Supporting Information for

Synthesis of Pyrroloindolines and Furoindolines via Cascade Dearomatization of Indole Derivatives with Carbenium Ion

Chuan Liu, Qin Yin, Li-Xin Dai and Shu-Li You*

State Key Laboratory of Organometallic Chemistry

Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences

345 Lingling Lu, Shanghai 200032, China

E-mail: slyou@sioc.ac.cn

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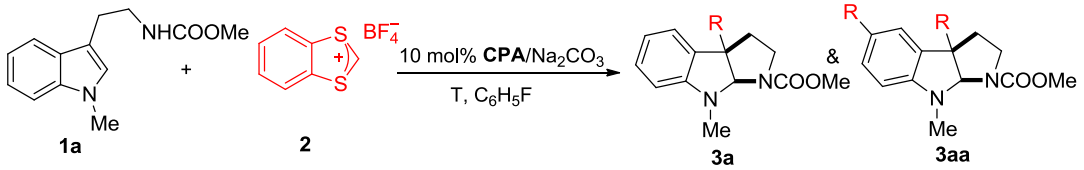
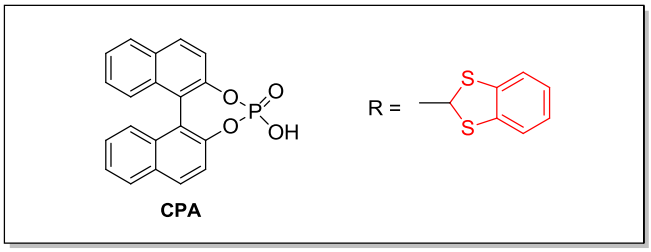
General methods. Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use.

^{1}H and ^{13}C NMR spectra were recorded on Varian instruments (300 MHz and 75 MHz or 400 MHz and 100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet or unresolved, coupling constant in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm).

Optimization of reaction conditions

(a) Temperature effect[a]

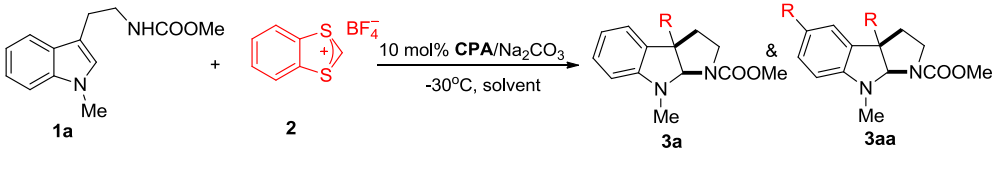


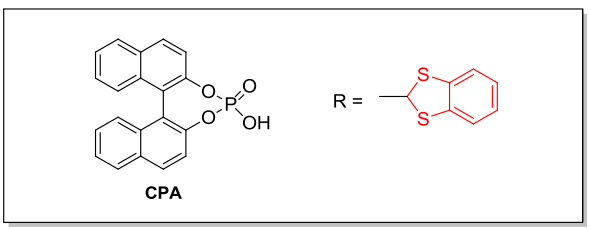


entry	T (^{o}C)	**3a**, yield (%)[b]	**3aa**, yield (%)[b]
1	rt	20	39
2	0	35	37
3	-10	74	17
4	-20	87	11
5	**-30**	**89**	**4**
6	-40	68/63	18/12

[a] Unless otherwise specified, all reactions were carried out using **1a** (0.1mmol, 1.0 equiv), **2** (0.11 mmol, 1.1 equiv) and Na_2CO_3 (0.11 mmol, 1.1 equiv) in C_6H_5F (1.5 mL) at noted temperature. [b] Determined by HPLC analysis.

(b) Solvent effect[a]

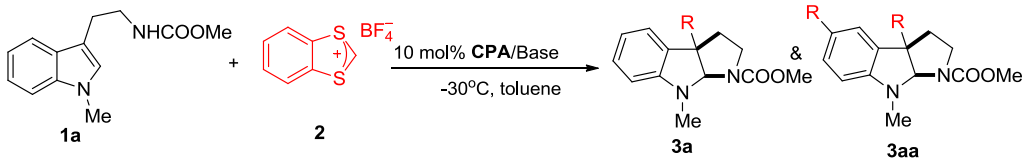


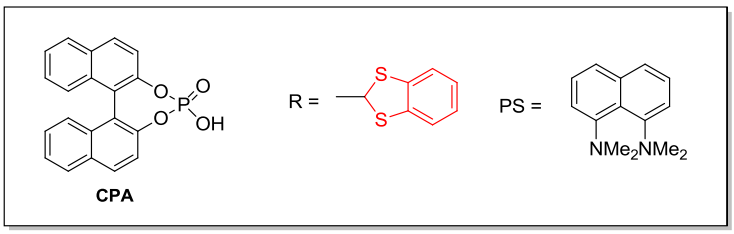


entry	solvent	**3a**, yield (%)[b]	**3aa**, yield (%)[b]
1	*n*-hexane	58	3
2	cyclohexane	69	5
3	**toluene**	**98**	**0.5**
4	C_6H_5F	89	4
5	C_6H_5Cl	86	2
6	DCM	36	26
7	EtOAc	91	6

[a] Unless otherwise specified, all reactions were carried out using **1a** (0.1mmol, 1.0 equiv), **2** (0.11 mmol, 1.1 equiv) and Na_2CO_3 (0.11 mmol, 1.1 equiv) in different solvent (1.5 mL) at -30 °C. [b] Determined by HPLC analysis.

(c) Base effect[a]

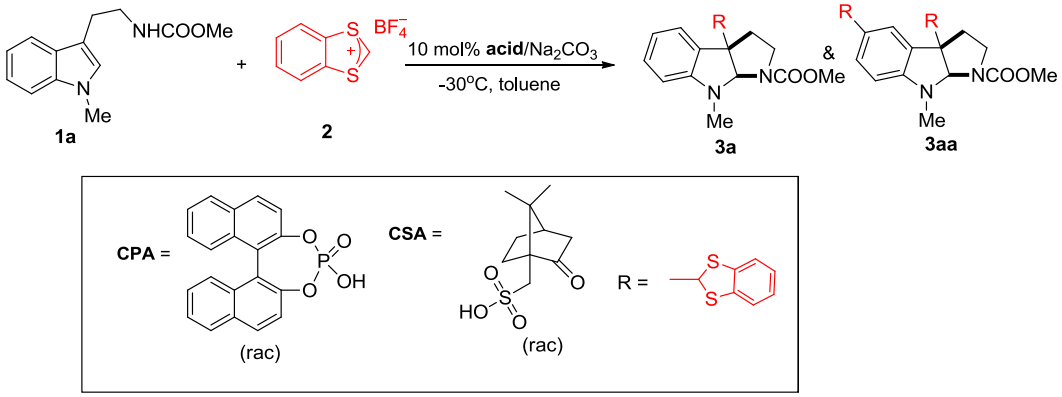




entry	Base	**3a**, yield (%)[b]	**3aa**, yield (%)[b]
1[c]	-	3	7
2	$NaHCO_3$	88	2
3	**Na_2CO_3**	**98**	**0.5**
4	K_2CO_3	84	2
5	Na_3PO_4	57	10
6	PS	39	7

[a] Unless otherwise specified, all reactions were carried out using **1a** (0.1mmol, 1.0 equiv), **2** (0.11 mmol, 1.1 equiv) and base (0.11 mmol, 1.1 equiv) in toluene (1.5 mL) at-30 °C. [b] Determined by HPLC analysis. [c] Without acid and Na_2CO_3.

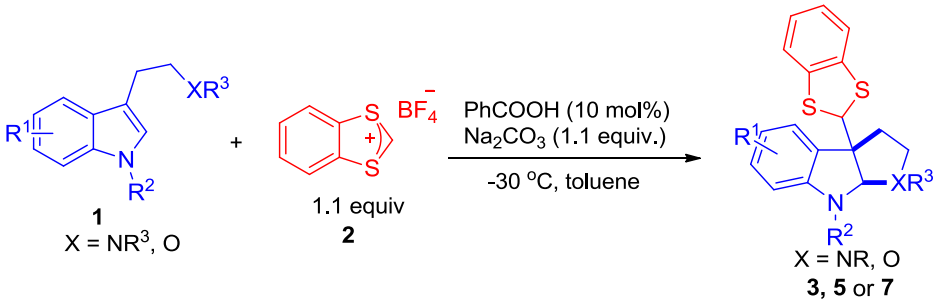
(d) Screening Brønsted acids[a]



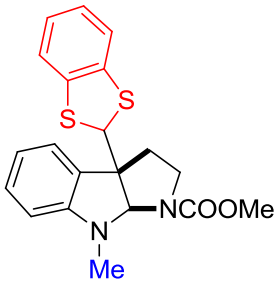
entry	Acid	**3a**, yield (%)[b]	**3aa**, yield (%)[b]
1	CPA	98(94[c])	0.5
2	$TsOH{\cdot}H_2O$	77	12
3	CSA	90	6
4	PhCOOH	93	1.5
5[c]	**PhCOOH**	**99(99[d])**	**<0.5**
6[e]	PhCOOH	3	5
7[f]	-	3	7
8[g]	-	88	7

[a] Unless otherwise specified, all reactions were carried out using **1a** (0.1mmol, 1.0 equiv), **2** (0.11 mmol, 1.1 equiv) and Na_2CO_3 (0.11 mmol, 1.1 equiv) in toluene (1.5 mL) at -30 °C. [b] Determined by HPLC analysis. [c] **1a** (0.22mmol, 1.1 equiv), **2** (0.2 mmol, 1.0 equiv), Na_2CO_3. (0.22 mmol, 1.1 equiv) in toluene (3.0 mL) at -30 °C, [d] Isolated yield. [e] without Na_2CO_3. [f] Without acid and Na_2CO_3. [g] Without acid.

General Procedure for Synthesis of Pyrroloindolines and Furoindolines



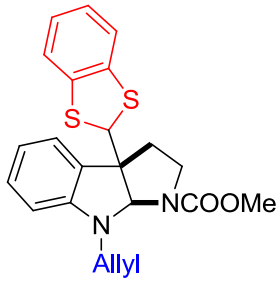
To a flame-dried Schlenk tube under argon were added indole derivative **1** (0.22 mmol, 110 mol%), benzoic acid (2.4 mg, 0.02 mmol, 10 mol%), sodium carbonate (23.3 mg, 0.22 mmol, 110 mol%) and toluene (2.0 mL). The reaction mixture was stirred at rt for 20 min and then cooled to -30 °C. Then 1,3-benzodithiolylium tetrafluoroborate (48.0 mg, 0.2 mmol, 100 mol%) and toluene (1 mL) were added. The reaction mixture was stirred at the same temperature for 6-24 h (monitored by TLC). After the reaction was complete, the reaction was diluted with EtOAc (5 mL), filtered, and washed with EtOAc. The collected organic filtrate was concentrated under reduced pressure to afford the crude product. Then the crude product was purified by silica gel column chromatography (PE/EA = 10/1-5/1) to afford compound **3**, **5** or **7**.



3a

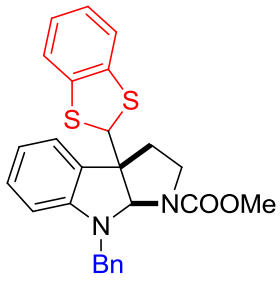
White solid, 76.1 mg, 99% yield, M.p. 128-130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.10 (m, 4H), 6.97 (s, 2H), 6.70-6.59 (m, 1H), 6.39 (d, *J* = 7.6 Hz, 1H), 5.46 and 5.41 (s, 1H), 5.25 and 5.20 (s, 1H), 3.92 and 3.76 (t, *J* = 9.6 Hz, 1H), 3.70 and 3.68 (s, 3H), 2.97 and 2.85 (s, 3 H), 2.97-2.85 (m, 1H), 2.26-2.17 (m, 1H), 2.12-2.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 154.9, 151.5, 151.3, 137.14, 137.09, 129.6, 128.7, 128.6, 125.3, 123.7, 123.5, 121.62, 121.57, 121.47, 117.4, 117.2, 106.2, 106.1,

84.0, 83.5, 63.6, 62.6, 59.3, 59.0, 52.3, 45.6, 45.5, 33.5, 33.1, 32.8, 32.3; ^{1}H NMR (400 MHz, d_6-DMSO, 80 ^{o}C) δ 7.24-7.18 (m, 3H), 7.10 (t, *J* = 8.0 Hz, 1H), 7.04-7.01 (m, 2H), 6.60 (t, *J* = 7.6 Hz, 1H), 6.44 (d, *J* = 7.6 Hz, 1H), 5.74 (s, 1H), 5.36 (s, 1H), 3.80 (t, *J* = 9.2 Hz, 1H), 3.62 (s, 3H), 2.91-2.84 (m, 1H), 2.84 (s, 3H), 2.27-2.19 (m, 1H), 2.13-2.08 (m, 1H). ^{13}C NMR (100 MHz, d_6-DMSO, 80 ^{o}C) δ 154.1, 151.2, 136.45, 136.42, 128.9, 128.8, 125.1, 125.0, 122.9, 121.2, 121.1, 116.9, 105.9, 83.3, 62.3, 58.6, 51.6, 44.6, 34.6, 32.4; IR (thin film): ν_{max} (cm^{-1}) = 3672, 2986, 2902, 1689, 1605, 1492, 1445, 1390, 1319, 1251, 1228, 1155, 1054, 938, 888, 771, 743, 684; HRMS (ESI) calcd for $C_{20}H_{21}N_2O_2S_2$([M+H]$^{+}$): 385.1039. Found: 385.1040.



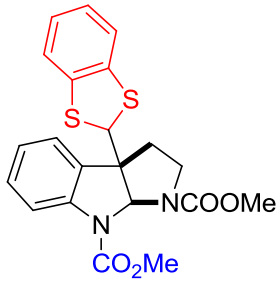
3b

Light yellow oil, 83.8 mg, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 6.0 Hz, 1H), 7.19-7.09 (m, 3H), 6.99 (d, *J* = 3.2 Hz, 2H), 6.68-6.63 (m, 1H), 6.40 (t, *J* = 8.0 Hz, 1H), 5.83-5.70 (m, 1H), 5.58 and 5.51 (s, 1H), 5.29 and 5.24 (s, 1H), 5.24-5.05 (m, 2H), 4.07-3.85 (m, 3H), 3.67 and 3.65 (s, 3H), 3.02-2.98 (m, 1H), 2.29-2.21 (m, 1H), 2.14-2.07 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 154.7, 150.4, 137.1, 134.2, 133.8, 129.5, 128.9, 128.7, 125.4, 125.3, 123.8, 123.4, 121.67, 121.63, 121.56, 117.4, 117.2, 115.9, 106.6, 106.3, 82.8, 82.1, 63.7, 62.8, 59.8, 59.4, 52.4, 48.7, 48.6, 45.2, 34.4, 33.8; IR (thin film): ν_{max} (cm^{-1}) = 3675, 2987, 2901, 1695, 1604, 1489, 1445, 1384, 1311, 1211, 1156, 1066, 908, 880, 737, 675, 646; HRMS (ESI) calcd for $C_{22}H_{23}N_2O_2S_2$([M+H]$^{+}$): 411.1195. Found: 411.1196.



3c

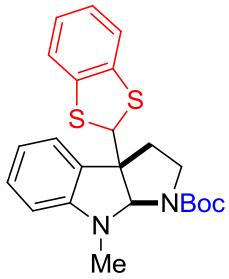
White solid, 92.0 mg, 97% yield, M.p. 75-77 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.19 (m, 6H), 7.15-7.07 (m, 3H), 6.99-6.97 (m, 2H), 6.67-6.63 (m, 1H), 6.33-6.30 (m, 1H), 5.66 and 5.57 (s, 1H), 5.24 and 5.07 (s, 1H), 4.75 and 4.57 (d, *J* = 16.4 Hz, 1H), 4.49 (d, *J* = 6.8 Hz, 1H), 3.99-3.94 and 3.81-3.77 (m, 1H), 3.63 and 3.40 (s, 3H), 3.12-3.01 (m, 1H), 2.30-2.22 (m, 1H), 2.17-2.12 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 154.6, 150.9, 150.6, 138.9, 137.2, 137.1, 129.7, 129.7, 128.8, 128.4, 128.3, 127.0, 126.6, 126.3, 125.5, 125.4, 124.0, 123.6, 121.6, 121.5, 117.7, 117.4, 106.8, 106.5, 82.9, 82.9, 64.0, 62.9, 59.7, 59.1, 52.4, 52.2, 50.4, 50.0, 45.2, 34.3, 33.4; IR (thin film): ν_{max} (cm^{-1}) = 3675, 2987, 2901, 1695, 1603, 1491, 1445, 1383, 1318, 1213, 1147, 1066, 978, 937, 881, 738, 696, 675, 666, 630; HRMS (ESI) calcd for $C_{26}H_{25}N_2O_2S_2$([M+H]$^{+}$): 461.1352. Found: 461.1351.



3d

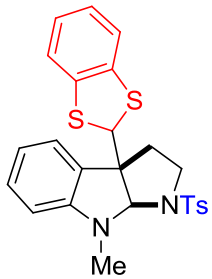
White foam, 78.8 mg, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.21 (m, 1H), 7.18-7.10 (m, 3H), 6.99-6.95 (m, 2H), 6.68-6.63 (m, 1H), 6.40 (d, *J* = 8.0 Hz, 1H), 5.47 and 5.42 (s, 1H), 5.27 and 5.22 (s, 1H), 3.93 and 3.77 (dd, *J* = 10.4, 8.4 Hz, 1H), 3.71 and 3.69 (s, 3H), 2.98 and 2.86 (s, 3H), 2.98-2.93 (m, 1H), 2.28-2.18 (m, 1H), 2.14-2.07 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 155.0, 151.6, 151.4, 137.22, 137.17, 129.7, 128.8, 128.7, 125.5, 125.4, 123.8, 123.6, 121.71, 121.66, 121.56, 117.5, 117.3, 106.26, 106.20, 84.1, 83.6, 63.6, 62.7, 59.4, 59.1, 52.4, 45.7, 45.6, 33.6, 33.2, 32.9, 32.4; IR (thin film): ν_{max} (cm^{-1}) = 3663, 2972, 2902, 1695, 1604, 1491, 1443,

1381, 1300, 1225, 1199, 1061, 1022, 999, 938, 880, 788, 738, 674, 624; HRMS (ESI) calcd for $C_{20}H_{21}N_2O_2S_2$([M+H]$^+$): 385.1039. Found: 385.1047.



3e

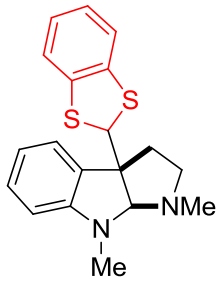
White foam, 86.5 mg, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.10 (m, 4H), 7.00-6.95 (m, 2H), 6.68-6.60 (m, 1H), 6.38 (d, *J* = 8.0 Hz, 1H), 5.45 and 5.31 (s, 1H), 5.23 (s, 1H), 3.95-3.91 and 3.75-3.70 (m, 1H), 2.96 and 2.86 (s, 3H), 2.96-2.86 (m, 1H), 2.26-2.21 (m, 1H), 2.10-2.01 (m, 1H), 1.75 and 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 153.6, 151.6, 137.3, 137.1, 129.6, 129.0, 128.8, 125.43, 125.35, 123.8, 123.4, 121.7, 121.6, 121.5, 117.4, 117.3, 106.0, 83.9, 83.2, 80.1, 79.6, 63.9, 62.7, 59.5, 59.2, 45.9, 44.7, 34.1, 33.4, 32.8, 32.5, 29.6, 28.3; IR (thin film): ν_{max} (cm^{-1}) = 3675, 2972, 2901, 1692, 1605, 1492, 1446, 1429, 1391, 1365, 1321, 1301, 1232, 1153, 1117, 1057, 990, 938, 891, 737, 675; HRMS (ESI) calcd for $C_{23}H_{27}N_2O_2S_2$([M+H]$^+$): 427.1508. Found: 427.1508.



3f

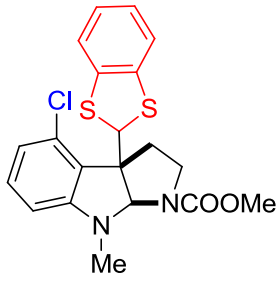
White solid, 92.3 mg, 96% yield, M.p. 142-144 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 6.8 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.12-7.10 (m, 1H), 7.00-6.93 (m, 3H), 6.65 (t, *J* = 7.2 Hz, 1H), 6.43 (d, *J* = 8.0 Hz, 1H), 5.31 (s, 1H), 4.95 (s, 1H), 3.52 (dd, *J* = 12.0, 7.2 Hz, 1H), 3.00 (s, 3H), 2.97-2.90 (m, 1H), 2.48 (s, 3H), 1.93 (dd, *J* = 12.0, 4.8 Hz, 1H), 1.73-1.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 143.3, 137.1, 137.0, 136.4, 129.9, 129.6, 127.8, 127.6, 125.5, 125.3, 123.9, 121.6, 121.3, 117.6, 106.5, 86.8, 64.4, 57.9, 48.2, 32.6,

31.5, 21.6; IR (thin film): ν_{max} (cm^{-1}) = 3674, 2971, 2901, 1681, 1604, 1489, 1445, 1432, 1382, 1343, 1302, 1232, 1154, 1118, 1089, 1008, 924, 868, 810, 782, 739, 708, 662; HRMS (ESI) calcd for $C_{25}H_{25}N_2O_2S_3$([M+H]$^+$): 481.1073. Found: 481.1072.



3g

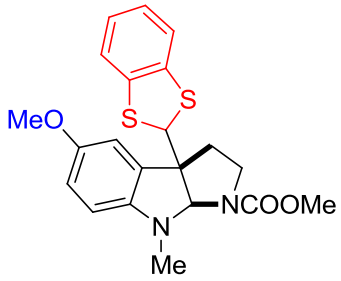
White solid, 26.4 mg, 39% yield, M.p. 82-84 ^oC.^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16-7.01 (m, 4H), 6.96-6.93 (m, 2H), 6.64 (t, *J* = 7.5 Hz, 1H), 6.44 (d, *J* = 7.8 Hz, 1H), 5.48 (s, 1H), 4.46 (s, 1H), 2.90 (s, 3H), 2.81-2.75 (m, 1H), 2.58-2.53 (m, 1H), 2.47 (s, 3H), 2.32-2.23 (m, 1H), 2.04-1.98 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 137.7, 137.4, 131.6, 129.1, 125.3, 125.2, 123.3, 121.8, 121.5, 117.6, 107.1, 91.5, 63.2, 61.1, 52.9, 37.5, 36.5, 36.1; IR (thin film): ν_{max} (cm^{-1}) = 3675, 2971, 2901, 1602, 1490, 1446, 1431, 1394, 1381, 1339, 1235, 1153, 1118, 1066, 1020, 926, 907, 868, 811, 740, 708, 663; HRMS (MALDI) calcd for $C_{19}H_{21}N_2O_2S_2$([M+H]$^+$): 341.1141. Found: 341.1140.



3h

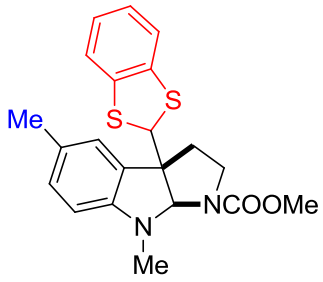
Vigorous oil, 72.3 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.16 (m, 1H), 7.10 (t, *J* = 8.0 Hz, 1H), 7.01-8.95 (m, 3H), 6.61 (d, *J* = 7.6 Hz, 1H), 6.32-6.26 (m, 1H), 6.11 and 6.08 (s, 1H), 5.60 and 5.58 (m, 1H), 4.07-4.02 and 3.88-3.82 (m, 1H), 3.69 and 3.64 (m, 3H), 3.05-3.00 (m, 1H), 2.88 and 2.76 (s, 3H), 2.62-2.53 (m, 1H), 2.22-2.18 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 154.67, 153.9, 153.5, 137.1, 136.8, 131.0, 129.6, 125.6, 125.55, 125.3, 124.6, 124.5, 122.0, 121.8, 121.7, 118.14, 118.12, 104.9, 104.5, 82.4, 82.0, 64.6, 63.6, 57.1, 57.0, 52.4, 45.0, 44.8, 33.7, 33.6,

33.4, 32.5; IR (thin film): ν_{max} (cm^{-1}) = 3672, 2986, 2902, 1698, 1598, 1445, 1383, 1345, 1262, 1229, 1190, 1158, 1076, 1006, 936, 881, 854, 811, 741, 665, 628; HRMS (ESI) calcd for $C_{20}H_{20}ClN_2O_2S_2$([M+H]$^+$): 419.0649. Found: 419.0648.



3i

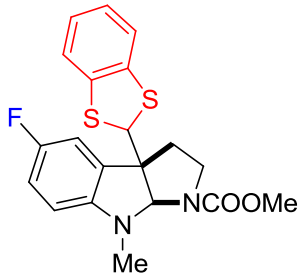
White solid, 80.9 mg, 98% yield, M.p. 152-154 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.15-7.12 (m, 2H), 7.00-6.99 (m, 2H), 6.91 and 6.88 (s, 1H), 6.73 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.34 (d, *J* = 8.4 Hz, 1H), 5.41 and 5.35 (s, 1H), 5.23 and 5.20 (s, 1H), 3.94-3.76 (m, 1H), 3.72 and 3.69 (s, 6H), 3.00-2.96 (m, 1H), 2.95 and 2.83 (s, 3H), 2.26-2.18 (m, 1H), 2.13-2.08 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 155.1, 152.6, 152.5, 146.2, 146.0, 137.2, 137.1, 133.3, 130.1, 130.0, 128.3, 125.4, 121.7, 121.64, 121.55, 114.2, 111.3, 111.0, 107.1, 85.1, 84.4, 63.9, 63.1, 59.2, 59.0, 56.0, 52.4, 45.7, 45.6, 33.9, 33.6, 33.4, 33.2; IR (thin film): ν_{max} (cm^{-1}) = 2950, 1695, 1595, 1496, 1444, 1381, 1277, 1217, 1197, 1117, 1057, 1029, 999, 951, 861, 801, 741, 675; HRMS (ESI) calcd for $C_{21}H_{23}N_2O_3S_2$([M+H]$^+$): 415.1145. Found: 415.1145.



3j

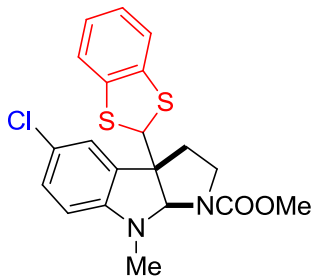
White foam, 78.1 mg, 98% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.15-7.10 (m, 2H), 7.06-6.95 (m, 4H), 6.31 (d, *J* = 7.6 Hz, 1H), 5.44 and 5.38 (s, 1H), 5.26 and 5.21 (s, 1H), 3.94-3.90 and 3.78-3.74 (m, 1H), 3.71 and 3.68 (s, 3H), 3.00-2.84 (m, 4H), 2.23 (s, 3H), 2.23-2.16 (m, 1H), 2.13-2.06 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 155.0, 149.6, 149.4, 137.3, 137.2, 130.0, 128.9, 128.8, 126.9, 126.6, 125.4, 125.3, 124.5, 124.3, 121.7, 121.6, 121.5, 106.4, 84.6, 84.0, 63.7, 62.8, 59.5, 59.2, 52.4, 45.6,

45.5, 33.7, 33.3, 32.9, 20.7; IR (thin film): ν_{max} (cm^{-1}) = 3672, 2985, 2903, 1695, 1601, 1493, 1446, 1407, 1381, 1254, 1230, 1204, 1152, 1054, 938, 895, 866, 802, 744, 672, 613; HRMS (ESI) calcd for $C_{21}H_{23}N_2O_2S_2$([M+H]$^+$): 399.1195. Found: 399.1195.



3k

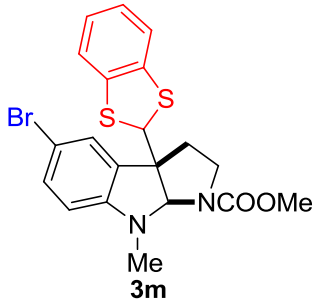
Light yellow oid, 78.4 mg, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.13 (m, 2H), 7.04-6.99 (m, 3H), 6.85 (td, *J* = 8.8, 2.4 Hz, 1H), 6.29 (dd, *J* = 8.8, 4.0 Hz, 1H), 5.43 and 5.37 (s, 1H), 5.18 and 5.15 (s, 1H), , 3.95-3.91 and 3.80-3.75 (m, 1H), 3.72 and 3.70 (s, 3H), 2.99-2.92 (m, 1H), 2.95 and 2.84 (s, 3H), 2.26-2.16 (m, 1H), 2.12-2.04 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.24, 157.21, 155.7, 155.0, 154.9, 148.0, 147.8, 137.1, 136.9, 129.9-129.7 (m), 125.6, 121.8, 121.7, 121.6, 115.8, 115.5, 111.8, 111.6, 111.5, 111.3, 106.6, 106.5, 84.9, 84.4, 63.8, 62.9, 58.9, 58.6, 52.5, 45.7, 45.6, 33.5, 33.3, 33.1, 33.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.0, -127.3; IR (thin film): ν_{max} (cm^{-1}) = 3672, 2972, 2902, 1693, 1609, 1494, 1444, 1382, 1227, 1192, 1053, 957, 906, 870, 804, 768, 728, 675, 647, 625; HRMS (ESI) calcd for $C_{20}H_{20}FN_2O_2S_2$([M+H]$^+$): 403.0945. Found: 403.0944.



3l

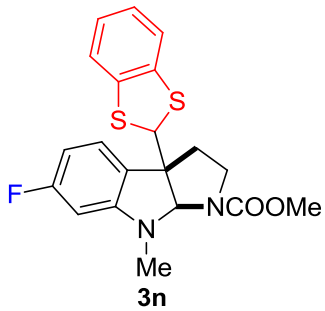
White foam, 82.5 mg, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 and 7.20 (s, 1H), 7.15-7.13 (m, 2H), 7.08 (d, *J* = 8.4 Hz, 1H), 7.01-6.96 (m, 2H), 6.28 (d, *J* = 8.4 Hz, 1H), 5.44 and 5.38 (s, 1H), 5.16 and 5.12 (s, 1H), 3.96-3.91 and 3.80-3.75 (m, 1H), 3.72 and 3.69 (s, 3H), 2.98-2.91 (m, 1H), 2.94 and 2.84 (s, 3H), 2.22-2.17 (m, 1H), 2.09-2.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 154.8, 150.2, 150.1, 137.0,

136.8, 130.3, 130.1, 129.4, 125.5, 124.2, 124.0, 121.8, 121.7, 121.6, 106.9, 84.4, 83.9, 63.8, 62.9, 58.9, 58.7, 52.5, 45.7, 45.6, 33.5, 33.2, 32.9, 32.4; IR (thin film): ν_{max} (cm^{-1}) = 3672, 2972, 2902, 1694, 1602, 1491, 1444, 1382, 1312, 1266, 1226, 1199, 1079, 1000, 945, 880, 804, 740, 673, 618; HRMS (ESI) calcd for $C_{20}H_{20}ClN_2O_2S_2$([M+H]$^+$): 419.0649. Found: 419.0646.



3m

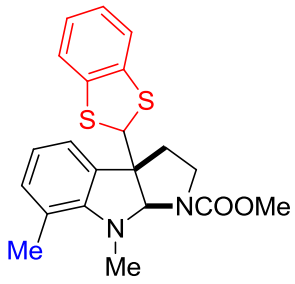
White solid, 84.6 mg, 91% yield, M.p. 115-117 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 and 7.32 (s, 1H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.15-7.09 (m, 2H), 7.00-6.93 (m, 2H), 6.24 (d, *J* = 8.4 Hz, 1H), 5.42 and 5.36 (s, 1H), 5.15 and 5.11 (s, 1H), 3.96-3.91 and 3.80-3.75 (m, 1H), 3.72 and 3.69 (s, 3H), 2.98-2.77 (m, 4H), 2.23-2.16 (m, 1H), 2.10-2.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 154.8, 150.7, 150.5, 137.0, 136.8, 132.3, 130.7, 130.5, 128.7, 127.0, 126.7, 125.5, 121.8, 121.7, 121.6, 118.9, 118.8, 109.6, 108.7, 108.5, 107.4, 84.4, 83.8, 63.8, 62.9, 58.9, 58.7, 52.5, 45.7, 45.5, 33.5, 33.2, 32.7, 32.3; IR (thin film): ν_{max} (cm^{-1}) = 3664, 2972, 2902, 1690, 1601, 1490, 1446, 1381, 1344, 1250, 1156, 1069, 1052, 918, 869, 806, 770, 744, 683, 656; HRMS (ESI) calcd for $C_{20}H_{20}BrN_2O_2S_2$([M+H]$^+$): 463.0144. Found: 463.0142.



3n

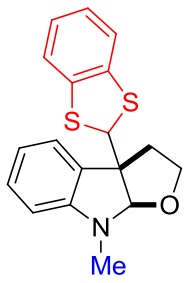
Light yellow foam, 75.6 mg, 93% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.18-7.09 (m, 3H), 7.04-6.94 (m, 2H), 6.34-6.26 (m, 1H), 6.07 (d, *J* = 10.0 Hz, 1H), 5.47 and 5.42 (s, 1H), 5.20 and 5.16 (s, 1H), 3.96-3.91 and 3.80-3.76 (m, 1H), 3.72 and 3.70 (s, 3H), 3.00-2.84 (m, 4H), 2.24-2.17 (m, 1H), 2.10-2.04 (m, 1H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 166.0, 163.6, 155.6, 154.8, 153.2, 153.1, 153.0, 152.9, 137.1, 137.0, 125.52, 125.47, 125.3, 124.6, 124.4, 124.3, 124.0, 123.8, 122.3, 121.7, 121.6, 121.5, 103.4, 103.2, 102.9, 94.2, 93.8, 84.5, 83.9, 63.2, 62.3, 59.3, 58.9, 52.5, 45.6, 45.5, 33.6, 33.2, 32.5, 32.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.1 and -112.2 (m); IR (thin film): ν_{max} (cm^{-1}) = 3675, 2987, 2901, 1695, 1614, 1600, 1496, 1444, 1382, 1326, 1230, 1201, 1172, 1078, 1056, 1001, 948, 881, 821, 739, 675, 618; HRMS (ESI) calcd for $C_{20}H_{20}FN_2O_2S_2$([M+H]$^+$): 403.0945. Found: 403.0943.



3o

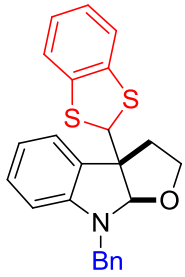
White foam, 78.0 mg, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.13 (m, 1H), 7.08-7.05 (m, 1H), 7.01-6.95 (m, 4H), 6.75-6.70 (m, 1H), 5.31 and 5.27 (s, 1H), 5.19 and 5.14 (s, 1H), 3.83-3.75 and 3.71-3.66 (m, 1H), 3.69 and 3.66 (s, 1H), 3.13 and 3.01 (s, 3H), 2.97-2.91 (m, 1H), 2.39-2.19 (m, 4H), 2.09-2.04 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 154.9, 151.1, 151.0, 137.1, 137.0, 136.9, 136.8, 132.4, 130.8, 130.7, 129.5, 126.8, 125.44, 125.37, 121.8, 121.7, 121.6, 121.1, 121.0, 120.9, 120.1, 119.8, 86.5, 86.0, 63.5, 62.5, 60.0, 59.8, 52.4, 52.2, 44.7, 44.6, 39.1, 38.9, 34.2, 19.0; IR (thin film): ν_{max} (cm^{-1}) = 3663, 2972, 2902, 1696, 1594, 1444, 1409, 1382, 1262, 1192, 1118, 1070, 994, 957, 896, 872, 789, 740, 674; HRMS (ESI) calcd for $C_{21}H_{23}N_2O_2S_2$([M+H]$^+$): 399.1195. Found: 399.1194.



5a

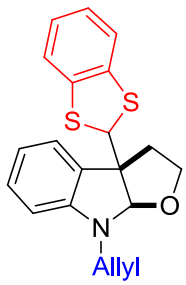
Vigorous oil, 62.7 mg, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 7.6 Hz, 1H), 7.09-7.01 (m, 3H), 6.90-6.88 (m, 2H), 6.57 (t, *J* = 7.6 Hz, 1H), 6.30 (d, *J* = 7.6

Hz, 1H), 5.28 (s, 1H), 5.22 (s, 1H), 3.88 (t, *J* = 8.0 Hz, 1H), 3.37-3.31 (m, 1H), 2.79 (s, 3H), 2.32-2.25 (m, 1H), 2.03 (dd, *J* = 11.6, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 137.32, 137.29, 129.4, 129.3, 125.4, 125.3, 123.8, 121.7, 121.5, 117.2, 105.3, 100.7, 67.2, 63.1, 58.7, 36.7, 30.9; IR (thin film): ν_{max} (cm^{-1}) = 3674, 2972, 2901, 1696, 1605, 1492, 1445, 1384, 1302, 1251, 1230, 1155, 1118, 1055, 1012, 943, 906, 872, 790, 730, 675, 646; HRMS (ESI) calcd for $C_{18}H_{18}NOS_2$([M+H]$^+$): 328.0824. Found: 328.0819.



5b

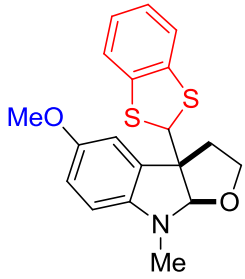
Vigorous oil, 72.2 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.24 (m, 4H), 7.22-7.20 (m, 2H), 7.11-7.04 (m, 3H), 6.95-6.93 (m, 2H), 6.65 (t, *J* = 8.0 Hz, 1H), 6.29 (d, *J* = 7.6 Hz, 1H), 5.40 (s, 1H), 5.39 (s, 1H), 4.44 (s, 2H), 3.99 (t, *J* = 7.6 Hz, 1H), 3.54-3.48 (m, 1H), 2.43-2.35 (m, 1H), 2.13 (dd, *J* = 12.0, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 137.9, 137.2, 137.1, 129.31, 129.26, 128.4, 127.1, 126.9, 125.4, 125.3, 123.7, 121.64, 121.57, 117.5, 105.6, 99.0, 66.9, 63.4, 58.7, 48.4, 37.5; IR (thin film): ν_{max} (cm^{-1}) = 3675, 2972, 2901, 1603, 1490, 1463, 1445, 1394, 1356, 1316, 1258, 1226, 1158, 1118, 1055, 1026, 1012, 941, 907, 872, 790, 733, 696, 675; HRMS (ESI) calcd for $C_{24}H_{22}NOS_2$([M+H]$^+$): 404.1137. Found: 404.1137.



5c

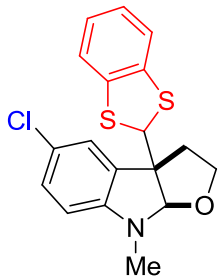
White solid, 66.8 mg, 94% yield, M.p. 76-78 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.15 (m, 1H), 7.14-7.10 (m, 2H), 7.08-7.06 (m, 1H), 6.97-6.95 (m, 2H), 6.65 (t, *J* = 7.6 Hz, 1H), 6.38 (d, *J* = 8.0 Hz, 1H), 5.80-5.73 (m, 1H), 5.38 (s, 1H), 5.36 (s, 1H),

5.20 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.08 (dd, *J* = 10.4, 1.6 Hz, 1H), 3.97 (t, *J* = 7.6 Hz, 1H), 3.85 (d, *J* = 5.6 Hz, 2H), 3.49-3.43 (m, 1H), 2.41-2.34 (m, 1H), 2.11 (dd, *J* = 12.0, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 137.3, 137.2, 133.5, 129.3, 129.2, 125.4, 125.3, 123.7, 121.7, 121.6, 117.3, 116.6, 105.6, 98.9, 66.8, 63.2, 58.9, 47.1, 37.4; IR (thin film): ν_{max} (cm^{-1}) = 3663, 2972, 2902, 1604, 1490, 1445, 1405, 1312, 1256, 1159, 1054, 939, 907, 793, 737, 697, 674; HRMS (ESI) calcd for $C_{20}H_{20}NOS_2$([M+H]$^+$): 354.0981. Found: 354.0981.



5d

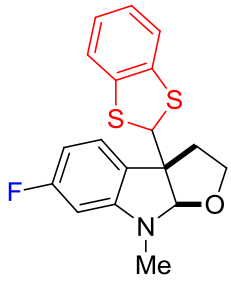
White foam, 71.1 mg, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14-7.11 (m, 2H), 6.99-6.96 (m, 2H), 6.92 (d, *J* = 1.6 Hz, 1H), 6.72 (d, *J* = 8.8 Hz, 1H), 6.31 (d, *J* = 8.4 Hz, 1H), 5.30 (s, 1H), 5.24 (s, 1H), 3.95 (t, *J* = 8.0 Hz, 1H), 3.70 (s, 3H), 3.46-3.40 (m, 1H), 2.84 (s, 3H), 2.38-2.30 (m, 1H), 2.12 (dd, *J* = 12.0, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 146.0, 137.3, 130.5, 125.4, 125.3, 125.2, 121.7, 121.5, 114.0, 111.4, 105.9, 101.6, 67.2, 63.4, 58.5, 56.0, 36.4, 31.7; IR (thin film): ν_{max} (cm^{-1}) = 3663, 3518, 2986, 2903, 1732, 1617, 1487, 1444, 1406, 1225, 1189, 1173, 1150, 1114, 1043, 917, 883, 836, 795, 743, 673, 634; HRMS (ESI) calcd for $C_{19}H_{20}NO_2S_2$([M+H]$^+$): 358.0930. Found: 358.0929.



5e

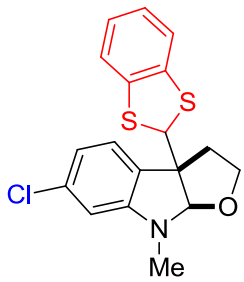
Vigorous oil, 72.6 mg, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.21 (m, 1H), 7.14-7.12 (m, 2H), 7.07 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.01-6.97 (m, 2H), 6.27 (d, *J* = 8.4 Hz, 1H), 5.25 (s, 1H), 5.24 (s, 1H), 3.96 (t, *J* = 8.0 Hz, 1H), 3.44-3.38 (m, 1H), 2.85 (s,

3H), 2.37-2.29 (m, 1H), 2.12-2.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 137.1, 137.0, 130.8, 129.1, 125.5, 125.4, 124.2, 121.73, 121.68, 121.6, 105.9, 101.0, 67.2, 63.3, 58.3, 36.6, 30.9; IR (thin film): ν_{max} (cm^{-1}) = 3663, 2972, 2903, 1603, 1565, 1477, 1444, 1421, 1380, 1246, 1048, 905, 866, 839, 790, 738, 675, 649, 622; HRMS (ESI) calcd for $C_{18}H_{17}ClNOS_2$([M+H]$^+$): 362.0435. Found: 362.0431



5f

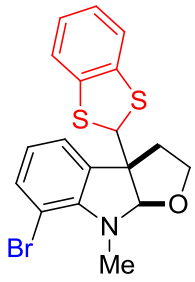
Vigorous oil, 67.0 mg, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.10 (m, 3H), 7.00-6.95 (m, 2H), 6.30-6.25 (m, 1H), 6.07 (dd, *J* = 10.0, 2.0 Hz, 1H), 5.30 (s, 1H), 5.29 (s, 1H), 3.97 (t, *J* = 8.0 Hz, 1H), 3.46-3.40 (m, 1H), 2.85 (s, 3H), 2.37-2.29 (m, 1H), 2.08 (dd, *J* = 12.0, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7 (d, *J* = 242.2 Hz), 153.1 (d, *J* = 12.1 Hz), 137.2 (d, *J* = 4.0 Hz), 125.5, 125.4, 124.6 (d, *J* = 2.3 Hz), 124.6, 124.4, 127.7, 121.6, 103.0 (d, *J* = 22.8 Hz), 101.2, 93.2 (d, *J* = 27.0 Hz), 67.3, 62.7, 58.8, 36.9, 30.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.51 (m); IR (thin film): ν_{max} (cm^{-1}) = 3673, 2972, 2903, 1614, 1601, 1496, 1444, 1379, 1328, 1239, 1176, 1054, 1005, 950, 902, 820, 739, 674; HRMS (ESI) calcd for $C_{18}H_{17}FNOS_2$([M+H]$^+$): 346.0730. Found: 346.0718



5g

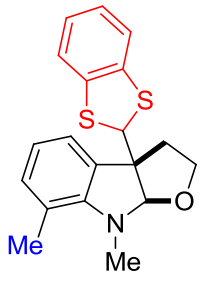
Light yellow oil, 72.4 mg, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14-7.10 (m, 3H), 7.01-6.97 (m, 2H), 6.58 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.34 (d, *J* = 2.0 Hz, 1H), 5.29 (s, 1H), 5.28 (s, 1H), 3.97 (t, *J* = 8.0 Hz, 1H), 3.45-3.38 (m, 1H), 2.85 (s, 3H), 2.37-2.30 (m, 1H), 2.08 (dd, *J* = 12.0, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

152.5, 137.13, 137.10, 135.2, 127.8, 125.5, 125.4 124.6, 121.7, 121.6, 116.9, 105.5, 100.9, 67.2, 62.9, 58.5, 36.8, 30.6; IR (thin film): ν_{max} (cm^{-1}) = 3663, 2972, 2903, 1680, 1603, 1495, 1476, 1444, 1412, 1323, 1232, 1117, 1052, 944, 906, 839, 801, 738, 675, 637; HRMS (ESI) calcd for $C_{18}H_{17}ClNOS_2$([M+H]$^+$): 362.0435. Found: 362.0432.



5h

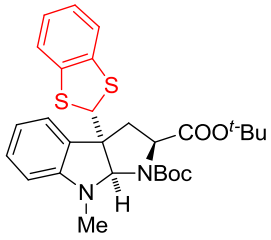
Vigorous oil, 83.9 mg, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.0 Hz, 1H), 7.15-7.09 (m, 3H), 7.00-6.97 (m, 2H), 6.54 (t, *J* = 7.6 Hz, 1H), 5.32 (s, 1H), 5.17 (s, 1H), 3.97 (t, *J* = 8.0 Hz, 1H), 3.50-3.43 (m, 1H), 3.23 (s, 3H), 2.40-2.32 (m, 1H), 2.08 (dd, *J* = 12.0, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 137.1, 136.8, 134.6, 133.2, 125.5, 125.4, 122.8, 121.8, 121.6, 119.6, 102.7 101.3, 66.7, 62.5, 58.7, 37.3, 35.6; IR (thin film): ν_{max} (cm^{-1}) = 3663, 2973, 2902, 1603, 1565, 1483, 1444, 1407, 1302, 1254, 1224, 1117, 1044, 947, 906, 809, 776, 730, 674, 647, 610; HRMS (ESI) calcd for $C_{18}H_{17}BrNOS_2$([M+H]$^+$): 405.9929. Found: 405.9927.



5i

White solid, 67.8 mg, 99% yield, M.p. 86-88^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.14 (m, 1H), 7.08-7.06 (m, 1H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.98-6.96 (m, 2H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.68 (t, *J* = 7.6 Hz, 1H), 5.40 (s, 1H), 5.17 (s, 1H), 3.96 (t, *J* = 8.0 Hz, 1H), 3.48-3.45 (m, 1H), 3.07 (s, 3H), 2.38 (s, 3H), 2.40-2.33 (m, 1H), 2.08 (dd, *J* = 12.0, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 137.4, 137.1, 132.5, 131.0, 125.45, 125.38, 121.9, 121.6, 121.4, 119.31, 119.29, 103.3, 66.6, 62.7, 59.2,

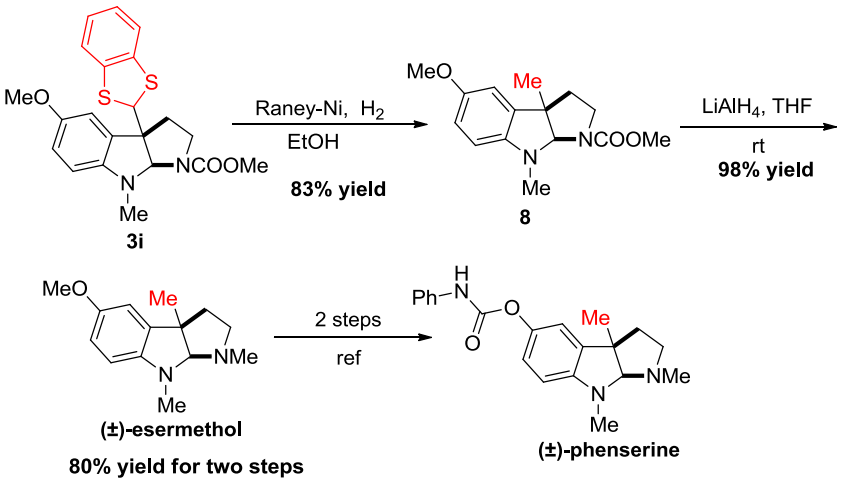
37.3, 36.7, 19.2; IR (thin film): ν_{max} (cm^{-1}) = 3663, 2972, 2903, 1734, 1590, 1470, 1445, 1410, 1372, 1320, 1227, 1068, 953, 909, 895, 866, 791, 738, 675, 647; HRMS (ESI) calcd for $C_{19}H_{20}NOS_2$([M+H]$^+$): 342.0981. Found: 342.0983.



7

White foam, 102.7 mg, 97% yield. ^{1}H NMR (400 MHz, 100 ^{o}C, d_6-DMSO) δ 7.19-7.00 (m, 6H), 6.57 (t, *J* = 7.2 Hz, 1H), 6.47 (d, *J* = 8.0 Hz, 1H), 5.49 (s, 1H), 5.17 (s, 1H), 3.80 (s, 1H), 2.93 (s, 3H), 2.54-2.48 (m, 1H), 2.34 (dd, *J* = 13.2, 8.0 Hz, 1H), 1.43 (s, 9H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 170.7, 154.3, 153.6, 150.9, 137.2, 129.6, 129.4, 129.1, 125.4, 125.3, 123.5, 121.8, 121.6, 121.4, 117.9, 117.5, 107.4, 107.3, 87.2, 85.8, 81.4, 81.0, 80.9, 805, 62.7, 61.8, 60.6, 60.0, 59.0, 58.20, 37.4, 37.3, 35.6, 35.4, 31.5, 28.3, 28.1, 27.9, 27.8, 27.4, 22.6, 14.1; IR (thin film): ν_{max} (cm^{-1}) = 2975, 2930, 1736, 1701, 1605, 1491, 1446, 1391,1366, 1252, 1150, 981, 845, 739, 674; HRMS (ESI) calcd for $C_{28}H_{35}N_2O_4S_2$([M+H]$^+$): 527.2033. Found: 527.2017.

Synthesis of esermethol

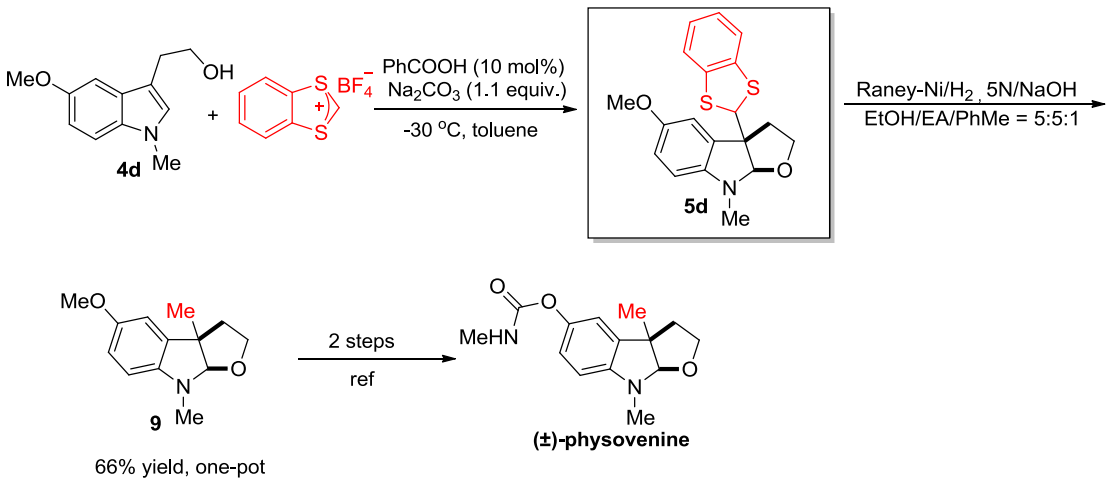


To a solution of **3i** (48.0 mg, 0.116 mmol) in ethanol (10 mL), Raney-Ni (0.5 g, slurry in water) was added and the reaction was kept under H_2 atmosphere (1 atm) for

6 h. Then the reaction mixture was filtered through a Celite pad and washed with EtOAc (3 x 5 mL) carefully. The collected organic layers were washed with brine (5 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Then the crude product was purified by silica gel column chromatography (PE/EA = 5/1) to afford compound **8**.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.69-6.66 (m, 2H), 6.34 (d, *J* = 7.2 Hz, 1H), 5.14 and 5.03 (s, 1H), 3.86-3.68 (m, 7H), 3.24-3.13 (s, 1H), 2.95 and 2.85 (s, 3H), 2.11-2.07 (m, 1H), 1.95-1.88 (m, 1H), 1.41 (s, 3H).

To a stirred solution of **8** (33.1 mg, 0.12 mmol) in THF (8 mL) at 0 ℃ was added $LiAlH_4$ portion wise (22.8 mg, 0.6 mmol). The reaction mixture was stirred for 2 hour at rt and then quenched with H_2O. The solvent was removed under reduced pressure and the resulting residue was diluted with water and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried with Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (DCM/MeOH = 10/1) to afford esermethol as a vigorous oil.[1] 27.2 mg, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.59-6.54 (m, 2H), 6.28 (d, *J* = 8.0 Hz, 1H), 3.98 (s, 1H), 3.67 (s, 3H), 2.81 (s, 3H), 2.67-2.62 (m, 1H), 2.59-2.53 (m, 1H), 2.46 (s, 3H), 1.87 (dd, *J* = 7.3, 5.4 Hz, 2H), 1.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 146.5, 138.2, 112.1, 109.7, 107.4, 98.2, 56.0, 53.1, 52.7, 40.8, 38.1, 38.0, 27.4.

