Supporting Information for

1,3-Iodo-Amination of 2-Methyl Indoles as C_{sp2}– C_{sp3} Dual Functionalization with Iodine Reagent

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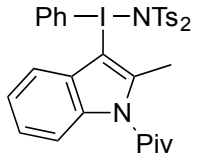
Table of contents

1. General Methods. ^{1}H NMR spectra were measured on a JEOL ECS-400 (400 MHz) spectrometer at ambient temperature. Data were recorded as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; sep = septet; m = multiplet; br = broad), coupling constant (Hz), integration, and assignment. ^{13}C NMR spectra were measured on a JEOL ECS-400 (100 MHz) spectrometer. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard (deuterochloroform at 77.0 ppm). High-resolution mass spectra were recorded by Thermo Fisher Scientific Exactive Orbitrap mass spectrometers. Infrared (IR) spectra were recorded on a JASCO FT/IR 4100 spectrometer. Single crystal X-ray diffraction data were collected at 173K on a Bruker SMART APEX II CCD diffractometer with Mo Kα (λ = 0.71073) radiation and graphite monochromator. For thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60GF254 0.25 mm) were used. The products were purified by neutral column chromatography on silica gel (Kanto Chemical Co., Inc. silica gel 60N, Prod. No. 37560-84; Merck silica gel 60, Prod. No. 1.09385.9929). Visualization was accomplished by UV light (254 nm), anisaldehyde, $KMnO_4$, and phosphomolybdic acid. In experiments that required dry solvents such as CH_2Cl_2, MeCN, $CHCl_3$, and THF were distilled in prior to use.

2. Procedure for Preparation of Indolyl(phenyl)iodonium Imides (2a) (Scheme 1; eq. 3).

A mixture of $PhI(OAc)_2$ (193.3 mg, 0.60 mmol) and Ts_2NH (195.2 mg, 0.60 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 30 min under argon atomosphere. Then, *N*-pivaloly 2-methyl indol (**1a**) (107.65 mg, 0.50 mmol) was added, and the solution was stirred at room temperature for 2 h. Volatile solvents were removed under reduced pressure. AcOEt (6 mL) was added to the residue, and ether was added dropwise until the solution became cloudy. Then the mixture was sonicated until a white solid appeared and then ether (2 mL) was added to the solution. The precipitated solid was washed with a mixture of AcOEt and hexane (2:1) (15 mL) to give desired product **2a** (322.6 mg, 87 % yield).



4-Methyl-*N*-((2-methyl-1-pivaloyl-1*H*-indol-3-yl)(phenyl)-λ^3-iodanyl)-*N*-tosylbenzenesulfonamide (2a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (s, 9H), 2.25 (s, 6H), 2.68 (s, 3H), 6.91 (d, *J* = 8.1 Hz, 4H), 7.21-7.26 (m, 1H), 7.27-7.34 (m, 4H), 7.45 (d, *J* = 8.1 Hz, 4H), 7.43-7.48 (m, 1H), 7.49-7.53 (m, 1H), 7.86-7.91 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 21.3 (2C), 27.9 (3C), 44.8, 82.0, 112.2, 115.9, 119.4, 123.5, 124.5, 126.7 (4C), 127.6, 128.4 (4C), 131.4, 131.7 (2C),

133.5 (2C), 135.8, 140.5 (2C), 141.2 (2C), 143.1, 185.2. IR (neat) 1730, 1451, 1263, 1131, 1082, 1035, 814, 746, 669 cm^{-1}. MS (ESI) calcd for $C_{34}H_{35}IN_2NaO_5S_2$ $[M+Na]^+$ 765.0924, found 765.0908.

Crystal data of 2a: Formula $C_{34}H_{35}IN_2O_5S_2$, colorless, crystal dimensions 0.20 × 0.20 × 0.10 mm^3, Triclinic, space group P -1, a = 12.2348(9) Å, b = 13.7713(10) Å, c = 21.3593(15) Å, α = 74.8147(9) °, β = 78.2115(10) °, γ = 80.1920(9) °, V = 3373.8(4) $Å^3$, Z = 4, ρ_{calc} = 1.462 g cm^{-3}, F(000) = 1512, μ(MoKα) = 1.115 mm^{-1}, T = 173 K. 19506 reflections collected, 14722 independent reflections with $I > 2\sigma(I)$ ($2\theta_{max}$ = 27.56°), and 805 parameters were used for the solution of the structure. The non-hydrogen atoms were refined anisotropically. R_1 = 0.0409 and wR_2 = 0.1113. GOF = 1.044. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1532903. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

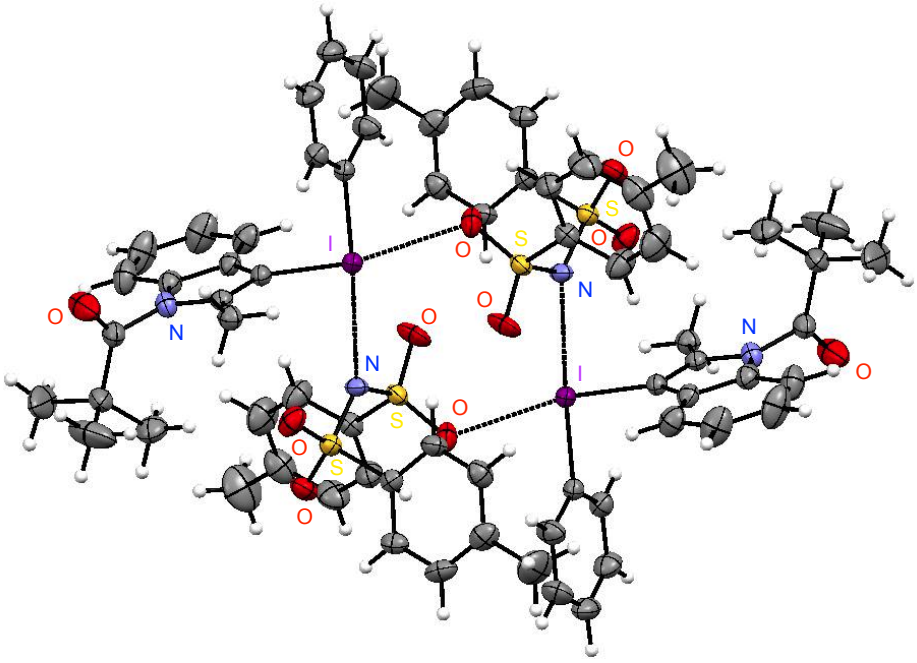


Figure S1. ORTEP drawing of **2a** (dimer structure).

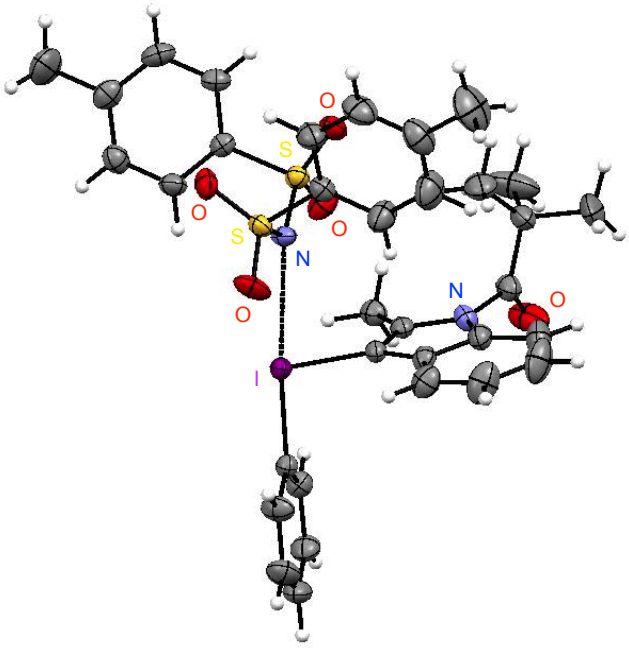
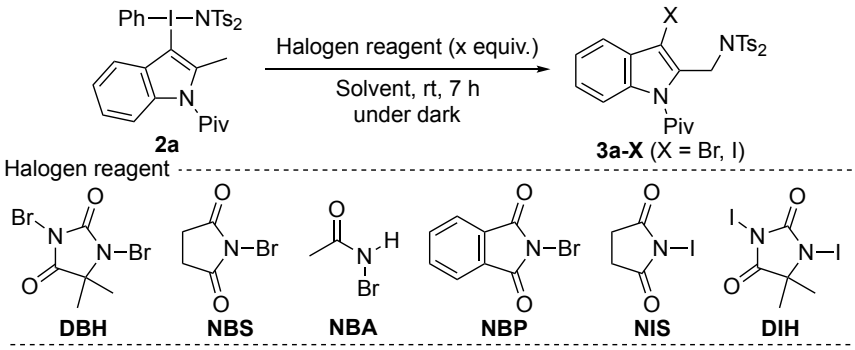


Figure S2. ORTEP drawing of **2a** (monomer unit).

3. Procedure for Iodo-amination of Indolyl(phenyl)iodonium Imides (2a) (Scheme 1; eq. 4).

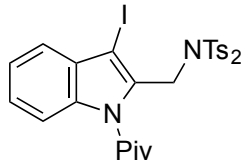
To a solution of 4-methyl-*N*-(phenyl(1-pivaloyl-2-methyl-1*H*-indol-3-yl)-λ^3-iodanyl)-*N*-tosylbenzenesulfonamide (**2a**) (74.3 mg, 0.10 mmol) in CH_2Cl_2 (1.0 mL) was added 1,3-diiodo-5,5-dimethylhydantoin (22.8 mg, 0.060 mmol). The mixture was stirred at room temperature for 7 h under argon atmosphere. Then, saturated Na_2SO_3 aqueous solution (10 mL) was added to the reaction mixture, and the product was extracted with AcOEt (15 mL × 3). The combined extracts were washed by water (10 mL) and brine (10 mL), and dried over Na_2SO_4. The organic phase was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5/1), to give the desired product **3a** (61.1 mg, 92 % yield).

Table S1. Screening for Halogen Reagent and Solvent for Halo-amination of **2a**.



Entry	Halogen reagent (equiv.)	Solvent	Yield (%)
1	DBH (0.6)	CH_2Cl_2	54
2	DBH (0.6)	CH_2Cl_2	67
3	DBH (0.6)	THF	7 (81)[a]
4	DBH (0.6)	MeCN	50
5	DBH (0.6)	$CHCl_3$	33
6	NBS (1.2)	CH_2Cl_2	70
7	NBA (1.2)	CH_2Cl_2	12
8	NBP (1.2)	CH_2Cl_2	74 (3)[b]
9	NIS (1.2)	CH_2Cl_2	83
10	DIH (0.6)	CH_2Cl_2	85

[a] The reaction was carried out without dark conditions. [b] Number in parenthese indicates the yield of *N*-pivaloyl 2-methyl-3-bromo indole.



***N*-((3-Iodo-1-pivaloyl-1*H*-indol-2-yl)methyl)-4-methyl-*N*-tosylbenzenesulfonamide (3a):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (s, 9H), 2.31 (s, 6H), 5.27 (s, 2H), 7.05 (d, J = 8.3 Hz, 4H), 7.17-7.31 (m, 4H), 7.63 (d, J = 8.3 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5 (2C), 28.1 (3C), 44.5, 46.8, 72.1, 112.7, 121.7, 122.1, 124.9, 127.8 (4C), 129.1 (4C), 130.2, 130.7, 135.7, 136.8 (2C), 144.5 (2C), 183.6. IR (neat) 1745, 1378, 1166, 996, 549 cm^{-1}. MS (ESI) calcd for $C_{28}H_{30}IN_2O_5S_2$ $[M+H]^+$ 665.0635, found 665.0641.

Crystal data for 3a: Formula $C_{28}H_{29}IN_2O_5S_2$, colorless, crystal dimensions 0.20 × 0.20 × 0.20 mm^3, Monoclinic, space group P 1 21/c 1, a = 11.244(3) Å, b = 10.311(3) Å, c = 24.381(7) Å, α = 90.00 °, β = 100.978(4) °, γ = 90.00 °, V = 2774.9(13) $Å^3$, Z = 4, ρ_{calc} = 1.591 g cm^{-3}, F(000) = 1344, μ(MoKα) = 1.346 mm^{-1}, T = 173 K. 15287 reflections collected, 6332 independent reflections with $I > 2\sigma(I)$ ($2\theta_{max}$ = 27.69°), and 348 parameters were used for the solution of the structure. The non-hydrogen atoms were refined anisotropically. R_1 = 0.0402 and wR_2 = 0.1056. GOF = 1.039. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1532904. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

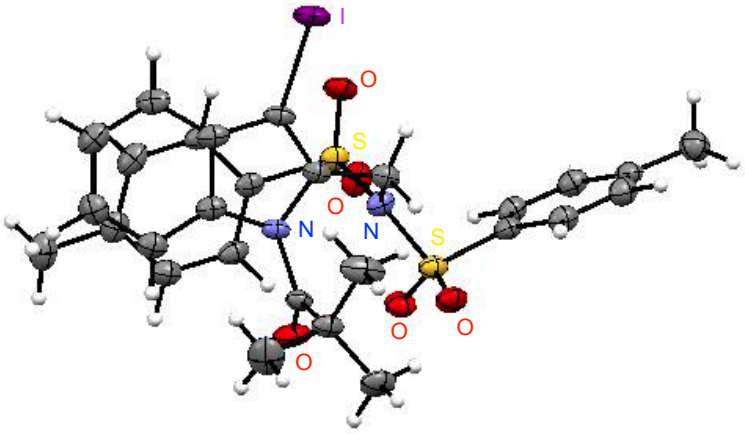


Figure S3. ORTEP drawing of **3a**.

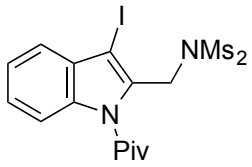
4. General procedure for Direct Iodo-amination of 2-Methyl Indole Derivatives (1) with $PhI(OAc)_2$ and DIH (Method A) (Scheme 2; eq. 5, Table 1, and Table 2).

A mixture of $PhI(OAc)_2$ (38.7 mg, 0.12 mmol), Ts_2NH (39.1 mg, 0.12 mmol) in CH_2Cl_2 (1.0 mL) was stirred at room temperature for 30 min under argon atomosphere. Then, *N*-pivaloyl 2-methyl indole (**1a**) (21.5 mg, 0.10 mmol) was added, and the solution was stirred at room temperature for 2 h. To the solution was added $NaHCO_3$ (22.1 mg, 0.24 mmol), and the obtained mixture was stirred at room temperature for 10 min, followed by addition of 1,3-diiodo-5,5-dimethylhydantoin (22.8 mg, 0.060 mmol). The mixture was stirred at room temperature for 5 h under argon atmosphere. Saturated Na_2SO_3 aqueous solution (10 mL) was added to the reaction mixture, and the product was extracted with AcOEt (15 mL × 3). The combined extracts were washed by water (10 mL) and brine (10 mL), and dried over Na_2SO_4. The organic phase was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5/1), to give the desired product **3a** (63.8 mg, 96% yield).

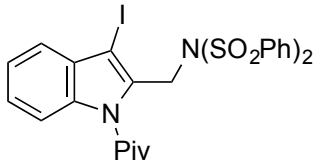
5. General procedure for Direct Iodo-amination of 2-Methyl Indole Derivatives (1) with DIH (Method B) (Scheme 2; eq. 6, Table 1, and Table 2).

To a solution of *N*-pivaloyl 2-methyl indole (**1a**) (21.5 mg, 0.10 mmol) in CH_2Cl_2 (1.0 mL) was added 1,3-diiodo-5,5-dimethylhydantoin (60.8 mg, 0.16 mmol), and the mixture was stirred at room temperature for 7 h under argon atomosphere. Saturated Na_2SO_3 aqueous solution (10 mL) was added to the reaction mixture, and the product was extracted with AcOEt (15 mL × 3). The combined extracts were washed with water (10 mL) and brine (10 mL), and dried over Na_2SO_4. The organic phase was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5/1), to give the desired product **2a**

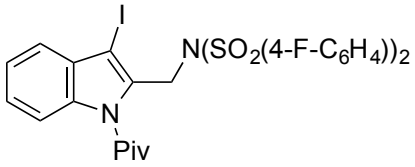
(61.1 mg, 92% yield).



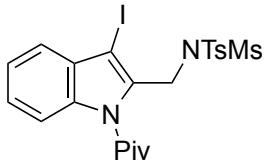
***N*-((3-Iodo-1-pivaloyl-1*H*-indol-2-yl)methyl)-*N*-(methylsulfonyl)methanesulfonamide (3b):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.49 (s, 9H), 3.23 (s, 6H), 5.18 (s, 2H), 7.24-7.30 (m, 1H), 7.31-7.37 (m, 1H), 7.39-7.44 (m, 1H), 7.47-7.51 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.2 (3C), 43.7 (2C), 44.2, 45.6, 70.6, 113.4, 122.2, 122.5, 125.0, 130.2, 132.7, 135.6, 184.4. IR (neat) 1692, 1363, 1154, 1004, 529 cm^{-1}. MS (ESI) calcd for $C_{16}H_{21}ClIN_2O_5S_2$ $[M+Cl]^-$ 546.9631, found 546.9641.



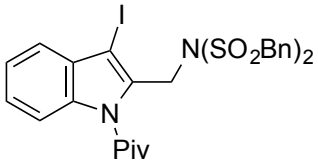
***N*-((3-Iodo-1-pivaloyl-1*H*-indol-2-yl)methyl)-*N*-(phenylsulfonyl)benzenesulfonamide (3c):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42 (s, 9H), 5.30 (s, 2H), 7.17-7.34 (m, 8H), 7.42-7.50 (m, 2H), 7.72-7.79 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.1 (3C), 44.4, 46.9, 72.5, 112.8, 121.9, 122.2, 125.0, 127.9 (4C), 128.5 (4C), 130.1, 130.7, 133.5 (2C), 135.6, 139.6 (2C), 183.7. IR (neat) 1731, 1374, 1167, 999, 546 cm^{-1}. MS (ESI) calcd for $C_{26}H_{26}IN_2O_5S_2$ $[M+H]^+$ 637.0033, found 637.0034.



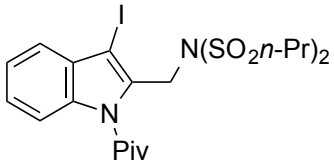
4-Fluoro-*N*-((4-fluorophenyl)sulfonyl)-*N*-((3-iodo-1-pivaloyl-1*H*-indol-2-yl)methyl)benzenesulfonamide (3d): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (s, 9H), 5.27 (s, 2H), 6.90-7.00 (m, 4H), 7.20-7.37 (m, 4H), 7.72-7.81 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.1 (3C), 44.5, 47.0, 72.3, 112.7, 115.8 (d, J_{C-F} = 23.0 Hz, 4C), 121.8, 122.5, 125.2, 130.0, 130.2, 130.9 (d, J_{C-F} = 9.6 Hz, 4C), 135.5 (d, J_{C-F} = 3.8 Hz, 2C), 135.7, 165.6 (d, J_{C-F} = 257.7 Hz, 2C), 183.7. ^{19}F NMR (369 MHz, $CDCl_3$) δ –102.9 IR (neat) 1745, 1590, 1492, 1384, 1173, 997, 547 cm^{-1}. MS (ESI) calcd for $C_{26}H_{24}F_2IN_2O_5S_2$ $[M+H]^+$ 673.0134, found 673.0132.



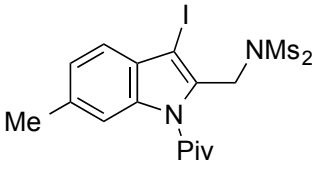
***N*-((3-Iodo-1-pivaloyl-1*H*-indol-2-yl)methyl)-4-methyl-*N*-(methylsulfonyl)benzenesulfonamide (3e):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (s, 9H), 2.27 (s, 3H), 3.36 (s, 3H), 5.19 (s, 2H), 6.94-7.01 (m, 2H), 7.20-7.26 (m, 1H), 7.29-7.34 (m, 3H), 7.51-7.58 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 28.1 (3C), 44.4, 44.6, 46.1, 71.3, 113.0, 121.9, 122.3, 124.9, 128.1 (2C), 129.0 (2C), 130.2, 131.5, 135.5, 135.6, 144.8, 184.0. IR (neat) 1686, 1364, 1163, 962, 558 cm^{-1}. MS (ESI) calcd for $C_{22}H_{26}IN_2O_5S_2$ $[M+H]^+$ 589.0322, found 589.0326.



***N*-(Benzylsulfonyl)-*N*-((3-iodo-1-pivaloyl-1*H*-indol-2-yl)methyl)-1-phenylmethanesulfonamide (3f):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (s, 9H), 4.28 (br, 2H), 4.52 (s, 4H), 7.21-7.42 (m, 13H), 7.46 (d, J = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.0 (3C), 44.0, 47.3, 62.9 (2C), 69.9, 113.0 122.1, 122.4, 125.1, 126.7 (2C), 128.9 (4C), 129.4 (2C), 130.0, 131.2 (4C), 132.6, 135.5, 183.9. IR (neat) 1691, 1377, 1158, 997, 544 cm^{-1}. MS (ESI) calcd for $C_{28}H_{30}IN_2O_5S_2$ $[M+H]^+$ 665.0635, found 665.0644.

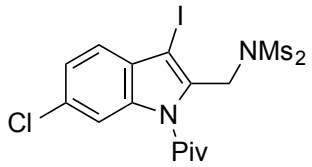


***N*-((3-Iodo-1-pivaloyl-1*H*-indol-2-yl)methyl)-*N*-(propylsulfonyl)propane-1-sulfonamide (3g):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (t, J = 7.5 Hz, 6H), 1.47 (s, 9H), 1.76-1.88 (m, 4H), 3.23-3.30 (m, 4H), 5.17 (s, 2H), 7.24-7.30 (m, 1H), 7.31-7.37 (m, 1H), 7.38-7.44 (m, 1H), 7.46-7.53 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.7 (2C), 16.6 (2C), 28.1 (3C), 44.2, 46.2, 58.5 (2C), 70.8, 113.2, 122.2, 122.4, 125.1, 130.1, 132.9, 135.7, 184.2. IR (neat) 2970, 1703, 1370, 1151, 999, 571 cm^{-1}. MS (ESI) calcd for $C_{20}H_{30}IN_2O_5S_2$ $[M+H]^+$ 569.0635, found 569.0641.

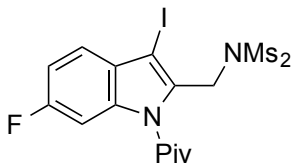


***N*-((3-Iodo-6-methyl-1-pivaloyl-1*H*-indol-2-yl)methyl)-*N*-(methylsulfonyl)methanesulfonamide (3h):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 (s, 9H), 2.49 (s, 3H), 3.21 (s, 6H), 5.16 (s, 2H), 7.09 (d, J = 8.2 Hz, 1H), 7.19 (s, 1H), 7.35 (d, J = 8.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0,

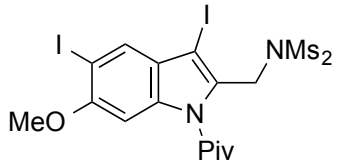
28.2 (3C), 43.7 (2C), 44.2, 45.7, 70.6, 113.3, 121.7, 124.2, 128.1, 131.7, 135.2, 136.0, 184.4. IR (neat) 1706, 1358, 1153, 965, 531 cm^{-1}. MS (ESI) calcd for $C_{17}H_{23}ClIN_2O_5S_2$ $[M+Cl]^-$ 560.9787, found 560.9794.



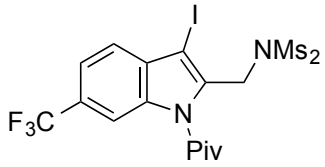
***N*-((6-Chloro-3-iodo-1-pivaloyl-1*H*-indol-2-yl)methyl)-*N*-(methylsulfonyl)methanesulfonamide (3i):** ^1H NMR (400 MHz, $CDCl_3$) δ 1.47 (s, 9H), 3.23 (s, 6H), 5.14 (s, 2H), 7.24 (dd, J = 8.5, 1.8 Hz, 1H), 7.39 (s, 1H), 7.41 (d, J = 8.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.2 (3C), 43.7 (2C), 44.3, 45.5, 69.8, 113.2, 123.1, 123.2, 128.8, 131.1, 133.3, 135.7, 183.8. IR (neat) 1712, 1358, 1153, 962, 531 cm^{-1}. MS (ESI) calcd for $C_{16}H_{20}Cl_2IN_2O_5S_2$ $[M+Cl]^-$ 580.9241, found 580.9251.



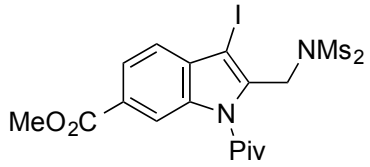
***N*-((6-Fluoro-3-iodo-1-pivaloyl-1*H*-indol-2-yl)methyl)-*N*-(methylsulfonyl)methanesulfonamide (3j):** ^1H NMR (400 MHz, $CDCl_3$) δ 1.48 (s, 9H), 3.23 (s, 6H), 5.15 (s, 2H), 7.04 (td, J = 9.2, 2.0 Hz, 1H), 7.13 (dd, J = 10.0, 2.0 Hz, 1H), 7.43 (dd, J = 9.2, 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.1 (3C), 43.6 (2C), 44.2, 45.6, 70.1, 100.2 (d, J_{C-F} = 28.6 Hz), 111.3 (d, J_{C-F} = 24.8 Hz), 123.3 (d, J_{C-F} = 10.5 Hz), 126.6, 133.1 (d, J_{C-F} = 3.8 Hz), 135.2 (d, J_{C-F} = 12.4 Hz), 161.2 (d, J_{C-F} = 246.1 Hz), 183.8. ^{19}F NMR (369 MHz, $CDCl_3$) δ –115.4. IR (neat) 1695, 1484, 1363, 1161, 975, 526 cm^{-1}. MS (ESI) calcd for $C_{16}H_{20}FClIN_2O_5S_2$ $[M+Cl]^-$ 564.9536, found 564.9538.



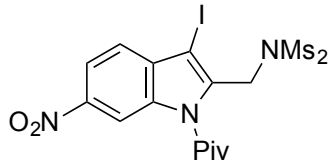
***N*-((3,5-Diiodo-6-methoxy-1-pivaloyl-1*H*-indol-2-yl)methyl)-*N*-(methylsulfonyl)methanesulfonamide (3k):** ^1H NMR (400 MHz, $CDCl_3$) δ 1.45 (s, 9H), 3.20 (s, 6H), 3.91 (s, 3H), 5.13 (s, 2H), 6.83 (s, 1H), 7.87 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.2 (3C), 43.7 (2C), 44.6, 45.7, 56.7, 68.8, 80.9, 95.5, 126.1, 131.6, 132.4, 136.3, 155.9, 183.9. IR (neat) 1702, 1360, 1151, 1041, 976, 529 cm^{-1}. MS (ESI) calcd for $C_{17}H_{22}ClI_2N_2O_6S_2$ $[M+Cl]^-$ 702.8703, found 702.8712.



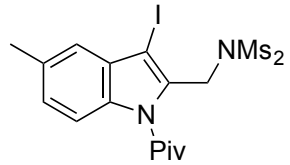
***N*-((3-Iodo-1-pivaloyl-6-(trifluoromethyl)-1*H*-indol-2-yl)methyl)-*N*-(methylsulfonyl)methanesulfonamide (3l):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48 (s, 9H), 3.25 (s, 6H), 5.18 (s, 2H), 7.51 (d, J = 8.4 Hz, 1H), 7.60 (d, J = 8.4 Hz, 1H), 7.68 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.2 (3C), 43.6 (2C), 44.4, 45.3, 69.2, 110.6 (q, $J_{C–F}$ = 3.8 Hz), 119.1 (q, $J_{C–F}$ = 3.8 Hz), 122.8, 124.3 (q, $J_{C–F}$ = 273.0 Hz), 127.1 (q, $J_{C–F}$ = 32.6 Hz), 132.5, 134.6, 135.4, 183.7. ^{19}F NMR (369 MHz, $CDCl_3$) δ –61.2. IR (neat) 1699, 1329, 1149, 1114, 974, 531 cm^{-1}. MS (ESI) calcd for $C_{17}H_{20}ClF_3IN_2O_5S_2$ $[M+Cl]^-$ 614.9504, found 614.9511.



Methyl 3-iodo-2-((*N*-(methylsulfonyl)methylsulfonamido)methyl)-1-pivaloyl-1*H*-indole-6-carboxylate (3m): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50 (s, 9H), 3.26 (s, 6H), 3.96 (s, 3H), 5.18 (s, 2H), 7.73 (dd, J = 8.4, 0.4 Hz, 1H), 7.94 (dd, J = 8.4, 1.4 Hz, 1H), 8.16-8.21 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.3 (3C), 43.6 (2C), 44.3, 45.3, 52.4, 69.5, 115.3, 121.9, 123.3, 126.7, 133.6, 135.0, 135.8, 167.0, 184.0. IR (neat) 1719, 1343, 1236, 1155, 979, 528 cm^{-1}. MS (ESI) calcd for $C_{18}H_{23}ClIN_2O_7S_2$ $[M+Cl]^-$ 604.9685, found 604.9692.

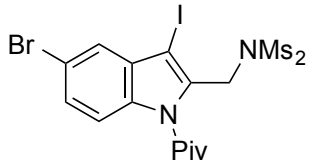


***N*-((3-Iodo-6-nitro-1-pivaloyl-1*H*-indol-2-yl)methyl)-*N*-(methylsulfonyl)methanesulfonamide (3n):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 (s, 9H), 3.22 (s, 6H), 5.11 (s, 2H), 7.58 (d, J = 8.9 Hz, 1H), 8.08 (d, J = 1.8 Hz, 1H), 8.14 (dd, J = 8.9, 1.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.2 (3C), 39.4, 43.8 (2C), 44.3, 62.4, 105.3, 117.3, 123.1, 131.1, 133.7, 136.8, 145.4, 176.3. IR (neat) 1793, 1514, 1335, 1159, 1011, 523 cm^{-1}. MS (APPI) calcd for $C_{14}H_{14}IN_2O_3$ $[M–NMs_2]^+$ 385.0044, found 385.0045.

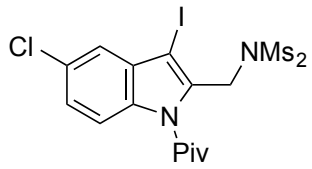


***N*-((3-Iodo-5-methyl-1-pivaloyl-1*H*-indol-2-yl)methyl)-*N*-(methylsulfonyl)methanesulfonamide (3o):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48 (s, 9H), 2.47 (s, 3H), 3.22 (s, 6H), 5.17 (s, 2H), 7.15

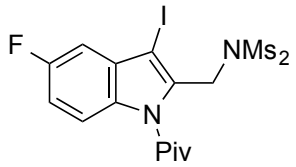
(dd, J = 8.5, 1.4 Hz, 1H), 7.26 (m, 1H), 7.32 (d, J = 8.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 28.2 (3C), 43.7 (2C), 43.9, 45.6, 70.6, 113.3, 121.8, 126.6, 130.4, 132.3, 132.7, 133.8, 184.2. IR (neat) 1728, 1362, 1157, 993, 521 cm^{-1}. MS (ESI) calcd for $C_{17}H_{23}ClIN_2O_5S_2$ $[M+Cl]^-$ 560.9787, found 560.9801.



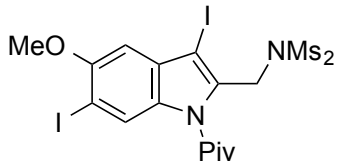
***N*-((5-Bromo-3-iodo-1-pivaloyl-1*H*-indol-2-yl)methyl)-*N*-(methylsulfonyl)methanesulfonamide (3p):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.45 (s, 9H), 3.24 (s, 6H), 5.15 (s, 2H), 7.27 (d, J = 8.9 Hz, 1H), 7.42 (dd, J = 8.9, 2.0 Hz, 1H), 7.64 (d, J = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.2 (3C), 43.7 (2C), 44.3, 45.4, 68.7, 114.7, 115.9, 124.8, 127.9, 132.0, 133.9, 134.3, 183.9. IR (neat) 1729, 1362, 1159, 992, 525 cm^{-1}. MS (ESI) calcd for $C_{16}H_{20}BrClIN_2O_5S_2$ $[M+Cl]^-$ 624.8736, found 624.8746.



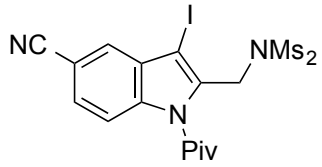
***N*-((5-Chloro-3-iodo-1-pivaloyl-1*H*-indol-2-yl)methyl)-*N*-(methylsulfonyl)methanesulfonamide (3q):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (s, 9H), 3.24 (s, 6H), 5.15 (s, 2H), 7.28 (dd, J = 9.2, 2.0 Hz, 1H), 7.33 (dd, J = 9.2, 0.5 Hz, 1H), 7.48 (dd, J = 2.0, 0.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.2 (3C), 43.7 (2C), 44.3, 45.4, 68.9, 114.4, 121.7, 125.3, 128.5, 131.5, 134.0, 134.1, 183.9. IR (neat) 1730, 1362, 1159, 992, 522 cm^{-1}. MS (ESI) calcd for $C_{16}H_{20}Cl_2IN_2O_5S_2$ $[M+Cl]^-$ 580.9241, found 580.9254.



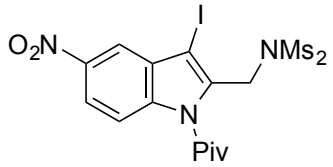
***N*-((5-Fluoro-3-iodo-1-pivaloyl-1*H*-indol-2-yl)methyl)-*N*-(methylsulfonyl)methanesulfonamide (3r):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 (s, 9H), 3.24 (s, 6H), 5.15 (s, 2H), 7.07 (d, J = 9.1, 2.5 Hz, 1H), 7.17 (dd, J = 8.7, 2.5 Hz, 1H), 7.35 (dd, J = 9.1, 4.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.2 (3C), 43.7 (2C), 44.2, 45.5, 69.4, 107.5 (d, J_{C-F} = 24.9 Hz), 113.4 (d, J_{C-F} = 25.9 Hz), 114.5 (d, J_{C-F} = 8.6 Hz), 131.4 (d, J_{C-F} = 10.5 Hz), 132.0, 134.4, 159.1 (d, J_{C-F} = 241.4 Hz), 184.0. ^{19}F NMR (369 MHz, $CDCl_3$) δ –120.1. IR (neat) 1698, 1366, 1160, 979, 510 cm^{-1}. MS (ESI) calcd for $C_{16}H_{20}ClFIN_2O_5S_2$ $[M+Cl]^-$ 564.9536, found 564.9548.



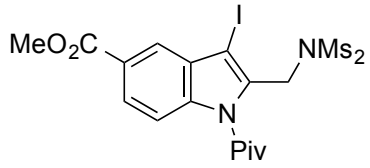
***N*-((3,6-Diiodo-5-methoxy-1-pivaloyl-1*H*-indol-2-yl)methyl)-*N*-(methylsulfonyl)methanesulfonamide (3s):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (s, 9H), 3.23 (s, 6H), 3.97 (s, 3H), 5.14 (s, 2H), 6.83 (s, 1H), 7.84 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.3 (3C), 43.7 (2C), 44.1, 45.5, 56.7, 70.0, 83.8, 102.2, 124.2, 131.1, 131.4, 133.5, 154.1, 183.6. IR (neat) 1694, 1365, 1161, 978, 531 cm^{-1}. MS (ESI) calcd for $C_{17}H_{22}ClI_2N_2O_6S_2$ $[M+Cl]^-$ 702.8703, found 702.8722.



***N*-((5-Cyano-3-iodo-1-pivaloyl-1*H*-indol-2-yl)methyl)-*N*-(methylsulfonyl)methanesulfonamide (3t):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (s, 9H), 3.26 (s, 6H), 5.15 (s, 2H), 7.44 (dd, *J* = 8.7, 0.7 Hz, 1H), 7.57 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.86 (dd, *J* = 1.6, 0.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.1 (3C), 43.6 (2C), 44.7, 45.2, 68.9, 106.1, 114.0, 119.1, 127.56, 127.59, 130.3, 135.1, 137.3, 183.7. IR (neat) 2230, 1709, 1347, 1156, 1005, 538 cm^{-1}. MS (ESI) calcd for $C_{17}H_{20}ClIN_3O_5S_2$ $[M+Cl]^-$ 571.9583, found 571.9599.

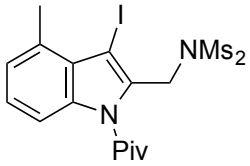


***N*-((3-Iodo-5-nitro-1-pivaloyl-1*H*-indol-2-yl)methyl)-*N*-(methylsulfonyl)methanesulfonamide (3u):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 (s, 9H), 3.27 (s, 6H), 5.15 (s, 2H), 7.45 (d, *J* = 9.4 Hz, 1H), 8.23 (dd, *J* = 9.4, 2.2 Hz, 1H), 8.46 (d, *J* = 2.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.1 (3C), 43.6 (2C), 44.8, 45.2, 69.9, 113.3, 119.1, 120.0, 130.2, 136.0, 138.4, 143.5, 183.6. IR (neat) 1714, 1520, 1361, 1154, 974, 532 cm^{-1}. MS (ESI) calcd for $C_{16}H_{20}ClIN_3O_7S_2$ $[M+Cl]^-$ 591.9481, found 591.9485.

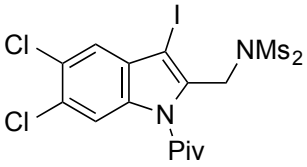


Methyl 3-iodo-2-((*N*-(methylsulfonyl)methylsulfonamido)methyl)-1-pivaloyl-1*H*-indole-5-carboxylate (3v): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.51 (s, 9H), 3.19 (s, 6H), 3.94 (s, 3H), 5.10 (s, 2H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 1.4 Hz, 1H), 7.92 (dd, *J* = 8.5, 1.4 Hz, 1H). ^{13}C NMR

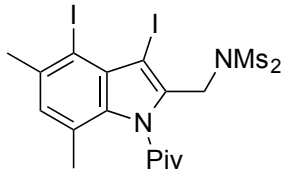
(100 MHz, $CDCl_3$) δ 27.2 (3C), 39.3, 43.9 (2C), 44.5, 52.3, 63.0, 110.8, 122.3, 123.1, 127.0, 130.2, 134.5, 134.8, 166.9, 176.5. IR (neat) 1781, 1716, 1351, 1248, 1159, 1072, 966, 521 cm^{-1}. MS (APCI) calcd for $C_{18}H_{23}IN_2O_7S_2$ $[M]^+$ 569.9986, found 569.9991.



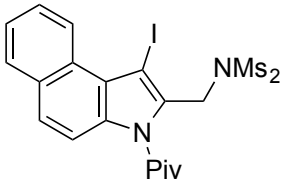
***N*-((3-Iodo-4-methyl-1-pivaloyl-1*H*-indol-2-yl)methyl)-*N*-(methylsulfonyl)methanesulfonamide (3w):** ^1H NMR (400 MHz, $CDCl_3$) δ 1.40 (s, 9H), 2.92 (s, 3H), 3.23 (s, 6H), 5.18 (s, 2H), 6.93-6.99 (m, 1H), 7.11-7.18 (m, 1H), 7.22-7.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3, 28.3 (3C), 43.6 (2C), 44.9, 46.3, 66.8, 111.3, 124.0, 124.4, 125.8, 131.3, 132.0, 136.1, 184.7. IR (neat) 1732, 1366, 1158, 961, 526 cm^{-1}. MS (ESI) calcd for $C_{17}H_{23}ClIN_2O_5S_2$ $[M+Cl]^-$ 560.9787, found 560.9792.



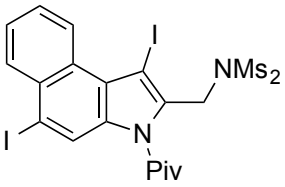
***N*-((5,6-Dichloro-3-iodo-1-pivaloyl-1*H*-indol-2-yl)methyl)-*N*-(methylsulfonyl)methanesulfonamide (3x):** ^1H NMR (400 MHz, $CDCl_3$) δ 1.46 (s, 9H), 3.24 (s, 6H), 5.12 (s, 2H), 7.52 (s, 1H), 7.58 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.2 (3C), 43.6 (2C), 44.3, 45.3, 68.3, 114.8, 123.1, 127.1, 129.2, 130.0, 134.0, 134.7, 183.4. IR (neat) 1712, 1353, 1156, 971, 530 cm^{-1}. MS (ESI) calcd for $C_{16}H_{19}Cl_3IN_2O_5S_2$ $[M+Cl]^-$ 614.8851, found 614.8857.



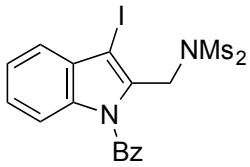
***N*-((3,4-Diiodo-5,7-dimethyl-1-pivaloyl-1*H*-indol-2-yl)methyl)-*N*-(methylsulfonyl)methanesulfonamide (3y):** ^1H NMR (400 MHz, $CDCl_3$) δ 1.09 (s, 9H), 2.56 (s, 3H), 2.60 (s, 3H), 3.28 (s, 6H), 5.08 (s, 2H), 7.24 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.0, 27.7 (3C), 30.1, 43.4 (2C), 45.6, 47.2, 71.6, 106.8, 119.8, 126.8, 130.6, 131.7, 135.1, 136.4, 186.6. IR (neat) 1712, 1372, 1157, 1030, 527 cm^{-1}. MS (ESI) calcd for $C_{18}H_{24}ClI_2N_2O_5S_2$ $[M+Cl]^-$ 700.8910, found 700.8916.



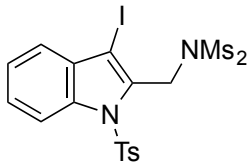
***N*-((1-Iodo-3-pivaloyl-3*H*-benzo[*e*]indol-2-yl)methyl)-*N*-(methylsulfonyl)methanesulfonamide (3z–H):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (s, 9H), 3.19 (s, 6H), 5.28 (s, 2H), 7.42 (d, *J* = 9.1 Hz, 1H), 7.49-7.56 (m, 1H), 7.65-7.71 (m, 2H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.2 (3C), 43.8 (2C), 45.5, 46.5, 66.7, 112.9, 120.2, 121.4, 124.8, 125.9, 126.2, 127.9, 128.8, 129.2, 130.2, 133.3, 184.6. IR (neat) 1731, 1361, 1154, 960, 529 cm^{-1}. MS (ESI) calcd for $C_{20}H_{23}ClIN_2O_5S_2$ $[M+Cl]^-$ 596.9787, found 596.9794.



***N*-((1,5-Diiodo-3-pivaloyl-3*H*-benzo[*e*]indol-2-yl)methyl)-*N*-(methylsulfonyl)methanesulfonamide (3z–I):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (s, 9H), 3.20 (s, 6H), 5.26 (s, 2H), 7.57-7.64 (m, 1H), 7.69-7.75 (m, 1H), 8.06 (s, 1H), 8.21-8.26 (m, 1H), 9.56-9.61 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.2 (3C), 43.7 (2C), 45.6, 46.3, 66.4, 95.7, 120.8, 121.7, 124.3, 126.3, 126.9, 127.9, 129.9, 130.2, 133.4, 133.7, 184.0. IR (neat) 1729, 1367, 1153, 1002, 528 cm^{-1}. MS (ESI) calcd for $C_{20}H_{22}ClI_2N_2O_5S_2$ $[M+Cl]^-$ 722.8754, found 722.8764.



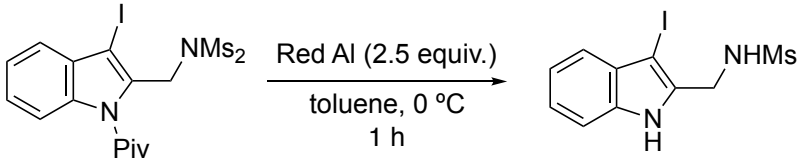
***N*-((1-Benzoyl-3-iodo-1*H*-indol-2-yl)methyl)-*N*-(methylsulfonyl)methanesulfonamide (3aa):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.28 (s, 6H), 5.54 (s, 2H), 6.46 (d, *J* = 8.7 Hz, 1H), 7.03-7.09 (m, 1H), 7.20-7.26 (m, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.50-7.56 (m, 2H), 7.76-7.73 (m, 1H), 7.80-7.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.7 (2C), 44.8, 75.2, 114.1, 122.1, 123.3, 125.3, 129.0 (2C), 130.4 (2C), 130.5, 133.8, 134.1, 134.9, 136.7, 169.4. IR (neat) 1685, 1375, 1158, 977, 745 cm^{-1}. MS (ESI) calcd for $C_{18}H_{17}IN_2NaO_5S_2$ $[M+Na]^+$ 554.9516, found 554.9519.



N-((3-Iodo-1-tosyl-1H-indol-2-yl)methyl)-N-(methylsulfonyl)methanesulfonamide (3ab): ^{1}H

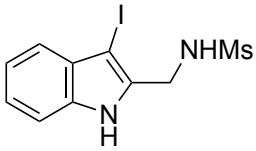
NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 3.49 (s, 6H), 5.46 (s, 2H), 7.16-7.23 (m, 2H), 7.28-7.35 (m, 1H), 7.35-7.43 (m, 2H), 7.61-7.68 (m, 2H), 8.03-8.09 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 42.8 (2C), 45.5, 80.8, 115.3, 122.5, 124.7, 126.5 (2C), 126.9, 130.1 (2C), 131.5, 132.8, 134.8, 136.7, 145.5. IR (neat) 1372, 1359, 1174, 1154, 996, 569 cm^{-1}. MS (ESI) calcd for $C_{18}H_{19}IN_2NaO_6S_3$ $[M+Na]^+$ 604.9342, found 604.9348.

6. Derivatization of 2-Aminomethyl-3-iodo indole Derivatives (3b) (Scheme 5).

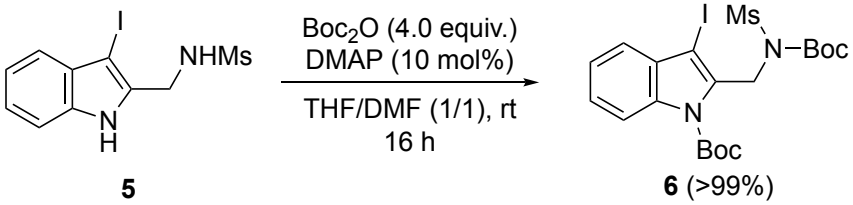


3b **5** (37%)

To a solution of **3b** (2.03 g, 3.50 mmol) in toluene (44 mL) was added Red-Al® (60 wt. % toluene solution; 2.85 mL, 8.75 mmol) dropwise at –20 ºC, and the reaction mixture was stirred at 0 ºC for 1 h under argon atmosphere. Saturated NH_4Cl aqueous solution (50 mL) was added to the mixture at 0 ºC, and the product was extracted with AcOEt (50 mL × 3). The organic phase was washed with brine (50 mL), and dried over Na_2SO_4. The solvent was removed under reduced pressure. The crude mixture was purified by column chromatography (eluent: hexane/AcOEt=2/1) to give the desired product **5** (455.2 mg, 37% yield).



