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Catalyst-free direct C(sp^3)–H sulfenylation of xanthene derivatives using air as oxidant

Qian Chen,*[a,b] Guodian Yu,[a] Xiaofeng Wang,[a] Yingcong Ou[a] and Yanping Huo[a]

[a]School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, China; [b]Key Laboratory of Functional Molecular Engineering of Guangdong Province, South China University of Technology, Guangzhou 510640, China

*qianchen@gdut.edu.cn

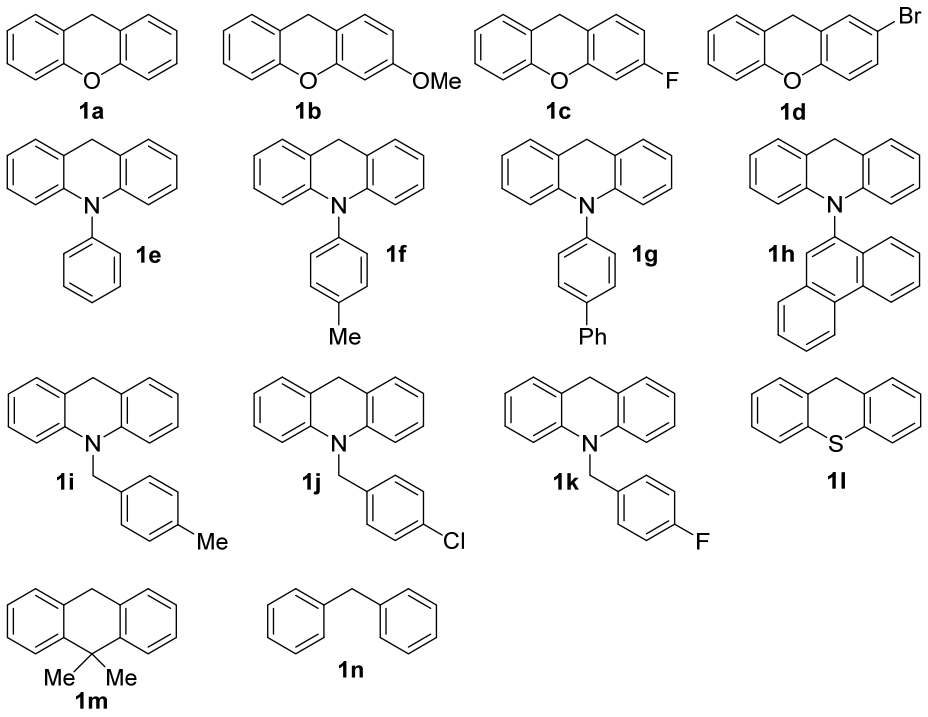
SUPPORTING INFORMATION

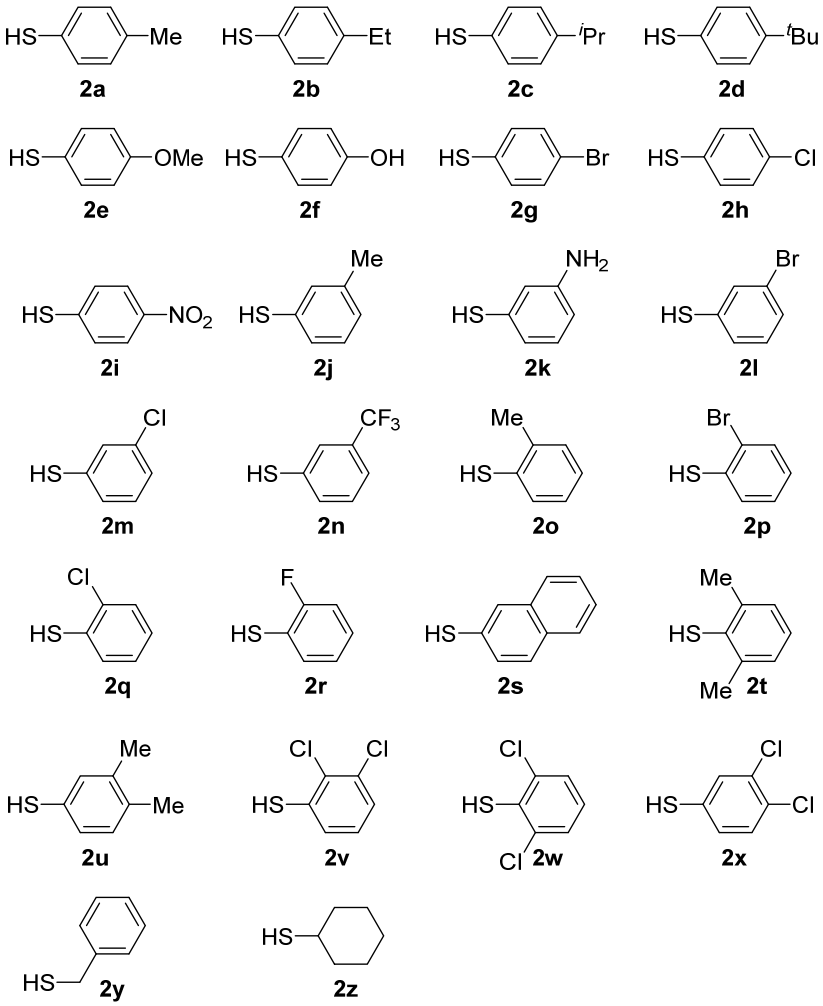
Content:

1. General information

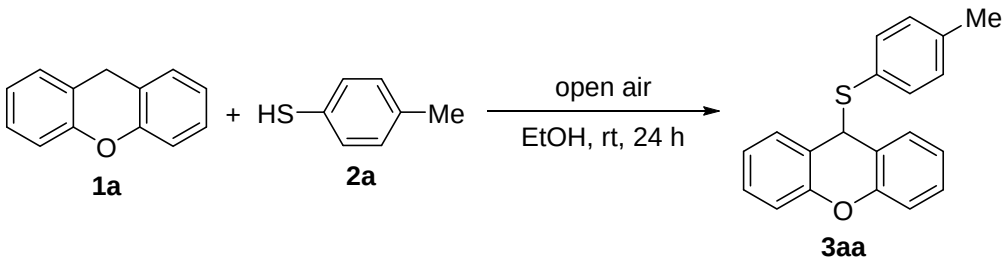
Unless otherwise stated, commercially available reagents including dry solvents were used without additional purification. Petroleum ether refers to the petroleum fraction b.p. 60~90 °C. Xanthenes were prepared according to the literature.[1] 9,10-Dihydroacridines and thioxanthene were prepared according to the literature.[2] All reactions were carried out in an oven-dried thick-walled glassware. Flash chromatography was performed using the indicated solvent system on silica gel standard grade (200~300 mesh). ^{1}H NMR spectra were recorded in $CDCl_3$ on Bruker 400 (400 MHz) spectrometer. ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker 400 (100 MHz) spectrometer. ^{19}F NMR spectra were recorded in $CDCl_3$ on Bruker 400 (376 MHz) spectrometer. Chemical shifts were reported relative to $CDCl_3$ (δ 7.26 ppm) for ^{1}H NMR and $CDCl_3$ (δ 77.16 ppm) for ^{13}C NMR. High-resolution mass spectra (HRMS) were recorded on ESI-TOF. Melting points (mp) were uncorrected and measured on micro melting point apparatus. Abbreviations for signal coupling are as follows: s = singlet, d = doublet; t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, br = broad.

2. Overview of substrates numbering





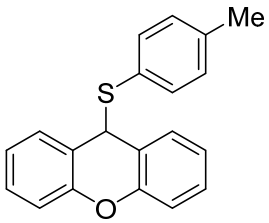
3. General procedure for the sulfenylation reaction



To a solution of xanthene **1a** (36 mg, 0.2 mmol) in EtOH (2 mL) was added thiophenol **2a** (50 mg, 0.4 mmol). The mixture was stirred at room temperature under air atmosphere for 24 h. The resulting mixture was then concentrated under reduced pressure. After removal of the solvent, the residue was then purified by flash column chromatography on silica gel with petroleum ether to give the desired **3aa** (51 mg, 84%) as a white solid.

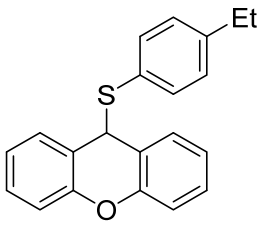
4. Characterizations of compounds 3

9-(*p*-Tolylthio)-9*H*-xanthene (3aa):



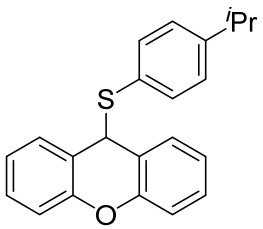
White solid (51 mg, 84%): mp 120–121 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, J = 7.6, 1.1 Hz, 2H), 7.24–7.20 (m, 2H), 7.08–7.04 (m, 2H), 6.97–6.91 (m, 4H), 6.82 (d, J = 8.0 Hz, 2H), 5.45 (s, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 139.1, 136.4, 129.7, 129.4, 128.5, 128.0, 123.2, 121.5, 116.4, 47.8, 21.4; HRMS (ESI-TOF) m/z: $[M - H]^+$ calcd for $C_{20}H_{15}OS$ 303.0838, found 303.0835.

9-((4-Ethylphenyl)thio)-9*H*-xanthene (3ab):



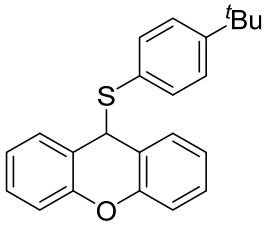
Colorless oil (55 mg, 87%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.25 (m, 2H), 7.21–7.19 (m, 2H), 7.06–7.02 (m, 2H), 6.97–6.93 (m, 4H), 6.85 (d, J = 8.1 Hz, 2H), 5.45 (s, 1H), 2.60 (q, J = 7.6 Hz, 2H), 1.20 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 145.2, 136.2, 129.3, 128.2, 128.0, 127.8, 122.9, 121.3, 116.1, 47.6, 28.4, 15.3; HRMS (ESI-TOF) m/z: $[M - H]^+$ calcd for $C_{21}H_{17}OS$ 317.0995, found 317.0993.

9-((4-Isopropylphenyl)thio)-9*H*-xanthene (3ac):



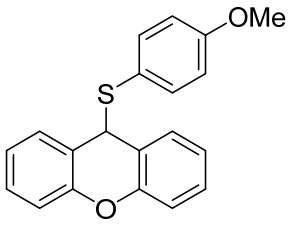
Colorless oil (60 mg, 90%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.19 (m, 4H), 7.05–6.93 (m, 6H), 6.87 (d, J = 8.2 Hz, 2H), 5.45 (s, 1H), 2.91–2.81 (m, 1H), 1.22 (d, J = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 150.1, 136.5, 129.6, 128.6 (2C), 126.7, 123.1, 121.6, 116.4, 48.0, 34.0, 24.1; HRMS (ESI-TOF) *m*/*z*: $[M - H]^+$ calcd for $C_{22}H_{19}OS$ 331.1151, found 331.1150.

