- **Supporting Information**

One-pot synthesis of 2,3-disubstituted dihydrobenzofurans and benzofurans *via* rhodium-catalyzed intramolecular C-H insertion reaction

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I. General Information.

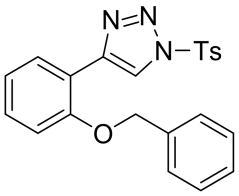
^{1}H NMR spectra were recorded in deuterated solvents on a Bruker 400 (400 MHz) spectrometer and calibrated to the residual solvent peak or tetramethylsilane (δ = 0 ppm). Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet, br = broad. J-values are in Hz. HRMS was measured by a Finnigan MA+ mass spectrometer or a GCT Premier (7000FWHM). Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure. All reactions were performed under argon using standard Schlenk techniques.

II. Experimental Section

1. Synthesis of starting materials 1

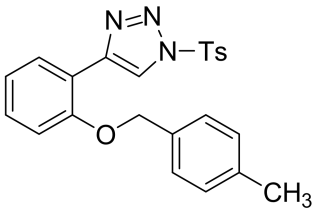
N-Sulfonyl-1,2,3-triazoles **1** were prepared from the corresponding alkynes and sulfonyl azides according to previously reported synthetic procedures. [1]

Following the reported procedure, copper(I) thiophene-2-carboxylate (0.1 mmol), sulfonyl azide (2 mmol), alkyne (2.6 mmol) in wet $CHCl_3$ (7 mL) was stirred at room temperature until the total consumption of sulfonyl azide. The mixture was then diluted with 15 mL of saturated NH_4Cl and extracted with EtOAc (3 x 15 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The mixture obtained was then filtrated over a pad of silica gel (3 x 10 cm) with a mixture of n-hexane/EtOAc (1:1) to afford the desired product.



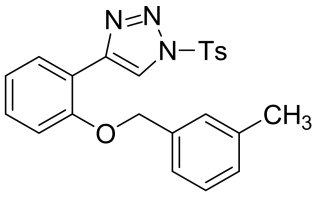
4-(2-(Benzyloxy)phenyl)-1-tosyl-1*H*-1,2,3-triazole (1a)

White solid; m.p.: 126-127 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.48 (s, 1H), 8.32 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.44-7.48 (m, 5H), 7.32-7.34 (m, 3H), 7.03-7.08 (m, 2H), 5.20 (s, 2H), 2.43 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.1, 146.9, 142.9, 138.4, 133.4, 130.3, 129.9, 128.9, 128.5, 128.4, 127.7, 122.4, 121.3, 118.1, 112.1, 70.7, 21.8; HRMS (ESI, m/z): calcd. for $C_{22}H_{20}N_3O_3S$ $(M+H)^+$: 406.1225, found: 406.1129.



4-(2-((4-Methylbenzyl)oxy)phenyl)-1-tosyl-1*H*-1,2,3-triazole (1b)

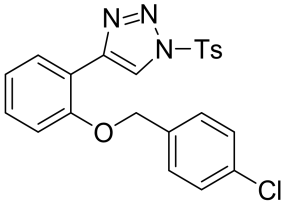
White solid; m.p.: 135-136 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (s, 1H), 8.31 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.29-7.34 (m, 5H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.02-7.08 (m, 2H), 5.16 (s, 2H), 2.42 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.2, 146.9, 142.9, 138.2, 133.5, 133.4, 130.3, 129.8, 129.5, 128.5, 128.1, 127.7, 122.4, 121.3, 118.1, 112.2, 70.6, 21.8, 21.3; HRMS (ESI, m/z): calcd. for $C_{23}H_{22}N_3O_3S$ $(M+H)^+$: 420.1382, found: 420.1375.



4-(2-((3-Methylbenzyl)oxy)phenyl)-1-tosyl-1*H*-1,2,3-triazole (1c)

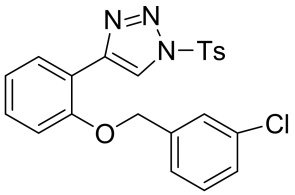
White solid; m.p.: 117-118 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (s, 1H), 8.32 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 2H), 7.30-7.35 (m, 5H), 7.22-7.25 (m, 2H), 7.02-7.05 (m, 2H), 5.16 (s, 2H), 2.44 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ

= 155.2, 146.9, 142.8, 138.7, 136.3, 133.5, 130.3, 129.8, 129.1, 128.7, 128.5, 128.3, 128.0, 124.7, 122.5, 121.3, 118.1, 112.1, 70.8, 21.8, 21.5; HRMS (ESI, m/z): calcd. for $C_{23}H_{22}N_3O_3S$ $(M+H)^+$: 420.1382, found: 420.1377.



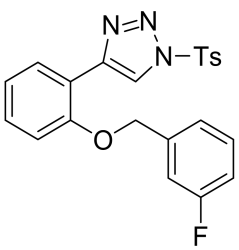
4-(2-((4-Chlorobenzyl)oxy)phenyl)-1-tosyl-1*H*-1,2,3-triazole (1d)

White solid; m.p.: 125-126 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (s, 1H), 8.30 (dd, J = 7.6, 1.2 Hz, 1H), 7.91 (d, J = 8.0 Hz, 2H), 7.29-7.43 (m, 7H), 7.08 (t, J = 7.6 Hz, 1H), 6.98-7.00 (d, J = 8.4 Hz, 1H), 5.17 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.9, 147.1, 142.8, 134.9, 134.3, 133.4, 130, 3, 129.8, 129.0, 128.9, 128.5, 128.2, 122.2, 121.6, 118.2, 112.2, 68.9, 21.8; HRMS (ESI, m/z): calcd. for $C_{22}H_{19}ClN_3O_3S$ $(M+H)^+$: 440.0836, found: 440.0839.



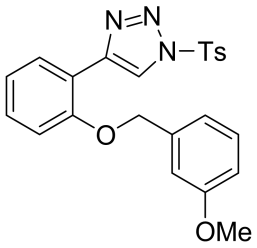
4-(2-((3-Chlorobenzyl)oxy)phenyl)-1-tosyl-1*H*-1,2,3-triazole (1e)

White solid; m.p.: 147-148 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (s, 1H), 8.30 (d, J = 7.2 Hz, 1H), 7.93 (d, J = 7.6 Hz, 2H), 7.30-7.35 (m, 7H), 7.09 (t, J = 7.2 Hz, 1H), 7.00 (d, J = 8.0 Hz, 1H), 5.17 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.9, 147.1, 142.7, 138.5, 134.8, 133.4, 133.3, 130.4, 130.2, 129.9, 128.6, 128.5, 128.3, 127.7, 125.7, 122.2, 121.6, 118.1, 112.1, 69.9, 21.8; HRMS (ESI, m/z): calcd. for $C_{22}H_{19}ClN_3O_3S$ $(M+H)^+$: 440.0836, found: 440.0840.



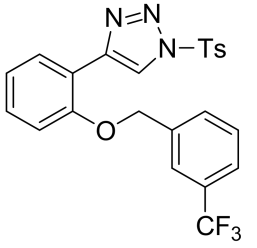
4-(2-((3-Fluorobenzyl)oxy)phenyl)-1-tosyl-1*H*-1,2,3-triazole (1f)

White solid; m.p.: 129-130 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (s, 1H), 8.30 (dd, J = 7.6, 1.6 Hz, 1H), 7.93 (d, J = 8.0 Hz, 2H), 7.41-7.45 (m, 1H), 7.30-7.36 (m, 3H), 7.22-7.25 (m, 1H), 7.07-7.15 (m, 3H), 6.99 (d, J = 8.0 Hz, 1H), 5.19 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8, 147.1, 142.8, 139.0, 133.4, 130.6, 130.5, 130.4, 129.9, 128.5, 128.3, 123.2, 123.1, 122.3, 121.6, 118.2, 115.5, 115.3, 114.5, 114.3, 112.0, 69.9, 69.8, 21.8; HRMS (ESI, m/z): calcd. for $C_{22}H_{19}FN_3O_3S$ $(M+H)^+$: 424.1131, found: 424.1136.



4-(2-((3-Methoxybenzyl)oxy)phenyl)-1-tosyl-1*H*-1,2,3-triazole (1g)

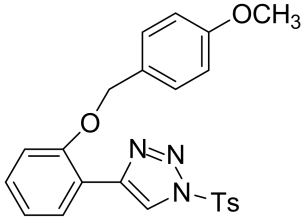
White solid; m.p.: 130-131 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (s, 1H), 8.31 (d, J = 7.6 Hz, 1H), 7.90 (d, J = 8.0 Hz, 2H), 7.30-7.40 (m, 4H), 7.96-7.09 (m, 5H), 5.17 (s, 2H), 3.85 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.1, 155.1, 146.9, 142.9, 137.9, 133.5, 130.3, 129.9, 129.8, 128.5, 128.1, 122.4, 121.4, 119.8, 118.1, 113.9, 113.1, 112.1, 70.6, 55.3, 21.8; HRMS (ESI, m/z): calcd. for $C_{23}H_{22}N_3O_4S$ $(M+H)^+$: 436.1331, found: 436.1327.



4-(2-((3-Trifluorobenzyl)oxy)phenyl)-1-tosyl-1*H*-1,2,3-triazole (1h)

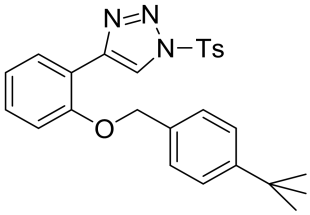
White solid; m.p.: 134-135 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (s, 1H), 8.33 (dd, J = 7.6, 1.6 Hz, 1H), 7.91 (d, J = 8.0 Hz, 2H), 7.61-7.71 (m, 4H), 7.32-7.34 (m, 3H), 7.10 (t, J = 7.6 Hz, 1H), 7.01 (d, J = 8.0 Hz, 1H), 5.25 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8, 147.1, 142.6, 137.4, 133.4, 130.9, 130.3, 129.9,

129.5, 128.5, 128.3, 125. 4, 125.3, 124.4, 124.3, 122.1, 121.7, 118.2, 112.0, 69.9, 21.8; HRMS (ESI, m/z): calcd. for $C_{23}H_{19}F_3N_3O_3S$ $(M+H)^+$: 474.1099, found: 474.1106.



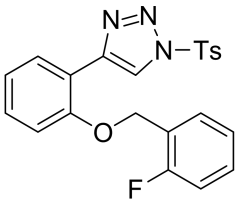
4-(2-((4-Methoxybenzyl)oxy)phenyl)-1-tosyl-1*H*-1,2,3-triazole (1i)

White solid; m.p.: 146-147 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (s, 1H), 8.30 (d, *J* = 7.6, 1H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.31-7.34 (m, 3H), 7.03-7.07 (m, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 5.12 (s, 2H), 3.87 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8, 155.2, 147.0, 142.9, 133.5, 130.3, 129.8, 128.5, 128.0,122.4, 121.2, 118.1, 114.2, 112.2, 70.5, 55.4, 21.8; HRMS (ESI, m/z): calcd. for $C_{23}H_{22}N_3O_4S$ $(M+H)^+$: 436.1331, found: 436.1329.



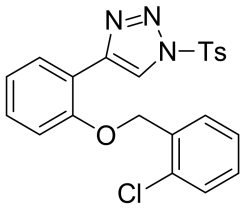
4-(2-((4-(*tert*-Butyl)benzyl)oxy)phenyl)-1-tosyl-1*H*-1,2,3-triazole (1j)

White solid; m.p.: 139-141 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (s, 1H), 8.30 (dd, *J* = 6.4, 1.2 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.30-7.33 (m, 3H), 7.00-7.08 (m, 1H), 5.17 (s, 2H), 2.42 (s, 3H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.3, 151.6, 146.9, 142.9, 133.6, 133.4, 130.3, 129.8, 128.4, 128.0, 127.6, 125.7, 122.5, 121.2, 118.1, 112.2, 70.5, 34.7, 31.4, 21.8; HRMS (ESI, m/z): calcd. for $C_{26}H_{28}N_3O_3S$ $(M+H)^+$: 462.1851, found: 462.1853.



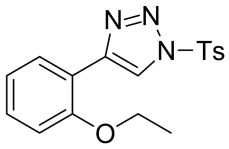
4-(2-((2-Fluorobenzyl)oxy)phenyl)-1-tosyl-1*H*-1,2,3-triazole (1k)

White solid; m.p.: 107-108 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (s, 1H), 8.30 (dd, J = 7.6, 1.2 Hz, 1H), 7.91 (d, J = 8.4 Hz, 2H), 7.40-7.45 (m, 2H), 7.32-7.34 (m, 3H), 7.18-7.25 (m, 2H), 7.05-7.09 (m, 2H), 5.27 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8, 146.9, 142.8, 133.4, 130.5, 130.4, 130.3, 130.1, 130.0, 129.8, 128.5, 128.2, 124.5, 124.4, 123.4, 122.4, 121.6, 118.3, 115.8, 115.6, 112.1, 64.5, 64.5, 21.8; HRMS (ESI, m/z): calcd. for $C_{22}H_{19}FN_3O_3S$ $(M+H)^+$: 424.1131, found: 424.1128.



4-(2-((2-Chlorobenzyl)oxy)phenyl)-1-tosyl-1*H*-1,2,3-triazole (1l)

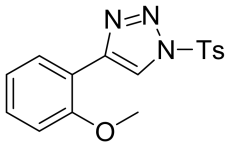
White solid; m.p.: 136-137 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (s, 1H), 8.30 (d, J = 7.6 Hz, 1H), 7.92 (d, J = 8.4 Hz, 2H), 7.45-7.50 (m, 2H), 7.25-7.34 (m, 5H), 7.08 (t, J = 7.6 Hz, 1H), 7.01 (d, J = 8.4 Hz, 1H), 5.32 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8, 147.0, 142.8, 134.0, 133.4, 133.2, 130.4, 129.9, 129.8, 129.7, 129.5, 128.5, 128.3, 127.2, 122.4, 121.6, 118.2, 112.2, 67.9, 21.8; HRMS (ESI, m/z): calcd. for $C_{22}H_{19}ClN_3O_3S$ $(M+H)^+$: 440.0836, found: 440.0831.



4-(2-Ethoxyphenyl)-1-tosyl-1*H*-1,2,3-triazole (1m)

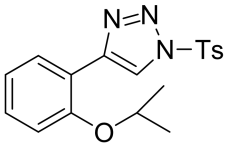
White solid; m.p.: 136-137 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (s, 1H), 8.31 (d, J = 7.6 Hz, 1H), 8.01 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.31 (t, J = 7.6 Hz, 1H), 7.04 7.31 (t, J = 7.6 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 4.18 (q, J = 6.8 Hz, 2H), 2.43 (s, 3H), 1.55 (t, J = 6.8 Hz, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.7, 140.9, 132.5, 129.1, 129.0, 128.4, 126.0, 124.8, 124.7, 121.4, 112.1, 111.8, 64.5, 21.4, 14.7;

HRMS (ESI, m/z): calcd. for $C_{17}H_{18}N_3O_3S$ $(M+H)^+$: 344.1069, found: 344.1068.



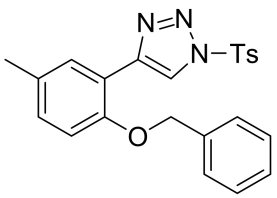
4-(2-Methoxyphenyl)-1-tosyl-1*H*-1,2,3-triazole (1n)

White solid; m.p.: 117-119 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (s, 1H), 8.31 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.33 (m, 1H), 7.06 (m, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 3.97 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.9, 147.1, 142.8, 133.4, 130.4, 129.9, 128.6, 127.9, 122.0, 120.9, 117.7, 110.8, 55.5, 21.8; HRMS (ESI, m/z): calcd. for $C_{16}H_{16}N_3O_3S$ $(M+H)^+$: 330.0912, found: 330.0907.



4-(2-Isopropoxyphenyl)-1-tosyl-1*H*-1,2,3-triazole (1o)

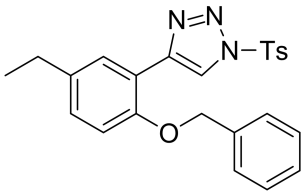
White solid; m.p.: 120-121 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (s, 1H), 8.29-8.31 (m, 1H), 8.01 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 8.27-8.32 (m, 1H), 7.03-7.04 (m, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 4.68-4.74 (m, 1H), 2.43 (s, 3H), 1.44 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.3, 147.0, 143.1, 133.5, 130.4, 129.7, 128.6, 128.2, 122.1, 120.7, 118.5, 112.9, 70.7, 22.3, 21.8; HRMS (ESI, m/z): calcd. for $C_{18}H_{20}N_3O_3S$ $(M+H)^+$: 358.1225, found: 358.1230.



4-(2-(Benzyloxy)-5-methylphenyl)-1-tosyl-1*H*-1,2,3-triazole (1p)

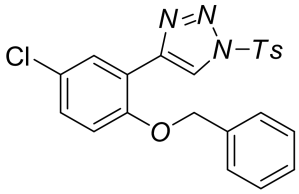
White solid; m.p.: 136-138 ºC;^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.48 (s, 1H), 8.12 (s, 1H), 7.88 (d, *J* = 7.6 Hz, 2H), 7.43-7.48 (m, 5H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.08-7.11

(m, 1H), 6.91-6.94 (m, 1H), 5.16 (s, 2H), 2.42 (s, 3H), 2.33 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.2, 146.9, 143.0, 136.6, 133.5, 130.6, 130.3, 128.8, 128.5, 127.6, 122.4, 117.7, 112.2, 70.8, 21.8, 20.5; HRMS (ESI, m/z): calcd. for $C_{23}H_{22}N_3O_3S$ $(M+H)^+$: 420.1382, found: 420.1378.



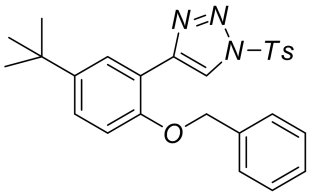
4-(2-(Benzyloxy)-5-ethylphenyl)-1-tosyl-1*H*-1,2,3-triazole (1q)

White solid; m.p.: 123-124 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.48 (s, 1H), 8.15 (s, 1H), 7.87 (d, J = 8.4 Hz, 2H), 7.41-7.45 (m, 5H), 7.33 (d, J = 8.4 Hz, 2H), 7.12-7.15 (m, 1H), 6.93-6.96 (m, 1H), 5.16 (s, 2H), 2.63 (q, J = 7.6 Hz, 2H), 2.41 (s, 3H), 1.22 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.3, 146.9, 143.1, 137.2, 136.6, 133.5, 130.3, 129.2, 128.8, 128.5, 128.4, 127.7, 127.4, 117.8, 112.2, 70.8, 28.1, 21.8, 15.8; HRMS (ESI, m/z): calcd. for $C_{24}H_{24}N_3O_3S$ $(M+H)^+$: 434.1538, found: 434.1546.



4-(2-(Benzyloxy)-5-chlorophenyl)-1-tosyl-1*H*-1,2,3-triazole (1r)

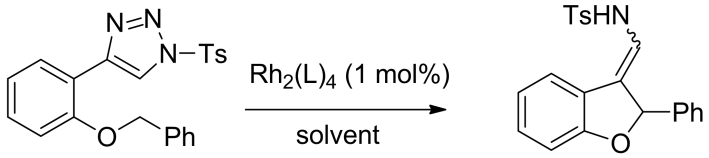
White solid; m.p.: 142-144 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (s, 1H), 8.29 (d, J = 2.8 Hz, 1H), 7.88 (d, J = 8.4 Hz, 2H), 7.41-7.45 (m, 5H), 7.33 ((d, J = 8.0 Hz, 3H), 7.23-7.25 (m, 1H), 6.94 (d, J = 8.4 Hz, 1H), 5.18 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.6, 147.1, 141.7, 135.9, 133.3, 130.9, 129.4, 128.9, 128.6, 128.5, 127.8, 127.6, 126.6, 122.5, 119.7, 113.5, 71.1, 21.8; HRMS (ESI, m/z): calcd. for $C_{22}H_{19}ClN_3O_3S$ $(M+H)^+$: 440.0836, found: 440.0835.



4-(2-(Benzyloxy)-5-(*tert*-butyl)phenyl)-1-tosyl-1*H*-1,2,3-triazole (1s)

White solid; m.p.: 109-110 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (s, 1H), 8.35 (d, J = 2.4 Hz, 1H), 7.88 (d, J = 8.4 Hz, 2H), 7.41-7.46 (m, 5H), 7.25-7.33 (m, 3H), 6.96 (d, J = 8.4 Hz, 1H), 5.18 (s, 2H), 2.42 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.1, 146.9, 144.1, 143.2, 136.6, 133.5, 130.3, 128.8, 128.4, 127.6, 126.7, 125.1, 122.4, 117.4, 111.8, 70.7, 34.3, 31.5, 21.8; HRMS (ESI, m/z): calcd. for $C_{26}H_{28}N_3O_3S$ $(M+H)^+$: 462.1851, found: 462.1854.

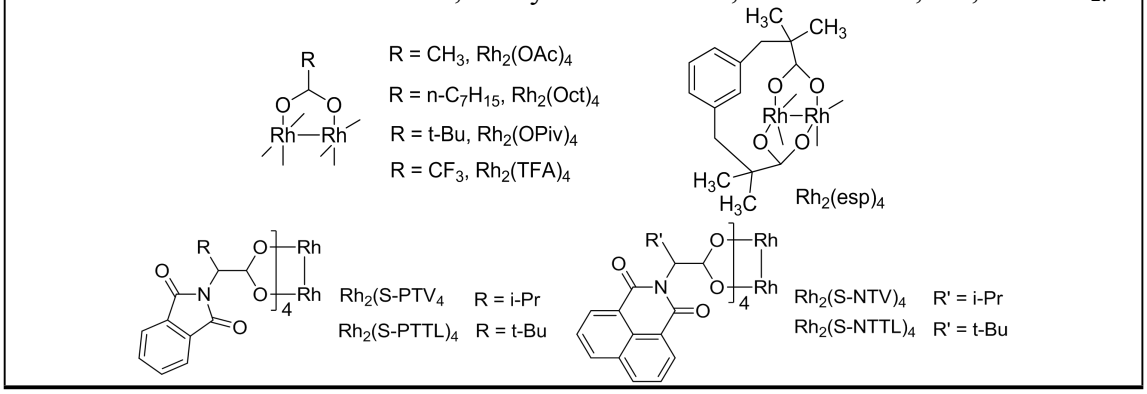
2. Optimization of Reaction Conditions



1a **2a**

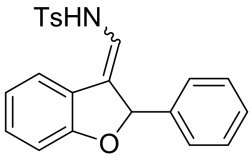
Entry	Cat. (1 mol%)	Solvent	T (ºC)	Yield (%)
1	$Rh_2(OAc)_4$	CH_2Cl_2	90	30
2	$Rh_2(Oct)_4$	CH_2Cl_2	90	51
3	$Rh_2(OPiv)_4$	CH_2Cl_2	90	57
4	$Rh_2(TFA)_4$	CH_2Cl_2	90	0
5	$Rh_2(esp)_4$	CH_2Cl_2	90	83
6	**Rh_2(S-PTV)$_4$**	**CH_2Cl_2**	**90**	**91**
7	Rh_2(S-PTTL)$_4$	CH_2Cl_2	90	82
8	Rh_2(S-NTV)$_4$	CH_2Cl_2	90	87
9	Rh_2(S-NTTL)$_4$	CH_2Cl_2	90	85
10	Rh_2(S-PTV)$_4$	CH_2Cl_2	80	<5
11	Rh_2(S-PTV)$_4$	CH_2Cl_2	100	90
12	Rh_2(S-PTV)$_4$	$CHCl_3$	90	90
13	Rh_2(S-PTV)$_4$	DCE	90	81
14	Rh_2(S-PTV)$_4$	toluene	90	73

Reaction conditions: **1a** 0.5 mmol, catalyst 0.005 mmol, solvent 4 mL, 2 h, under N_2.



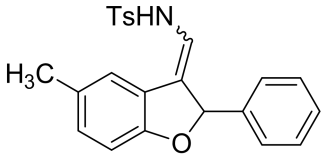
3. General procedure for the synthesis of 2

To a reaction tube with screw stopper were added triazoles **1** (0.5 mmol, 1.0 equiv) and Rh_2(*S*-PTV)$_4$ (0.005 mmol, 0.01 equiv). The tube was evacuated and backfilled with N_2 for 3 times. DCM (4.0 mL) was added to this tube via a syringe under N_2. The reaction mixture was sealed and stirred for 2-4 hours at 90 ºC. The crude product was purified by silica gel chromatography (hexane: ethyl acetate) to afford the desired product **2** as a white solid.



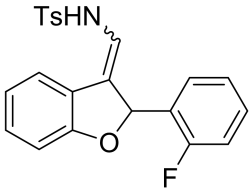
***N*-((2-Phenylbenzofuran-3(2*H*)-ylidene)methyl)-4-methylbenzenesulfonamide (2a)**

White solid; m.p.: 147-149 ºC ; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, J = 7.6 Hz, 0.56H), 7.43 (d, J = 7.6 Hz, 1.44H), 7.21-7.36 (m, 7H), 7.14 (t, J = 7.6 Hz, 1H), 6.91 (t, J = 7.6 Hz, 1H), 6.85 (d, J = 8.0 Hz, 0.28H), 6.77 (d, J = 8.0 Hz, 0.72H), 6.77 (dd, J = 9.2, 1.6 Hz, 0.72H), 6.51 (d, J = 10.4 Hz, 0.28 H), 6.05 (s, 0.28H), 5.95 (s, 0.72H), 5.91 (d, J = 10.4 Hz, 0.28H), 6.66 (d, J = 11.2 Hz, 0.28H), 2,42 (s, 2.16H), 2.40 (s, 0.84H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.8, 160.8, 143.9, 136.7, 136.6, 130.2, 129.9, 129.8, 129.4, 128.9, 128.8, 127.7, 127.3, 126.7, 126.5, 124.8, 123.4, 122.4, 121.2, 119.2, 115.9, 113.2, 110.5, 110.2, 86.6, 85.1, 21.6; HRMS (GC-TOF) for $C_{22}H_{19}NO_3S$: calcd. 377.1086, Found 377.1085.



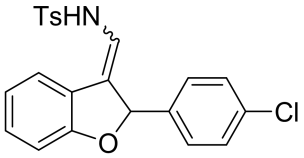
***N*-((5-Methyl-2-phenylbenzofuran-3(2*H*)-ylidene)methyl)-4-methylbenzenesulfonamide (2b)**

White solid; m.p.: 143-145 ºC ; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, J = 8.4 Hz, 1H), 7.32-7.43 (m, 3H), 7.24-7.32 (m, 5H), 7.09-7.12 (m, 1H), 7.04 (s, 0.61 H), 6.99 (d, J = 8.0 Hz, 0.39 H), 6.99 (d, J = 8.4 Hz, 0.61H), 6.65 (d, J = 7.6 Hz, 1H), 6.54 (d, J = 10.4 Hz, 0.39H), 6.02 (s, 0.39H), 5.92 (d, J = 2.4 Hz, 0.61H), 5.88 (d, J = 10.4 Hz, 0.39H), 5.65 (d, J = 11.2 Hz, 0.39H), 2.42 (s, 1.83H), 2.40 (s, 1.17H), 2.31 (s, 1.83H), 2.30 (s, 1.17H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 158.9, 144.1, 143.9, 140.2, 136.9, 130.8 ,130.6, 130.1, 129.9, 129.8, 129.7, 129.5, 128.9, 128.8, 127.7, 127.3, 126.7, 126.5, 124.6, 123.7, 122.7, 119.5, 115.6, 112.9, 110.1, 109.7, 86.7, 85.2, 21.6, 20.9; HRMS (GC-TOF) for $C_{23}H_{21}NO_3S$: calcd. 391.1242, Found 391.1241.



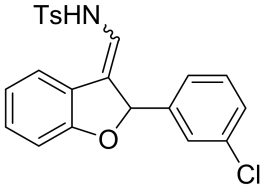
***N*-((2-(2-Fluorophenyl)benzofuran-3(2*H*)-ylidene)methyl)-4-methylbenzenesulfonamide (2c)**

White solid; m.p.: 219-221 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, J = 7.6 Hz, 0.36 H), 7.66 (t, J = 8.0 Hz, 0.36 H), 7.53 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 7.6 Hz, 0.18 H), 7.30-7.32 (m, 2.36 H), 7.21 (d, J = 8.0 Hz, 2H), 7.13-7.18 (m, 1.54H), 7.03-7.11 (m, 2.18H), 6.90-7.00 (m, 1.54H), 6,81 (d, J = 8.0 Hz, 1H), 6.70-6.73 (m, 1H), 6.65 (d, J = 8.0 Hz, 0.18H), 6.31(d, J = 2.0 Hz, 1H), 5.88 (d, J = 10.4 Hz, 1H), 5.23 (d, J = 10.4 Hz, 0.18H), 2.45 (s, 0.54H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.5, 160.9, 159.0, 143.9, 136.7, 131.1, 131.0, 129.9, 129.5, 128.4,,128.3, 127.4, 126.5, 125.1, 125.0, 124.4, 124.1, 123.9, 122.4, 121.3, 119.4, 116.1, 115.9, 113.2, 110.1, 77.9, 21.6; HRMS (GC-TOF) for $C_{22}H_{18}FNO_3S$: calcd. 395.0991, Found 395.0989.



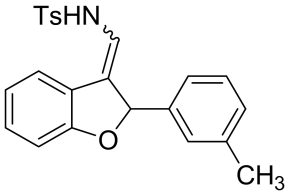
***N*-((2-(4-Chlorophenyl)benzofuran-3(2*H*)-ylidene)methyl)-4-methylbenzenesulfonamide (2d)**

White solid; m.p.: 197-199 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 7.6 Hz, 2H), 7.32 (d, J = 7.6 Hz, 1H), 7.23-7.25 (m, 3H), 7.11-7.16 (m, 4H), 6.92 (t, J = 7.6 Hz, 1H), 6.73-6.77 (m, 2H), 5.95 (s, 1H), 5.76 (d, J = 10.4 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.7, 144.2, 136.5, 135.6, 135.4, 129.9, 129.6, 129.5, 129.0, 126.4, 124.6, 123.4, 121.3, 119.3, 113.4, 110.2, 84.1, 21.6; HRMS (GC-TOF) for $C_{22}H_{18}ClNO_3S$: calcd. 411.0696, Found 411.0692.



***N*-((2-(3-Chlorophenyl)benzofuran-3(2*H*)-ylidene)methyl)-4-methylbenzenesulfonamide (2e)**

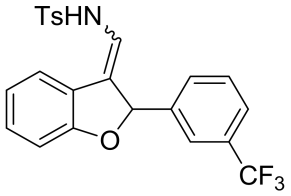
White solid; m.p.: 140-142 ºC ; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, J = 8.4 Hz, 2H), 7.28-7.32 (m, 2H), 7.22-7.27 (m, 4H), 7.13-7.26 (m, 2H), 6.76 (t, J = 8.4 Hz, 1H), 6.71-6.77 (m, 2H), 5.94 (s, 1H), 5.77-5.85 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.6, 144.2, 139.1, 139.0, 136.4, 135.5, 130.5, 130.0, 129.9, 129.6, 127.6, 126.3, 125.9, 125.8, 124.6, 124.5, 123.0, 122.9, 121.4, 119.3, 113.5, 110.2, 84.1, 21.6; HRMS (GC-TOF) for $C_{22}H_{18}ClNO_3S$: calcd. 411.0696, Found 411.0699.



***N*-((2-(3-Methylphenyl)benzofuran-3(2*H*)-ylidene)methyl)-4-**

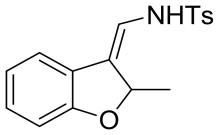
methylbenzenesulfonamide (2f)

White solid; m.p.: 129-131 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 7.6 Hz, 1H), 7.11-7.21 (m, 5H), 7.04-7.07 (m, 2H), 6.91 (d, J = 7.6 Hz, 1H), 6.76 (d, J = 8.0 Hz, 1H), 6.68 (dd, J = 11.2, 2.8 Hz, 1H), 5.90 (d, J = 2.8 Hz, 1H), 5.78 (d, J = 11.2 Hz, 1H), 2.40 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.9, 143.9, 139.5, 136.8, 136.7, 130.6, 129.8, 129.4, 129.3, 128.3, 126.5, 124.8, 124.7, 123.5, 119.2, 113.2, 110.2, 85.2, 21.6, 21.3; HRMS (GC-TOF) for $C_{23}H_{21}NO_3S$: calcd. 391.1242, Found 391.1245.



***N*-((2-(3-Trifluorophenyl)benzofuran-3(2*H*)-ylidene)methyl)-4-methylbenzenesulfonamide (2g)**

White solid; m.p.: 158-159 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, J = 7.6 Hz, 1H), 7.49 (s, 1H), 7.41-7.45 (m, 3H), 7.32-7.37 (m, 2H), 7.14-7.20 (m, 3H), 6.92-6.96 (m, 1H), 6.73-6.78 (m, 2H), 6.04 (d, J = 2.4 Hz, 1H), 5.91 (d, J = 11.2 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.6, 144.2, 138.1, 136.4, 131.8, 131.5, 131.0, 129.9, 129.7, 129.6, 126.3, 124.7, 124.5, 124.4, 122.9, 121.4, 119.3, 113.6, 110.3, 84.0, 21.5; HRMS (GC-TOF) for $C_{23}H_{18}F_3NO_3S$: calcd. 445.0959, Found 445.0963.



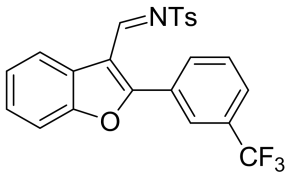
***N*-((2-Methylbenzofuran-3(2*H*)-ylidene)methyl)-4-methyl-benzenesulfonamide (2h)**

White solid; m.p.: 153-155 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, J = 7.6 Hz, 1H), 7.32 (d, J = 7.6 Hz, 1H), 7.22-7.25 (m, 1H), 7.10 (t, J = 7.6 Hz, 1H), 6.94-6.97 (m, 1H), 6.82 (t, J = 7.6 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 6.54 (d, J = 9.6 Hz, 1H),

5.30-5.34 (m, 1H), 2.41 (s, 3H), 1.27 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.7, 144.3, 136.6, 130.0, 129.4, 127.0, 126.7, 124.2, 120.7, 119.6, 111.1, 110.3, 79.5, 21.6, 19.6; HRMS (GC-TOF) for $C_{17}H_{17}NO_3S$: calcd. 315.0929, Found 315.0927.

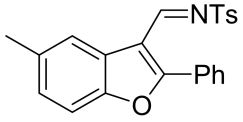
4. General procedure for the synthesis of 3

To a reaction tube with screw stopper were added triazoles **1** (0.5 mmol, 1.0 equiv) and Rh_2(S-PTV)$_4$ (0.005 mmol, 0.01 equiv). The tube was evacuated and backfilled with N_2 for 3 times. DCM (4.0 mL) was added to this tube via a syringe under N_2. The reaction mixture was sealed and stirred for 2-4 hours at 90 ºC. After cooling to 40 ºC, Pd/C (5%) was added. The mixture was stirred at 45 ºC under N_2 or air (1 atm) for another 2h. Silica gel was added to the reaction mixture and the solvent was removed under reduced pressure, the crude product was purified by silica gel chromatography (hexane: ethyl acetate) to afford the desired product **3** as a white solid.



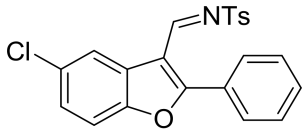
4-Methyl-*N*-((2-(3-trifluorophenyl)benzofuran-3-yl)methylene)benzenesulfonamide (3b)

White solid; m.p.: 145-147 ºC ;^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.31 (s, 1H), 8.30 (d, J = 7.6 Hz, 1H), 8.06 (s, 1H), 7.91-7.96 (m, 3H), 7.85 (d, J = 7.6 Hz, 1H), 7.74 (t, J = 7.6 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.34-7.41 (m, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =163.8, 162.5, 154.6, 144.5, 135.4, 132.2, 130.0, 129.8, 129.1, 128.0, 127.9, 127.8, 126.9, 125.7, 125.6, 125.2, 124.9, 123.8, 114.1, 111.4, 21.7; HRMS (GC-TOF) for $C_{23}H_{16}F_3NO_3S$: calcd. 443.0803, Found 443.0801.



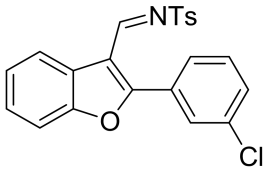
4-Methyl-*N*-((5-methyl-2-phenylbenzofuran-3-yl)methylene)benzenesulfonate (3c)

White solid; m.p.: 190-192 ºC ; ^{1}H NMR (400 MHz, *d6*-DMSO): δ = 9.07 (s, 1H), 7.87-7.91 (m, 5H), 7.66-7.68 (m, 4H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 1H), 2.44 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =163.8, 153.0, 144.2, 155.9, 134.8, 129.8, 129.4, 129.1, 128.4, 127.9, 127.7, 125.1, 123.4, 113.4, 110.7, 21,6, 21.5; HRMS (GC-TOF) for $C_{23}H_{19}NO_3S$: calcd. 389.1086, Found 389.1085.



4-Methyl-*N*-((5-chloro-2-phenylbenzofuran-3-yl)methylene)benzenesulfonate (3d)

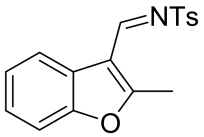
White solid; m.p.: 246-148 ºC ; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.31 (s, 1H), 8.26 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 5.6 Hz, 2H), 7.59-7.61 (m, 3H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.35-7.37 (m, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =167.3, 163.1, 152.8, 144.5, 135.6, 131.8, 130.7, 129.5, 129.1, 127.9, 127.8, 126.7, 126.5, 123.3, 112.3, 21.7; HRMS (GC-TOF) for $C_{22}H_{16}ClNO_3S$: calcd. 409.0539, Found 409.0534.



4-Methyl-*N*-((2-(3-chlorophenyl)benzofuran-3-yl)methylene)benzenesulfonamide (3e)

White solid; m.p.: 142-144 ºC ; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.31 (s, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.79 (s, 1H), 7.64 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.52-7.57 (m, 3H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.39-7.45 (m, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =164.2, 162.7, 154.5, 144.5, 135.5, 135.4, 131.4, 130.7, 129.9, 128.7, 128.0, 127.3,126.8, 125.8, 125.1, 125.0, 123.7, 113.8, 111.3, 21.7; HRMS (GC-

TOF) for $C_{22}H_{16}ClNO_3S$: calcd. 409.0539, Found 409.0533.

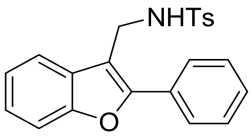


4-Methyl-*N*-((2-methylbenzofuran-3-yl)methylene)benzenesulfonate (3f)

White solid; m.p.: 159-161 ºC ; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.22 (s, 1H), 8.12 (d, J = 6.8 Hz, 1H), 7.91 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.4 Hz, 1H), 7.30-7.35 (m, 4H), 2.74 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =168.1, 161.8, 154.4, 144.2, 136.1, 129.7, 127.7, 125.7, 124.6, 124.5, 122.6, 113.7, 110.8, 21.6, 13.4; HRMS (GC-TOF) for $C_{17}H_{15}NO_3S$: calcd. 313.0773, Found 313.0775.

