Supporting Information

SITE-SELECTIVE INTRODUCTION OF AN ENAMIDO GROUP AT THE C(3)-POSITION OF INDOLES

Tomoya Miura,* Qiang Zhao, Yuuta Funakoshi, and Masahiro Murakami*

Department of Synthetic Chemistry and Biological Chemistry, Kyoto University, Katsura, Kyoto 615-8510

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General Methods.

IR measurements were performed on a FTIR SHIMADZU DR-8000 spectrometer fitted with a Pike Technologies MIRacle Single Reflection ATR adapter. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury-vx400 (^{1}H at 400.44 MHz and ^{13}C at 100.69 MHz), a JEOL JNM-ECS400 (^{1}H at 399.78 MHz and ^{13}C at 100.53 MHz) or a JEOL JNM-ECA600 (^{1}H at 600.17 MHz and ^{13}C at 150.92 MHz) spectrometer. NMR data were obtained in $CDCl_3$. Proton chemical shifts were referenced to the residual proton signal of the solvent at 7.26 ppm ($CHCl_3$). Carbon chemical shifts were referenced to the carbon signal of the solvent at 77.0 ppm ($CDCl_3$). High-resolution mass spectra were recorded on a Thermo Scientific Exactive (ESI) spectrometer. Flash column chromatography was performed with silica gel 60N (Kanto). Preparative thin-layer chromatography (PTLC) was performed on silica gel plates with PF254 indicator (Merck).

Materials.

($^{t}BuCO_2$)$_4Rh_2$ (Aldrich), iodine (Wako), cesium carbonate (Aldrich), Pd/C (Aldrich) were used as received from the commercial source. Chloroform (Wako, dehydrated, amylene as stabilizer) was distilled from phosphorus oxide (Wako). Ethanol (Wako, super dehydrated) and acetonitrile (Wako, super dehydrated) were used as received from the commercial source. 1-Sulfonyl-1,2,3-triazoles **1a**–**m** were prepared according to the literature procedure.[1] The analytical data of compounds **1a**,[2] **1b**,[2] **1c**,[2] **1d**,[3] **1e**,[3] **1f**,[4] **1g**,[5] **1h**,[5] **1i**,[2] **1j**,[6] **1k**,[7] **1l**,[3] and **1m**[1] have already been reported. Phenylacetylene (**4**, Aldrich) was obtained from commercial sources and distilled before use. 1,2-Dimethyl-1*H*-indole (**2a**, TCI), 1-methyl-1*H*-indole (TCI), 5-bromo-1-methyl-1*H*-indole (Aldrich), 4-bromo-1-methyl-1*H*-indole (Aldrich) were used as received from the commercial source. 2,3-Dihydro-1*H*-pyrrolo[1,2-*a*]indole **2b** was prepared according to the literature procedure.[8] 1,7-Dimethyl-1*H*-indole, 1,5-dimethyl-1*H*-indole, 5-methoxy-1-methyl-1*H*-indole were prepared according to the literature procedure.[9]

CAUTION!

Sulfonyl azides are potentially explosive materials and must be handled with caution, although we have never encountered any difficulty in handling them.

Procedure for the Reaction of *N*-Sulfonyl-1,2,3-Triazole 1a with 1,2-Dimethyl-1*H*-Indole (2a) (Table 1 & 2).

In a nitrogen-filled glove-box, ($^{t}BuCO_2$)$_4Rh_2$ (1.22 mg, 1.0 mol %), 4-phenyl-1-tosyl-1,2,3-triazole (**1a**, 59.9 mg, 0.20 mmol), 1,2-dimethyl-1*H*-indole (**2a**, 43.6 mg, 0.30 mmol), and $CHCl_3$ (2 mL) were added to an oven-dried 20 mL Schlenk flask equipped with a stirrer bar. The flask was sealed with a cap. The reaction mixture was heated at 80 °C for 8 hours. The resulting mixture was cooled to room temperature and concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography (chloroform/ethyl acetate = 100:1) to give the product **3a** (80.8 mg, 0.19 mmol, 97%).

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1 Raushel, J.; Fokin, V. V. *Org. Lett.* **2010**, *12*, 4952.
2 Miura, T.; Yamauchi, M.; Murakami, M. *Chem. Commun*. **2009**, 1470.
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4 Miura, T.; Hiraga, K.; Biyajima, T.; Nakamuro, T.; Murakami, M. *Org. Lett.* **2013**, *15*, 3298.
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8 Ishikura, M.; Ida, W.; Yanada, K. *Tetrahedron* **2006**, *62*, 1015.
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One-Pot Procedure for the Synthesis of 3a Starting from Phenylacetylene (4) (Eq 2).

Phenylacetylene (**4**, 21.7 mg, 0.21 mmol), TsN_3 (42.0 mg, 0.21 mmol), CuTC (3.82 mg, 10 mol %), $(^tBuCO_2)_4Rh_2$ (1.22 mg, 1.0 mol %), 1,2-dimethyl-1*H*-indole (**2a**, 43.7 mg, 0.30 mmol), and $CHCl_3$ (2 mL) were added to an oven-dried 4 mL-vial equipped with a stirrer bar. The vial was sealed with a cap containing an inner Teflon film. The reaction mixture was stirred at room temperature for 3 hours. Then, the resulting mixture was heated at 80 ℃ for 8 hours. After the mixture was cooled to room temperature, it was concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography (chloroform/ethyl acetate = 100:1) to give the product **3a** (70.1 mg, 0.17 mmol, 79%).

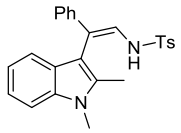
Procedure for the Hydrogenation Reaction of 3a, 3n, and 3q (Eq 3).

A side-arm tube equipped with a stirrer bar was charged with **3a** (81.8 mg, 0.20 mmol), Pd/C (10 wt % support carbon, dry, 21.3 mg, 10 mol %), and ethanol (2 mL). The tube was connected to a hydrogen balloon and immersed in a dry ice/acetone bath. After ten vacuum/H_2-filling cycles, the cooling bath was removed. The reaction mixture was stirred for 10–18 hours at room temperature. Then, the resulting mixture was passed through a pad of Celite and eluted with ethyl acetate. The filtrate was concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography (chloroform/ethyl acetate = 100:1) to give the product **6** (70.9 mg, 86%).

Procedure for the Iodine-Catalyzed Cyclization Reaction of 6 (Eq 4).[10]

A mixture of indole derivative **6** (80.8 mg, 0.20 mmol), iodine (51.4 mg, 0.20 mmol), Cs_2CO_3 (133.0 mg, 2.0 mmol), and acetonitrile (2 mL) was stirred at room temperature for 60 hours. The reaction was quenched with a saturation solution of $Na_2S_2O_3$ (5 mL) and then extracted with ethyl acetate (3 × 10 mL). The combined organic phases were washed with brine (20 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 3:1) to give the product **8** (62.0 mg, 77%).

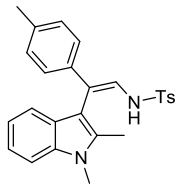
3a:



IR (ATR): 3252, 2924, 1632, 1595, 1333, 1155 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.07 (s, 3H), 2.48 (s, 3H), 3.72 (s, 3H), 6.37 (br, 1H), 6.68 (d, *J* = 7.6 Hz, 1H), 6.83–6.89 (m, 1H), 7.03–7.09 (br, 1H), 7.15–7.37 (m, 9H), 7.69 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 10.8, 21.5, 29.7, 106.3, 108.8, 117.7, 118.4, 119.7, 121.2, 121.7, 125.8, 126.2, 126.6, 126.8, 128.3, 129.7, 135.6, 136.9, 137.0, 139.5, 143.7; HRMS (ESI^+): Calcd for $C_{25}H_{25}N_2O_2S$, $M+H^+$ 417.1631. Found m/z 417.1622.

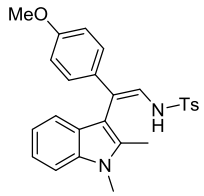
10 Li, Y.-X.; Wang, H.-X.; Ali, S.; Xia, X.-F.; Liang, Y.-M. *Chem. Commun.* **2012**, *48*, 2343.

3b:



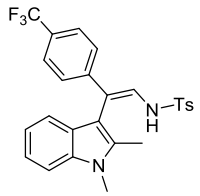
IR (ATR): 3256, 2916, 1634, 1472, 1327, 1151, 1088 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.06 (s, 3H), 2.32 (s, 3H), 2.47 (s, 3H), 3.71 (s, 3H), 6.29 (d, *J* = 11.6 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 6.81–6.87 (m, 1H), 6.99–7.19 (m, 6H), 7.27–7.35 (m, 3H), 7.68 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 10.8, 21.0, 21.5, 29.7, 106.4, 108.8, 117.7, 118.5, 119.7, 121.0, 121.2, 125.7, 126.2, 126.9, 129.0, 129.7, 135.6, 136.4, 136.7, 136.97, 137.02, 143.7; HRMS (ESI^+): Calcd for $C_{26}H_{27}N_2O_2S$, $M+H^+$ 431.1788. Found m/z 431.1777.

3c:



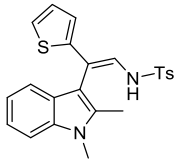
IR (ATR): 3229, 2928, 1510, 1325, 1242, 1171, 1146, 1030 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.06 (s, 3H), 2.47 (s, 3H), 3.71 (s, 3H), 3.77 (s, 3H), 6.29 (d, *J* = 11.6 Hz, 1H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 8.8 Hz, 2H), 6.82–6.88 (m, 1H), 6.95 (d, *J* = 11.6 Hz, 1H), 7.09–7.20 (m, 3H), 7.27–7.35 (m, 3H), 7.68 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 10.8, 21.5, 29.7, 55.2, 106.5, 108.8, 113.7, 117.6, 118.5, 119.6, 120.1, 121.1, 126.2, 126.86, 126.94, 129.7, 132.2, 135.5, 136.96, 137.01, 143.6, 158.6; HRMS (ESI^+): Calcd for $C_{26}H_{27}N_2O_3S$, $M+H^+$ 447.1737. Found m/z 447.1727.

3d:



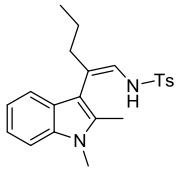
IR (ATR): 3258, 3051, 2925, 1607, 1472, 1323, 1155, 1109, 1067 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.05 (s, 3H), 2.47 (s, 3H), 3.72 (s, 3H), 6.40 (d, *J* = 11.6 Hz, 1H), 6.62 (d, *J* = 7.6 Hz, 1H), 6.82–6.88 (m, 1H), 7.12 (d, *J* = 12.0 Hz, 1H), 7.15–7.21 (m, 1H), 7.27–7.36 (m, 5H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 10.9, 21.6, 29.8, 105.6, 109.1, 116.2, 118.3, 120.0, 121.5, 123.6, 124.3 (q, *J* = 270.2 Hz), 125.3 (q, *J* = 3.7 Hz), 125.9, 126.0, 126.9, 128.4 (q, *J* = 32.2 Hz), 129.9, 135.8, 136.9, 137.2, 143.3, 144.0; HRMS (ESI^+): Calcd for $C_{26}H_{24}F_3N_2O_2S$, $M+H^+$ 485.1505. Found m/z 485.1494.

3e:



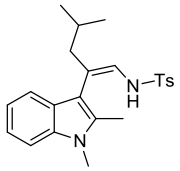
IR (ATR): 3258, 2922, 1634, 1472, 1151, 1088 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.10 (s, 3H), 2.47 (s, 3H), 3.71 (s, 3H), 6.26 (d, *J* = 11.6 Hz, 1H), 6.69–6.75 (m, 2H), 6.84–6.90 (m, 1H), 7.04 (d, *J* = 11.2 Hz, 1H), 7.13–7.19 (m, 2H), 7.23–7.34 (m, 4H), 7.66 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 10.9, 21.6, 29.8, 106.3, 108.9, 113.8, 118.6, 119.7, 120.5, 121.28, 121.32, 124.7, 125.8, 126.1, 126.9, 129.8, 135.4, 137.0, 137.1, 141.2, 143.8; HRMS (ESI^+): Calcd for $C_{23}H_{23}N_2O_2S_2$, $M+H^+$ 423.1195. Found m/z 423.1183.

3f:



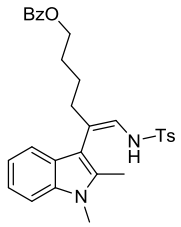
IR (ATR): 3279, 2928, 1651, 1597, 1472, 1335, 1157, 1090 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 0.82 (t, *J* = 7.2 Hz, 3H), 1.20–1.31 (m, 2H), 2.15 (s, 3H), 2.14–2.33 (m, 2H), 2.46 (s, 3H), 3.66 (s, 3H), 5.95 (d, *J* = 11.2 Hz, 1H), 6.37 (dt, *J* = 11.2, 0.8 Hz, 1H), 6.81–6.85 (m, 1H), 6.86–6.93 (m, 1H), 7.11–7.17 (m, 1H), 7.22–7.31 (m, 3H), 7.60 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 10.7, 13.6, 21.51, 21.54, 29.6, 37.9, 107.3, 108.7, 118.3, 118.9, 119.3, 120.7, 121.0, 126.3, 126.8, 129.6, 134.0, 136.86, 136.89, 143.4; HRMS (ESI^+): Calcd for $C_{22}H_{27}N_2O_2S$, $M+H^+$ 383.1788. Found m/z 383.1777.

3g:



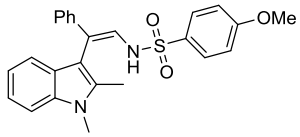
IR (ATR): 3267, 2951, 1653, 1472, 1396, 1319, 1157, 1088 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 0.78 (d, *J* = 6.0 Hz, 3H), 0.80 (d, *J* = 6.4 Hz, 3H), 1.30–1.43 (m, 1H), 2.06 (ddd, *J* = 13.6, 6.8, 1.2 Hz, 1H), 2.15 (s, 3H), 2.20 (ddd, *J* = 13.6, 6.8, 0.8 Hz, 1H), 2.46 (s, 3H), 3.66 (s, 3H), 5.95 (d, *J* = 11.6 Hz, 1H), 6.33 (dt, *J* = 11.6, 0.8 Hz, 1H), 6.79–6.83 (m, 1H), 6.86–6.92 (m, 1H), 7.11–7.17 (m, 1H), 7.21–7.31 (m, 3H), 7.61 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 10.8, 21.6, 22.4, 26.3, 29.6, 45.3, 107.5, 108.8, 118.0, 118.4, 119.4, 121.1, 121.3, 126.2, 126.9, 129.6, 134.0, 136.92, 136.94, 143.5; HRMS (ESI^+): Calcd for $C_{23}H_{29}N_2O_2S$, $M+H^+$ 397.1944. Found m/z 397.1938.

3h:



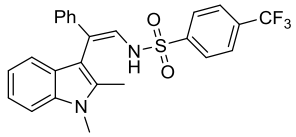
IR (ATR): 3261, 2941, 1713, 1472, 1273, 1157, 1090 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 1.34–1.44 (m, 2H), 1.65–1.75 (m, 2H), 2.14 (s, 3H), 2.24–2.42 (m, 2H), 2.43 (s, 3H), 3.64 (s, 3H), 4.16–4.27 (m, 2H), 5.99 (d, *J* = 11.6 Hz, 1H), 6.40 (d, *J* = 11.2 Hz, 1H), 6.81–6.93 (m, 2H), 7.11–7.18 (m, 1H), 7.21–7.29 (m, 3H), 7.38–7.46 (m, 2H), 7.52–7.63 (m, 3H), 7.92–7.98 (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 10.7, 21.5, 24.7, 28.1, 29.6, 35.3, 64.6, 106.9, 108.8, 118.17, 118.25, 119.5, 121.0, 121.1, 126.2, 126.8, 128.3, 129.4, 129.6, 130.3, 132.8, 134.1, 136.8, 136.9, 143.5, 166.5; HRMS (ESI^+): Calcd for $C_{30}H_{33}N_2O_4S$, $M+H^+$ 517.2156. Found m/z 517.2152.

3i:



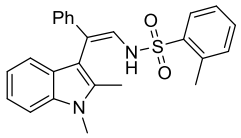
IR (ATR): 3252, 2920, 1593, 1337, 1252, 1155, 1092 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.06 (s, 3H), 3.71 (s, 3H), 3.90 (s, 3H), 6.29 (d, *J* = 11.2 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 6.81–6.89 (m, 1H), 6.95–7.07 (m, 3H), 7.13–7.32 (m, 7H), 7.73 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 10.9, 29.7, 55.7, 106.4, 108.9, 114.3, 117.6, 118.5, 119.7, 121.2, 121.8, 125.8, 126.2, 126.6, 128.4, 129.1, 131.6, 135.7, 137.1, 139.6, 163.1; HRMS (ESI^+): Calcd for $C_{25}H_{25}N_2O_3S$, $M+H^+$ 433.1580. Found m/z 433.1569.

3j:



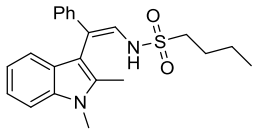
IR (ATR): 3252, 3051, 1634, 1474, 1404, 1321, 1157, 1136, 1061 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.07 (s, 3H), 3.72 (s, 3H), 6.49 (d, *J* = 11.2 Hz, 1H), 6.58 (d, *J* = 7.6 Hz, 1H), 6.79–6.85 (m, 1H), 7.06 (d, *J* = 11.2 Hz, 1H), 7.12–7.33 (m, 7H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 10.8, 29.7, 106.0, 109.0, 118.0, 119.3, 119.8, 120.8, 121.4, 123.2 (q, *J* = 270.9 Hz), 125.9, 126.1, 126.3 (q, *J* = 3.6 Hz), 127.0, 127.3, 128.4, 134.5 (q, *J* = 32.9 Hz), 135.7, 137.1, 139.1, 143.2; HRMS (ESI^-): Calcd for $C_{25}H_{20}F_3N_2O_2S$, $M-H^-$ 469.1203. Found m/z 469.1203.

3k:



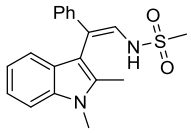
IR (ATR): 3267, 3057, 1634, 1472, 1447, 1323, 1153, 1130, 1063 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.14 (s, 3H), 2.31 (s, 3H), 3.74 (s, 3H), 6.43 (d, *J* = 11.2 Hz, 1H), 6.85–7.03 (m, 3H), 7.13–7.37 (m, 9H), 7.45–7.52 (m, 1H), 7.95 (dd, *J* = 7.6, 0.8 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 10.9, 20.3, 29.8, 106.3, 108.9, 117.5, 118.4, 119.9, 121.4, 121.8, 125.7, 126.3, 126.4, 126.6, 128.3, 128.6, 128.9, 132.6, 132.9, 135.6, 137.1, 138.3, 139.4; HRMS (ESI^+): Calcd for $C_{25}H_{25}N_2O_2S$, $M+H^+$ 417.1631. Found m/z 417.1620.

3l:



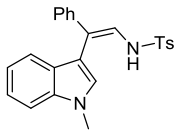
IR (ATR): 3252, 2957, 1636, 1472, 1325, 1142 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 0.91 (t, *J*= 7.6 Hz, 3H), 1.35–1.46 (m, 2H), 1.60–1.74 (m, 2H), 2.24 (s, 3H), 3.04 (t, *J* = 8.0 Hz, 2H), 3.77 (s, 3H), 6.25 (d, *J* = 11.6 Hz, 1H), 7.02–7.10 (m, 2H), 7.18–7.40 (m, 8H); ^{13}C NMR ($CDCl_3$): δ = 11.0, 13.4, 21.4, 25.4, 29.8, 53.6, 106.3, 109.0, 116.7, 118.5, 119.7, 121.3, 122.0, 125.7, 126.5, 126.6, 128.4, 135.6, 137.2, 139.3; HRMS (ESI^-): Calcd for $C_{22}H_{25}N_2O_2S$, $M-H^-$ 381.1642. Found m/z 381.1645.

3m:



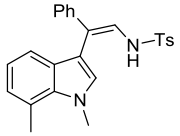
IR (ATR): 3279, 1637, 1472, 1447, 1391, 1321, 1302, 1146 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.23 (s, 3H), 2.98 (s, 3H), 3.76 (s, 3H), 6.25 (d, *J* = 10.8 Hz, 1H), 6.99–7.10 (m, 2H), 7.18–7.31 (m, 7H), 7.36 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 11.0, 29.8, 41.1, 106.3, 109.1, 117.6, 118.5, 119.8, 121.4, 121.5, 125.8, 126.4, 126.8, 128.4, 135.6, 137.2, 139.3; HRMS (ESI^+): Calcd for $C_{19}H_{21}N_2O_2S$, $M+H^+$ 341.1318. Found m/z 341.1308.

3n:



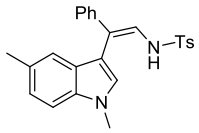
IR (ATR): 3252, 1636, 1447, 1329, 1304, 1153 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.48 (s, 3H), 3.81 (s, 3H), 6.55 (d, *J* = 11.2 Hz, 1H), 6.75–6.80 (m, 1H), 6.83 (s, 1H), 6.88–6.97 (m, 2H), 7.19–7.29 (m, 5H), 7.31–7.39 (m, 4H), 7.73 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 21.6, 32.9, 109.51, 109.53, 118.0, 119.7, 119.8, 120.8, 122.2, 126.4, 126.5, 126.8, 126.9, 128.2, 128.6, 129.8, 136.9, 137.0, 140.1, 143.8; HRMS (ESI^+): Calcd for $C_{24}H_{23}N_2O_2S$, $M+H^+$ 403.1475. Found m/z 403.1463.

3o:



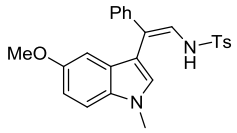
IR (ATR): 3271, 3034, 1489, 1333, 1163, 1088 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.48 (s, 3H), 2.80 (s, 3H), 4.06 (s, 3H), 6.50 (d, *J* = 11.6 Hz, 1H), 6.57–6.62 (m, 1H), 6.71 (s, 1H), 6.75 (t, *J* = 8.0 Hz, 1H), 6.89–6.96 (m, 2H), 7.15–7.28 (m, 5H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 19.6, 21.5, 36.9, 109.1, 117.8, 118.1, 120.0, 120.9, 121.5, 124.8, 126.3, 126.7, 126.9, 127.5, 128.2, 129.8, 130.1, 135.8, 136.8, 140.0, 143.7; HRMS (ESI^+): Calcd for $C_{25}H_{25}N_2O_2S$, $M+H^+$ 417.1631. Found m/z 417.1623.

3p:



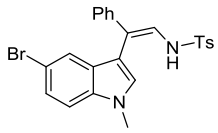
IR (ATR): 3304, 3044, 1634, 1595, 1493, 1456, 1331, 1161 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.26 (s, 3H), 2.47 (s, 3H), 3.78 (s, 3H), 6.52 (d, *J* = 11.2 Hz, 1H), 6.63–6.66 (m, 1H), 6.77 (s, 1H), 6.96 (d, *J* = 11.6 Hz, 1H), 7.08 (dd, *J* = 8.4 Hz, 1.2 Hz, 1H), 7.18–7.38 (m, 8H), 7.73 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 21.3, 21.5, 32.9, 108.8, 109.3, 117.9, 119.1, 120.8, 123.9, 126.3, 126.6, 126.7, 126.8, 128.2, 128.7, 129.0, 129.8, 135.5, 137.0, 140.2, 143.7; HRMS (ESI^+): Calcd for $C_{25}H_{25}N_2O_2S$, $M+H^+$ 417.1631. Found m/z 417.1624.

3q:



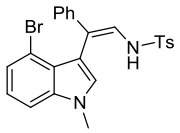
IR (ATR): 3271, 3051, 1620, 1489, 1335, 1217, 1165 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.45 (s, 3H), 3.60 (s, 3H), 3.77 (s, 3H), 6.40 (d, *J* = 2.4 Hz, 1H), 6.58 (d, *J* = 11.6 Hz, 1H), 6.78 (s, 1H), 6.88–6.95 (m, 2H), 7.20–7.37 (m, 8H), 7.72 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 21.5, 33.0, 55.5, 101.5, 108.8, 110.3, 112.5, 118.0, 120.7, 126.4, 126.7, 126.8, 127.0, 128.2, 128.9, 129.8, 132.4, 137.0, 139.9, 143.7, 154.2; HRMS (ESI^+): Calcd for $C_{25}H_{25}N_2O_3S$, $M+H^+$ 433.1580. Found m/z 433.1574.