9-((4-(*tert*-Butyl)phenyl)thio)-9*H*-xanthene (3ad):



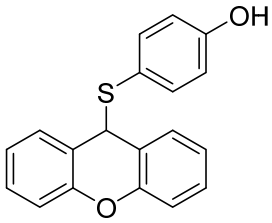
Colorless oil (67 mg, 96%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.18 (m, 4H), 7.14 (d, J = 8.4 Hz, 2H), 7.04–7.00 (m, 2H), 6.94 (d, J = 8.2 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 5.45 (s, 1H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 152.3, 136.1, 129.6, 128.6, 128.4, 125.6, 123.1, 121.6, 116.4, 48.0, 34.8, 31.4; HRMS (ESI-TOF) *m*/*z*: $[M - H]^+$ calcd for $C_{23}H_{21}OS$ 345.1308, found 345.1309.

9-((4-Methoxyphenyl)thio)-9*H*-xanthene (3ae):



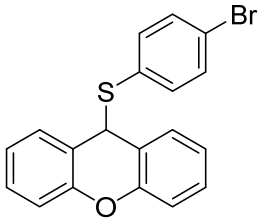
Blue oil (57 mg, 89%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, J = 7.6, 1.5 Hz, 2H), 7.22–7.18 (m, 2H), 7.07–7.03 (m, 2H), 6.91 (d, J = 8.2 Hz, 2H), 6.77 (d, J = 8.8 Hz, 2H), 6.62 (d, J = 8.8 Hz, 2H), 5.39 (s, 1H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 152.3, 138.2, 129.7, 128.5, 123.2, 122.1, 121.5, 116.3, 114.1, 55.4, 48.0; HRMS (ESI-TOF) *m*/*z*: $[M - H]^+$ calcd for $C_{20}H_{15}O_2S$ 319.0787, found 319.0784.

4-((9*H*-xanthen-9-yl)thio)phenol (3af):



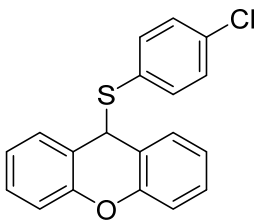
Red oil (55 mg, 90%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, J = 7.6, 1.3 Hz, 2H), 7.22–7.18 (m, 2H), 7.08–7.04 (m, 2H), 6.91 (d, J = 8.2 Hz, 2H), 6.71 (d, J = 8.7 Hz, 2H), 6.55 (d, J = 8.7 Hz, 2H), 5.39 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 152.3, 138.5, 129.7, 128.5, 123.2, 122.2, 121.4, 116.3, 115.6, 47.9; HRMS (ESI-TOF) *m*/*z*: $[M - H]^+$ calcd for $C_{19}H_{13}O_2S$ 305.0631, found 305.0629.

9-((4-Bromophenyl)thio)-9*H*-xanthene (3ag):



Blue oil (38 mg, 52%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, J = 7.6, 1.2 Hz, 2H), 7.24–7.22 (m, 4H), 7.09–7.05 (m, 2H), 6.93 (d, J = 8.2 Hz, 2H), 6.69 (d, J = 8.4 Hz, 2H), 5.50 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 138.0, 131.6, 130.4, 129.6, 128.8, 123.9, 123.4, 121.0, 116.5, 47.9; HRMS (ESI-TOF) *m*/*z*: $[M - H]^+$ calcd for $C_{19}H_{12}{}^{79}BrOS$ 366.9787, found 366.9786.

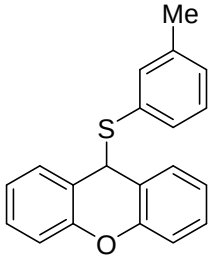
9-((4-Chlorophenyl)thio)-9*H*-xanthene (3ah):



Yellow oil (22 mg, 34%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, J = 7.6, 1.1 Hz, 2H), 7.24–7.19 (m, 2H), 7.09–7.05 (m, 4H), 6.92 (d, J = 8.2 Hz, 2H), 6.75 (d, J = 8.4

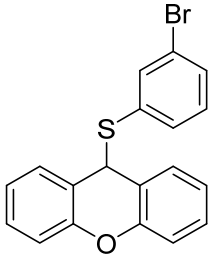
Hz, 2H), 5.49 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 137.8, 135.6, 129.7, 129.6, 128.8, 128.7, 123.4, 121.0, 116.5, 47.9; HRMS (ESI-TOF) *m*/*z*: $[M - H]^+$ calcd for $C_{19}H_{12}{}^{35}ClOS$ 323.0292, found 323.0291.

9-(*m*-Tolylthio)-9*H*-xanthene (3aj):



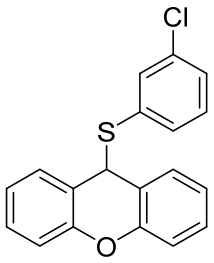
Colorless oil (53 mg, 87%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.23–7.18 (m, 2H), 7.10–7.03 (m, 3H), 7.00 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.92 (dd, *J* = 8.2, 1.0 Hz, 2H), 6.73 (d, *J* = 7.6 Hz, 1H), 6.67 (s, 1H), 5.48 (s, 1H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 138.3, 137.2, 133.4, 131.1, 129.7 (2C), 128.6, 128.3, 123.2, 121.5, 116.3, 47.8, 21.2; HRMS (ESI-TOF) *m*/*z*: $[M - H]^+$ calcd for $C_{20}H_{15}OS$ 303.0838, found 303.0835.

9-((3-Bromophenyl)thio)-9*H*-xanthene (3al):



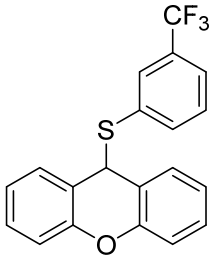
Yellow oil (41 mg, 56%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.23 (dd, *J* = 7.3, 7.3 Hz, 2H), 7.09 (dd, *J* = 7.4, 7.4 Hz, 2H), 6.98–6.92 (m, 4H), 6.79 (d, *J* = 7.7 Hz, 1H), 5.53 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 139.0, 135.0, 133.4, 132.0, 129.7, 129.6, 128.9, 123.4, 122.0, 120.9, 116.4, 48.2; HRMS (ESI-TOF) *m*/*z*: $[M - H]^+$ calcd for $C_{19}H_{12}{}^{79}BrOS$ 366.9787, found 366.9786.

9-((3-Chlorophenyl)thio)-9*H*-xanthene (3am):



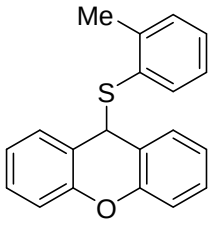
Colorless oil (25 mg, 40%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 7.6 Hz, 2H), 7.26–7.21 (m, 3H), 7.10–7.06 (m, 2H), 7.02 (dd, J = 7.9, 7.9 Hz, 1H), 6.93 (d, J = 8.2 Hz, 2H), 6.80 (s, 1H), 6.75 (d, J = 7.7 Hz, 1H), 5.53 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 136.2, 134.5, 133.9, 133.1, 129.6, 129.4, 129.1, 128.9, 123.4, 120.9, 116.4, 48.1; HRMS (ESI-TOF) m/z: $[M - H]^+$ calcd for $C_{19}H_{12}{}^{35}ClOS$ 323.0292, found 323.0291.

9-((3-(Trifluoromethyl)phenyl)thio)-9*H*-xanthene (3an):



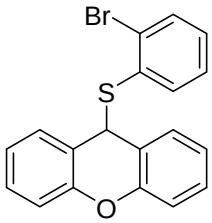
Yellow oil (16 mg, 23%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.8 Hz, 1H), 7.37 (dd, J = 7.6, 1.4 Hz, 2H), 7.24–7.15 (m, 3H), 7.11–7.07 (m, 2H), 6.97–6.96 (m, 2H), 6.86 (d, J = 8.2 Hz, 2H), 5.57 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 139.8, 133.4 (q, J = 3.7 Hz), 132.0 (q, J = 33.3 Hz), 130.5, 129.5, 128.8, 128.6, 125.6 (q, J = 3.7 Hz), 123.4, 120.5, 122.1 (q, J = 273 Hz), 116.3, 47.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9; HRMS (ESI-TOF) m/z: $[M - H]^+$ calcd for $C_{20}H_{12}F_3OS$ 357.0555, found 357.0558.

9-(*o*-Tolylthio)-9*H*-xanthene (3ao):



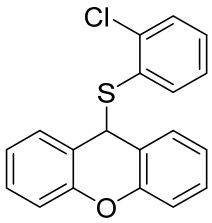
Yellow oil (56 mg, 92%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.19 (m, 3H), 7.17–7.09 (m, 3H), 7.04–6.98 (m, 6H), 5.41 (s, 1H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 143.9, 138.0, 131.4, 130.3, 129.4, 129.3, 128.7, 126.1, 123.2, 121.7, 116.5, 47.9, 20.6; HRMS (ESI-TOF) *m*/*z*: $[M - H]^+$ calcd for $C_{20}H_{15}OS$ 303.0838, found 303.0835.

9-((2-Bromophenyl)thio)-9*H*-xanthene (3ap):



Colorless oil (48 mg, 65%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.9 Hz, 1H), 7.27–7.23 (m, 2H), 7.19–7.15 (m, 1H), 7.11–7.04 (m, 6H), 6.98 (dd, J = 7.4, 7.4 Hz, 2H), 5.70 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 138.7, 133.9, 133.3, 131.7, 130.6, 129.2, 129.0, 127.7, 123.2, 121.2, 116.7, 47.0; HRMS (ESI-TOF) *m*/*z*: $[M - H]^+$ calcd for $C_{19}H_{12}{}^{79}BrOS$ 366.9787, found 366.9786.

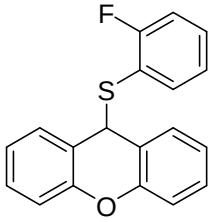
9-((2-Chlorophenyl)thio)-9*H*-xanthene (3aq):



Colorless oil (36 mg, 55%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.9 Hz, 1H), 7.27–7.18 (m, 3H), 7.09–7.04 (m, 4H), 7.01–6.94 (m, 4H), 5.66 (s, 1H); ^{13}C NMR

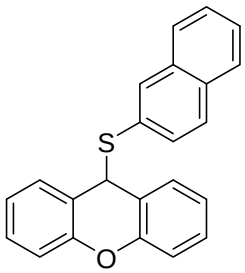
(100 MHz, $CDCl_3$) δ 152.5, 140.3, 138.8, 131.8, 130.6, 129.9, 129.2, 129.0, 127.0, 123.2, 121.3, 116.7, 46.7; HRMS (ESI-TOF) *m*/*z*: $[M - H]^+$ calcd for $C_{19}H_{12}{}^{35}ClOS$ 323.0292, found 323.0291.

