Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry

2-Phenyl-4-bis(methylthio)methyleneoxazol-5-one: versatile template for diversity oriented synthesis of heterocycles: synthesis of novel 4-bis(methylthio)methylene-2-phenyl-1-aryl/alkylimidazol-5-(4*H*)-ones and other heterocycles

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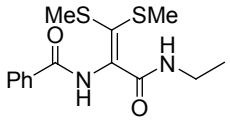
Supplementary information

Contents

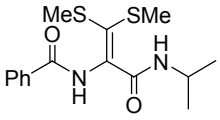
***N*-(3-(Ethylamino)-1,1-bis(methylthio)-3-oxoprop-1-en-2-yl)benzamide (4a).**



4a

White solid, yield: 198 mg (85%), mp 154-155^{0}C. R_f = 0.2 (EtOAc/hexane:4/6). ν_{max} (KBr)/cm^{-1} 1580, 1628, 3176, 3329. ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 1.27 (3H, t, *J* = 7.2 Hz, CH_3), 2.35 (3H, s, SCH_3), 2.36 (3H, s, SCH_3), 3.49 (2H, q, *J* = 7.2 Hz, CH_2), 6.17 (1H, br s, NH), 7.56-7.44 (3H, m, ArH), 7.85 (2H, d, *J* = 8.4 Hz, ArH), 8.38 (1H, br s, NH). ^{13}C NMR δ_C (400 MHz, $CDCl_3$) 14.3, 16.3, 17.8, 34.9, 124.7, 127.5, 128.7, 132.3, 133.1, 136.7, 164.0, 164.4.MS (MALDI/TOF): *m/z* calcd for $C_{14}H_{18}N_2O_2S_2$ 333.0709 $[M + Na]^+$; found 332.990.

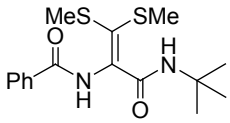
***N*-(3-(*i*-propylamino)-1,1-bis(methylthio)-3-oxoprop-1-en-2-yl)benzamide (4b).**



4b

White solid, yield: 195 mg (80%), mp 168^{0}C. R_f = 0.2 (EtOAc/hexane: 3/7). ν_{max} (KBr)/cm^{-1} 1290, 1544, 1626, 3204, 3312. ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 1.29 (6H, d, *J* = 6.4 Hz, $(CH_3)_2$), 2.33 (3H, s, SCH_3), 2.34 (3H, s, SCH_3), 4.26 (1H, sept, *J* = 8 Hz, CH), 6.01 (1H, br s, NH), 7.44-7.56 (3H, m, ArH), 7.84-7.86 (2H, d, *J* = 7.2 Hz, ArH), 8.39 (1H, br s, NH). ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 16.4, 17.8, 22.4, 42.1, 123.9, 127.5, 128.7, 132.3, 133.2, 137.1, 163.0, 164.4.MS (MALDI/TOF): *m/z* calcd for $C_{15}H_{20}N_2O_2S_2$ $[M + Na]^+$ 347.0864; found 347.1238.

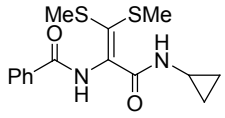
***N*-(3-(*t*-butylamino)-1,1-bis(methylthio)-3-oxoprop-1-en-2-yl)benzamide (4c).**



4c

White solid, yield: 206 mg (81%), mp 190-191^{0}C. R_f = 0.2 (EtOAc/hexane: 3/7). ν_{max} (KBr)/cm^{-1} 1289, 1535, 1631, 3178, 3345. ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 1.47 (9H, s, $(CH_3)_3$), 2.33 (3H, s, SCH_3), 6.02 (1H, br s, NH), 7.42-7.55 (3H, m, ArH), 7.85 (2H, d, *J* = 8.4 Hz, ArH), 8.4 (1H, br s, NH). ^{13}C NMR δ_C (100MHz, $CDCl_3$) 16.4, 17.8, 52.0, 123.5, 127.5, 128.7, 132.2, 133.3, 138.0, 162.7, 164.4. MS (MALDI/TOF): *m/z* calcd for $C_{16}H_{22}N_2O_2S_2$ $[M + Na]^+$ 361.1021; found 361.1712.

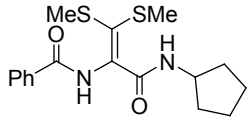
***N*-(3-(Cyclopropylamino)-1,1-bis(methylthio)-3-oxoprop-1-en-2-yl)benzamide (4d).**



4d

White solid, yield: 190 mg (78%), mp 168-169^{0}C. R_f = 0.25 (EtOAc/hexane: 3/7). ν_{max} (KBr)/cm^{-1} 1287, 1529, 1572, 1635, 2919, 3181, 3310. ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 0.70-0.74 (2H, m, -CH_2-), 0.81-0.84 (2H, m, -CH_2-), 2.32 (3H, s, SCH_3), 2.33 (3H, s, SCH_3), 2.87 (1H, sext, *J* = 7.2 Hz, NCH), 6.28 (1H, br s, NH), 7.44-7.56 (3H, m, ArH), 7.84 (2H, d, *J* = 8.4 Hz, ArH), 8.39 (1H, br s, NH).^{13}C NMR δ_C (400 MHz, $CDCl_3$) 6.47, 16.3, 17.8, 23.0, 124.4, 127.5, 128.7, 132.3, 133.0, 136.7, 164.4, 165.4. MS (MALDI/TOF): *m/z* calcd for $C_{15}H_{18}N_2O_2S_2$ $[M + Na]^+$ 345.0907; found 345.1533.

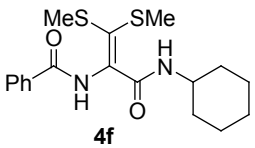
***N*-(3-(Cyclopentylamino)-1,1-bis(methylthio)-3-oxoprop-1-en-2-yl)benzamide (4e).**



4e

White solid, yield: 198 mg (75%), mp 176-178^{0}C. R_f = 0.2 (EtOAc/hexane: 4/6). ν_{max} (KBr)/cm^{-1} 1296, 1471, 1549, 1636, 3058, 3263. ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 1.63-1.73 (6H, m, -CH_2-), 2.01-2.05 (2H, m, -CH_2-), 2.32 (3H, s, SCH_3), 2.33 (3H, s, SCH_3), 4.34-4.39 (1H, m, NCH), 6.19-6.21 (1H, d, *J* = 6.4 Hz, NH), 7.43-7.55 (3H, m, ArH), 7.84-7.86 (2H, d, *J* = 8.8 Hz, ArH), 8.43 (1H, br s, NH). ^{13}C NMR δ_C (100 MHz, $CDCl_3$)16.4, 17.9, 23.8, 32.6, 51.8, 124.3, 127.5, 128.7, 132.3, 133.1, 140.0, 163.4, 164.4. MS (MALDI/TOF): *m/z* calcd for $C_{17}H_{22}N_2O_2S_2$ $[M + Na]^+$ 373.1021; found 373.2133.

***N*-(3-(Cyclohexylamino)-1,1-bis(methylthio)-3-oxoprop-1-en-2-yl)benzamide (4f).**

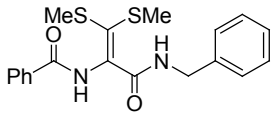


4f

White solid, yield: 227 mg (78%), mp 196-197^{0}C. R_f = 0.3 (EtOAc/hexane: 4/6). ν_{max} (KBr)/cm^{-1} 1082, 1301, 1479, 1544, 1631, 3350. ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 1.17-1.33 (3H, m, -CH_2-), 1.36-1.47 (2H, m, -CH_2-), 1.60-1.65 (1H, m, -CH_2-), 1.71-1.77 (4H, m, -CH_2-), 2.33 (3H, s, SCH_3), 2.35 (3H, s, SCH_3), 3.35-3.39 (1H, m, NCH), 6.09 (1H, d, *J* = 8.0 Hz, NH), 7.44-7.56 (3H, m, ArH), 7.86 (2H, dd, J_1 = 8.0 Hz, J_2 = 8.4 Hz, ArH), 8.39 (1H, br s, NH). ^{13}C NMR δ_C (100 MHz, CDCl3)

16.3, 17.9, 24.8, 25.6, 32.7, 48.8, 124.0, 127.5, 128.7, 132.2, 133.2, 137.2, 163.0, 164.4. MS (MALDI/TOF): *m/z* calcd for $C_{18}H_{24}N_2O_2S_2$ $[M + Na]^+$ 387.1177; found 387.2050.

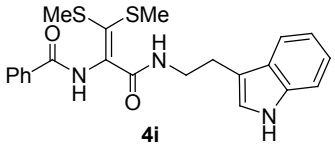
***N*-(3-(Benzylamino)-1,1-bis(methylthio)-3-oxoprop-1-en-2-yl)benzamide (4g).**



4g

White solid, yield: 232 mg (78%), mp 177-178^{0}C. R_f = 0.2 (MeOH/DCM: 0.2/9.8). ν_{max} (KBr)/cm^{-1} 1644, 1720, 3237, 3237. ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 2.29 (3H, s, SCH_3), 2.35 (3H, s, SCH_3), 4.66 (2H, d, J = 5.6 Hz, CH_2), 6.41-6.42 (1H, t, J = 4.8 Hz, NH), 7.28-7.37 (3H, m, ArH), 7.45-7.58 (5H, m, ArH), 7.87 (2H, d, J = 7.2 Hz, ArH), 8.41 (1H, br s, NH). ^{13}C NMR δ_C (400 MHz, $CDCl_3$) 16.4, 17.8, 44.4, 125.0, 127.5, 127.7, 128.2, 128.6, 128.8, 132.3, 133.0, 136.4, 137.8, 164.0, 164.4. MS (MALDI/TOF): *m/*z calcd for $C_{19}H_{20}N_2O_2S_2$ $[M + Na]^+$ 395.0864; found 395.1975.

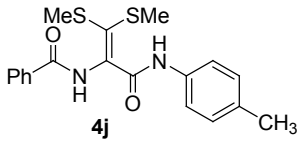
***N*-(3-(2-(1*H*-indol-3-yl)ethylamino)-1,1-bis(methylthio)-3-oxoprop-1-en-2-yl)benzamide (4i).**



4i

White solid, yield: 287 mg (85%), mp 136-137^{0}C. ν_{max} (KBr)/cm^{-1} 1459, 1574, 1642, 1664, 3208, 3327, 3371. R_f = 0.3 (MeOH/DCM: 0.2/9.8). ^{1}H NMR δ_H (400 MHz, DMSO-d_6) 2.28 (3H, s, SCH_3), 2.30 (3H, s, SCH_3), 2.91 (2H, t, J = 8 Hz, CH_2), 3.41 (2H, t, J = 8 Hz, NCH_2), 6.97 (1H, dd, J_1= 7.2 Hz, J_2 = 0.8 Hz, ArH), 7.06 (1H, dd, J_1= 7.2 Hz, J_2 = 1.2 Hz, ArH), 7.20 (1H, d, J = 2 Hz, ArH), 7.33 (1H, d, J = 8 Hz, ArH), 7.49-7.61 (4H, m, ArH), 7.94 (2H, d, J = 8 Hz, ArH), 8.18 (1H, t, J = 5.6 Hz, NH), 9.65 (1H, br s, NH), 10.80 (1H br s, NH). ^{13}C NMR δ_C (400 MHz, DMSO-d_6) 16.3, 17.0, 24.8, 111.3, 111.8, 118.2, 118.2, 120.8, 122.7, 127.2, 127.7, 128.4, 130.5, 131.8, 133.4, 134.9, 136.3, 163.9, 164.4. MS (MALDI/TOF): *m/z* calcd for $C_{22}H_{23}N_3O_2S_2$ $[M + Na]^+$ 448.1130; found 448.1527.

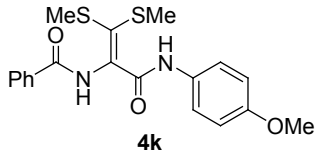
***N*-(3-(4-Methylphenylamino)-1,1-bis(methylthio)-3-oxoprop-1-en-2-yl)benzamide (4j).**



4j

White solid, yield: 208 mg (70%), mp 206-208^{0}C. R_f = 0.3 (EtOAc/hexane: 3/7). ν_{max} (KBr)/cm^{-1} 1477, 1510, 1604, 1664, 3287. ^{1}H NMR δ_H (400 MHz, $CDCl_3$). 2.29 (3H, s, SCH_3), 2.32 (3H, s, SCH_3), 2.33 (3H, s, SCH_3), 7.09 (2H, d, *J* = 8.0, ArH), 7.43-7.54 (5H, m, ArH), 7.87 (2H, d, *J* = 7.8 Hz, ArH), 8.36 (1H, br s, NH), 8.51 (1H, br s, NH). ^{13}C NMR δ_C (100 MHz, CDCl3) 16.4, 17.8, 20.9, 120.2, 127.6, 128.7, 129.4, 132.3, 132.6, 132.9, 134.1, 135.1, 135.4, 162.2, 165.0. MS (MALDI/TOF): *m/z* calcd for $C_{19}H_{20}N_2O_2S_2$ $[M + Na]^+$ 395.0864; found 395.2066.

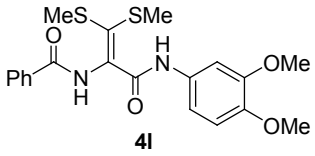
***N*-(3-(4-methoxyphenylamino)-1,1-bis(methylthio)-3-oxoprop-1-en-2-yl)benzamide (4k).**



4k

White solid, yield: 95 mg (65%), mp 174-1175^{0}C. R_f = 0.3 (MeOH/DCM: 2/8). ν_{max} (KBr)/cm^{-1} 1239, 1511, 1646, 3246. ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 2.37 (3H, s, SCH_3), 2.38 (3H, s, SCH_3), 3.79 (3H, s, OCH_3), 6.89 (1H, d, *J* = 8.4 Hz, ArH), 7.45-7.57 (5H, m, ArH), 7.87 (2H, d, *J* = 8.4 Hz, ArH), 8.01 (1H, br s, NH), 8.37 (1H, br s, NH). ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 16.4, 17.9, 55.5, 114.2, 122.0, 127.0, 127.6, 128.7, 130.9, 132.4, 132.8, 136.0, 156.7, 162.0, 164.9. MS (FAB): *m/z* calcd for $C_{20}H_{22}N_2O_4S_2$ $[M + Na]^+$ 441.0919; found 441.2707.

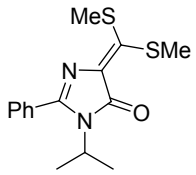
***N*-(3-(3,4-Dimethoxyphenylamino)-1,1-bis(methylthio)-3-oxoprop-1-en-2-yl)benzamide (4l).**



4l

White solid, yield: 217 mg (69%), mp 210-211^{0}C. R_f = 0.2 (EtOAc/hexane: 4/6). ν_{max} (KBr)/cm^{-1} 1236, 1513, 1580, 1609, 1651, 3080, 3251. ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 2.25 (3H, s, SCH_3), 2.29 (3H, s, SCH_3), 3.79 (3H, s, OCH3), 3.81 (3H, s, OCH3), 6.70 (1H, d, *J* = 8.8 Hz, ArH), 7.02 (1H, dd, J_1 = 8.8 Hz, J_2 = 2.2 Hz, ArH), 7.37-7.51 (4H, m, ArH), 7.85 (2H, d, *J* = 7.32, ArH), 8.54 (2H, br s, NH), 8.55 (1H, br s, NH). MS (MALDI/TOF): *m/z* calcd for $C_{20}H_{22}N_2O_4S_2$ $[M + Na]^+$ 441.0919: found 441.1702.

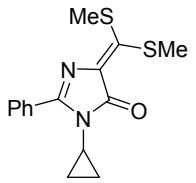
4-(Bis(methylthio)methylene)-1-isopropyl-2-phenyl-1*H*-imidazol-5-(4*H*)-one (5b).



5b

Yellow solid, yield: 91 mg (48%), mp 110^{0}C. R_f = 0.7 (EtOAc/hexane: 3/7). ν_{max} (KBr)/cm^{-1} 1278, 1368, 1495, 1561, 1669. ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 1.47 (6H, d, J = 6.8, $(CH_3)_2$), 2.60 (3H, s, SCH_3), 2.75 (3H, s, SCH_3), 4.16 (1H, sept, J = 6.8 Hz, NCH), 7.44-7.48 (3H, m, ArH), 7.53-7.55 (2H, m, ArH). ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 18.0, 20.0, 20.0, 47.6, 128.4, 128.6, 130.1, 130.3, 135.7, 154.6, 156.1, 165.3. MS (MALDI/TOF): *m/z* calcd for $C_{15}H_{18}N_2OS_2$ $[M + H]^+$ 307.0939; found 307.1093.

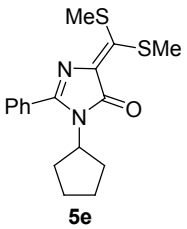
4-(Bis(methylthio)methylene)-1-cyclopropyl-2-phenyl-1*H*-imidazol-5-(4*H*)-one (5d).



5d

White solid, yield: 126 mg (67%), mp 99-100^{0}C. R_f = 0.2 (EtOAc/hexane: 4/6). ν_{max} (KBr)/cm^{-1} 1294, 1396, 1487, 1550, 1667. ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 0.57 (2H, m, CH_2), 0.89 (2H, m, CH_2), 2.57 (3H, s, SCH_3), 2.76 (3H, s, SCH_3), 2.87 (1H, br m, NCH), 7.37-7.42 (3H, m, ArH), 7.82 (2H, d, J = 6.8, 2H, ArH).^{13}C NMR δ_C (100 MHz, $CDCl_3$) 8.5, 18.5, 19.9, 24.4, 128.3, 128.6, 129.0, 130.7, 133.3, 155.3, 156.7, 165.0 MALDI/TOF): *m/z* calcd for $C_{15}H_{16}N_2OS_2$ $[M + H]^+$ 305.078; found 2305.2065.

4-(Bis(methylthio)methylene)-1-cyclopentyl-2-phenyl-1*H*-imidazol-5-(4*H*)-one (5e).

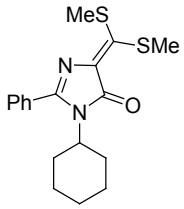


5e

Yellow low melting solid, yield: 123 mg (65%), R_f = 0.6 (EtOAc/hexane: 3/7). ν_{max} (KBr)/cm^{-1} 1370, 1496, 1562, 1676. ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 1.43-1.49 (2H, m, -CH_2-), 1.71-1.79 (2H, m, -CH_2-), 1.86-1.96 (2H, m, CH_2), 2.20-2.29 (2H, quint, J = 8.8 Hz, CH_2), 2.57 (3H, s, SCH_3), 2.73

(3H, s, SCH_3), 4.18-4.22 (1H, m, CH), 7.39-7.44 (3H, m, ArH), 7.52-7.54 (2H, m, ArH). ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 18.0, 19.7, 25.4, 29.4, 56.1, 126.1, 128.6, 128.6, 128.8, 129.8, 130.5, 156.6, 164.6. MS (FAB, *m/z*, %): 333(50, $[M + H]^+$). Elemental analysis for $C_{17}H_{20}N_2OS_2$: calcd: C, 61.41; H, 6.06; N, 8.43. Found: C, 61.48; H, 6.11; N, 8.36.

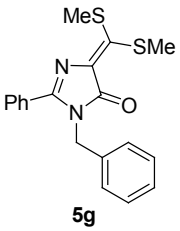
4-(Bis(methylthio)methylene)-1-cyclohexyl-2-phenyl-1*H*-imidazol-5-(4*H*)-one (5f).



5f

Pale yellow solid, yield: 122 mg (64%), mp 97-98^{0}C. R_f = 0.6 (EtOAc/hexane: 4/6). ν_{max} (KBr)/cm^{-1} 1371, 1444, 1494, 1564, 1583, 1665. ^1H NMR δ_H (400 MHz, $CDCl_3$) 1.18-1.08 (4H, m, -CH_2-), 1.37-1.78 (4H, m, -CH_2-), 2.34-2.43 (2H, m, -CH_2-), 2.6 (3H, s, SCH_3), 2.7 (3H, s, SCH_3), 3.68-3.71 (1H, m, NCH), 7.40-7.45 (3H, m, ArH), 7.49-7.51 (2H, m, ArH). ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 18.0, 19.5, 24.9, 25.9, 29.4, 55.6, 128.4, 128.5, 130.1, 130.2, 135.7, 154.5, 156.3, 165.1. MS (FAB, *m/z,* %): 347 (100, $[M + H]^+$, 346 (60, $[M]^+$). Elemental analysis for $C_{18}H_{22}N_2OS_2$: cacld: C, 62.39; H, 6.40; N, 8.08. Found: C, 62.46, H, 6.48, N, 8.02.

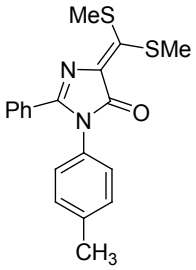
4-(Bis(methylthio)methylen)-1-benzyl-4-(bis(methylthio)methylen)-2-phenyl-1*H*-imidazol-5(4*H*)-one (5g).



5g

White solid, yield: 111 mg (59%), mp 129-130^{0}C. R_f = 0.5 (EtOAc/hexane: 2/8).). ν_{max} (KBr)/cm^{-1} 1307, 1391, 1438, 1494, 1557, 1681. ^1H NMR δ_H (400 MHz, $CDCl_3$) 2.65 (3H, s, SCH_3), 2.82 (3H, s, SCH_3), 4.91 (2H, s, CH_2), 7.10 (2H, d, *J* = 7.0 Hz, ArH), 7.21-7.28 (3H, m, ArH), 7.36-7.37 (2H, m, ArH), 7.41-7.42 (1H, m, ArH), 7.53-7.54 (2H, m, ArH). ^{13}C NMR δ_C (100 MHz, CDCl3) 18.2, 19.7, 45.2, 126.8, 127.4, 128.3, 128.5, 128.6, 129.6, 130.5, 134.5, 136.8, 155.1, 156.5, 165.0. MS (MALDI/TOF): *m/z* calcd for $C_{19}H_{18}N_2OS_2$ $[M + H]^+$ 355.0939; found 355.1284.

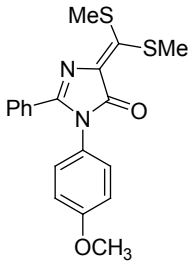
4-(Bis(methylthio)methylene)-2-phenyl-1-(4-methylphenyl)-1*H*-imidazol-5(4*H*)-one (5j).



5j

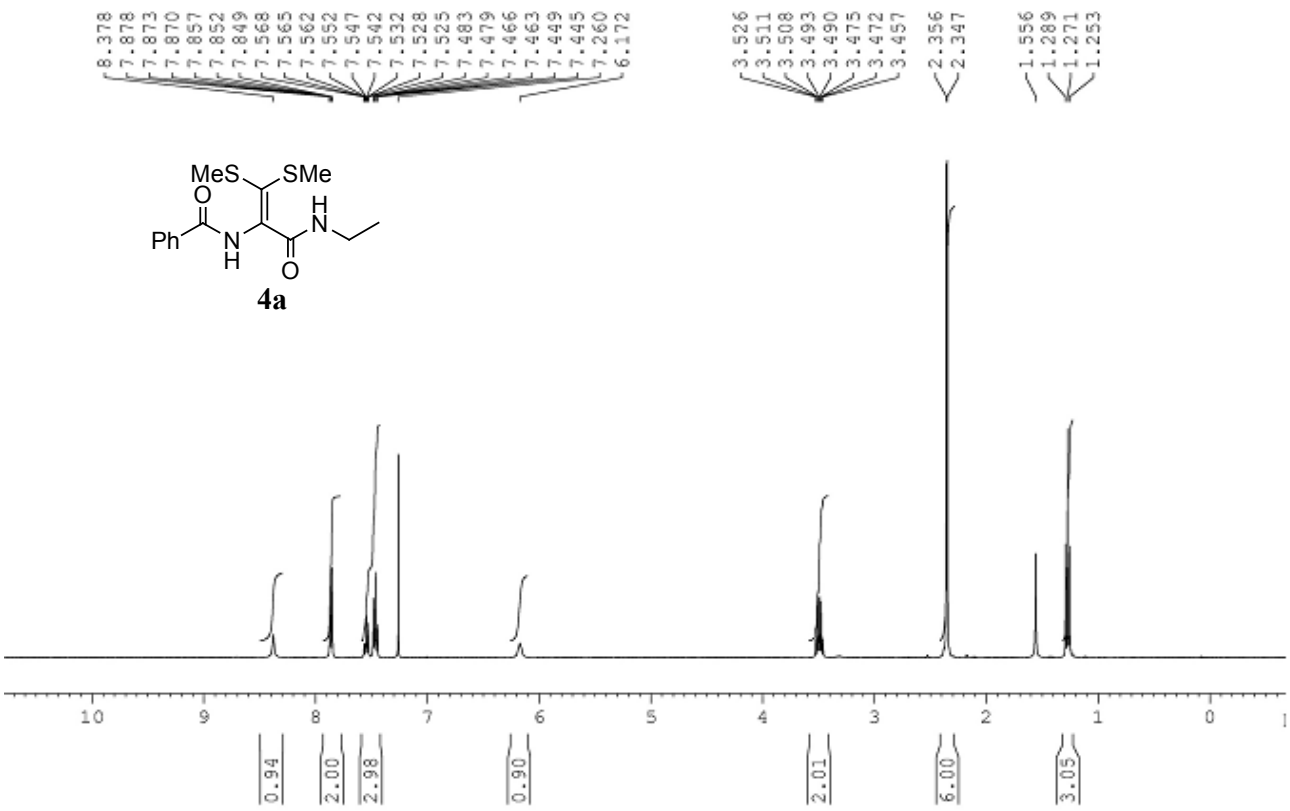
Yellow solid, yield: 110 mg (58%), mp 165-166^{0}C. R_f = 0.5 (EtOAc/hexane: 2/8). ν_{max} (KBr)/cm^{-1} 1384, 1493, 1557, 1680, 2853, 2922, 3349. ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 2.37 (3H, s, SCH_3), 2.66 (3H, s, SCH_3), 2.90 (3H, s, CH_3), 7.04 (2H, d, J = 8.0 Hz, ArH), 7.19 (2H, d, J = 8.0 Hz, ArH), 7.24-7.37 (3H, m, ArH), 7.46 (2H, dd, J_1 = 7.8 Hz, J_2 = 1.5 Hz, ArH). ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 18.4, 20.0, 21.2, 127.1, 128.2, 128.7, 129.2, 129.9, 130.3, 132.2, 134.2, 138.1, 153.1, 156.7, 164.2. MS (ESI): *m/z* 355.2 ([M + H]$^+$, 100%). Elemental analysis for $C_{19}H_{18}N_2OS_2$: calcd: C, 64.38; H, 5.12; N, 7.90. Found: C, 64.46; H, 5.16; N, 7.86.

4-(Bis(methylthio)methylene)-1-(4-methoxyphenyl)-2-phenyl-1*H*-imidazol-5(4*H*)-one (5k).



5k

Yellow solid, yield: 122 mg (64%), mp 166-168^{0}C. R_f = 0.3 (EtOAc/hexane: 4/6). ν_{max} (KBr)/cm^{-1} 1244, 1297, 1492, 1512, 1558, 1672. ^{1}H NMR δ_H (400 MHz, $CDCl_3$) 2.63 (3H, s, CH_3), 2.87 (3H, s, SCH_3), 3.79 (3H, s, OCH_3), 6.88 (2H, d, J = 8.5 Hz, ArH), 7.05 (2H, d, J = 8.5 Hz, ArH), 7.22-7.35 (3H, m, ArH), 7.45 (2H, d, J = 7.5 Hz, ArH). ^{13}C NMR δ_C (100 MHz, $CDCl_3$) 18.6, 20.2, 55.4, 114.6, 127.3, 128.2, 128.4, 128.6, 128.9, 130.7, 132.8, 153.2, 157.9, 159.3, 163.7. MS (ESI, *m/z*, %): 371 (100, [M + H]$^+$). Elemental analysis for $C_{19}H_{18}N_2O_2S_2$: calcd: C, 61.60; H, 4.90; N, 7.56. Found: C, 61.67; H, 4.94; N, 7.49.



