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Supporting Information for

Regioselective C_{sp2}–H Dual Functionalization of Indoles Using Hypervalent Iodines(III): Bromo–Amination via 1,3-Migration of Imides on Indolyl(phenyl)iodonium Imides

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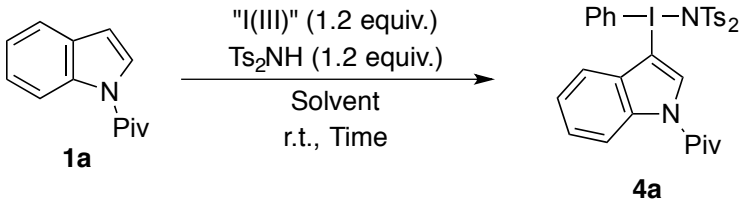
1. General Methods. ^{1}H NMR spectra were measured on a JEOL ECS-400 (400 MHz) spectrometer at ambient temperature. Data were recorded as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; sep = septet; m = 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 MeCN, CH_2Cl_2, and $ClCH_2CH_2Cl$ were distilled in prior to use.

2. General procedure for Preparation of Indolyl(phenyl)iodonium Imides (4).

A mixture of PhI(OAc)(NTs_2) were used with PhI$(OAc)_2$ (96.6 mg, 0.30 mmol), Ts_2NH (39.1 mg, 0.12 mmol) in MeCN (1.4 mL) and CH_2Cl_2 (0.7 mL) was stirred at room temperature for 30 min under argon atomosphere. Then, *N*-pivaloly indols **1a** (50.3 mg, 0.25 mmol) was added, and the solution was stirred at room temperature for 7 h. The volatile solvents were removed under reduced pressure. Et_2O (5 mL) was added, then the precipitated solid was washed with a mixture of ether and AcOEt (2:1) (15 mL) to give desired product **4a** (163.9 mg, 90 % yield).

Table S1. Isolation of Indolyl(phenyl)iodonium Imides (**4a**)

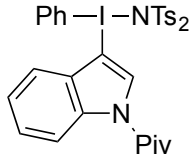


1a **4a**

Entry	"I(III)"	Solvent	Time (h)	Yield (%)
1	PhI$(OAc)_2$ (DIB)	MeCN	3	95
2	PhI$(OAc)_2$ (DIB)	CH_2Cl_2	7	83

3	$PhI(OAc)_2$ (DIB)	$CHCl_3$	24	59 (8)[a]
4	$PhI(OAc)_2$ (DIB)	Toluene	24	42 (36)[a]
5	$PhI(OAc)_2$ (DIB)	THF	24	0 (66)[a]
6	$PhI(OAc)_2$ (DIB)	MeOH	7	11
7	$PhI(OAc)_2$ (DIB)	$MeCN:CH_2Cl_2$ (2:1)	7	90
8	$PhI(OAc)_2$ (DIB)	$CF_3CH_2OH:CH_2Cl_2$ (2:1)	3	65
9	$PhI(OCOCF_3)_2$ (BTI)	$MeCN:CH_2Cl_2$ (2:1)	3	43
10	$PhI(OH)(OTs)_2$ (HTIB)	$MeCN:CH_2Cl_2$ (2:1)	3	19

[a]Numbers in parentheses indicate the recovery of **1a**.



4-Methyl-*N*-(phenyl(1-pivaloyl-1*H*-indol-3-yl)-λ^3-iodanyl)-*N*-tosylbenzenesulfonamide (4a): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.44 (s, 9H), 2.20 (s, 6H), 6.87 (d, J = 8.0 Hz, 4H), 7.27 (t, J = 7.5 Hz, 2H), 7.33 (t, J = 7.5 Hz, 1H), 7.39-7.48 (m, 7H), 8.08 (d, J = 7.5 Hz, 2H), 8.45 (d, J = 8.3 Hz, 1H), 8.85 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2 (2C), 28.4 (3C), 41.7, 86.0, 115.4, 117.6, 119.4, 125.1, 126.76 (4C), 126.81, 127.7, 128.5 (4C), 131.6 (3C), 134.9 (2C), 135.5, 136.3, 140.8 (2C), 141.0 (2C), 177.1. IR (neat) 1703, 1444, 1281, 1134, 1077, 1035, 1014, 814, 741, 670 cm^{-1}. MS (ESI) calcd for $C_{33}H_{33}IN_2NaO_5S_2$ $[M+Na]^+$ 751.0768, found 751.0754.

Crystal data for 4a: Formula $C_{33}H_{33}IN_2O_5S_2$•$2CHCl_3$, colorless, crystal dimensions 0.30 × 0.20 × 0.10 mm^3, Monoclinic, space group P2(1)/n, a = 18.254(3) Å, b = 9.5783(15) Å, c = 23.967(4) Å, α = 90.00 °, β = 97.1187(2) °, γ = 90.00 °, V = 4157.7(11) Å^3, Z = 4, ρ_{calc} = 1.545 g cm^{-3}, F(000) = 1944, μ(MoKα) = 1.298 mm^{-1}, T = 173 K. 22389 reflections collected, 9335 independent reflections with $I > 2\sigma(I)$ ($2\theta_{max}$ = 27.56°), and 539 parameters were used for the solution of the structure. The non-hydrogen atoms were refined anisotropically. R_1 = 0.0678 and wR_2 = 0.1797. GOF = 1.061. 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-1023214. 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].

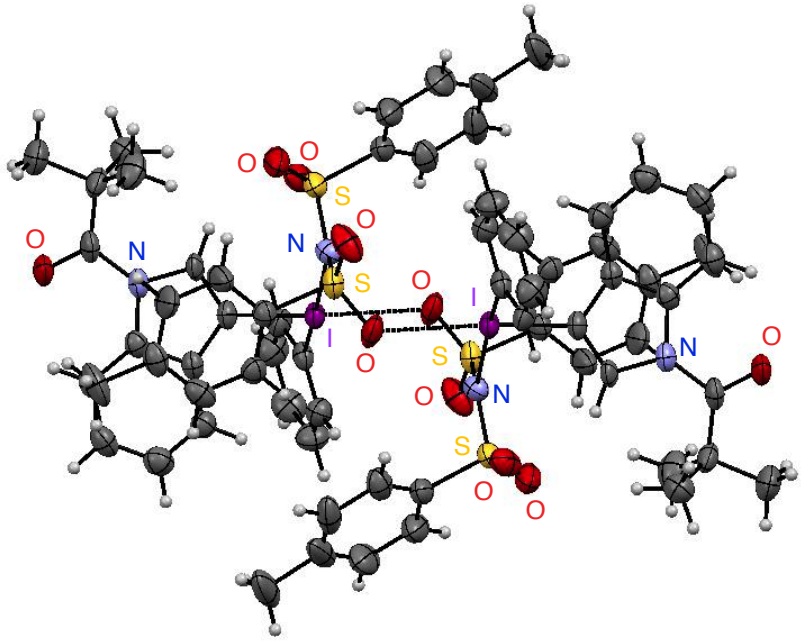


Figure S1. ORTEP drawing of **4a** (dimer structure).

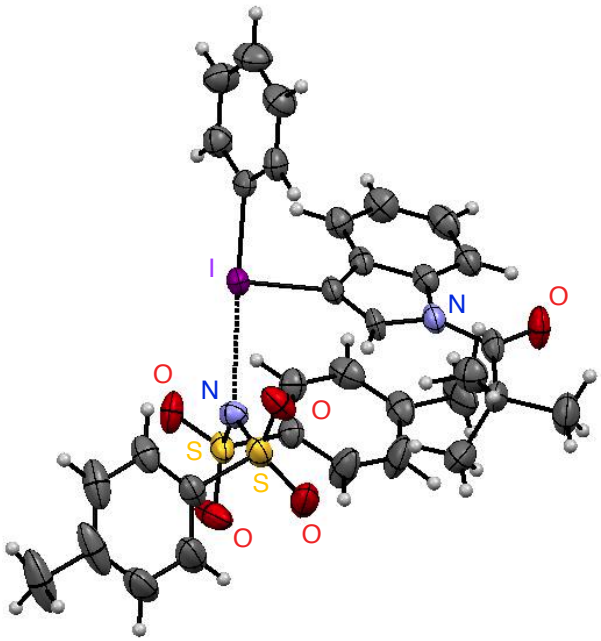
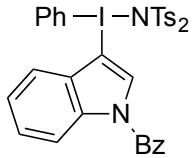
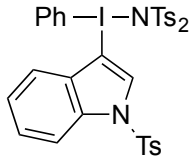


Figure S2. ORTEP drawing of **4a** (monomer unit).

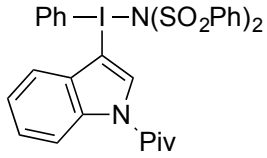


***N*-((1-Benzoyl-1*H*-indol-3-yl)(phenyl)-λ^3-iodanyl)-4-methyl-*N*-tosylbenzenesulfonamide (4b):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.21 (s, 6H), 6.85 (d, *J* = 8.1 Hz, 4H), 7.26 (t, *J* = 7.7 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 4H), 7.34-7.55 (m, 6H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.69 (d, *J* = 7.2 Hz, 2H), 8.00 (d, *J*

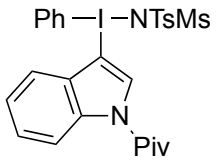
= 7.7 Hz, 2H), 8.23 (s, 1H), 8.38 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2 (2C), 86.7, 115.6, 116.7, 119.9, 125.5, 126.7 (5C), 128.4 (4C), 128.9, 129.2 (2C), 129.9 (2C), 131.5 (3C), 132.0, 133.2, 134.7 (2C), 135.7, 136.8, 140.7 (2C), 141.1 (2C), 167.9. IR (neat) 1695, 1445, 1282, 1134, 1081, 1029, 1010, 808, 761, 664 cm^{-1}. MS (ESI) calcd for $C_{35}H_{29}IN_2NaO_5S_2$ $[M+Na]^+$ 771.0455, found 771.0448.



4-Methyl-*N*-(phenyl(1-tosyl-1*H*-indol-3-yl)-λ^3-iodanyl)-*N*-tosylbenzenesulfonamide (4c): ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.29 (s, 9H), 7.12 (d, *J* = 8.0 Hz, 4H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.43-7.49 (m, 4H), 7.52 (d, *J* = 8.0 Hz, 4H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 2H), 8.00 (d, *J* = 8.4 Hz, 1H), 8.26 (d, *J* = 7.8 Hz, 2H), 9.03 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 20.8 (2C), 21.1, 90.3, 113.7, 117.3, 120.8, 125.2, 126.1 (4C), 126.9, 127.1 (2C), 128.2 (4C), 128.6, 130.6 (2C), 131.7 (2C), 132.0, 133.1, 133.4, 134.7 (2C), 135.0, 139.5 (2C), 143.8 (2C), 146.6. IR (neat) 1364, 1283, 1136, 1081, 1030, 1010, 812, 762, 672 cm^{-1}. MS (ESI) calcd for $C_{35}H_{31}IN_2NaO_6S_3$ $[M+Na]^+$ 821.0281, found 821.0267.

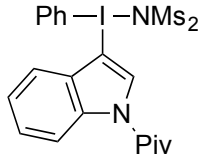


***N*-(phenyl(1-pivaloyl-1*H*-indol-3-yl)-λ^3-iodanyl)-*N*-(phenylsulfonyl)benzenesulfonamide (4d):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.43 (s, 9H), 7.10 (t, *J* = 8.0 Hz, 4H), 7.22 (t, *J* = 7.7 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.40-7.49 (m, 3H), 7.55 (d, *J* = 8.0 Hz, 4H), 8.07 (d, *J* = 7.7 Hz, 2H), 8.46 (d, *J* = 8.1 Hz, 1H), 8.84 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.3 (3C), 41.7, 85.9, 115.3, 117.7, 119.3, 125.2, 126.6 (4C), 126.9, 127.7, 127.9 (4C), 130.6 (2C), 131.6 (2C), 131.7, 134.9 (2C), 135.4, 136.3, 143.9 (2C), 1771. IR (neat) 1712, 1444, 1279, 1131, 1078, 1038, 793, 744, 720, 688 cm^{-1}. MS (ESI) calcd for $C_{31}H_{29}IN_2NaO_5S_2$ $[M+Na]^+$ 723.0455, found 723.0444.

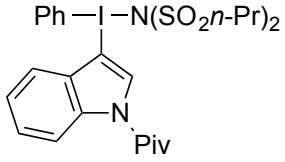


4-Methyl-*N*-(methylsulfonyl)-*N*-(phenyl(1-pivaloyl-1*H*-indol-3-yl)-λ^3-iodanyl)benzenesulfonamide (4e): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.48 (s, 9H), 2.23 (s, 3H), 2.80 (s, 3H), 6.99 (d, *J* = 7.5 Hz, 2H), 7.30-7.38 (m, 3H), 7.40-7.52 (m, 3H), 7.56 (d, *J* = 7.5 Hz, 2H), 8.07 (d, *J* = 8.3 Hz, 2H), 8.47 (d, *J* = 8.6 Hz, 1H), 8.75 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3, 28.4 (3C),

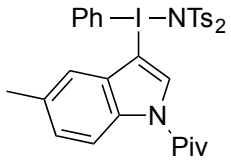
41.7, 42.7, 86.2, 115.7, 117.7, 119.3, 125.2, 126.7 (2C), 127.0, 127.6, 128.7 (2C), 131.67 (2C), 131.73, 134.7 (2C), 135.1, 136.3, 141.2, 141.6, 177.0. IR (neat) 1710, 1443, 1267, 1120, 1080, 1051, 823, 747, 717 cm^{-1}. MS (ESI) calcd for $C_{27}H_{29}IN_2NaO_5S_2$ $[M+Na]^+$ 675.0455, found 675.0450.



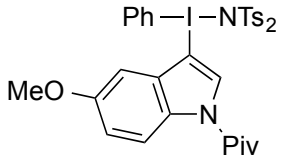
***N*-(Methylsulfonyl)-*N*-(phenyl(1-pivaloyl-1*H*-indol-3-yl)-λ^3-iodanyl)methanesulfonamide (4f):** **4f** could not be prepared. The yield of **4f** was assigned from that of **4a** by analogy of the ^{1}H-NMR spectra of the crude product based on internal standard (1,4-bis(trimethylsilyl)benzene).



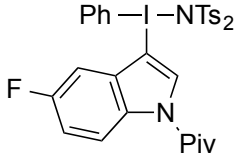
***N*-(Phenyl(1-pivaloyl-1*H*-indol-3-yl)-λ^3-iodanyl)-*N*-(propylsulfonyl)propane-1-sulfonamide (4g):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.5 Hz, 6H), 1.56 (s, 9H), 1.60-1.70 (m, 4H), 2.95-3.00 (m, 4H), 7.36-7.43 (m, 3H), 7.44-7.50 (m, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 8.11 (d, *J* = 7.5 Hz, 2H), 8.49 (d, *J* = 8.6 Hz, 1H), 8.65 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.0 (2C), 17.5 (2C), 28.5 (3C), 41.8, 56.1 (2C), 86.8, 116.6, 117.8, 119.3, 125.4, 127.3, 127.5, 131.9 (2C), 132.0, 134.46 (2C), 134.53, 136.4, 176.7. IR (neat) 1706, 1442, 1270, 1095, 1046, 948, 822, 741, 608 cm^{-1}. MS (ESI) calcd for $C_{25}H_{33}IN_2NaO_5S_2$ $[M+Na]^+$ 655.0768, found 655.0771.



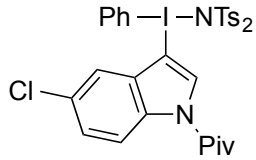
4-Methyl-*N*-((5-methyl-1-pivaloyl-1*H*-indol-3-yl)(phenyl)-λ^3-iodanyl)-*N*-tosylbenzenesulfonamide (4h): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.44 (s, 9H), 2.23 (s, 6H), 2.43 (s, 3H), 6.88 (d, *J* = 8.0 Hz, 4H), 7.19 (s, 1H), 7.24 (d, *J* = 8.6 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.42-7.48 (m, 1H), 7.45 (d, *J* = 8.0 Hz, 4H), 8.06 (d, *J* = 7.8 Hz, 2H), 8.32 (d, *J* = 8.6 Hz, 1H), 8.78 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.26 (2C), 21.33, 28.4 (2C), 41.7, 85.4, 115.4, 117.4, 119.0, 126.8 (4C), 127.8, 128.4, 128.5 (4C), 131.6, 131.7 (2C), 134.5, 134.6 (2C), 135.2, 135.4, 140.7 (2C), 140.9 (2C), 176.9. IR (neat) 1699, 1469, 1294, 1131, 1078, 1037, 1014, 806, 760, 742, 671 cm^{-1}. MS (ESI) calcd for $C_{34}H_{35}IN_2NaO_5S_2$ $[M+Na]^+$ 765.0924, found 765.0908.



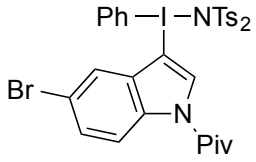
***N*-((5-Methoxy-1-pivaloyl-1*H*-indol-3-yl)(phenyl)-λ^3-iodanyl)-4-methyl-*N*-tosylbenzenesulfonamide (4i):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.43 (s, 9H), 2.20 (s, 6H), 3.80 (s, 3H), 6.86 (s, 1H), 6.87 (d, *J* = 8.3 Hz, 4H), 6.99 (dd, *J* = 9.2, 2.3 Hz, 1H), 7.27 (t, *J* = 7.7 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 4H), 7.36-7.48 (m, 1H), 8.09 (d, *J* = 7.7 Hz, 2H), 8.33 (d, *J* = 9.2 Hz, 1H), 8.79 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2 (2C), 28.4 (2C), 41.6, 55.9, 85.7, 101.6, 115.4, 115.8, 118.6, 126.7 (4C), 128.4 (4C), 128.8, 130.7, 131.50 (2C), 131.54, 134.9 (2C), 135.6, 140.8 (2C), 141.2 (2C), 157.5, 176.8. IR (neat) 1711, 1471, 1260, 1128, 1075, 1039, 802, 737, 664 cm^{-1}. MS (ESI) calcd for $C_{34}H_{35}IN_2NaO_6S_2$ $[M+Na]^+$ 781.0873, found 781.0867.



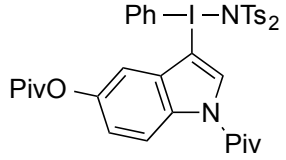
***N*-((5-Fluoro-1-pivaloyl-1*H*-indol-3-yl)(phenyl)-λ^3-iodanyl)-4-methyl-*N*-tosylbenzenesulfonamide (4j):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.42 (s, 9H), 2.22 (s, 6H), 6.90 (d, *J* = 8.2 Hz, 4H), 7.05 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.13 (td, *J* = 9.2, 2.3 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 4H), 7.46 (t, *J* = 7.5 Hz, 1H), 8.06 (d, *J* = 7.5 Hz, 2H), 8.42 (dd, *J* = 9.2, 4.6 Hz, 1H), 8.91 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2 (2C), 28.4 (3C), 41.7, 85.7, 105.2 (d, J_{C-F} = 25.0 Hz), 114.7 (d, J_{C-F} = 25.0 Hz), 115.6, 119.2 (d, J_{C-F} = 9.5 Hz), 126.7 (4C), 128.5 (4C), 129.1 (d, J_{C-F} = 10.7 Hz), 131.56 (2C), 131.63, 132.6, 135.1 (2C), 136.9, 141.06 (2C), 141.13 (2C), 160.2 (d, J_{C-F} = 243.2 Hz), 177.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ −115.8. IR (neat) 1716, 1469, 1441, 1280, 1179, 1133, 1077, 1031, 1011, 813, 761, 738, 671 cm^{-1}. MS (ESI) calcd for $C_{33}H_{32}FIN_2NaO_5S_2$ $[M+Na]^+$ 769.0674, found 769.0662.



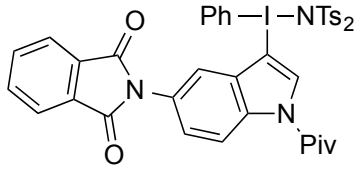
***N*-((5-Chloro-1-pivaloyl-1*H*-indol-3-yl)(phenyl)-λ^3-iodanyl)-4-methyl-*N*-tosylbenzenesulfonamide (4k):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.42 (s, 9H), 2.21 (s, 6H), 6.88 (d, *J* = 8.1 Hz, 4H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.32-7.38 (m, 2H), 7.40 (d, *J* = 8.1 Hz, 4H), 7.47 (t, *J* = 7.8 Hz, 1H), 8.07 (d, *J* = 7.8 Hz, 2H), 8.37 (d, *J* = 9.8 Hz, 1H), 8.91 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2 (2C), 28.3 (3C), 41.7, 85.4, 115.8, 118.8, 118.9, 126.7 (4C), 126.9, 128.5 (4C), 129.2, 130.7, 131.5 (2C), 131.6, 134.6, 135.1 (2C), 136.7, 141.0 (2C),141.1 (2C), 177.0. IR (neat) 1715, 1442, 1260, 1076, 1044, 810, 763, 735, 665 cm^{-1}. MS (ESI) calcd for $C_{33}H_{32}ClIN_2NaO_5S_2$ $[M+Na]^+$ 785.0378, found 785.0363.



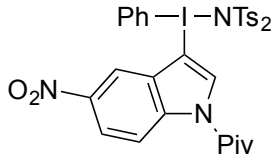
***N*-((5-Bromo-1-pivaloyl-1*H*-indol-3-yl)(phenyl)-λ^3-iodanyl)-4-methyl-*N*-tosylbenzenesulfonamide (4l):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.43 (s, 9H), 2.22 (s, 6H), 6.87 (d, *J* = 8.1 Hz, 4H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 4H), 7.46-7.62 (m, 3H), 8.06 (d, *J* = 7.8 Hz, 2H), 8.30 (d, *J* = 7.1 Hz, 1H), 8.89 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2 (2C), 28.3 (3C), 41.8, 85.1, 115.7, 118.4, 119.1, 121.9, 126.7 (4C), 128.5 (4C), 129.5, 129.6, 131.6 (2C), 131.7, 135.1 (3C), 136.6, 140.87 (2C), 140.93 (2C), 177.0. IR (neat) 1714, 1441, 1281, 1133, 1081, 1040, 808, 763, 672 cm^{-1}. MS (ESI) calcd for $C_{34}H_{35}IN_2NaO_6S_2$ $[M+Na]^+$ 781.0873, found 781.0867.



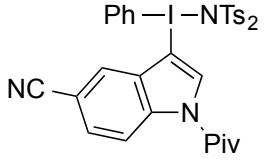
3-(((4-Methyl-*N*-tosylphenyl)sulfonamido)(phenyl)-λ^3-iodanyl)-1-pivaloyl-1*H*-indol-5-yl pivalate (4m): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.37 (s, 9H), 1.45 (s, 9H), 2.21 (s, 6H), 6.90 (d, *J* = 8.1 Hz, 4H), 7.11 (dd, *J* = 9.2, 2.3 Hz, 1H), 7.16 (d, *J* = 2.3 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 4H), 7.48 (t, *J* = 7.8 Hz, 1H), 8.08 (d, *J* = 7.8 Hz, 2H), 8.45 (d, *J* = 9.2 Hz, 1H), 8.83 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.1 (2C), 27.1 (3C), 28.3 (3C), 39.0, 41.6, 85.7, 111.8, 115.7, 118.3, 120.6, 126.6 (4C), 128.4 (4C), 128.6, 129.6, 131.4 (2C), 133.7, 135.0 (2C), 136.5, 140.88 (2C), 140.92 (2C), 148.3, 176.9 (2C). IR (neat) 1748, 1712, 1459, 1276, 1133, 1113, 1078, 1034, 822, 770, 741, 671 cm^{-1}. MS (ESI) calcd for $C_{38}H_{41}IN_2NaO_7S_2$ $[M+Na]^+$ 851.1292, found 851.1279.



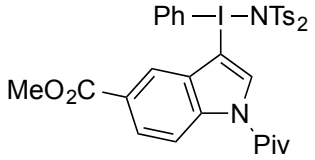
***N*-((5-(1,3-Dioxoisoindolin-2-yl)-1-pivaloyl-1*H*-indol-3-yl)(phenyl)-λ^3-iodanyl)-4-methyl-*N*-tosylbenzenesulfonamide (4n):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.43 (s, 9H), 2.19 (s, 6H), 6.85 (d, *J* = 8.1 Hz, 4H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 4H), 7.41-7.50 (m, 2H), 7.62 (d, *J* = 1.8 Hz, 1H), 7.76-7.82 (m, 2H), 7.86-7.94 (m, 2H), 8.17 (d, *J* = 7.8 Hz, 2H), 8.51 (d, *J* = 8.9 Hz, 1H), 8.91 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2 (2C), 28.3 (3C), 41.7, 86.6, 116.0, 117.7, 118.3, 123.7 (2C), 125.0, 126.6 (4C), 128.3, 128.4 (4C), 128.6, 129.8, 131.6 (4C), 134.5 (2C), 135.2, 135.4 (2C), 136.3, 140.8 (2C), 141.3 (2C), 167.1 (2C), 177.0. IR (neat) 1719, 1468, 1377, 1279, 1132, 1077, 1036, 814, 751, 716, 669 cm^{-1}. MS (ESI) calcd for $C_{41}H_{36}IN_3NaO_7S_2$ $[M+Na]^+$ 896.0932, found 896.0908.



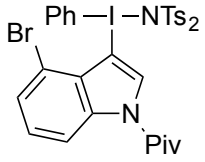
4-Methyl-*N*-((5-nitro-1-pivaloyl-1*H*-indol-3-yl)(phenyl)-λ^3-iodanyl)-*N*-tosylbenzenesulfonamide (4o): **4o** could not be prepared. The yield of **4o** was assigned from that of **4a** by analogy of the ^{1}H-NMR spectra of the crude product based on internal standard (1,4-bis(trimethylsilyl)benzene).



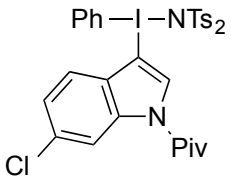
***N*-((5-Cyano-1-pivaloyl-1*H*-indol-3-yl)(phenyl)-λ^3-iodanyl)-4-methyl-*N*-tosylbenzenesulfonamide (4p):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.43 (s, 9H), 2.23 (s, 6H), 6.87 (d, *J* = 8.0 Hz, 4H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 4H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.63 (dd, *J* = 8.9, 1.4 Hz, 1H), 7.72 (d, *J* = 1.4 Hz, 2H), 8.09 (d, *J* = 7.8 Hz, 2H), 8.51 (d, *J* = 8.9 Hz, 1H), 9.02 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3 (2C), 28.2 (3C), 41.9, 86.3, 108.5, 115.8, 118.58, 118.62, 124.1, 126.6 (4C), 128.2, 128.5 (4C), 129.4, 131.7 (2C), 131.9, 135.3 (2C), 137.6, 138.1, 140.8 (2C), 141.0 (2C), 177.1. IR (neat) 2223, 1721, 1457, 1280, 1133, 1078, 1039, 821, 763, 672 cm^{-1}. MS (ESI) calcd for $C_{34}H_{32}IN_3NaO_5S_2$ $[M+Na]^+$ 776.0720, found 776.0707.



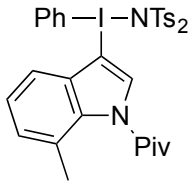
Methyl 3-(((4-methyl-*N*-tosylphenyl)sulfonamido)(phenyl)-λ^3-iodanyl)-1-pivaloyl-1*H*-indole-5-carboxylate (4q): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.45 (s, 9H), 2.23 (s, 6H), 3.95 (s, 3H), 6.91 (d, *J* = 8.1 Hz, 4H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.44-7.50 (m, 1H), 7.46 (d, *J* = 8.1 Hz, 4H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.44-7.50 (m, 1H), 7.46 (d, *J* = 8.1 Hz, 4H), 8.06-8.14 (m, 4H), 8.50 (d, *J* = 7.5 Hz, 1H), 8.97 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2 (2C), 28.2 (3C), 41.8, 52.3, 86.5, 115.6, 117.5, 121.2, 126.7 (4C), 126.8, 127.6, 127.8, 128.6 (4C), 131.5 (2C), 131.6, 135.1 (2C), 137.0, 138.8, 140.77 (2C), 140.90 (2C), 166.4, 177.2. IR (neat) 1718, 1434, 1291, 1263, 1130, 1075, 1041, 806, 764, 738, 665 cm^{-1}. MS (ESI) calcd for $C_{35}H_{35}IN_2NaO_7S_2$ $[M+Na]^+$ 809.0823, found 809.0807.



***N*-((4-Bromo-1-pivaloyl-1*H*-indol-3-yl)(phenyl)-λ^3-iodanyl)-4-methyl-*N*-tosylbenzenesulfonamide (4r):** **4r** could not be prepared. The yield of **4r** was assigned from that of **4a** by analogy of the ^{1}H-NMR spectra of the crude product based on internal standard (1,4-bis(trimethylsilyl)benzene).



***N*-((6-Chloro-1-pivaloyl-1*H*-indol-3-yl)(phenyl)-λ^3-iodanyl)-4-methyl-*N*-tosylbenzenesulfonamide (4s):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.42 (s, 9H), 2.21 (s, 6H), 6.87 (d, *J* = 8.2 Hz, 4H), 7.24-7.30 (m, 3H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 4H), 7.46 (t, *J* = 7.5 Hz, 1H), 8.10 (d, *J* = 7.5 Hz, 2H), 8.48 (d, *J* = 1.7 Hz, 1H), 8.83 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2 (2C), 28.3 (3C), 41.7, 86.3, 115.7, 117.8, 120.2, 125.6, 126.4, 126.6 (4C), 128.4 (4C), 131.5 (2C), 131.6, 133.0, 135.2 (2C), 135.9, 136.4, 141.0 (2C), 141.2 (2C), 177.0. IR (neat) 1714, 1421, 1265, 1131, 1077, 1042, 805, 766, 670 cm^{-1}. MS (ESI) calcd for $C_{33}H_{32}ClIN_2NaO_5S_2$ $[M+Na]^+$ 785.0378, found 785.0364.



4-Methyl-*N*-((7-methyl-1-pivaloyl-1*H*-indol-3-yl)(phenyl)-λ^3-iodanyl)-*N*-tosylbenzenesulfonamide (4t): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.46 (s, 9H), 2.19 (s, 6H), 2.29 (s, 3H), 6.86 (d, *J* = 8.1 Hz, 4H), 7.20 (d, *J* = 6.9 Hz, 1H), 7.21-7.31 (m, 4H), 7.40-7.48 (m, 1H), 7.45 (d, *J* = 8.1 Hz, 4H), 8.04 (d, *J* = 7.5 Hz, 2H), 8.63 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.0, 21.2 (2C), 28.8 (3C), 42.7, 84.0, 115.8, 117.4, 124.8, 125.7, 126.8 (4C), 128.4 (4C), 128.7, 128.9, 131.4, 131.5 (2C), 134.6 (2C), 135.3, 135.6, 140.7 (2C), 141.3 (2C), 178.8. IR (neat) 1724, 1442, 1276, 1131, 1077, 1035, 811, 762, 738, 672 cm^{-1}. MS (ESI) calcd for $C_{34}H_{35}IN_2NaO_5S_2$ $[M+Na]^+$ 765.0924, found 765.0913.

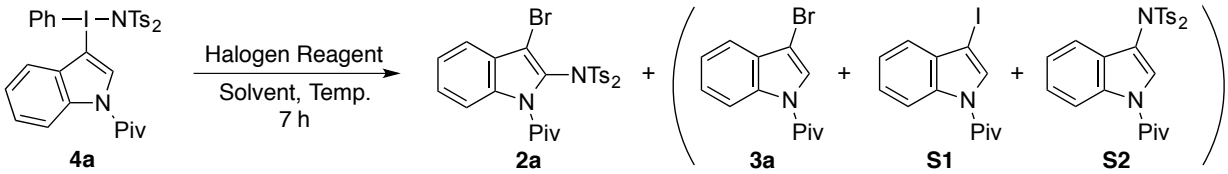
3. General procedure for the Dual Functionalization from Indolyl(phenyl)iodonium Imides (4) (Method A).

To a solution of **4a** (72.9 mg, 0.10 mmol) in $ClCH_2CH_2Cl$ (1.0 mL) was added 1,3-dibromo-5,5-dimethylhydantoin (17.2 mg, 0.06 mmol), and the mixture was stirred at 40 ºC 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), 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** (55.4 mg, 92% yield).

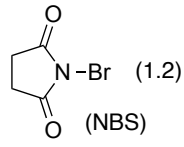
4. General procedure for the Dual Functionalization from Indoles (1) (Method B).

A mixture of $PhI(OAc)_2$ (38.7 mg, 0.12 mmol), Ts_2NH (39.1 mg, 0.12 mmol) in $ClCH_2CH_2Cl$ (1.0 mL) was stirred at room temperature for 30 min under argon atomosphere. Then, *N*-pivaloyl indole **1a** (20.1 mg, 0.10 mmol) and 1,3-dibromo-5,5-dimethylhydantoin (17.2 mg, 0.06 mmol) were added, and the solution was stirred at 40 ºC for 7 h. 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 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** (52.4 mg, 87% yield).

Table S2. Dual Coupling Reaction via Bromo-Amination of Indolyl(phenyl)iodonium Imides (**4a**) with Halogen Reagents.

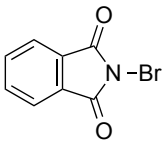


Halogen Reagent (equiv.), Solvent, Temp. (°C), Yield (%)



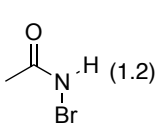
(1.2)

CH_2Cl_2, r.t.
59% (9%)[a]
CH_2Cl_2, 40 °C
75% (7%)[a]



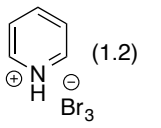
(1.2)

CH_2Cl_2, r.t.
63% (7%)[b]



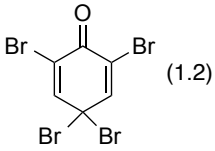
(1.2)

CH_2Cl_2, r.t.
70% (10%)[a]



(1.2)

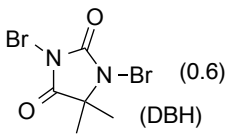
CH_2Cl_2, r.t.
11% (70%)[a]


(1.2)

CH_2Cl_2, r.t.
0% (53%)[b]
(17%)[c](30%)[d]

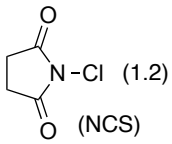
Br_2 (1.2)

CH_2Cl_2, r.t.
20% (23%)[a]
(16%)[b](16%)[d]



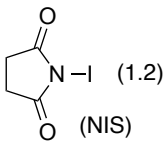
(0.6)

CH_2Cl_2, r.t.
90% (5%)[c]
$CHCl_3$, r.t.
75%
THF, r.t.
1%(89%)[c]
DMF, r.t.
14%(21%)[a](23%)[b]
$ClCH_2CH_2Cl_2$, 40 °C
92%



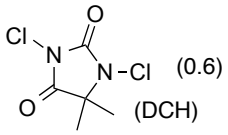
(1.2)

CH_2Cl_2, r.t.
N.R.



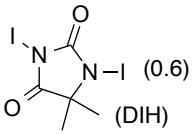
(1.2)

CH_2Cl_2, r.t.
0%(99%)[b]



(0.6)

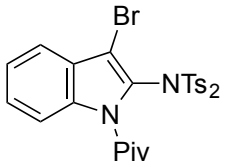
CH_2Cl_2, r.t.
N.R.



(0.6)

CH_2Cl_2, r.t.
0% (80%)[b](9%)[d]

[a]Numbers in parentheses indicate the yield of **3a**. [b]Numbers in parentheses indicates the yield of **S1**. [c]Numbers in parentheses indicate the recovery of **4a**. [d]Numbers in parentheses indicate the yield of **S2**.



***N*-(3-Bromo-1-pivaloyl-1*H*-indol-2-yl)-4-methyl-*N*-tosylbenzenesulfonamide (2a):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.50 (s, 9H), 2.48 (s, 6H), 7.24-7.30 (m, 1H), 7.33 (d, J = 8.0 Hz, 4H), 7.41 (t, J = 7.5 Hz, 1H), 7.52 (d, J = 7.5 Hz, 1H), 7.55 (d, J = 7.5 Hz, 1H), 7.98 (d, J = 8.0 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.8 (2C), 28.1 (3C), 43.2, 103.4, 113.8, 121.0, 122.2, 125.6, 125.9, 126.1, 129.2 (4C), 130.4 (4C), 133.7, 135.5 (2C), 145.4 (2C), 181.2. IR (neat) 1716, 1373, 1295, 1167, 660 cm^{-1}. MS (ESI) calcd for $C_{27}H_{27}BrN_2NaO_5S_2$ $[M+Na]^+$ 625.0437, found 625.0428.

Crystal data for 2a: Formula $C_{27}H_{27}BrN_2O_5S_2$, colorless, crystal dimensions 0.40 × 0.30 × 0.30 mm^3, orthorthombic, space group Pbca, a = 11.3613(5) Å, b = 15.8902(6) Å, c = 29.9856(12) Å, α = 90.00 °, β = 90.00 °, γ = 90.00 °, V = 5413.4(4) Å^3, Z = 8, ρ_{calc} = 1.481 g cm^{-3}, F(000) = 2480,

μ(MoKα) = 1.713 mm^{-1}, T = 173 K. 28834 reflections collected, 6153 independent reflections with $I > 2\sigma(I)$ ($2\theta_{max}$ = 27.51°), and 339 parameters were used for the solution of the structure. The non-hydrogen atoms were refined anisotropically. R_1 = 0.0292 and wR_2 = 0.0767. GOF = 1.105. 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-1023213. 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].

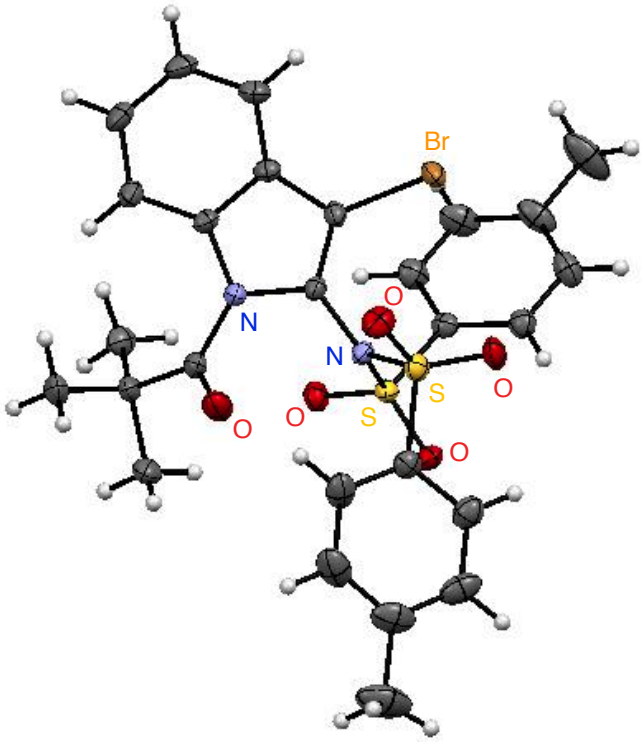
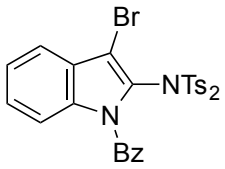
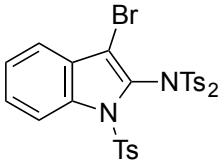


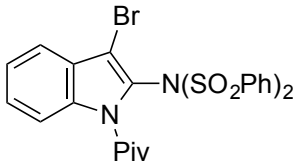
Figure S3. ORTEP drawing of **2a**.



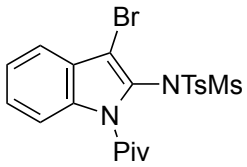
***N*-(1-Benzoyl-3-bromo-1*H*-indol-2-yl)-4-methyl-*N*-tosylbenzenesulfonamide (2b):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.44 (s, 6H), 6.47 (t, J = 8.6 Hz, 1H), 7.08-7.14 (m, 1H), 7.21-7.27 (m, 1H), 7.30 (d, J = 8.3 Hz, 4H), 7.44 (t, J = 7.7 Hz, 2H), 7.55 (d, J = 7.6 Hz, 1H), 7.61 (t, J = 7.7 Hz, 1H), 7.68 (d, J = 7.7 Hz, 2H), 8.01 (d, J = 8.3 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.8 (2C), 105.8, 114.4, 120.8, 123.0, 126.0, 126.1, 126.4, 128.6 (2C), 129.2 (4C), 130.2 (4C), 130.5 (2C), 133.4, 133.9, 134.7, 135.7 (2C), 145.4 (2C), 166.4. IR (neat) 1702, 1381, 1302, 1168, 654 cm^{-1}. MS (ESI) calcd for $C_{29}H_{23}BrN_2NaO_5S_2$ $[M+Na]^+$ 645.0124, found 645.0115.



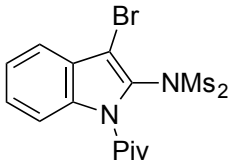
***N*-(3-Bromo-1-tosyl-1*H*-indol-2-yl)-4-methyl-*N*-tosylbenzenesulfonamide (2c):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.33 (s, 3H), 2.47 (s, 6H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.26-7.31 (m, 1H), 7.31-7.38 (m, 5H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 2H), 8.02 (d, *J* = 8.3 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 21.8 (2C), 107.7, 114.4, 121.1, 123.9, 126.5, 126.9, 127.4, 128.1 (2C), 129.3 (4C), 129.6 (2C), 130.4 (4C), 134.3, 135.99, 136.02 (2C), 145.0, 145.6 (2C). IR (neat) 1595, 1378, 1176, 1161, 1082, 658 cm^{-1}. MS (ESI) calcd for $C_{29}H_{25}BrN_2NaO_6S_3$ $[M+Na]^+$ 694.9950, found 694.9941.



***N*-(3-Bromo-1-pivaloyl-1*H*-indol-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide (2d):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.49 (s, 9H), 7.27 (t, *J* = 7.7 Hz, 1H), 7.39-7.45 (m, 1H), 7.49-7.58 (m, 6H), 7.68 (tt, *J* = 7.5, 1.2 Hz, 2H), 8.09 (dd, *J* = 8.6, 1.2 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0 (3C), 43.2, 103.7, 113.9, 121.0, 122.3, 125.5, 125.8, 126.1, 128.6 (4C), 130.4 (4C), 133.6, 134.4 (2C), 138.3 (2C), 181.1. IR (neat) 1714, 1379, 1298, 1168, 685 cm^{-1}. MS (ESI) calcd for $C_{25}H_{23}BrN_2NaO_5S_2$ $[M+Na]^+$ 597.0124, found 597.0115.

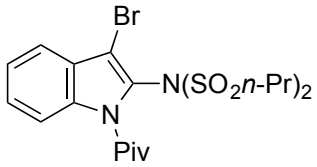


***N*-(3-Bromo-1-pivaloyl-1*H*-indol-2-yl)-4-methyl-*N*-(methylsulfonyl)benzenesulfonamide (2e):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.60 (s, 9H), 2.44 (s, 3H), 3.83 (s, 3H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.38-7.44 (m, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.8, 28.1 (3C), 43.3, 44.0, 103.8, 114.0, 121.0, 122.5, 125.4, 125.6, 126.1, 129.7 (2C), 129.8 (2C), 133.4, 134.5, 146.0, 182.3. IR (neat) 1718, 1361, 1300, 1171, 663 cm^{-1}. MS (ESI) calcd for $C_{21}H_{23}BrN_2NaO_5S_2$ $[M+Na]^+$ 549.0124, found 549.0112.

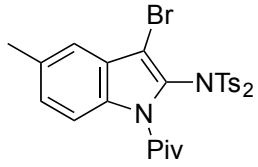


***N*-(3-Bromo-1-pivaloyl-1*H*-indol-2-yl)-*N*-(methylsulfonyl)methanesulfonamide (2f):** ^{1}H

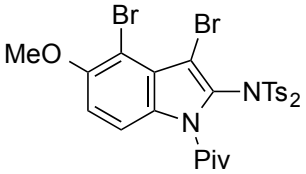
NMR (500 MHz, $CDCl_3$) δ 1.52 (s, 9H), 3.63 (s, 6H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0 (3C), 43.4, 43.8 (2C), 102.5, 114.0, 121.0, 122.8, 125.0, 125.4, 126.3, 133.4, 182.7. IR (neat) 1714, 1357, 1290, 1161, 621 cm^{-1}. MS (ESI) calcd for $C_{15}H_{19}BrN_2NaO_5S_2$ $[M+Na]^+$ 472.9811, found 472.9810.



***N*-(3-Bromo-1-pivaloyl-1*H*-indol-2-yl)-*N*-(propylsulfonyl)propane-1-sulfonamide (2g):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.13 (t, *J* = 7.4 Hz, 6H), 1.52 (s, 9H), 1.92-2.09 (m, 4H), 3.68-3.80 (m, 2H), 3.94-4.06 (m, 2H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.1 (2C), 16.9 (2C), 28.0 (3C), 43.4, 58.5 (2C), 102.8, 113.9, 120.9, 122.7, 125.36, 125.42, 126.1, 133.4, 182.7. IR (neat) 1712, 1374, 1299, 1163, 619 cm^{-1}. MS (ESI) calcd for $C_{19}H_{27}BrN_2NaO_5S_2$ $[M+Na]^+$ 529.0437, found 529.0432.

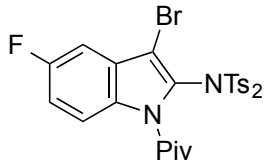


***N*-(3-Bromo-5-methyl-1-pivaloyl-1*H*-indol-2-yl)-4-methyl-*N*-tosylbenzenesulfonamide (2h):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.49 (s, 9H), 2.46 (s, 3H), 2.47 (s, 6H), 7.23 (d, *J* = 8.6 Hz, 1H), 7.29 (s, 1H), 7.32 (d, *J* = 8.3 Hz, 4H), 7.45 (d, *J* = 8.6 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2, 21.8 (2C), 28.1 (3C), 43.1, 103.2, 113.7, 120.4, 125.7, 125.9, 127.5, 129.2 (4C), 130.4 (5C), 132.0, 135.5 (2C), 145.4 (2C), 181.0. IR (neat) 1712, 1374, 1282, 1164, 662 cm^{-1}. MS (ESI) calcd for $C_{28}H_{29}BrN_2NaO_5S_2$ $[M+Na]^+$ 639.0593, found 639.0585.

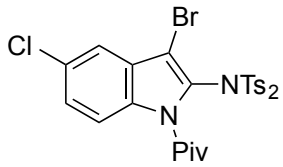


***N*-(3,4-Dibromo-5-methoxy-1-pivaloyl-1*H*-indol-2-yl)-4-methyl-*N*-tosylbenzenesulfonamide (2i):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.46 (s, 9H), 2.48 (s, 6H), 3.94 (s, 3H), 7.09 (d, *J* = 9.2 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 4H), 7.43 (d, *J* = 9.2 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.8 (2C), 28.2 (3C), 43.4, 57.7, 102.3, 104.2, 112.1, 113.3, 123.0, 128.6, 129.2 (4C), 129.9, 130.6 (4C), 135.6 (2C), 145.6 (2C), 151.9, 181.0. IR (neat) 1723, 1471, 1382, 1277, 1175, 1084, 648 cm^{-1}. MS (ESI) calcd for $C_{28}H_{28}Br_2N_2NaO_6S_2$ $[M+Na]^+$ 732.9648, found

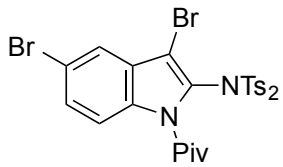
732.9642.



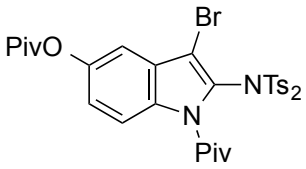
***N*-(3-Bromo-5-fluoro-1-pivaloyl-1*H*-indol-2-yl)-4-methyl-*N*-tosylbenzenesulfonamide (2j):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.48 (s, 9H), 2.48 (s, 6H), 7.12-7.21 (m, 2H), 7.33 (d, J = 8.2 Hz, 4H), 7.49 (dd, J = 8.5, 3.8 Hz, 1H), 7.96 (d, J = 8.2 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.8 (2C), 28.1 (3C), 43.2, 102.8 (d, $J_{C–F}$ = 3.6 Hz), 106.0 (d, $J_{C–F}$ = 25.0 Hz), 114.5 (d, $J_{C–F}$ = 26.2 Hz), 115.2 (d, $J_{C–F}$ = 8.3 Hz), 126.5 (d, $J_{C–F}$ = 9.5 Hz), 127.5, 129.2 (4C), 130.1, 130.4 (4C), 135.3 (2C), 145.6 (2C), 158.7 (d, $J_{C–F}$ = 239.7 Hz), 180.8. ^{19}F NMR (471 MHz, $CDCl_3$) δ –119.8. IR (neat) 1723, 1373, 1300, 1171, 662 cm^{-1}. MS (ESI) calcd for $C_{27}H_{26}BrFN_2NaO_5S_2$ $[M+Na]^+$ 643.0343, found 643.0330.



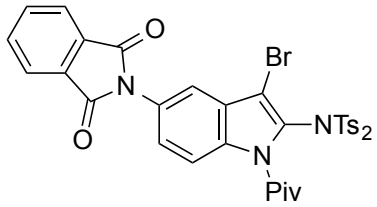
***N*-(3-Bromo-5-chloro-1-pivaloyl-1*H*-indol-2-yl)-4-methyl-*N*-tosylbenzenesulfonamide (2k):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.48 (s, 9H), 2.48 (s, 6H), 7.33 (d, J = 8.2 Hz, 4H), 7.36 (dd, J = 8.9, 2.3 Hz, 1H), 7.47 (d, J = 8.9 Hz, 1H), 7.50 (d, J = 2.3 Hz, 1H), 7.95 (d, J = 8.2 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.8 (2C), 28.1 (3C), 43.2, 102.4, 115.1, 120.4, 126.3, 126.7, 127.3, 128.2, 129.3 (4C), 130.4 (4C), 131.9, 135.3 (2C), 145.6 (2C), 180.7. IR (neat) 1721, 1373, 1297, 1164, 1130, 661 cm^{-1}. MS (ESI) calcd for $C_{27}H_{26}BrClN_2NaO_5S_2$ $[M+Na]^+$ 659.0047, found 659.0037.



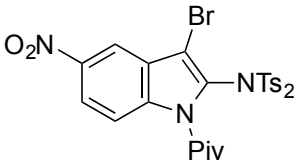
***N*-(3,5-Bibromo-1-pivaloyl-1*H*-indol-2-yl)-4-methyl-*N*-tosylbenzenesulfonamide (2l):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.47 (s, 9H), 2.48 (s, 6H), 7.33 (d, J = 8.3 Hz, 4H), 7.42 (d, J = 8.9 Hz, 1H), 7.50 (dd, J = 8.9, 1.8 Hz, 1H), 7.66 (d, J = 1.8 Hz, 1H), 7.95 (d, J = 8.3 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.8 (2C), 28.1 (3C), 43.2, 102.2, 115.3, 115.6, 123.5, 127.2, 128.8 (2C), 129.3 (4C), 130.4 (4C), 132.2, 135.3 (2C), 145.6 (2C), 180.7. IR (neat) 1725, 1373, 1299, 1165, 661 cm^{-1}. MS (ESI) calcd for $C_{27}H_{26}Br_2N_2NaO_5S_2$ $[M+Na]^+$ 702.9542, found 702.9536.



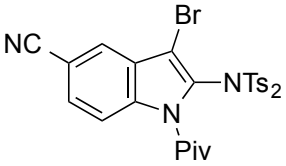
3-Bromo-2-((4-methyl-*N*-tosylphenyl)sulfonamido)-1-pivaloyl-1*H*-indol-5-yl pivalate (2m): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.39 (s, 9H), 1.48 (s, 9H), 2.47 (s, 6H), 7.10 (dd, *J* = 8.9, 2.8 Hz, 1H), 7.21 (d, *J* = 2.8 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 4H), 7.53 (d, *J* = 8.9 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.8 (2C), 27.2 (3C), 28.1 (3C), 39.1, 43.2, 103.1, 113.1, 114.6, 120.3, 126.2, 127.1, 129.2 (4C), 130.4 (4C), 131.2, 135.4 (2C), 145.5 (2C), 146.3, 177.5, 180.9. IR (neat) 1744, 1723, 1384, 1272, 1166, 652 cm^{-1}. MS (ESI) calcd for $C_{32}H_{35}BrN_2NaO_7S_2$ $[M+Na]^+$ 725.0961, found 725.0955.



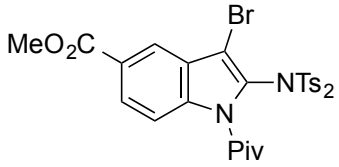
***N*-(3-Bromo-5-(1,3-dioxoisoindolin-2-yl)-1-pivaloyl-1*H*-indol-2-yl)-4-methyl-*N*-tosylbenzenesulfonamide (2n):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.51 (s, 9H), 2.48 (s, 6H), 7.34 (d, *J* = 8.2 Hz, 4H), 7.45 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.60 (d, *J* = 2.0 Hz, 1H), 7.67 (d, *J* = 8.9 Hz, 1H), 7.79-7.85 (m, 2H), 7.94-8.03 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.8 (2C), 28.1 (3C), 43.2, 103.4, 114.5, 119.7, 123.8 (2C), 124.7, 126.1, 126.2, 127.5, 129.3 (4C), 130.5 (4C), 131.7 (2C), 132.8, 134.5 (2C), 135.4 (2C), 145.5 (2C), 167.5 (2C), 180.8. IR (neat) 1718, 1479, 1376, 1308, 1166, 1079, 661 cm^{-1}. MS (ESI) calcd for $C_{35}H_{30}BrN_3NaO_7S_2$ $[M+Na]^+$ 770.0601, found 770.0594.



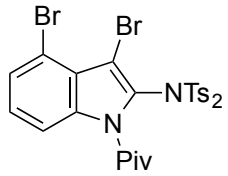
***N*-(3-Bromo-5-nitro-1-pivaloyl-1*H*-indol-2-yl)-4-methyl-*N*-tosylbenzenesulfonamide (2o):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.50 (s, 9H), 2.50 (s, 6H), 7.35 (d, *J* = 8.3 Hz, 4H), 7.61 (d, *J* = 9.3 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 4H), 8.30 (dd, *J* = 9.3, 2.3 Hz, 1H), 8.48 (d, *J* = 2.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.8 (2C), 28.1 (3C), 43.5, 104.0, 114.1, 118.0, 120.8, 125.3, 129.4 (4C), 130.4 (5C), 135.0 (2C), 136.0, 143.1, 146.0 (2C), 180.6. IR (neat) 1730, 1348, 1308, 1166, 873, 650 cm^{-1}. MS (ESI) calcd for $C_{27}H_{26}BrN_3NaO_7S_2$ $[M+Na]^+$ 670.0288, found 670.0283.



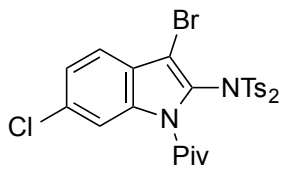
***N*-(3-Bromo-5-cyano-1-pivaloyl-1*H*-indol-2-yl)-4-methyl-*N*-tosylbenzenesulfonamide (2p):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.48 (s, 9H), 2.49 (s, 6H), 7.34 (d, *J* = 8.3 Hz, 4H), 7.60 (d, *J* = 8.6 Hz, 1H), 7.64 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.88 (d, *J* = 1.4 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.8 (2C), 28.0 (3C), 43.4, 102.8, 105.9, 114.6, 118.9, 125.5, 126.4, 128.2, 128.6, 129.3 (4C), 130.4 (4C), 134.9, 135.0 (2C), 145.9 (2C), 180.6. IR (neat) 2225, 1728, 1372, 1308, 1165, 664 cm^{-1}. MS (ESI) calcd for $C_{28}H_{26}BrN_3NaO_5S_2$ $[M+Na]^+$ 650.0389, found 650.0381.



Methyl 3-bromo-2-((4-methyl-*N*-tosylphenyl)sulfonamido)-1-pivaloyl-1*H*-indole-5-carboxylate (2q): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.50 (s, 9H), 2.48 (s, 6H), 3.96 (s, 3H), 7.33 (d, *J* = 8.4 Hz, 4H), 7.57 (dd, *J* = 8.9, 0.6 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 4H), 8.10 (dd, *J* = 8.9, 1.7 Hz, 1H), 8.25 (dd, *J* = 1.7, 0.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.8 (2C), 28.1 (3C), 43.3, 52.3, 104.1, 113.6, 123.6, 124.3, 125.3, 126.8, 127.5, 129.3 (4C), 130.4 (4C), 135.2 (2C), 135.8, 145.7 (2C), 166.7, 180.9. IR (neat) 1720, 1379, 1289, 1166, 650 cm^{-1}. MS (ESI) calcd for $C_{29}H_{29}BrN_2NaO_7S_2$ $[M+Na]^+$ 683.0492, found 683.0483.

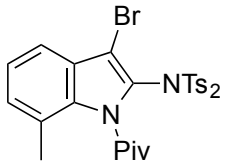


***N*-(3,4-Dibromo-1-pivaloyl-1*H*-indol-2-yl)-4-methyl-*N*-tosylbenzenesulfonamide (2r):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.46 (s, 9H), 2.48 (s, 6H), 7.20 (dd, *J* = 8.3, 7.8 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 4H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 8.5 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.8 (2C), 28.2 (3C), 43.6, 102.2, 113.0, 115.6, 121.9, 125.9, 127.4, 127.9, 129.2 (4C), 130.6 (4C), 134.7, 135.6 (2C), 145.6 (2C), 181.4. IR (neat) 1718, 1377, 1310, 1165, 662 cm^{-1}. MS (ESI) calcd for $C_{27}H_{26}Br_2N_2NaO_5S_2$ $[M+Na]^+$ 702.9542, found 702.9535.



***N*-(3-Bromo-6-chloro-1-pivaloyl-1*H*-indol-2-yl)-4-methyl-*N*-tosylbenzenesulfonamide (2s):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.49 (s, 9H), 2.48 (s, 6H), 7.25 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 4H), 7.44 (d, *J* = 8.6 Hz, 1H), 7.54 (d, *J* = 1.5 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 4H). ^{13}C

NMR (125 MHz, $CDCl_3$) δ 21.8 (2C), 28.1 (3C), 43.2, 103.1, 113.7, 122.0, 123.1, 124.1, 126.7, 129.2 (4C), 130.4 (4C), 132.0, 133.6, 135.3 (2C), 145.6 (2C), 180.7. IR (neat) 1726, 1374, 1292, 1165, 1072, 648 cm^{-1}. MS (ESI) calcd for $C_{27}H_{26}BrClN_2NaO_5S_2$ $[M+Na]^+$ 659.0047, found 659.0040.

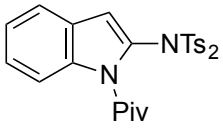


***N*-(3-Bromo-7-methyl-1-pivaloyl-1*H*-indol-2-yl)-4-methyl-*N*-tosylbenzenesulfonamide (2t):** ^1H NMR (500 MHz, $CDCl_3$) δ 1.32 (s, 9H), 2.36 (s, 3H), 2.48 (brs, 6H), 7.14-7.21 (m, 2H), 7.21-7.46 (m, 5H), 7.65-7.86 (br, 2H), 8.02-8.25 (br, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.8, 21.8 (2C), 28.6 (3C), 44.7, 102.7, 118.7, 122.3, 122.4, 125.4, 127.6, 128.9, 129.3 (4C), 130.6 (4C), 131.3 (2C), 136.1, 145.9 (2C), 184.4. IR (neat) 1737, 1380, 1264, 1173, 662 cm^{-1}. MS (ESI) calcd for $C_{28}H_{29}BrN_2NaO_5S_2$ $[M+Na]^+$ 639.0593, found 639.0586.

5. Transformation of 2a into Various 2-Amino Indole derivatives.

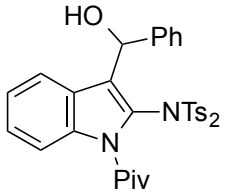
5.1. General procedure for the Electrophilic Addition of 2a with *t*-BuLi.