9-((2-Fluorophenyl)thio)-9*H*-xanthene (3ar):



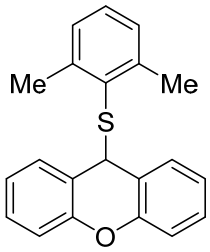
Colorless oil (37 mg, 60%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.33–7.27 (m, 1H), 7.25–7.18 (m, 4H), 7.04–6.98 (m, 5H), 6.91–6.89 (m, 2H), 5.59 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8 (d, J = 245 Hz), 152.3, 138.5, 131.5 (d, J = 8.1 Hz), 129.4, 128.9, 124.3 (d, J = 3.9 Hz), 123.3, 121.3, 119.7, 116.6, 115.7 (d, J = 23.6 Hz), 47.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.8; HRMS (ESI-TOF) *m*/*z*: $[M - H]^+$ calcd for $C_{19}H_{12}FOS$ 307.0587, found 307.0587.

9-(Naphthalen-2-ylthio)-9*H*-xanthene (3as):



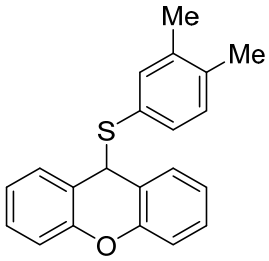
White solid (55 mg, 81%): mp 130–131 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.0 Hz, 1H), 7.62–7.54 (m, 2H), 7.50–7.41 (m, 2H), 7.39 (s, 1H), 7.31 (d, J = 7.6 Hz, 2H), 7.23–7.17 (m, 2H), 7.07–7.01 (m, 3H), 6.88 (d, J = 9.2 Hz, 2H), 5.58 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 136.2, 133.4, 133.1, 132.6, 129.5, 129.0, 128.5, 127.84, 127.82, 127.6, 126.6, 126.1, 123.1, 121.3, 116.3, 47.9; HRMS (ESI-TOF) *m*/*z*: $[M - H]^+$ calcd for $C_{23}H_{15}OS$ 339.0838, found 339.0838.

9-((2,6-Dimethylphenyl)thio)-9*H*-xanthene (3at):



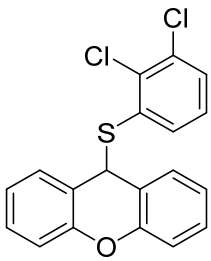
White solid (61 mg, 95%): mp 122–123 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.23 (m, 2H), 7.19–7.13 (m, 3H), 7.07 (d, J = 7.4 Hz, 2H), 6.93 (dd, J = 7.4, 7.4 Hz, 2H), 6.80 (d, J = 7.6 Hz, 2H), 5.25 (s, 1H), 2.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 144.6, 132.1, 129.2, 128.8, 128.7, 128.2, 123.1, 121.8, 116.6, 46.0, 21.7; HRMS (ESI-TOF) m/z: $[M - H]^+$ calcd for $C_{21}H_{17}OS$ 317.0995, found 317.0993.

9-((3,4-Dimethylphenyl)thio)-9*H*-xanthene (3au):



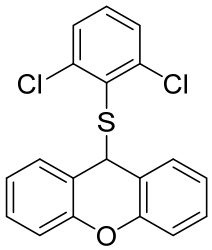
Colorless oil (61 mg, 95%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 8.6 Hz, 2H), 7.20 (dd, J = 7.7, 7.7 Hz, 2H), 7.04 (dd, J = 7.4, 7.4 Hz, 2H), 6.93 (d, J = 8.2 Hz, 2H), 6.88 (d, J = 7.7 Hz, 1H), 6.68 (d, J = 7.8 Hz, 1H), 6.65 (s, 1H), 5.43 (s, 1H), 2.21 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 137.7, 137.6, 136.9, 133.8, 129.8, 129.7, 128.5, 128.2, 123.2, 121.7, 116.3, 47.9, 19.7, 19.5; HRMS (ESI-TOF) m/z: $[M - H]^+$ calcd for $C_{21}H_{17}OS$ 317.0995, found 317.0993.

9-((2,3-Dichlorophenyl)thio)-9*H*-xanthene (3av):



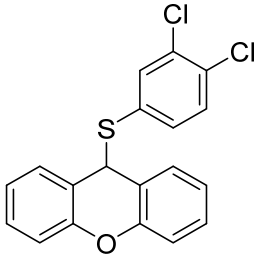
Yellow oil (38 mg, 53%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, J = 6.5, 3.1 Hz, 1H), 7.28–7.23 (m, 2H), 7.12–7.06 (m, 4H), 7.02–6.98 (m, 2H), 6.97–6.91 (m, 2H), 5.70 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 138.3, 136.6, 134.3, 133.7, 131.3, 129.1 (2C), 127.0, 123.3, 121.0, 116.7, 47.0; HRMS (ESI-TOF) m/z: $[M - H]^+$ calcd for $C_{19}H_{11}{}^{35}Cl_2OS$ 356.9902, found 356.9902.

9-((2,6-Dichlorophenyl)thio)-9*H*-xanthene (3aw):



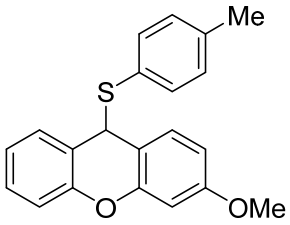
Colorless oil (43 mg, 60%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.2 Hz, 2H), 7.30–7.25 (m, 2H), 7.22–7.13 (m, 3H), 6.95–6.88 (m, 4H), 5.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 143.0, 132.0, 130.7, 129.2, 128.6, 128.5, 123.1, 121.0, 116.9, 46.5; HRMS (ESI-TOF) m/z: $[M - H]^+$ calcd for $C_{19}H_{11}{}^{35}Cl_2OS$ 356.9902, found 356.9902.

9-((3,4-Dichlorophenyl)thio)-9*H*-xanthene (3ax):



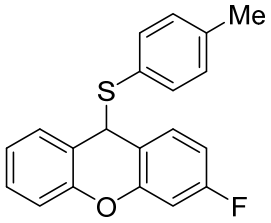
Colorless oil (45 mg, 63%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 2.2 Hz, 1H), 7.26–7.23 (m, 2H), 7.12 (dd, J = 6.3, 1.3 Hz, 2H), 7.05 (d, J = 8.1 Hz, 2H), 7.03–6.96 (m, 3H), 6.86 (d, J = 8.3 Hz, 1H), 5.63 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 141.2, 139.4, 136.0, 130.2, 129.7, 129.2, 129.1, 127.2, 123.4, 121.0, 116.70, 47.1; HRMS (ESI-TOF) m/z: $[M - H]^+$ calcd for $C_{19}H_{11}{}^{35}Cl_2OS$ 356.9902, found 356.9902.

3-Methoxy-9-(*p*-tolylthio)-9*H*-xanthene (3ba):



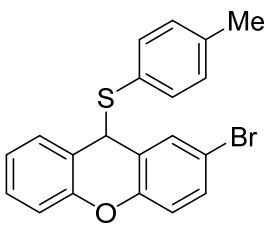
Yellow oil (34 mg, 51%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (dd, J = 7.6, 1.6 Hz, 1H), 7.22–7.16 (m, 2H), 7.05–7.01 (m, 1H), 6.94–6.91 (m, 3H), 6.83 (d, J = 8.1 Hz, 2H), 6.65 (dd, J = 8.5, 2.6 Hz, 1H), 6.48 (d, J = 2.5 Hz, 1H), 5.42 (s, 1H), 3.80 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 153.0, 152.0, 138.8, 136.2, 130.2, 129.6, 129.2, 128.3, 128.2, 123.0, 121.7, 116.1, 113.5, 110.4, 100.7, 55.5, 47.5, 21.3; HRMS (ESI-TOF) *m*/*z*: $[M - H]^+$ calcd for $C_{21}H_{17}O_2S$ 333.0944, found 333.0942.

3-Fluoro-9-(*p*-tolylthio)-9*H*-xanthene (3ca):



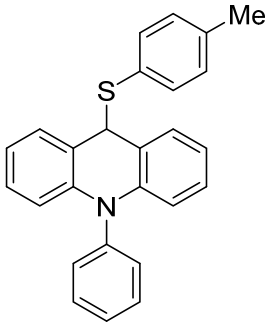
Colorless oil (28 mg, 43%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, J = 7.6, 1.5 Hz, 1H), 7.25–7.19 (m, 2H), 7.09–7.05 (m, 1H), 6.95–6.90 (m, 3H), 6.80–6.74 (m, 3H), 6.65 (dd, J = 9.7, 2.5 Hz, 1H), 5.41 (s, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, J = 242 Hz), 153.0 (d, J = 12.6 Hz), 151.8, 139.3, 136.4, 130.8 (d, J = 9.8 Hz), 129.7, 129.5, 128.7, 127.7, 123.6, 121.4, 116.3, 110.8, 110.5, 103.6 (d, J = 25.0 Hz), 47.2, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.7; HRMS (ESI-TOF) *m*/*z*: $[M - H]^+$ calcd for $C_{20}H_{14}FOS$ 321.0744, found 321.0742.

2-Bromo-9-(*p*-tolylthio)-9*H*-xanthene (3da):



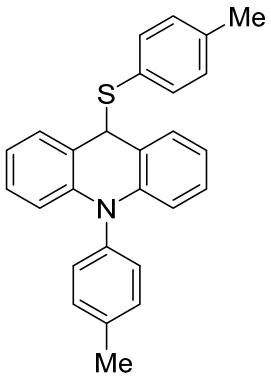
Yellow oil (42 mg, 55%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, J = 7.7, 1.5 Hz, 2H), 7.25–7.22 (m, 1H), 7.21–7.16 (m, 1H), 7.06–7.02 (m, 1H), 6.93–6.87 (m, 3H), 6.83–6.74 (m, 3H), 5.31 (s, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 151.2, 139.5, 136.5, 132.1, 131.4, 129.7, 129.5, 128.8, 127.5, 123.6, 123.6, 120.8, 118.1, 116.4, 115.0, 47.3, 21.4; HRMS (ESI-TOF) m/z: $[M - H]^+$ calcd for $C_{20}H_{14}{}^{79}BrOS$ 380.9943, found 380.9940.

10-Phenyl-9-(*p*-tolylthio)-9,10-dihydroacridine (3ea):



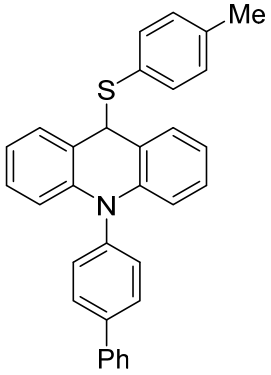
Yellow oil (71 mg, 93%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 7.5, 7.5 Hz, 2H), 7.47–7.43 (m, 1H), 7.32 (d, J = 7.5 Hz, 2H), 6.98–6.94 (m, 4H), 6.91–6.87 (m, 4H), 6.78 (d, J = 8.0 Hz, 2H), 6.09 (d, J = 8.2 Hz, 2H), 5.74 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 140.4, 138.7, 137.0, 131.1, 130.7, 129.7, 129.2, 128.8, 128.4, 127.6, 120.7, 120.5, 114.0, 53.0, 21.3; HRMS (ESI-TOF) m/z: $[M - H]^+$ calcd for $C_{26}H_{20}NS$ 378.1311, found 378.1306; $[M - TolS]^+$ calcd for $C_{19}H_{14}N$ 256.1119, found 256.1121.