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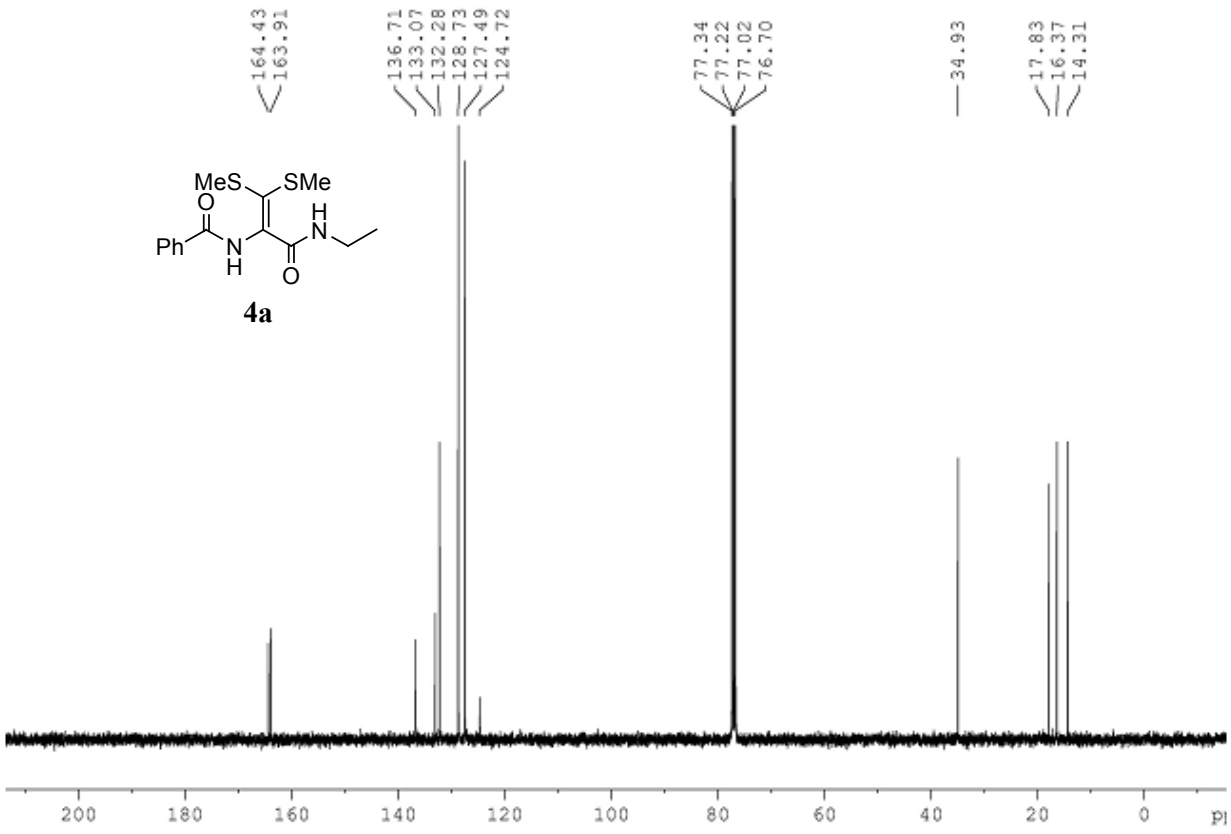

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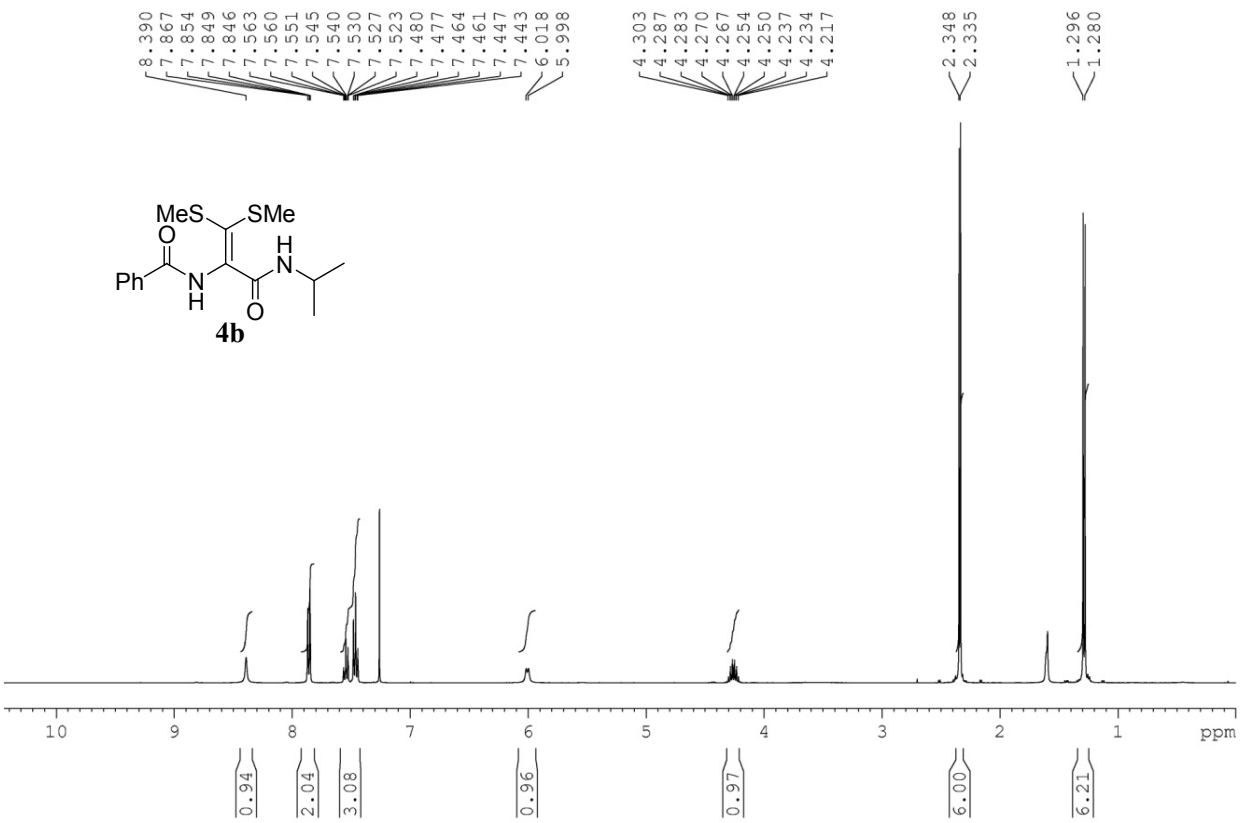

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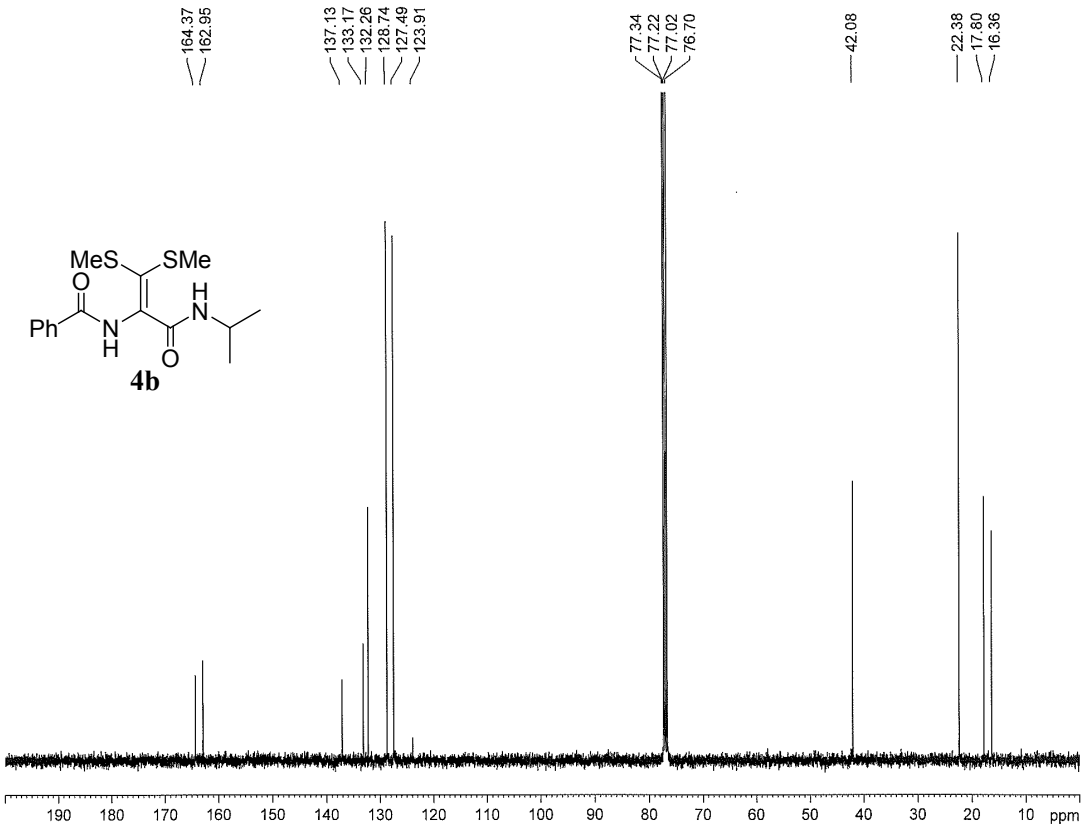

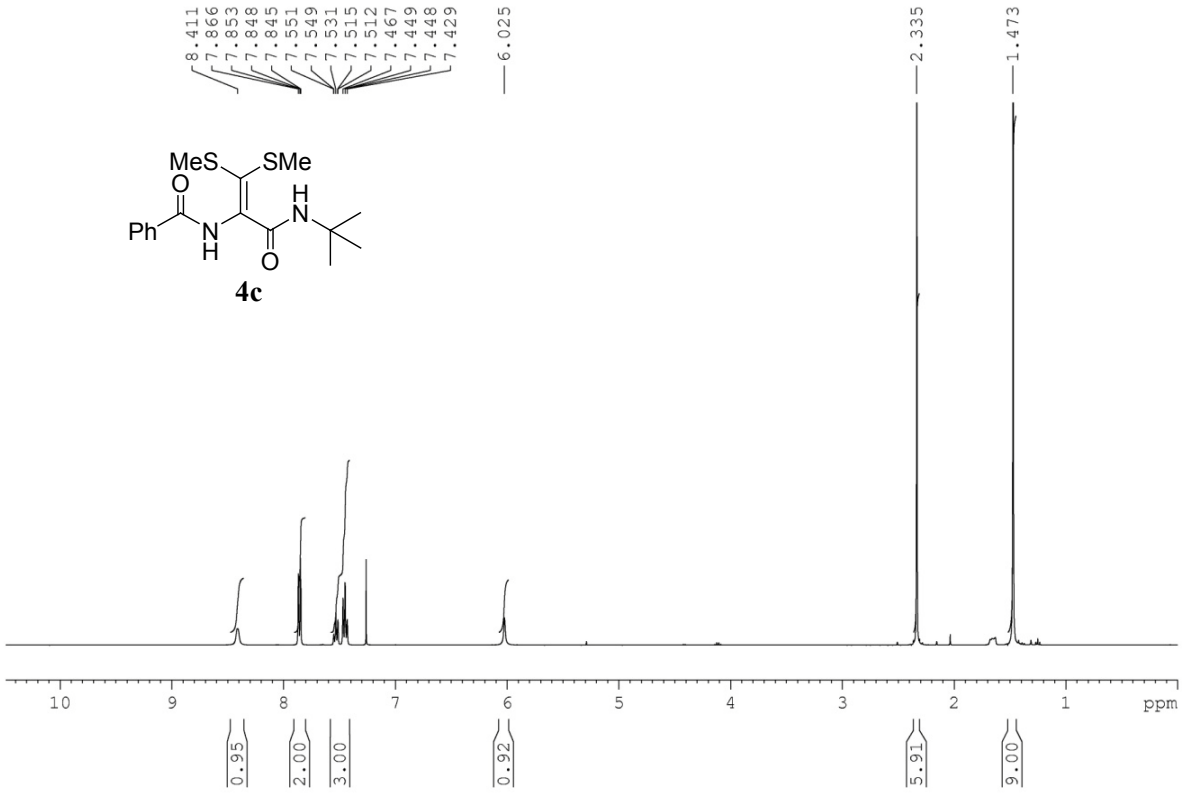

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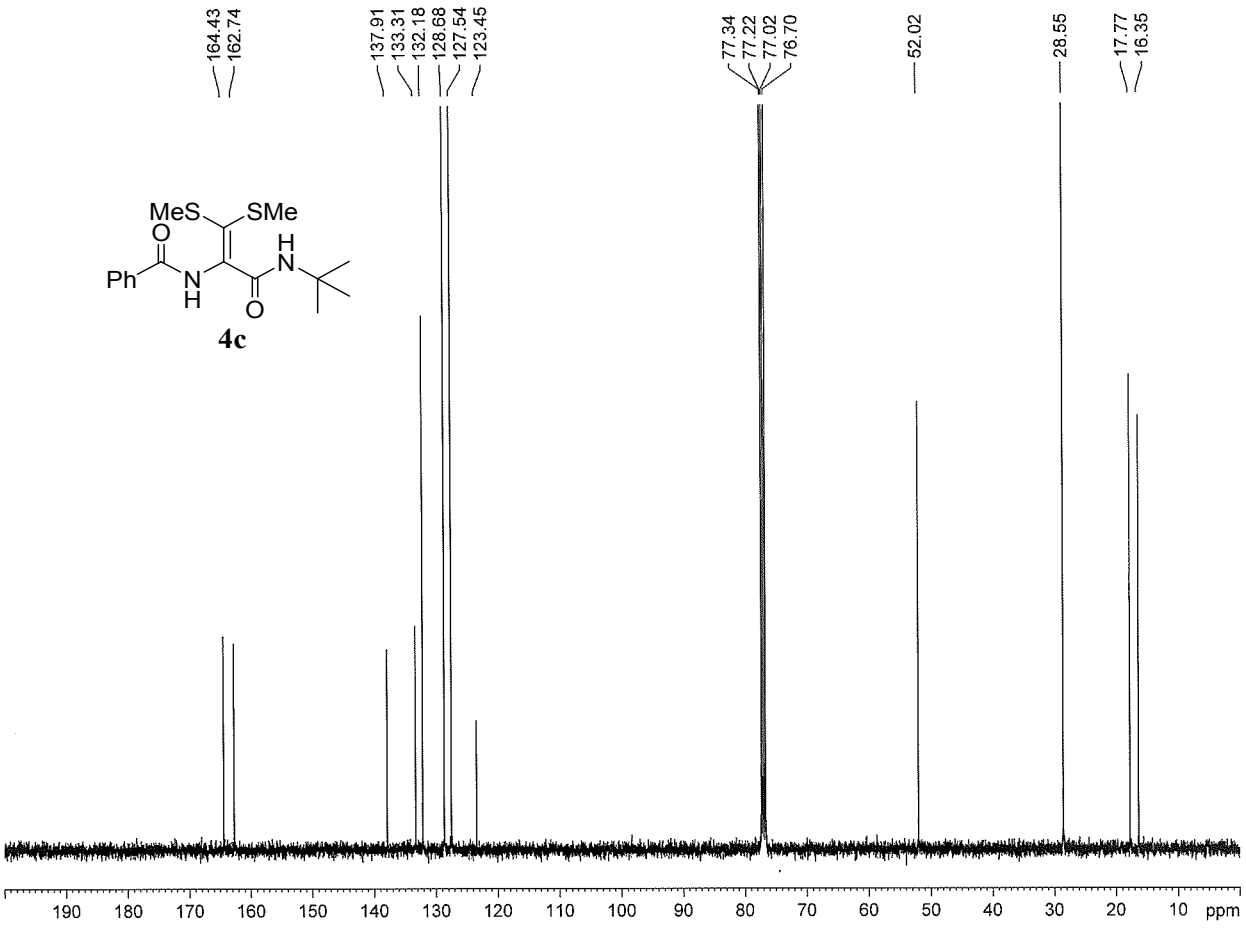

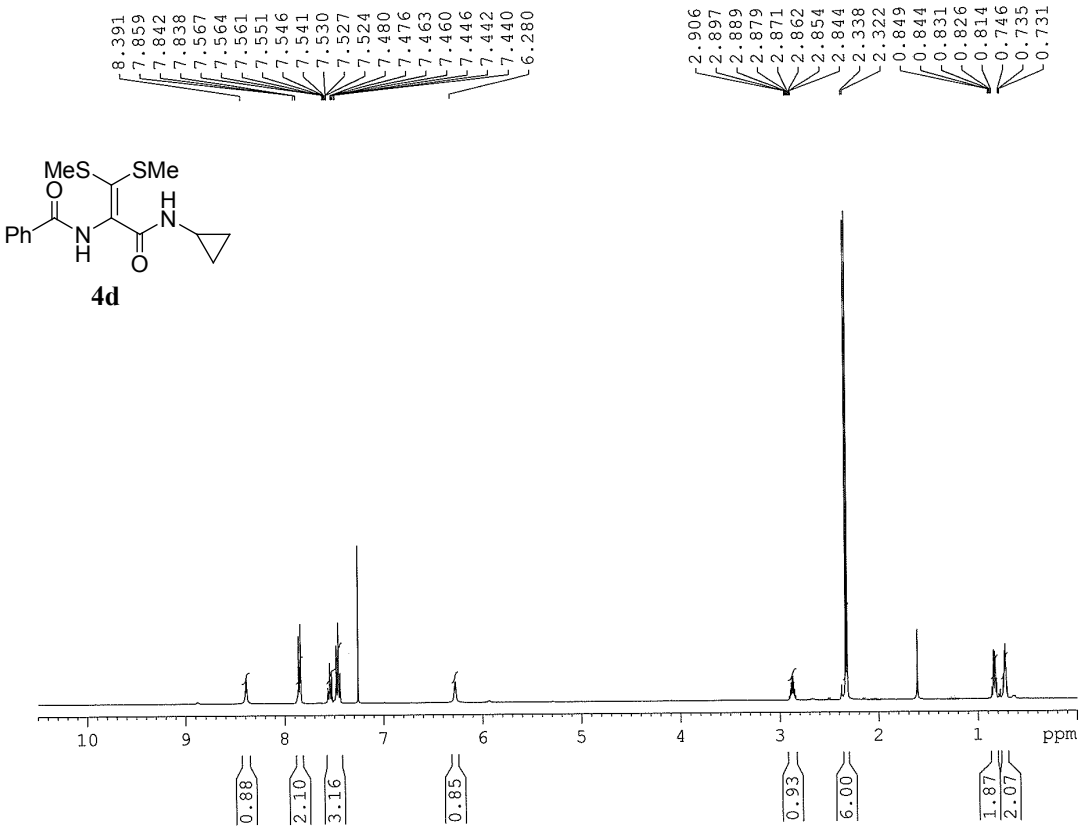

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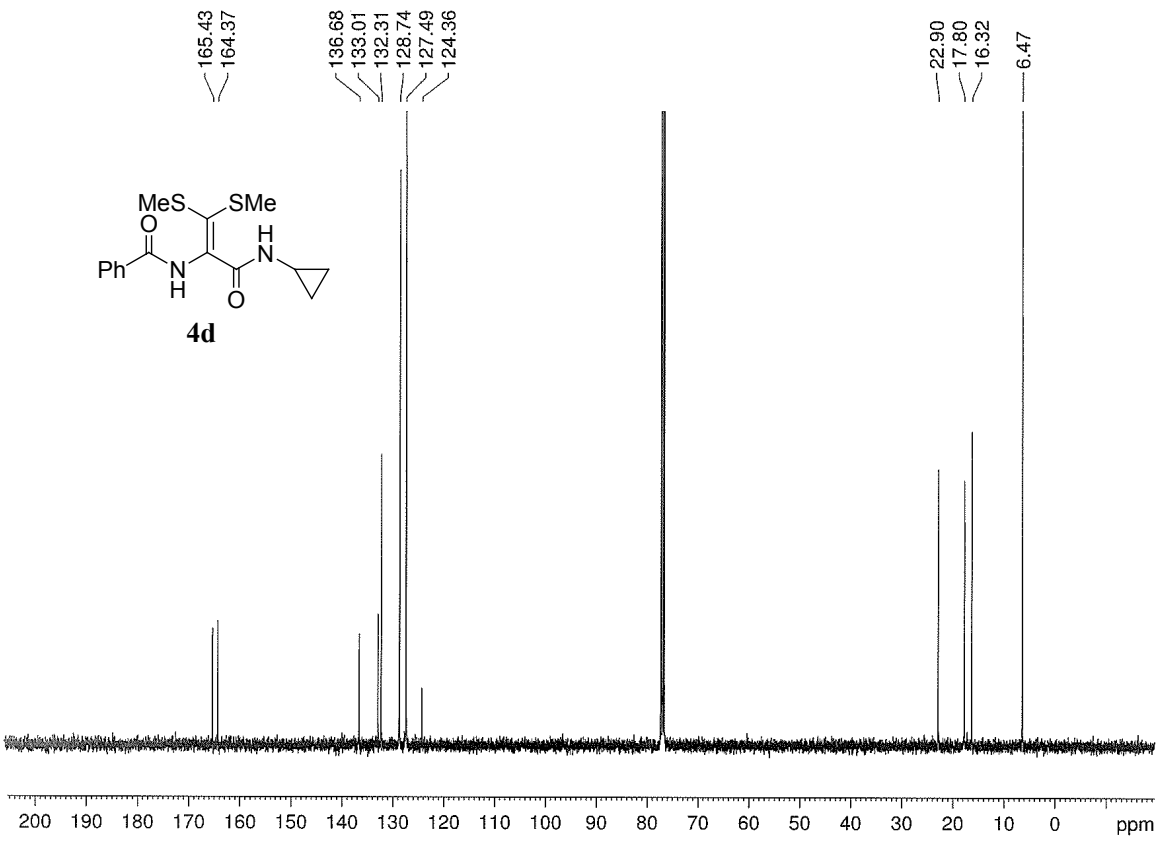

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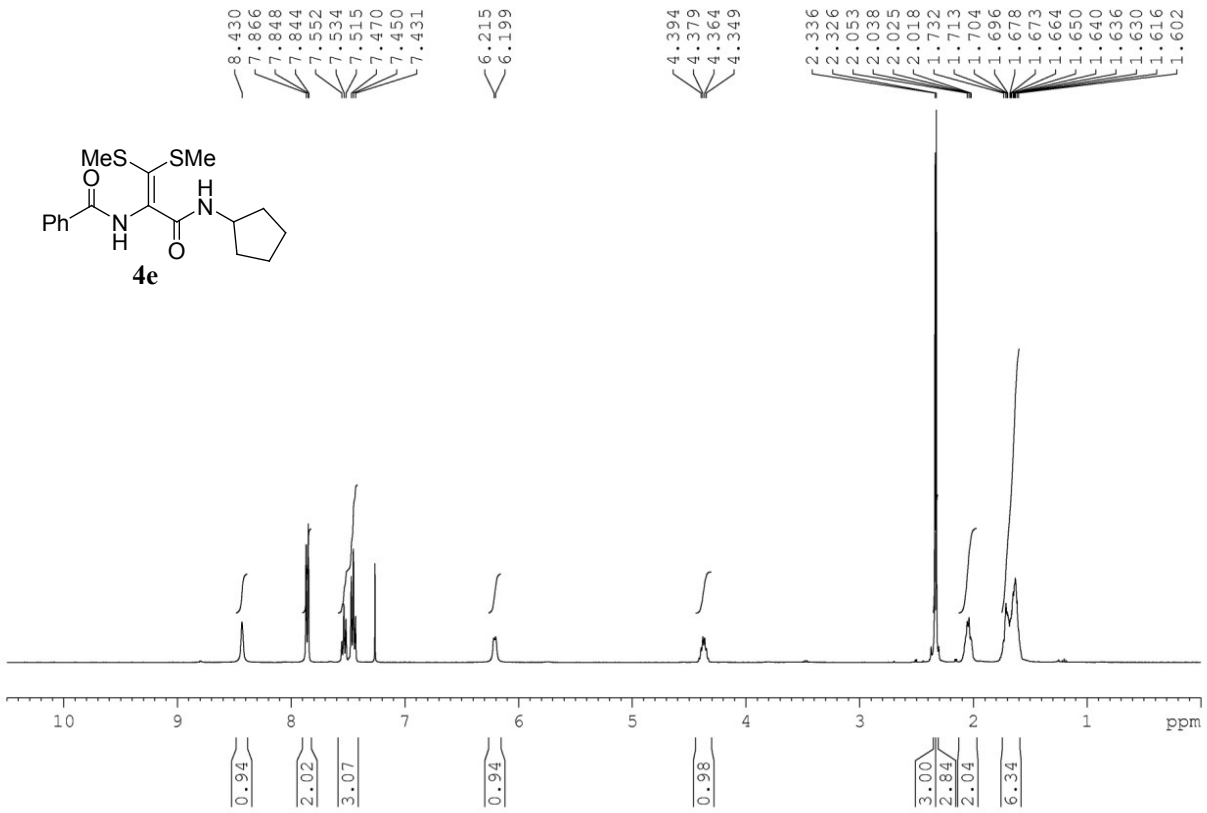

