

Electronic Supplementary information

Environmentally friendly catechol-based synthesis of dibenzosultams

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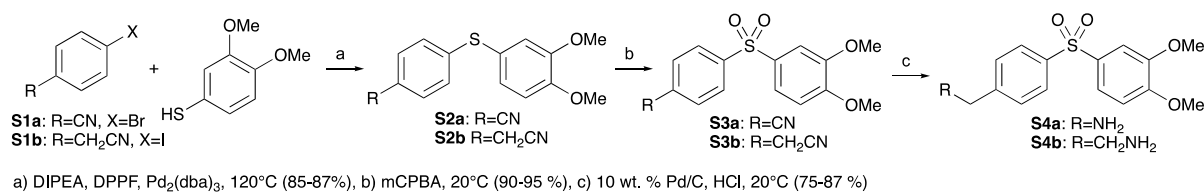
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Extended synthesis



Scheme S1. Procedure for synthesis of amines.

SA. General procedure for sulfone-carbon coupling

To a suspension of the selected aryl halide (**S1a-b**) in toluene (6 mL), thiol (1.2 equiv.), DIPEA (3 equiv.), DPPF (0.04 equiv.) and tris(dibenzylidene-acetone)dipalladium(0) (0.02 equiv.) was added and stirred at 120 °C for 24 h. The solution was concentrated, mounted on silica and purified by flash chromatography to afford the desired thioether (**S2a-b**).

SB. General procedure for sulfide oxidation

To a solution of the selected thioether (**S2a-b**) in chloroform (10 mL) at 0 °C *m*CPBA (3 equiv.) was added. The reaction was stirred at 19 °C and monitored by LCMS until complete oxidation (2 h). The white suspension was partitioned between chloroform (30 mL) and an aqueous solution of sodium sulfite (10 % w/v) and sodium carbonate (10 % w/v) (30 mL). The aqueous phase was extracted with chloroform (2 x 50 mL), and the combined organic layers were washed with sodium carbonate (10 % w/v) (2 x 30 mL) and brine (30 mL), dried over Na₂SO₄, gravity filtered and concentrated to afford the desired sulfone (**S3a-b**) without further purification.

SC. General procedure for nitrile reduction

To a solution of the selected nitrile (**S3a-b**) in MeOH/DCM, concentrated HCl (1.0 equiv.) and 10 % palladium on carbon was added in portions and the mixture was stirred at 19 °C for 18 h in hydrogen atmosphere. The mixture was filtered using LCMS filters (approximately 6 filters) and concentrated. The solid was triturated with DCM and concentrated again to yield the desired amine (**S4a-b**) without further purification.

4-((3,4-dimethoxyphenyl)thio)benzonitrile (S2a). Following general procedure SA, 4-bromobenzonitrile (**S1a**) (1.0 g, 5.49 mmol) was reacted with 3,4-dimethoxythiophenol (1.12 g, 6.59 mmol) to afford 1.3 g (87 %) of the title compound as a white solid after normal phase column chromatography (pentane/DCM, compound eluted at 80-100 % DCM); mp: 131-134 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, *J* = 8.3 Hz, 2H), 7.10 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 2.1 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 3.88 (s, 3H), 3.81 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 150.49, 149.76, 147.09, 132.18, 128.67, 125.94, 120.36, 118.82, 117.71, 112.01, 107.95, 56.00, 55.92.

2-(4-((3,4-dimethoxyphenyl)thio)phenyl)acetonitrile (S2b). Following general procedure SA, 4-iodophenyl-acetonitrile (**S1b**) (1.0 g, 5.49 mmol) was reacted with 3,4-dimethoxythiophenol (841 g, 4.94 mmol) to afford 1.0 g (85 %) of the title compound as a sticky oil after normal phase column chromatography (pentane/DCM, compound eluted at 80-100 % DCM); ¹H NMR (400 MHz, CDCl₃) δ 7.05 (d, *J* = 1.4 Hz, 4H), 6.97 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.90 (d, *J* = 2.1 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 3.76 (s, 3H), 3.71 (s, 3H), 3.55 (s, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 149.30, 149.13, 138.43, 128.15, 127.89, 127.15, 126.78, 126.77, 123.12, 117.51, 116.47, 116.43, 55.64, 55.49, 55.45, 22.52.

4-((3,4-dimethoxyphenyl)sulfonyl)benzonitrile (S3a). Following general procedure SB, **S2a** (920 mg, 3.39 mmol) was reacted with *m*CPBA (2.28 g, 10.2 mmol, 3.0 equiv.) to afford

980 mg (95 %) of the title compound as a white solid; mp: 169-172 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.02 – 7.99 (m, 2H), 7.79 – 7.76 (m, 2H), 7.56 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.34 (d, *J* = 2.2 Hz, 1H), 6.95 (d, *J* = 8.5 Hz, 1H), 3.91 (s, 3H), 3.91 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 153.86, 149.67, 146.60, 133.13, 131.45, 127.98, 127.97, 122.58, 117.33, 116.66, 111.19, 110.04, 56.44, 56.41. NMR data were in agreement with those reported in the literature.¹

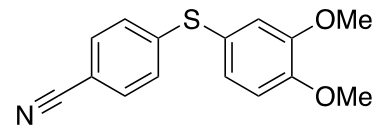
2-(4-((3,4-dimethoxyphenyl)sulfonyl)phenyl)acetonitrile (S3b). Following general procedure SB, **S2b** (1.0, 3.50 mmol) was reacted with mCPBA (2.48 g, 11.1 mmol, 3.16 equiv.) to afford 1.0 g (90 %) of the title compound as a white solid; mp: 173-174 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.93 – 7.90 (m, 2H), 7.54 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.47 – 7.44 (m, 2H), 7.35 (d, *J* = 2.1 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 3.90 (s, 6H), 3.80 (s, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 153.36, 149.46, 142.42, 135.25, 132.62, 128.92, 128.23, 122.13, 116.82, 111.02, 109.92, 56.42, 56.29, 23.65.

(4-((3,4-dimethoxyphenyl)sulfonyl)phenyl)methanamine (S4a). Following general procedure SC, **S3a** (980 mg, 3.23 mmol) was reacted with 10 % palladium on carbon (444 mg, 0.42 mmol, 0.13 equiv.) in 40 mL MeOH/DCM (1:1) to afford 730 mg (75 %) of the title compound as a white solid; mp: 247-250 °C; ¹H NMR (400 MHz, CD₃OD) δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.58 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.41 (d, *J* = 2.2 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 1H), 4.21 (s, 2H), 3.88 (s, 3H), 3.86 (s, 3H); ¹³C NMR (101 MHz, CD₃OD) δ 155.09, 150.95, 144.40, 139.79, 133.78, 131.09, 129.07, 123.25, 112.56, 111.20, 56.74, 56.72, 43.55.

2-(4-((3,4-dimethoxyphenyl)sulfonyl)phenyl)ethan-1-amine (S4b). Following general procedure SC, **S3b** (100 mg, 0.31 mmol) was reacted with 10 % palladium on carbon (67 mg, 0.063 mmol, 0.2 equiv.) in 14 mL MeOH/DCM (2:5) to afford 88 mg (87 %) of the title compound as a white solid; mp: 250 °C (decomposition); ¹H NMR (400 MHz, CD₃OD) δ 7.75 (s, 2H), 7.38 (s, 3H), 7.24 (s, 1H), 6.93 (s, 1H), 3.70 (s, 6H), 3.00 (d, *J* = 50.8 Hz, 4H); ¹³C NMR (101 MHz, CD₃OD) δ 154.63, 150.58, 143.88, 142.11, 133.82, 131.06, 128.83, 123.02, 112.55, 110.96, 56.94, 56.92, 41.43, 34.04.

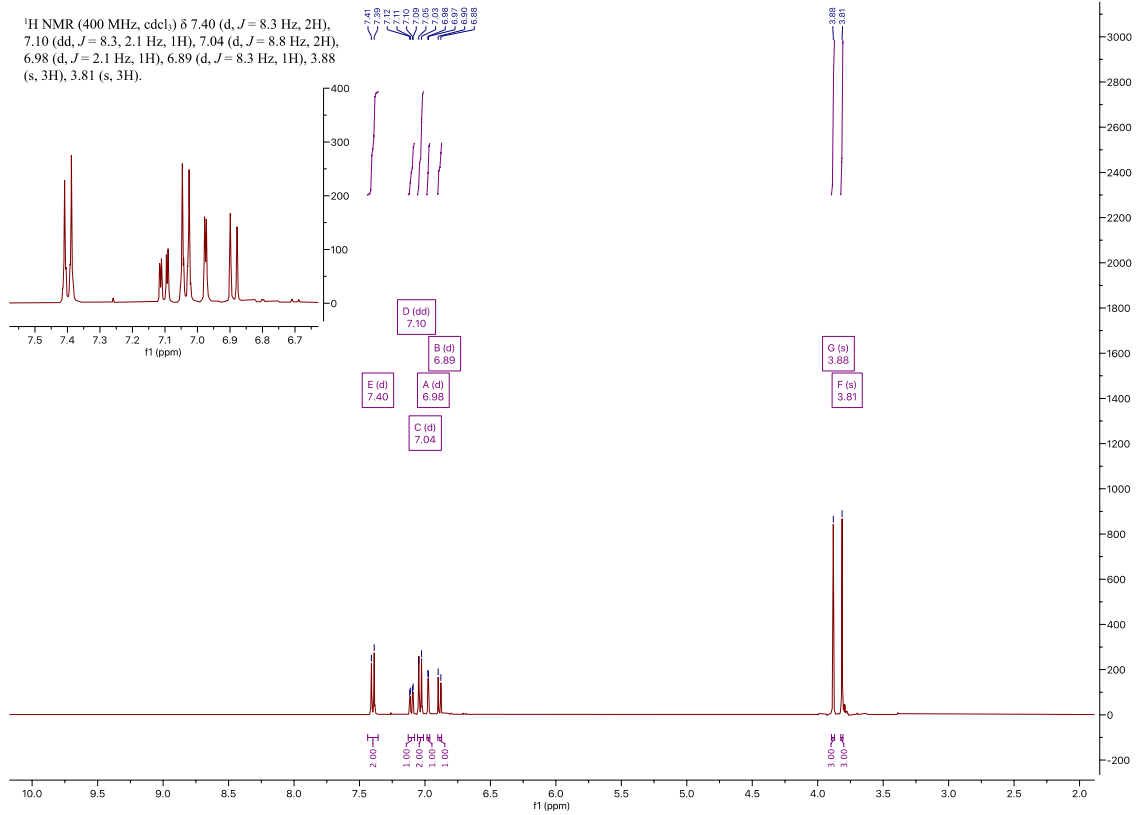
¹H. Yue, C. Zhu and M. Rueping. *Angew. Chem. Int. Ed.* 2017, **57**, 1371-1375.

¹H-NMR and ¹³C-NMR spectra



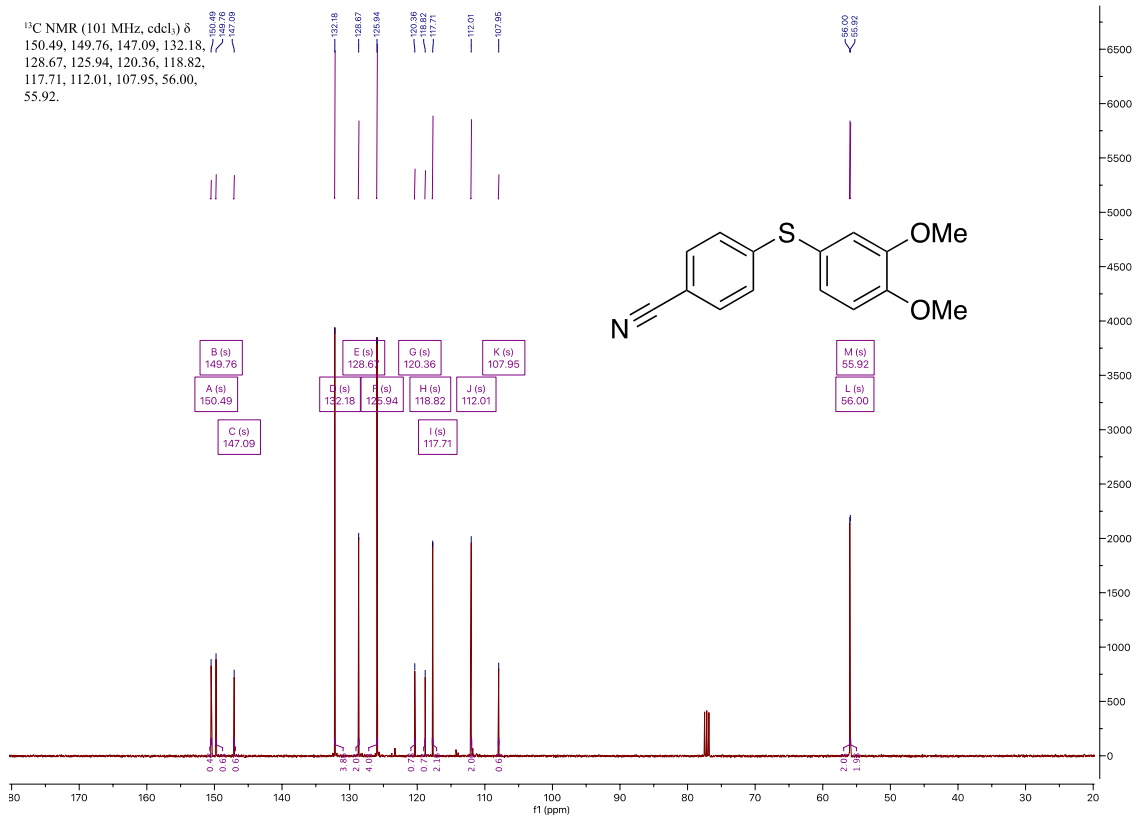
¹H NMR (400 MHz, CDCl₃) of S2a

¹H NMR (400 MHz, cdcl₃) δ 7.40 (d, *J* = 8.3 Hz, 2H), 7.10 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 2.1 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 3.88 (s, 3H), 3.81 (s, 3H).



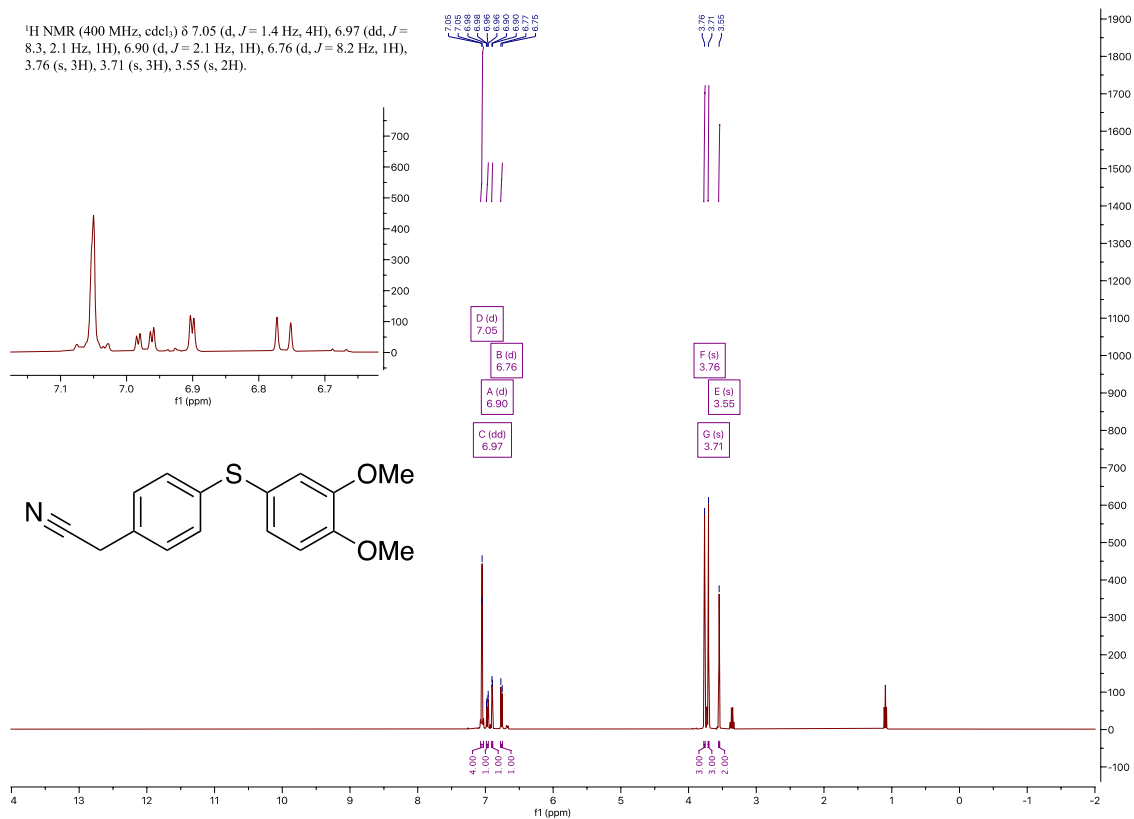
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¹³C NMR (101 MHz, cdcl₃) δ 150.49, 149.76, 147.09, 132.18, 128.67, 125.94, 120.36, 118.82, 117.71, 112.01, 107.95, 56.00, 55.92.



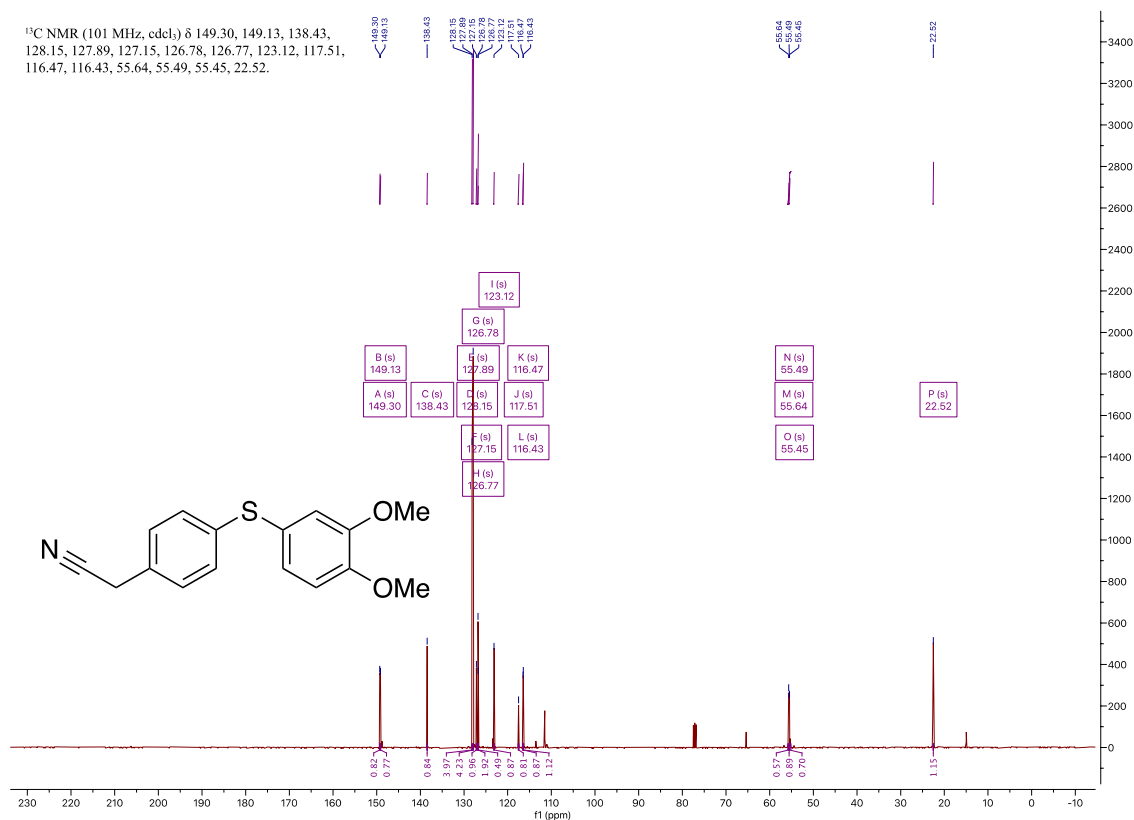
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¹H NMR (400 MHz, cdcl₃) δ 7.05 (d, *J* = 1.4 Hz, 4H), 6.97 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.90 (d, *J* = 2.1 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 3.76 (s, 3H), 3.71 (s, 3H), 3.55 (s, 2H).

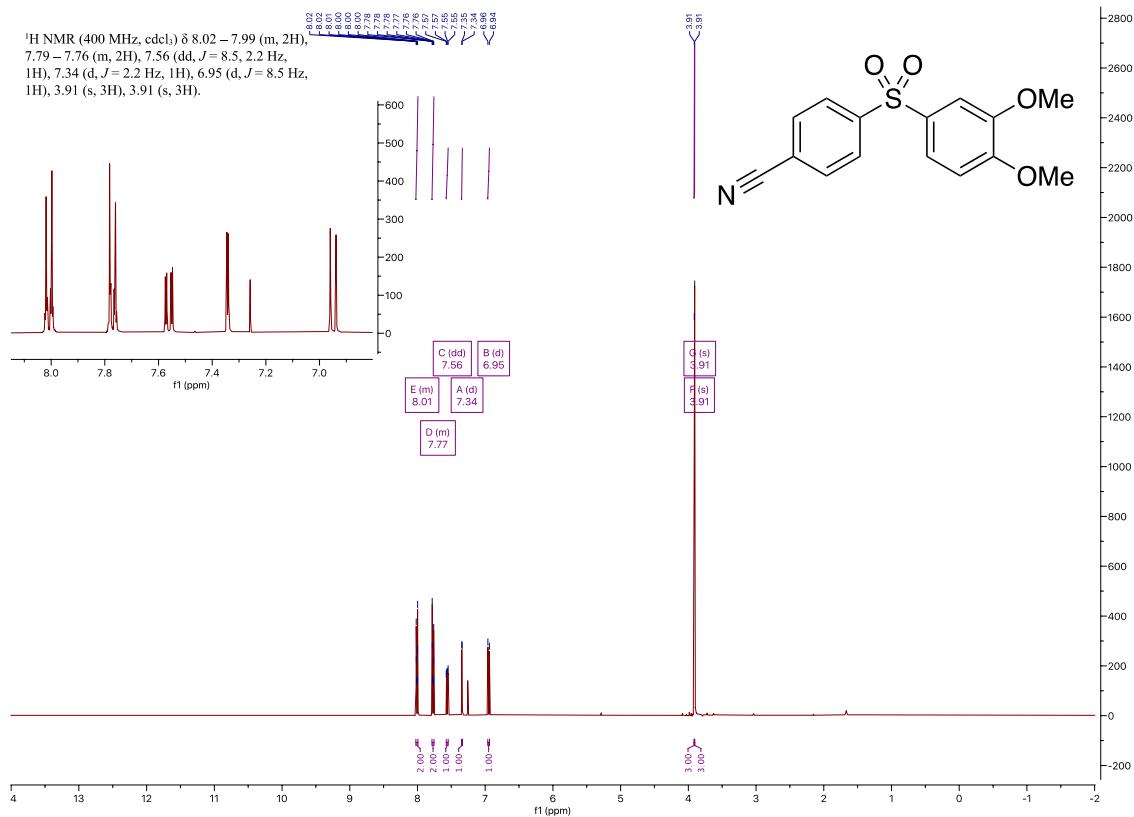


¹³C NMR (101 MHz, CDCl₃) of S2b

¹³C NMR (101 MHz, cdcl₃) δ 149.30, 149.13, 138.43, 128.15, 127.89, 127.15, 126.78, 126.77, 123.12, 117.51, 116.47, 116.43, 55.64, 55.49, 55.45, 22.52.



¹H NMR (400 MHz, CDCl₃) of S3a

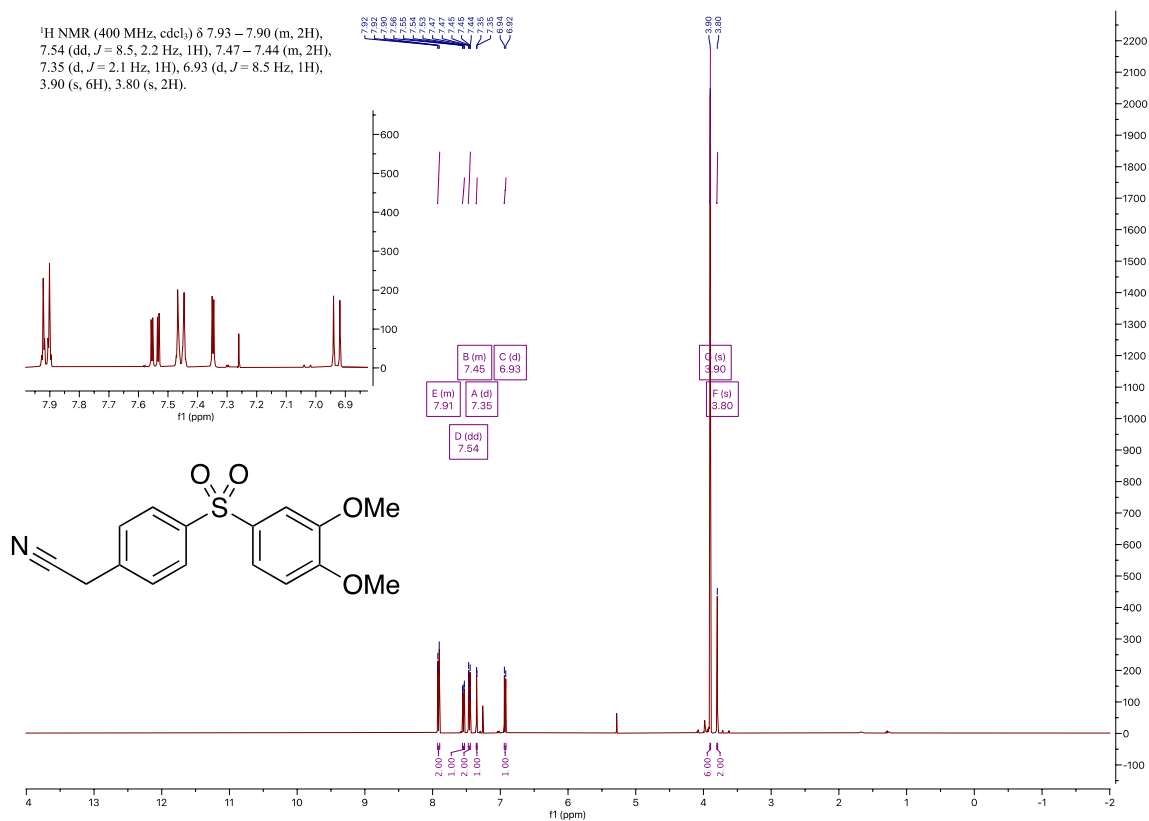


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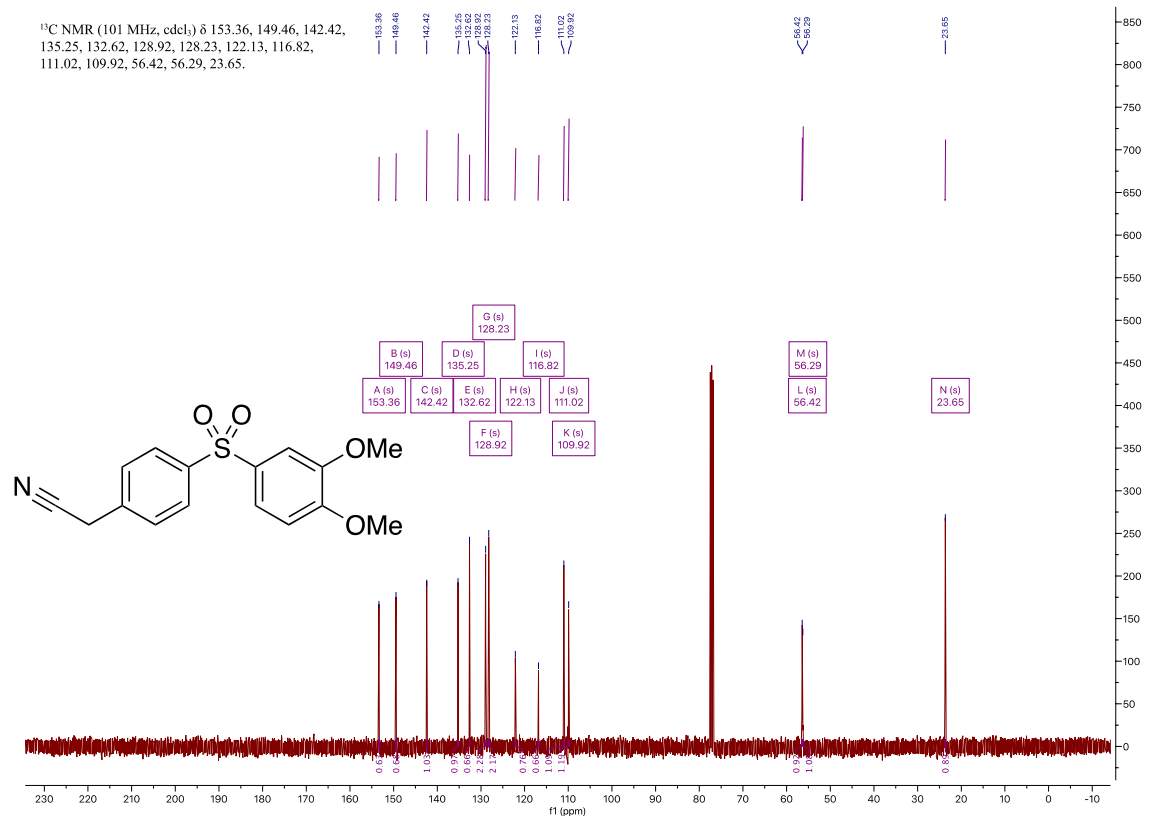
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¹H NMR (400 MHz, cdcl₃) δ 7.93 – 7.90 (m, 2H), 7.54 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.47 – 7.44 (m, 2H), 7.35 (d, *J* = 2.1 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 3.90 (s, 6H), 3.80 (s, 2H).



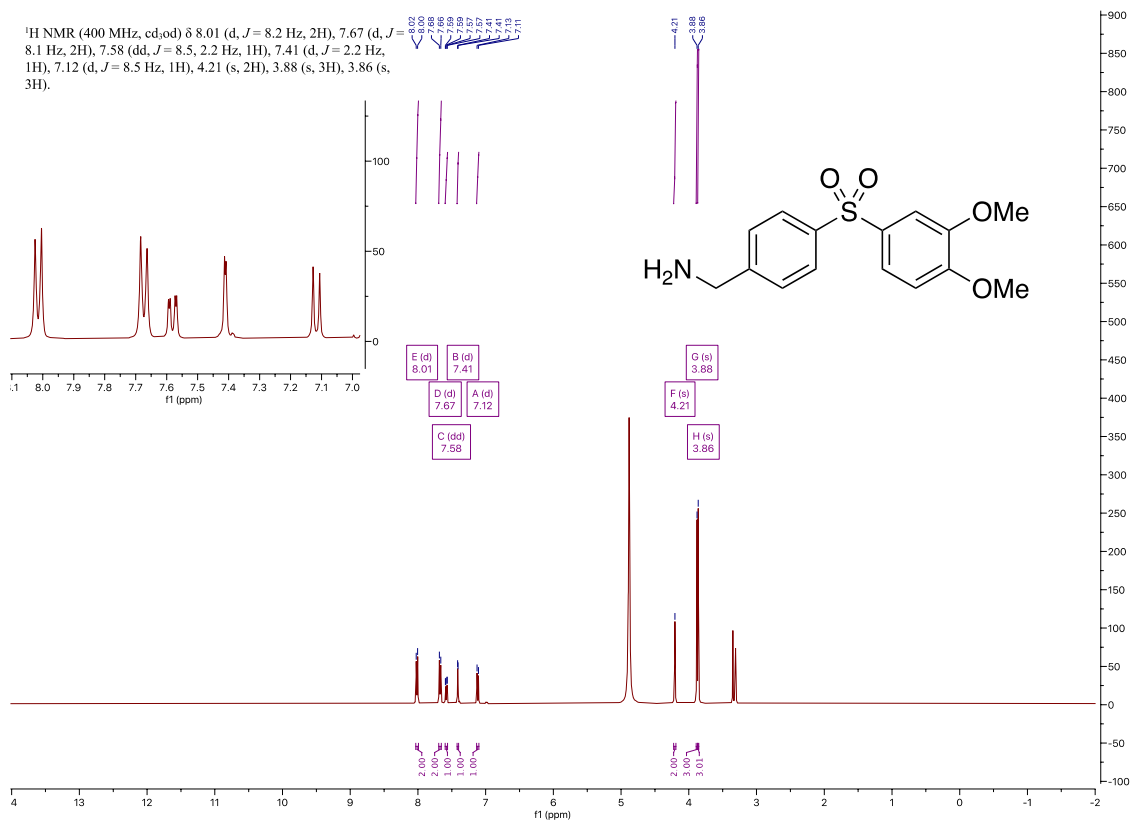
¹³C NMR (101 MHz, CDCl₃) of S3b

¹³C NMR (101 MHz, cdcl₃) δ 153.36, 149.46, 142.42, 135.25, 132.62, 128.92, 128.23, 122.13, 116.82, 111.02, 109.92, 56.42, 56.29, 23.65.