5. General procedure for the synthesis of 4

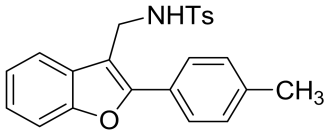
To a reaction tube with screw stopper were added triazoles **1** (0.5 mmol, 1.0 equiv) and Rh_2(S-PTV)$_4$ (0.005 mmol, 0.01 equiv). The tube was evacuated and backfilled with N_2 for 3 times. DCM (4.0 mL) was added to this tube via a syringe under N_2. The reaction mixture was sealed and stirred for 2-4 hours at 90 ºC. After **1** was consumed completely and cooled to 40 ºC, Pd/C (5%) added. The mixture was stirred at 45 ºC under H_2 (1 atm) for another 3h. Silica gel was added to the reaction mixture and the solvent was removed under reduced pressure, the crude product was purified by silica gel chromatography (hexane: ethyl acetate) to afford the desired product **4** as a white solid.



***N*-((2-Phenylbenzofuran-3-yl)methyl)-4-methylbenzenesulfonamide (4a)**

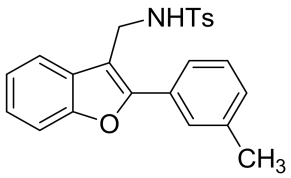
White solid; m.p.: 164-166 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, J = 8.4 Hz, 2H), 7.60-7.63 (m, 2H), 7.39-7.47 (m, 4H), 7.26-7.34 (m, 4H), 7.20 (t, J = 7.2 Hz,

1H), 4.56 (br, 1H), 4.43 (d, *J* = 5.6 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.9, 153.4, 143.7, 136.3, 129.7, 129.1, 128.9, 128.7,127.3, 127.2, 124.9, 123.1, 119.4, 111.2, 110.1, 37.7, 21.6; HRMS (GC-TOF) for $C_{22}H_{19}NO_3S$: calcd. 377.1086, Found 377.1089.



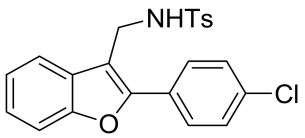
***N*-((2-*p*-Tolyl)benzofuran-3-yl)methyl)-4-methylbenzenesulfonamide (4b)**

White solid; m.p.: 175-177 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 7.76 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.29-7.31 (m, 4H), 7.17-7.22 (m, 3H), 4.51 (br, 1H), 4.42 (d, *J* = 5.6 Hz, 2H), 2.46 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.8, 143.6, 139.3, 136.4, 129.7, 129.6, 129.5, 129.4, 128.8, 127.4, 127.1, 124.7, 123.0, 119.2, 111.2, 109.4, 37.7, 21.6, 21.4; HRMS (GC-TOF) for $C_{23}H_{21}NO_3S$: calcd. 391.1242, Found 391.1244.



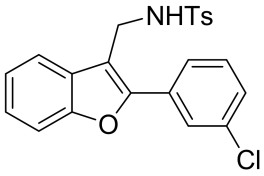
***N*-((2-(*m*-Tolyl)benzofuran-3-yl)methyl)-4-methylbenzenesulfonamide (4c)**

White solid; m.p.: 147-148 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H) , 7.25-7.30 (m, 3H), 7.16-7.21 (m, 2H), 4.66 (t, *J* = 5.2 Hz, 1H), 4.41 (d, *J* = 5.2, 2H), 2.43 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.9, 153.6, 143.6, 138.7, 136.4, 129.9, 129.7, 129.6, 128.8, 128.7, 127.8, 127.3, 124.9, 124.3, 123.0, 119.3, 111.2, 109.9, 37.8, 21.5, 21.4; HRMS (GC-TOF) for $C_{23}H_{21}NO_3S$: calcd. 391.1242, Found 391.1240.



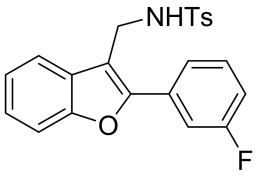
***N*-((2-(4-Chlorophenyl)benzofuran-3-yl)methyl)-4-methylbenzenesulfonamide (4d)**

White solid; m.p.: 146-147 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.29-7.39 (m, 6H), 7.18-7.22 (m, 1H), 4.57 (br, 1H), 4.39 (d, *J* = 5.2 Hz, 2H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.8, 152.2, 143.8, 136.2, 135.1, 129.7, 129.1, 128.6, 128.4, 128.1, 127.3, 125.2, 123.2, 119.3, 111.2, 110.4, 37.6, 21.6; HRMS (GC-TOF) for $C_{22}H_{18}ClNO_3S$: calcd. 411.0696, Found 411.0700.



***N*-((2-(3-Chlorophenyl)benzofuran-3-yl)methyl)-4-methylbenzenesulfonamide (4e)**

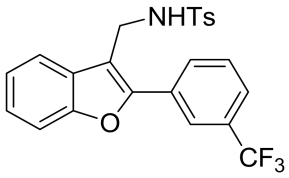
White solid; m.p.: 153-155 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72-7.77 (m, 2H), 7.67 (s, 1H), 7.60-7.62 (m, 1H), 7.45-7.51 (m, 2H), 7.29-7.40 (m, 5H), 7.19-7.23 (m, 1H), 4.57 (br, 1H), 4.43 (dd, *J* = 5.2, 3.2 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 153.9, 151.7, 143.8, 143.7, 136.3, 136.2, 135.0, 131.4, 130.1, 129.8, 129.7, 129.1, 128.9, 128.7, 128.4, 127.4, 127.3, 127.2, 127.1, 125.4, 125.2, 124.9, 123.3, 123.0, 119.5, 119.3, 111.3, 111.2, 111.1, 109.9, 37.7, 37.6, 21.6; HRMS (GC-TOF) for $C_{22}H_{18}ClNO_3S$: calcd. 411.0696, Found 411.0696.



***N*-((2-(3-Flurophenyl)benzofuran-3-yl)methyl)-4-methylbenzenesulfonamide (4f)**

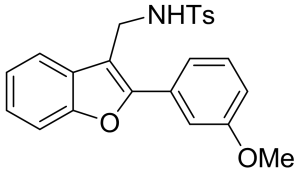
White solid; m.p.: 171-173 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.26-7.41 (m, 7H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 8.0 Hz, 1H), 4.59 (br, 1H), 4.42 (d, *J* = 5.2 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$): δ = 153.8, 151.9, 143.8, 136.2, 131.7, 130.5, 129.7, 128.5, 127.3, 125.4, 123.2, 122.8, 119.5, 116.0, 114.1, 111.1, 37.5, 21.6; HRMS (GC-TOF) for $C_{22}H_{18}FNO_3S$: calcd.395.0991, Found 395.0991.



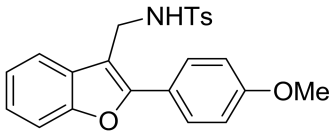
***N*-((2-(3-Trifluoromethyl)phenyl)benzofuran-3-yl)methyl)-4-methyl benzenesulfonamide (4g)**

White solid; m.p.: 169-171 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (s, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.20-7.25 (m, 3H), 4.76 (t, *J* = 5.2 Hz, 1H), 4.41 (d, *J* = 5.2 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.9, 151.5, 143.8, 136.1, 131.6, 131.3, 130.5, 130.2, 129.7, 129.4, 128.4, 127.2, 125.6, 125.5, 124.0, 123.9, 123.3, 119.6, 111.3, 37.6, 21.5; HRMS (GC-TOF) for $C_{23}H_{18}F_3NO_3S$: calcd. 445.0959, Found 445.0962.



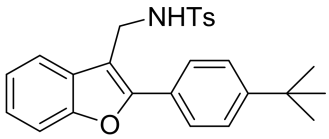
***N*-((2-(3-Methoxyphenyl)benzofuran-3-yl)methyl)-4-methylbenzenesulfonamide (4h)**

White solid; m.p.: 135-137 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.25-7.32 (m, 6H), 7.16-7.20 (m, 2H), 6.93-6.96 (m, 1H), 4.63 (t, *J* = 5.2 Hz, 1H), 4.42 (d, *J* = 5.2 Hz, 2H), 3.86 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.0, 153.8, 153.2, 143.7, 136.3, 130.9, 129.9, 129.7, 128.6, 127.3, 125.0, 123.1, 119.5, 119.3, 115.4, 112.2, 111.2, 110.2, 55.5, 37.7, 21.6; HRMS (GC-TOF) for $C_{23}H_{21}NO_4S$: calcd. 407.1191, Found 407.1194.



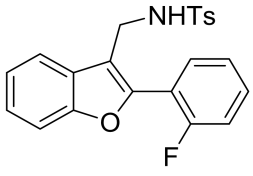
***N*-((2-(4-Methoxyphenyl)benzofuran-3-yl)methyl)-4-methylbenzenesulfonamide (4i)**

White solid; m.p.: 169-171 ºC; ^{1}H NMR (400 MHz, CDCl3): δ = 7.76 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.26-7.31 (m, 4H), 7.15-7.18 (m, 1H), 6.92 (d, *J* = 8.4 Hz, 2H), 4.54 (br, 1H), 4.39 (d, *J* = 5.2 Hz, 2H), 3.86 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl3): δ = 160.3, 153.7, 153.6, 143.7, 136.3, 129.7, 128.8, 128.6, 127.4, 124.5, 122.9, 122.3, 118.9, 114.4, 111.1, 108.5, 55.4, 37.8, 21.6; HRMS (GC-TOF) for $C_{23}H_{21}NO_4S$: calcd. 407.1191, Found 407.1193.



***N*-((2-(4-(*tert*-Butyl)phenyl)benzofuran-3-yl)methyl)-4-methyl Benzenesulfonamide (4j)**

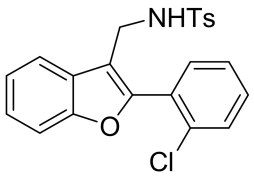
White solid; m.p.: 177-179 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.39-7.45 (m, 3H), 7.27-7.32 (m, 4H), 7.16-7.20 (m, 1H), 4.56 (br, 1H), 4.42 (d, *J* = 5.2 Hz, 1H), 2.46 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 153.8, 153.6, 152.4, 136.4, 129.7, 128.8, 127.4, 126.9, 126.8, 125.8, 124.7, 122.9, 119.2, 111.2, 109.5, 37.8, 34.8, 31.2, 21.6; HRMS (GC-TOF) for $C_{26}H_{27}NO_3S$: calcd. 433.1712, Found 433.1710.



***N*-((2-(2-Fluorophenyl)benzofuran-3-yl)methyl)-4-methylbenzenesulfonamide (4k)**

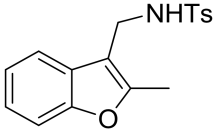
White solid; m.p.: 159-161 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 7.6 Hz, 2H), 7.56-7.60 (m, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.38-7.42 (m, 1H), 7.31-7.35 (m,

1H), 7.22-7.26 (m, 4H), 7.11 (t, *J* = 9.2 Hz, 1H), 4.66 (br, 1H), 4.27 (d, *J* = 6.0 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.7, 147.6, 143.5, 136.5, 131.2, 131.1, 130.7, 129.6, 128.1, 127.2, 125.2, 124.7, 123.2, 120.2, 116.3, 116.1, 113.3, 111.2, 37.8, 21.5; HRMS (GC-TOF) for $C_{22}H_{18}FNO_3S$: calcd. 395.0991, Found 395.0988.



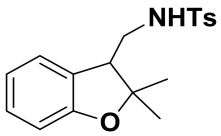
***N*-((2-(2-Chlorophenyl)benzofuran-3-yl)methyl)-4-methylbenzenesulfonamide (4l)**

White solid; m.p.: 181-183 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.45-7.48 (m, 2H), 7.40-7.42 (m, 2H), 7.32-7.37 (m, 2H), 7.23-7.27 (m, 3H), 4.60 (t, *J* = 5.2 Hz, 1H), 4.21 (d, *J* = 5.2 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 154.6, 150.7, 143.5, 136.4, 133.9, 132.2, 130.9, 130.2, 129.7, 128.7, 127.6, 127.2, 126.9, 125.2, 123.1, 120.3, 113.3, 111.4, 38.0, 21.5; HRMS (GC-TOF) for $C_{22}H_{18}ClNO_3S$: calcd. 411.0696, Found 411.0696.



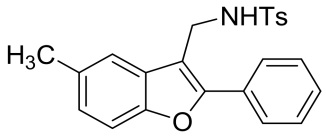
***N*-((2-Methylbenzofuran-3-yl)methyl)methyl)-4-methylbenzenesulfonamide (4m)**

White solid; m.p.: 105-107 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.23-7.27 (m, 3H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.12-7.15 (m, 1H), 4.54 (br, 1H), 4.19 (d, *J* = 5.2 Hz, 2H), 2.41 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.8, 153.2, 143.5, 136.7, 129.6, 127.8, 127.1, 123.1, 122.6, 118.6, 110.7, 109.7, 37.2, 21.5, 11.9; HRMS (GC-TOF) for $C_{17}H_{17}NO_3S$: calcd. 315.0929, Found 315.0926.



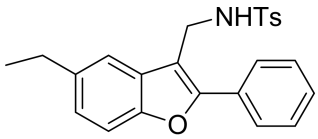
***N*-((2,2-dimethyl-2,3-dihydrobenzofuran-3-yl)methyl)-4-methyl benzenesulfonamide (4o)**

White solid; m.p.: 73-75 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.10-7.15 (m, 2H), 6.81 (t, *J* = 7.2 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 4.59 (br, 1H), 3.08-3.21 (m, 3H), 2.43 (s, 3H), 1.39 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.2, 143.7, 136.4, 129.8, 129.1, 127.9, 127.1, 124.9, 120.4, 110.1, 88.2, 50.1, 43.8, 28.9, 22.0, 21.5; HRMS (GC-TOF) for $C_{18}H_{21}NO_3S$: calcd. 331.1242, Found 331.1239.



***N*-((5-Methyl-2-phenylbenzofuran-3-yl)methyl)-4-methylbenzenesulfonamide (4p)**

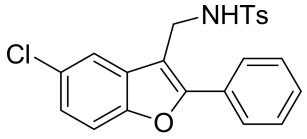
White solid; m.p.: 184-185 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.0 Hz, 2H), 7.58-7.60 (m, 2H), 7.37-7.39 (m, 3H), 7.29-7.32 (m, 3H), 7.06-7.08 (m, 1H), 6.93 (s, 1H), 4.57 (t, *J* = 4.8, 1H), 4.38 (d, *J* = 4.8, 1H), 2.46 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =153.6, 153.3, 143.7, 136.3, 132.6, 129.8, 129.7, 129.0, 128.9, 128.7, 127.4, 127.1, 126.2, 118.9, 110.7, 109.7, 37.7, 21.6, 21.3; HRMS (GC-TOF) for $C_{23}H_{21}NO_3S$: calcd. 391.1242, Found 391.1244.



***N*-((5-Ethyl-2-phenylbenzofuran-3-yl)methyl)-4-methylbenzenesulfonamide (4q)**

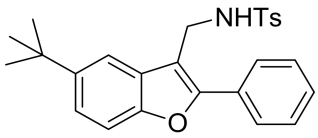
White solid; m.p.: 167-168 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.0 Hz, 2H), 7.59-7.61 (m, 2H), 7.29-7.39 (m, 6H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.96 (s, 1H), 4.56 (br, 1H), 4.40 (d, *J* = 5.2 Hz, 2H), 2.65 (q, *J* = 7.6 Hz, 2H), 2.46 (s, 3H), 2.65 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.6, 152.4, 143.7, 139.3, 136.3,

129.8, 129.7, 129.0, 128.9, 128.7, 127.4, 127.1, 125.2, 117.7, 110.8, 109.7, 37.7, 28.8, 21.6, 16.3; HRMS (GC-TOF) for $C_{24}H_{23}NO_3S$: calcd. 405.1399, Found 409.1400.



***N*-((5-Chloro-2-phenylbenzofuran-3-yl)methyl)-4-methylbenzenesulfonamide (4r)**

White solid; m.p.: 168-169 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 8.0 Hz, 2H), 7.60-7.62 (m, 2H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.39-7.41 (m, 3H), 7.27-7.32 (m, 3H), 7.19 (t, *J* = 7.6 Hz, 1H), 4.57 (br, 1H), 4.42 (d, *J* = 5.2 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.8, 153.4, 143.7, 136.3, 129.7, 129.1, 128.9, 128.7, 127.3, 127.2, 124.9, 123.0, 119.4, 111.2, 110.0, 37.7, 21.6; HRMS (GC-TOF) for $C_{22}H_{18}ClNO_3S$: calcd. 411.0696, Found 411.0694.

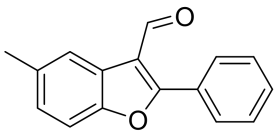


***N*-((5-(*tert*-Butyl)-2-phenylbenzofuran-3-yl)methyl)-4-methylbenzenesulfonamide (4s)**

White solid; m.p.: 132-134 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 8.0 Hz, 2H), 7.37-7.43 (m, 6H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.14 (s, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 5.86 (br, 1H), 5.00 (m, 2H), 2.65 (q, *J* = 7.6 Hz, 2H), 2.43 (s, 3H), 1.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.3, 146.2, 144.1, 136.3, 132.5, 130.1, 129.8, 128.9, 128.7, 128.3, 127.6, 127.4, 114.3, 114.1, 112.2, 70.9, 56.5, 34.2, 31.2, 21.8; HRMS (GC-TOF) for $C_{26}H_{27}NO_3S$: calcd. 433.1712, Found 433.1714.

6. Synthesis of 5 and 6

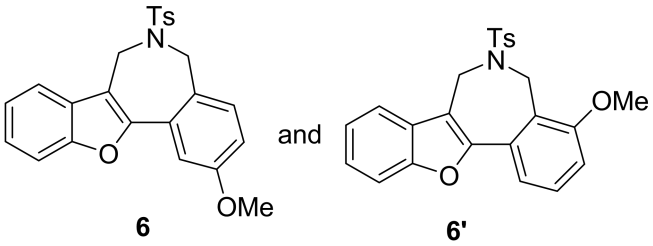
3c (195 mg, 0.5 mmol, 1.0 equiv) was dissolved in CH_3OH (10 mL), followed by addition of K_2CO_3 (276 mg, 2.0 mmol, 4.0 equiv) and H_2O (360 mg, 20.0 mmol, 40.0 equiv). The solution was stirred at room temperature until the total consumption of starting material. Crude product was collected as White solid (105 mg, 89%).



5-Methyl-2-phenylbenzofuran-3-carbaldehyde 5

White solid; m.p.: 88-89 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.33 (s, 1H), 8.08 (s, 1H), 7.83-7.86 (m, 2H), 7.55-7.58 (m, 3H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.8, 165.5, 152.5, 134.7, 131.0, 129.1, 128.8, 127.2, 125.4, 122.5, 117.4, 110.6, 21.4; HRMS (GC-TOF) for $C_{16}H_{12}O_2$: calcd. 236.0837, Found 236.0835.

4g (102 mg, 0.25 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (5 mL). Then aq HCHO (1.1equiv) and TFA (57 mg, 0.5 mmol, 2.0 equiv) were added. The solution was stirred at room temperature for overnight. Crude product was purified by chromatography to give **6** and **6'** as a white solid (92 mg, 88%).



6 **6'**

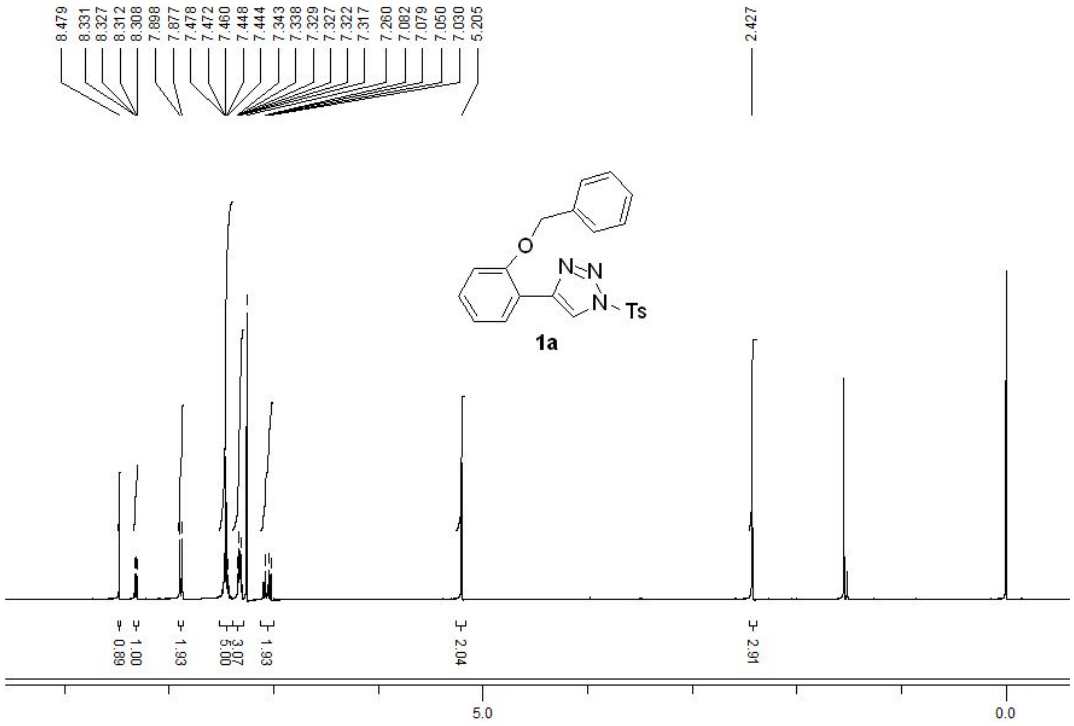
2/4-Metheoxy-6-tosyl-6,7-dihydro-5H-benzo[c]-benzofuro[2,3-e]azepine 6/6'

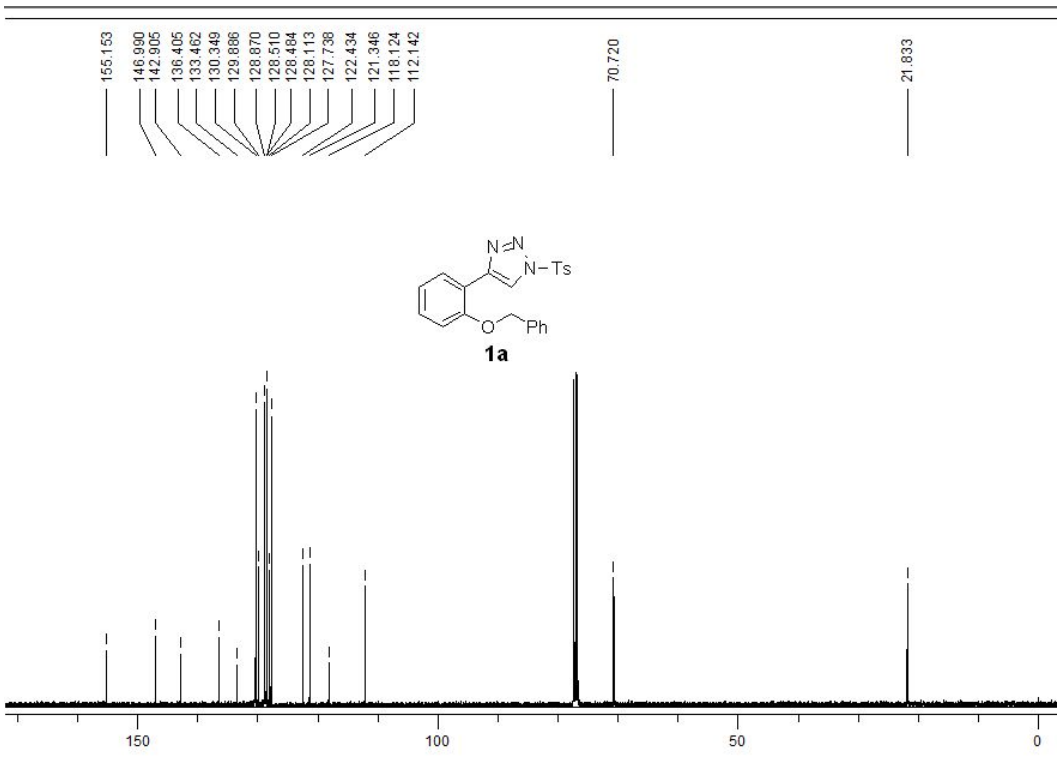
White solid; m.p.: 68-73 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 7.43-7.48 (m, 3H)，7.23-7.36 (m, 5H)，6.99 (d, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 4.91 (s, 2H), 4.73 (s, 1H), 4.56 (s, 1H), 3.89 (s, 1.36H), 3.86 (s, 1.64H), 2.29 (s, 1.36H), 2.26 (s, 1.64H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.5, 156.5, 153.7, 153.6, 149.0, 148.7, 142.9, 142.7, 136.5, 136.3, 130.9, 130.5, 130.4, 129.1, 129.0, 128.6, 128.0, 127.0, 126.8, 125.5, 125.4, 123.2, 123.0, 122.9, 118.9, 118.7, 114.7, 114.6, 114.0, 111.3, 111.2, 111.1, 111.0, 56.3, 55.5, 52.3, 46.3, 46.2, 43.7, 21.4, 21.3; HRMS (GC-TOF) for $C_{24}H_{21}NO_4S$: calcd. 419.1191, Found 419.1189.

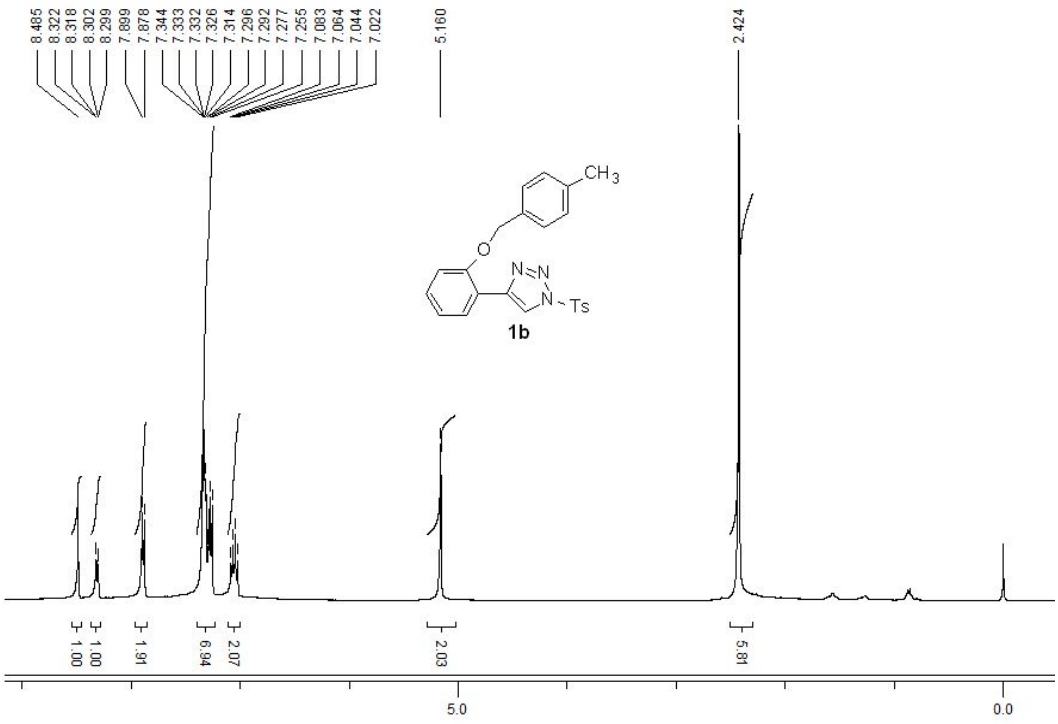
• III Reference:

(1) (a) S. Chuprakov, S. W. Kwok, L. Zhang, L. Lercher and V. V. Fokin, *J. Am. Chem. Soc.*, 2009, **131**, 18034; (b) T. Miura, T. Biyajima, T. Fujii and M. Murakami, *J. Am. Chem. Soc.*, 2012, **134**, 194.