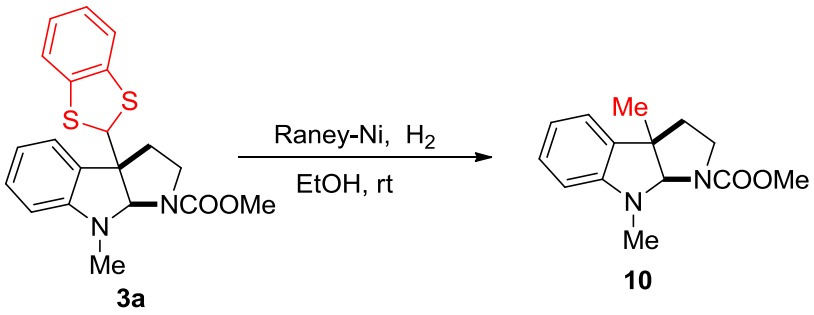
Formal synthesis of physovenine



1 R. Tsuji, M. Nakagawa and A. Nishida, *Heterocycles* 2002, **58**, 587-594.

To a flame-dried Schlenk tube under argon were added **4d** (47.1 mg, 0.22 mmol, 110 mol%), benzoic acid (2.4 mg, 0.02 mmol, 10 mol%), sodium carbonate (23.3 mg, 0.22 mmol, 110 mol%) and toluene (2.0 mL). The reaction mixture was stirred at rt for 20 min and then cooled to -30 ^{o}C. Then 1,3-benzodithiolylium tetrafluoroborate (48.0 mg, 0.2 mmol, 100 mol%) and toluene (1 mL) were added. The reaction mixture was stirred at the same temperature for 10 h (monitored by TLC). Then the reaction was diluted with EtOAc (5 mL), filtered, and washed with EtOAc (10 mL). To this mixture were added 0.2 mL 5N/NaOH, Raney-Ni (0.5 g, slurry in water) and 15 mL EtOH. After that the reaction was kept under H_2 atmosphere (1 atm) for 6 h. Then the reaction mixture was filtered through a Celite pad and washed with EtOAc (3 x 5 mL) carefully. The collected organic layers were washed with brine (5 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Then the crude product was purified by silica gel column chromatography (PE/EA = 5/1) to afford compound **9** as a light yellow oil,[2] 29.1 mg, 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.65-6.60 (m, 2H), 6.24 (d, *J* = 8.4 Hz, 1H), 4.99 (s, 1H), 3.90 (t, *J* = 8.4 Hz, 1H), 3.70 (s, 3H), 3.45-3.39 (m, 1H), 2.83 (s, 3H), 2.10-1.96 (m, 2H), 1.40 (s, 3H).

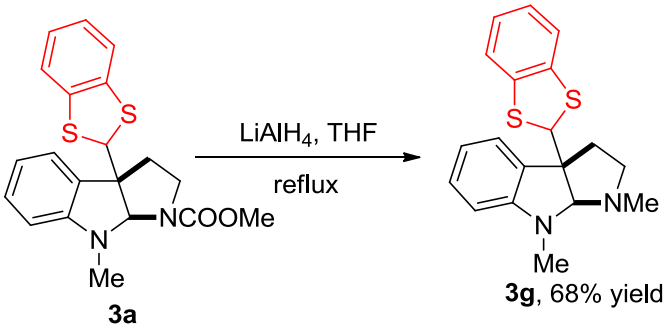
Transformations of product 3



To a solution of **3a** (38.4 mg, 0.1 mmol, 1.0 equiv) in ethanol (15 mL), Raney-Ni (0.5 g, slurry in water) was added and the reaction was kept under H_2 atmosphere (1 atm) overnight. Then the reaction mixture was filtered through a Celite pad and washed with EtOAc (3 x 5 mL) carefully. The collected organic layers were washed with

2 S. Horne, N. Taylor, S. Collins and R. Russell, *J. Chem. Soc., Perkin Trans. 1* 2001, **12**, 3047–3052.

brine (5 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Then the crude product was purified by silica gel column chromatography (PE/EA = 8/1-3/1) to afford compound **10** as a light yellow oil,[3] 19.4 mg, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.2 Hz, 1H), 6.68 (t, *J* = 7.2 Hz, 1H), 6.39 (d, *J* = 7.2 Hz, 1H), 5.21 and 5.09 (s, 1H), 3.86-3.72 (m, 4H), 3.20-3.06 (m, 1H), 2.98 and 2.88 (s, 3H), 2.16-2.05 (m, 1H), 1.96-1.89 (m, 1H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 150.3, 134.0, 128.2, 121.8, 117.6, 117.4, 106.0, 105.9, 89.0, 88.3, 52.8, 52.4, 51.7, 46.3, 46.1, 39.0, 38.5, 33.1, 32.5, 24.8, 24.4.

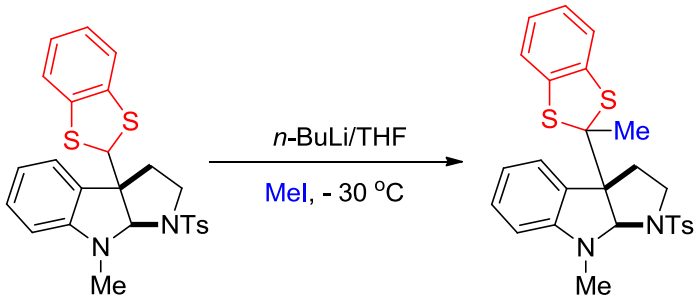


3a **3g**, 68% yield

A flame-dried 25 mL round bottom flask was cooled to room temperature and filled with argon. To this flask was added $LiAlH_4$ (38.0 mg, 1.0 mmol), the atmosphere exchanged with argon three times before the addition of THF (6 mL) and the slow addition of **3a** (76.8 mg, 0.20 mmol). Then mixture was refluxed at 80 ^{o}C. After the reaction was complete (monitored by TLC), the reaction mixture was quenched with water, extracted with ether. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (PE/EA = 1/5) to afford compound **3g** as a white solid, 46.1 mg, 68% yield, M.p. 82-84^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16-7.01 (m, 4H), 6.96-6.93 (m, 2H), 6.64 (t, *J* = 7.5 Hz, 1H), 6.44 (d, *J* = 7.8 Hz, 1H), 5.48 (s, 1H), 4.46 (s, 1H), 2.90 (s, 3H), 2.81-2.75 (m, 1H), 2.58-2.53 (m, 1H), 2.47 (s, 3H), 2.32-2.23 (m, 1H), 2.04-1.98 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 137.7, 137.4, 131.6, 129.1, 125.3, 125.2, 123.3, 121.8, 121.5, 117.6, 107.1, 91.5, 63.2, 61.1, 52.9, 37.5, 36.5, 36.1; IR (thin film): ν_{max} (cm^{-1}) = 3675,

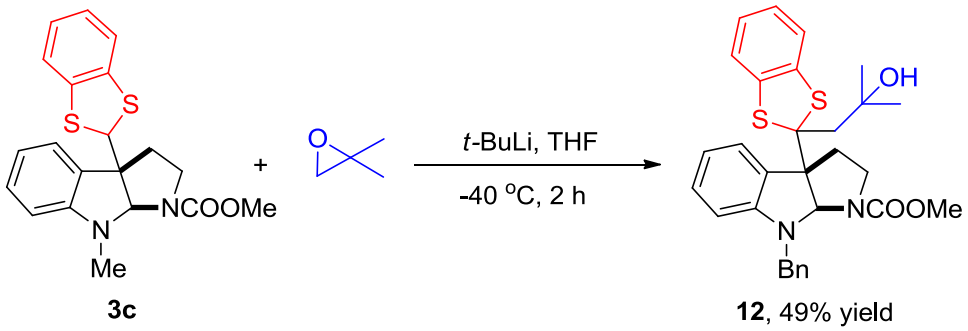
3 M. Kawahara, A. Nishida and M. Nakagawa, *Org. Lett*. 2000, **2**, 675−678.

2971, 2901, 1602, 1490, 1446, 1431, 1381, 1339, 1235, 1153, 1118, 1066, 1020, 926, 907, 868, 811, 740, 708, 663; HRMS (ESI) calcd for $C_{19}H_{21}N_2O_2S_2$([M+H]$^+$): 341.1141. Found: 341.1140.



3f **11**, 68% yield

A solution of *n*-BuLi (0.15 mmol, 60 uL, 2.5 M in hexanes) was added dropwise to a solution of **3f** (48.0 mg, 0.1 mmol) in anhydrous THF (2 mL) at -30 ℃ under argon atmosphere. The reaction mixture was stirred at -30 ℃ for 30 min. Then MeI (0.2 mmol, 10 μL) was added via syringe under argon atmosphere. The solution was stirred for 30 min and then water (2 mL) was added. The organic layer was separated, and the aqueous layer was extracted with Et_2O (2 x 5 mL). The collected organic layers were washed with brine (5 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (PE/EA = 15/1) to afford compound **11** as a white foam, 33.6 mg, 68% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 2H), 7.35-7.26 (m, 3H), 7.20 (t, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 6.3 Hz, 1H), 7.01-6.87 (m, 3H), 6.70 (t, *J* = 7.2 Hz, 1H), 6.43 (d, *J* = 7.8 Hz, 1H), 5.51 (s, 1H), 3.61-3.55 (m, 1H), 3.02 (s, 3H), 2.98-2.86 (m, 1H), 2.47 (s, 3H), 2.14-2.08 (m, 2H), 1.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.7, 143.3, 137.9, 137.8, 136.8, 130.0 129.6, 127.7, 127.2, 125.4, 125.2, 124.1, 121.8, 121.5, 117.5, 106.4, 87.2, 67.4, 48.2, 35.8, 31.4, 28.0, 21.6; IR (thin film): ν_{max} (cm^{-1}) = 3663, 2972, 2902, 1602, 1490, 1445, 1380, 1343, 1300, 1251, 1156, 1118, 1078, 1013, 918, 868, 810, 739, 705, 684, 656; HRMS (ESI) calcd for $C_{26}H_{27}N_2O_2S_3$([M+H]$^+$): 495.1229. Found: 495.1230.



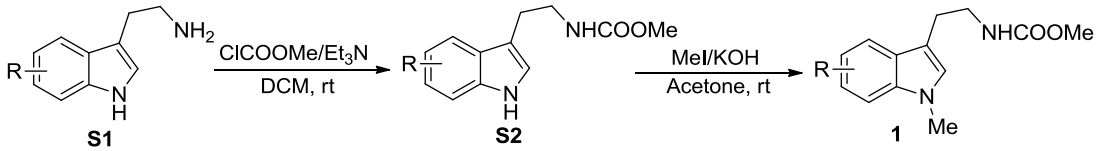
To a solution of **3c** (92.1 mg, 0.20 mmol, 1.00 equiv) in THF (3 mL) at –40 °C was added a 1.5 M solution of *t*-BuLi (270 uL, 0.4 mmol, 2.0 equiv) dropwise via syringe. The mixture was stirred for 0.5 h, then the epoxide (22 mg, 0.3 mmol, 1.5 equiv) was added dropwise to the reaction mixture at –78 °C via syringe. The resultant solution was stirred for an additional 1 h at –40 °C and EtOAc (5 mL) was added to quench the reaction. Then combined organic layers were washed with brine (5 mL), extracted with EtOAc (2 x 5mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Then the crude product was purified by silica gel column chromatography (PE/EA = 10/2-10/3) to afford compound **12** as a white foam, 52.3 mg, 49% yield. ^{1}H NMR (400 MHz, d_6-DMSO, 80 °C) δ 8.22 (s, 1H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.25-7.13 (m, 6H), 7.03-6.97 (m, 3H), 6.62 (t, *J* = 7.6 Hz, 1H), 6.27 (d, *J* = 7.6 Hz, 1H), 5.67 (s, 1H), 4.47 (s, 2H), 4.01-3.98 (m, 1H), 3.81 (t, *J* = 9.2 Hz,, 1H), 3.46 (s, 3H), 3.06 (brs, 1H), 2.84-2.75 (m, 1H), 2.48-2.41 (m, 1H), 2.20-2.17 (m, 2H), 1.25 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO, 80 °C) δ 159.5, 139.0, 138.0, 137.8, 129.4, 128.2, 127.9, 127.0, 126.6, 125.2, 125.1, 124.5, 121.3, 120.8, 118.6, 118.3, 117.1, 105.8, 83.4, 74.3, 70.3, 52.1, 49.2, 48.8, 44.8, 35.6, 30.9; IR (thin film): ν_{max} (cm^{-1}) = 3497, 2964, 1699, 1600, 1490, 1449, 1388, 1355, 1317, 1255, 1217, 1152, 1104, 944, 742, 698; HRMS (ESI) calcd for $C_{30}H_{33}N_2O_3S_2$([M+H]$^+$): 533.1927. Found: 533.1924.

General Procedures for Synthesis of Substrates

All *N*-methyl tryptophols were prepared according to the previously reptorted

procedures[4] and the *N*-protected tryptamine derivatives **1a-b**[5], **1d**[6], **1e**[7], **1f**[8], and **1g**[9] were prepared according to the reported procedures.

General One-pot Procedure for Synthesis of Substrates[5]

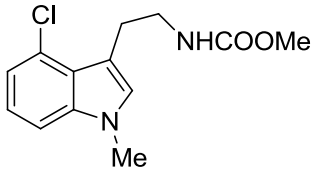


To an oven-dried round-bottom flask were added appropriate tryptamine **S1** (5.0 mmol, 1.00 equiv) and DCM (30 ml), followed by triethylamine (0.85 mL, 6.0 mmol, 1.2 equiv). The mixture was cooled to 0 ℃ and methyl chloroformate (0.4 ml, 5.5 mmol, 1.10 equiv) was added slowly. Then the ice bath was removed and the reaction mixture was stirred at room temperature for about 3 h. After the reaction was complete (monitored by TLC), the mixture was quenched with water (20 mL) and extracted with DCM (3 x 15 mL). The combined organic layers were washed with water, brine, separated, dried with Na_2SO_4, filtered and concentrated under reduced pressure. The residue was used directly for the next step without further purification.

To a solution of the above obtained **S2** in acetone (30 mL) was added powdered potassium hydroxide (1.4 g, 25 mmol, 5.0 equiv) at 0 ^{o}C. After 10 min, methyliodide (0.35 ml, 5.0 mmol, 1.0 equiv) was added to the acetone solution with vigorous stirring. Then the reaction mixture was stirred for 0.5 h at room temperature. The same amount of potassium hydroxide (1.4 g, 25 mmol, 5.0 equiv) and methyl iodide (0.35 mL, 5.0 mmol, 1.0 equiv) were added again and stirred overnight. The mixture was filtered and concentrated. The residue was dissolved in EtOAc (30 mL) and

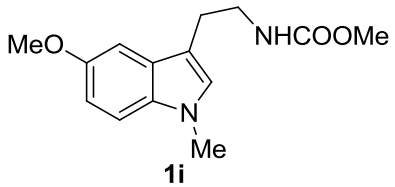
4 C. Liu, W. Zhang, L.-X. Dai and S.-L. You, *Org. Biomol. Chem.* 2012, **10**, 7177-7183.
5 Y. Yang, X. Jiang, F.-L. Qing, *J. Org. Chem*. 2012, **77**, 7538-7547.
6 W.-H. Chiou, C.-L. Kao, J.-C. Tsai, Y.-M. Chang, *Chem. Commun*. 2013, **49**, 8232-8234.
7 H. Song, J. Yang, W. Chen, Y. Qin, *Org. Lett.* 2006, **8**, 6011-6014.
8 O. Lozano, G. Blessley, T. Martinez del Campo, A. L. Thompson, G. T. Giuffredi, M. Bettati, M. Walker, R. Borman, V. Gouverneur, *Angew. Chem., Int. Ed*. 2011, **50**, 8105-8109
9 C.-L. Fang, S. Horne, N. Taylor, R. Rodrigo, *J. Am. Chem. Soc.* 1994, **116**, 9480-9486.

washed subsequently with water, sat. $NaHCO_3$. The aqueous phase was extracted with EtOAc (3 x 15 mL) and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on silica gel using 20-40% EtOAc in hexane to provide the desired product **1**.



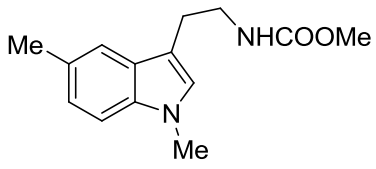
1h

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.90 (s, 1H), 4.81 (s, 1H), 3.74 (s, 3H), 3.67 (s, 3H), 3.56-3.51 (m, 2H), 3.17 (t, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 138.3, 128.4, 126.0, 124.1, 121.8, 119.7, 111.5, 107.9 51.8, 42.4, 32.6, 26.4; IR (thin film): ν_{max} (cm^{-1}) = 3335, 2923, 1687, 1612, 1534, 1479, 1459, 1420, 1371, 1342, 1321, 1281, 1252, 1188, 1140, 1075, 1026, 1000, 927, 865, 816, 772, 739, 699, 680, 657, 627; HRMS (ESI) calcd for $C_{13}H_{16}ClN_2O_2$([M+H]$^+$): 267.0895. Found: 267.0897.



1i

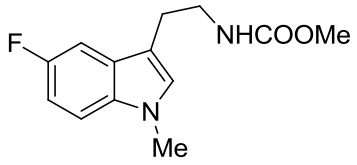
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.8 Hz, 1H), 7.00 (s, 1H), 6.87 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.80 (s, 1H), 4.95 (s, 1H), 3.83 (s, 3H), 3.65 (s, 3H), 3.63 (s, 3H), 3.47-3.33 (m, 2H), 2.88 (t, *J* = 6.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 153.6, 132.3, 127.8, 127.2, 111.7, 110.6, 109.9, 100.4, 55.7, 51.7, 41.3, 32.5, 25.5; IR (thin film): ν_{max} (cm^{-1}) = 3341, 2941, 1699, 1621, 1578, 1520, 1490, 1454, 1424, 1378, 1298, 1249, 1224, 1176, 1137, 1068, 1034, 899, 878, 833, 791, 751, 665, 650, 631; HRMS (ESI) calcd for $C_{14}H_{19}N_2O_2$([M+H]$^+$): 263.1390. Found: 263.1392.



1j

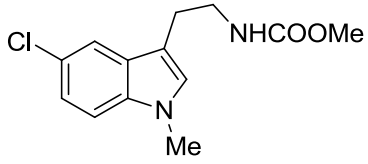
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.04 (d, *J* = 8.4

Hz, 1H), 6.80 (s, 1H), 4.83 (s, 1H), 3.68 (s, 3H), 3.64 (s, 3H), 3.47 (dt, *J* = 12.4, 6.4 Hz, 2H), 2.90 (t, *J* = 6.8 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 135.5, 128.0, 127.7, 126.8, 123.2, 118.4, 110.6, 108.9, 51.9, 41.3, 32.5 25.5, 21.4; IR (thin film): ν_{max} (cm^{-1}) = 3335, 2918, 1689, 1538, 1493, 1457, 1384, 1362, 1306, 1283, 1254, 1186, 1143, 1068, 1031, 1001, 927, 890, 858, 815, 797, 778, 694, 671, 653, 616; HRMS (ESI) calcd for $C_{14}H_{19}N_2O_2$([M+H]$^+$): 247.1441. Found: 247.1445.



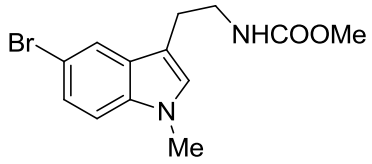
1k

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.15 (m, 2H), 6.97-6.92 (m, 1H), 6.89 (s, 1H), 4.88 (s, 1H), 3.70 (s, 3H), 3.65 (s, 3H), 3.49-3.39 (m, 2H), 2.87 (t, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5 (d, *J* = 232.8 Hz), 157.0, 133.6, 128.4, 121.9, 118.2, 110.0, 109.8 (d, *J* = 11.0 Hz), 103.5 (d, *J* = 23.1 Hz), 51.9, 41.2, 32.8, 25.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -125.9; IR (thin film): ν_{max} (cm^{-1}) = 3321, 2972, 2902, 1686, 1540, 1490, 1458, 1425, 1305, 1283, 1258, 1242, 1210, 1180, 1066, 1030, 908, 838, 800, 712, 672, 655; HRMS (ESI) calcd for $C_{13}H_{16}FN_2O_2$([M+H]$^+$): 251.1190. Found: 251.1193.



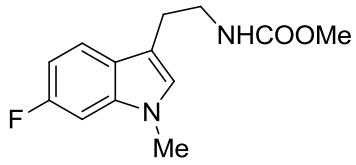
1l

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.18-7.15 (m, 2H), 6.88 (s, 1H), 4.85 (s, 1H), 3.70 (s, 3H), 3.65 (s, 3H), 3.46-3.42 (m, 2H), 2.88 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 135.4, 128.7, 128.1, 124.7, 121.8, 118.2, 111.0, 110.2, 51.9, 41.3, 32.7, 25.4; IR (thin film): ν_{max} (cm^{-1}) = 3329, 2971, 2902, 1684, 1538, 1479, 1422, 1283, 1256, 1187, 1144, 1080, 1062, 1030, 908, 839, 798, 779, 699, 660, 623; HRMS (ESI) calcd for $C_{13}H_{16}ClN_2O_2$([M+H]$^+$): 267.0895. Found: 267.0895.



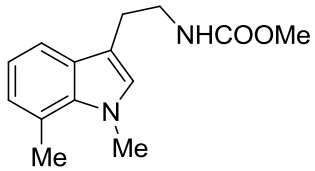
1m

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 1.6 Hz,, 1H), 7.27 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.13 (d, *J* = 8.8 Hz, 1H), 6.85 (s, 1H), 4.83 (s, 1H), 3.70 (s, 3H), 3.65 (s, 3H), 3.46-3.42 (m, 2H), 2.87 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 135.6, 129.3, 127.9, 124.4, 121.3, 112.2, 111.0, 110.7, 51.9, 41.3, 32.7, 25.4; IR (thin film): ν_{max} (cm^{-1}) = 3663, 3330, 2912, 1687, 1537, 1476, 1421, 1394, 1381, 1301, 1282, 1256, 1189, 1143, 1075, 1047, 1030, 996, 865, 850, 820, 794, 779, 696, 660, 614; HRMS (ESI) calcd for $C_{13}H_{16}BrN_2O_2$([M+H]$^+$): 311.0390. Found: 311.0388.



1n

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.37 (m, 1H), 6.85 (dd, *J* = 10.0, 2.0 Hz, 1H), 6.80-6.75 (m, 1H), 6.75 (s, 1H), 4.76 (s, 1H), 3.58 (s, 3H), 3.56 (s, 3H), 3. 38-3.36 (m, 2H), 2.82 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9 (d, *J* = 236.4 Hz), 157.0, 137.0 (d, *J* = 12.0 Hz), 126.9, 124.2, 119.5 (d, *J* = 10.4 Hz), 111.6, 107.5 (d, *J* = 24.4 Hz), 95.5 (d, *J* = 25.9 Hz), 51.9, 41.3, 32.6, 25.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -121.0; IR (thin film): ν_{max} (cm^{-1}) = 3675, 3325, 2972, 2901, 1685, 1623, 1538, 1479, 1455, 1407, 1394, 1382, 1283, 1257, 1192, 1106, 1067, 1055, 1028, 916, 838, 800, 694, 657; HRMS (ESI) calcd for $C_{13}H_{16}FN_2O_2$([M+H]$^+$): 251.1190. Found: 251.1190.

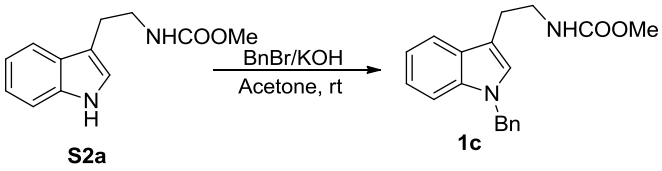


1o

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.0 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.2 Hz, 1H), 6.74 (s, 1H), 4.83 (s, 1H), 3.97 (s, 3H), 3.64 (s, 3H), 3.48-3.43 (m, 2H), 2.89 (t, *J* = 6.8 Hz, 2H), 2.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9,

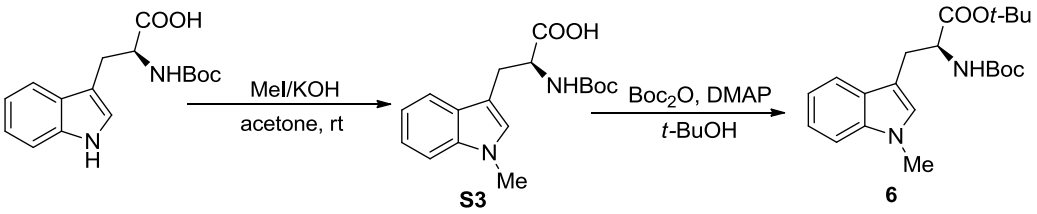
135.7, 128.6, 128.4, 124.2, 121.2, 119.1, 116.8, 110.8, 51.9, 41.2, 36.4, 25.4, 19.6; IR (thin film): ν_{max} (cm^{-1}) = 3675, 3333, 2987, 2901, 1695, 1543, 1453, 1405, 1394, 1360, 1321, 1288, 1252, 1192, 1140, 1056, 891, 813, 779, 745, 690, 610; HRMS (ESI) calcd for $C_{14}H_{19}N_2O_2$([M+H]$^+$): 247.1441. Found: 247.1440.

General Procedure for Synthesis of Substrate 1c



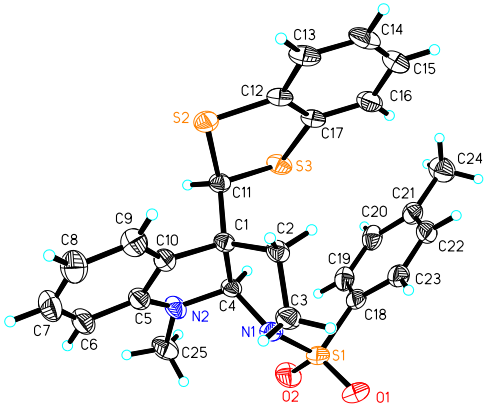
To a solution of **S2a** (436 mg, 2.0 mmol) in acetone (20 mL) was added powdered potassium hydroxide (560 mg, 10 mmol, 5.0 equiv) at 0 ^oC. After 10 min, benzyl bromide (223 μL, 2.0 mmol, 1.0 equiv) was added to the acetone solution with vigorous stirring and the reaction mixture was stirred for 0.5 h at room temperature. Then the same amount of potassium hydroxide (560 mg, 10 mmol, 5.0 equiv) and benzyl bromide (223 μL, 2.0 mmol, 1.0 equiv) were added again and the reaction mixture was stirred overnight. The mixture was filtered and concentrated. The residue was dissolved in EtOAc (20 mL) and washed subsequently with water and sat. $NaHCO_3$. The aqueous phase was extracted with EtOAc (3 x 10 mL) and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was was purified by flash chromatography on silica gel using 20-40% EtOAc in hexane to provide **1c** as a white solid, 570 mg, 92% yield, M.p. 64-66^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.29-7.21 (m, 4H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.12-7.07 (m, 3H), 6.93 (s, 1H), 5.24 (s, 2H), 4.81 (s, 1H), 3.63 (s, 3H), 3.51-3.46 (m, 2H), 2.95 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 137.4, 136.6, 128.7, 127.9, 127.5, 126.7, 126.1, 121.8, 119.1, 118.9, 112.0, 109.7, 51.9, 49.8, 41.3, 25.7; IR (thin film): ν_{max} (cm^{-1}) = 3672, 3359, 2986, 2903, 1689, 1532, 1438, 1407, 1381, 1323, 1251, 1174, 1138, 1065, 895, 806, 781, 734, 698, 660; HRMS (ESI) calcd for $C_{19}H_{21}N_2O_2$([M+H]$^+$): 309.1598. Found: 309.1597.

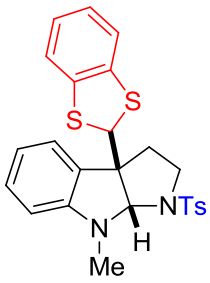
General procedure for synthesis of 6



To a solution of *N*-Boc-L-trytophan (608 mg, 2.0 mmol) in acetone (20 mL) was added powdered potassium hydroxide (560 mg, 10 mmol, 5.0 equiv) at 0 ^{o}C. After 10 min, MeI (0.14 mL, 2.0 mmol, 1.0 equiv) was added to the acetone solution with vigorous stirring and the reaction mixture was stirred for 0.5 h at room temperature. Then the same amount of potassium hydroxide (560 mg, 10 mmol, 5.0 equiv) and MeI (0.14 mL, 2.0 mmol, 1.0 equiv) were added again and the reaction mixture was stirred overnight. The mixture was filtered and concentrated. The residue was disolved in EtOAc (20 mL) and the organic layer was washed subsequently with water and sat. $NaHCO_3$. The aqueous phase was extracted with EtOAc (3 x 15 mL) and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was used directly for next step without further purification.

To a solution of **S3** in *t*-BuOH (20 mL) was added DMAP (72 mg, 0.6 mmol, 0.3 equiv) and Boc_2O (1.85 mL, 8.0 mmol, 4.0 equiv) at rt. The reaction mixture was stirred for 72 h at rt and then concentrated. The residue was dissolved in EtOAc (20 mL). The organic layer was washed with sat. NH_4Cl. The aqueous phase was extracted with EtOAc (3 x 15 mL) and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on silica gel using 20% EtOAc in hexane to provide compound **6** as a white solid, 532.3 mg, 71% yield, M.p. 80-82 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.87 (s, 1H), 5.04 (d, *J* = 8.0 Hz, 1H), 4.54-4.49 (m, 1H), 3.74 (s, 3H), 3.27-3.19 (m, 2H), 1.42 (s, 9H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 155.2, 136.7, 128.3, 127.3, 121.5, 119.1, 118.8, 109.0, 108.9, 81.6, 79.4, 54.6, 32.6, 28.3, 27.9, 27.8; IR (thin film): ν_{max} (cm^{-1}) = 3357, 2977, 1702, 1513, 1472, 1364, 1324, 1274, 1236, 1151, 1066, 1015, 847, 769, 742; HRMS (ESI) calcd for $C_{21}H_{31}N_2O_4$([M+H]$^{+}$): 375.2278. Found: 375.2277.





3f

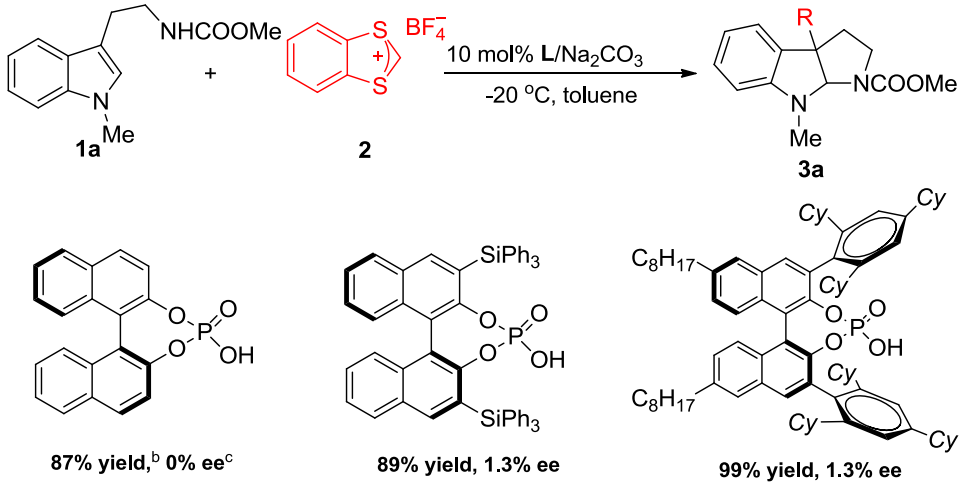
Table 1. Crystal data and structure refinement for 190.

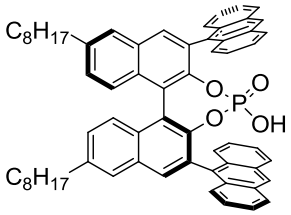
Identification code	190
Empirical formula	C25 H24 N2 O2 S3
Formula weight	480.64
Temperature	296(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P 21/n
Unit cell dimensions	a = 11.461(2) A alpha = 90 deg.
	b = 12.938(3) A beta = 93.48(3) deg.
	c = 15.619(3) A gamma = 90 deg.
Volume	2311.7(8) A^3
Z, Calculated density	4, 1.381 Mg/m^3
Absorption coefficient	3.137 mm^-1
F(000)	1008
Crystal size	0.38 x 0.31 x 0.24 mm
Theta range for data collection	4.44 to 65.99 deg.
Limiting indices	-12<=h<=13, -15<=k<=14, -18<=l<=18
Reflections collected / unique	16134 / 3959 [R(int) = 0.0266]
Completeness to theta = 65.99	98.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7529 and 0.5484
Refinement method	Full-matrix least-squares on F^2

Data / restraints / parameters	3959 / 0 / 290
Goodness-of-fit on F^2	1.028
Final R indices [I>2sigma(I)]	R1 = 0.0419, wR2 = 0.1136
R indices (all data)	R1 = 0.0426, wR2 = 0.1143
Extinction coefficient	0.0059(4)
Largest diff. peak and hole	0.409 and -0.487 e.A^-3

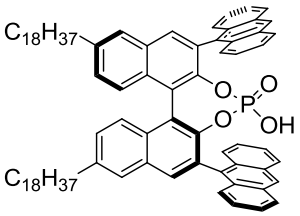
General procedure for chiral Brønsted acid catalyzed intermolecular enantioselective cascade dearomatization reaction of indole derivatives with carbenium ion[a]

To a flame-dried Schlenk tube under argon were added indole derivative **1** (0.22 mmol, 110 mol%), chiral Brønsted acid (0.02 mmol, 10 mol%), sodium carbonate (23.3 mg, 0.22 mmol, 110 mol%) and toluene (2.0 mL). The reaction mixture was stirred at rt for 20 min and then cooled to -20 ^{o}C. Then 1,3-benzodithiolylium tetrafluoroborate (48.0 mg, 0.2 mmol, 100 mol%) and toluene (1 mL) were added. The reaction mixture was stirred at the same temperature for 6-24 h (monitored by TLC). After the reaction was complete, the reaction was diluted with EtOAc (5 mL), filtered, and washed with EtOAc. The collected organic filtrate was concentrated under reduced pressure to afford the crude product. Then the crude product was purified by silica gel column chromatography (PE/EA = 8/1) to afford compound **3a**. The preliminary results for the enantioselective synthesis are summarized below.

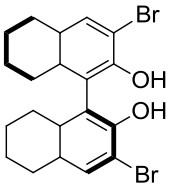




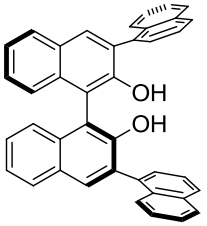
76% yield, 10% ee



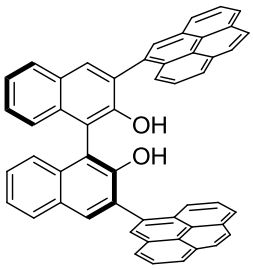
51% yield, 1.4% ee



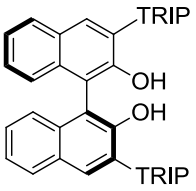
99% yield, 1.7% ee



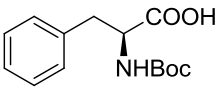
99% yield, 1.3% ee



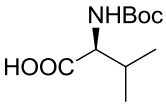
86% yield, 2.0 % ee



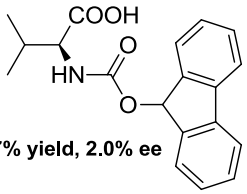
94% yield, 1.0 % ee



93% yield, 2.0% ee

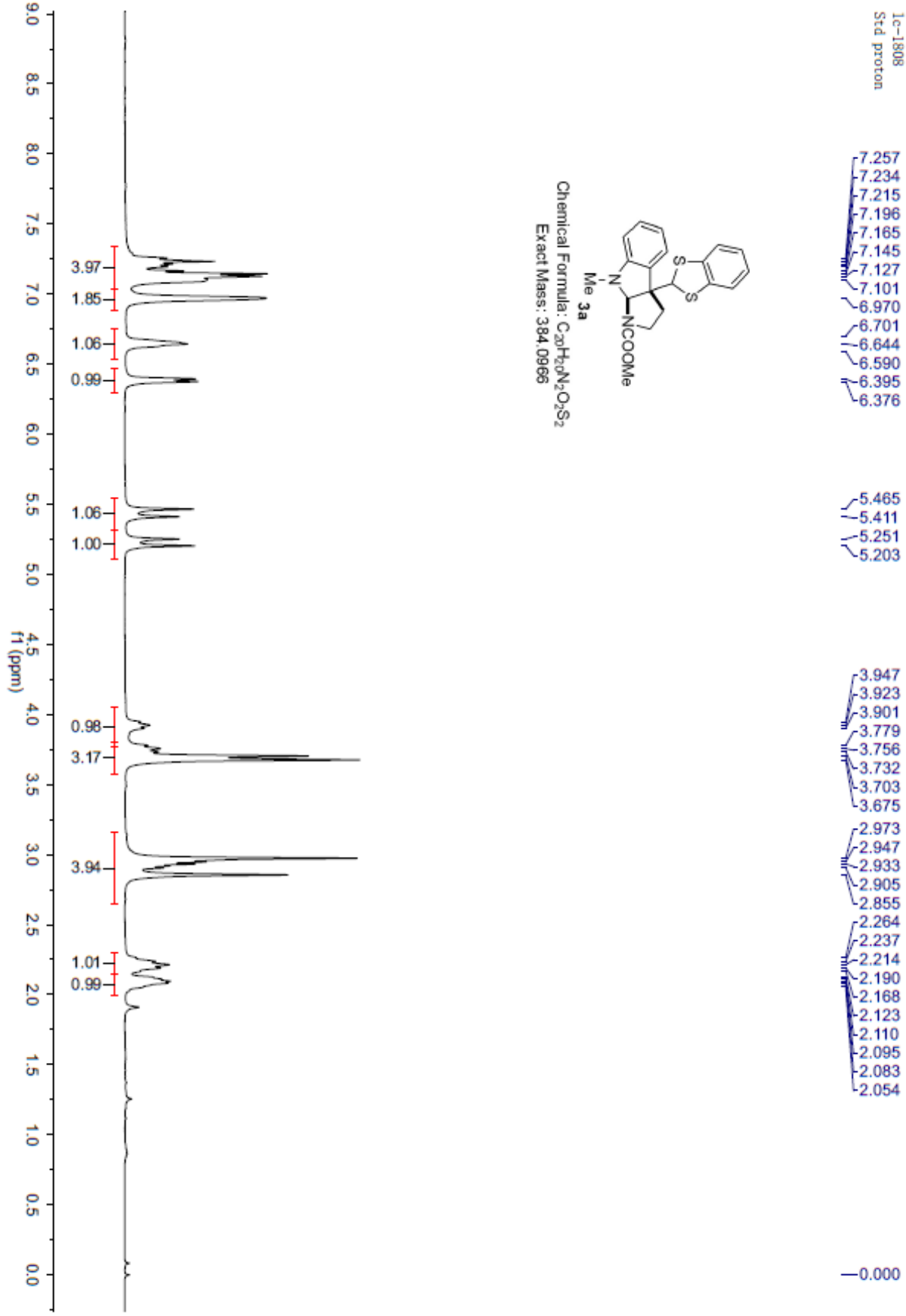


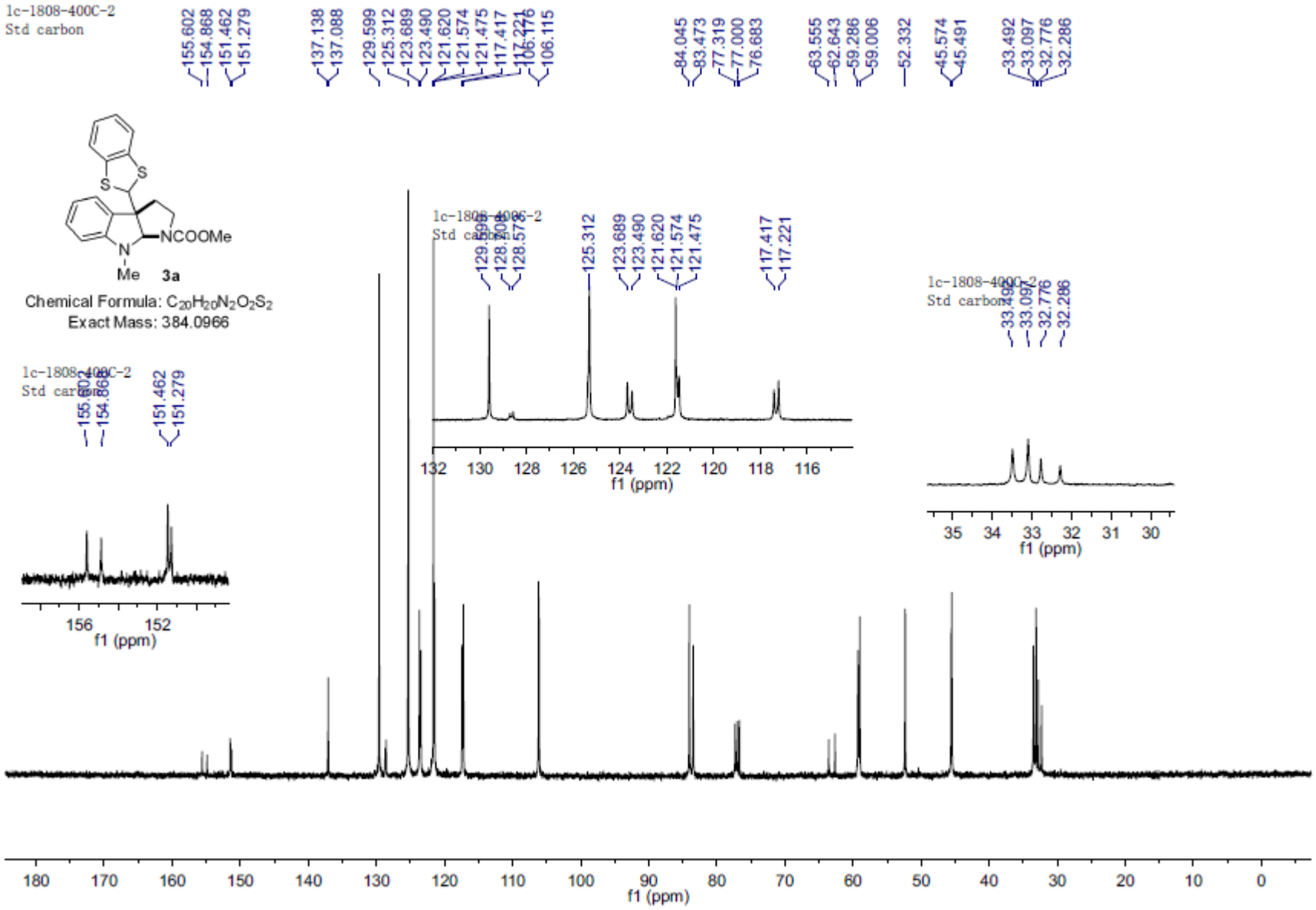
99% yield, 2.0% ee

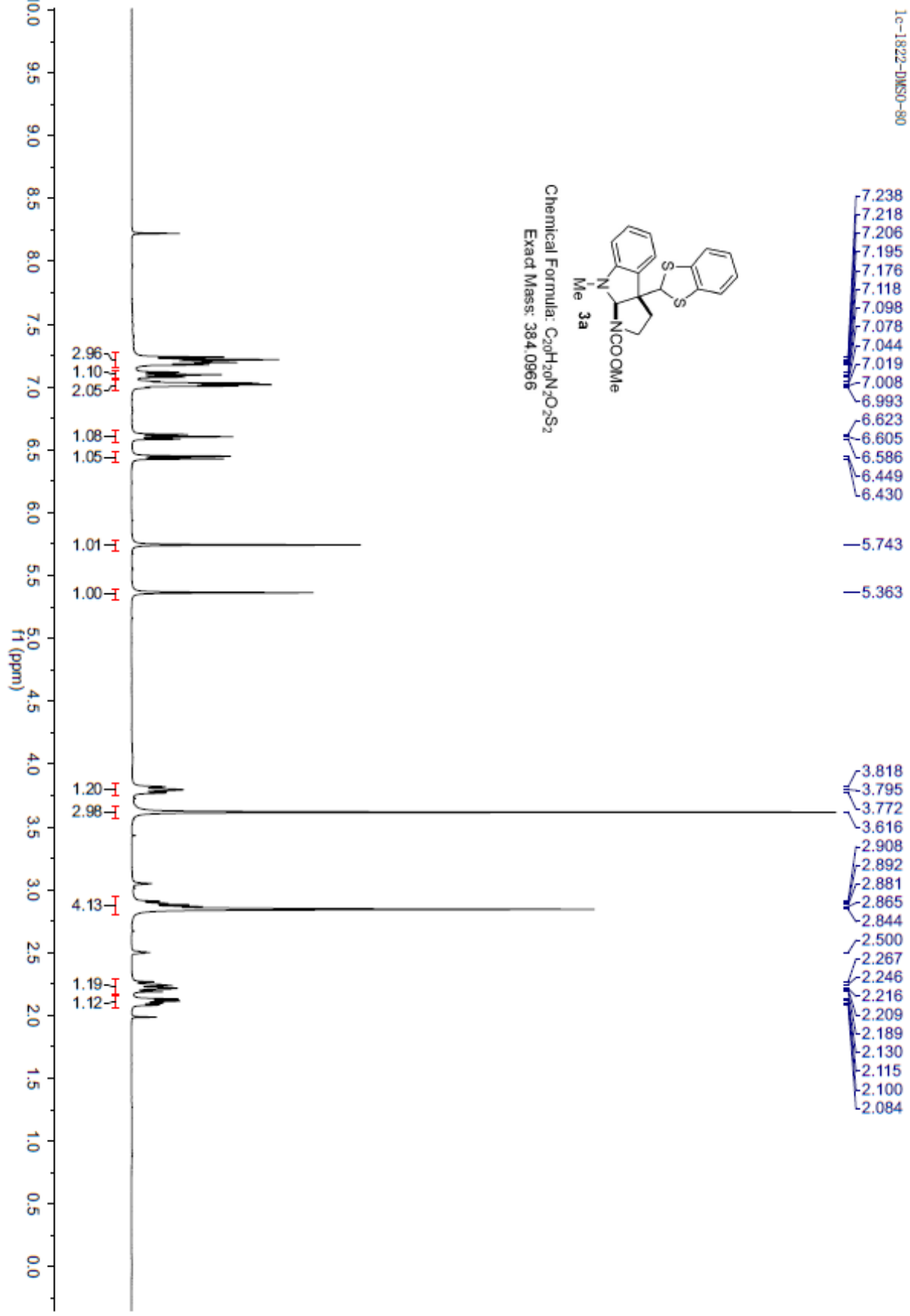


97% yield, 2.0% ee

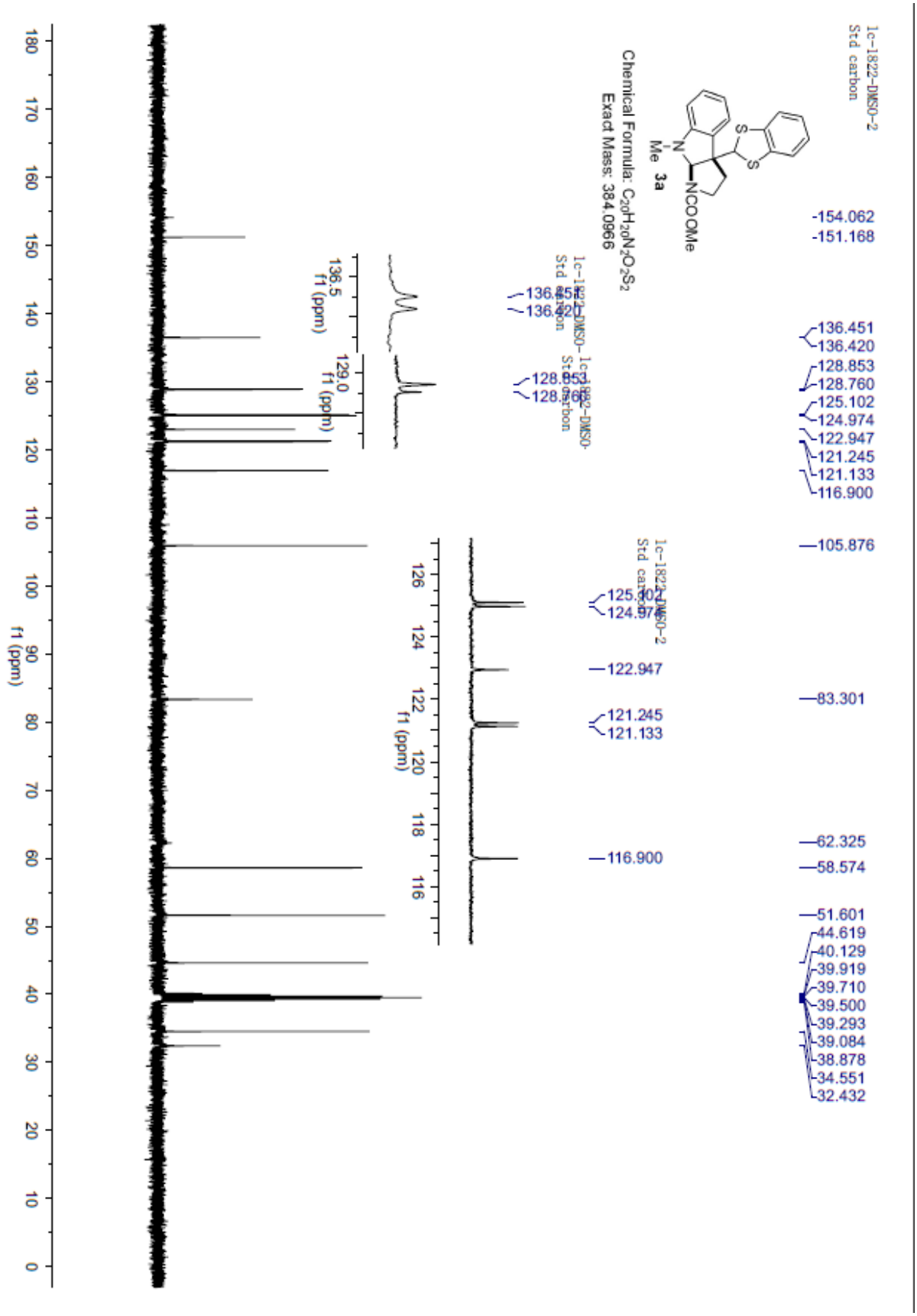
[a] Reaction conditions: **1a** (0.2mmol), **2** (0.22 mmol), Na_2CO_3 (0.22 mmol) in toluene (3 mL) at rt.[b] Isolated yield. [c] Determined by HPLC analysis.