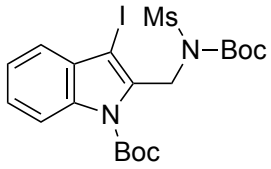
***N*-((3-Iodo-1*H*-indol-2-yl)methyl)methanesulfonamide (5):** ^1H NMR (400 MHz, MeCN-d_3) δ 2.89 (s, 3H), 4.41 (s, 2H), 5.72 (brs, 1H), 7.11-7.17 (m, 1H), 7.18-7.25 (m, 1H), 7.29-7.35 (m, 1H), 7.38-7.43 (m, 1H), 9.78 (brs, 1H). ^{13}C NMR (100 MHz, MeCN-d_3) δ 40.4, 41.5, 59.0, 112.7, 121.2, 121.5, 124.1, 131.1, 136.6, 137.4. IR (neat) 3381, 3303, 1310, 1148, 1068, 589 cm^{-1}. MS (ESI) calcd for $C_{10}H_{12}IN_2O_2S$ $[M+H]^+$ 350.9659, found 350.9651.



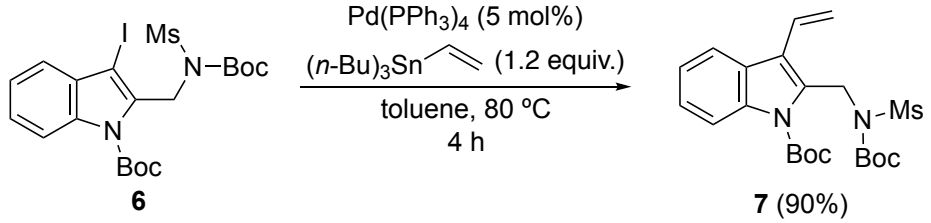
5 **6** (>99%)

To a solution of **5** (70.0 mg, 0.20 mmol) in DMF (0.8 mL) and THF (0.8 mL) was added Boc_2O (183.0 μL, 0.80 mmol) and DMAP (2.4 mg, 0.020 mmol), and the mixture was stirred at room

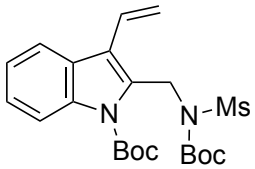
temperature for 16 h. The solvent was removed under reduced pressure and the crude mixture was purified by column chromatography (eluent: hexane/AcOEt=5/1) to give the desired product **6** (109.0 mg, >99% yield).



***tert*-Butyl 2-((*N*-(*tert*-butoxycarbonyl)methylsulfonamido)methyl)-3-iodo-1*H*-indole-1-carboxylate (6):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.51 (s, 9H), 1.70 (s, 9H), 3.04 (s, 3H), 5.45 (s, 2H), 7.27-7.33 (m, 1H), 7.33-7.39 (m, 1H), 7.41-7.47 (m, 1H), 7.93-7.98 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.9 (3C), 28.1 (3C), 42.3, 43.9, 74.0, 84.6, 85.3, 115.4, 121.8, 123.4, 125.7, 130.8, 135.2, 135.7, 149.4, 151.6. IR (neat) 1729, 1353, 1237, 1143, 543 cm^{-1}. MS (ESI) calcd for $C_{20}H_{28}IN_2O_6S$ $[M+H]^+$ 551.0707, found 551.0707.

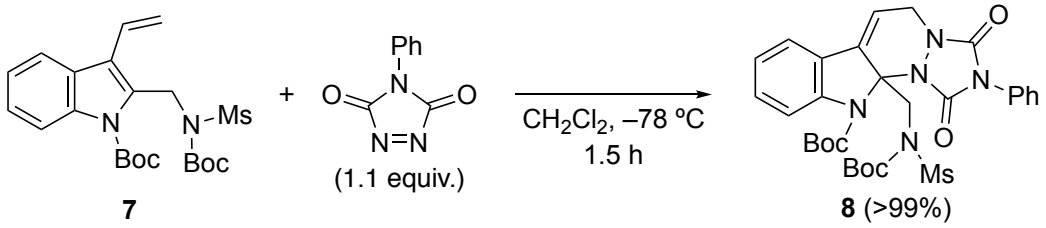


To a solution of **6** (110.1 mg, 0.20 mmol) and $Pd(PPh_3)_4$ (11.6 mg, 0.010 mmol) in toluene (1 mL) was added tributylvinyltin (70.2 μL, 0.24 mmol), and the reaction mixture was stirred at 80 ºC for 4 h under argon atmosphere. Water (10 mL) was added to the mixture and the organic phase was extracted with AcOEt (10 mL × 3). The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by column chromatography (10% w/w anhydrous K_2CO_3-silica gel, eluent: hexane/AcOEt=7/1) to give the desired product **7** (81.5 mg, 90% yield).



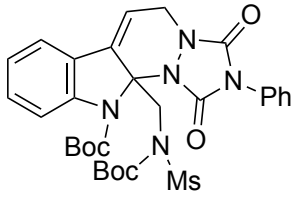
***tert*-Butyl 2-((*N*-(*tert*-butoxycarbonyl)methylsulfonamido)methyl)-3-vinyl-1*H*-indole-1-carboxylate (7):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.51 (s, 9H), 1.70 (s, 9H), 2.95 (s, 3H), 5.43 (s, 2H), 5.51 (dd, J = 11.6, 1.4 Hz, 1H), 5.77 (dd, J = 18.0, 1.4 Hz, 1H), 6.92 (dd, J = 18.0, 11.6 Hz, 1H), 7.23-7.29 (m, 1H), 7.29-7.35 (m, 1H), 7.80 (d, J = 7.6 Hz, 1H), 8.02 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.8 (3C), 28.2 (3C), 41.3, 41.9, 84.5, 84.7, 115.3, 118.0, 120.1, 120.6, 123.0, 124.8, 127.2, 127.9, 132.2, 136.0, 150.2, 151.6. IR (neat) 1727, 1453, 1240, 1140 cm^{-1}.

MS (ESI) calcd for $C_{22}H_{31}N_2O_6S$ $[M+H]^+$ 451.1897, found 451.1894.



7 **8** (>99%)

To a solution of **7** (45.1 mg, 0.10 mmol) in CH_2Cl_2 (2 mL) was added 4-phenyl-1,2,4-triazoline-3,5-dione (19.3 mg, 0.11 mmol) at –78 ºC, the mixture was stirred at –78 ºC for 1.5 h under argon atmosphere. The solvent was removed under reduced pressure and the crude mixture was purified by column chromatography (eluent: hexane/AcOEt=1/1) to give the desired product **8** (61.9 mg, >99% yield).



***tert*-Butyl 11a-((*N*-(*tert*-butoxycarbonyl)methylsulfonamido)methyl)-1,3-dioxo-2-phenyl-2,3,5, 11a-tetrahydro-1*H*,11*H*-[1,2,4]triazolo[1',2':1,2]pyridazino[3,4-*b*]indole-11-carboxylate (8):** ^{1}H NMR (400 MHz, MeCN-d_3 (60 ºC)) δ 1.37 (s, 9H), 1.59 (s, 9H), 2.89 (brs, 3H), 4.57 (dd, J = 17.2, 2.8 Hz, 1H), 4.70 (dd, J = 17.2, 7.2 Hz, 1H), 4.80 (d, J = 16.0 Hz, 1H), 5.26 (d, J = 16.0 Hz, 1H), 6.42 (dd, J = 6.8, 2.8 Hz, 1H), 7.04-7.10 (m, 1H), 7.28-7.35 (m, 1H), 7.36-7.43 (m, 3H), 7.43-7.53 (m, 3H), 7.91 (d, J = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, MeCN-d_3 (60 ºC)) δ 28.1 (3C), 28.7 (3C), 43.3, 45.6, 46.5, 83.2, 84.2, 86.4, 115.4, 116.5, 121.7, 124.4, 125.6, 127.9 (2C), 129.5, 130.1 (2C), 131.9, 133.3, 139.6, 145.9, 149.4, 152.1, 152.9, 155.2. IR (neat) 1716, 1407, 1356, 1154, 753 cm^{-1}. MS (ESI) calcd for $C_{30}H_{35}N_5O_8S$ $[M+H]^+$ 626.2279, found 626.2268.

Crystal data for 8: Formula $C_{30}H_{35}N_5O_8S$, colorless, crystal dimensions 0.20 × 0.20 × 0.10 mm^3, Monoclinic, space group P 1 21/c 1', a = 15.0230(15) Å, b = 12.3995(12) Å, c = 17.7457(17) Å, α = 90.00 °, β = 112.6609(12) °, γ = 90.00 °, V = 3050.4(5) Å^3, Z = 4, ρ_{calc} = 1.362 g cm^{-3}, F(000) = 1320, μ(MoKα) = 0.165 mm^{-1}, T = 173 K. 17156 reflections collected, 6907 independent reflections with $I > 2\sigma(I)$ ($2\theta_{max}$ = 27.48°), and 404 parameters were used for the solution of the structure. The non-hydrogen atoms were refined anisotropically. R_1 = 0.0449 and wR_2 = 0.1090. GOF = 0.993. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1589706. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

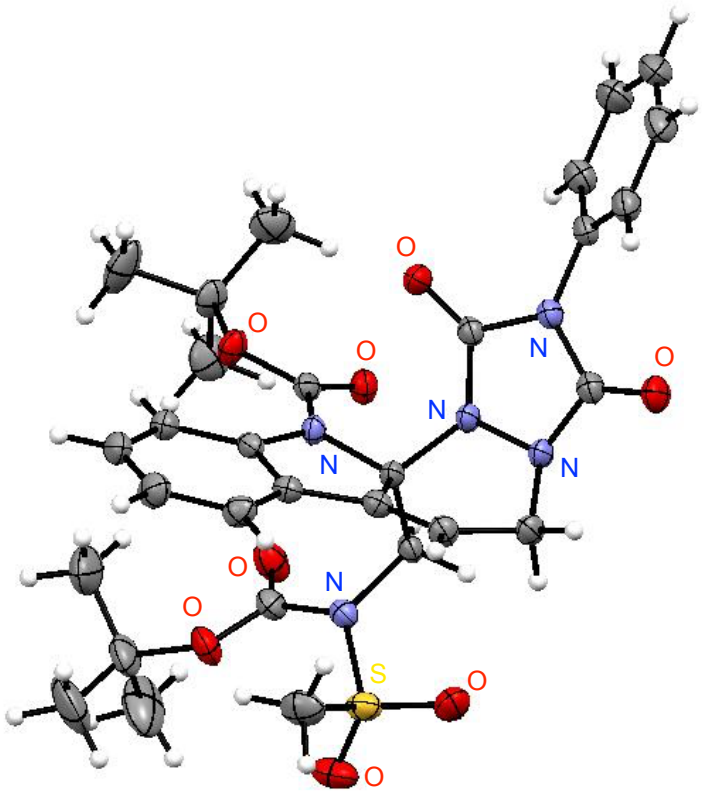
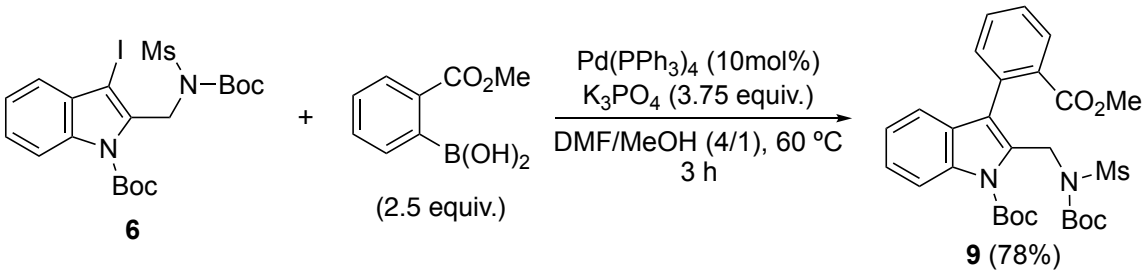
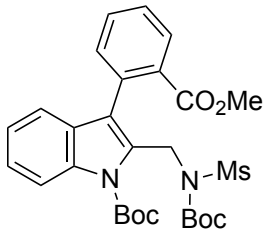


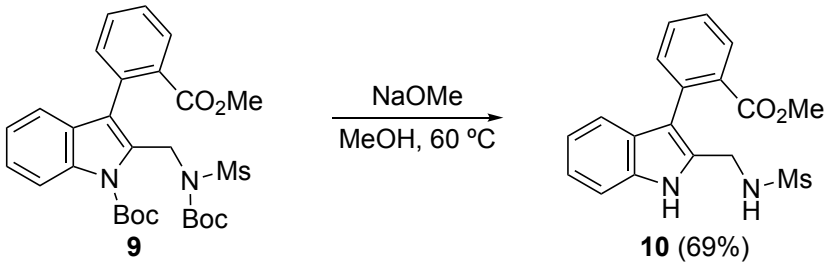
Figure S4. ORTEP drawing of **8**.



A solution of **6** (79.5 mg, 0.144 mmol), $Pd(PPh_3)_4$ (16.6 mg, 0.0144 mmol), 2-(Methoxycarbonyl)phenylboronic Acid (64.8 mg, 0.360 mmol), K_3PO_4 (115.0 mg, 0.540 mmol) in DMF (1.2 mL) and MeOH (300 µL) was stirred at 60 ºC for 3 h under argon atmosphere. Saturated NH_4Cl aqueous solution (10 mL) was added to the mixture at 0 ºC, and the product was extracted with AcOEt (10 mL × 3). The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by column chromatography (eluent: hexane/$CHCl_3$/AcOEt=10/10/1) to give the desired product **9** (62.9 mg, 78% yield).

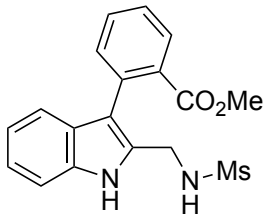


***tert*-Butyl 2-((*N*-(*tert*-butoxycarbonyl)methylsulfonamido)methyl)-3-(2-(methoxycarbonyl)phenyl)-1*H*-indole-1-carboxylate (9):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (s, 9H), 1.73 (s, 9H), 2.83 (s, 3H), 3.59 (s, 3H), 5.20 (d, *J* = 16.4 Hz, 1H), 5.38 (d, *J* = 16.4 Hz, 1H), 7.05-7.11 (m, 1H), 7.11-7.18 (m, 1H), 7.26-7.32 (m, 1H), 7.41-7.46 (m, 1H), 7.46-7.52 (m, 1H), 7.58-7.65 (m, 1H), 7.98-8.08 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.7 (3C), 28.2 (3C), 41.7, 41.8, 51.9, 84.1, 84.4, 115.2, 119.3, 122.8, 123.8, 124.5, 127.9, 129.9, 130.5, 130.9, 131.4, 132.0, 132.7, 133.6, 135.1, 150.4, 151.5, 167.0. IR (neat) 1731, 1362, 1347, 1146, 1091, 751 cm^{-1}. MS (ESI) calcd for $C_{28}H_{35}N_2O_8S$ $[M+H]^+$ 559.2109, found 559.2110.



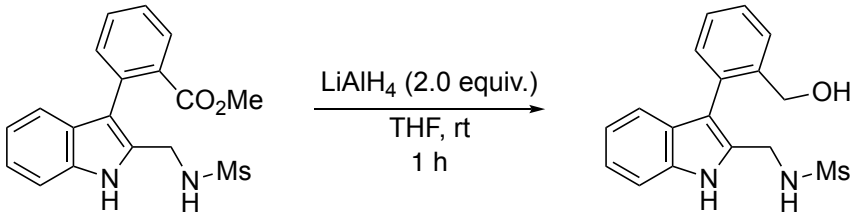
9 **10** (69%)

A solution of **9** (158.7 mg, 0.284 mmol) and NaOMe (153.4 mg, 2.84 mmol) in MeOH (2.8 mL) was refluxed for 16 h under argon atmosphere. Saturated NH_4Cl aqueous solution (10 mL) was added to the mixture, and the product was extracted with AcOEt (10 mL × 3). The organic phase was dried over Na_2SO_4, and concentrated under reduced pressure. The crude mixture was purified by column chromatography (eluent: hexane/ AcOEt=2/1) to give the desired product **10** (66.2 mg, 69% yield).



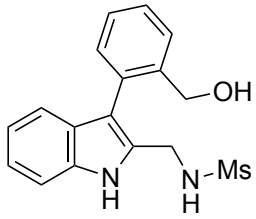
Methyl 2-(2-(methylsulfonamidomethyl)-1*H*-indol-3-yl)benzoate (10): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.90 (s, 3H), 3.60 (s, 3H), 4.17 (dd, *J* = 15.4, 4.4 Hz, 1H), 4.31 (dd, *J* = 15.4, 8.2 Hz, 1H), 5.39 (dd, *J* = 8.2, 4.4 Hz, 1H), 7.01-7.08 (m, 1H), 7.14-7.21 (m, 1H), 7.21-7.27 (m, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.36-7.41 (m, 1H), 7.41-7.48 (m, 1H), 7.52-7.59 (m, 1H), 7.86-7.92 (m, 1H), 8.99 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.2, 40.6, 52.4, 111.2, 114.4, 119.0, 120.0, 122.6, 127.2,

128.0, 129.8, 131.0, 131.5, 132.0, 132.9, 134.1, 135.4, 168.9. IR (neat) 3387, 3285, 1707, 1430, 1325, 1152, 1093, 743 cm^{-1}. MS (ESI) calcd for $C_{18}H_{19}N_2O_4S$ $[M+H]^+$ 359.1060, found 359.1057.

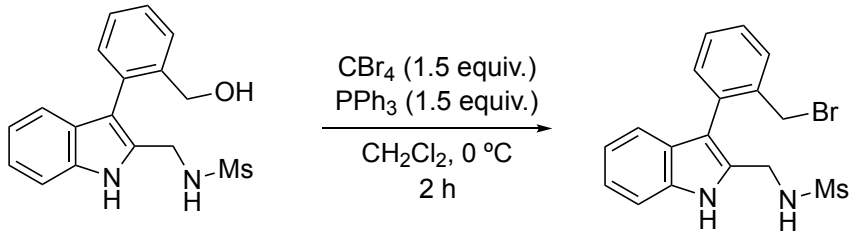


10 **S1** (>99%)

To a solution of **10** (65.2 mg, 0.182 mmol) in THF (1.8 mL) was added $LiAlH_4$ (13.8 mg, 0.364 mmol) at 0 ºC, and the mixture was stirred at room temperature for 1 h under argon atmosphere. Saturated Na_2SO_4 aqueous solution (10 mL) was added to the mixture at 0 ºC, and Na_2SO_4 (5 g) was added to the solution. The resulting mixture was filtered with Celite, and the filtrate was extracted with AcOEt (10 mL × 3). The organic phase was dried over Na_2SO_4, and concentrated under reduced pressure. The crude mixture was purified by column chromatography (eluent: hexane/AcOEt=1/1 to 1/2) to give the desired product **S1** (59.8 g, >99% yield).



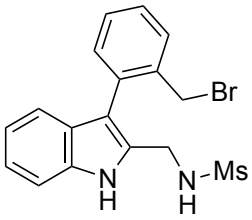
***N*-((3-(2-(Hydroxymethyl)phenyl)-1*H*-indol-2-yl)methyl)methanesulfonamide (S1):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.00 (brs, 1H), 2.90 (s, 3H), 4.10 (dd, *J* = 15.4, 4.0 Hz, 1H), 4.30 (dd, *J* = 15.4, 8.4 Hz, 1H), 4.35 (d, *J* = 12.0 Hz, 1H), 4.48 (d, *J* = 12.0 Hz, 1H), 5.89 (dd, *J* = 8.4, 4.0 Hz, 1H), 7.03-7.11 (m, 1H), 7.16-7.27 (m, 2H), 7.29-7.35 (m, 1H), 7.37-7.48 (m, 3H), 7.49-7.55 (m 1H), 8.93 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.5, 40.5, 63.3, 111.3, 114.5, 119.4, 120.1, 122.8, 128.09, 128.15 (2C), 129.6, 131.6, 132.1, 133.4, 135.4, 139.9. IR (neat) 3383, 1455, 1306, 1142, 1057, 744 cm^{-1}. MS (ESI) calcd for $C_{17}H_{19}N_2O_3S$ $[M+H]^+$ 331.1111, found 331.1111.



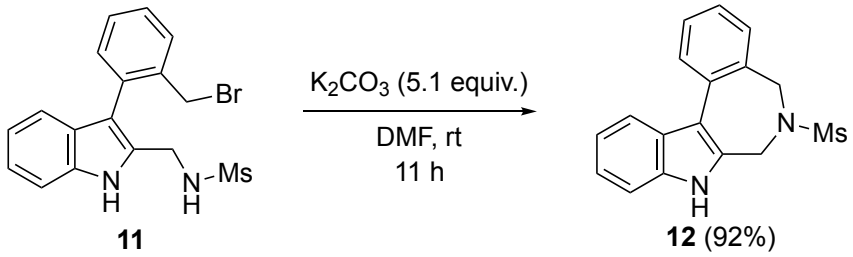
S1 **11** (72%)

To a solution of **S1** (58.2 mg, 0.176 mmol) in CH_2Cl_2 (1.8 mL) was added PPh_3 (72.1 mg, 0.275

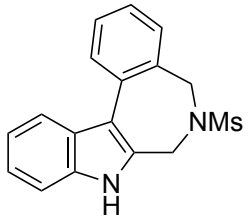
mmol) and CBr_4 (91.2 mg, 0.275 mmol) at 0 ºC, and the mixture was stirred room temperature for 1 h under argon atmosphere. The crude mixture was purified by column chromatography (eluent: hexane/AcOEt=2/3) to give the desired product **11** (49.5 mg, 72% yield).



***N*-((3-(2-(Bromomethyl)phenyl)-1*H*-indol-2-yl)methyl)methanesulfonamide (11):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.97 (s, 3H), 4.27 (dd, *J* = 15.6, 5.2 Hz, 1H), 4.361 (d, *J* = 9.8 Hz, 1H), 4.362 (dd, *J* = 15.6, 7.8 Hz, 1H), 4.42 (d, *J* = 9.8 Hz, 1H), 4.94 (dd, *J* = 7.8, 5.2 Hz, 1H), 7.04-7.11 (m, 1H), 7.13-7.19 (m, 1H), 7.20-7.28 (m, 2H), 7.35-7.47 (m, 3H), 7.56-7.61 (m 1H), 9.03 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.3, 38.8, 40.9, 111.4, 113.8, 119.1, 120.3, 123.0, 127.9, 128.6, 128.9, 130.7, 131.3, 132.4, 133.6, 135.6, 137.9. IR (neat) 3377, 3316, 1405, 1306, 1156, 1054, 749 cm^{-1}. MS (ESI) calcd for $C_{17}H_{18}BrN_2O_2S$ $[M+H]^+$ 393.0267, found 393.0264.

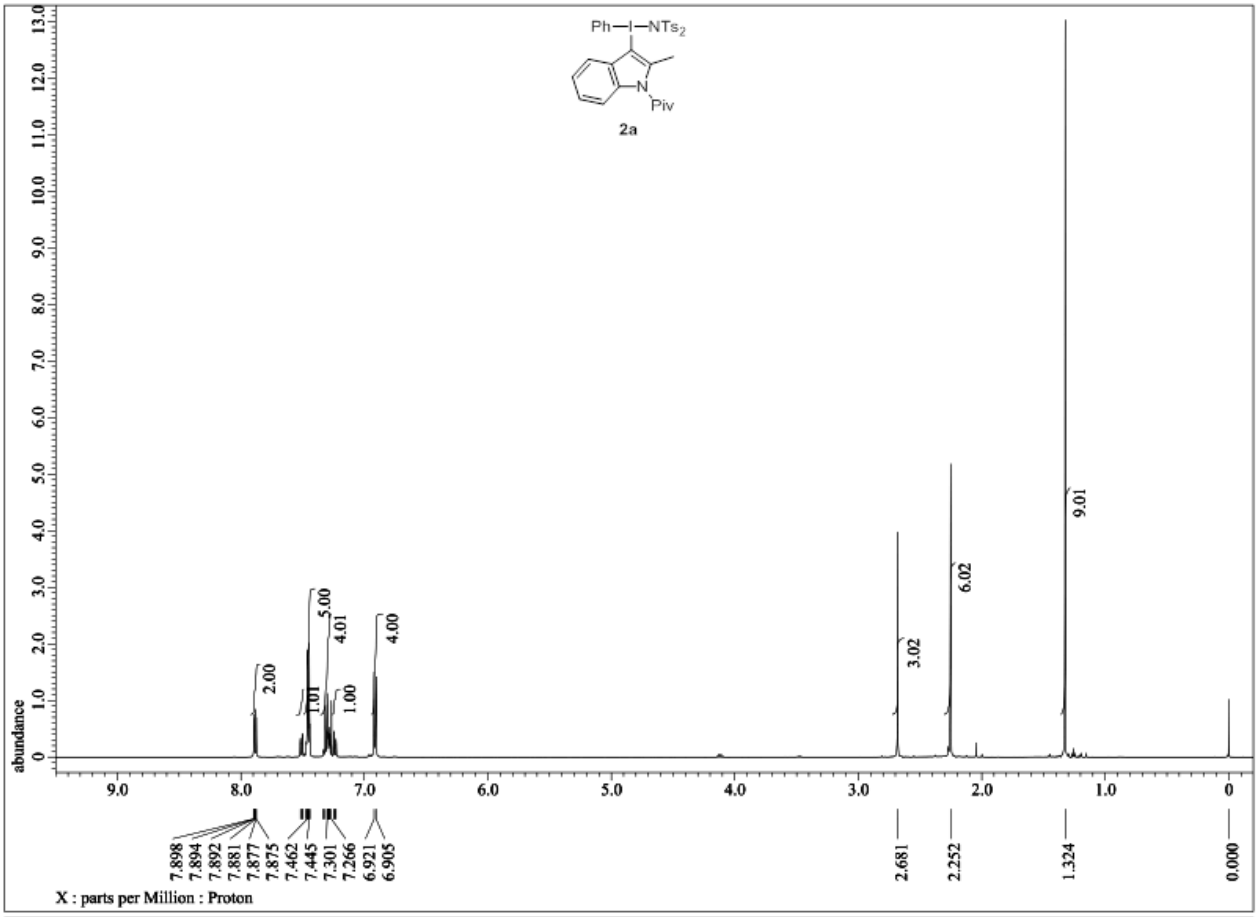


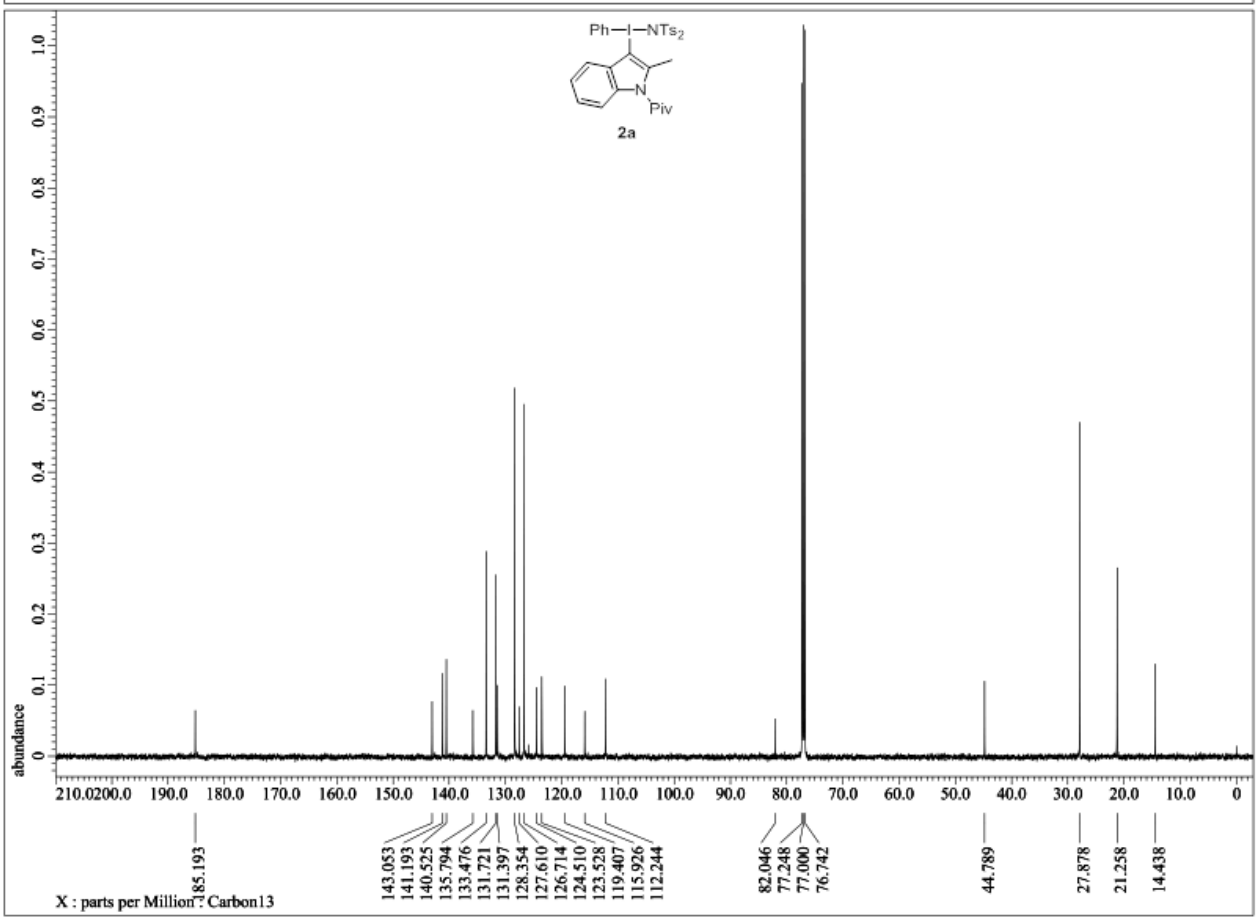
To a solution of **11** (49.5 mg, 0.126 mmol) in DMF (1.3 mL) was added K_2CO_3 (87.0 mg, 0.630 mmol), and the mixture was stirred room temperature for 3 h under argon atmosphere. Saturated NH_4Cl aqueous solution (10 mL) was added to the mixture, and the product was extracted with AcOEt (10 mL × 3). The organic phase was dried over Na_2SO_4, and concentrated under reduced pressure. The crude mixture was purified by column chromatography (eluent: hexane/AcOEt=2/3) to give the desired product **12** (36.2 mg, 92% yield).

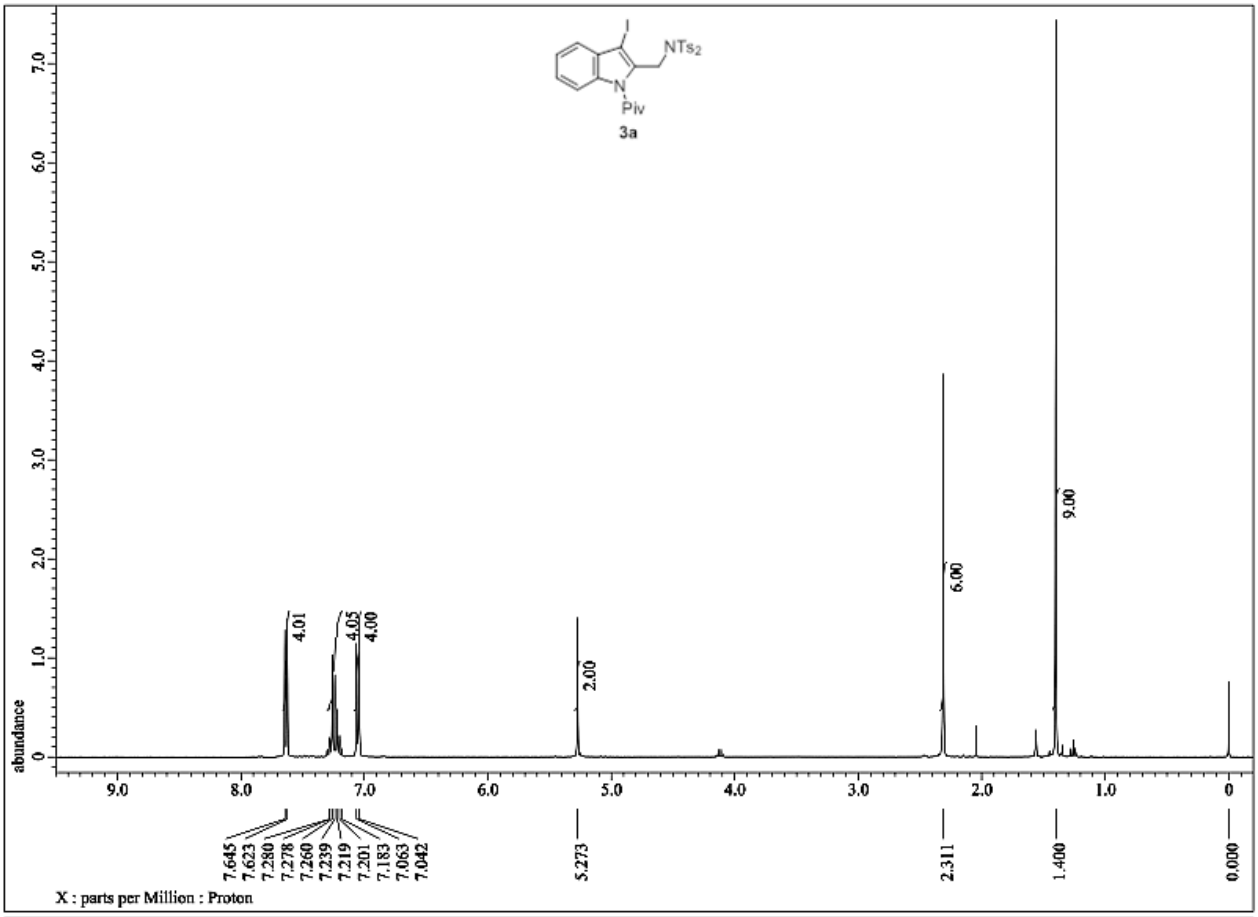


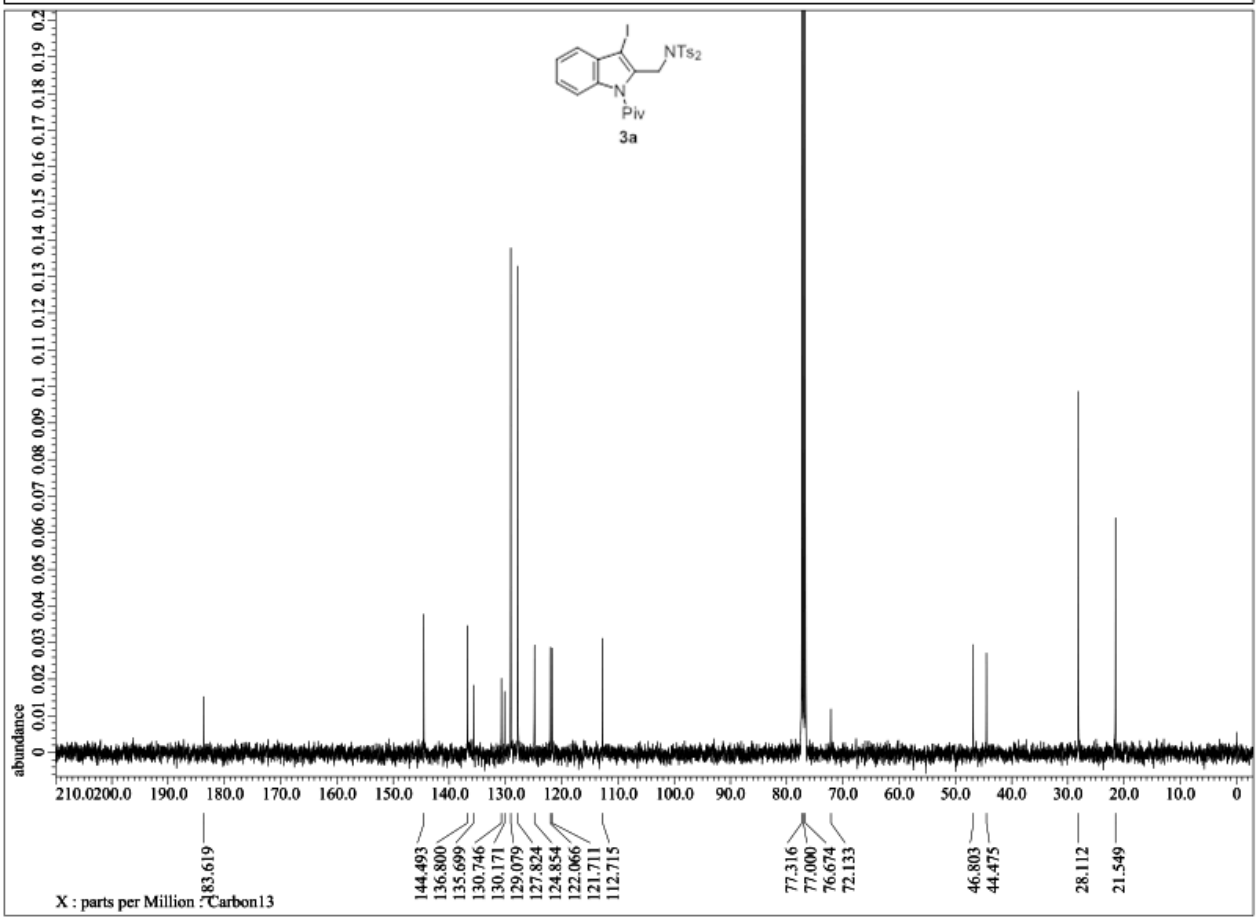
6-(Methylsulfonyl)-5,6,7,8-tetrahydrobenzo[5,6]azepino[3,4-*b*]indole (12): ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.59 (s, 3H), 4.33 (s, 2H), 4.76 (s, 2H), 7.07-7.14 (m, 1H), 7.15-7.21 (m, 1H), 7.21-7.27 (m, 1H), 7.38-7.45 (m, 2H), 7.45-7.52 (m 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.87-7.92 (m, 1H), 11.59 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 36.9, 45.9, 50.6, 111.2, 111.6, 118.8,

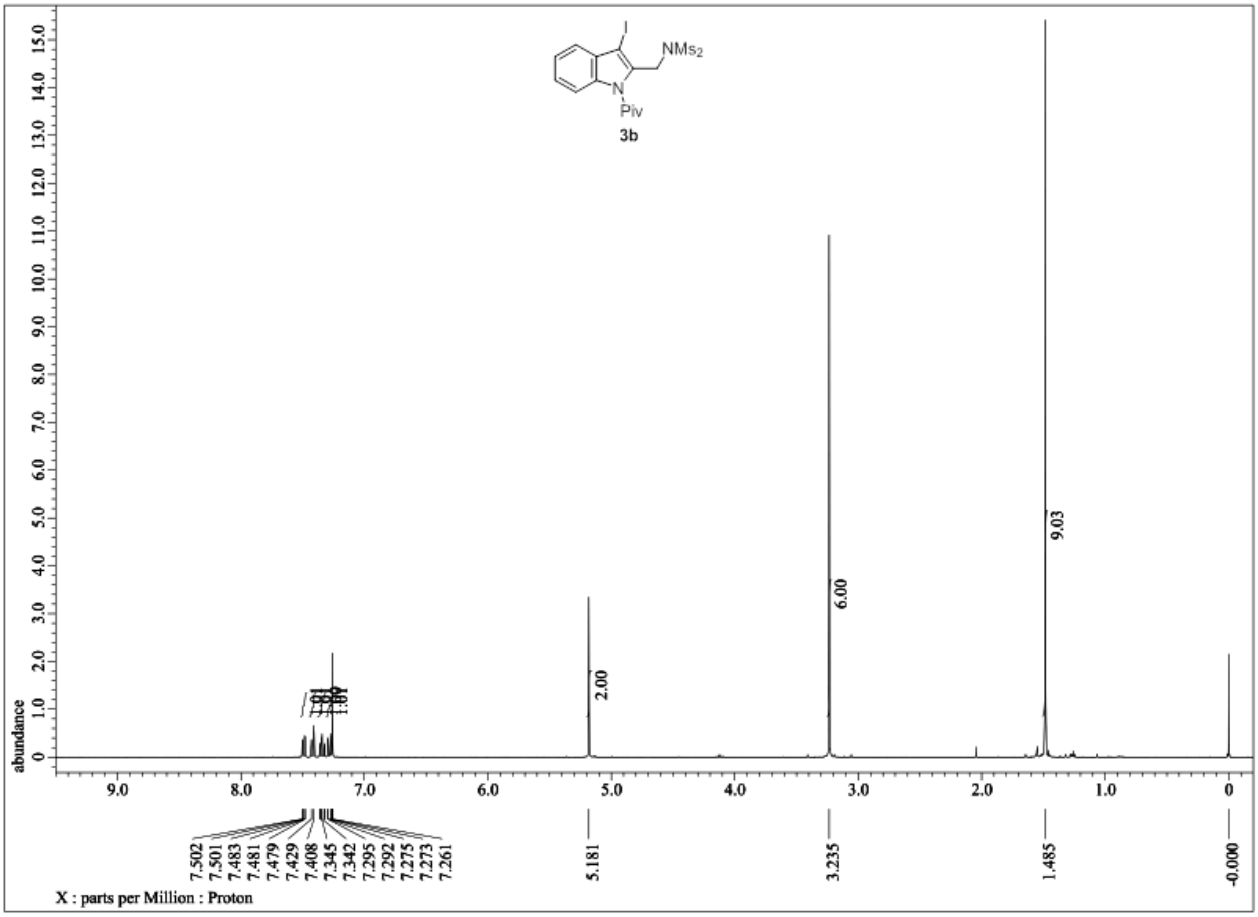
120.0, 122.0, 125.1, 125.9, 127.2, 128.5, 130.0, 133.2, 134.3, 134.9, 136.1. IR (neat) 3375, 2920, 1728, 1456, 1320, 1139, 1071 752 cm^{-1}. MS (ESI) calcd for $C_{17}H_{17}N_2O_2S$ $[M+H]^+$ 313.1005, found 313.1007.