To a solution of **2a** (60.2 mg, 0.10 mmol) in THF (1.0 mL) was dropwised the cooled t-BuLi (0.12 mL, 0.21 mmol, 1.8 M in pentane) at –96 ºC over 10 min, and the solution was stirred at –96 ºC for 20 min under argon atomosphere. Then, dried $MgCl_2$ (20.0 mg, 0.21 mmol) was added. After the obtained mixture was stirred at –96 ºC for 20 min, electrophiles were added and the reaction solution was at –96 ºC (electrophile: PhCHO, TMSOTf) or –60 ºC (electrophile: Piv_2O, 1-formylmorphorine, Me_2SO_4) for 1–2 h. Saturated NH_4Cl 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 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 = 8/1), to give the desired product **5aa–10a**.

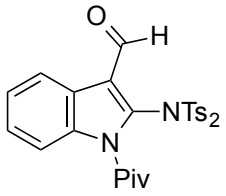


4-Methyl-*N*-(1-pivaloyl-1*H*-indol-2-yl)-*N*-tosylbenzenesulfonamide (5a): ^1H NMR (500 MHz, $CDCl_3$) δ 1.49 (s, 9H), 2.48 (s, 6H), 6.15 (s, 1H), 7.18 (t, J = 7.6 Hz, 1H), 7.29-7.37 (m, 5H), 7.47-7.53 (m, 2H), 7.91 (d, J = 8.6 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.8 (2C), 28.0 (3C), 43.4, 110.3, 113.6, 121.6, 121.8, 124.7, 125.5, 127.2, 129.1 (4C), 130.0 (4C), 134.6, 134.8 (2C), 145.4 (2C), 182.3. IR (neat) 1713, 1370, 1294, 1171 cm^{-1}. MS (ESI) calcd for $C_{27}H_{29}N_2O_5S_2$

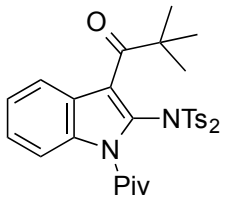
$[M+H]^+$ 525.1512, found 525.1508.



***N*-(3-(Hydroxy(phenyl)methyl)-1-pivaloyl-1*H*-indol-2-yl)-4-methyl-*N*-tosylbenzenesulfonamide (6a):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.48 (s, 9H), 2.22 (s, 3H), 2.50 (s, 3H), 2.86 (d, *J* = 2.3 Hz, 1H), 5.45 (d, *J* = 2.3 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 7.6 Hz, 1H), 7.19-7.28 (m, 6H), 7.28-7.33 (m, 1H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 1H), 7.86 (d, *J* = 8.5 Hz, 2H), 8.03 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 21.8, 28.3 (3C), 43.3, 66.6, 113.8, 121.4, 123.1, 124.2, 124.3, 124.9, 126.2, 127.0, 127.1 (2C), 127.6 (2C), 129.1 (2C), 129.4 (2C), 129.5 (2C), 130.5 (2C), 134.7, 135.1, 135.2, 140.1, 145.55, 145.64, 181.7. IR (neat) 2928, 1711, 1377, 1291, 1163 cm^{-1}. MS (ESI) calcd for $C_{34}H_{34}N_2NaO_6S_2$ $[M+Na]^+$ 653.1750, found 653.1739.

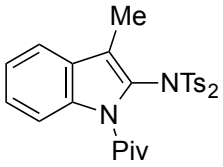


***N*-(3-Formyl-1-pivaloyl-1*H*-indol-2-yl)-4-methyl-*N*-tosylbenzenesulfonamide (7a):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.48 (s, 9H), 2.50 (s, 6H), 7.30-7.41 (m, 1H), 7.37 (d, *J* = 8.4 Hz, 4H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 4H), 8.37 (d, *J* = 7.8 Hz, 1H), 8.97 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.9 (2C), 28.0 (3C), 43.7, 113.3, 119.3, 123.1, 123.2, 123.9, 126.0, 129.5 (4C), 130.3 (4C), 133.5 (2C), 134.1, 134.2, 146.4 (2C), 181.9, 185.4. IR (neat) 1724, 1674, 1381, 1311, 1166 cm^{-1}. MS (ESI) calcd for $C_{28}H_{28}N_2NaO_6S_2$ $[M+Na]^+$ 575.1281, found 575.1267.

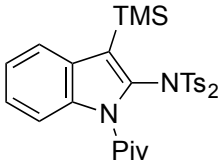


***N*-(1,3-Dipivaloyl-1*H*-indol-2-yl)-4-methyl-*N*-tosylbenzenesulfonamide (8a):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.27 (s, 9H), 1.43 (s, 9H), 2.48 (s, 6H), 7.25-7.30 (m, 1H), 7.32 (d, *J* = 8.4 Hz, 4H), 7.35-7.40 (m, 1H), 7.52 (d, *J* = 8.6 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 21.8 (2C), 27.4 (3C), 28.3 (3C), 43.6, 44.1, 113.6, 121.9, 122.5, 123.3, 123.6, 124.6, 126.3, 128.7 (4C), 130.8 (4C), 132.9, 135.7 (2C), 145.0 (2C), 181.6, 205.6. IR (neat) 2930, 1718, 1672, 1379, 1289, 1165 cm^{-1}. MS (ESI) calcd for $C_{32}H_{36}N_2NaO_6S_2$ $[M+Na]^+$ 631.1907, found 631.1896.



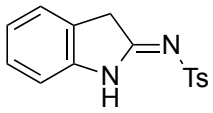
4-Methyl-*N*-(3-methyl-1-pivaloyl-1*H*-indol-2-yl)-*N*-tosylbenzenesulfonamide (9a): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.50 (s, 9H), 1.51 (s, 3H), 2.47 (s, 6H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.30-7.39 (m, 1H), 7.33 (d, *J* = 7.8 Hz, 4H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 7.8 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 8.2, 21.8 (2C), 28.1 (3C), 43.0, 113.8, 120.2, 120.5, 121.1, 124.6, 124.9, 126.9, 129.1 (4C), 130.2 (4C), 134.2, 135.4 (2C), 145.2 (2C), 181.9. IR (neat) 1719, 1374, 1292, 1163 cm^{-1}. MS (ESI) calcd for $C_{28}H_{30}N_2NaO_5S_2$ $[M+Na]^+$ 561.1488, found 561.1484.



4-Methyl-*N*-(1-pivaloyl-3-(trimethylsilyl)-1*H*-indol-2-yl)-*N*-tosylbenzenesulfonamide (10a): ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.05 (s, 9H), 1.39 (s, 9H), 2.47 (s, 6H), 7.21 (t, *J* = 7.9 Hz, 1H), 7.30-7.37 (m, 1H), 7.32 (d, *J* = 8.3 Hz, 4H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.11 (3C), 21.7 (2C), 28.3 (3C), 43.3, 113.8, 120.4, 120.9, 123.2, 124.0, 129.0 (4C), 130.4 (4C), 130.9, 131.2, 135.4, 136.2 (2C), 144.9 (2C), 181.4. IR (neat) 2922, 1715, 1447, 1375, 1294, 1170, 658 cm^{-1}. MS (ESI) calcd for $C_{30}H_{36}N_2NaO_5S_2Si$ $[M+Na]^+$ 619.1727, found 619.1711.

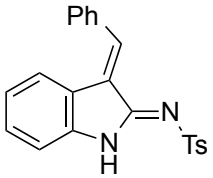
5.2. Transformation of 2a into 1-Amino-indole Derivatives 13aa–15aa.

To a solution of the Raney Nickel (300 mg) in 1,4-dioxiane (4.0 mL) and H_2O (0.8 mL) was added **2a** (120.4 mg, 0.20 mmol), and the solution was refluxed for 48 h under argon atomosphere. The mixture was filtrated and washed with $CHCl_3$ (10 mL). The solution was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (eluent: hexane/AcOEt = 2/1), to give the desired product **10a** (64.3 mg, 88% yield).



(*Z*)-*N*-(Indolin-2-ylidene)-4-methylbenzenesulfonamide (11a): ^{1}H NMR (500 MHz, $CDCl_3/CF_3CO_2H$) δ 2.44 (s, 3H), 4.24 (s, 2H), 7.21-7.29 (m, 2H), 7.33-7.43 (m, 4H), 7.88 (d, J = 8.3 Hz, 2H), 11.8 (brs, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 37.6, 113.1, 124.6, 125.9, 127.3 (2C), 129.1, 130.3 (2C), 135.3, 140.6, 146.2, 170.7. IR (neat) 2952, 1590, 1486, 1302, 1144 cm^{-1}. MS (ESI) calcd for $C_{15}H_{15}N_2O_2S$ $[M+H]^+$ 287.0849, found 287.0845.

To a solution of **11a** (36.3 mg, 0.10 mmol) in CH_2Cl_2 (1.0 mL) was added BF_3•Et_2O (18.5 μL, 0.15 mmol) and PhCHO (15.3 μL, 0.15 mmol), and the mixture was stirred at room temperature for 7 h under argon atomosphere. Saturated $NaHCO_3$ 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 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 = 2/1), to give the desired product **12aa** (36.3 mg, 97% yield, E:Z = 92:8).



***N*-((*Z*)-3-((*E*)-Benzylidene)indolin-2-ylidene)-4-methylbenzenesulfonamide (12aa):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.41 (s, 3H), 6.92 (t, J = 7.8 Hz, 1H), 7.04 (d, J = 8.0 Hz, 1H), 7.21-7.28 (m, 1H), 7.30 (d, J = 8.2 Hz, 2H), 7.41-7.49 (m, 3H), 7.58-7.63 (m, 2H), 7.65 (d, J = 7.8 Hz, 1H), 7.94 (d, J = 8.2 Hz, 2H), 8.11 (s, 1H), 10.12 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 111.3, 121.3, 122.8, 123.1, 126.5 (2C), 128.7 (2C), 129.4 (4C), 129.5, 130.1, 130.2, 134.3, 139.1, 140.2, 141.8, 143.1, 160.6. IR (neat) 3280, 1571, 1461, 1312, 1280, 1134, 1085 cm^{-1}. MS (ESI) calcd for $C_{22}H_{19}N_2O_2S$ $[M+H]^+$ 375.1162, found 375.1154.

Crystal data for 12aa: Formula $C_{22}H_{18}N_2O_2S$, yellow, crystal dimensions 0.30 × 0.10 × 0.10 mm^3, triclinic, space group P-1, a = 9.9285(7) Å, b = 10.1079(7) Å, c = 10.4705(7) Å, α = 66.6900(10) °, β = 76.0070(10) °, γ = 89.8540(10) °, V = 931.25(11) Å^3, Z = 2, ρ_{calc} = 1.335 g cm^{-3}, F(000) = 392, μ(MoKα) = 0.193 mm^{-1}, T = 173 K. 5301 reflections collected, 4050 independent reflections with $I > 2\sigma(I)$ ($2\theta_{max}$ = 28.43°), and 245 parameters were used for the solution of the structure. The non-hydrogen atoms were refined anisotropically. R_1 = 0.0458 and wR_2 = 0.1094. GOF = 1.040. 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-1023215. 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].

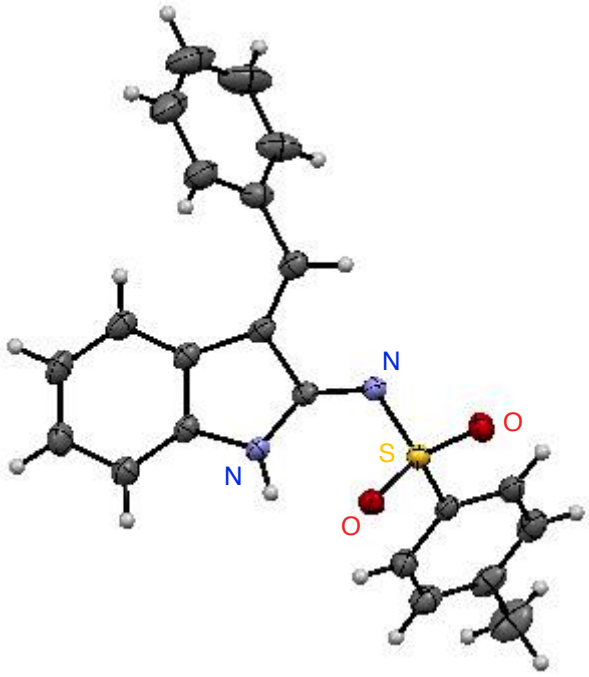
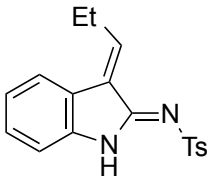


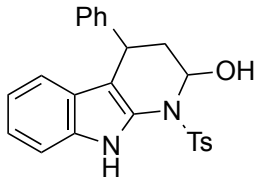
Figure S4. ORTEP drawing of **12aa**.



4-Methyl-*N*-((2*Z*,3*E*)-3-propylideneindolin-2-ylidene)benzenesulfonamide (12ab): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22 (t, *J* = 7.7 Hz, 3H), 2.39 (s, 3H), 2.70 (quint, *J* = 7.7 Hz, 2H), 7.05 (d, *J* = 7.8 Hz, 1H), 7.08 (td, *J* = 7.8, 1.0 Hz, 1H), 7.22-7.30 (m, 3H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 2H), 10.12 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.8, 21.5, 23.2, 111.2, 122.3, 123.4, 123.6, 126.4 (2C), 129.1, 129.4 (2C), 129.7, 139.2, 141.2, 143.0, 147.3, 159.9. IR (neat) 3301, 1575, 1464, 1277, 1131, 1083 cm^{-1}. MS (ESI) calcd for $C_{18}H_{19}N_2O_2S$ $[M+H]^+$ 327.1162, found 327.1154.

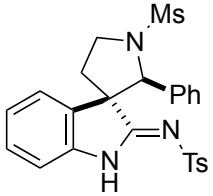
To a solution of **12aa** (37.4 mg, 0.10 mmol), 4-nitrobenzoic acid (3.3 mg, 0.02 mmol), and pyrrolidine (1.7 μL, 0.02 mol) in THF (1.0 mL) was added acetaldehyde (24.9 μL, 0.40 mmol, ca. 90% aq.) at –78 ºC, and the mixture was stirred at –78 ºC for 24 h under argon atomosphere. Saturated $NaHCO_3$ aqueous 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 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 = 2/1), to give the desired product **12aa** (35.2 mg, 82% yield).



4-Phenyl-1-tosyl-2,3,4,9-tetrahydro-1*H*-pyrido[2,3-*b*]indol-2-ol (13aa): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.03-1,09 (m, 1H), 2.21 (ddd, *J* = 14.5, 6.0, 3.0 Hz, 1H), 2.38 (s. 3H), 2.94 (brs, 1H), 4.18 (dd, *J* = 11.5, 6.0 Hz, 1H), 5.74 (s, 1H), 6.60 (d, *J* = 7.8 Hz, 1H), 6.85 (t, *J* = 7.8 Hz, 1H), 6.87-6.93 (m, 2H), 7.11 (t, *J* = 7.8 Hz, 1H), 7.14-7.20 (m, 3H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 2H), 9.04 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 34.0, 37.3, 79.8, 101.9, 110.7, 119.4, 119.7, 121.5, 125.6, 126.6, 126.9 (2C), 127.8 (2C), 128.4 (2C), 129.1, 130.1 (2C), 133.5, 134.0, 143.3, 144.8. IR (neat) 3480, 1593, 1468, 1362, 1162 cm^{-1}. MS (ESI) calcd for $C_{24}H_{23}N_2O_3S$ $[M+H]^+$ 419.1424, found 419.1424.

To a solution of **12aa** (37.4 mg, 0.10 mmol) and 2-methansulfonylethylamine (24.3 mg, 0.12 mmol) in THF (1.0 mL) was added 1,8-diazabicyclo[5.4.0]undec-7-ene (15.6 μL, 0.105 mmol), and the mixture was stirred at room temperature for 7 h under argon atomosphere. Saturated NH_4Cl 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 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 = 3/1), to give the desired product **13aa** (42.6 mg, 86% yield, *E*:*Z* = >99:<1).



(*Z*)-4-Methyl-*N*-(1'-(methylsulfonyl)-2'-phenylspiro[indoline-3,3'-pyrrolidin]-2-ylidene)benzenesulfonamide (14aa): ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.20-2.28 (m, 1H), 2.41-2.50 (m, 1H), 2.45 (s, 3H), 2.83 (s, 3H), 3.90-3.98 (m, 2H), 4.89 (s, 1H), 5.82 (d, *J* = 7.8 Hz, 1H), 6.68 (td, *J* = 7.8, 1.0 Hz, 1H), 6.71-7.30 (br, 2H), 6.93 (d, *J* = 7.8 Hz, 1H), 7.10-7.25 (m, 3H), 7.13 (td, *J* = 7.8, 1.0 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.87 (d, *J* = 8.2 Hz, 2H), 10.0 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 35.2, 35.9, 46.8, 62.1, 69.3, 110.7 (2C), 123.4, 125.4, 126.4 (2C), 127.2 (2C), 128.1,

128.2, 129.0, 129.8 (2C), 138.2, 139.1, 140.3 (2C), 144.0, 172.0. IR (neat) 3282, 1589, 1322, 1145, 1085 cm^{-1}. MS (ESI) calcd for $C_{25}H_{26}N_3O_4S_2$ $[M+H]^+$ 496.1359, found 496.1353.

Crystal data for 14aa: Formula $C_{25}H_{25}N_3O_4S_2 \cdot C_4H_8O_2$, colorless, crystal dimensions 0.20 × 0.10 × 0.10 mm^3, triclinic, space group P-1, a = 9.5145(9) Å, b = 11.3505(10) Å, c = 12.4229(11) Å, α = 79.1933(10) °, β = 86.0059(12) °, γ = 82.6050(12) °, V = 1305.4(2) $Å^3$, Z = 2, ρ_{calc} = 1.375 g cm^{-3}, F(000) = 570, μ(MoKα) = 0.247 mm^{-1}, T = 173 K. 7744 reflections collected, 5883 independent reflections with $I > 2\sigma(I)$ ($2\theta_{max}$ = 28.74°), and 364 parameters were used for the solution of the structure. The non-hydrogen atoms were refined anisotropically. R_1 = 0.0528 and wR_2 = 0.1411. 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-1023217. 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].

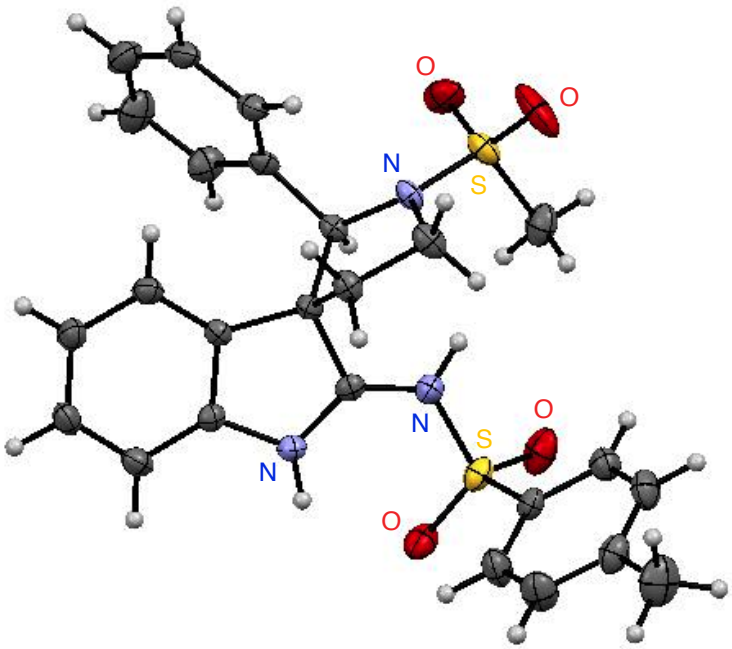
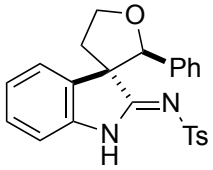


Figure S5. ORTEP drawing of **14aa**.

To a solution of **12aa** (37.4 mg, 0.10 mmol) in THF (1.0 mL) was added 2-bromoethanol (15.3 μL, 0.15 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (15.3 μL, 0.15 mmol), and the mixture was stirred at room temperature for 7 h under argon atomosphere. Saturated NH_4Cl 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 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 = 2/1), to give the desired product **14aa** (38.1 mg, 91%

yield, *E*:*Z* = 85:15).



(*Z*)-4-Methyl-*N*-(2-phenyl-4,5-dihydro-2*H*-spiro[furan-3,3'-indolin]-2'-ylidene)benzenesulfonamide (15aa): ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.37 (ddd, *J* = 12.6, 8.3, 5.2 Hz, 1H), 2.46 (s, 3H), 2.89 (ddd, *J* = 12.6, 9.8, 7.2 Hz, 1H), 4.35 (td, *J* = 9.8, 5.2 Hz, 1H), 4.44 (td, *J* = 8.3, 7.2 Hz, 1H), 5.09 (s, 1H), 6.71 (d, *J* = 7.5 Hz, 2H), 6.76 (d, *J* = 7.8 Hz, 1H), 6.89 (t, *J* = 7.5 Hz, 2H), 6.94-7.01 (m, 2H), 7.07 (t, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 2H), 9.86 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 39.2, 62.9, 67.1, 89.1, 110.5, 123.5, 124.6, 125.2 (2C), 126.7 (2C), 127.49 (2C), 127.53, 128.2, 129.6 (2C), 131.2, 135.5, 138.5, 139.6, 143.6, 170.1. IR (neat) 3060, 1657, 1446, 1275, 1149 cm^{-1}. MS (ESI) calcd for $C_{24}H_{23}N_2O_3S$ $[M+H]^+$ 419.1424, found 419.1416.

Crystal data for 15aa: Formula $C_{24}H_{22}N_2O_3S$, colorless, crystal dimensions 0.20 × 0.10 × 0.10 mm^3, triclinic, space group P-1, *a* = 6.8453(4) Å, *b* = 11.1232(7) Å, *c* = 14.3467(9) Å, α = 95.8640(10) °, β = 94.6170(2) °, γ = 106.1630(10) °, *V* = 1036.91(11) $Å^3$, *Z* = 2, ρ_{calc} = 1.340 g cm^{-3}, F(000) = 440, μ(MoKα) = 0.185 mm^{-1}, *T* = 173 K. 5925 reflections collected, 4519 independent reflections with $I > 2\sigma(I)$ ($2\theta_{max}$ = 28.44°), and 272 parameters were used for the solution of the structure. The non-hydrogen atoms were refined anisotropically. R_1 = 0.0437 and wR_2 = 0.1124. GOF = 1.079. 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-1023216. 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].

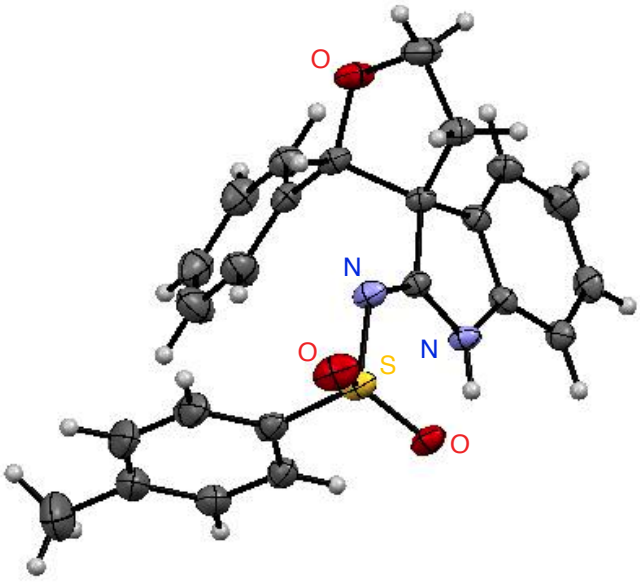
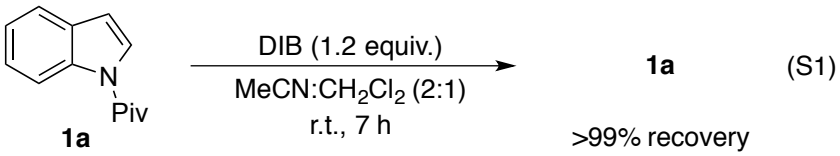


Figure S6. ORTEP drawing of **15aa**.

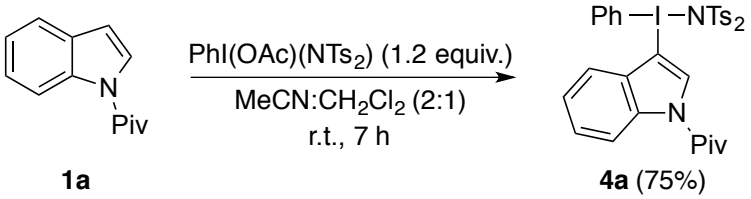
6. Mechanism Study for Dual Functionalization of Indols.

6.1. Preparation of Indolyl(phenyl)iodonium compounds with Indole and Hypervalent iodines (Eqs S1 and S2)

To a solution of **1a** (50.3 mg, 0.25 mmol) in MeCN (1.4 mL) and CH_2Cl_2 (0.7 mL) was added hypervalent iodine reagens (DIB or PhI(OAc)(NTs_2), 0.30 mmol) at room temperature under argon atomosphere, and the solution was stirred at room temperature. The volatile solvents were removed under reduced pressure. The yield of products was determined by ^{1}H-NMR spectra of the crude product based on internal standerd (1,4-bis(trimethylsilyl)benzene) (eqs S1 and S2).



(S1)



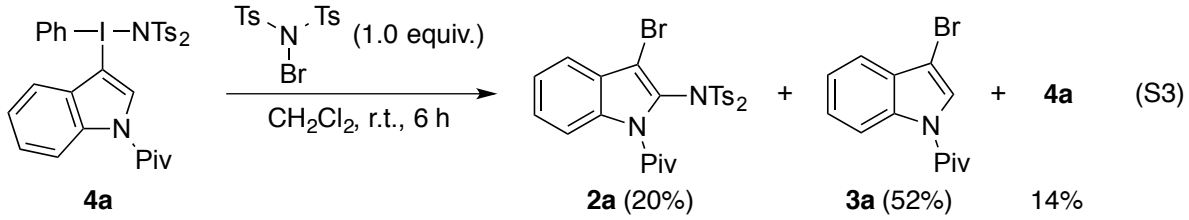
(S2)

When DIB was used as a hypervalentiodine reagent for the preparation of indolyl(phenyl)iodonium imide, the desired product (**1a**) was not obtained (eq S1). However, the use of PhI(OAc)(NTs_2) for the present reaction provided **4a** in 75% yield (eq S2). These results (eqs S1 and S2) suggest that

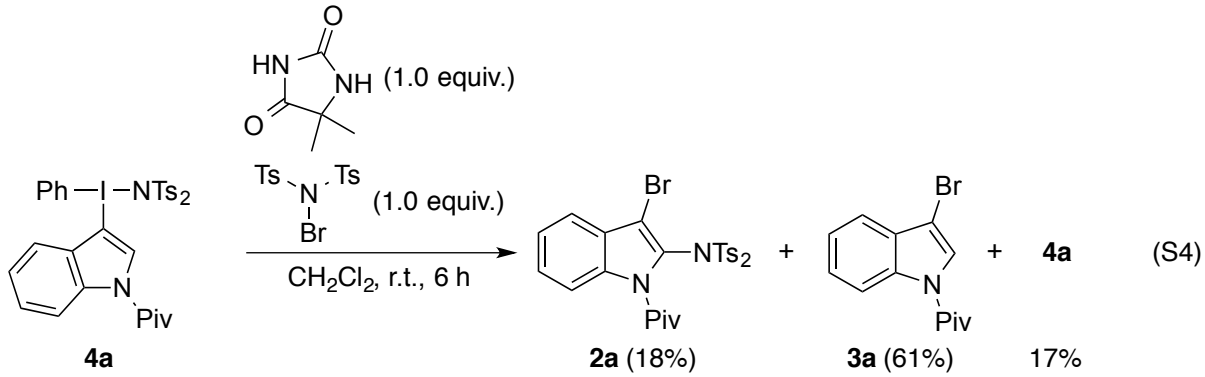
bis(tosyl)imide group (having weak conjugated basicity) increases the electrophilicity of the iodine atom on the hypervalent iodine to promote the electrophilic reaction into indole (**1**).

6.2. Effect of Bromo Reagent for Dual Functionalization of Indoles (Eqs S3 and S4)

To a solution of **4a** (72.9 mg, 0.10 mmol) in $ClCH_2CH_2Cl$ (2.0 mL) was added *N*-bromo-bis(tosyl)imide (40.4 mg, 0.10 mmol) at room temperature under argon atomosphere, and the solution was stirred for 7 h. 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), brine (10 mL) and dried over Na_2SO_4. The organic phase was concentrated under reduced pressure. The yield of products was determined by ^{1}H-NMR spectra of the crude product based on internal standerd (1,4-bis(trimethylsilyl)benzene) to give the desired product **2a** (20%) together with *N*-pivaloyl-3-bromo-indole **3a** (52%) and **4a** (14%) (eq S3).



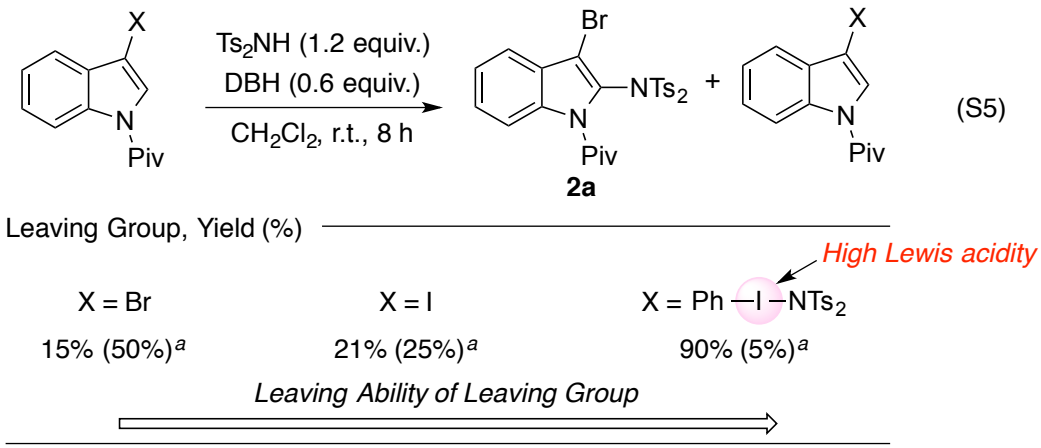
To a solution of **4a** (72.9 mg, 0.10 mmol) and 5,5-dimethylhydantoin (12.8 mg, 0.10 mmol) in Cl CH_2CH_2Cl (2.0 mL) was added *N*-bromo-bis(tosyl)imide (40.4 mg, 0.10 mmol) at room temperature under argon atomosphere, and the solution was stirred for 7 h. Saturated Na_2SO_3 aqueous solution (10 mL) 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), brine (10 mL) and dried over Na_2SO_4. The organic phase was concentrated under reduced pressure. The yield of products was determined by ^{1}H-NMR spectra of the crude product based on internal standerd (1,4-bis(trimethylsilyl)benzene) to give the desired product **2a** (18%) together with *N*-pivaloyl-3-bromo-indole **3a** (61%) and **4a** (17%) (eq S4).



These results (eqs S3 and S4) suggest that 1,3-dibromo-5,5-dimethylhidantoin (DBH) directly promotes the dual functionalization of indoles as a bromo reagent, but forms *N*-bromo-bis(tosyl)imide from bis(tosyl)imide. Furthermore, the results in Table S2 suggest that the amide moiety on bromo reagents is important to the bromination of indoles.

6.3. Effect of Leaving Group for Dual Functionalization of Indoles (Eq S5).

To a solution of *N*-pivaloyl-3-halo-indoles (0.10 mmol) and bis(tosyl)imide (39.1 mg, 0.10 mmol) in CH_2Cl_2 (1.0 mL) was added 1,3-dibromo-5,5-dimethylhydantoin (17.2 mg, 0.06 mmol) at room temperature under argon atomosphere, and the solution was stirred for 7 h. 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), brine (10 mL) and dried over Na_2SO_4. The organic phase was concentrated under reduced pressure. The yield of products was determined by ^{1}H-NMR spectra of the crude product based on internal standerd (1,4-bis(trimethylsilyl)benzene) (eq S5).

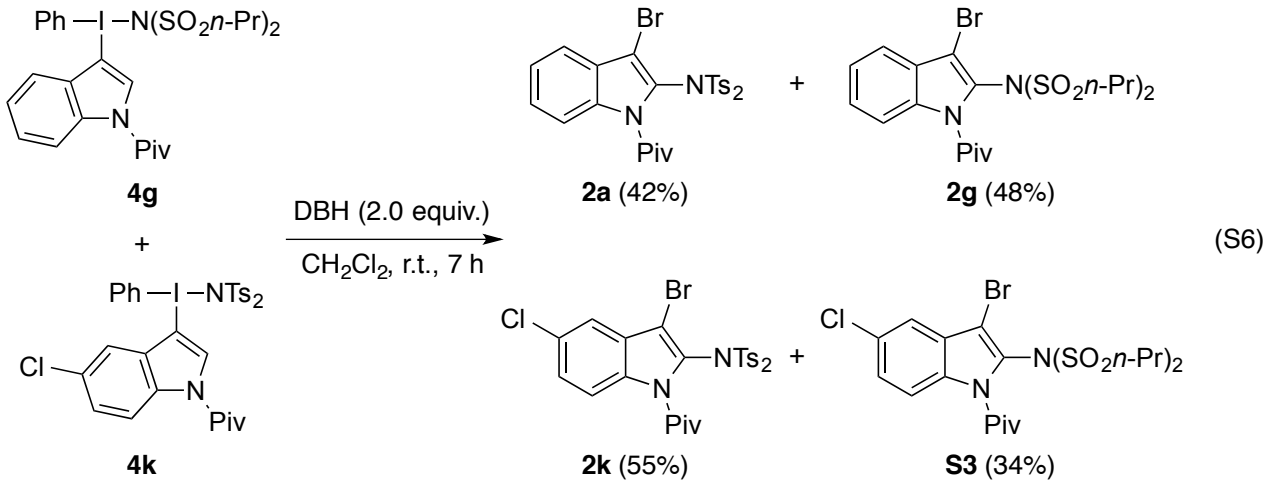


[a]Numbers in parentheses indicate the recovery of substrate.

This suggests that the high Lewis acidity of the iodine (III) atom and the leaving ability of the bis(tosyl)imide(phenyl)-λ^3-iodanyl group at the 3-position on the indoles accelerates the C_{sp2}–H dual functionalization, to give the desired product **2**. The present reaction requires both a high leaving ability and a strong Lewis acidity of the iodine (III) atom for the λ^3-iodanyl group at the 3-position on indole to promote not only the electrophilic addition at the 3-position with a bromo reagent as Lewis acid, but olso the aromatization of the adduct of bis(sulfonyl)imide at the 2-position as a leaving group.

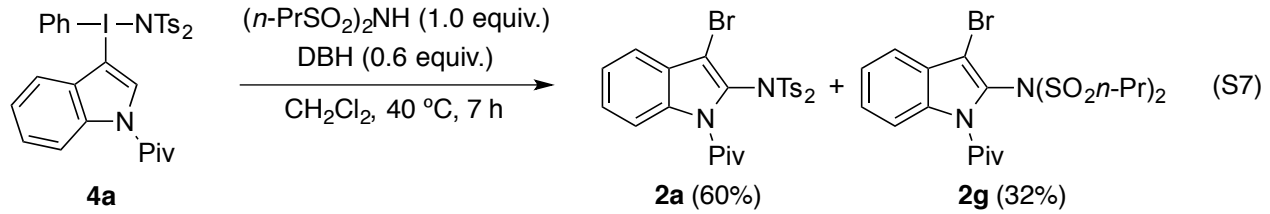
6.4. Crossover Reaction of Dual Functionalization of Indoles (Eqs S6–S8).

To a solution of **4g** (63.3 mg, 0.10 mmol) and **4k** (76.3 mg, 0.10 mmol) in CH_2Cl_2 (2.0 mL) was added 1,3-dibromo-5,5-dimethylhydantoin (114.4 mg, 0.40 mmol) at room temperature under argon atomosphere, and the solution was stirred for 7 h. 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), brine (10 mL) and dried over Na_2SO_4. The organic phase was concentrated under reduced pressure. The yield of products was determined by ^{1}H-NMR spectra of the crude product based on internal standerd (1,4-bis(trimethylsilyl)benzene) to give *N*-pivaloyl-2-bis(tosyl)-amino-3-bromo-indole **2a** (42 %), *N*-pivaloyl-2-bis(*n*-propane sulfonyl)-amino-3-bromo-indole **2g** (48 %), *N*-pivaloyl-2-bis(tosyl)-amino-3-bromo-5-chloro-indole **2k** (55 %), *N*-pivaloyl-2-bis(*n*-propanesulfonyl)-amino-3-bromo-5-chloro-indole **S3** (34 %) (eq S6).



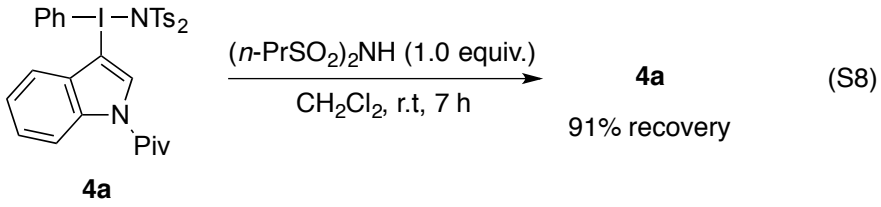
(S6)

To a solution of **4a** (72.9 mg, 0.10 mmol) and bis(*n*-propanesulfonyl)imide (22.9 mg, 0.10 mmol) in CH_2Cl_2 (1.0 mL) was added 1,3-dibromo-5,5-dimethylhydantoin (17.2 mg, 0.06 mmol) at room temperature under argon atomosphere, and the solution was stirred at 40 ºC for 7 h. 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), brine (10 mL) and dried over Na_2SO_4. The organic phase was concentrated under reduced pressure. The yield of products was determined by ^{1}H-NMR spectra of the crude product based on internal standerd (1,4-bis(trimethylsilyl)benzene) to give *N*-pivaloyl-2-bistosylimidyl-3-bromo indole **2a** (60 %), *N*-pivaloyl-2-bis(*n*-propylsulfonyl) imidyl-3-bromo indole **2g** (32 %) (eq S7).



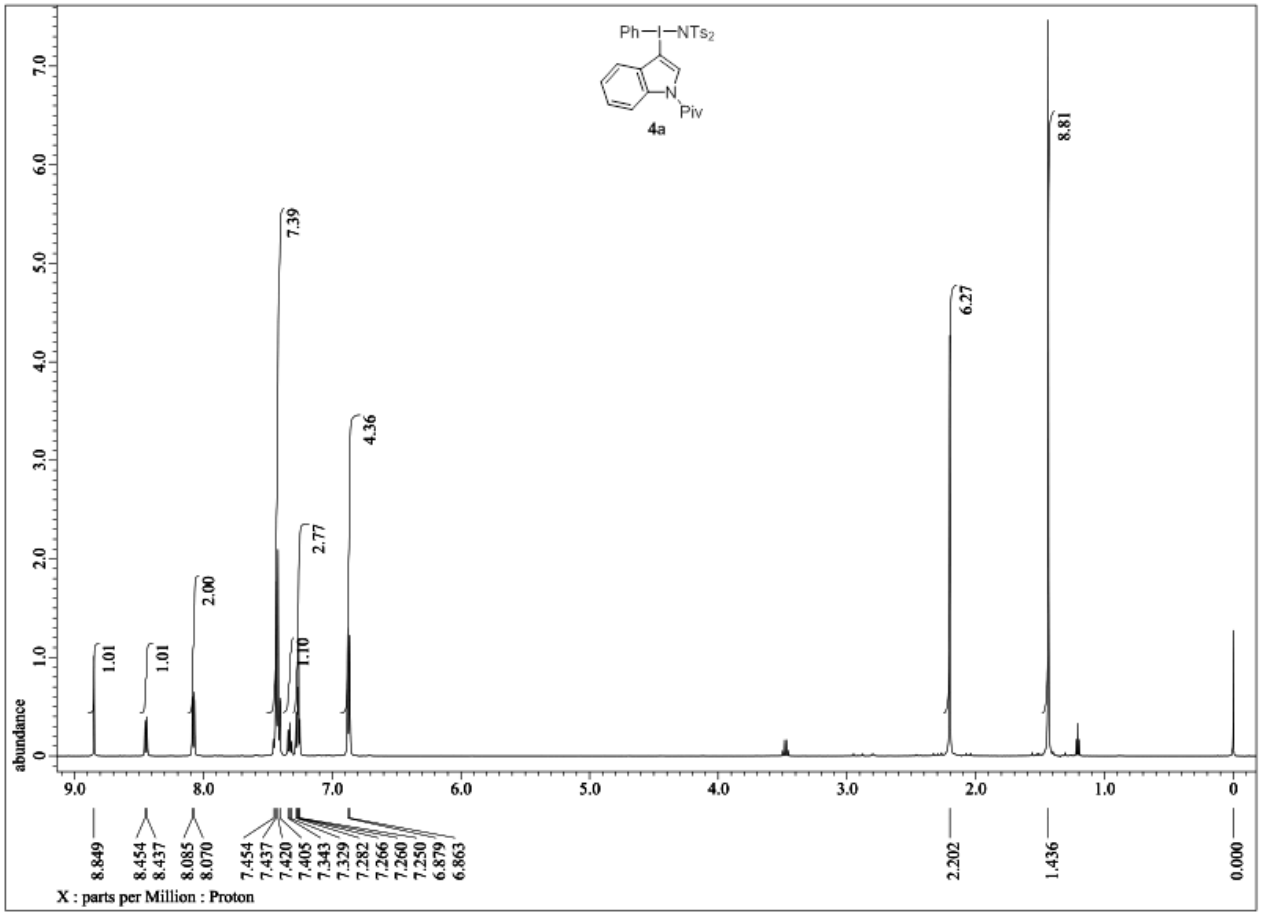
(S7)

To a solution of **4a** (72.9 mg, 0.10 mmol) in CH_2Cl_2 (1.0 mL) was added bis(*n*-propanesulfonyl)imide (22.9 mg, 0.10 mmol) at room temperature under argon atomosphere, and the solution was stirred for 7 h. 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 sovent was removed under reduced pressure. The yield of products was determined by ^{1}H-NMR spectra of the crude product based on internal standerd (1,4-bis(trimethylsilyl)benzene) and it was found that **4a** was recoverd in 91% yield (eq S8).



4a (S8)

These results (eqs S6–S8) suggest that bis(sulfonyl)imide combined with hypervalent iodine **4** releases a bis(sulfonyl)imide anion via the addition of a bromonium species. Subsequent intermolecular nucleophilic substitution by the bis(sulfonyl)imide anion at the 2-position of indoles then occurs, but intramolecular substitution does not.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Piv
4a
abundance
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7.260
7.250
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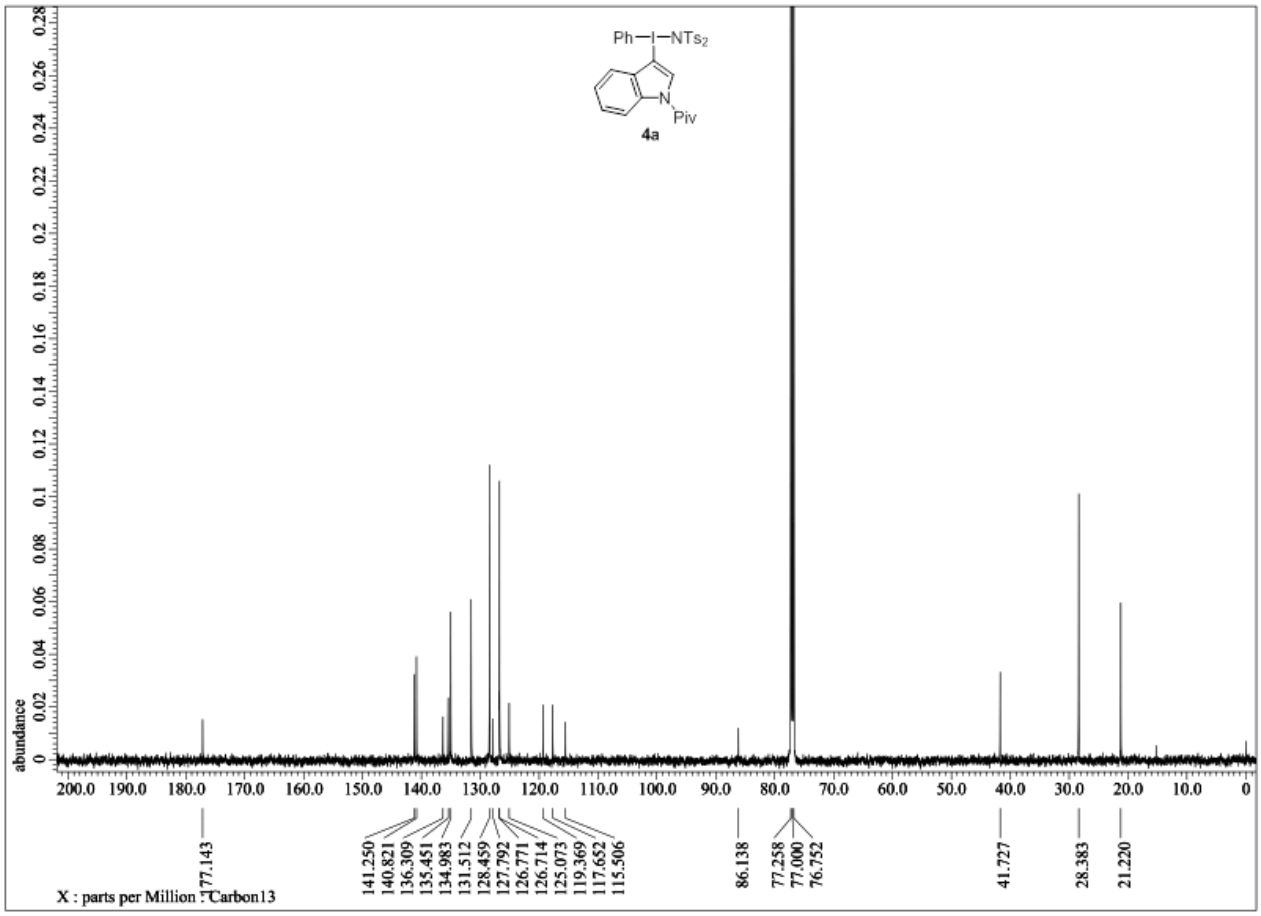
8.81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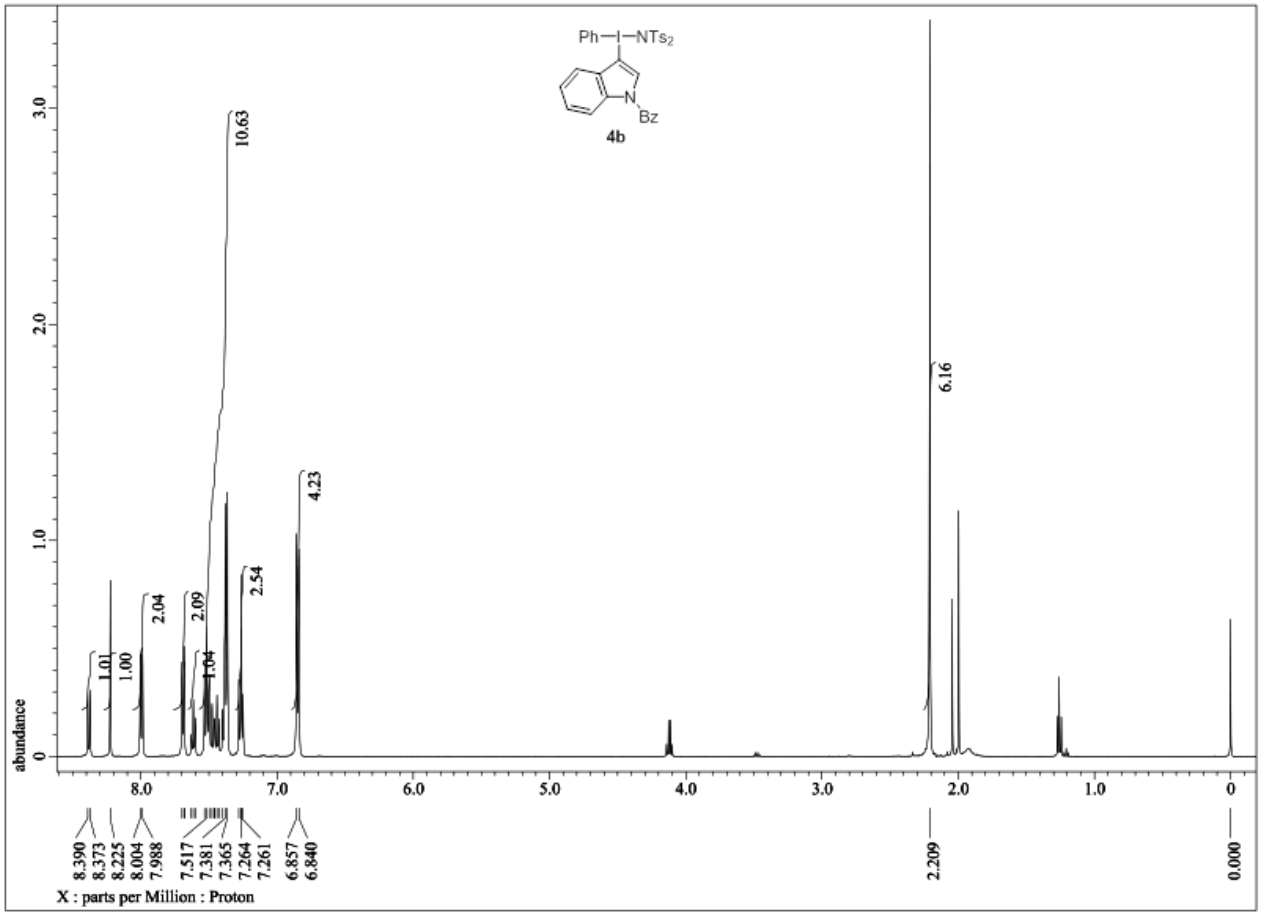
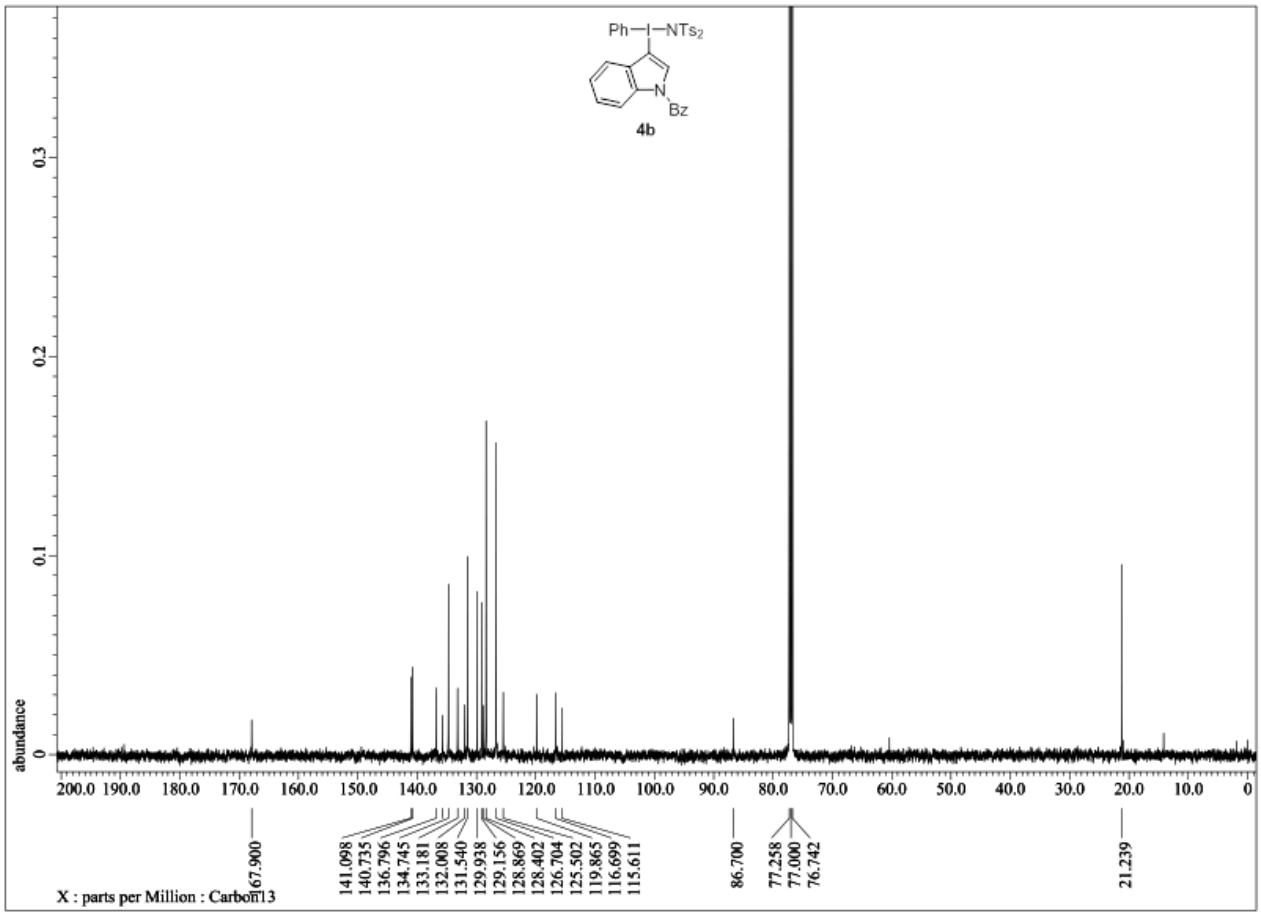
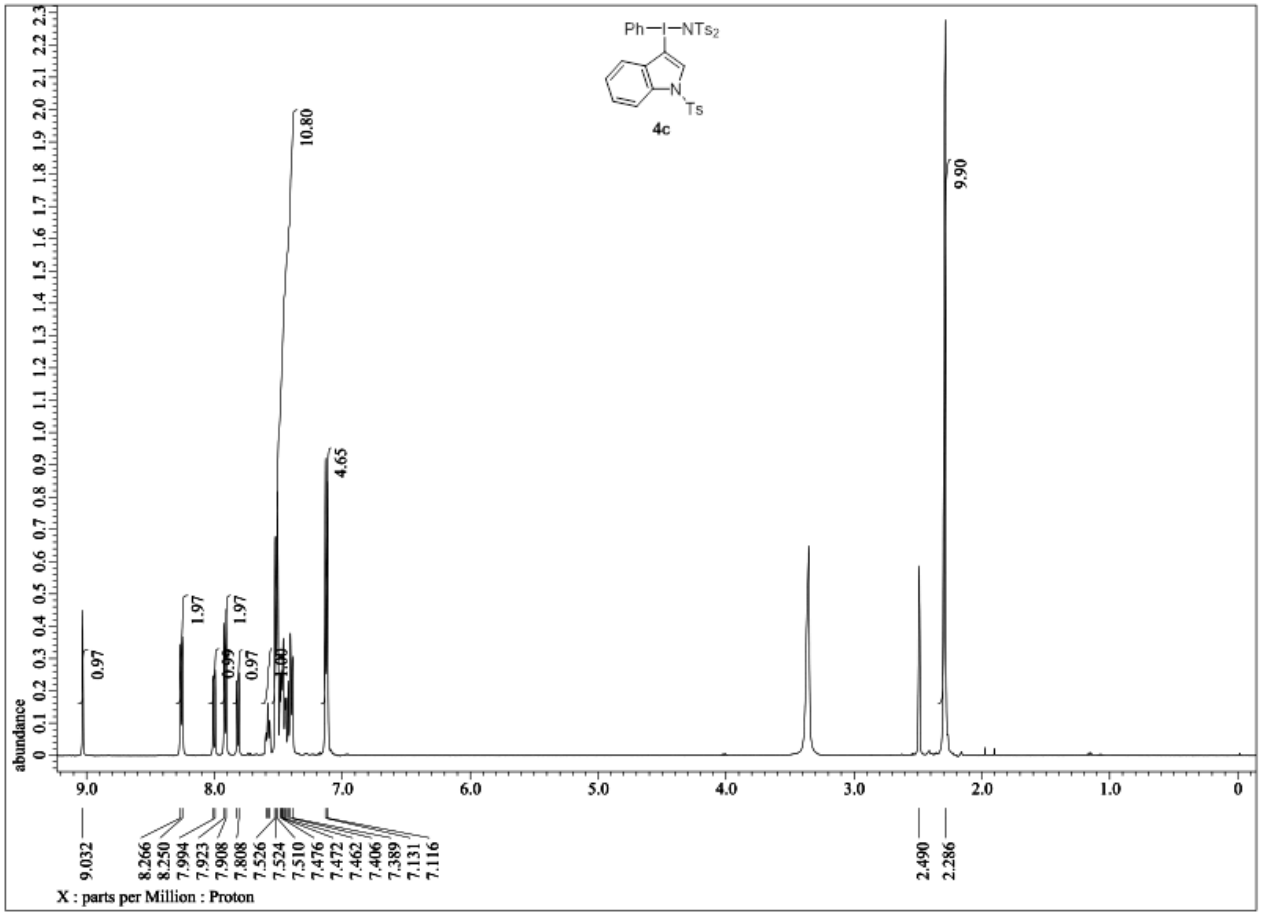
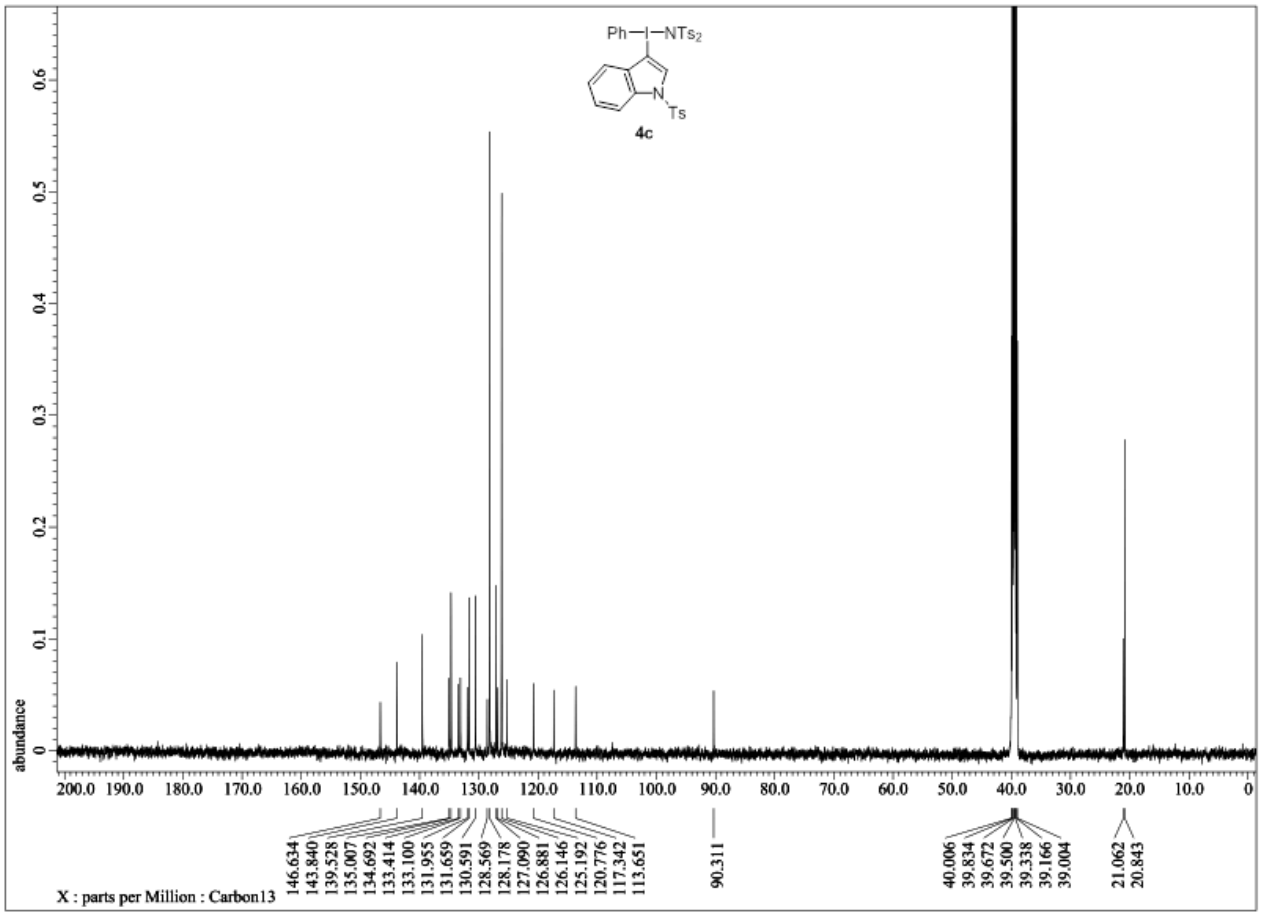
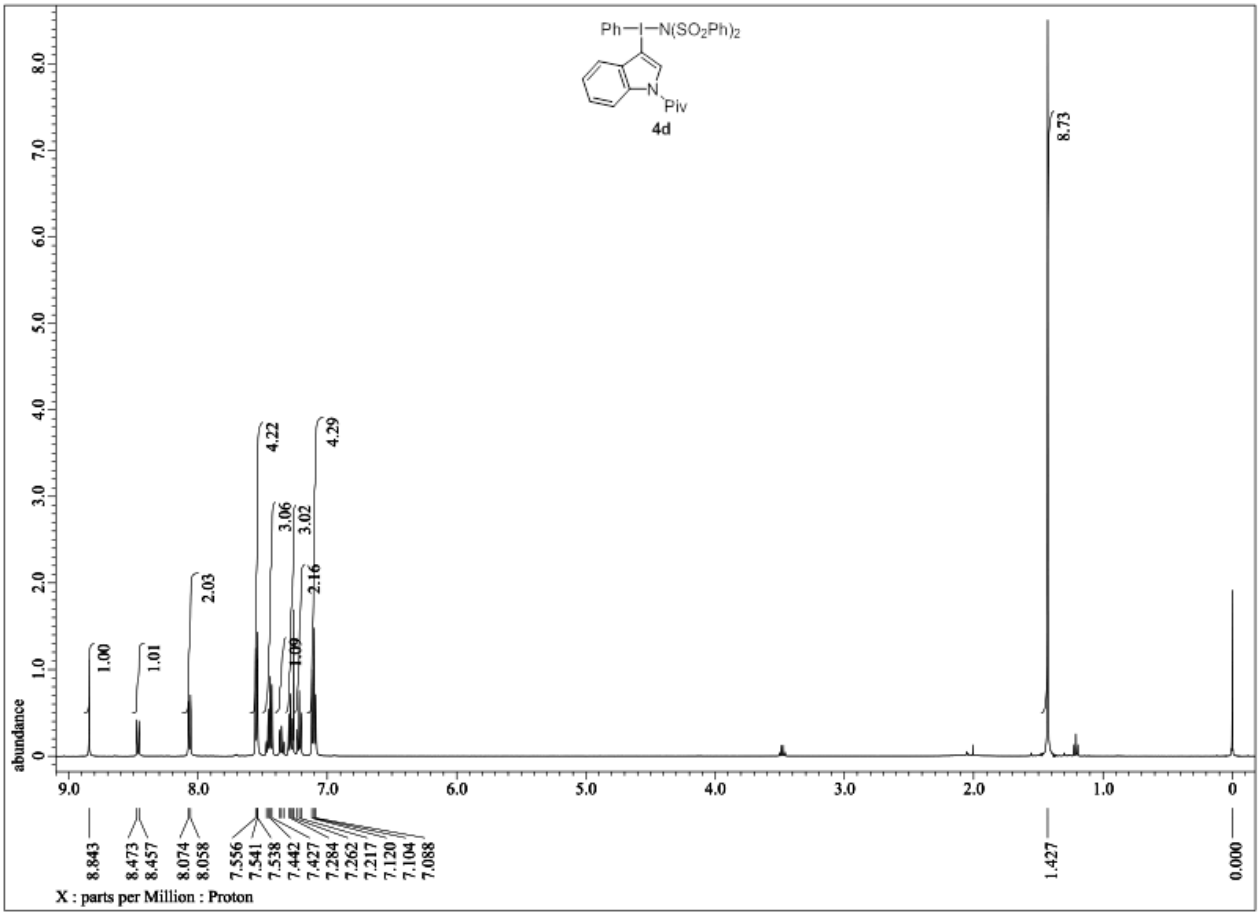
28.383
21.220

