Oxidative Cycloaddition and Cross-Coupling Processes on Unactivated Benzene Derivatives

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Supporting Information

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I. General information and materials

Unless otherwise indicated, ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, in $CDCl_3$ solutions. Chemical shifts are reported in ppm on the δ scale. Multiplicities are described as s (singlet), d (doublet), dd, ddd, etc. (doublet of doublets, doublet of doublets of doublets, etc.), t (triplet), q (quartet), p (pentuplet), m (multiplet), and further qualified as app (apparent) br (broad) c (complex). Coupling constants, J, are reported in Hz. IR spectra (cm–1) were recorded from thin films. Mass spectra (m/e) were measured in the electrospray (ESI) mode.

II. Experimental procedures

General procedure for the formation of cycloadduct 11:

A solution of hypevalent iodine (0.32 mmol, 1.6 equiv.) in $(CF_3)_2CHOH$ ("HFIP", 0.35 ml) was added dropwise on 30 second to a vigorously stirred solution of phenol **9** (0.20 mmol, 1 equiv.) and the corresponding aromatic compound (10 equiv.) in HFIP/DCM (2:1; ml) at -4 °C. The mixture was then stirred for 30 seconds and quenched with $NaHCO_3$. The phases were separated and the aqueous phase extracted with EtOAc. The organic phases were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by silica gel chromatography with a mixture of ethyl acetate/hexane to give the corresponding cycloaddition product **11**.

4a-iodo-8-(2-(phenylsulfonyl)ethyl)-4a,9b-dihydrodibenzo[b,d]furan (11a-g or 12a): Pale yellow oil: 0.032 mmol, 14.8 mg, 34-51% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.69 – 7.54 (m, 4H), 7.49 (s, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 6.73 – 6.66 (m, 2H), 6.02 (dd, *J* = 9.6, 4.4 Hz, 1H), 5.82 (dd, *J* = 9.6, 6.1 Hz, 1H), 5.36 (dd, *J* = 11.3, 4.4 Hz, 1H), 4.35 (d, *J* = 11.3 Hz, 1H), 3.40 – 3.33 (m, 2H), 3.08 – 3.00 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3, 139.3, 133.9, 133.3, 129.5, 128.9, 128.2, 128.1, 126.9, 126.6, 121.9, 109.8, 101.15, 81.3, 58.0, 49.9, 28.5; HRMS (ESI): Calc. for $C_{20}H_{18}IO_3S$ $(M+H)^+$: 465.0016; found: 465.0011.

4a-iodo-8-(2-(propylsulfonyl)ethyl)-4a,9b-dihydrodibenzo[b,d]furan (11h): Pale yellow oil: 0.037 mmol, 16.2 mg, 55% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.04 (dd, *J* = 8.2, 1.7 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 6.70 (dd, *J* = 6.1, 1.7 Hz, 1H), 6.05 (dd, *J* = 9.6, 4.4 Hz, 1H), 5.84 (dd, *J* = 9.6, 6.1 Hz, 1H), 5.39 (dd, *J* = 11.2, 4.4 Hz, 1H), 4.40 (d, *J* = 11.2 Hz, 1H), 3.25 – 3.09 (m, 4H), 2.91 – 2.84 (m, 2H), 1.92 – 1.79 (sx, *J* = 7.6 Hz, 2H), 1.04 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.5, 133.3, 129.7, 129.1, 128.3, 126.9, 126.8, 121.9, 110.0, 101.2, 81.4, 55.2, 54.7, 49.9, 27.9, 16.0, 13.3; HRMS (ESI): Calc. for $C_{17}H_{20}IO_3S$ $(M+H)^+$: 431.0172; found: 431.0171.

4a-iodo-8-(2-((4-methoxyphenyl)sulfonyl)ethyl)-4a,9b-dihydrodibenzo[b,d]furan (11i): Pale yellow oil: 0.048 mmol, 24.0 mg, 48% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.8 Hz, 2H), 7.48 (s, 1H), 7.01 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 8.1 Hz, 1H), 6.71 (d, *J* = 8.2 Hz, 1H), 6.67 (dd, *J* = 6.2, 1.7 Hz, 1H), 6.02 (dd, *J* = 9.6, 4.4 Hz, 1H), 5.82 (dd, *J* = 9.6, 6.1 Hz, 1H), 5.36 (dd, *J* = 11.2, 4.4 Hz, 1H), 4.34 (d, *J* = 11.1 Hz, 1H), 3.88 (s, 3H), 3.37 – 3.30 (m, 2H), 3.04 – 2.97 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9, 157.2, 133.2, 130.8, 130.4, 129.6, 128.9, 128.0, 126.8, 126.1, 121.9, 114.7, 109.8, 101.2, 81.3, 58.3, 55.8, 49.9, 28.7; HRMS (ESI): Calc. for $C_{21}H_{20}IO_4S$ $(M+H)^+$: 495.0121; found: 495.014.

4a-iodo-8-(2-((4-nitrophenyl)sulfonyl)ethyl)-4a,9b-dihydrodibenzo[b,d]furan (11j): Pale yellow oil: 0.071 mmol, 36.4 mg, 41% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.7 Hz, 2H), 8.07 (dd, *J* = 7.5, 5.7 Hz, 2H), 7.45 (s, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 6.66 (dd, *J* = 10.9, 4.9 Hz, 2H), 6.00 (dd, *J* = 9.6, 4.3 Hz, 1H), 5.81 (dd, *J* = 9.6, 6.1 Hz, 1H), 5.36 (dd, *J* = 11.4, 4.3 Hz, 1H), 4.33 (d, *J* = 11.3 Hz, 1H), 3.45 (dd, *J* = 9.4, 6.5 Hz, 2H), 3.07 (dd, *J* = 9.4, 6.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4, 150.9, 145.0, 133.3, 129.7, 129.1, 128.6, 128.2, 126.7, 126.4, 124.5, 122.0, 109.9, 100.7, 81.4, 57.9, 49.8, 28.5; HRMS (ESI): Calc. for $C_{20}H_{17}INO_5S$ $(M+H)^+$: 509.9867; found: 509.9878.

2-((2-(5a-iodo-5a,9a-dihydrodibenzo[b,d]furan-2-yl)ethyl)sulfonyl)benzo[d]thiazole (11k): Pale yellow oil: 0.019 mmol, 10.2 mg, 45% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.6 Hz, 1H), 8.02 (d, *J* = 7.4 Hz, 1H), 7.68 – 7.56 (m, 2H), 7.52 (s, 1H), 6.98 (dd, *J* = 8.2, 1.7 Hz, 1H), 6.70 (d, *J* = 8.2 Hz, 1H), 6.66 (dd, *J* = 6.1, 1.8 Hz, 1H), 6.00 (dd, *J* = 9.6, 4.4 Hz, 1H), 5.81 (dd, *J* = 9.6, 6.1 Hz, 1H), 5.28 (dd, *J* = 11.3, 4.4 Hz, 1H), 4.26 (d, *J* = 11.4 Hz, 1H), 3.81 (td, *J* = 7.2, 3.2 Hz, 2H), 3.24 – 3.16 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 157.4, 152.8, 137.0, 133.2, 129.2, 128.9, 128.2, 128.1, 127.8, 126.8, 126.7, 125.7, 122.5,

121.9, 109.8, 101.1, 81.3, 56.4, 49.8, 28.4; HRMS (ESI): Calc. for $C_{21}H_{17}INO_3S_2$ $(M+H)^+$: 521.9689; found: 521.9692.

General procedure for the formation of cycloadduct 12:

A solution of bis(*tert*-butylcarbonyloxy)iodobenzene (0.32 mmol, 1.6 equiv.) in $(CF_3)_2CHOH$ ("HFIP", 0.35 ml) was added dropwise on 30 second to a vigorously stirred solution of phenol **9** (0.20 mmol, 1 equiv.) and the corresponding aromatic compound (2.00 mmol, 10.0 equiv.) in HFIP/DCM (2:1; ml) at -4 °C. The mixture was then stirred for 30 seconds and quenched with $NaHCO_3$. The phases were separated and the aqueous phase extracted with EtOAc. The organic phases were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by silica gel chromatography with a mixture of ethyl acetate/hexane to give the corresponding cycloaddition product **12**.

4a-iodo-9b-methyl-8-(2-(phenylsulfonyl)ethyl)-4a,9b-dihydrodibenzo[b,d]furan (12b):

Pale yellow oil: 0.019 mmol, 9.2 mg, 54% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.70 – 7.53 (m, 4H), 7.48 (s, 1H), 6.90 (dd, *J* = 8.1, 1.7 Hz, 1H), 6.70 (d, *J* = 8.2 Hz, 1H), 6.56 (dd, *J* = 6.3, 1.7 Hz, 1H), 5.57 (dd, *J* = 6.3, 1.5 Hz, 1H), 5.16 (d, *J* = 11.0 Hz, 1H), 4.34 (d, *J* = 10.9 Hz, 1H), 3.41 – 3.33 (m, 2H), 3.08 – 3.00 (m, 2H), 1.92 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3, 139.3, 133.9, 133.8, 131.3, 129.5, 129.4, 128.9, 128.7, 128.2, 126.5, 122.7, 109.7, 97.1, 85.3, 58.1, 50.3, 28.5, 20.6; HRMS (ESI): Calc. for $C_{21}H_{20}IO_3S$ $(M+H)^+$: 479.0172; found: 479.0165.

9b-ethyl-4a-iodo-8-(2-(phenylsulfonyl)ethyl)-4a,9b-dihydrodibenzo[b,d]furan (12c):

Pale yellow oil: 0.020 mmol, 9.9 mg, 47% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.4 Hz, 2H), 7.69 – 7.53 (m, 4H), 7.47 (s, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.69 (d, *J* = 8.2 Hz, 1H), 6.61 (d, *J* = 6.4 Hz, 1H), 5.57 (d, *J* = 6.4 Hz, 1H), 5.18 (d, *J* = 10.9 Hz, 1H), 4.31 (d, *J* = 10.9 Hz, 1H), 3.41 – 3.32 (m, 2H), 3.08 – 3.00 (m, 2H), 2.41 – 2.19 (m, 2H), 1.12 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4, 139.3, 136.7, 133.9, 133.8, 129.5, 129.4, 128.8, 128.7, 128.2, 126.7, 121.0, 109.7, 97.7, 84.4, 58.1, 50.4, 28.5, 27.1, 11.7; HRMS (ESI): Calc. for $C_{22}H_{22}IO_3S$ $(M+H)^+$: 493.0329; found: 493.0319.

4a-iodo-9b-isopropyl-8-(2-(phenylsulfonyl)ethyl)-4a,9b-dihydrodibenzo[b,d]furan (12d):

Pale yellow oil: 0.015 mmol, 7.7 mg, 40% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (s, *J* = 7.3 Hz, 2H), 7.70 – 7.55 (m, 5H), 7.44 (s, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 6.69 (d, *J* = 8.1 Hz,

1H), 6.63 (dd, *J* = 6.5, 1.9 Hz, 1H), 5.62 (d, *J* = 6.2 Hz, 1H), 5.22 (d, *J* = 10.4 Hz, 1H), 4.24 (d, *J* = 10.1 Hz, 1H), 3.39 – 3.30 (m, 2H), 3.07 – 3.00 (m, 2H), 2.56 (h, *J* = 6.5 Hz, 1H), 1.14 (dd, *J* = 6.8, 2.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.6, 140.7, 139.3, 134.0, 133.9, 129.5, 129.4, 128.8, 128.7, 128.3, 126.8, 120.5, 109.7, 98.3, 83.4, 58.1, 50.6, 32.1, 28.6, 21.9, 21.1; HRMS (ESI): Calc. for $C_{23}H_{24}IO_3S$ $(M+H)^+$: 507.0485; found: 507.0489.

tert-butyl((5a-iodo-2-(2-(phenylsulfonyl)ethyl)-5a,9a-dihydrodibenzo[b,d]furan-9a-yl)methoxy)dimethylsilane (12e): Pale yellow oil: 0.014 mmol, 8.8 mg, 35% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.2 Hz, 2H), 7.71 – 7.53 (m, 4H), 7.48 (s, 1H), 6.93 – 6.87 (m, 1H), 6.67 (dd, *J* = 9.3, 4.8 Hz, 2H), 5.81 (d, *J* = 6.4 Hz, 1H), 5.25 (d, *J* = 10.9 Hz, 1H), 4.31 (s, 2H), 3.41 – 3.32 (m, 2H), 3.09 – 2.99 (m, 2H), 0.91 (s, 9H), 0.09 (d, *J* = 2.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4, 139.3, 137.8, 134.0, 133.9, 133.5, 129.5, 129.5, 129.0, 128.9, 128.5, 128.2, 126.7, 121.2, 109.7, 99.3, 81.7, 63.9, 58.1, 50.3, 28.5, 26.0, 18.5, -5.2, -5.3; HRMS (ESI): Calc. for $C_{27}H_{34}IO_4SSi$ $(M+H)^+$: 609.0986; found: 609.0978.

4a-iodo-8-(3-(phenylsulfonyl)propyl)-4a,9b-dihydrodibenzo[b,d]furan (12f): Pale yellow oil: 0.013 mmol, 6.2 mg, 31% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.3 Hz, 2H), 7.69 – 7.52 (m, 4H), 7.47 (s, 1H), 6.90 (d, *J* = 8.1 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 1H), 6.69 (dd, *J* = 6.1, 1.9 Hz, 1H), 6.06 (dd, *J* = 9.7, 4.5 Hz, 1H), 5.85 (dd, *J* = 9.6, 6.1 Hz, 1H), 5.34 (dd, *J* = 11.1, 4.5 Hz, 1H), 4.34 (d, *J* = 10.9 Hz, 1H), 3.09 (dd, *J* = 8.7, 7.2 Hz, 2H), 2.69 (t, *J* = 7.3 Hz, 2H), 2.04 (dq, *J* = 11.3, 7.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.0, 139.4, 133.8, 133.3, 132.0, 129.4, 129.0, 128.2, 127.8, 127.0, 126.8, 121.8, 109.6, 102.0, 81.1, 55.6, 49.8, 33.8, 24.7; HRMS (ESI): Calc. for $C_{21}H_{20}IO_3S$ $(M+H)^+$: 479.0172; found: 479.0182.

8-(2-(phenylsulfonyl)ethyl)-4a,9b-dihydrodibenzo[b,d]furan (12g): Pale yellow oil: 0.041 mmol, 14.2 mg, 40% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.2 Hz, 2H), 7.70 – 7.52 (m, 4H), 6.98 (s, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 8.2 Hz, 1H), 6.12 (dd, *J* = 9.8, 5.5 Hz, 1H), 5.97 – 5.88 (m, 2H), 5.77 (dd, *J* = 9.7, 3.3 Hz, 1H), 5.42 (dd, *J* = 12.1, 4.6 Hz, 1H), 4.17 (d, *J* = 12.0 Hz, 1H), 3.33 (dd, *J* = 10.4, 6.2 Hz, 2H), 2.99 (dd, *J* = 10.4, 6.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4, 139.3, 133.9, 130.1, 129.8, 129.4, 128.2, 128.1, 127.6, 126.5, 124.6, 121.3, 121.2, 110.0, 78.7, 58.1, 40.8, 28.4; HRMS (ESI): Calc. for $C_{20}H_{18}O_3SNa$ $(M+Na)^+$: 361.0869; found: 361.0860.

10-(2-(phenylsulfonyl)ethyl)-6a,11b-dihydronaphtho[2,1-b]benzofuran (12h): Pale yellow oil: 0.095 mmol, 37.1 mg, 72% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.3 Hz, 2H), 7.68 – 7.49 (m, 5H), 7.38 – 7.19 (m, 4H), 7.07 (d, *J* = 7.2 Hz, 1H), 6.87 – 6.79 (m, 2H), 6.72 (d, *J* = 8.1 Hz, 1H), 6.48 (d, *J* = 8.8 Hz, 1H), 5.85 – 5.76 (m, 2H), 4.64 (d, *J* = 10.5 Hz, 1H), 3.33 – 3.23 (m, 2H), 2.98 – 2.89 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.2, 139.2, 133.8, 132.7, 130.6, 130.5, 129.8, 129.6, 129.4, 128.6, 128.5, 128.4, 128.2, 128.0, 127.7, 124.6, 124.5, 110.0, 81.4, 58.0, 43.7, 28.3; HRMS (ESI): Calc. for $C_{24}H_{20}O_3SNa$ $(M+Na)^+$: 411.1025; found: 411.1028.

2-(2-(phenylsulfonyl)ethyl)-6,11-dihydro-6,11-[1,2]benzenodibenzo[b,e]oxepine (13): A solution of bis(*tert*-butylcarbonyloxy)iodobenzene (0.17 mmol, 1.6 equiv.) in $(CF_3)_2CHOH$ ("HFIP", 0.35 ml) was added dropwise on 30 second to a vigorously stirred solution of phenol **9** (0.11 mmol, 1 equiv.) and the anthracene (0.55 mmol, 5.0 equiv.) in HFIP/DCM (2:1; ml) at -4 °C. The mixture was then stirred for 30 seconds and quenched with $NaHCO_3$. The phases were separated and the aqueous phase extracted with EtOAc. The organic phases were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by silica gel chromatography with a mixture of ethyl acetate/hexane to afford **13** in 58% yield (0.034 mmol, 14.8 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.2 Hz, 2H), 7.62 – 7.54 (m, 2H), 7.53 – 7.42 (m, 5H), 7.38 – 7.32 (m, 2H), 7.25 – 7.22 (m, 2H), 6.93 (d, *J* = 2.2 Hz, 1H), 6.71 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.44 (d, *J* = 8.3 Hz, 1H), 5.88 (s, *J* = 6.6 Hz, 1H), 4.51 (s, 1H), 3.33 – 3.24 (m, 2H), 2.95 – 2.87 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.7, 144.8, 139.3, 134.8, 133.7, 129.3, 129.3, 128.8, 128.7, 128.4, 128.1, 127.5, 127.4, 124.5, 120.3, 78.8, 57.8, 52.3, 28.0; HRMS (ESI): Calc. for $C_{28}H_{23}O_3S$ $(M+H)^+$: 439.1362; found: 439.1353.

7-(2-((4-methoxyphenyl)sulfonyl)ethyl)-3a,8b-dihydrofuro[3,2-b]benzofuran (14): A solution of bis(*tert*-butylcarbonyloxy)iodobenzene (0.08 mmol, 1.6 equiv.) in $(CF_3)_2CHOH$ ("HFIP", 0.35 ml) was added dropwise on 30 second to a vigorously stirred solution of phenol **9i** (0.05 mmol, 1 equiv.) and the furan (0.75 mmol, 15.0 equiv.) in TFE at -25 °C. After completion the reaction was quenched with $NaHCO_3$. The phases were separated and the aqueous phase extracted with EtOAc. The organic phases were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by silica gel chromatography with a mixture of ethyl acetate/hexane to afford **14** in 95% yield (0.047 mmol, 16.8 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.9 Hz, 2H), 7.17 (d, *J* = 1.4 Hz, 1H), 7.01 (d, *J* = 8.8 Hz, 3H), 6.76 (d, *J* = 8.3 Hz, 1H), 6.61 (d, *J* = 2.5 Hz, 1H), 5.97 (s, 2H), 5.28 (t, *J* = 2.3 Hz, 1H),

3.89 (s, 3H), 3.35 – 3.27 (m, 2H), 3.02 – 2.95 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9, 158.5, 151.3, 131.7, 131.5, 130.6, 130.4, 130.1, 126.3, 125.4, 114.6, 111.2, 100.2, 89.4, 85.1, 58.2, 55.8, 28.5; HRMS (ESI): Calc. for $C_{19}H_{18}O_5SNa$ $(M+Na)^+$: 381.0767; found: 381.0779.

General procedure for the formation of cycloadduct 17: A solution of bis(*tert*-butylcarbonyloxy)iodobenzene (0.22 mmol, 1.6 equiv.) in $(CF_3)_2CHOH$ ("HFIP", 0.35 ml) was added dropwise on 30 second to a vigorously stirred solution of sulfonamide **15** (0.14 mmol, 1 equiv.) and the corresponding aromatic compound (0.70 mmol, 5.0 equiv.) in HFIP/DCM (2:1; ml) at -4 °C. The mixture was then stirred for 30 seconds and quenched with $NaHCO_3$. The phases were separated and the aqueous phase extracted with EtOAc. The organic phases were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by silica gel chromatography with a mixture of ethyl acetate/hexane to give the corresponding cycloaddition product **17**.

10-methyl-7-(methylsulfonyl)-7,11b-dihydro-6aH-benzo[c]carbazole (17a): Pale yellow oil: 0.074 mmol, 23.3 mg, 61% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 4H), 7.05 (dd, *J* = 14.5, 7.5 Hz, 2H), 6.75 (s, 1H), 6.43 (dd, *J* = 9.9, 2.1 Hz, 1H), 5.83 (dd, *J* = 9.9, 2.5 Hz, 1H), 5.53 (dt, *J* = 9.8, 2.3 Hz, 1H), 4.64 (d, *J* = 9.8 Hz, 1H), 2.94 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.6, 135.0, 135.0, 131.6, 130.7, 129.2, 128.8, 128.1, 128.1, 127.9, 126.5, 125.3, 116.2, 64.0, 43.9, 37.7, 21.1; HRMS (ESI): Calc. for $C_{18}H_{18}NO_2S$ $(M+H)^+$: 312.1058; found: 312.1051.

7-(ethylsulfonyl)-10-methyl-7,11b-dihydro-6aH-benzo[c]carbazole (17b): Pale yellow oil: 0.081 mmol, 26.4 mg, 59% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 9.1, 6.7 Hz, 4H), 7.07 (d, *J* = 6.7 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.72 (s, 1H), 6.41 (dd, *J* = 9.9, 2.0 Hz, 1H), 5.84 (dd, *J* = 9.9, 2.4 Hz, 1H), 5.53 (dt, *J* = 9.8, 2.3 Hz, 1H), 4.62 (d, *J* = 9.7 Hz, 1H), 3.18 – 3.08 (m, 2H), 2.22 (s, 3H), 1.38 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.8, 134.7, 134.4, 131.6, 130.7, 129.3, 129.2, 128.6, 128.1, 128.0, 127.9, 127.1, 125.2, 115.4, 64.0, 45.9, 44.0, 21.1, 8.2; HRMS (ESI): Calc. for $C_{19}H_{20}NO_2S$ $(M+H)^+$: 326.1209; found: 326.1207.

10-methyl-7-tosyl-7,11b-dihydro-6aH-benzo[c]carbazole (17c): Pale yellow oil: 0.030 mmol, 11.7 mg, 32% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 2H), 7.24 – 7.18

(m, 4H), 7.14 – 6.99 (m, 4H), 6.55 (s, 1H), 6.38 (d, *J* = 9.9 Hz, 1H), 5.86 (dd, *J* = 9.8, 2.3 Hz, 1H), 5.39 (d, *J* = 9.6 Hz, 1H), 3.80 (d, *J* = 9.7 Hz, 1H), 2.40 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.0, 138.0, 135.9, 135.9, 135.3, 131.6, 130.8, 129.9, 129.2, 129.1, 128.5, 128.0, 127.8, 127.8, 127.2, 127.1, 124.8, 118.1, 63.8, 43.4, 21.7, 21.2; HRMS (ESI): Calc. for $C_{24}H_{22}NO_2S$ $(M+H)^+$: 388.1369; found: 388.1374.

7-(isopropylsulfonyl)-10-methyl-7,11b-dihydro-6aH-benzo[c]carbazole (17d): Pale yellow oil: 0.032 mmol, 11.0 mg, 38% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 5H), 7.06 (d, *J* = 6.8 Hz, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.70 (s, 1H), 6.41 (d, *J* = 9.9 Hz, 1H), 5.86 (dd, *J* = 9.9, 2.2 Hz, 1H), 5.51 (d, *J* = 9.7 Hz, 1H), 4.63 (d, *J* = 9.7 Hz, 1H), 3.40 (h, *J* = 6.8 Hz, 1H), 2.21 (s, 3H), 1.45 – 1.37 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.4, 134.1, 133.7, 131.7, 129.3, 129.1, 128.5, 128.1, 128.0, 127.8, 127.5, 125.2, 114.7, 64.4, 54.0, 43.9, 21.1, 17.2, 16.8; HRMS (ESI): Calc. for $C_{20}H_{22}NO_2S$ $(M+H)^+$: 340.1366; found: 340.1358.

7-(benzylsulfonyl)-10-methyl-7,11b-dihydro-6aH-benzo[c]carbazole (17e): Pale yellow oil: 0.048 mmol, 18.5 mg, 45% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 4H), 7.26 – 7.23 (m, 3H), 7.19 (t, *J* = 6.1 Hz, 2H), 7.00 (dd, *J* = 9.8, 4.2 Hz, 2H), 6.70 (s, 1H), 6.30 (dd, *J* = 9.9, 1.9 Hz, 1H), 5.69 (dd, *J* = 9.9, 2.5 Hz, 1H), 4.96 (dt, *J* = 10.1, 2.2 Hz, 1H), 4.40 (d, *J* = 2.6 Hz, 2H), 3.92 (d, *J* = 10.1 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.4, 134.9, 134.2, 131.8, 130.8, 130.7, 129.2, 129.2, 129.0, 128.6, 128.0, 127.9, 127.8, 127.7, 127.3, 125.2, 114.7, 64.7, 57.3, 43.2, 21.2; HRMS (ESI): Calc. for $C_{24}H_{22}NO_2S$ $(M+H)^+$: 388.1369; found: 388.1381.

10-chloro-7-(methylsulfonyl)-7,11b-dihydro-6aH-benzo[c]carbazole (17f): Pale yellow oil: 0.043 mmol, 14.3 mg, 51% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 4H), 7.18 (ddd, *J* = 8.5, 2.0, 0.9 Hz, 1H), 7.12 – 7.06 (m, 1H), 6.93 – 6.88 (m, 1H), 6.45 (dd, *J* = 9.9, 2.0 Hz, 1H), 5.83 (dd, *J* = 9.9, 2.5 Hz, 1H), 5.55 (dt, *J* = 9.8, 2.3 Hz, 1H), 4.65 (d, *J* = 9.8 Hz, 1H), 2.98 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 137.0, 130.7, 130.6, 130.3, 130.1, 129.8, 129.1, 128.8, 128.5, 128.4, 128.1, 127.4, 125.9, 125.1, 117.1, 64.1, 43.8, 38.3; HRMS (ESI): Calc. for $C_{17}H_{14}NO_2SClNa$ $(M+Na)^+$: 354.0326; found: 354.0320.

10-isopropyl-7-(methylsulfonyl)-7,11b-dihydro-6aH-benzo[c]carbazole (17g): Pale yellow oil: 0.023 mmol, 7.8 mg, 52% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 4H), 7.07

(d, *J* = 6.7 Hz, 2H), 6.78 (s, 1H), 6.43 (dd, *J* = 9.9, 2.0 Hz, 1H), 5.85 (dd, *J* = 9.9, 2.5 Hz, 1H), 5.53 (dt, *J* = 9.9, 2.3 Hz, 1H), 4.65 (d, *J* = 9.7 Hz, 1H), 2.95 (s, 3H), 2.79 (h, *J* = 6.9 Hz, 1H), 1.15 (dd, *J* = 6.9, 3.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.0, 137.8, 134.8, 131.7, 130.8, 129.2, 128.9, 128.1, 128.1, 128.0, 127.7, 126.5, 122.8, 116.1, 63.9, 43.9, 37.9, 33.9, 24.4, 24.0; HRMS (ESI): Calc. for $C_{20}H_{22}NO_2S$ $(M+H)^+$: 340.1366; found: 340.1361.

7-(methylsulfonyl)-10-propyl-7,11b-dihydro-6aH-benzo[c]carbazole (17h): Pale yellow oil: 0.061 mmol, 20.7 mg, 51% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 4H), 7.05 (dd, *J* = 12.8, 7.5 Hz, 2H), 6.74 (s, 1H), 6.43 (dd, *J* = 9.9, 2.0 Hz, 1H), 5.84 (dd, *J* = 9.9, 2.5 Hz, 1H), 5.53 (dt, *J* = 9.8, 2.3 Hz, 1H), 4.64 (d, *J* = 9.8 Hz, 1H), 2.95 (s, 3H), 2.51 – 2.43 (m, 2H), 1.53 (sx, *J* = 7.4 Hz, 2H), 0.89 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.9, 137.8, 134.9, 131.6, 130.7, 129.2, 128.8, 128.7, 128.1, 128.1, 127.9, 126.5, 124.6, 116.1, 64.0, 43.9, 37.8, 37.8, 24.8, 14.0; HRMS (ESI): Calc. for $C_{20}H_{22}NO_2S$ $(M+H)^+$: 340.1366; found: 340.1368.

7-(methylsulfonyl)-10-(2-(phenylsulfonyl)ethyl)-7,11b-dihydro-6aH-benzo[c]carbazole (17i): Pale yellow oil: 0.016 mmol, 7.6 mg, 54% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.2 Hz, 2H), 7.68 – 7.49 (m, 5H), 7.39 – 7.28 (m, 5H), 7.08 (dd, *J* = 5.7, 2.4 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.71 (s, 1H), 6.42 (dd, *J* = 9.9, 2.0 Hz, 1H), 5.81 (dd, *J* = 9.9, 2.5 Hz, 1H), 5.52 (dt, *J* = 9.9, 2.3 Hz, 1H), 4.60 (d, *J* = 9.8 Hz, 1H), 3.29 – 3.20 (m, 3H), 2.99 – 2.91 (m, 2H), 2.95 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.2, 139.0, 135.6, 134.3, 134.0, 131.2, 130.6, 129.5, 129.2, 129.0, 128.7, 128.4, 128.2, 128.0, 126.2, 124.7, 116.3, 64.0, 57.6, 43.8, 38.2, 28.4; HRMS (ESI): Calc. for $C_{25}H_{23}NO_4SNa$ $(M+Na)^+$: 488.0961; found: 488.0957.