IV. NMR Spectra



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7.292
7.277
7.255
7.083
7.064
7.044
7.022
5.160
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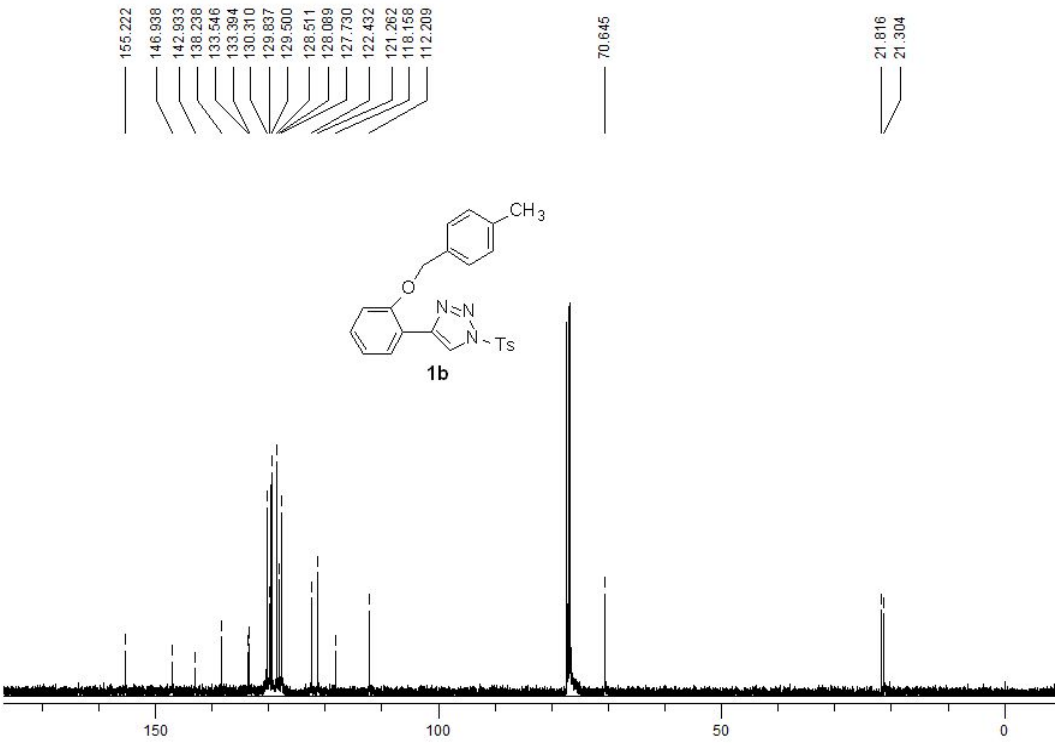
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121.262
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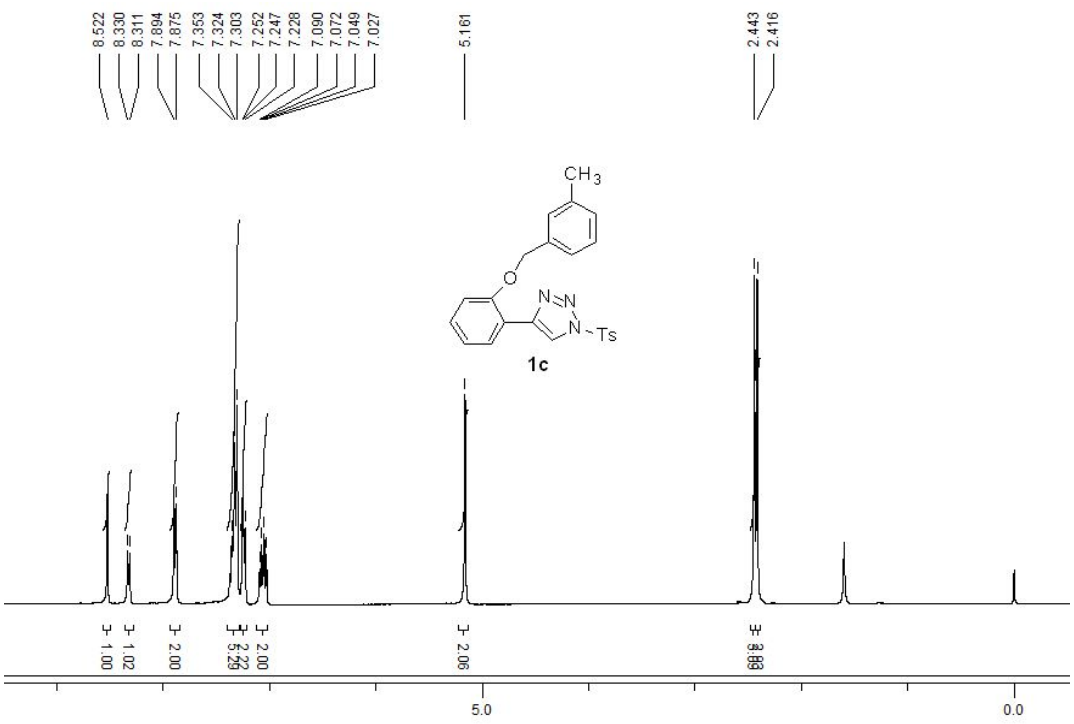
50
0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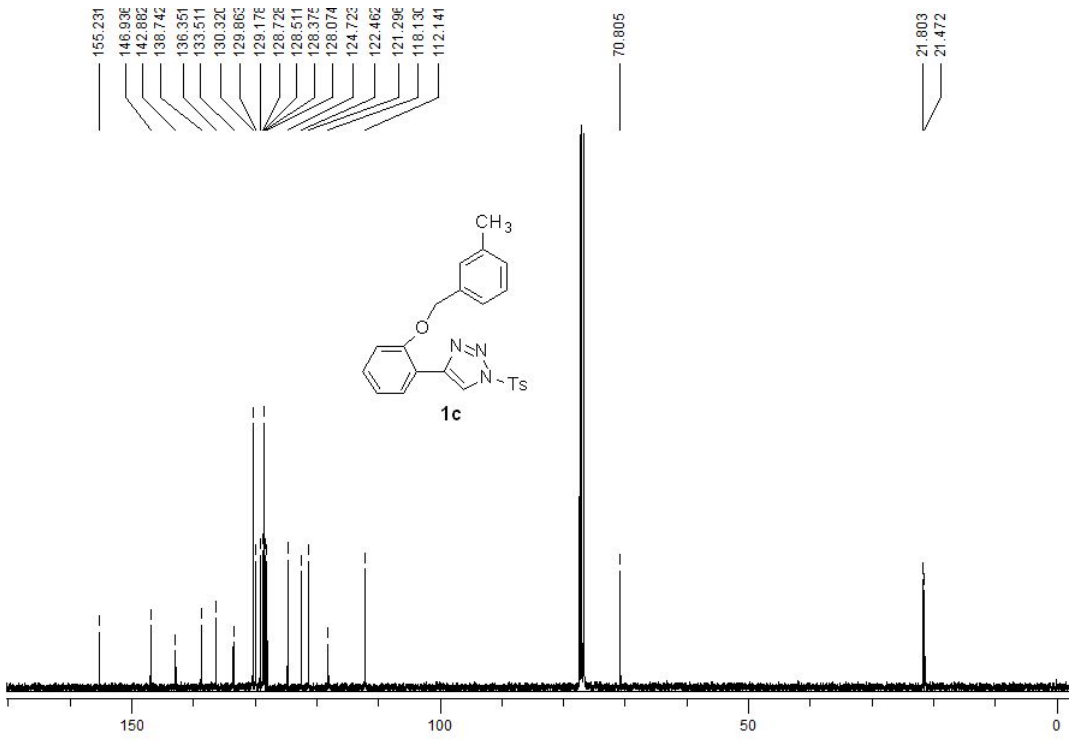
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1c
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50
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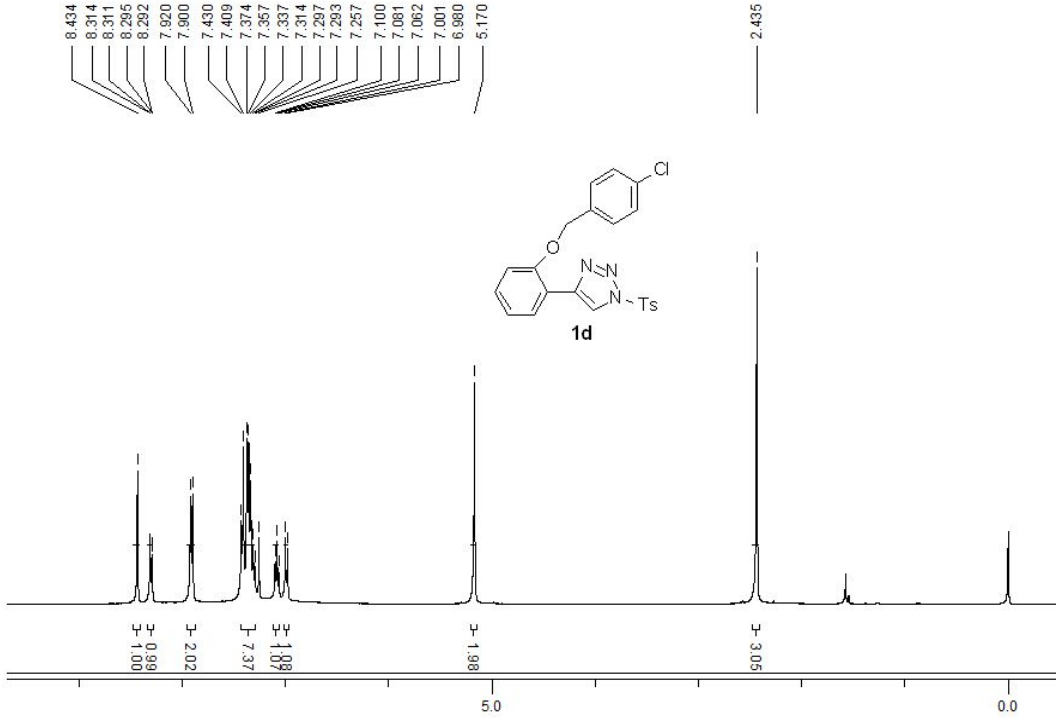
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7.081
7.062
7.001
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5.170
2.435
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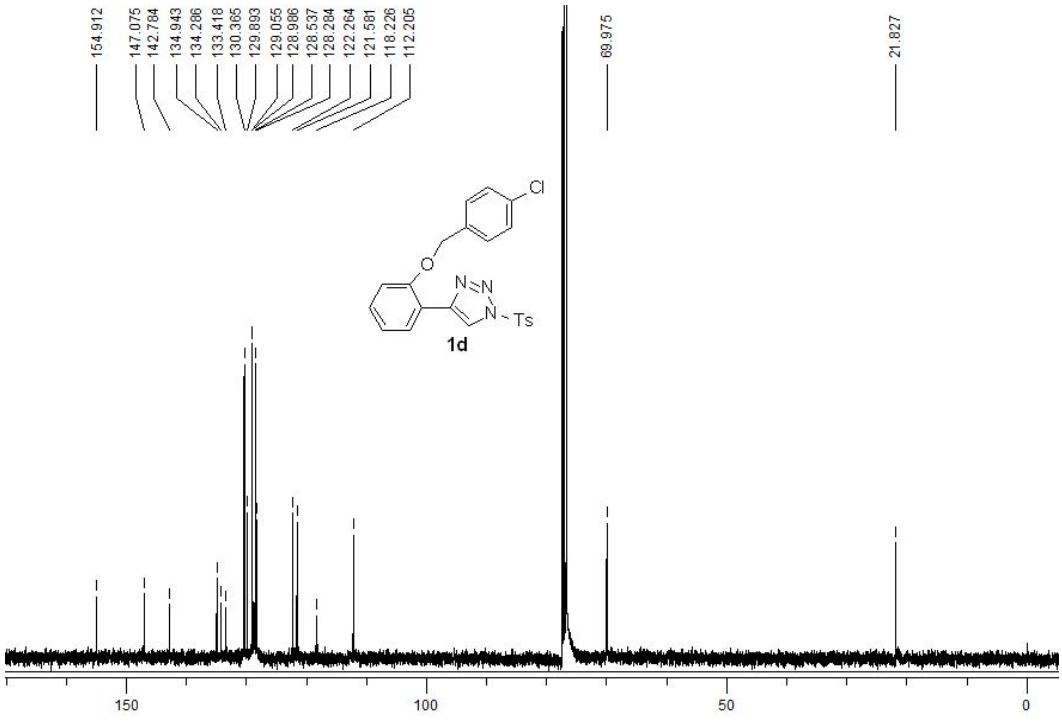
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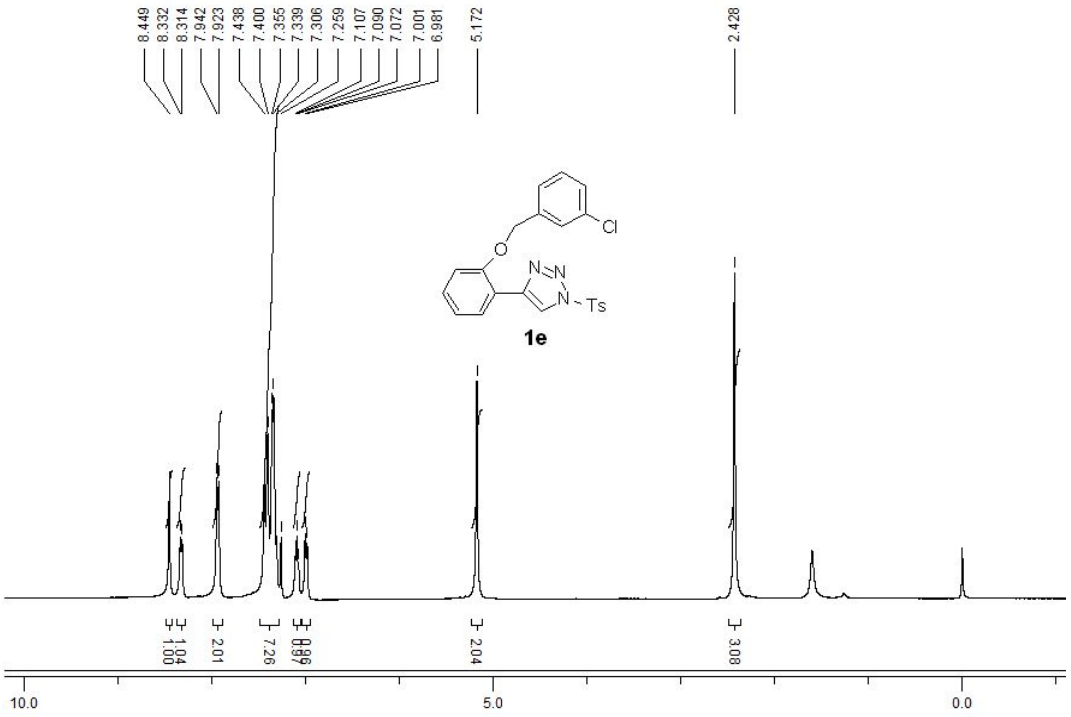
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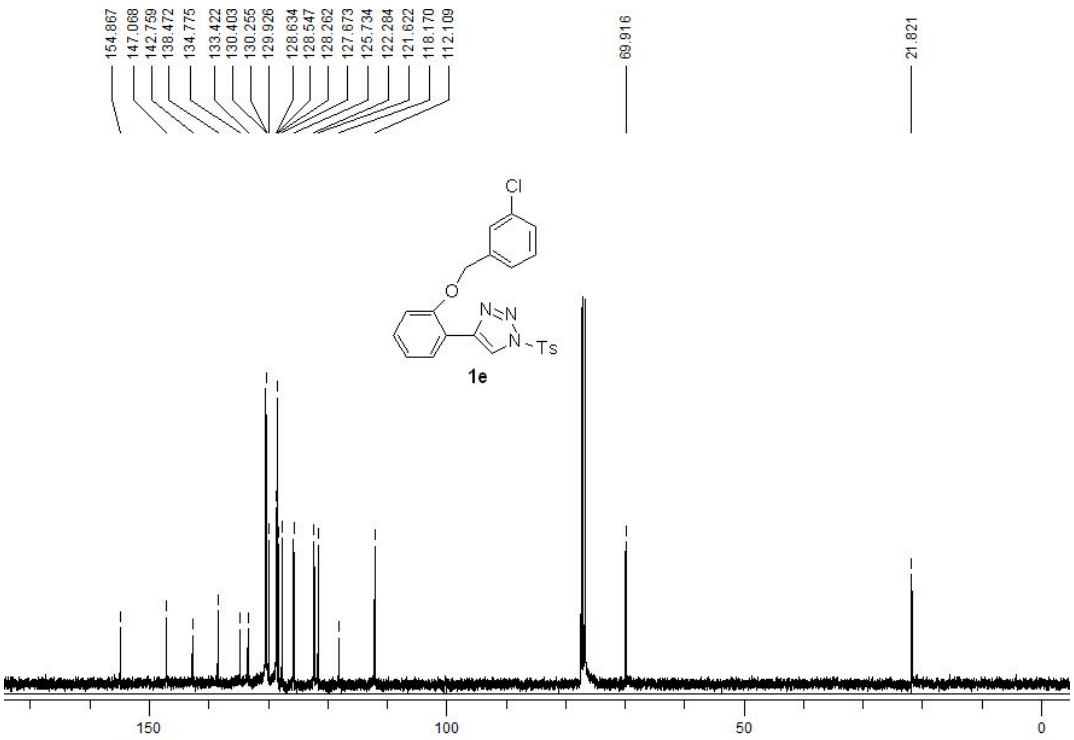
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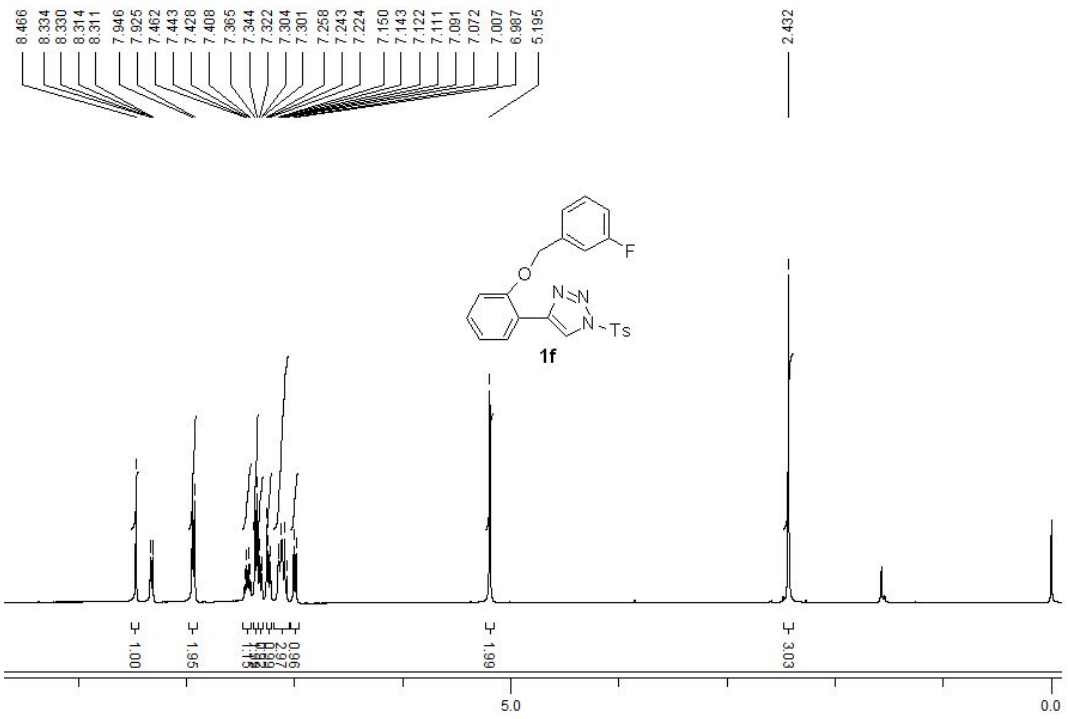
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7.258
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7.143
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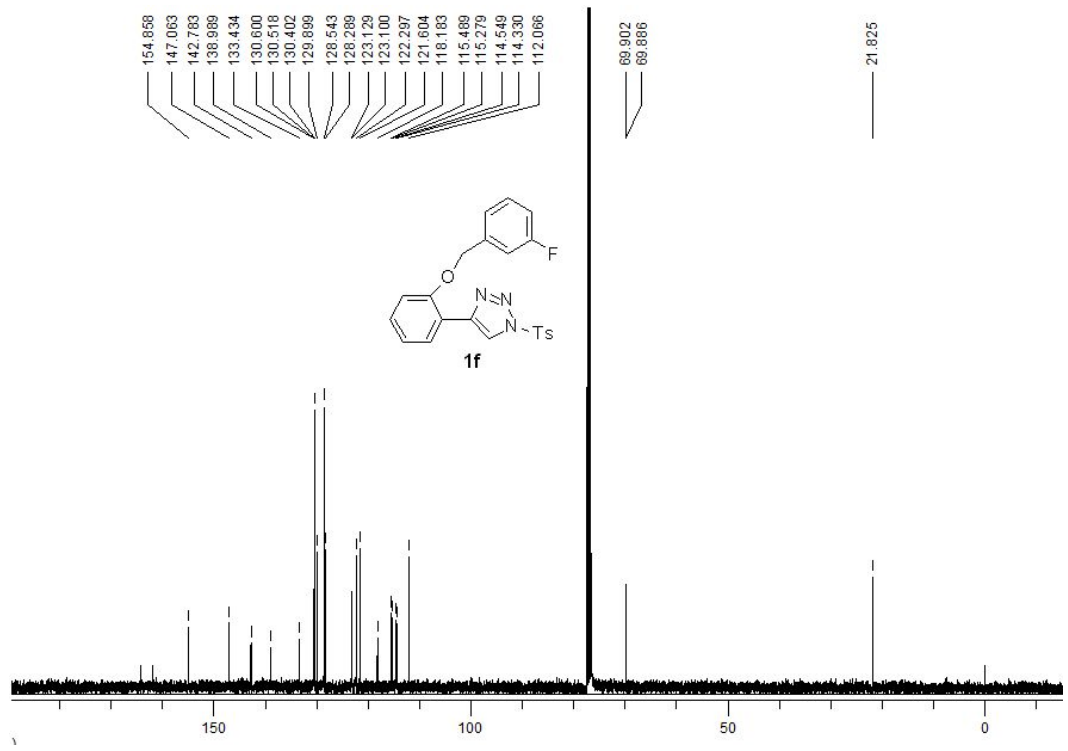
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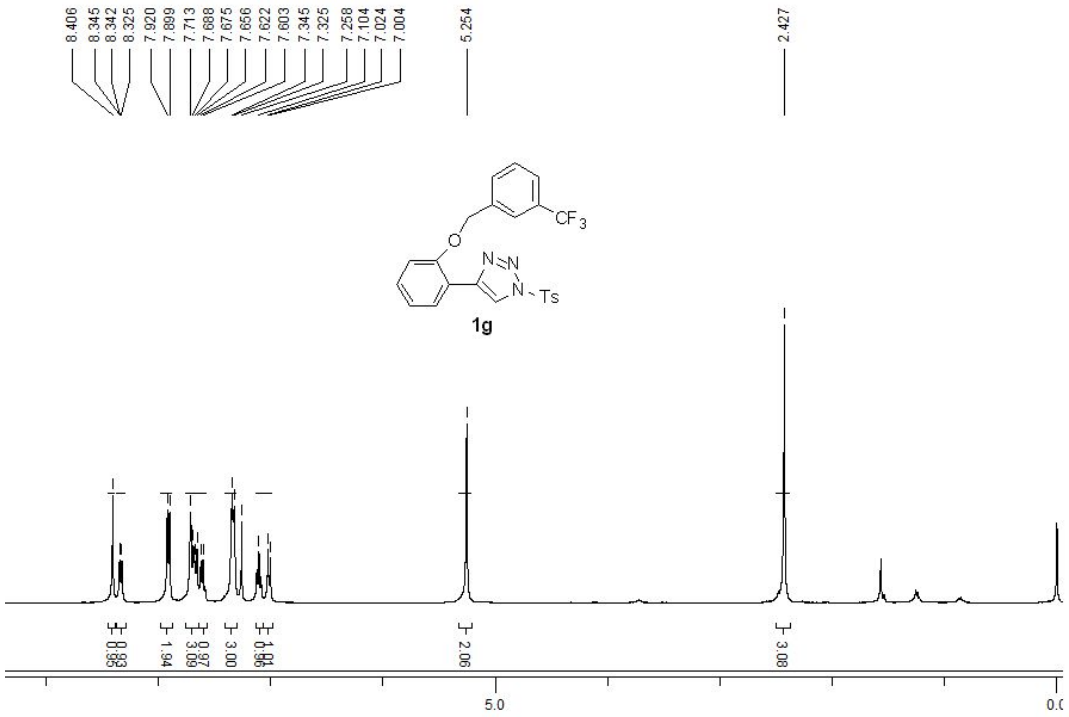
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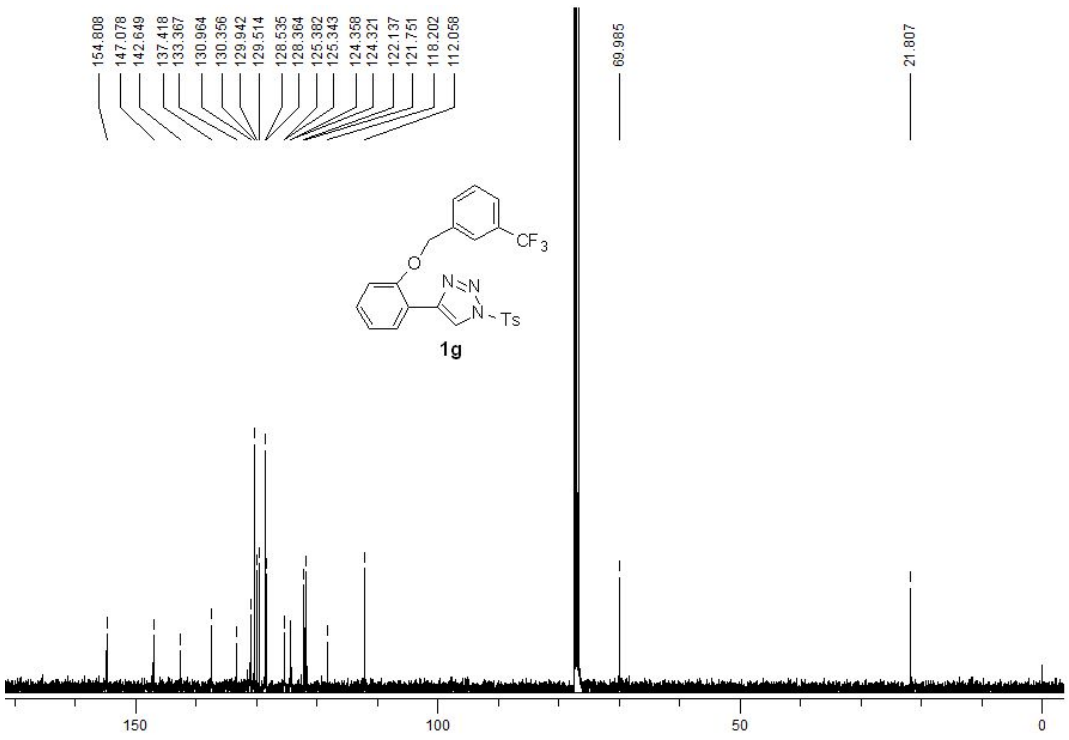
5.0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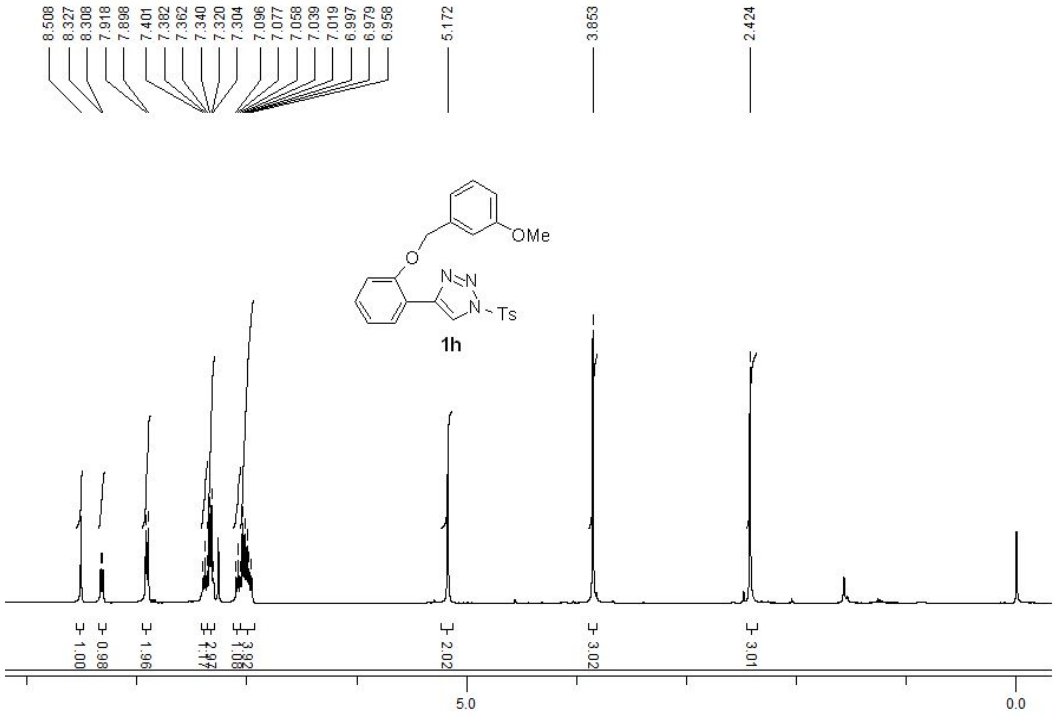
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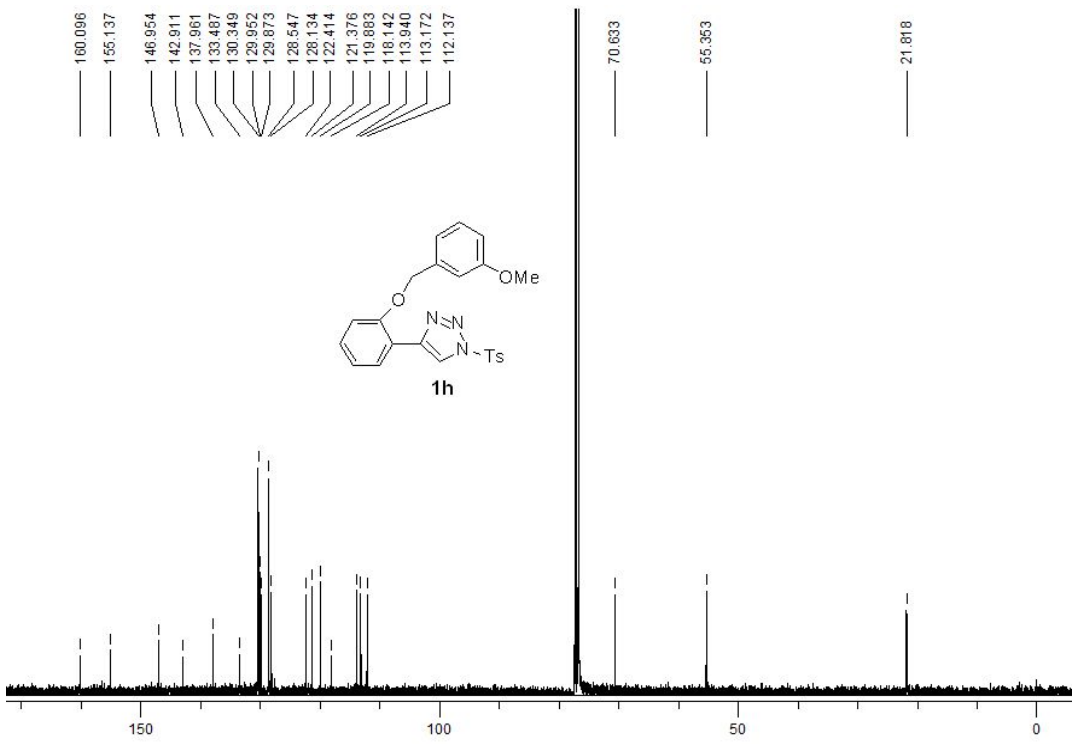
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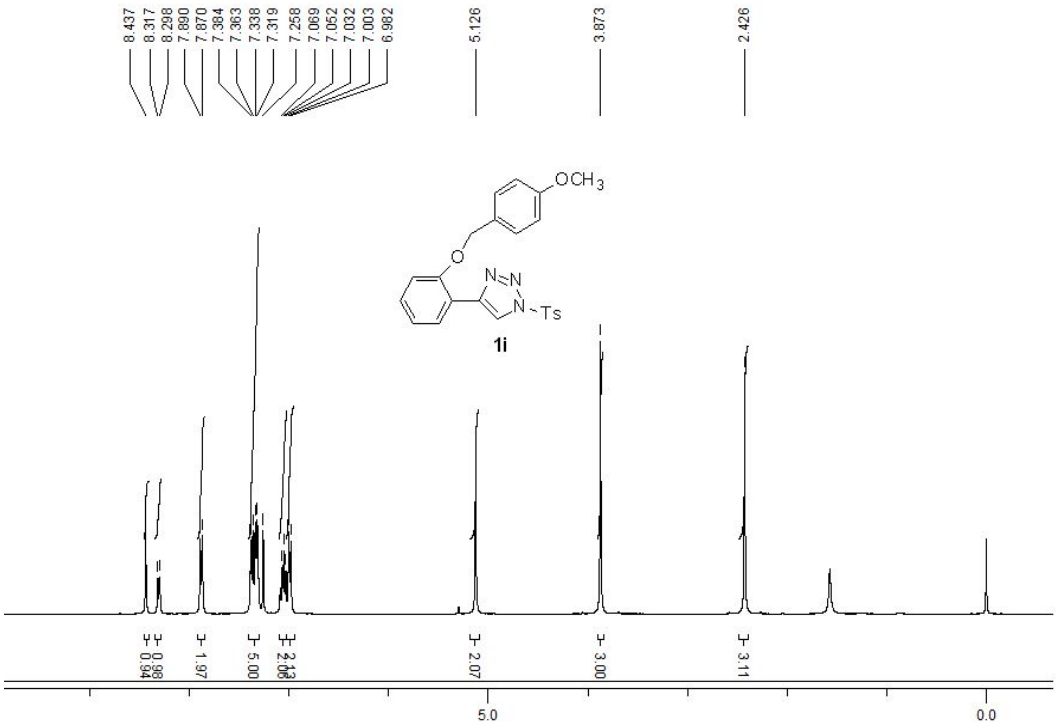
