

Supporting information

Cascade Rh(II) and Yb(III) Catalyzed Synthesis of Substituted Naphthofurans *via* Transannulation of of *N*-Sulfonyl -1,2,3-triazoles with β -naphthols

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1) General Comments:

All the starting materials synthesis was carried out under nitrogen atmosphere. Synthesis of naphtho[2,1-*b*]furans were carried under oxygen atmosphere. All *N*-sulfonyl 1,2,3-triazoles¹ and β -naphthol derivatives² were synthesized according to the literature procedure. Dry toluene was prepared by distilling over sodium and stored over activated 4Å molecular sieves under N₂ atmosphere. Column chromatography was performed using Rankem Silica gel (100-200 mesh) and the solvent system used unless otherwise specified, was ethyl acetate-hexanes with various percentage of polarity depending on the nature of the substrate.

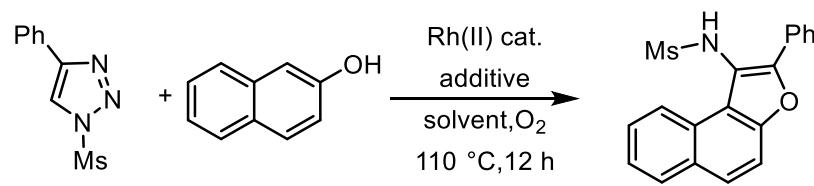
2. Analytical Methods:

NMR data were recorded on 400 and 500 MHz spectrometers. ¹H and ¹³C NMR spectra were referenced to signals of either deuterated solvents or residual protiated solvents. Infrared spectra were recorded on a Thermo Nicolet iS10 FT spectrometer. HRMS were recorded by electron spray ionization (ESI) method on a Q-TOF Micro with lock spray source.

¹ J. Raushel, V. V. Fokin, *Org. Lett.* **2010**, *12*, 4952-4955.

² AlHujran, T. A.; Dawe, L. N.; Collins, J.; Georghiou, P. E., *J. Org. Chem.* **2011**, *76*, 971-973.

3.1. Synthesis of Naphthofurans: Optimization



Entry	Catalyst (mol %)	Oxidant (mol %)	Solvent	Time (h)	Yield (%)
1	Rh ₂ (OAc) ₄ (2)	CuTC (10)	Toluene	14	45
2	Rh ₂ (Oct) ₄ (2)	CuTC (10)	Toluene	14	28
3	Rh ₂ (S-NTTL) ₄ (2)	CuTC (10)	Toluene	14	25
4	Rh ₂ (OAc) ₄ (2)	CuTC (10)	DCM	12	29
5	Rh ₂ (OAc) ₄ (2)	CuTC (10)	Trifluorotoluene	12	17
6	Rh ₂ (OAc) ₄ (2)	CuTC (10)	Toluene	12	26
7	Rh ₂ (OAc) ₄ (2)	Cu(OAc) ₂ .H ₂ O (10)	Toluene	12	20
8	Rh ₂ (OAc) ₄ (2)	Oxone	Toluene	12	21
9	Rh ₂ (OAc) ₄ (2)	Cu ₂ O (10)	Toluene	12	36
10	Rh ₂ (OAc) ₄ (2)	AgOTf (10)	Toluene	10	31
11	Rh ₂ (OAc) ₄ (2)	Sc(OTf) ₃ (10)	Toluene	12	31
12	Rh ₂ (OAc) ₄ (2)	Yb(OTf) ₃ (10)	Toluene	12	40
13	Rh ₂ (OAc) ₄ (2)	Zn(OTf) ₂ (10)	Toluene	10	36
14	Rh ₂ (OAc) ₄ (2)	Yb(OTf) ₃ (20)	Toluene	12	61
15	Rh ₂ (OAc) ₄ (4)	Yb(OTf) ₃ (20)	Toluene	12	65
16 ^d	Rh₂(OAc)₄ (4)	Yb(OTf)₃ (20)	Toluene	12	75
17	Rh ₂ (OAc) ₄ (4)	Ni(OTf) ₂ (20)	Toluene	12	44
18	Rh ₂ (OAc) ₄ (4)	Hf(OTf) ₃ (20)	Toluene	12	60
19	Rh ₂ (OAc) ₄ (4)	Cu(OTf) ₃ (20)	Toluene	12	32

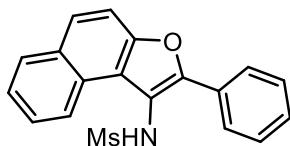
20	Rh ₂ (OAc) ₄ (4)	Yt(OTf) ₃ (20)	Toluene	12	37
21	Rh ₂ (OAc) ₄ (4)	La(OTf) ₃ (20)	Toluene	12	46
22	Rh ₂ (OAc) ₄ (4)	In(OTf) ₃ (20)	Toluene	12	48
23	Rh ₂ (OAc) ₄ (4)	Yb(OTf) ₃ (20)	Toluene	12	40
24	Rh ₂ (TFA) ₄ (4)	Yb(OTf) ₃ (20)	Toluene	12	60
25	Rh ₂ (Oct) ₄ (4)	Yb(OTf) ₃ (20)	Toluene	12	28
26	Rh ₂ (esp) ₄ (4)	Yb(OTf) ₃ (20)	Toluene	12	43
27	Rh ₂ (Piv) ₄ (4)	Yb(OTf) ₃ (20)	Toluene	12	39

Reaction Conditions: ^[a]2 equiv. of mesyltriazole was used;

3.2. General procedure for the synthesis of naphtho[2,1-*b*]furan (3)

N-Sulfonyl-1,2,3 triazole **1** (155 mg, 0.694 mmol, 2 equiv), β -naphthol derivative **2** (50 mg, 0.347 mmol, 1 equiv), Rh₂(OAc)₄ (6 mg, 0.003 mmol) and Yb(OTf)₃ (43 mg, 0.069 mmol) were taken in an oven dried 10 mL Schlenk tube. The Schlenk tube was filled with oxygen through successive evacuation and refilled with oxygen. To ensure the continuous oxygen supply, one oxygen filled balloon was put on side tube of the Schlenk tube. The mouth of the Schlenk tube was sealed with a septum and dry toluene (5.0 mL) was added to the reaction mixture. The reaction was stirred at 110 °C for the 12 h. After the specified time, the reaction mixture was cooled to room temperature and diluted with EtOAc. Evaporation of solvent under reduced pressure and purification of resultant crude through column chromatography using (Hexane:EtOAc:9:1) as eluent afforded the naphthofuran derivatives.

N-(2-Phenylnaphtho[2,1-*b*]furan-1-yl)methanesulfonamide (**3a**)



Yield: 75 % (87 mg); White solid; *Rf* = 0.35 in 2:8 EtOAc/Hexane.

MP: 196–198 °C.

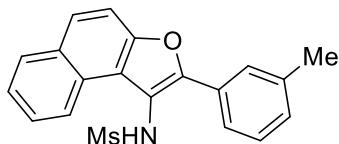
IR (ν_{max} , cm⁻¹): 3448, 2972, 1637, 1309, 1075, 750.

¹H NMR (400 MHz, DMSO, 24 °C): δ 8.71 (d, *J* = 8.4 Hz, 1H), 8.54 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.66-7.63 (m, 2H), 7.55-7.51 (m, 3H), 7.44 (t, *J* = 7.2 Hz, 1H), 6.47 (s, 1H), 2.82 (s, 3H).

¹³C{¹H} NMR (125 MHz, DMSO, 24 °C) δ 151.7, 151.0, 131.1, 129.4, 129.2, 129.0, 128.8, 127.5, 126.8, 126.7, 126.6, 125.0, 123.1, 121.1, 114.2, 112.3, 41.1.

HRMS: m/z: [M+H]⁺ Calcd. for C₁₉H₁₆NO₃S, 338.0850, found 338.0836.

N-(2-(*m*-Tolyl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3b)



Yield: 52 % (63 mg); White solid; *Rf* = 0.40 in 2:8 EtOAc/Hexane.

MP: 156-158 °C.

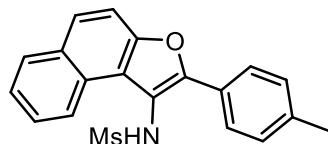
IR (ν_{max} , cm⁻¹): 3474, 2972, 1637, 1315, 1143, 747.

¹H NMR (400 MHz, DMSO, 24 °C): δ 9.99 (s, 1H), 8.85 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 7.6 Hz, 1H), 7.94-7.88 (m, 3H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.55 (t, *J* = 7.0 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 6.8 Hz, 1H), 2.76 (s, 3H), 2.42 (s, 3H).

¹³C{¹H} NMR (100 MHz, DMSO, 24 °C) δ 150.9, 150.2, 138.3, 130.6, 130.0, 128.9, 128.8, 128.7, 127.1, 126.9, 126.6, 126.4, 125.0, 123.7, 123.4, 121.2, 114.9, 112.4, 41.8, 21.1.

HRMS: m/z: [M+H]⁺ Calcd. for C₂₀H₁₈NO₃S, 352.1007, found 352.1000.

N-(2-(*p*-Tolyl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3c)



Yield: 93 % (113 mg); White solid; *Rf* = 0.33 in 2:8 EtOAc/Hexane.

MP: 204-206 °C.

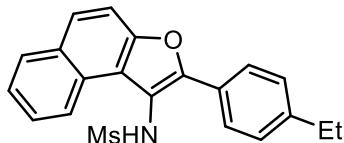
IR (ν_{max} , cm⁻¹): 3470, 2977, 1637, 1319, 1150, 818.

¹H NMR (400 MHz, DMSO, 24 °C): δ 9.93 (s, 1H), 8.83 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 2H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 2.76 (s, 3H), 2.40 (s, 3H).

$^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, DMSO, 24 °C) δ 150.1, 150.0, 138.9, 130.6, 129.5, 128.8, 127.0, 126.4, 126.3, 126.2, 126.1, 124.9, 123.3, 121.2, 114.3, 112.3, 41.7, 21.0.

HRMS: m/z: [M+H]⁺ Calcd. for C₂₀H₁₈NO₃S, 352.1007, found 352.0991.

N-(2-(4-Ethylphenyl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3d)



Yield: 85 % (107 mg); White solid; R_f = 0.37 in 2:8 EtOAc/Hexane.

MP: 188-190 °C.

IR (ν_{max} , cm⁻¹): 3311, 2965, 1683, 1312, 1143, 836.

^1H NMR (400 MHz, DMSO, 24 °C): δ 9.94 (s, 1H), 8.83 (d, J = 8.5 Hz, 1H), 8.06 - 8.03(m, 3H), 7.89 (d, J = 9.0 Hz, 1H), 7.82 (d, J = 9.0 Hz, 1H), 7.68-7.64 (m, 1H), 7.57-7.54 (m, 1H), 7.43 (d, J = 8.5 Hz, 2H), 2.77 (s, 3H), 2.71-2.67 (m, 2H), 1.26-1.23 (m, 3H)

$^{13}\text{C}\{\text{H}\}$ NMR (125 MHz, DMSO, 24 °C) δ 151.0, 150.0, 145.1, 130.5, 128.8, 128.3, 127.0, 126.5, 126.3(2C), 126.2, 124.9, 123.3, 121.2, 114.3, 112.3, 41.6, 28.0, 15.2.

HRMS: m/z: [M+H]⁺ Calcd. for C₂₁H₂₀NO₃S, 366.1163, found 366.1157.

N-(2-(4-(tert-Butyl)phenyl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3e)



Yield: 67 % (92 mg); White solid; R_f = 0.42 in 2:8 EtOAc/Hexane.

MP: 250-252 °C.

IR (ν_{max} , cm⁻¹): 3478, 2959, 1632, 1315, 1161, 835.

^1H NMR (400 MHz, CDCl₃, 24 °C): δ 8.73 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 7.0 Hz, 2H), 7.87 (d, J = 8.5 Hz, 1H), 7.70-7.68 (m, 1H), 7.59-7.55 (m, 2H), 7.48-7.44 (m, 3H), 2.74 (s, 3H), 1.31 (s, 9H).

$^{13}\text{C}\{\text{H}\}$ NMR (125 MHz, DMSO, 24 °C) δ 152.5, 151.9, 150.9, 131.1, 128.9, 127.4, 126.5 (3C), 125.8 (2C), 124.9, 123.2, 121.1, 113.6, 112.3, 41.1, 34.9, 31.2.

HRMS: m/z: [M+H]⁺ Calcd. for C₂₃H₂₄NO₃S, 394.1476, found 394.1467.

N-(2-(4-Methoxyphenyl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3f)



Yield: 28 % (36 mg); White solid; $R_f = 0.37$ in 2:8 EtOAc/Hexane.

MP: 235-237 °C.

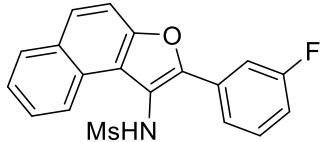
IR (ν_{max} , cm⁻¹): 3480, 2920, 1637, 1310, 1144, 809.

¹H NMR (400 MHz, CDCl₃, 24 °C): δ 8.69 (d, $J = 8.4$ Hz, 1H), 8.00 (d, $J = 8.4$ Hz, 2H), 7.95 (d, $J = 8.4$ Hz, 1H), 7.76-7.73 (m, 1H), 7.64-7.62 (m, 2H), 7.51 (t, $J = 7.6$ Hz, 1H), 7.04 (d, $J = 8.4$ Hz, 2H), 6.37 (s, 1H), 3.89 (s, 3H), 2.84 (s, 3H).

¹³C{¹H} NMR (125 MHz, DMSO, 24 °C) δ 160.4, 151.6, 150.3, 131.0, 129.2, 128.6, 127.4, 126.7, 126.5, 125.4, 123.8, 121.8, 121.7, 114.9, 113.9, 112.8, 55.8, 42.1.

HRMS: m/z: [M+H]⁺ Calcd. for C₂₀H₁₈NO₄S, 368.0956, found 368.0951.

N-(2-(3-Fluorophenyl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3g)



Yield: 77 % (95 mg); White solid; $R_f = 0.31$ in 2:8 EtOAc/Hexane.

MP: 218-220 °C.

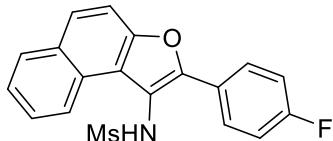
IR (ν_{max} , cm⁻¹): 3473, 2971, 1637, 1313, 1140, 778.

¹H NMR (500 MHz, DMSO, 24 °C): δ 10.05 (s, 1H), 8.82 (d, $J = 8.5$ Hz, 1H), 8.07 (d, $J = 8.0$ Hz, 1H), 7.98-7.91 (m, 3H), 7.85 (d, $J = 9.0$ Hz, 1H), 7.70-7.67 (m, 1H), 7.65-7.61 (m, 1H), 7.59-7.56 (m, 1H), 7.35-7.31 (m, 1H), 2.83 (s, 3H).

¹³C{¹H} NMR (125 MHz, DMSO, 24 °C) δ 162.3 (d, $J = 242.0$ Hz), 150.5, 149.4, 149.3, 131.2 (d, $J = 8.5$ Hz), 131.0 (d, $J = 8.9$ Hz), 130.6, 128.9, 127.2, 127.0, 126.6, 125.2, 123.3, 122.5 (d, $J = 2.4$ Hz), 120.9, 116.0 (d, $J = 21.0$ Hz), 115.9, 113.0 (d, $J = 23.8$ Hz), 41.6.

HRMS: m/z: [M+H]⁺ Calcd. for C₁₉H₁₅FNO₃S, 356.0756, found 356.0750.

N-(2-(4-Fluorophenyl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3h)



Yield: 69% (85 mg); White solid; R_f = 0.29 in 2:8 EtOAc/Hexane.

MP: 210-212 °C.

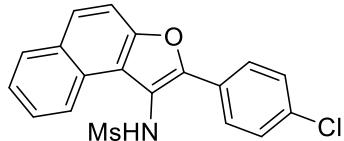
IR (ν_{max} , cm⁻¹): 3471, 2972, 1637, 1315, 1141, 816.

¹H NMR (500 MHz, DMSO, 24 °C): δ 9.98 (s, 1H), 8.81 (d, J = 6.8 Hz, 1H), 8.17-8.14 (m, 2H), 8.05 (d, J = 6.4 Hz, 1H), 7.90 (d, J = 7.2 Hz, 1H), 7.82 (d, J = 7.2 Hz, 1H), 7.67 (t, J = 7.2 Hz, 1H), 7.56 (t, J = 7.2 Hz, 1H), 7.44-7.41 (m, 2H), 2.79 (s, 3H).

¹³C{¹H} NMR (125 MHz, DMSO, 24 °C) δ 162.4 (d, J = 246.0 Hz), 150.3, 150.1, 130.6, 128.9, 128.8 (d, J = 8.3 Hz), 127.0, 126.7, 126.4, 125.5 (d, J = 3.1 Hz), 125.1, 123.4, 121.0, 116.1 (d, J = 21.8 Hz), 114.8, 112.4, 41.7.

HRMS: m/z: [M+H]⁺ Calcd. for C₁₉H₁₅FNO₃S, 356.0756, found 356.0749.

N-(2-(4-Chlorophenyl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3i)



Yield: 62 % (80 mg); White solid; R_f = 0.32 in 2:8 EtOAc/Hexane.

MP: 217-219 °C.

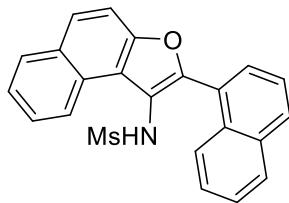
IR (ν_{max} , cm⁻¹): 3459, 2925, 1630, 1320, 1148, 806.

¹H NMR (400 MHz, DMSO, 24 °C): δ 10.03 (s, 1H), 8.82 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 8.4 Hz, 2H), 8.06 (d, J = 8.0 Hz, 1H), 7.95-7.91 (m, 1H), 7.83 (d, J = 8.8 Hz, 1H), 7.70-7.64 (m, 3H), 7.59-7.55 (m, 1H), 2.83 (s, 3H).

¹³C{¹H} NMR (100 MHz, DMSO, 24 °C) δ 150.4, 149.4, 133.7, 130.6, 129.1 (2C), 128.9, 128.1, 127.7, 127.0, 126.5, 125.1, 123.4, 121.0, 115.4, 112.4, 41.7.

HRMS: m/z: [M+Na]⁺ Calcd. for C₁₉H₁₄ClNO₃SnA, 394.0280, found 394.0268.

N-(2-(Naphthalen-1-yl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3j)



Yield: 61 % (82 mg); White solid; $R_f = 0.25$ in 2:8 EtOAc/Hexane.

MP: 220-222 °C.

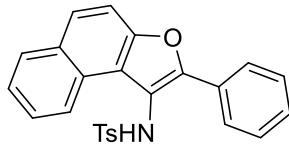
IR (ν_{max} , cm⁻¹): 3447, 2925, 1636, 1267, 1142, 751.

¹H NMR (400 MHz, DMSO, 24 °C): δ 10.13 (s, 1H), 8.88 (d, $J = 8.4$ Hz, 1H), 8.68 (s, 1H), 8.29 (d, $J = 8.8$ Hz, 1H), 8.13-8.08 (m, 3H), 8.01-7.99 (m, 1H), 7.95 (d, $J = 8.8$ Hz, 1H), 7.89 (d, $J = 8.8$ Hz, 1H), 7.72-7.68 (m, 1H), 7.63-7.57 (m, 3H), 2.79 (s, 3H).

¹³C{¹H} NMR (100 MHz, DMSO, 24 °C) δ 150.9, 150.4, 140.0, 136.6, 131.1, 129.4, 129.1(2C), 129.0, 128.8, 127.6, 127.1, 127.0 (2C), 126.5, 126.4, 126.2, 125.4, 124.1, 121.2, 115.0, 112.9, 41.7.

HRMS: m/z: [M+H]⁺ Calcd. for C₂₃H₁₈NO₃S, 388.1007, found 388.0997.

4-Methyl-N-(2-phenylnaphtho[2,1-*b*]furan-1-yl)benzenesulfonamide (3k)



Yield: 53 % (76 mg); White solid; $R_f = 0.37$ in 2:8 EtOAc/Hexane.

MP: 230-232 °C.

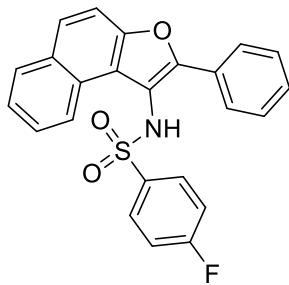
IR (ν_{max} , cm⁻¹): 3452, 2932, 1637, 1315, 1140, 840.

¹H NMR (400 MHz, CDCl₃, 24 °C): δ 8.58-8.56 (m, 1H), 7.90-7.88 (m, 1H), 7.72 (d, $J = 8.8$ Hz, 1H), 7.63-7.58 (m, 3H), 7.50-7.44 (m, 3H), 7.26-7.23 (m, 3H), 6.86 (d, $J = 8.0$ Hz, 2H), 6.62 (s, 1H), 2.21 (s, 3H).

¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C) δ 151.8, 151.0, 143.8, 136.5, 131.0, 129.4 (2C), 129.2, 128.8, 128.5, 128.4, 127.5, 126.8, 126.5, 126.4, 125.0, 123.5, 121.0, 114.3, 112.3, 21.4.

HRMS: m/z: [M+H]⁺ Calcd. for C₂₅H₂₀NO₃S, 414.1163, found 394.414.1150.

4-Fluoro-N-(2-phenylnaphtho[2,1-*b*]furan-1-yl)benzenesulfonamide (3l)



Yield: 60 % (87 mg); Brown solid; R_f = 0.38 in 2:8 EtOAc/Hexane.

MP: 220-222 °C.

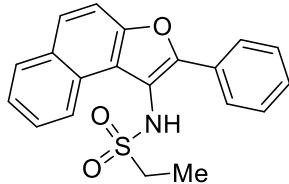
IR (ν_{max} , cm⁻¹): 3478, 2921, 1637, 1331, 1152, 805.

¹H NMR (500 MHz, DMSO, 24 °C): δ 10.48 (s, 1H), 8.63-8.61 (m, 1H), 8.03-8.01 (m, 1H), 7.88 (d, J = 6.8 Hz, 1H), 7.81-7.79 (m, 1H), 7.75-7.73 (m, 2H), 7.56-7.50 (m, 4H), 7.30-7.28 (m, 3H), 7.02-6.99 (m, 2H).

¹³C{¹H} NMR (125 MHz, DMSO, 24 °C) δ 165.2 (d, J = 250.0 Hz), 151.0, 150.2, 137.0 (d, J = 2.8 Hz), 130.5, 129.5 (d, J = 9.6 Hz), 128.7, 128.6, 128.5, 128.4, 127.0, 126.6, 126.1, 126.0, 124.9, 123.2, 121.0, 115.9 (d, J = 22.7 Hz), 114.4, 112.4.

HRMS: m/z: [M+H]⁺ Calcd. for C₂₄H₁₇FNO₃S, 418.0913, found 418.0911.

N-(2-Phenylnaphtho[2,1-*b*]furan-1-yl)ethanesulfonamide (3m)



Yield: 50 % (61 mg); White solid; R_f = 0.37 in 2:8 EtOAc/Hexane.

MP: 169-171 °C.

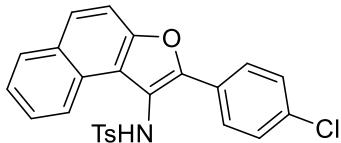
IR (ν_{max} , cm⁻¹): 3375, 2931, 1632, 1320, 1143, 762.

¹H NMR (400 MHz, DMSO, 24 °C): δ 9.90 (s, 1H), 8.85 (d, J = 8.0 Hz, 1H), 8.07-8.05 (m, 3H), 7.90 (d, J = 8.8 Hz, 1H), 7.82 (d, J = 8.8 Hz, 1H), 7.66 (t, J = 7.2 Hz, 1H), 7.57-7.55 (m, 3H), 7.50-7.48 (m, 1H), 2.81-2.79 (m, 2H), 1.08 (t, J = 6.8 Hz, 3H).

¹³C{¹H} NMR (100 MHz, DMSO, 24 °C) δ 150.9, 150.2, 130.6, 129.3, 128.9, 128.8, 127.1 (2C), 126.7, 126.6, 126.3, 125.0, 123.3, 121.4, 115.1, 112.4, 48.0, 7.8.

HRMS: m/z: [M+H]⁺ Calcd. for C₂₀H₁₈NO₃S, 352.1007, found 352.0995.

N-(2-(4-Chlorophenyl)naphtho[2,1-*b*]furan-1-yl)-4-methylbenzenesulfonamide (3n)



Yield: 46 % (71 mg); White solid; $R_f = 0.39$ in 2:8 EtOAc/Hexane.

MP: 194-196 °C.

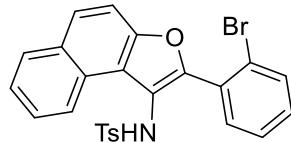
IR (ν_{max} , cm⁻¹): 3419, 2929, 1633, 1161, 815.

¹H NMR (500 MHz, DMSO, 24 °C): δ 10.32 (s, 1H), 8.68-8.66 (m, 1H), 8.05-8.03 (m, 1H), 7.90 (d, $J = 8.5$ Hz, 1H), 7.78 (d, $J = 9.0$ Hz, 1H), 7.67 (d, $J = 8.5$ Hz, 2H), 7.57-7.52 (m, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.30 (d, $J = 8.5$ Hz, 2H), 7.01 (d, $J = 8.0$ Hz, 2H), 2.24 (s, 3H).

¹³C{¹H} NMR (125 MHz, DMSO, 24 °C) δ 150.3, 149.7, 143.1, 137.8, 133.1, 130.5, 129.2, 128.7, 128.3, 127.6, 127.4, 127.1, 126.8, 126.5, 126.2, 124.9, 123.3, 121.1, 115.2, 112.3, 20.8.

HRMS: m/z: [M+H]⁺ Calcd. for C₂₅H₁₉ClNO₃S, 448.0774, found 448.0769.

N-(2-(2-Bromophenyl)naphtho[2,1-*b*]furan-1-yl)-4-methylbenzenesulfonamide (3o)



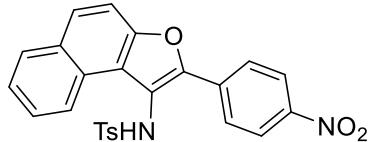
Yield: 38 % (65 mg); White solid; $R_f = 0.39$ in 2:8 EtOAc/Hexane.

¹H NMR (400 MHz, CDCl₃, 24 °C): δ 9.04 (d, $J = 8.0$ Hz, 1H), 7.94 (d, $J = 8.2$ Hz, 1H), 7.78 (d, $J = 8.8$ Hz, 1H), 7.68-7.65 (m, 1H), 7.59-7.52 (m, 2H), 7.48-7.46 (m, 1H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.19-7.13 (m, 2H), 7.06-7.04 (m, 1H), 6.85 (s, 1H), 6.82 (d, $J = 8.0$ Hz, 2H), 2.24 (s, 3H).

¹³C{¹H} NMR (125 MHz, DMSO, 24 °C) δ 150.9, 150.6, 142.3, 137.2, 133.2, 132.3, 130.9, 130.4, 129.3, 129.2, 128.7, 127.3, 127.1, 126.7, 126.3, 126.1, 125.0, 123.3, 122.7, 120.3, 116.4, 112.5, 20.9.

HRMS: m/z: [M+Na]⁺ Calcd. for C₂₅H₁₈BrNO₃SNa, 514.0088, found 514.0085.

4-Methyl-N-(2-(4-nitrophenyl)naphtho[2,1-*b*]furan-1-yl)benzenesulfonamide (3p)



Yield: 27 % (43 mg); Pale yellow solid; $R_f = 0.37$ in 2:8 EtOAc/Hexane.

MP: 110-112 °C.

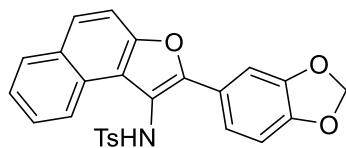
IR (ν_{max} , cm⁻¹): 3458, 2930, 1637, 1515, 1336, 760.

¹H NMR (400 MHz, DMSO, 24 °C): δ 10.51 (s, 1H), 8.69-8.67 (m, 1H), 8.09-8.05 (m, 3H), 7.98-7.91 (m, 3H), 7.84 (d, J = 8.8 Hz, 1H), 7.60-7.54 (m, 2H), 7.38 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 2.10 (s, 3H).

¹³C{¹H} NMR (100 MHz, DMSO, 24 °C) δ 151.1, 148.2, 146.1, 143.2, 137.8(2C), 134.7, 130.5, 129.3, 128.8, 128.0, 127.1, , 126.6(2C), 126.5, 125.2, 123.5, 123.3, 121.0, 112.4, 20.6.

HRMS: m/z: [M+H]⁺ Calcd. for C₂₅H₁₉N₂O₅S, 459.1014, found 459.0998.

N-(2-(Benzo[d][1,3]dioxol-5-yl)naphtho[2,1-*b*]furan-1-yl)-4-methylbenzenesulfonamide (3q)



Yield: 37 % (59 mg); White solid; R_f = 0.33 in 2:8 EtOAc/Hexane.

MP: 204-206 °C.

IR (ν_{max} , cm⁻¹): 3468, 2957, 1618, 1241, 1088, 811.

¹H NMR (400 MHz, DMSO, 24 °C): δ 10.19 (s, 1H), 8.68 (d, J = 7.2 Hz, 1H), 8.02 (d, J = 7.6 Hz, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.61-7.46 (m, 2H), 7.37 (d, J = 7.6 Hz, 2H), 7.20 (d, J = 8.0 Hz, 1H), 7.15 (s, 1H), 7.05 (d, J = 7.2 Hz, 2H), 6.82 (d, J = 8.0 Hz, 1H), 6.05 (s, 2H), 2.24 (s, 3H).

¹³C{¹H} NMR (100 MHz, DMSO, 24 °C) δ 151.0, 149.7, 147.6, 147.1, 142.8, 138.0, 130.5, 129.2, 128.6, 127.0, 126.5, 126.0, 124.8, 123.3, 122.5, 121.3, 120.8, 113.6, 112.2, 108.2, 106.4, 101.4, 54.9, 20.8.

HRMS: m/z: [M+H]⁺ Calcd. for C₂₆H₂₀NO₅S, 458.1062, found 458.1062.

N-(7-(Benzylxy)-2-phenylnaphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3r)



Yield: 37 % (57 mg); White solid; R_f = 0.30 in 2:8 EtOAc/Hexane.

MP: 194-196 °C.

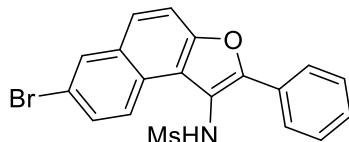
IR (ν_{max} , cm⁻¹): 3447, 2925, 1637, 1327, 1148, 740.

¹H NMR (400 MHz, DMSO, 24 °C): δ 9.96 (s, 1H), 8.76-8.73 (m, 1H), 8.10 (d, J = 8.0 Hz, 2H), 7.79 (s, 2H), 7.62-7.33 (m, 10H), 5.26 (s, 2H), 2.76 (s, 3H).

¹³C{¹H} NMR (100 MHz, DMSO, 24 °C) δ 155.6, 150.7, 149.3, 137.0, 132.1, 129.2, 129.0, 128.5, 128.0, 127.9, 126.5 (2C), 125.6, 124.8, 121.9, 121.4, 118.3, 114.7, 112.8, 109.4, 69.4, 41.6.

HRMS: m/z: [M+H]⁺ Calcd. for C₂₆H₂₂NO₄S, 444.1269, found 444.1249.

N-(7-bromo-2-phenylnaphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3s)



Yield: 45 % (65 mg); White solid; *Rf* = 0.30 in 2:8 EtOAc/Hexane.

MP: 230-232 °C.