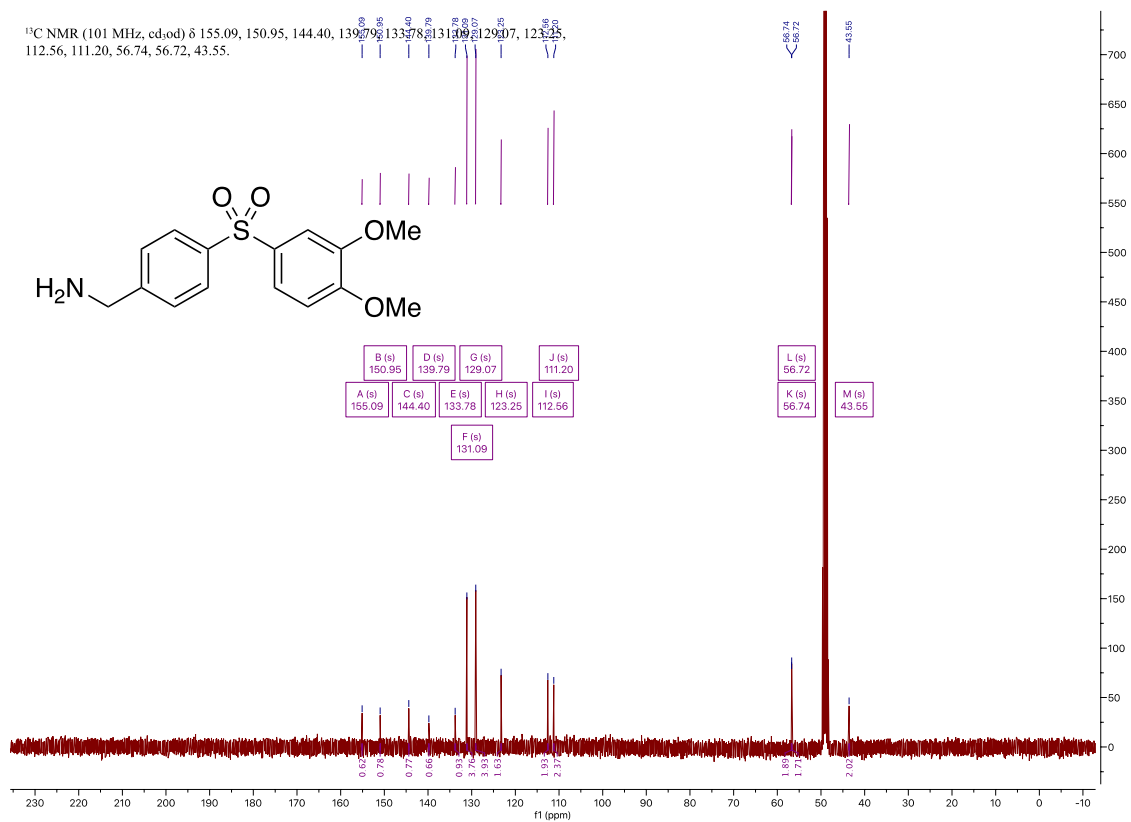
¹H NMR (400 MHz, CD₃OD) of S4a

¹H NMR (400 MHz, cd₃od) δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.58 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.41 (d, *J* = 2.2 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 1H), 4.21 (s, 2H), 3.88 (s, 3H), 3.86 (s, 3H).

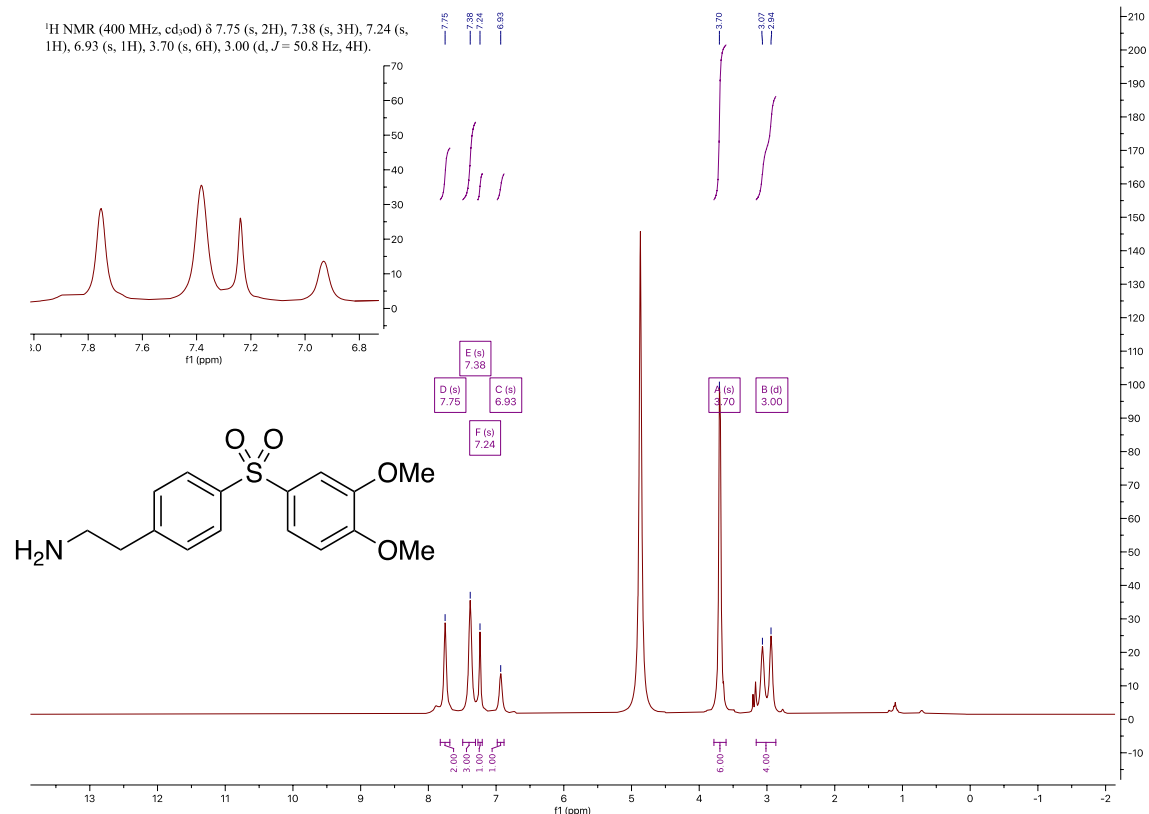


¹³C NMR (101 MHz, CD₃OD) of S4a

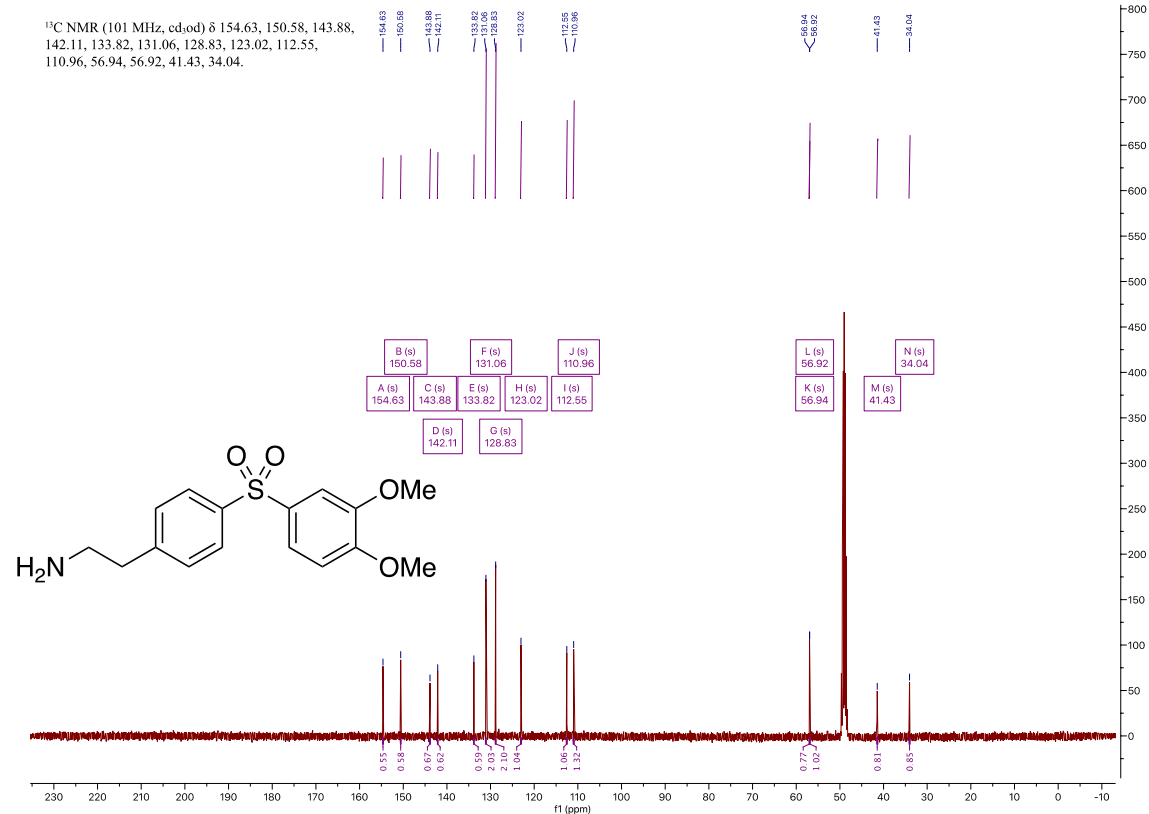
¹³C NMR (101 MHz, cd₃od) δ 155.09, 150.95, 144.40, 139.79, 133.78, 131.09, 129.07, 123.25, 112.56, 111.20, 56.74, 56.72, 43.55.



¹H NMR (400 MHz, CD₃OD) of S4b

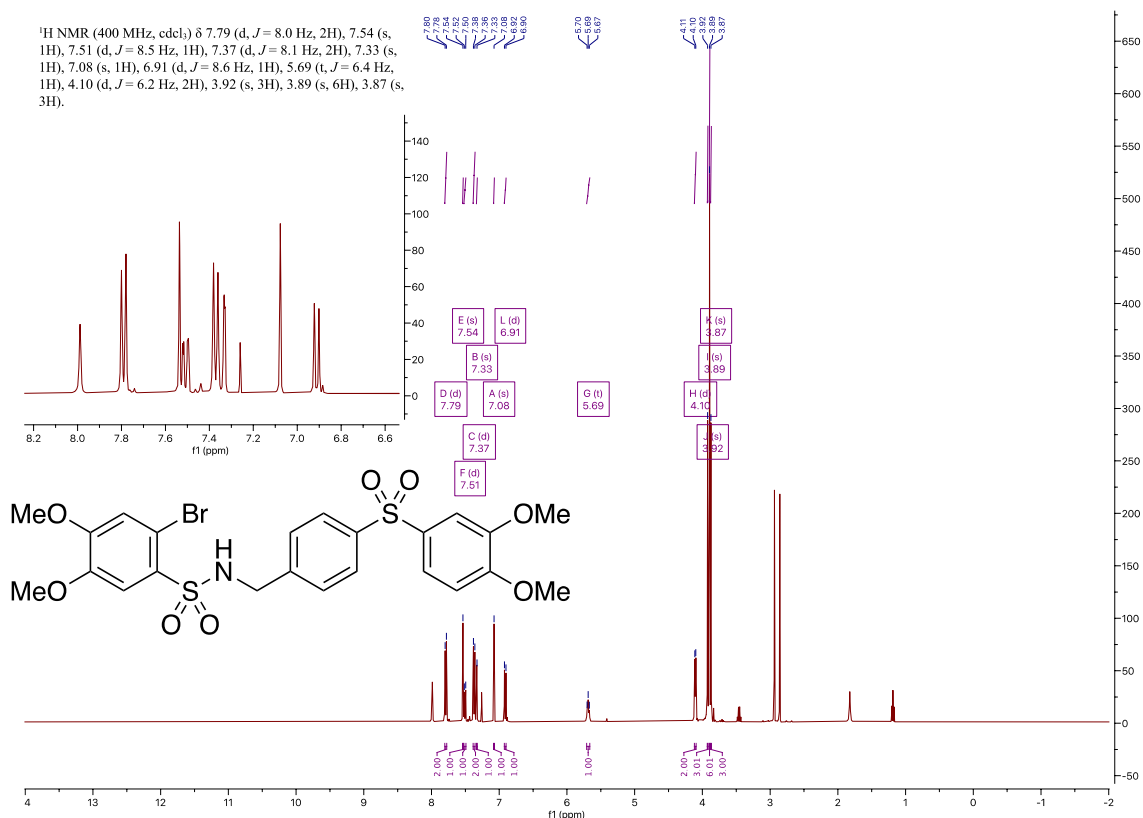


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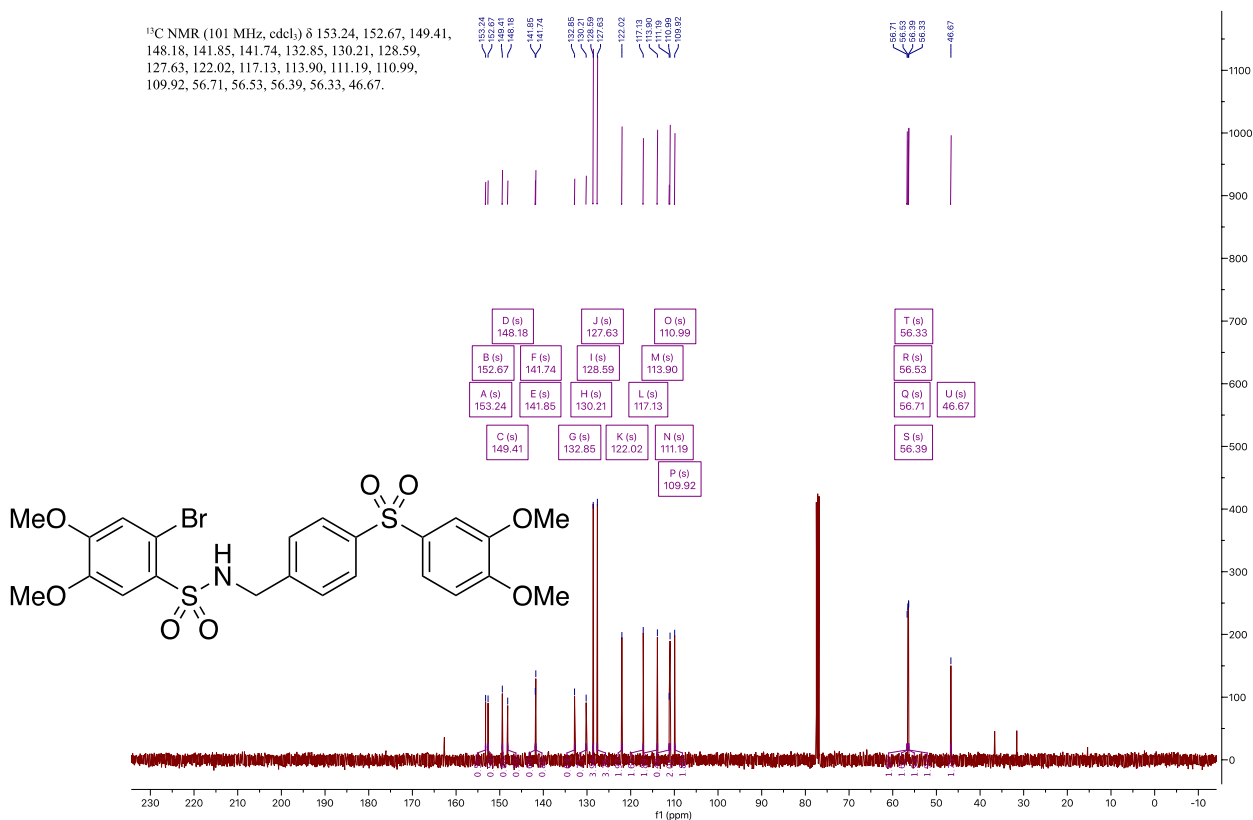
¹H NMR (400 MHz, CDCl₃) of 4a

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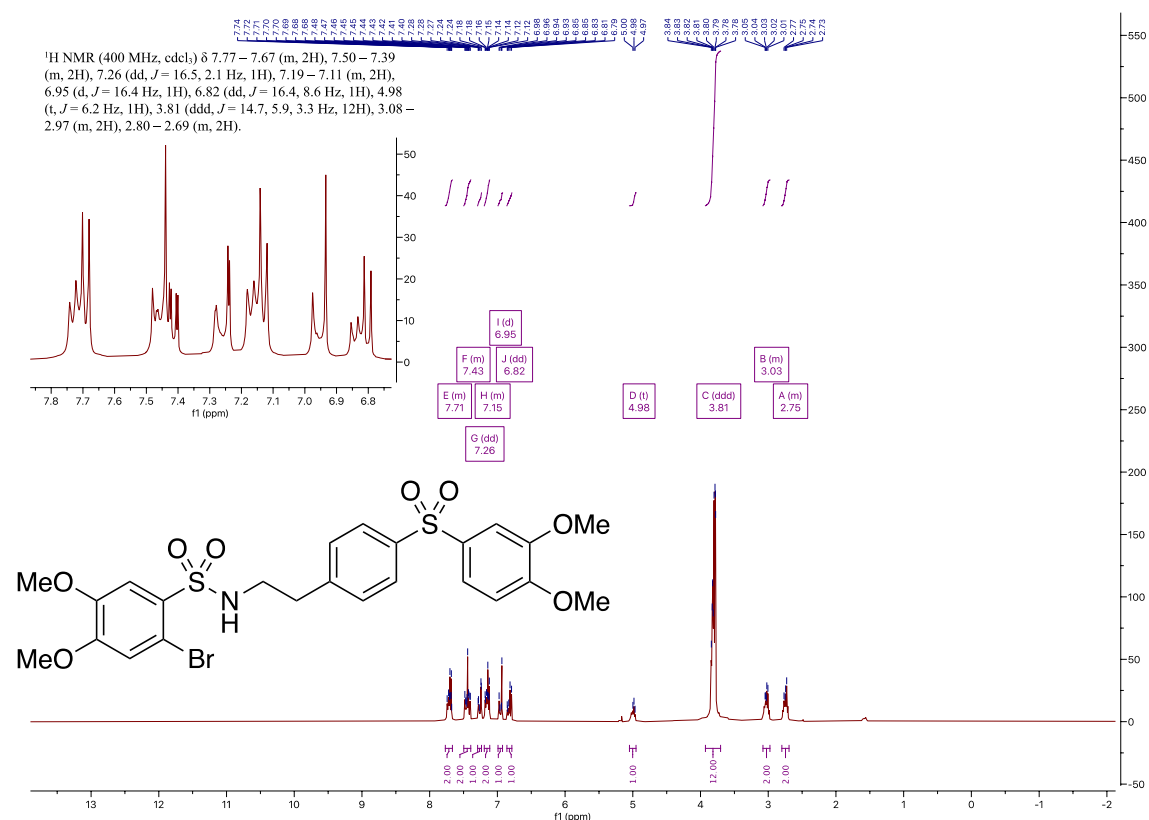


¹³C NMR (101 MHz, CDCl₃) of 4a

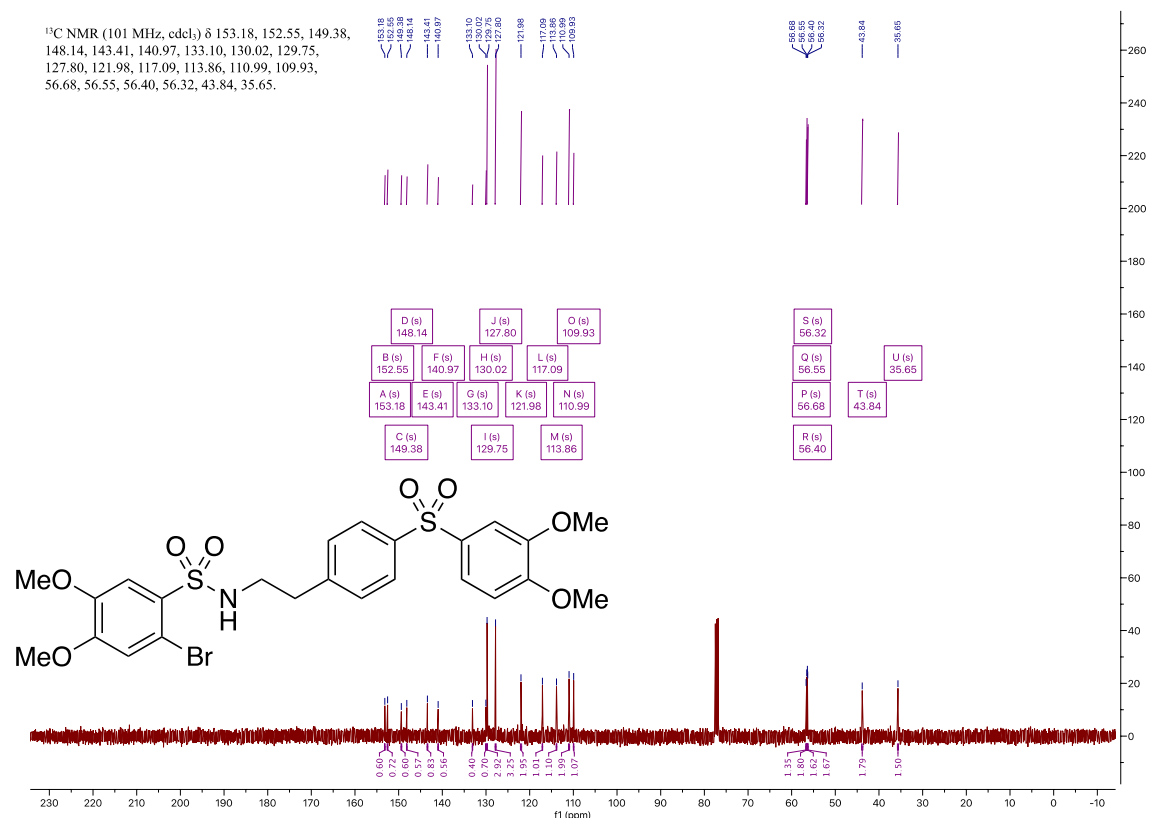
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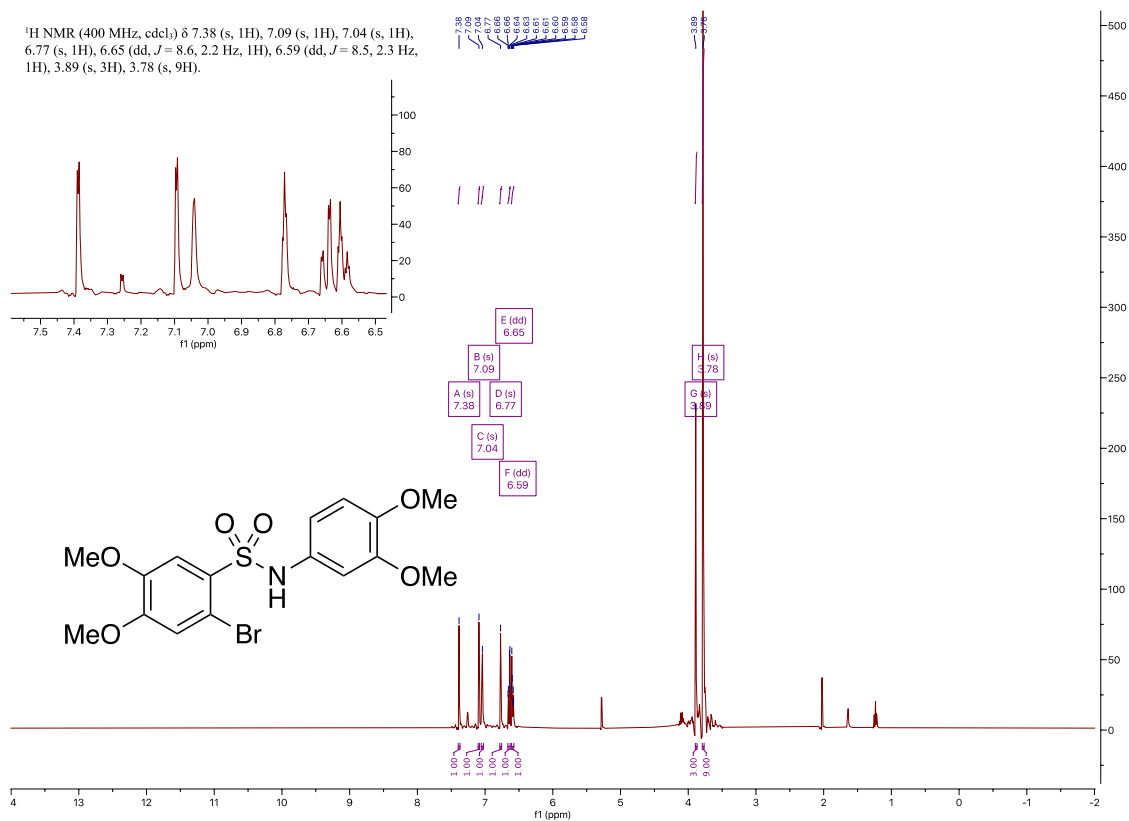


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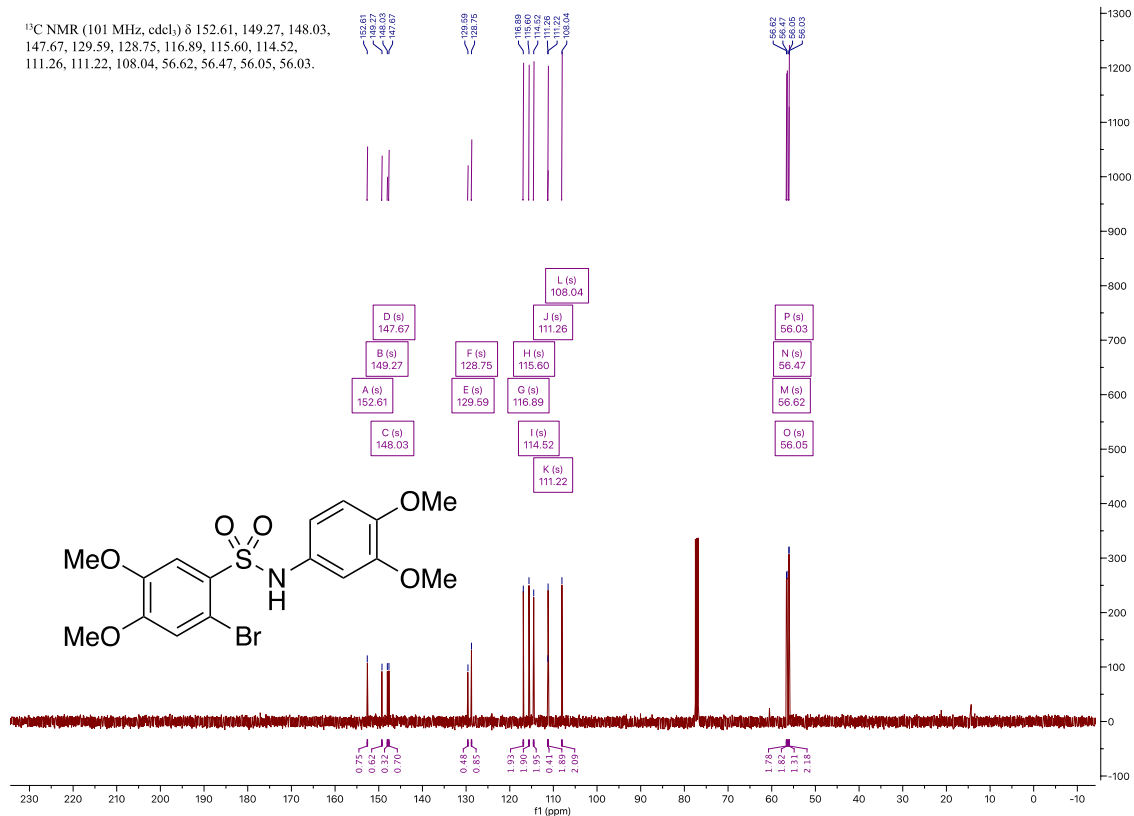
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¹H NMR (400 MHz, cdcl₃) δ 7.38 (s, 1H), 7.09 (s, 1H), 7.04 (s, 1H), 6.77 (s, 1H), 6.65 (dd, J = 8.6, 2.2 Hz, 1H), 6.59 (dd, J = 8.5, 2.3 Hz, 1H), 3.89 (s, 3H), 3.78 (s, 9H).