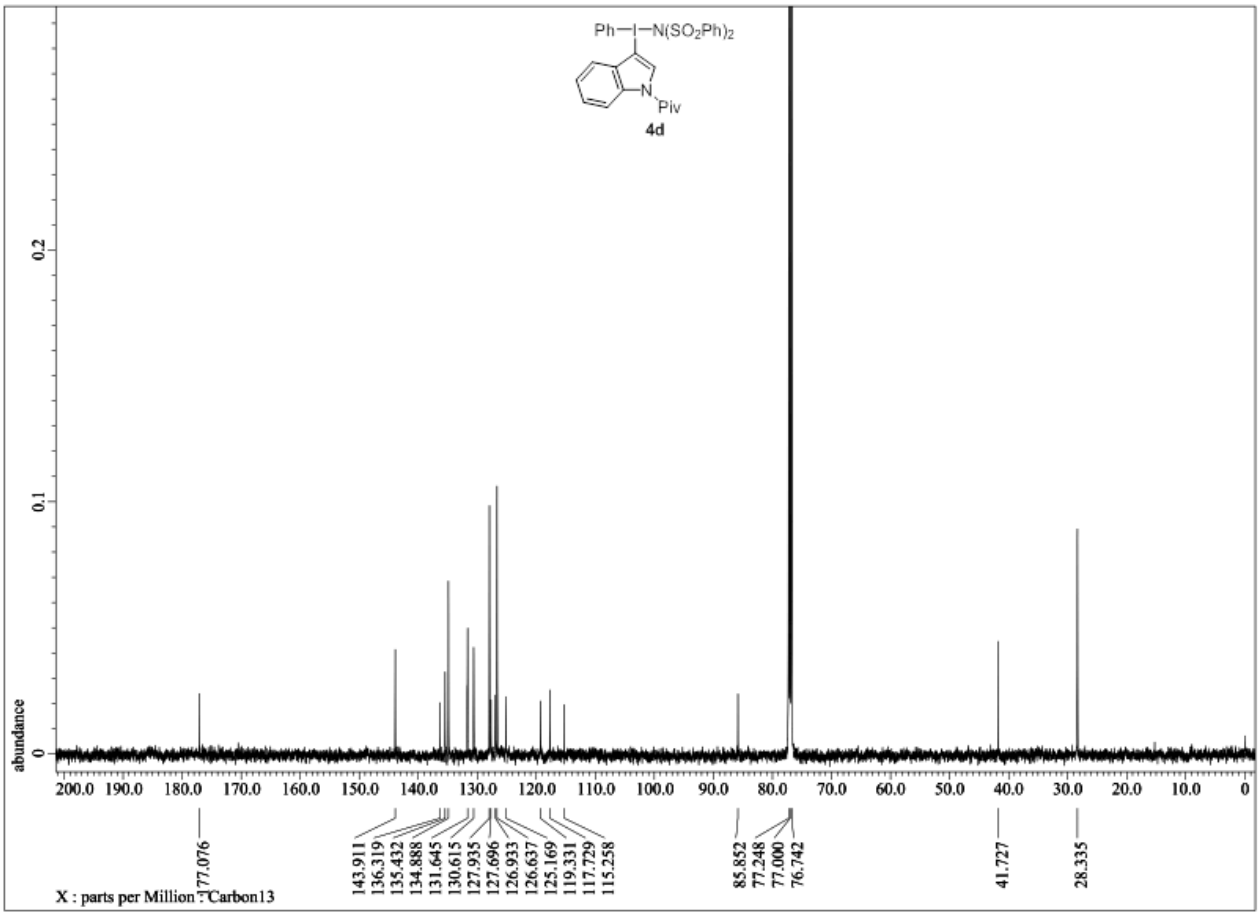

Ph—I—NTs2
N
Bz
4b
abundance
X : parts per Million : Proton
10.63
6.16
4.23
2.54
2.09
2.04
1.01
1.00
1.04
8.390
8.373
8.225
8.004
7.988
7.517
7.381
7.365
7.264
7.261
6.857
6.840
2.209
0.000

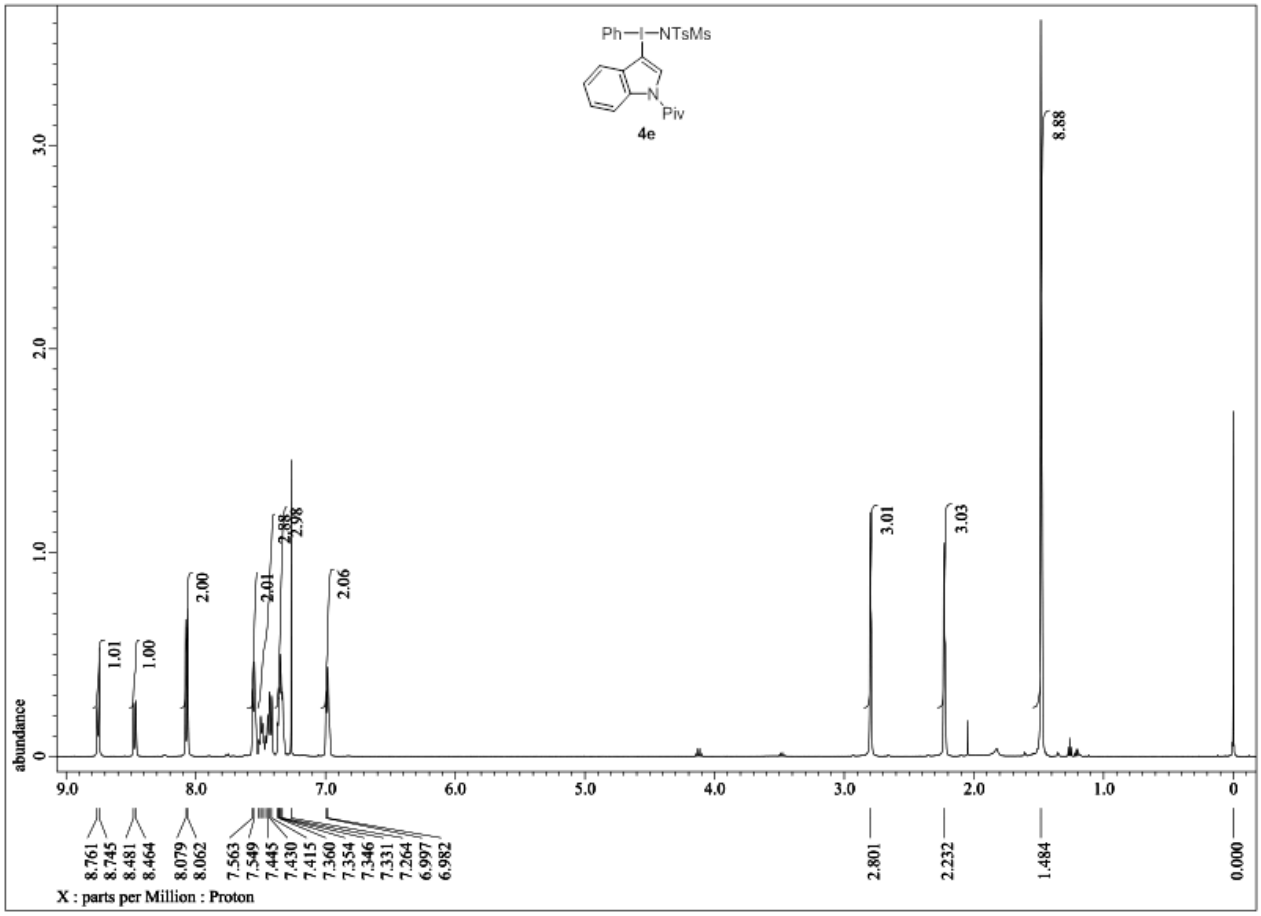

Ph—I—NTs2
N
Bz
4b
abundance
X : parts per Million : Carbon13
167.900
141.098
140.735
136.796
134.745
133.181
132.008
131.540
129.938
129.156
128.869
128.402
126.704
125.502
119.865
116.699
115.611
86.700
77.258
77.000
76.742
21.239

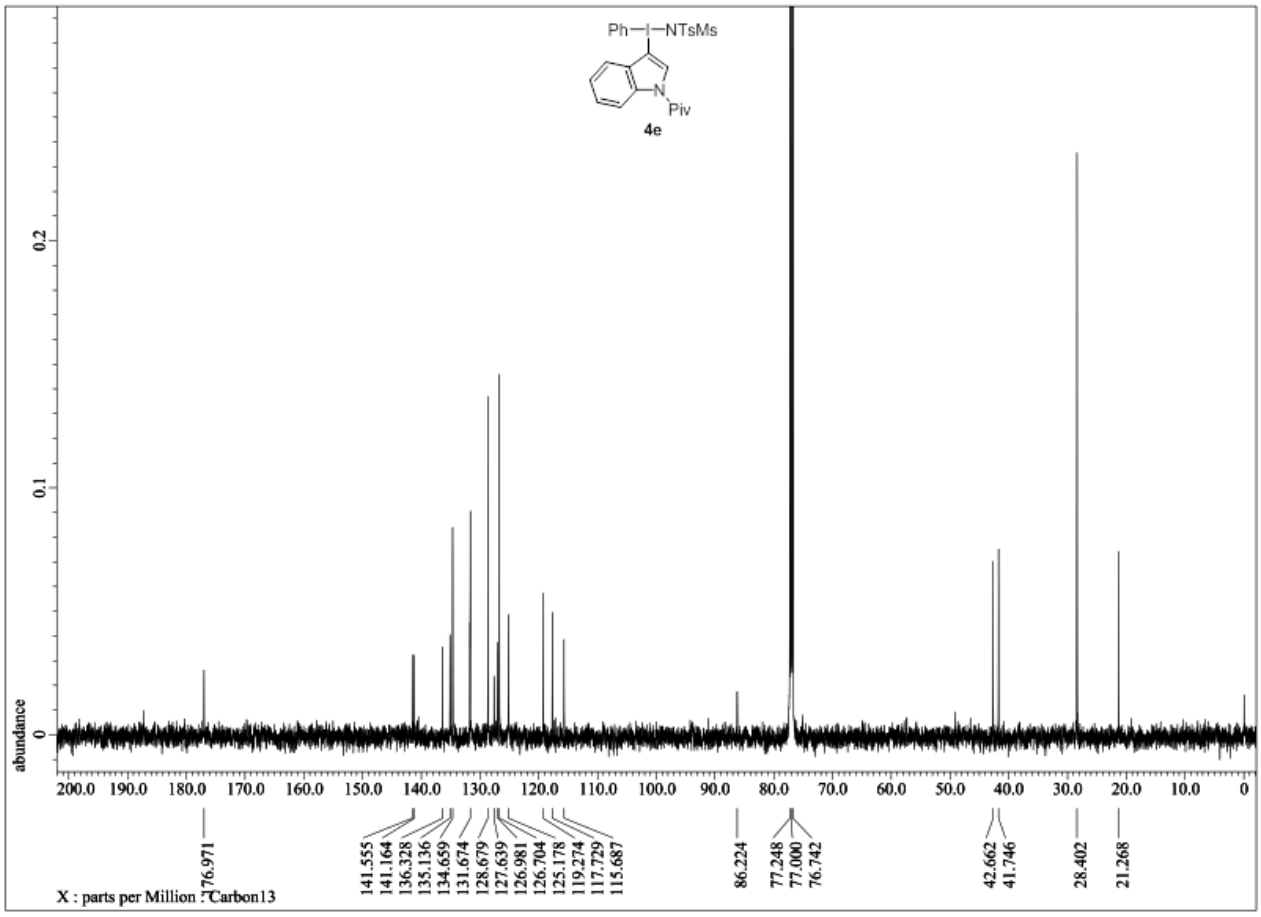

Ph—I—NTs2
N
Ts
4c
10.80
9.90
4.65
1.97
1.97
0.97
0.99
0.97
1.00
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.032
8.266
8.250
7.994
7.923
7.908
7.808
7.526
7.524
7.510
7.476
7.472
7.462
7.406
7.389
7.131
7.116
2.490
2.286
X : parts per Million : Proton

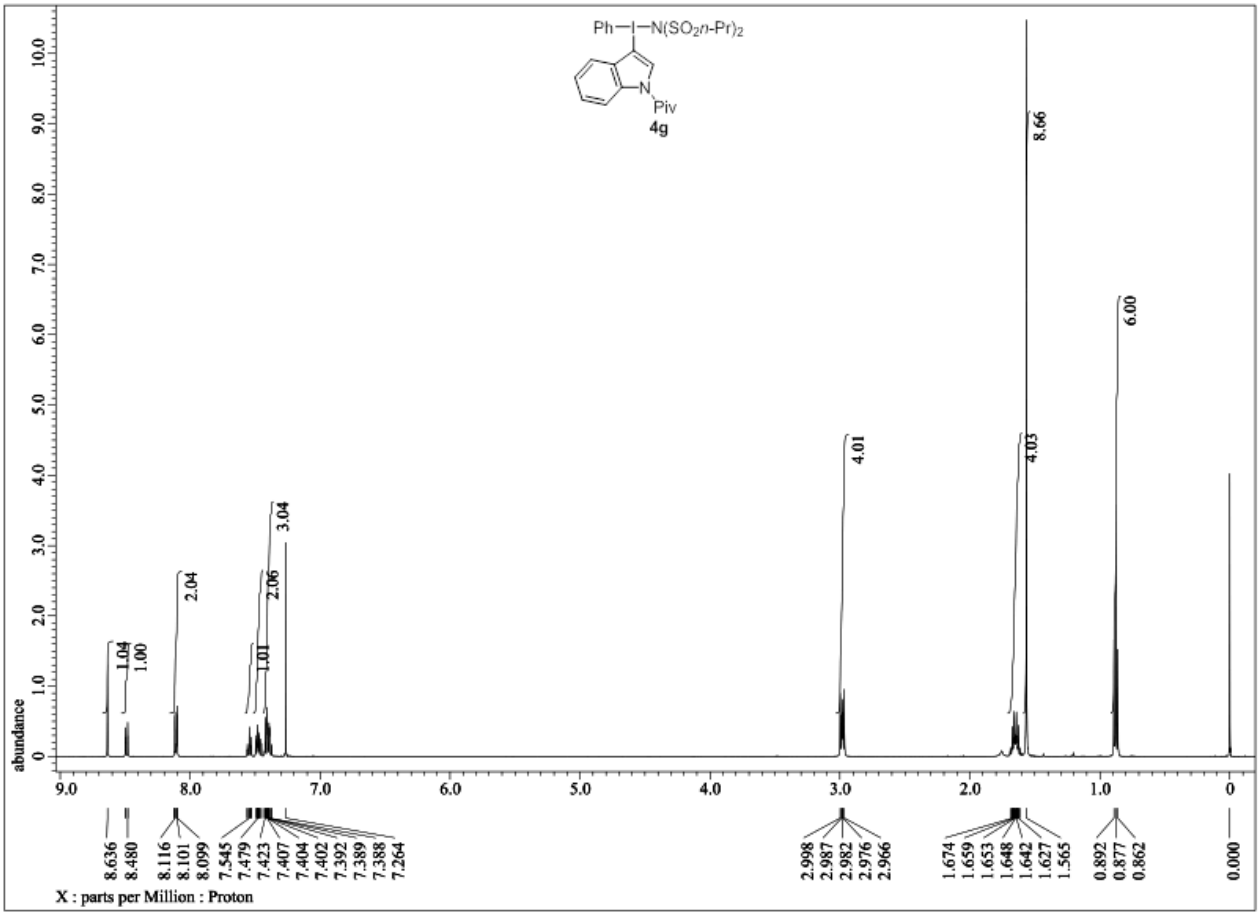

Ph—I—NTs2
N
Ts
4c
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
146.634
143.840
139.528
135.007
134.692
133.414
133.100
131.955
131.659
130.591
128.569
128.178
127.090
126.881
126.146
125.192
120.776
117.342
113.651
90.311
40.006
39.834
39.672
39.500
39.338
39.166
39.004
21.062
20.843
X : parts per Million : Carbon13

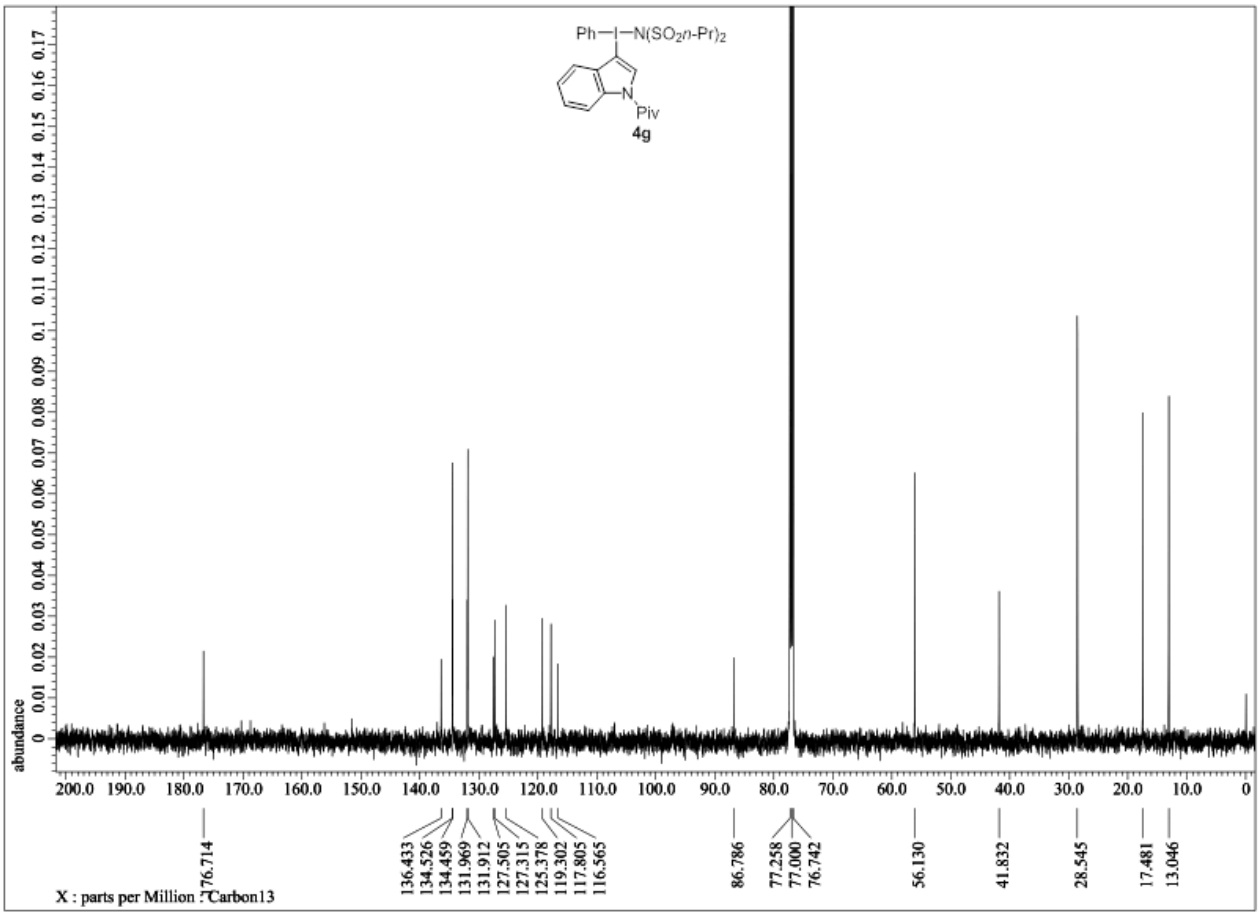

Ph—I—N(SO2Ph)2
Piv
4d
abundance
1.00
1.01
2.03
4.22
3.06
3.02
4.29
2.16
1.09
8.73
8.843
8.473
8.457
8.074
8.058
7.556
7.541
7.538
7.442
7.427
7.284
7.262
7.217
7.120
7.104
7.088
1.427
0.000
X : parts per Million : Proton

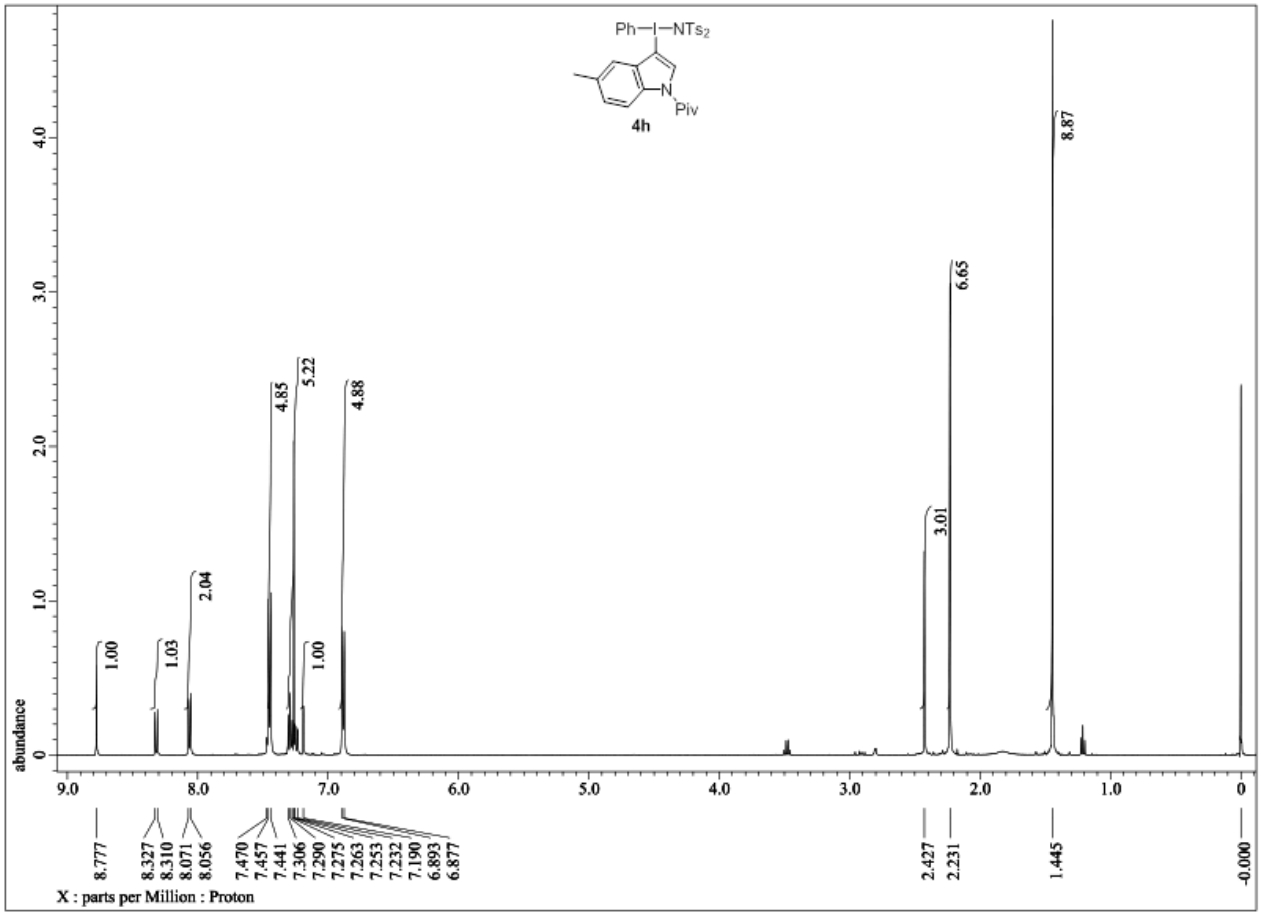

Ph—I—N(SO2Ph)2
Piv
4d
abundance
77.076
143.911
136.319
135.432
134.888
131.645
130.615
127.935
127.696
126.933
126.637
125.169
119.331
117.729
115.258
85.852
77.248
77.000
76.742
41.727
28.335
X : parts per Million : Carbon13

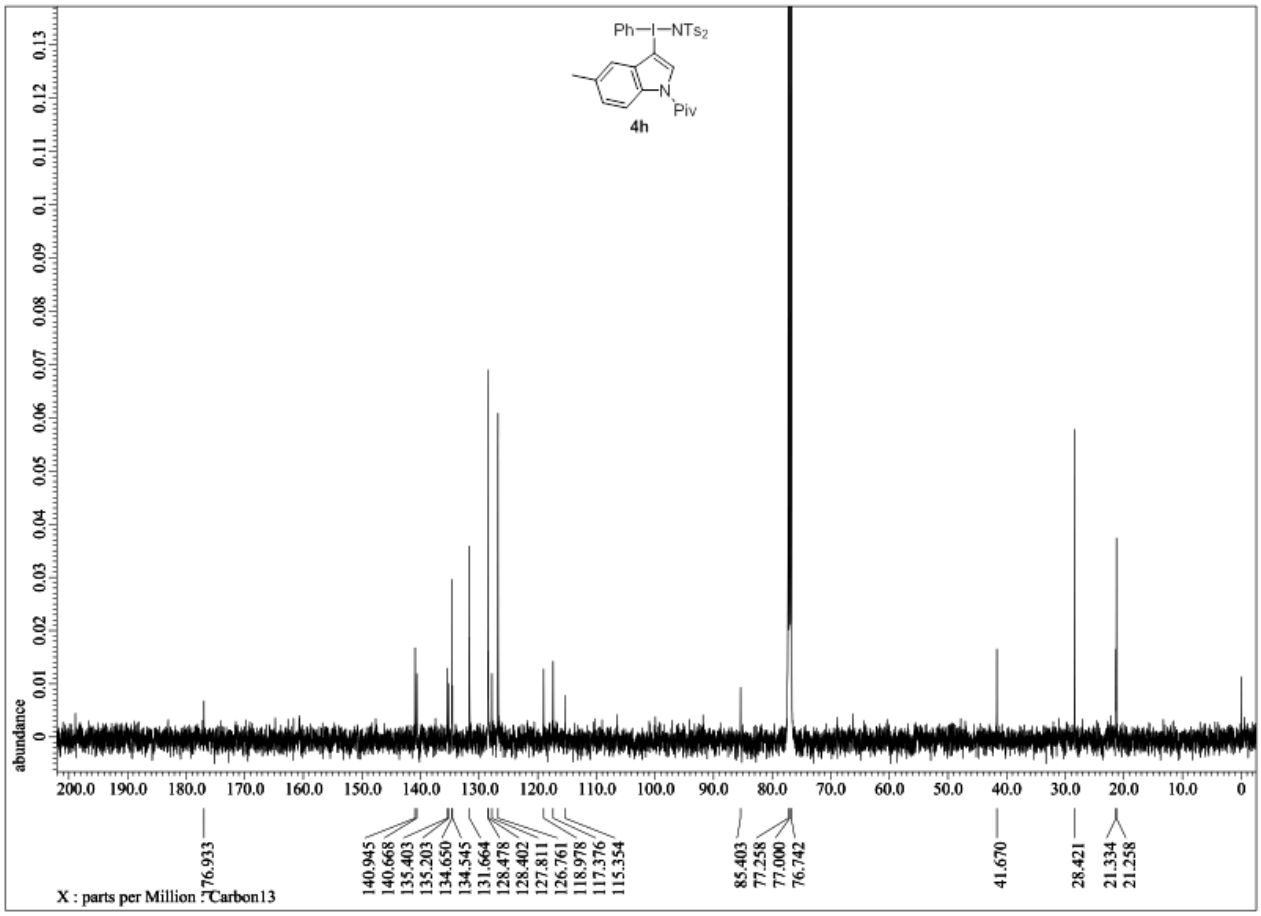

Ph—I—NTsMs
N
Piv
4e
abundance
X : parts per Million : Proton
8.761
8.745
8.481
8.464
8.079
8.062
7.563
7.549
7.445
7.430
7.415
7.360
7.354
7.346
7.331
7.264
6.997
6.982
2.801
2.232
1.484
0.000

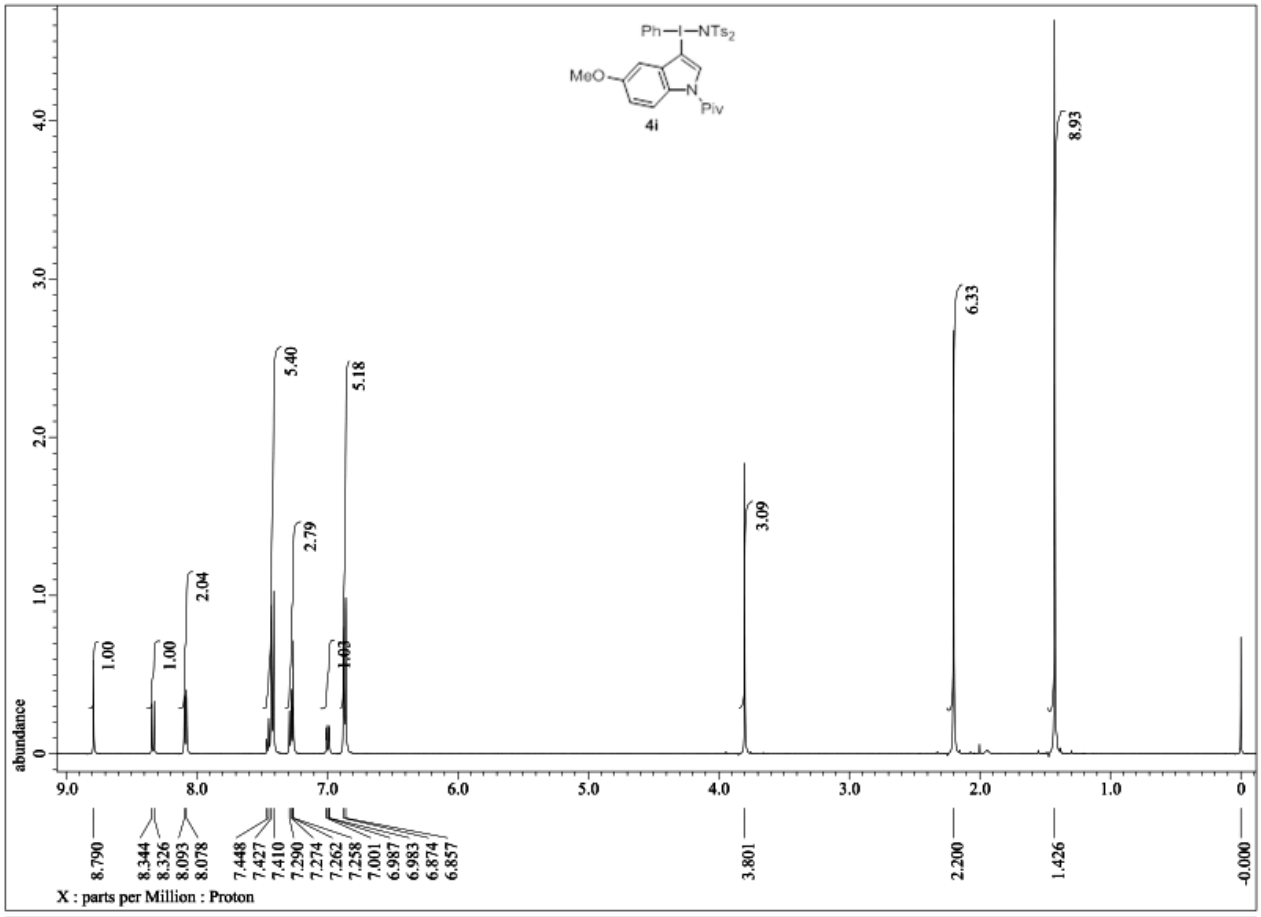

Ph—I—NTsMs
N
Piv
4e
abundance
X : parts per Million : Carbon13
76.971
141.555
141.164
136.328
135.136
134.659
131.674
128.679
127.639
126.981
126.704
125.178
119.274
117.729
115.687
86.224
77.248
77.000
76.742
42.662
41.746
28.402
21.268

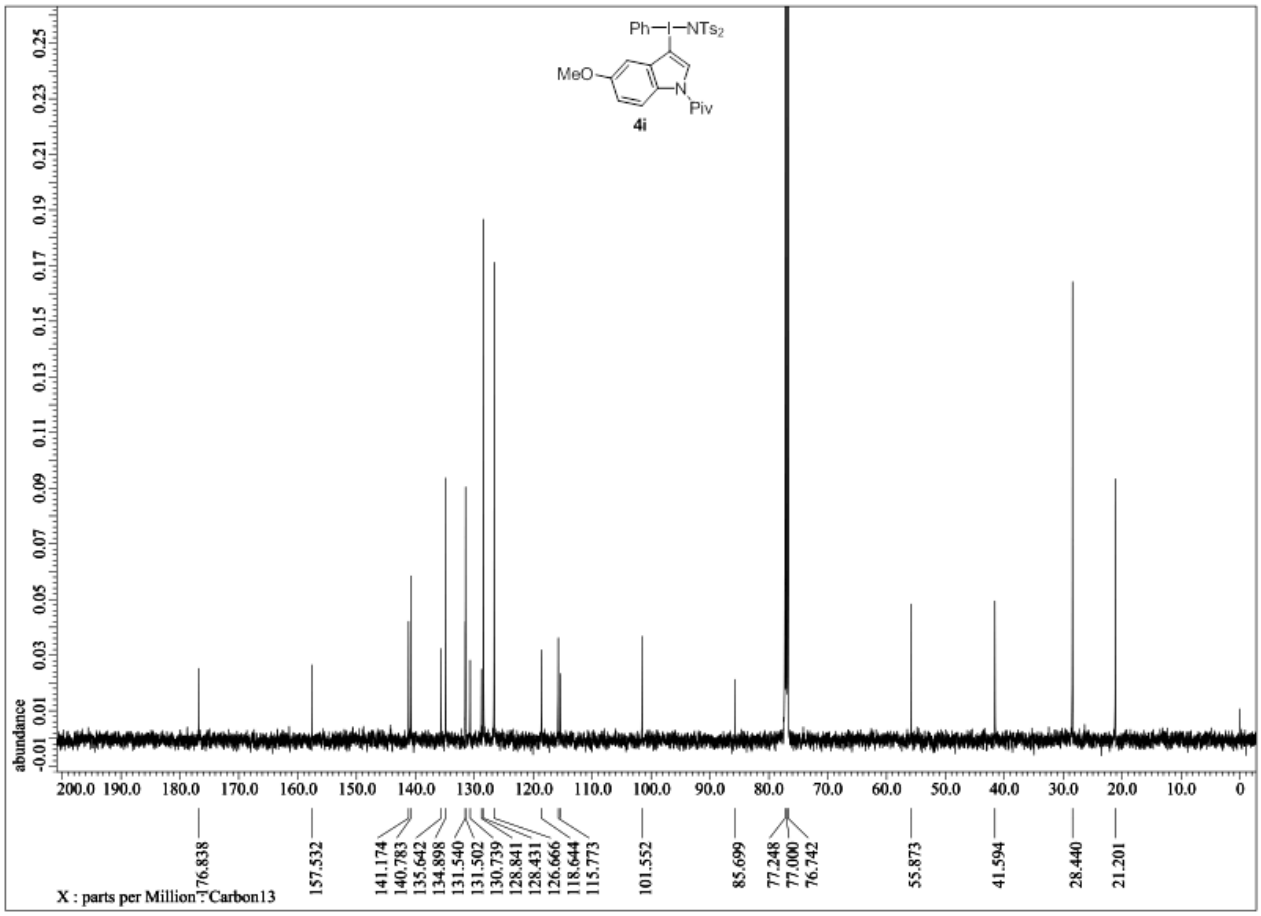

Ph—I—N(SO2n-Pr)2
Piv
4g
8.66
6.00
4.01
4.03
3.04
2.04
2.06
1.04
1.00
1.01
abundance
X : parts per Million : Proton

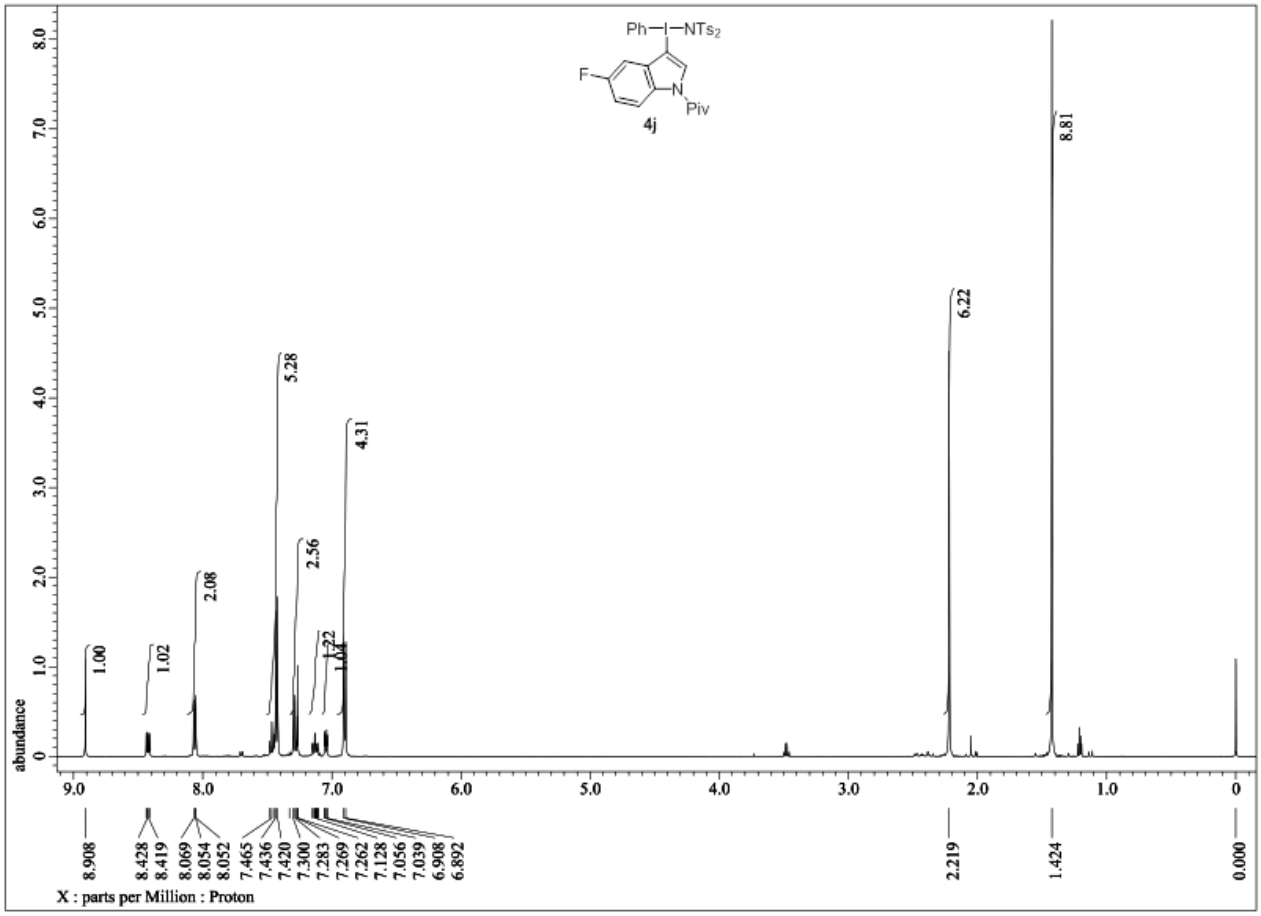

Ph—I—N(SO2n-Pr)2
Piv
4g
abundance
X : parts per Million : Carbon13

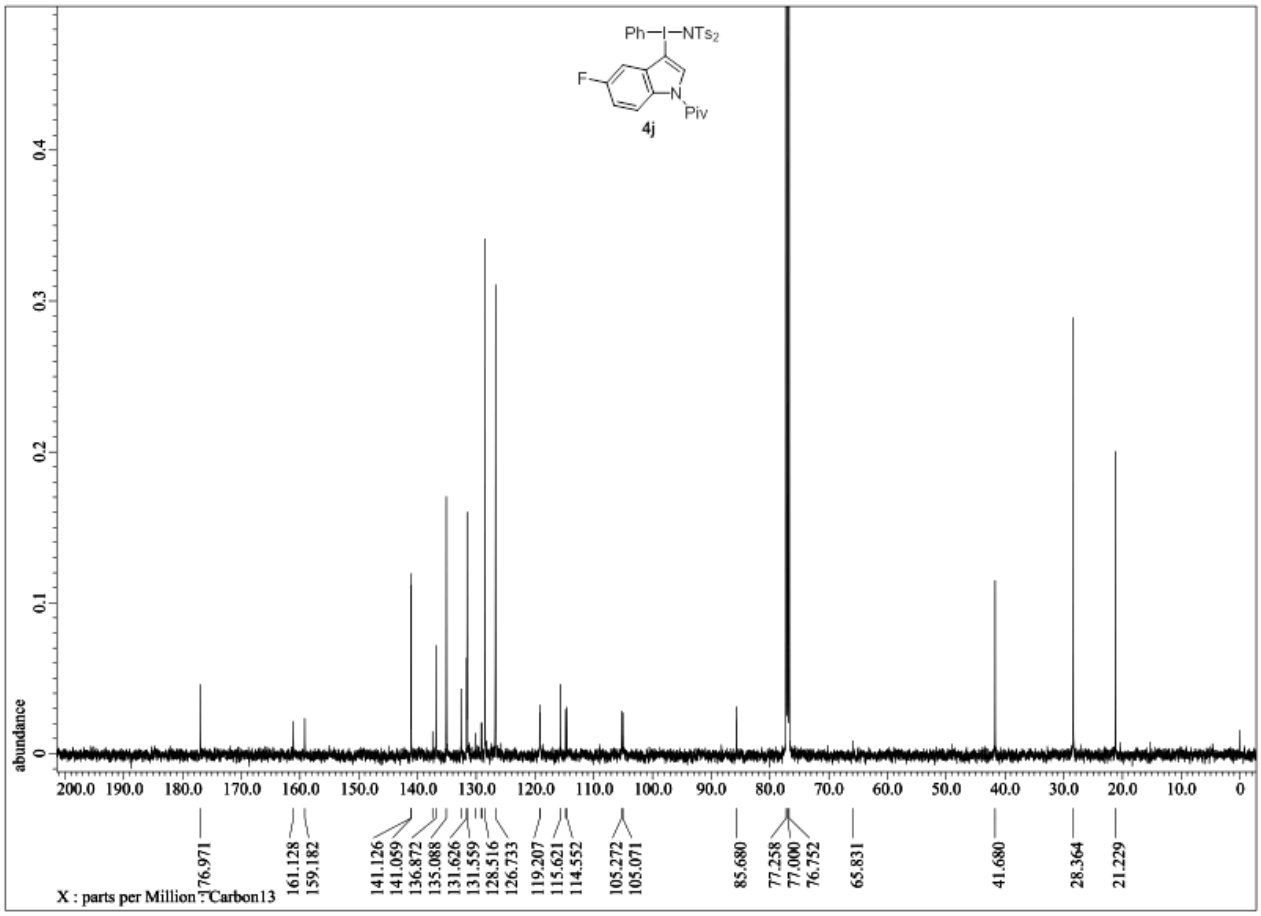

Ph—I—NTs2
N
Piv
4h
abundance
X : parts per Million : Proton
8.87
6.65
4.85
5.22
4.88
3.01
2.04
1.00
1.03
1.00
8.777
8.327
8.310
8.071
8.056
7.470
7.457
7.441
7.306
7.290
7.275
7.263
7.253
7.232
7.190
6.893
6.877
2.427
2.231
1.445
-0.000

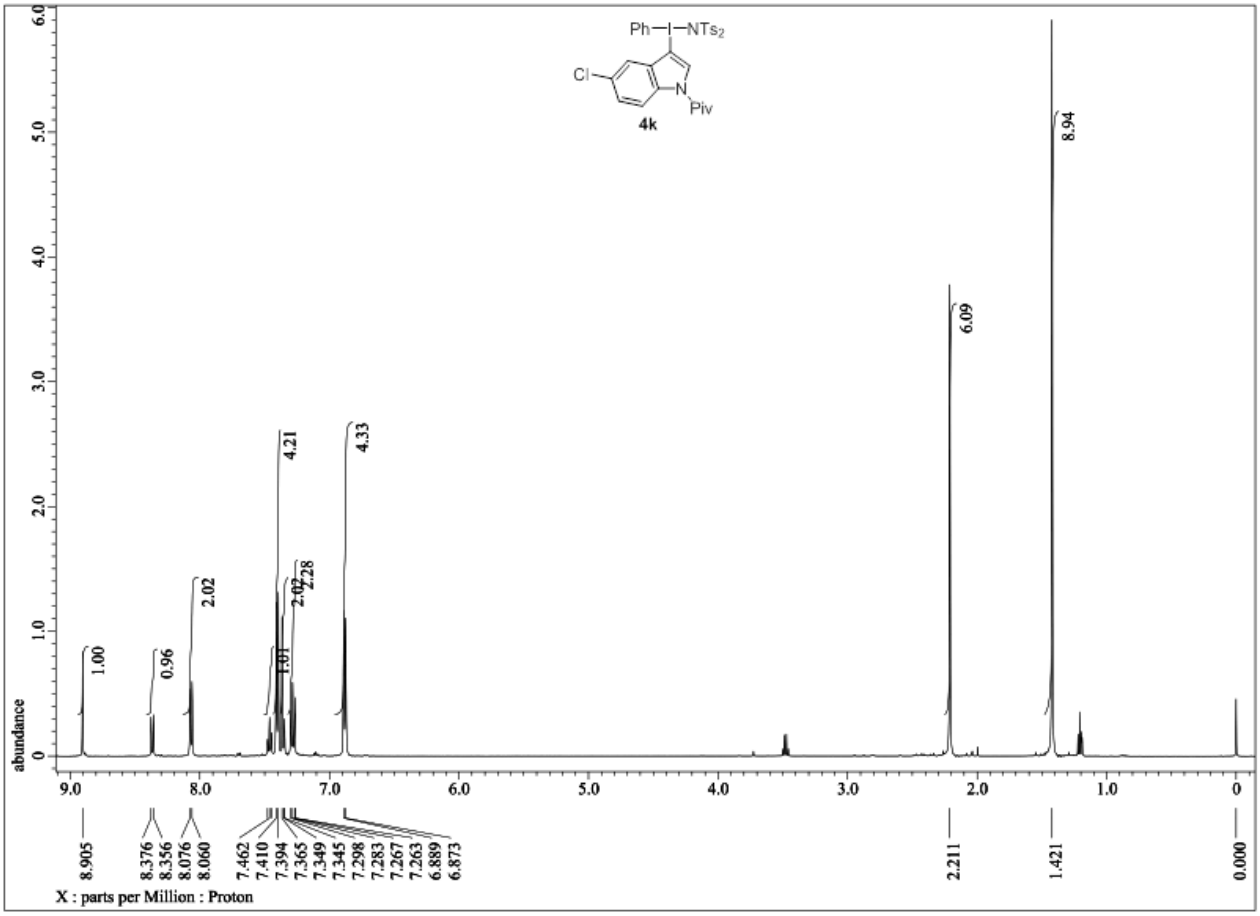

Ph—I—NTs2
N
Piv
4h
abundance
X : parts per Million : Carbon13
76.933
140.945
140.668
135.403
135.203
134.650
134.545
131.664
128.478
128.402
127.811
126.761
118.978
117.376
115.354
85.403
77.258
77.000
76.742
41.670
28.421
21.334
21.258

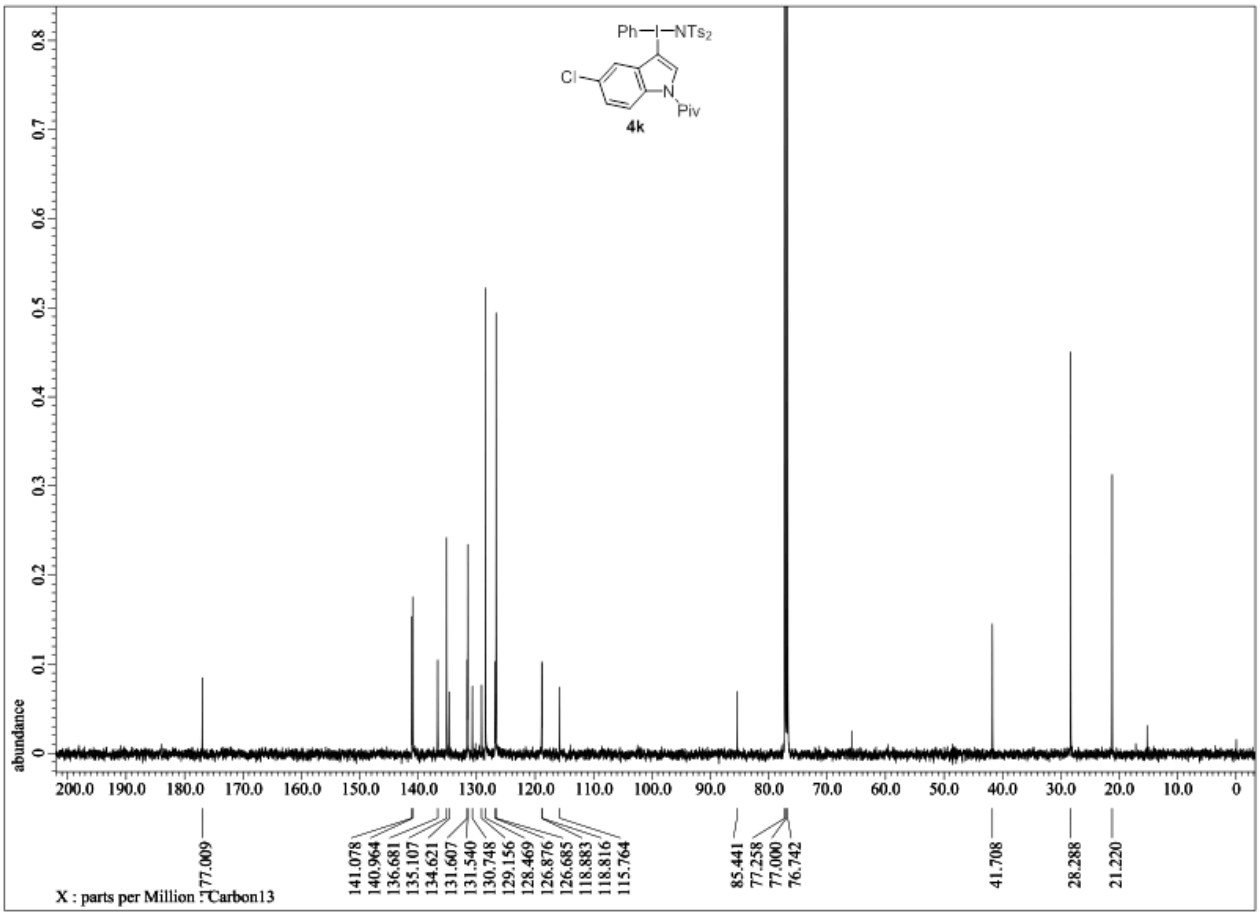

Ph—I—NTs2
MeO
N
Piv
4i
abundance
X : parts per Million : Proton
8.790
8.344
8.326
8.093
8.078
7.448
7.427
7.410
7.290
7.274
7.262
7.258
7.001
6.987
6.983
6.874
6.857
3.801
2.200
1.426
-0.000

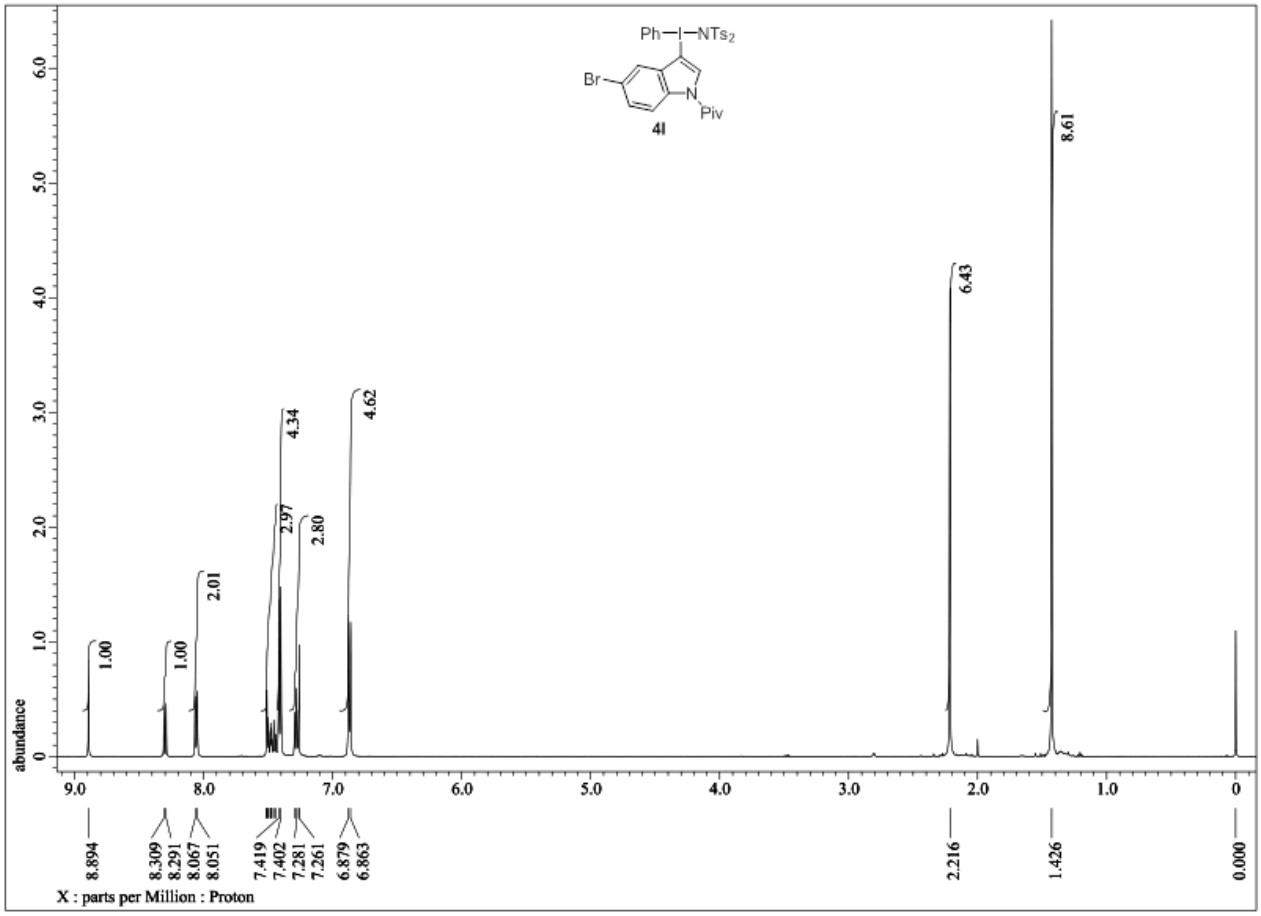

Ph—I—NTs2
MeO
N
Piv
4i
abundance
X : parts per Million : Carbon13
76.838
157.532
141.174
140.783
135.642
134.898
131.540
131.502
130.739
128.841
128.431
126.666
118.644
115.773
101.552
85.699
77.248
77.000
76.742
55.873
41.594
28.440
21.201