3r:



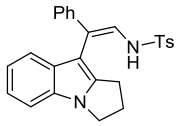
IR (ATR): 3271, 3071, 1637, 1475, 1371, 1333, 1161, 1088 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.46 (s, 3H), 3.78 (s, 3H), 6.54 (d, *J* = 11.6 Hz, 1H), 6.85 (s, 1H), 6.91–6.97 (m, 2H), 7.17–7.40 (m, 9H), 7.66 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 21.6, 33.1, 108.9, 111.1, 113.2, 117.1, 121.6, 121.8, 125.2, 126.1, 126.6, 126.9, 128.2, 128.3, 129.8, 130.0, 135.7, 136.5, 139.5, 144.0; HRMS (ESI^-): Calcd for $C_{24}H_{20}BrN_2O_2S$, $M-H^-$ 479.0434. Found m/z 479.0434.

3s:



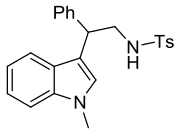
IR (ATR): 3242, 1651, 1599, 1327, 1163, 1146, 1119 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.44 (s, 3H), 3.78 (s, 3H), 6.48 (d, *J* = 11.6 Hz, 1H), 6.72 (s, 1H), 7.01–7.10 (m, 2H), 7.13–7.32 (m, 9H), 7.65 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 21.5, 33.1, 108.8, 114.2, 118.2, 122.9, 123.1, 124.0, 125.6, 125.7, 126.4, 126.7, 128.1, 129.7, 129.9, 137.1, 138.2, 140.4, 143.7; HRMS (ESI^-): Calcd for $C_{24}H_{20}BrN_2O_2S$, $M\text{-}H^-$ 479.0434. Found m/z 479.0434.

3t:



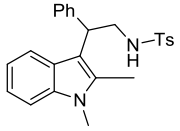
IR (ATR): 3258, 1634, 1450, 1323, 1161, 1090 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.47 (s, 3H), 2.50–2.60 (m, 4H), 4.08–4.15 (m, 2H), 6.42 (d, *J* = 11.2 Hz, 1H), 6.62 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.79–6.85 (m, 1H), 6.87–6.93 (m, 1H), 7.08–7.37 (m, 9H), 7.73 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 21.6, 24.0, 27.4, 43.9, 100.9, 109.7, 117.6, 119.2, 119.6, 120.3, 120.8, 126.4, 126.7, 126.9, 128.3, 129.8, 130.6, 132.8, 137.1, 139.6, 143.8, 144.1; HRMS (ESI^+): Calcd for $C_{26}H_{25}N_2O_2S$, $M+H^+$ 429.1631. Found m/z 429.1621.

5:



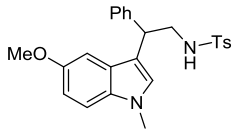
IR (ATR): 3277, 3034, 1597, 1452, 1323, 1153, 1092 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.44 (s, 3H), 3.49–3.70 (m, 2H), 3.73 (s, 3H), 4.31 (t, *J* = 7.6 Hz, 1H), 4.36 (t, *J* = 6.4 Hz, 1H), 6.77 (s, 1H), 6.97–7.02 (m, 1H), 7.16–7.31 (m, 10H), 7.66 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 21.5, 32.7, 42.5, 47.5, 109.4, 113.9, 119.15, 119.20, 122.0, 126.7, 126.8, 127.0, 127.1, 127.9, 128.7, 129.7, 136.8, 137.2, 141.1, 143.4; HRMS (ESI^+): Calcd for $C_{24}H_{25}N_2O_2S$, $M+H^+$ 405.1631. Found m/z 405.1621.

6:



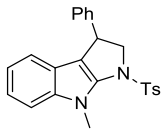
IR (ATR): 3279, 3034, 1599, 1472, 1408, 1323, 1157 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.32 (s, 3H), 2.45 (s, 3H), 3.54–3.78 (m, 4H), 3.80–3.90 (m, 1H), 4.38–4.52 (m, 2H), 6.90 (t, *J* = 7.6 Hz, 1H), 7.10–7.35 (m, 10H), 7.61 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 10.4, 21.4, 29.6, 42.4, 46.3, 108.1, 108.9, 118.6, 119.1, 120.7, 125.9, 126.4, 127.0, 127.5, 128.4, 129.6, 135.3, 136.3, 136.8, 141.5, 143.2; HRMS (ESI^+): Calcd for $C_{25}H_{27}N_2O_2S$, $M+H^+$ 419.1788. Found m/z 419.1783.

7:



IR (ATR): 3279, 2930, 1489, 1325, 1157, 1092 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.44 (s, 3H), 3.49–3.67 (m, 2H), 3.68 (s, 3H), 3.74 (s, 3H), 4.30 (t, *J* = 7.6 Hz, 1H), 4.54 (t, *J* = 6.4 Hz, 1H), 6.73 (d, *J* = 2.4 Hz, 1H), 6.74 (s, 1H), 6.84–6.90 (m, 1H), 7.16 (d, *J* = 8.8 Hz, 1H), 7.19–7.31 (m, 7H), 7.66 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 21.4, 32.8, 42.6, 47.3, 55.7, 101.1, 110.1, 112.0, 113.3, 126.9, 127.05, 127.13, 127.2, 127.9, 128.7, 129.6, 132.6, 136.7, 141.1, 143.3, 153.7; HRMS (ESI^+): Calcd for $C_{25}H_{27}N_2O_3S$, $M+H^+$ 435.1737. Found m/z 435.1729.

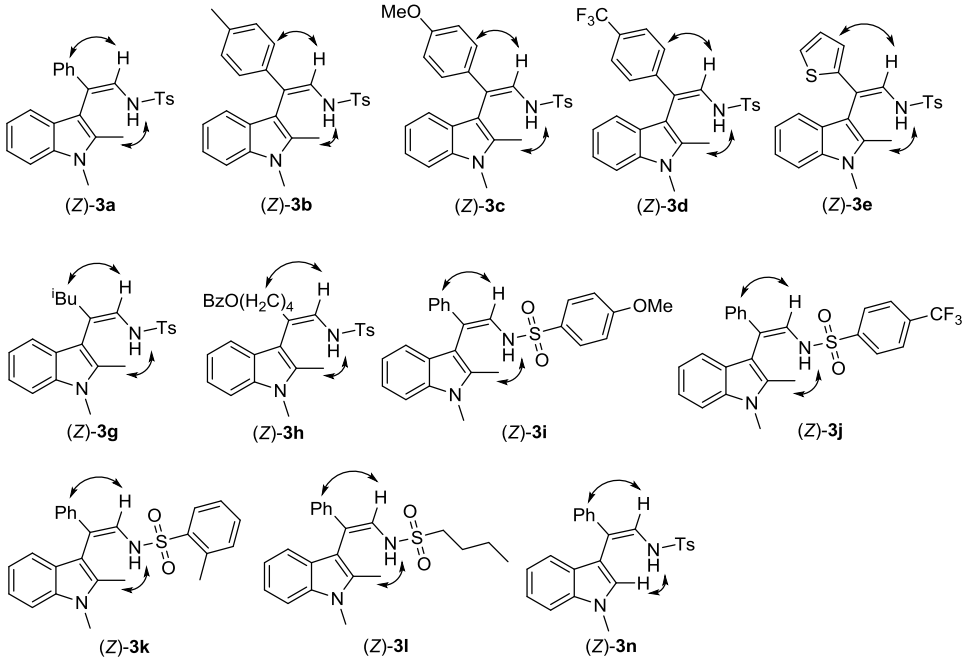
8:

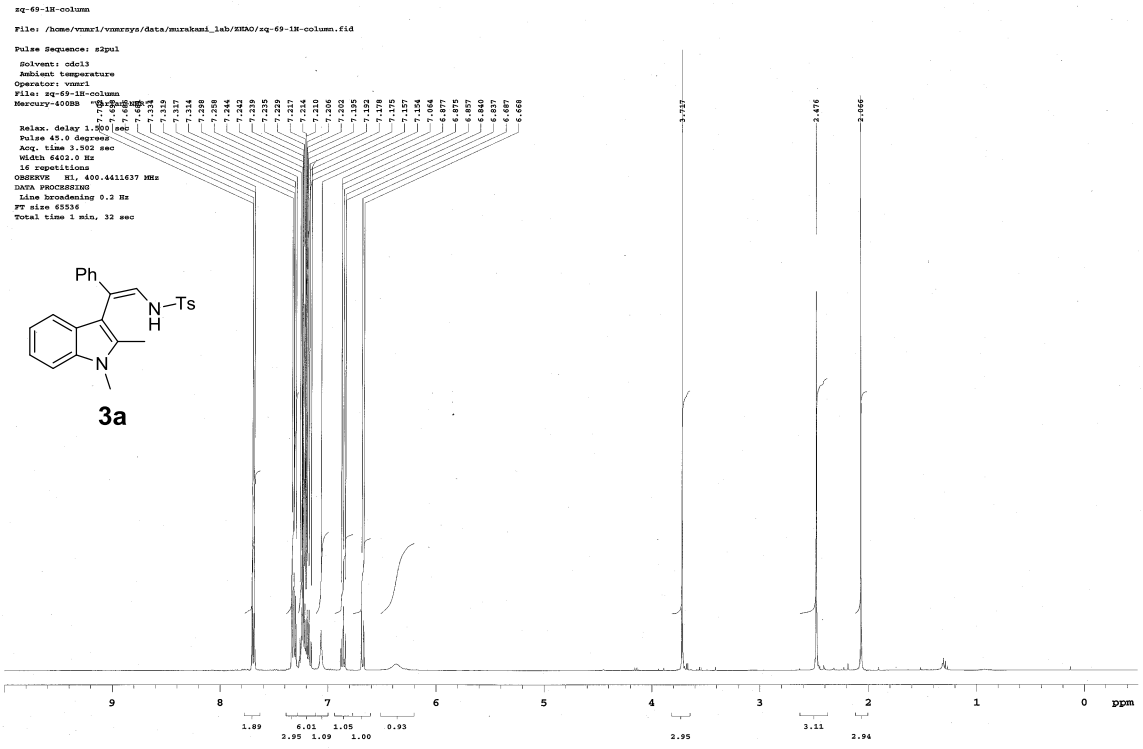


IR (ATR): 3044, 1558, 1456, 1354, 1169, 1090 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.35 (s, 3H), 3.89 (t, *J* = 8.0 Hz, 1H), 4.01 (s, 3H), 4.15 (dd, *J* = 12.4, 7.2 Hz, 1H), 4.71 (dd, *J* = 12.8, 8.4 Hz, 1H), 6.85–6.91 (m, 2H), 7.00–7.25 (m, 8H), 7.35–7.42 (m, 3H); ^{13}C NMR ($CDCl_3$): δ = 21.6, 31.9, 42.4, 67.4, 110.2, 110.4, 118.6, 120.3, 121.1, 122.8, 126.5, 127.2, 127.9, 128.4, 129.6, 132.1, 140.5, 141.7, 143.7, 144.5; HRMS (ESI^+): Calcd for $C_{24}H_{23}N_2O_2S$, $M+H^+$ 403.1475. Found m/z 403.1461.

Determination of Stereochemistries:

The stereochemistry of the product **3a**, **3b**, **3c**, **3d**, **3e**, **3g**, **3h**, **3i**, **3j**, **3k**, **3l**, and **3n** was determined by nOe experiments. Curved arrows shown below indicate the observed NOE. The other products were assigned by analogy.

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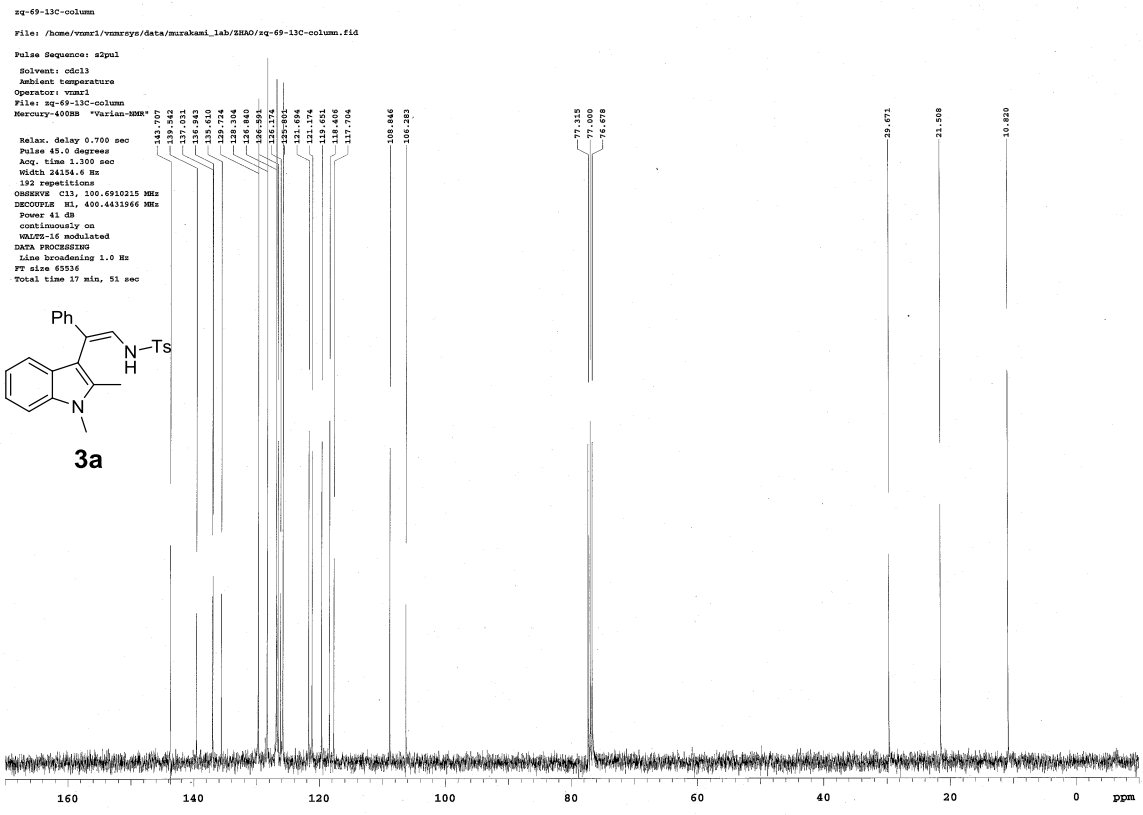
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: zq-69-1H-column
Mercury-400BB "Varian-MMR"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411637 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
Ph
N
Ts
H
N
3a
3.737
2.476
2.066
9
8
7
6
5
4
3
2
1
0
ppm
1.89
6.01
1.05
0.93
2.95
1.09
1.00
2.95
3.11
2.94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Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: zq-69-13C-column
Mercury-400BB "Varian-MMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
192 repetitions
OBSERVE C13, 100.6910215 MHz
DECOUPLE H1, 400.4431966 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min, 51 sec
Ph
N
Ts
H
N
3a
143.707
139.562
137.031
136.943
135.610
129.724
128.304
126.840
126.591
126.174
125.801
121.664
121.174
119.651
118.406
117.704
108.846
106.283
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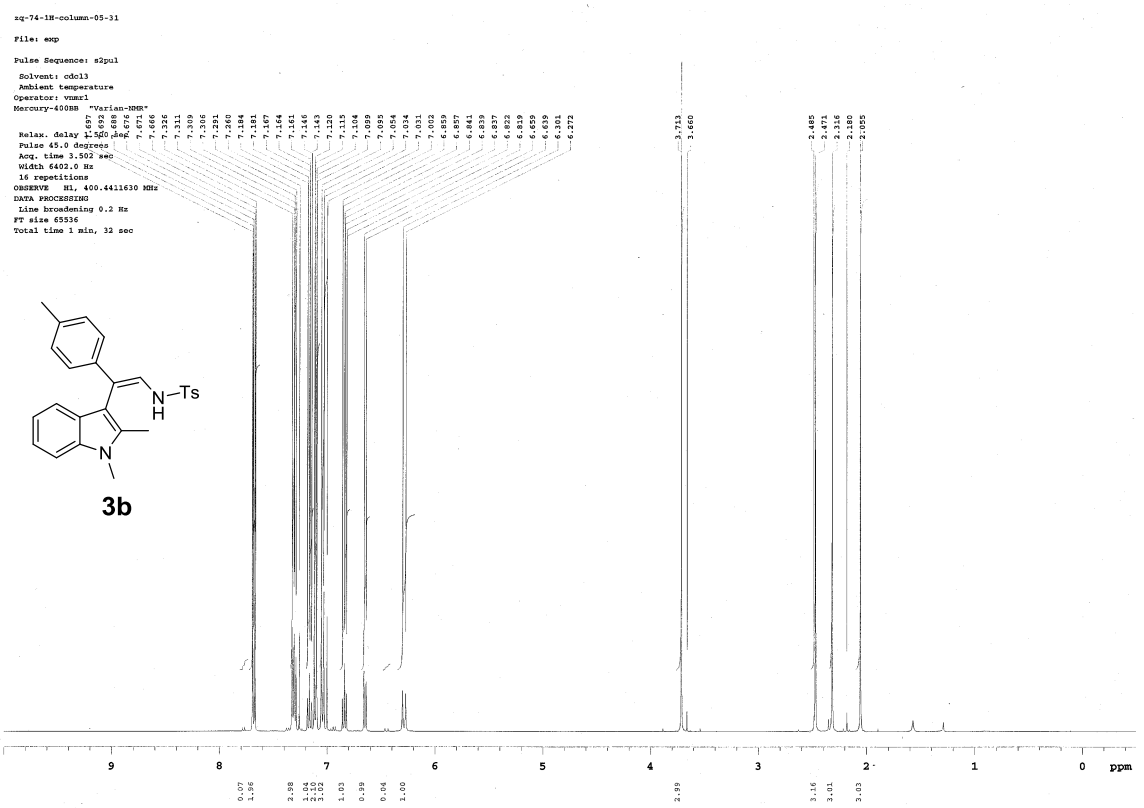
76.678
29.671
21.508
10.820
160
140
120
100
80
60
40
20
0
ppm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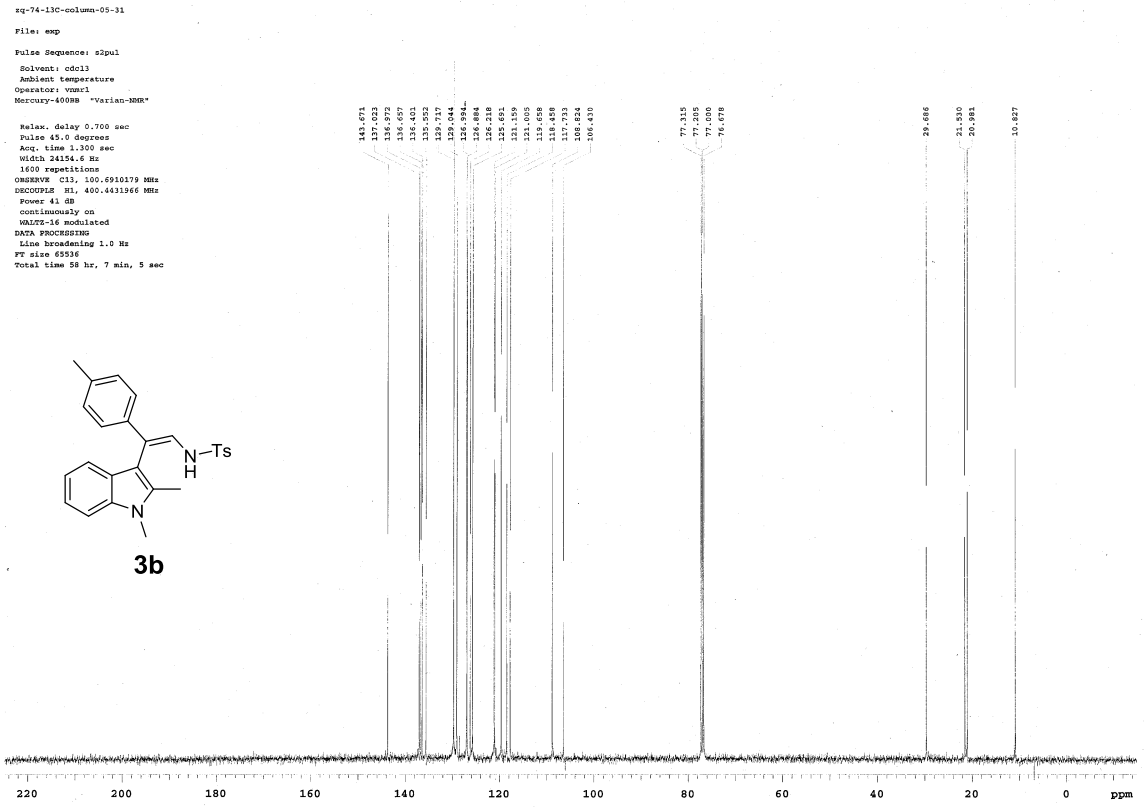
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmrl
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411630 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
N–Ts
H
N
3b
ppm


zq-74-13C-column-05-31
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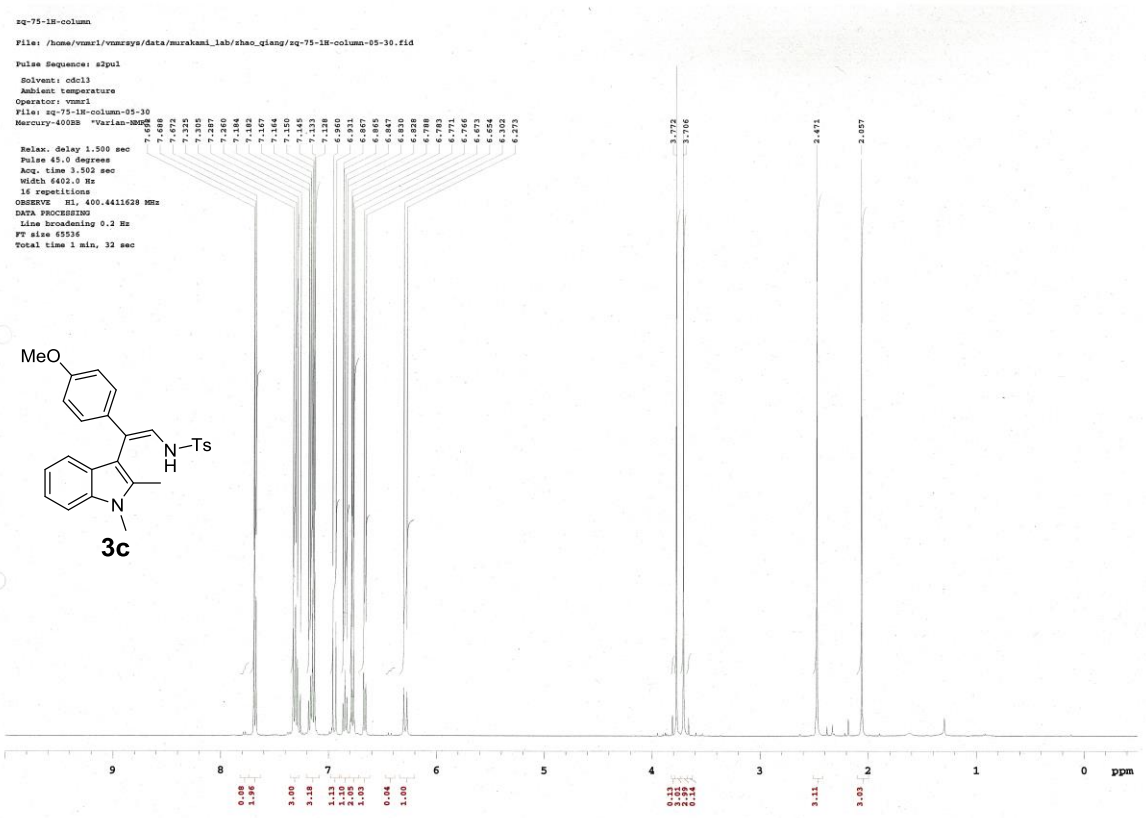
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmrl
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
1600 repetitions
OBSERVE C13, 100.6910179 MHz
DECOUPLE H1, 400.4431966 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 58 hr, 7 min, 5 sec
N–Ts
H
N
3b
ppm