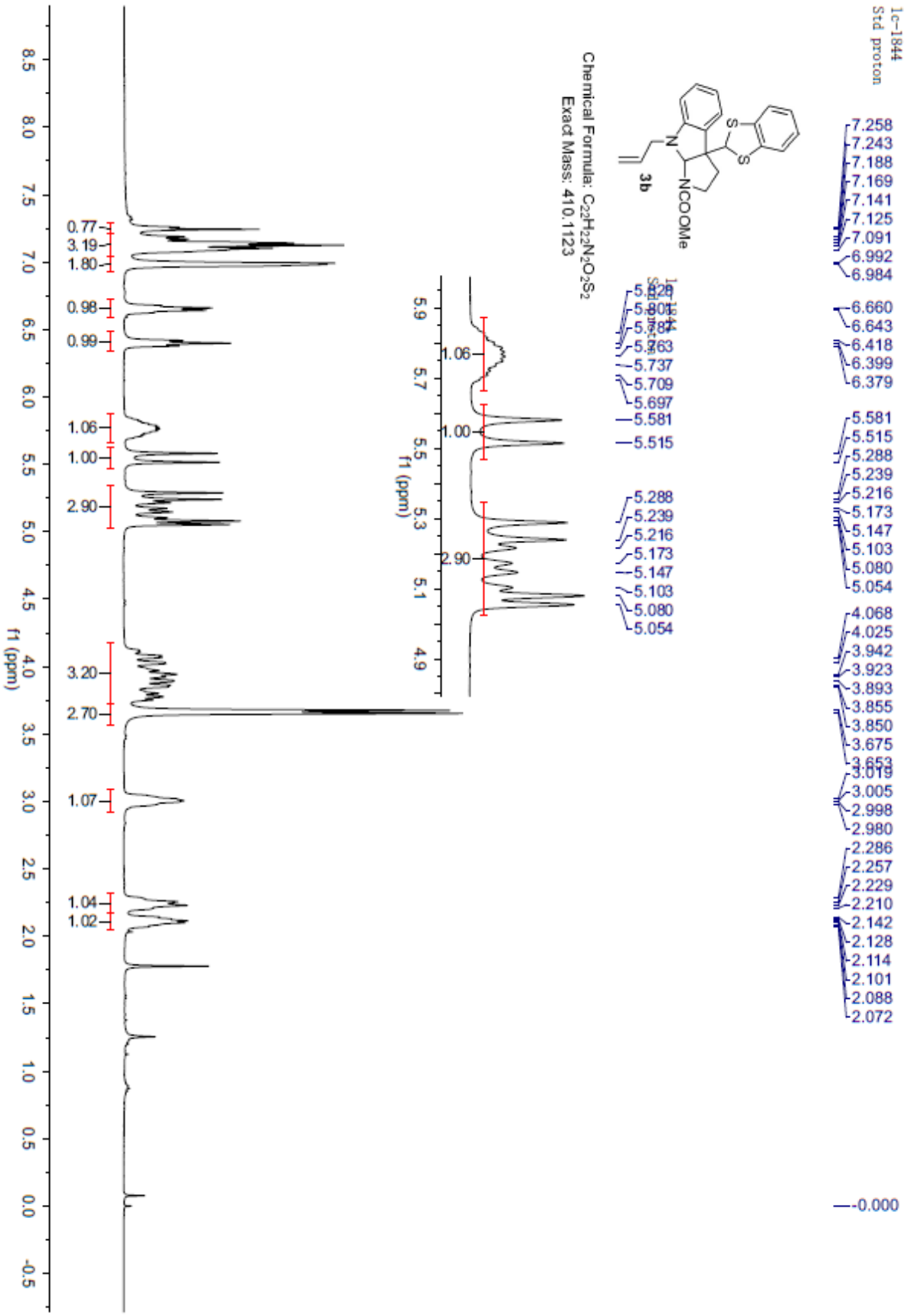

1c-1808
Std proton
7.257
7.234
7.215
7.196
7.165
7.145
7.127
7.101
6.970
6.701
6.644
6.590
6.395
6.376
5.465
5.411
5.251
5.203
3.947
3.923
3.901
3.779
3.756
3.732
3.703
3.675
2.973
2.947
2.933
2.905
2.855
2.264
2.237
2.214
2.190
2.168
2.123
2.110
2.095
2.083
2.054
0.000
Chemical Formula: C20H20N2O2S2
Exact Mass: 384.0966
Me
3a
NCOOMe
S
S
N
3.97
1.85
1.06
0.99
1.06
1.00
0.98
3.17
3.94
1.01
0.99
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

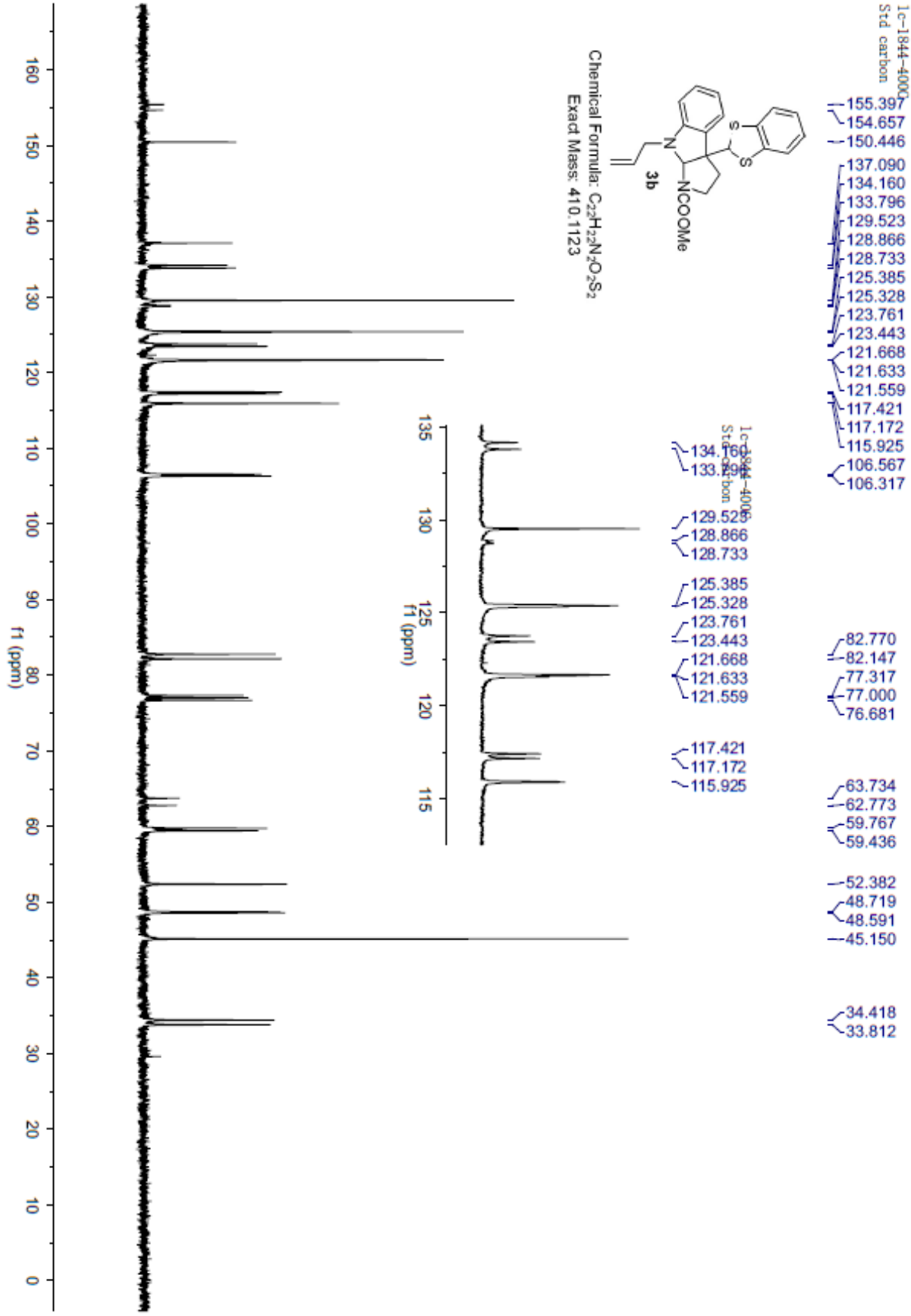

1c-1808-400C-2
Std carbon
155.602
154.868
151.462
151.279
137.138
137.088
129.599
125.312
123.689
123.490
121.620
121.574
121.475
117.417
117.221
106.176
106.115
84.045
83.473
77.319
77.000
76.683
63.555
62.643
59.286
59.006
52.332
45.574
45.491
33.492
33.097
32.776
32.286
NCOOMe
N
Me
3a
Chemical Formula: C20H20N2O2S2
Exact Mass: 384.0966
f1 (ppm)

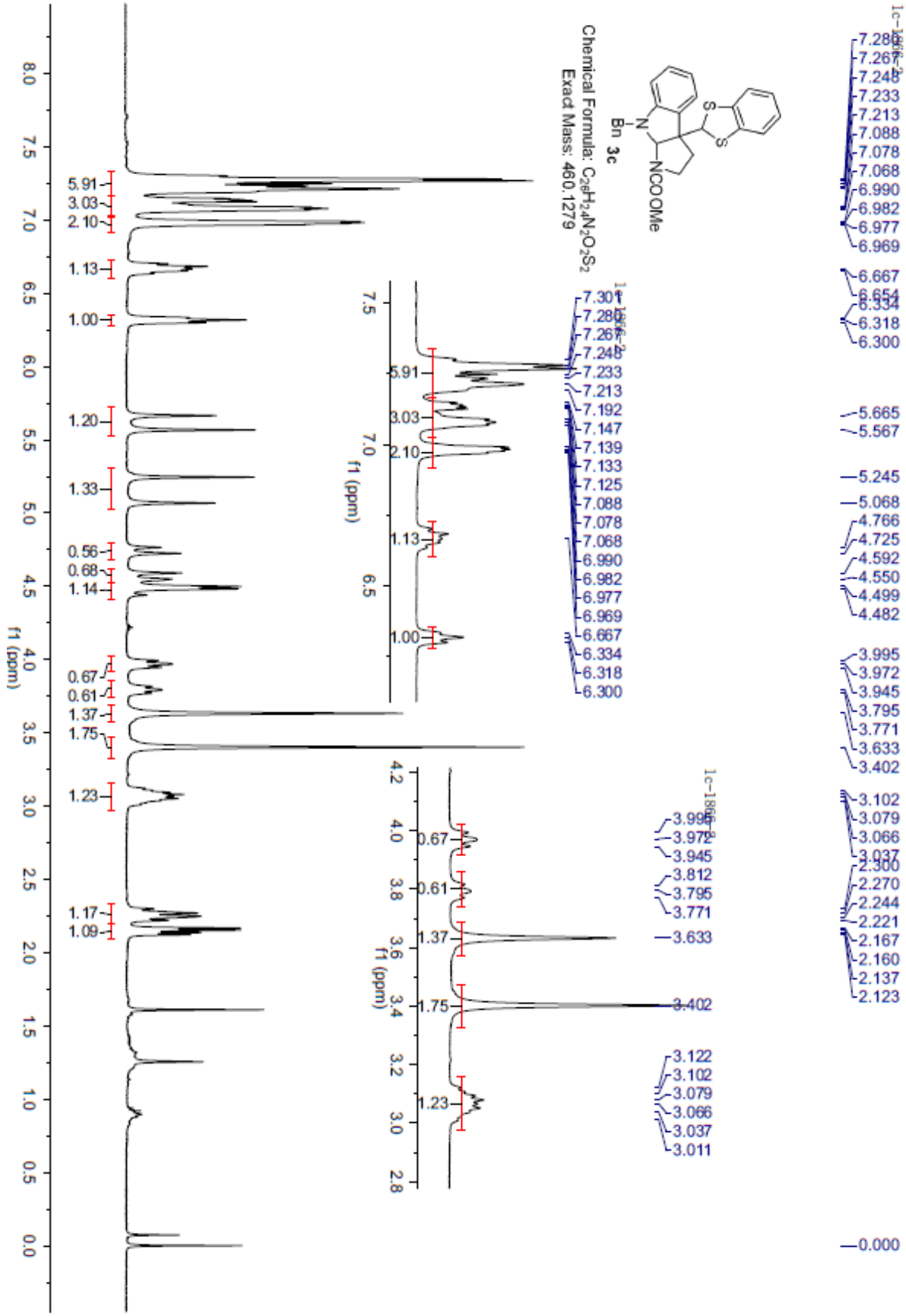

1c-1822-DMSO-80
Chemical Formula: $C_{20}H_{20}N_2O_2S_2$
Exact Mass: 384.0966
Me 3a
NCOOMe
7.238
7.218
7.206
7.195
7.176
7.118
7.098
7.078
7.044
7.019
7.008
6.993
6.623
6.605
6.586
6.449
6.430
5.743
5.363
3.818
3.795
3.772
3.616
2.908
2.892
2.881
2.865
2.844
2.500
2.267
2.246
2.216
2.209
2.189
2.130
2.115
2.100
2.084
2.96
1.10
2.05
1.08
1.05
1.01
1.00
1.20
2.98
4.13
1.19
1.12
f1 (ppm)

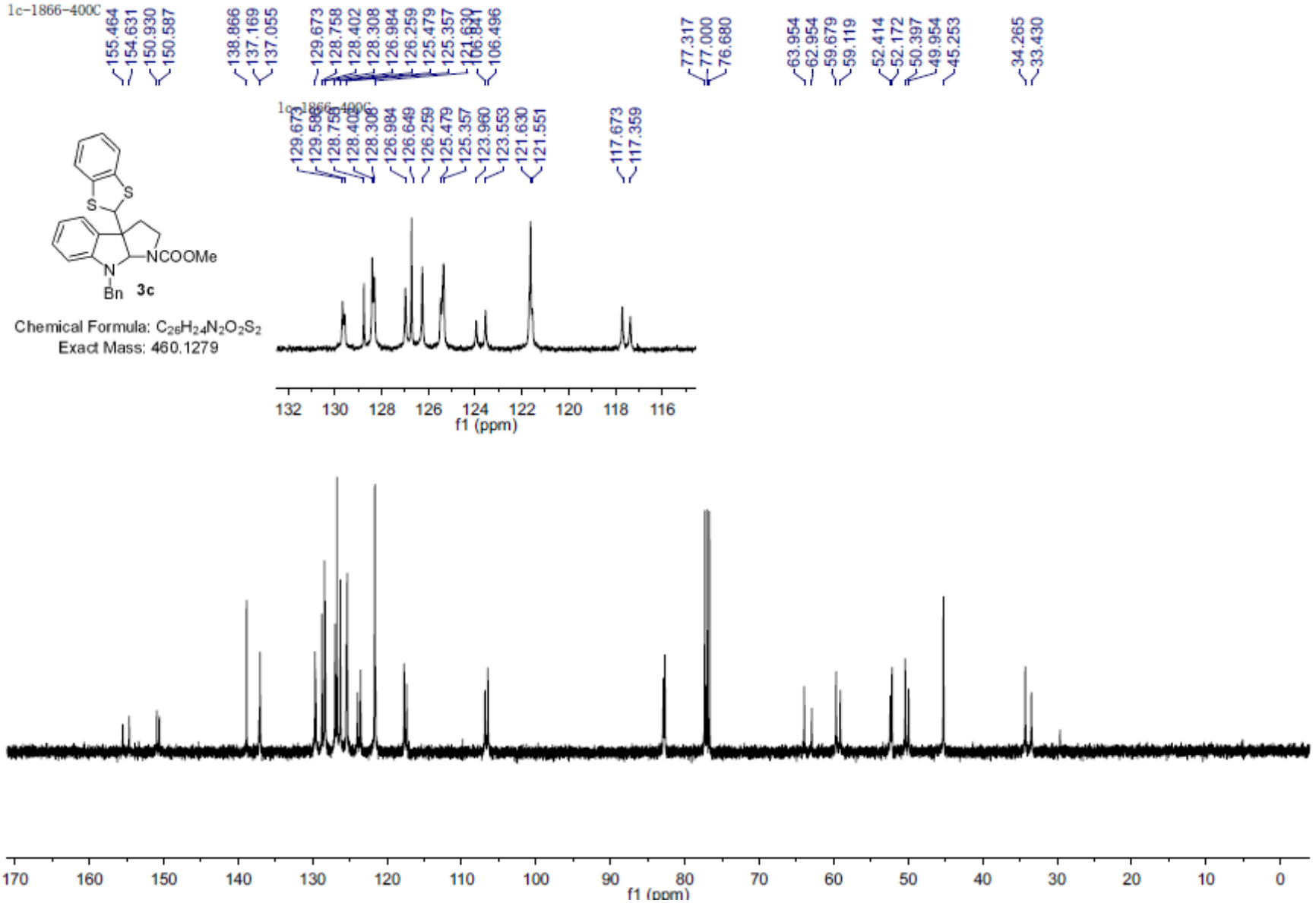
DMSO, 80 °C

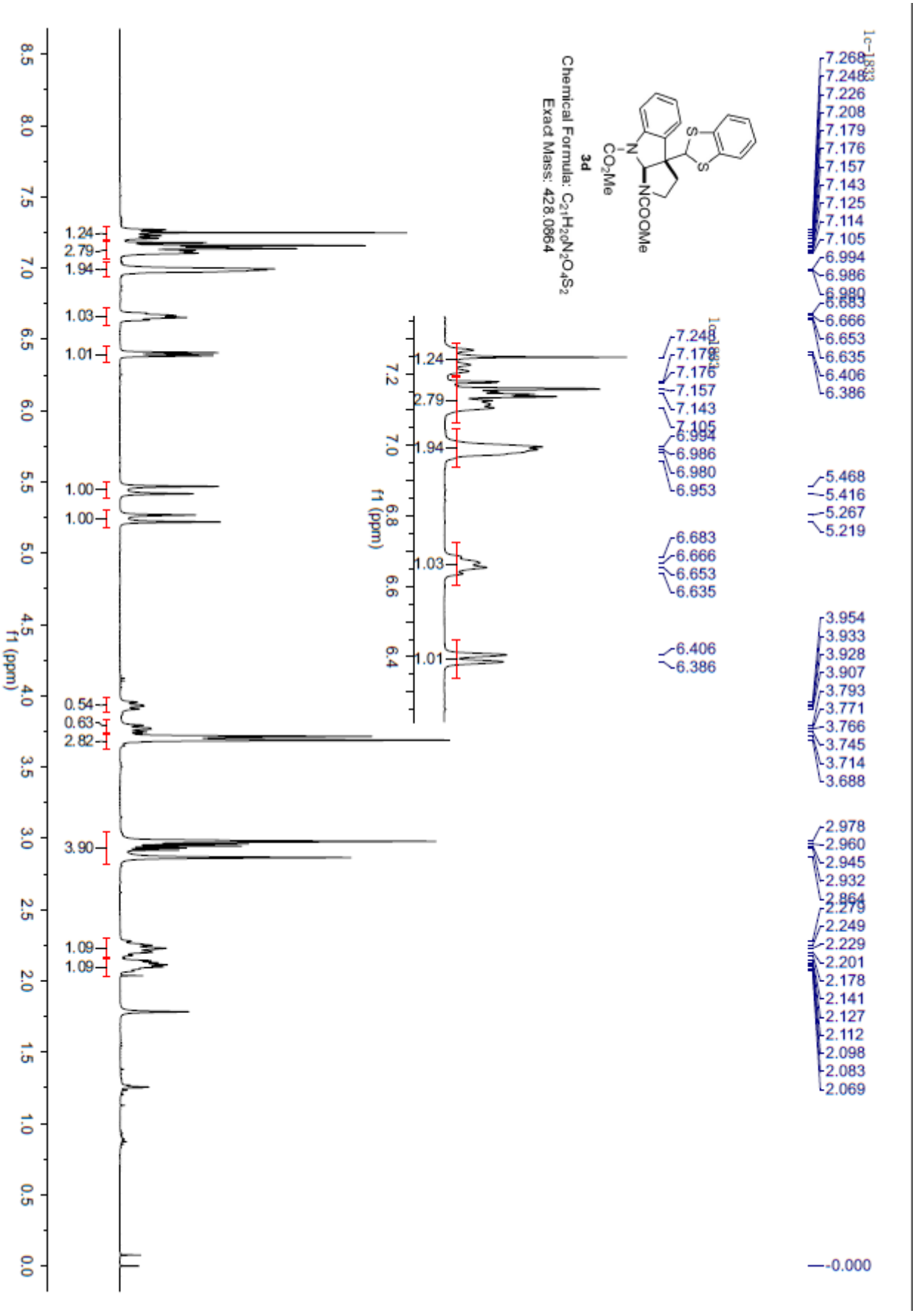

1c-1822-DMSO-2
Std carbon
Chemical Formula: $C_{20}H_{20}N_2O_2S_2$
Exact Mass: 384.0966
Me 3a
NCOOMe
-154.062
-151.168
136.451
136.420
128.853
128.760
125.102
124.974
122.947
121.245
121.133
116.900
105.876
83.301
62.325
58.574
51.601
44.619
40.129
39.919
39.710
39.500
39.293
39.084
38.878
34.551
32.432
f1 (ppm)

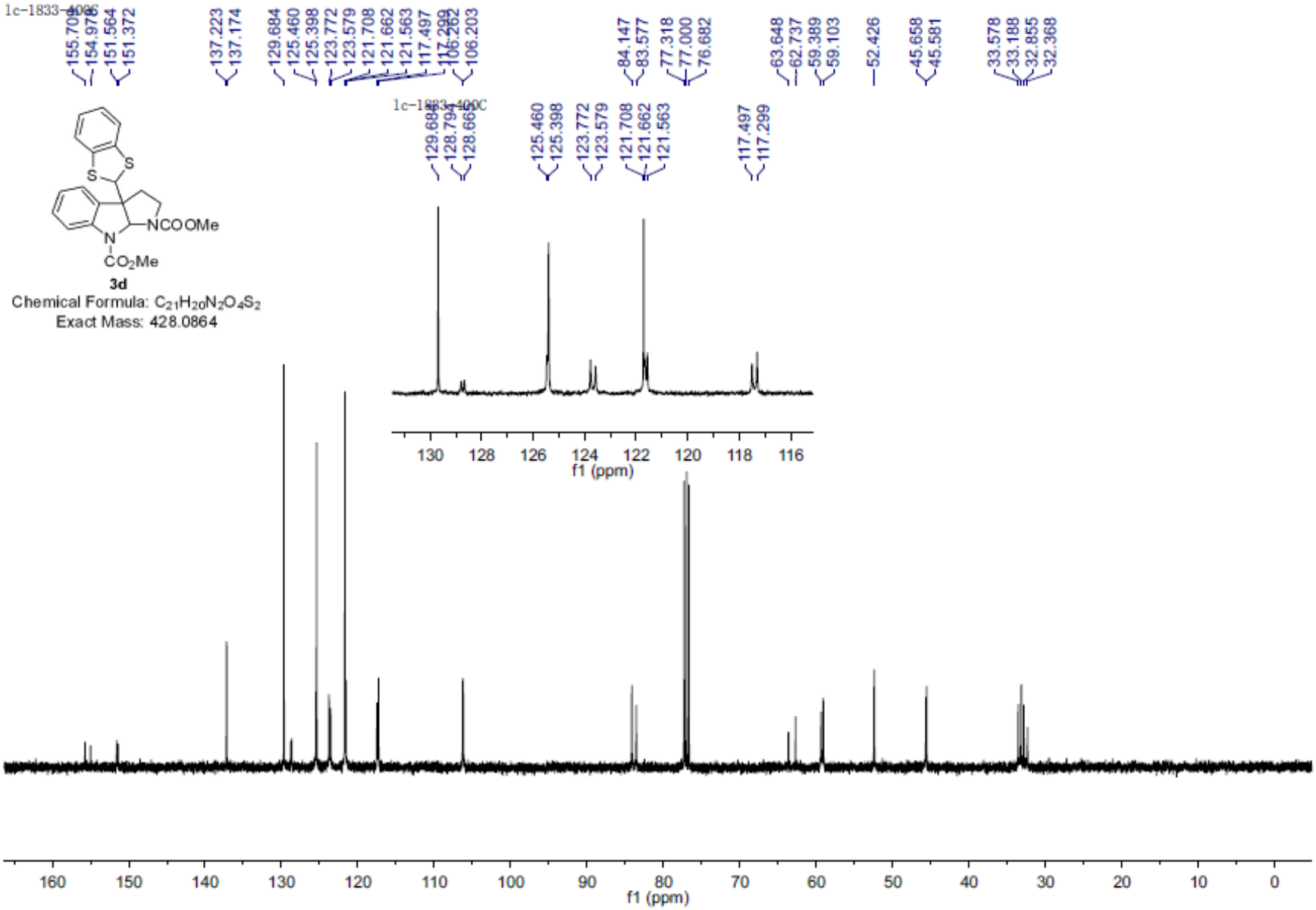

1c-1844
Std proton
Chemical Formula: C22H22N2O2S2
Exact Mass: 410.1123
3b
NCOOMe
7.258
7.243
7.188
7.169
7.141
7.125
7.091
6.992
6.984
6.660
6.643
6.418
6.399
6.379
5.581
5.515
5.288
5.239
5.216
5.173
5.147
5.103
5.080
5.054
4.068
4.025
3.942
3.923
3.893
3.855
3.850
3.675
3.653
3.019
3.005
2.998
2.980
2.286
2.257
2.229
2.210
2.142
2.128
2.114
2.101
2.088
2.072
-0.000
0.77
3.19
1.80
0.98
0.99
1.06
1.00
2.90
3.20
2.70
1.07
1.04
1.02
f1 (ppm)

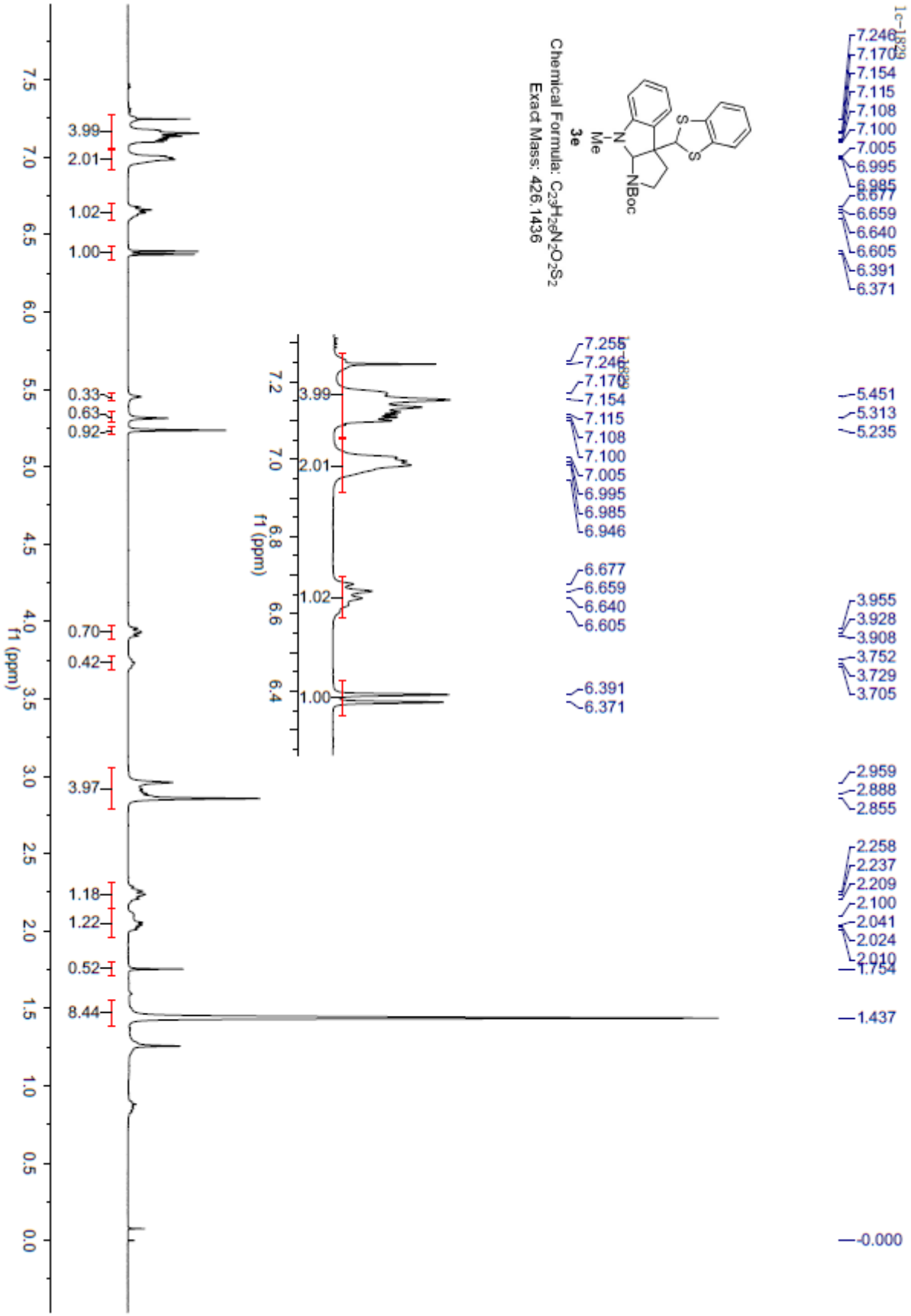

1c-1844-400C
Std carbon
155.397
154.657
150.446
137.090
134.160
133.796
129.523
128.866
128.733
125.385
125.328
123.761
123.443
121.668
121.633
121.559
117.421
117.172
115.925
106.567
106.317
82.770
82.147
77.317
77.000
76.681
63.734
62.773
59.767
59.436
52.382
48.719
48.591
45.150
34.418
33.812
3b
NCOOMe
Chemical Formula: C22H22N2O2S2
Exact Mass: 410.1123
f1 (ppm)

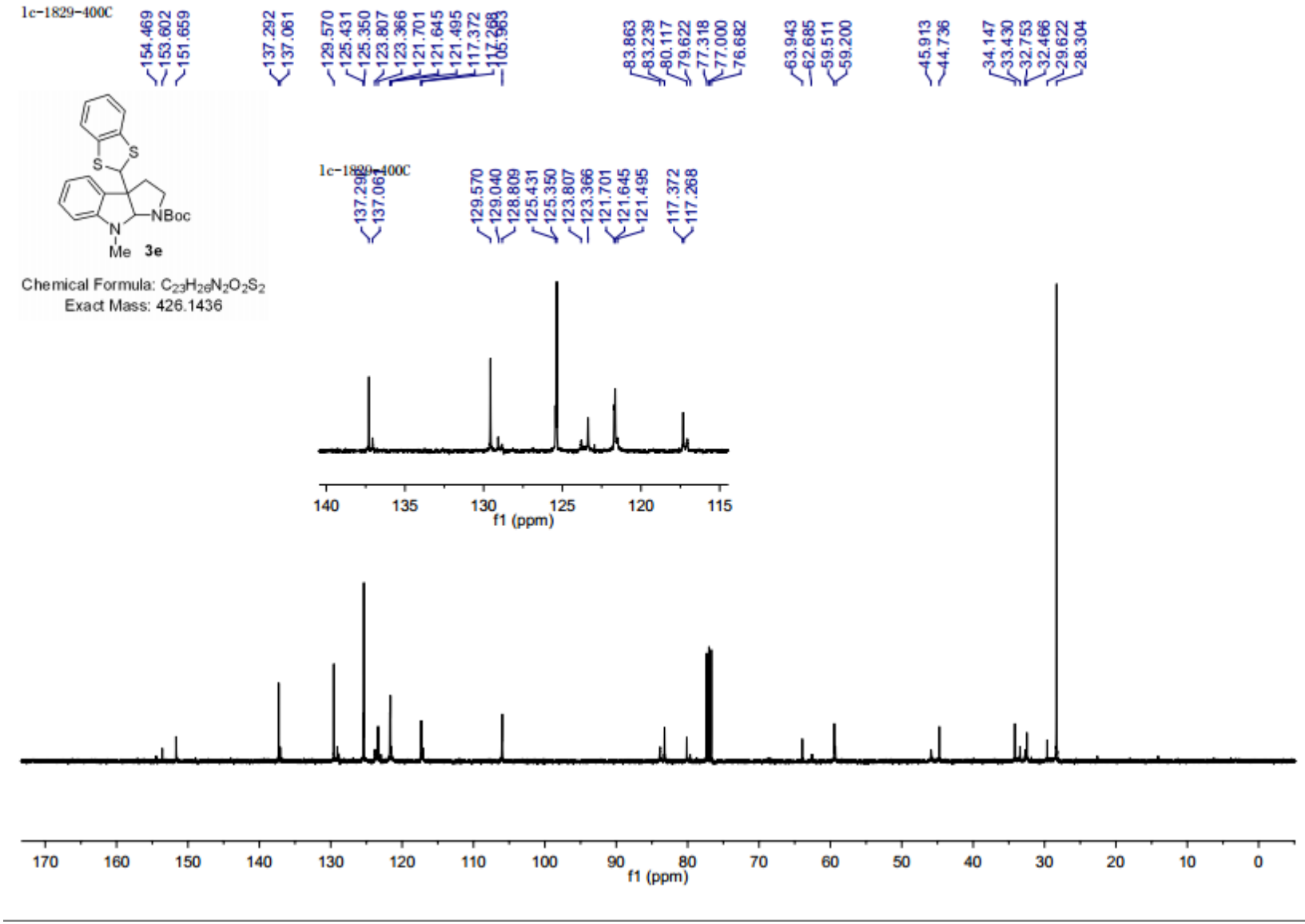

Chemical Formula: C26H24N2O2S2
Exact Mass: 460.1279
Bn
3c
NCOOMe
f1 (ppm)

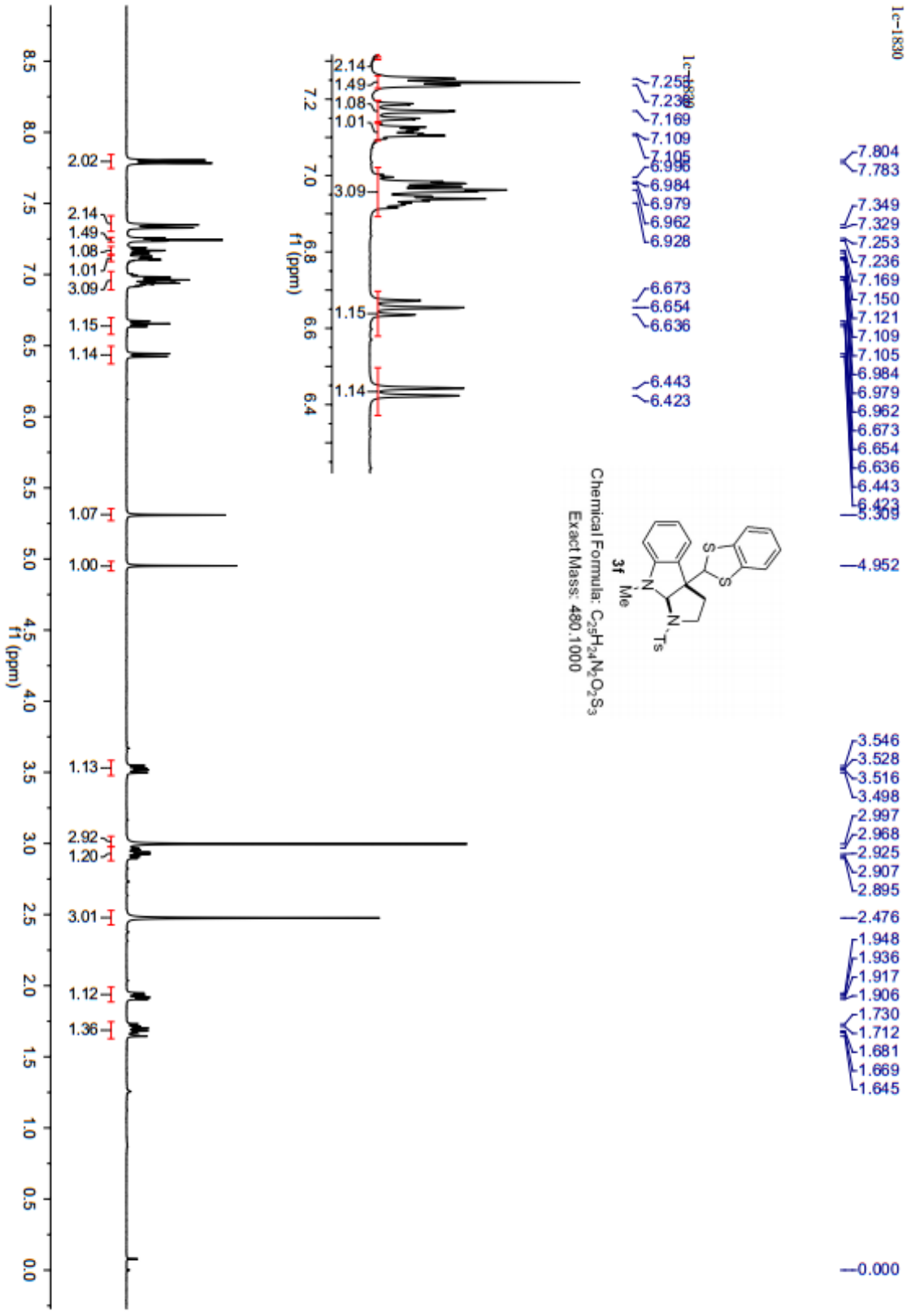

1c-1866-400C
155.464
154.631
150.930
150.587
138.866
137.169
137.055
129.673
128.758
128.402
128.308
126.984
126.259
125.479
125.357
121.630
121.551
106.496
77.317
77.000
76.680
63.954
62.954
59.679
59.119
52.414
52.172
50.397
49.954
45.253
34.265
33.430
117.673
117.359
NCOOMe
N
Bn
3c
Chemical Formula: C26H24N2O2S2
Exact Mass: 460.1279
f1 (ppm)
f1 (ppm)

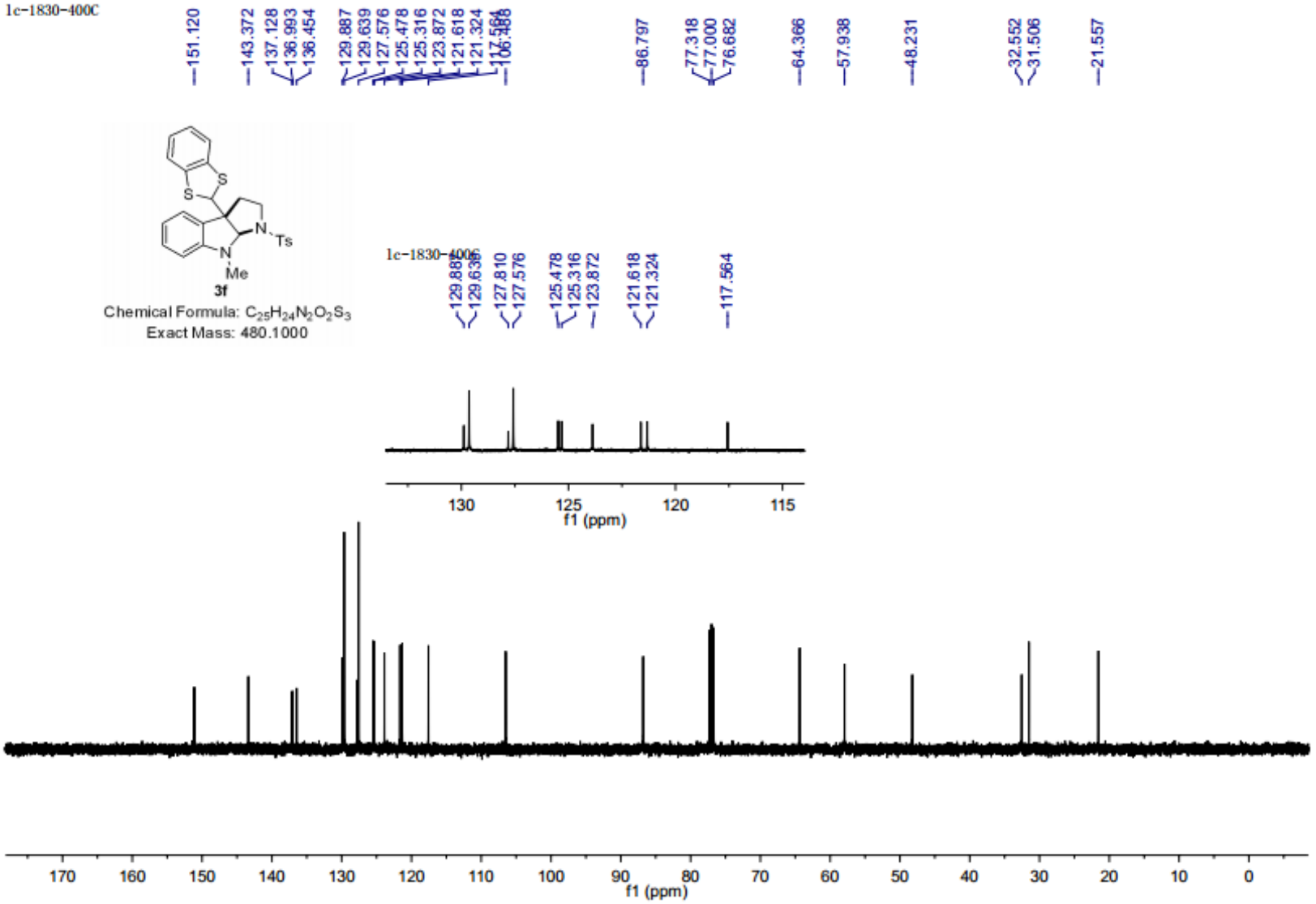

3d
Chemical Formula: C21H20N2O4S2
Exact Mass: 428.0864
CO2Me
NCOOMe
f1 (ppm)
1.24
2.79
1.94
1.03
1.01
1.00
1.00
0.54
0.63
2.82
3.90
1.09
1.09
7.268
7.248
7.226
7.208
7.179
7.176
7.157
7.143
7.125
7.114
7.105
6.994
6.986
6.980
6.683
6.666
6.653
6.635
6.406
6.386
5.468
5.416
5.267
5.219
3.954
3.933
3.928
3.907
3.793
3.771
3.766
3.745
3.714
3.688
2.978
2.960
2.945
2.932
2.279
2.249
2.229
2.201
2.178
2.141
2.127
2.112
2.098
2.083
2.069
-0.000

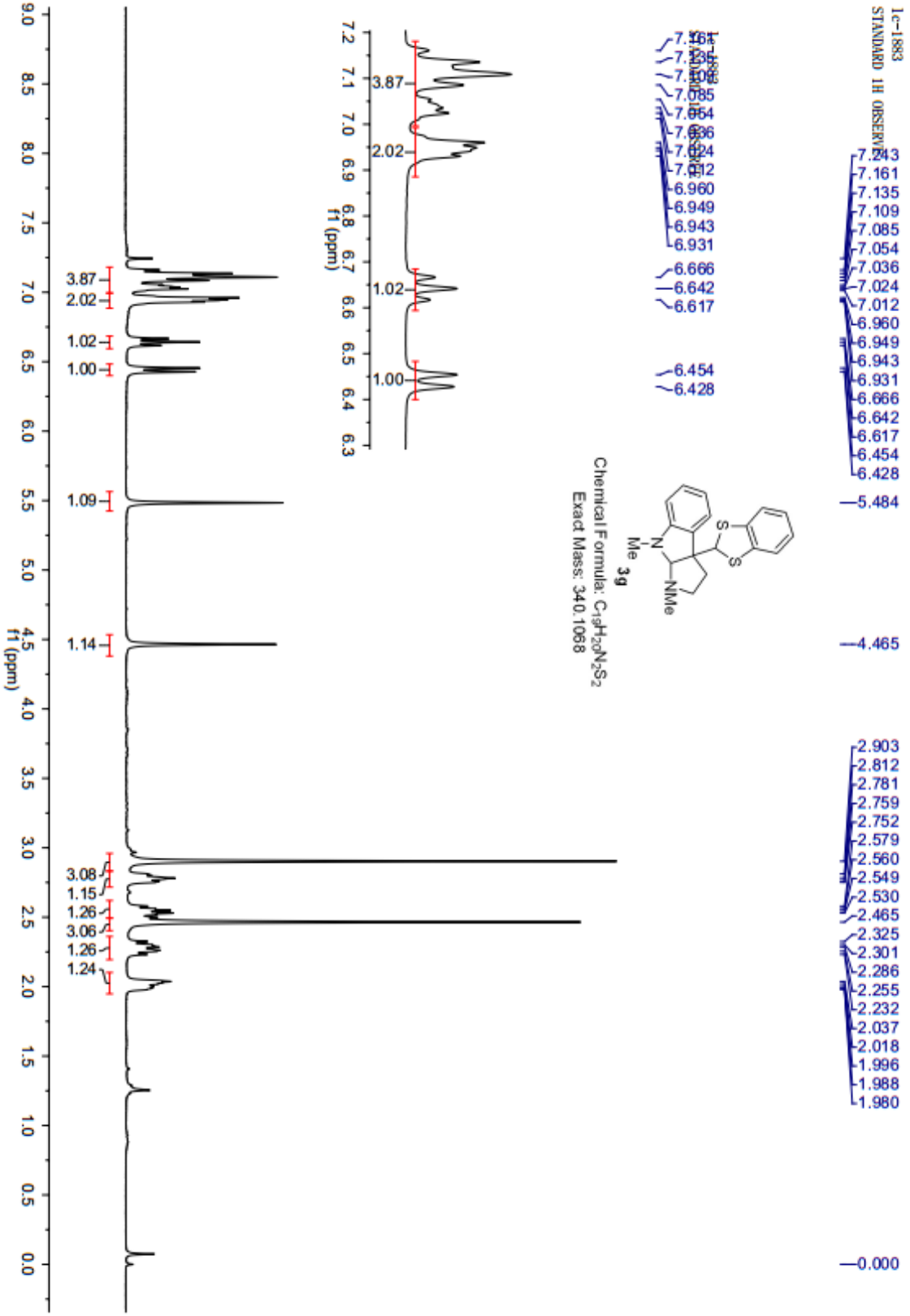

1c-1833-400C
155.709
154.976
151.564
151.372
137.223
137.174
129.684
125.460
125.398
123.772
123.579
121.708
121.662
121.563
117.497
117.299
106.262
106.203
84.147
83.577
77.318
77.000
76.682
63.648
62.737
59.389
59.103
52.426
45.658
45.581
33.578
33.188
32.855
32.368
1c-1833-400C
129.684
128.794
128.665
125.460
125.398
123.772
123.579
121.708
121.662
121.563
117.497
117.299
130
128
126
124
122
120
118
116
f1 (ppm)
S
S
NCOOMe
N
CO2Me
3d
Chemical Formula: C21H20N2O4S2
Exact Mass: 428.0864
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

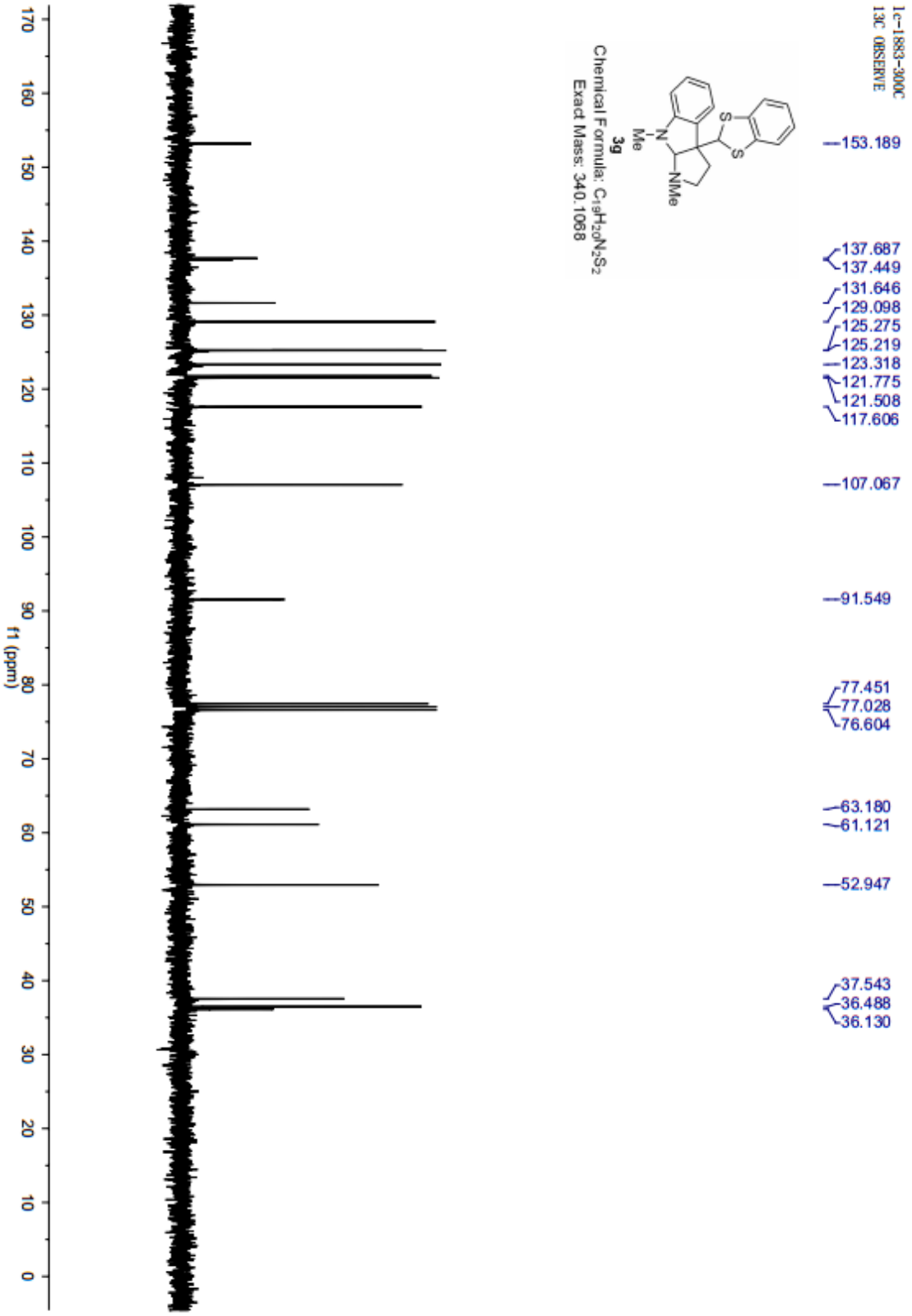

1c-1829
Chemical Formula: C23H26N2O2S2
Exact Mass: 426.1436
3e
Me
N
NBoc
S
S
f1 (ppm)
3.99
2.01
1.02
1.00
0.33
0.63
0.92
0.70
0.42
3.97
1.18
1.22
0.52
8.44
7.246
7.170
7.154
7.115
7.108
7.100
7.005
6.995
6.985
6.677
6.659
6.640
6.605
6.391
6.371
5.451
5.313
5.235
3.955
3.928
3.908
3.752
3.729
3.705
2.959
2.888
2.855
2.258
2.237
2.209
2.100
2.041
2.024
2.010
1.754
1.437
0.000


1c-1829-400C
154.469
153.602
151.659
137.292
137.061
129.570
125.431
125.350
123.807
123.366
121.701
121.645
121.495
117.372
117.268
105.883
83.863
83.239
80.117
79.622
77.318
77.000
76.682
63.943
62.685
59.511
59.200
45.913
44.736
34.147
33.430
32.753
32.466
29.622
28.304
S
S
NBoc
N
Me
3e
Chemical Formula: C23H26N2O2S2
Exact Mass: 426.1436
1c-1829-400C
137.292
137.061
129.570
129.040
128.809
125.431
125.350
123.807
123.366
121.701
121.645
121.495
117.372
117.268
140
135
130
125
120
115
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


1c-1830
7.804
7.783
7.349
7.329
7.253
7.236
7.169
7.150
7.121
7.109
7.105
6.984
6.979
6.962
6.673
6.654
6.636
6.443
6.423
5.309
4.952
3.546
3.528
3.516
3.498
2.997
2.968
2.925
2.907
2.895
2.476
1.948
1.936
1.917
1.906
1.730
1.712
1.681
1.669
1.645
0.000
3f
Me
Ts
Chemical Formula: C25H24N2O2S3
Exact Mass: 480.1000
f1 (ppm)

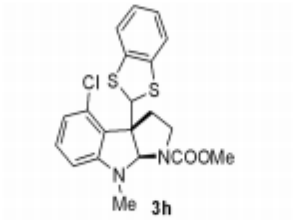

1c-1830-400C
151.120
143.372
137.128
136.993
136.454
129.887
129.639
127.576
125.478
125.316
123.872
121.618
121.324
86.797
77.318
77.000
76.682
64.366
57.938
48.231
32.552
31.506
21.557
3f
Chemical Formula: C25H24N2O2S3
Exact Mass: 480.1000
1c-1830-400C
129.887
129.639
127.810
127.576
125.478
125.316
123.872
121.618
121.324
117.564
130
125
120
115
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


1c-1883
STANDARD 1H OBSERVE
7.243
7.161
7.135
7.109
7.085
7.054
7.036
7.024
7.012
6.960
6.949
6.943
6.931
6.666
6.642
6.617
6.454
6.428
5.484
4.465
2.903
2.812
2.781
2.759
2.752
2.579
2.560
2.549
2.530
2.465
2.325
2.301
2.286
2.255
2.232
2.037
2.018
1.996
1.988
1.980
0.000
Chemical Formula: C19H20N2S2
Exact Mass: 340.1068
Me
3g
NMe
S
S
N
3.87
2.02
1.02
1.00
1.09
1.14
3.08
1.15
1.26
3.06
1.26
1.24
f1 (ppm)


1c-1883-300C
13C OBSERVE
153.189
137.687
137.449
131.646
129.098
125.275
125.219
123.318
121.775
121.508
117.606
107.067
91.549
77.451
77.028
76.604
63.180
61.121
52.947
37.543
36.488
36.130
3g
Chemical Formula: C19H20N2S2
Exact Mass: 340.1068
Me
N
NMe
S
S
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

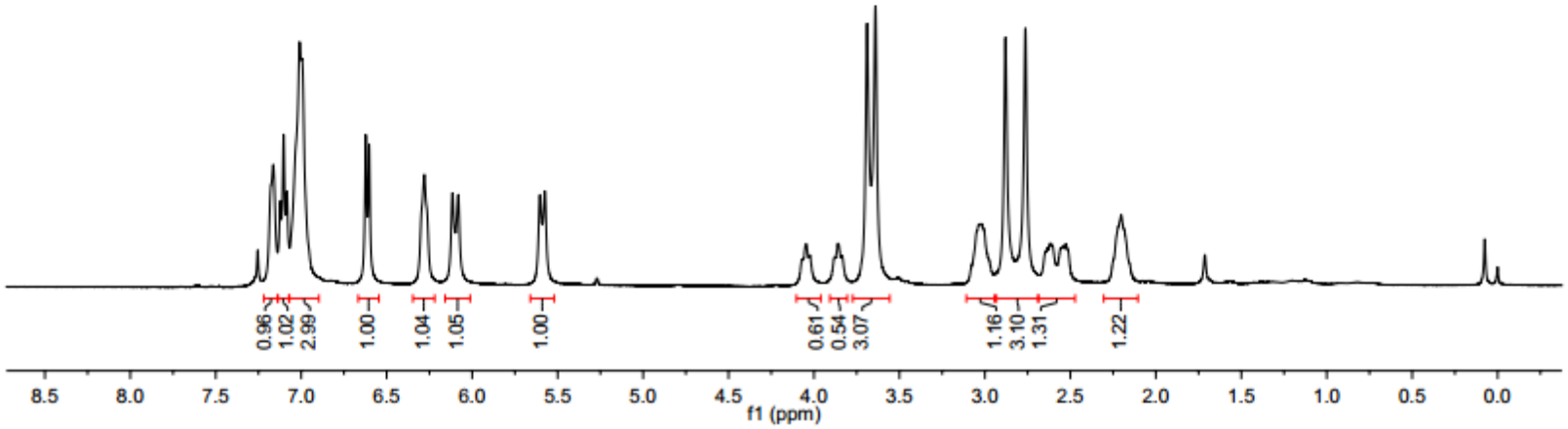
1c-1865

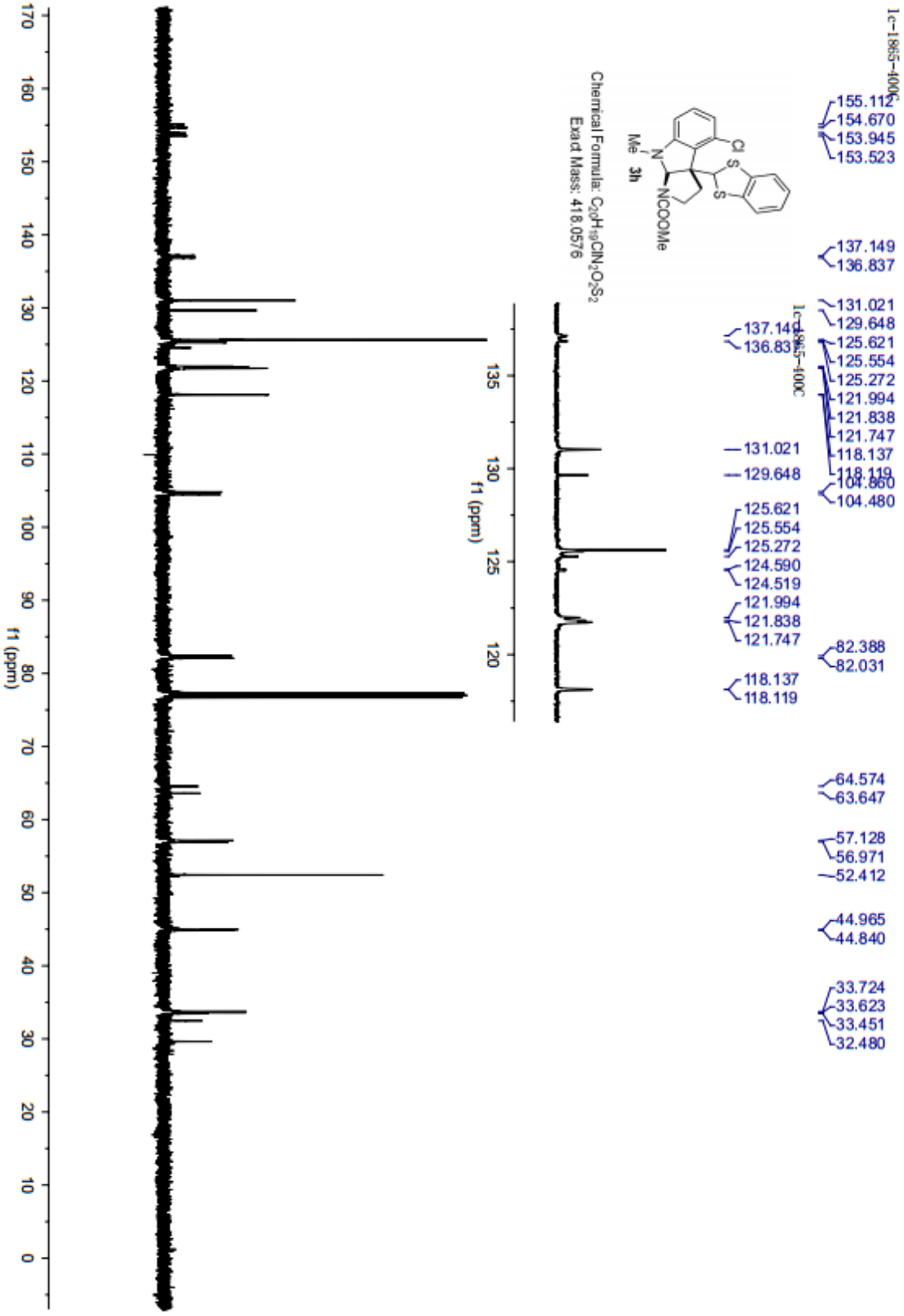
7.254 7.177 7.164 7.163 7.122 7.103 7.083 7.009 6.995 6.948 6.622 6.603 6.321 6.280 6.265 6.115 6.082 5.604 5.575 4.072 4.047 4.022 3.885 3.860 3.825 3.689 3.640 3.048 3.037 3.003 2.879 2.763 2.617 2.526 2.218 2.203 2.178 0.000