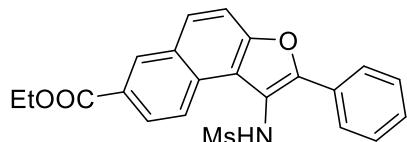
IR (ν_{max} , cm⁻¹): 3416, 2964, 1638, 1334, 1142, 767.

¹H NMR (500 MHz, DMSO, 24 °C): δ 10.05 (s, 1H), 8.77 (d, *J* = 9.0 Hz, 1H), 8.35 (d, *J* = 2.0 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 2H), 7.90-7.86 (m, 2H), 7.82 (dd, *J* = 9.0, 1.5 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 2H), 7.50-7.44 (m, 1H), 2.77 (s, 3H).

¹³C{¹H} NMR (125 MHz, DMSO, 24 °C) δ 151.3, 150.3, 132.1, 130.7, 129.5, 129.2, 129.0, 128.6, 126.6, 125.8, 125.6, 125.5, 121.3, 118.1, 114.8, 113.7, 41.5.

HRMS: m/z: [M+Na]⁺ Calcd. for C₁₉H₁₄BrNO₃Na, 437.9775, found 437.9763.

Ethyl 1-(methylsulfonamido)-2-phenylnaphtho[2,1-*b*]furan-7-carboxylate (3t)



Yield: 75 % (106 mg); White solid; *Rf* = 0.27 in 2:8 EtOAc/Hexane.

MP: 130-132 °C.

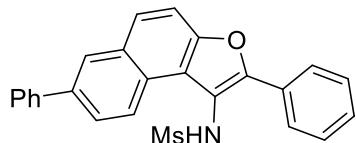
IR (ν_{max} , cm⁻¹): 3469, 2925, 1711, 1633, 1147, 749.

¹H NMR (400 MHz, DMSO, 24 °C): δ 10.07 (s, 1H), 8.92 (d, *J* = 8.4 Hz, 1H), 8.75 (s, 1H), 8.14-8.12 (m, 4H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.59-7.49 (m, 3H), 4.41-4.39 (m, 2H), 2.80 (s, 3H), 1.39-1.37 (m, 3H).

¹³C{¹H} NMR (100 MHz, DMSO, 24 °C) δ 165.8, 151.5, 151.4, 131.2, 129.8, 129.4, 129.0 (3C), 128.6, 127.9, 126.6, 126.2, 125.4, 123.8, 121.2, 114.9, 113.5, 60.9, 41.6, 14.3.

HRMS: m/z: [M+H]⁺ Calcd. for C₂₂H₂₀NO₅S, 410.1062, found 410.1051.

N-(2,7-Diphenylnaphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3u)



Yield: 27 % (60 mg); White solid; R_f = 0.37 in 2:8 EtOAc/Hexane.

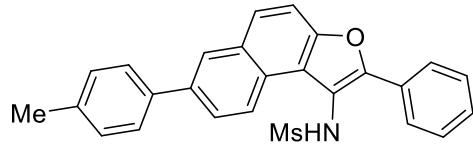
MP: 240-242 °C.

IR (ν_{max} , cm⁻¹): 3452, 2924, 1636, 1144, 762.

¹H NMR (400 MHz, DMSO, 24 °C): δ 10.03 (s, 1H), 8.91 (d, J = 8.8 Hz, 1H), 8.39 (s, 1H), 8.13 (d, J = 8.0 Hz, 2H), 8.02-7.99 (m, 2H), 7.88-7.86 (m, 3H), 7.61-7.45 (m, 5H), 7.43-7.40 (m, 1H), 2.78 (s, 3H).
¹³C{¹H} NMR (100 MHz, DMSO, 24 °C) δ 150.9, 150.4, 139.9, 136.6, 131.0, 129.3, 129.0, 128.9, 128.8, 127.5, 127.1, 126.9, 126.5, 126.4, 126.1, 125.3, 124.0, 121.1, 114.9, 112.8, 41.6.

HRMS: m/z: [M+H]⁺ Calcd. for C₂₅H₂₀NO₃S, 414.1163, found 414.1152.

N-(2-Phenyl-7-(*p*-tolyl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3v)



Yield: 33 % (49 mg); White solid; R_f = 0.33 in 2:8 EtOAc/Hexane.

MP: 252-254 °C.

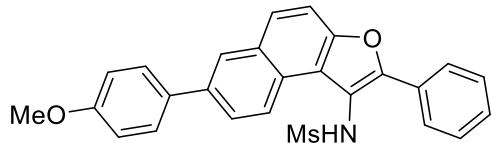
IR (ν_{max} , cm⁻¹): 3473, 2972, 1633, 1317, 1148, 776.

¹H NMR (400 MHz, DMSO, 24 °C): δ 10.03 (s, 1H), 8.89 (d, J = 8.8 Hz, 1H), 8.35 (s, 1H), 8.13 (d, J = 7.6 Hz, 2H), 8.00-7.98 (m, 2H), 7.87 (d, J = 8.8 Hz, 1H), 7.76 (d, J = 8.0 Hz, 2H), 7.59 (t, J = 7.6 Hz, 2H), 7.51-7.47 (m, 1H), 7.33 (d, J = 7.6 Hz, 2H), 2.79 (s, 3H), 2.38 (s, 3H).

¹³C{¹H} NMR (100 MHz, DMSO, 24 °C) δ 150.9, 150.3, 137.0, 136.9, 136.5, 131.1, 129.7, 129.3, 129.0, 128.9, 127.0, 126.8, 126.5, 126.0, 125.9, 125.2, 124.0, 121.2, 114.9, 112.8, 41.7, 20.7.

HRMS: m/z: [M+H]⁺ Calcd. for C₂₆H₂₂NO₃S, 428.1320, found 428.1310.

N-(7-(4-Methoxyphenyl)-2-phenylnaphtho[2,1-*b*]furanyl)methanesulfonamide (3w)



Yield: 37 % (57 mg); White solid; $R_f = 0.30$ in 2:8 EtOAc/Hexane.

MP: 168-170 °C.

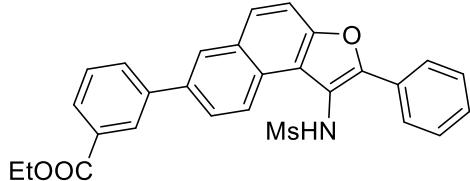
IR (ν_{max} , cm⁻¹): 3480, 2970, 1635, 1312, 1149, 812.

¹H NMR (400 MHz, DMSO, 24 °C): δ 10.03 (s, 1H), 8.87 (d, $J = 8.4$ Hz, 1H), 8.31 (s, 1H), 8.13 (d, $J = 7.2$ Hz, 2H), 7.97 (d, $J = 8.4$ Hz, 2H), 7.86-7.80 (m, 3H), 7.59-7.57 (m, 2H), 7.50-7.48 (m, 1H), 7.09 (d, $J = 7.6$ Hz, 2H), 3.83 (s, 3H), 2.78 (s, 3H).

¹³C{¹H} NMR (100 MHz, DMSO, 24 °C) δ 159.0, 150.8, 150.3, 136.3, 132.2, 131.1, 129.3, 129.0, 128.9, 128.0, 127.0, 126.5, 125.7, 125.5, 125.1, 124.0, 121.2, 114.9, 114.5, 112.7, 55.2, 41.7.

HRMS: m/z: [M+H]⁺ Calcd. for C₂₆H₂₂NO₄S, 444.1269, found 444.1264.

Ethyl 3-(1-(methylsulfonamido)-2-phenylnaphtho[2,1-b]furan-7-yl)benzoate (3x)



Yield: 75 % (126 mg); White solid; $R_f = 0.20$ in 2:8 EtOAc/Hexane.

MP: 149-151 °C.

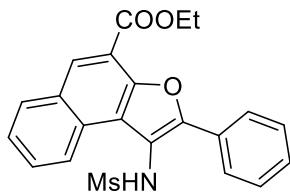
IR (ν_{max} , cm⁻¹): 3450, 2926, 1712, 1638, 1306, 1148, 805.

¹H NMR (400 MHz, DMSO, 24 °C): δ 10.05 (s, 1H), 8.94 (d, $J = 8.8$ Hz, 1H), 8.44 (s, 1H), 8.38 (s, 1H), 8.15-8.13 (m, 3H), 8.05 (d, $J = 8.4$ Hz, 2H), 8.00 (d, $J = 7.6$ Hz, 1H), 7.88 (d, $J = 8.8$ Hz, 1H), 7.71-7.65 (m, 1H), 7.61-7.57 (m, 2H), 7.51-7.47 (m, 1H), 4.38 (q, $J = 7.0$ Hz, 2H), 2.79 (s, 3H), 1.37 (t, $J = 7.0$ Hz, 3H).

¹³C{¹H} NMR (100 MHz, DMSO, 24 °C) δ 165.7, 151.0, 150.5, 140.5, 135.5, 131.8, 131.0, 130.8, 129.6, 129.3, 129.0, 128.8, 128.1, 127.3, 127.2, 126.7, 126.5, 126.4, 125.2, 124.3, 121.1, 114.9, 113.0, 61.0, 41.7, 14.2.

HRMS: m/z: [M+Na]⁺ Calcd. for C₂₈H₂₃NO₅Na, 508.1194, found 508.3100.

Ethyl 1-(methylsulfonamido)-2-phenylnaphtho[2,1-b]furan-4-carboxylate (3y)



Yield: 62 % (88 mg); White solid; R_f = 0.30 in 2:8 EtOAc/Hexane.

MP: 112-114 °C.

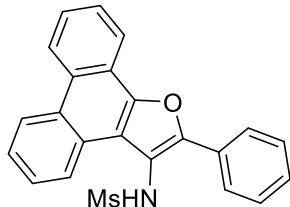
IR (ν_{max} , cm⁻¹): 3438, 2925, 1713, 1637, 1312, 1143, 763.

¹H NMR (400 MHz, DMSO, 24 °C): δ 10.07 (s, 1H), 8.90 (d, J = 8.4 Hz, 1H), 8.55 (s, 1H), 8.27 (d, J = 8.0 Hz, 1H), 8.17 (d, J = 7.6 Hz, 2H), 7.82 (d, J = 7.4 Hz, 1H), 7.67-7.60 (m, 3H), 7.53-7.51 (m, 1H), 4.48-4.51 (m, 2H), 2.81 (s, 3H), 1.48 (s, 3H).

¹³C{¹H} NMR (125 MHz, DMSO, 24 °C) δ 163.7, 151.3, 147.2, 130.3, 129.9, 129.5, 129.0 (3C), 128.8, 128.6, 126.4, 125.9, 123.2, 122.9, 115.4, 114.8, 61.1, 41.7, 14.3.

HRMS: m/z: [M+H]⁺ Calcd. for C₂₂H₂₀NO₅S, 410.1062, found 410.1056.

N-(2-Phenylphenanthro[9,10-b]furan-3-yl)methanesulfonamide (3z)



Yield: 28% (38 mg); White solid; R_f = 0.40 in 2:8 EtOAc/Hexane.

MP: 238-240 °C.

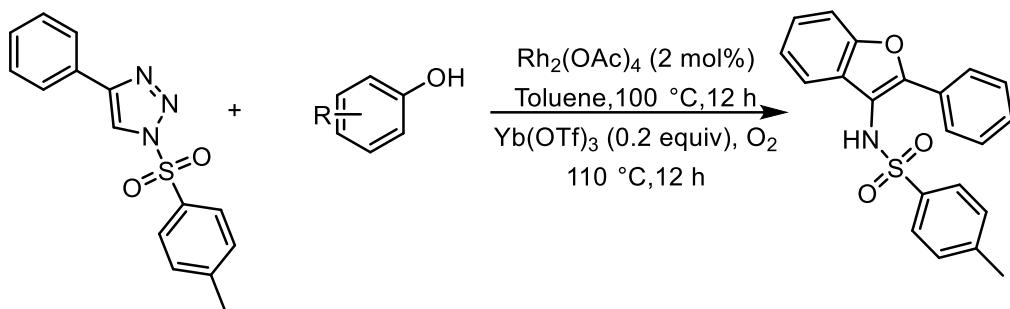
IR (ν_{max} , cm⁻¹): 3480, 2922, 1637, 1322, 1147, 761.

¹H NMR (400 MHz, DMSO, 24 °C): δ 10.04 (s, 1H), 8.91-8.89 (m, 3H), 8.44 (d, J = 7.6Hz, 1H), 8.21 (d, J = 7.6Hz, 2H), 7.82-7.69 (m, 4H), 7.61 (t, J = 7.4 Hz, 2H), 7.51-7.48 (m, 1H), 2.78 (s, 3H).

¹³C{¹H} NMR (100 MHz, DMSO, 24 °C) δ 150.8, 146.7, 129.3, 129.1, 129.0, 128.9, 128.1, 127.9, 127.2, 127.1, 126.6, 126.5, 126.1, 124.1 (2C), 124.0, 121.2, 120.1, 118.7, 115.7, 41.8.

HRMS: m/z: [M+H]⁺ Calcd. for C₂₃H₁₈NO₃S, 388.1007, found 388.1005.

3.3. Typical procedure for Rhodium(III) catalyzed benzofuran synthesis (3aa & 3ab) :



N-Sulfonyl-1,2,3triazole **1a** (100 mg, 0.334 mmol, 1 equiv) phenol derivative (38 mg, 0.401 mmol, 1.2 equiv) and $\text{Rh}_2(\text{OAc})_4$ (3 mg, 0.007 mmol) were taken in an oven dried 10 mL Schlenk tube. The tube was filled with nitrogen through successive evacuation and refilled with nitrogen and dry toluene (2.0 mL) was introduced to the reaction mixture *via* syringe. The reaction was stirred at 100 °C for 3 h. After the consumption of triazole monitored by TLC analysis, $\text{Yb}(\text{OTf})_3$ (41 mg, 0.066 mmol) was added and the reaction was continued further 12 h under oxygen atmosphere. After the TLC analysis, the reaction mixture was cooled to room temperature and diluted with EtOAc. Evaporation of solvent and purification of crude through column chromatography using (Hexane: EtOAc: 9:1) as eluent gave the benzofurans.

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



Yield: 38 % (53 mg); Yellow liquid; R_f = 0.48 in 2:8 EtOAc/Hexane.

IR (ν_{max} , cm⁻¹): 3425, 2955, 1619, 1325, 1150, 813.

¹H NMR (400 MHz, CDCl₃, 24 °C): δ 7.94 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 7.39-7.29 (m, 5H), 7.12 (d, J = 8.0 Hz, 2H), 6.89(s, 1H), 6.46(s, 1H), 2.33(s, 3H), 1.23(s, 9H).

¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C) δ 152.2, 151.1, 146.3, 144.1, 137.1, 129.8, 129.2, 129.1, 128.6, 127.7, 126.7, 126.6, 123.2, 115.3, 112.7, 110.8, 34.8, 31.7, 21.6.

HRMS: m/z: [M+H]⁺ Calcd. for C₂₅H₂₆NO₃S, 420.1633, found 420.1626.

N-(4,6-Dimethyl-2-phenylbenzofuran-3-yl)-4-methylbenzenesulfonamide (3ab)



Yield: 29 % (28 mg); White solid; $R_f = 0.52$ in 2:8 EtOAc/Hexane.

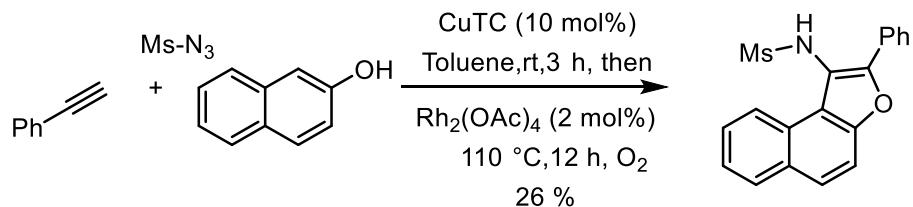
IR (ν_{max} , cm^{-1}): 3429, 3064, 2961, 1614, 828.

^1H NMR (500 MHz, CDCl_3 , 24 °C): δ 7.51-7.49 (m, 2H), 7.42 (d, $J = 8.5$ Hz, 2H), 7.18-7.13 (m, 3H), 7.10 (s, 1H), 6.89 (d, $J = 8.0$ Hz, 2H), 6.84 (s, 1H), 6.38 (s, 1H), 2.60 (s, 3H), 2.42 (s, 3H), 2.24 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 24 °C) δ 153.8, 151.4, 143.7, 136.6, 135.5, 131.3, 129.3, 129.2, 128.2 (2C), 127.5, 127.0, 126.5, 123.4, 112.9, 109.4, 21.7, 21.5, 18.5.

HRMS: m/z: [M+H]⁺ Calcd. for $\text{C}_{23}\text{H}_{22}\text{NO}_3\text{S}$, 392.1320, found 392.1319.

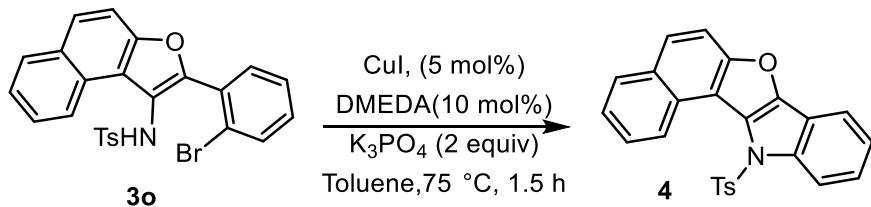
3.4 One-pot synthesis of naphthofuran 3a:



In an over dried 10 mL Schlenk tube, equipped with stir bar, CuTC (0.1 mmol, 0.2 equiv) was dissolved in toluene (4 mL) and stirred at room temperature under N_2 atmosphere. To the stirred solution phenylacetylene (0.55 mmol, 1.1 equiv) followed by mesyl azide (0.5 mmol, 1 equiv) were added and the resulting mixture was stirred for 3 h. After complete conversion of the starting material as monitored by TLC analysis, $\text{Rh}_2(\text{OAc})_4$ (0.02 mmol, 4 mol%) and β -naphthol (0.5 mmol, 1 equiv) were added to the Schlenk tube equipped with oxygen atmosphere and stirred at 110 °C for 12 h. After completion of reaction, as monitored by TLC analysis, the reaction mixture was cooled to room temperature and purified by column chromatography using hexane/ethyl acetate mixture to afford the **3a** in 26% (44 mg) of yield.

4. Synthetic application of the developed method:

4.1. Synthesis of compound 12*H*-naphtho[1',2':4,5]furo[3,2-*b*]indole (4):



In an oven dried 10 mL reaction tube, equipped with stir bar, **3o** (0.1 mmol) was dissolved in 1 mL of toluene. Subsequently, CuI (5 mol%), *N,N'*-dimethylethylenediamine (DMEDA) (10 mol%) and K₃PO₄ (2 equiv) were added under nitrogen atmosphere. The reaction tube was sealed and stirred at 75 °C for 1.5 h. After the TLC analysis, it was cooled to room temperature and purified by column chromatography using ethyl acetate / hexane (9:91) mixture as eluent to afford the polyheteroaromatic compound **4** in 89% of yield.

Yield: 89 % (37 mg); White solid; *R*_f = 0.34 in 2:8 EtOAc/Hexane.

MP: 128-130 °C.

IR (ν_{max} , cm⁻¹): 3483, 2926, 1637, 1326, 1417.

¹H NMR (400 MHz, CDCl₃, 24 °C): δ 9.02 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.58-7.51 (m, 2H), 7.48-7.46 (m, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.16-7.15 (m, 2H), 7.05-7.03 (m, 1H), 6.83-6.80 (m, 2H), 2.23 (s, 3H).

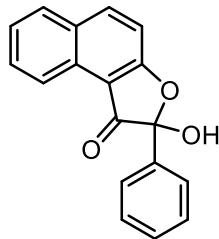
¹³C{¹H} NMR (125 MHz, DMSO, 24 °C) δ 152.0, 150.0, 143.5, 135.7, 133.0, 132.1, 131.1, 130.4, 130.3, 129.4, 128.7, 127.9, 127.3, 127.2(2C), 126.8, 125.3, 124.4, 121.7, 120.7, 116.5, 112.2, 21.5.

HRMS: m/z: [M+Na]⁺ Calcd. for C₂₅H₁₇NO₃SnA, 434.0826, found 434.0781.

4. 2. Synthesis of naphtho[2,1-*b*]furan-1(*2H*)-ones:

In an oven dried 10 mL Schlenk tube equipped with stir bar, **3a** or **3s** (0.1 mmol) was dissolved in 2 mL DMF. Subsequently, Pd(OAc)₂ (10 mol%), Cu(OAc)₄ (1 equiv) were added under oxygen atmosphere. The reaction mixture was stirred at 100 °C for 12 h. After the TLC analysis, the reaction mixture was cooled to room temperature and diluted with water, extracted with DCM. The obtained organic layer was washed with cold water and dried over Na₂SO₄. Evaporation of solvent and purification of crude through column chromatography using (Hexane: EtOAc: 9:1) as eluent to afford the product.

2-Hydroxy-2-phenylnaphtho[2,1-*b*]furan-1(2*H*)-one (5):



Yield: 58 % (16 mg); White solid; R_f = 0.38 in 2:8 EtOAc/Hexane.

MP: 85-87 °C.

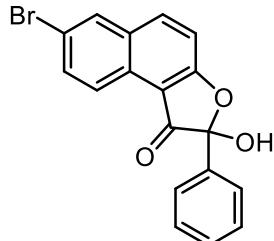
IR (ν_{max} , cm⁻¹): 3396, 1709, 1258, 1077, 748

¹H NMR (400 MHz, CDCl₃, 24 °C): δ 8.47 (d, J = 8.00 Hz, 1H), 8.10 (d, J = 8.8 Hz, 1H), 7.77 (d, J = 8.00 Hz, 1H), 7.69-7.68 (m, 2H), 7.54 (t, J = 7.6 Hz, 1H), 7.44-7.38 (m, 4H), 7.29 (d, J = 7.2 Hz, 1H), 4.92 (bs, 1H).

¹³C{¹H} NMR (125 MHz, DMSO, 24 °C) δ 197.6, 173.5, 141.6, 136.4, 130.4, 129.3, 129.2, 129.1, 129.0, 128.6, 125.8, 125.5, 121.9, 114.2, 109.7, 105.3.

HRMS: m/z: [M+H]⁺ Calcd. for C₈H₁₃O₃, 277.0864, found 277.0873.

7-Bromo-2-hydroxy-2-phenylnaphtho[2,1-*b*]furan-1(2*H*)-one (6)



Yield: 47 % (17 mg); White solid; R_f = 0.43 in 2:8 EtOAc/Hexane.

MP: 108-110 °C.

IR (ν_{max} , cm⁻¹): 3389, 1710, 1498, 1277, 1066, 740.

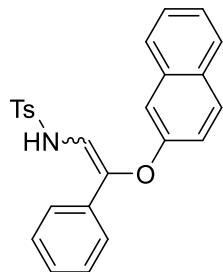
¹H NMR (400 MHz, CDCl₃, 24 °C): δ 8.67 (s, 1H), 8.41 (dd, J = 8.8, 2.8 Hz, 2H), 8.36 (s, 1H), 7.87-7.84 (m, 1H), 7.61 (d, J = 8.8 Hz, 1H), 7.52-7.51(m, 2H), 7.41-7.40(m, 3H),

¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C) δ 197.8, 174.0, 140.4, 135.2, 133.3, 130.7, 130.6, 130.0, 128.9, 127.9, 126.0, 124.4, 119.3, 114.9, 110.5, 105.0.

HRMS: m/z: [M+H]⁺ Calcd. for C₁₈H₁₂BrO₃, 354.9969, found 354.9996.

5. Synthesis of 4-Methyl-N-(2-(naphthalen-2-yloxy)-2-phenylvinyl)benzenesulfonamide (7):

In an over dried 10 mL sealed tube, equipped with stir bar tosyl triazole **1b** (0.5 mmol, 1 equiv) followed by β -naphthol (0.6 mmol, 1.2 equiv) and $\text{Rh}_2(\text{OAc})_4$ (0.01 mmol, 2 mol%) were added and the resulting mixture was stirred for 12 h in toluene. After complete conversion of starting material as monitored by TLC analysis the reaction mixture was cooled to room temperature and purified by column chromatography using hexane/ethyl acetate mixture to afford the **7** in 43% of yield.



Yield: 43 % (89 mg); White solid; $R_f = 0.37$ in 2:8 EtOAc/Hexane.

IR (ν_{max} , cm^{-1}): 3430, 2978, 1166, 1329, 743.

^1H NMR (400 MHz, DMSO, 24 °C): δ 10.35 (d, $J = 10.4$ Hz, 1H), 7.83-7.77 (m, 4H), 7.53 (d, $J = 8.0$ Hz, 1H), 7.44-7.40 (m, 1H), 7.38-7.32 (m, 3H), 7.27-7.23 (m, 3H), 7.18-7.14 (m, 3H), 6.99-6.96 (m, 1H), 2.36 (s, 3H).

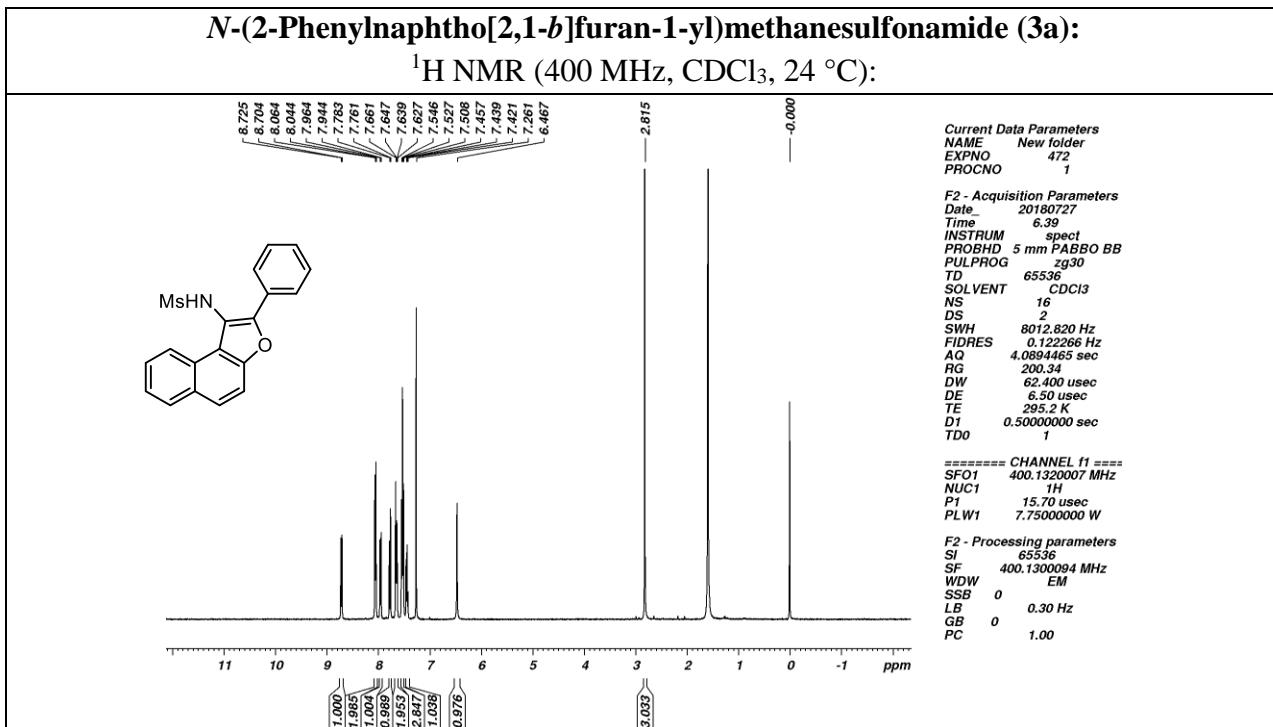
$^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, DMSO, 24 °C) δ 154.6, 143.7, 138.2, 134.9, 134.1, 133.7, 130.2, 129.9, 129.6, 129.1, 128.0, 127.8, 127.1, 126.9, 124.6, 124.4, 119.0, 114.9, 109.6, 21.3.

HRMS: m/z: [M+Na]⁺ Calcd. for $\text{C}_{25}\text{H}_{21}\text{NO}_3\text{SNa}$, 438.1139, found 438.1127.