10-(*p*-Tolyl)-9-(*p*-tolylthio)-9,10-dihydroacridine (3fa):



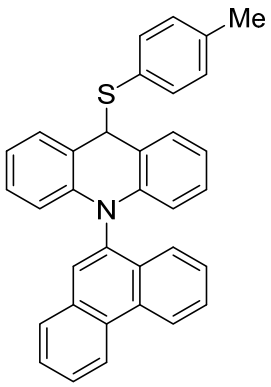
Yellow oil (75 mg, 96%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.28 (m, 4H), 6.99–6.92 (m, 4H), 6.89–6.85 (m, 2H), 6.76 (d, J = 7.8 Hz, 4H), 6.12 (d, J = 8.3 Hz, 2H), 5.73 (s, 1H), 2.45 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 138.5, 138.1, 137.5, 136.9, 131.2, 130.6, 129.6, 129.1, 128.7, 127.4, 120.4, 120.3, 113.9, 52.9, 21.3, 21.2; HRMS (ESI-TOF) m/z: $[M - H]^+$ calcd for $C_{27}H_{22}NS$ 392.1467, found 392.1461; $[M - TolS]^+$ calcd for $C_{20}H_{16}N$ 270.1277, found 270.1274.

10-([1,1'-Biphenyl]-4-yl)-9-(*p*-tolylthio)-9,10-dihydroacridine (3ga):



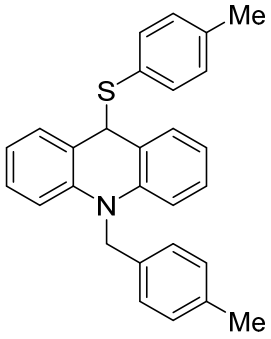
Yellow oil (82 mg, 90%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.5 Hz, 2H), 7.68 (d, J = 7.1 Hz, 2H), 7.50 (dd, J = 7.5, 7.5 Hz, 2H), 7.43–7.39 (m, 1H), 7.34 (dd, J = 7.5, 1.4 Hz, 2H), 7.03–6.95 (m, 6H), 6.93–6.89 (m, 2H), 6.80 (d, J = 8.0 Hz, 2H), 6.21 (d, J = 7.7 Hz, 2H), 5.76 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 141.3, 140.4, 139.5, 138.7, 137.1, 131.4, 129.8, 129.4, 129.2, 129.1, 128.8, 127.8, 127.6, 127.3, 120.7, 120.5, 114.1, 52.9, 21.4; HRMS (ESI-TOF) m/z: $[M - H]^+$ calcd for $C_{32}H_{24}NS$ 454.1624, found 454.1618; $[M - TolS]^+$ calcd for $C_{25}H_{18}N$ 332.1434, found 332.1431.

10-(Phenanthren-9-yl)-9-(*p*-tolylthio)-9,10-dihydroacridine (3ha):



White solid (85 mg, 89%): mp 133–134 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84–8.75 (m, 2H), 8.25–7.61 (m, 5H), 7.56–7.27 (m, 3H), 7.19–6.99 (m, 4H), 6.95–6.35 (m, 6H), 5.96 (d, J = 8.2 Hz, 1H), 5.86 (s, 0.6H), 5.84 (s, 0.4H), 2.49 (s, 1.8H), 2.49 (s, 1.2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 141.4, 138.7, 138.5, 137.1, 136.7, 135.3, 135.1, 132.5, 132.4, 132.1, 131.9, 130.9, 130.49, 130.47, 130.45, 129.8, 129.7, 129.6, 129.5, 129.4, 129.3, 129.2, 129.12, 129.06, 128.99, 128.9, 128.8, 128.7, 127.9, 127.7, 127.61, 127.57, 127.33, 127.26, 127.0, 124.7, 124.4, 123.4, 123.0, 122.9, 122.8, 120.7, 120.6, 120.4, 120.3, 114.3, 114.0, 53.4, 52.7, 21.5, 21.4; HRMS (ESI-TOF) *m*/*z*: [M - H]$^{+}$ calcd for $C_{34}H_{24}NS$ 478.1624, found 478.1622; [M - TolS]$^{+}$ calcd for $C_{27}H_{18}N$ 356.1434, found 356.1433.

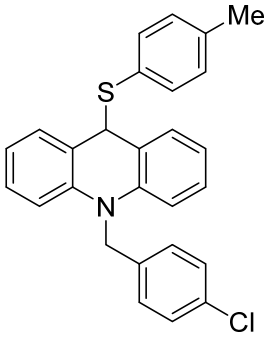
10-(4-Methylbenzyl)-9-(*p*-tolylthio)-9,10-dihydroacridine (3ia):



White solid (75 mg, 95%): mp 127–128 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, J = 7.5, 1.3 Hz, 2H), 7.12–7.05 (m, 4H), 7.00–6.96 (m, 4H), 6.92–6.82 (m, 4H), 6.62 (d, J = 8.2 Hz, 2H), 5.57 (s, 1H), 4.74 (s, 2H), 2.34 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 138.7, 136.8, 136.6, 133.9, 129.6, 129.2, 129.12, 129.10, 128.1,

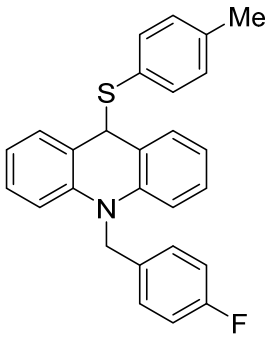
126.0, 122.5, 120.7, 113.4, 53.4, 50.8, 21.4, 21.2; HRMS (ESI-TOF) *m*/*z*: $[M - TolS]^+$ calcd for $C_{21}H_{18}N$ 284.1434, found 284.1430.

10-(4-Chlorobenzyl)-9-(*p*-tolylthio)-9,10-dihydroacridine (3ja):



Colorless oil (79 mg, 92%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 7.5 Hz, 2H), 7.18 (dd, J = 7.5, 1.4 Hz, 2H), 7.10–7.02 (m, 4H), 6.97 (d, J = 7.8 Hz, 2H), 6.92–6.88 (m, 2H), 6.84 (d, J = 8.0 Hz, 2H), 6.56 (d, J = 8.2 Hz, 2H), 5.53 (s, 1H), 4.73 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 138.6, 136.7, 135.5, 132.7, 129.8, 129.1, 129.0, 128.9, 128.0, 127.5, 122.6, 120.9, 113.1, 53.1, 50.2, 21.2; HRMS (ESI-TOF) *m*/*z*: $[M - TolS]^+$ calcd for $C_{20}H_{15}{}^{35}ClN$ 304.0888, found 304.0888.

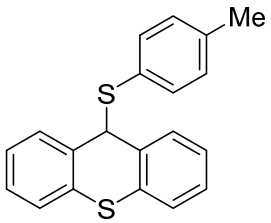
10-(4-Fluorobenzyl)-9-(*p*-tolylthio)-9,10-dihydroacridine (3ka):



Colorless oil (74 mg, 90%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, J = 7.5, 1.3 Hz, 2H), 7.11–7.04 (m, 4H), 6.99–6.94 (m, 4H), 6.92–6.88 (m, 2H), 6.84 (d, J = 8.0 Hz, 2H), 6.58 (d, J = 8.2 Hz, 2H), 5.54 (s, 1H), 4.75 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8 (d, J = 245 Hz), 141.2, 138.6, 136.7, 132.5 (d, J = 3.2 Hz), 129.1, 129.0 (2C), 127.9, 127.6 (d, J = 7.9 Hz), 122.5, 120.8, 115.7 (d, J = 21.5 Hz),

113.1, 53.1, 50.2, 21.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.4; HRMS (ESI-TOF) *m*/*z*: $[M - TolS]^+$ calcd for $C_{20}H_{15}FN$ 288.1183, found 288.1181.

9-(*p*-Tolylthio)-9*H*-thioxanthene (3la):

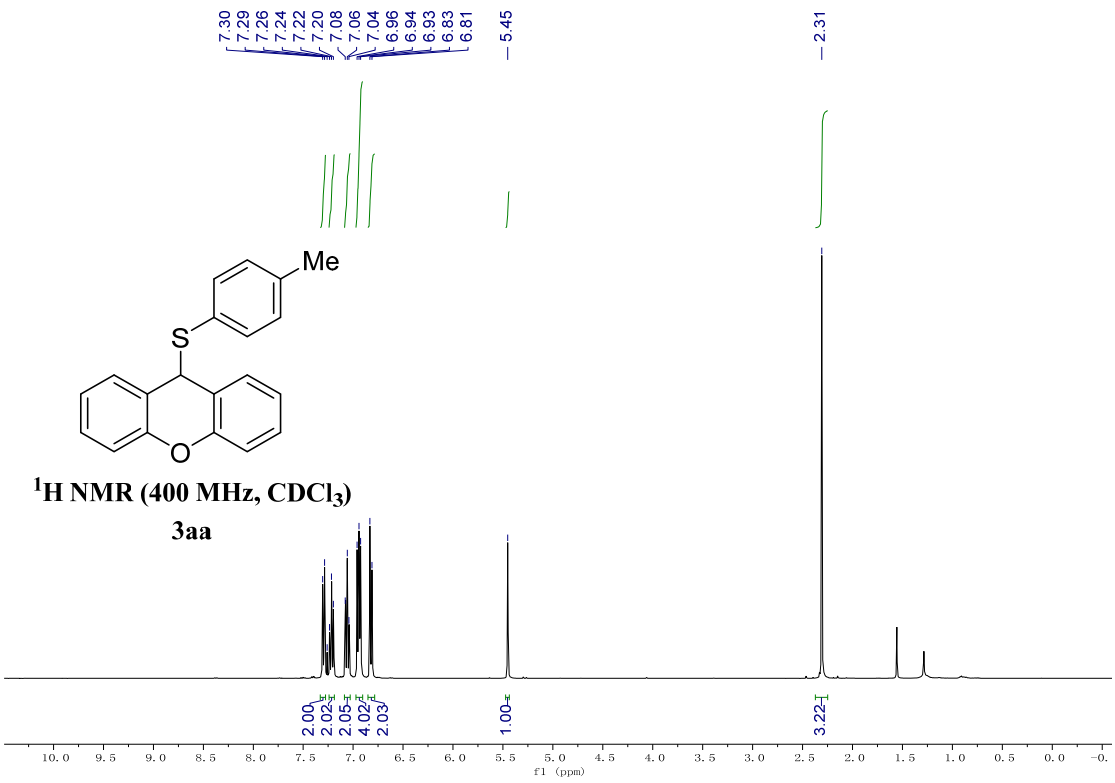


White solid (60 mg, 93%): mp 131–132 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.7 Hz, 2H), 7.23–7.19 (m, 2H), 7.11–7.06 (m, 4H), 7.03–6.99 (m, 4H), 5.43 (s, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 136.3, 133.4, 133.3, 129.9, 129.6, 129.3, 127.4, 126.8, 126.2, 57.1, 21.4; HRMS (ESI-TOF) *m*/*z*: $[M - H]^+$ calcd for $C_{20}H_{15}S_2$ 319.0610, found 319.0602.

