOAc = 2:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 3H), 5.32 (s, 2H), 7.33-7.50 (m, 8H), 7.65 (dd, *J* = 2.1, 8.9 Hz, 1H), 7.81-7.85 (m, 3H), 7.91 (d, *J* = 1.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 62.4, 68.0, 119.5, 121.2, 127.6, 127.9, 128.1, 128.3, 128.5, 128.6, 131.5, 133.3, 135.8, 136.9, 154.3. IR (neat) 3060, 3034, 2935, 2895, 2815, 1715, 1632, 1599, 1509, 1467, 1390, 1362, 1315, 1270, 1105, 1038, 957, 886, 857, 816 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{17}NO_3$ $(M+Na)^+$ 330.1100, found 330.1100.



3a

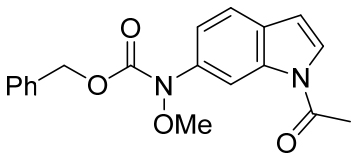
Benzyl (1-acetyl-1H-indol-4-yl)(methoxy)carbamate (3a). Yellow solid. Mp: 86.3 °C. Rf = 0.35 [hexane/EtOAc = 2:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.65 (s, 3H), 3.75 (s, 3H), 5.25 (s, 2H), 6.66 (d,

J = 8.2 Hz, 1H), 7.28-7.41 (m, 5H), 8.43 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.0, 62.3, 67.9, 107.4, 116.5, 121.1, 125.1, 125.6, 126.7, 128.0, 128.2, 128.5, 131.3, 135.8, 136.5, 154.9, 168.6. IR (neat) 3163, 3113, 3068, 2968, 2935, 1732, 1708, 1535, 1482, 1428, 1392, 1369, 1323, 1310, 1260, 1221, 1179, 1165, 1098, 1055, 1031, 952, 933, 914, 891, 863, 822 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{18}N_2O_4$ $(M+Na)^+$ 361.1159, found 361.1159.



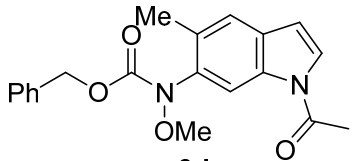
3b

Benzyl (1-acetyl-1H-indol-5-yl)(methoxy)carbamate (3b). Colorless solid. Mp: 63.4 °C. Rf = 0.38 [hexane/EtOAc = 2:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.65 (s, 3H), 3.77 (s, 3H), 5.27 (s, 2H), 6.63 (d, *J* = 4.1 Hz, 1H), 7.31-7.39 (m, 5H), 7.42-7.45 (m, 2H), 7.64 (d, *J* = 2.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.85, 62.15, 67.88, 109.17, 115.63, 116.64, 120.80, 126.19, 128.03, 128.21, 128.53, 130.61, 133.80, 135.30. 135.92. 154.62. 168.47. IR (neat) 3019, 2976, 2923, 1707, 1613, 1584, 1540, 1466, 1382, 1319, 1278, 1263, 1236, 1214, 1184, 1090, 1029, 983, 933, 881 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{18}N_2O_4$ $(M+Na)^+$ 361.1159, found 361.1159.



3c

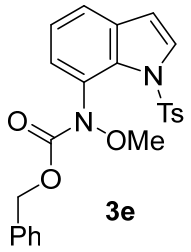
Benzyl (1-acetyl-1H-indol-6-yl)(methoxy)carbamate (3c). Orange solid. Mp: 91.4 °C. Rf = 0.36 [hexane/EtOAc = 2:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.64 (s, 3H), 3.78 (s, 3H), 5.27 (s, 2H), 6.63 (d, *J* = 4.1 Hz, 1H), 7.30-7.40 (m, 6H), 7.45 (d, *J* = 2.8 Hz, 1H), 7.54 (d, *J* = 8.9 Hz, 1H), 8.54 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.9, 62.2, 67.9, 108.8, 112.4, 120.0, 120.7, 126.1, 128.0, 128.1, 128.5, 129.0, 135.3, 135.9, 136.7, 154.6, 168.5. IR (neat) 2979, 2921, 1720, 1698, 1530, 1481, 1437, 1388, 1366, 1330, 1299, 1220, 1090, 1026, 931, 916, 885, 833 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{18}N_2O_4$ $(M+Na)^+$ 361.1159, found 361.1159.



3d

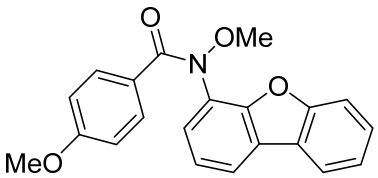
Benzyl (1-acetyl-5-methyl-1H-indol-6-yl)(methoxy)carbamate (3d). Orange solid. Mp: 113.7 °C. Rf = 0.32 [hexane/EtOAc = 2:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.61 (s, 3H), 3.76 (s, 3H), 5.21 (s, 2H), 6.57 (d, *J* = 3.4 Hz, 1H), 7.28-7.47 (m, 7H), 8.39 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$)

δ 17.8, 23.8, 61.7, 67.7, 108.6, 116.9, 122.2, 126.7, 127.9, 128.0, 128.4, 131.0, 132.2, 133.6, 135.2, 136.1, 155.5, 168.3. IR (neat) 3141, 3116, 2979, 2958, 2932, 2817, 1732, 1712, 1692, 1531, 1458, 1442, 1378, 1329, 1310, 1272, 1254, 1225, 1212, 1154, 1113, 1091, 1073, 1032, 1005, 962, 935, 905, 888, 875 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{20}N_2O_4$ $(M+Na)^+$ 375.1315, found 375.1315.



3e

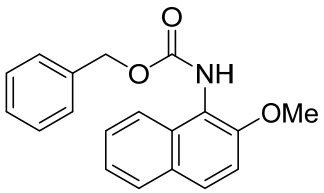
Benzyl methoxy(1-tosyl-1H-indol-7-yl)carbamate (3e). Brown oil. Rf = 0.36 [hexane/EtOAc = 2:1 (v/v)]. ^1H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H), 3.66 (s, 3H), 5.26 (s, 2H), 6.69 (d, *J* = 3.4 Hz, 1H), 7.10 (d, *J* = 8.3 Hz, 2H), 7.24-7.40 (m, 6H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.69 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 61.2, 67.6, 109.4, 122.3, 123.8, 126.1, 126.3, 126.9, 127.6, 127.8, 128.2, 129.2, 130.4, 131.2, 134.6, 135.6, 135.9, 144.2, 154.7. IR (neat) 3033, 2934, 1729, 1596, 1547, 1496, 1480, 1456, 1411, 1378, 1362, 1338, 1253, 1221, 1101, 1064, 1030, 985, 909, 806 cm^{-1}. HRMS (ESI) calcd. for $C_{24}H_{22}N_2O_5S$ $(M+Na)^+$ 473.1142, found 473.1142.



3f

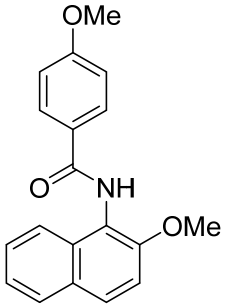
***N*-(Dibenzo[b,d]furan-4-yl)-*N*,4-dimethoxybenzamide (3f).** Orange solid. Mp: 110.6 °C. Rf = 0.36 [hexane/EtOAc = 2:1 (v/v)]. ^1H NMR (400 MHz, $CDCl_3$) δ 3.74 (s, 3H), 3.96 (s, 3H), 6.73 (d, *J* = 8.7 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.35-7.39 (m, 2H), 7.49 (dt, *J* = 0.9, 7.3 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 8.7 Hz, 2H), 7.90 (dd, *J* = 0.9, 7.8 Hz, 1H), 7.94 (d, *J* = 7.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.2, 62.1, 112.0, 113.2, 120.8, 121.1, 123.2, 123.2, 123.7, 125.4, 126.0, 126.10, 126.14, 127.7, 130.6, 150.9, 156.2, 161.7, 168.6. IR (neat) 2937, 1673, 1606, 1510, 1452, 1426, 1306, 1257, 1220, 1194, 1027, 845 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{17}NO_4$ $(M+Na)^+$ 370.1050, found 370.1050.

8. Analytical data of Products 2, 4, 6, and



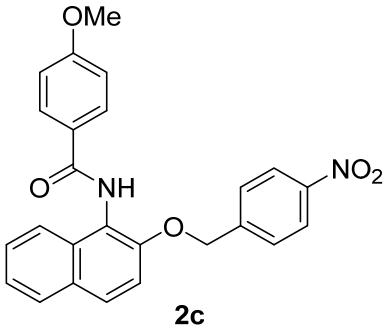
2a

Benzyl (2-methoxynaphthalen-1-yl)carbamate (2a). 103.0 mg (0.335 mmol, 84%). Colorless solid. Mp: 123.3 °C. Rf = 0.40 [hexane/EtOAc = 2:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.93 (s, 3H), 5.25 (s, 2H), 6.53 (br, 1H), 7.28-7.51 (m, 8H), 7.80 (m, 2H), 7.91 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.3, 67.2, 112.9, 118.5, 122.5, 123.8, 126.8, 127.7, 127.9, 128.1, 128.4, 128.5, 129.0, 131.2, 136.4, 151.7, 156.4. IR (neat) 3256, 1693, 1506, 1338, 1262, 1242, 1112 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{17}NO_3$ $(M+Na)^+$ 330.1100, found 330.1100.



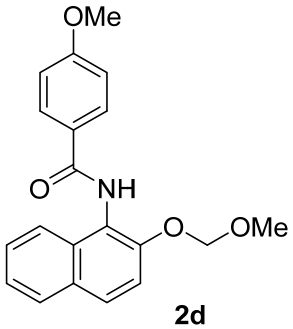
2b

4-Methoxy-*N*-(2-methoxynaphthalen-1-yl)benzamide (2b). 119.3 mg (0.388 mmol, 97%). Colorless solid. Mp: 167.8 °C. Rf = 0.43 [hexane/EtOAc = 1:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (s, 3H), 3.95 (s, 3H), 7.02 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 8.9 Hz, 1H), 7.36 (t, *J* = 6.9 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.72 (br, 1H), 7.80-7.84 (m, 3H), 8.01 (d, *J* = 5.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.41, 56.36, 112.79, 113.75, 119.20, 123.02, 123.82, 126.66, 127.95, 128.39, 129.05, 129.41, 130.68, 151.28. 162.39. 166.30. IR (neat) 3230, 3053, 3016, 2992, 2965, 2935, 2836, 1634, 1606, 1599, 1577, 1530, 1495, 1474, 1461, 1441, 1392, 1345, 1292, 1251, 1214, 1189, 1145, 1122, 1081, 1054, 1030, 938, 867, 853, 844, 812, 806 cm^{-1}. HRMS (ESI) calcd. for $(M+Na)^+$ 3301101, found 330.1101.



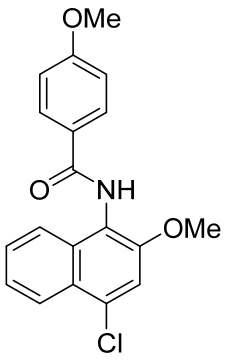
2c

4-Methoxy-*N*-{2-[(4-nitrobenzyl)oxy]naphthalen-1-yl}benzamide (2c). 135.9 mg (0.317 mmol, 79%). Colorless solid. Mp: 193.0 °C. Rf = 0.23 [hexane/EtOAc = 2:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (s, 3H), 5.31 (s, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 9.2 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.50-7.57 (m, 4H), 7.61 (br, 1H), 7.82 (d, *J* = 6.4 Hz, 2H), 7.91-7.95 (m, 3H), 8.14 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 70.5, 114.0, 114.8, 122.8, 123.8, 124.6, 126.4, 127.1, 127.6, 128.1, 128.9, 129.3, 129.8, 131.2, 144.3, 147.5, 150.5, 162.6. IR (neat) 3225, 2993, 2953, 2844, 1648, 1630, 1605, 1582, 1515, 1498, 1452, 1350, 1337, 1296, 1280, 1246, 1202, 1182, 1174, 1146, 1131, 1106, 1095, 1056, 1024, 906, 862, 850, 833 cm^{-1}. HRMS (ESI) calcd. for $C_{25}H_{20}N_2O_5$ $(M+Na)^+$ 451.1265, found 451.1265.



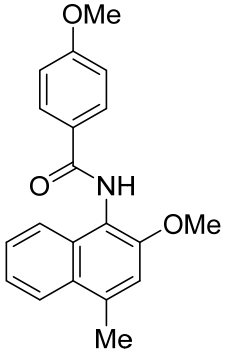
2d

4-Methoxy-*N*-[2-(methoxymethoxy)naphthalen-1-yl]benzamide (2d). 82.2 mg (0.244 mmol, 61%). Colorless solid. Mp: 183.4 °C. Rf = 0.15 [hexane/EtOAc = 2:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.48 (s, 3H), 3.90 (s, 3H), 5.26 (s, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 7.40 (dt, *J* = 0.8, 7.2 Hz, 1H), 7.46-7.52 (m, 2H), 7.81 (t, *J* = 8.0 Hz, 3H), 7.86 (d, *J* = 8.4 Hz, 1H), 8.00 (br d, *J* = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 56.4, 95.9, 113.9, 116.6, 120.9, 123.3, 124.5, 126.7, 128.1, 128.5, 129.4, 130.0, 130.7, 149.6, 162.6. IR (neat) 2952, 2926, 2852, 2340, 1727, 1653, 1559, 1495, 1263, 1107, 795 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{19}NO_4$ $(M+Na)^+$ 360.1206, found 360.1206.



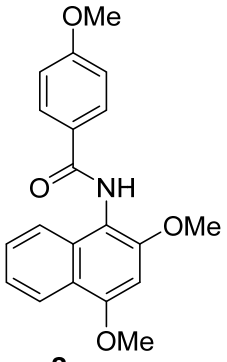
2e

***N*-(4-Chloro-2-methoxynaphthalen-1-yl)-4-methoxybenzamide (2e).** 58.1 mg (0.2 mmol scale, 0.170 mmol, 85%). Colorless solid. Mp: 197.3 °C. Rf = 0.44 [hexane/EtOAc = 1:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (s, 3H), 3.95 (s, 3H), 7.02 (d, *J* = 8.3 Hz, 2H), 7.45-7.49 (m, 2H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.64 (br, 1H), 7.87 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 6.2 Hz, 2H), 8.21 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 56.6, 113.6, 113.8, 118.6, 123.4, 124.6, 125.0, 126.3, 126.4, 127.5, 129.5, 131.5, 131.8, 150.9, 162.6, 166.4. IR (neat) 3263, 3073, 3009, 2964, 2934, 2901, 2837, 1646, 1627, 1602, 1566, 1526, 1487, 1461, 1441, 1419, 1385, 1330, 1311, 1296, 1248, 1218, 1175, 1157, 1126, 1096, 1054, 1026, 948, 914, 901, 857, 846, 839 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{16}ClNO_3$ $(M+Na)^+$ 364.0711, found 364.0711.



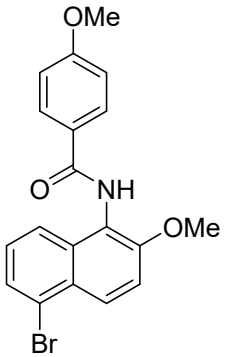
2f

4-Methoxy-*N*-(2-methoxy-4-methylnaphthalen-1-yl)benzamide (2f). 56.6 mg (0.2 mmol scale, 0.176 mmol, 88%). Colorless solid. Mp: 197.1 °C. Rf = 0.52 [hexane/EtOAc = 1:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.73 (s, 3H), 3.90 (s, 3H), 3.94 (s, 3H), 7.02 (d, *J* = 8.3 Hz, 2H), 7.18 (br, 1H), 7.40 (t, *J* = 6.9 Hz, 1H), 7.48 (t, *J* = 6.9 Hz, 1H), 7.65 (s, 1H), 7.85 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9, 56.4, 56.5, 113.8, 114.0, 117.2, 123.4, 123.7, 124.3, 126.5, 126.8, 128.1, 129.4, 131.0, 135.5, 151.0, 162.4, 166.4. IR (neat) 3233, 3065, 3013, 2992, 2965, 2935, 2844, 1634, 1602, 1578, 1529, 1497, 1474, 1460, 1440, 1391, 1349, 1296, 1262, 1250, 1189, 1159, 1132, 1112, 1098, 1053, 1028, 936, 853, 845, 816 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{19}NO_3$ $(M+Na)^+$ 344.1257, found 344.1257.



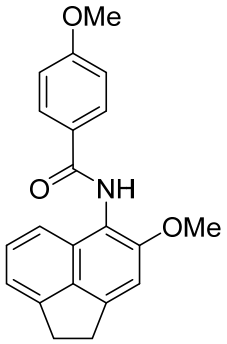
2g

***N*-(2,4-dimethoxynaphthalen-1-yl)-4-methoxybenzamide (2g).** 57.9 mg (0.2 mmol scale, 0.172 mmol, 86%). Colorless solid. Mp: 185.4 °C. Rf = 0.22 [hexane/EtOAc = 1:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (s, 3H), 3.95 (s, 3H), 4.04 (s, 3H), 6.68 (s, 1H), 7.01 (d, *J* = 8.3 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.52 (br, 1H), 7.77 (m, 1H), 8.00 (d, *J* = 8.3 Hz, 2H), 8.19 (d, *J* = 8.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 55.8, 56.7, 93.2, 111.9, 113.8, 121.3, 122.2, 122.4, 123.3, 127.0, 127.6, 129.4, 131.6, 152.3, 156.1, 162.4, 166.6. IR (neat) 3283, 3003, 2962, 2936, 2842, 1637, 1602, 1524, 1494, 1381, 1354, 1274, 1250, 1218, 1175, 1157, 1137, 1110, 1097, 1025, 983, 931, 845 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{19}NO_4$ $(M+Na)^+$ 360.1206, found 360.1206.



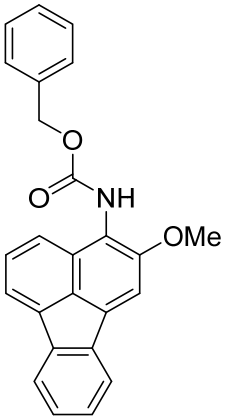
2h

***N*-(5-Bromo-2-methoxynaphthalen-1-yl)-4-methoxybenzamide (2h).** 73.9 mg (0.2 mmol scale, 0.191 mmol, 96%). Colorless solid. Mp: 191.1 °C. Rf = 0.24 [hexane/EtOAc = 2:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (s, 3H), 3.97 (s, 3H), 7.02 (d, *J* = 8.3 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 9.6 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 1H), 7.71 (br, 1H), 7.82 (d, *J* = 8.9 Hz, 1H), 8.00 (d, *J* = 6.2 Hz, 2H), 8.25 (d, *J* = 8.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 56.3, 113.6, 113.8, 119.4, 122.9, 123.2, 126.4, 126.9, 127.4, 127.8, 127.9, 129.5, 132.0, 151.8, 162.6, 166.4. IR (neat) 3247, 1637, 1606, 1596, 1578, 1530, 1488, 1460, 1442, 1392, 1334, 1293, 1262, 1249, 1189, 1127, 1090, 1067, 1049, 1029, 939, 852, 844 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{16}BrNO_3$ $(M+Na)^+$ 408.0206, found 408.0206.



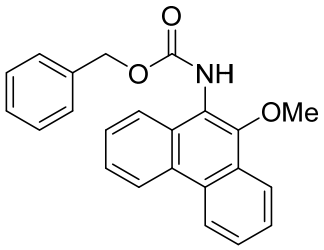
2i

4-Methoxy-*N*-(4-methoxy-1,2-dihydroacenaphthylen-5-yl)benzamide (2i). 51.8 mg (0.2 mmol scale, 0.155 mmol, 78%). Colorless solid. Mp: 213.5 °C. Rf = 0.42 [hexane/EtOAc = 1:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.40 (m, 4H), 3.90 (s, 3H), 3.94 (s, 3H), 7.01 (d, *J* = 7.6 Hz, 2H), 7.15 (m, 2H), 7.43 (t, *J* = 6.9 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.75 (br, 1H), 8.00 (d, *J* = 6.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.4, 30.6, 55.5, 56.7, 106.8, 113.8, 116.0, 117.3, 119.0, 127.0, 128.1, 128.7, 129.4, 134.7, 145.9, 146.3, 152.9, 162.3, 165.9. IR (neat) 3227, 2928, 2837, 1636, 1605, 1526, 1502, 1460, 1399, 1374, 1352, 1316, 1281, 1249, 1219, 1190, 1174, 1093, 1060, 1029, 963, 945, 922, 841 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{19}NO_3$ $(M+Na)^+$ 356.1257, found 356.1257.



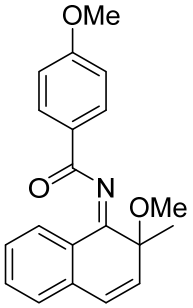
2j

Benzyl (2-methoxyfluoranthen-3-yl)carbamate (2j). 69.7 mg (0.2 mmol scale, 0.182 mmol, 91%). Yellow solid. Mp: 217.6 °C. Rf = 0.44 [hexane/EtOAc = 2:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.05 (s, 3H), 5.26 (s, 3H), 6.74 (br, 1H), 7.35-7.43 (m, 7H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.70 (s, 1H), 7.79 (d, *J* = 6.9 Hz, 1H), 7.82-7.87 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.9, 67.4, 107.3, 118.5, 119.8, 121.1, 121.5, 123.6, 127.5, 127.6, 127.8, 128.2, 128.3, 128.45, 128.53, 136.2. 136.3, 136.7, 138.8, 140.0, 152.9, 155.3. IR (neat) 3270, 3033, 1705, 1521, 1489, 1461, 1454, 1442, 1354, 1275, 1249, 1219, 1176, 1161, 1147, 1110, 1168, 1042, 1024, 852 cm^{-1}. HRMS (ESI) calcd. for $C_{25}H_{19}NO_3$ $(M+Na)^+$ 404.1257, found 404.1257.



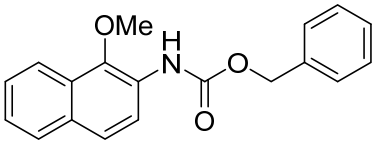
2k

Benzyl (10-methoxyphenanthren-9-yl)carbamate (2k). 42.2 mg (0.2 mmol scale, 0.118 mmol, 59%). Colorless solid. Mp: 174.2 °C. Rf = 0.48 [hexane/EtOAc = 2:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.93 (s, 3H), 5.27 (s, 2H), 6.60 (br, 1H), 7.35-7.43 (m, 4H), 7.60-7.67 (m, 3H), 7.69 (t, *J* = 6.9 Hz, 1H), 8.00 (m, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 8.67 (m, 1H), 8.69 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 61.7, 67.6, 121.7, 122.9, 123.0, 123.1, 123.7, 126.1, 127.0, 127.2, 127.4, 127.6, 127.9, 128.4, 128.6, 128.7, 130.2, 131.1, 136.3, 146.5, 149.9. IR (neat) 3254, 3076, 3029, 2954, 1690, 1531, 1489, 1450, 1362, 1328, 1245, 1214, 1197, 1177, 1125, 1111, 1074, 1019, 987, 961 cm^{-1}. HRMS (ESI) calcd. for $C_{23}H_{19}NO_3$ $(M+Na)^+$ 380.1257, found 380.1257.



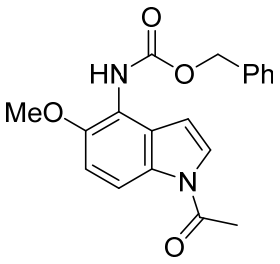
6l

(*E*)-4-methoxy-*N*-[2-methoxy-2-methylnaphthalen-1(2*H*)-ylidene]benzamide (6l). 43.1 mg (0.2 mmol scale, 0.134 mmol, 67%). Colorless solid. Mp: 170.1 °C. Rf = 0.43 [hexane/EtOAc = 2:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.58 (s, 3H), 2.75 (s, 3H), 3.84 (s, 3H), 5.97 (d, *J* = 9.6 Hz, 1H), 6.57 (d, *J* = 9.6 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.89 (d, *J* = 8.7 Hz, 2H), 8.19 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.7, 54.5, 55.4, 80.2, 113.4, 127.0, 127.4, 127.5, 127.7, 128.2, 129.2, 130.8, 132.9, 134.7. 135.0, 162.7, 166.4, 178.7. IR (neat) 3053, 2989, 2967, 2938, 2842, 2828, 1923, 1643, 1594, 1508, 1482, 1458, 1451, 1393, 1360, 1315, 1302, 1270, 1255, 1240, 1226, 1208, 1184, 1165, 1092, 1057, 1025, 1006, 971, 942, 884, 849, 810 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{19}NO_3$ $(M+Na)^+$ 344.1257, found 344.1257.



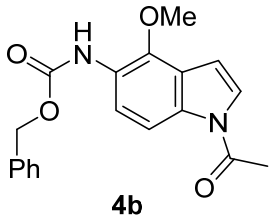
2m

Benzyl (1-methoxynaphthalen-2-yl)carbamate (2m). 19.4 mg (0.2 mmol scale, 0.063 mmol, 32%). Brown oil. Rf = 0.48 [hexane/EtOAc = 3:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 3H), 5.27 (s, 2H), 7.35-7.52 (m, 8H), 7.65 (d, *J* = 9.2 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 8.35 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 61.4, 67.2, 118.8, 121.0, 121.7, 124.7, 126.3, 127.2, 127.7, 128.2, 128.40, 128.42, 128.7, 130.9, 136.0, 142.3, 153.5. IR (neat) 3412, 3323, 3062, 3032, 2938, 2843, 1730, 1631, 1602, 1519, 1503, 1455, 1427, 1363, 1290, 1259, 1209, 1193, 1148, 1092, 1060, 931 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{17}NO_3$ $(M+Na)^+$ 330.1100, found 330.1100.



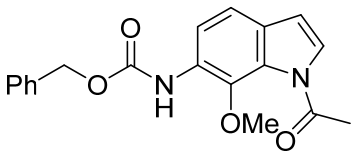
4a

Benzyl (1-acetyl-5-methoxy-1H-indol-4-yl)carbamate (4a). 54.0 mg (0.2 mmol scale, 0.160 mmol, 80%). Colorless solid. Mp: 155.8 °C. Rf = 0.56 [hexane/EtOAc = 1:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.61 (s, 3H), 3.88 (s, 3H), 5.23 (s, 2H), 6.74 (s, 1H), 6.92-6.96 (m, 2H), 7.34-7.45 (m, 6H), 8.27 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.8, 56.4, 67.3, 108.8, 108.9, 113.8, 117.5, 125.4, 125.8, 128.25, 128.34, 128.5, 131.2, 136.1, 147.6, 154.1, 168.4. IR (neat) 3283, 3149, 3063, 3032, 3006, 2970, 2954, 2934, 2833, 1697, 1619, 1590, 1545, 1519, 1487, 1452, 1423, 1385, 1370, 1326, 1263, 1232, 1184, 1151, 1124, 1099, 1063, 1044, 970, 940, 923, 913, 845 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{18}N_2O_4$ $(M+Na)^+$ 361.1159, found 361.1159.



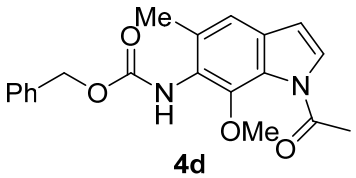
4b

Benzyl (1-acetyl-4-methoxy-1H-indol-5-yl)carbamate (4b). 54.3 mg (0.2 mmol scale, 0.161 mmol, 80%). Colorless solid. Mp: 97.3 °C. Rf = 0.54 [hexane/EtOAc = 1:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.63 (s, 3H), 4.00 (s, 3H), 5.23 (s, 2H), 6.73 (s, 1H), 7.28 (br, 1H), 7.37-7.45 (m, 6H), 8.41 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.9, 61.1, 67.0, 105.8, 111.9, 116.9, 122.0, 125.2, 125.6, 128.35, 128.38, 128.6, 133.1, 136.1, 140.6, 153.5, 168.3. IR (neat) 3429, 3161, 3138, 3071, 3030, 2999, 2971, 2948, 2893, 1959, 1843, 1715, 1693, 1619, 1593, 1551, 1527, 1469, 1455, 1440, 1420, 1388, 1372, 1340, 1261, 1241, 1199, 1176, 1135, 1094, 1065, 1027, 990, 971, 963, 947, 914 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{18}N_2O_4$ $(M+Na)^+$ 361.1159, found 361.1159.



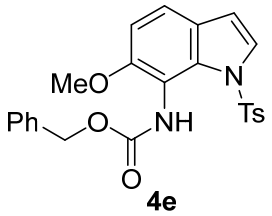
4c

Benzyl (1-acetyl-7-methoxy-1H-indol-6-yl)carbamate (4c). 49.2 mg (0.2 mmol scale, 0.146 mmol, 73%). Dark red oil. Rf = 0.27 [hexane/EtOAc = 2:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.67 (s, 3H), 3.70 (s, 3H), 5.24 (s, 2H), 6.59 (d, *J* = 3.7 Hz, 1H), 7.31 (d, *J* = 8.7 Hz, 1H), 7.33-7.45 (m, 7H), 8.11 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.7, 60.7, 67.0, 109.0, 115.9, 117.0, 126.7, 126.8, 128.2, 128.3, 128.6, 129.2, 129.3, 136.0, 136.8, 153.5, 167.7. IR (neat) 3414, 3324, 3153, 3089, 3063, 3031, 3006, 2938, 2830, 1718, 1614, 1585, 1547, 1521, 1464, 1417, 1364, 1311, 1259, 1228, 1192, 1086, 1051, 1028, 964, 906, 816 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{18}N_2O_4$ $(M+Na)^+$ 361.1159, found 361.1159.



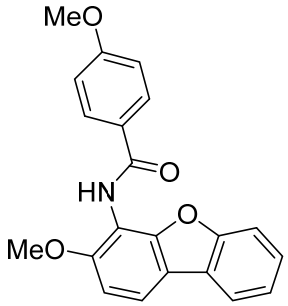
4d

Benzyl(1-acetyl-7-methoxy-5-methyl-1H-indol-6-yl)carbamate (4d). 35.1 mg (0.2 mmol scale, 0.100 mmol, 50%). Orange solid. Mp: 98.0 °C. Rf = 0.19 [hexane/EtOAc = 2:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3H), 2.66 (s, 3H), 3.66 (s, 3H), 5.22 (s, 2H), 6.45 (br, 1H), 6.54 (d, *J* = 3.4 Hz, 1H), 7.20 (s, 1H), 7.30-7.47 (m, 5H), 7.50 (d, *J* = 4.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.3, 24.9, 61.0, 67.2, 108.3, 117.8, 125.8, 126.3, 127.9, 128.1, 128.2, 128.5, 132.7, 133.1, 136.4, 143.9, 155.1,168.1. IR (neat) 3254, 3017, 2960, 2934, 2837, 1722, 1694, 1576, 1549, 1517, 1474, 1455, 1432, 1363, 1331, 1302, 1287, 1238, 1197, 1092, 1050, 1029, 1019, 954, 919, 896, 868, 844 cm^{-1}. HRMS (ESI) calcd. for $C_{20}H_{20}N_2O_4$ $(M+Na)^+$ 375.1315, found 375.1315.



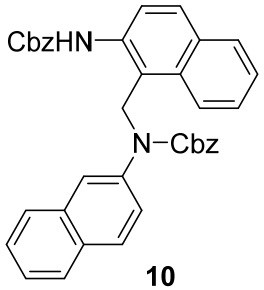
4e

Benzyl (6-methoxy-1-tosyl-1H-indol-7-yl)carbamate (4e). 37.8 mg (0.2 mmol scale, 0.084 mmol, 42%). Colorless solid. Mp: 146.0 °C. Rf = 0.28 [hexane/EtOAc = 2:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3H), 3.79 (s, 3H), 4.96 (s, 2H), 6.63 (d, *J* = 3.4 Hz, 1H), 6.95 (br, 1H), 7.10 (br, 2H), 7.28-7.50 (m, 5H), 7.55 (m, *J* = 5.5 Hz, 2H), 7.68 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 56.8, 66.5, 107.6, 112.2, 120.3, 126.1, 126.8, 127.6, 127.9, 128.1, 128.4, 129.8, 131.7, 136.4, 136.6, 144.4, 153.7. IR (neat) 3322, 3032, 2958, 2932, 2849, 1735, 1617, 1594, 1547, 1504, 1451, 1414, 1344, 1279, 1248, 1219, 1177, 1165, 1138, 1114, 1090, 1067, 1032, 1014, 898, 871, 814 cm^{-1}. HRMS (ESI) calcd. for $C_{24}H_{22}N_2O_5S$ $(M+Na)^+$ 473.1142, found 473.1142.



4f

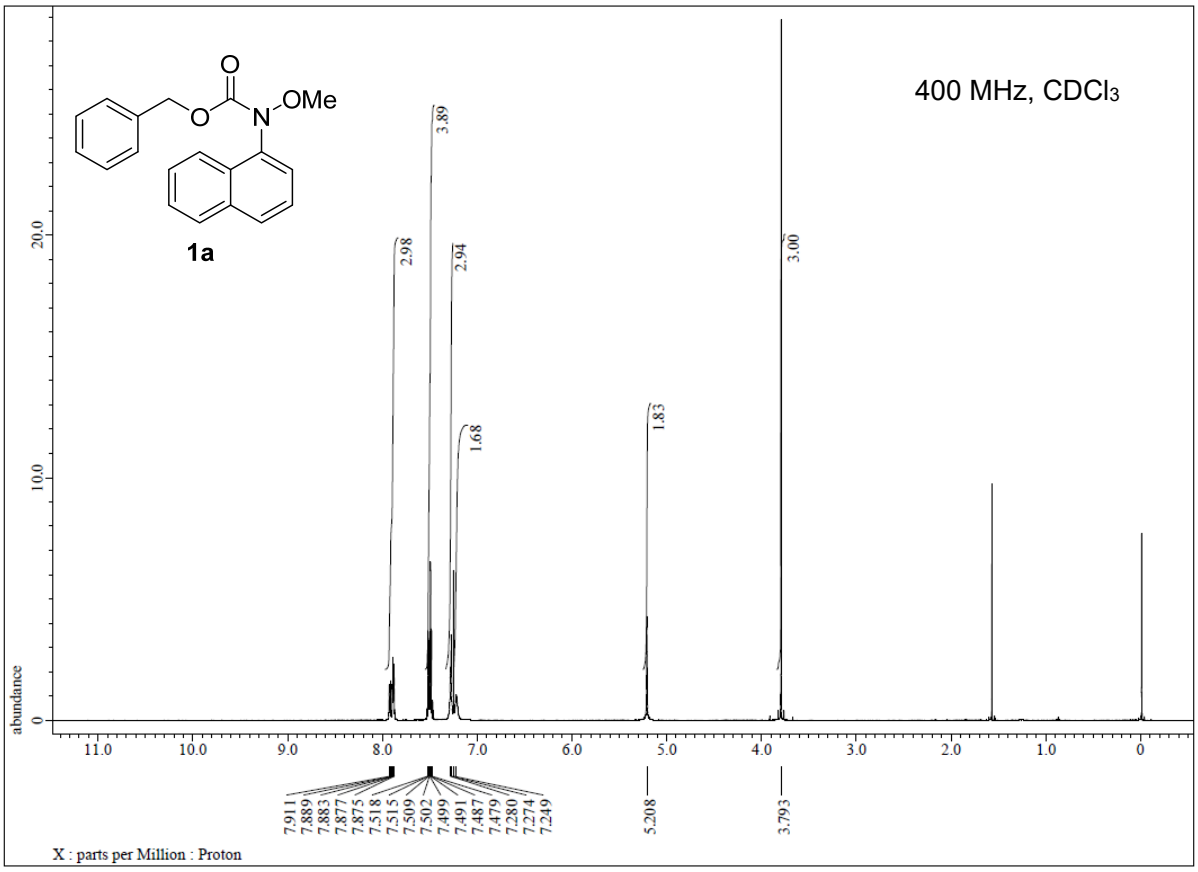
4-methoxy-*N*-(3-methoxydibenzo[b,d]furan-4-yl)benzamide (4f). 66.4 mg (0.2 mmol scale, 0.191 mmol, 96%). Colorless solid. Mp: 173.0 °C. Rf = 0.50 [hexane/EtOAc = 1:1 (v/v)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (s, 3H), 3.94 (s, 3H), 6.99-7.02 (m, 3H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 8.3 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.70 (br, 1H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 56.5, 106.6, 111.3, 111.8, 113.7, 117.9, 119.0, 119.9, 122.7, 124.3, 126.1, 126.4, 129.6, 151.2, 152.6, 156.6, 162.5, 165.2. IR (neat) 3392, 3078, 3017, 2961, 2936, 2906, 2837, 1666, 1643, 1605, 1576, 1512, 1470, 1456, 1439, 1415, 1355, 1325, 1313, 1255, 1239, 1216, 1194, 1178, 1123, 1091, 1024, 958, 942, 925, 882, 855, 840, 816 cm^{-1}. HRMS (ESI) calcd. for $C_{21}H_{17}NO_4$ $(M+Na)^+$ 370.1050, found 370.1050.