6. Spectral data of the synthesized compounds:

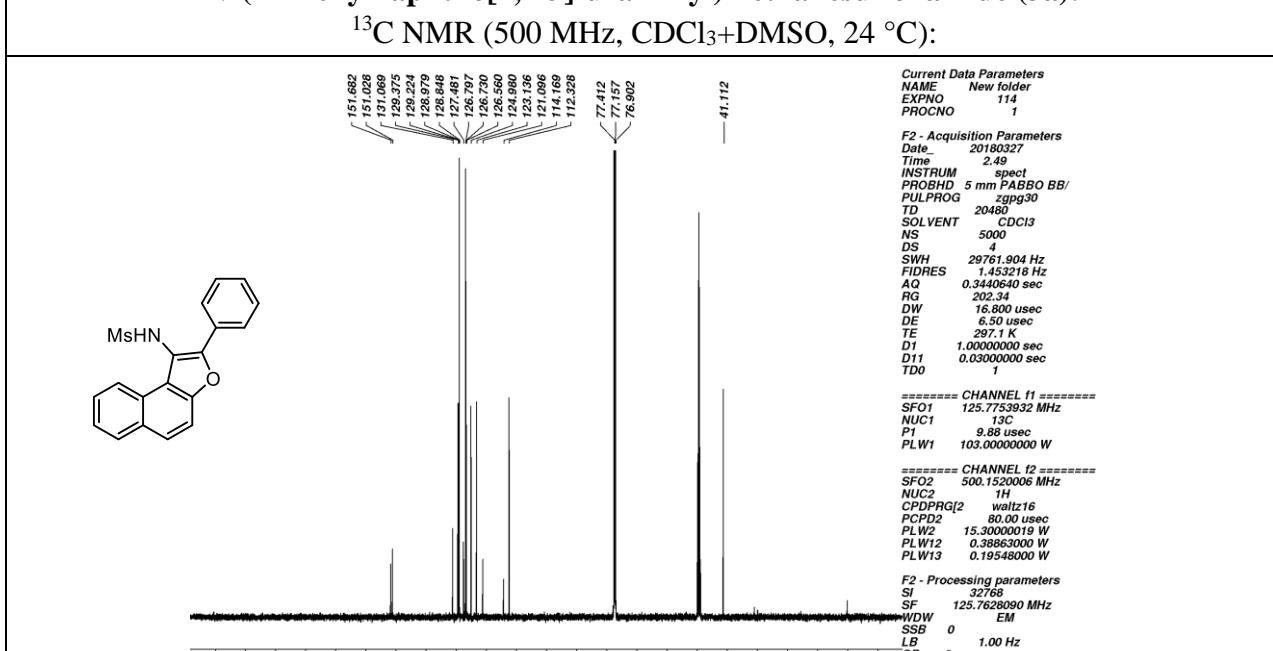
N-(2-Phenylnaphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3a):

¹H NMR (400 MHz, CDCl₃, 24 °C):



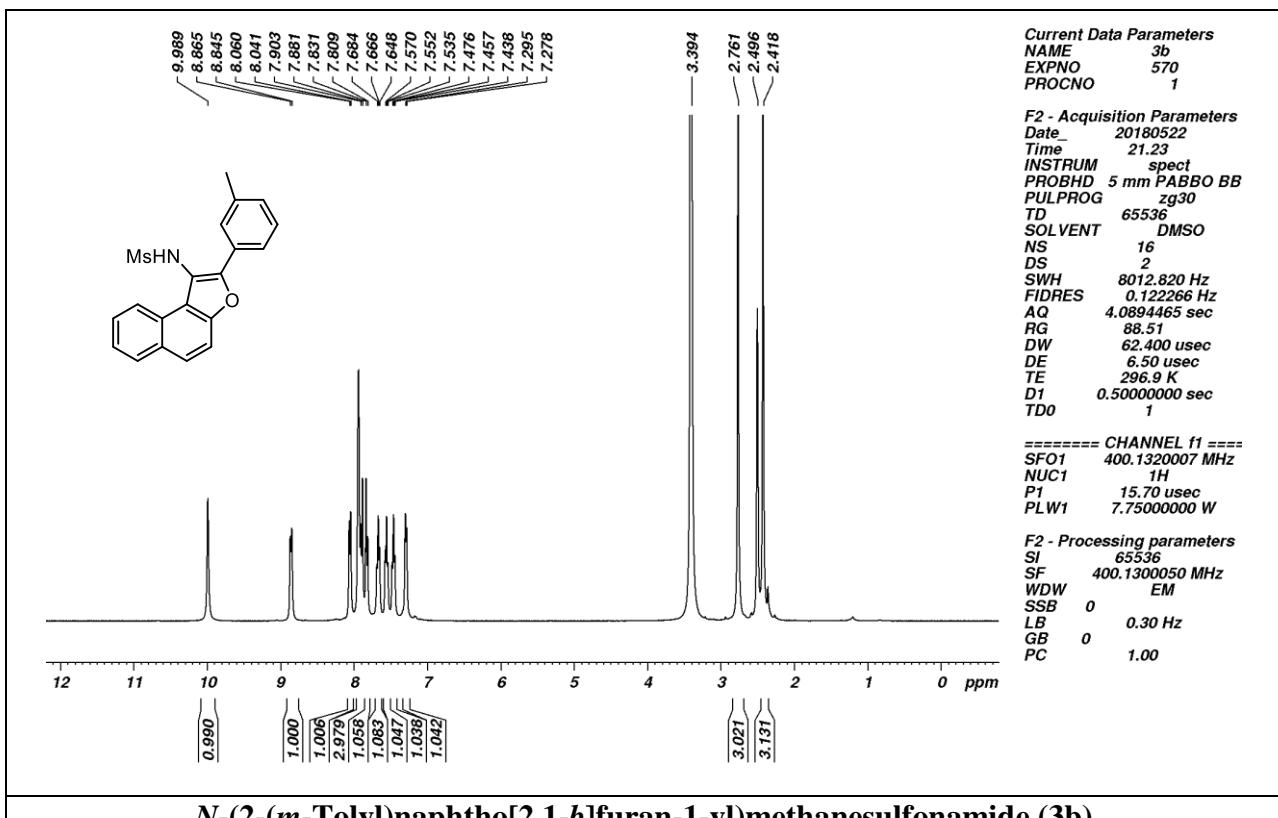
N-(2-Phenylnaphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3a):

¹³C NMR (500 MHz, CDCl₃+DMSO, 24 °C):



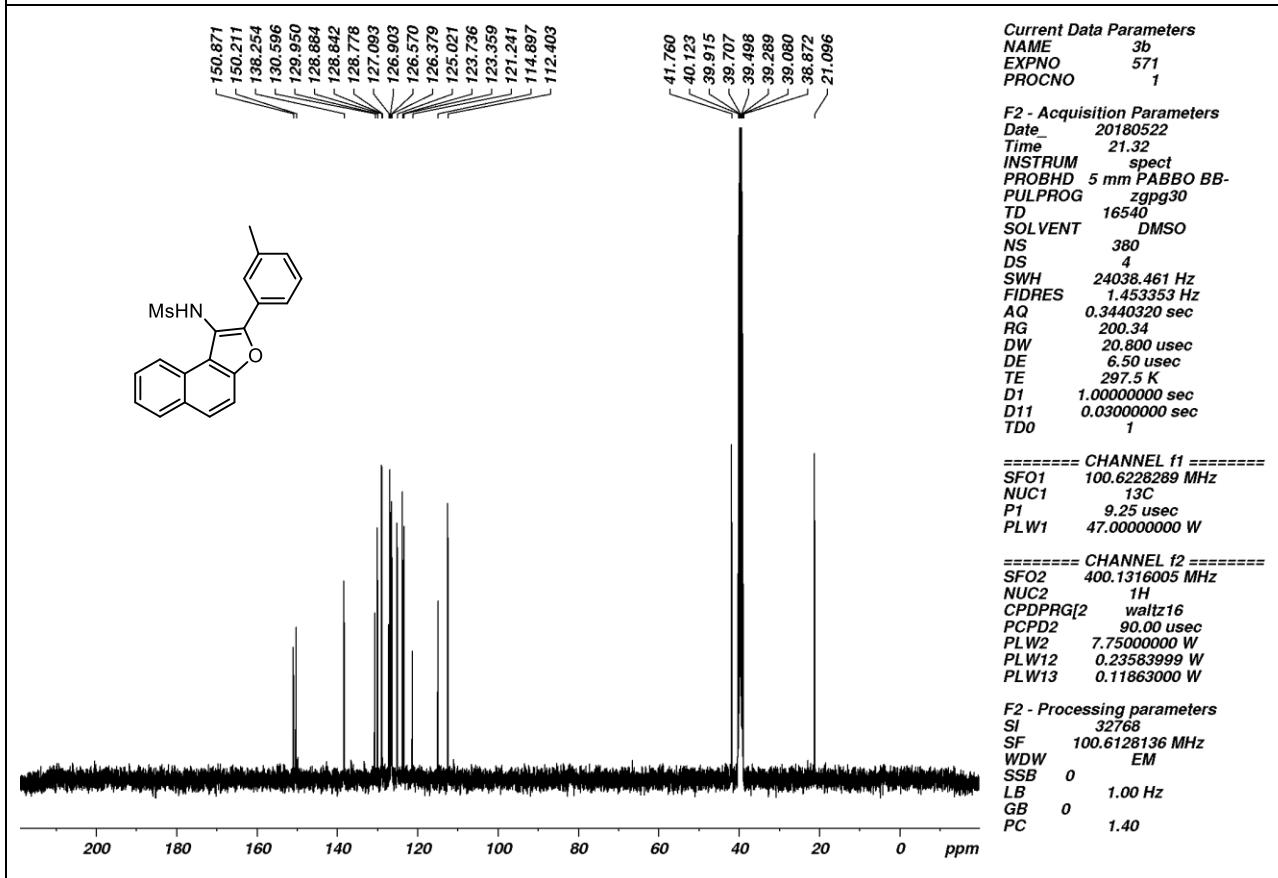
N-(2-(*m*-Tolyl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3b)

¹H NMR (400 MHz, DMSO, 24 °C):



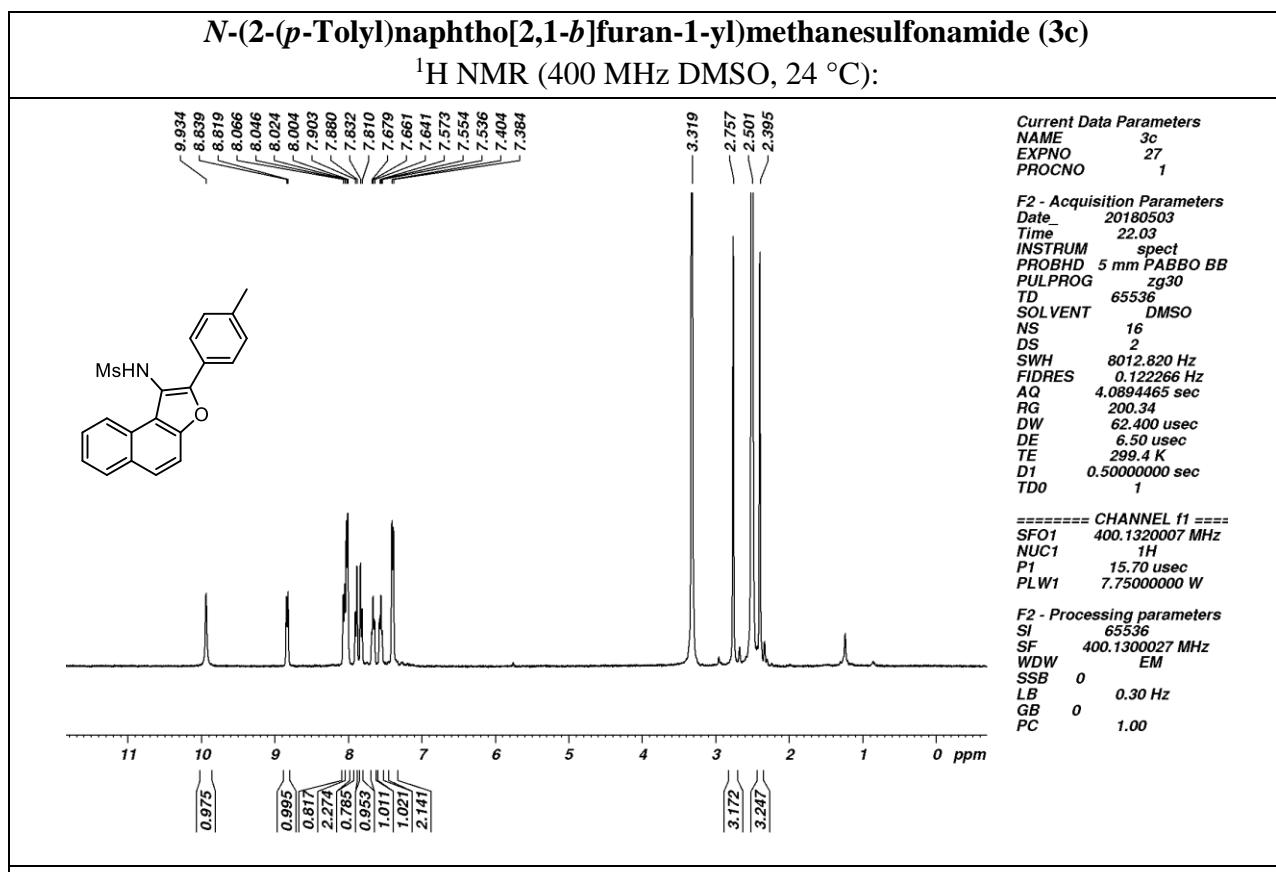
N-(2-(*m*-Tolyl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3b)

¹³C NMR (400 MHz, DMSO, 24 °C):



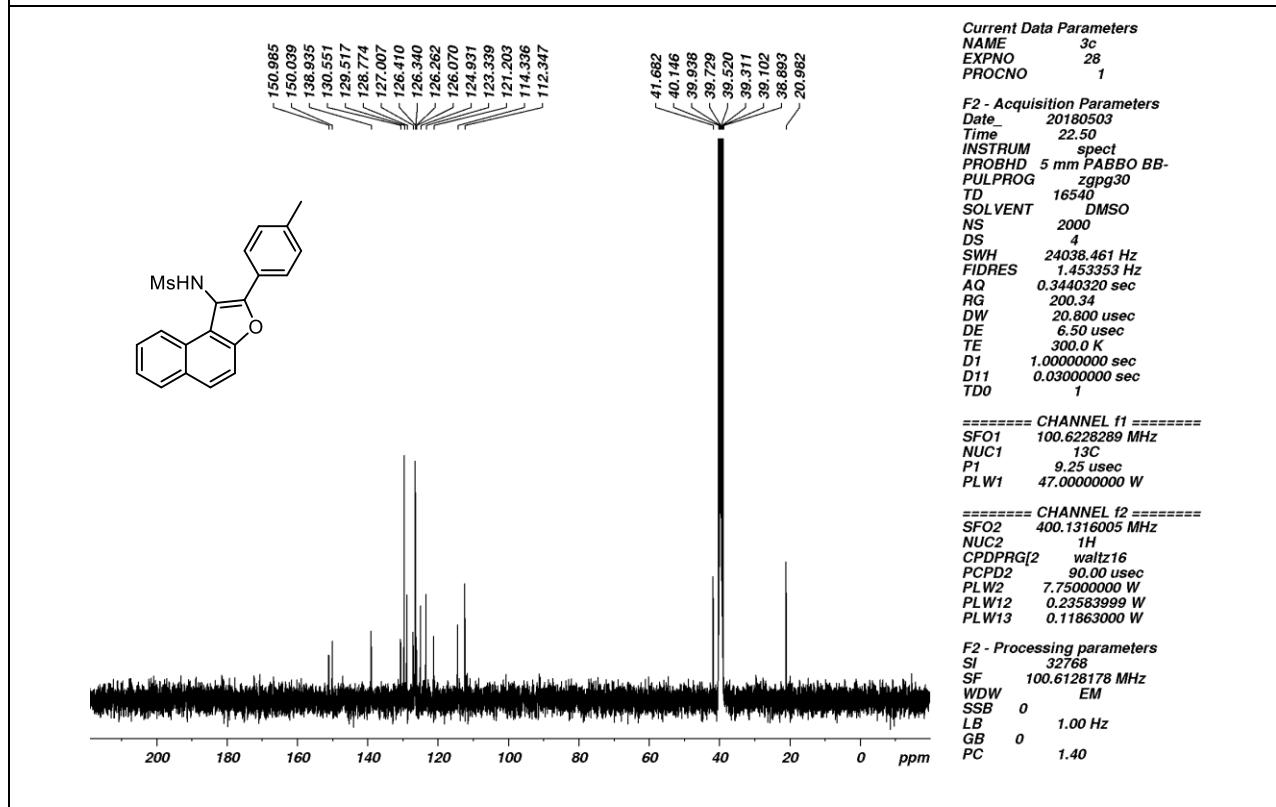
***N*-(2-(*p*-Tolyl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3c)**

¹H NMR (400 MHz DMSO, 24 °C):



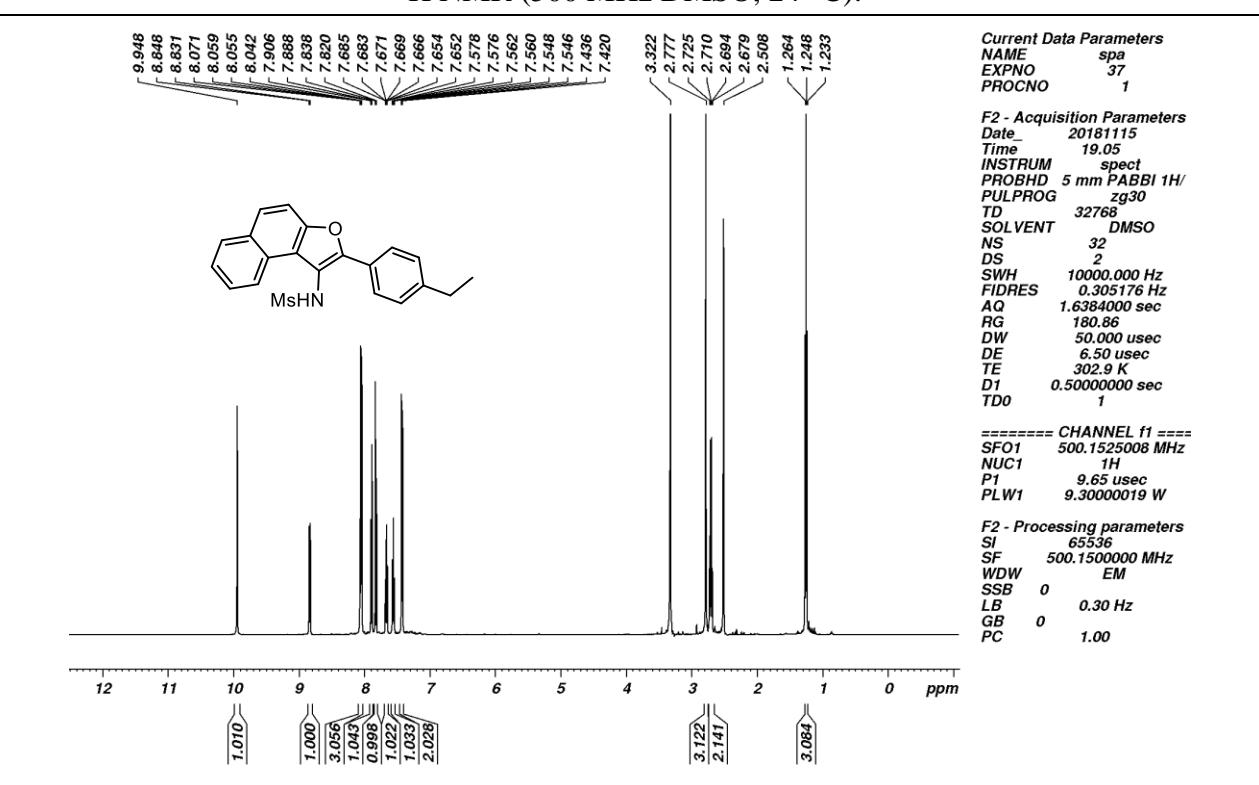
***N*-(2-(*p*-Tolyl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3c)**

¹³C NMR (400 MHz, DMSO, 24 °C):



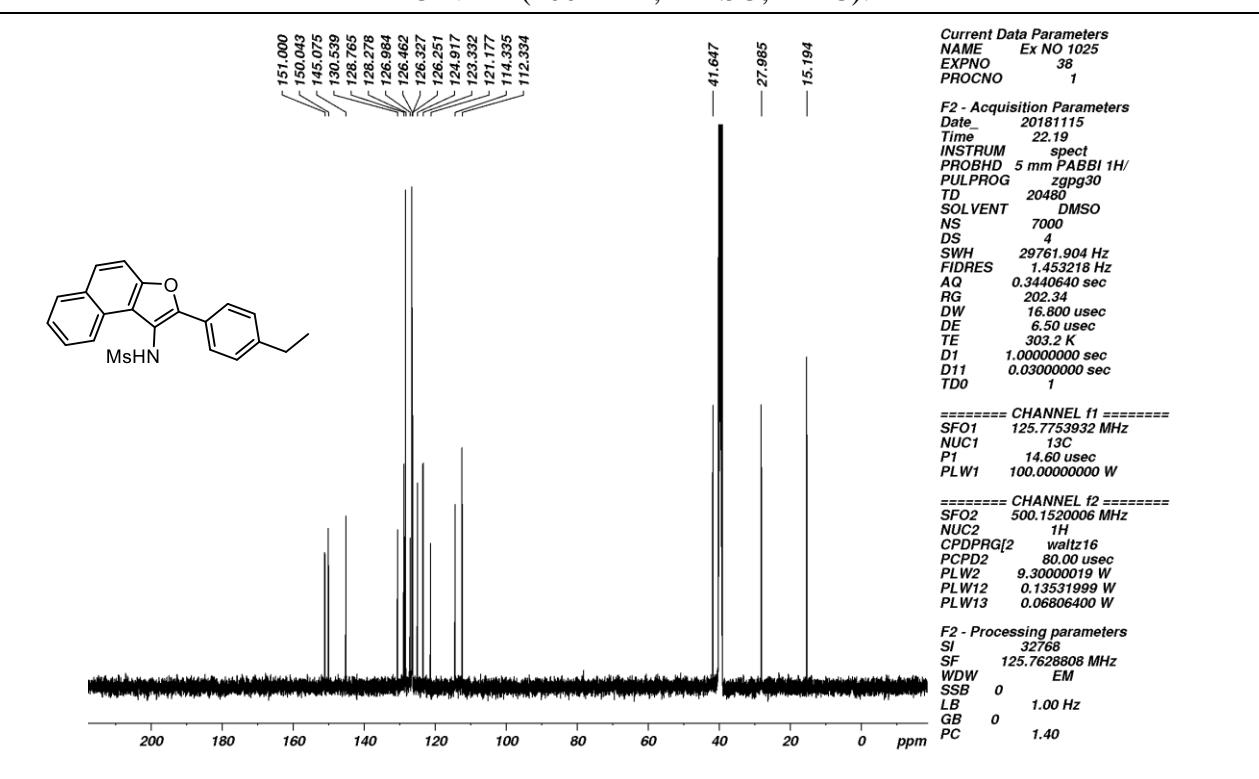
***N*-(2-(4-Ethylphenyl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3d)**

¹H NMR (500 MHz DMSO, 24 °C):



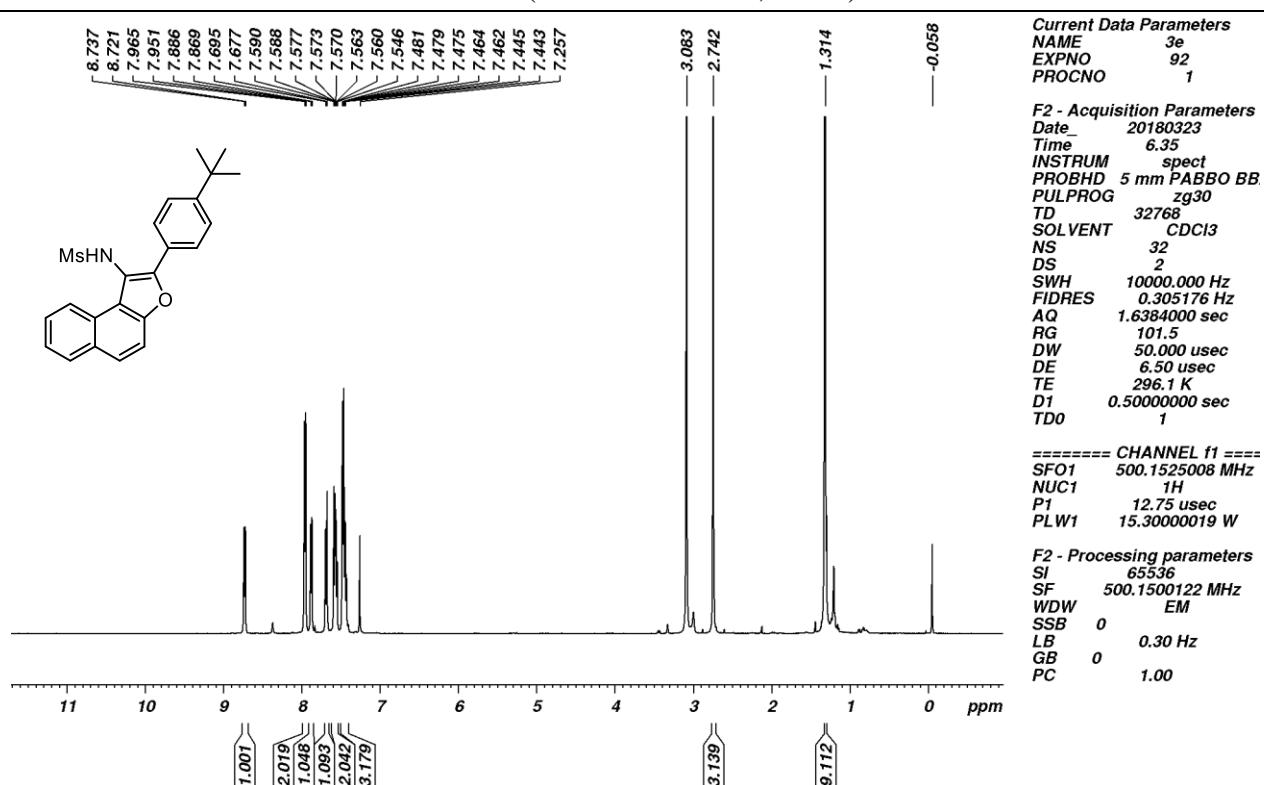
***N*-(2-(4-Ethylphenyl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3d)**

¹³C NMR (400 MHz, DMSO, 24 °C):



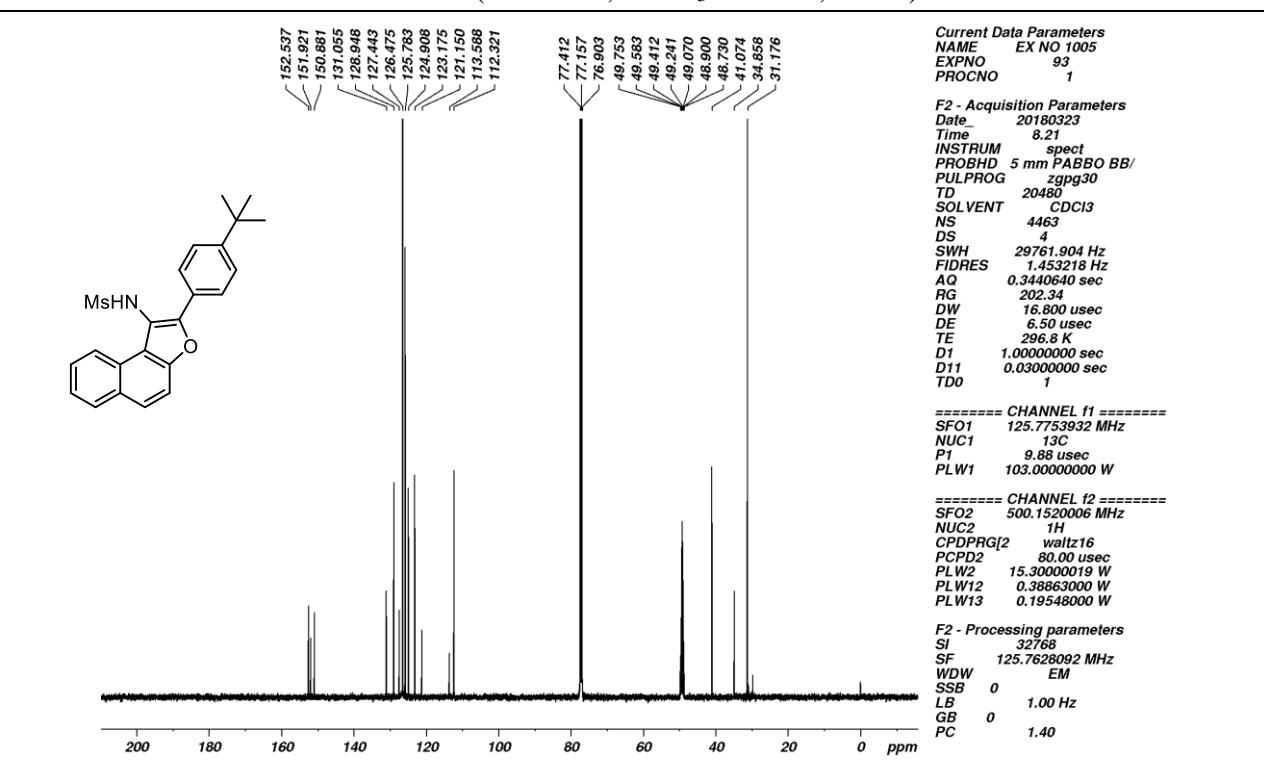
N-(2-(4-(*tert*-Butyl)phenyl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3e)

¹H NMR (500 MHz DMSO, 24 °C):



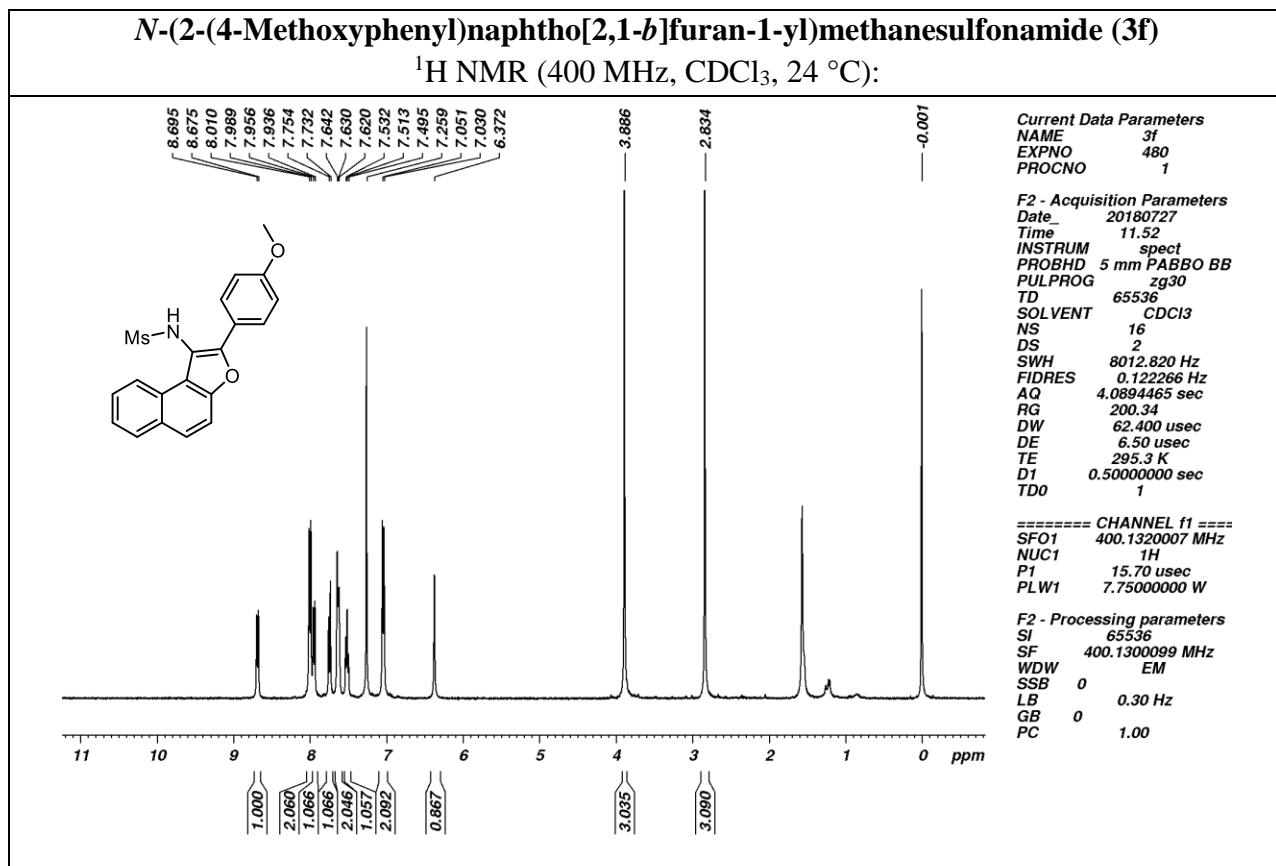
N-(2-(4-(*tert*-Butyl)phenyl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3e)

¹³C NMR (500 MHz, CDCl₃+DMSO, 24 °C):



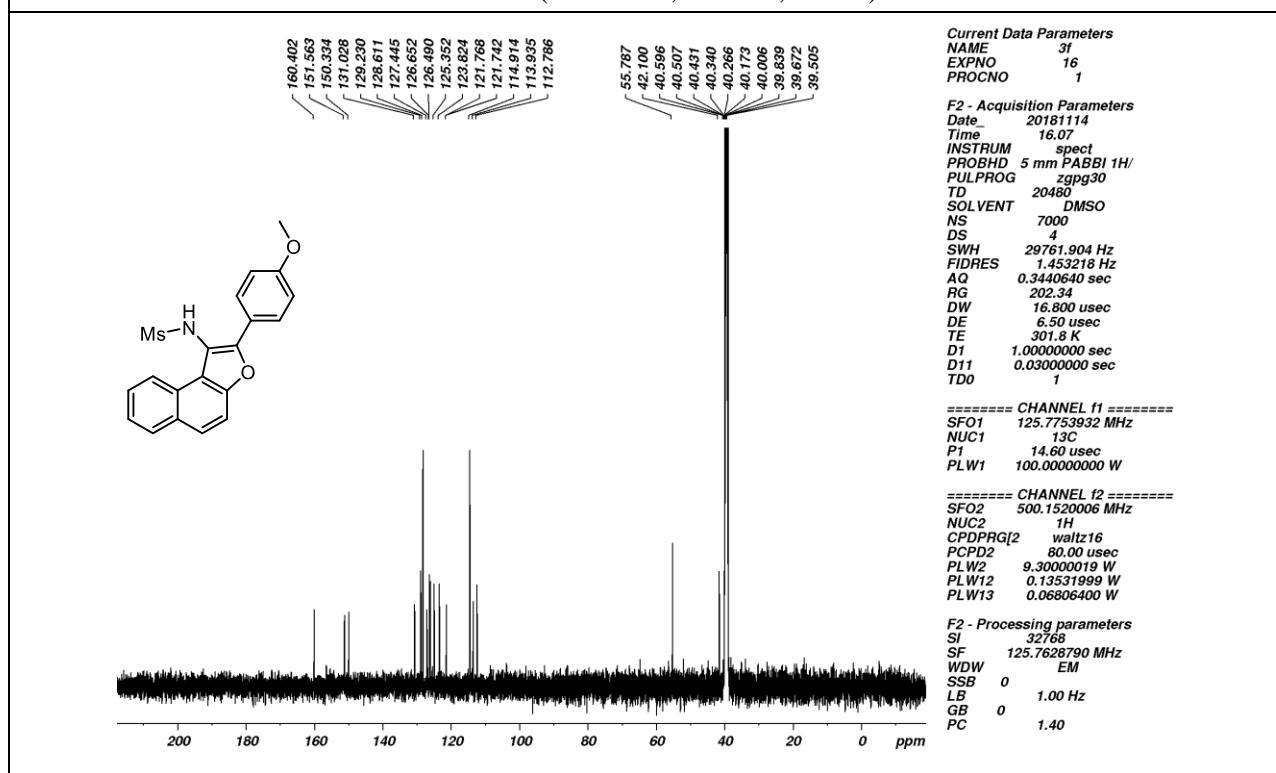
N-(2-(4-Methoxyphenyl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3f)