zq-75-1H-column
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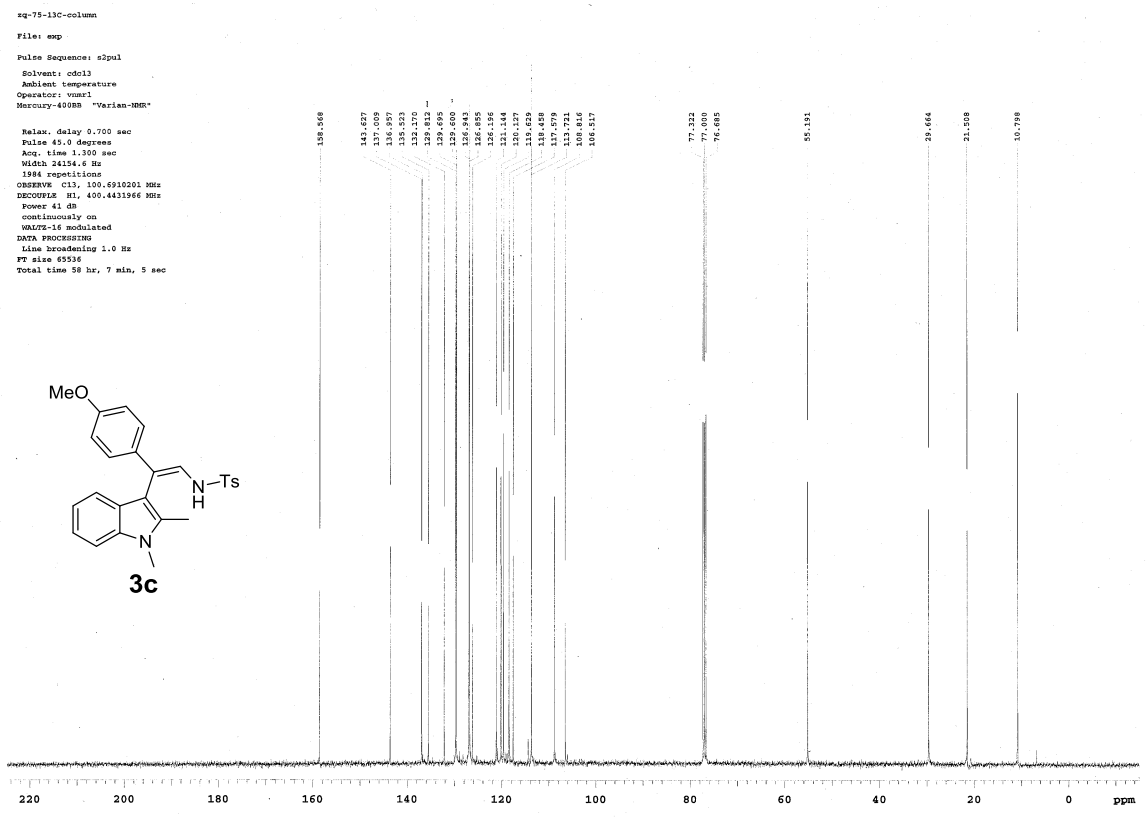
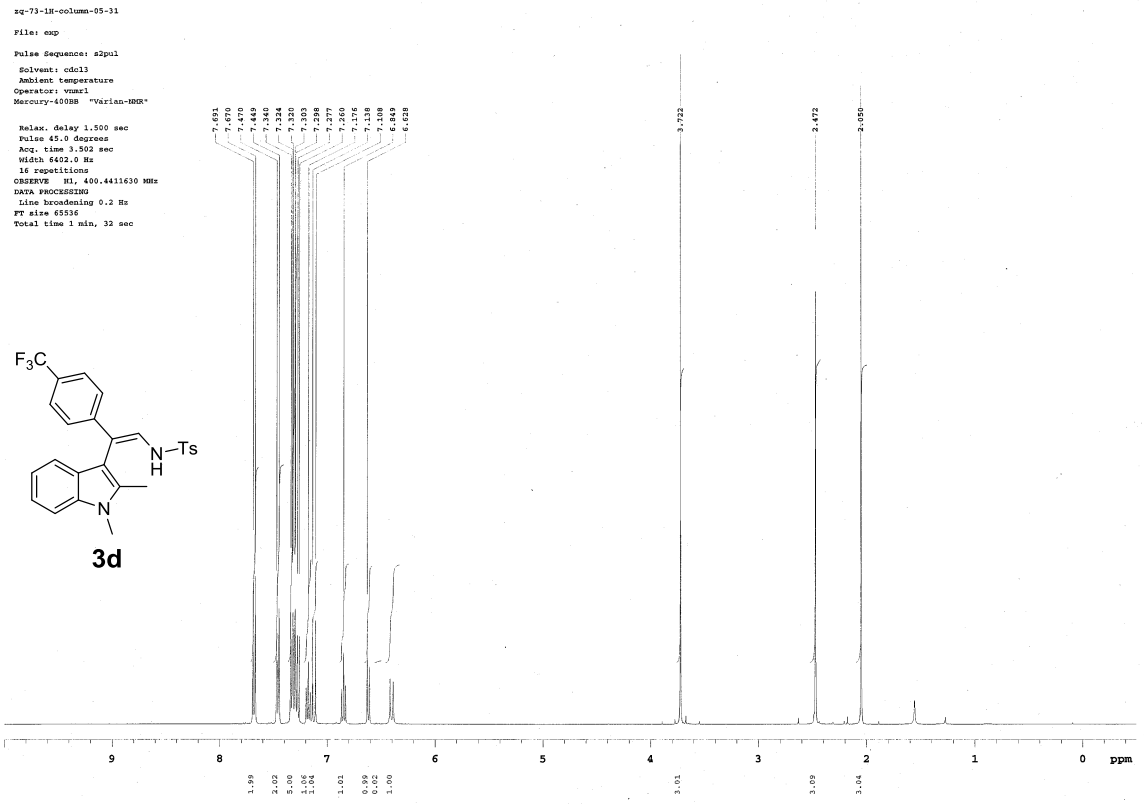
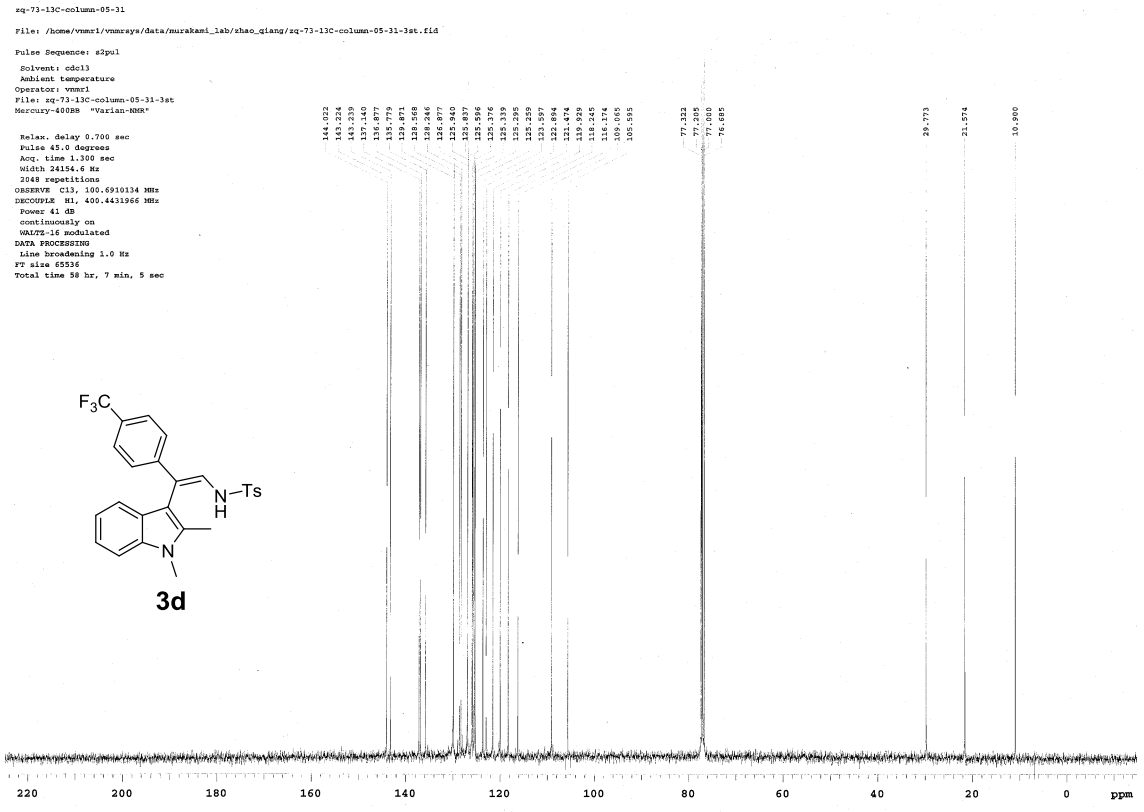
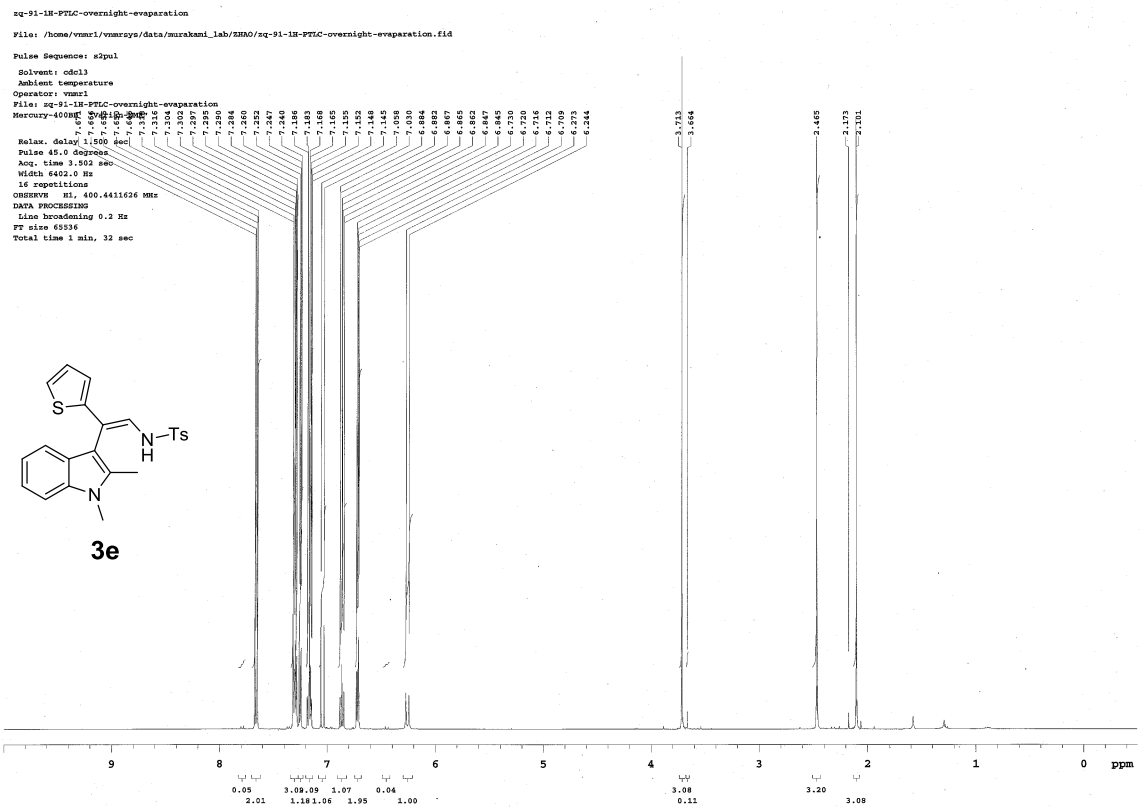
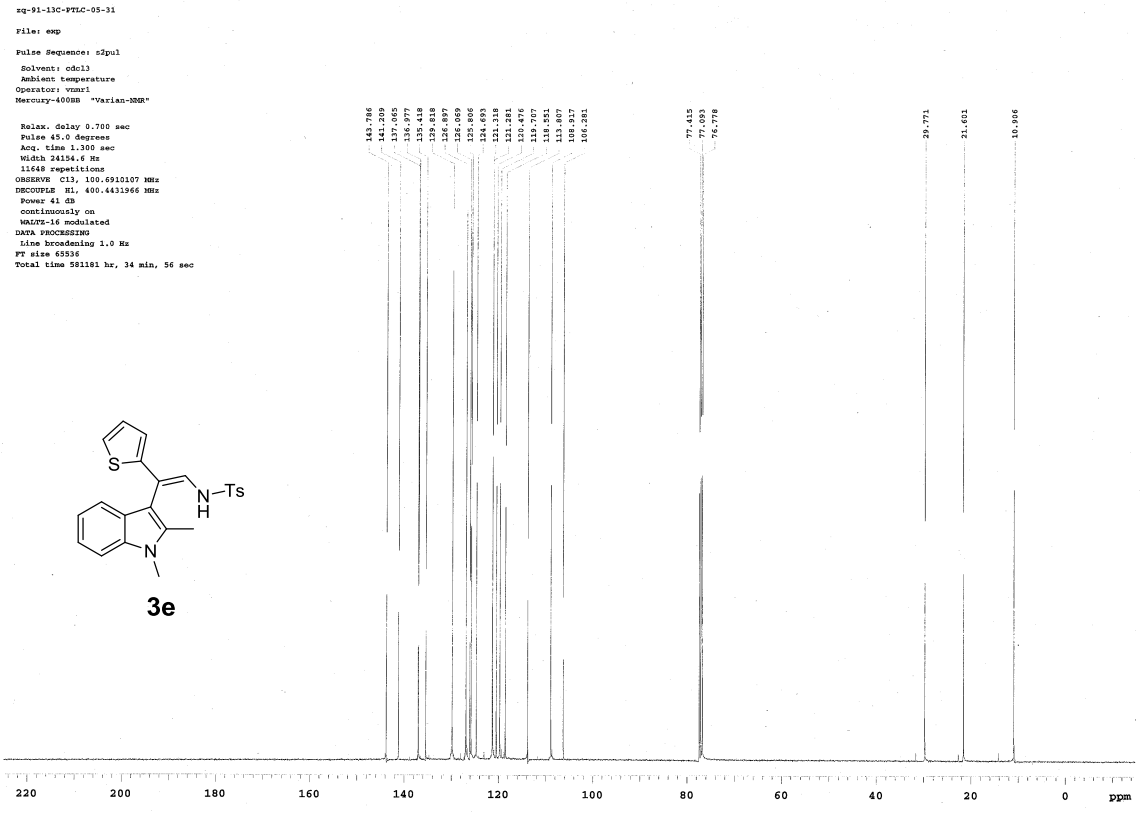
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: zq-75-1H-column-05-30
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411628 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
MeO
N
Ts
H
3c
ppm

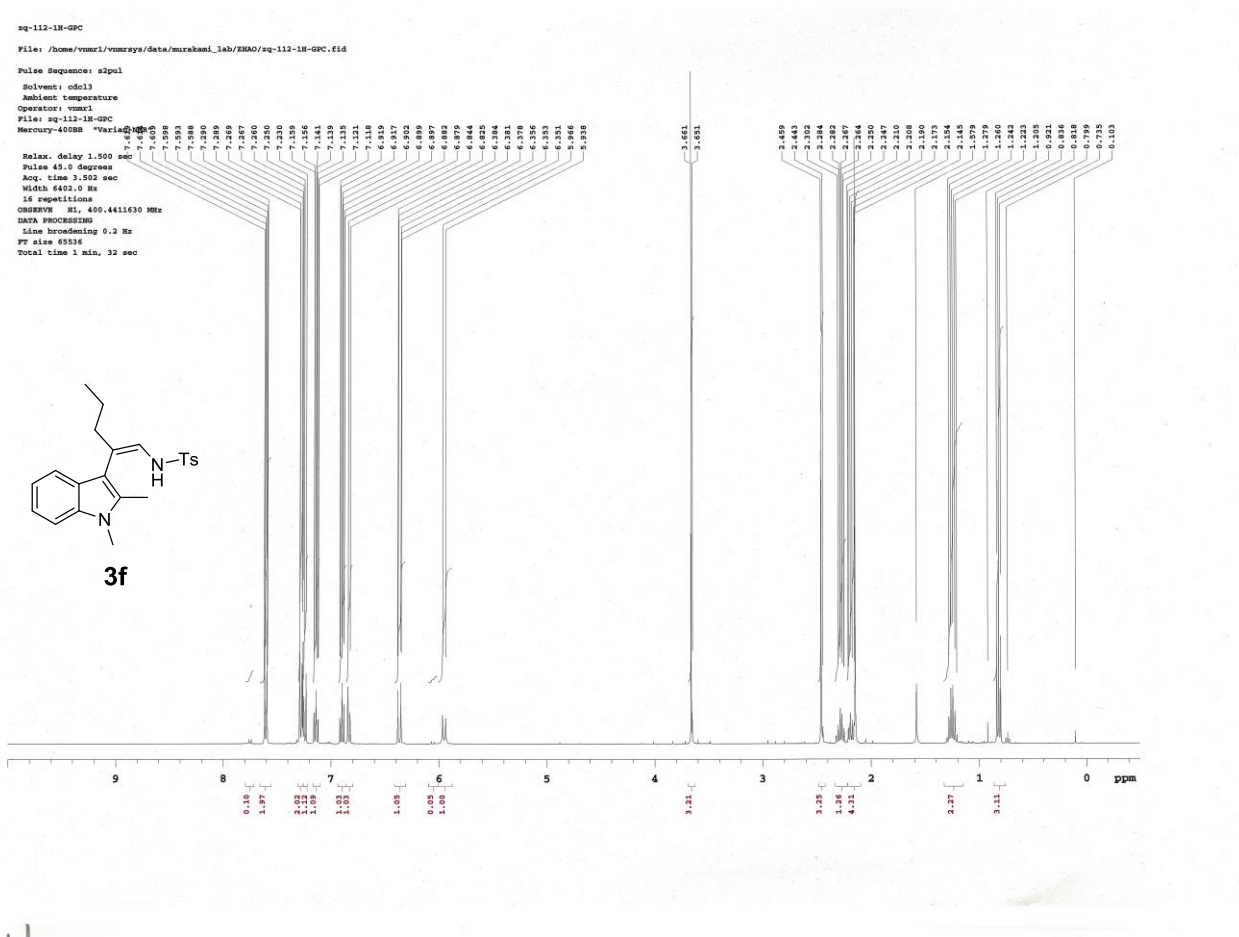

zq-75-13C-column
File: exp
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
1984 repetitions
OBSERVE C13, 100.6910201 MHz
DECOUPLE H1, 400.4431966 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 58 hr, 7 min, 5 sec
MeO
N
Ts
H
3c
ppm

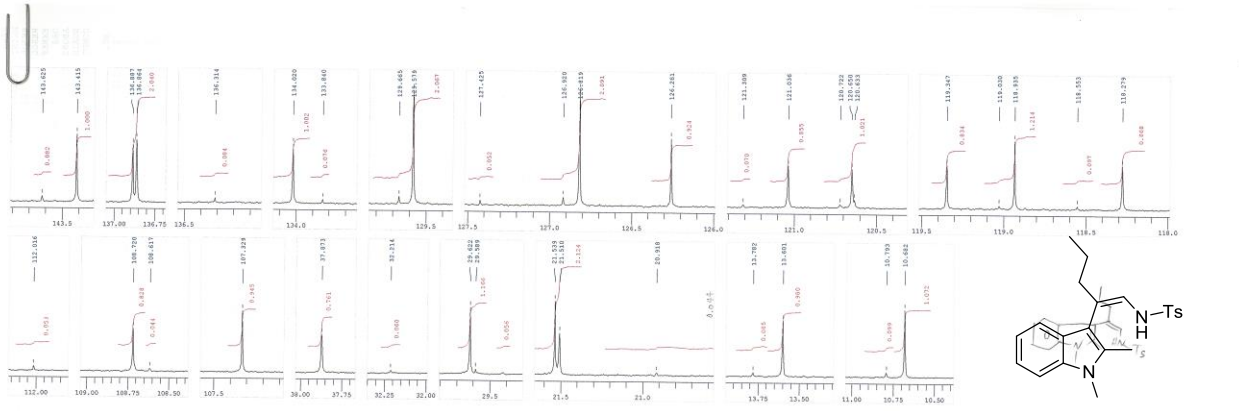

zq-73-1H-column-05-31
File: exp
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmrl
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411630 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
7.691
7.670
7.470
7.449
7.340
7.324
7.320
7.303
7.298
7.277
7.260
7.176
7.138
7.108
6.849
6.628
3.722
2.472
2.050
F3C
N
Ts
H
N
3d
9
8
7
6
5
4
3
2
1
0
ppm
1.99
2.02
5.00
1.04
1.01
0.99
0.02
1.00
3.01
3.09
3.04

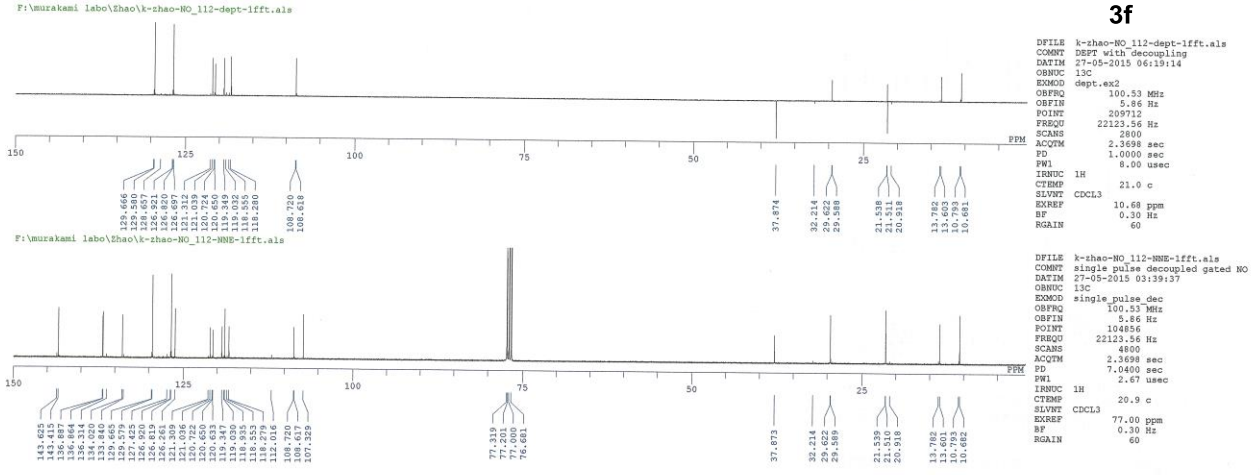

zq-73-13C-column-05-31
File: /home/vnmrl/vnmrsys/data/murakami_lab/zhao_qiang/zq-73-13C-column-05-31-3st.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmrl
File: zq-73-13C-column-05-31-3st
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
2048 repetitions
OBSERVE C13, 100.6910134 MHz
DECOUPLE H1, 400.4431966 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 58 hr, 7 min, 5 sec
144.022
143.224
143.239
137.140
136.877
135.779
130.871
130.668
130.246
126.877
125.940
125.837
125.596
125.376
125.339
125.295
125.259
123.597
122.894
121.474
119.929
118.245
116.174
109.065
105.595
77.322
77.205
77.000
76.685
29.773
21.574
10.900
F3C
N
Ts
H
N
3d
220
200
180
160
140
120
100
80
60
40
20
0
ppm

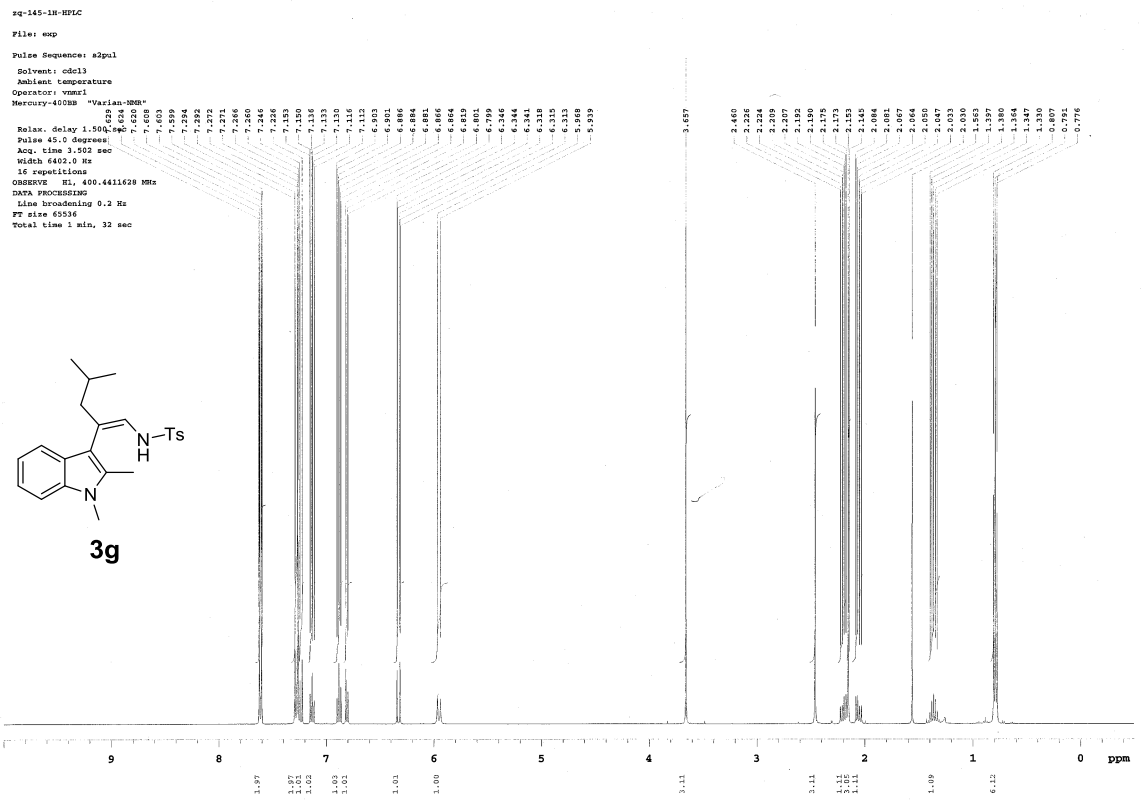

zq-91-1H-PTLC-overnight-evaparation
File: /home/vnmr1/vnmrsys/data/murakami_lab/ZHAO/zq-91-1H-PTLC-overnight-evaparation.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: zq-91-1H-PTLC-overnight-evaparation
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411626 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
3e
ppm