(7-(methylsulfonyl)-7,11b-dihydro-6aH-benzo[c]carbazol-10-yl)methanol (17j): Pale yellow oil: 0.064 mmol, 21.0 mg, 53% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.1 Hz, 1H), 7.37 – 7.29 (m, 3H), 7.21 (d, *J* = 7.9 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.98 (s, 1H), 6.43 (d, *J* = 9.9 Hz, 1H), 5.84 (dd, *J* = 9.9, 2.2 Hz, 1H), 5.56 (d, *J* = 9.9 Hz, 1H), 4.66 (d, *J* = 9.9 Hz, 1H), 4.56 (s, 2H), 2.97 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.9, 139.5, 137.8, 135.4, 131.8, 131.3, 130.6, 129.3, 128.9, 128.3, 128.3, 128.0, 127.8, 126.2, 123.7, 118.4, 116.0, 65.0, 60.6, 43.8, 38.1; HRMS (ESI): Calc. for $C_{18}H_{17}NO_3SNa$ $(M+Na)^+$: 350.0821; found: 350.0811.

2-(7-(methylsulfonyl)-7,11b-dihydro-6aH-benzo[c]carbazol-10-yl)ethanol (17k): Pale yellow oil: 0.042 mmol, 14.2 mg, 62% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.1 Hz, 1H), 7.39 – 7.31 (m, 3H), 7.12 (dd, *J* = 7.3, 3.0 Hz, 2H), 6.84 (s, 1H), 6.47 (dd, *J* = 9.9, 2.0 Hz, 1H), 5.88 (dd, *J* = 9.9, 2.5 Hz, 1H), 5.58 (dt, *J* = 9.9, 2.3 Hz, 1H), 4.69 (d, *J* = 9.9 Hz, 1H), 3.81 (t, *J* = 6.5 Hz, 2H), 3.01 (s, 3H), 2.79 (t, *J* = 6.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.5, 135.5, 135.3, 131.4, 130.7, 130.1, 129.3, 129.2, 128.9, 128.2, 128.2, 128.0, 126.3, 125.5, 125.3, 116.2, 64.0, 63.7, 43.8, 38.8, 38.1; HRMS (ESI): Calc. for $C_{19}H_{19}NO_3SNa$ $(M+Na)^+$: 364.0978; found: 364.0972.

10-(2-((tert-butyldimethylsilyl)oxy)ethyl)-7-(methylsulfonyl)-7,11b-dihydro-6aH-benzo[c]carbazole (17l): Pale yellow oil: 0.048 mmol, 21.8 mg, 52% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.1 Hz, 1H), 7.29 (dd, *J* = 9.0, 4.2 Hz, 3H), 7.09 – 7.03 (m, 2H), 6.80 (s, 1H), 6.42 (dd, *J* = 9.9, 1.9 Hz, 1H), 5.83 (dd, *J* = 9.9, 2.4 Hz, 1H), 5.53 (dt, *J* = 9.8, 2.2 Hz, 1H), 4.63 (d, *J* = 9.8 Hz, 1H), 3.71 (t, *J* = 6.6 Hz, 2H), 2.93 (s, 3H), 2.69 (t, *J* = 6.6 Hz, 2H), 0.81 (d, *J* = 6.6 Hz, 10H), -0.12 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.2, 136.7, 134.9, 131.5, 130.7, 129.4, 129.2, 128.8, 128.2, 128.1, 127.9, 126.5, 125.6, 121.2, 116.1, 64.4, 64.0, 43.9, 39.1, 37.7, 26.0, 18.4, -5.3, -5.4; HRMS (ESI): Calc. for $C_{25}H_{33}NO_3SNa$ $(M+Na)^+$: 478.1843; found: 478.1850.

7-(methylsulfonyl)-10-(trimethylsilyl)-7,11b-dihydro-6aH-benzo[c]carbazole (17m): Pale yellow oil: 0.038 mmol, 14.2 mg, 43% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 1H), 7.40 – 7.31 (m, 3H), 7.08 (d, *J* = 5.5 Hz, 2H), 6.44 (dd, *J* = 9.9, 2.0 Hz, 1H), 5.86 (dd, *J* = 9.9, 2.5 Hz, 1H), 5.54 (dt, *J* = 10.0, 2.3 Hz, 1H), 4.67 (d, *J* = 10.0 Hz, 1H), 2.98 (s, 3H), 0.19 – 0.15 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.6, 136.6, 134.0, 133.9, 131.6, 130.7, 129.3, 129.2, 129.0, 128.1, 128.0, 126.1, 115.1, 63.7, 43.8, 38.4, -0.9; HRMS (ESI): Calc. for $C_{20}H_{24}NO_2SSi$ $(M+H)^+$: 370.1292; found: 370.1299.

10-isopropyl-7-(methylsulfonyl)-7,11b-dihydro-6aH-benzo[c]carbazol-5-yl methanesulfonate (18) and 4-(N-(4-isopropylphenyl)methylsulfonamido)naphthalen-1-yl methanesulfonate (19) :

A solution of bis(*tert*-butylcarbonyloxy)iodobenzene (0.08 mmol, 1.6 equiv.) in $(CF_3)_2CHOH$ ("HFIP", 0.2 ml) was added dropwise on 30 second to a vigorously stirred solution of sulfonamide **15a** (10.7 mg , 0.05 mmol, 1 equiv.) and the O-Mesyl-Naphthol (0.35 mmol, 7.0 equiv.) in HFIP/DCM (2:1; ml) at -4 °C. The mixture was then stirred for 30 seconds and

quenched with $NaHCO_3$. The phases were separated and the aqueous phase extracted with EtOAc. The organic phases were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by silica gel chromatography with a mixture of ethyl acetate/hexane to afford **18 and 19** in 72% yield (0.036 mmol, 15.6 mg) as a 1:1.2 ratio. **18:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.33 (m, 5H), 7.11 (d, *J* = 8.2 Hz, 1H), 6.78 (s, 1H), 5.93 (d, *J* = 2.9 Hz, 1H), 5.70 (dd, *J* = 9.8, 3.0 Hz, 1H), 4.68 (d, *J* = 9.7 Hz, 1H), 3.09 (s, 3H), 2.99 (s, 3H), 2.80 (p, *J* = 6.9 Hz, 1H), 1.16 (d, *J* = 4.0 Hz, 3H), 1.14 (d, *J* = 4.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.1, 145.9, 137.5, 133.7, 133.0, 129.8, 129.2, 128.3, 126.9, 123.4, 122.8, 115.8, 114.5, 63.3, 43.8, 38.3, 38.1, 33.9, 24.4, 24.0. HRMS (ESI): Calc. for $C_{21}H_{24}NO_5S_2$ $(M+H)^+$: 434.1090; found: 434.1083.

19: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 (dd, *J* = 7.1, 2.4 Hz, 1H), 8.14 (dd, *J* = 7.0, 2.5 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.68 – 7.62 (m, 2H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 3.25 (s, 3H), 3.24 (s, 3H), 2.86 (p, *J* = 6.9 Hz, 1H), 1.19 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.9, 145.6, 138.7, 136.3, 133.8, 128.6, 128.4, 128.1, 127.7, 127.4, 125.9, 124.4, 122.1, 118.2, 40.1, 38.4, 33.7, 24.0. HRMS (ESI): Calc. for $C_{21}H_{23}NO_5S_2Na$ $(M+Na)^+$: 456.0910; found: 456.0913.

(9s,10s)-10-(N-p-tolylmethylsulfonamido)-9,10-dihydroanthracen-9-yl pivalate (20) :

A solution of bis(*tert*-butylcarbonyloxy)iodobenzene (0.096 mmol, 1.6 equiv.) in $(CF_3)_2CHOH$ ("HFIP", 0.2 ml) was added dropwise on 30 second to a vigorously stirred solution of sulfonamide **15a** (11.1 mg, 0.060 mmol, 1 equiv.) and the anthracene (0.299 mmol, 5.0 equiv.) in HFIP/DCM (2:1; ml) and Na_2CO_3 at -4 °C. The mixture was then stirred for 30 seconds and quenched with $NaHCO_3$. The phases were separated and the aqueous phase extracted with EtOAc. The organic phases were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by silica gel chromatography with a mixture of ethyl acetate/hexane to afford **20** in 46% yield (0.027 mmol, 12.1 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.5 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.1 Hz, 2H), 7.02 (d, *J* = 7.8 Hz, 2H), 6.85 (d, *J* = 7.0 Hz, 2H), 6.84 (s, 1H), 6.16 (d, *J* = 8.2 Hz, 2H), 5.52 (s, 1H), 3.00 (s, 3H), 2.26 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.2, 139.7, 138.4, 133.2, 131.9, 131.7, 129.7, 129.4, 128.5, 128.5, 125.2, 66.4, 60.3, 41.1, 39.1, 27.4, 21.3. HRMS (ESI): Calc. for $C_{27}H_{30}NO_4S$ $(M+H)^+$: 464.1890; found: 464.1882.

General procedure for the formation of coupling product 5:

Trifluoroacetic acid (0.55 mmol, 5.0 equiv.) was added to a solution of cycloaddition product **21** (0.11 mnol, 1.0 equiv.) in DCM at room temperature and the solution was heated at 40 °C. After completion, the solution was evaporated under reduced pressure and purified by silica gel chromatography with a mixture of ethyl acetate/hexane to give the corresponding coupling product **5**.

2'-iodo-5-(2-(phenylsulfonyl)ethyl)-[1,1'-biphenyl]-2-ol (5a): Pale yellow oil: 0.032 mmol, 15.0 mg, 97% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 – 7.92 (m, 3H), 7.67 – 7.54 (m, 3H), 7.43 (dd, *J* = 7.4, 6.6 Hz, 1H), 7.24 (d, *J* = 1.6 Hz, 1H), 7.08 (ddd, *J* = 15.8, 8.0, 1.9 Hz, 2H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.83 (d, *J* = 2.1 Hz, 1H), 3.41 – 3.32 (m, 2H), 3.06 – 2.98 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.2, 141.5, 139.9, 139.2, 133.9, 131.3, 131.0, 130.3, 130.1, 129.8, 129.5, 129.4, 128.9, 128.3, 116.4, 100.6, 57.9, 28.1; IR υ (cm−1) 3418, 1634, 1511, 1446, 1306, 1149; HRMS (ESI): Calc. for $C_{20}H_{18}IO_3S$ $(M+H)^+$: 465.0016; found: 465.0013.

2'-iodo-5'-methyl-5-(2-(phenylsulfonyl)ethyl)-[1,1'-biphenyl]-2-ol (5b): Pale yellow oil: 0.051 mmol, 24.5 mg, 91% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.1 Hz, 2H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.67 – 7.53 (m, 3H), 7.07 (d, *J* = 1.9 Hz, 1H), 7.04 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.92 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 6.82 (d, *J* = 2.2 Hz, 1H), 3.41 – 3.33 (m, 2H), 3.05 – 2.97 (m, 2H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.2, 141.2, 139.6, 139.2, 139.1, 133.9, 131.8, 131.3, 131.2, 130.3, 129.7, 129.5, 129.4, 128.3, 116.3, 96.3, 57.9, 28.1, 21.0; HRMS (ESI): Calc. for $C_{21}H_{23}INO_3S$ $(M+NH_4)^+$: 496.0438; found: 496.0416.

5'-ethyl-2'-iodo-5-(2-(phenylsulfonyl)ethyl)-[1,1'-biphenyl]-2-ol (5c): Pale yellow oil: 0.041 mmol, 20.0 mg, 98% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.1 Hz, 2H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.67 – 7.55 (m, 3H), 7.09 (d, *J* = 2.1 Hz, 1H), 7.05 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.98 – 6.91 (m, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.83 (d, *J* = 2.1 Hz, 1H), 4.71 (s, 1H), 3.41 – 3.33 (m, 2H), 3.05 – 2.98 (m, 2H), 2.62 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.5 Hz , 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.2, 145.4, 141.2, 139.8, 139.2, 133.9, 131.4, 130.6, 130.3, 130.0, 129.7, 129.5, 129.4, 128.3, 116.3, 96.5, 57.9, 28.4, 28.1, 15.4; HRMS (ESI): Calc. for $C_{22}H_{22}IO_3S$ $(M+H)^+$: 493.0329; found: 493.0324.

2'-iodo-5'-isopropyl-5-(2-(phenylsulfonyl)ethyl)-[1,1'-biphenyl]-2-ol (5d): Pale yellow oil: 0.059 mmol, 29.7 mg, 90% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.2 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.67 – 7.57 (m, 4H), 7.12 (d, *J* = 2.2 Hz, 1H), 7.05 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 2H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.84 (d, *J* = 2.1 Hz, 1H), 3.42 – 3.34 (m, 2H), 3.06 – 2.97 (m, 2H), 2.94 – 2.83 (m, 1H), 1.23 (t, *J* = 6.7 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.2, 150.2, 141.2, 139.8, 139.1, 137.5, 134.0, 131.5, 130.3, 129.7, 129.5, 129.4, 129.3, 128.8, 128.6, 128.3, 116.3, 96.6, 57.9, 33.8, 28.1, 23.9, 23.9; IR υ (cm−1) 3426, 1509, 1446, 1306, 1149; HRMS (ESI): Calc. for $C_{23}H_{24}IO_3S$ $(M+H)^+$: 507,0485; found: 507,0493.

5-(2-(phenylsulfonyl)ethyl)-[1,1'-biphenyl]-2-ol (5e): Pale yellow oil: 0.082 mmol, 27.7 mg, 97% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.2 Hz, 2H), 7.67 – 7.55 (m, 3H), 7.50 – 7.37 (m, 5H), 7.02 – 6.96 (m, 2H), 6.87 (d, *J* = 8.1 Hz, 1H), 3.42 – 3.33 (m, 2H), 3.06 – 2.97 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.5, 139.2, 136.8, 133.9, 130.2, 129.7, 129.5, 129.4, 129.1, 129.0, 128.6, 128.2, 128.2, 116.4, 57.9, 28.1; IR υ (cm−1) 3425, 1446, 1305, 1149; HRMS (ESI): Calc. for $C_{40}H_{36}NaO_6S_2$ $(2M+Na)^+$: 699.1846; found: 699.1823.

2'-iodo-5-(2-((4-methoxyphenyl)sulfonyl)ethyl)-[1,1'-biphenyl]-2-ol (5f): Pale yellow oil: 0.025 mmol, 12.3 mg, 87% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 1H), 7.85 (d, *J* = 8.9 Hz, 2H), 7.43 (dt, *J* = 7.5, 3.7 Hz, 1H), 7.08 (ddd, *J* = 15.7, 7.9, 1.9 Hz, 2H), 7.02 (d, *J* = 8.9 Hz, 2H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.83 (d, *J* = 2.1 Hz, 1H), 3.88 (s, 3H), 3.38 – 3.30 (m, 2H), 3.05 – 2.95 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.0, 151.2, 141.6, 139.9, 131.3, 131.0, 130.5, 130.3, 130.1, 129.8, 129.6, 128.9, 128.4, 116.4, 114.7, 100.6, 58.2, 55.9, 28.3; IR υ (cm−1) 3418, 1594, 1497, 1262, 1144; HRMS (ESI): Calc. for $C_{21}H_{20}IO_4S$ $(M+H)^+$: 495.0121; found: 495.0116.

2-(naphthalen-1-yl)-4-(2-(phenylsulfonyl)ethyl)phenol (5g): Pale yellow oil: 0.030 mmol, 11.5 mg, 98% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 5.3, 3.2 Hz, 4H), 7.63 (d, *J* = 7.3 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 5H), 7.49 (dd, *J* = 8.5, 1.3 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.12 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.00 (d, *J* = 2.2 Hz, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 3.42 – 3.35 (m, 2H), 3.09 – 3.01 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.3, 139.3, 134.1, 133.9, 133.7, 131.8, 131.0, 129.5, 129.5, 129.2, 128.7, 128.3, 128.2, 127.0, 126.8, 126.6, 125.9, 125.6, 116.2, 57.9, 28.1; HRMS (ESI): Calc. for $C_{24}H_{24}NO_3S$ $(M+NH_4)^+$: 406.1471; found: 406.1453.

N-(4-methyl-2-(naphthalen-1-yl)phenyl)ethanesulfonamide (5h): Pale yellow oil: 0.074 mmol, 24.0 mg, 97% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.62 – 7.46 (m, 5H), 7.41 (dd, *J* = 7.0, 1.1 Hz, 1H), 7.30 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.22 (d, *J* = 1.9 Hz, 1H), 2.83 (q, *J* = 7.4 Hz, 2H), 2.41 (s, 3H), 0.80 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.0, 134.8, 134.0, 132.6, 132.1, 131.8, 131.6, 130.0, 129.2, 128.9, 127.6, 127.2, 126.7, 125.8, 125.2, 120.8, 46.1, 20.9, 7.9; IR υ (cm−1) 3357, 1498, 1333, 1153; HRMS (ESI): Calc. for $C_{19}H_{20}NO_2S$ $(M+H)^+$: 326.1209; found: 326.1203.

N-(2-(naphthalen-1-yl)-4-propylphenyl)methanesulfonamide (5i): Pale yellow oil: 0.051 mmol, 17.2 mg, 83% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.61 – 7.51 (m, 2H), 7.46 (d, *J* = 3.2 Hz, 2H), 7.39 (d, *J* = 7.0 Hz, 1H), 7.30 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.15 (d, *J* = 1.9 Hz, 1H), 2.69 (s, 3H), 2.67 – 2.59 (m, 2H), 1.68 (sx, *J* = 7.4 Hz, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.8, 135.0, 134.1, 132.7, 131.8, 131.7, 131.5, 129.4, 129.2, 128.9, 127.7, 127.2, 126.7, 125.8, 125.1, 120.9, 39.4, 37.4, 24.6, 13.9; HRMS (ESI): Calc. for $C_{20}H_{22}NO_2S$ $(M+H)^+$: 340.1366; found: 340.1359.

N-(4-isopropyl-2-(naphthalen-1-yl)phenyl)methanesulfonamide (5j): Pale yellow oil: 0.105 mmol, 35.8 mg, 97% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.48 – 7.45 (m, 2H), 7.40 (dd, *J* = 7.0, 1.1 Hz, 1H), 7.35 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.19 (d, *J* = 2.1 Hz, 1H), 2.95 (h, *J* = 6.9 Hz, 1H), 2.69 (s, 3H), 1.27 (d, *J* = 1.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.0, 135.1, 134.1, 132.7, 131.8, 131.7, 129.6, 129.2, 128.9, 127.7, 127.4, 127.2, 126.7, 125.8, 125.1, 121.0, 39.5, 33.7, 24.1; HRMS (ESI): Calc. for $C_{20}H_{22}NO_2S$ $(M+H)^+$: 340.1366; found: 340.1352.

N-(4-(2-hydroxyethyl)-2-(naphthalen-1-yl)phenyl)methanesulfonamide (5k): Pale yellow oil: 0.016 mmol, 5.5 mg, 76% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.55 (ddd, *J* = 7.6, 6.5, 5.0 Hz, 2H), 7.45 (d, *J* = 3.7 Hz, 2H), 7.40 – 7.33 (m, 2H), 7.20 (d, *J* = 2.0 Hz, 1H), 6.01 (s, 1H), 3.91 (t, *J* = 6.5 Hz, 2H), 2.91 (t, *J* = 6.5 Hz, 2H), 2.72 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.7, 134.6, 134.1, 133.5, 132.1, 131.9, 131.7, 130.0, 129.4, 129.0, 127.8, 127.3, 126.8, 125.8, 125.0, 120.9, 63.6, 39.6, 38.6; IR υ (cm−1) 3349, 1496, 1329, 1155; HRMS (ESI): Calc. for $C_{19}H_{19}NNaO_3S$ $(M+Na)^+$: 364.0978; found: 364.0968.

4-(methylsulfonamido)-3-(naphthalen-1-yl)phenethyl 2,2,2-trifluoroacetate (5l): Pale yellow oil: 0.038 mmol, 16.5 mg, 79% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.62 – 7.51 (m, 2H), 7.50 – 7.32 (m, 5H), 7.19 (d, *J* = 1.9 Hz, 1H), 4.59 (t, *J* = 6.8 Hz, 2H), 3.09 (t, *J* = 6.8 Hz, 2H), 2.73 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.2, 133.1, 132.1, 131.9, 131.7, 129.9, 129.6, 129.0, 127.7, 127.4, 126.9, 125.8, 124.9, 120.7, 68.2, 39.6, 34.1; HRMS (ESI): Calc. for $C_{21}H_{18}F_3NNaO_4S$ $(M+Na)^+$: 460.0801; found: 460.0795.

N-(2-(naphthalen-1-yl)-4-(2-(phenylsulfonyl)ethyl)phenyl)methanesulfonamide (5m): Pale yellow oil: 0.011 mmol, 5.0 mg, 94% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (t, *J* = 6.8 Hz, 4H), 7.72 – 7.63 (m, 2H), 7.62 – 7.51 (m, 4H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.37 – 7.31 (m, 2H), 7.08 (d, *J* = 1.6 Hz, 1H), 5.98 (s, 1H), 3.44 – 3.36 (m, 2H), 3.15 – 3.06 (m, 2H), 2.71 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.2, 134.4, 134.0, 132.0, 131.6, 131.4, 129.6, 129.6, 129.4, 129.1, 128.3, 127.7, 127.4, 126.9, 125.8, 124.8, 120.8, 57.5, 39.7, 28.2; HRMS (ESI): Calc. for $C_{25}H_{24}NO_4S_2$ $(M+H)^+$: 466.1141; found: 466.1133.

General procedure for the formation of coupling product 23:

A solution of bis(*tert*-butylcarbonyloxy)iodobenzene (0.17 mmol, 1.6 equiv.) in $(CF_3)_2CHOH$ ("HFIP", 0.35 ml) was added dropwise on 30 second to a vigorously stirred solution of sulfamide **22** (0.11 mmol, 1 equiv.) and naphthalene (0.55 mmol, 5.0 equiv.) in HFIP/DCM (2:1; ml) at -4 °C. The mixture was then stirred for 30 seconds and quenched with $NaHCO_3$. The phases were separated and the aqueous phase extracted with EtOAc. The organic phases were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by silica gel chromatography with a mixture of ethyl acetate/hexane to give the corresponding coupling product **23**.

N-(4-methyl-2-(naphthalen-1-yl)phenyl)pyrrolidine-1-sulfonamide (23a): Pale yellow oil: 0.035 mmol, 12.9 mg, 55% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.57 – 7.48 (m, 3H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 3.36 (t, *J* = 6.6 Hz, 4H), 2.28 (s, 3H), 1.72 – 1.65 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.2, 138.2, 135.9, 135.1, 132.0, 129.7, 128.9, 128.4, 128.0, 127.1, 126.4, 125.6, 125.5, 123.8, 49.0, 25.8, 21.0; HRMS (ESI): Calc. for $C_{21}H_{23}N_2O_2S$ $(M+H)^+$: 367.1475; found: 367.1471.

N-(4-ethyl-2-(naphthalen-1-yl)phenyl)pyrrolidine-1-sulfonamide (23b): Pale yellow oil: 0.057 mmol, 21.6 mg, 64% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.3 Hz, 1H), 7.90 (d, *J* = 7.4 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.58 – 7.45 (m, 5H), 7.11 (d, *J* = 8.5 Hz, 2H), 3.36 (t, *J* = 6.6 Hz, 4H), 2.58 (q, *J* = 7.6 Hz, 2H), 1.71 – 1.64 (m, 4H), 1.17 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.2, 140.3, 138.2, 135.1, 132.1, 128.9, 128.5, 128.4, 128.1, 127.1, 126.4, 125.6, 125.5, 123.8, 49.0, 28.4, 25.8, 15.5; IR υ (cm−1) 1595, 1506, 1343, 1156; HRMS (ESI): Calc. for $C_{22}H_{24}N_2NaO_2S$ $(M+Na)^+$: 403.1451; found: 403.1431.

N-(4-isopropyl-2-(naphthalen-1-yl)phenyl)pyrrolidine-1-sulfonamide (23c): Pale yellow oil: 0.031 mmol, 12.4 mg, 54% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.3 Hz, 1H), 7.90 (d, *J* = 7.4 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 2H), 7.59 – 7.45 (m, 5H), 7.13 (d, *J* = 8.5 Hz, 2H), 3.35 (t, *J* = 6.5 Hz, 4H), 2.92 – 2.76 (m, 1H), 1.71 – 1.63 (m, 4H), 1.18 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.8, 140.3, 138.2, 135.1, 132.1, 128.9, 128.4, 128.0, 127.1, 126.4, 125.6, 125.5, 123.8, 49.0, 33.7, 25.8, 24.0. IR υ (cm−1) 1498, 1343, 1156; HRMS (ESI): Calc. for $C_{23}H_{27}N_2O_2S$ $(M+H)^+$: 395.1788; found: 395.1797.

N-(4-chloro-2-(naphthalen-1-yl)phenyl)pyrrolidine-1-sulfonamide (23d): Pale yellow oil: 0.054 mmol, 21.0 mg, 81% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 – 8.21 (m, 1H), 7.92 – 7.79 (m, 4H), 7.58 – 7.48 (m, 3H), 7.48 – 7.40 (m, 3H), 7.23 (d, *J* = 8.9 Hz, 2H), 3.33 (d, *J* = 6.4 Hz, 4H), 1.72 – 1.66 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.5, 137.4, 135.1, 131.9, 131.1, 129.5, 129.4, 129.2, 128.6, 128.7, 127.4, 126.6, 125.8, 125.6, 123.5, 49.0, 25.8. HRMS (ESI): Calc. for $C_{20}H_{19}ClKN_2O_2S$ $(M+K)^+$: 425.0487; found: 425.0466.

N-(2-(naphthalen-1-yl)-4-(trimethylsilyl)phenyl)pyrrolidine-1-sulfonamide (23e): Pale yellow oil: 0.056 mmol, 23.7 mg, 52% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.0 Hz, 1H), 7.90 – 7.82 (m, 3H), 7.52 (q, *J* = 8.0 Hz, 4H), 7.43 (q, *J* = 8.6 Hz, 4H), 3.37 (s, 4H), 1.72 – 1.65 (m, 4H), 0.21 (s, *J* = 3.2 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.3, 137.7, 137.3, 135.1, 134.2, 132.2, 129.1, 128.4, 128.4, 127.2, 126.5, 125.6, 123.8, 123.5, 49.0, 25.8, -1.0; IR υ (cm−1) 1592, 1499, 1347, 1157; HRMS (ESI): Calc. for $C_{46}H_{56}N_4NaO_4S_2Si$ $(2M+Na)^+$: 871.3174; found: 871.3148.

Diethyl 8-(2-(phenylsulfonyl)ethyl)-1,4,4a,9b-tetrahydro-1,4-pidiazanodibenzo[b,d]furan-10,11-dicarboxylate (26) :

To a solution of **12a** (36.7 mg, 0.079 mmol, 1.0 equiv.) in benzene (1.0 ml) was added DEAD (0.094 mmol, 1.2 equiv.). The reaction was heated at 60°C and the reaction was followed by TLC. After completion, the mixture was rapidly purified by silica gel chromatography with a mixture of ethyl acetate/hexane and the residue was treated with LiOH in THF/H_2O (1:1) at 40°C. After 24h, the reaction was quenched with NH_4Cl. The phases were separated and the aqueous phase extracted with EtOAc. The organic phases were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by silica gel chromatography with a mixture of ethyl acetate/hexane to afford **26** in 59 % yield (0.047 mmol, 29.5 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.3 Hz, 2H), 7.72 – 7.64 (m, 1H), 7.63 – 7.50 (m, 3H), 6.91 (d, *J* = 7.7 Hz, 1H), 6.62 (s, 1H), 6.55 (d, *J* = 8.2 Hz, 1H), 6.35 (s, 1H), 5.20 – 5.00 (m, 2H), 4.89 (s, 1H), 4.34 – 4.10 (m, 4H), 3.39 – 3.29 (m, 2H), 3.07 – 2.96 (m, 2H), 1.35 – 1.22 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.2, 157.2, 139.2, 133.9, 129.8, 129.5, 128.2, 125.4, 109.8, 80.7, 63.4, 63.2, 58.0, 54.4, 51.0, 28.4, 14.6, 14.5; HRMS (ESI): Calc. for $C_{26}H_{27}IN_2O_7S$ $(M+H)^+$: 638.0578; found: 638.0568.