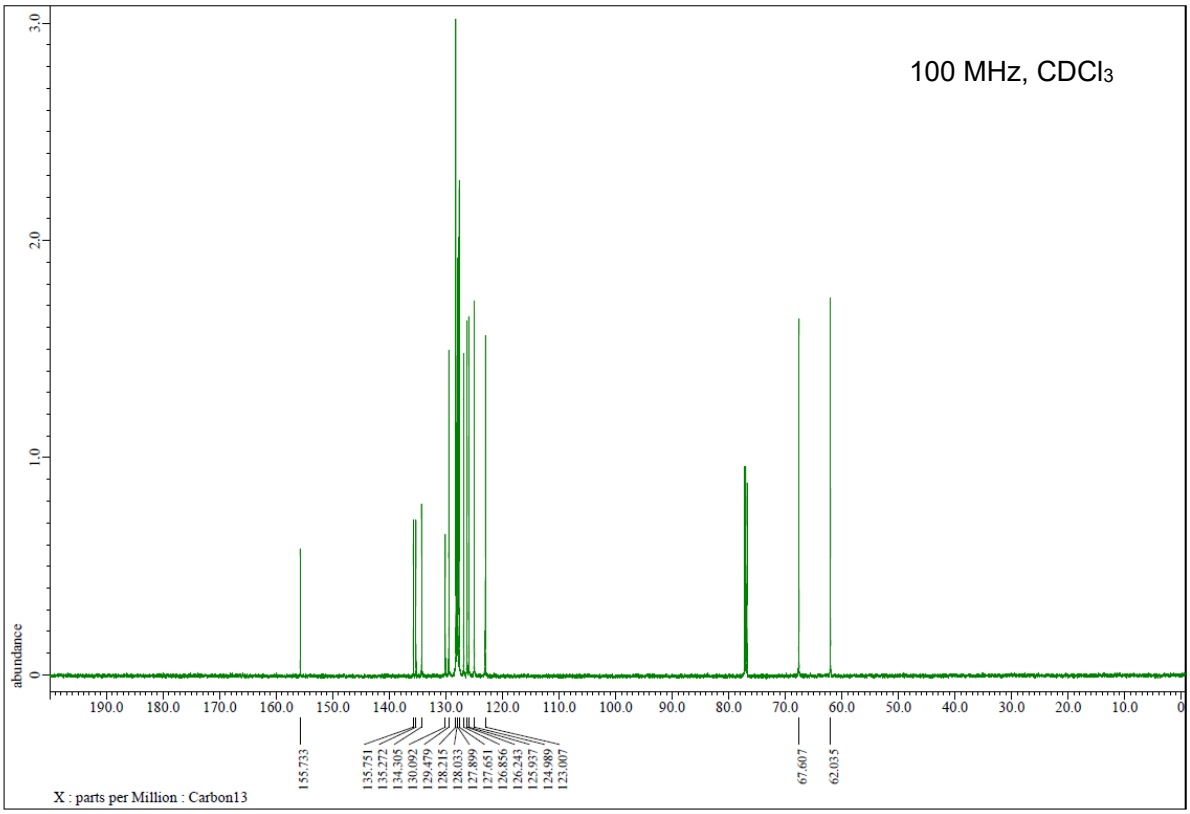


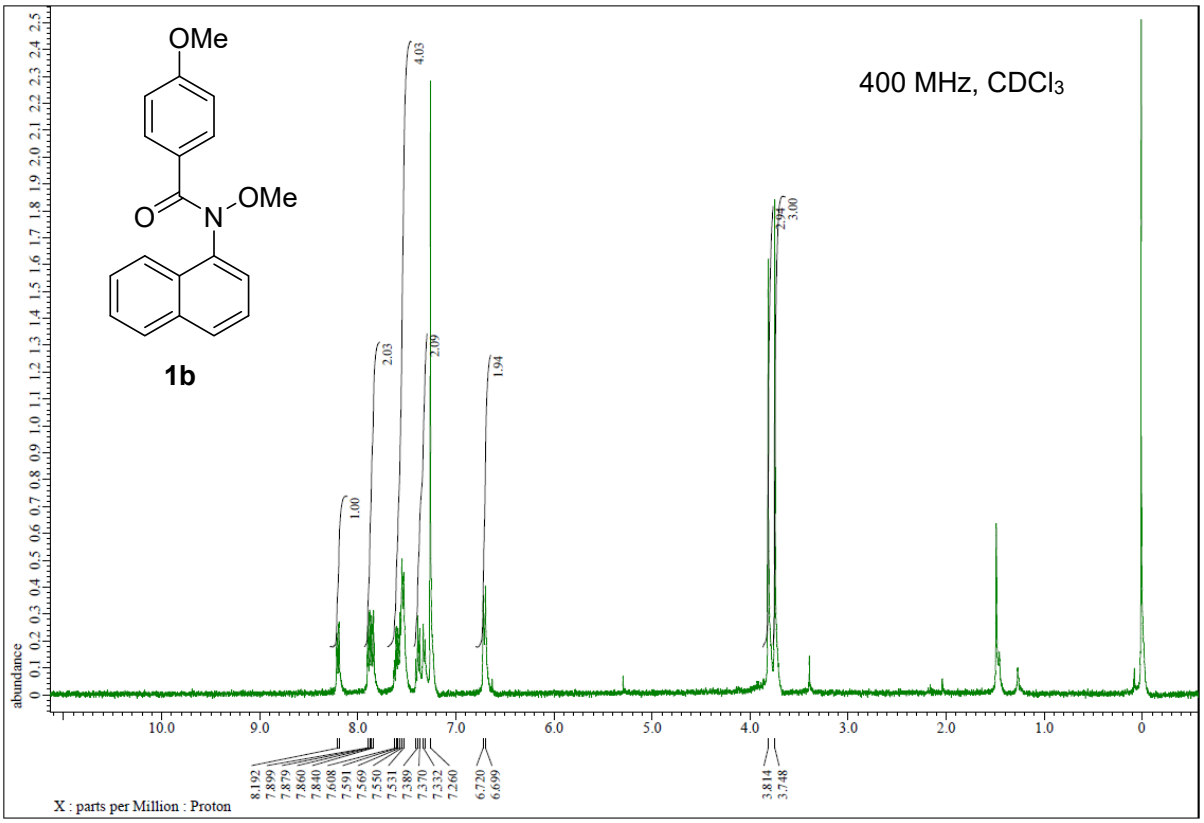
10

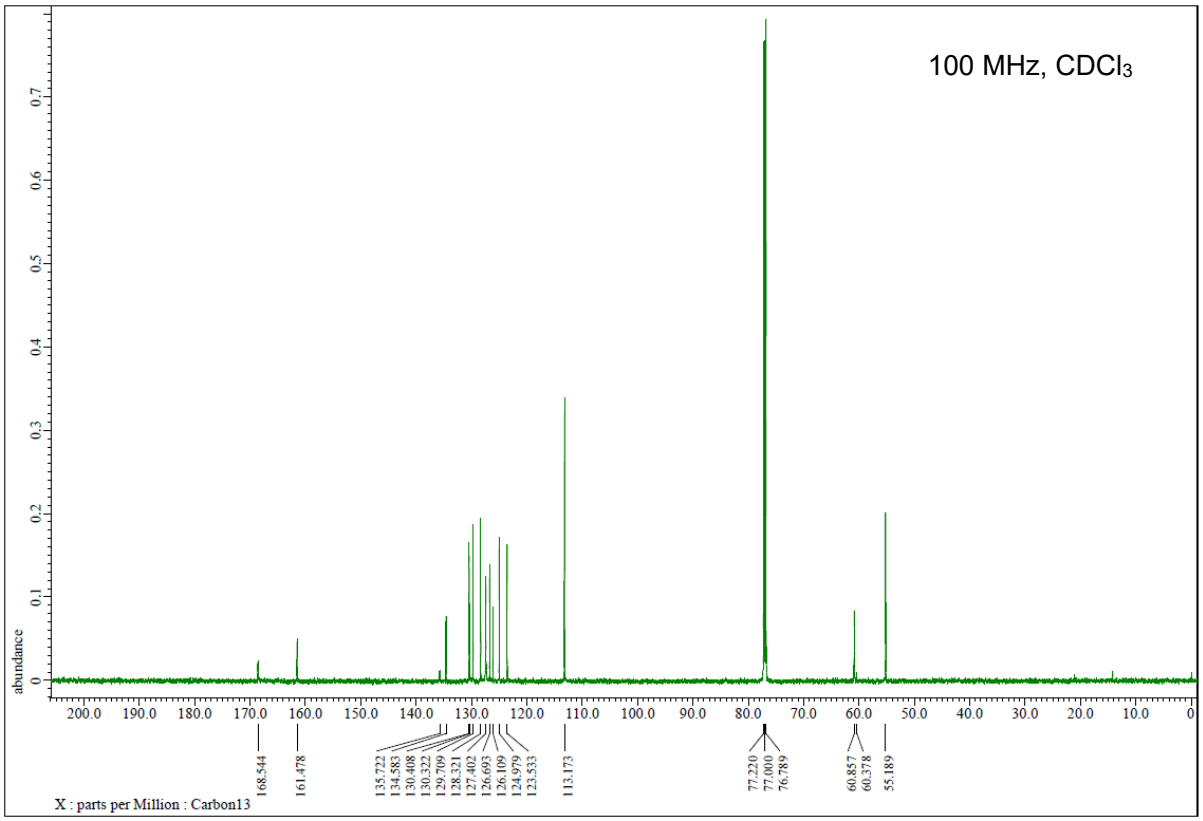
10, Colorless solid. Mp: 230.5 °C. Rf=0.36 [hexane/EtOAc = 3:1 (v/v)]. ^{1}H NMR (400 MHz,$CDCl_3$) δ 5.12 (s, 2H), 5.26 (s, 2H), 5.36 (s, 2H), 6.91 (t, *J* = 7.2 Hz, 1H), 7.10-7.12 (m, 3H), 7.20-7.23 (m, 5H), 7.34 (t, J = 7.2, 1H), 7.40 (t, J = 7.2, 2H), 7.46-7.55 (m, 5H), 7.68-7.84 (m, 5H), 7.99(br, 1H), 9.42(br, 1H). ^{13}C NMR(100 MHz, $CDCl_3$) δ 47.2, 66.7, 67.8, 122.6, 124.0, 124.5, 126.1, 126.2, 126.5, 127.4, 127.7, 127.86, 127.91, 128.0, 128.1, 128.3, 128.5, 129.0, 129.3, 131.0, 132.3, 132.6, 133.5, 135.6, 136.1, 136.7, 139.2, 154.7, 156.9. IR (neat) 3247, 3060, 3032, 2957, 2925, 2854, 1730, 1682, 1626, 1601, 1586, 1508, 1455, 1430, 1410, 1341, 1287, 1263, 1241, 1218, 1120, 1090, 1039, 990, 861, 816, 749, 697 cm^{-1}. HRMS (ESI) calcd. for $(M+Na)^+$ 589.2098, found 589.2098.

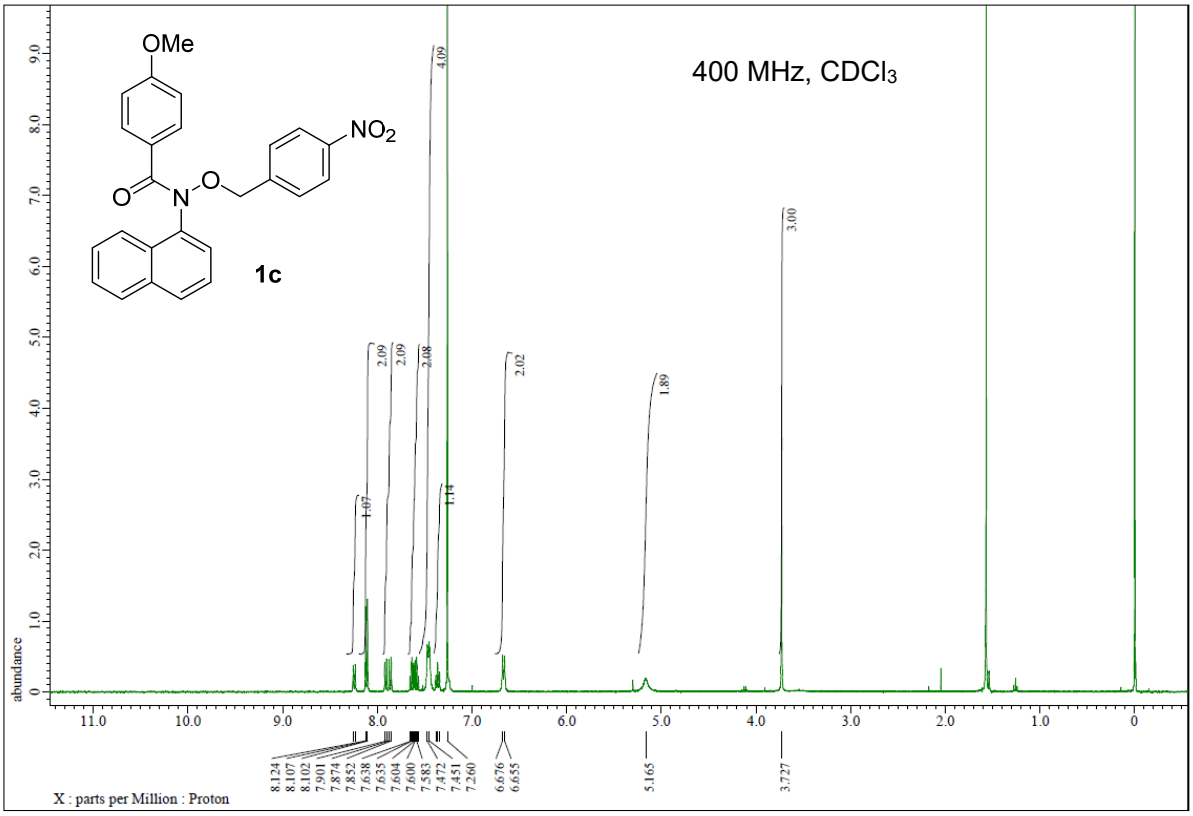
8. NMR charts of substrates **1** and **3**

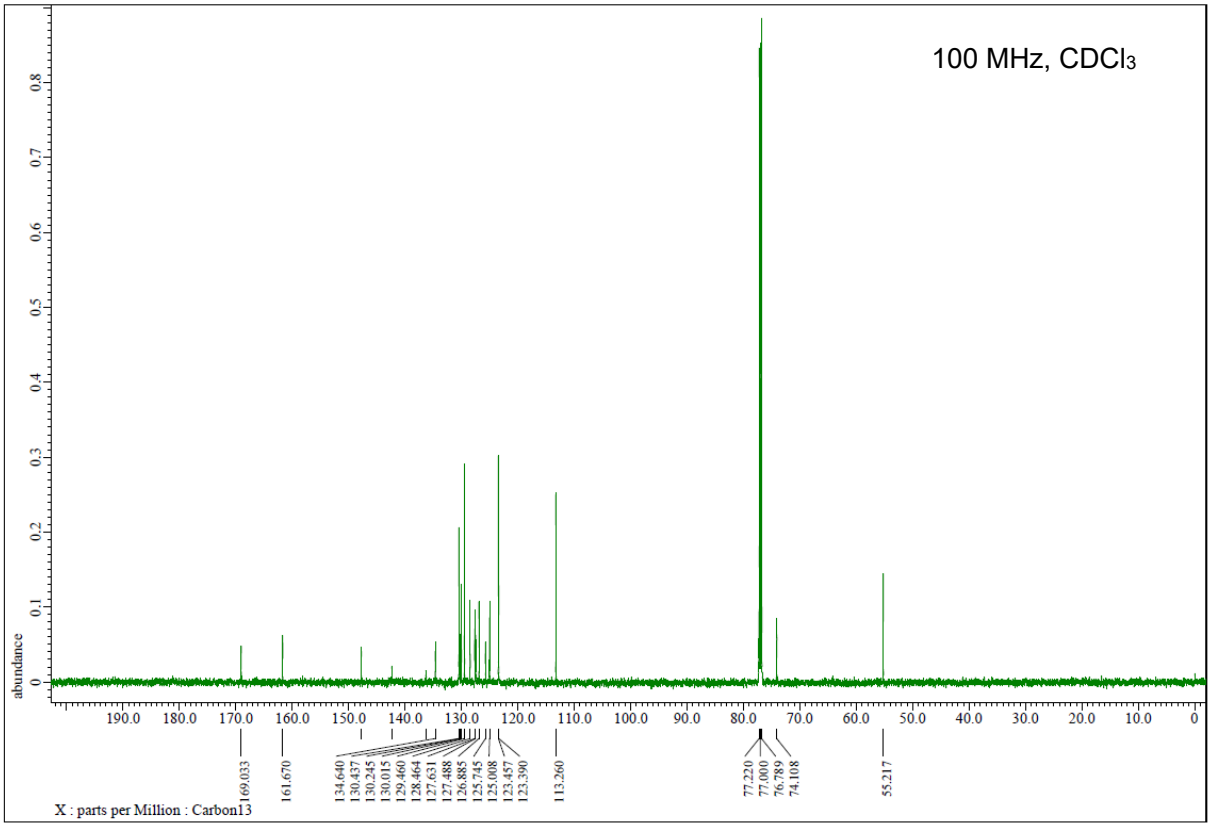


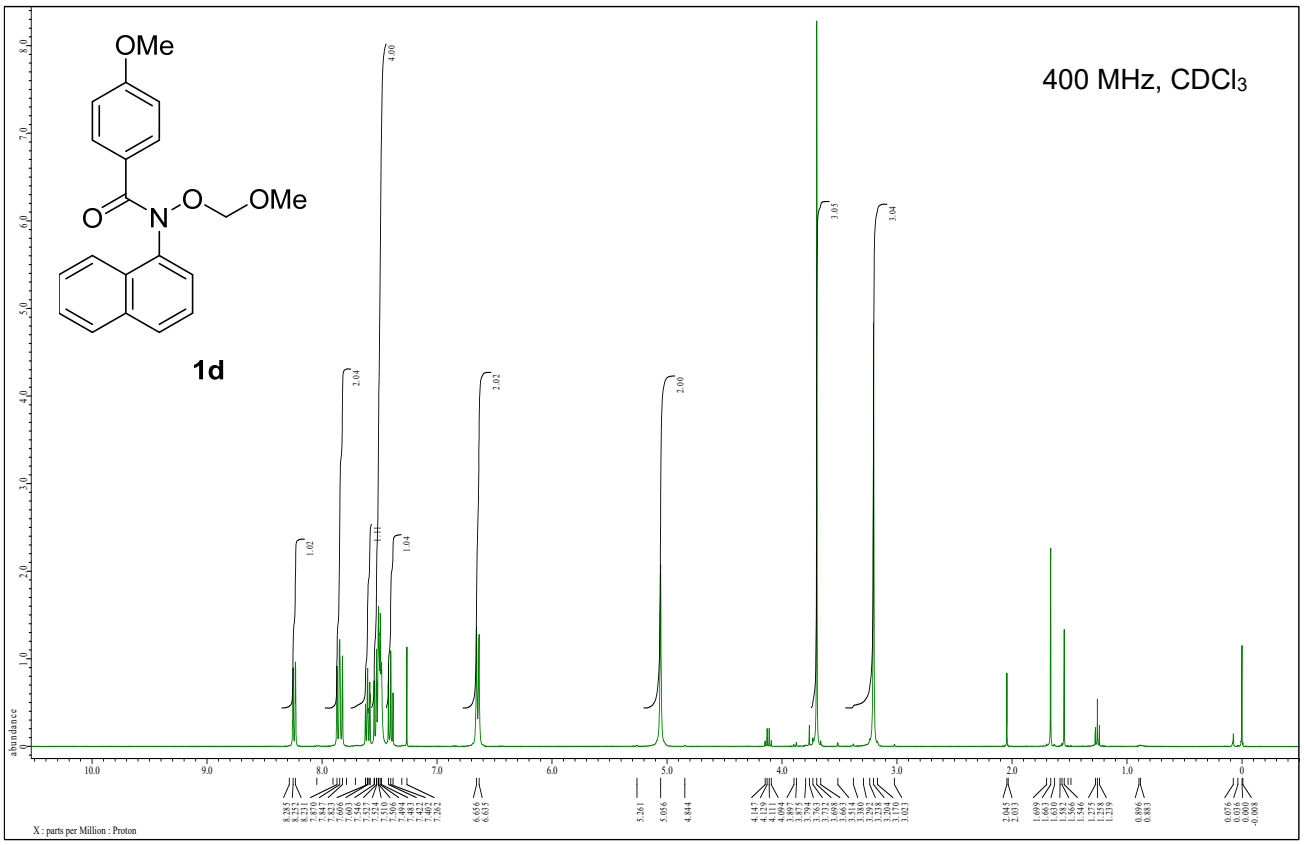


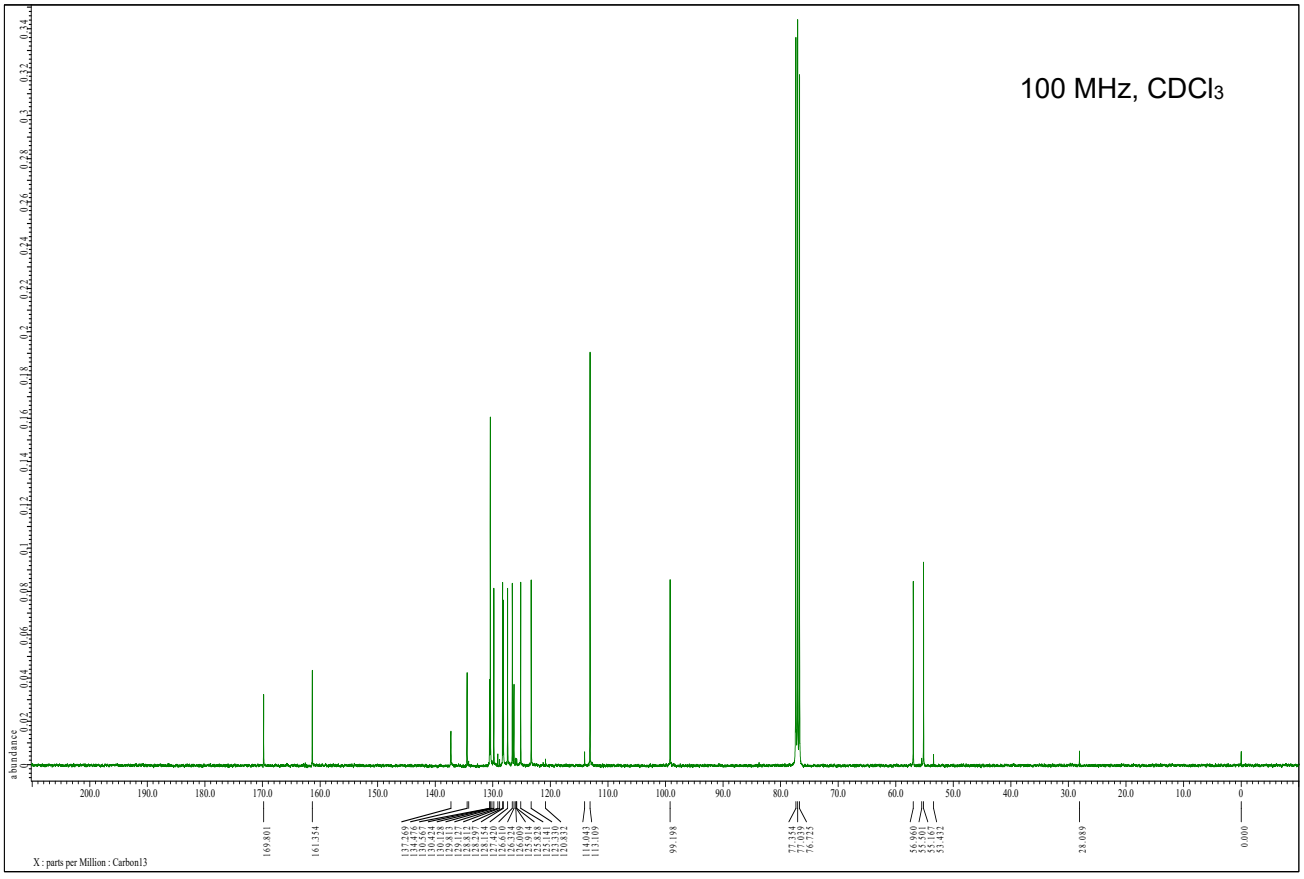

OMe
OMe
O
N
1b
400 MHz, CDCl3
4.03
2.03
2.09
1.94
1.00
2.94
3.00
abundance
X : parts per Million : Proton
8.192
7.899
7.879
7.860
7.840
7.608
7.591
7.569
7.550
7.531
7.389
7.370
7.332
7.260
6.720
6.699
3.814
3.748

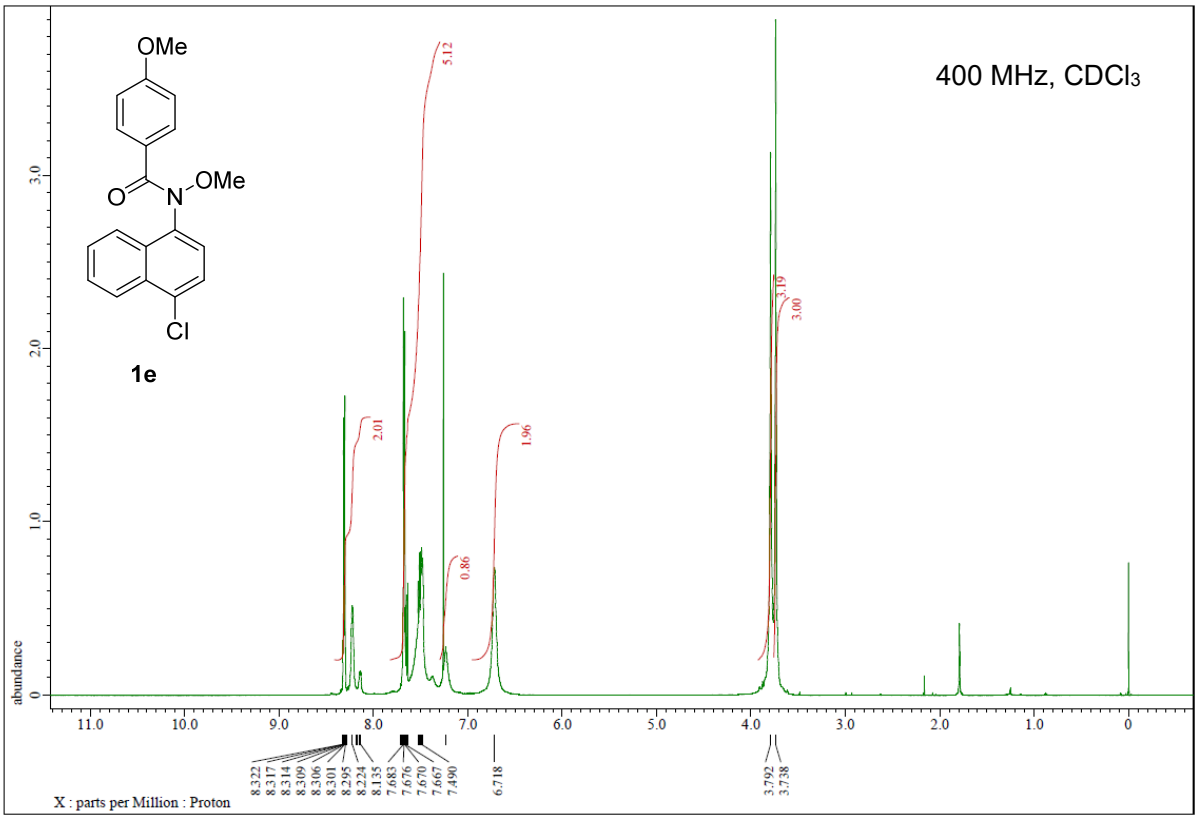

100 MHz, CDCl3
abundance
X : parts per Million : Carbon13
168.544
161.478
135.722
134.583
130.408
130.322
129.709
128.321
127.402
126.693
126.109
124.979
123.533
113.173
77.220
77.000
76.789
60.857
60.378
55.189

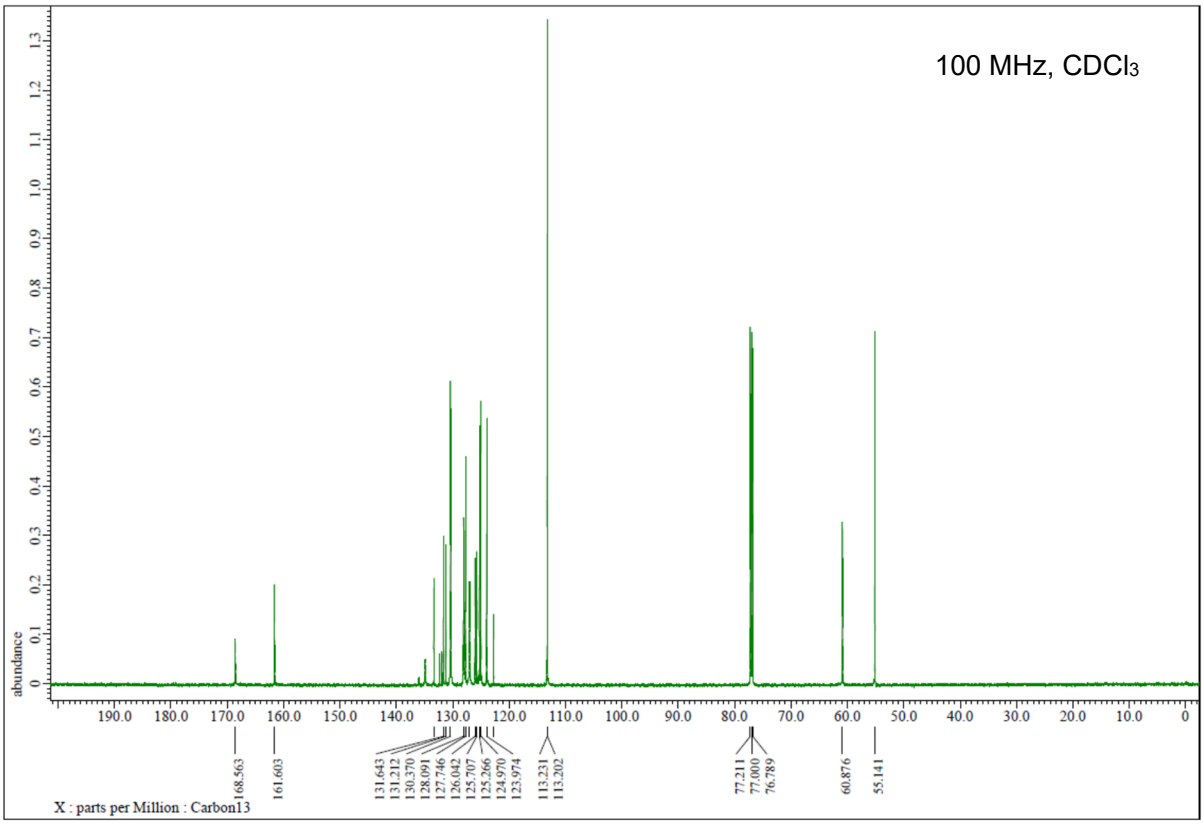

OMe
NO2
O
N
O
1c
400 MHz, CDCl3
4.09
3.00
2.09
2.09
2.08
2.02
1.89
1.07
1.14
abundance
X : parts per Million : Proton
8.124
8.107
8.102
7.901
7.874
7.852
7.638
7.635
7.604
7.600
7.583
7.472
7.451
7.260
6.676
6.655
5.165
3.727

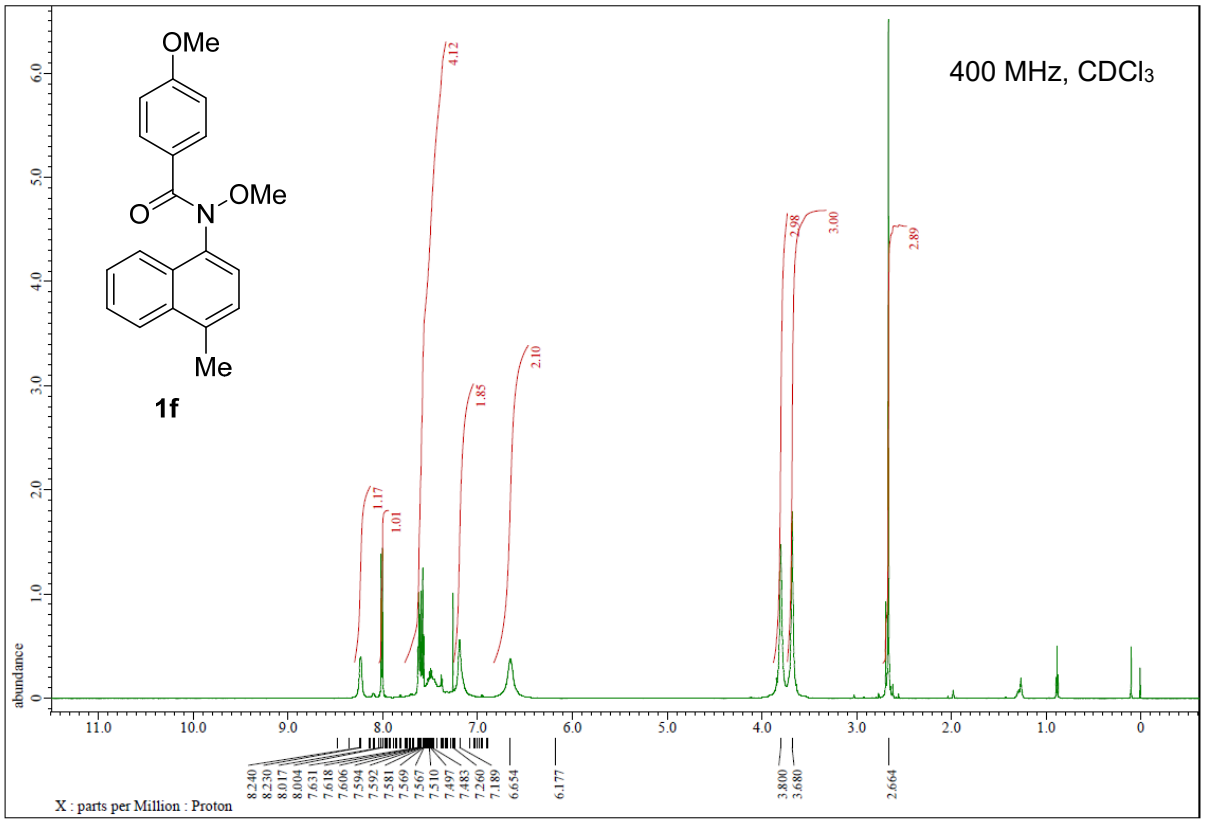

100 MHz, CDCl3
abundance
X : parts per Million : Carbon13
169.033
161.670
134.640
130.437
130.245
130.015
129.460
128.464
127.631
127.488
126.885
125.745
125.008
123.457
123.390
113.260
77.220
77.000
76.789
74.108
55.217