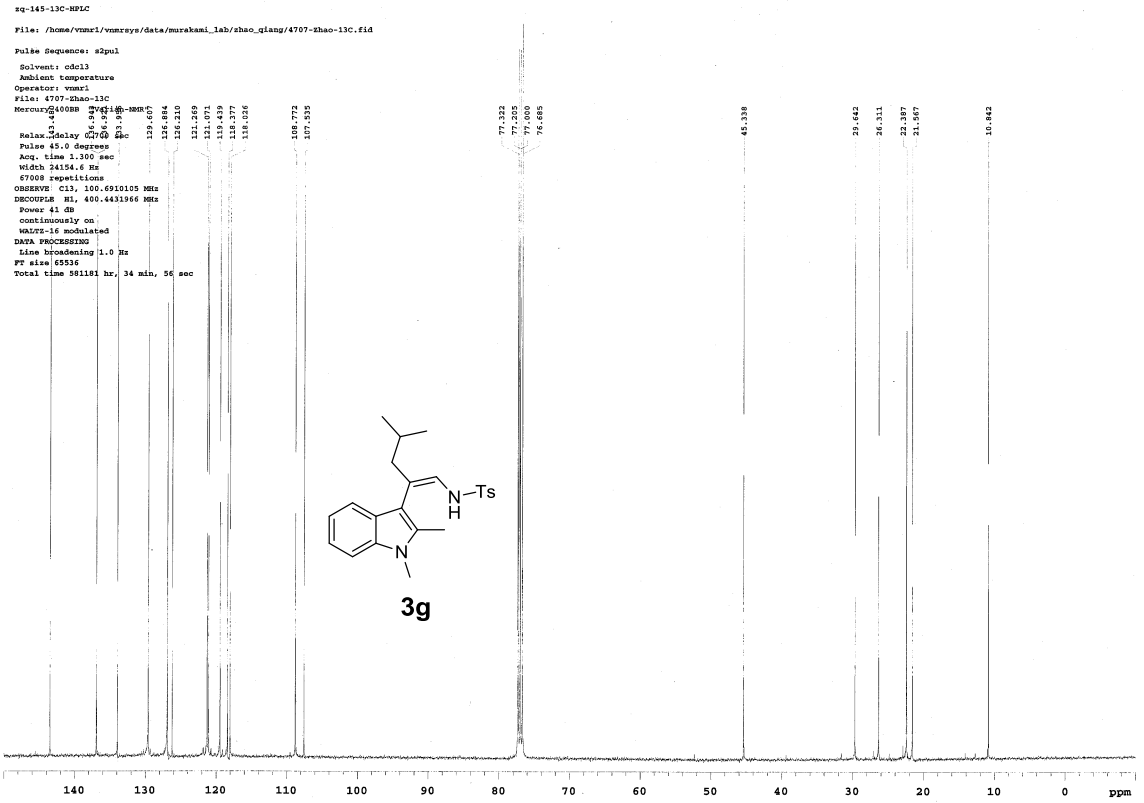

zq-91-13C-PTLC-05-31
File: exp
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
11648 repetitions
OBSERVE C13, 100.6910107 MHz
DECOUPLE H1, 400.4431966 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 581181 hr, 34 min, 56 sec
3e
ppm

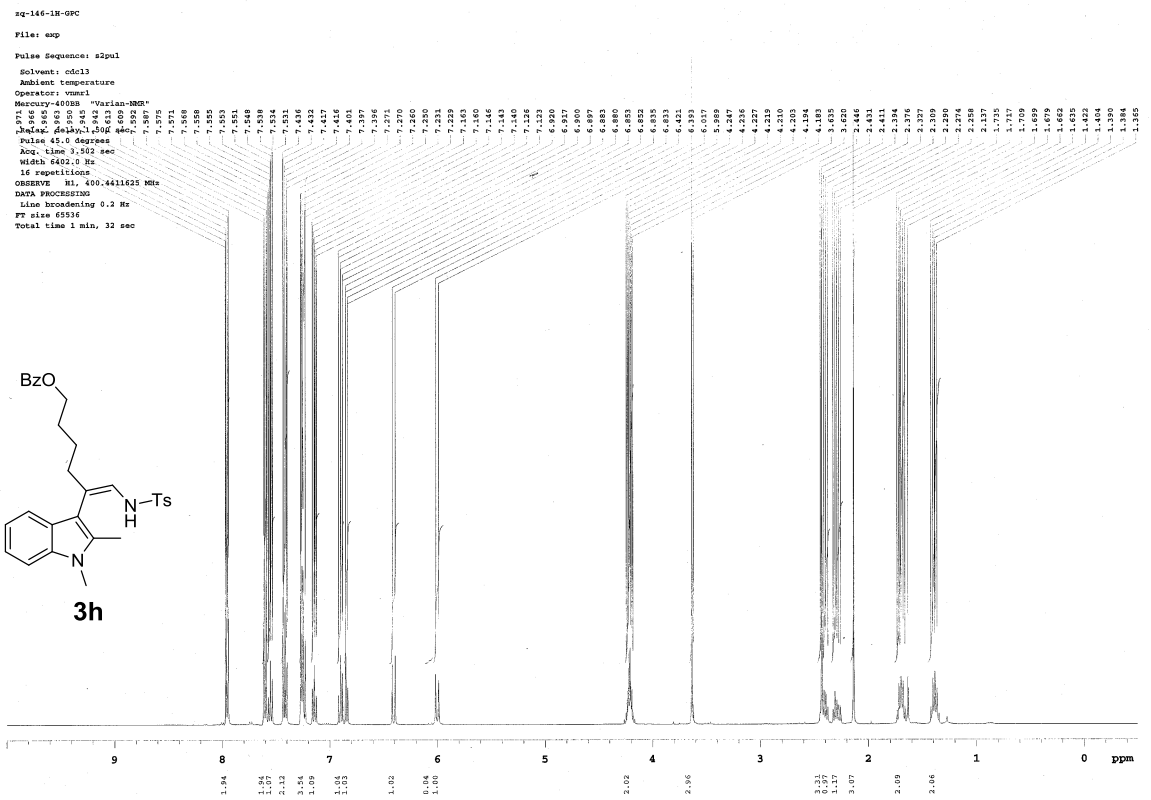

sq-112-1H-GPC
File: /home/vnmr1/vnmrsys/data/murakami_lab/ZHAO/sq-112-1H-GPC.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: sq-112-1H-GPC
Mercury-400BB "VarianNMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411630 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
N—Ts
H
3f
ppm

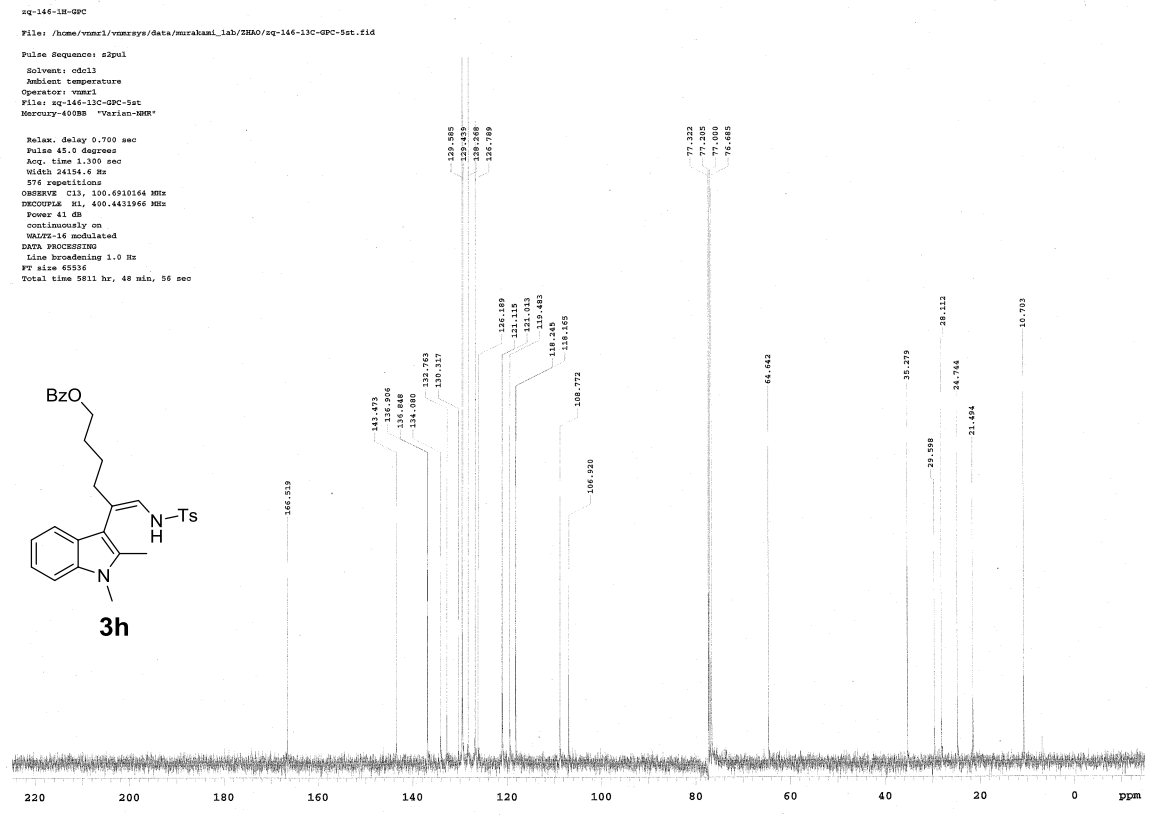

N—Ts
H
3f

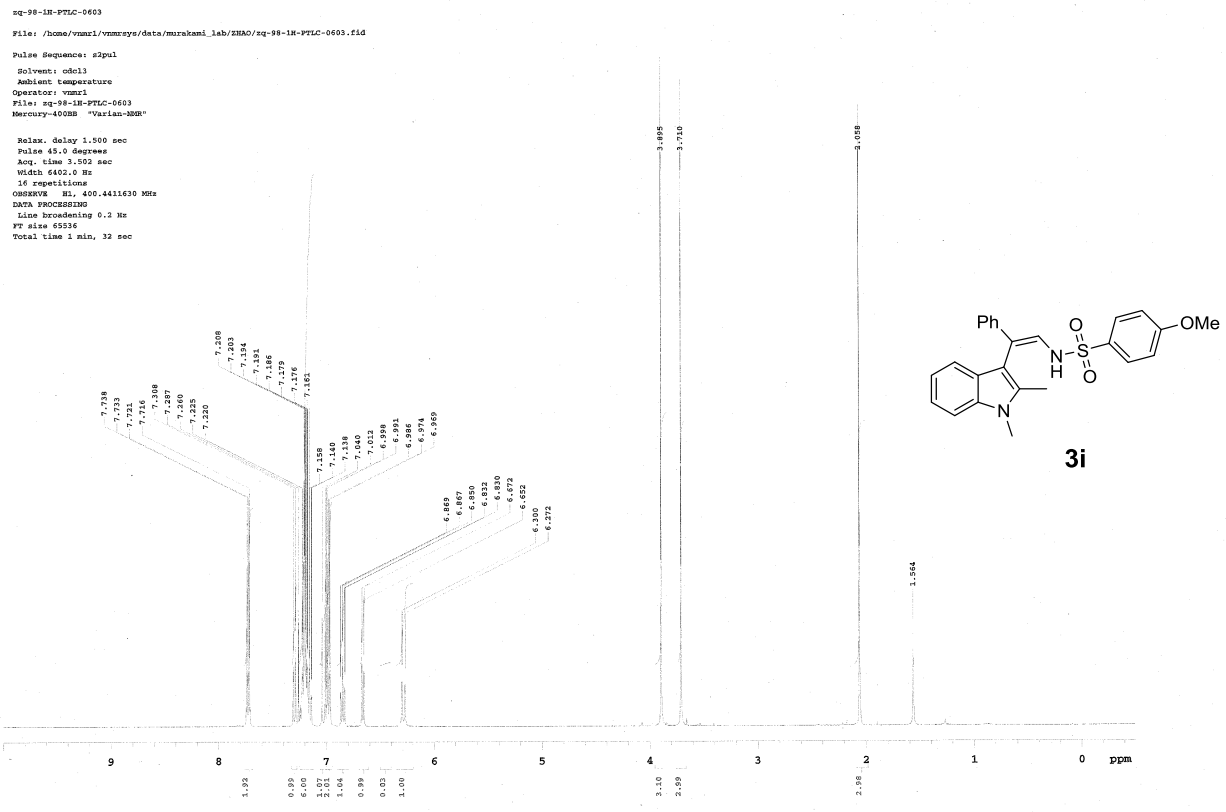

F:\murakami labo\Zhao\k-zhao-NO_112-dept-1fft.als
PPM
DFILE k-zhao-NO_112-dept-1fft.als
COMNT DEPT with decoupling
DATIM 27-05-2015 06:19:14
OBNUC 13C
EXMOD dept.ex2
OBFRQ 100.53 MHz
OBFIN 5.86 Hz
POINT 209712
FREQU 22123.56 Hz
SCANS 2800
ACQTM 2.3698 sec
PD 1.0000 sec
PW1 8.00 usec
IRNUC 1H
CTEMP 21.0 c
SLVNT CDCL3
EXREF 10.68 ppm
BF 0.30 Hz
RGAIN 60
F:\murakami labo\Zhao\k-zhao-NO_112-NNE-1fft.als
PPM
DFILE k-zhao-NO_112-NNE-1fft.als
COMNT single pulse decoupled gated NO
DATIM 27-05-2015 03:39:37
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBFIN 5.86 Hz
POINT 104856
FREQU 22123.56 Hz
SCANS 4800
ACQTM 2.3698 sec
PD 7.0400 sec
PW1 2.67 usec
IRNUC 1H
CTEMP 20.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.30 Hz
RGAIN 60

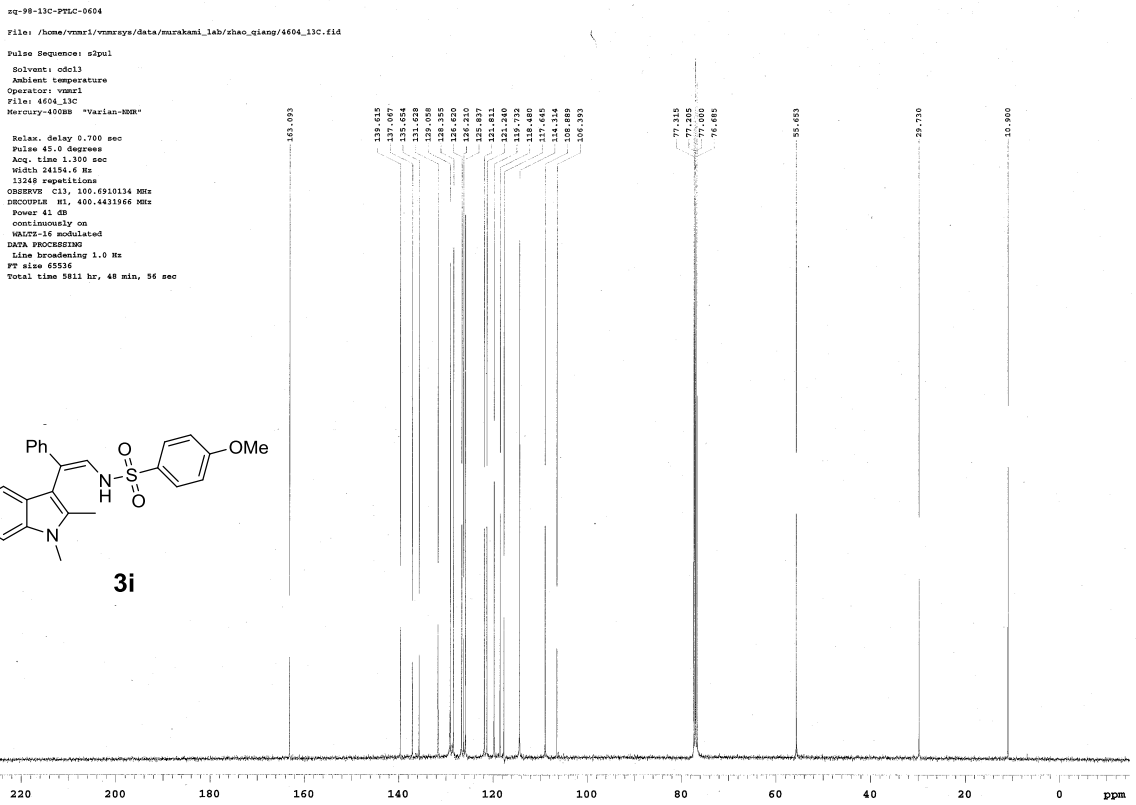

zq-145-1H-HPLC
File: exp
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411628 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
N
Ts
H
N
3g
ppm

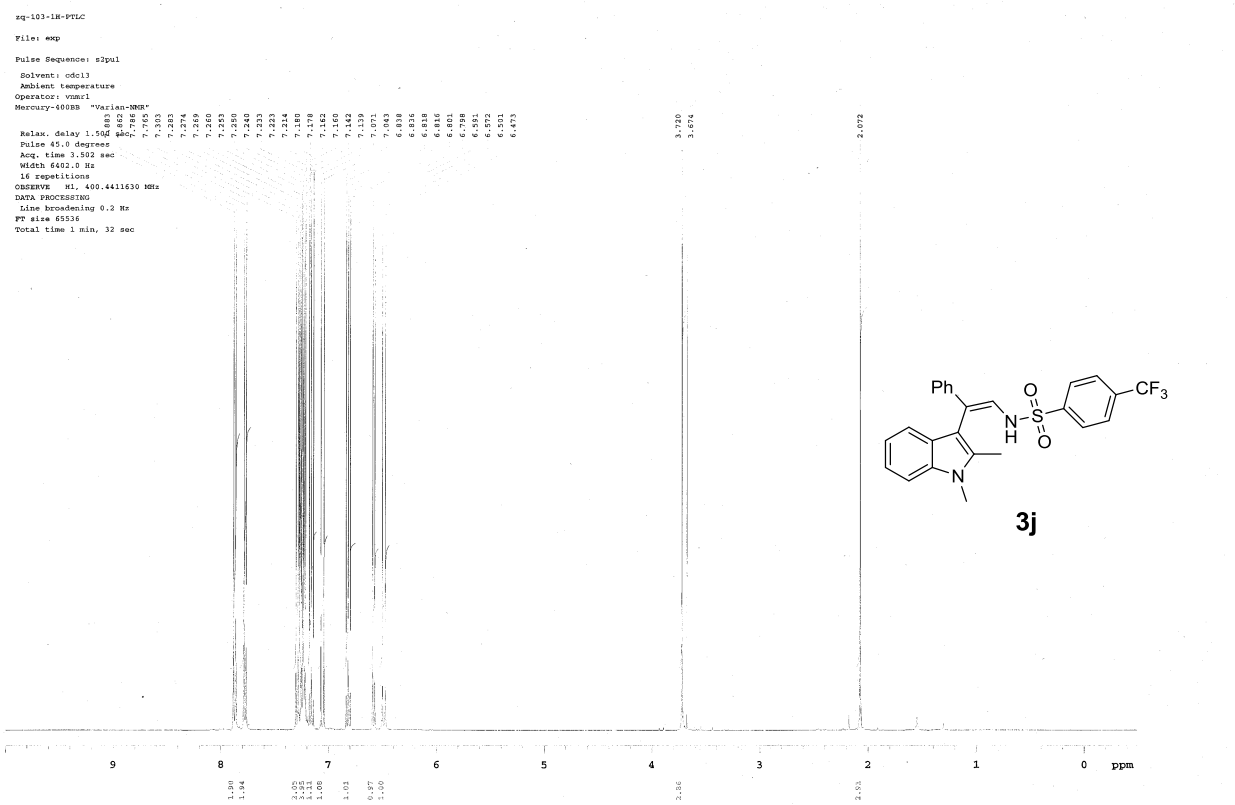

zq-145-13C-HPLC
File: /home/vnmr1/vnmrsys/data/murakami_lab/zhao_qiang/4707-Zhao-13C.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 4707-Zhao-13C
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
67008 repetitions
OBSERVE C13, 100.6910105 MHz
DECOUPLE H1, 400.4431966 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 581181 hr, 34 min, 56 sec
N
Ts
H
N
3g
ppm

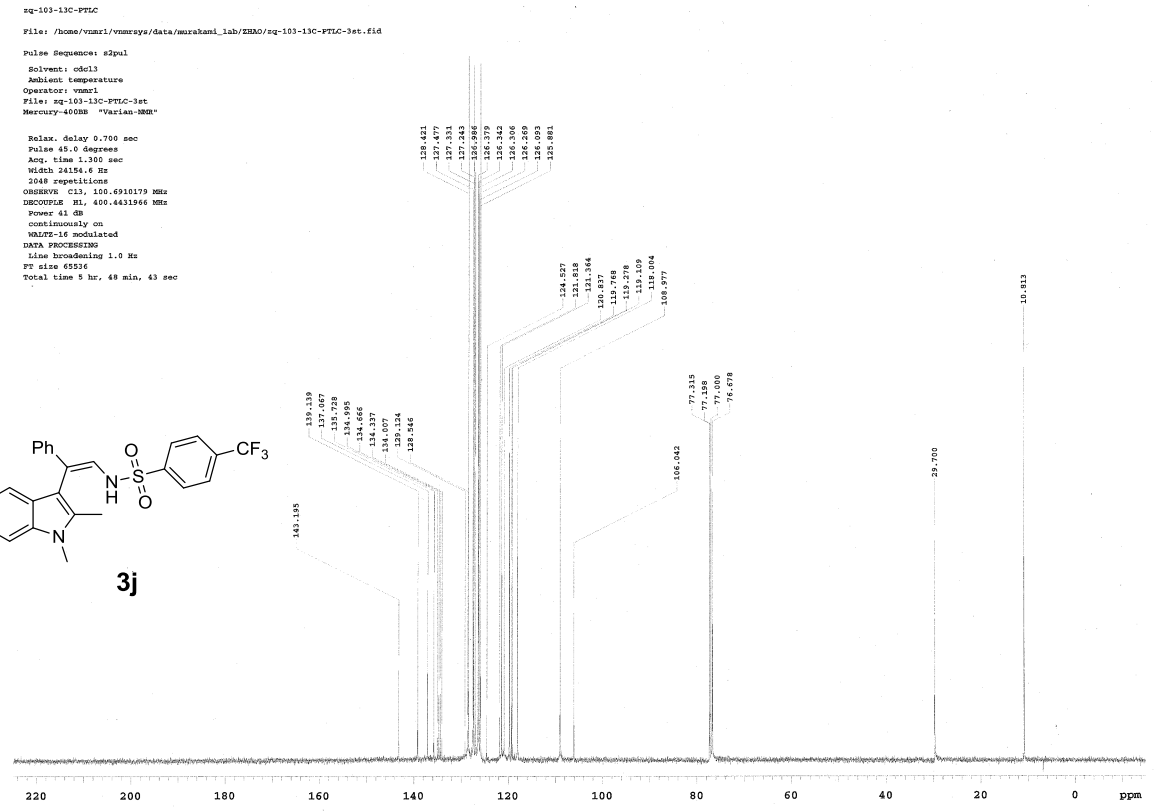

zq-146-1H-GPC
File: exp
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmrl
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411625 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
BzO
N
Ts
H
N
3h
ppm