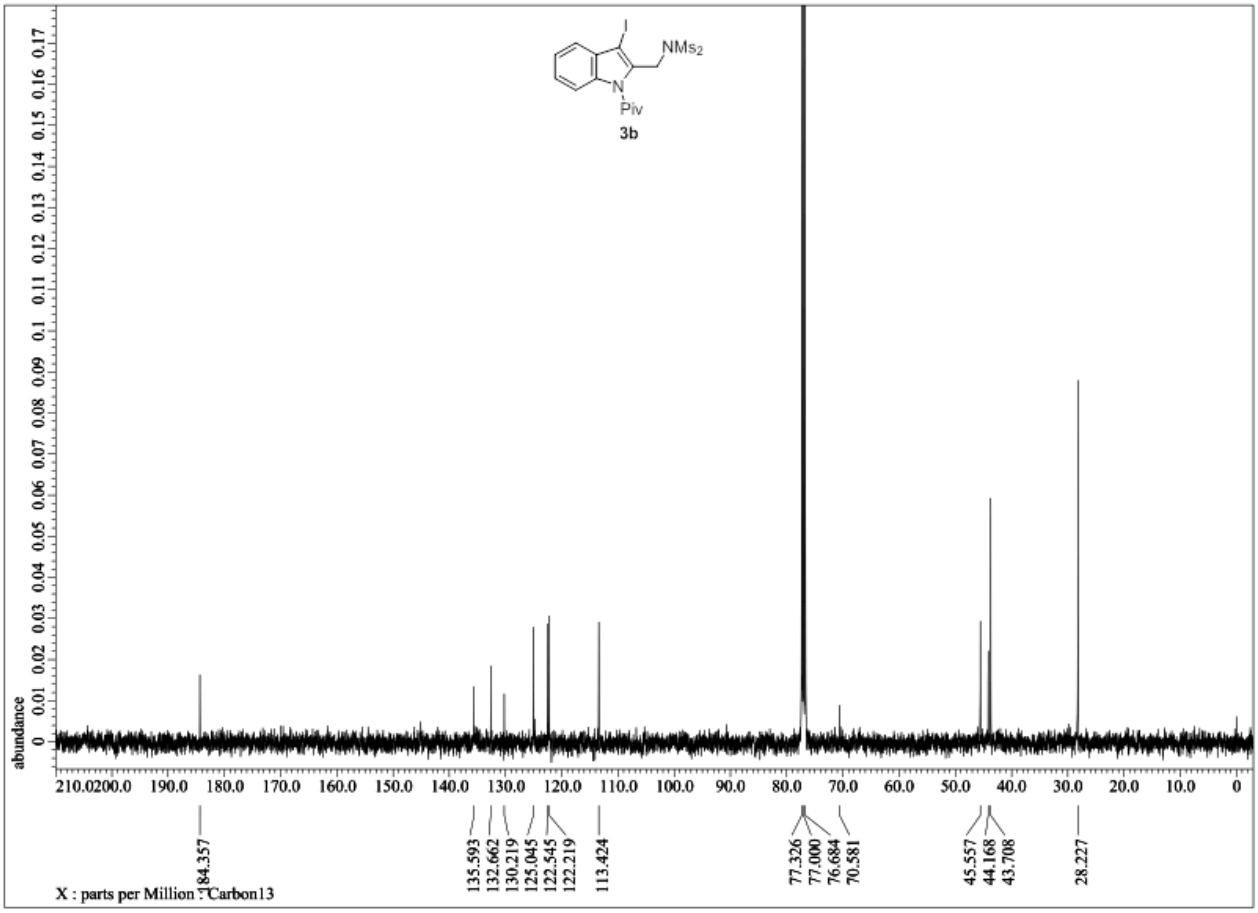

Ph—I—NTs2
N
Piv
2a
abundance
2.00
1.01
5.00
4.01
1.00
4.00
3.02
6.02
9.01
7.898
7.894
7.892
7.881
7.877
7.875
7.462
7.445
7.301
7.266
6.921
6.905
2.681
2.252
1.324
0.000
X : parts per Million : Proton

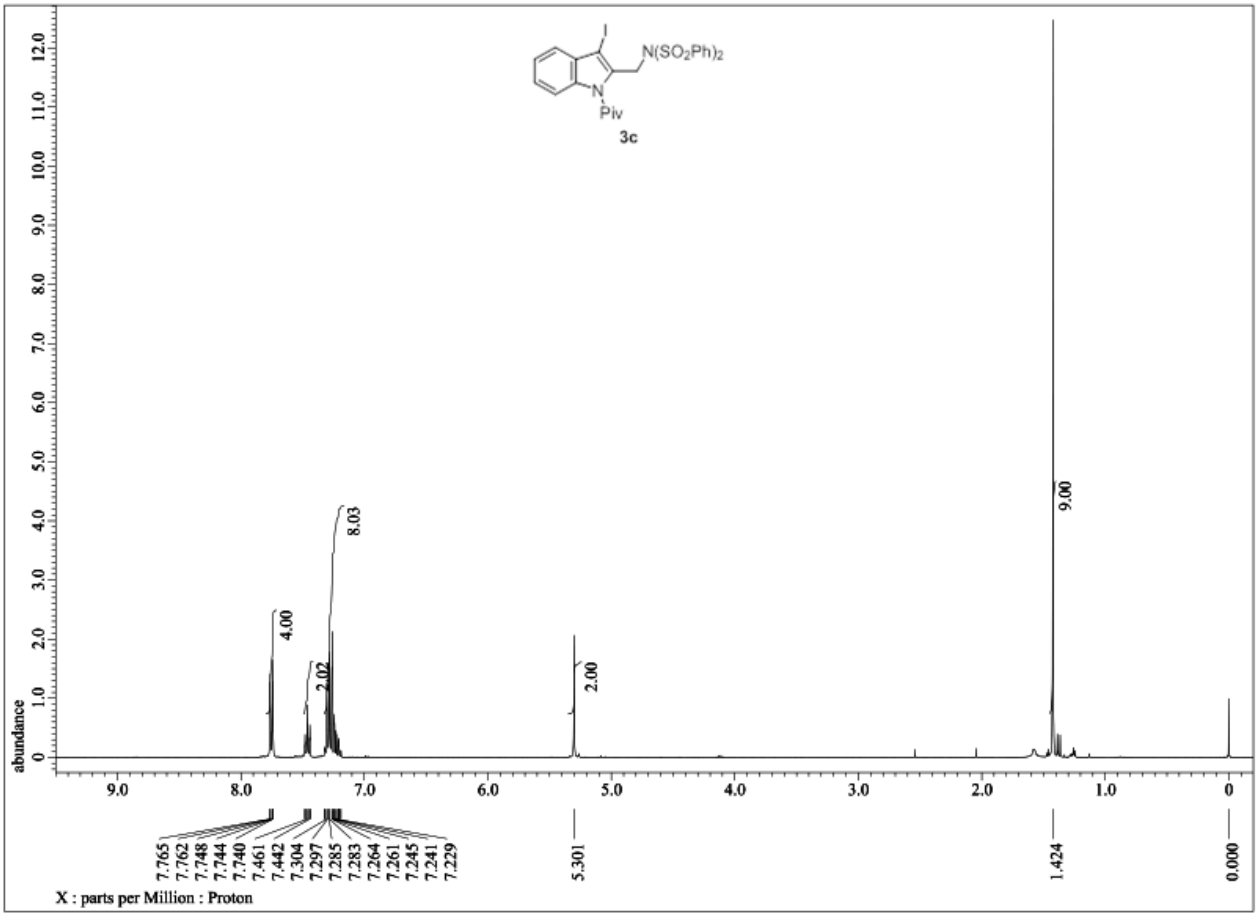

Ph—I—NTs2
N
Piv
2a
abundance
185.193
143.053
141.193
140.525
135.794
133.476
131.721
131.397
128.354
127.610
126.714
124.510
123.528
119.407
115.926
112.244
82.046
77.248
77.000
76.742
44.789
27.878
21.258
14.438
X : parts per Million : Carbon13

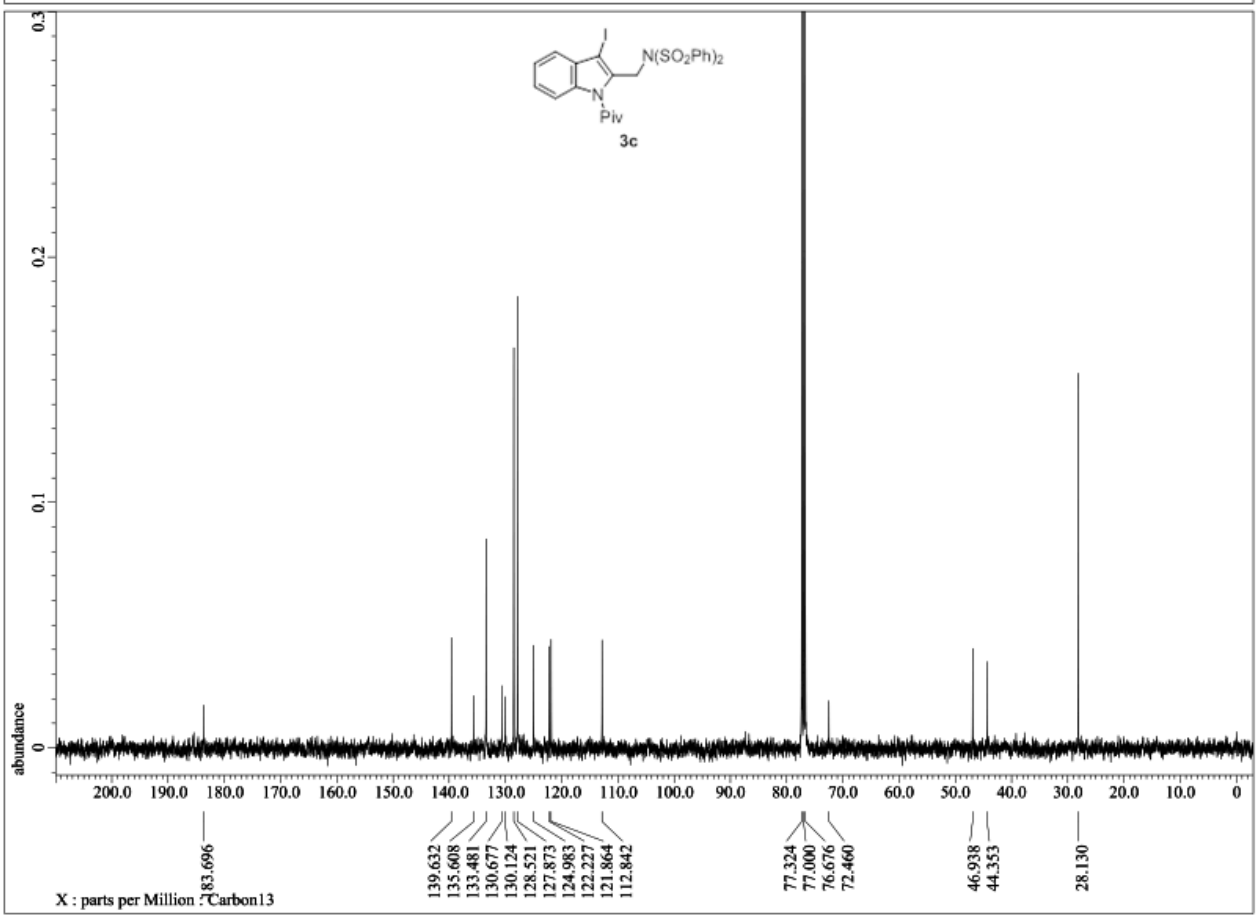

I
NTs2
N
Piv
3a
abundance
X : parts per Million : Proton
4.01
4.05
4.00
2.00
6.00
9.00
7.645
7.623
7.280
7.278
7.260
7.239
7.219
7.201
7.183
7.063
7.042
5.273
2.311
1.400
0.000

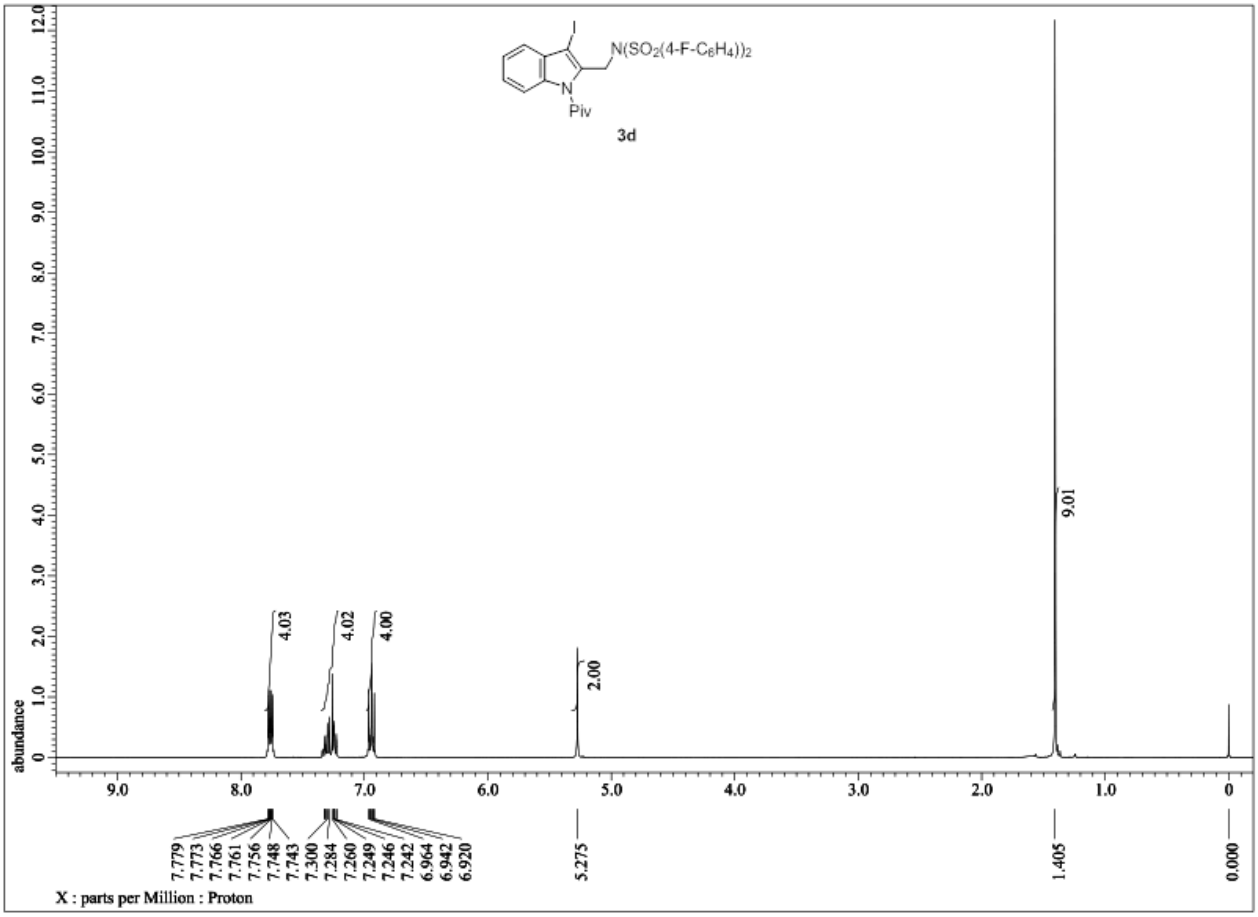

I
NTs2
N
Piv
3a
abundance
X : parts per Million : Carbon13
183.619
144.493
136.800
135.699
130.746
130.171
129.079
127.824
124.854
122.066
121.711
112.715
77.316
77.000
76.674
72.133
46.803
44.475
28.112
21.549

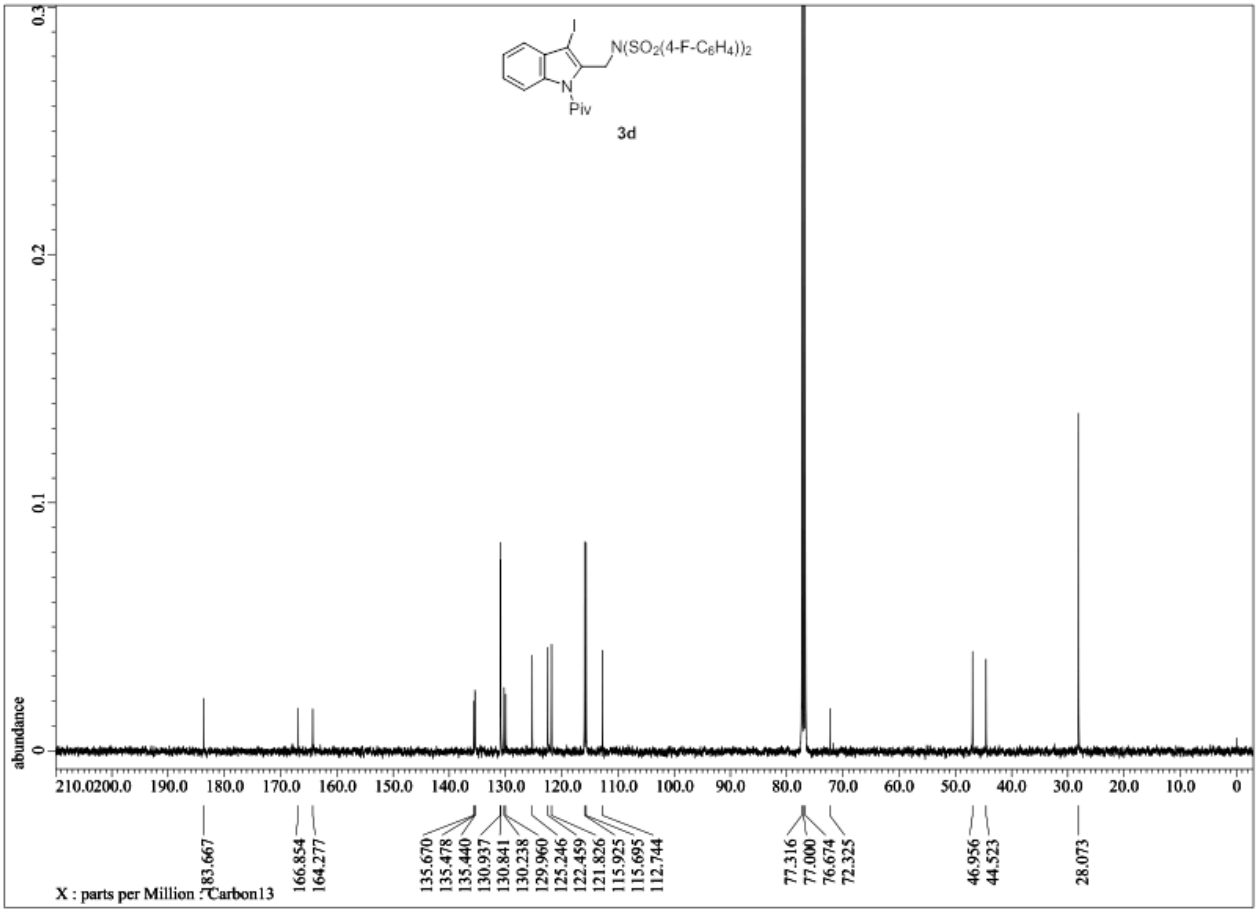

I
NMs2
N
Piv
3b
abundance
9.03
6.00
2.00
7.502
7.501
7.483
7.481
7.479
7.429
7.408
7.345
7.342
7.295
7.292
7.275
7.273
7.261
5.181
3.235
1.485
-0.000
X : parts per Million : Proton

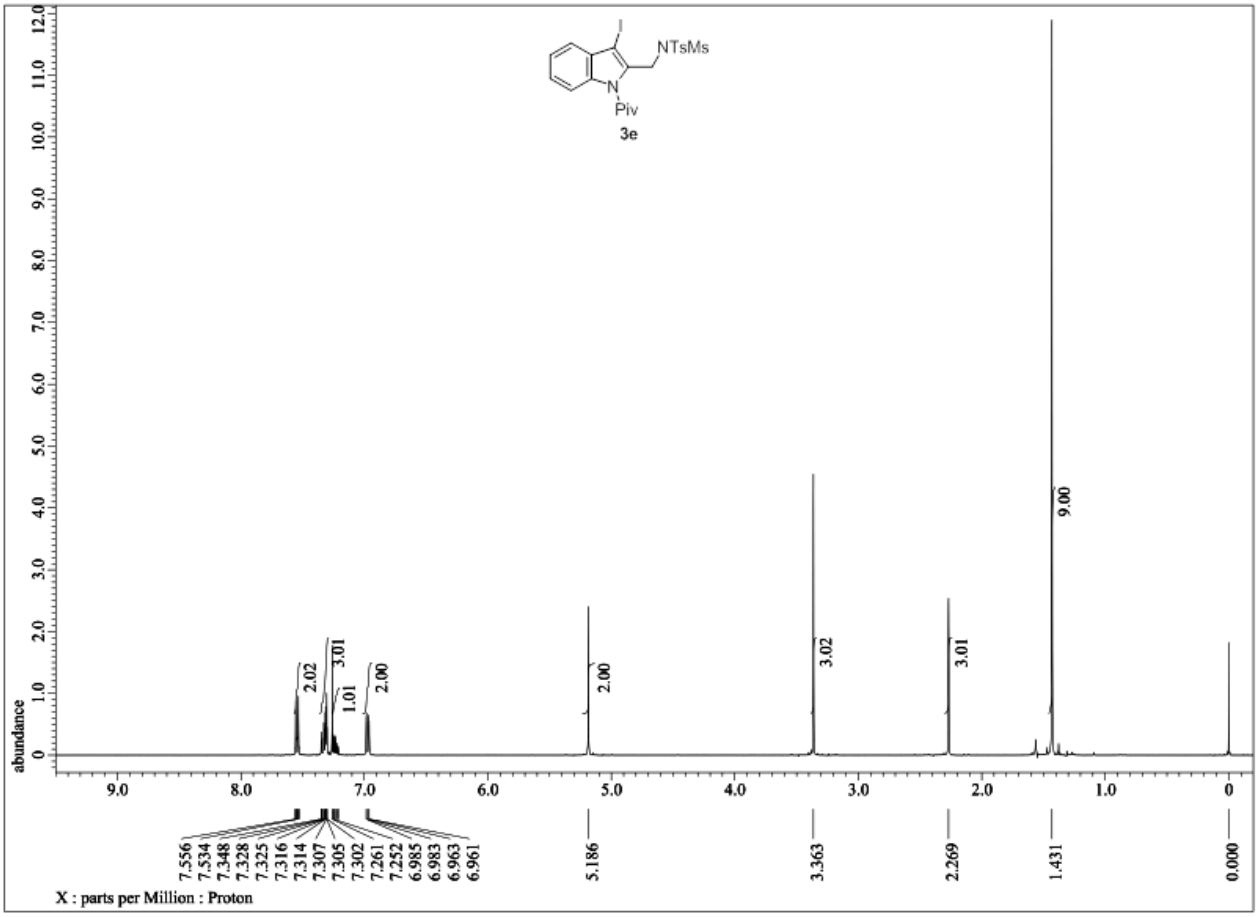

I
NMs2
N
Piv
3b
abundance
84.357
135.593
132.662
130.219
125.045
122.545
122.219
113.424
77.326
77.000
76.684
70.581
45.557
44.168
43.708
28.227
X : parts per Million : Carbon13

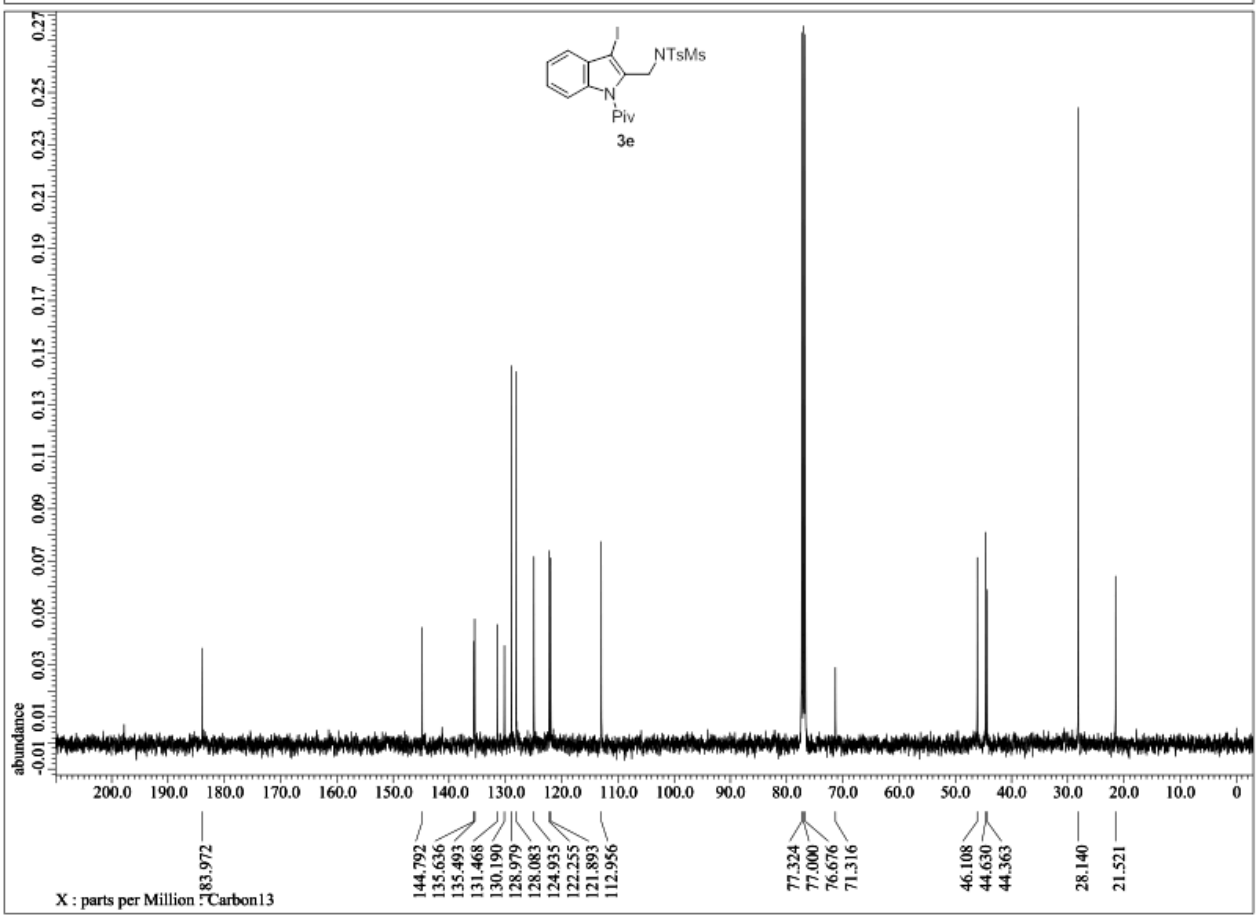

I
N(SO2Ph)2
N
Piv
3c
abundance
4.00
2.02
8.03
2.00
9.00
7.765
7.762
7.748
7.744
7.740
7.461
7.442
7.304
7.297
7.285
7.283
7.264
7.261
7.245
7.241
7.229
5.301
1.424
0.000
X : parts per Million : Proton

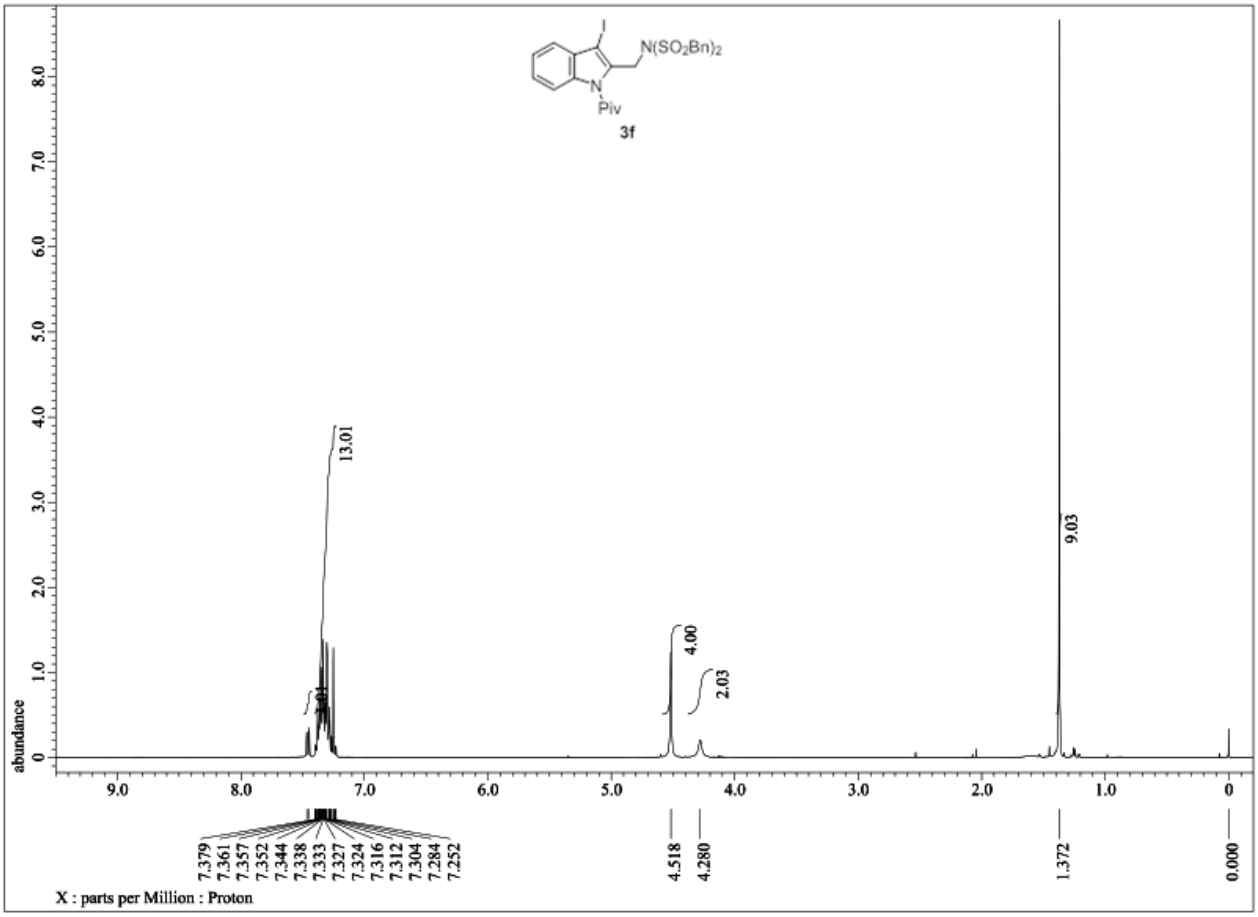

I
N(SO2Ph)2
N
Piv
3c
abundance
83.696
139.632
135.608
133.481
130.677
130.124
128.521
127.873
124.983
122.227
121.864
112.842
77.324
77.000
76.676
72.460
46.938
44.353
28.130
X : parts per Million : Carbon13

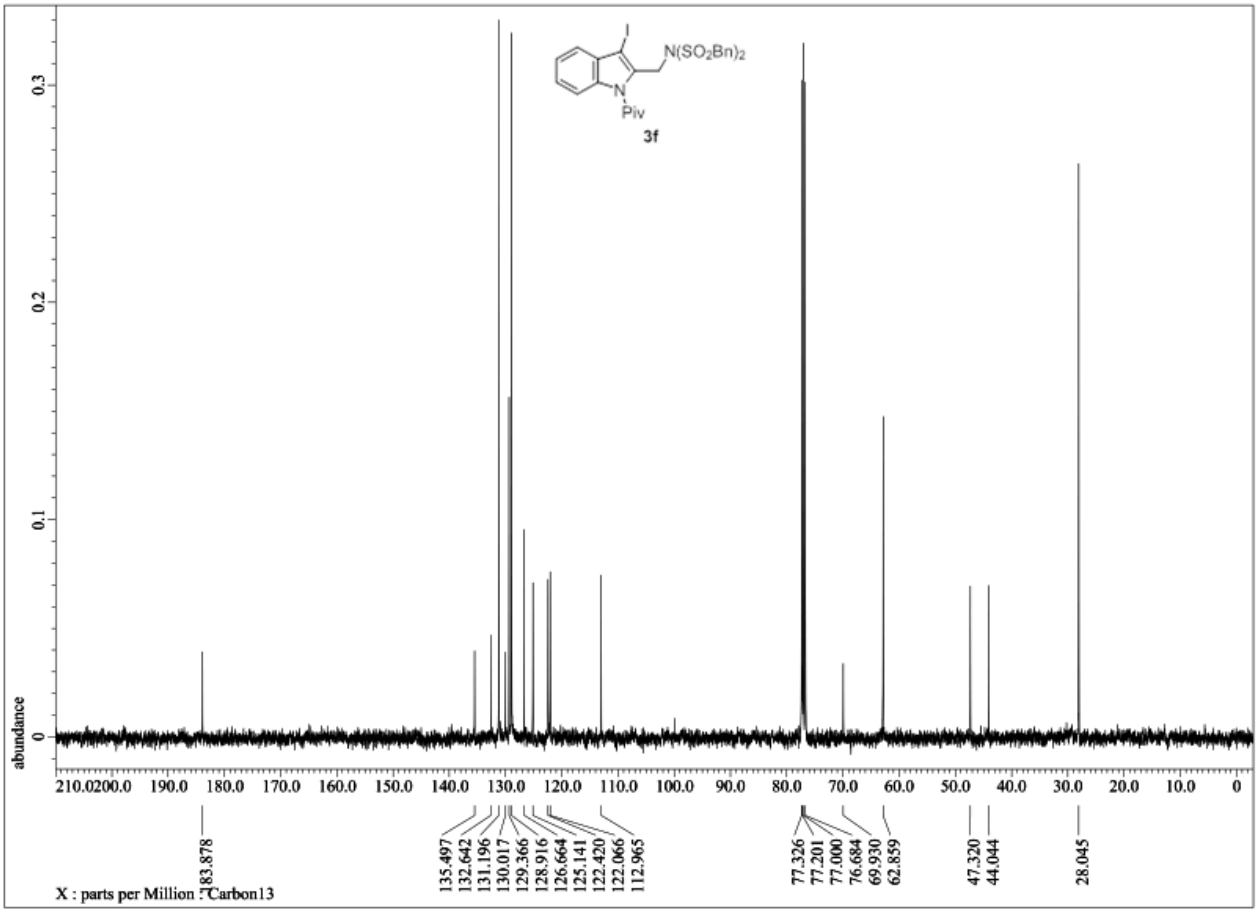

N(SO2(4-F-C6H4))2
Piv
3d
abundance
4.03
4.02
4.00
2.00
9.01
7.779
7.773
7.766
7.761
7.756
7.748
7.743
7.300
7.284
7.260
7.249
7.246
7.242
6.964
6.942
6.920
5.275
1.405
0.000
X : parts per Million : Proton

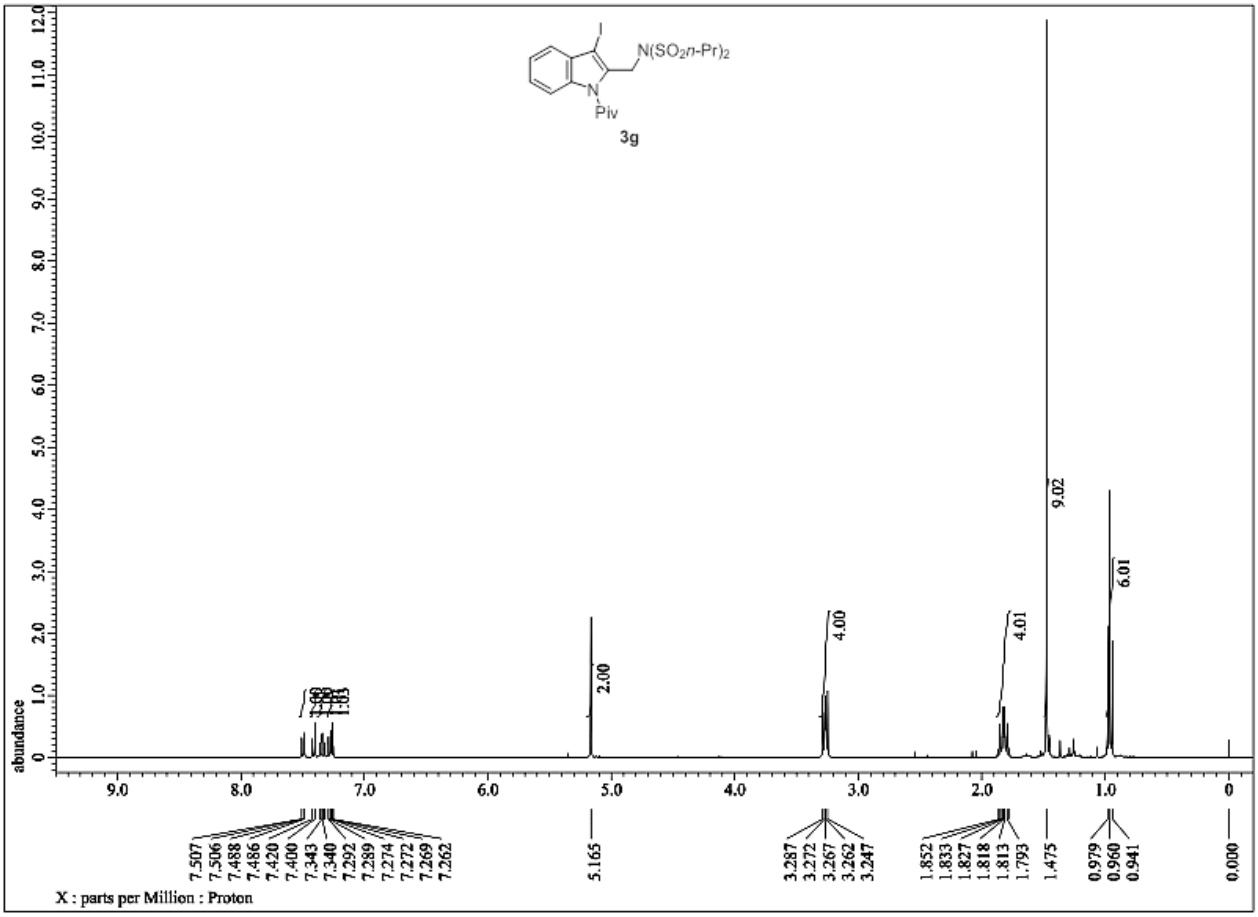

N(SO2(4-F-C6H4))2
Piv
3d
abundance
183.667
166.854
164.277
135.670
135.478
135.440
130.937
130.841
130.238
129.960
125.246
122.459
121.826
115.925
115.695
112.744
77.316
77.000
76.674
72.325
46.956
44.523
28.073
X : parts per Million : Carbon13

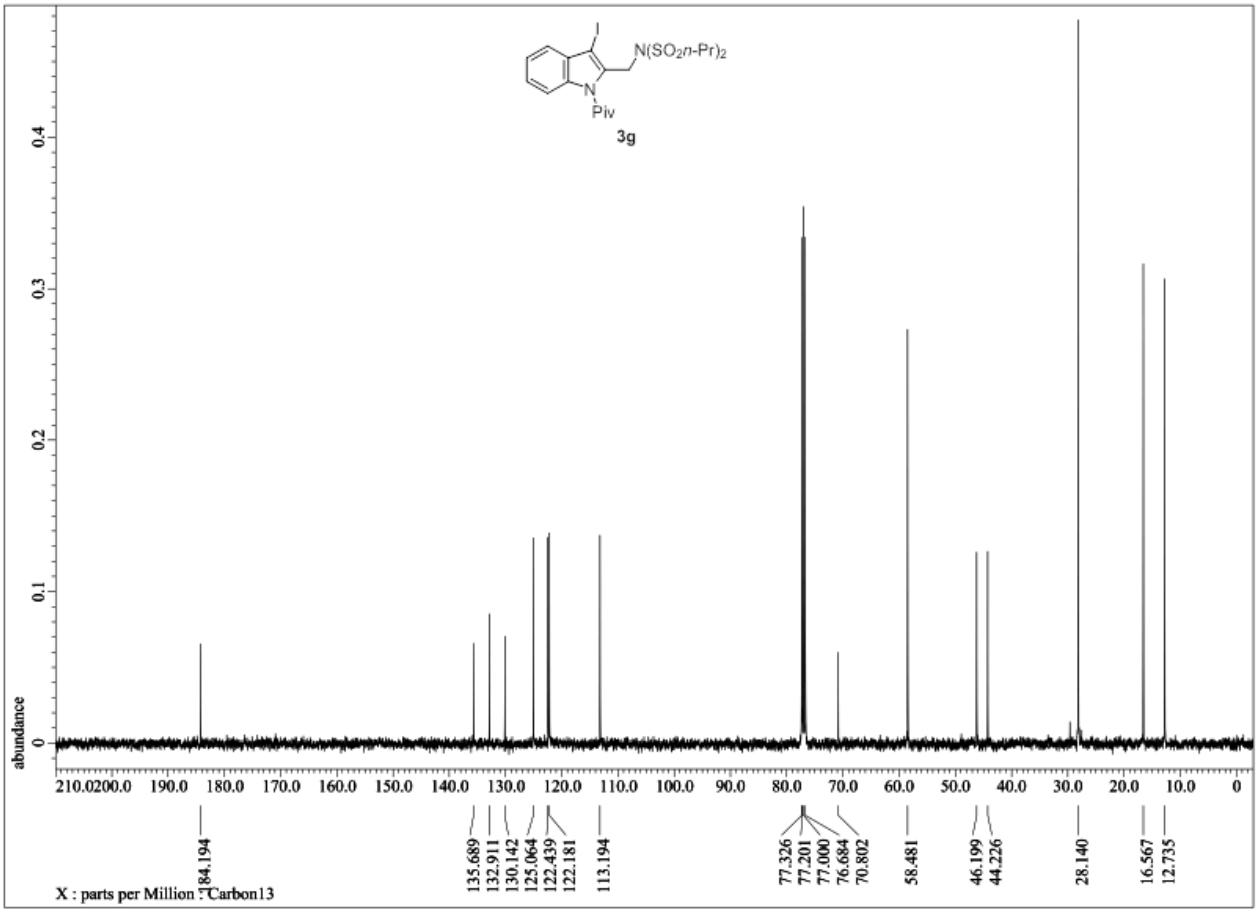

NTsMs
Piv
3e
abundance
2.02
3.01
1.01
2.00
2.00
3.02
3.01
9.00
7.556
7.534
7.348
7.328
7.325
7.316
7.314
7.307
7.305
7.302
7.261
7.252
6.985
6.983
6.963
6.961
5.186
3.363
2.269
1.431
0.000
X : parts per Million : Proton

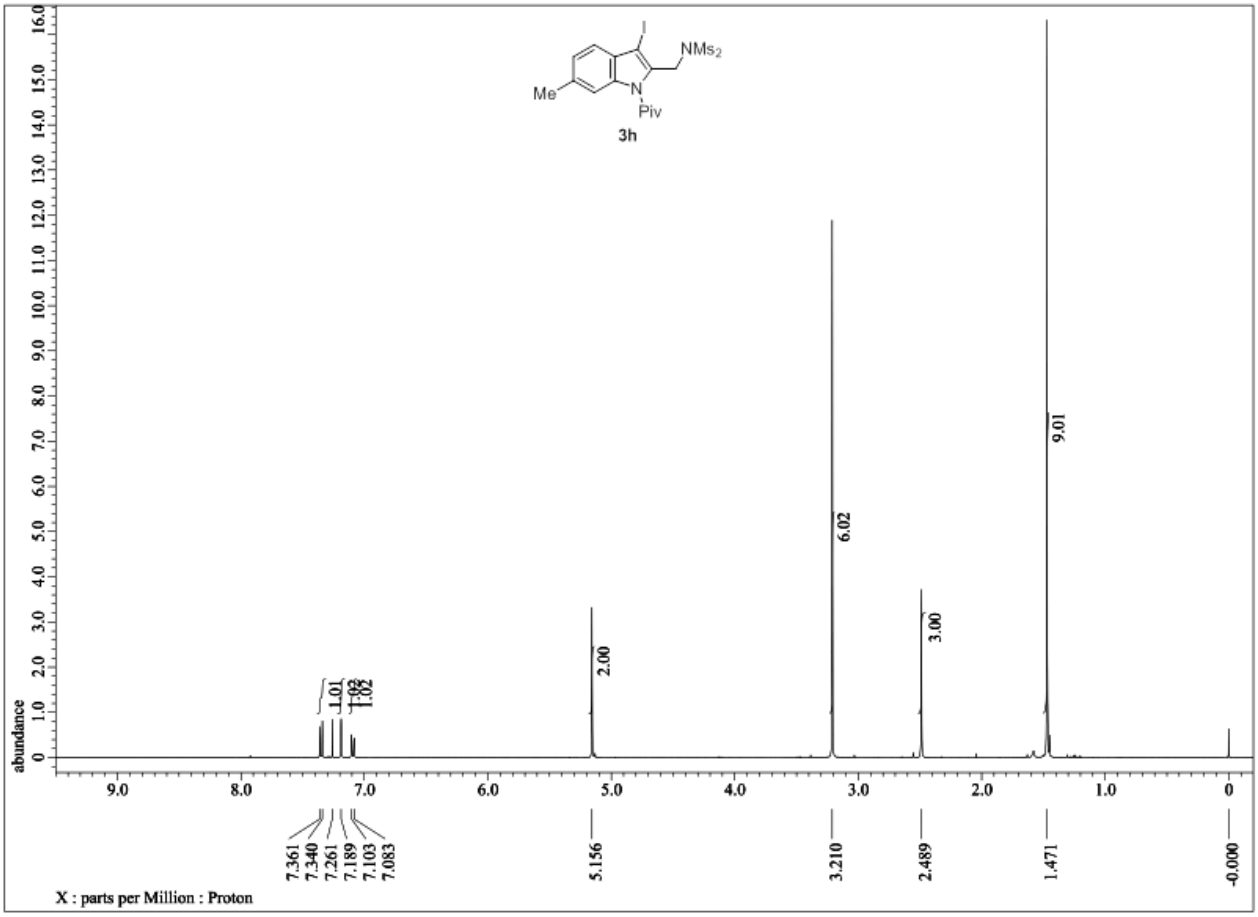

NTsMs
Piv
3e
abundance
183.972
144.792
135.636
135.493
131.468
130.190
128.979
128.083
124.935
122.255
121.893
112.956
77.324
77.000
76.676
71.316
46.108
44.630
44.363
28.140
21.521
X : parts per Million : Carbon13

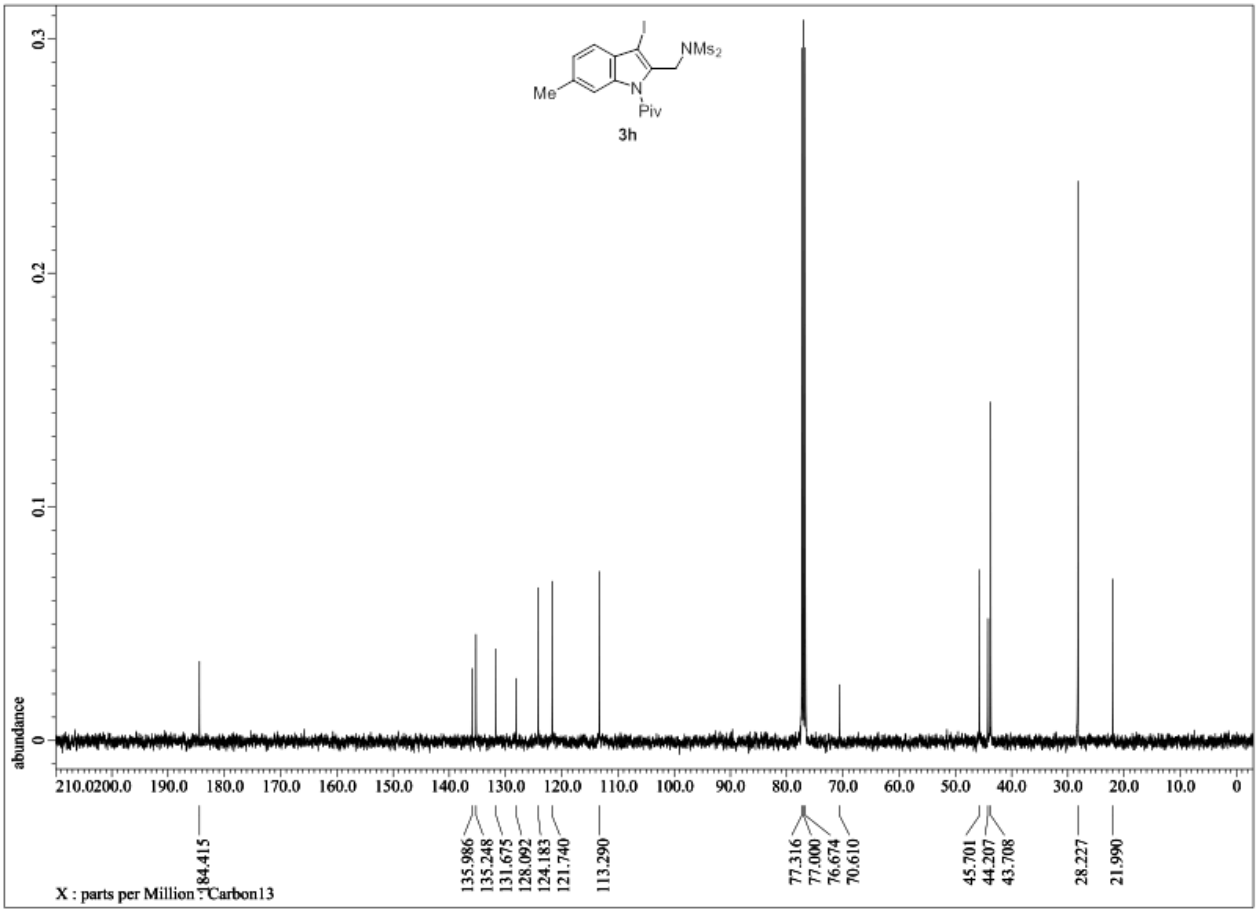

N(SO2Bn)2
Piv
3f
abundance
13.01
4.00
2.03
9.03
7.379
7.361
7.357
7.352
7.344
7.338
7.333
7.327
7.324
7.316
7.312
7.304
7.284
7.252
4.518
4.280
1.372
0.000
X : parts per Million : Proton