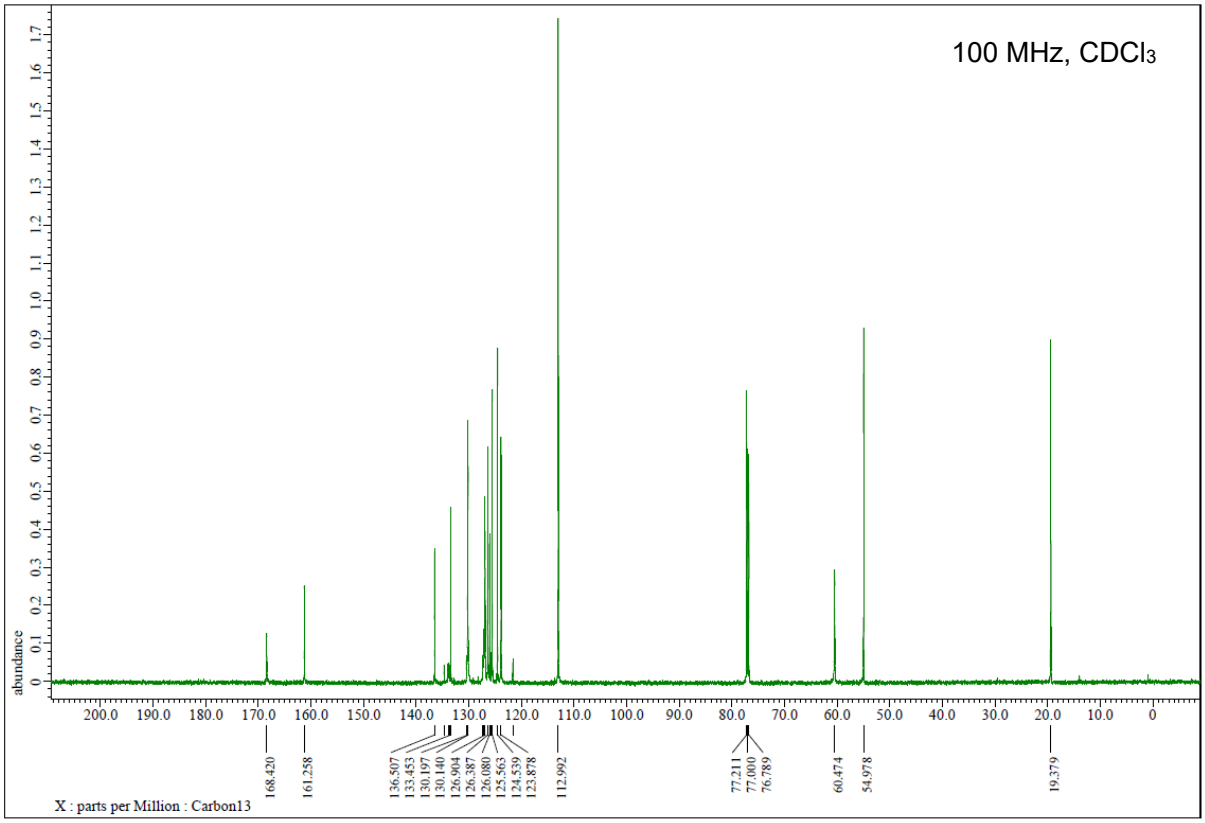

OMe
O
N
O
OMe
1d
400 MHz, CDCl3
X : parts per Million : Proton

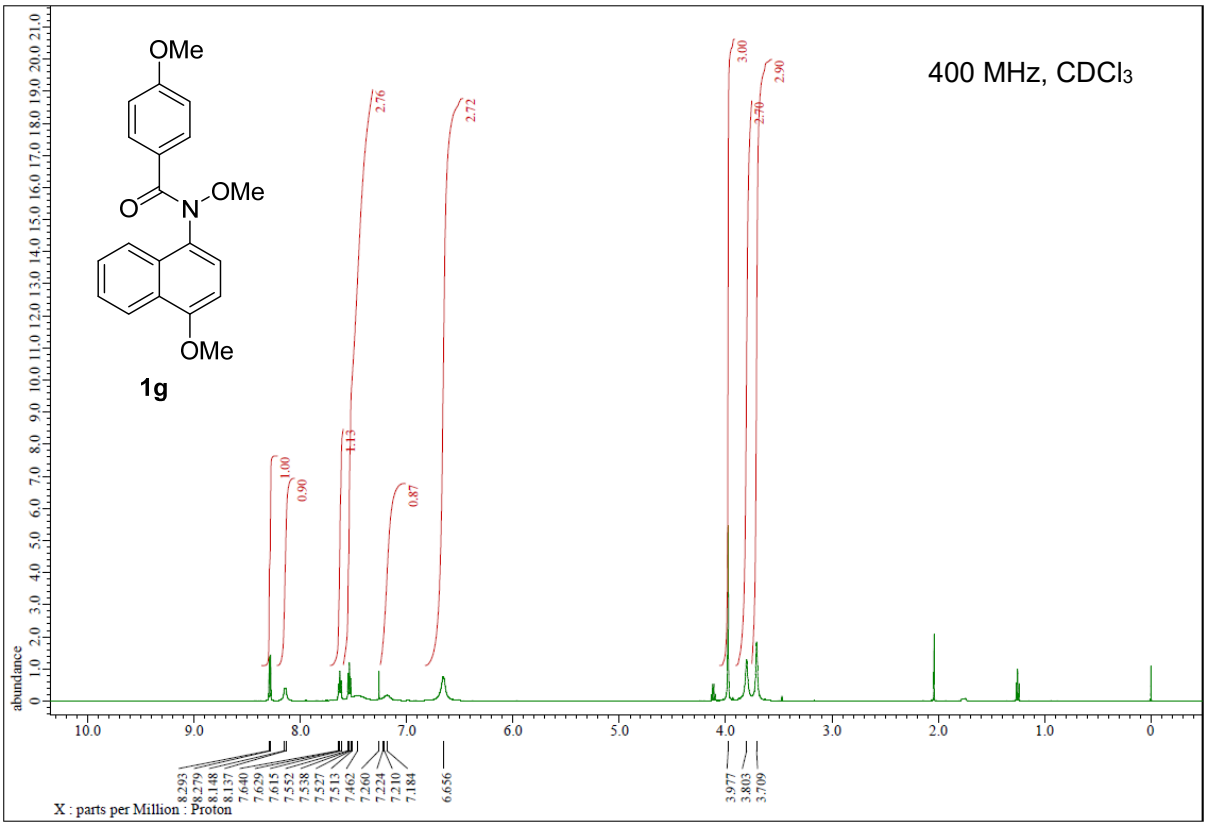

100 MHz, CDCl3
X : parts per Million : Carbon13

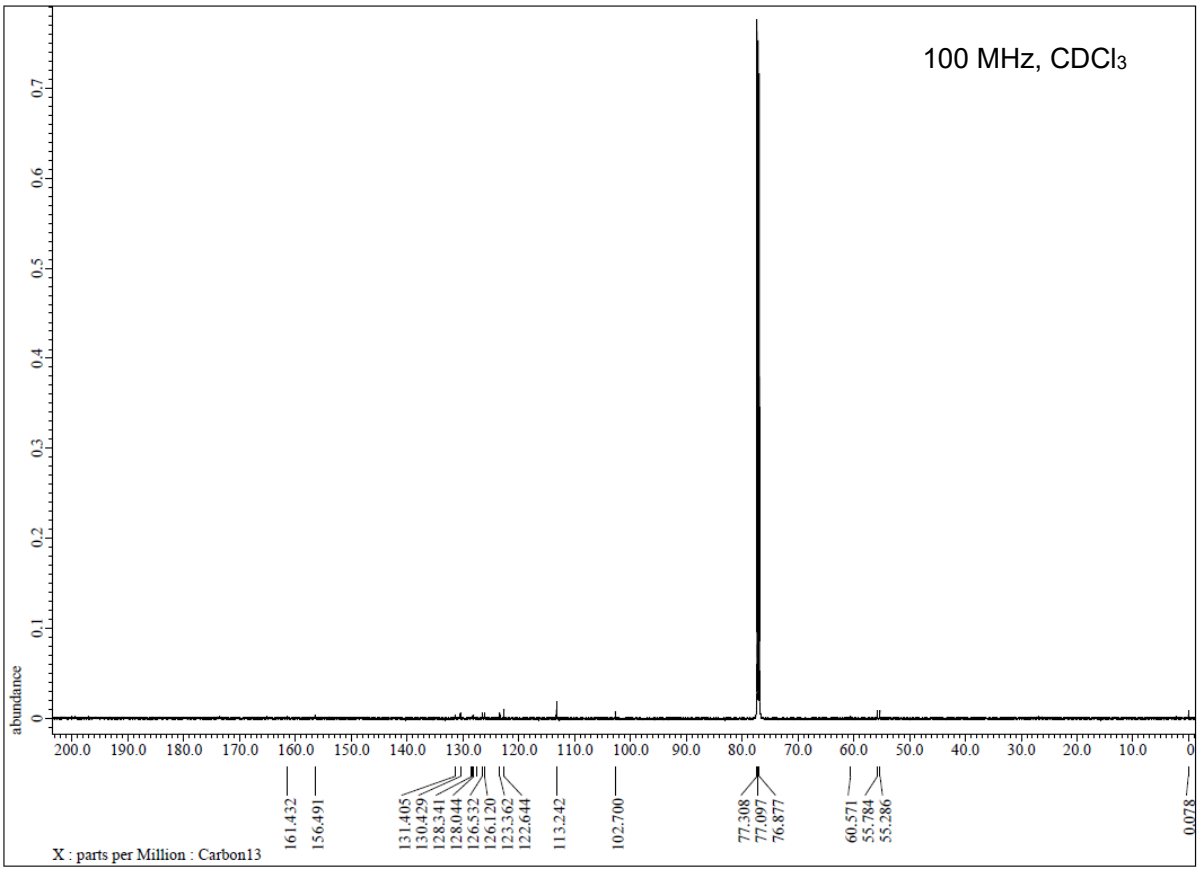

OMe
O
N
OMe
Cl
1e
400 MHz, CDCl3
5.12
3.19
3.00
2.01
1.96
0.86
abundance
X : parts per Million : Proton
8.322
8.317
8.314
8.309
8.306
8.301
8.295
8.224
8.135
7.683
7.676
7.670
7.667
7.490
6.718
3.792
3.738

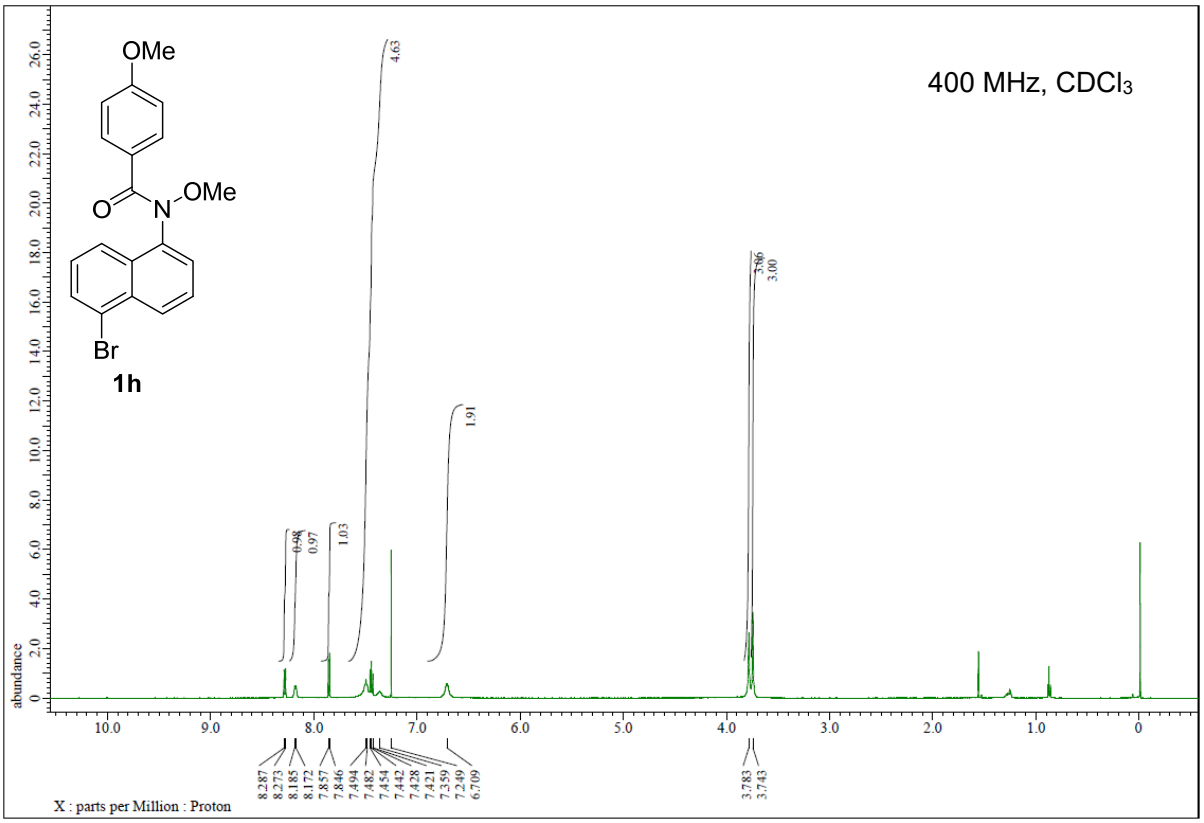

100 MHz, CDCl3
abundance
X : parts per Million : Carbon13
168.563
161.603
131.643
131.212
130.370
128.091
127.746
126.642
125.707
125.266
124.970
123.974
113.231
113.202
77.211
77.000
76.789
60.876
55.141

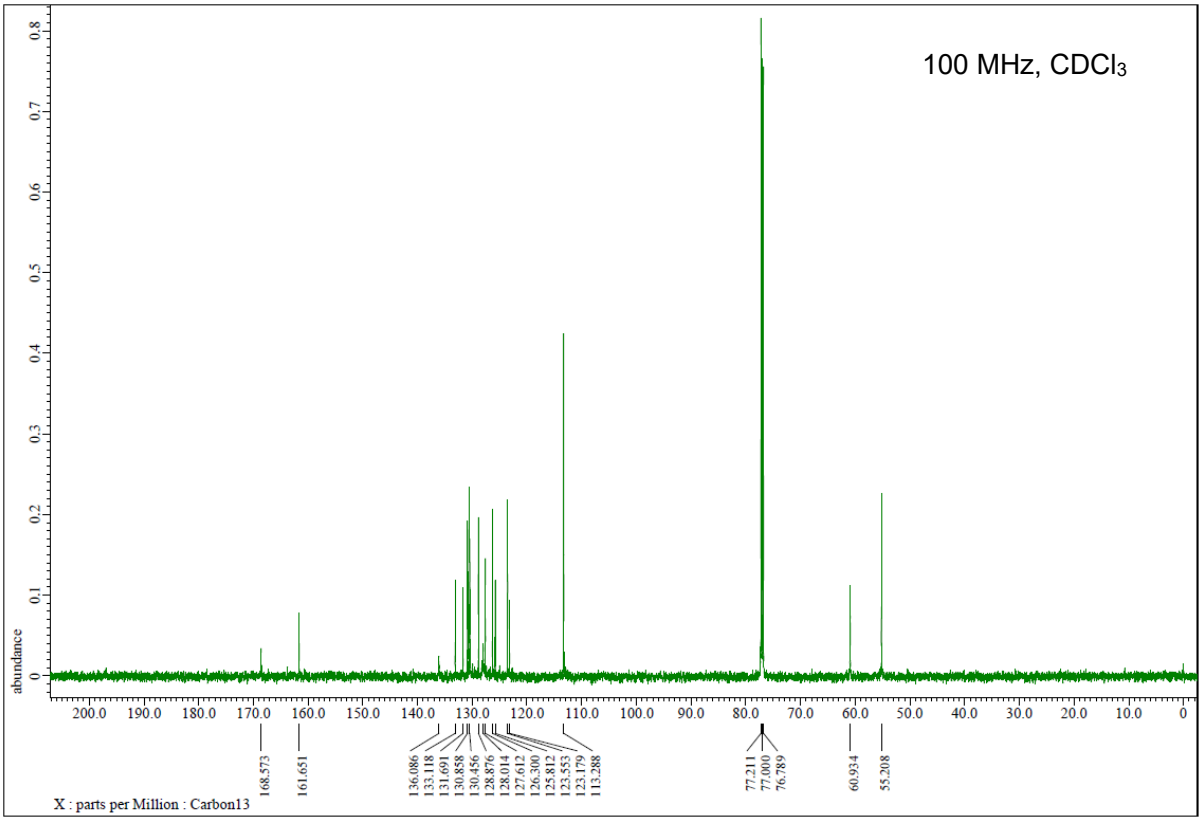

OMe
O
N
OMe
Me
1f
400 MHz, CDCl3
4.12
2.98
3.00
2.89
1.85
2.10
1.17
1.01
abundance
X : parts per Million : Proton

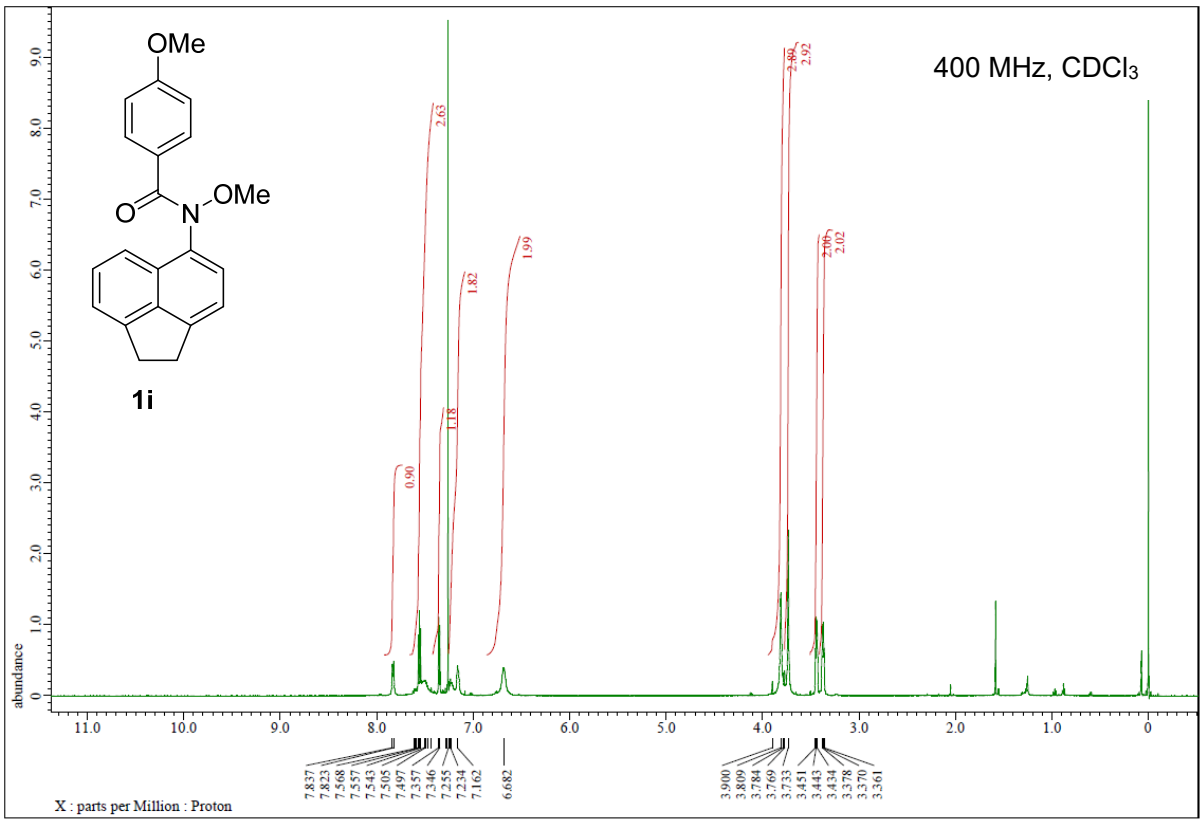

100 MHz, CDCl3
abundance
X : parts per Million : Carbon13

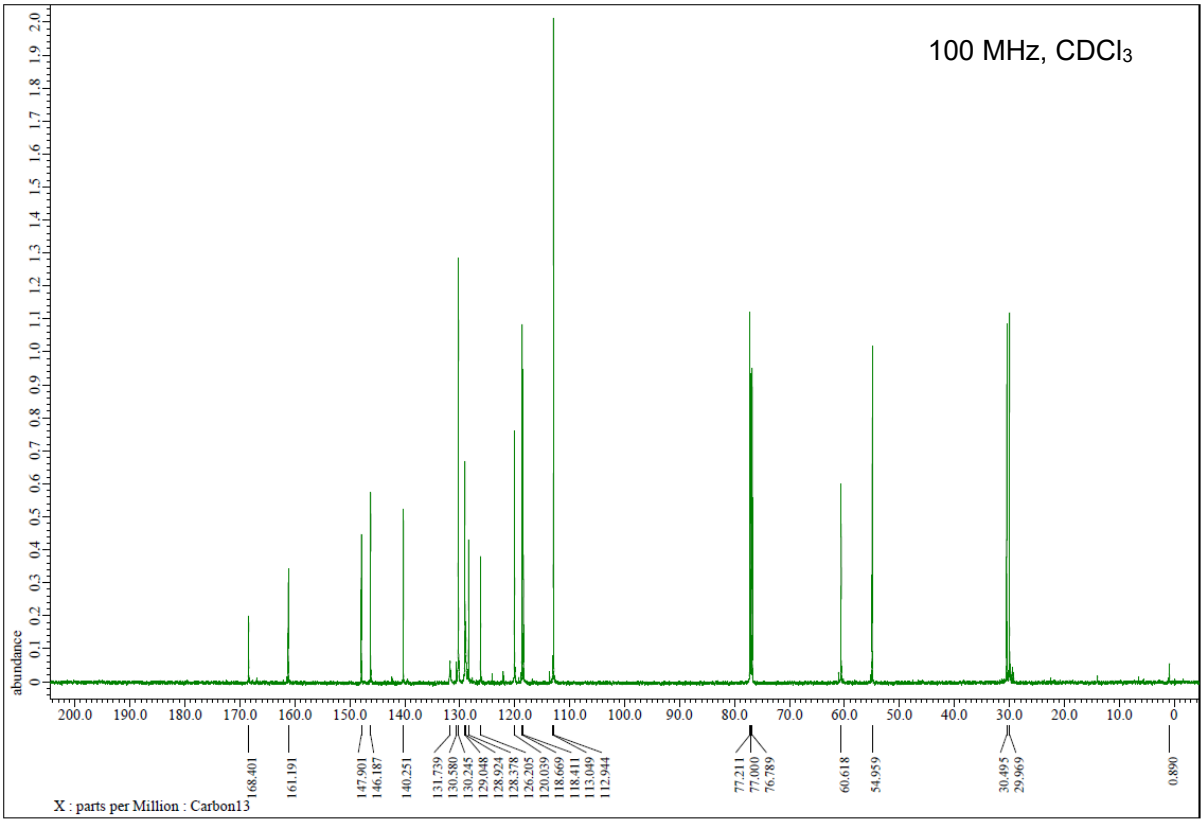

OMe
O
N
OMe
OMe
1g
400 MHz, CDCl3
abundance
X : parts per Million : Proton

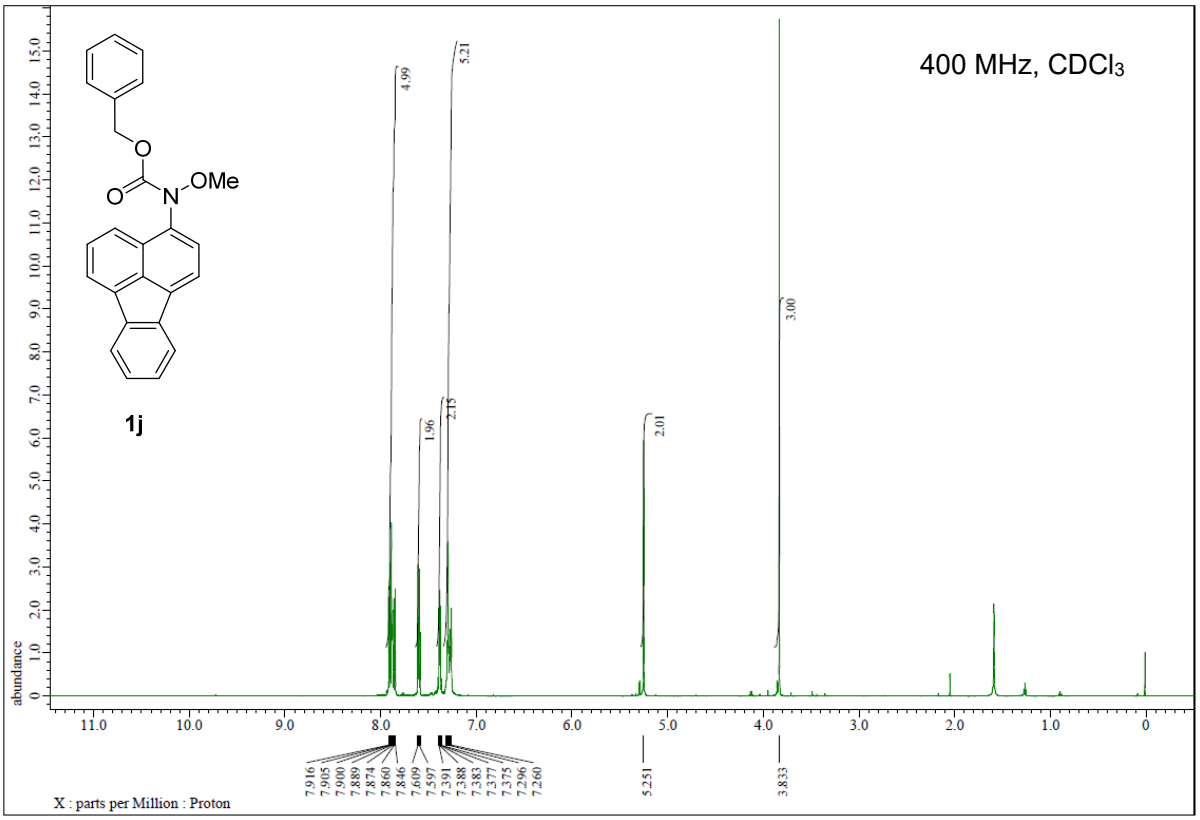

100 MHz, CDCl3
abundance
X : parts per Million : Carbon13

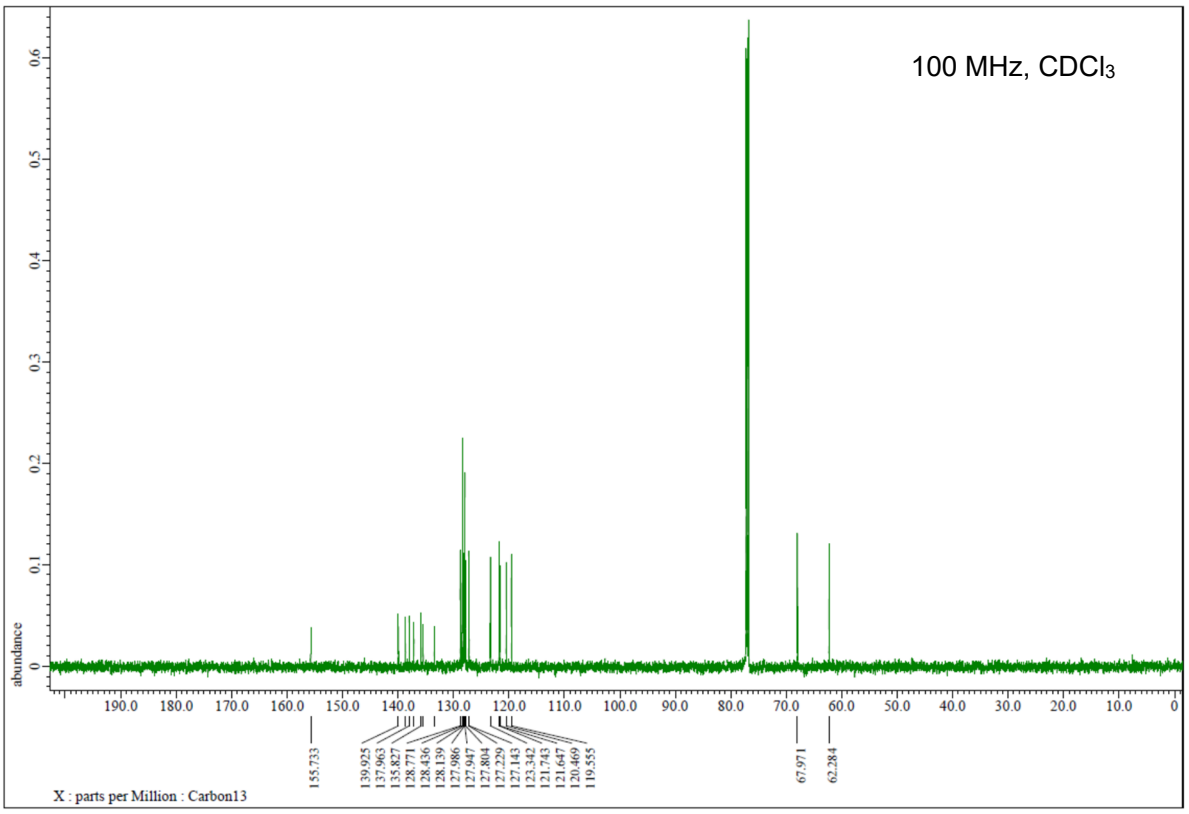

OMe
O
N
OMe
Br
1h
400 MHz, CDCl3
4.63
1.91
1.03
0.98
0.97
3.86
3.00
abundance
X : parts per Million : Proton
8.287
8.273
8.185
8.172
7.857
7.846
7.494
7.482
7.454
7.442
7.428
7.421
7.359
7.249
6.709
3.783
3.743

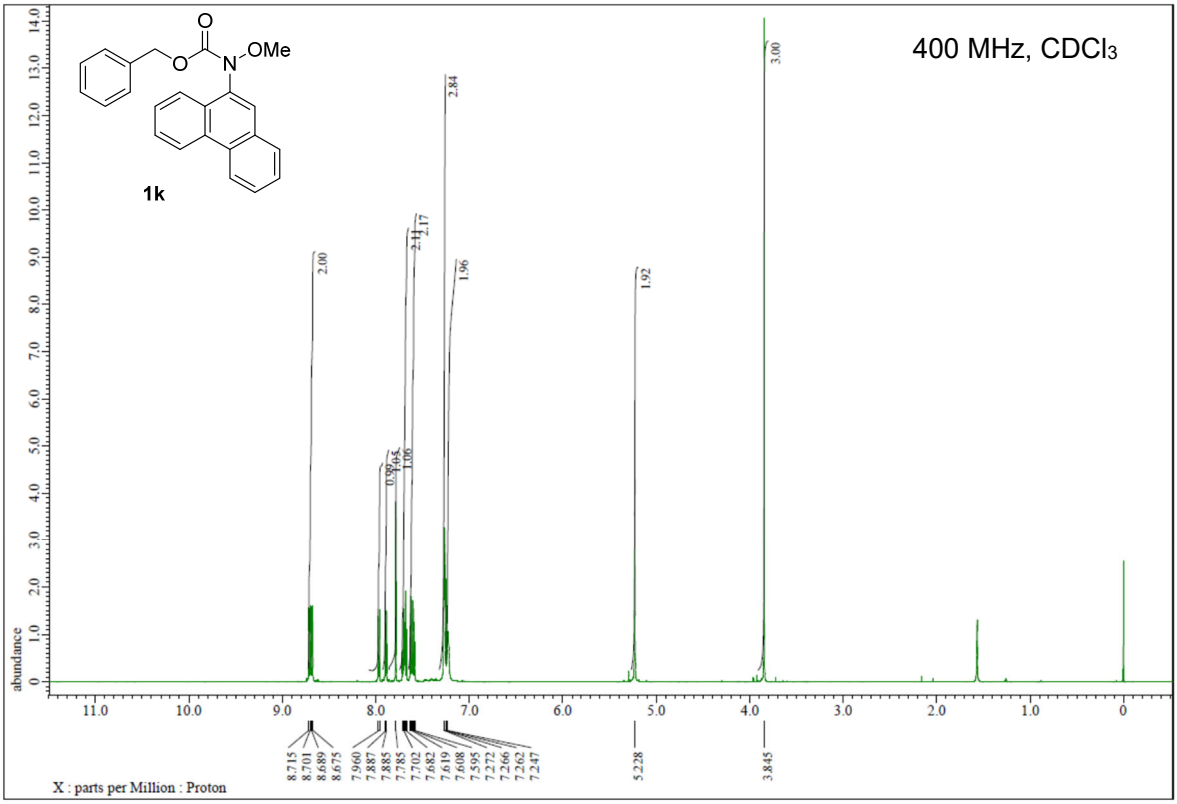

100 MHz, CDCl3
abundance
X : parts per Million : Carbon13
168.573
161.651
136.086
133.118
131.691
130.858
130.456
128.876
128.014
127.612
126.300
125.812
123.553
123.179
113.288
77.211
77.000
76.789
60.934
55.208