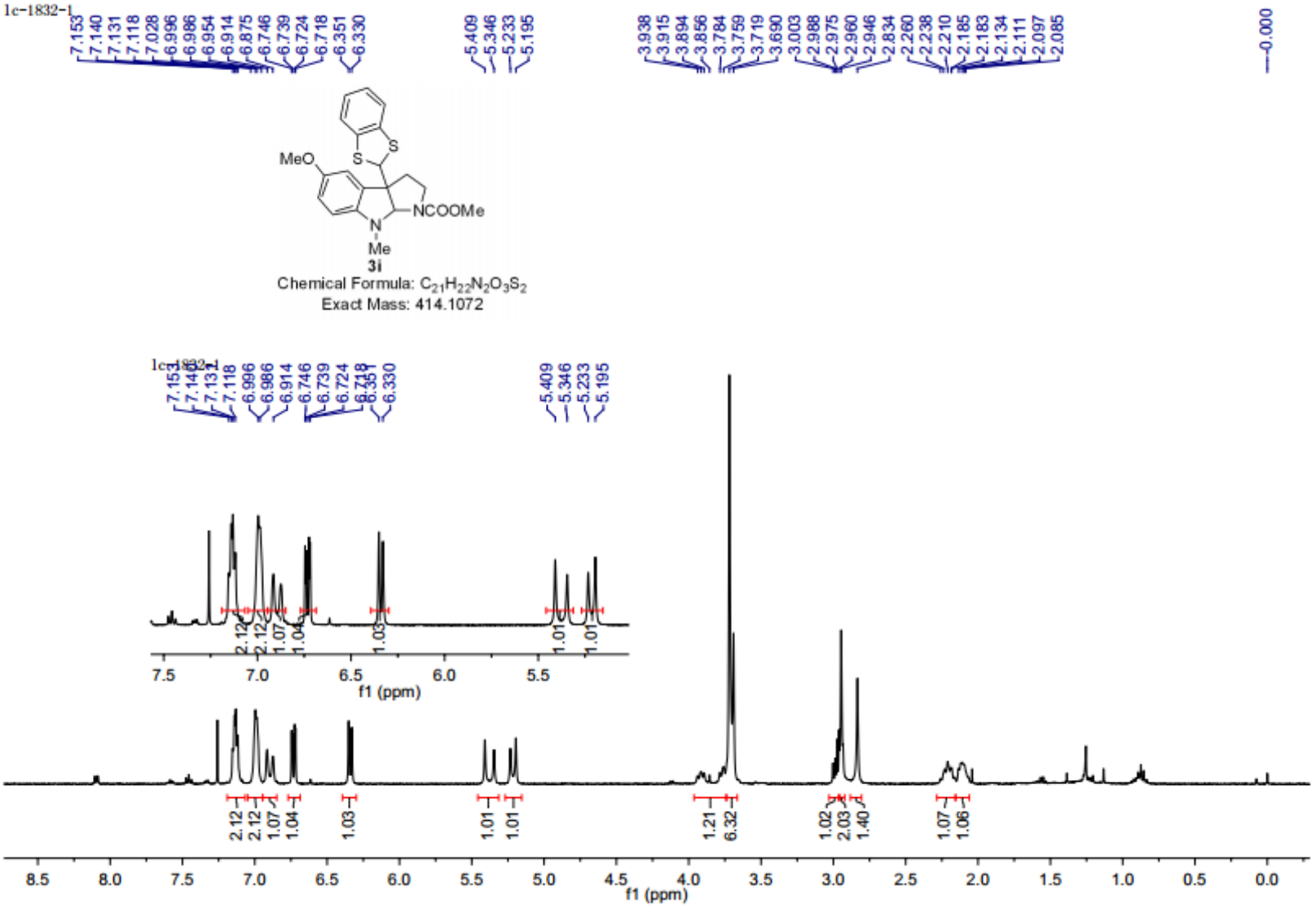


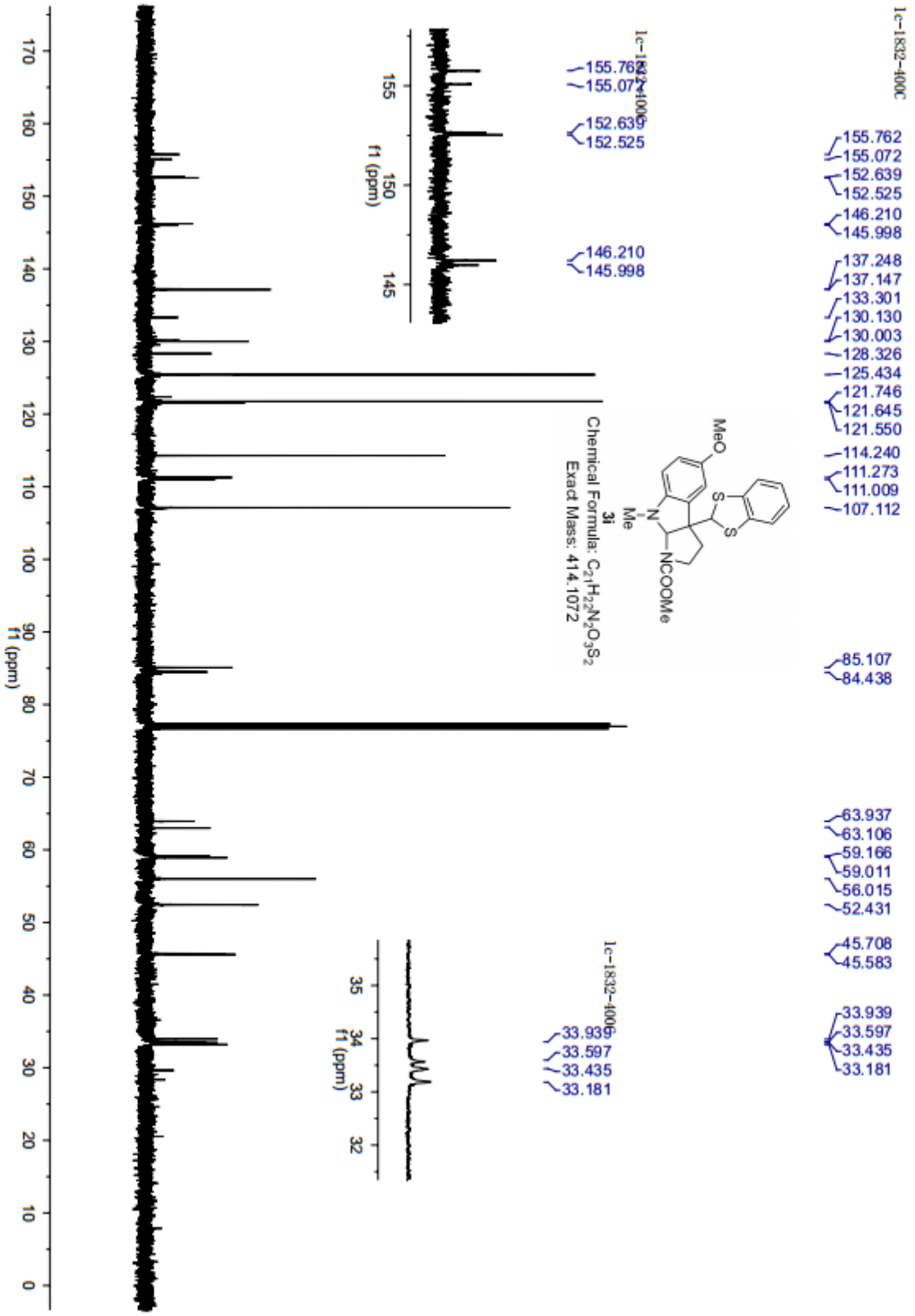
3h

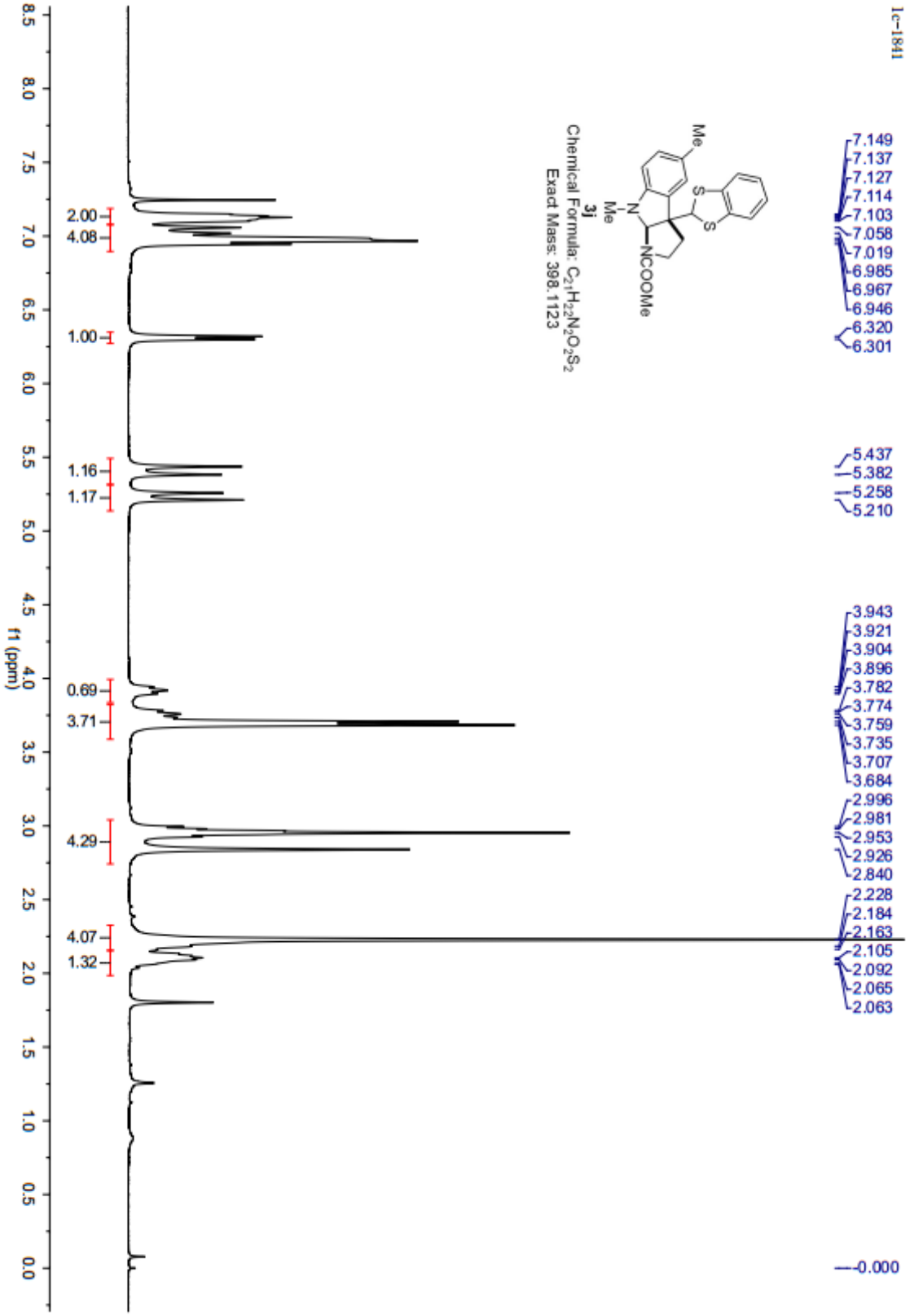
Chemical Formula: $C_{20}H_{19}ClN_2O_2S_2$
Exact Mass: 418.0576

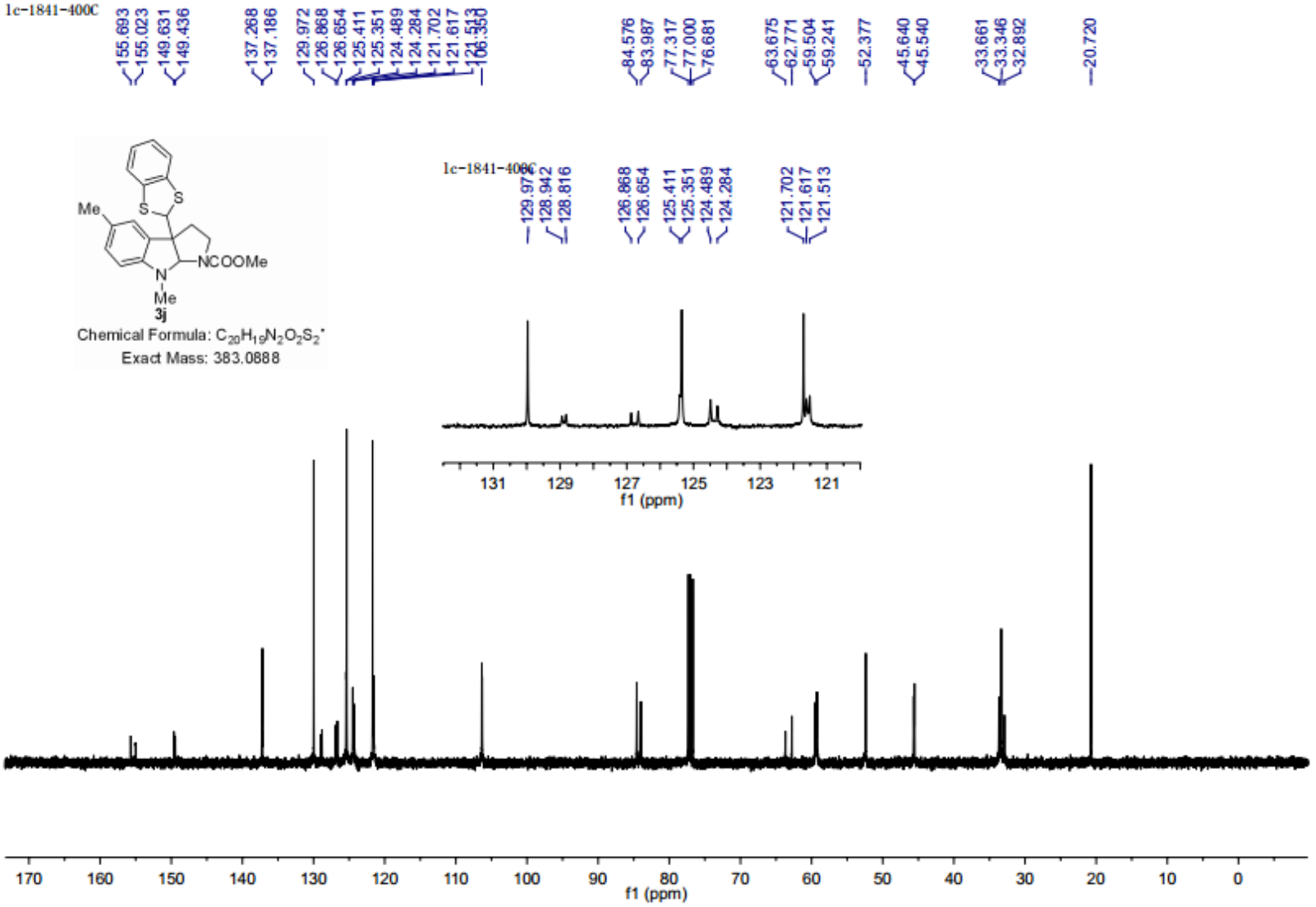


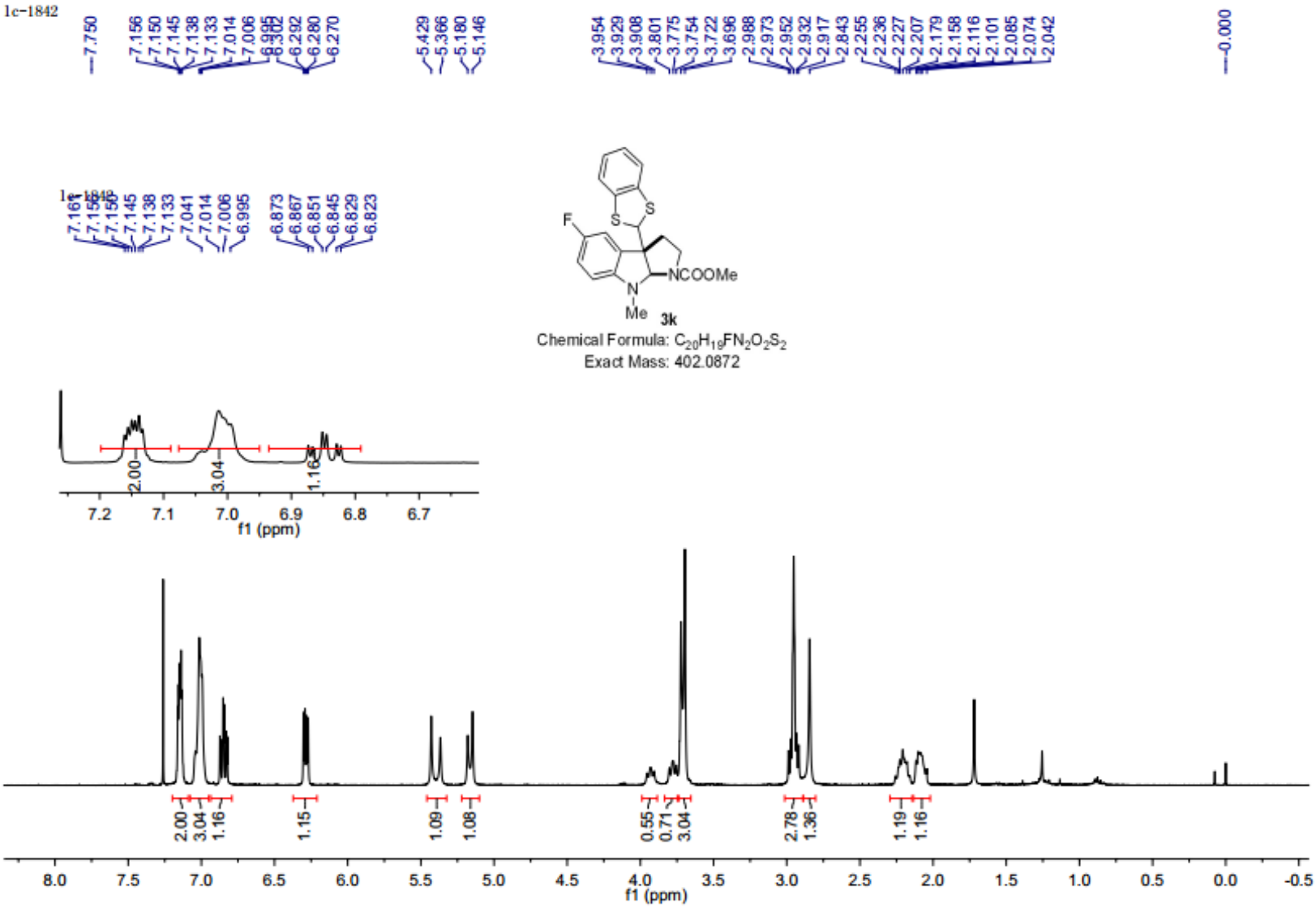

1c-1865-400C
155.112
154.670
153.945
153.523
137.149
136.837
131.021
129.648
125.621
125.554
125.272
121.994
121.838
121.747
118.137
118.119
104.860
104.480
82.388
82.031
64.574
63.647
57.128
56.971
52.412
44.965
44.840
33.724
33.623
33.451
32.480
Chemical Formula: C20H19ClN2O2S2
Exact Mass: 418.0576
Me
3h
NCOOMe
Cl
S
S
N
f1 (ppm)

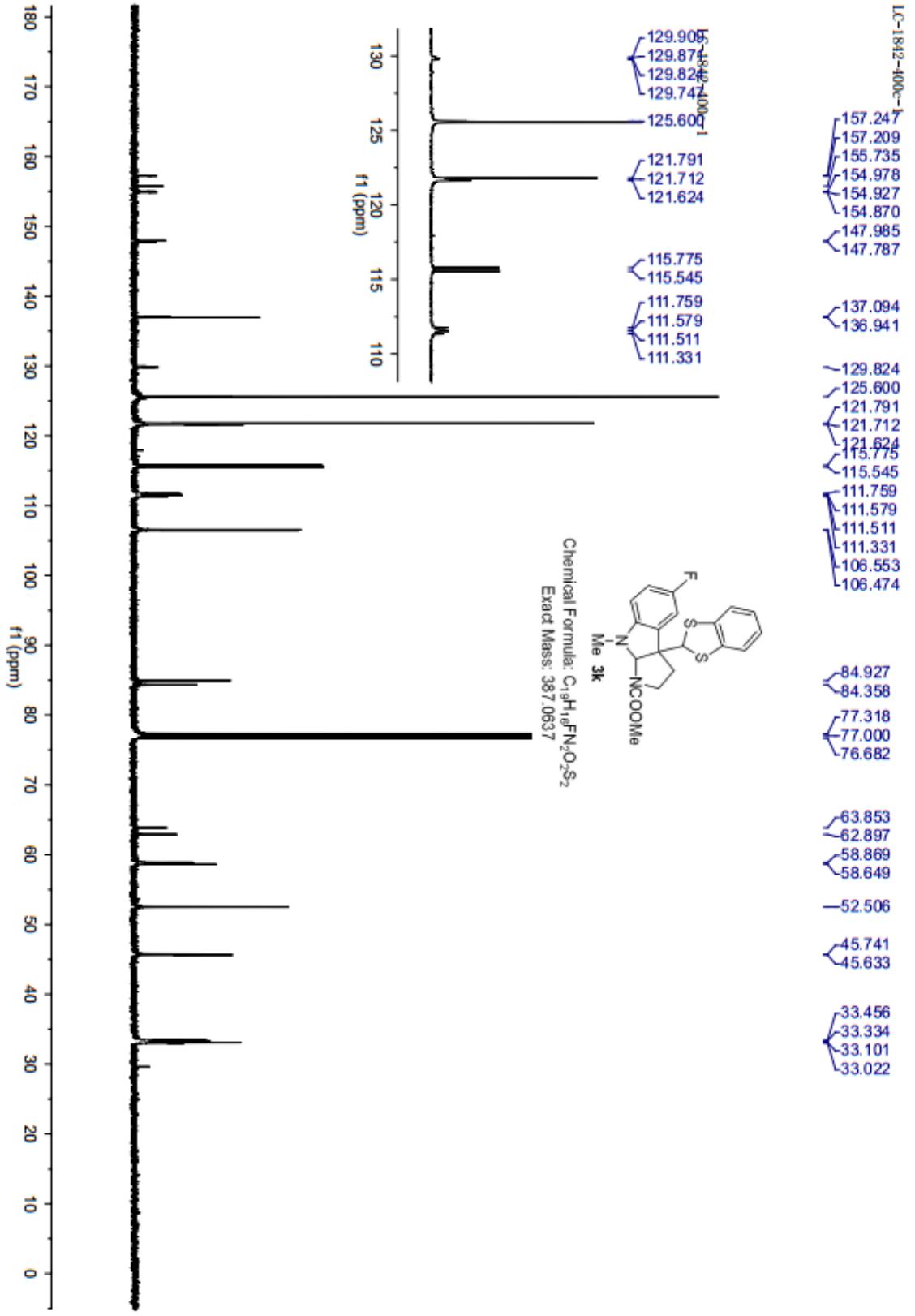

1c-1832-1
7.153
7.140
7.131
7.118
7.028
6.996
6.986
6.954
6.914
6.875
6.746
6.739
6.724
6.718
6.351
6.330
5.409
5.346
5.233
5.195
3.938
3.915
3.894
3.856
3.784
3.759
3.719
3.690
3.003
2.988
2.975
2.960
2.946
2.834
2.260
2.238
2.210
2.185
2.183
2.134
2.111
2.097
2.085
0.000
MeO
S
S
NCOOMe
N
Me
3i
Chemical Formula: C21H22N2O3S2
Exact Mass: 414.1072
2.12
2.12
1.07
1.04
1.03
1.01
1.01
1.21
6.32
1.02
2.03
1.40
1.07
1.06
f1 (ppm)

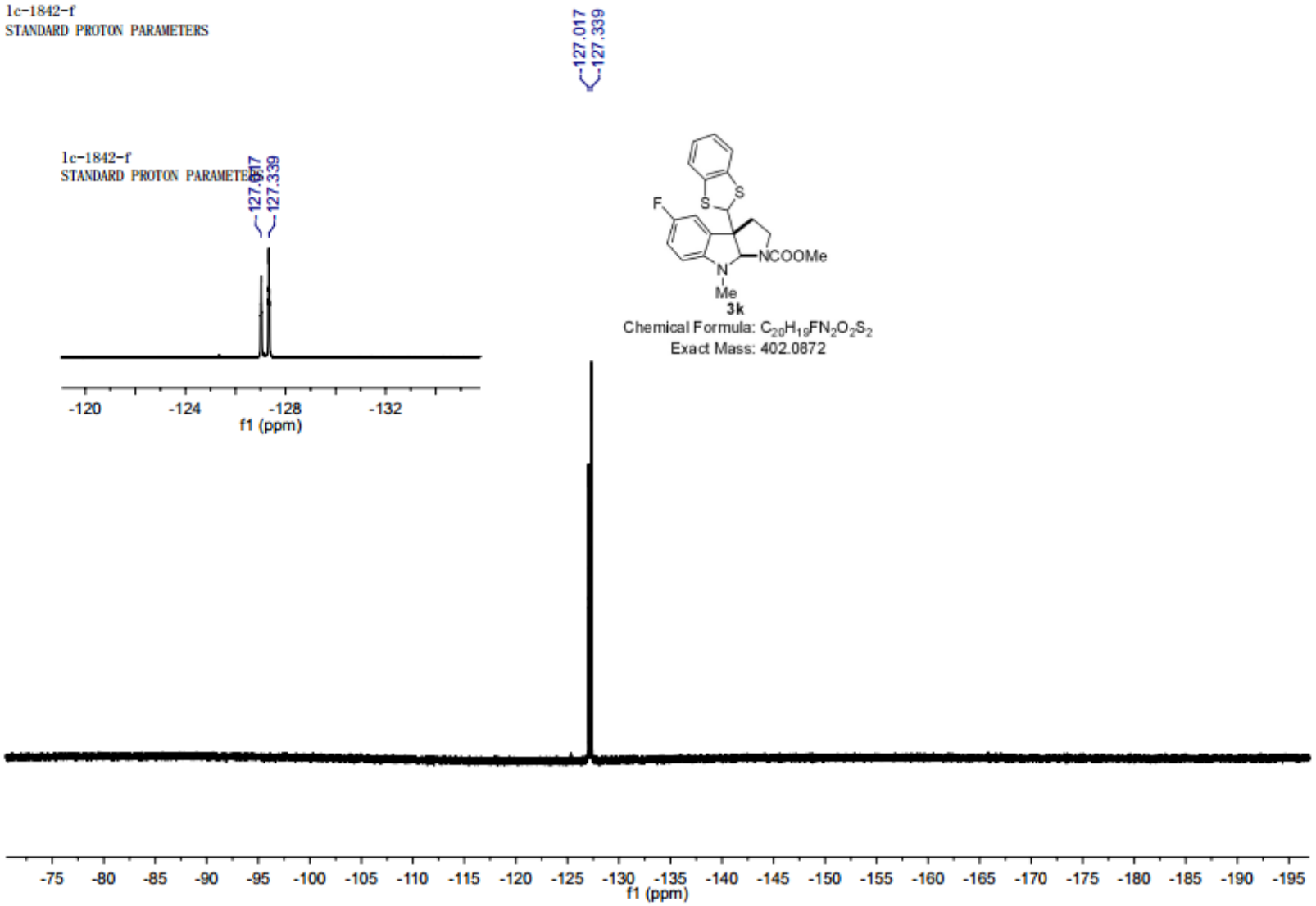

1c-1832-400C
155.762
155.072
152.639
152.525
146.210
145.998
137.248
137.147
133.301
130.130
130.003
128.326
125.434
121.746
121.645
121.550
114.240
111.273
111.009
107.112
85.107
84.438
63.937
63.106
59.166
59.011
56.015
52.431
45.708
45.583
33.939
33.597
33.435
33.181
MeO
N
Me
S
S
NCOOMe
3i
Chemical Formula: C21H22N2O3S2
Exact Mass: 414.1072
f1 (ppm)

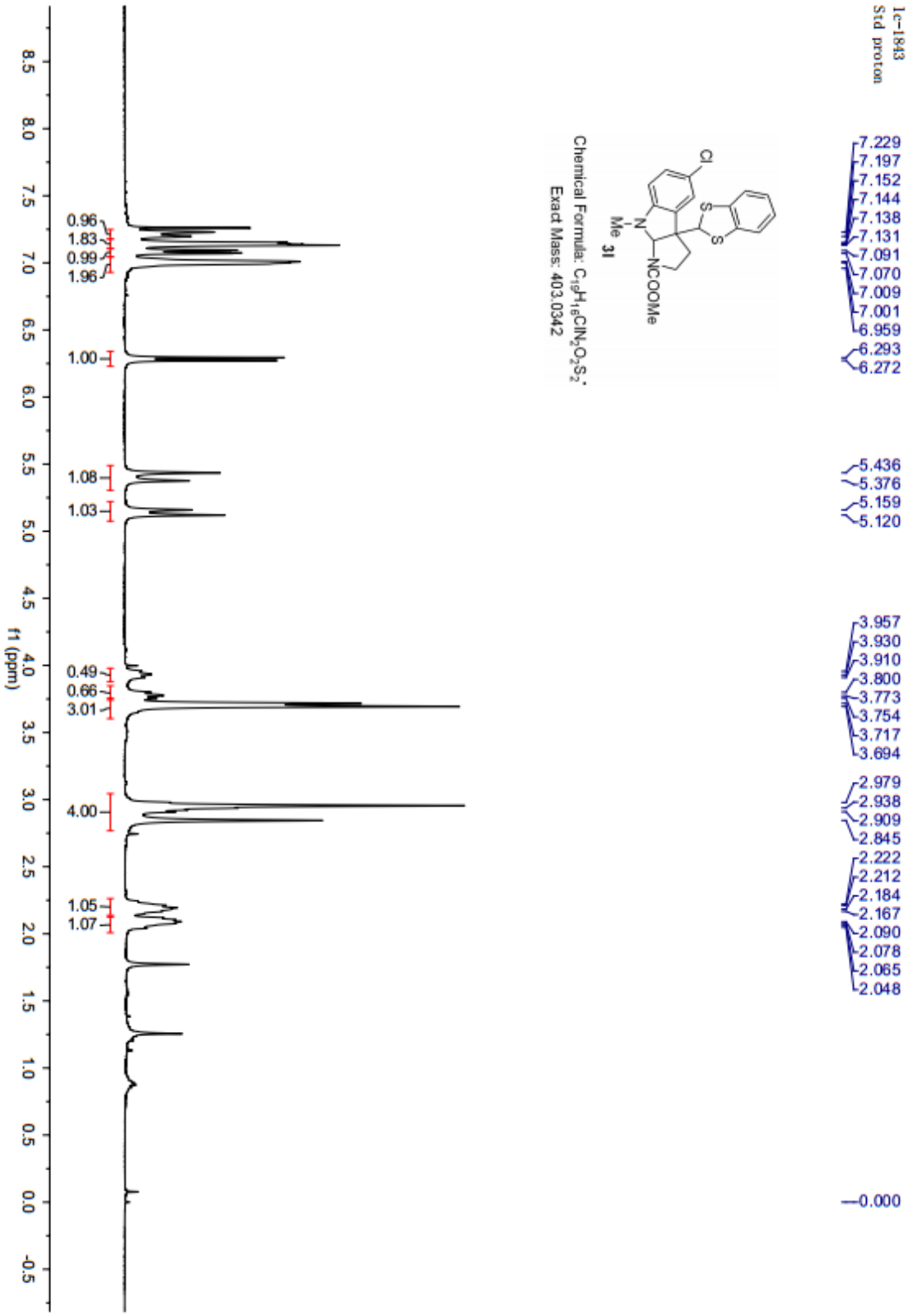

1c-1841
3j
Chemical Formula: C21H22N2O2S2
Exact Mass: 398.1123
Me
N
Me
NCOOMe
S
S
7.149
7.137
7.127
7.114
7.103
7.058
7.019
6.985
6.967
6.946
6.320
6.301
5.437
5.382
5.258
5.210
3.943
3.921
3.904
3.896
3.782
3.774
3.759
3.735
3.707
3.684
2.996
2.981
2.953
2.926
2.840
2.228
2.184
2.163
2.105
2.092
2.065
2.063
0.000
2.00
4.08
1.00
1.16
1.17
0.69
3.71
4.29
4.07
1.32
f1 (ppm)

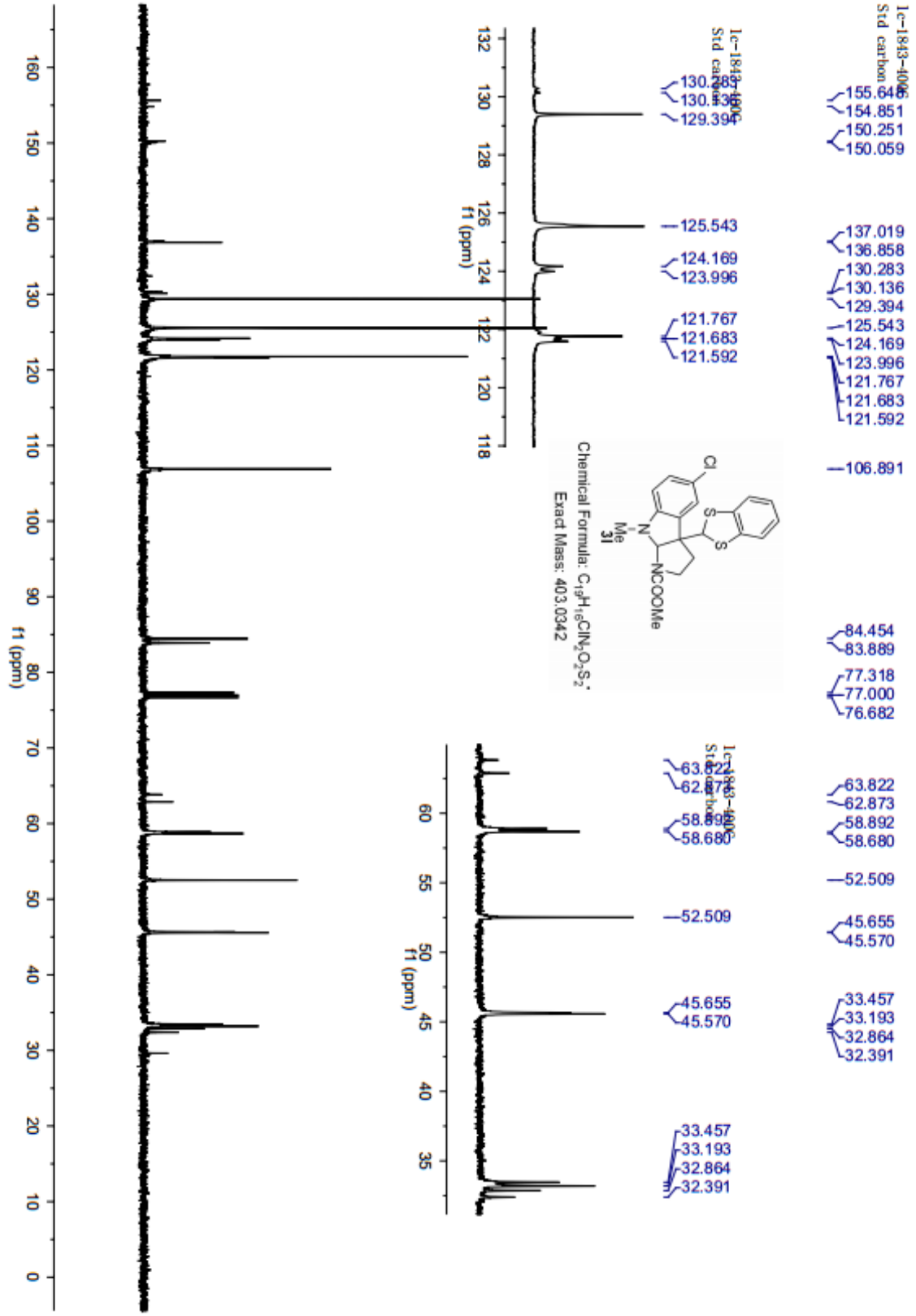

1c-1841-400C
155.693
155.023
149.631
149.436
137.268
137.186
129.972
126.868
126.654
125.411
125.351
124.489
124.284
121.702
121.617
121.513
84.576
83.987
77.317
77.000
76.681
63.675
62.771
59.504
59.241
52.377
45.640
45.540
33.661
33.346
32.892
20.720
Me
S
S
N
NCOOMe
Me
3j
Chemical Formula: C20H19N2O2S2+
Exact Mass: 383.0888
1c-1841-400C
129.972
128.942
128.816
126.868
126.654
125.411
125.351
124.489
124.284
121.702
121.617
121.513
131
129
127
125
123
121
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

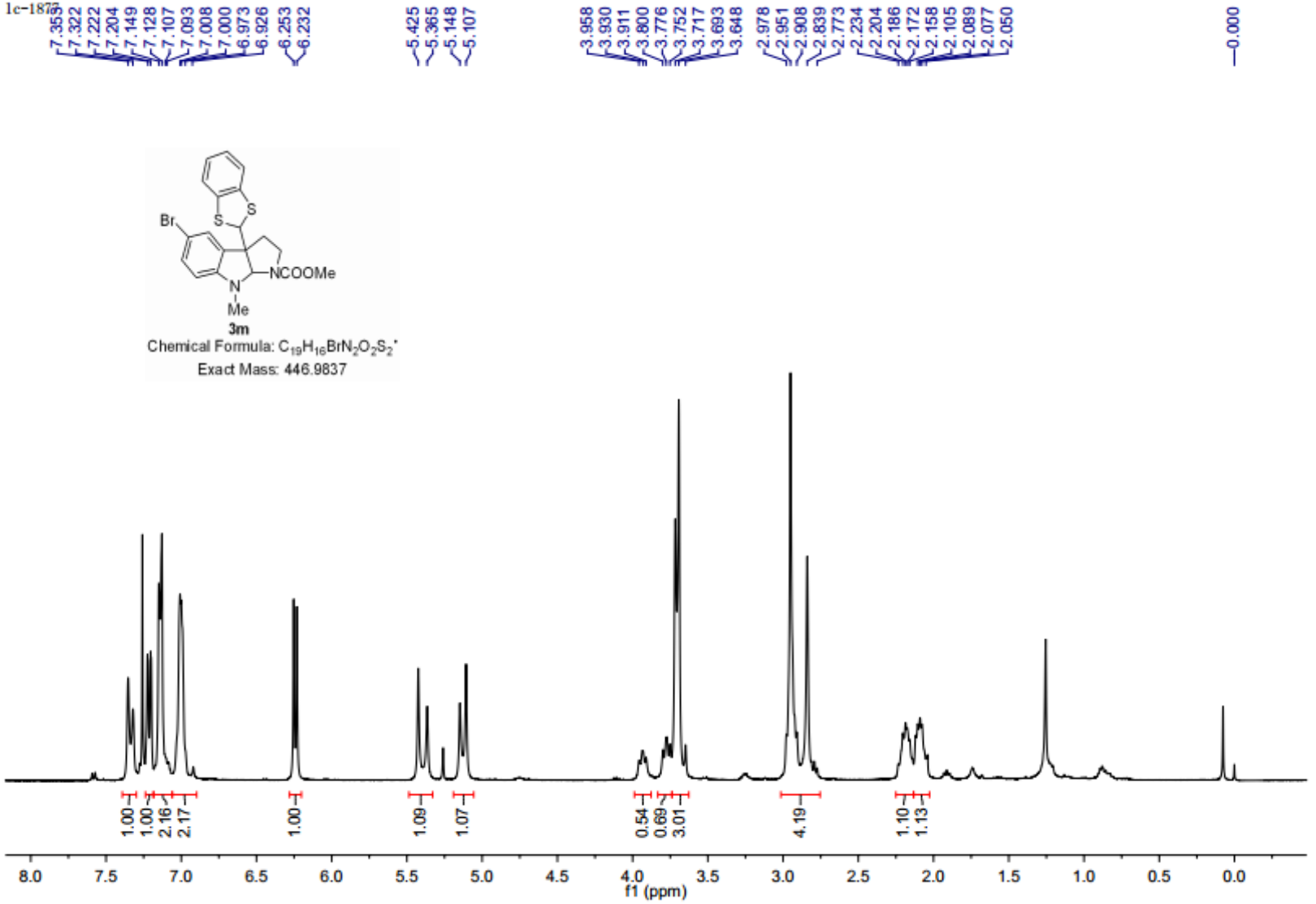

1c-1842
7.750
7.156
7.150
7.145
7.138
7.133
7.014
7.006
6.995
6.302
6.292
6.280
6.270
5.429
5.366
5.180
5.146
3.954
3.929
3.908
3.801
3.775
3.754
3.722
3.696
2.988
2.973
2.952
2.932
2.917
2.843
2.255
2.236
2.227
2.207
2.179
2.158
2.116
2.101
2.085
2.074
2.042
0.000
1c-1842
7.161
7.156
7.150
7.145
7.138
7.133
7.041
7.014
7.006
6.995
6.873
6.867
6.851
6.845
6.829
6.823
F
S
S
NCOOMe
N
Me
3k
Chemical Formula: C20H19FN2O2S2
Exact Mass: 402.0872
2.00
3.04
1.16
7.2
7.1
7.0
6.9
6.8
6.7
f1 (ppm)
2.00
3.04
1.16
1.15
1.09
1.08
0.55
0.71
3.04
2.78
1.36
1.19
1.16
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

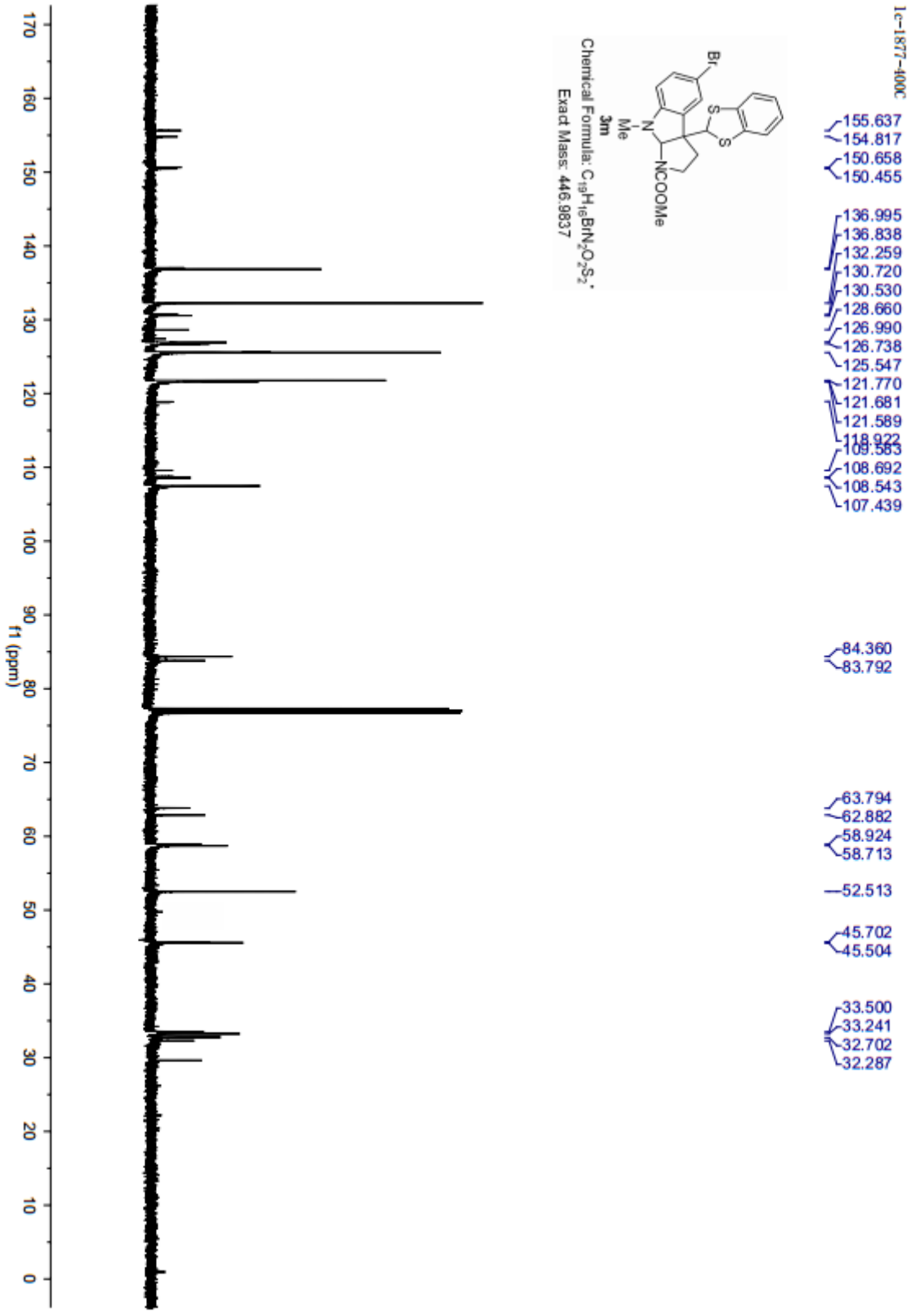

LC-1842-400c-1
157.247
157.209
155.735
154.978
154.927
154.870
147.985
147.787
137.094
136.941
129.824
125.600
121.791
121.712
121.624
115.775
115.545
111.759
111.579
111.511
111.331
106.553
106.474
84.927
84.358
77.318
77.000
76.682
63.853
62.897
58.869
58.649
52.506
45.741
45.633
33.456
33.334
33.101
33.022
LC-1842-400c-1
129.906
129.874
129.824
129.741
125.600
121.791
121.712
121.624
115.775
115.545
111.759
111.579
111.511
111.331
f1 (ppm)
Chemical Formula: C19H16FN2O2S2
Exact Mass: 387.0637
Me 3k
f1 (ppm)


1c-1842-f
STANDARD PROTON PARAMETERS
127.017
127.339
1c-1842-f
STANDARD PROTON PARAMETERS
127.017
127.339
-120
-124
-128
-132
f1 (ppm)
F
S
S
N
NCOOMe
Me
3k
Chemical Formula: C20H19FN2O2S2
Exact Mass: 402.0872
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
-185
-190
-195
f1 (ppm)


1c-1843
Std proton
7.229
7.197
7.152
7.144
7.138
7.131
7.091
7.070
7.009
7.001
6.959
6.293
6.272
5.436
5.376
5.159
5.120
3.957
3.930
3.910
3.800
3.773
3.754
3.717
3.694
2.979
2.938
2.909
2.845
2.222
2.212
2.184
2.167
2.090
2.078
2.065
2.048
0.000
Chemical Formula: C19H16ClN2O2S2+
Exact Mass: 403.0342
Cl
S
S
N
Me
3l
NCOOMe
0.96
1.83
0.99
1.96
1.00
1.08
1.03
0.49
0.66
3.01
4.00
1.05
1.07
f1 (ppm)

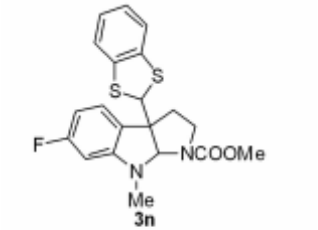

1c-1843-400C
Std carbon
155.646
154.851
150.251
150.059
137.019
136.858
130.283
130.136
129.394
125.543
124.169
123.996
121.767
121.683
121.592
106.891
84.454
83.889
77.318
77.000
76.682
63.822
62.873
58.892
58.680
52.509
45.655
45.570
33.457
33.193
32.864
32.391
Chemical Formula: C19H16ClN2O2S2+
Exact Mass: 403.0342
3l
Me
N
NCOOMe
S
S
Cl
f1 (ppm)


1c-1877
7.353
7.322
7.222
7.204
7.149
7.128
7.107
7.093
7.008
7.000
6.973
6.926
6.253
6.232
5.425
5.365
5.148
5.107
3.958
3.930
3.911
3.800
3.776
3.752
3.717
3.693
3.648
2.978
2.951
2.908
2.839
2.773
2.234
2.204
2.186
2.172
2.158
2.105
2.089
2.077
2.050
0.000
Br
S
S
N
NCOOMe
Me
3m
Chemical Formula: C19H16BrN2O2S2+
Exact Mass: 446.9837
1.00
1.00
2.16
2.17
1.00
1.09
1.07
0.54
0.69
3.01
4.19
1.10
1.13
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


1c-1877-400C
155.637
154.817
150.658
150.455
136.995
136.838
132.259
130.720
130.530
128.660
126.990
126.738
125.547
121.770
121.681
121.589
118.922
109.583
108.692
108.543
107.439
84.360
83.792
63.794
62.882
58.924
58.713
52.513
45.702
45.504
33.500
33.241
32.702
32.287
Br
S
S
N
Me
NCOOMe
3m
Chemical Formula: C19H16BrN2O2S2+
Exact Mass: 446.9837
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

1c-1845

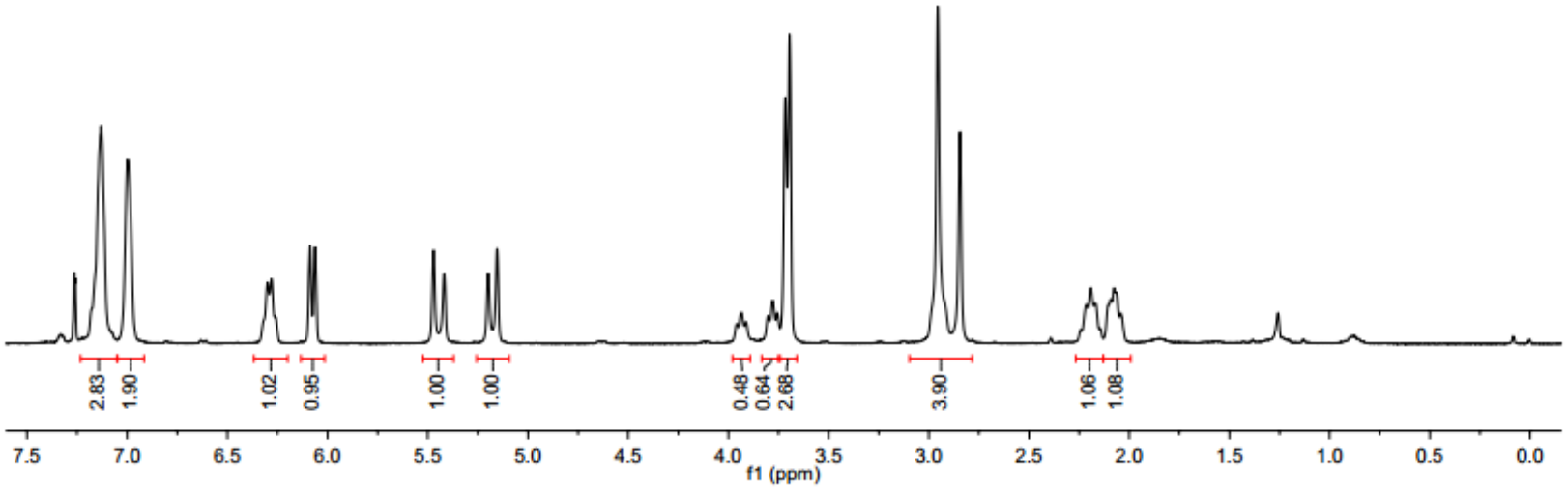
7.176 7.130 7.086 7.039 6.997 6.945 6.341 6.299 6.279 6.264 6.087 6.062 5.471 5.418 5.198 5.155 3.959 3.936 3.912 3.802 3.778 3.757 3.716 3.695 3.005 2.955 2.845 2.241 2.214 2.192 2.168 2.105 2.103 2.075 2.064 2.037 0.000

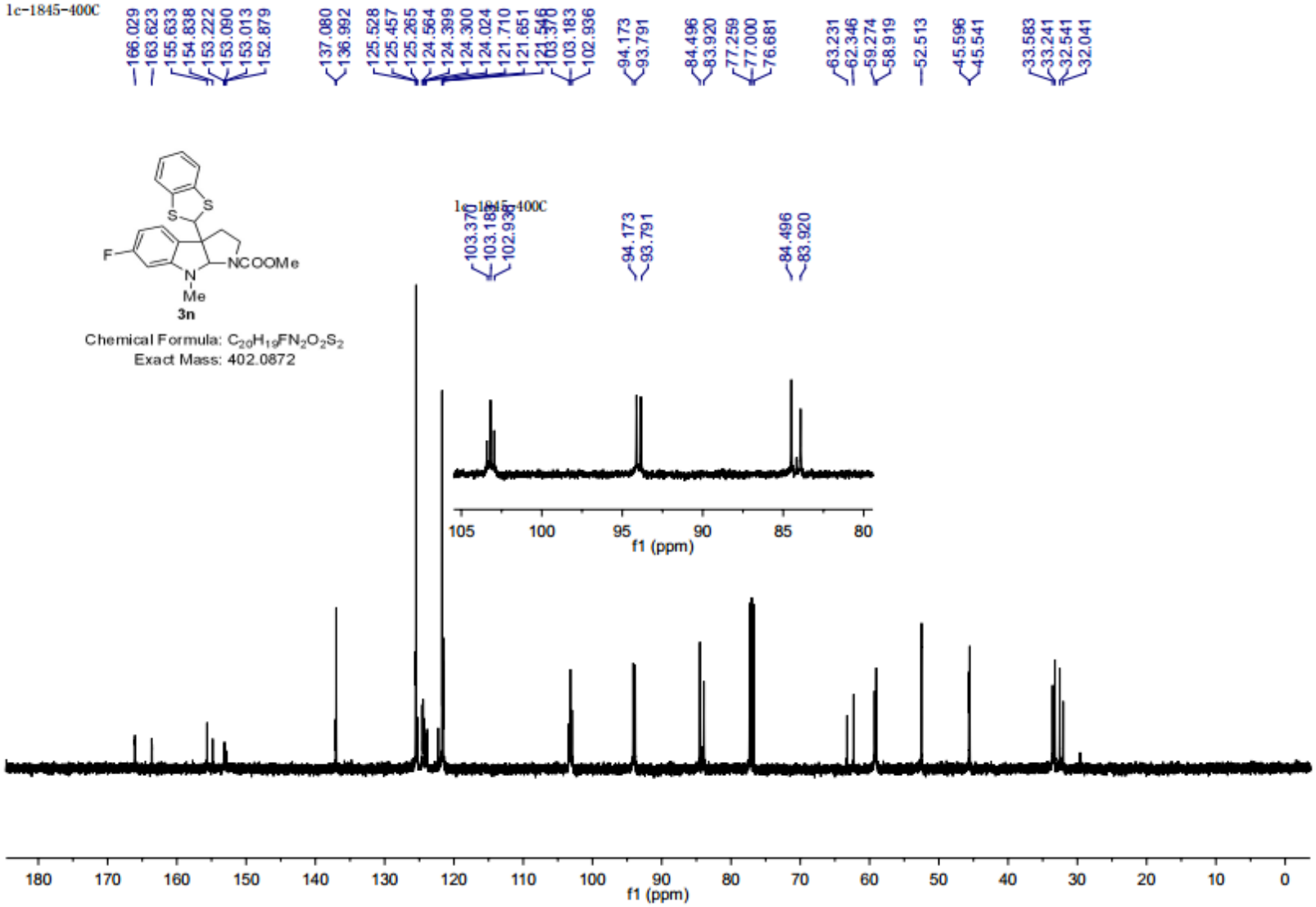


3n

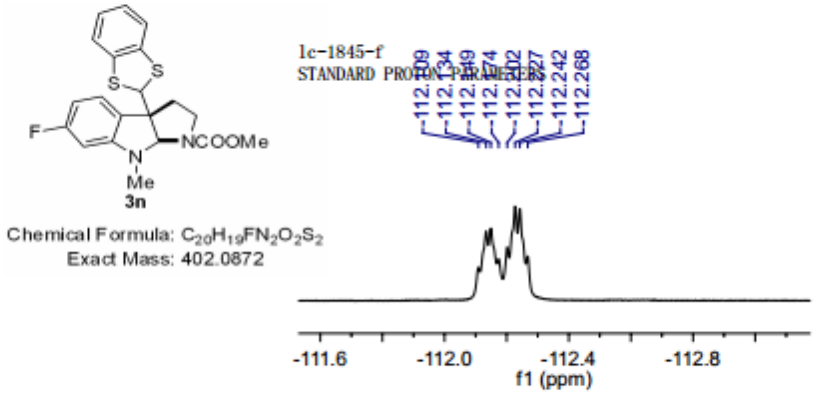
Chemical Formula: $C_{20}H_{19}FN_2O_2S_2$