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2.426
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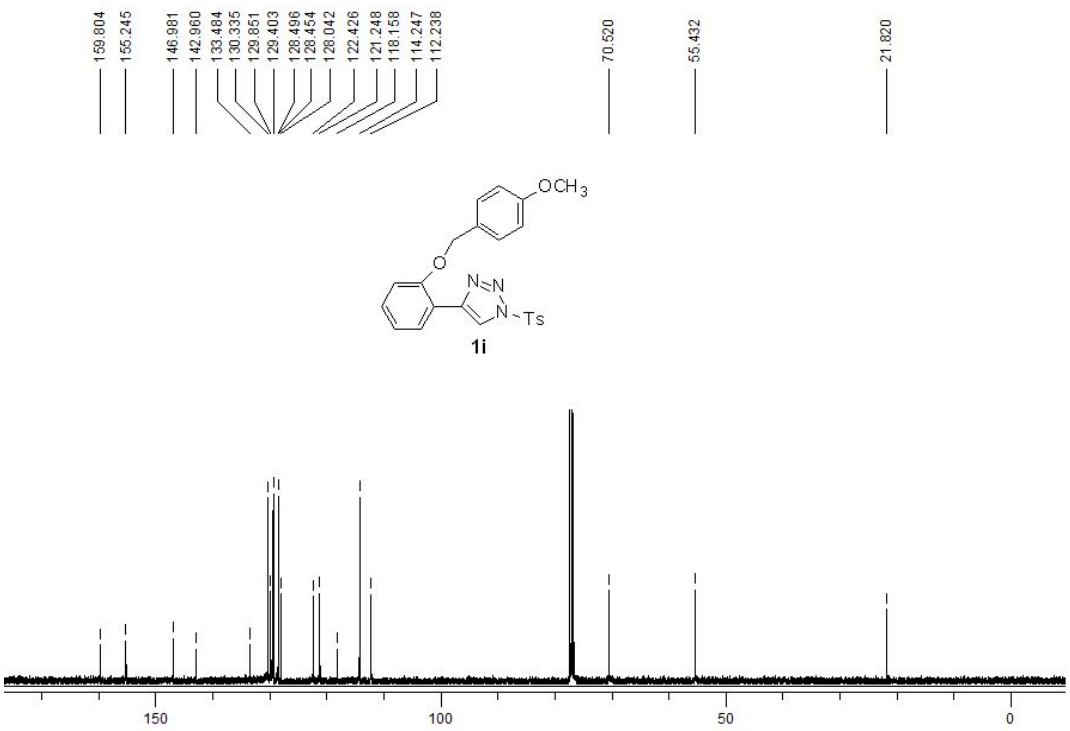
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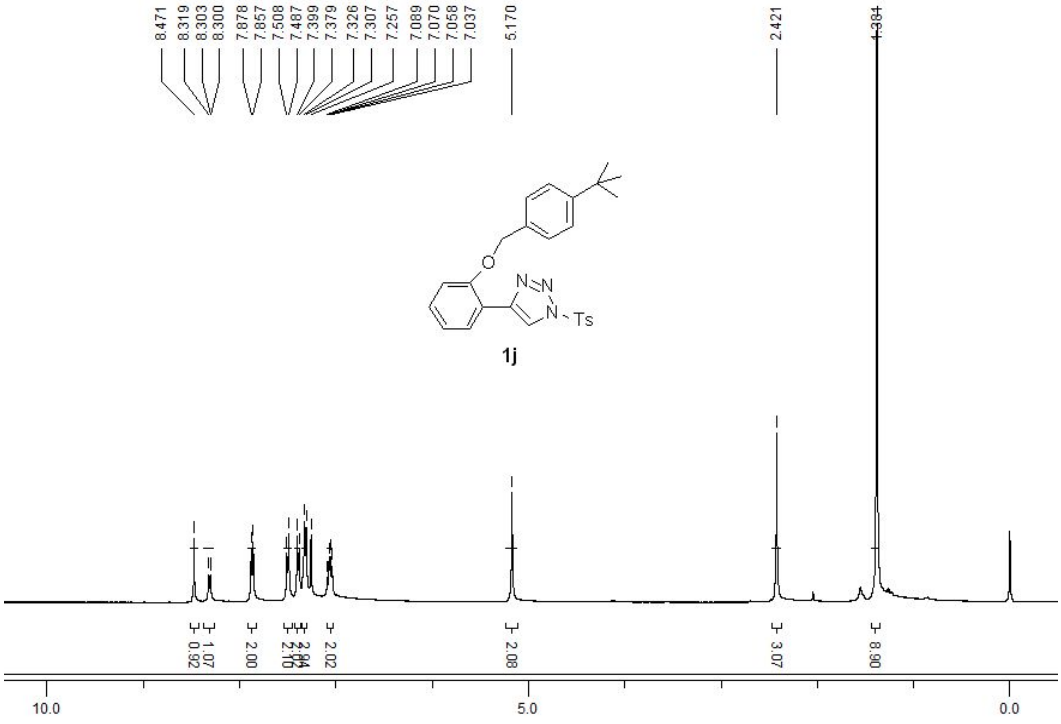
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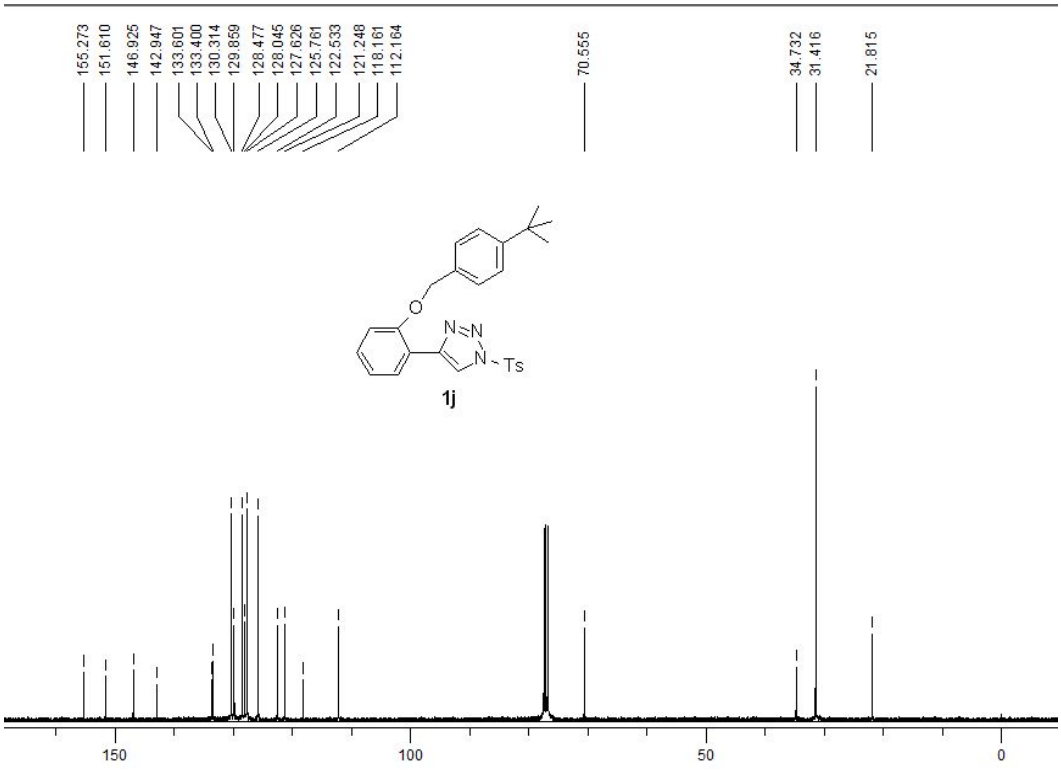
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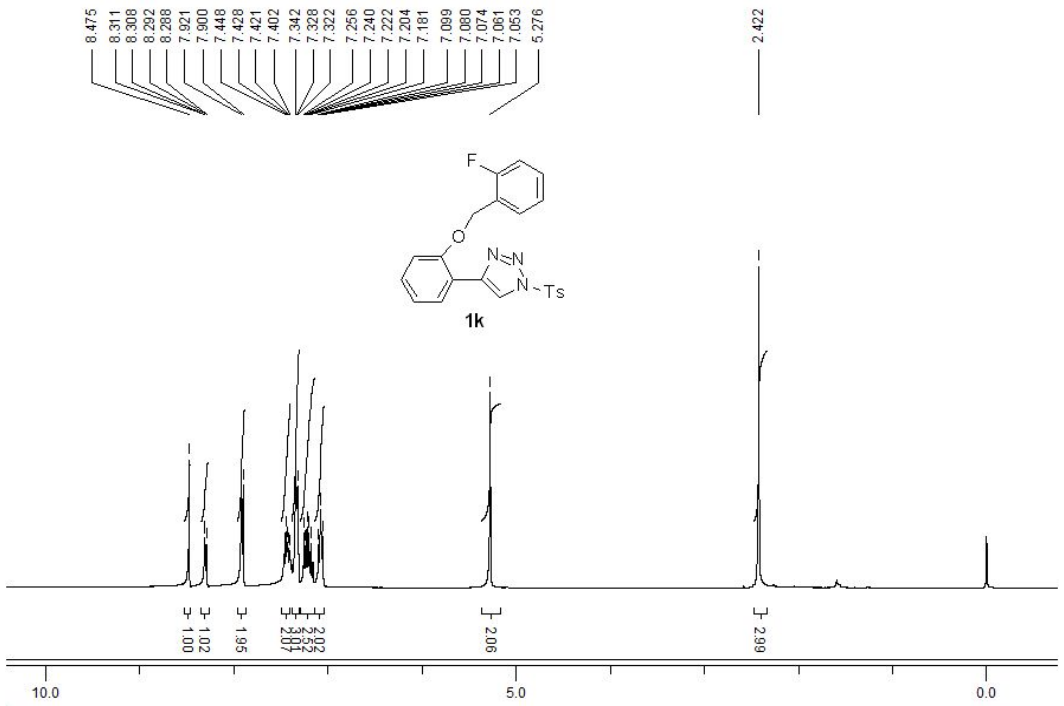
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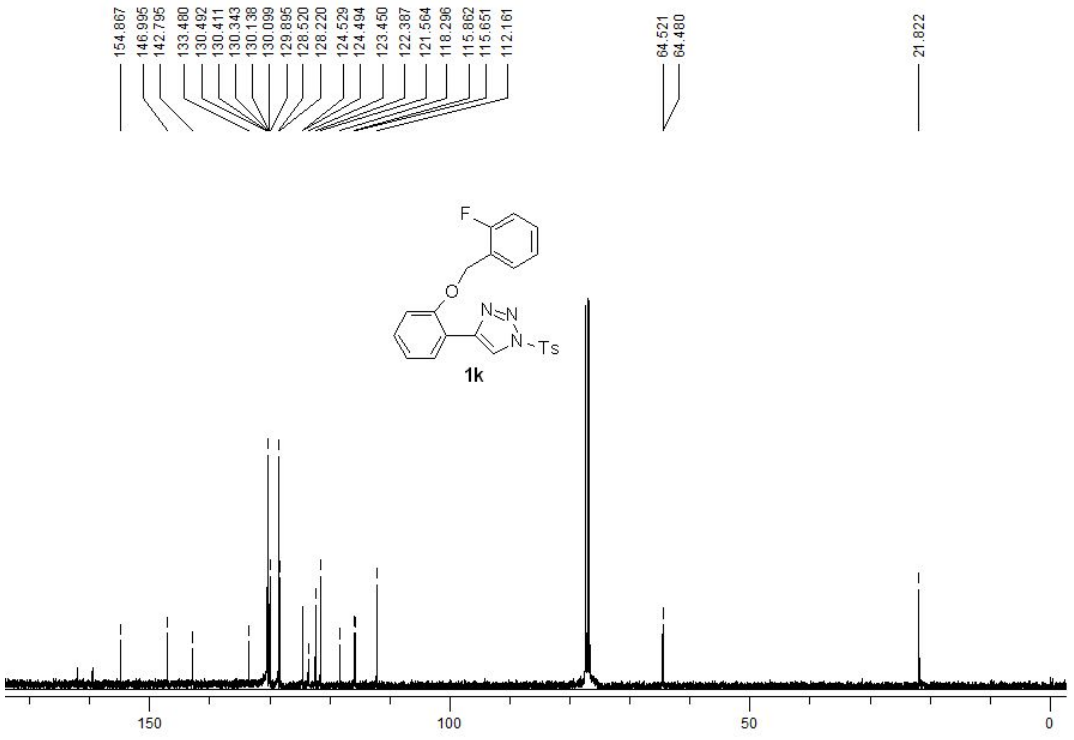
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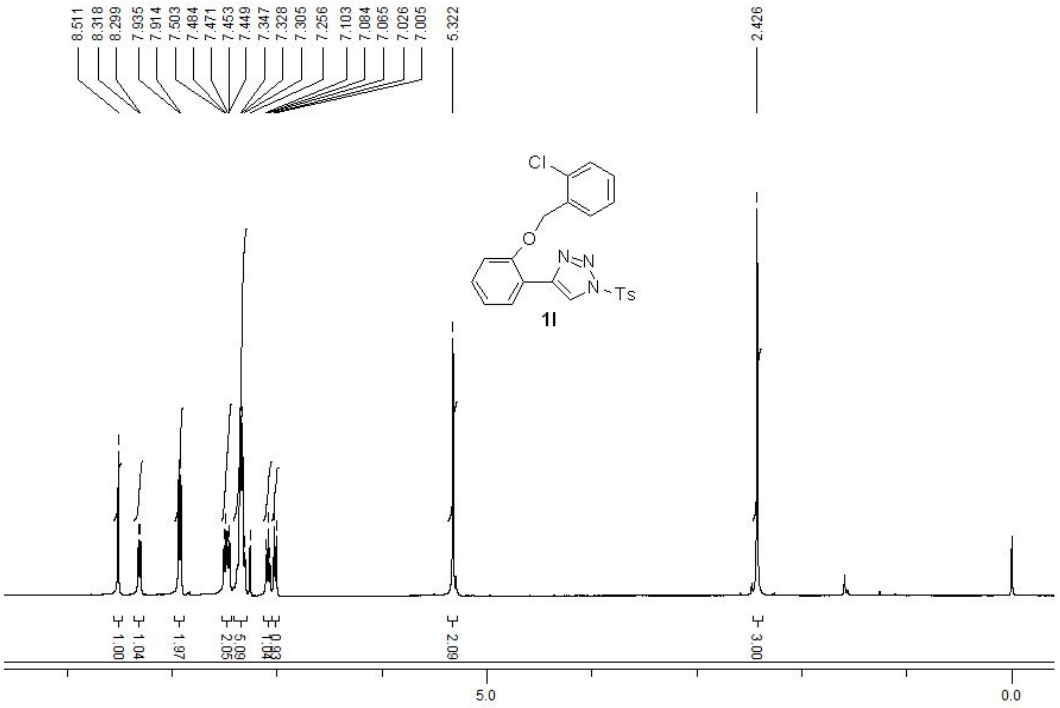
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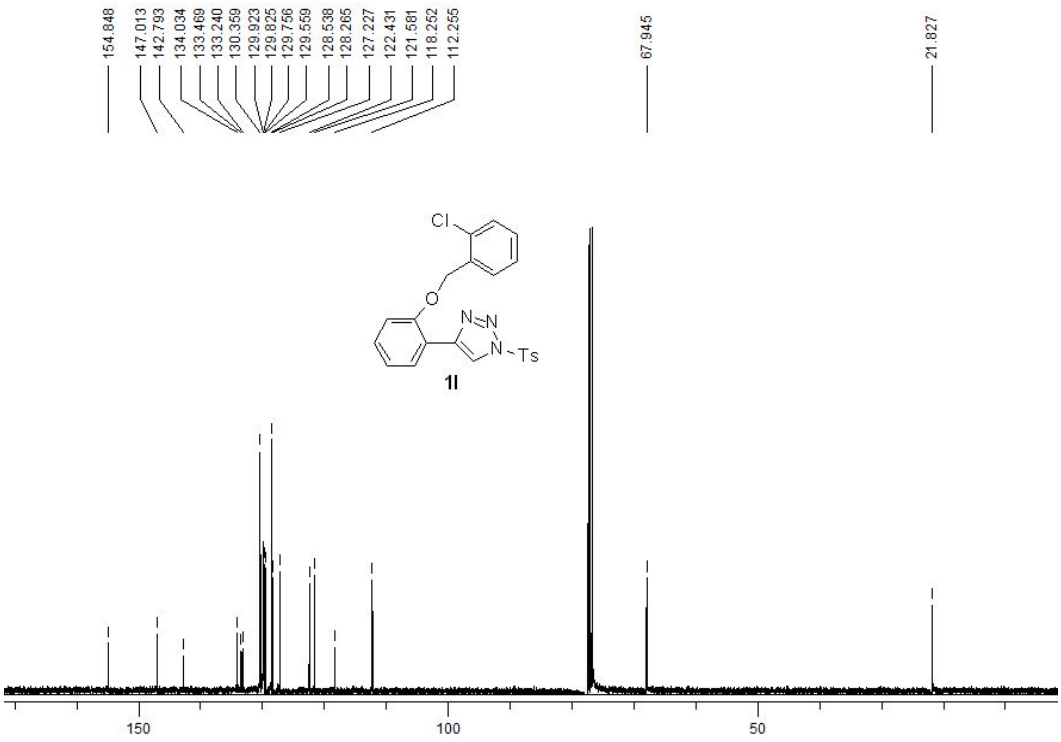
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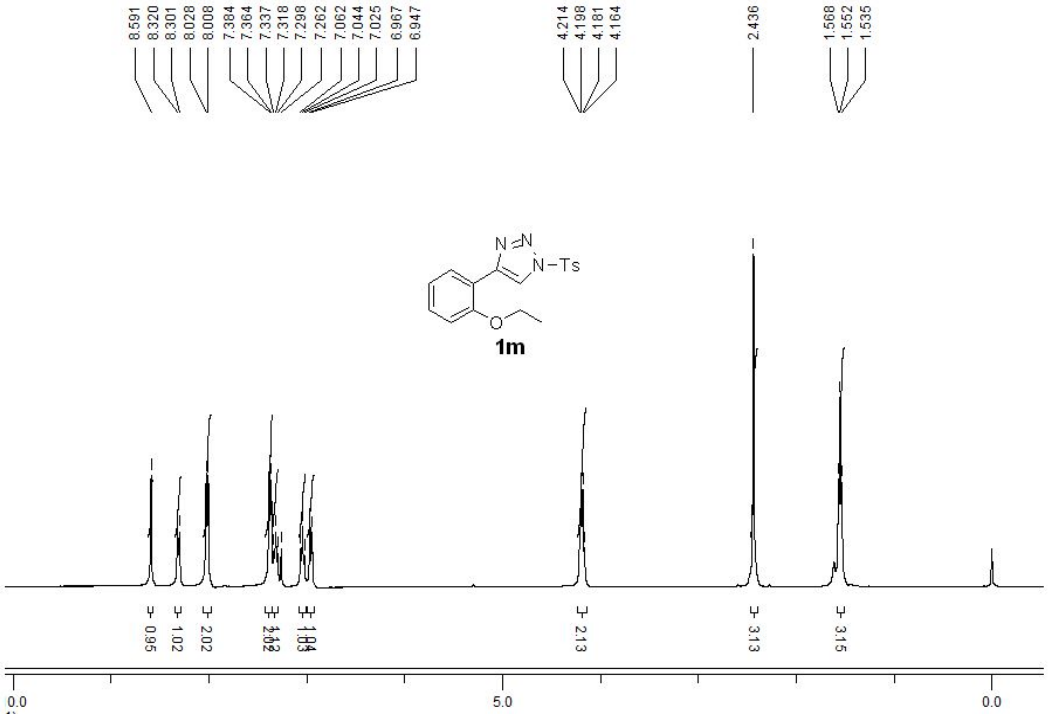
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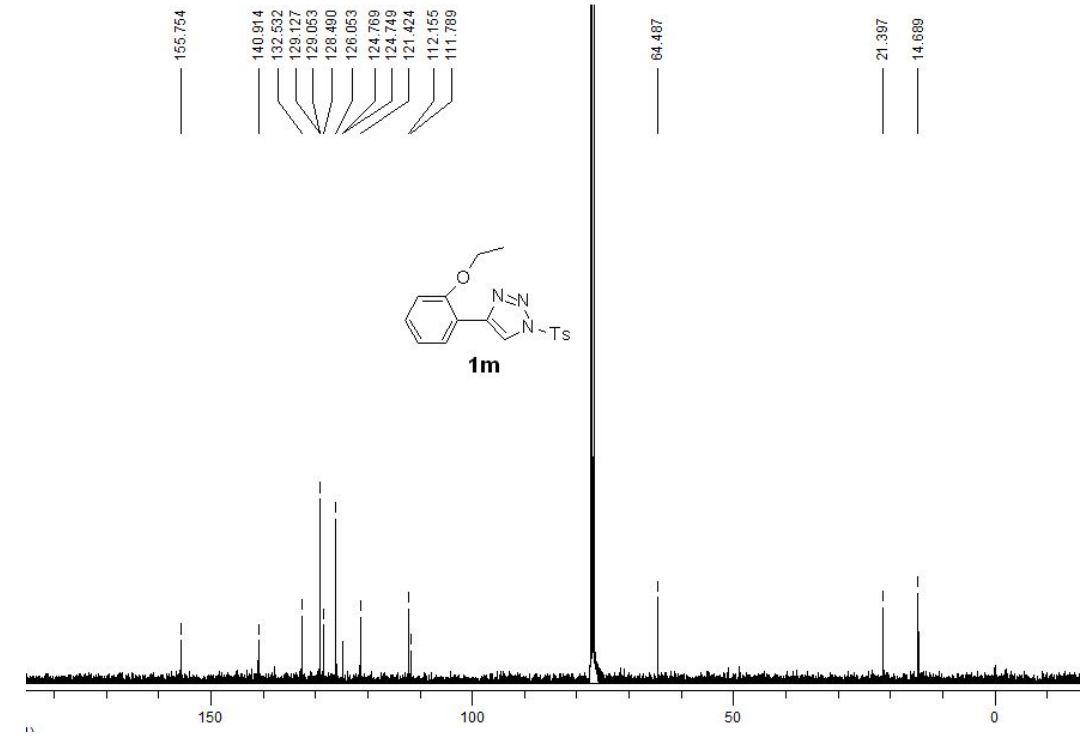
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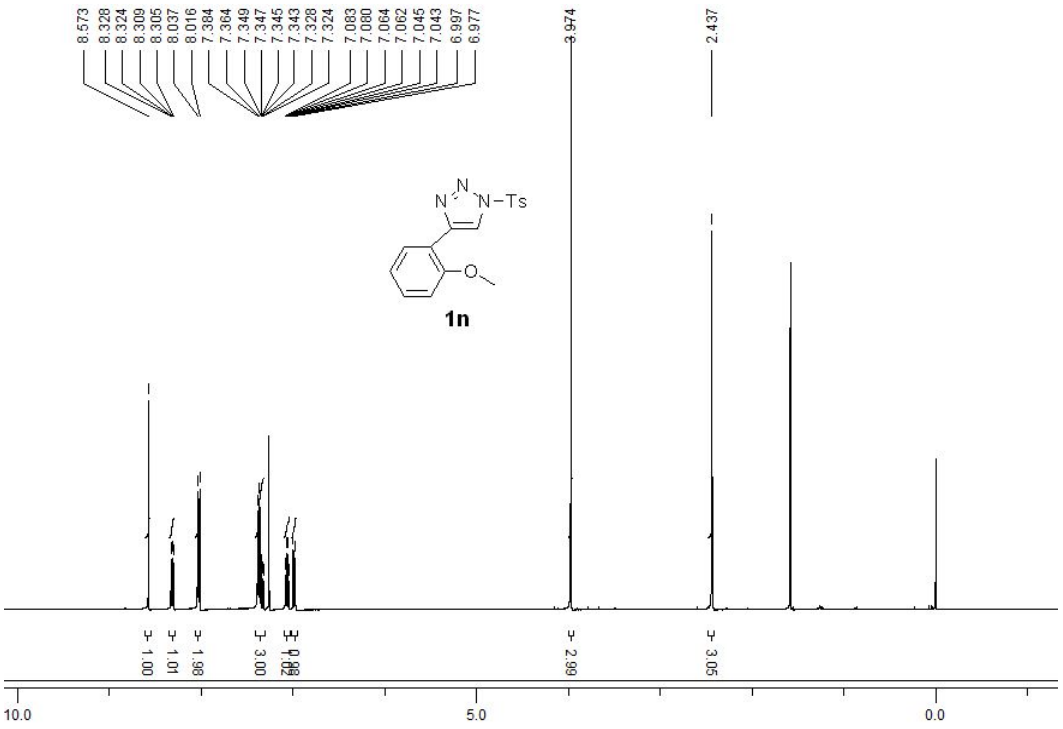
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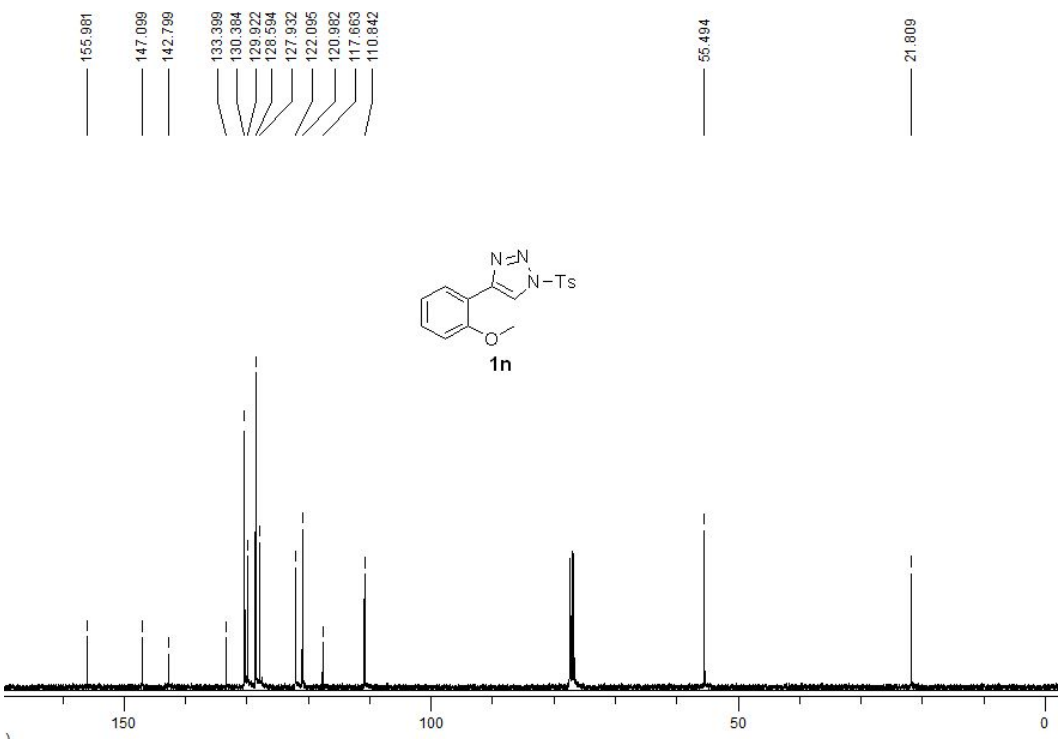
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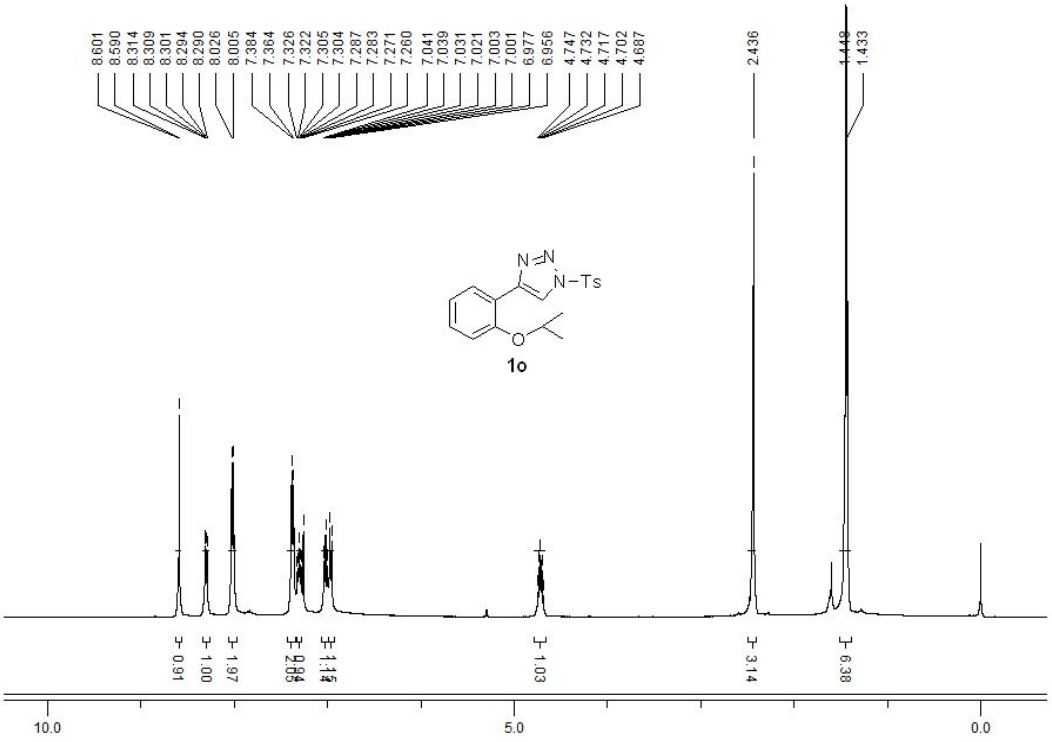
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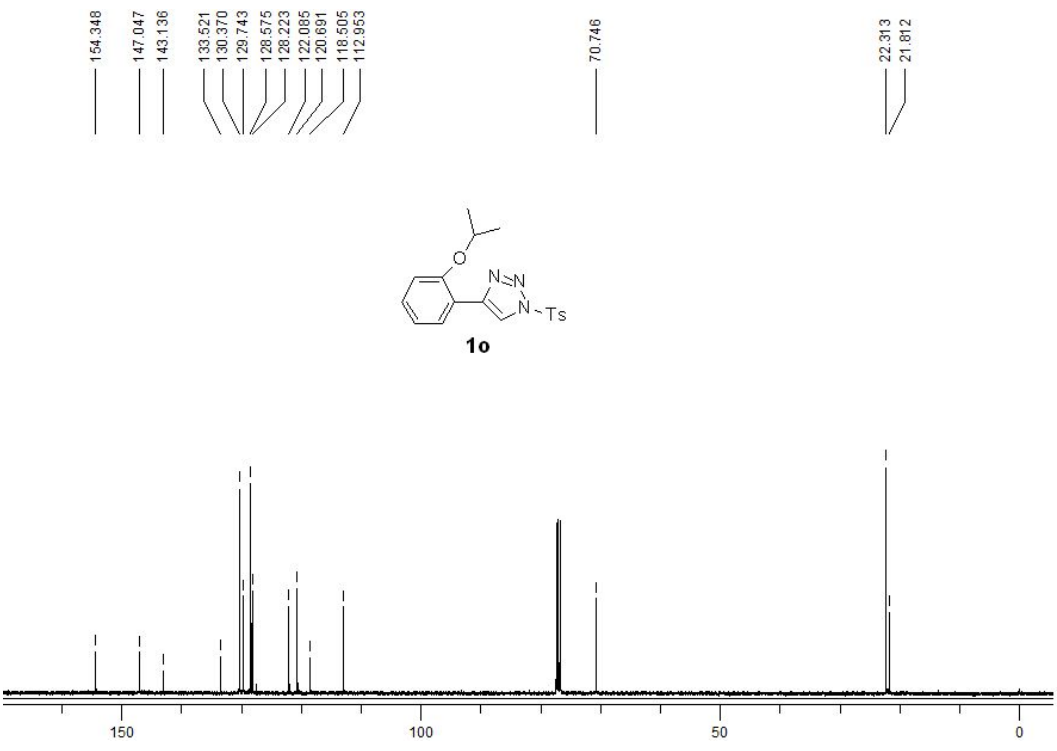
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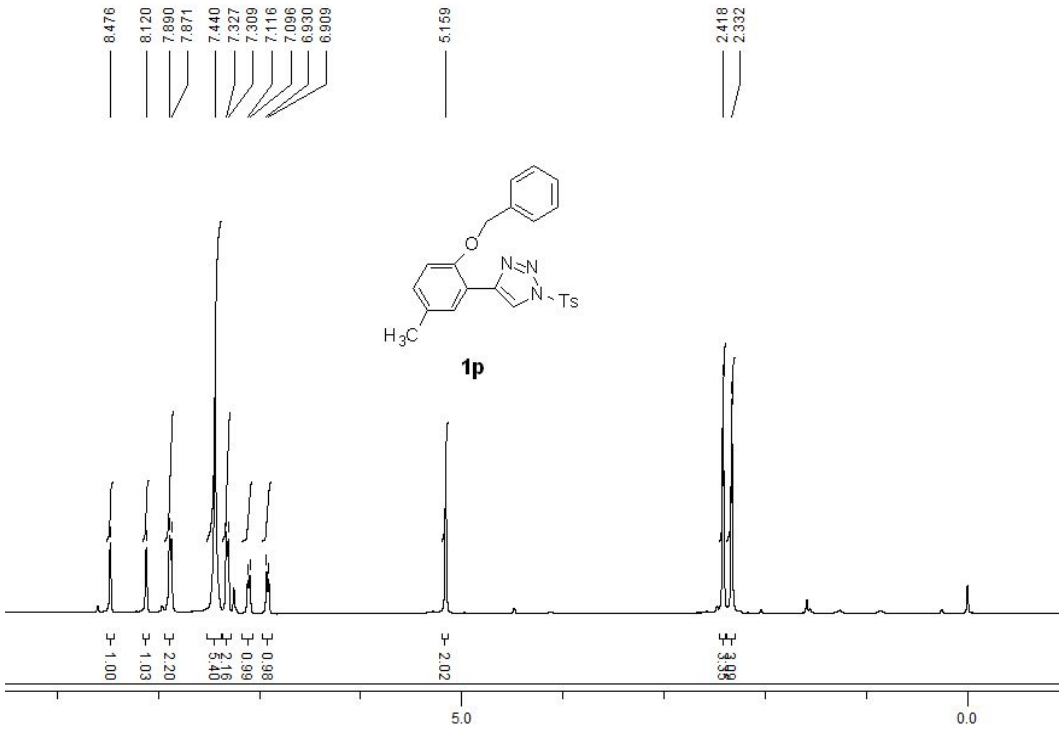
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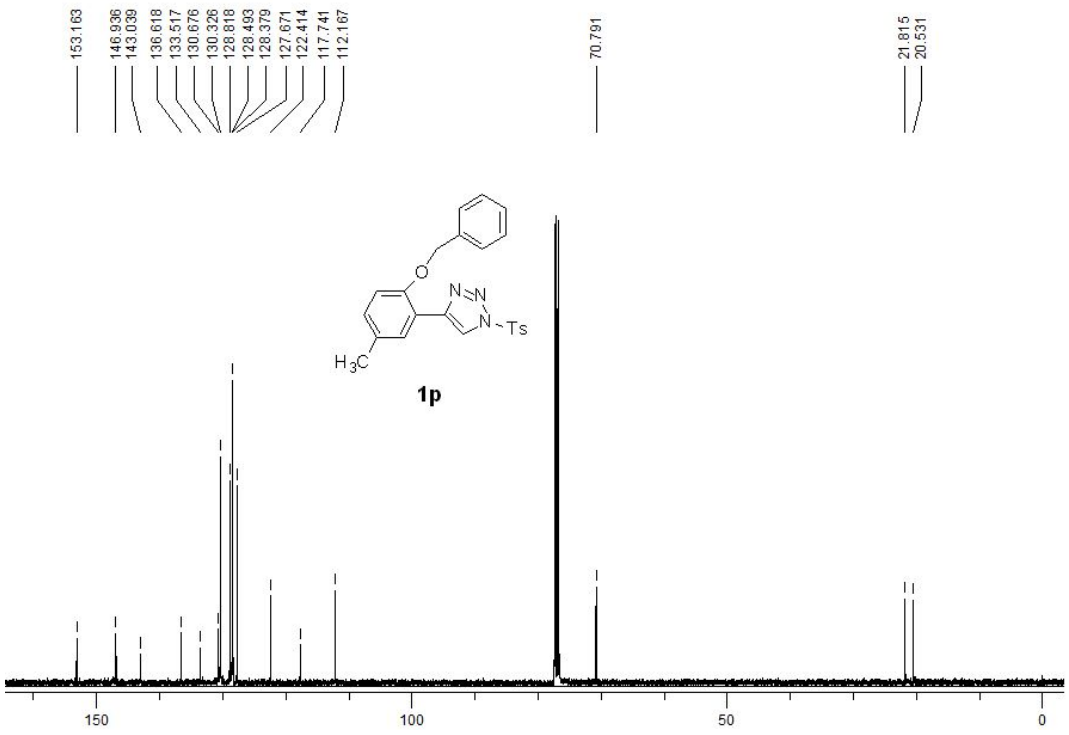
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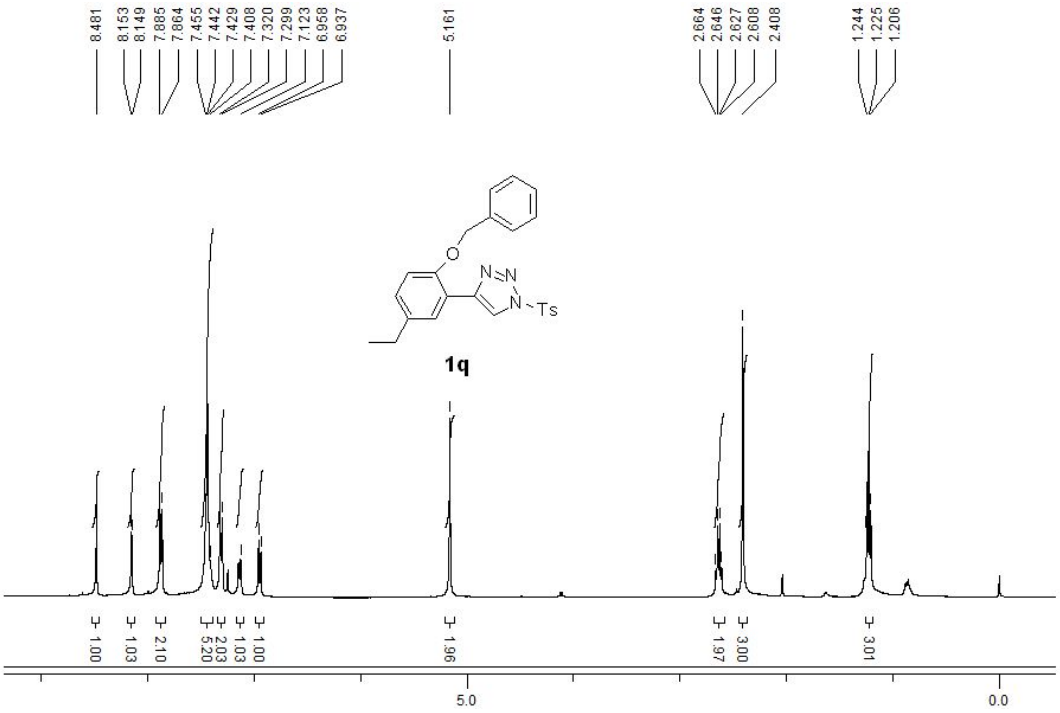
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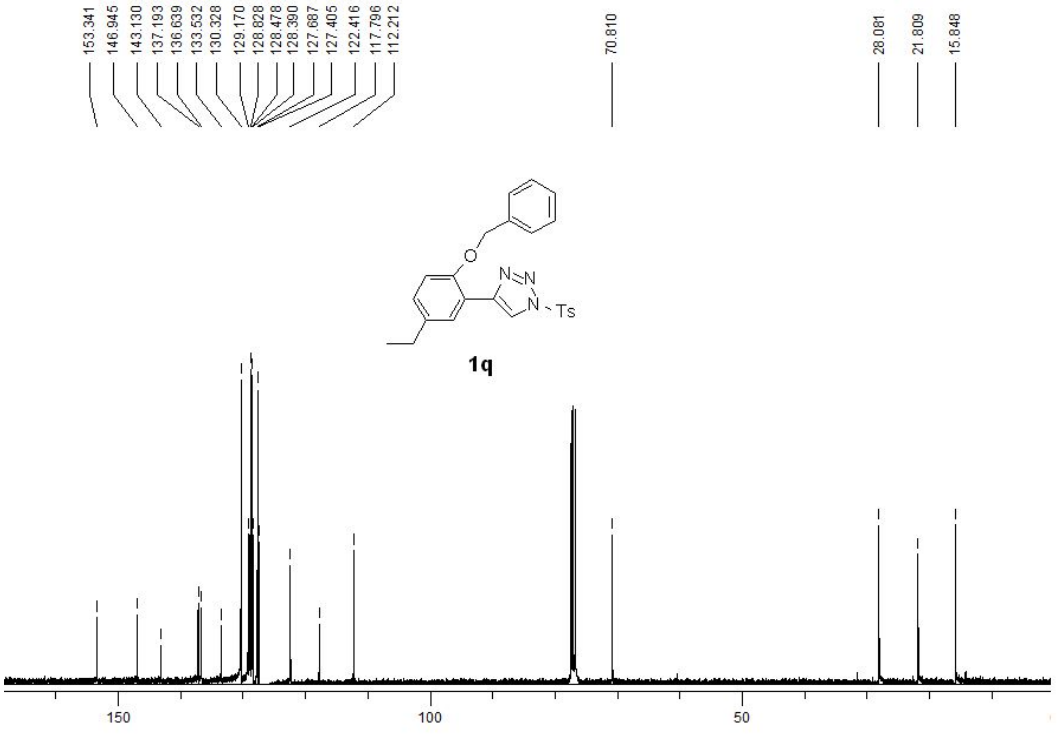
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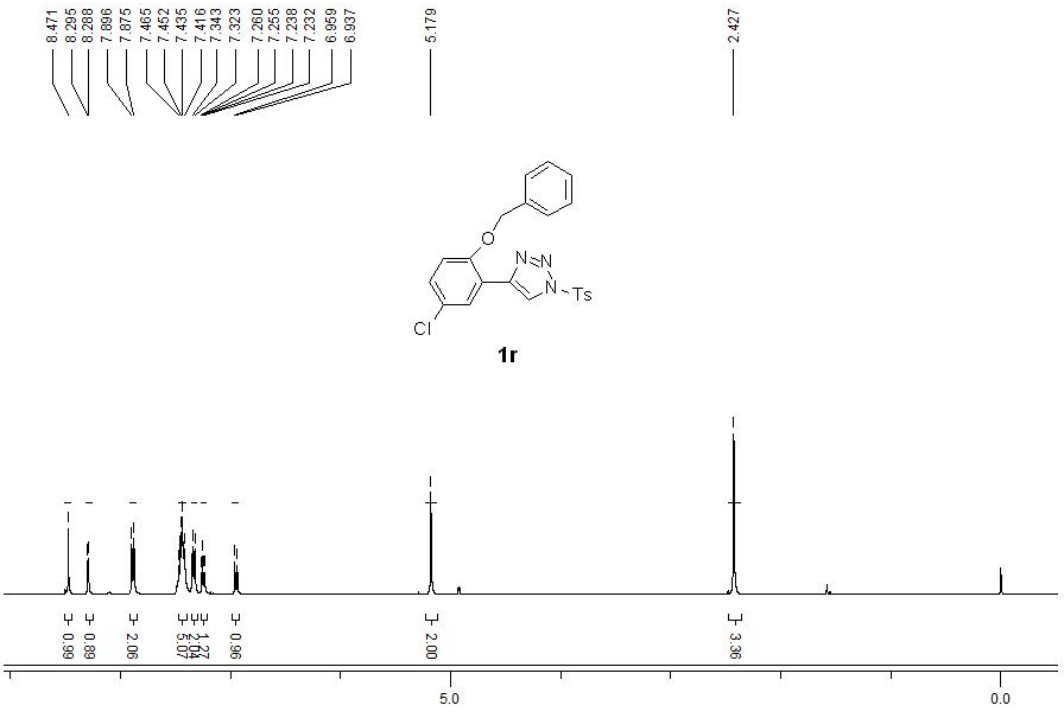
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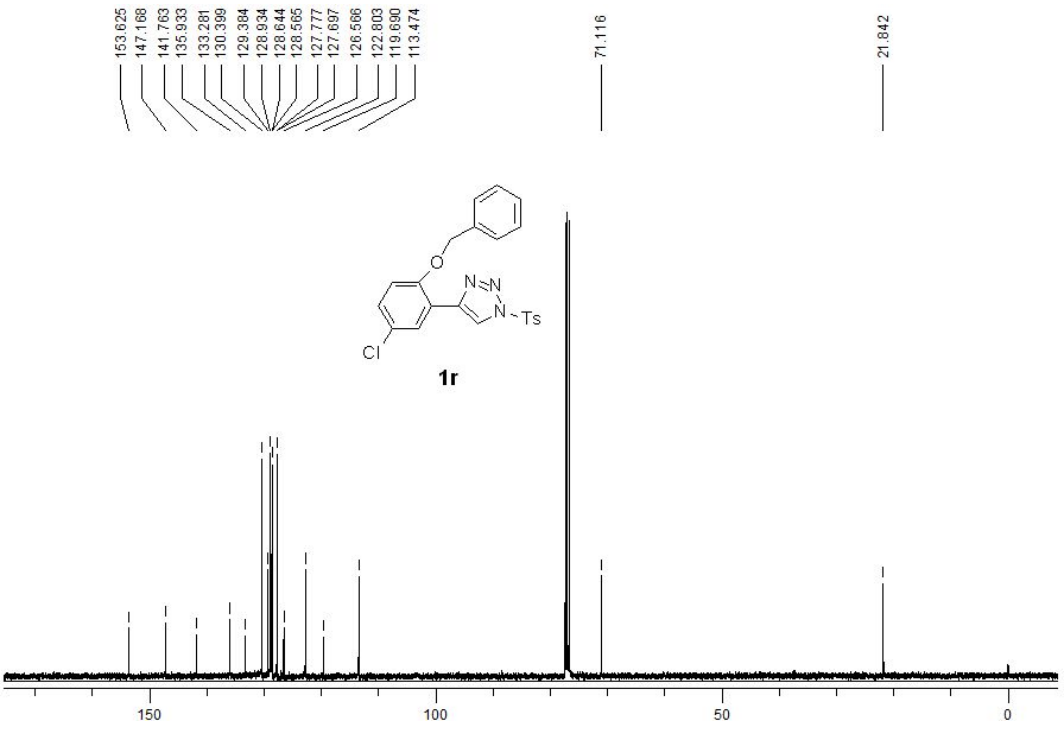