References:

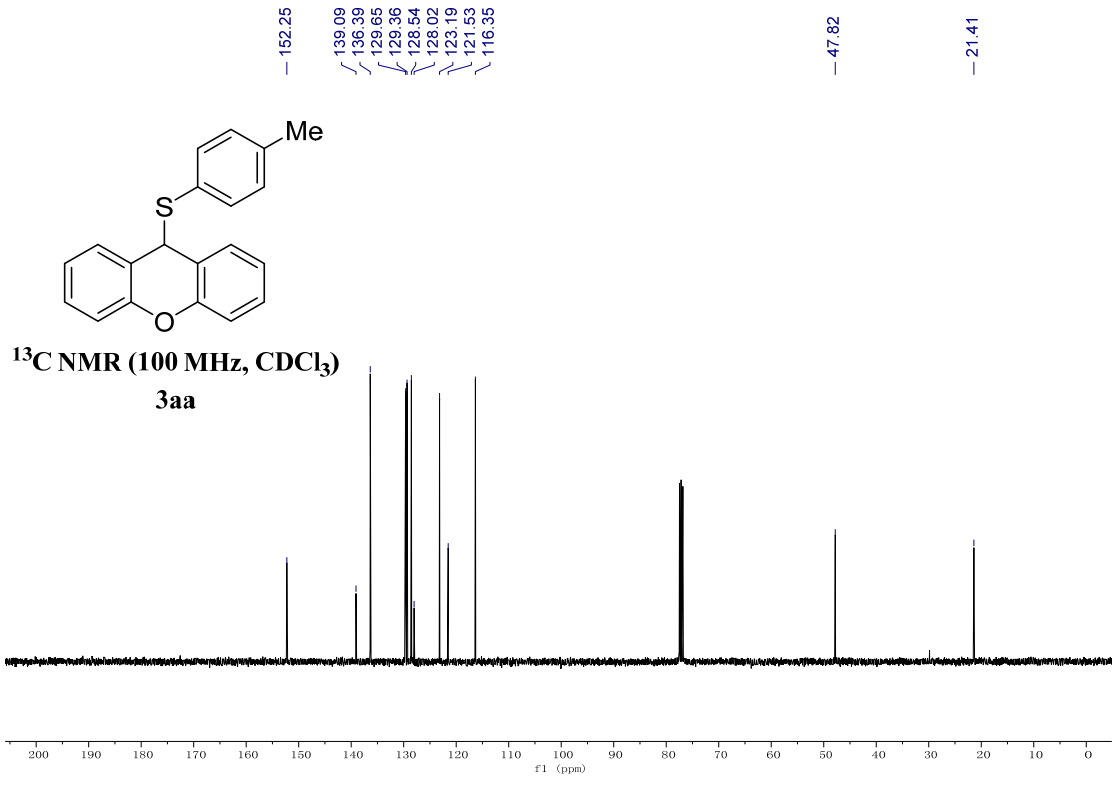
1. C. A. Menéndez, F. Nador, G. Radivoy and D. C. Gerbino, *Org. Lett.*, 2014, **16**, 2846.
2. Á. Pintér, A. Sud, D. Sureshkumar and M. Klussmann, *Angew. Chem., Int. Ed.*, 2010, **49**, 5004.

5. Copies of ^{1}H and ^{13}C NMR spectra for compounds 3



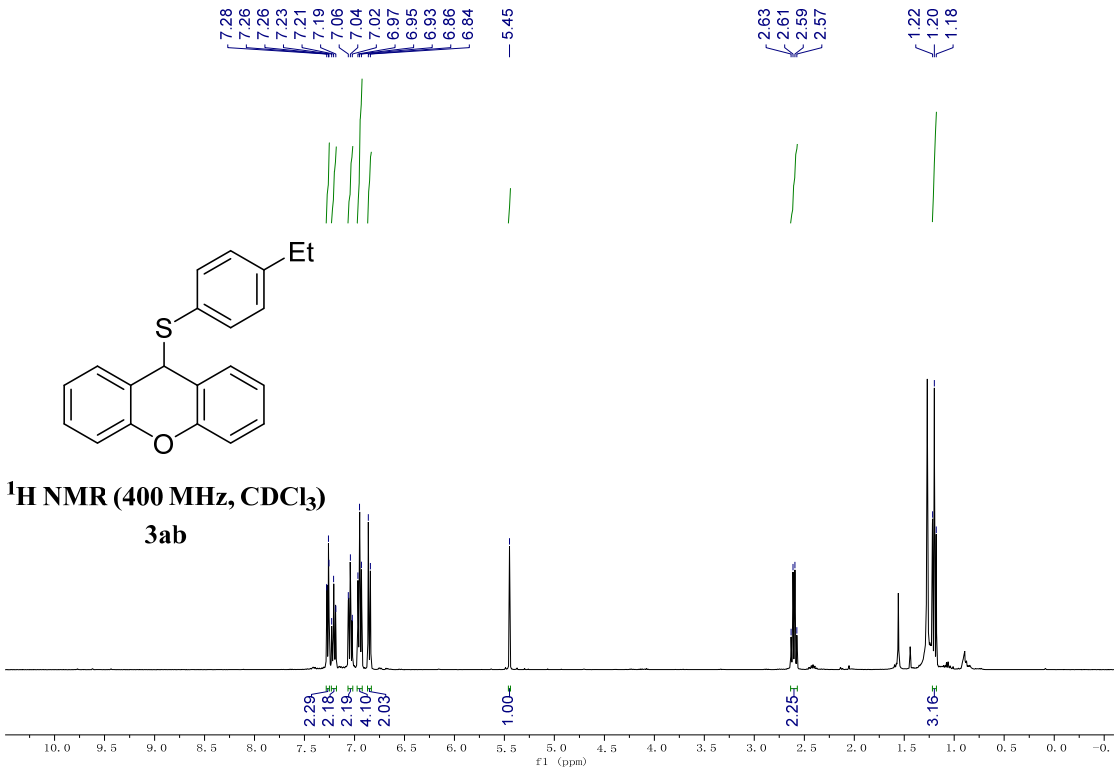
^{1}H NMR (400 MHz, $CDCl_3$)

3aa



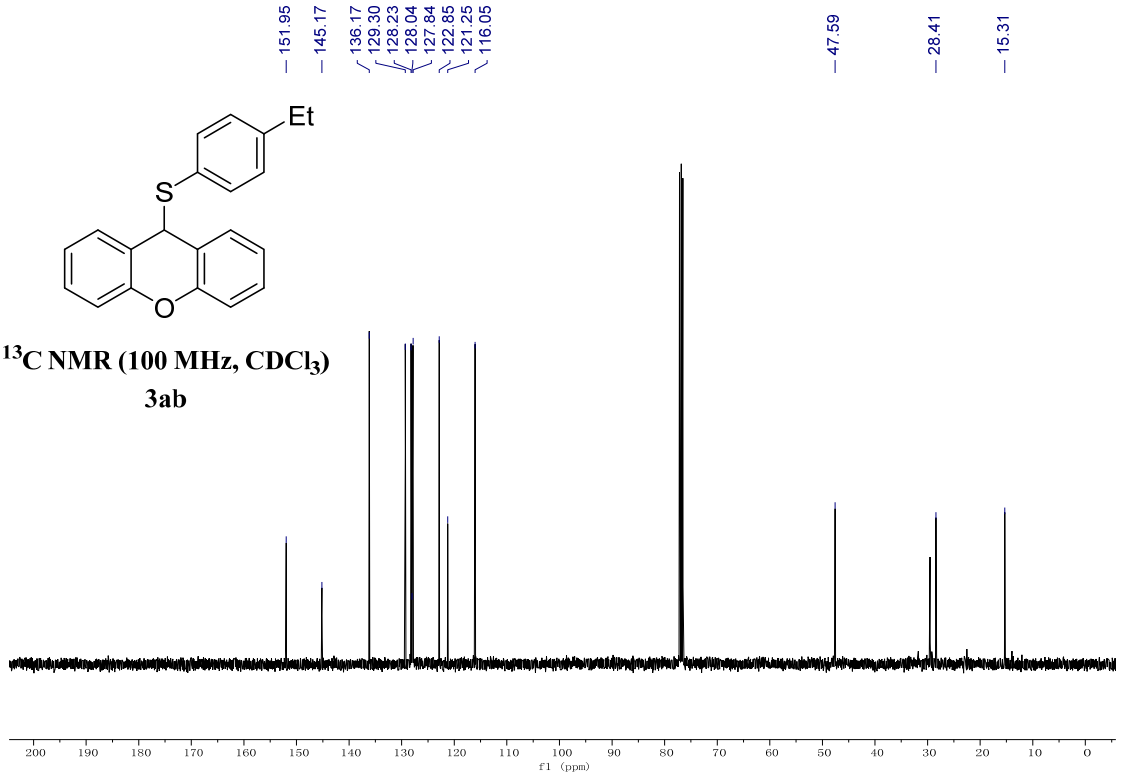
^{13}C NMR (100 MHz, $CDCl_3$)

3aa



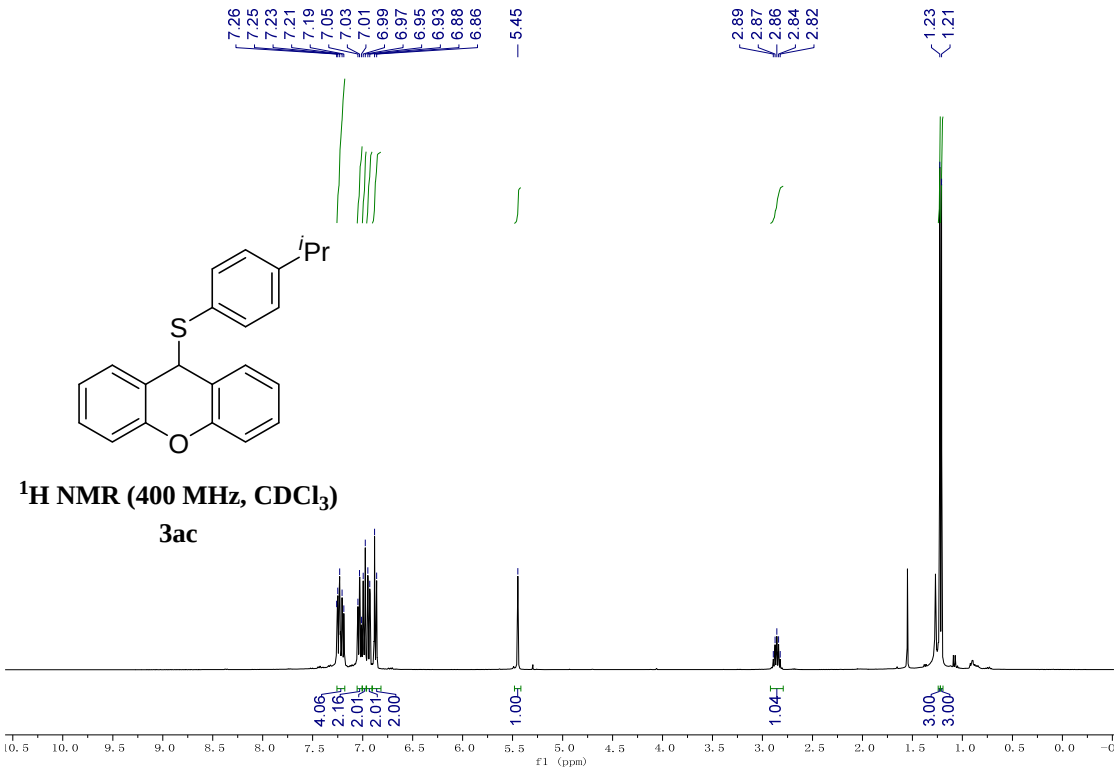
^{1}H NMR (400 MHz, $CDCl_3$)