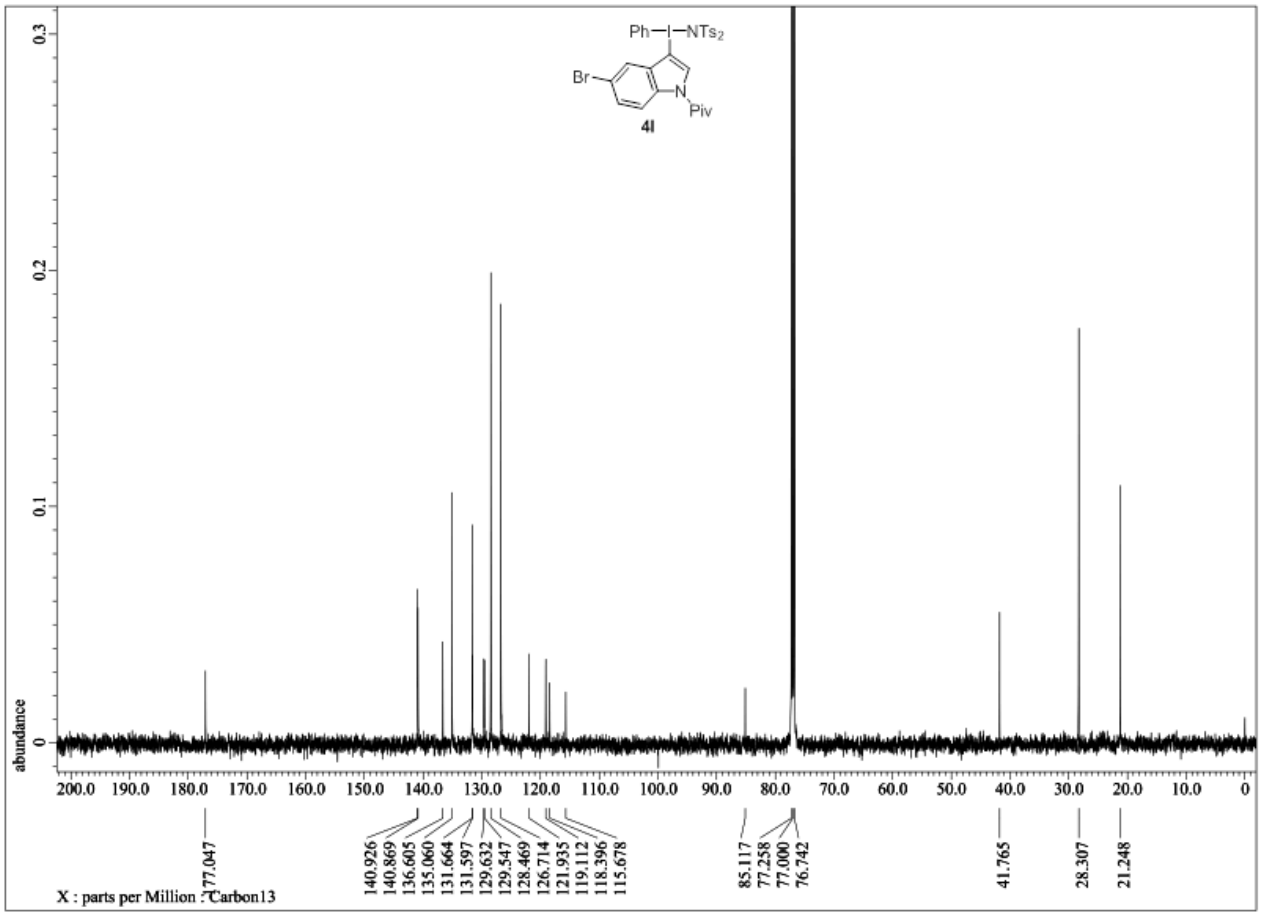

Ph—I—NTs2
F
N
Piv
4j
abundance
X : parts per Million : Proton
8.908
8.428
8.419
8.069
8.054
8.052
7.465
7.436
7.420
7.300
7.283
7.269
7.262
7.128
7.056
7.039
6.908
6.892
2.219
1.424
0.000

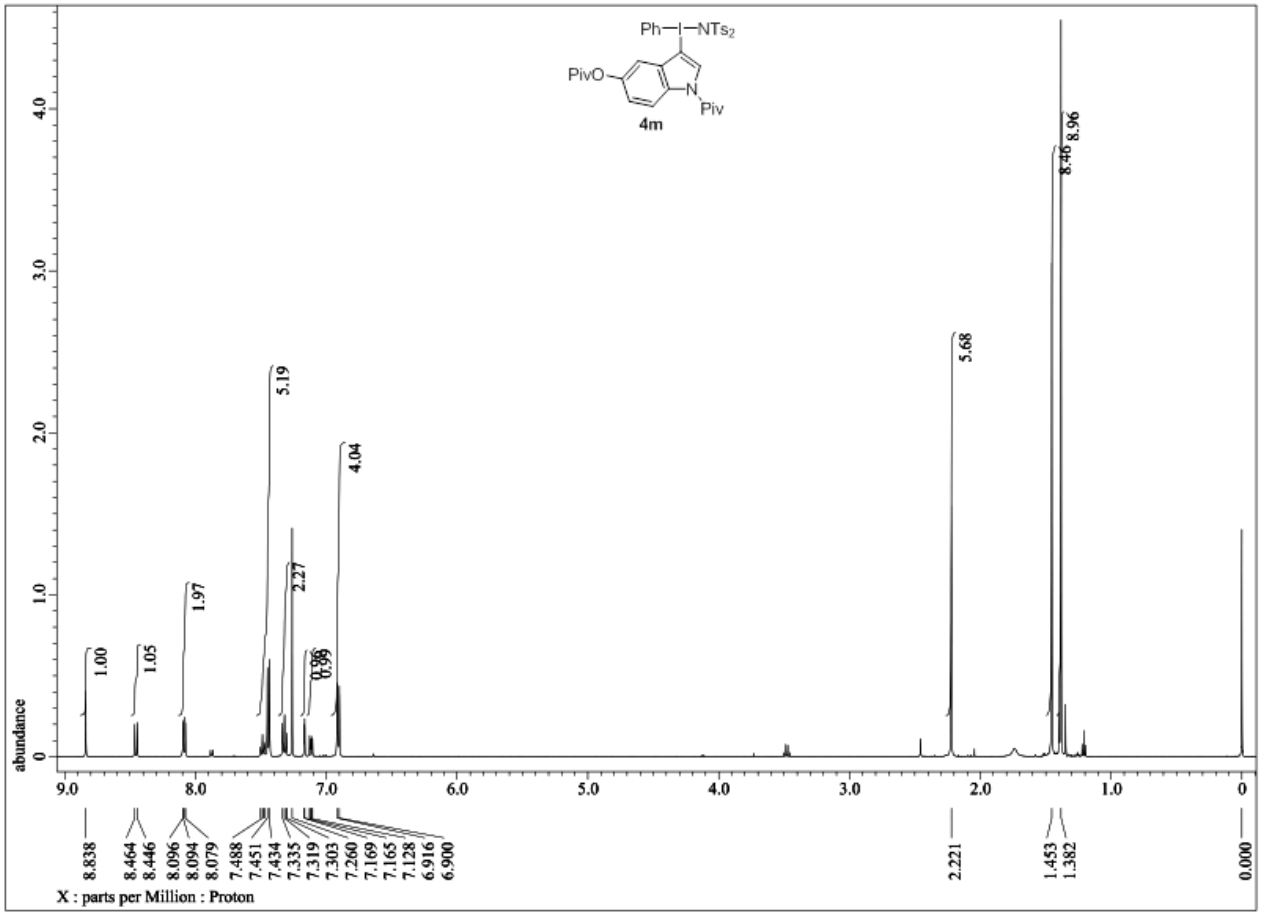

Ph—I—NTs2
F
N
Piv
4j
abundance
X : parts per Million : Carbon13
76.971
161.128
159.182
141.126
141.059
136.872
135.088
131.626
131.559
128.516
126.733
119.207
115.621
114.552
105.272
105.071
85.680
77.258
77.000
76.752
65.831
41.680
28.364
21.229

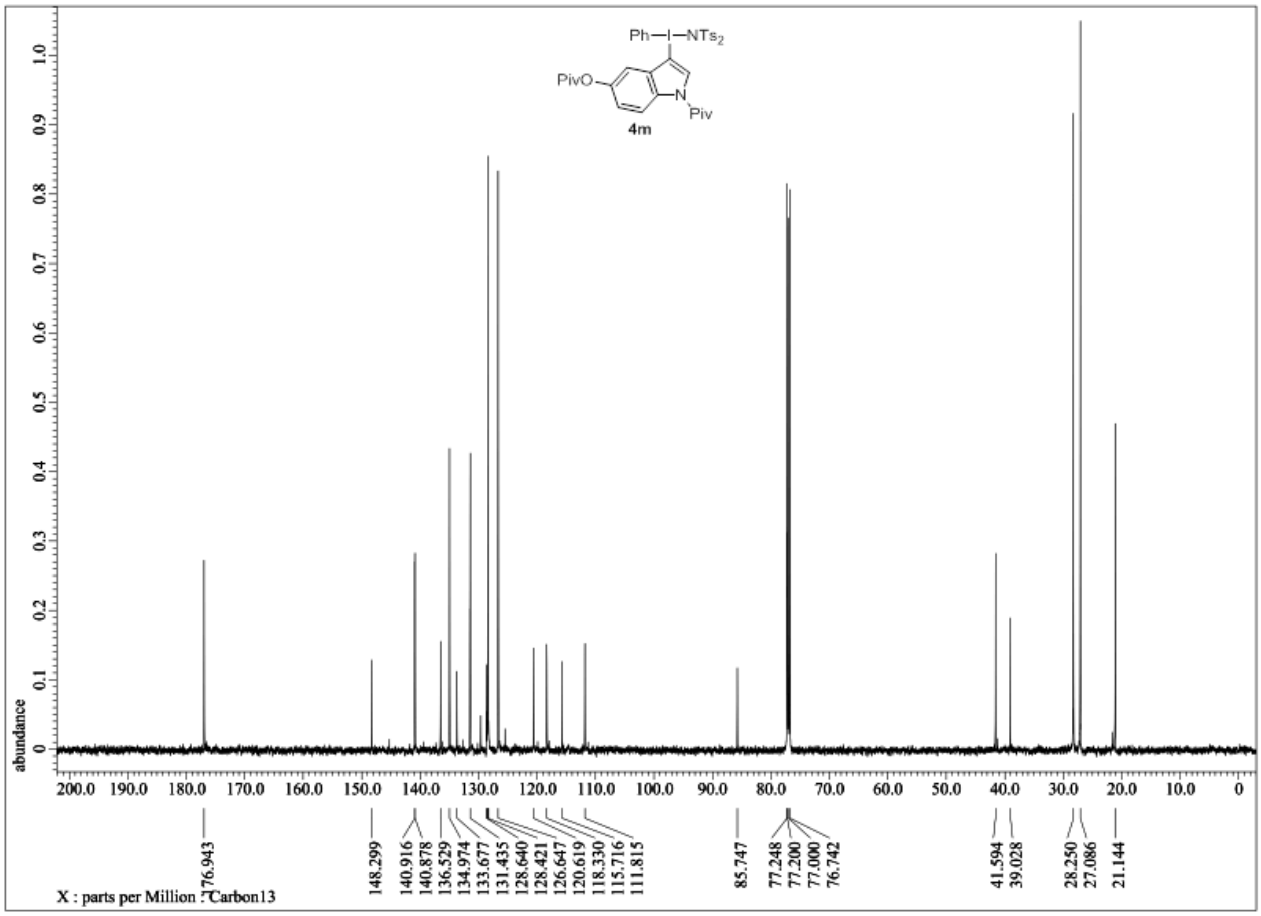

Ph—I—NTs2
Cl
N
Piv
4k
abundance
X : parts per Million : Proton
1.00
0.96
2.02
1.01
4.21
2.02
2.28
4.33
6.09
8.94
8.905
8.376
8.356
8.076
8.060
7.462
7.410
7.394
7.365
7.349
7.345
7.298
7.283
7.267
7.263
6.889
6.873
2.211
1.421
0.000

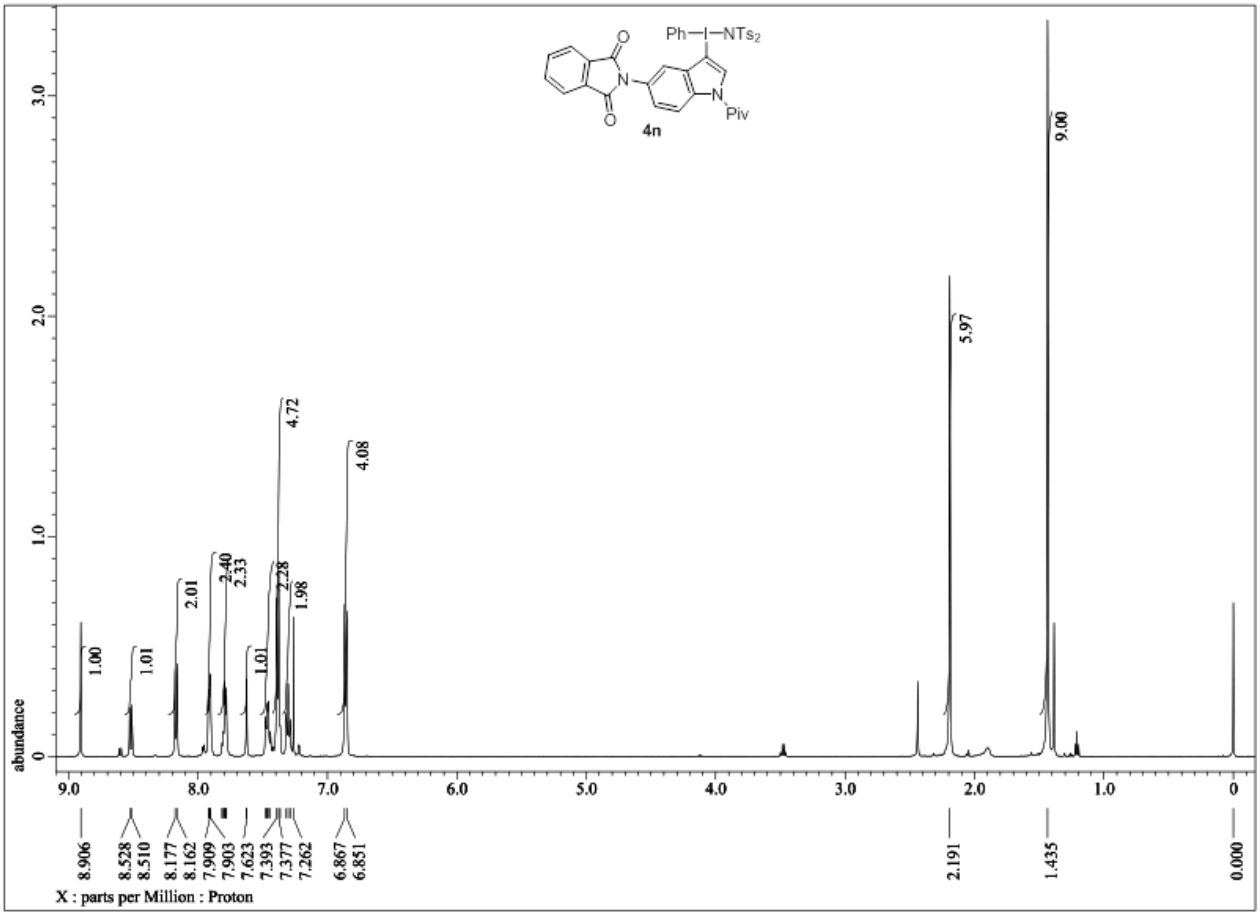

Ph—I—NTs2
Cl
N
Piv
4k
abundance
X : parts per Million : Carbon13
77.009
141.078
140.964
136.681
135.107
134.621
131.607
131.540
130.748
129.156
128.469
126.876
126.685
118.883
118.816
115.764
85.441
77.258
77.000
76.742
41.708
28.288
21.220

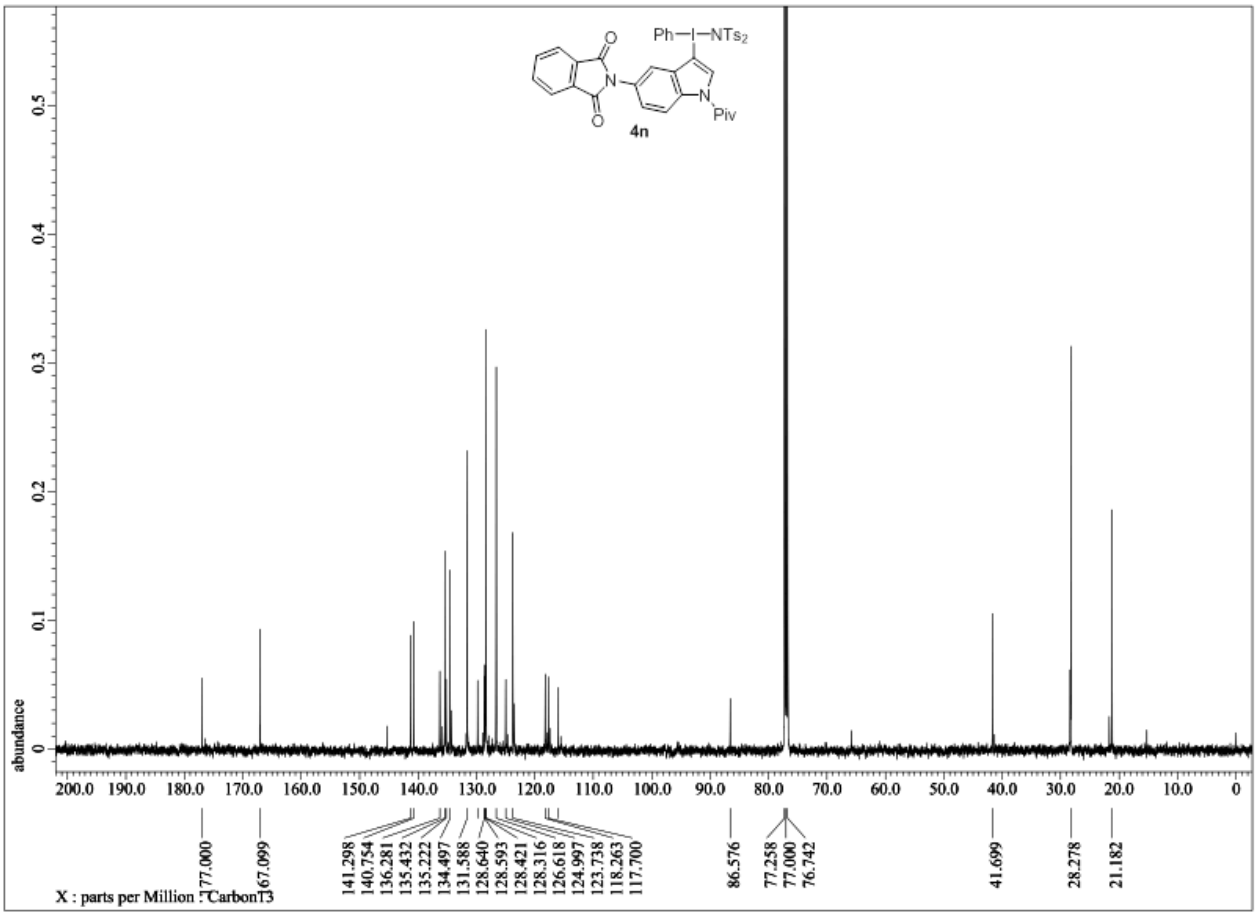

Ph—I—NTs2
Br
N
Piv
4l
abundance
X : parts per Million : Proton
1.00
1.00
2.01
2.97
4.34
2.80
4.62
6.43
8.61
8.894
8.309
8.291
8.067
8.051
7.419
7.402
7.281
7.261
6.879
6.863
2.216
1.426
0.000

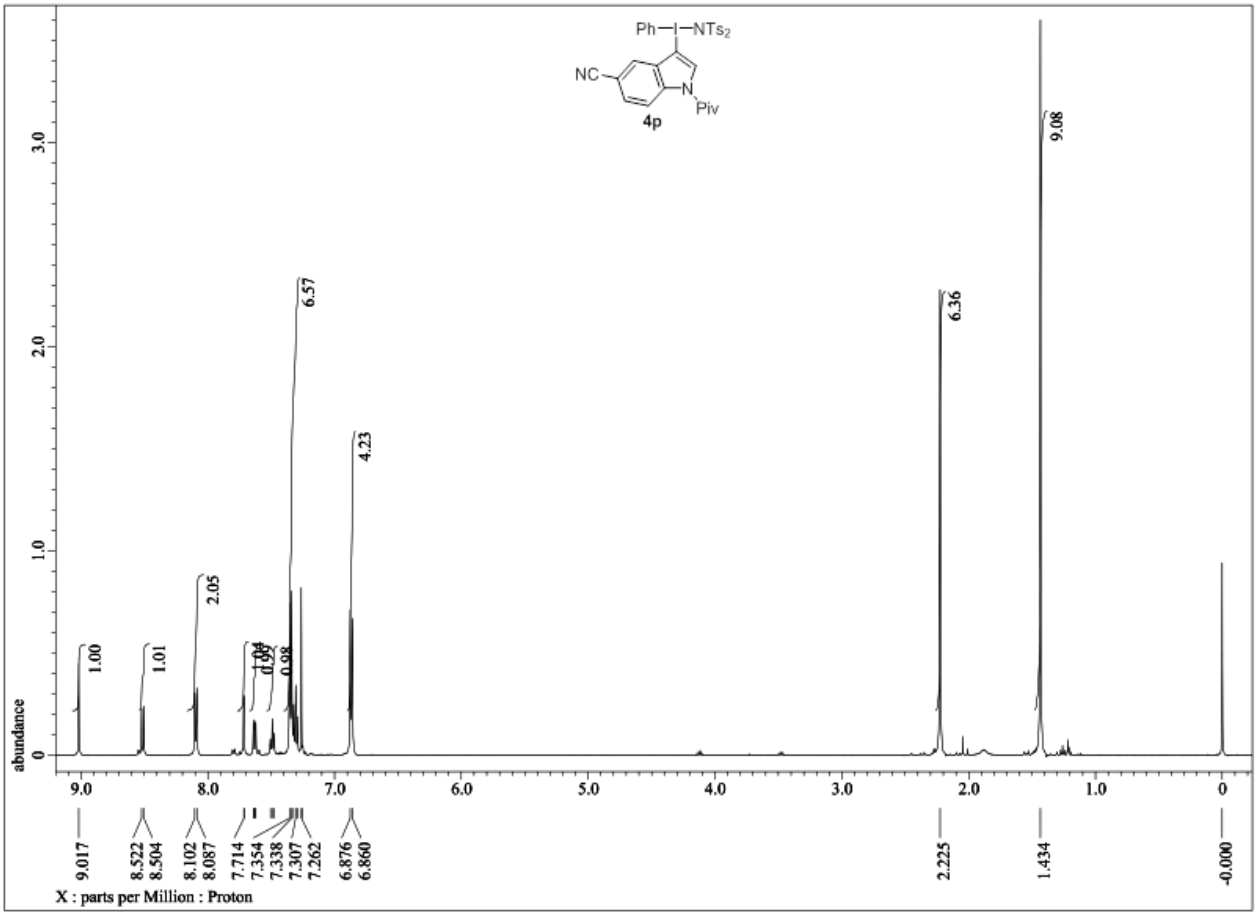

Ph—I—NTs2
Br
N
Piv
4l
abundance
X : parts per Million : Carbon13
77.047
140.926
140.869
136.605
135.060
131.664
131.597
129.632
129.547
128.469
126.714
121.935
119.112
118.396
115.678
85.117
77.258
77.000
76.742
41.765
28.307
21.248

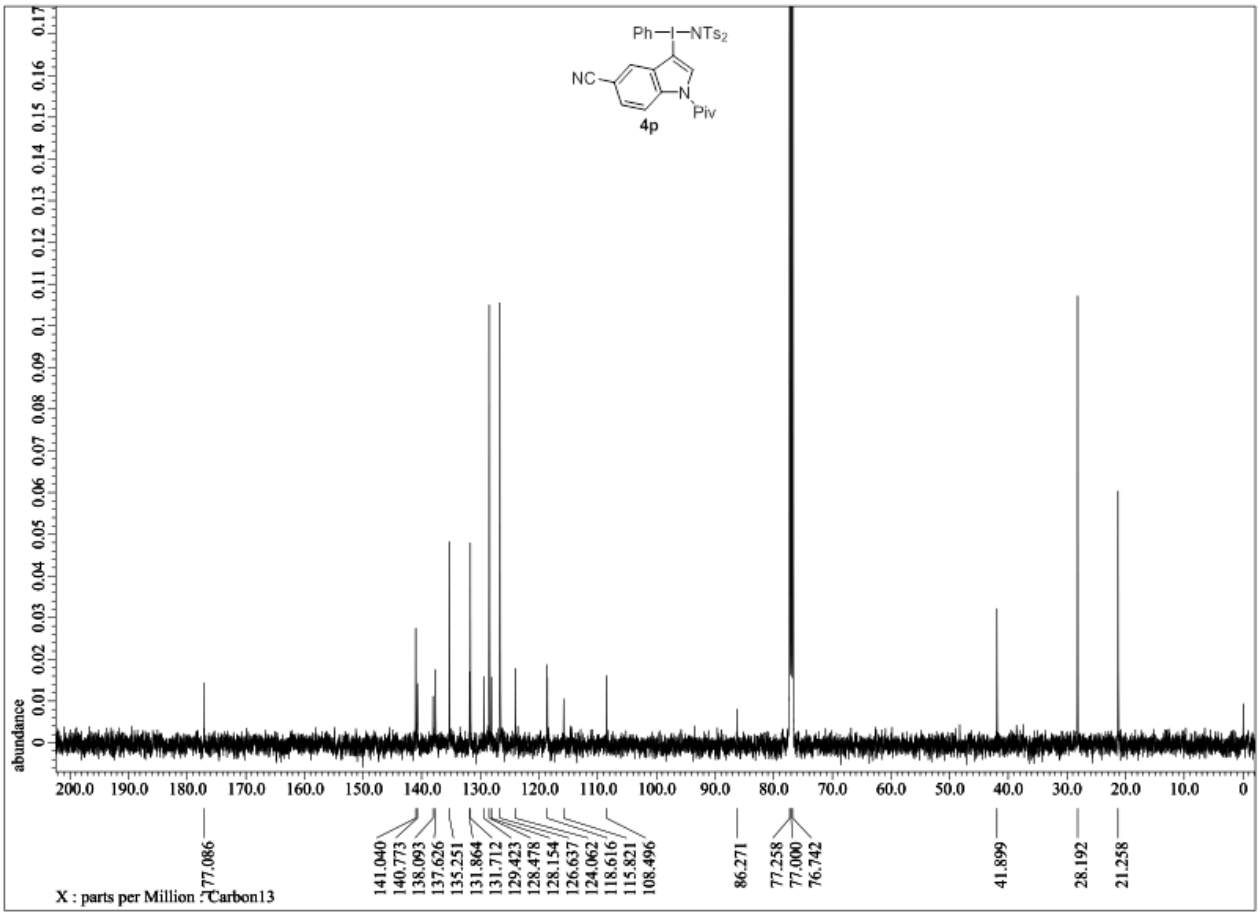

Ph—I—NTs2
PivO
N
Piv
4m
abundance
X : parts per Million : Proton
8.838
8.464
8.446
8.096
8.094
8.079
7.488
7.451
7.434
7.335
7.319
7.303
7.260
7.169
7.165
7.128
6.916
6.900
2.221
1.453
1.382
0.000

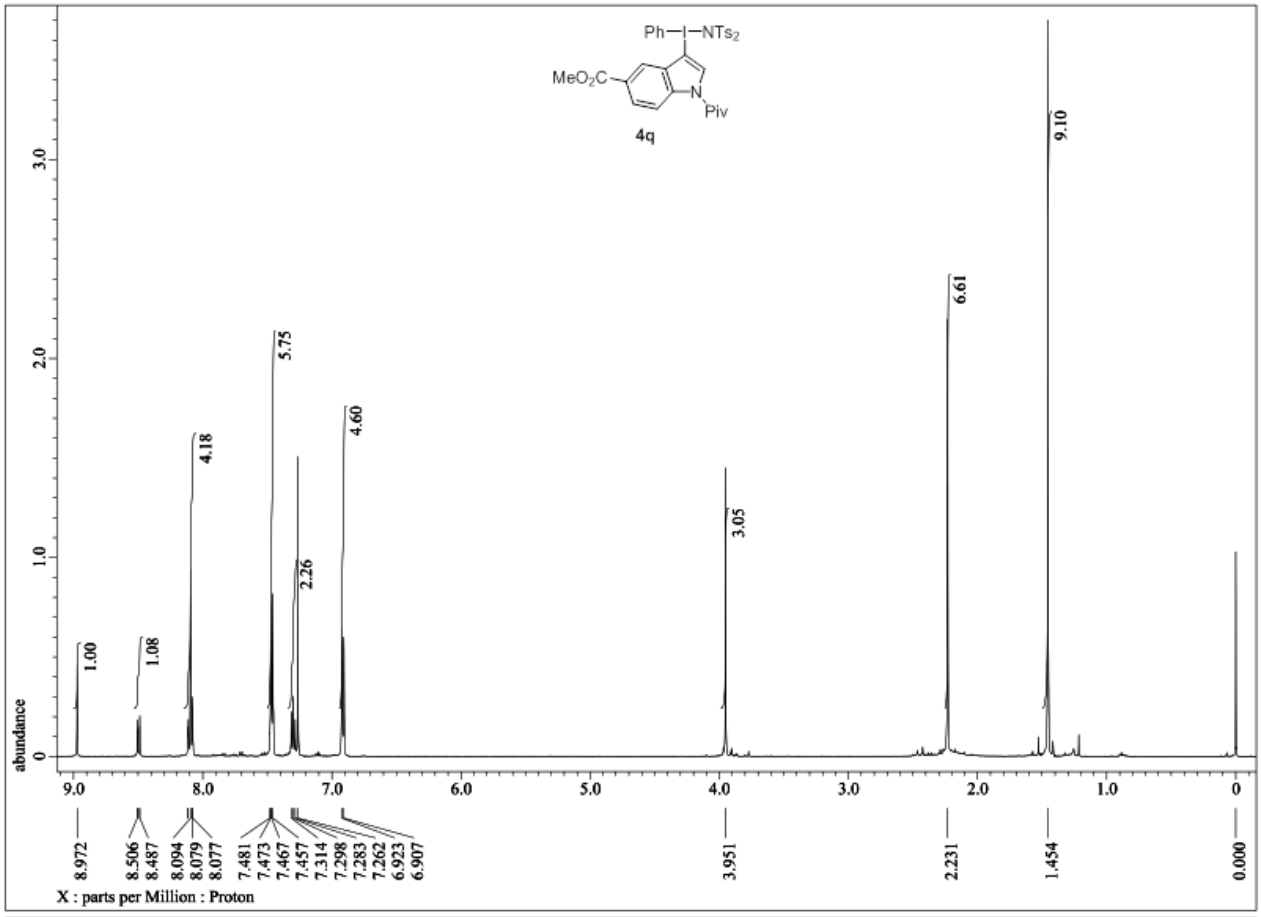

Ph—I—NTs2
PivO
N
Piv
4m
abundance
X : parts per Million : Carbon13
76.943
148.299
140.916
140.878
136.529
134.974
133.677
131.435
128.640
128.421
126.647
120.619
118.330
115.716
111.815
85.747
77.248
77.200
77.000
76.742
41.594
39.028
28.250
27.086
21.144

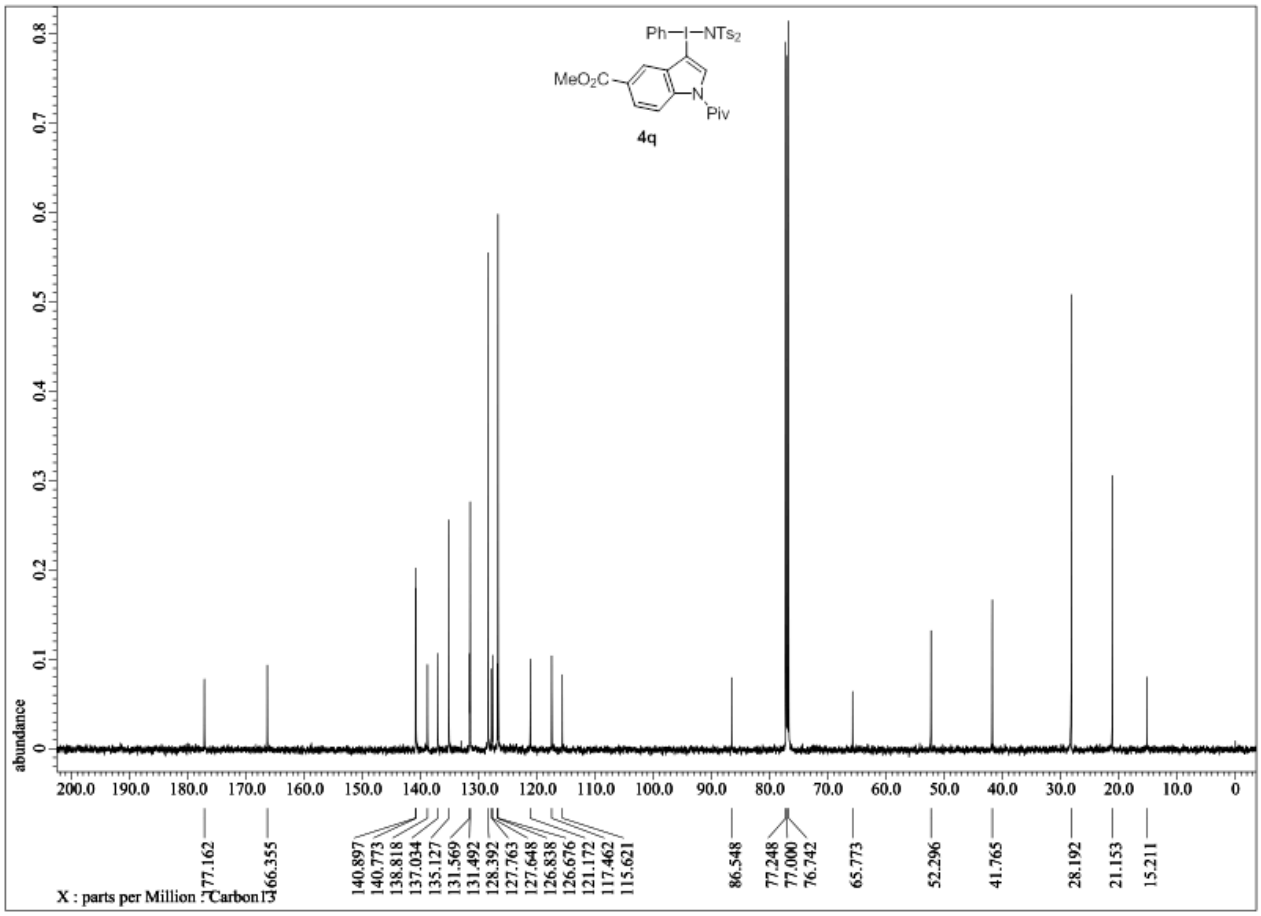

Ph—I—NTs2
Piv
4n
abundance
X : parts per Million : Proton
1.00
1.01
2.01
2.40
2.33
1.01
2.28
1.98
4.72
4.08
5.97
9.00
8.906
8.528
8.510
8.177
8.162
7.909
7.903
7.623
7.393
7.377
7.262
6.867
6.851
2.191
1.435
0.000

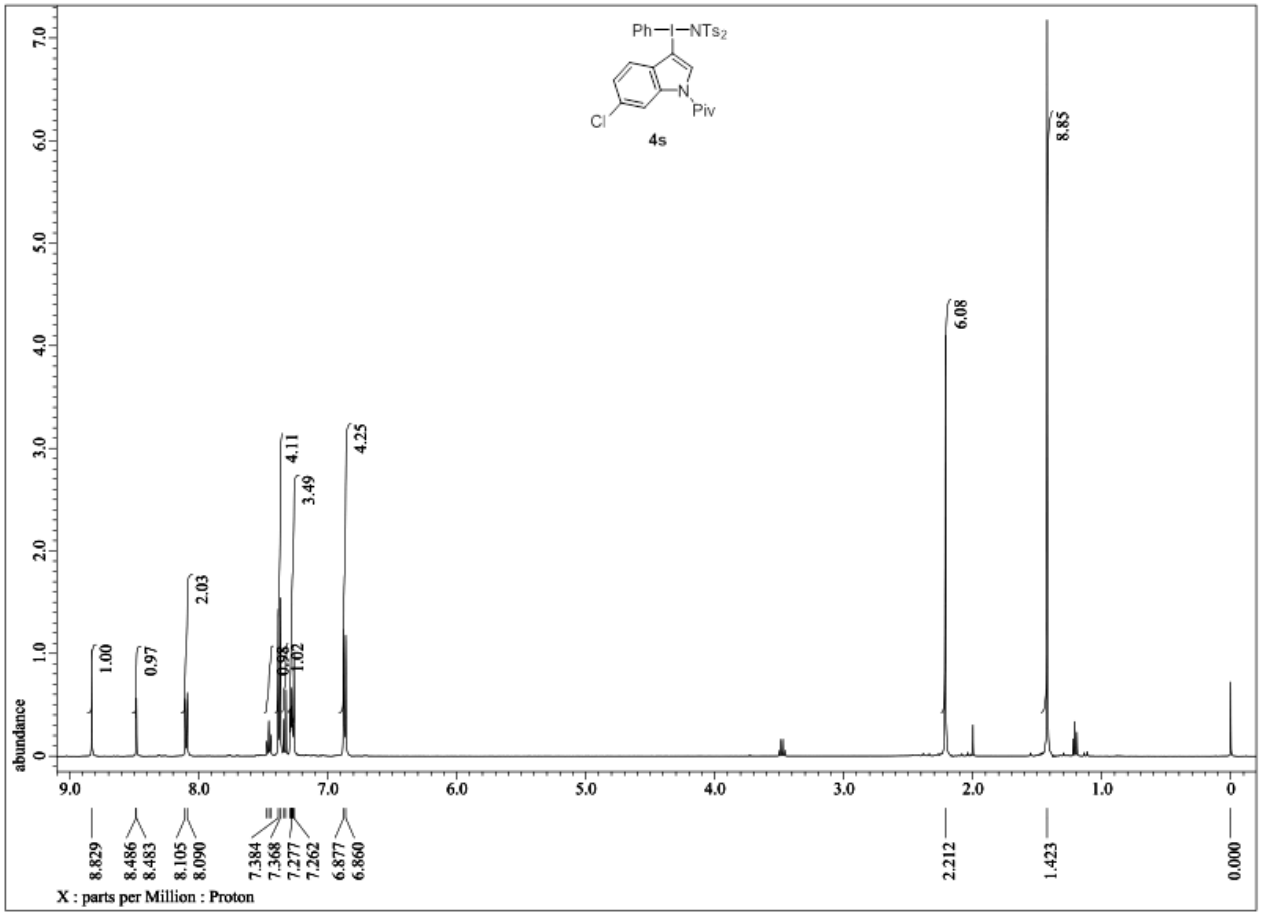

Ph—I—NTs2
Piv
4n
abundance
X : parts per Million : CarbonT3
77.000
67.099
141.298
140.754
136.281
135.432
135.222
134.497
131.588
128.640
128.593
128.421
128.316
126.618
124.997
123.738
118.263
117.700
86.576
77.258
77.000
76.742
41.699
28.278
21.182

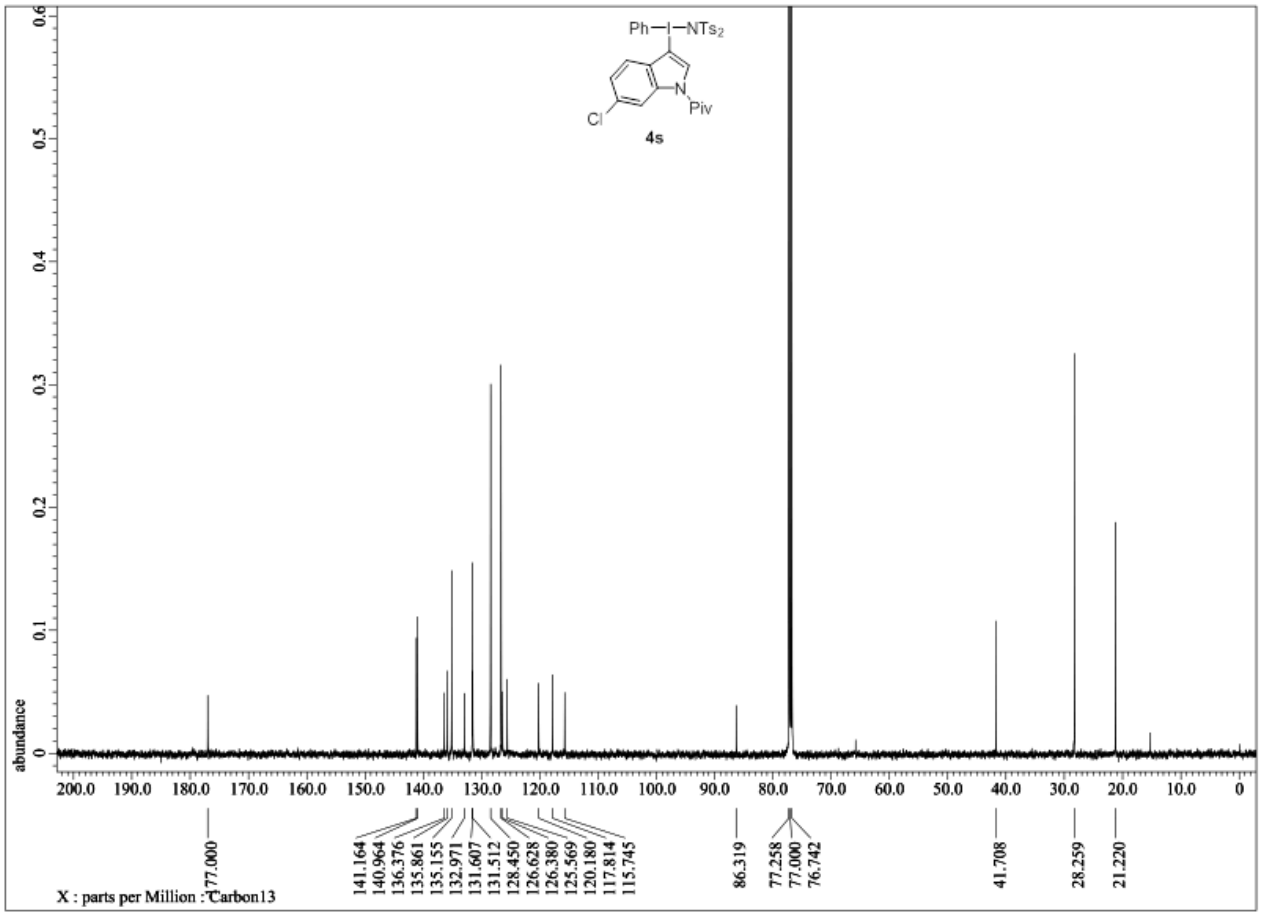

Ph—I—NTs2
NC
N
Piv
4p
abundance
9.08
6.57
6.36
4.23
2.05
1.00
1.01
9.017
8.522
8.504
8.102
8.087
7.714
7.354
7.338
7.307
7.262
6.876
6.860
2.225
1.434
-0.000
X : parts per Million : Proton

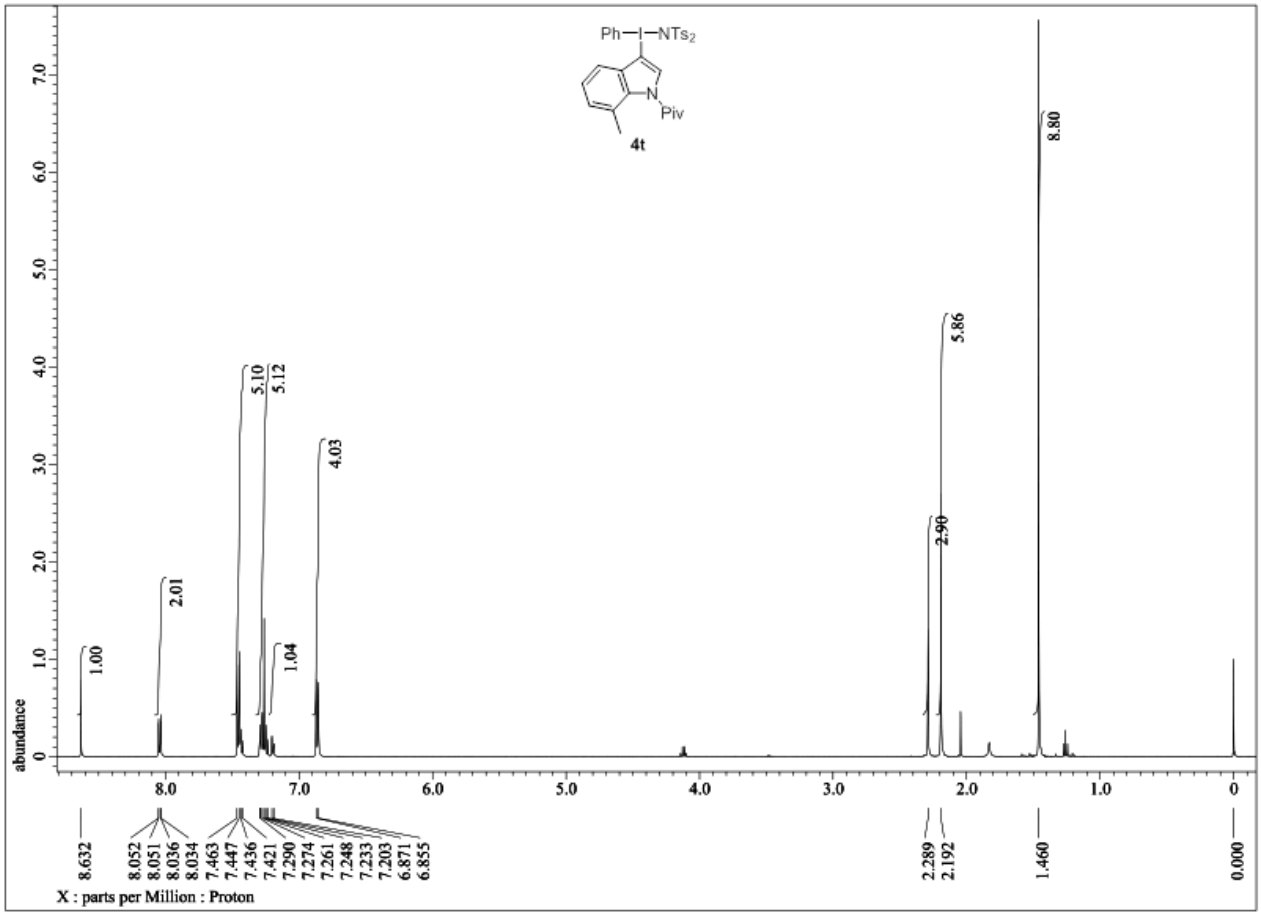

Ph—I—NTs2
NC
N
Piv
4p
abundance
77.086
141.040
140.773
138.093
137.626
135.251
131.864
131.712
129.423
128.478
128.154
126.637
124.062
118.616
115.821
108.496
86.271
77.258
77.000
76.742
41.899
28.192
21.258
X : parts per Million : Carbon13

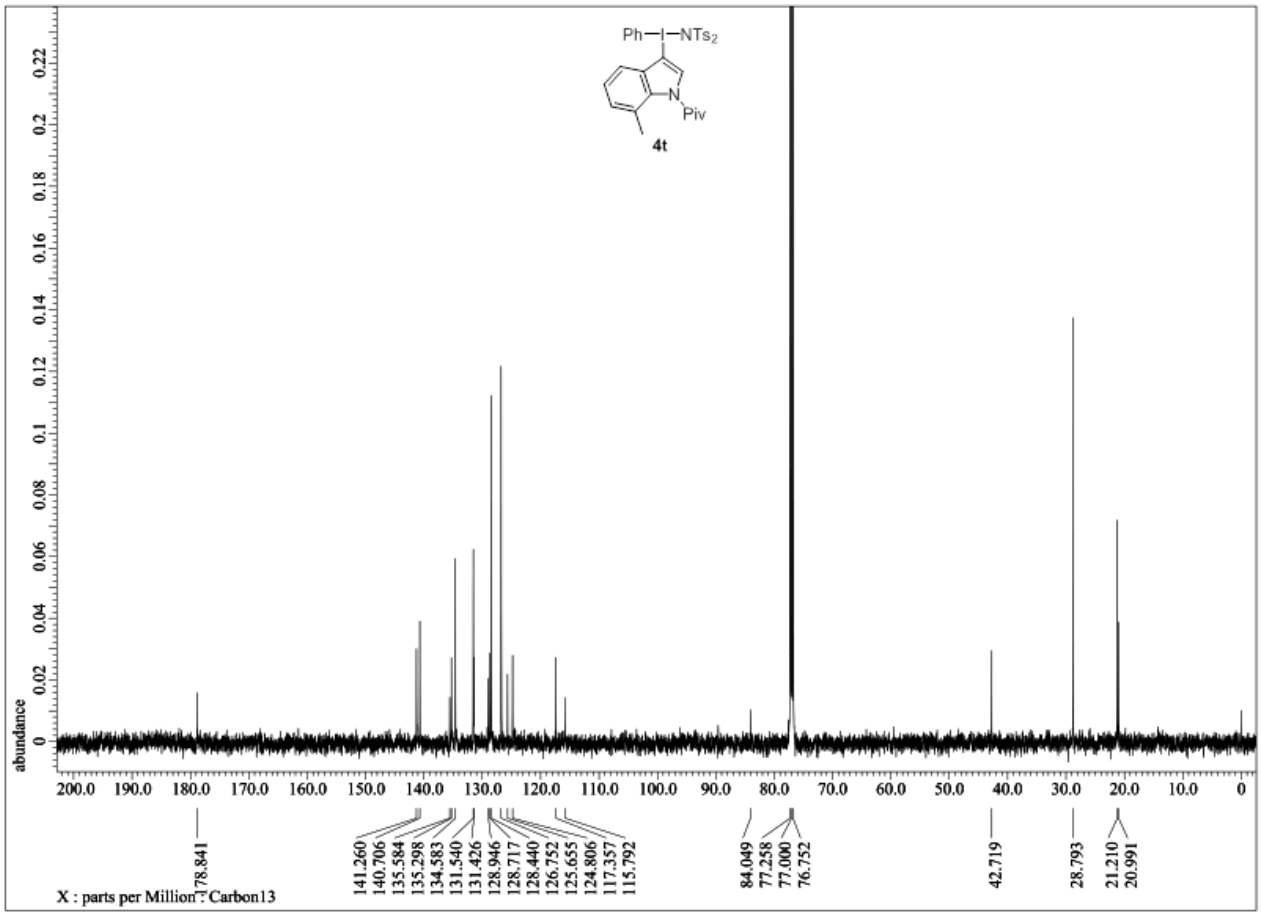

Ph—I—NTs2
MeO2C
N
Piv
4q
abundance
1.00
1.08
4.18
5.75
2.26
4.60
3.05
6.61
9.10
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.972
8.506
8.487
8.094
8.079
8.077
7.481
7.473
7.467
7.457
7.314
7.298
7.283
7.262
6.923
6.907
3.951
2.231
1.454
0.000
X : parts per Million : Proton

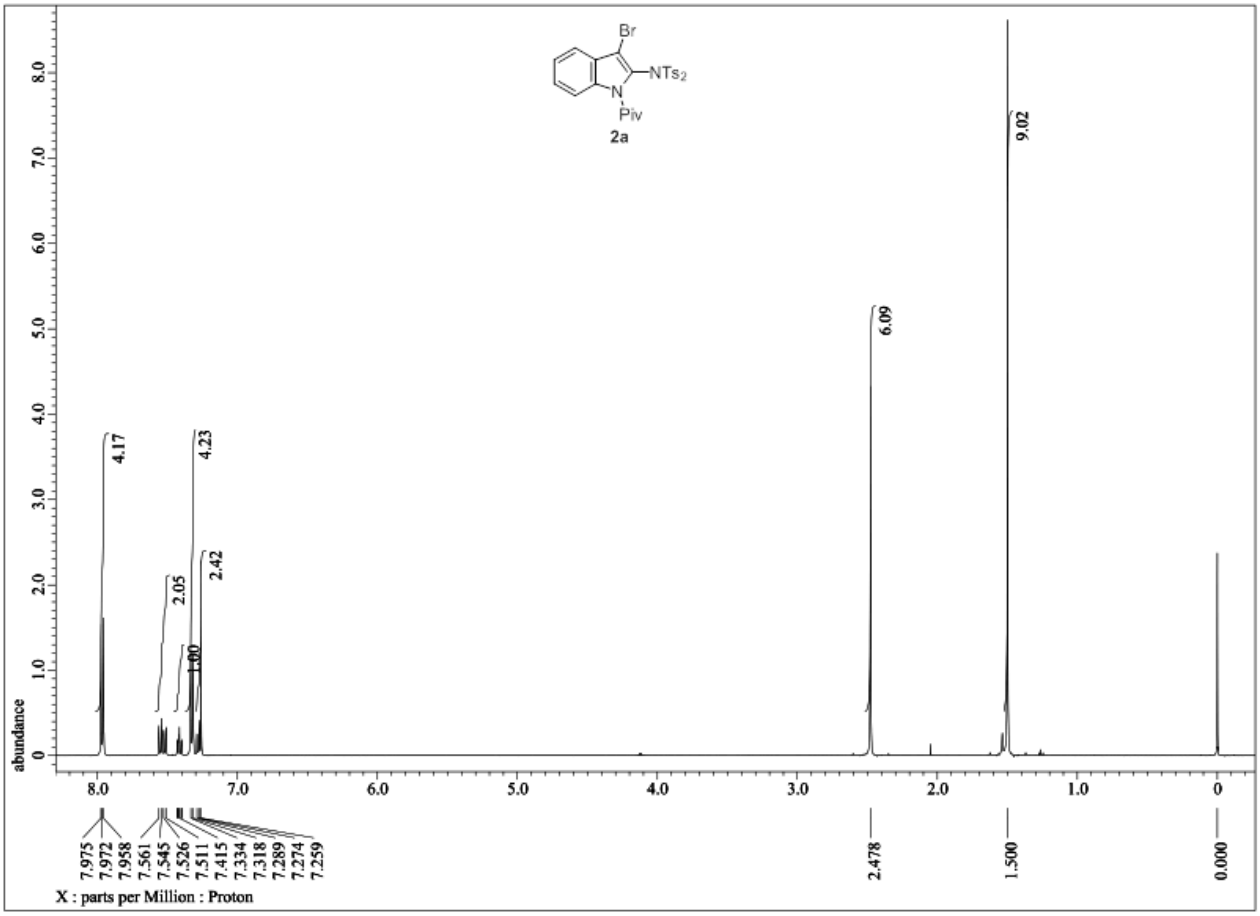

Ph—I—NTs2
MeO2C
N
Piv
4q
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
77.162
166.355
140.897
140.773
138.818
137.034
135.127
131.569
131.492
128.392
127.763
127.648
126.838
126.676
121.172
117.462
115.621
86.548
77.248
77.000
76.742
65.773
52.296
41.765
28.192
21.153
15.211
X : parts per Million : Carbon13

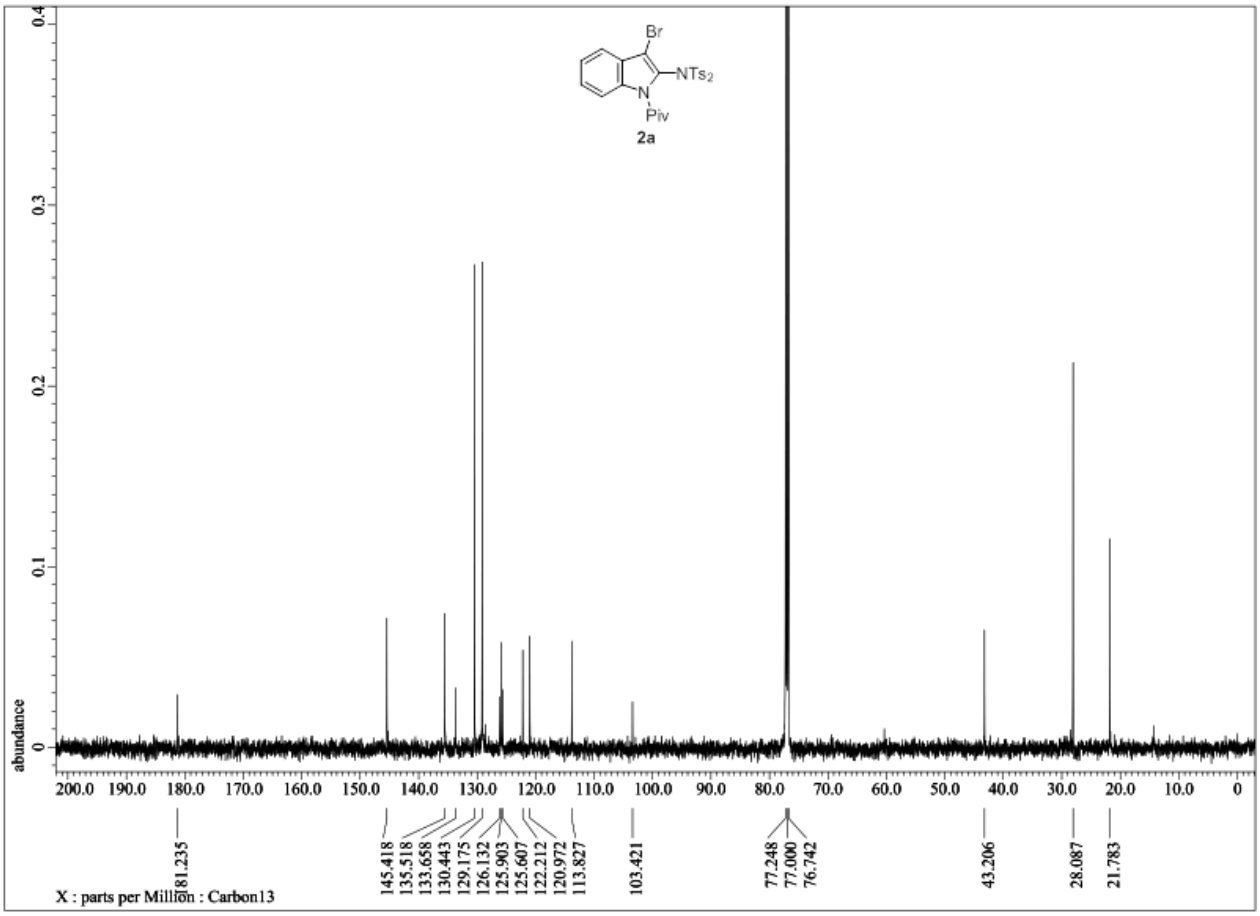

Ph—I—NTs2
Cl
N
Piv
4s
abundance
X : parts per Million : Proton
1.00
0.97
2.03
0.98
1.02
4.11
3.49
4.25
6.08
8.85
8.829
8.486
8.483
8.105
8.090
7.384
7.368
7.277
7.262
6.877
6.860
2.212
1.423
0.000