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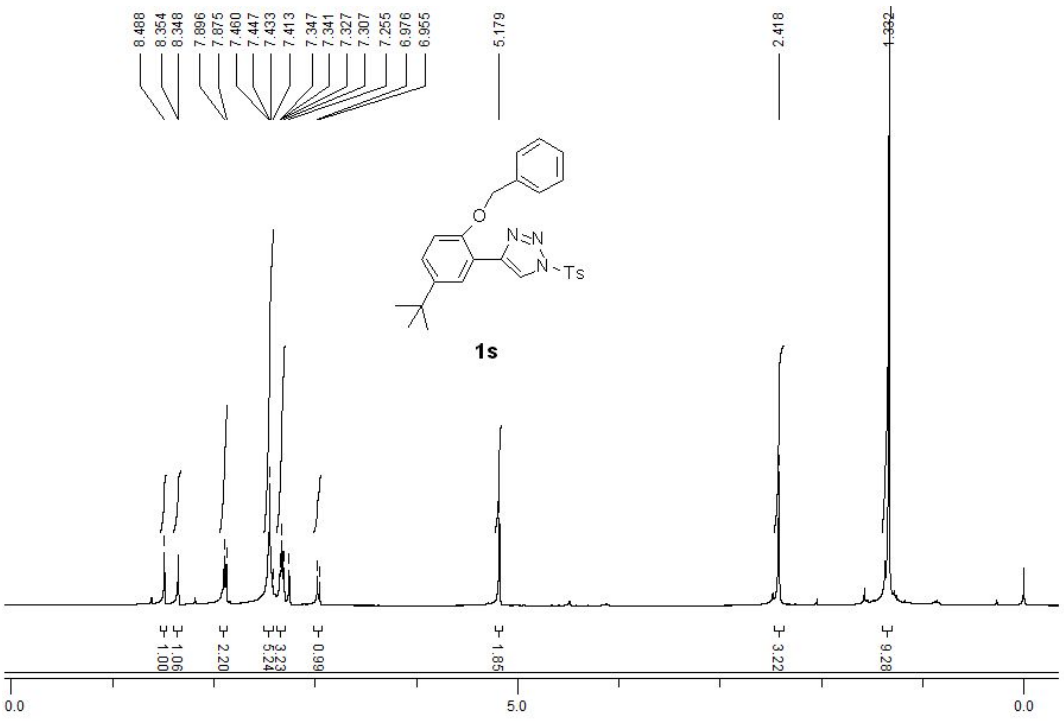
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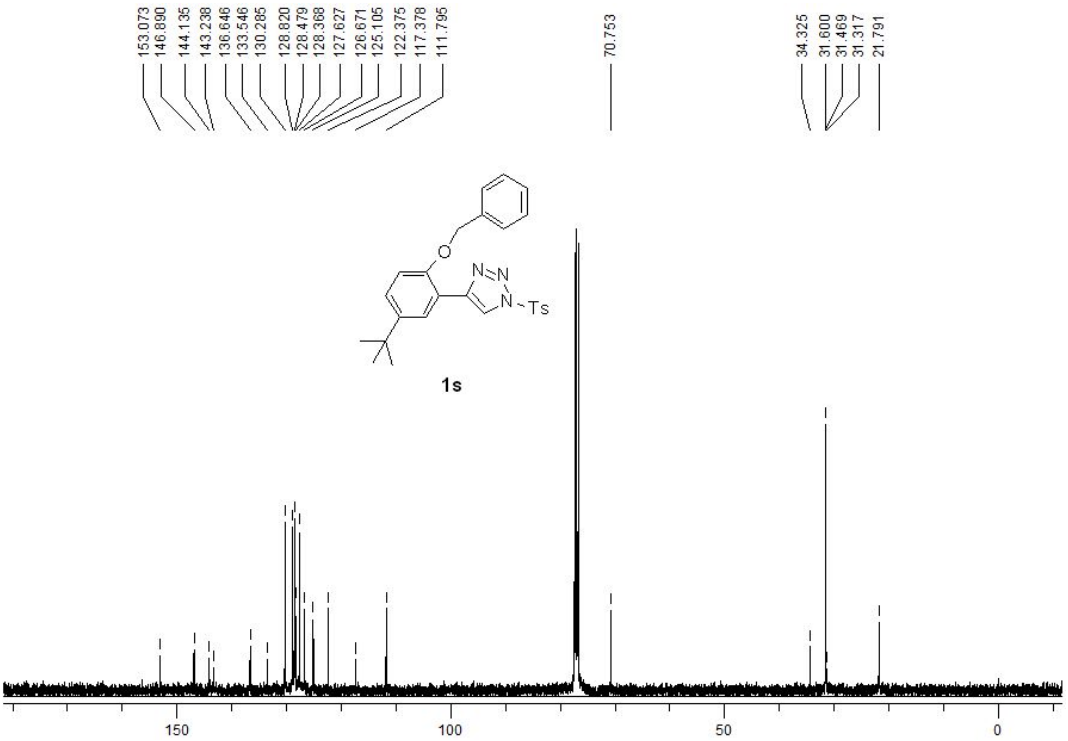
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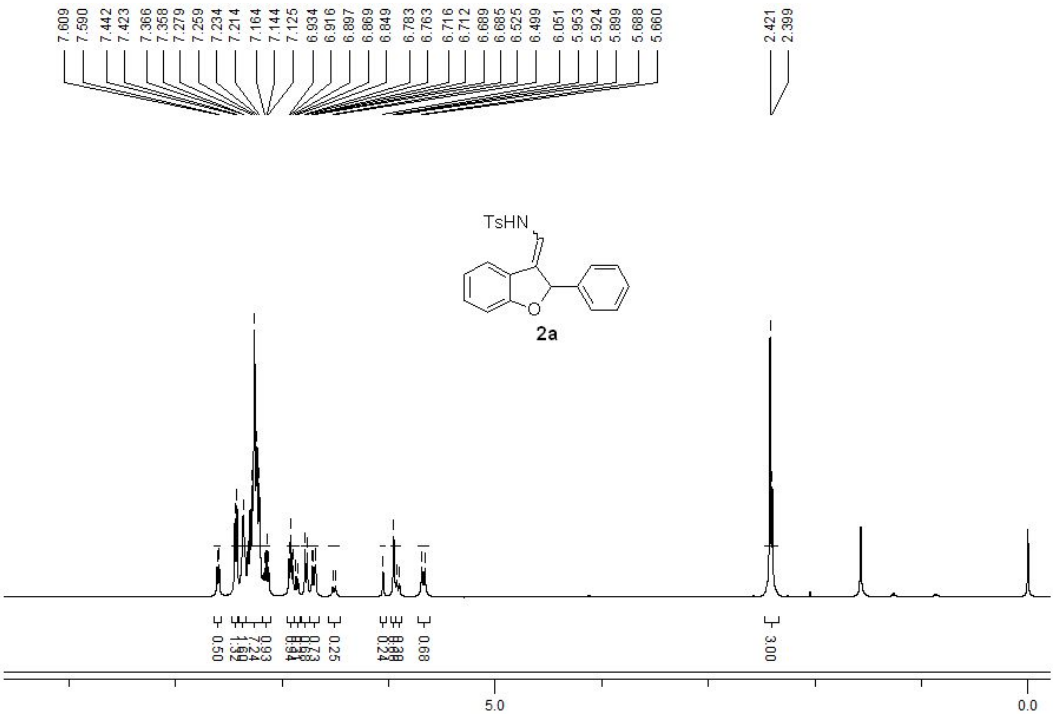
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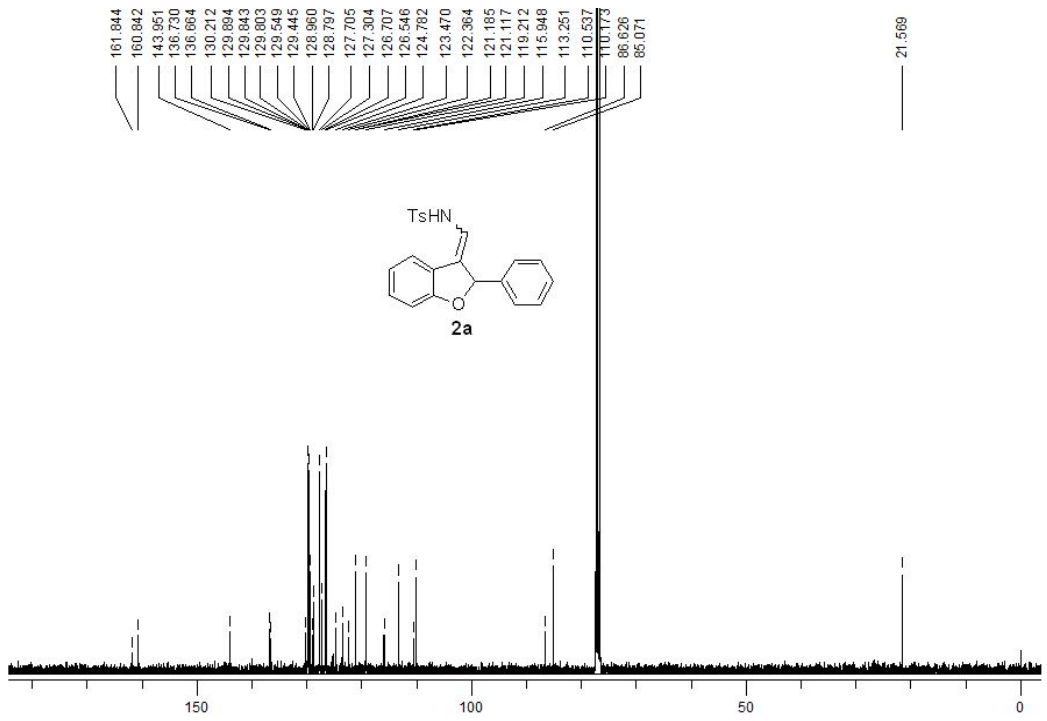
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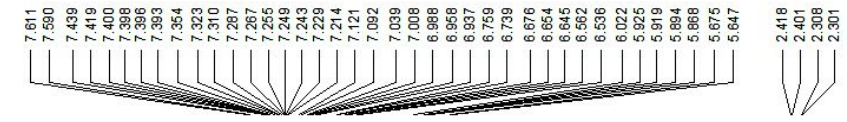
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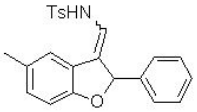
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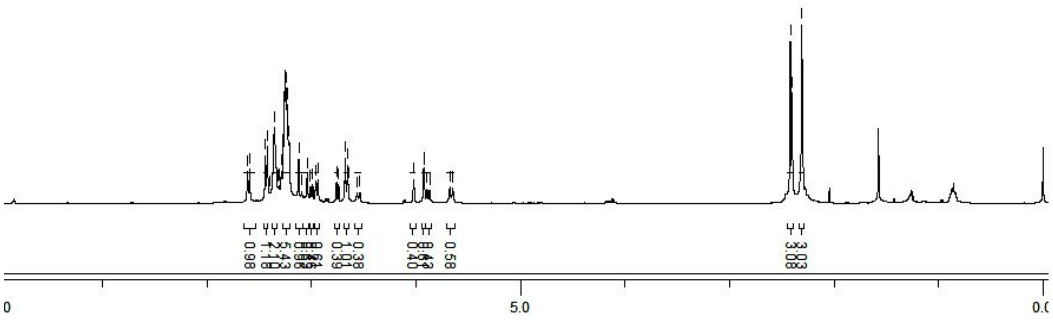
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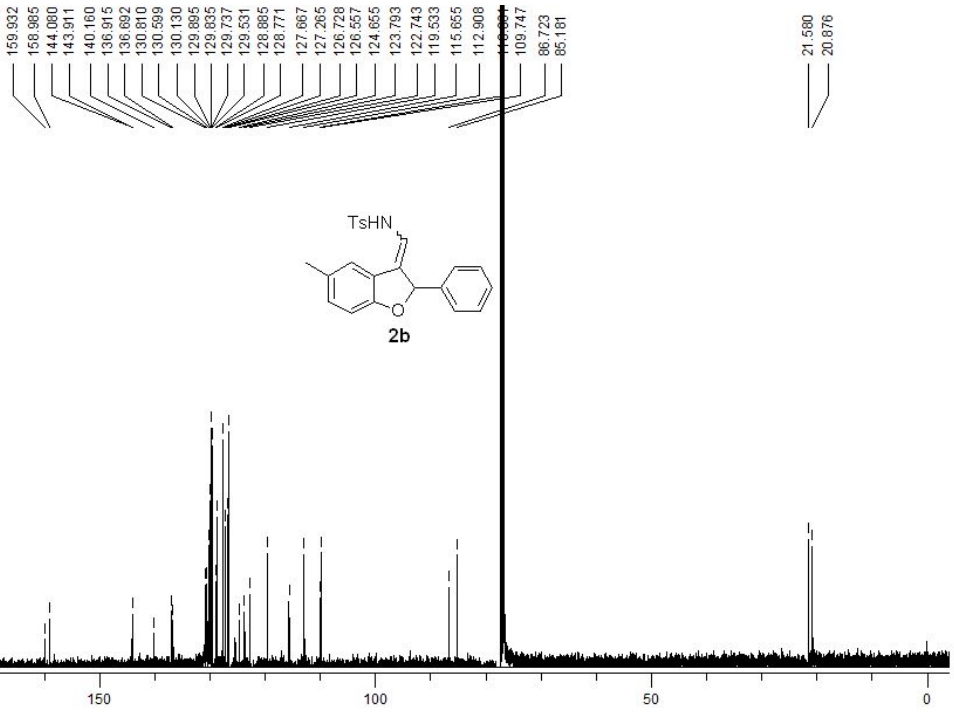
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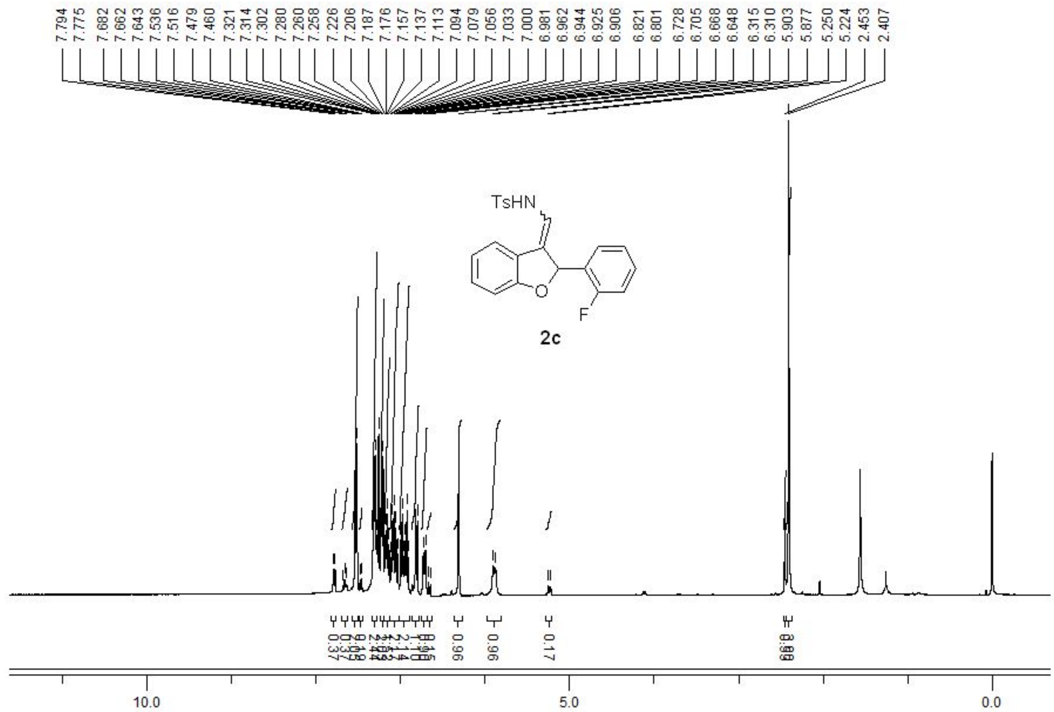
2b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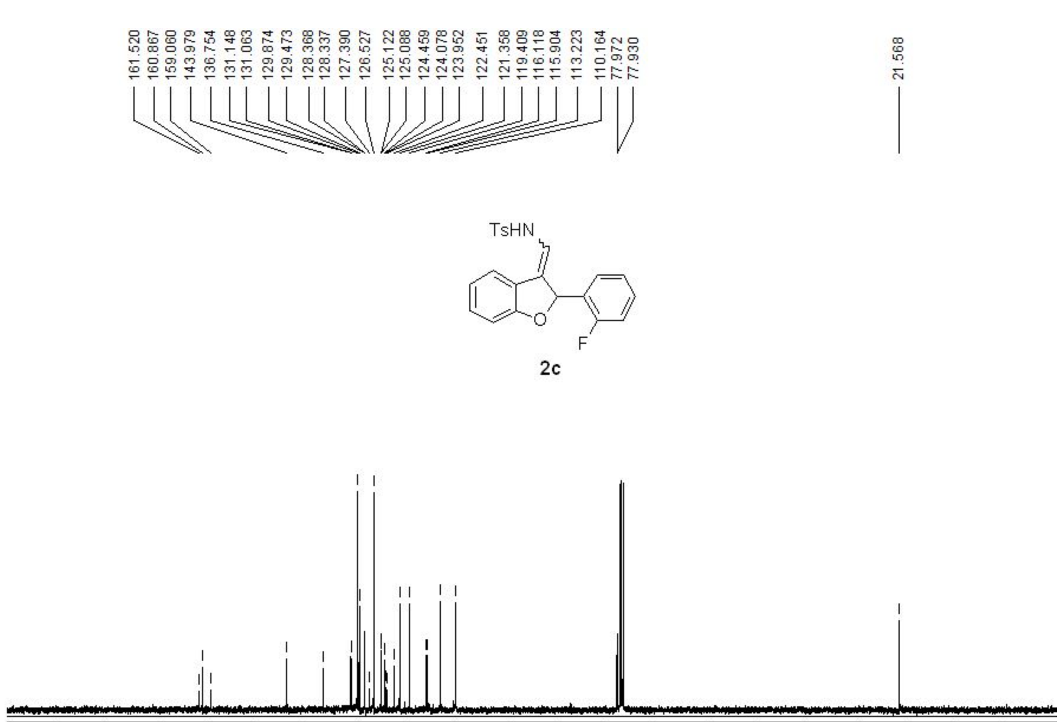
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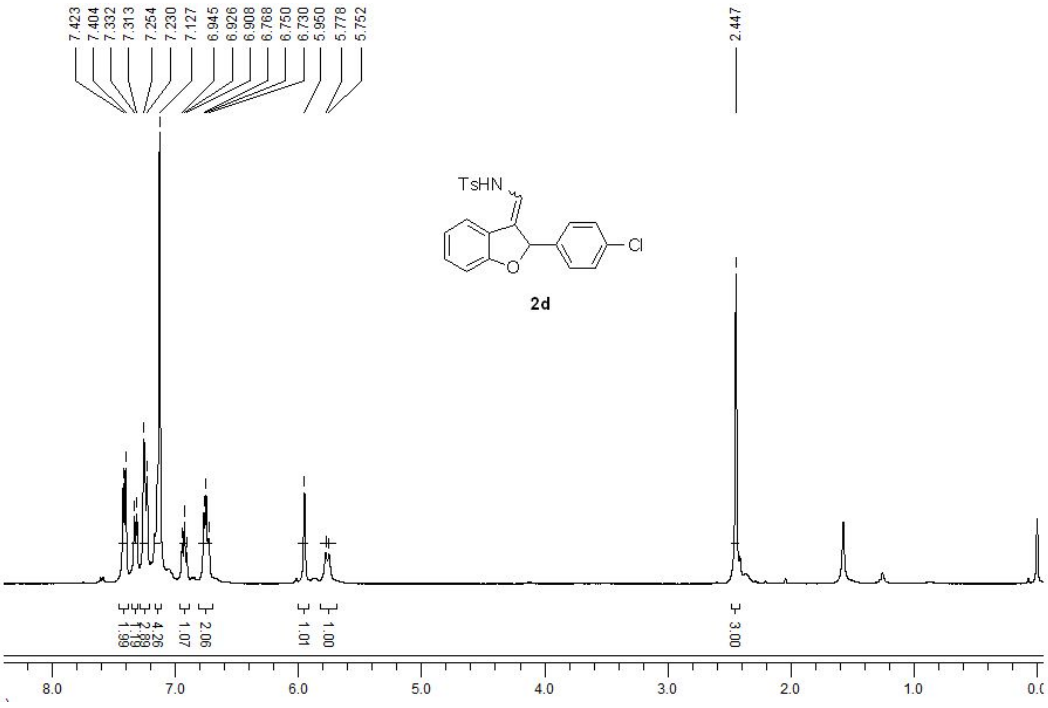
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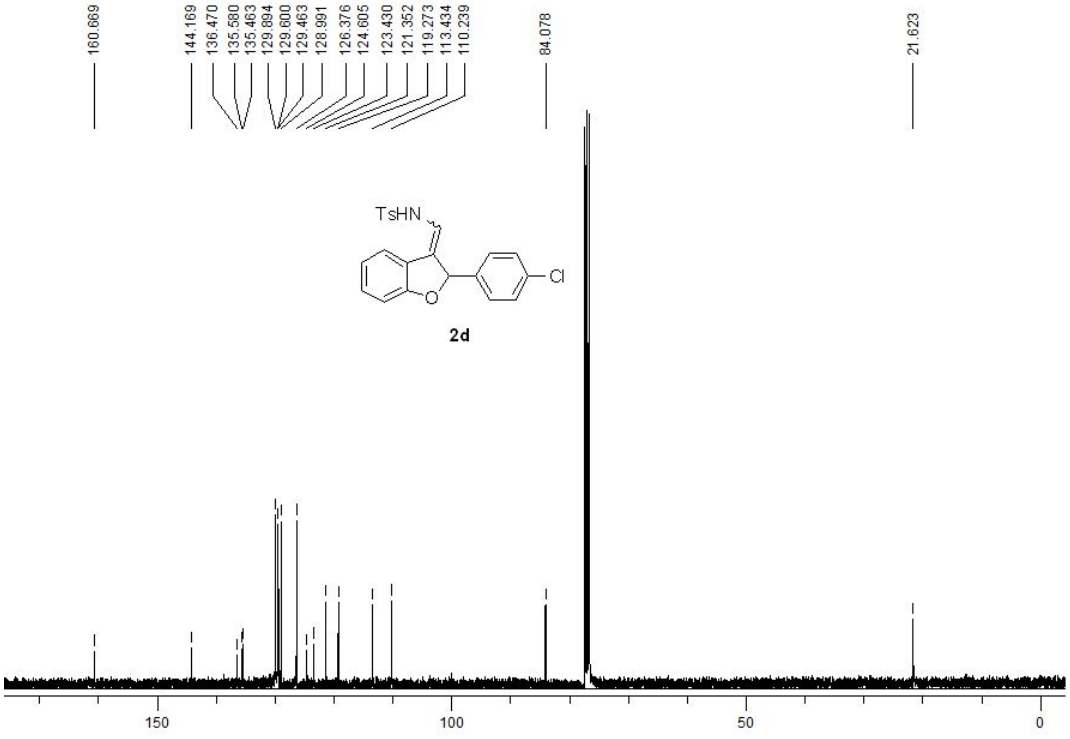
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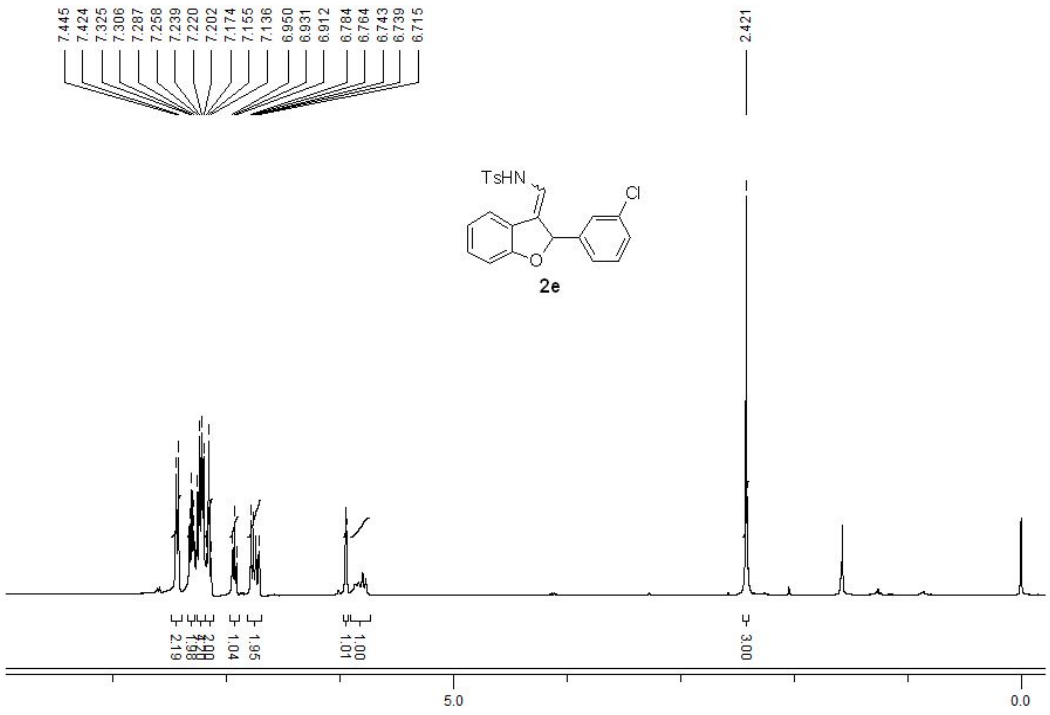
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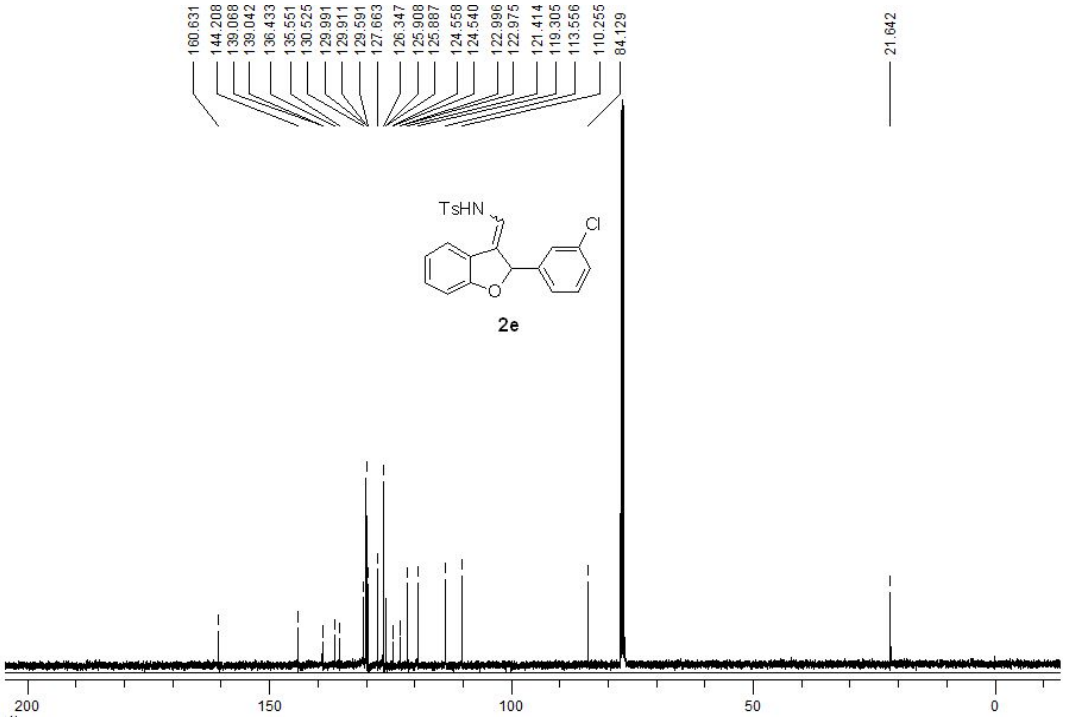
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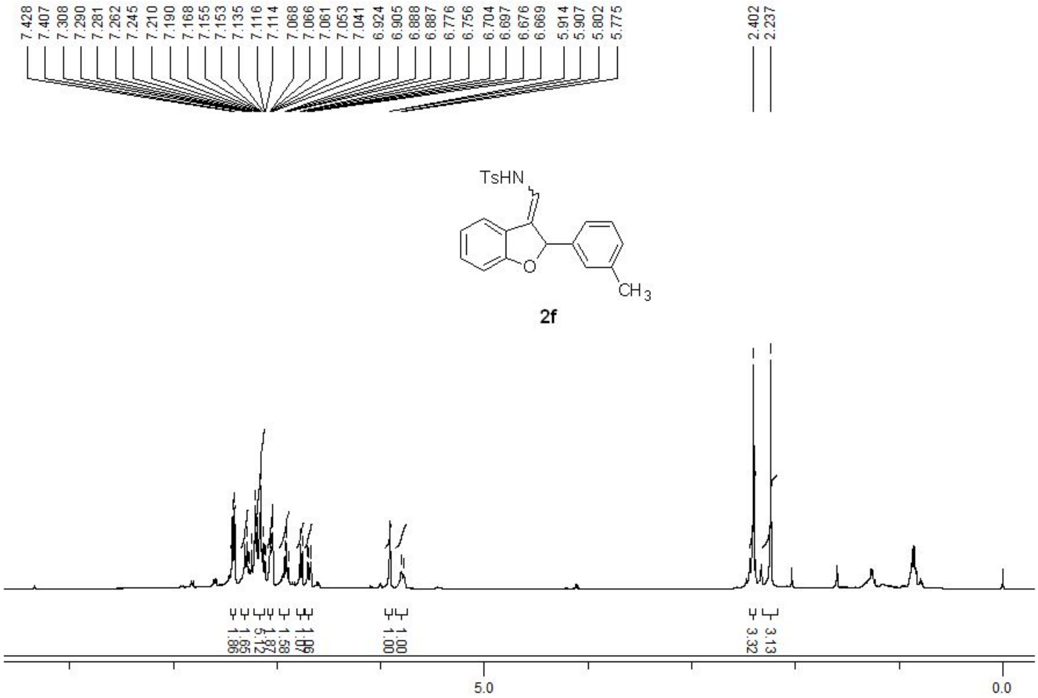
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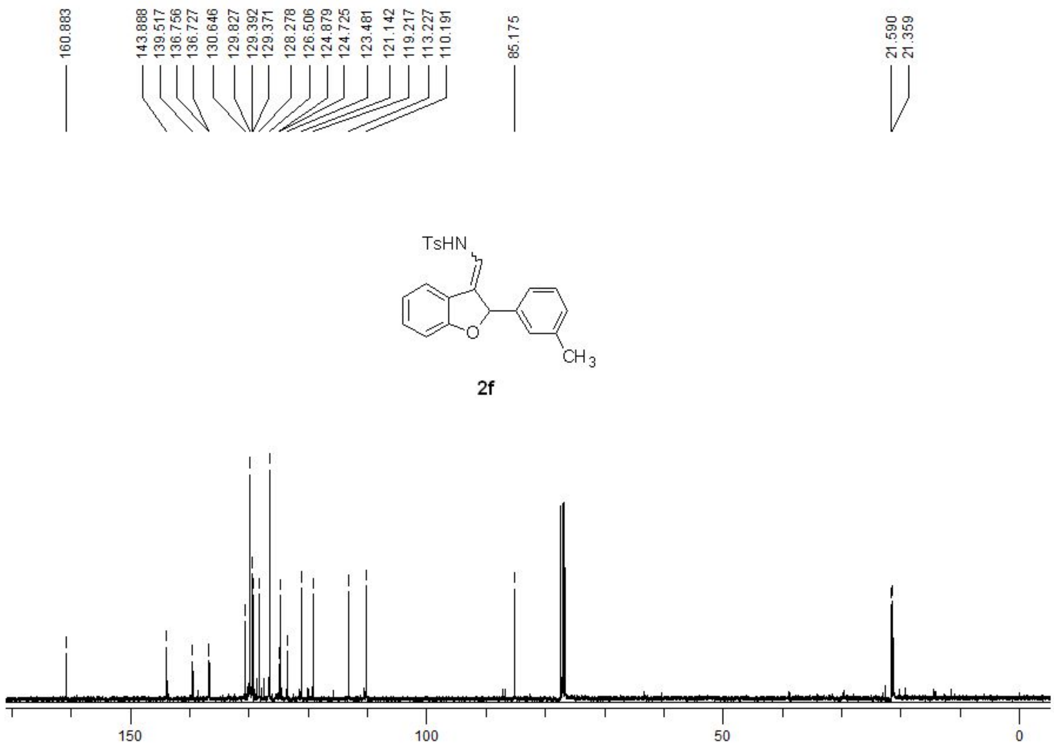
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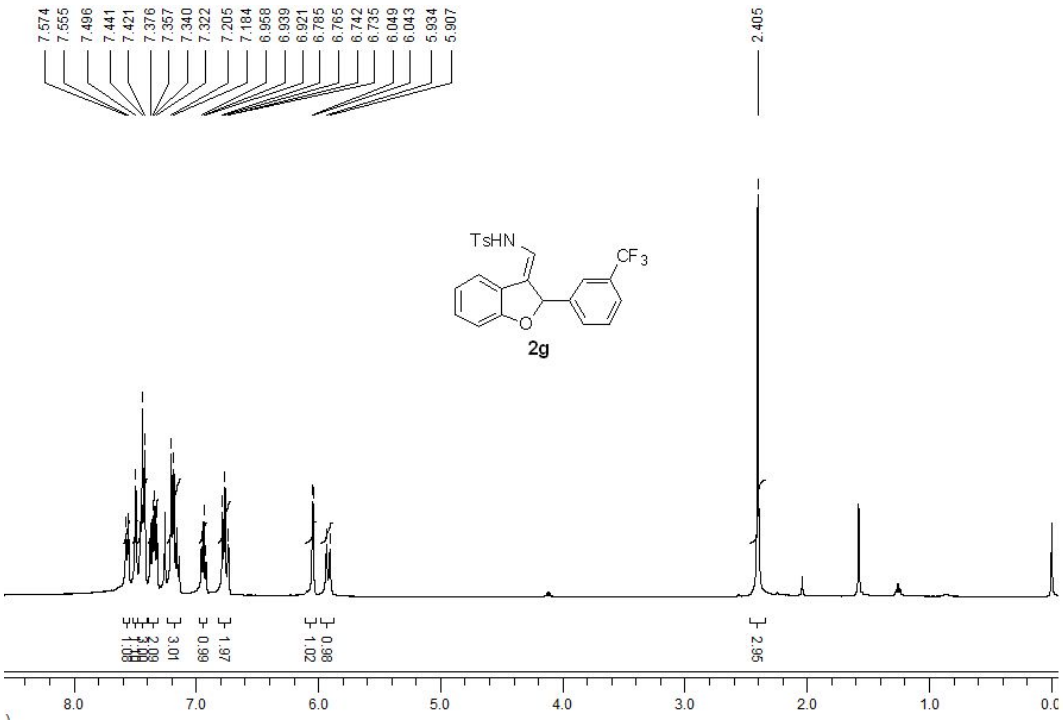
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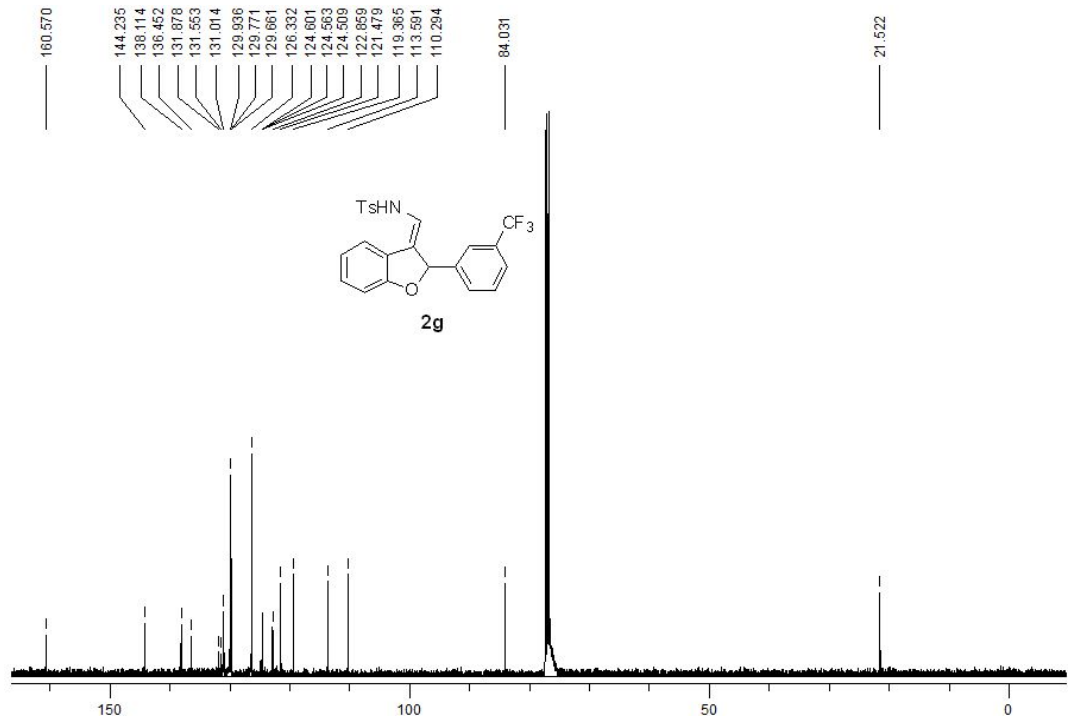
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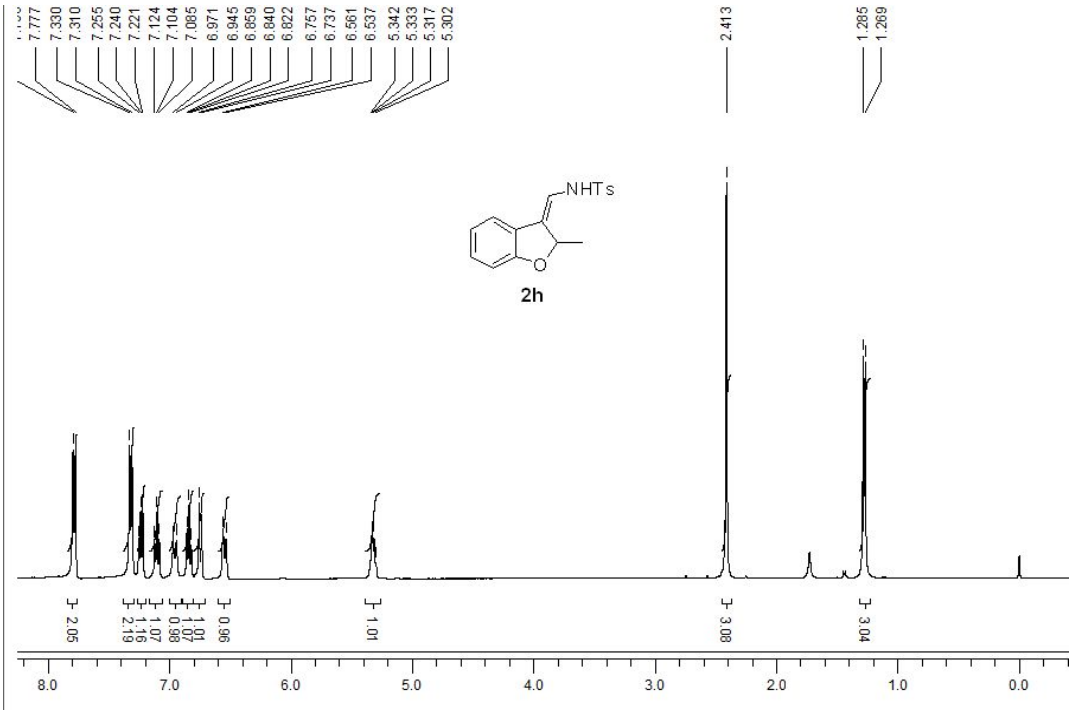