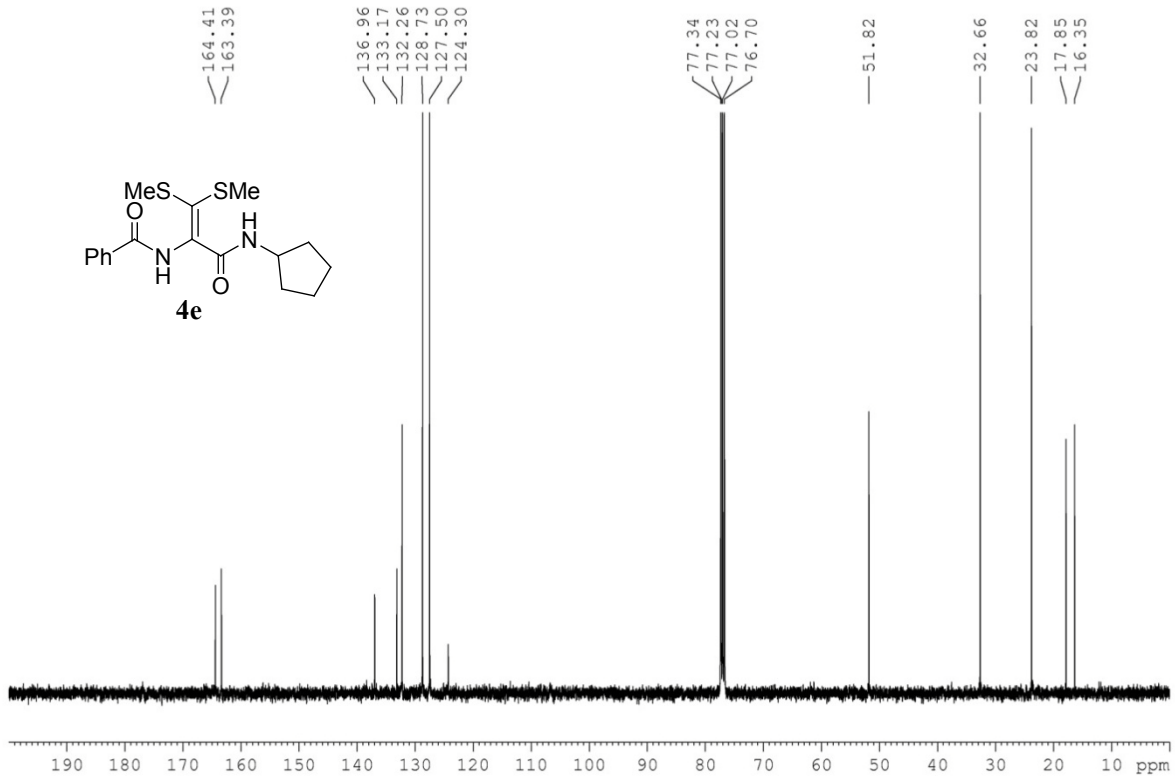

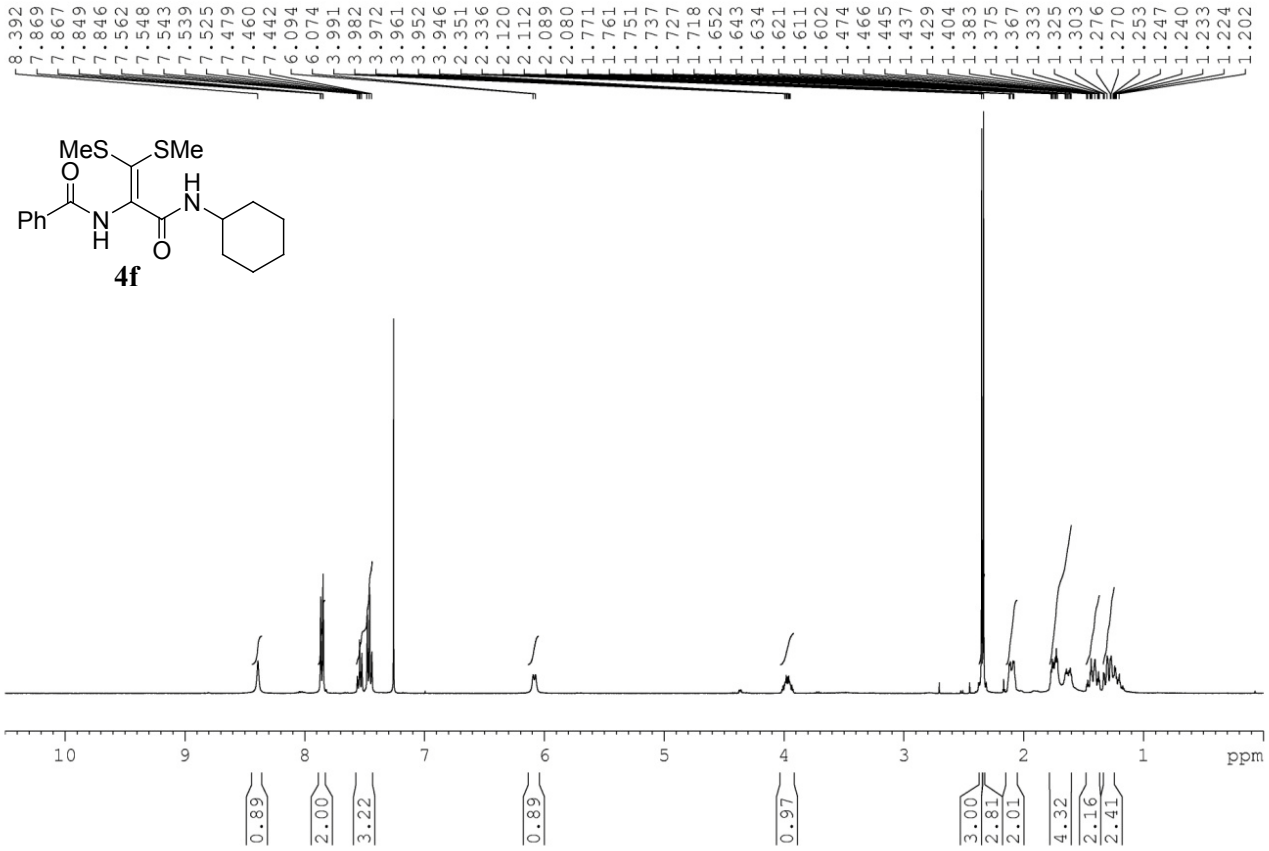

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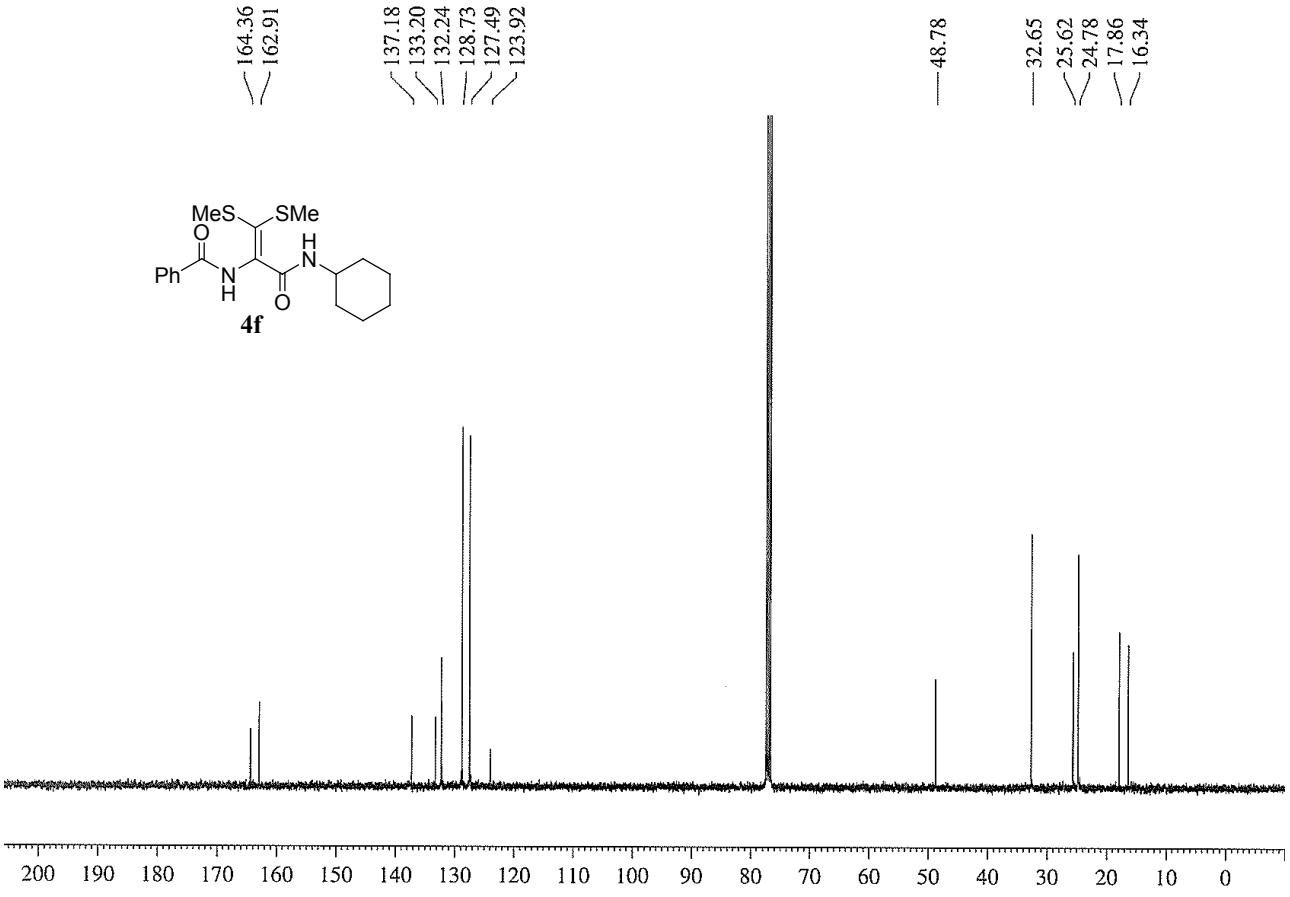

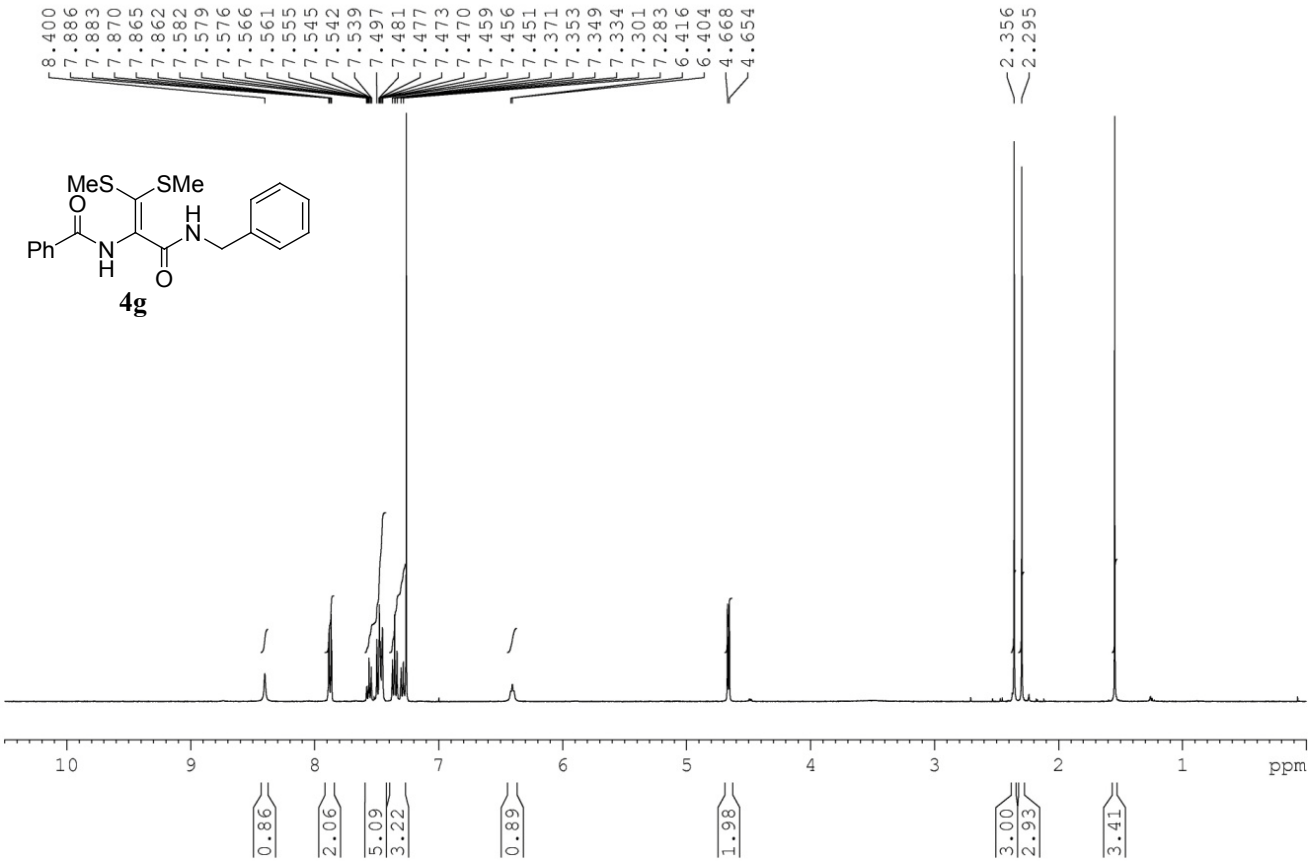

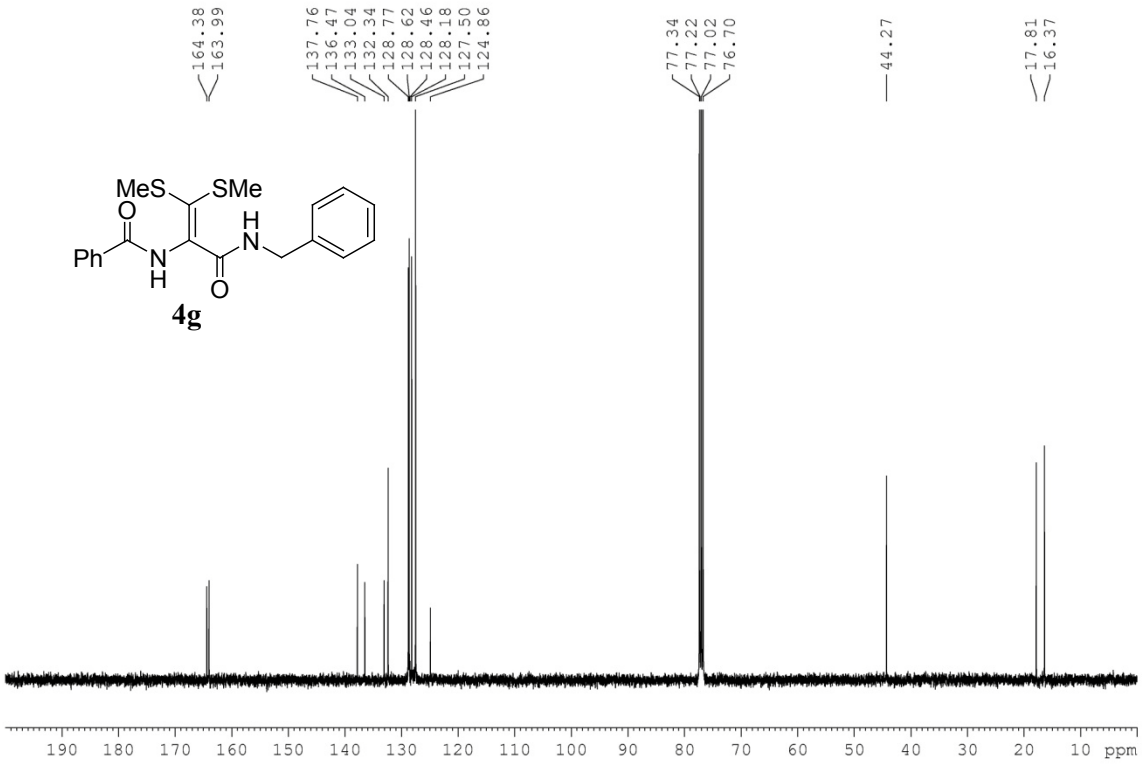

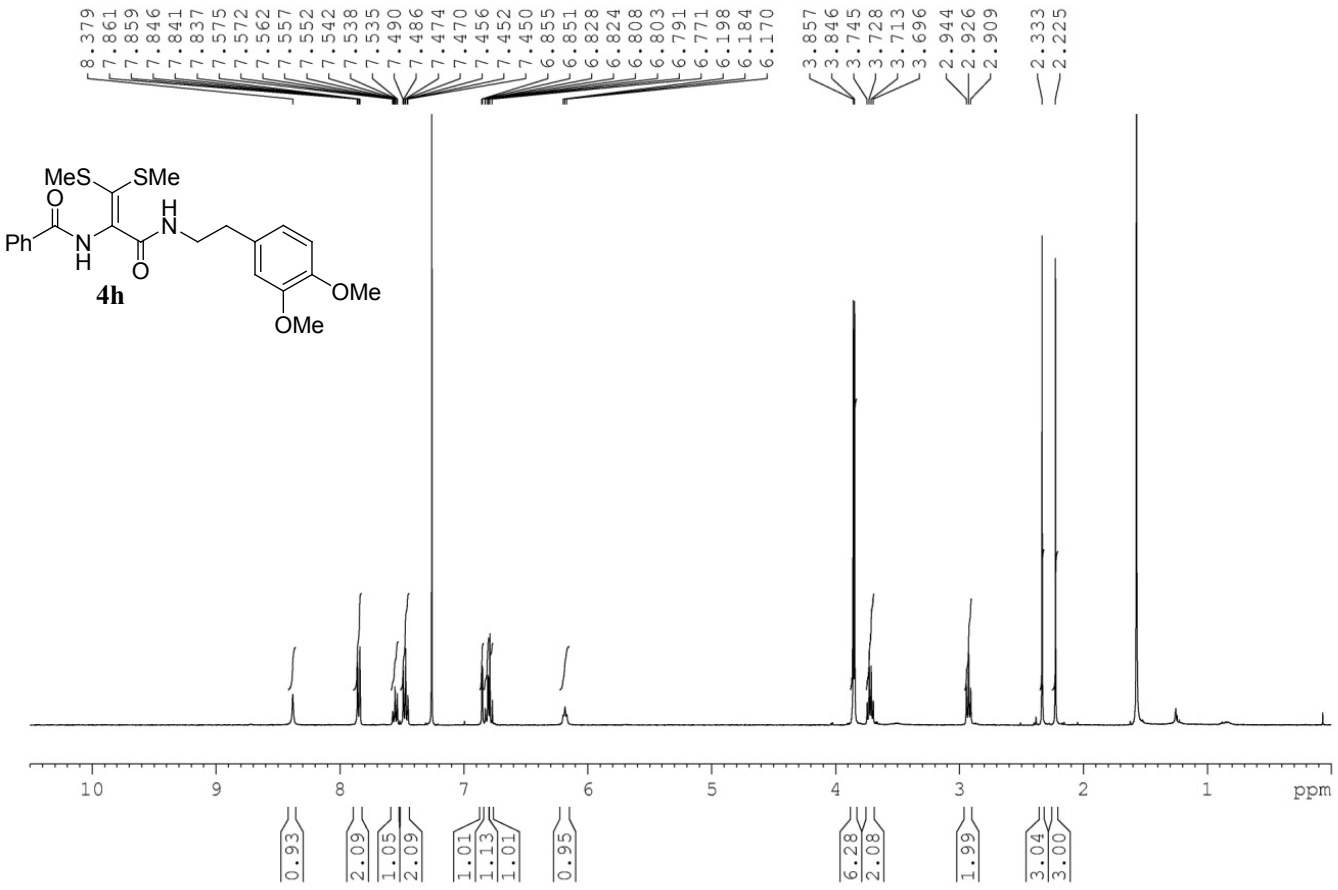

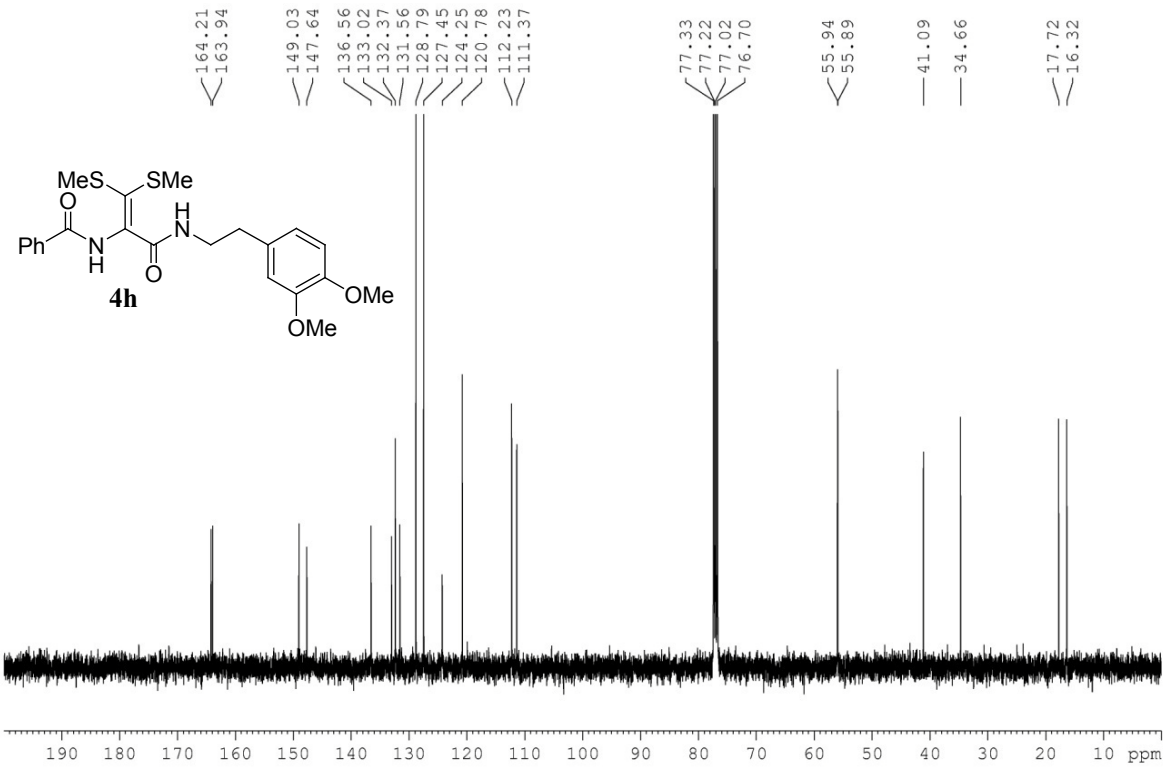

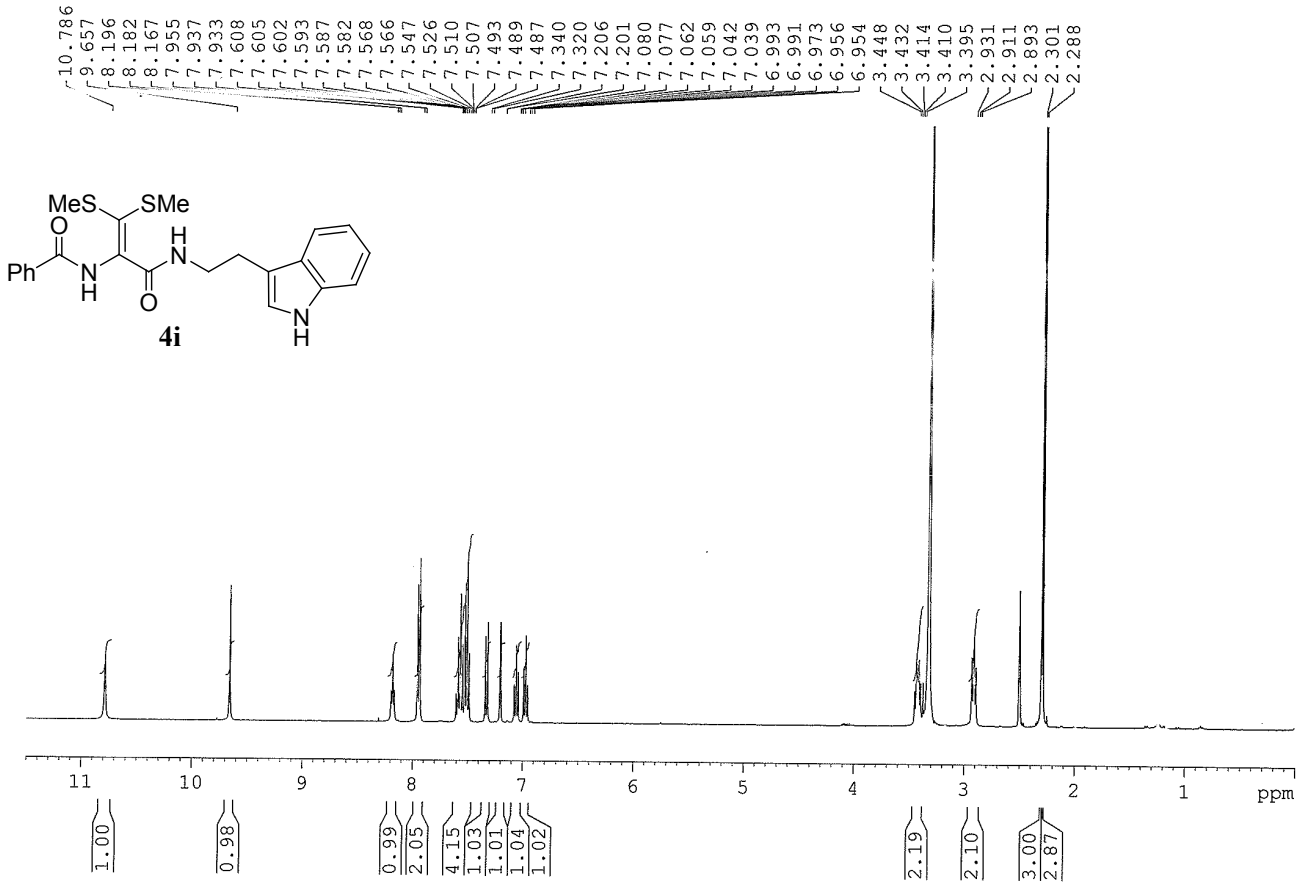

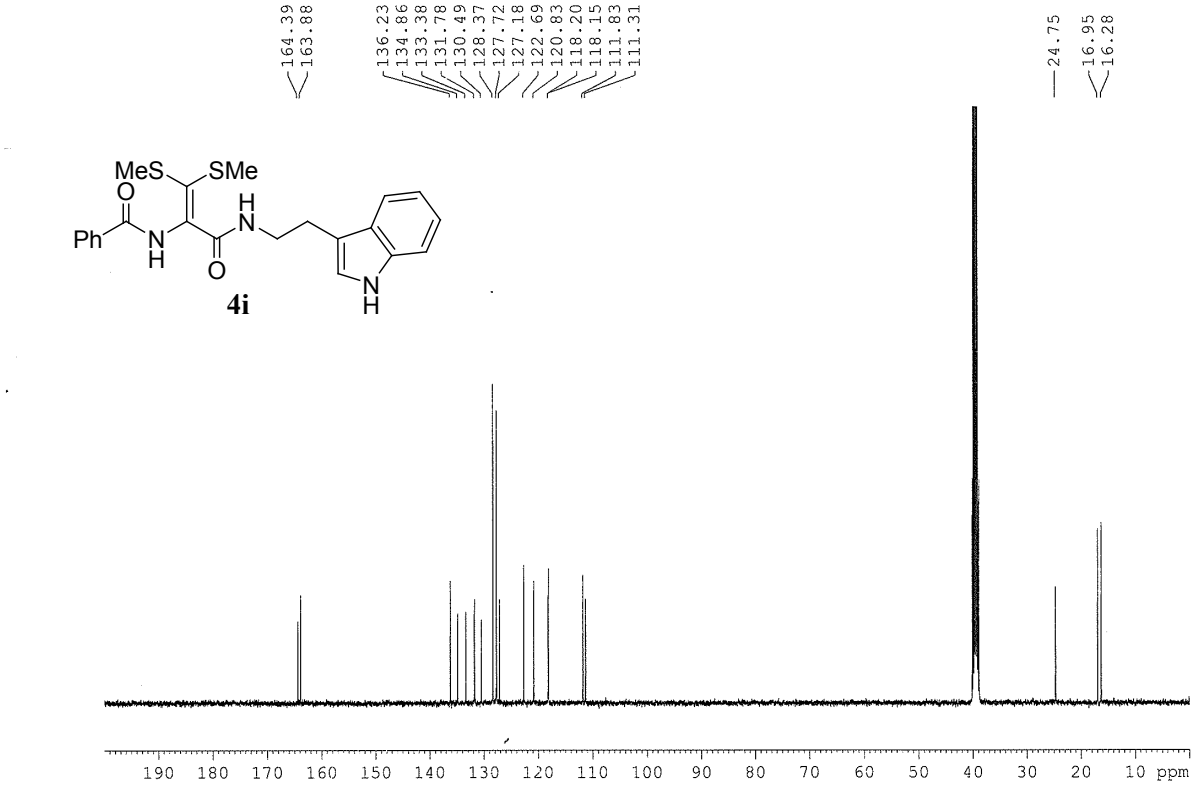

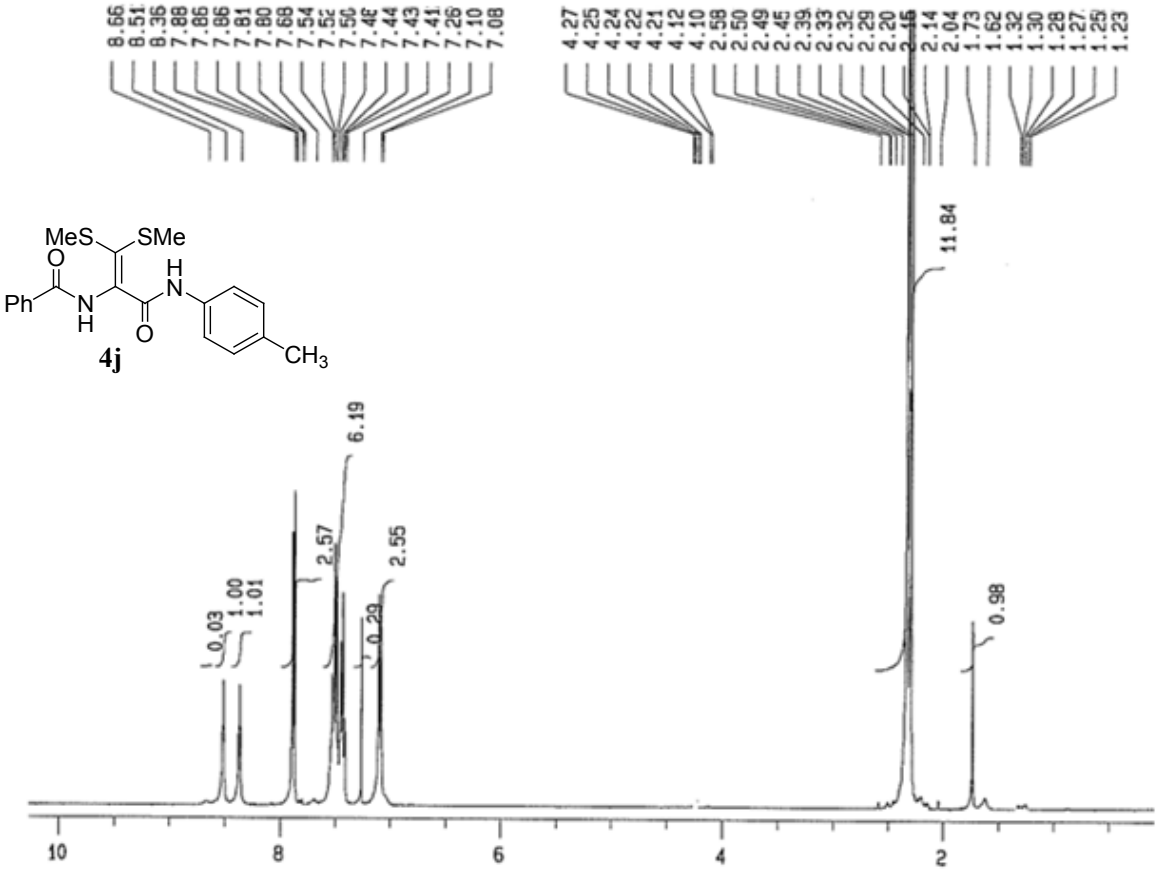
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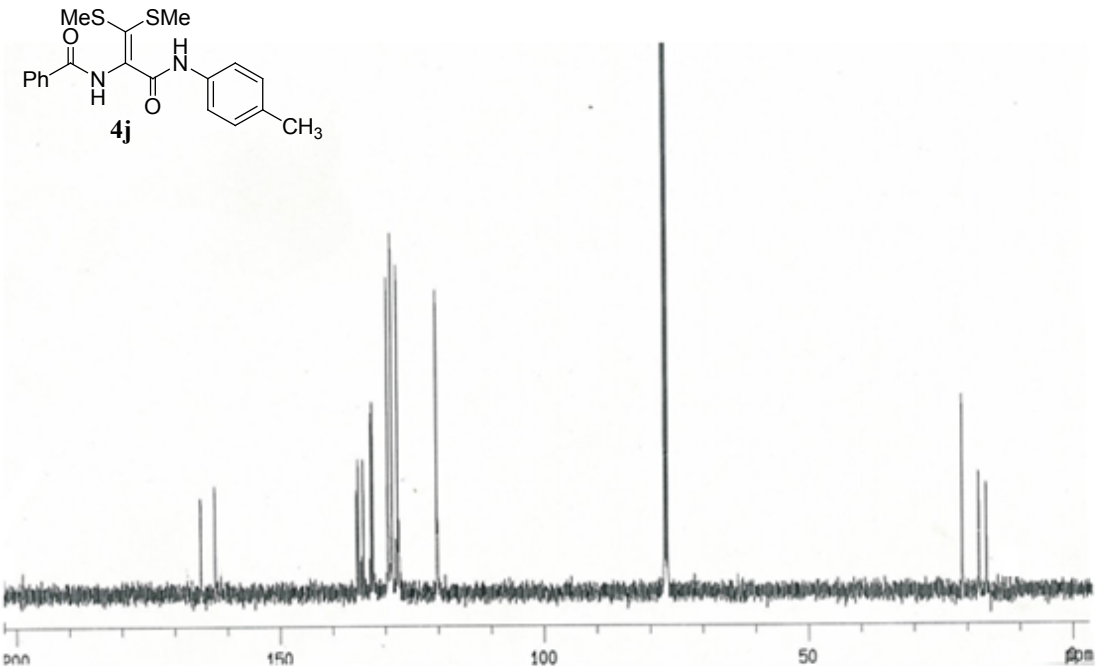