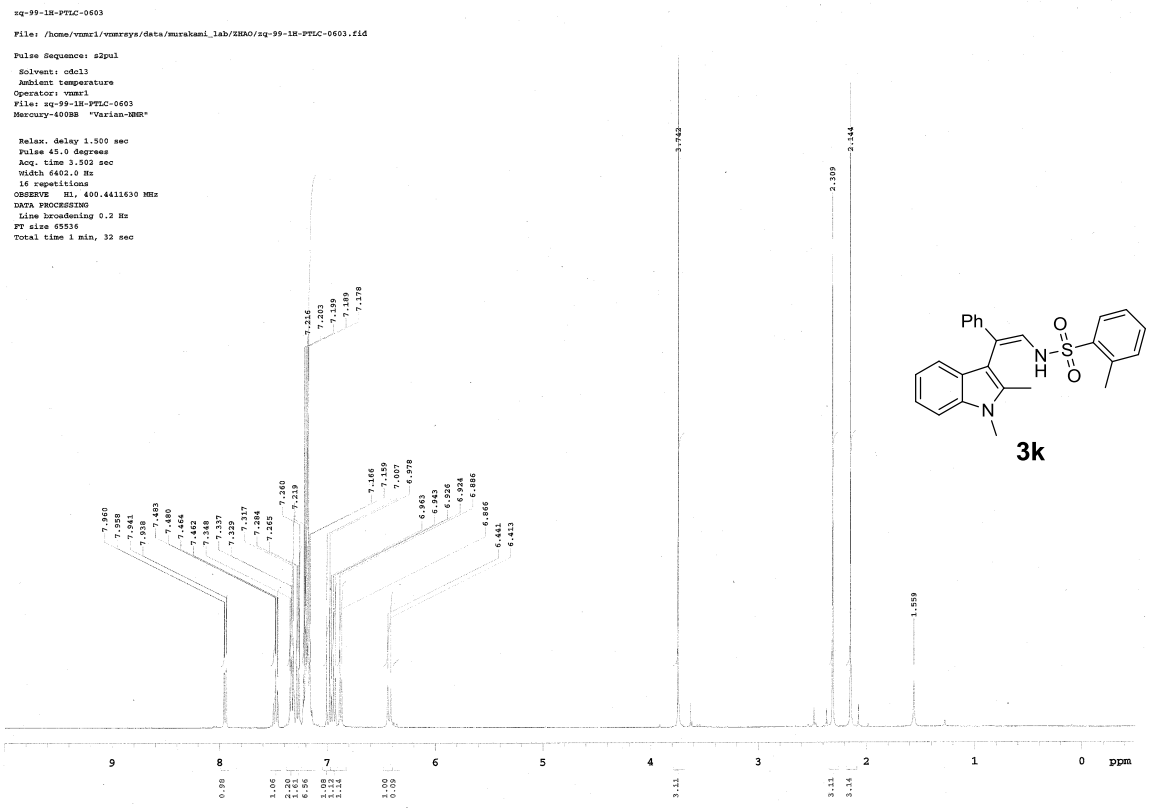

zq-146-1H-GPC
File: /home/vnmr1/vnmrsys/data/murakami_lab/ZHAO/zq-146-13C-GPC-5st.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: zq-146-13C-GPC-5st
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
576 repetitions
OBSERVE C13, 100.6910164 MHz
DECOUPLE H1, 400.4431966 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 5811 hr, 48 min, 56 sec
BzO
N
Ts
H
N
3h
ppm

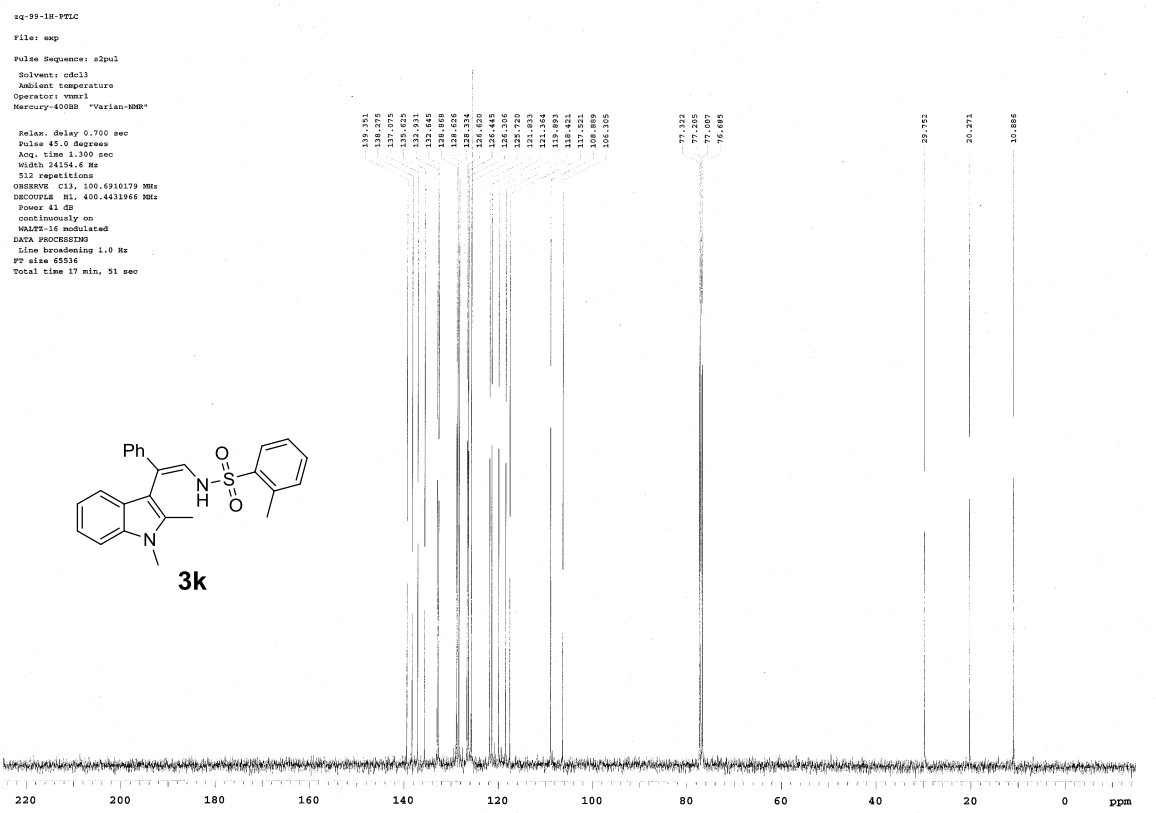

zq-98-1H-PTLC-0603
File: /home/vnmr1/vnmrsys/data/murakami_lab/ZHAO/zq-98-1H-PTLC-0603.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: zq-98-1H-PTLC-0603
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411630 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
Ph
OMe
3i
ppm

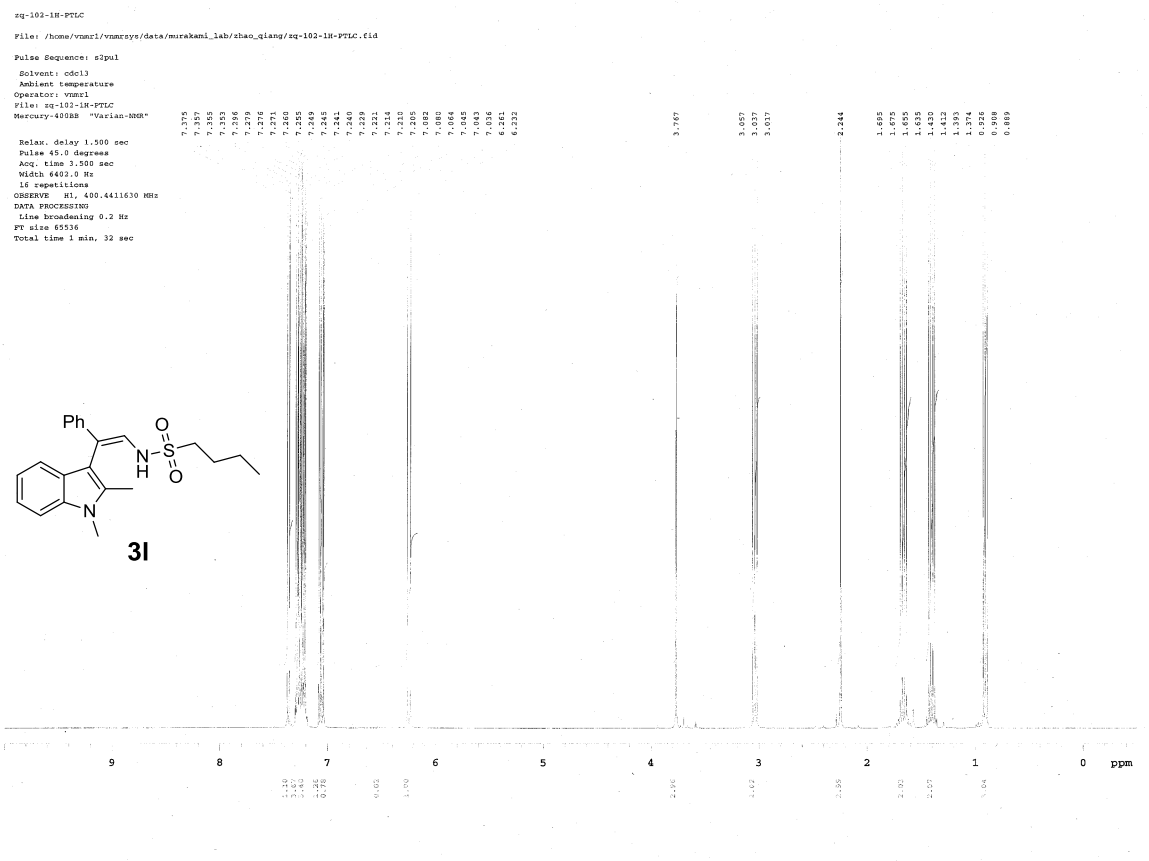

zq-98-13C-PTLC-0604
File: /home/vnmr1/vnmrsys/data/murakami_lab/zhao_qiang/4604_13C.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: 4604_13C
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
13248 repetitions
OBSERVE C13, 100.6910134 MHz
DECOUPLE H1, 400.4431966 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 5811 hr, 48 min, 56 sec
Ph
OMe
3i
ppm

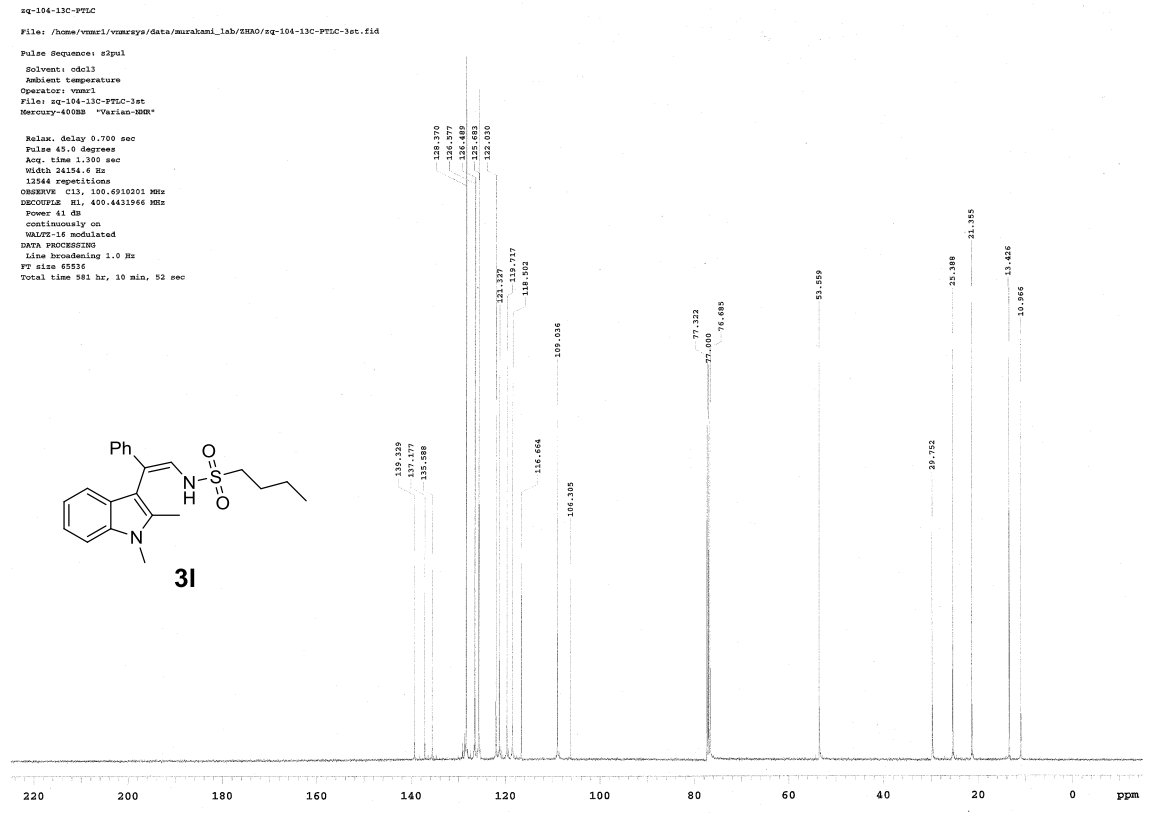

zq-103-1H-PTLC
File: exp
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411630 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
Ph
CF3
N
H
O
S
3j
ppm

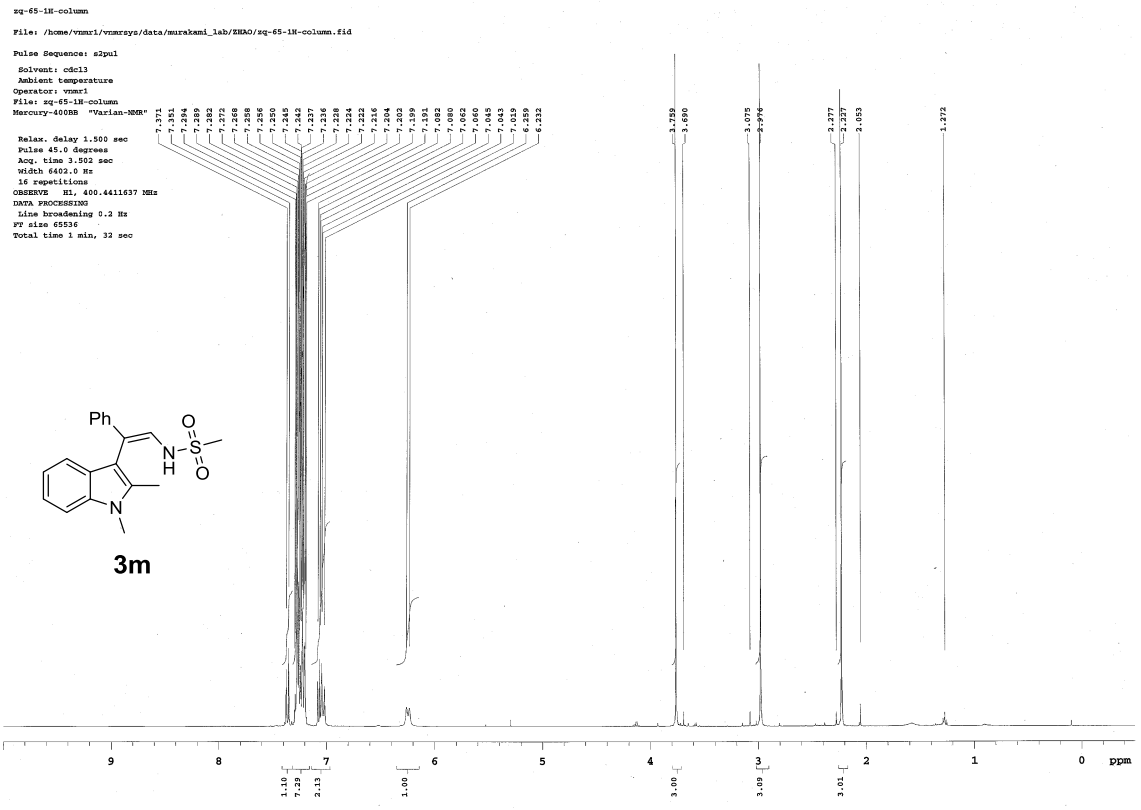

zq-103-13C-PTLC
File: /home/vnmr1/vnmrsys/data/murakami_lab/ZHAO/zq-103-13C-PTLC-3st.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: zq-103-13C-PTLC-3st
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
2048 repetitions
OBSERVE C13, 100.6910179 MHz
DECOUPLE H1, 400.4431966 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 5 hr, 48 min, 43 sec
Ph
CF3
3j
ppm

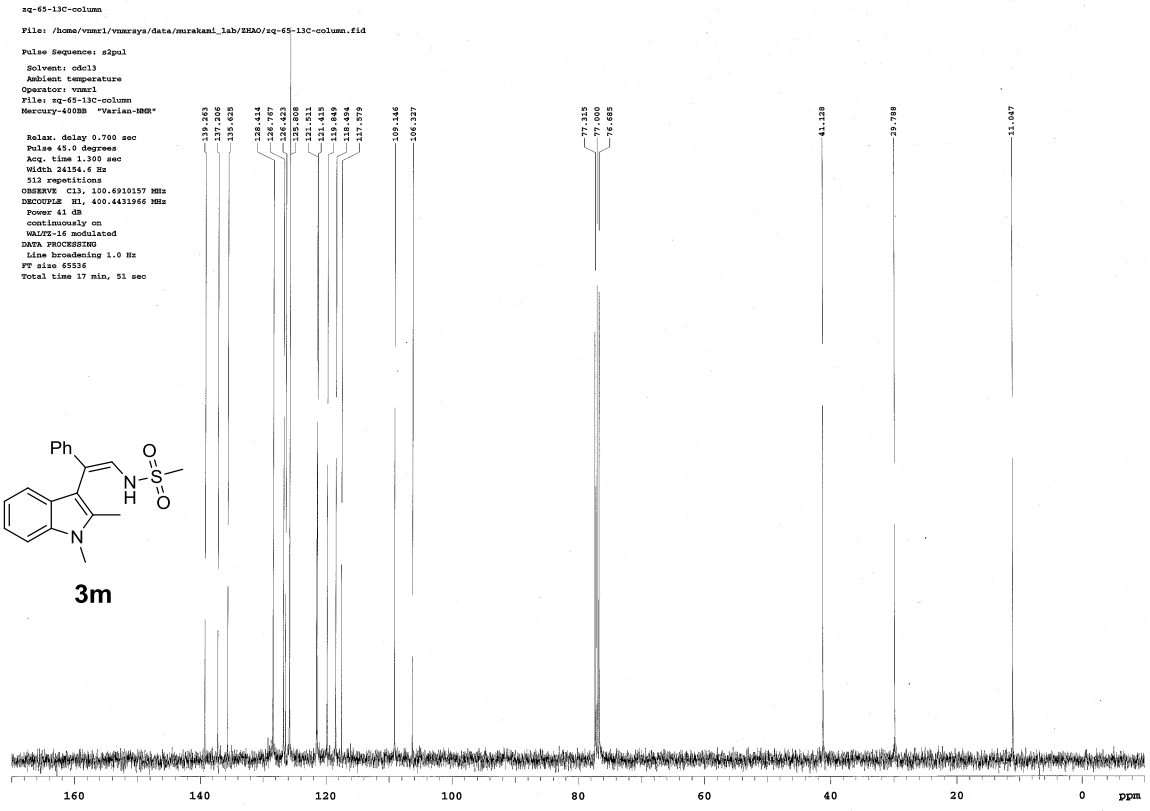

zq-99-1H-PTLC-0603
File: /home/vnmr1/vnmrsys/data/murakami_lab/ZHAO/zq-99-1H-PTLC-0603.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: zq-99-1H-PTLC-0603
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411630 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
7.960
7.958
7.941
7.938
7.493
7.480
7.464
7.462
7.348
7.337
7.329
7.317
7.284
7.265
7.260
7.219
7.216
7.203
7.189
7.178
7.166
7.159
7.007
6.978
6.963
6.943
6.926
6.924
6.886
6.866
6.441
6.413
3.742
2.309
2.144
1.559
Ph
O
S
O
N
H
N
3k
9
8
7
6
5
4
3
2
1
0
ppm
0.98
1.06
2.20
2.16
6.56
1.08
1.12
1.14
1.00
0.09
3.11
3.11
3.14

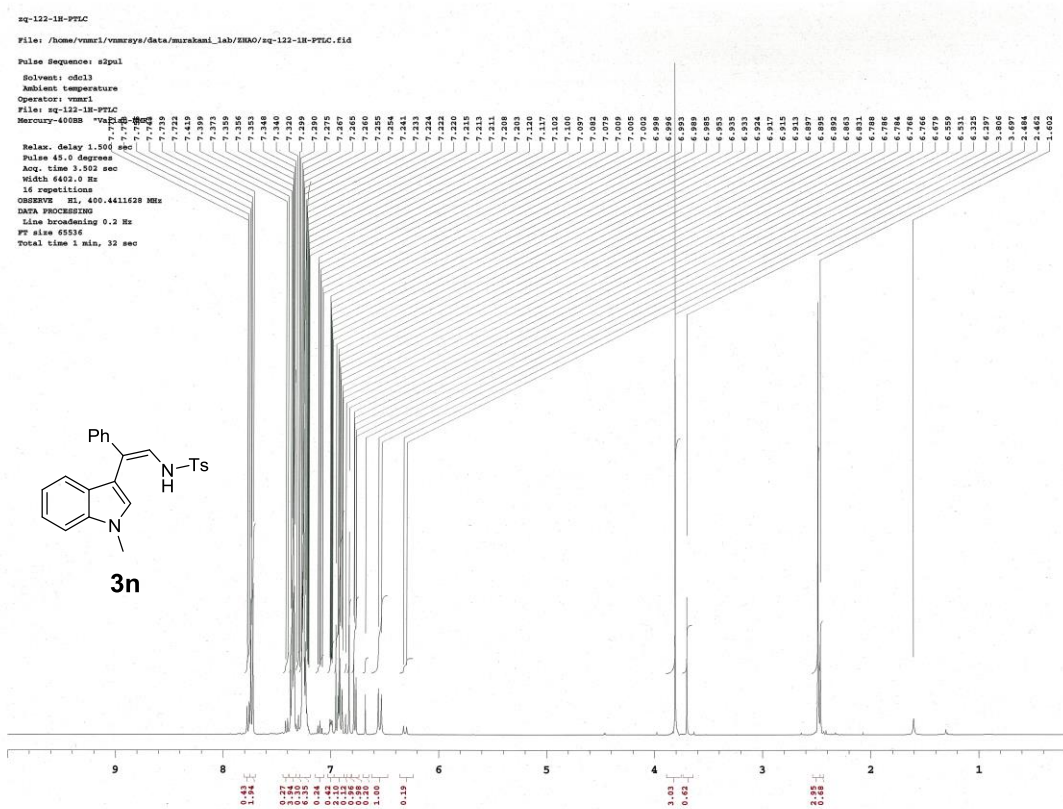

zq-99-1H-PTLC
File: exp
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
512 repetitions
OBSERVE C13, 100.6910179 MHz
DECOUPLE H1, 400.4431965 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min, 51 sec
139.351
138.275
137.075
135.625
132.491
132.445
128.868
128.626
128.334
126.620
126.445
126.306
125.720
121.833
121.364
119.693
118.421
117.521
108.889
106.305
77.322
77.205
77.007
76.685
29.752
20.271
10.886
Ph
O
S
O
N
H
N
3k
220
200
180
160
140
120
100
80
60
40
20
0
ppm

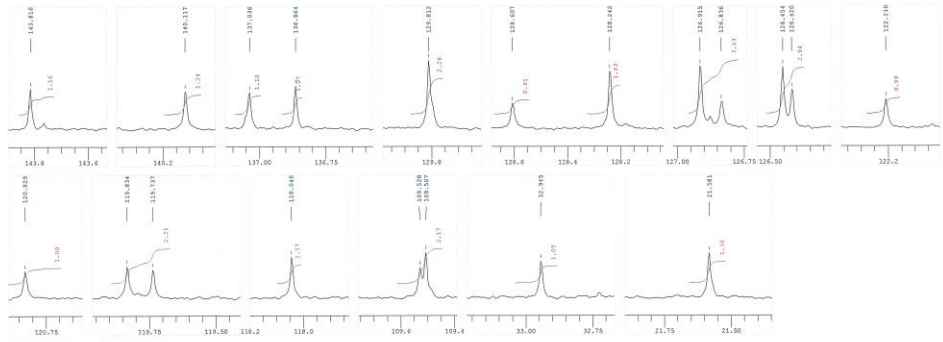

zq-102-1H-PTLC
File: /home/vnmr1/vnmrsys/data/murakami_lab/zhao_qiang/zq-102-1H-PTLC.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: zq-102-1H-PTLC
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411630 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
7.375
7.357
7.355
7.353
7.296
7.279
7.276
7.271
7.260
7.255
7.249
7.245
7.241
7.240
7.229
7.221
7.214
7.210
7.205
7.082
7.080
7.064
7.045
7.043
7.036
6.261
6.232
3.767
3.057
3.037
3.017
2.244
1.695
1.675
1.655
1.635
1.430
1.412
1.393
1.374
0.926
0.908
0.889
Ph
O
N
S
O
H
N
3l
9
8
7
6
5
4
3
2
1
0
ppm