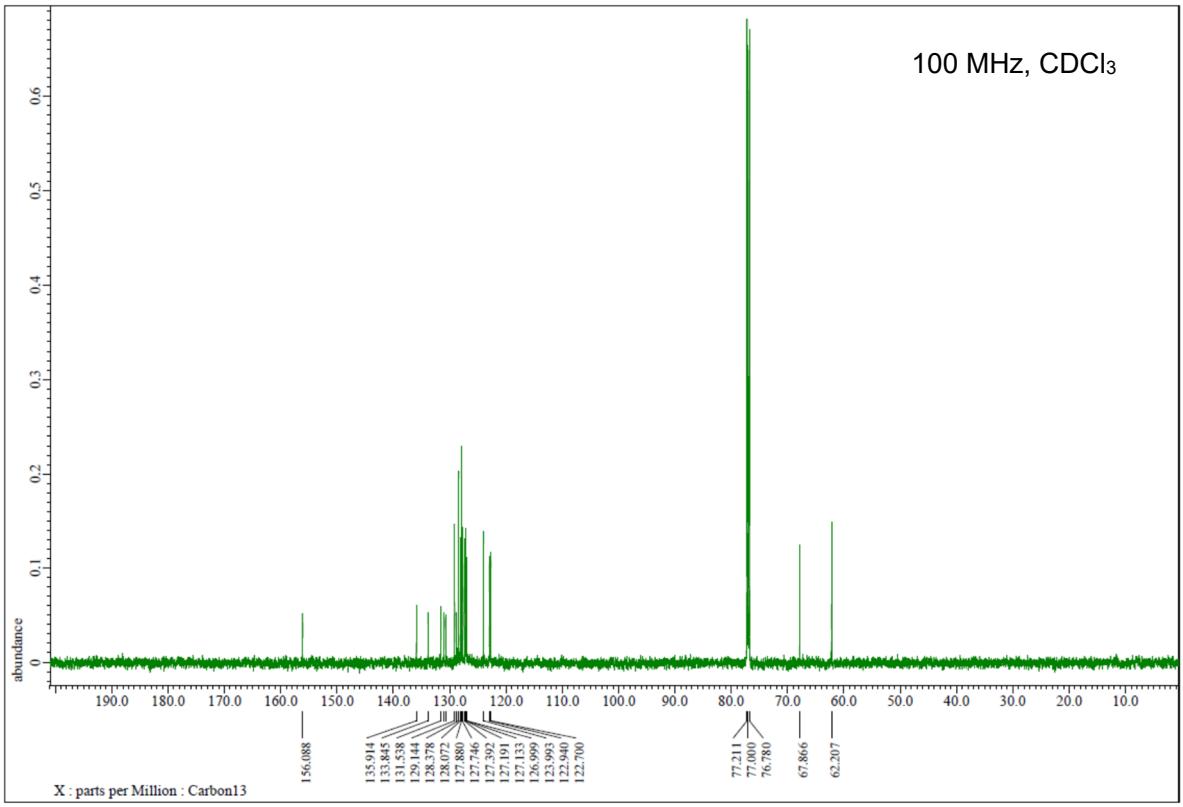

OMe
O
N
OMe
1i
400 MHz, CDCl3
abundance
X : parts per Million : Proton

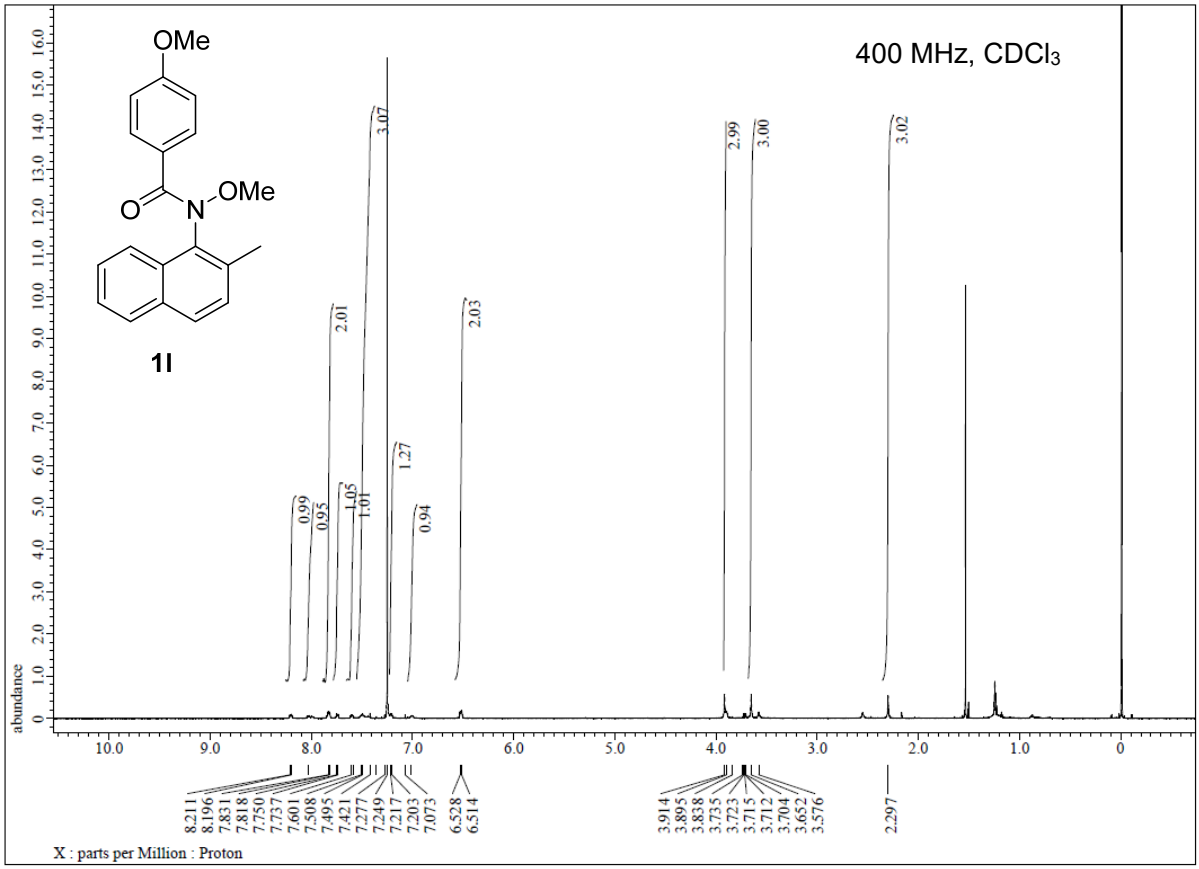

100 MHz, CDCl3
abundance
X : parts per Million : Carbon13

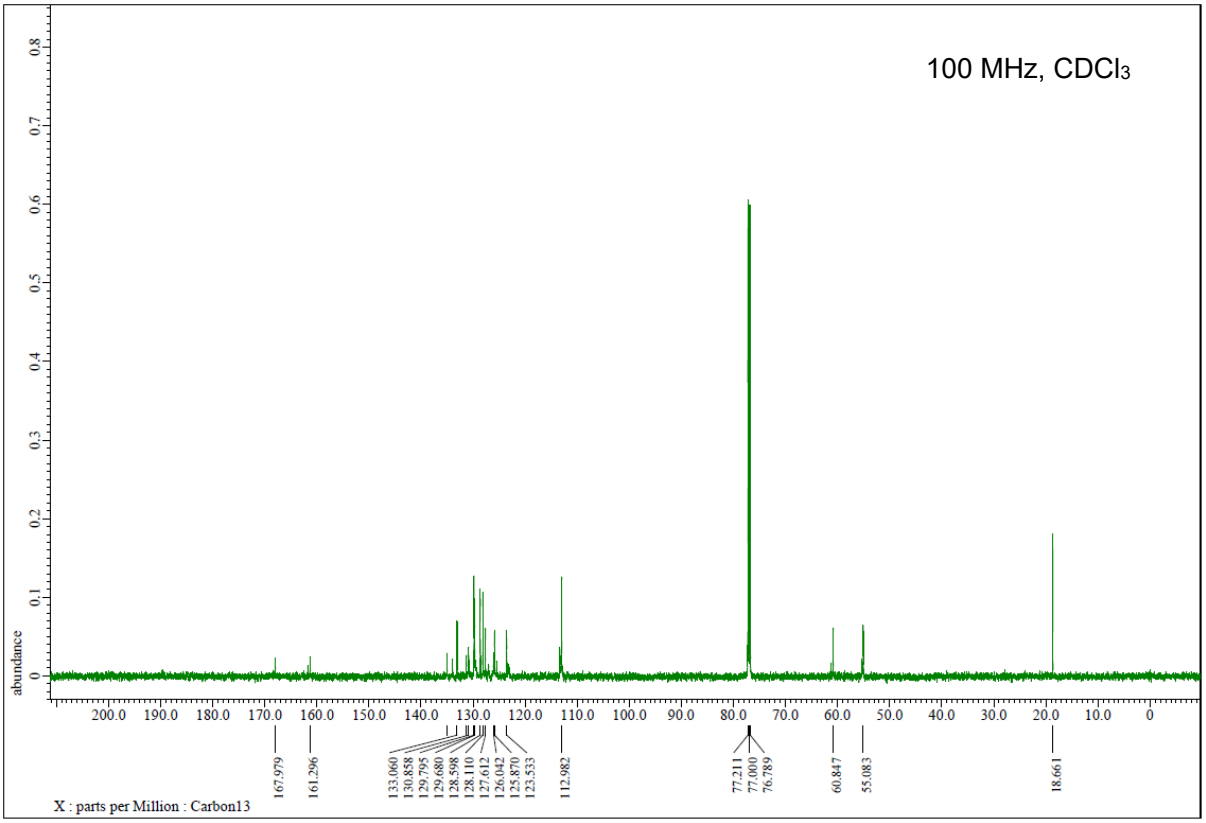

400 MHz, CDCl3
1j
abundance
X : parts per Million : Proton

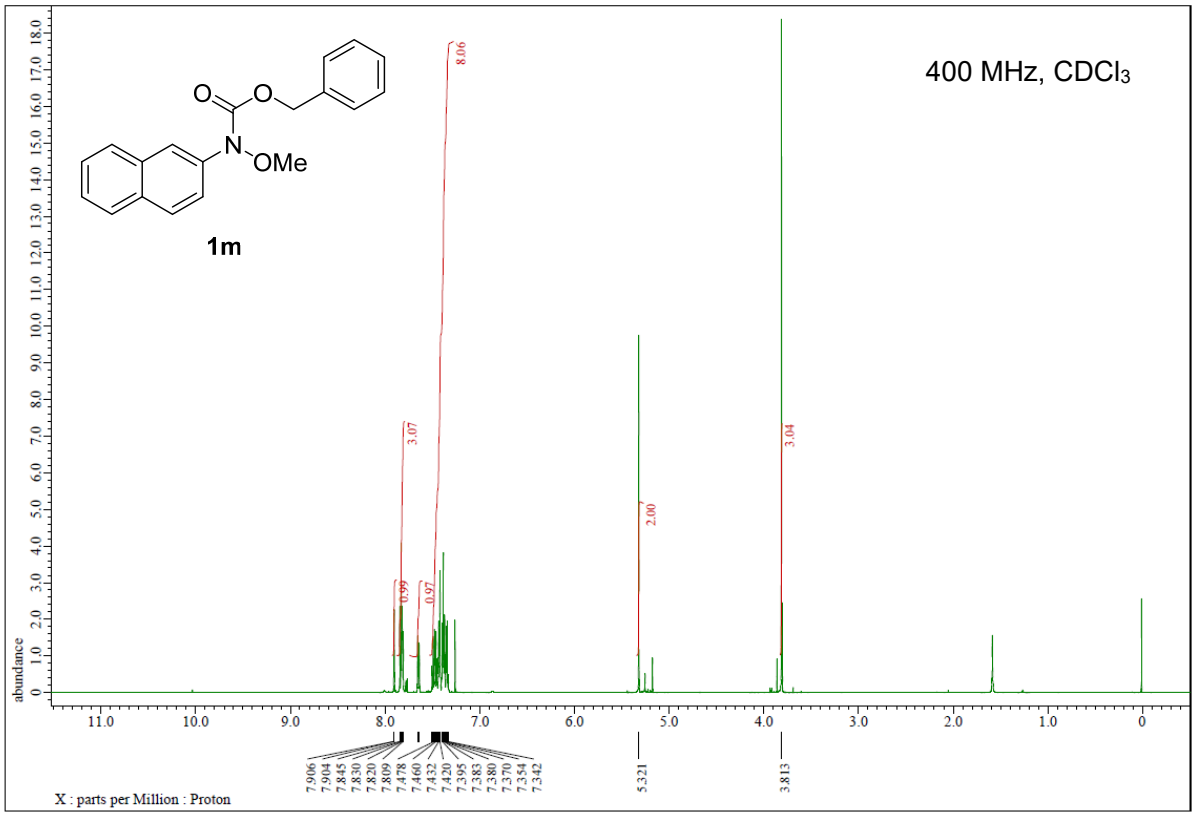

100 MHz, CDCl3
abundance
X : parts per Million : Carbon13

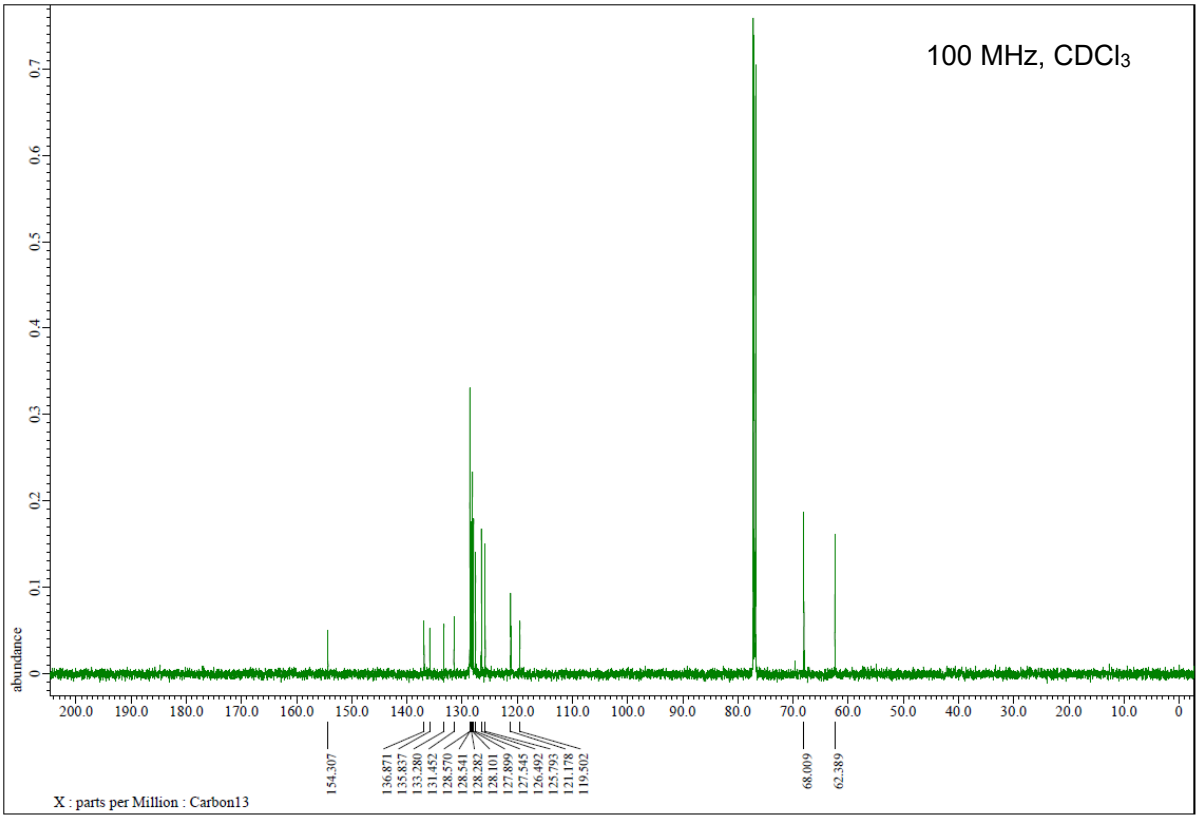

400 MHz, CDCl3
1k
abundance
X : parts per Million : Proton

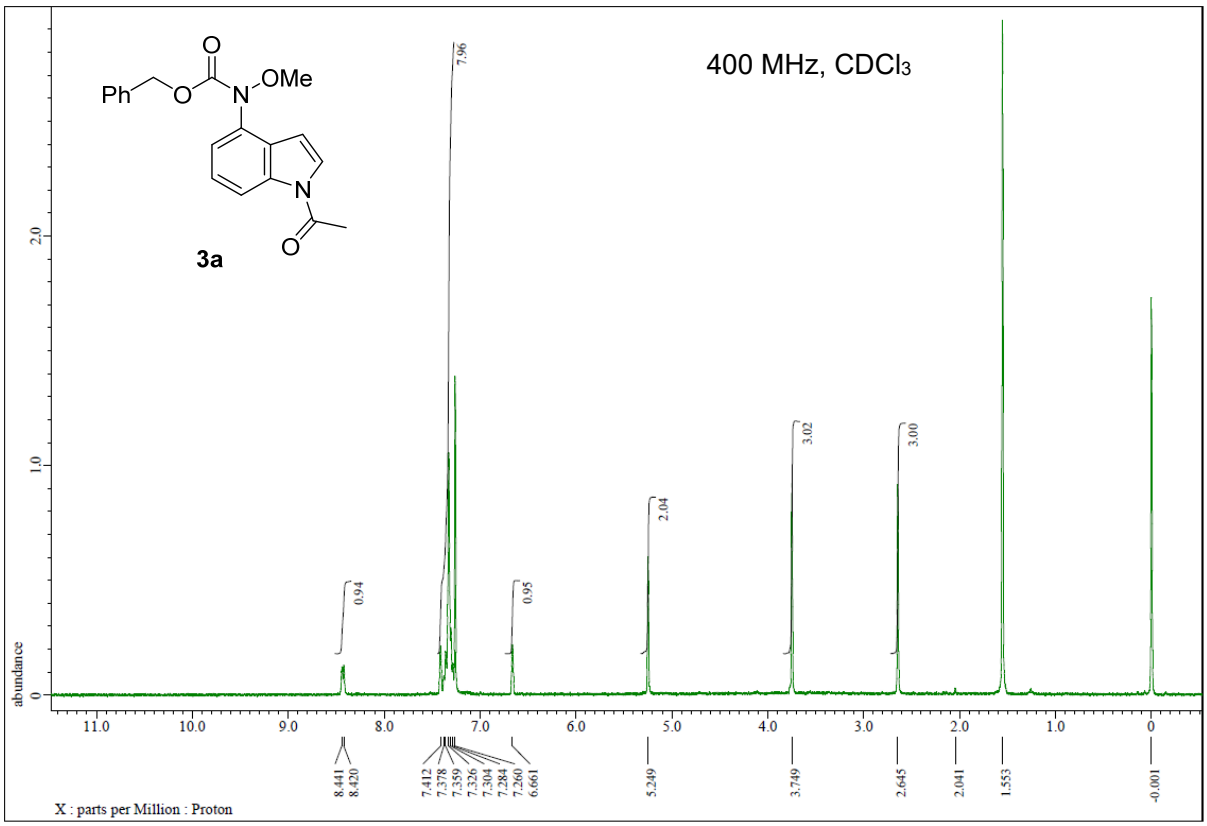

100 MHz, CDCl3
abundance
X : parts per Million : Carbon13

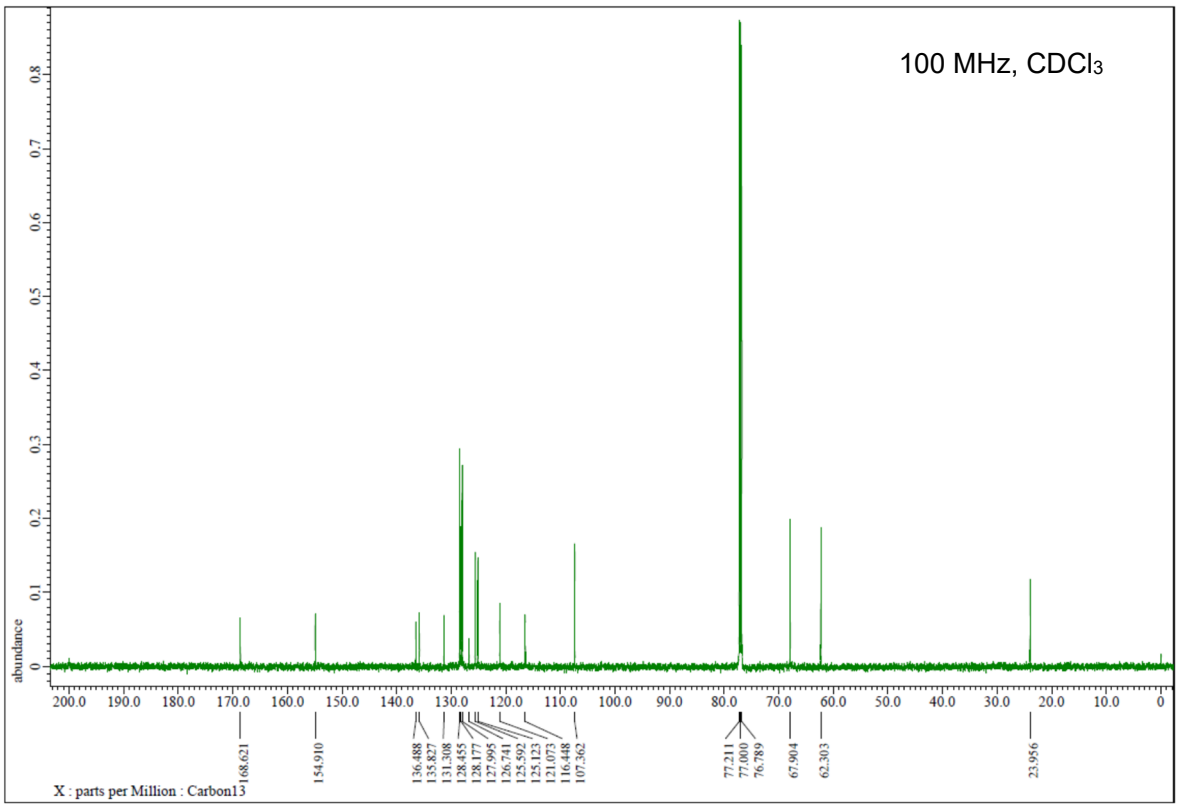

OMe
O
N
OMe
1l
400 MHz, CDCl3
abundance
X : parts per Million : Proton

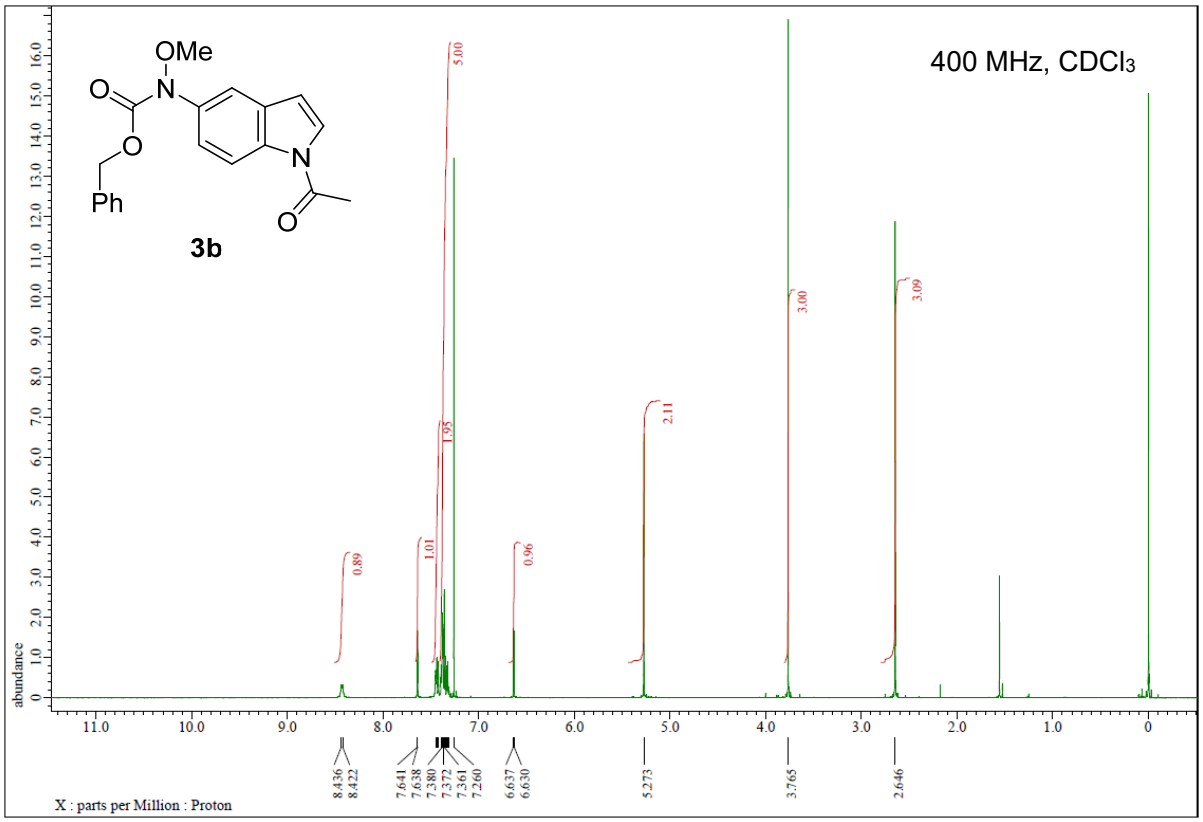

100 MHz, CDCl3
abundance
X : parts per Million : Carbon13

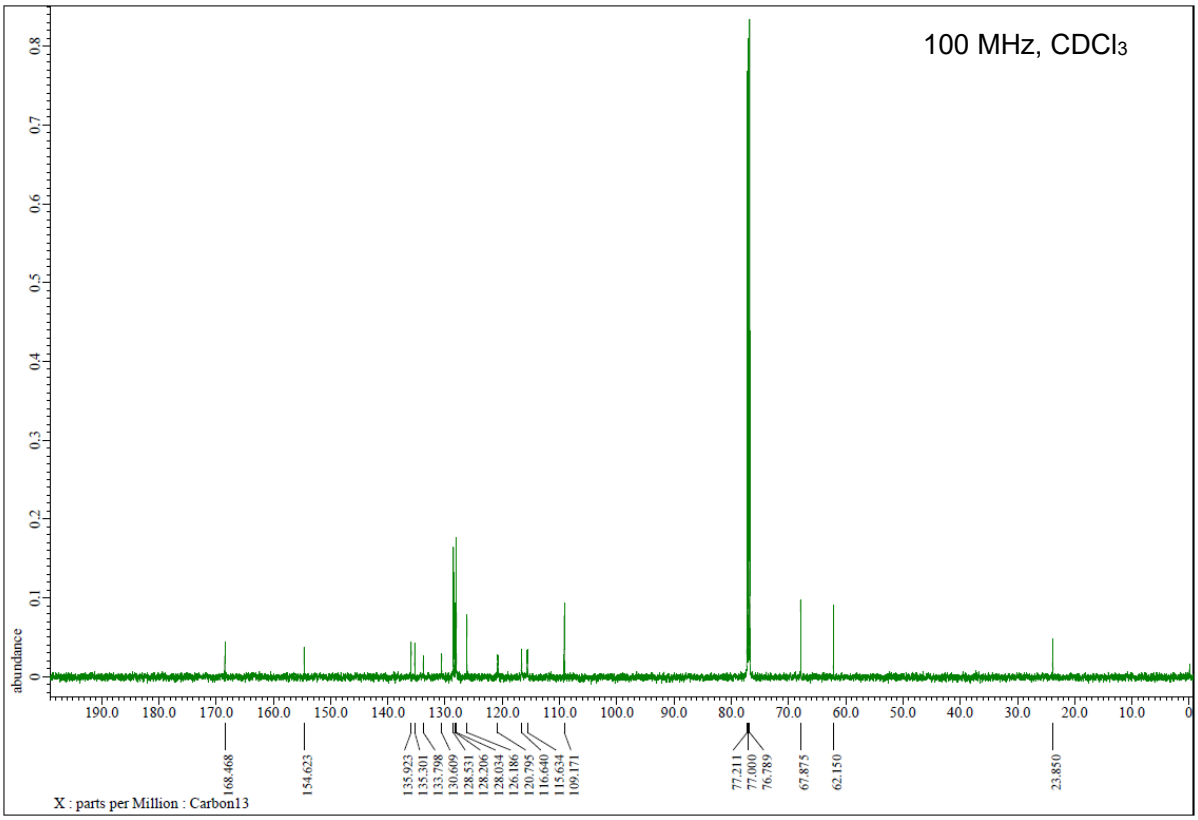

400 MHz, CDCl3
1m
abundance
X : parts per Million : Proton


100 MHz, CDCl3
abundance
X : parts per Million : Carbon13

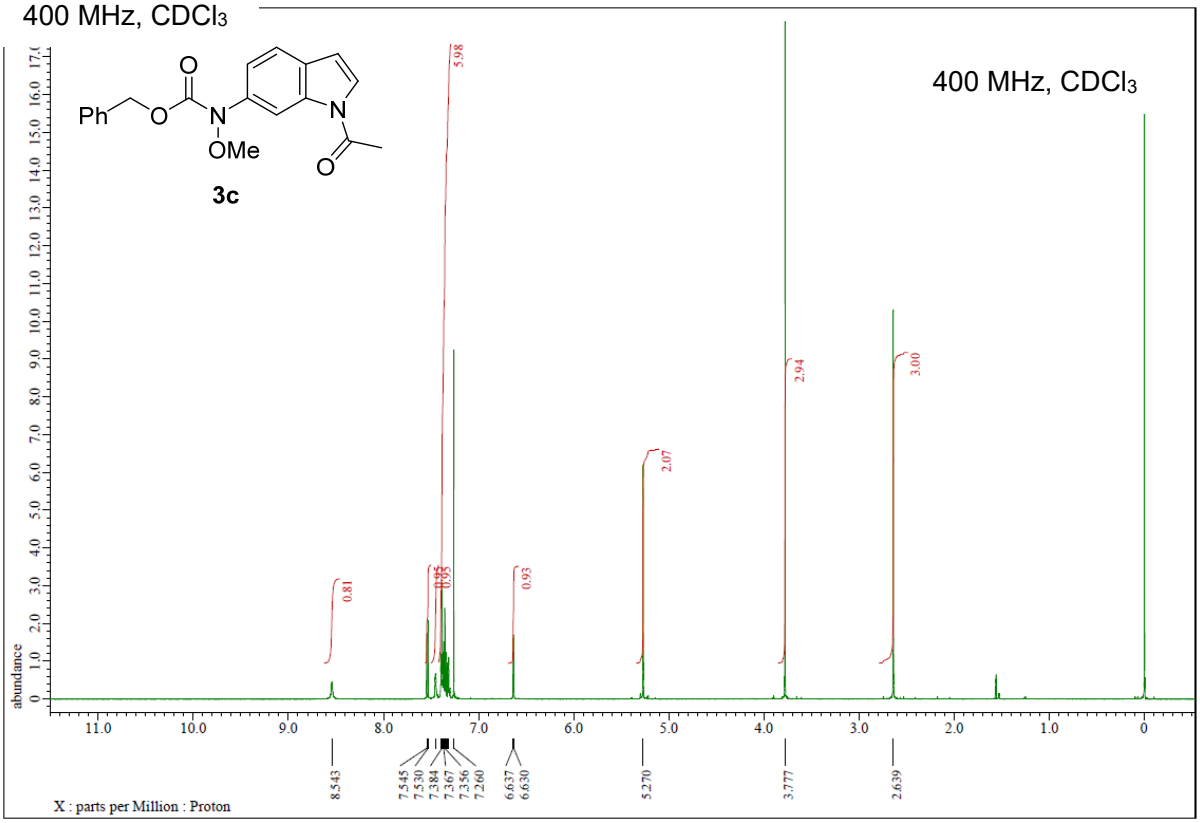

400 MHz, CDCl3
3a
abundance
X : parts per Million : Proton


100 MHz, CDCl3
abundance
X : parts per Million : Carbon13

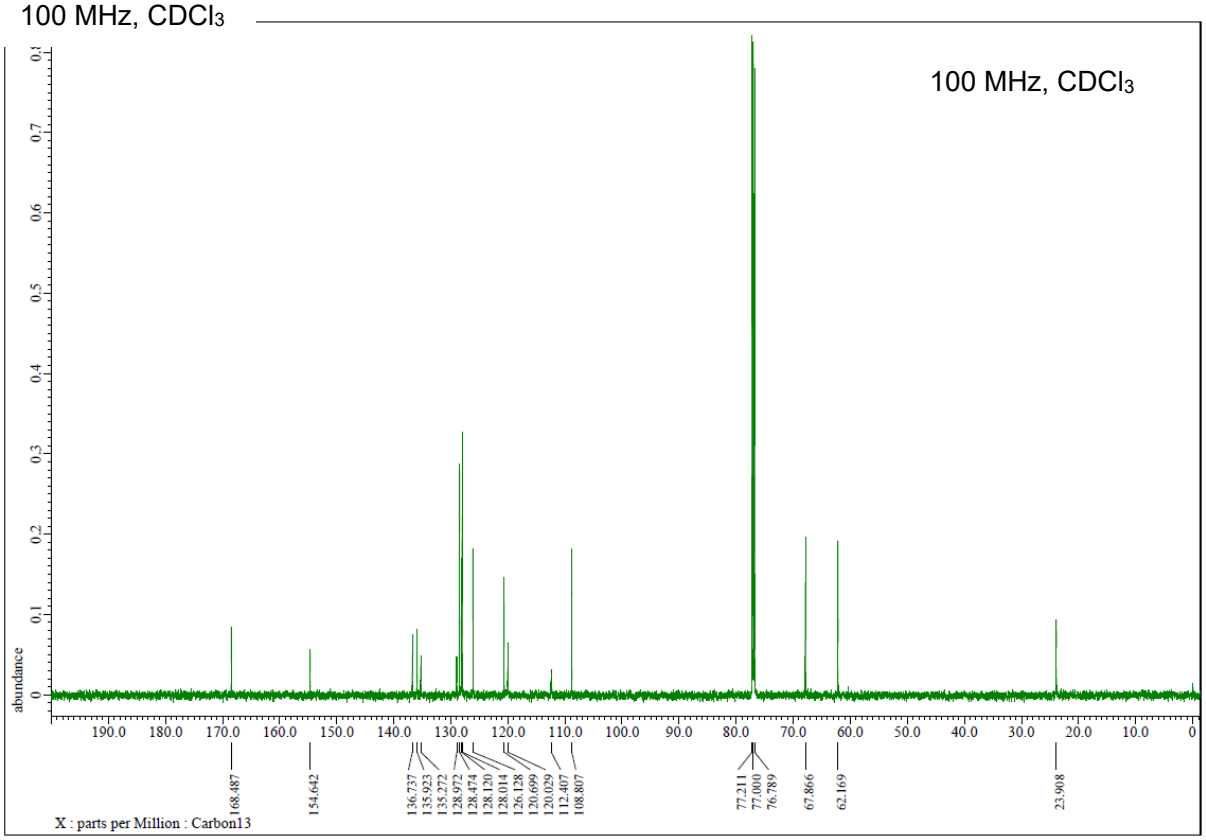

OMe
N
O
O
Ph
N
O
3b
400 MHz, CDCl3
5.00
3.00
3.09
2.11
1.95
1.01
0.96
0.89
abundance
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.436
8.422
7.641
7.638
7.380
7.372
7.361
7.260
6.637
6.630
5.273
3.765
2.646
X : parts per Million : Proton

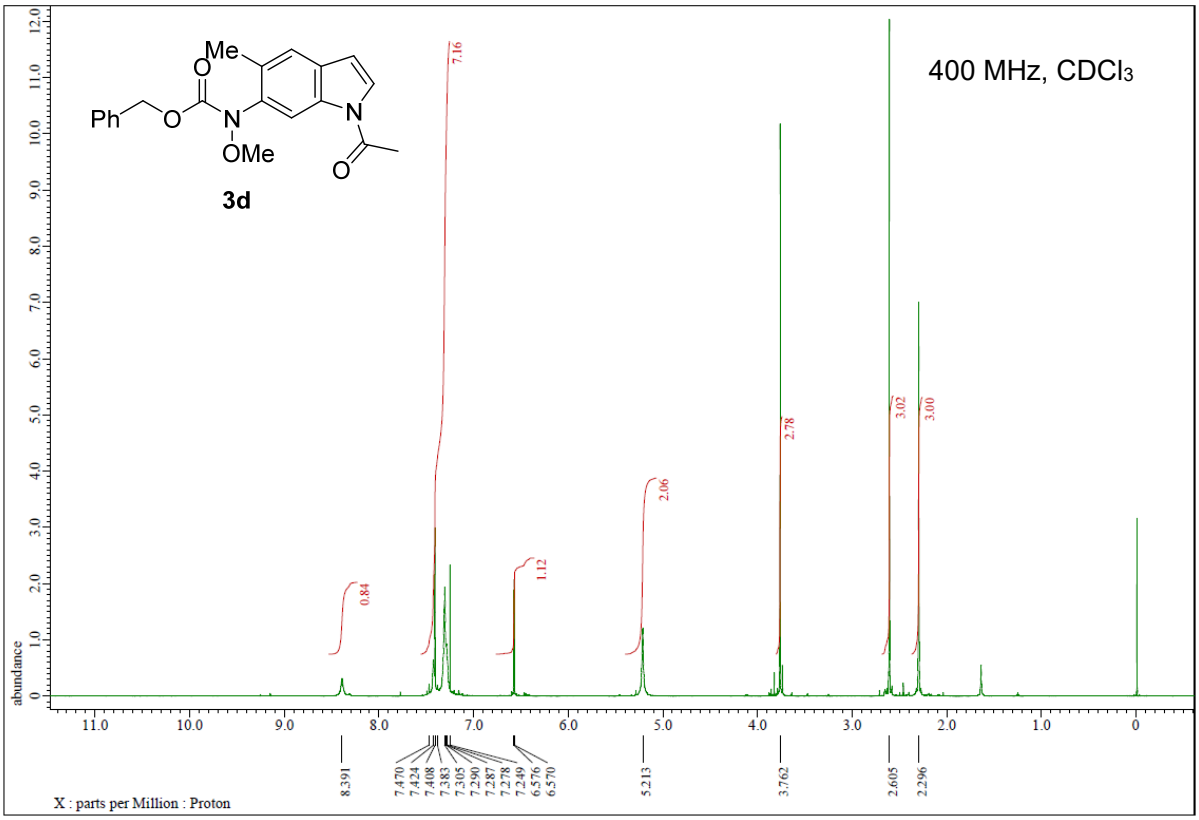

100 MHz, CDCl3
abundance
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
168.468
154.623
135.923
135.301
133.798
130.669
128.531
128.206
128.034
126.186
120.795
116.640
115.634
109.171
77.211
77.000
76.789
67.875
62.150
23.850
X : parts per Million : Carbon13