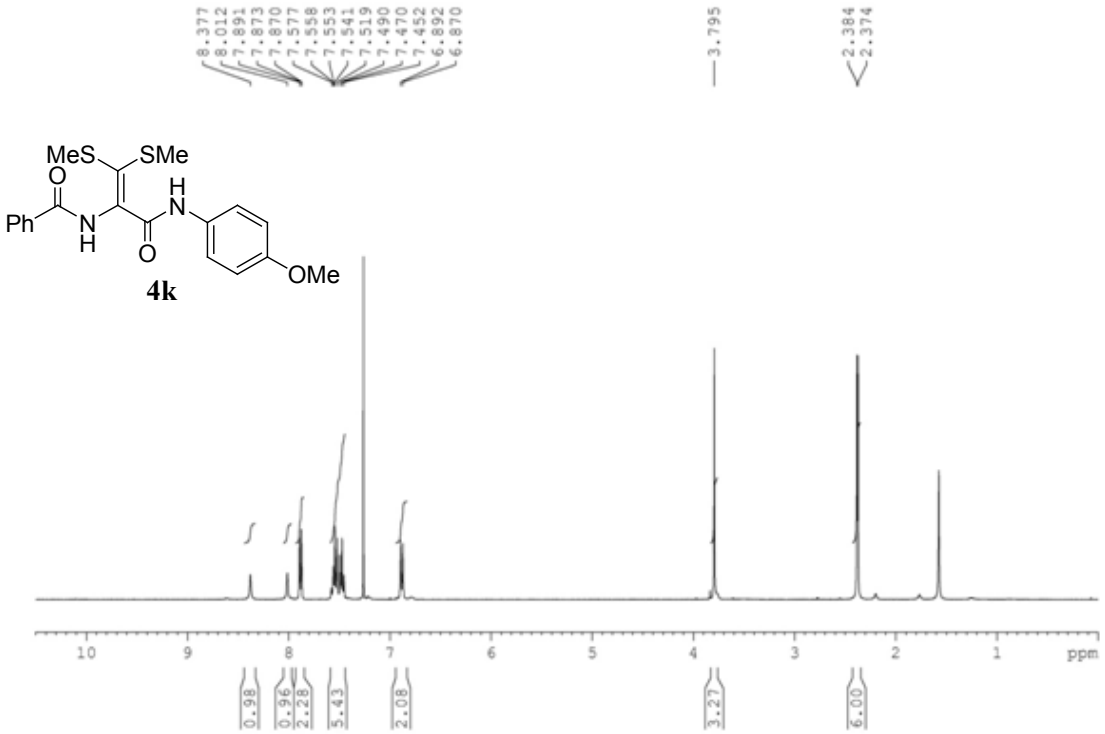

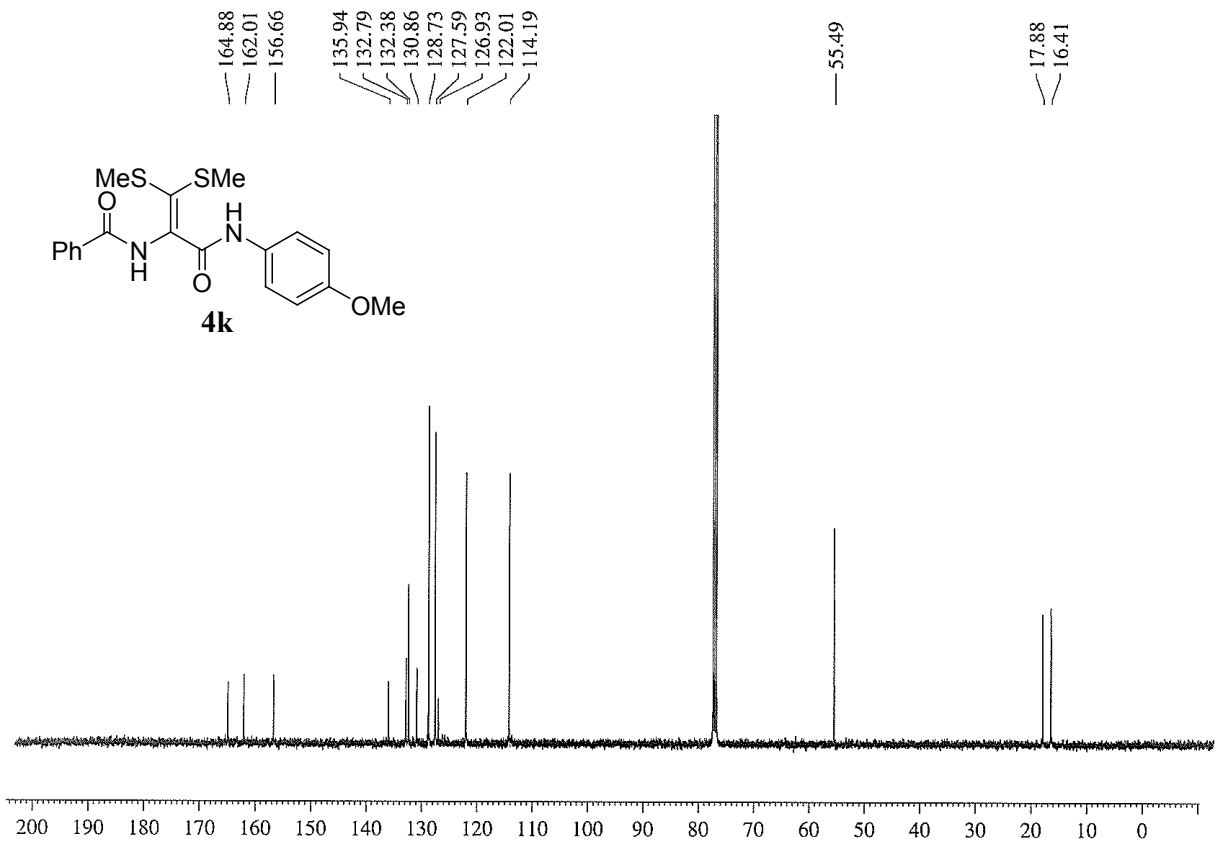

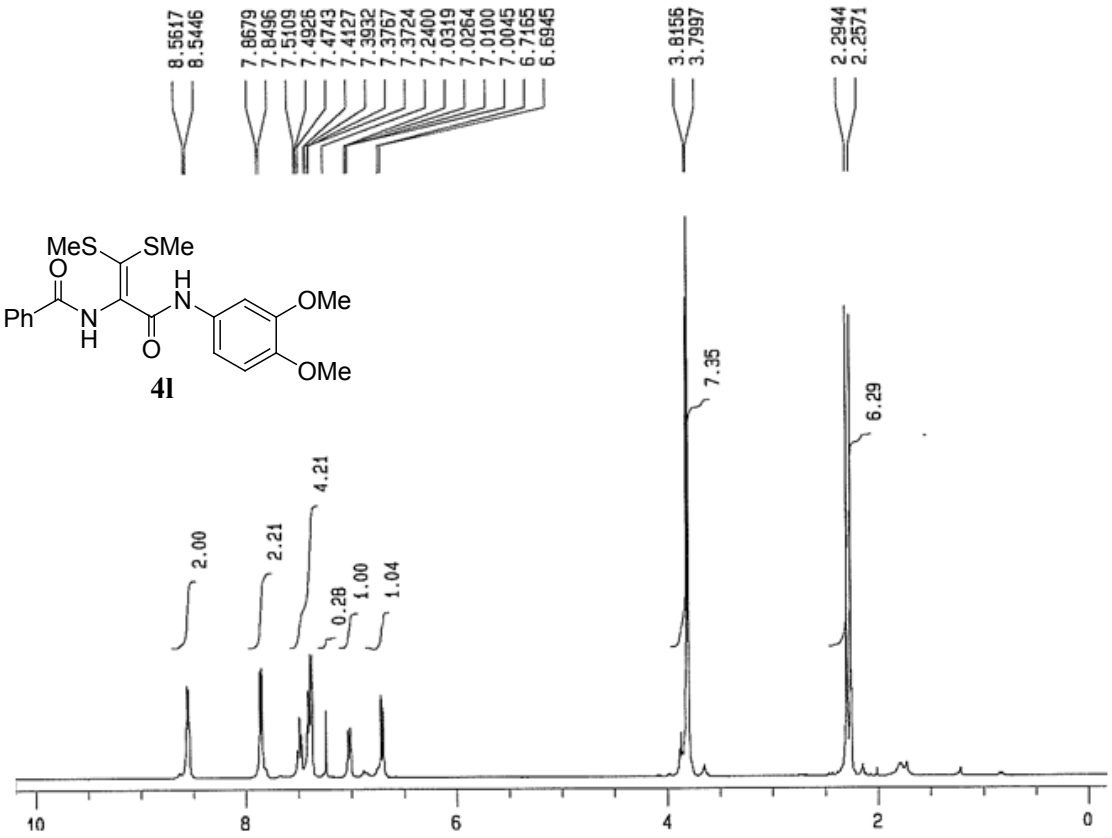

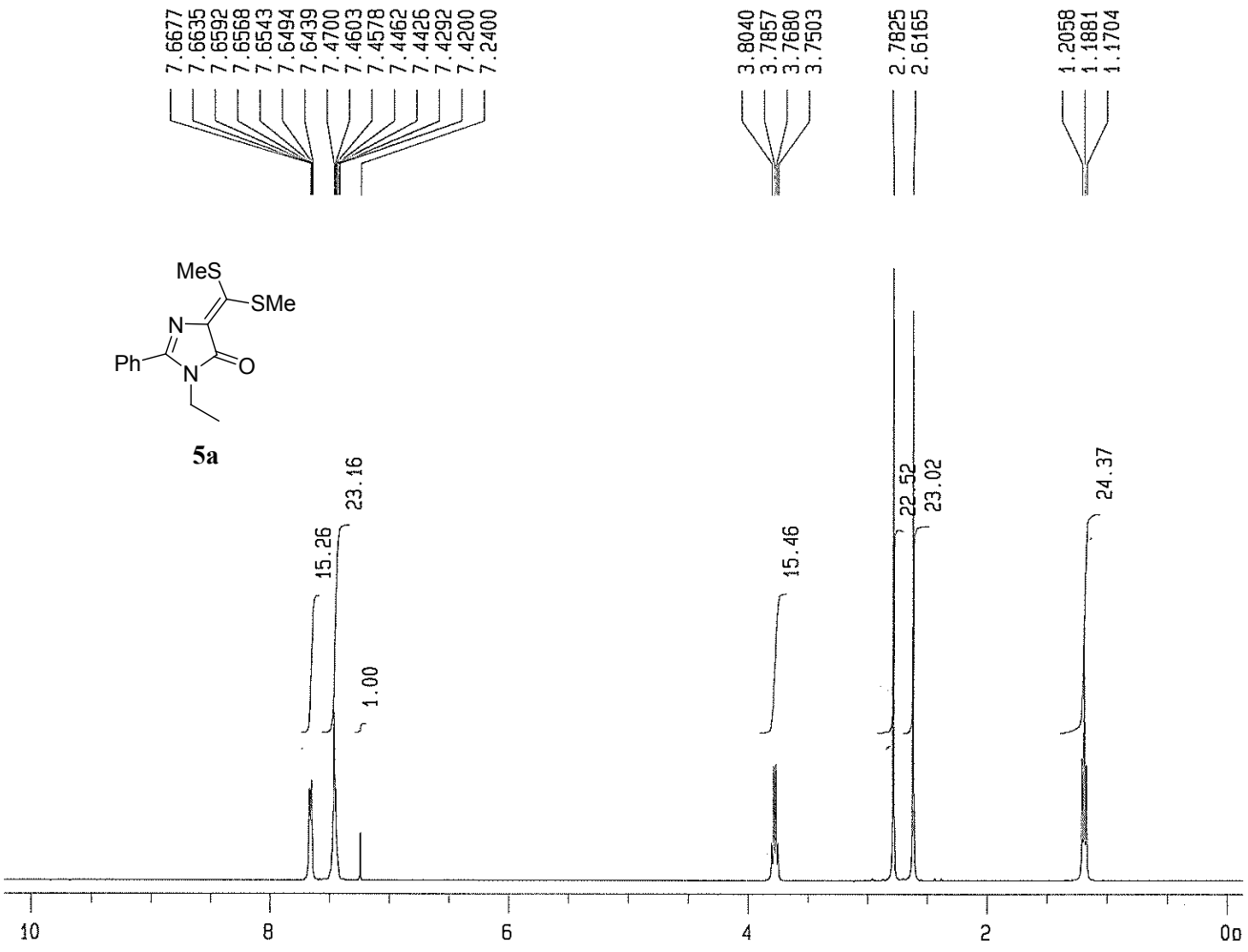

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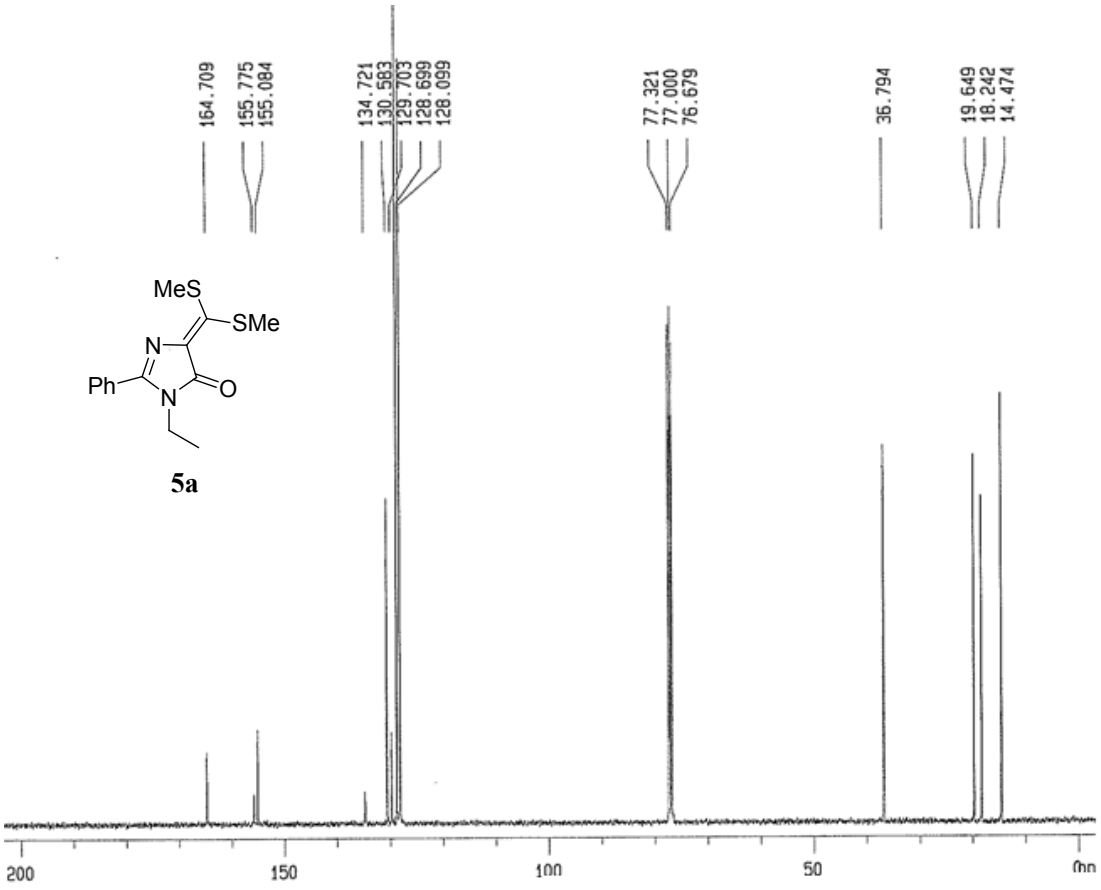

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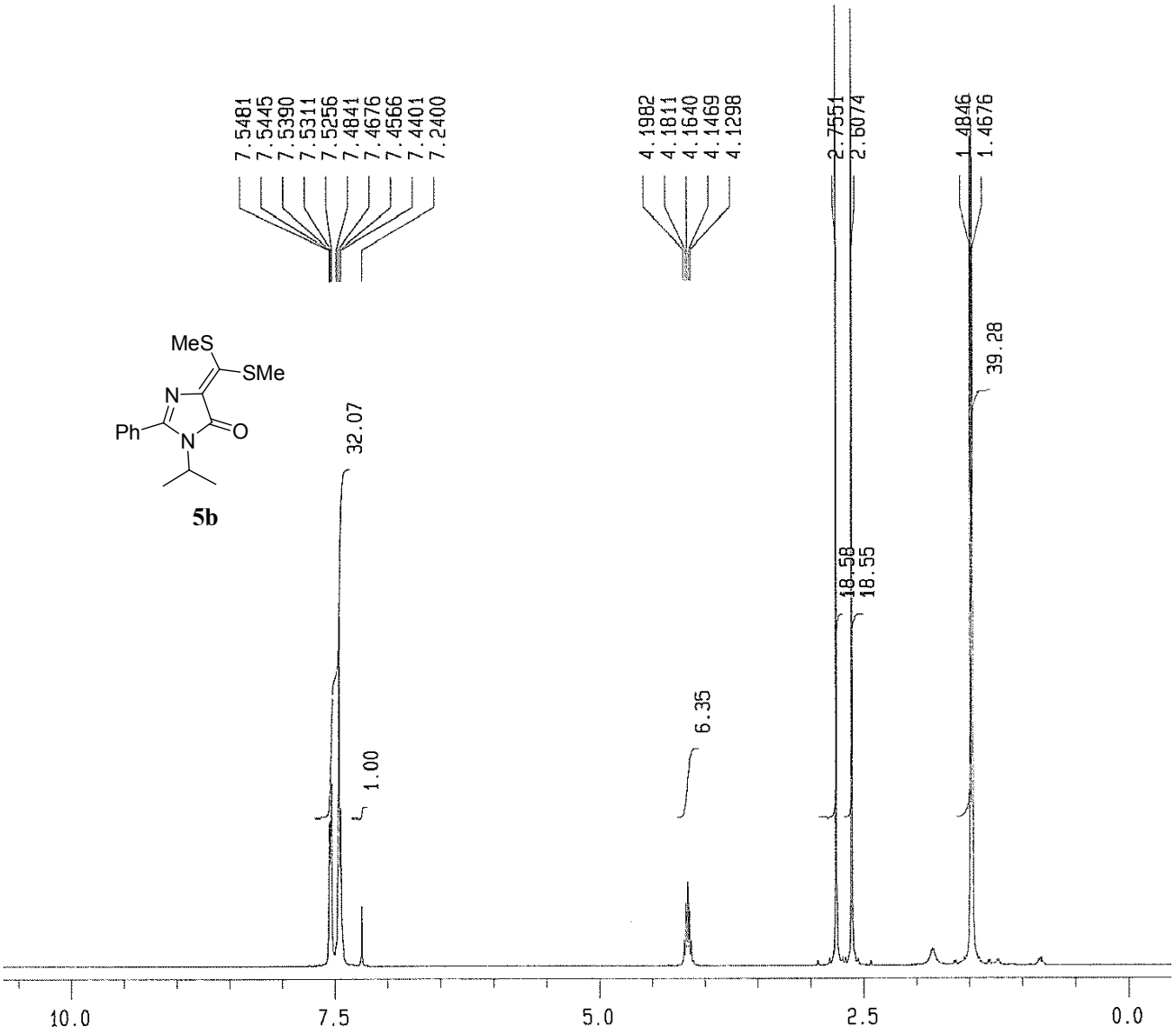

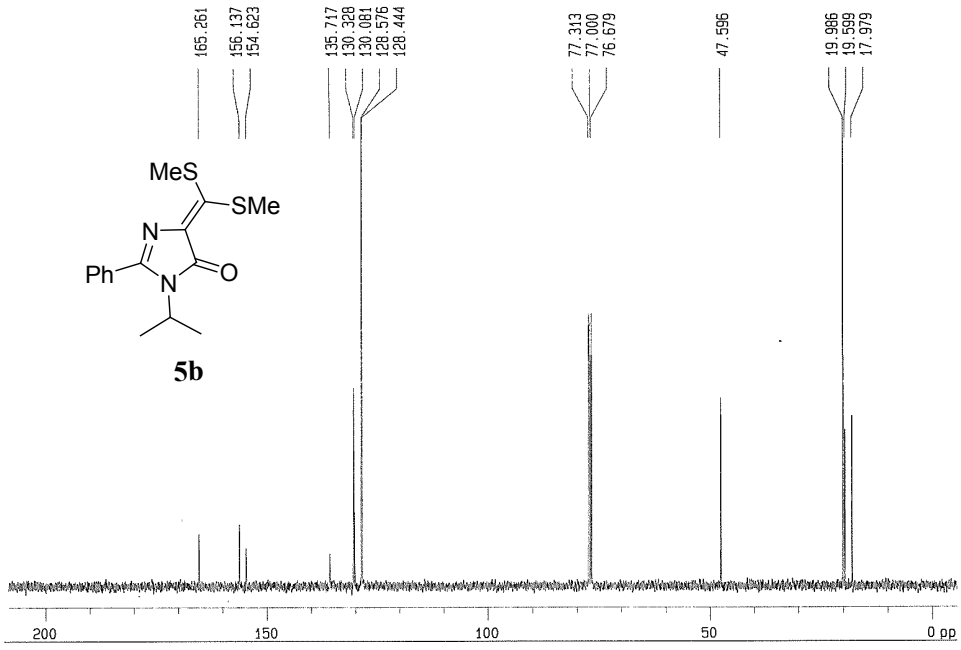

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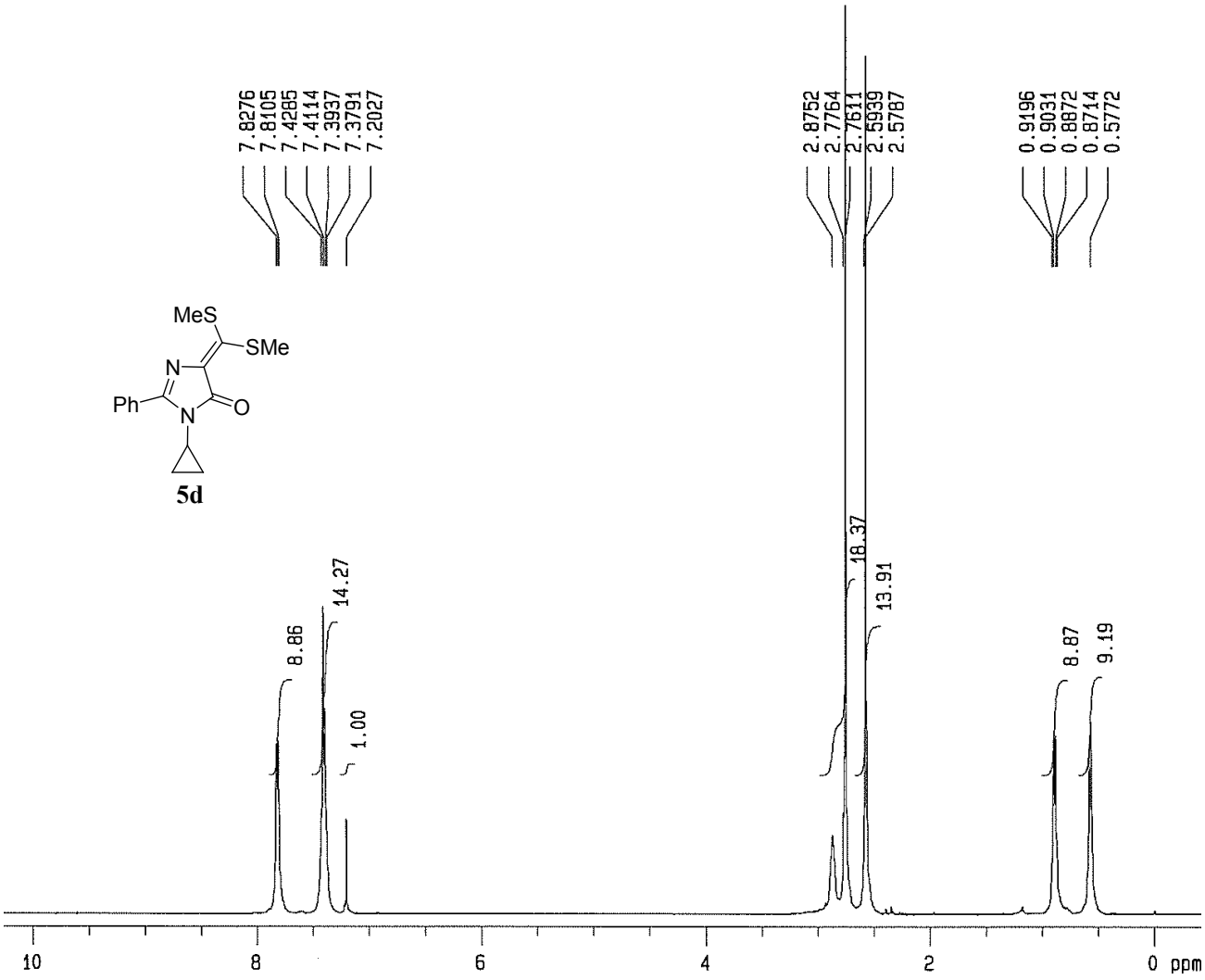