10-methyl-7-(methylsulfonyl)-6,6a,7,11b-tetrahydro-5H-benzo[c]carbazole (27) :

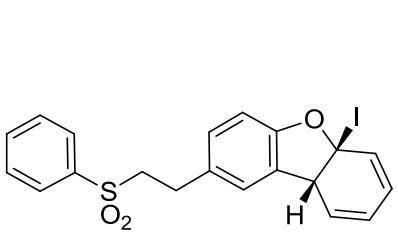
To a solution of **17a** (23.2 mg, 0.075 mmol, 1.0 equiv.) in MeOH (2.0 mL) was added Pd/C (0.0038mmol, 0.05 equiv.). The mixture was stirred at room temperature and the reaction was followed by Mass Spectroscopy. After completion the mixture was filtered through Celite and concentrated under vacuum. The residue was purified by silica gel chromatography with a mixture of ethyl acetate/hexane to afford **28** in 66% yield (0.049 mmol, 15.4 mg).^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.3 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.21 (td, *J* = 7.4, 1.3 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.90 (s, 1H), 4.81 – 4.71 (m, 2H), 2.93 (d, *J* = 7.0 Hz, 3H), 2.69 (t, *J* = 6.0 Hz, 2H), 2.38 – 2.26 (m, 1H), 2.23 (s, 3H), 2.03 – 1.89 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 138.2, 135.0, 134.6, 134.4, 129.3, 129.0, 128.8, 127.0, 126.7, 125.9, 115.2, 63.1, 44.9, 36.4, 29.8, 26.2, 21.1. HRMS (ESI): Calc. for $C_{18}H_{20}NO_2S$ $(M+H)^+$: 314.1209; found: 314.1211.

10-methyl-7-(methylsulfonyl)-6,6a,7,11b-tetrahydro-5H-benzo[c]carbazole-5,6-diol (28) :

To a solution of **17a** (18.7 mg, 0.060 mmol, 1.0 equiv.) in THF (1.5 mL) was added OsO_4 (0.012 mmol, 0.2 equiv.) and NMO (0.120 mmol, 2.0 equiv.). The mixture was stirred at room temperature and the reaction was followed by TLC. After completion, $Na_2S_2O_3$ was

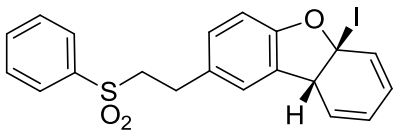
added, followed by Celite and EtOAc. The mixture was stirred during 30 minutes, filtered through Celite and concentrated under vacuum. The residue was purified by silica gel chromatography with a mixture of ethyl acetate/hexane to afford **28** in 60% yield (0.036 mmol, 12.5 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, *J* = 4.0 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.99 (s, 1H), 4.85 (t, *J* = 9.9 Hz, 1H), 4.81 – 4.74 (m, 2H), 4.01 (dd, *J* = 7.4, 2.8 Hz, 1H), 2.97 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.6, 135.5, 135.0, 134.2, 133.1, 130.0, 129.4, 129.2, 129.0, 127.9, 125.3, 117.2, 70.9, 69.5, 65.3, 44.7, 37.0, 21.2. HRMS (ESI): Calc. for $C_{18}H_{20}NO_4S$ $(M+H)^+$: 346.1108; found: 346.1102.