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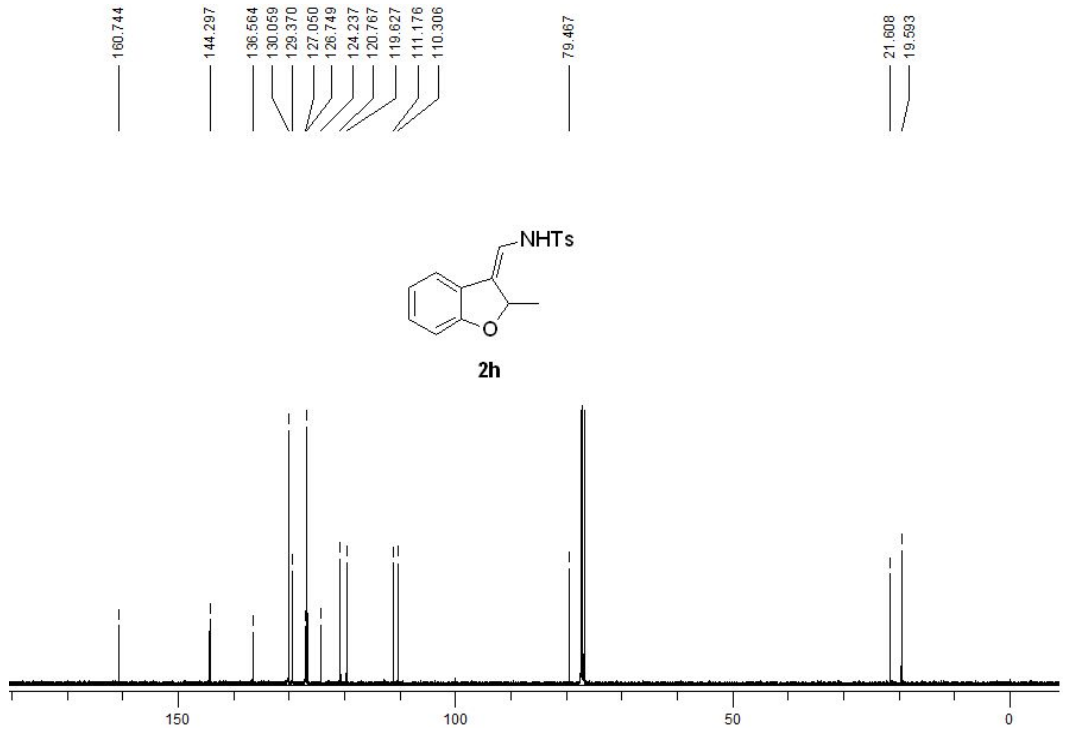
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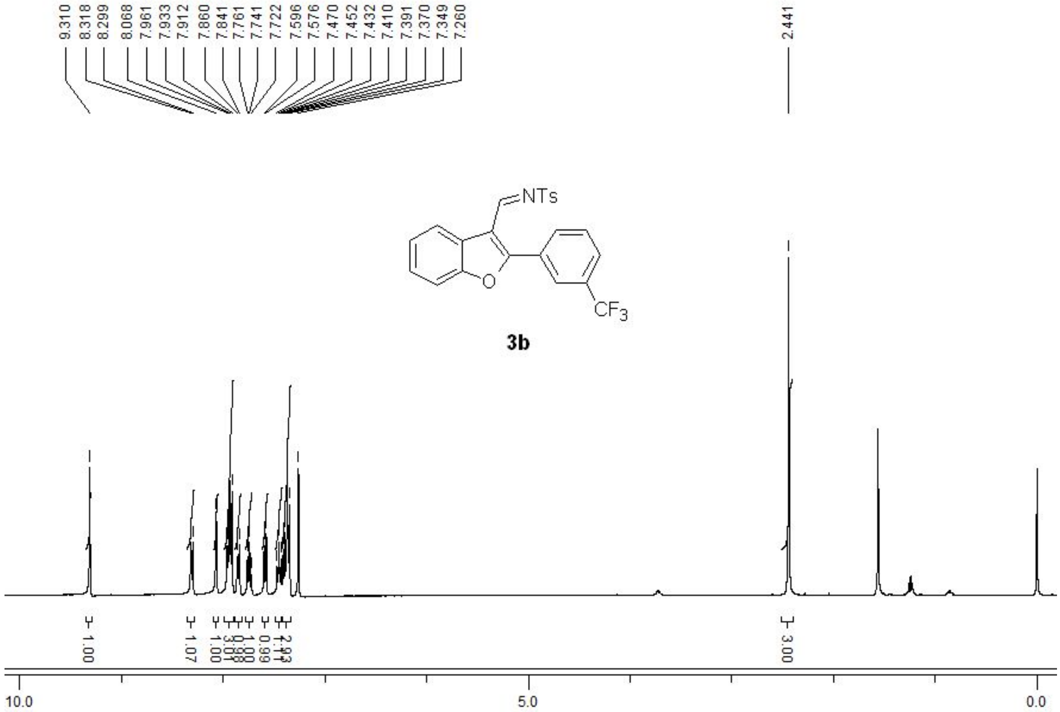
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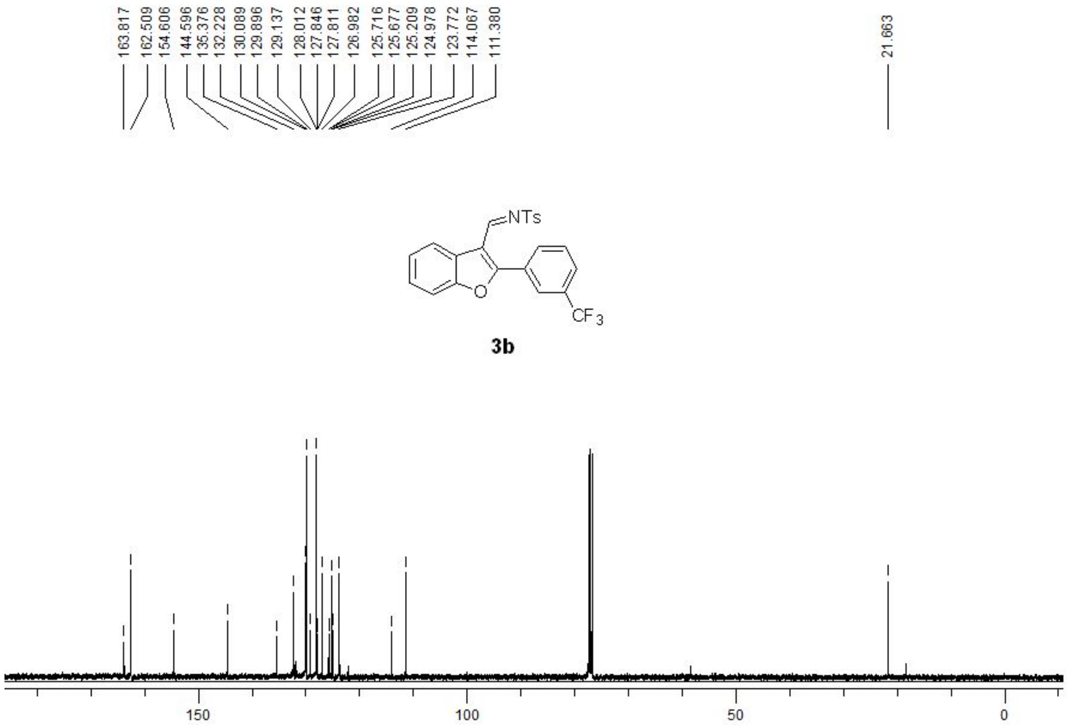
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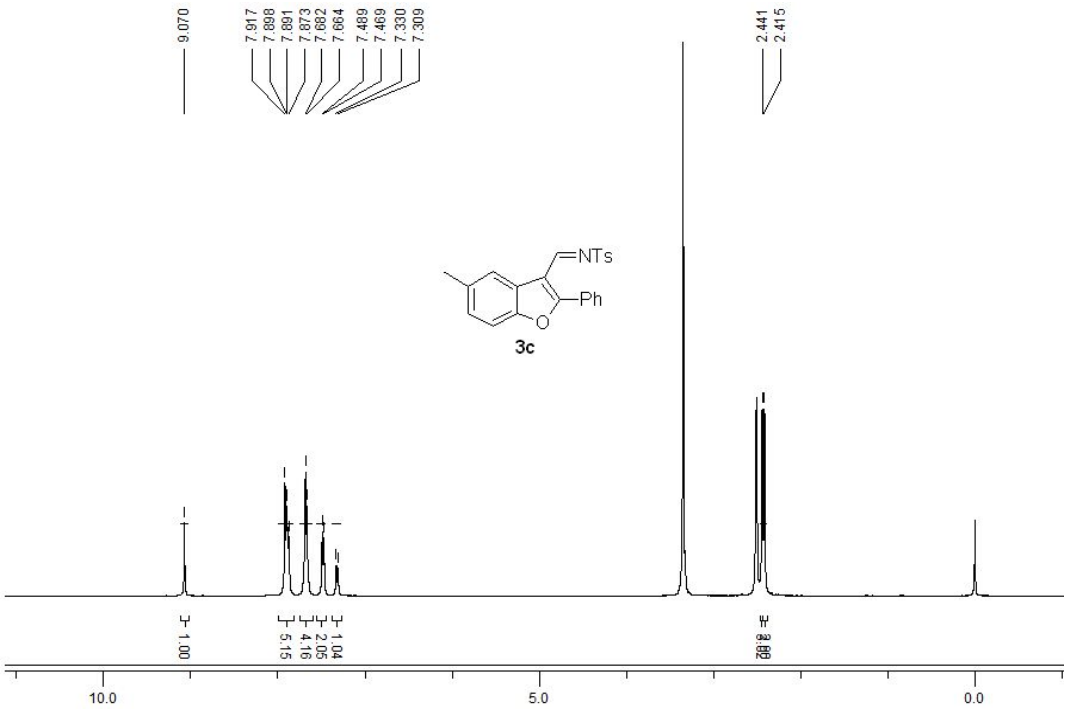
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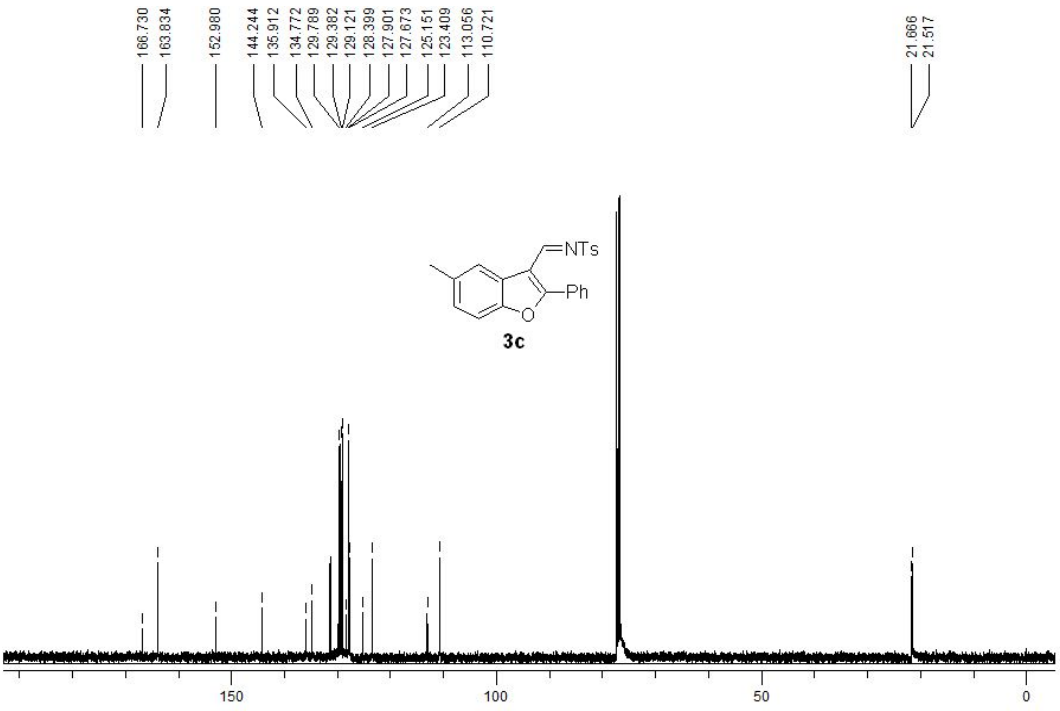
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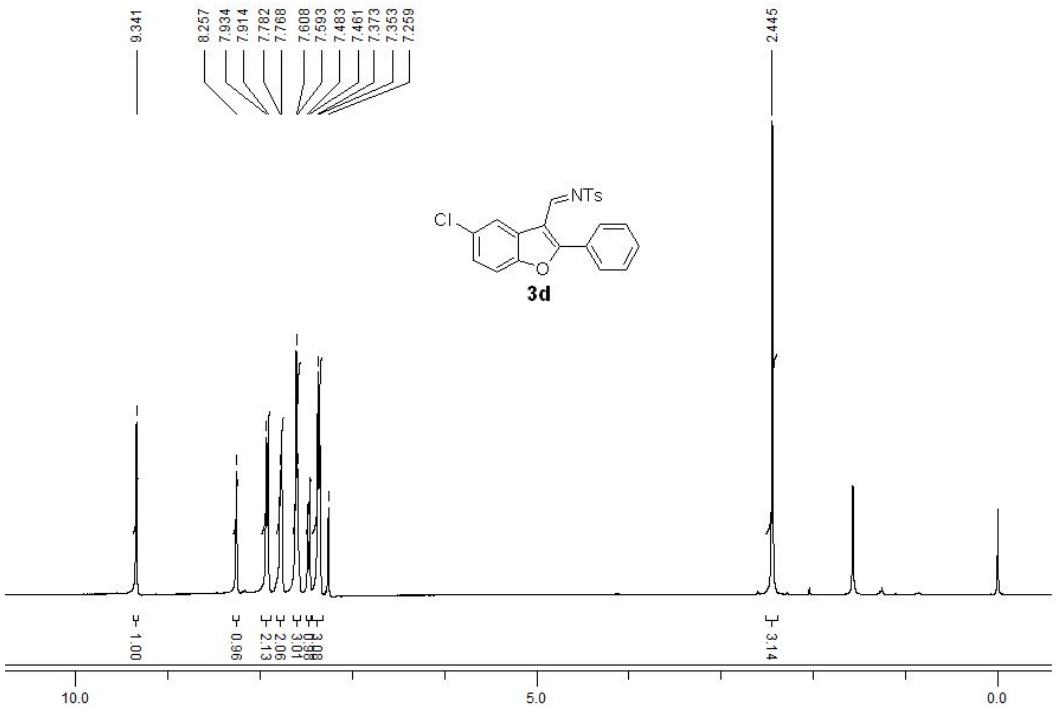
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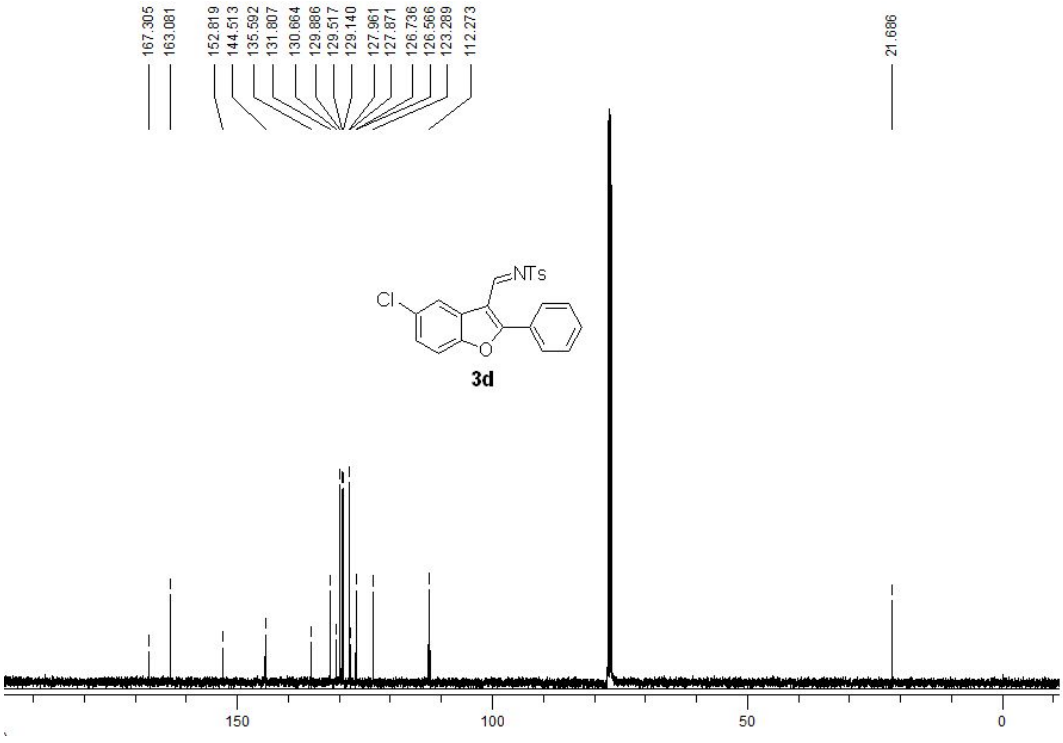
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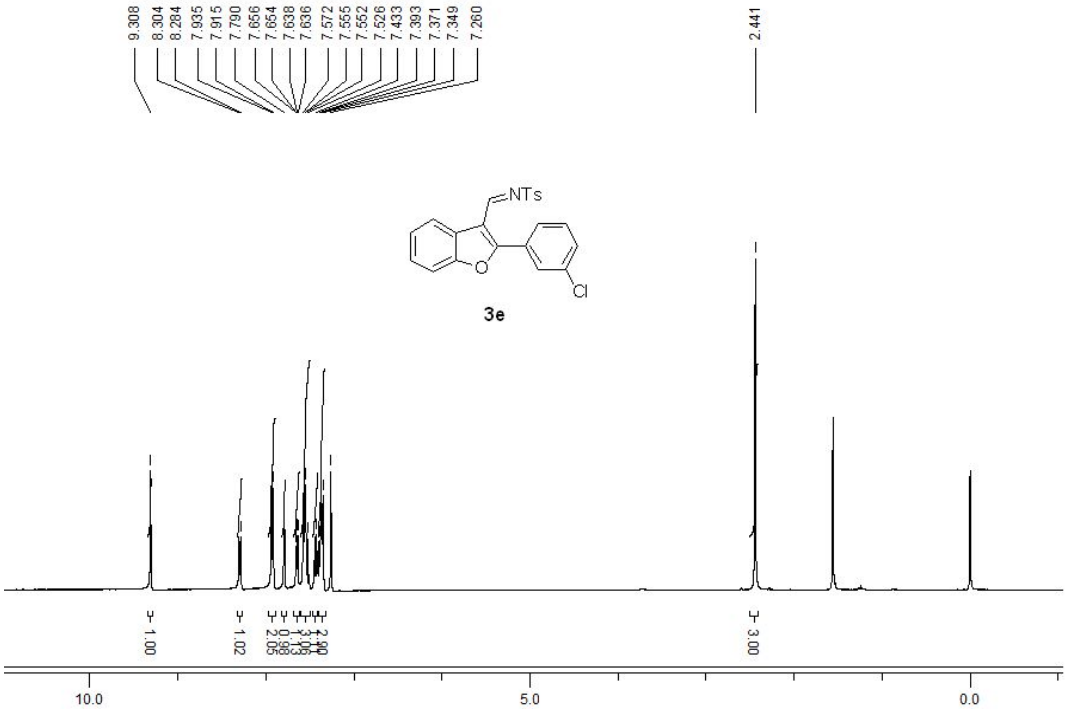
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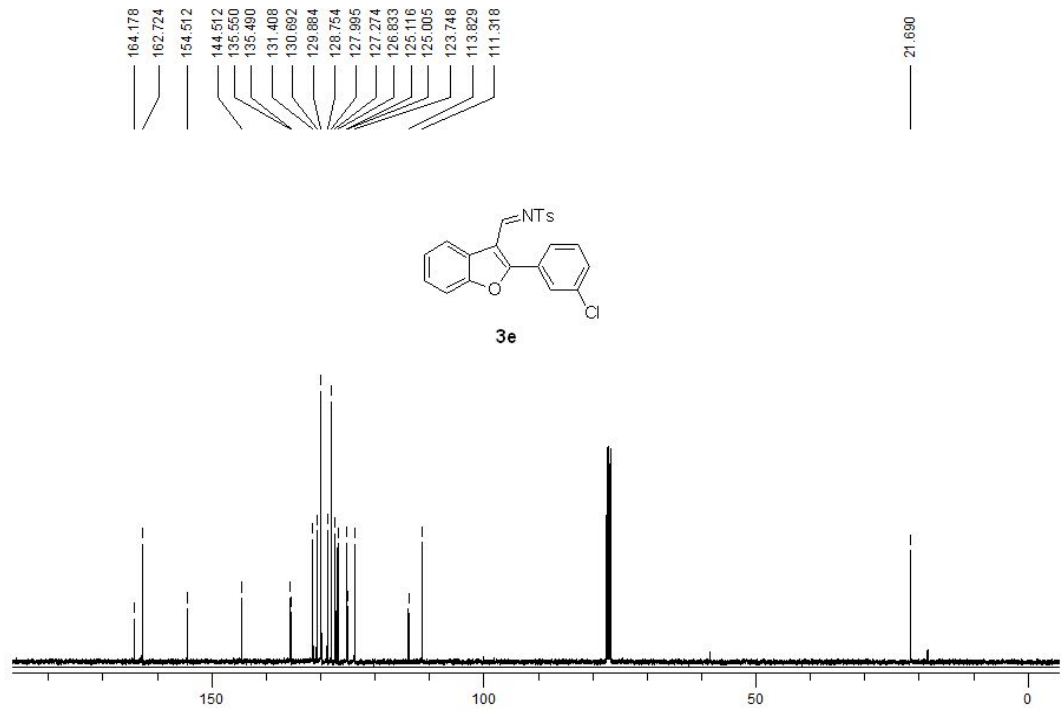
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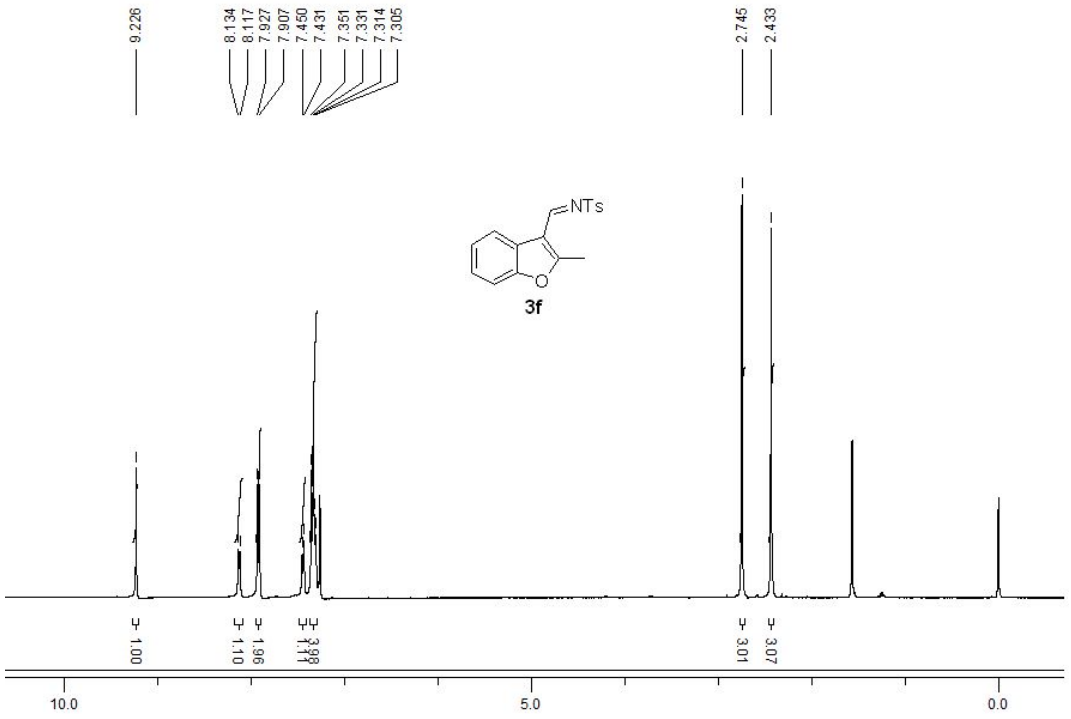
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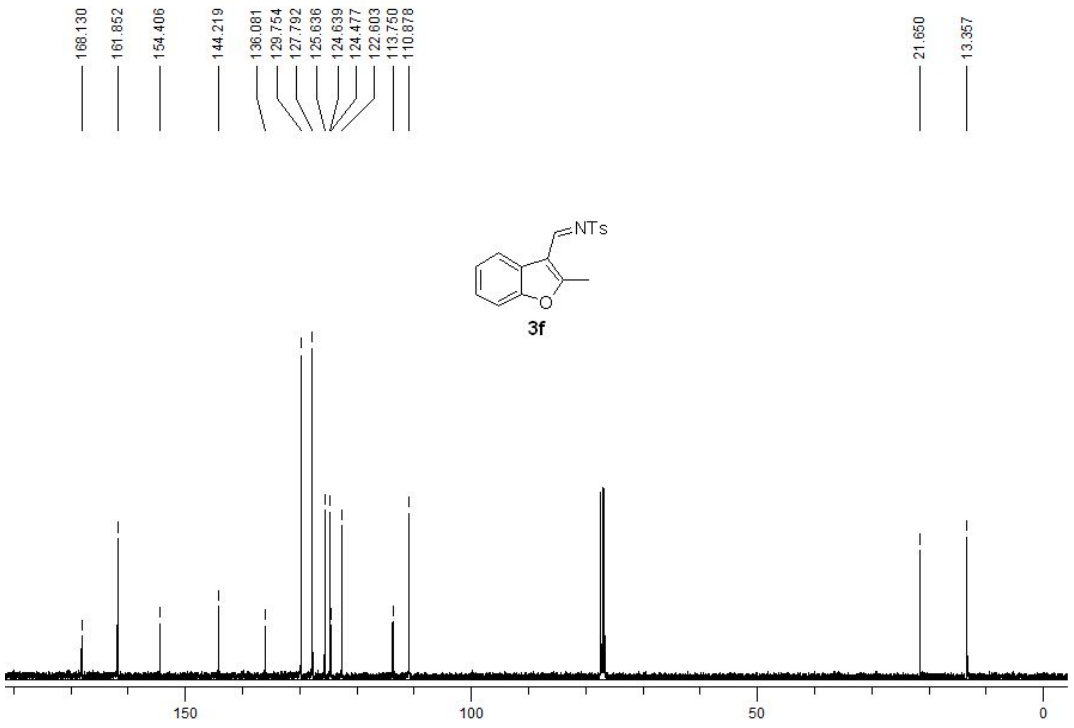
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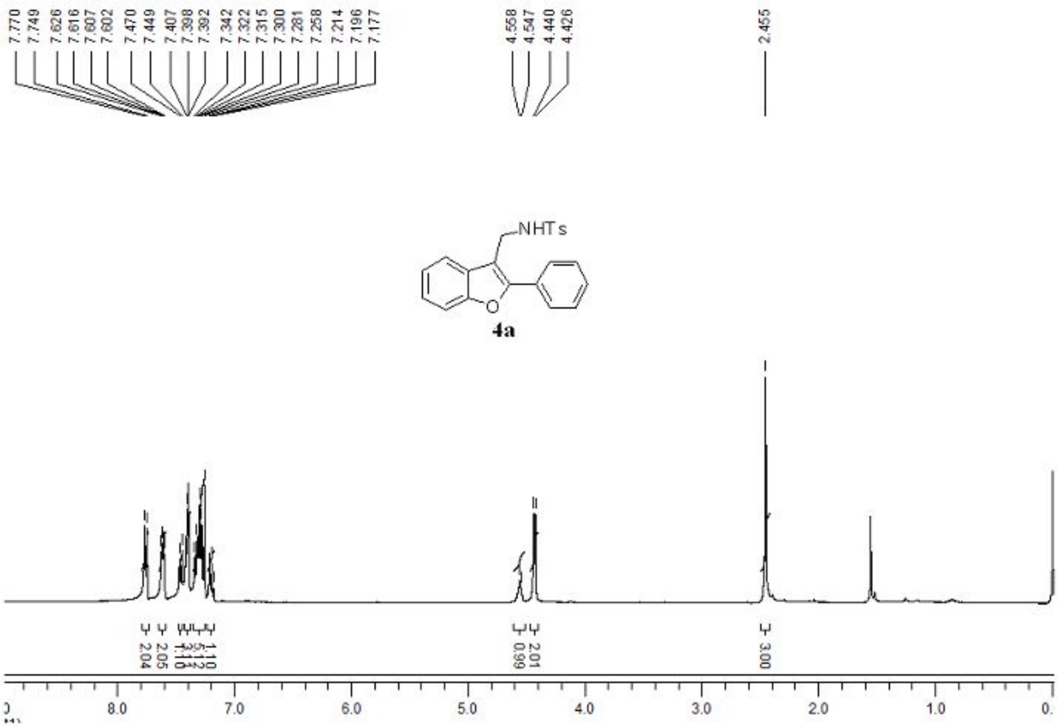
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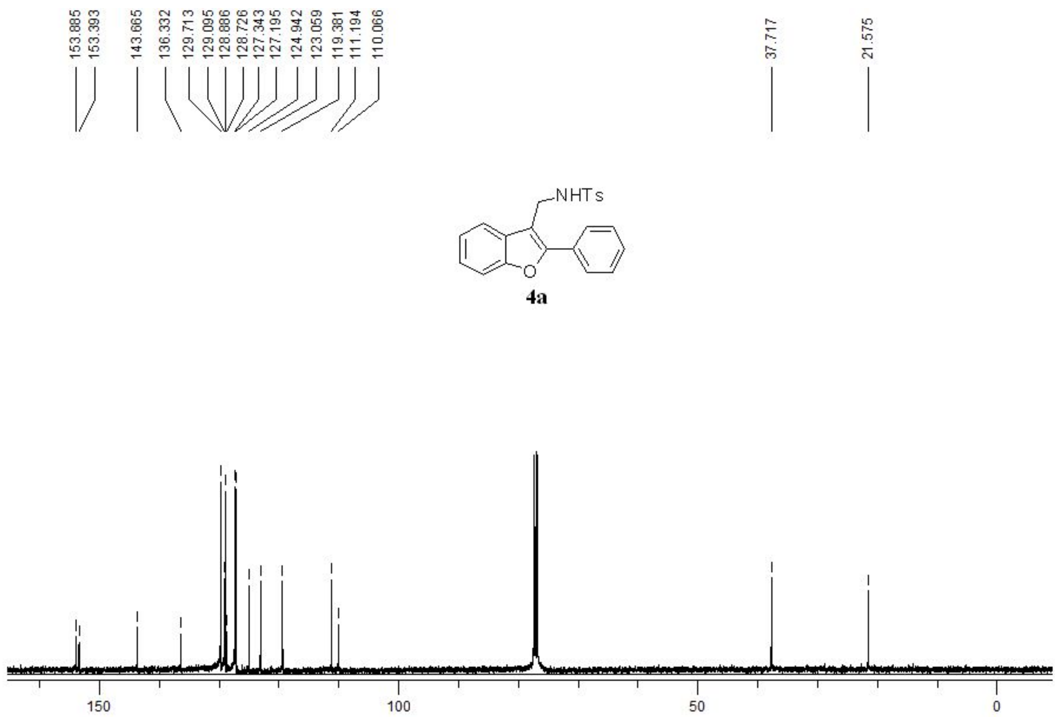
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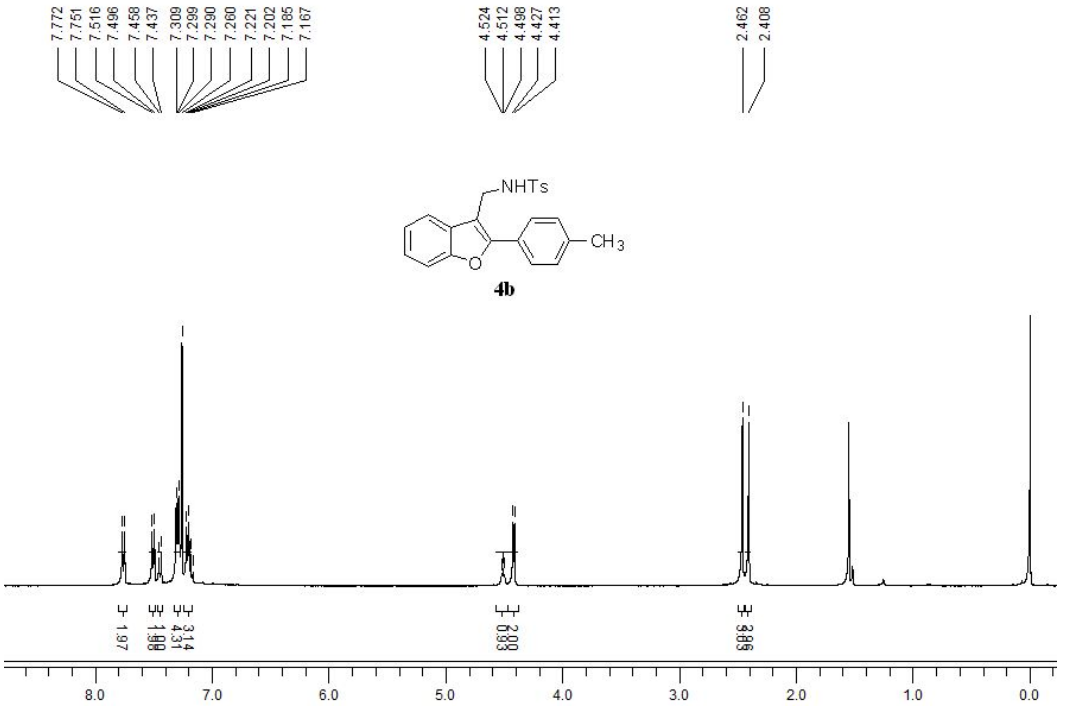
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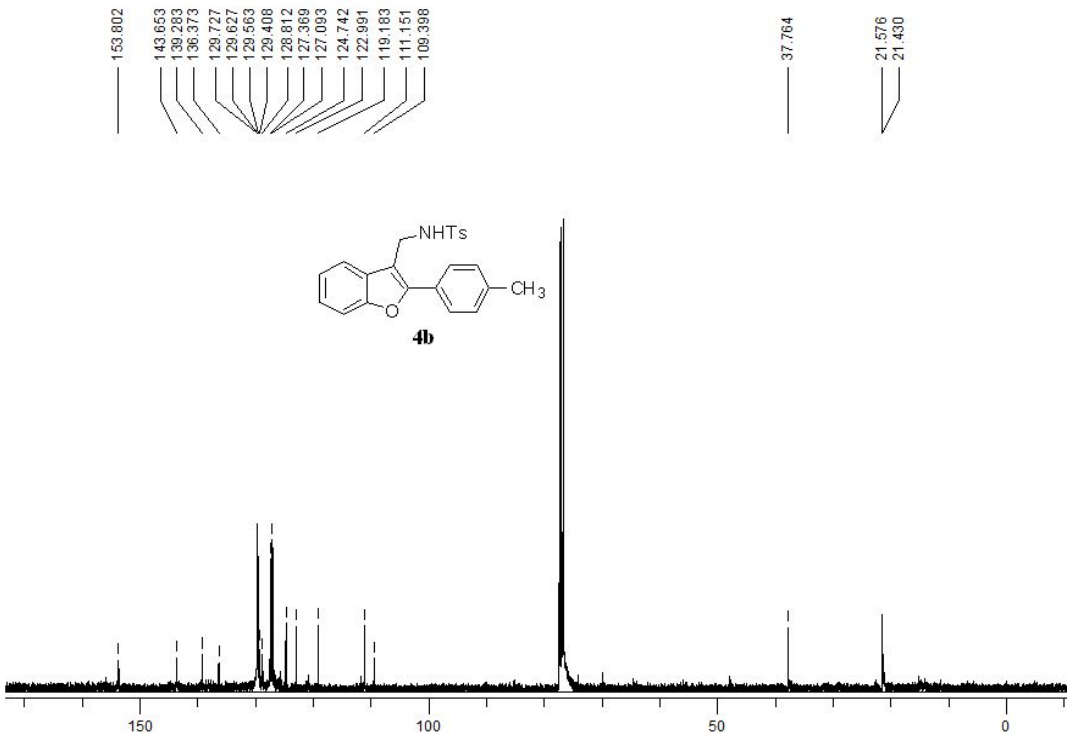
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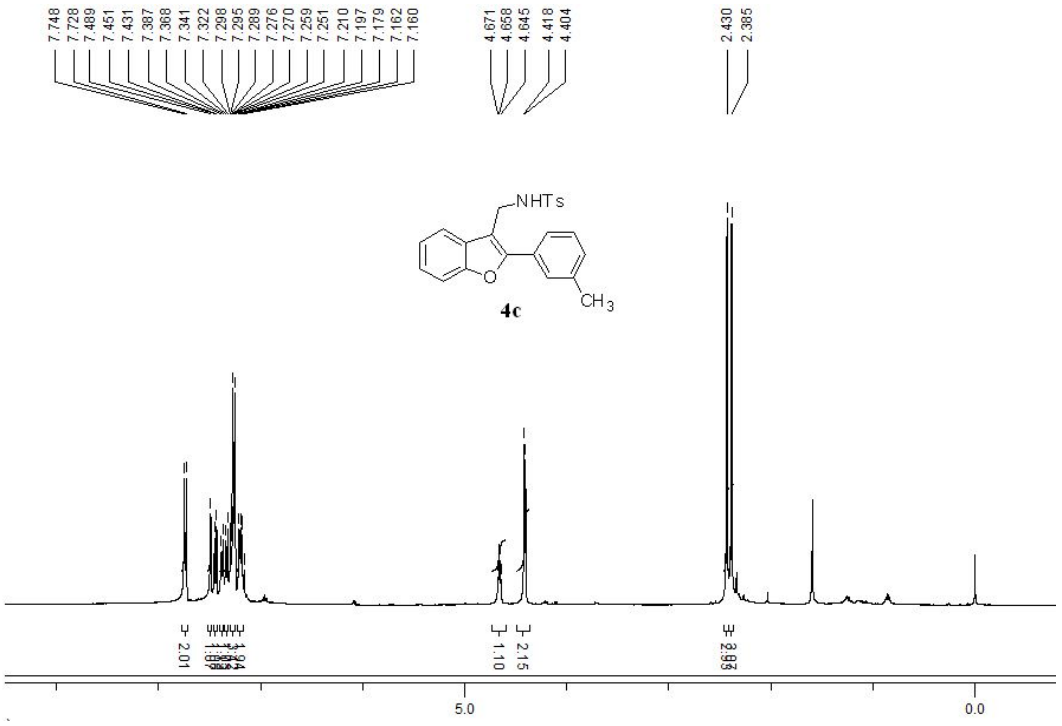
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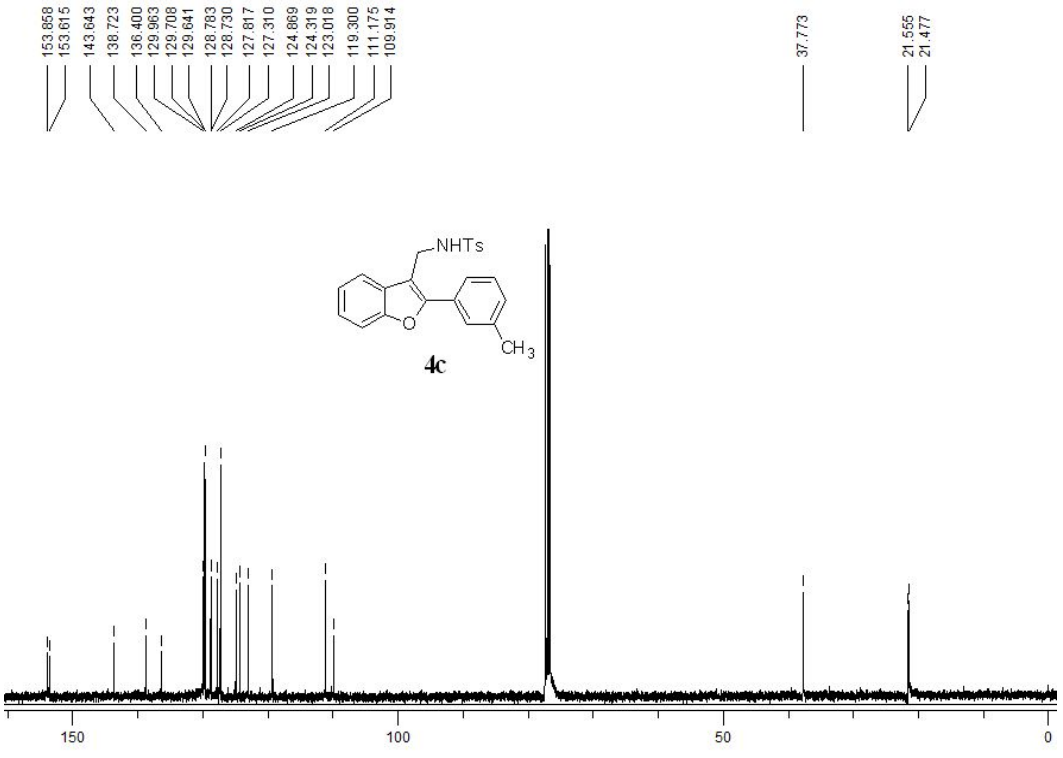
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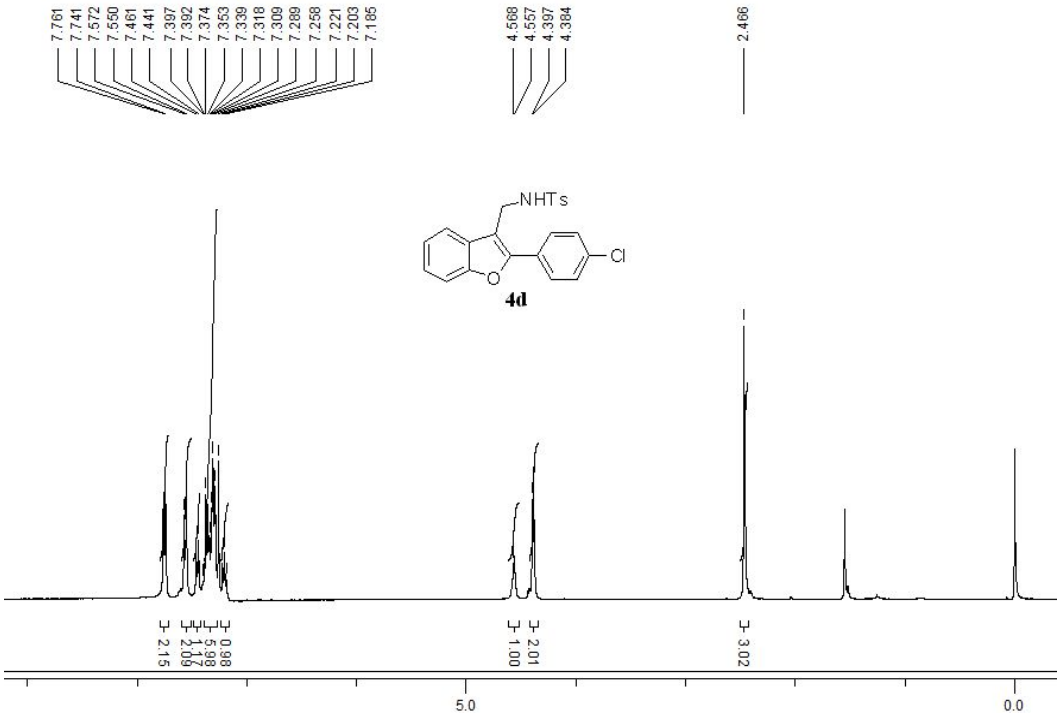
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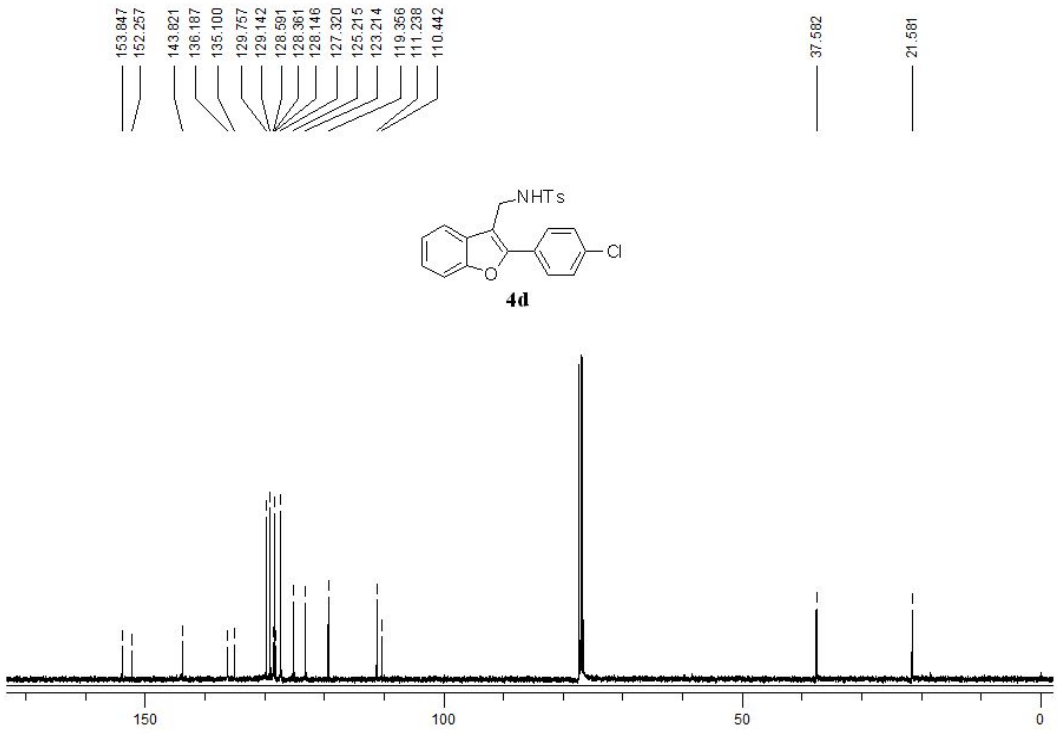
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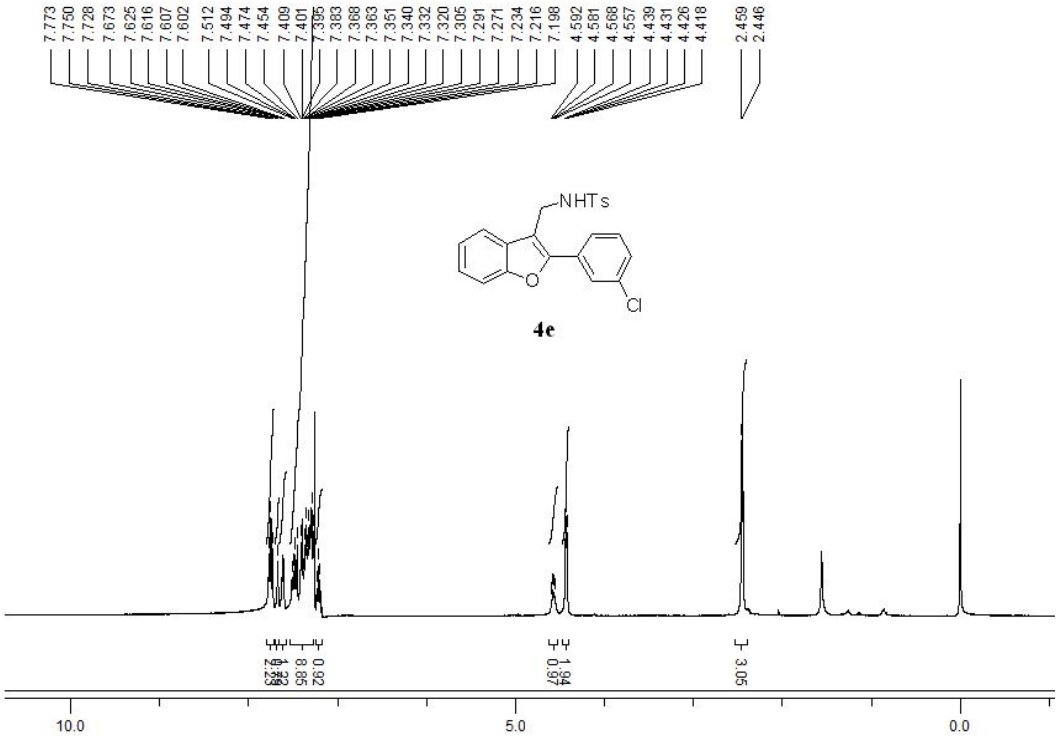