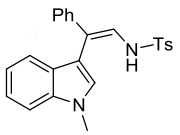

zq-104-13C-PTLC
File: /home/vnmr1/vnmrsys/data/murakami_lab/ZHAO/zq-104-13C-PTLC-3st.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: zq-104-13C-PTLC-3st
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
12544 repetitions
OBSERVE C13, 100.6910201 MHz
DECOUPLE H1, 400.4431966 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 581 hr, 10 min, 52 sec
128.370
126.577
126.489
125.683
122.030
121.337
119.717
118.502
116.664
109.036
106.305
77.322
77.000
76.685
53.559
29.752
25.388
21.355
13.426
10.966
139.329
137.177
135.588
Ph
O
N
S
O
H
N
3l
220
200
180
160
140
120
100
80
60
40
20
0
ppm


sq-65-1H-column
File: /home/vnmr1/vnmrsys/data/murakami_lab/ZHAO/sq-65-1H-column.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: sq-65-1H-column
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411637 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
7.371
7.351
7.284
7.269
7.262
7.272
7.268
7.258
7.256
7.250
7.245
7.242
7.237
7.236
7.228
7.224
7.222
7.216
7.204
7.202
7.199
7.191
7.082
7.080
7.063
7.060
7.045
7.043
7.019
6.259
6.232
3.769
3.690
3.075
2.976
2.277
2.257
2.053
1.272
Ph
N
H
O
S
O
N
3m
9
8
7
6
5
4
3
2
1
0
ppm
1.10
7.29
2.13
1.00
3.00
3.09
3.01


sq-65-13C-column
File: /home/vnmr1/vnmrsys/data/murakami_lab/ZHAO/sq-65-13C-column.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: sq-65-13C-column
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
512 repetitions
OBSERVE C13, 100.6910157 MHz
DECOUPLE H1, 400.4431966 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 min, 51 sec
139.263
137.206
135.628
128.414
126.767
126.423
125.808
121.511
121.415
119.849
118.494
117.979
109.146
106.327
77.315
77.000
76.685
41.128
29.788
11.047
Ph
N
H
O
S
O
N
3m
160
140
120
100
80
60
40
20
0
ppm

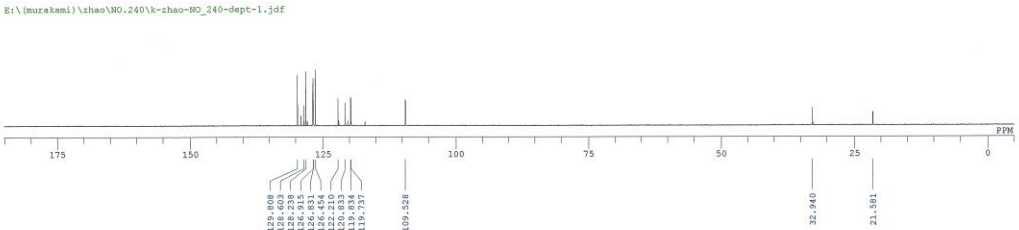




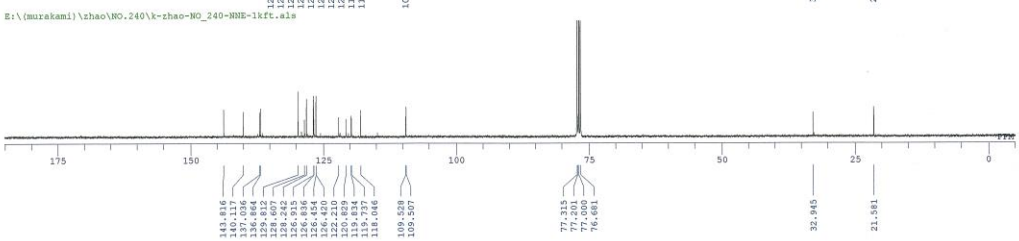


3n

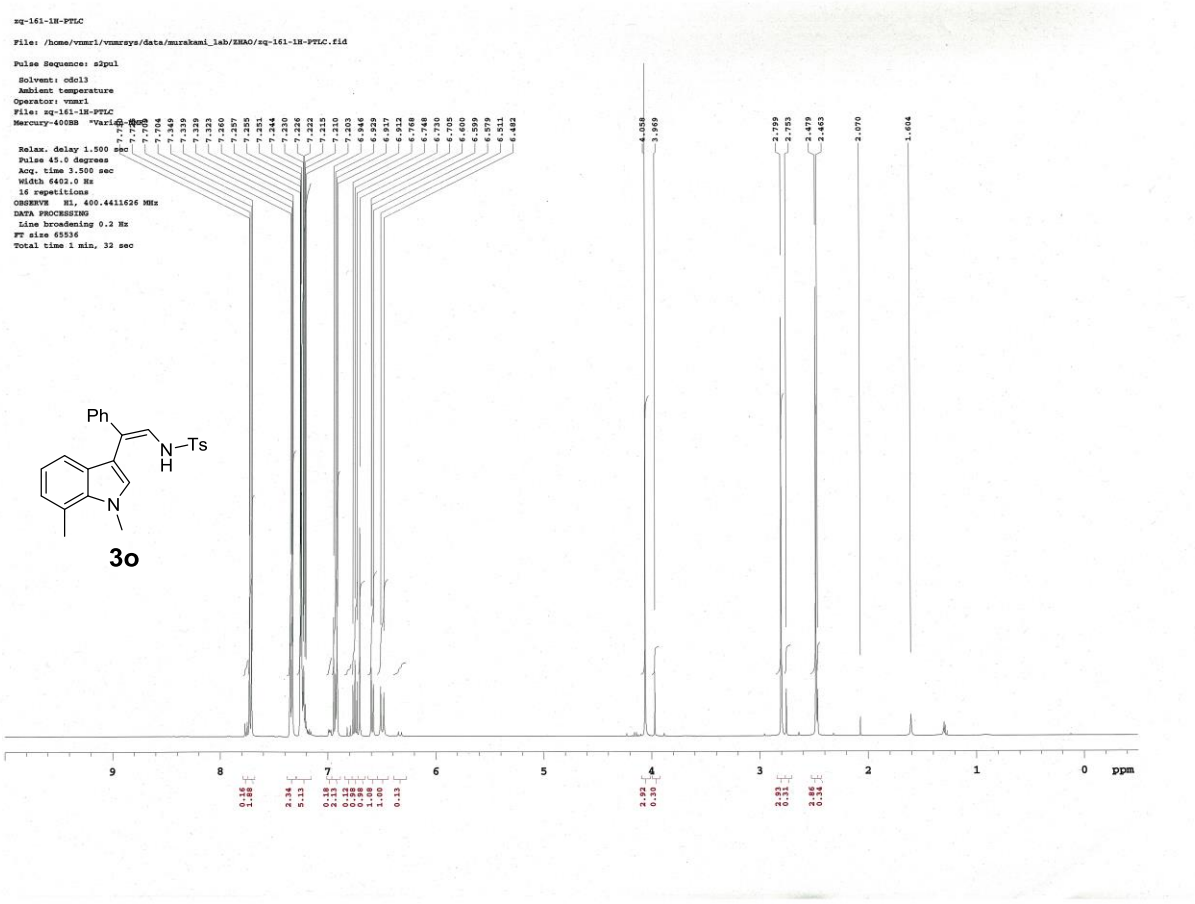
132713

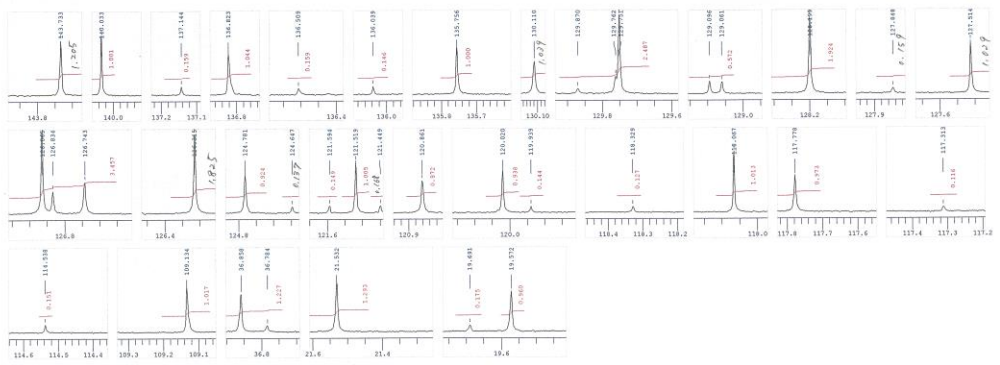


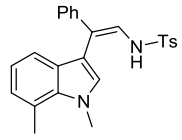

```
DFILE   k-zhao-NO_240-dept-1.jdf
COMMT   DEPT with decoupling
DATIM   26-05-2015 11:55:42
OBNUC   13C
EXMOD   dept.ex2
OBFRQ        100.53 MHz
OBFIN          5.86 Hz
POINT         65536
FREQU      27654.87 Hz
SCANS           853
ACQTM        2.3698 sec
PD           1.0000 sec
PW1            8.00 usec
IRNUC   1H
CTEMP         21.3 c
SLVNT   CDCL3
EXREF        77.00 ppm
BF            1.00 Hz
RGAIN           60
```

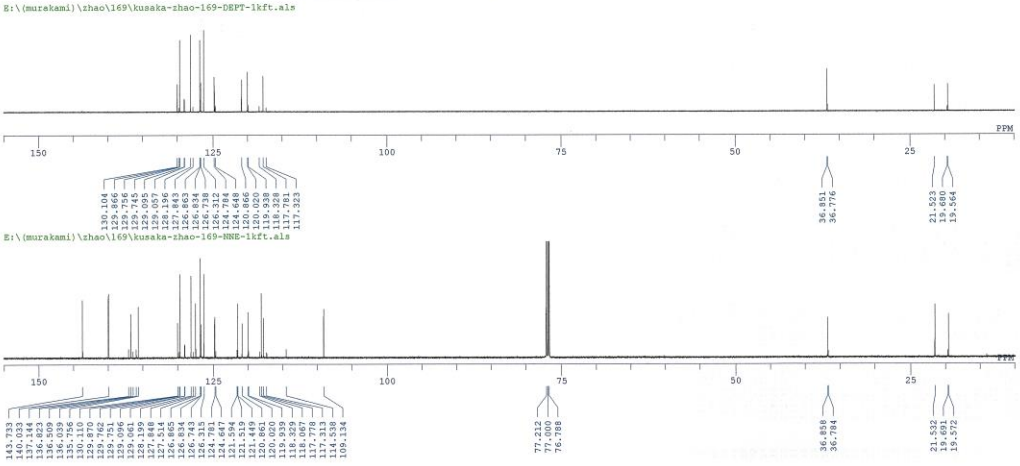



```
DFILE   k-zhao-NO_240-NNE-1kft.als
COMMT   single pulse decoupled gated NO
DATIM   26-05-2015 09:50:05
OBNUC   13C
EXMOD   single_pulse_dec
OBFRQ        100.53 MHz
OBFIN          5.86 Hz
POINT         65536
FREQU      27654.87 Hz
SCANS           501
ACQTM        2.3698 sec
PD           7.0400 sec
PW1            2.67 usec
IRNUC   1H
CTEMP         21.0 c
SLVNT   CDCL3
EXREF        77.00 ppm
BF            1.00 Hz
RGAIN           60
```



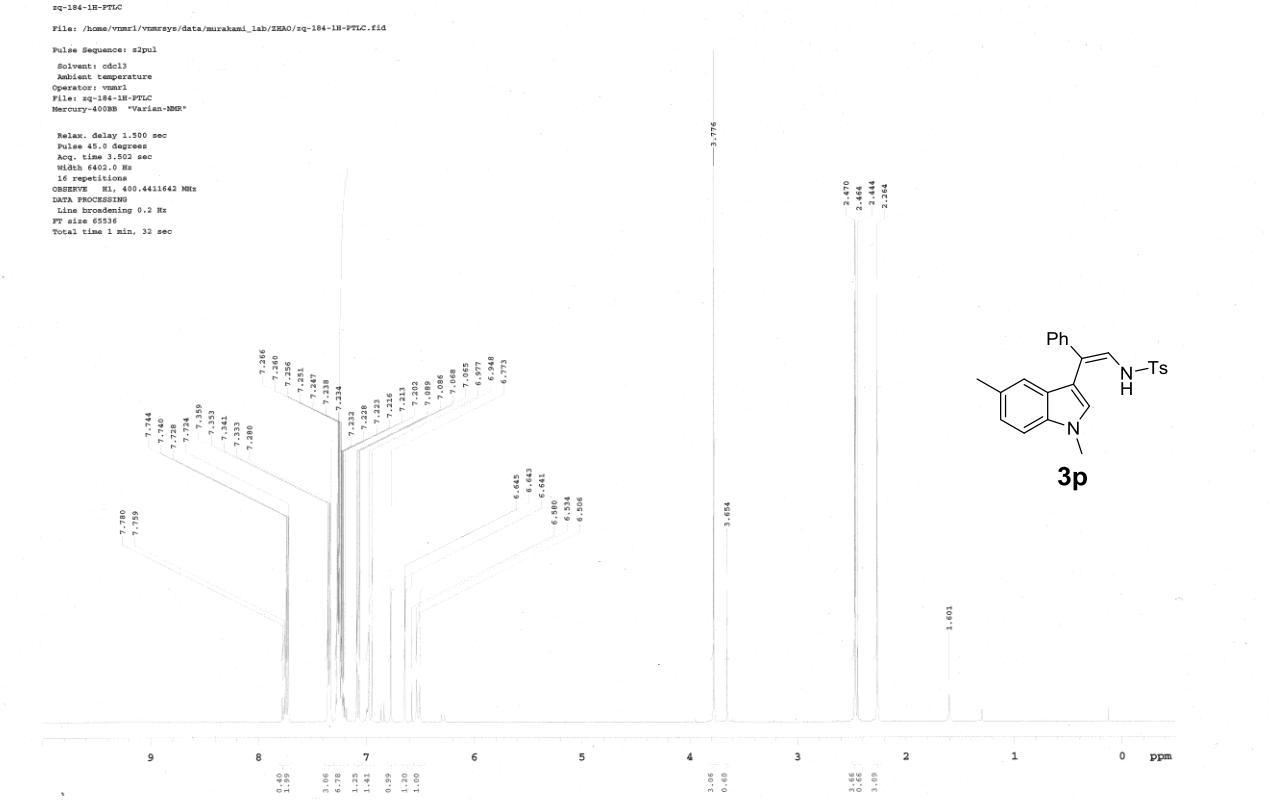


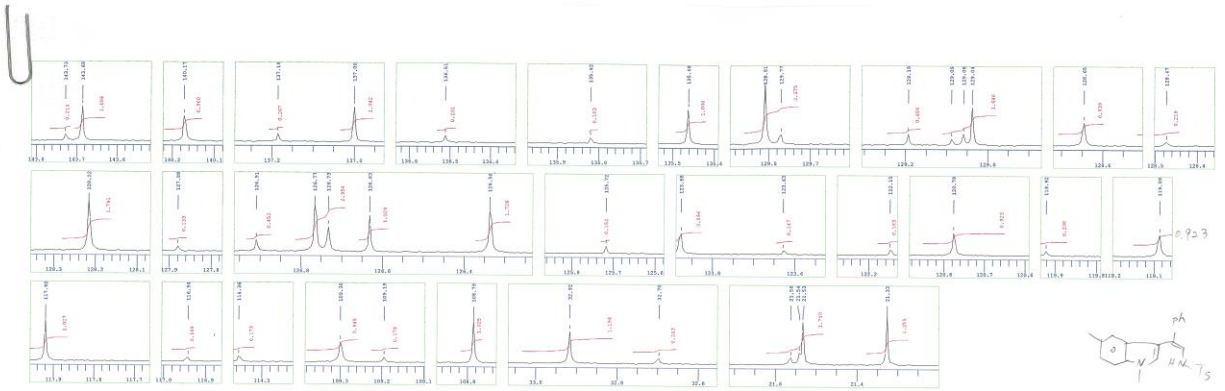


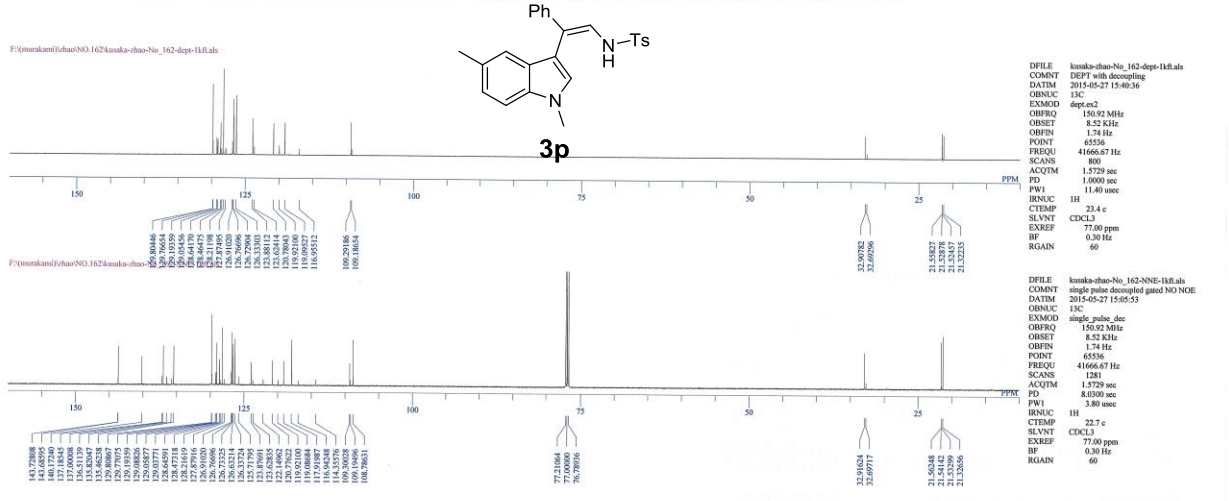


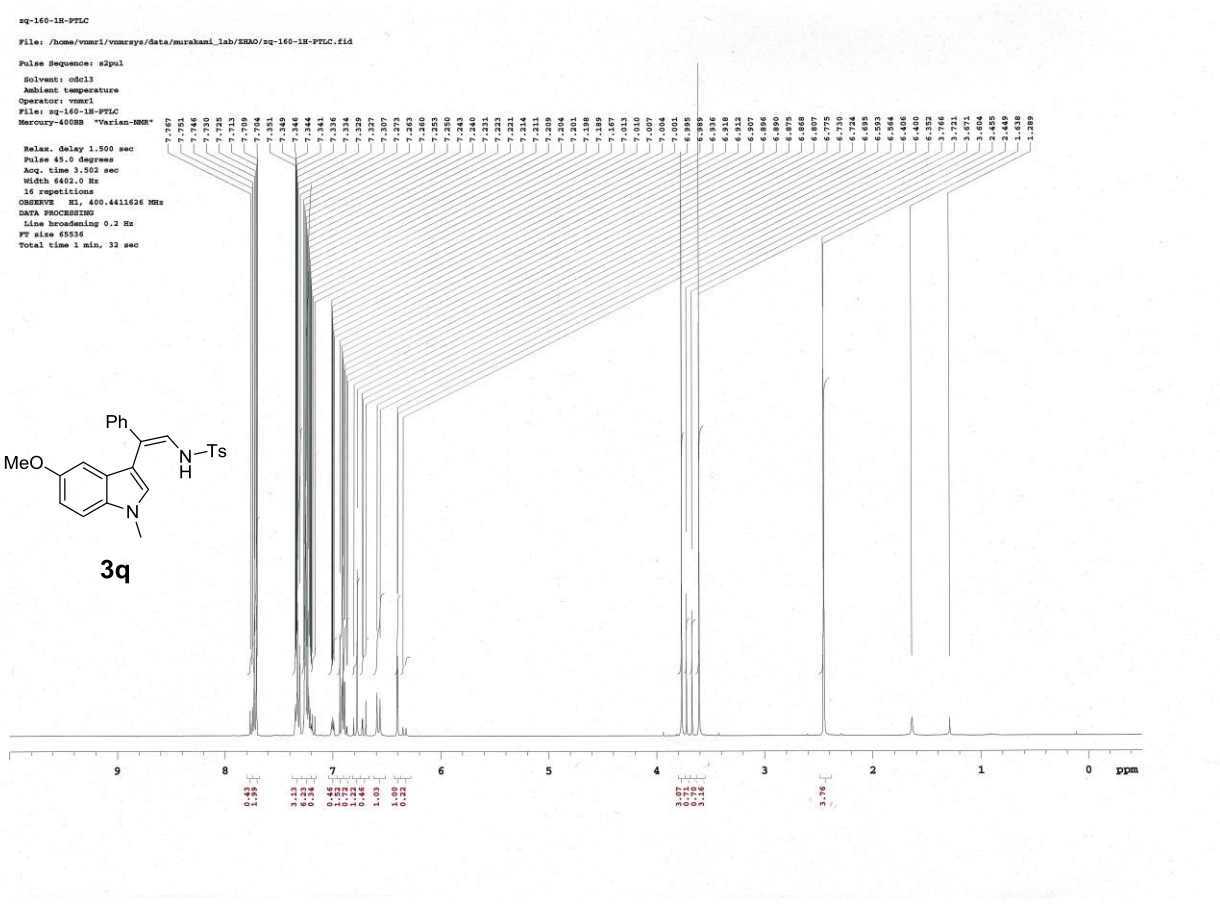

```
DFILE  kusaka-zhao-169-DEPT-1kft.als
COMNT  DEPT with decoupling
DATIM  08-06-2015 14:59:04
OBNUC  13C
EXMOD  dept.ex2
OBFRQ       150.92 MHz
OBFIN         7.12 Hz
POINT       131072
FRQU      30193.24 Hz
SCANS          250
ACQTM       2.1706 sec
PD          1.2000 sec
PW1          11.40 usec
IRNUC  1H
CTEMP        22.9 c
SLVNT  CDCL3
EXREF       77.00 ppm
BF           0.23 Hz
RGAIN          60
```

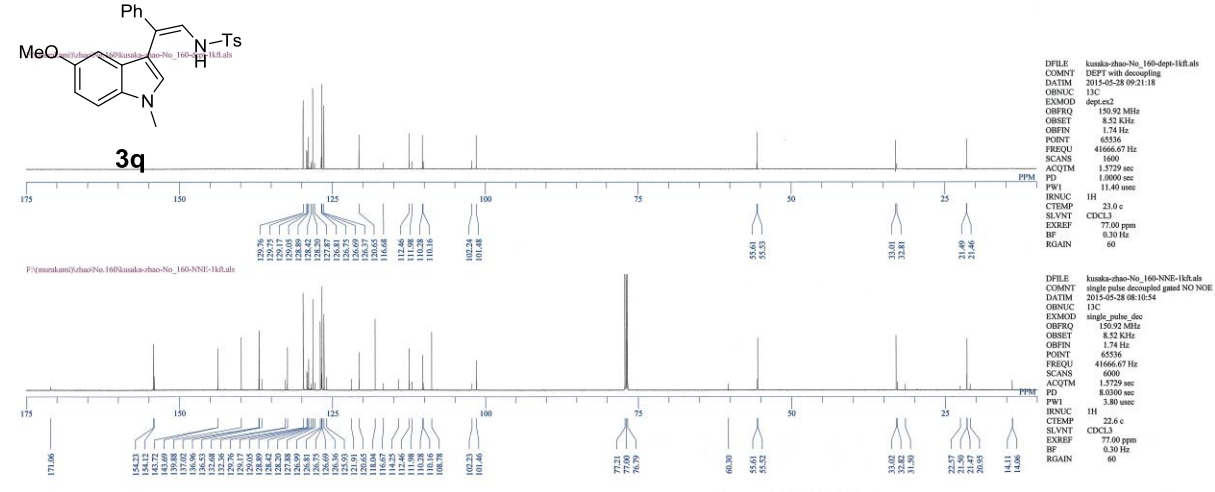
```
DFILE  kusaka-zhao-169-NNE-1kft.als
COMNT  single pulse decoupled gated NO-
DATIM  08-06-2015 14:42:33
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ       150.92 MHz
OBFIN         7.12 Hz
POINT       131072
FRQU      30193.24 Hz
SCANS          1281
ACQTM       2.1706 sec
PD          8.0000 sec
PW1          3.80 usec
IRNUC  1H
CTEMP        22.3 c
SLVNT  CDCL3
EXREF       77.00 ppm
BF           0.23 Hz
RGAIN          60
```