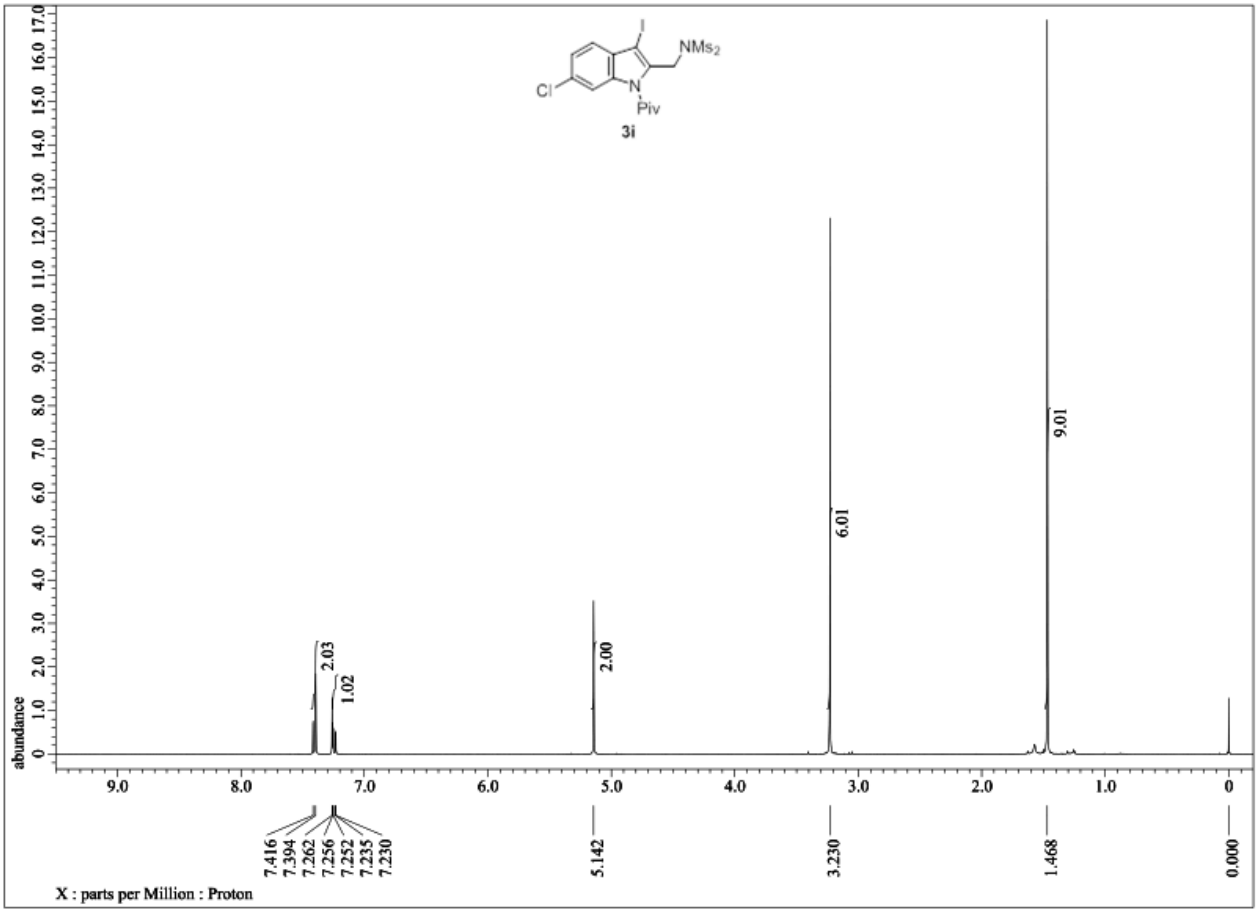

N(SO2Bn)2
Piv
3f
abundance
83.878
135.497
132.642
131.196
130.017
129.366
128.916
126.664
125.141
122.420
122.066
112.965
77.326
77.201
77.000
76.684
69.930
62.859
47.320
44.044
28.045
X : parts per Million : Carbon13

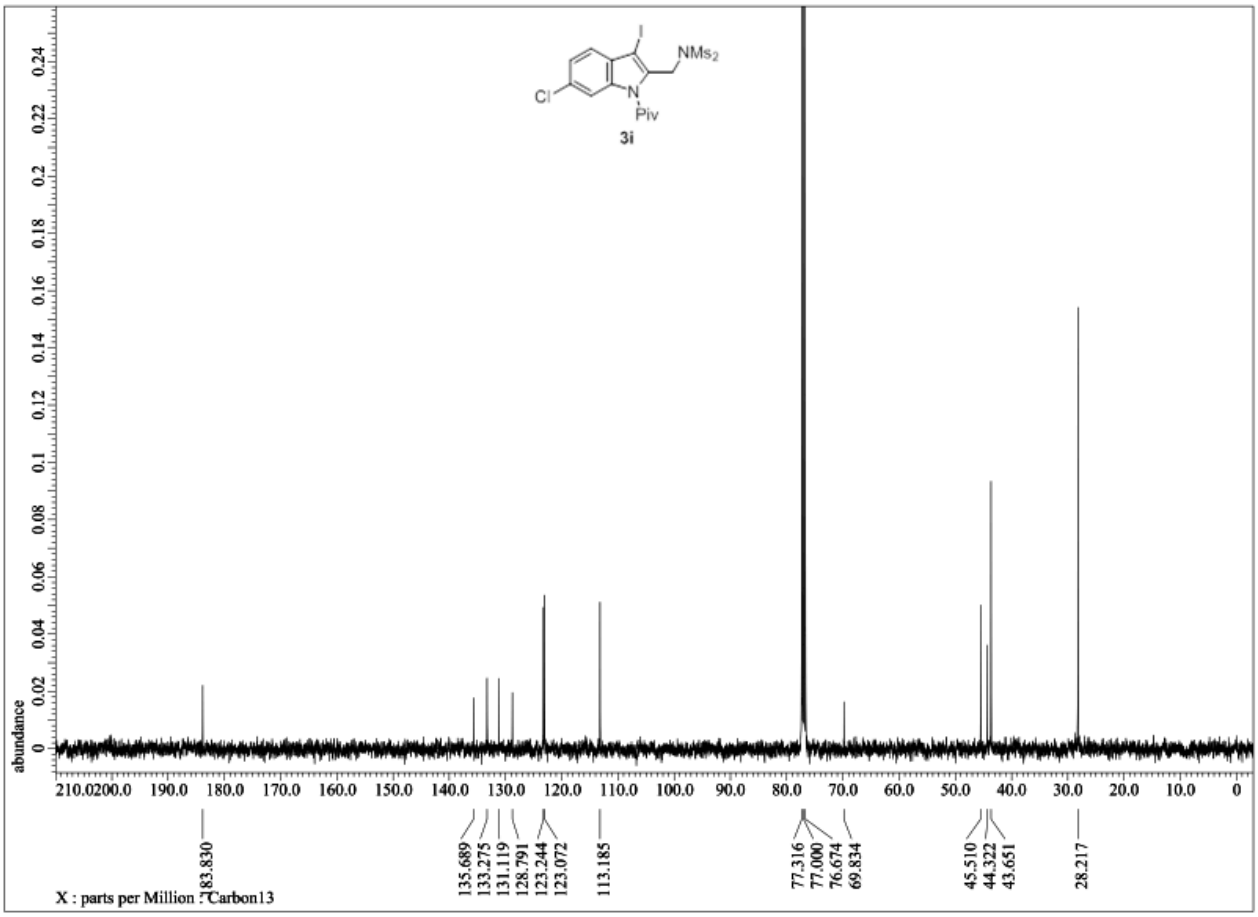

I
N(SO2n-Pr)2
N
Piv
3g
abundance
9.02
6.01
4.00
4.01
2.00
7.507
7.506
7.488
7.486
7.420
7.400
7.343
7.340
7.292
7.289
7.274
7.272
7.269
7.262
5.165
3.287
3.272
3.267
3.262
3.247
1.852
1.833
1.827
1.818
1.813
1.793
1.475
0.979
0.960
0.941
0.000
X : parts per Million : Proton

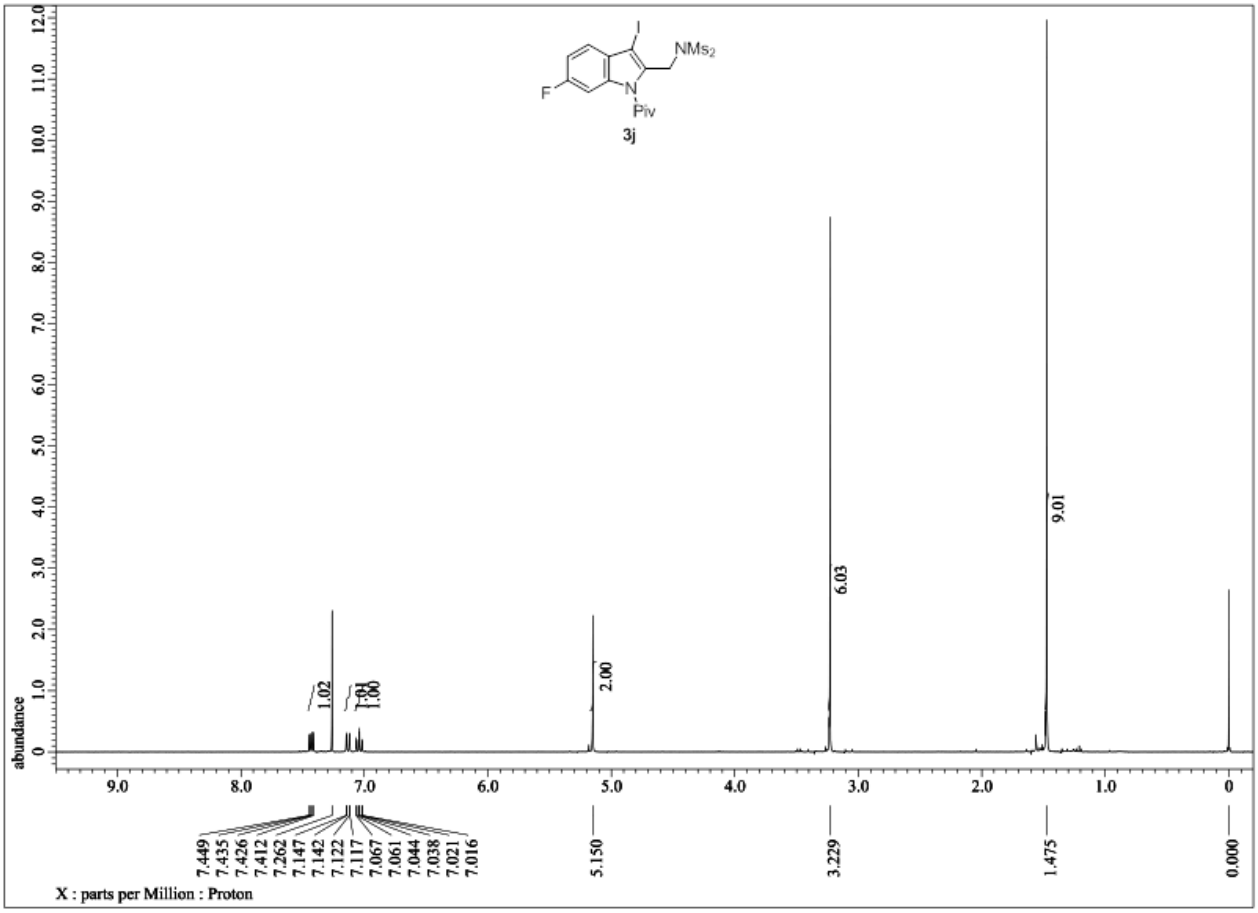

I
N(SO2n-Pr)2
N
Piv
3g
abundance
84.194
135.689
132.911
130.142
125.064
122.439
122.181
113.194
77.326
77.201
77.000
76.684
70.802
58.481
46.199
44.226
28.140
16.567
12.735
X : parts per Million : Carbon13

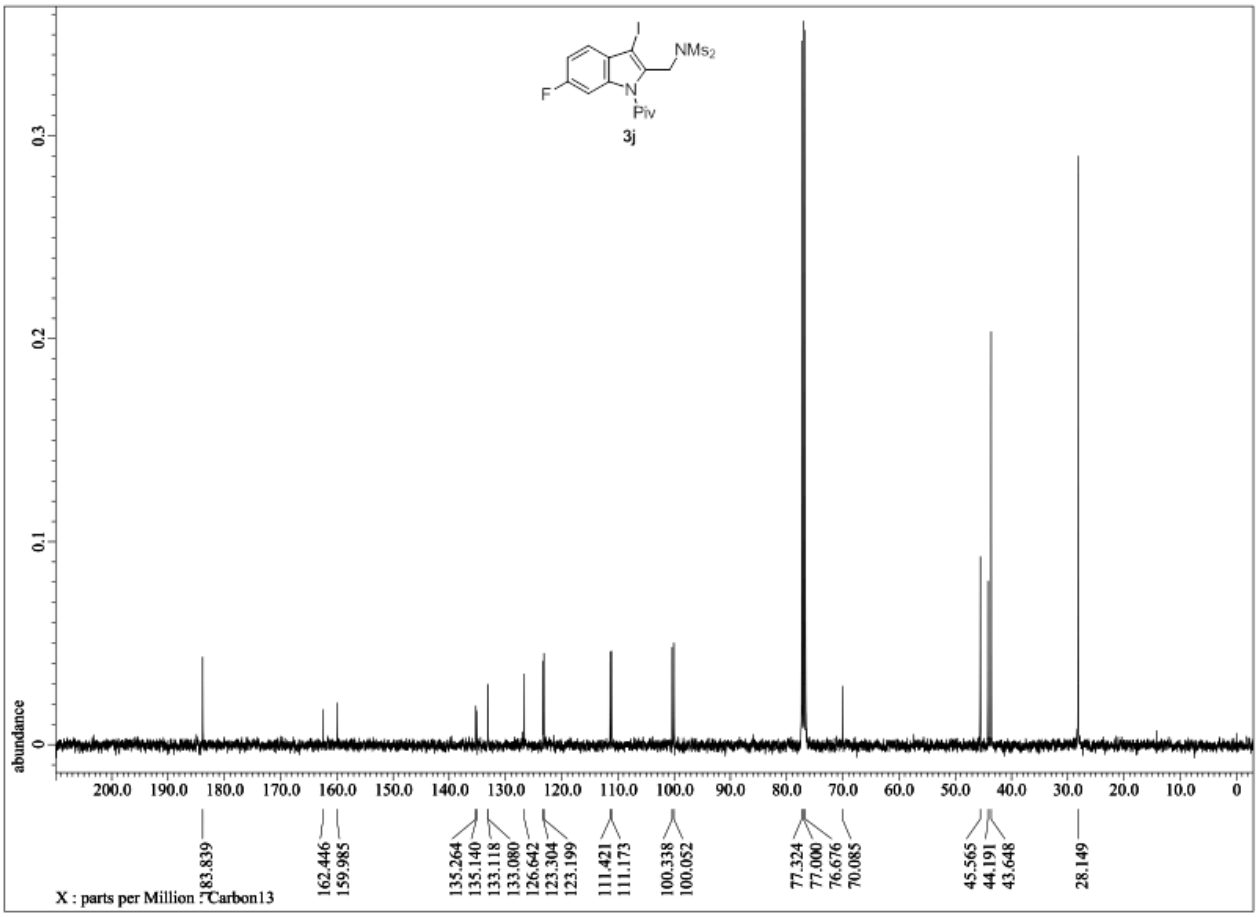

I
NMs2
Me
N
Piv
3h
abundance
X : parts per Million : Proton
7.361
7.340
7.261
7.189
7.103
7.083
5.156
3.210
2.489
1.471
-0.000
2.00
6.02
3.00
9.01

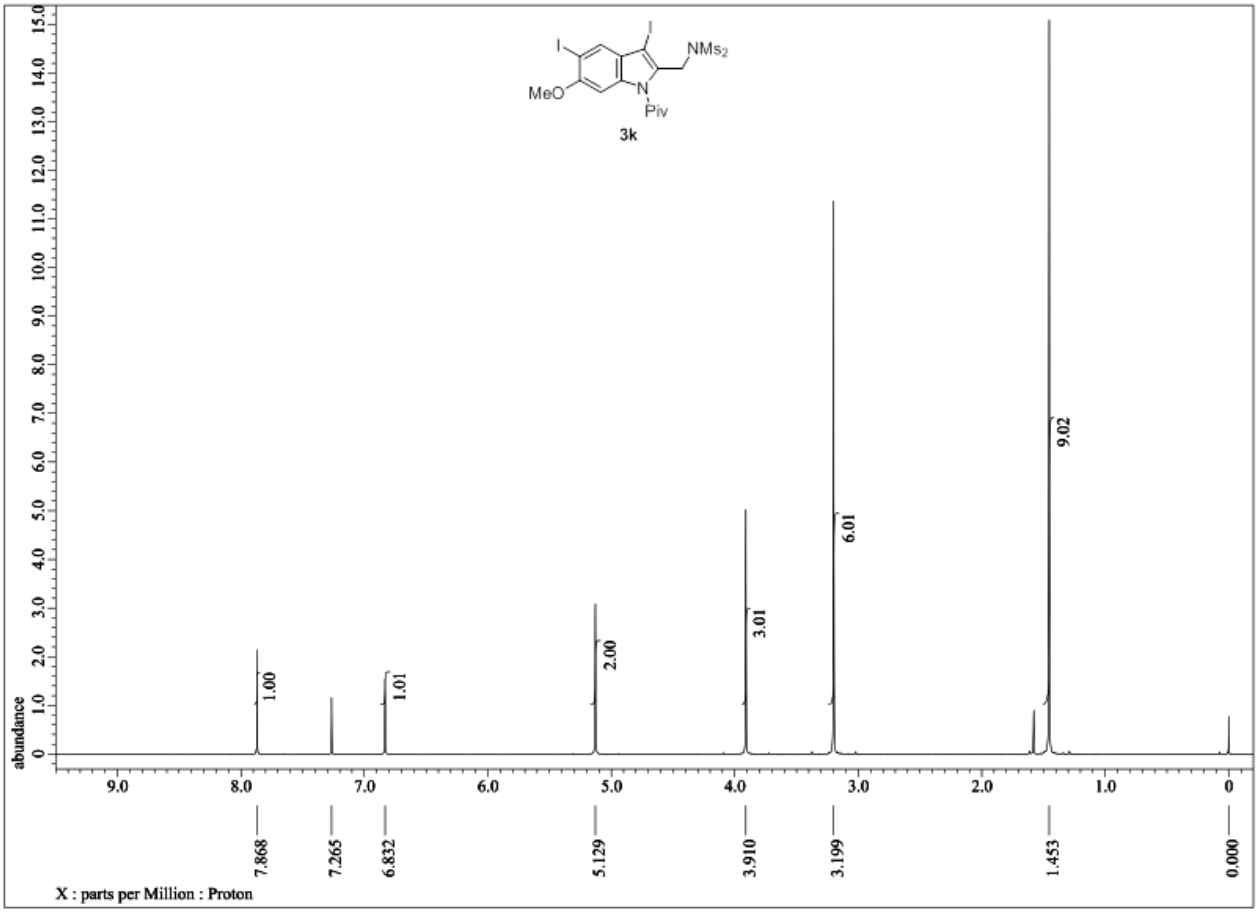

I
NMs2
Me
N
Piv
3h
abundance
X : parts per Million : Carbon13
84.415
135.986
135.248
131.675
128.092
124.183
121.740
113.290
77.316
77.000
76.674
70.610
45.701
44.207
43.708
28.227
21.990

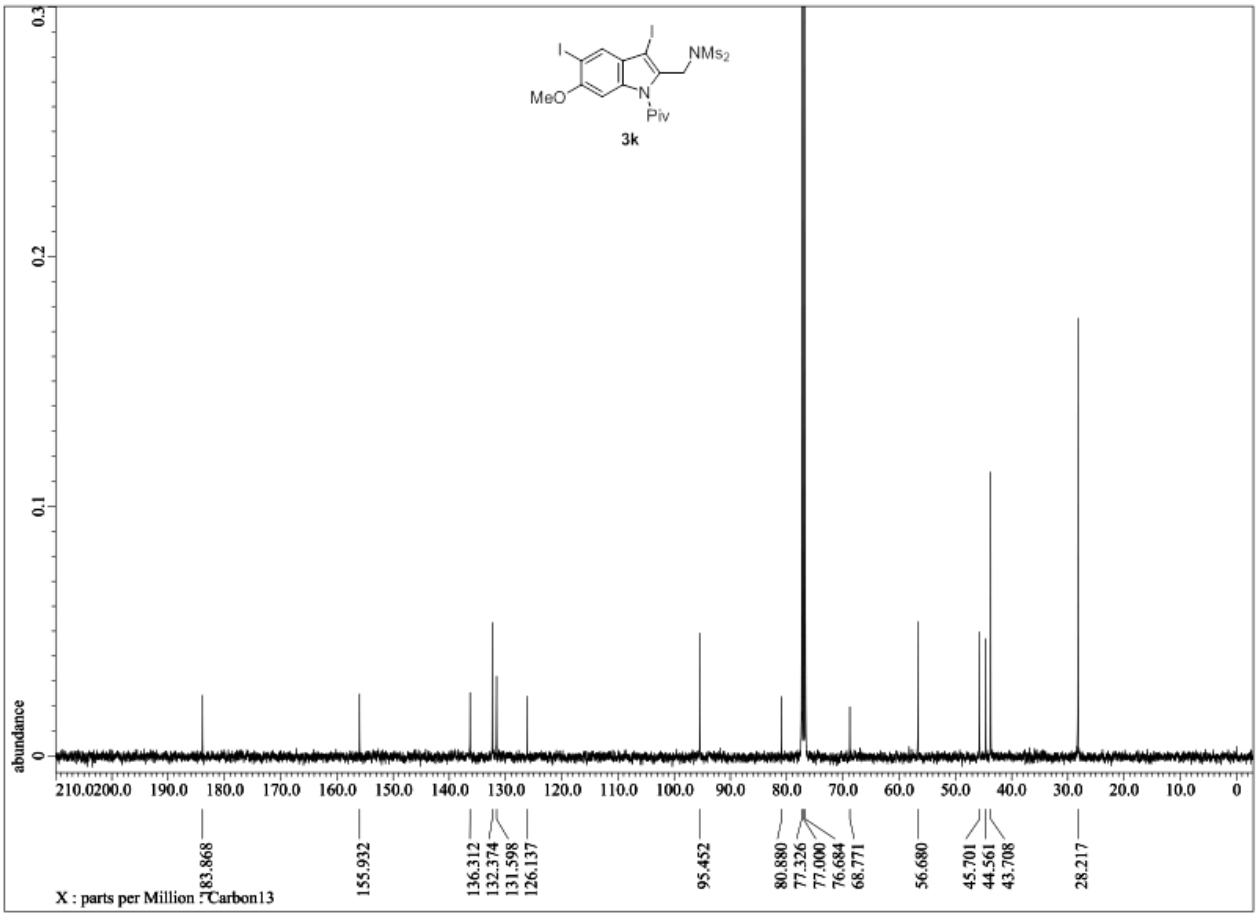

I
NMs2
Cl
N
Piv
3i
abundance
2.03
1.02
2.00
6.01
9.01
7.416
7.394
7.262
7.256
7.252
7.235
7.230
5.142
3.230
1.468
0.000
X : parts per Million : Proton

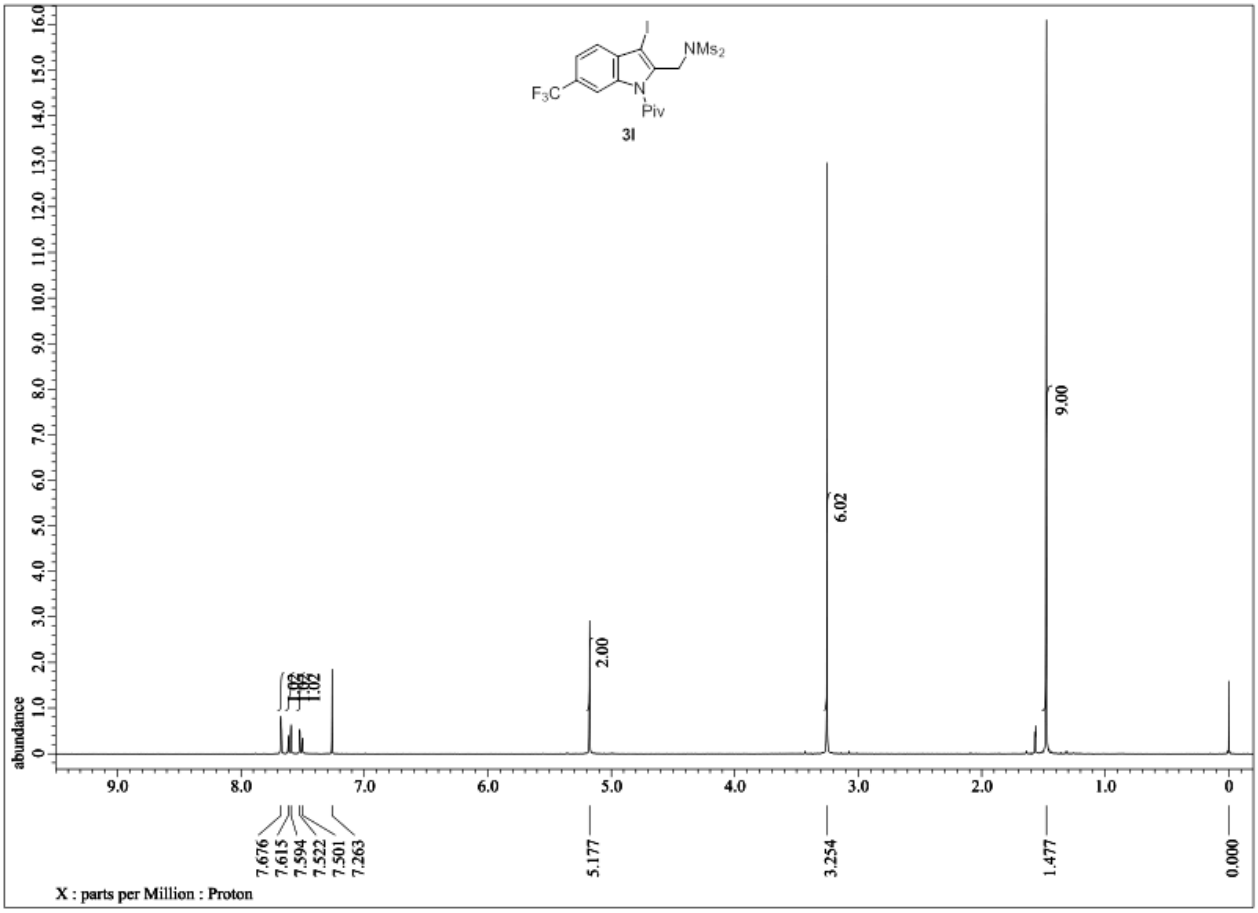

I
NMs2
Cl
N
Piv
3i
abundance
183.830
135.689
133.275
131.119
128.791
123.244
123.072
113.185
77.316
77.000
76.674
69.834
45.510
44.322
43.651
28.217
X : parts per Million : Carbon13

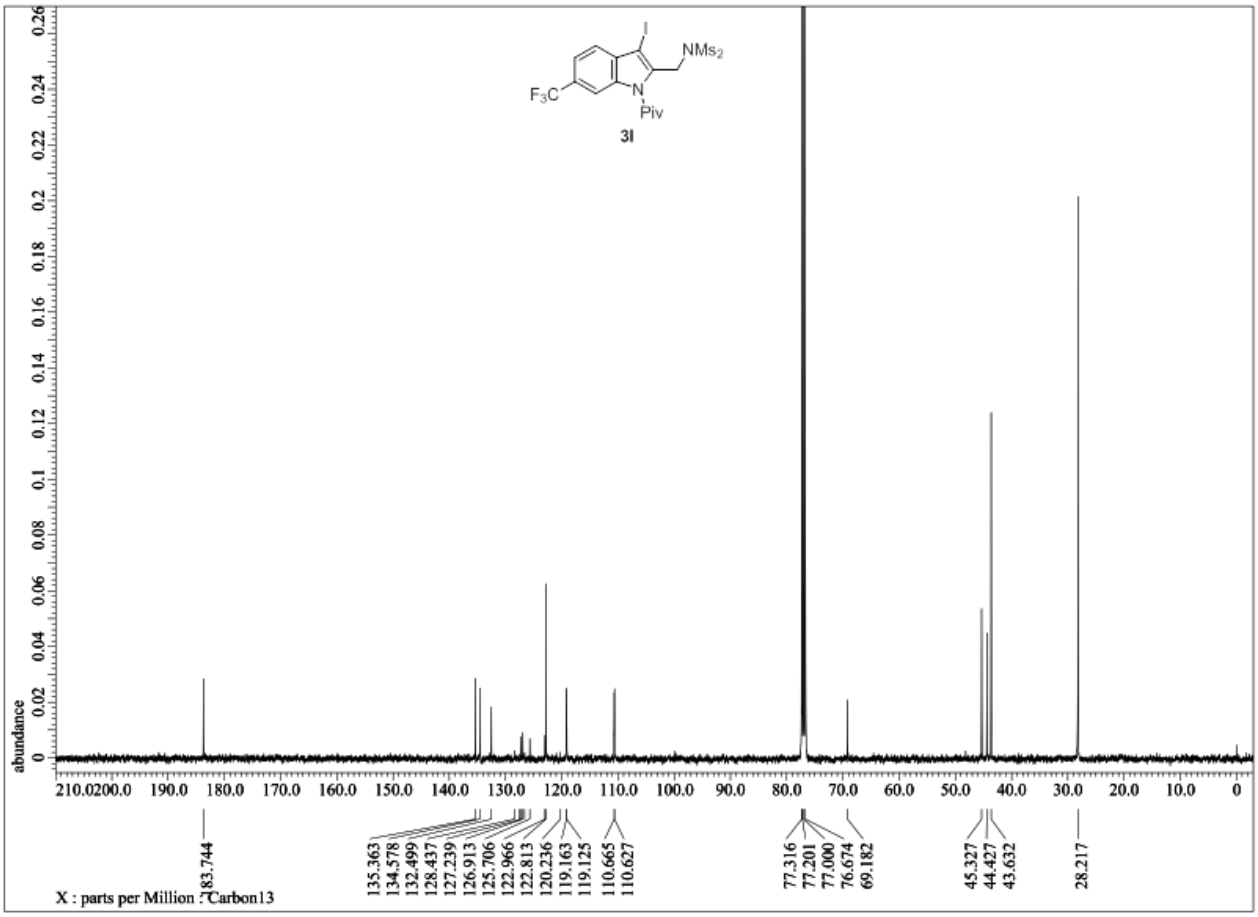

I
NMs2
F
N
Piv
3j
abundance
1.02
1.01
1.00
2.00
6.03
9.01
7.449
7.435
7.426
7.412
7.262
7.147
7.142
7.122
7.117
7.067
7.061
7.044
7.038
7.021
7.016
5.150
3.229
1.475
0.000
X : parts per Million : Proton

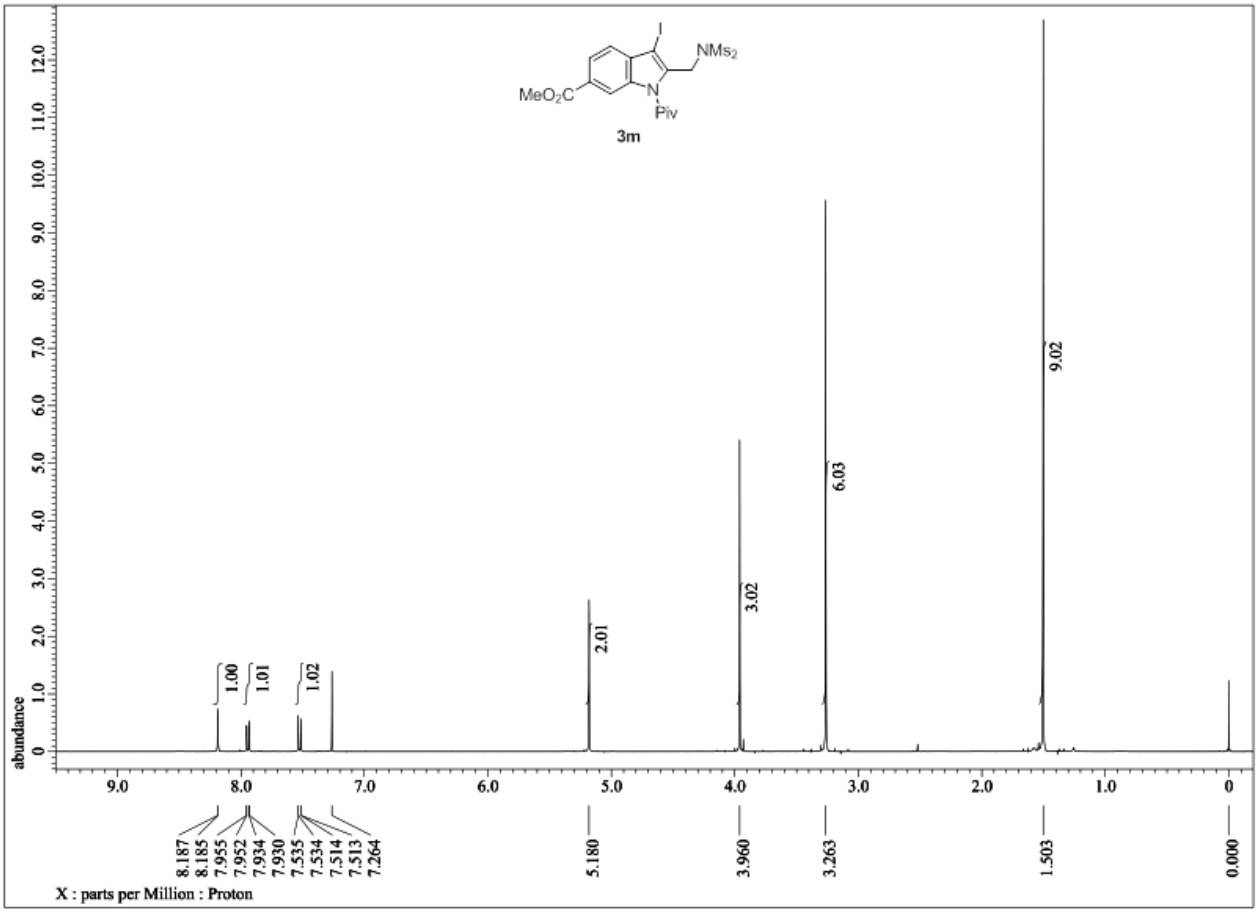

I
NMs2
F
N
Piv
3j
abundance
183.839
162.446
159.985
135.264
135.140
133.118
133.080
126.642
123.304
123.199
111.421
111.173
100.338
100.052
77.324
77.000
76.676
70.085
45.565
44.191
43.648
28.149
X : parts per Million : Carbon13

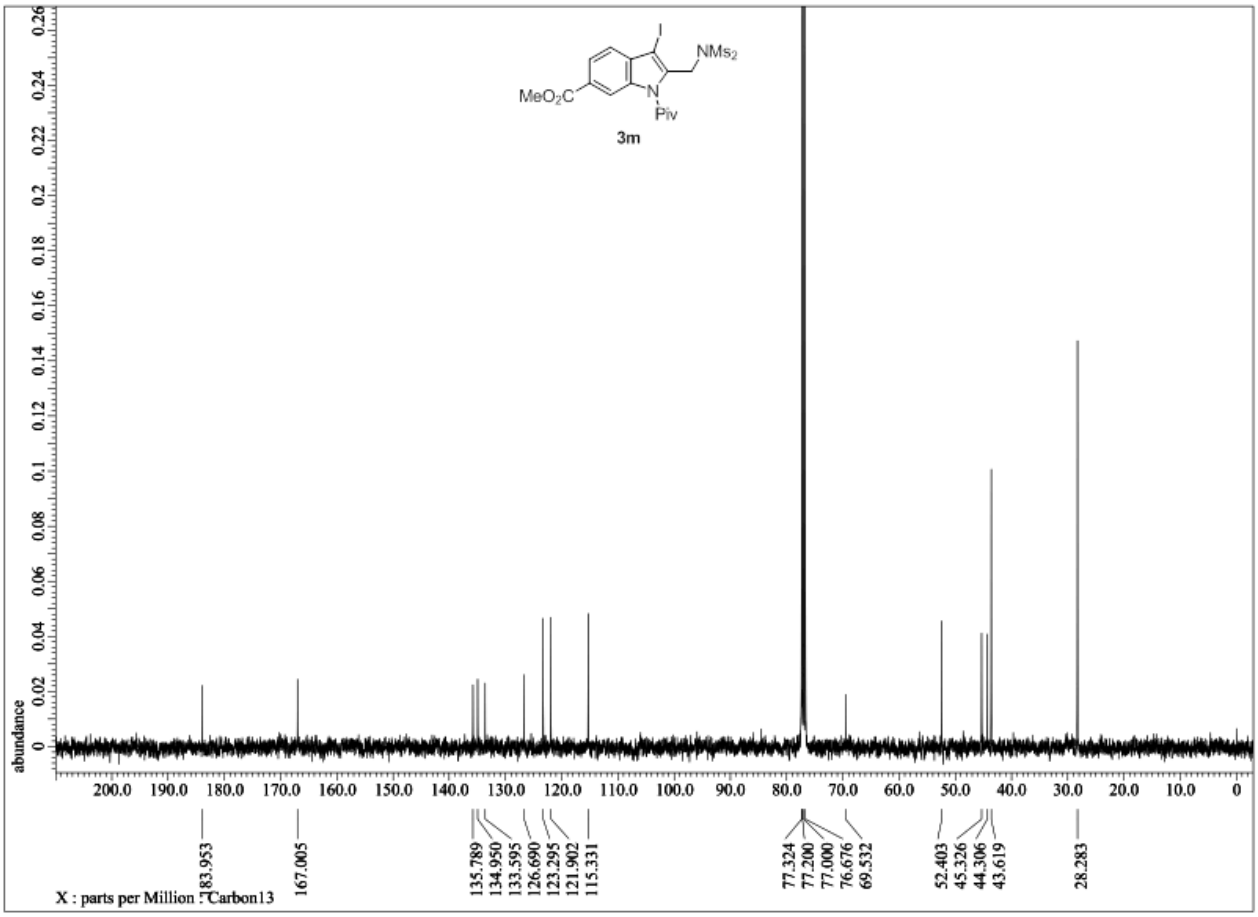

I
I
NMs2
MeO
N
Piv
3k
abundance
1.00
1.01
2.00
3.01
6.01
9.02
7.868
7.265
6.832
5.129
3.910
3.199
1.453
0.000
X : parts per Million : Proton

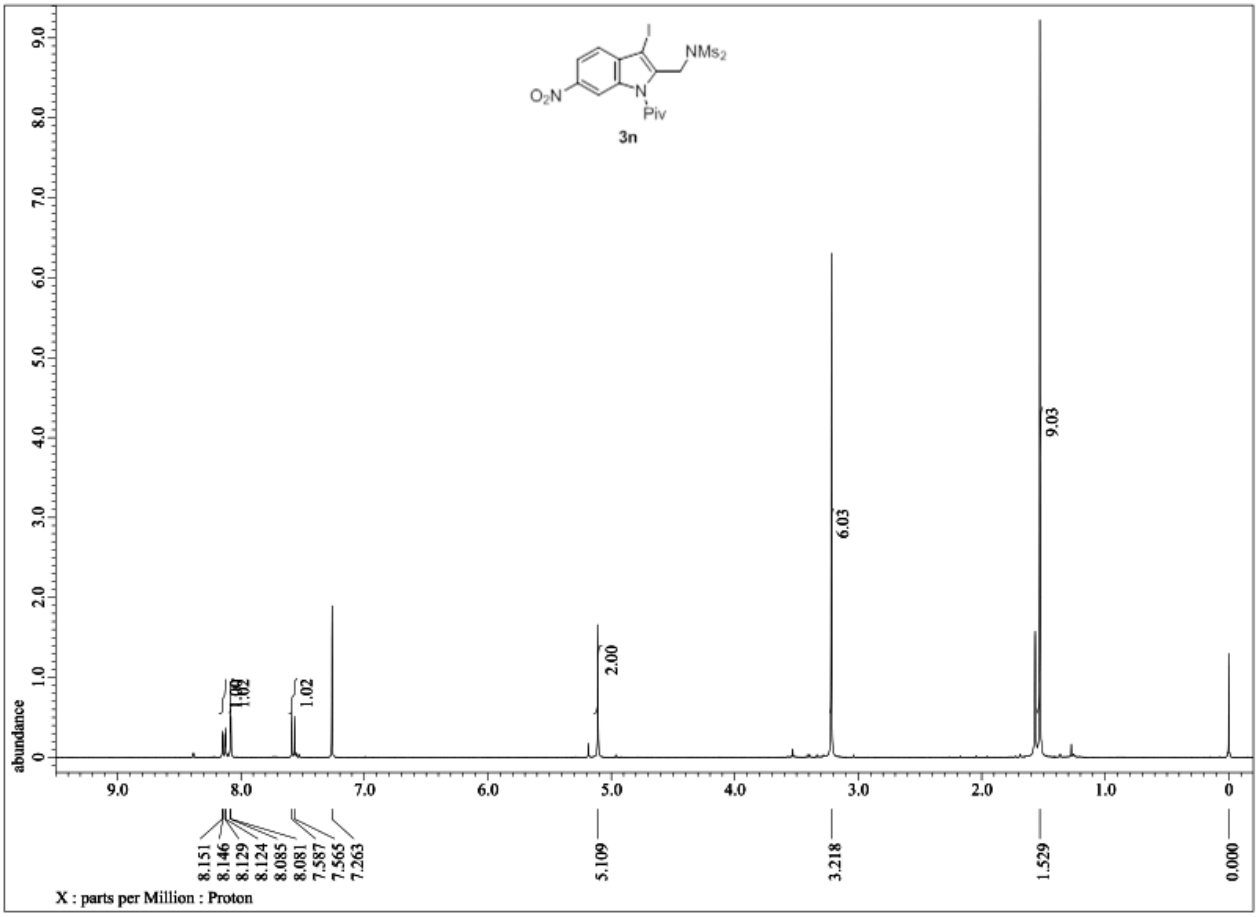

I
I
NMs2
MeO
N
Piv
3k
abundance
183.868
155.932
136.312
132.374
131.598
126.137
95.452
80.880
77.326
77.000
76.684
68.771
56.680
45.701
44.561
43.708
28.217
X : parts per Million : Carbon13

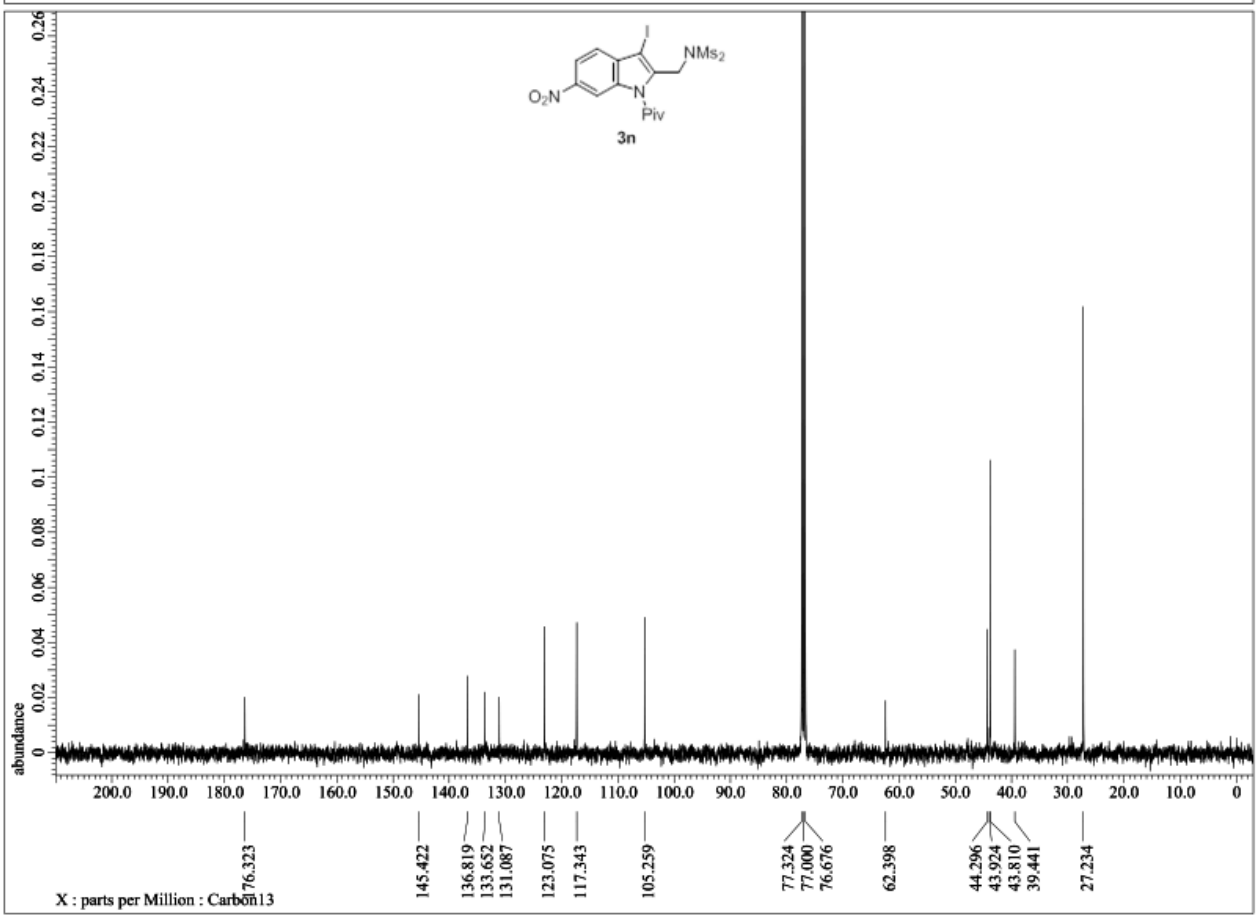

I
NMs2
F3C
N
Piv
3l
abundance
2.00
6.02
9.00
7.676
7.615
7.594
7.522
7.501
7.263
5.177
3.254
1.477
0.000
X : parts per Million : Proton