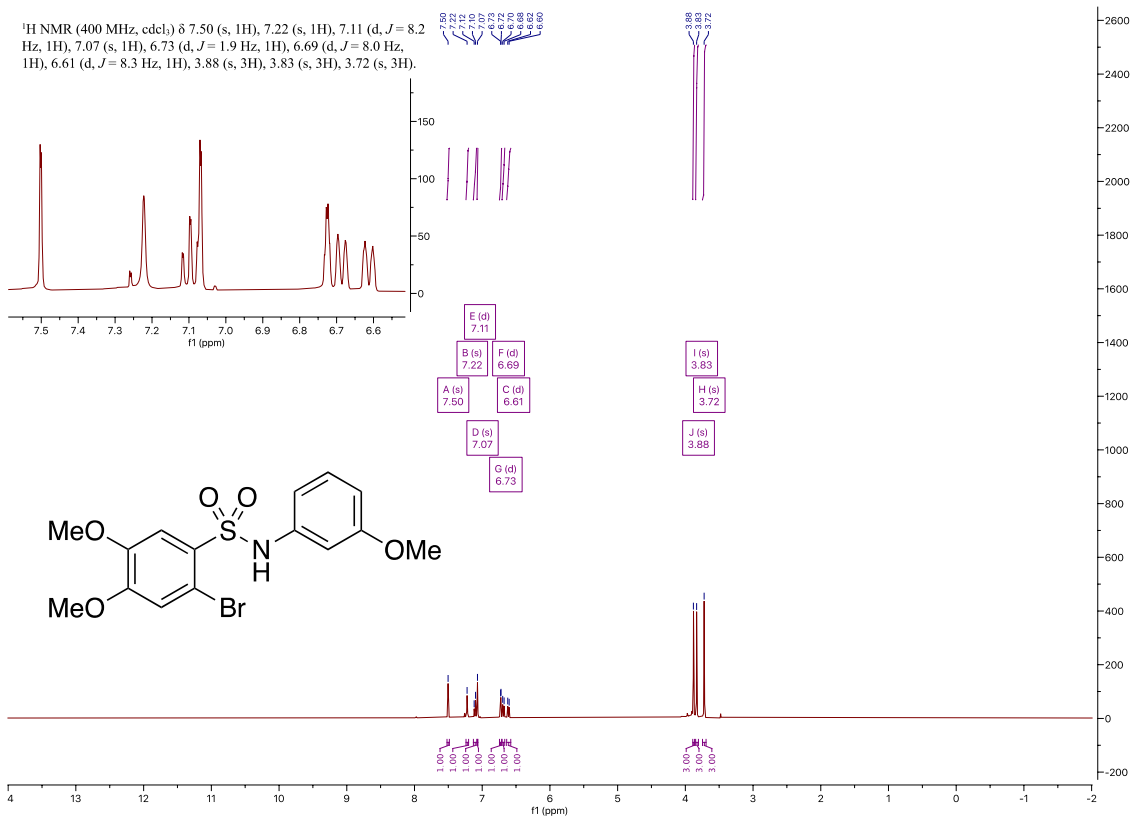


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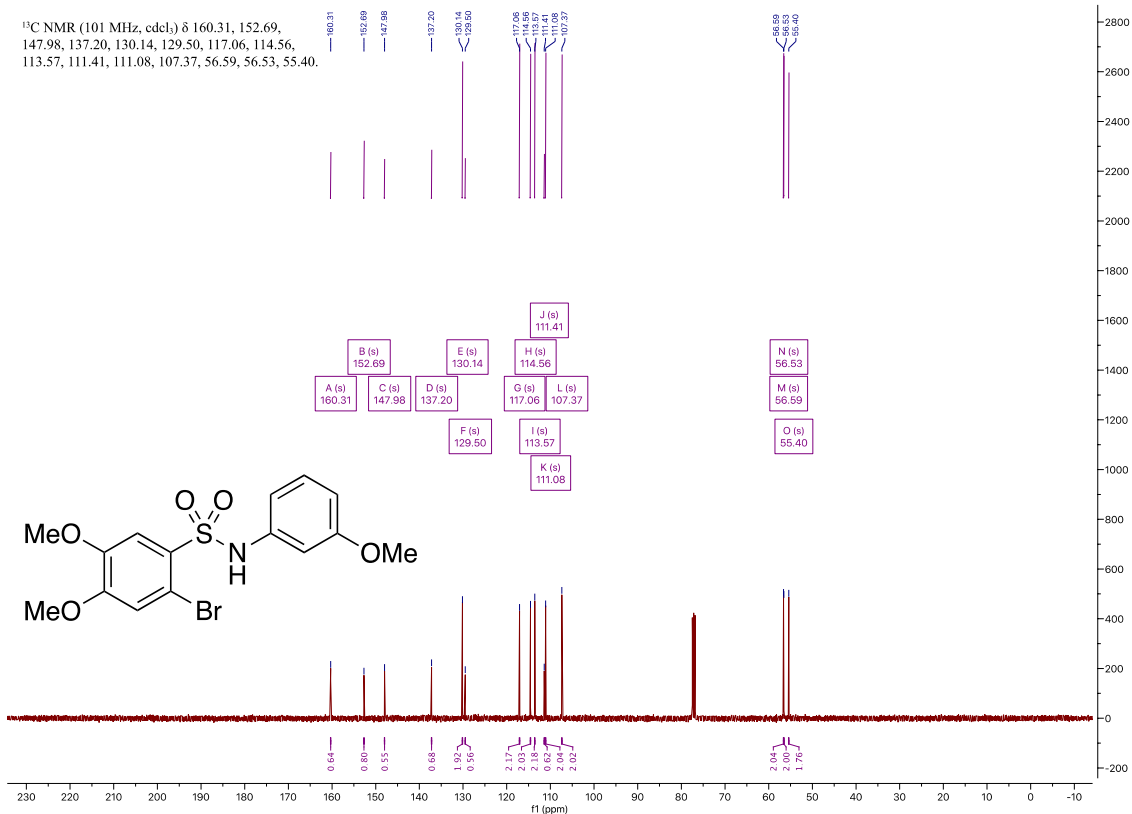
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¹H NMR (400 MHz, CDCl₃) of 4d

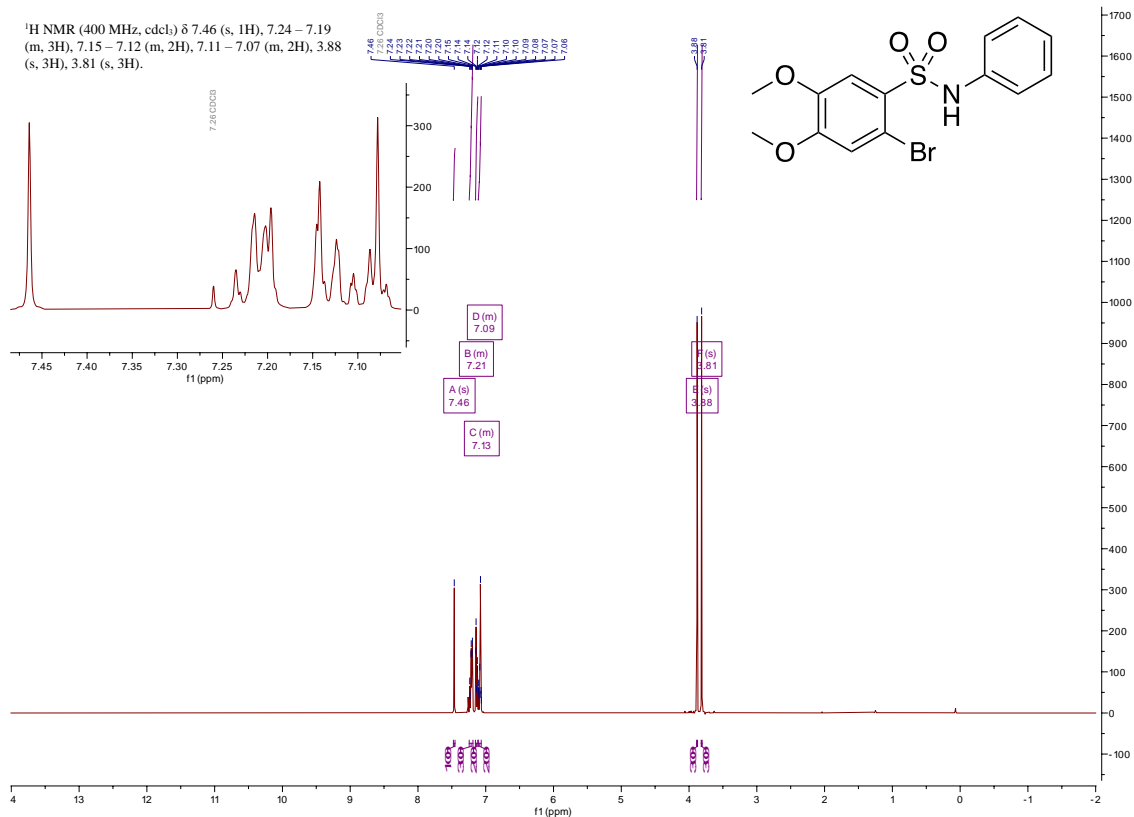


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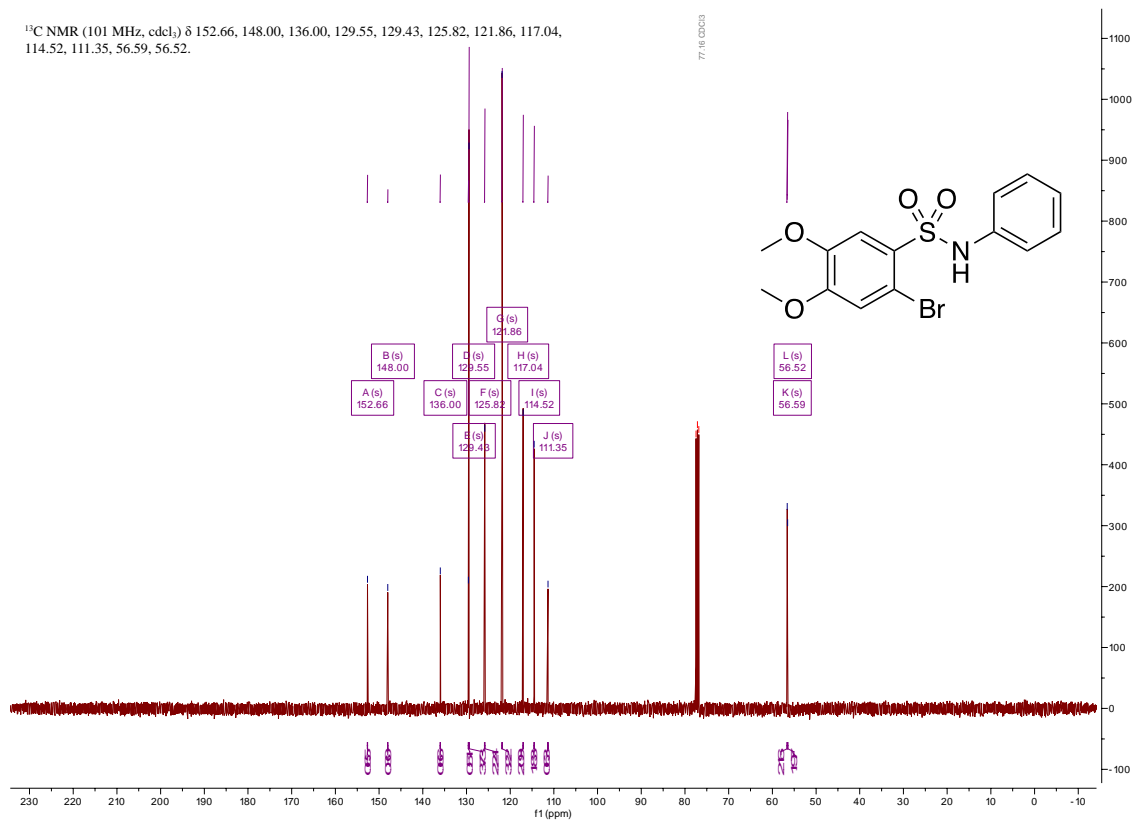
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¹H NMR (400 MHz, cdcl₃) δ 7.46 (s, 1H), 7.24 – 7.19 (m, 3H), 7.15 – 7.12 (m, 2H), 7.11 – 7.07 (m, 2H), 3.88 (s, 3H), 3.81 (s, 3H).



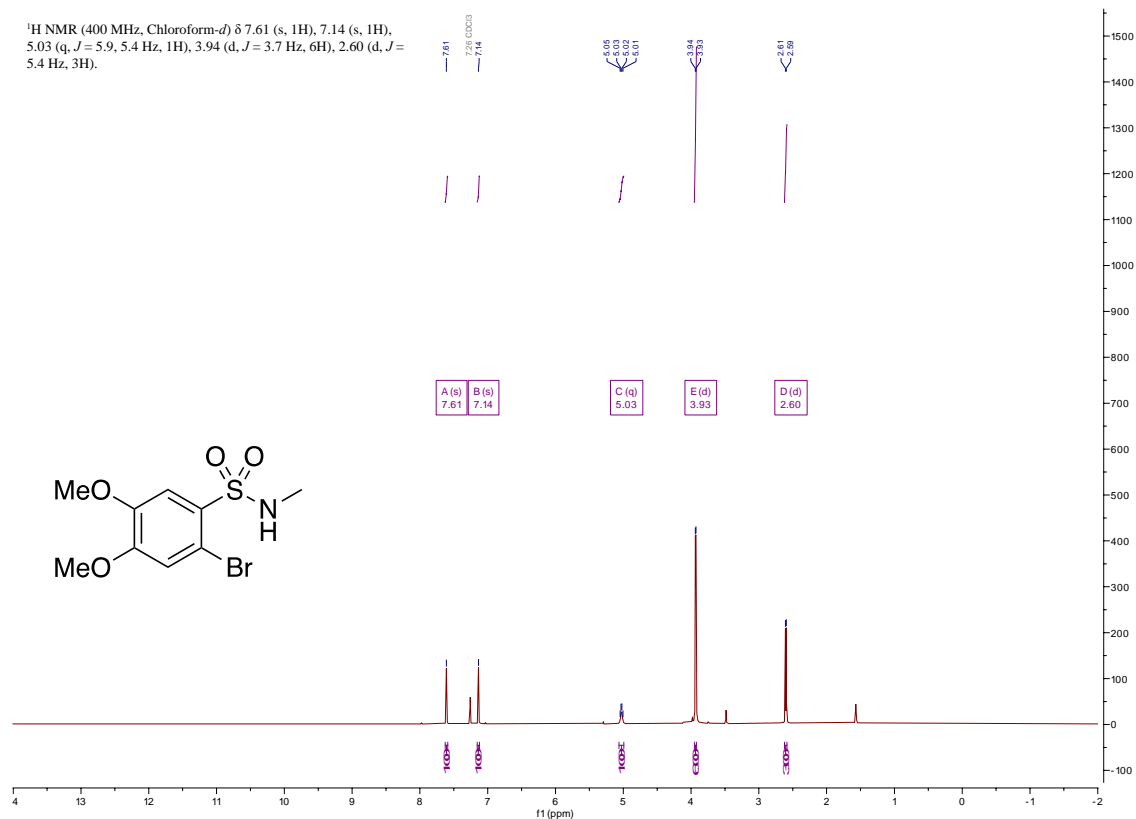
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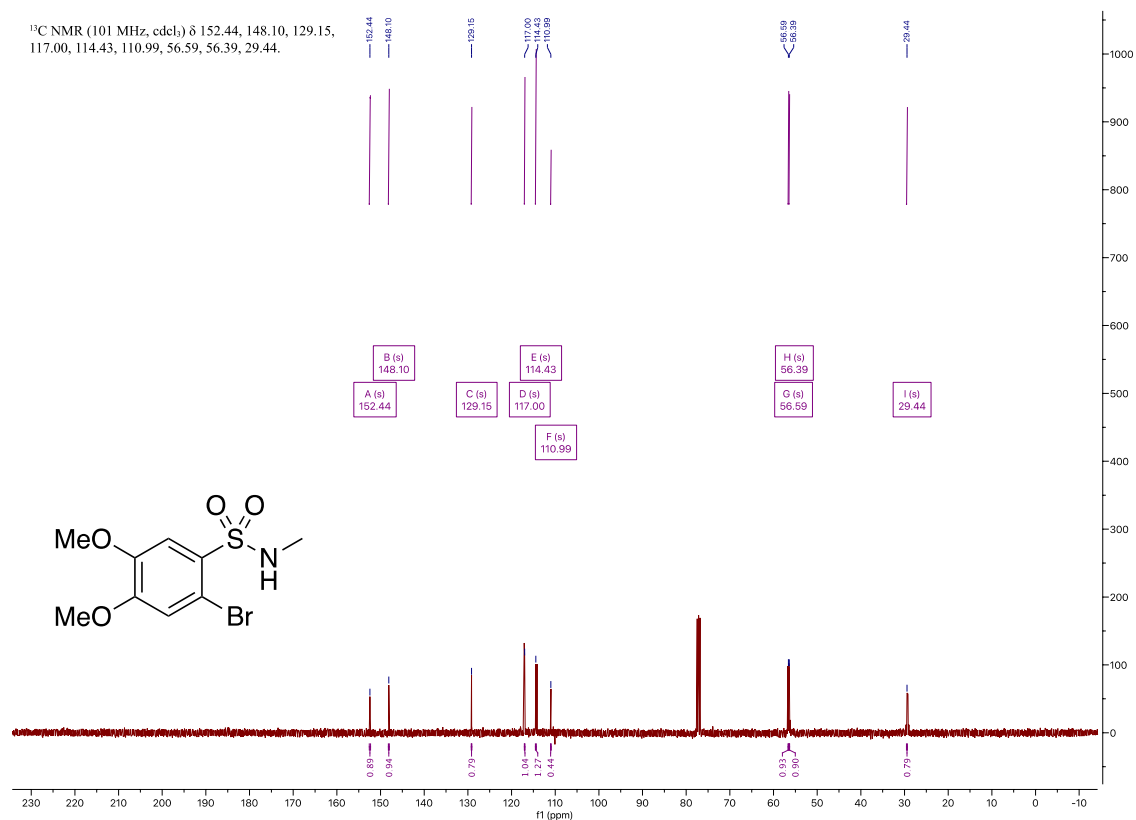
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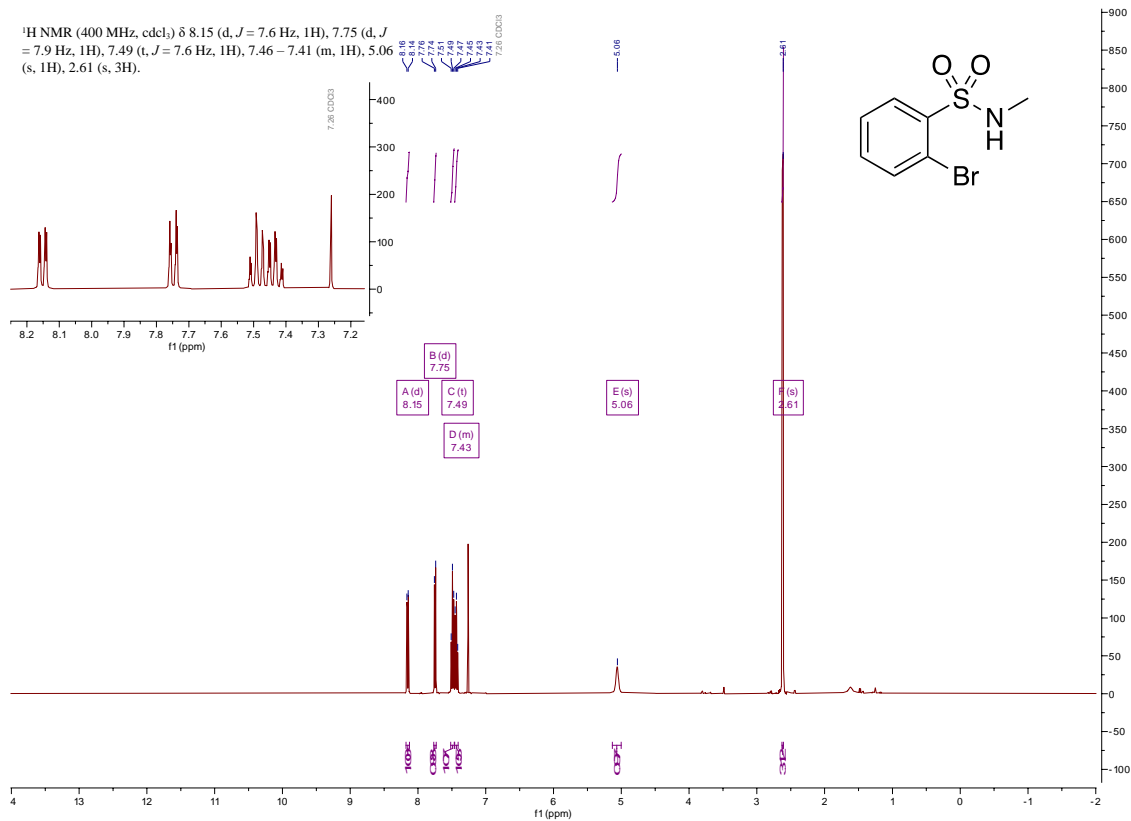
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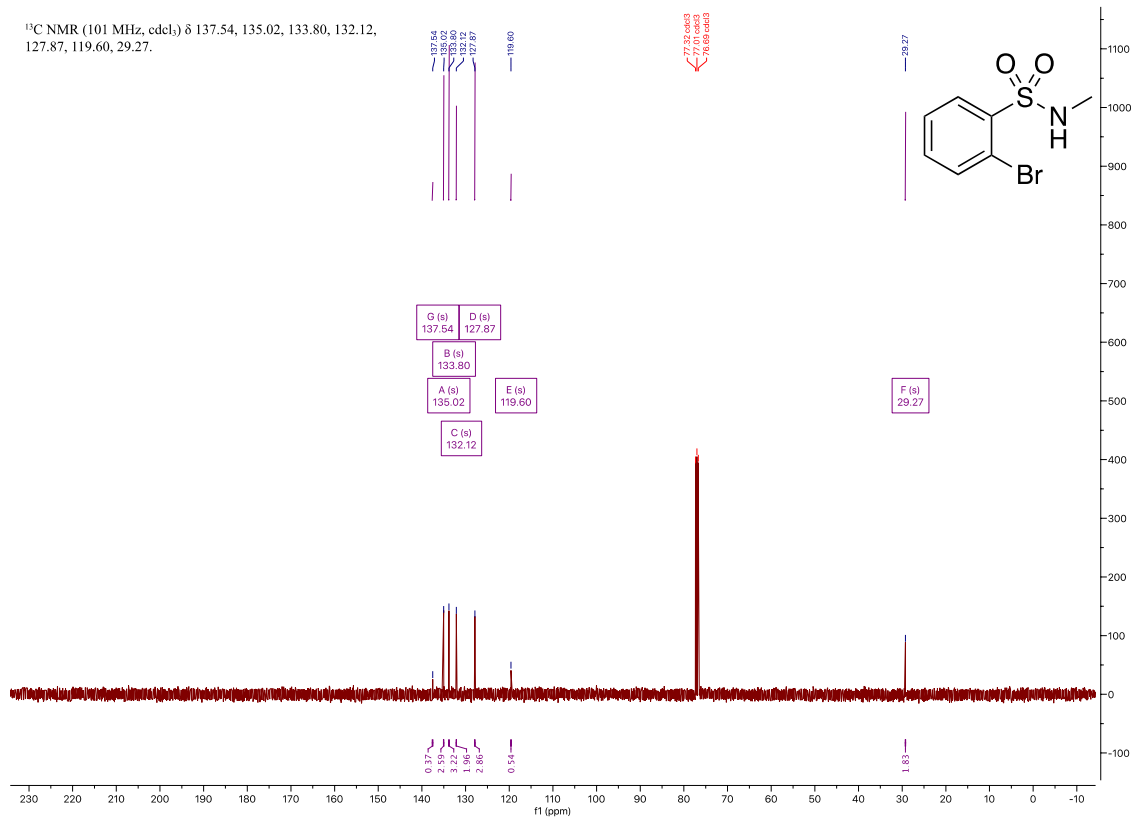
^1H NMR (400 MHz, CDCl_3) of 4g

^1H NMR (400 MHz, cdCl_3) δ 8.15 (d, $J = 7.6$ Hz, 1H), 7.75 (d, $J = 7.9$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 1H), 7.46–7.41 (m, 1H), 5.06 (s, 1H), 2.61 (s, 3H).

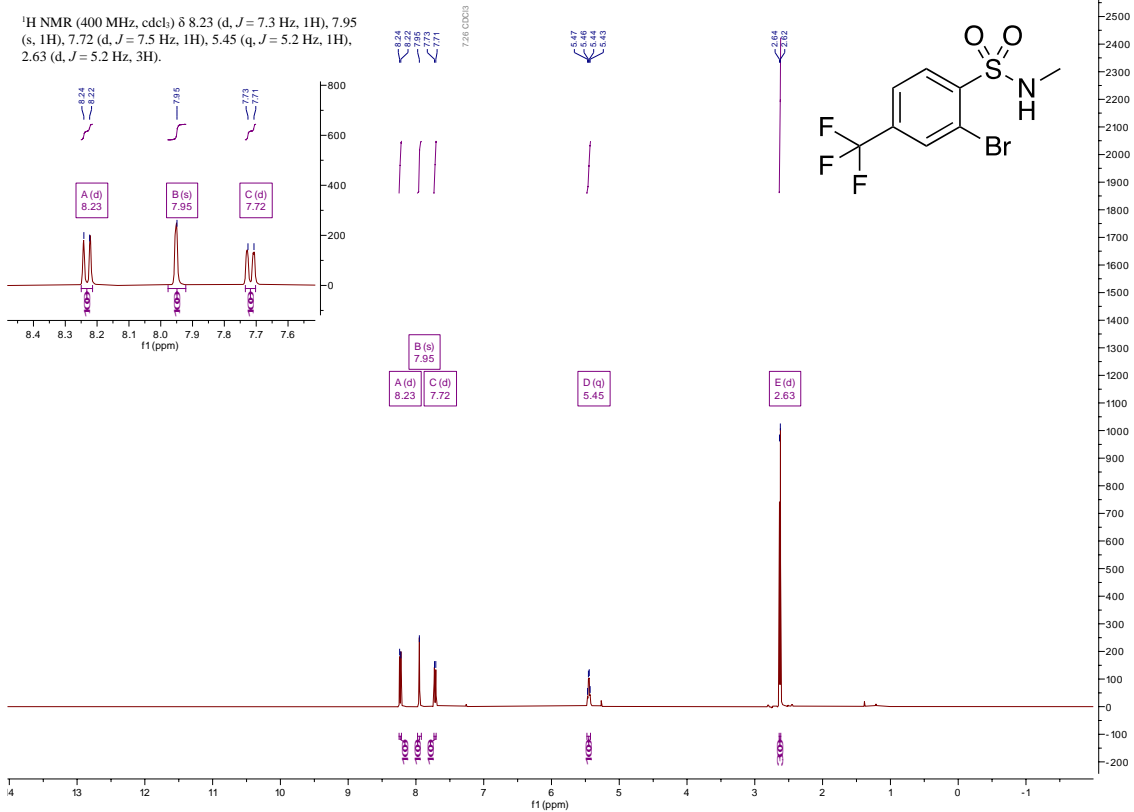


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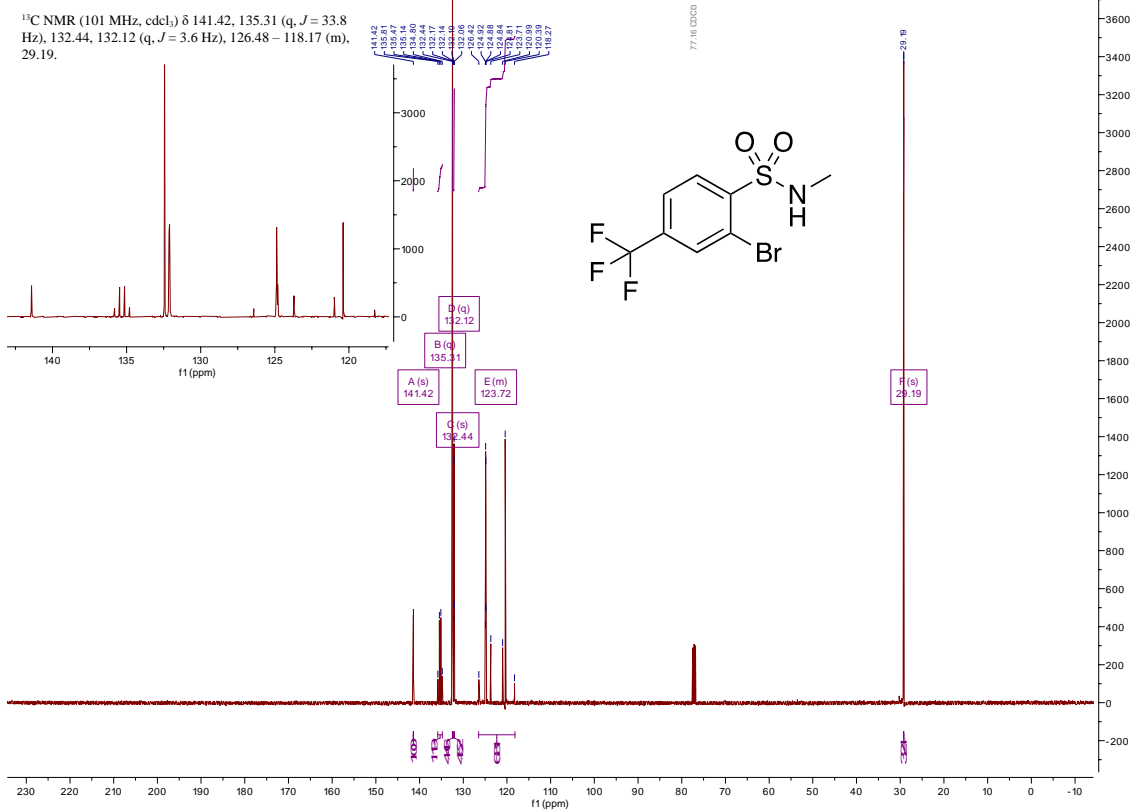
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^1H NMR (400 MHz, CDCl_3) of 4h

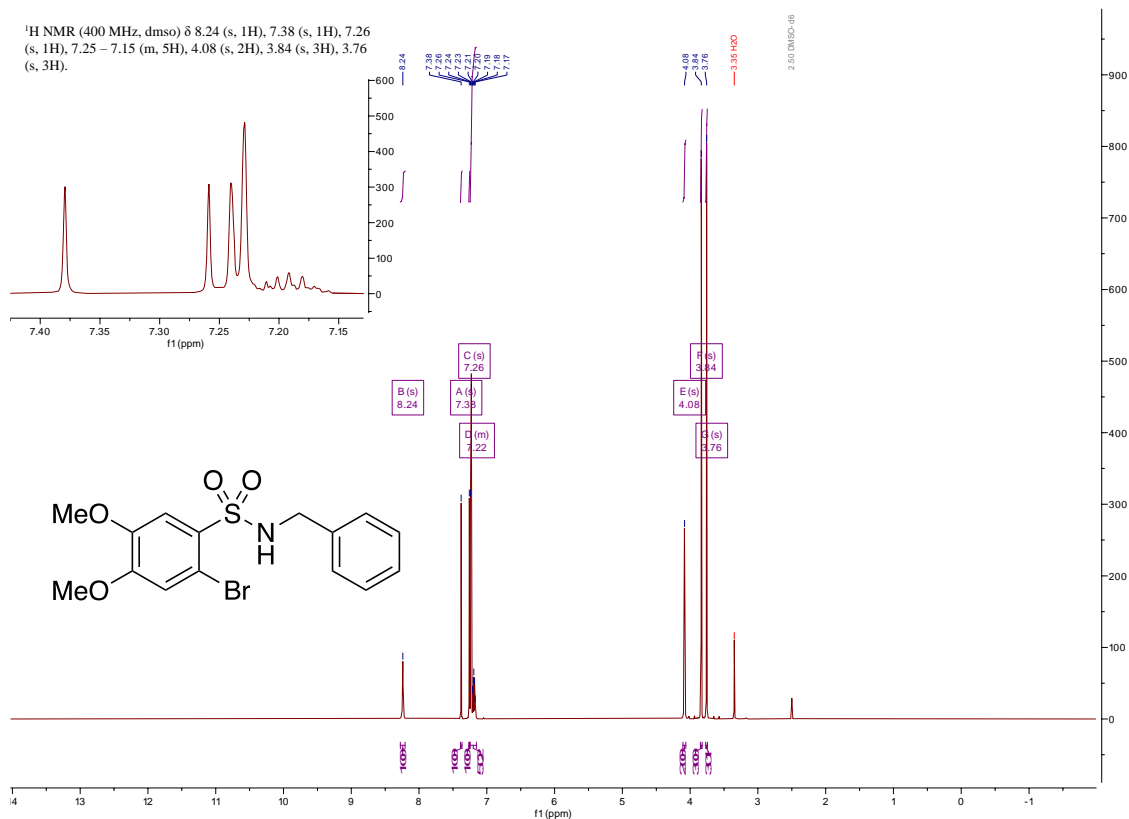


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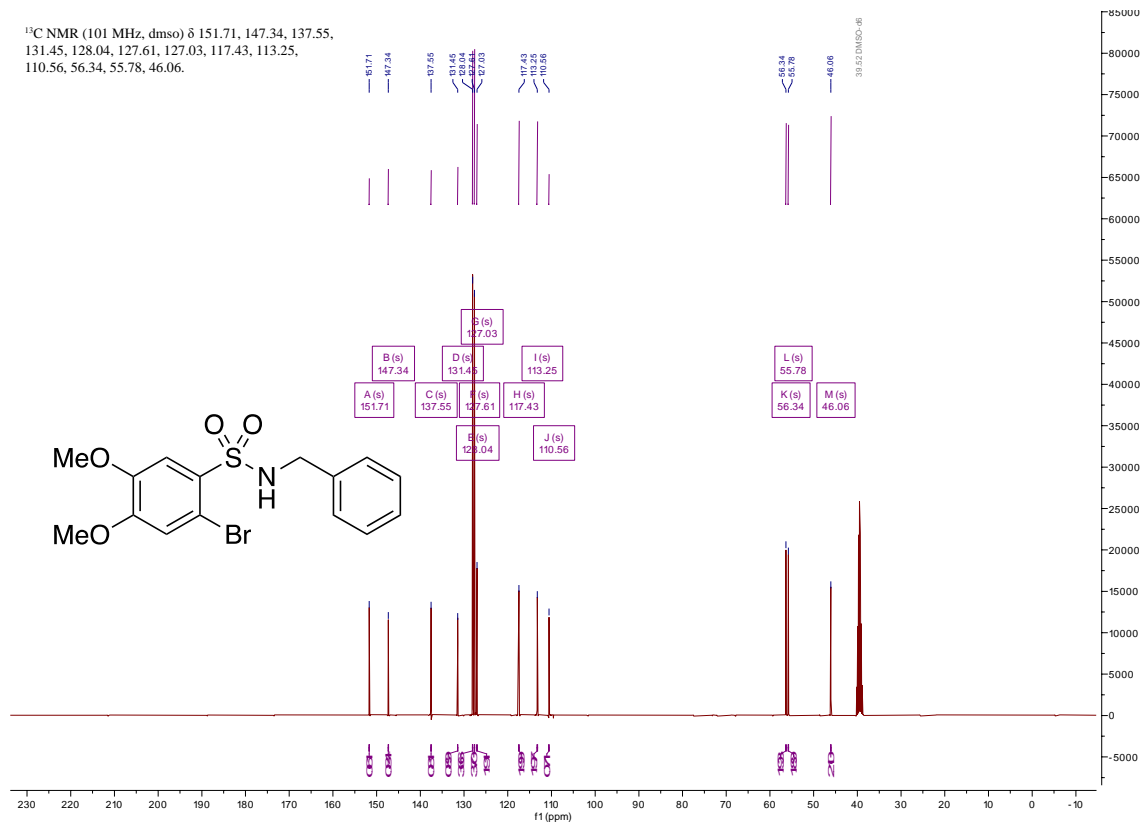
¹H NMR (400 MHz, (CD₃)₂SO) of 4i

¹H NMR (400 MHz, dmsO) δ 8.24 (s, 1H), 7.38 (s, 1H), 7.26 (s, 1H), 7.25 – 7.15 (m, 5H), 4.08 (s, 2H), 3.84 (s, 3H), 3.76 (s, 3H).