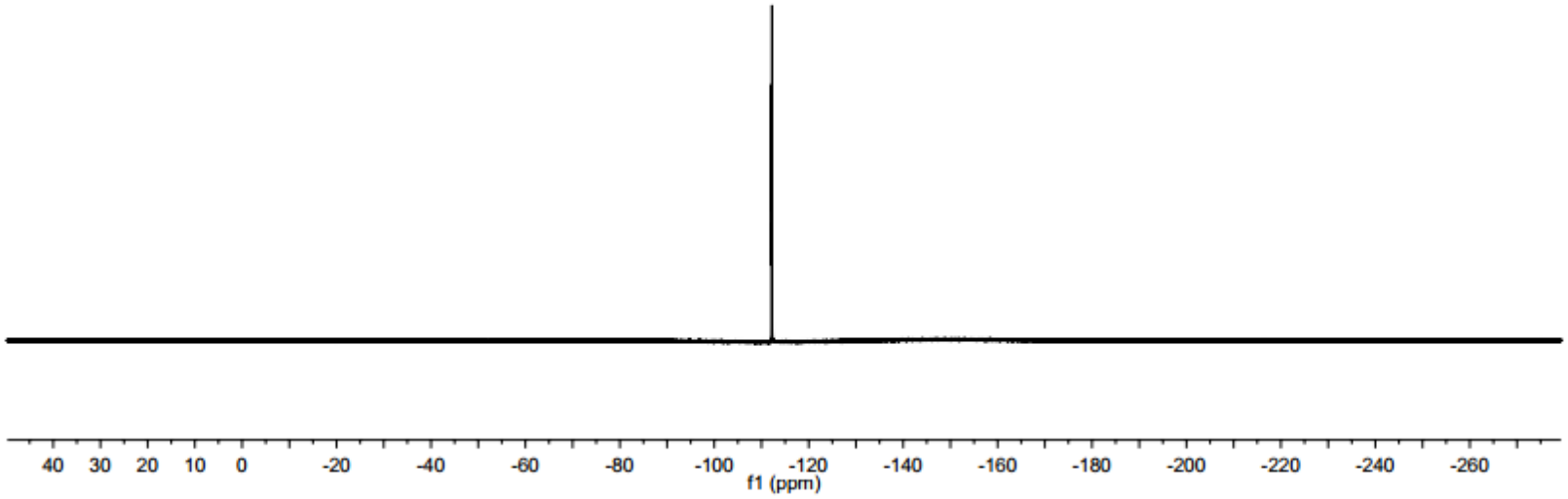
Exact Mass: 402.0872

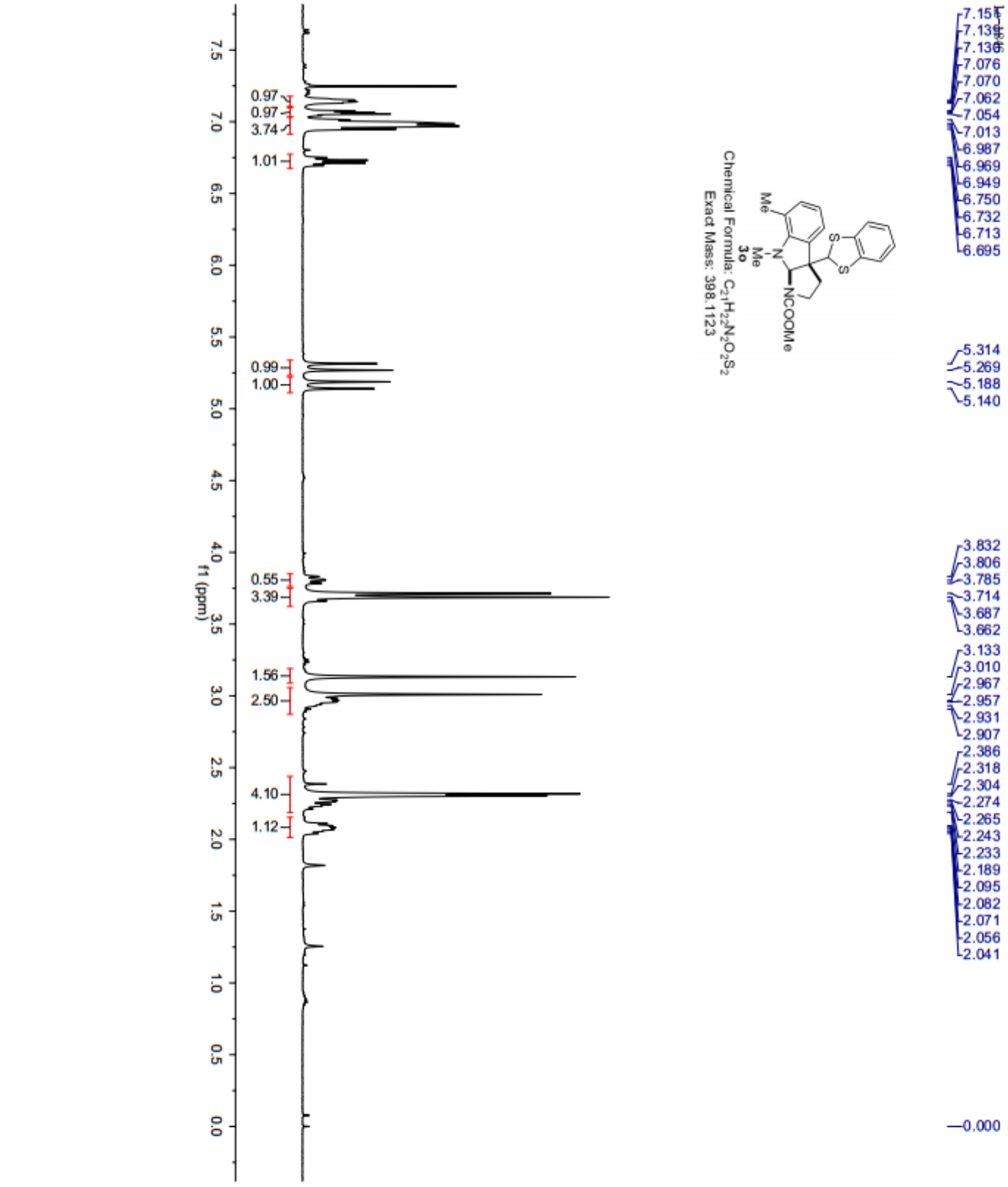


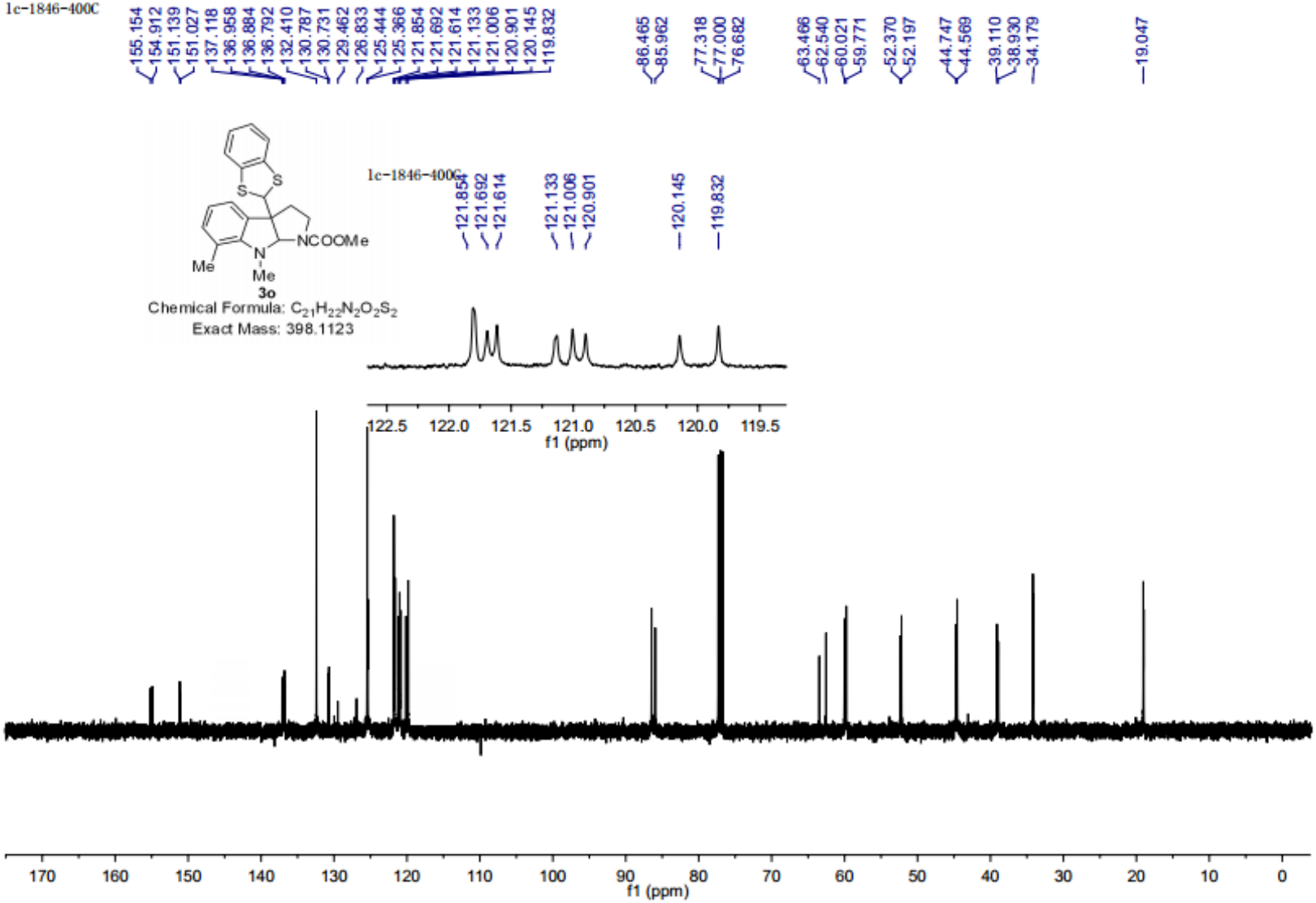

1c-1845-400C
166.029
163.623
155.633
154.838
153.222
153.090
153.013
152.879
137.080
136.992
125.528
125.457
125.265
124.564
124.399
124.300
124.024
121.710
121.651
103.370
103.183
102.936
94.173
93.791
84.496
83.920
77.259
77.000
76.681
63.231
62.346
59.274
58.919
52.513
45.596
45.541
33.583
33.241
32.541
32.041
F
S
S
N
NCOOMe
Me
3n
Chemical Formula: C20H19FN2O2S2
Exact Mass: 402.0872
f1 (ppm)

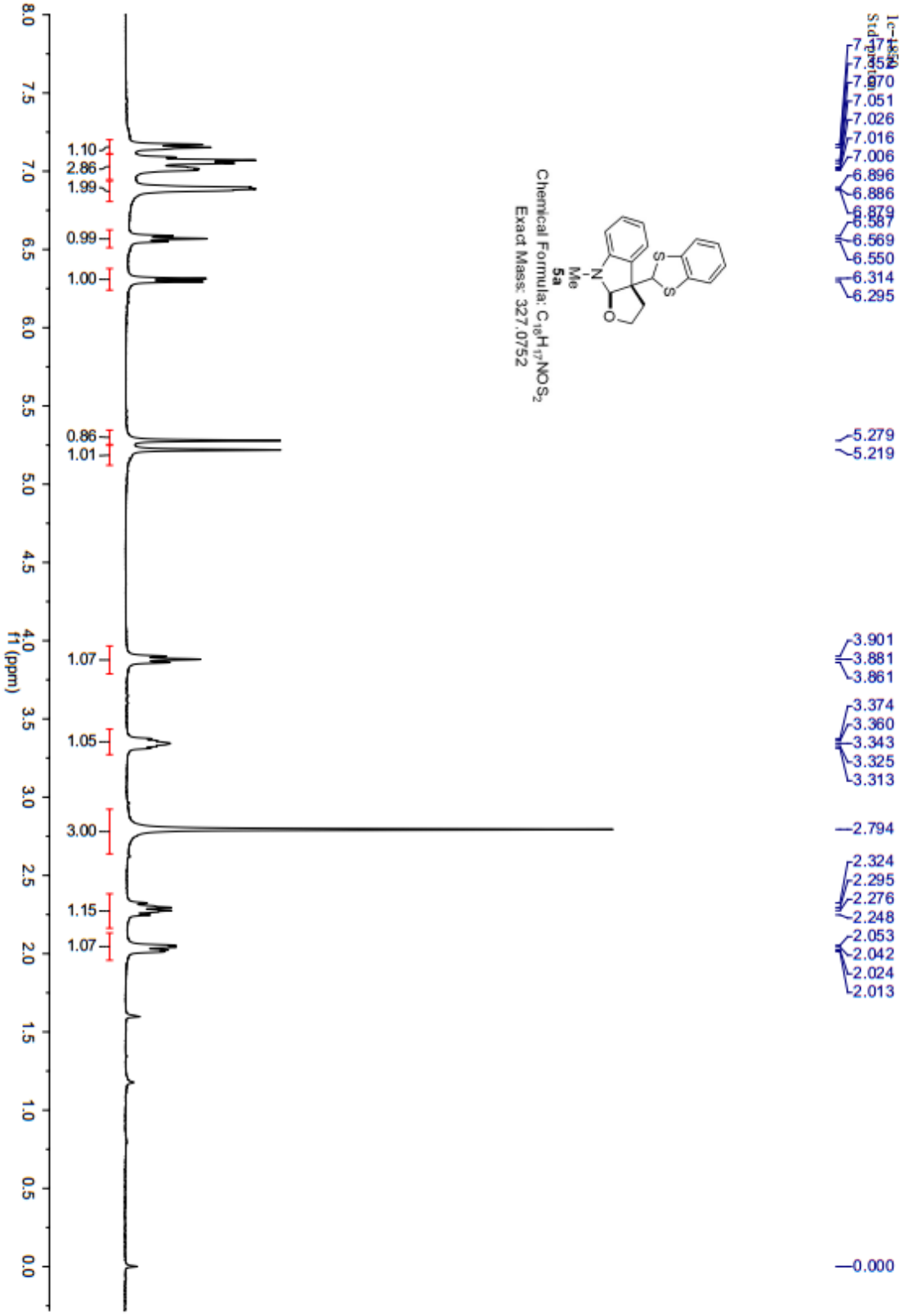
1c-1845-f
STANDARD PROTON PARAMETERS





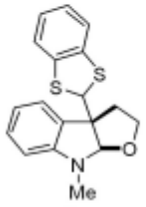

7.151
7.139
7.136
7.076
7.070
7.062
7.054
7.013
6.987
6.969
6.949
6.750
6.732
6.713
6.695
5.314
5.269
5.188
5.140
3.832
3.806
3.785
3.714
3.687
3.662
3.133
3.010
2.967
2.957
2.931
2.907
2.386
2.318
2.304
2.274
2.265
2.243
2.233
2.189
2.095
2.082
2.071
2.056
2.041
0.000
0.97
0.97
3.74
1.01
0.99
1.00
0.55
3.39
1.56
2.50
4.10
1.12
f1 (ppm)
Chemical Formula: C21H22N2O2S2
Exact Mass: 398.1123
3o
Me
N
Me
NCOOMe
S
S


1c-1846-400C
155.154
154.912
151.139
151.027
137.118
136.958
136.884
136.792
132.410
130.787
130.731
129.462
126.833
125.444
125.366
121.854
121.692
121.614
121.133
121.006
120.901
120.145
119.832
86.465
85.962
77.318
77.000
76.682
63.466
62.540
60.021
59.771
52.370
52.197
44.747
44.569
39.110
38.930
34.179
19.047
NCOOMe
Me
N
Me
3o
Chemical Formula: C21H22N2O2S2
Exact Mass: 398.1123
1c-1846-400C
121.854
121.692
121.614
121.133
121.006
120.901
120.145
119.832
122.5
122.0
121.5
121.0
120.5
120.0
119.5
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

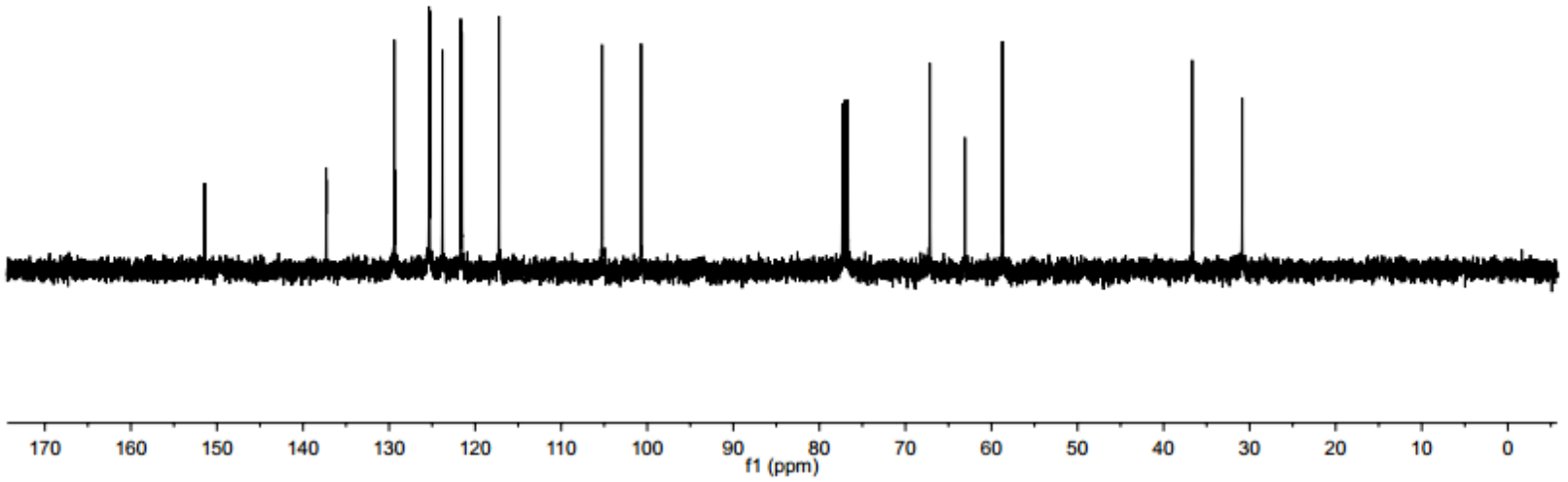

Chemical Formula: $C_{18}H_{17}NOS_2$
Exact Mass: 327.0752
5a
Me
N
O
S
S
f1 (ppm)
1.10
2.86
1.99
0.99
1.00
0.86
1.01
1.07
1.05
3.00
1.15
1.07
7.970
7.051
7.026
7.016
7.006
6.896
6.886
6.879
6.569
6.550
6.314
6.295
5.279
5.219
3.901
3.881
3.861
3.374
3.360
3.343
3.325
3.313
2.794
2.324
2.295
2.276
2.248
2.053
2.042
2.024
2.013
0.000

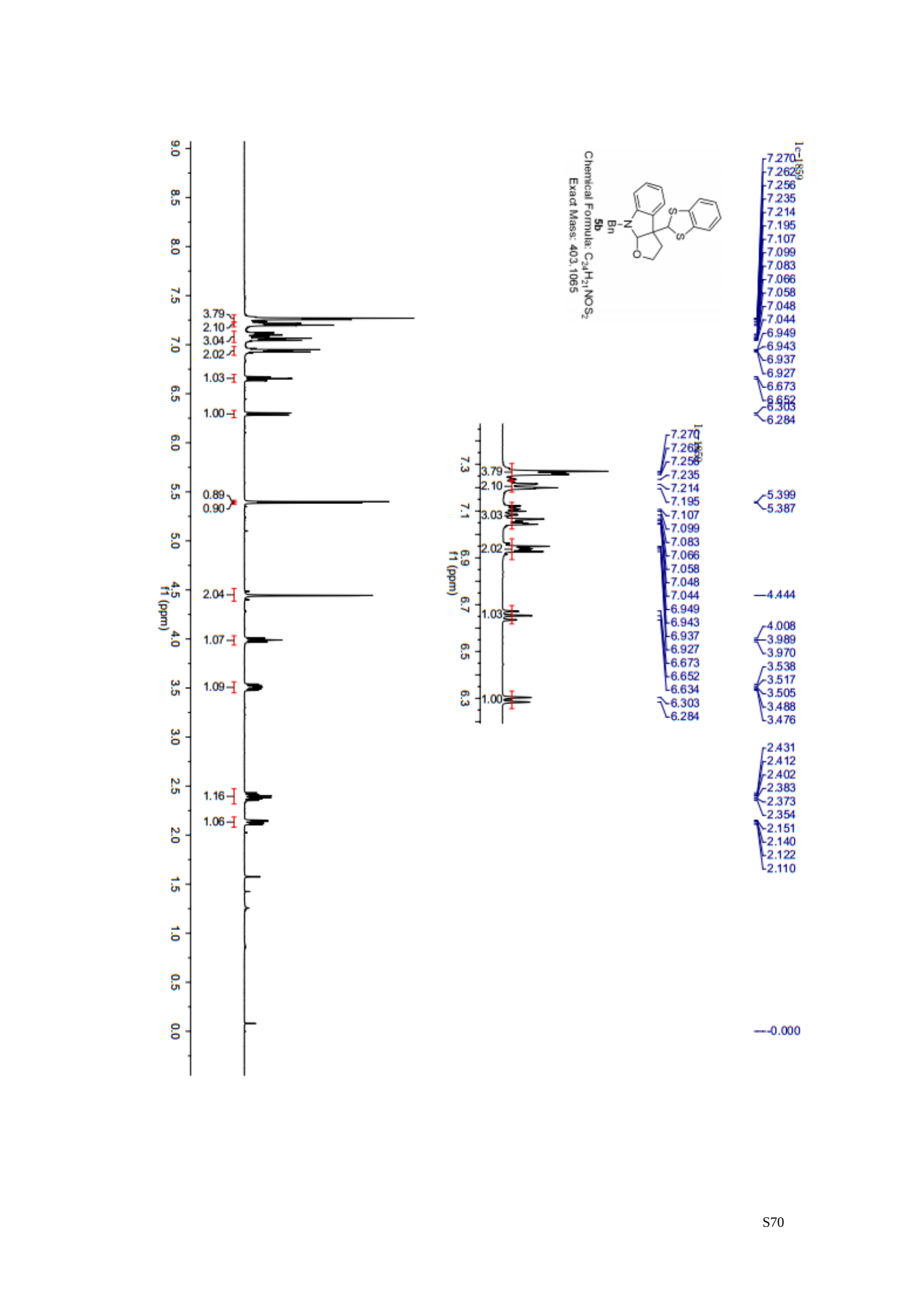
1c-1850-400C
Std carbon

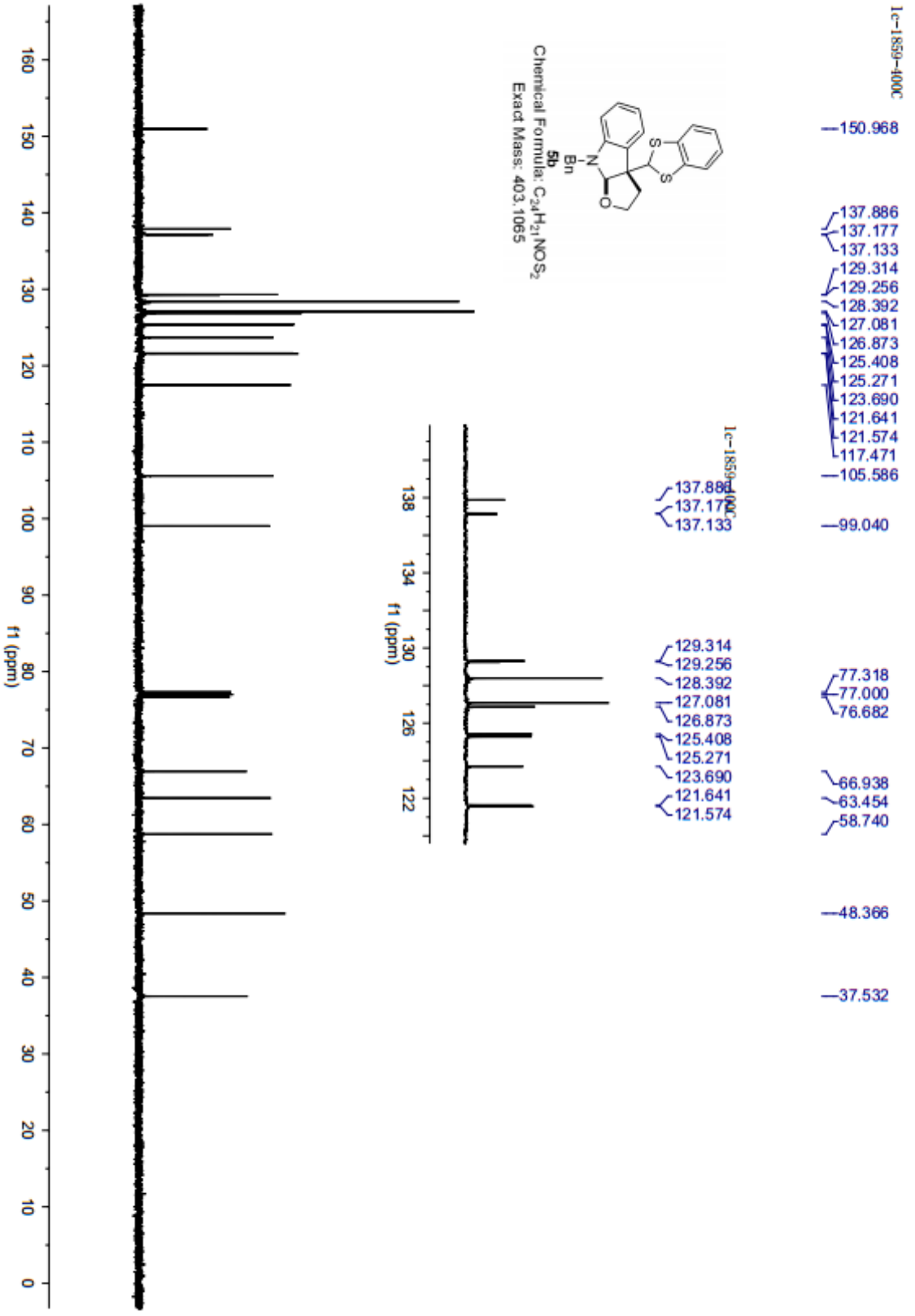
151.432
137.315
137.288
129.391
129.298
125.360
125.289
123.792
121.670
121.532
117.233
105.259
100.714
77.316
77.000
76.681
67.164
63.085
58.726
36.675
30.868

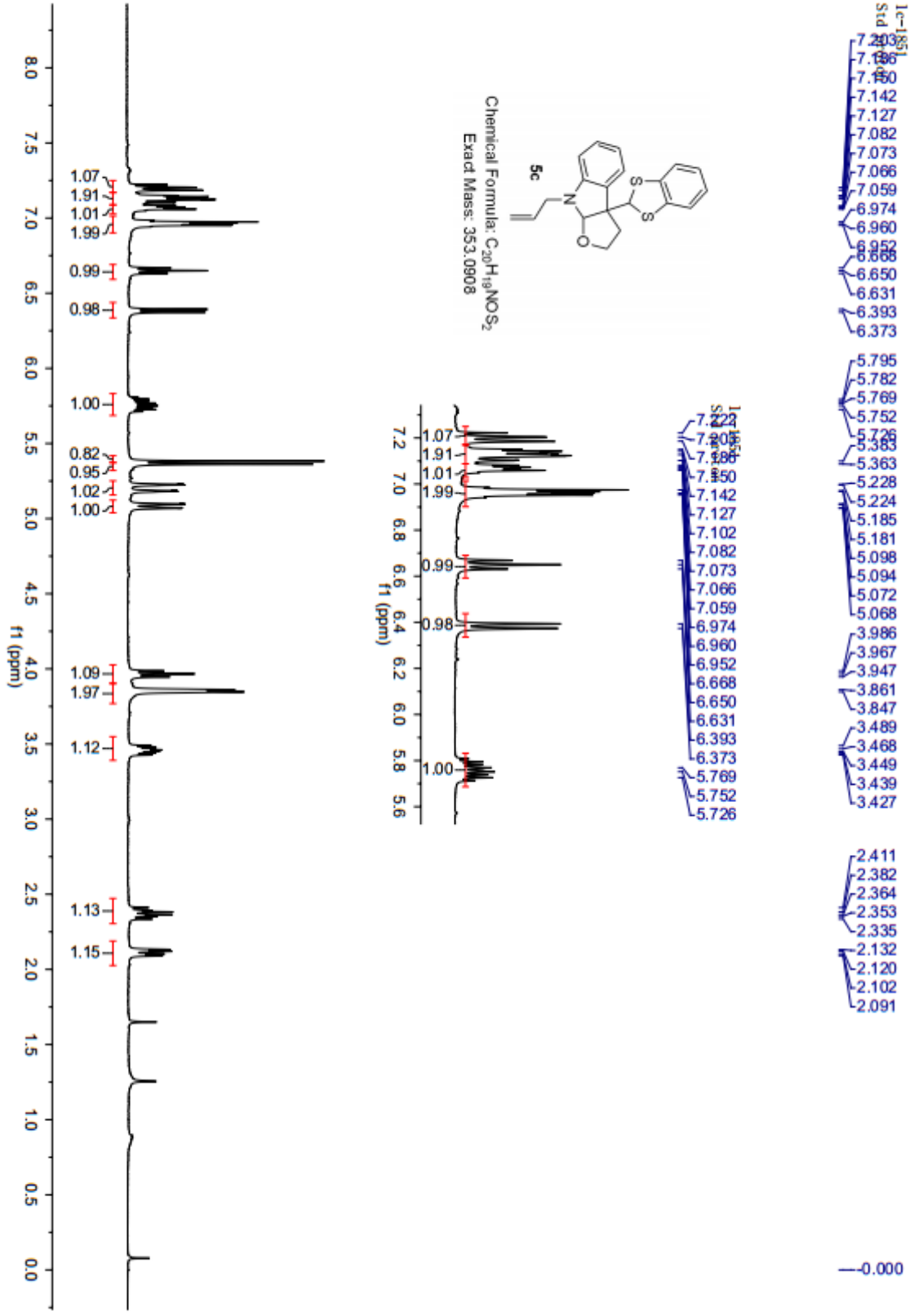


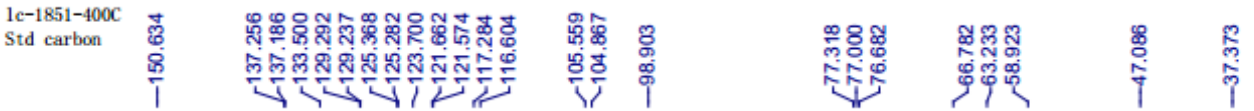
5a
Chemical Formula: $C_{18}H_{17}NOS_2$
Exact Mass: 327.0752

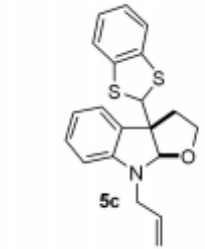



5b
Bn
Chemical Formula: C24H21NOS2
Exact Mass: 403.1065
f1 (ppm)
3.79
2.10
3.04
2.02
1.03
1.00
0.89
0.90
2.04
1.07
1.09
1.16
1.06
7.270
7.262
7.256
7.235
7.214
7.195
7.107
7.099
7.083
7.066
7.058
7.048
7.044
6.949
6.943
6.937
6.927
6.673
6.652
6.634
6.303
6.284
5.399
5.387
4.444
4.008
3.989
3.970
3.538
3.517
3.505
3.488
3.476
2.431
2.412
2.402
2.383
2.373
2.354
2.151
2.140
2.122
2.110
0.000

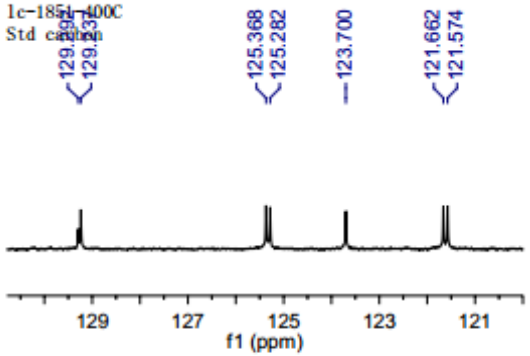

1c-1859-400C
Chemical Formula: $C_{24}H_{21}NOS_2$
Exact Mass: 403.1065
5b
Bn
150.968
137.886
137.177
137.133
129.314
129.256
128.392
127.081
126.873
125.408
125.271
123.690
121.641
121.574
117.471
105.586
99.040
77.318
77.000
76.682
66.938
63.454
58.740
48.366
37.532
f1 (ppm)

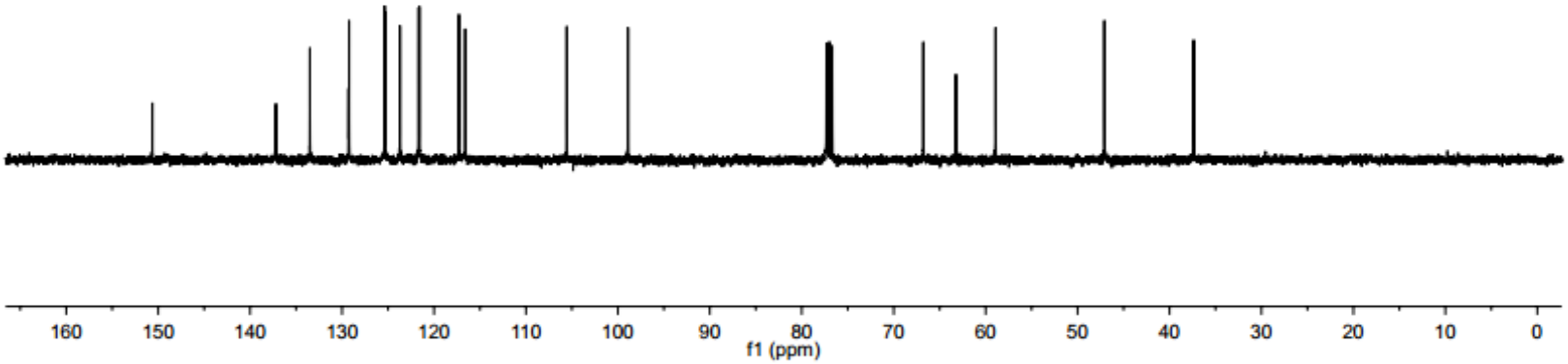

1c-185
Std
Chemical Formula: C20H19NOS2
Exact Mass: 353.0908
5c
f1 (ppm)
1.07
1.91
1.01
1.99
0.99
0.98
1.00
0.82
0.95
1.02
1.00
1.09
1.97
1.12
1.13
1.15
7.203
7.186
7.150
7.142
7.127
7.082
7.073
7.066
7.059
6.974
6.960
6.952
6.650
6.631
6.393
6.373
5.795
5.782
5.769
5.752
5.383
5.363
5.228
5.224
5.185
5.181
5.098
5.094
5.072
5.068
3.986
3.967
3.947
3.861
3.847
3.489
3.468
3.449
3.439
3.427
2.411
2.382
2.364
2.353
2.335
2.132
2.120
2.102
2.091
0.000

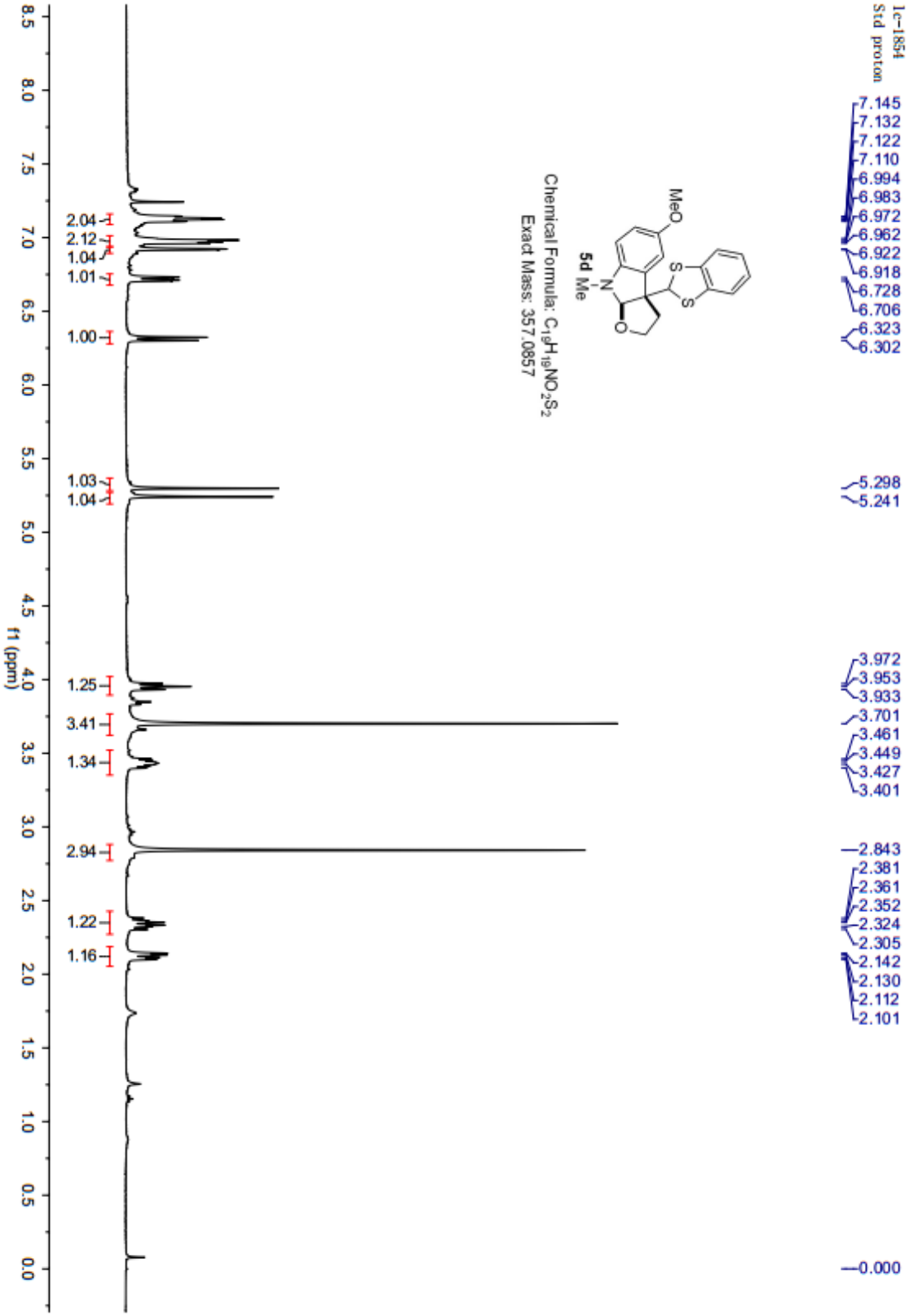


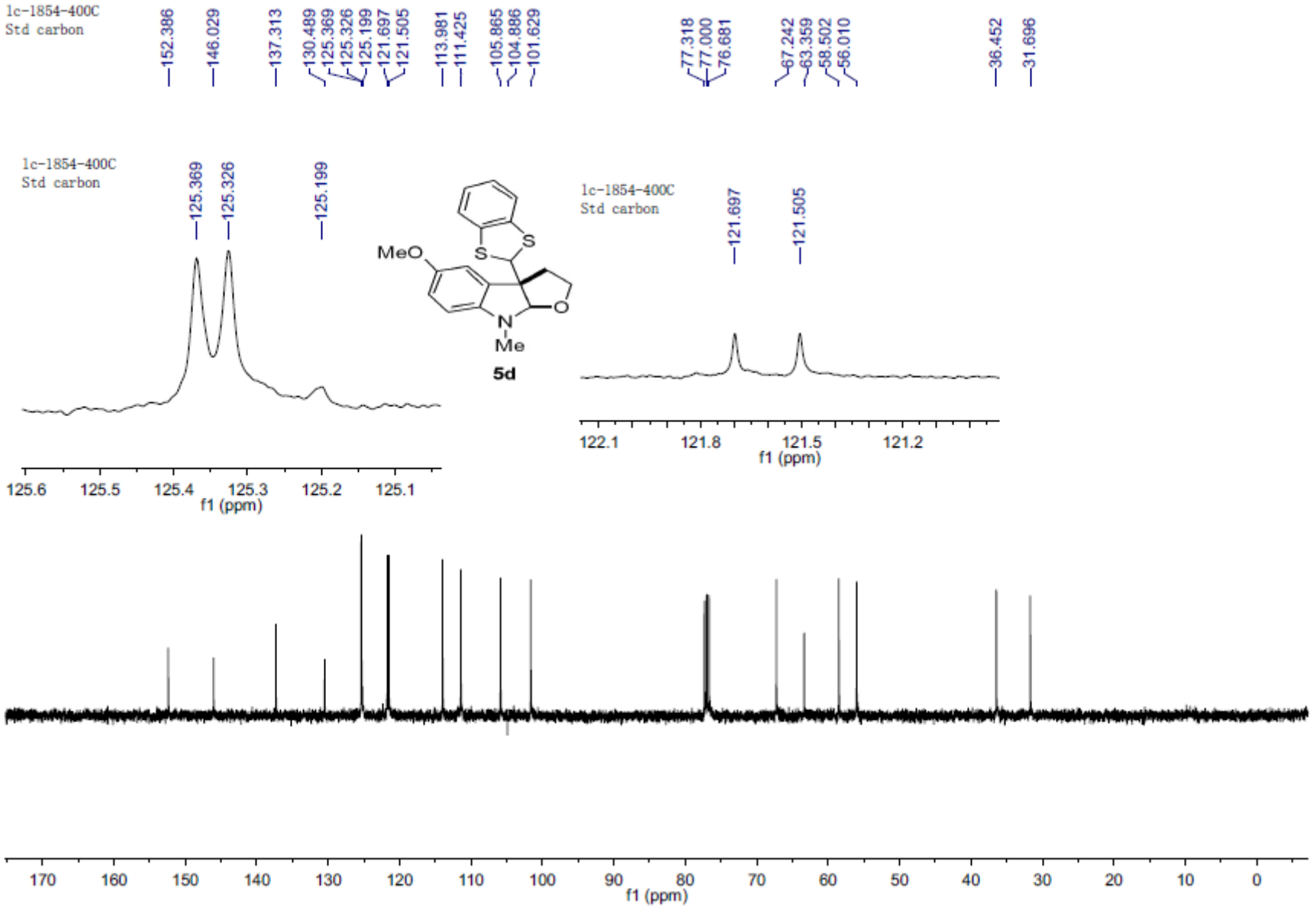


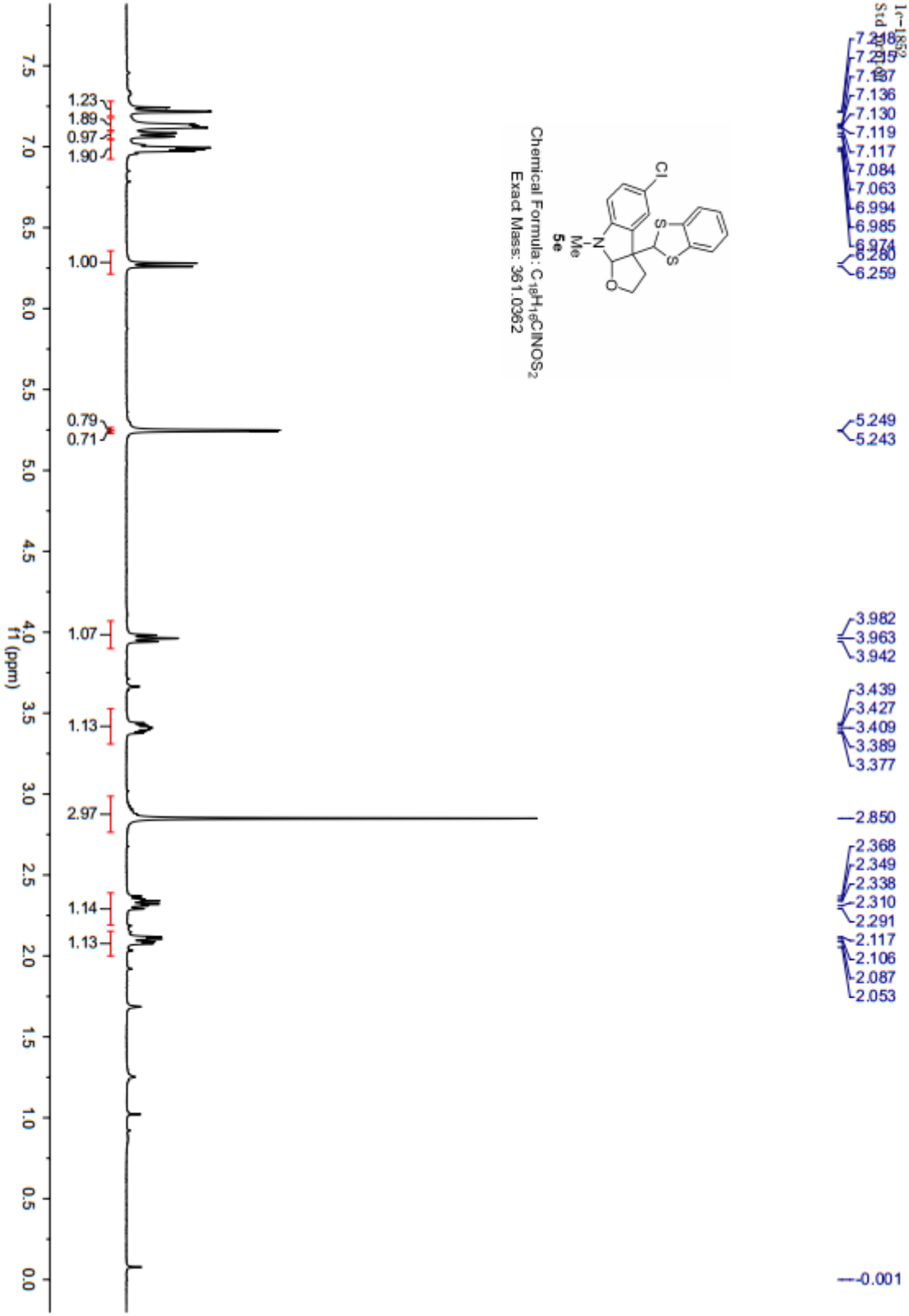
Chemical Formula: $C_{20}H_{19}NOS_2$
Exact Mass: 353.0908

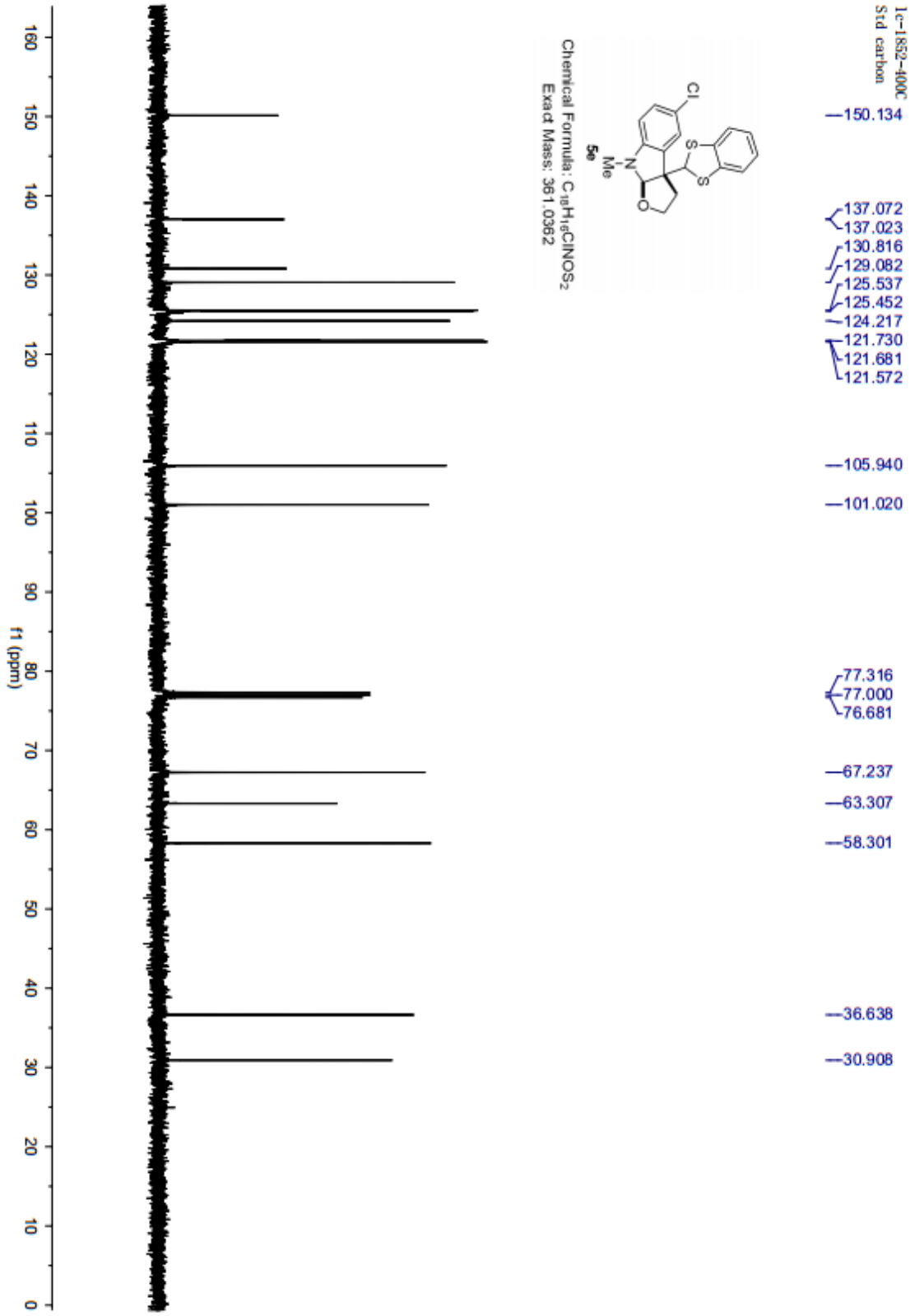


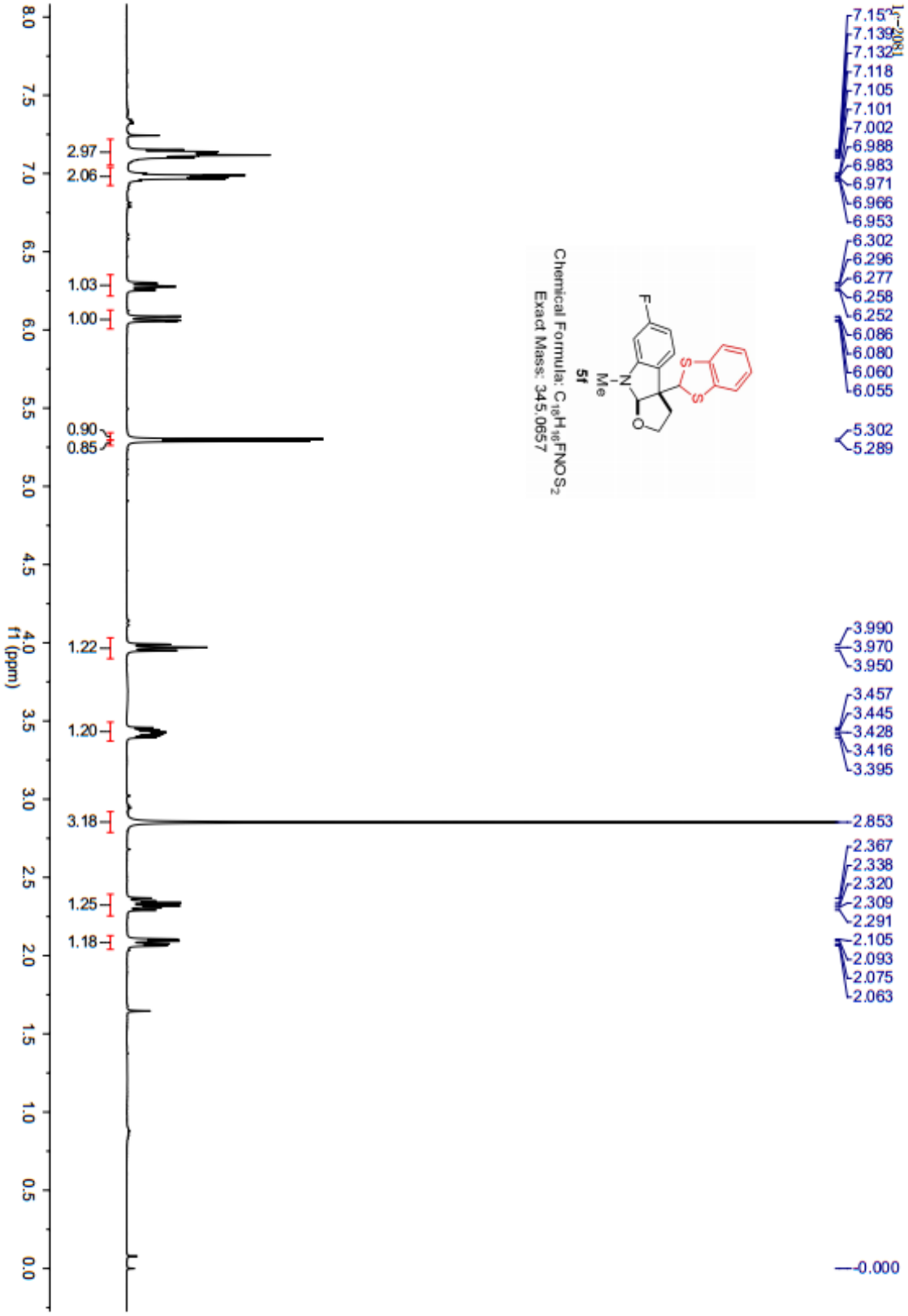


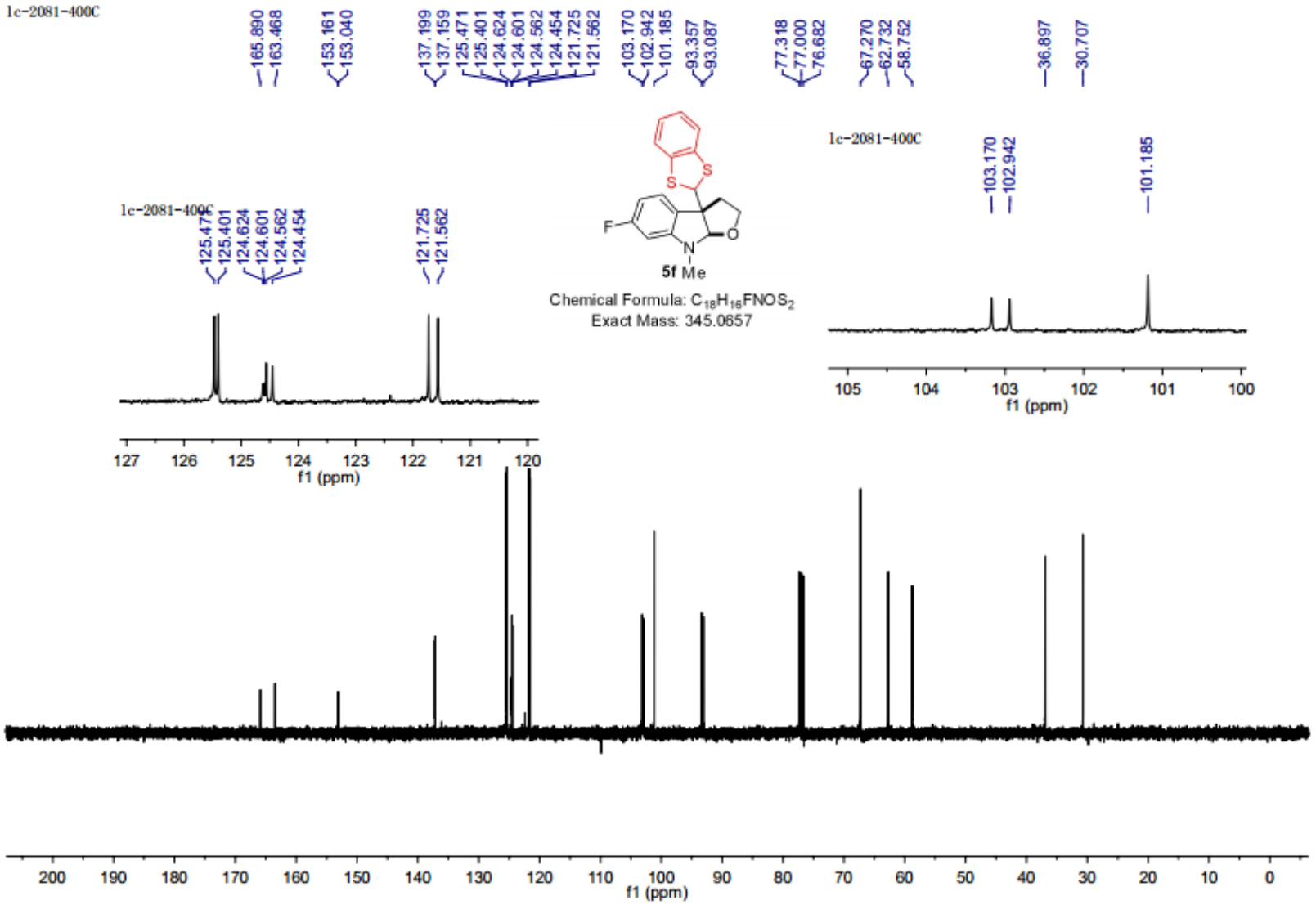

1c-1854
Std proton
7.145
7.132
7.122
7.110
6.994
6.983
6.972
6.962
6.922
6.918
6.728
6.706
6.323
6.302
5.298
5.241
3.972
3.953
3.933
3.701
3.461
3.449
3.427
3.401
2.843
2.381
2.361
2.352
2.324
2.305
2.142
2.130
2.112
2.101
0.000
Chemical Formula: C19H19NO2S2
Exact Mass: 357.0857
5d Me
MeO
N
O
S
S
2.04
2.12
1.04
1.01
1.00
1.03
1.04
1.25
3.41
1.34
2.94
1.22
1.16
f1 (ppm)