III. Copies of ^{1}H and ^{13}C NMR spectra



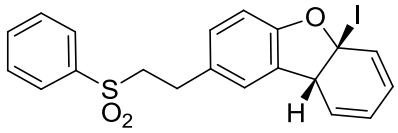
11a-g

$CDCl_3$, 300 MHz



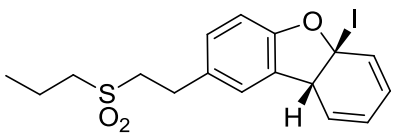
11a-g

$CDCl_3$, 300 MHz



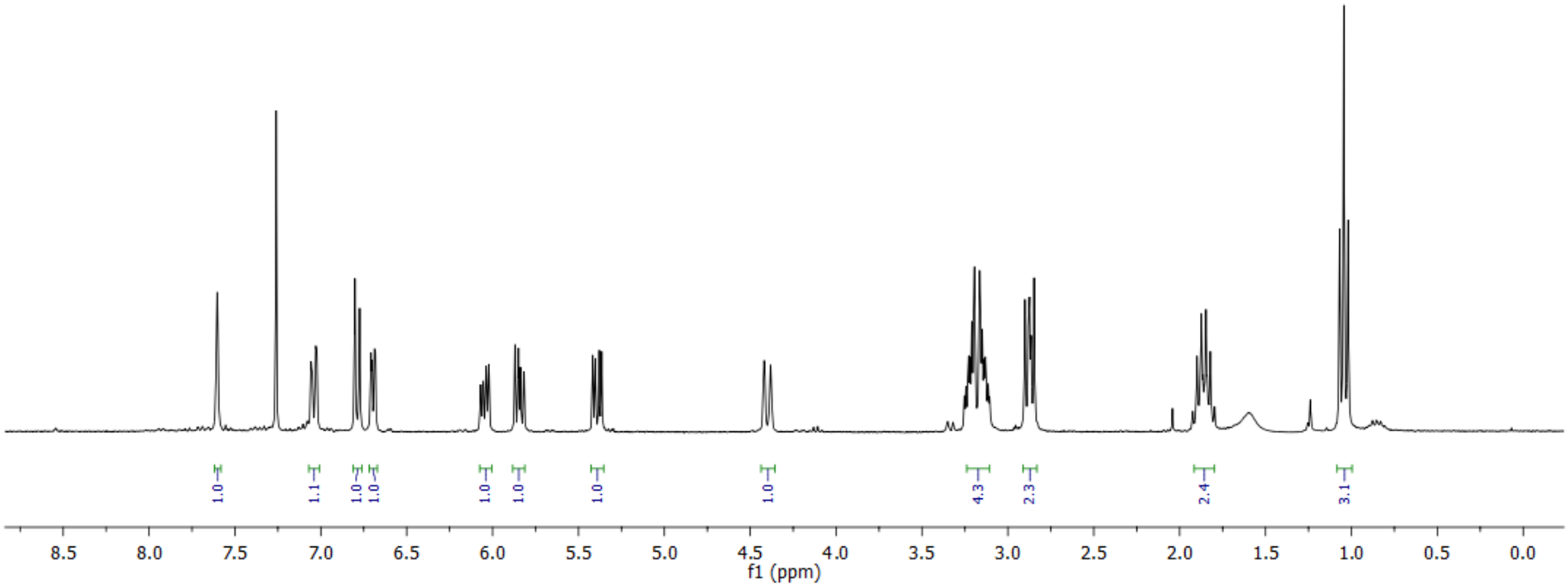
11a-g

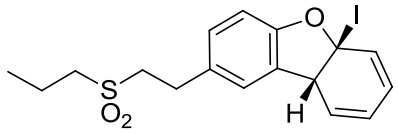
$CDCl_3$, 75 MHz



11h

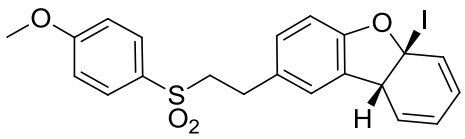
$CDCl_3$, 300 MHz





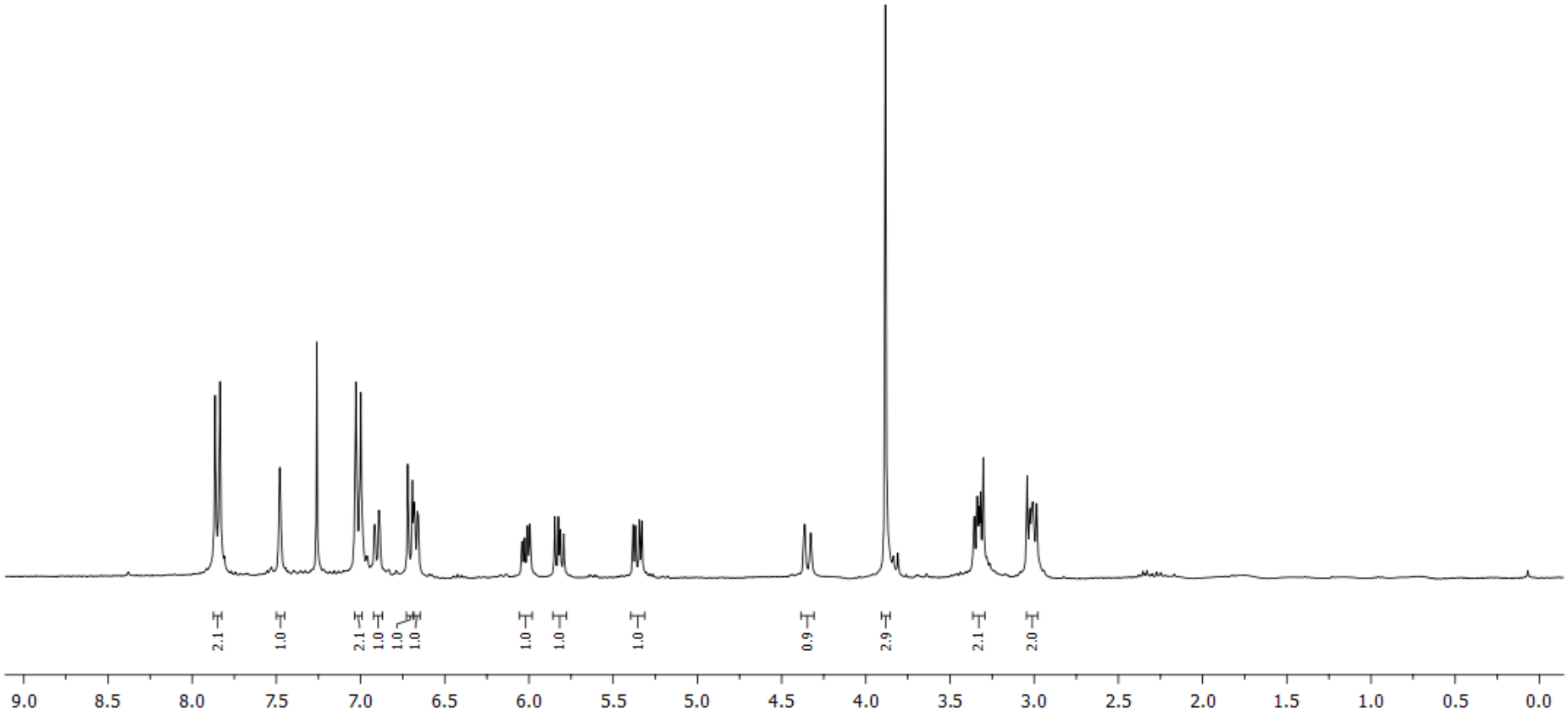
11h

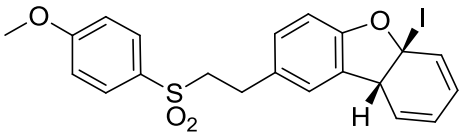
$CDCl_3$, 75 MHz



11i

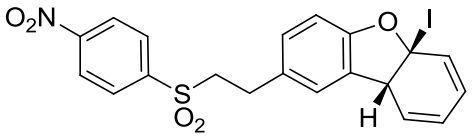
$CDCl_3$, 300 MHz





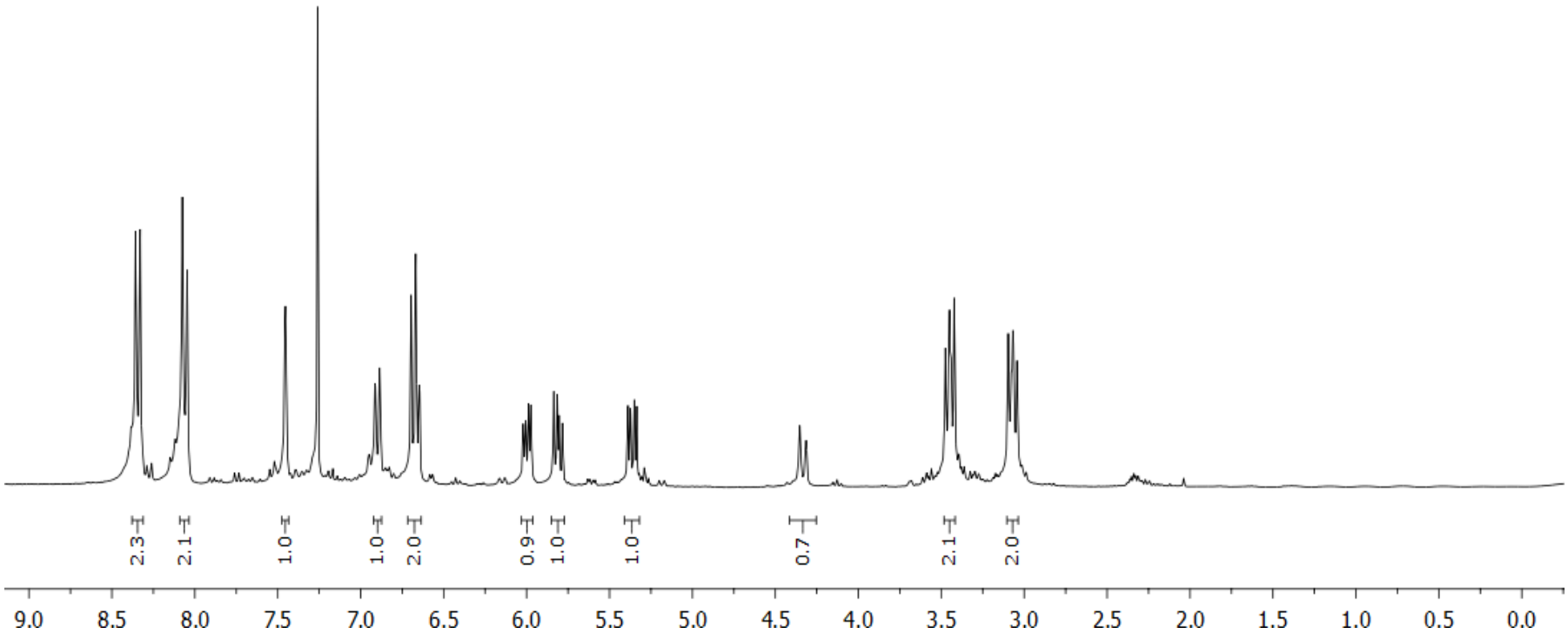
11i

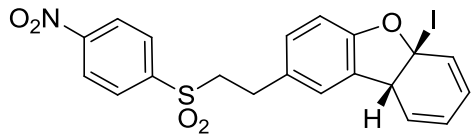
$CDCl_3$, 75 MHz



11j

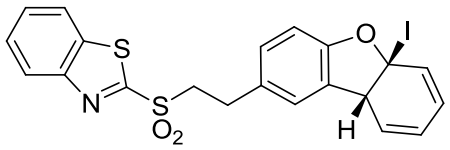
$CDCl_3$, 300 MHz





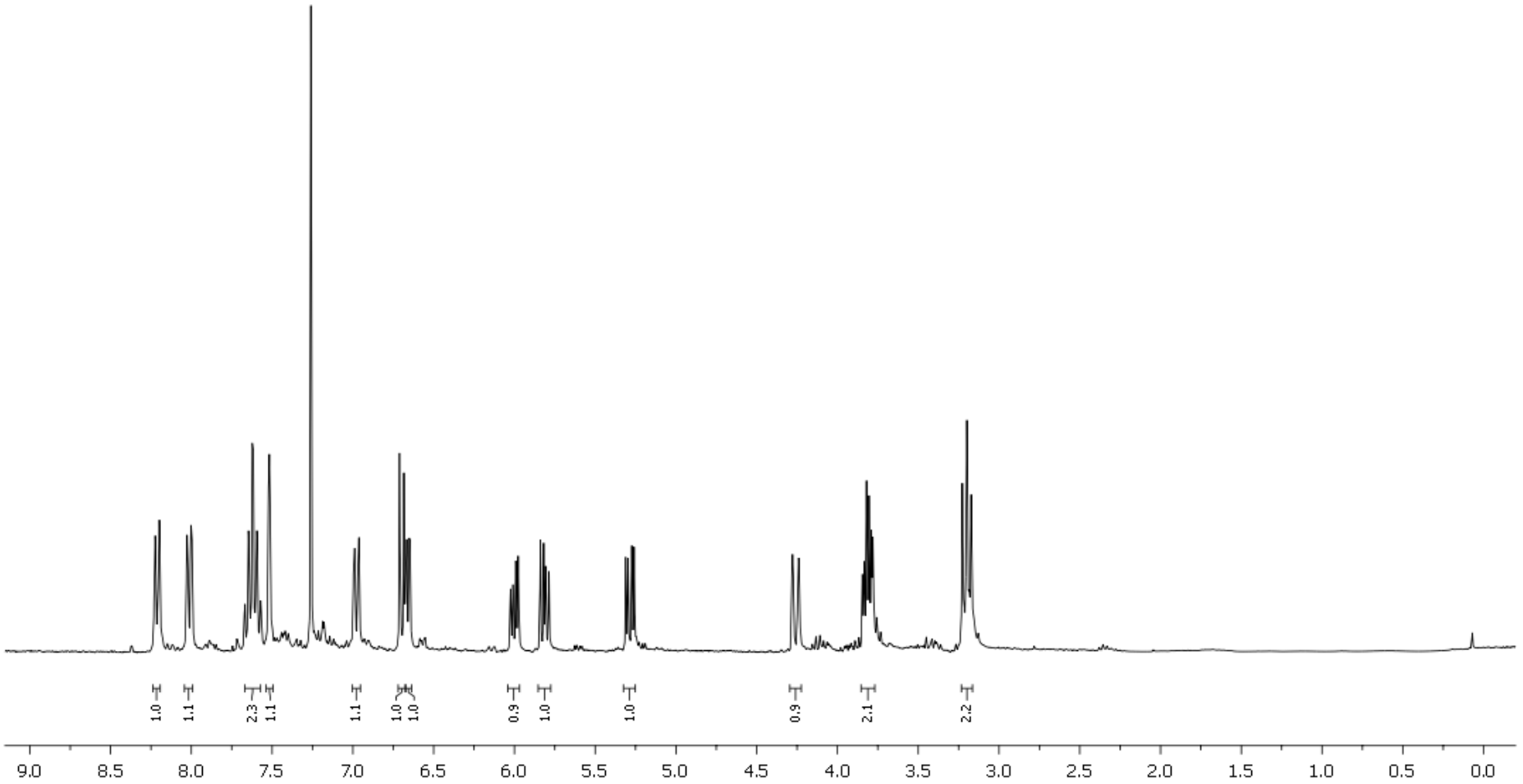
11j

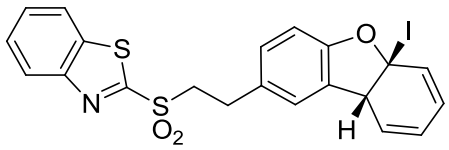
$CDCl_3$, 75 MHz



11k

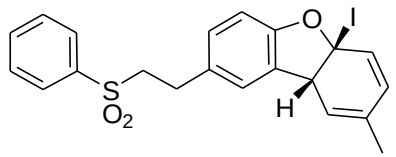
$CDCl_3$, 300 MHz





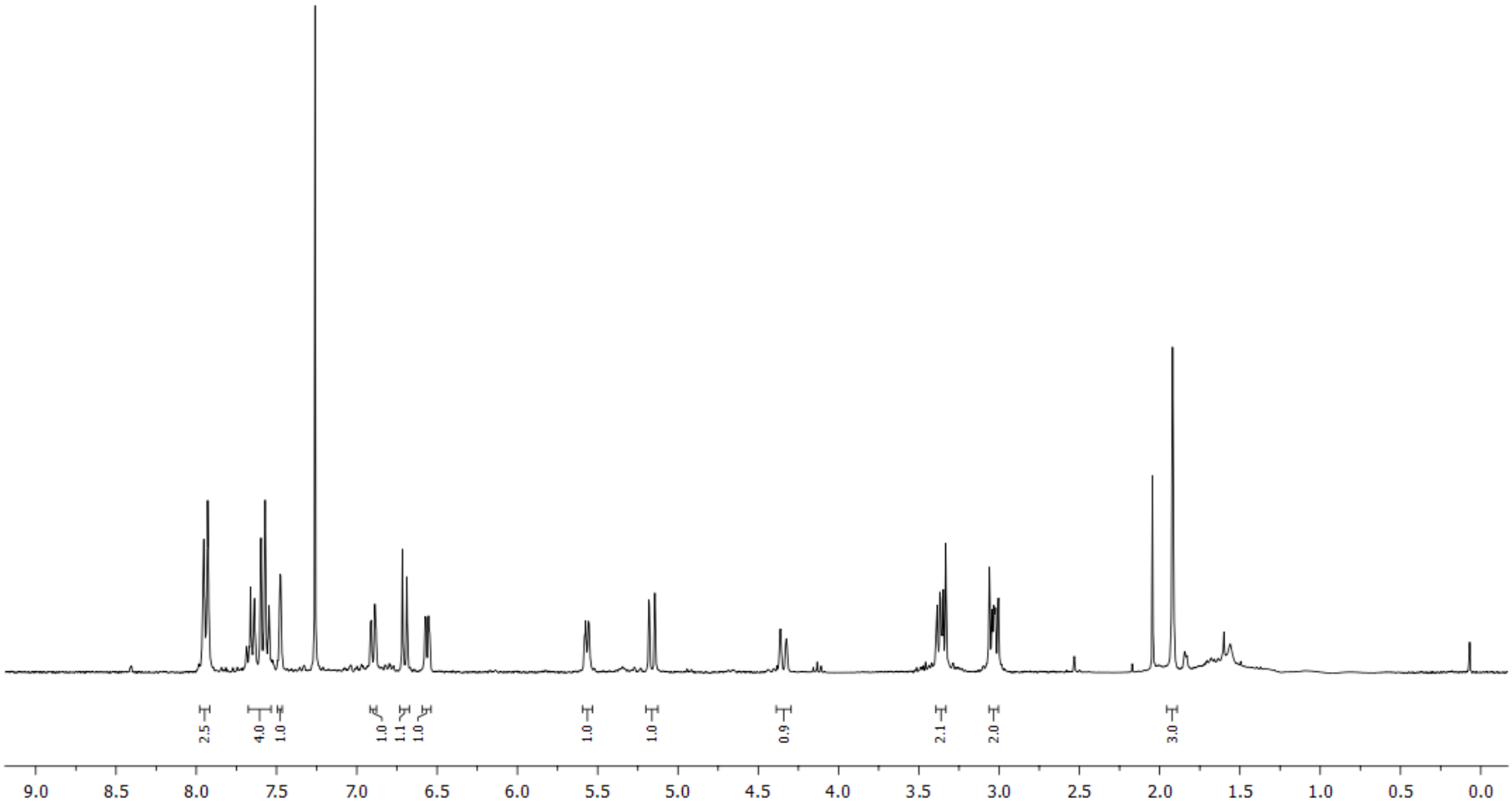
11k

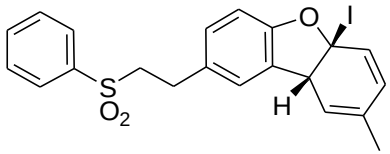
$CDCl_3$, 75 MHz



12b

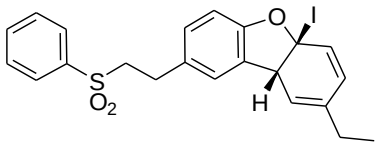
$CDCl_3$, 300 MHz





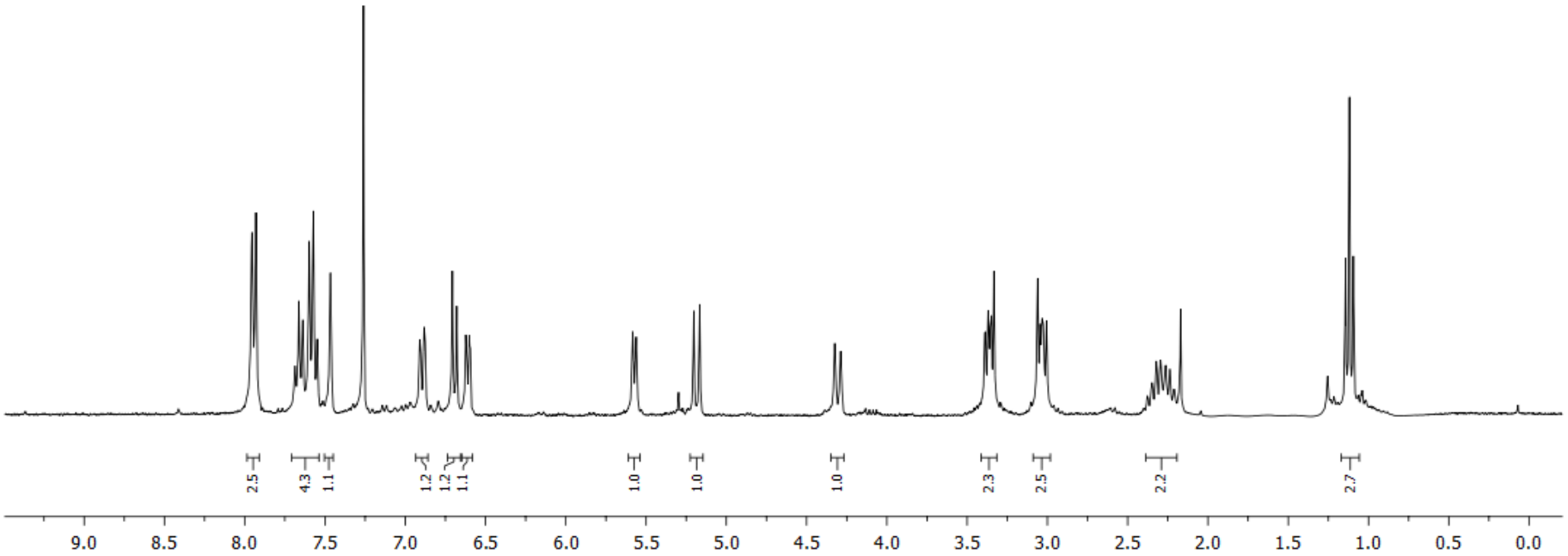
12b

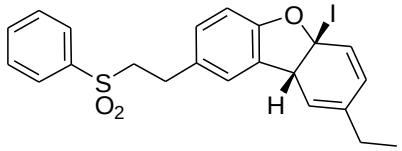
$CDCl_3$, 75 MHz



12c

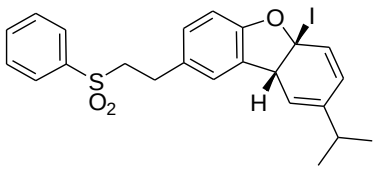
$CDCl_3$, 300 MHz





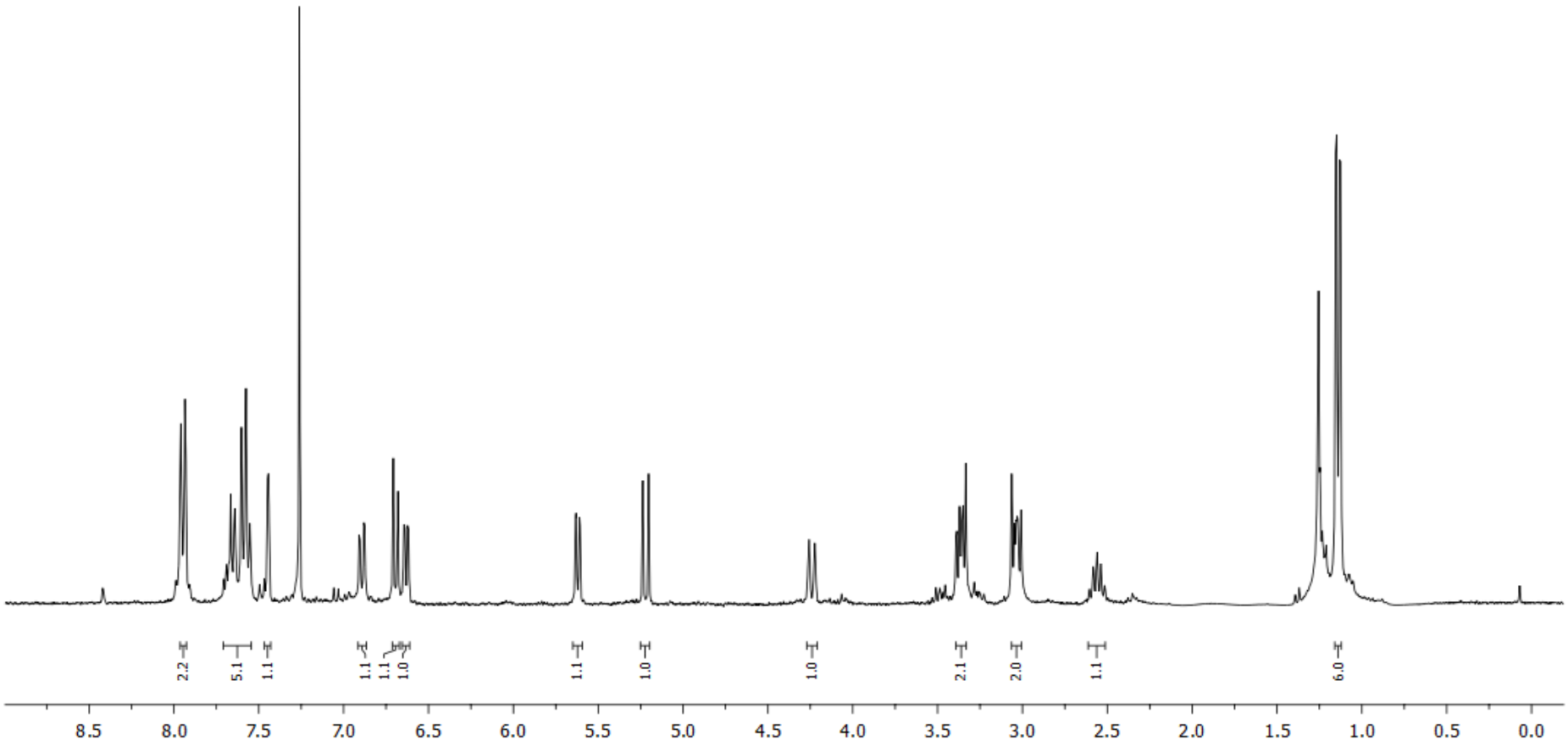
12c

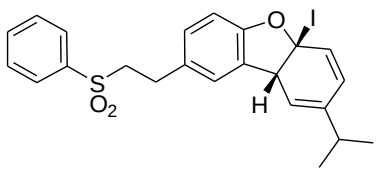
$CDCl_3$, 75 MHz



12d

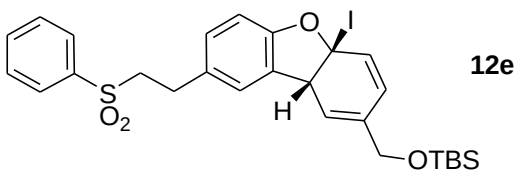
$CDCl_3$, 300 MHz





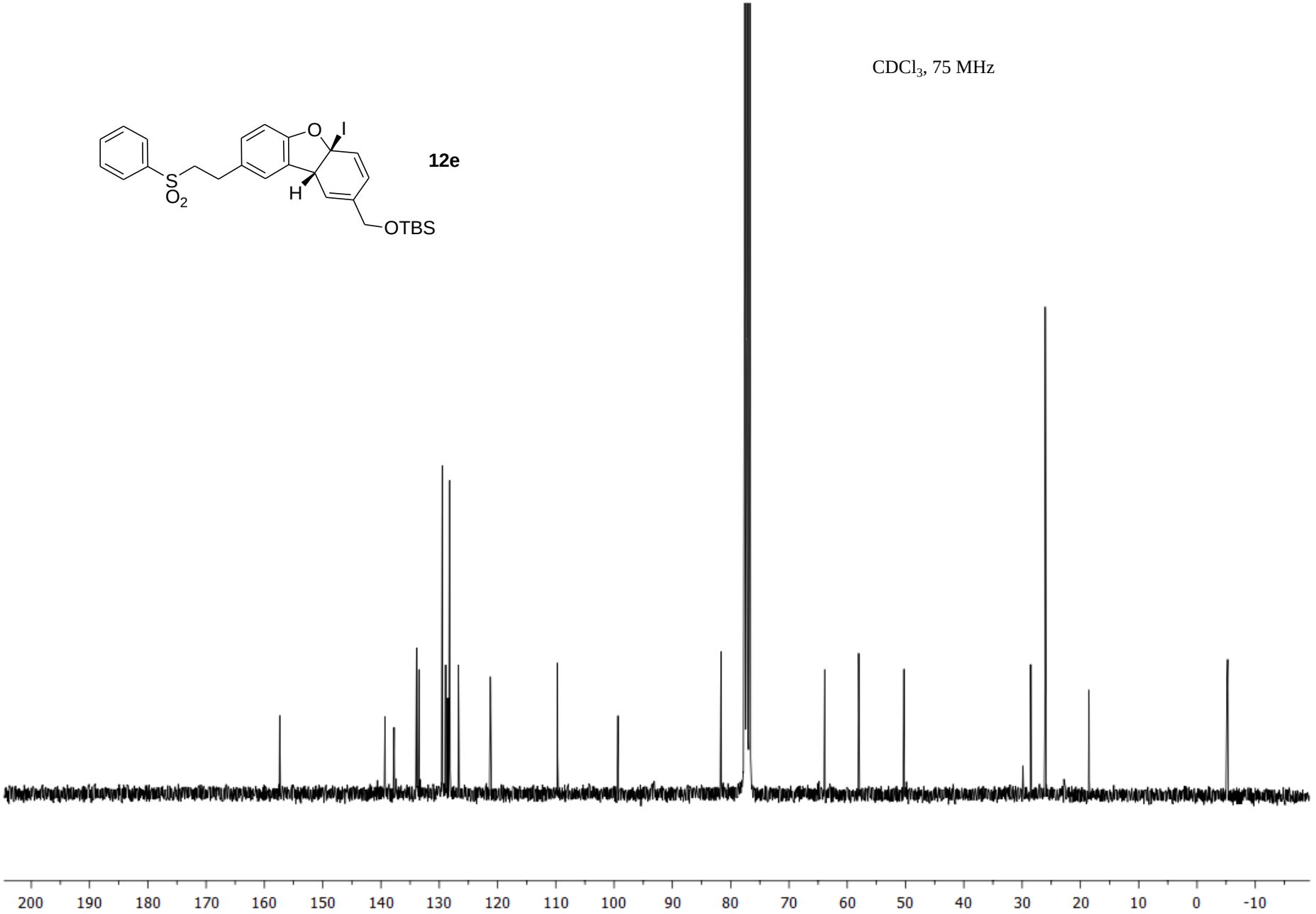
12d

$CDCl_3$, 75 MHz

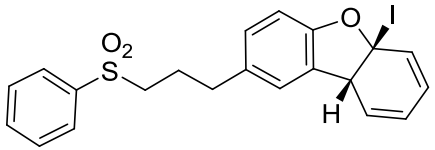


12e

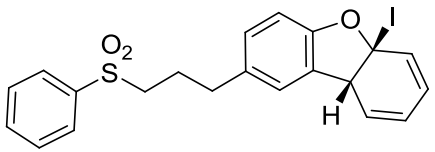
$CDCl_3$, 300 MHz