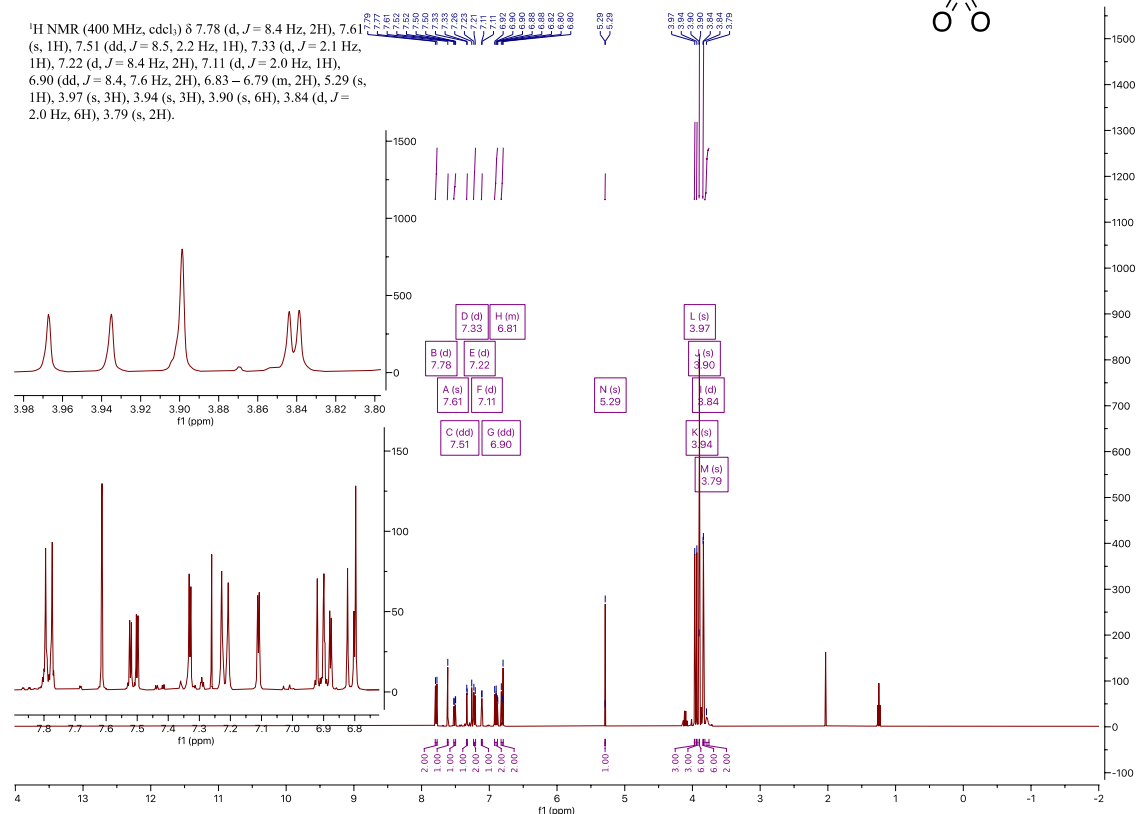


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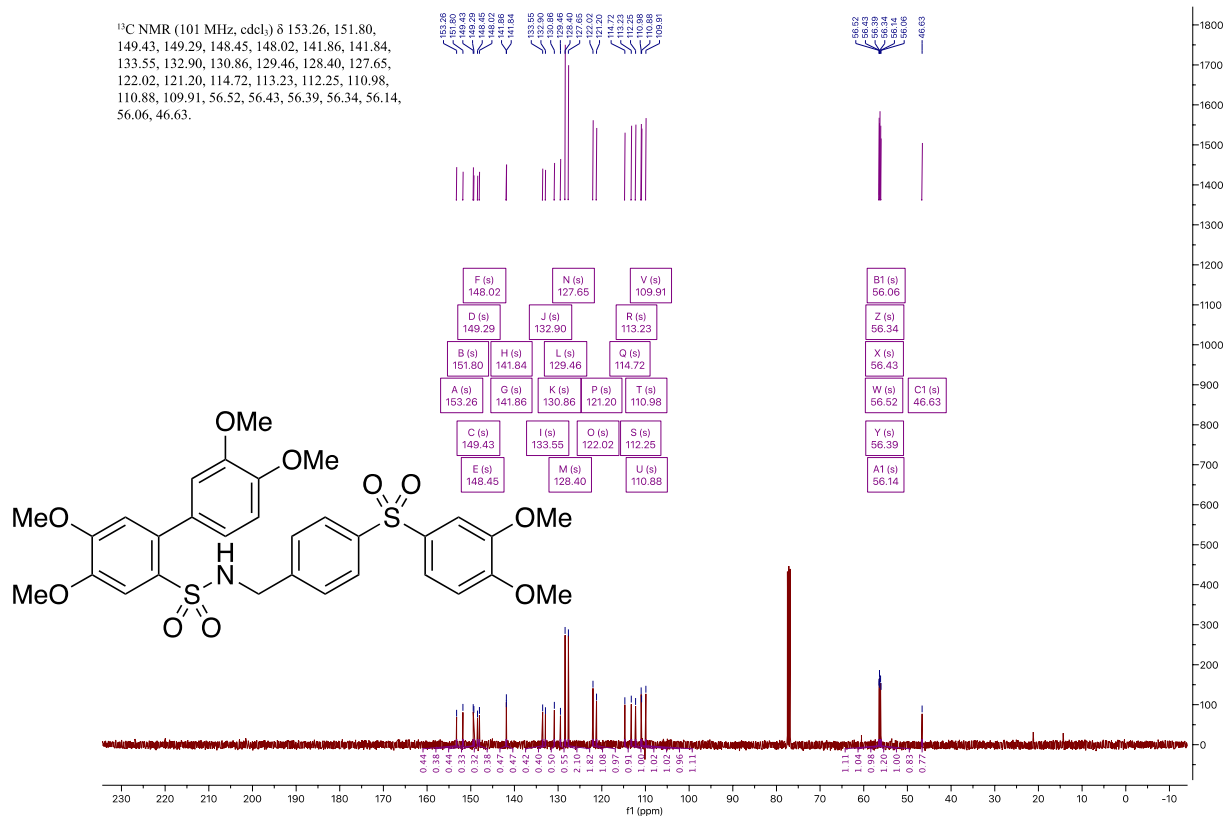
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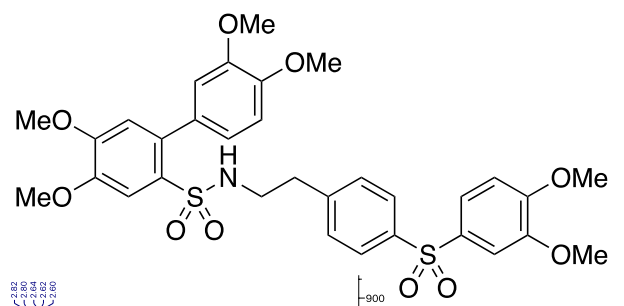


¹H NMR (400 MHz, CDCl₃) of 5a

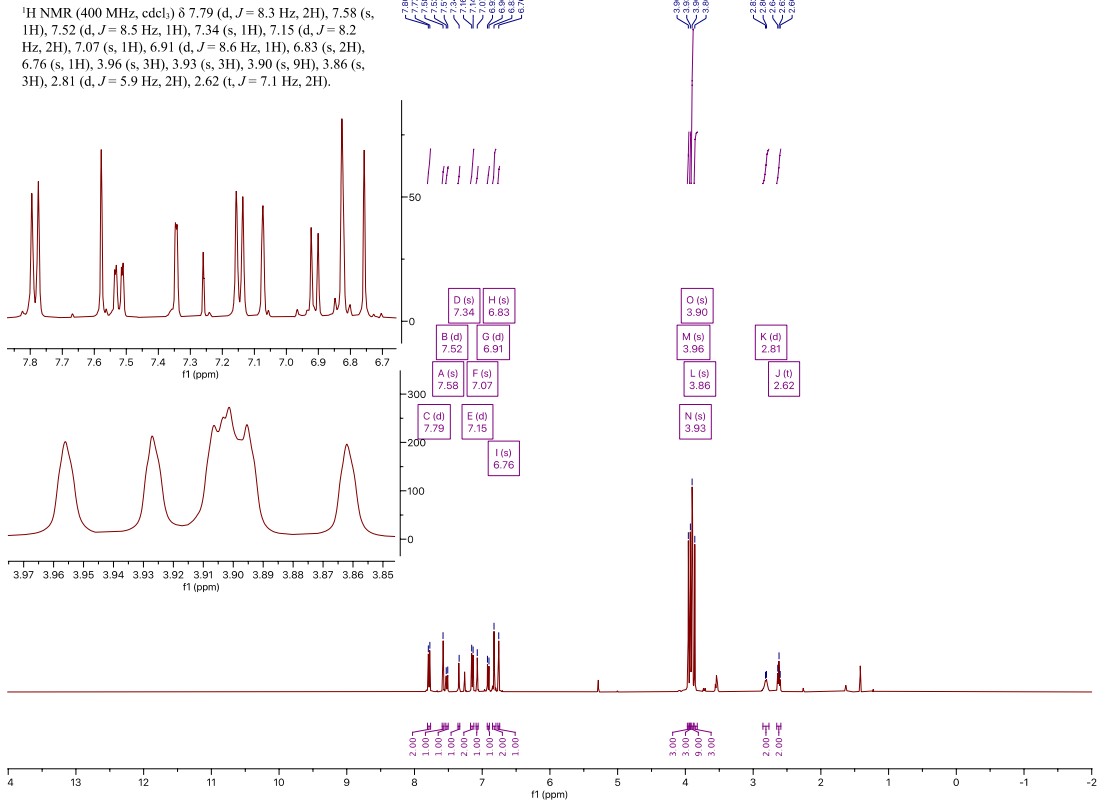


¹³C NMR (101 MHz, CDCl₃) of 5a

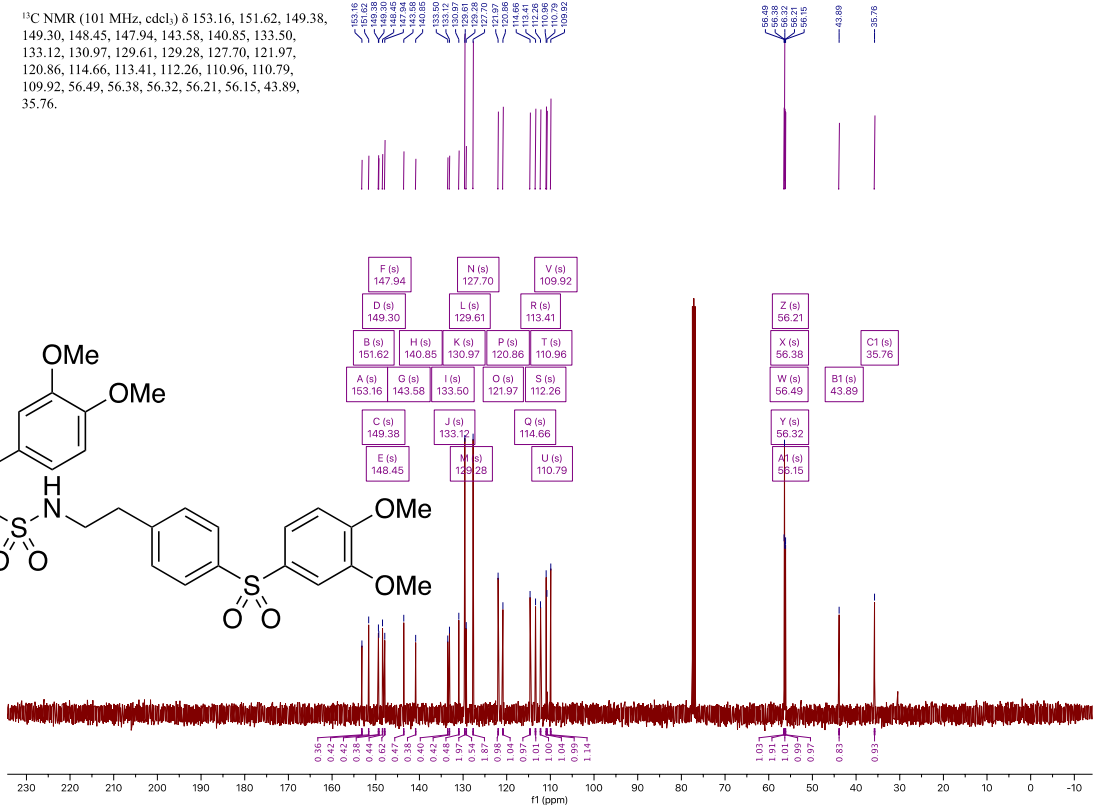




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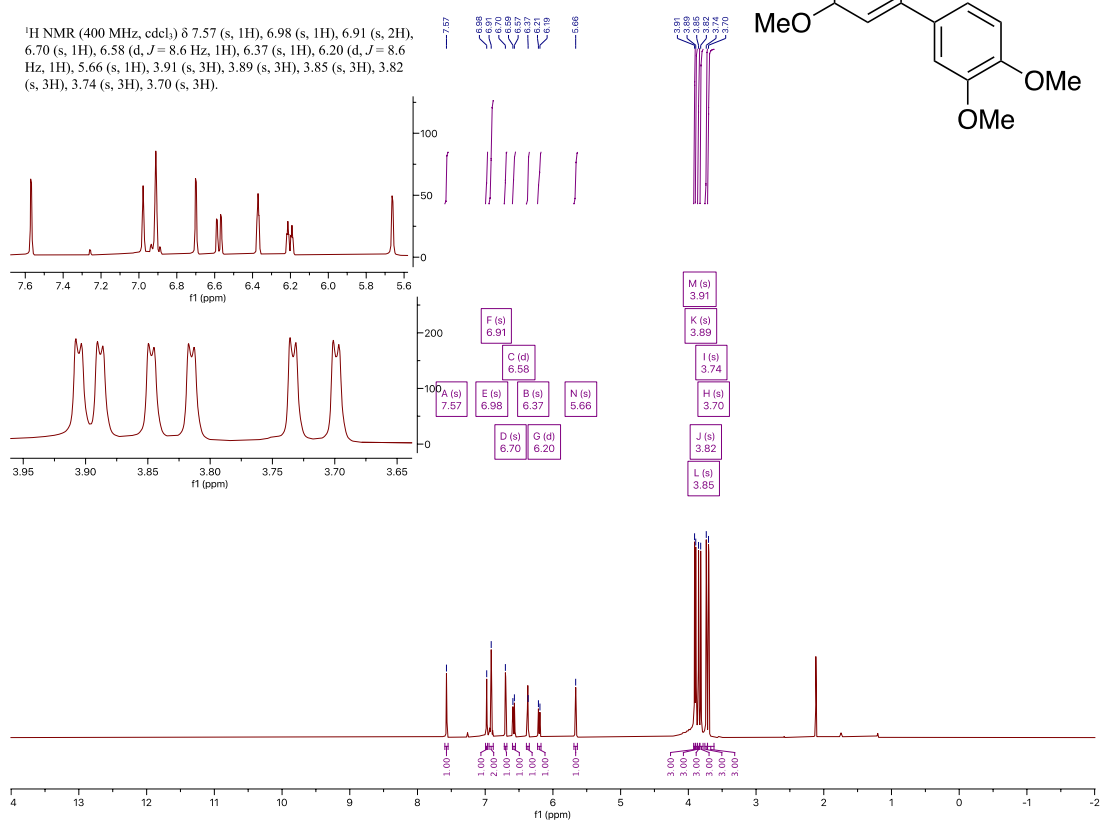


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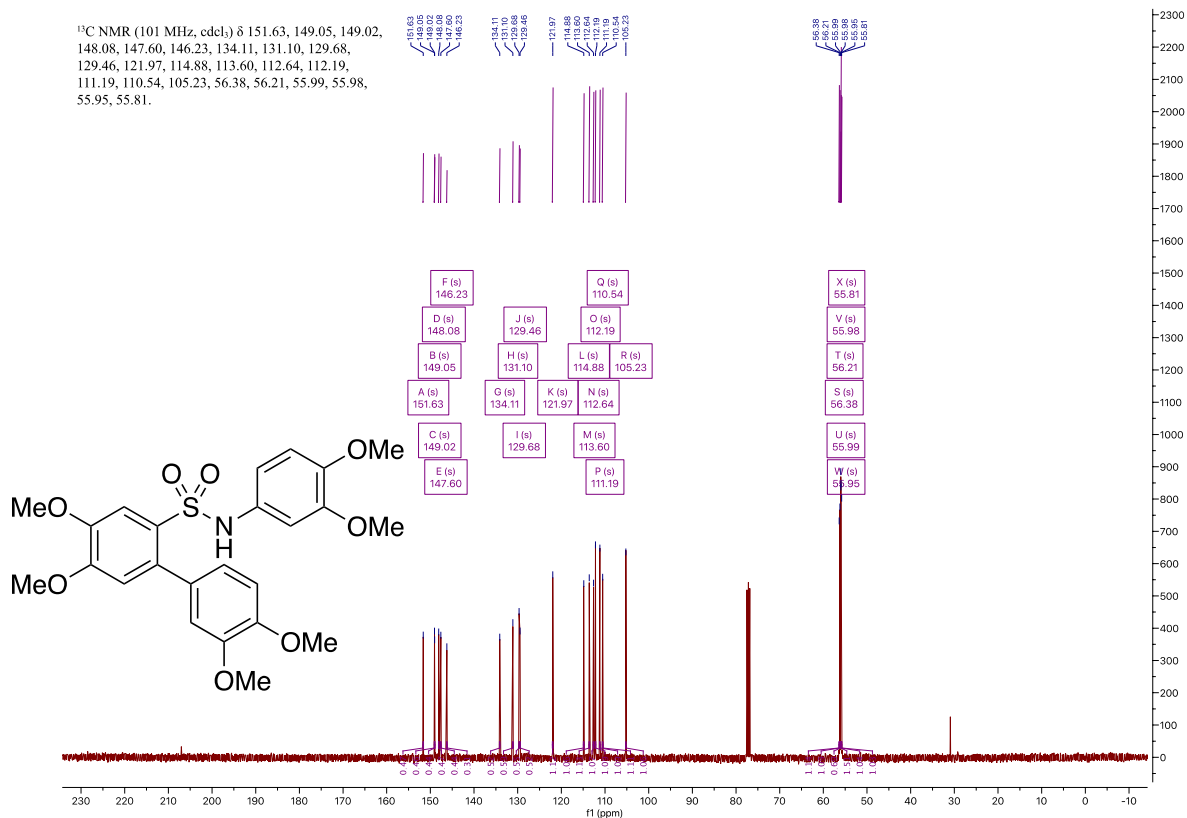
¹H NMR (400 MHz, CDCl₃) of 5c

¹H NMR (400 MHz, cdcl₃) δ 7.57 (s, 1H), 6.98 (s, 1H), 6.91 (s, 2H), 6.70 (s, 1H), 6.58 (d, *J* = 8.6 Hz, 1H), 6.37 (s, 1H), 6.20 (d, *J* = 8.6 Hz, 1H), 5.66 (s, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 3.85 (s, 3H), 3.82 (s, 3H), 3.74 (s, 3H), 3.70 (s, 3H).



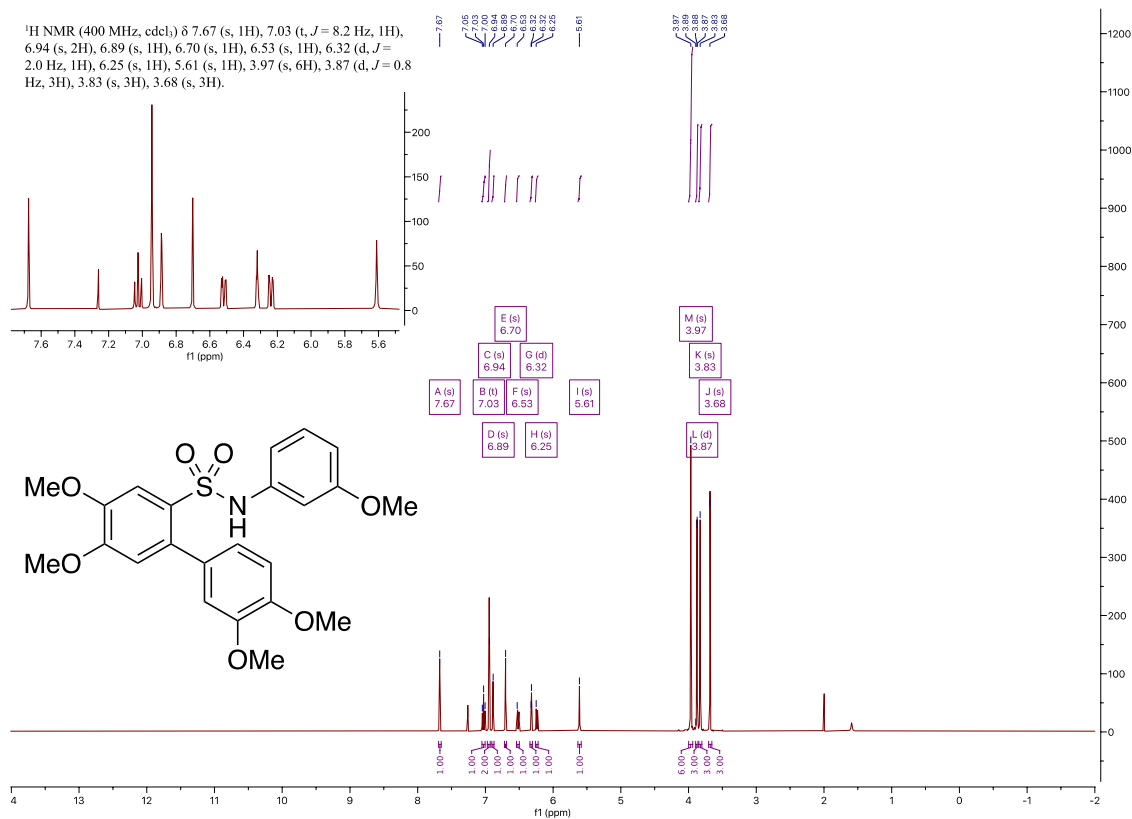
¹³C NMR (101 MHz, CDCl₃) of 5c

¹³C NMR (101 MHz, cdcl₃) δ 151.63, 149.05, 149.02, 148.08, 147.60, 146.23, 134.11, 131.10, 129.68, 129.46, 121.97, 114.88, 113.60, 112.64, 112.19, 111.19, 110.54, 105.23, 56.38, 56.21, 55.99, 55.98, 55.95, 55.81.



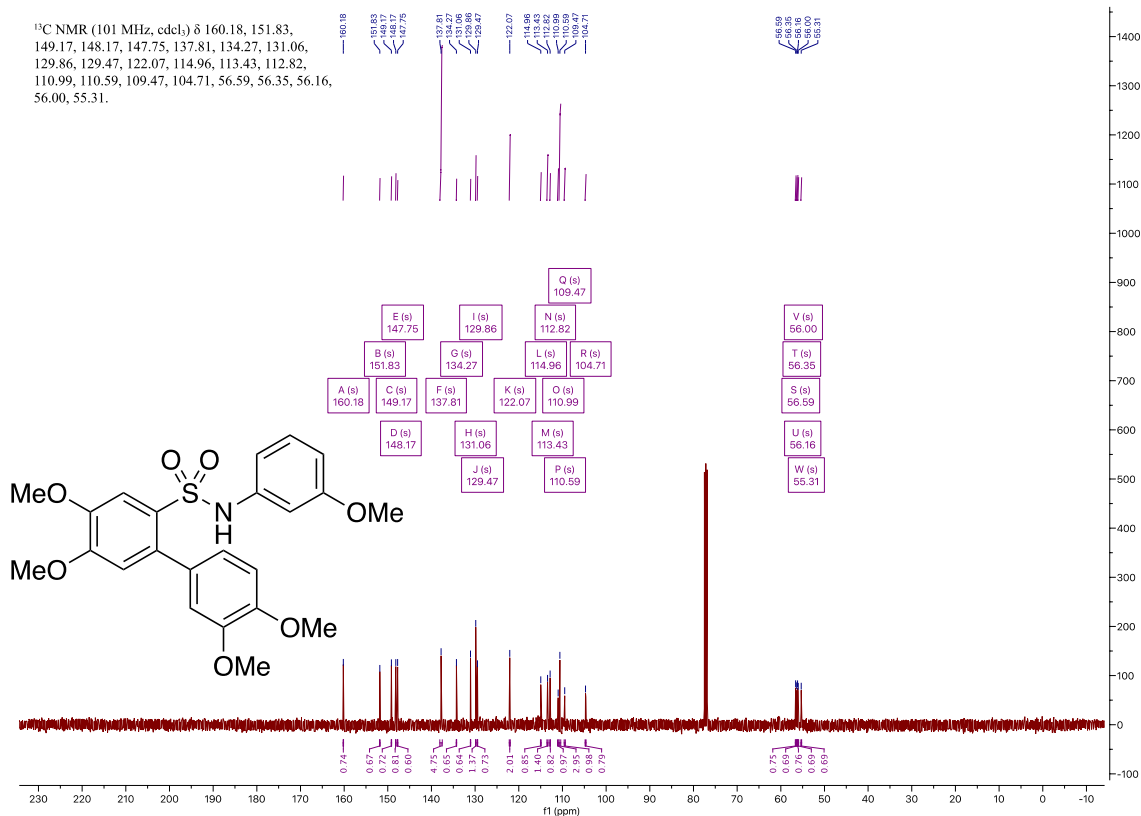
¹H NMR (400 MHz, CDCl₃) of 5d

¹H NMR (400 MHz, cdcl₃) δ 7.67 (s, 1H), 7.03 (t, *J* = 8.2 Hz, 1H), 6.94 (s, 2H), 6.89 (s, 1H), 6.70 (s, 1H), 6.53 (s, 1H), 6.32 (d, *J* = 2.0 Hz, 1H), 6.25 (s, 1H), 5.61 (s, 1H), 3.97 (s, 6H), 3.87 (d, *J* = 0.8 Hz, 3H), 3.83 (s, 3H), 3.68 (s, 3H).



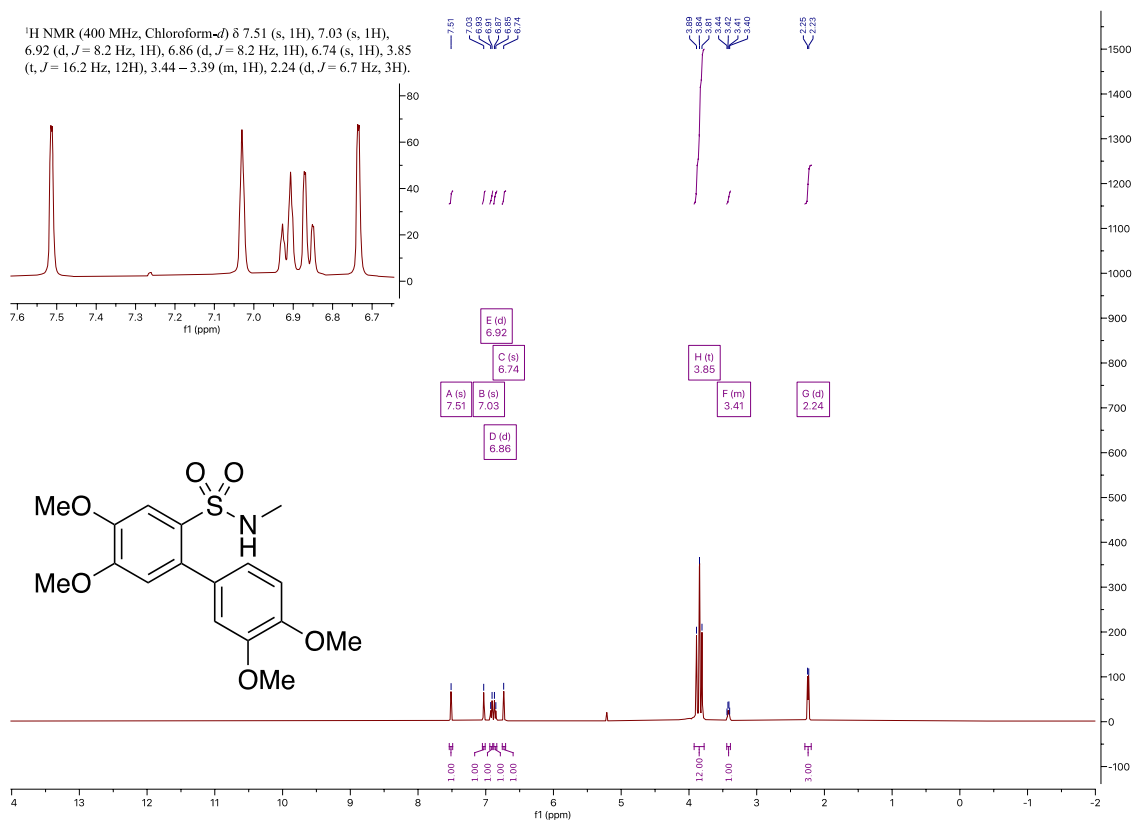
¹³C NMR (101 MHz, CDCl₃) of 5d

¹³C NMR (101 MHz, cdcl₃) δ 160.18, 151.83, 149.17, 148.17, 147.75, 137.81, 134.27, 131.06, 129.86, 129.47, 122.07, 114.96, 113.43, 112.82, 110.99, 110.59, 109.47, 104.71, 56.59, 56.35, 56.16, 56.00, 55.31.



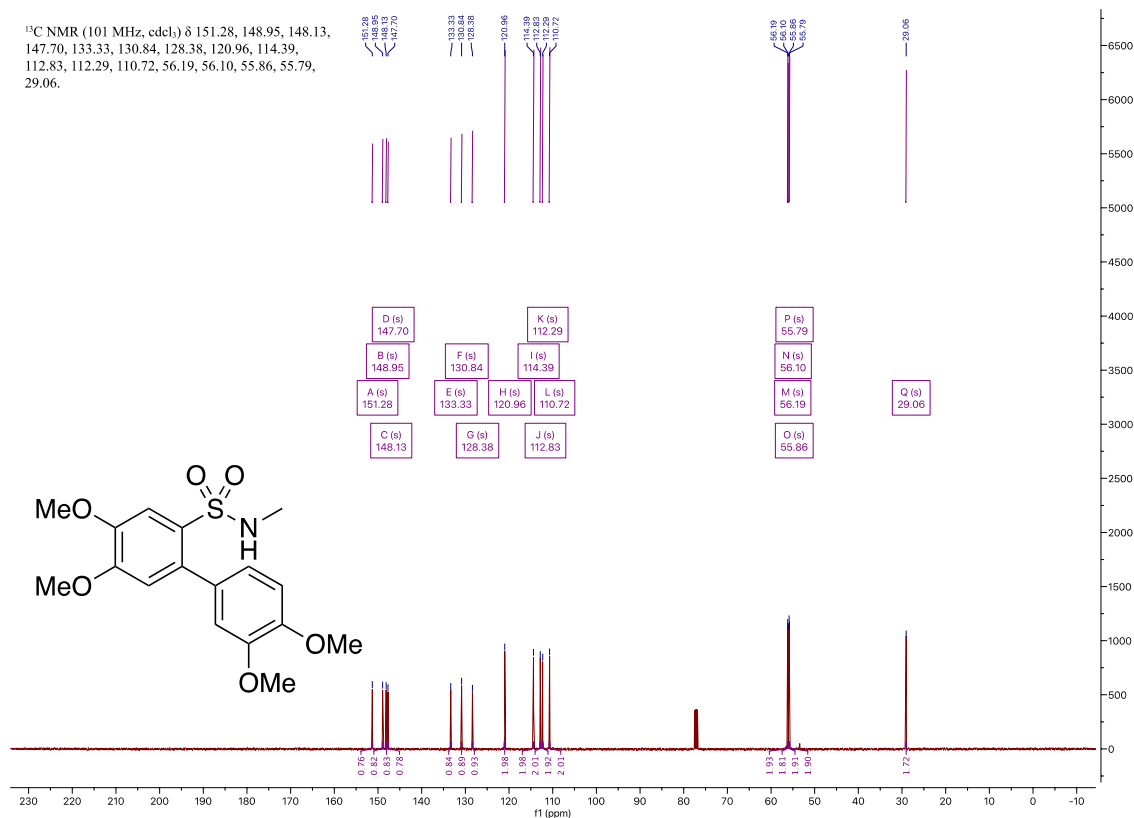
¹H NMR (400 MHz, CDCl₃) of 5f

¹H NMR (400 MHz, Chloroform-*d*) δ 7.51 (s, 1H), 7.03 (s, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.74 (s, 1H), 3.85 (t, *J* = 16.2 Hz, 1H), 3.44–3.39 (m, 1H), 2.24 (d, *J* = 6.7 Hz, 3H).