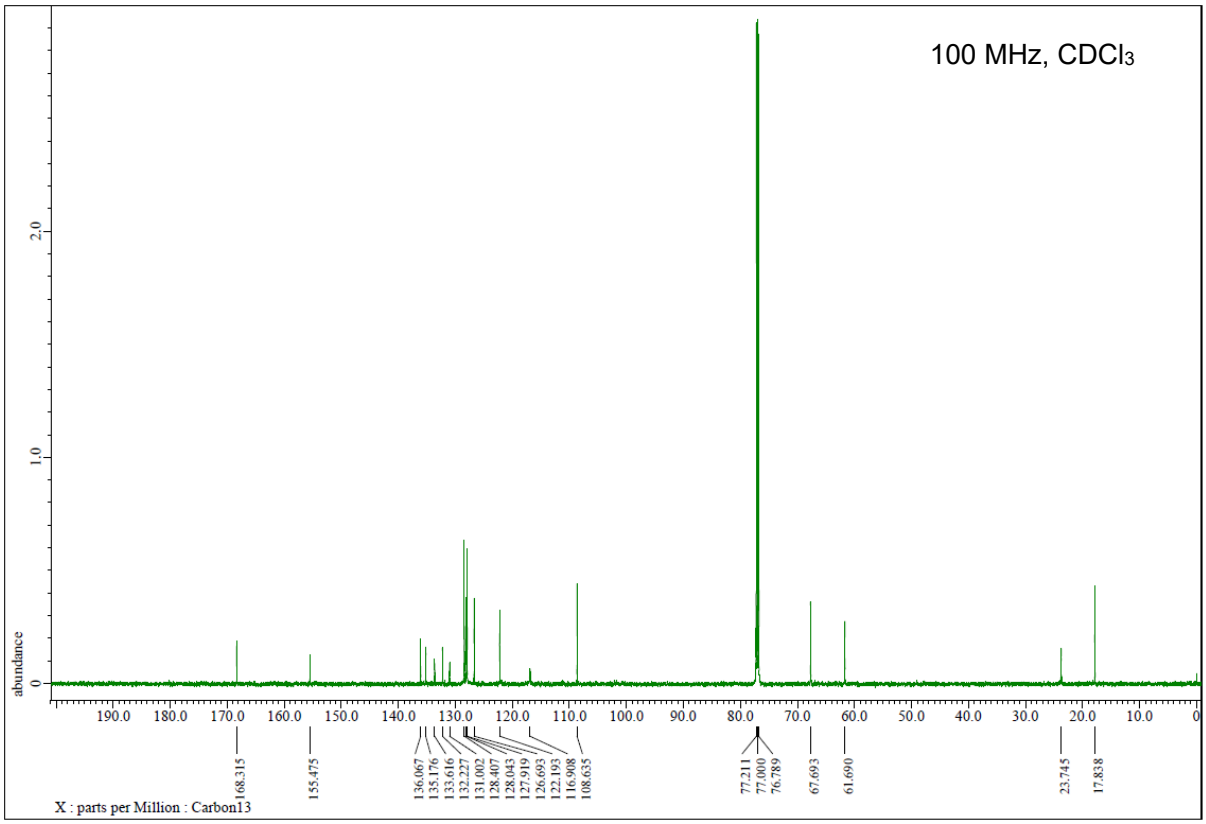
400 MHz, $CDCl_3$

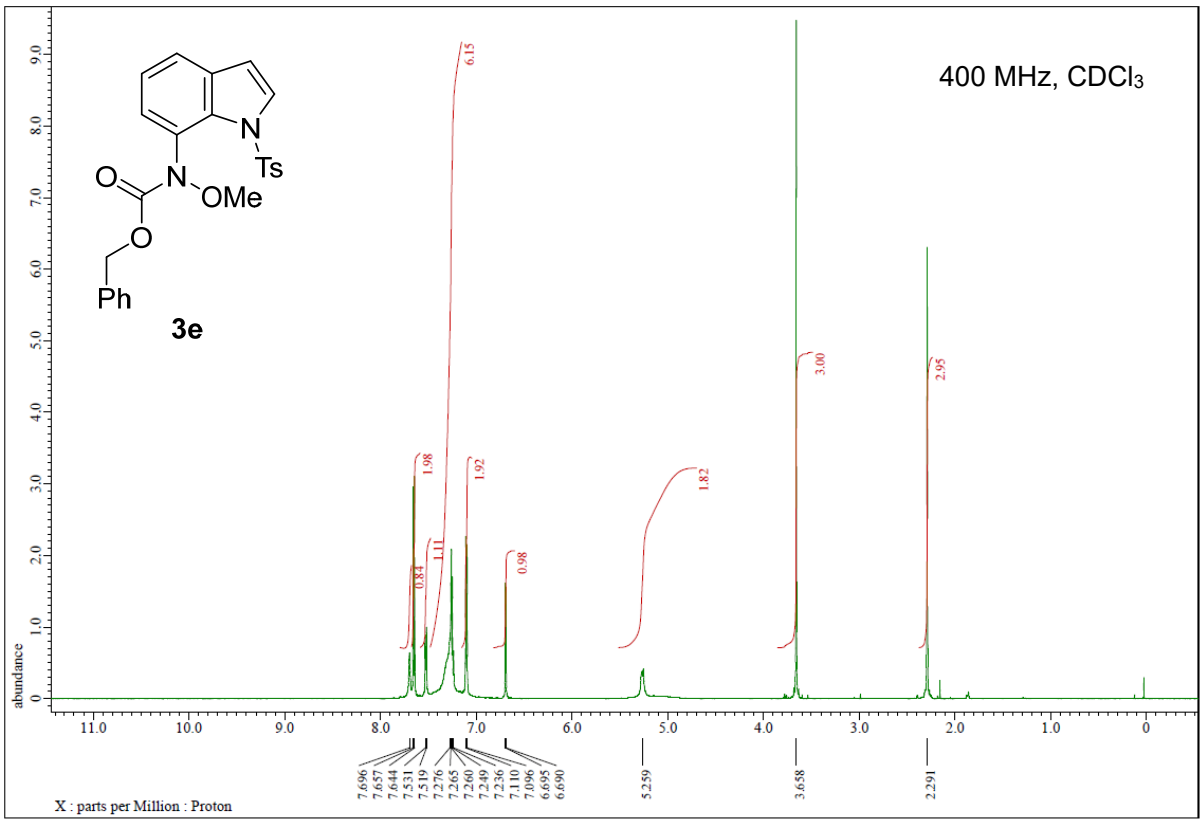


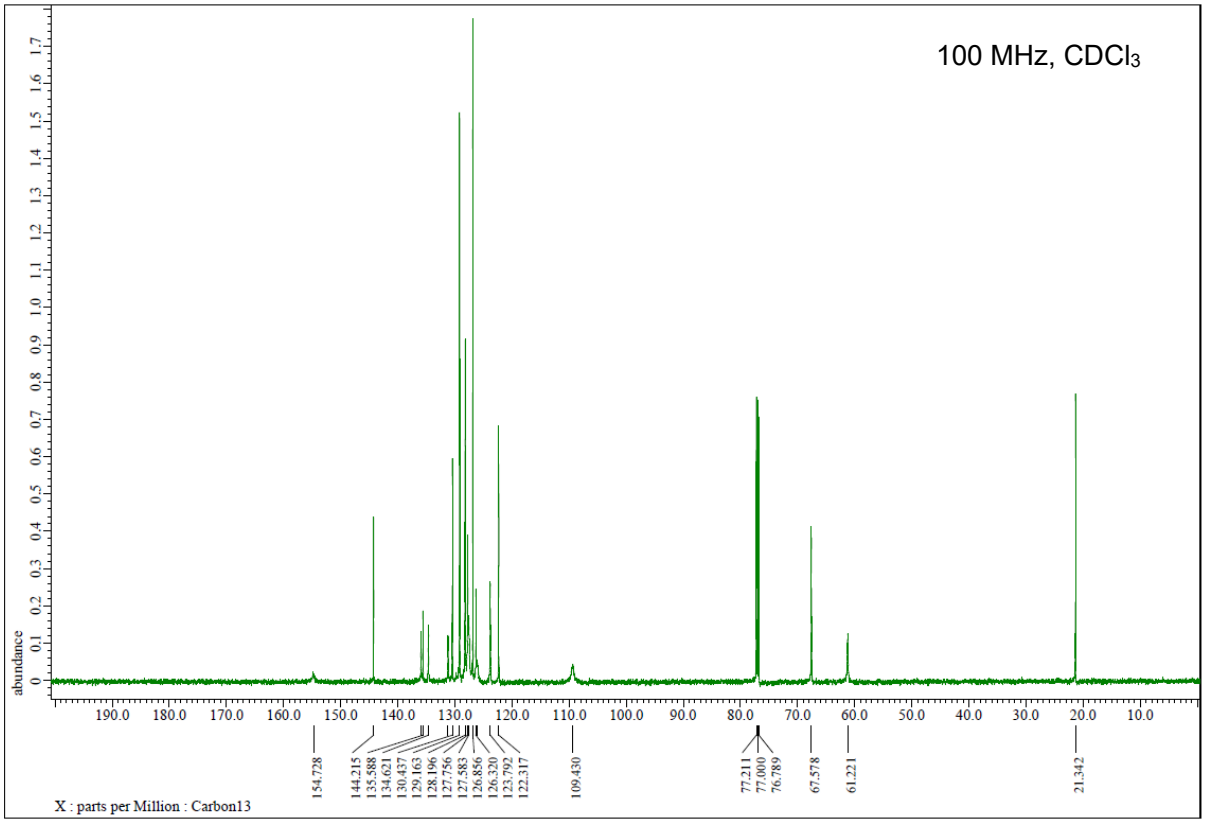
100 MHz, $CDCl_3$

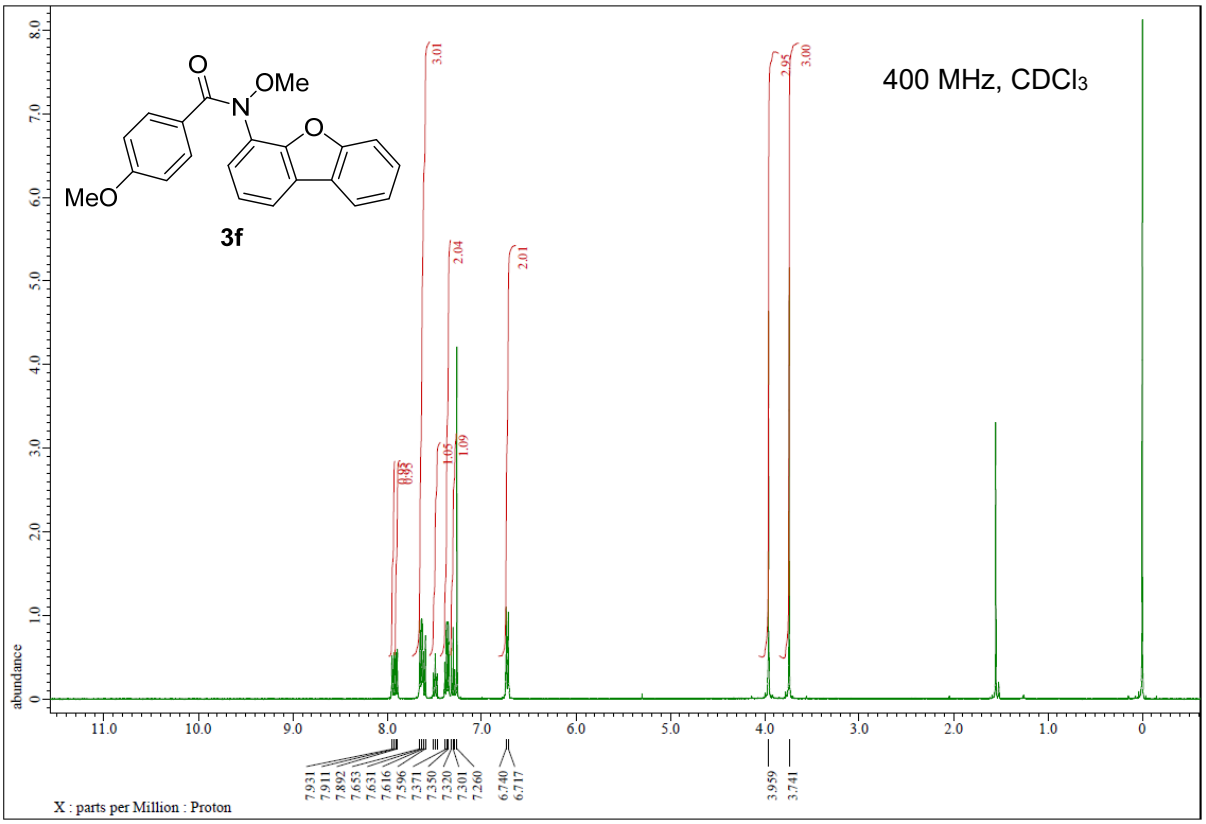


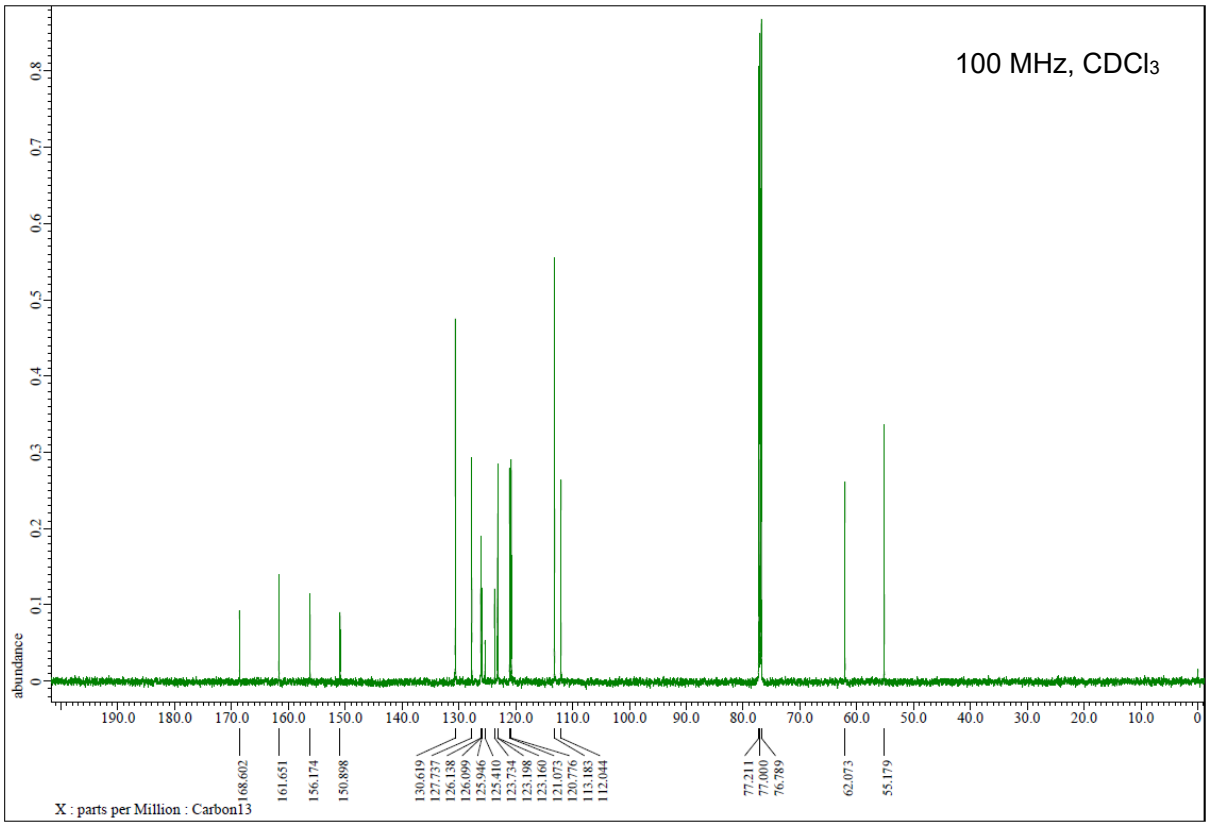

Me
O
Ph
O
N
OMe
N
O
3d
400 MHz, CDCl3
7.16
2.78
3.02
3.00
2.06
1.12
0.84
abundance
X : parts per Million : Proton
8.391
7.470
7.424
7.408
7.383
7.305
7.290
7.287
7.278
7.249
6.576
6.570
5.213
3.762
2.605
2.596


100 MHz, CDCl3
abundance
X : parts per Million : Carbon13
168.315
155.475
136.067
135.176
133.616
132.227
131.002
128.407
128.043
127.919
126.693
122.193
116.908
108.635
77.211
77.000
76.789
67.693
61.690
23.745
17.838

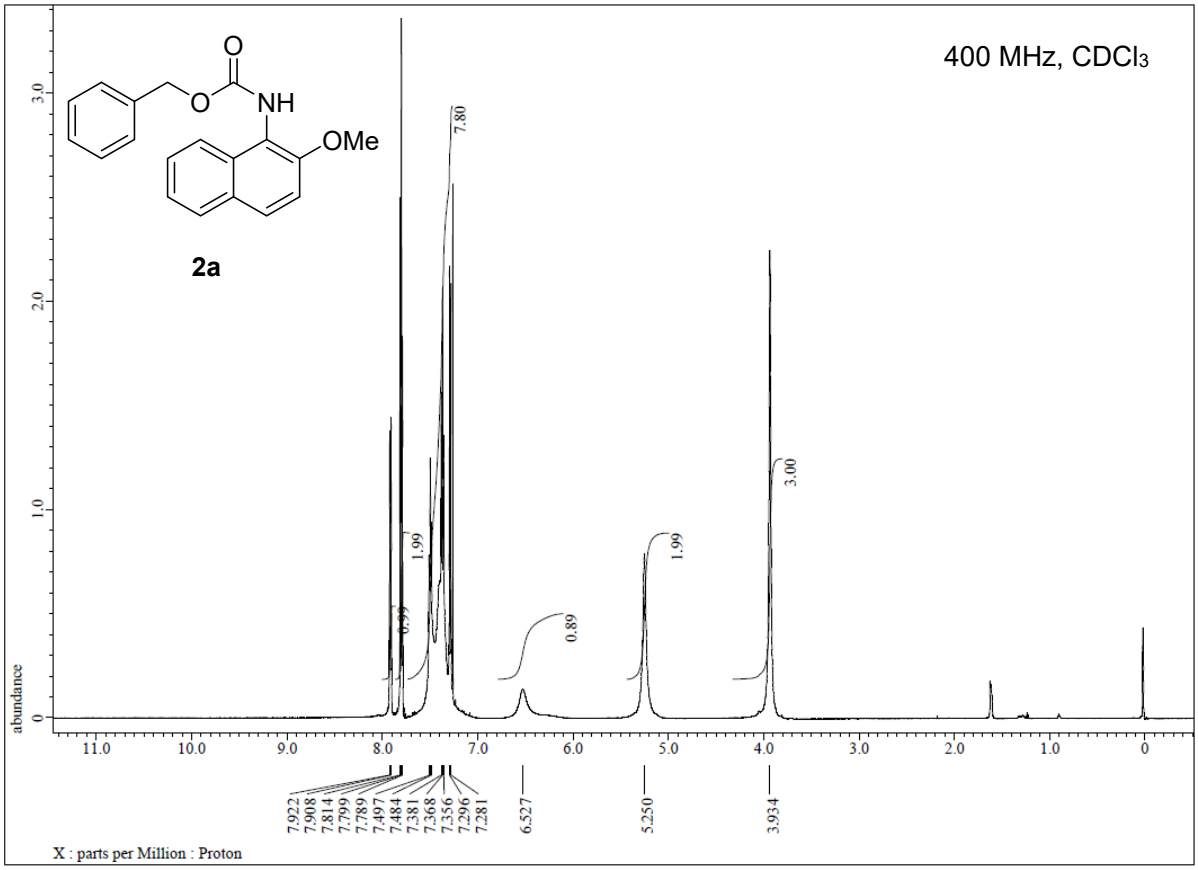

400 MHz, CDCl3
N
Ts
O
N
OMe
O
Ph
3e
6.15
1.98
1.92
1.82
1.11
0.98
0.84
3.00
2.95
abundance
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.696
7.657
7.644
7.531
7.519
7.276
7.265
7.260
7.249
7.236
7.110
7.096
6.695
6.690
5.259
3.658
2.291
X : parts per Million : Proton

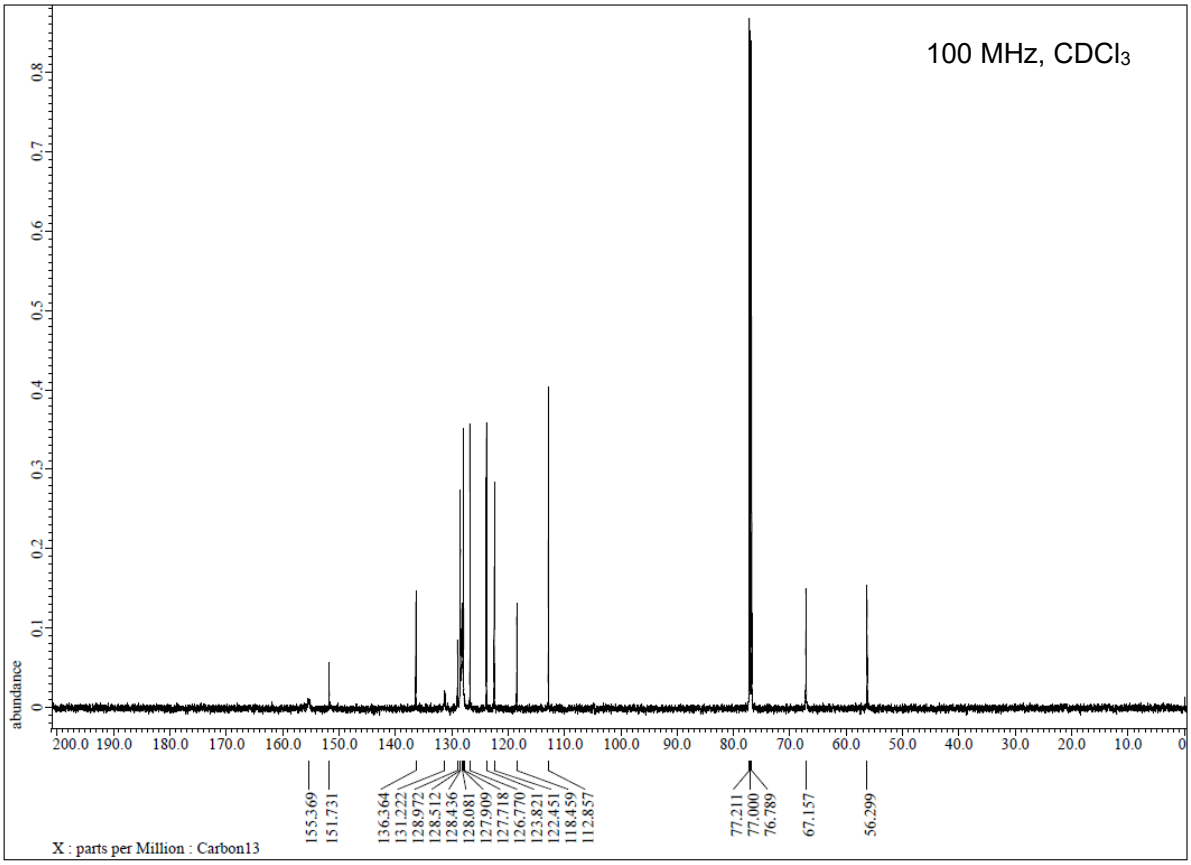

100 MHz, CDCl3
abundance
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
154.728
144.215
135.588
134.621
130.437
129.163
128.196
127.756
127.583
126.856
126.320
123.792
122.317
109.430
77.211
77.000
76.789
67.578
61.221
21.342
X : parts per Million : Carbon13

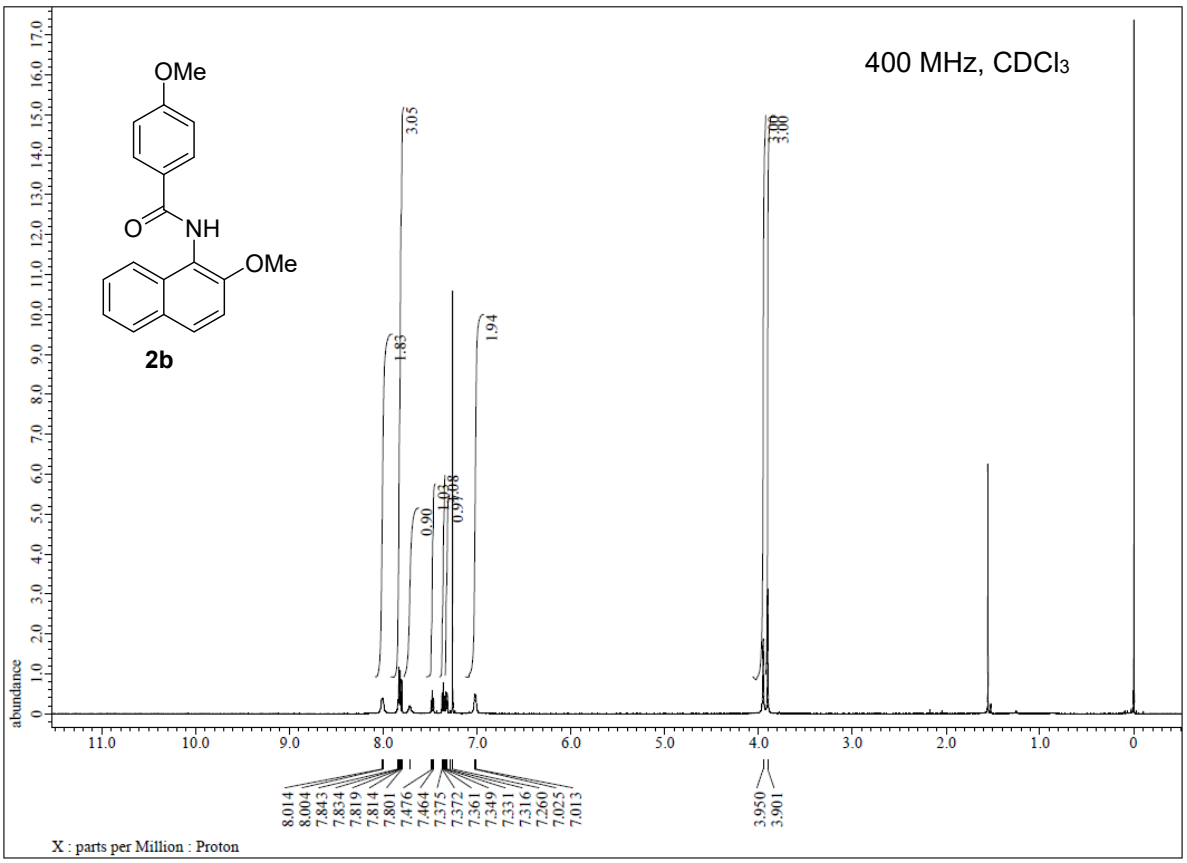

400 MHz, CDCl3
3f
MeO
OMe
O
N
O
abundance
X : parts per Million : Proton
7.931
7.911
7.892
7.653
7.631
7.616
7.596
7.371
7.350
7.320
7.301
7.260
6.740
6.717
3.959
3.741

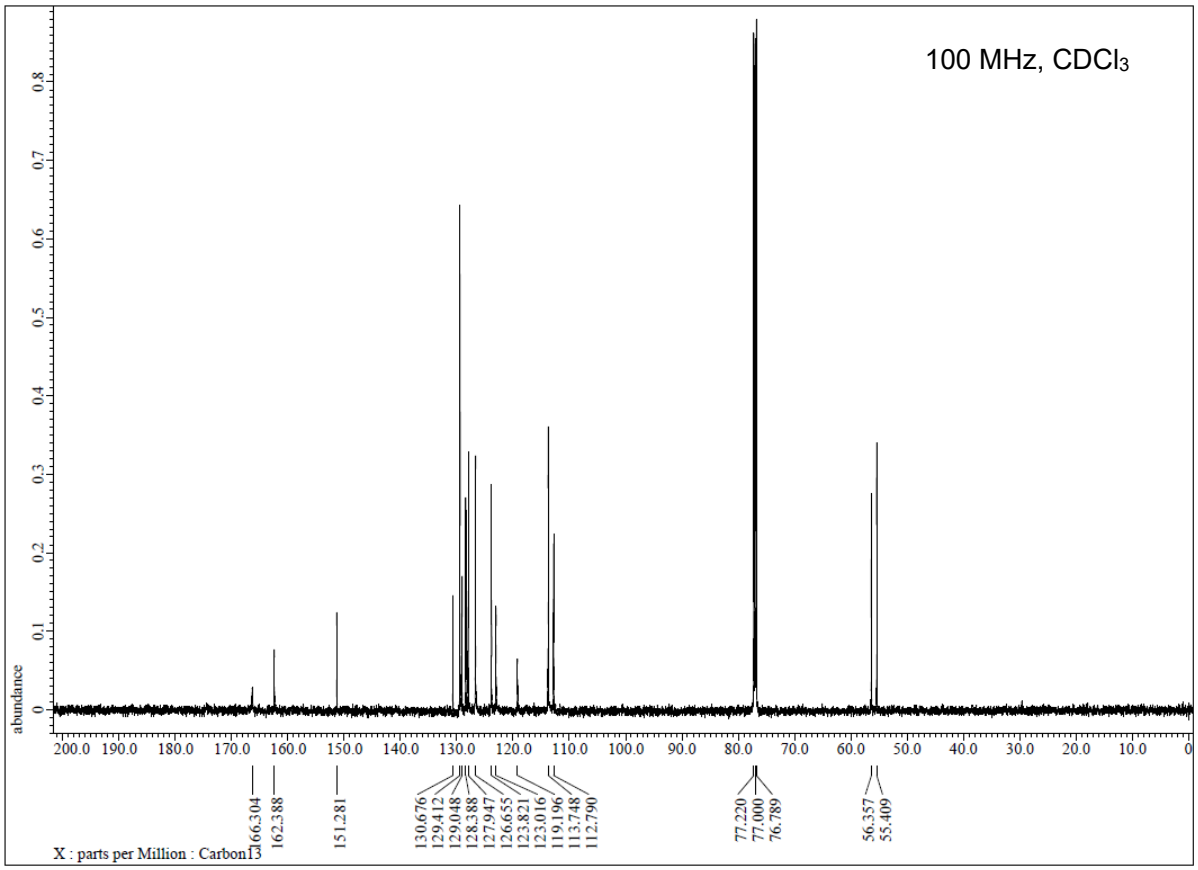

100 MHz, CDCl3
abundance
X : parts per Million : Carbon13
168.602
161.651
156.174
150.898
130.619
127.737
126.138
126.099
125.946
125.410
123.734
123.198
123.160
121.073
120.776
113.183
112.044
77.211
77.000
76.789
62.073
55.179

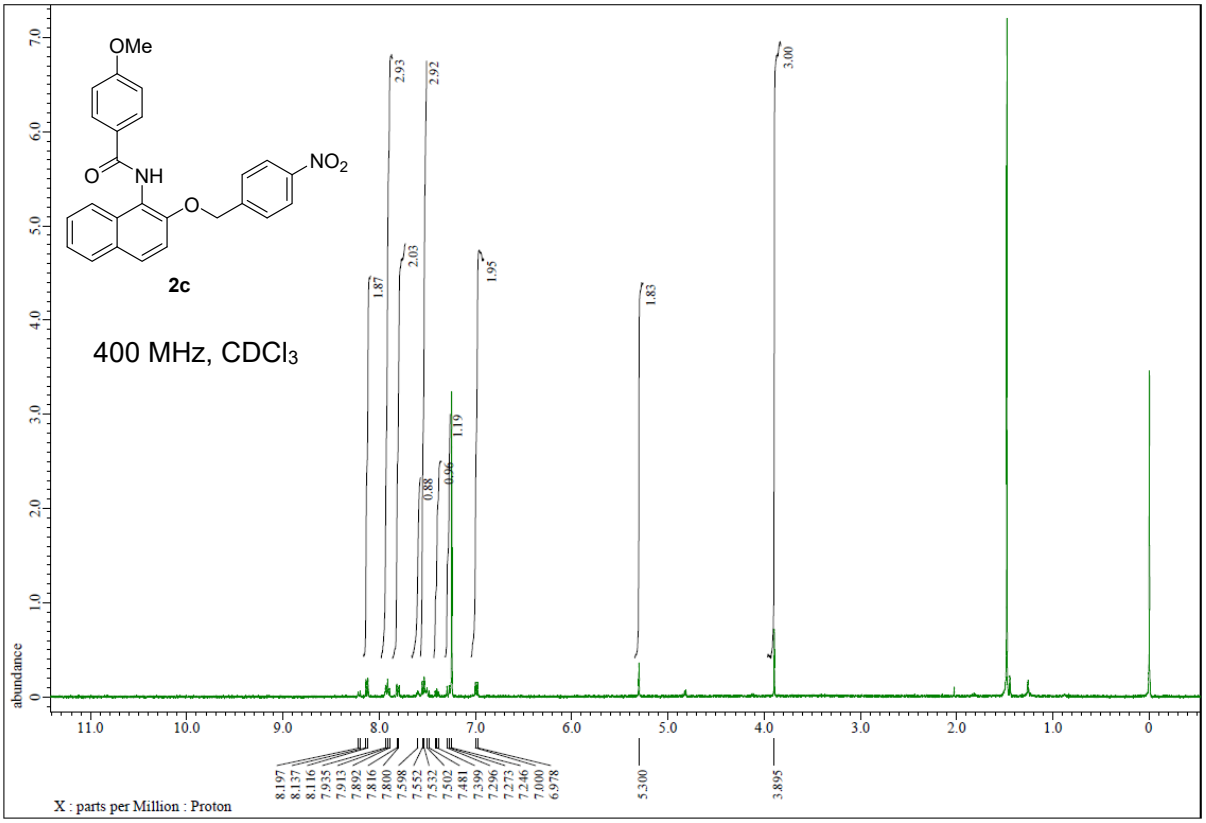
9. NMR charts of products 2, 4, 6k, and 10