$CDCl_3$, 300 MHz



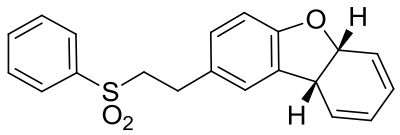
12f



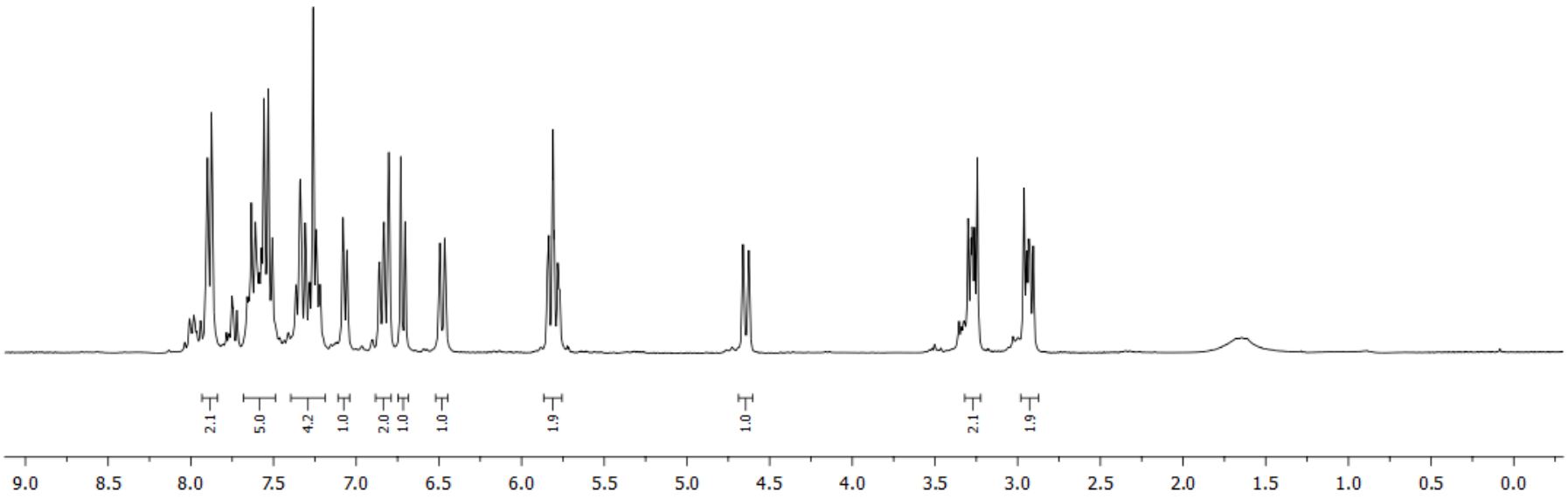
12f

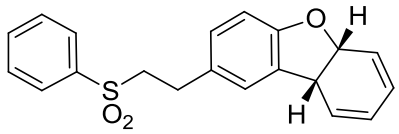
$CDCl_3$, 75 MHz

$CDCl_3$, 300 MHz



12g

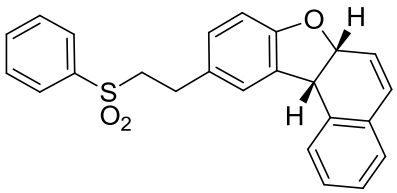




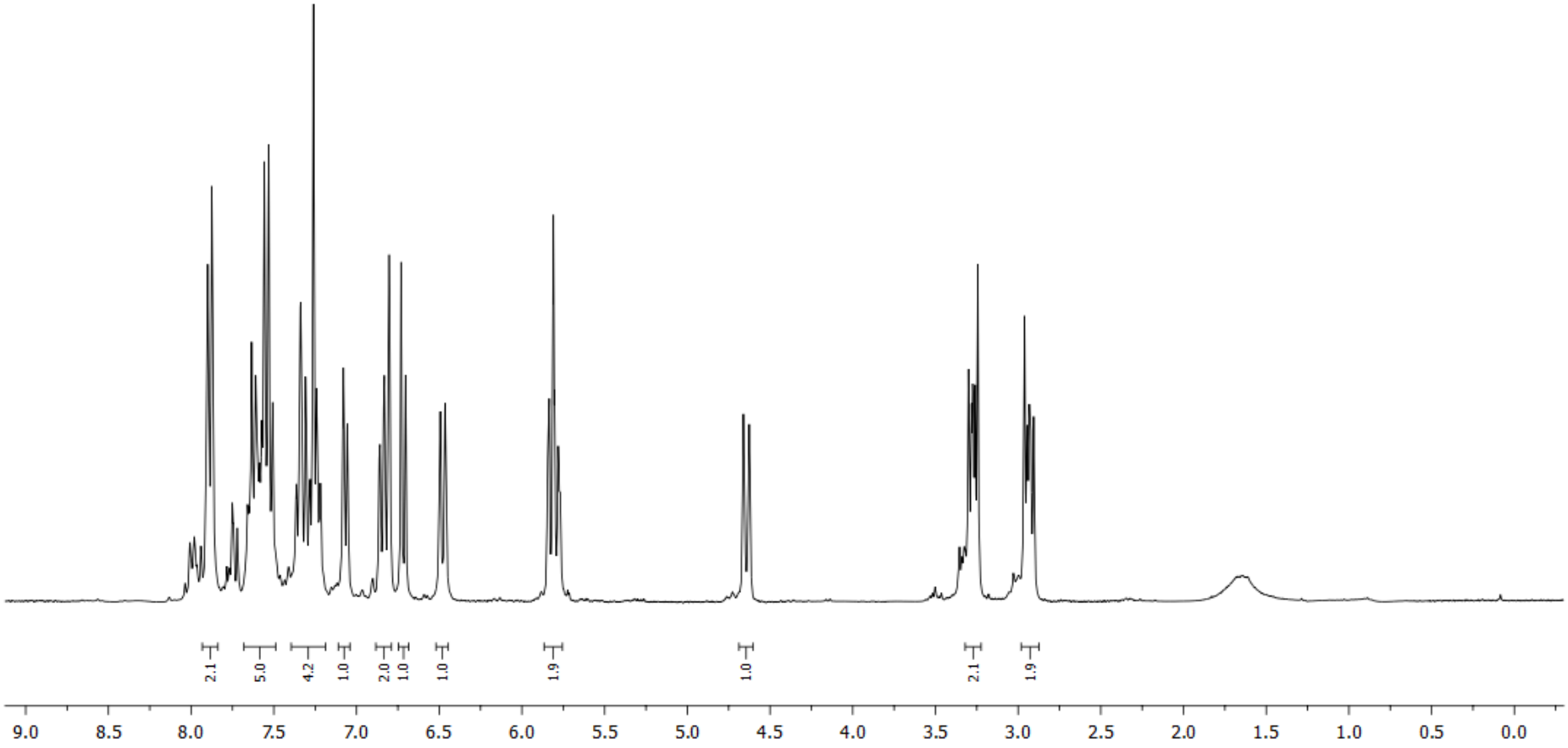
12g

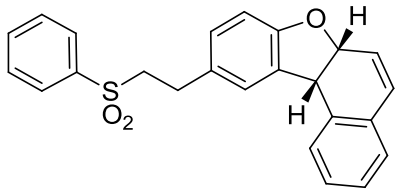
$CDCl_3$, 75 MHz

$CDCl_3$, 300 MHz



12h

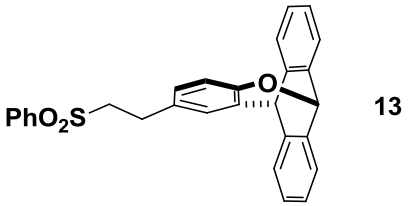




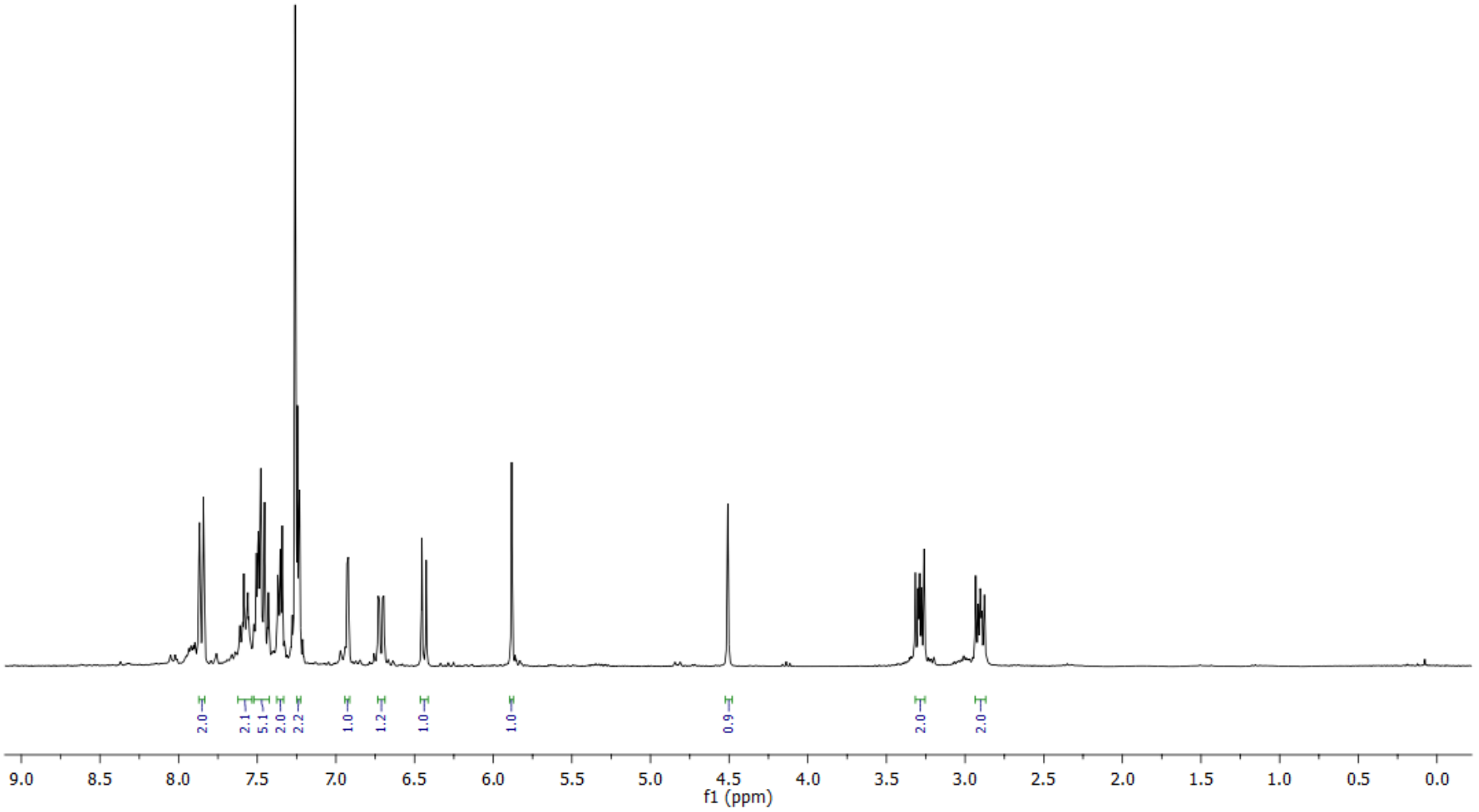
12h

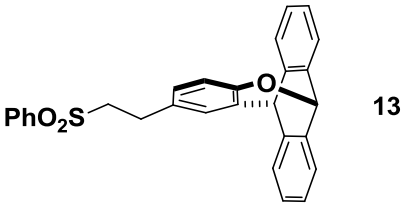
$CDCl_3$, 75 MHz

$CDCl_3$, 300 MHz



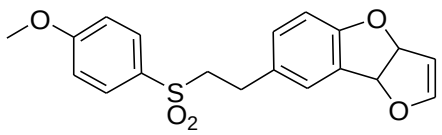
13





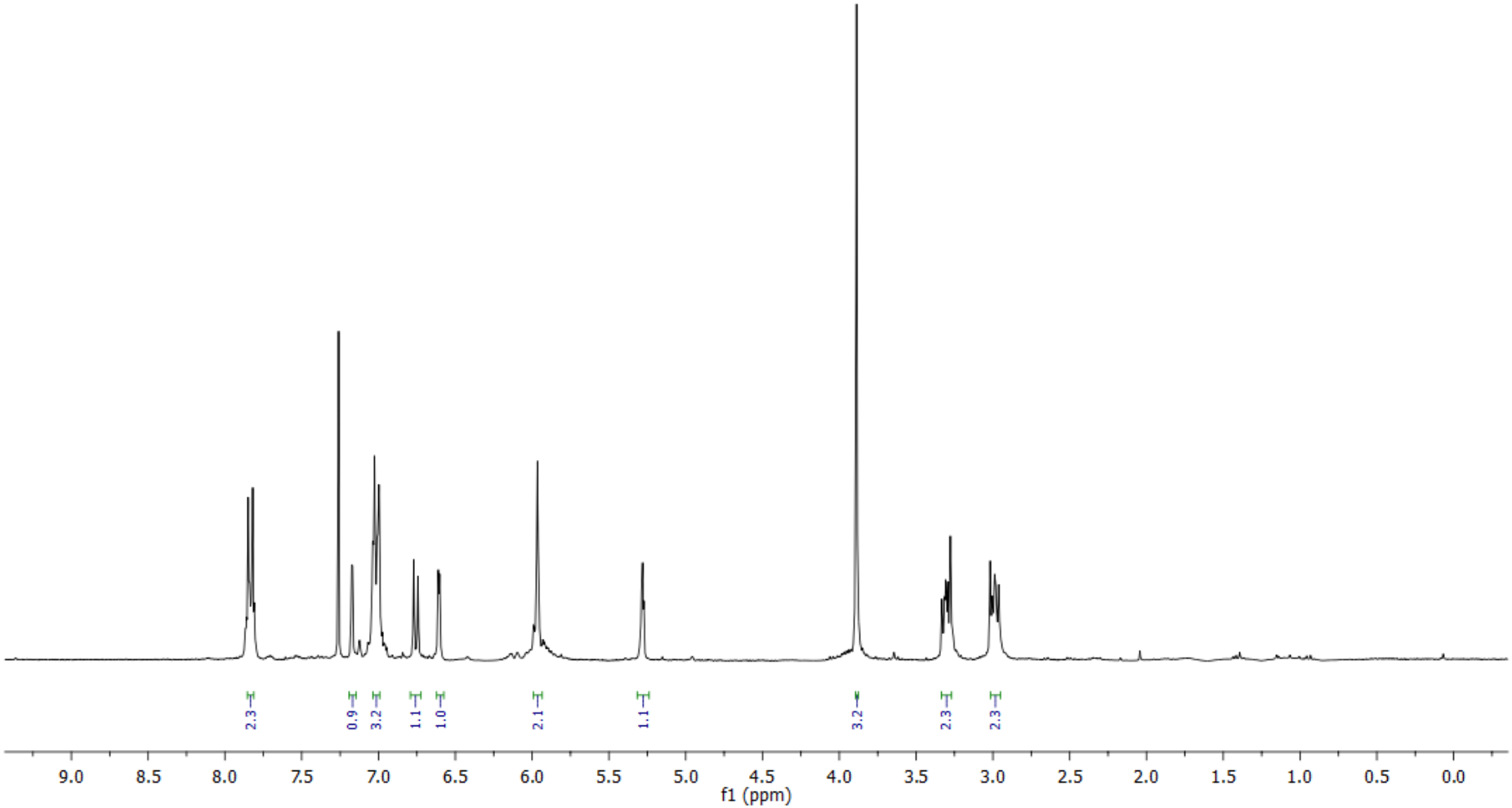
13

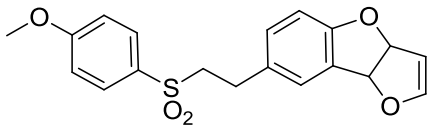
$CDCl_3$, 75 MHz



14

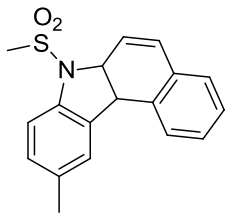
$CDCl_3$, 300 MHz





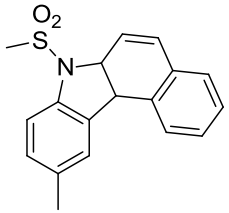
14

$CDCl_3$, 75 MHz



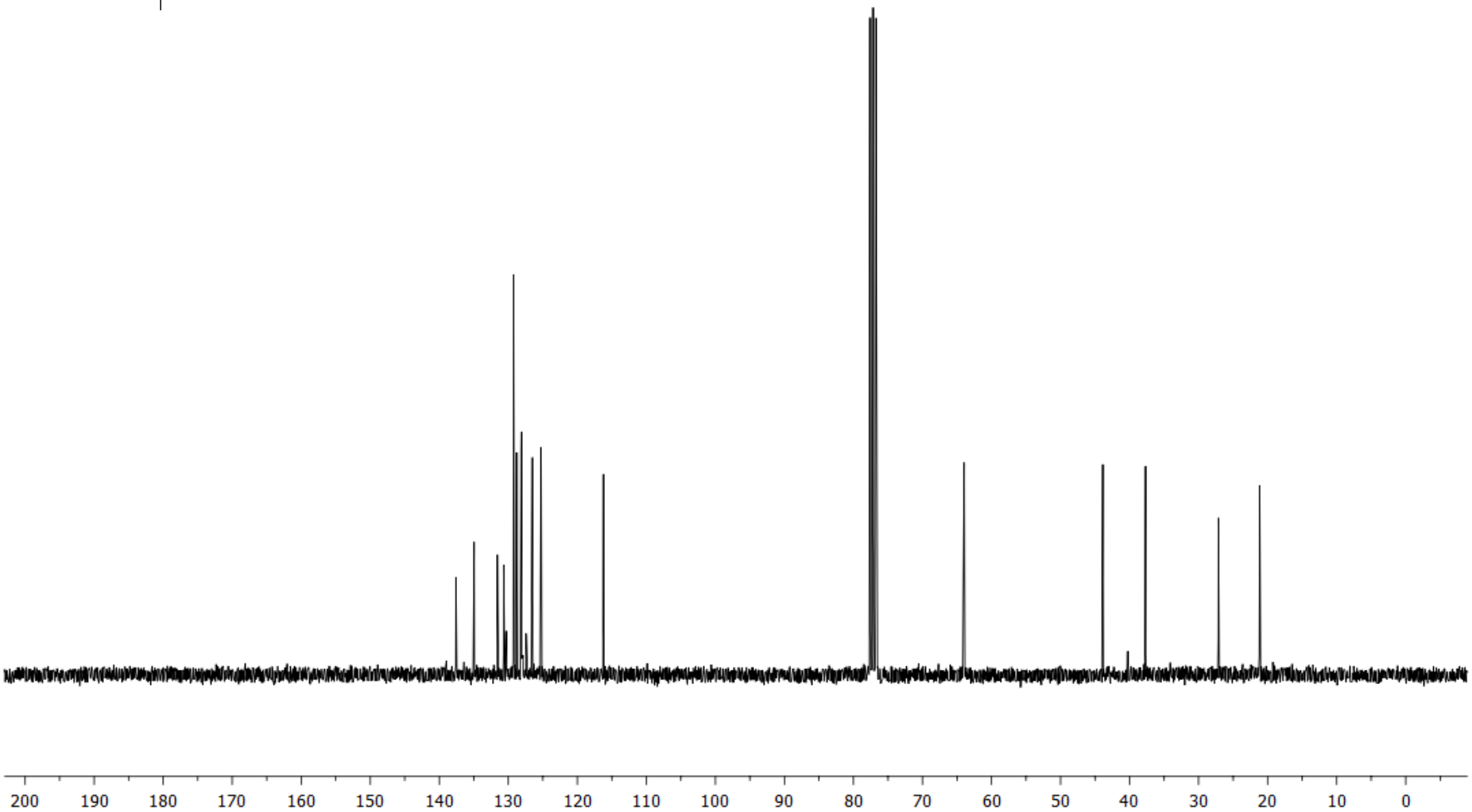
17a

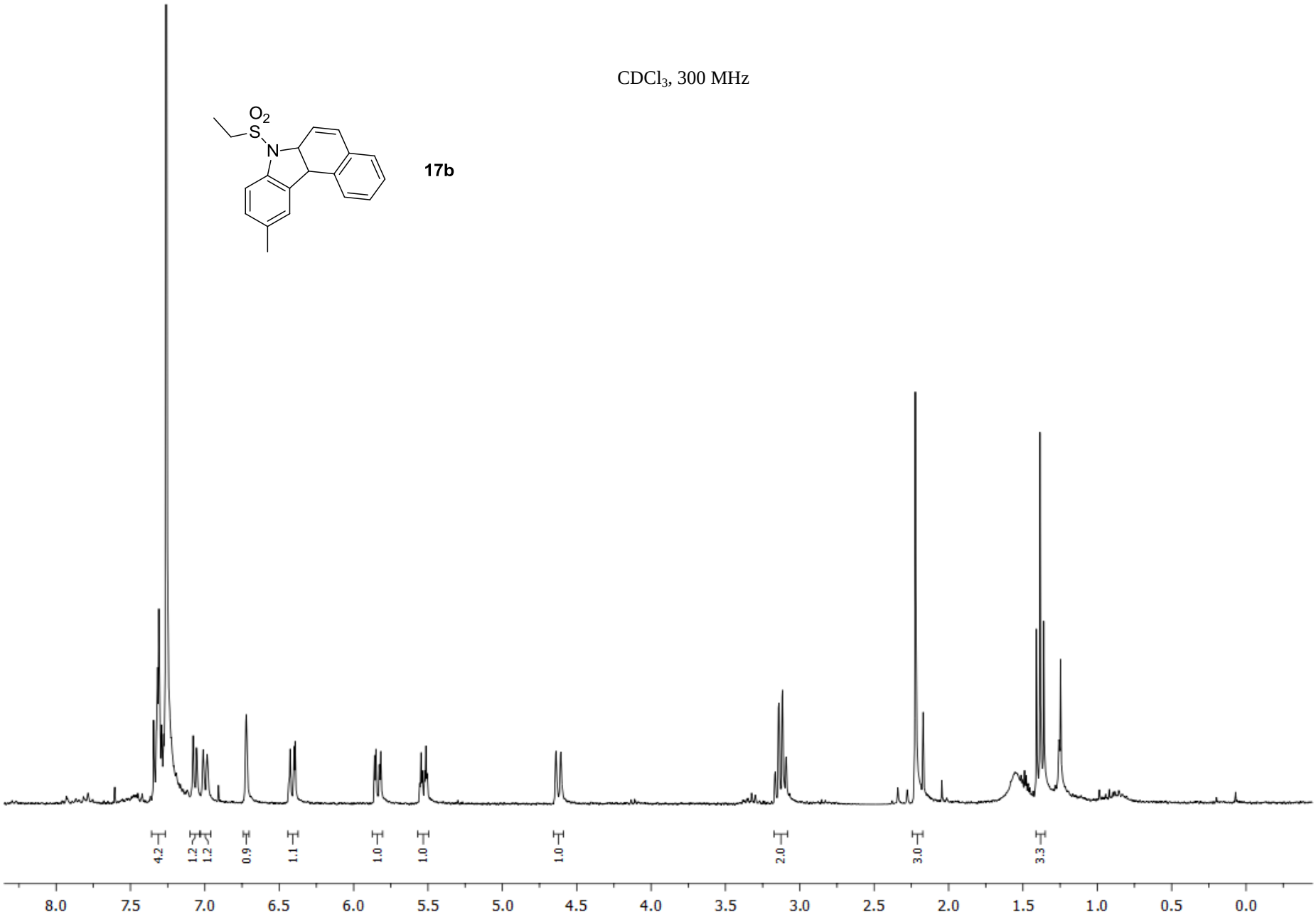
$CDCl_3$, 300 MHz

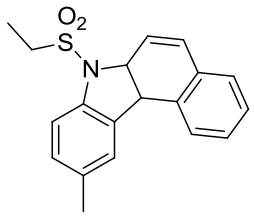


17a

$CDCl_3$, 75 MHz

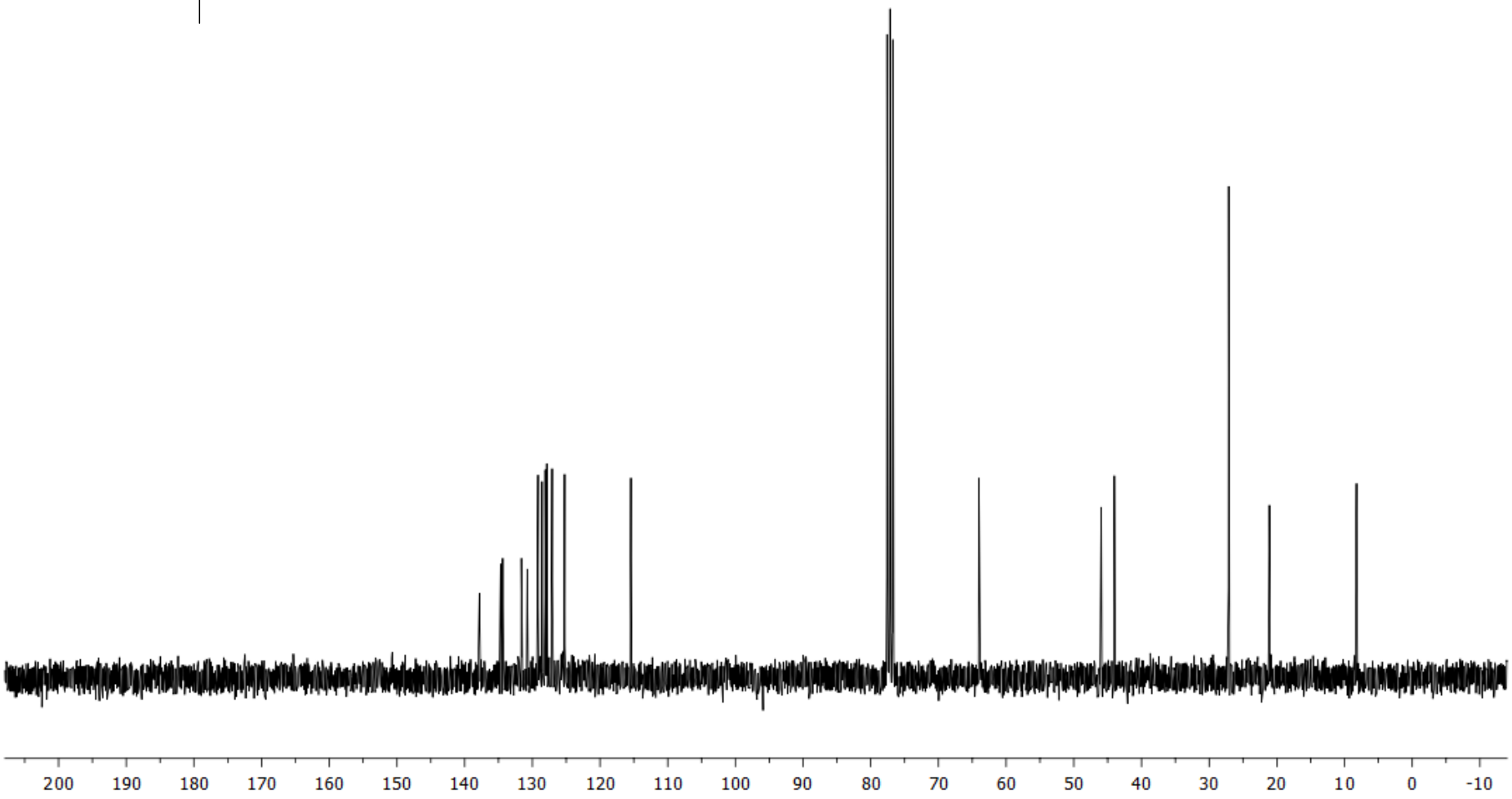


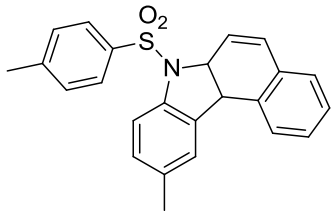




17b

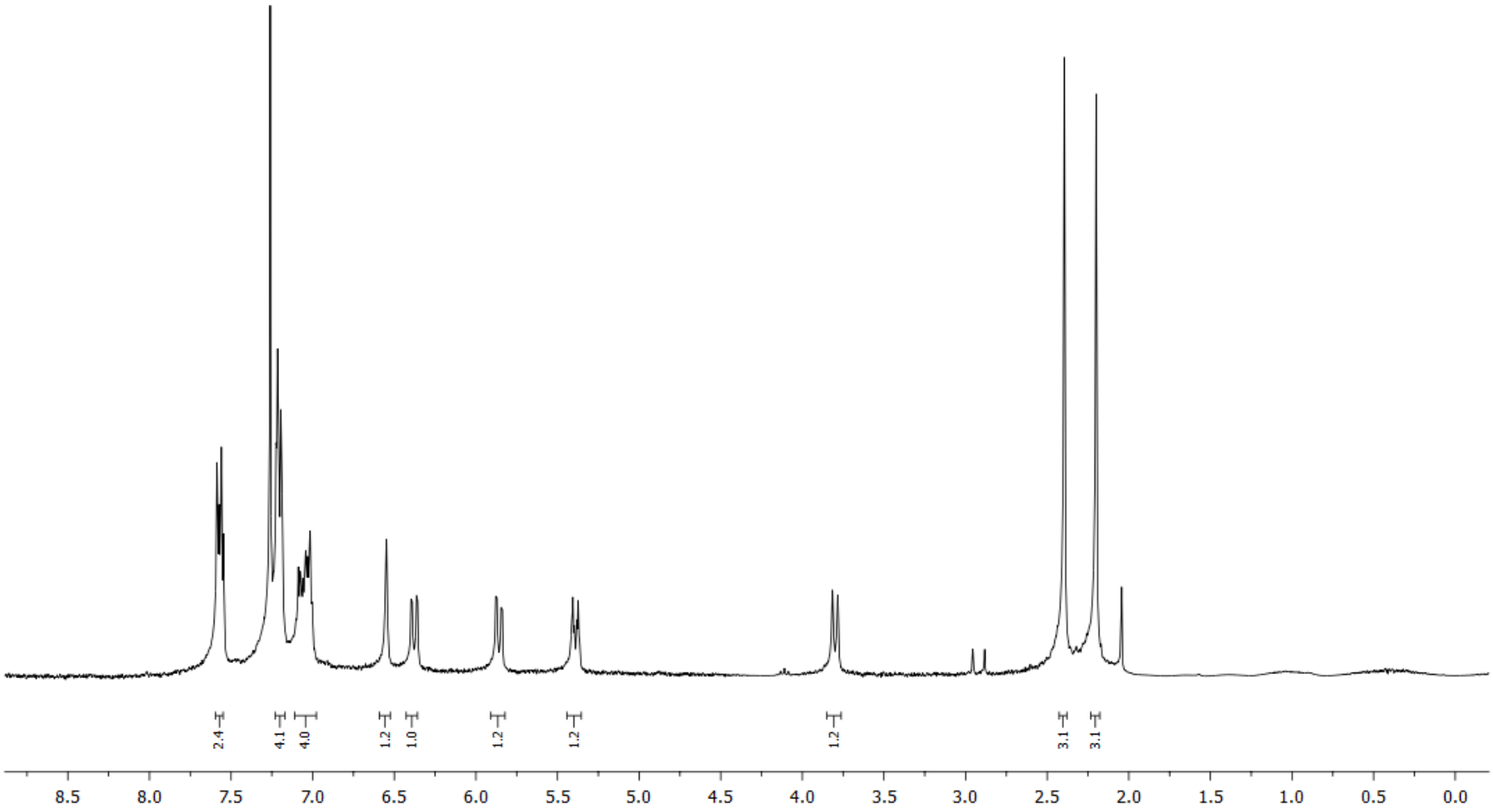
$CDCl_3$, 75 MHz

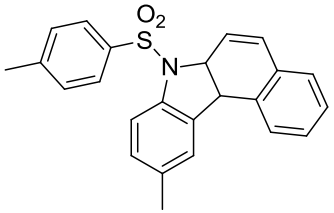




17c

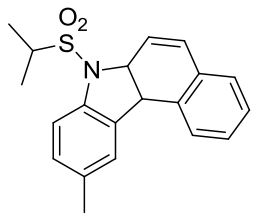
$CDCl_3$, 300 MHz





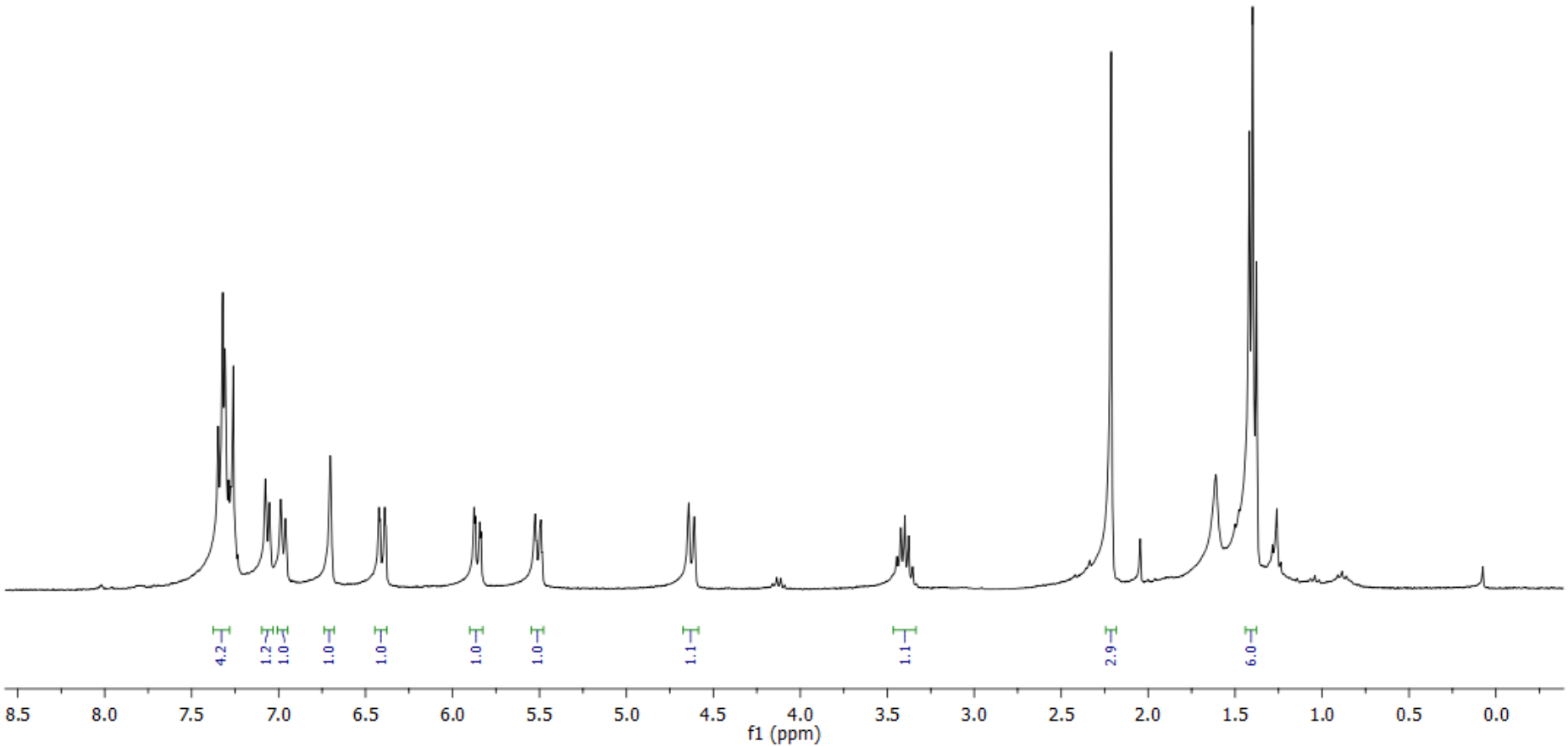
17c

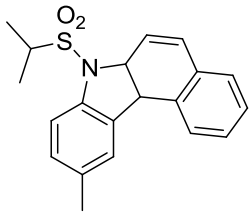
$CDCl_3$, 75 MHz



17d

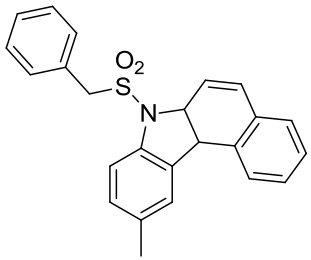
$CDCl_3$, 300 MHz





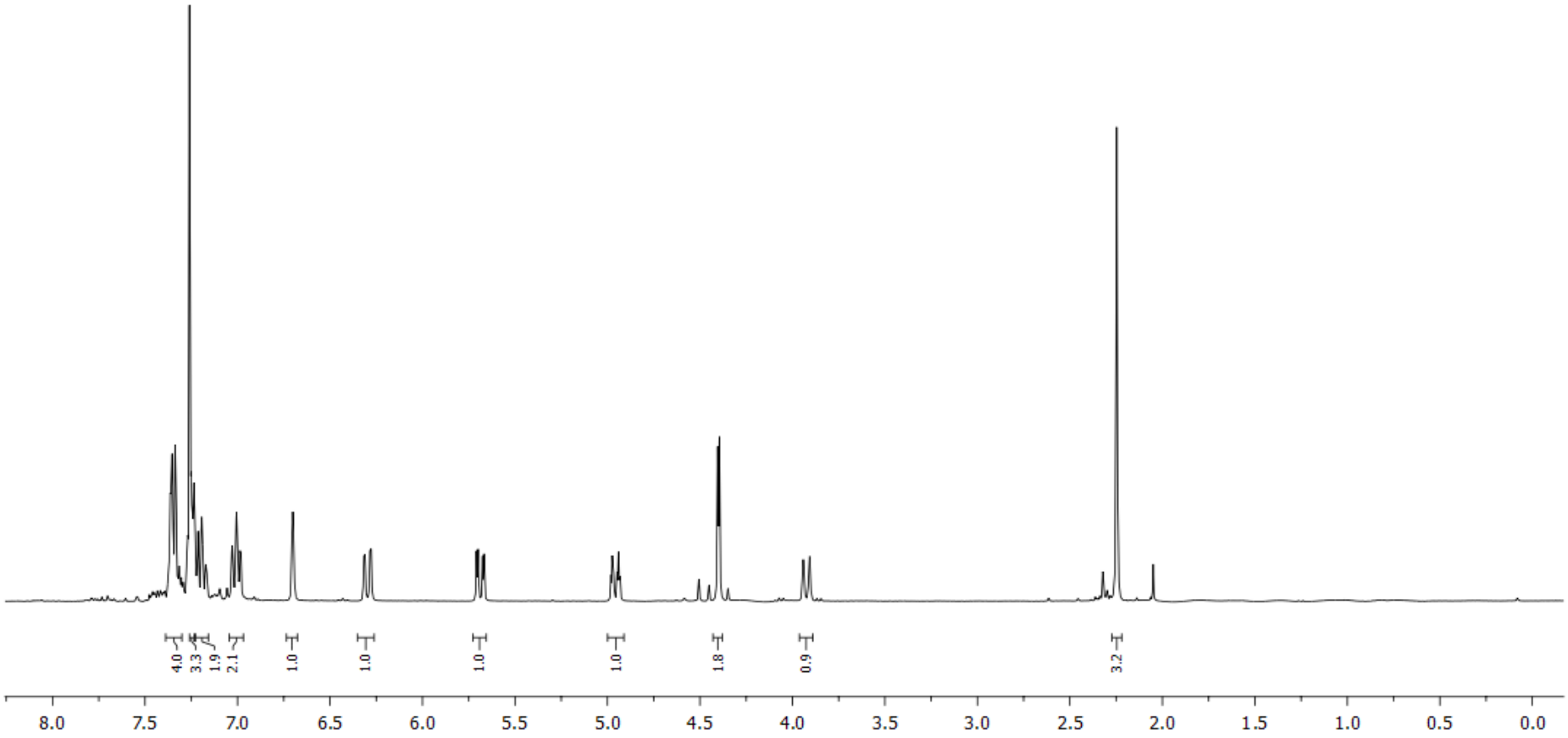
17d

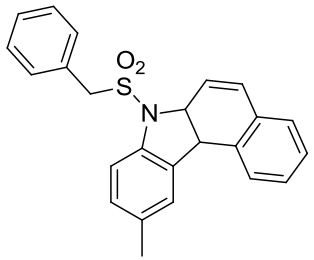
$CDCl_3$, 75 MHz



17e