1c-1854-400C
Std carbon
152.386
146.029
137.313
130.489
125.369
125.326
125.199
121.697
121.505
113.981
111.425
105.865
104.886
101.629
77.318
77.000
76.681
67.242
63.359
58.502
56.010
36.452
31.696
1c-1854-400C
Std carbon
125.369
125.326
125.199
125.6
125.5
125.4
125.3
125.2
125.1
f1 (ppm)
MeO
S
S
O
N
Me
5d
1c-1854-400C
Std carbon
121.697
121.505
122.1
121.8
121.5
121.2
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Chemical Formula: $C_{18}H_{16}ClNOS_2$
Exact Mass: 361.0362
5e
Cl
N
Me
S
S
O
1.23
1.89
0.97
1.90
1.00
0.79
0.71
1.07
1.13
2.97
1.14
1.13
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
7.136
7.130
7.119
7.117
7.084
7.063
6.994
6.985
6.974
6.259
5.249
5.243
3.982
3.963
3.942
3.439
3.427
3.409
3.389
3.377
2.850
2.368
2.349
2.338
2.310
2.291
2.117
2.106
2.087
2.053
0.001

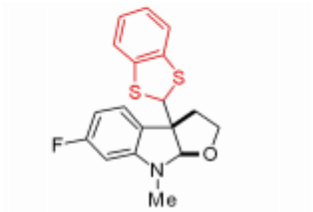

1c-1852-400C
Std carbon
Chemical Formula: C18H16ClNOS2
Exact Mass: 361.0362
5e
Me
Cl
S
S
N
O
150.134
137.072
137.023
130.816
129.082
125.537
125.452
124.217
121.730
121.681
121.572
105.940
101.020
77.316
77.000
76.681
67.237
63.307
58.301
36.638
30.908
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Chemical Formula: C18H16FNOS2
Exact Mass: 345.0657
5f
F
N
Me
O
S
S
7.154
7.139
7.132
7.118
7.105
7.101
7.002
6.988
6.983
6.971
6.966
6.953
6.302
6.296
6.277
6.258
6.252
6.086
6.080
6.060
6.055
5.302
5.289
3.990
3.970
3.950
3.457
3.445
3.428
3.416
3.395
2.853
2.367
2.338
2.320
2.309
2.291
2.105
2.093
2.075
2.063
0.000
2.97
2.06
1.03
1.00
0.90
0.85
1.22
1.20
3.18
1.25
1.18
f1 (ppm)


1c-2081-400C
165.890
163.468
153.161
153.040
137.199
137.159
125.471
125.401
124.624
124.601
124.562
124.454
121.725
121.562
103.170
102.942
101.185
93.357
93.087
77.318
77.000
76.682
67.270
62.732
58.752
36.897
30.707
5f Me
Chemical Formula: C18H16FNOS2
Exact Mass: 345.0657
f1 (ppm)

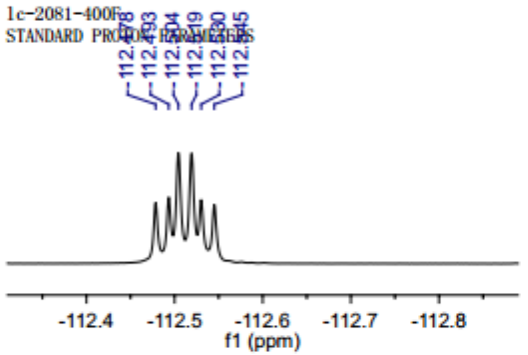
1c-2081-400F
STANDARD PROTON PARAMETERS

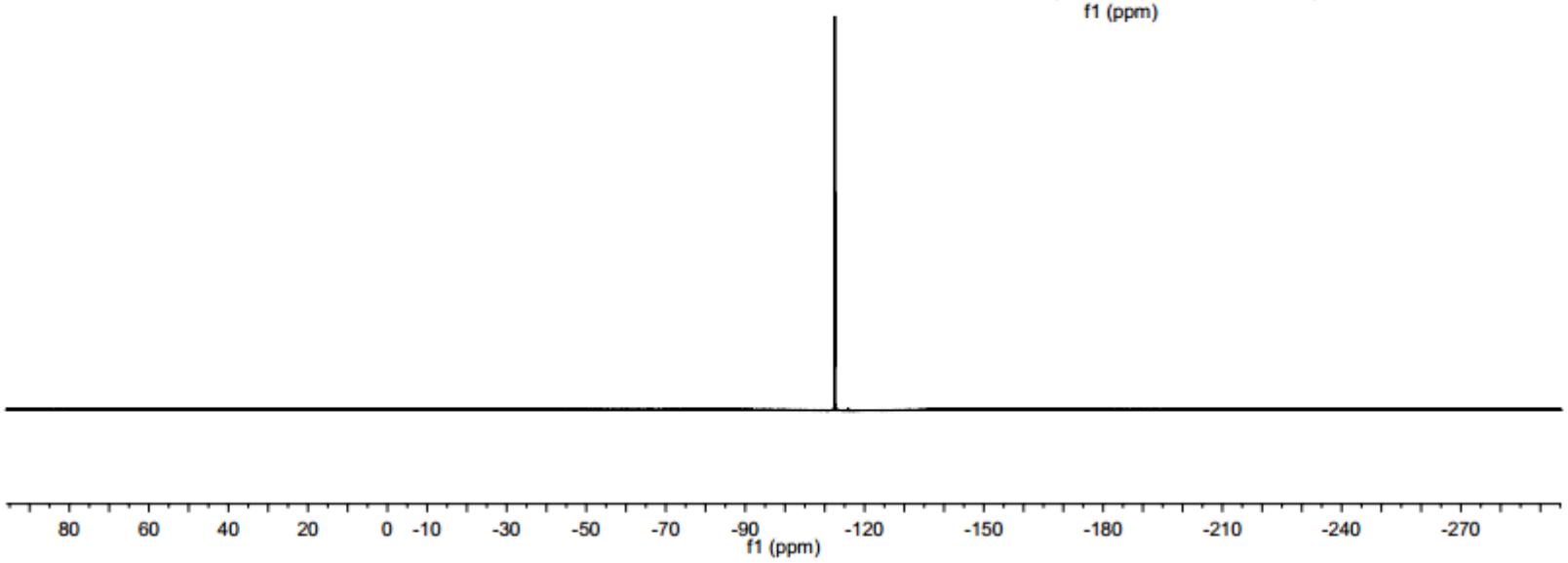
-112.478
-112.493
-112.504
-112.519
-112.530
-112.545

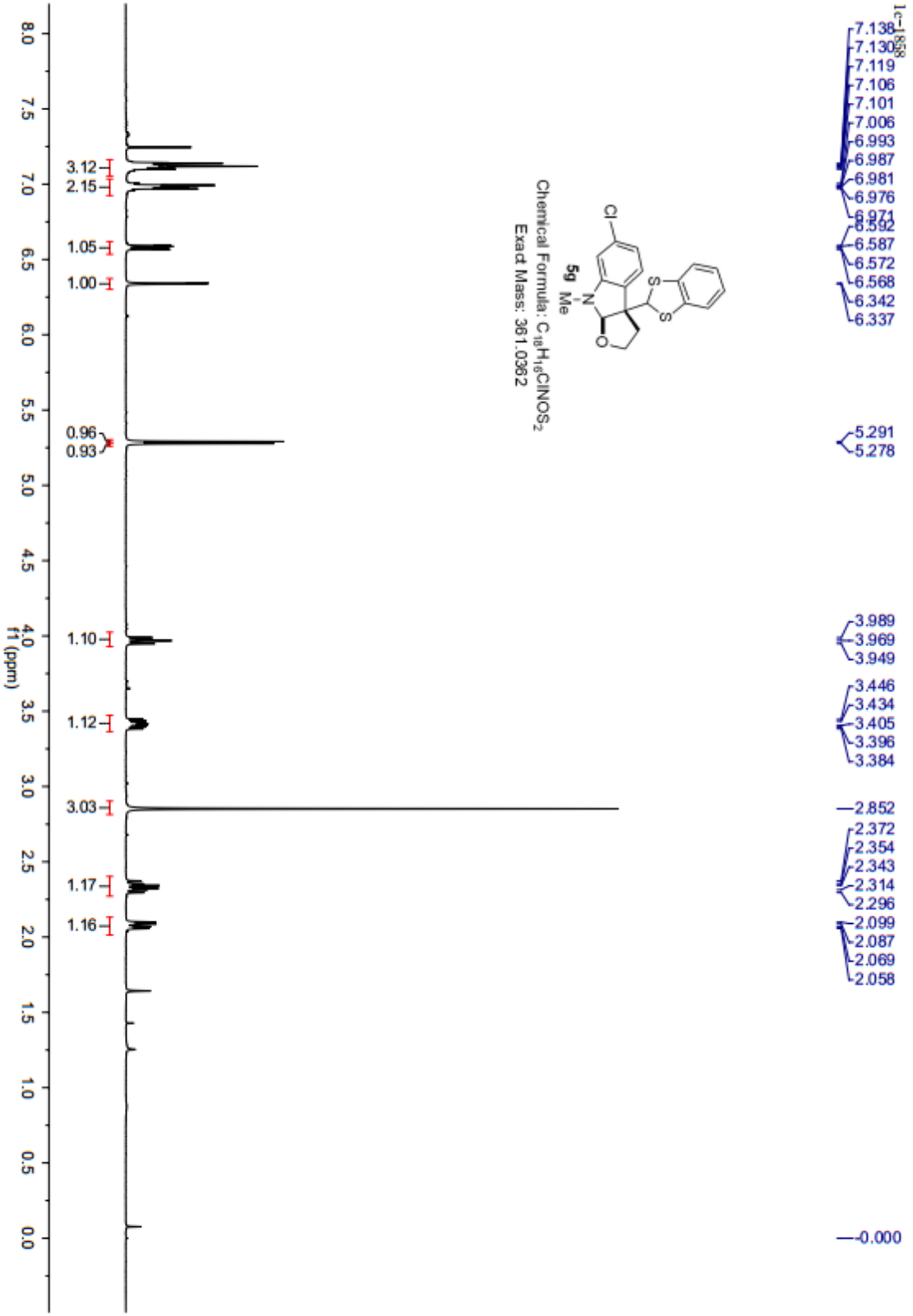


5f

Chemical Formula: $C_{18}H_{16}FNOS_2$
Exact Mass: 345.0657

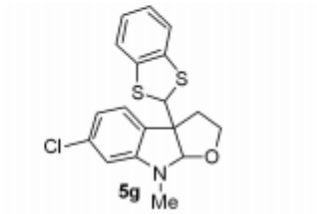





1c-1858
7.138
7.130
7.119
7.106
7.101
7.006
6.993
6.987
6.981
6.976
6.971
6.592
6.587
6.572
6.568
6.342
6.337
5.291
5.278
3.989
3.969
3.949
3.446
3.434
3.405
3.396
3.384
2.852
2.372
2.354
2.343
2.314
2.296
2.099
2.087
2.069
2.058
0.000
3.12
2.15
1.05
1.00
0.96
0.93
1.10
1.12
3.03
1.17
1.16
f1 (ppm)
Chemical Formula: C18H16ClNOS2
Exact Mass: 361.0362
5g
Me
Cl
N
O
S
S

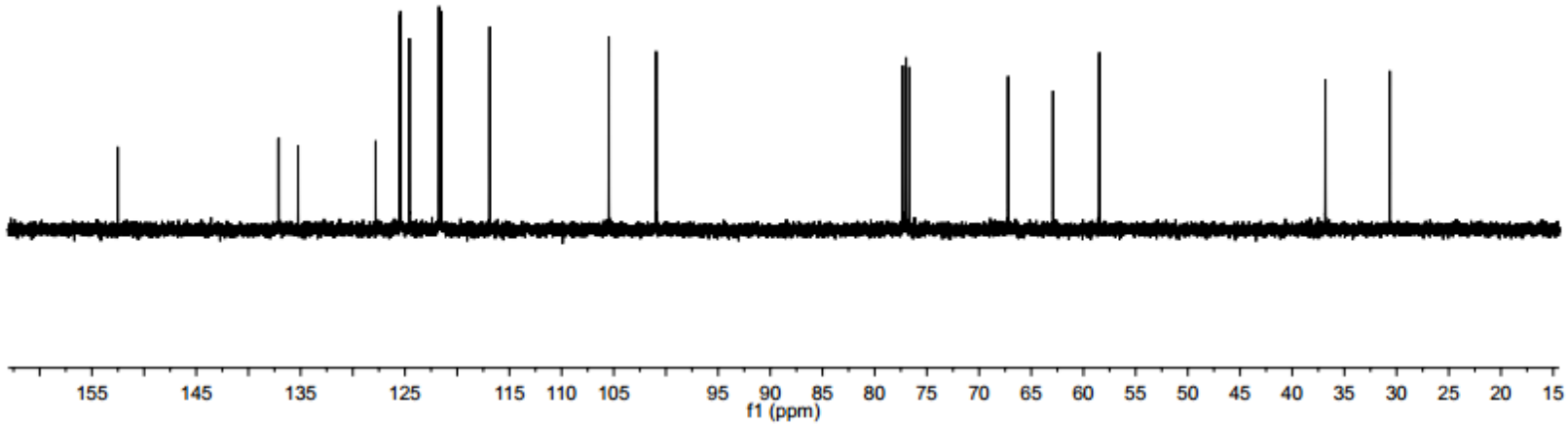
1c-1858-4006

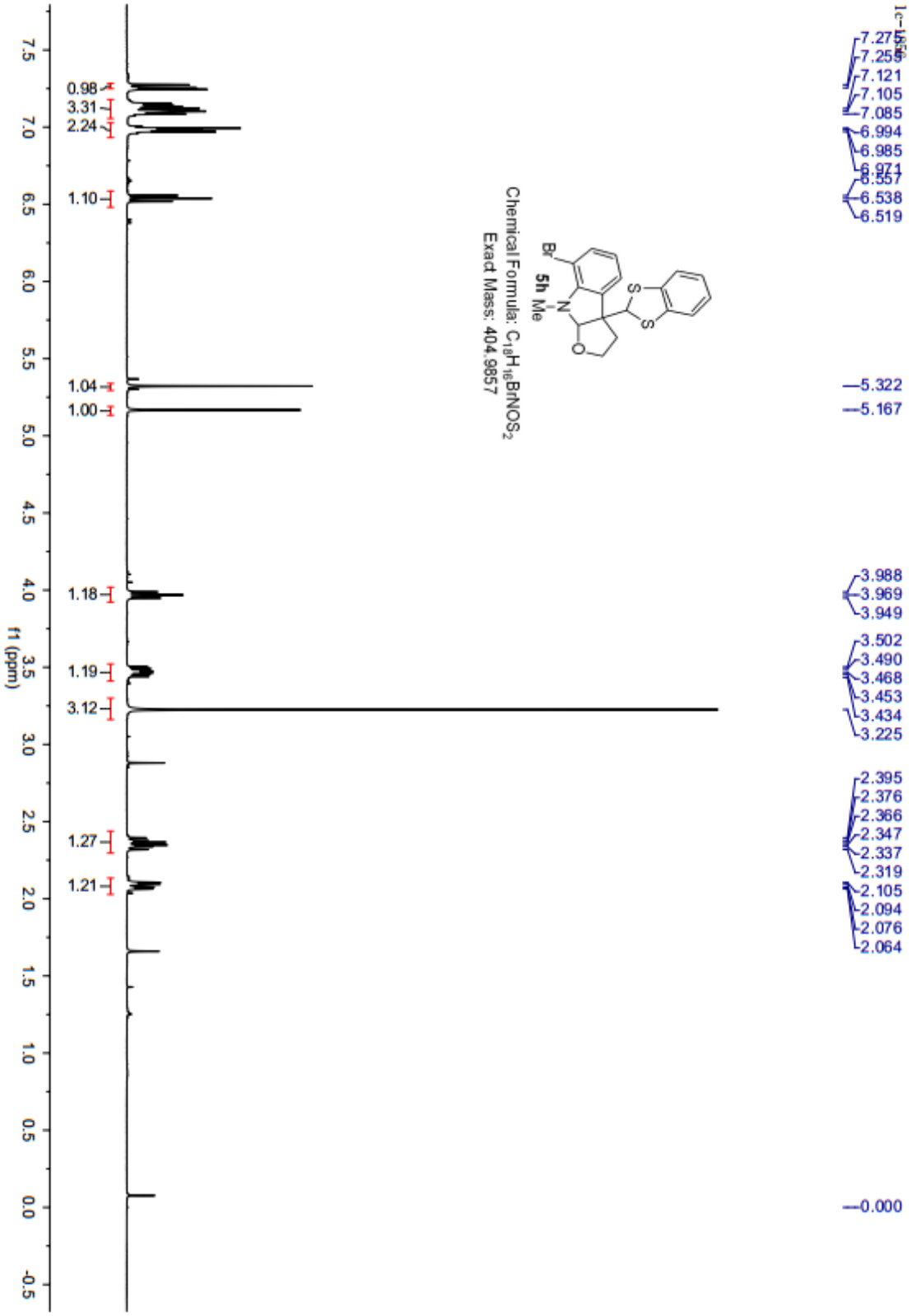
152.516
137.129
137.095
135.245
127.812
125.510
125.439
124.570
121.741
121.572
116.886
105.473
100.937
77.318
77.000
76.682
67.220
62.923
58.479
36.823
30.652

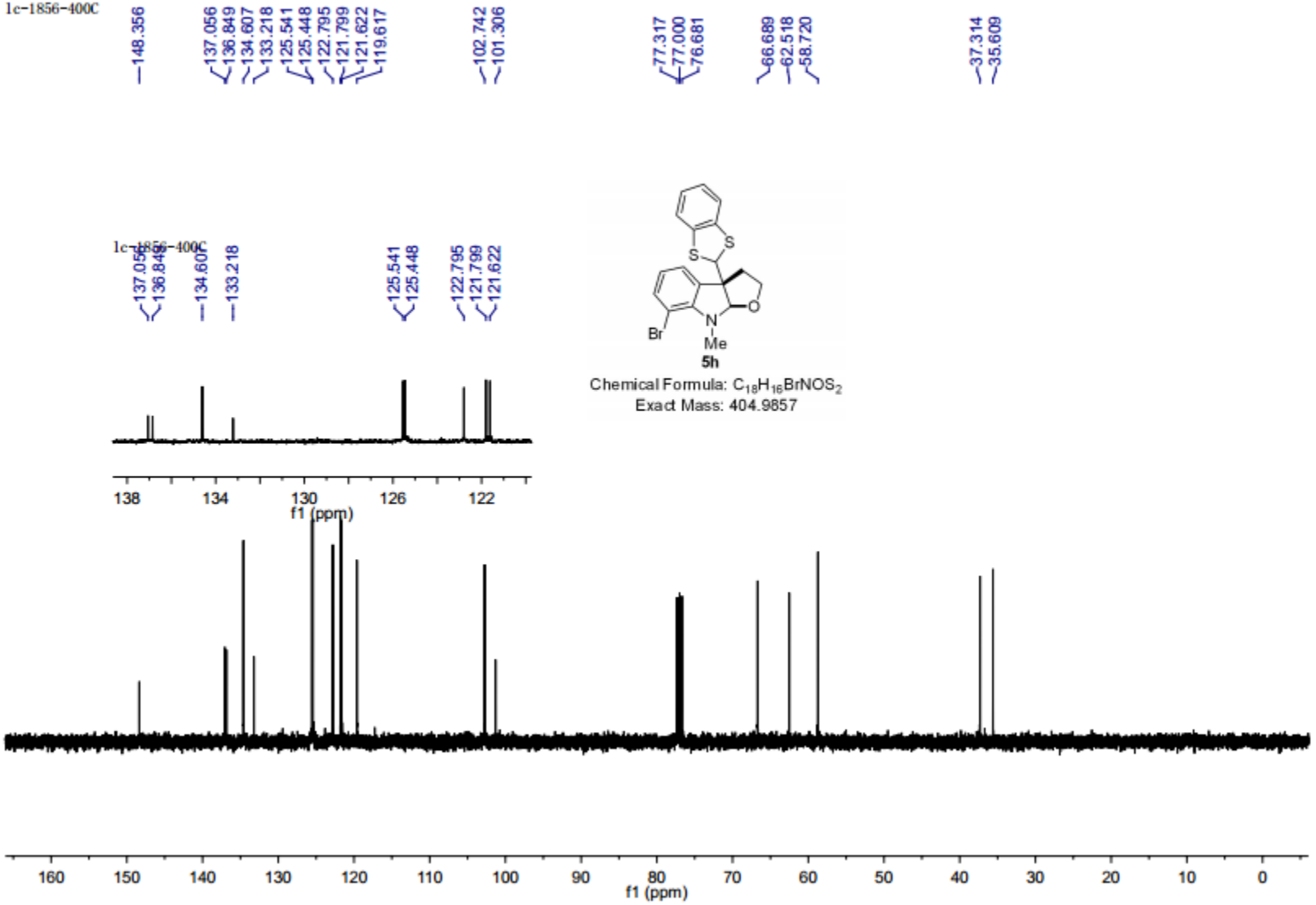


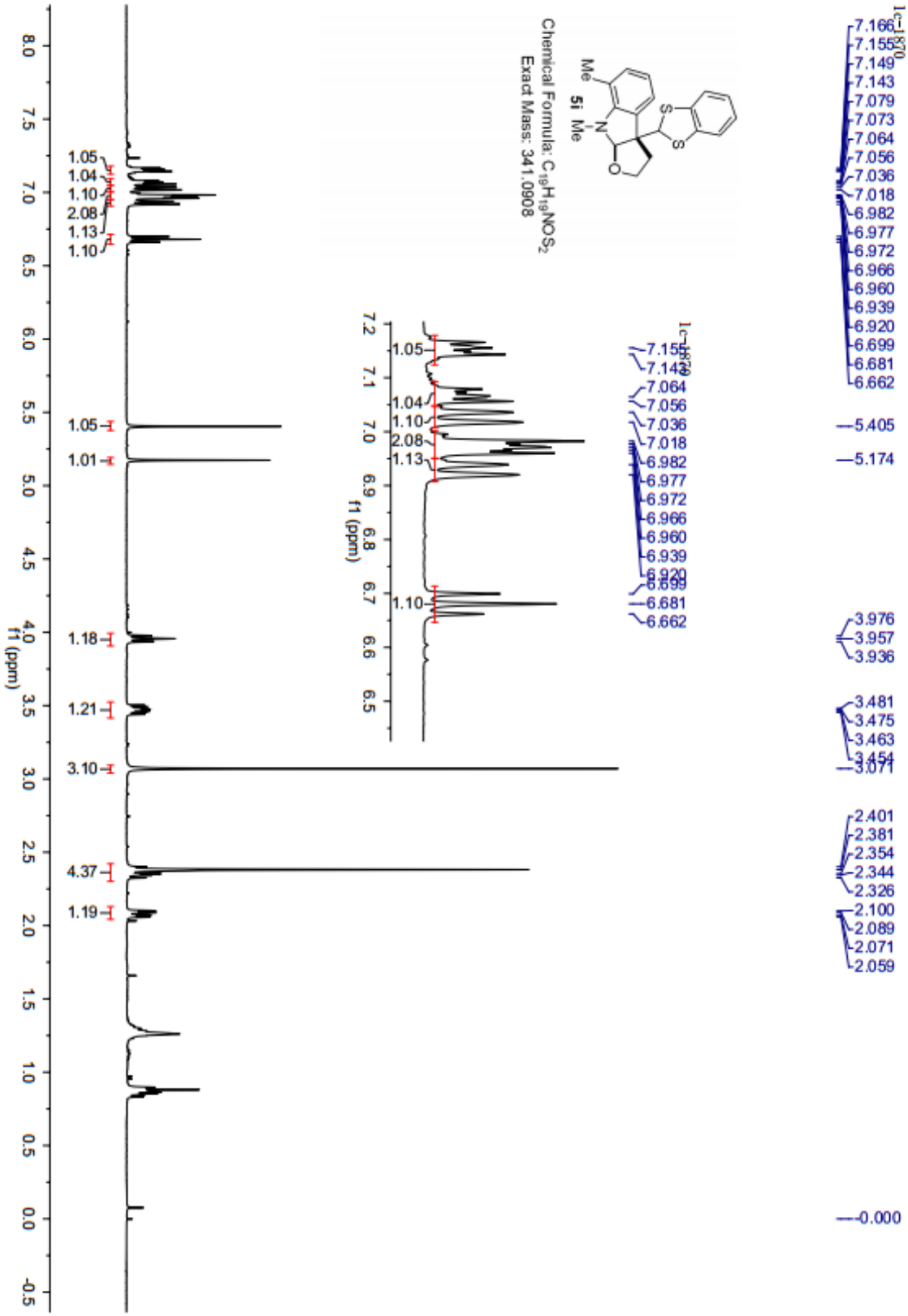
5g

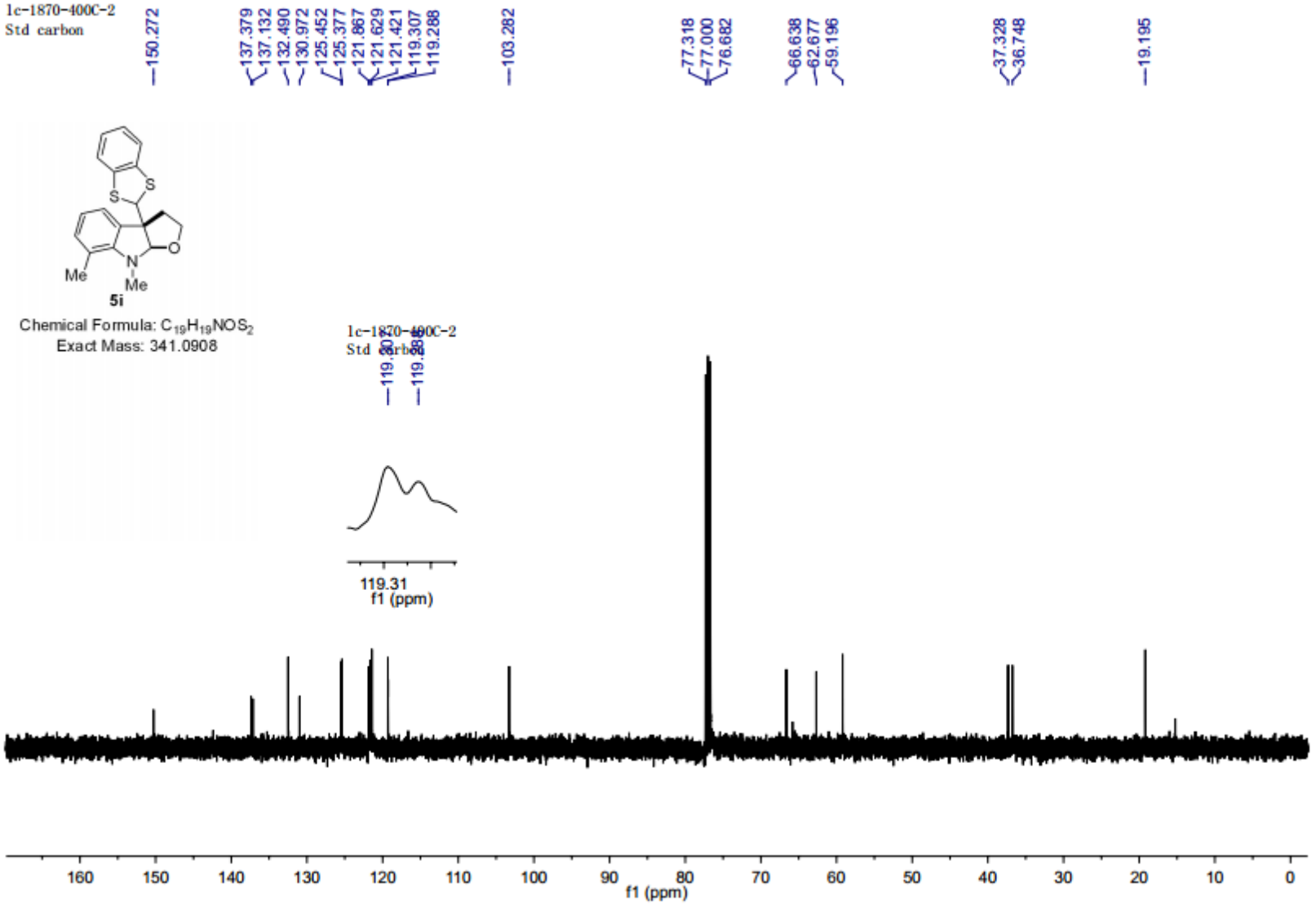
Chemical Formula: $C_{18}H_{16}ClNOS_2$
Exact Mass: 361.0362

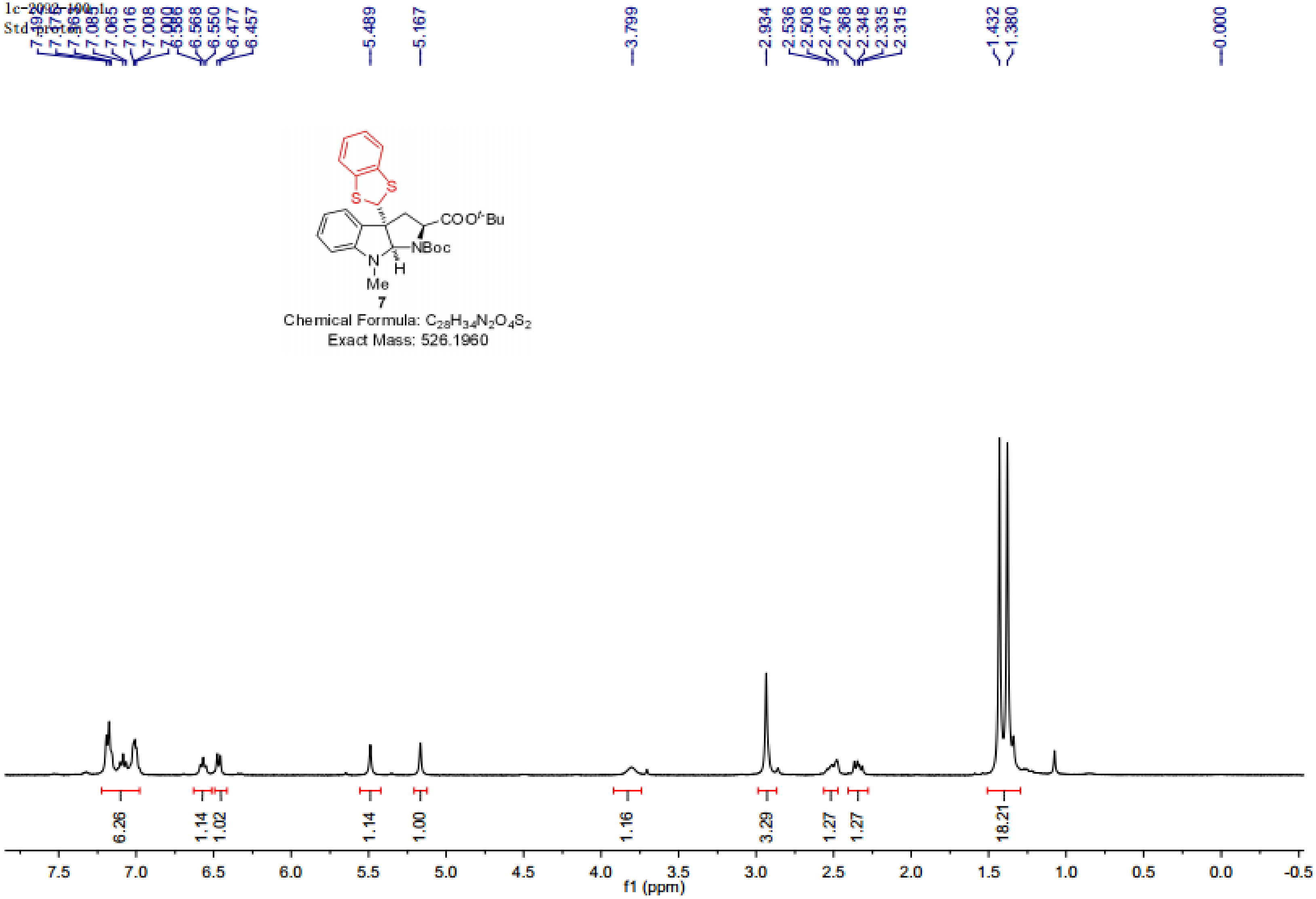



Chemical Formula: $C_{18}H_{16}BrNOS_2$
Exact Mass: 404.9857
5h
Me
Br
N
S
S
O
0.98
3.31
2.24
1.10
1.04
1.00
1.18
1.19
3.12
1.27
1.21
7.275
7.255
7.121
7.105
7.085
6.994
6.985
6.971
6.557
6.538
6.519
5.322
5.167
3.988
3.969
3.949
3.502
3.490
3.468
3.453
3.434
3.225
2.395
2.376
2.366
2.347
2.337
2.319
2.105
2.094
2.076
2.064
0.000
f1 (ppm)


1c-1856-400C
148.356
137.056
136.849
134.607
133.218
125.541
125.448
122.795
121.799
121.622
119.617
102.742
101.306
77.317
77.000
76.681
66.689
62.518
58.720
37.314
35.609
1c-1856-400C
137.056
136.849
134.607
133.218
125.541
125.448
122.795
121.799
121.622
138
134
130
126
122
f1 (ppm)
S
S
N
O
Br
Me
5h
Chemical Formula: C18H16BrNOS2
Exact Mass: 404.9857
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

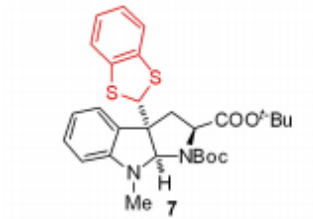

Chemical Formula: $C_{19}H_{19}NOS_2$
Exact Mass: 341.0908
5i
Me
Me
f1 (ppm)
1.05
1.04
1.10
2.08
1.13
1.10
1.05
1.01
1.18
1.21
3.10
4.37
1.19
7.166
7.155
7.149
7.143
7.079
7.073
7.064
7.056
7.036
7.018
6.982
6.977
6.972
6.966
6.960
6.939
6.920
6.699
6.681
6.662
5.405
5.174
3.976
3.957
3.936
3.481
3.475
3.463
3.454
3.071
2.401
2.381
2.354
2.344
2.326
2.100
2.089
2.071
2.059
0.000


1c-1870-400C-2
Std carbon
150.272
137.379
137.132
132.490
130.972
125.452
125.377
121.867
121.629
121.421
119.307
119.288
103.282
77.318
77.000
76.682
66.638
62.677
59.196
37.328
36.748
19.195
Me
Me
5i
Chemical Formula: C19H19NOS2
Exact Mass: 341.0908
1c-1870-400C-2
Std carbon
119.31
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


1c-2092-400nl
Std proton
7.192
7.176
7.163
7.085
7.065
7.016
7.008
7.000
6.586
6.568
6.550
6.477
6.457
5.489
5.167
3.799
2.934
2.536
2.508
2.476
2.368
2.348
2.335
2.315
1.432
1.380
0.000
S
S
COO^{t}Bu
NBoc
N
H
Me
7
Chemical Formula: $C_{28}H_{34}N_2O_4S_2$
Exact Mass: 526.1960
6.26
1.14
1.02
1.14
1.00
1.16
3.29
1.27
1.27
18.21
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

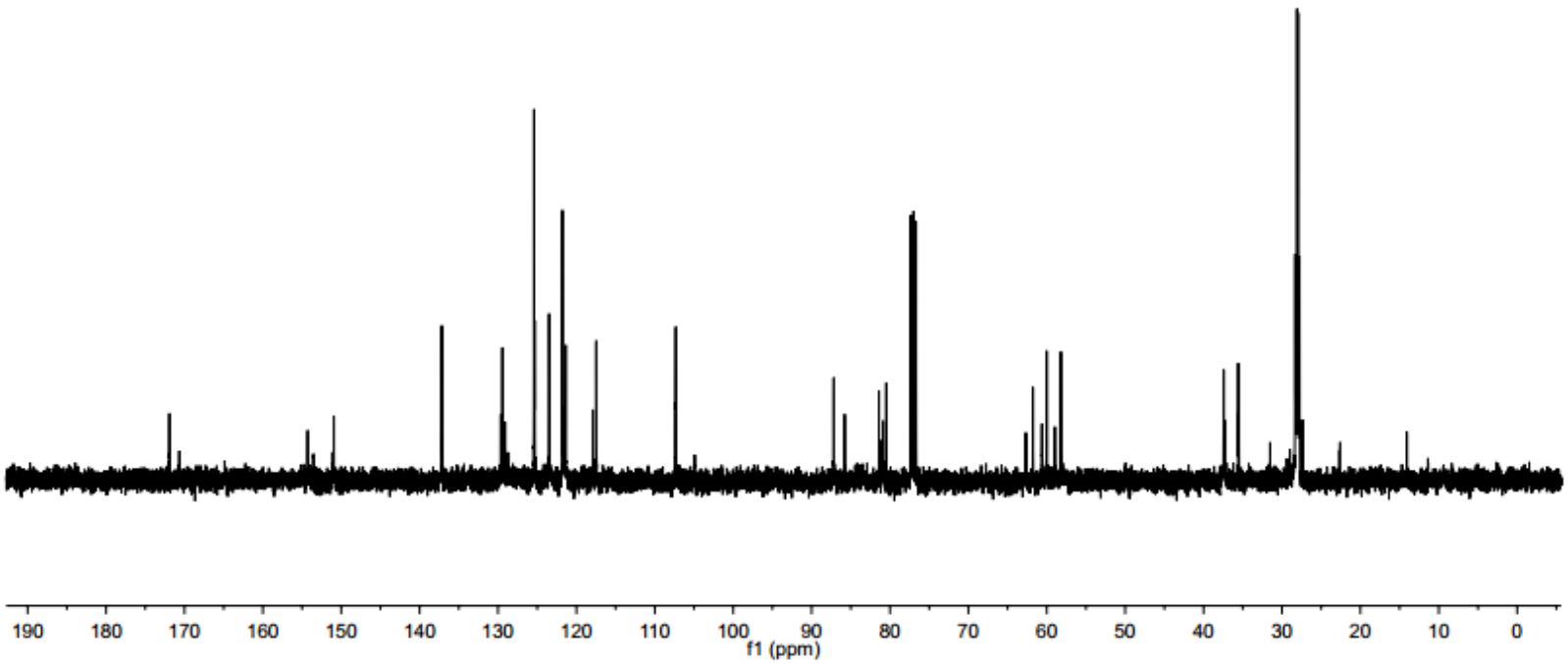
1c-2012-400C
Std carbon

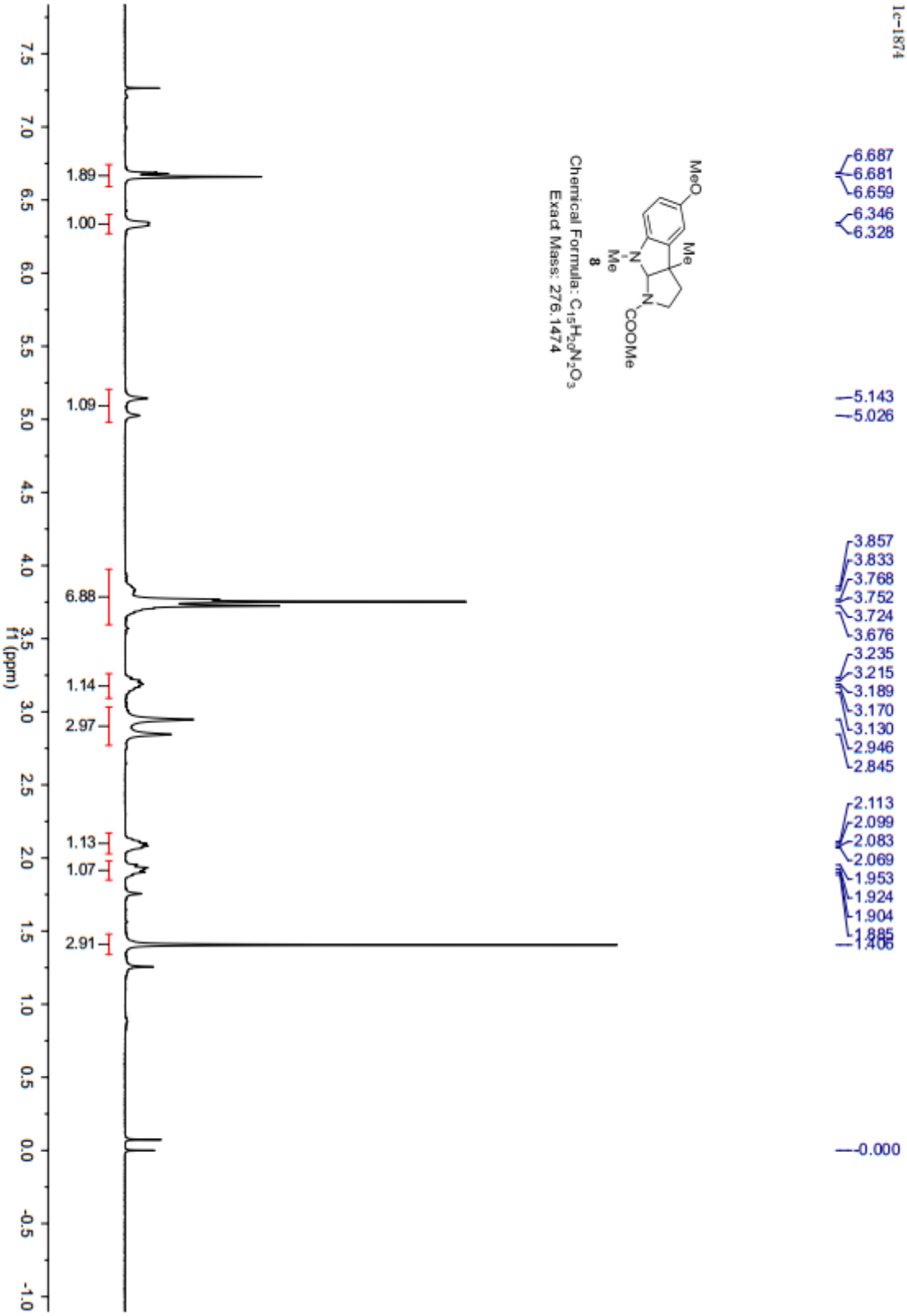
171.915
170.656
154.285
153.555
150.945
137.174
129.434
125.409
125.329
123.483
121.788
121.355
117.903
117.468
107.375
107.332
87.173
85.783
81.402
81.048
80.888
80.471
77.319
77.000
76.682
62.668
61.768
60.619
60.011
58.969
58.202
37.427
37.265
35.570
35.453
31.512
28.315
28.083
27.947
27.761
27.375
22.611
14.097

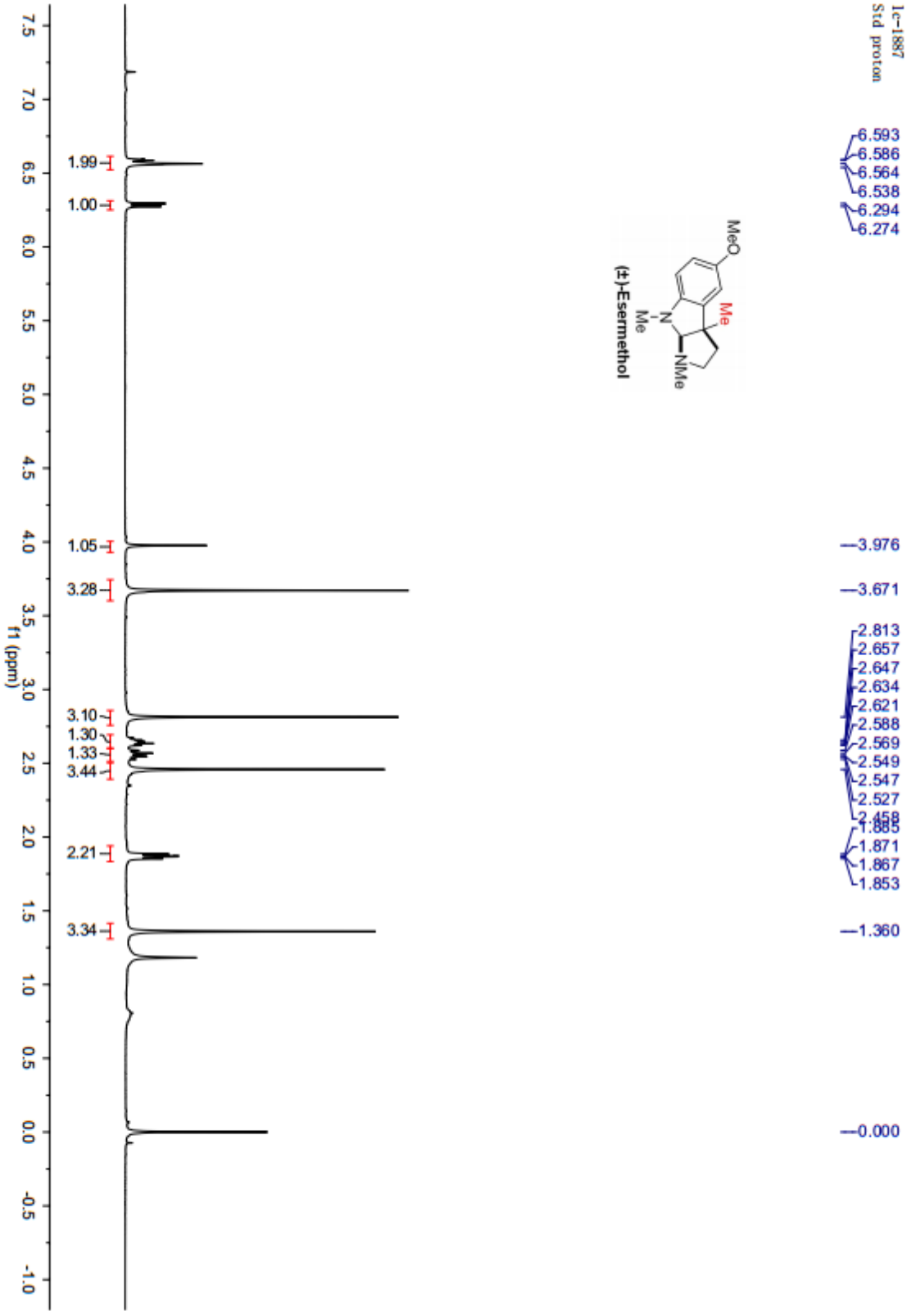


7

Chemical Formula: $C_{28}H_{34}N_2O_4S_2$
Exact Mass: 526.1960

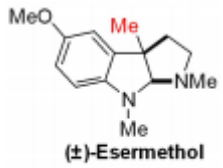



1c-1874
6.687
6.681
6.659
6.346
6.328
5.143
5.026
3.857
3.833
3.768
3.752
3.724
3.676
3.235
3.215
3.189
3.170
3.130
2.946
2.845
2.113
2.099
2.083
2.069
1.953
1.924
1.904
1.406
-0.000
1.89
1.00
1.09
6.88
1.14
2.97
1.13
1.07
2.91
f1 (ppm)
MeO
Me
N
N
Me
COOMe
8
Chemical Formula: C15H20N2O3
Exact Mass: 276.1474

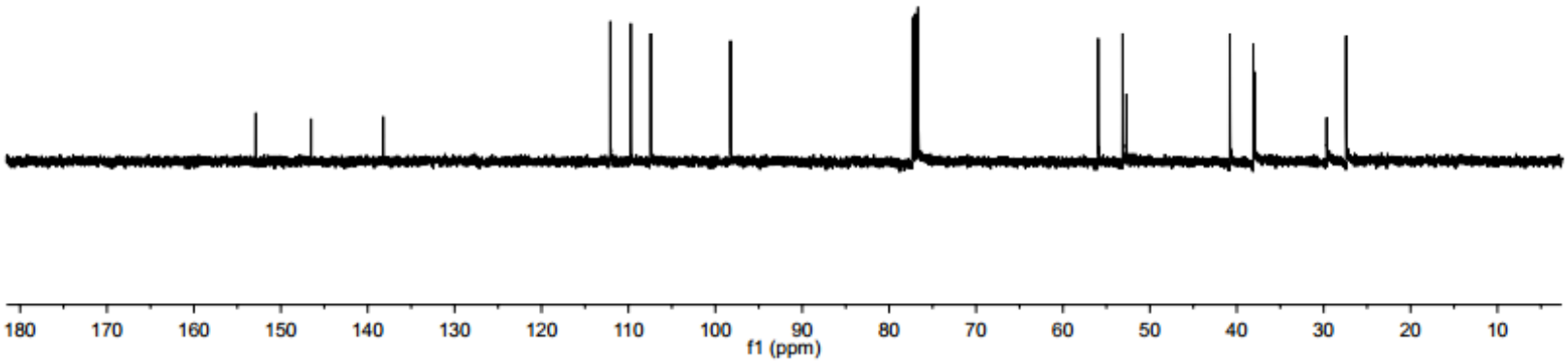

1c-1887
Std proton
6.593
6.586
6.564
6.538
6.294
6.274
3.976
3.671
2.813
2.657
2.647
2.634
2.621
2.588
2.569
2.549
2.547
2.527
2.458
1.885
1.871
1.867
1.853
1.360
0.000
MeO
Me
NMe
Me
(±)-Esermethol
1.99
1.00
1.05
3.28
3.10
1.30
1.33
3.44
2.21
3.34
f1 (ppm)