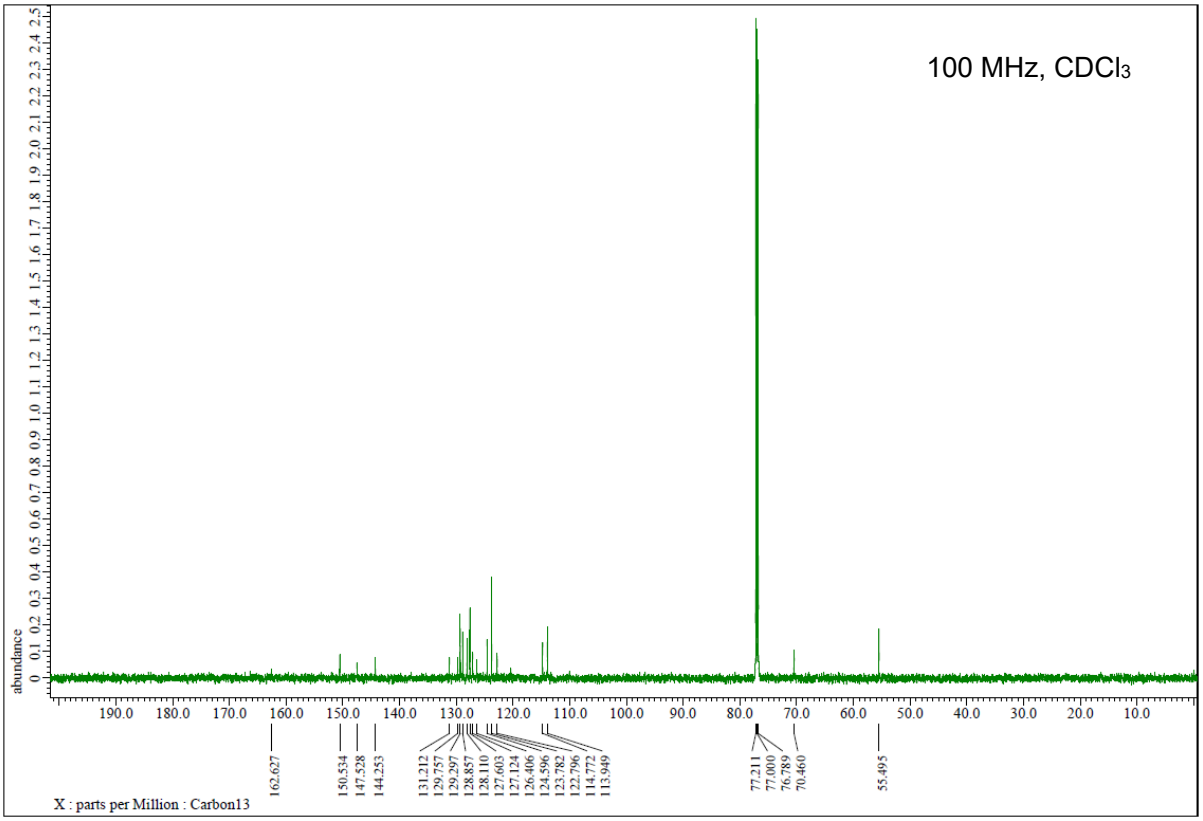


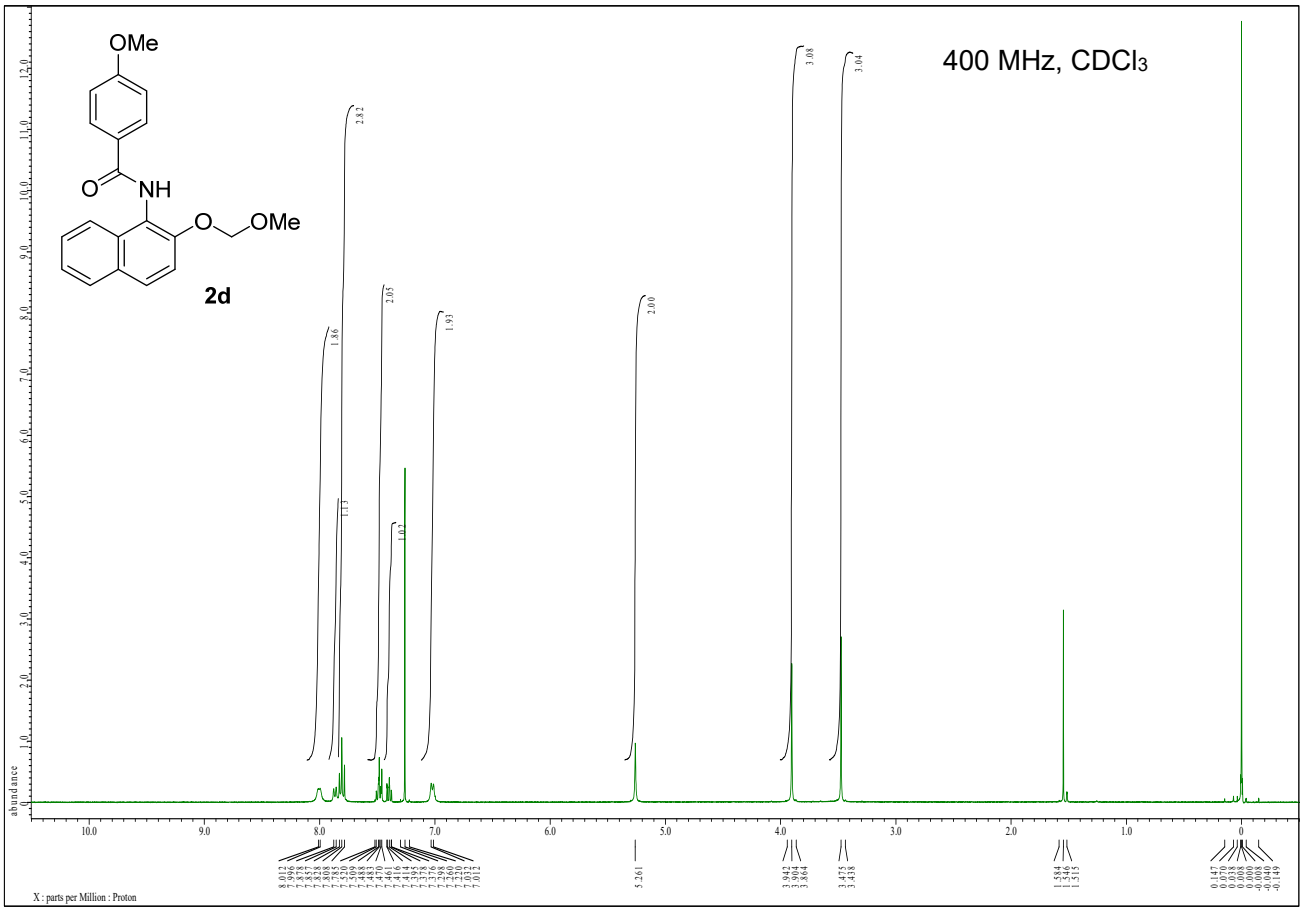


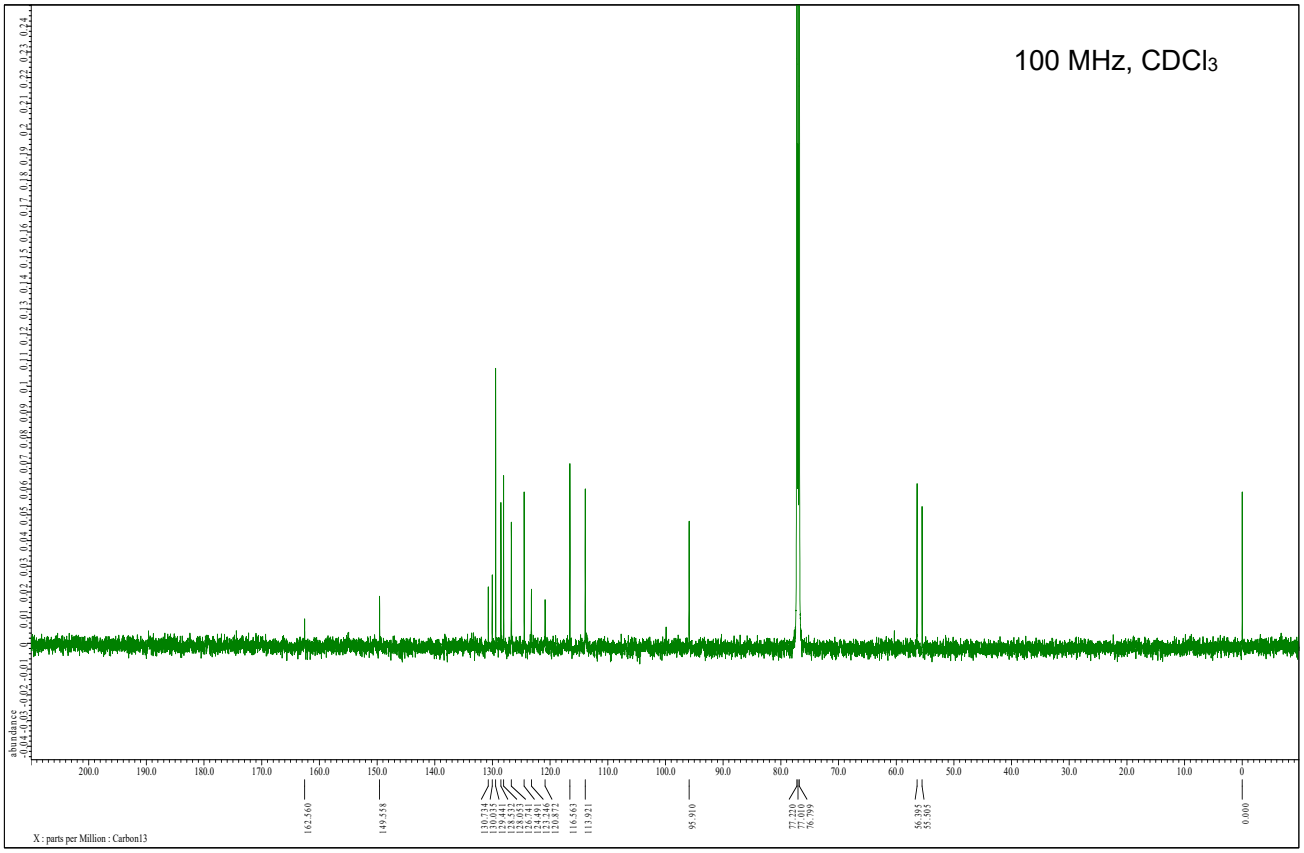

400 MHz, CDCl3
OMe
O
NH
OMe
2b
abundance
X : parts per Million : Proton

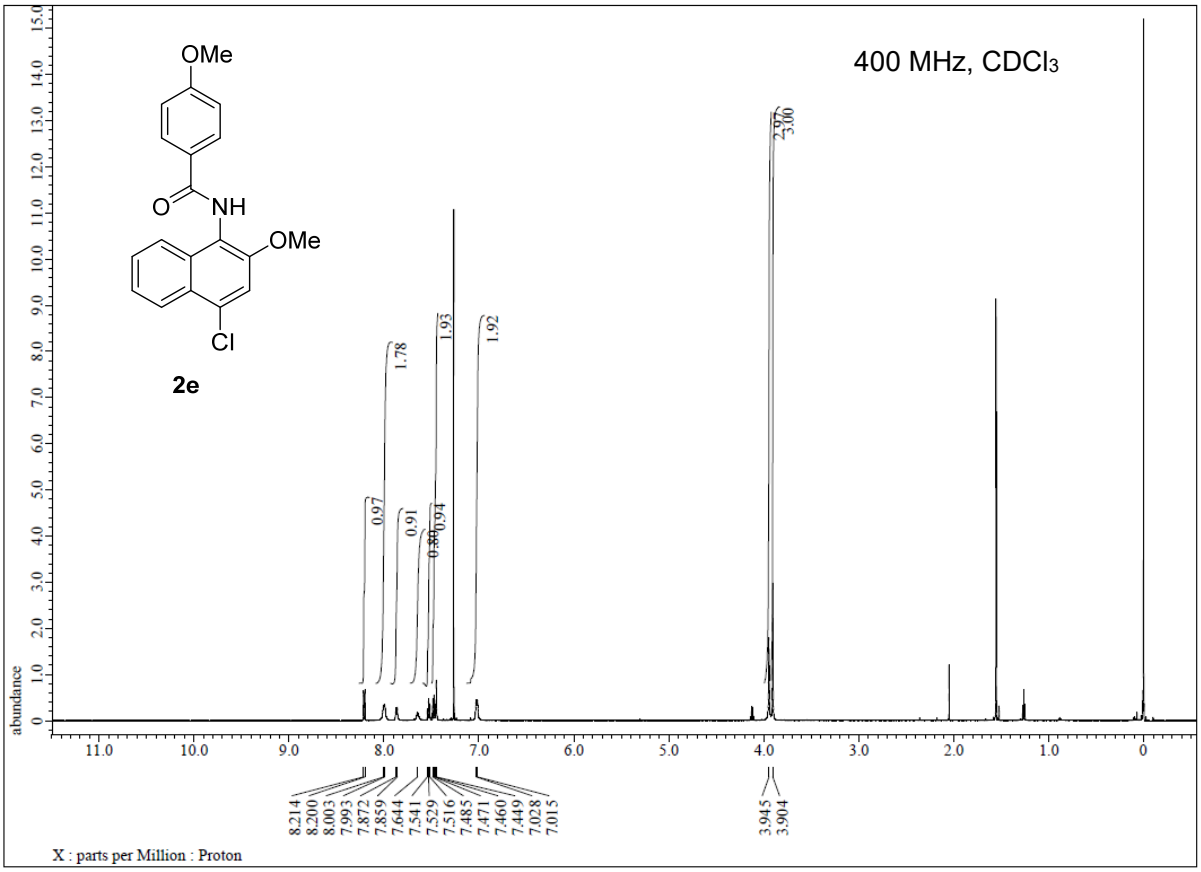

100 MHz, CDCl3
abundance
X : parts per Million : Carbon13

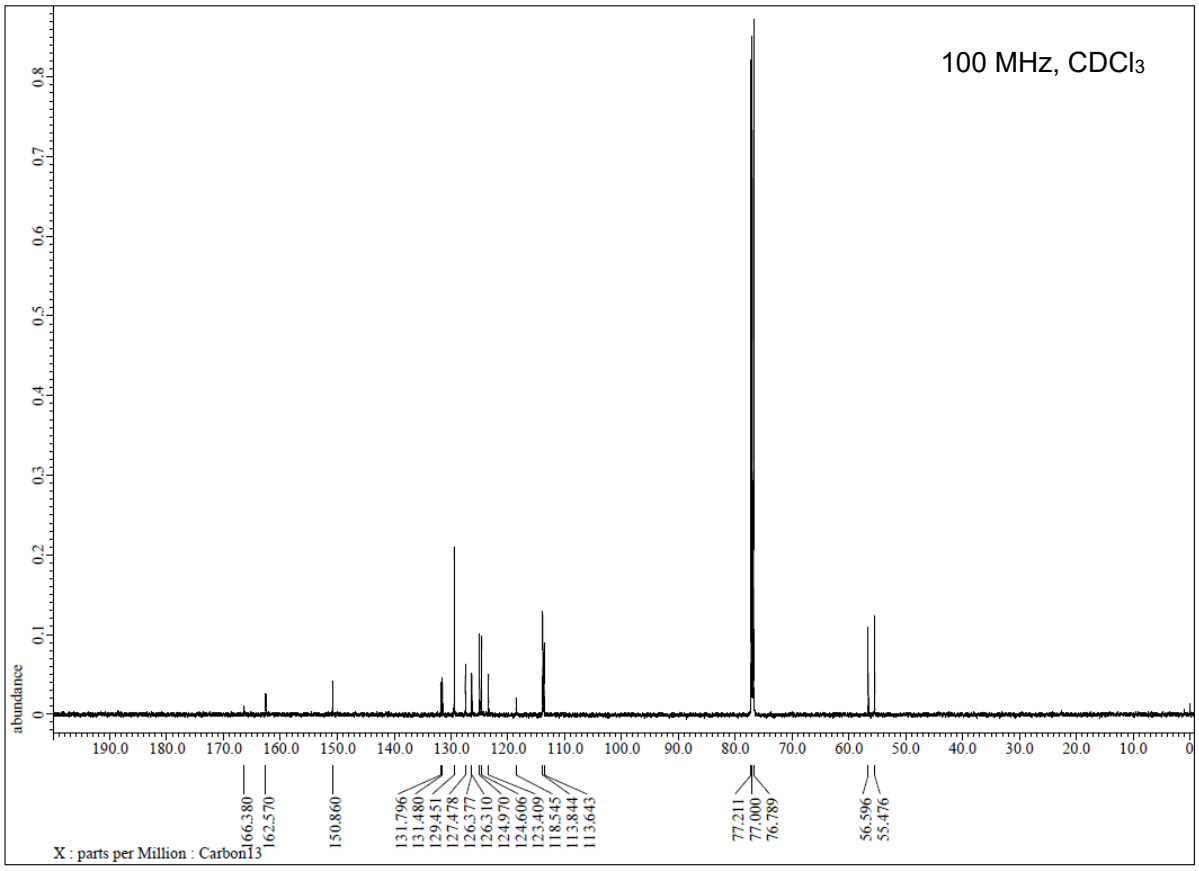

OMe
NH
O
O
NO2
2c
400 MHz, CDCl3
abundance
X : parts per Million : Proton

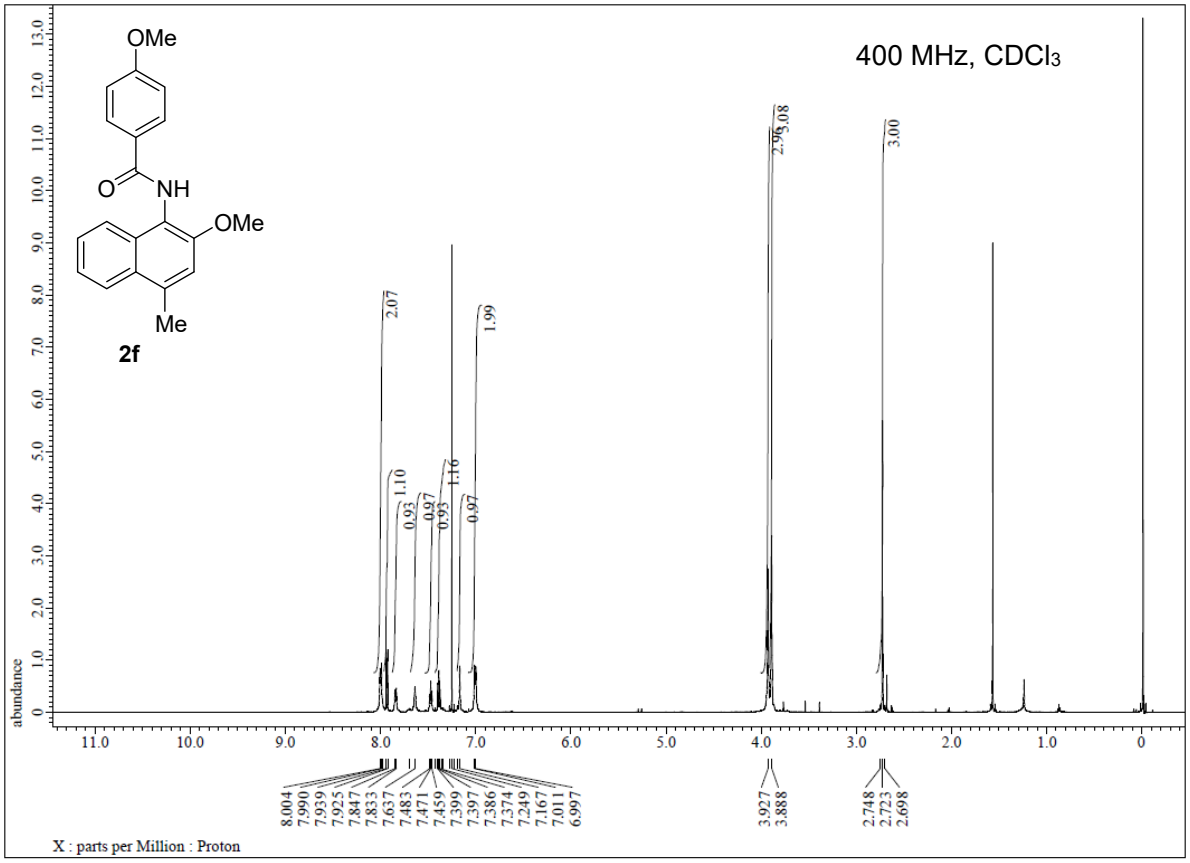

100 MHz, CDCl3
abundance
X : parts per Million : Carbon13

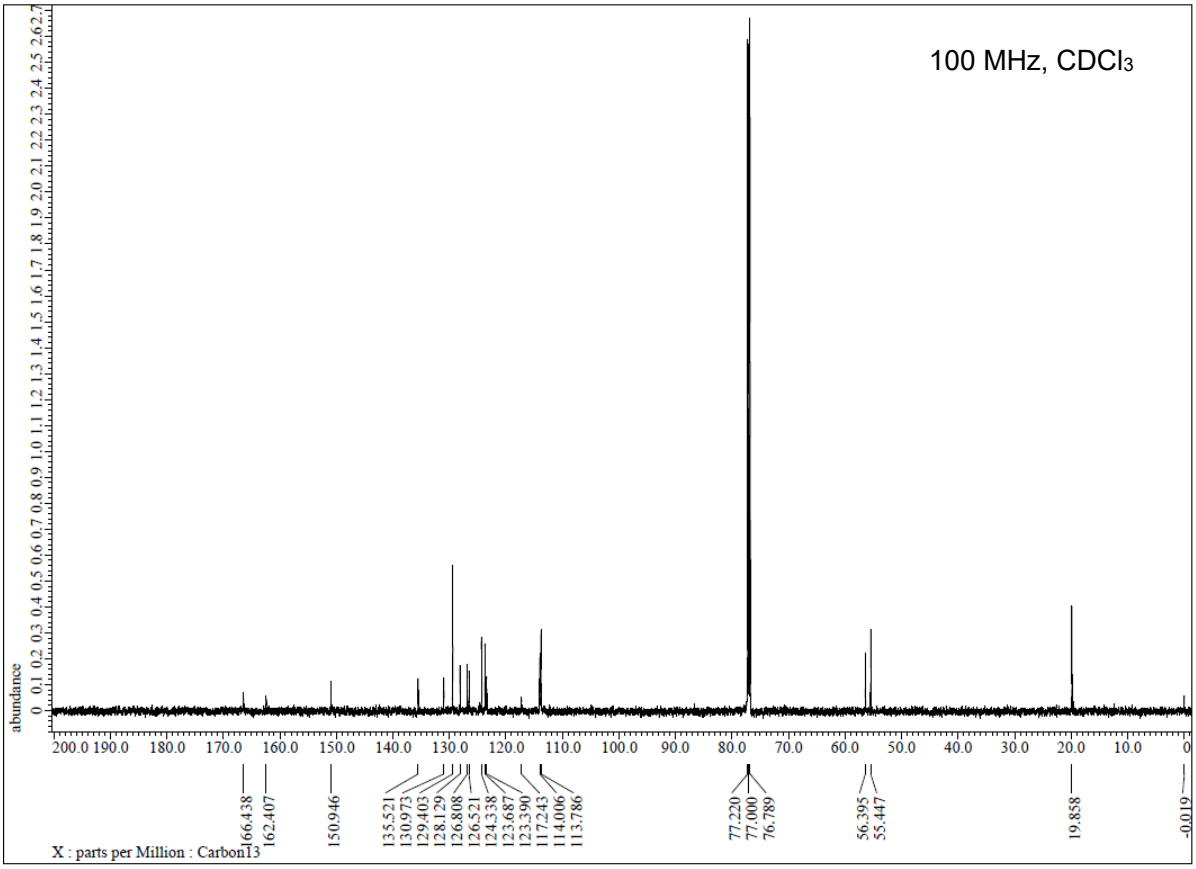

OMe
O
NH
O
O
OMe
2d
400 MHz, CDCl3
2.82
3.08
3.04
2.05
2.00
1.93
1.86
1.13
1.02
abundance
X : parts per Million : Proton