¹H NMR (400 MHz, CDCl₃, 24 °C):



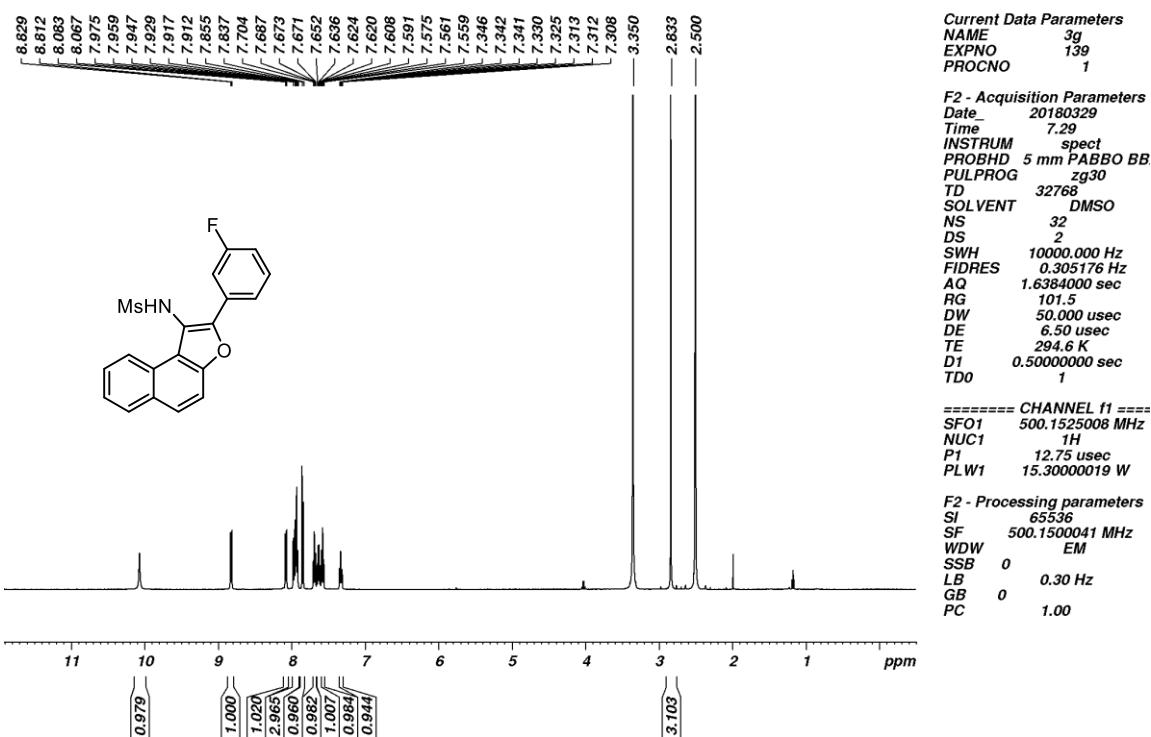
N-(2-(4-Methoxyphenyl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3f)

¹³C NMR (500 MHz, DMSO, 24 °C):



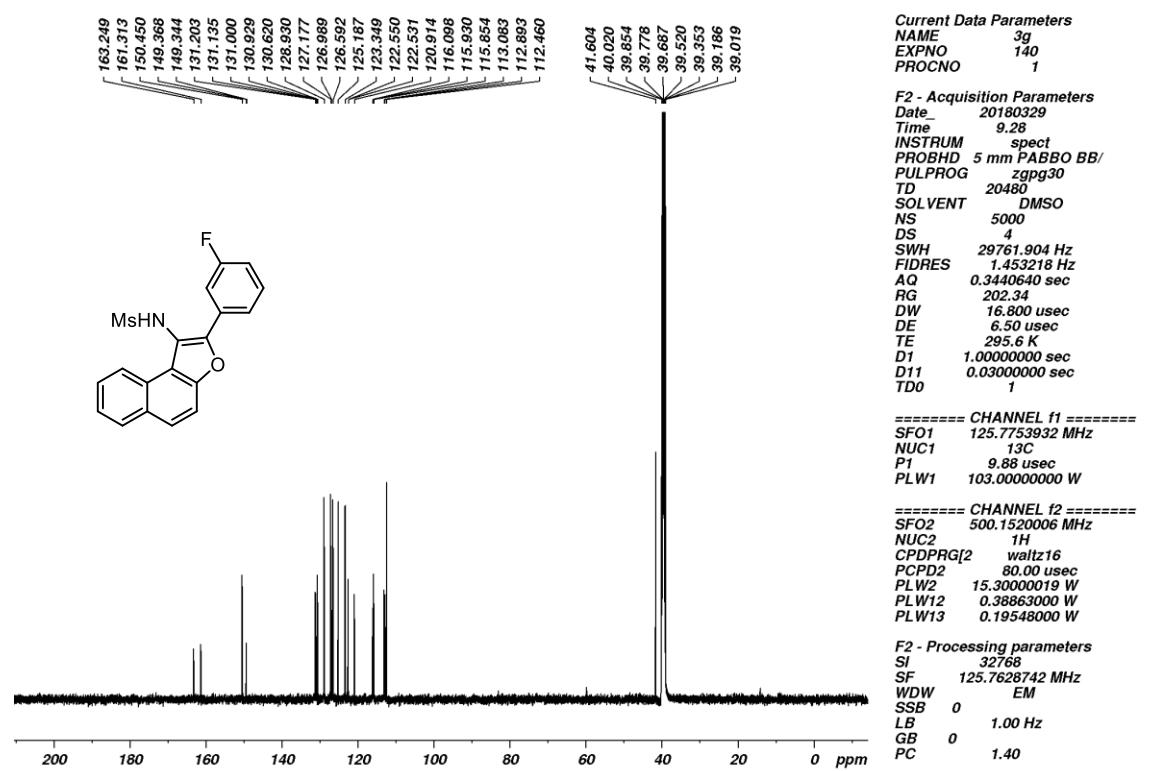
N-(2-(3-Fluorophenyl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3g)

¹H NMR (500 MHz, DMSO, 24 °C):

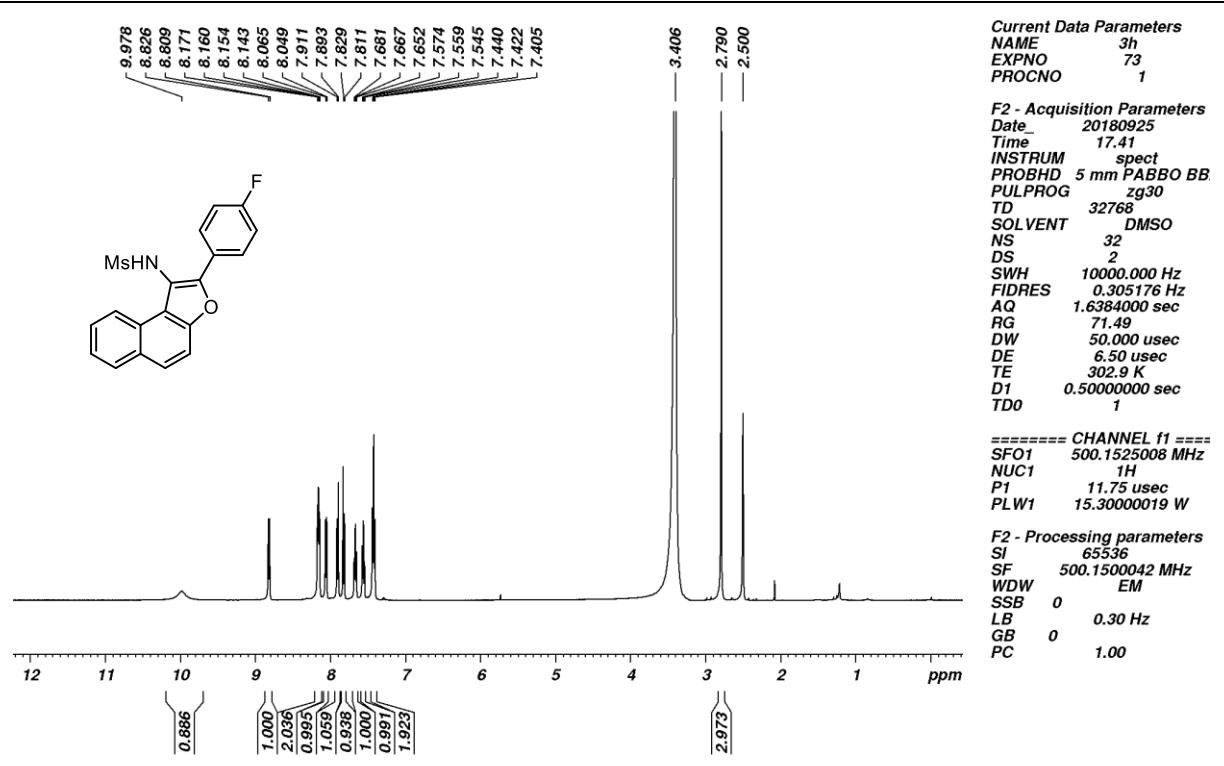


N-(2-(3-Fluorophenyl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3g)

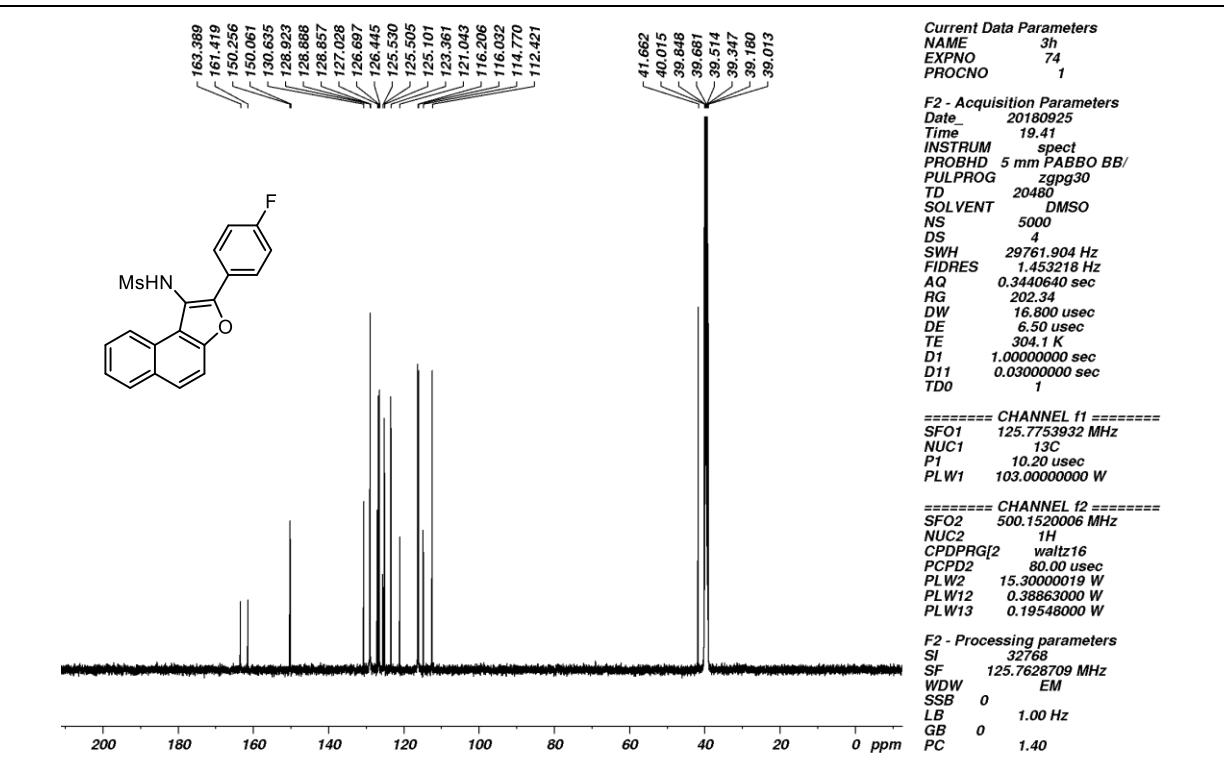
¹³C NMR (500 MHz, DMSO, 24 °C):



N-(2-(4-Fluorophenyl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3h)
¹H NMR (500 MHz, DMSO, 24 °C):

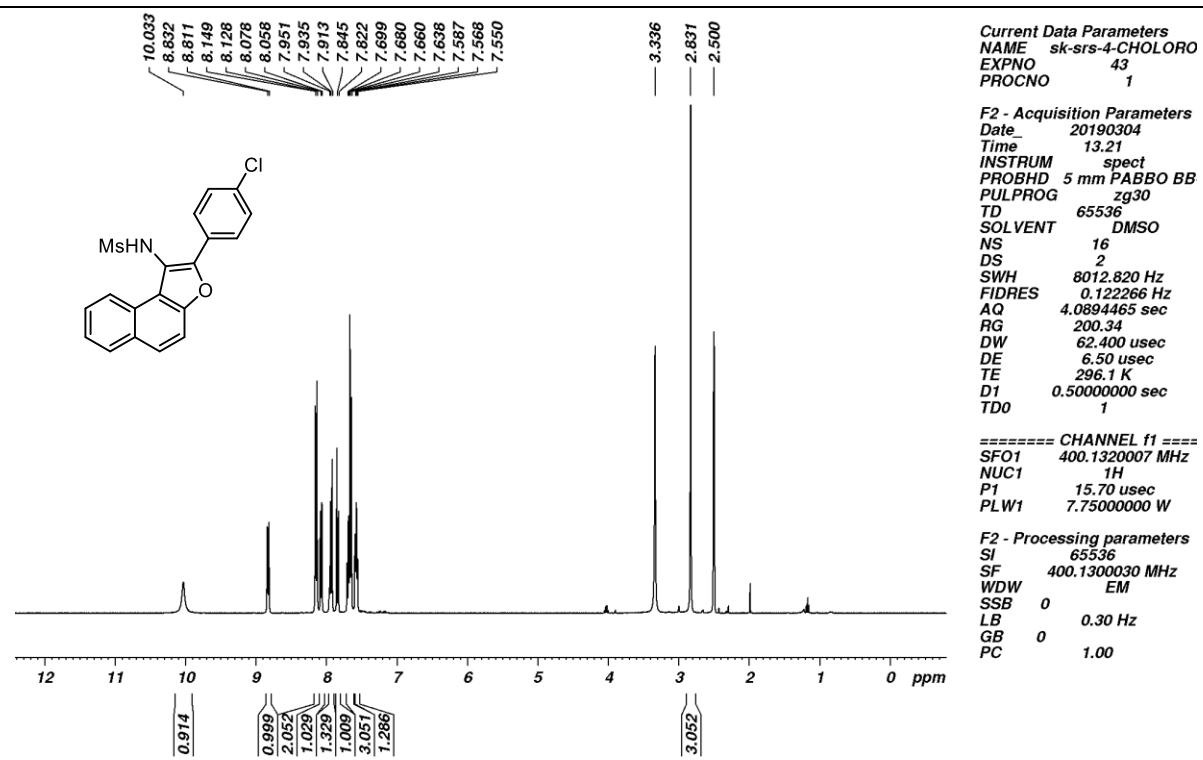


N-(2-(4-Fluorophenyl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3h)
¹³C NMR (500 MHz, DMSO, 24 °C):



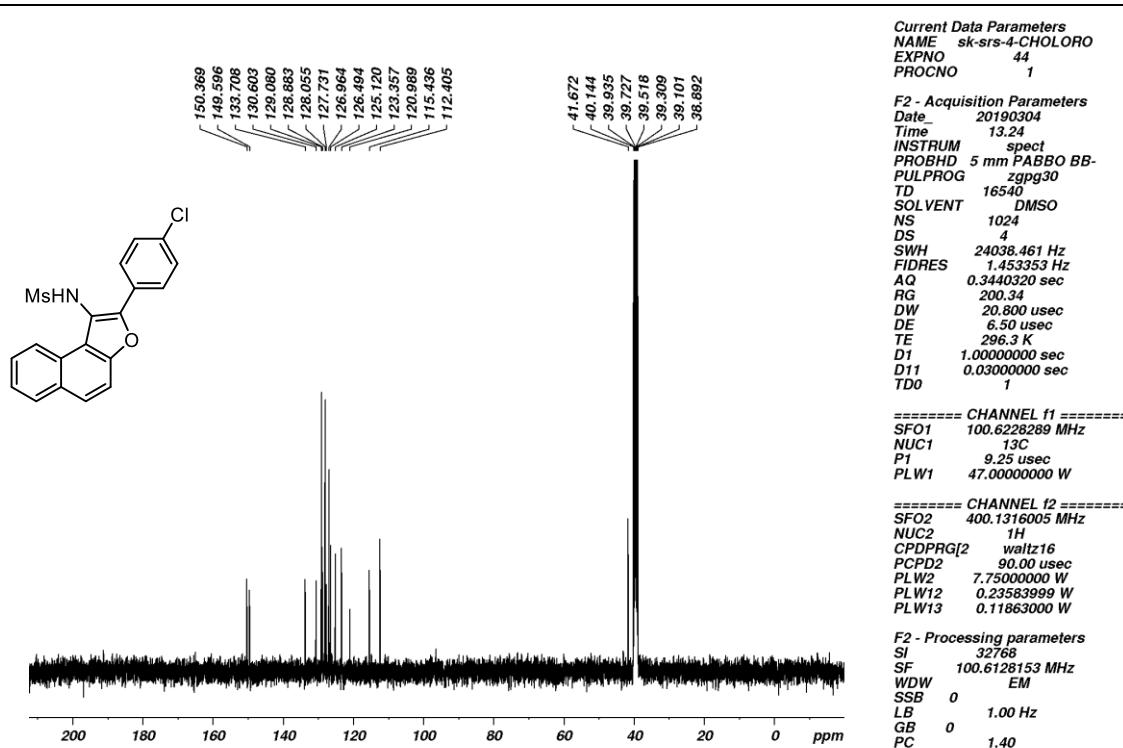
N-(2-(4-Chlorophenyl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3i)

¹H NMR (400 MHz, DMSO, 24 °C):



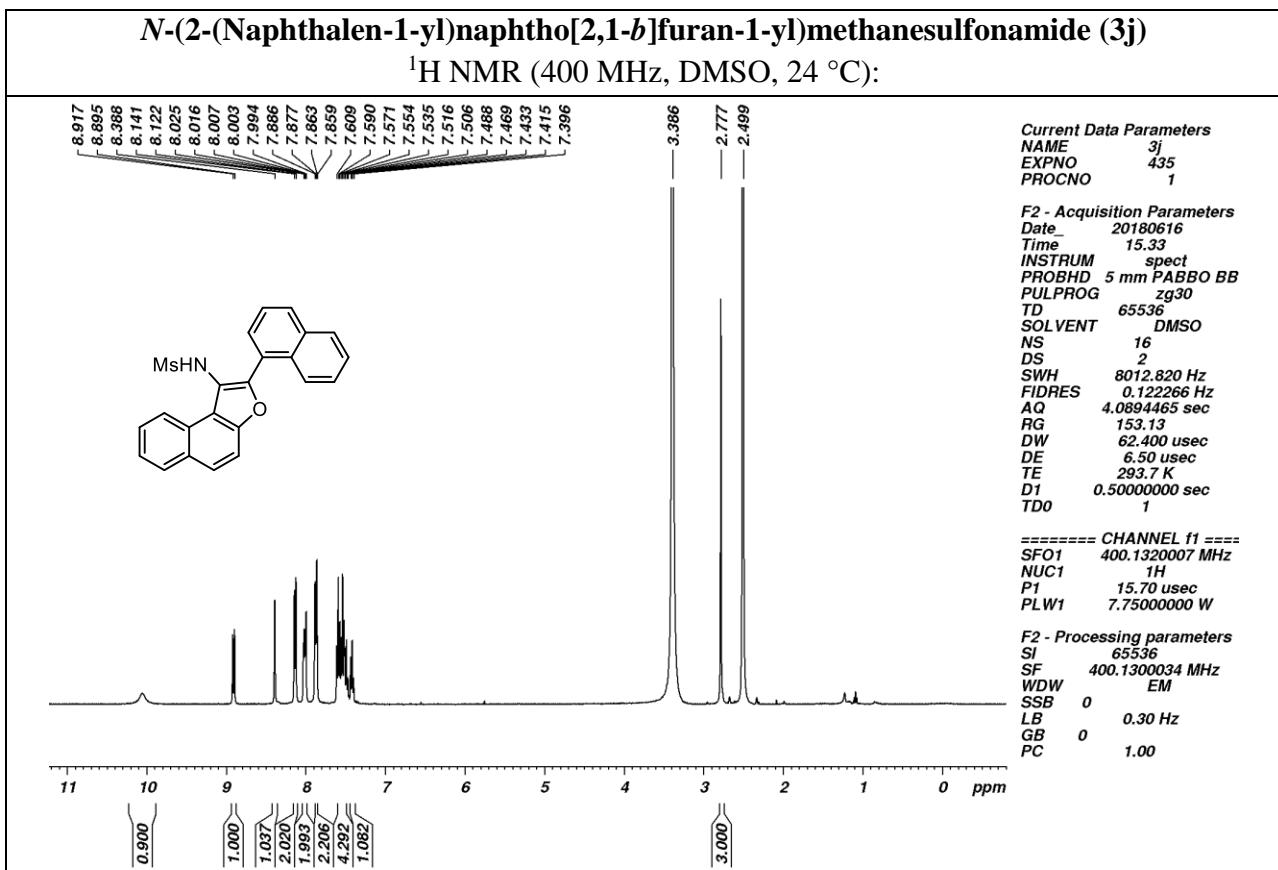
N-(2-(4-Chlorophenyl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3i)

¹³C NMR (400 MHz, DMSO, 24 °C):



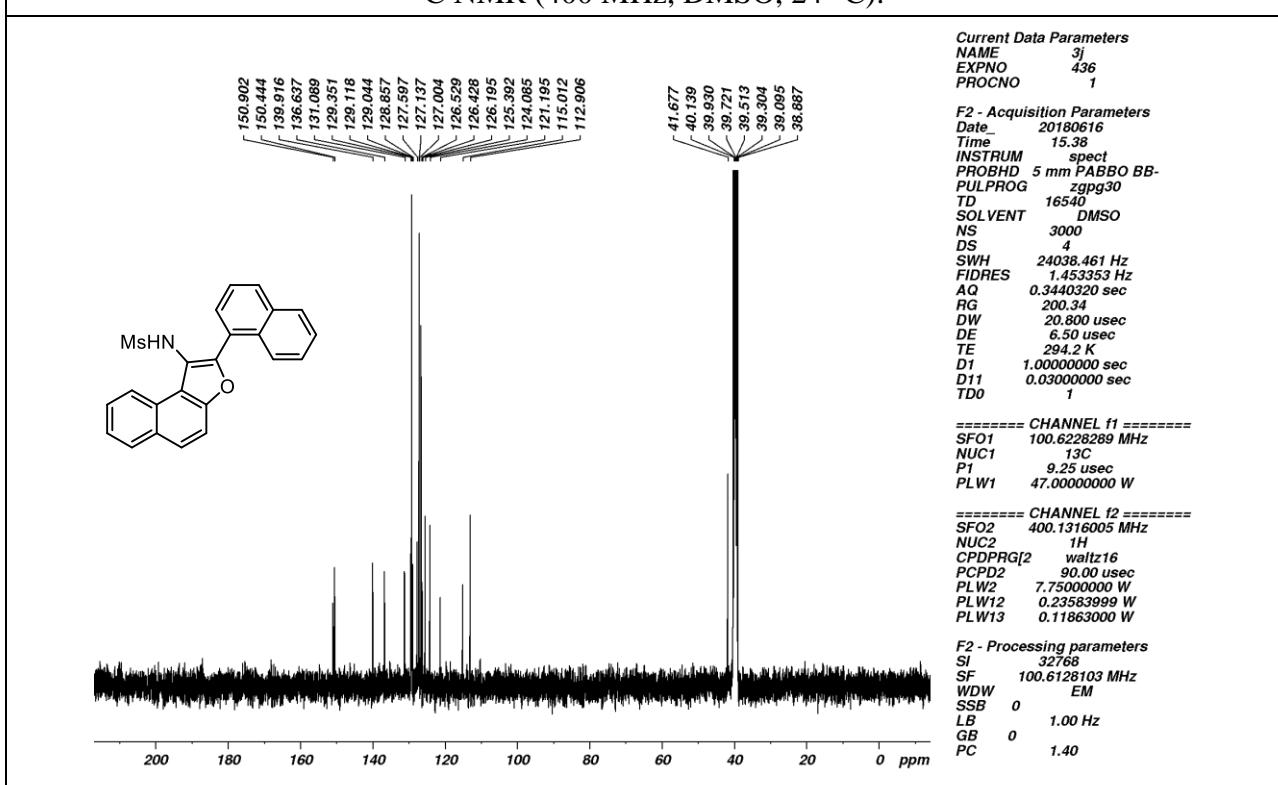
N-(2-(Naphthalen-1-yl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3j)

¹H NMR (400 MHz, DMSO, 24 °C):



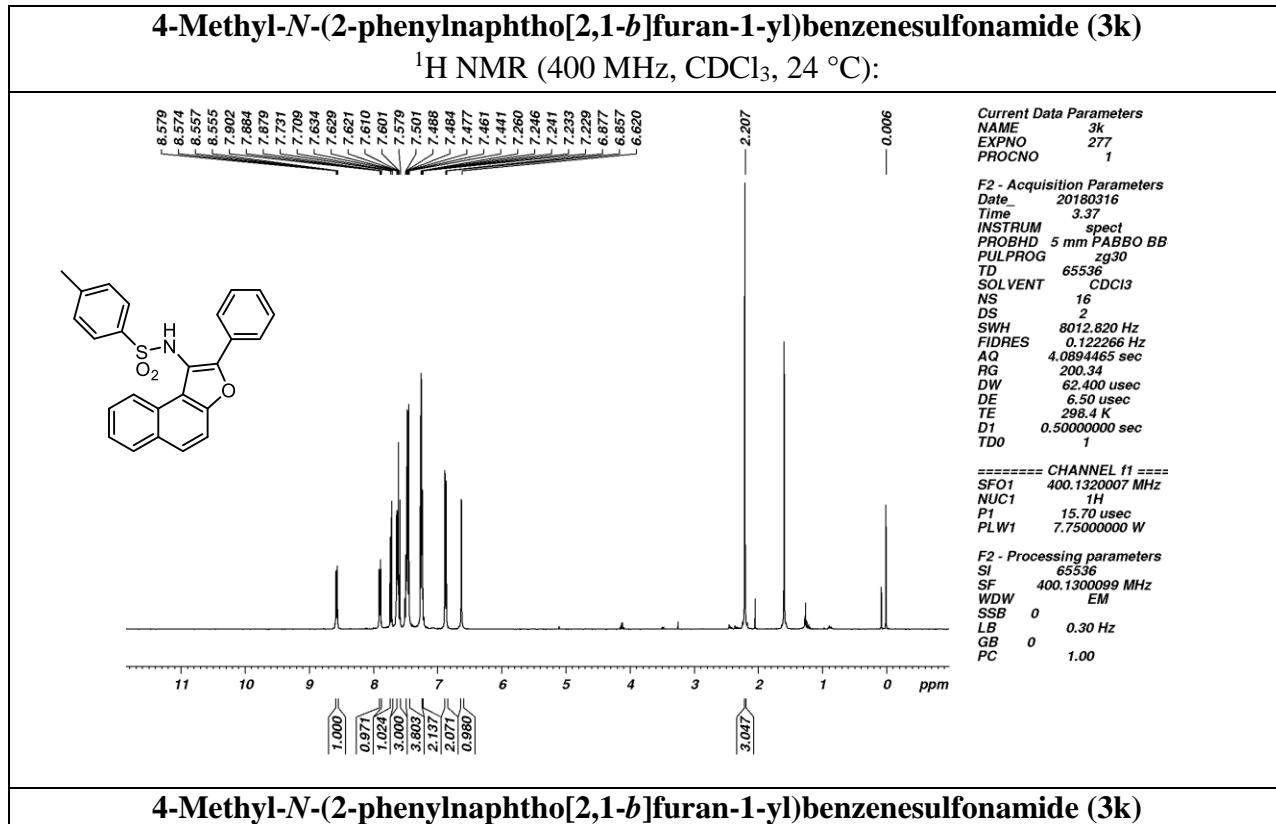
N-(2-(Naphthalen-1-yl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3j)

¹³C NMR (400 MHz, DMSO, 24 °C):



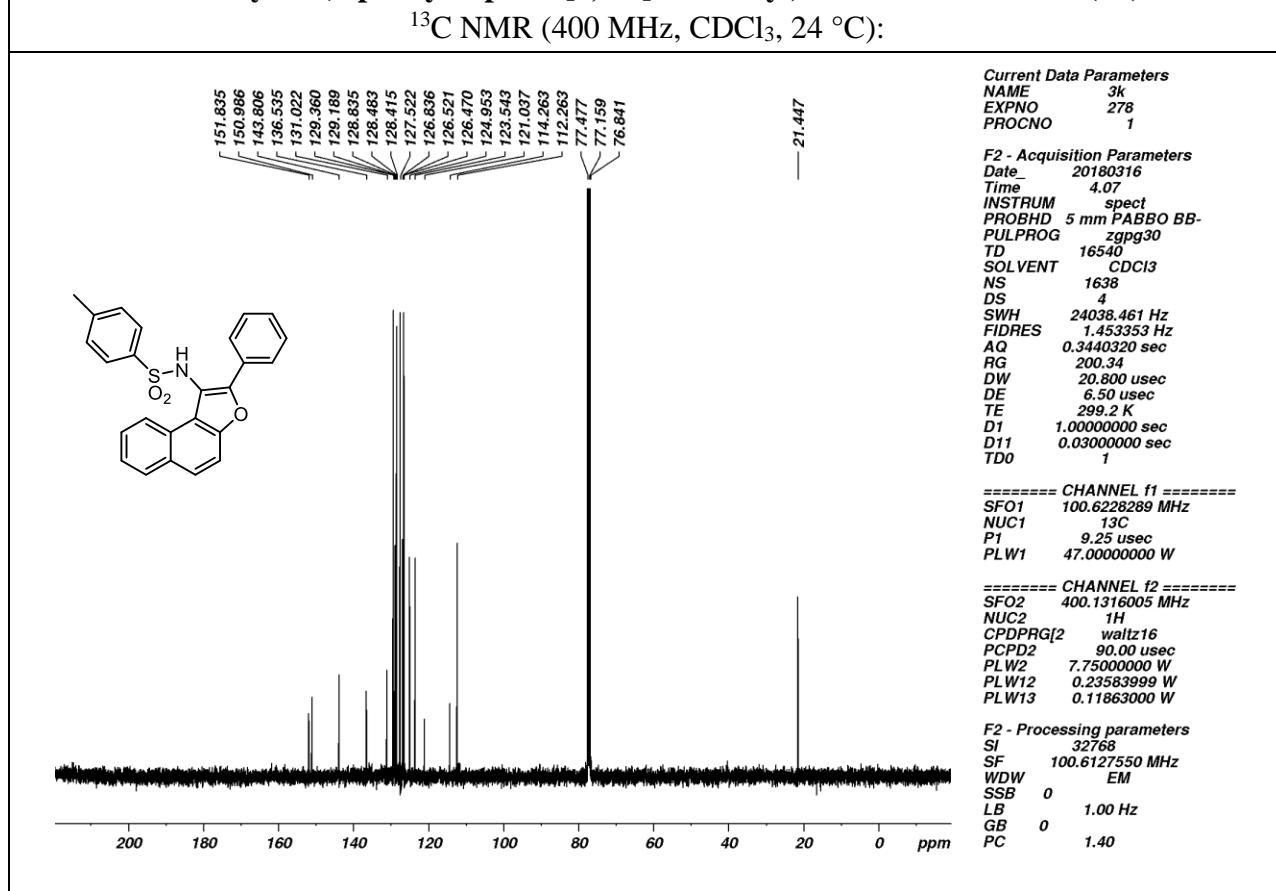
4-Methyl-N-(2-phenylnaphtho[2,1-*b*]furan-1-yl)benzenesulfonamide (3k)