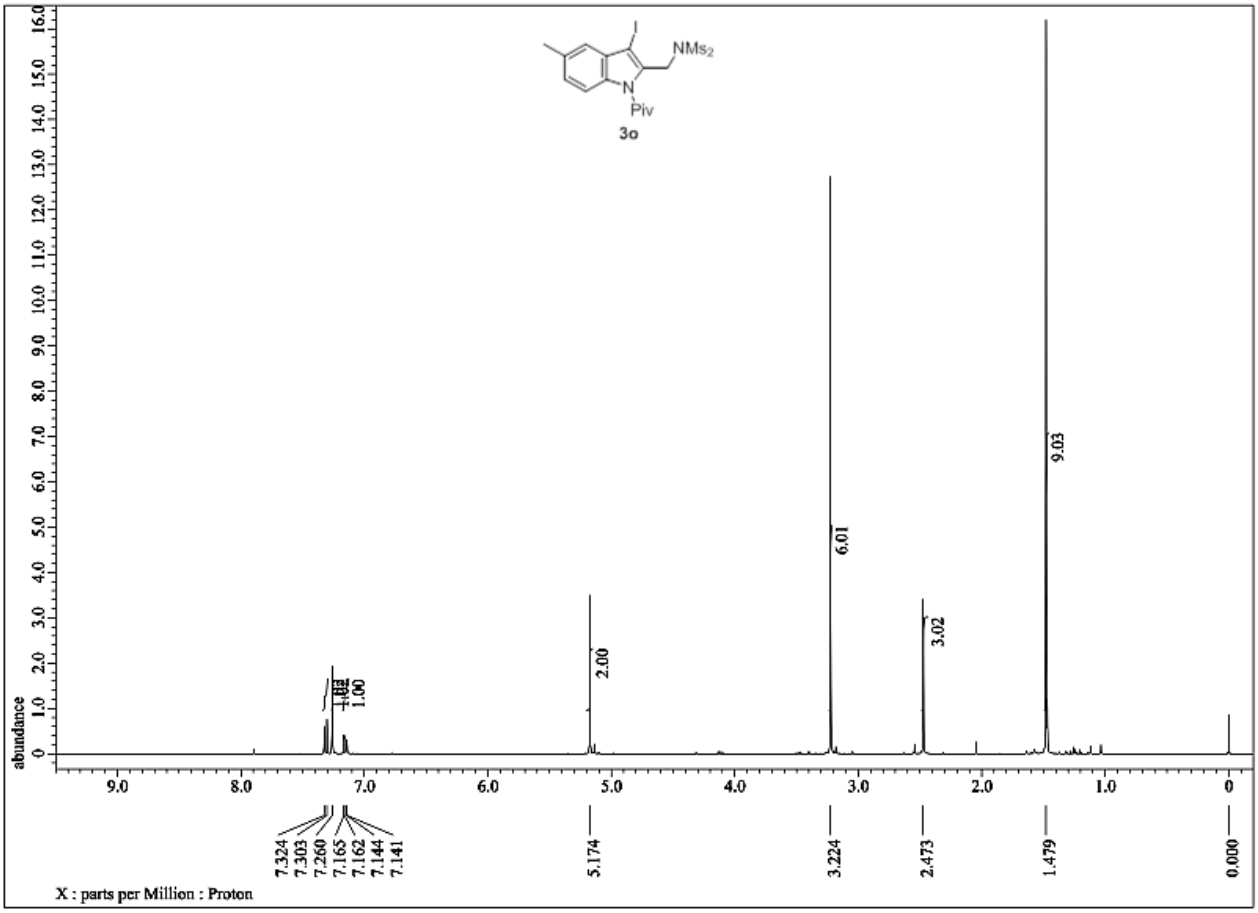

I
NMs2
F3C
N
Piv
3l
abundance
183.744
135.363
134.578
132.499
128.437
127.239
126.913
125.706
122.966
122.813
120.236
119.163
119.125
110.665
110.627
77.316
77.201
77.000
76.674
69.182
45.327
44.427
43.632
28.217
X : parts per Million : Carbon13

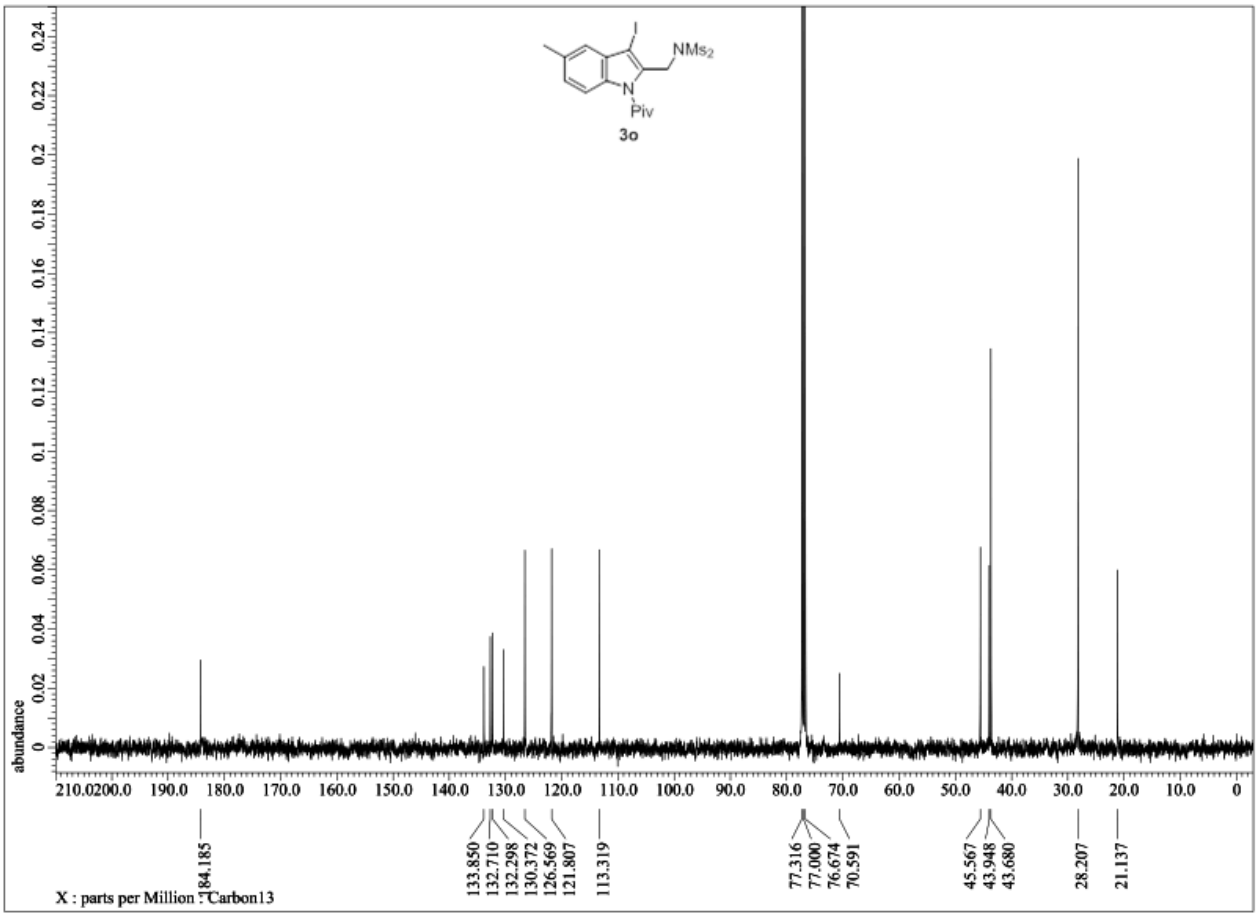

I
NMs2
MeO2C
N
Piv
3m
abundance
X : parts per Million : Proton
1.00
1.01
1.02
2.01
3.02
6.03
9.02
8.187
8.185
7.955
7.952
7.934
7.930
7.535
7.534
7.514
7.513
7.264
5.180
3.960
3.263
1.503
0.000

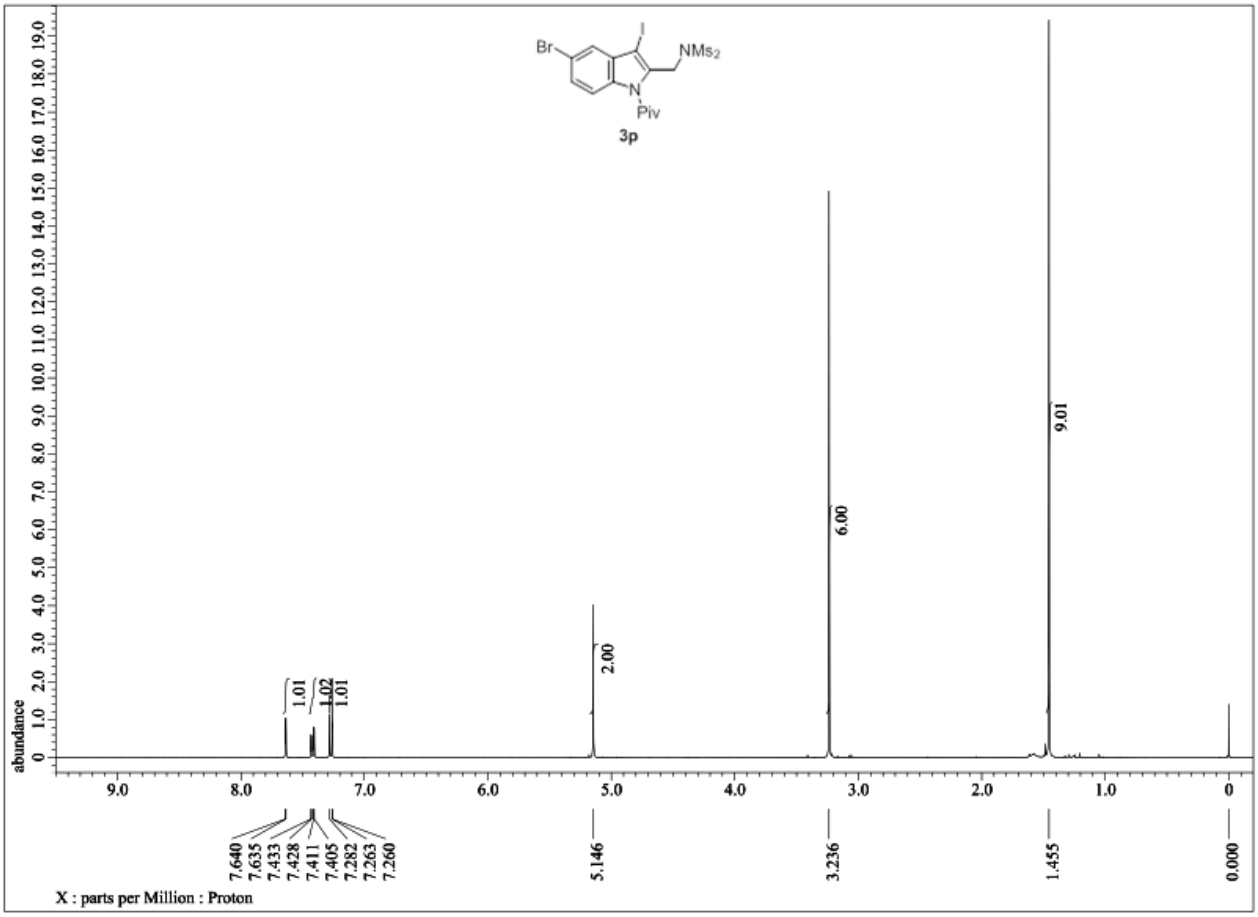

I
NMs2
MeO2C
N
Piv
3m
abundance
X : parts per Million : Carbon13
183.953
167.005
135.789
134.950
133.595
126.690
123.295
121.902
115.331
77.324
77.200
77.000
76.676
69.532
52.403
45.326
44.306
43.619
28.283

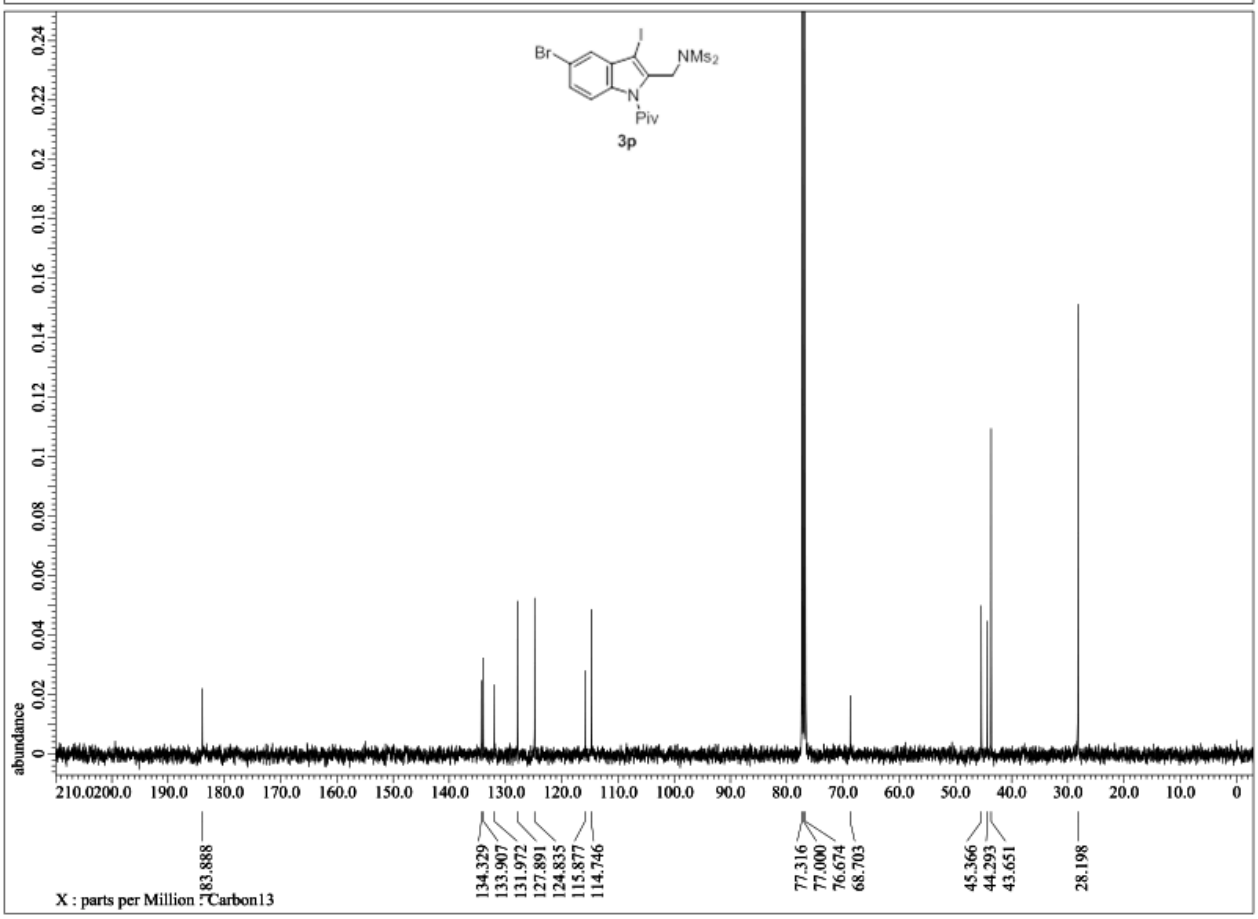

I
NMs2
O2N
N
Piv
3n
abundance
9.03
6.03
2.00
1.02
8.151
8.146
8.129
8.124
8.085
8.081
7.587
7.565
7.263
5.109
3.218
1.529
0.000
X : parts per Million : Proton

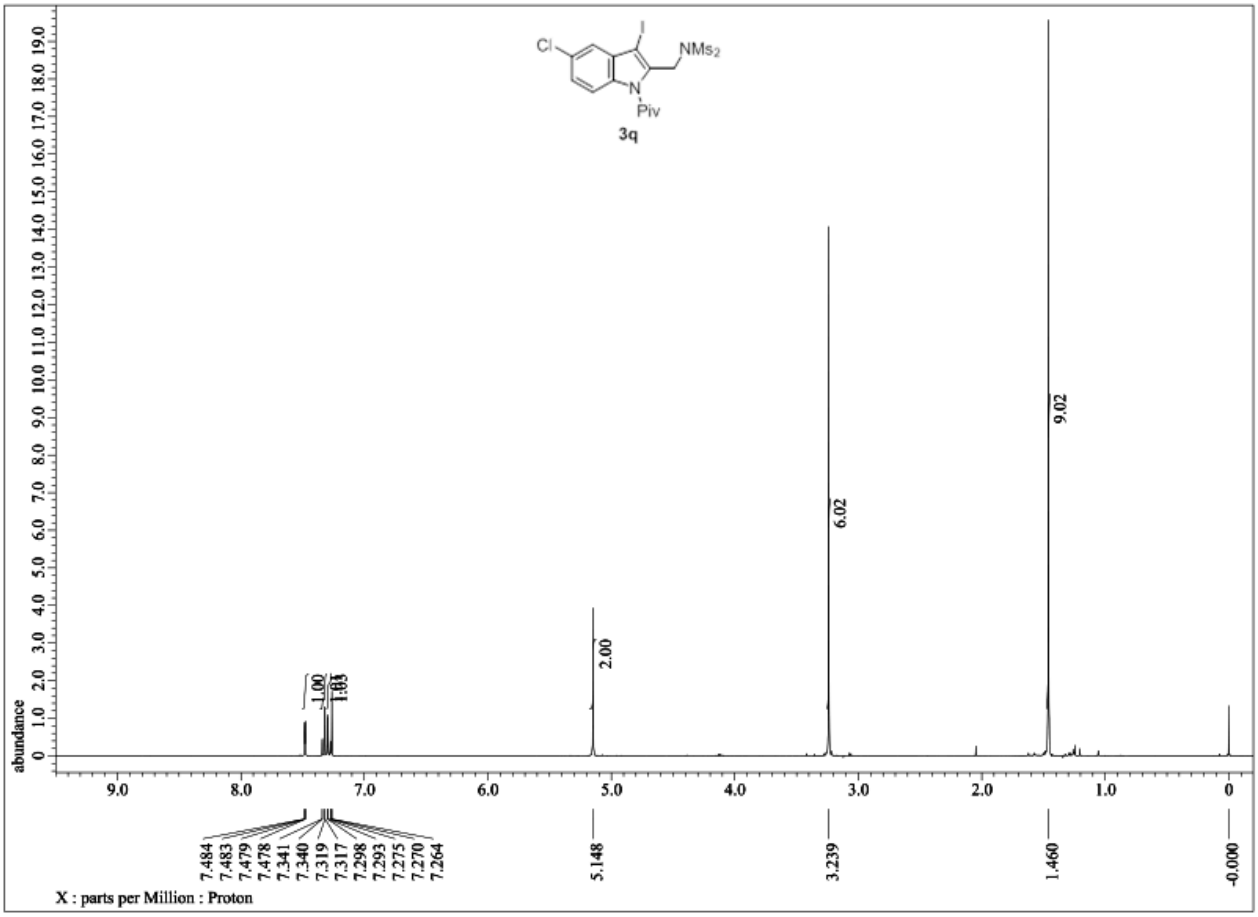

I
NMs2
O2N
N
Piv
3n
abundance
76.323
145.422
136.819
133.652
131.087
123.075
117.343
105.259
77.324
77.000
76.676
62.398
44.296
43.924
43.810
39.441
27.234
X : parts per Million : Carbon13

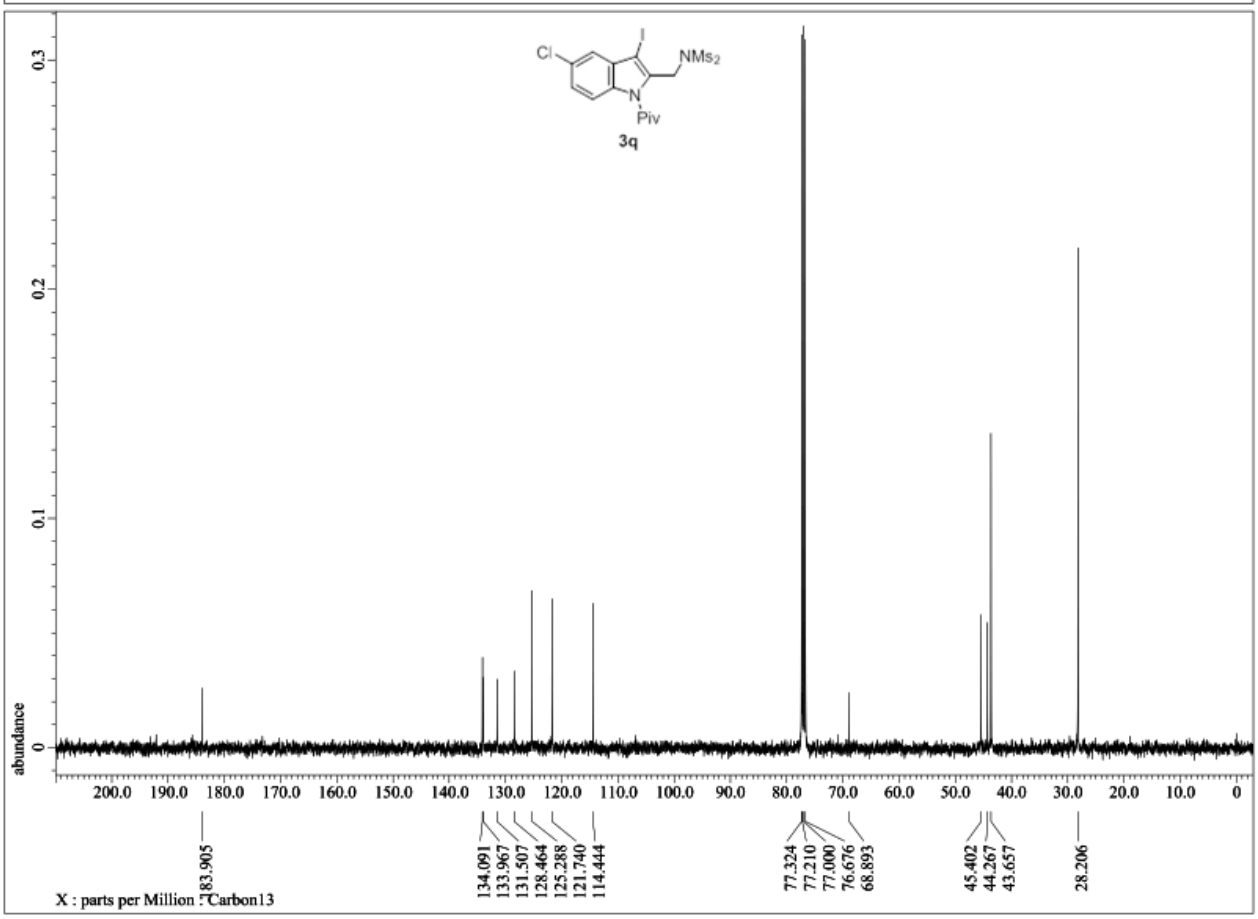

I
NMs2
N
Piv
3o
abundance
9.03
6.01
3.02
2.00
1.00
7.324
7.303
7.260
7.165
7.162
7.144
7.141
5.174
3.224
2.473
1.479
0.000
X : parts per Million : Proton

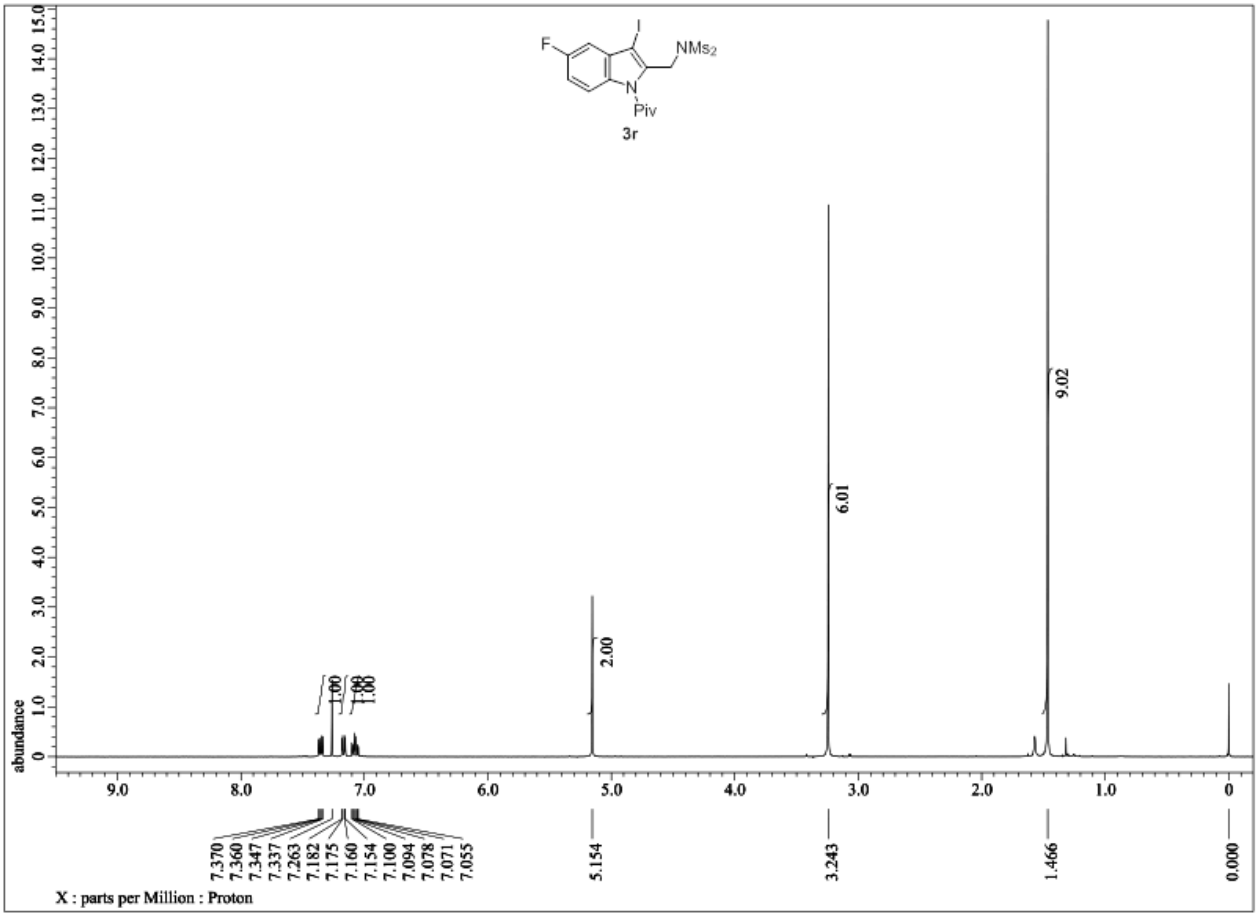

I
NMs2
N
Piv
3o
abundance
184.185
133.850
132.710
132.298
130.372
126.569
121.807
113.319
77.316
77.000
76.674
70.591
45.567
43.948
43.680
28.207
21.137
X : parts per Million : Carbon13

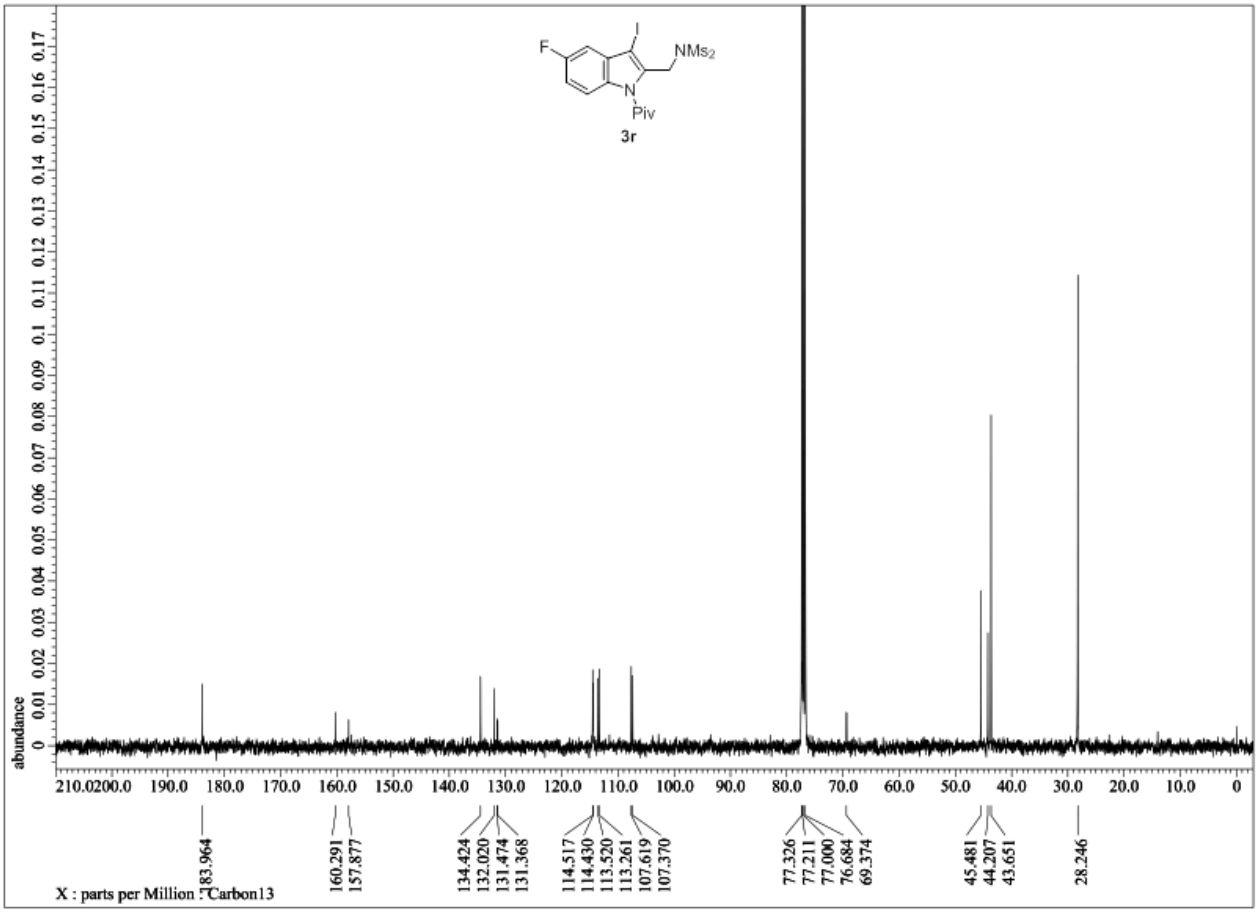

Br
I
NMs2
N
Piv
3p
abundance
1.01
1.02
1.01
2.00
6.00
9.01
7.640
7.635
7.433
7.428
7.411
7.405
7.282
7.263
7.260
5.146
3.236
1.455
0.000
X : parts per Million : Proton

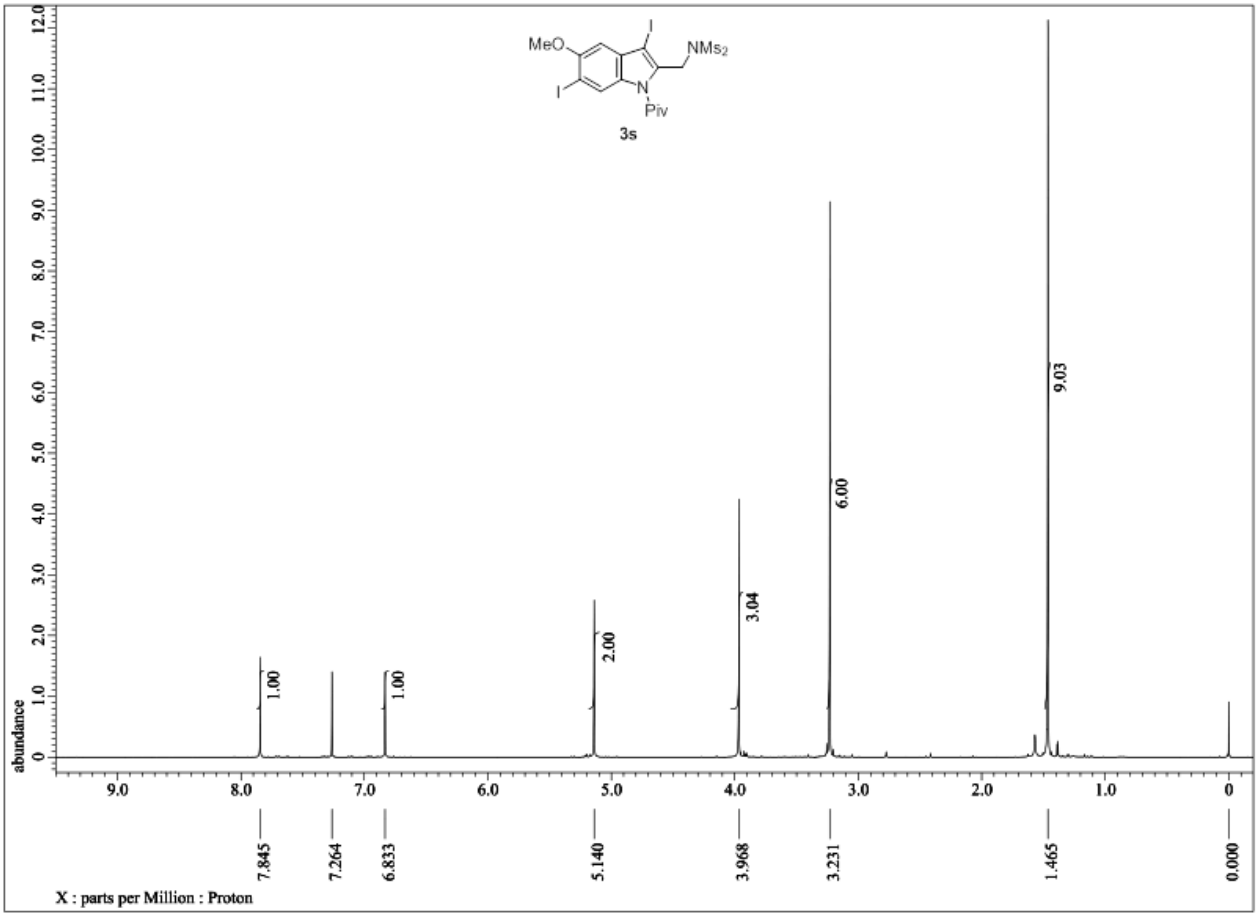

Br
I
NMs2
N
Piv
3p
abundance
183.888
134.329
133.907
131.972
127.891
124.835
115.877
114.746
77.316
77.000
76.674
68.703
45.366
44.293
43.651
28.198
X : parts per Million : Carbon13

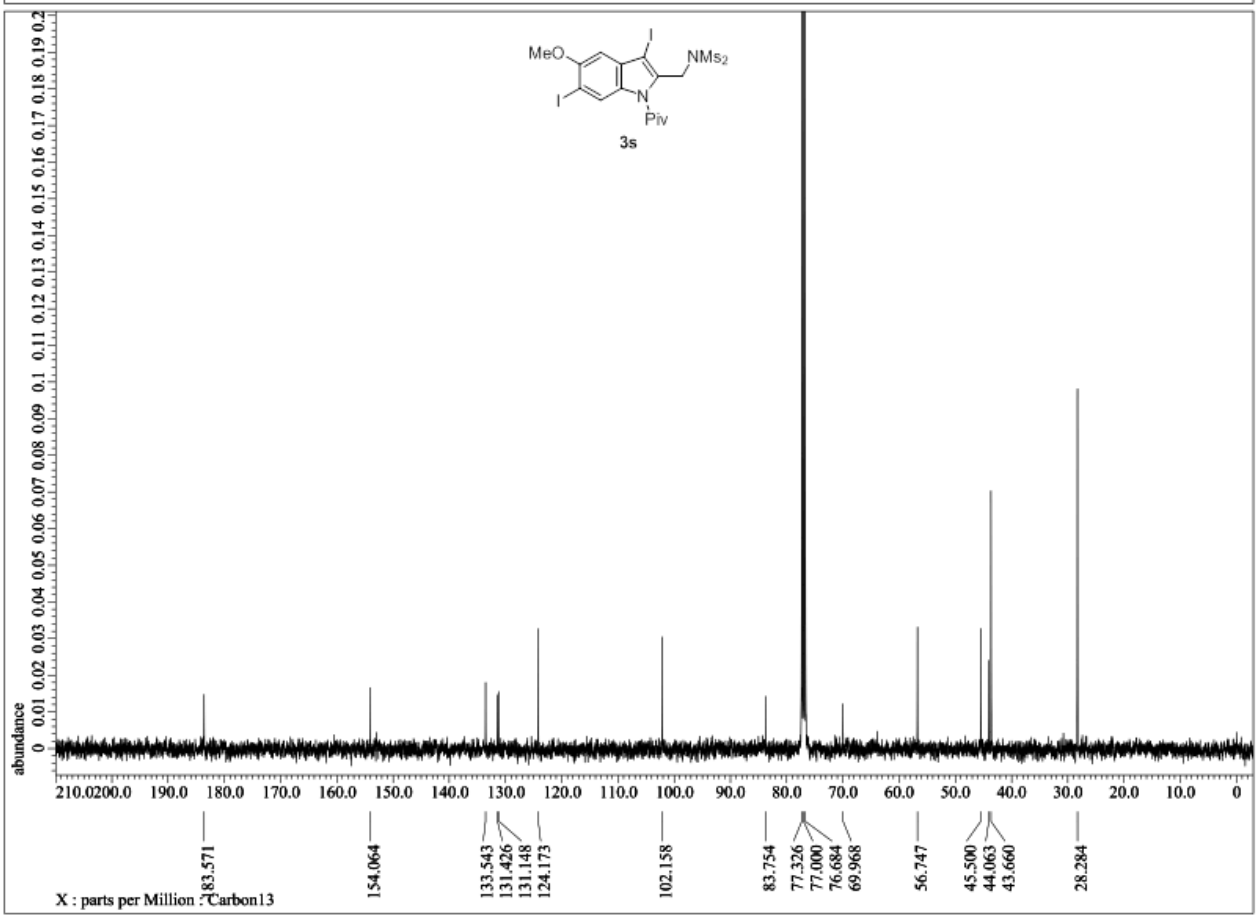

Cl
I
NMs2
N
Piv
3q
abundance
9.02
6.02
2.00
1.00
1.03
1.01
7.484
7.483
7.479
7.478
7.341
7.340
7.319
7.317
7.298
7.293
7.275
7.270
7.264
5.148
3.239
1.460
-0.000
X : parts per Million : Proton

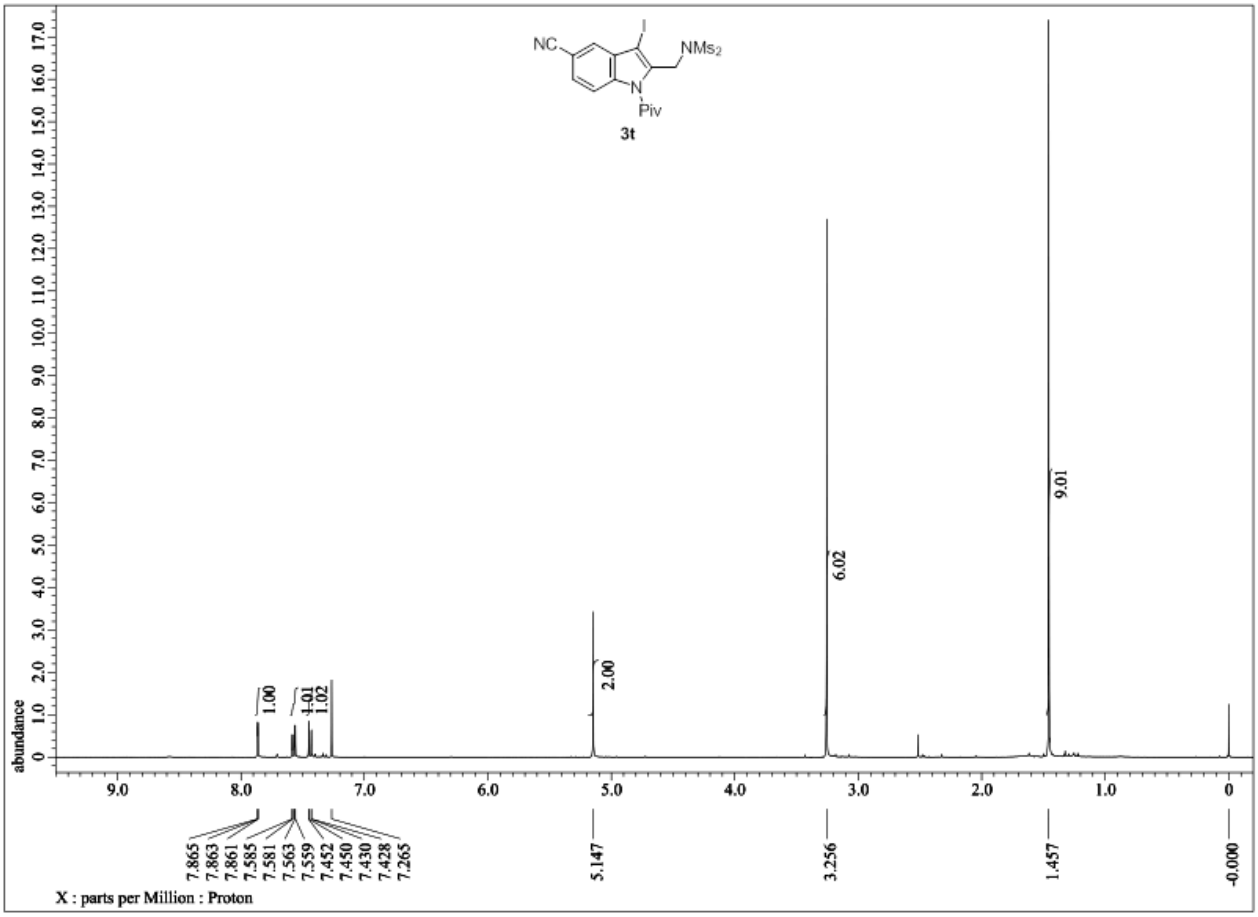

Cl
I
NMs2
N
Piv
3q
abundance
183.905
134.091
133.967
131.507
128.464
125.288
121.740
114.444
77.324
77.210
77.000
76.676
68.893
45.402
44.267
43.657
28.206
X : parts per Million : Carbon13

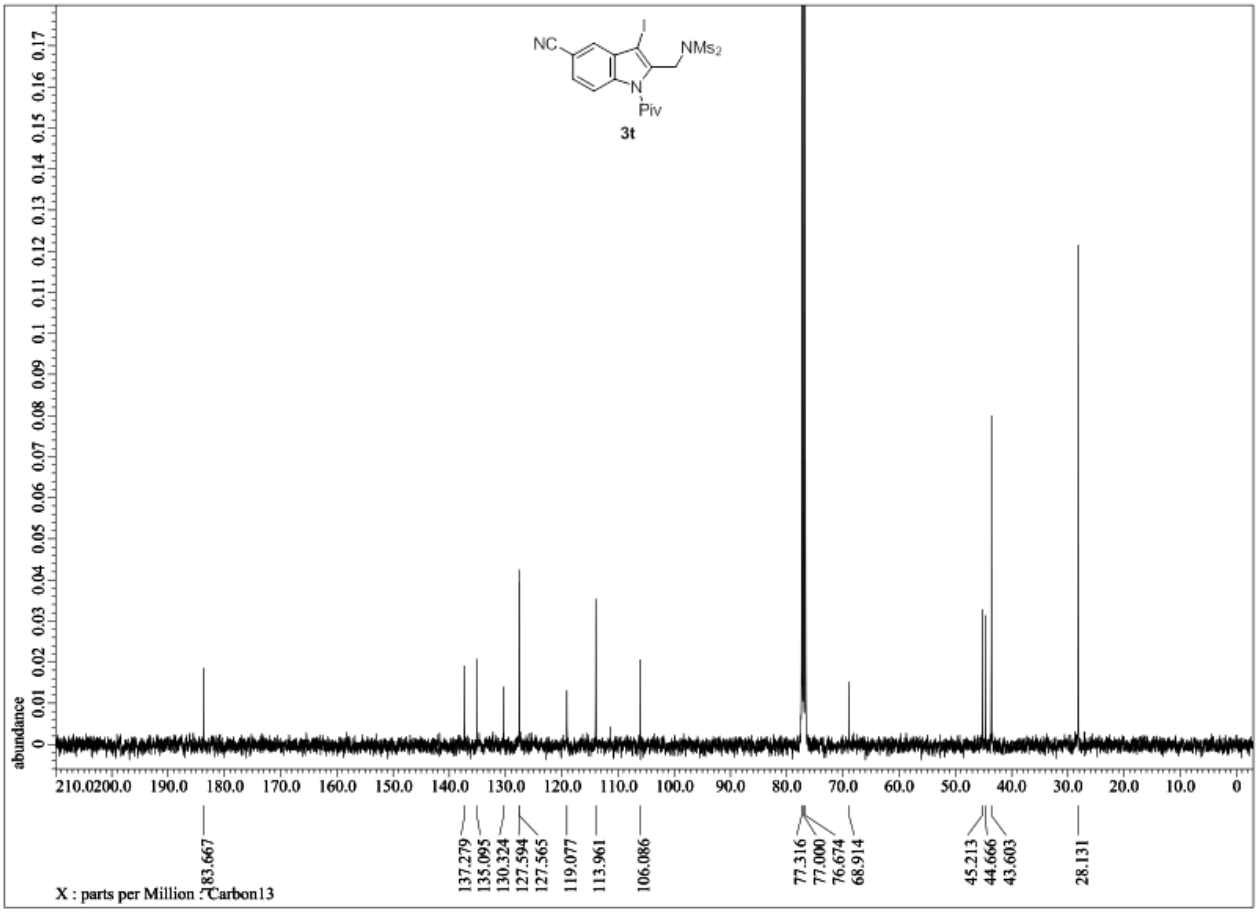

F
I
NMs2
N
Piv
3r
abundance
9.02
6.01
2.00
7.370
7.360
7.347
7.337
7.263
7.182
7.175
7.160
7.154
7.100
7.094
7.078
7.071
7.055
5.154
3.243
1.466
0.000
X : parts per Million : Proton