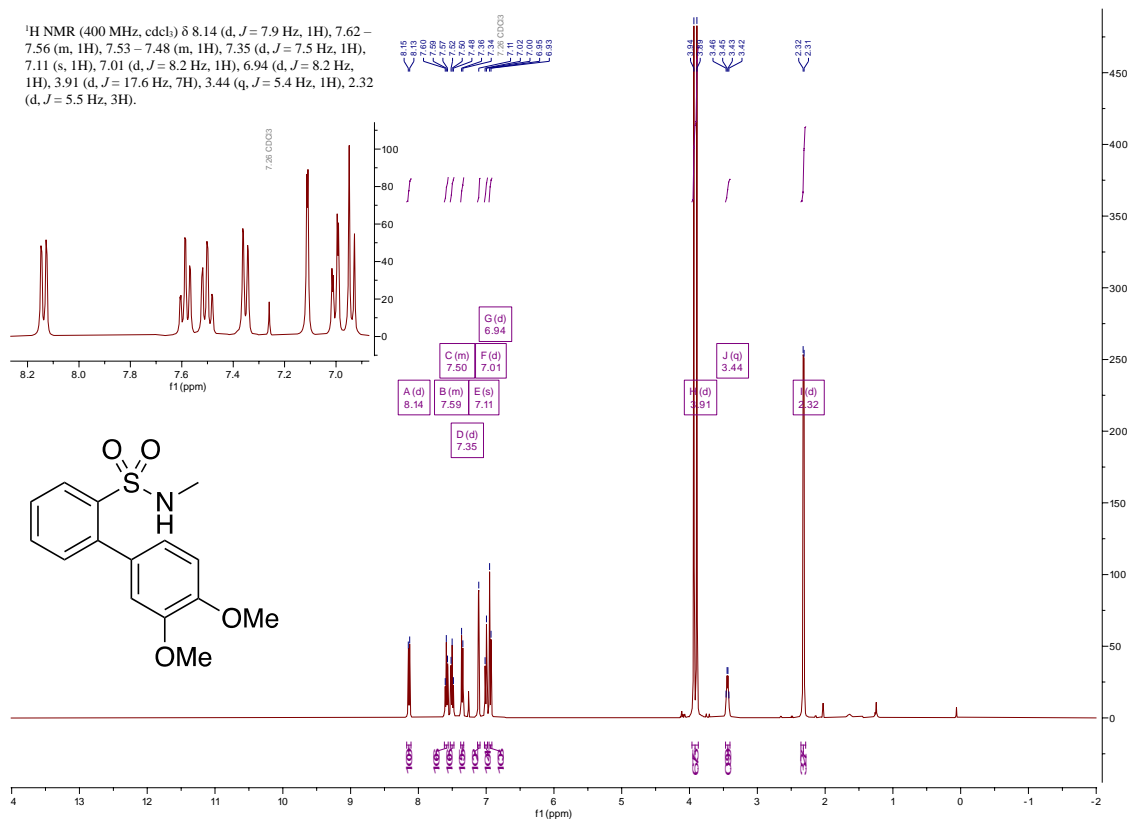
¹³C NMR (101 MHz, CDCl₃) of 5f

¹³C NMR (101 MHz, cdcl₃) δ 151.28, 148.95, 148.13, 147.70, 133.33, 130.84, 128.38, 120.96, 114.39, 112.83, 112.29, 110.72, 56.19, 56.10, 55.86, 55.79, 29.06.



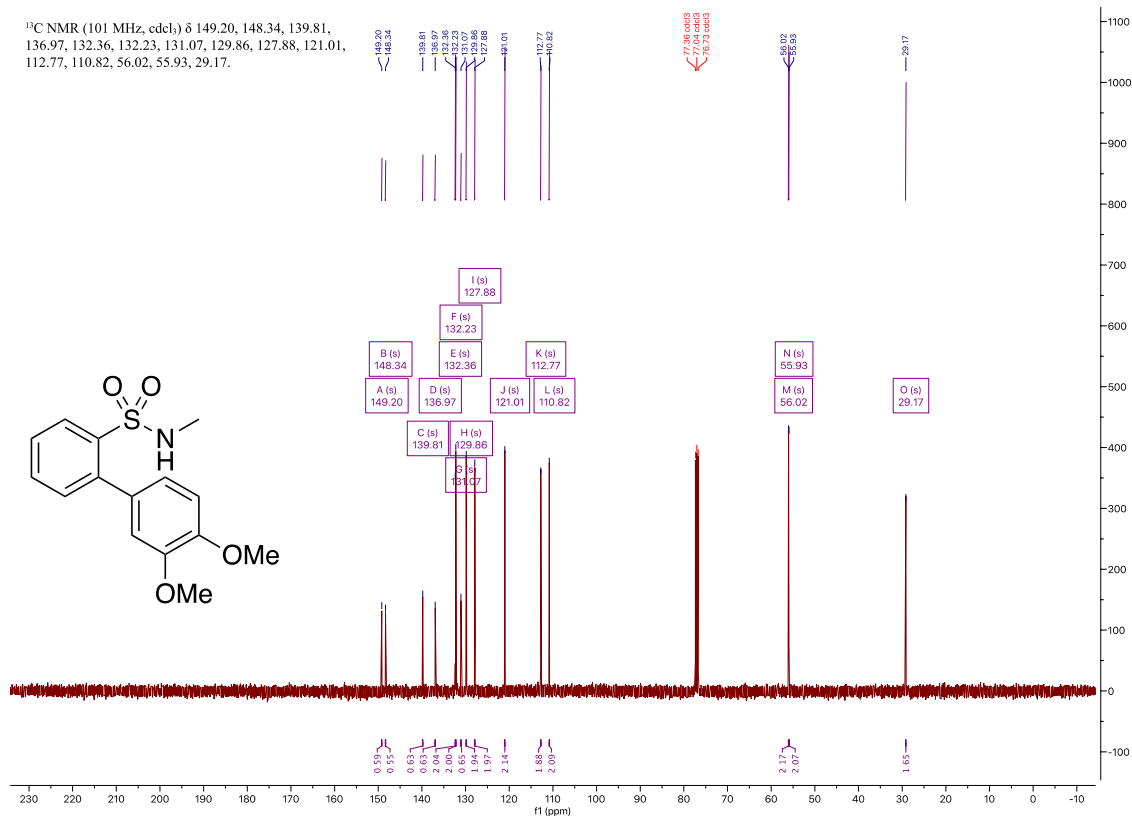
¹H NMR (400 MHz, CDCl₃) of 5g

¹H NMR (400 MHz, cdcl₃) δ 8.14 (d, *J* = 7.9 Hz, 1H), 7.62–7.56 (m, 1H), 7.53–7.48 (m, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.11 (s, 1H), 7.01 (d, *J* = 8.2 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 3.91 (d, *J* = 17.6 Hz, 7H), 3.44 (q, *J* = 5.4 Hz, 1H), 2.32 (d, *J* = 5.5 Hz, 3H).

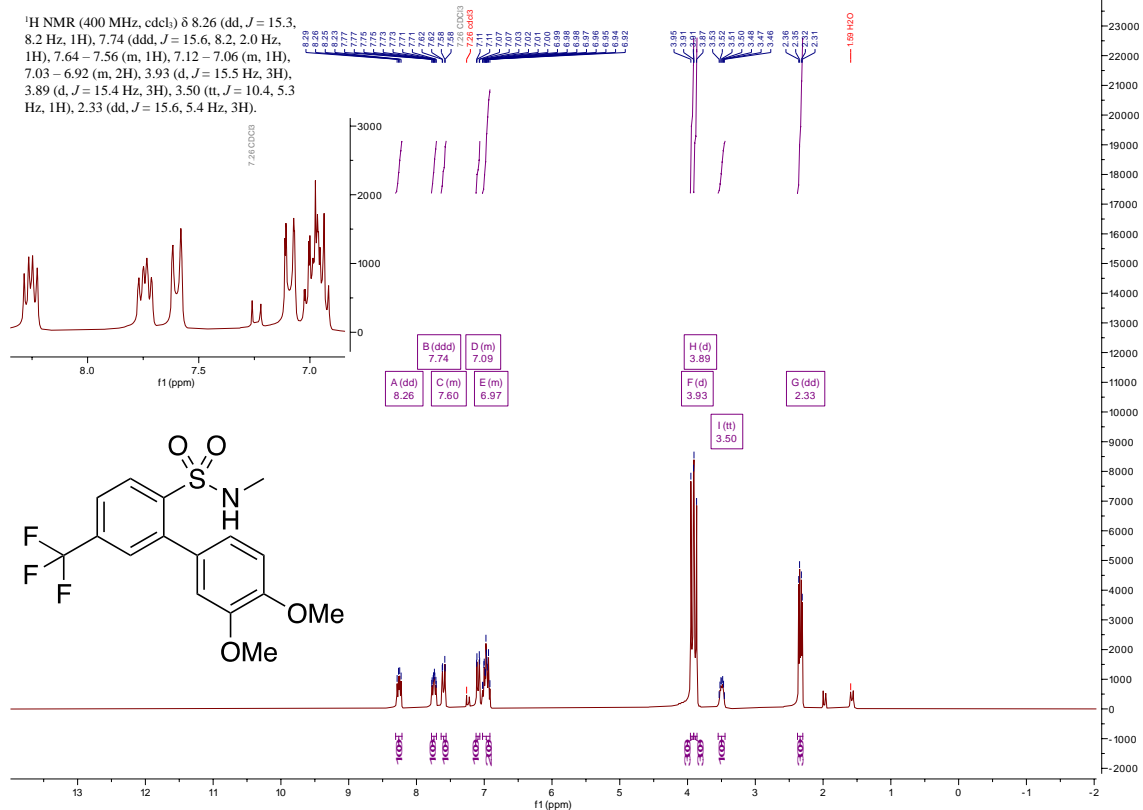


¹³C NMR (101 MHz, CDCl₃) of 5g

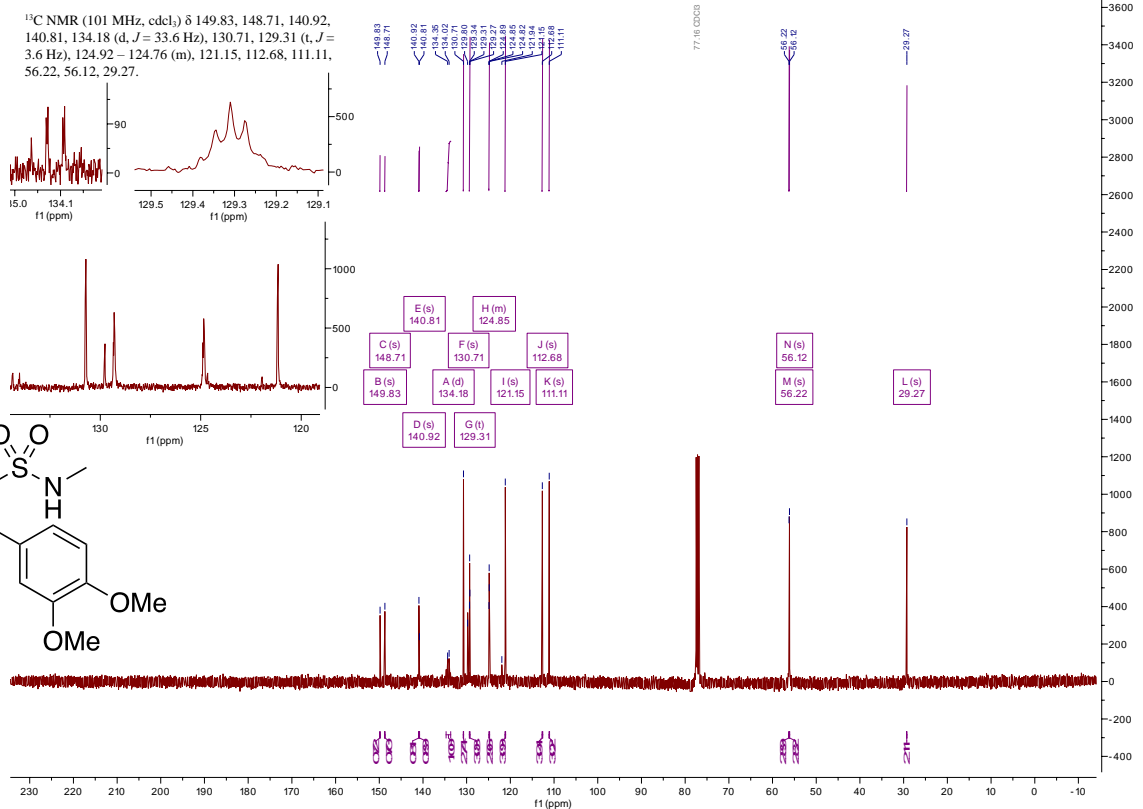
¹³C NMR (101 MHz, cdcl₃) δ 149.20, 148.34, 139.81, 136.97, 132.36, 132.23, 131.07, 129.86, 127.88, 121.01, 112.77, 110.82, 56.02, 55.93, 29.17.



¹H NMR (400 MHz, CDCl₃) of 5h

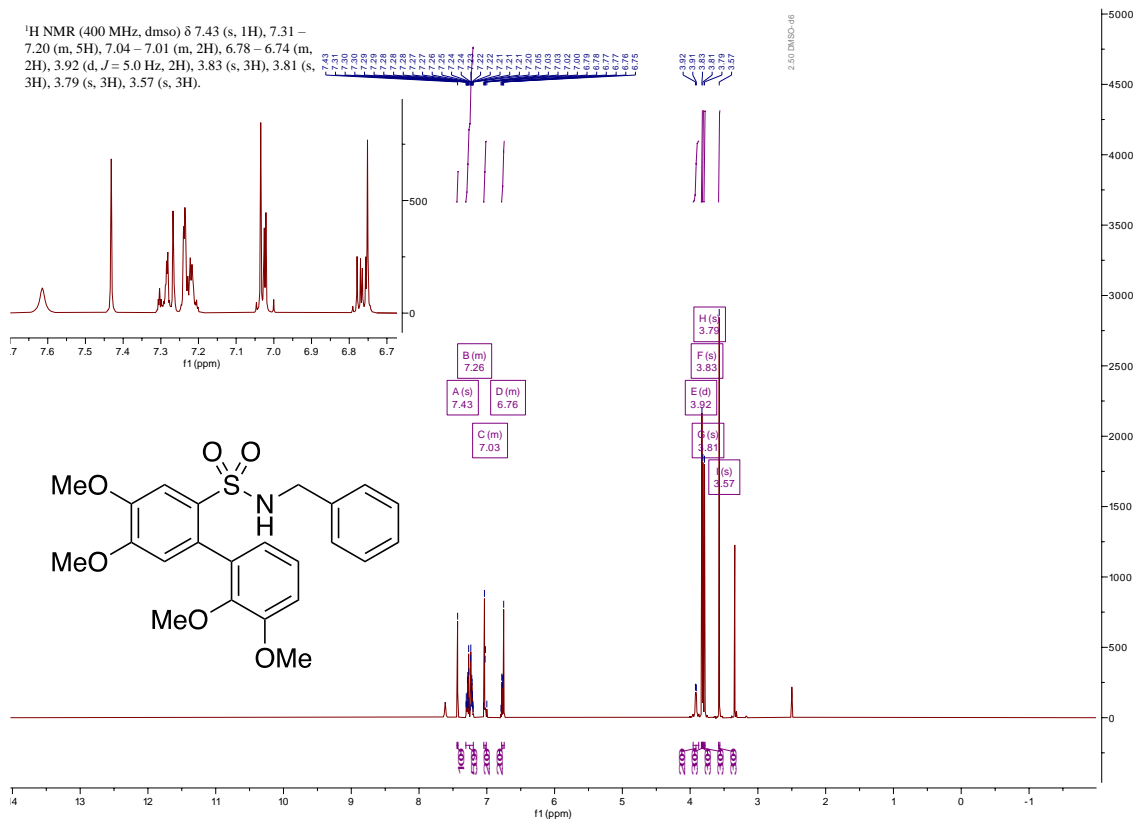


¹³C NMR (101 MHz, CDCl₃) of 5h



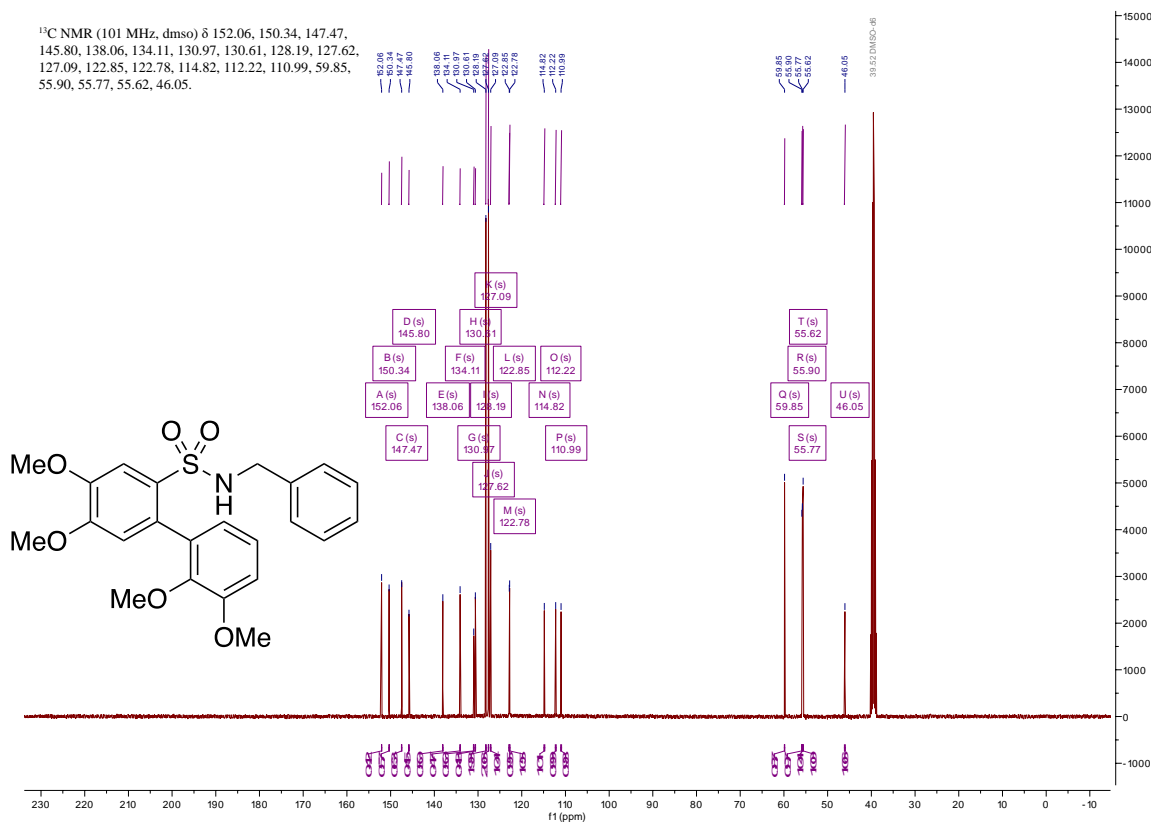
¹H NMR (400 MHz, (CD₃)₂SO) of 5i

¹H NMR (400 MHz, dmsO) δ 7.43 (s, 1H), 7.31 – 7.20 (m, 5H), 7.04 – 7.01 (m, 2H), 6.78 – 6.74 (m, 2H), 3.92 (d, J = 5.0 Hz, 2H), 3.83 (s, 3H), 3.81 (s, 3H), 3.79 (s, 3H), 3.57 (s, 3H).



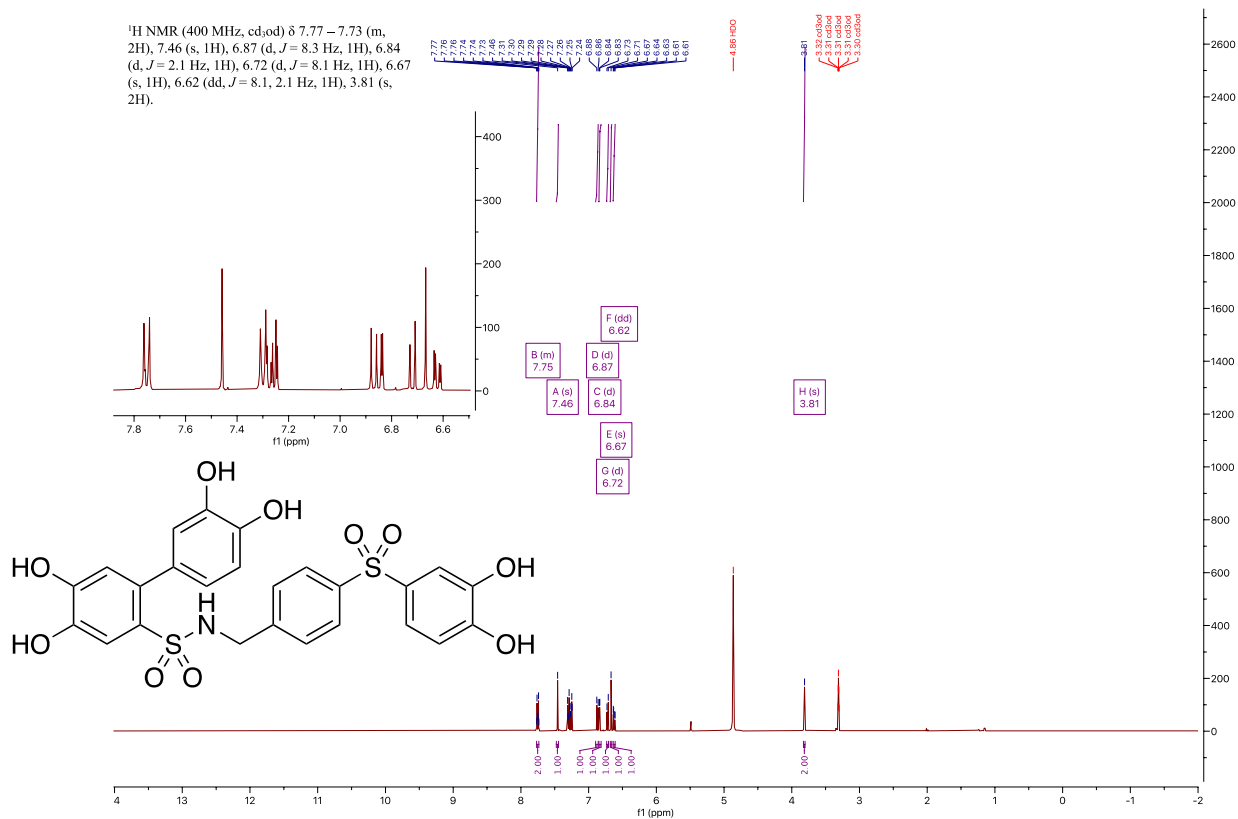
¹³C NMR (101 MHz, (CD₃)₂SO) of 5i

¹³C NMR (101 MHz, dmsO) δ 152.06, 150.34, 147.47, 145.80, 138.06, 134.11, 130.97, 130.61, 128.19, 127.62, 127.09, 122.85, 122.78, 114.82, 112.22, 110.99, 59.85, 55.90, 55.77, 55.62, 46.05.



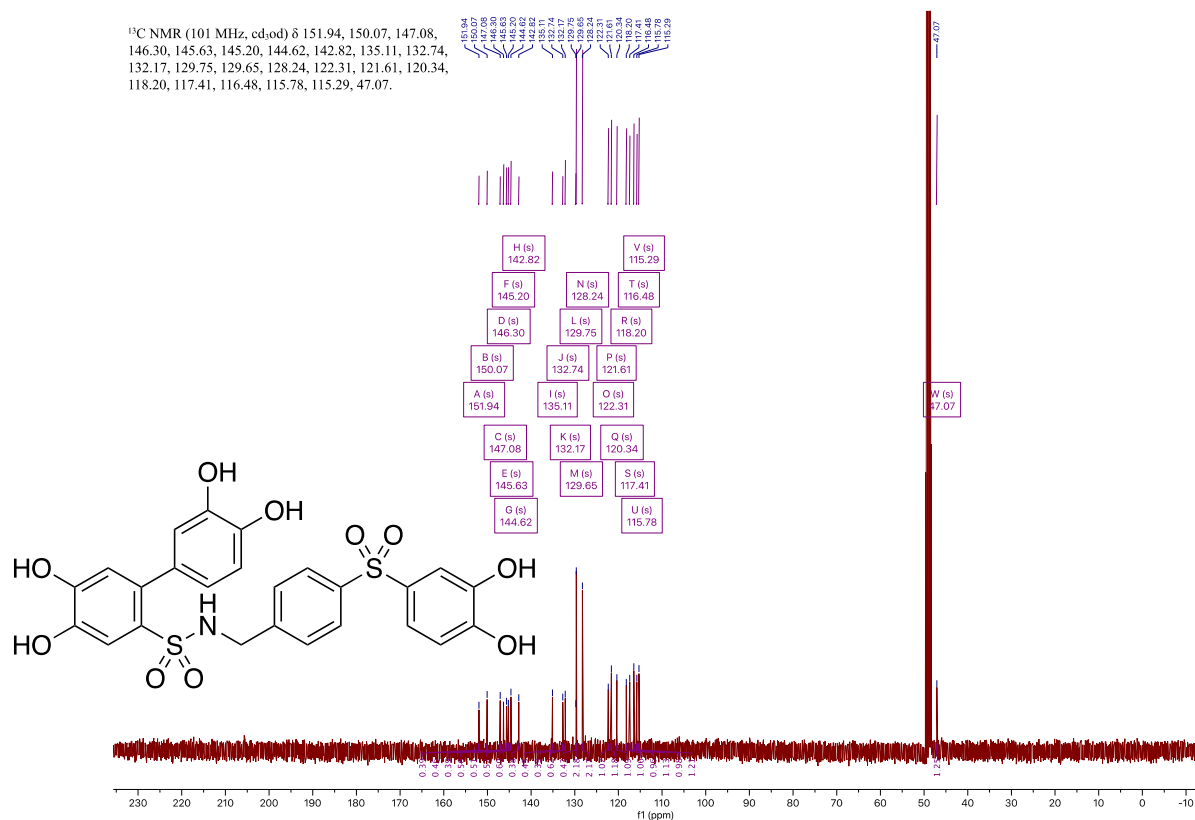
¹H NMR (400 MHz, CD₃OD) of 1a

¹H NMR (400 MHz, cd₃od) δ 7.77 (m, 2H), 7.46 (s, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 6.84 (d, *J* = 2.1 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 1H), 6.67 (s, 1H), 6.62 (dd, *J* = 8.1, 2.1 Hz, 1H), 3.81 (s, 2H).



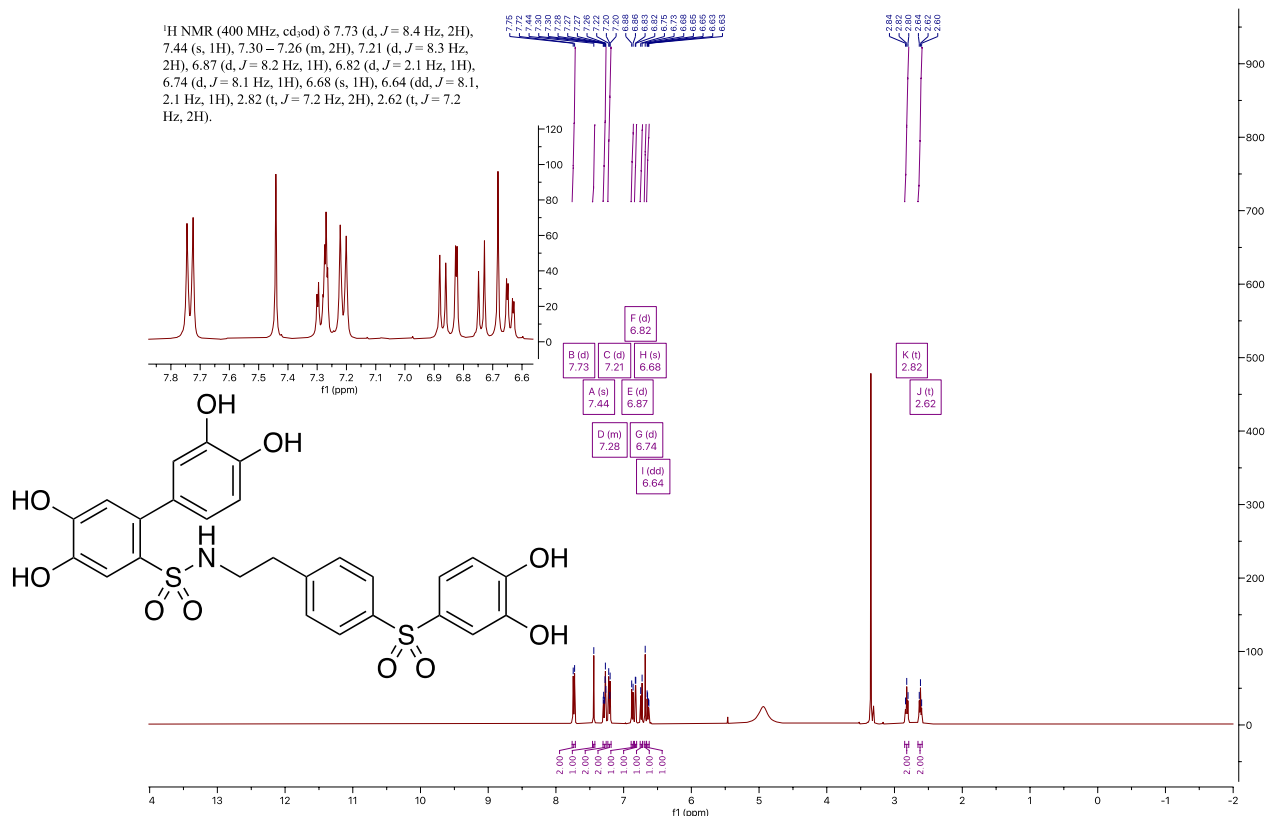
¹³C NMR (101 MHz, CD₃OD) of 1a

¹³C NMR (101 MHz, cd₃od) δ 151.94, 150.07, 147.08, 146.30, 145.63, 145.20, 144.62, 142.82, 135.11, 132.74, 132.17, 129.75, 129.65, 128.24, 122.31, 121.61, 120.34, 118.20, 117.41, 116.48, 115.78, 115.29, 47.07.



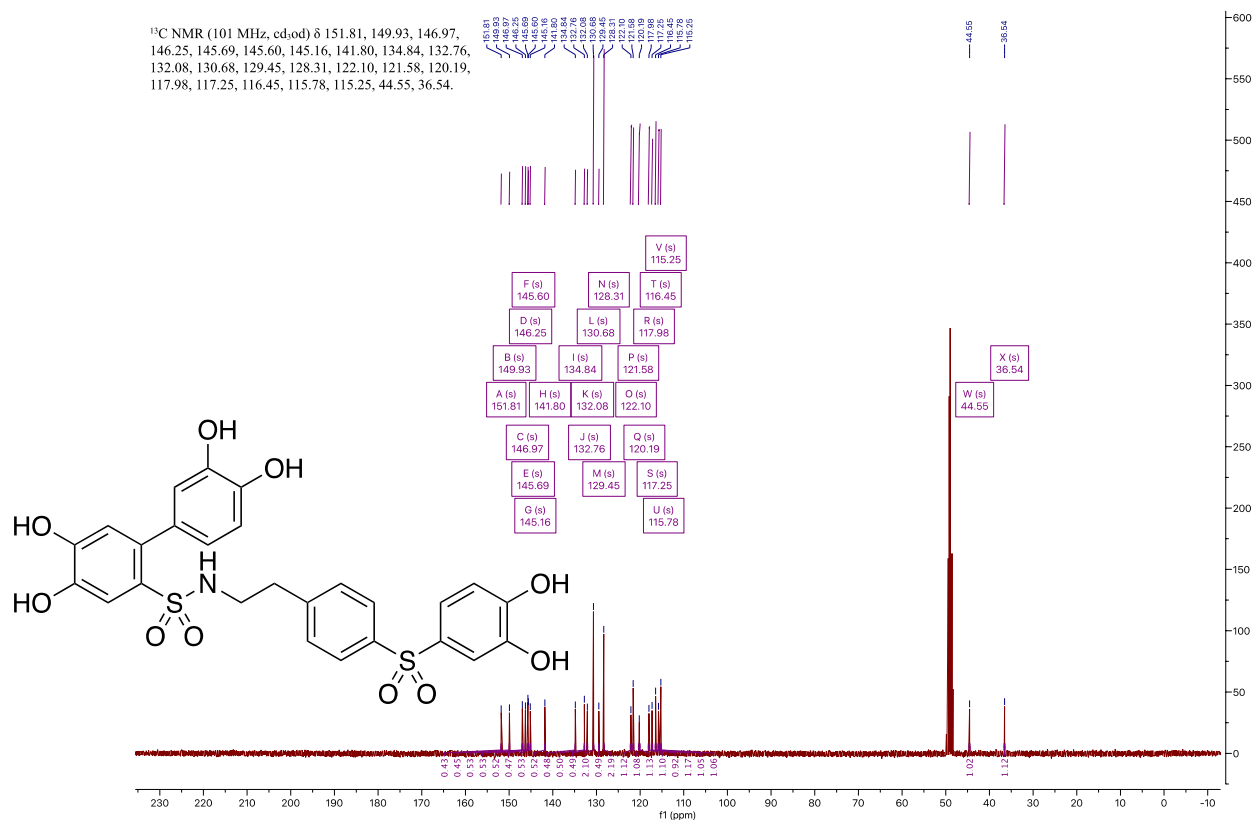
¹H NMR (400 MHz, CD₃OD) of 1b

¹H NMR (400 MHz, cd₃od) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.44 (s, 1H), 7.30–7.26 (m, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 1H), 6.82 (d, *J* = 2.1 Hz, 1H), 6.74 (d, *J* = 8.1 Hz, 1H), 6.68 (s, 1H), 6.64 (dd, *J* = 8.1, 2.1 Hz, 1H), 2.82 (t, *J* = 7.2 Hz, 2H), 2.62 (t, *J* = 7.2 Hz, 2H).