¹H NMR (400 MHz, CDCl₃, 24 °C):



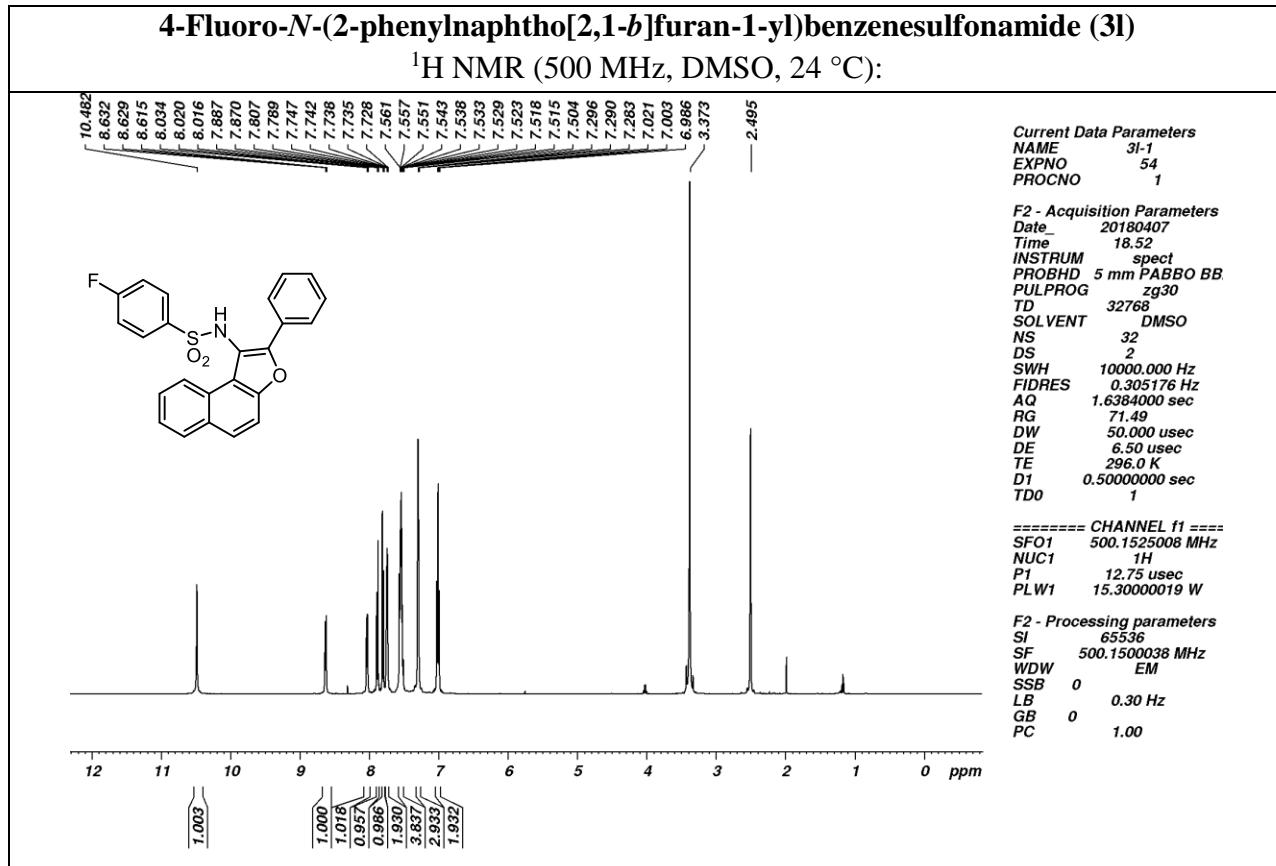
4-Methyl-N-(2-phenylnaphtho[2,1-*b*]furan-1-yl)benzenesulfonamide (3k)

¹³C NMR (400 MHz, CDCl₃, 24 °C):



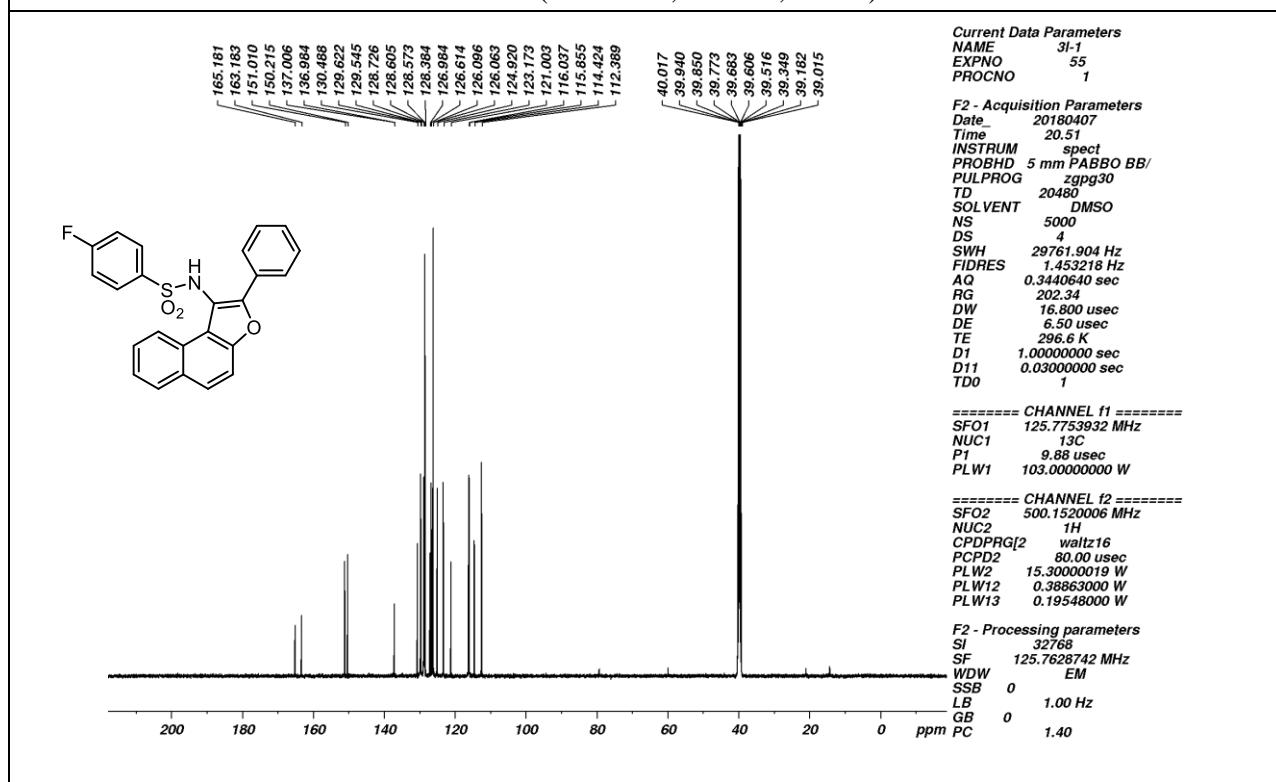
4-Fluoro-N-(2-phenylnaphtho[2,1-*b*]furan-1-yl)benzenesulfonamide (3l)

¹H NMR (500 MHz, DMSO, 24 °C):



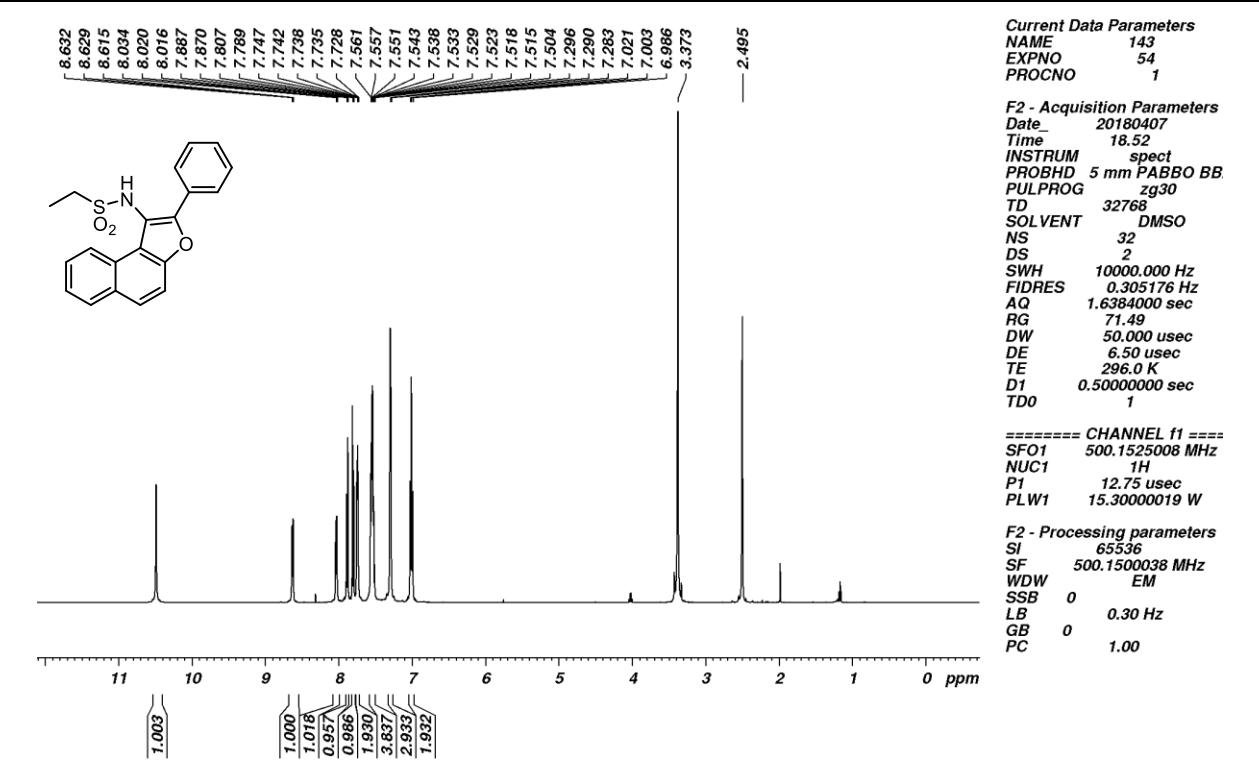
4-Fluoro-N-(2-phenylnaphtho[2,1-*b*]furan-1-yl)benzenesulfonamide (3l)

¹³C NMR (500 MHz, DMSO, 24 °C):



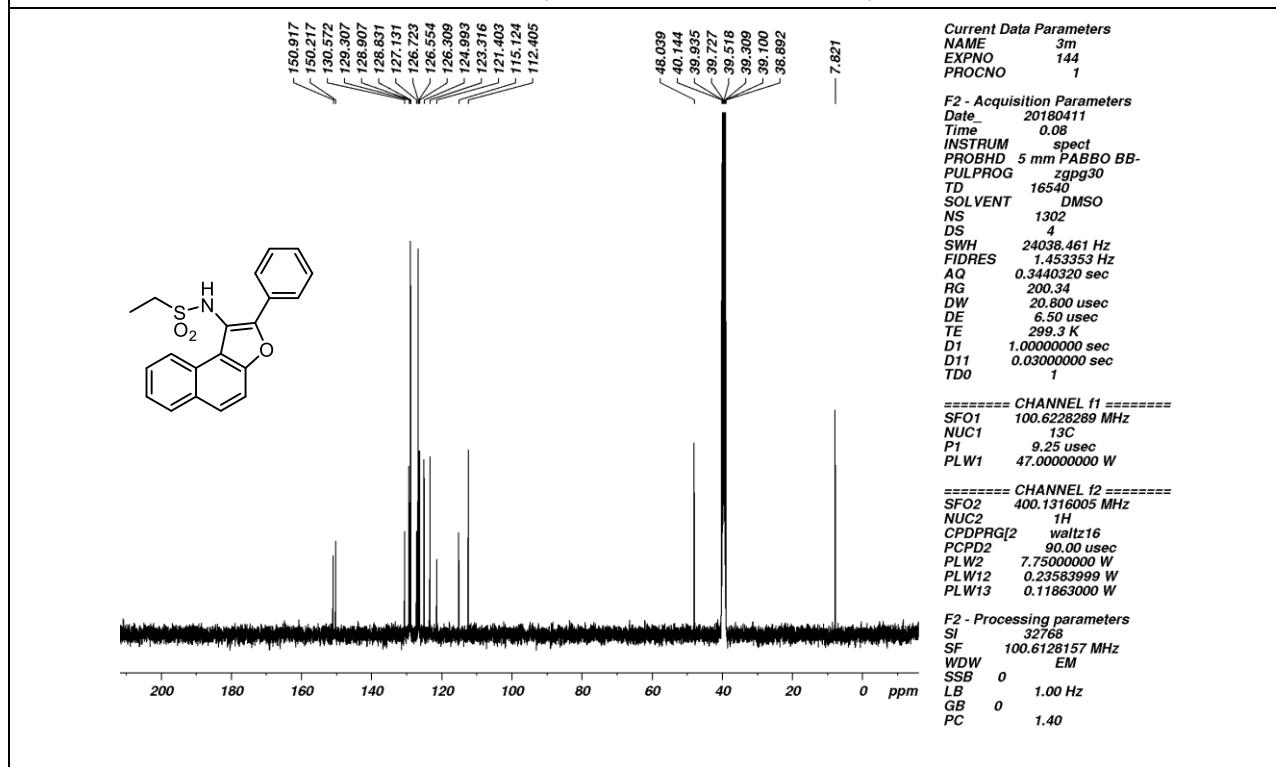
N-(2-Phenylnaphtho[2,1-*b*]furan-1-yl)ethanesulfonamide (3m)

¹H NMR (400 MHz, DMSO, 24 °C):



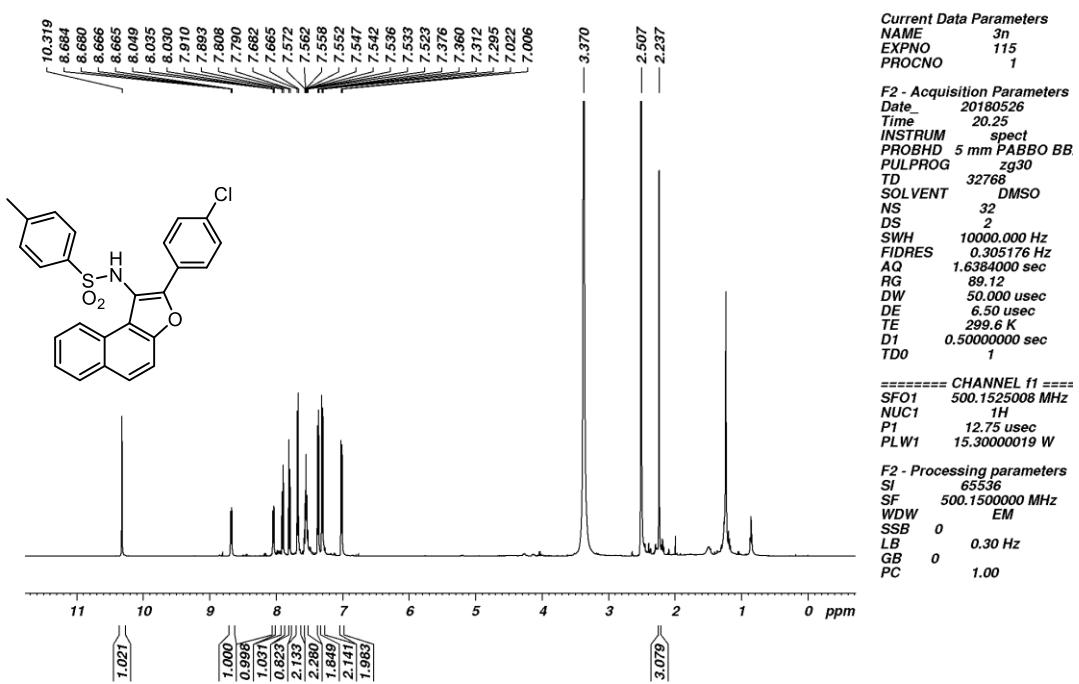
N-(2-Phenylnaphtho[2,1-*b*]furan-1-yl)ethanesulfonamide (3m)

¹³C NMR (400 MHz, DMSO, 24 °C):



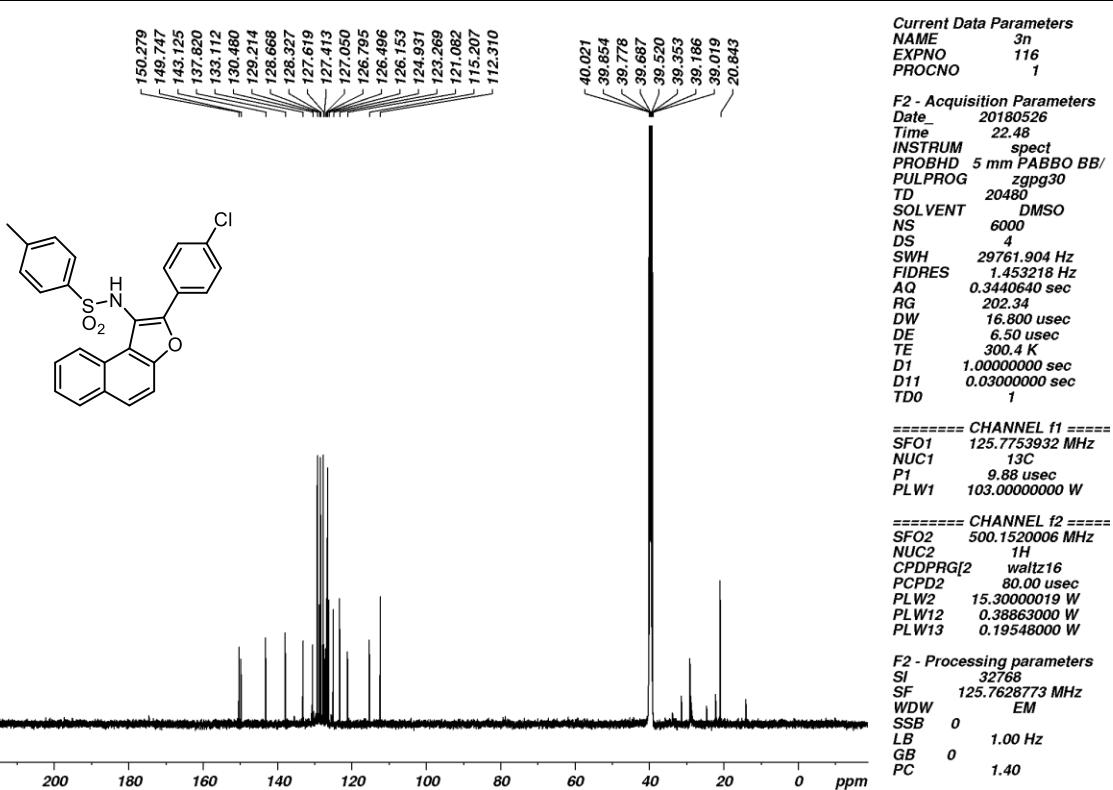
N-(2-(4-Chlorophenyl)naphtho[2,1-*b*]furan-1-yl)-4-methylbenzenesulfonamide (3n) ^1H

NMR (500 MHz, DMSO, 24 °C):

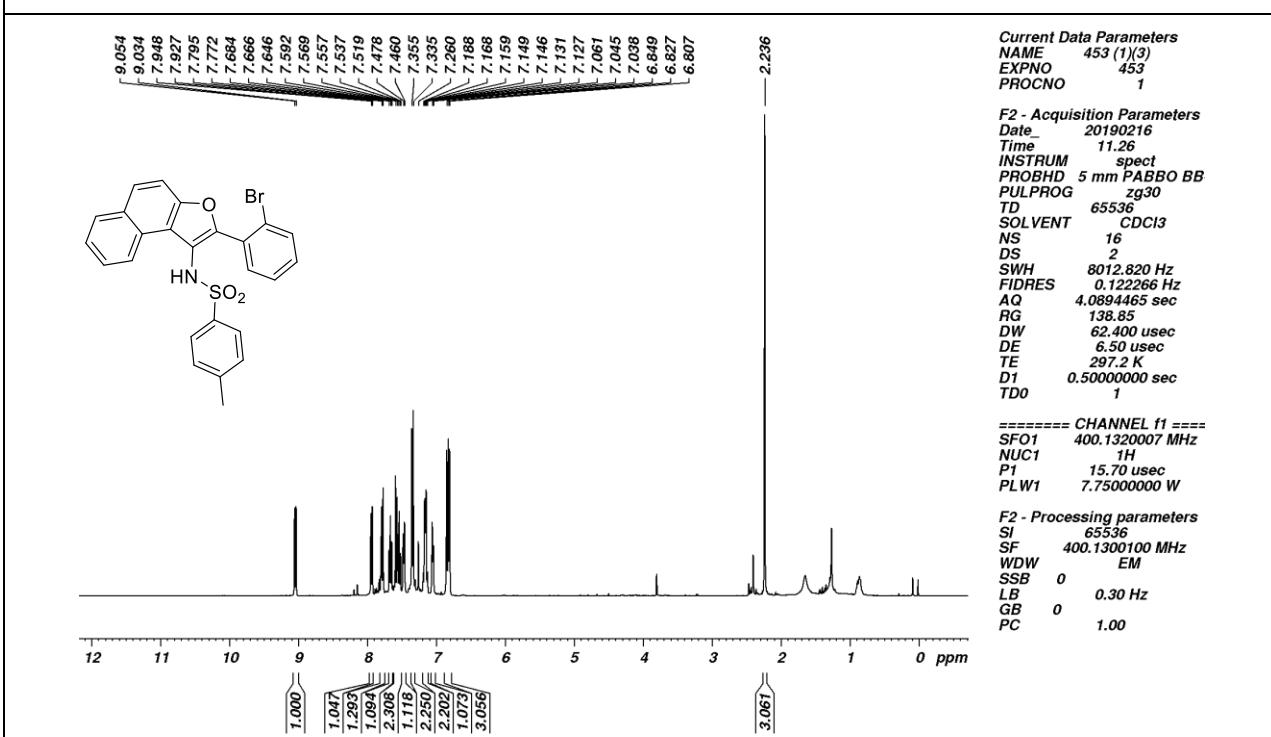


N-(2-(4-Chlorophenyl)naphtho[2,1-*b*]furan-1-yl)-4-methylbenzenesulfonamide (3n) ^{13}C

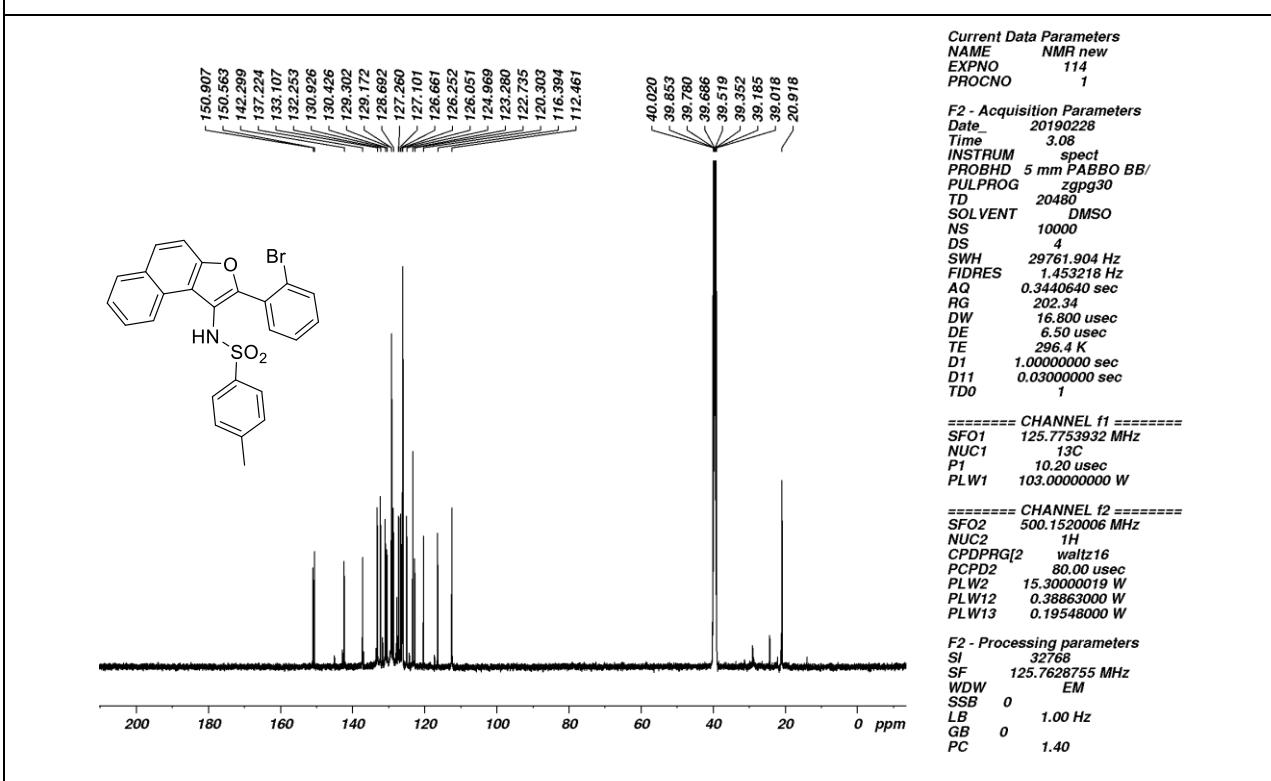
NMR (500 MHz, DMSO, 24 °C):



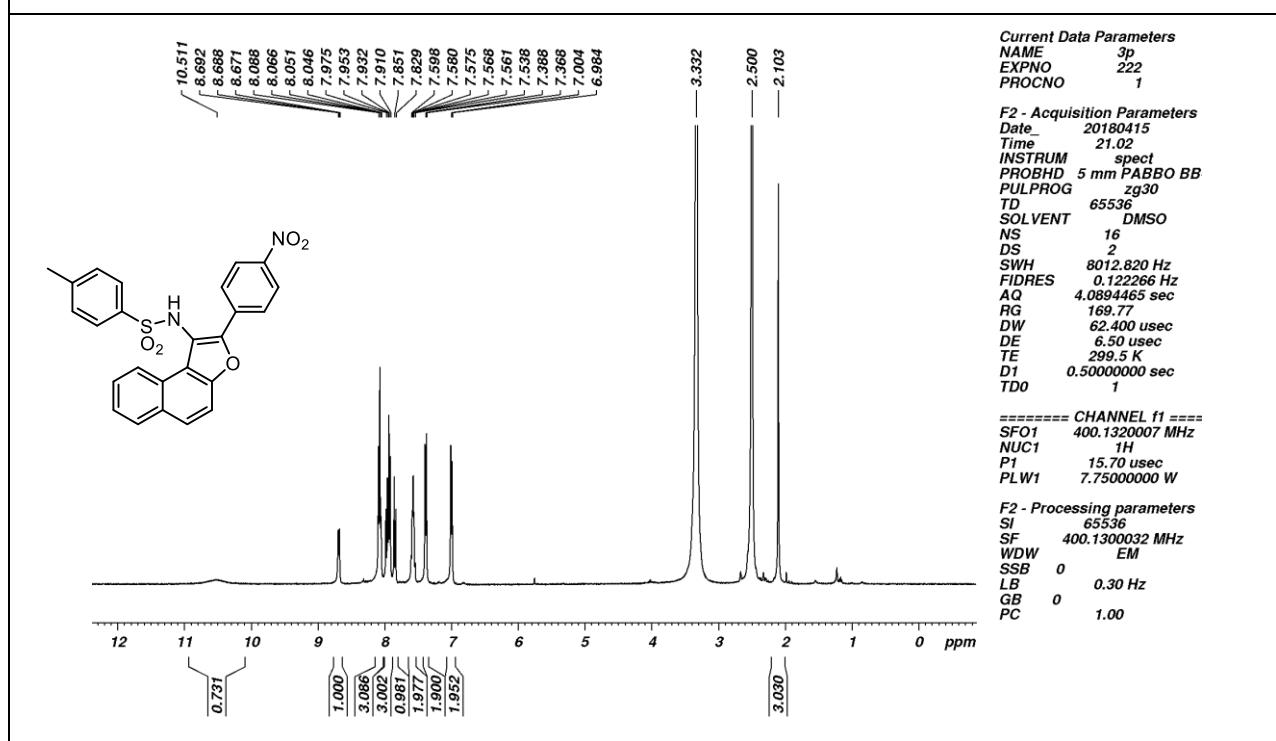
**N-(2-(2-Bromophenyl)naphtho[2,1-*b*]furan-1-yl)-4-methylbenzenesulfonamide (3o)¹H NMR
(400 MHz, CDCl₃, 24 °C):**