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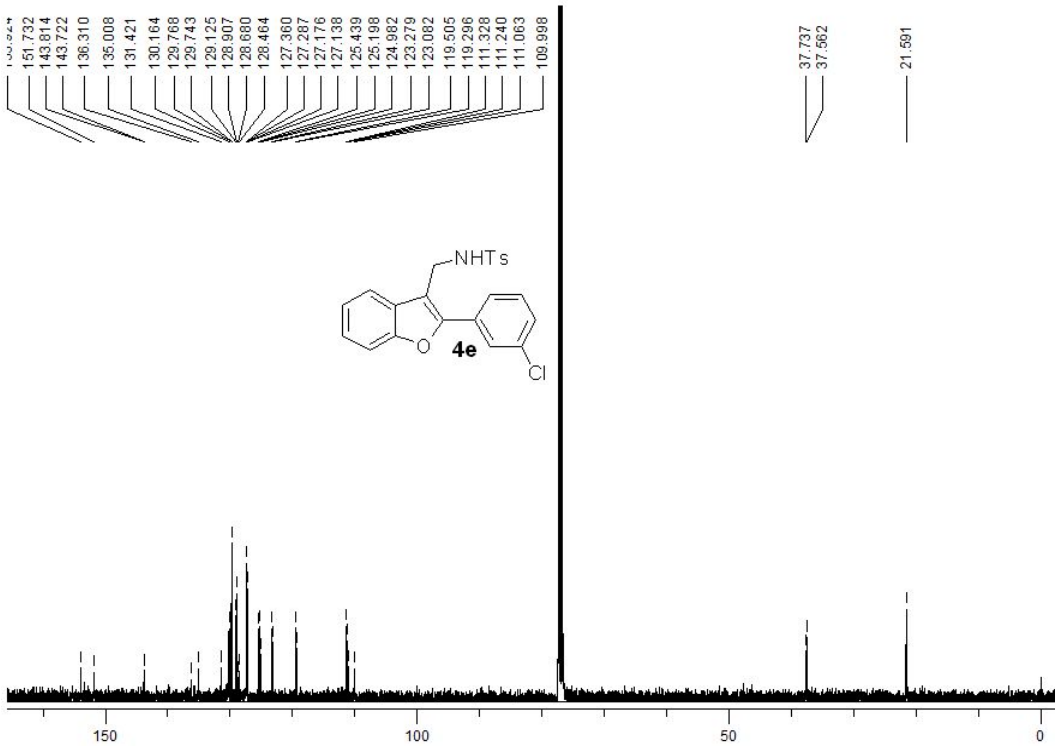
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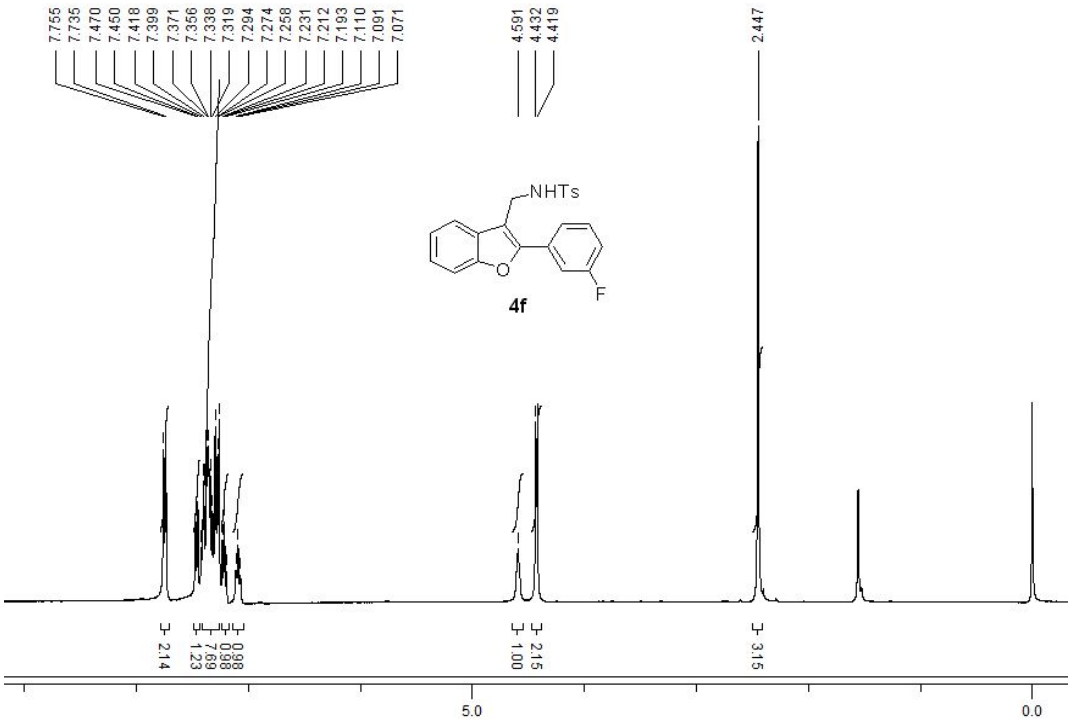
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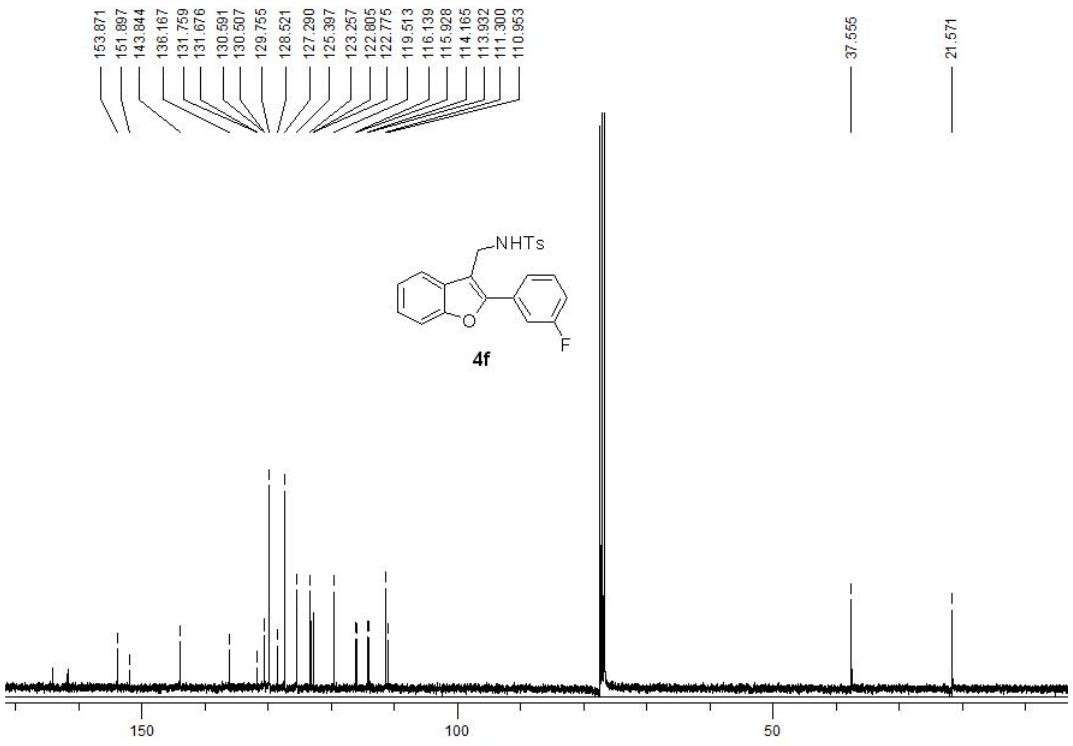
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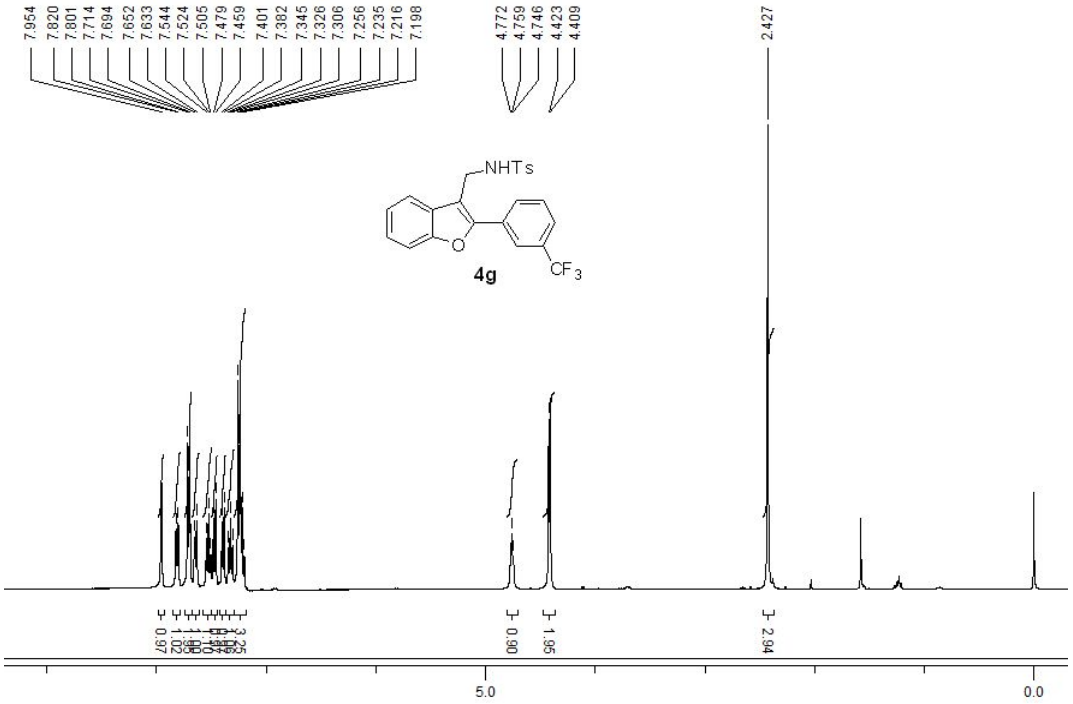
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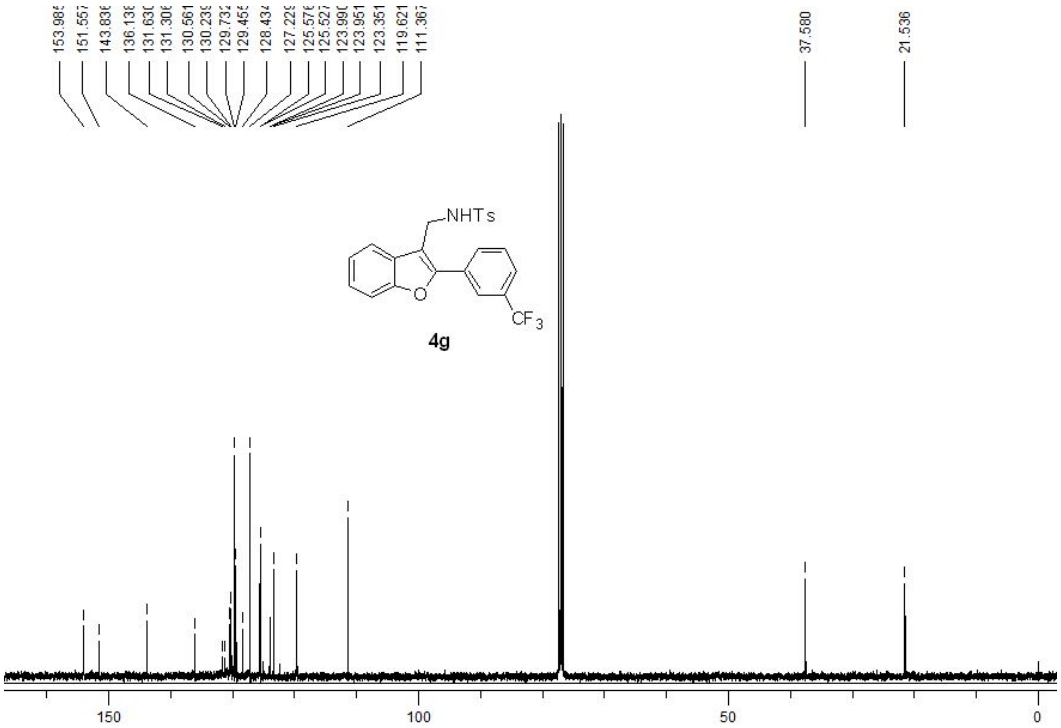
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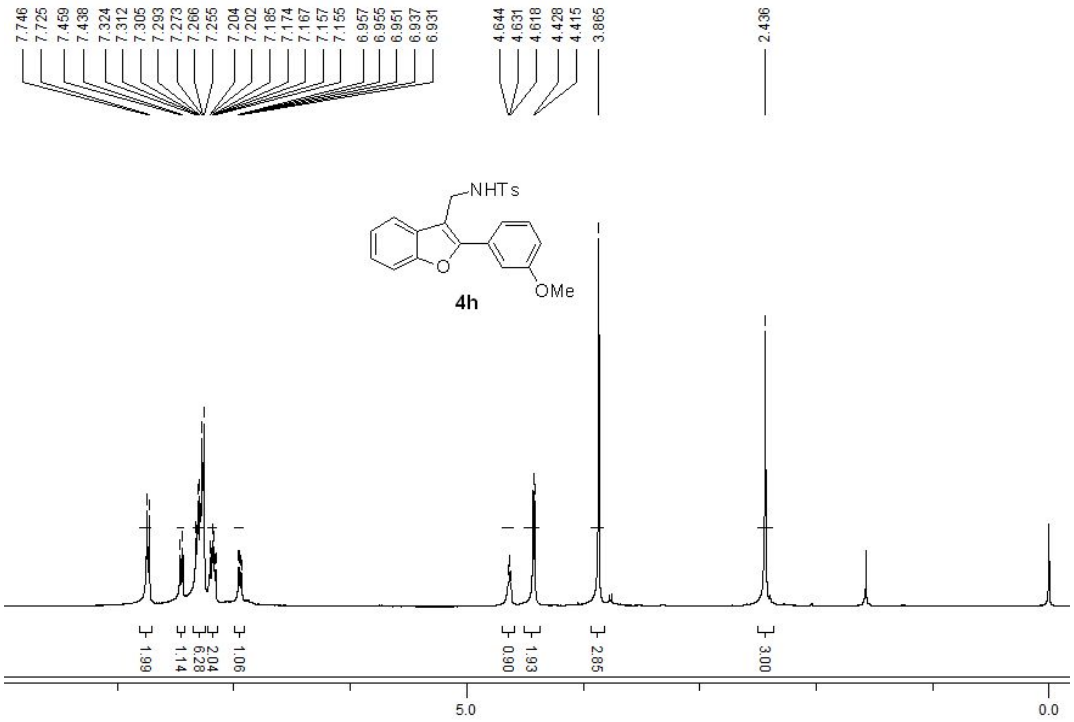
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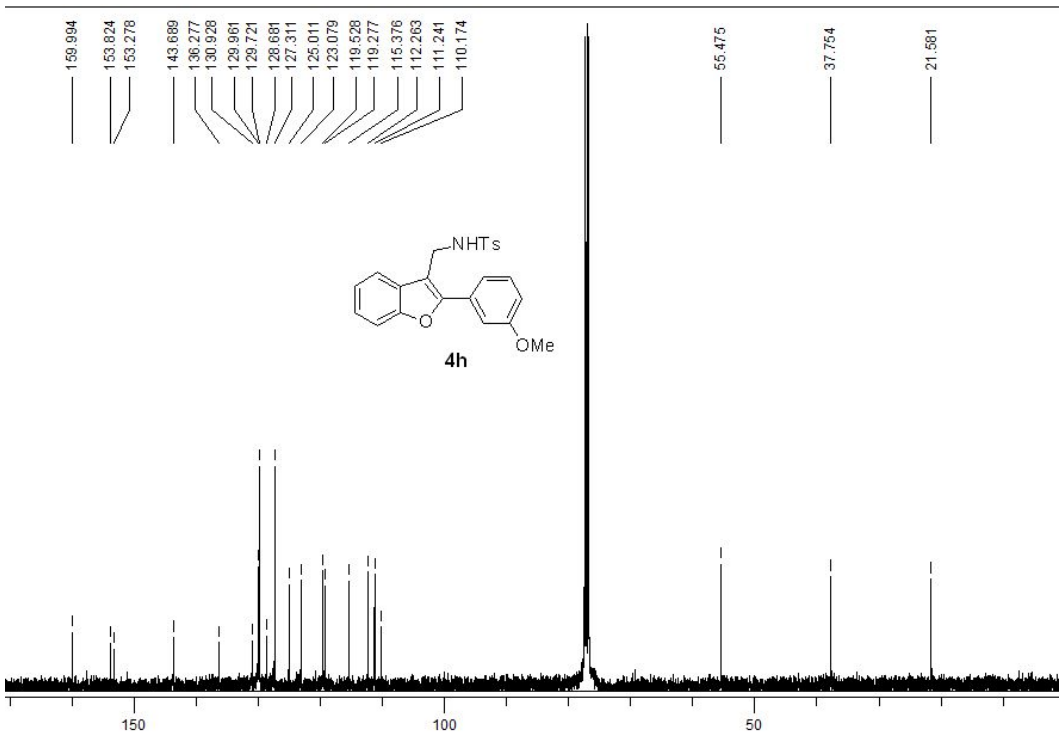
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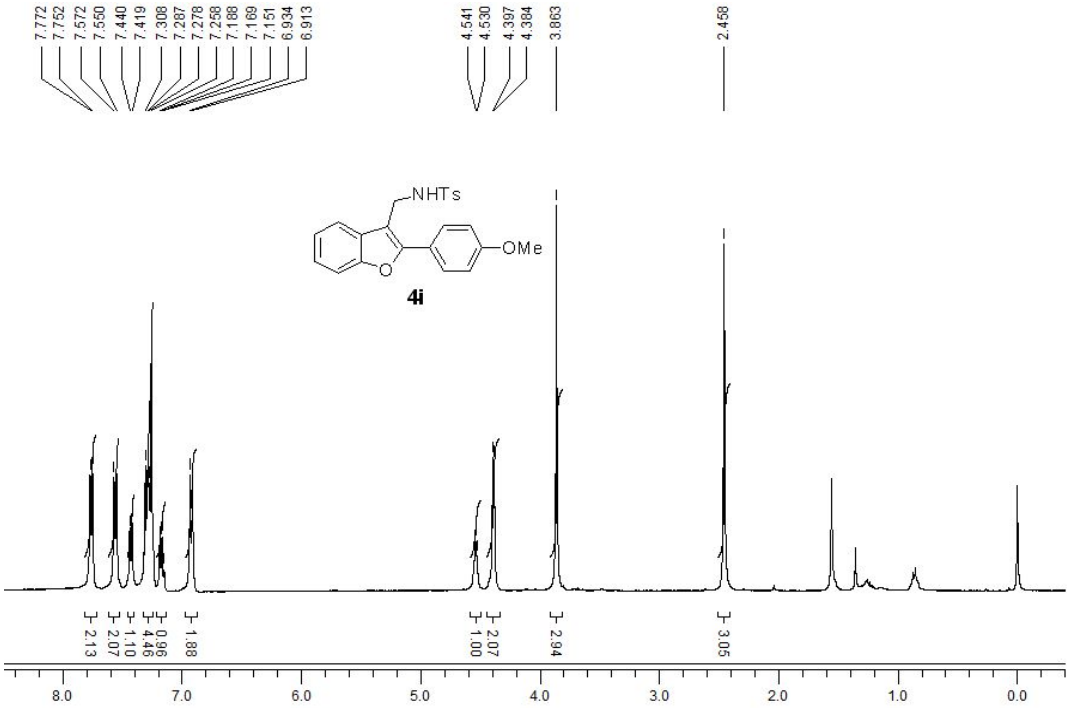
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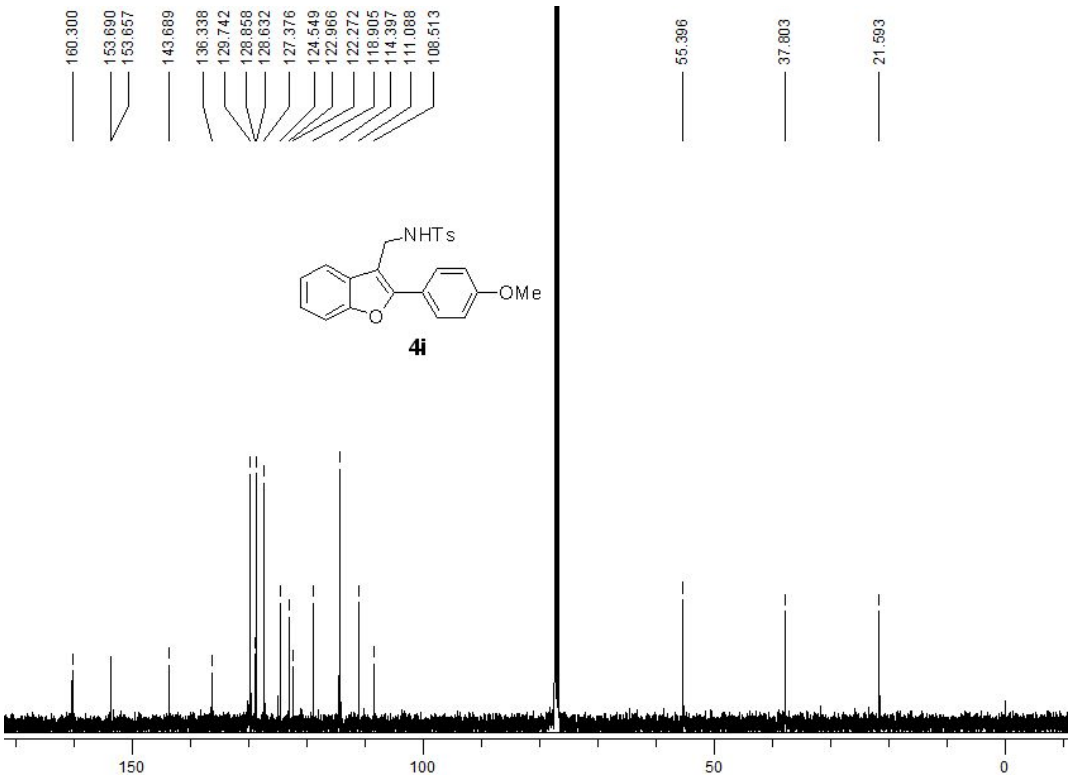
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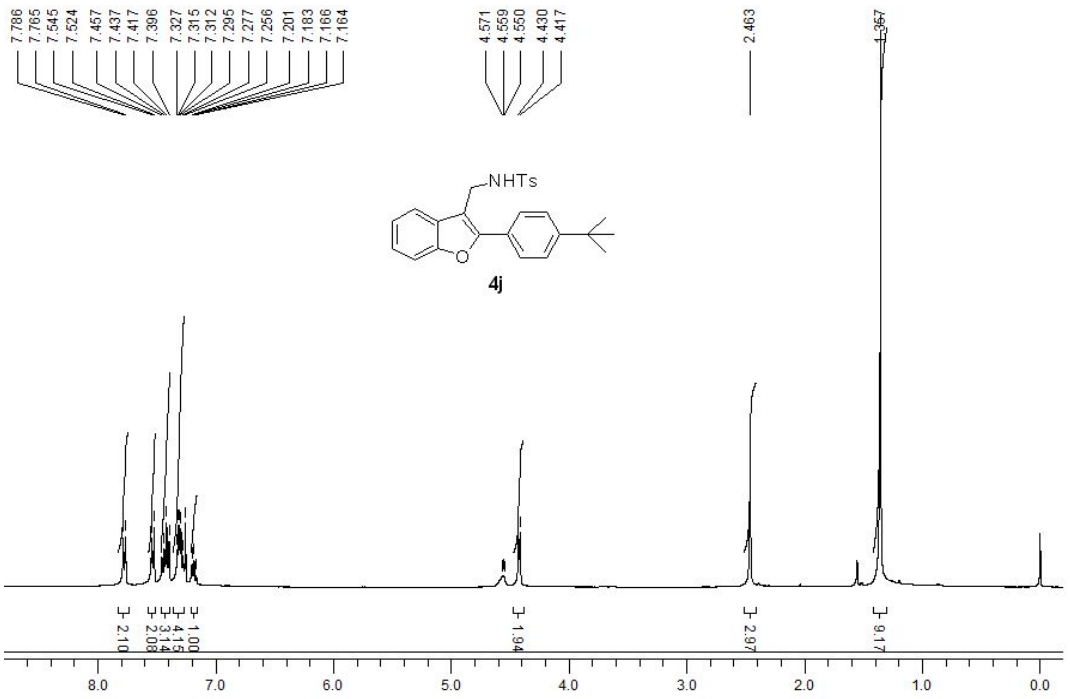
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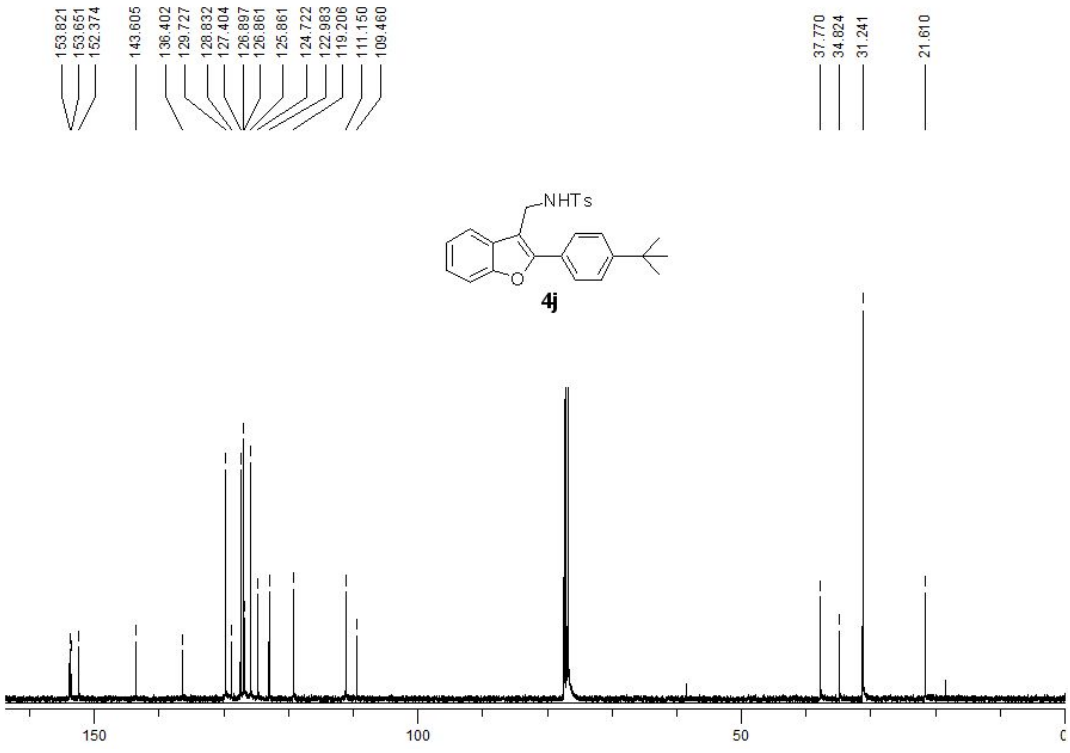
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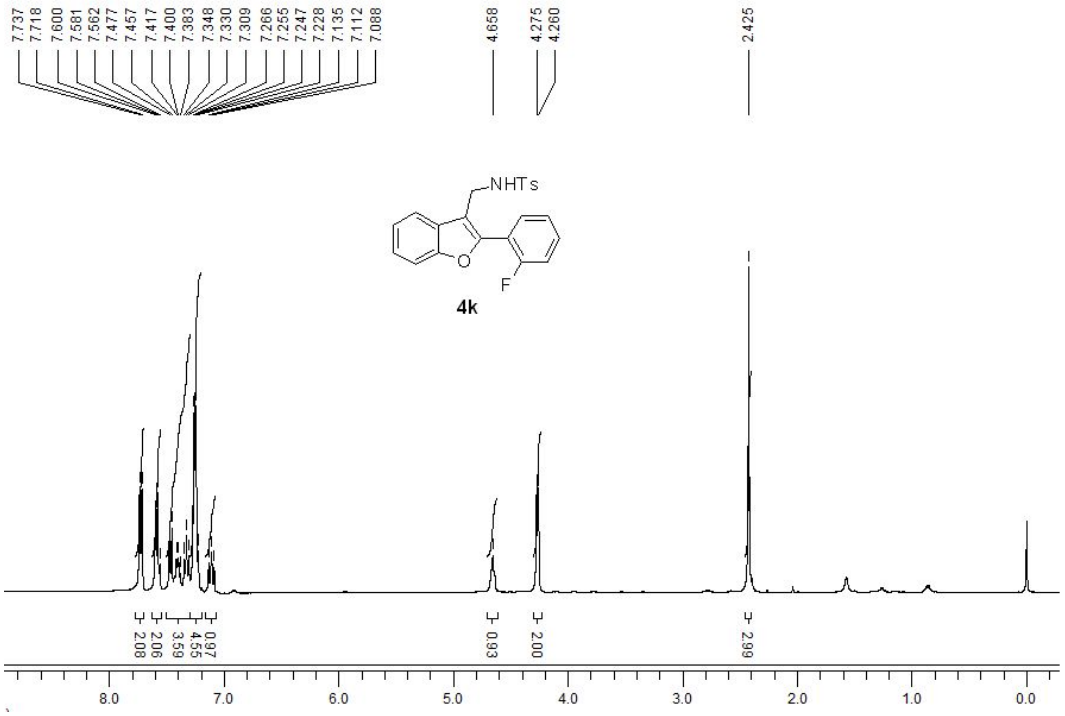
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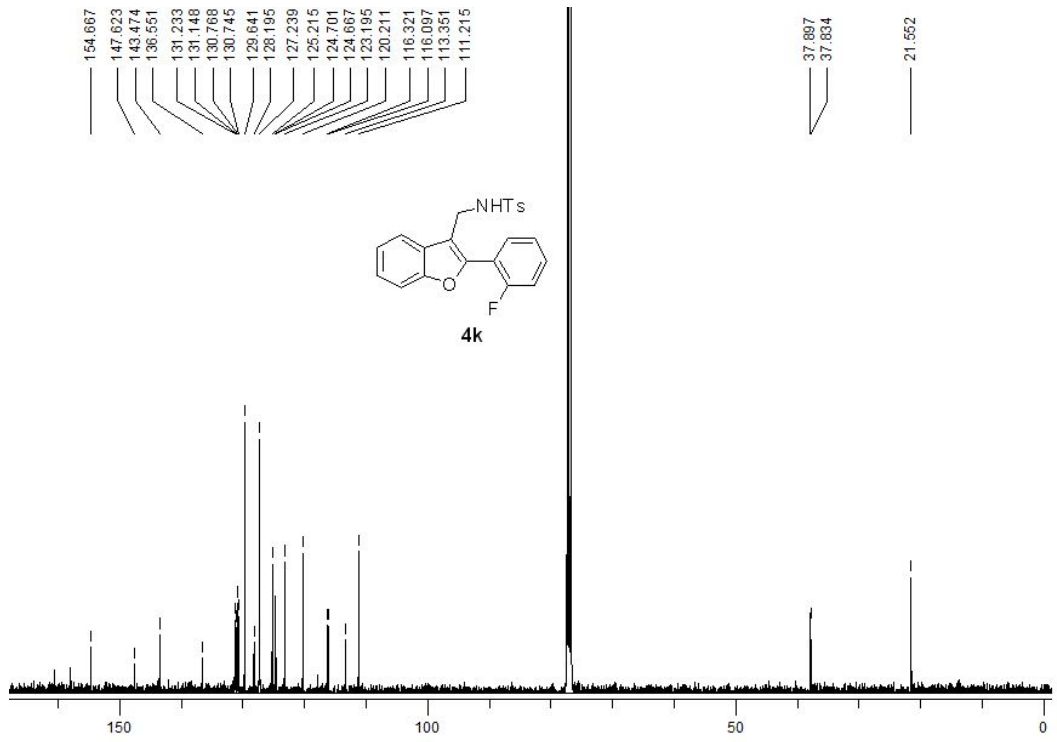
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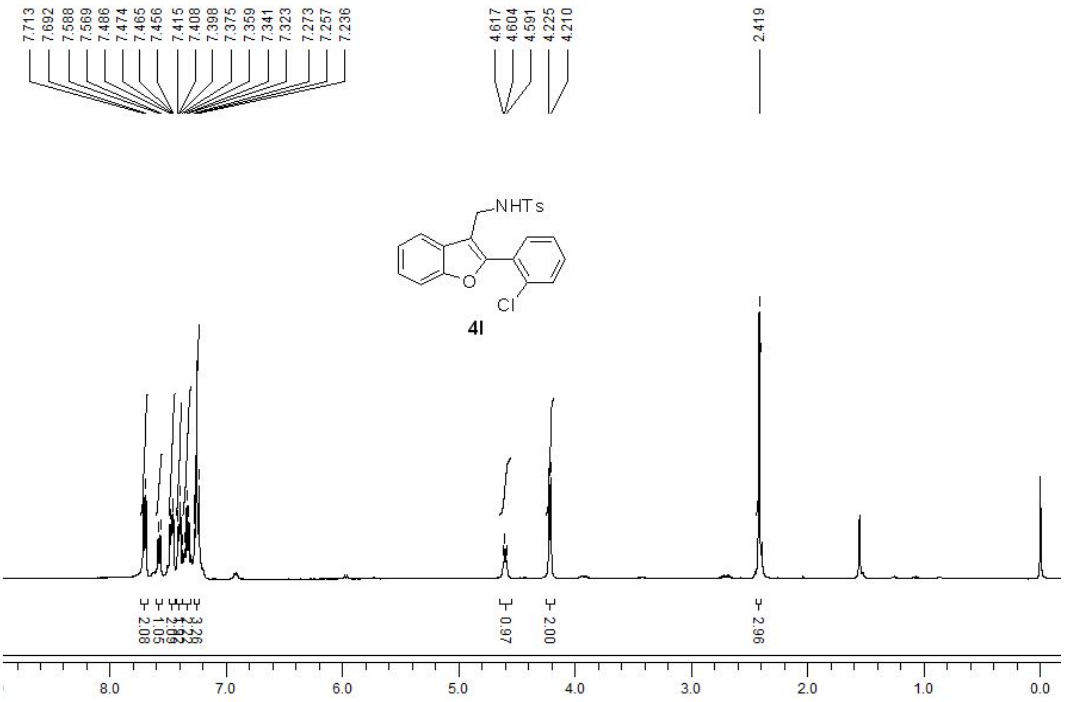
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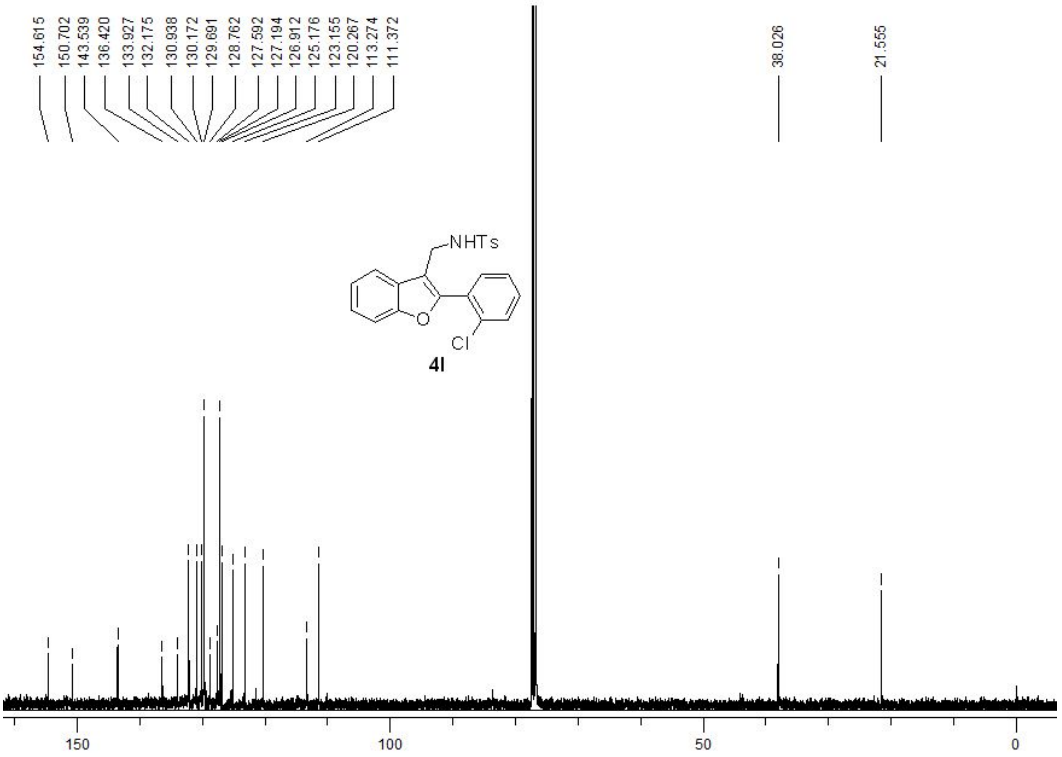
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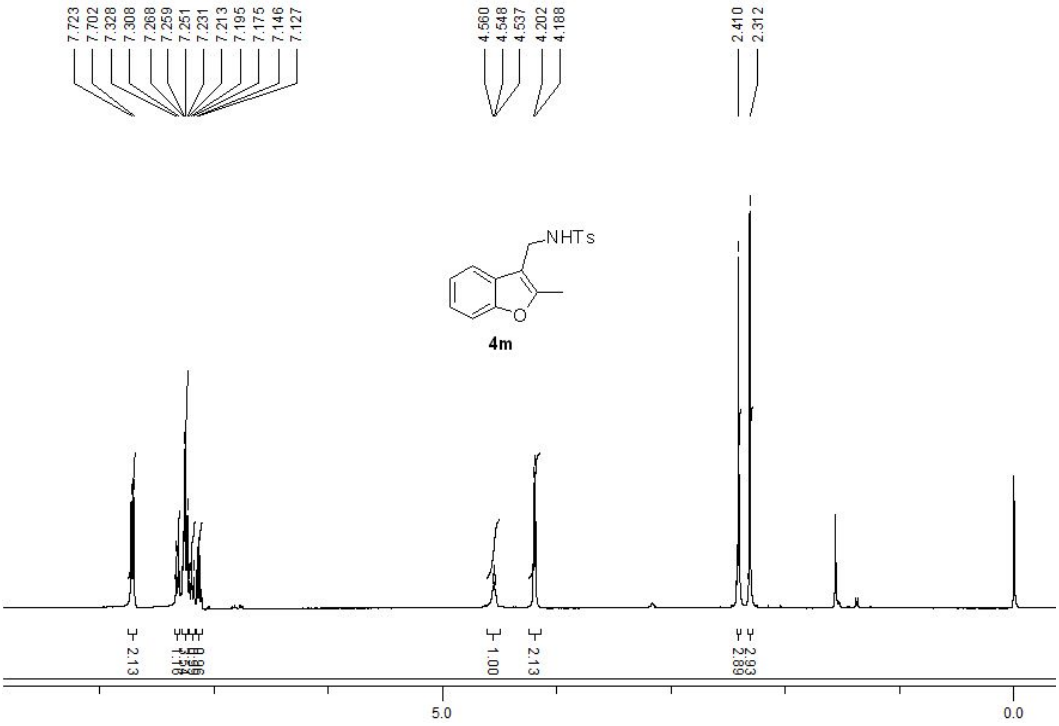
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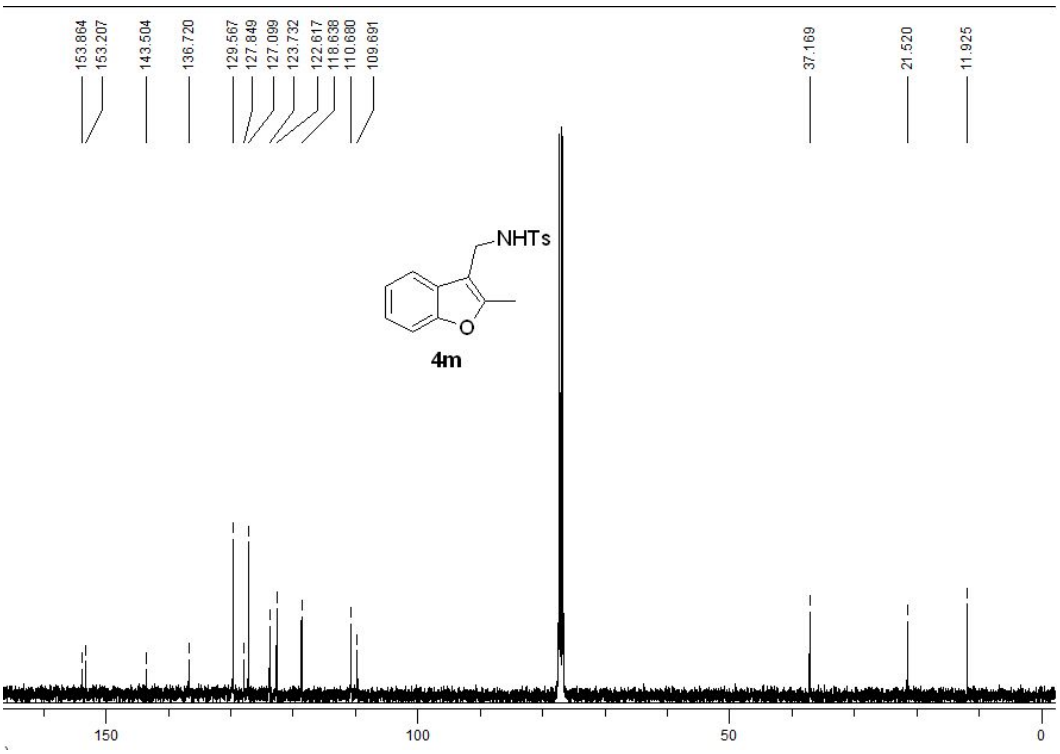
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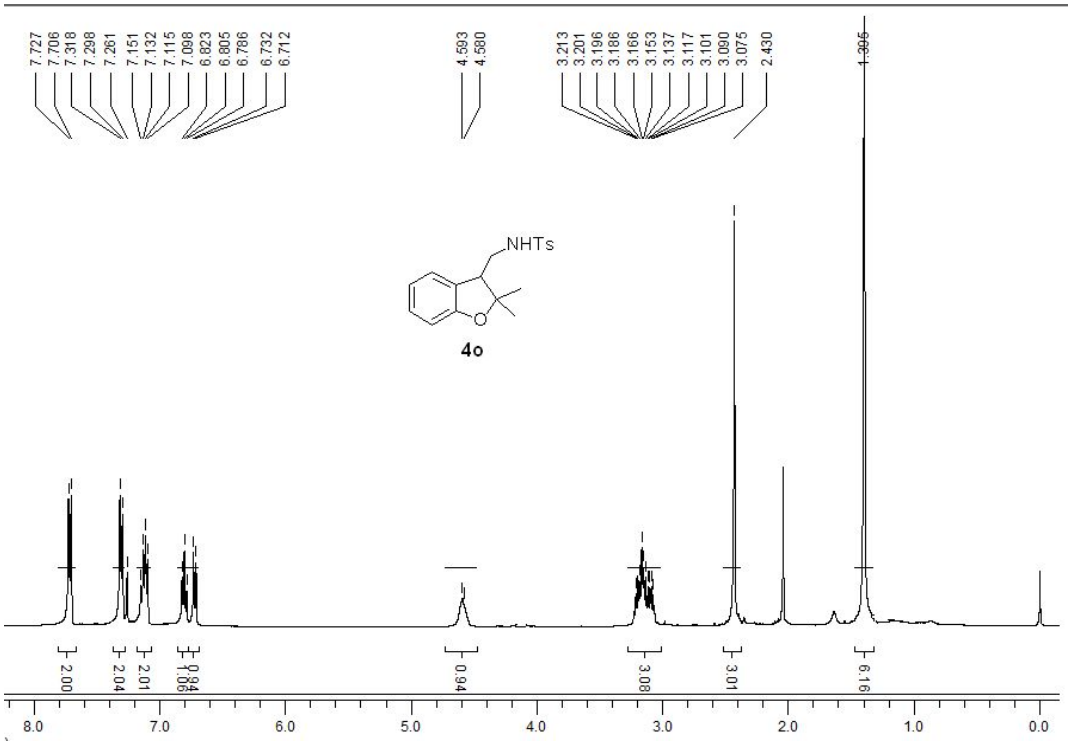
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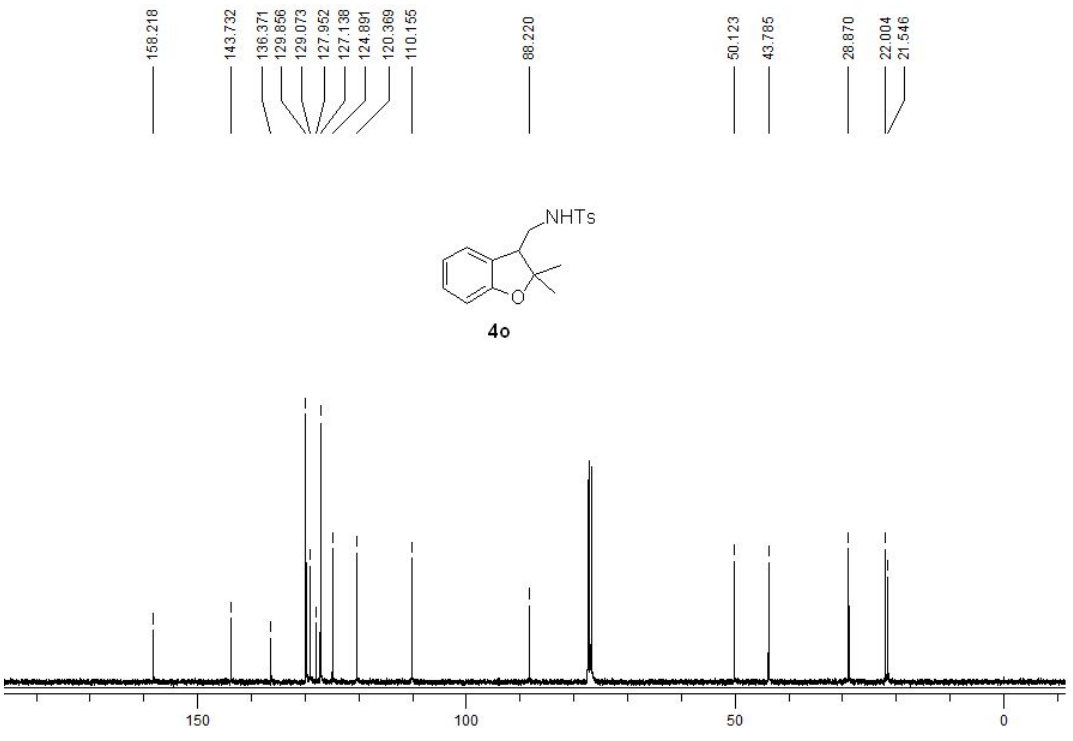
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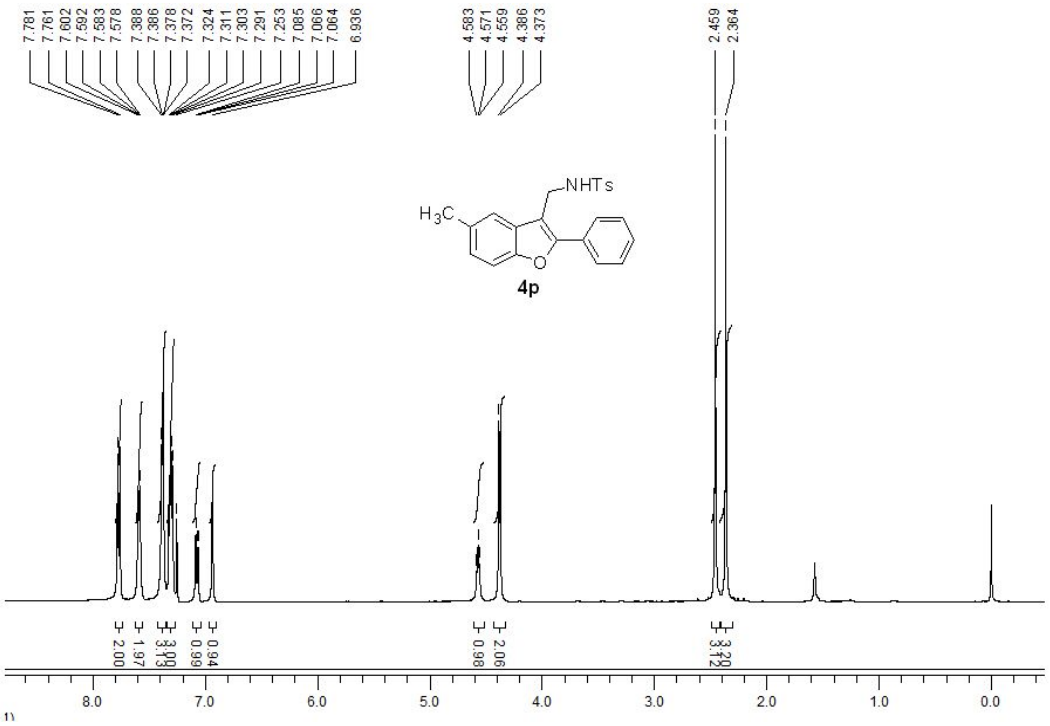