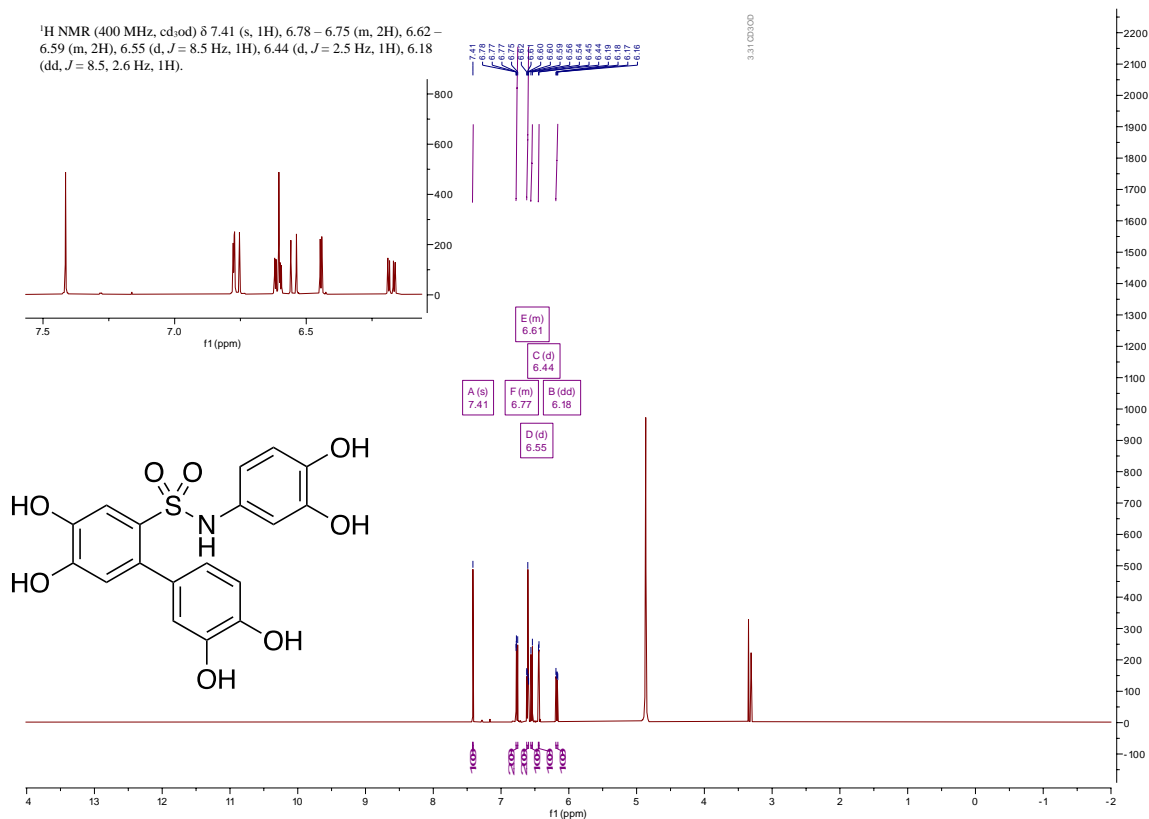
¹³C NMR (101 MHz, CD₃OD) of 1b

¹³C NMR (101 MHz, cd₃od) δ 151.81, 149.93, 146.97, 146.25, 145.69, 145.60, 145.16, 141.80, 134.84, 132.76, 132.08, 130.68, 129.45, 128.31, 122.10, 121.58, 120.19, 117.98, 117.25, 116.45, 115.78, 115.25, 44.55, 36.54.



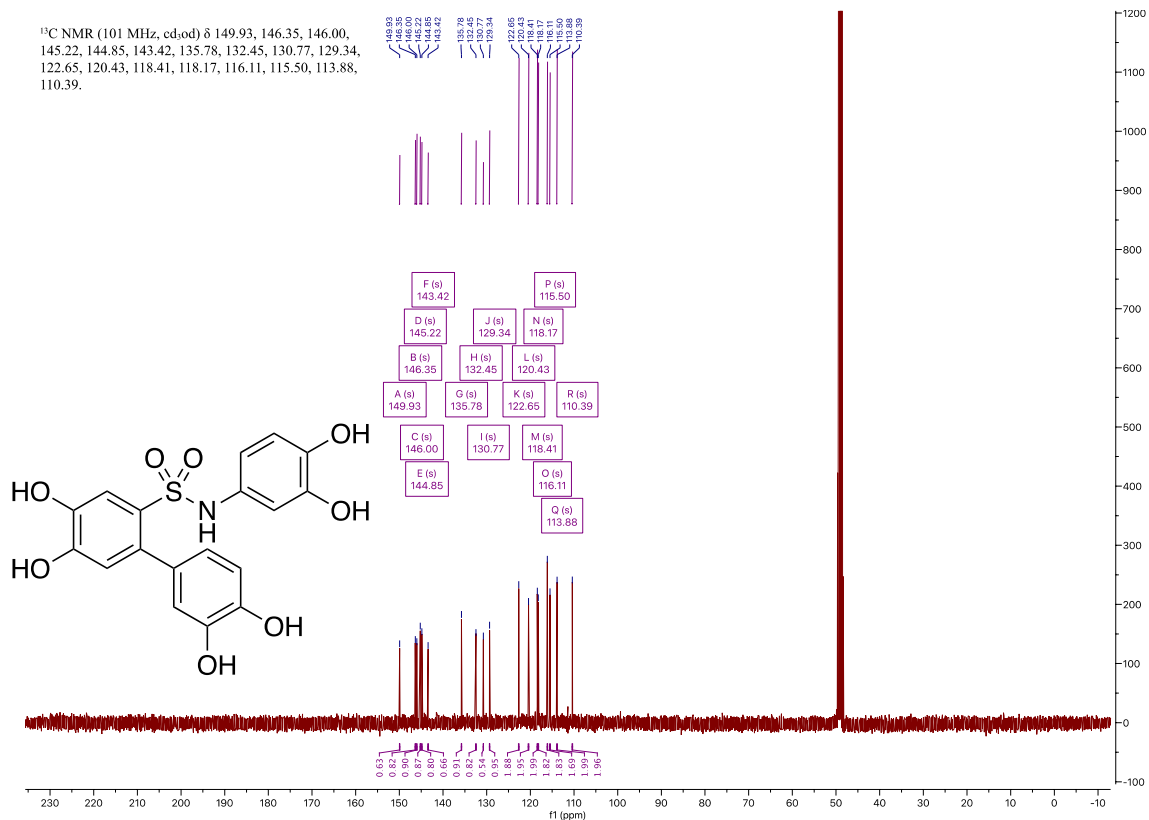
¹H NMR (400 MHz, CD₃OD) of 1c

¹H NMR (400 MHz, cd₃od) δ 7.41 (s, 1H), 6.78 – 6.75 (m, 2H), 6.62 – 6.59 (m, 2H), 6.55 (d, *J* = 8.5 Hz, 1H), 6.44 (d, *J* = 2.5 Hz, 1H), 6.18 (dd, *J* = 8.5, 2.6 Hz, 1H).

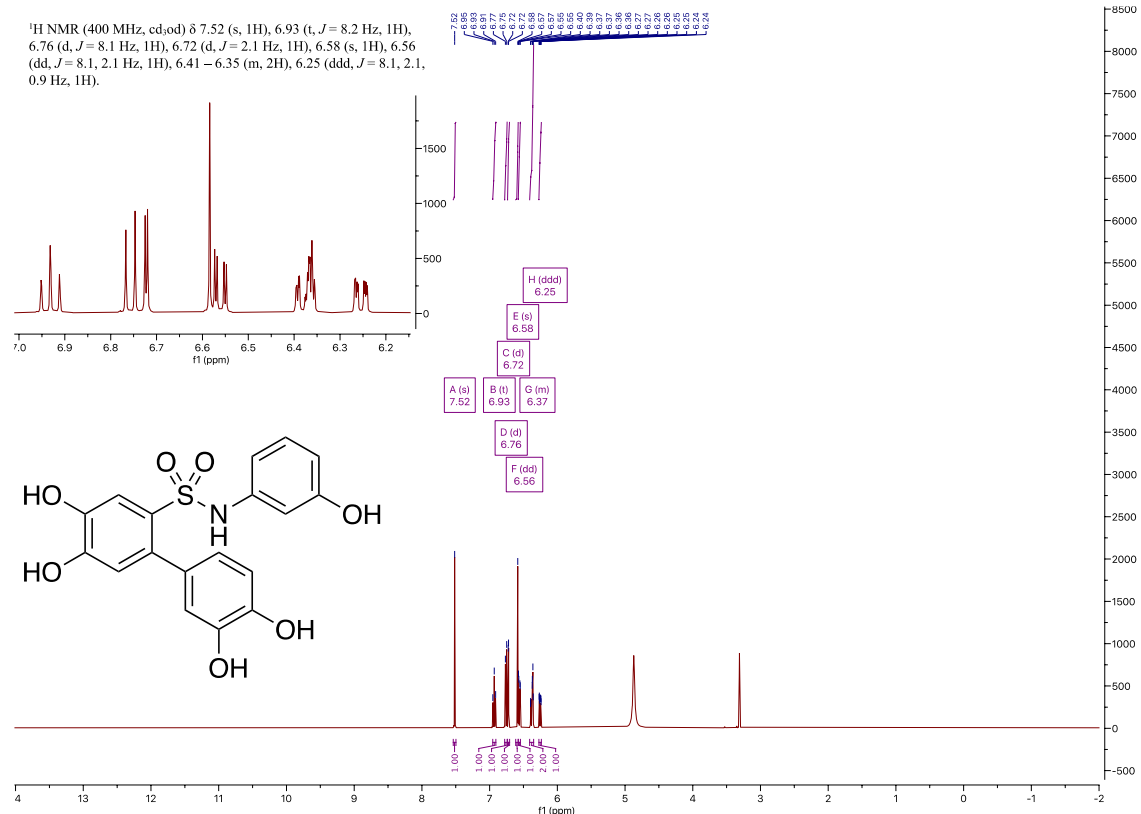


¹³C NMR (101 MHz, CD₃OD) of 1c

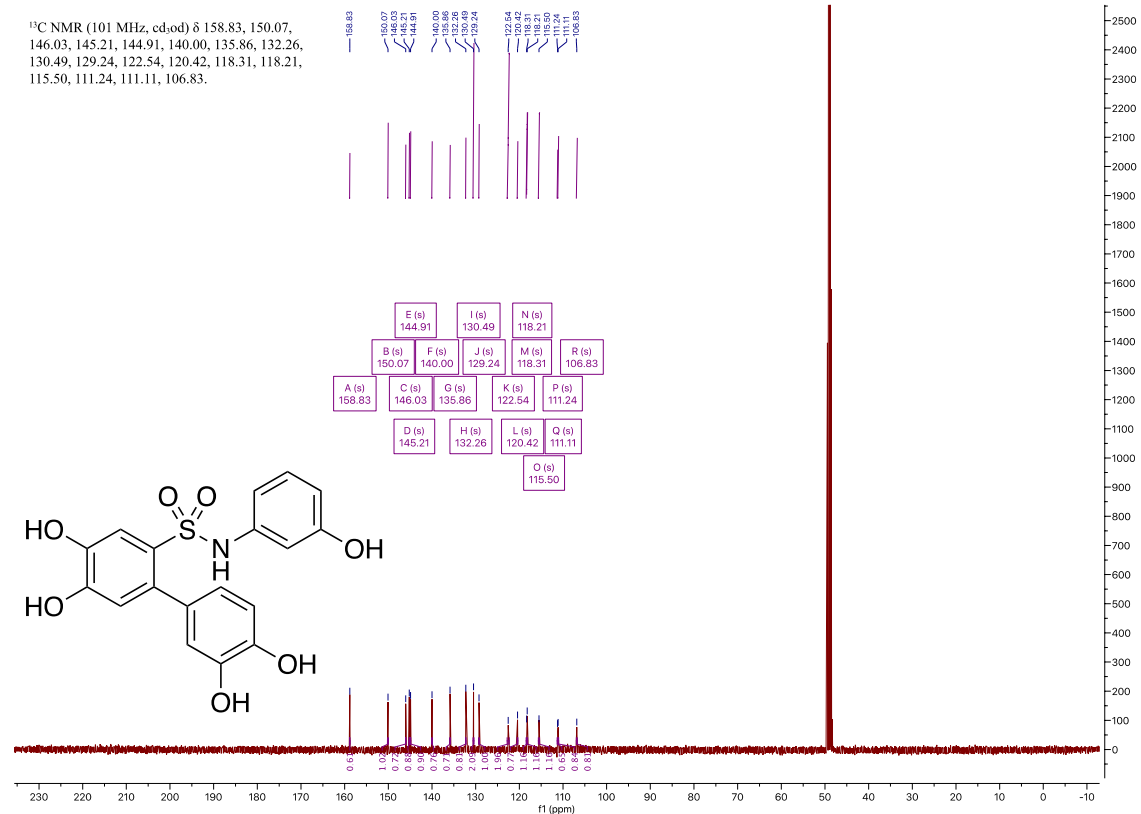
¹³C NMR (101 MHz, cd₃od) δ 149.93, 146.35, 146.00, 145.22, 144.85, 143.42, 135.78, 132.45, 130.77, 129.34, 122.65, 120.43, 118.41, 118.17, 116.11, 115.50, 113.88, 110.39.



^1H NMR (400 MHz, CD_3OD) of 1d

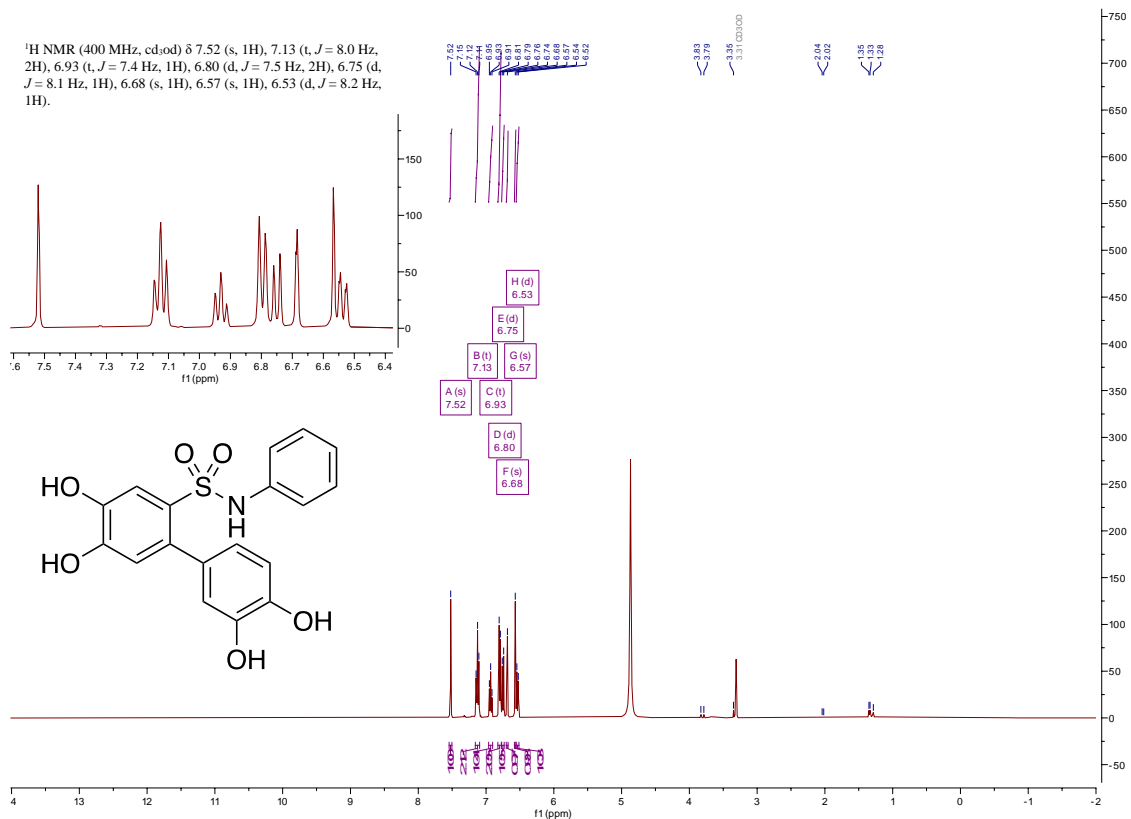


^{13}C NMR (101 MHz, CD_3OD) of 1d



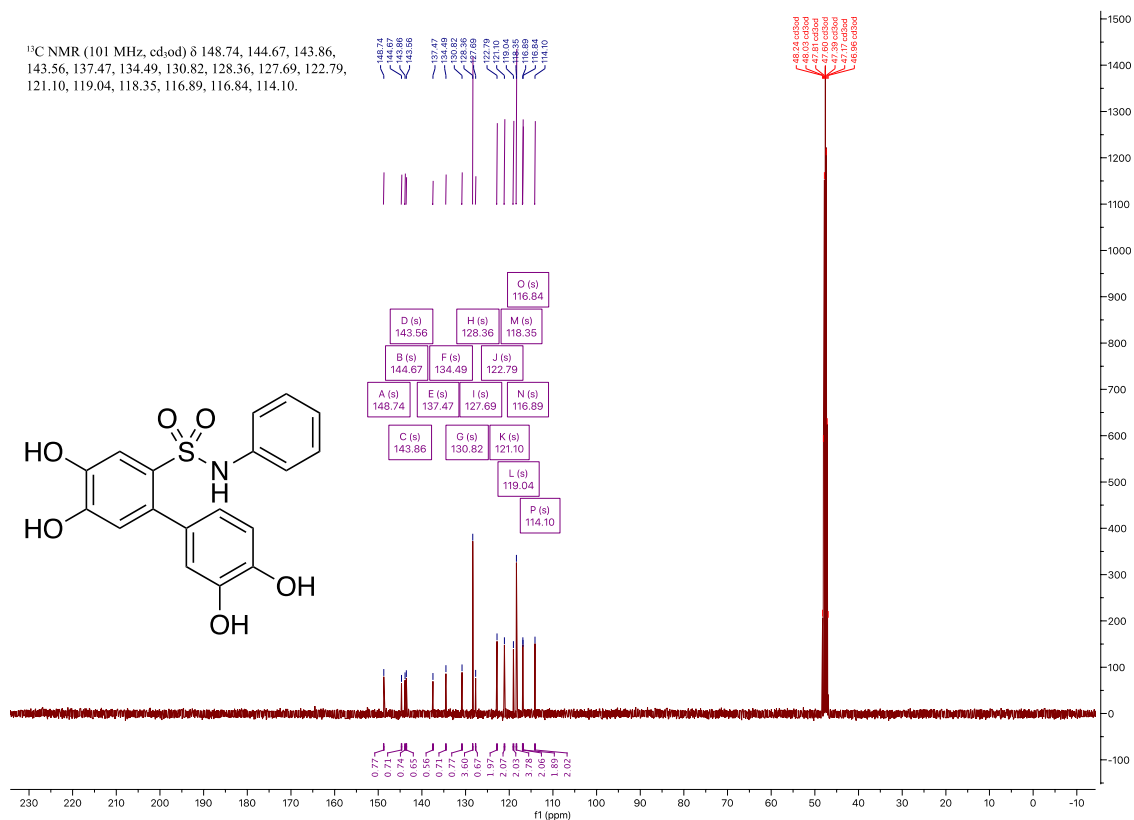
¹H NMR (400 MHz, CD₃OD) of 1e

¹H NMR (400 MHz, cd₃od) δ 7.52 (s, 1H), 7.13 (t, *J* = 8.0 Hz, 2H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 7.5 Hz, 2H), 6.75 (d, *J* = 8.1 Hz, 1H), 6.68 (s, 1H), 6.57 (s, 1H), 6.53 (d, *J* = 8.2 Hz, 1H).



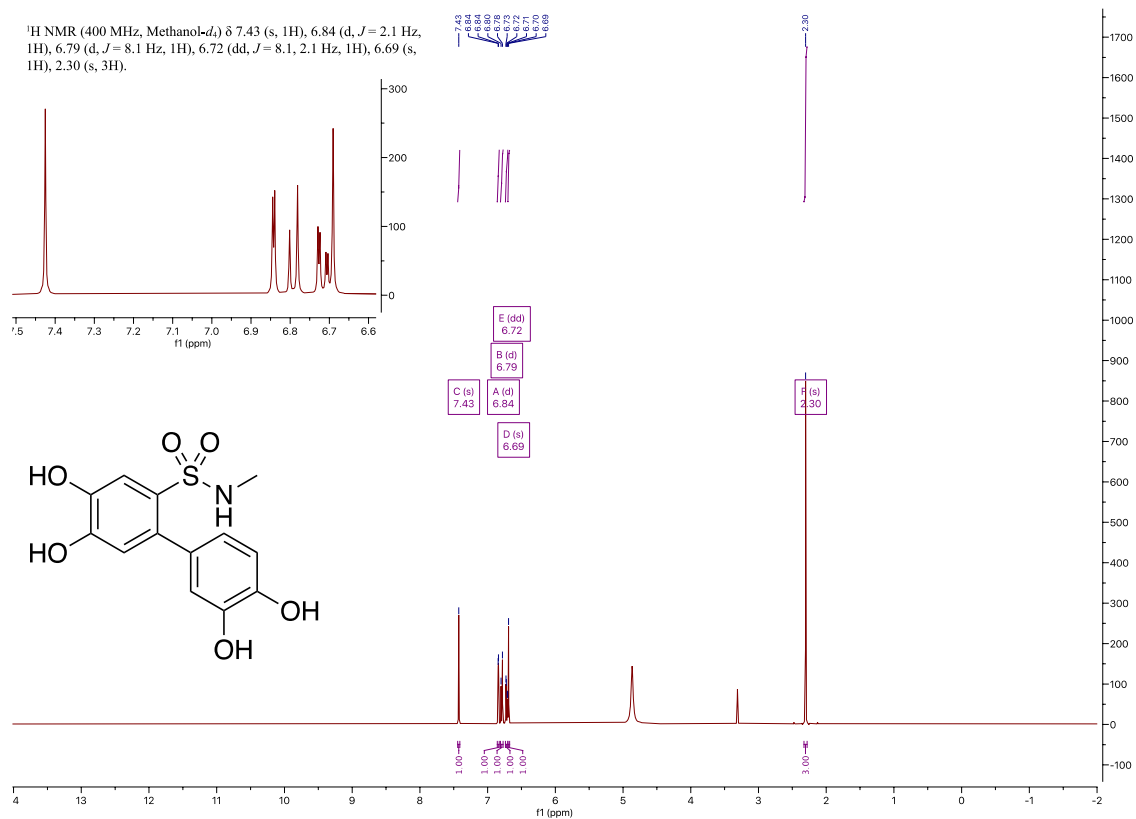
¹³C NMR (101 MHz, CD₃OD) of 1e

¹³C NMR (101 MHz, cd₃od) δ 148.74, 144.67, 143.86, 143.56, 137.47, 134.49, 130.82, 128.36, 127.69, 122.79, 121.10, 119.04, 118.35, 116.89, 116.84, 114.10.



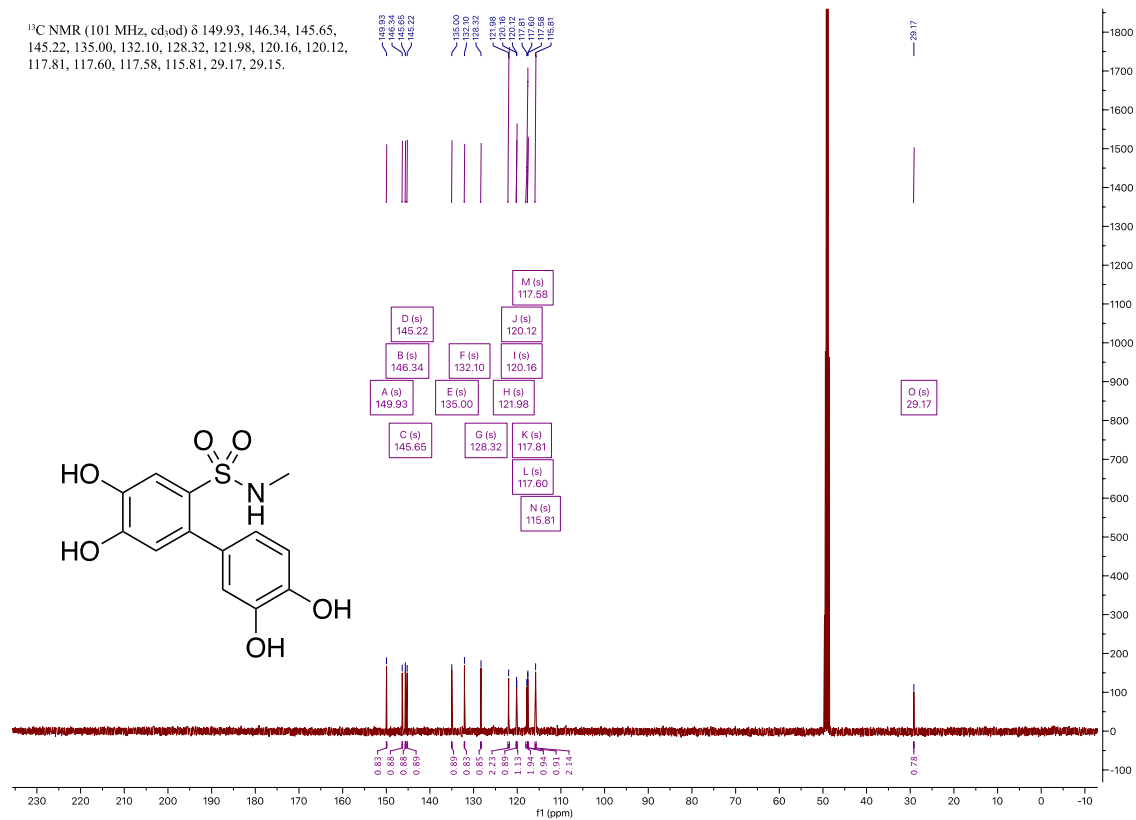
¹H NMR (400 MHz, CD₃OD) of 1f

¹H NMR (400 MHz, Methanol-*d*₄) δ 7.43 (s, 1H), 6.84 (d, *J* = 2.1 Hz, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.72 (dd, *J* = 8.1, 2.1 Hz, 1H), 6.69 (s, 1H), 2.30 (s, 3H).



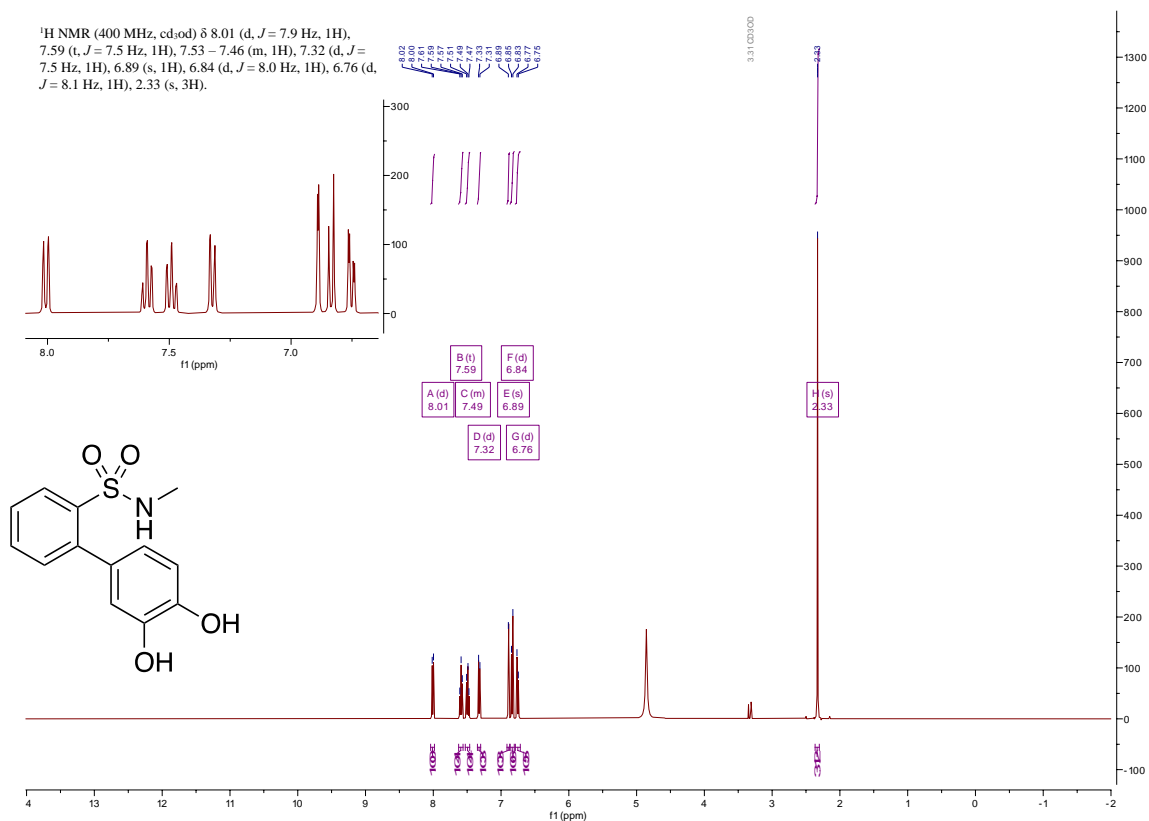
¹³C NMR (101 MHz, CD₃OD) of 1f

¹³C NMR (101 MHz, cd₃od) δ 149.93, 146.34, 145.65, 145.22, 135.00, 132.10, 128.32, 121.98, 120.16, 120.12, 117.81, 117.60, 117.58, 115.81, 29.17, 29.15.



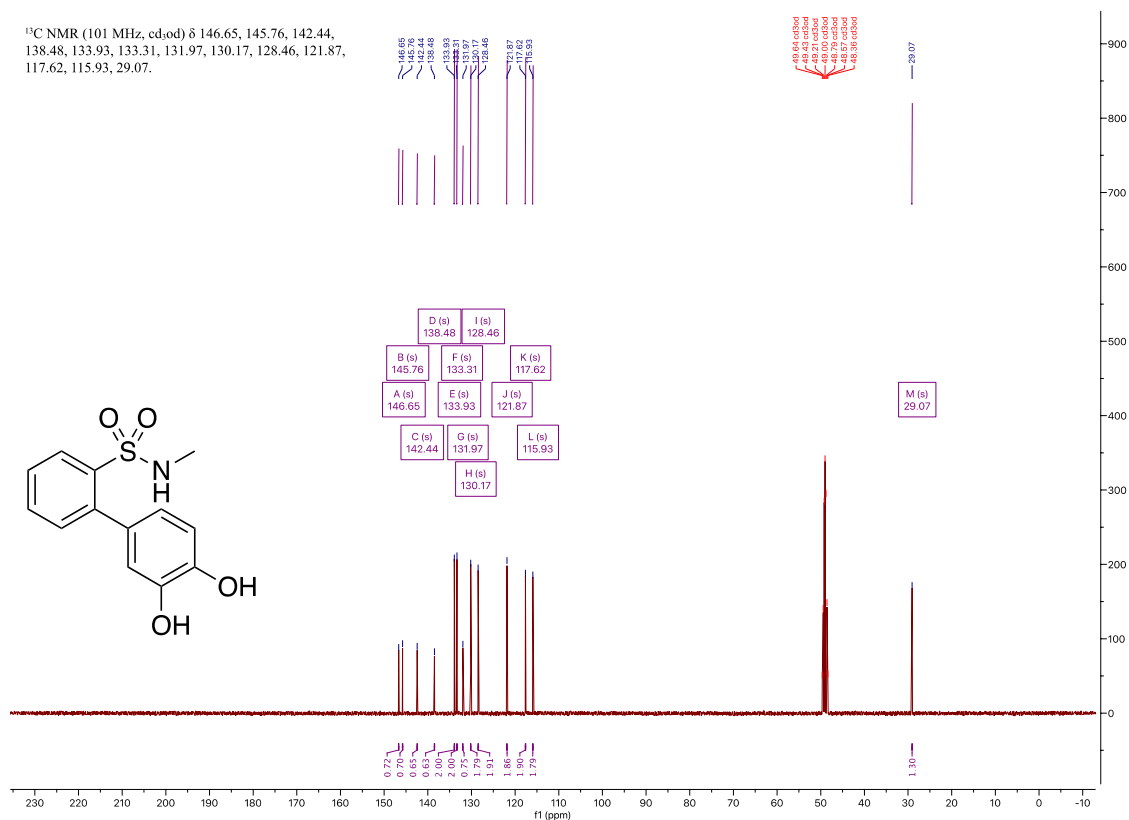
¹H NMR (400 MHz, CD₃OD) of 1g

¹H NMR (400 MHz, cd₃od) δ 8.01 (d, *J* = 7.9 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.53 – 7.46 (m, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 6.89 (s, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 2.33 (s, 3H).