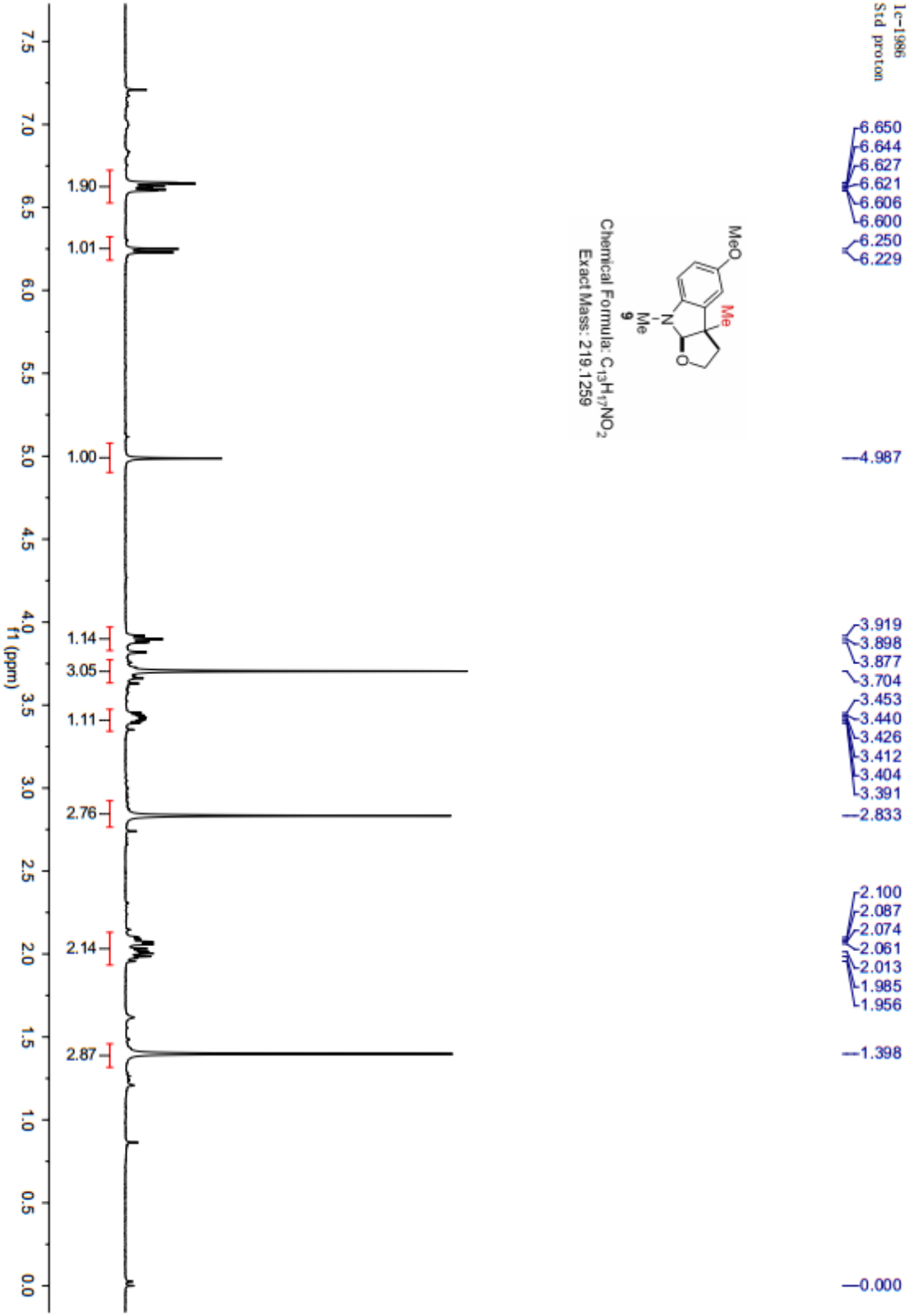
1c-1887-400C
Std carbon

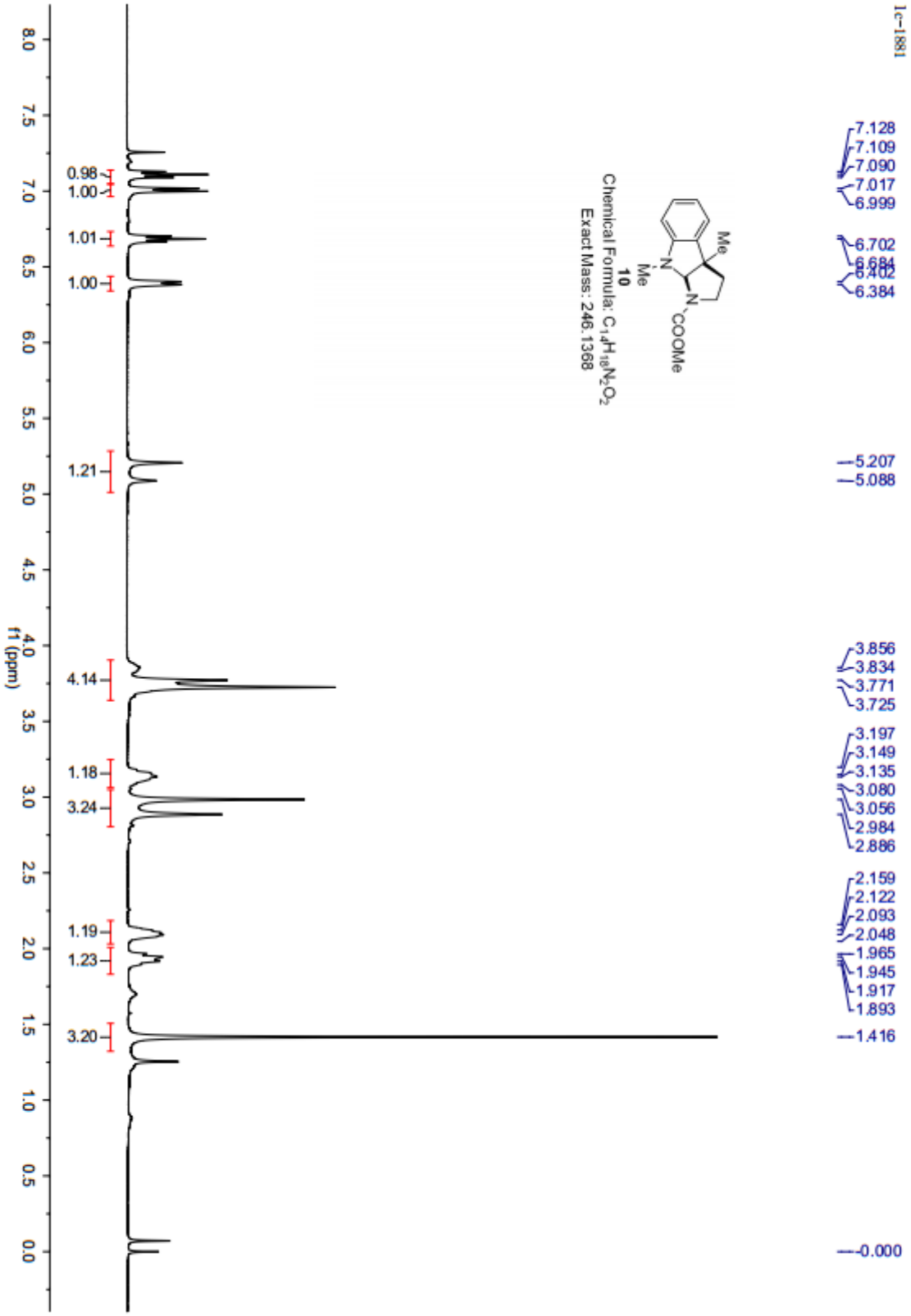
152.870
146.528
138.218
112.077
109.736
107.423
98.249
77.318
77.000
76.682
55.950
53.127
52.695
40.790
38.095
37.975
27.412

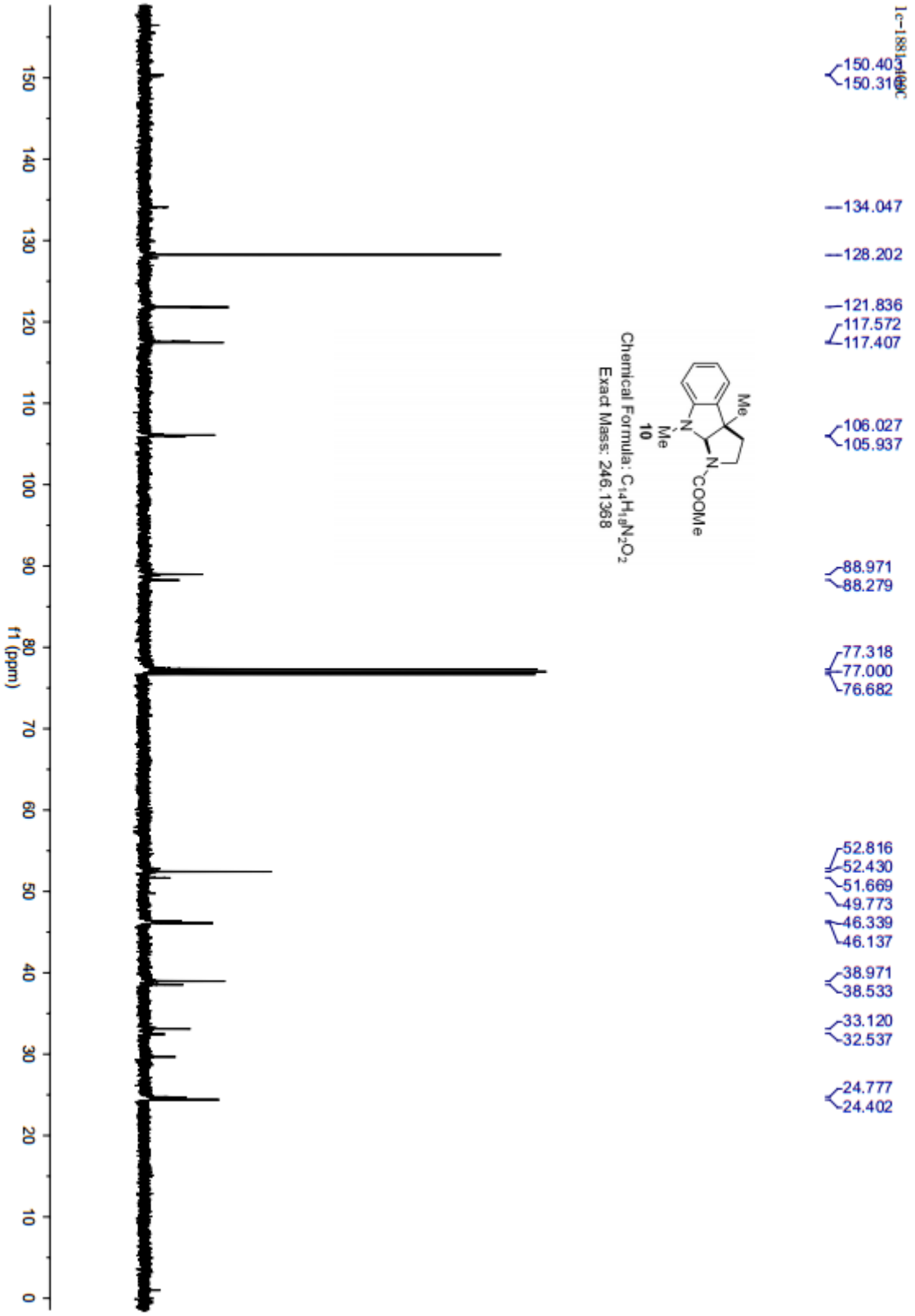


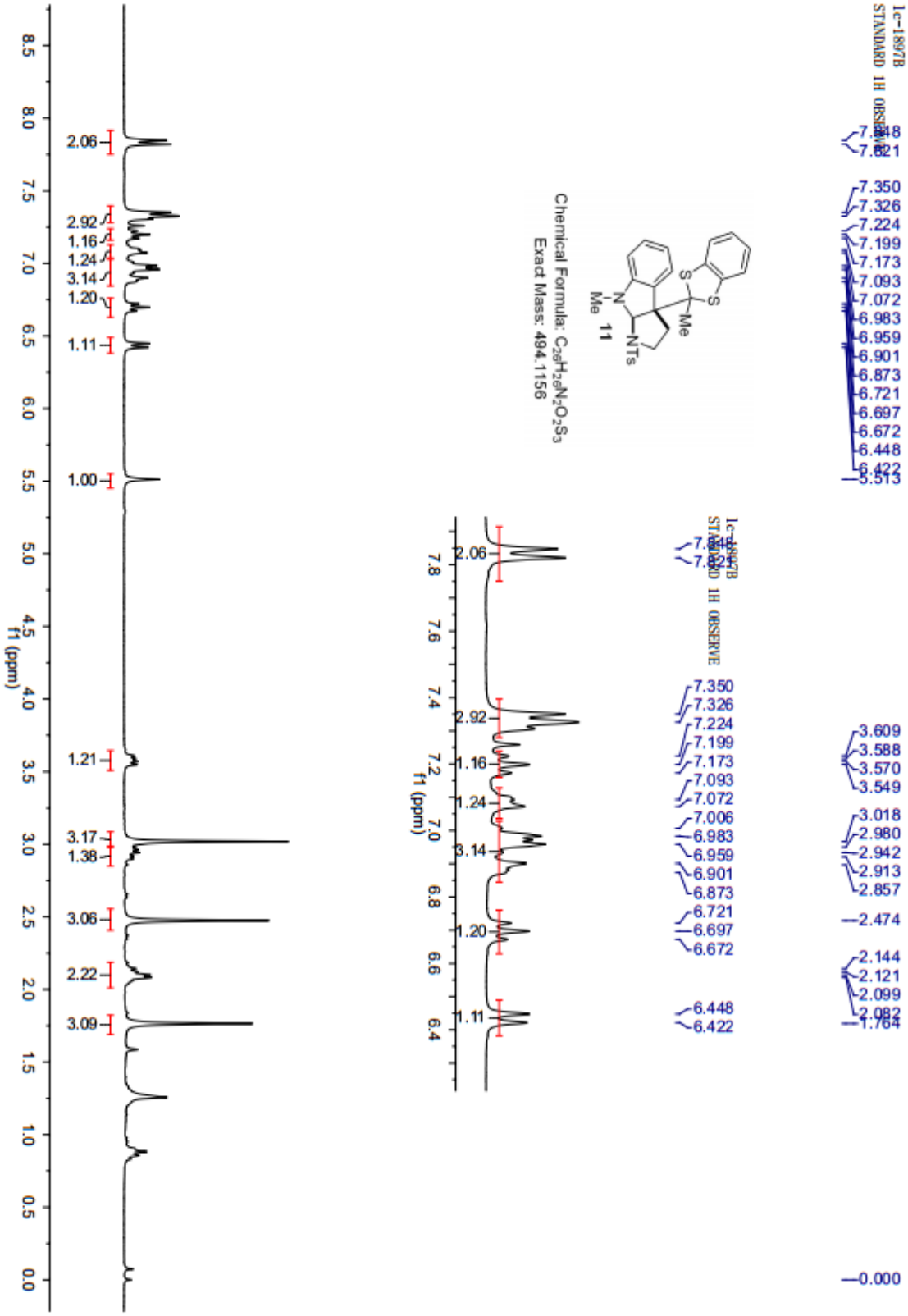
(±)-Esermethol

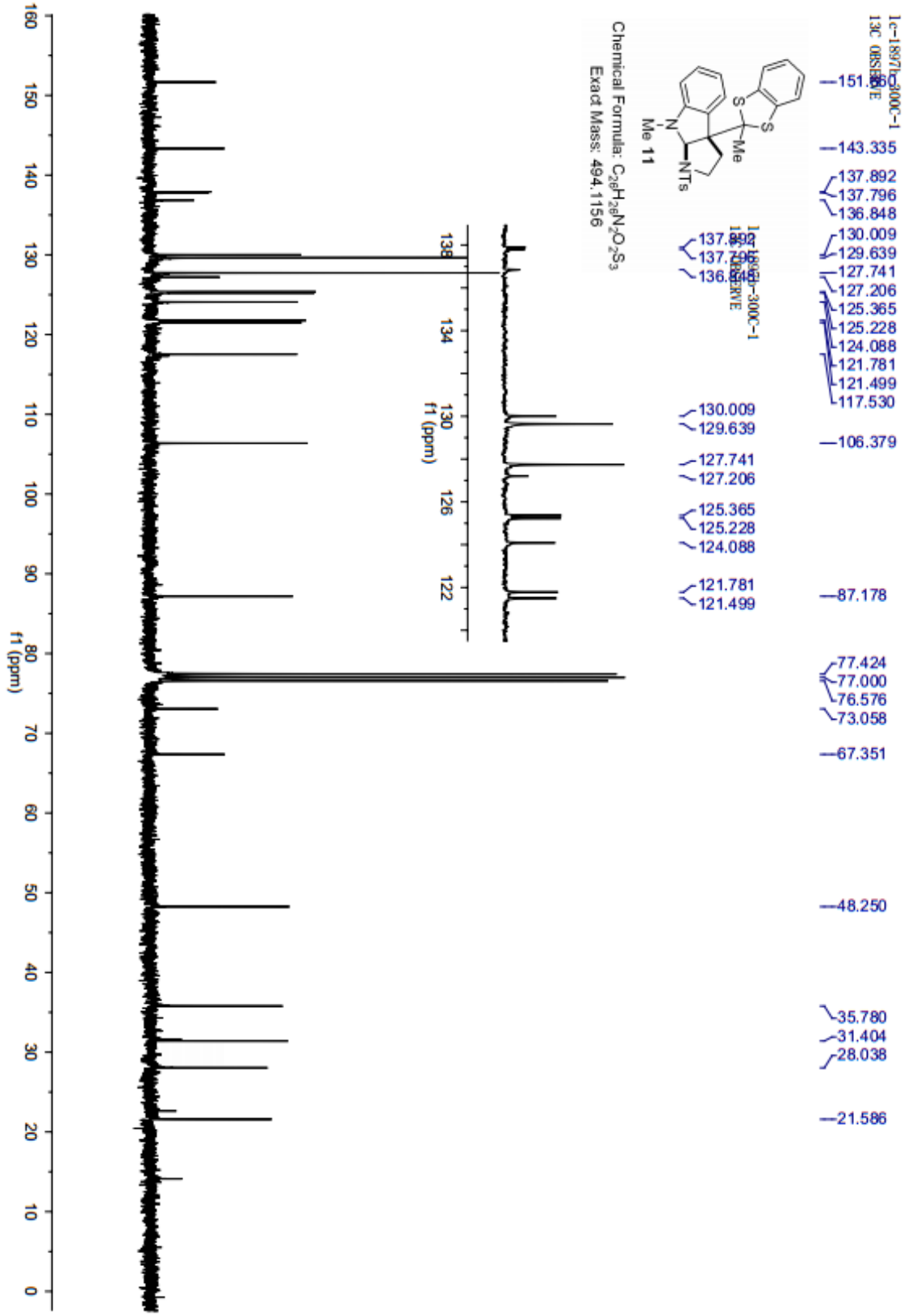


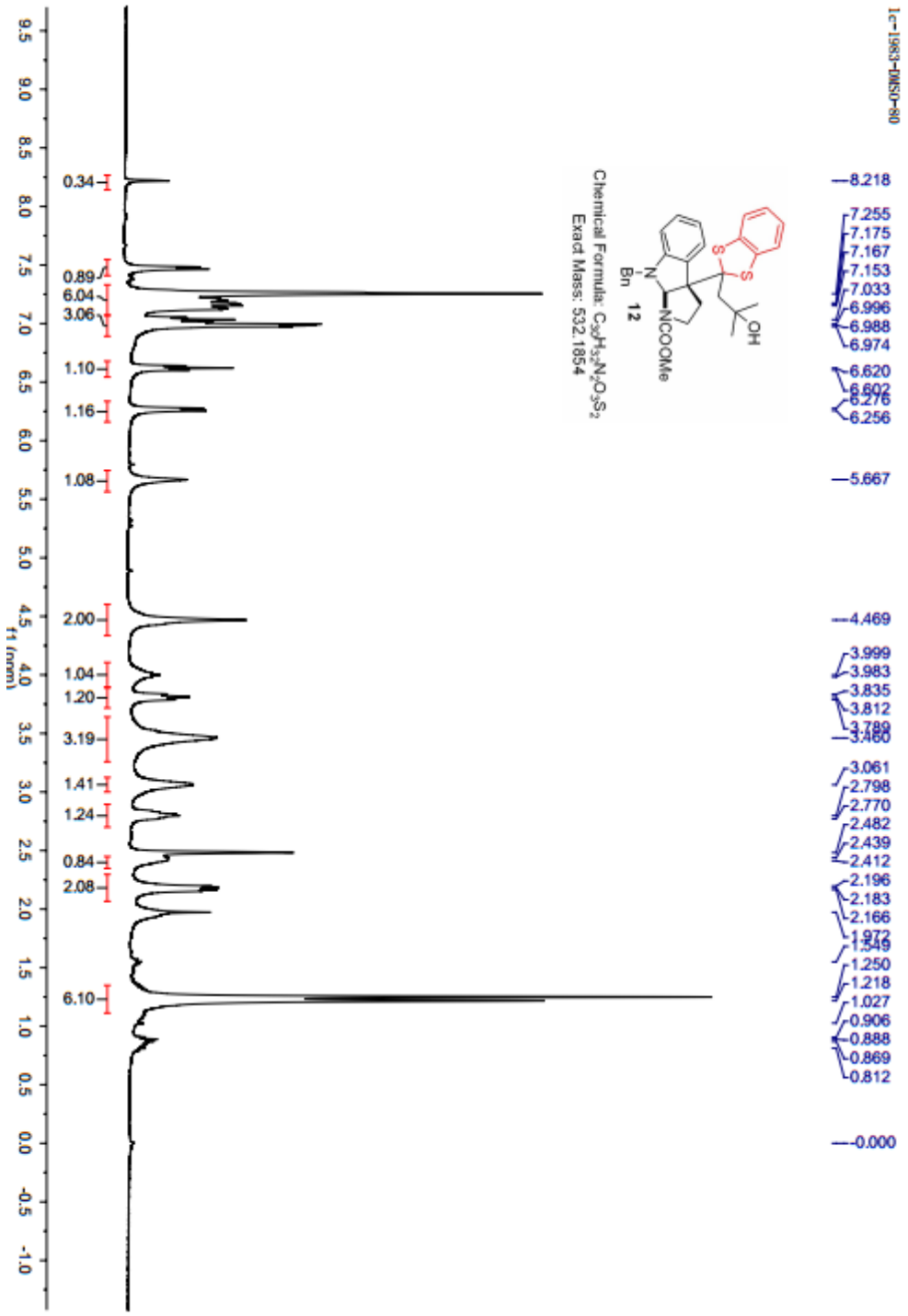

lc-1986
Std proton
6.650
6.644
6.627
6.621
6.606
6.600
6.250
6.229
4.987
3.919
3.898
3.877
3.704
3.453
3.440
3.426
3.412
3.404
3.391
2.833
2.100
2.087
2.074
2.061
2.013
1.985
1.956
1.398
0.000
MeO
Me
N
Me
O
9
Chemical Formula: C13H17NO2
Exact Mass: 219.1259
1.90
1.01
1.00
1.14
3.05
1.11
2.76
2.14
2.87
f1 (ppm)

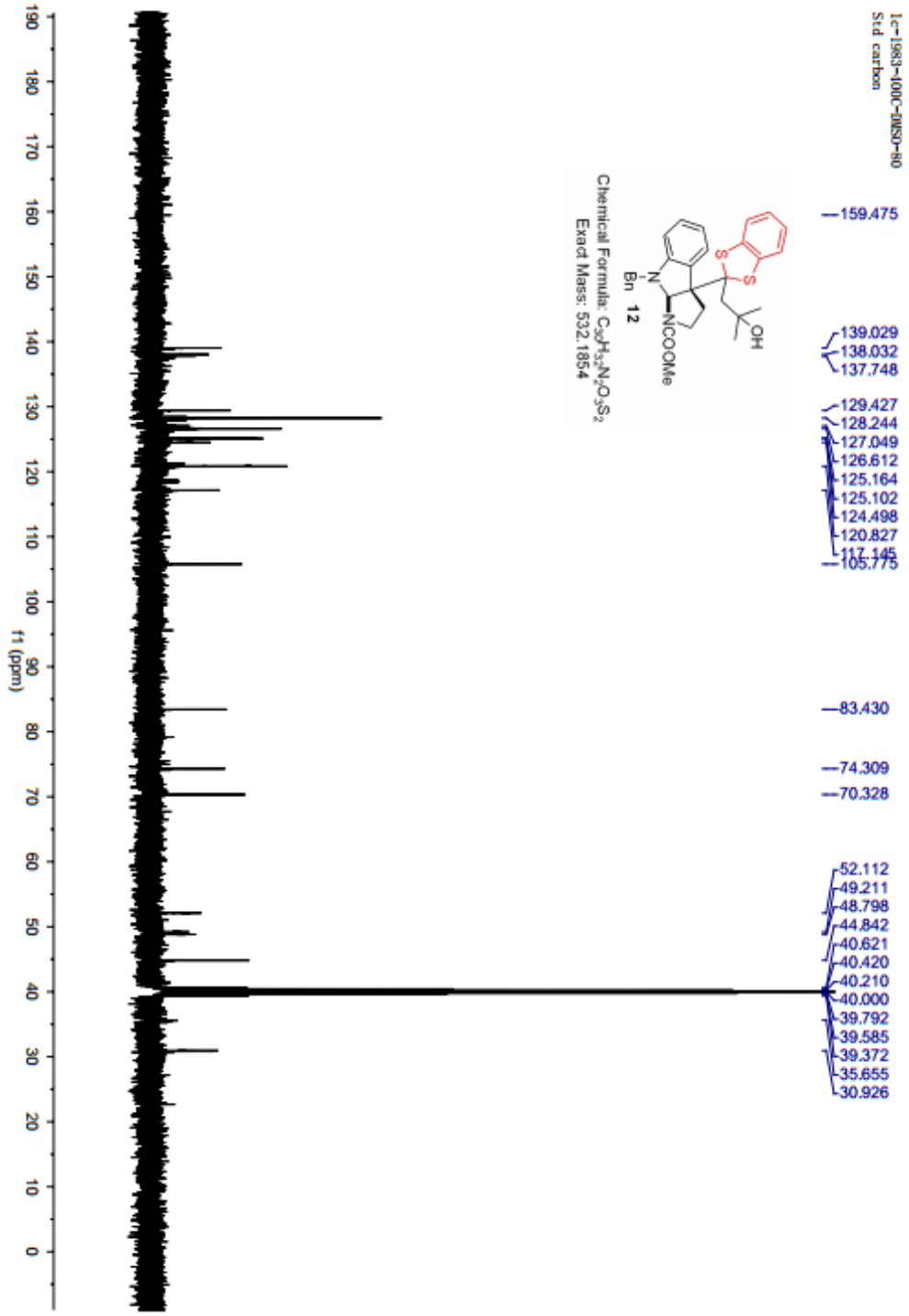

1c-1881
7.128
7.109
7.090
7.017
6.999
6.702
6.684
6.402
6.384
5.207
5.088
3.856
3.834
3.771
3.725
3.197
3.149
3.135
3.080
3.056
2.984
2.886
2.159
2.122
2.093
2.048
1.965
1.945
1.917
1.893
1.416
0.000
0.98
1.00
1.01
1.00
1.21
4.14
1.18
3.24
1.19
1.23
3.20
f1 (ppm)
Chemical Formula: C14H18N2O2
Exact Mass: 246.1368
10
Me
Me
N
N
COOMe

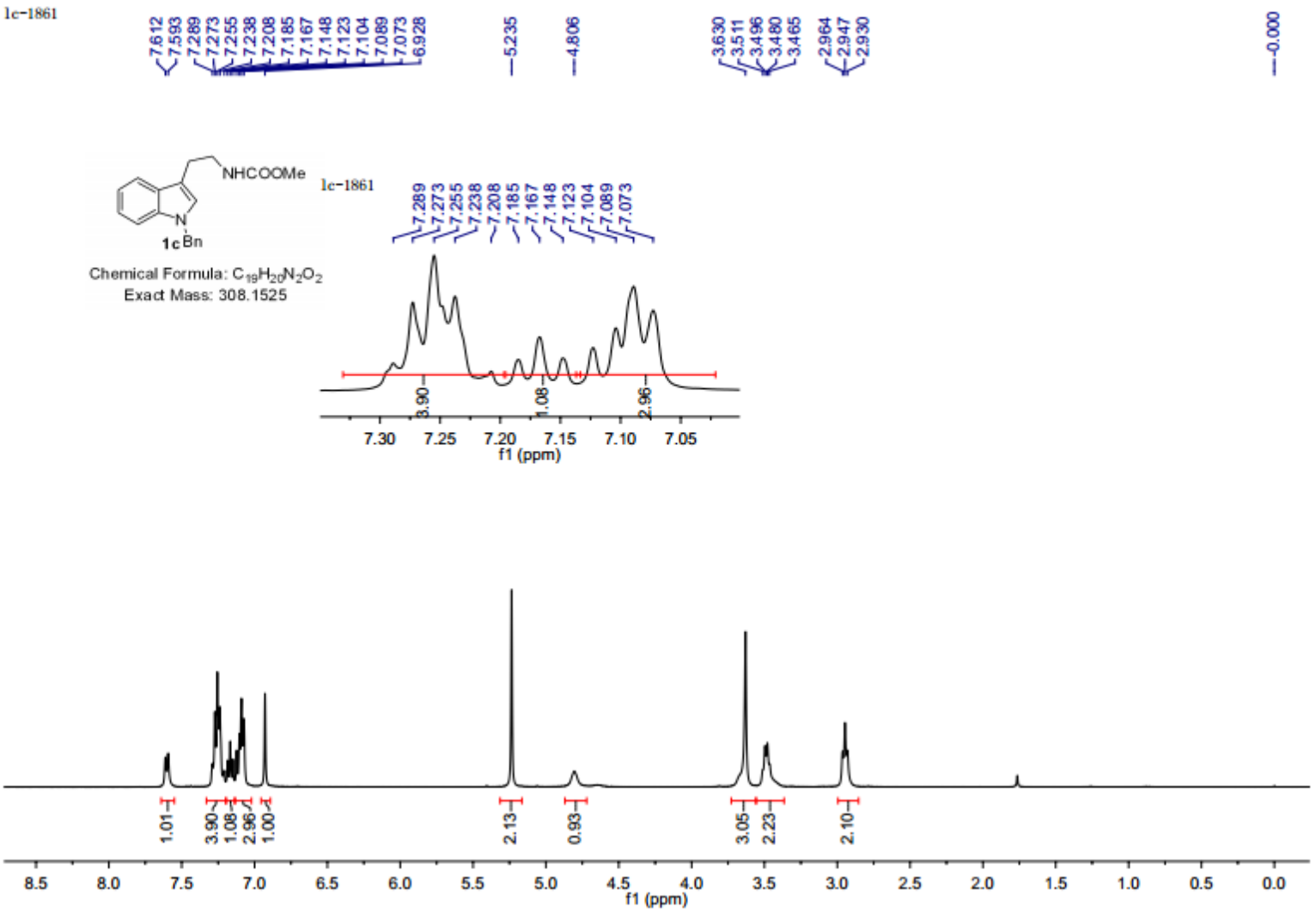

1c-188
150.403
150.316
134.047
128.202
121.836
117.572
117.407
106.027
105.937
88.971
88.279
77.318
77.000
76.682
52.816
52.430
51.669
49.773
46.339
46.137
38.971
38.533
33.120
32.537
24.777
24.402
Me
N
Me
10
N
COOMe
Chemical Formula: C14H18N2O2
Exact Mass: 246.1368
f1 (ppm)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

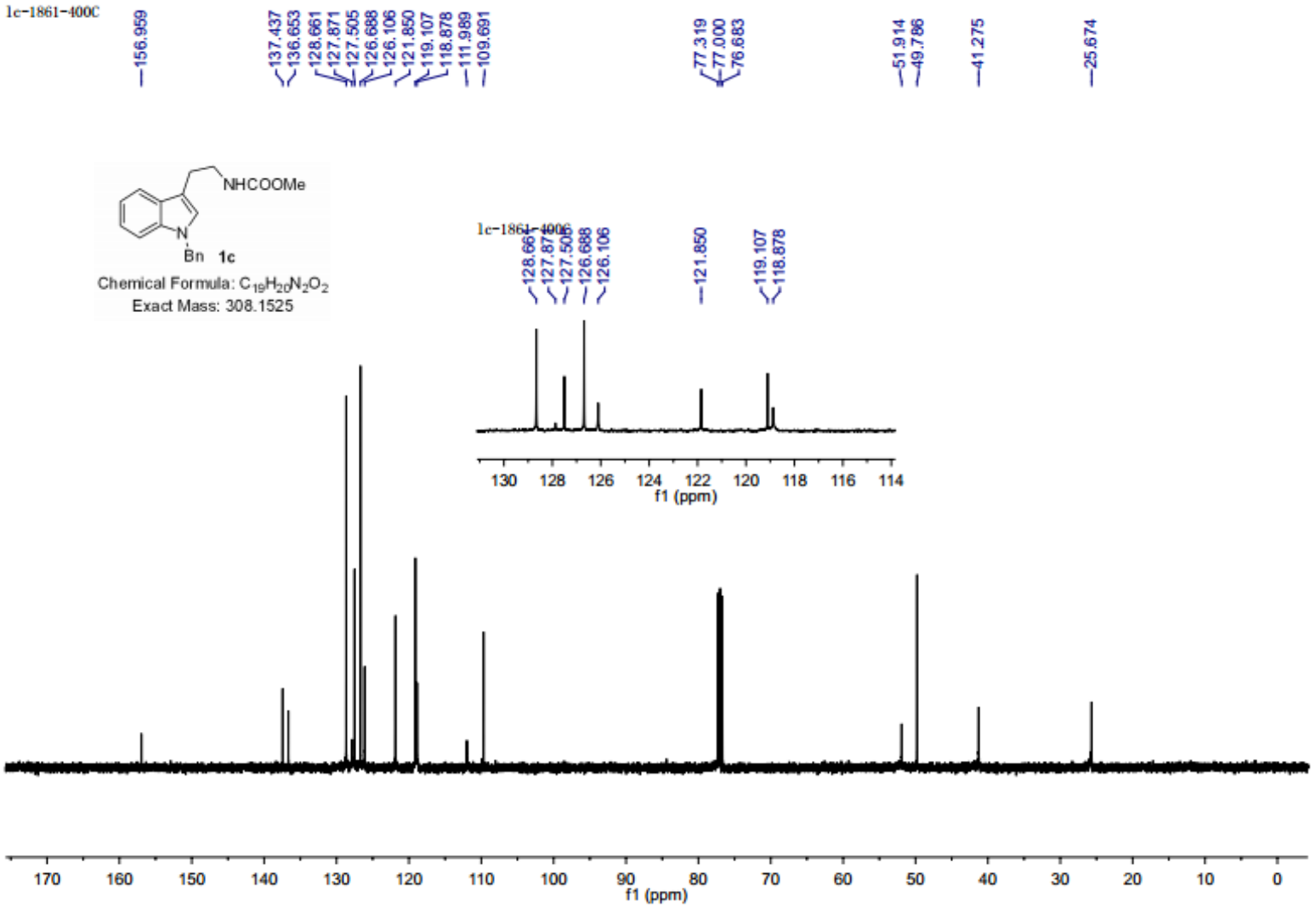

1c-1897B
STANDARD 1H OBSERVE
7.848
7.821
7.350
7.326
7.224
7.199
7.173
7.093
7.072
6.983
6.959
6.901
6.873
6.721
6.697
6.672
6.448
6.422
5.513
3.609
3.588
3.570
3.549
3.018
2.980
2.942
2.913
2.857
2.474
2.144
2.121
2.099
2.082
1.764
0.000
Chemical Formula: C29H29N2O2S3
Exact Mass: 494.1156
Me
N
S
S
Me
NTs
11
2.06
2.92
1.16
1.24
3.14
1.20
1.11
1.00
1.21
3.17
1.38
3.06
2.22
3.09
f1 (ppm)

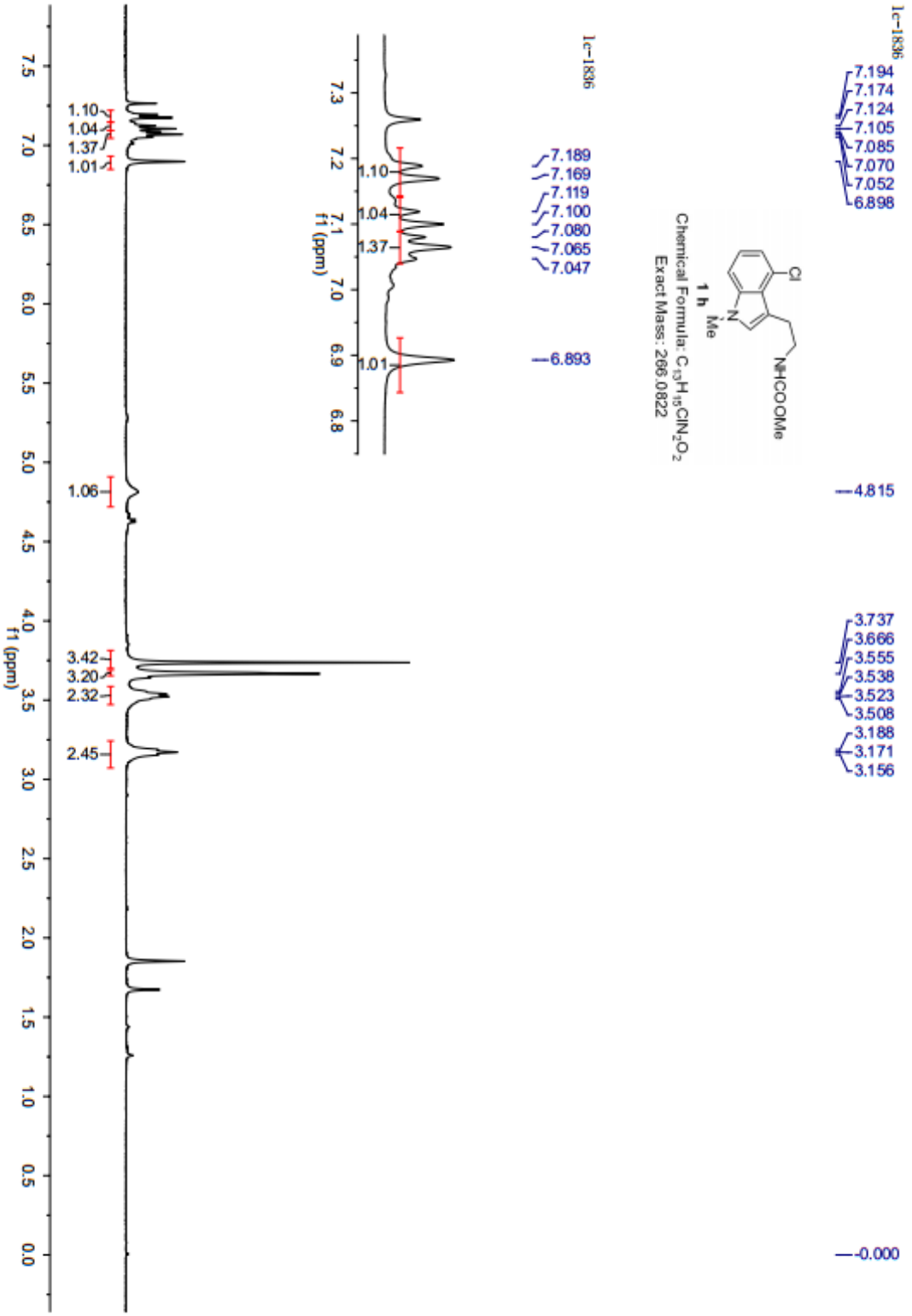

Chemical Formula: C28H28N2O2S3
Exact Mass: 494.1156
Me 11
NTs
Me
151.866
143.335
137.892
137.796
136.848
130.009
129.639
127.741
127.206
125.365
125.228
124.088
121.781
121.499
117.530
106.379
87.178
77.424
77.000
76.576
73.058
67.351
48.250
35.780
31.404
28.038
21.586
f1 (ppm)

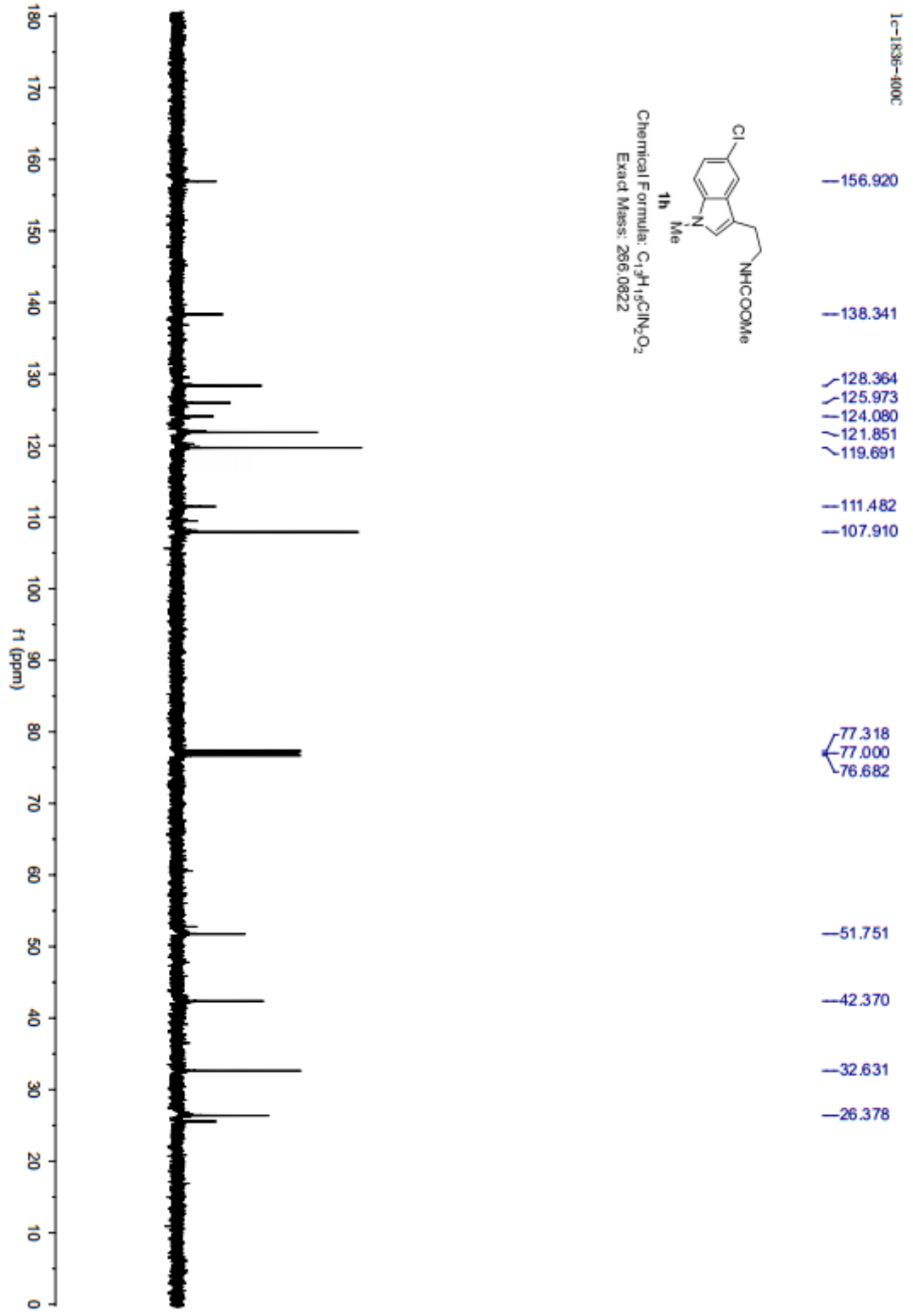

1c=1983-DMSO-80
Chemical Formula: $C_{30}H_{32}N_2O_3S_2$
Exact Mass: 532.1854
Bn
12
NCOOMe
OH
8.218
7.255
7.175
7.167
7.153
7.033
6.996
6.988
6.974
6.620
6.602
6.276
6.256
5.667
4.469
3.999
3.983
3.835
3.812
3.789
3.460
3.061
2.798
2.770
2.482
2.439
2.412
2.196
2.183
2.166
1.972
1.549
1.250
1.218
1.027
0.906
0.888
0.869
0.812
0.000
0.34
0.89
6.04
3.06
1.10
1.16
1.08
2.00
1.04
1.20
3.19
1.41
1.24
0.84
2.08
6.10
f1 (ppm)

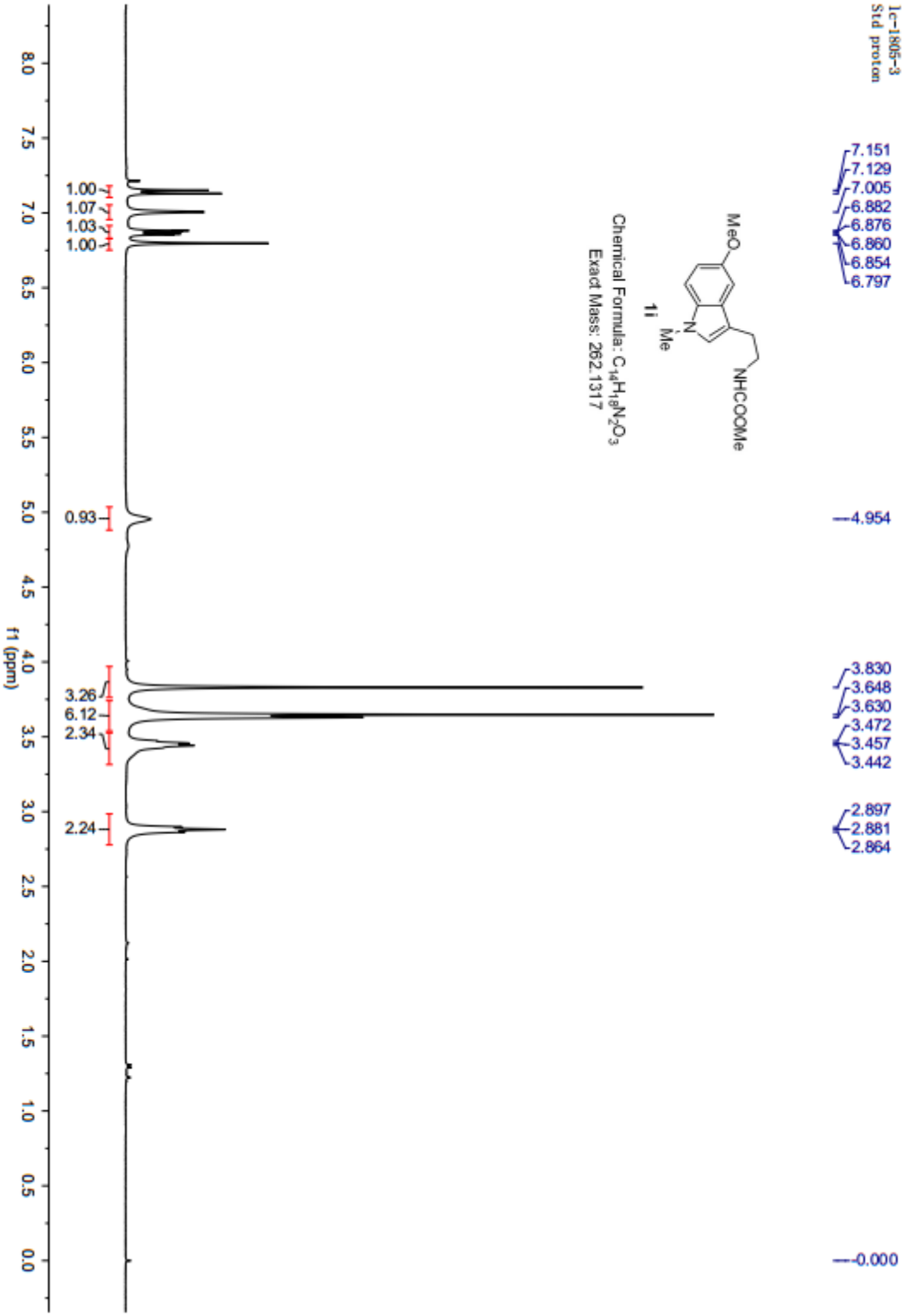

1c-1983-400C-DMSO-80
Std carbon
159.475
139.029
138.032
137.748
129.427
128.244
127.049
126.612
125.164
125.102
124.498
120.827
117.145
105.775
83.430
74.309
70.328
52.112
49.211
48.798
44.842
40.621
40.420
40.210
40.000
39.792
39.585
39.372
35.655
30.926
Chemical Formula: C29H32N2O3S2
Exact Mass: 532.1854
Bn 12
NCOOMe
OH
f1 (ppm)

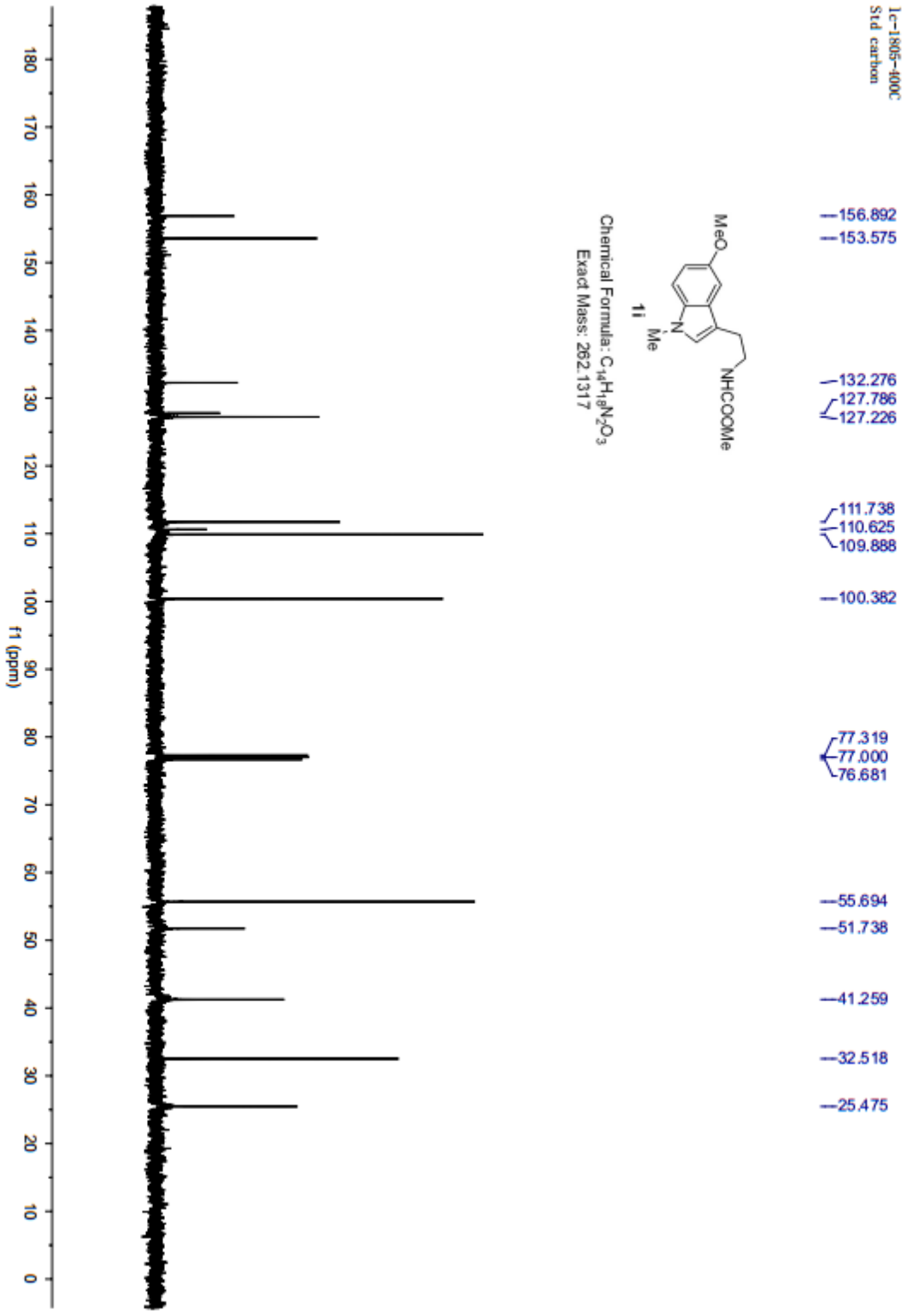

1c-1861
7.612
7.593
7.289
7.273
7.255
7.238
7.208
7.185
7.167
7.148
7.123
7.104
7.089
7.073
6.928
5.235
4.806
3.630
3.511
3.496
3.480
3.465
2.964
2.947
2.930
0.000
NHCOOMe
N
1cBn
Chemical Formula: C19H20N2O2
Exact Mass: 308.1525
1c-1861
7.289
7.273
7.255
7.238
7.208
7.185
7.167
7.148
7.123
7.104
7.089
7.073
3.90
1.08
2.96
7.30
7.25
7.20
7.15
7.10
7.05
f1 (ppm)
1.01
3.90
1.08
2.96
1.00
2.13
0.93
3.05
2.23
2.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

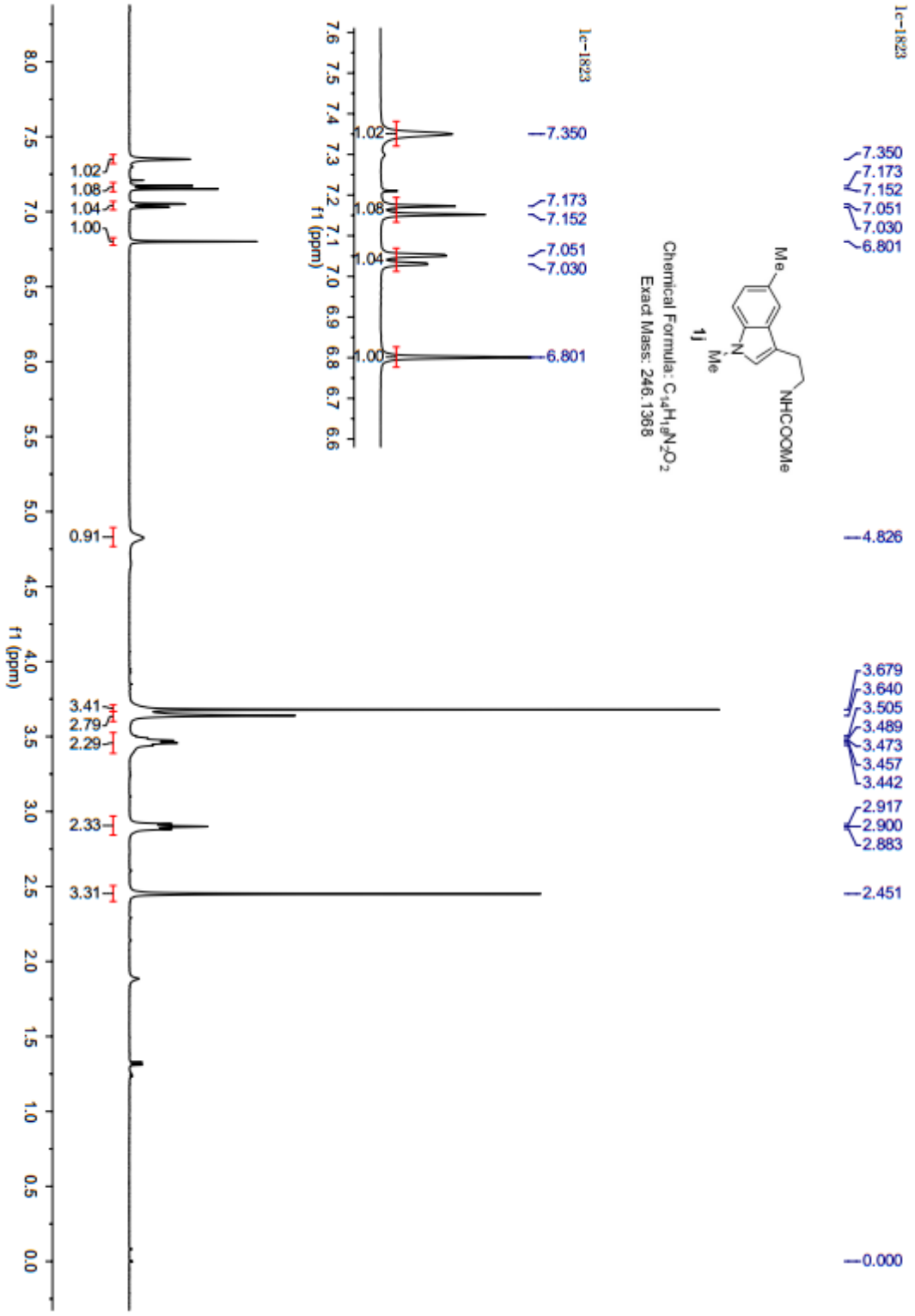

1c-1861-400C
156.959
137.437
136.653
128.661
127.871
127.505
126.688
126.106
121.850
119.107
118.878
111.989
109.691
77.319
77.000
76.683
51.914
49.786
41.275
25.674
NHCOOMe
N
Bn 1c
Chemical Formula: C19H20N2O2
Exact Mass: 308.1525
1c-1861-400C
128.661
127.871
127.505
126.688
126.106
121.850
119.107
118.878
130 128 126 124 122 120 118 116 114
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