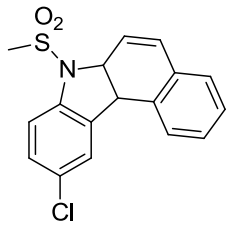
$CDCl_3$, 300 MHz





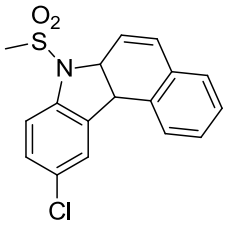
17e

$CDCl_3$, 75 MHz



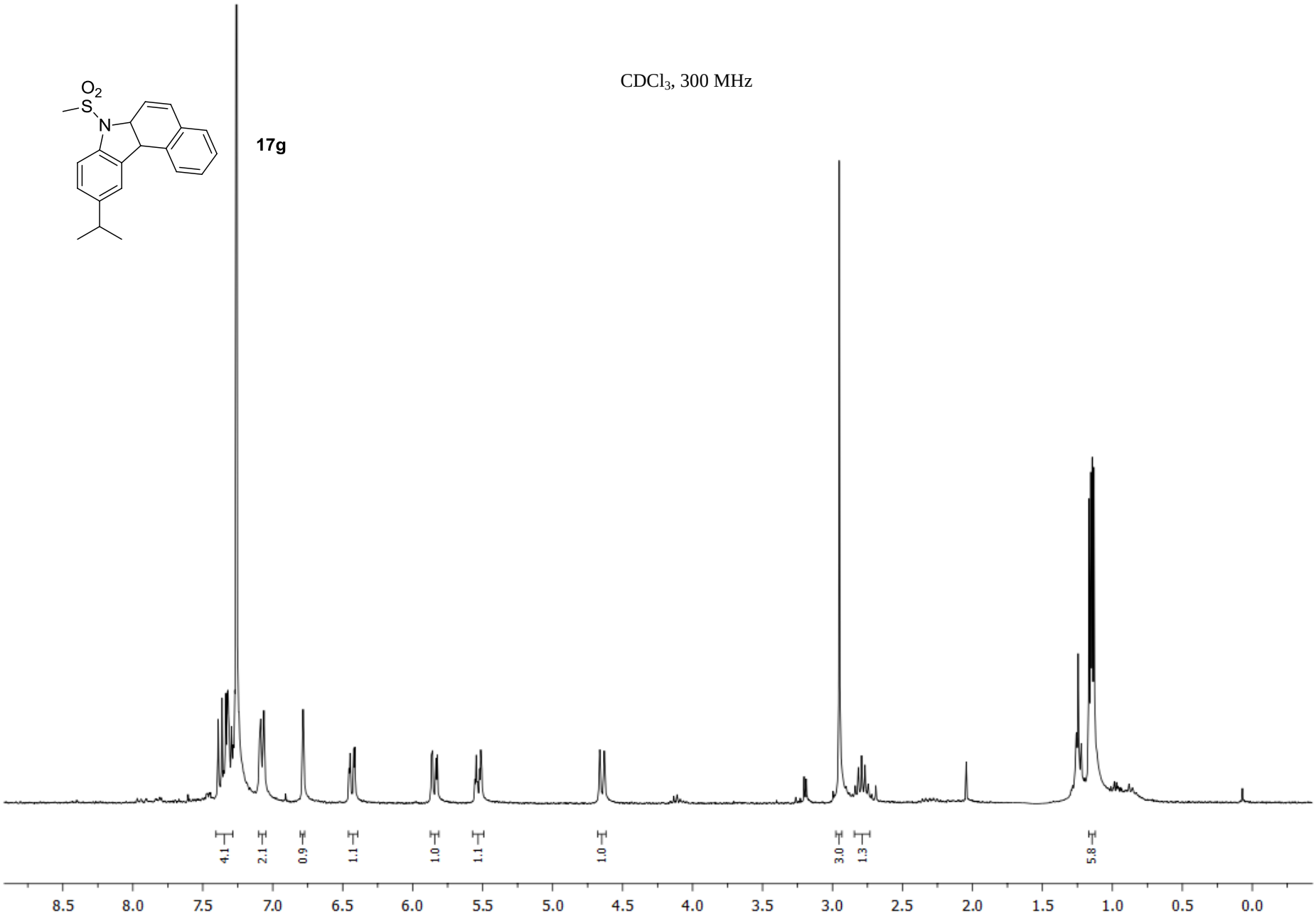
17f

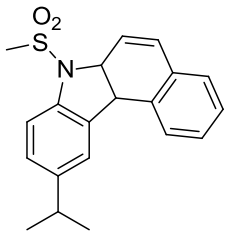
$CDCl_3$, 300 MHz



17f

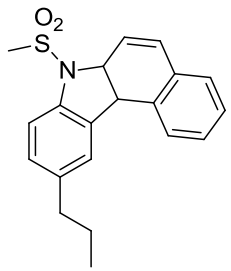
$CDCl_3$, 75 MHz





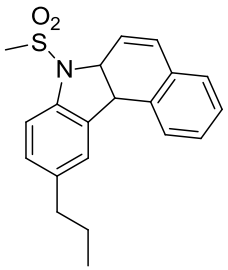
17g

$CDCl_3$, 75 MHz



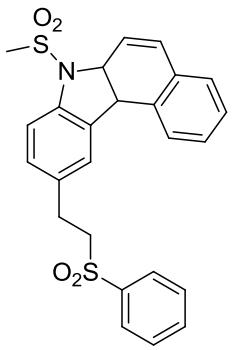
17h

$CDCl_3$, 300 MHz



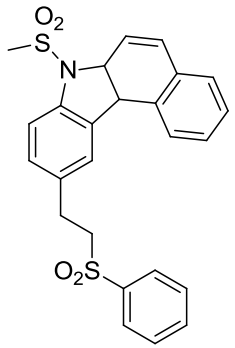
17h

$CDCl_3$, 75 MHz



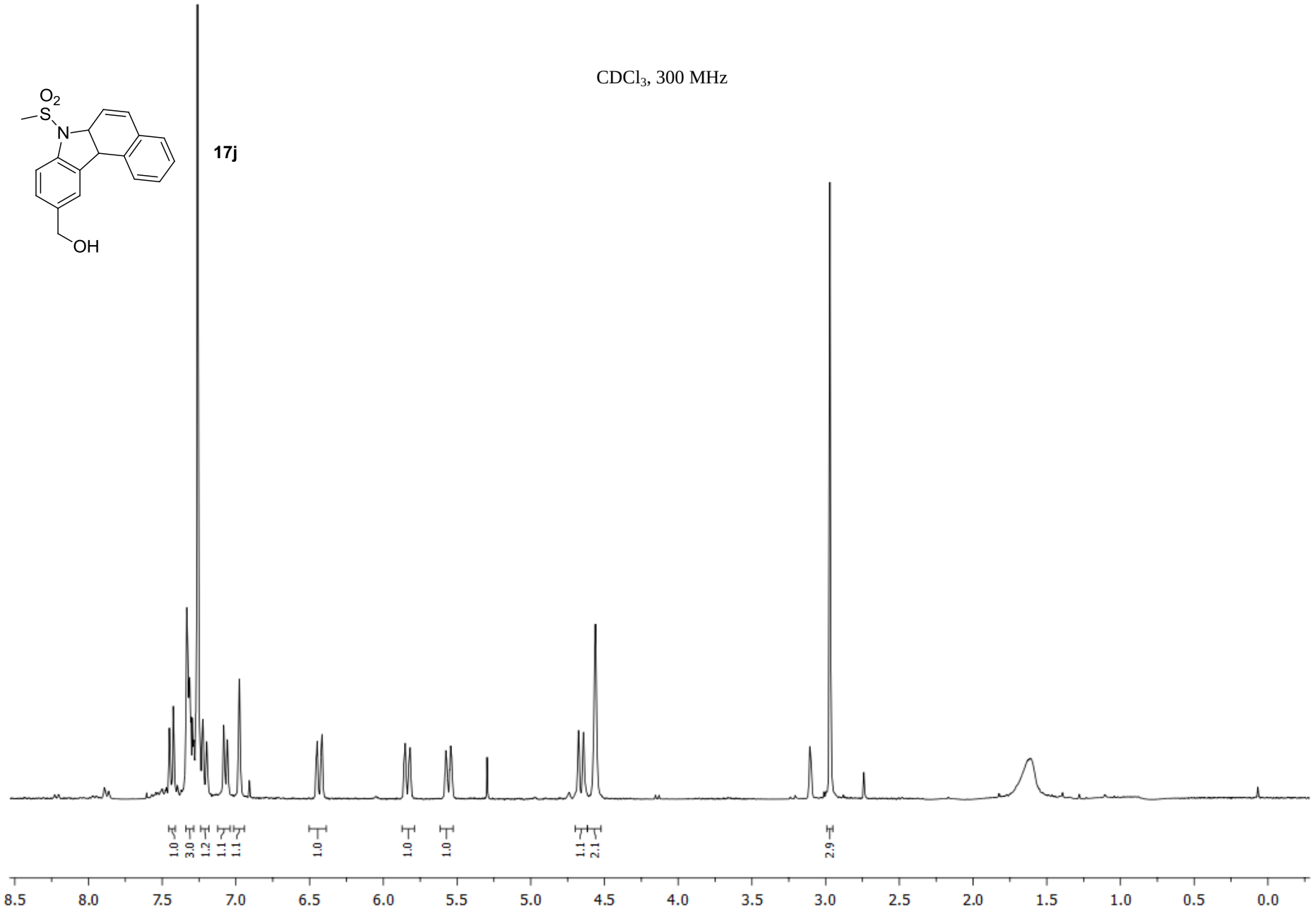
17i

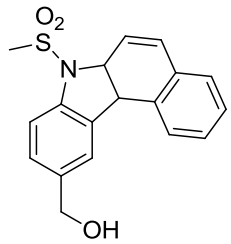
$CDCl_3$, 300 MHz



17i

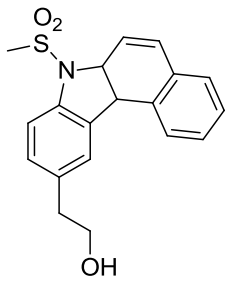
$CDCl_3$, 75 MHz





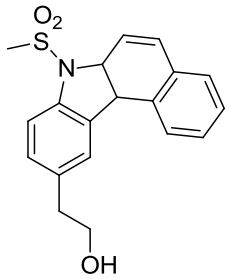
17j

$CDCl_3$, 75 MHz



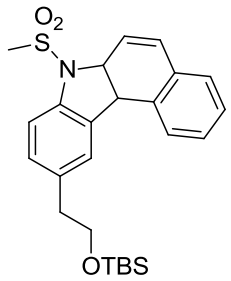
17k

$CDCl_3$, 300 MHz



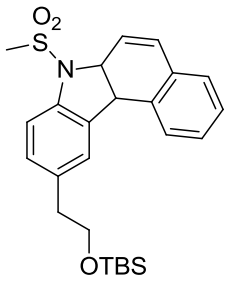
17k

$CDCl_3$, 75 MHz



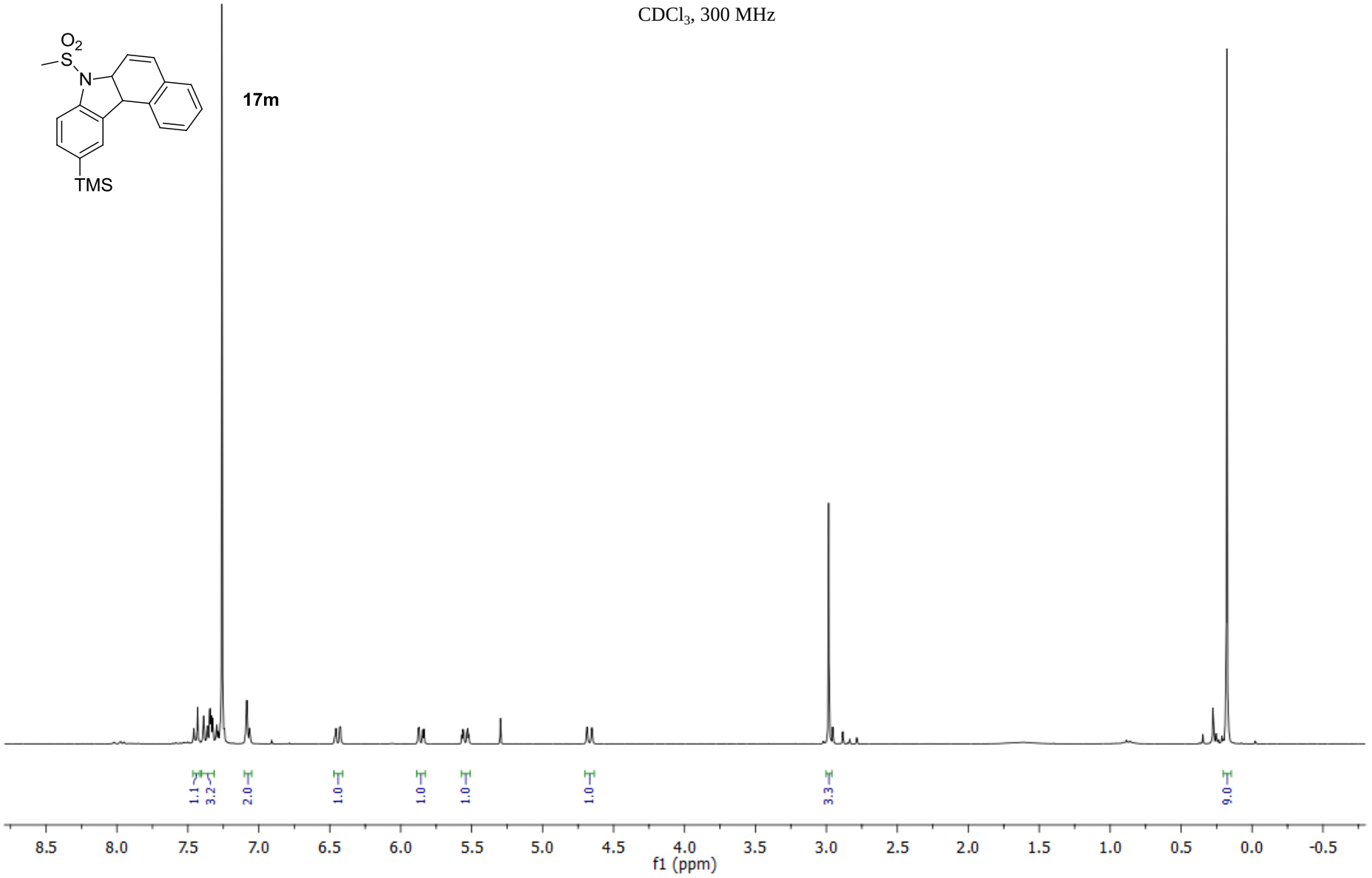
17l

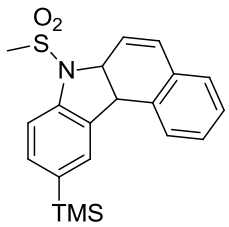
$CDCl_3$, 300 MHz



17l

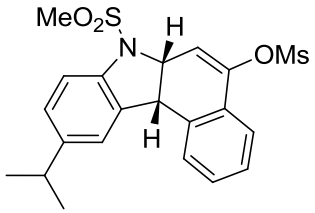
$CDCl_3$, 75 MHz





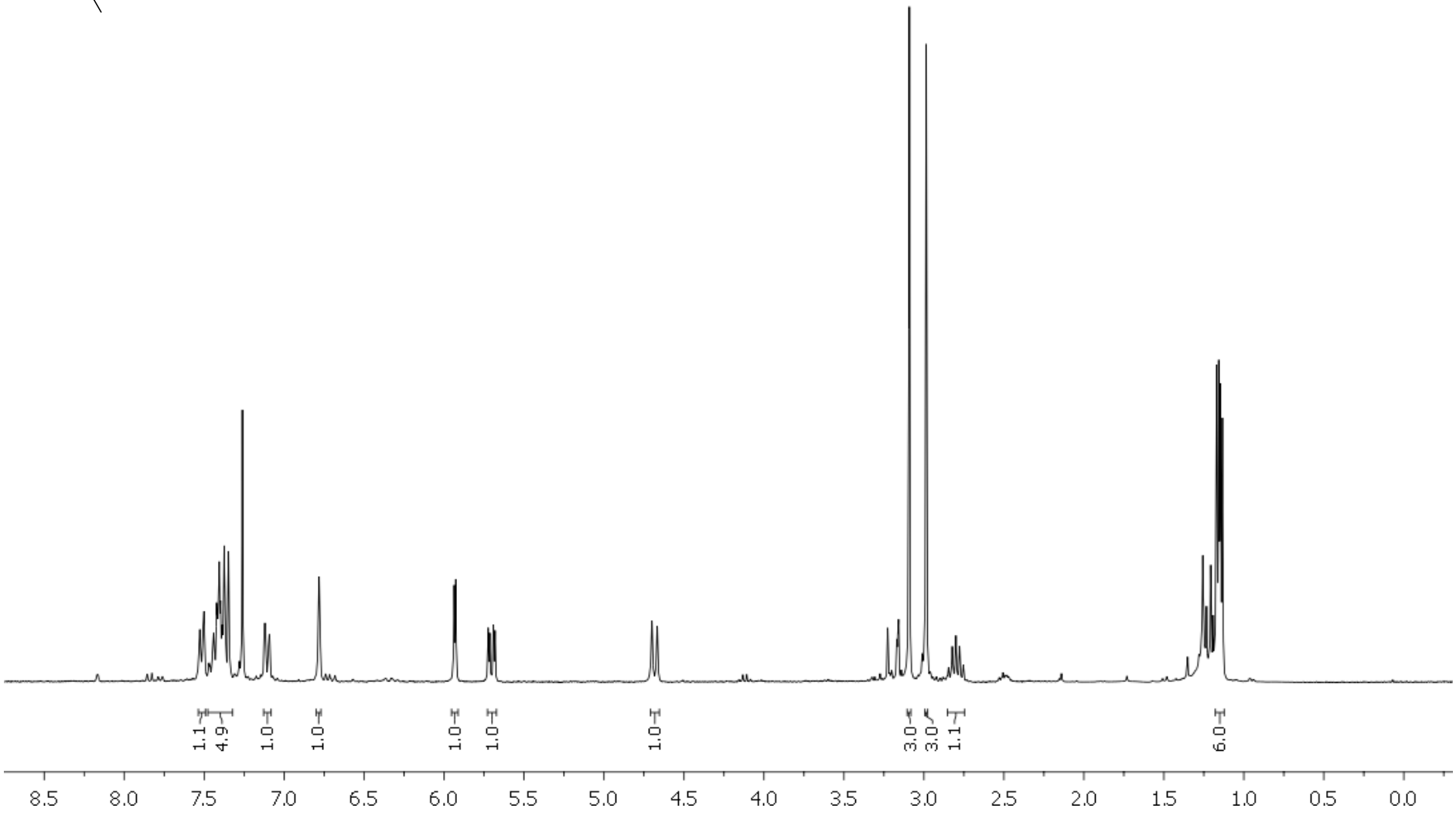
17m

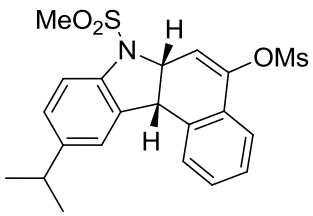
$CDCl_3$, 75 MHz



18

$CDCl_3$, 300 MHz

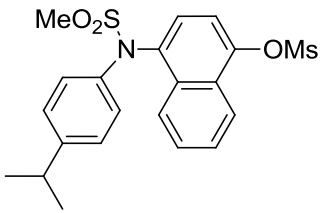




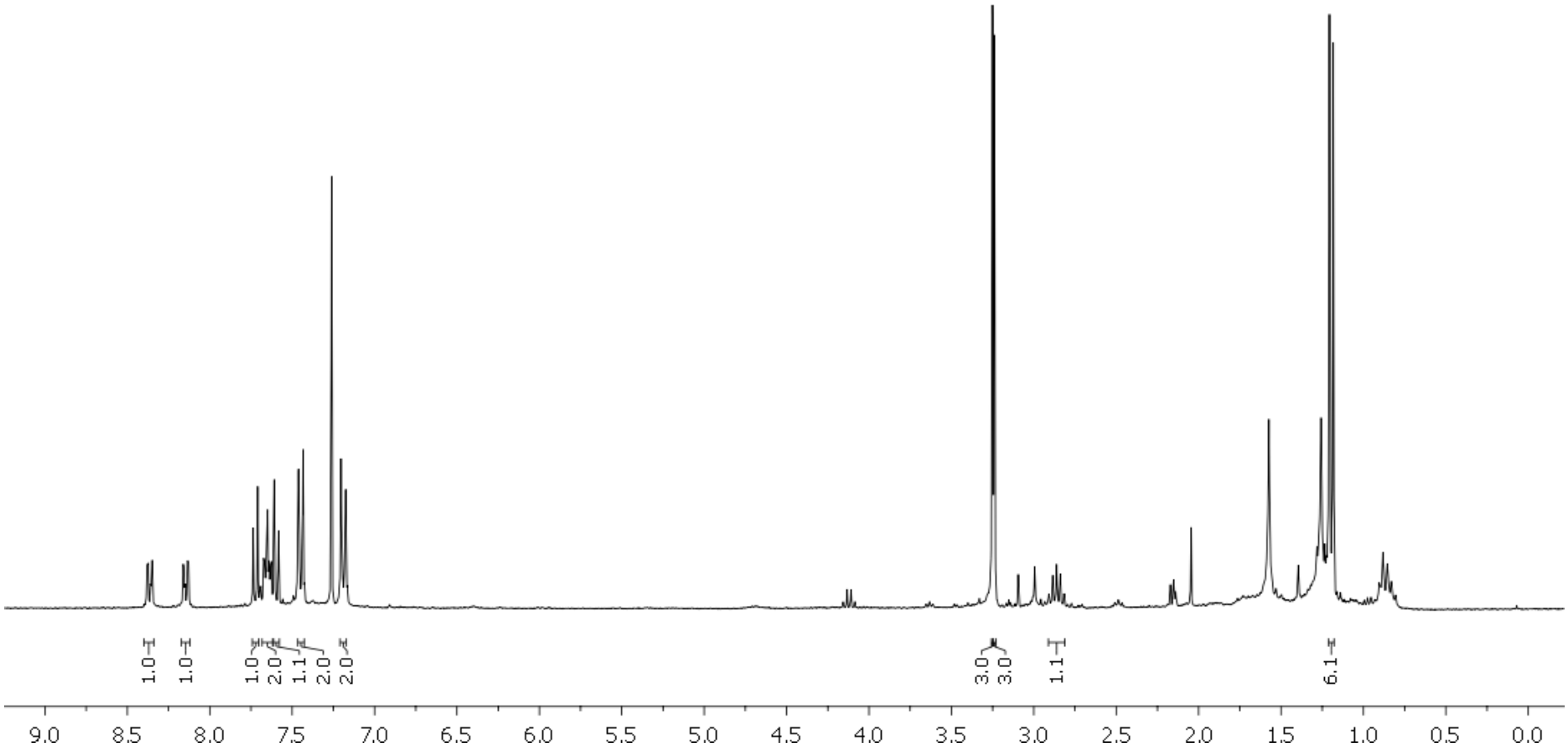
18

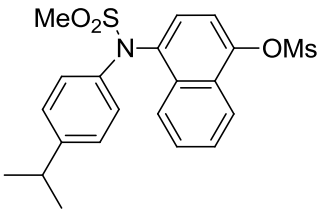
$CDCl_3$, 75 MHz

$CDCl_3$, 300 MHz



19

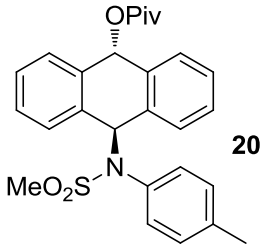




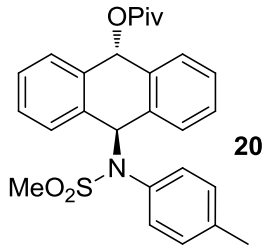
19

$CDCl_3$, 75 MHz

$CDCl_3$, 300 MHz

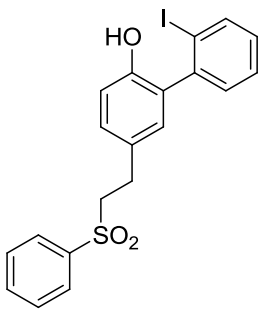


20



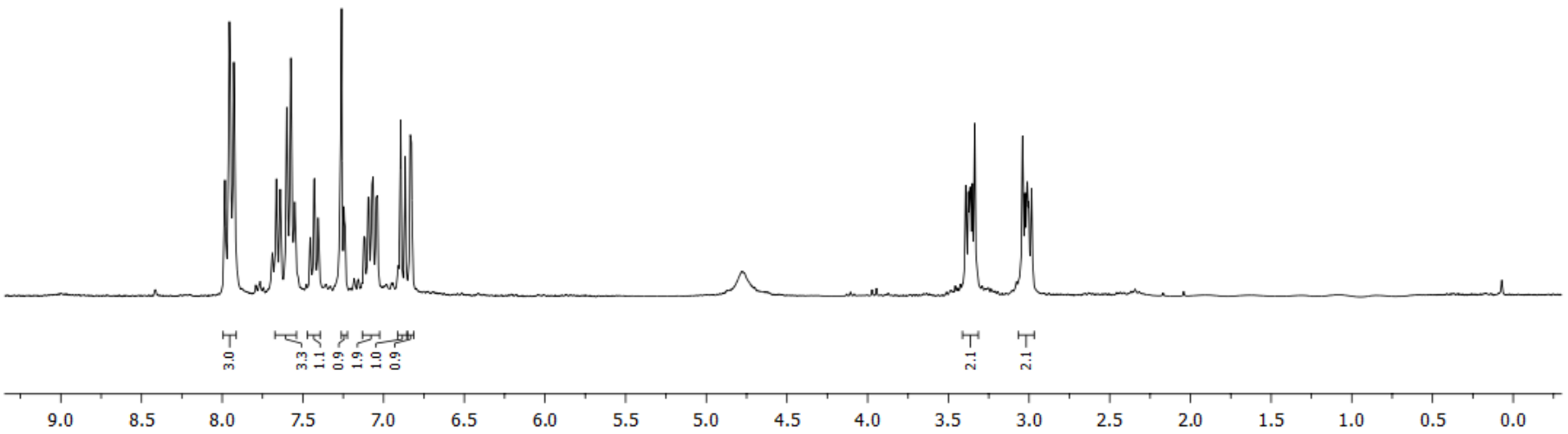
20