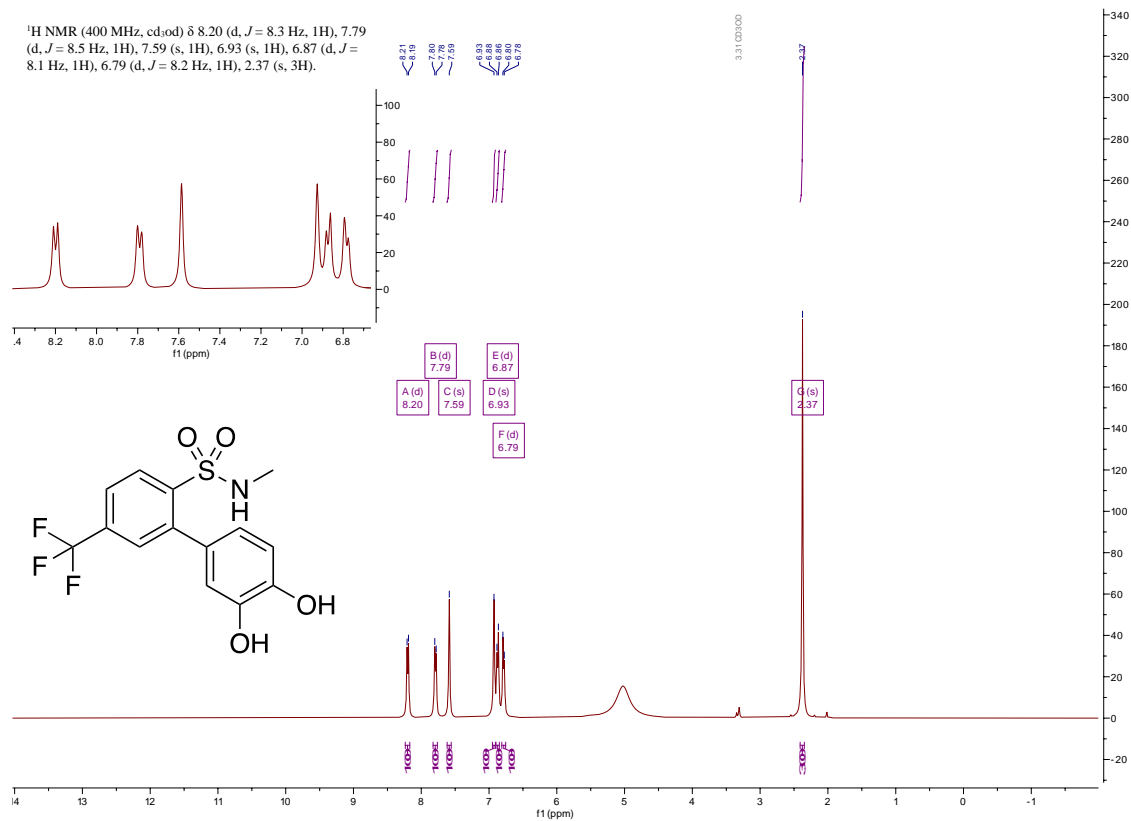
¹³C NMR (101 MHz, CD₃OD) of 1g

¹³C NMR (101 MHz, cd₃od) δ 146.65, 145.76, 142.44, 138.48, 133.93, 133.31, 131.97, 130.17, 128.46, 121.87, 117.62, 115.93, 29.07.



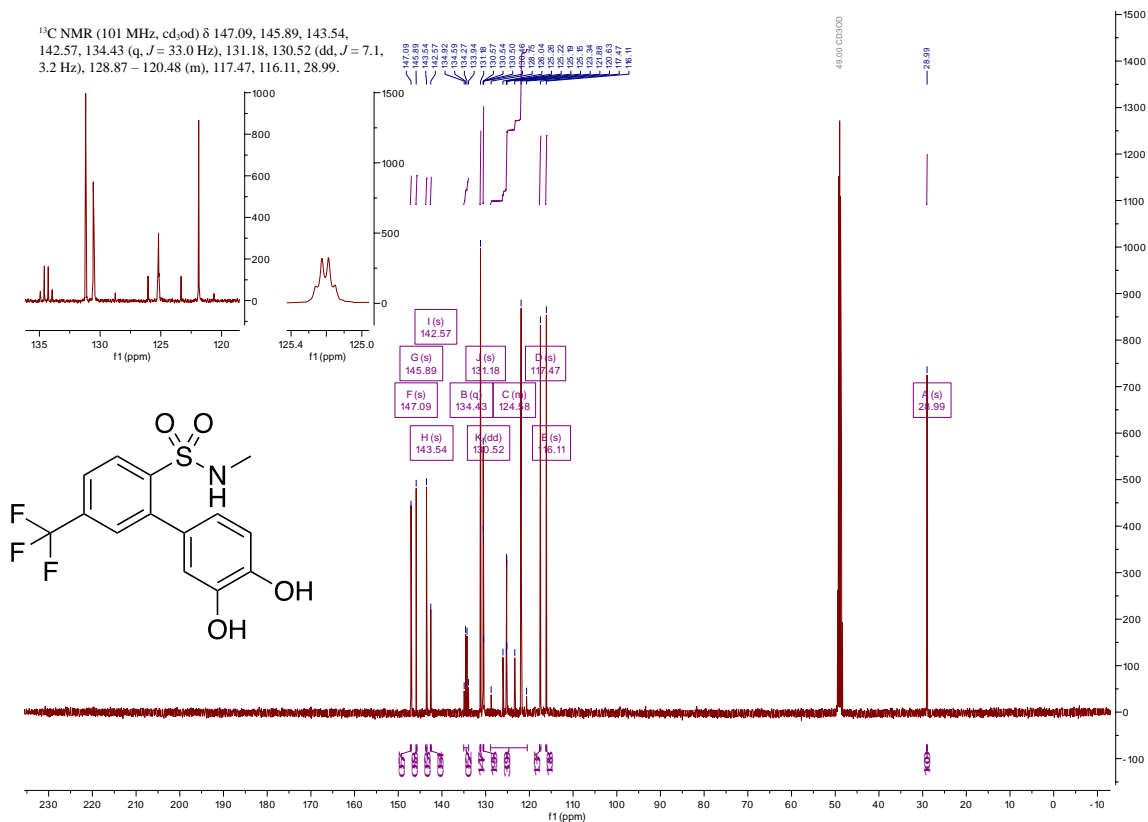
¹H NMR (400 MHz, CD₃OD) of 1h

¹H NMR (400 MHz, cd₃od) δ 8.20 (d, *J* = 8.3 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.59 (s, 1H), 6.93 (s, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 2.37 (s, 3H).



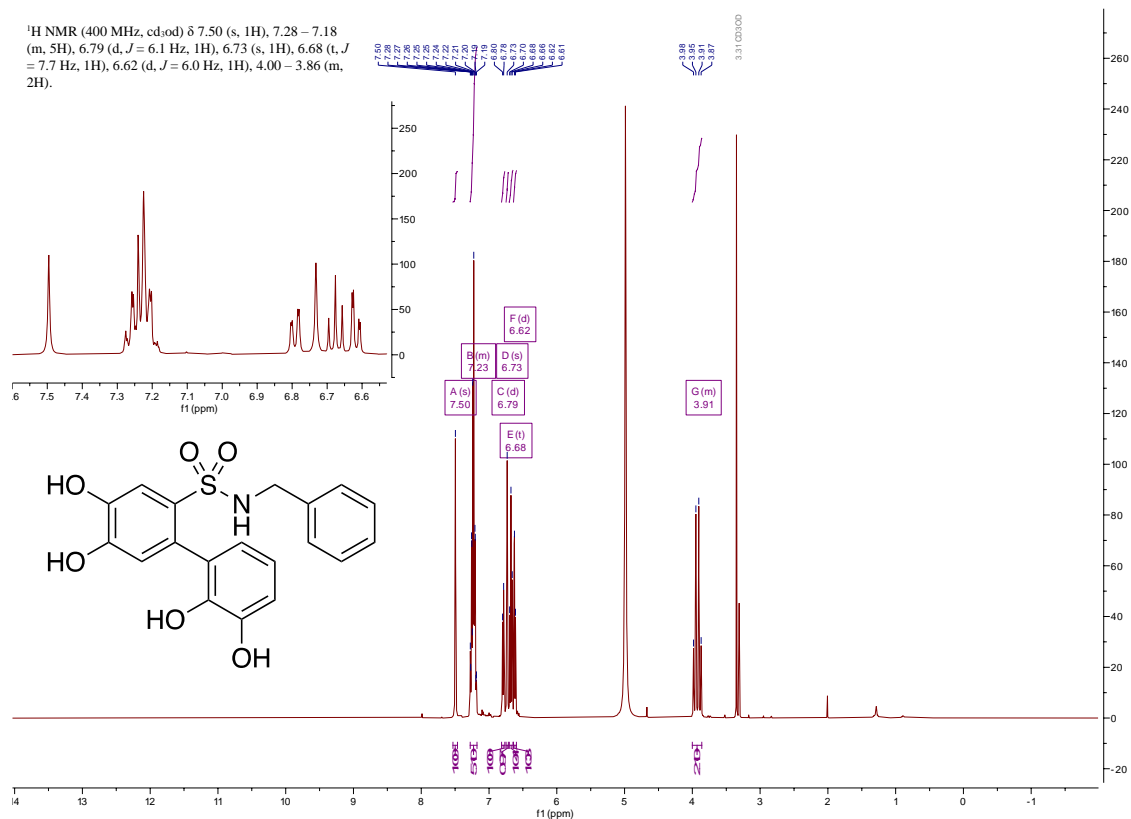
¹³C NMR (101 MHz, CD₃OD) of 1h

¹³C NMR (101 MHz, cd₃od) δ 147.09, 145.89, 143.54, 142.57, 134.43 (q, *J* = 33.0 Hz), 131.18, 130.52 (dd, *J* = 7.1, 3.2 Hz), 128.87 – 120.48 (m), 117.47, 116.11, 28.99.



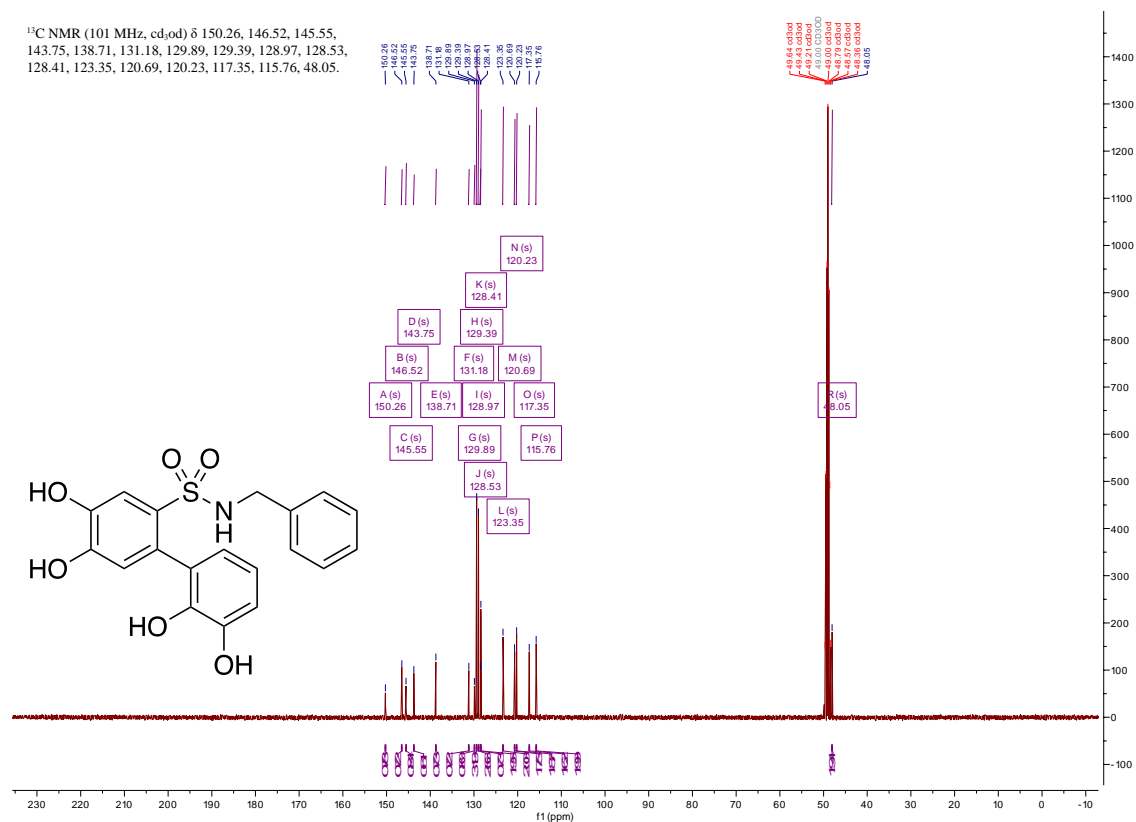
¹H NMR (400 MHz, CD₃OD) of 1i

¹H NMR (400 MHz, cd₃od) δ 7.50 (s, 1H), 7.28 – 7.18 (m, 5H), 6.79 (d, J = 6.1 Hz, 1H), 6.73 (s, 1H), 6.68 (t, J = 7.7 Hz, 1H), 6.62 (d, J = 6.0 Hz, 1H), 4.00 – 3.86 (m, 2H).



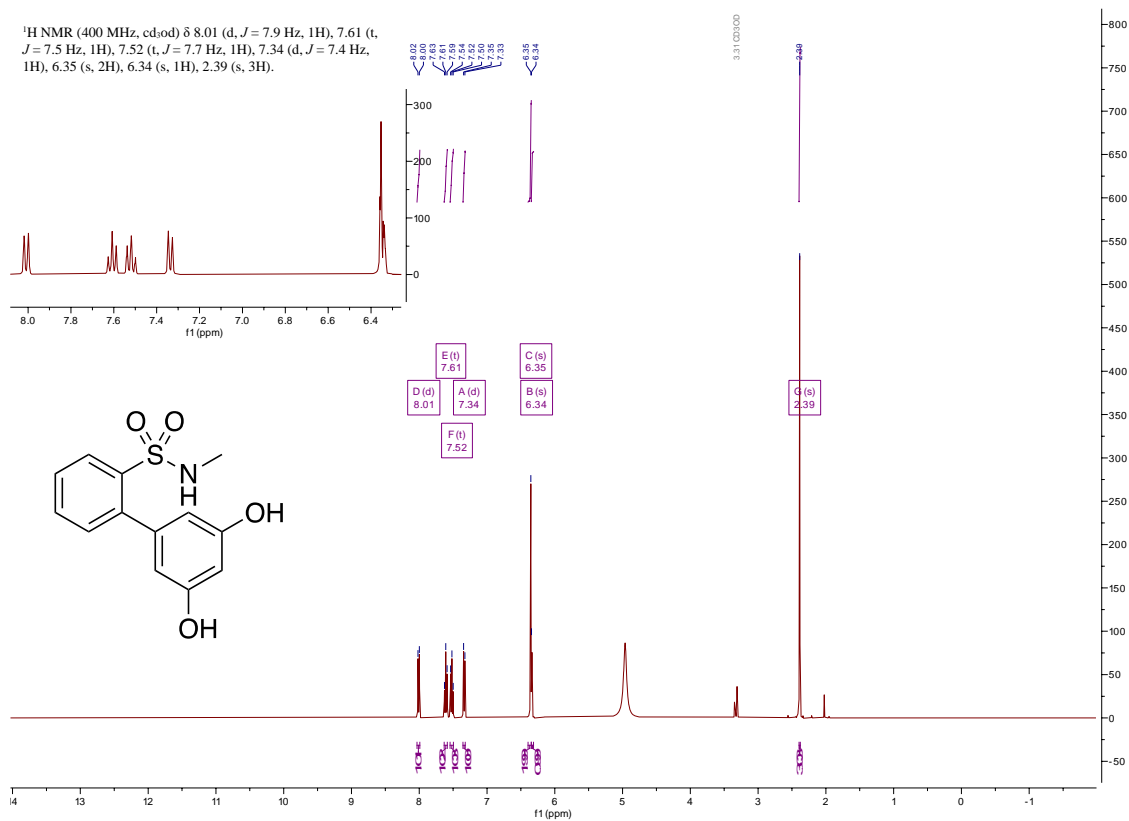
¹³C NMR (101 MHz, CD₃OD) of 1i

¹³C NMR (101 MHz, cd₃od) δ 150.26, 146.52, 145.55, 143.75, 138.71, 131.18, 129.89, 129.39, 128.97, 128.53, 128.41, 123.35, 120.69, 120.23, 117.35, 115.76, 48.05.



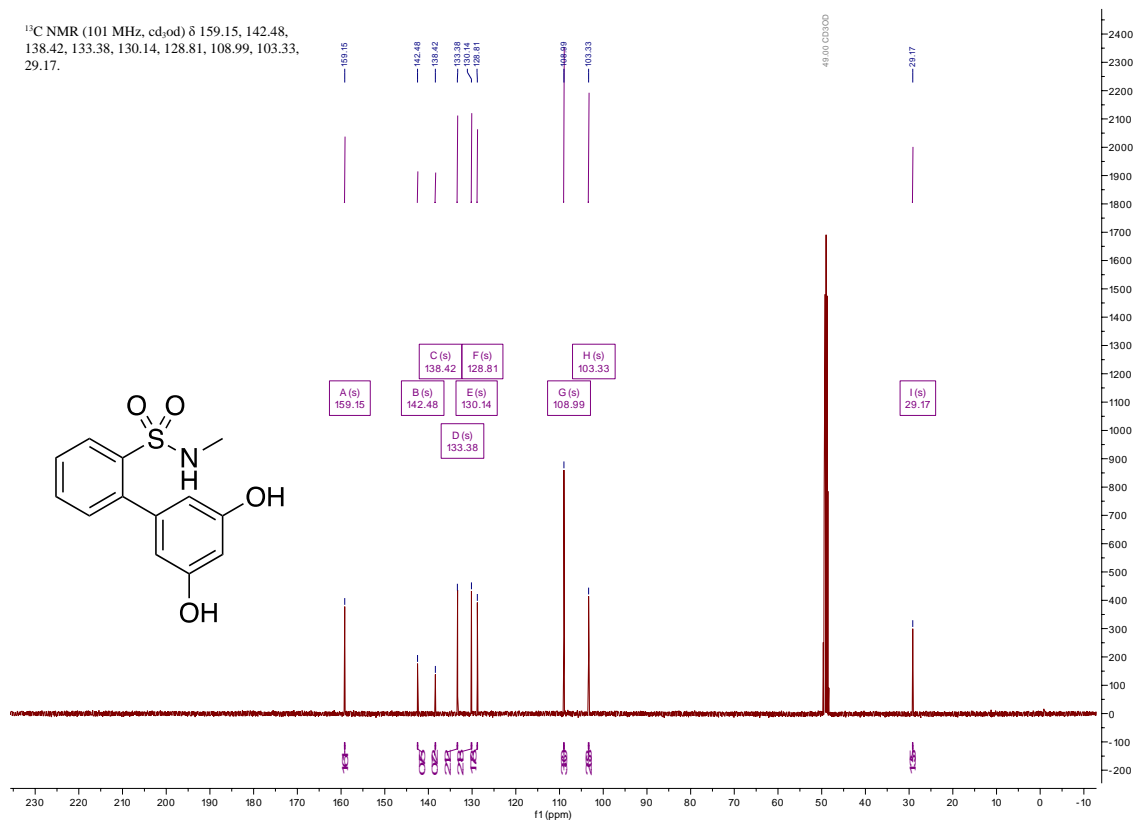
¹H NMR (400 MHz, CD₃OD) of 1j

¹H NMR (400 MHz, cd₃od) δ 8.01 (d, *J* = 7.9 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 6.35 (s, 2H), 6.34 (s, 1H), 2.39 (s, 3H).



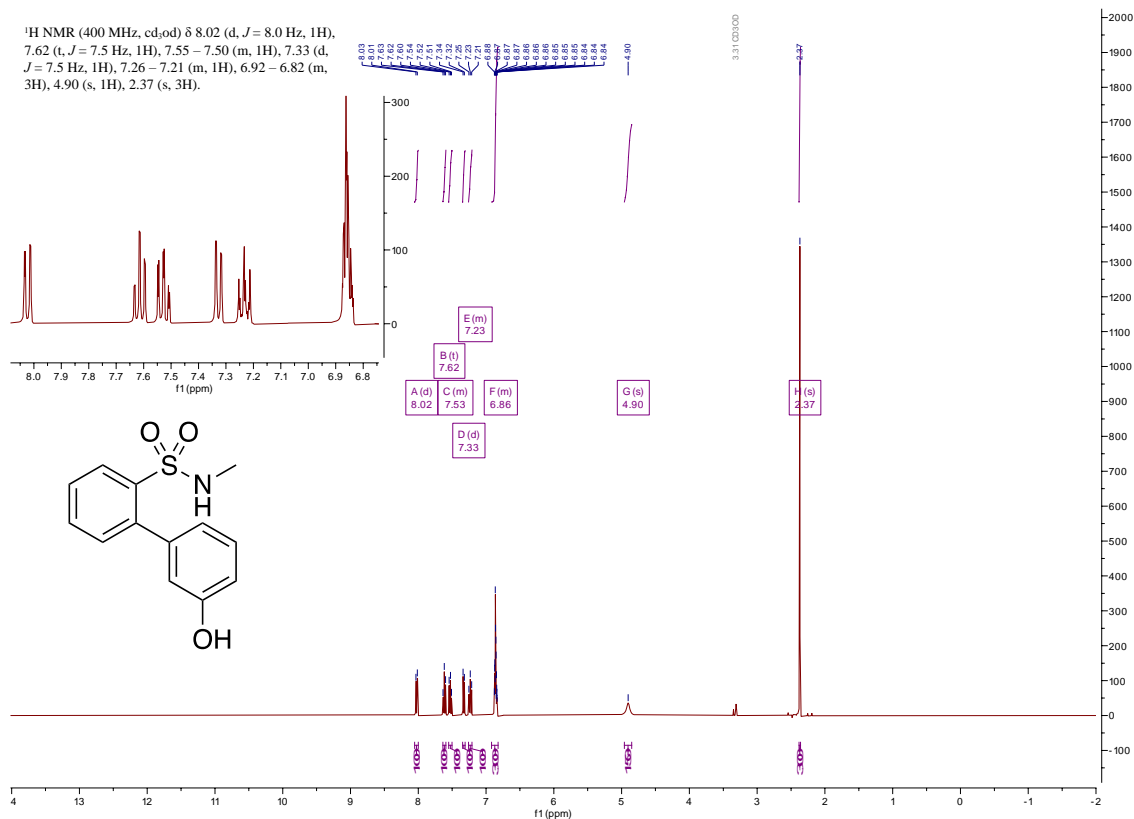
¹³C NMR (101 MHz, CD₃OD) of 1j

¹³C NMR (101 MHz, cd₃od) δ 159.15, 142.48, 138.42, 133.38, 130.14, 128.81, 108.99, 103.33, 29.17.



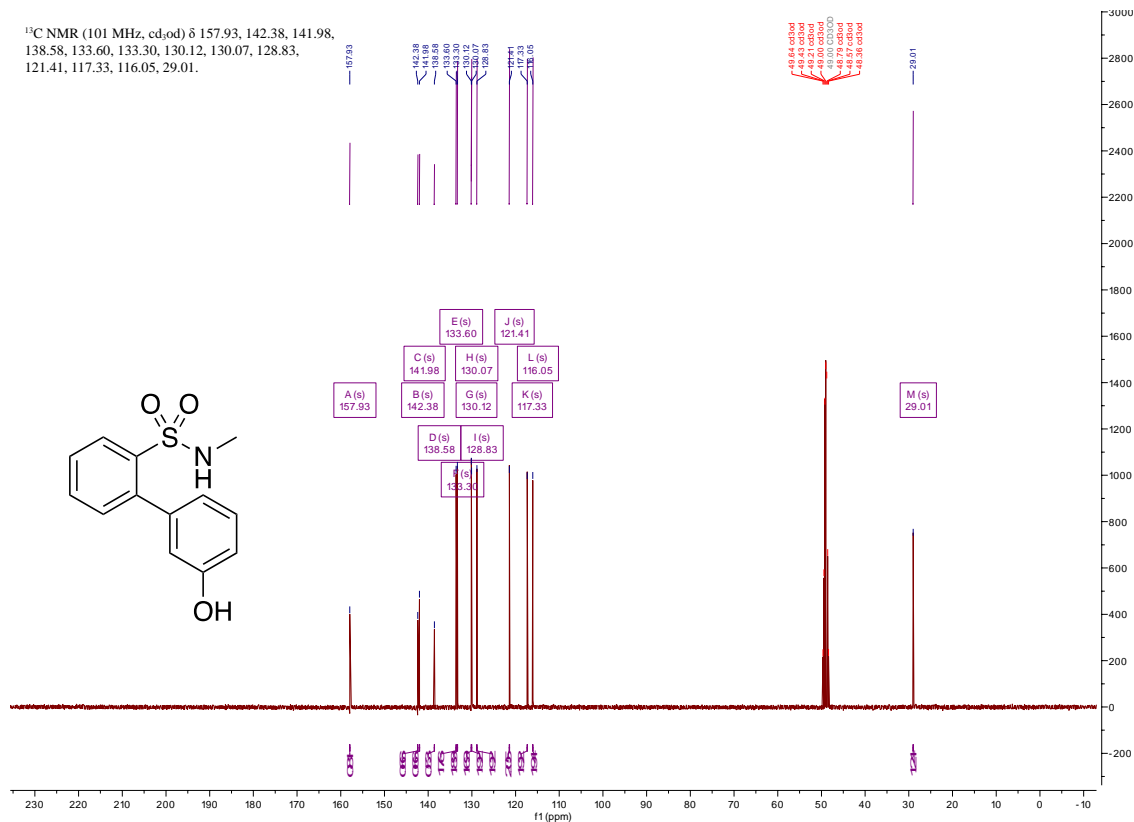
¹H NMR (400 MHz, CD₃OD) of 1k

¹H NMR (400 MHz, cd₃od) δ 8.02 (d, J = 8.0 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.33 (d, J = 7.5 Hz, 1H), 7.26 – 7.21 (m, 1H), 6.92 – 6.82 (m, 3H), 4.90 (s, 1H), 2.37 (s, 3H).



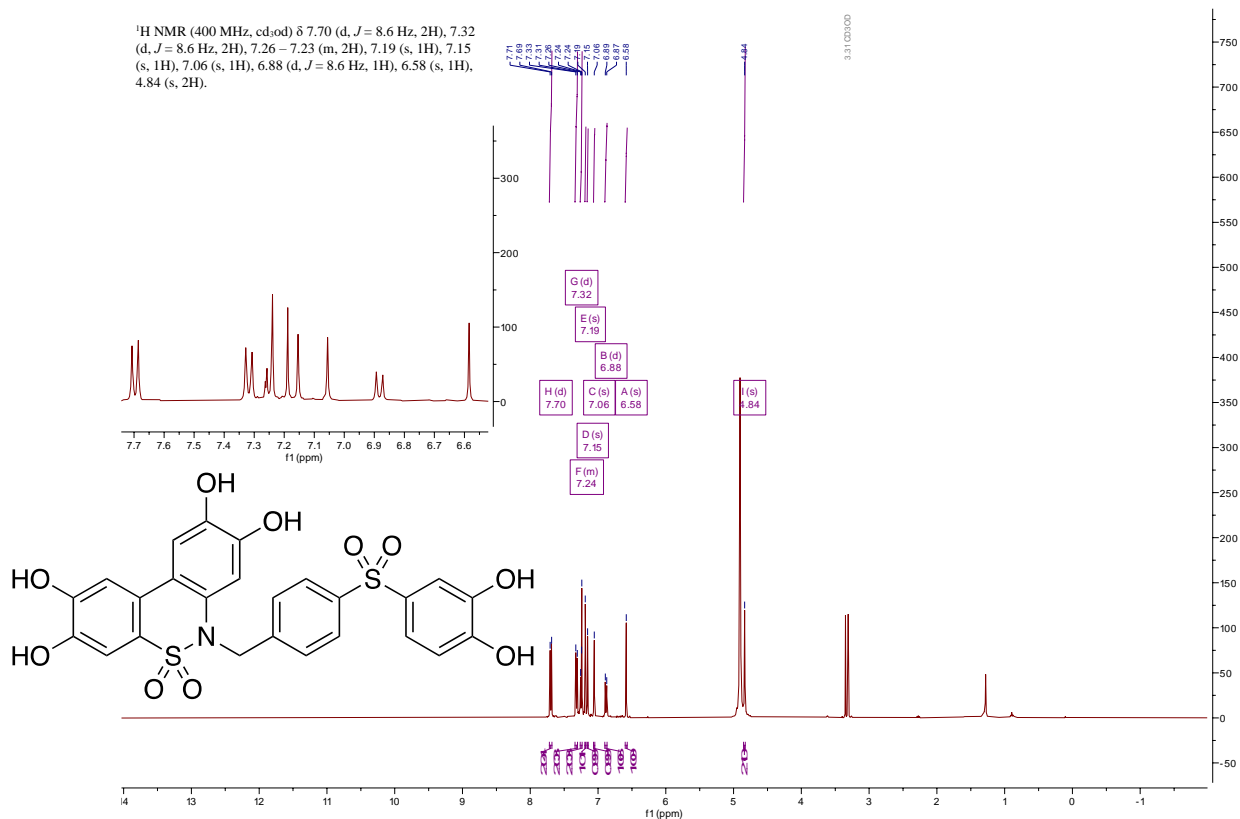
¹³C NMR (101 MHz, CD₃OD) of 1k

¹³C NMR (101 MHz, cd₃od) δ 157.93, 142.38, 141.98, 138.58, 133.60, 133.30, 130.12, 130.07, 128.83, 121.41, 117.33, 116.05, 29.01.



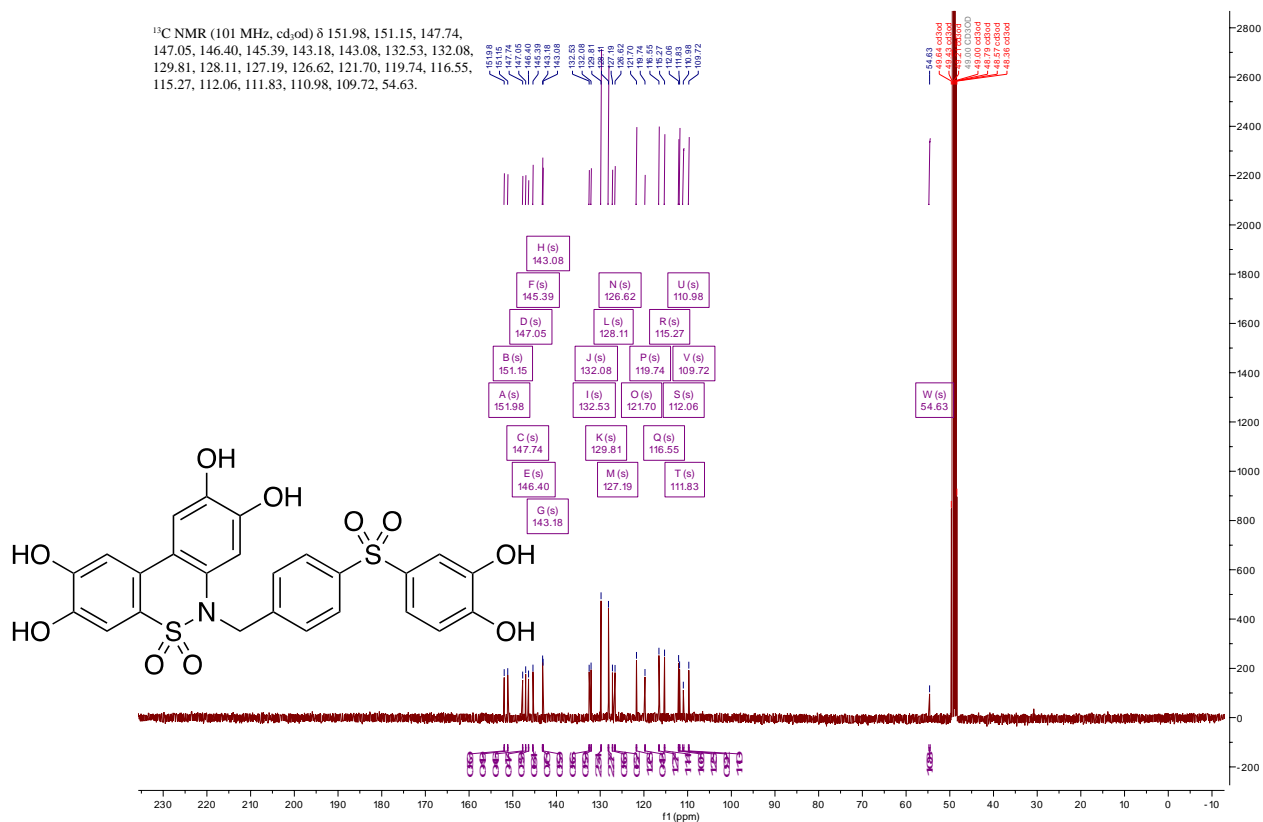
¹H NMR (400 MHz, CD₃OD) of 2a

¹H NMR (400 MHz, cd₃od) δ 7.70 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 7.26 – 7.23 (m, 2H), 7.19 (s, 1H), 7.15 (s, 1H), 7.06 (s, 1H), 6.88 (d, *J* = 8.6 Hz, 1H), 6.58 (s, 1H), 4.84 (s, 2H).