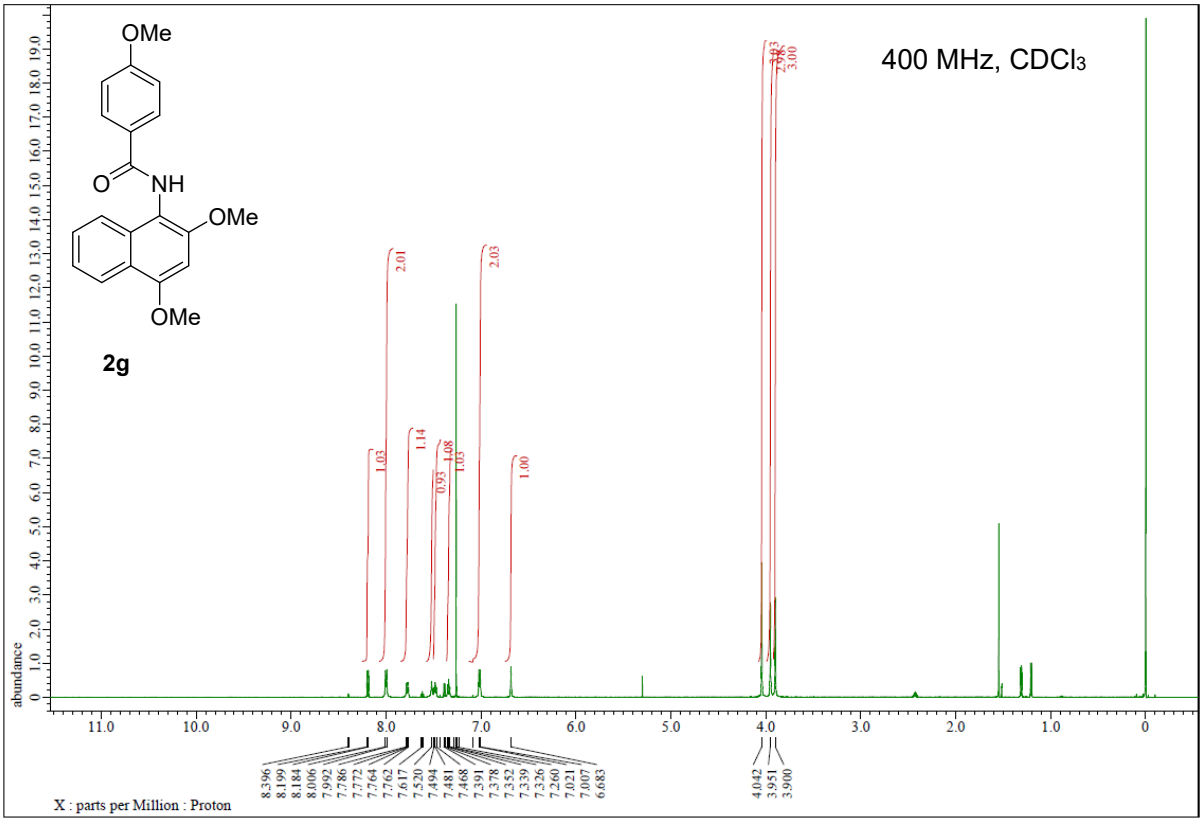

100 MHz, CDCl3
abundance
X : parts per Million : Carbon13

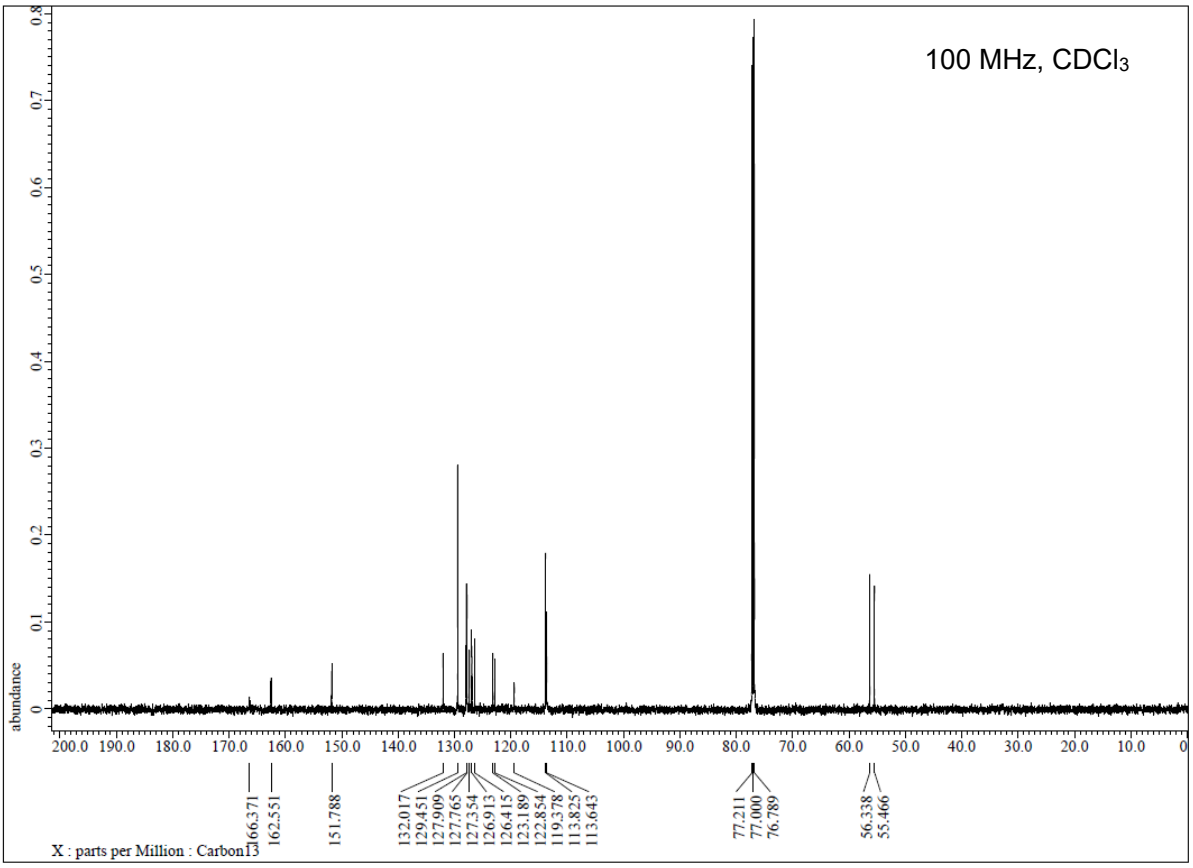

OMe
O
NH
OMe
Cl
2e
400 MHz, CDCl3
abundance
X : parts per Million : Proton

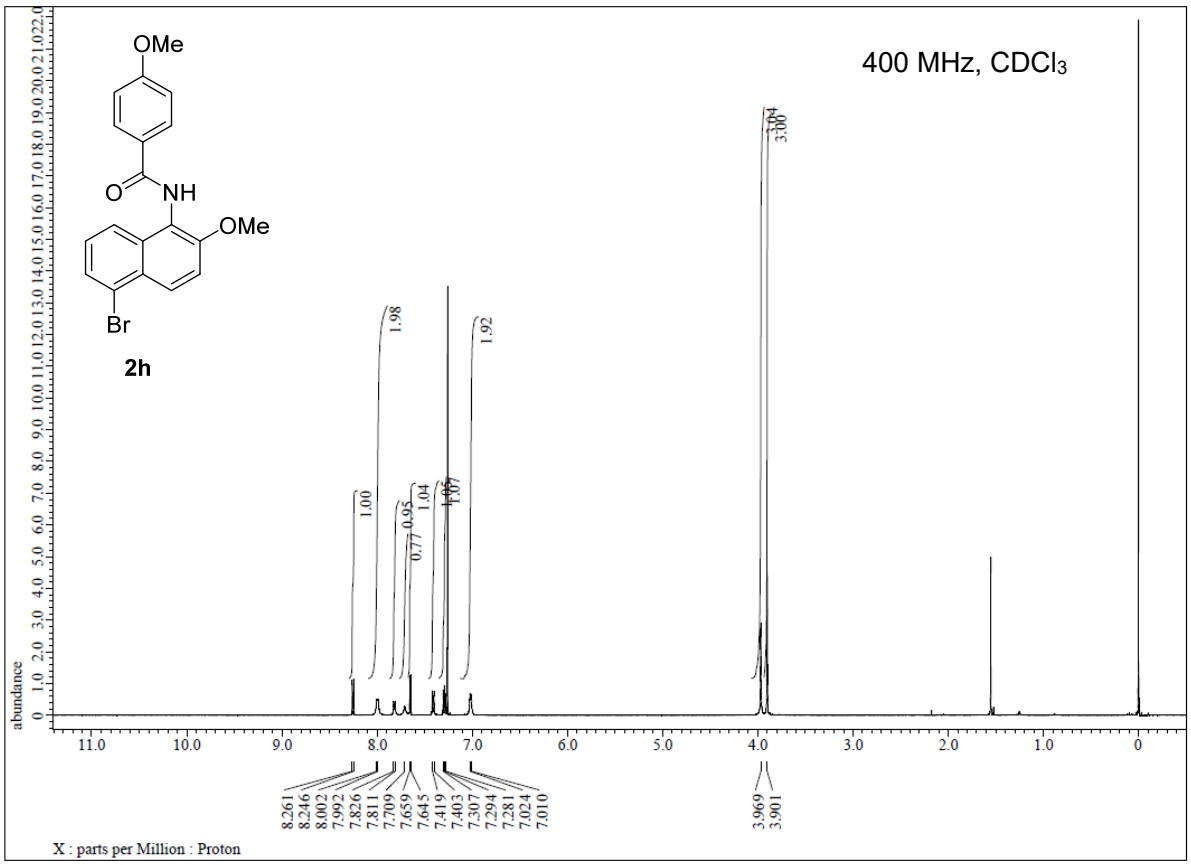

100 MHz, CDCl3
abundance
X : parts per Million : Carbon13

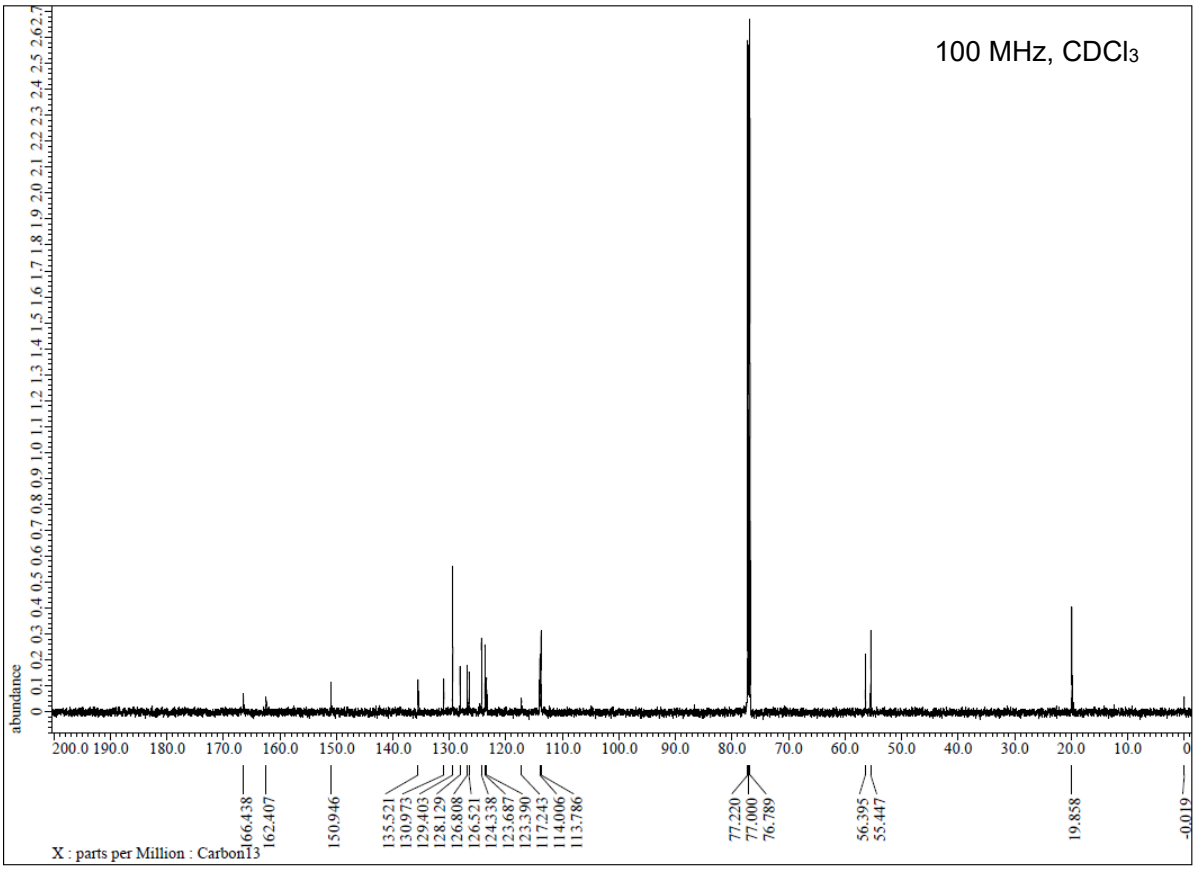

OMe
O
NH
OMe
Me
2f
400 MHz, CDCl3
abundance
X : parts per Million : Proton

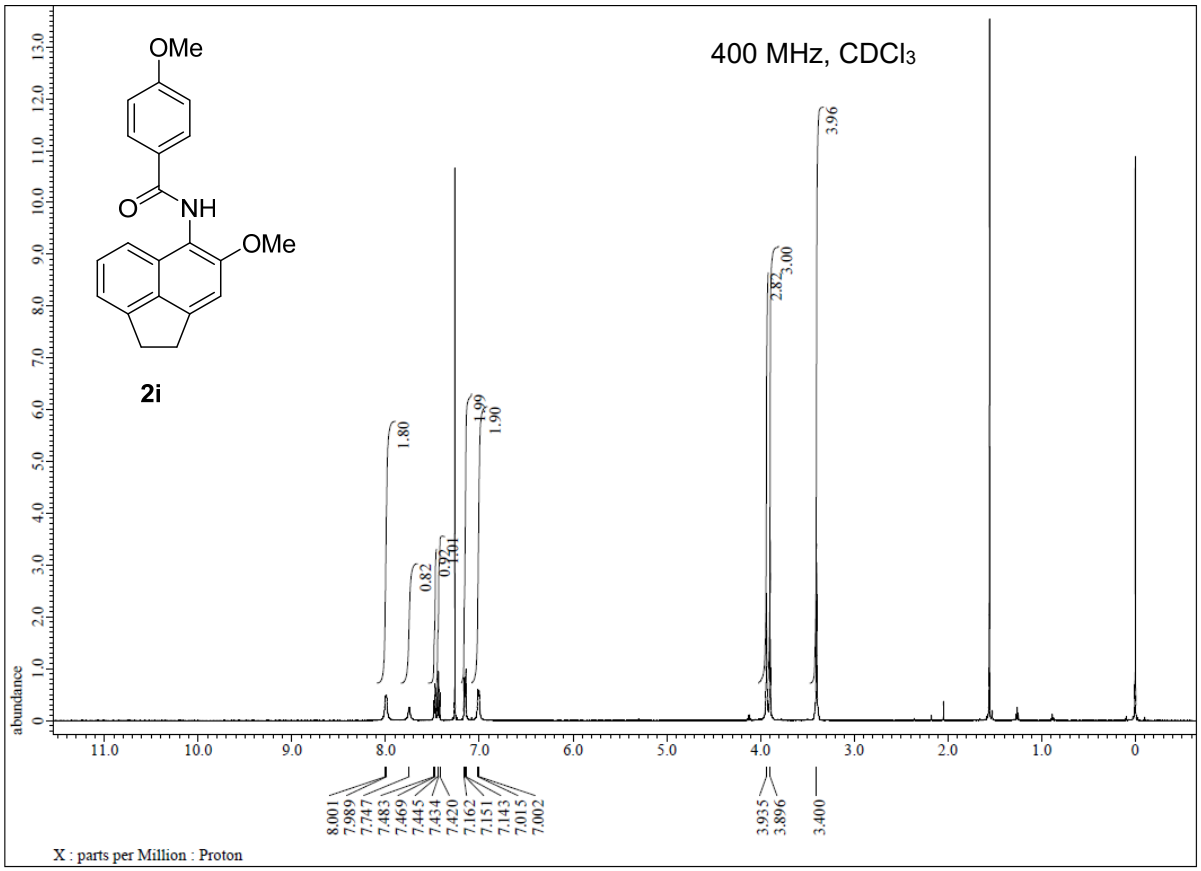

100 MHz, CDCl3
abundance
X : parts per Million : Carbon13

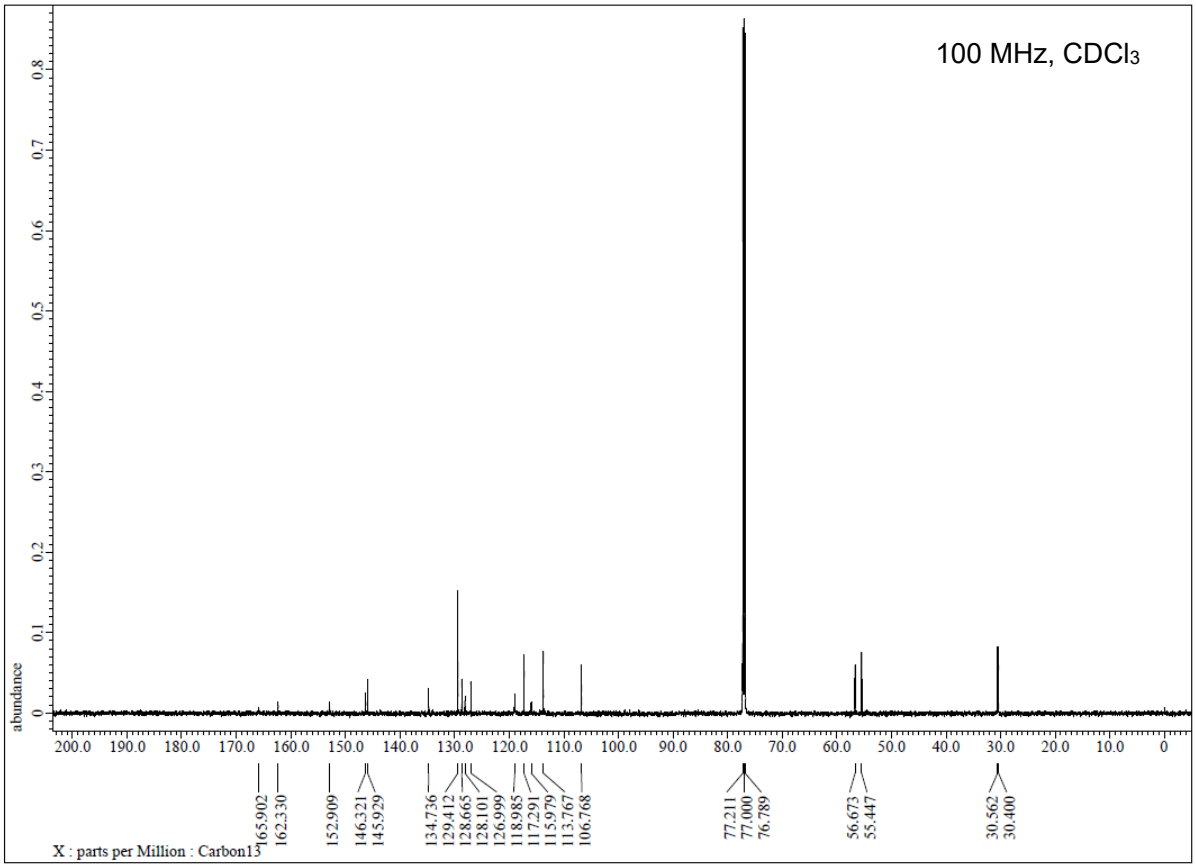

OMe
O
NH
OMe
OMe
2g
400 MHz, CDCl3
abundance
X : parts per Million : Proton

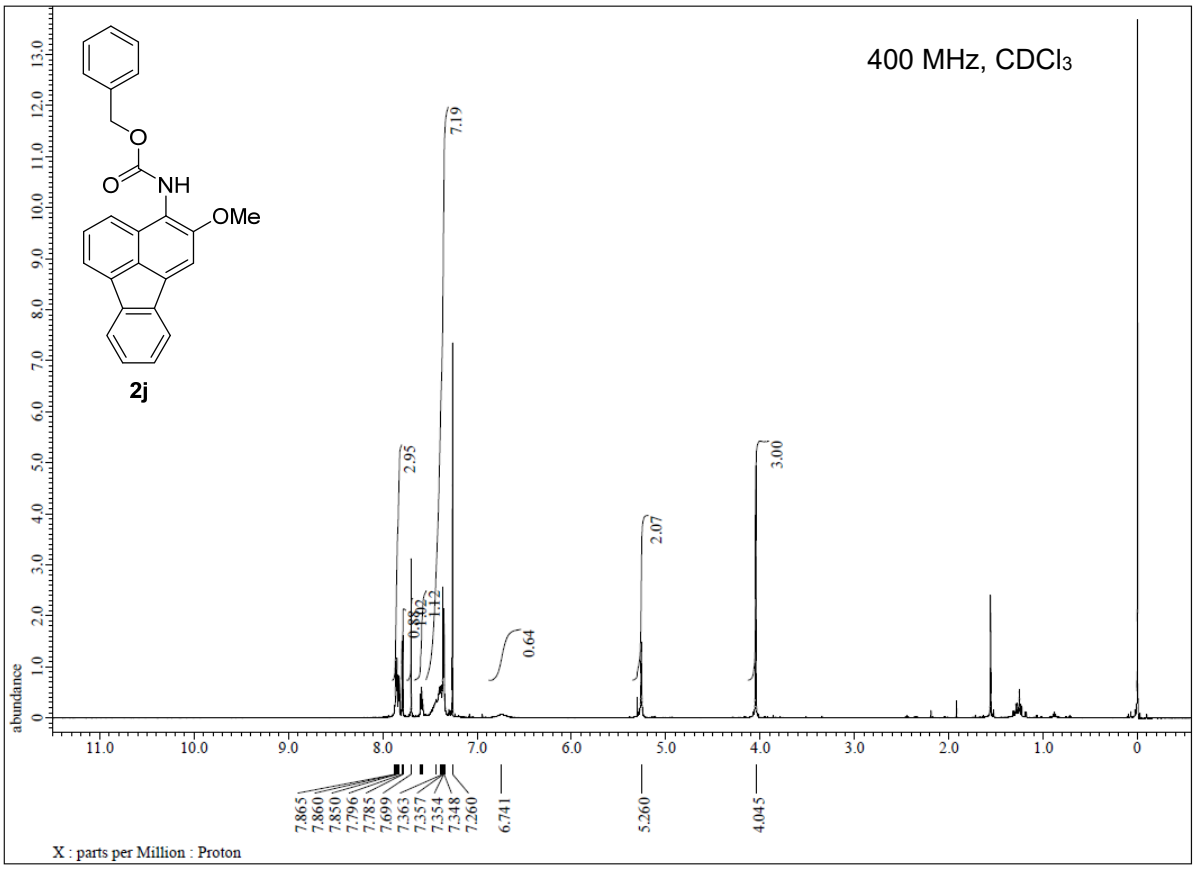

100 MHz, CDCl3
abundance
X : parts per Million : Carbon13

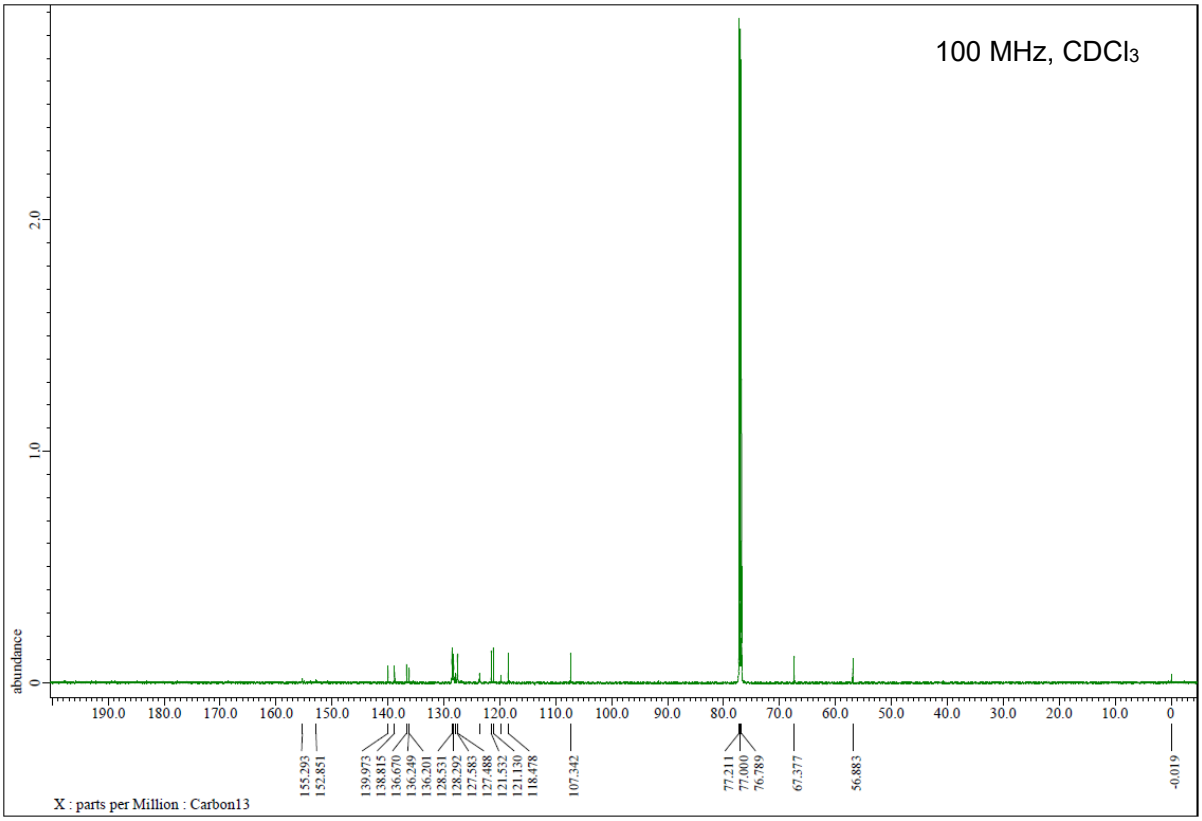

OMe
O
NH
OMe
Br
2h
400 MHz, CDCl3
abundance
X : parts per Million : Proton

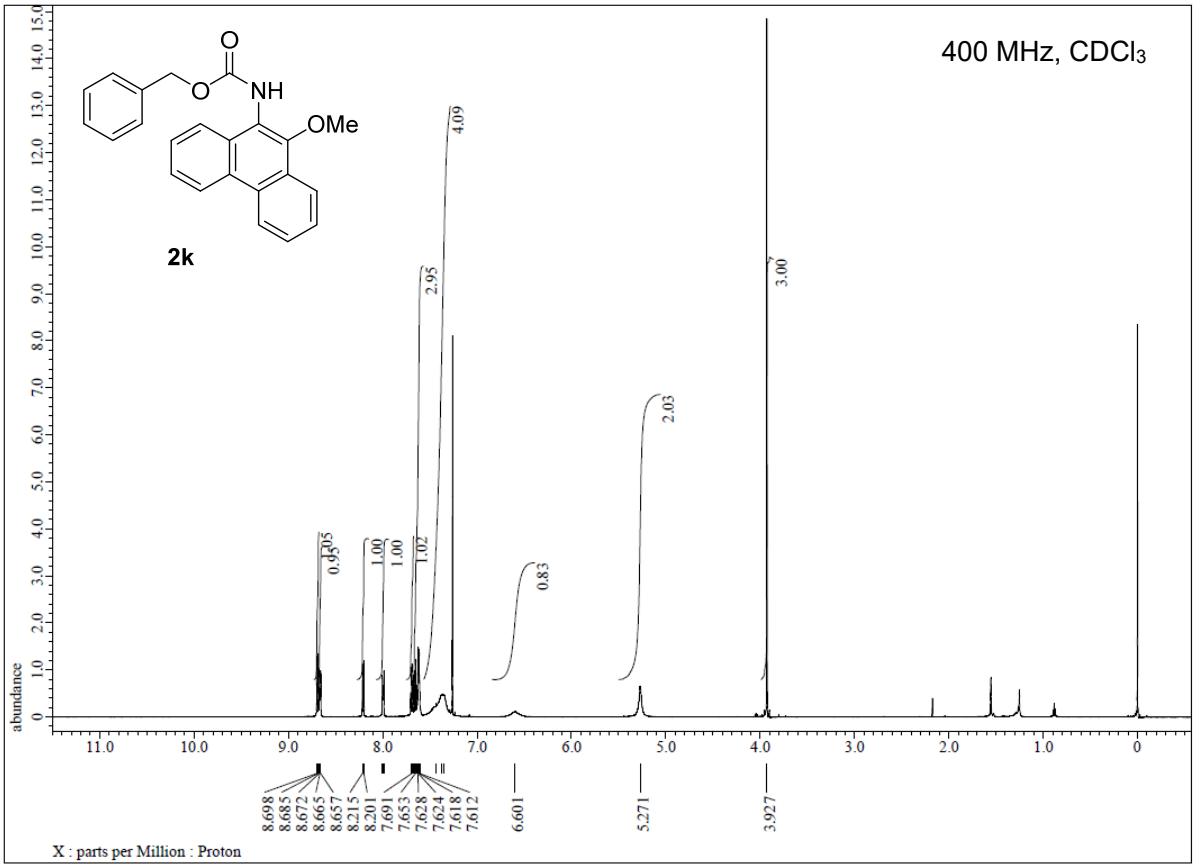

100 MHz, CDCl3
abundance
X : parts per Million : Carbon13

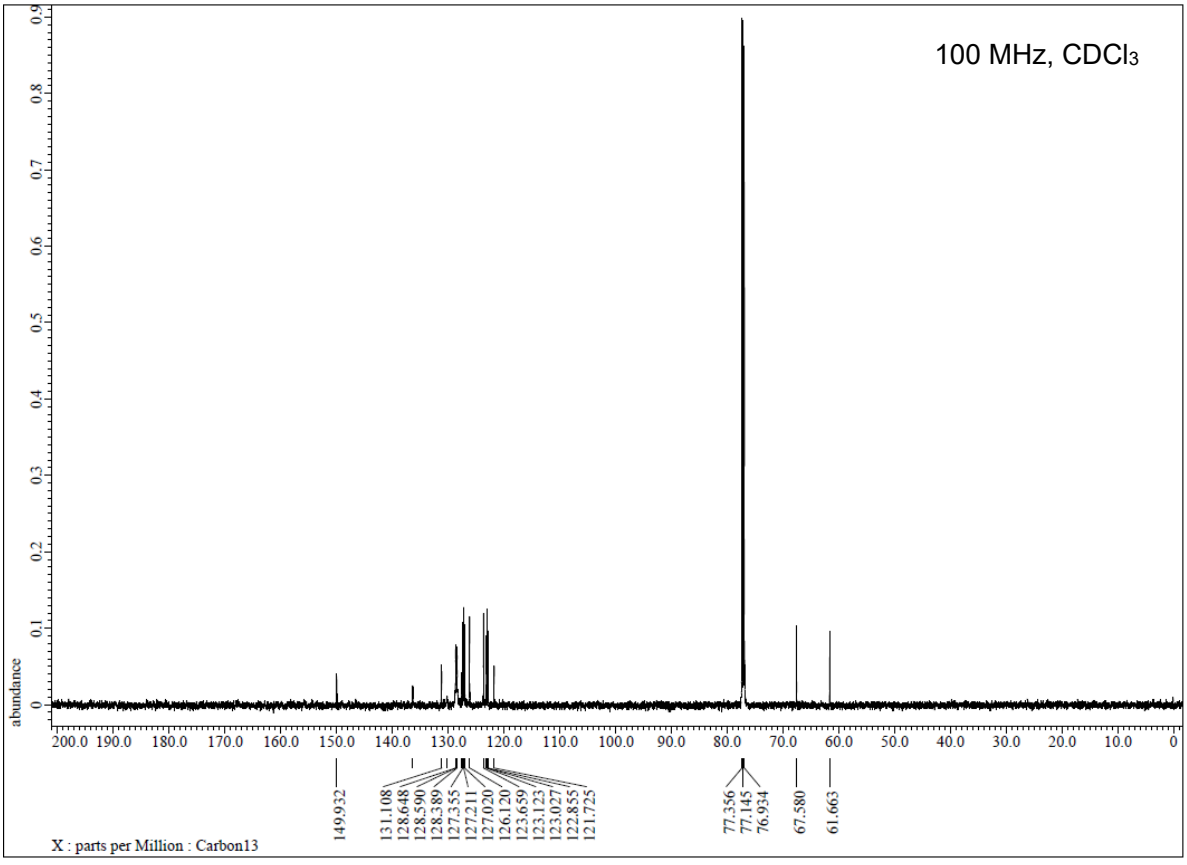

OMe
O
NH
OMe
2i
400 MHz, CDCl3
3.96
3.00
2.82
1.80
0.82
0.92
1.01
1.99
1.90
abundance
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.001
7.989
7.747
7.483
7.469
7.445
7.434
7.420
7.162
7.151
7.143
7.015
7.002
3.935
3.896
3.400
X : parts per Million : Proton

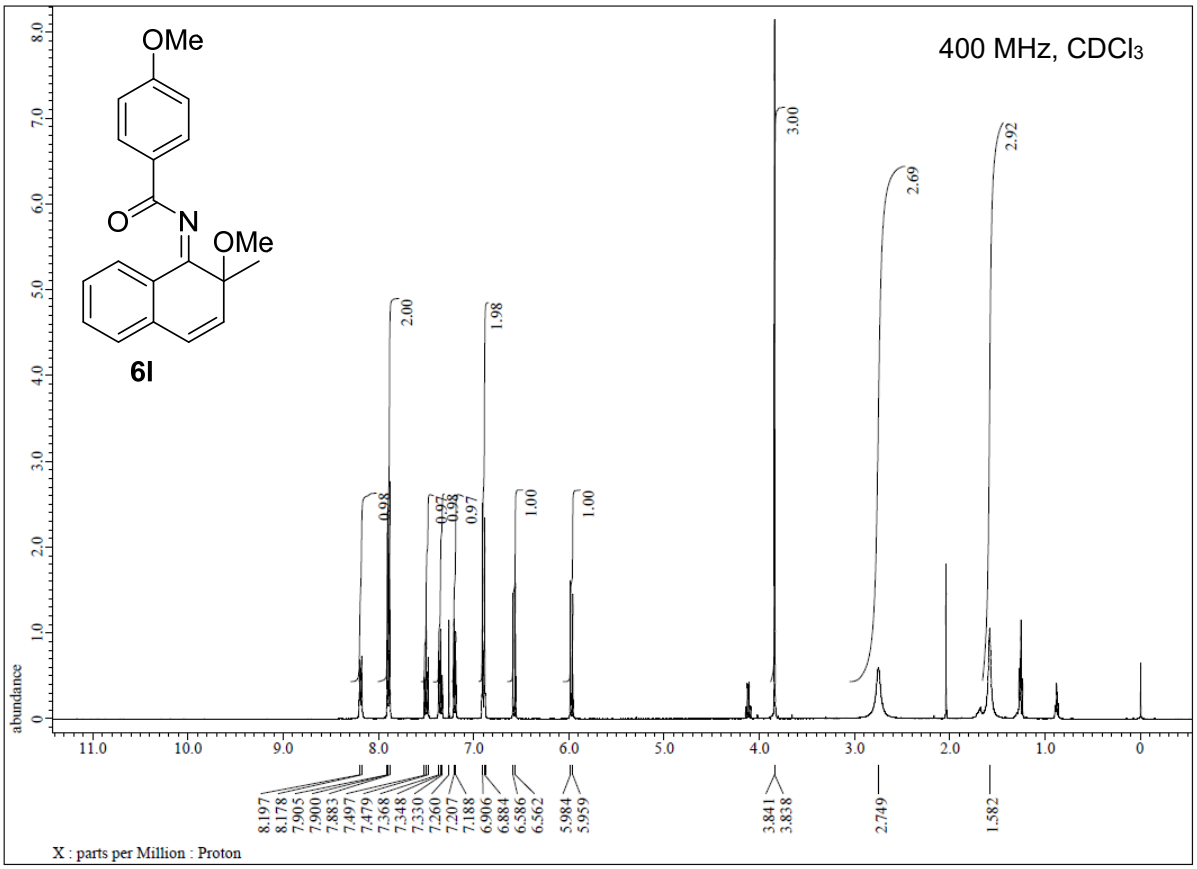

100 MHz, CDCl3
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
165.902
162.330
152.909
146.321
145.929
134.736
129.412
128.665
128.101
126.999
118.985
117.291
115.979
113.767
106.768
77.211
77.000
76.789
56.673
55.447
30.562
30.400
X : parts per Million : Carbon13

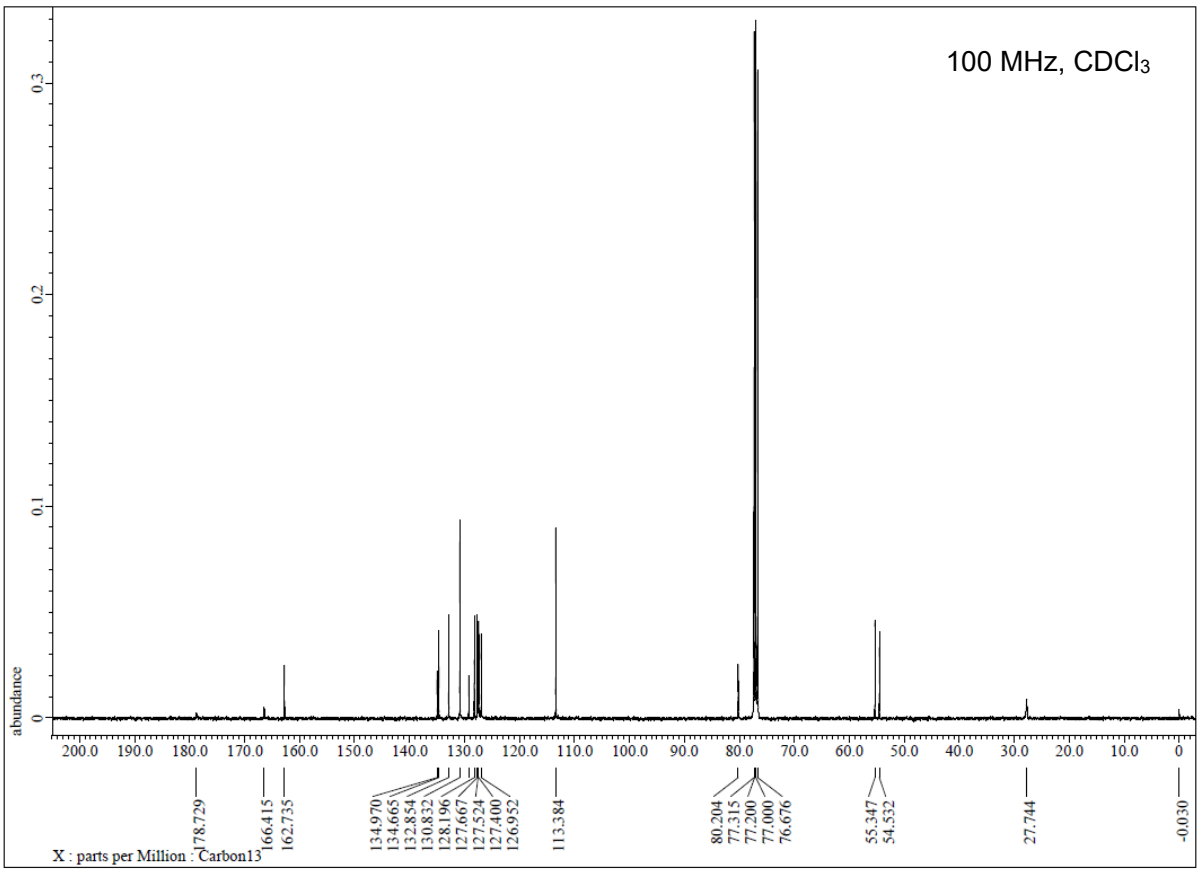

400 MHz, CDCl3
O
O
NH
OMe
2j
abundance
X : parts per Million : Proton

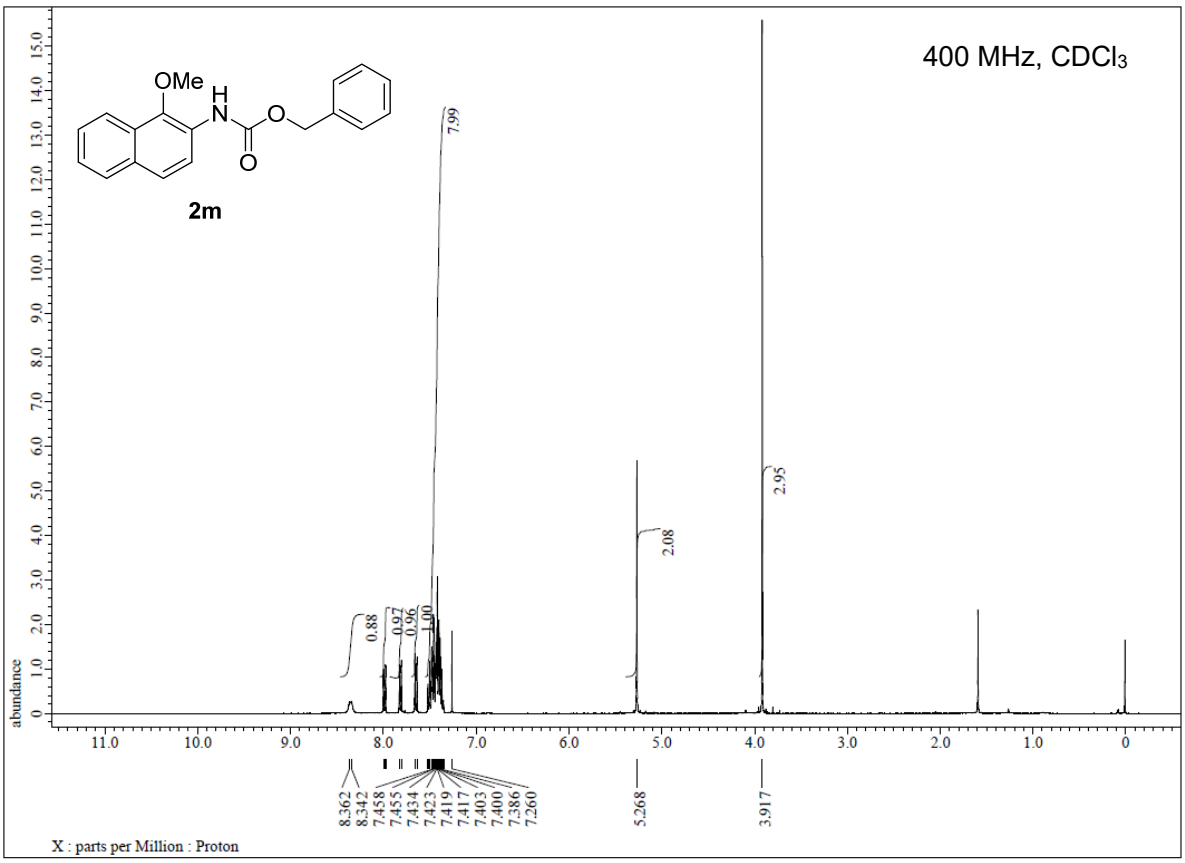

100 MHz, CDCl3
abundance
X : parts per Million : Carbon13

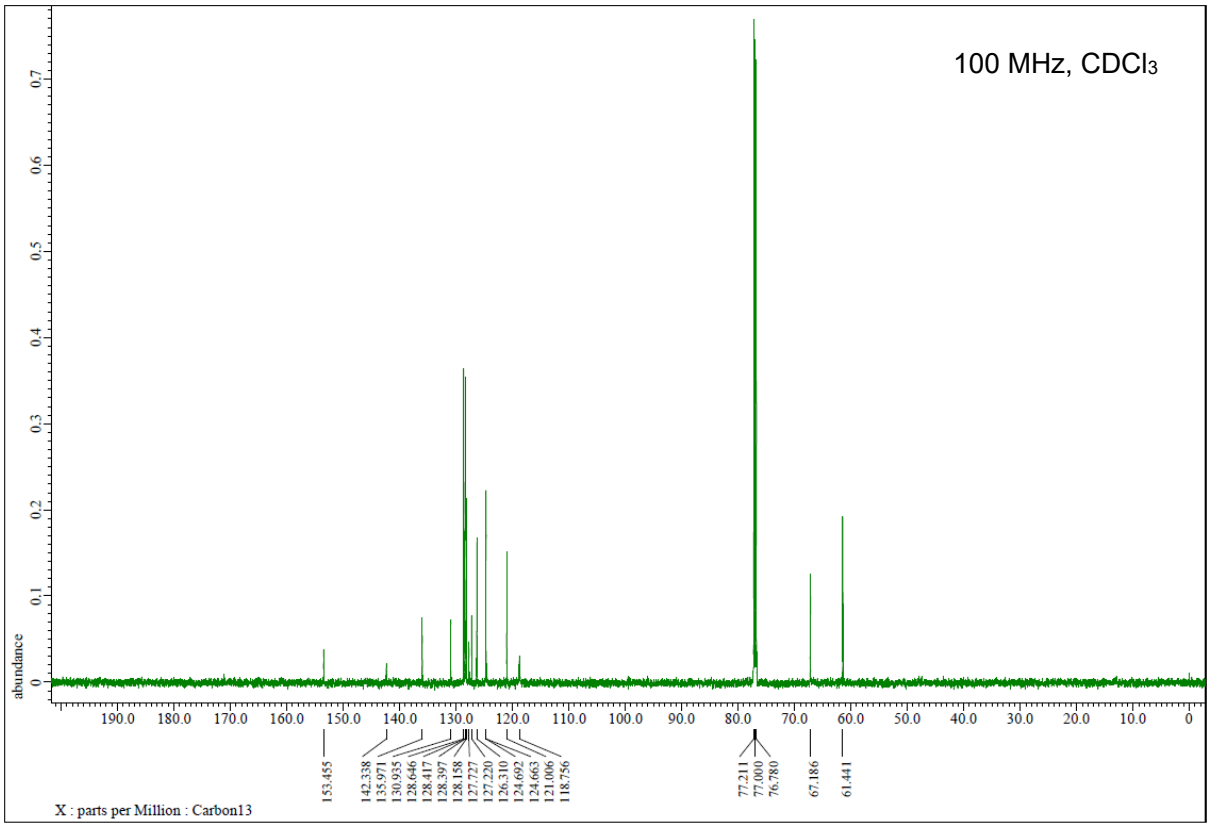

400 MHz, CDCl3
O
O
NH
OMe
2k
4.09
2.95
3.00
2.03
0.83
0.95
1.00
1.00
1.02
abundance
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.698
8.685
8.672
8.665
8.657
8.215
8.201
7.691
7.653
7.628
7.624
7.618
7.612
6.601
5.271
3.927
X : parts per Million : Proton

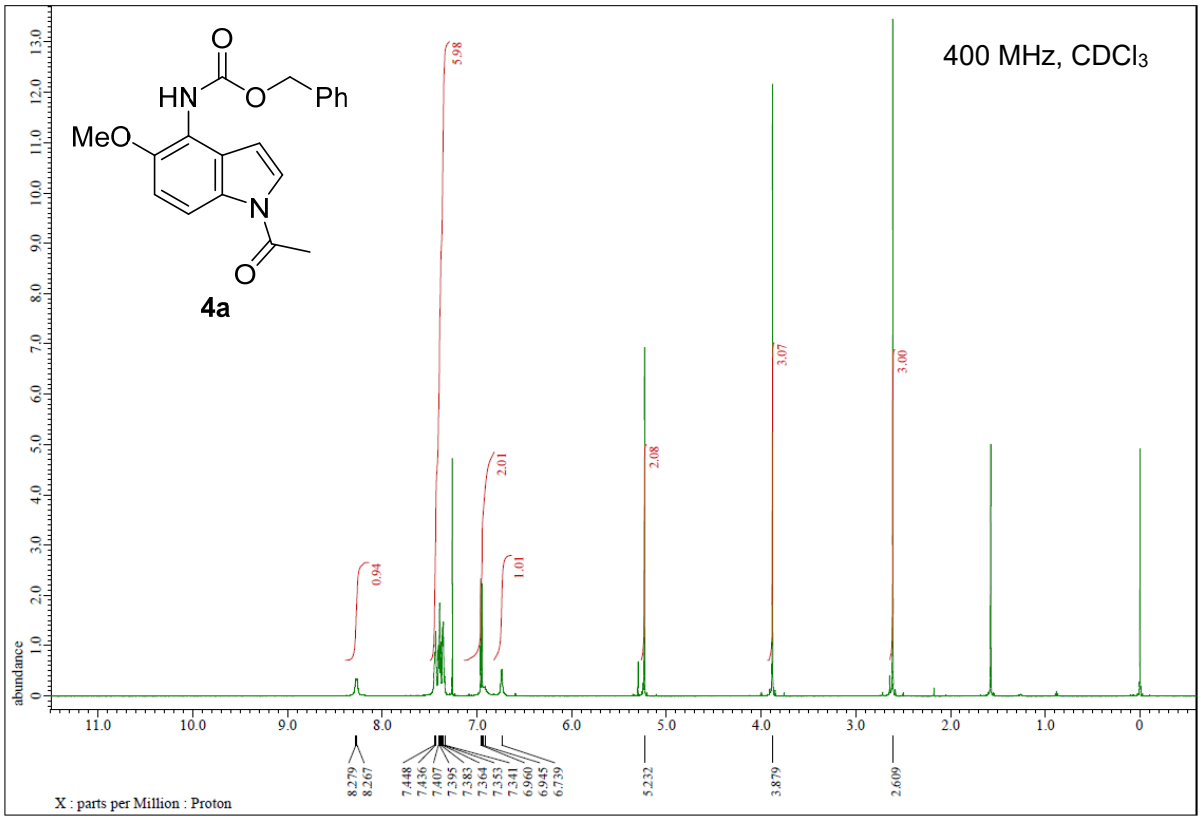

100 MHz, CDCl3
abundance
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
149.932
131.108
128.648
128.590
128.389
127.355
127.211
127.020
126.120
123.659
123.123
123.027
122.855
121.725
77.356
77.145
76.934
67.580
61.663
X : parts per Million : Carbon13

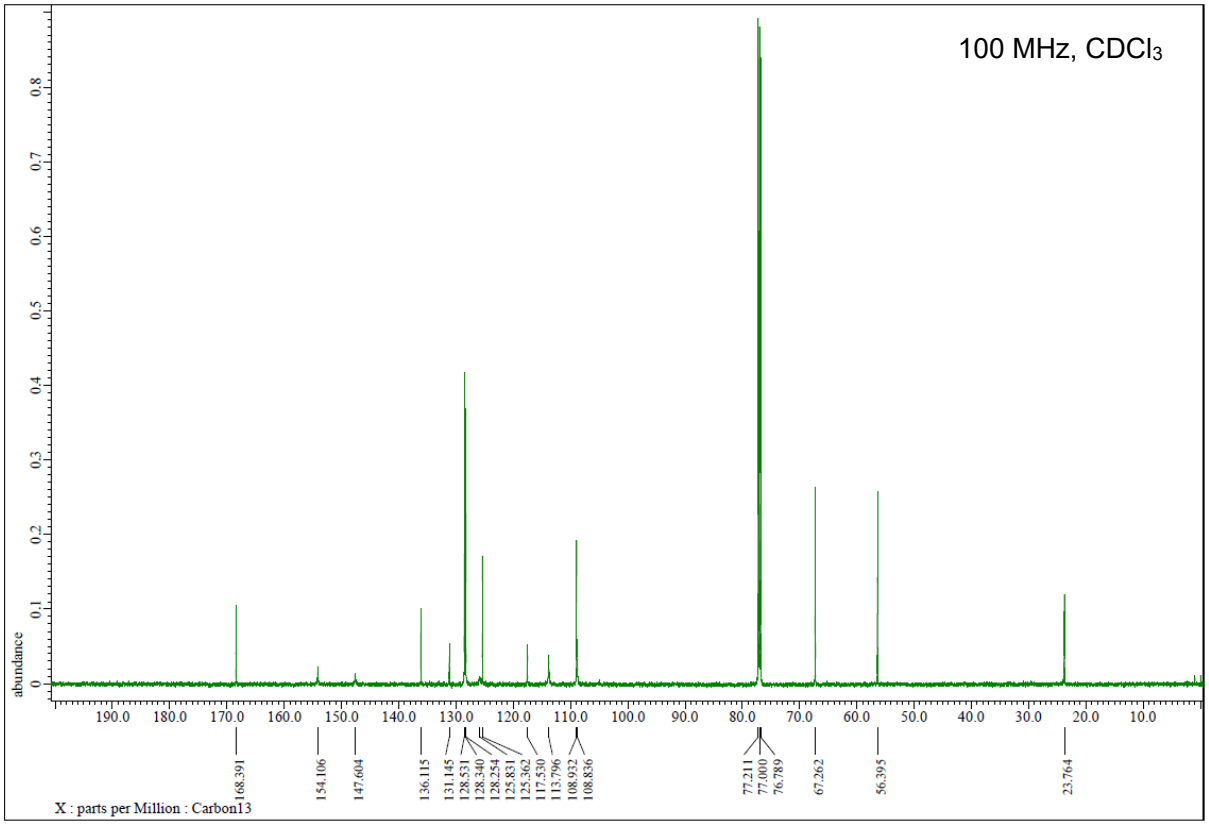

OMe
O
N
OMe
6l
400 MHz, CDCl3
abundance
X : parts per Million : Proton

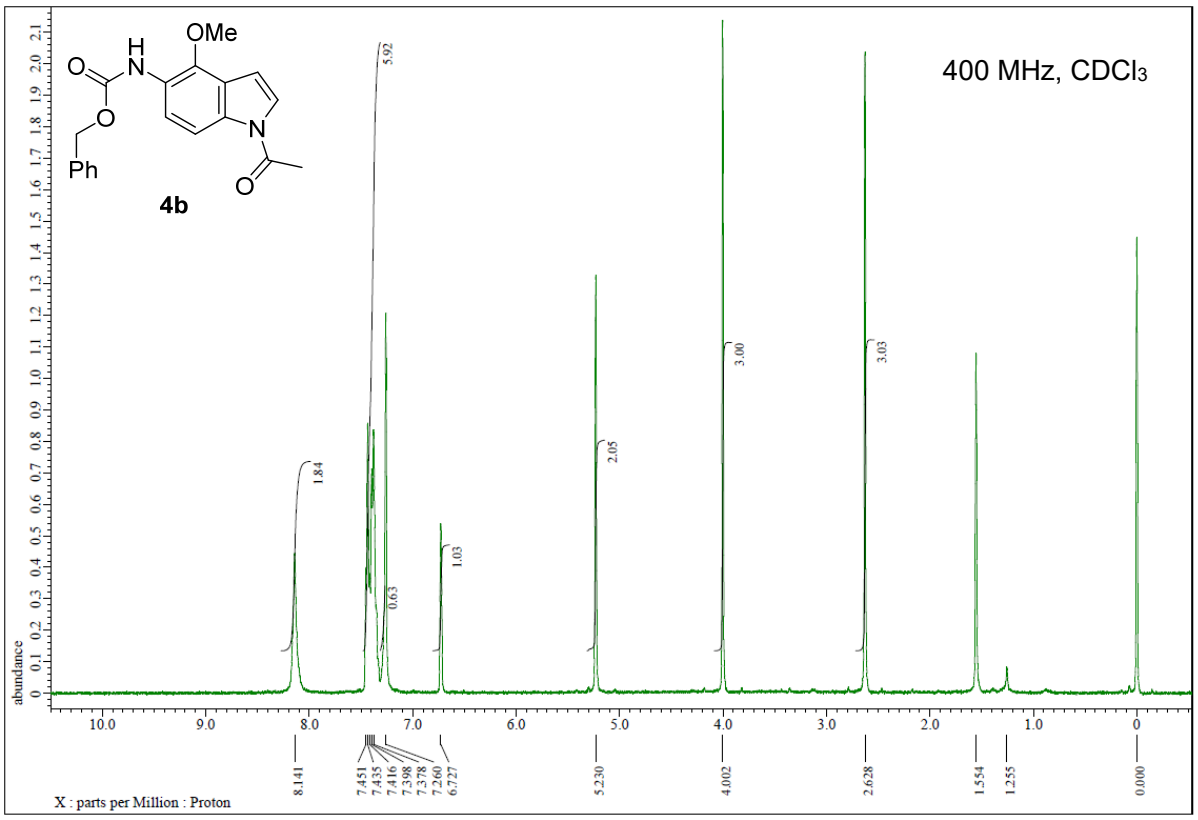

100 MHz, CDCl3
abundance
X : parts per Million : Carbon13

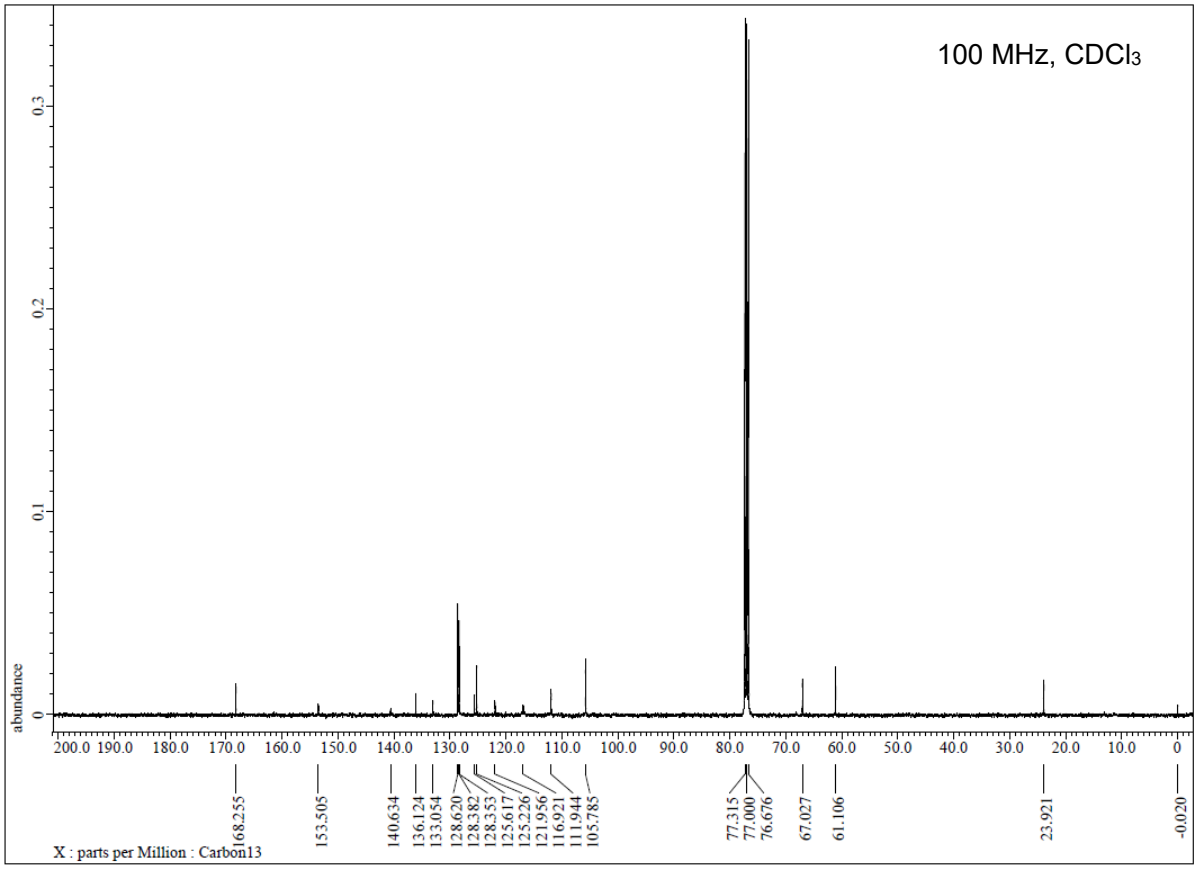

400 MHz, CDCl3
OMe
H
N
O
O
2m
7.99
2.95
2.08
0.88
0.97
0.96
1.00
abundance
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.362
8.342
7.458
7.455
7.434
7.423
7.419
7.417
7.403
7.400
7.386
7.260
5.268
3.917
X : parts per Million : Proton