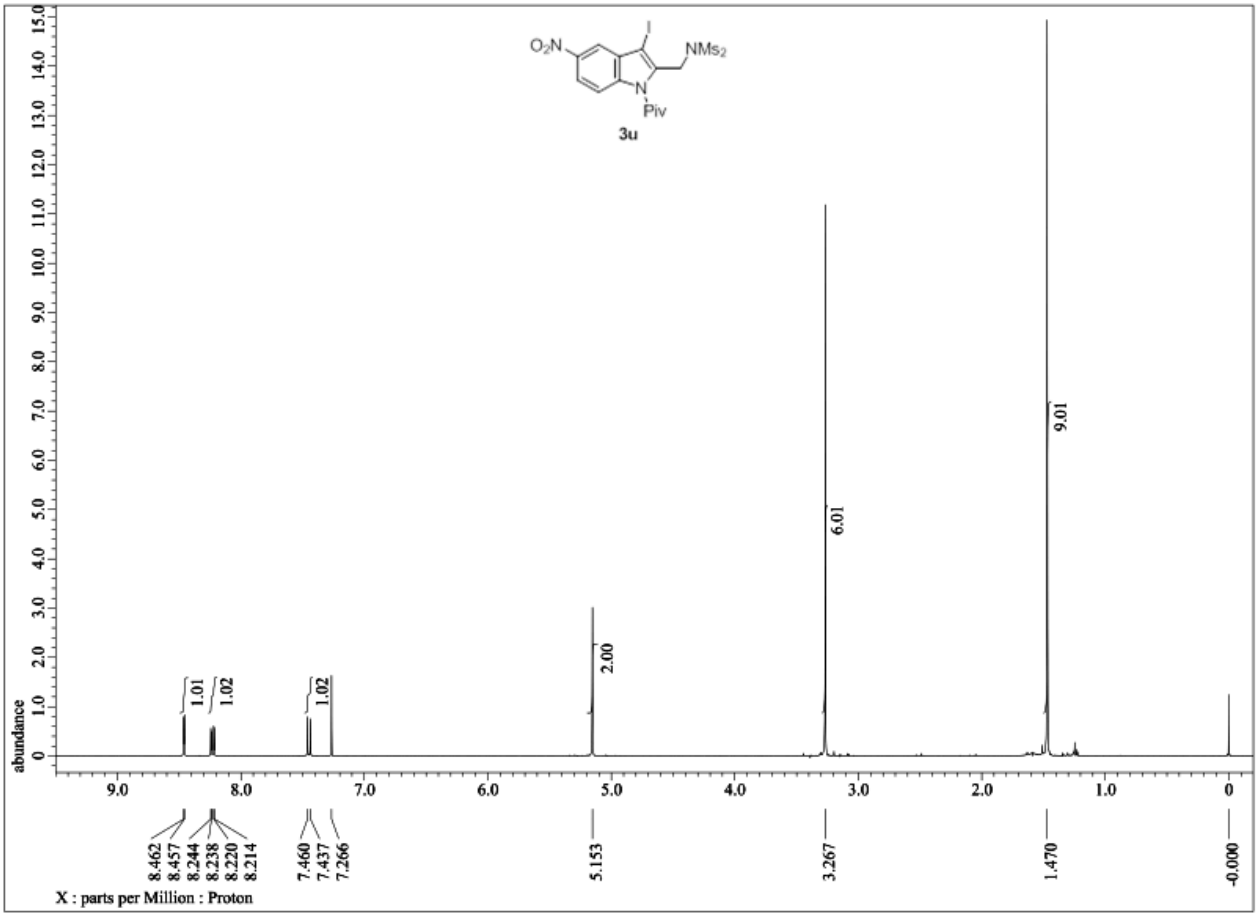

F
I
NMs2
N
Piv
3r
abundance
183.964
160.291
157.877
134.424
132.020
131.474
131.368
114.517
114.430
113.520
113.261
107.619
107.370
77.326
77.211
77.000
76.684
69.374
45.481
44.207
43.651
28.246
X : parts per Million : Carbon13

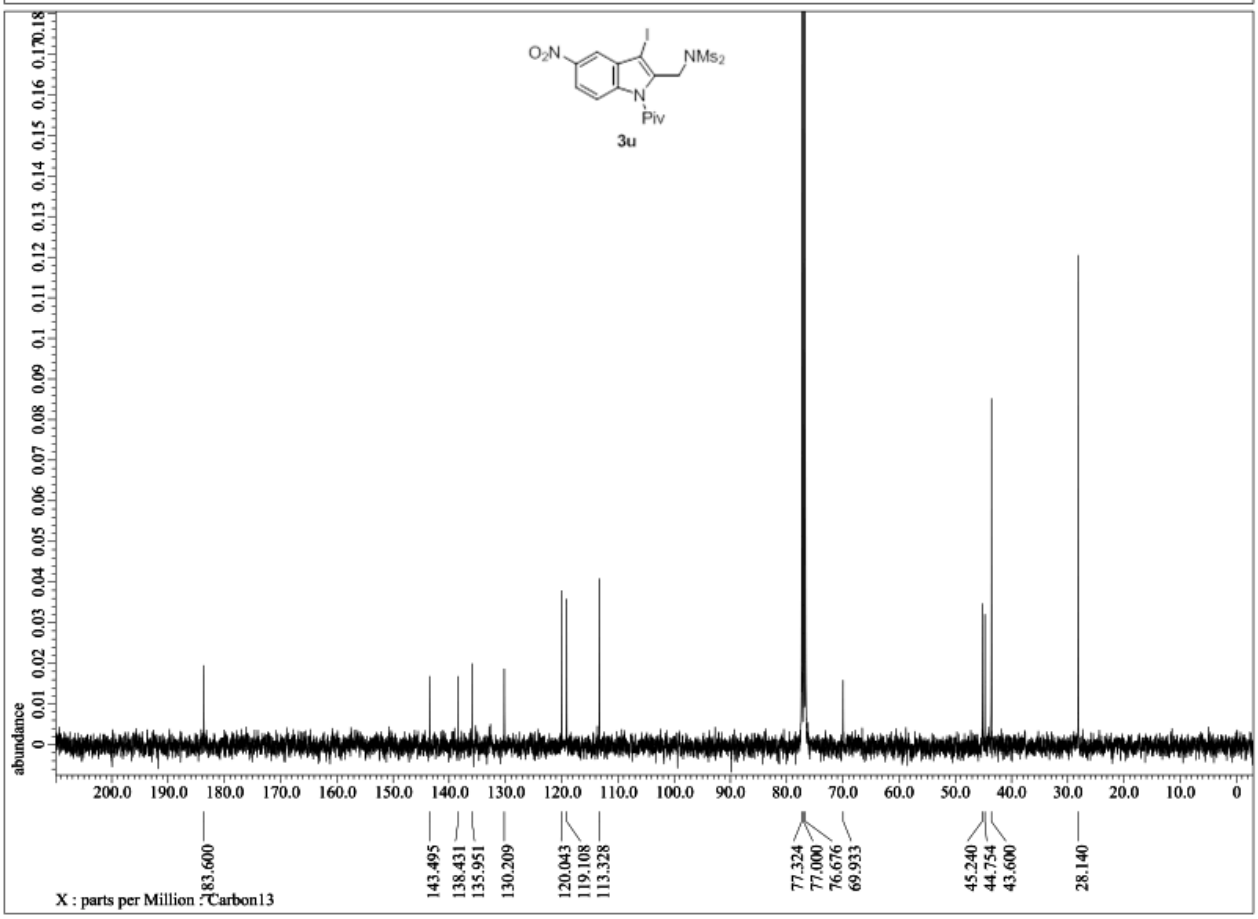

MeO
I
NMs2
I
N
Piv
3s
abundance
1.00
1.00
2.00
3.04
6.00
9.03
7.845
7.264
6.833
5.140
3.968
3.231
1.465
0.000
X : parts per Million : Proton

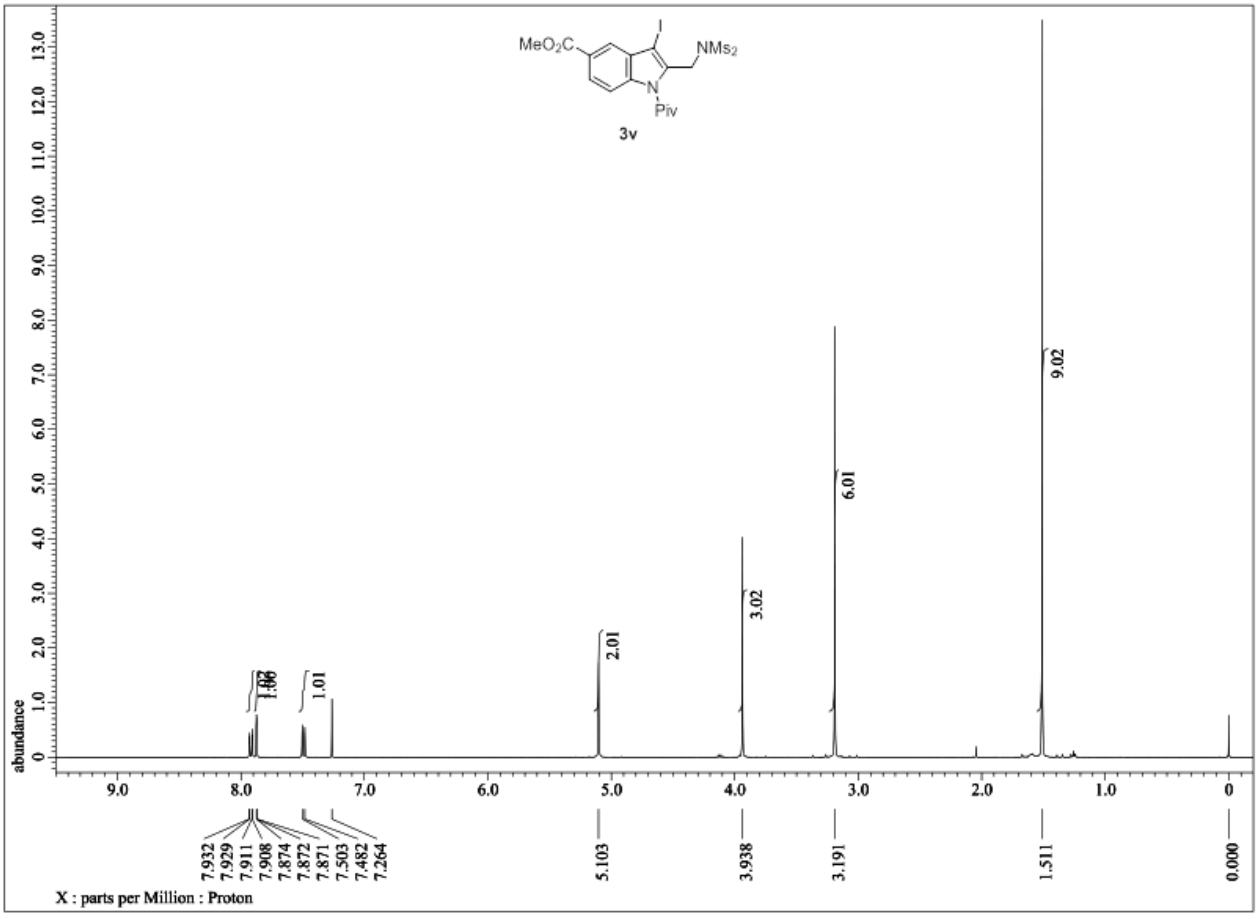

MeO
I
NMs2
I
N
Piv
3s
abundance
83.571
154.064
133.543
131.426
131.148
124.173
102.158
83.754
77.326
77.000
76.684
69.968
56.747
45.500
44.063
43.660
28.284
X : parts per Million : Carbon13

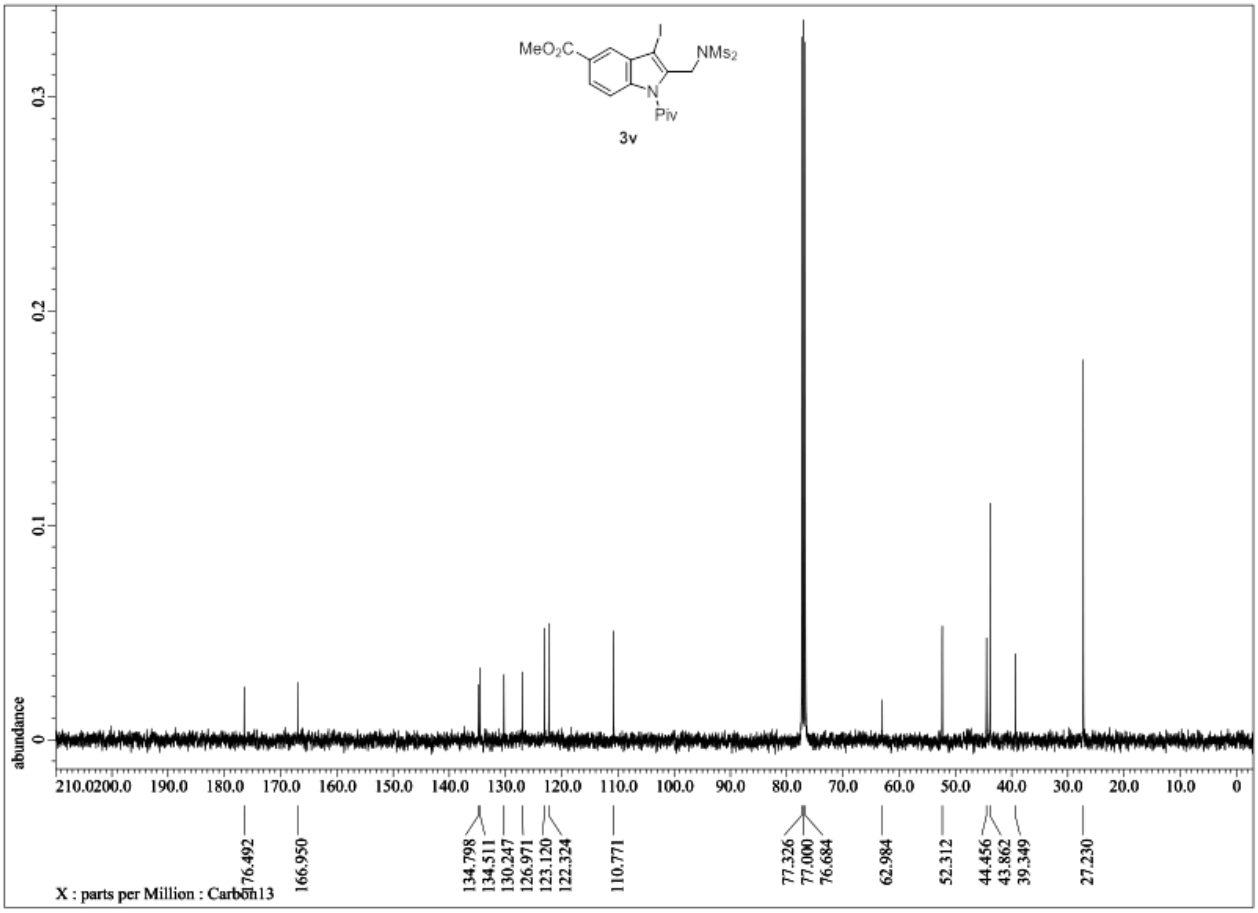

NC
I
NMs2
N
Piv
3t
abundance
1.00
1.01
1.02
2.00
6.02
9.01
7.865
7.863
7.861
7.585
7.581
7.563
7.559
7.452
7.450
7.430
7.428
7.265
5.147
3.256
1.457
-0.000
X : parts per Million : Proton

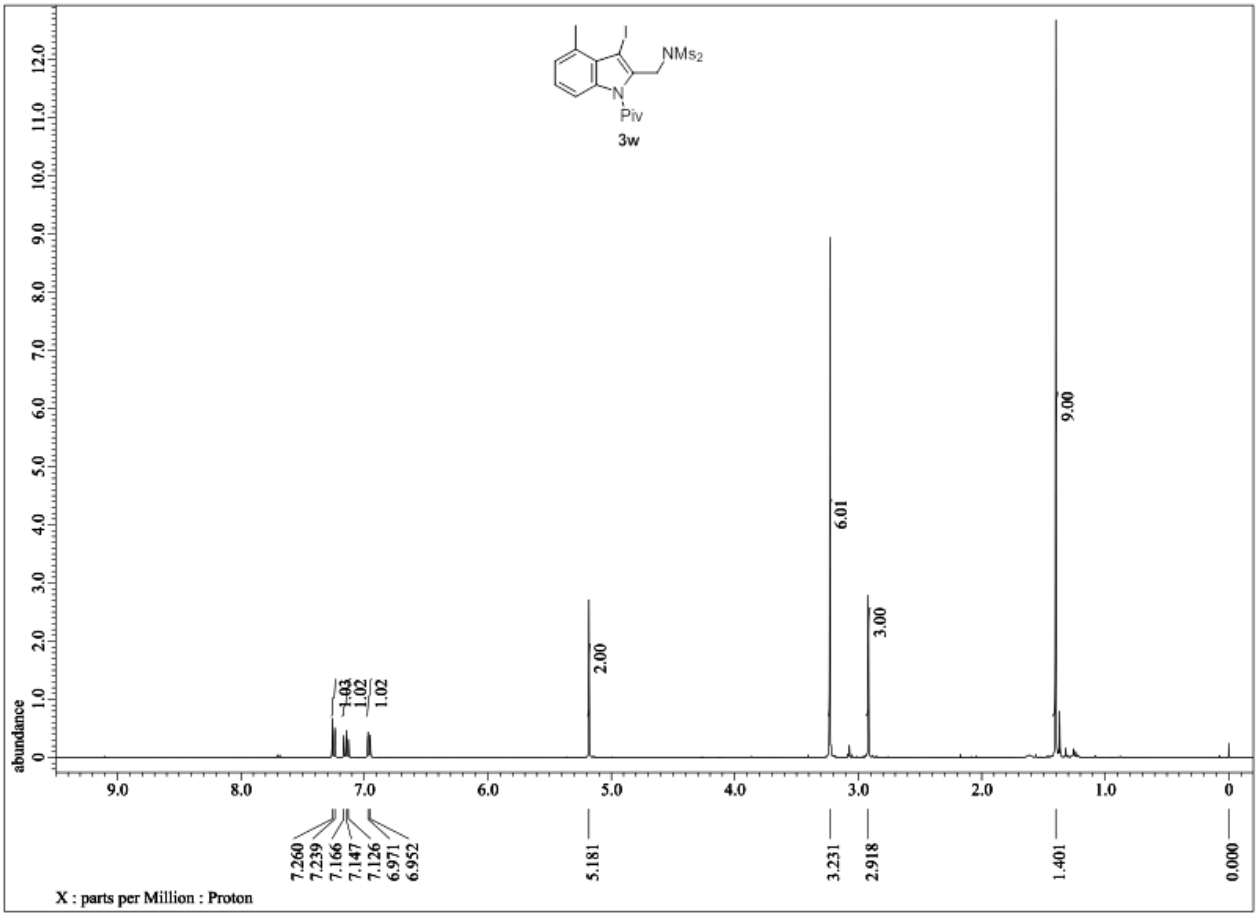

NC
I
NMs2
N
Piv
3t
abundance
183.667
137.279
135.095
130.324
127.594
127.565
119.077
113.961
106.086
77.316
77.000
76.674
68.914
45.213
44.666
43.603
28.131
X : parts per Million : Carbon13

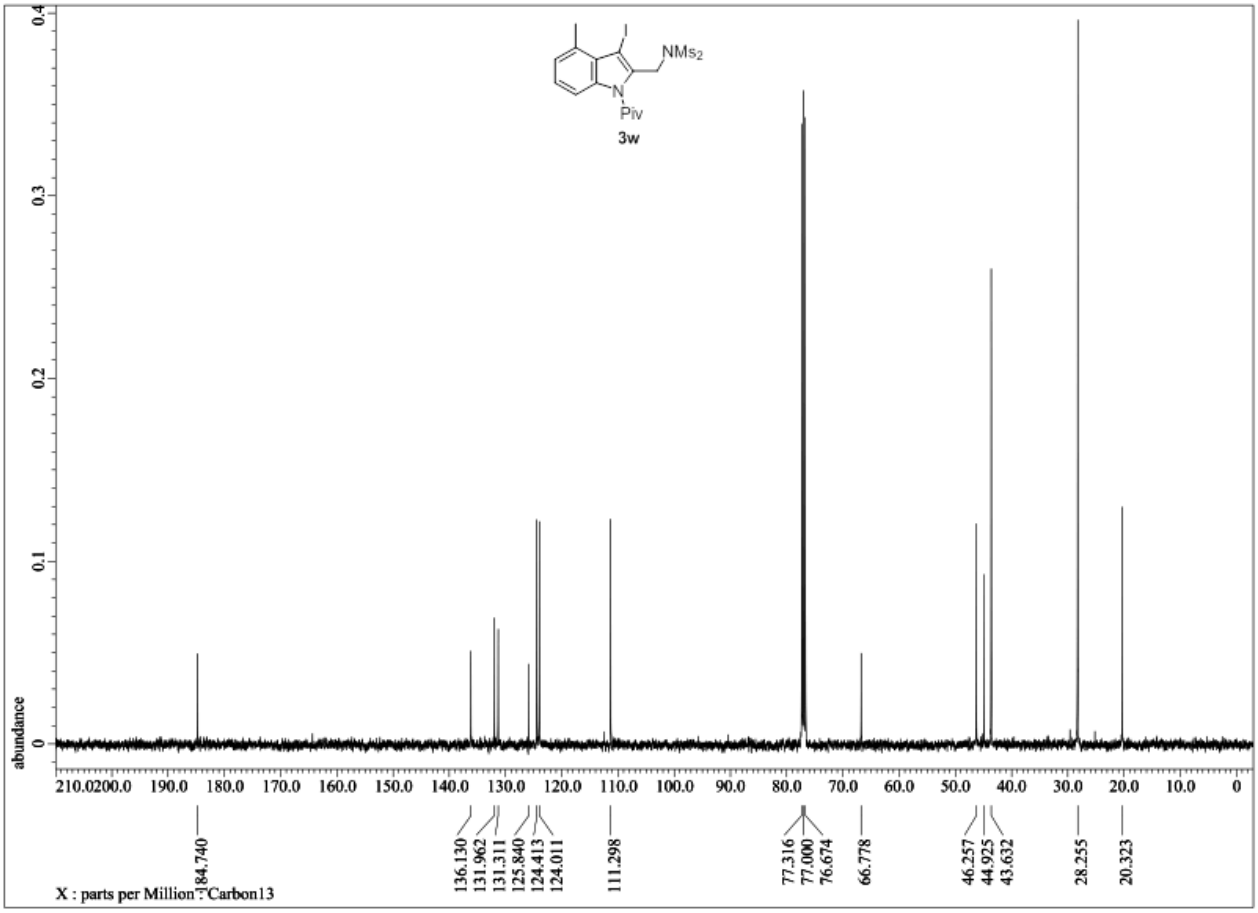

O2N
I
NMs2
N
Piv
3u
abundance
1.01
1.02
1.02
2.00
6.01
9.01
8.462
8.457
8.244
8.238
8.220
8.214
7.460
7.437
7.266
5.153
3.267
1.470
-0.000
X : parts per Million : Proton

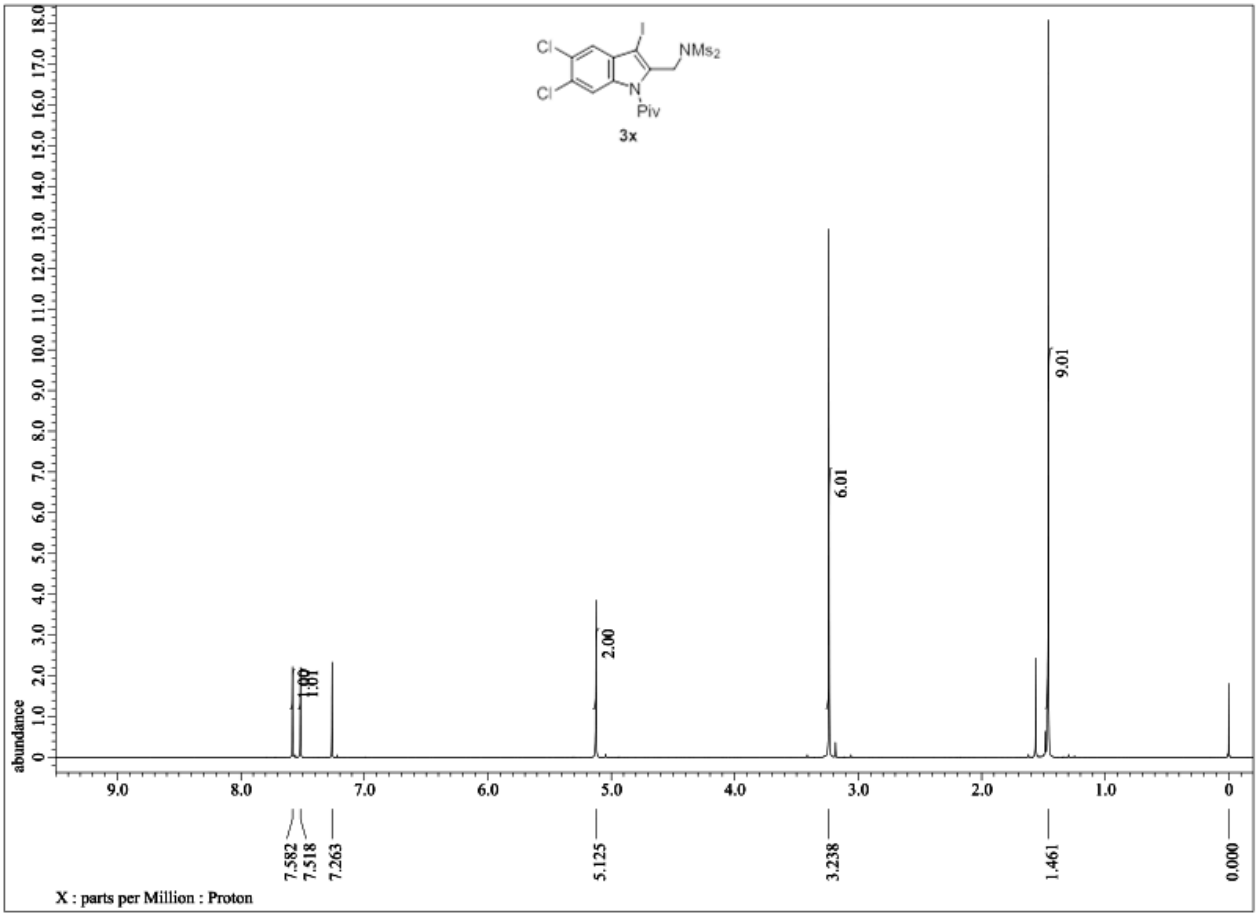

O2N
I
NMs2
N
Piv
3u
abundance
183.600
143.495
138.431
135.951
130.209
120.043
119.108
113.328
77.324
77.000
76.676
69.933
45.240
44.754
43.600
28.140
X : parts per Million : Carbon13

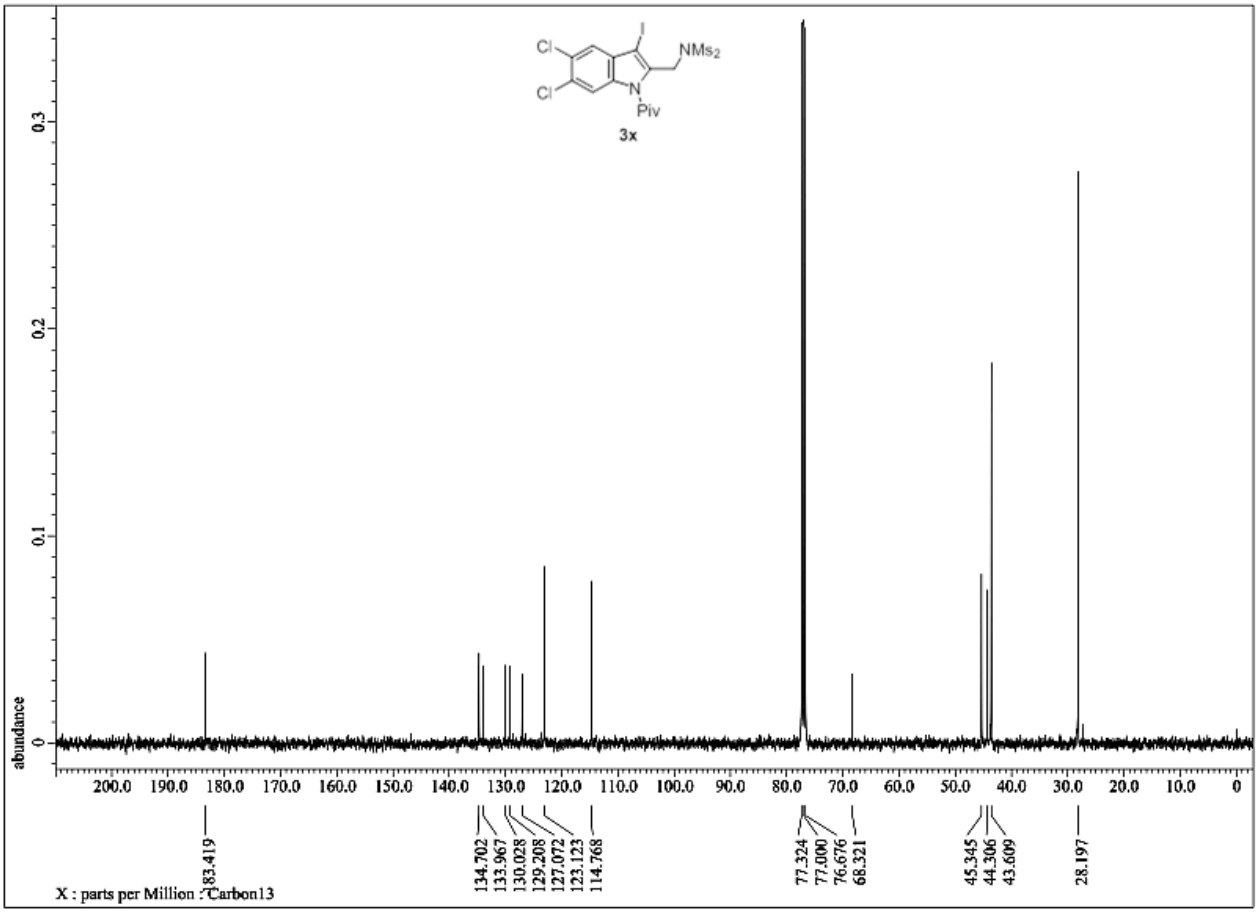

MeO2C
I
NMs2
N
Piv
3v
abundance
9.02
6.01
3.02
2.01
1.01
7.932
7.929
7.911
7.908
7.874
7.872
7.871
7.503
7.482
7.264
5.103
3.938
3.191
1.511
0.000
X : parts per Million : Proton

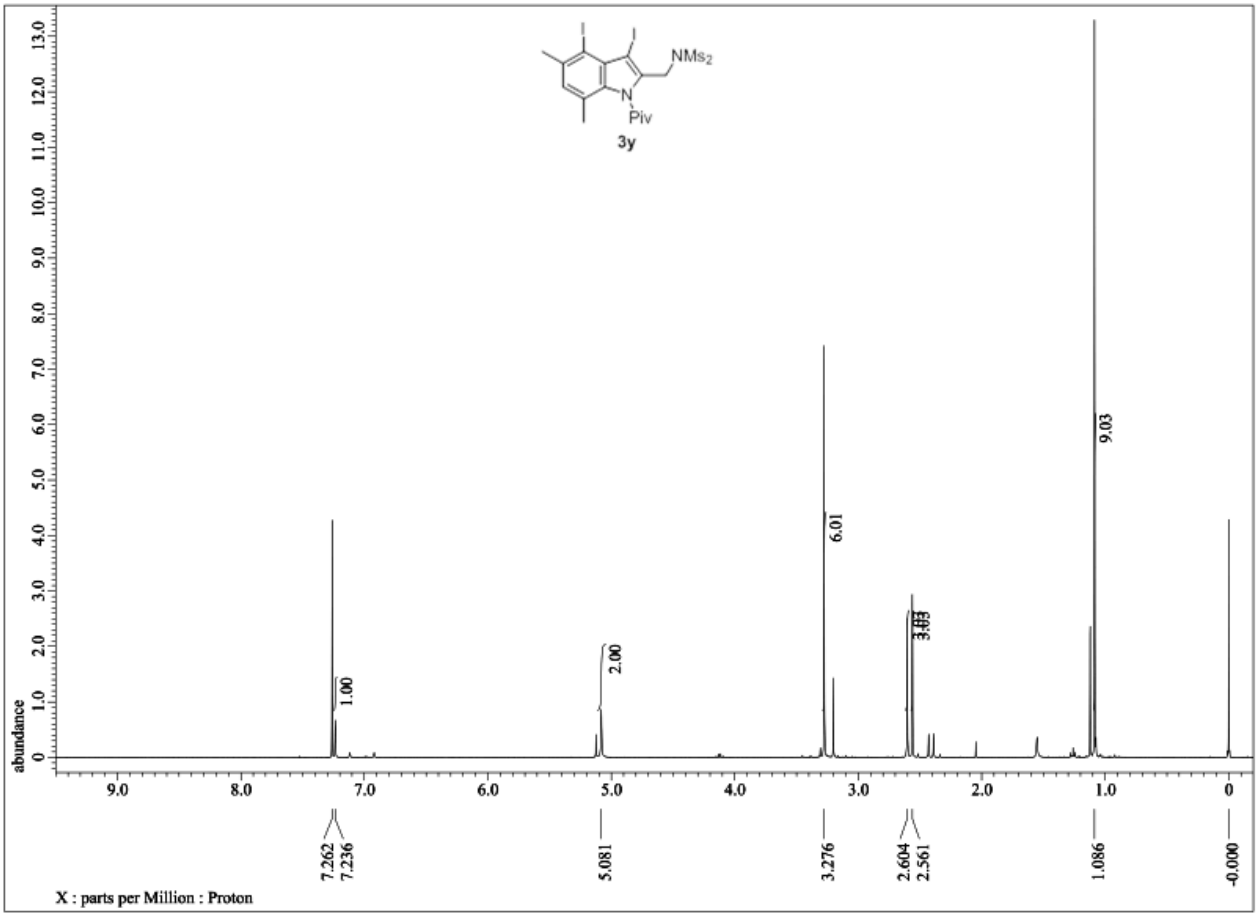

MeO2C
I
NMs2
N
Piv
3v
abundance
76.492
166.950
134.798
134.511
130.247
126.971
123.120
122.324
110.771
77.326
77.000
76.684
62.984
52.312
44.456
43.862
39.349
27.230
X : parts per Million : Carbon13

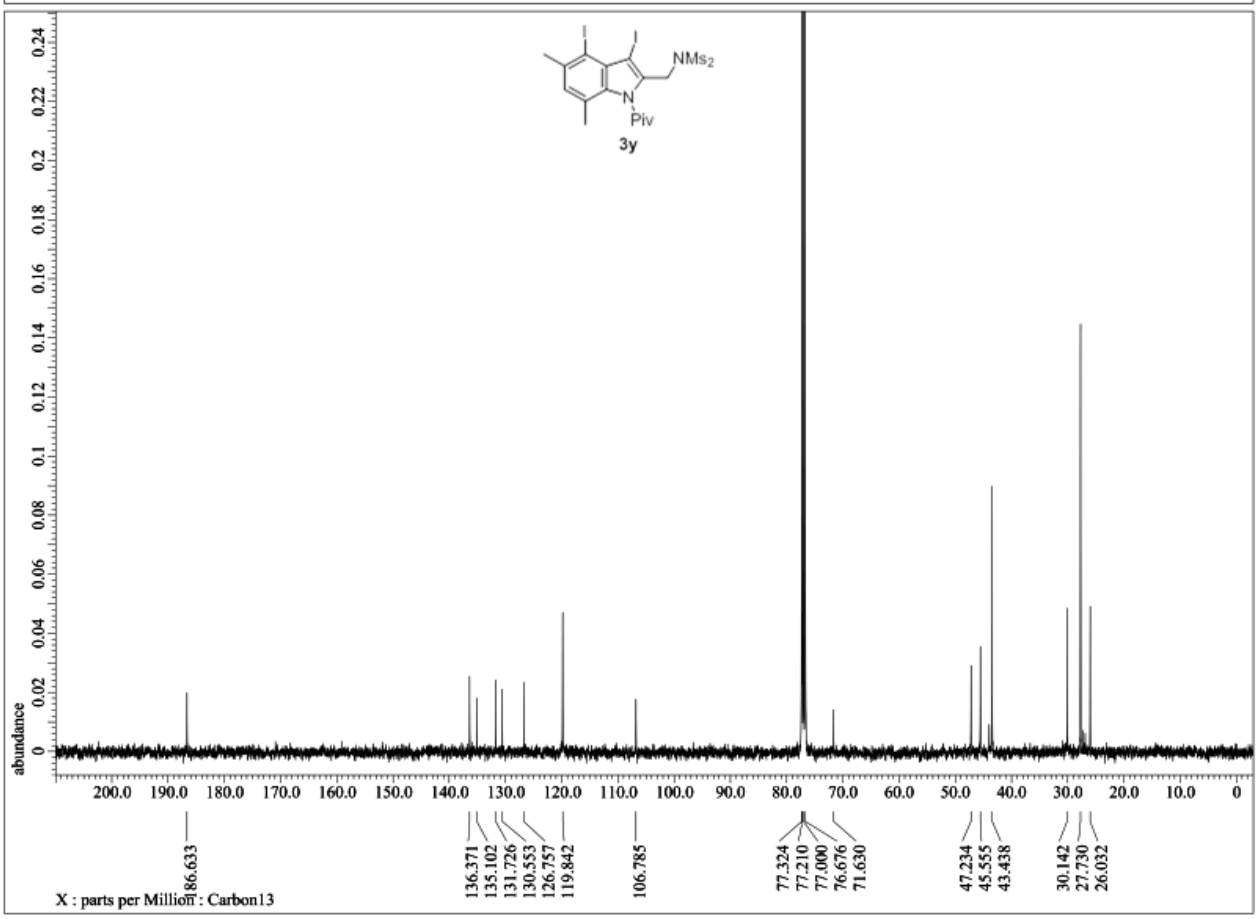

NMs2
Piv
3w
abundance
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
1.03
1.02
1.02
2.00
6.01
3.00
9.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.260
7.239
7.166
7.147
7.126
6.971
6.952
5.181
3.231
2.918
1.401
0.000
X : parts per Million : Proton

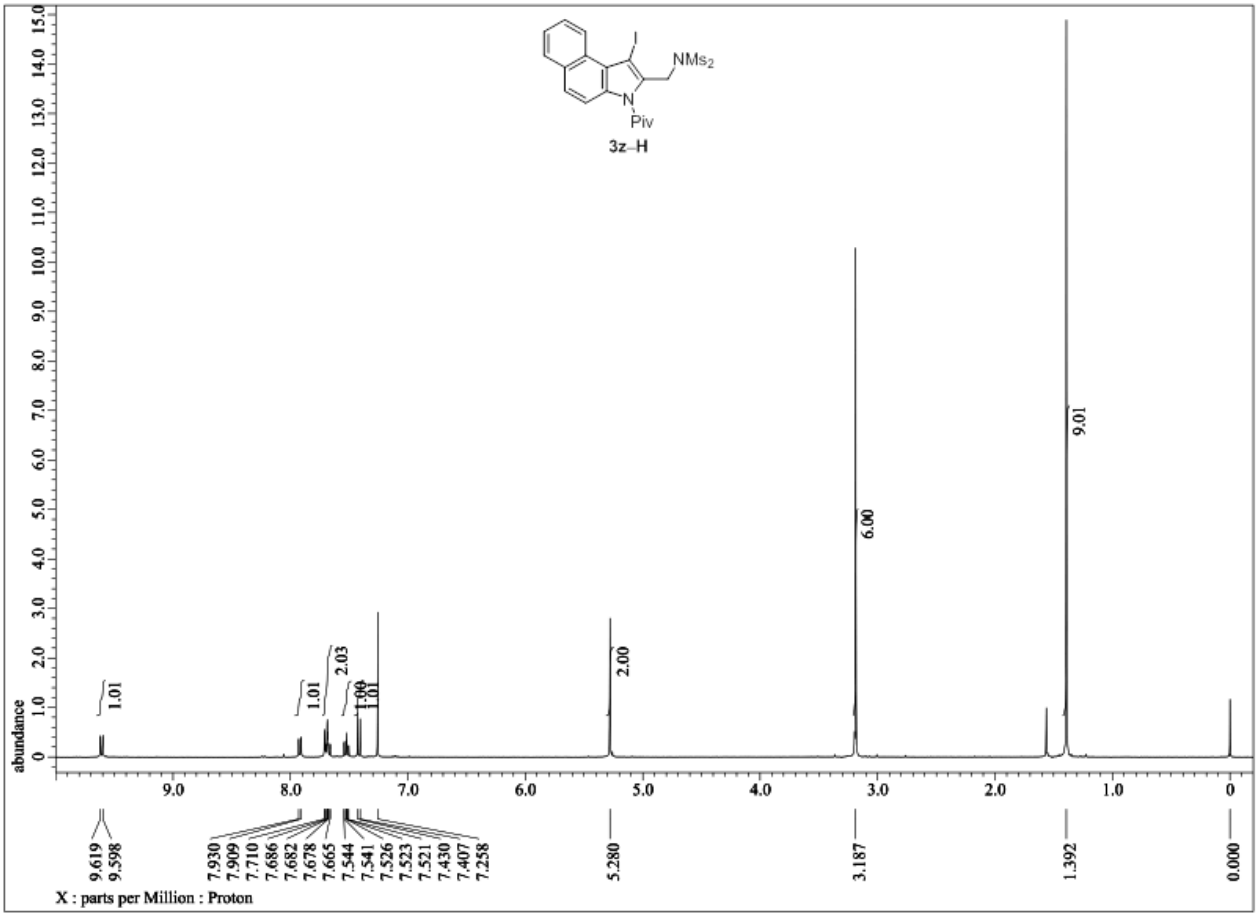

NMs2
Piv
3w
abundance
0.4
0.3
0.2
0.1
0
210.0200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
184.740
136.130
131.962
131.311
125.840
124.413
124.011
111.298
77.316
77.000
76.674
66.778
46.257
44.925
43.632
28.255
20.323
X : parts per Million : Carbon13


Cl
Cl
I
NMs2
N
Piv
3x
abundance
9.01
6.01
2.00
1.07
1.01
7.582
7.518
7.263
5.125
3.238
1.461
0.000
X : parts per Million : Proton


Cl
Cl
I
NMs2
N
Piv
3x
abundance
183.419
134.702
133.967
130.028
129.208
127.072
123.123
114.768
77.324
77.000
76.676
68.321
45.345
44.306
43.609
28.197
X : parts per Million : Carbon13


NMs2
N
Piv
3y
abundance
1.00
2.00
6.01
9.03
7.262
7.236
5.081
3.276
2.604
2.561
1.086
-0.000
X : parts per Million : Proton


NMs2
N
Piv
3y
abundance
186.633
136.371
135.102
131.726
130.553
126.757
119.842
106.785
77.324
77.210
77.000
76.676
71.630
47.234
45.555
43.438
30.142
27.730
26.032
X : parts per Million : Carbon13