3ab



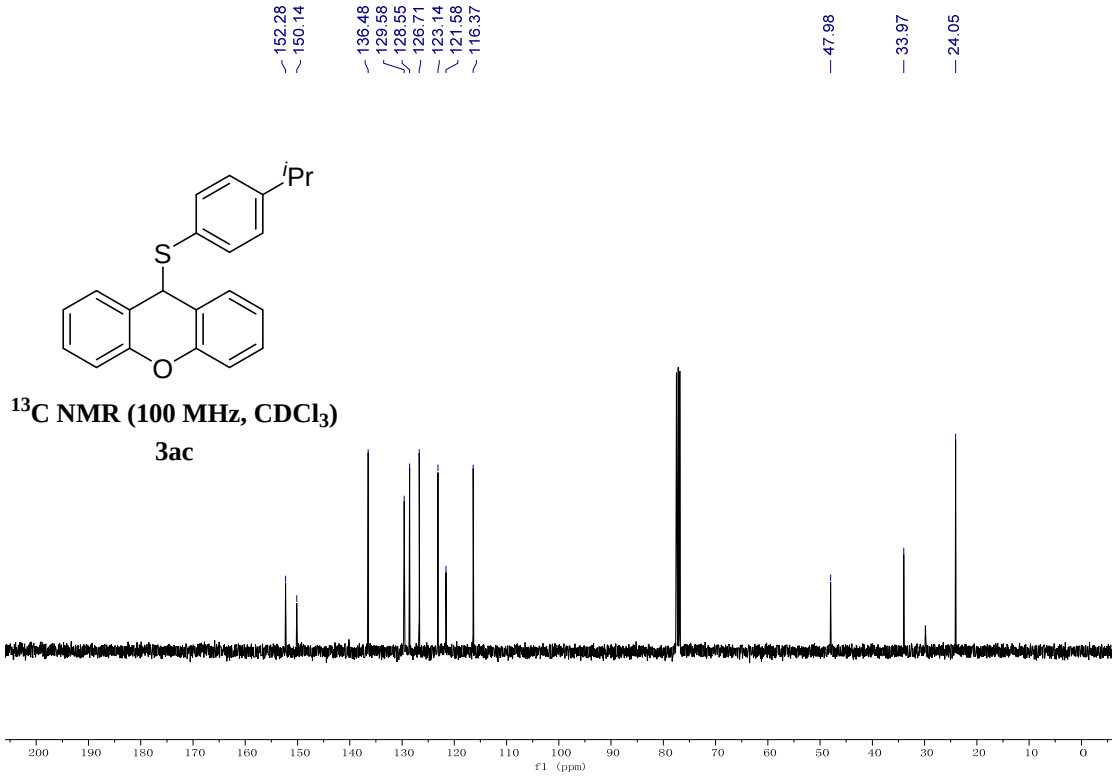
^{13}C NMR (100 MHz, $CDCl_3$)

3ab



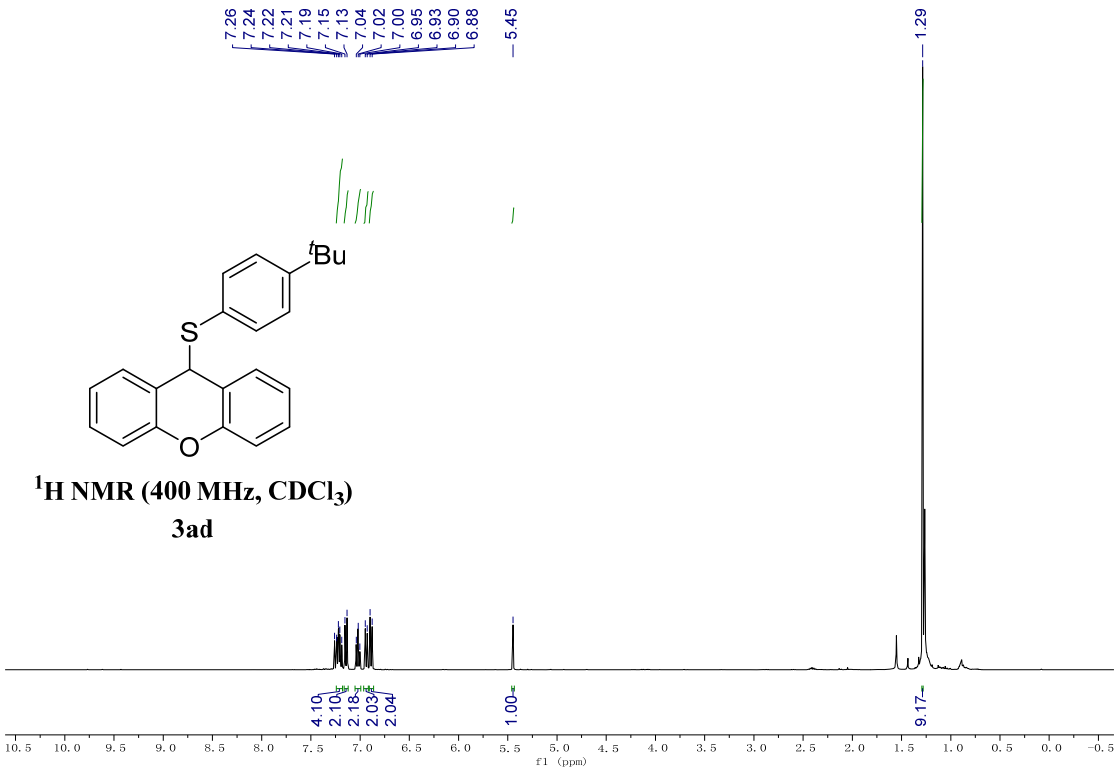
^{1}H NMR (400 MHz, $CDCl_3$)

3ac



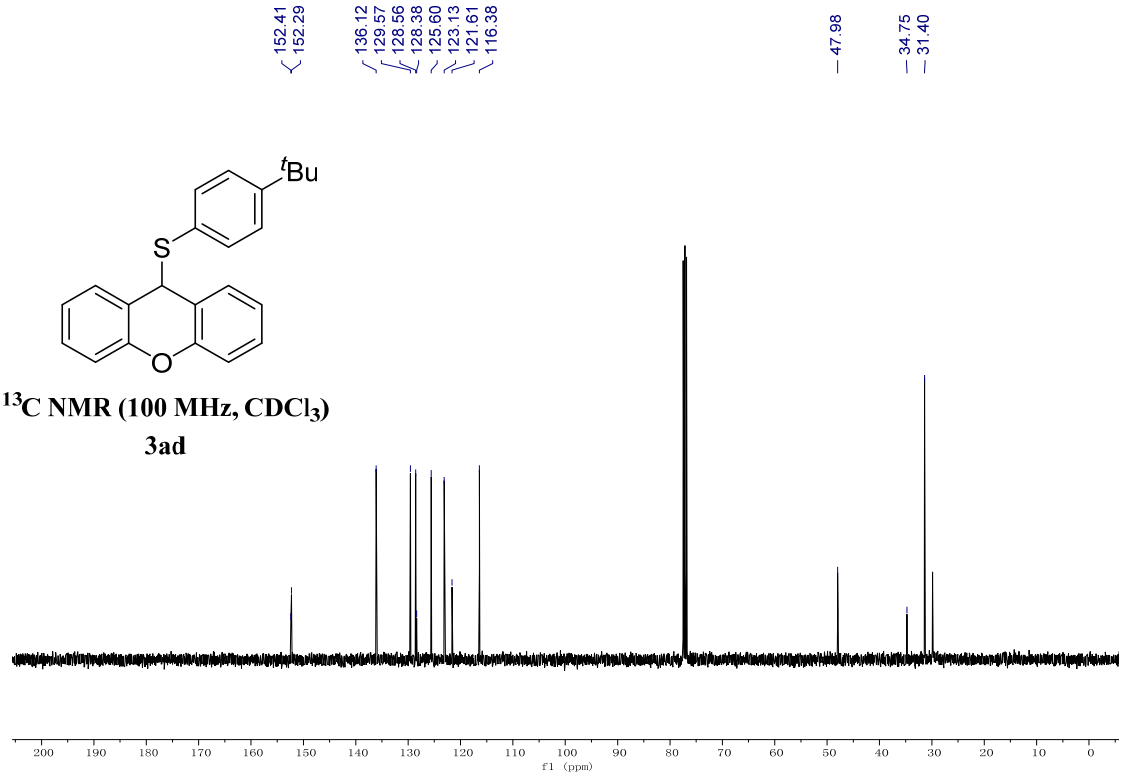
^{13}C NMR (100 MHz, $CDCl_3$)

3ac



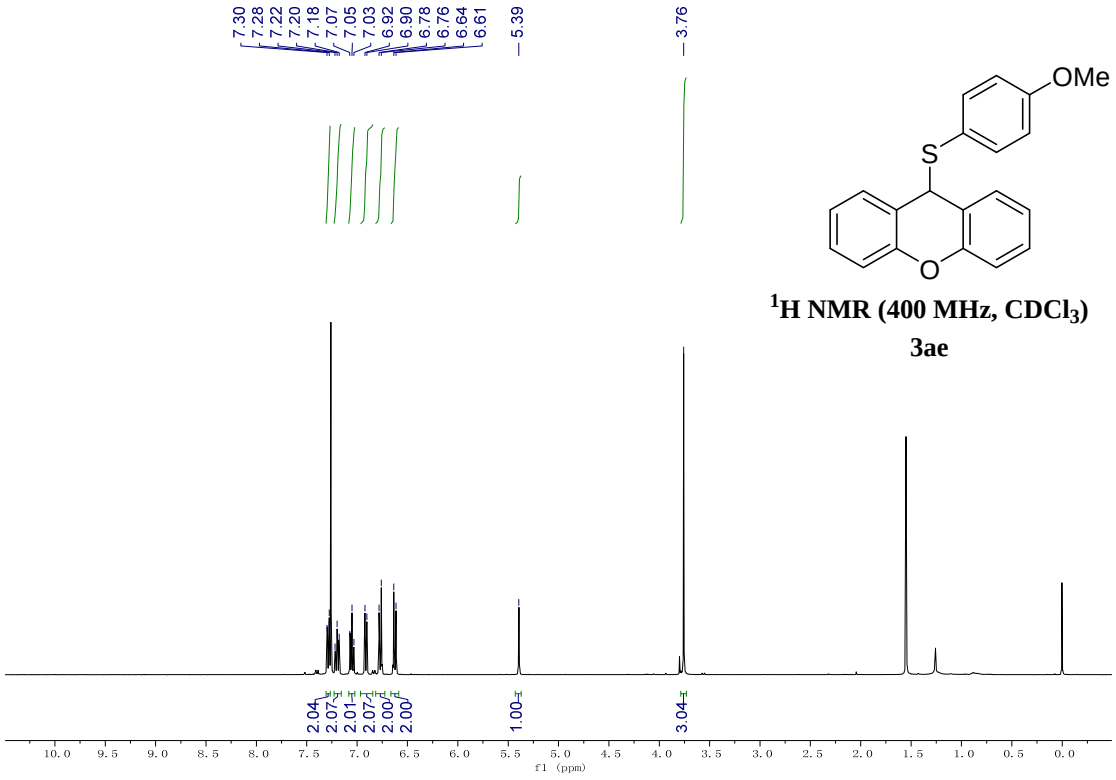
^{1}H NMR (400 MHz, $CDCl_3$)