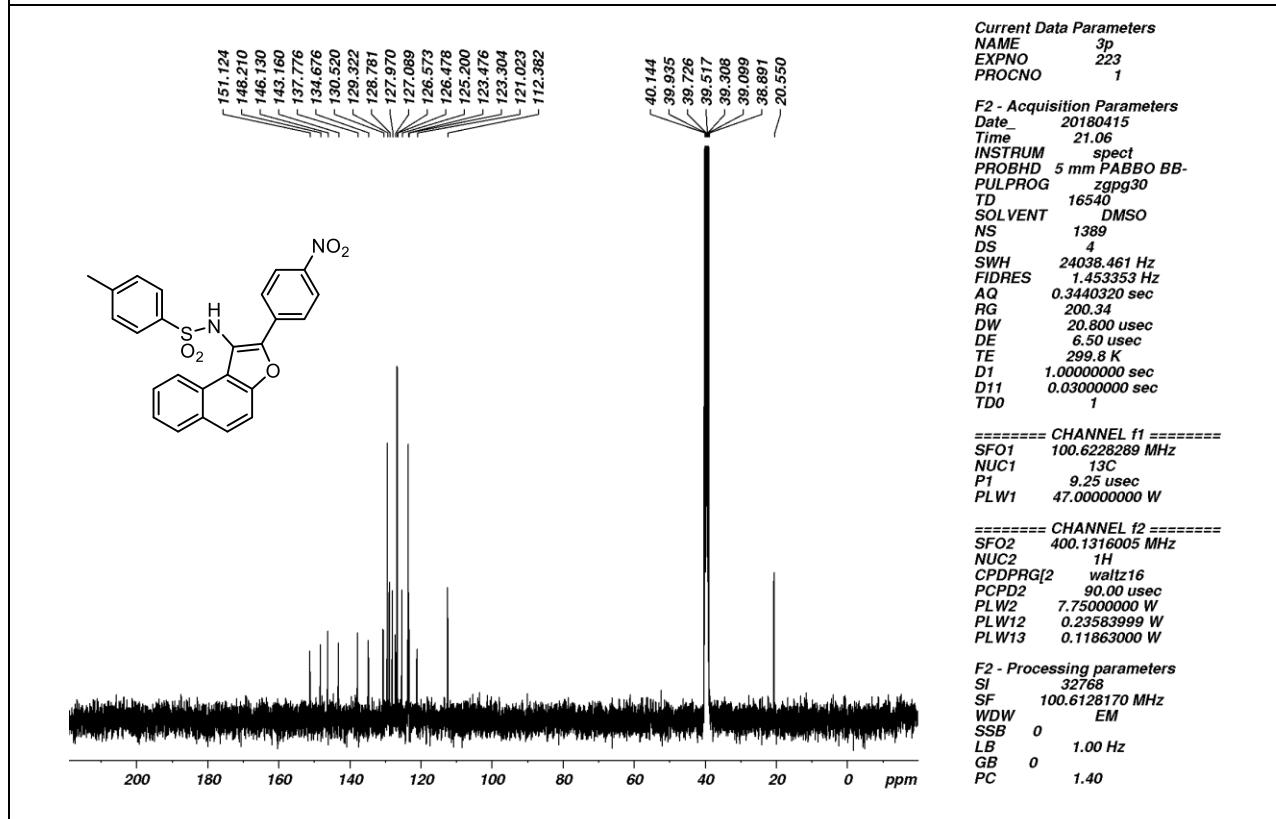
**N-(2-(2-Bromophenyl)naphtho[2,1-*b*]furan-1-yl)-4-methylbenzenesulfonamide (3o)¹³C
NMR (500 MHz, DMSO, 24 °C):**



4-Methyl-N-(2-(4-nitrophenyl)naphtho[2,1-*b*]furan-1-yl)benzenesulfonamide (3p) ^1H NMR
(400 MHz, DMSO, 24 °C):

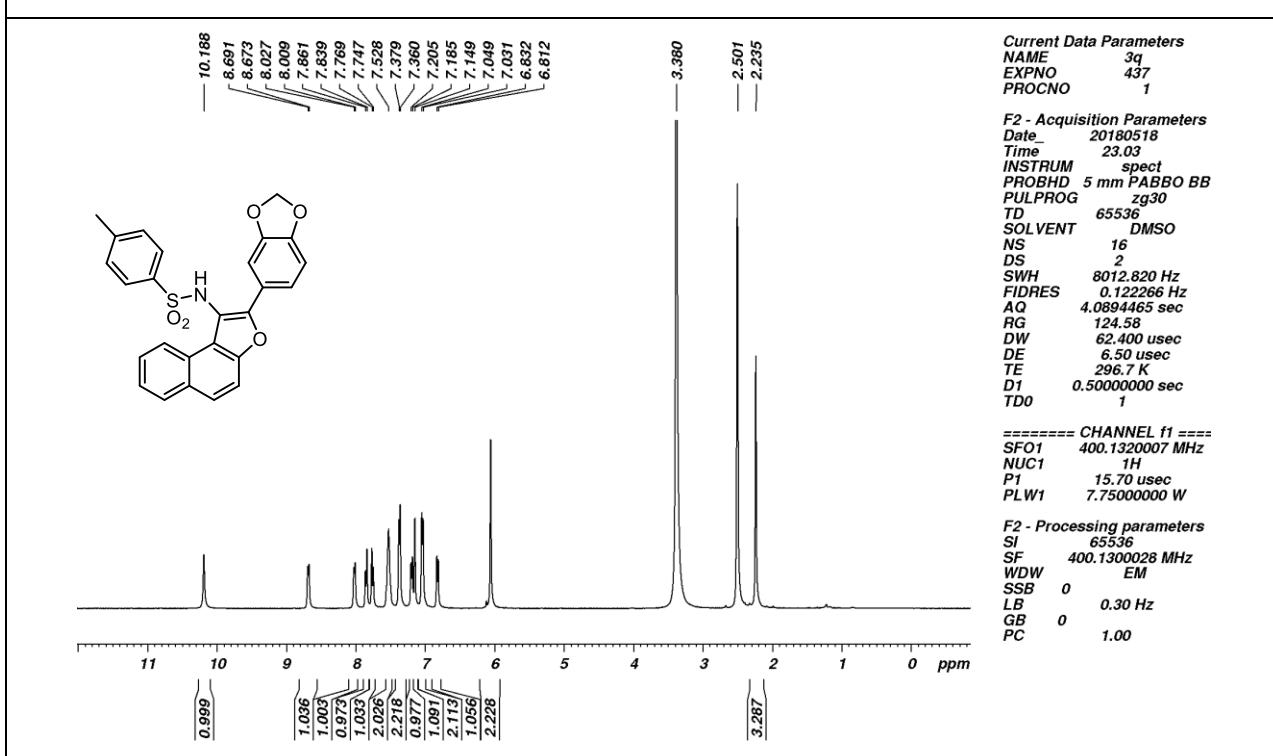


4-Methyl-N-(2-(4-nitrophenyl)naphtho[2,1-*b*]furan-1-yl)benzenesulfonamide (3p) ^{13}C NMR
(400 MHz, DMSO, 24 °C):



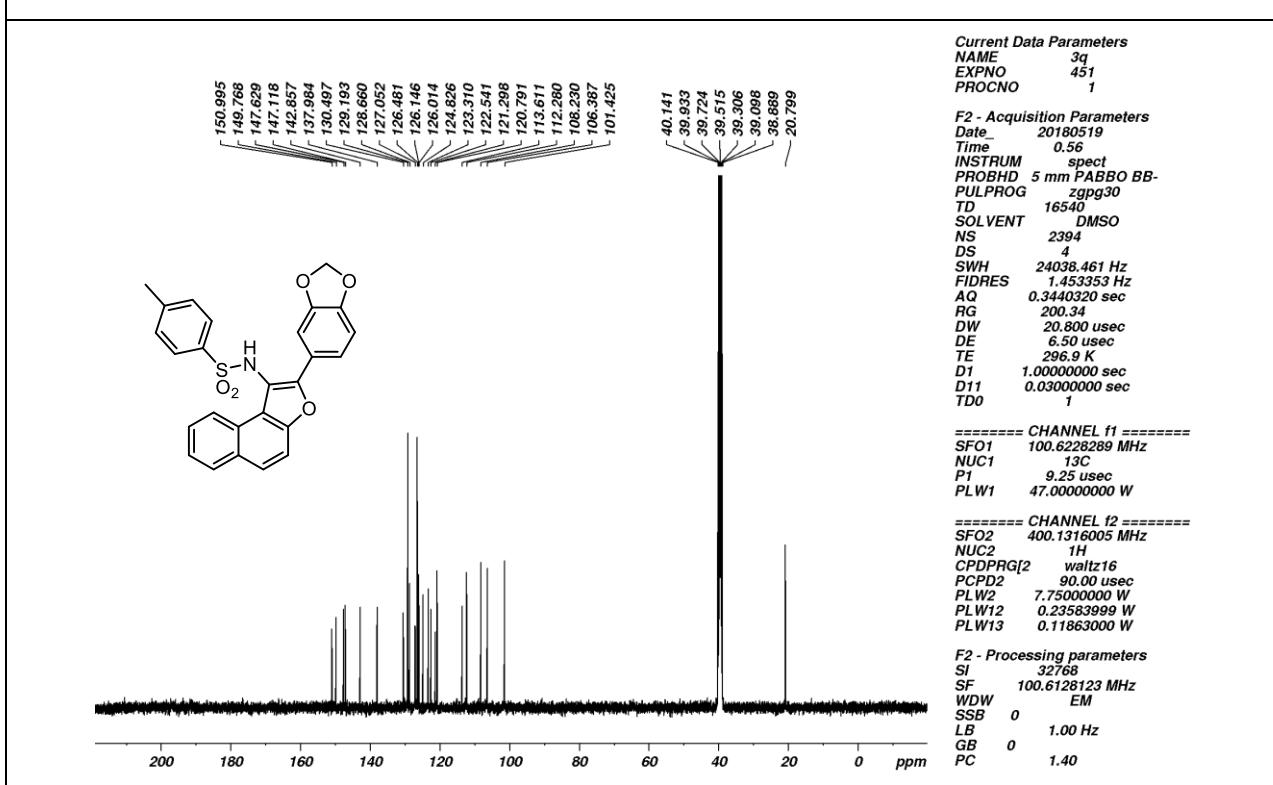
N-(2-(Benzo[*d*][1,3]dioxol-5-yl)naphtho[2,1-*b*]furan-1-yl)-4-methylbenzenesulfonamide (3q)

¹H NMR (400 MHz, DMSO, 24 °C):



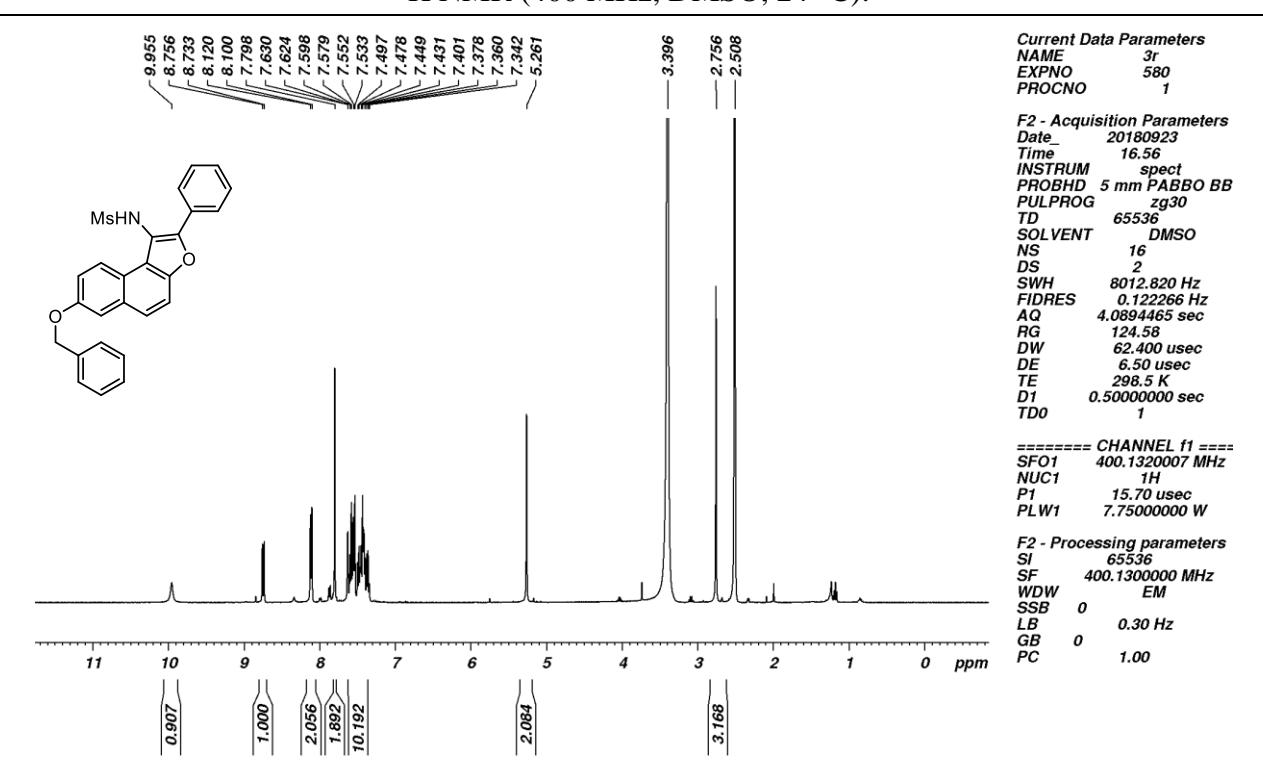
N-(2-(Benzo[*d*][1,3]dioxol-5-yl)naphtho[2,1-*b*]furan-1-yl)-4-methylbenzenesulfonamide (3q)

¹³C NMR (400 MHz, DMSO, 24 °C):



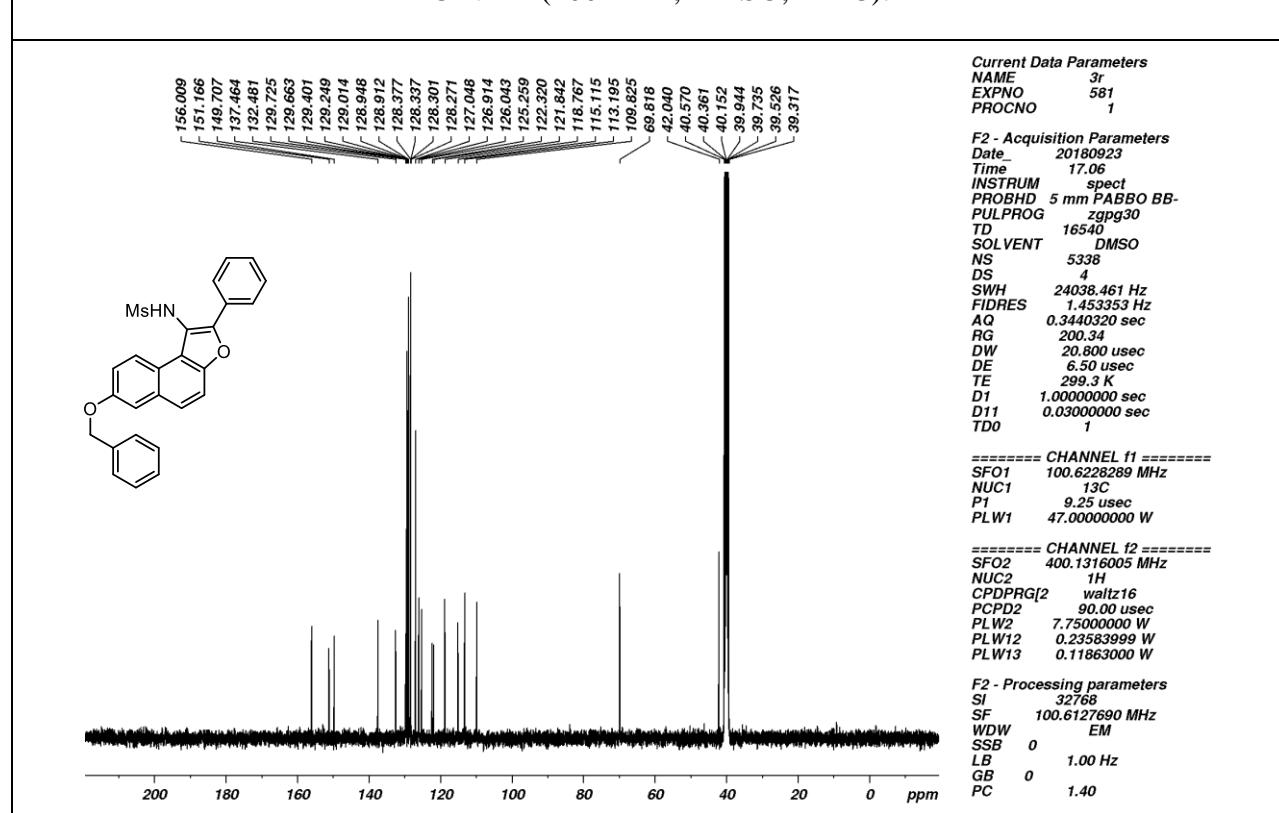
N-(7-(BenzylOxy)-2-phenylnaphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3r)

¹H NMR (400 MHz, DMSO, 24 °C):



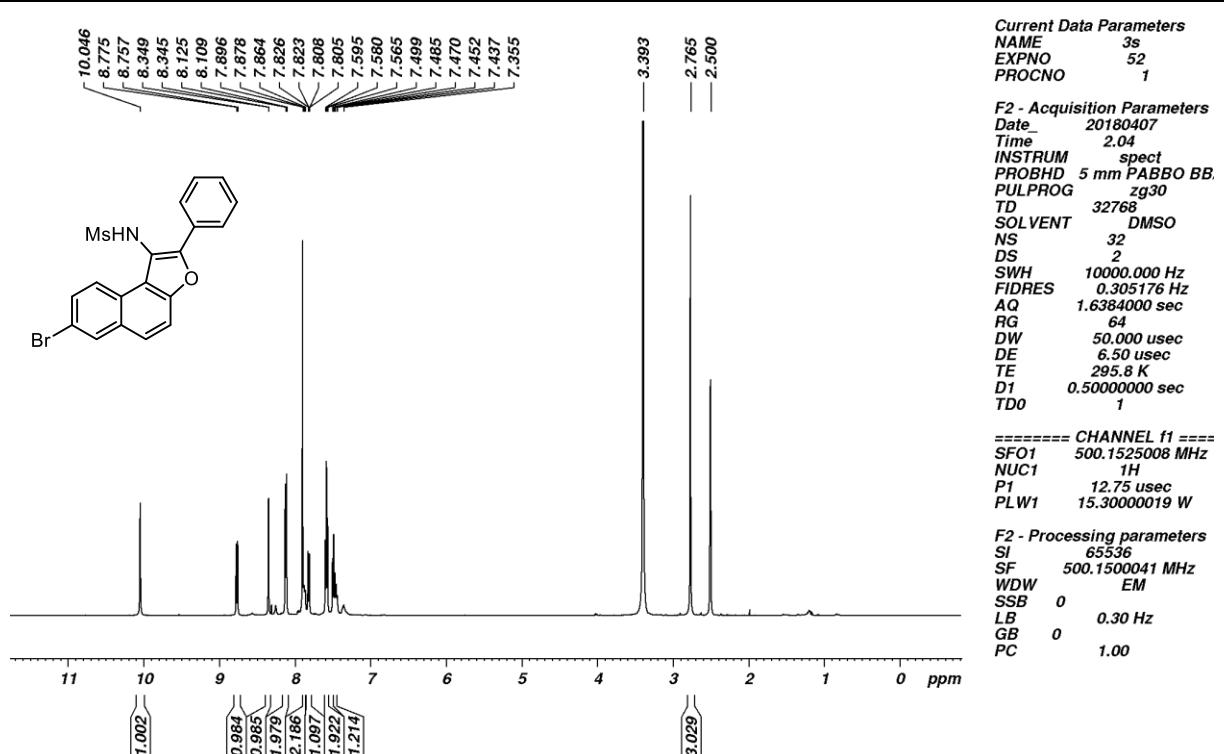
N-(7-(BenzylOxy)-2-phenylnaphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3r)

¹³C NMR (400 MHz, DMSO, 24 °C):



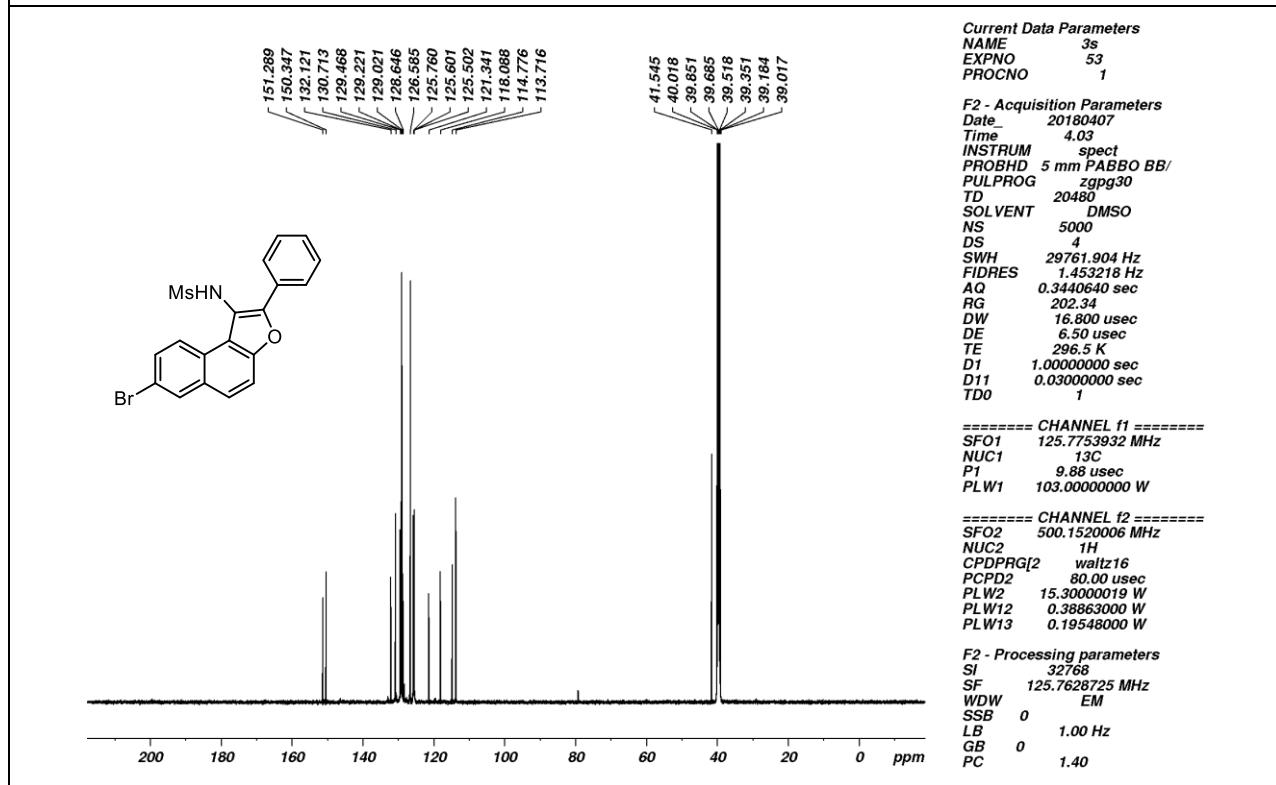
***N*-(7-bromo-2-phenylnaphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3s)**

¹H NMR (500 MHz, DMSO, 24 °C):



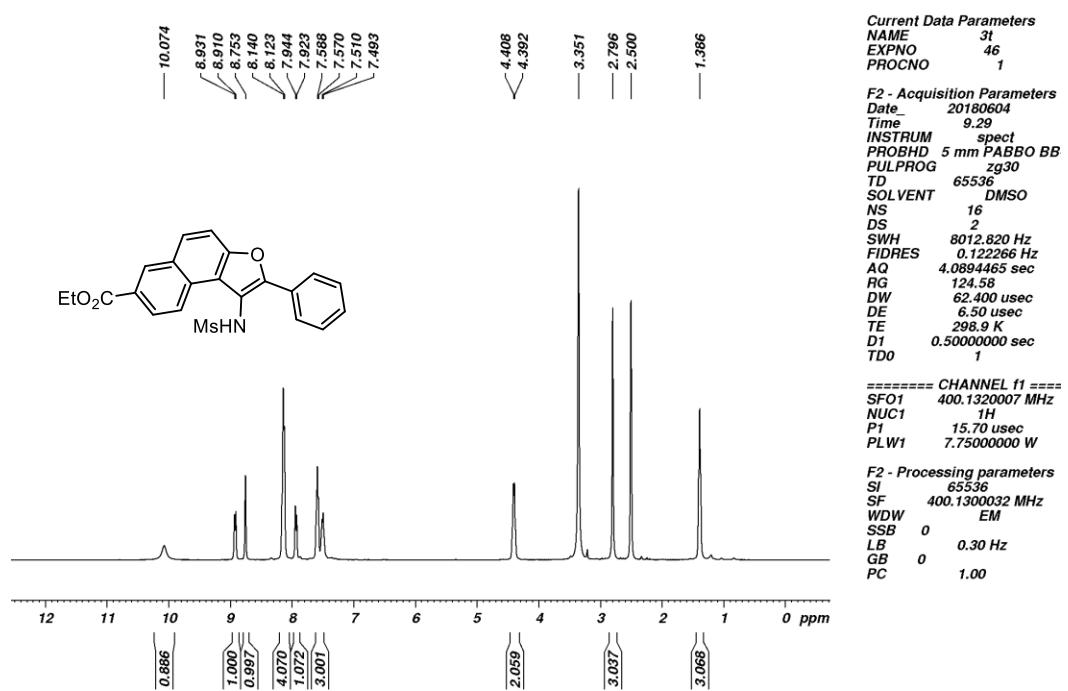
***N*-(7-bromo-2-phenylnaphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3s)**

¹³C NMR (500 MHz, DMSO, 24 °C):



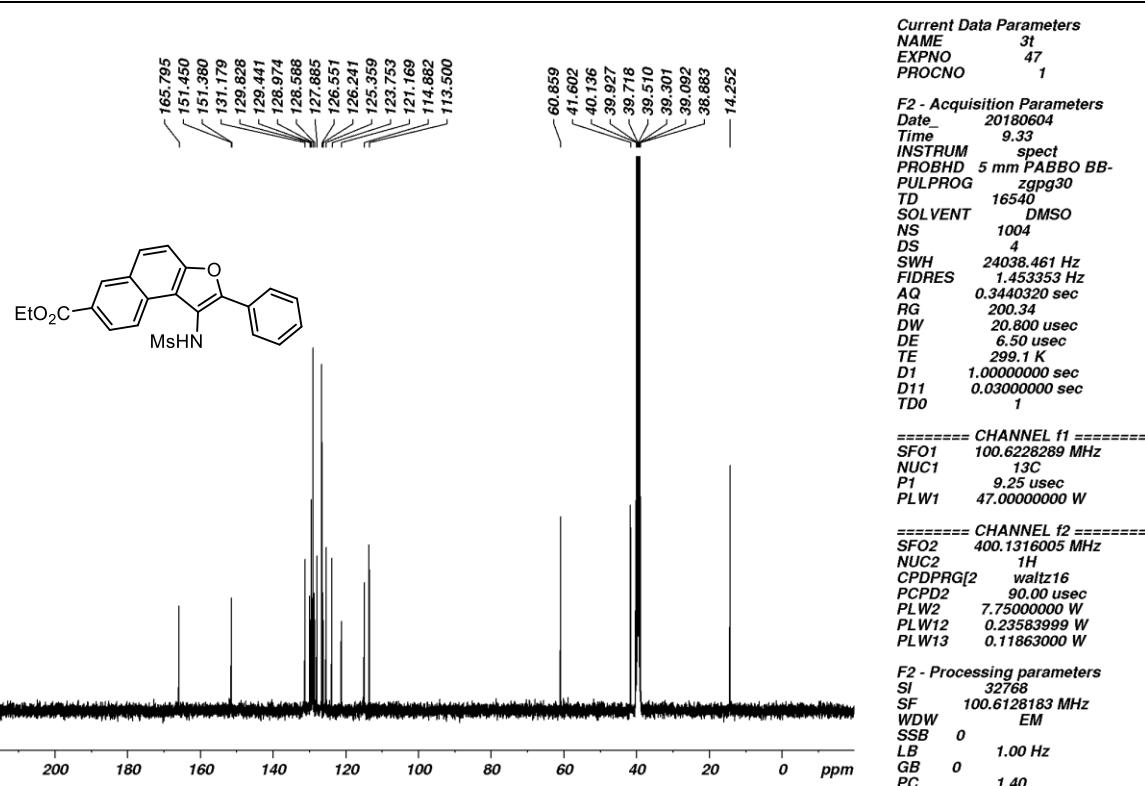
Ethyl 1-(methylsulfonamido)-2-phenylnaphtho[2,1-*b*]furan-7-carboxylate (3t)

¹H NMR (400 MHz, DMSO, 24 °C):



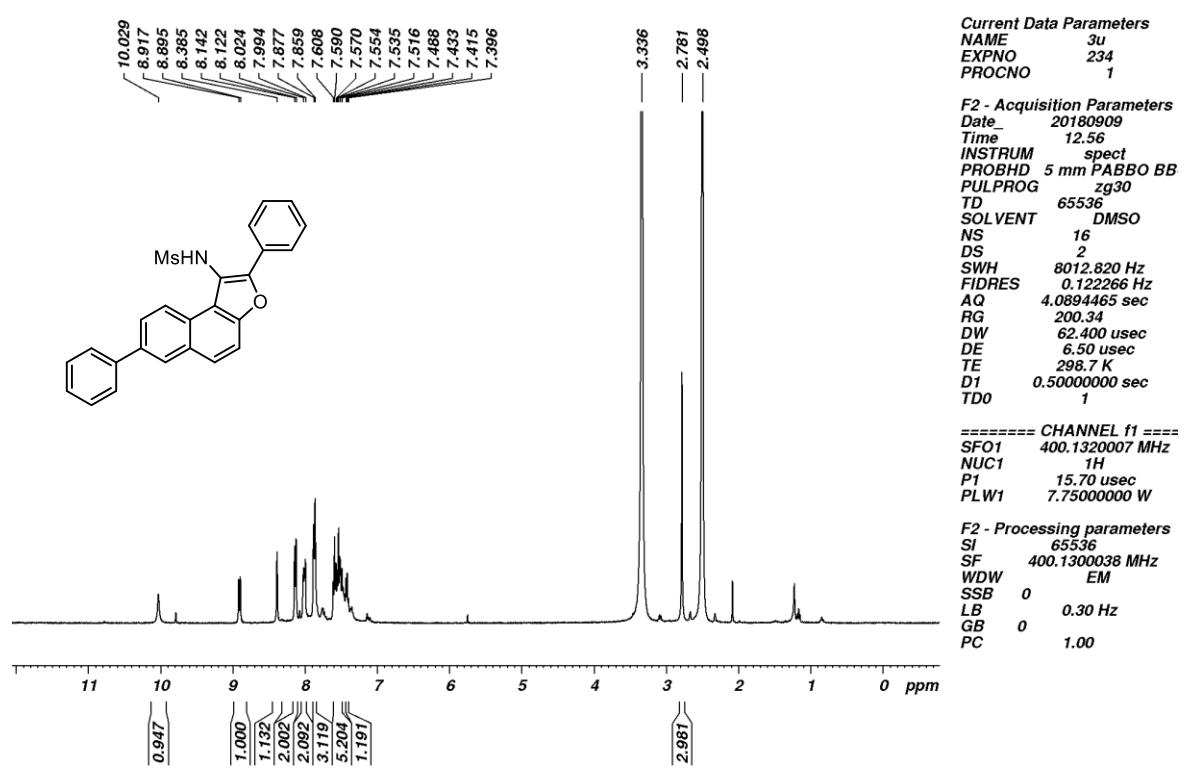
Ethyl 1-(methylsulfonamido)-2-phenylnaphtho[2,1-*b*]furan-7-carboxylate (3t)

¹³C NMR (400 MHz, DMSO, 24 °C):