NMs2
N
Piv
3z–H
abundance
X : parts per Million : Proton
1.01
1.01
2.03
1.00
1.01
2.00
6.00
9.01
9.619
9.598
7.930
7.909
7.710
7.686
7.682
7.678
7.665
7.544
7.541
7.526
7.523
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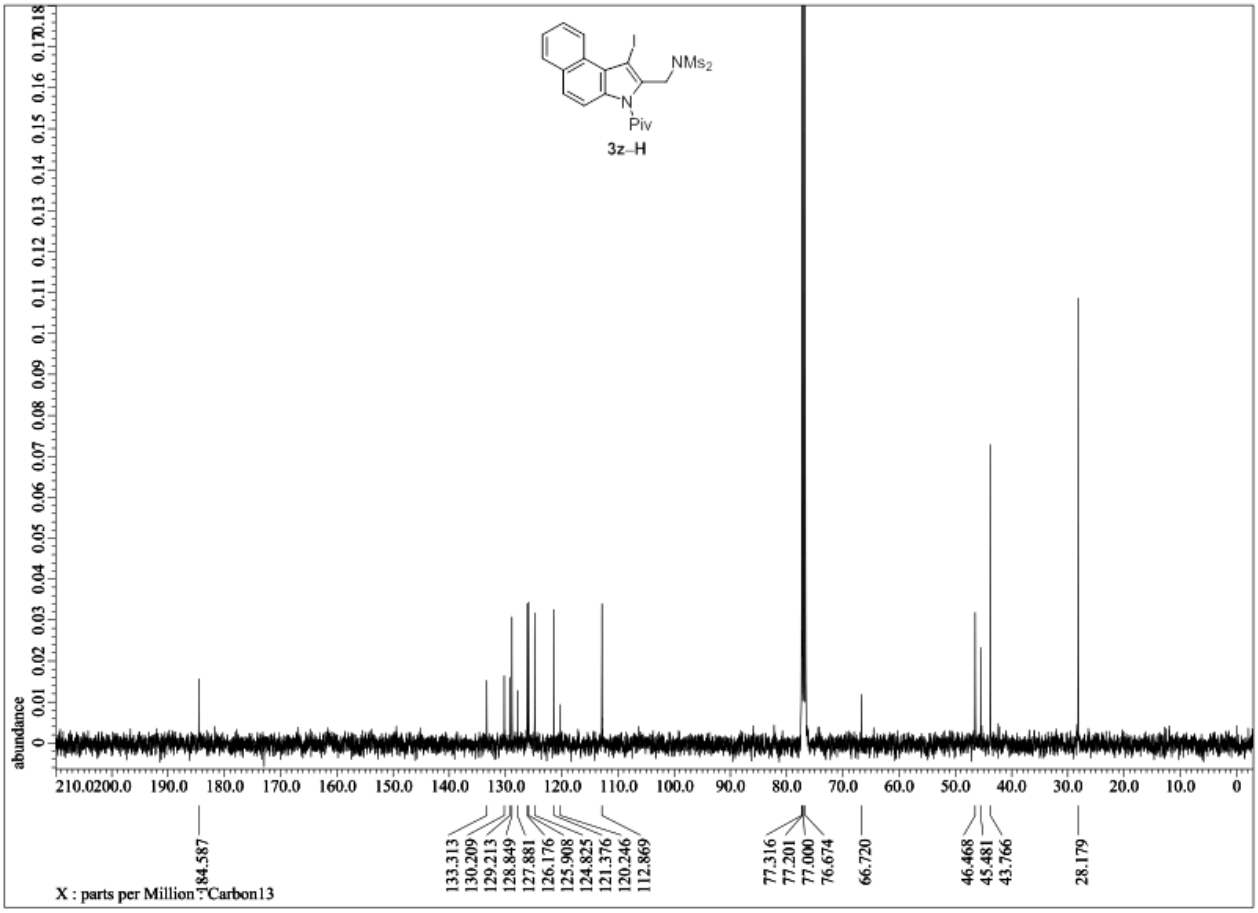
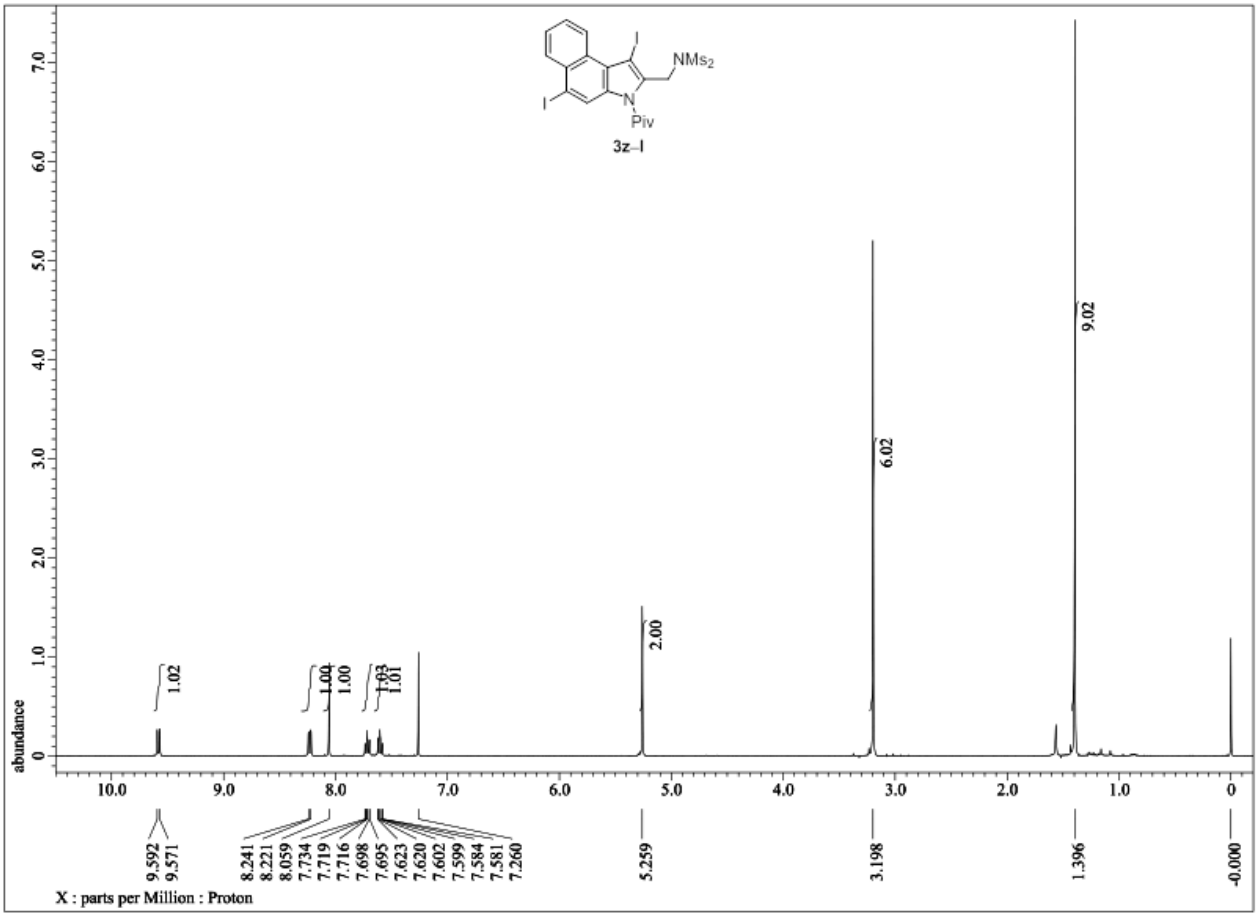
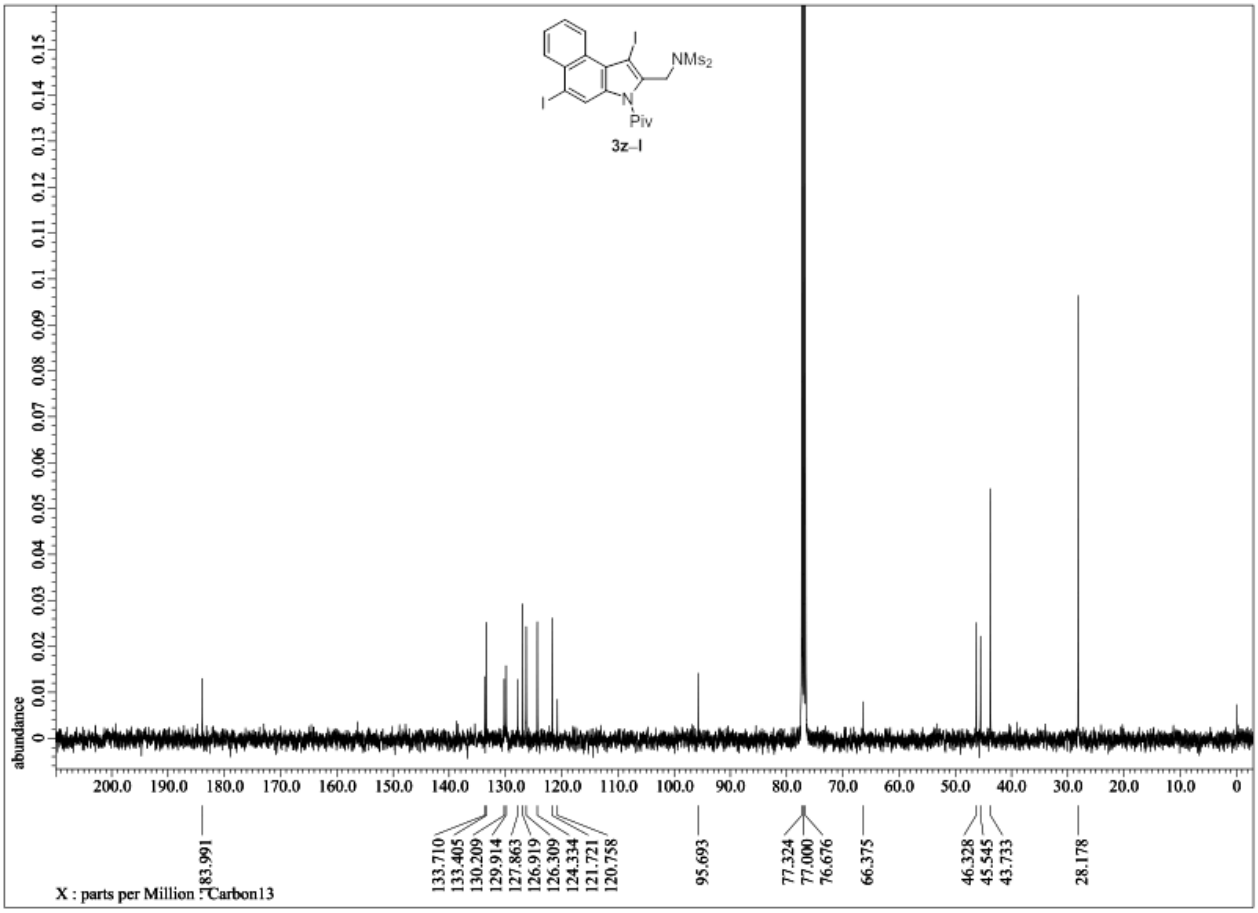
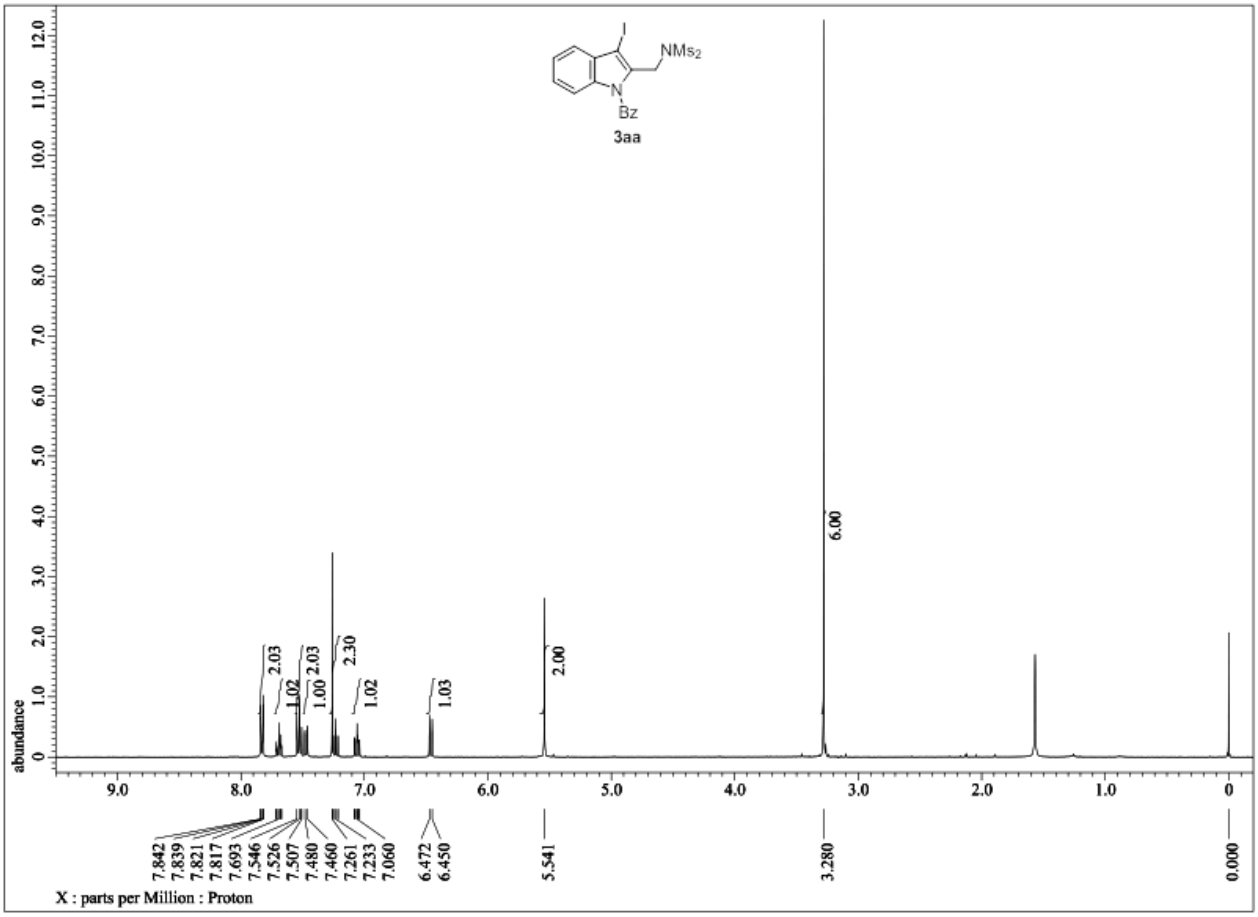
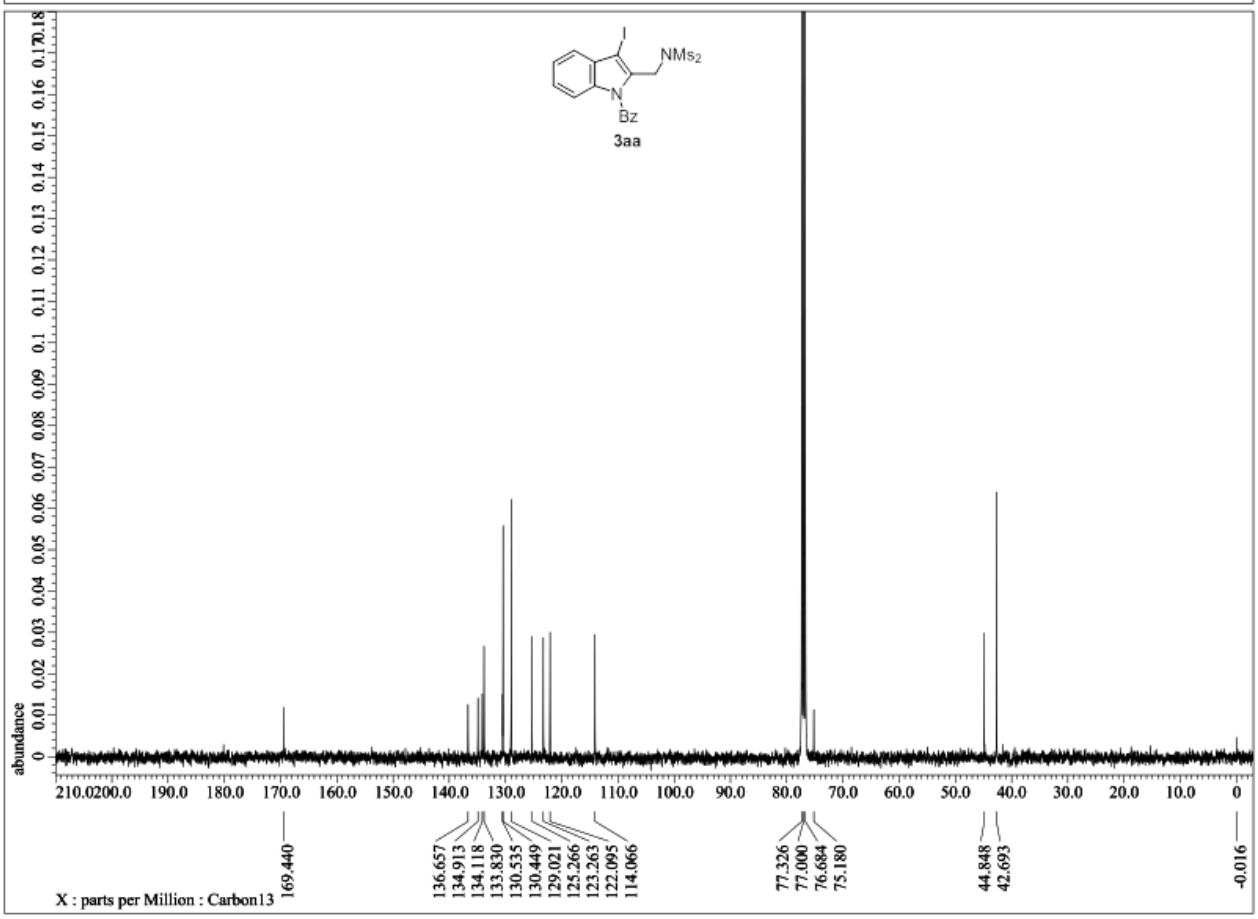
7.430
7.407
7.258
5.280
3.187
1.392
0.000

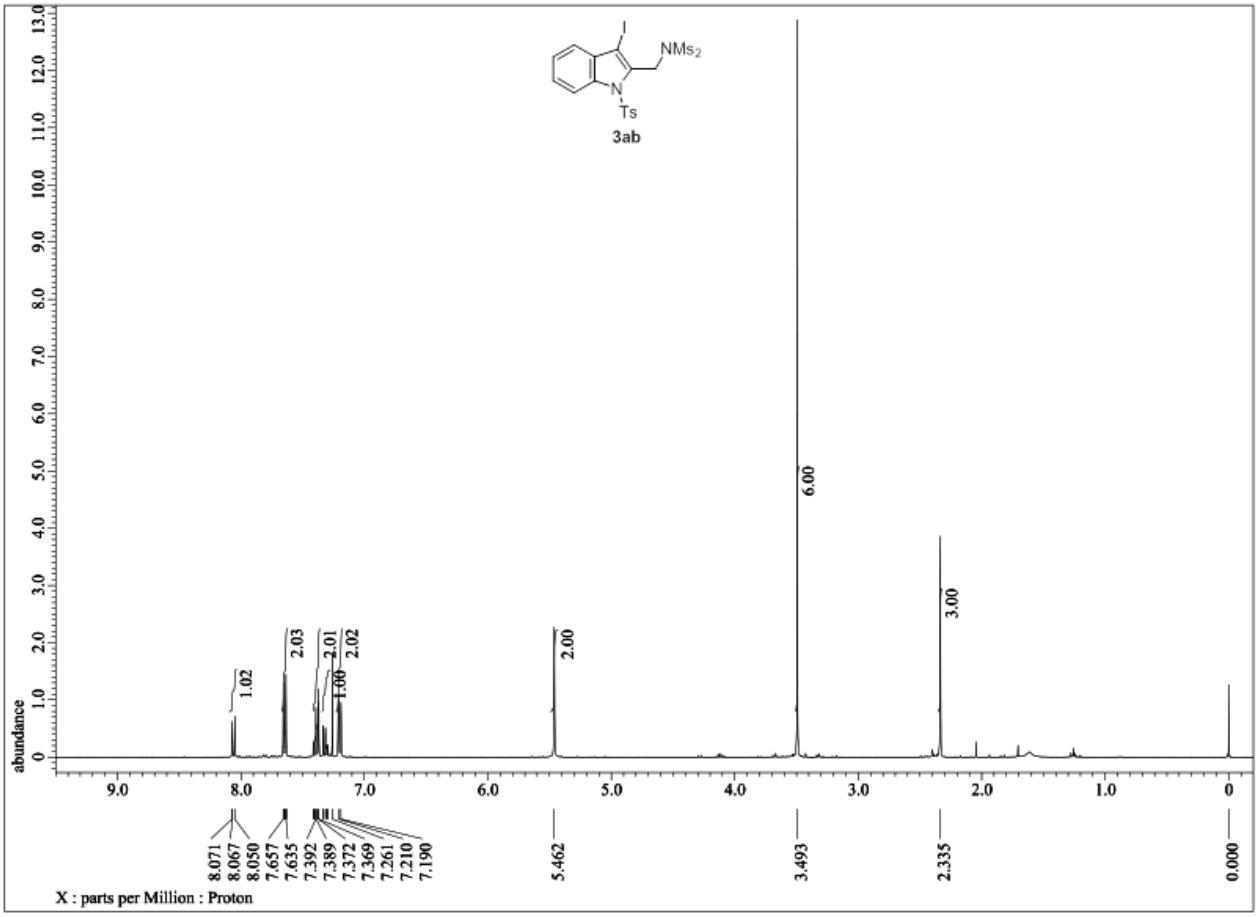

NMs2
N
Piv
3z–H
abundance
X : parts per Million : Carbon13
84.587
133.313
130.209
129.213
128.849
127.881
126.176
125.908
124.825
121.376
120.246
112.869
77.316
77.201
77.000
76.674
66.720
46.468
45.481
43.766
28.179

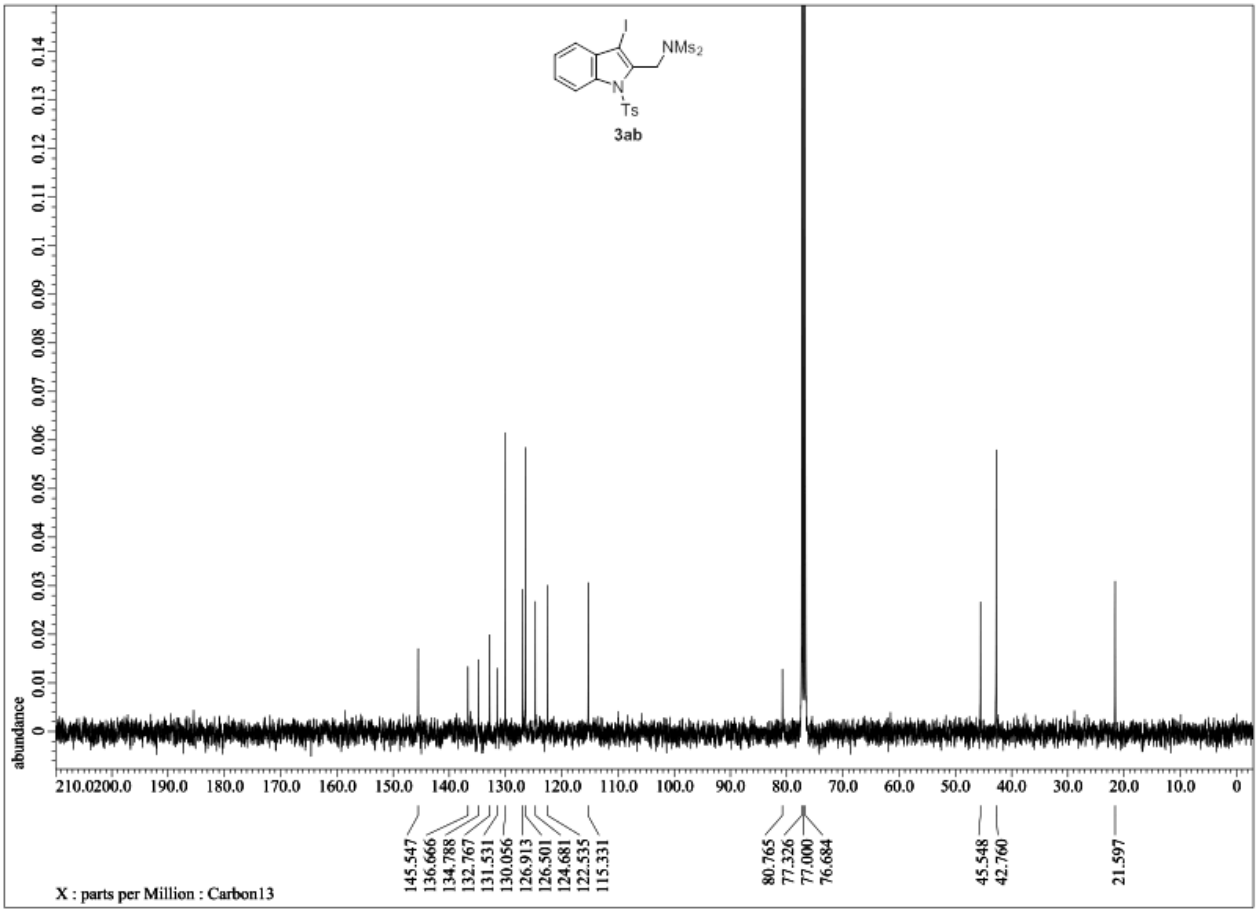

NMs2
I
N
Piv
I
3z–I
abundance
X : parts per Million : Proton
1.02
1.00
1.00
1.03
1.01
2.00
6.02
9.02
9.592
9.571
8.241
8.221
8.059
7.734
7.719
7.716
7.698
7.695
7.623
7.620
7.602
7.599
7.584
7.581
7.260
5.259
3.198
1.396
-0.000

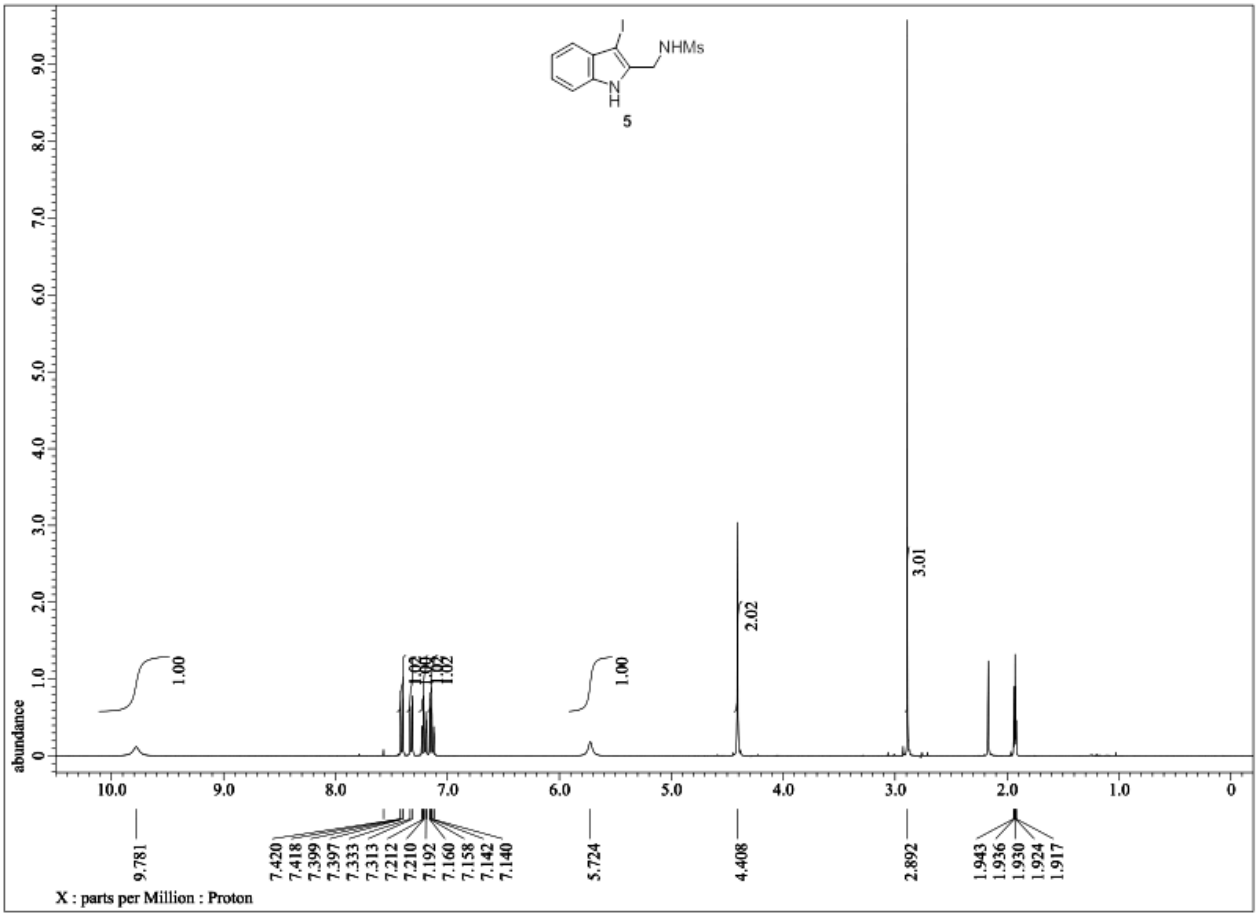

NMs2
I
N
Piv
I
3z–I
abundance
X : parts per Million : Carbon13
183.991
133.710
133.405
130.209
129.914
127.863
126.919
126.309
124.334
121.721
120.758
95.693
77.324
77.000
76.676
66.375
46.328
45.545
43.733
28.178

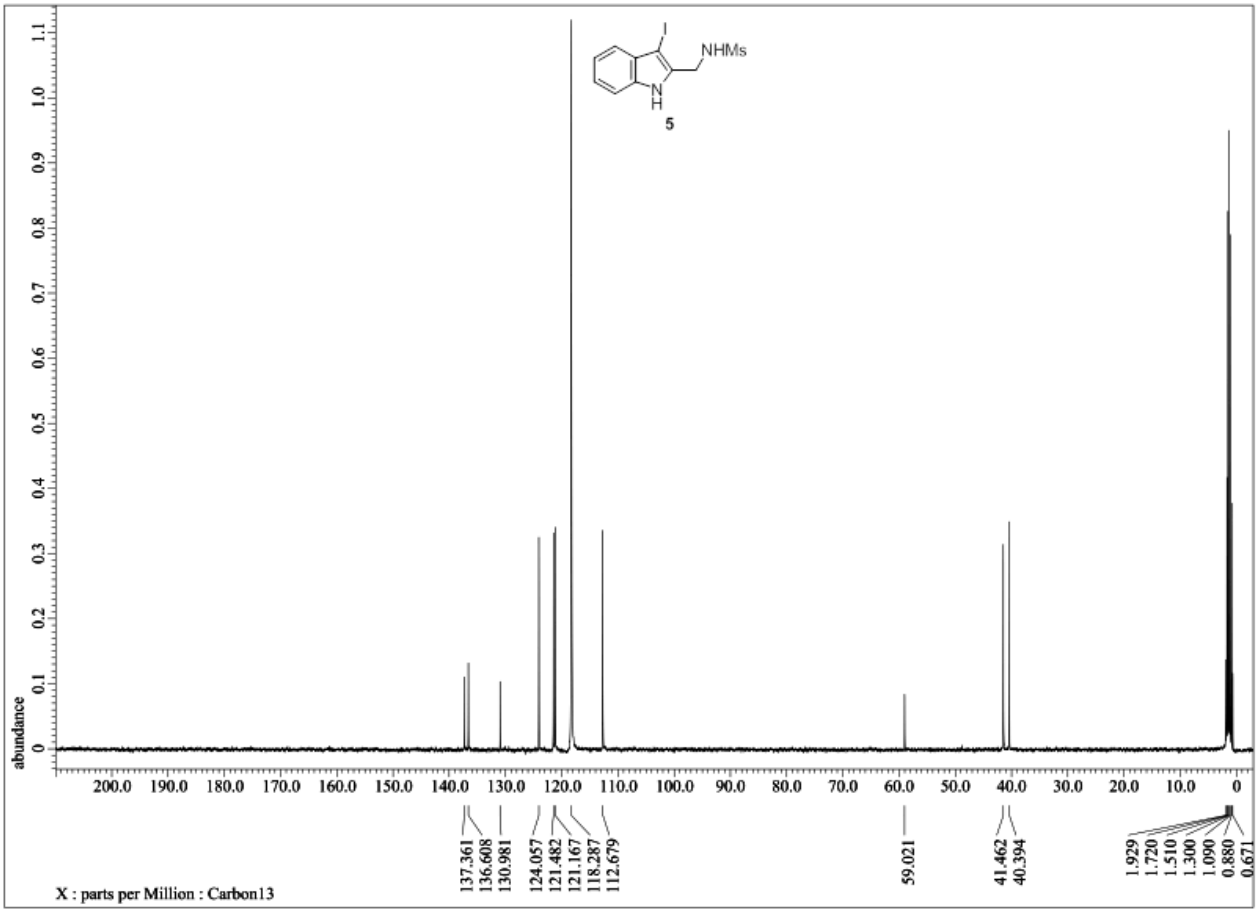

I
NMs2
N
Bz
3aa
abundance
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.03
1.02
2.03
1.00
2.30
1.02
1.03
2.00
6.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.842
7.839
7.821
7.817
7.693
7.546
7.526
7.507
7.480
7.460
7.261
7.233
7.060
6.472
6.450
5.541
3.280
0.000
X : parts per Million : Proton

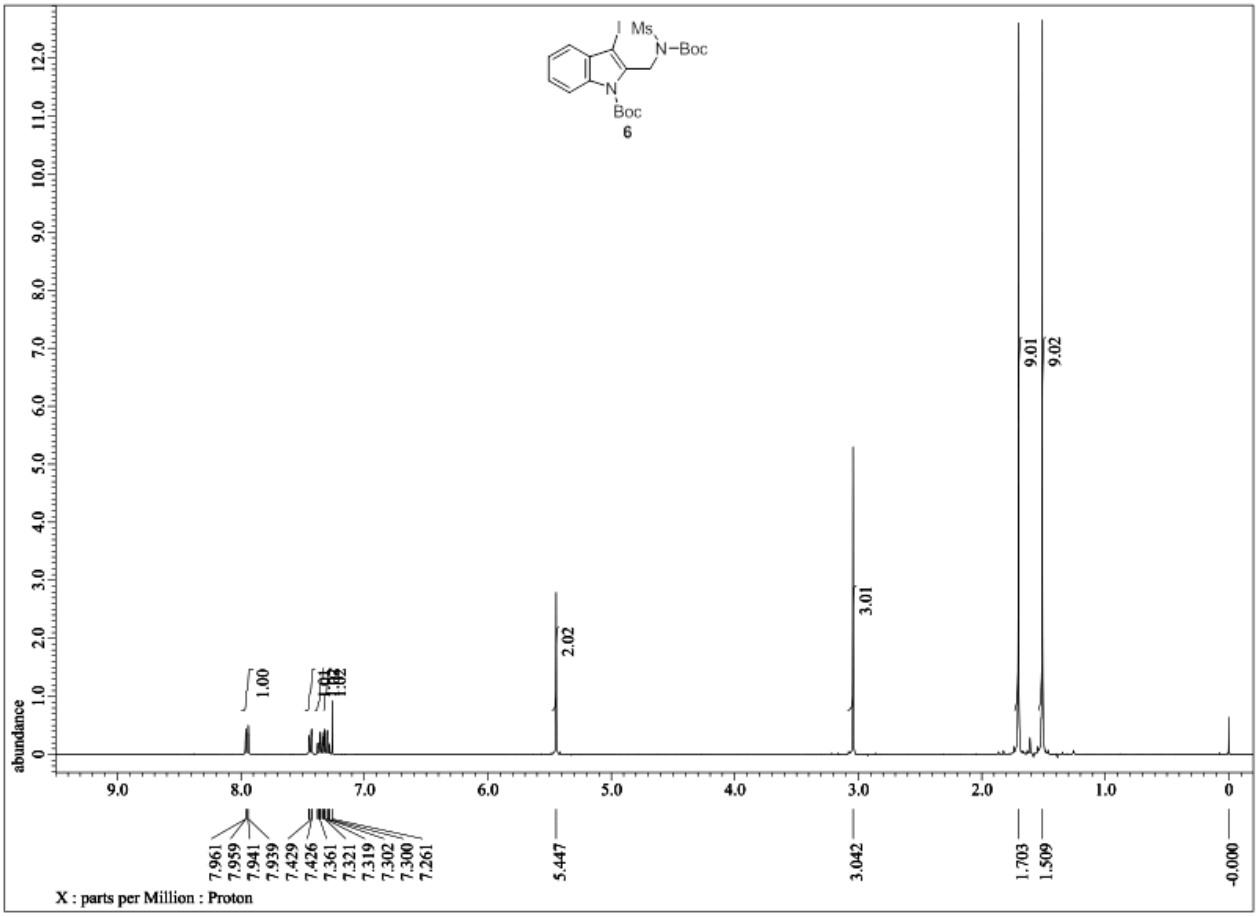

I
NMs2
N
Bz
3aa
abundance
0.18
0.17
0.16
0.15
0.14
0.13
0.12
0.11
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
210.0200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
169.440
136.657
134.913
134.118
133.830
130.535
130.449
129.021
125.266
123.263
122.095
114.066
77.326
77.000
76.684
75.180
44.848
42.693
-0.016
X : parts per Million : Carbon13

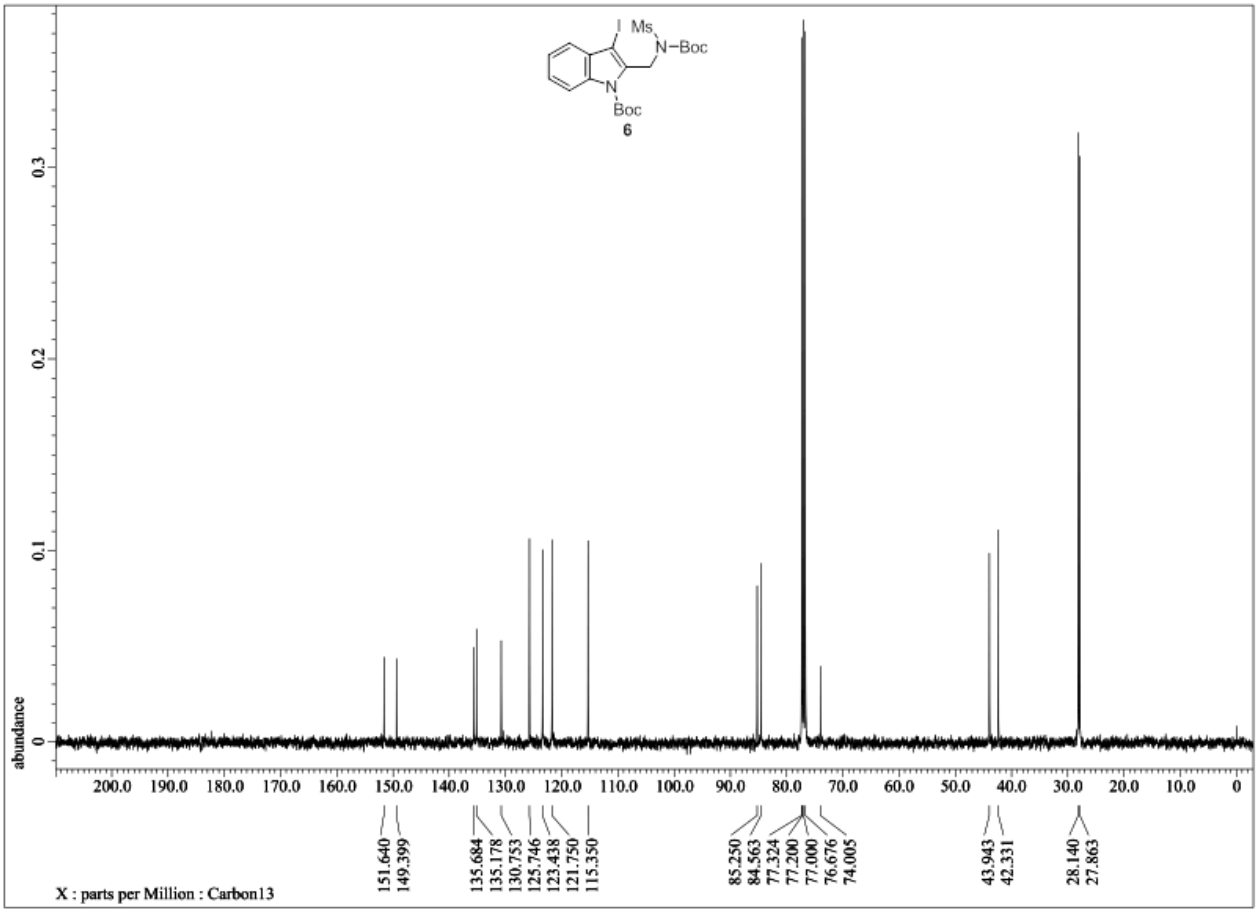

I
NMs2
N
Ts
3ab
abundance
1.02
2.03
2.01
1.00
2.02
2.00
6.00
3.00
8.071
8.067
8.050
7.657
7.635
7.392
7.389
7.372
7.369
7.261
7.210
7.190
5.462
3.493
2.335
0.000
X : parts per Million : Proton

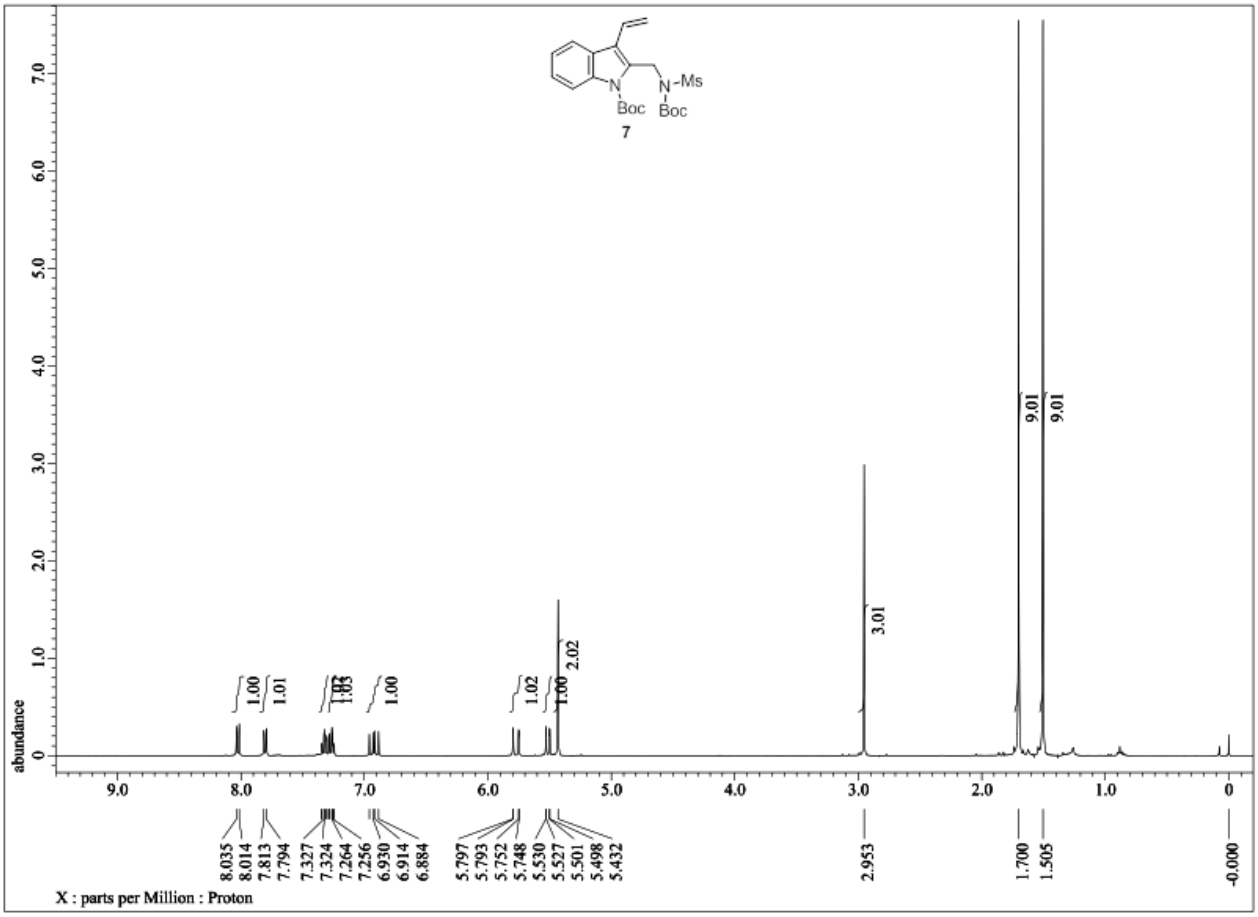

I
NMs2
N
Ts
3ab
abundance
145.547
136.666
134.788
132.767
131.531
130.056
126.913
126.501
124.681
122.535
115.331
80.765
77.326
77.000
76.684
45.548
42.760
21.597
X : parts per Million : Carbon13

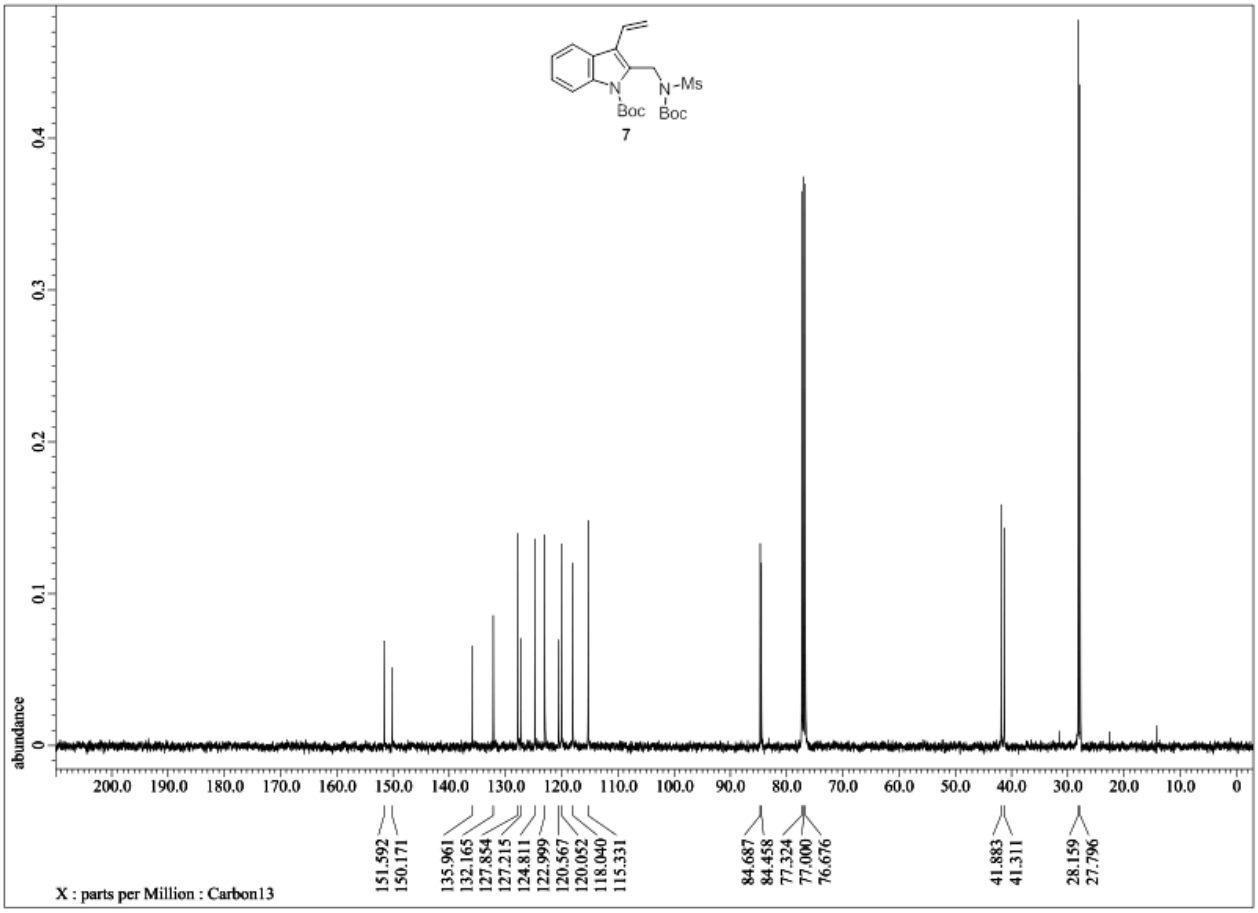

I
NHMs
N
H
5
abundance
1.00
1.00
2.02
3.01
9.781
7.420
7.418
7.399
7.397
7.333
7.313
7.212
7.210
7.192
7.160
7.158
7.142
7.140
5.724
4.408
2.892
1.943
1.936
1.930
1.924
1.917
X : parts per Million : Proton

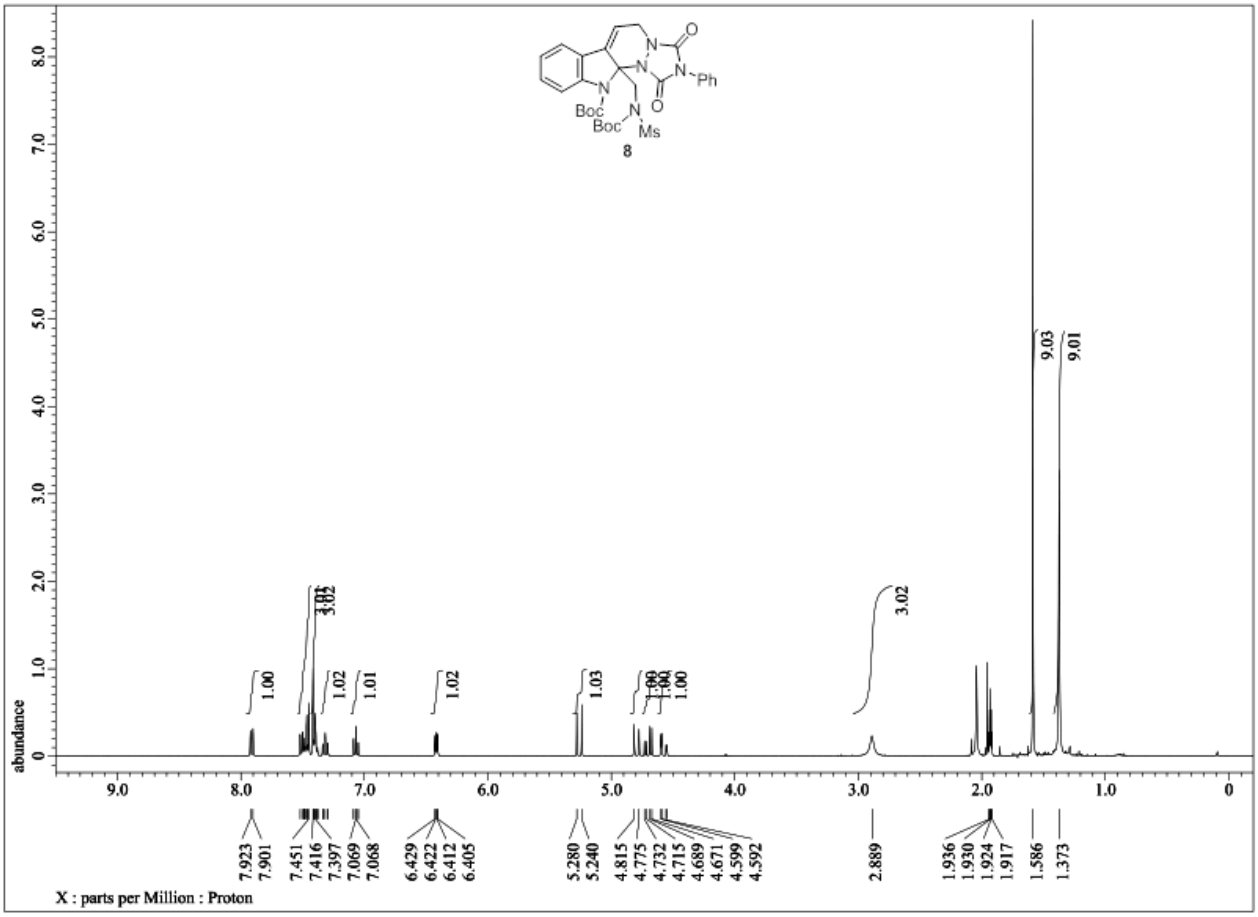

I
NHMs
N
H
5
abundance
137.361
136.608
130.981
124.057
121.482
121.167
118.287
112.679
59.021
41.462
40.394
1.929
1.720
1.510
1.300
1.090
0.880
0.671
X : parts per Million : Carbon13