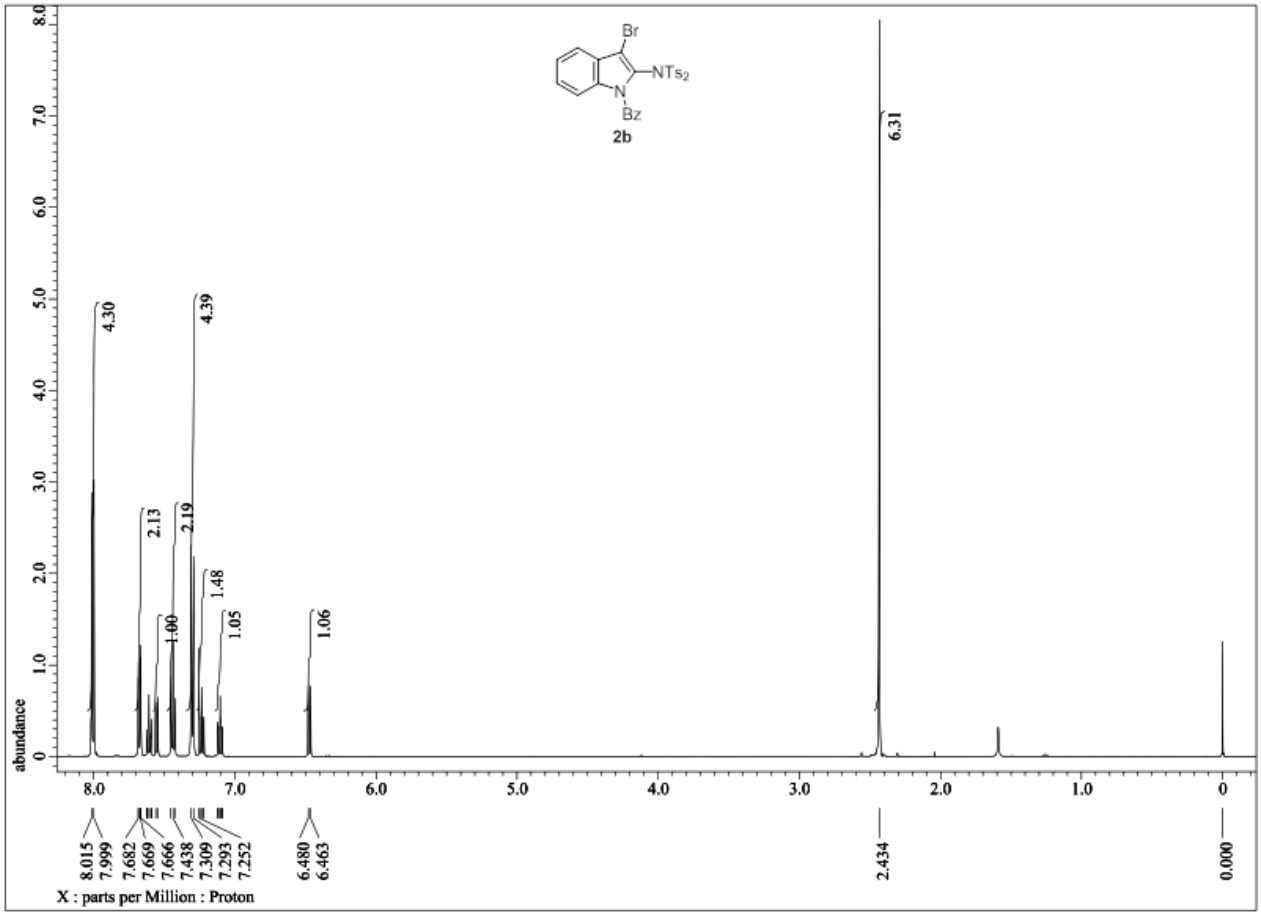

Ph—I—NTs2
Cl
N
Piv
4s
abundance
X : parts per Million : Carbon13
77.000
141.164
140.964
136.376
135.861
135.155
132.971
131.607
131.512
128.450
126.628
126.380
125.569
120.180
117.814
115.745
86.319
77.258
77.000
76.742
41.708
28.259
21.220

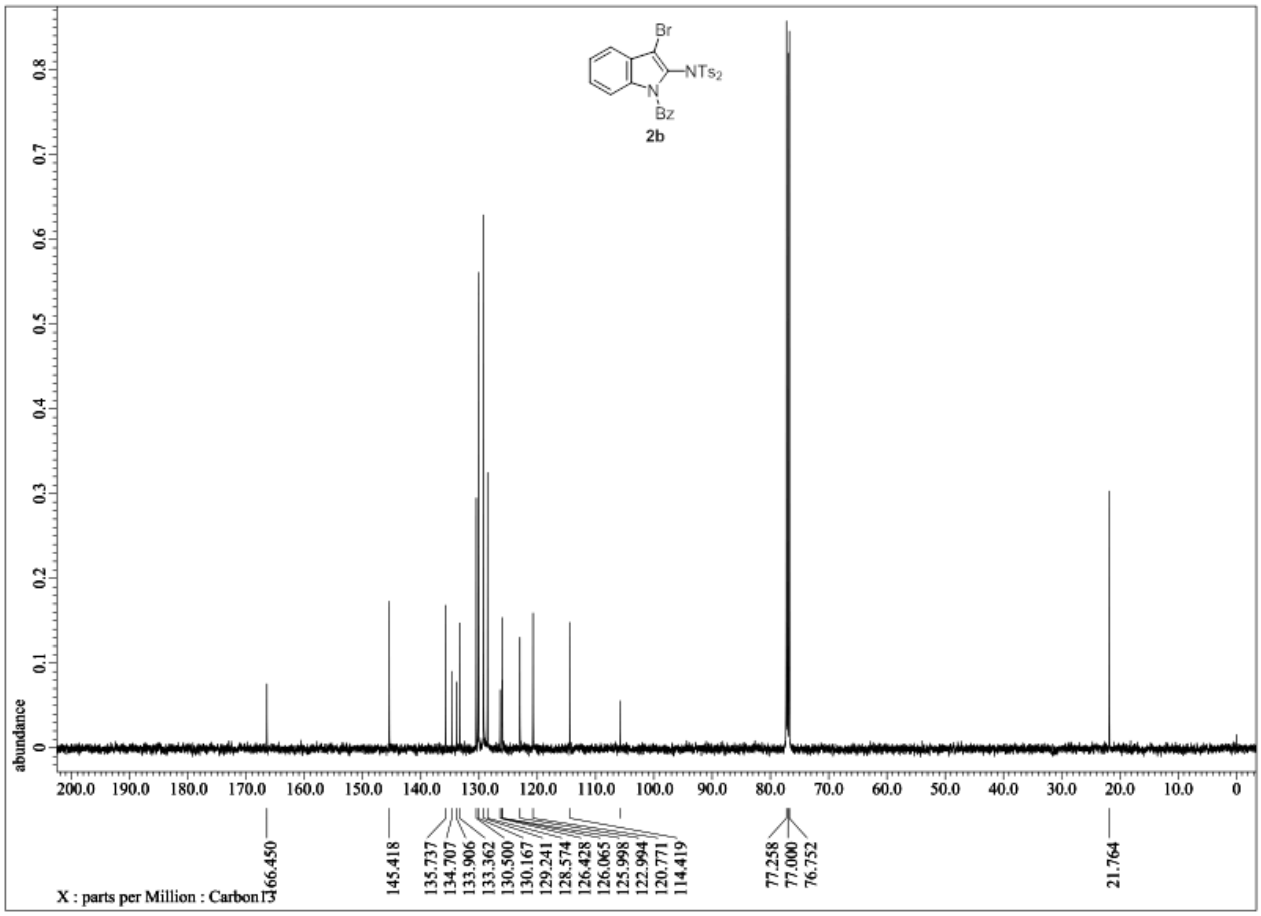

Ph—I—NTs2
N
Piv
4t
abundance
1.00
2.01
1.04
4.03
5.10
5.12
2.90
5.86
8.80
8.632
8.052
8.051
8.036
8.034
7.463
7.447
7.436
7.421
7.290
7.274
7.261
7.248
7.233
7.203
6.871
6.855
2.289
2.192
1.460
0.000
X : parts per Million : Proton

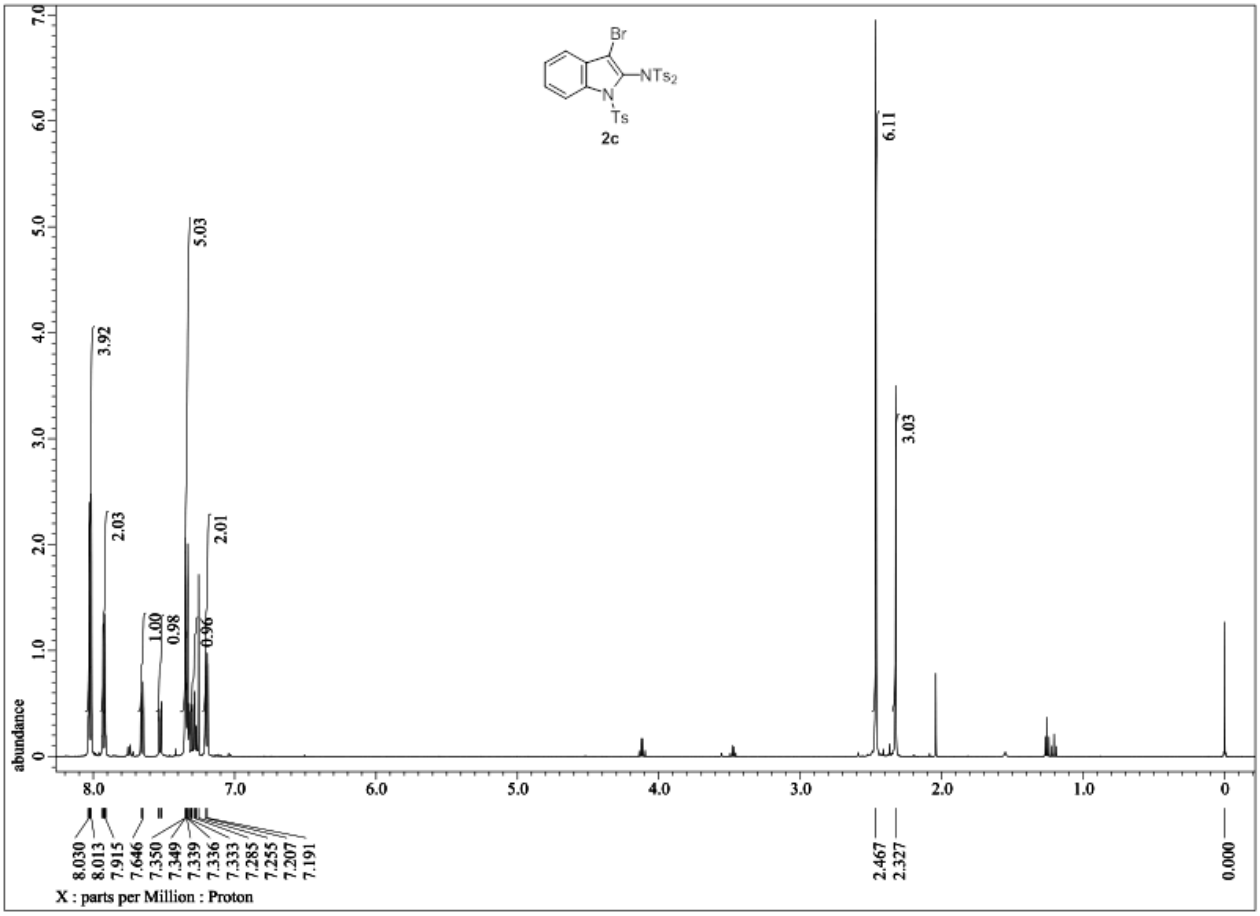

Ph—I—NTs2
N
Piv
4t
abundance
78.841
141.260
140.706
135.584
135.298
134.583
131.540
131.426
128.946
128.717
128.440
126.752
125.655
124.806
117.357
115.792
84.049
77.258
77.000
76.752
42.719
28.793
21.210
20.991
X : parts per Million : Carbon13

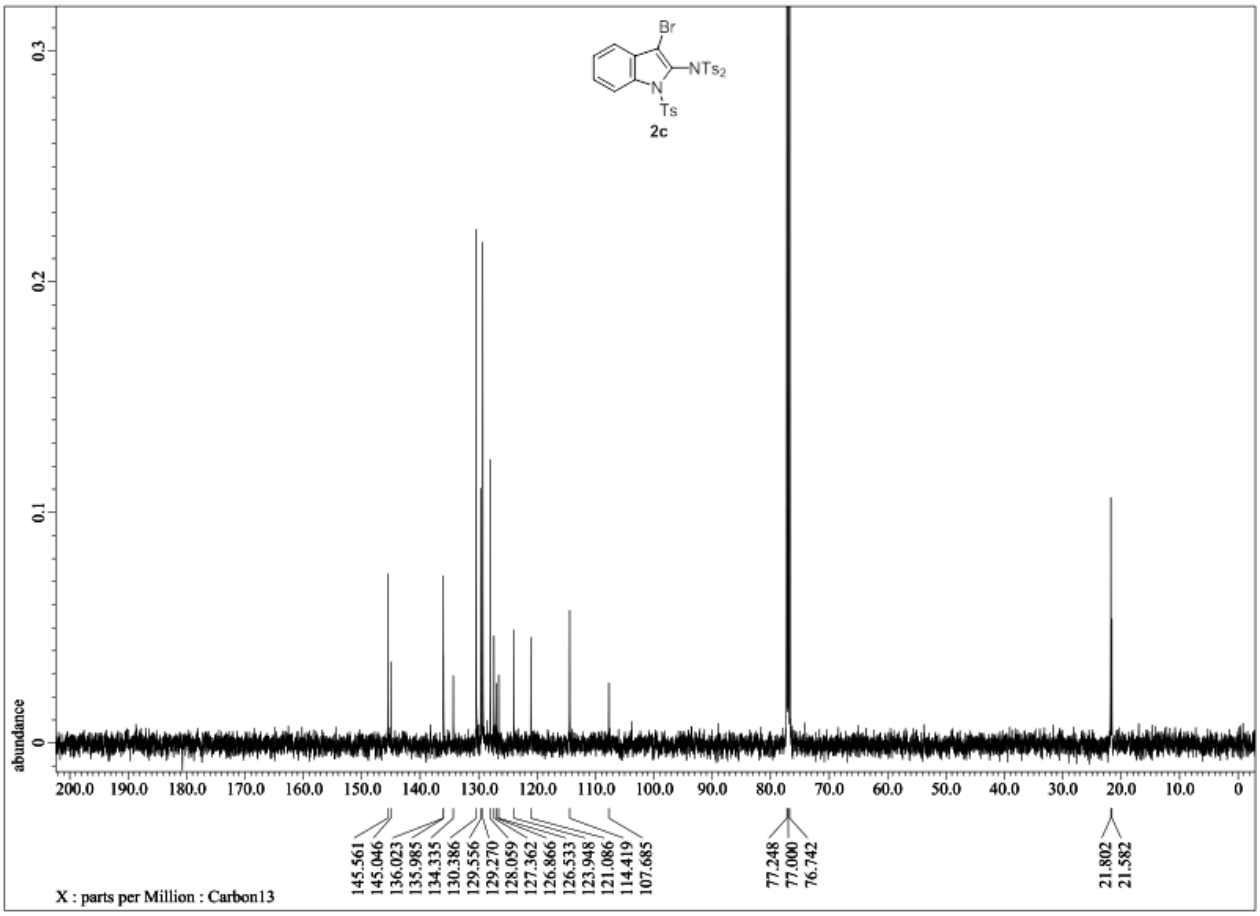

Br
NTs2
N
Piv
2a
9.02
6.09
4.17
4.23
2.42
2.05
1.00
abundance
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.975
7.972
7.958
7.561
7.545
7.526
7.511
7.415
7.334
7.318
7.289
7.274
7.259
2.478
1.500
0.000
X : parts per Million : Proton

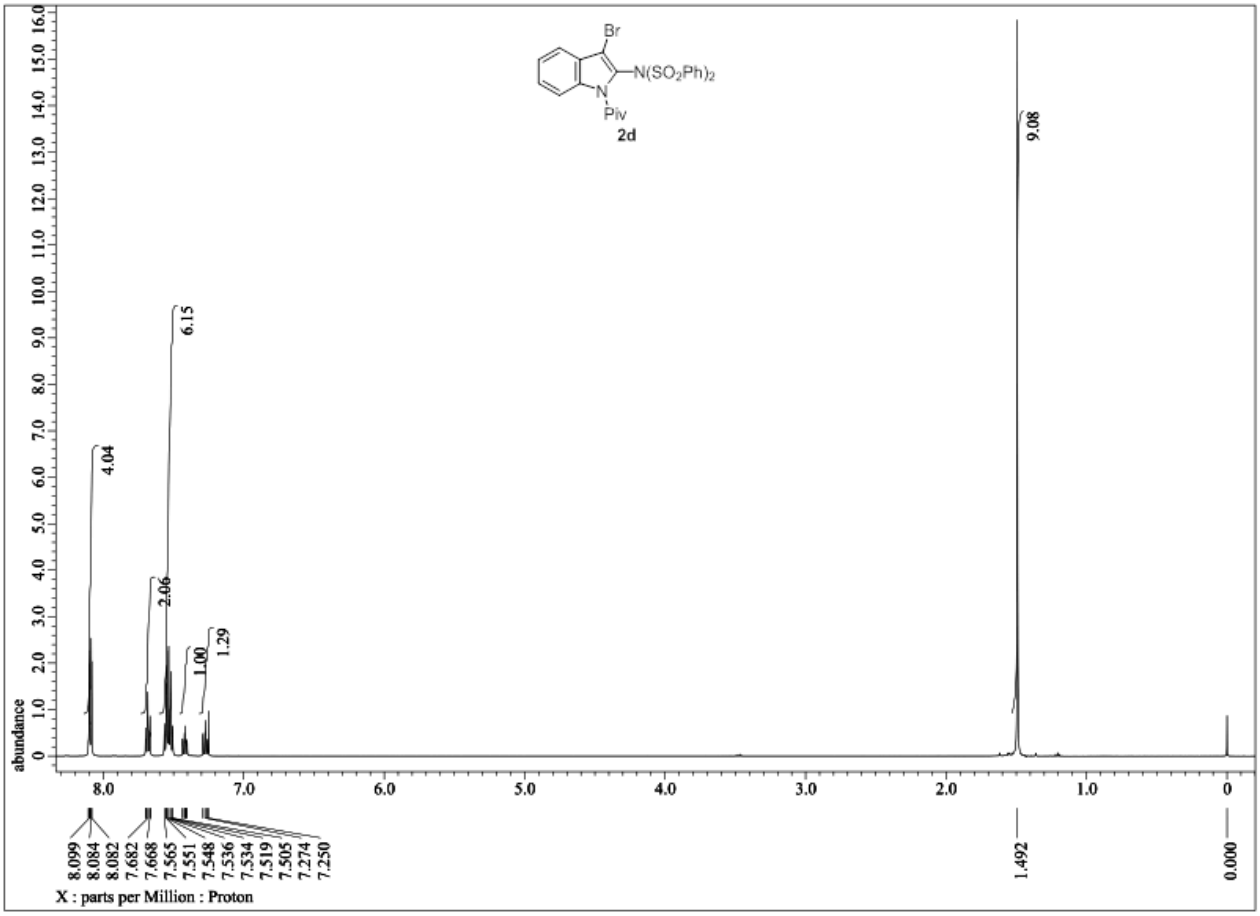

Br
NTs2
N
Piv
2a
abundance
0.4
0.3
0.2
0.1
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
181.235
145.418
135.518
133.658
130.443
129.175
126.132
125.903
125.607
122.212
120.972
113.827
103.421
77.248
77.000
76.742
43.206
28.087
21.783
X : parts per Million : Carbon13

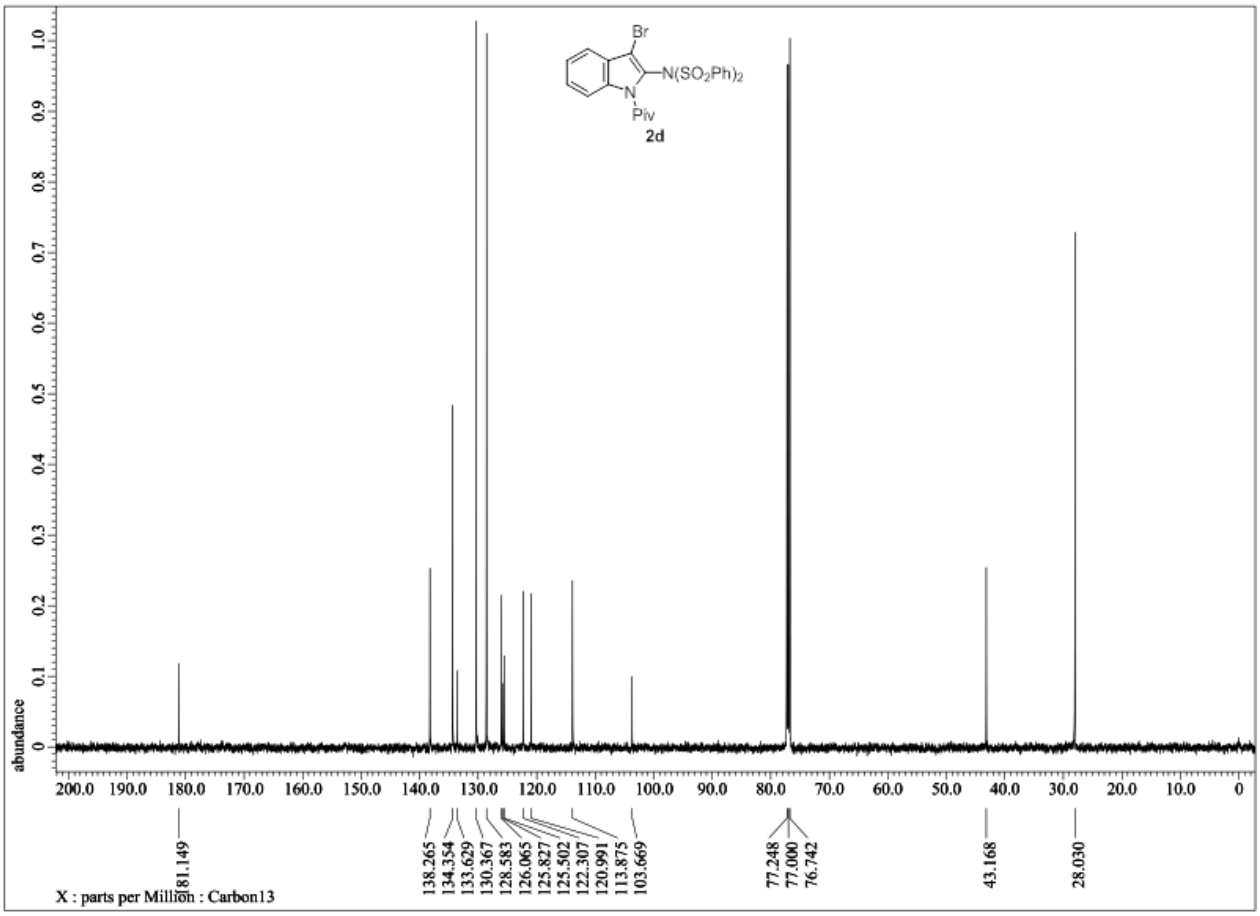

Br
NTs2
N
Bz
2b
6.31
4.30
4.39
2.13
2.19
1.48
1.00
1.05
1.06
abundance
8.015
7.999
7.682
7.669
7.666
7.438
7.309
7.293
7.252
6.480
6.463
2.434
0.000
X : parts per Million : Proton

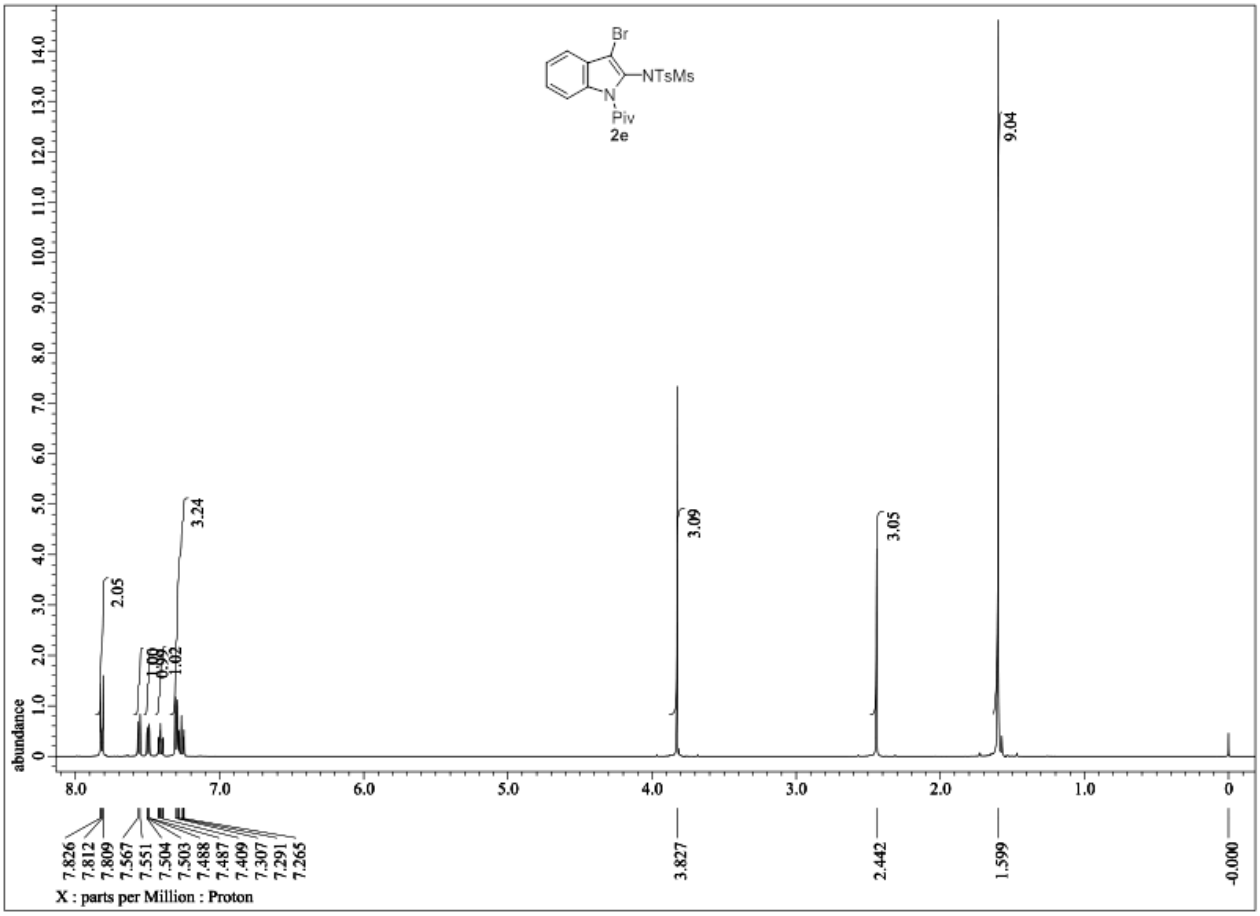

Br
NTs2
N
Bz
2b
abundance
166.450
145.418
135.737
134.707
133.906
133.362
130.500
130.167
129.241
128.574
126.428
126.065
125.998
122.994
120.771
114.419
77.258
77.000
76.752
21.764
X : parts per Million : Carbon13

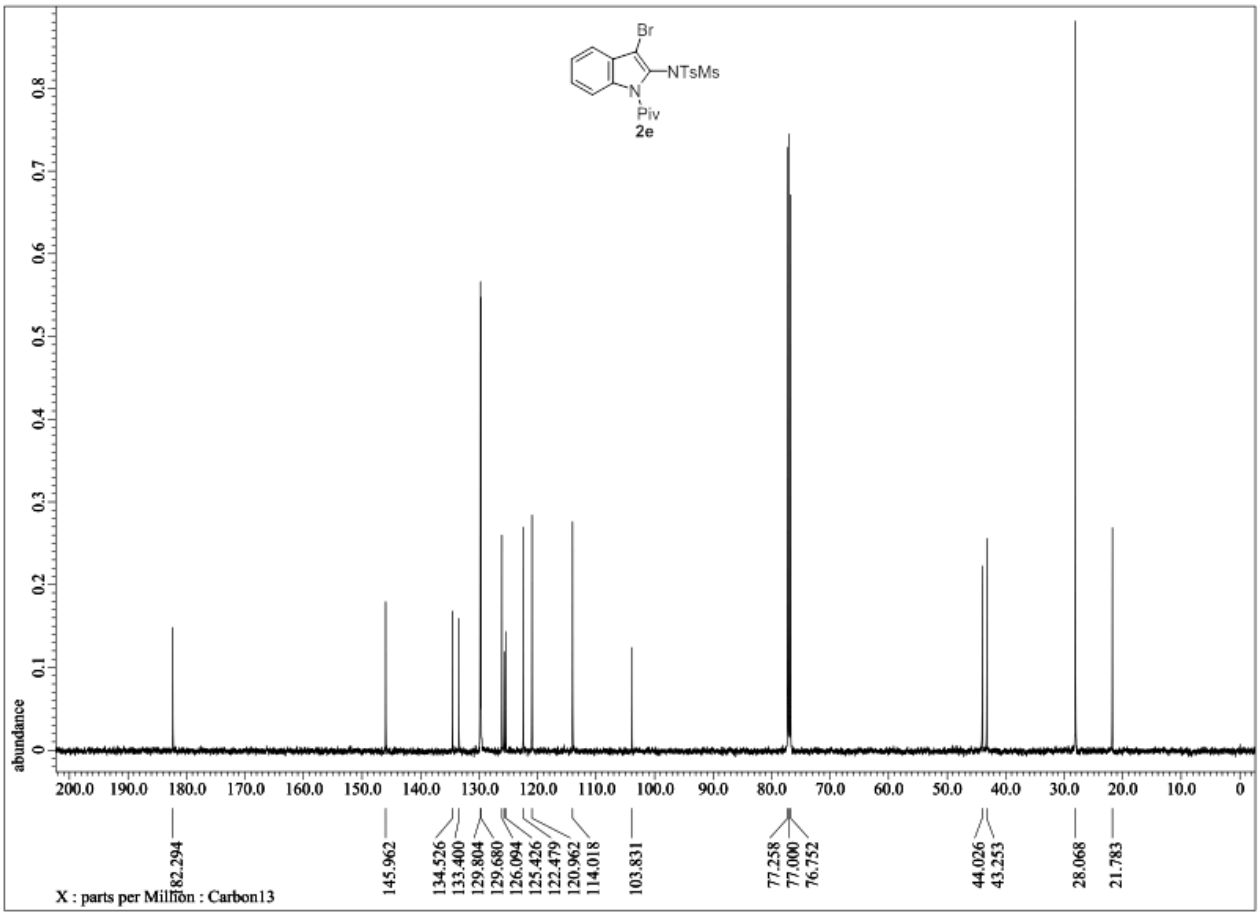

Br
NTs2
N
Ts
2c
6.11
5.03
3.92
3.03
2.03
2.01
1.00
0.98
0.96
abundance
8.030
8.013
7.915
7.646
7.350
7.349
7.339
7.336
7.333
7.285
7.255
7.207
7.191
2.467
2.327
0.000
X : parts per Million : Proton

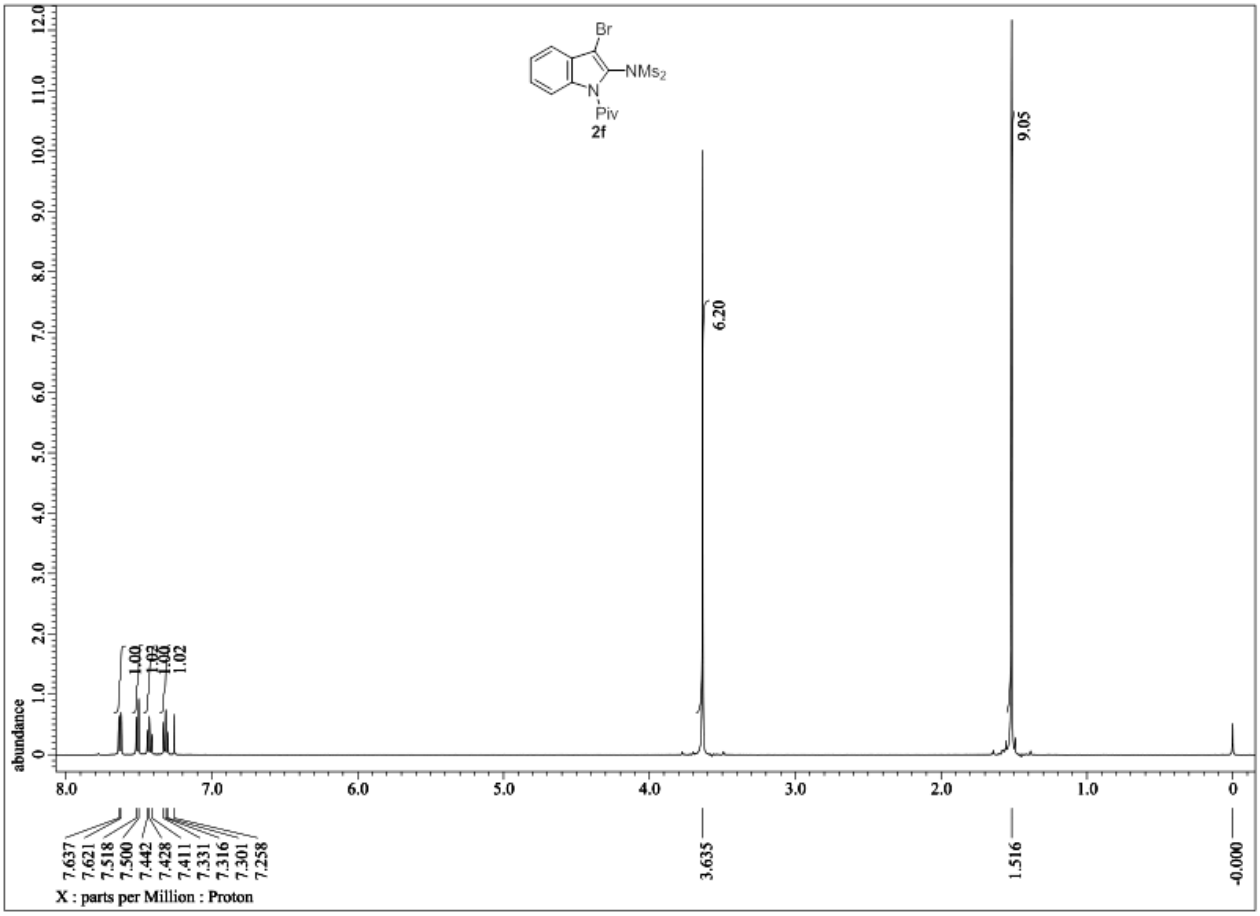

Br
NTs2
N
Ts
2c
abundance
145.561
145.046
136.023
135.985
134.335
130.386
129.556
129.270
128.059
127.362
126.866
126.533
123.948
121.086
114.419
107.685
77.248
77.000
76.742
21.802
21.582
X : parts per Million : Carbon13

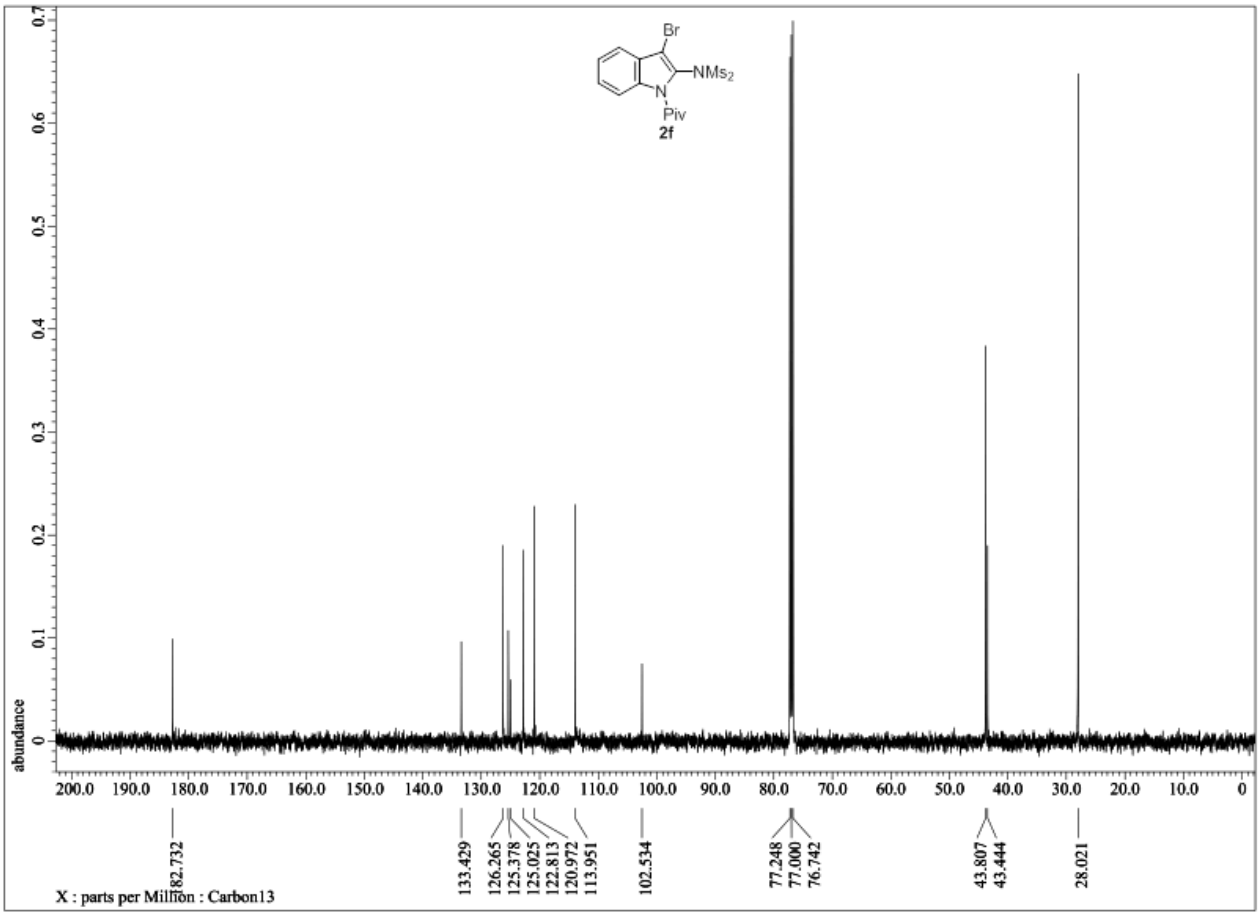

Br
N(SO2Ph)2
N
Piv
2d
9.08
6.15
4.04
2.06
1.29
1.00
abundance
8.099
8.084
8.082
7.682
7.668
7.565
7.551
7.548
7.536
7.534
7.519
7.505
7.274
7.250
1.492
0.000
X : parts per Million : Proton

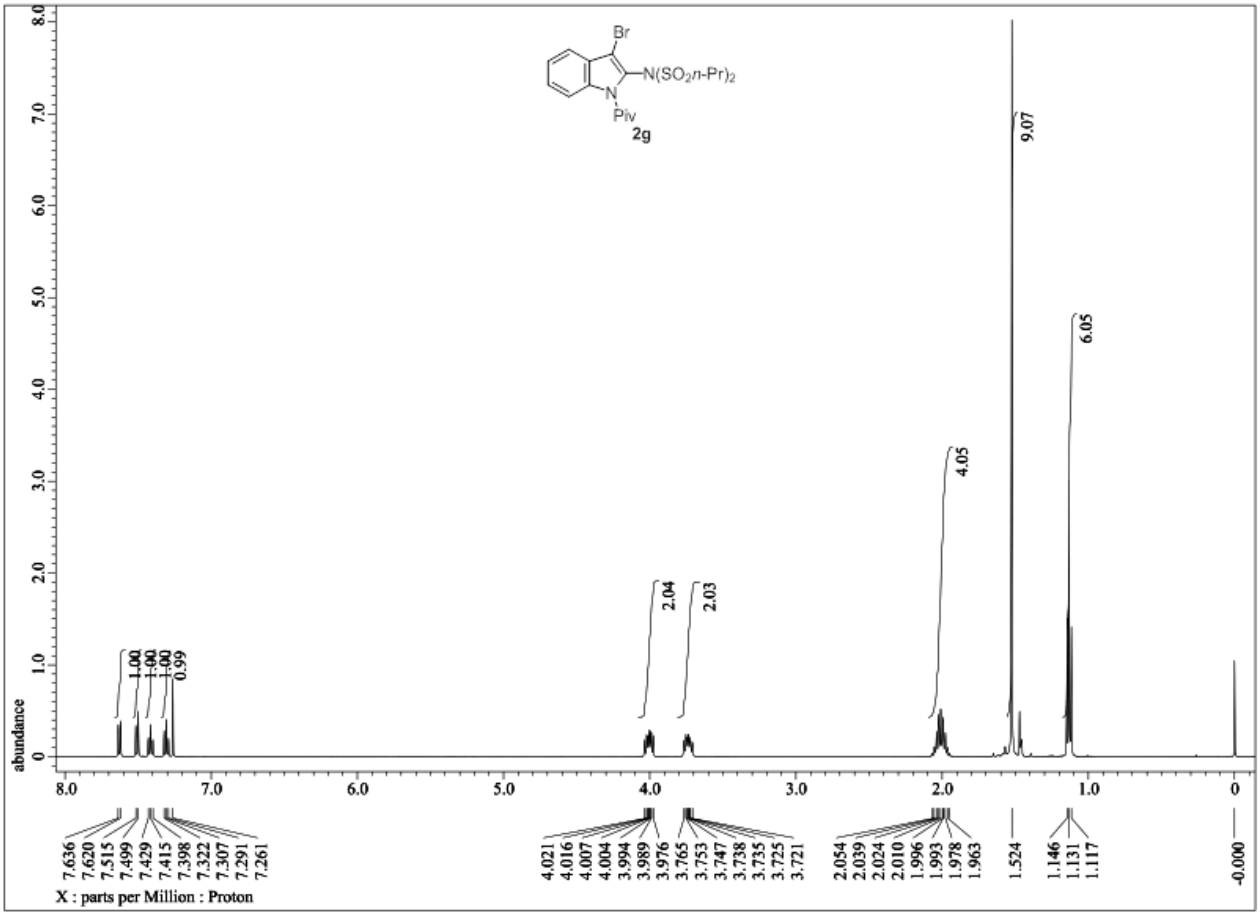

Br
N(SO2Ph)2
N
Piv
2d
abundance
181.149
138.265
134.354
133.629
130.367
128.583
126.065
125.827
125.502
122.307
120.991
113.875
103.669
77.248
77.000
76.742
43.168
28.030
X : parts per Million : Carbon13

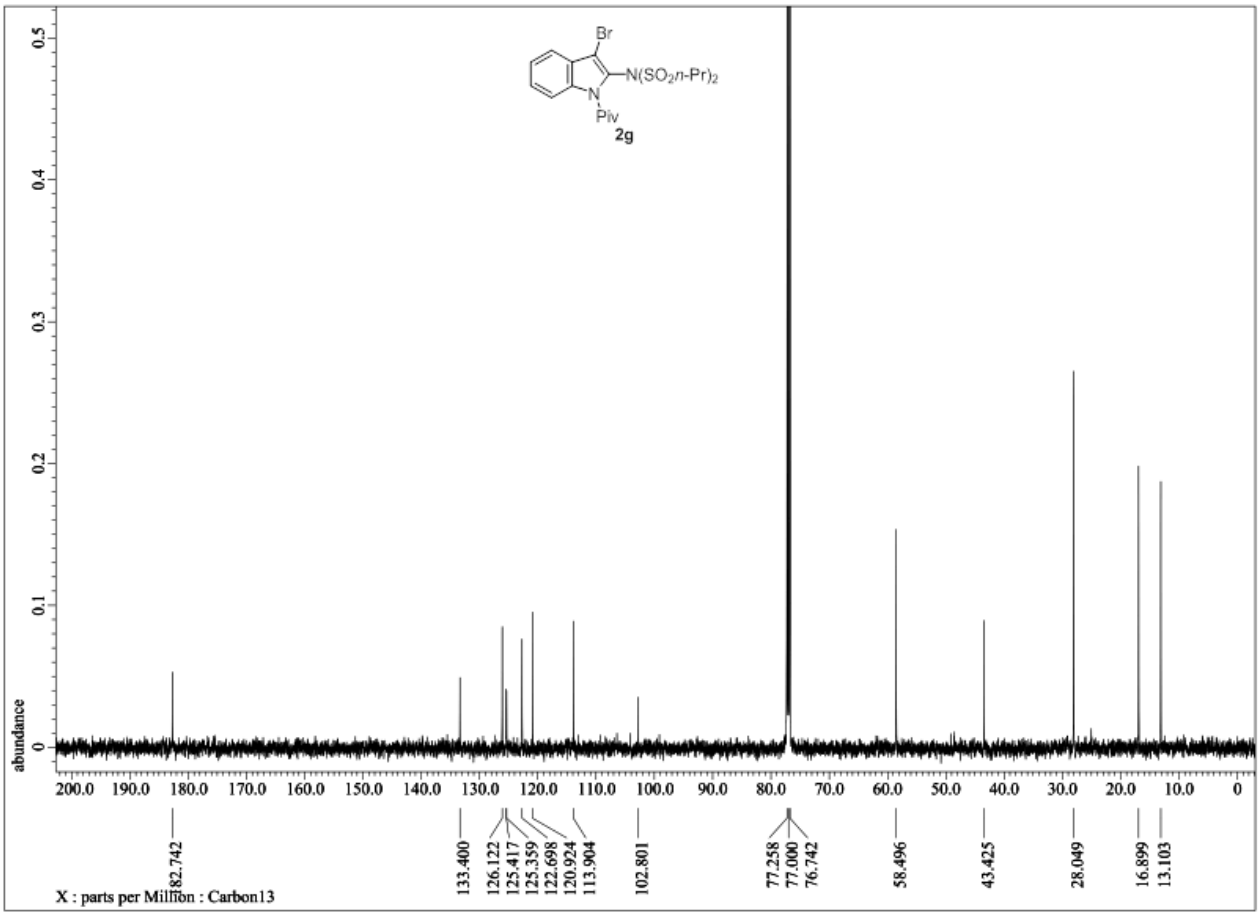

Br
NTsMs
N
Piv
2e
9.04
3.24
3.09
3.05
2.05
1.00
0.99
1.02
abundance
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.826
7.812
7.809
7.567
7.551
7.504
7.503
7.488
7.487
7.409
7.307
7.291
7.265
3.827
2.442
1.599
-0.000
X : parts per Million : Proton

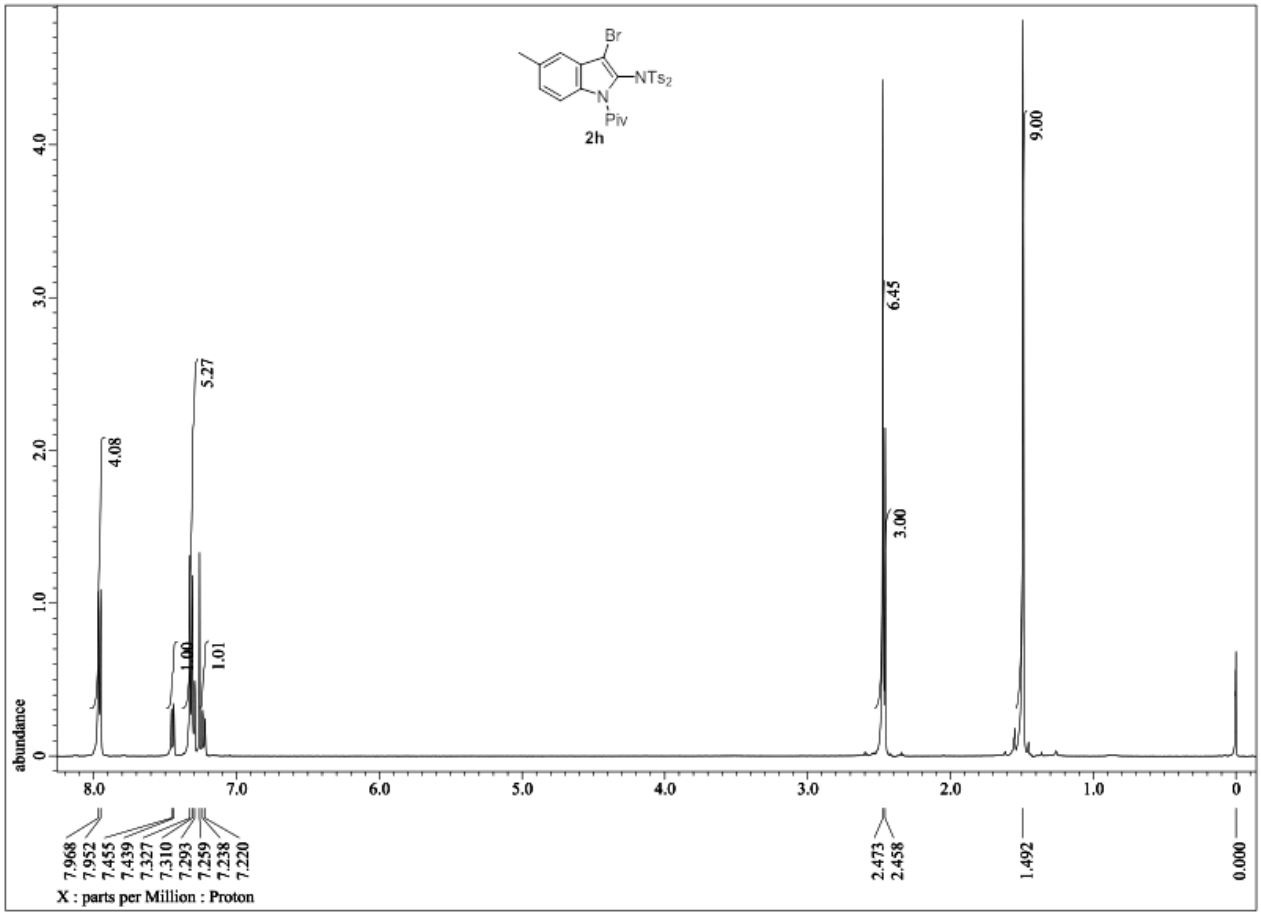

Br
NTsMs
N
Piv
2e
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
182.294
145.962
134.526
133.400
129.804
129.680
126.094
125.426
122.479
120.962
114.018
103.831
77.258
77.000
76.752
44.026
43.253
28.068
21.783
X : parts per Million : Carbon13

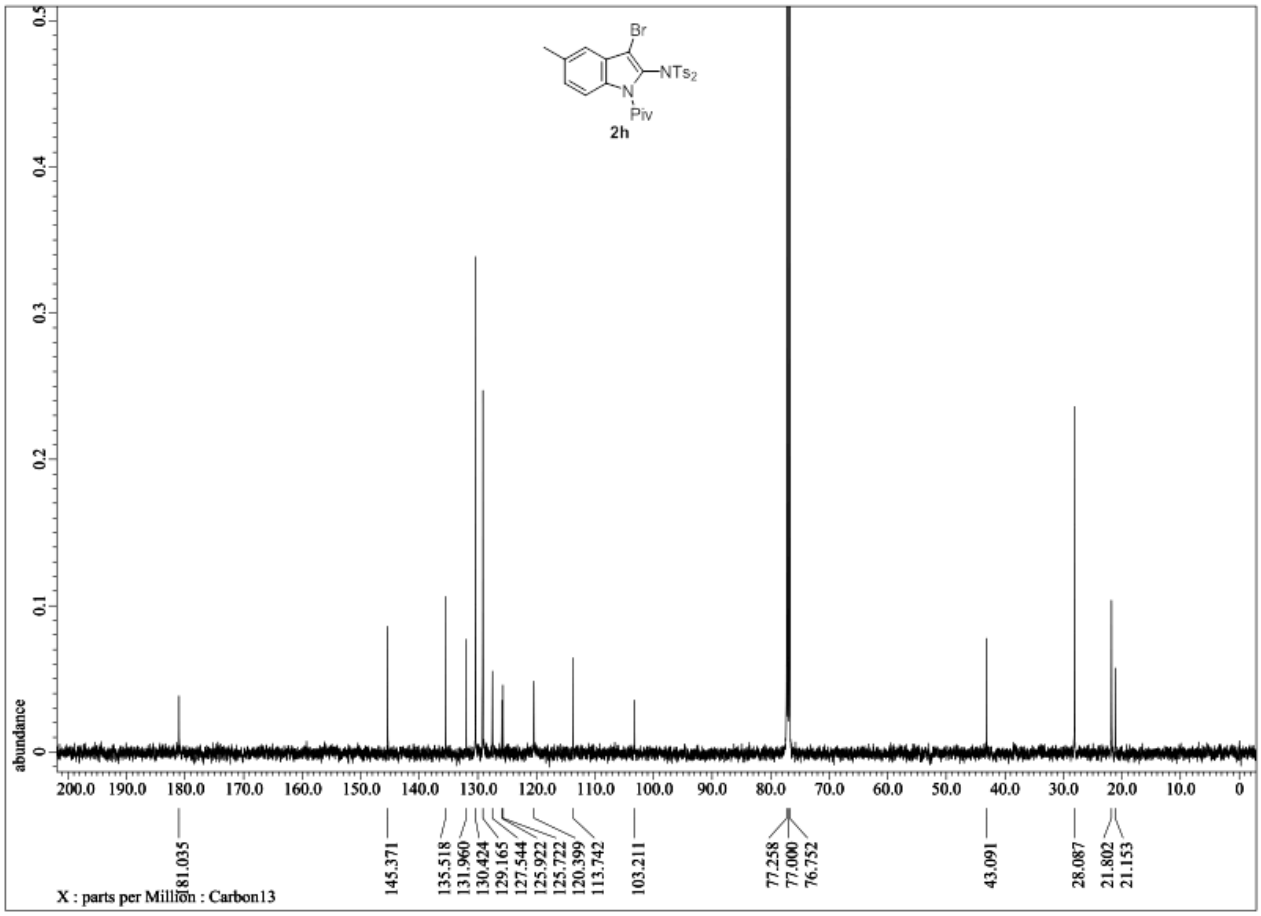

Br
NMs2
N
Piv
2f
9.05
6.20
1.00
1.02
abundance
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.637
7.621
7.518
7.500
7.442
7.428
7.411
7.331
7.316
7.301
7.258
3.635
1.516
-0.000
X : parts per Million : Proton

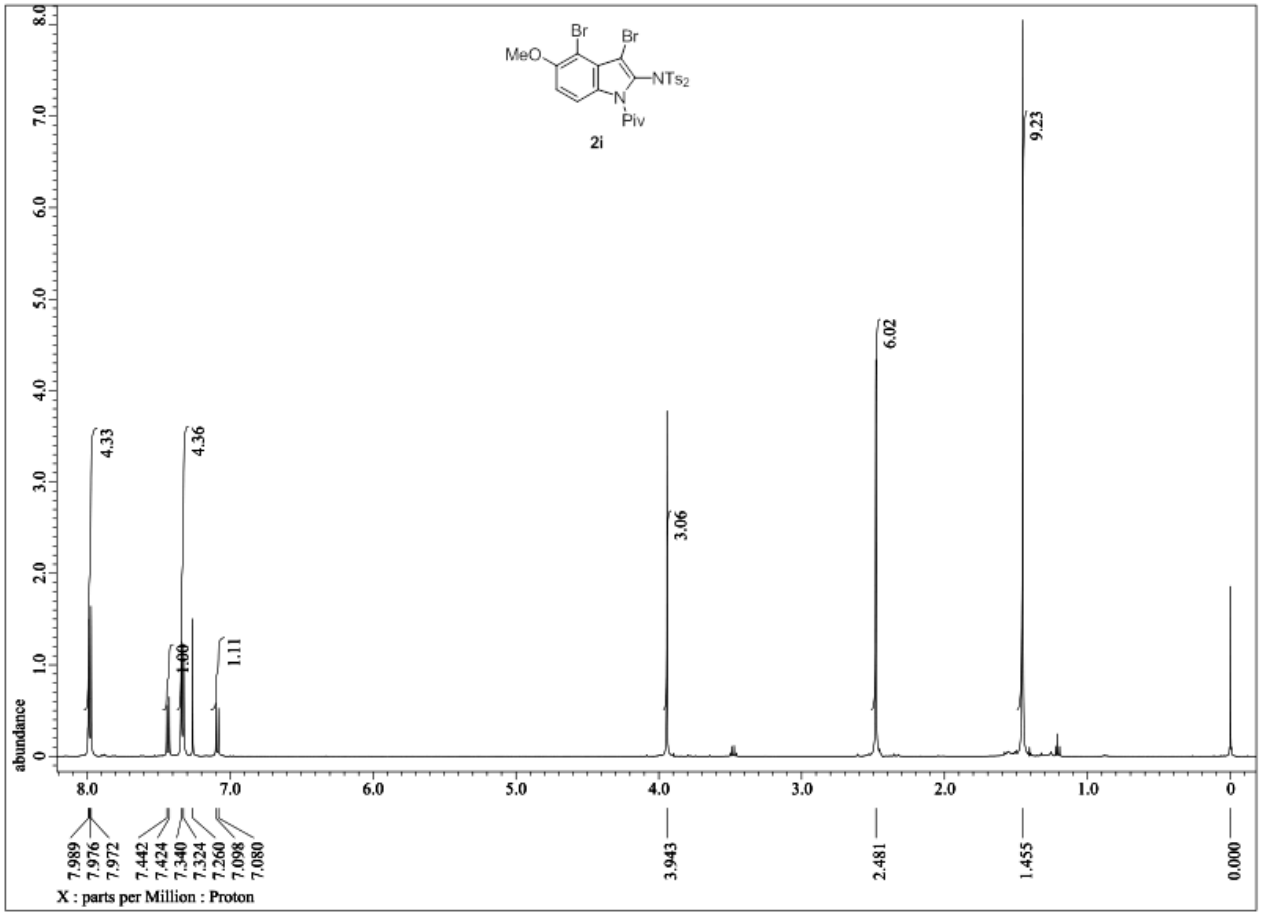

Br
NMs2
N
Piv
2f
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
182.732
133.429
126.265
125.378
125.025
122.813
120.972
113.951
102.534
77.248
77.000
76.742
43.807
43.444
28.021
X : parts per Million : Carbon13

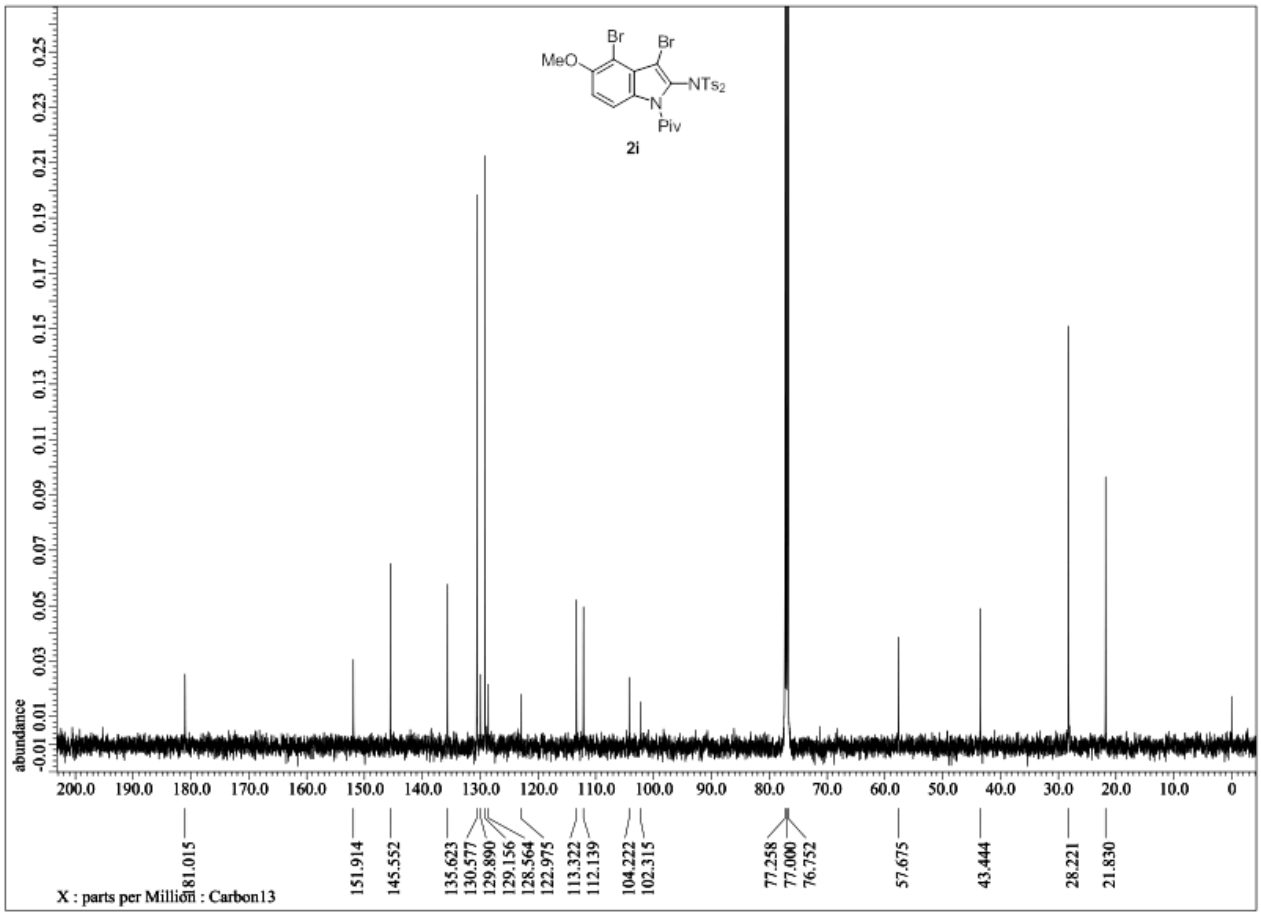

Br
N(SO2n-Pr)2
N
Piv
2g
9.07
6.05
4.05
2.04
2.03
1.00
1.00
1.00
1.00
0.99
abundance
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.636
7.620
7.515
7.499
7.429
7.415
7.398
7.322
7.307
7.291
7.261
4.021
4.016
4.007
4.004
3.994
3.989
3.976
3.765
3.753
3.747
3.738
3.735
3.725
3.721
2.054
2.039
2.024
2.010
1.996
1.993
1.978
1.963
1.524
1.146
1.131
1.117
-0.000
X : parts per Million : Proton

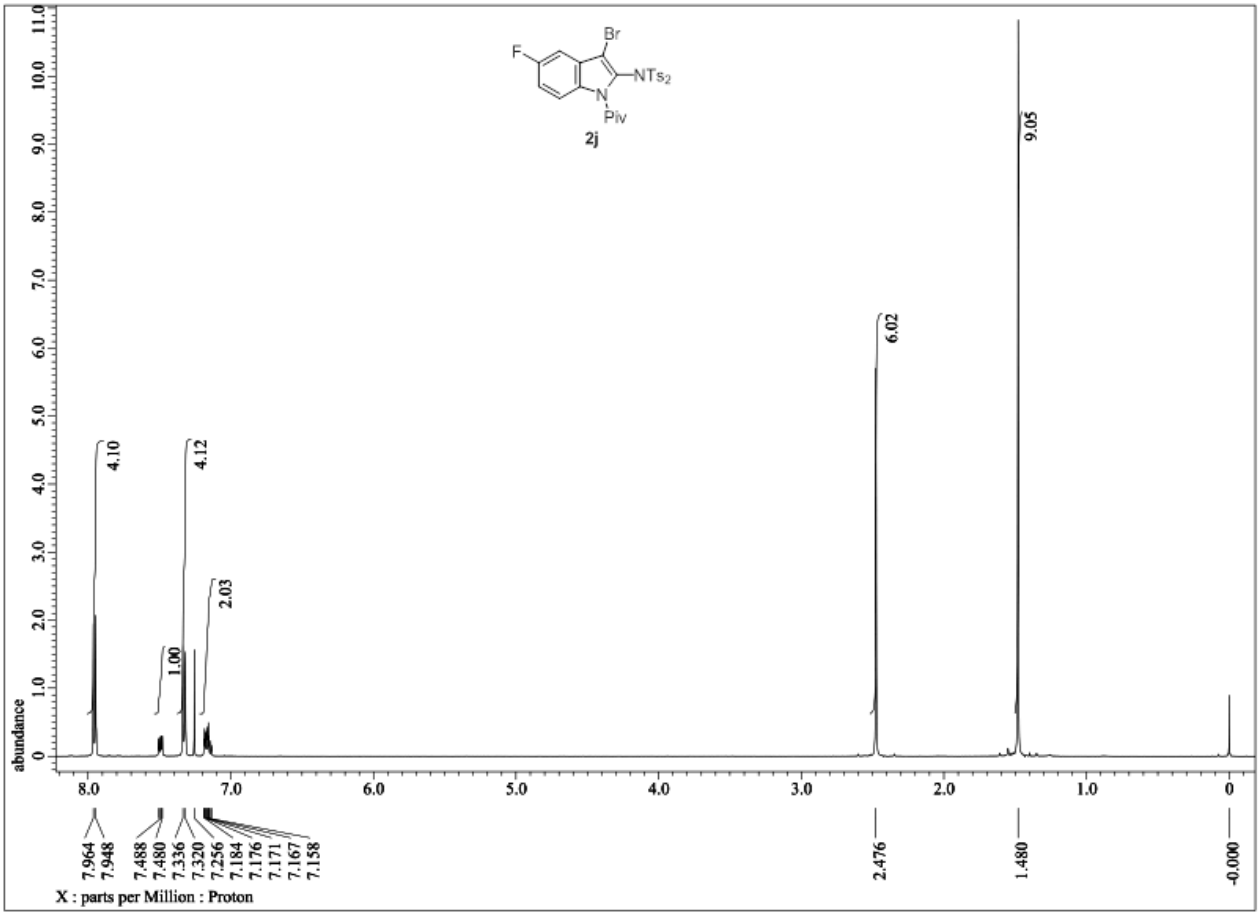

Br
N(SO2n-Pr)2
N
Piv
2g
abundance
0.5
0.4
0.3
0.2
0.1
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
182.742
133.400
126.122
125.417
125.359
122.698
120.924
113.904
102.801
77.258
77.000
76.742
58.496
43.425
28.049
16.899
13.103
X : parts per Million : Carbon13

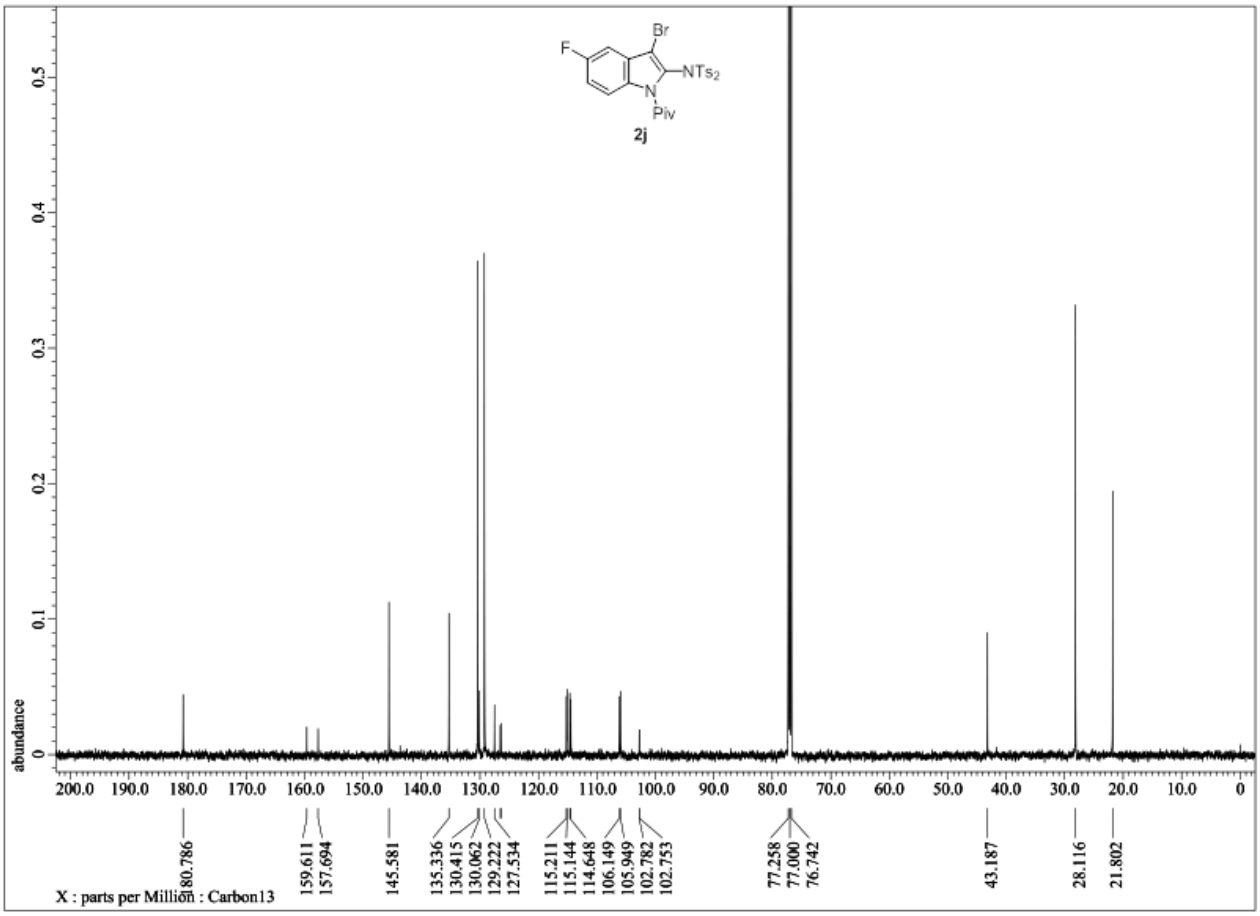

Br
NTs2
N
Piv
2h
abundance
X : parts per Million : Proton
7.968
7.952
7.455
7.439
7.327
7.310
7.293
7.259
7.238
7.220
2.473
2.458
1.492
0.000
4.08
1.00
5.27
1.01
6.45
3.00
9.00

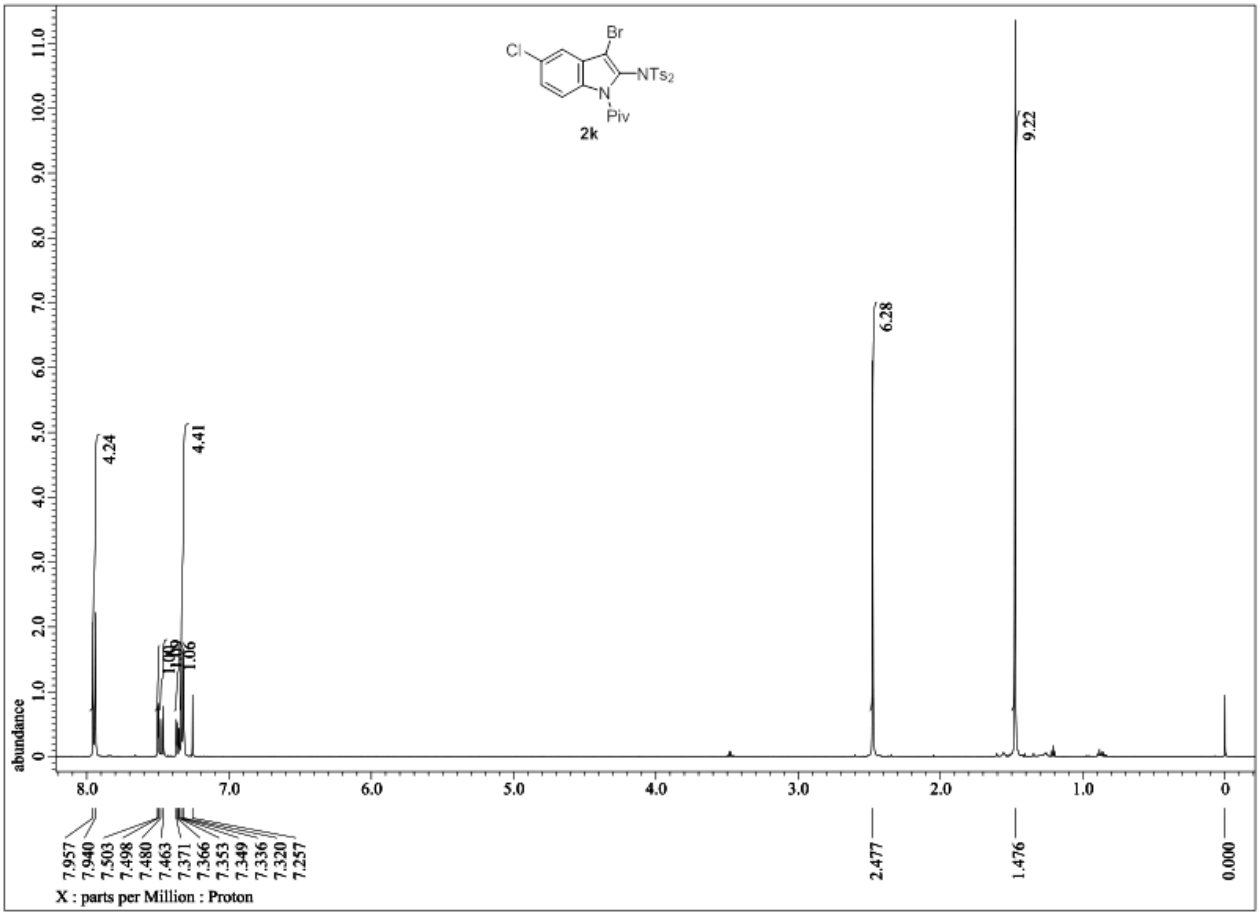

Br
NTs2
N
Piv
2h
abundance
X : parts per Million : Carbon13
181.035
145.371
135.518
131.960
130.424
129.165
127.544
125.922
125.722
120.399
113.742
103.211
77.258
77.000
76.752
43.091
28.087
21.802
21.153

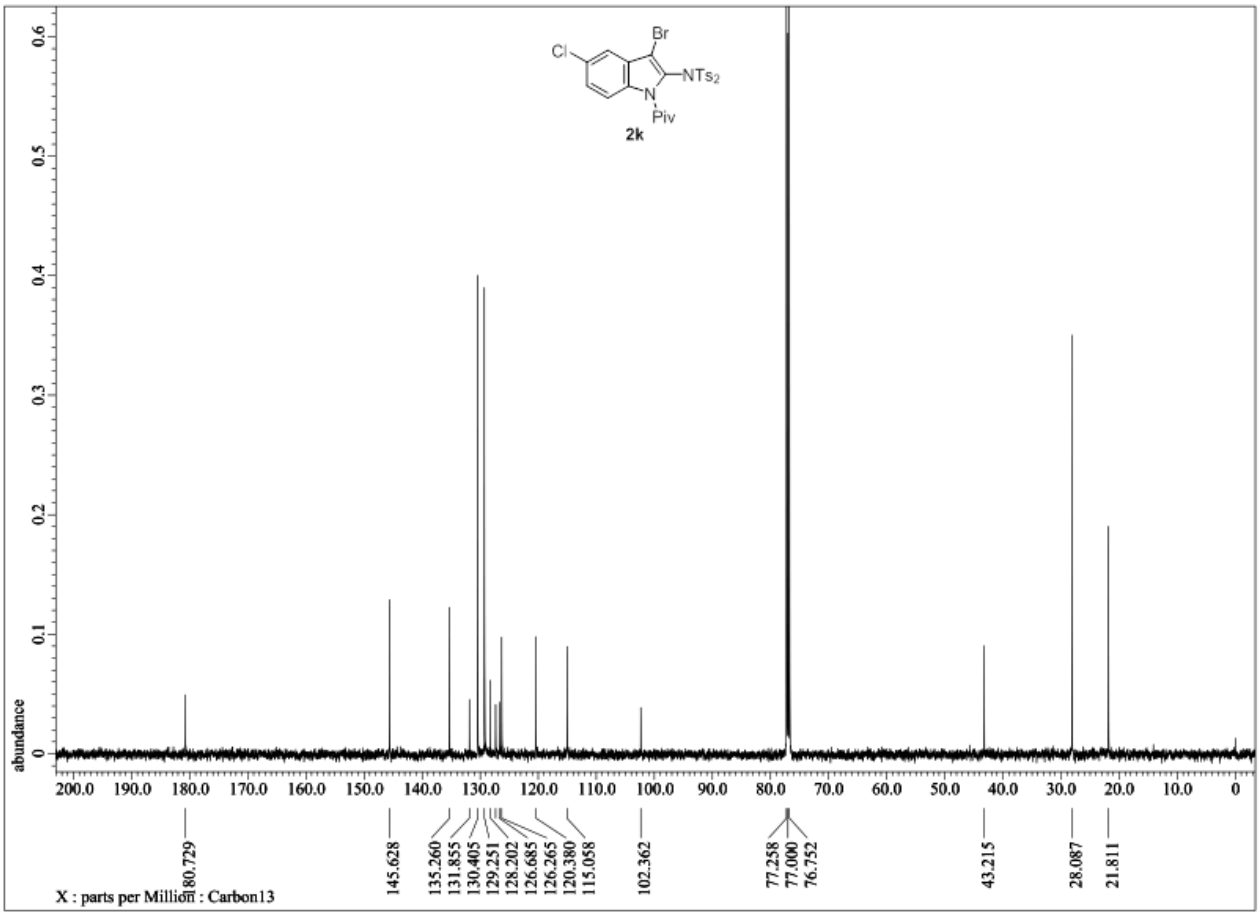

Br
Br
MeO
NTs2
N
Piv
2i
9.23
6.02
4.33
4.36
3.06
1.11
1.00
abundance
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.989
7.976
7.972
7.442
7.424
7.340
7.324
7.260
7.098
7.080
3.943
2.481
1.455
0.000
X : parts per Million : Proton

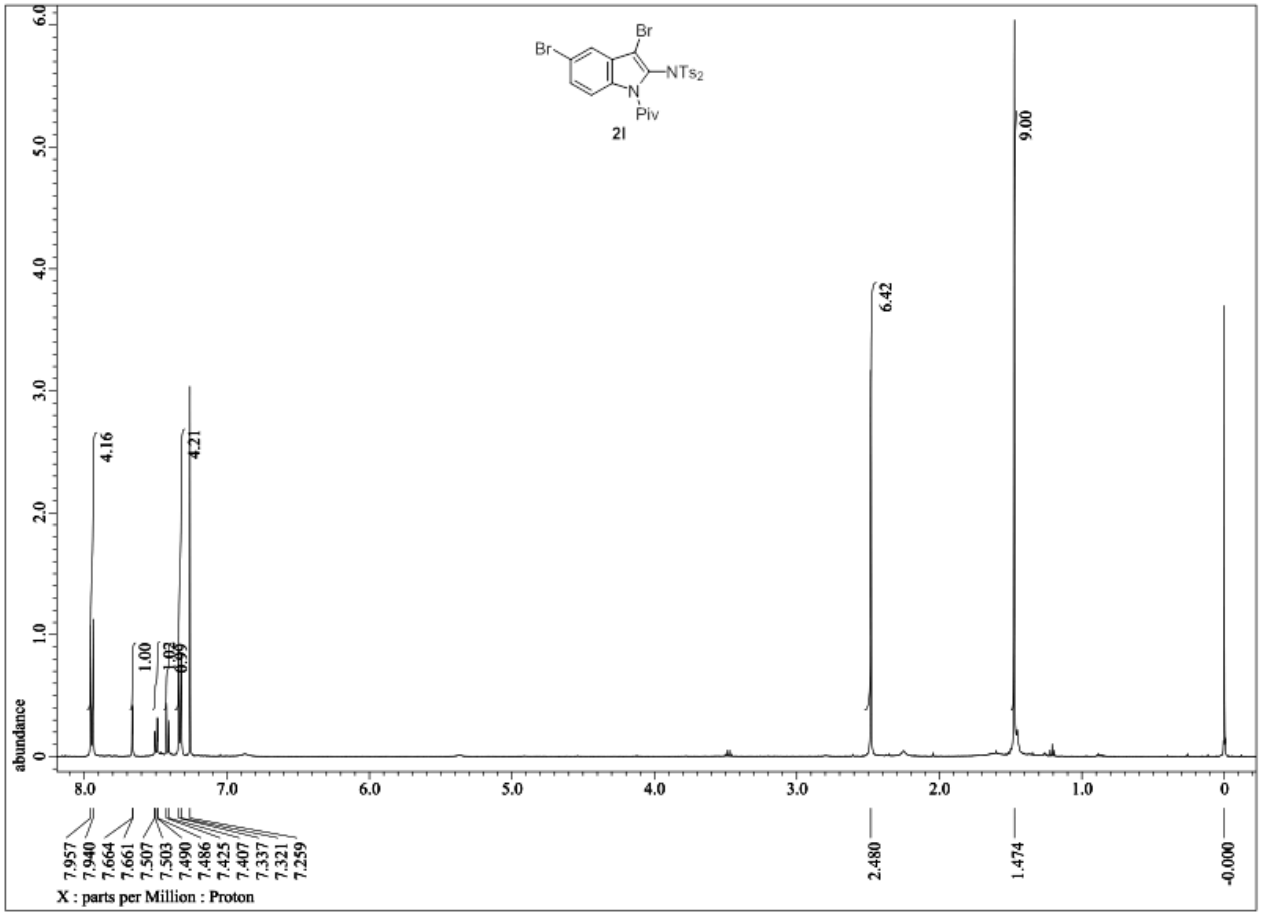

Br
Br
MeO
NTs2
N
Piv
2i
abundance
0.25
0.23
0.21
0.19
0.17
0.15
0.13
0.11
0.09
0.07
0.05
0.03
0.01
-0.01
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
181.015
151.914
145.552
135.623
130.577
129.890
129.156
128.564
122.975
113.322
112.139
104.222
102.315
77.258
77.000
76.752
57.675
43.444
28.221
21.830
X : parts per Million : Carbon13

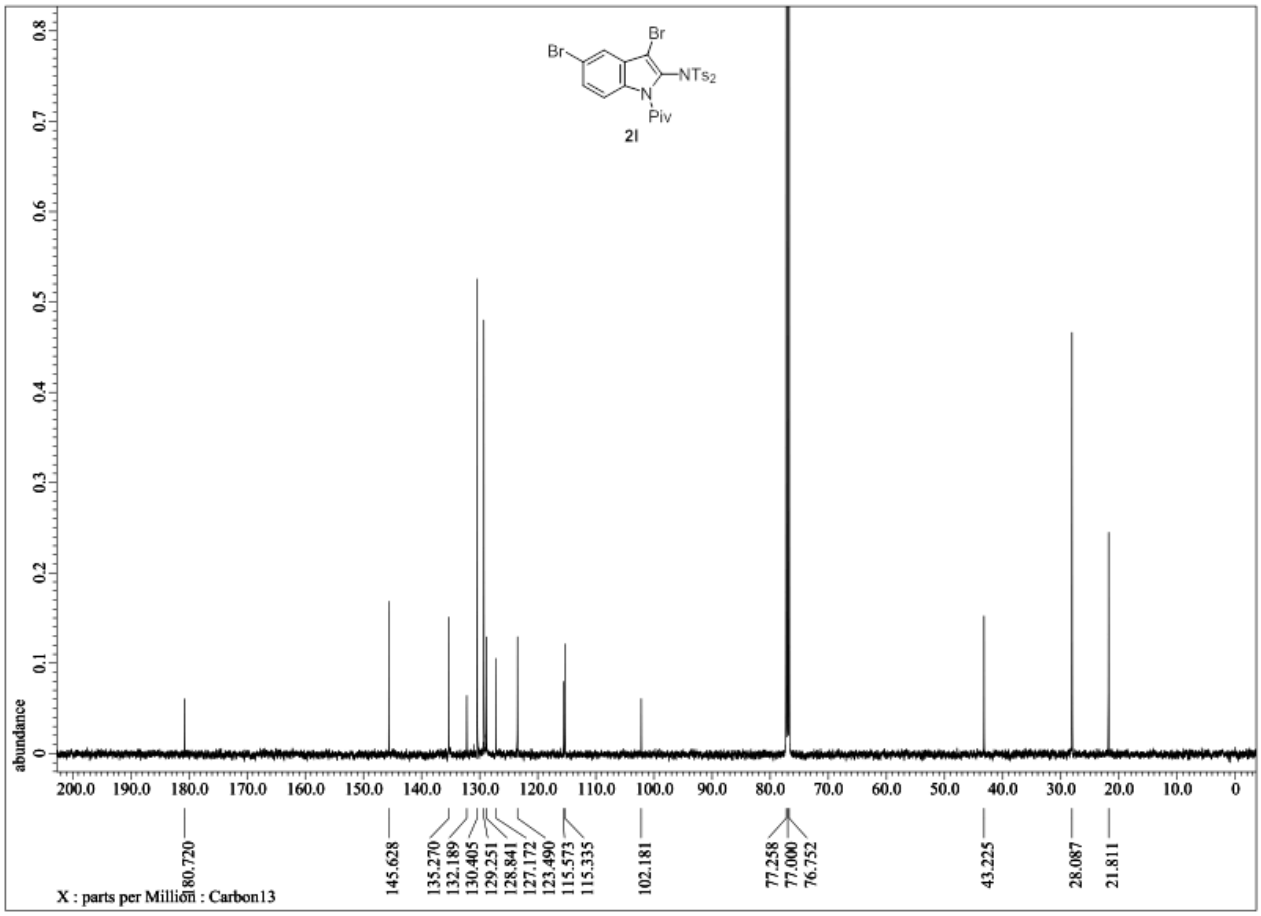

Br
F
NTs2
N
Piv
2j
9.05
6.02
4.10
4.12
2.03
1.00
abundance
X : parts per Million : Proton
7.964
7.948
7.488
7.480
7.336
7.320
7.256
7.184
7.176
7.171
7.167
7.158
2.476
1.480
-0.000

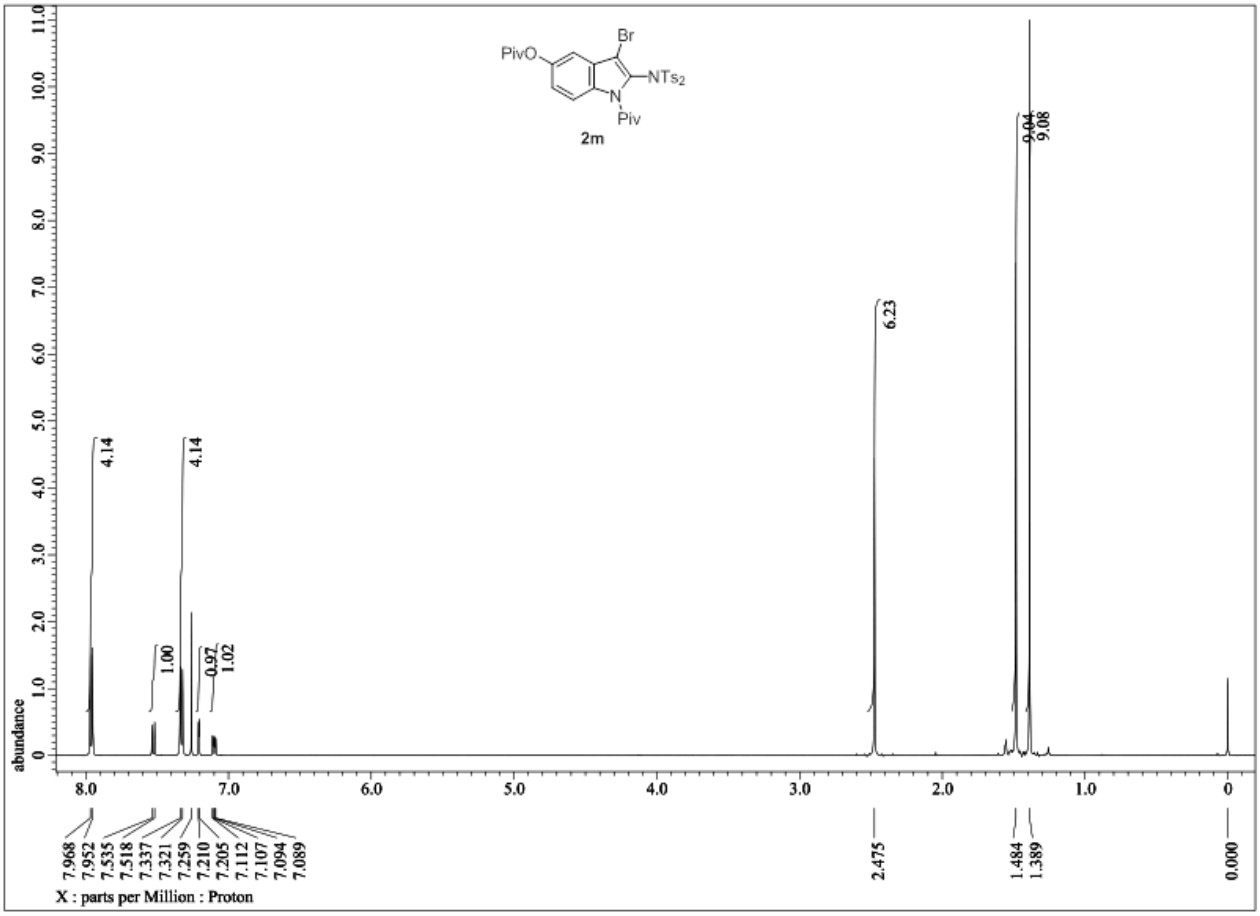

Br
F
NTs2
N
Piv
2j
abundance
X : parts per Million : Carbon13
180.786
159.611
157.694
145.581
135.336
130.415
130.062
129.222
127.534
115.211
115.144
114.648
106.149
105.949
102.782
102.753
77.258
77.000
76.742
43.187
28.116
21.802

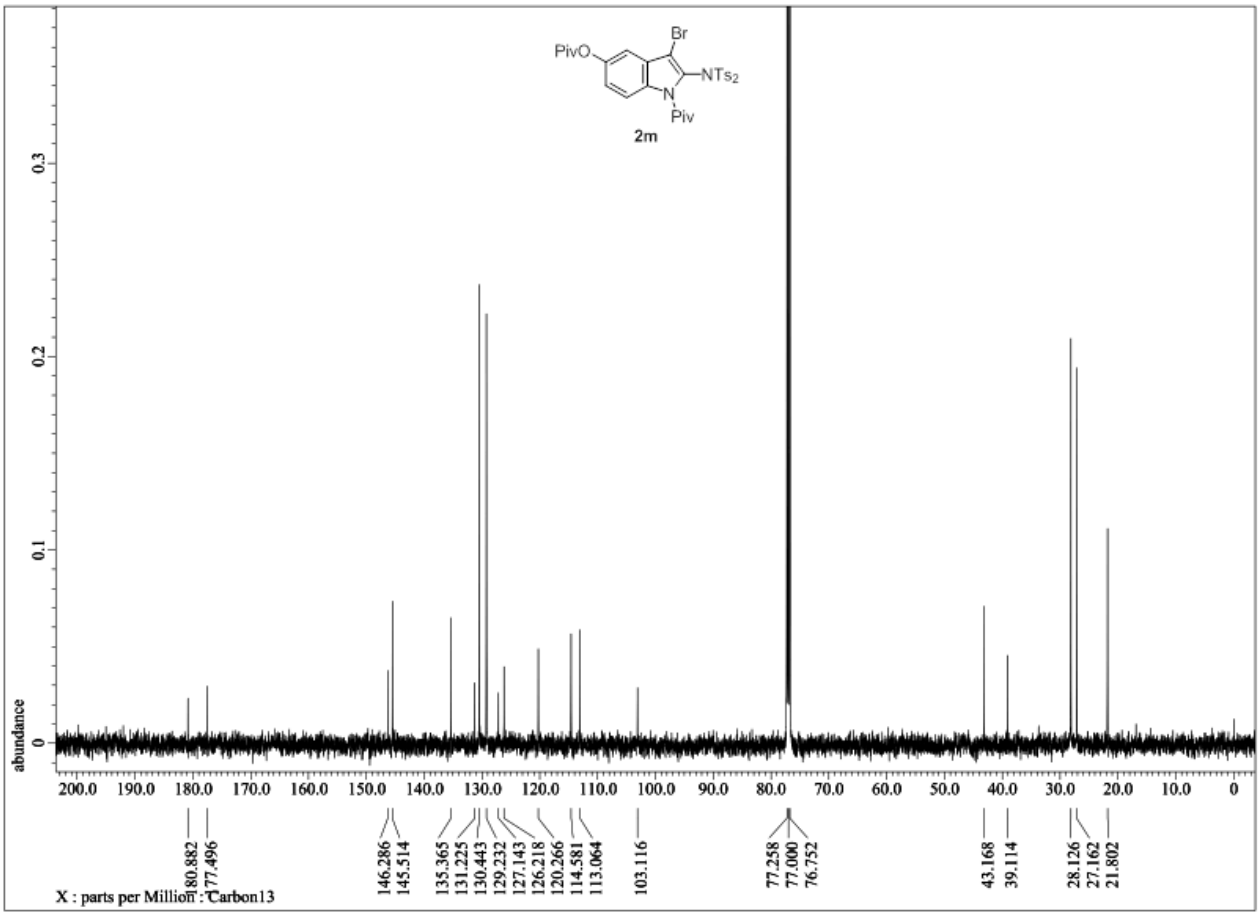

Br
Cl
NTs2
N
Piv
2k
9.22
6.28
4.24
4.41
1.06
abundance
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.957
7.940
7.503
7.498
7.480
7.463
7.371
7.366
7.353
7.349
7.336
7.320
7.257
2.477
1.476
0.000
X : parts per Million : Proton

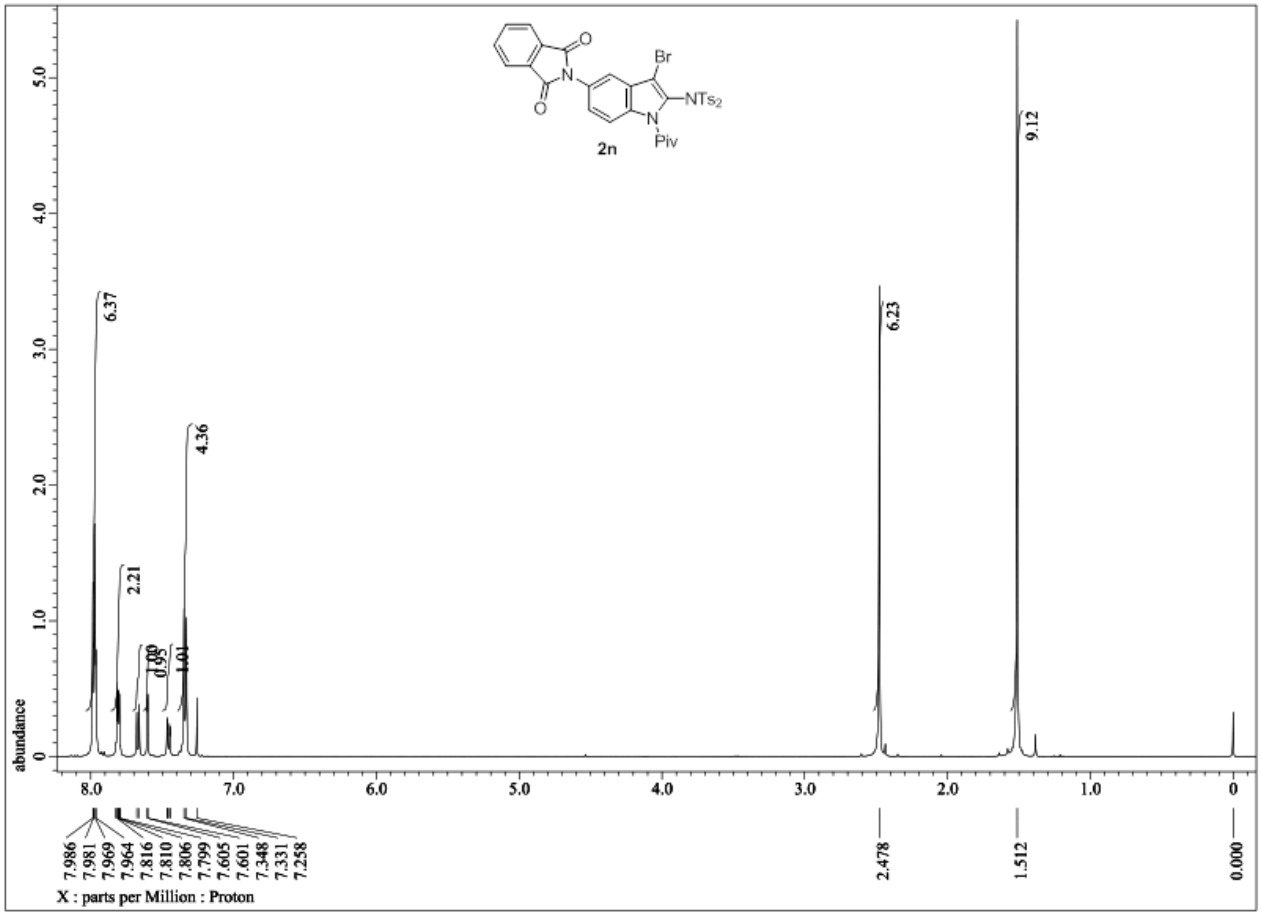

Br
Cl
NTs2
N
Piv
2k
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
180.729
145.628
135.260
131.855
130.405
129.251
128.202
126.685
126.265
120.380
115.058
102.362
77.258
77.000
76.752
43.215
28.087
21.811
X : parts per Million : Carbon13

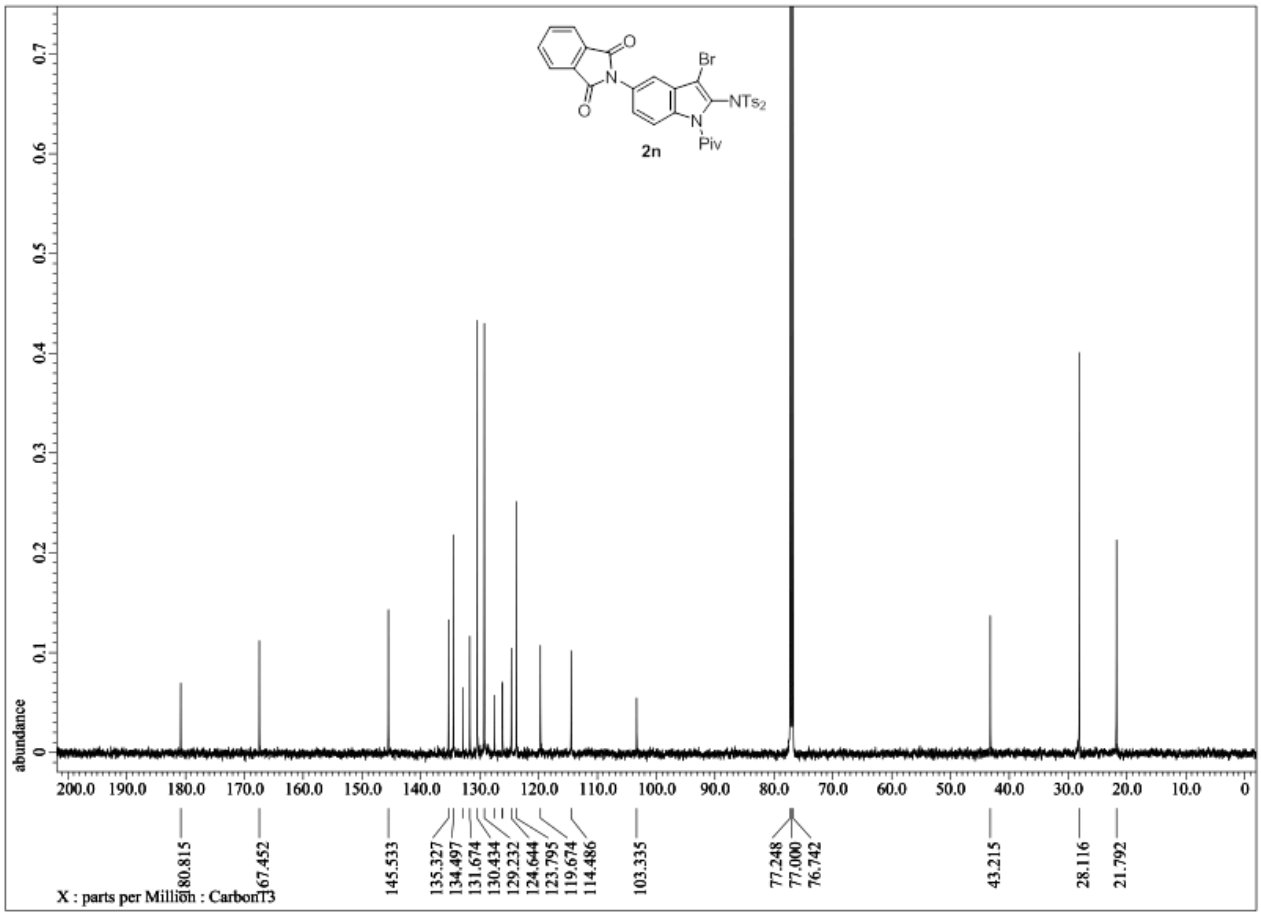

Br
Br
NTs2
N
Piv
2l
9.00
6.42
4.16
4.21
1.00
abundance
X : parts per Million : Proton
7.957
7.940
7.664
7.661
7.507
7.503
7.490
7.486
7.425
7.407
7.337
7.321
7.259
2.480
1.474
-0.000

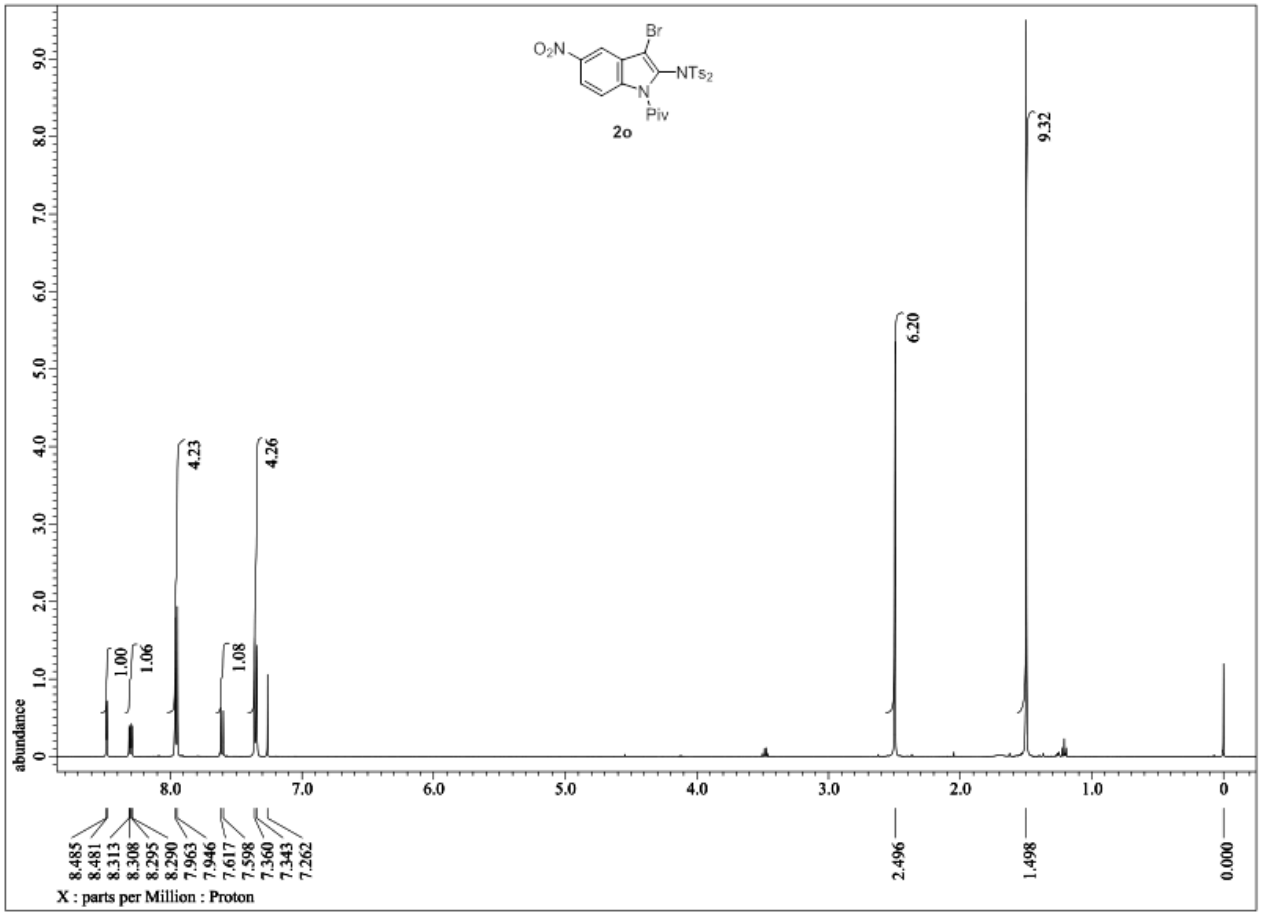

Br
Br
NTs2
N
Piv
2l
abundance
X : parts per Million : Carbon13
180.720
145.628
135.270
132.189
130.405
129.251
128.841
127.172
123.490
115.573
115.335
102.181
77.258
77.000
76.752
43.225
28.087
21.811

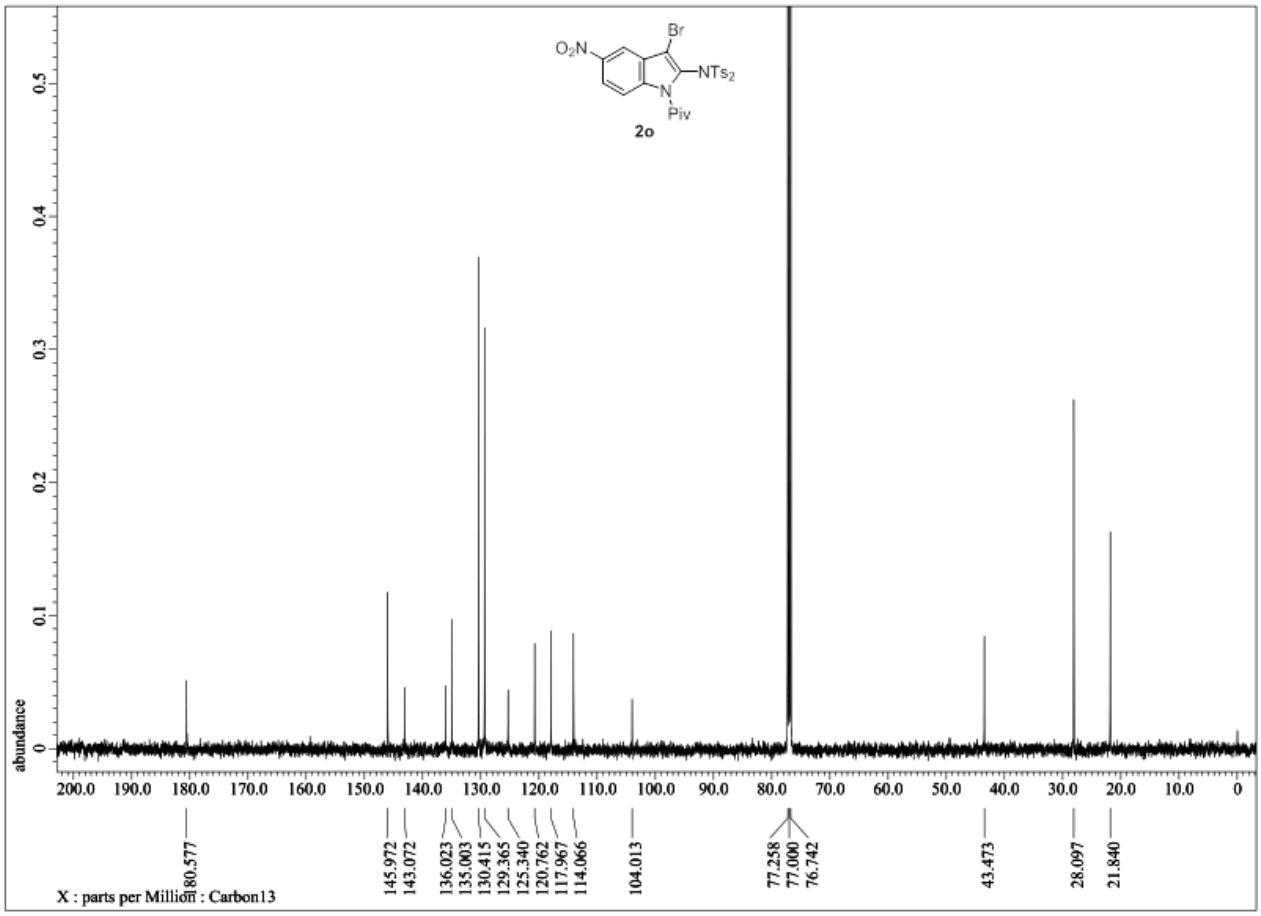

PivO
Br
NTs2
N
Piv
2m
abundance
X : parts per Million : Proton
4.14
4.14
1.00
0.97
1.02
6.23
9.04
9.08
7.968
7.952
7.535
7.518
7.337
7.321
7.259
7.210
7.205
7.112
7.107
7.094
7.089
2.475
1.484
1.389
0.000

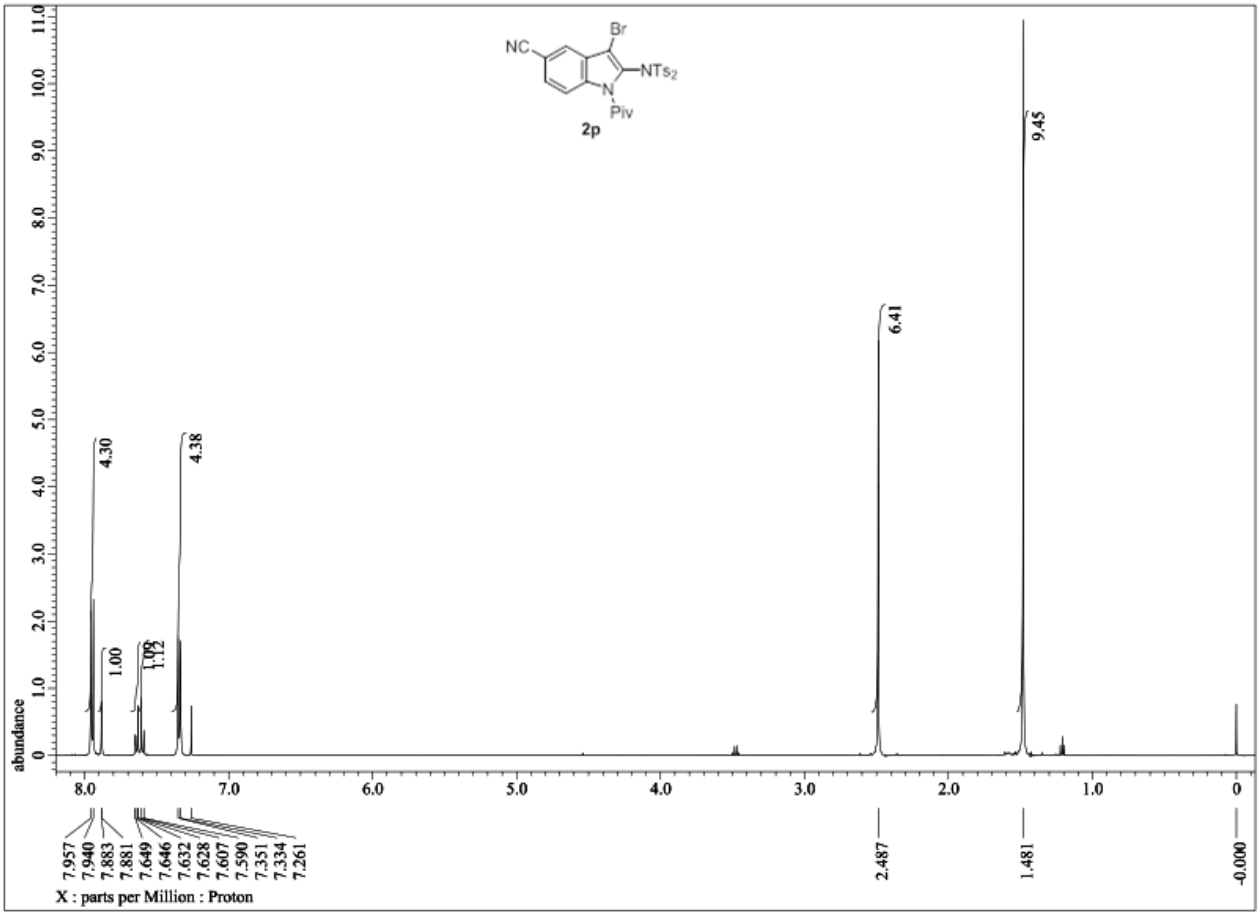

PivO
Br
NTs2
N
Piv
2m
abundance
X : parts per Million : Carbon13
80.882
77.496
146.286
145.514
135.365
131.225
130.443
129.232
127.143
126.218
120.266
114.581
113.064
103.116
77.258
77.000
76.752
43.168
39.114
28.126
27.162
21.802

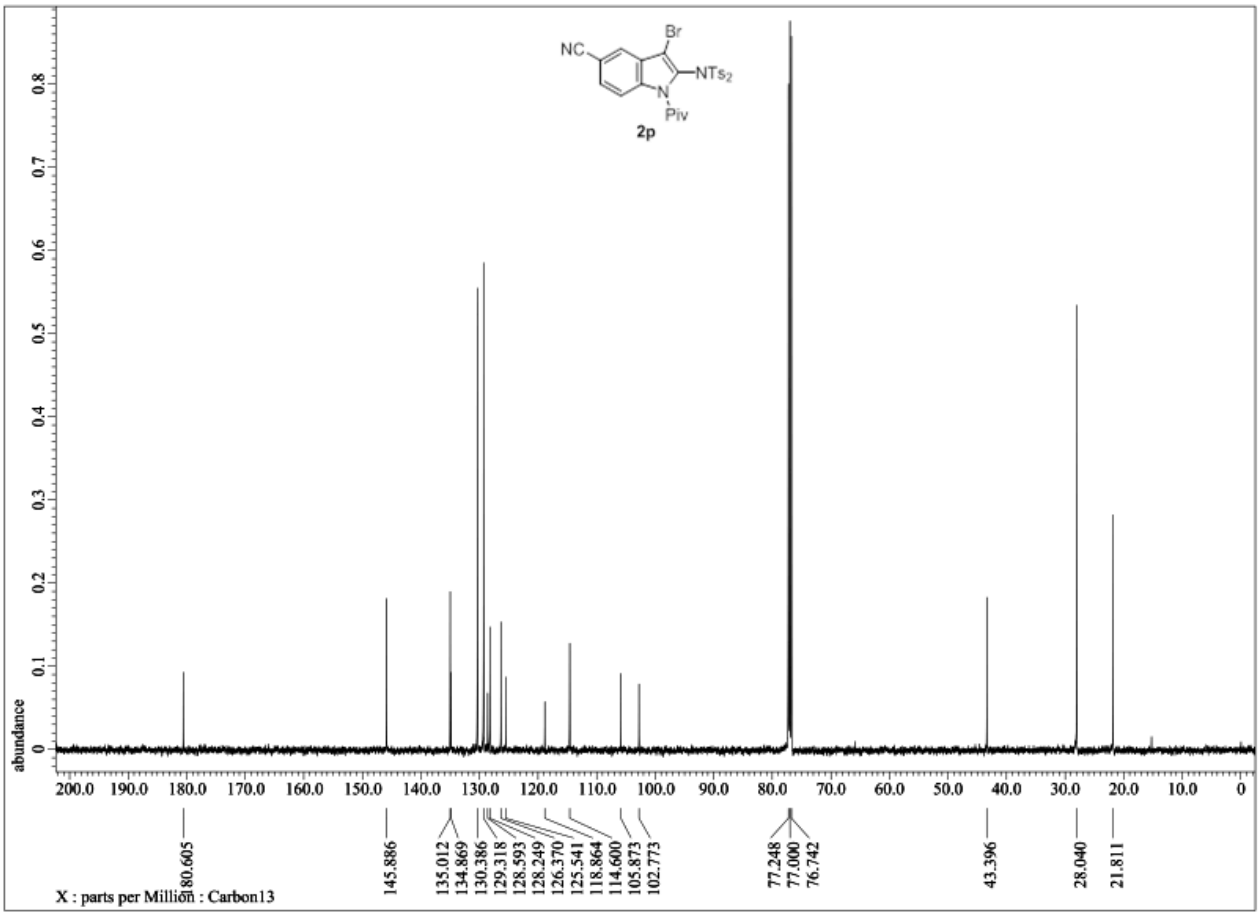

Br
NTs2
N
Piv
2n
6.37
2.21
1.00
0.95
1.01
4.36
6.23
9.12
abundance
X : parts per Million : Proton
7.986
7.981
7.969
7.964
7.816
7.810
7.806
7.799
7.605
7.601
7.348
7.331
7.258
2.478
1.512
0.000

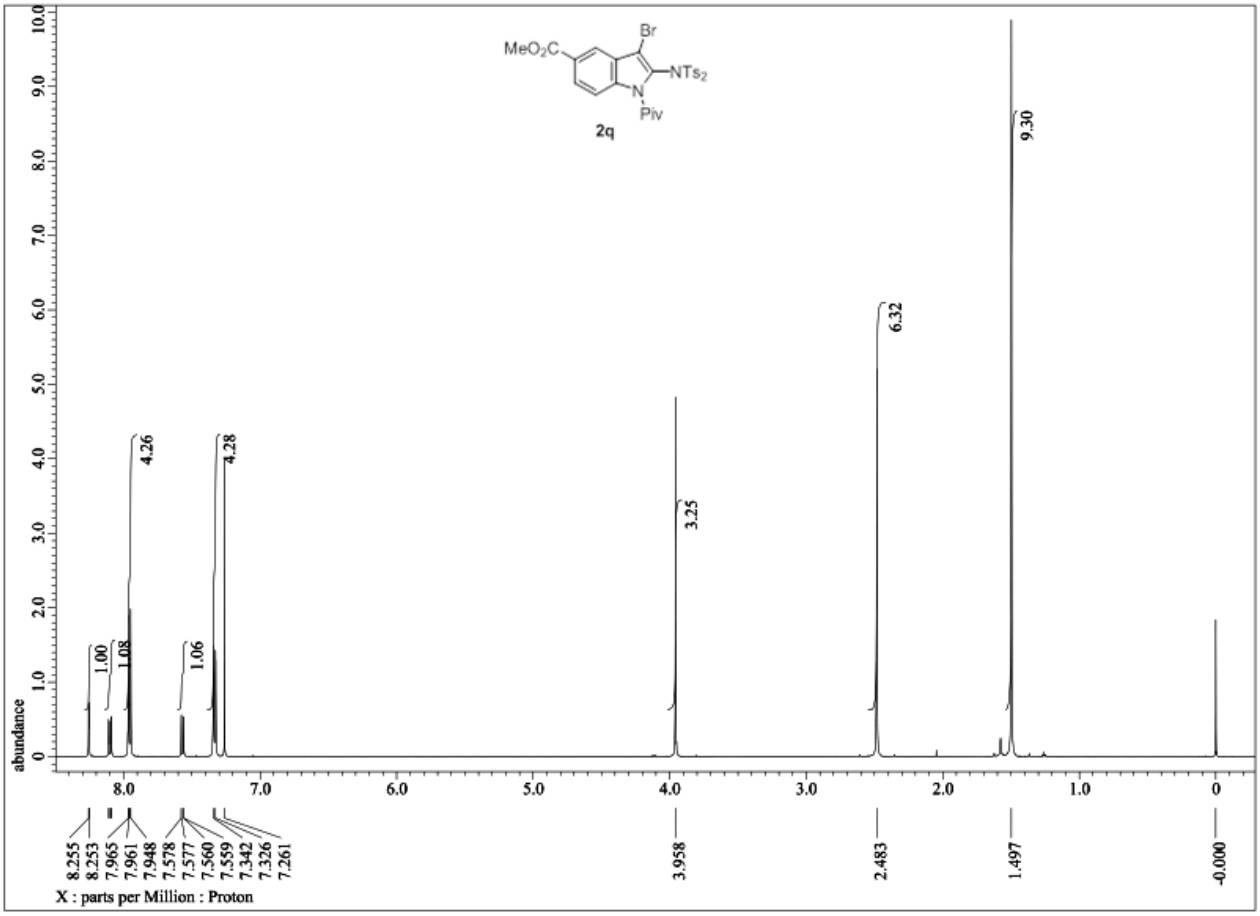

Br
NTs2
N
Piv
2n
abundance
X : parts per Million : Carbon13
180.815
167.452
145.533
135.327
134.497
131.674
130.434
129.232
124.644
123.795
119.674
114.486
103.335
77.248
77.000
76.742
43.215
28.116
21.792

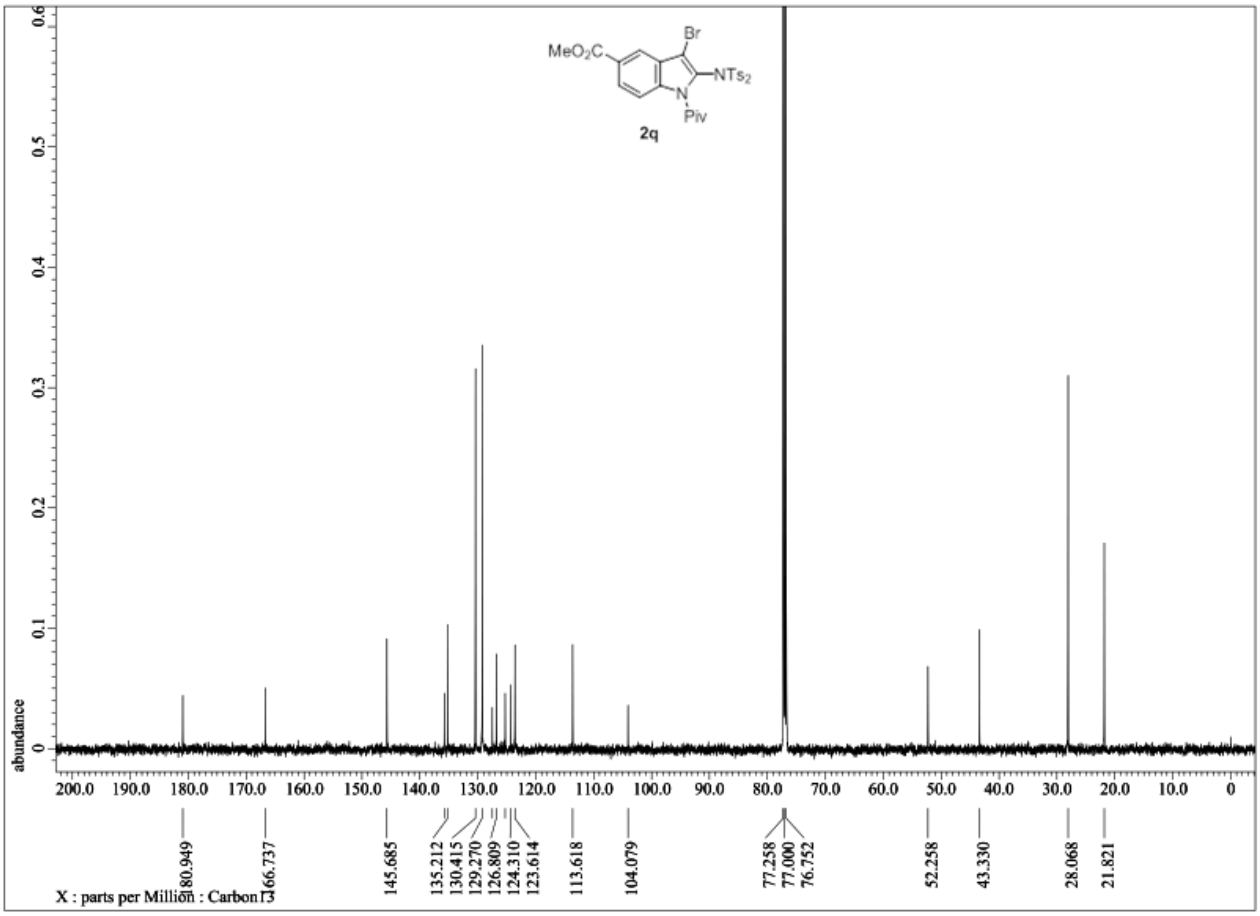

Br
O2N
NTs2
N
Piv
2o
9.32
6.20
4.23
4.26
1.00
1.06
1.08
abundance
8.485
8.481
8.313
8.308
8.295
8.290
7.963
7.946
7.617
7.598
7.360
7.343
7.262
2.496
1.498
0.000
X : parts per Million : Proton

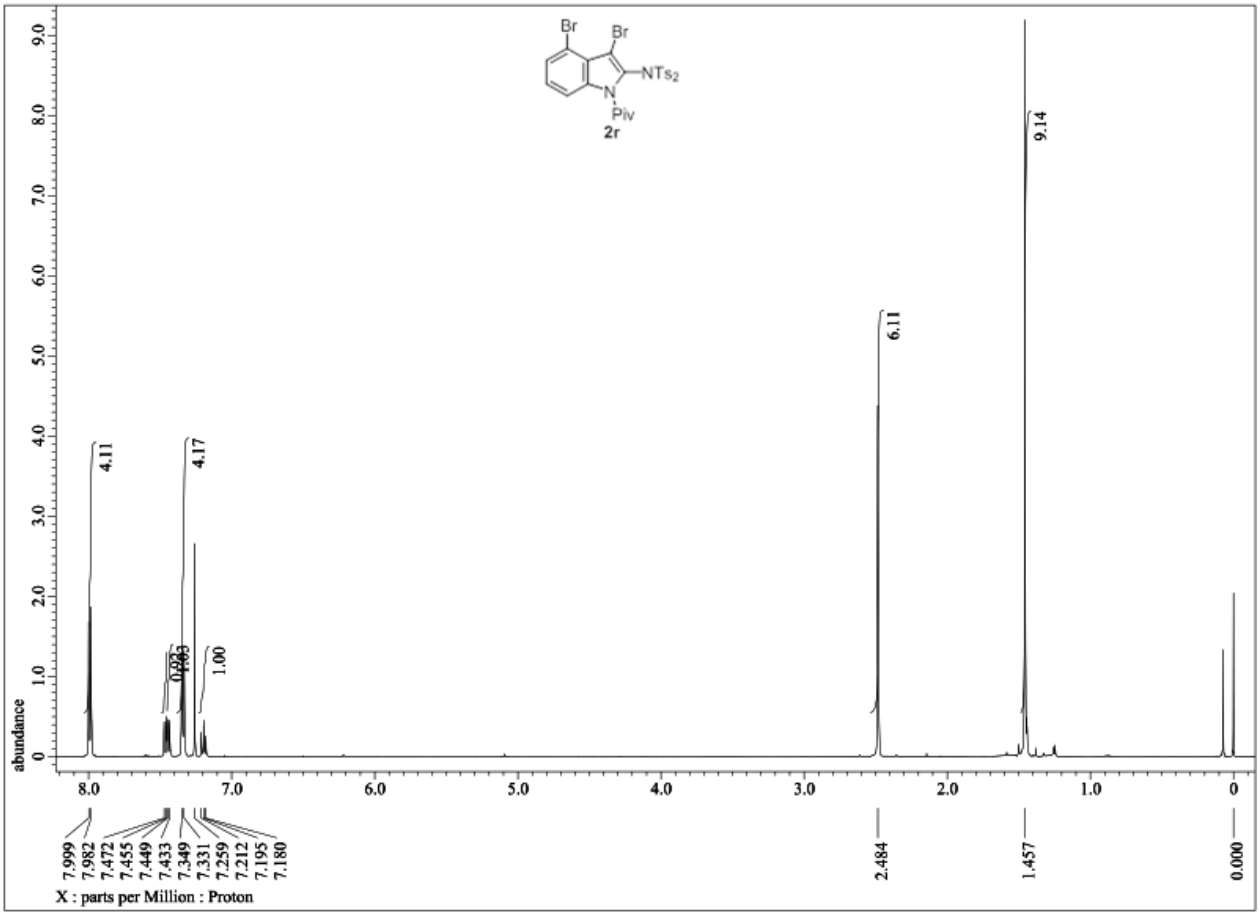

Br
O2N
NTs2
N
Piv
2o
abundance
180.577
145.972
143.072
136.023
135.003
130.415
129.365
125.340
120.762
117.967
114.066
104.013
77.258
77.000
76.742
43.473
28.097
21.840
X : parts per Million : Carbon13

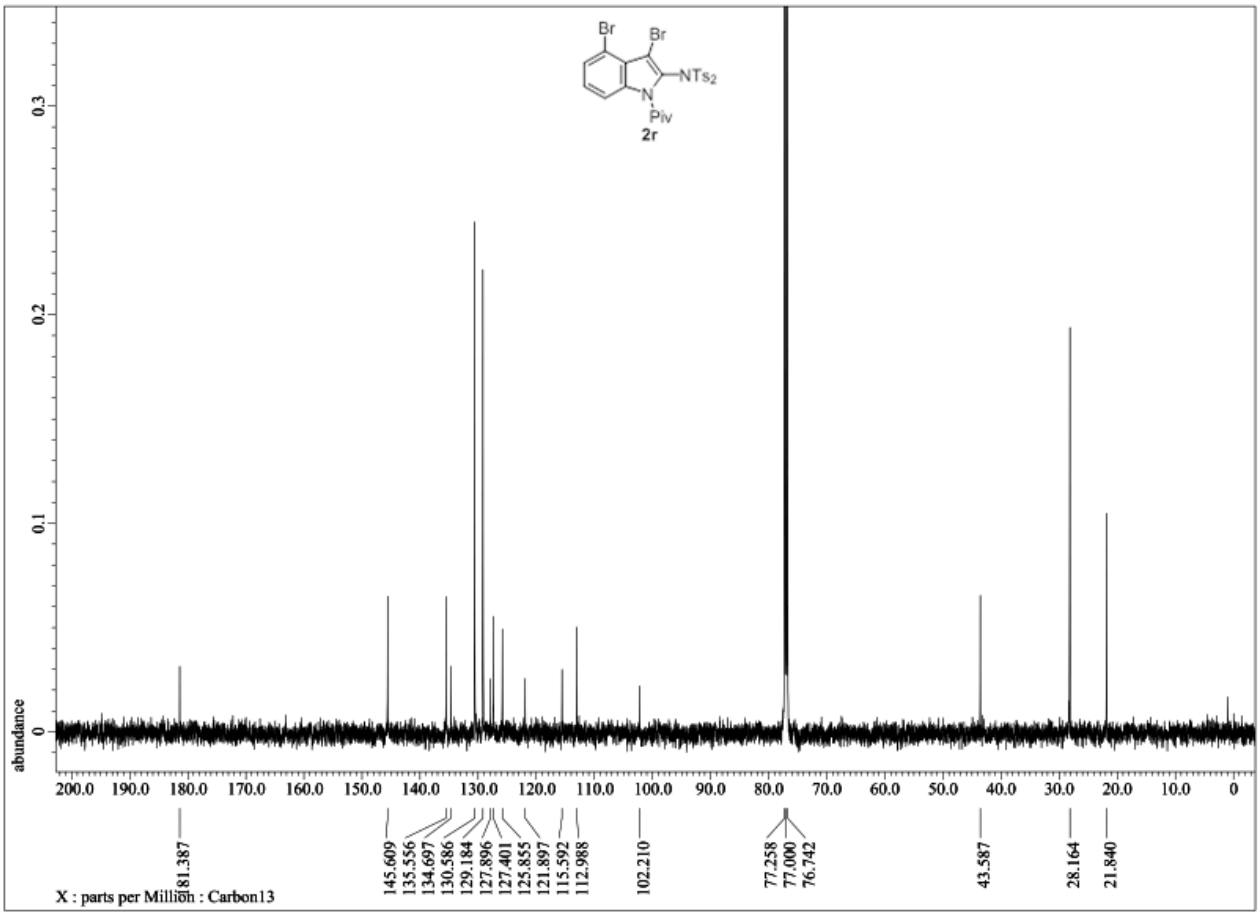

Br
NC
NTs2
N
Piv
2p
9.45
6.41
4.30
4.38
1.00
1.09
1.12
abundance
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.957
7.940
7.883
7.881
7.649
7.646
7.632
7.628
7.607
7.590
7.351
7.334
7.261
2.487
1.481
-0.000
X : parts per Million : Proton

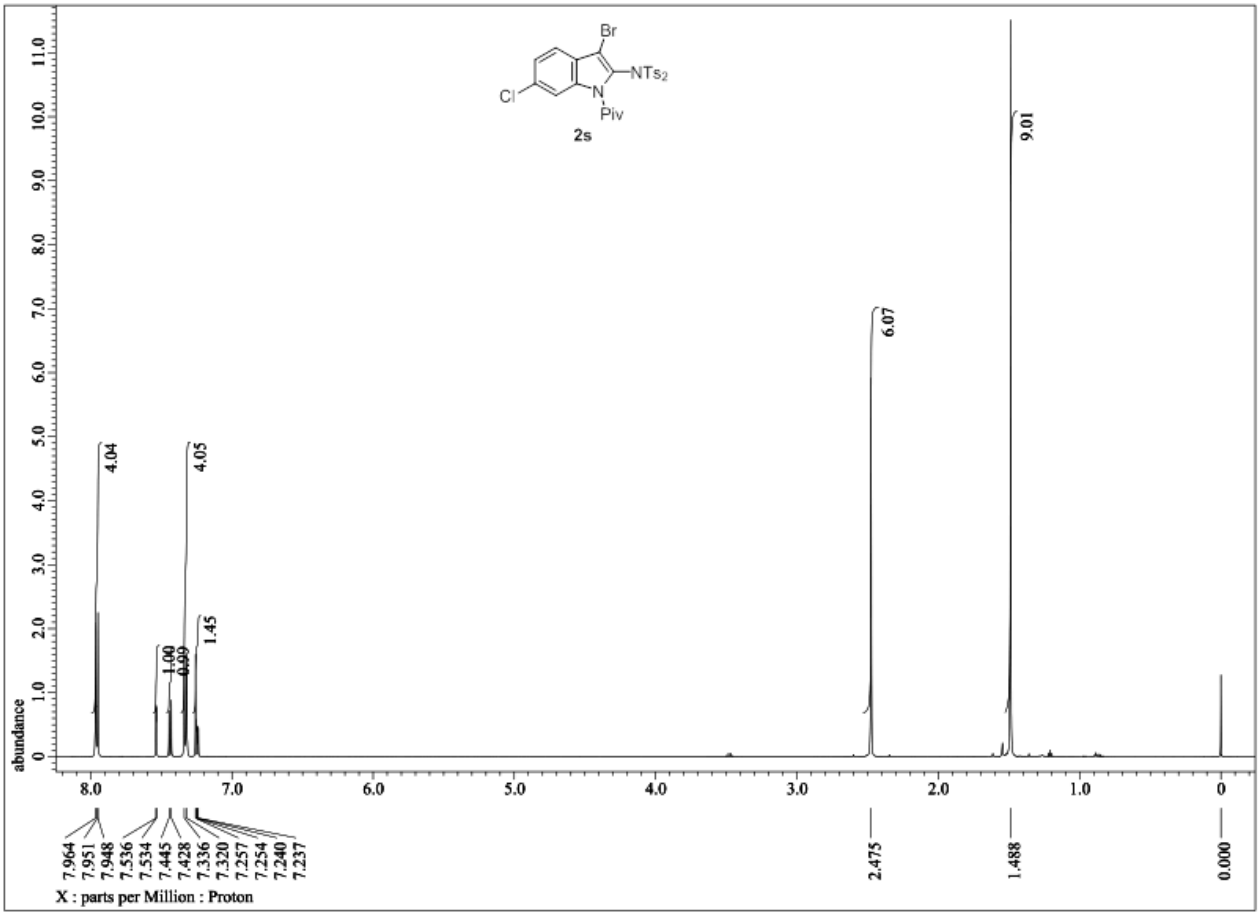

Br
NC
NTs2
N
Piv
2p
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
180.605
145.886
135.012
134.869
130.386
129.318
128.593
128.249
126.370
125.541
118.864
114.600
105.873
102.773
77.248
77.000
76.742
43.396
28.040
21.811
X : parts per Million : Carbon13

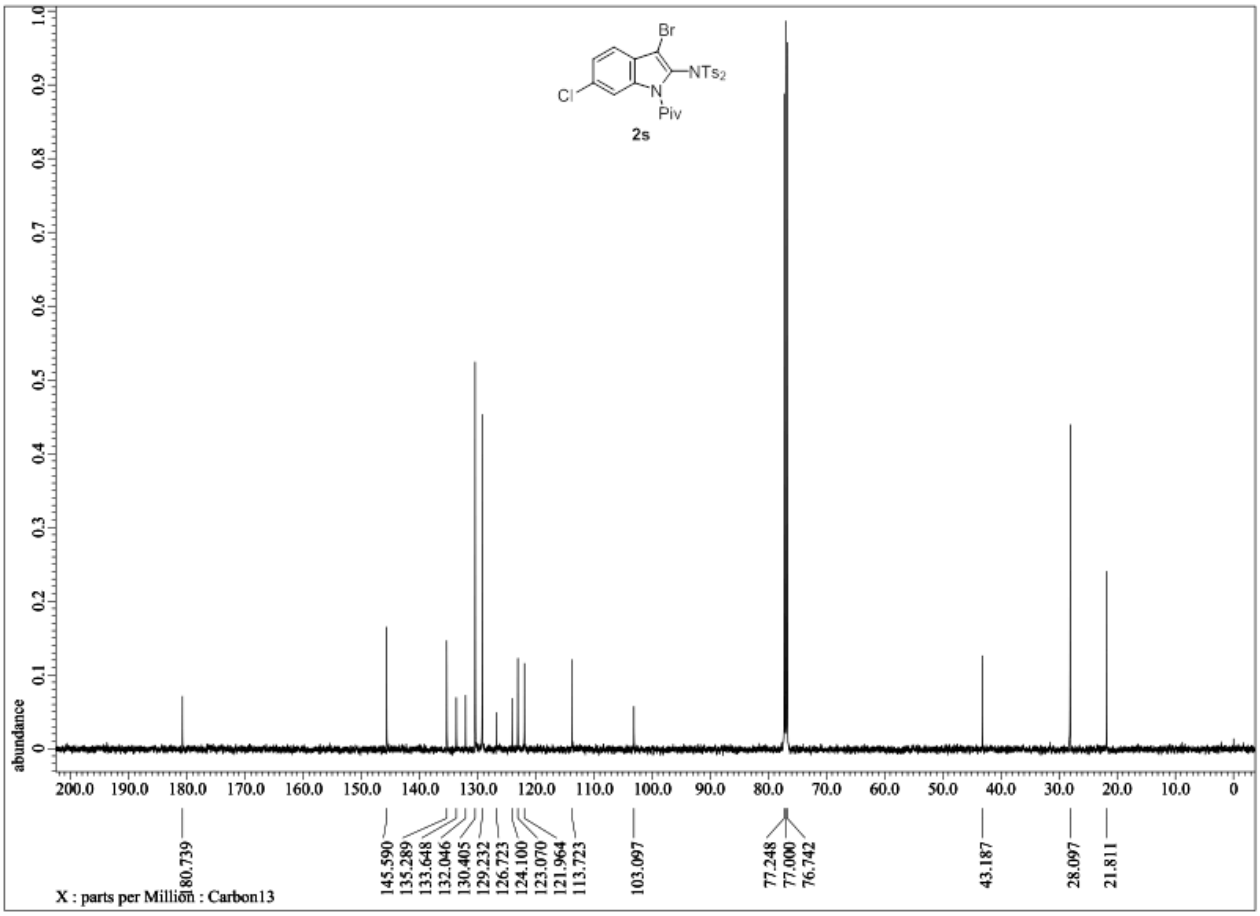

MeO2C
Br
NTs2
N
Piv
2q
9.30
6.32
4.26
4.28
3.25
1.00
1.08
1.06
abundance
8.255
8.253
7.965
7.961
7.948
7.578
7.577
7.560
7.559
7.342
7.326
7.261
3.958
2.483
1.497
-0.000
X : parts per Million : Proton

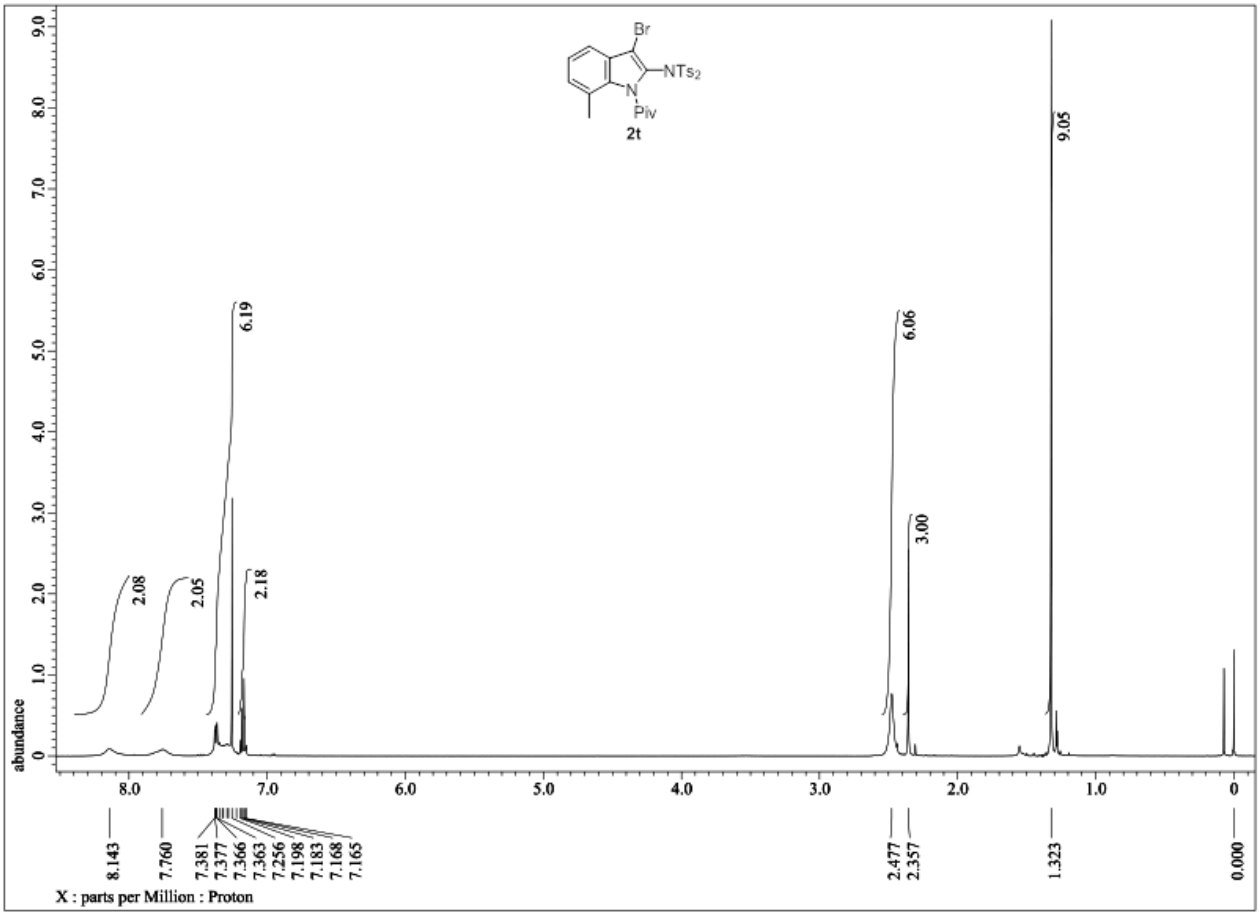

MeO2C
Br
NTs2
N
Piv
2q
abundance
180.949
166.737
145.685
135.212
130.415
129.270
126.809
124.310
123.614
113.618
104.079
77.258
77.000
76.752
52.258
43.330
28.068
21.821
X : parts per Million : Carbon 13

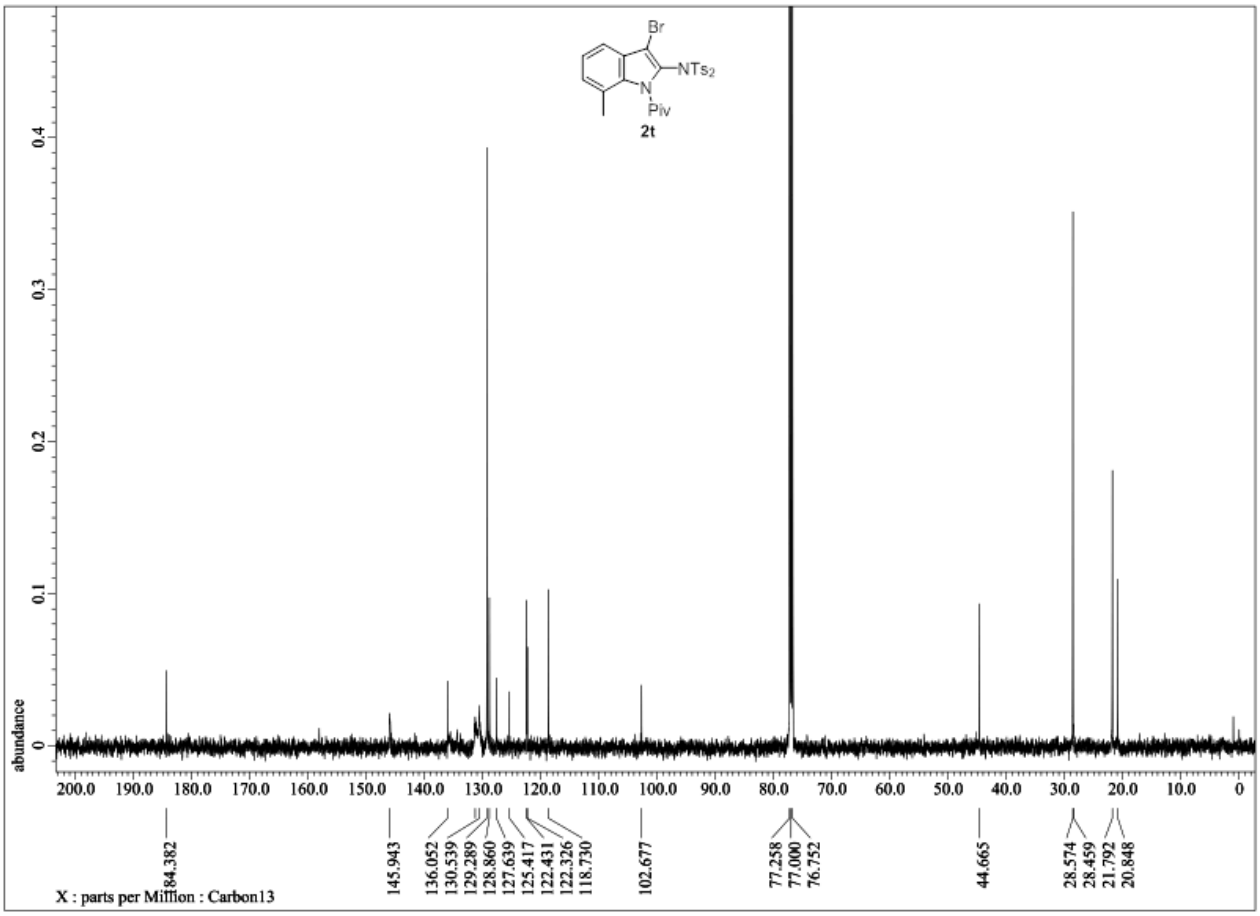

Br
Br
NTs2
N
Piv
2r
9.14
6.11
4.11
4.17
1.00
abundance
7.999
7.982
7.472
7.455
7.449
7.433
7.349
7.331
7.259
7.212
7.195
7.180
2.484
1.457
0.000
X : parts per Million : Proton

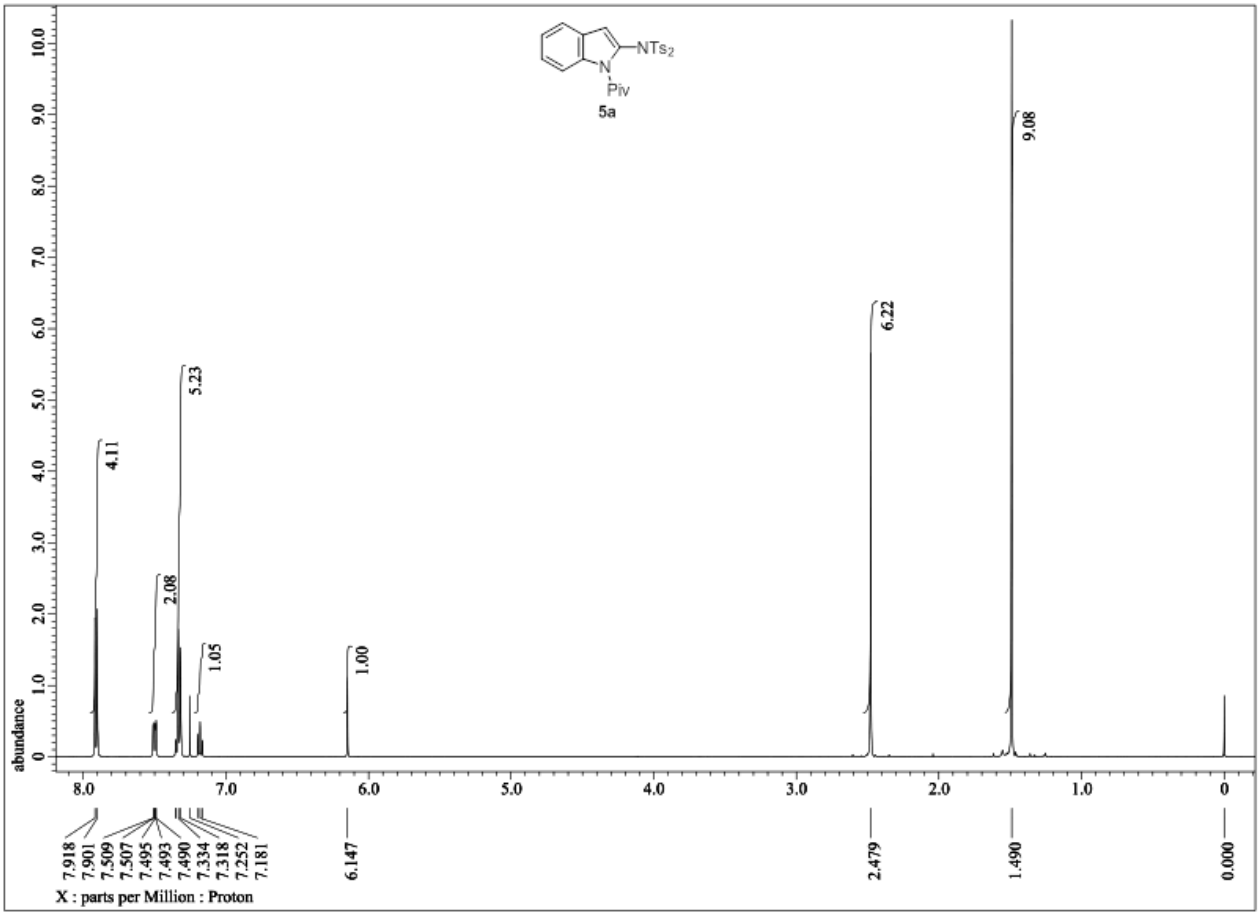

Br
Br
NTs2
N
Piv
2r
abundance
181.387
145.609
135.556
134.697
130.586
129.184
127.896
127.401
125.855
121.897
115.592
112.988
102.210
77.258
77.000
76.742
43.587
28.164
21.840
X : parts per Million : Carbon13

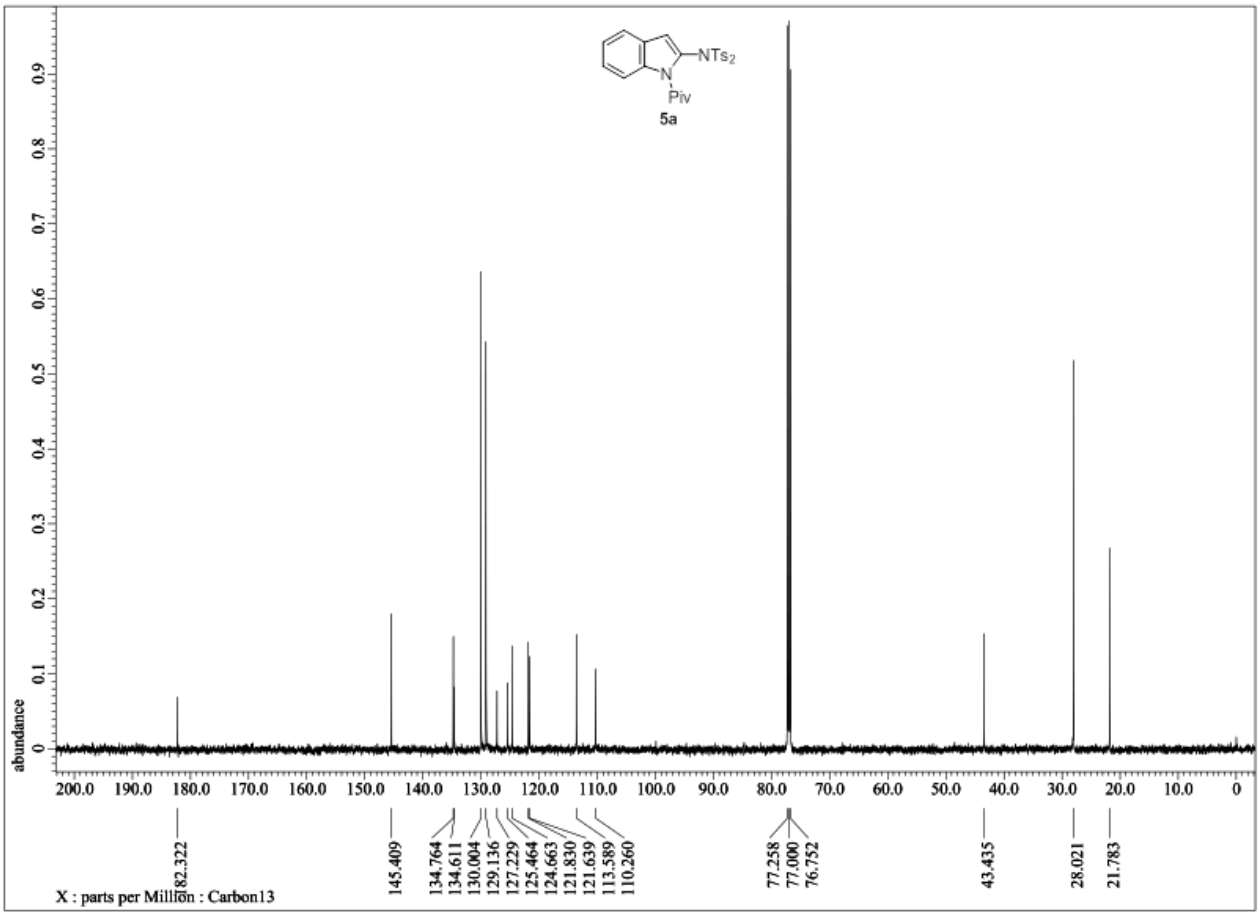

Br
NTs2
Cl
N
Piv
2s
abundance
X : parts per Million : Proton
4.04
4.05
1.45
1.00
0.99
6.07
9.01
7.964
7.951
7.948
7.536
7.534
7.445
7.428
7.336
7.320
7.257
7.254
7.240
7.237
2.475
1.488
0.000

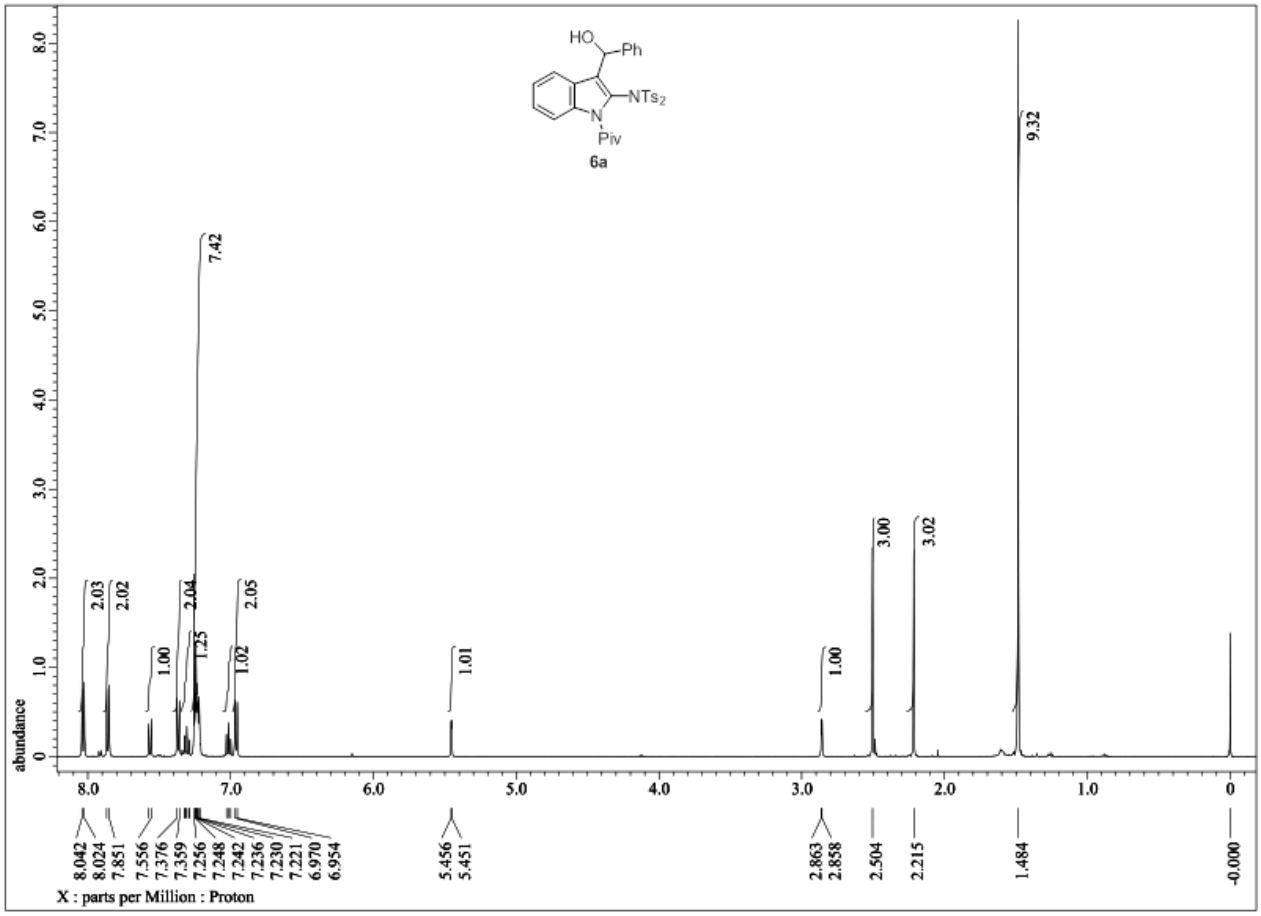

Br
NTs2
Cl
N
Piv
2s
abundance
X : parts per Million : Carbon13
180.739
145.590
135.289
133.648
132.046
130.405
129.232
126.723
124.100
123.070
121.964
113.723
103.097
77.248
77.000
76.742
43.187
28.097
21.811

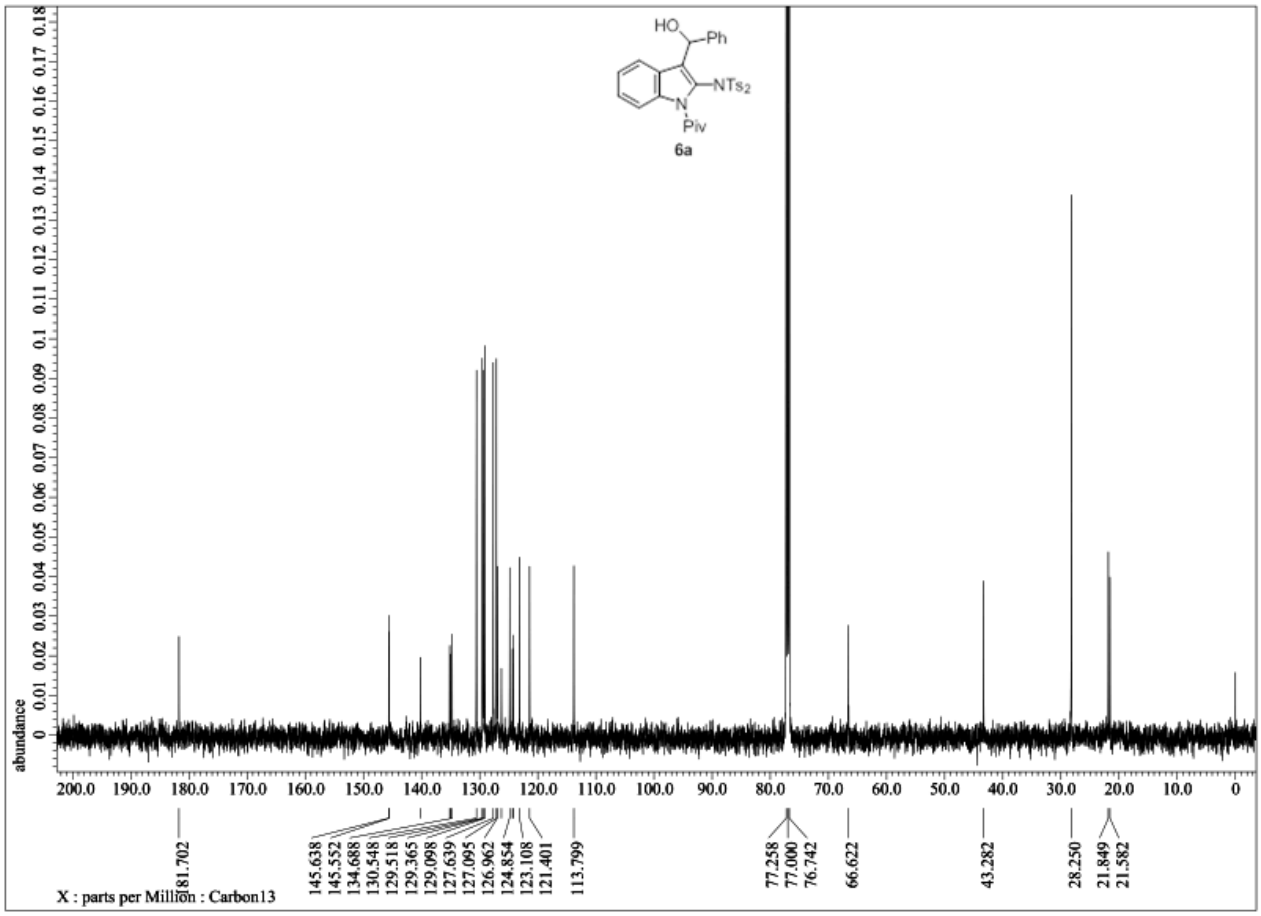

Br
NTs2
N
Piv
2t
9.05
6.19
6.06
3.00
2.08
2.05
2.18
abundance
8.143
7.760
7.381
7.377
7.366
7.363
7.256
7.198
7.183
7.168
7.165
2.477
2.357
1.323
0.000
X : parts per Million : Proton

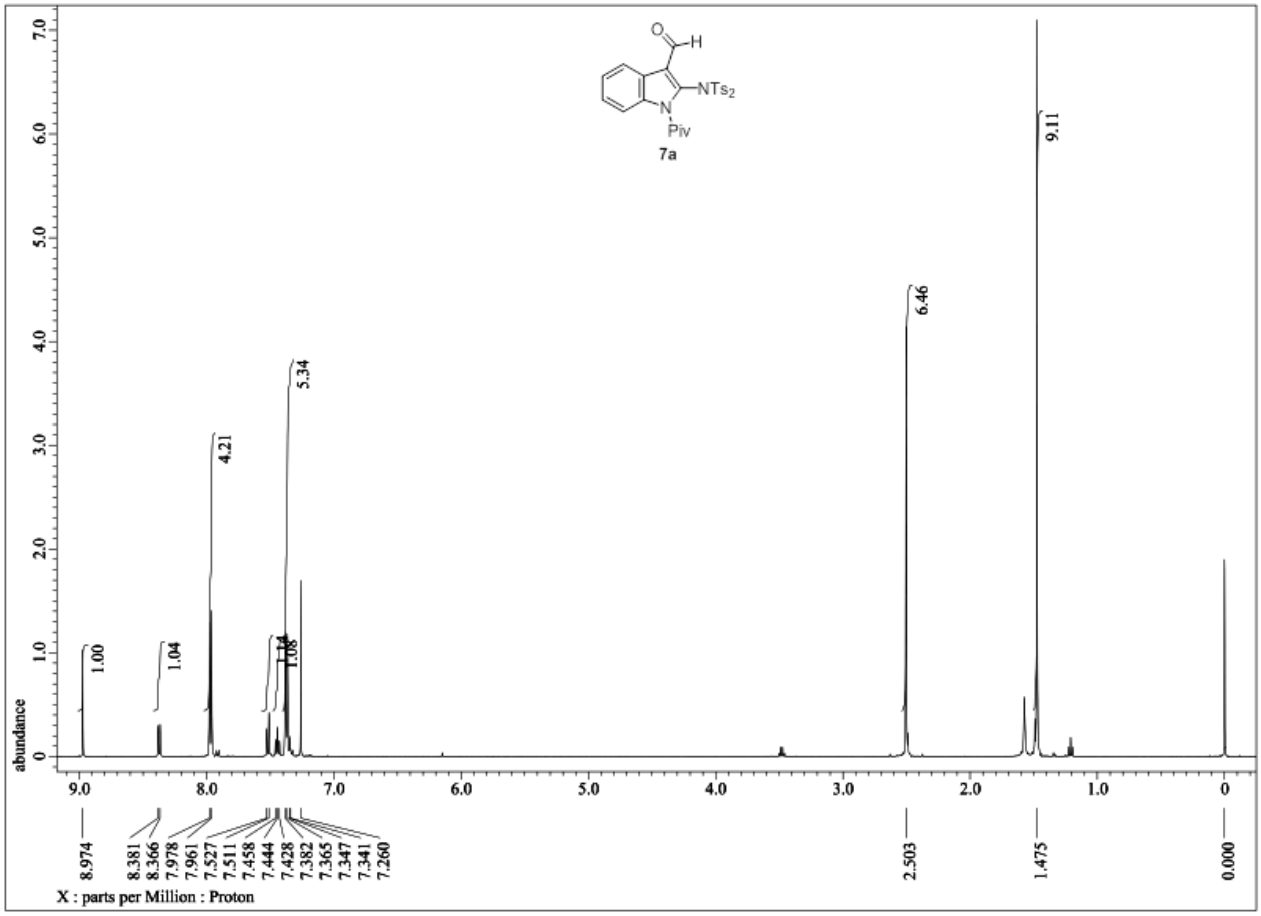

Br
NTs2
N
Piv
2t
abundance
184.382
145.943
136.052
130.539
129.289
128.860
127.639
125.417
122.431
122.326
118.730
102.677
77.258
77.000
76.752
44.665
28.574
28.459
21.792
20.848
X : parts per Million : Carbon13

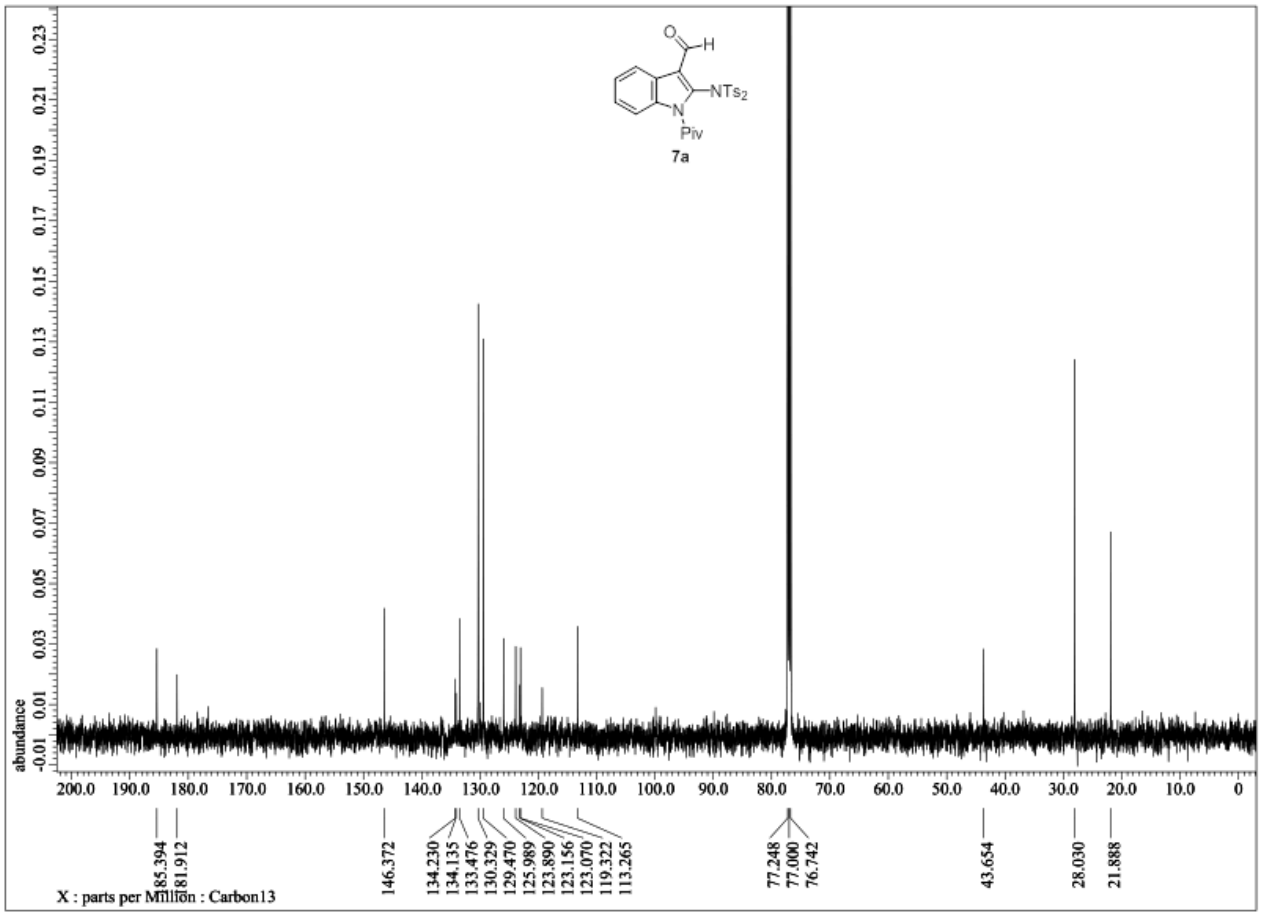

NTs2
N
Piv
5a
abundance
4.11
2.08
5.23
1.05
1.00
6.22
9.08
7.918
7.901
7.509
7.507
7.495
7.493
7.490
7.334
7.318
7.252
7.181
6.147
2.479
1.490
0.000
X : parts per Million : Proton

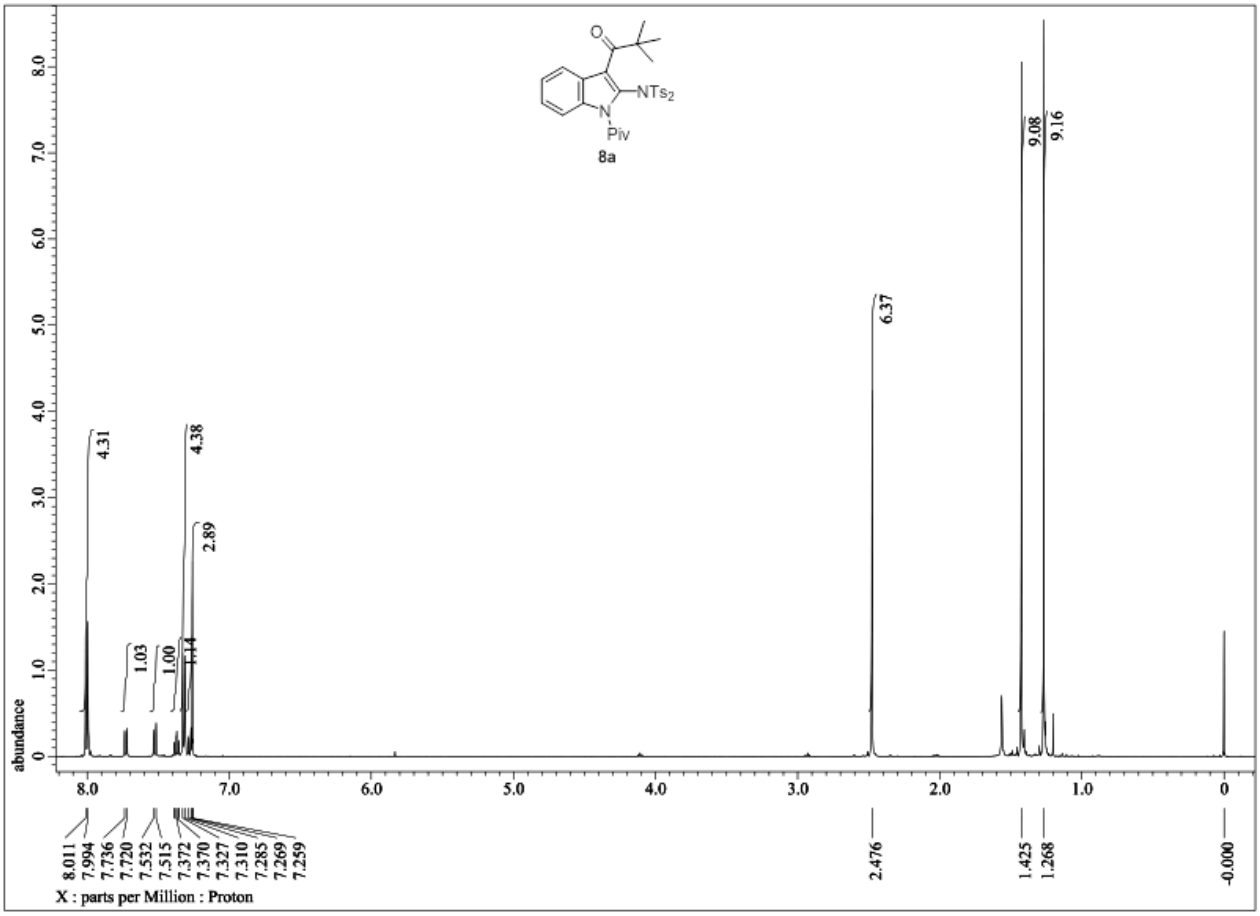

NTs2
N
Piv
5a
abundance
82.322
145.409
134.764
134.611
130.004
129.136
127.229
125.464
124.663
121.830
121.639
113.589
110.260
77.258
77.000
76.752
43.435
28.021
21.783
X : parts per Million : Carbon13

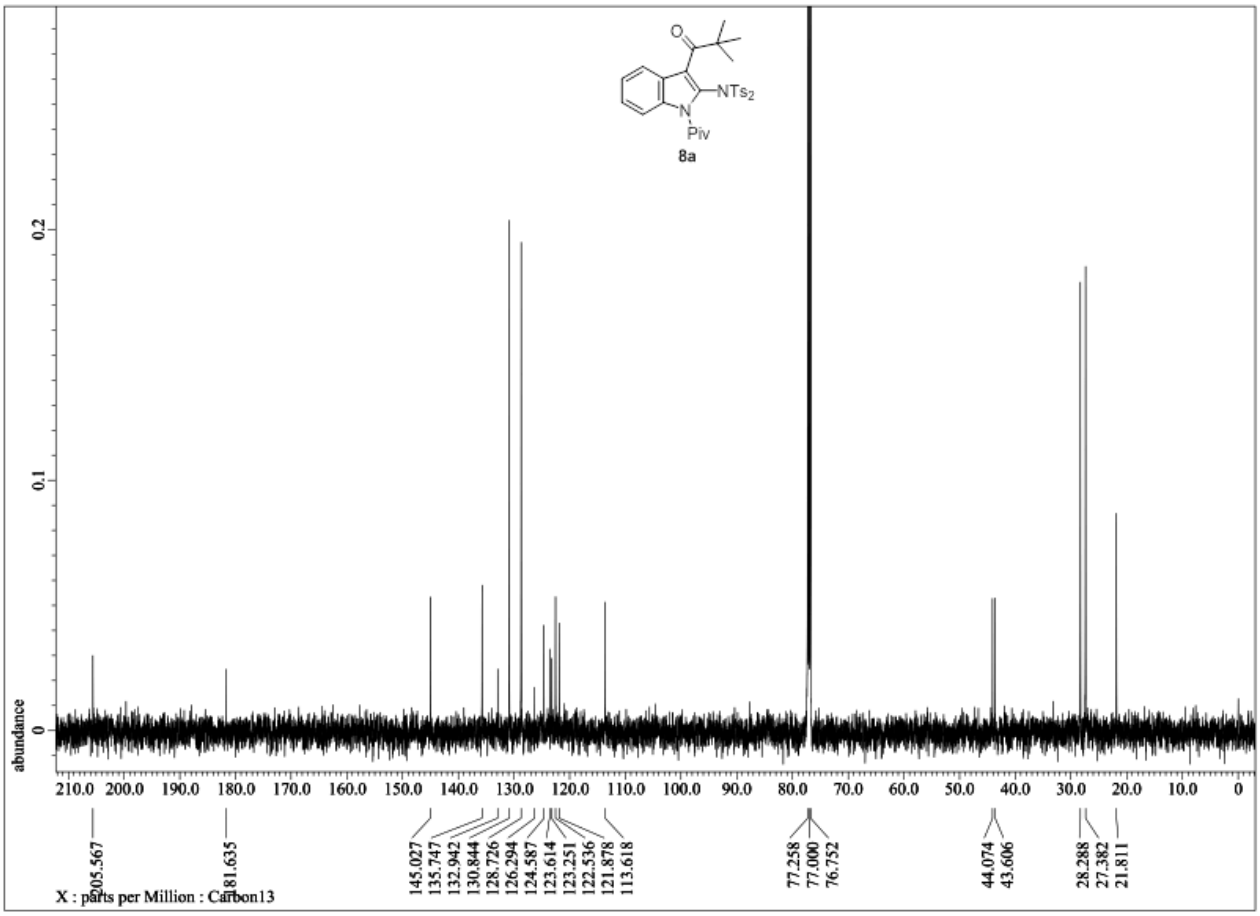

HO
Ph
NTs2
N
Piv
6a
abundance
X : parts per Million : Proton
9.32
7.42
3.00
3.02
2.03
2.02
2.04
2.05
1.25
1.00
1.02
1.01
1.00
8.042
8.024
7.851
7.556
7.376
7.359
7.256
7.248
7.242
7.236
7.230
7.221
6.970
6.954
5.456
5.451
2.863
2.858
2.504
2.215
1.484
-0.000

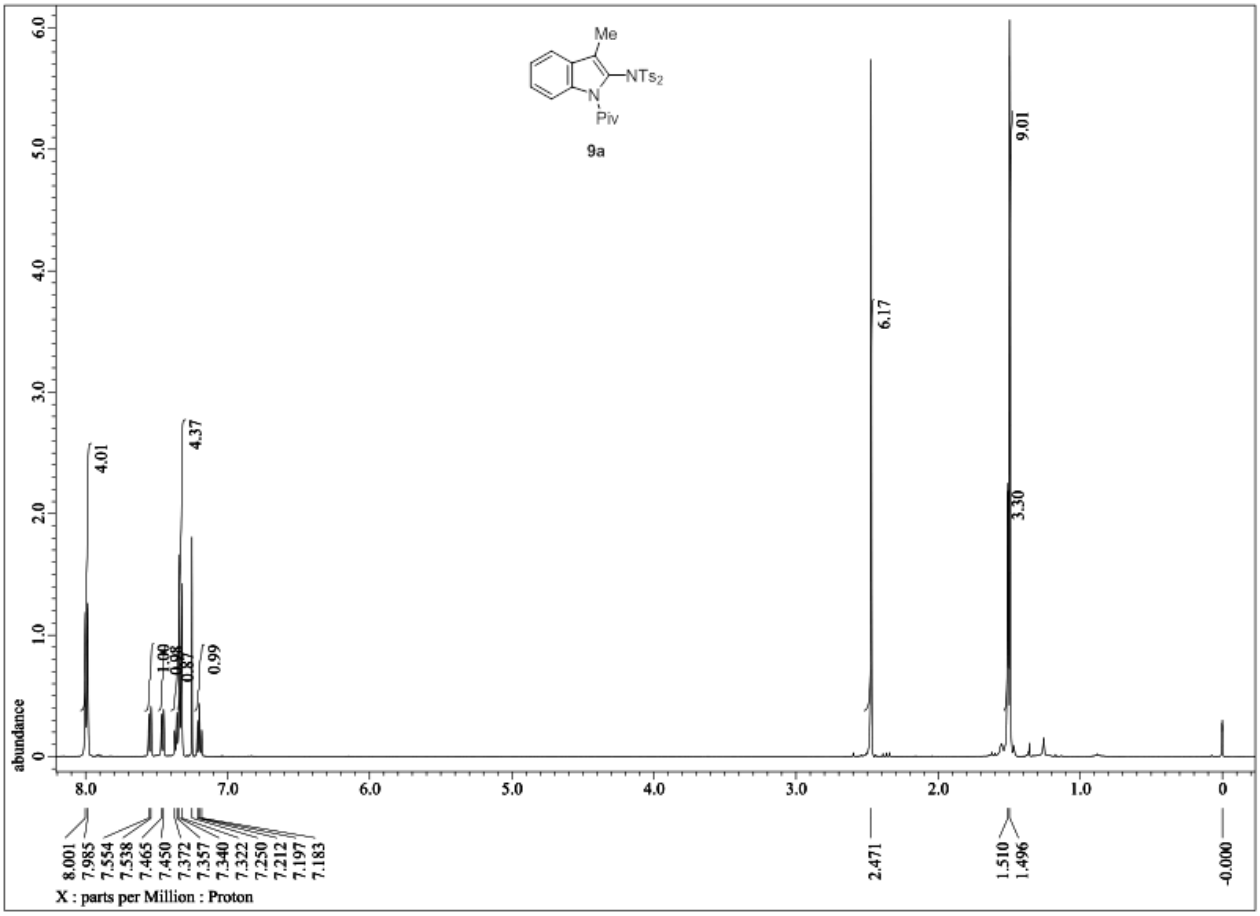

HO
Ph
NTs2
N
Piv
6a
abundance
X : parts per Million : Carbon13
181.702
145.638
145.552
134.688
130.548
129.518
129.365
129.098
127.639
127.095
126.962
124.854
123.108
121.401
113.799
77.258
77.000
76.742
66.622
43.282
28.250
21.849
21.582

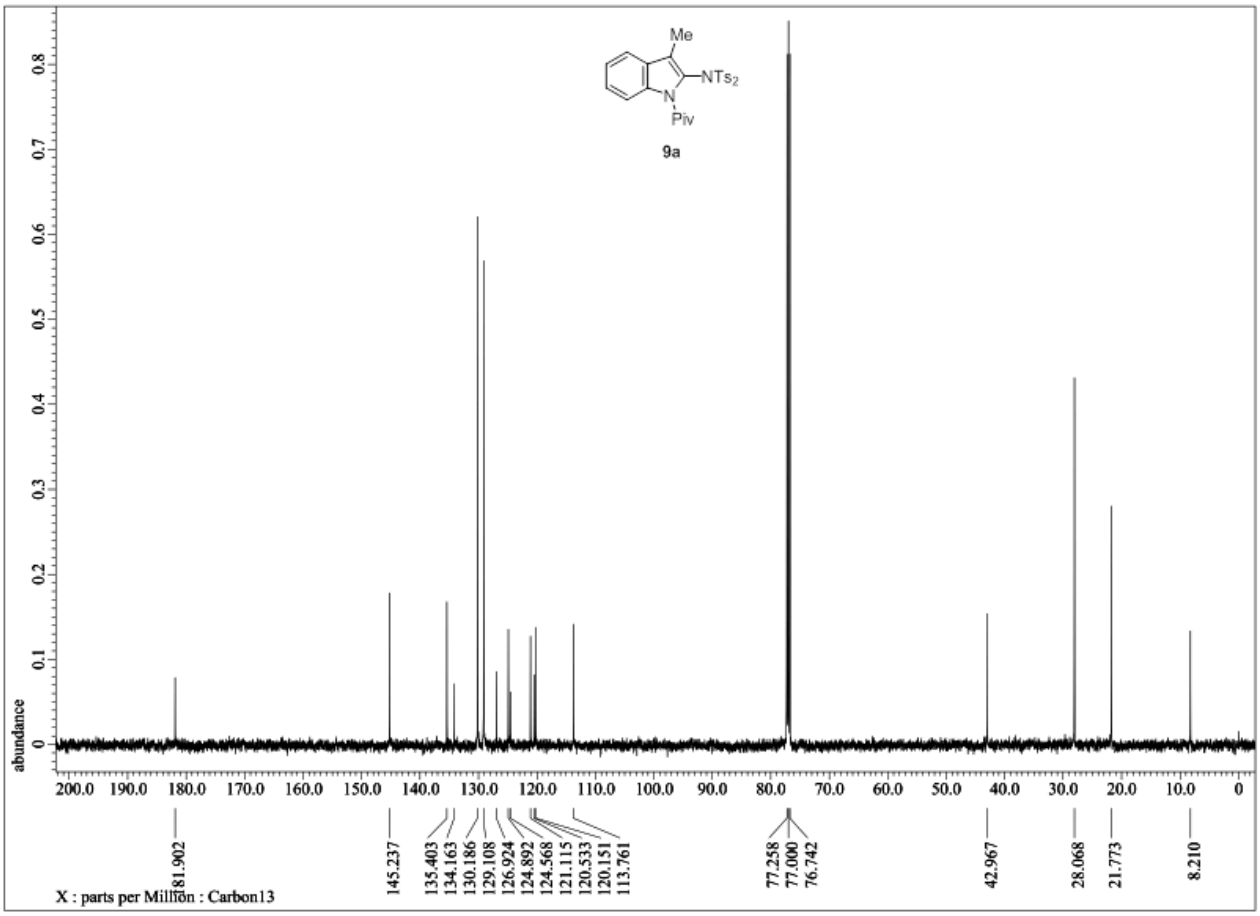

O
H
NTs2
N
Piv
7a
9.11
6.46
5.34
4.21
1.00
1.04
1.08
abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.974
8.381
8.366
7.978
7.961
7.527
7.511
7.458
7.444
7.428
7.382
7.365
7.347
7.341
7.260
2.503
1.475
0.000
X : parts per Million : Proton

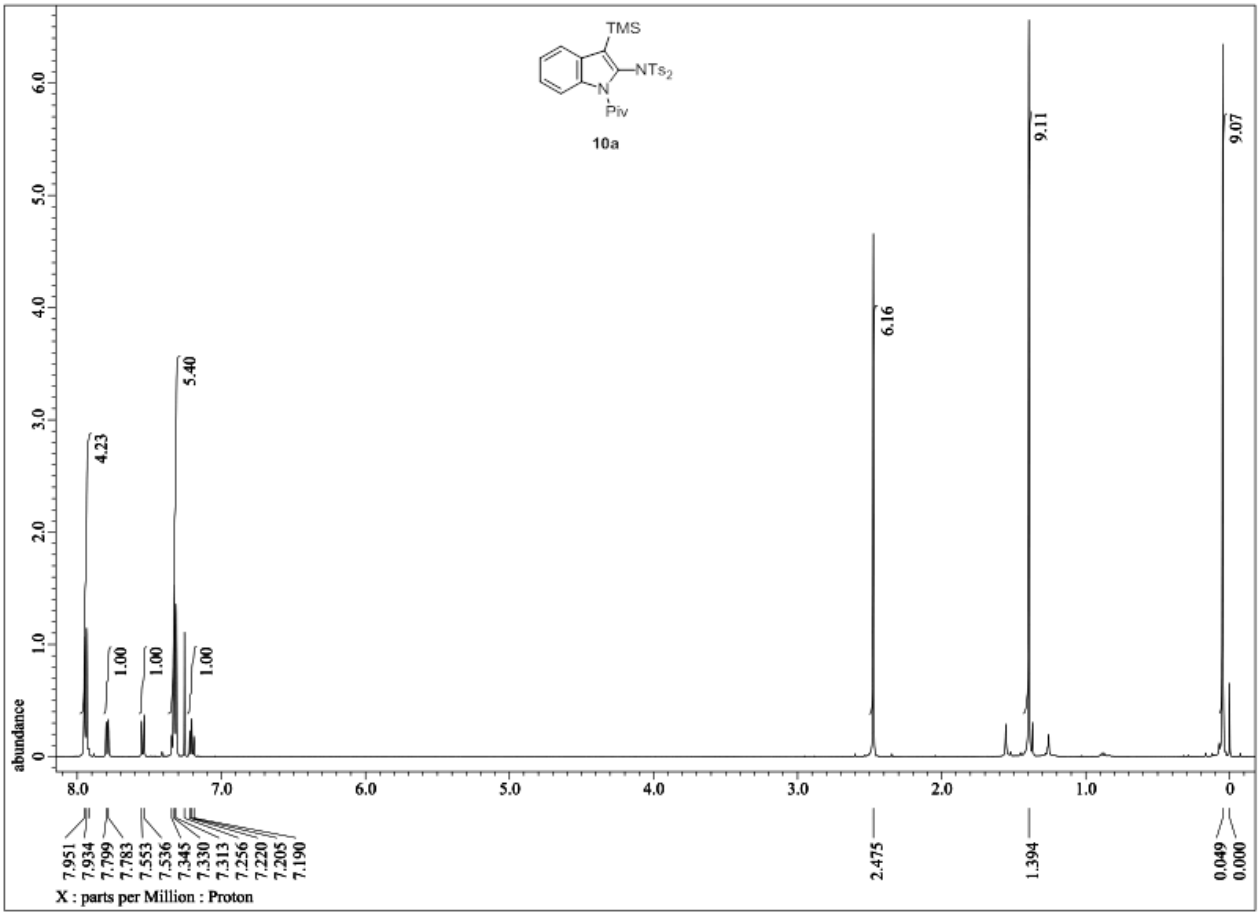

O
H
NTs2
N
Piv
7a
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
185.394
181.912
146.372
134.230
134.135
133.476
130.329
129.470
125.989
123.890
123.156
123.070
119.322
113.265
77.248
77.000
76.742
43.654
28.030
21.888
X : parts per Million : Carbon13

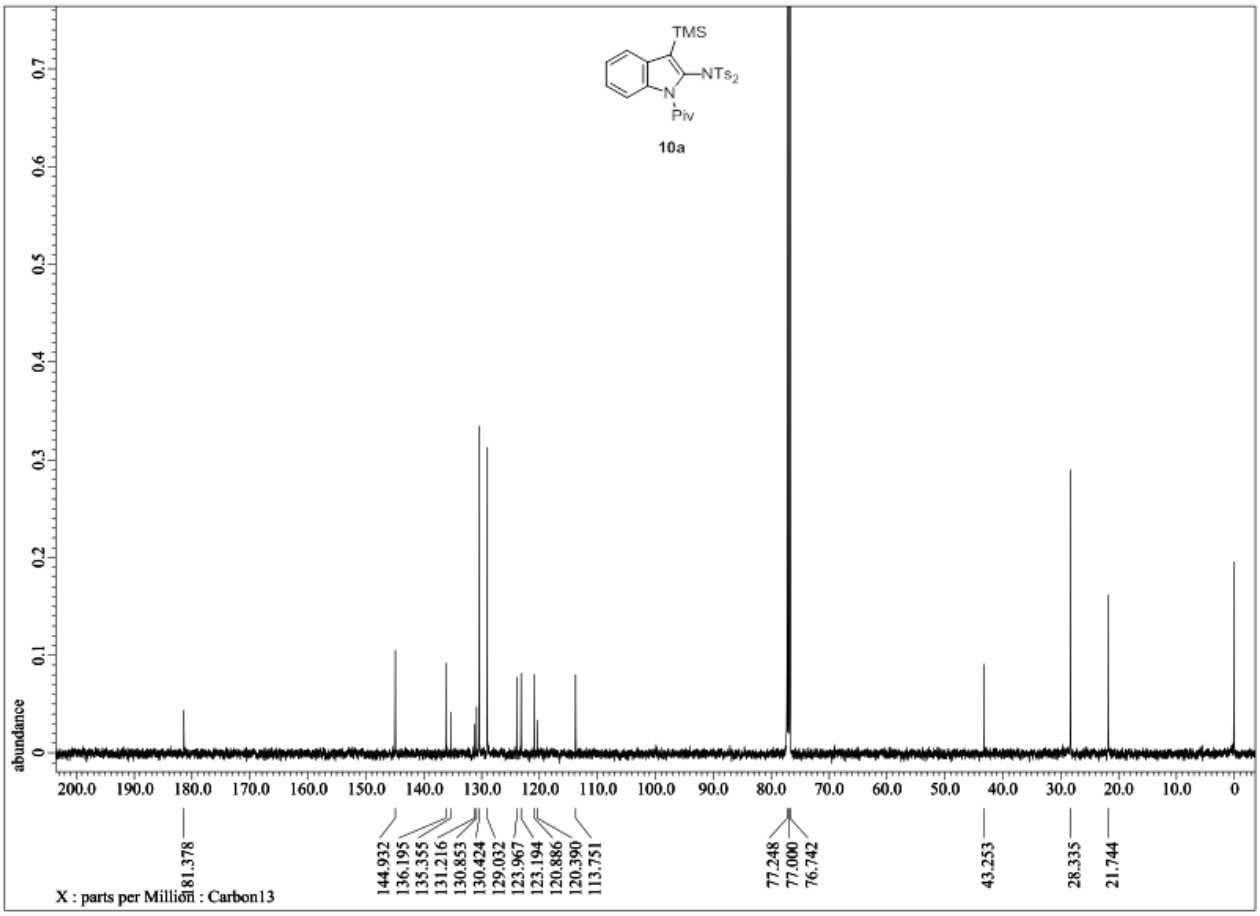

8a
NTs2
Piv
abundance
4.31
4.38
2.89
1.03
1.00
1.14
6.37
9.08
9.16
8.011
7.994
7.736
7.720
7.532
7.515
7.372
7.370
7.327
7.310
7.285
7.269
7.259
2.476
1.425
1.268
-0.000
X : parts per Million : Proton

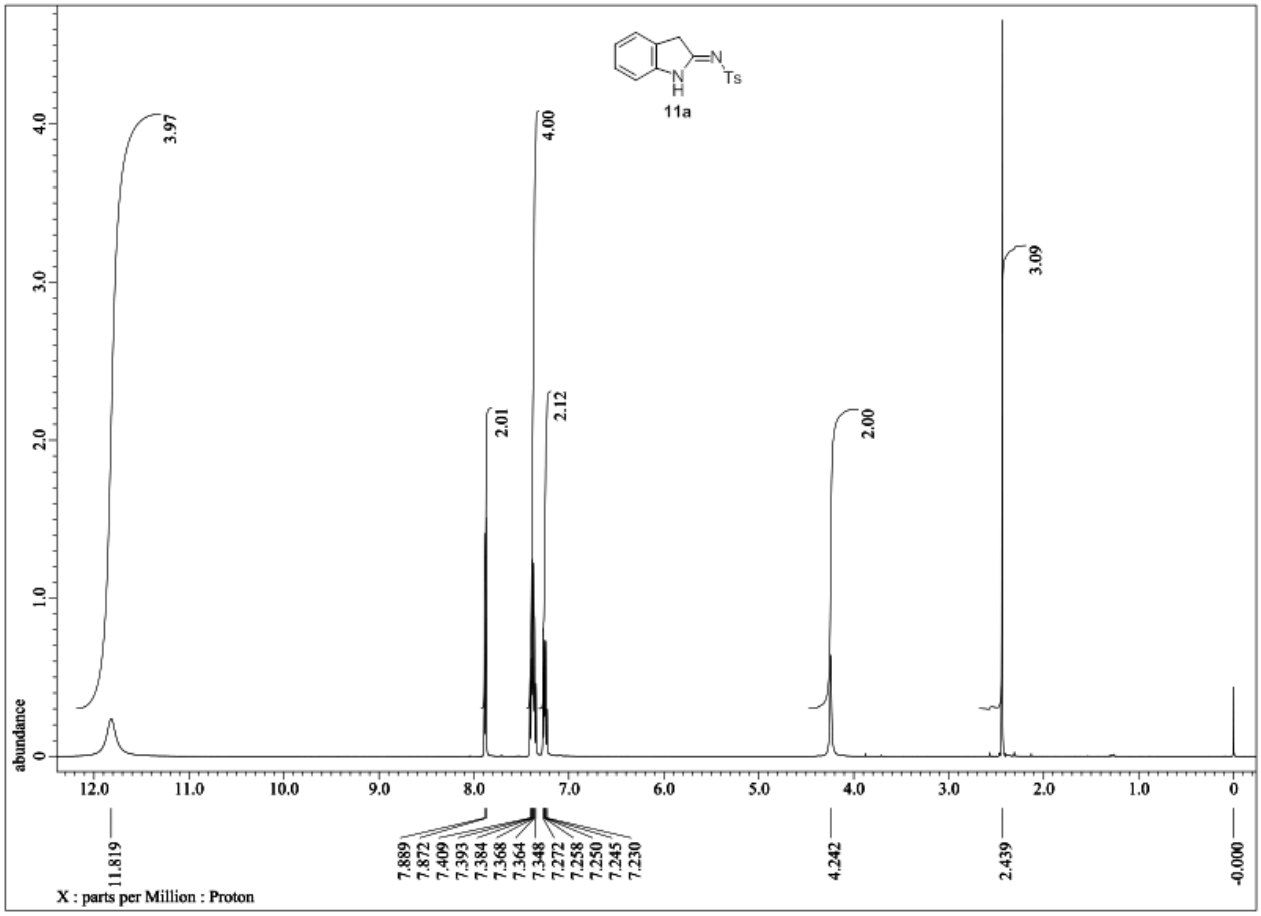

8a
NTs2
Piv
abundance
205.567
181.635
145.027
135.747
132.942
130.844
128.726
126.294
124.587
123.614
123.251
122.536
121.878
113.618
77.258
77.000
76.752
44.074
43.606
28.288
27.382
21.811
X : parts per Million : Carbon13

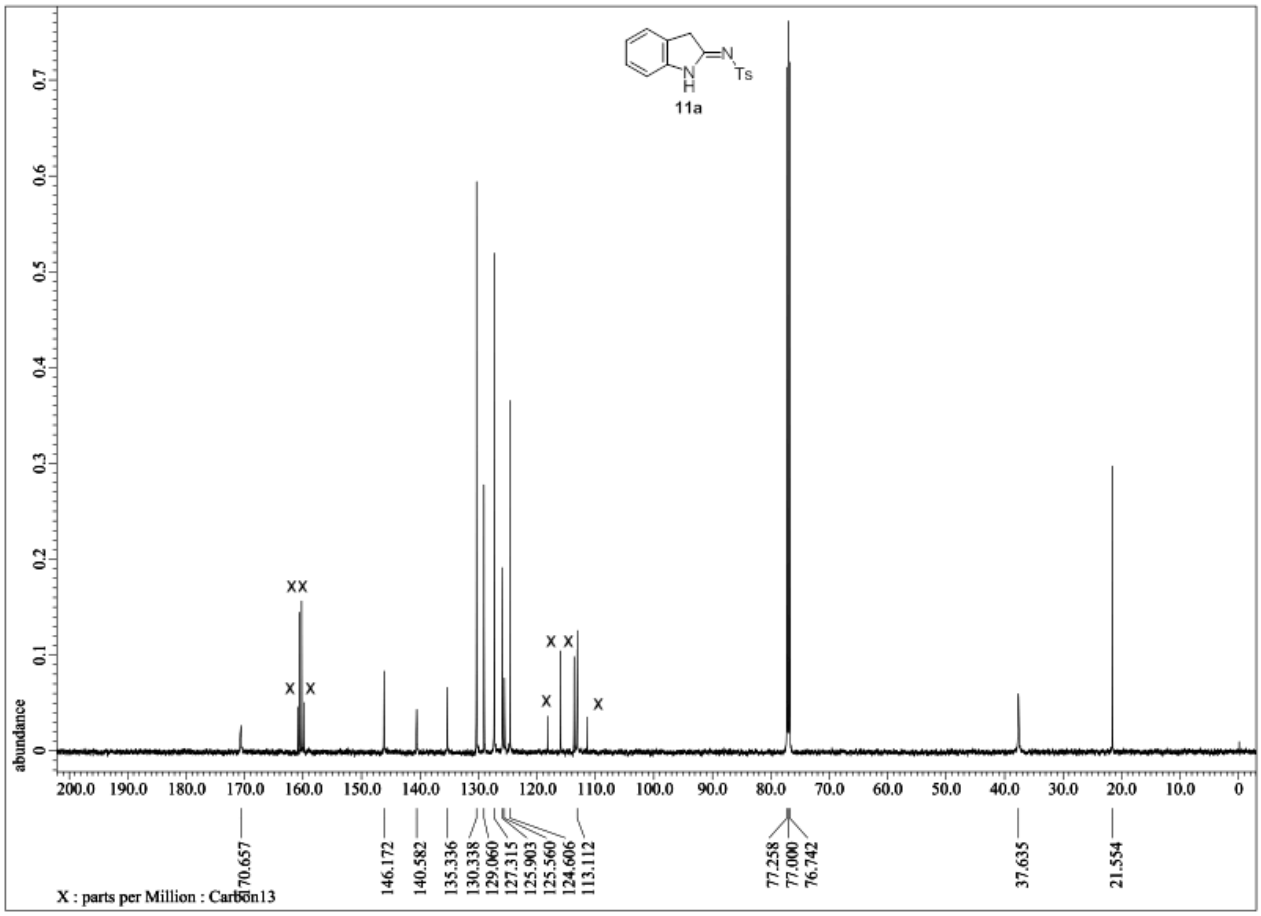

Me
NTs2
N
Piv
9a
abundance
X : parts per Million : Proton
4.01
4.37
6.17
9.01
3.30
0.99
8.001
7.985
7.554
7.538
7.465
7.450
7.372
7.357
7.340
7.322
7.250
7.212
7.197
7.183
2.471
1.510
1.496
-0.000

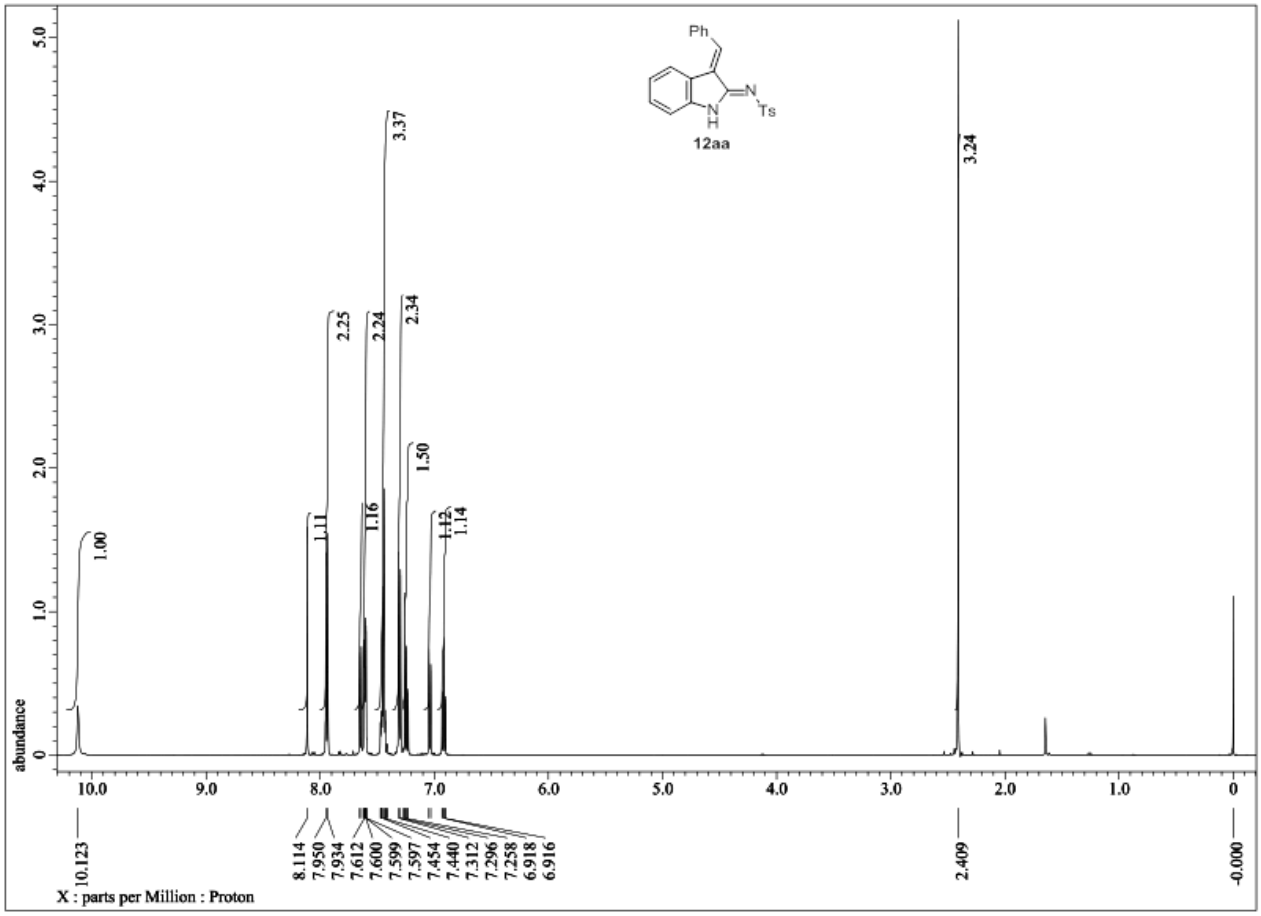

Me
NTs2
N
Piv
9a
abundance
X : parts per Million : Carbon13
181.902
145.237
135.403
134.163
130.186
129.108
126.924
124.892
124.568
121.115
120.533
120.151
113.761
77.258
77.000
76.742
42.967
28.068
21.773
8.210

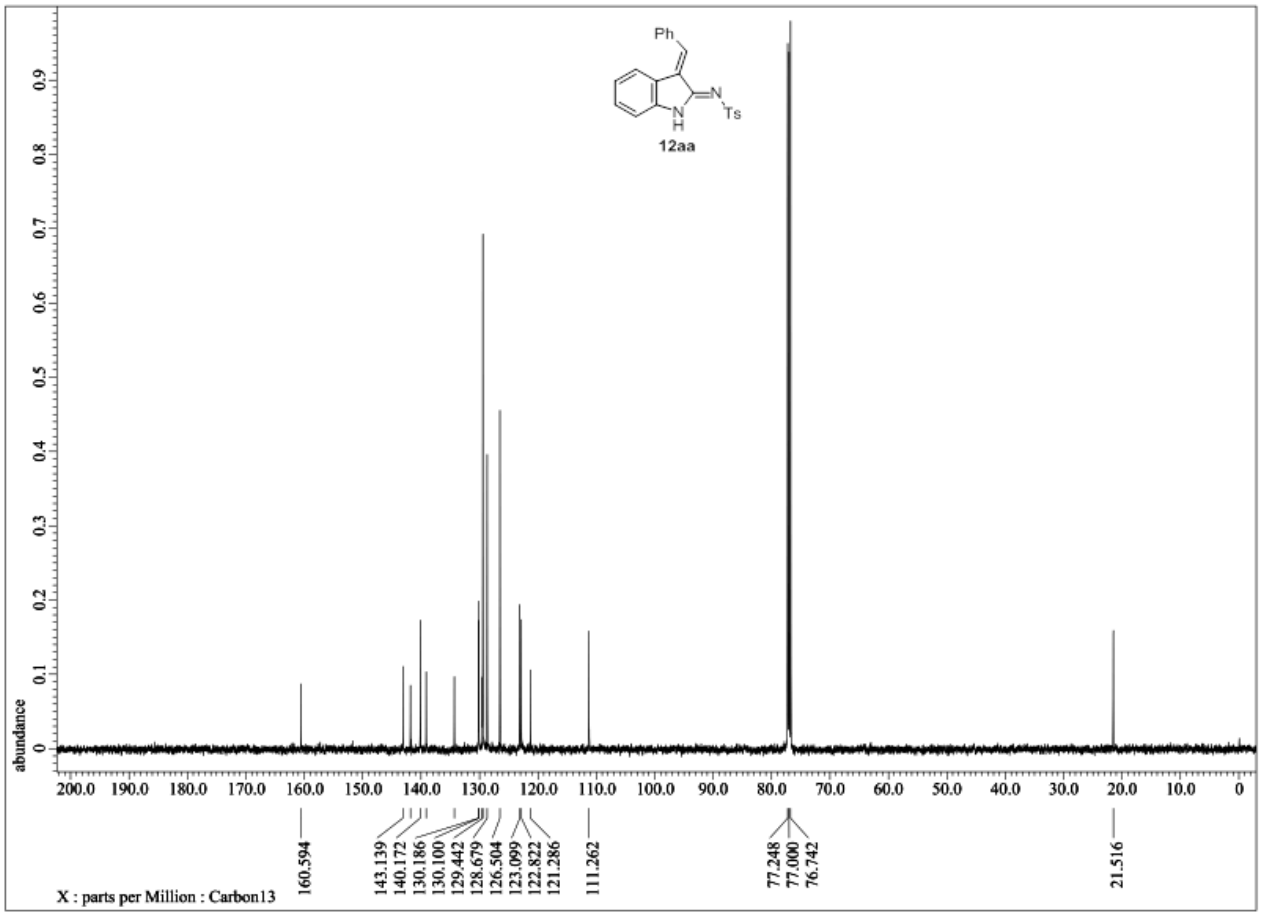

TMS
NTs2
N
Piv
10a
abundance
X : parts per Million : Proton
7.951
7.934
7.799
7.783
7.553
7.536
7.345
7.330
7.313
7.256
7.220
7.205
7.190
4.23
1.00
1.00
5.40
1.00
6.16
2.475
9.11
1.394
9.07
0.049
0.000

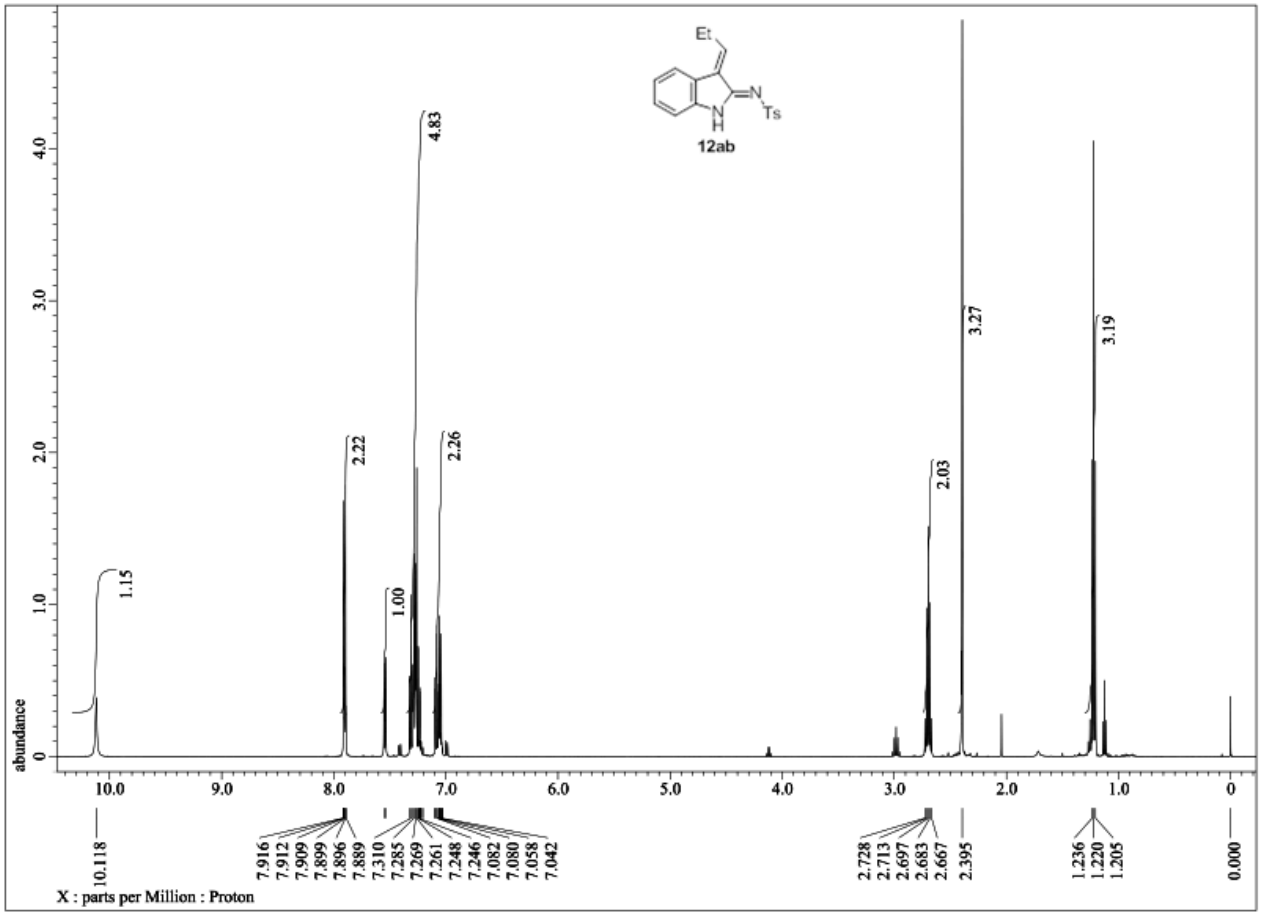

TMS
NTs2
N
Piv
10a
abundance
X : parts per Million : Carbon13
181.378
144.932
136.195
135.355
131.216
130.853
130.424
129.032
123.967
123.194
120.886
120.390
113.751
77.248
77.000
76.742
43.253
28.335
21.744

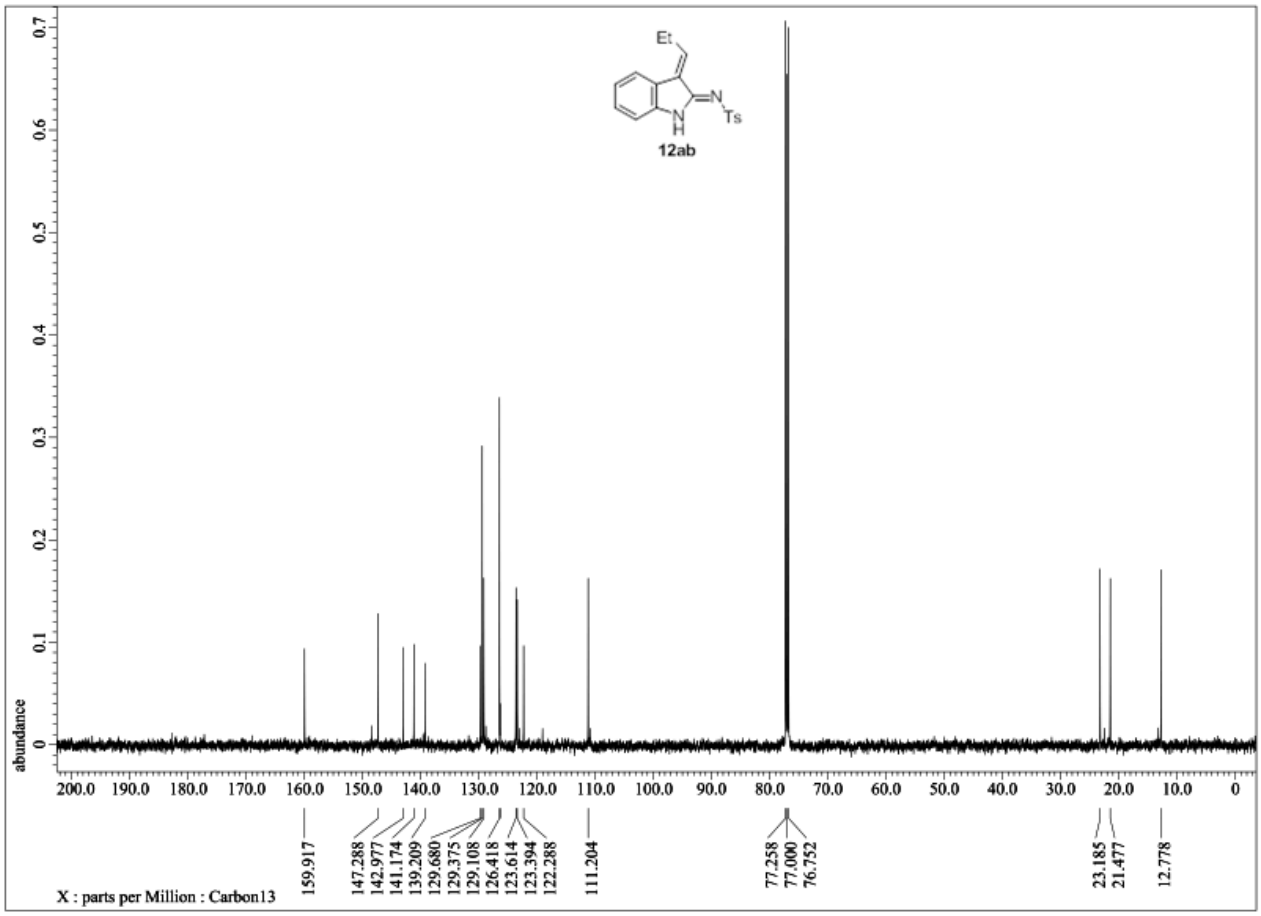

11a
3.97
4.00
3.09
2.01
2.12
2.00
abundance
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
11.819
7.889
7.872
7.409
7.393
7.384
7.368
7.364
7.348
7.272
7.258
7.250
7.245
7.230
4.242
2.439
-0.000
X : parts per Million : Proton

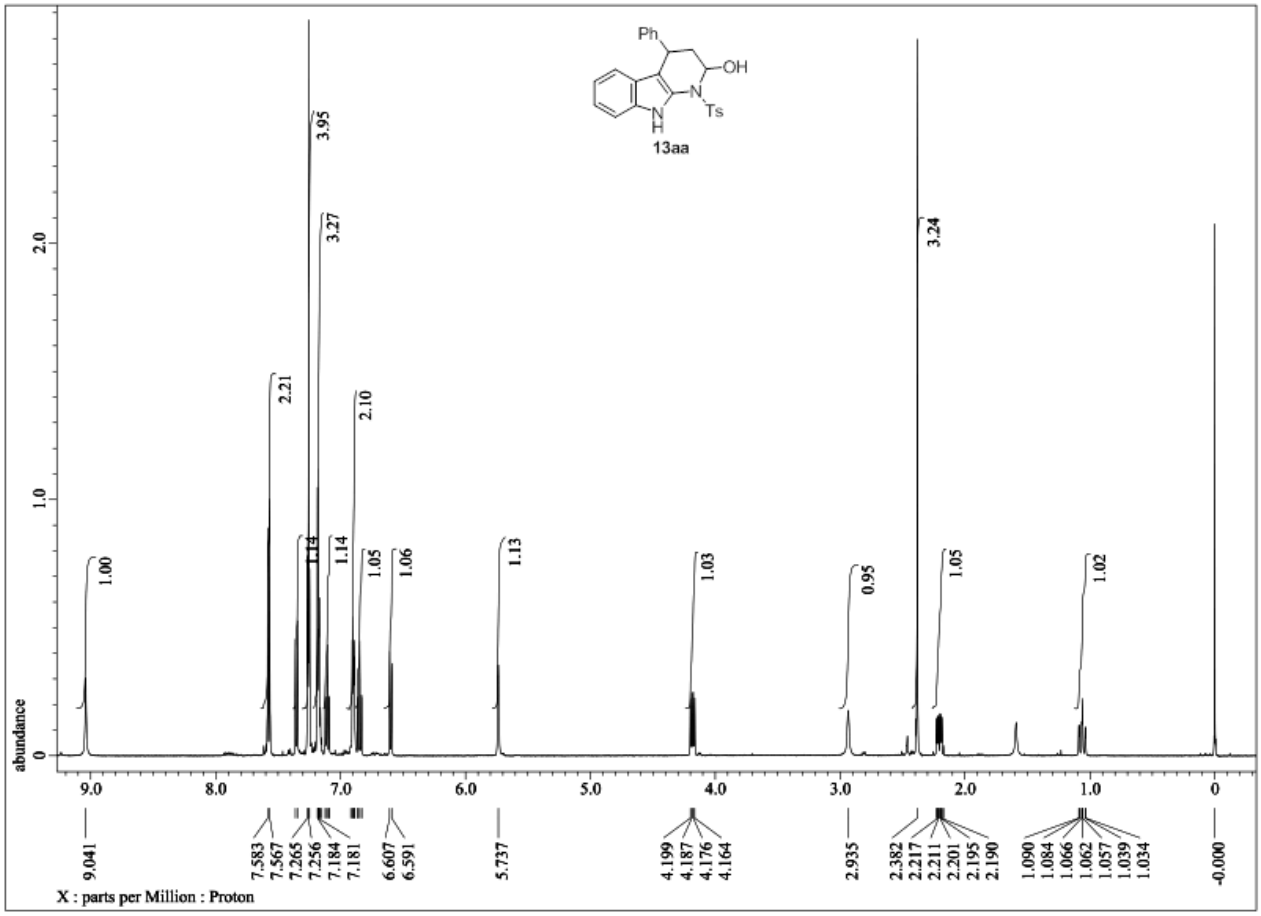

11a
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
170.657
146.172
140.582
135.336
130.338
129.060
127.315
125.903
125.560
124.606
113.112
77.258
77.000
76.742
37.635
21.554
X : parts per Million : Carbon13

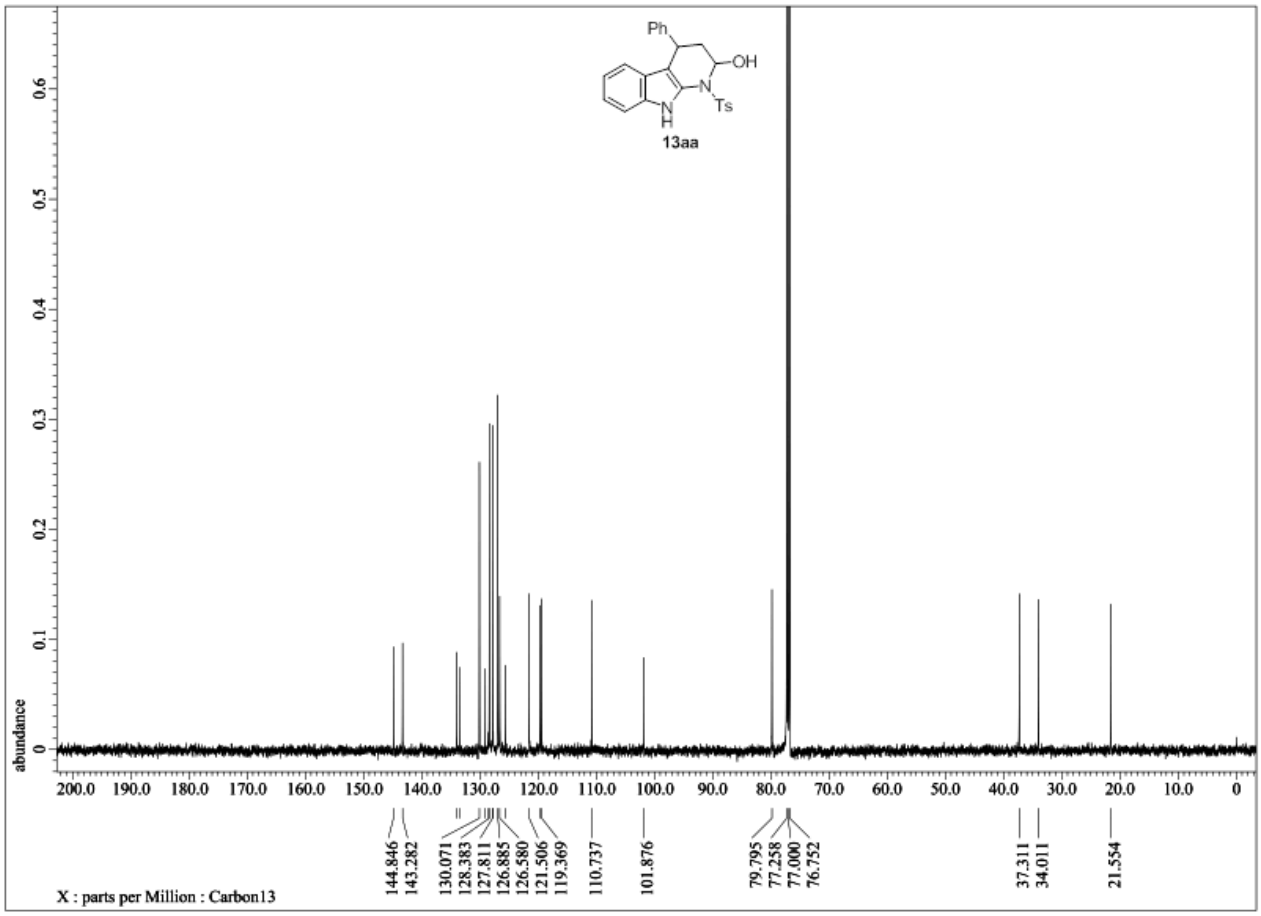

Ph
N
Ts
H
12aa
3.37
3.24
2.25
2.24
2.34
1.50
1.16
1.11
1.12
1.14
1.00
abundance
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.123
8.114
7.950
7.934
7.612
7.600
7.599
7.597
7.454
7.440
7.312
7.296
7.258
6.918
6.916
2.409
-0.000
X : parts per Million : Proton

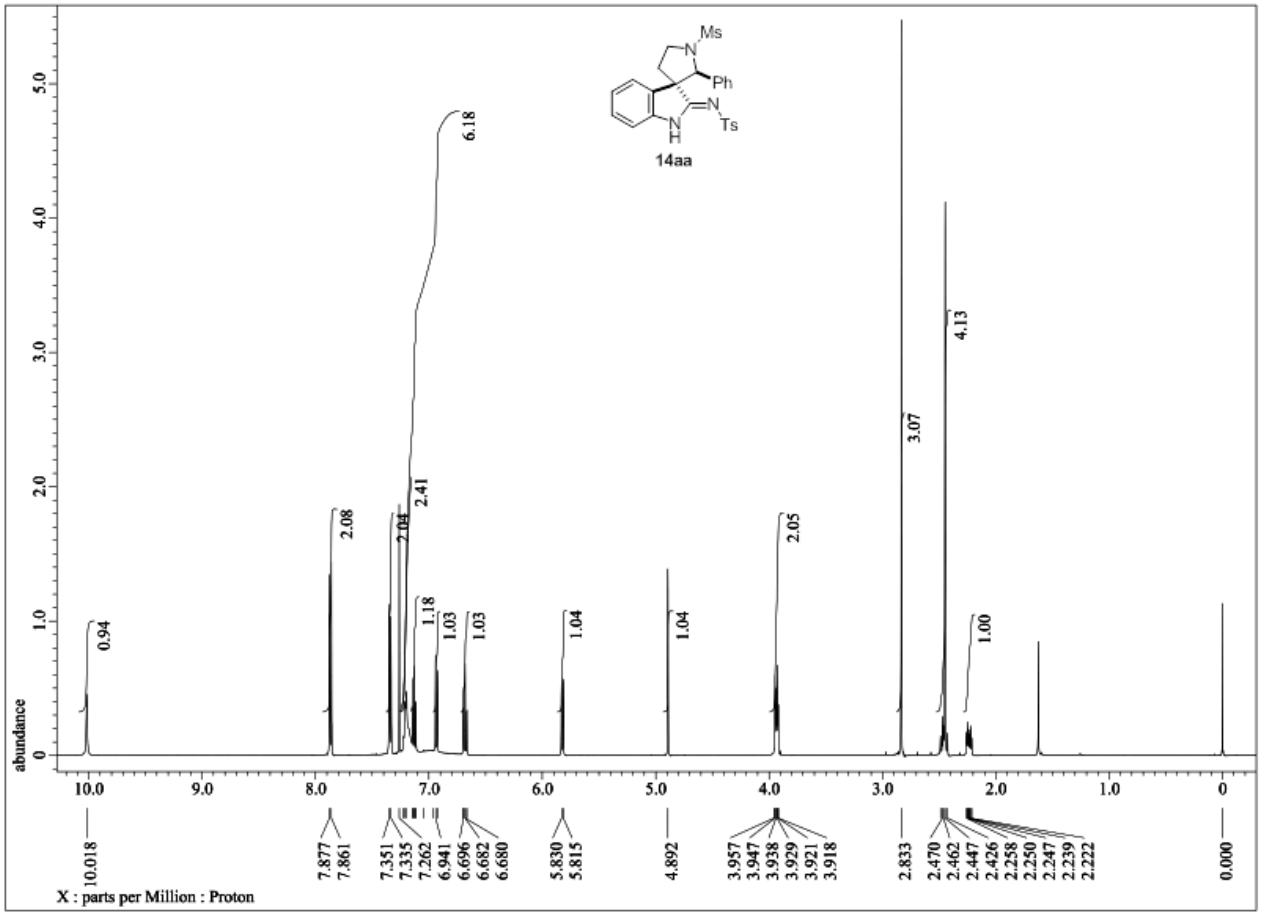

Ph
N
Ts
H
12aa
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
160.594
143.139
140.172
130.186
130.100
129.442
128.679
126.504
123.099
122.822
121.286
111.262
77.248
77.000
76.742
21.516
X : parts per Million : Carbon13

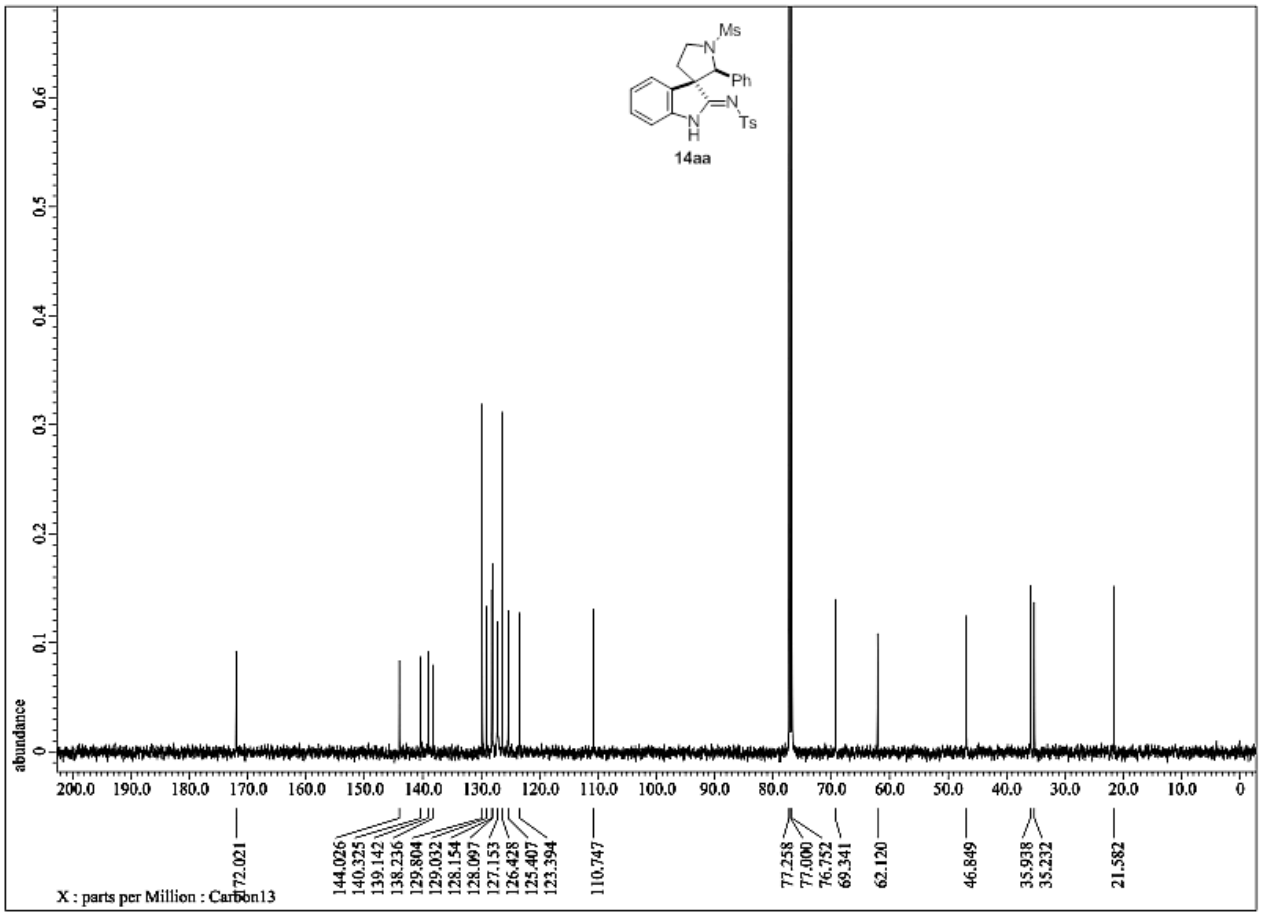

Et
N
Ts
H
12ab
4.83
2.22
2.26
1.15
1.00
2.03
3.27
3.19
abundance
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.118
7.916
7.912
7.909
7.899
7.896
7.889
7.310
7.285
7.269
7.261
7.248
7.246
7.082
7.080
7.058
7.042
2.728
2.713
2.697
2.683
2.667
2.395
1.236
1.220
1.205
0.000
X : parts per Million : Proton

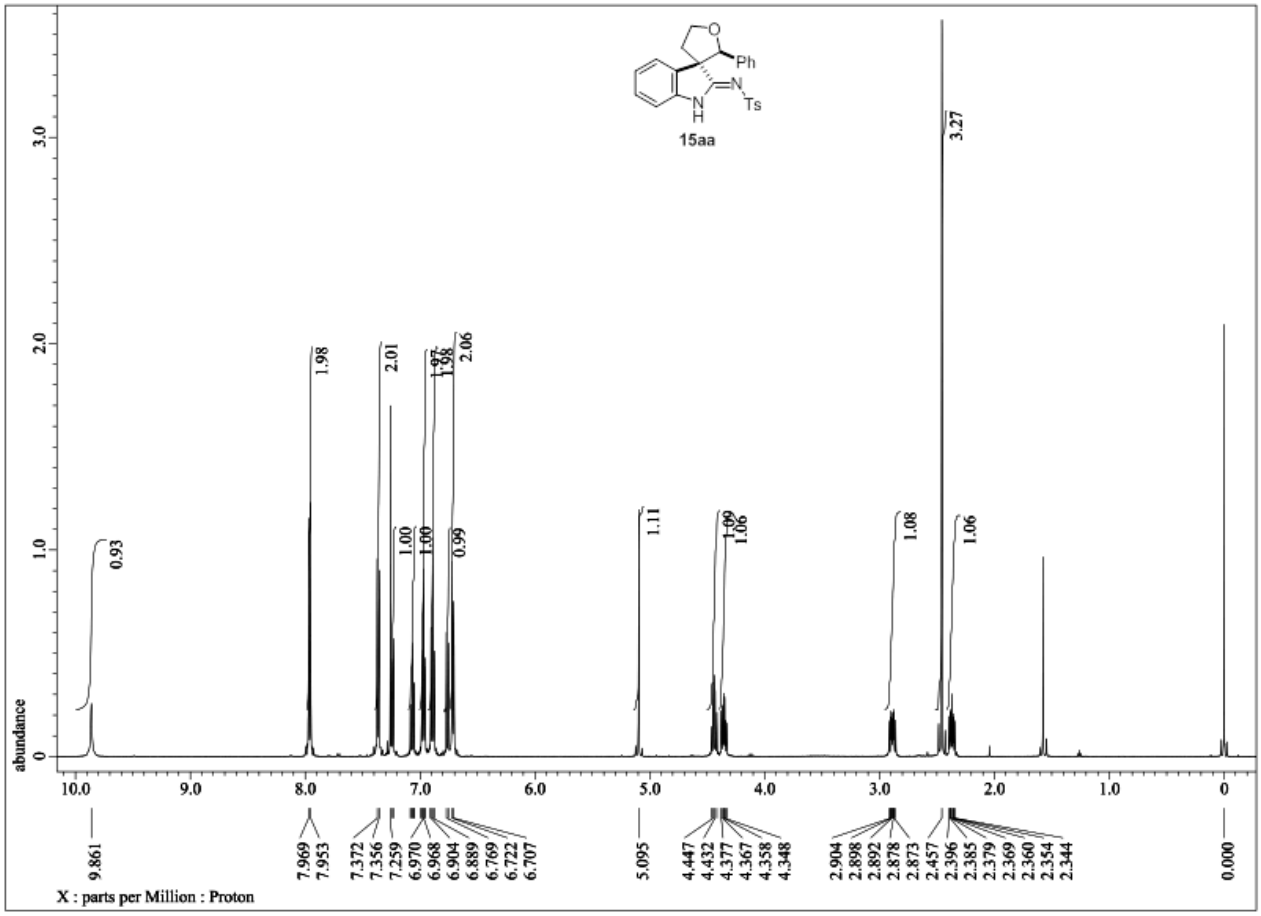

Et
N
Ts
H
12ab
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
159.917
147.288
142.977
141.174
139.209
129.680
129.375
129.108
126.418
123.614
123.394
122.288
111.204
77.258
77.000
76.752
23.185
21.477
12.778
X : parts per Million : Carbon13

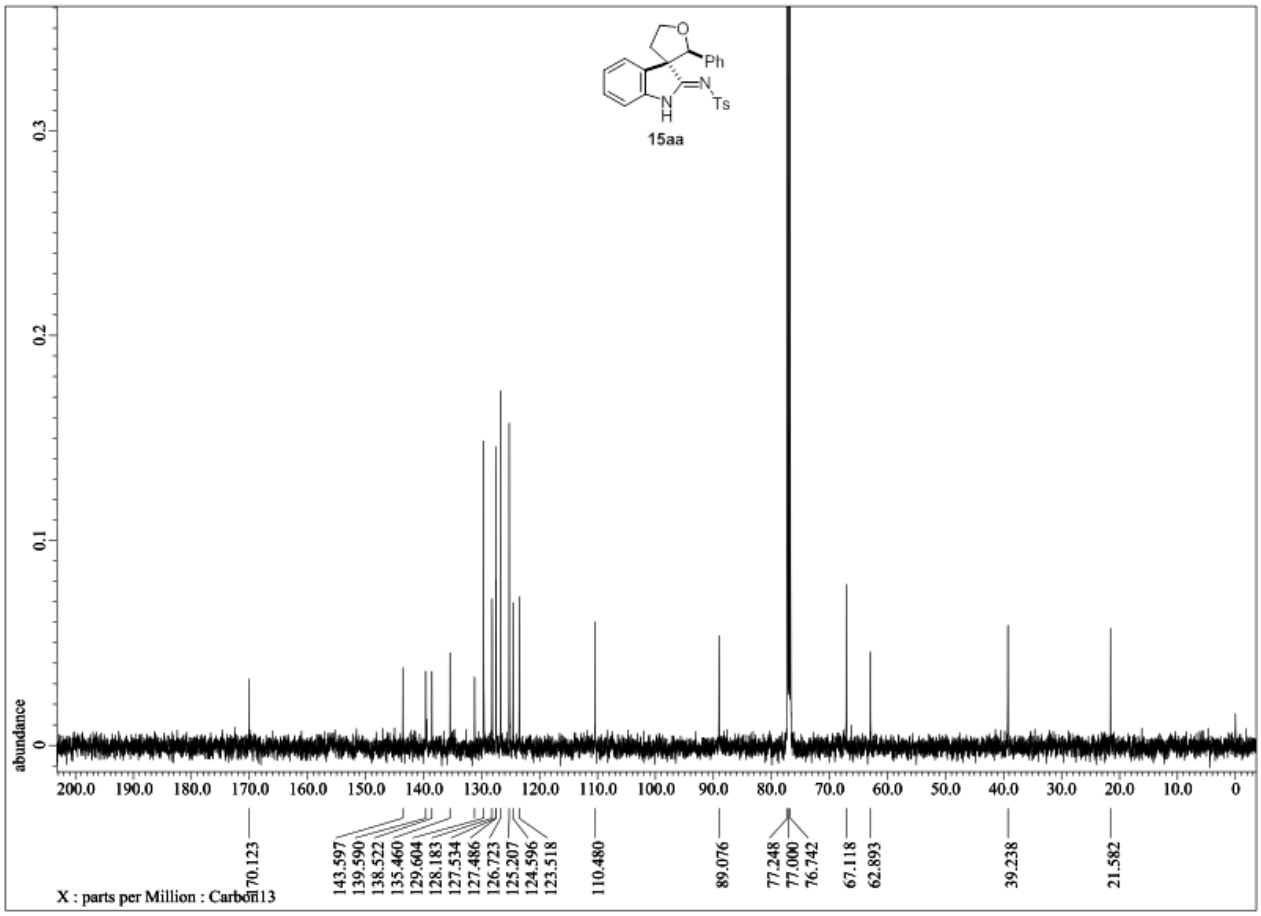

Ph
OH
N
Ts
H
13aa
abundance
X : parts per Million : Proton


Ph
OH
N
Ts
H
13aa
abundance
X : parts per Million : Carbon13


Ms
N
Ph
N
Ts
H
14aa
abundance
X : parts per Million : Proton


Ms
N
Ph
N
Ts
H
14aa
abundance
X : parts per Million : Carbon13


15aa
abundance
X : parts per Million : Proton


15aa
abundance
X : parts per Million : Carbon13