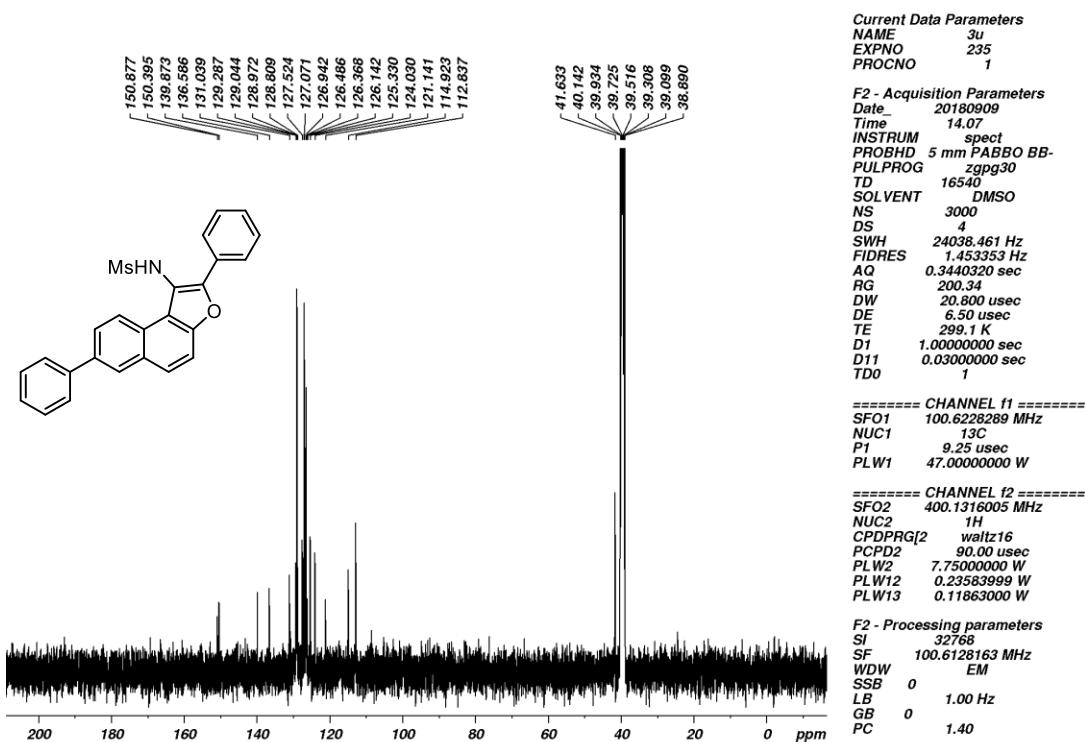
N-(2,7-Diphenylnaphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3u)

¹H NMR (400 MHz, DMSO, 24 °C):



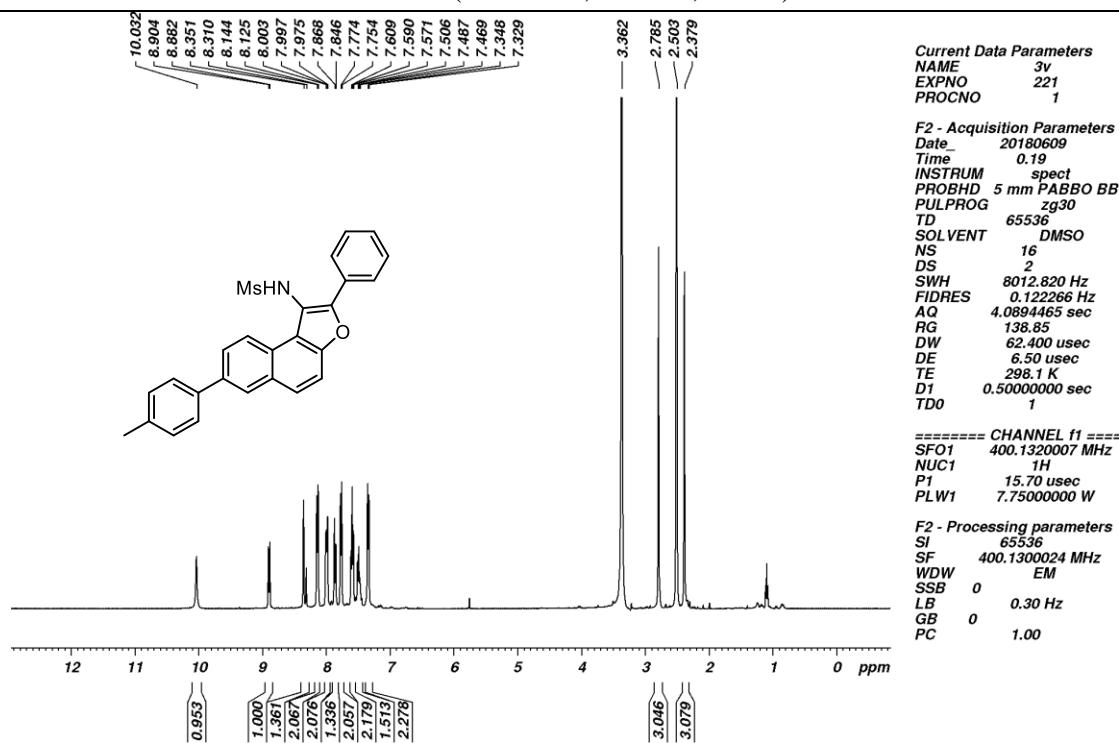
N-(2,7-Diphenylnaphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3u)

¹³C NMR (400 MHz, DMSO, 24 °C):



N-(2-Phenyl-7-(*p*-tolyl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3v)

¹H NMR (400 MHz, DMSO, 24 °C):



Current Data Parameters
NAME 3v
EXPNO 221
PROCNO 1

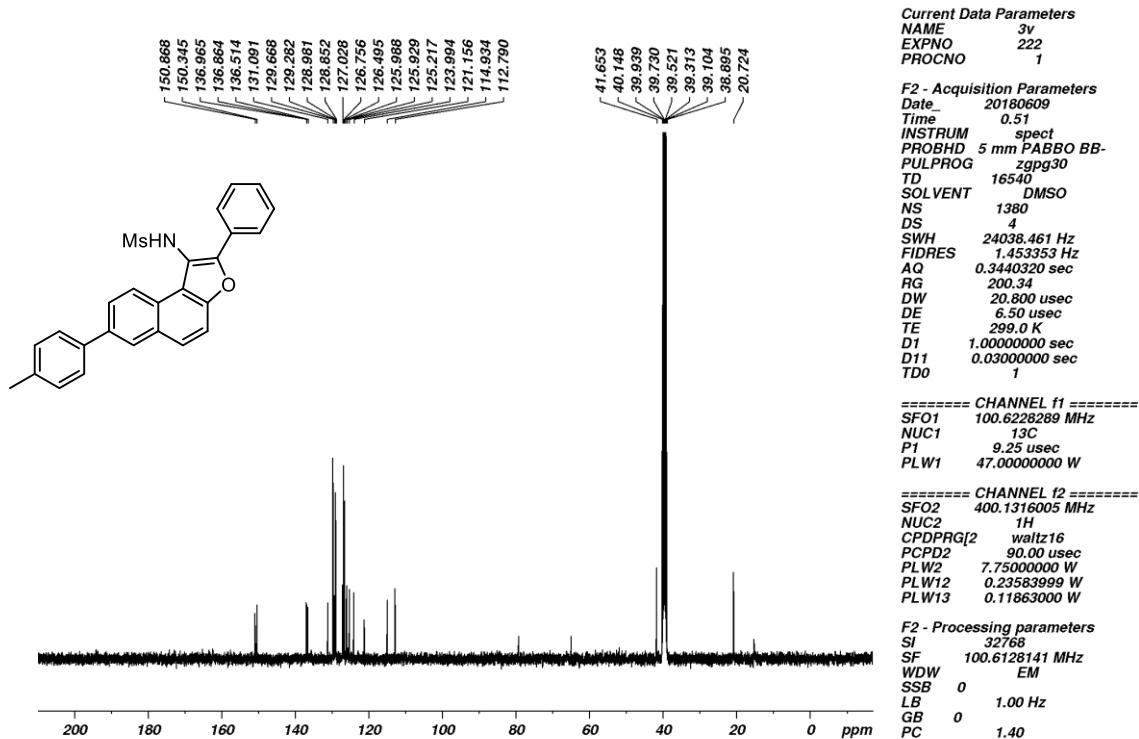
F2 - Acquisition Parameters
Date_ 20180609
Time 0.19
INSTRUM spect
PROBHD 5 mm PABBO BB
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 138.85
DW 62.400 usec
DE 6.50 usec
TE 298.1 K
D1 0.5000000 sec
TD0 1

===== CHANNEL f1 =====
SF01 400.1320007 MHz
NUC1 1H
P1 15.70 usec
PLW1 7.75000000 W

F2 - Processing parameters
SI 65536
SF 400.1300024 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

N-(2-Phenyl-7-(*p*-tolyl)naphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3v)

¹³C NMR (400 MHz, DMSO, 24 °C):



Current Data Parameters
NAME 3v
EXPNO 222
PROCNO 1

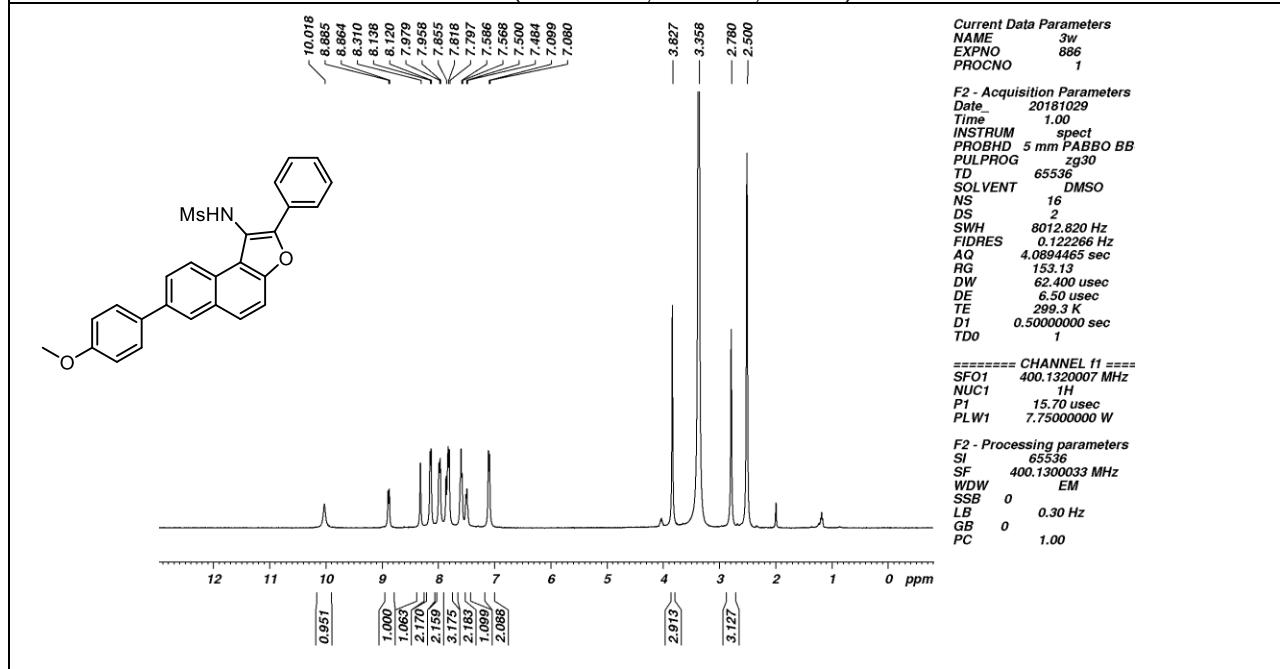
F2 - Acquisition Parameters
Date_ 20180609
Time 0.51
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 16540
SOLVENT DMSO
NS 1380
DS 4
SWH 24038.461 Hz
FIDRES 1.453353 Hz
AQ 0.3440320 sec
RG 200.34
DW 20.800 usec
DE 6.50 usec
TE 299.0 K
D1 1.0000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
SF01 100.6228289 MHz
NUC1 13C
P1 9.25 usec
PLW1 47.000000000 W

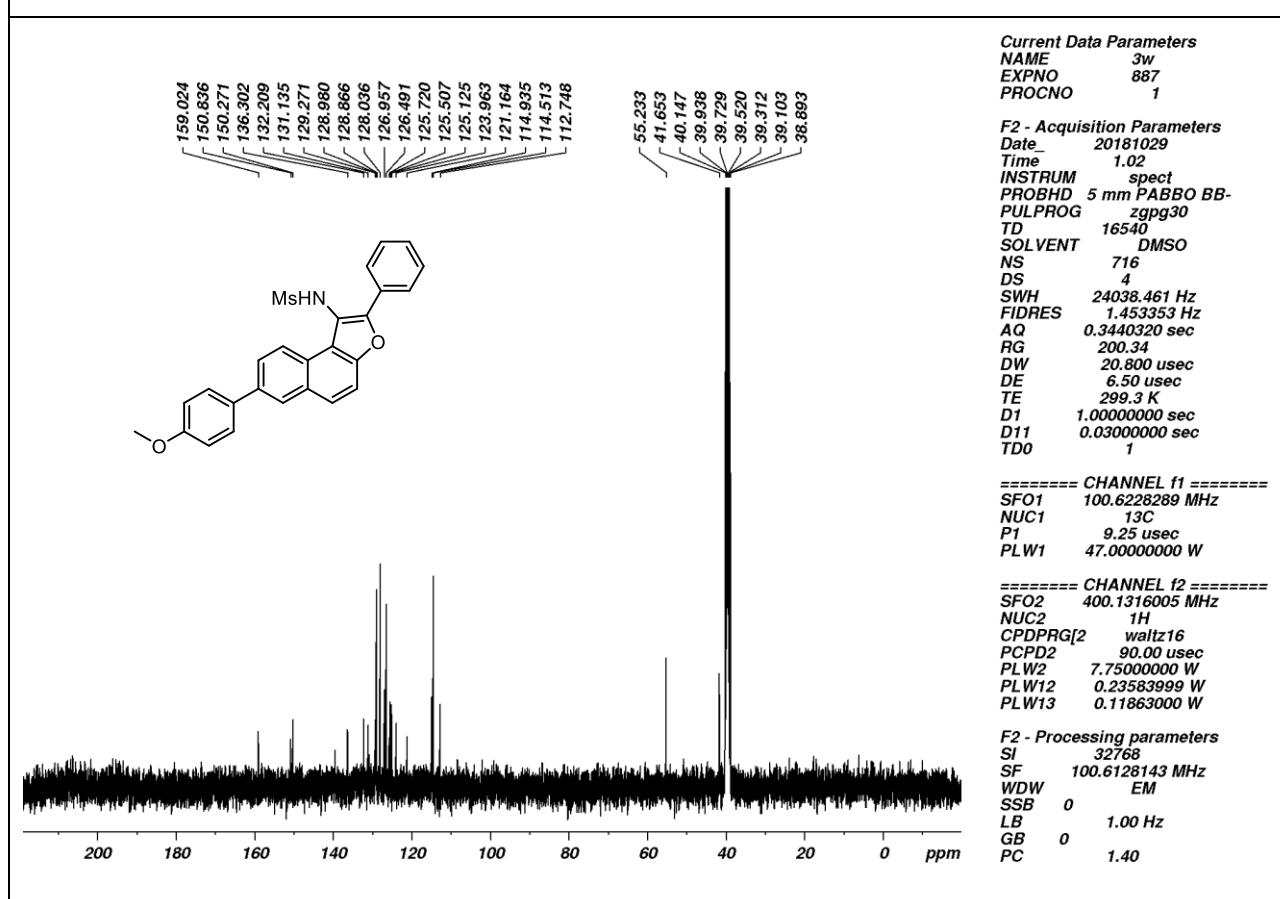
===== CHANNEL f2 =====
SF02 400.1316005 MHz
NUC2 1H
CPDPRG[2] waltz16
PCPD2 90.00 usec
PLW2 7.75000000 W
PLW12 0.23583999 W
PLW13 0.11863000 W

F2 - Processing parameters
SI 32768
SF 100.6128141 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

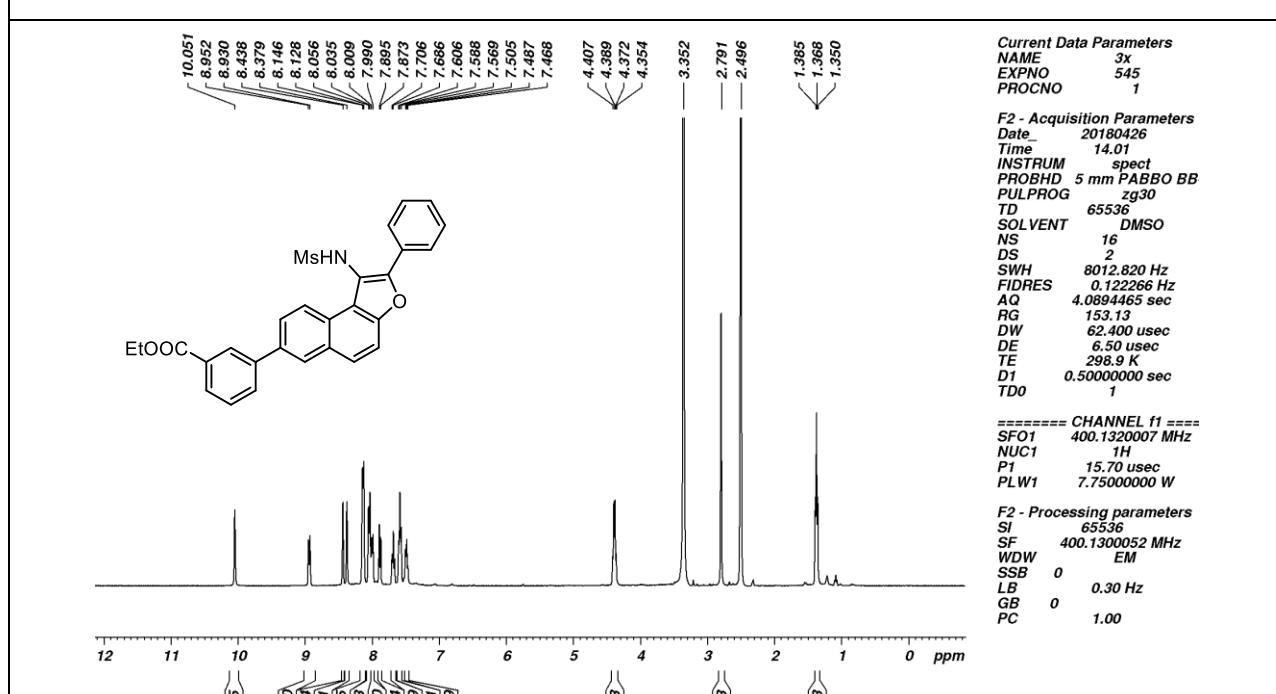
N-(7-(4-Methoxyphenyl)-2-phenylnaphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3w) ^1H NMR (400 MHz, DMSO, 24 °C):



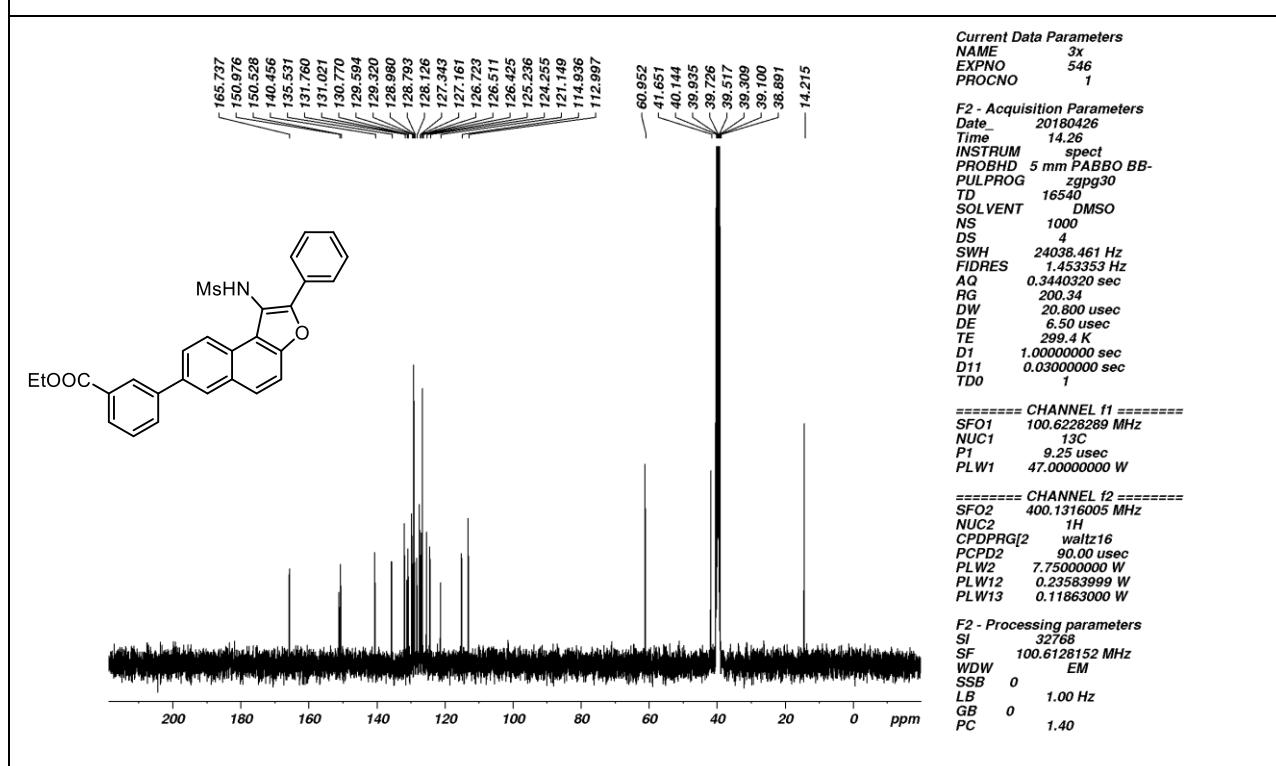
N-(7-(4-Methoxyphenyl)-2-phenylnaphtho[2,1-*b*]furan-1-yl)methanesulfonamide (3w) ^{13}C NMR (400 MHz, DMSO, 24 °C):



Ethyl 3-(1-(methylsulfonamido)-2-phenylnaphtho[2,1-*b*]furan-7-yl)benzoate (3x) ^1H NMR
(400 MHz, DMSO, 24 °C):

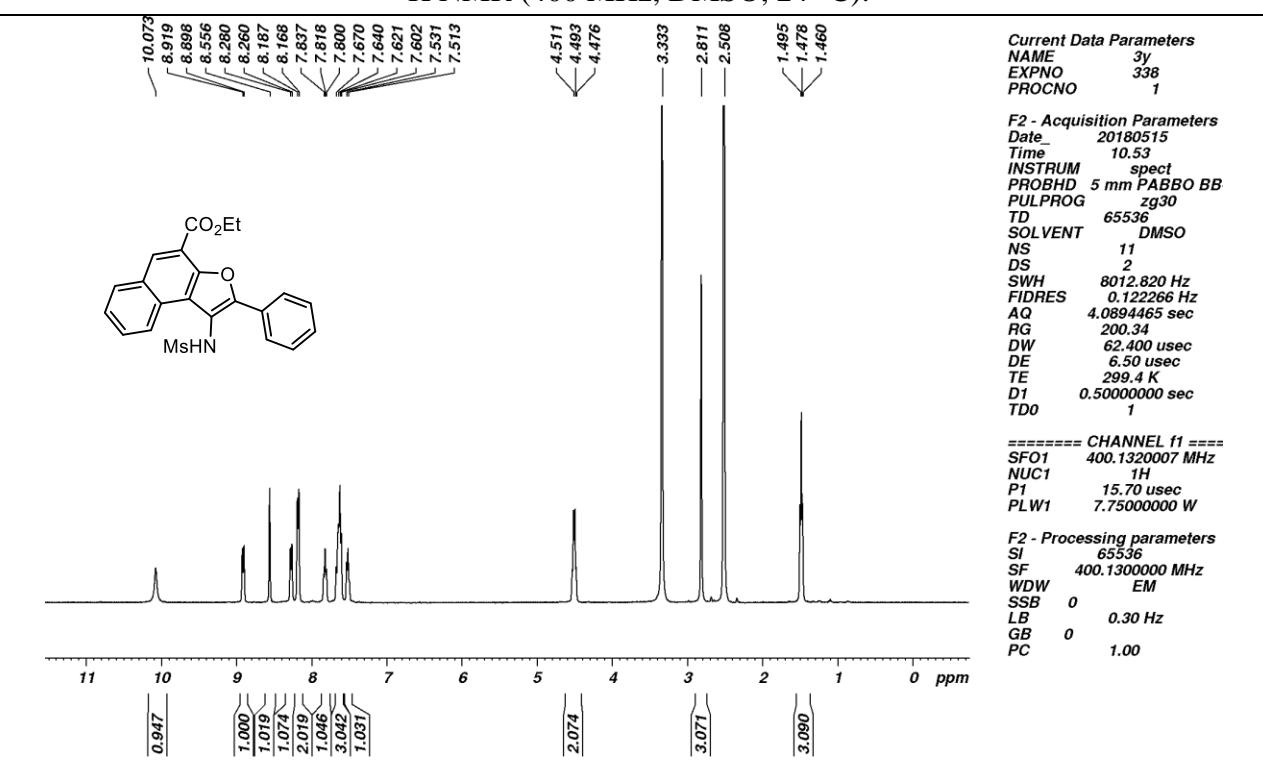


Ethyl 3-(1-(methylsulfonamido)-2-phenylnaphtho[2,1-*b*]furan-7-yl)benzoate (3x) ^{13}C NMR
(400 MHz, DMSO, 24 °C):



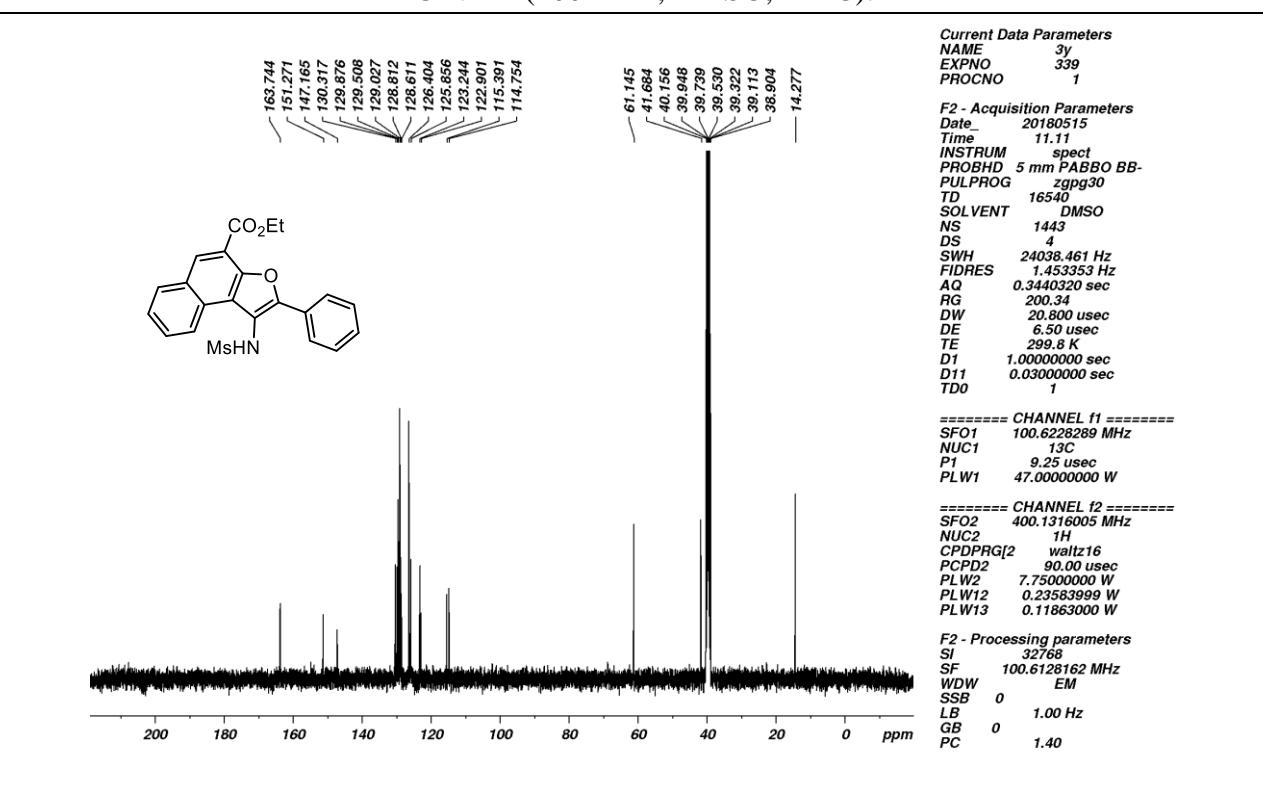
Ethyl 1-(methylsulfonamido)-2-phenylnaphtho[2,1-*b*]furan-4-carboxylate (3y)

¹H NMR (400 MHz, DMSO, 24 °C):



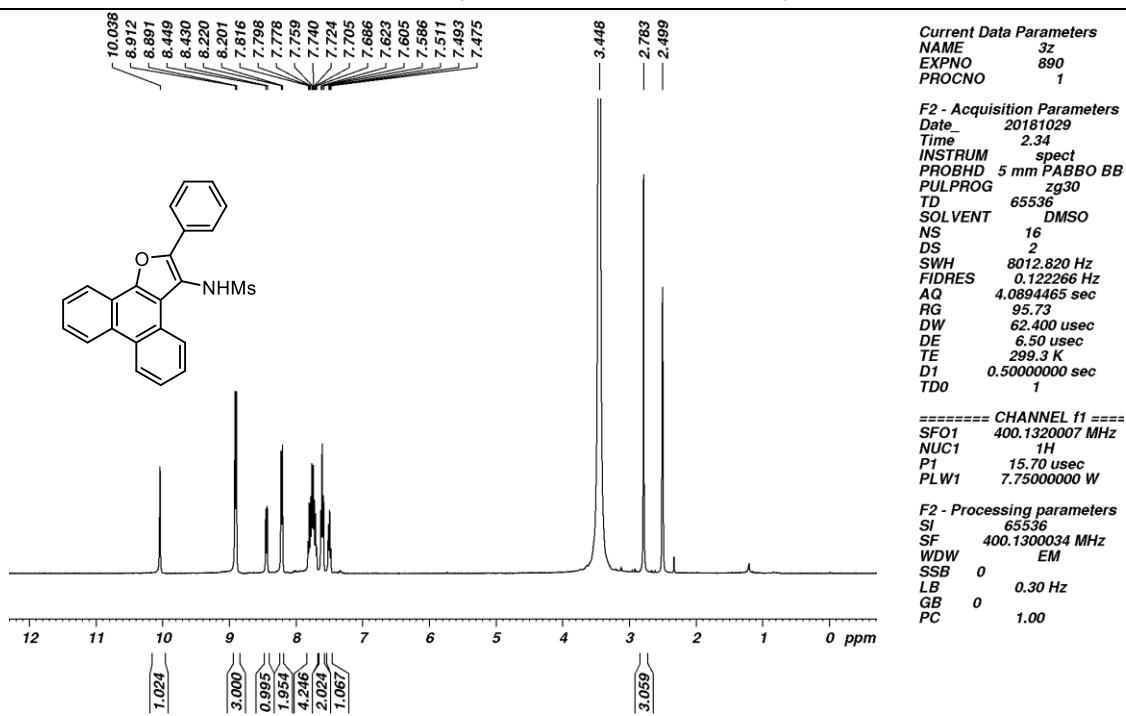
Ethyl 1-(methylsulfonamido)-2-phenylnaphtho[2,1-*b*]furan-4-carboxylate (3y)

¹³C NMR (400 MHz, DMSO, 24 °C):