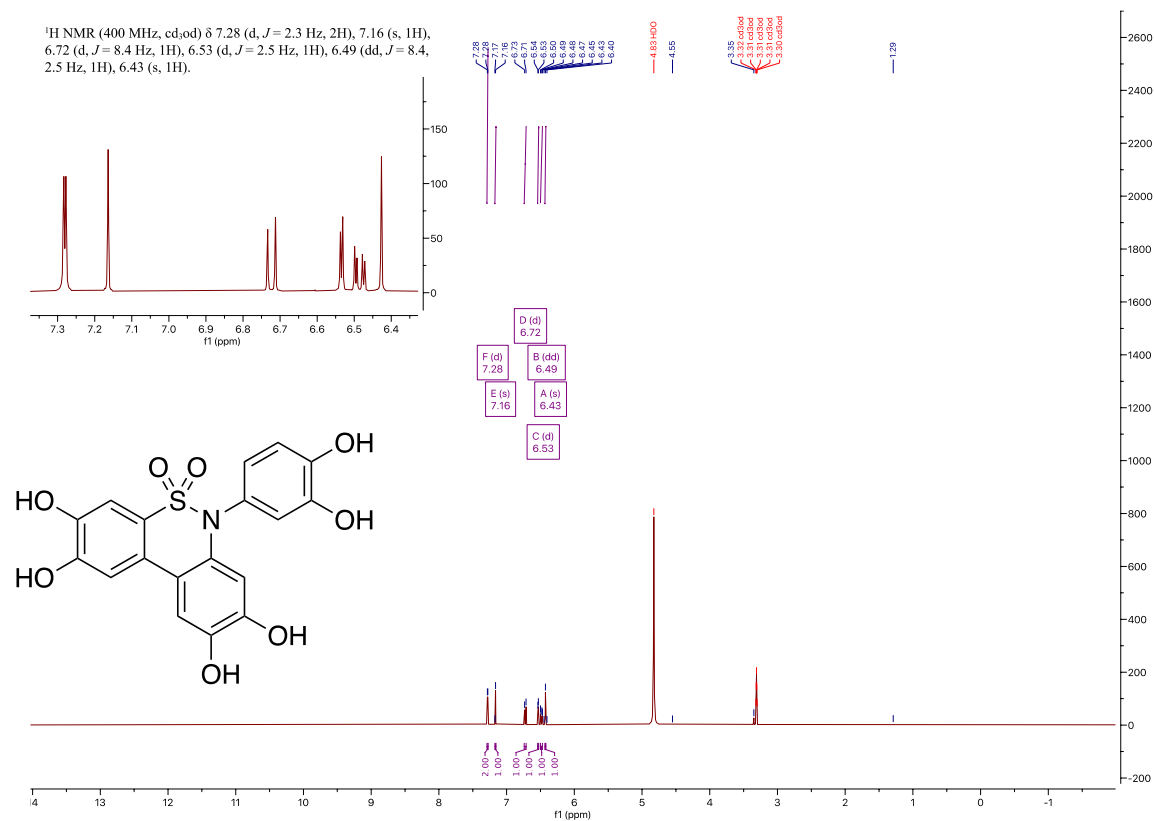
¹³C NMR (101 MHz, CD₃OD) of 2a

¹³C NMR (101 MHz, cd₃od) δ 151.98, 151.15, 147.74, 147.05, 146.40, 145.39, 143.18, 143.08, 132.53, 132.08, 129.81, 128.11, 127.19, 126.62, 121.70, 119.74, 116.55, 115.27, 112.06, 111.83, 110.98, 109.72, 54.63.



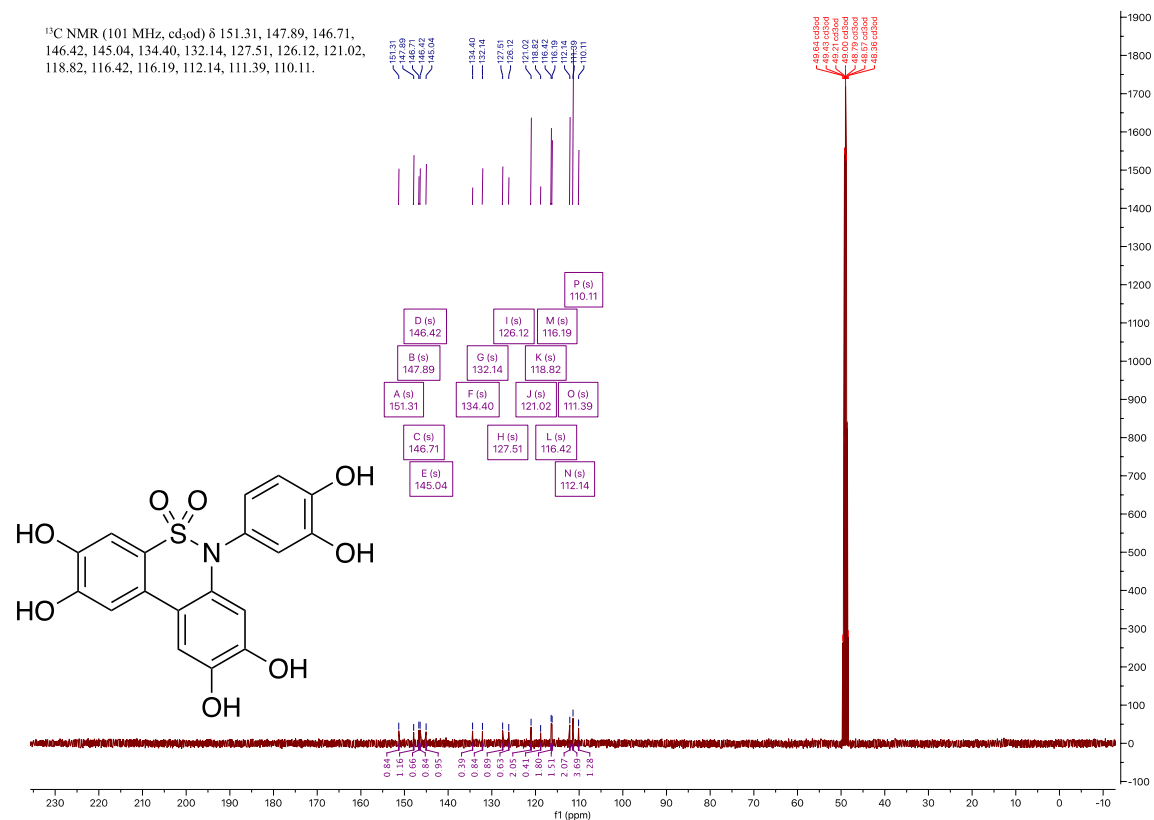
¹H NMR (400 MHz, CD₃OD) of 2c

¹H NMR (400 MHz, cd₃od) δ 7.28 (d, *J* = 2.3 Hz, 2H), 7.16 (s, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.53 (d, *J* = 2.5 Hz, 1H), 6.49 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.43 (s, 1H).



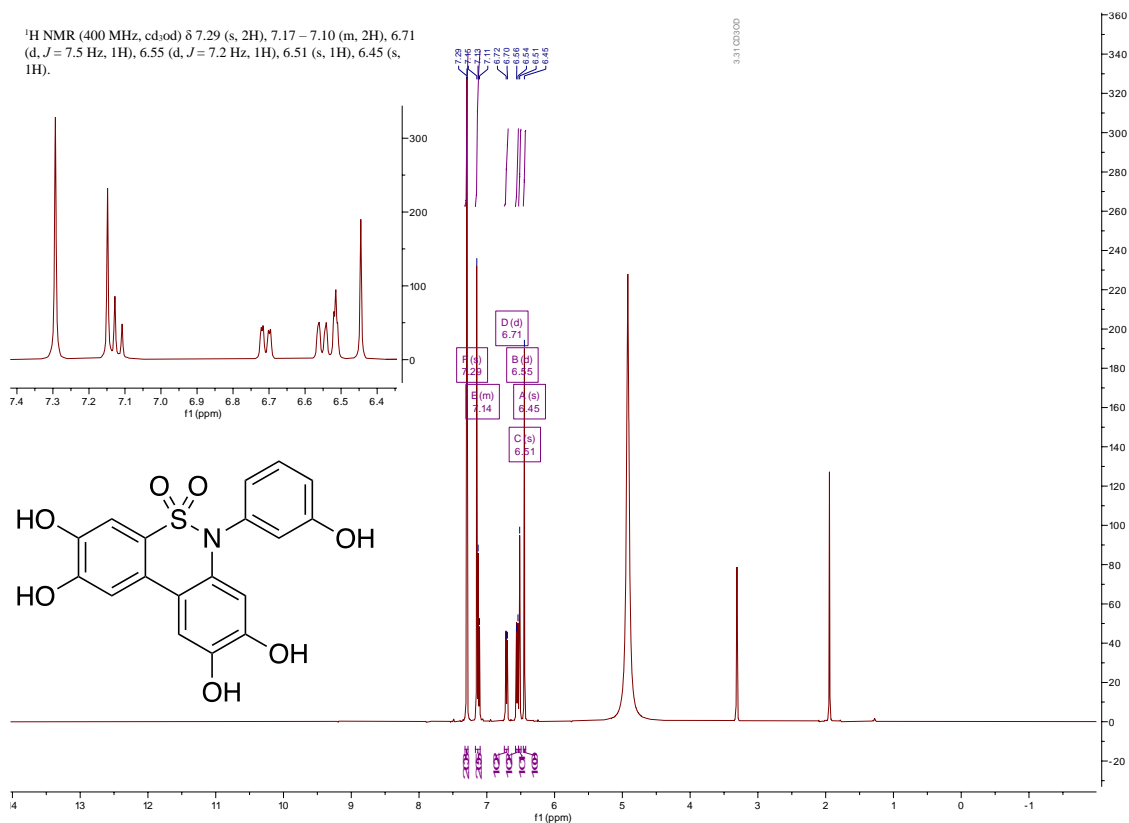
¹³C NMR (101 MHz, CD₃OD) of 2c

¹³C NMR (101 MHz, cd₃od) δ 151.31, 147.89, 146.71, 145.04, 134.40, 132.14, 127.51, 126.12, 121.02, 118.82, 116.42, 116.19, 112.14, 111.39, 110.11.



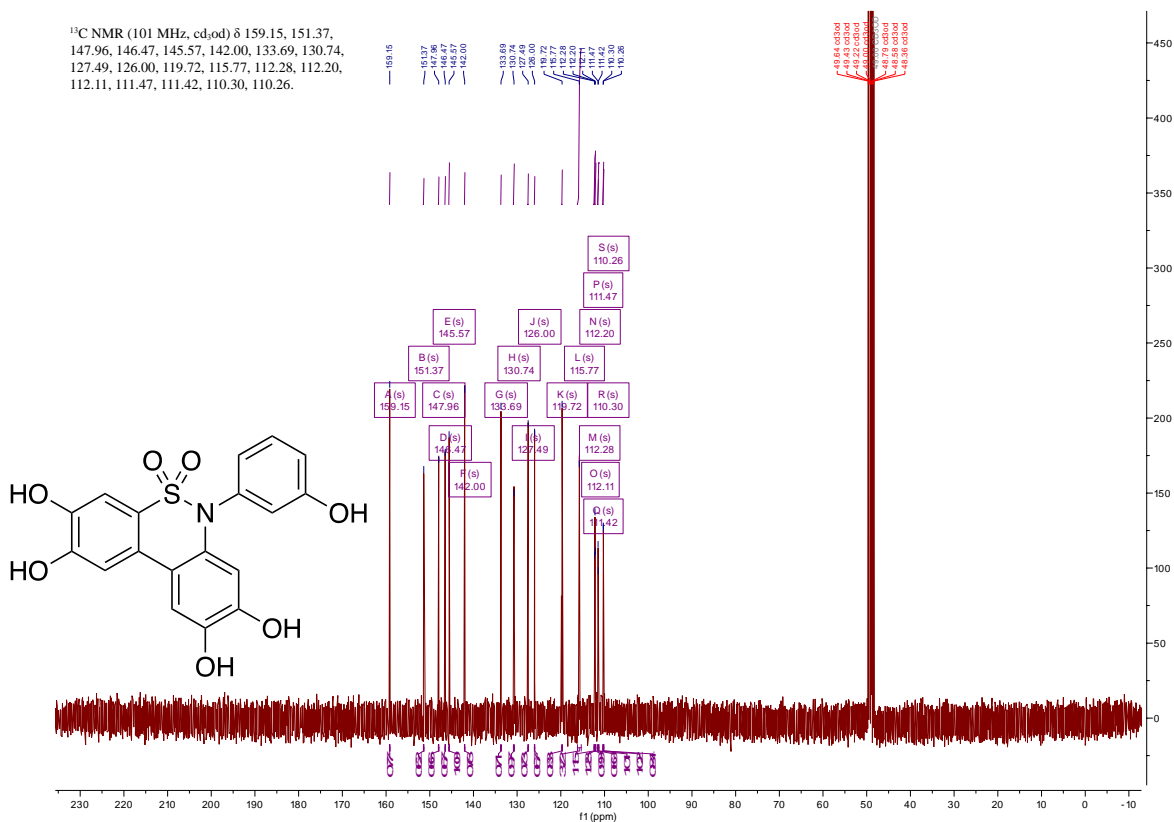
¹H NMR (400 MHz, CD₃OD) of 2d

¹H NMR (400 MHz, cd₃od) δ 7.29 (s, 2H), 7.17 – 7.10 (m, 2H), 6.71 (d, *J* = 7.5 Hz, 1H), 6.55 (d, *J* = 7.2 Hz, 1H), 6.51 (s, 1H), 6.45 (s, 1H).



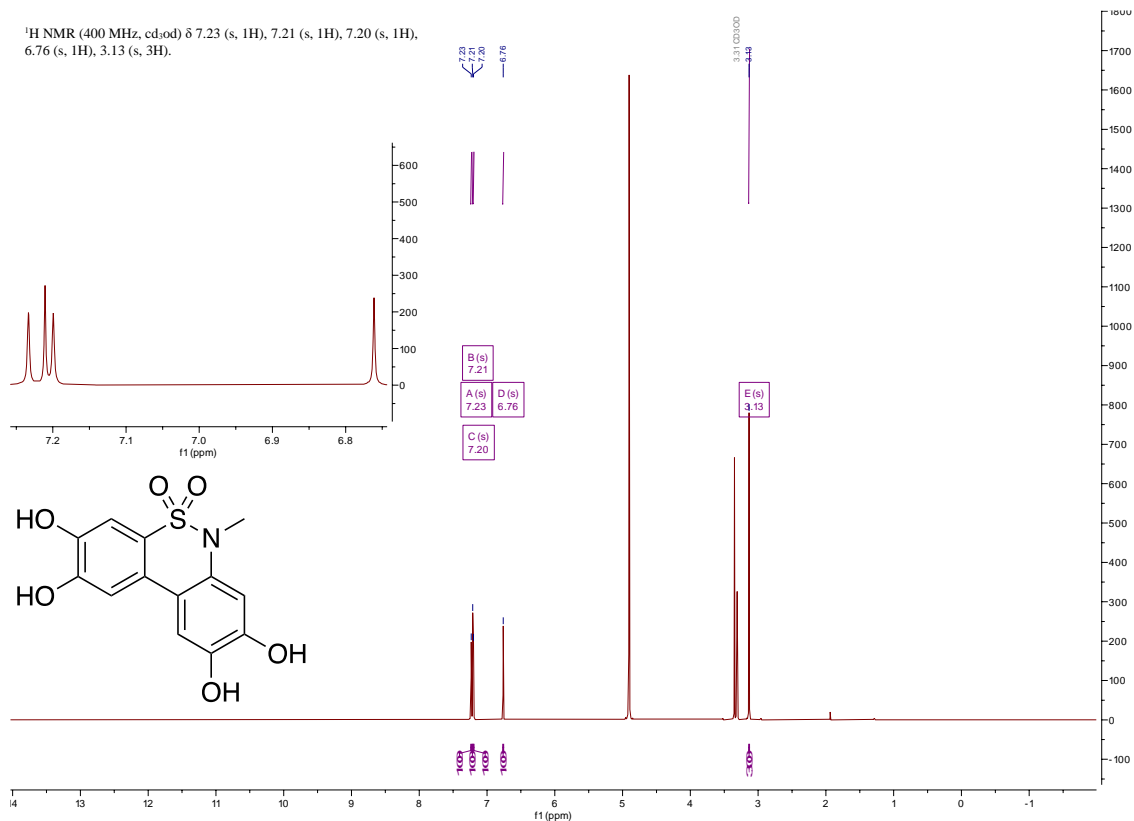
¹³C NMR (101 MHz, CD₃OD) of 2d

¹³C NMR (101 MHz, cd₃od) δ 159.15, 151.37, 147.96, 146.47, 145.57, 142.00, 133.69, 130.74, 127.49, 126.00, 119.72, 115.77, 112.28, 112.20, 112.11, 111.47, 111.42, 110.30, 110.26.



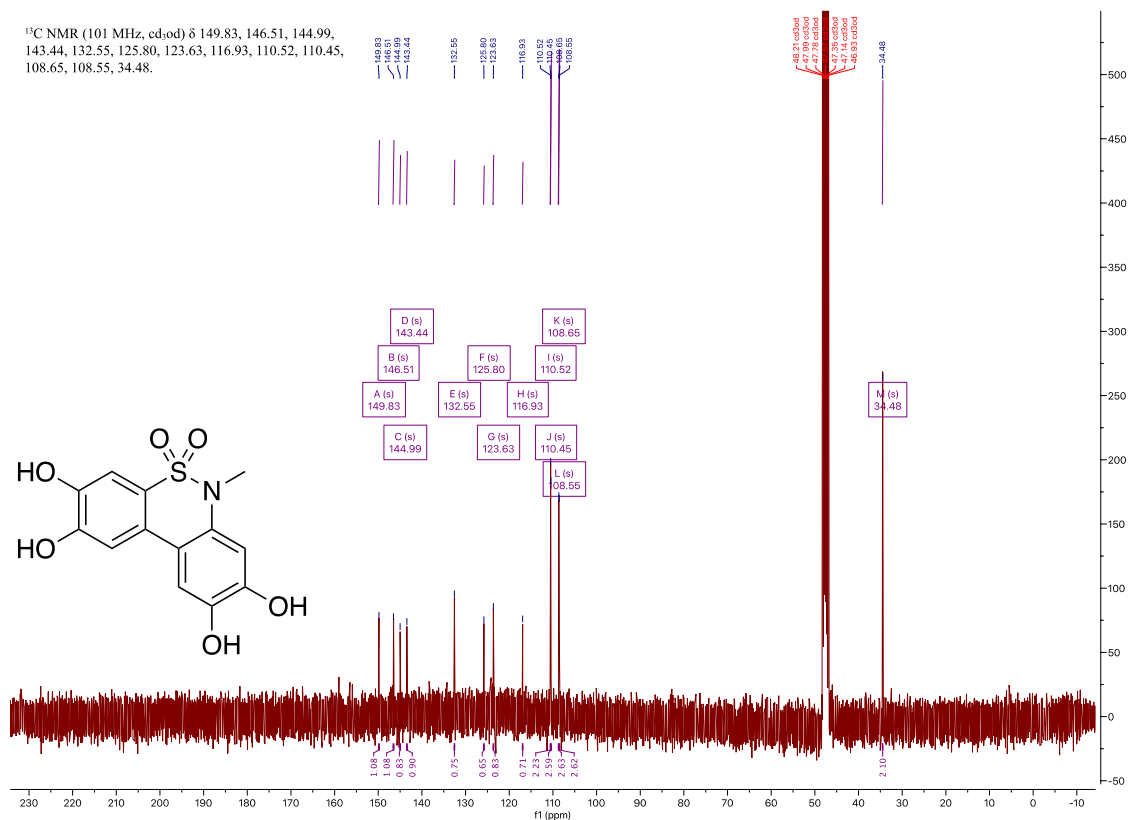
¹H NMR (400 MHz, CD₃OD) of 2f

¹H NMR (400 MHz, cd₃od) δ 7.23 (s, 1H), 7.21 (s, 1H), 7.20 (s, 1H), 6.76 (s, 1H), 3.13 (s, 3H).



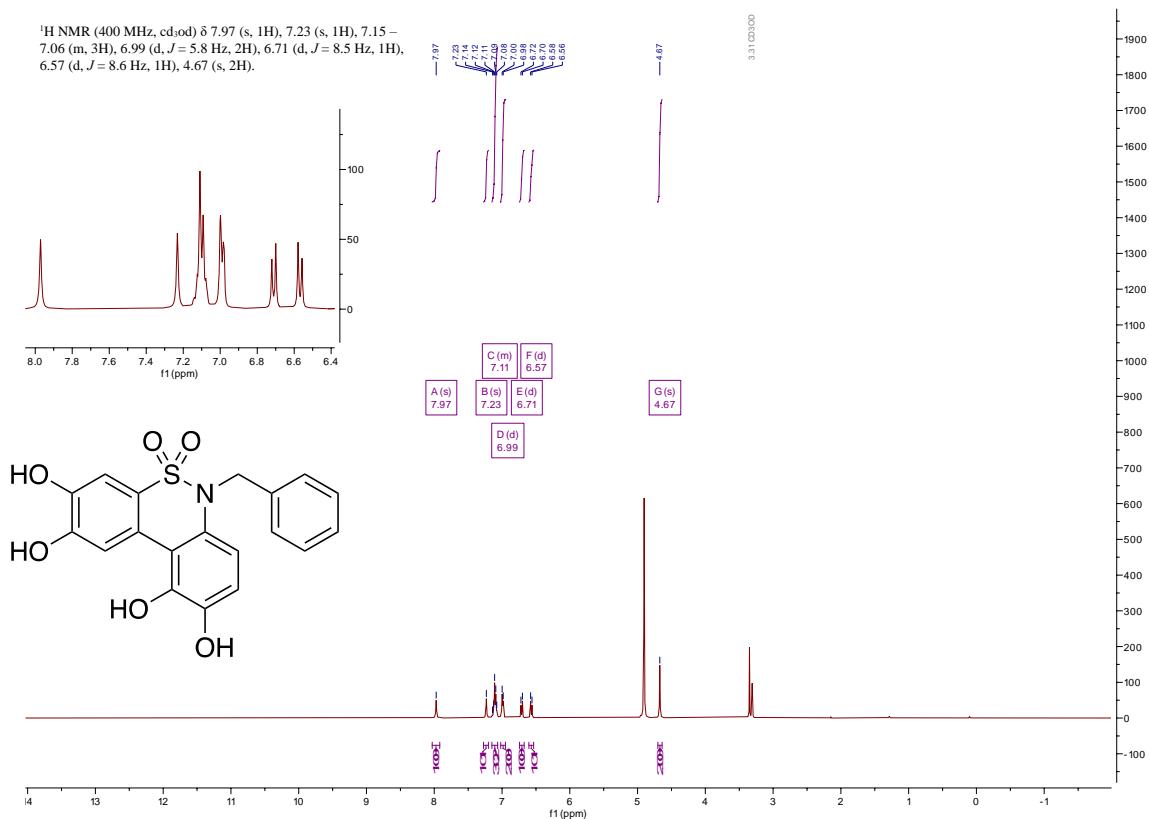
¹³C NMR (101 MHz, CD₃OD) of 2f

¹³C NMR (101 MHz, cd₃od) δ 149.83, 146.51, 144.99, 143.44, 132.55, 125.80, 123.63, 116.93, 110.52, 110.45, 108.65, 108.55, 34.48.



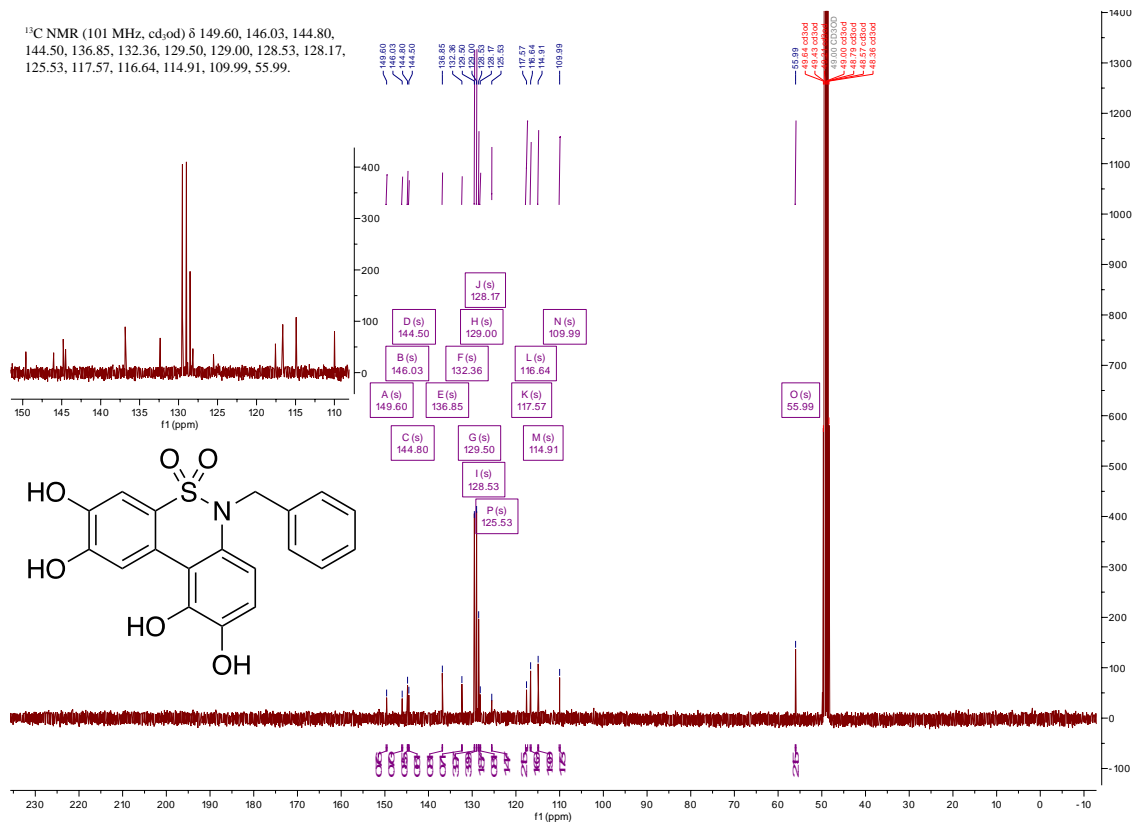
¹H NMR (400 MHz, CD₃OD) of 2i

¹H NMR (400 MHz, cd₃od) δ 7.97 (s, 1H), 7.23 (s, 1H), 7.15 – 7.06 (m, 3H), 6.99 (d, *J* = 5.8 Hz, 2H), 6.71 (d, *J* = 8.5 Hz, 1H), 6.57 (d, *J* = 8.6 Hz, 1H), 4.67 (s, 2H).



¹³C NMR (101 MHz, CD₃OD) of 2i

¹³C NMR (101 MHz, cd₃od) δ 149.60, 146.03, 144.80, 144.50, 136.85, 132.36, 129.50, 129.00, 128.53, 128.17, 125.53, 117.57, 116.64, 114.91, 109.99, 55.99.



Chromatographic data

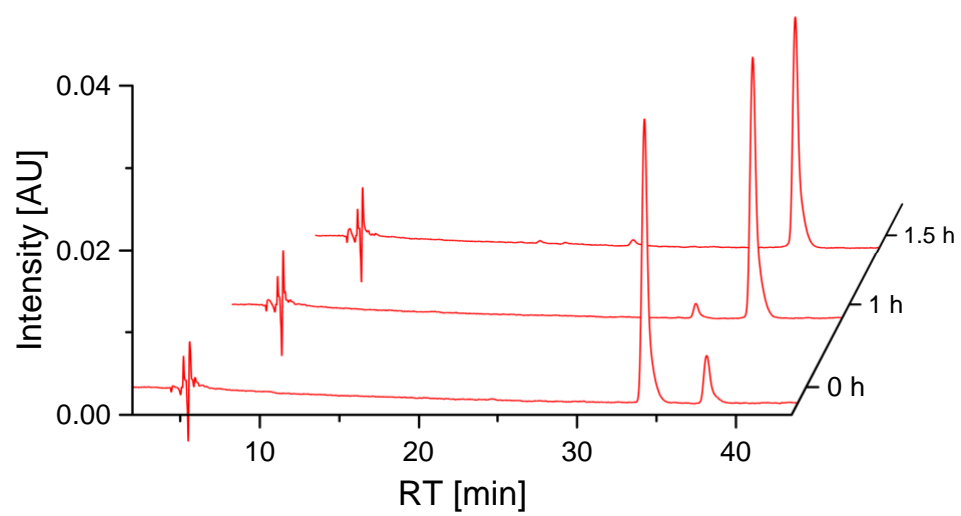


Figure S1. Chromatograms at 292 nm of **1g** in **TRIS 8** at 70 °C.

Cyclic voltammetry data

General information

Cyclic voltammetry was performed on an IKA Electrasyn2.0 potentiostat using a glassy carbon disk working electrode and a platinum plated copper counter electrode. The reference electrode is a silver wire in 0,01 M AgNO₃ in ACN.

Protocol

Compound **1g**: 13 mg of compound **1g** was dissolved in 5 mL of nitrogen purged 0.1 M tetrabutylammonium hexafluorophosphate solution in ACN. The solution was then purged with nitrogen again prior to data collection. A sweep of 100 mV/s between 0 V and 2 V was performed (Figure S2).

Data

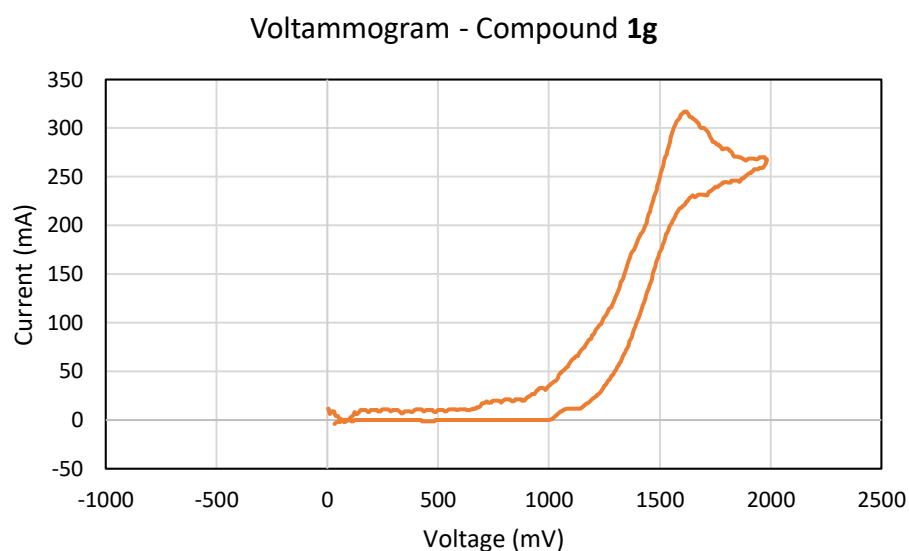


Figure S2. Voltammogram for compound **1g**.