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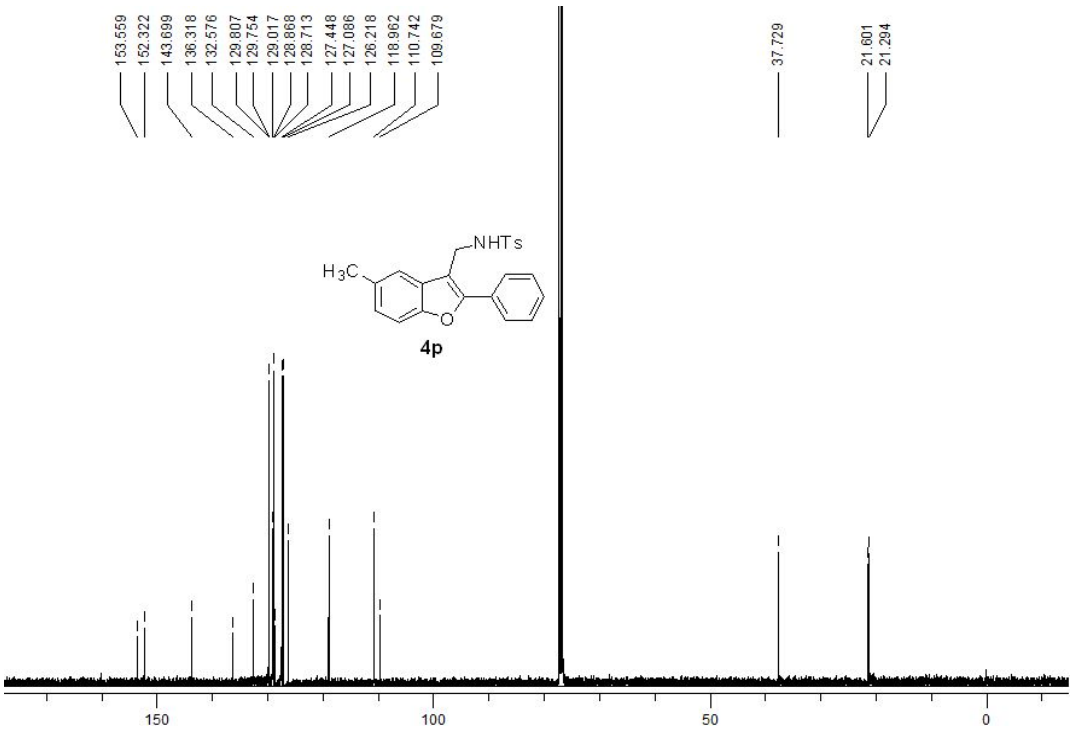
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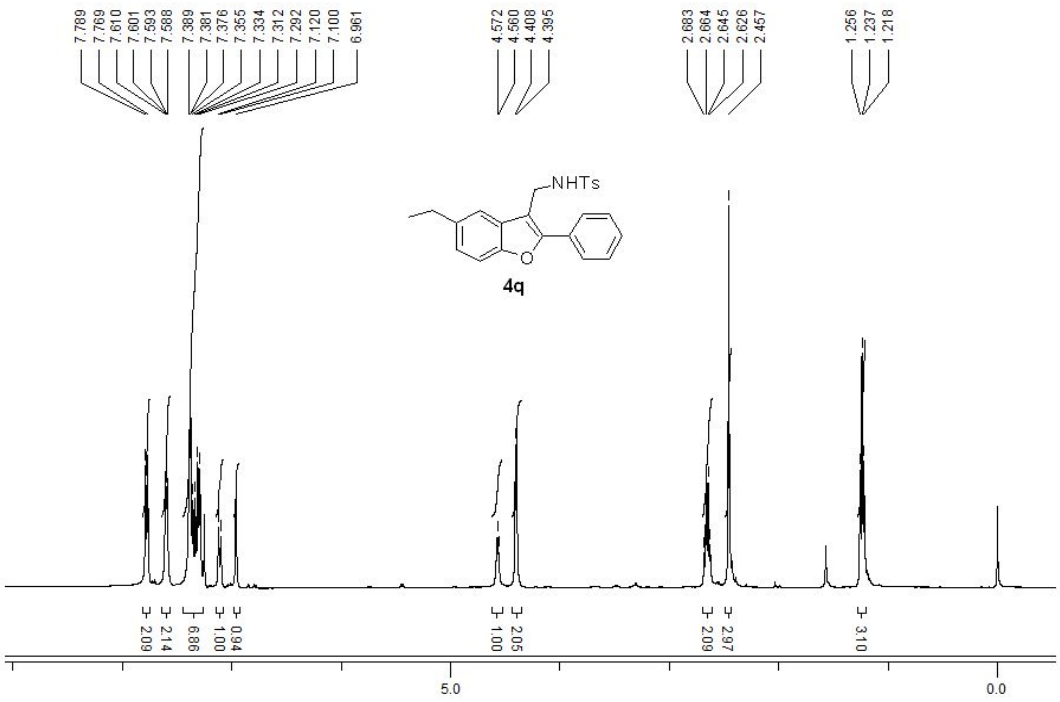
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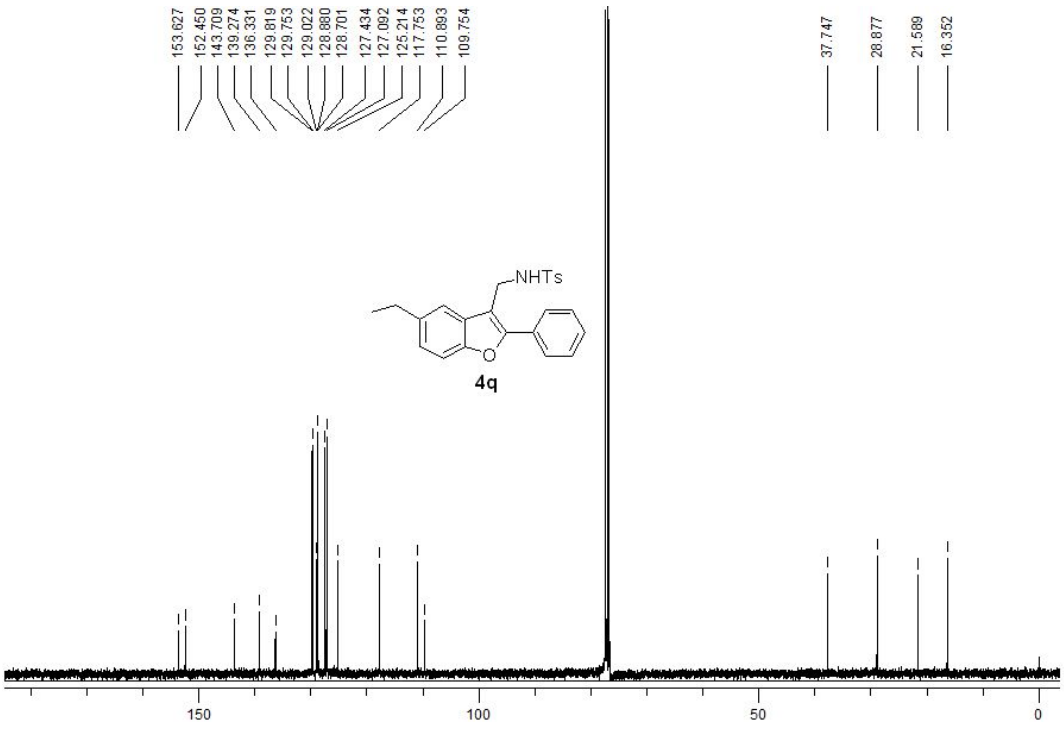
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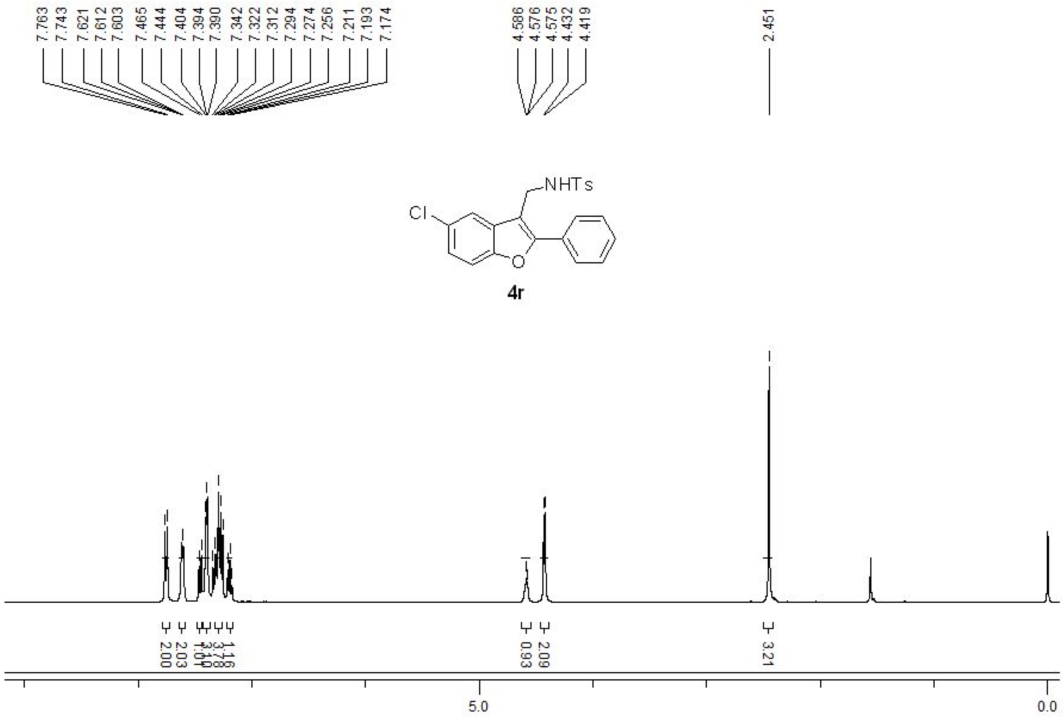
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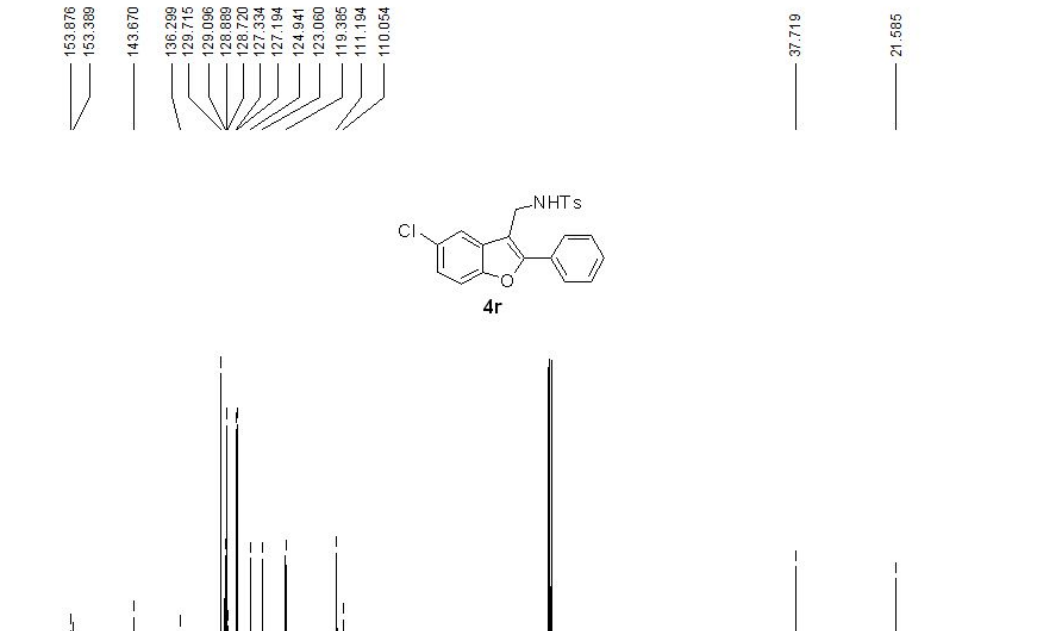
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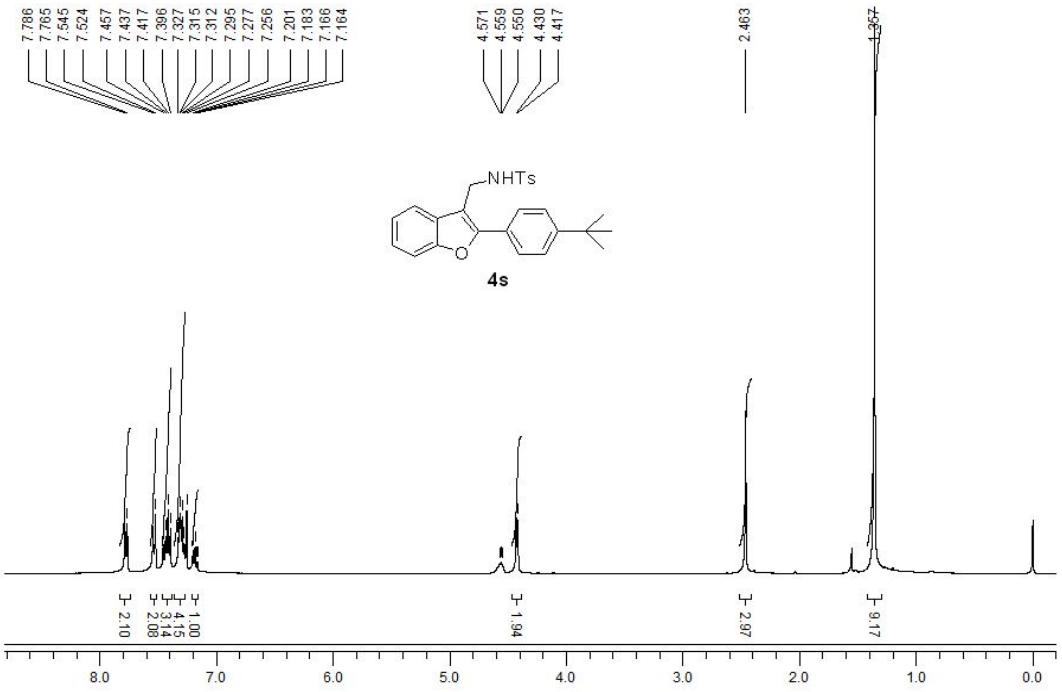
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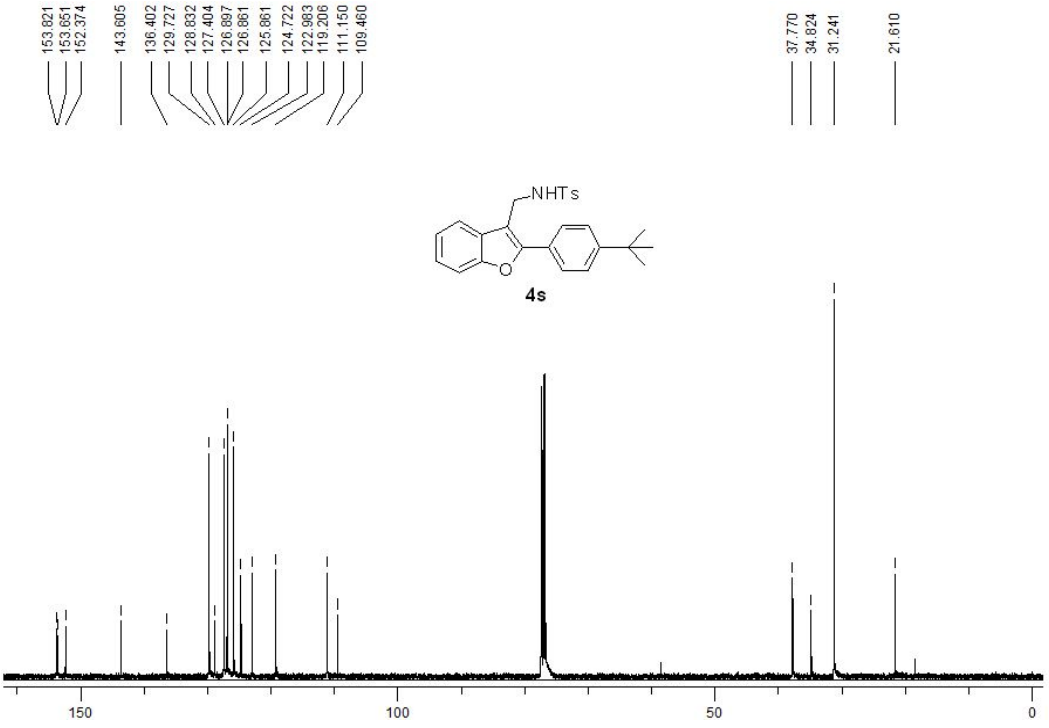
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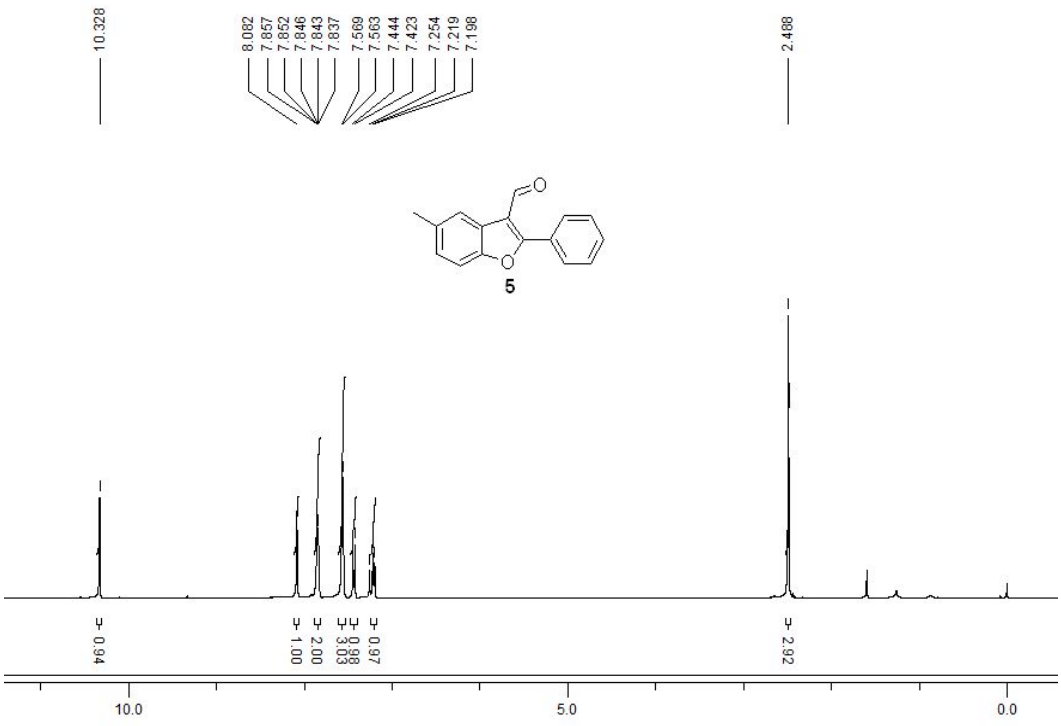
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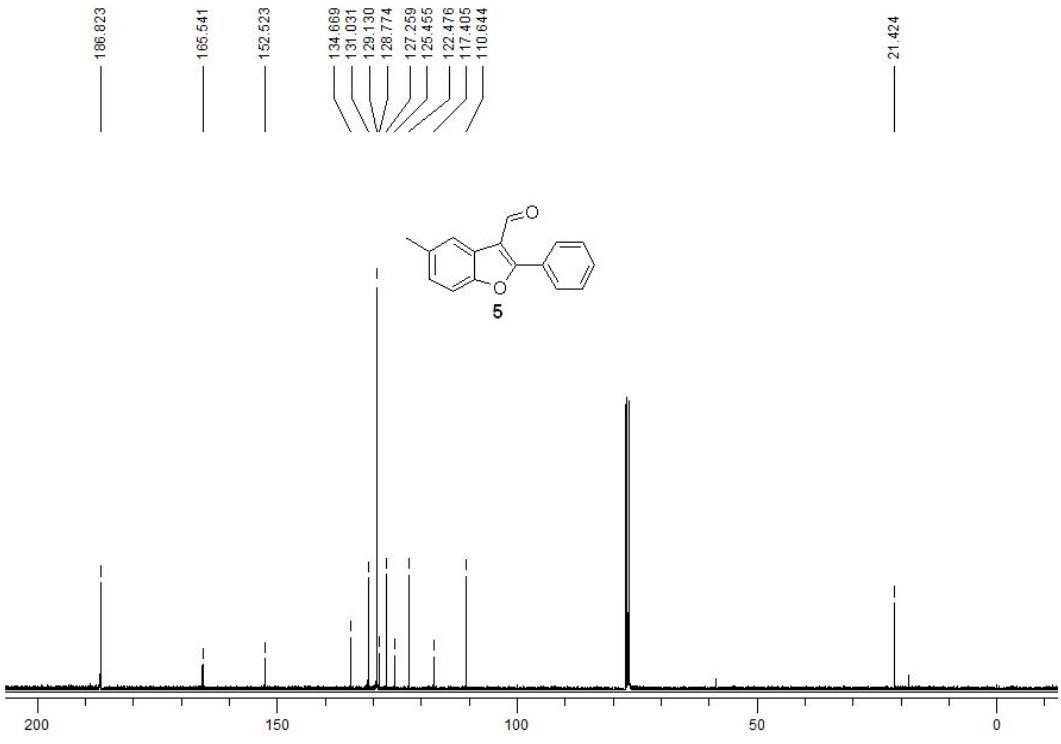
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152.523
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131.031
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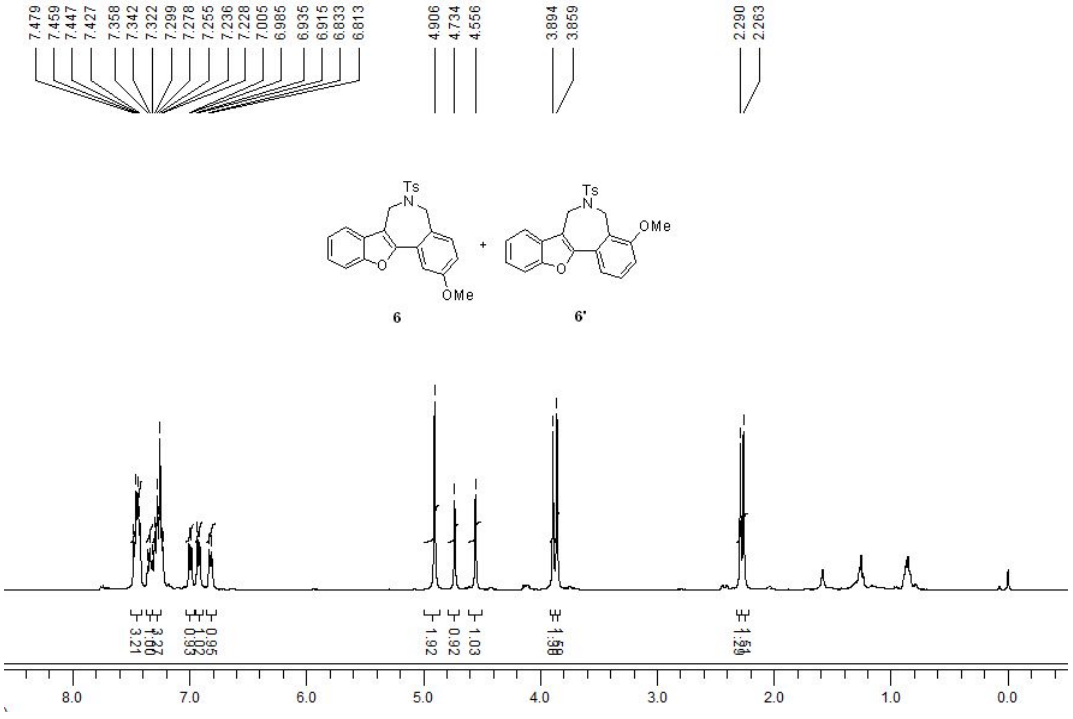
127.259
125.455
122.476
117.405
110.644
21.424
5
200
150
100
50
0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7.228
7.005
6.985
6.935
6.915
6.833
6.813
4.906
4.734
4.556
3.894
3.859
2.290
2.263
Ts
N
OMe
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6'
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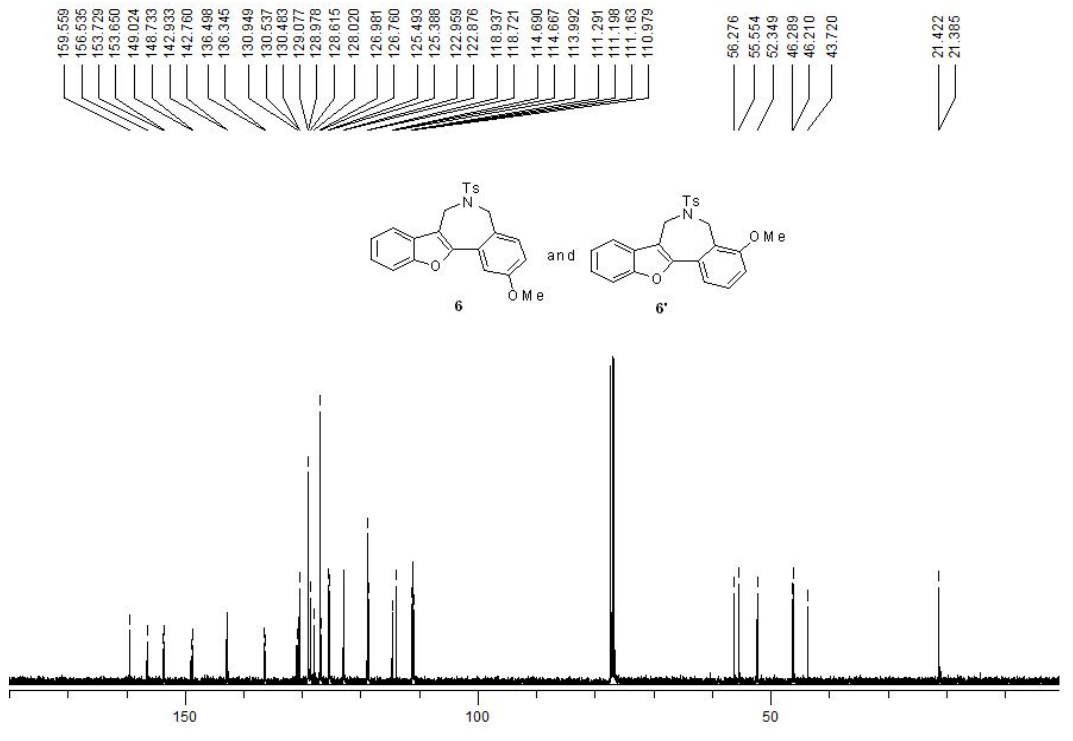
1.0
0.0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153.650
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130.483
129.077
128.978
128.615
128.020
126.981
126.760
125.493
125.388
122.959
122.876
118.937
118.721
114.690
114.667
113.992
111.291
111.198
111.163
110.979
56.276
55.554
52.349
46.289
46.210
43.720
21.422
21.385
Ts
N
OMe
and
6
6'
150
100
50

NOE of Compounds 2e and 2h