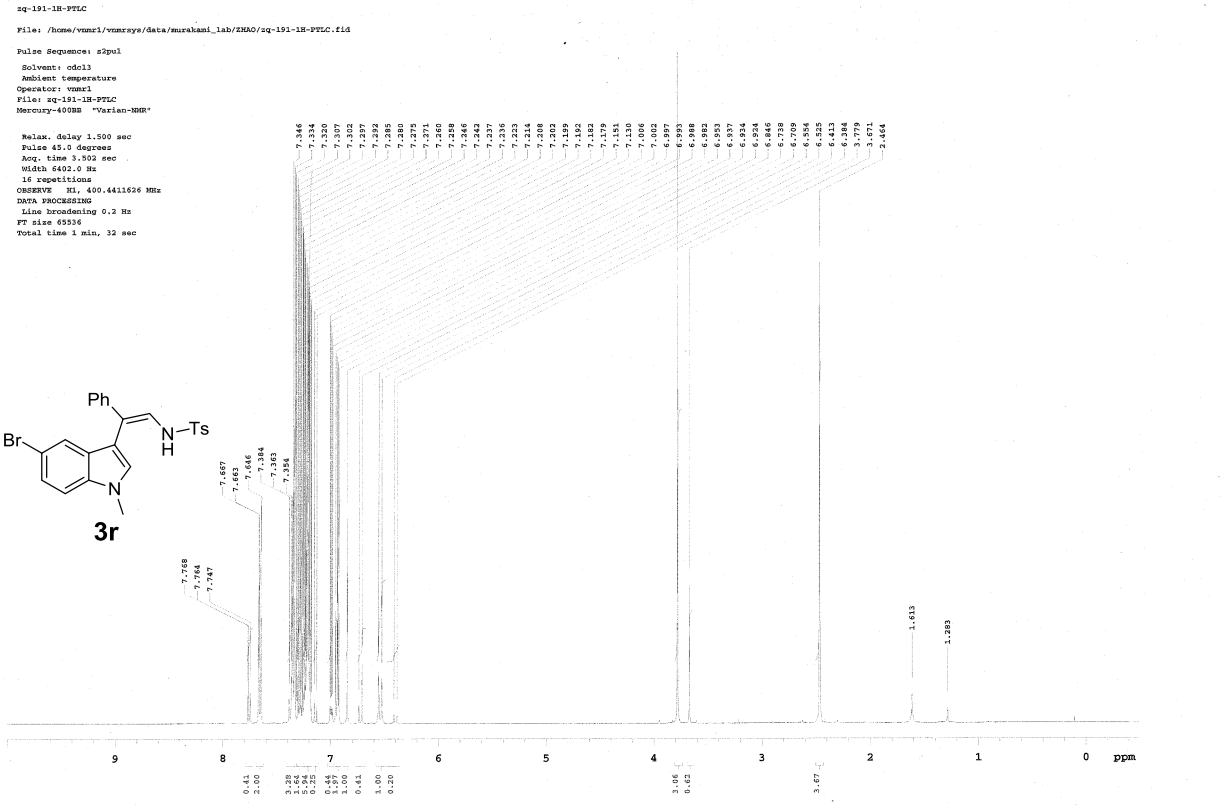

sq-184-1H-PTLC
File: /home/vnmr1/vnmrsys/data/murakami_lab/ZHAO/sq-184-1H-PTLC.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: sq-184-1H-PTLC
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411642 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
3.776
2.470
2.464
2.444
2.264
1.601
3.654
Ph
N–Ts
H
N
3p
ppm

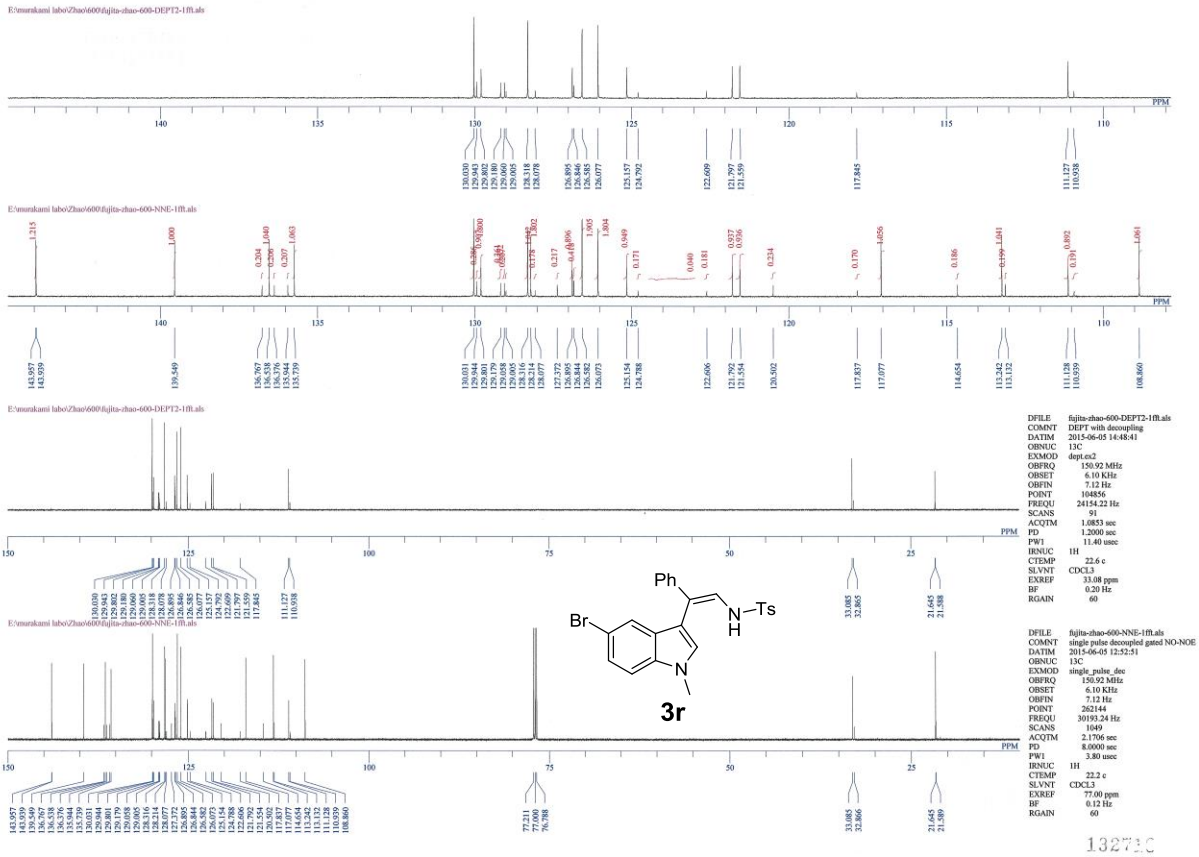



Ph
N–Ts
H
N
3p
PPM
DFILE kusaka-zhao-No_162-dept-1kfl.als
COMNT DEPT with decoupling
DATIM 2015-05-27 15:40:36
OBNUC 13C
EXMOD dept.ex2
OBFRQ 150.92 MHz
OBSET 8.52 KHz
OBFIN 1.74 Hz
POINT 65536
FREQU 41666.67 Hz
SCANS 800
ACQTM 1.5729 sec
PD 1.0000 sec
PW1 11.40 usec
IRNUC 1H
CTEMP 23.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.30 Hz
RGAIN 60
DFILE kusaka-zhao-No_162-NNE-1kfl.als
COMNT single pulse decoupled gated NO NOE
DATIM 2015-05-27 15:05:53
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
OBSET 8.52 KHz
OBFIN 1.74 Hz
POINT 65536
FREQU 41666.67 Hz
SCANS 1281
ACQTM 1.5729 sec
PD 8.0300 sec
PW1 3.80 usec
IRNUC 1H
CTEMP 22.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.30 Hz
RGAIN 60


sq-160-1H-PTLC
File: /home/vnmr1/vnmrsys/data/murakami_lab/EHAO/sq-160-1H-PTLC.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: sq-160-1H-PTLC
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411626 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
Ph
MeO
N
Ts
H
N
3q
ppm

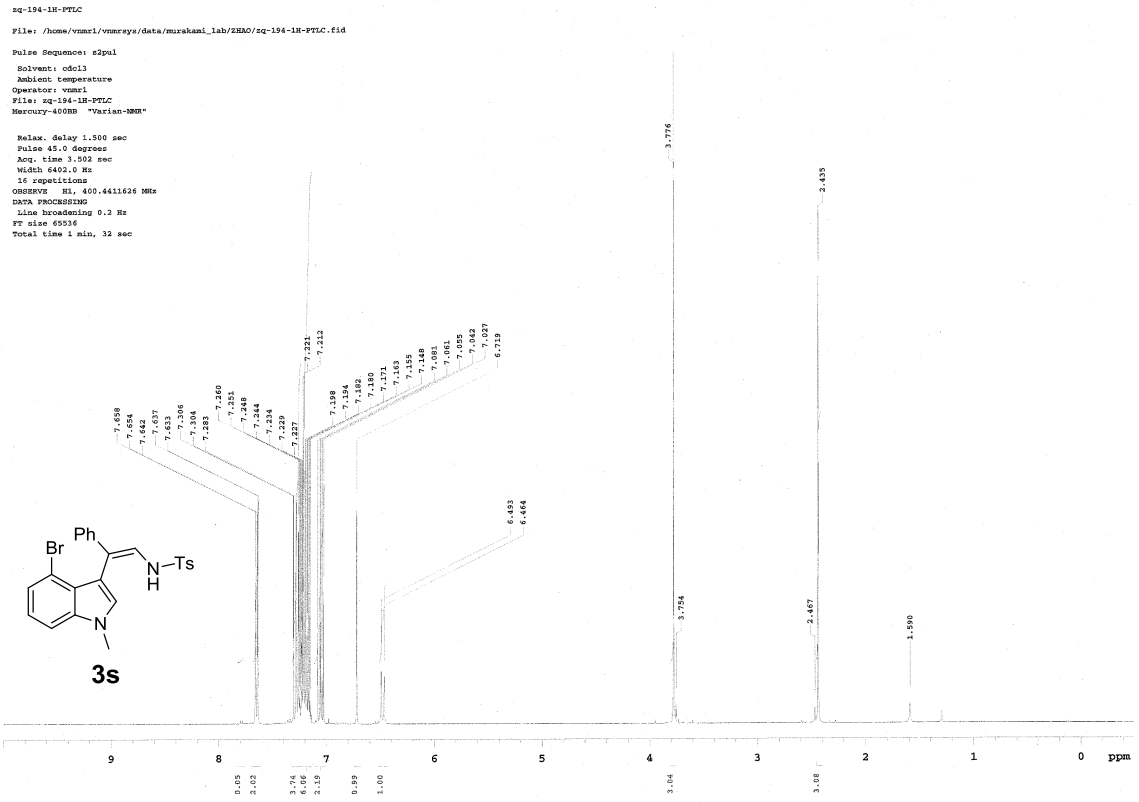

Ph
MeO
N
Ts
H
N
3q
PPM
DFILE kusaka-zhao-No_160-dept-1kft.als
COMNT DEPT with decoupling
DATIM 2015-05-28 09:21:18
OBNUC 13C
EXMOD dept.ex2
OBFRQ 150.92 MHz
OBSET 8.52 KHz
OBFIN 1.74 Hz
POINT 65536
FREQU 41666.67 Hz
SCANS 1600
ACQTM 1.5729 sec
PD 1.0000 sec
PW1 11.40 usec
IRNUC 1H
CTEMP 23.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.30 Hz
RGAIN 60
DFILE kusaka-zhao-No_160-NNE-1kft.als
COMNT single pulse decoupled gated NO NOE
DATIM 2015-05-28 08:10:54
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
OBSET 8.52 KHz
OBFIN 1.74 Hz
POINT 65536
FREQU 41666.67 Hz
SCANS 6000
ACQTM 1.5729 sec
PD 8.0300 sec
PW1 3.80 usec
IRNUC 1H
CTEMP 22.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.30 Hz
RGAIN 60

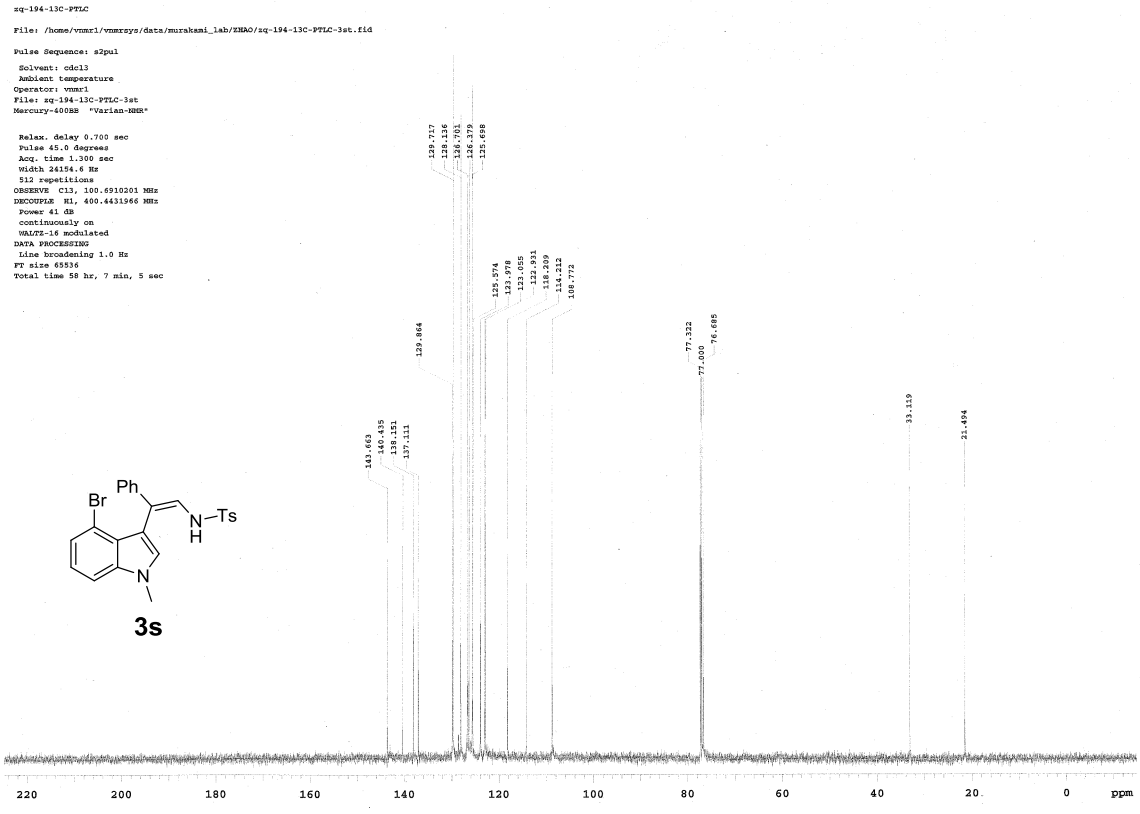


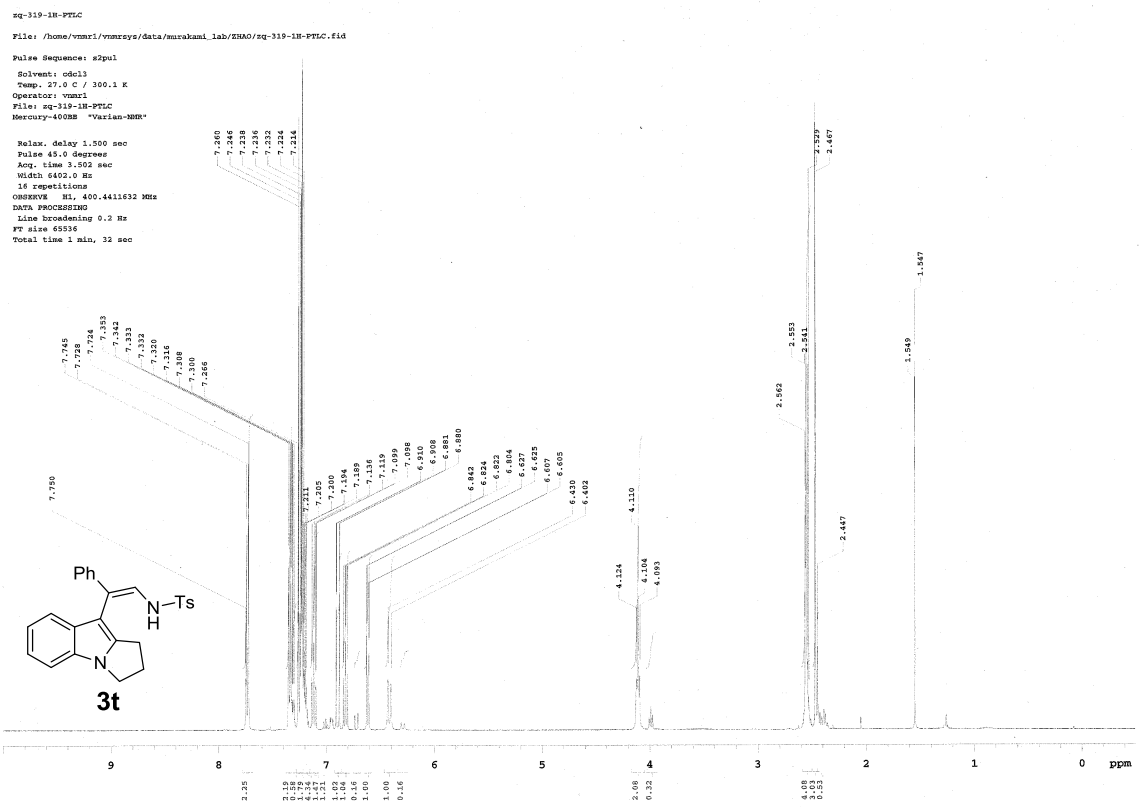


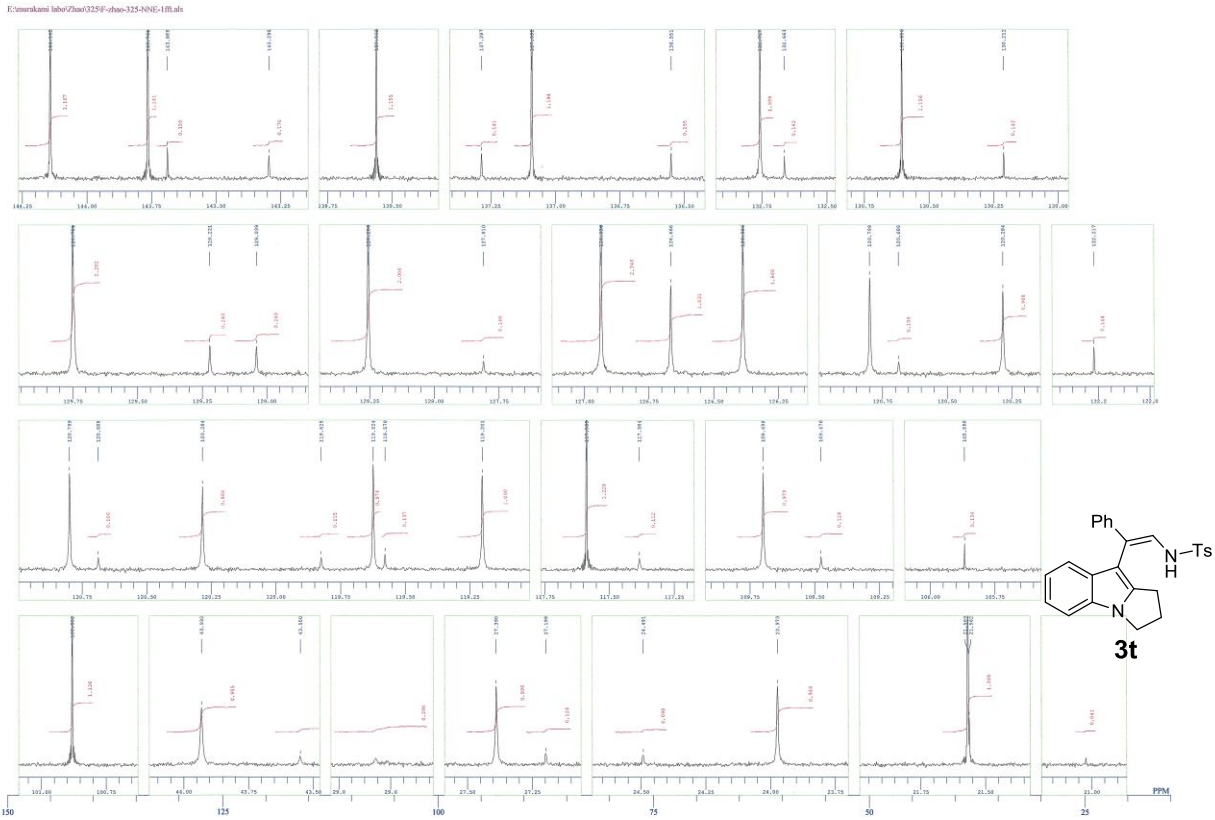
DFILE fujita-zhao-600-DEPT2-1ffl.als
COMNT DEPT with decoupling
DATIM 2015-06-05 14:48:41
OBNUC 13C
EXMOD dept.ex2
OBFRQ 150.92 MHz
OBSET 6.10 KHz
OBFIN 7.12 Hz
POINT 104856
FREQU 24154.22 Hz
SCANS 91
ACQTM 1.0853 sec
PD 1.2000 sec
PW1 11.40 usec
IRNUC 1H
CTEMP 22.6 c
SLVNT CDCL3
EXREF 33.08 ppm
BF 0.20 Hz
RGAIN 60

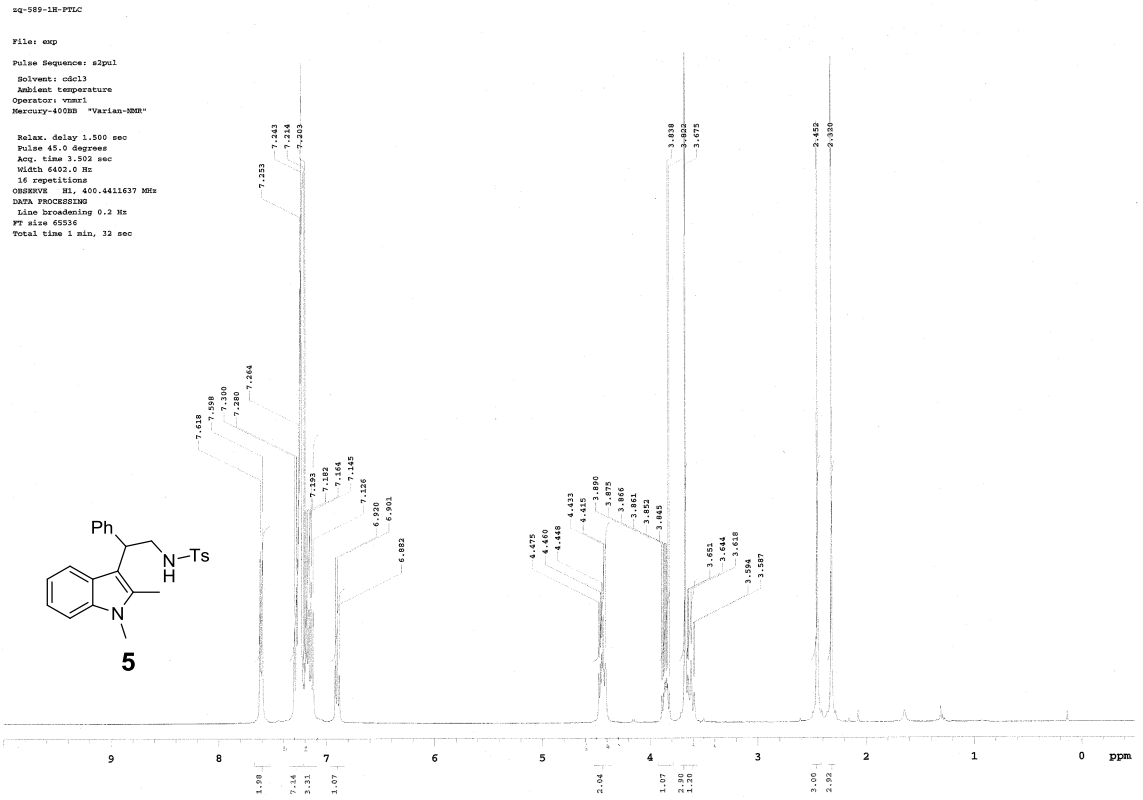
DFILE fujita-zhao-600-NNE-1ffl.als
COMNT single pulse decoupled gated NO-NOE
DATIM 2015-06-05 12:52:51
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
OBSET 6.10 KHz
OBFIN 7.12 Hz
POINT 262144
FREQU 30193.24 Hz
SCANS 1049
ACQTM 2.1706 sec
PD 8.0000 sec
PW1 3.80 usec
IRNUC 1H
CTEMP 22.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60