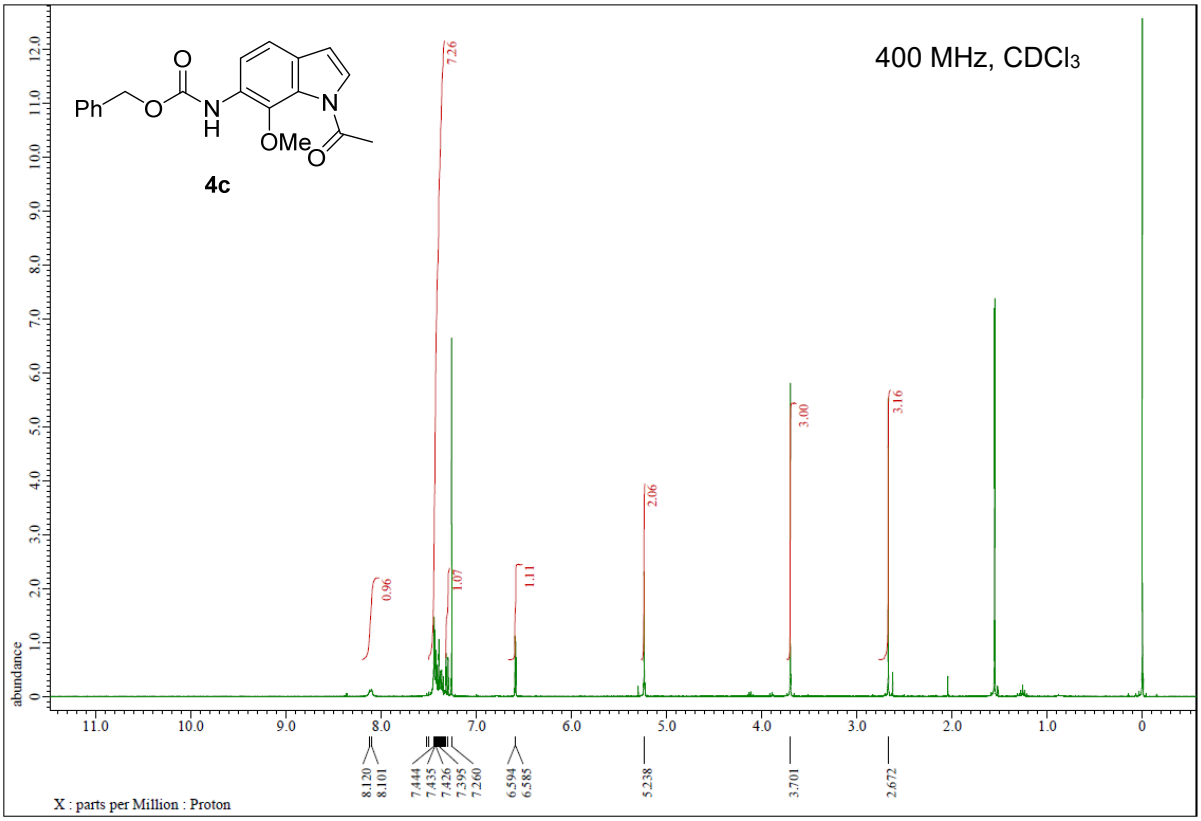

100 MHz, CDCl3
abundance
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
153.455
142.338
135.971
130.935
128.646
128.417
128.397
128.158
127.727
127.220
126.310
124.692
124.663
121.006
118.756
77.211
77.000
76.780
67.186
61.441
X : parts per Million : Carbon13

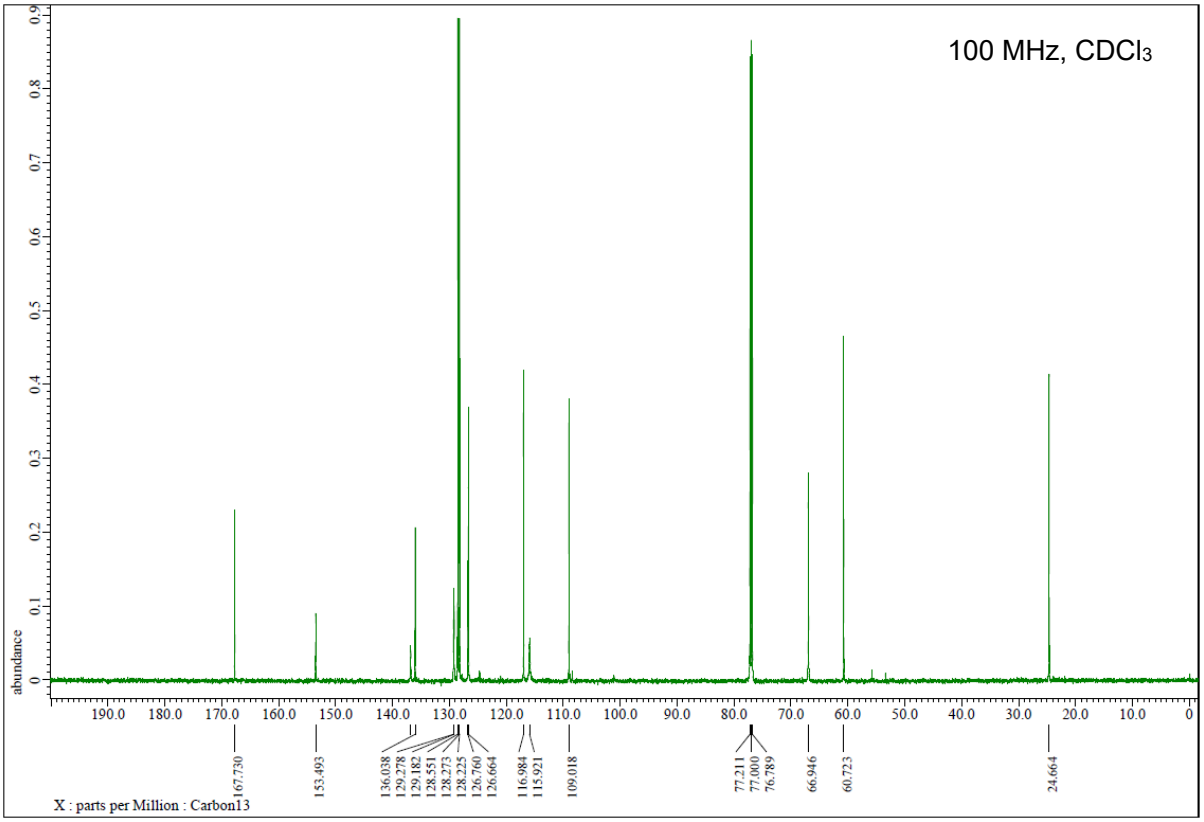

400 MHz, CDCl3
HN
O
O
Ph
MeO
N
O
4a
abundance
X : parts per Million : Proton
5.98
2.01
2.08
3.07
3.00
1.01
0.94
8.279
8.267
7.448
7.436
7.407
7.395
7.383
7.364
7.355
7.341
6.960
6.945
6.739
5.232
3.879
2.609

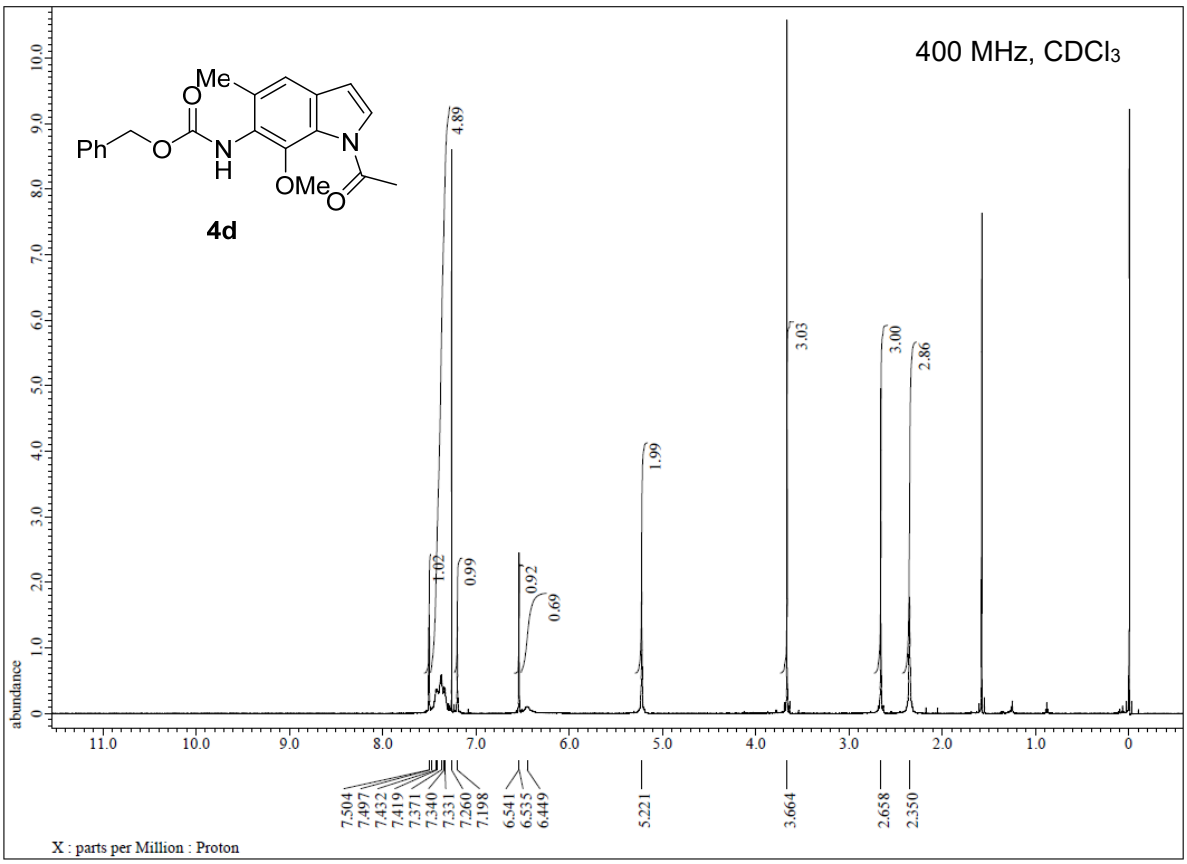

100 MHz, CDCl3
abundance
X : parts per Million : Carbon13
168.391
154.106
147.604
136.115
131.145
128.531
128.340
128.254
125.831
125.362
117.530
113.796
108.932
108.836
77.211
77.000
76.789
67.262
56.395
23.764

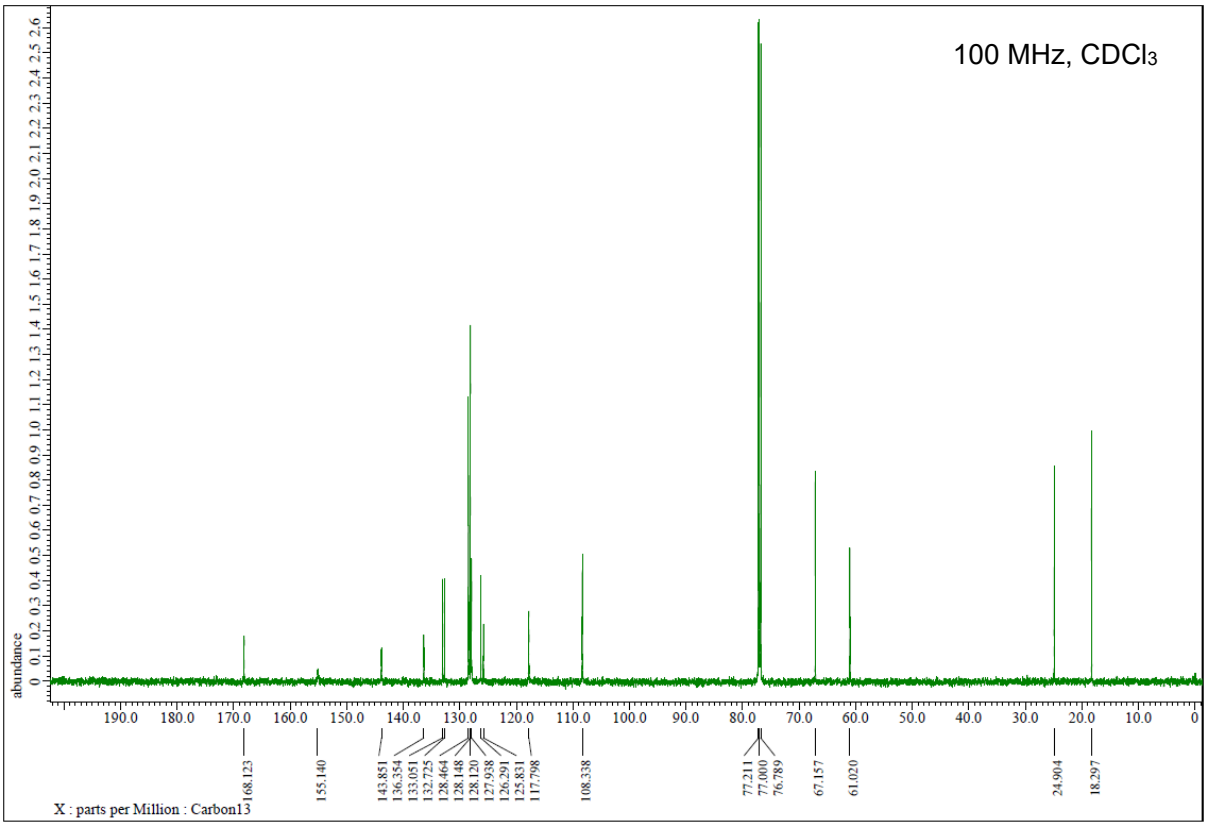

OMe
H
N
O
O
Ph
N
O
4b
400 MHz, CDCl3
abundance
X : parts per Million : Proton
8.141
7.451
7.435
7.416
7.398
7.378
7.260
6.727
5.230
4.002
2.628
1.554
1.255
0.000

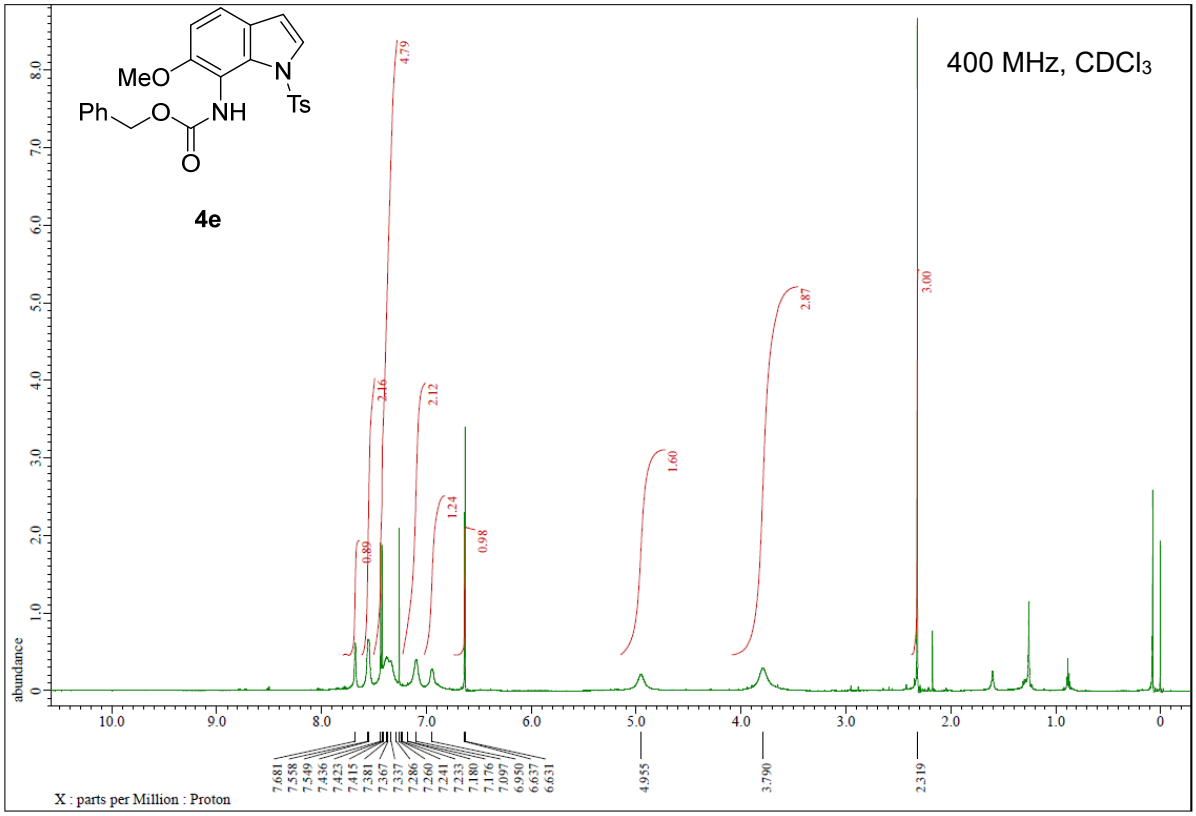

100 MHz, CDCl3
abundance
X : parts per Million : Carbon13
168.255
153.505
140.634
136.124
133.054
128.620
128.382
128.353
125.617
125.226
121.956
116.921
111.944
105.785
77.315
77.000
76.676
67.027
61.106
23.921
-0.020

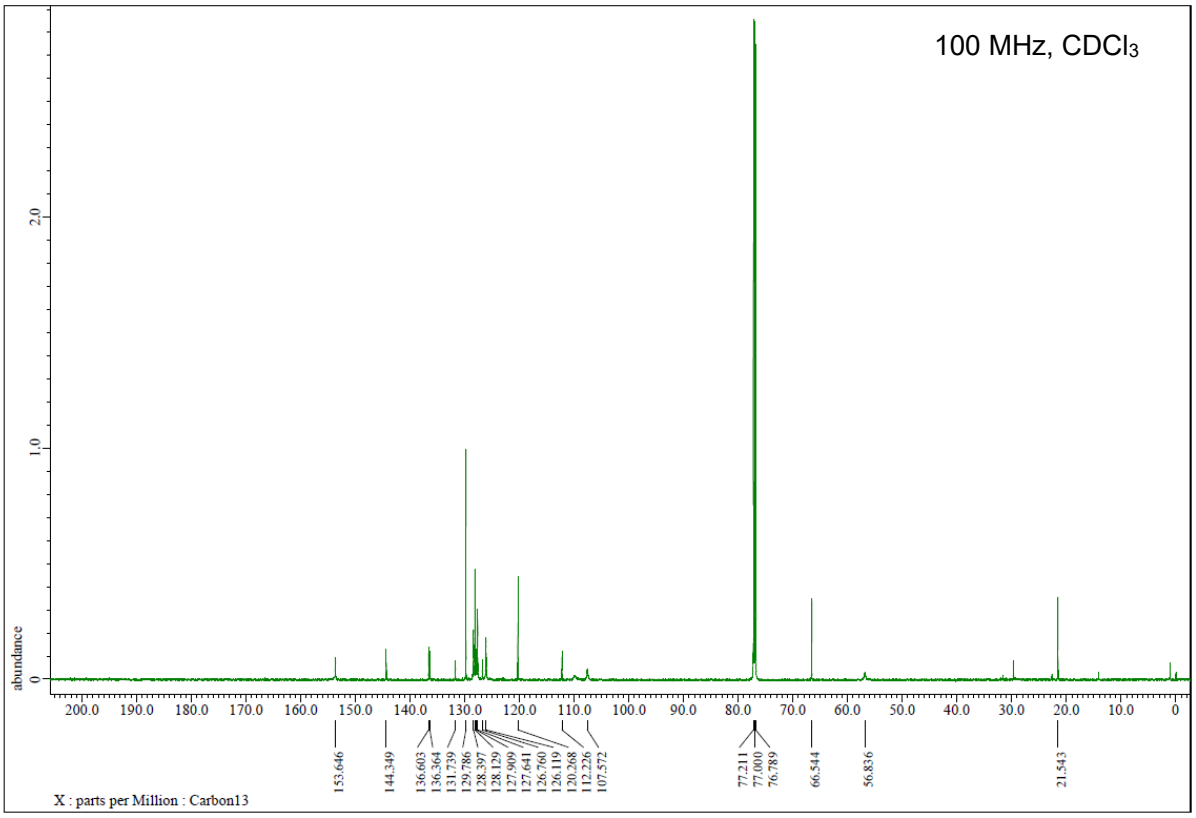

400 MHz, CDCl3
4c
abundance
X : parts per Million : Proton

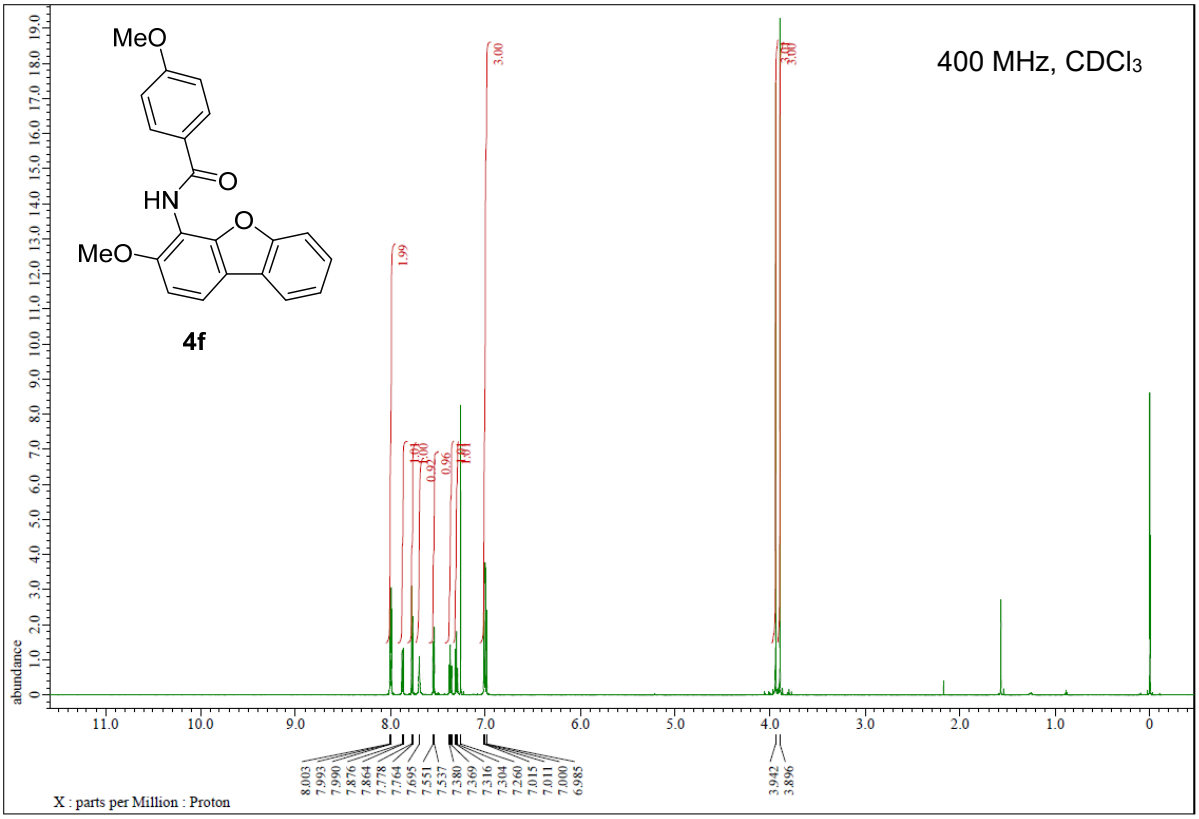

100 MHz, CDCl3
abundance
X : parts per Million : Carbon13

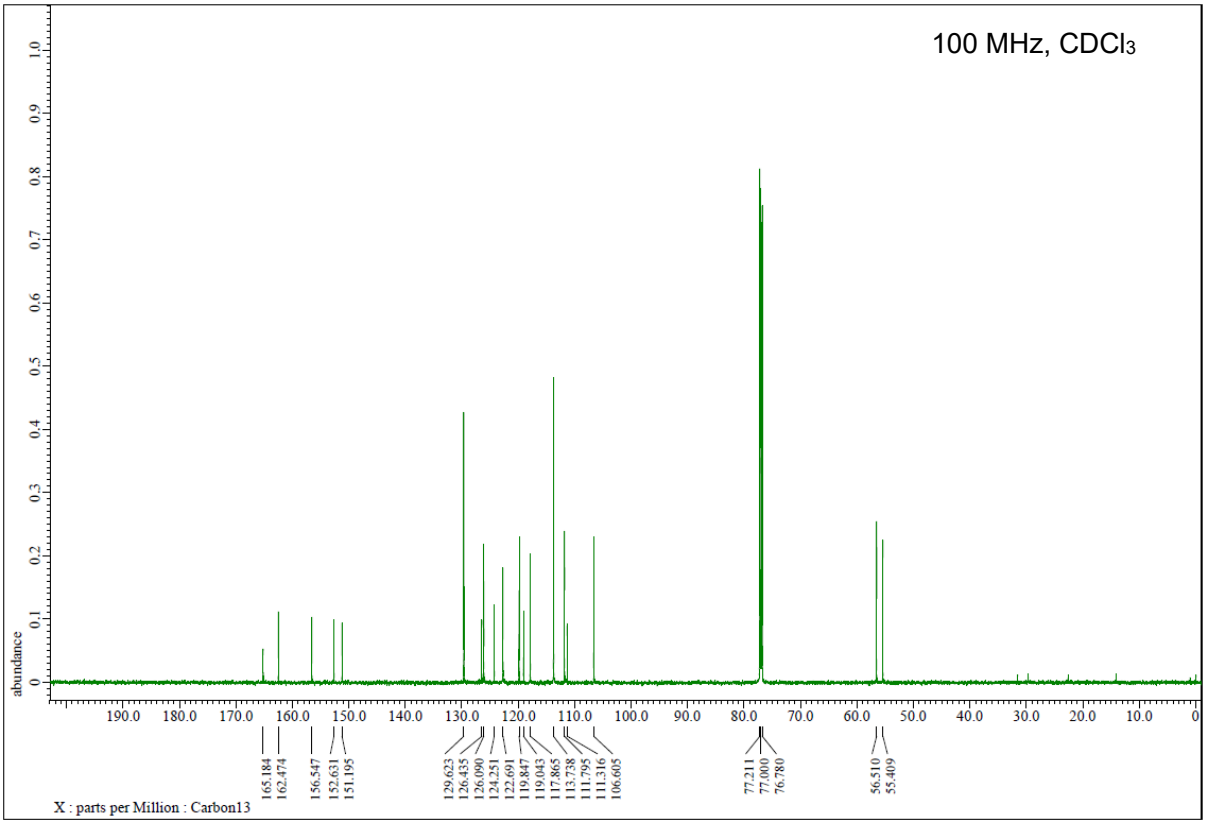

400 MHz, CDCl3
Me
O
Ph
O
N
H
OMe
N
O
4d
4.89
1.02
0.99
0.92
0.69
1.99
3.03
3.00
2.86
abundance
7.504
7.497
7.432
7.419
7.371
7.340
7.331
7.260
7.198
6.541
6.535
6.449
5.221
3.664
2.658
2.350
X : parts per Million : Proton

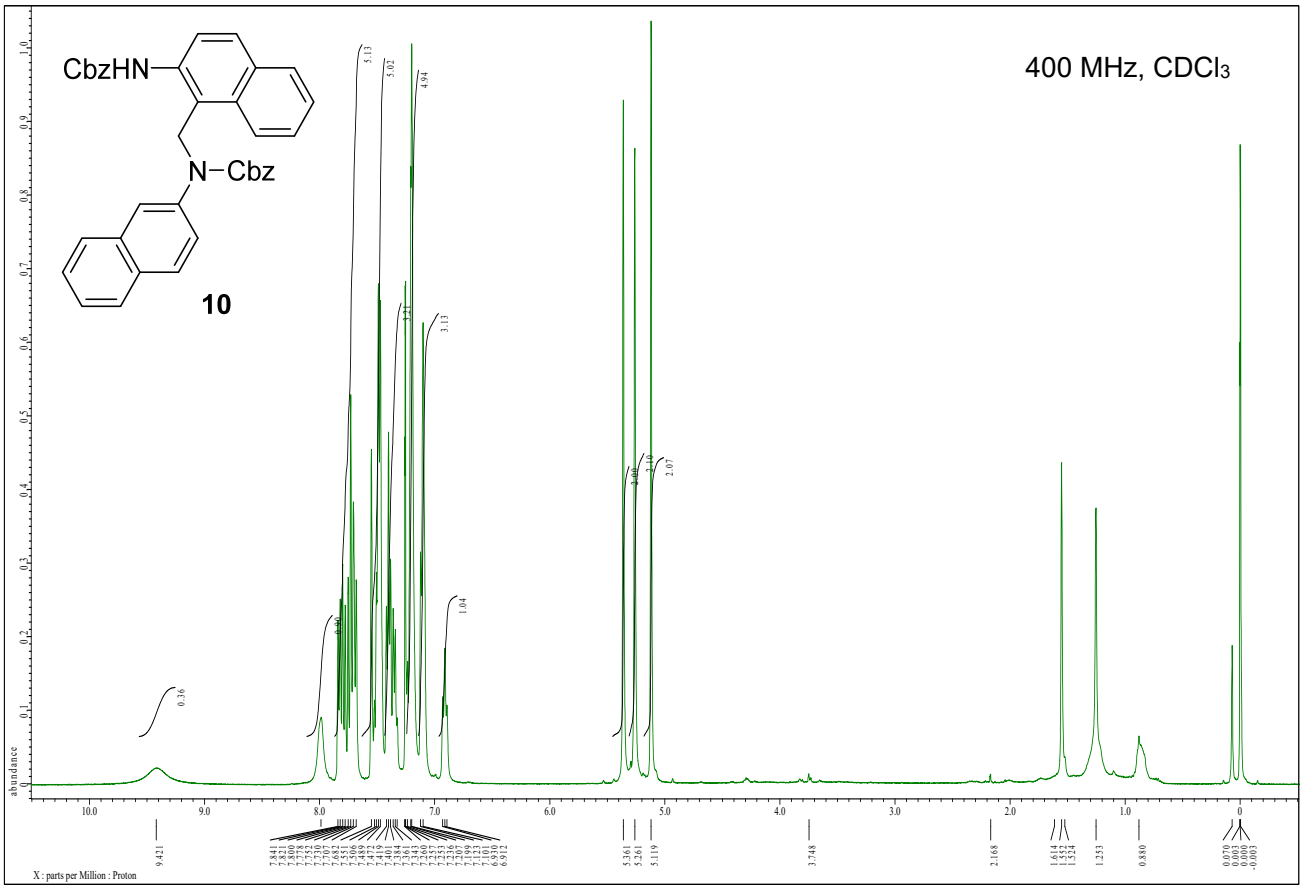

100 MHz, CDCl3
abundance
168.123
155.140
143.851
136.354
133.051
132.725
128.464
128.148
128.120
127.938
126.291
125.831
117.798
108.338
77.211
77.000
76.789
67.157
61.020
24.904
18.297
X : parts per Million : Carbon13

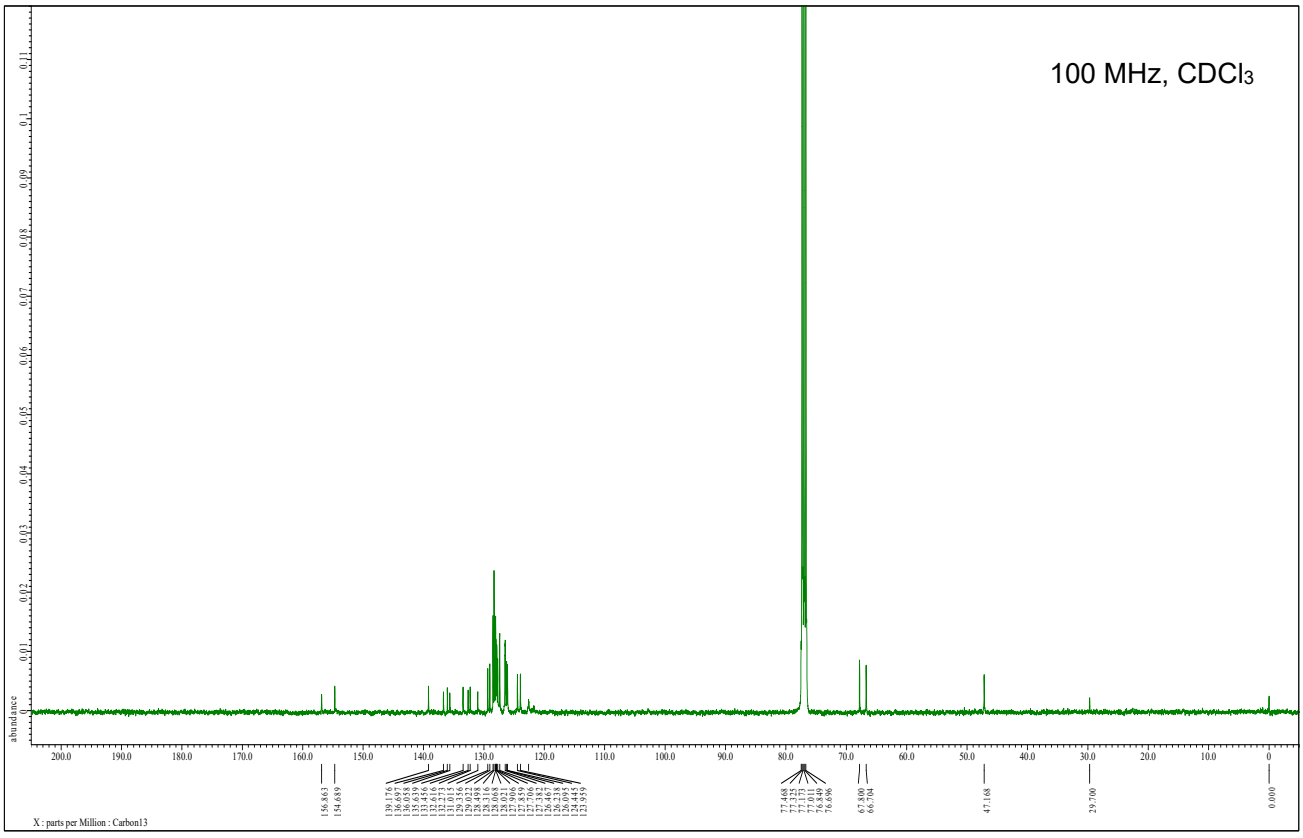

MeO
N
Ts
Ph
O
NH
O
4e
400 MHz, CDCl3
4.79
2.16
2.12
1.24
0.98
0.89
1.60
2.87
3.00
abundance
X : parts per Million : Proton


100 MHz, CDCl3
abundance
X : parts per Million : Carbon13


MeO
HN
O
O
MeO
4f
400 MHz, CDCl3
abundance
X : parts per Million : Proton


100 MHz, CDCl3
abundance
X : parts per Million : Carbon13


CbzHN
N−Cbz
10
400 MHz, CDCl3
X : parts per Million : Proton


100 MHz, CDCl3
X : parts per Million : Carbon13