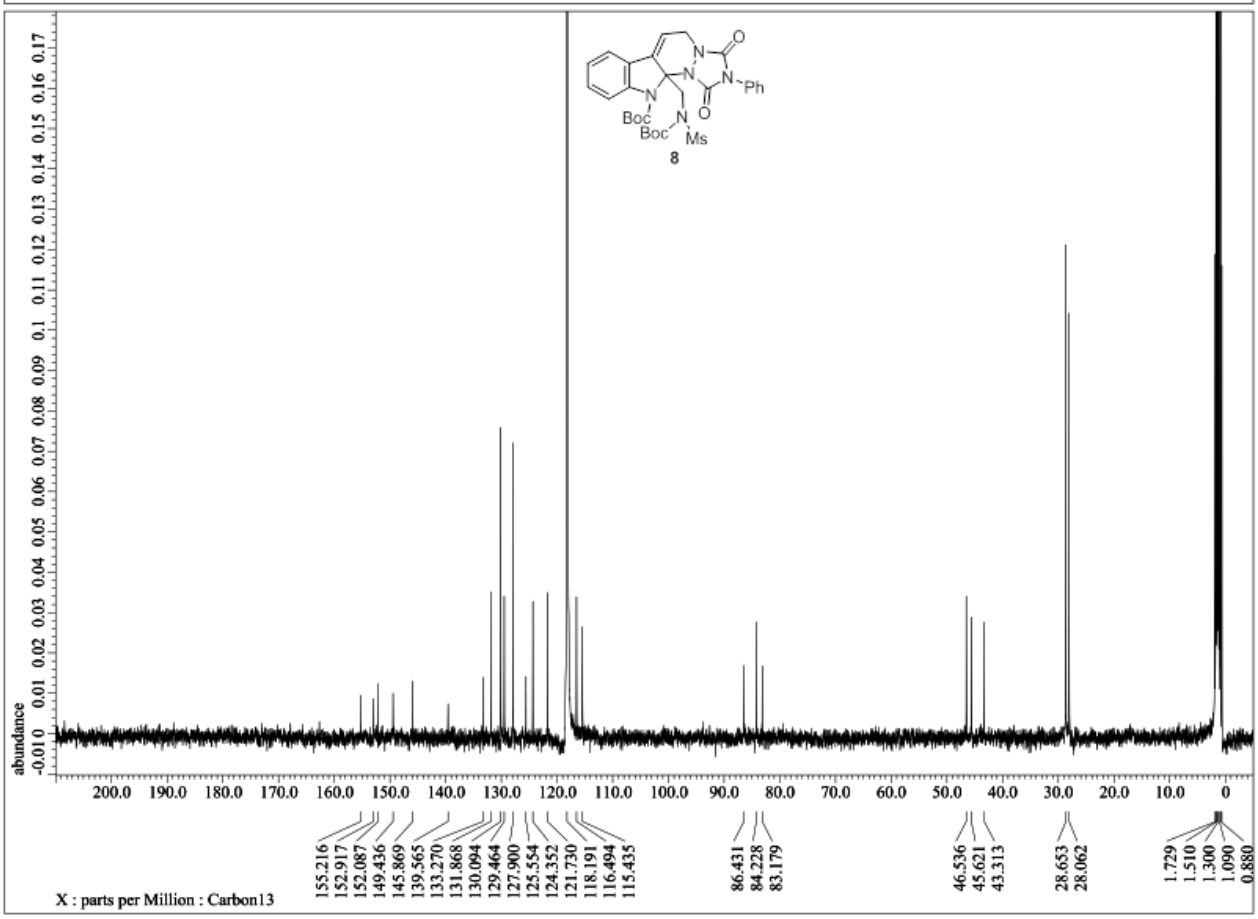

I
Ms
N–Boc
N
Boc
6
abundance
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
1.00
2.02
3.01
9.01
9.02
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.961
7.959
7.941
7.939
7.429
7.426
7.361
7.321
7.319
7.302
7.300
7.261
5.447
3.042
1.703
1.509
-0.000
X : parts per Million : Proton

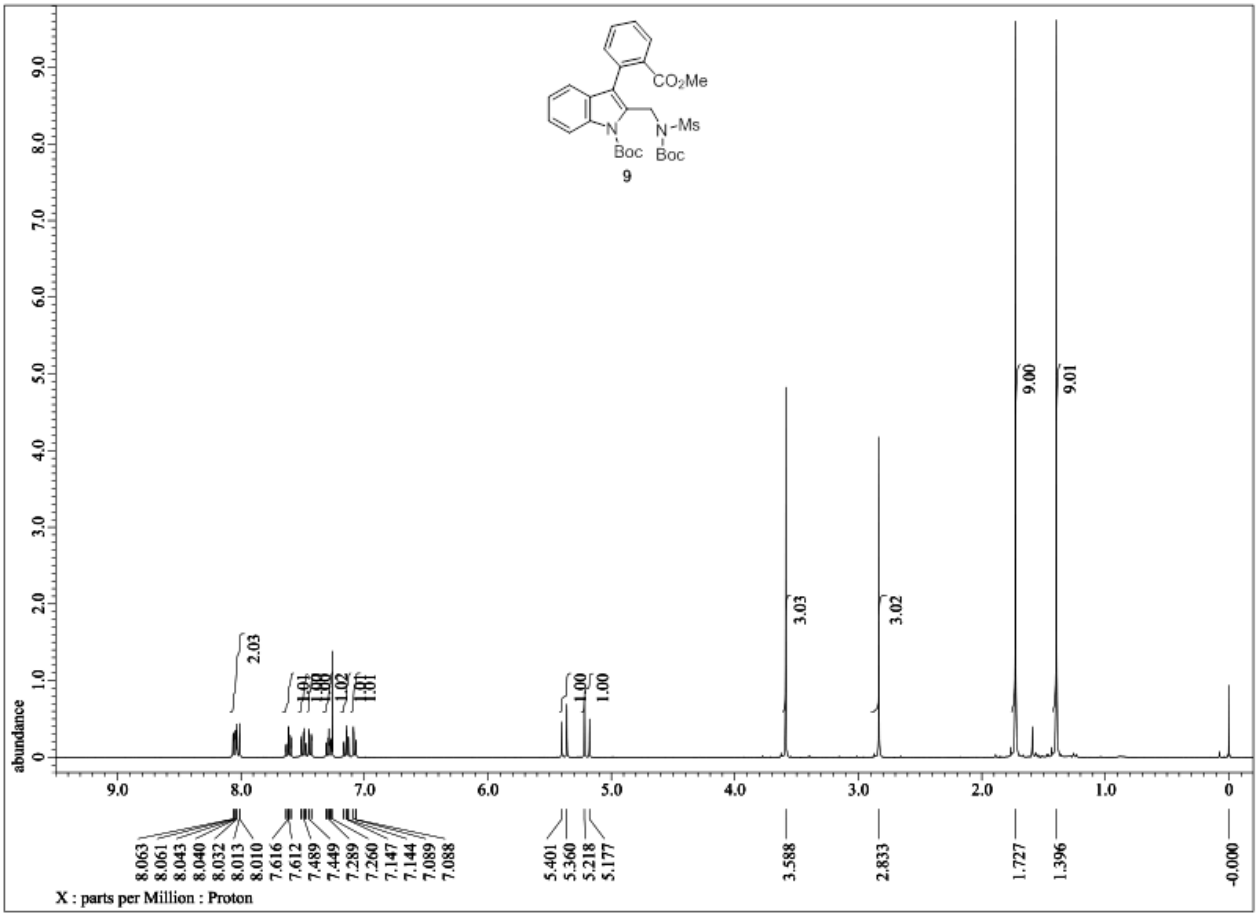

I
Ms
N–Boc
N
Boc
6
abundance
0.3
0.2
0.1
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
151.640
149.399
135.684
135.178
130.753
125.746
123.438
121.750
115.350
85.250
84.563
77.324
77.200
77.000
76.676
74.005
43.943
42.331
28.140
27.863
X : parts per Million : Carbon13

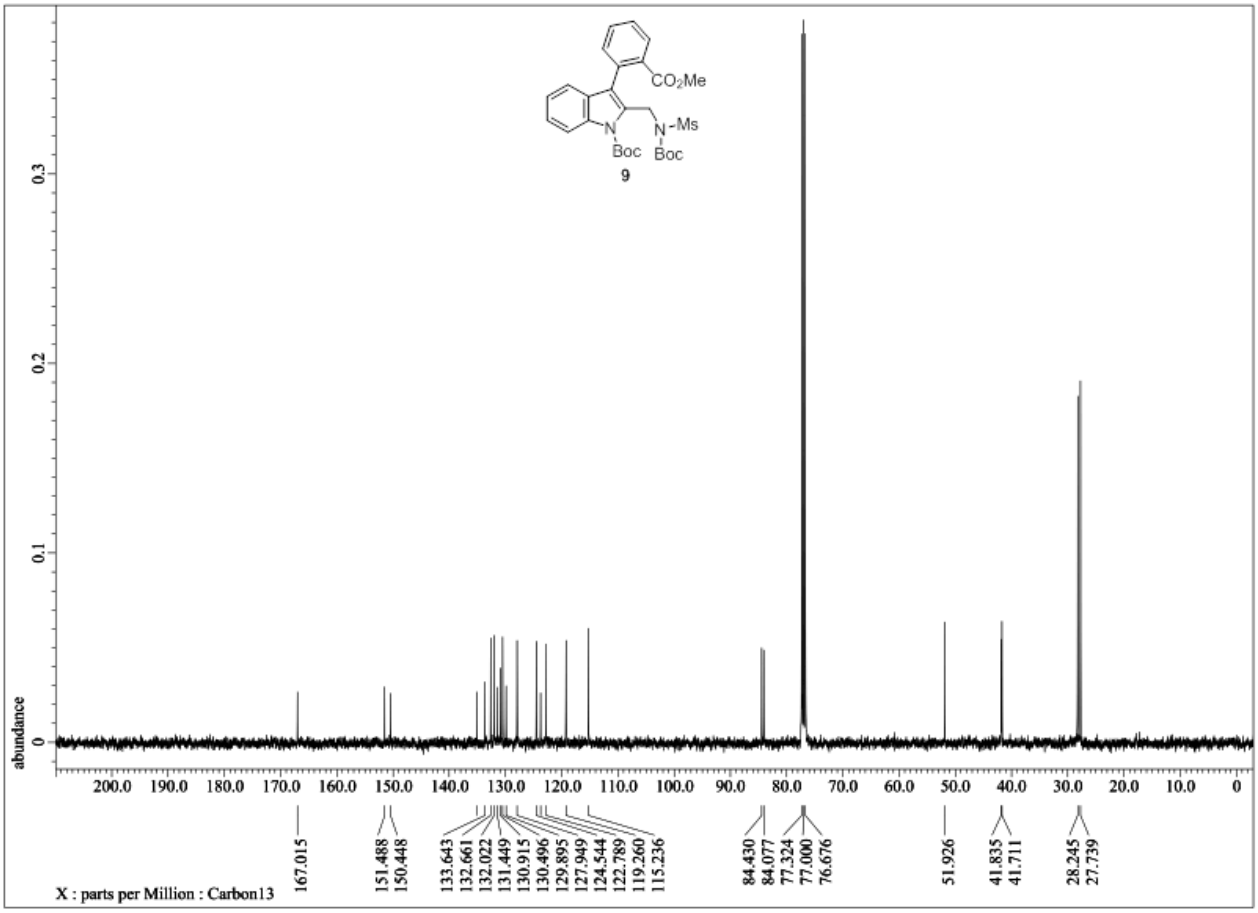

7
abundance
X : parts per Million : Proton
8.035
8.014
7.813
7.794
7.327
7.324
7.264
7.256
6.930
6.914
6.884
5.797
5.793
5.752
5.748
5.530
5.527
5.501
5.498
5.432
2.953
1.700
1.505
-0.000

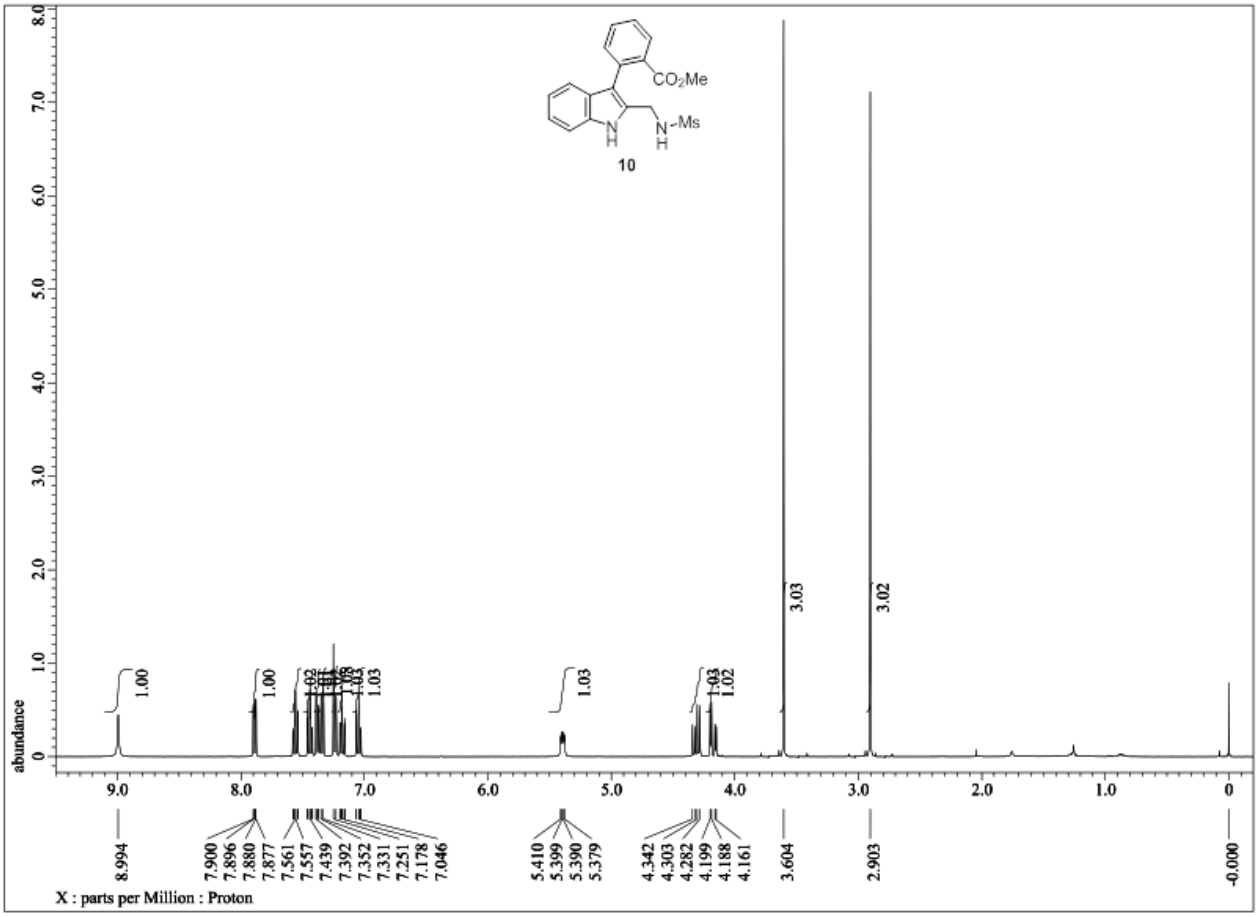

7
abundance
X : parts per Million : Carbon13
151.592
150.171
135.961
132.165
127.854
127.215
124.811
122.999
120.567
120.052
118.040
115.331
84.687
84.458
77.324
77.000
76.676
41.883
41.311
28.159
27.796

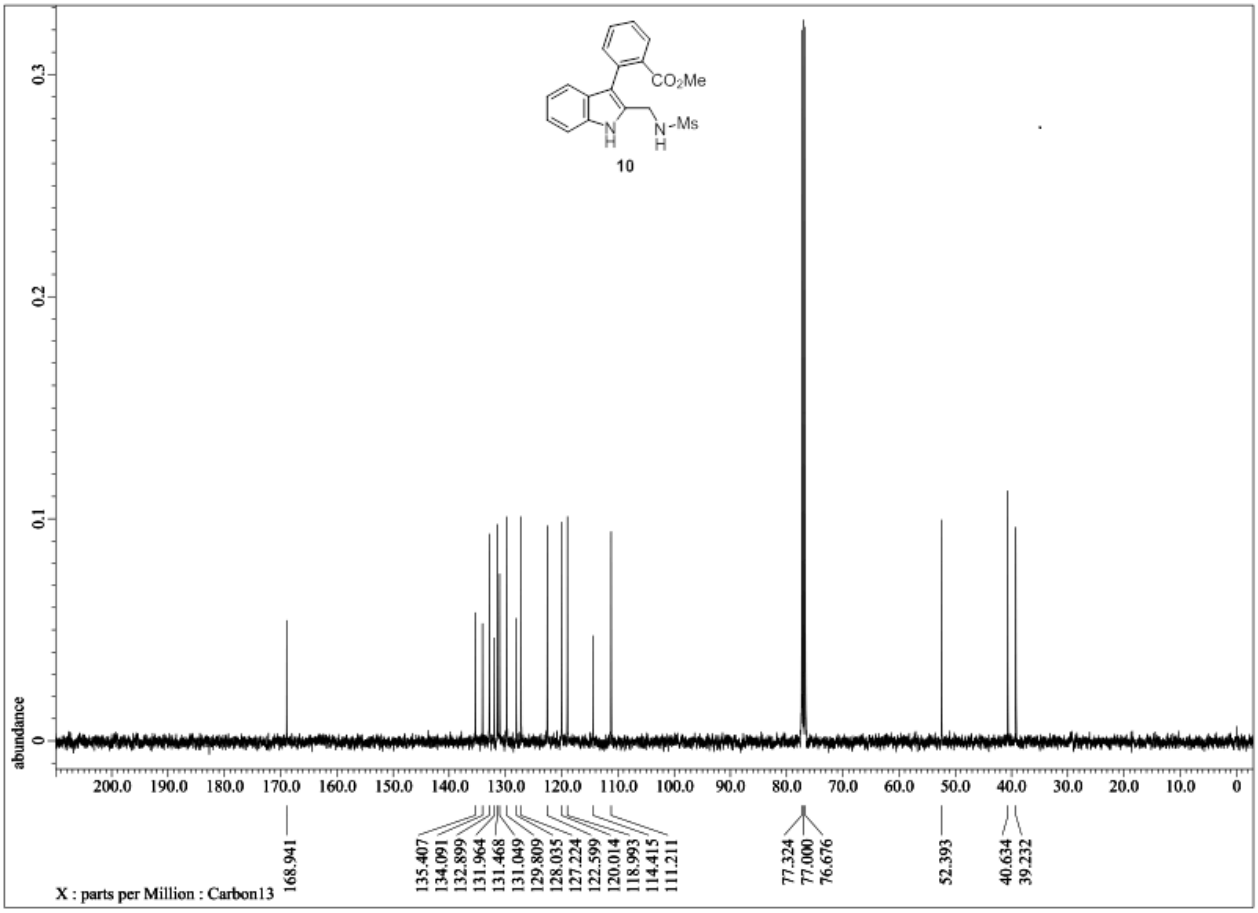

8
abundance
X : parts per Million : Proton
7.923
7.901
7.451
7.416
7.397
7.069
7.068
6.429
6.422
6.412
6.405
5.280
5.240
4.815
4.775
4.732
4.715
4.689
4.671
4.599
4.592
2.889
1.936
1.930
1.924
1.917
1.586
1.373
9.03
9.01
3.02

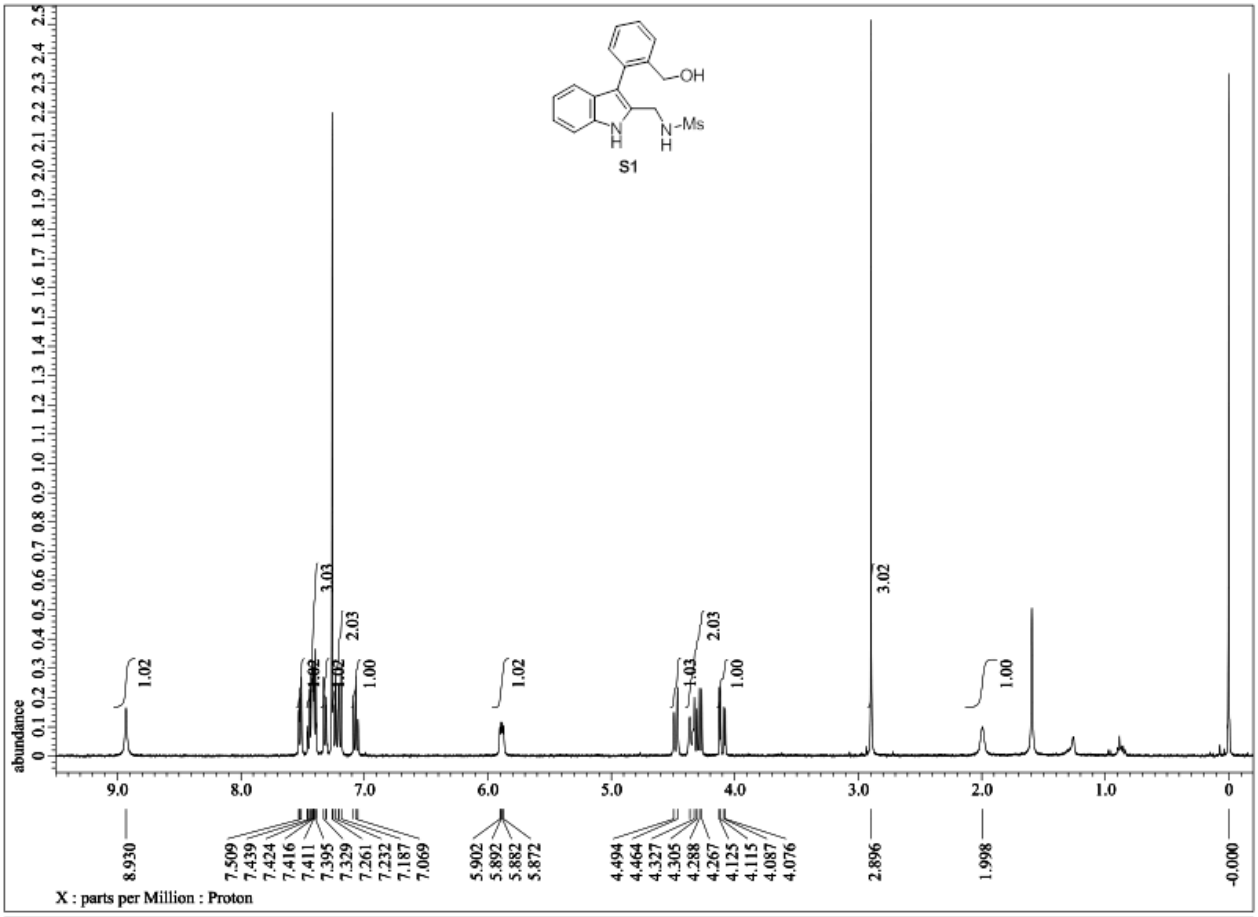

8
abundance
X : parts per Million : Carbon13
155.216
152.917
152.087
149.436
145.869
139.565
133.270
131.868
130.094
129.464
127.900
125.554
124.352
121.730
118.191
116.494
115.435
86.431
84.228
83.179
46.536
45.621
43.313
28.653
28.062
1.729
1.510
1.300
1.090
0.880

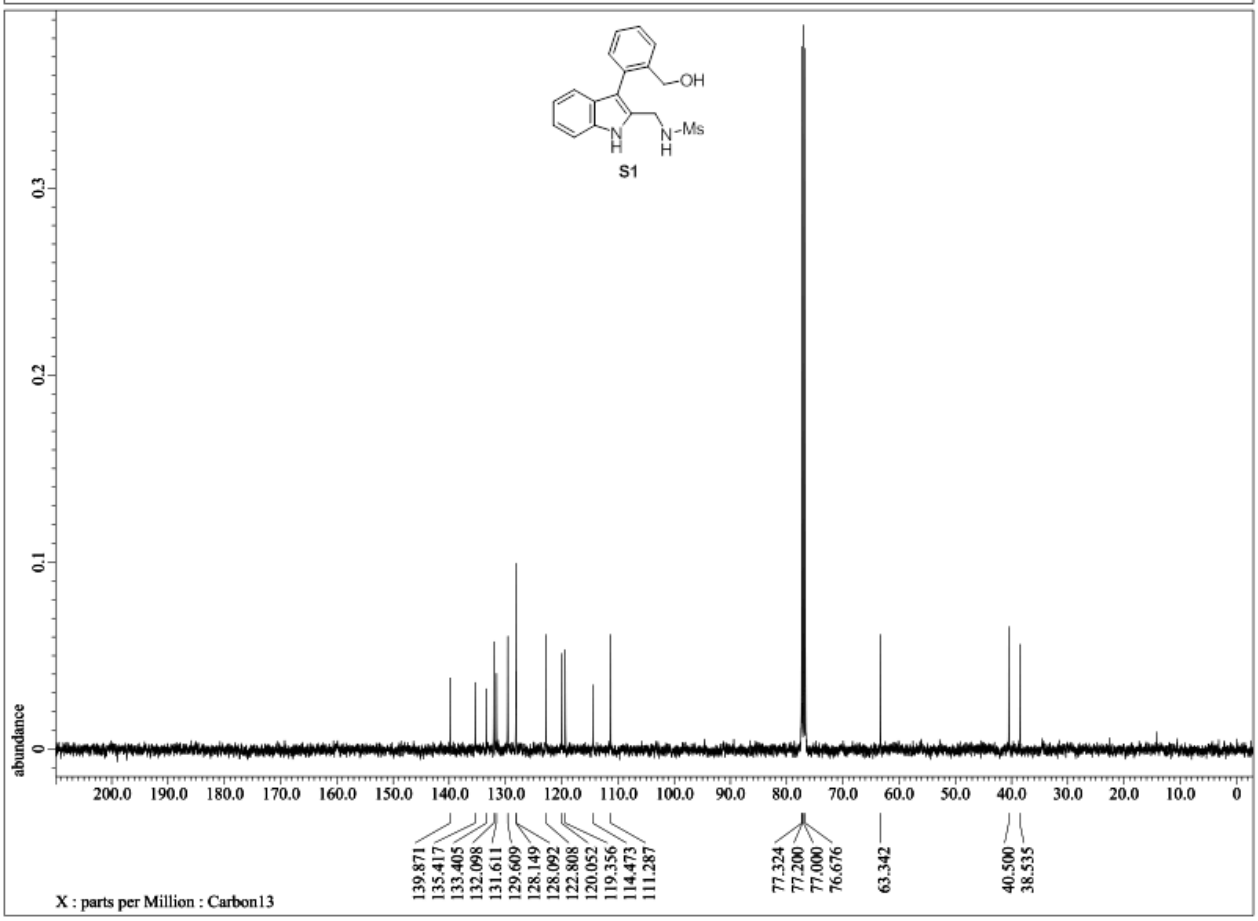

CO2Me
N-Ms
Boc Boc
9
abundance
2.03
1.01
1.00
1.02
1.01
1.00
1.00
3.03
3.02
9.00
9.01
8.063
8.061
8.043
8.040
8.032
8.013
8.010
7.616
7.612
7.489
7.449
7.289
7.260
7.147
7.144
7.089
7.088
5.401
5.360
5.218
5.177
3.588
2.833
1.727
1.396
-0.000
X : parts per Million : Proton

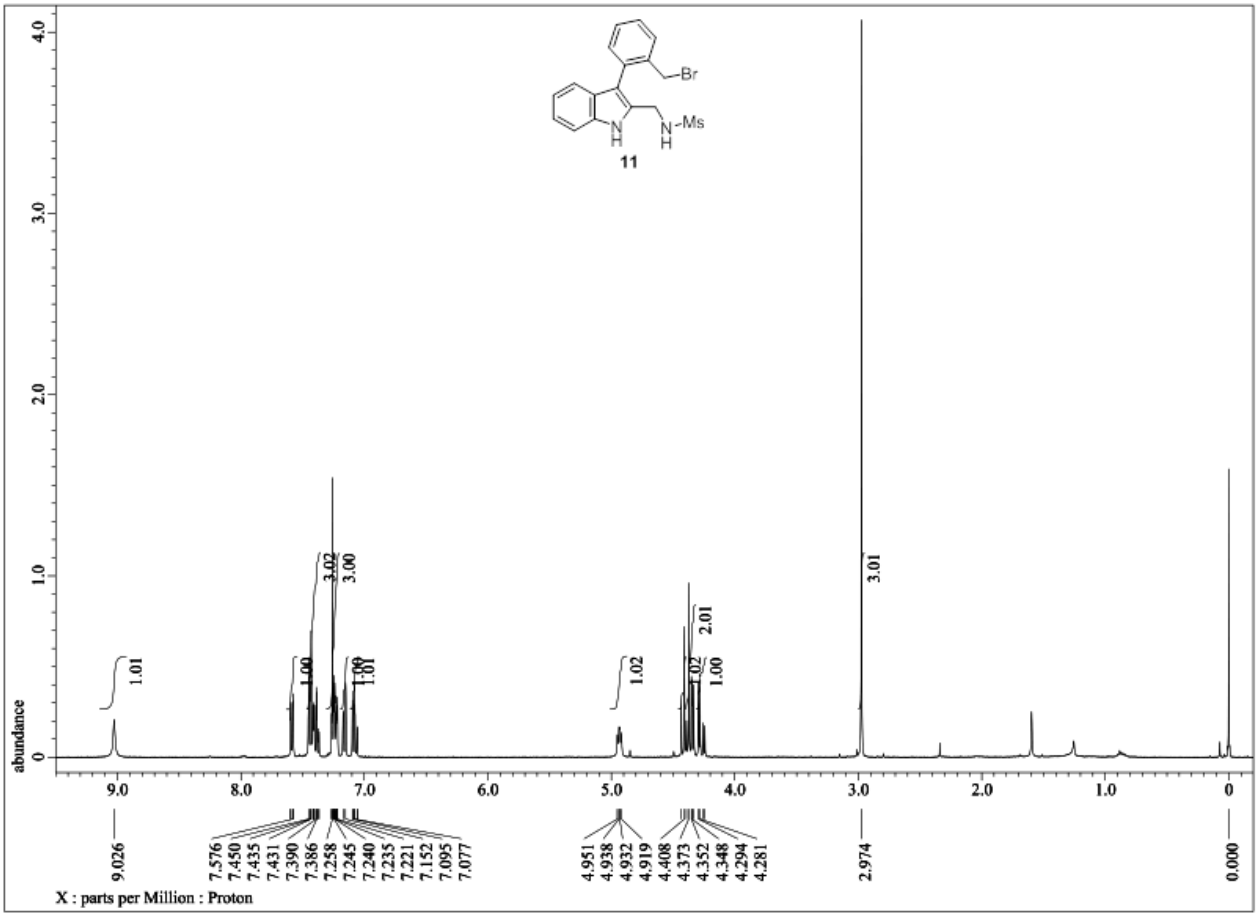

CO2Me
N-Ms
Boc Boc
9
abundance
167.015
151.488
150.448
133.643
132.661
132.022
131.449
130.915
130.496
129.895
127.949
124.544
122.789
119.260
115.236
84.430
84.077
77.324
77.000
76.676
51.926
41.835
41.711
28.245
27.739
X : parts per Million : Carbon13

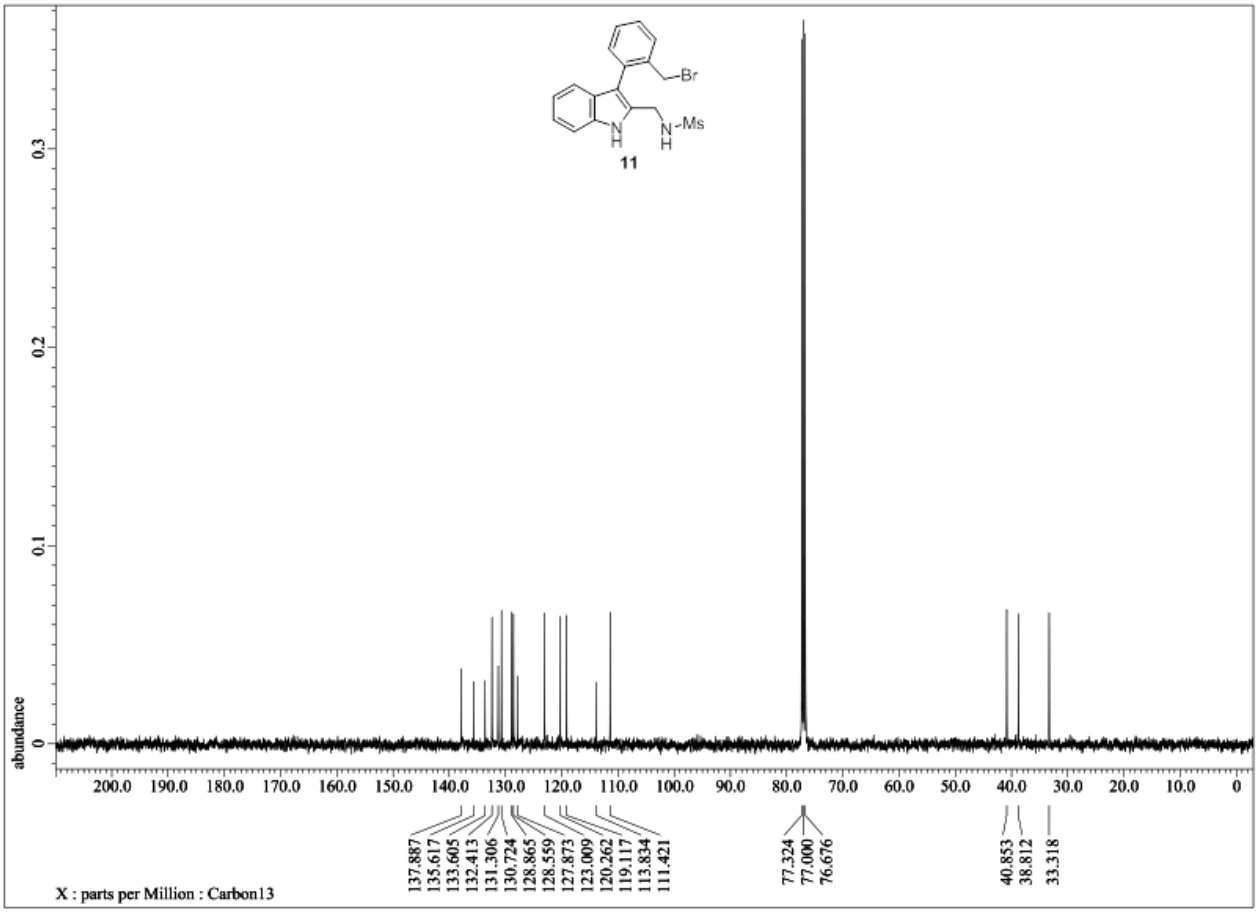

CO2Me
N-Ms
H
N
H
10
abundance
1.00
1.00
1.03
1.03
1.03
1.02
3.03
3.02
8.994
7.900
7.896
7.880
7.877
7.561
7.557
7.439
7.392
7.352
7.331
7.251
7.178
7.046
5.410
5.399
5.390
5.379
4.342
4.303
4.282
4.199
4.188
4.161
3.604
2.903
-0.000
X : parts per Million : Proton

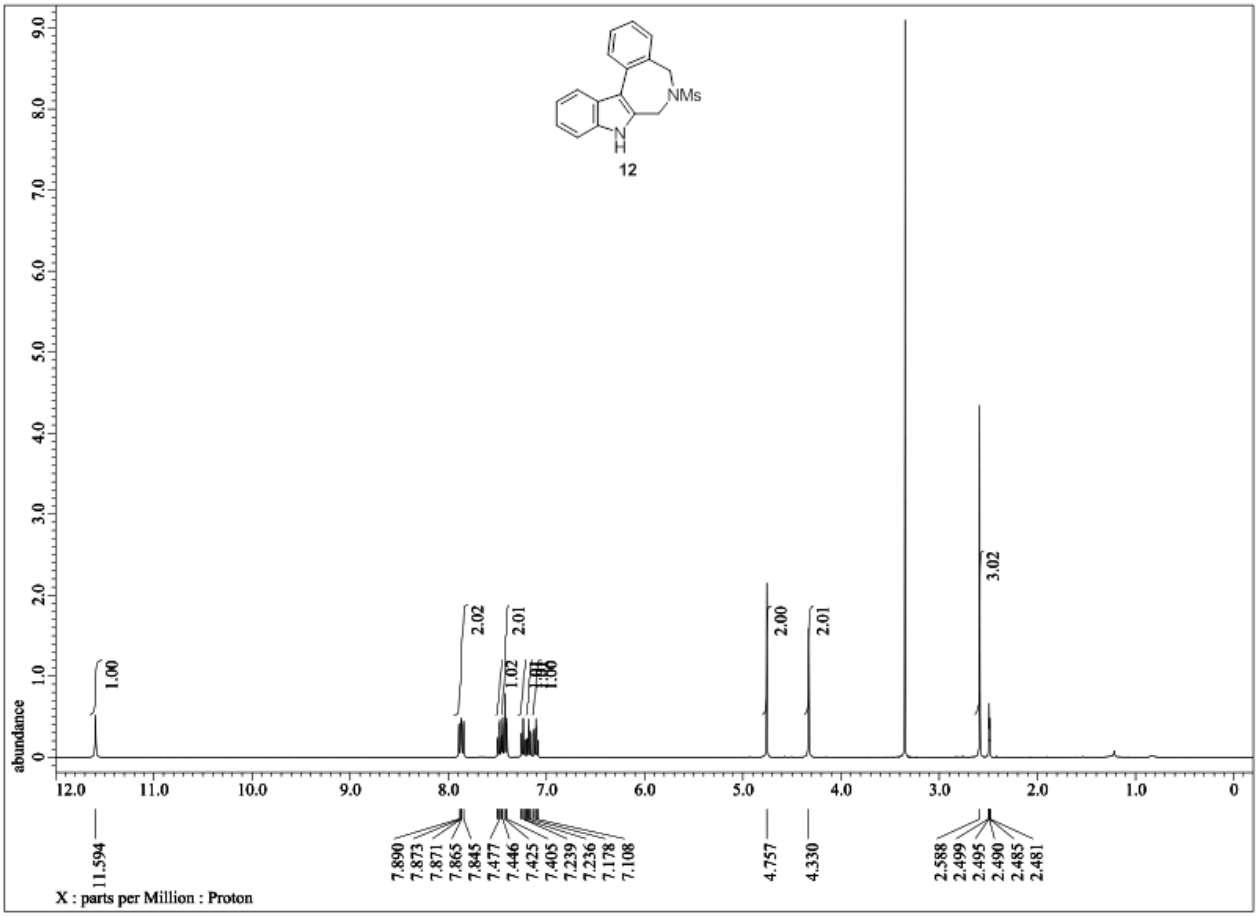

CO2Me
N-Ms
H
N
H
10
abundance
168.941
135.407
134.091
132.899
131.964
131.468
131.049
129.809
128.035
127.224
122.599
120.014
118.993
114.415
111.211
77.324
77.000
76.676
52.393
40.634
39.232
X : parts per Million : Carbon13

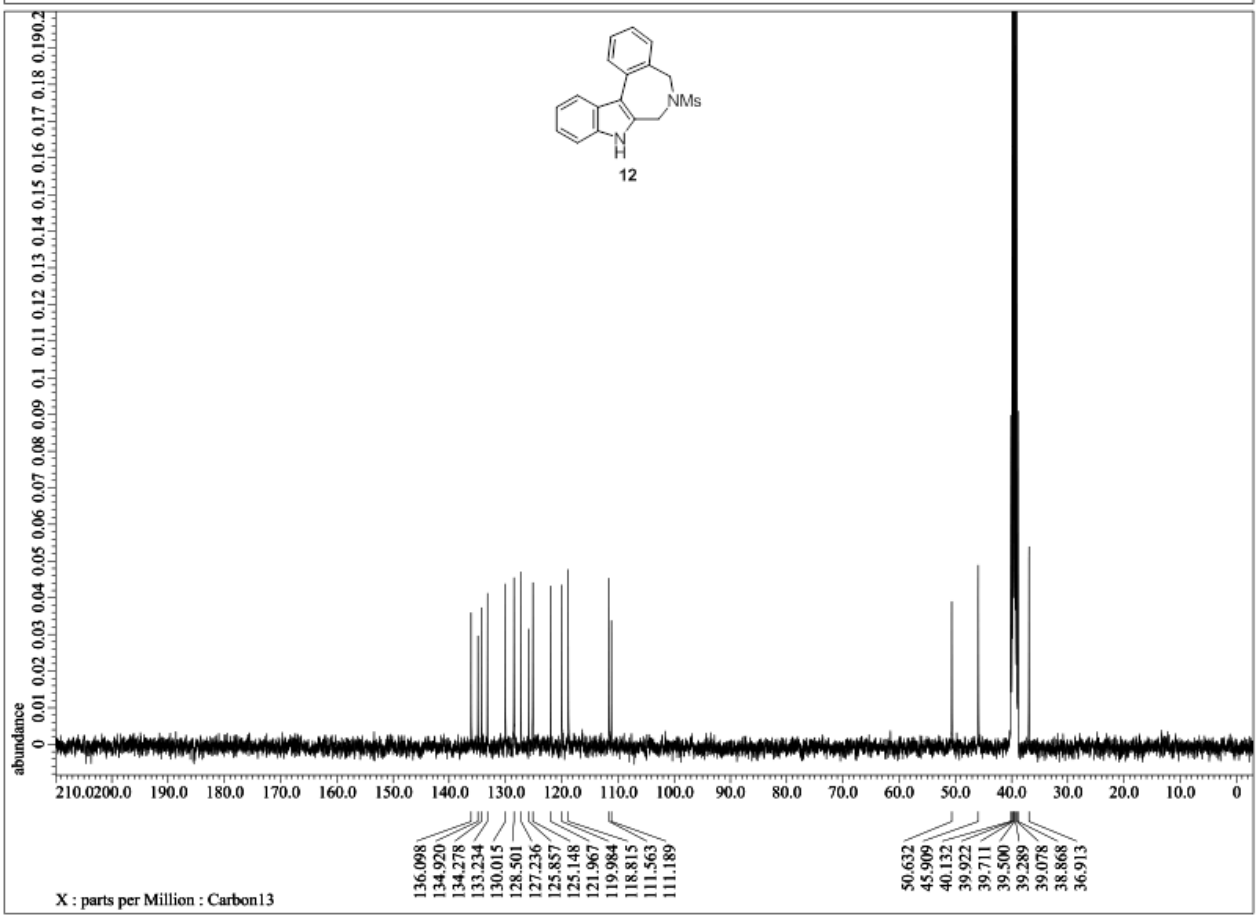

OH
N-Ms
H
N
H
S1
abundance
1.02
3.03
1.02
2.03
1.00
1.02
1.03
2.03
1.00
3.02
1.00
8.930
7.509
7.439
7.424
7.416
7.411
7.395
7.329
7.261
7.232
7.187
7.069
5.902
5.892
5.882
5.872
4.494
4.464
4.327
4.305
4.288
4.267
4.125
4.115
4.087
4.076
2.896
1.998
-0.000
X : parts per Million : Proton


OH
N-Ms
H
N
H
S1
abundance
139.871
135.417
133.405
132.098
131.611
129.609
128.149
128.092
122.808
120.052
119.356
114.473
111.287
77.324
77.200
77.000
76.676
63.342
40.500
38.535
X : parts per Million : Carbon13


Br
N-Ms
H
N
H
11
abundance
4.0
3.0
2.0
1.0
0
1.01
1.00
3.02
3.00
1.00
1.01
1.02
1.02
2.01
1.00
3.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.026
7.576
7.450
7.435
7.431
7.390
7.386
7.258
7.245
7.240
7.235
7.221
7.152
7.095
7.077
4.951
4.938
4.932
4.919
4.408
4.373
4.352
4.348
4.294
4.281
2.974
0.000
X : parts per Million : Proton


Br
N-Ms
H
N
H
11
abundance
0.3
0.2
0.1
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
137.887
135.617
133.605
132.413
131.306
130.724
128.865
128.559
127.873
123.009
120.262
119.117
113.834
111.421
77.324
77.000
76.676
40.853
38.812
33.318
X : parts per Million : Carbon13


NMs
H
12
abundance
1.00
2.02
2.01
1.02
2.00
2.01
3.02
11.594
7.890
7.873
7.871
7.865
7.845
7.477
7.446
7.425
7.405
7.239
7.236
7.178
7.108
4.757
4.330
2.588
2.499
2.495
2.490
2.485
2.481
X : parts per Million : Proton


NMs
H
12
abundance
136.098
134.920
134.278
133.234
130.015
128.501
127.236
125.857
125.148
121.967
119.984
118.815
111.563
111.189
50.632
45.909
40.132
39.922
39.711
39.500
39.289
39.078
38.868
36.913
X : parts per Million : Carbon13