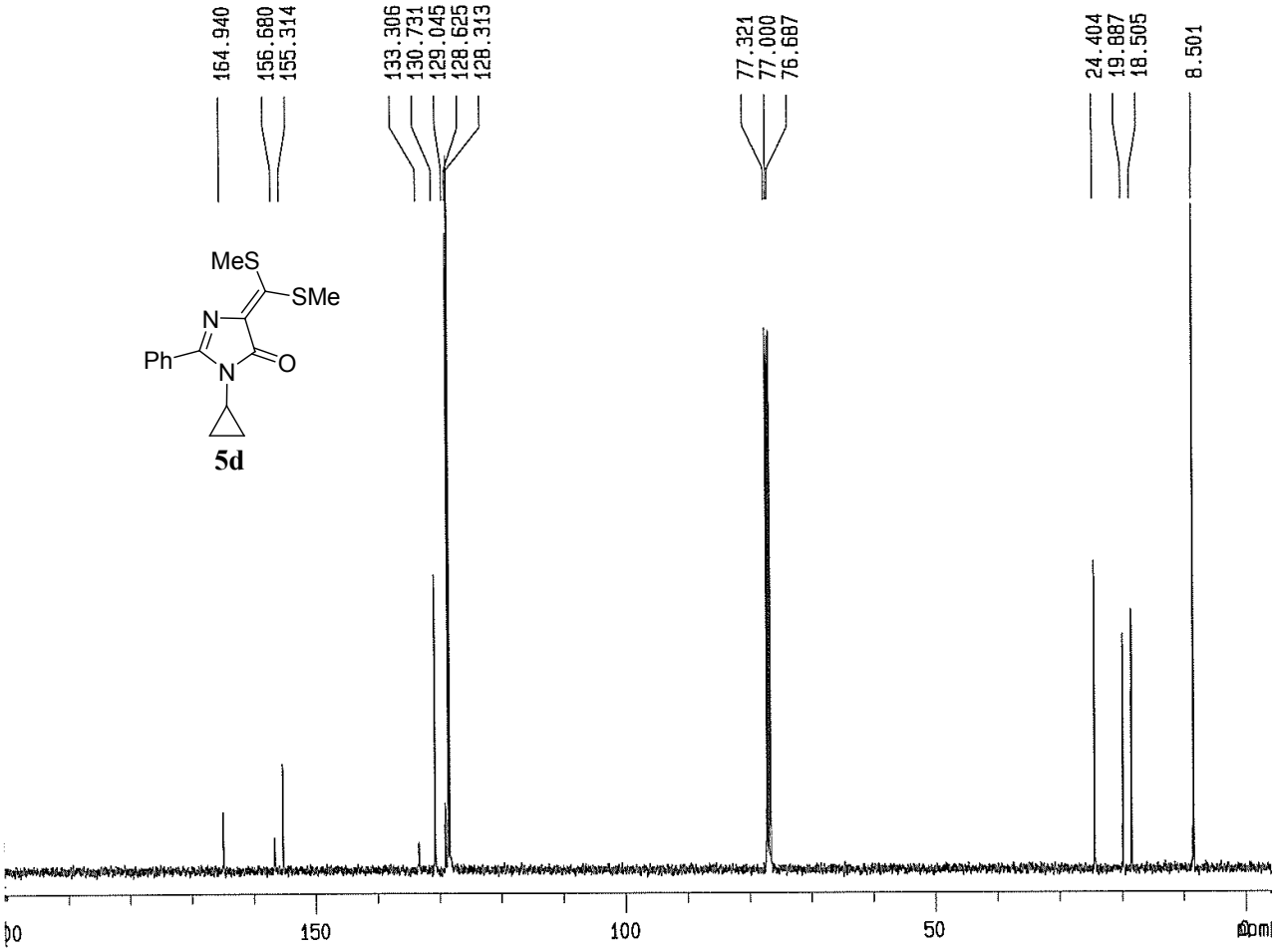

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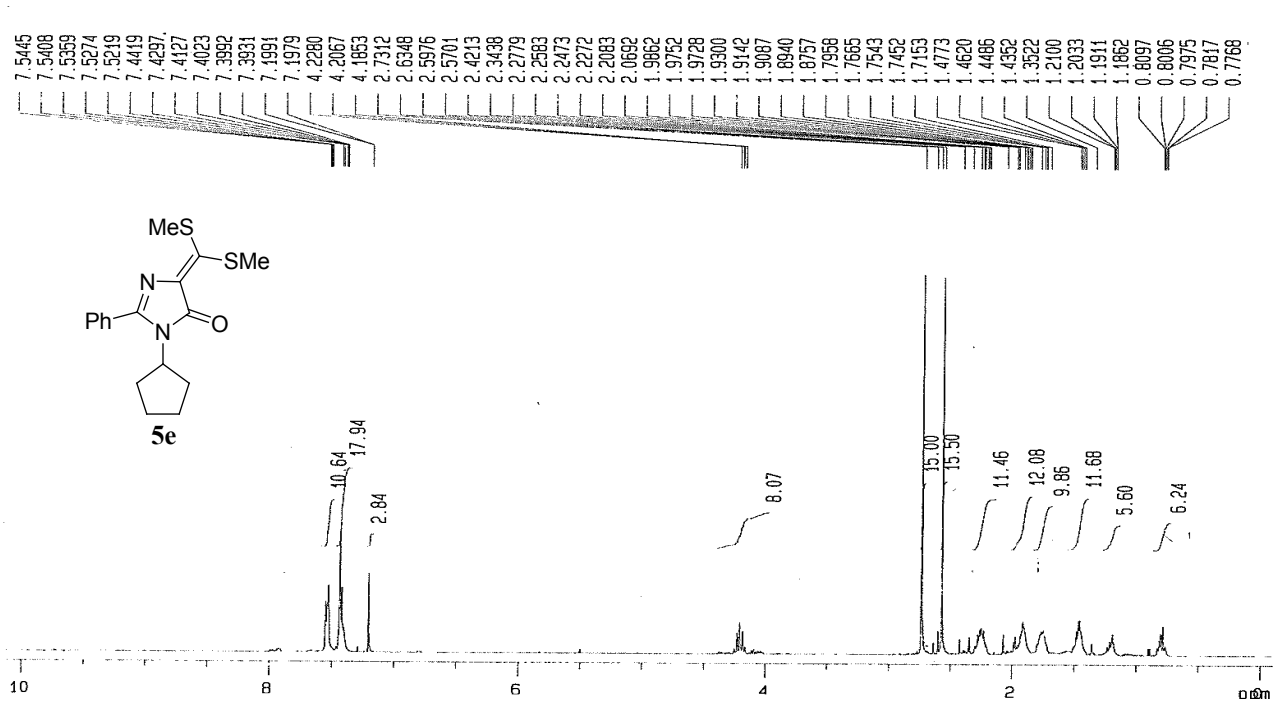
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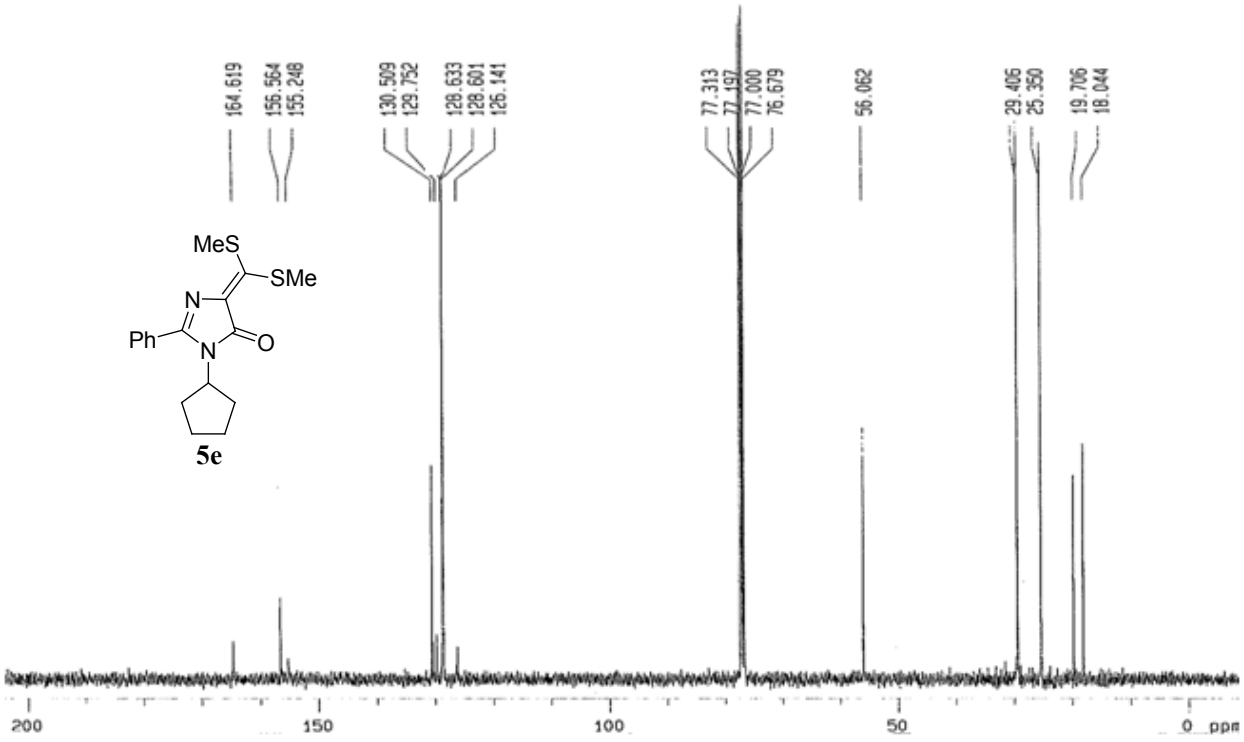

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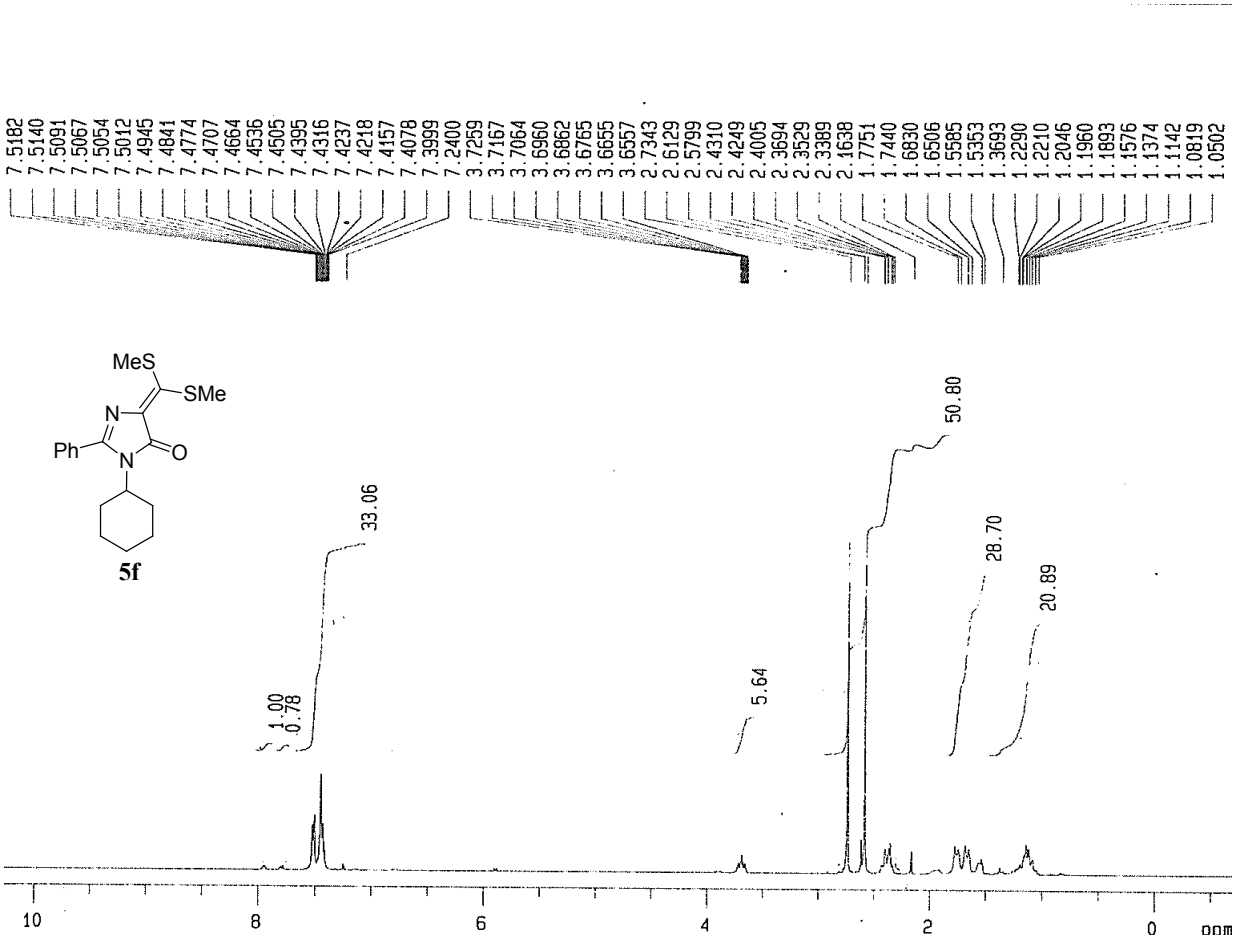
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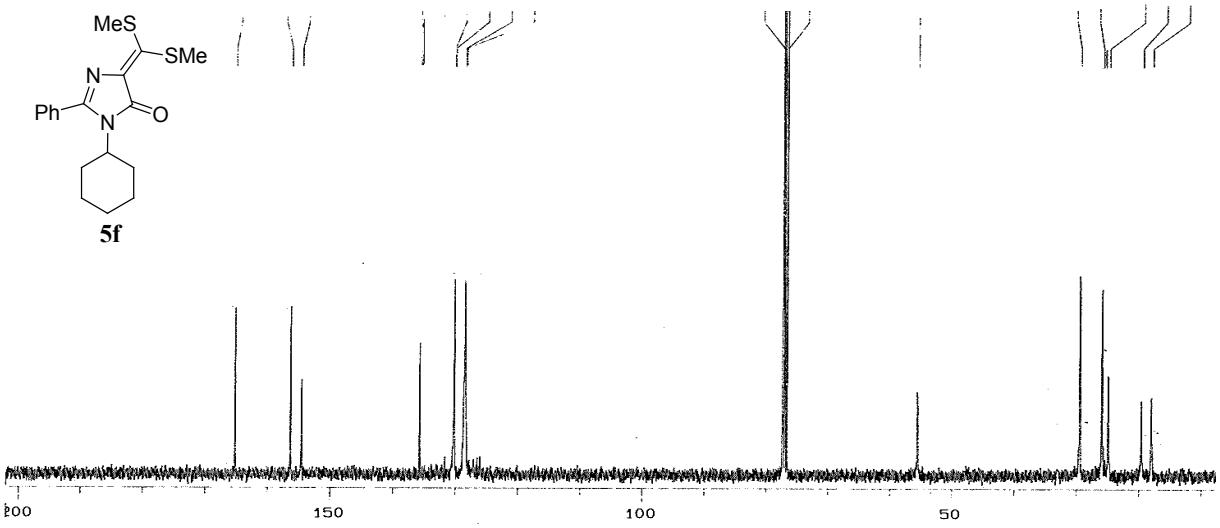
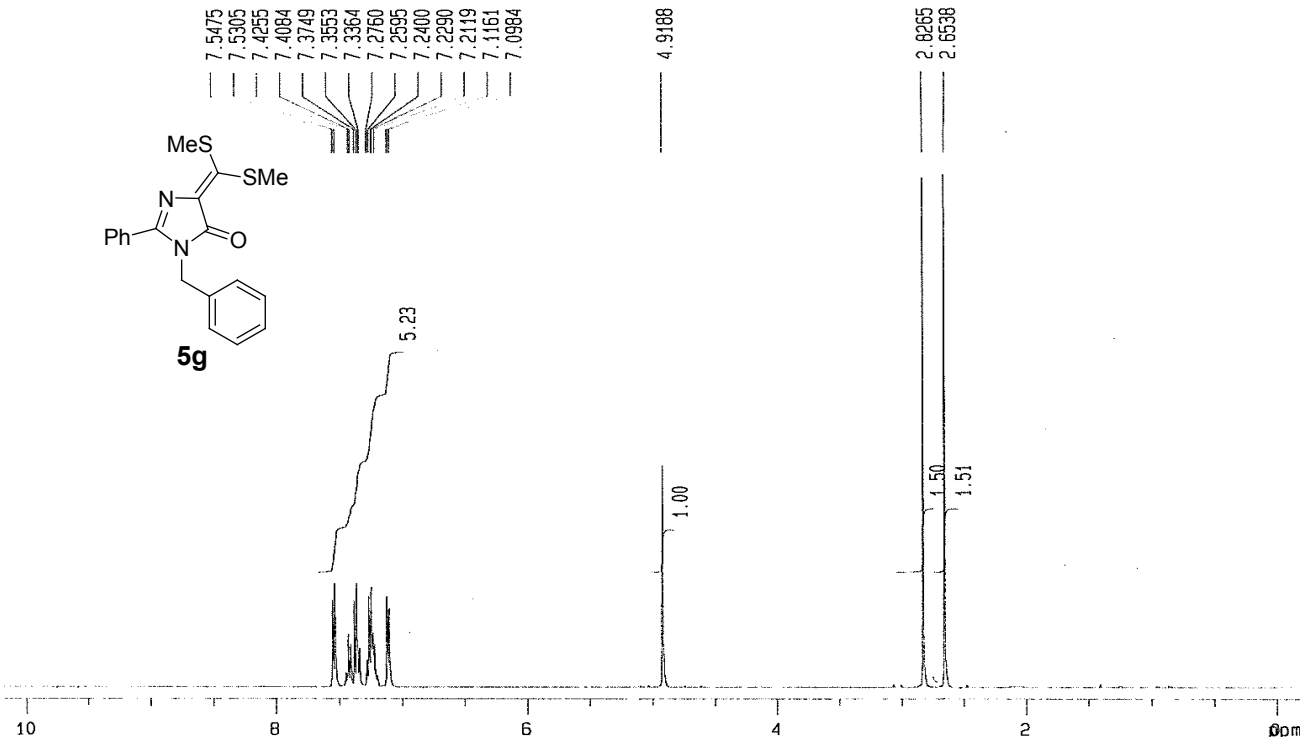
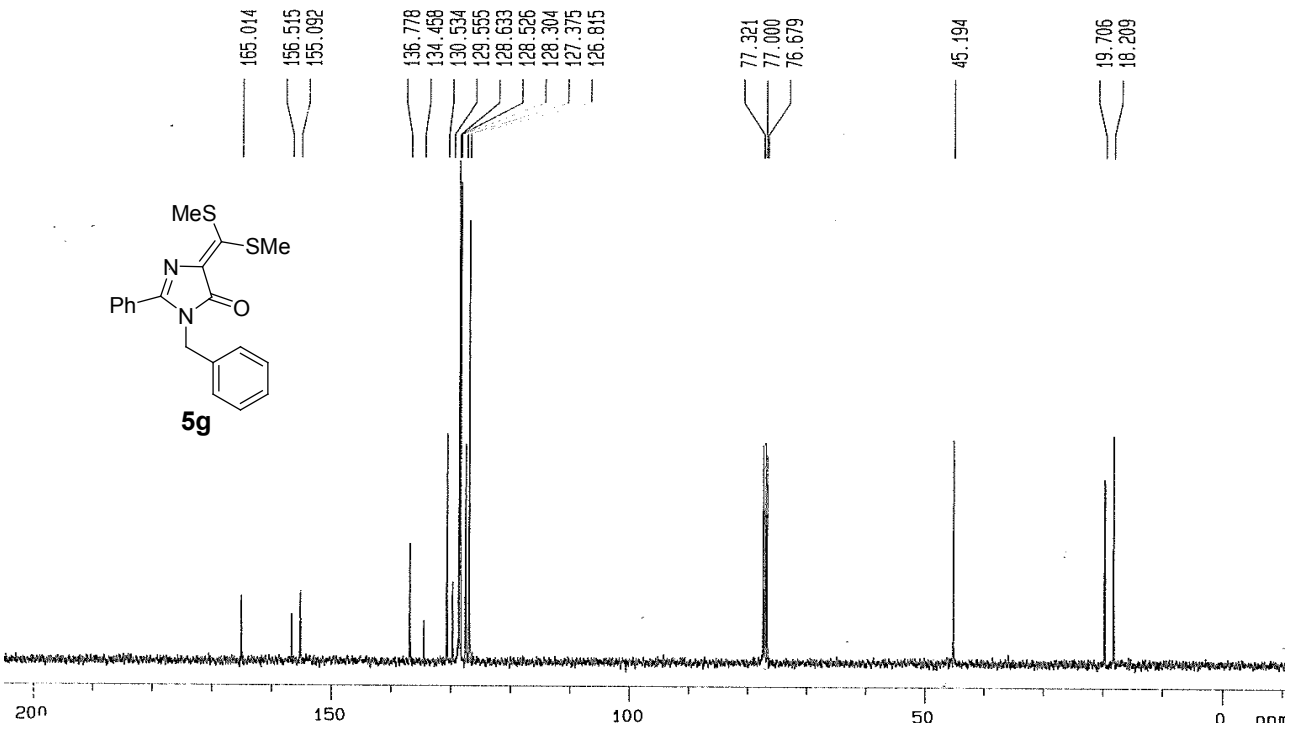
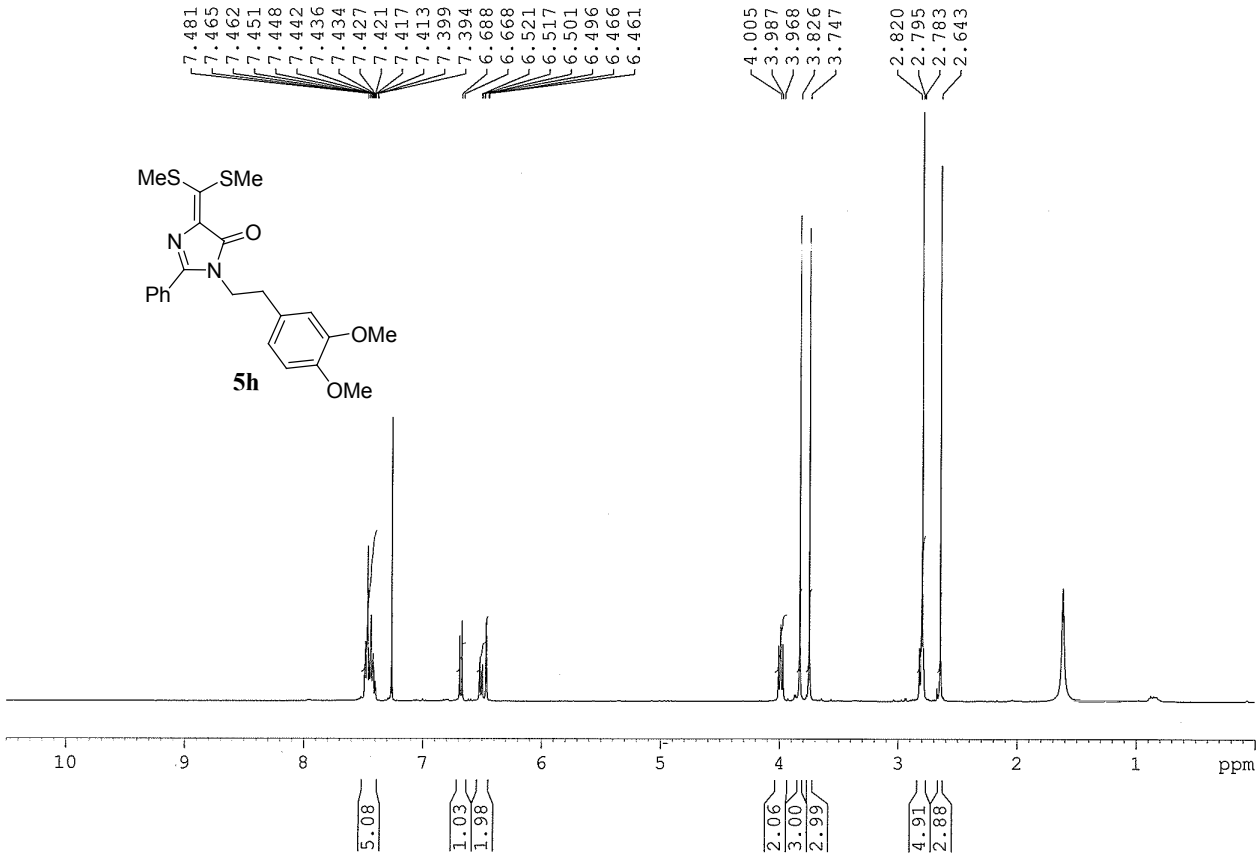
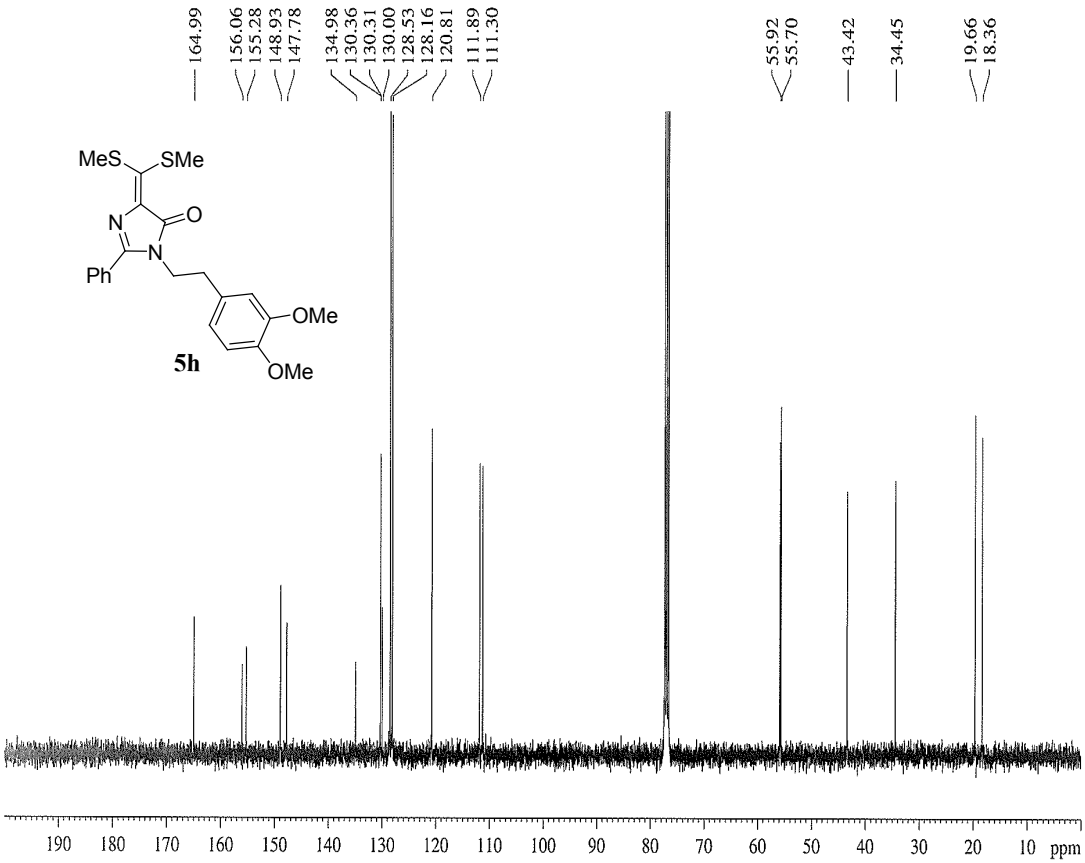
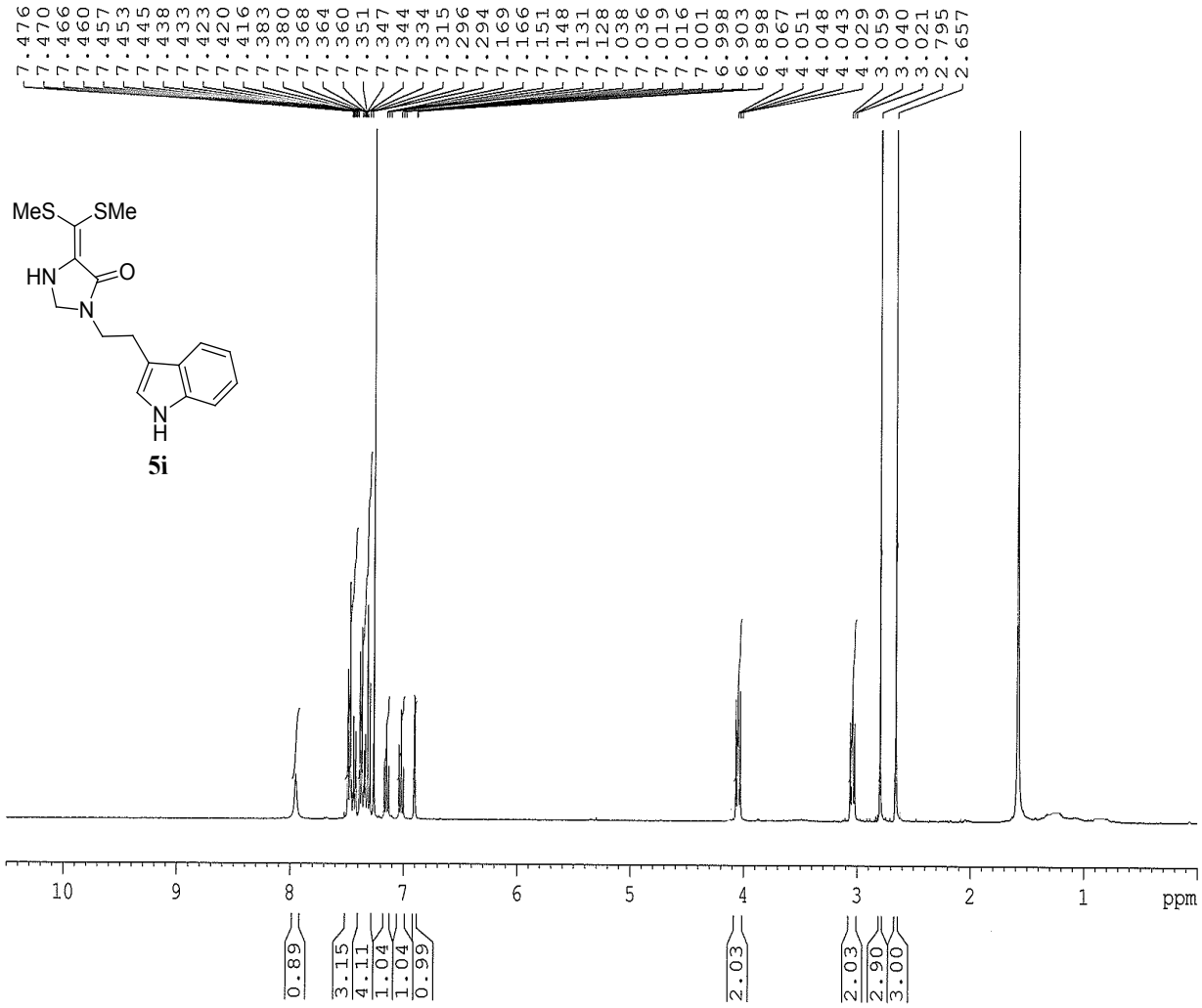