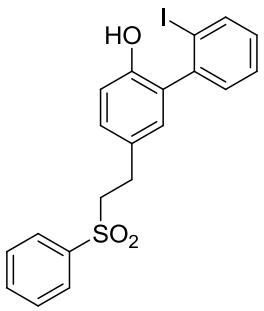
$CDCl_3$, 75 MHz



5a

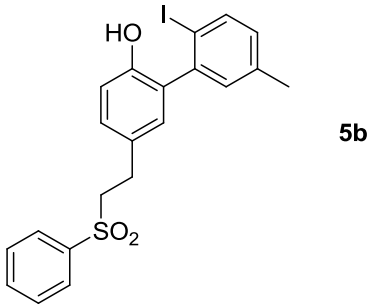
$CDCl_3$, 300 MHz





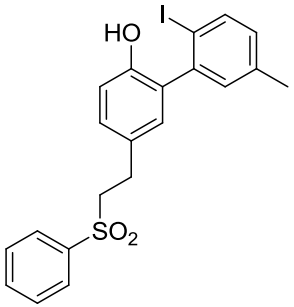
5a

$CDCl_3$, 75 MHz



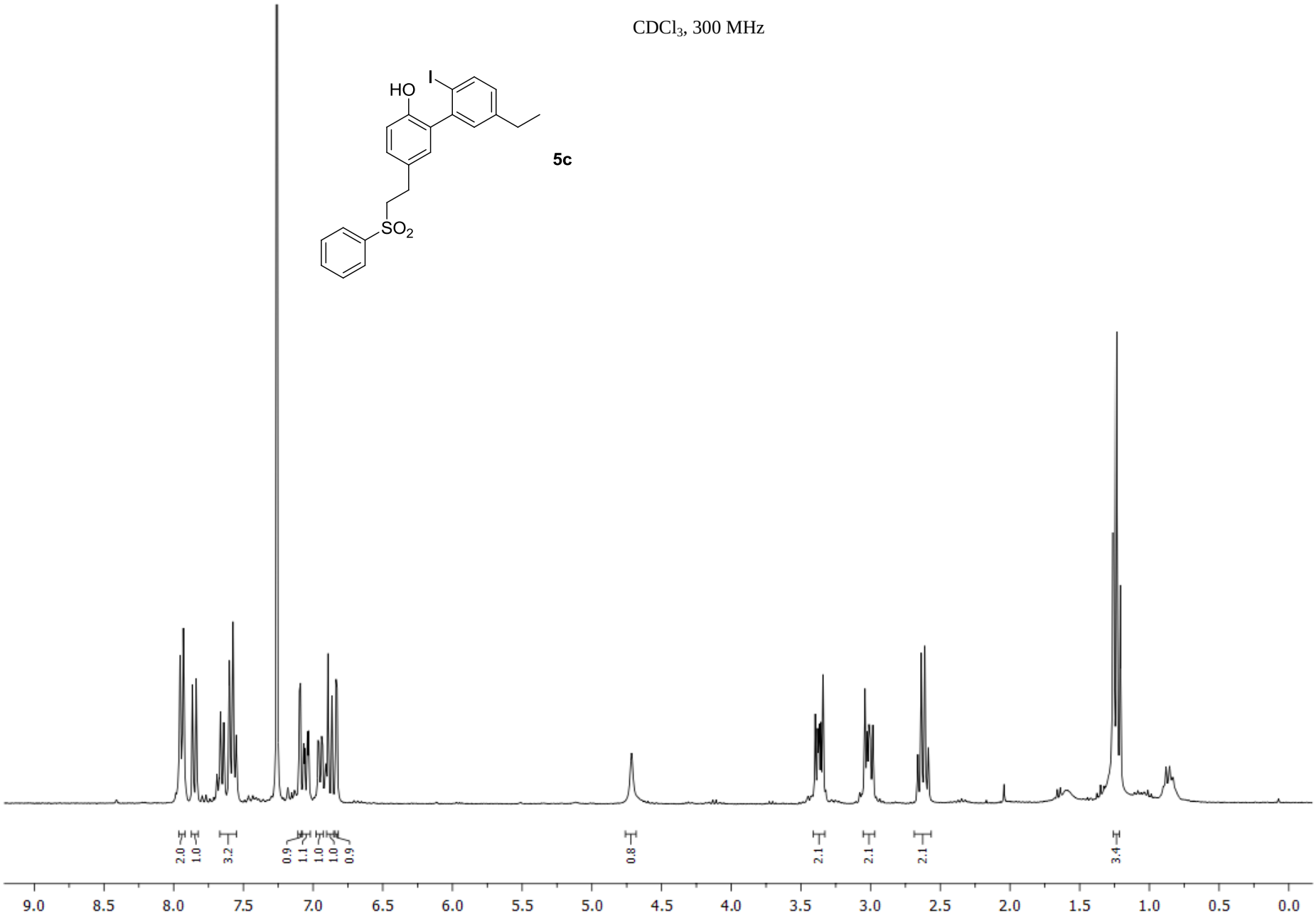
5b

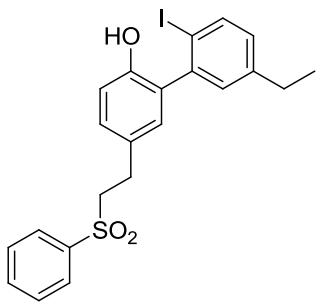
$CDCl_3$, 300 MHz



5b

$CDCl_3$, 75 MHz

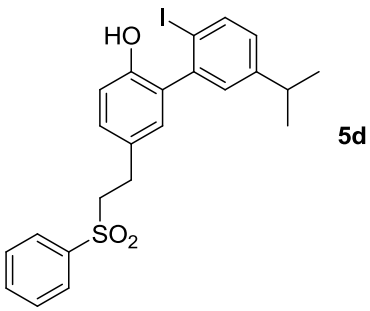




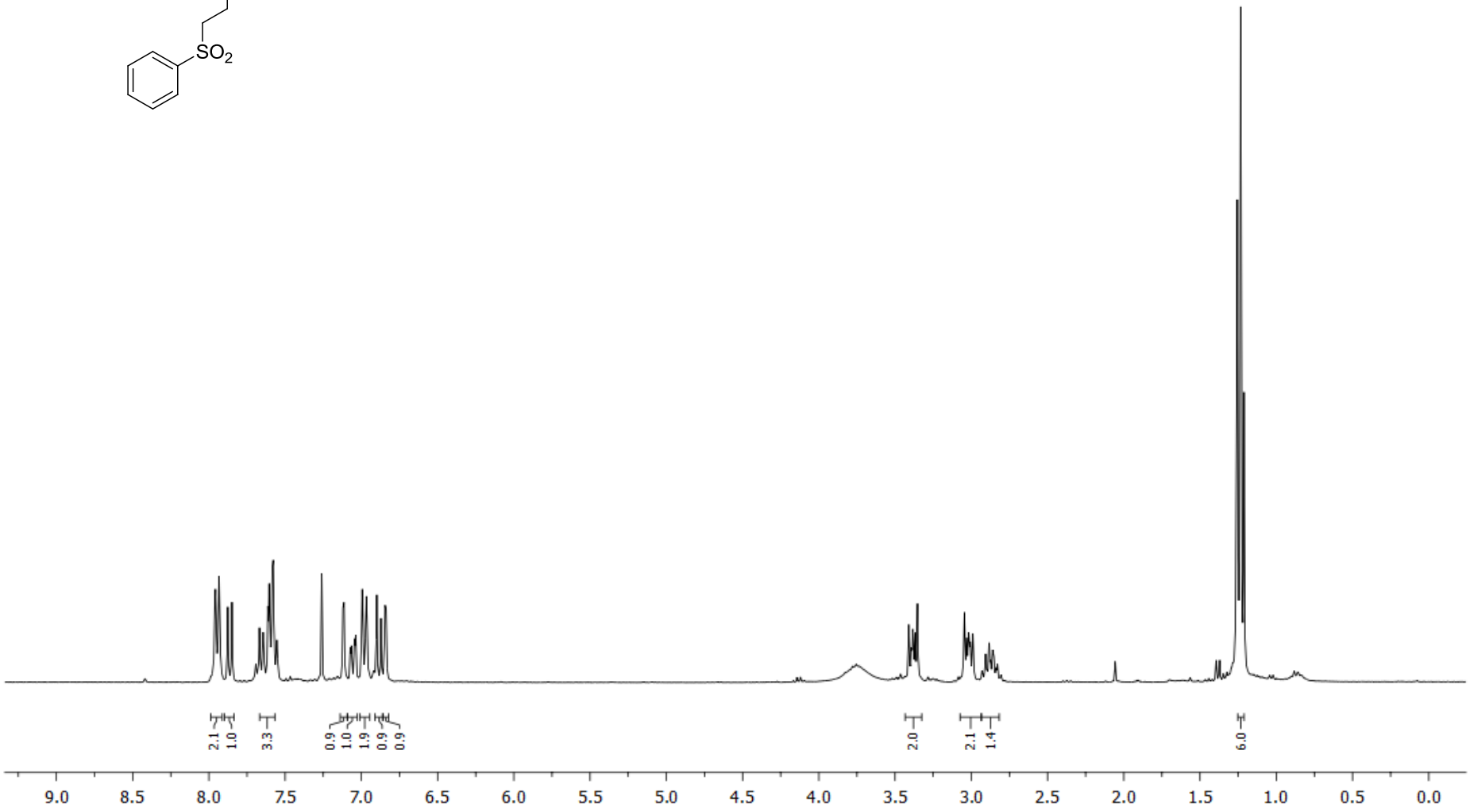
5c

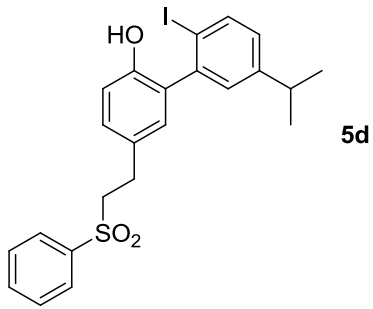
$CDCl_3$, 75 MHz

$CDCl_3$, 300 MHz



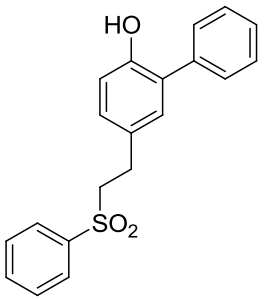
5d





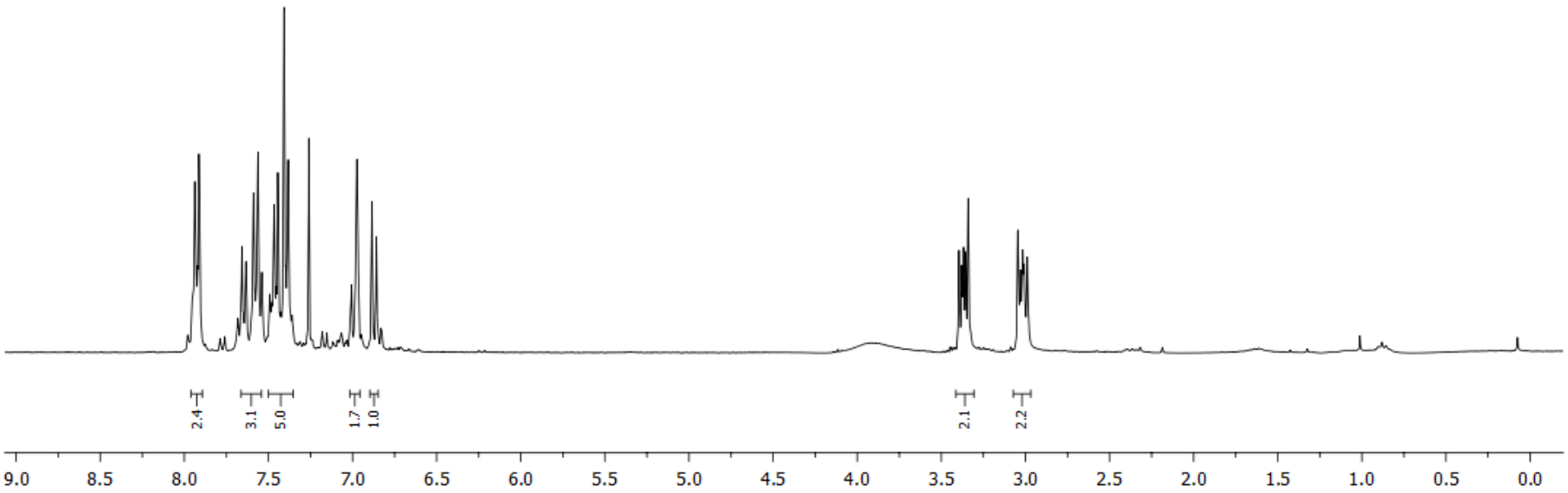
5d

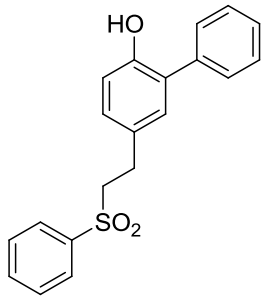
$CDCl_3$, 75 MHz



5e

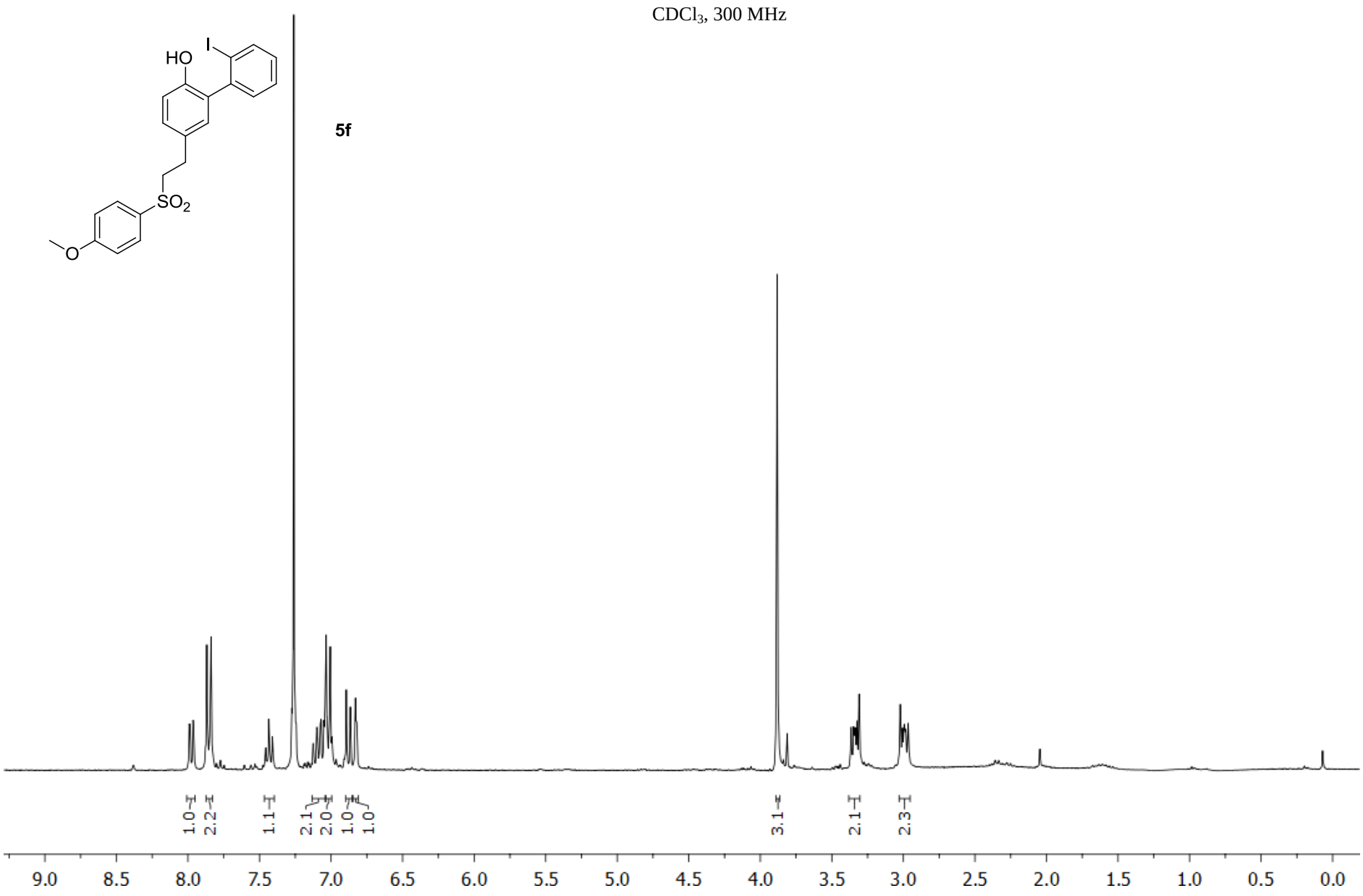
$CDCl_3$, 300 MHz

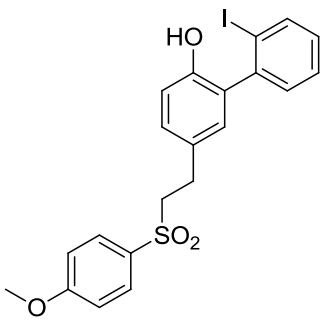




5e

$CDCl_3$, 75 MHz

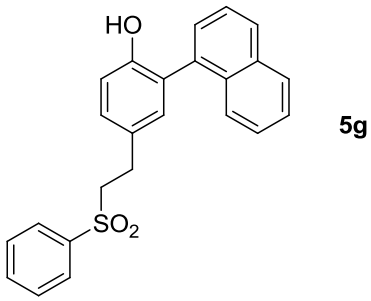




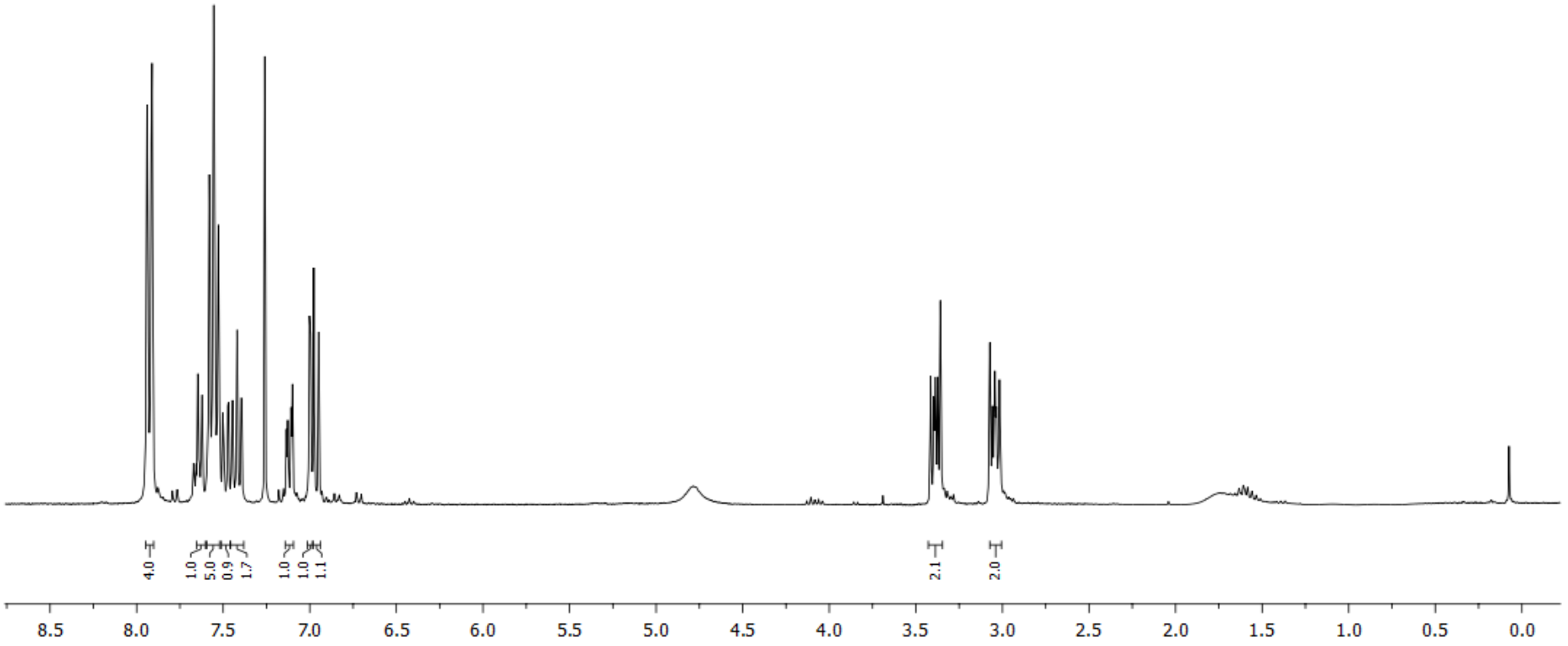
5f

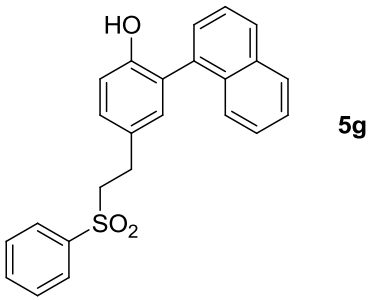
$CDCl_3$, 75 MHz

$CDCl_3$, 300 MHz



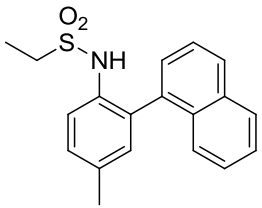
5g





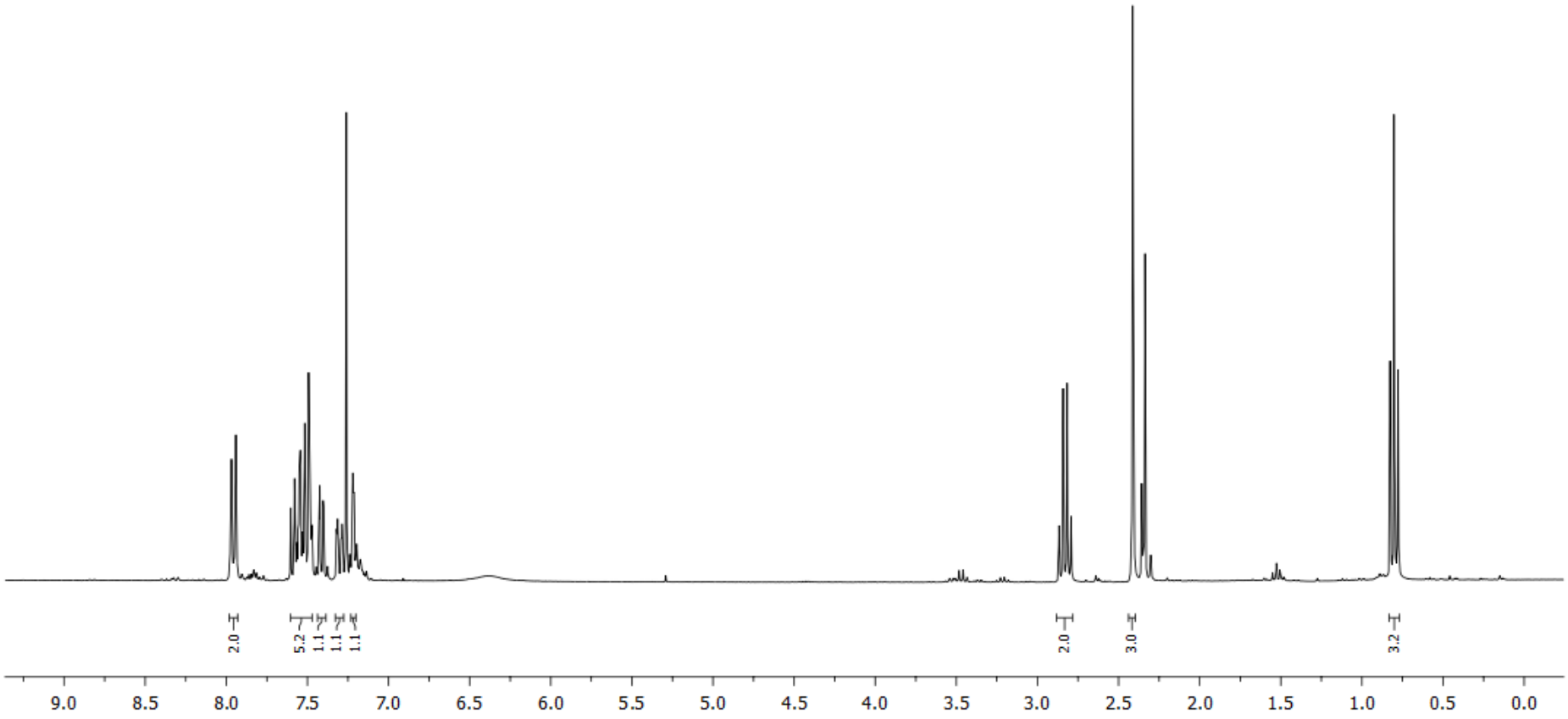
5g

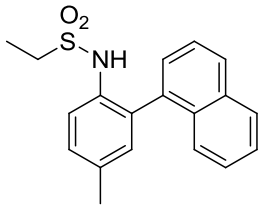
$CDCl_3$, 75 MHz



5h

$CDCl_3$, 300 MHz

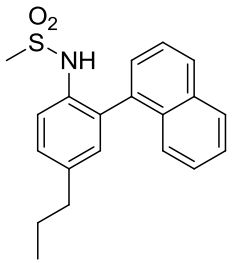




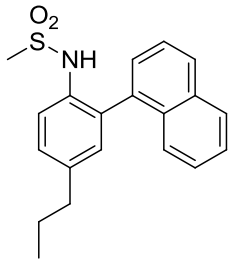
5h

$CDCl_3$, 75 MHz

$CDCl_3$, 300 MHz

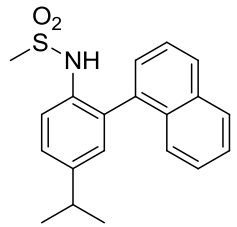


5i



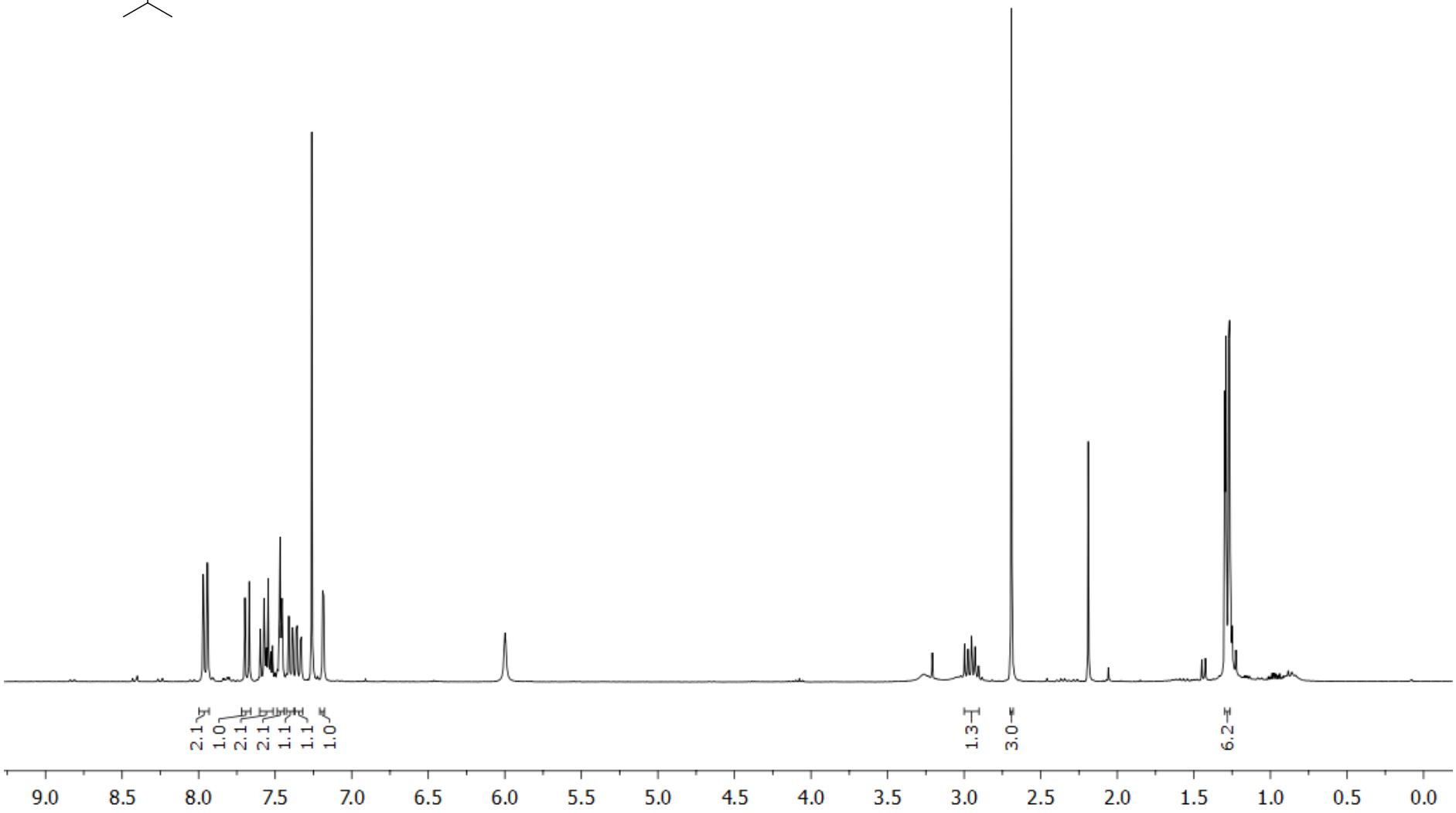
5i

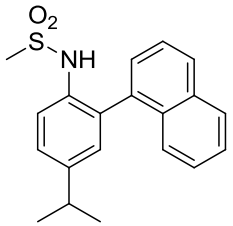
$CDCl_3$, 75 MHz



5j

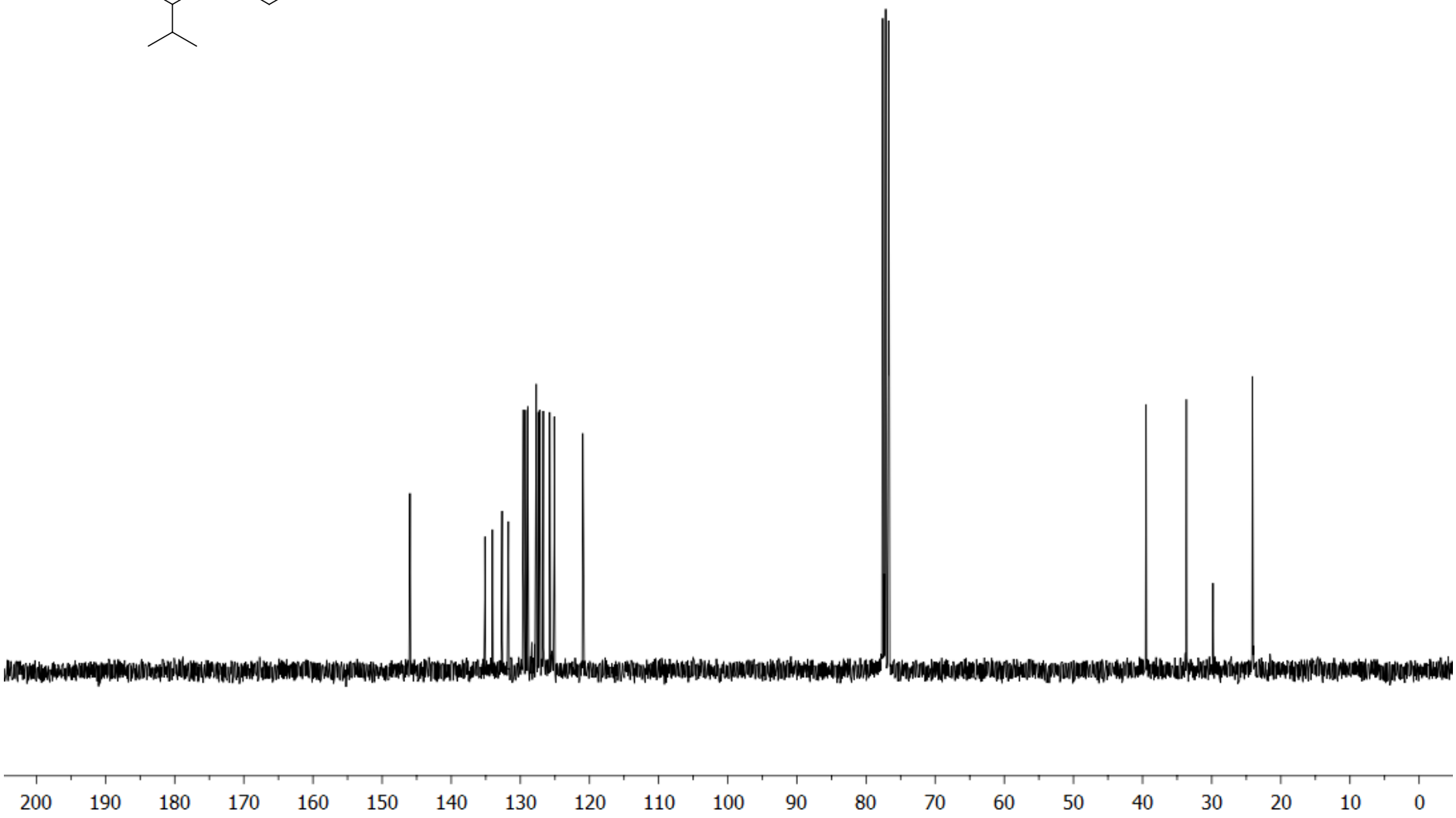
$CDCl_3$, 300 MHz



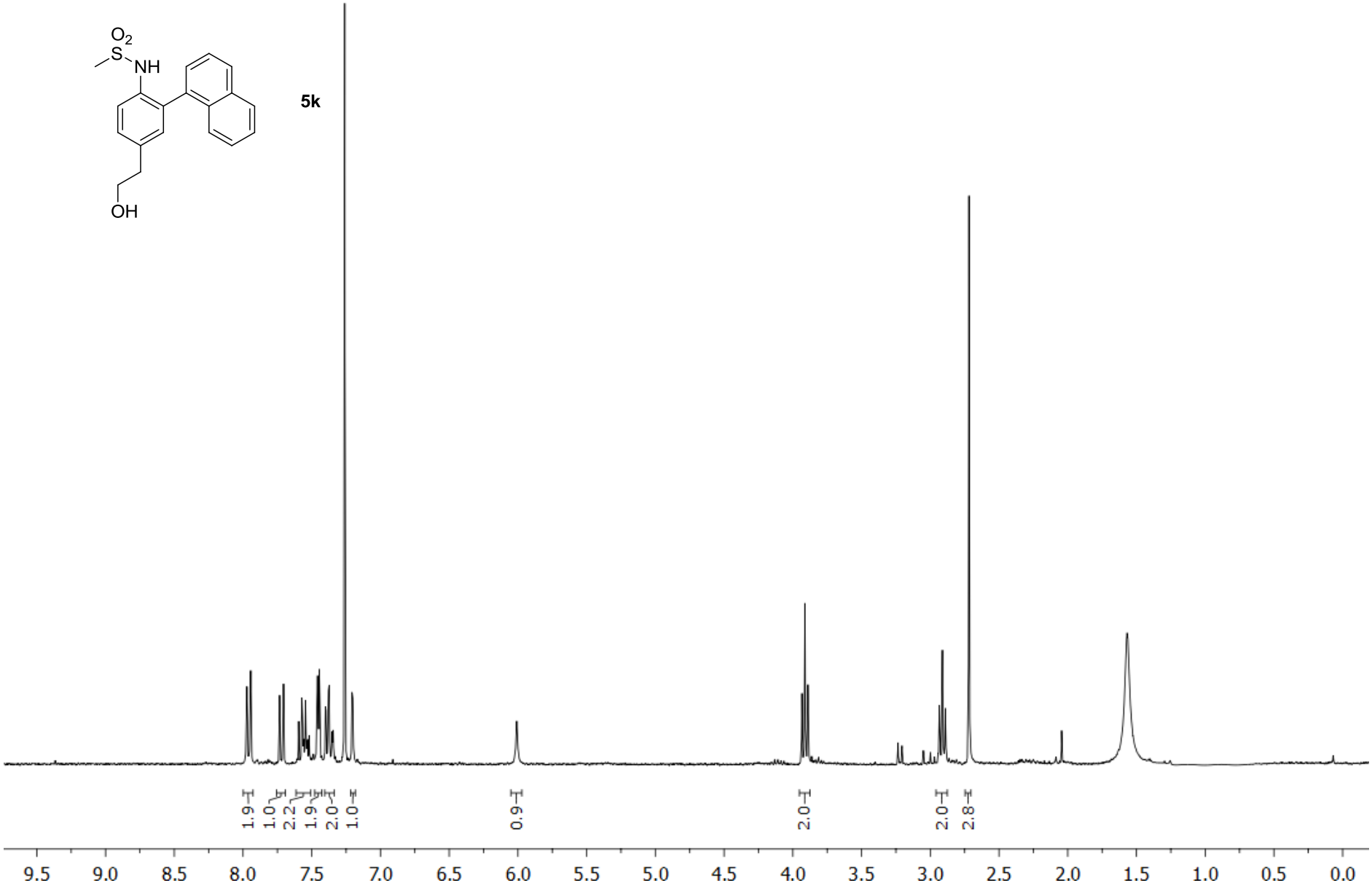


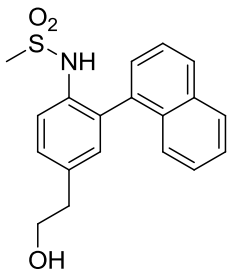
5j

$CDCl_3$, 75 MHz



$CDCl_3$, 300 MHz