3ad



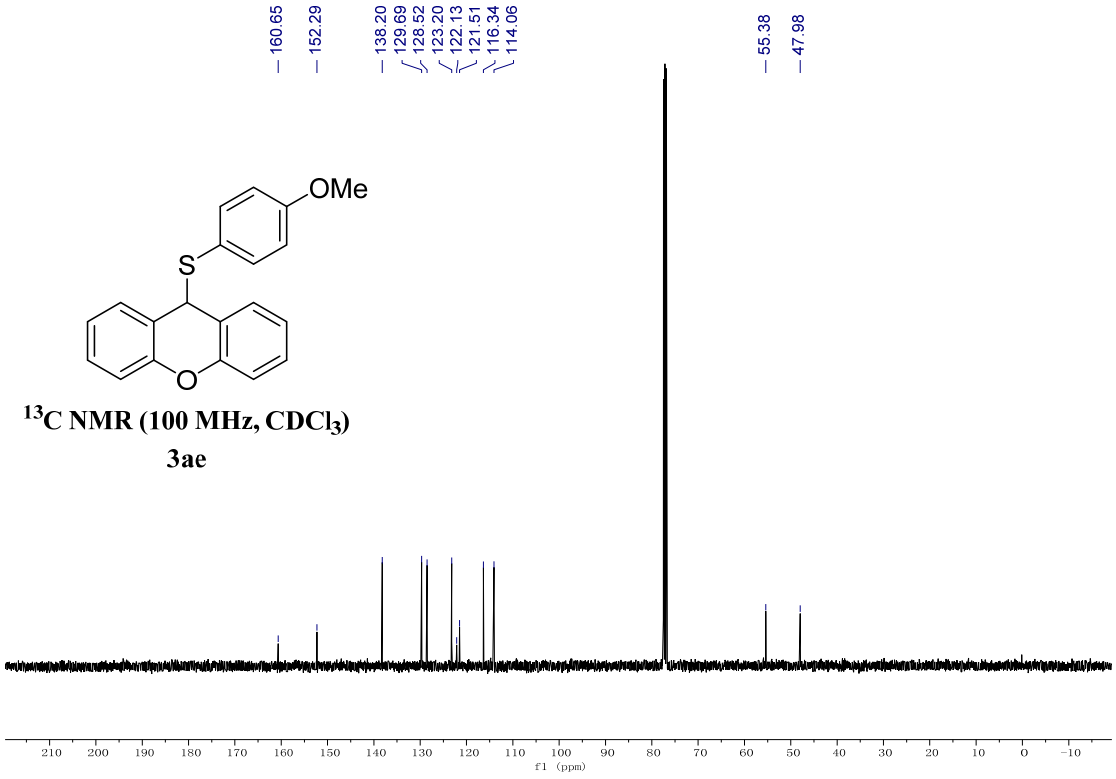
^{13}C NMR (100 MHz, $CDCl_3$)

3ad



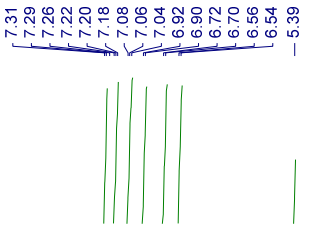
^{1}H NMR (400 MHz, $CDCl_3$)

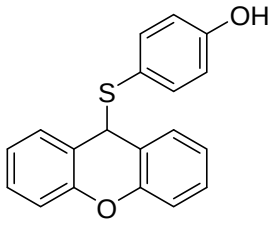
3ae



^{13}C NMR (100 MHz, $CDCl_3$)

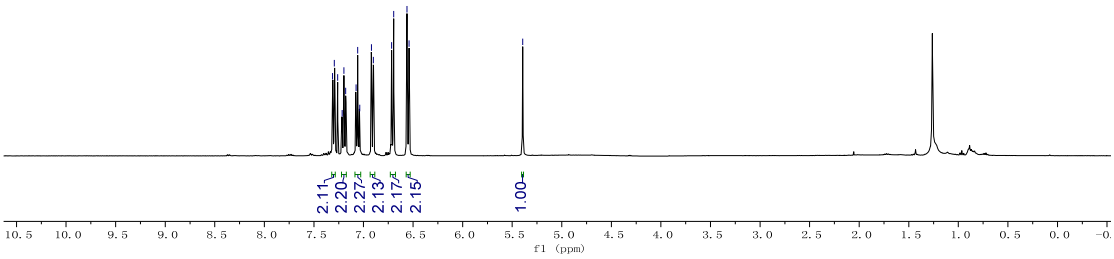
3ae

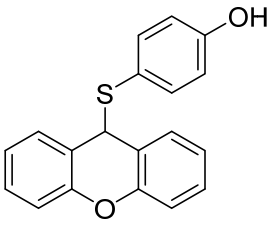




^{1}H NMR (400 MHz, $CDCl_3$)

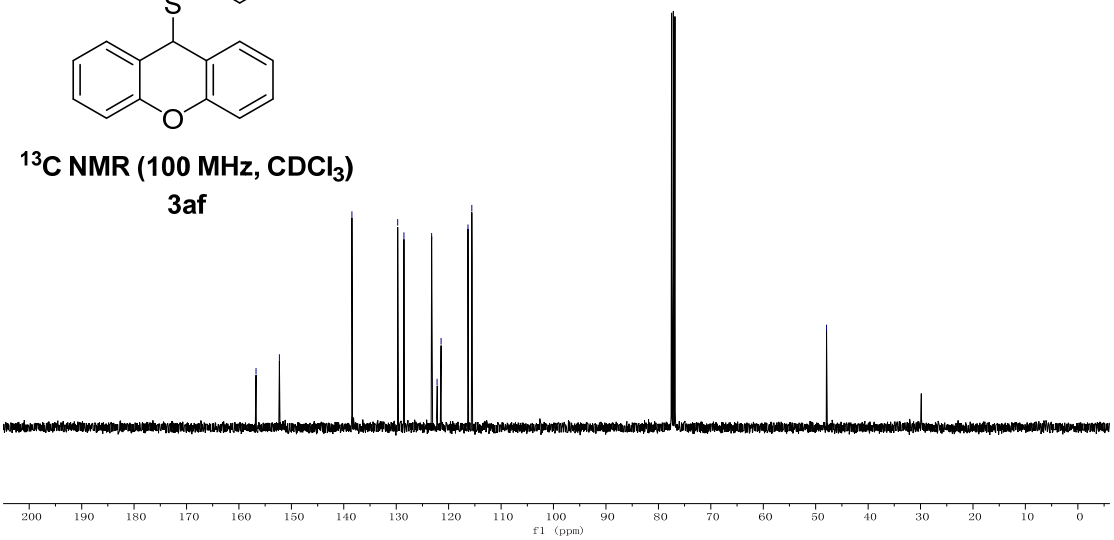
3af

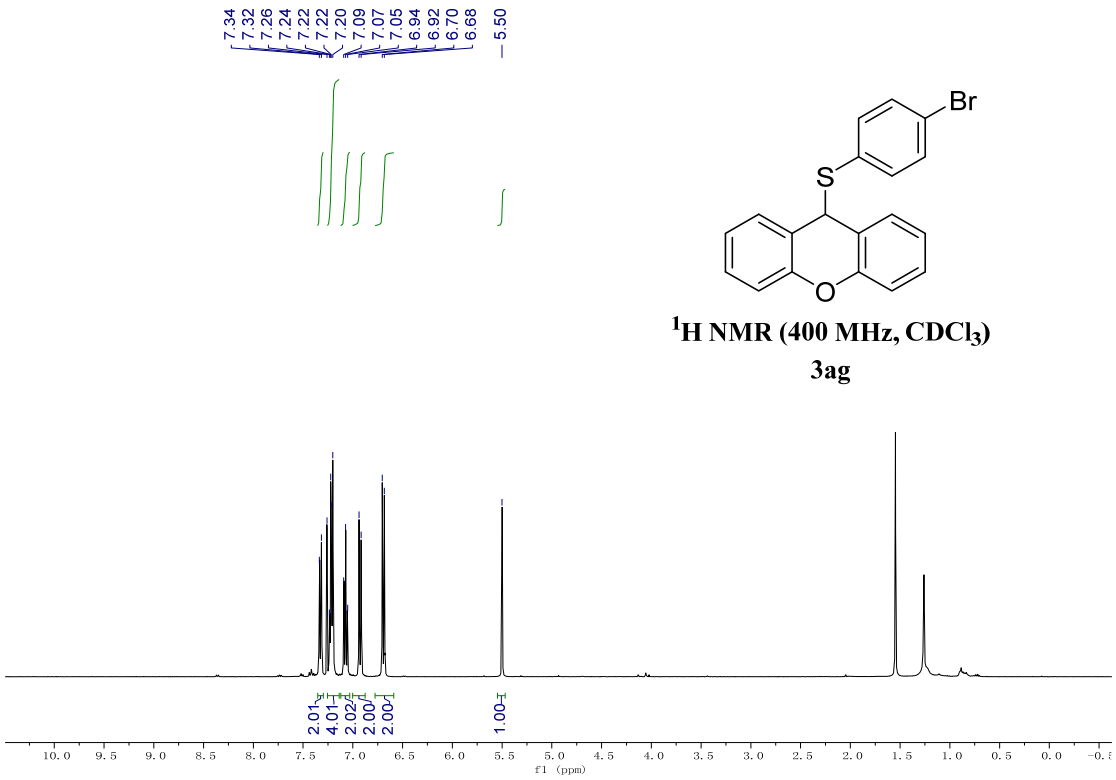




^{13}C NMR (100 MHz, $CDCl_3$)