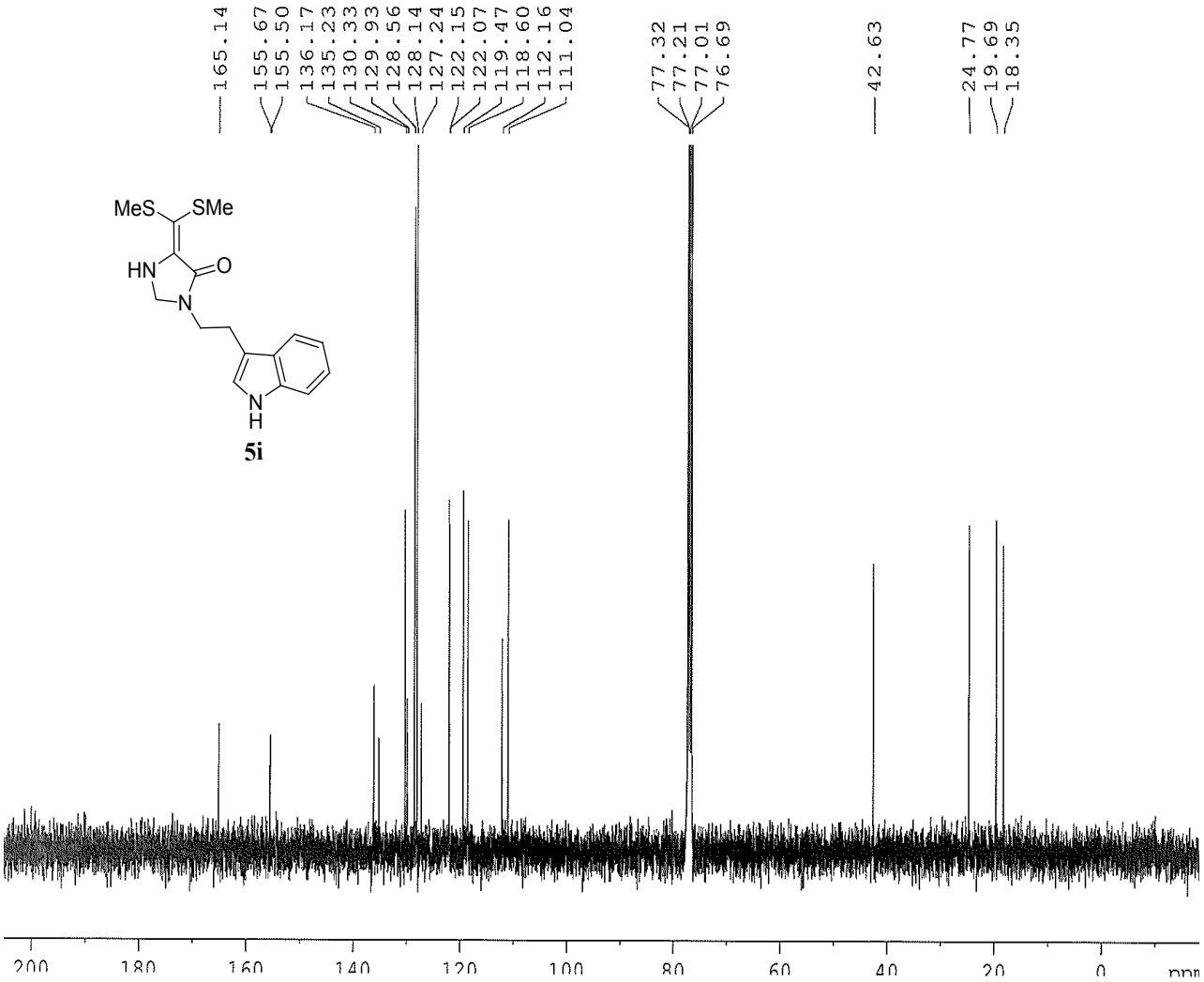


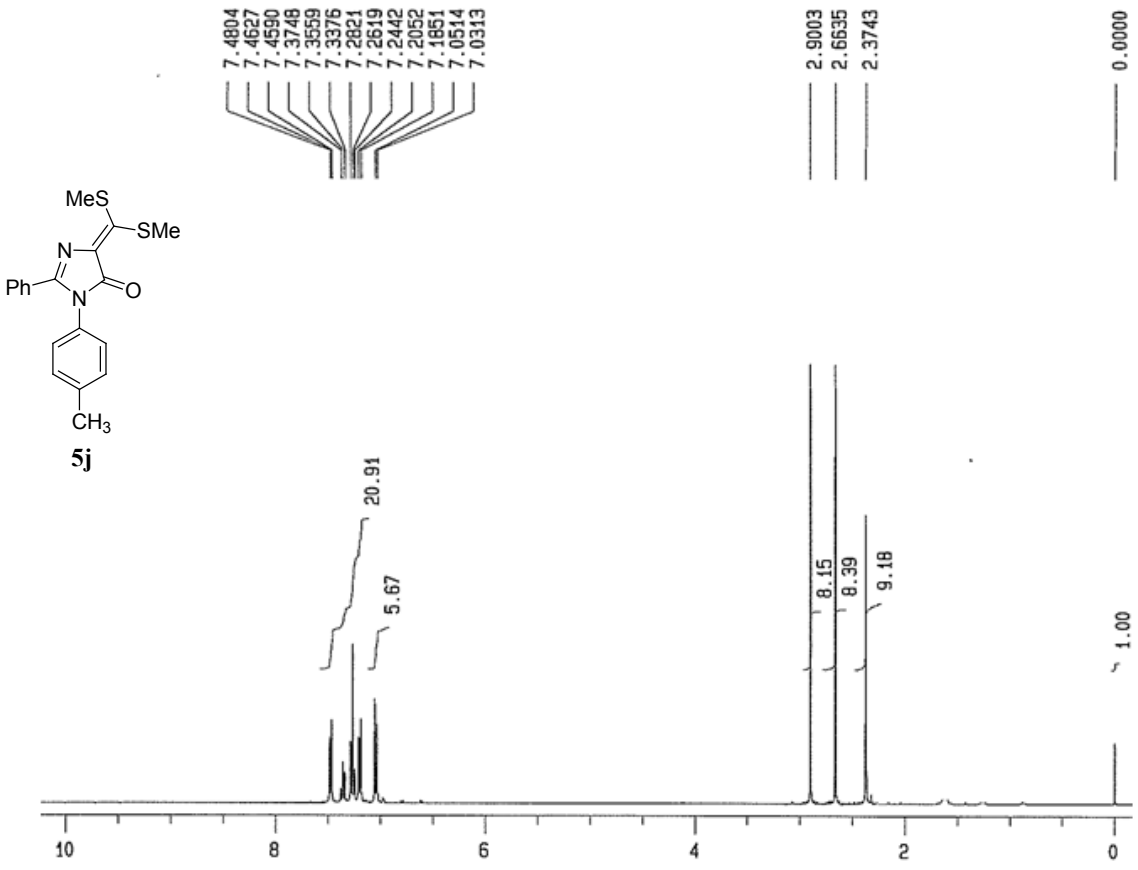


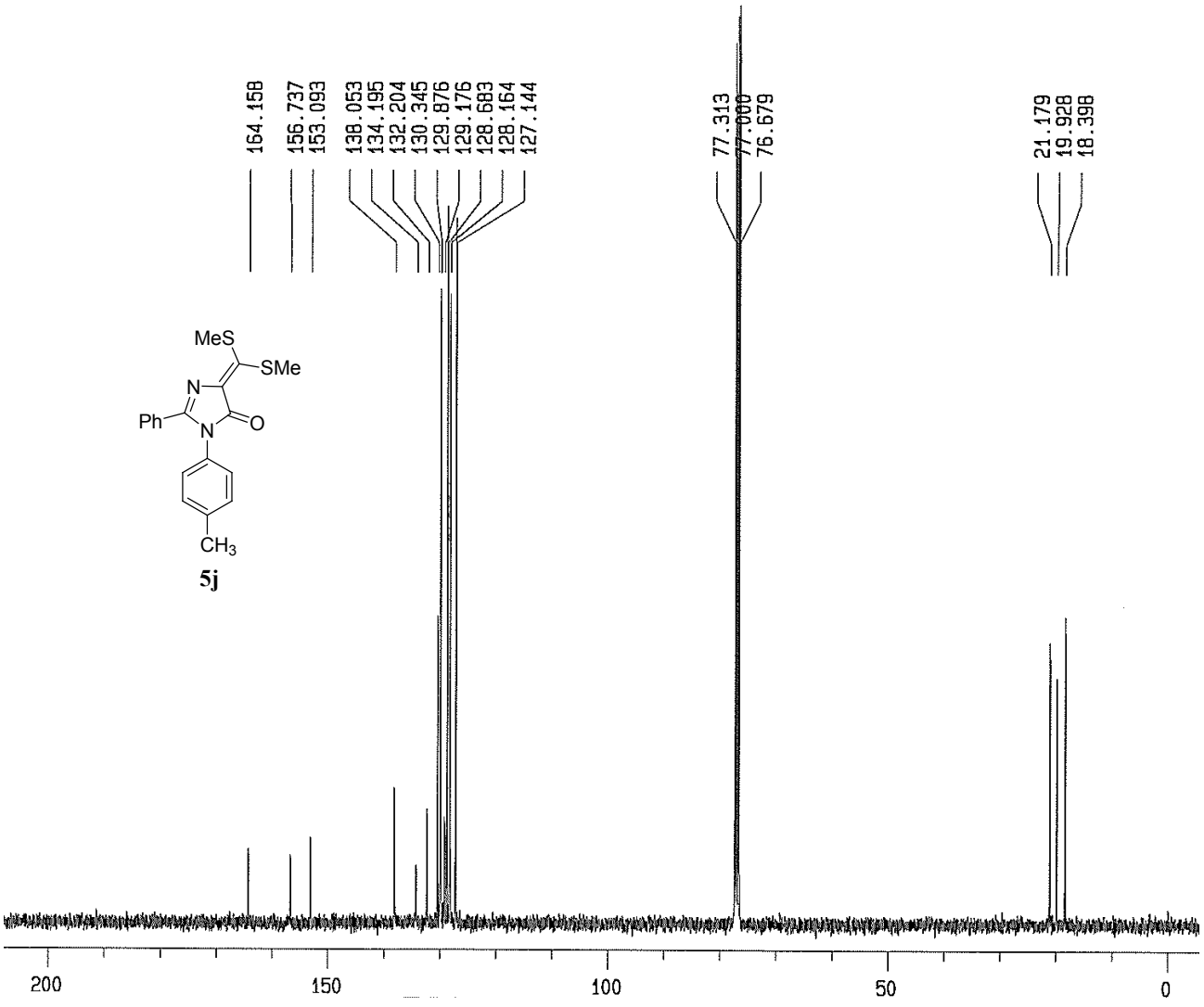




5i







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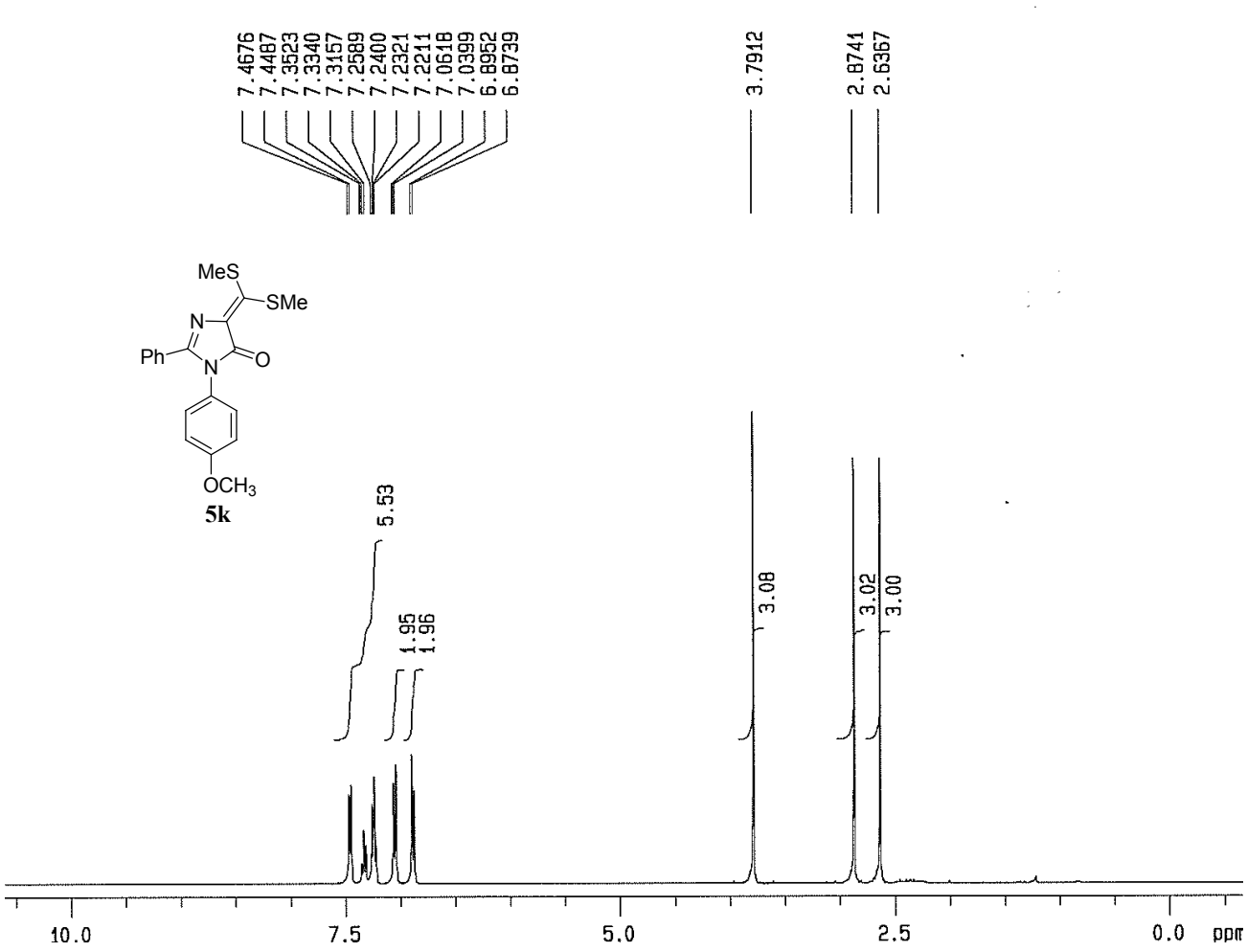

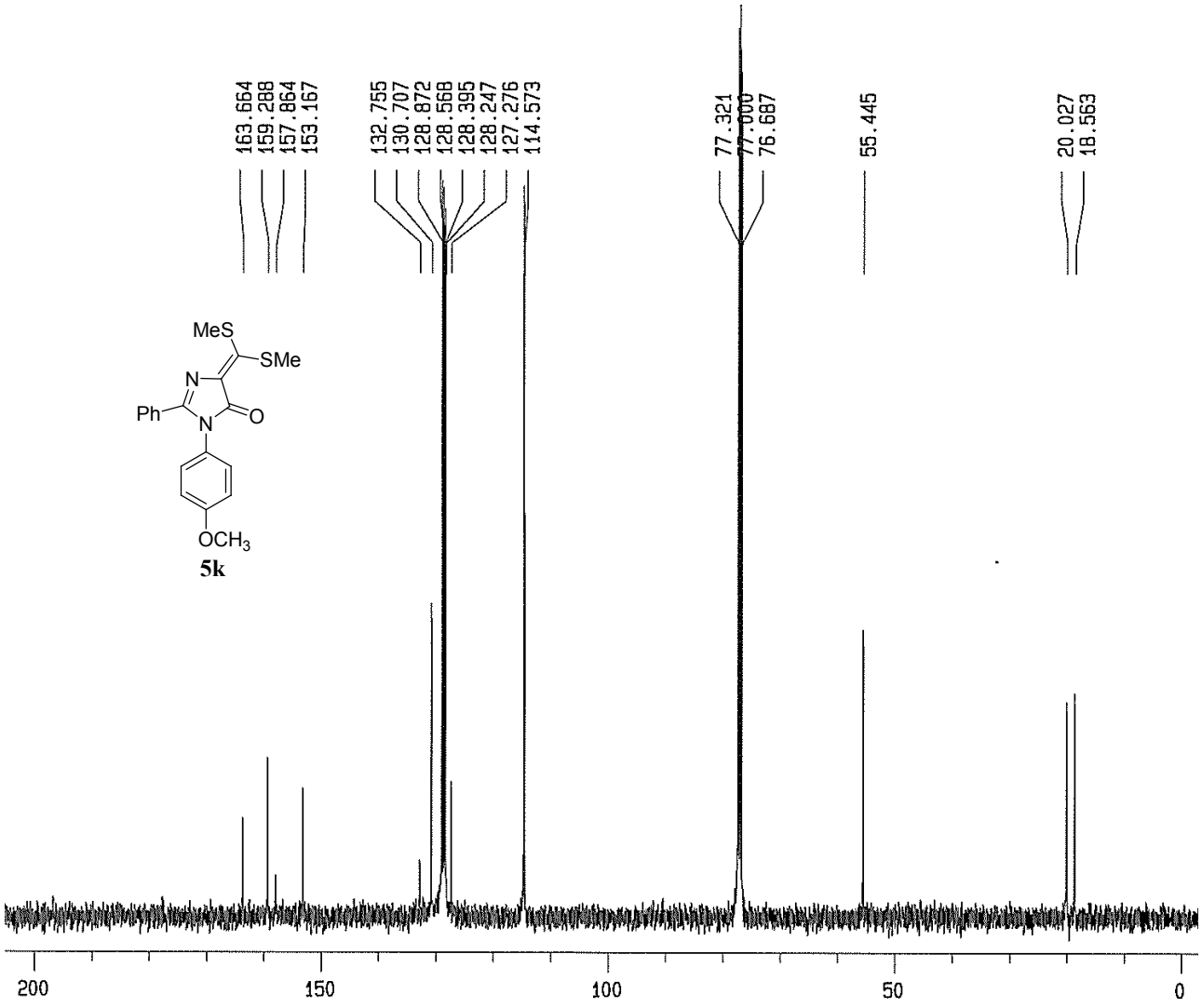

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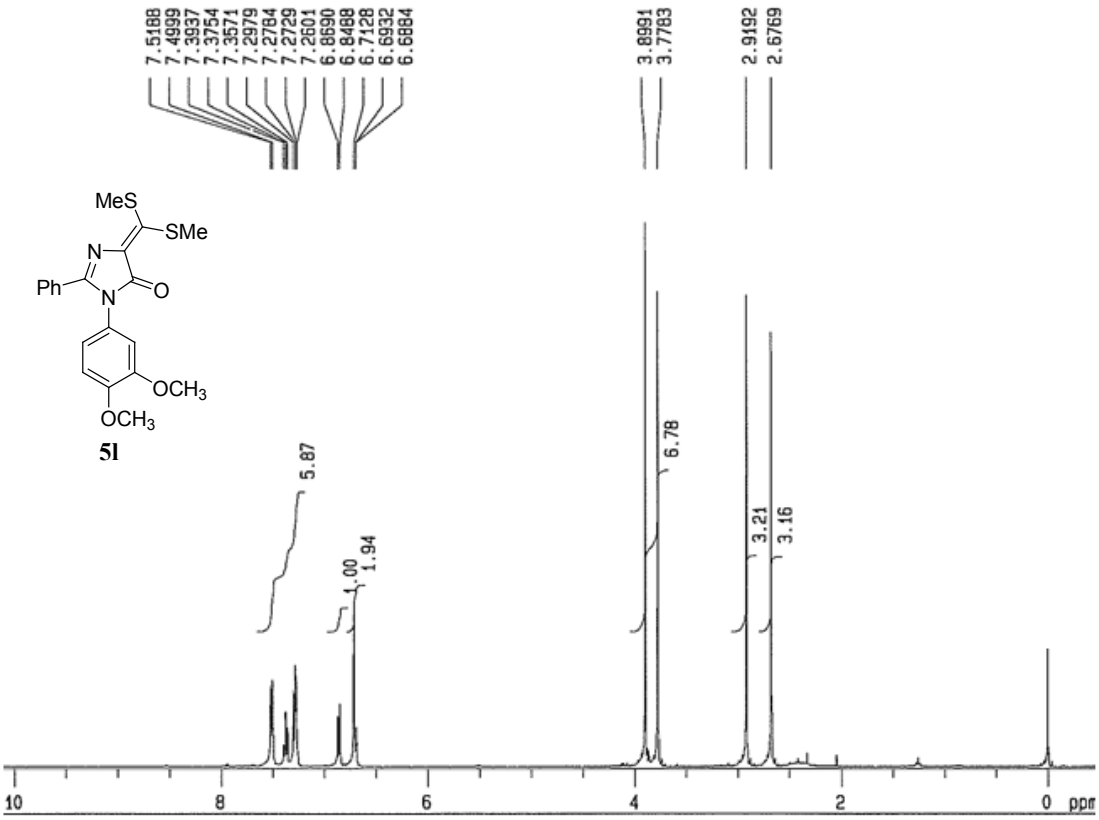

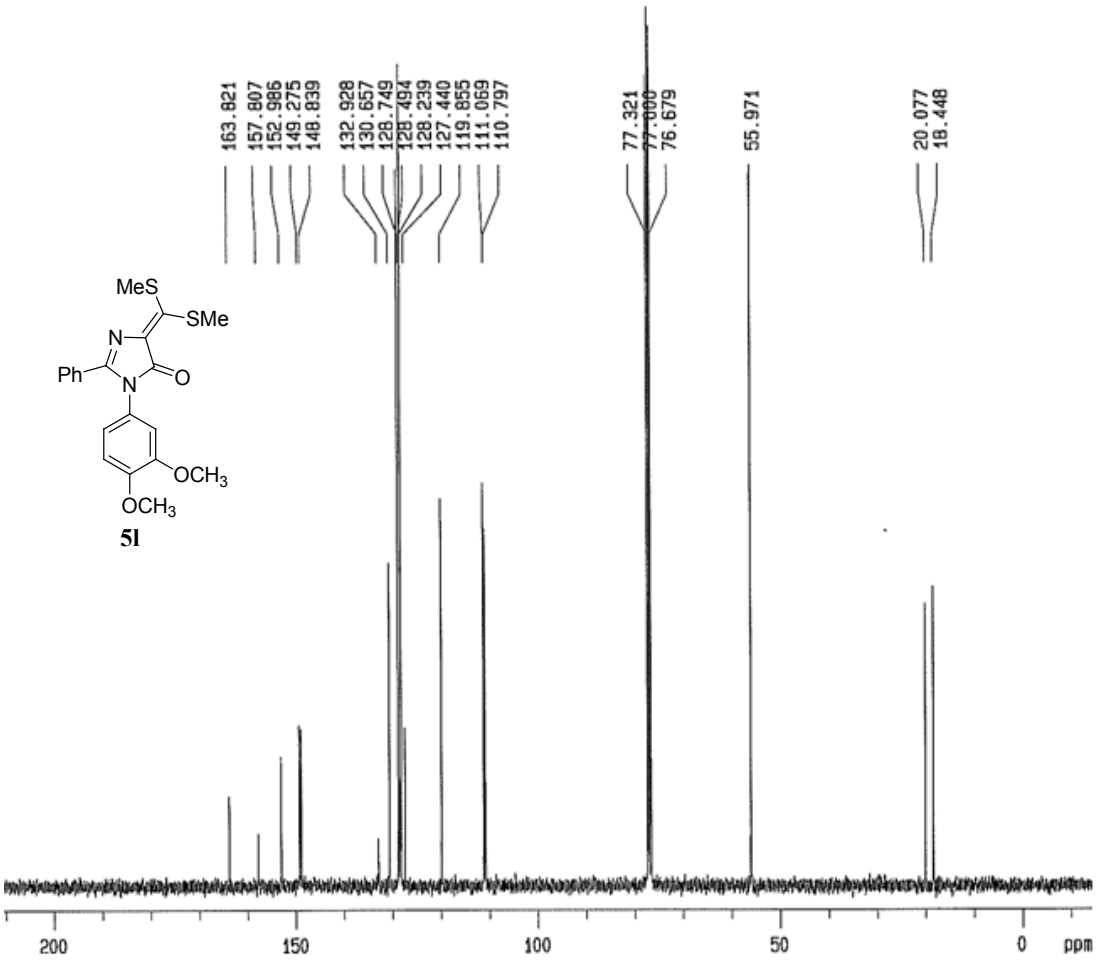

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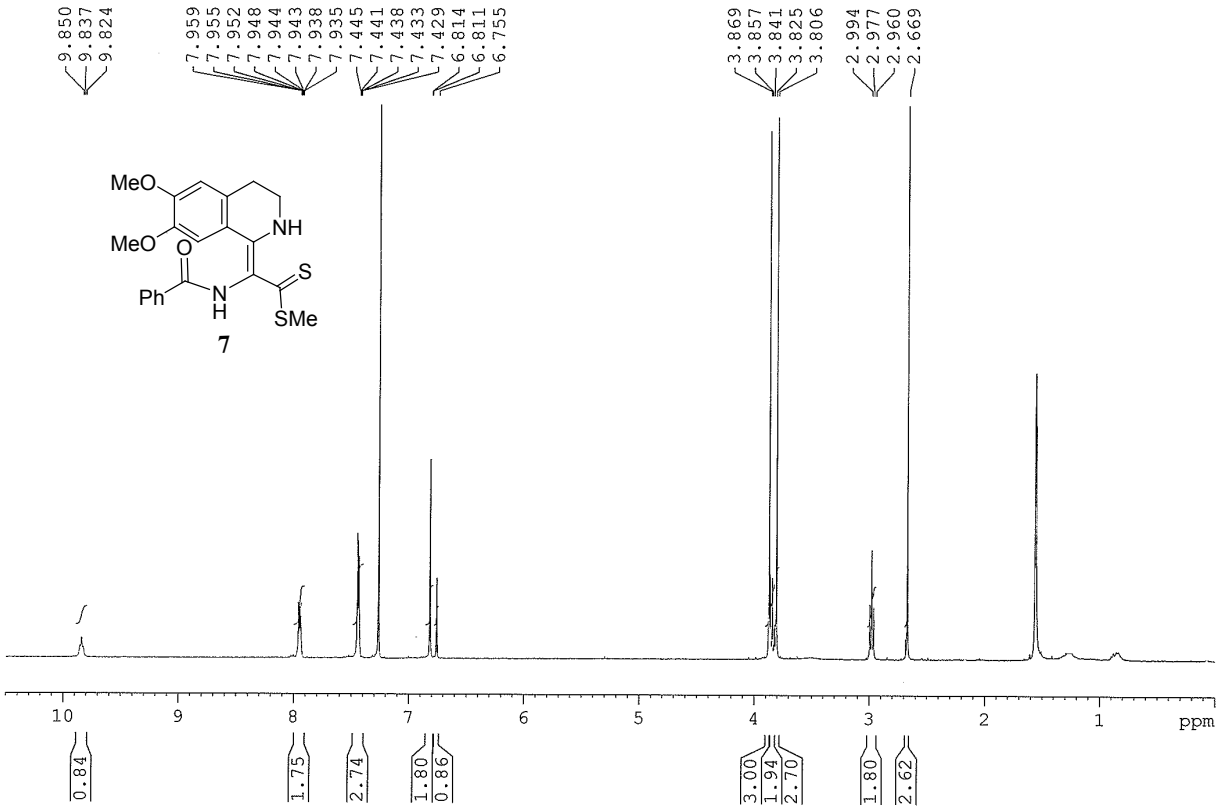