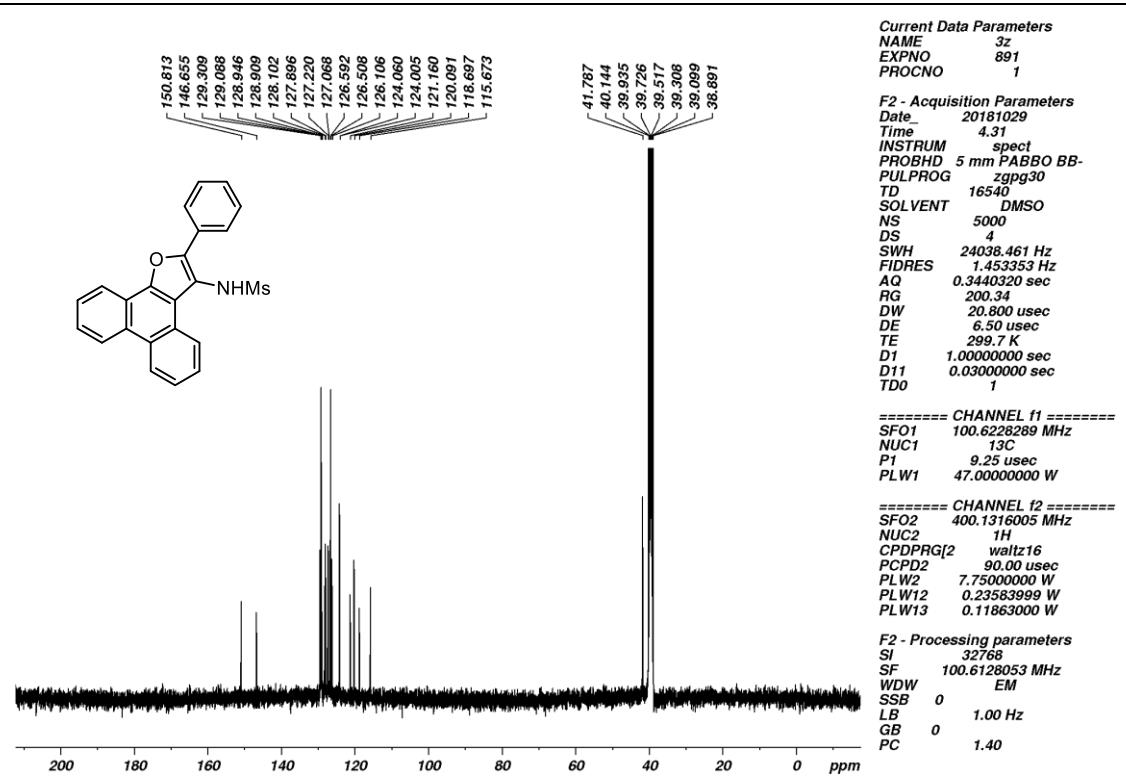
N-(2-Phenylphenanthro[9,10-*b*]furan-3-yl)methanesulfonamide (3z)

¹H NMR (400 MHz, DMSO, 24 °C):

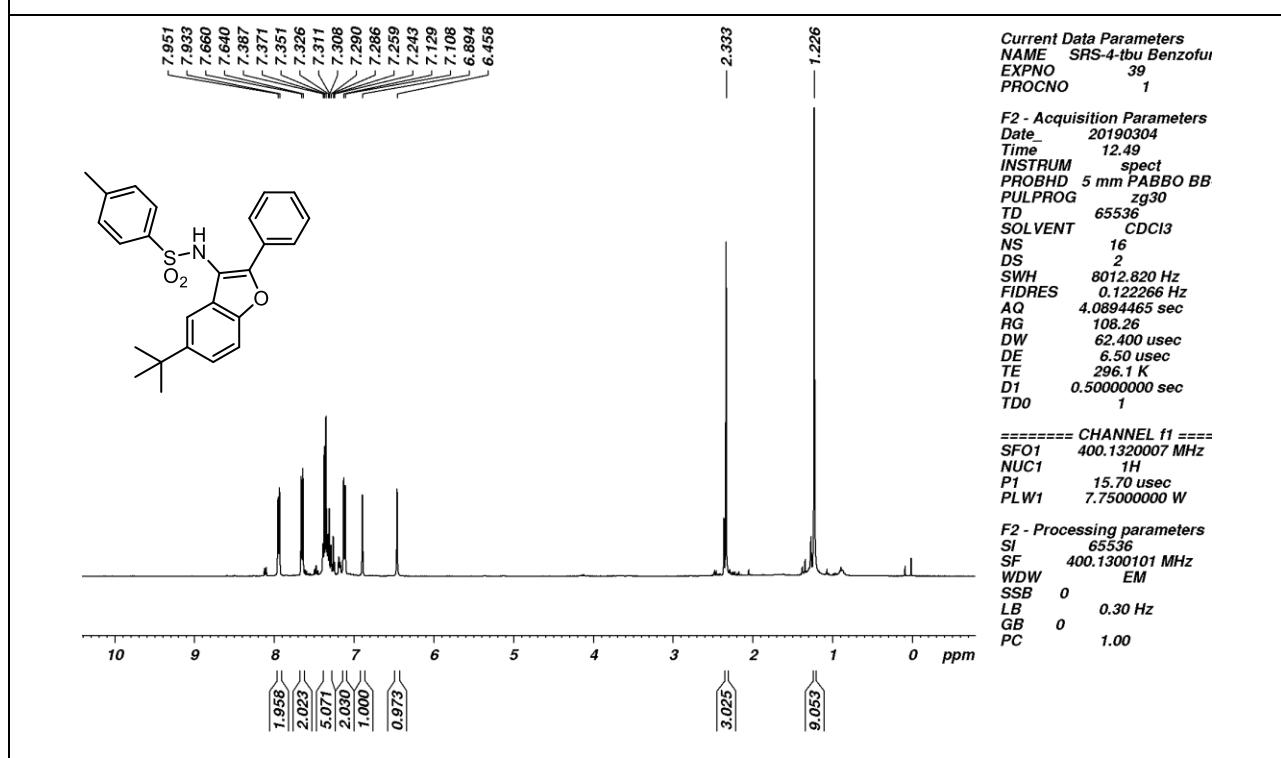


N-(2-Phenylphenanthro[9,10-*b*]furan-3-yl)methanesulfonamide (3z)

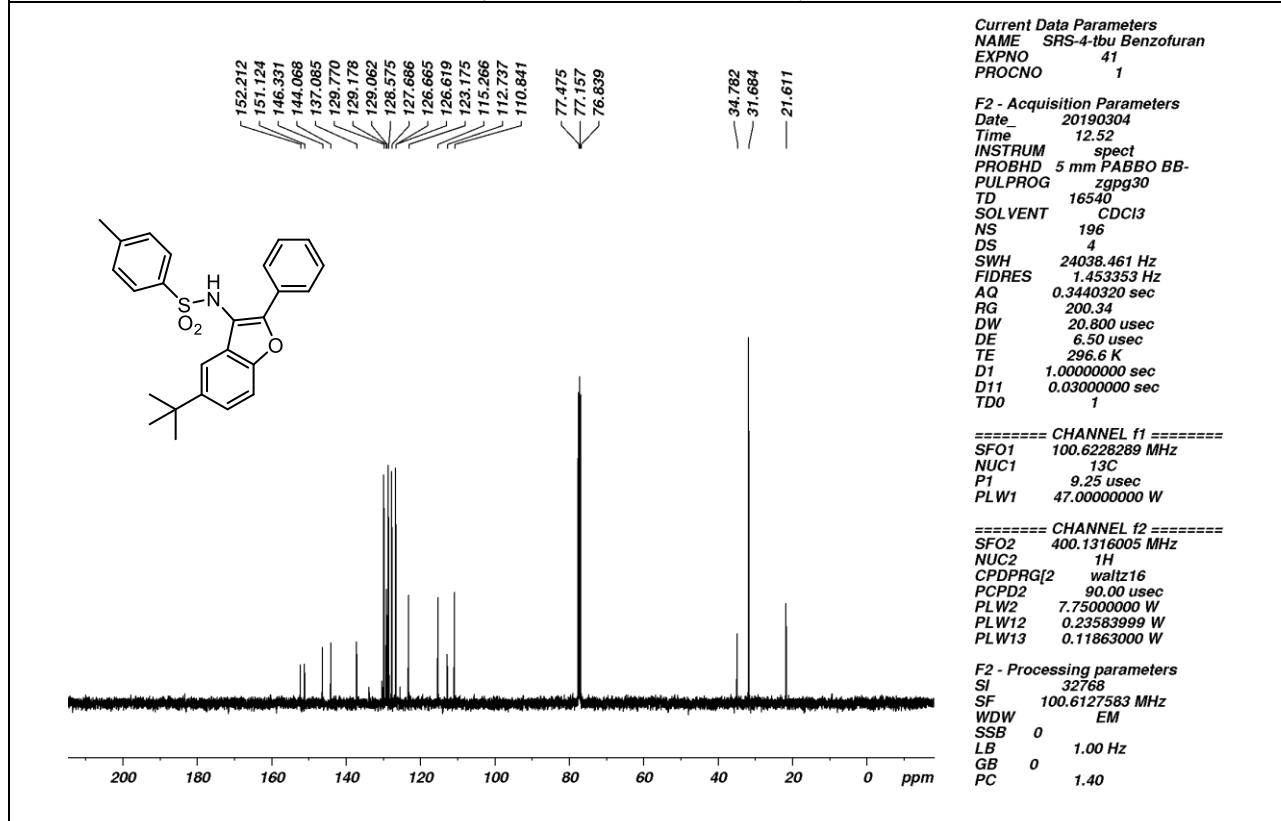
¹³C NMR (400 MHz, DMSO, 24 °C):



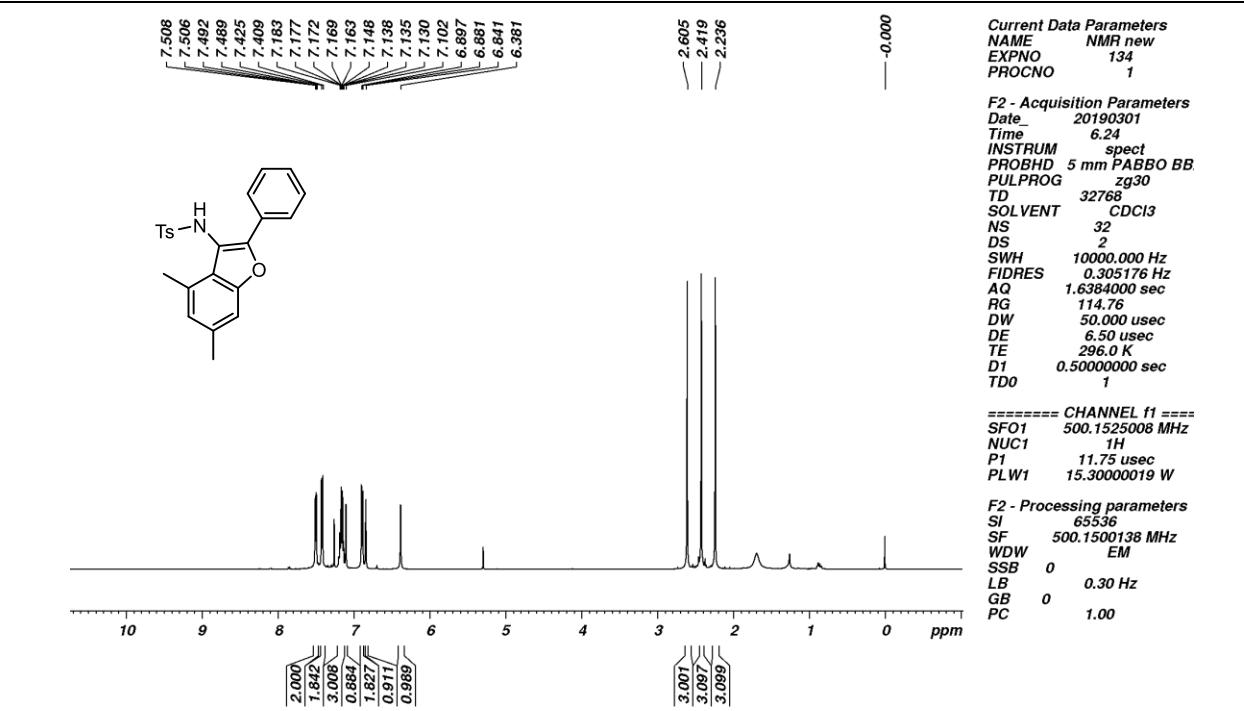
N-(5-(*Tert*-butyl)-2-phenylbenzofuran-3-yl)-4-methylbenzenesulfonamide (3aa): ^1H NMR (400 MHz, CDCl_3 , 24 °C):



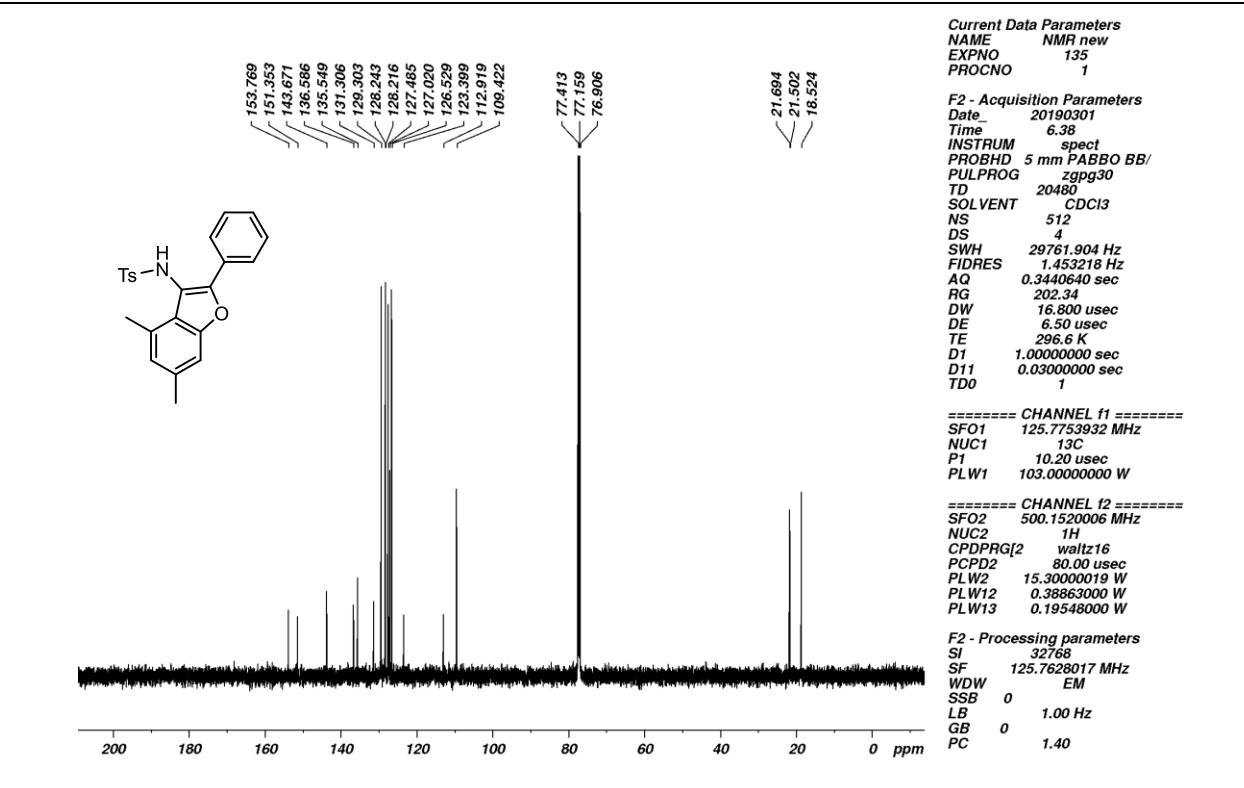
N-(5-(*Tert*-butyl)-2-phenylbenzofuran-3-yl)-4-methylbenzenesulfonamide (3aa) : ^{13}C NMR (400 MHz, CDCl_3 , 24 °C):



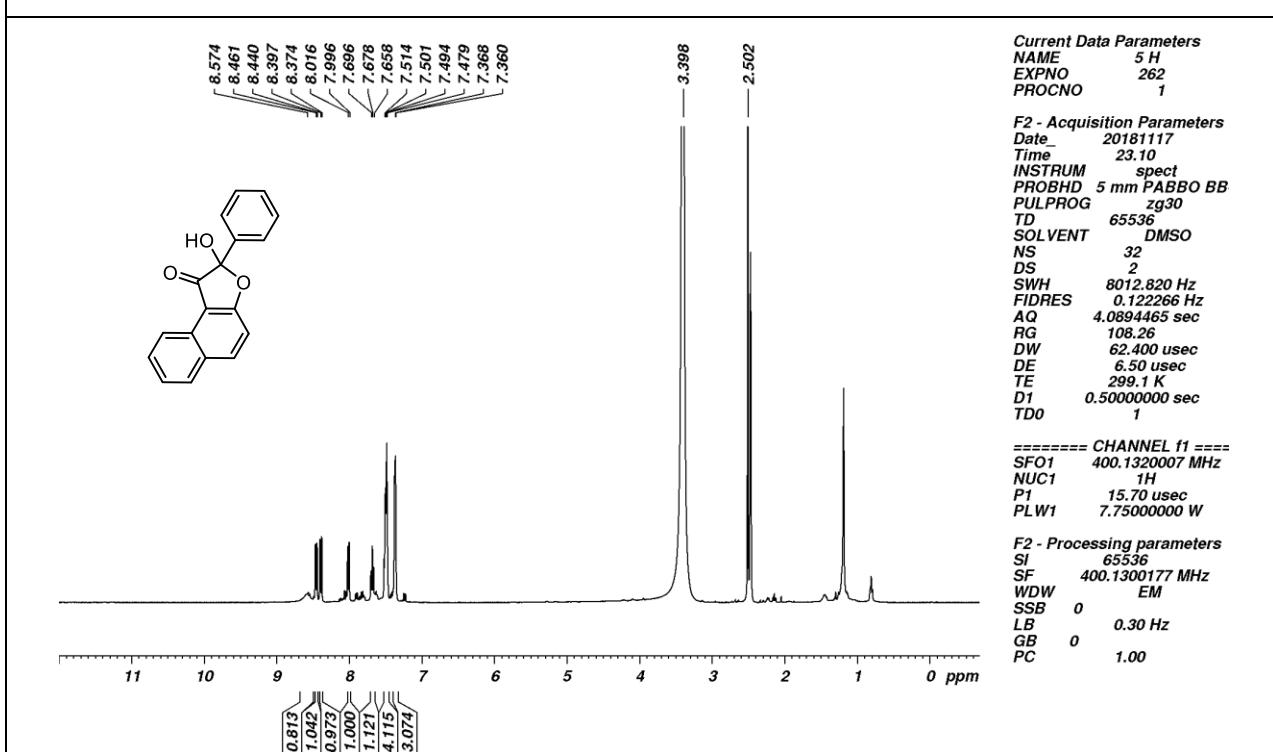
N-(4,6-Dimethyl-2-phenylbenzofuran-3-yl)-4-methylbenzenesulfonamide (3ab) : ^1H NMR
 (500 MHz, CDCl_3 , 24 °C):



N-(4,6-Dimethyl-2-phenylbenzofuran-3-yl)-4-methylbenzenesulfonamide (3ab) : ^{13}C NMR
 (500 MHz, CDCl_3 , 24 °C):

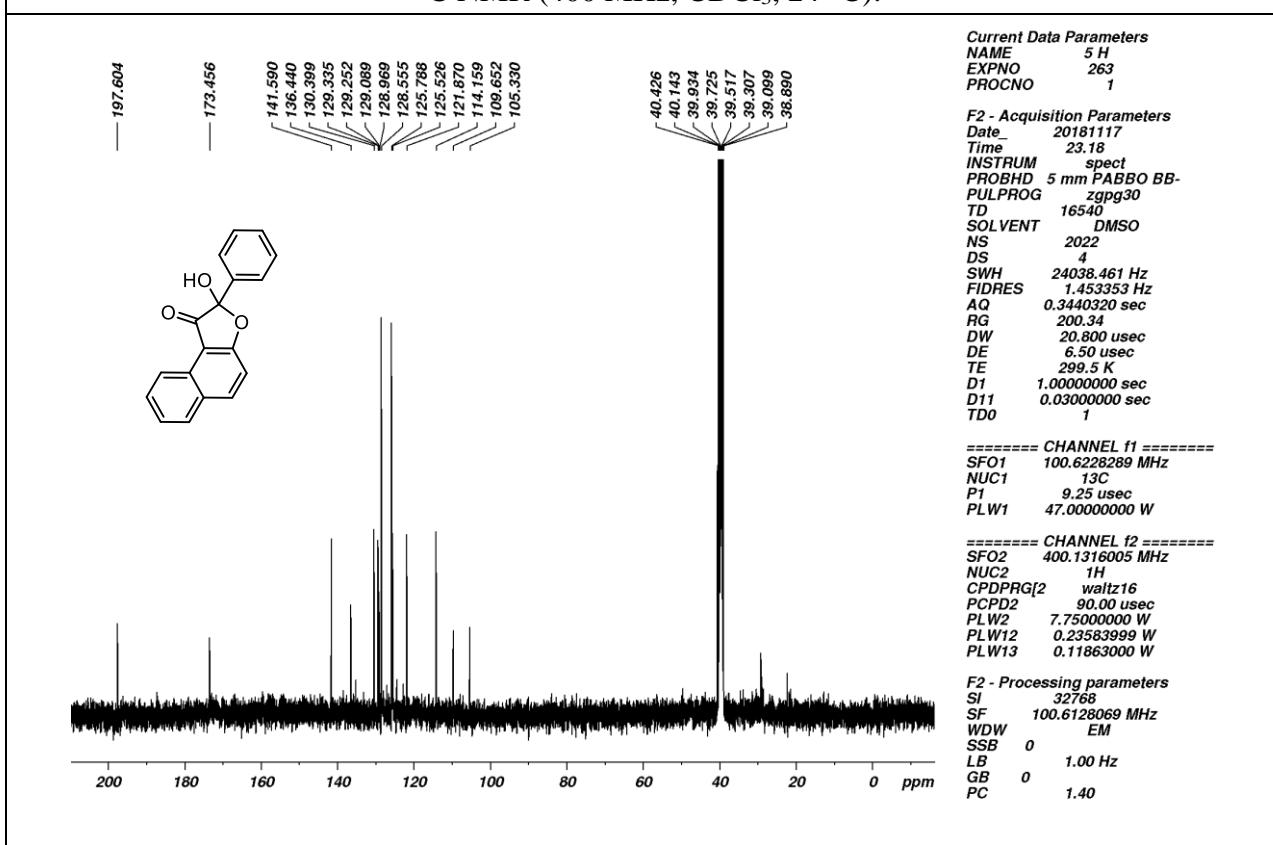


2-Hydroxy-2-phenylnaphtho[2,1-*b*]furan-1(2*H*)-one (5): ^1H NMR (400 MHz, CDCl_3 , 24 °C):

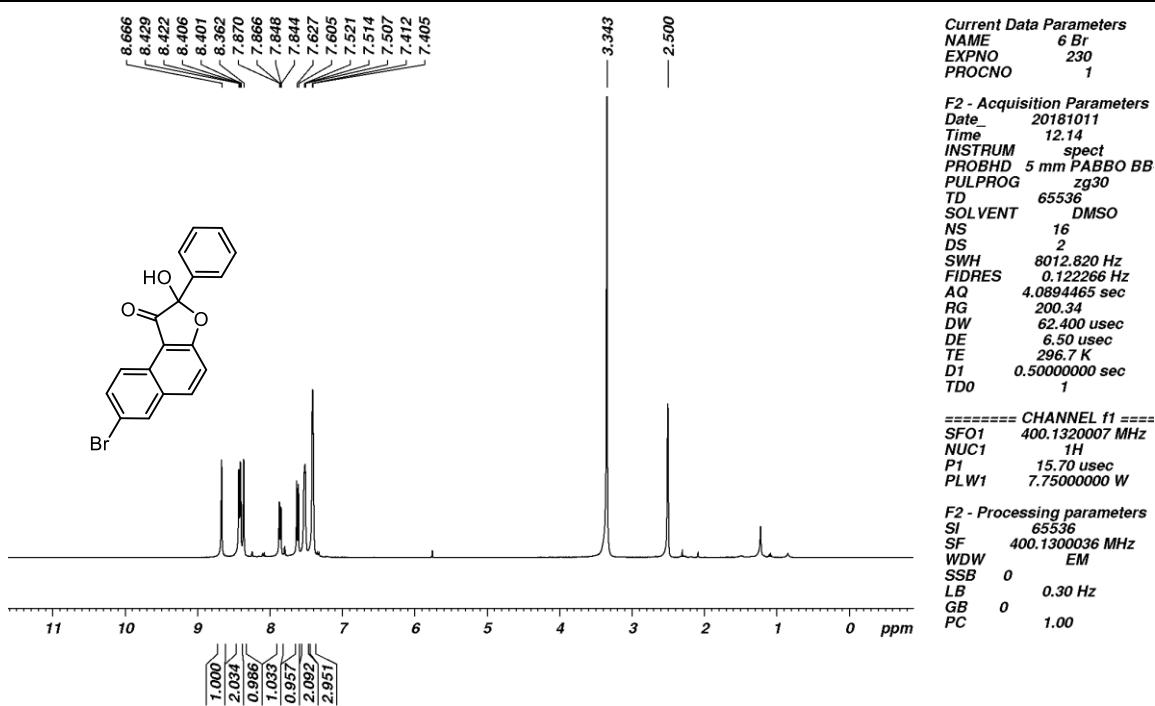


2-Hydroxy-2-phenylnaphtho[2,1-*b*]furan-1(2*H*)-one (5):

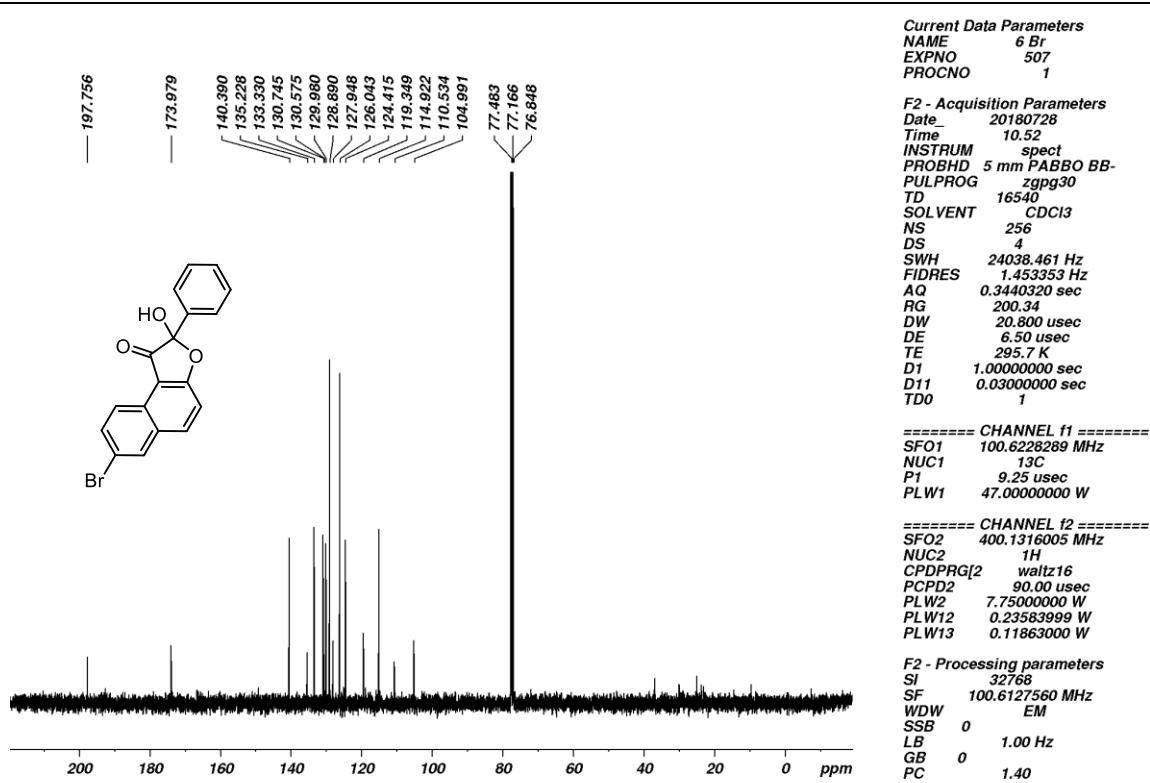
^{13}C NMR (400 MHz, CDCl_3 , 24 °C):



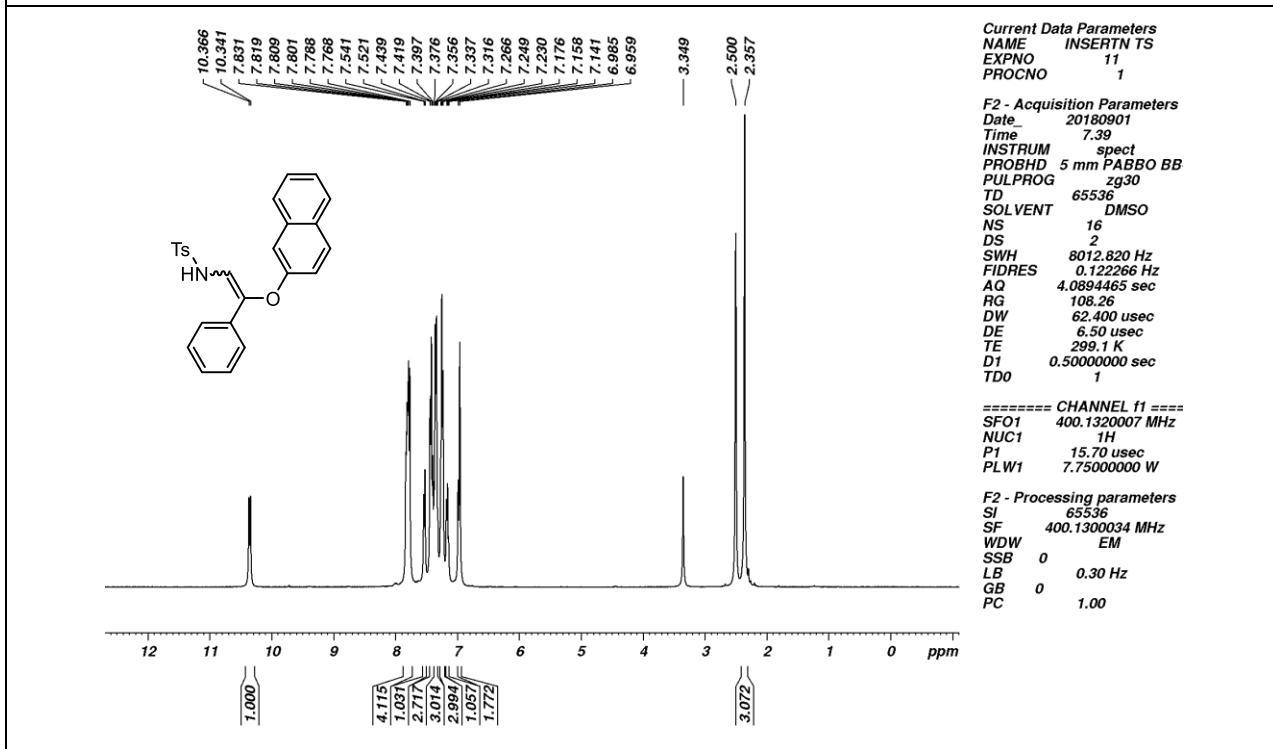
7-Bromo-2-hydroxy-2-phenylnaphtho[2,1-*b*]furan-1(2*H*)-one (6**) : ^1H NMR (400 MHz, DMSO, 24 °C):**



7-Bromo-2-hydroxy-2-phenylnaphtho[2,1-*b*]furan-1(2*H*)-one (6**) : ^{13}C NMR (400 MHz, CDCl₃, 24 °C):**



4-Methyl-N-(2-(naphthalen-2-yloxy)-2-phenylvinyl)benzenesulfonamide (7) : ^1H NMR (400 MHz, DMSO, 24 °C):



4-Methyl-N-(2-(naphthalen-2-yloxy)-2-phenylvinyl)benzenesulfonamide (7) : ^{13}C NMR (400 MHz, DMSO, 24 °C):