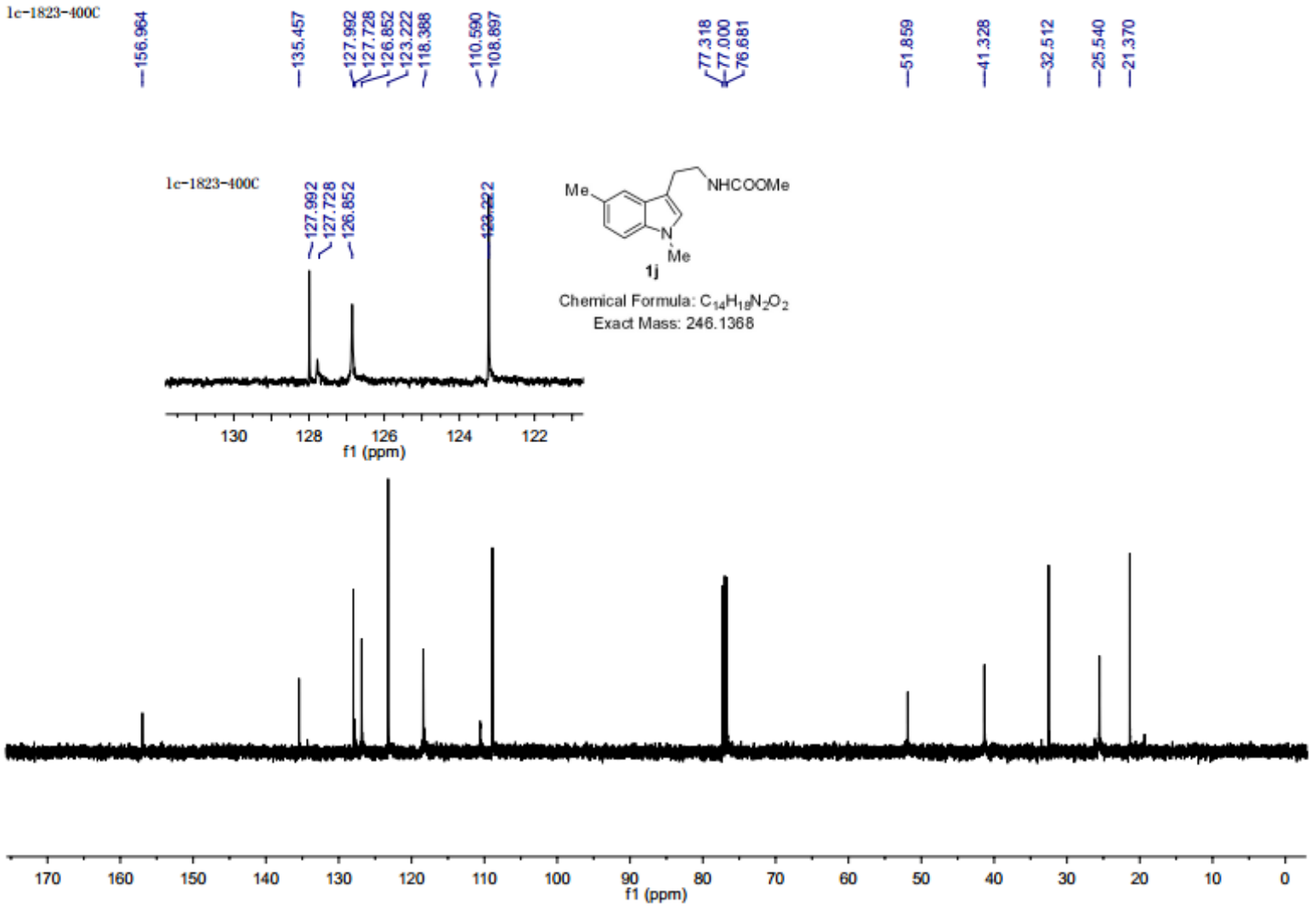

1c-1836
7.194
7.174
7.124
7.105
7.085
7.070
7.052
6.898
4.815
3.737
3.666
3.555
3.538
3.523
3.508
3.188
3.171
3.156
0.000
1 h
Me
N
Cl
NHCOOMe
Chemical Formula: C13H15ClN2O2
Exact Mass: 266.0822
1c-1836
7.189
7.169
7.119
7.100
7.080
7.065
7.047
6.893
1.10
1.04
1.37
1.01
f1 (ppm)
1.10
1.04
1.37
1.01
1.06
3.42
3.20
2.32
2.45
f1 (ppm)

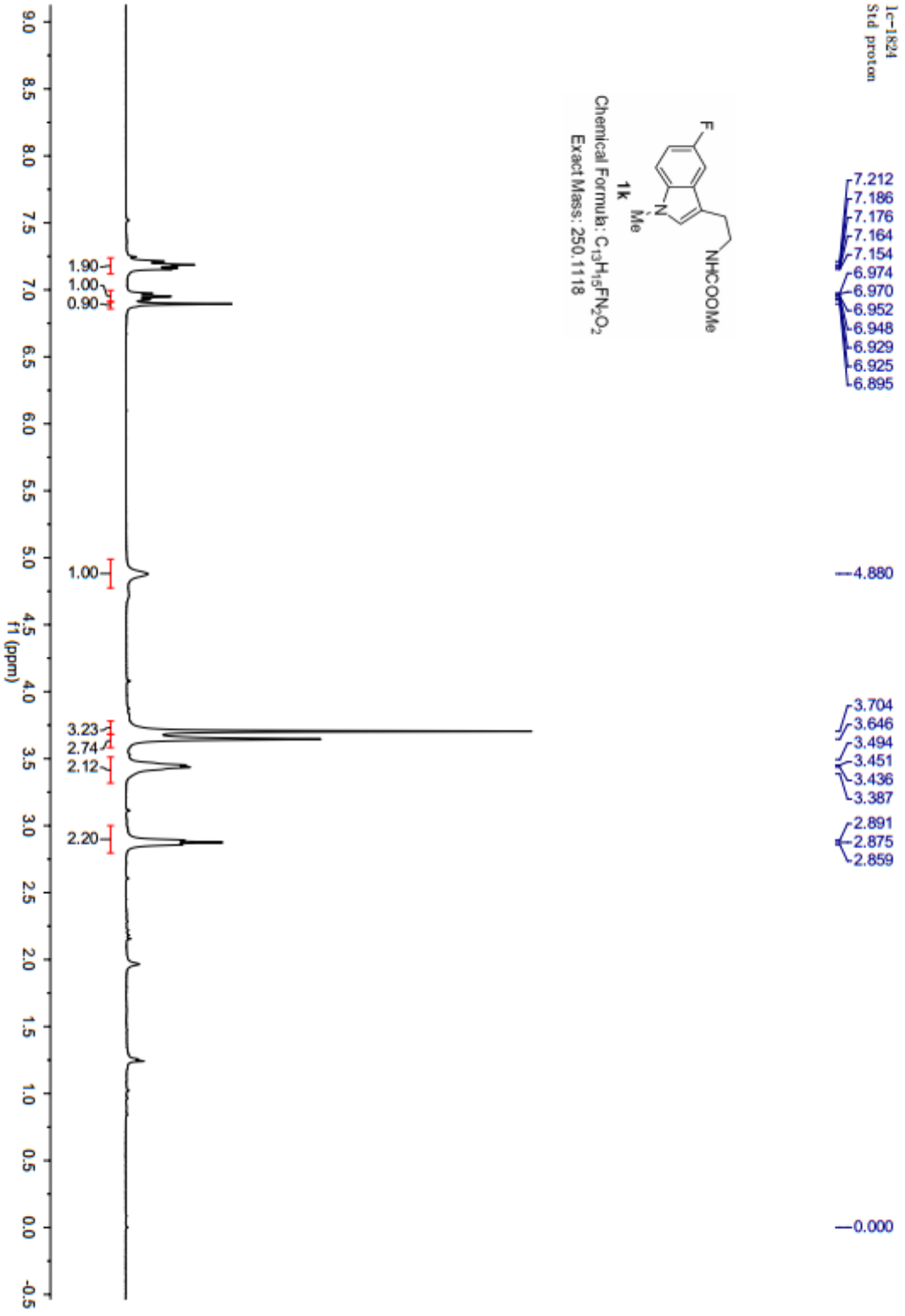

1c-1836-400C
156.920
138.341
128.364
125.973
124.080
121.851
119.691
111.482
107.910
77.318
77.000
76.682
51.751
42.370
32.631
26.378
Cl
NHCOOMe
N
Me
1h
Chemical Formula: C13H15ClN2O2
Exact Mass: 266.0822
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

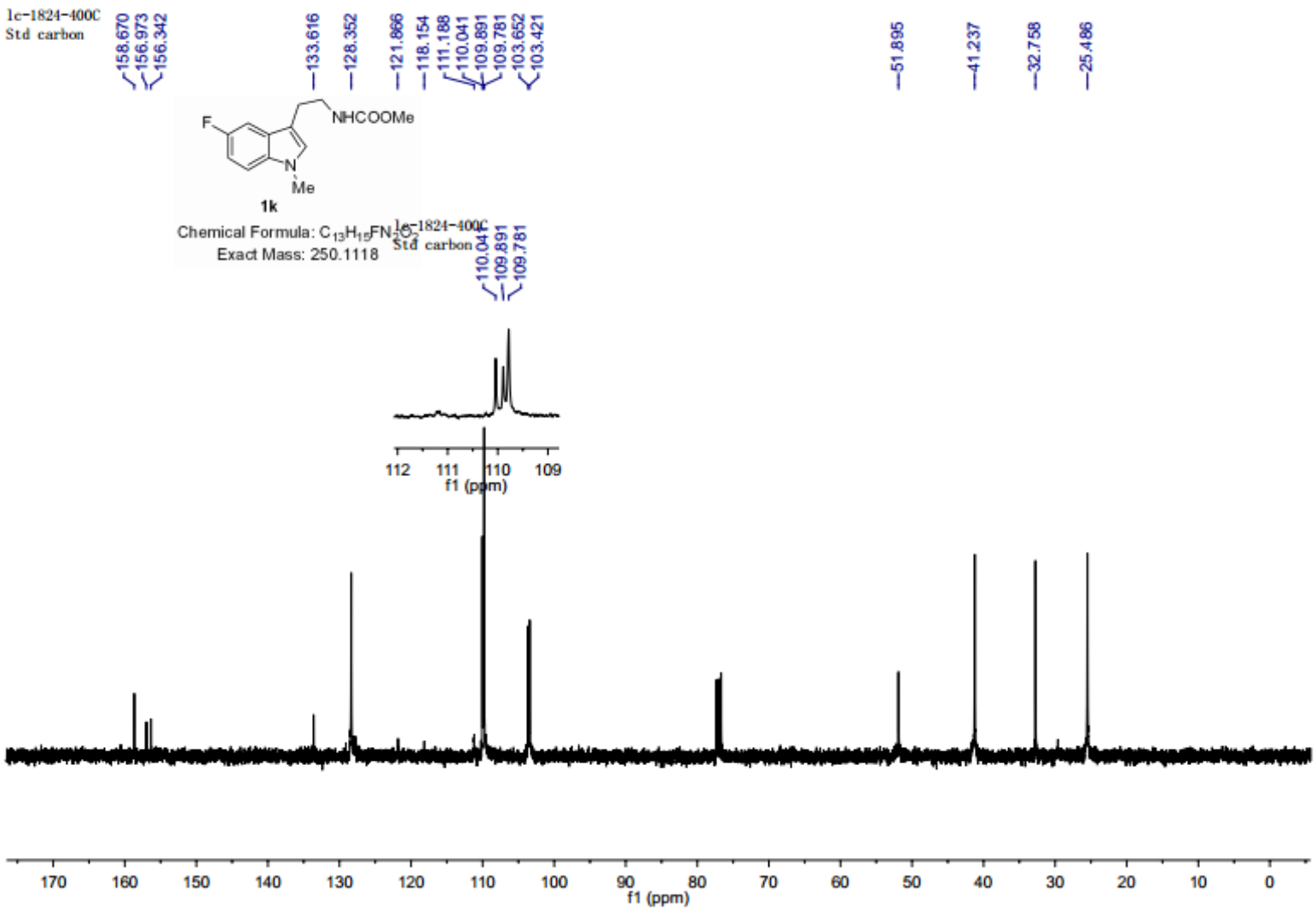

1c-1805-3
Std proton
7.151
7.129
7.005
6.882
6.876
6.860
6.854
6.797
4.954
3.830
3.648
3.630
3.472
3.457
3.442
2.897
2.881
2.864
0.000
1.00
1.07
1.03
1.00
0.93
3.26
6.12
2.34
2.24
f1 (ppm)
Chemical Formula: C14H18N2O3
Exact Mass: 262.1317
1i
MeO
NHCOOMe
N
Me


1c-1805-400C
Std carbon
156.892
153.575
132.276
127.786
127.226
111.738
110.625
109.888
100.382
77.319
77.000
76.681
55.694
51.738
41.259
32.518
25.475
MeO
NHCOOMe
N
Me
1i
Chemical Formula: C14H18N2O3
Exact Mass: 262.1317
f1 (ppm)

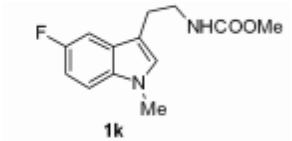

1c-1823
Chemical Formula: C14H18N2O2
Exact Mass: 246.1368
1j
Me
N
Me
NHCOOMe
7.350
7.173
7.152
7.051
7.030
6.801
4.826
3.679
3.640
3.505
3.489
3.473
3.457
3.442
2.917
2.900
2.883
2.451
0.000
1.02
1.08
1.04
1.00
0.91
3.41
2.79
2.29
2.33
3.31
f1 (ppm)


1c-1823-400C
156.964
135.457
127.992
127.728
126.852
123.222
118.388
110.590
108.897
77.318
77.000
76.681
51.859
41.328
32.512
25.540
21.370
1c-1823-400C
127.992
127.728
126.852
123.222
Me
NHCOOMe
N
Me
1j
Chemical Formula: C14H18N2O2
Exact Mass: 246.1368
130
128
126
124
122
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


1c-1824
Std proton
7.212
7.186
7.176
7.164
7.154
6.974
6.970
6.952
6.948
6.929
6.925
6.895
4.880
3.704
3.646
3.494
3.451
3.436
3.387
2.891
2.875
2.859
0.000
1k
Me
NHCOOMe
F
N
Chemical Formula: C13H15FN2O2
Exact Mass: 250.1118
1.90
1.00
0.90
1.00
3.23
2.74
2.12
2.20
f1 (ppm)

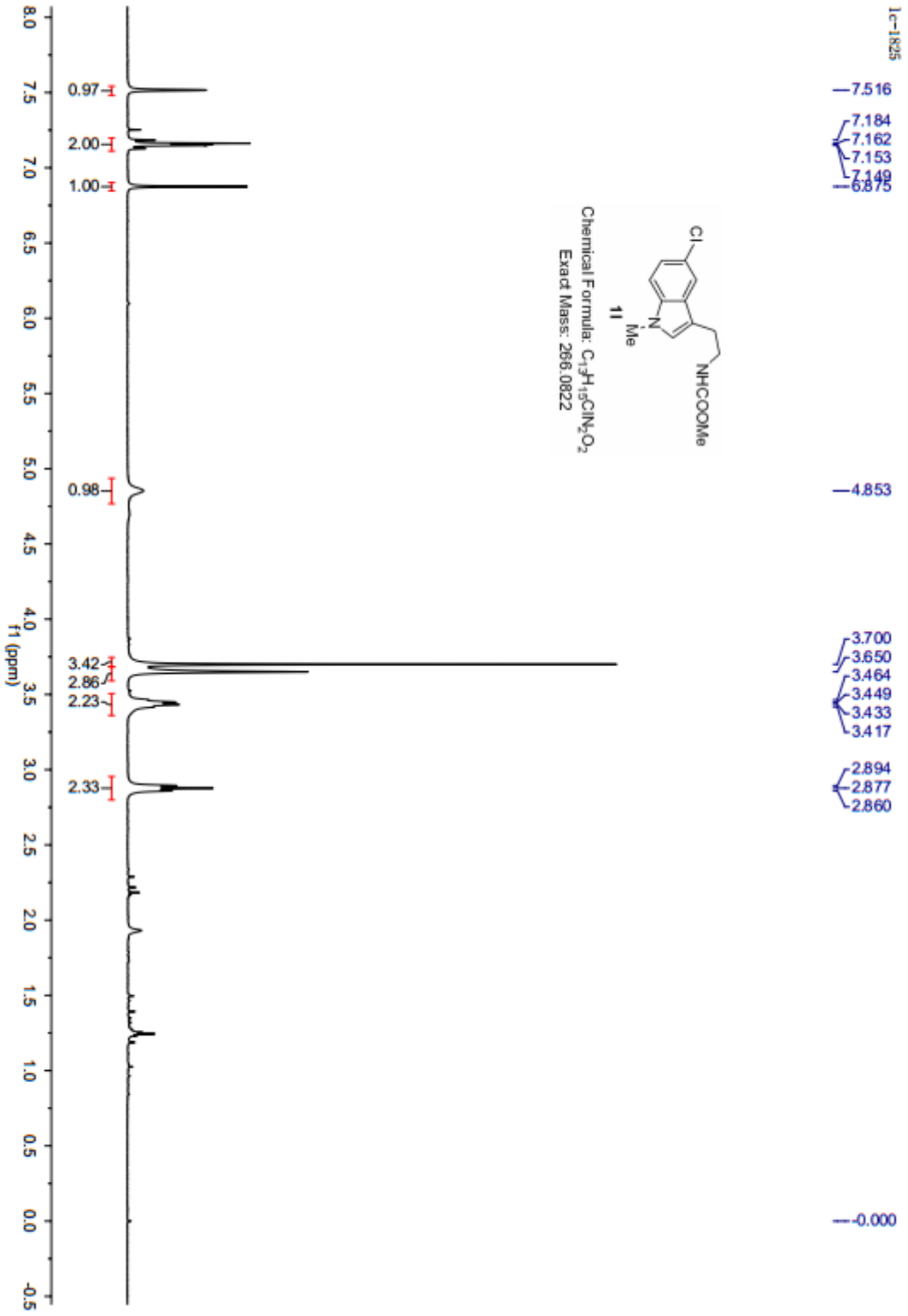

1c-1824-400C
Std carbon
158.670
156.973
156.342
133.616
128.352
121.866
118.154
111.188
110.041
109.891
109.781
103.652
103.421
51.895
41.237
32.758
25.486
F
NHCOOMe
N
Me
1k
Chemical Formula: C13H15FN2O2
Exact Mass: 250.1118
1c-1824-400C
Std carbon
110.041
109.891
109.781
112
111
110
109
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

lc-1824-f
Std Fluorine



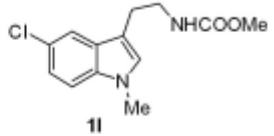
1k

Chemical Formula: $C_{13}H_{15}FN_2O_2$
Exact Mass: 250.1118


1e-1825
7.516
7.184
7.162
7.153
7.149
6.875
4.853
3.700
3.650
3.464
3.449
3.433
3.417
2.894
2.877
2.860
-0.000
0.97
2.00
1.00
0.98
3.42
2.86
2.23
2.33
f1 (ppm)
Chemical Formula: C13H15ClN2O2
Exact Mass: 266.0822
11
Cl
N
Me
NHCOOMe

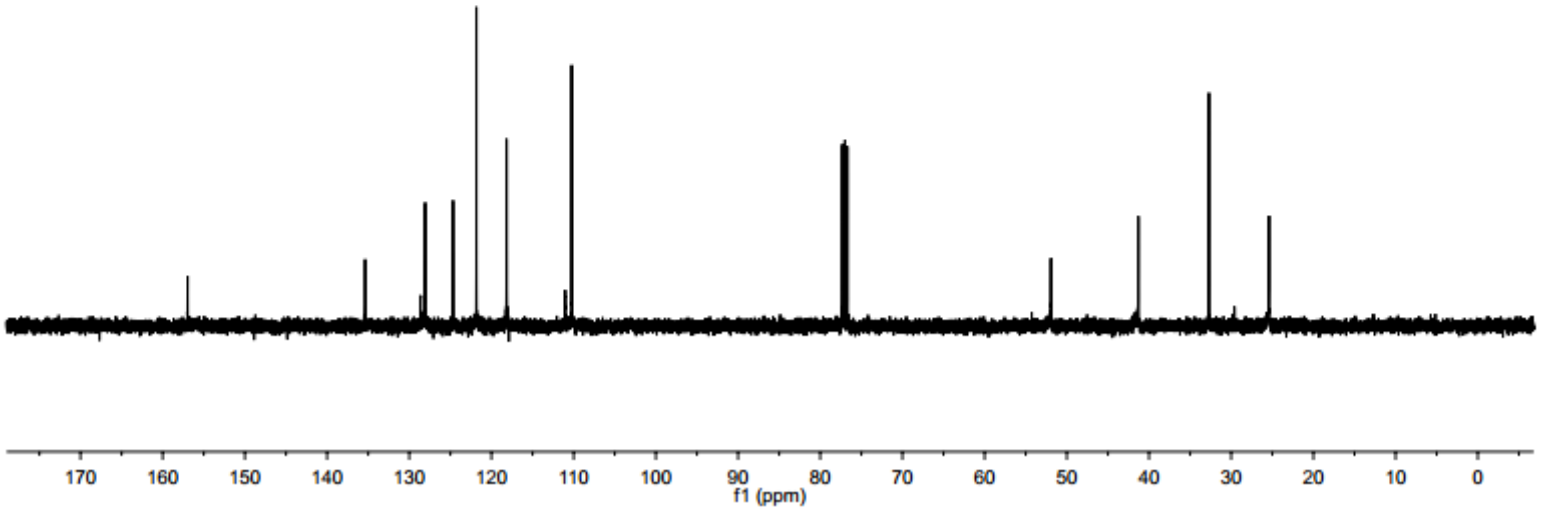
1c-1825-400C

156.959
135.370
128.670
128.063
124.667
121.831
118.160
111.025
110.244
77.319
77.000
76.682
51.935
41.285
32.704
25.391



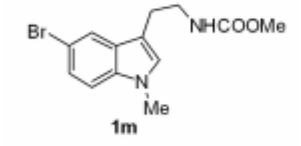
1l

Chemical Formula: $C_{13}H_{15}ClN_2O_2$
Exact Mass: 266.0822



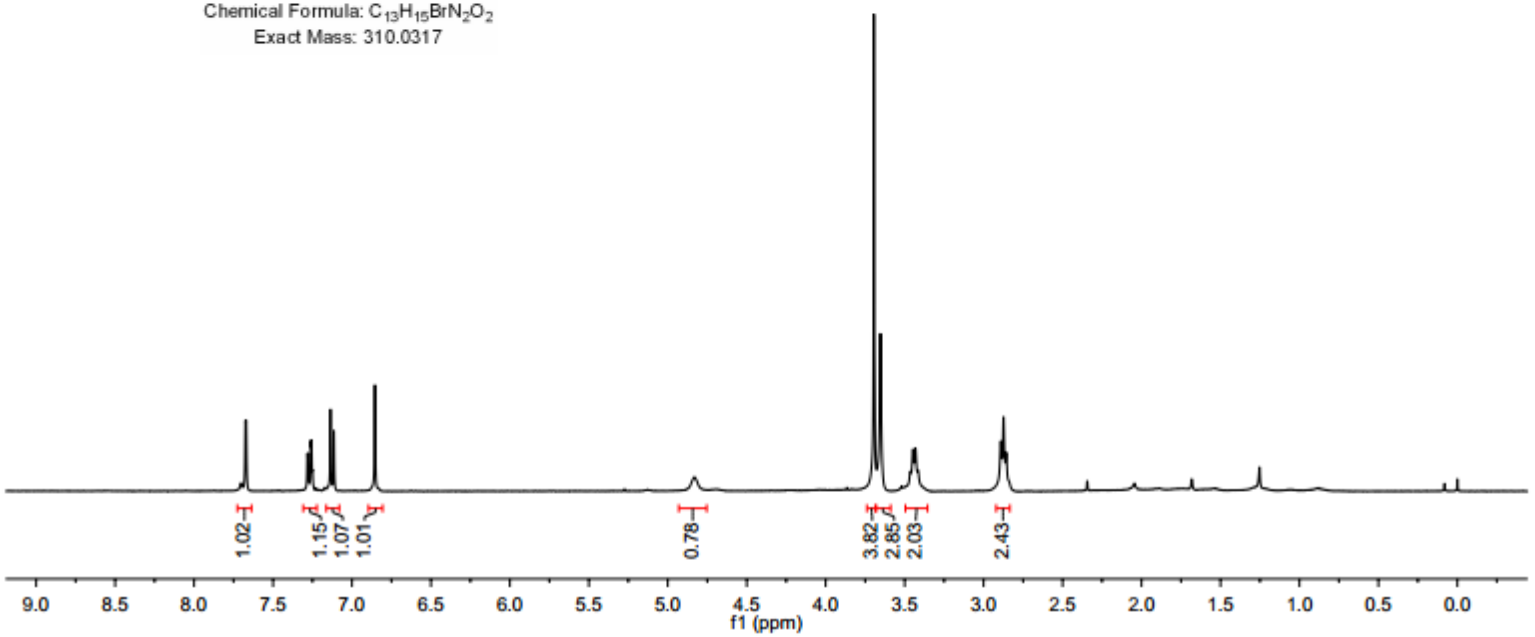
1c-1872

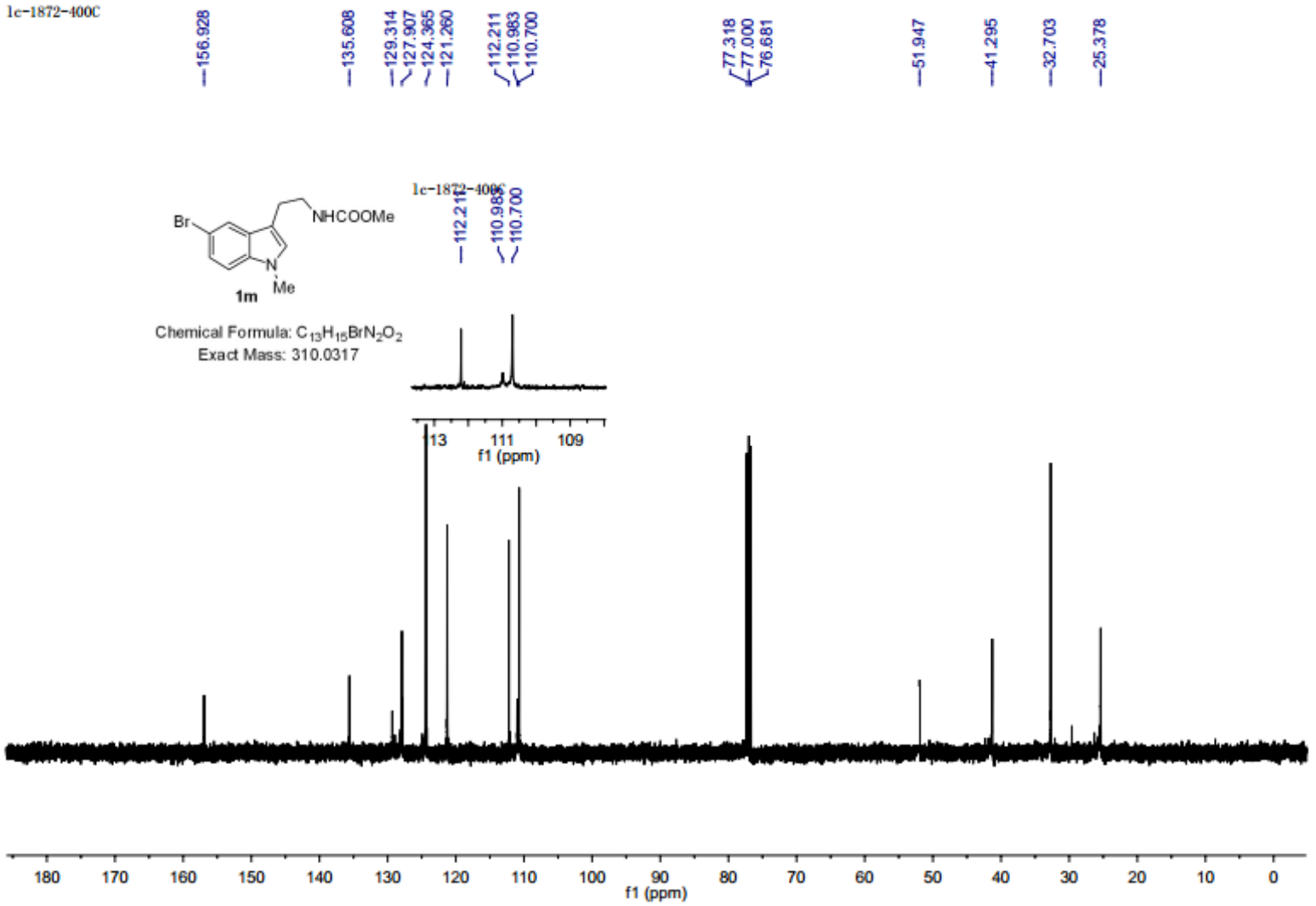
7.674
7.670
7.282
7.278
7.260
7.256
7.136
7.115
6.854
4.830
3.695
3.653
3.464
3.448
3.432
3.416
2.891
2.874
2.857
0.000

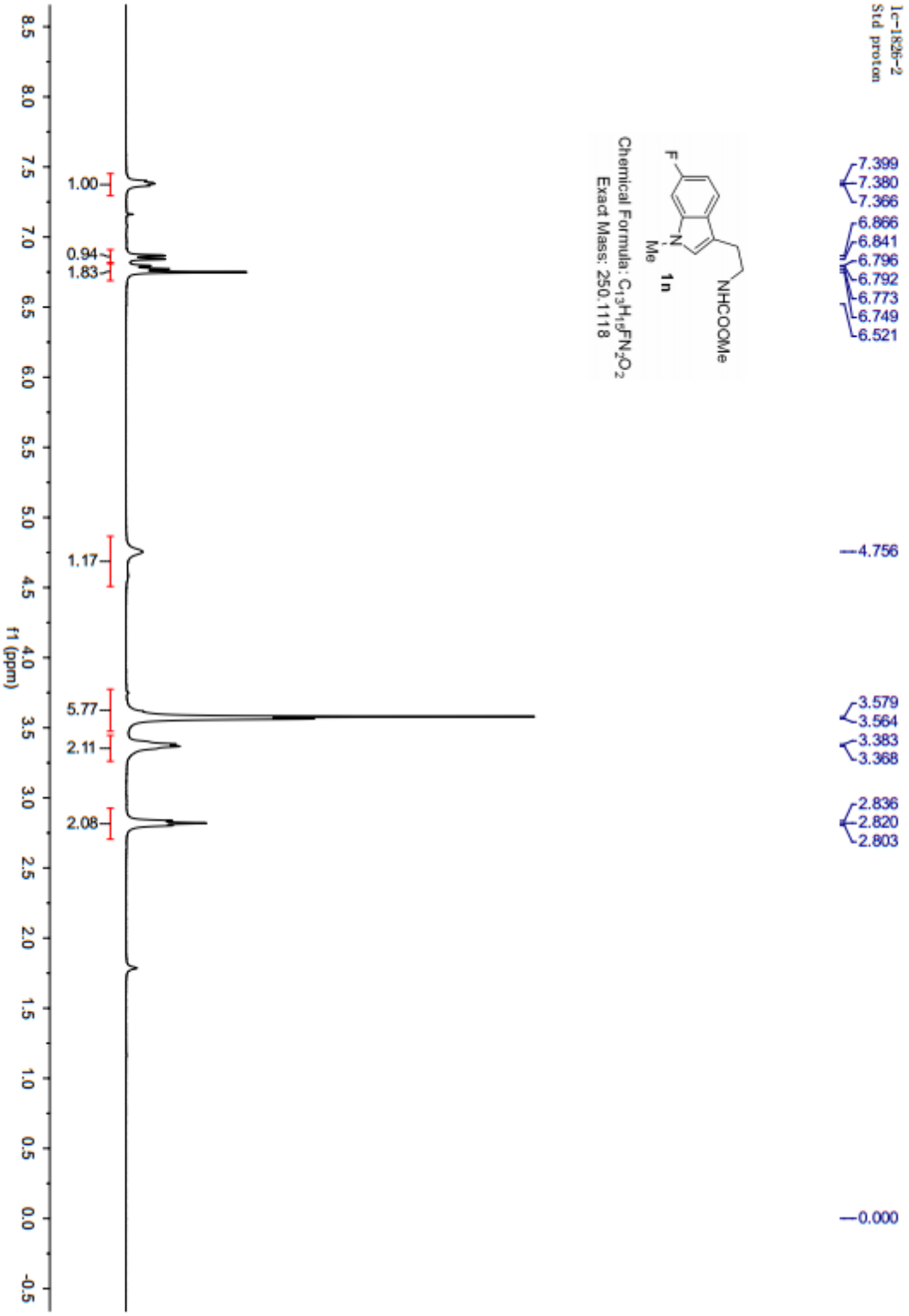


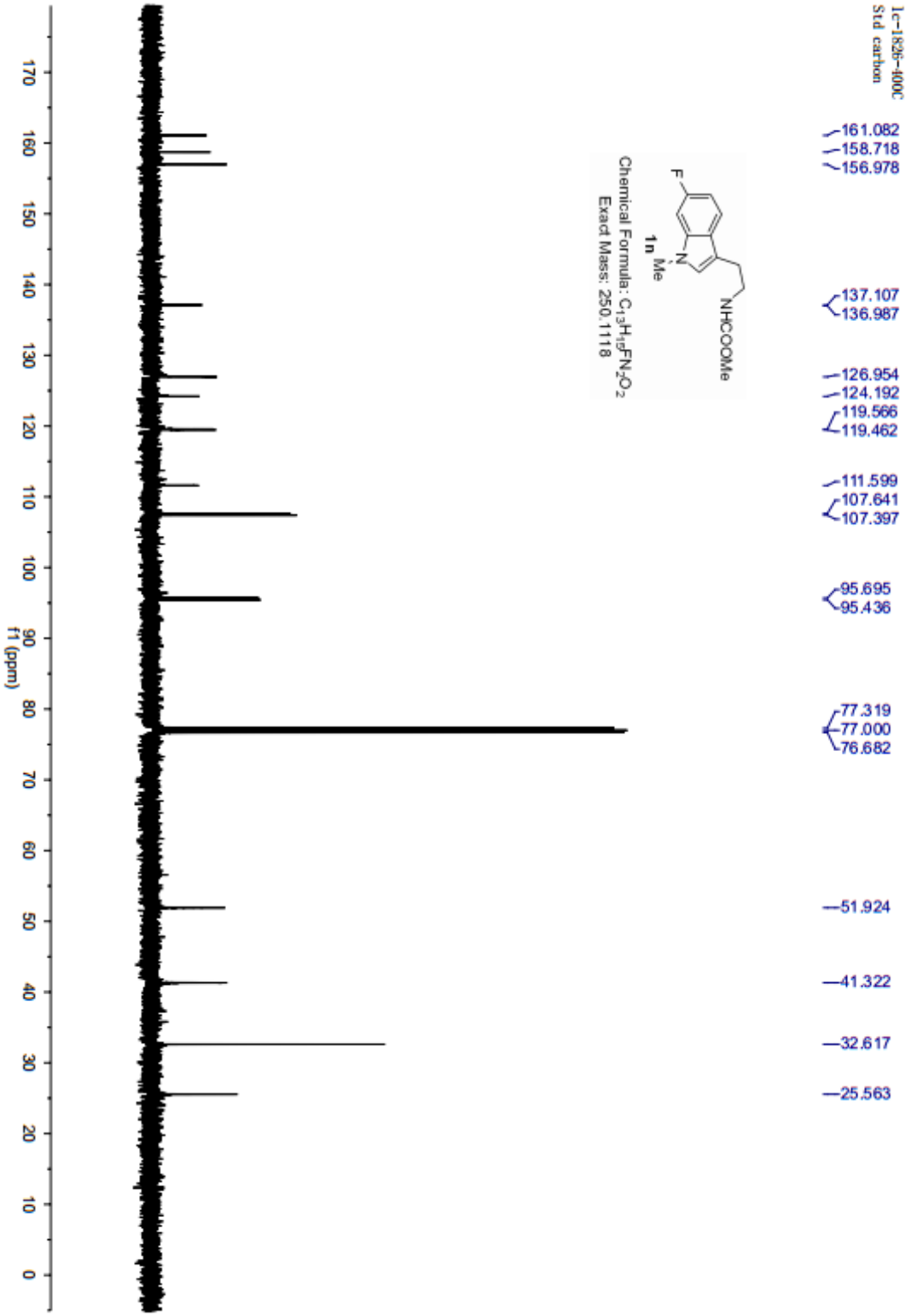
1m

Chemical Formula: $C_{13}H_{15}BrN_2O_2$
Exact Mass: 310.0317

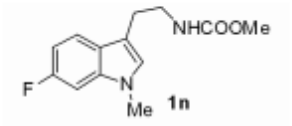



1c-1872-400C
156.928
135.608
129.314
127.907
124.365
121.260
112.211
110.983
110.700
77.318
77.000
76.681
51.947
41.295
32.703
25.378
Br
NHCOOMe
N
Me
1m
Chemical Formula: C13H15BrN2O2
Exact Mass: 310.0317
f1 (ppm)
f1 (ppm)


1c-1826-2
Std proton
Chemical Formula: $C_{13}H_{15}FN_2O_2$
Exact Mass: 250.1118
F
N
Me
1n
NHCOOMe
7.399
7.380
7.366
6.866
6.841
6.796
6.792
6.773
6.749
6.521
4.756
3.579
3.564
3.383
3.368
2.836
2.820
2.803
0.000
1.00
0.94
1.83
1.17
5.77
2.11
2.08
f1 (ppm)

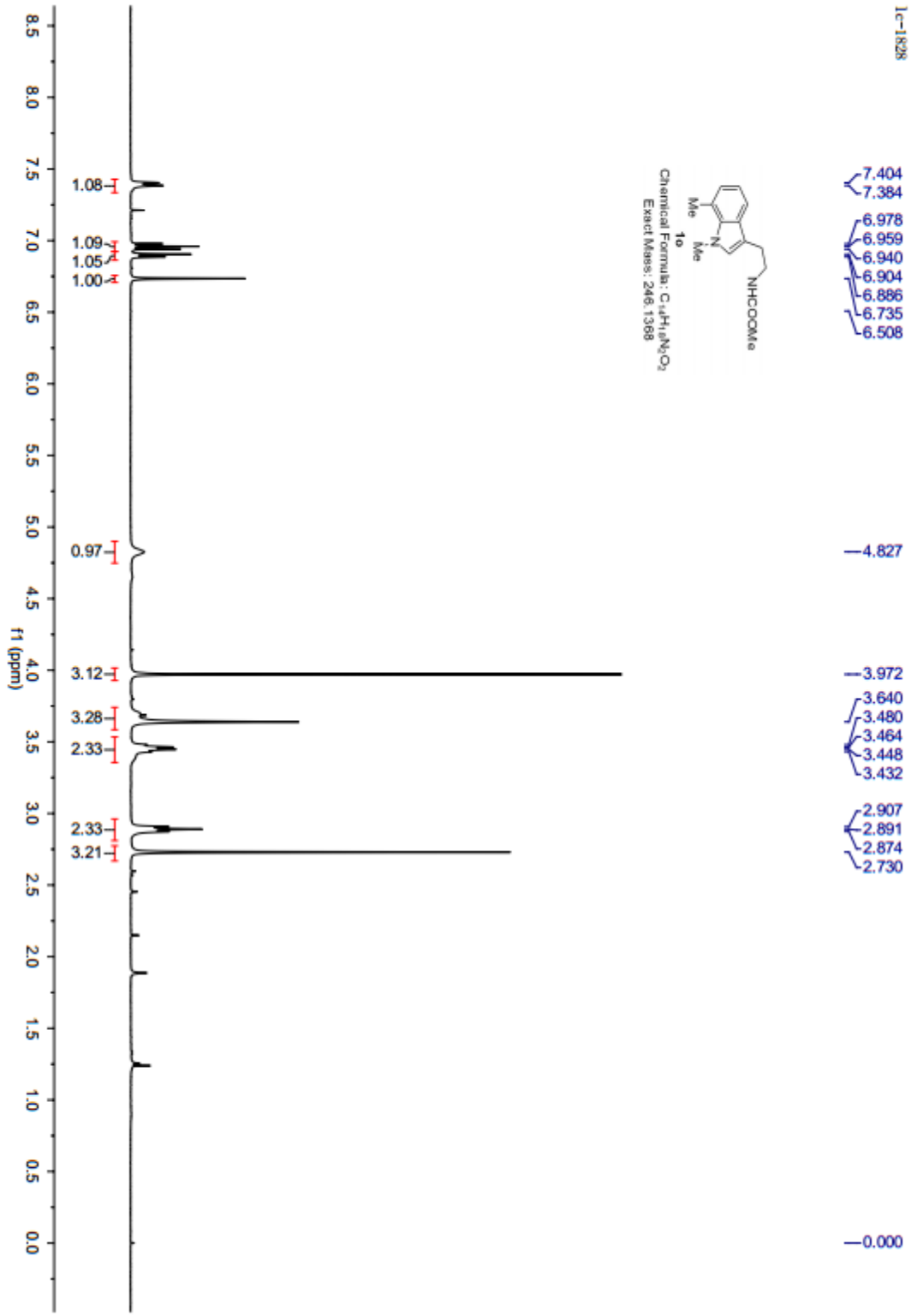

1c-1826-400C
Std carbon
161.082
158.718
156.978
137.107
136.987
126.954
124.192
119.566
119.462
111.599
107.641
107.397
95.695
95.436
77.319
77.000
76.682
51.924
41.322
32.617
25.563
F
N
Me
1n
NHCOOMe
Chemical Formula: C13H15FN2O2
Exact Mass: 250.1118
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

1c-1826-f
STANDARD PROTON PARAMETERS



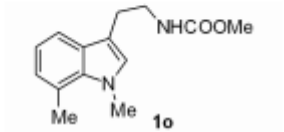
1n

Chemical Formula: $C_{13}H_{15}FN_2O_2$
Exact Mass: 250.1118


1c-1828
7.404
7.384
6.978
6.959
6.940
6.904
6.886
6.735
6.508
4.827
3.972
3.640
3.480
3.464
3.448
3.432
2.907
2.891
2.874
2.730
0.000
1.08
1.09
1.05
1.00
0.97
3.12
3.28
2.33
2.33
3.21
f1 (ppm)
Me
N
Me
1o
NHCOOMe
Chemical Formula: C14H18N2O2
Exact Mass: 246.1368

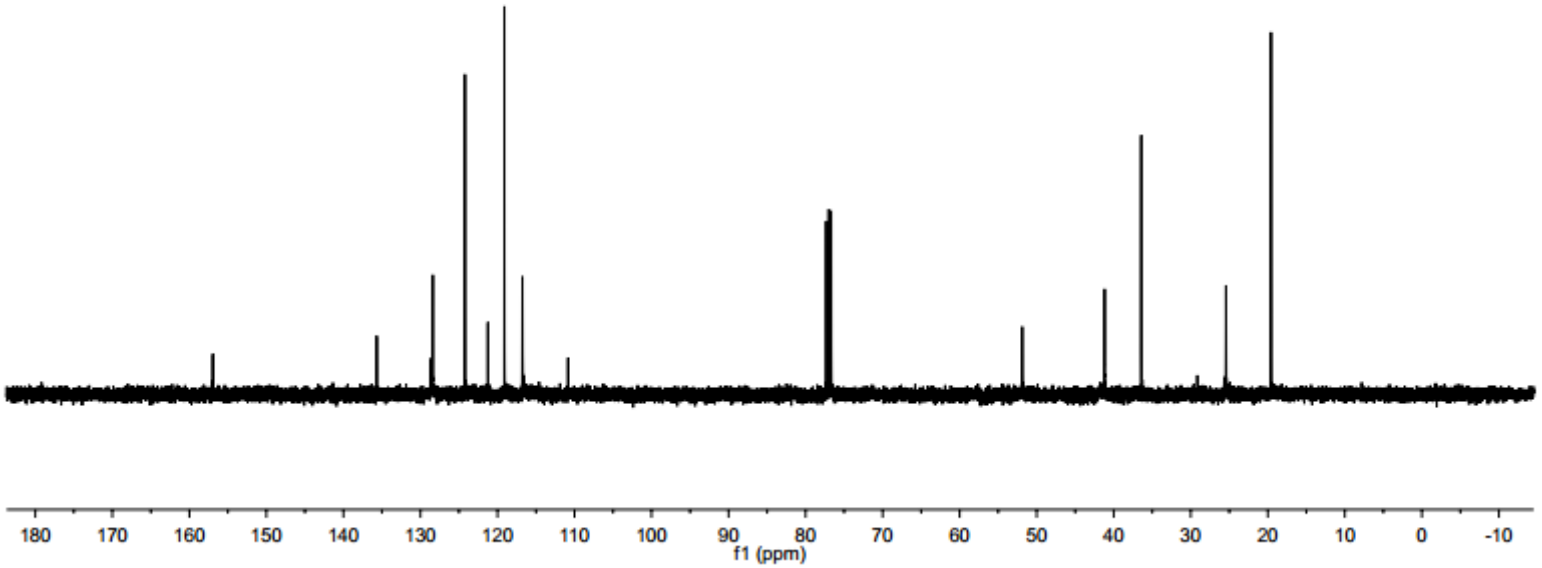
1c-1828-400C

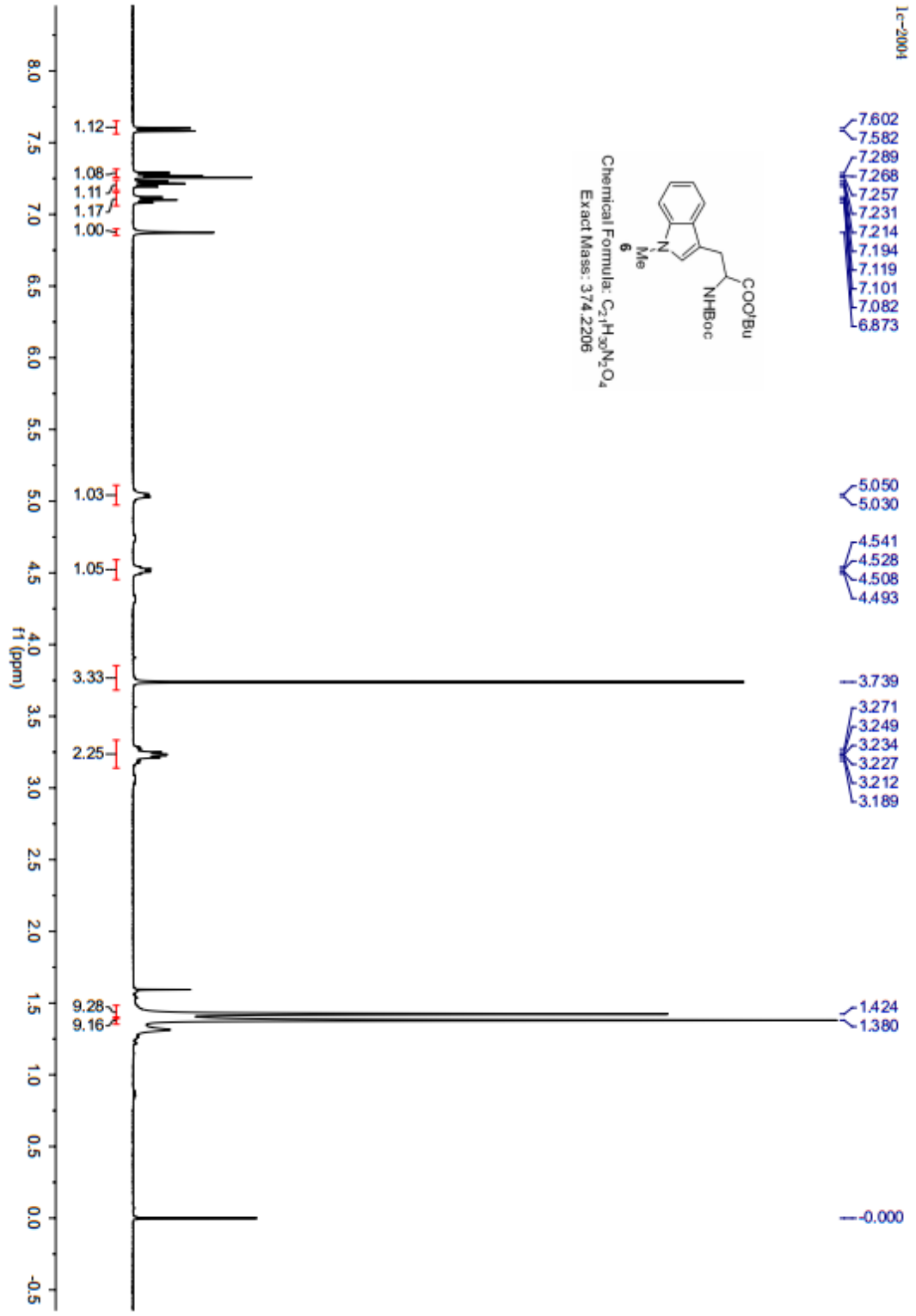
156.954
135.678
128.627
128.399
124.231
121.249
119.109
116.765
110.847
77.318
77.000
76.681
51.876
41.191
36.422
25.425
19.589

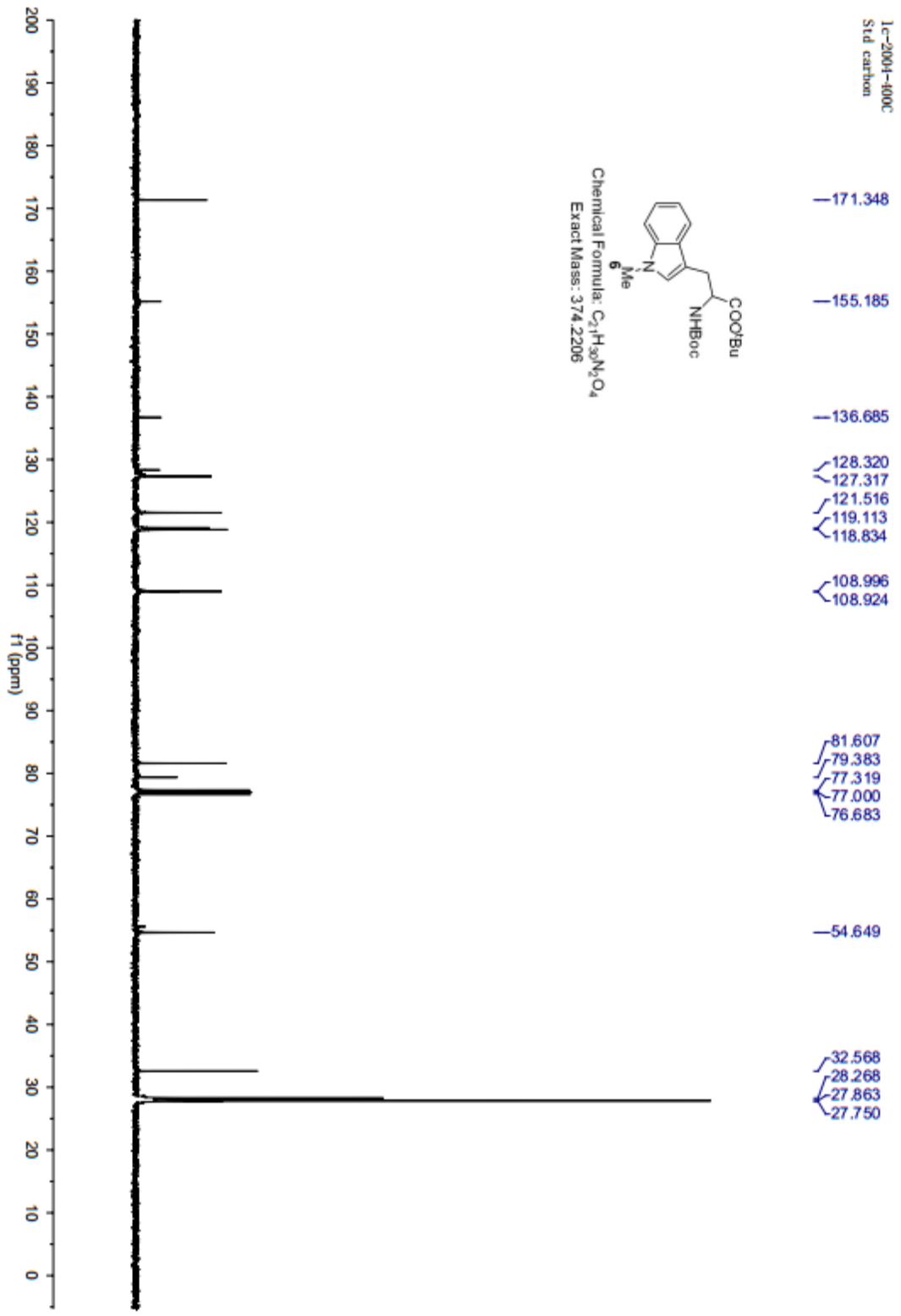


1o

Chemical Formula: $C_{14}H_{18}N_2O_2$
Exact Mass: 246.1368




1e-200H
Chemical Formula: $C_{21}H_{30}N_2O_4$
Exact Mass: 374.2206
6
Me
N
NHBoc
COO'Bu
7.602
7.582
7.289
7.268
7.257
7.231
7.214
7.194
7.119
7.101
7.082
6.873
5.050
5.030
4.541
4.528
4.508
4.493
3.739
3.271
3.249
3.234
3.227
3.212
3.189
1.424
1.380
-0.000
1.12
1.08
1.11
1.17
1.00
1.03
1.05
3.33
2.25
9.28
9.16
f1 (ppm)


1c-200H-400C
Std carbon
171.348
155.185
136.685
128.320
127.317
121.516
119.113
118.834
108.996
108.924
81.607
79.383
77.319
77.000
76.683
54.649
32.568
28.268
27.863
27.750
Chemical Formula: C21H30N2O4
Exact Mass: 374.2206
Me
6
N
NHBoc
CO2tBu
f1 (ppm)