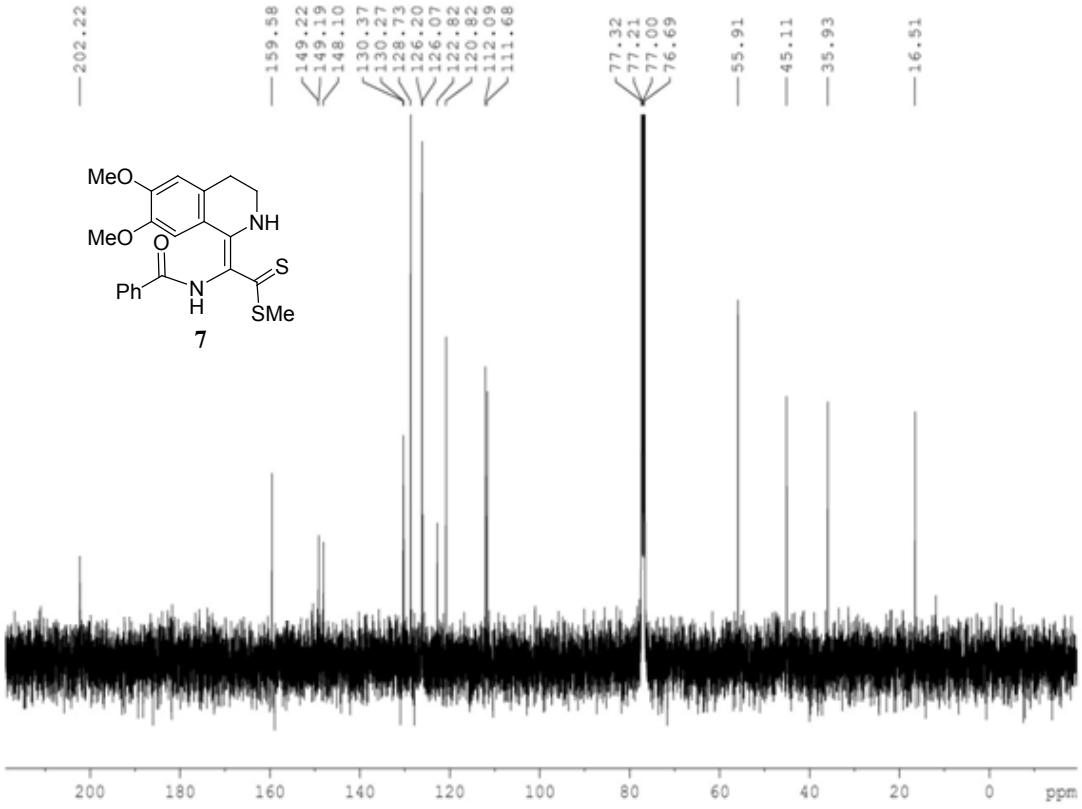

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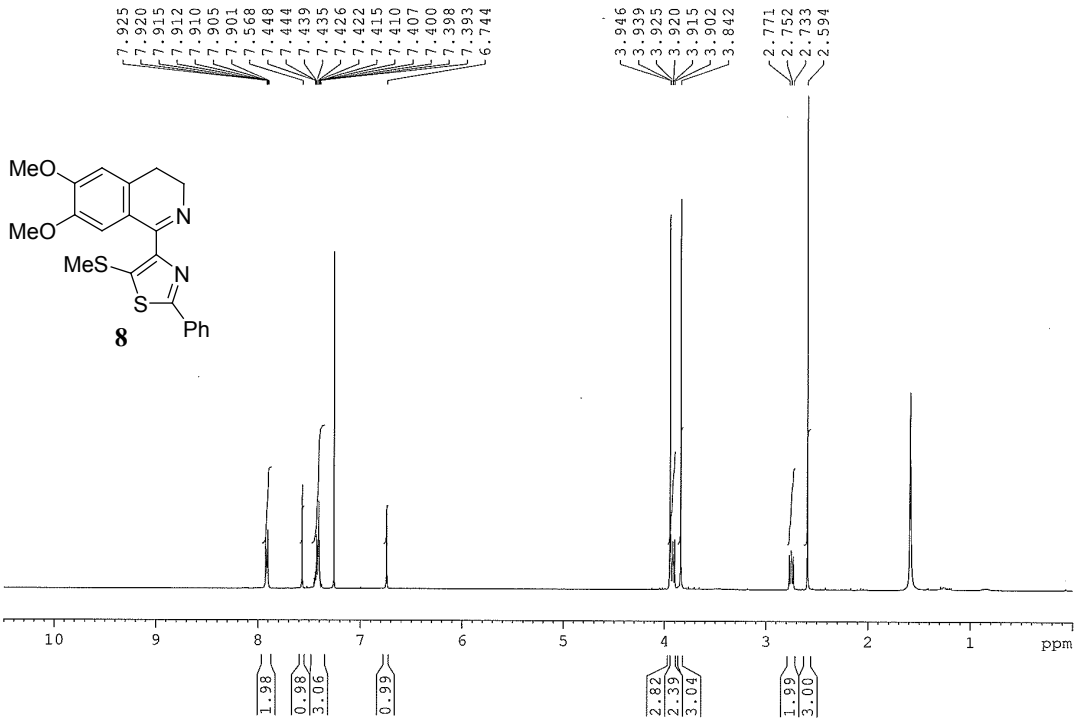
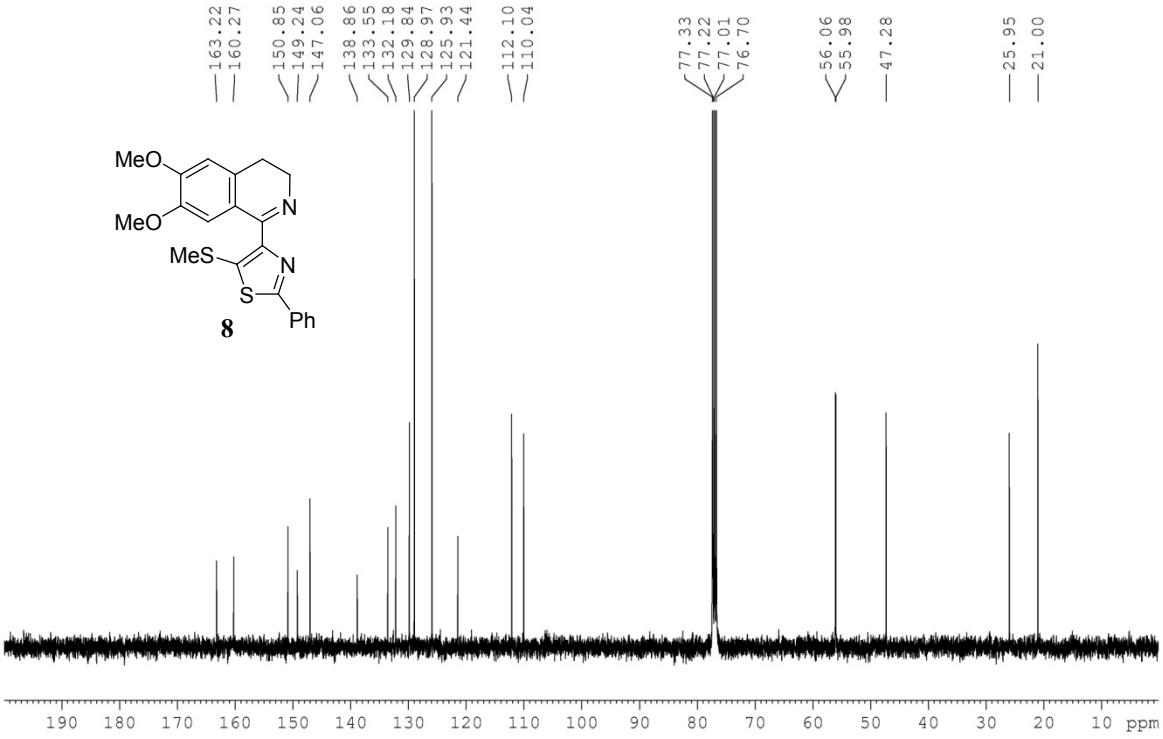
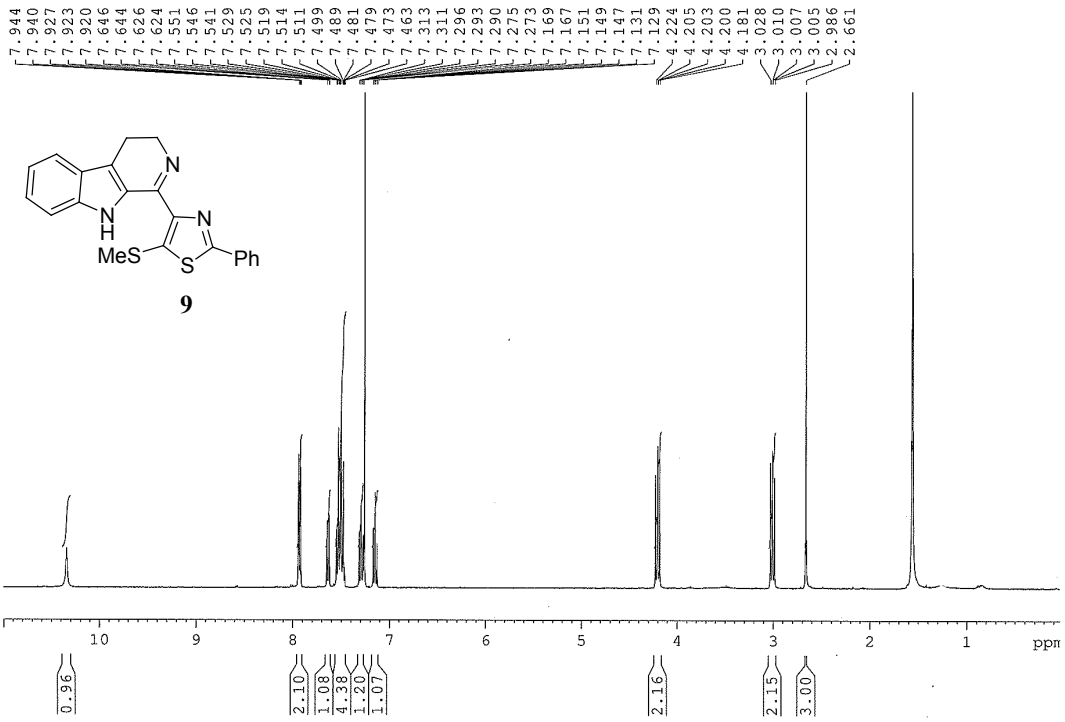
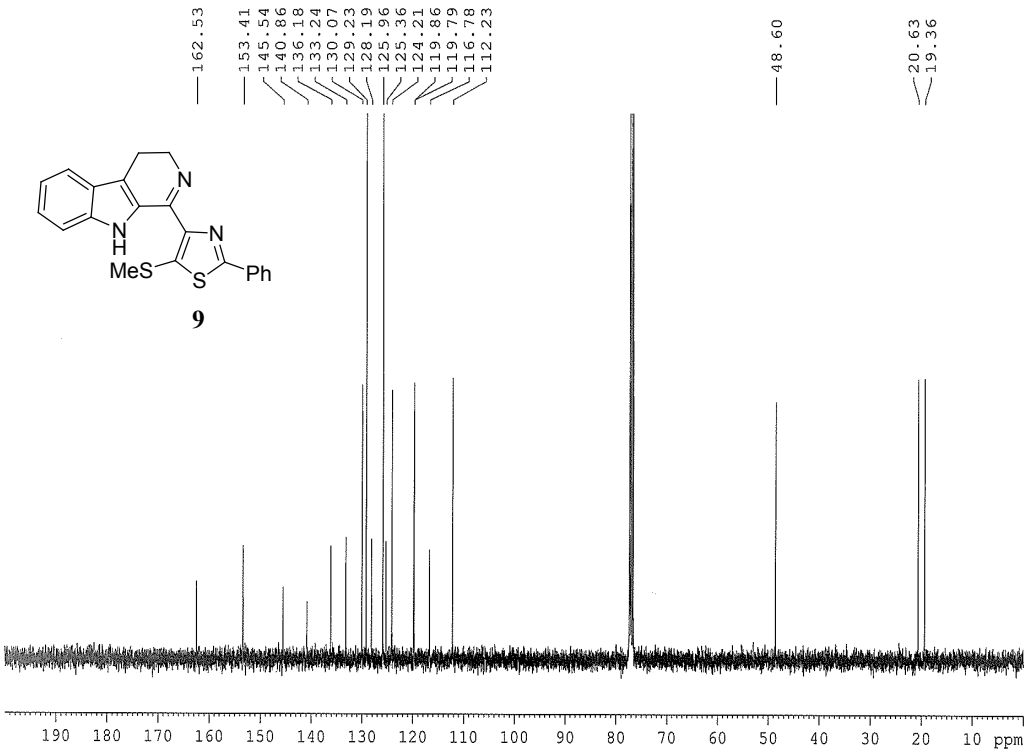
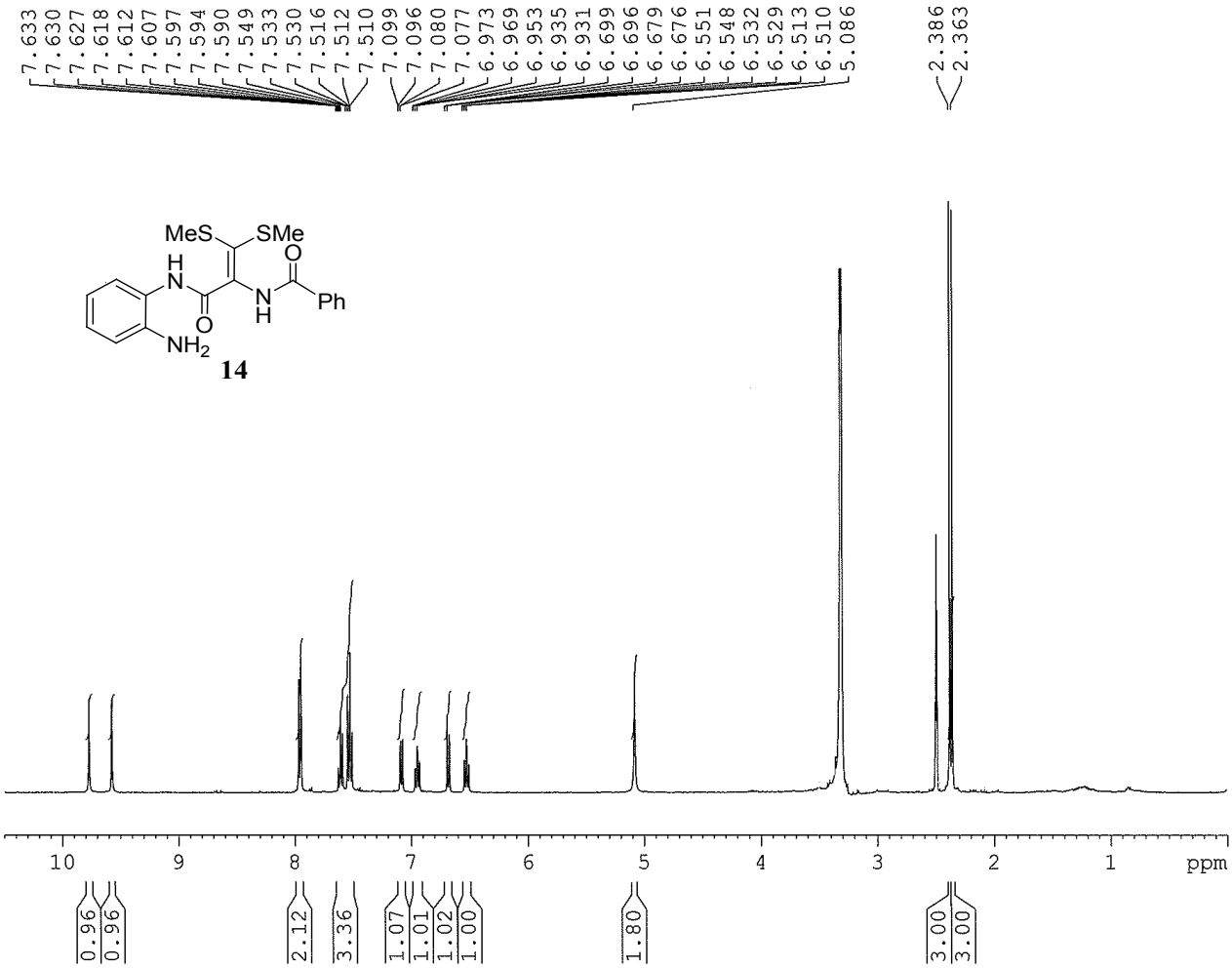


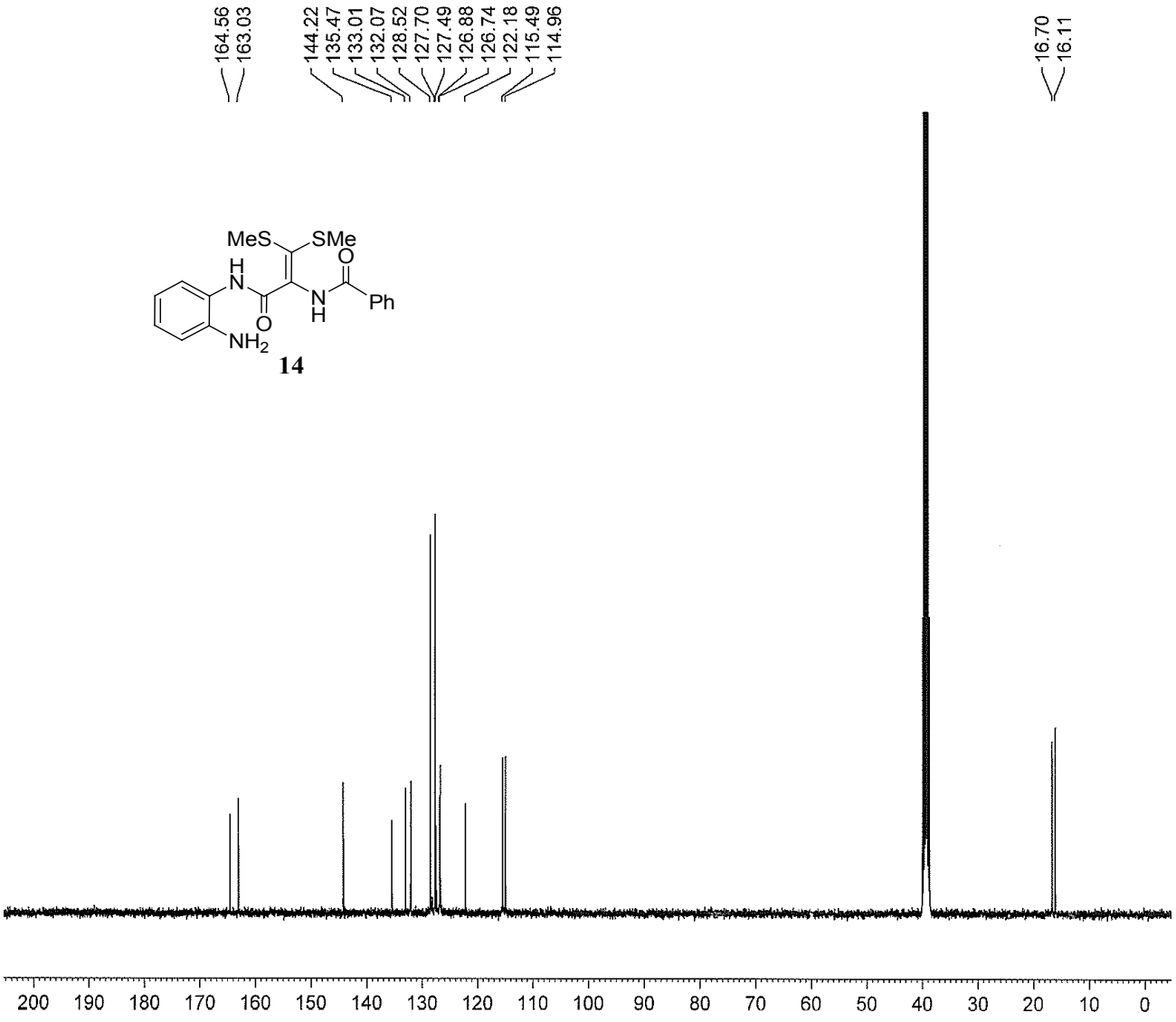

163.22
160.27
150.85
149.24
147.06
138.86
133.55
132.18
129.84
128.97
125.93
121.44
112.10
110.04
77.33
77.22
77.01
76.70
56.06
55.98
47.28
25.95
21.00
MeO
MeO
MeS
N
N
S
Ph
8
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



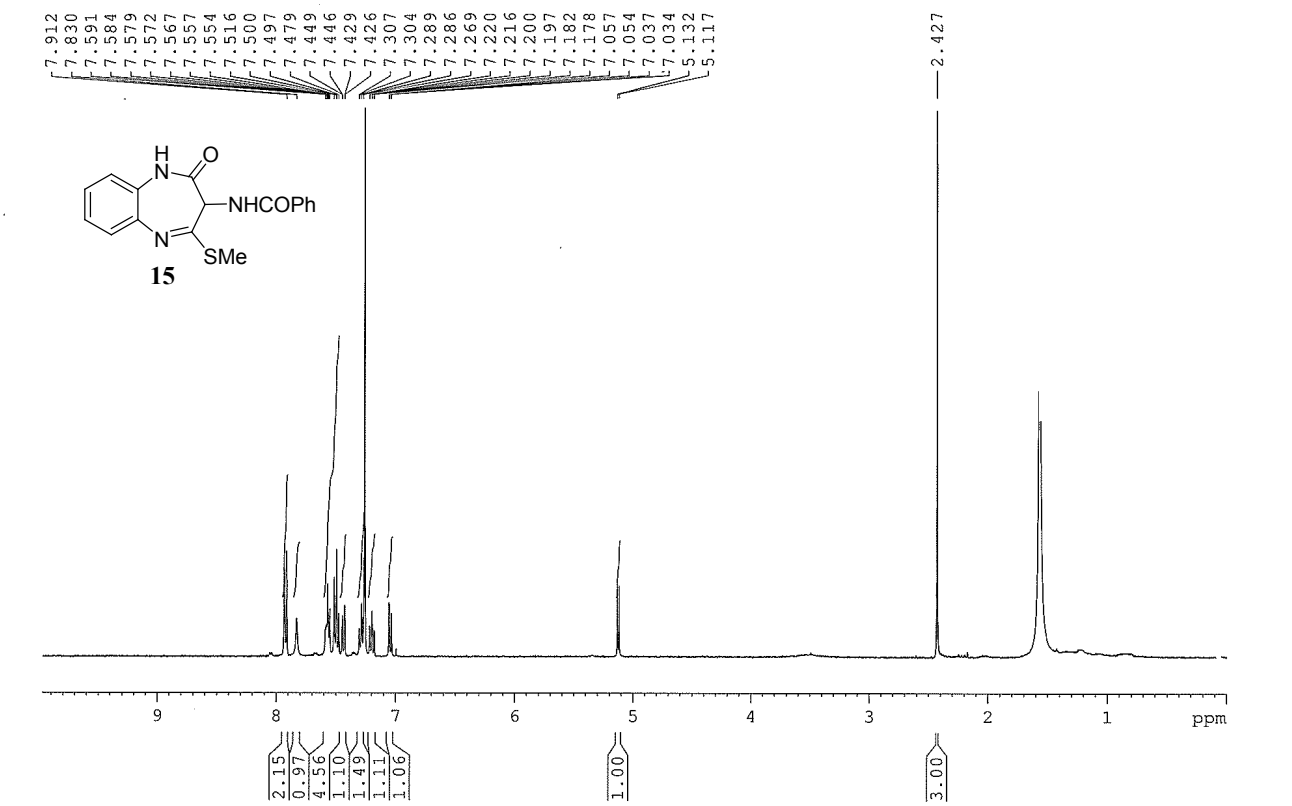


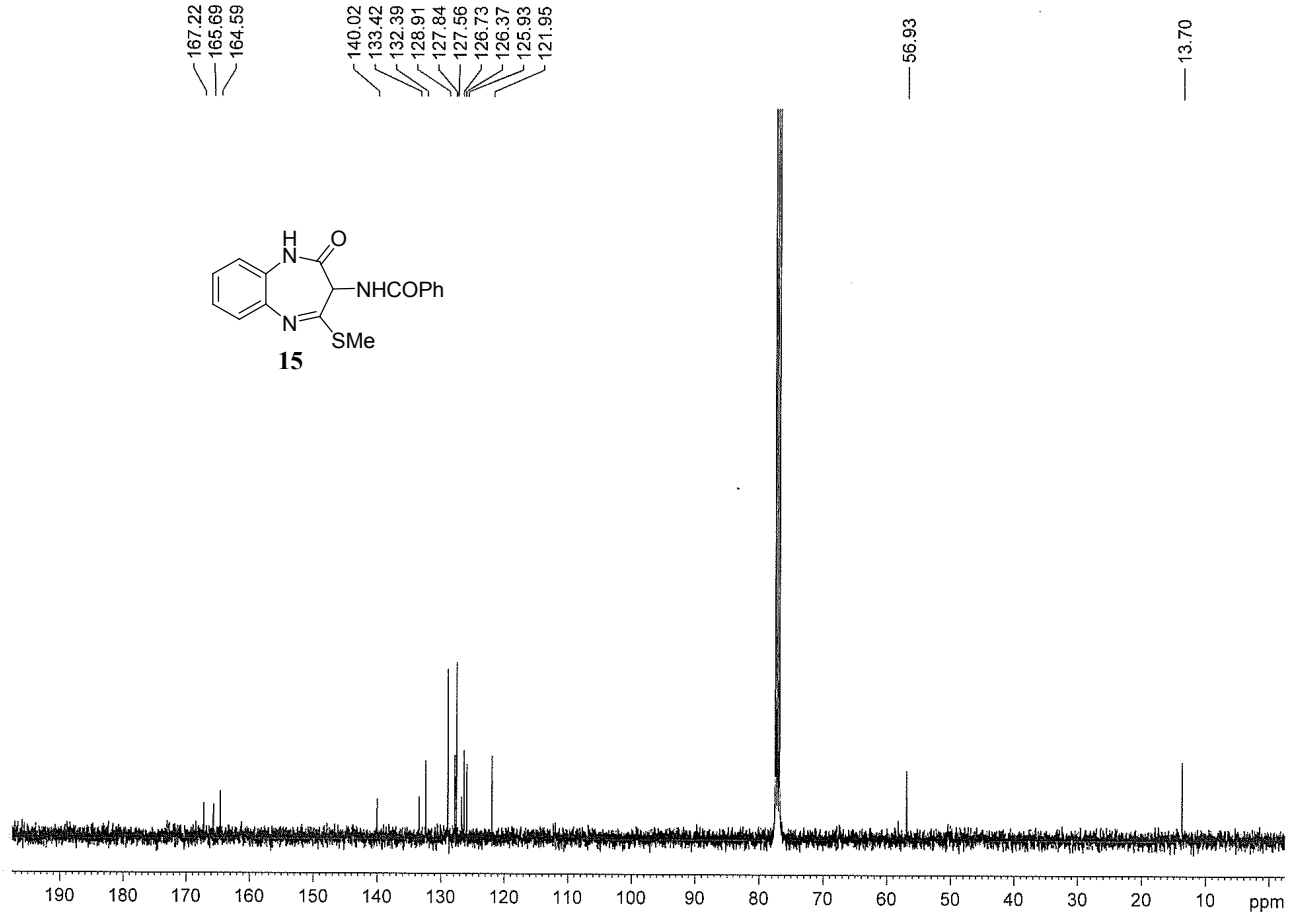
9



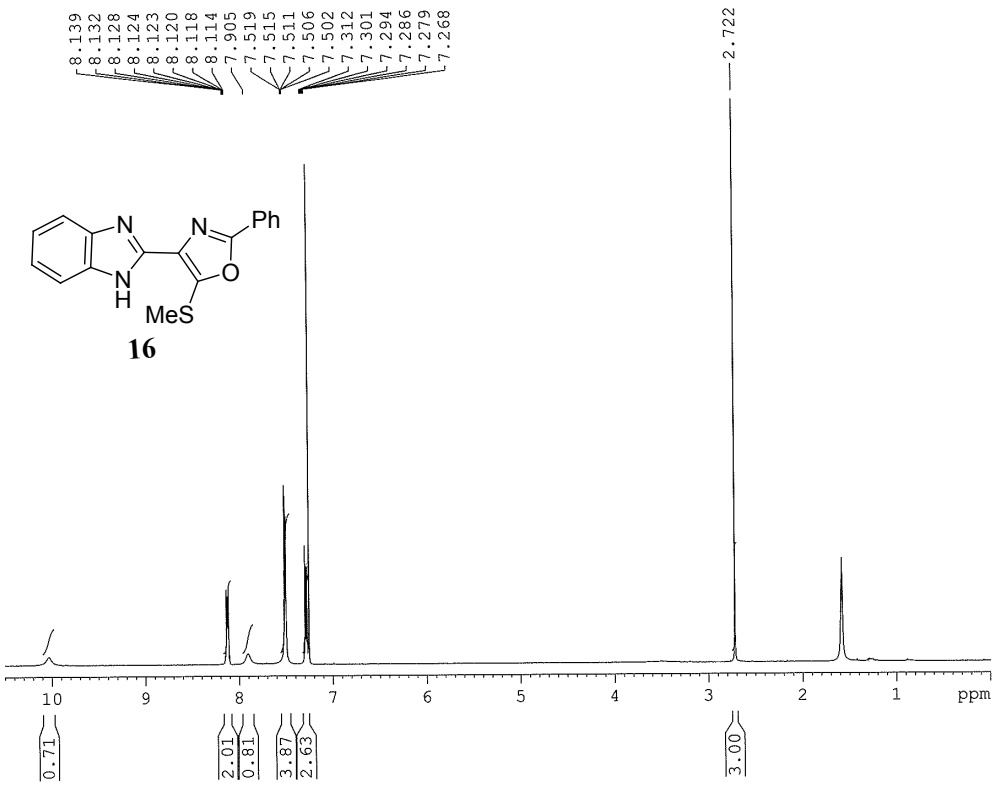

164.56
163.03
144.22
135.47
133.01
132.07
128.52
127.70
127.49
126.88
126.74
122.18
115.49
114.96
16.70
16.11
MeS
SMe
O
H
N
N
H
Ph
O
NH2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