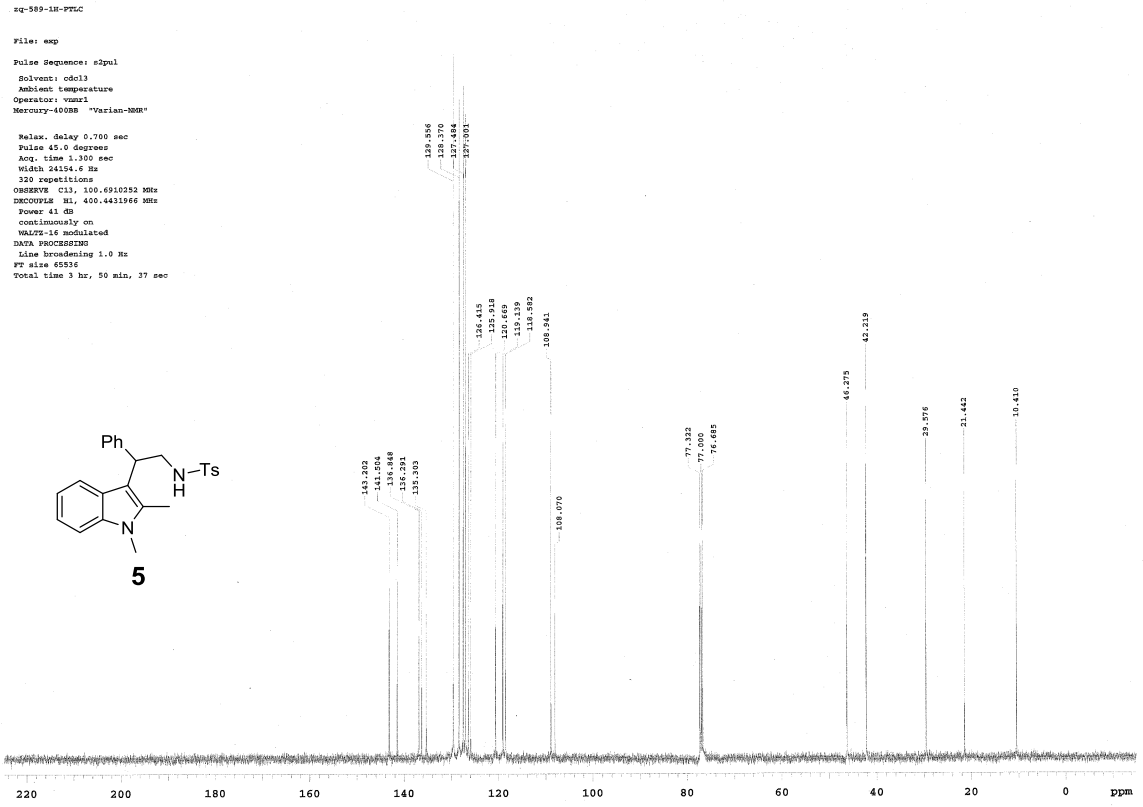

zq-194-1H-PTLC
File: /home/vnmr1/vnmrsys/data/murakami_lab/ZHAO/zq-194-1H-PTLC.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: zq-194-1H-PTLC
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411626 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
Br
Ph
N
Ts
H
N
3s
ppm

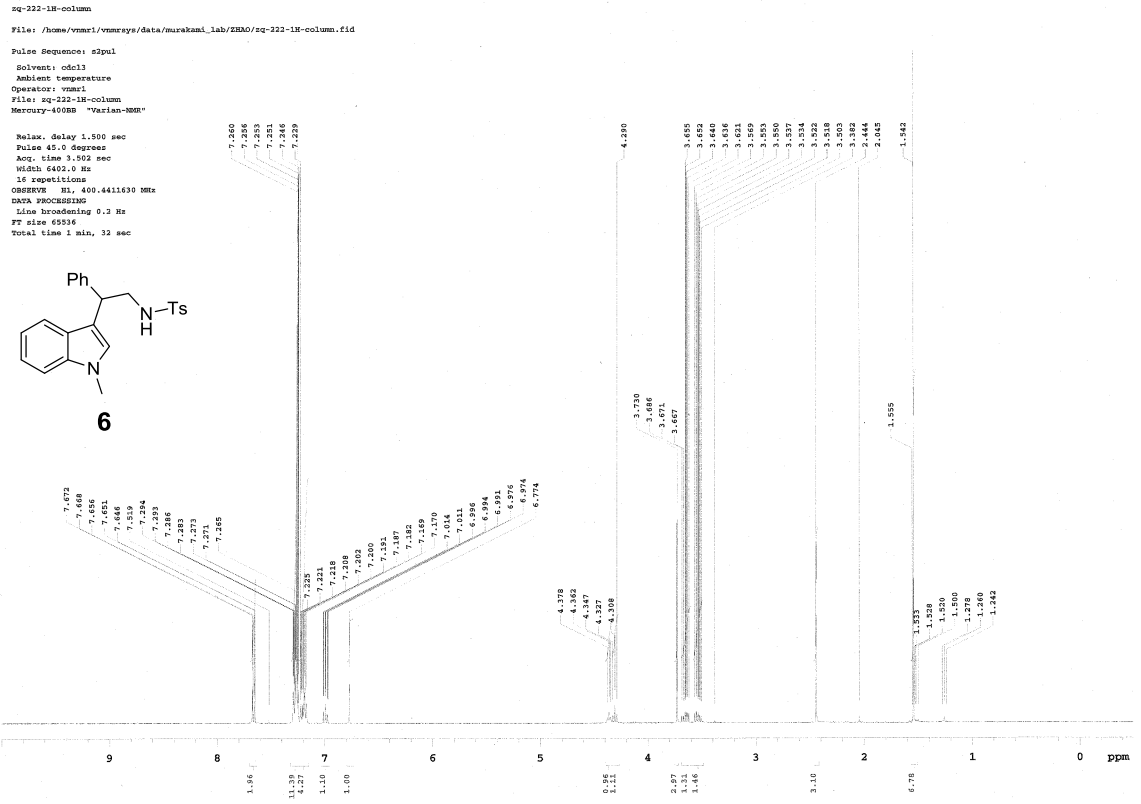

zq-194-13C-PTLC
File: /home/vnmr1/vnmrsys/data/murakami_lab/ZHAO/zq-194-13C-PTLC-3st.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: zq-194-13C-PTLC-3st
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
512 repetitions
OBSERVE C13, 100.6910201 MHz
DECOUPLE H1, 400.4431966 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 58 hr, 7 min, 5 sec
Br
Ph
N
Ts
H
N
3s
ppm

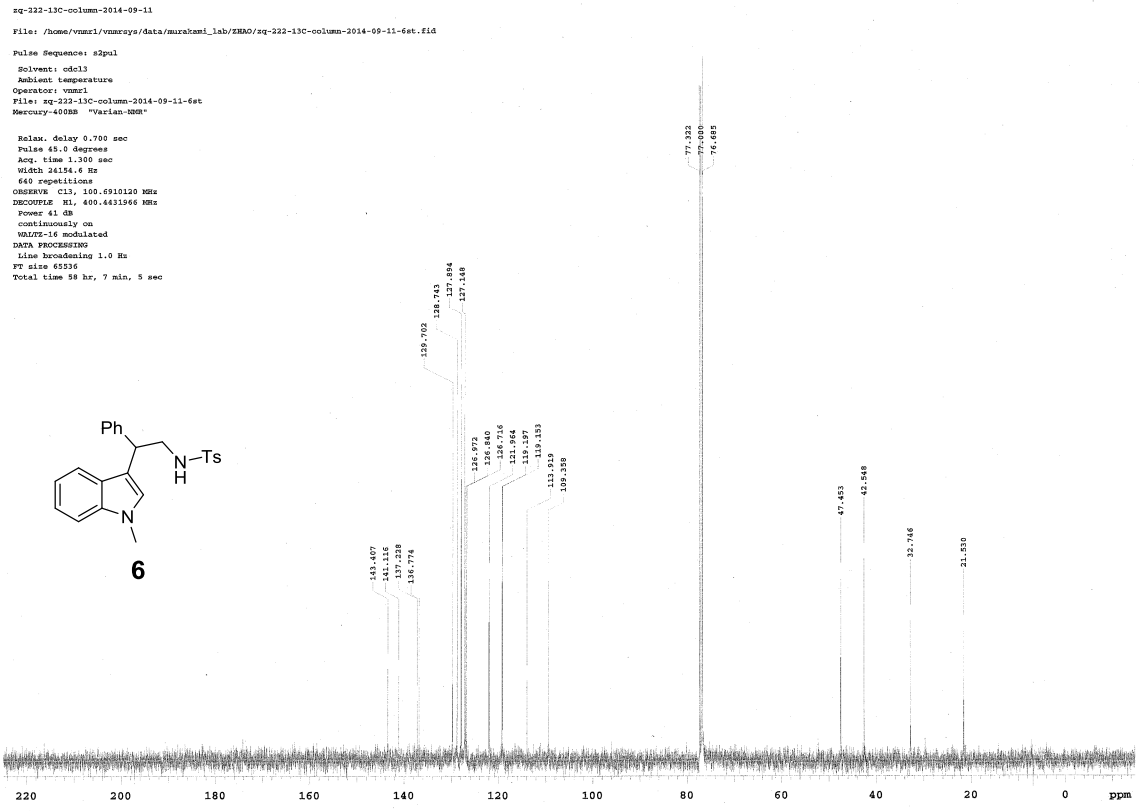

sq-319-1H-PTLC
File: /home/vnmr1/vnmrsys/data/murakami_lab/ZHAO/sq-319-1H-PTLC.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 27.0 C / 300.1 K
Operator: vnmr1
File: sq-319-1H-PTLC
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411632 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
Ph
N
Ts
H
3t
ppm

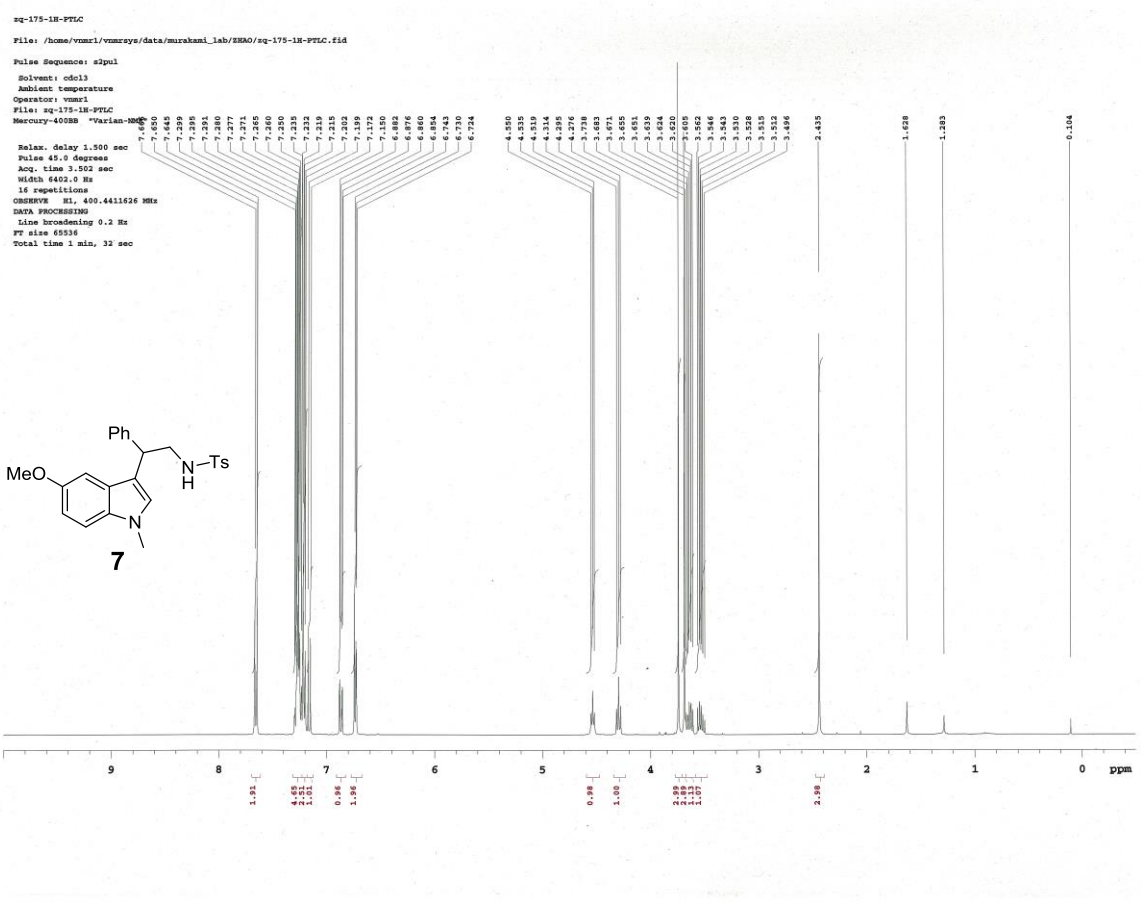

E:\murakami labo\Zhao\325\F-zhao-325-NNE-1ffl.als
Ph
N
Ts
H
3t
PPM

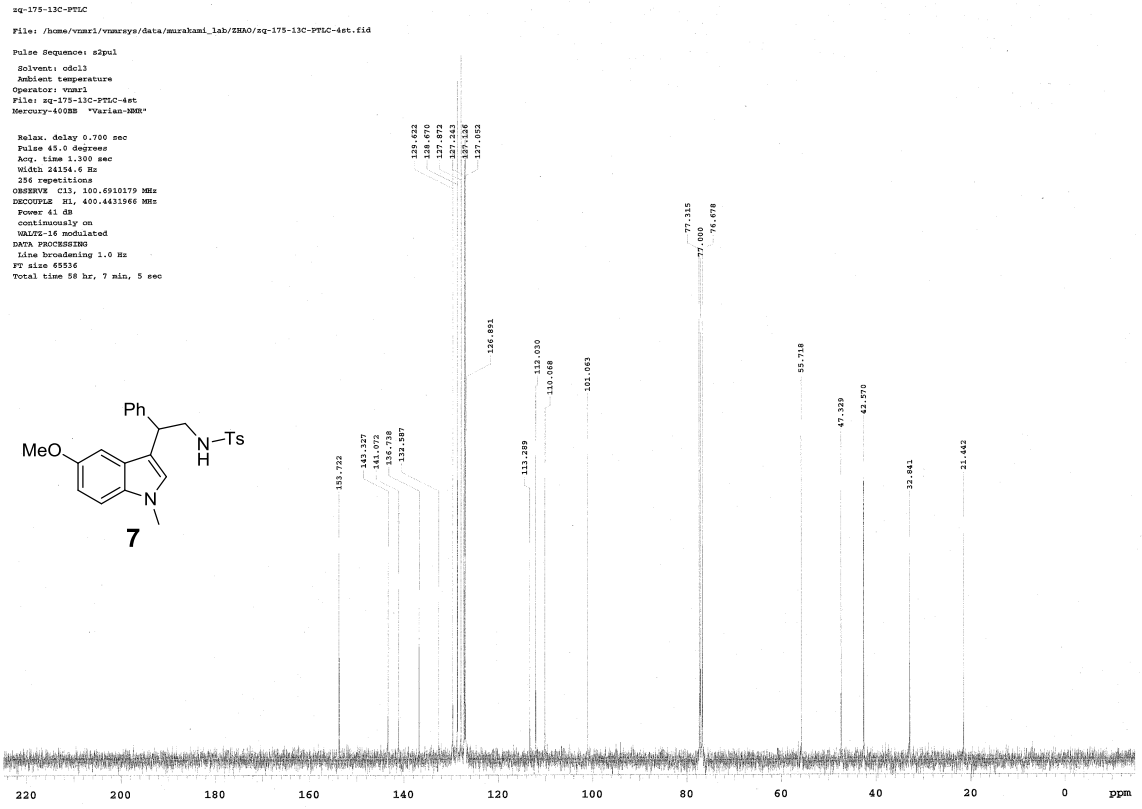

zq-589-1H-PTLC
File: exp
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411637 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
Ph
N–Ts
H
N
5
ppm

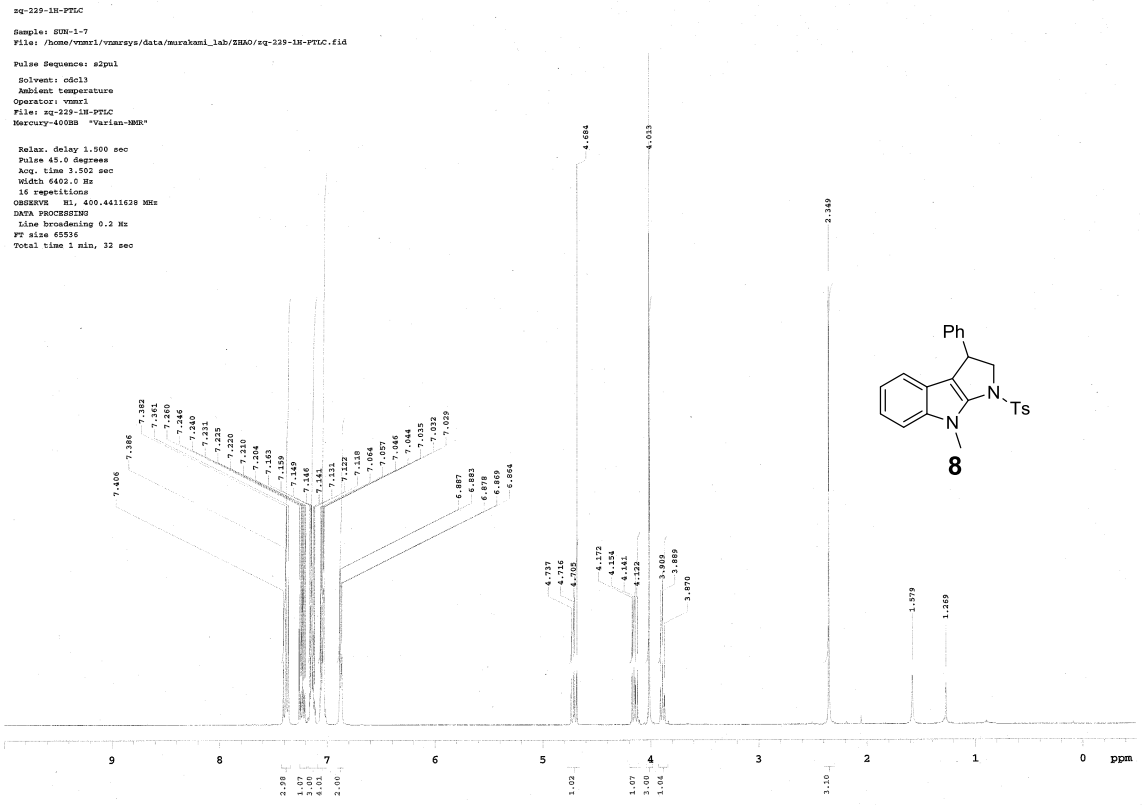

zq-589-1H-PTLC
File: exp
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
320 repetitions
OBSERVE C13, 100.6910252 MHz
DECOUPLE H1, 400.4431966 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 3 hr, 50 min, 37 sec
Ph
N–Ts
H
N
5
ppm

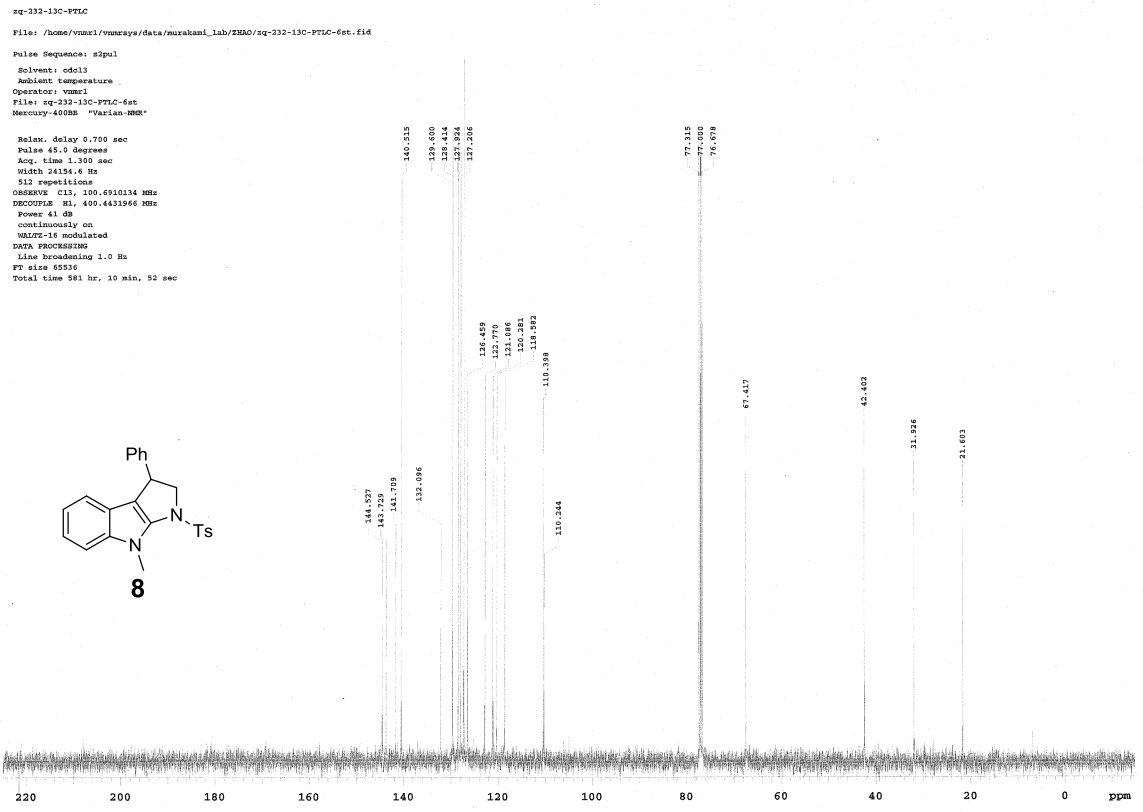

sq-222-1H-column
File: /home/vnmr1/vnmrsys/data/murakami_lab/ZHAO/sq-222-1H-column.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: sq-222-1H-column
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411630 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
Ph
N–Ts
H
N
6
ppm


sq-222-13C-column-2014-09-11
File: /home/vnmr1/vnmrsys/data/murakami_lab/ZHAO/sq-222-13C-column-2014-09-11-6st.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: sq-222-13C-column-2014-09-11-6st
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
640 repetitions
OBSERVE C13, 100.6910120 MHz
DECOUPLE H1, 400.4431966 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 58 hr, 7 min, 5 sec
Ph
N–Ts
H
N
6
ppm


sq-175-1H-PTLC
File: /home/vnmr1/vnmrsys/data/murakami_lab/ZHAO/sq-175-1H-PTLC.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: sq-175-1H-PTLC
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411626 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
Ph
MeO
N
Ts
H
N
7
ppm


sq-175-13C-PTLC
File: /home/vnmr1/vnmrsys/data/murakami_lab/ZHAO/sq-175-13C-PTLC-4st.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: sq-175-13C-PTLC-4st
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
256 repetitions
OBSERVE C13, 100.6910179 MHz
DECOUPLE H1, 400.4431966 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 58 hr, 7 min, 5 sec
Ph
MeO
N
Ts
H
N
7
ppm


zq-229-1H-PTLC
Sample: SUN-1-7
File: /home/vnmr1/vnmrsys/data/murakami_lab/ZHAO/zq-229-1H-PTLC.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: zq-229-1H-PTLC
Mercury-400BB "Varian-NMR"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.502 sec
Width 6402.0 Hz
16 repetitions
OBSERVE H1, 400.4411628 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 32 sec
Ph
N
Ts
N
8
ppm


zq-232-13C-PTLC
File: /home/vnmr1/vnmrsys/data/murakami_lab/ZHAO/zq-232-13C-PTLC-6st.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: vnmr1
File: zq-232-13C-PTLC-6st
Mercury-400BB "Varian-NMR"
Relax. delay 0.700 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
512 repetitions
OBSERVE C13, 100.6910134 MHz
DECOUPLE H1, 400.4431966 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 581 hr, 10 min, 52 sec
Ph
N
Ts
N
8
ppm