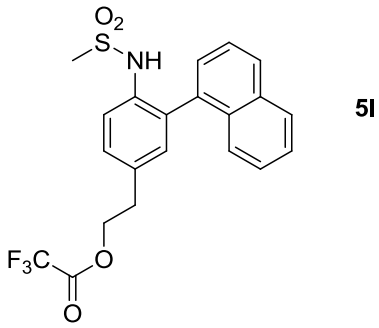




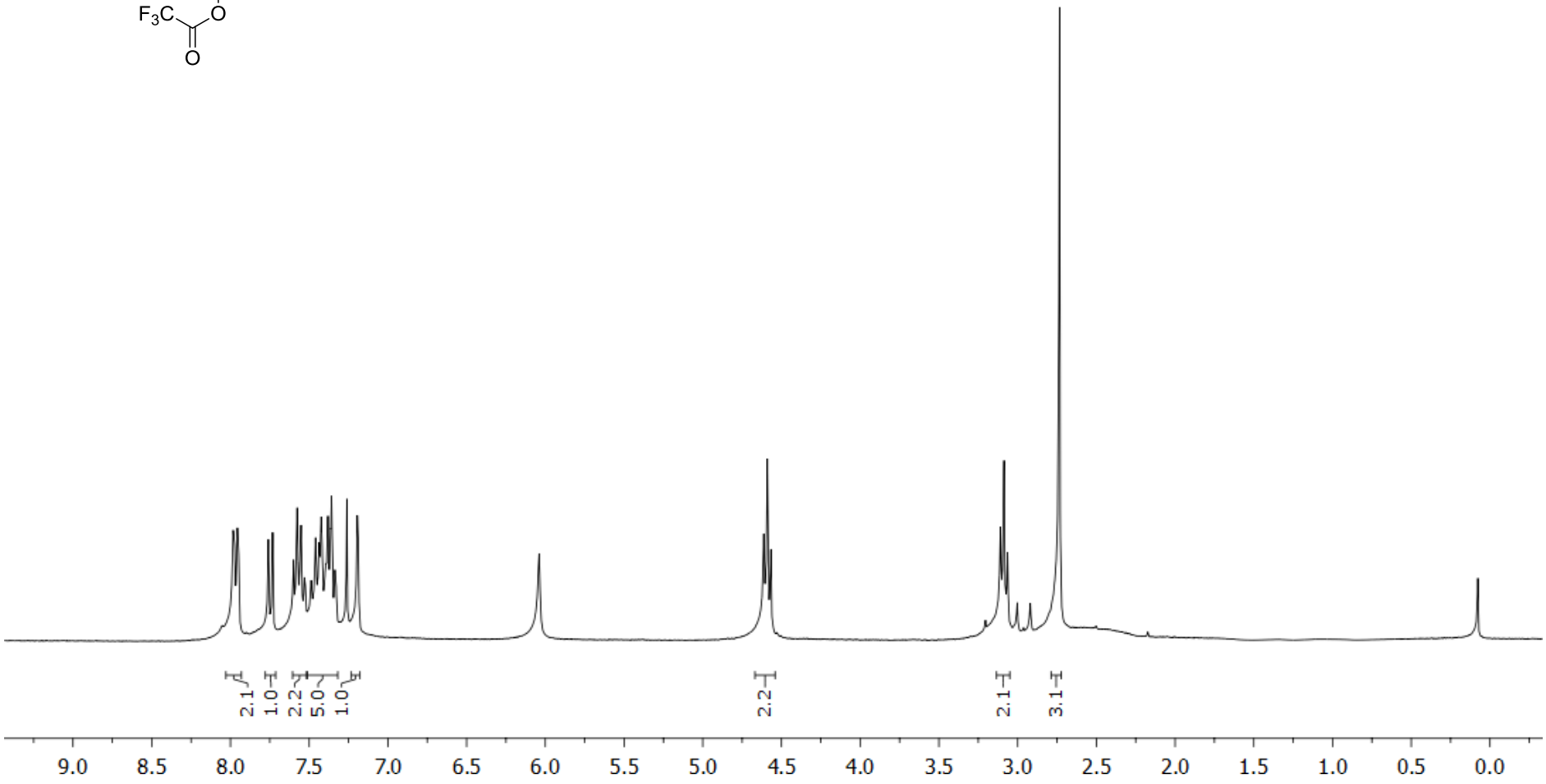
5k

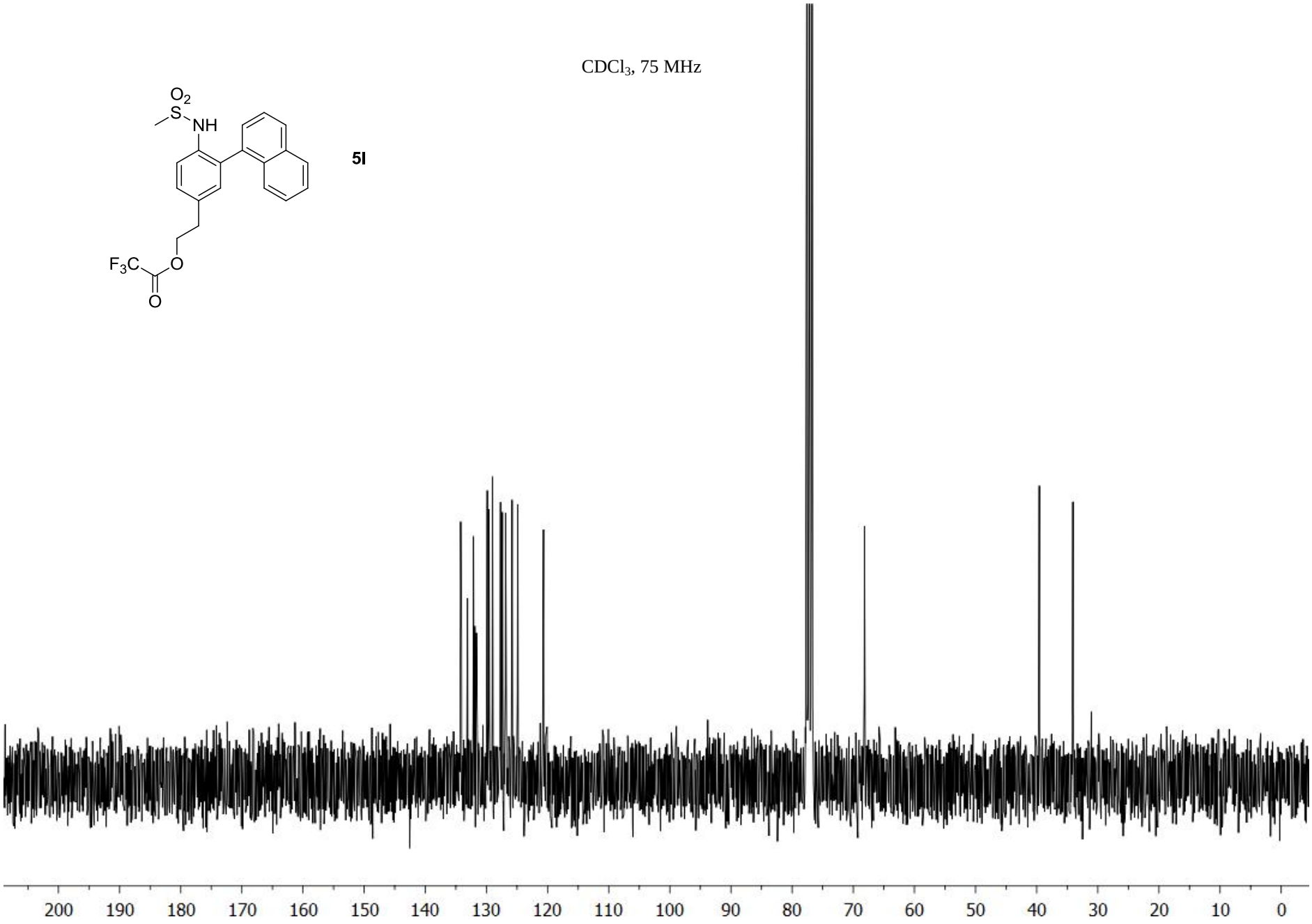
$CDCl_3$, 75 MHz

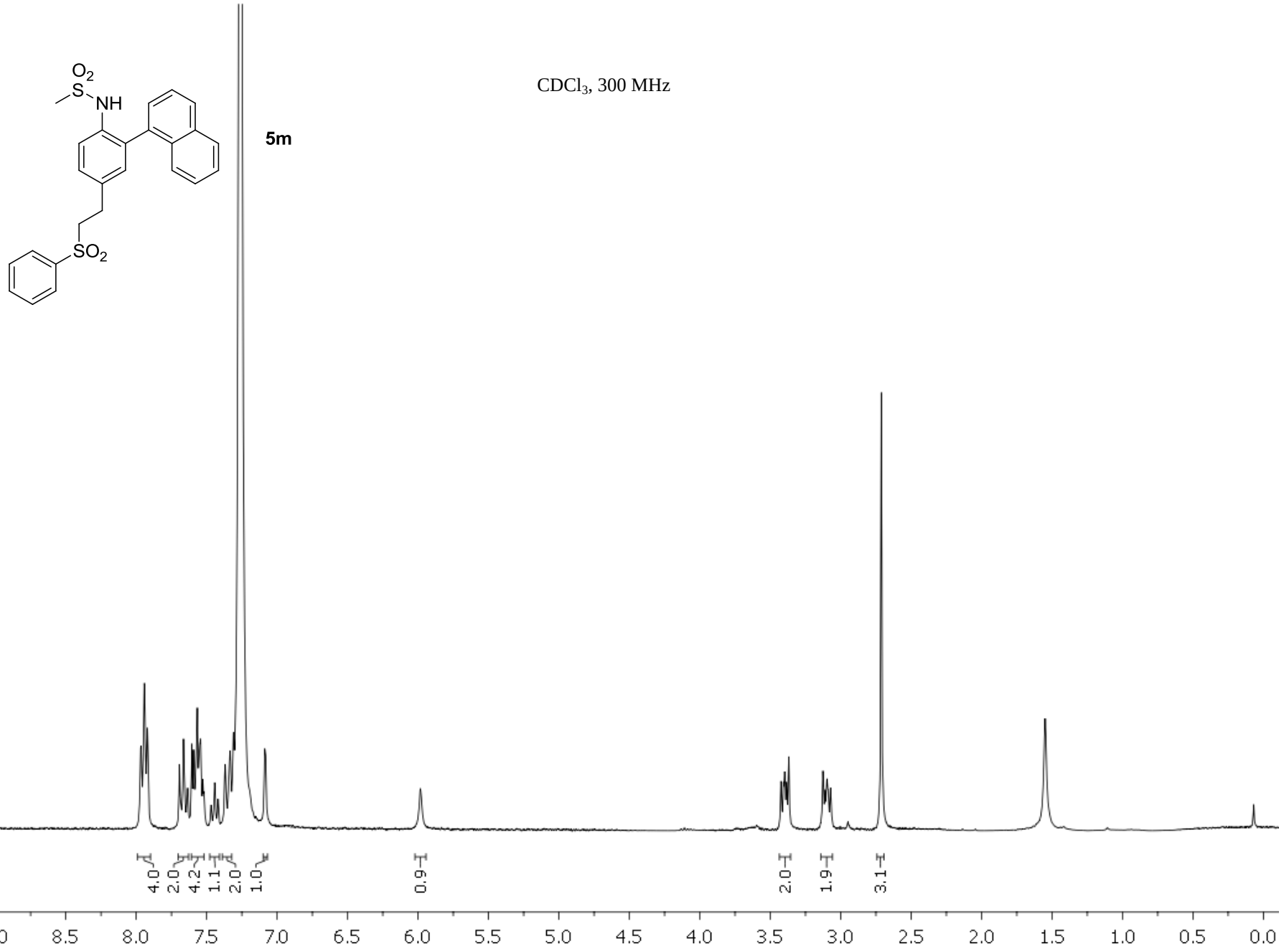
$CDCl_3$, 300 MHz

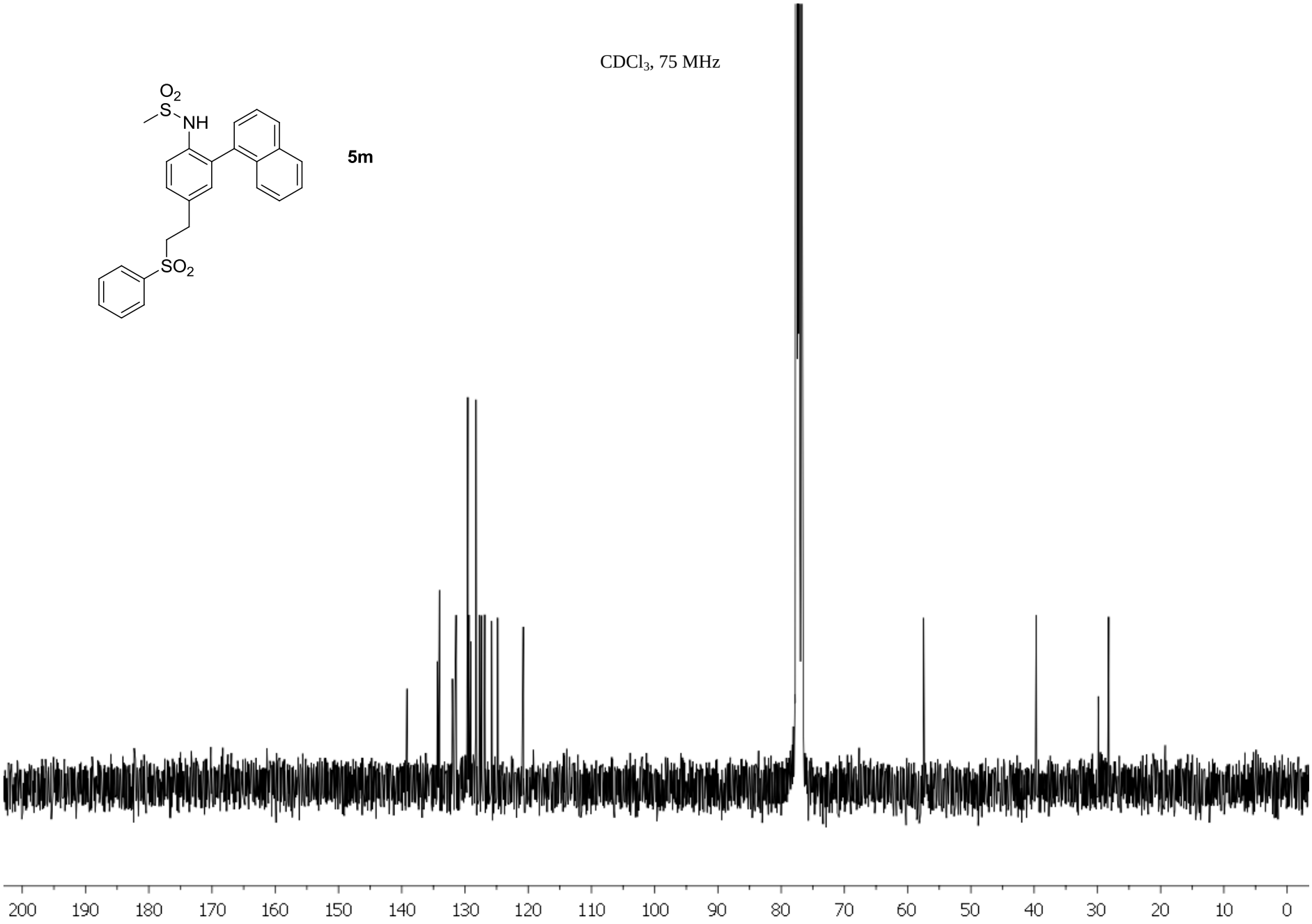


5l

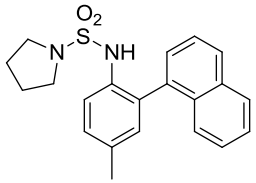




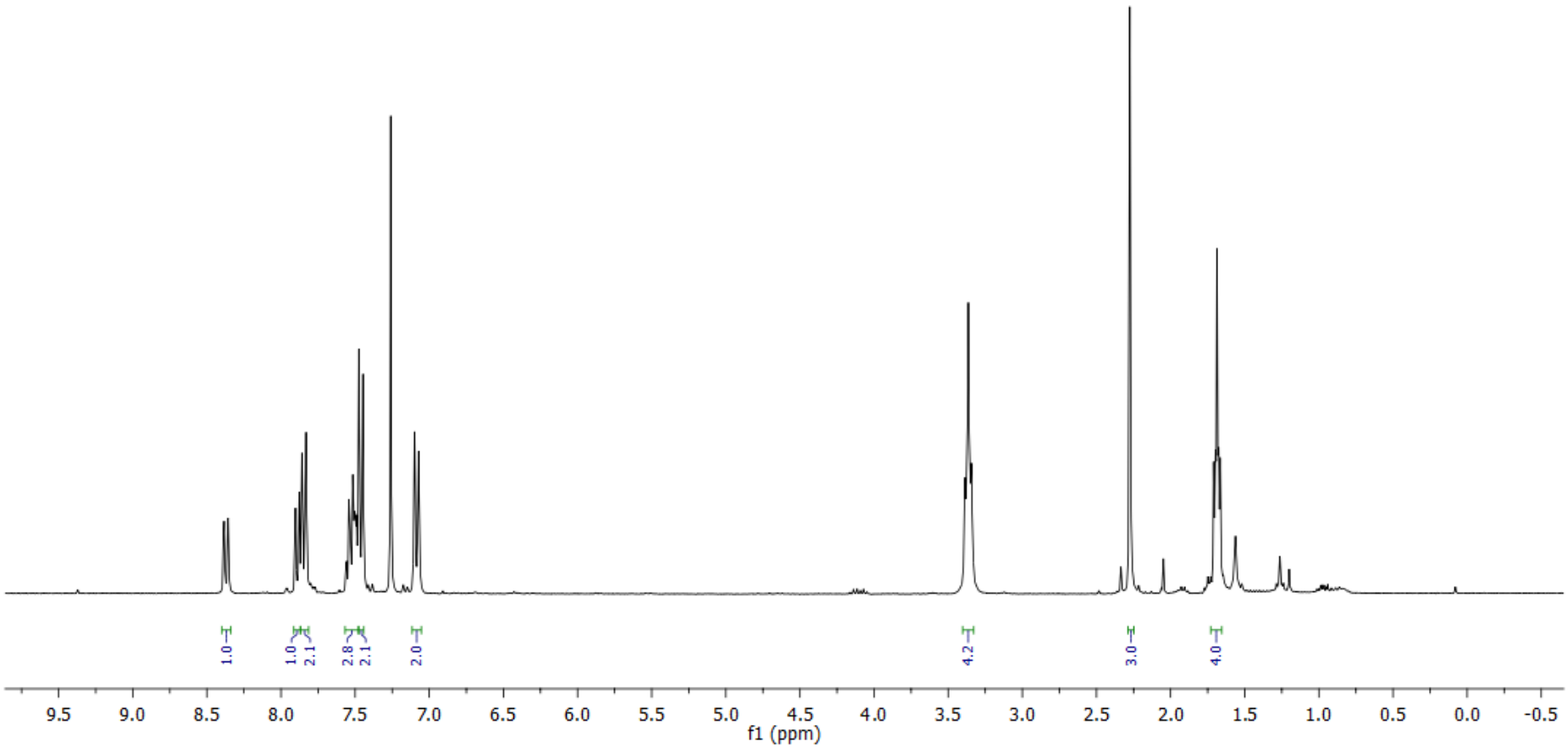


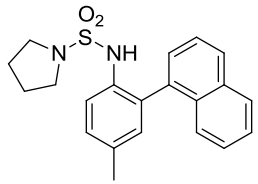


$CDCl_3$, 300 MHz



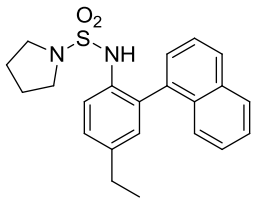
23a





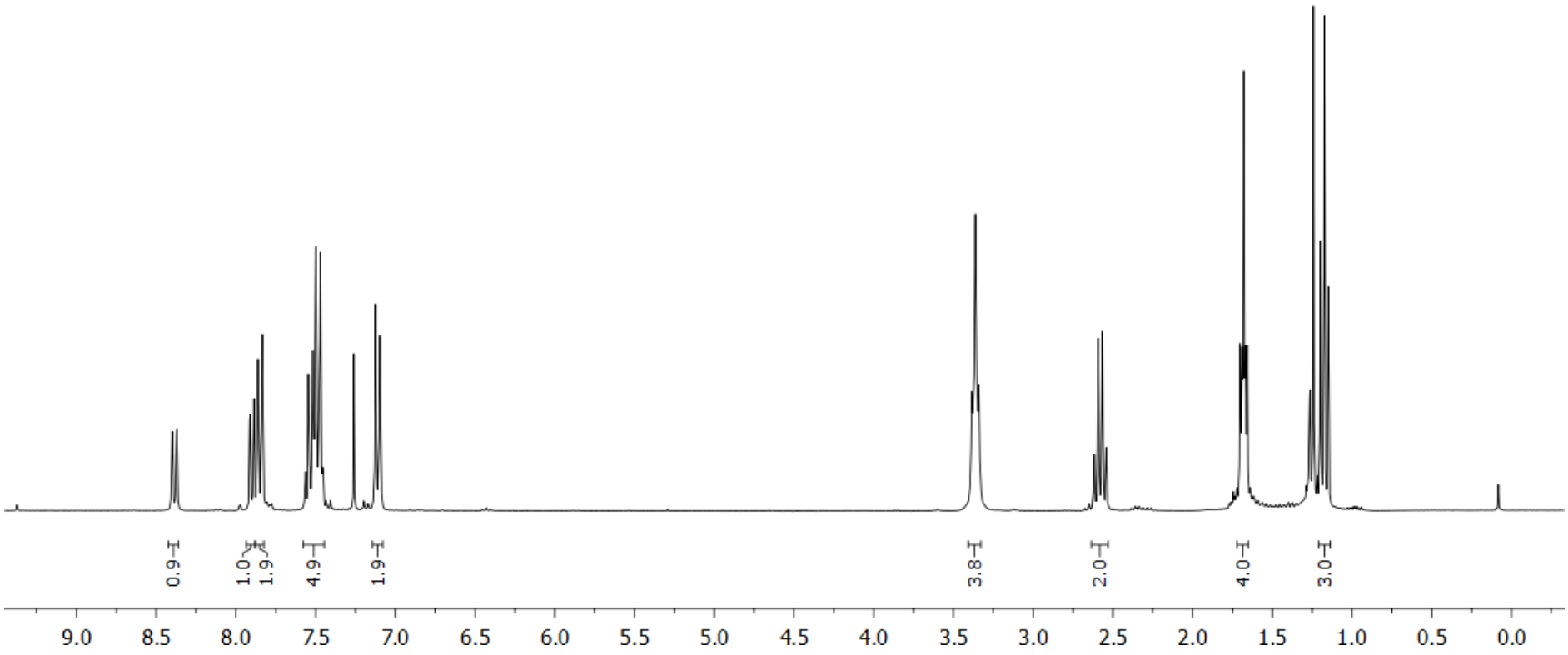
23a

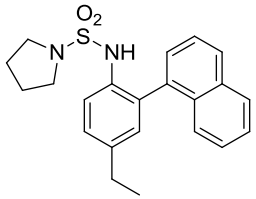
$CDCl_3$, 75 MHz



23b

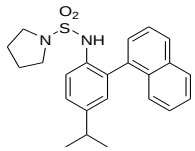
$CDCl_3$, 300 MHz





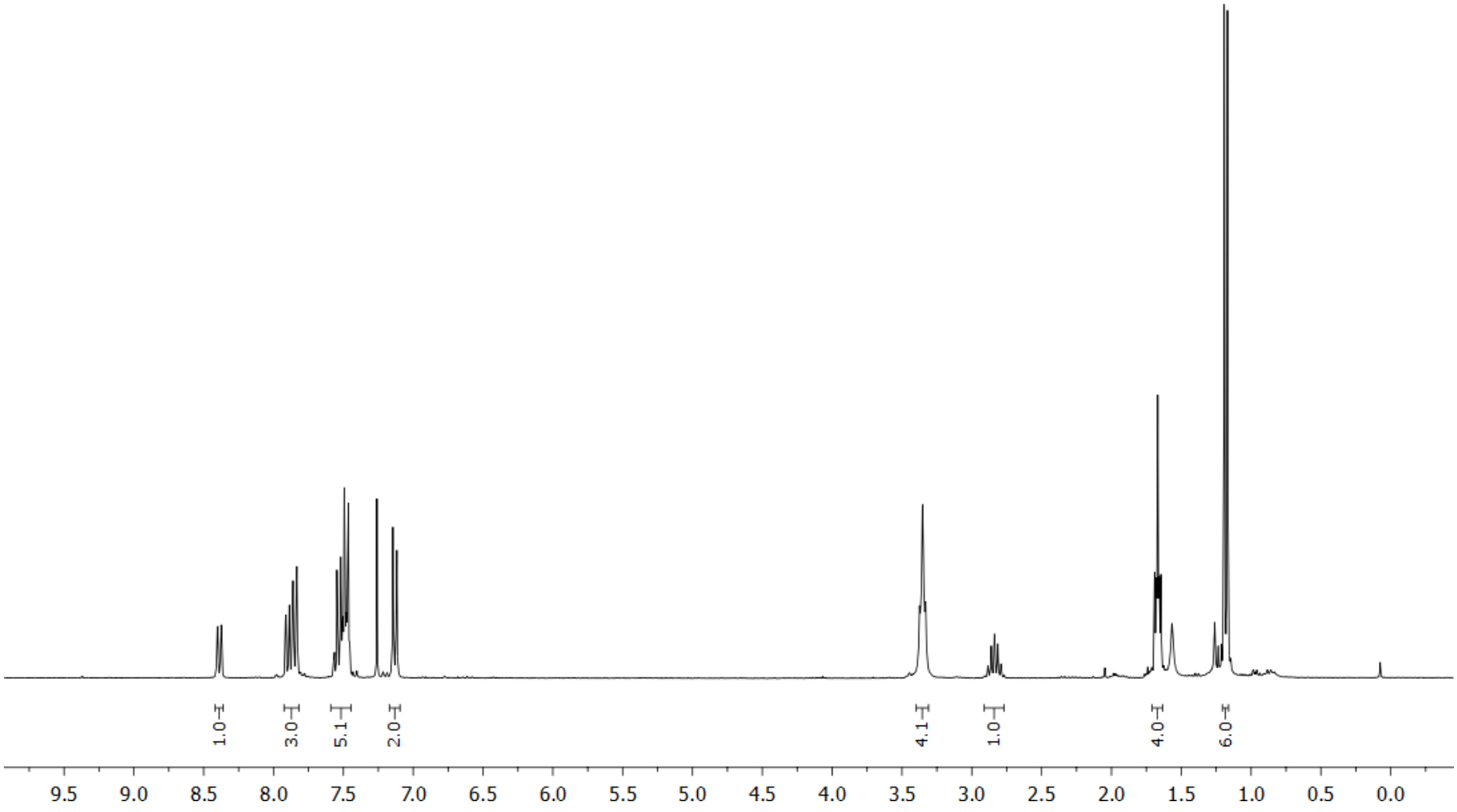
23b

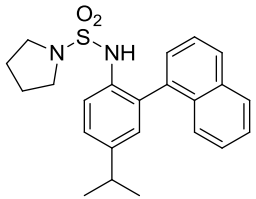
$CDCl_3$, 75 MHz



23c

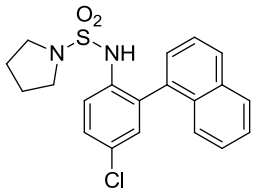
$CDCl_3$, 300 MHz





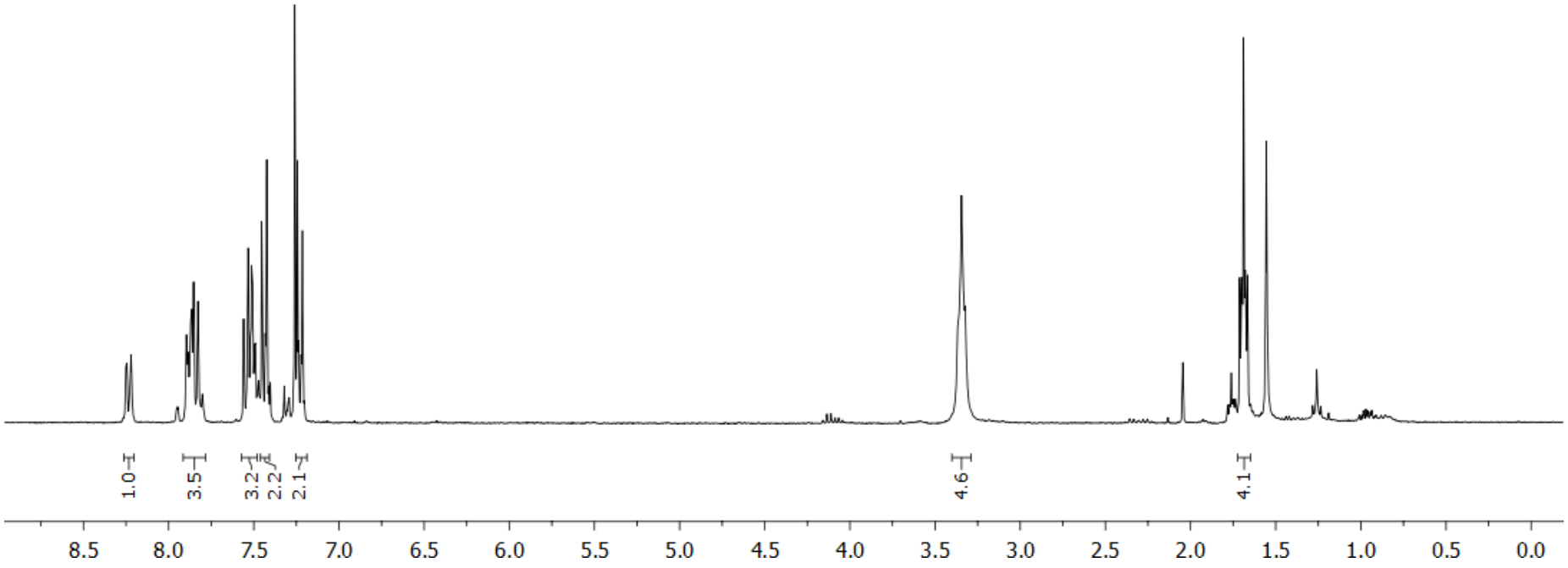
23c

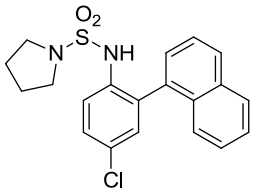
$CDCl_3$, 75 MHz



23d

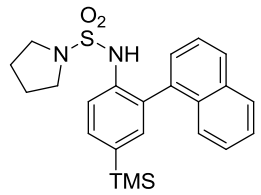
$CDCl_3$, 300 MHz





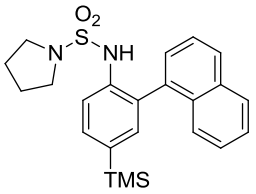
23d

$CDCl_3$, 75 MHz



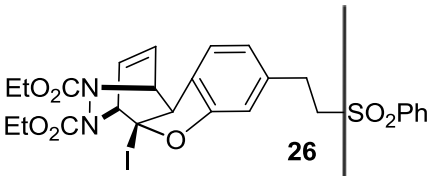
23e

$CDCl_3$, 300 MHz

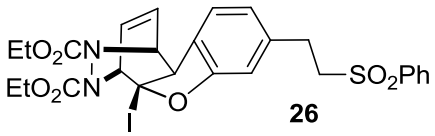


23e

$CDCl_3$, 75 MHz

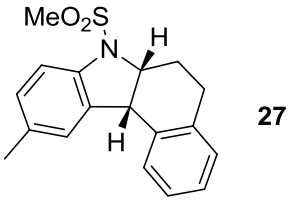


26



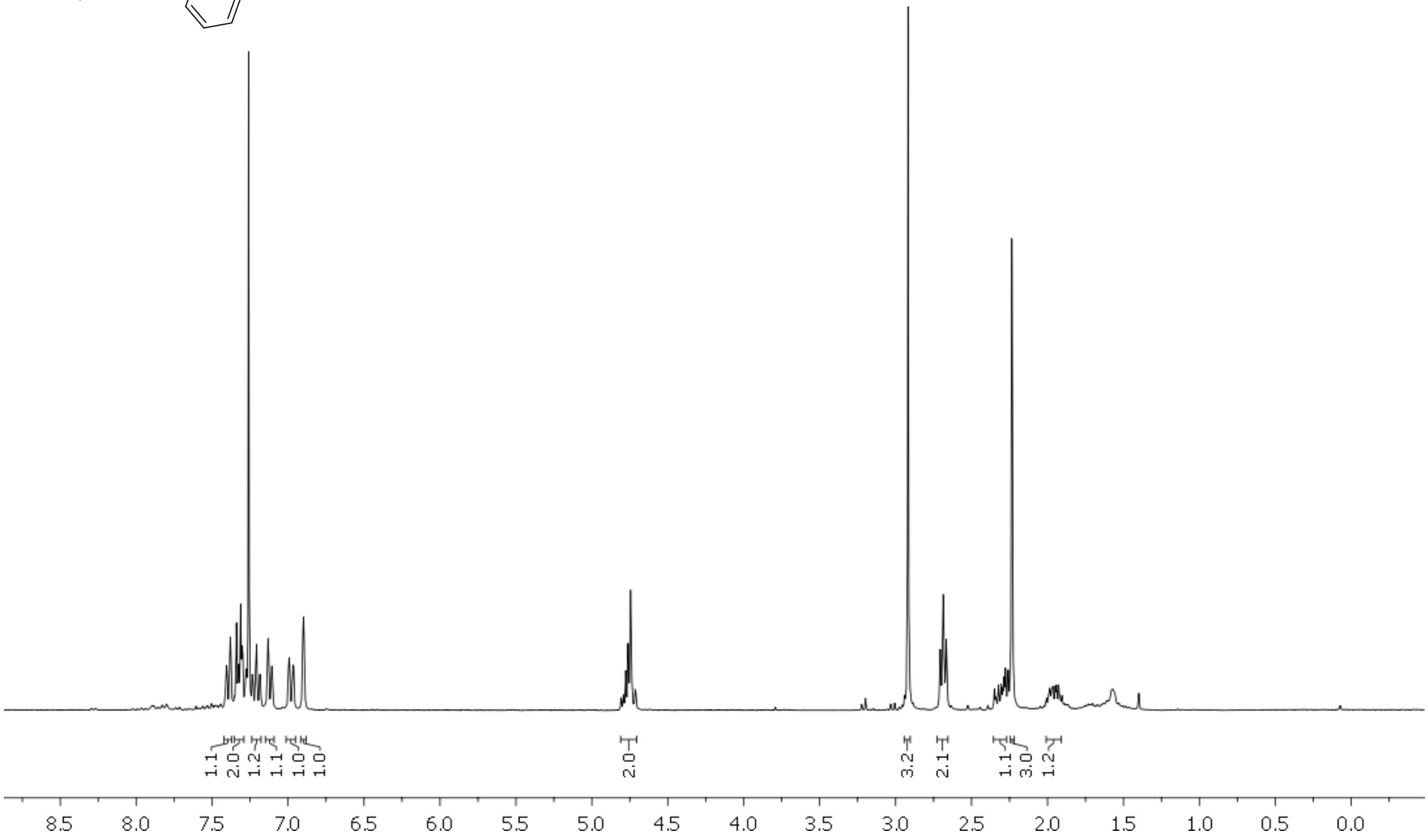
26

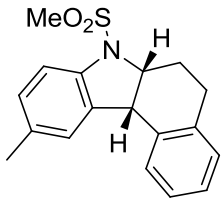
$CDCl_3$, 75 MHz



27

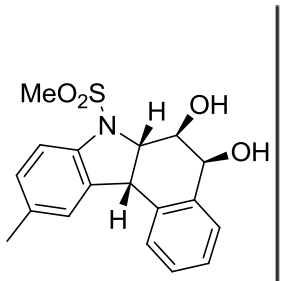
$CDCl_3$, 300 MHz





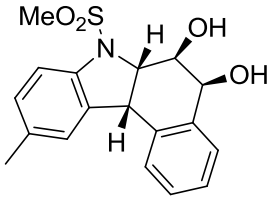
27

$CDCl_3$, 75 MHz



28

$CDCl_3$, 300 MHz



28

$CDCl_3$, 75 MHz

CD_3OD

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0