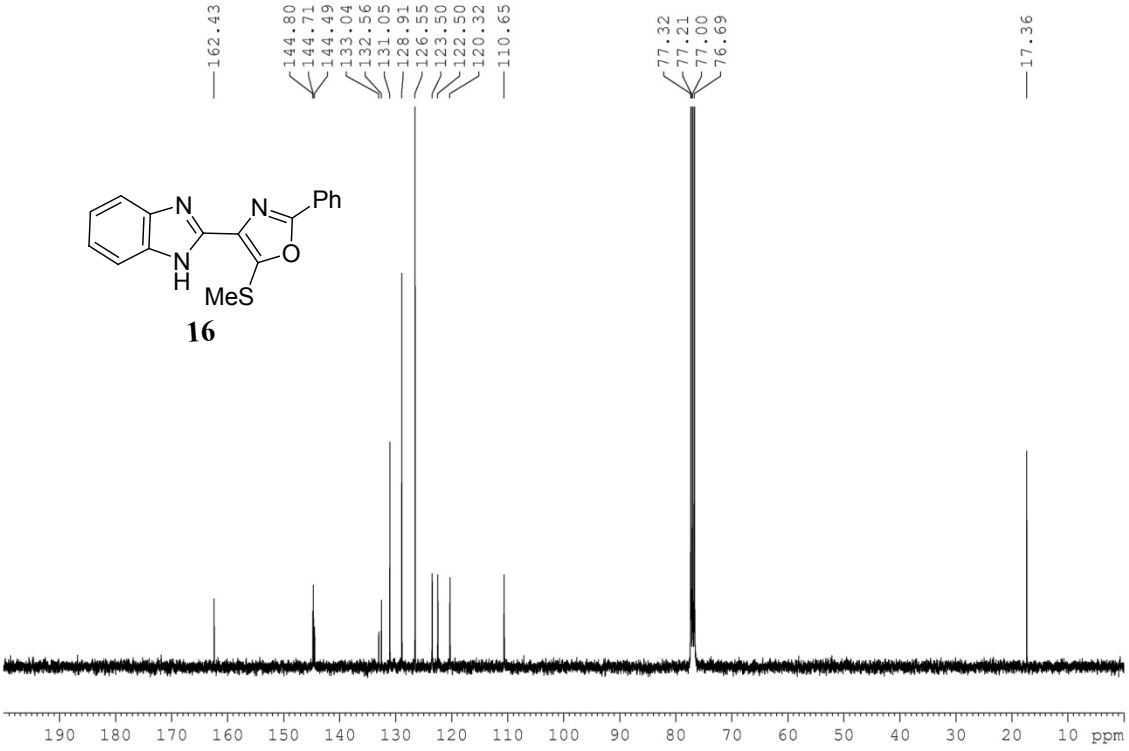
14



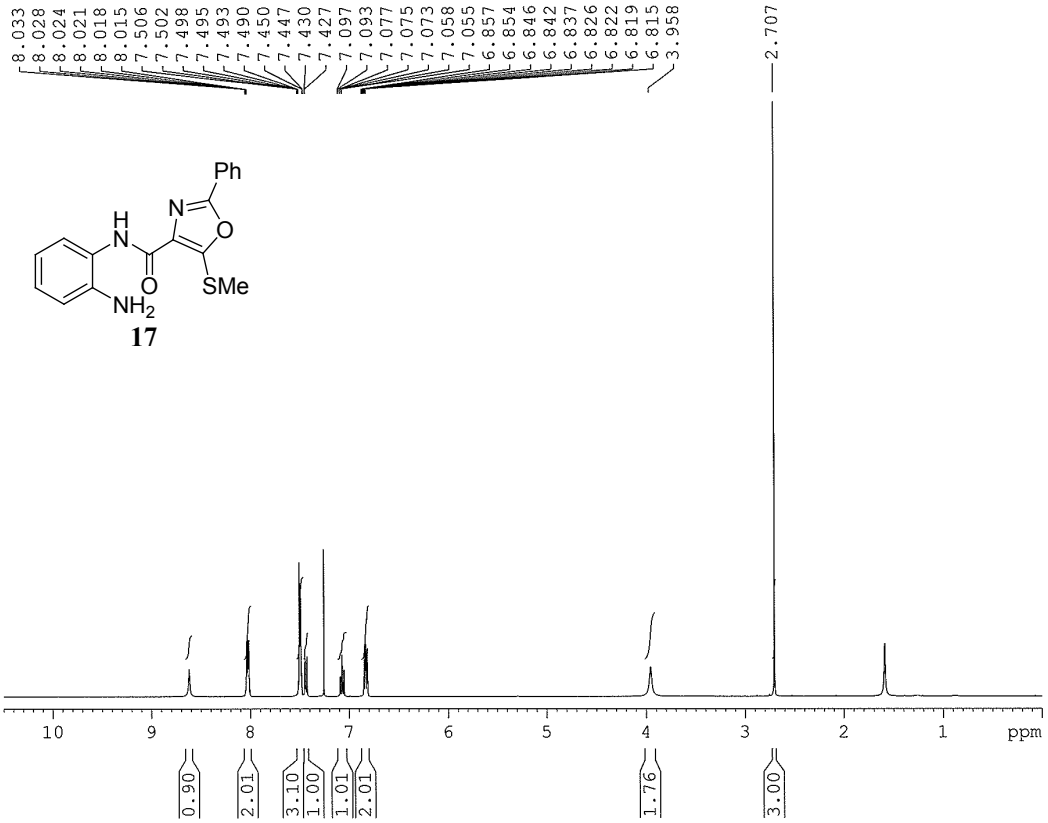

167.22
165.69
164.59
140.02
133.42
132.39
128.91
127.84
127.56
126.73
126.37
125.93
121.95
56.93
13.70
H
N
O
NHCOPh
N
SMe
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

15

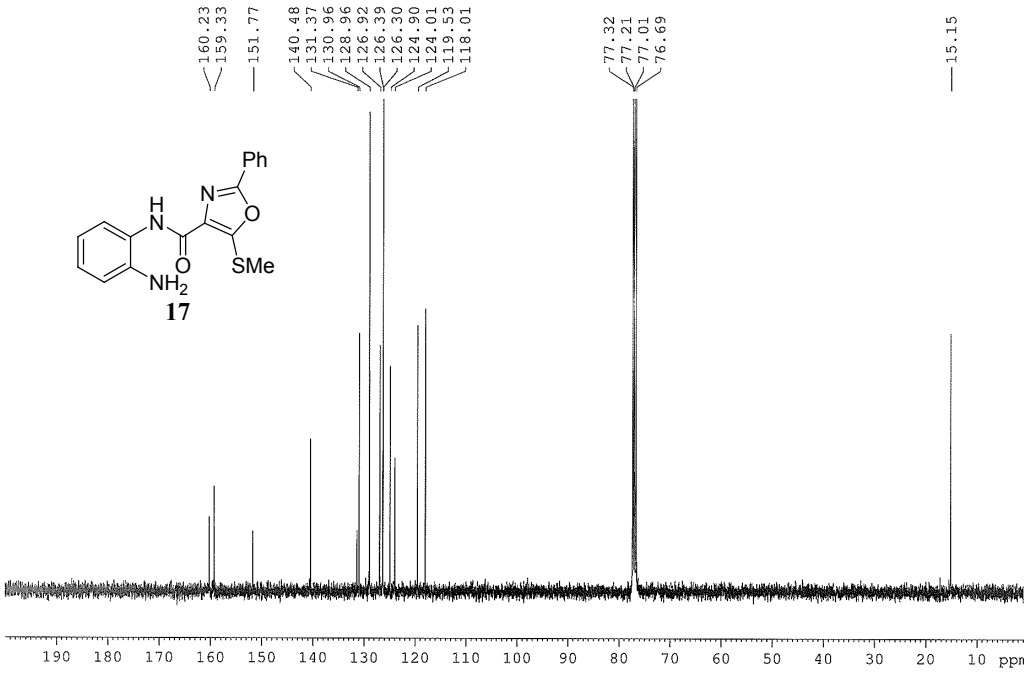

8.139
8.132
8.128
8.124
8.123
8.120
8.118
8.114
7.905
7.519
7.515
7.511
7.506
7.502
7.312
7.301
7.294
7.286
7.279
7.268
2.722
N
N
H
N
O
Ph
MeS
16
10
9
8
7
6
5
4
3
2
1
ppm
0.71
2.01
0.81
3.87
2.63
3.00


162.43
144.80
144.71
144.49
133.04
132.56
131.05
128.91
126.55
123.50
122.50
120.32
110.65
77.32
77.21
77.00
76.69
17.36
N
N
H
N
O
Ph
MeS
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

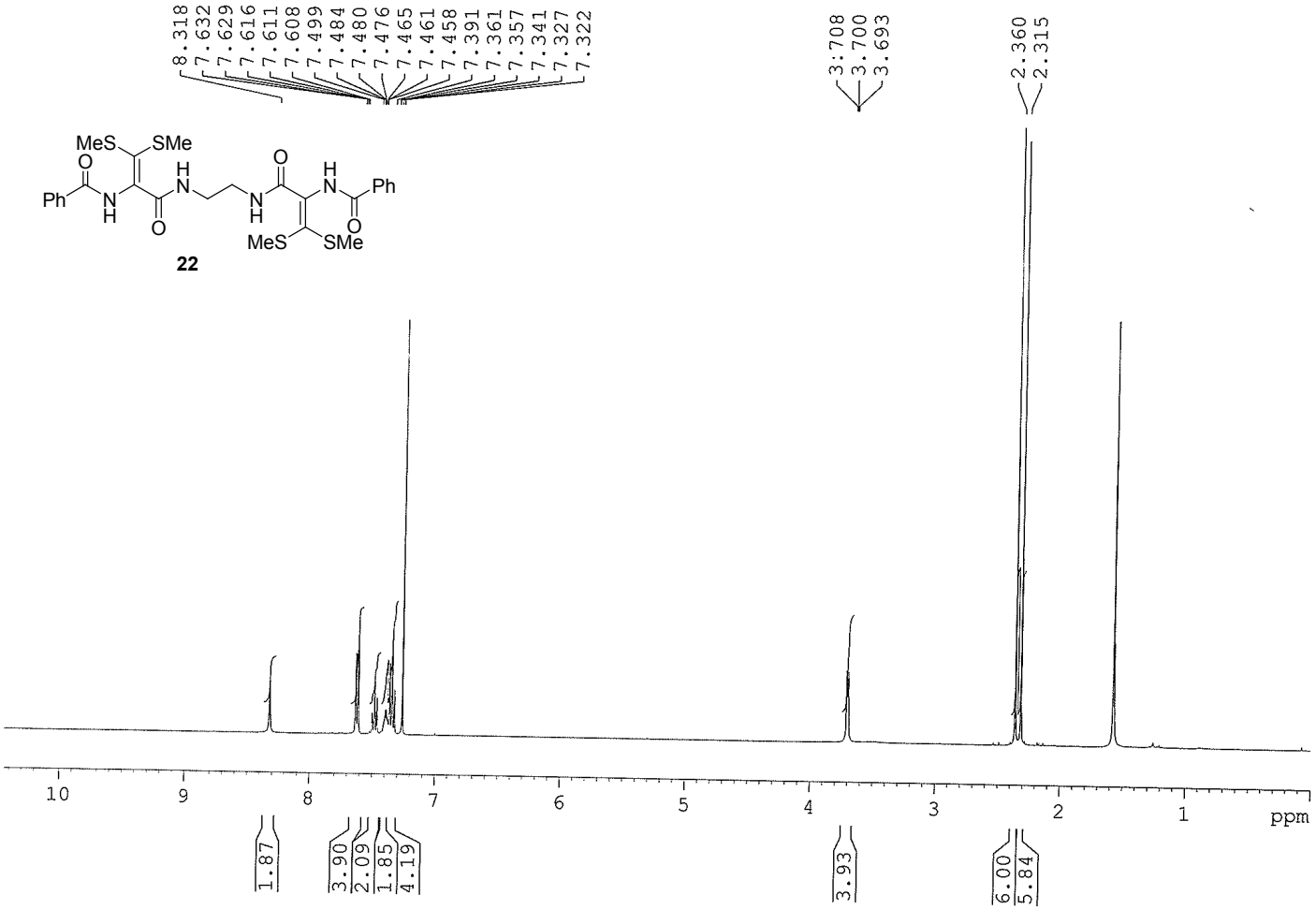
16

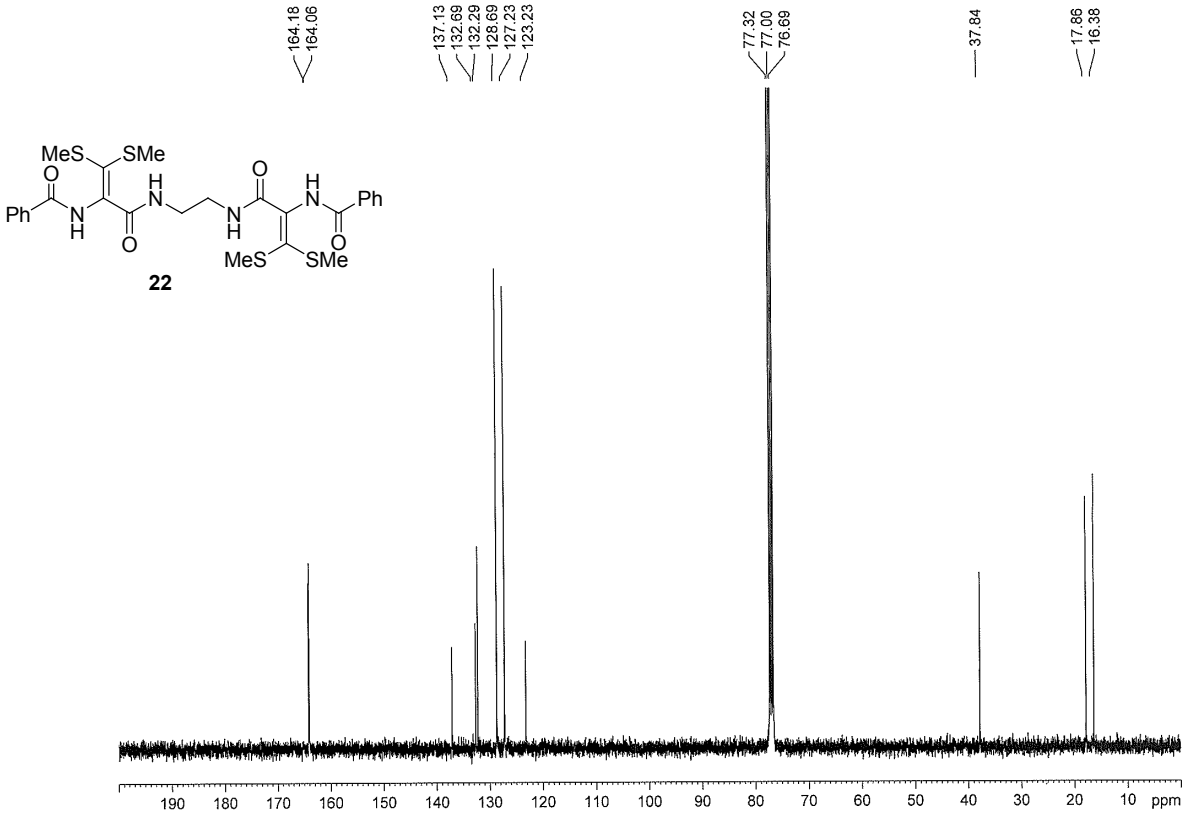

8.033
8.028
8.024
8.021
8.018
8.015
7.506
7.502
7.498
7.495
7.493
7.490
7.450
7.447
7.430
7.427
7.097
7.093
7.077
7.075
7.073
7.058
7.055
6.857
6.854
6.846
6.842
6.837
6.826
6.822
6.819
6.815
3.958
2.707
Ph
N
H
N
O
O
SMe
NH2
10
9
8
7
6
5
4
3
2
1
ppm
0.90
2.01
3.10
1.00
1.01
2.01
1.76
3.00

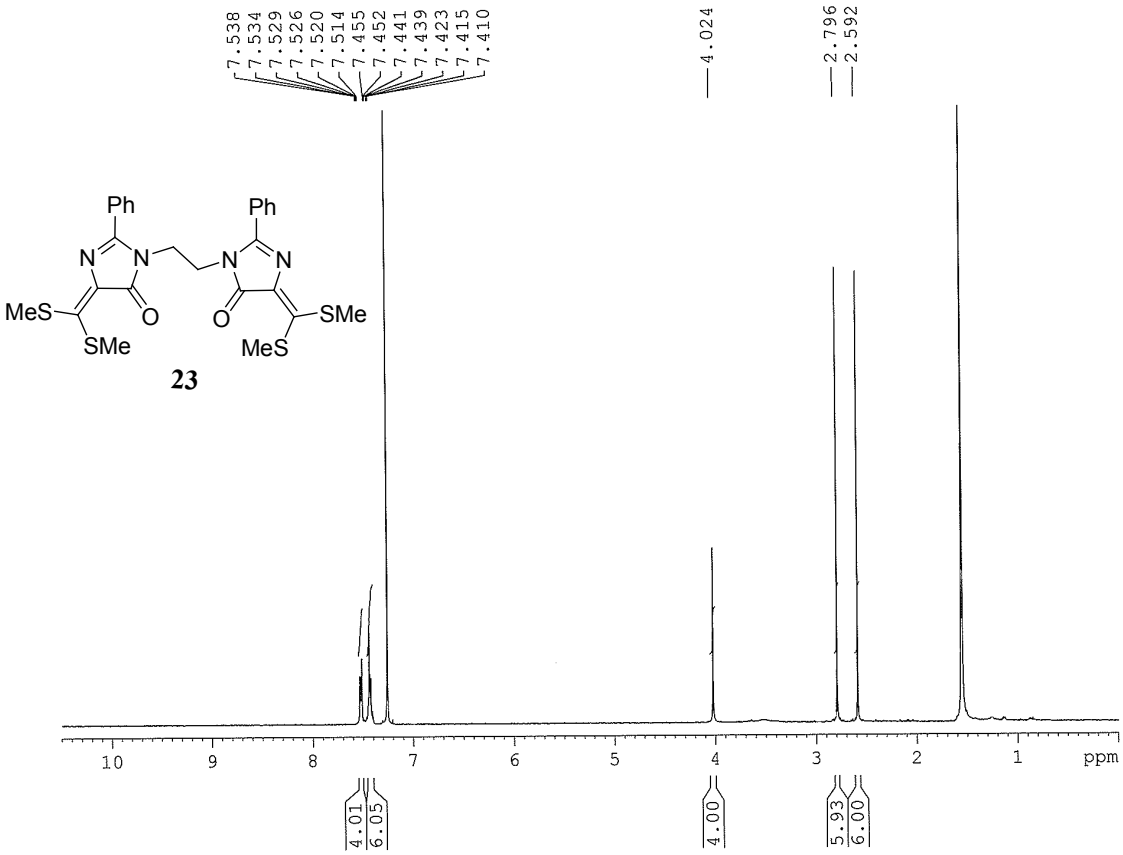
17


160.23
159.33
151.77
140.48
131.37
130.96
128.96
126.92
126.39
126.30
124.90
124.01
119.53
118.01
77.32
77.21
77.01
76.69
15.15
Ph
N
O
H
N
O
SMe
NH2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

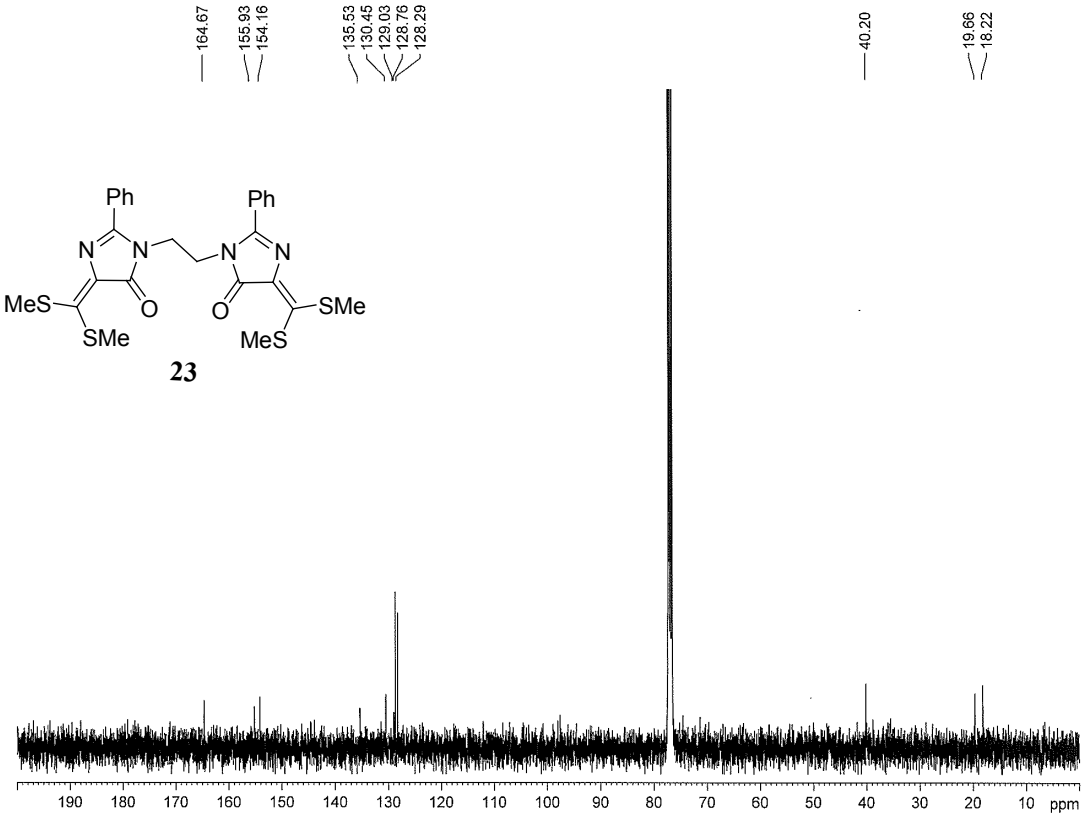
17



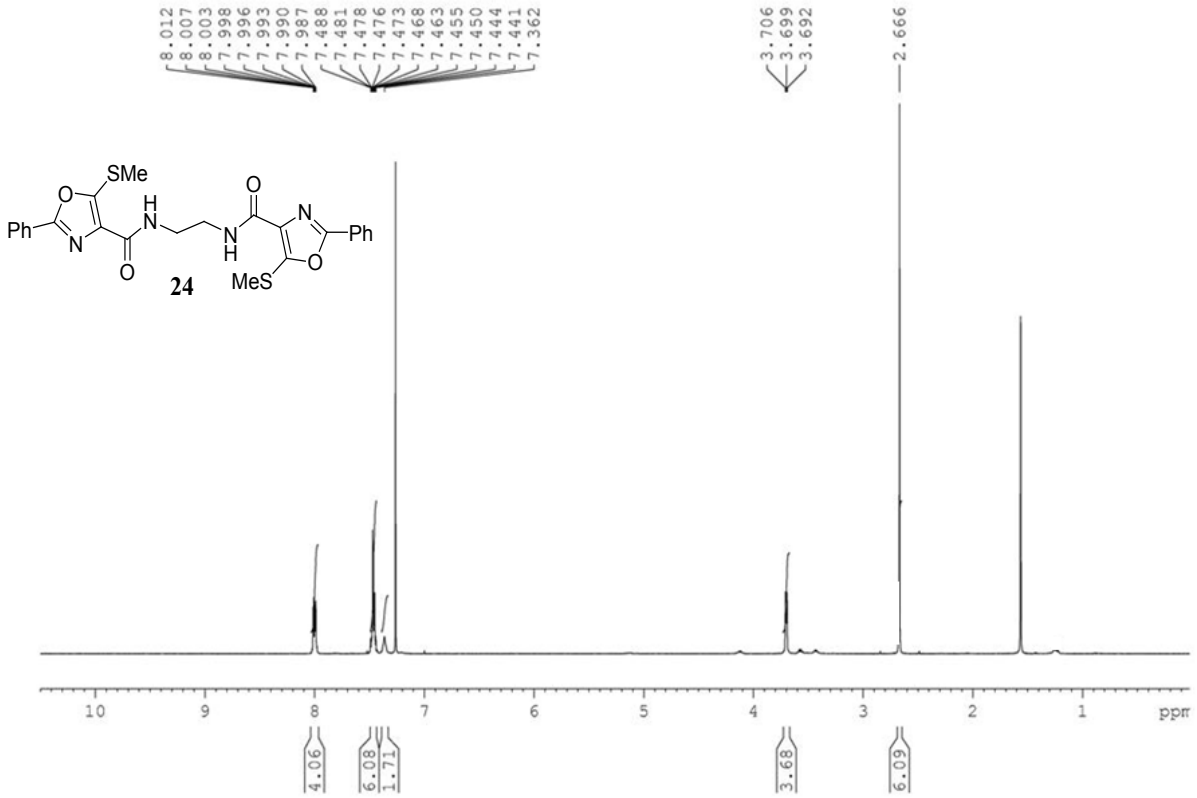


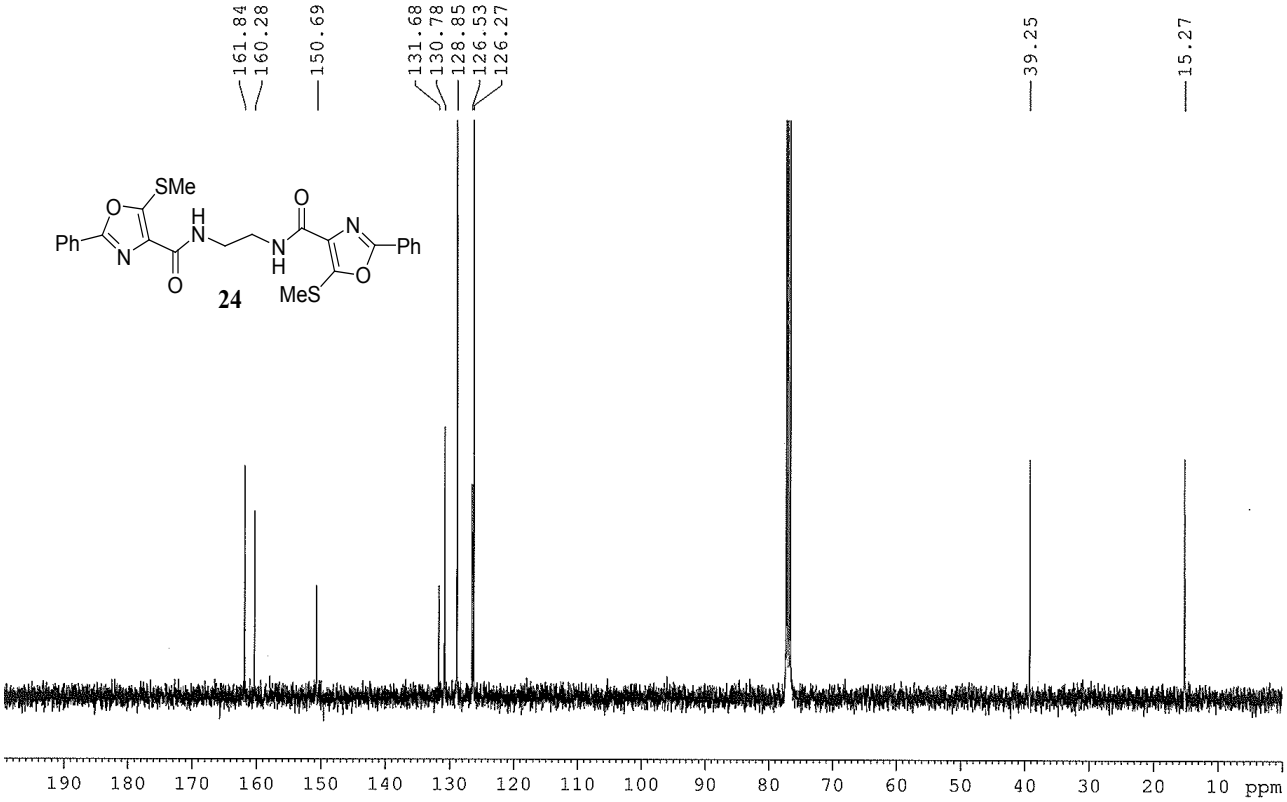

7.538
7.534
7.529
7.526
7.520
7.514
7.455
7.452
7.441
7.439
7.423
7.415
7.410
4.024
2.796
2.592
Ph
Ph
N
N
N
N
MeS
SMe
O
O
SMe
MeS
10
9
8
7
6
5
4
3
2
1
ppm
4.01
6.05
4.00
5.93
6.00

23


164.67
155.93
154.16
135.53
130.45
129.03
128.76
128.29
40.20
19.66
18.22
Ph
Ph
N
N
N
N
O
O
MeS
SMe
SMe
MeS
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

23


8.012
8.007
8.003
7.998
7.996
7.993
7.990
7.987
7.488
7.481
7.478
7.476
7.473
7.468
7.463
7.455
7.450
7.444
7.441
7.362
3.706
3.699
3.692
2.666
SMe
O
H
N
O
N
Ph
N
O
N
H
Ph
O
MeS
24
10
9
8
7
6
5
4
3
2
1
ppm
4.06
6.08
1.71
3.68
6.09


161.84
160.28
150.69
131.68
130.78
128.85
126.53
126.27
39.25
15.27
SMe
O
Ph
N
H
N
O
N
H
O
N
Ph
O
MeS
24
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm