Direct use of allyl alcohols for palladium catalyzed synthesis of 3-allylbenzo[*b*]thiophenes, benzofuranes and indoles in aqueous media.

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Supporting Information

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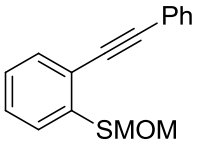
1. General Information.

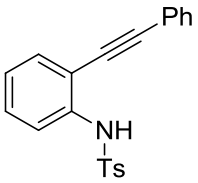
All melting points were determined on a microscopic melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR) spectrometer using $CDCl_3$ as solvent and TMS as internal standard. Coupling constants (J) are reported in hertz (Hz), and spin multiplicities are presented by the following symbols: s (singlet), br-s (broad singlet), d (doublet), br-d (broad doublet), t (triplet), q (quartet), quint (quintet) and m (multiplet). High resolution mass spectra were obtained using a high resolution EI or ESI-TOF mass spectrometer. Infrared spectra (IR) were recorded on a FT-IR spectrophotometer and are reported as wavelength numbers (cm^{-1}). All evaporations were performed under reduced pressure. For column chromatography, silica gel (63 - 200 mm) was employed.

2. Preparation of substrates.

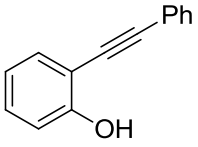
(*o*-alkynylphenyl) (methoxymethyl) sulfide **15** and 2-Alkynyl-*N*-tosylaniline **24** were prepared according to the published procedure.[1a, f] The substrate **1**, **2**, **3**, **17** and **22** were known compounds.[1a-e]



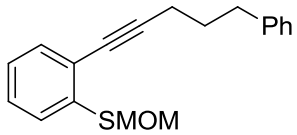
Methoxymethyl 2-(phenylethynyl)phenyl sulfide (**1**) [1a]



4-Methyl-*N*-{2-(phenylethynyl)phenyl}benzenesulfonamide (**2**) [1b]



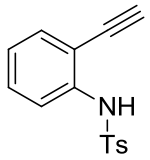
2-(2-Phenylethynyl)- phenol (**3**) [1c]



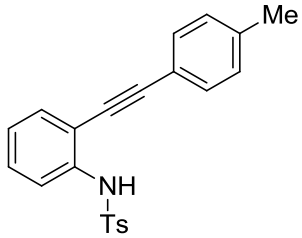
Methoxymethyl 2-(5-phenylpent-1-yn-1-yl) phenyl sulfide (**15**)

To a mixture of 2-iodophenyl methoxymethyl sulfide[1a] (280 mg, 1.0 mmol), $(PPh_3)_2PdCl_2$ (14.0 mg, 0.02 mmol), and CuI (7.6 mg, 0.04 mmol) in triethylamine (7 ml) under argon was added 5-phenyl-1-pentyne (216.3 mg, 1.5 mmol). The reaction mixture was stirred for 4.5 at 50℃. The mixture was diluted with ether, washed with saturated aqueous ammonium chloride, water and brine and dried over Mg_2SO_4. The crude product was purified by flash chromatography using hexane / ether (30 / 1) as eluent to obtain **15** in 86% yield (254.3 mg).

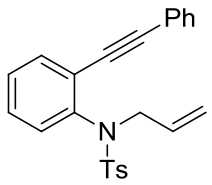
yellow oil, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.96 (2H, quint, *J* = 6.8 Hz), 2.50 (2H, t, *J* = 6.8Hz), 2.85 (2H, t, *J* = 7.6Hz), 3.44 (3H, s), 5.05 (2H, s), 7.20-7.29 (7H, m), 7.20-7.29 (7H, m) 7.38-7.40 (1H, m), 7.54-7.56 (1H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 19.1, 30.4, 34.8, 56.1, 76.2, 79.1, 96.1, 123.8, 125.7, 125.9, 128.1, 128.3, 128.4 (2C), 128.6 (2C), 132.5, 138.7, 141.7; IR (KBr): 2936, 2221, 1603, 1463, 1182, 1085, 751 cm^{-1}; HRMS-EI: m/z [M^+] calcd for $C_{19}H_{20}S$: 296.1235 ; found 296.1236



N-(2-Ethynyl-phenyl)-4-methyl-benzenesulfonamide (**17**) [1d]



4-Methyl-*N*-{2-(phenylethynyl)phenyl}benzenesulfonamide (**22**) [1e]



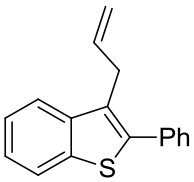
N-Allyl -*N*-{2-(phenylethynyl)phenyl}-4-methyl benzenesulfonamide (**24**)

To a solution of **2** (200 mg, 0.576 mmol) in acetone (7 mL) were added allyl bromide (78 μL, 0.922 mmol) and K_2CO_3 (119.4 mg, 0.864 mmol) at rt, and the mixture was refluxed for 4.5 h. After removal of solvent, the residue was dissolved in AcOEt. The organic layer was successively washed with water, saturated NaCl aq. solution, dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography using hexane / AcOEt (20 / 1) as eluent to obtain **24** in 99% yield (220.5 mg).

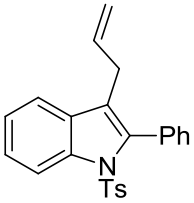
Colorless prism, mp 83-85 °C (Hexane / AcOEt), ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.21 (3H, s), 4.38 (2H, d, *J* = 6.8 Hz), 5.05 (1H, dd, *J* = 1.2, 10.0 Hz), 5.10 (1H, dd, *J* = 1.2, 17.2 Hz), 5.87 (1H, tdd, *J* = 6.8, 10.0, 17.2 Hz), 7.08-7.10 (2H, m), 7.26-7.34 (8H, m), 7.48-7.50 (1H, m), 7.63-7.65 (2H, m) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 53.2, 86.4, 94.2, 118.7, 122.8, 123.7, 127.6 (2C), 128.1, 128.2 (2C), 128.5, 128.8, 129.5 (2C), 131.4 (2C), 132.4, 133.2, 133.4, 137.2, 139.8, 143.2 ; IR (KBr) 3064, 2979, 2213, 1643, 1598, 1495, 1342, 1164, 752 cm^{-1} ; HRMS-ESI$^+$: *m/z* $[M+Na]^+$ calcd for $C_{24}H_{21}NNaO_2S$: 410.1191; found 410.1203.

3. Typical experimental procedure for the allylative cyclization reaction.

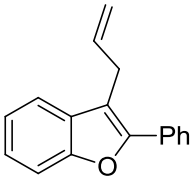
A 30 mL two-neck round-bottom flask containing a magnetic stirring bar, $Pd_2(dba)_3{\cdot}CHCl_3$ (10.4 mg, 0.01 mmol), TPPMS (14.6 mg, 0.04 mmol) and H_2O (3 mL) was fitted with a rubber septum and a three-way stopcock connected to a balloon filled with argon. After it was sonicated for 2 min, a solution of alkyne substrate **1**-**3** (0.4 mmol) and allylic alcohol (0.8 mmol) in dioxane (6 mL) was added to the mixture. The apparatus was purged with argon by pump-filling via the three-way stopcock. The mixture was refluxed for 0.5-2 h. After cooling, the mixture was diluted with ethyl acetate (40 mL) and saturated NaCl aq. (40 mL). The layers were separated and the aqueous layer was extracted with ethyl acetate (30 mL). The combined organic layers were dried over Mg_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel. The fraction eluted with hexane/ethyl acetate (150/1) afforded the allylated products **4**-**6**.



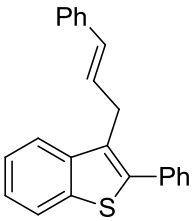
3-Allyl-2-phenylbenzo[*b*]thiophene (**4a**)[2]



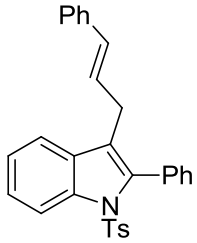
3-Allyl-2-phenyl-1-tosyl-1*H*-indole (**5a**): 98% Yield, White solid, mp 75-77 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (3H, s), 3.19 (2H, dt, *J* = 2.0, 5.2 Hz), 4.58 (1H, dq, *J* = 2.0, 17.2 Hz), 4.89 (1H, dq, *J* = 1.6, 10.4 Hz), 5.82-5.89 (1H, m), 7.05 (2H, d, *J* = 8.8 Hz), 7.26-7.29 (3H, m), 7.34-7.43 (7H, m), 8.32 (1H, d, *J* = 8 Hz) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 28.5, 115.5, 116.5, 119.5, 121.5, 124.0, 125.0, 126.8, 127.4, 128.6, 129.1, 131.0, 131.1, 131.2, 134.8, 135.8, 137.5, 137.6, 144.4 ; IR (KBr) 3057, 2978, 2882, 1597, 1452, 1364, 1176, 750, 702, 665, 579, 544 cm^{-1} ; HRMS-EI: *m/z* [M^+] calcd for $C_{24}H_{21}NO_2S$: 387.1293; found 387.1294.



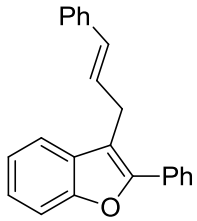
3-Allyl-2-phenylbenzofuran (**6a**)[3]



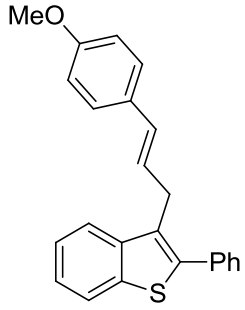
3-Cinnamyl-2-phenylbenzo[*b*]thiophene (**4b**): 91% Yield, Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (2H, dd, *J* = 1.6, 5.6 Hz), 6.37 (1H, d, *J* = 15.6 Hz), 6.48 (1H, dt, *J* = 5.4, 16.0 Hz), 7.16-7.21 (1H, m), 7.23-7.47 (10H, m), 7.56-7.59 (2H, m), 7.76-7.78 (1H, m), 7.84-7.87 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.5, 122.2, 122.6, 124.27, 124.3, 126.1 (2C), 127.1, 128.1, 128.2, 128.5 (2C), 128.6 (2C), 129.0, 129.5 (2C), 131.1, 134.4, 137.3, 139.1, 139.8, 140.5; IR (KBr) : 1597, 1488, 1438, 966, 744 cm^{-1}; HRMS-EI: *m/z* [M^+] calcd for $C_{23}H_{18}S$: 326.1129 ; found 326.1128.



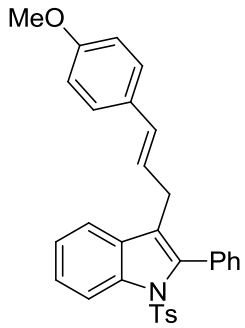
3-Cinnamyl-2-phenyl-1-tosyl-1*H*-indole (**5b**): 97% Yield, White solid, mp 136-137 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (3H, s), 3.35 (2H, dd, *J* = 2.0, 6.0 Hz), 5.86 (1H, dt, *J* = 2.0, 15.6 Hz), 6.24 (1H, dt, *J* = 5.6, 16.0 Hz), 7.05-7.08 (2H, m), 7.11-7.99 (3H, m), 7.22-7.33 (5H, m), 7.36-7.45 (7H, m), 8.35 (1H, dt, *J* = 0.5, 8.8 Hz) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 27.7, 116.6, 119.5, 121.7, 124.2, 125.0, 126.0, 126.9, 127.1, 127.5, 127.8, 128.4, 128.6, 129.2, 130.5, 131.0, 131.2, 131.3, 134.8, 137.2, 137.6, 137.7, 144.4; IR (KBr) 3027, 2895, 1598, 1496, 1450, 1362, 1187, 1173, 666, 576, 543 cm^{-1} ; HRMS-EI: *m/z* [M^+] calcd for $C_{30}H_{25}NO_2S$: 463.1606; found 463.1606.



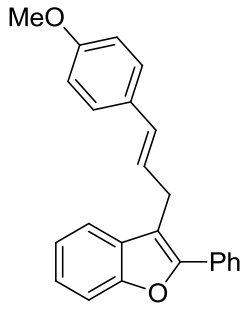
3-Cinnamyl-2-phenylbenzofuran (**6b**)[3]



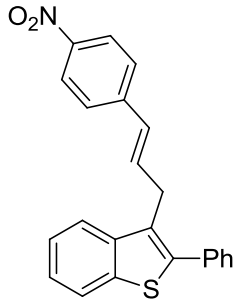
(*E*)-3-{3-(4-Methoxyphenyl)allyl}-2-phenylbenzo[*b*]thiophene (**4c**): 95% yield, Colorless solid, mp 78-80 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76-3.77 (2H, m), 3.76 (3H, s), 6.32-6.33 (2H, m), 6.79-6.82 (2H, m), 7.22-7.23 (2H, m), 7.31-4.46 (5H, m), 7.56-7.59 (2H, m), 7,76-7.78 (1H, m), 7.83-7.86 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.4, 55.3, 113.9 (2C), 122.2, 122.7, 124.3, 124.3, 125.9, 127.2 (2C), 128.1, 128.6 (2C), 129.3, 129.5 (2C), 130.2, 130.4, 134.4, 139.1, 139.7, 140.6, 158.9; IR (KBr): 1602, 1504, 1247, 837, 765 cm^{-1}; HRMS-EI: *m/z* [M^+] calcd for $C_{24}H_{20}OS$: 356.1235; found 356.1233.



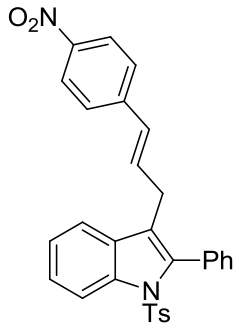
(*E*)-3-{3-(4-Methoxyphenyl)allyl}-2-phenyl-1-tosyl-1*H*-indole (**5c**): 96% Yield, White solid, mp 155-156 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (3H, s), 3.32 (2H, dd, *J* = 1.6, 5.6 Hz), 3.76 (3H, s), 5.83 (1H, d, *J* = 15.6 Hz), 6.08 (1H, dt, *J* = 5.6, 16.0 Hz), 6.77 (2H, d, *J* = 8.4 Hz), 7.05-7.08 (4H, m), 7.26-7.32 (3H, m), 7.36-7.44 (7H, m), 8.36 (1H, dd, *J* = 0.8, 8.4 Hz) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 27.7, 55.3, 113.8, 116.6, 119.7, 122.0, 124.2, 125.0, 125.6, 126.9, 127.1, 127.4, 128.6, 129.2, 129.8, 130.0, 131.0, 131.2, 131.3, 134.8, 137.6 (2C), 144.4, 158.8 ; IR (KBr) 3030, 2897, 1607, 1511, 1363, 1252, 1174, 665, 578 cm^{-1} ; HRMS-EI : *m/z* [M^+] calcd for $C_{31}H_{27}NO_3S$: 493.1712; found 493.1710.



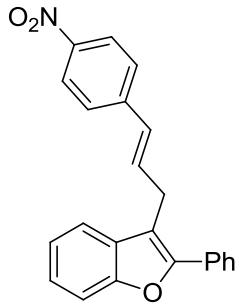
(*E*)-3-{3-(4-Methoxyphenyl)allyl}-2-phenylbenzofuran (**6c**): 80% Yield, White solid, 100-102 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (3H, s), 3.77 (2H, d, *J* = 5.6 Hz), 6.28-6.44 (2H, m), 6.79 (2H, dd, *J* = 1.6, 8.4 Hz), 7.20-7.55 (9H, m), 7.80 (2H, d, *J* = 5.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.6, 55.2, 111.0, 113.4, 113.9 (2C), 119.8, 122.5, 124.4, 124.9, 127.0 (3C), 127.3 (2C), 128.3, 128.7 (2C), 130.1, 130.4, 130.9, 151.6, 154.0, 158.9; IR (KBr) 3055, 3028, 3008, 2955, 2905, 2891, 2835, 1671, 1653, 1309, 1180, 1060, 519 cm^{-1}; HRMS-EI: *m/z* [M^+] calcd for $C_{24}H_{20}O_2$: 340.1462; found 340.1463.



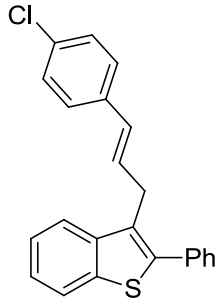
(*E*)-3-{3-(4-Nitrophenyl)allyl}-2-phenylbenzo[*b*]thiophene (**4d**): 88% Yield, Yellow solid, mp 185-187 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (2H, dd, *J* = 2, 5.8 Hz), 6.41 (1H, d, *J* = 16.0 Hz), 6.67 (1H, dt, *J* = 5.6, 16.0 Hz), 7.35-7.48 (7H, m), 7.55 (2H, br-d, *J* = 6.8 Hz), 7.73 (1H, br-d, *J* = 7.2 Hz), 7.87 (1H, br-d, *J* = 6.8 Hz), 8.12 (2H, d, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.6, 122.3, 122.4, 123.9 (2C), 124.4, 124.5, 126.6 (2C), 128.0, 128.3, 128.7 (2C), 129.3, 129.5 (2C), 133.5, 134.1, 139.2, 140.2, 140.4, 143.8, 146.6 ; IR (KBr):1647, 1598, 1509, 1337, 765 cm^{-1}; HRMS-EI: *m/z* [M^+] calcd for $C_{23}H_{17}NO_2S$: 371.0980 ; found 371.0981.



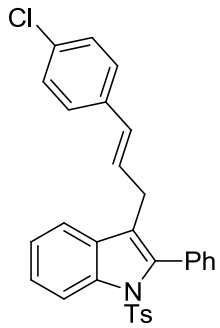
(*E*)-3-{3-(4-Nitrophenyl)allyl}-2-phenyl-1-tosyl-1*H*-indole (**5d**): 99% Yield, Yellow solid, mp 190-191 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (3H, s), 3.41 (2H, dd, *J* = 2.0, 5.6 Hz), 5.97 (1H, d, *J* = 16.0 Hz), 6.41 (1H, dt, *J* = 5.6, 16.0 Hz), 7.09 (2H, d, *J* = 8.0 Hz), 7.23-7.46 (12H, m), 8.09 (2H, d, *J* = 8.8 Hz), 8.37 (1H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 28.0, 116.5, 119.2, 120.5, 123.9, 124.2, 125.2, 126.5, 126.9, 127.6, 128.8(2C), 129.3, 130.7, 131.0(2C), 133.1, 135.0, 137.4, 137.9, 143.6, 144.5, 146.5 ; IR (KBr) 3059, 2921, 1596, 1513, 1340, 1174, 754, 664, 577 cm-^{1} ; HRMS-EI: *m/z* [M^+] calcd for $C_{30}H_{24}N_2O_4S$: 508.1457; found 508.1456.



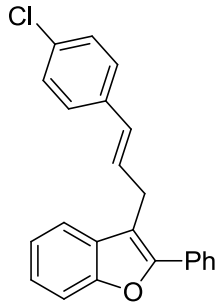
(*E*)-3-{3-(4-Nitrophenyl)allyl}-2-phenylbenzofuran (**6d**): 84% Yield, Yellow solid, mp 119-121 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88 (2H, dd, *J* = 2.0, 5.6 Hz), 6.52 (1H, d, *J* = 16.0 Hz), 6.67-6.74 (1H, m), 7.23-7.56 (9H, m), 7.78 (2H, d, *J* = 8.8 Hz), 8.12 (2H, d, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.9, 111.3, 112.2, 119.5, 122.7, 123.9 (2C), 124.7, 126.7 (2C), 127.0 (2C), 128.6, 128.8 (2C), 129.3, 130.1, 130.7, 132.5, 143.7, 146.7, 152.0, 154.1; IR (KBr) 3052, 2900, 2875, 2824, 1684, 1379, 1261, 1025, 970, 842, 488 cm^{-1}; HRMS-EI: *m/z* [M^+] calcd for $C_{23}H_{17}NO_3$: 355.1210; found 355.1208.



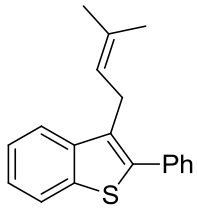
(*E*)-3-{3-(4-Chlorophenyl)allyl}-2-phenylbenzo[*b*]thiophene (**4e**): 93% Yield, Colorless solid, mp 118-120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (2H, dd, *J* = 1.6, 5.6 Hz), 6.30 (1H, br-d, *J* = 16.0 Hz), 6.43 (1H, dt, *J* = 5.6, 16.0 Hz), 7.19-7.23 (4H, m), 7.29-7.46 (6H, m), 7.54-7.57 (2H, m), 7.73-7.75 (1H, m), 7.84-7.86 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.3, 122.2, 122.5, 124.3, 124.4 (2C), 127.3, 128.1, 128.5, 128.6 , 128.7 (2C), 128.8 (2C), 129.5 (2C), 129.8, 132.6, 134.2, 135.7, 139.0, 139.9, 140.4; IR (KBr): 1484, 1435, 1087, 836, 763 cm^{-1}; HRMS-EI: *m/z* [M^+] calcd for $C_{23}H_{17}ClS$: 360.0739 ; found 360.0734.



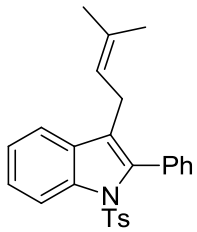
(*E*)-3-{3-(4-Chlorophenyl)allyl}-2-phenyl-1-tosyl-1*H*-indole (**5e**): 93% Yield, White solid, mp 169-170 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (3H, s), 3.34 (2H, dd, *J* = 1.6, 5.6 Hz), 5.85 (1H, d, *J* = 16.0 Hz), 6.20 (1H, dt, *J* = 6.0, 16.0 Hz), 7.03-7.08 (4H, m), 7.19 (2H, dt, *J* = 2.8, 8.0 Hz), 7.25-7.45 (10H, m), 8.36 (1H, dd, *J* = 0.8, 8.4 Hz) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 27.7, 116.5, 119.4, 121.4, 124,2, 125.1, 126.9, 127.2, 127.5, 128.5, 128.6, 128.7, 129.2, 129.3, 131.0, 131.1 (2C), 132.7, 134.9, 135.7, 137.5, 137.7, 144.4 ; IR (KBr) 3054, 2891, 1597, 1452, 1366, 1187, 755, 663, 577 cm^{-1} ; HRMS-EI: *m/z* [M^+] calcd for $C_{26}H_{25}NO_2S$: 497.1216, found 497.1214.



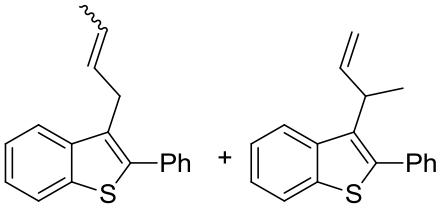
(*E*)-3-{3-(4-Chlorophenyl)allyl}-2-phenylbenzofuran (**6e**): 82% Yield, White solid, mp 59-61 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (2H, d, *J* = 4.0 Hz), 6.44-6.50 (2H, m), 7.22-7.24 (5H, m), 7.30-7.41 (2H, m), 7.45-7.50 (2H, m), 7.52-7.57 (2H, m), 7.77- 7.80 (2H, m) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.6, 111.1, 112.8, 119.6, 122.5, 124.4, 126.9 (2C), 127.3 (2C), 127.9, 128.3, 128.5 (2C), 128.7 (2C), 129.8, 130.3, 130.8, 132.7, 135.6, 151.7, 154.0; IR (KBr) 3041, 2894, 1652, 1485, 1448, 1260, 1178, 1098, 973, 841, 690 cm^{-1}; HRMS-EI: *m/z* [M^+] calcd for $C_{23}H_{17}ClO$: 346.0935; found 346.0938.



3-(3-Methylbut-2-en-1-yl)-2-phenylbenzo[*b*]thiophen (**4f**): 82% Yield, White solid, mp 60-62 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.72 (3H, d, *J* = 1.6 Hz), 1.72 (3H, d, *J* = 0.8 Hz), 3.72 (2H, d, *J* = 6.8 Hz), 5.28-5.32 (1H, m), 7.31-7.46 (5H, m), 7.51-7.54 (2H, m), 7.70-7.73 (1H, m), 7.82-7.84 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.0, 25.7, 26.3, 122.2, 122.5, 122.5, 124.1, 124.2, 127.9, 128.5 (2C), 129.8 (2C), 131.4, 132.3, 134.7, 138.5, 139.2, 140.6; IR (KBr): 1597, 1483, 1436, 1186, 757 cm^{-1}; HRMS-EI: *m/z* [M^+] calcd for $C_{23}H_{17}NO_2S$: 278.1129 ; found 278.1130.

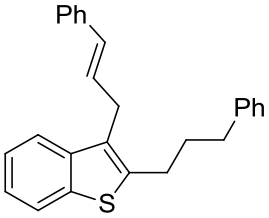


3-(3-Methylbut-2-en-1-yl)-2-phenyl-1-tosyl-1*H*-indole (**5f**): 98% yield, Pale yellow solid, mp 74-76 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.51 (3H, s), 1.59 (3H, s), 2.26 (3H, s), 3.14 (2H, d, *J* = 6.8 Hz), 5.00 (1H, t, *J* = 6.8 Hz), 7.03 (2H, d, *J* = 8.4 Hz), 7.24-7.43 (10H, m), 8.31 (1H, br-d, *J* = 8.4 Hz) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.7, 21.5, 23.7, 25.6, 116.1, 119.5, 121.8, 123.5, 123.8, 124.8, 126.8 (2C), 127.4, 128.4, 129.2, 131.0, 131.4, 132.1, 135.1, 136.5, 137.3, 144.3 ; IR (KBr) 3059, 2906, 1596, 1451, 1366, 1169, 1117, 929, 803, 751, 701, 580, 545 cm^{-1}; HRMS-EI: *m/z* [M^+] calcd for $C_{26}H_{25}NO_2S$: 415.1606, found 415.1608.

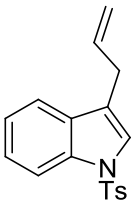


4g **4h**

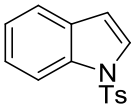
3-(But-2-en-1-yl)-2-phenylbenzo[*b*]thiophene (**4g**) and 3-(but-3-en-2-yl)-2-phenylbenzo[*b*]thiophene (**4h**) : as a inseparable mixture of (*E*)-**4g** , (*Z*)-**4g** and **4h** in a 1 : 0.2 : 1 ratio determined by ^{1}H-NMR spectra.; 80% yield, colorless oil, , ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.51 (3/2.2 H, d, *J* = 7.2 Hz : **4h**), 1.66 (3/2.2 H, dd, *J* = 1.6, 6.4 Hz : **4g** *E* isomer), 1.72 (0.6/2.2 H, d-like, *J* = 4.8 Hz : **4g** *Z* isomer), 3.56 (2/2.2 H, dt, *J* = 1.6, 5.6 Hz : **4g** *E* isomer), 3.62-3.63 (0.4/2.2 H, m : **4g** *Z* isomer), 3.97-4.05 (1/2.2 H, m : **4h**), 5.11 (1/2.2 H, ddd, *J* = 1.2, 2.0, 17.2 Hz : **4h**), 5.13 (1/2.2 H, ddd, *J* = 1.2, 2.0, 10.4 Hz : **4h**), 5.42-5.51 (1/2.2 H, m : **4g** *E* isomer), 5.54-5.57 (0.4/2.2 H, m : **4g** *Z* isomer), 5.65-5.72 (1/2.2 H, m : **4g** *E* isomer), 6.20 (1/2.2 H, ddd, *J* = 4.8, 10.4, 17.2 Hz : **4h**), 7.29-7.90 (19.8/2.2 H, m) ; ^{13}C NMR (100 MHz, $CDCl_3$, **4g** *E* isomer and **4h**) δ 17.9 (1/2C), 18.8 (1/2C), 30.1 (1/2C), 36.2 (1/2C), 114.1 (1/2C), 122.1 (1/2C), 122.3 (1/2C), 122.7 (1/2C), 123.6 (1/2C), 123.8 (1/2C), 124.1 (1/2C), 124.2 (1/2C), 124.2 (1/2C), 126.6 (1/2C), 127.9 (1/2C), 128.1 (1/2C), 128.5 (3/2C), 128.5, 128.7 (1/2C), 129.5, 129.9 (1/2C), 130.0, 134.4 (1/2C), 134.5 (1/2C), 134.7 (1/2C), 138.8 (1/2C), 138.9 (1/2C), 139.1 (1/2C), 139.6 (1/2C), 140.6 (1/2C), 141.5 (1/2C); IR (KBr) 2976, 2885, 1598, 1437, 744, 697 cm^{-1}; HRMS-EI: *m/z* [M^+] calcd for $C_{18}H_{16}S$: 264.0973, found 264.0975.



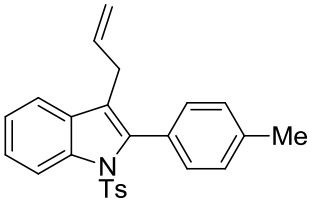
3-Cinnamyl-2-(3-phenylpropyl)benzo[*b*]thiophene (**16**): 66% Yield, yellow oil, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.00-2.08 (2 H, quint, *J* = 7.6 Hz), 2.70 (2 H, t, *J* = 7.6 Hz), 2.91 (2 H, t, *J* = 7.6 Hz), 3.64 (2 H, d, *J* = 5.6 Hz), 6.23-6.36 (2 H, m), 7.14-7.33 (12 H, m), 7.66 (1 H, d, *J* = 8.0 Hz), 7.77 (1 H, d, *J* = 8.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 28.0, 29.8, 32.9, 35.3, 121.5, 122.2, 123.5, 123.9, 125.9, 126.0 (2C), 127.1, 127.6, 128.3, 128.4 (5C), 128.6, 130.6, 137.3, 138.4, 140.2, 141.0, 141.7; IR (KBr): 3025, 2934, 2854, 1601 cm^{-1}; HRMS-EI : *m/z* [M^+] calcd for $C_{26}H_{24}S$: 368.1599; found: 368.1598



3-Allyl-1-tosyl-1*H*-indole (**18**) : Spectral data are consistent with previously reported data.[4]



1-Tosyl-1*H*-indole (**19**) : Spectral data are consistent with previously reported data.[5]



3-Allyl-2-(*p*-tolyl)-1-tosyl-1*H*-indole (**23**): 95% Yield, White solid, mp 104-105 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (3H, s), 2.44 (3H, s), 3.18 (2H, dt, *J* = 2.0, 5.2 Hz), 4.55 (1H, dd, *J* = 2.0, 17.2 Hz), 4.89 (1H, dd, *J* = 2.0, 10.0 Hz), 5.81-5.88 (1H, m), 7.04 (2H, br-d, *J* = 8.4 Hz), 7.24-7.39 (8H, m), 8.31 (1H, dd, *J* = 0.8, 8.0 Hz) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 28.6, 115.4, 116.5, 119.4, 121.3, 124.0, 124.8, 124.9, 126.8, 128.2 (2C), 129.1, 130.8, 131.3, 134.7, 135.9, 137.5, 137.8, 138.4, 144.4 ; IR (KBr) 3060, 2979, 2915, 1598, 1451, 1367, 1175, 934, 745, 686, 657, 581 cm^{-1}; HRMS-EI: *m/z* [M^+] calcd for $C_{26}H_{25}NO_2S$: 401.1449, found 401.1451.

4. References

1 (*a*) Y. Jiang, T. Kusakabe, K. Takahashi, K. Kato, *Org. Biomol. Chem.*, 2014, **12**, 3380; (*b*) T. Kurisaki, T. Naniwa, H. Yamamoto, H. Imagawa, M. Nishizawa, *Tetrahedron Lett.*, **2007**, *48*, 1871; (c) A. Arcaidi, S. Cacchi, M. D. Rosario, G. Fabrizi, F. Marinelli, *J. Org. Chem.* **1996**, *61*, 9280; (d) M. Hatano, K. Mikami, *J. Am. Chem. Soc.*, **2003**, *125*, 4704; (e) X. Han, X. Lu, *Org. Lett.*, **2010**, *12*, 3336. (f) M. Mori, D. Tanaka, N. Saito, Y. Sato, *Organometallics*, **2008**, *27*, 6313.

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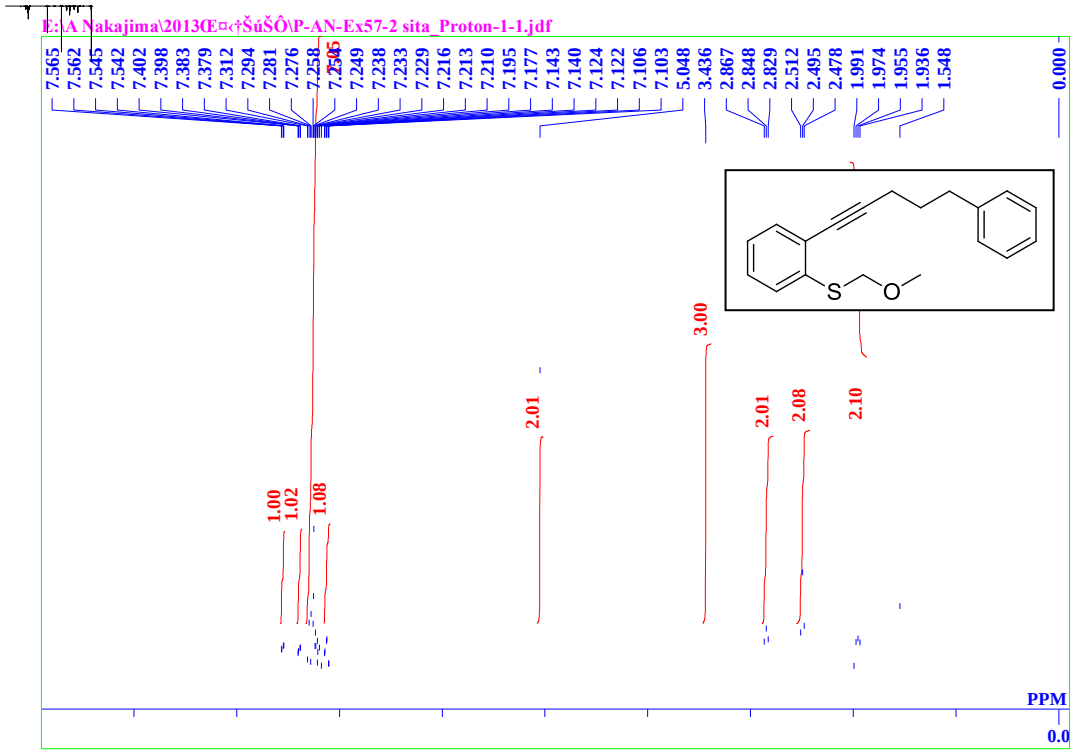
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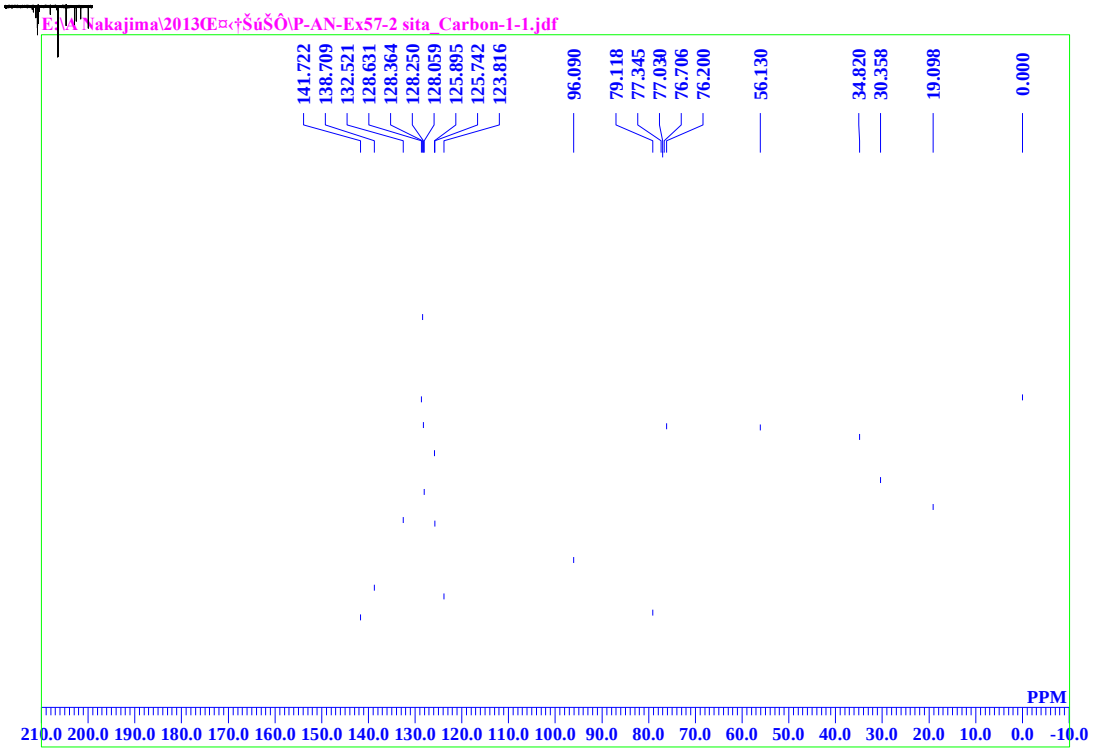
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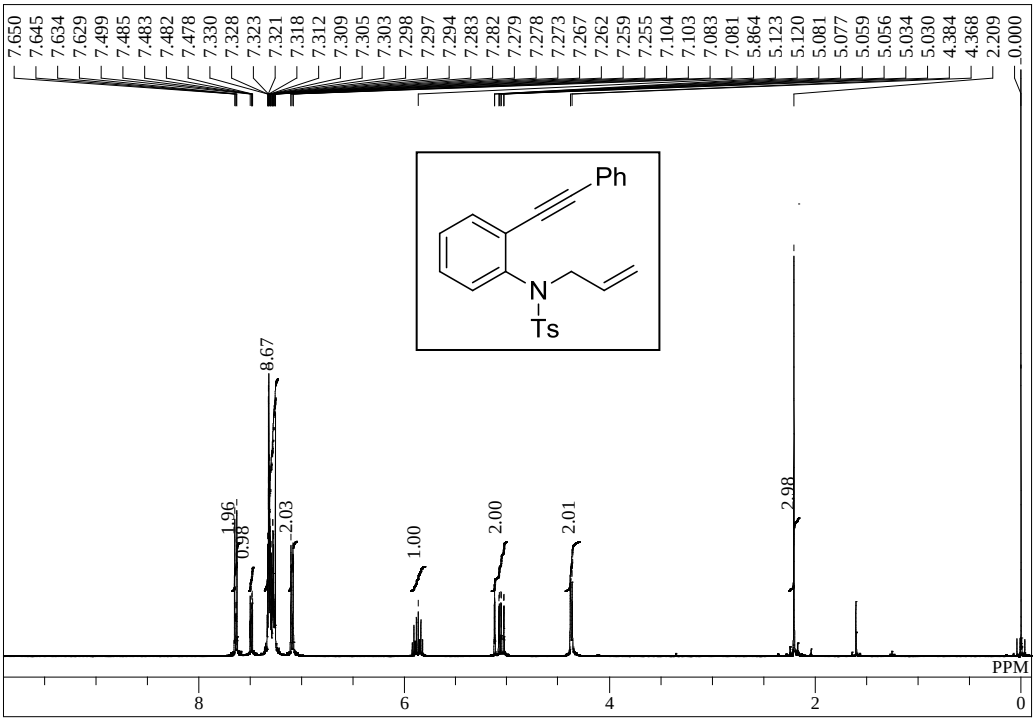

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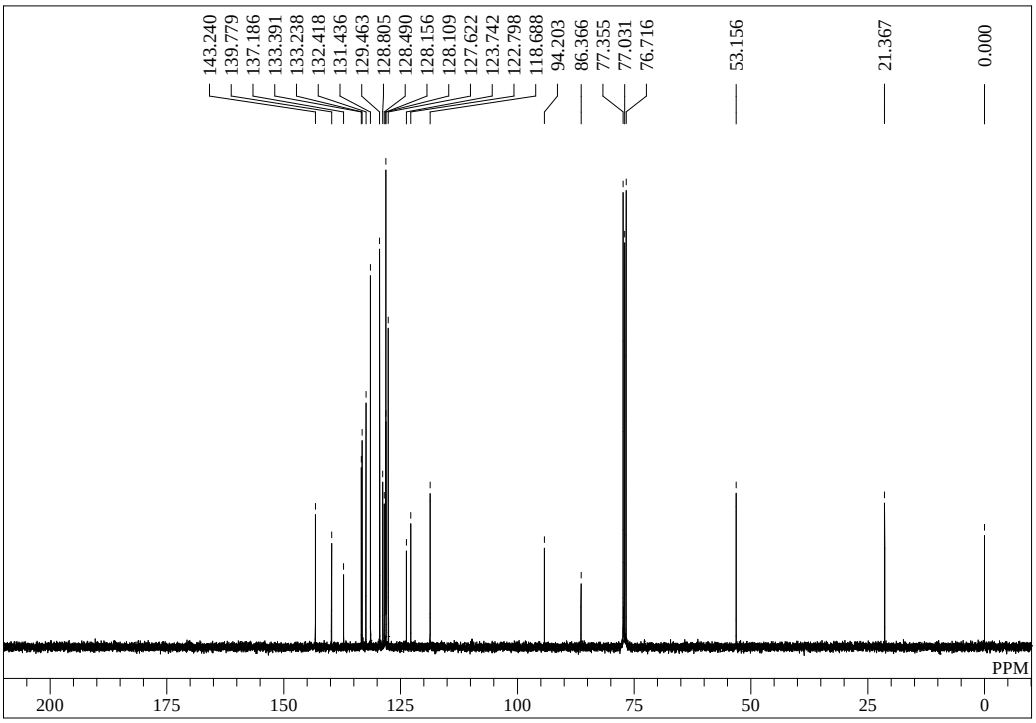

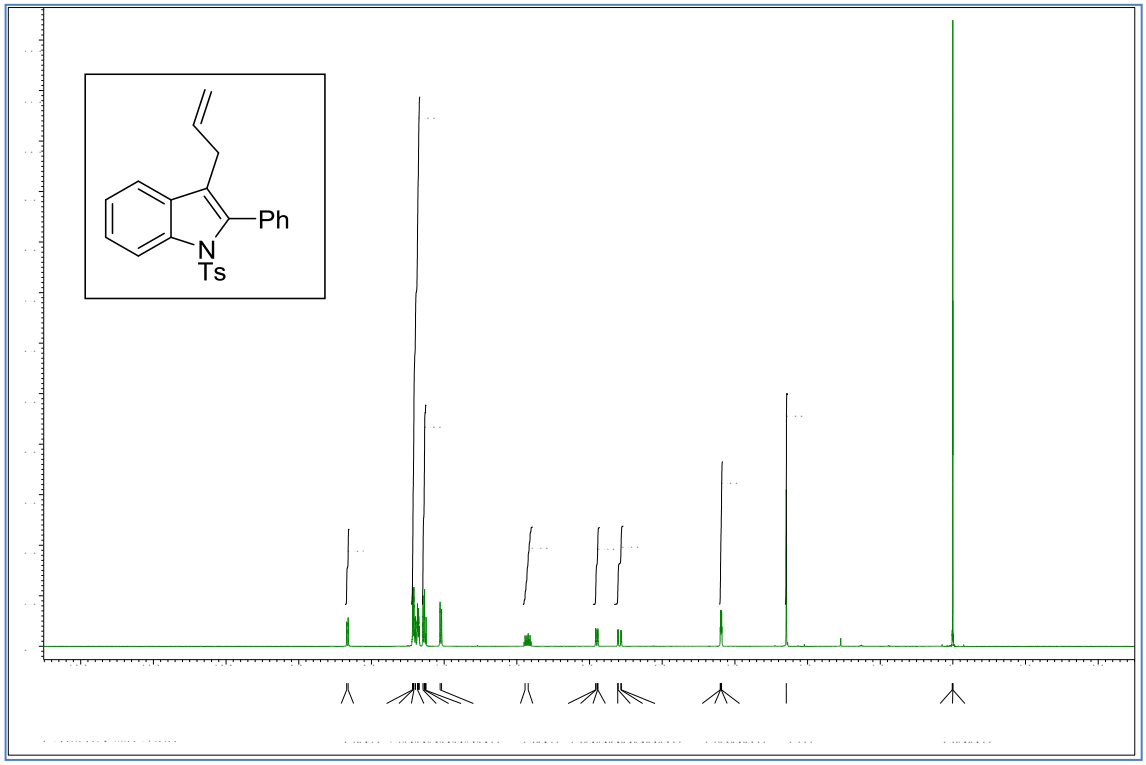
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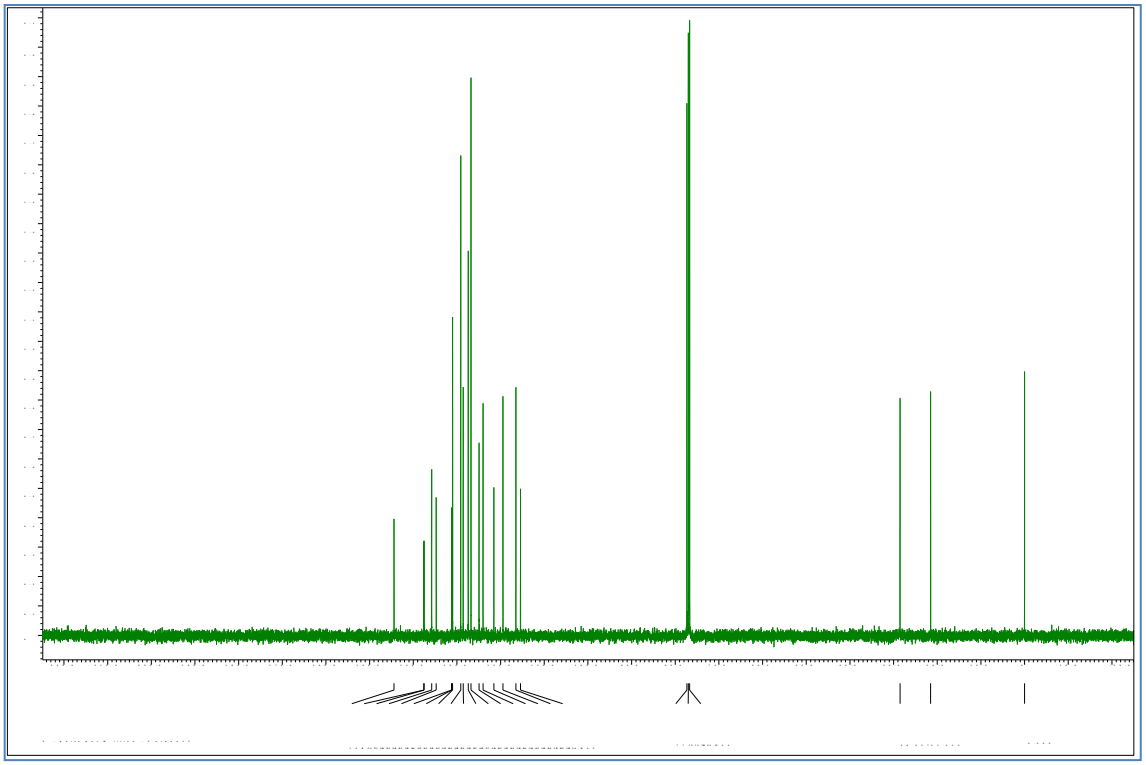

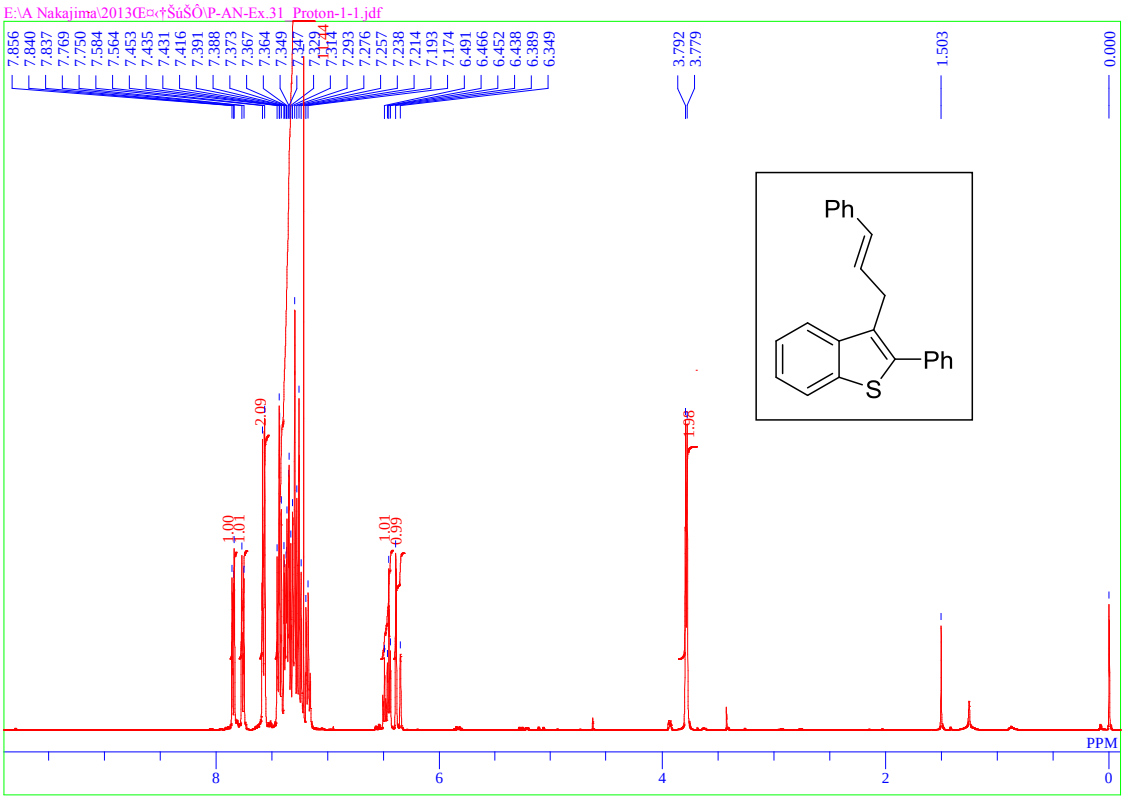
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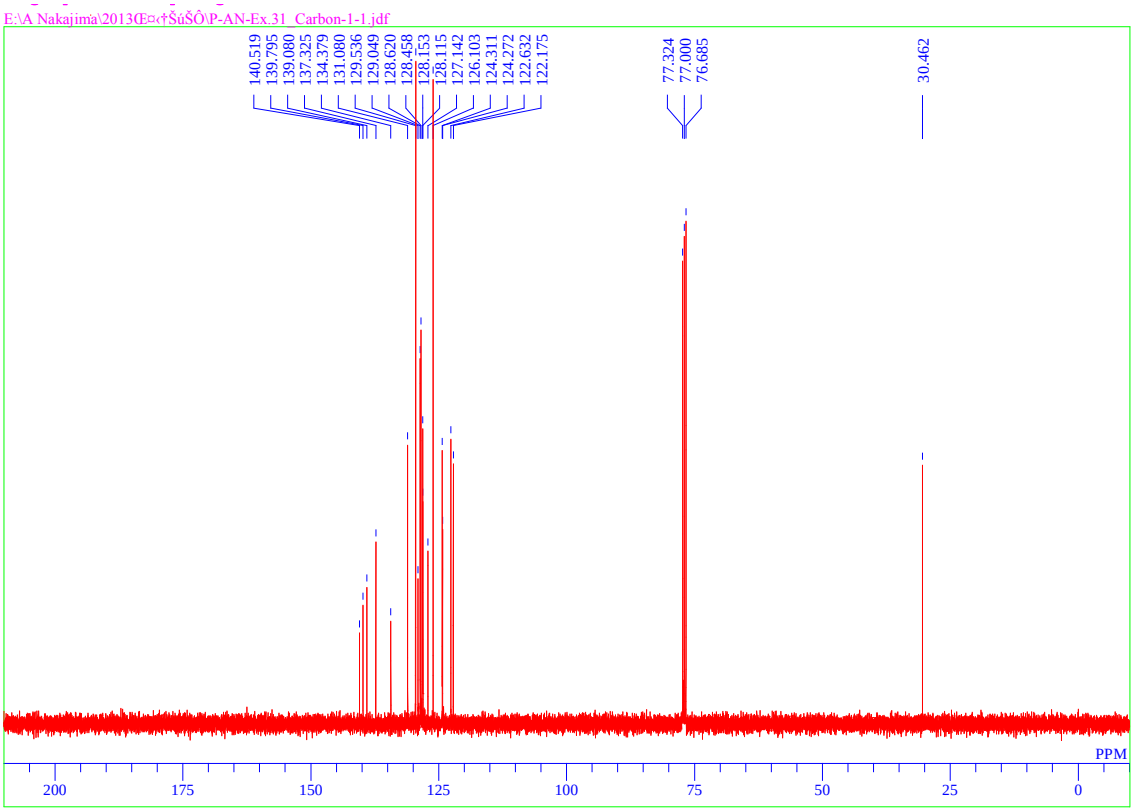
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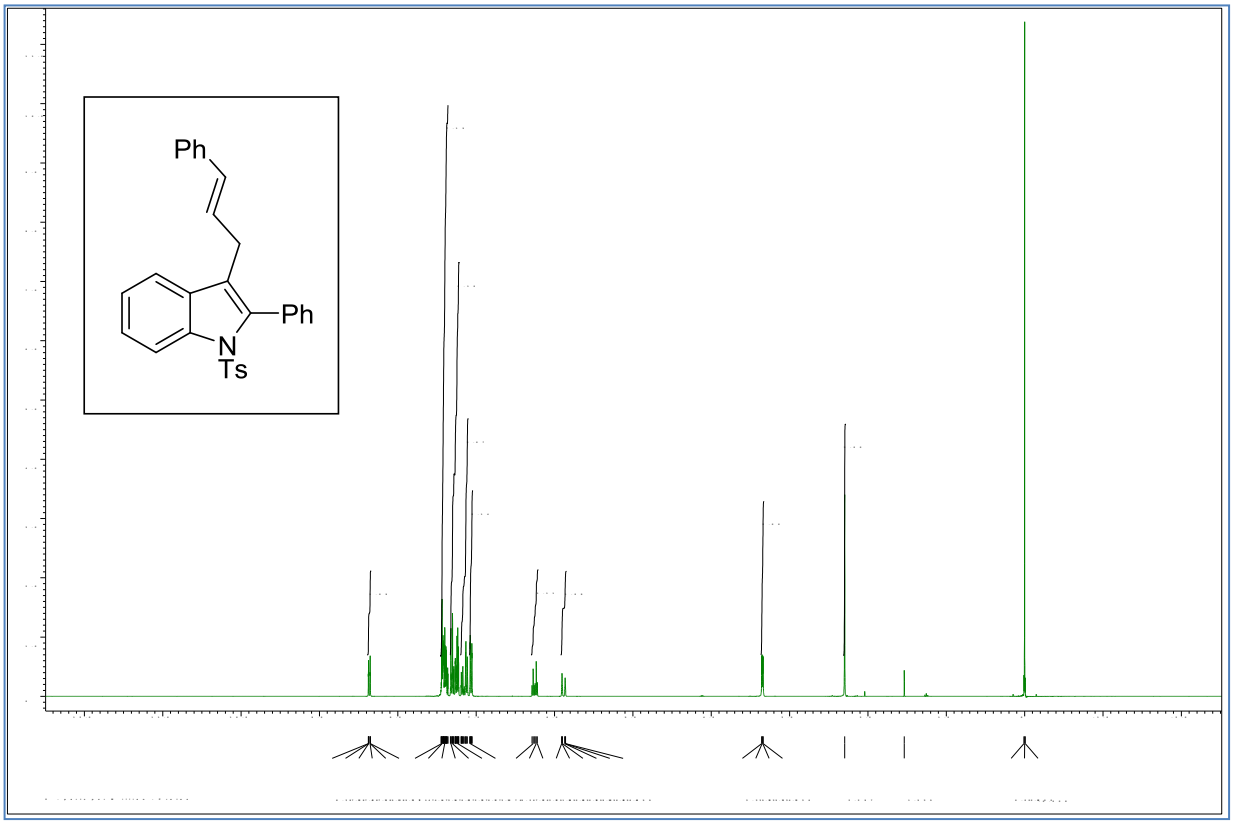
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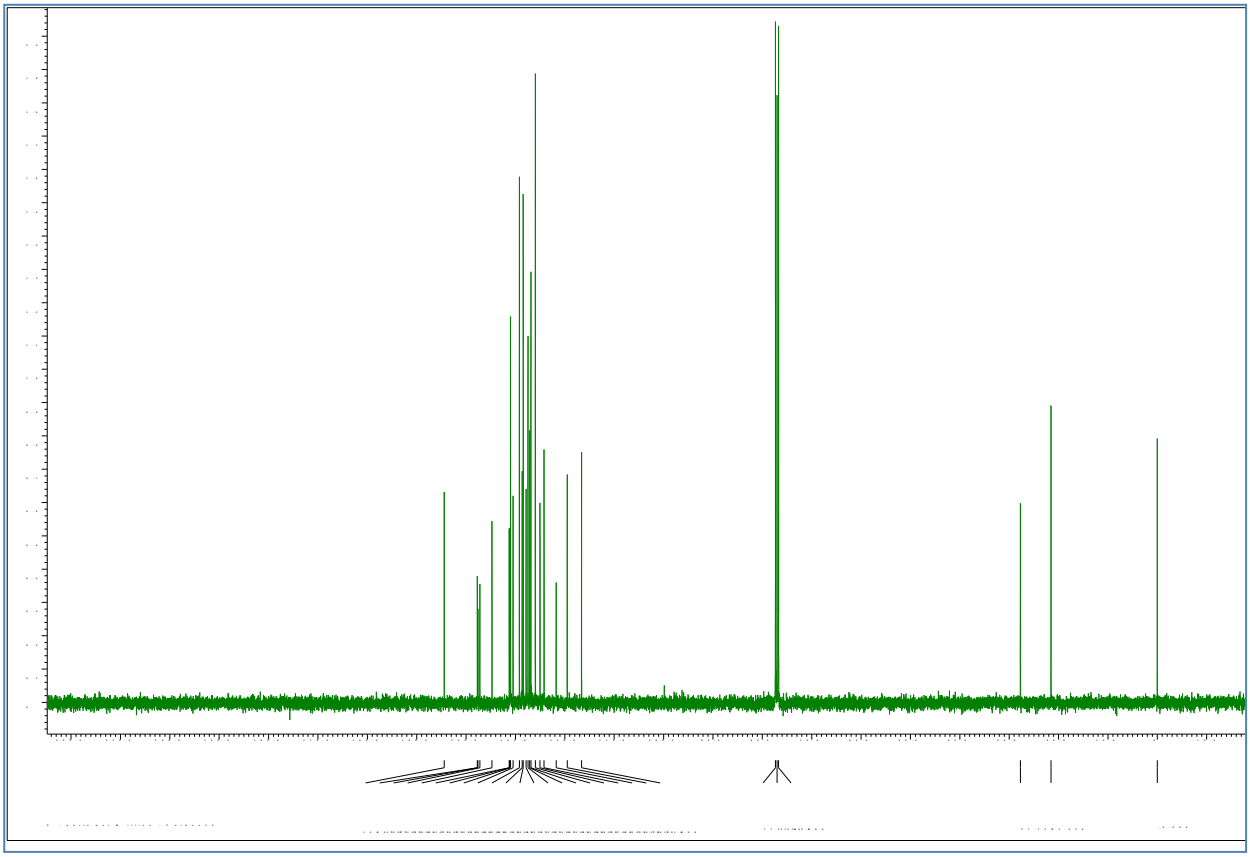
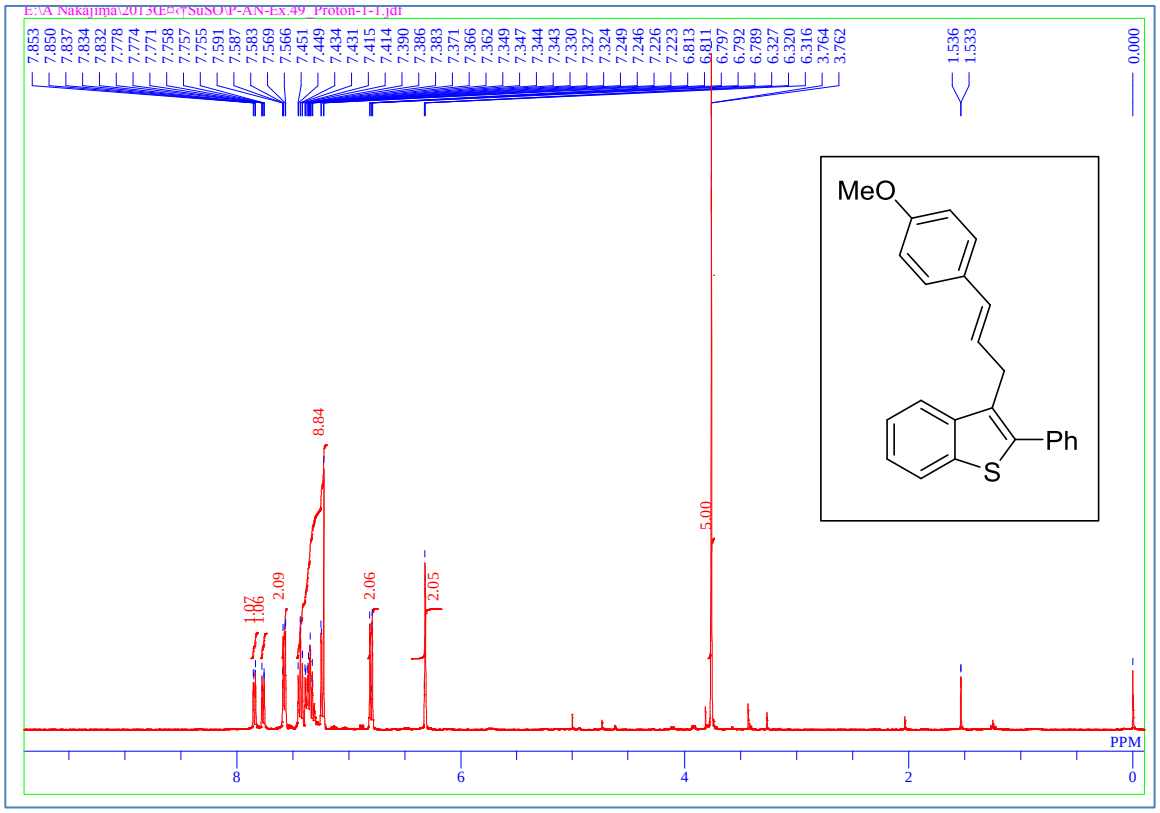
Ph
N
Ts

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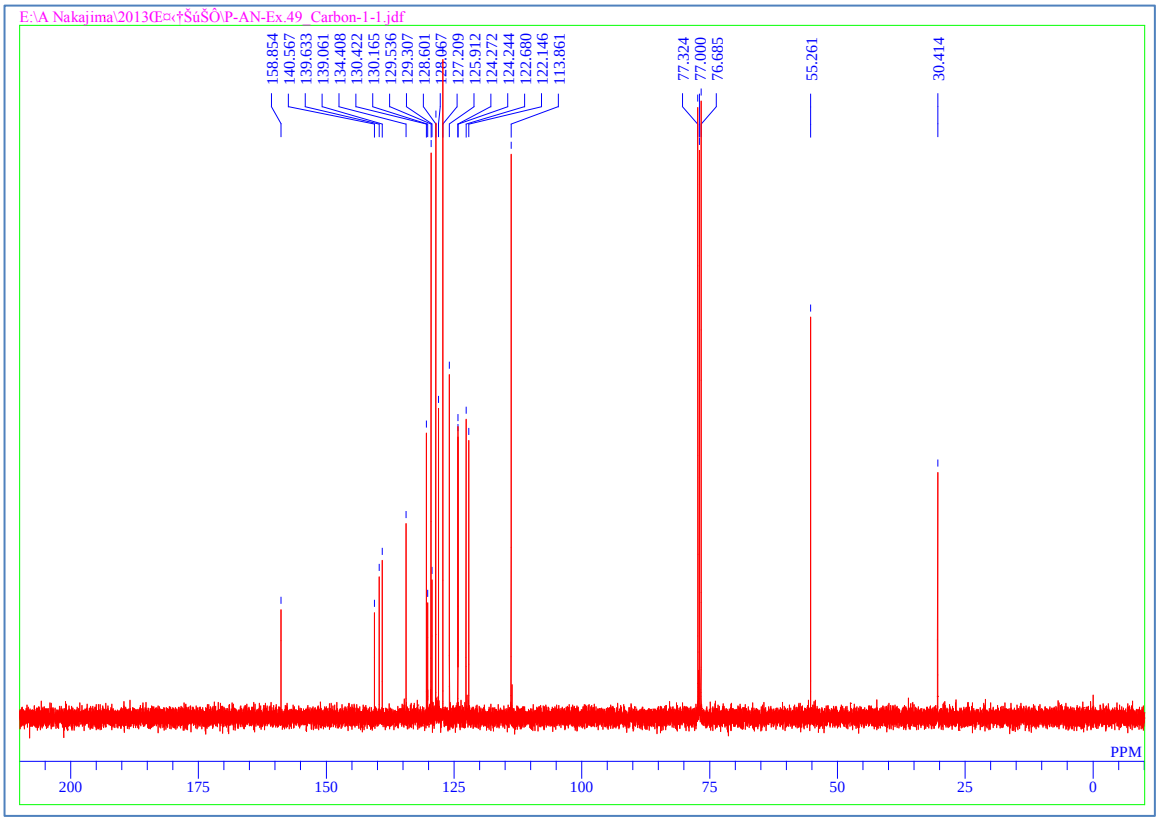
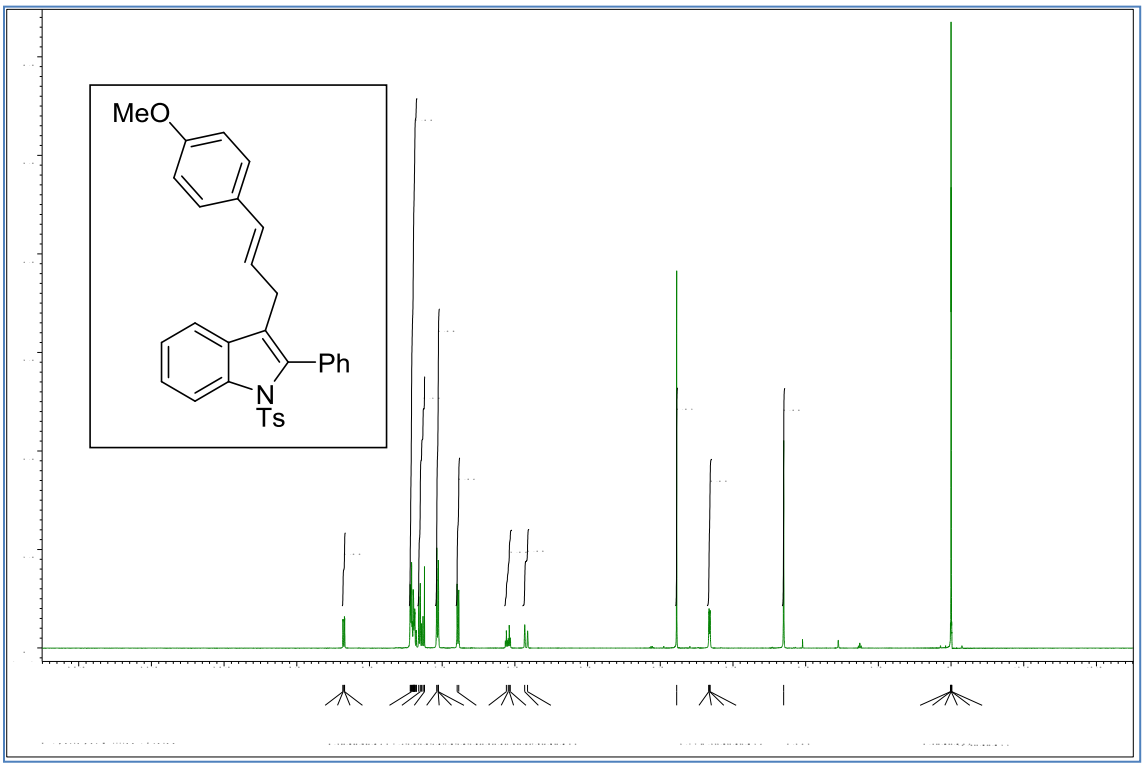
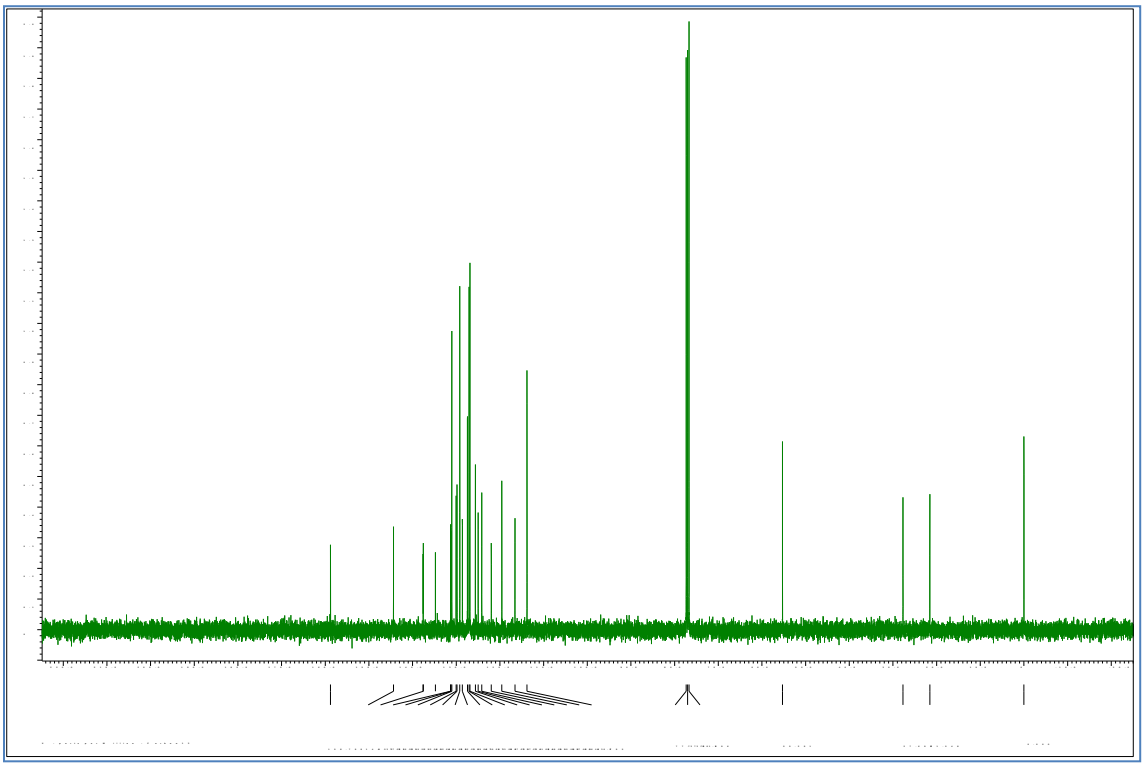
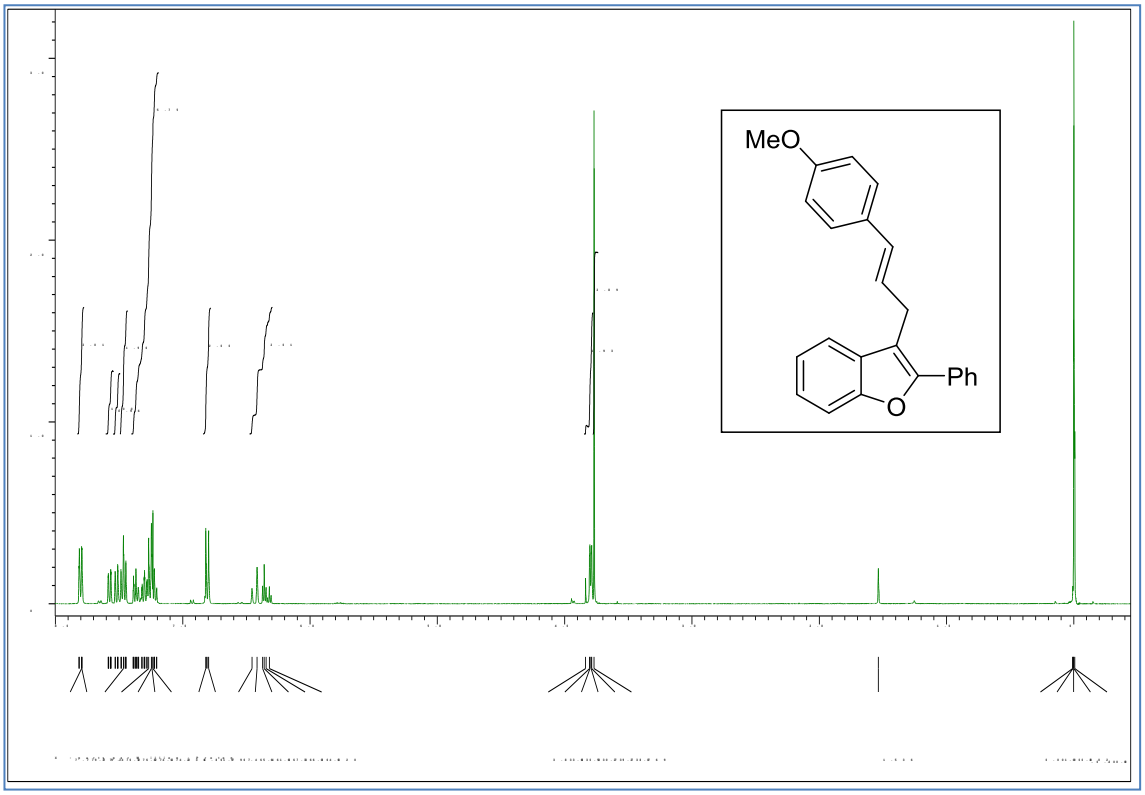
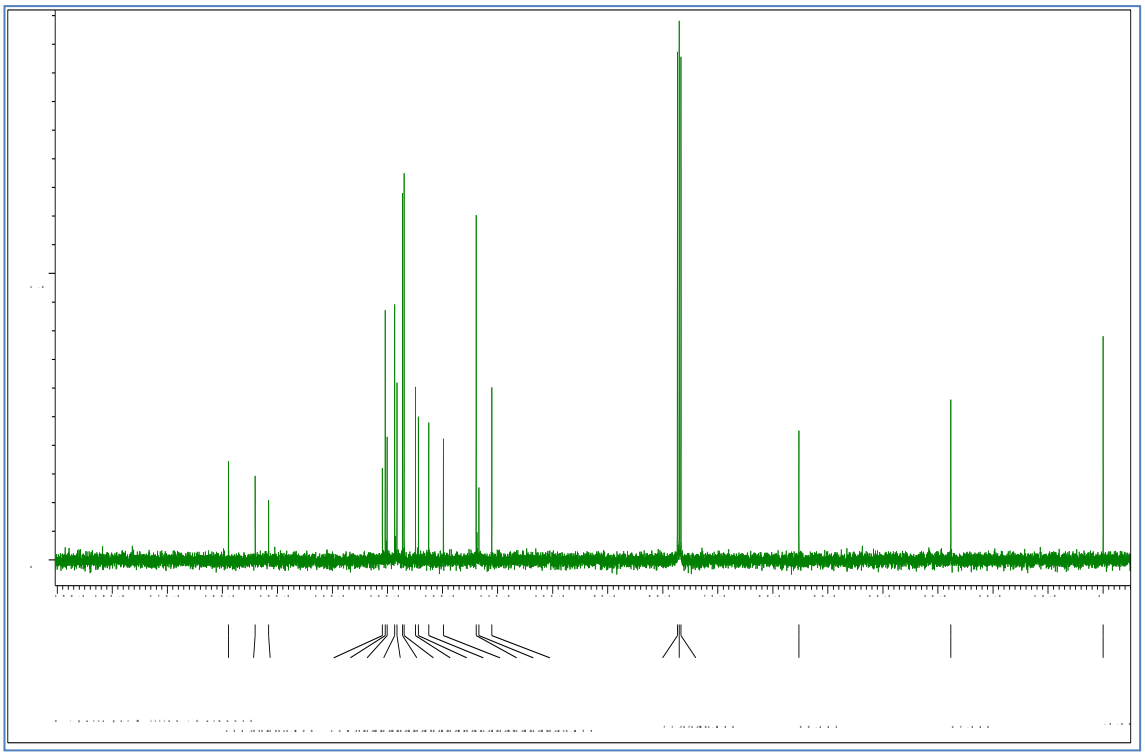
7.850
7.837
7.834
7.832
7.778
7.774
7.771
7.758
7.757
7.755
7.591
7.587
7.583
7.569
7.566
7.451
7.449
7.434
7.431
7.415
7.414
7.390
7.386
7.383
7.371
7.366
7.362
7.349
7.347
7.344
7.343
7.330
7.327
7.324
7.249
7.246
7.226
7.223
6.813
6.811
6.797
6.792
6.789
6.327
6.320
6.316
3.764
3.762
1.536
1.533
0.000
MeO
Ph
S
8.84
5.00
1.07
1.06
2.09
2.06
2.05
PPM
8
6
4
2
0

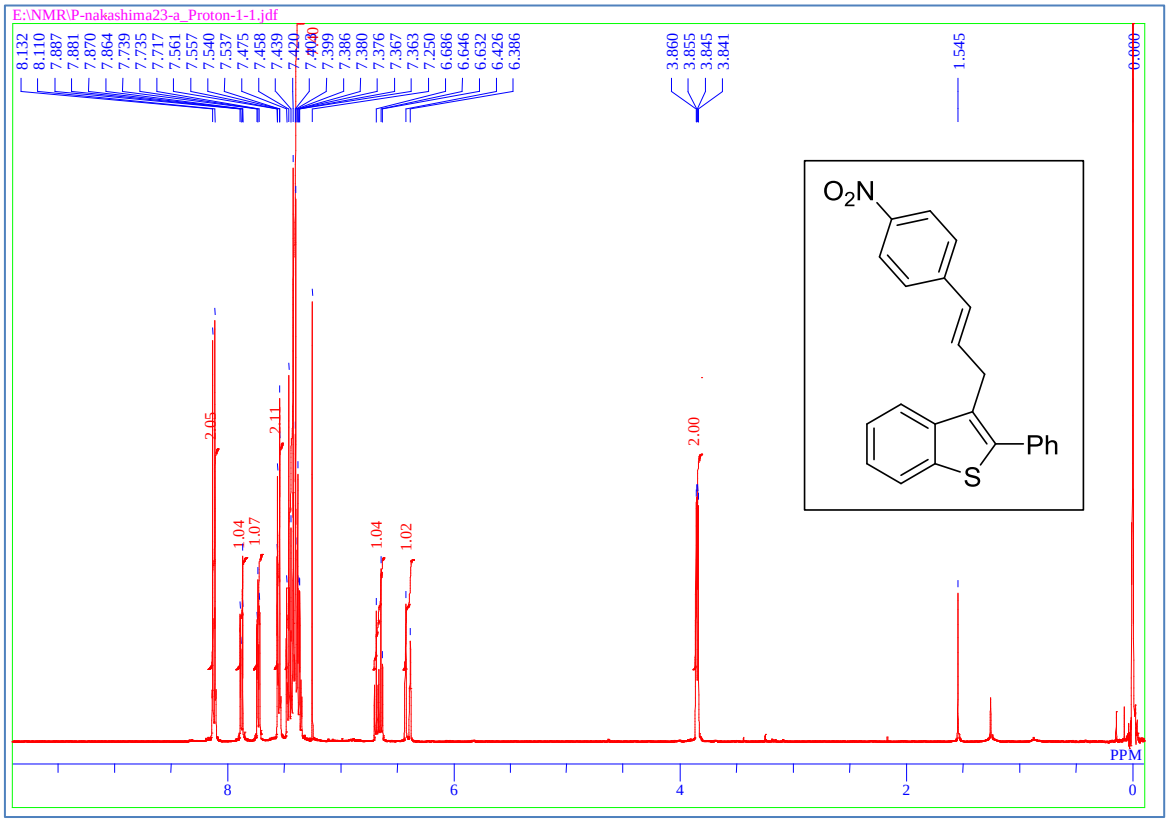

E:\A Nakajima\2013\Eメ†ŠúŠÔ\P-AN-Ex.49_Carbon-1-1.jdf
158.854
140.567
139.633
139.061
134.408
130.422
130.165
129.536
129.307
128.601
128.067
127.209
125.912
124.272
124.244
122.680
122.146
113.861
77.324
77.000
76.685
55.261
30.414
PPM
200
175
150
125
100
75
50
25
0

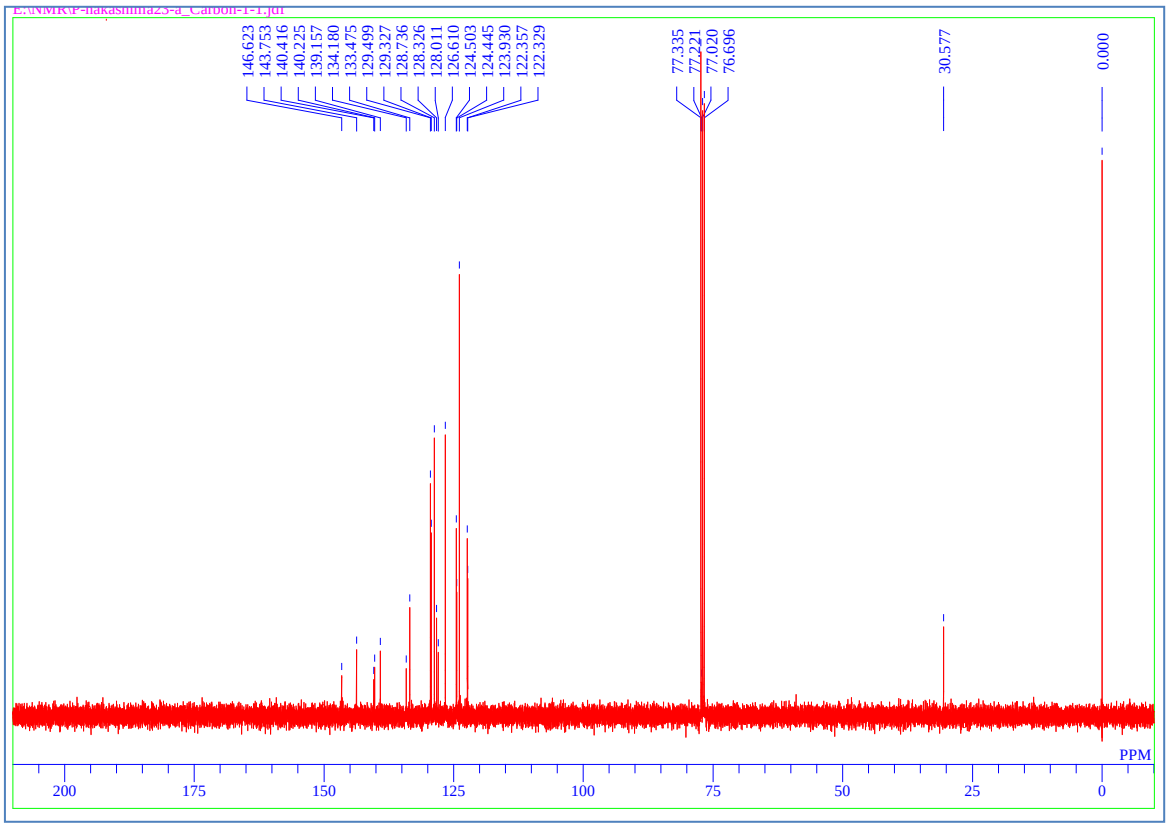

MeO
Ph
N
Ts

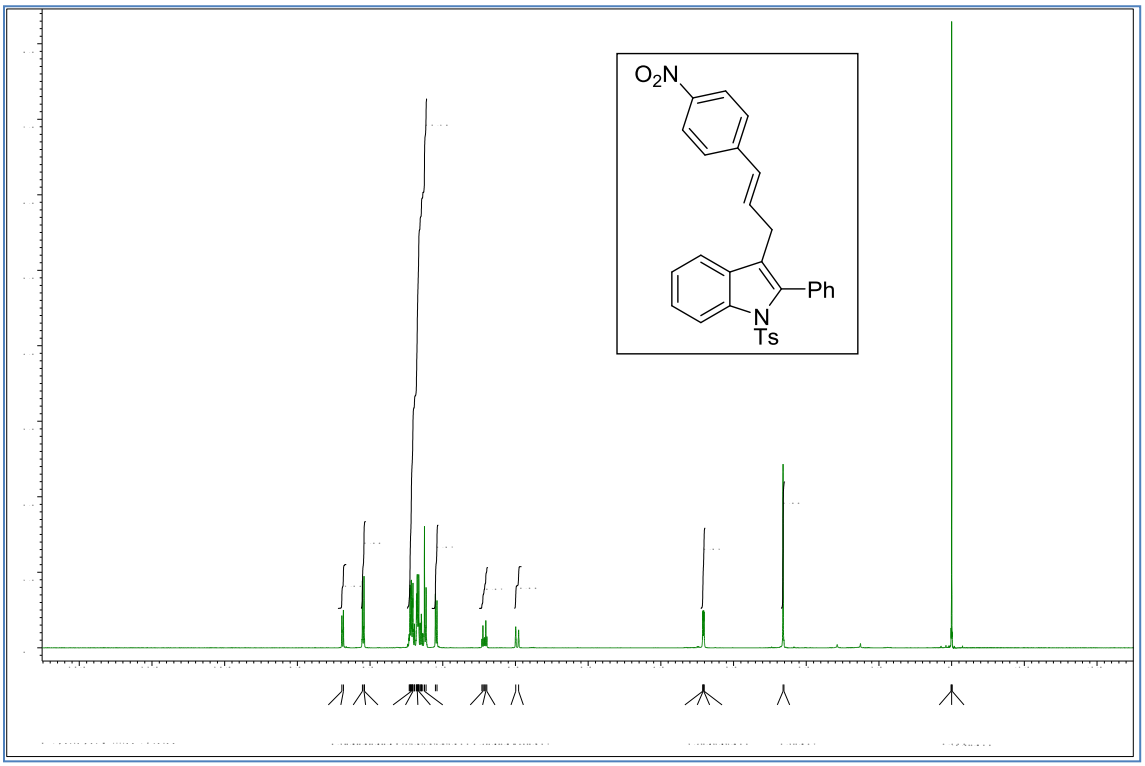


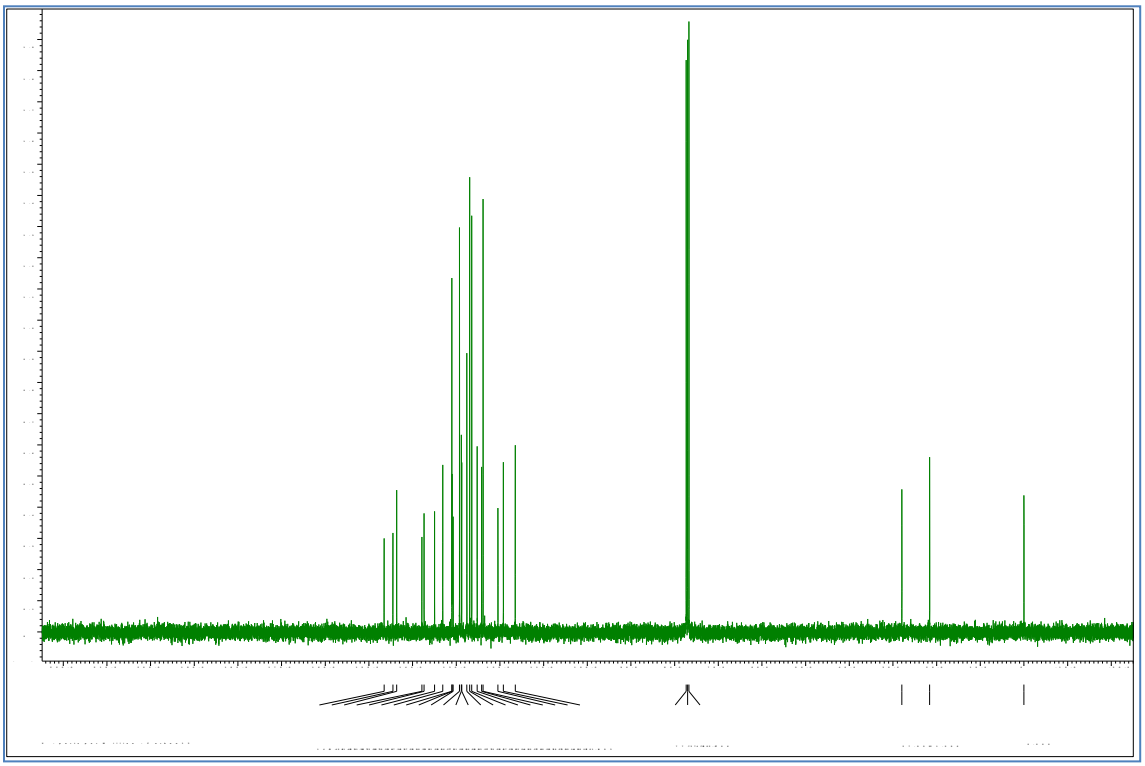

MeO
Ph
O

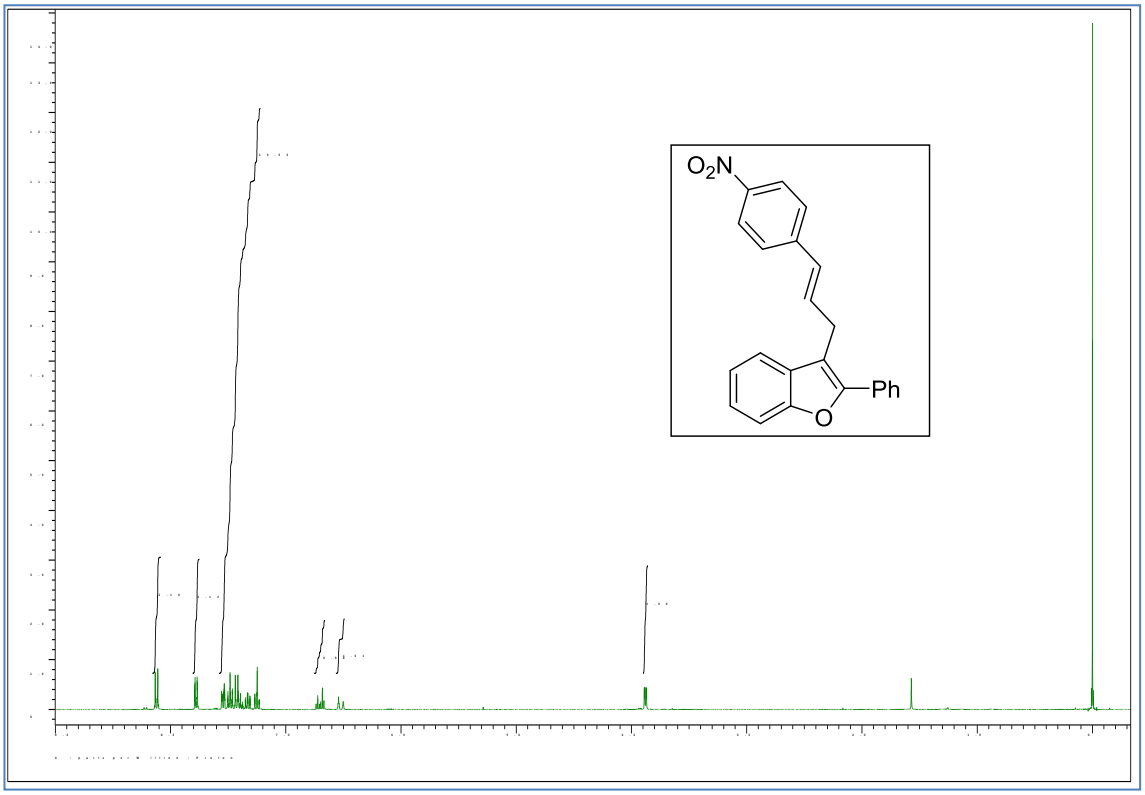


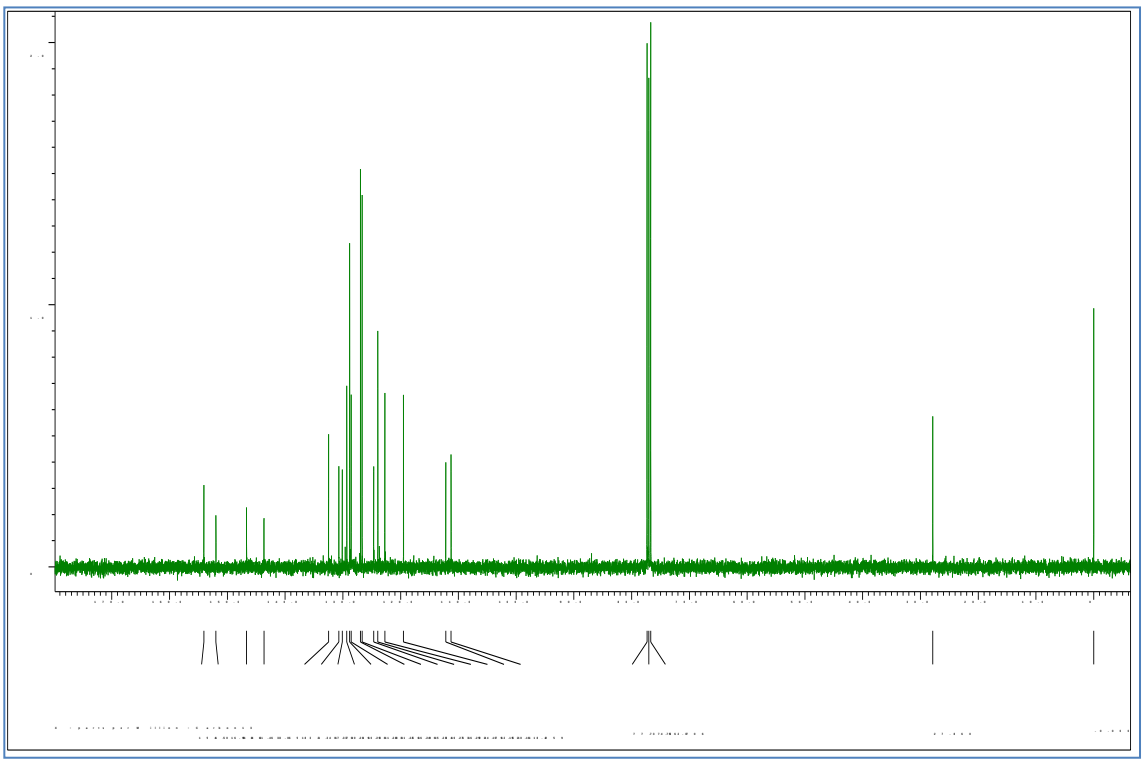

E:\NMR\P-nakashima23-a_Proton-1-1.jdf
8.132
8.110
7.887
7.881
7.870
7.864
7.739
7.735
7.717
7.561
7.557
7.540
7.537
7.475
7.458
7.439
7.420
7.400
7.399
7.386
7.380
7.376
7.367
7.363
7.250
6.686
6.646
6.632
6.426
6.386
3.860
3.855
3.845
3.841
1.545
0.000
2.05
1.04
1.07
2.11
1.04
1.02
2.00
O2N
Ph
S
PPM
8
6
4
2
0

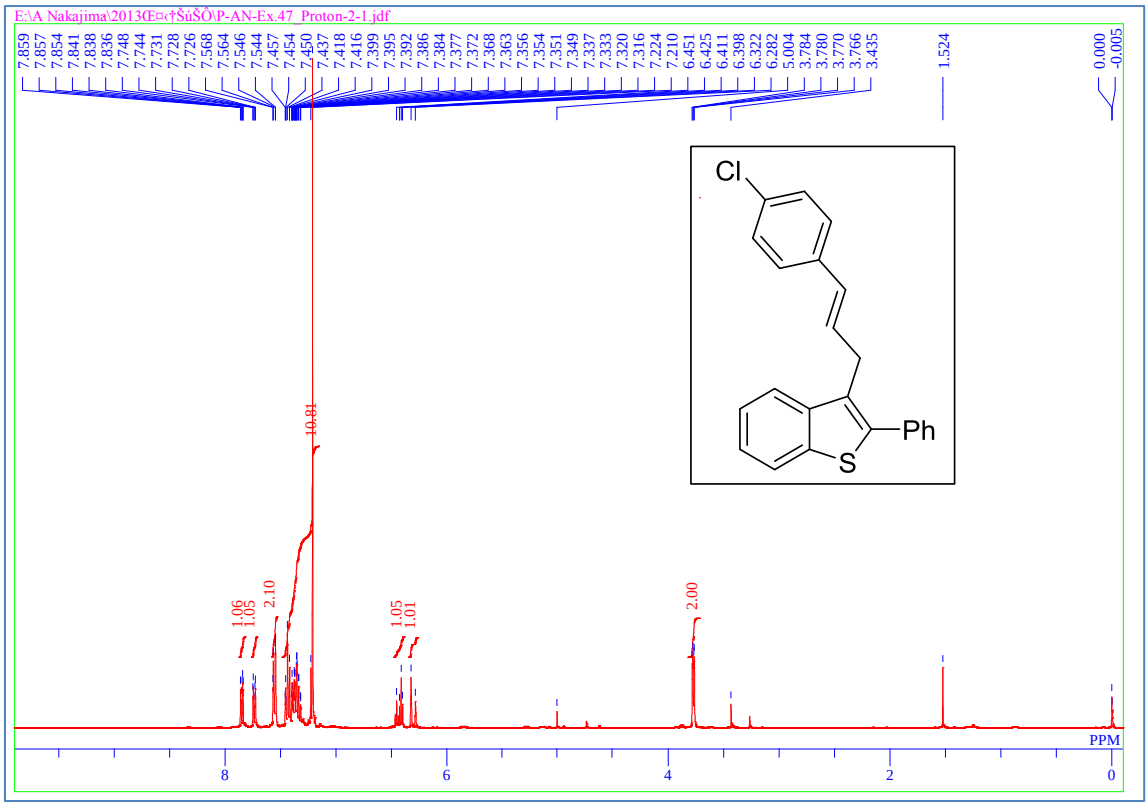

146.623
143.753
140.416
140.225
139.157
134.180
133.475
129.499
129.327
128.736
128.326
128.011
126.610
124.503
124.445
123.930
122.357
122.329
77.335
77.221
77.020
76.696
30.577
0.000
PPM
200
175
150
125
100
75
50
25
0

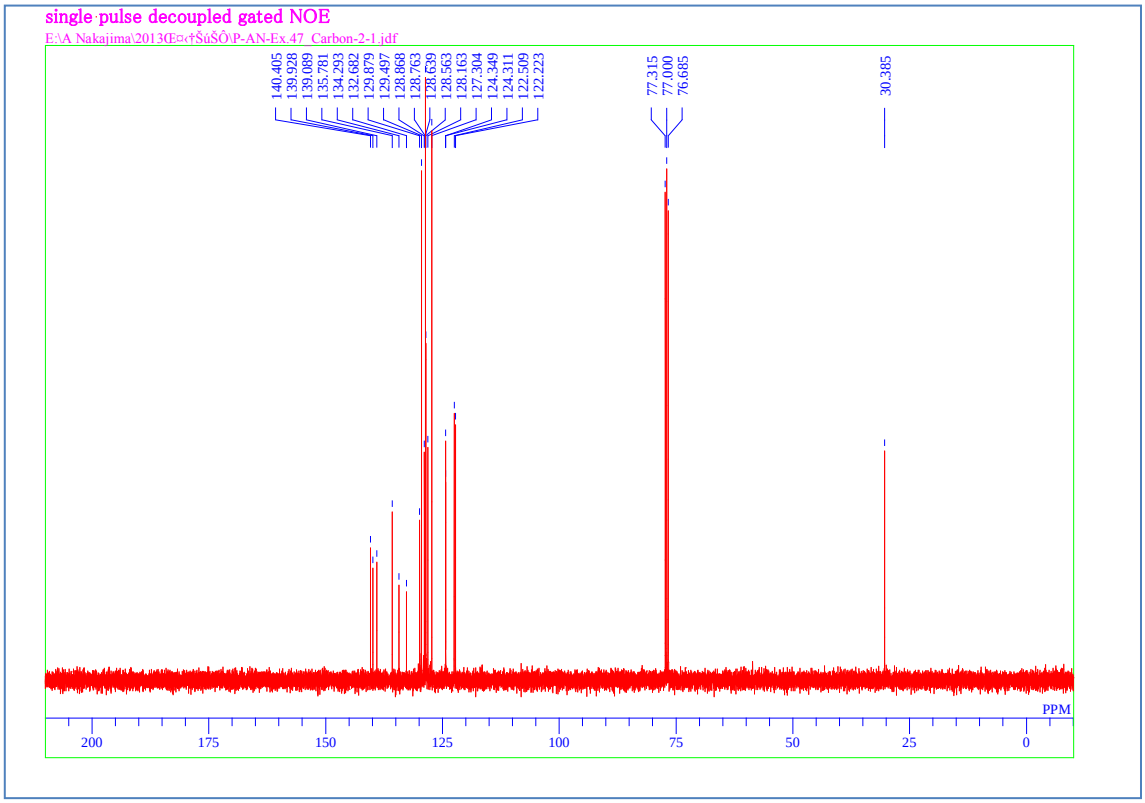

O2N
Ph
N
Ts

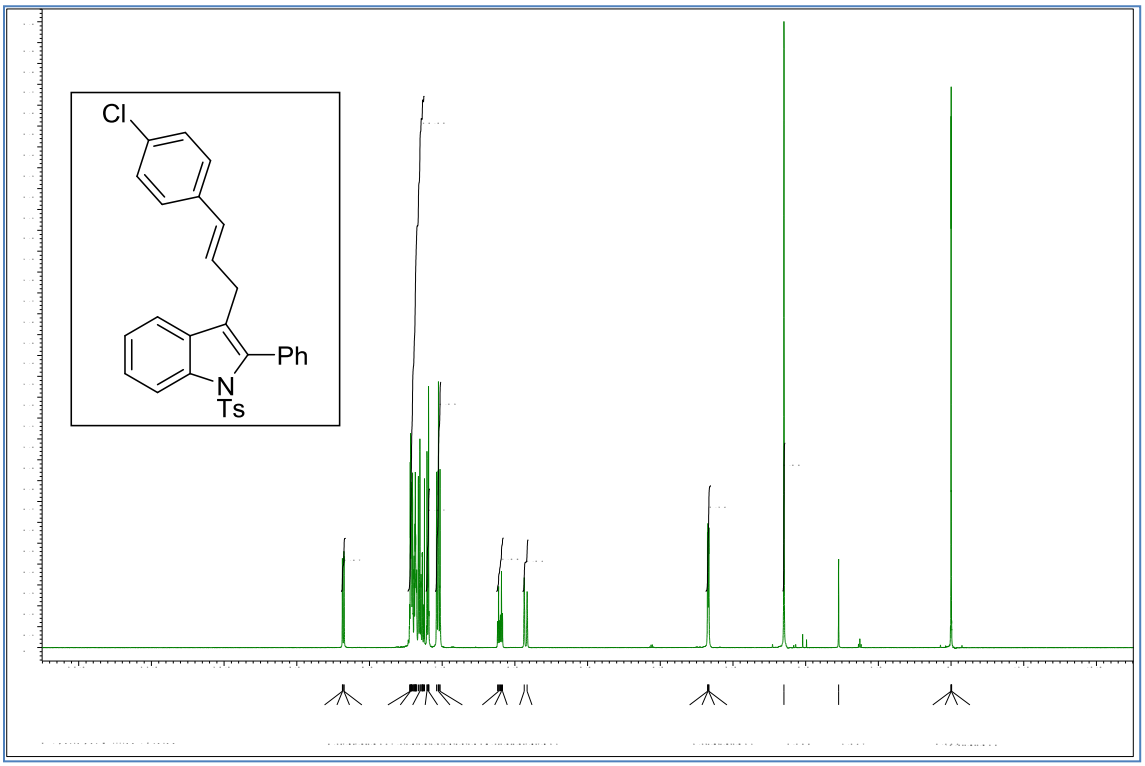


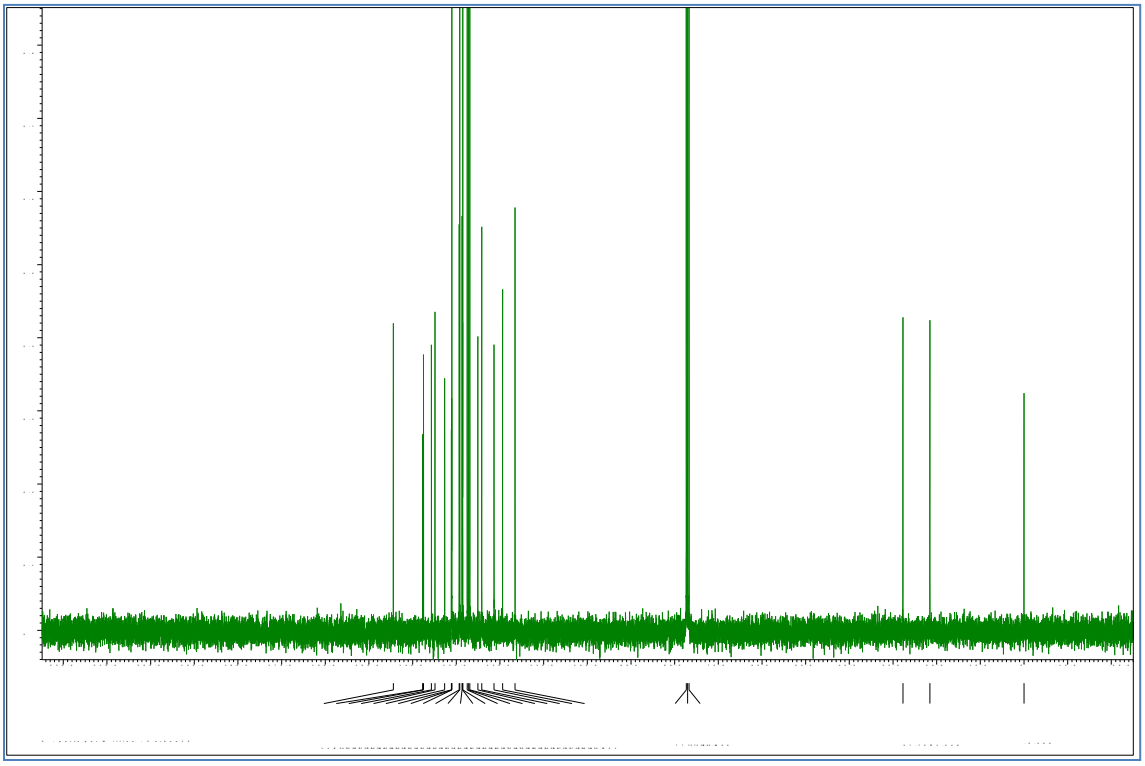

O2N
Ph
O

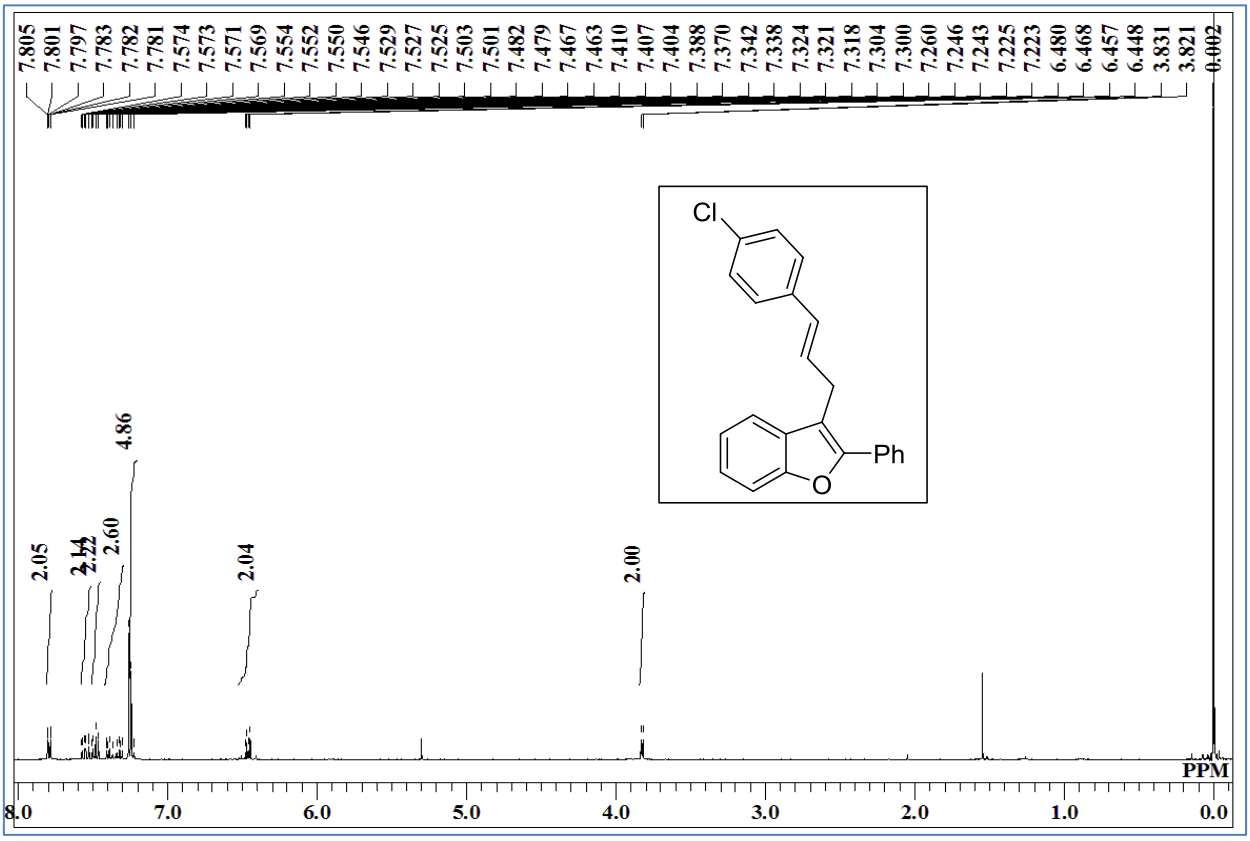


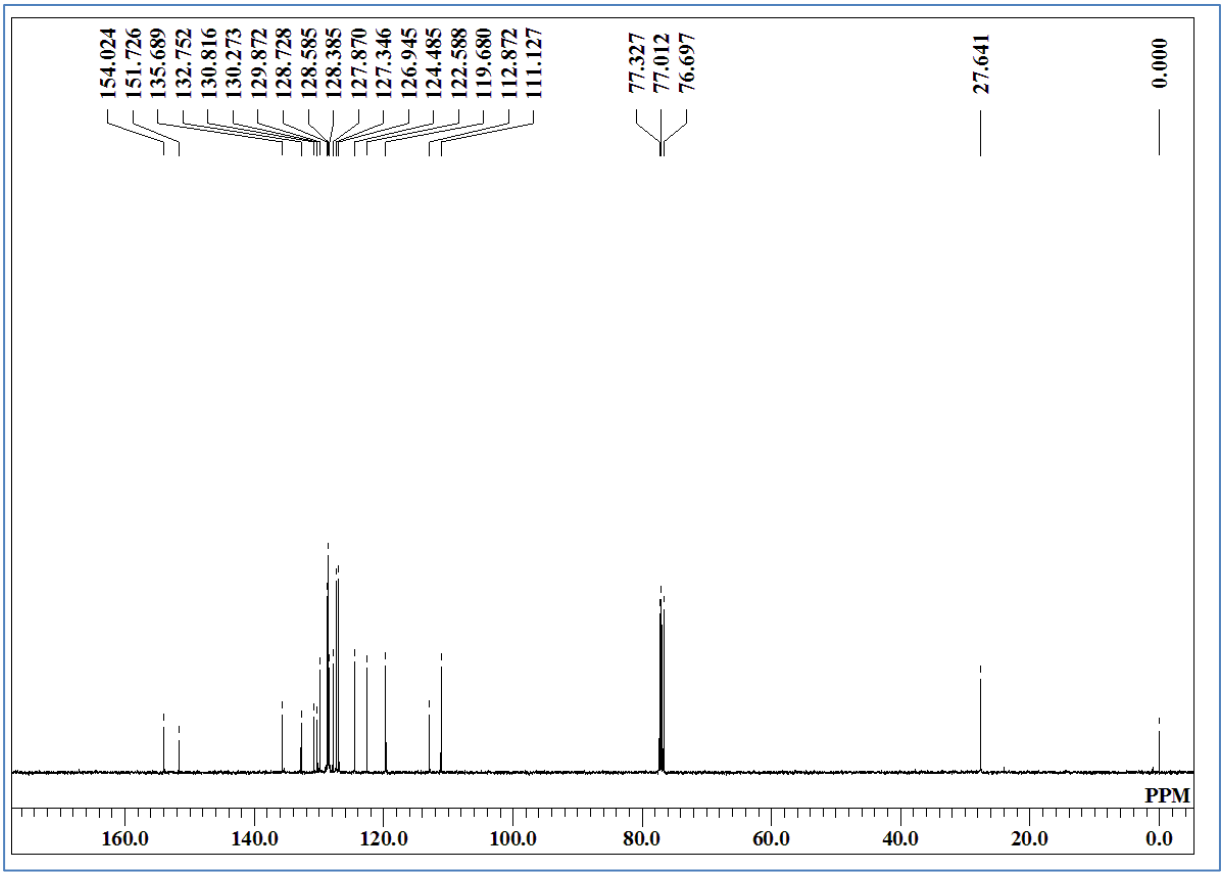

E:\A Nakajima\2013Œ¤‹†ŠúŠÔ\P-AN-Ex.47_Proton-2-1.jdf
7.859
7.857
7.854
7.841
7.838
7.836
7.748
7.744
7.731
7.728
7.726
7.568
7.564
7.546
7.544
7.457
7.454
7.450
7.437
7.418
7.416
7.399
7.395
7.392
7.386
7.384
7.377
7.372
7.368
7.363
7.356
7.354
7.351
7.349
7.337
7.333
7.320
7.316
7.224
7.210
6.451
6.425
6.411
6.398
6.322
6.282
5.004
3.784
3.780
3.770
3.766
3.435
1.524
0.000
-0.005
Cl
Ph
S
10.81
1.06
1.05
2.10
1.05
1.01
2.00
PPM
8
6
4
2
0

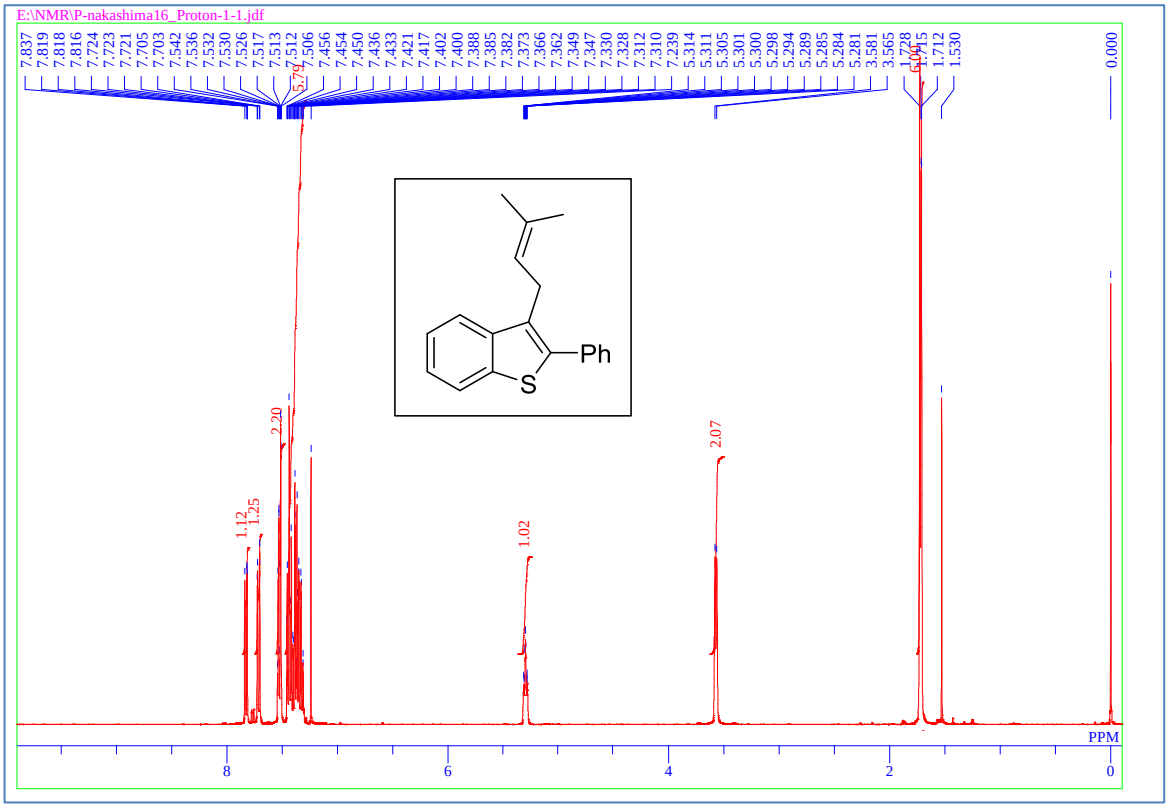

single pulse decoupled gated NOE
E:\A Nakajima\2013Œ¤‹†ŠúŠÔ\P-AN-Ex.47_Carbon-2-1.jdf
140.405
139.928
139.089
135.781
134.293
132.682
129.879
129.497
128.868
128.763
128.639
128.563
128.163
127.304
124.349
124.311
122.509
122.223
77.315
77.000
76.685
30.385
PPM
200
175
150
125
100
75
50
25
0

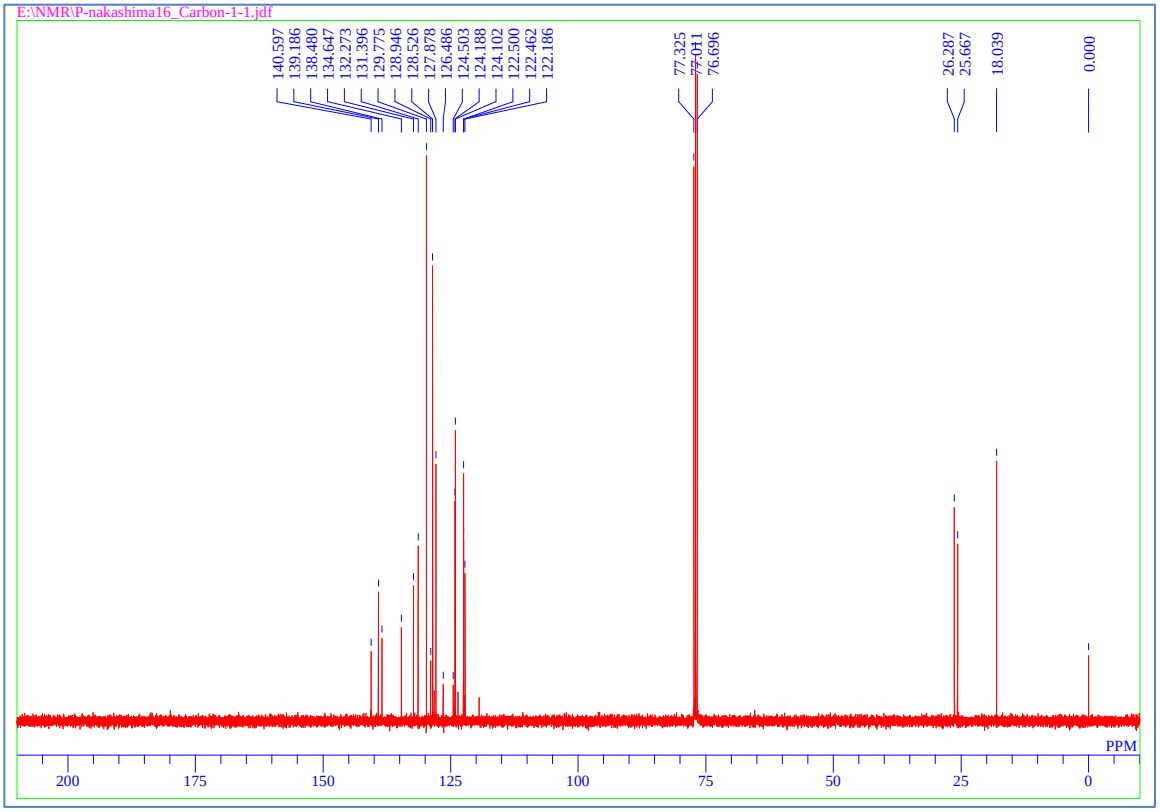

Cl
Ph
N
Ts

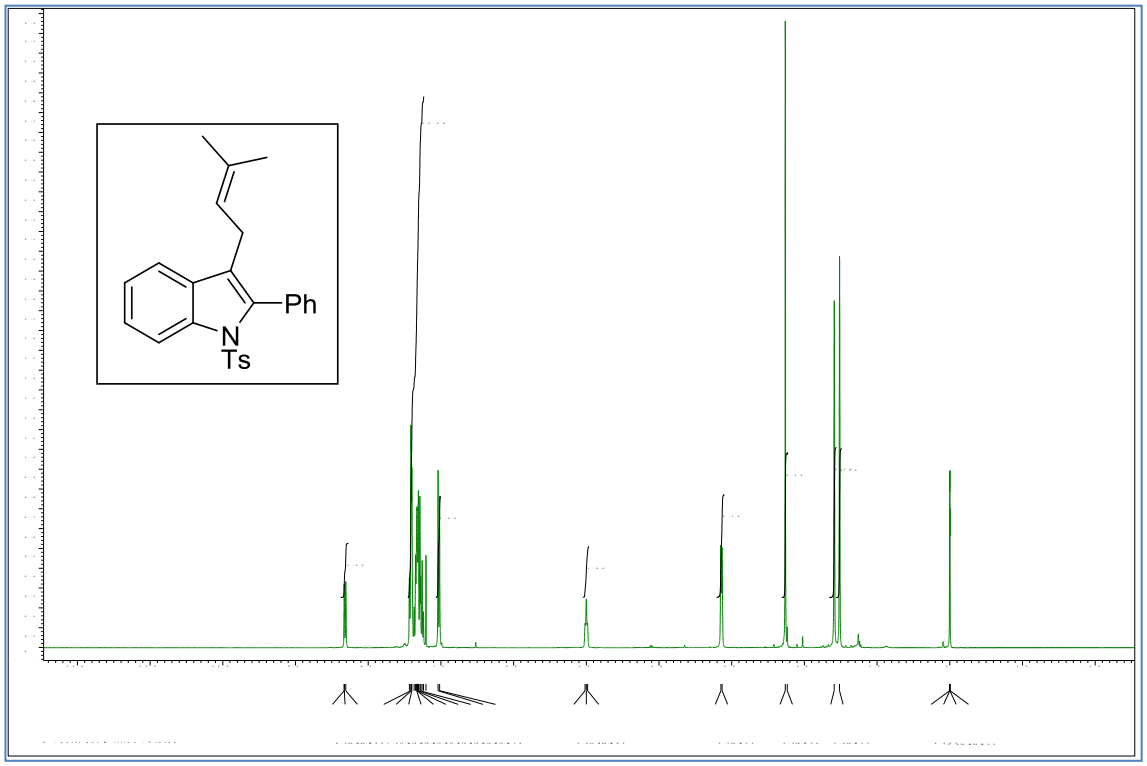


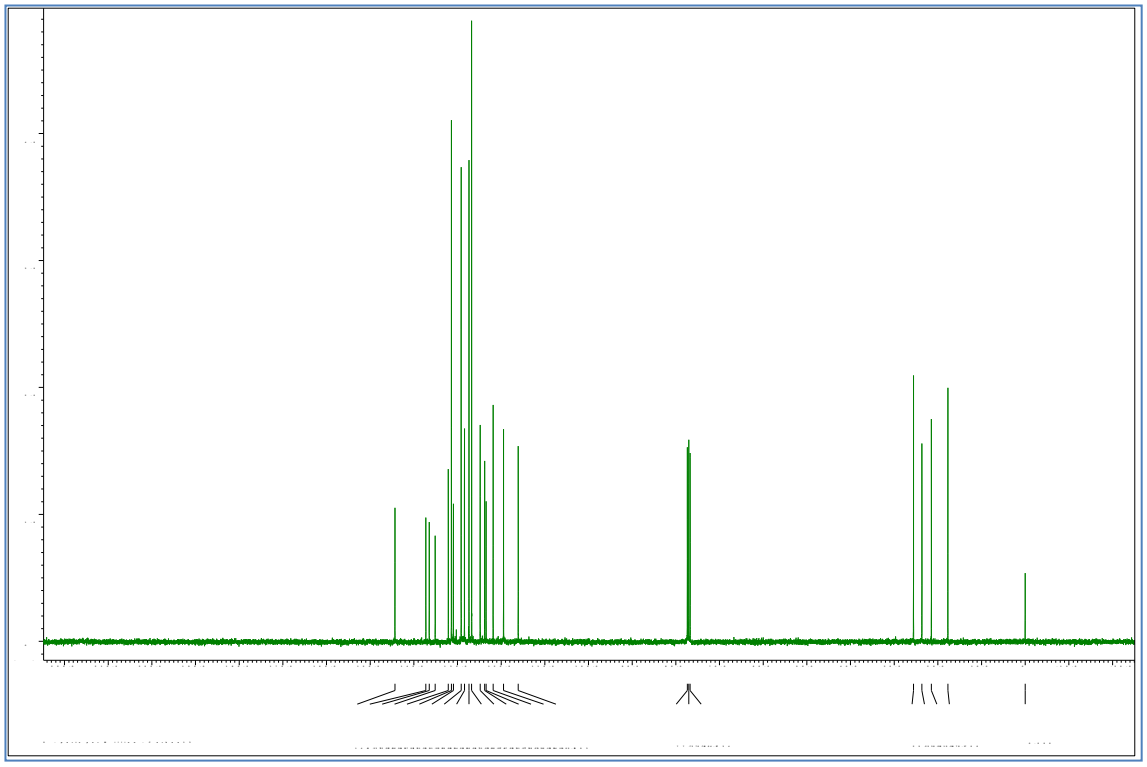

7.805
7.801
7.797
7.783
7.782
7.781
7.574
7.573
7.571
7.569
7.554
7.552
7.550
7.546
7.529
7.527
7.525
7.503
7.501
7.482
7.479
7.467
7.463
7.410
7.407
7.404
7.388
7.370
7.342
7.338
7.324
7.321
7.318
7.304
7.300
7.260
7.246
7.243
7.225
7.223
6.480
6.468
6.457
6.448
3.831
3.821
0.002
Cl
Ph
O
4.86
2.60
2.22
2.14
2.05
2.04
2.00
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


154.024
151.726
135.689
132.752
130.816
130.273
129.872
128.728
128.585
128.385
127.870
127.346
126.945
124.485
122.588
119.680
112.872
111.127
77.327
77.012
76.697
27.641
0.000
PPM
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0

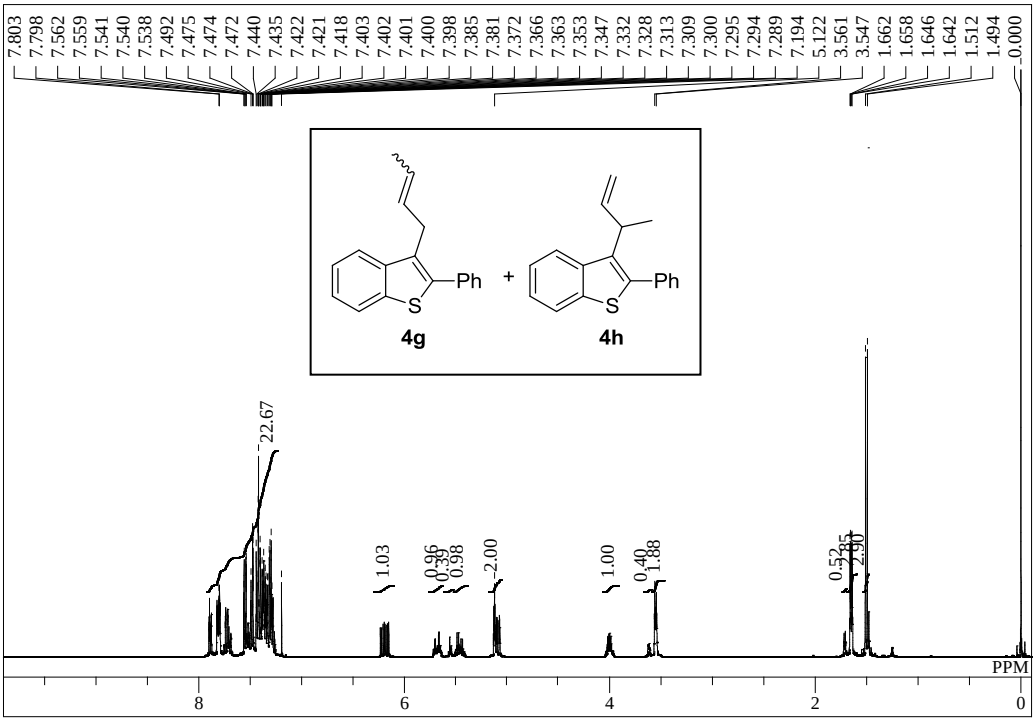

E:\NMR\P-nakashima16_Proton-1-1.jdf
7.837 7.819 7.818 7.816 7.724 7.723 7.721 7.705 7.703 7.542 7.536 7.532 7.530 7.526 7.517 7.513 7.512 7.506 7.456 7.454 7.450 7.436 7.433 7.421 7.417 7.402 7.400 7.388 7.385 7.382 7.373 7.366 7.362 7.349 7.347 7.330 7.328 7.312 7.310 7.239 5.314 5.311 5.305 5.301 5.300 5.298 5.294 5.289 5.285 5.284 5.281 3.581 3.565 1.728 1.715 1.712 1.530 0.000
5.79
6.06
Ph
S
2.20
2.07
1.12
1.25
1.02
PPM
8
6
4
2
0


E:\NMR\P-nakashima16_Carbon-1-1.jdf
140.597 139.186 138.480 134.647 132.273 131.396 129.775 128.946 128.526 127.878 126.486 124.503 124.188 124.102 122.500 122.462 122.186
77.325 77.041 76.696
26.287 25.667 18.039 0.000
PPM
200
175
150
125
100
75
50
25
0

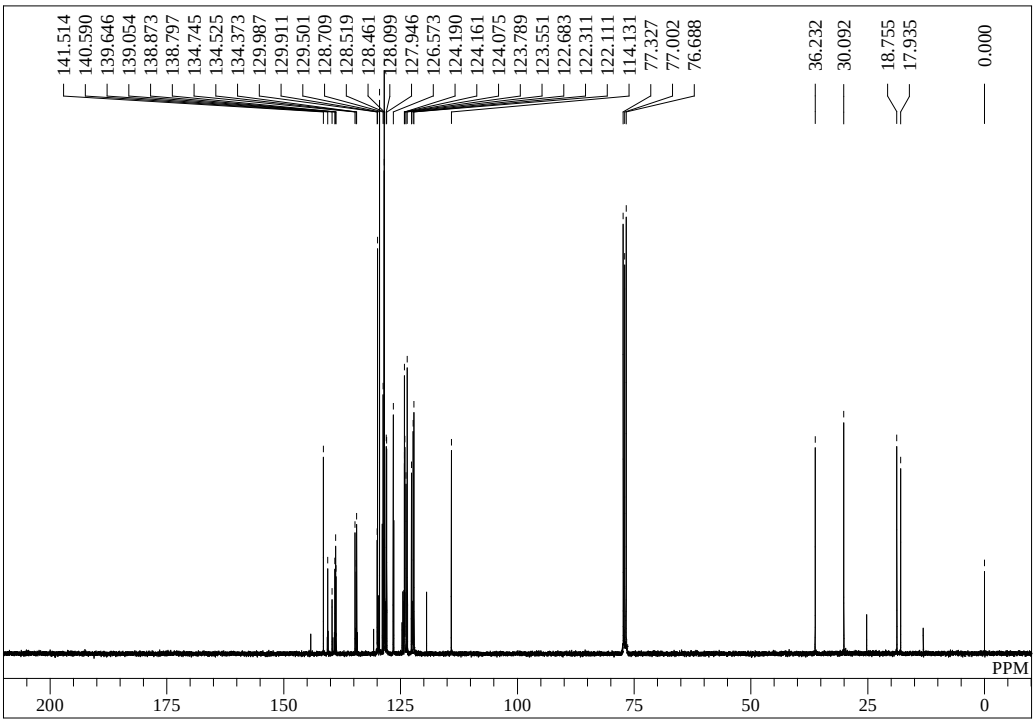

Ph
N
Ts



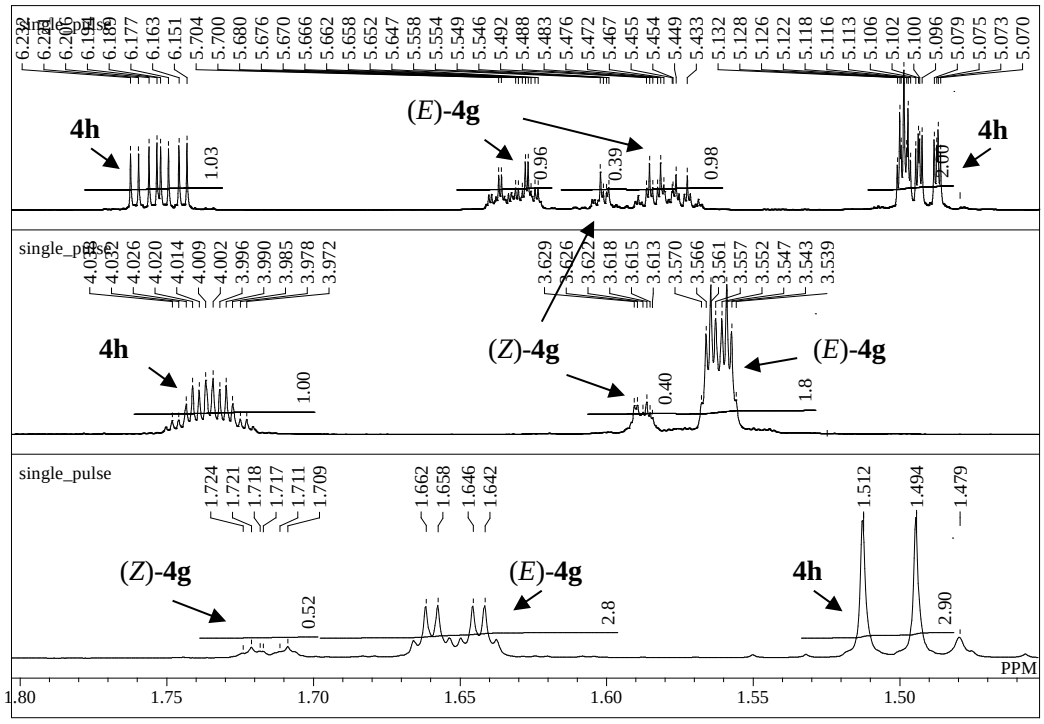
single_pulse

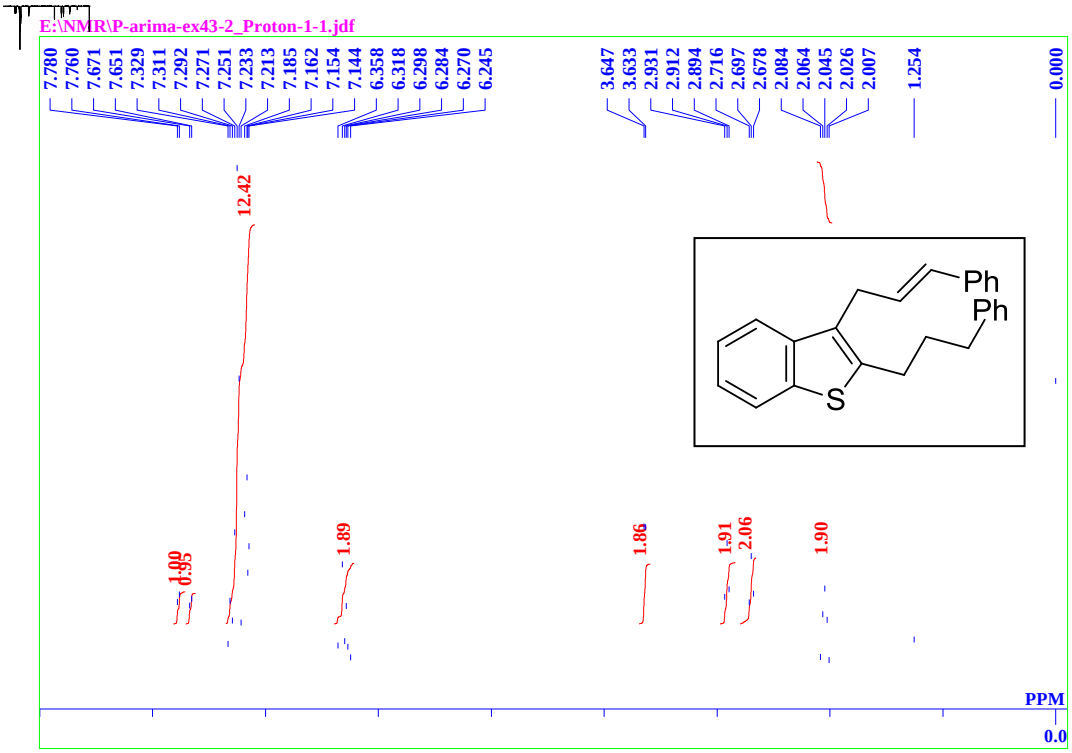


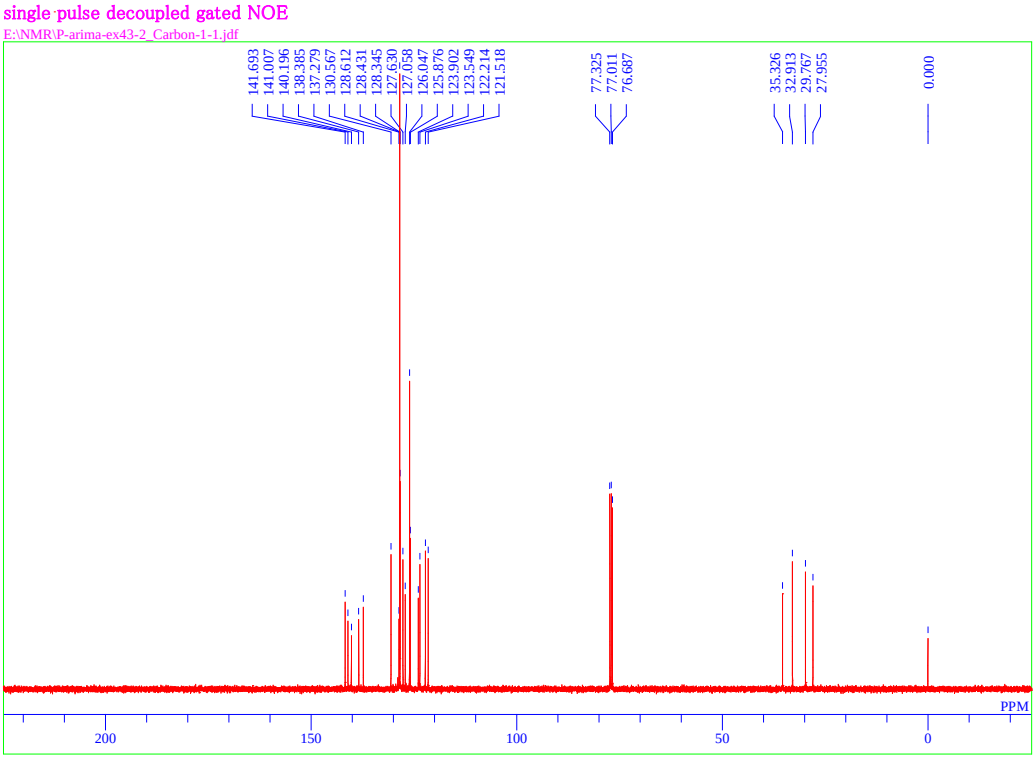
single pulse decoupled gated NOE



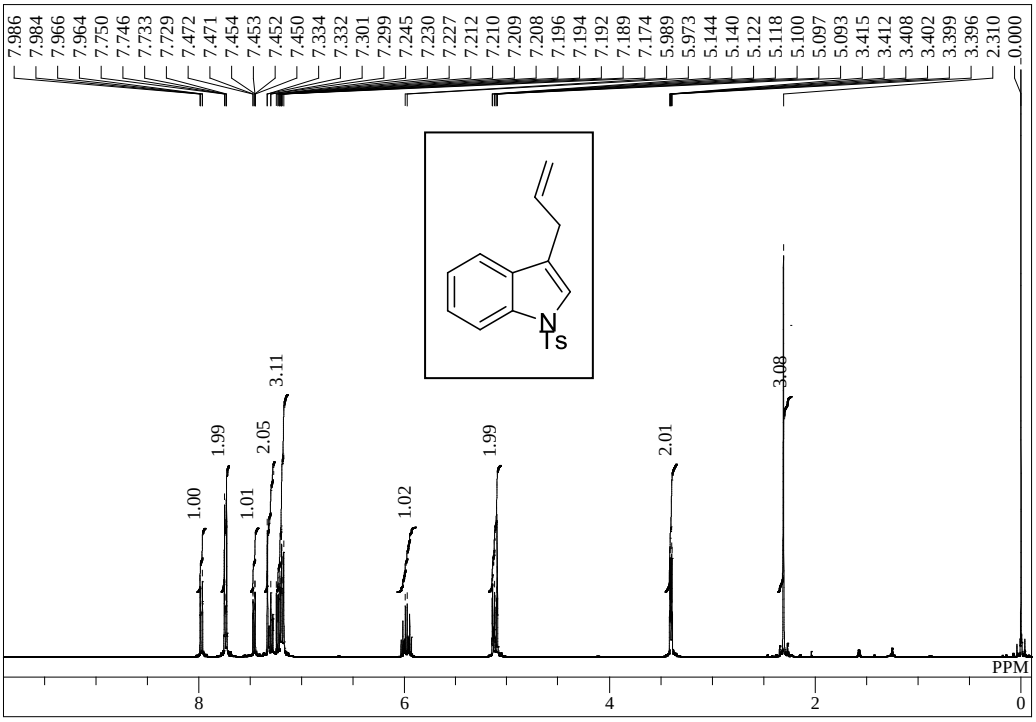
Enlarged NMR spectra of **4g** and **4h**



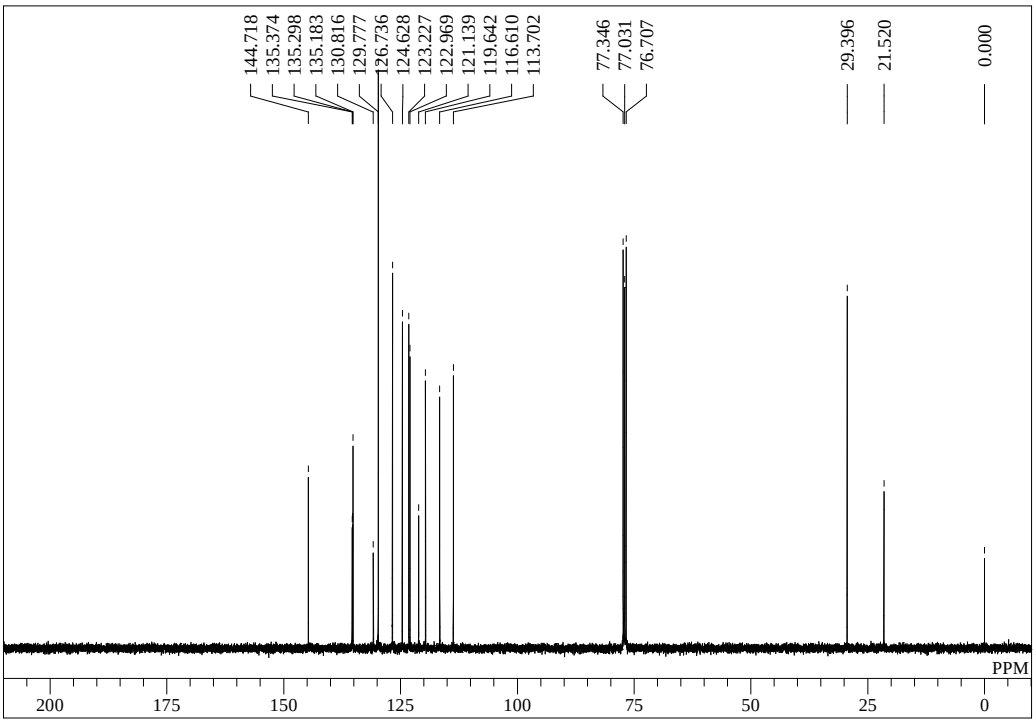

E:\NMR\P-arima-ex43-2_Proton-1-1.jdf
7.780
7.760
7.671
7.651
7.329
7.311
7.292
7.271
7.251
7.233
7.213
7.185
7.162
7.154
7.144
6.358
6.318
6.298
6.284
6.270
6.245
3.647
3.633
2.931
2.912
2.894
2.716
2.697
2.678
2.084
2.064
2.045
2.026
2.007
1.254
0.000
12.42
1.00
0.95
1.89
1.86
1.91
2.06
1.90
Ph
Ph
S
PPM
0.0


single pulse decoupled gated NOE
E:\NMR\P-arima-ex43-2_Carbon-1-1.jdf
141.693
141.007
140.196
138.385
137.279
130.567
128.612
128.431
128.345
127.630
127.058
126.047
125.876
123.902
123.549
122.214
121.518
77.325
77.011
76.687
35.326
32.913
29.767
27.955
0.000
PPM
200
150
100
50
0

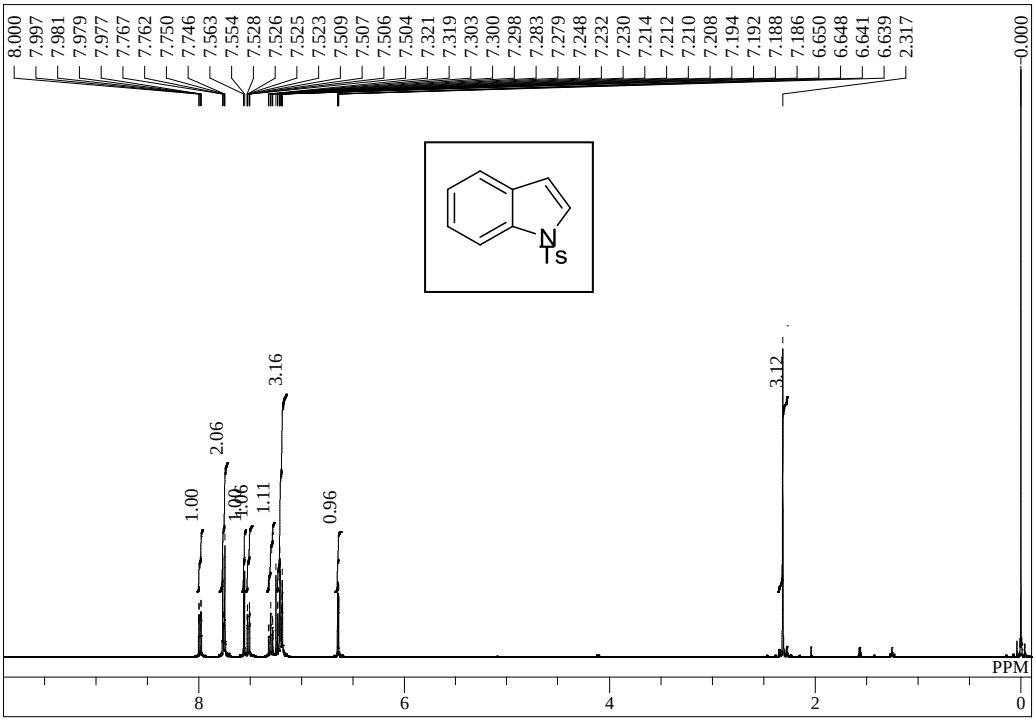
single_pulse



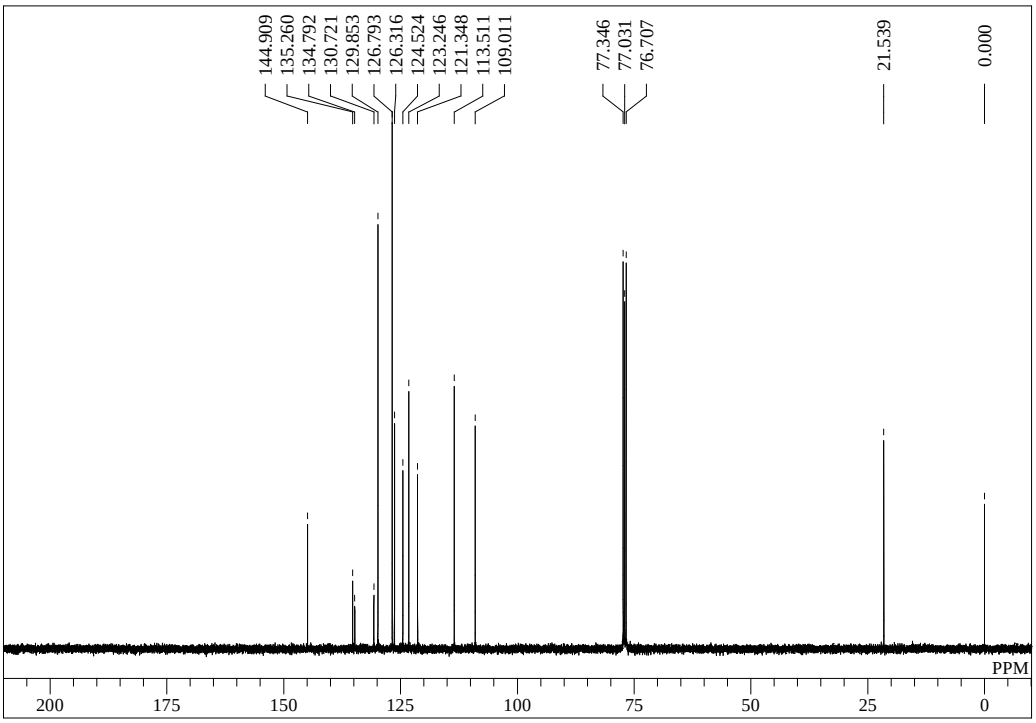
single pulse decoupled gated NOE

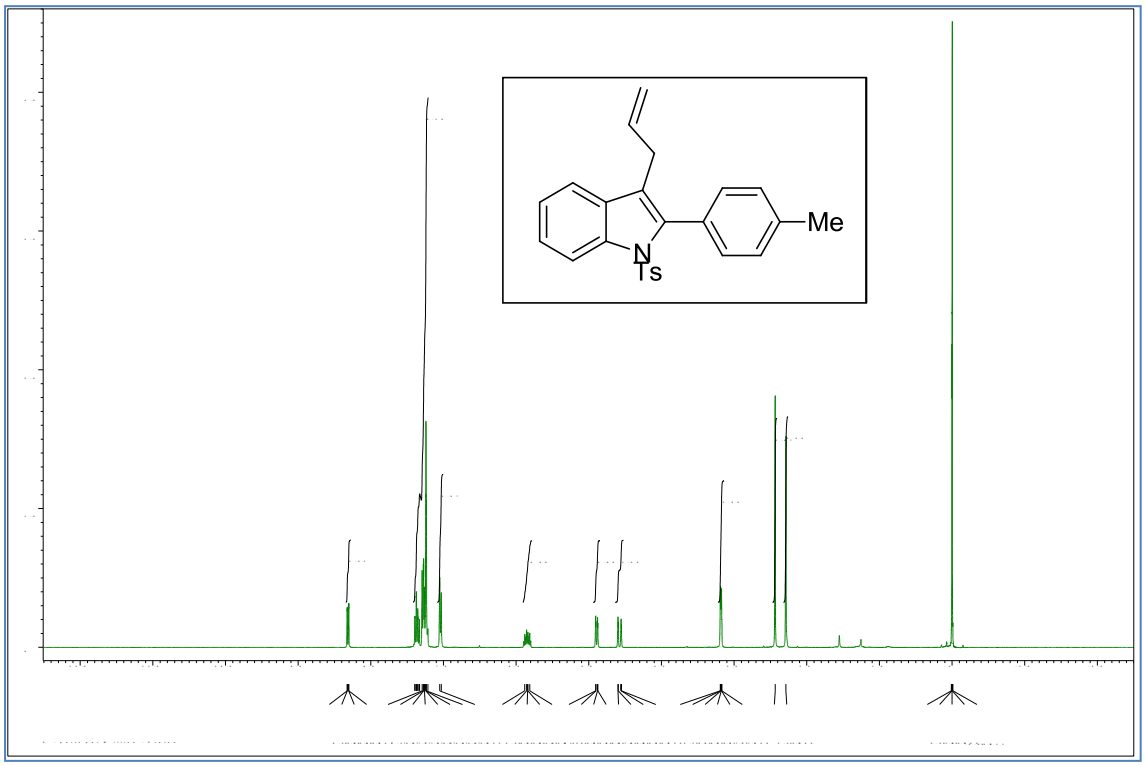


single_pulse



single pulse decoupled gated NOE




Me
N
Ts