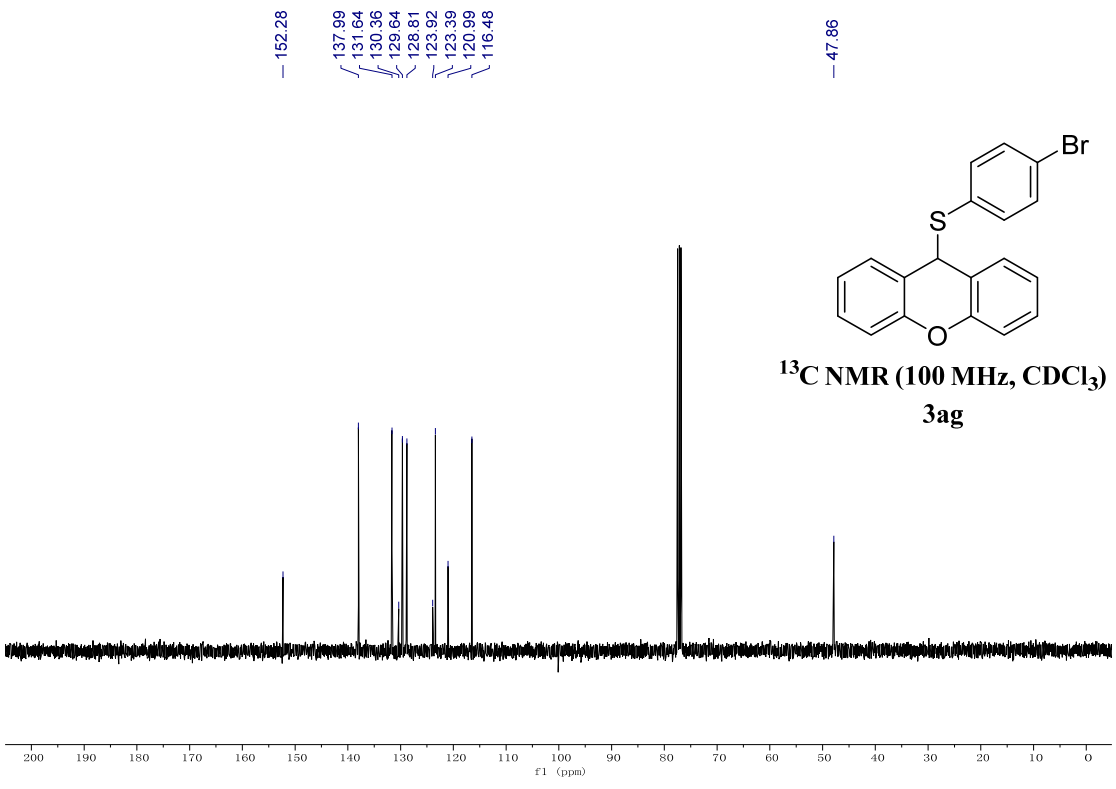
3af





^{1}H NMR (400 MHz, $CDCl_3$)

3ag



^{13}C NMR (100 MHz, $CDCl_3$)

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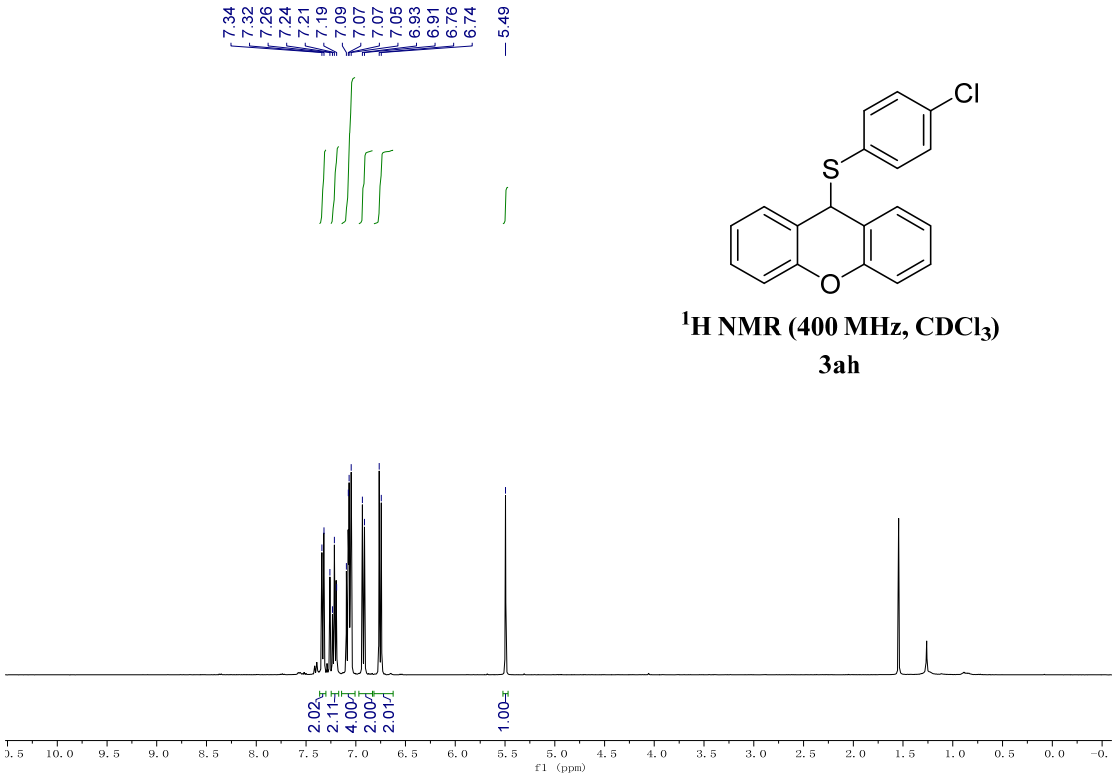
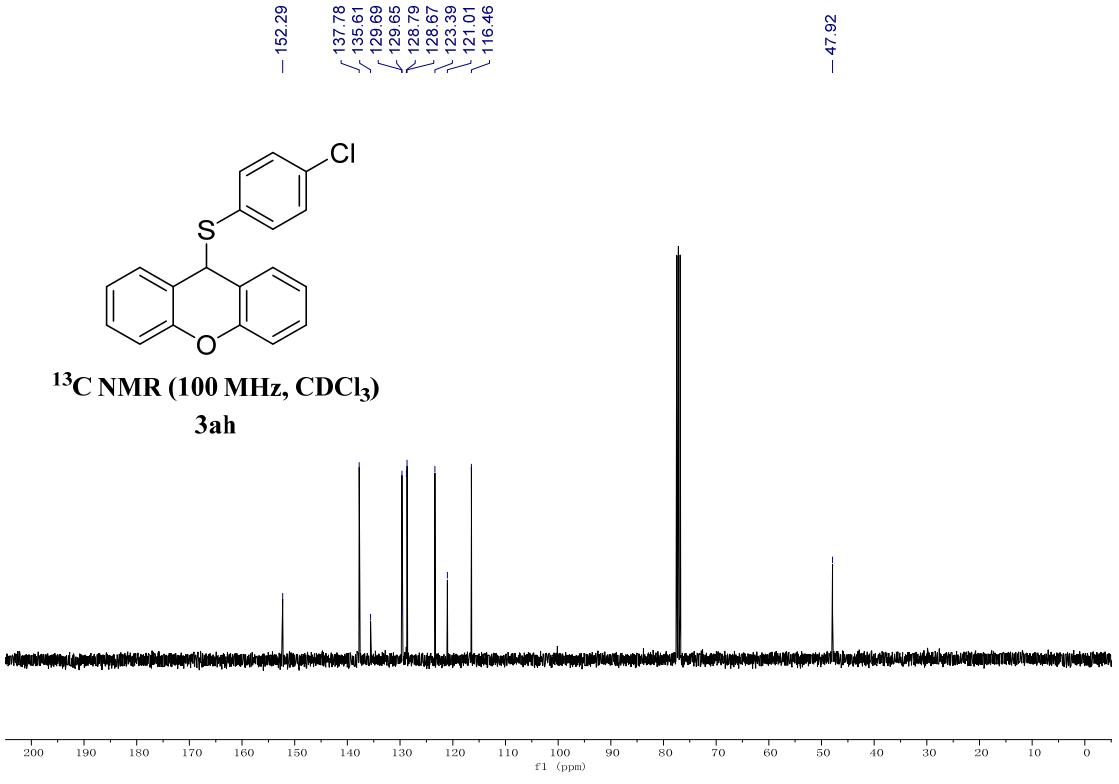


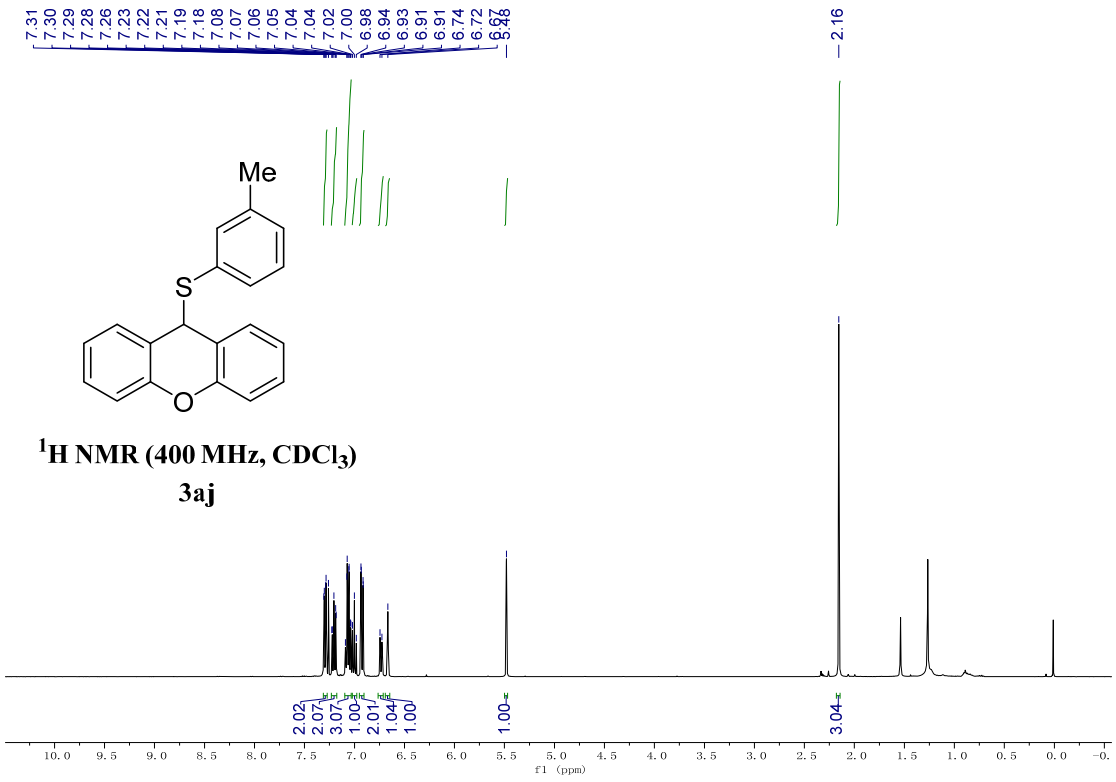
^{1}H NMR (400 MHz, $CDCl_3$)

3ah



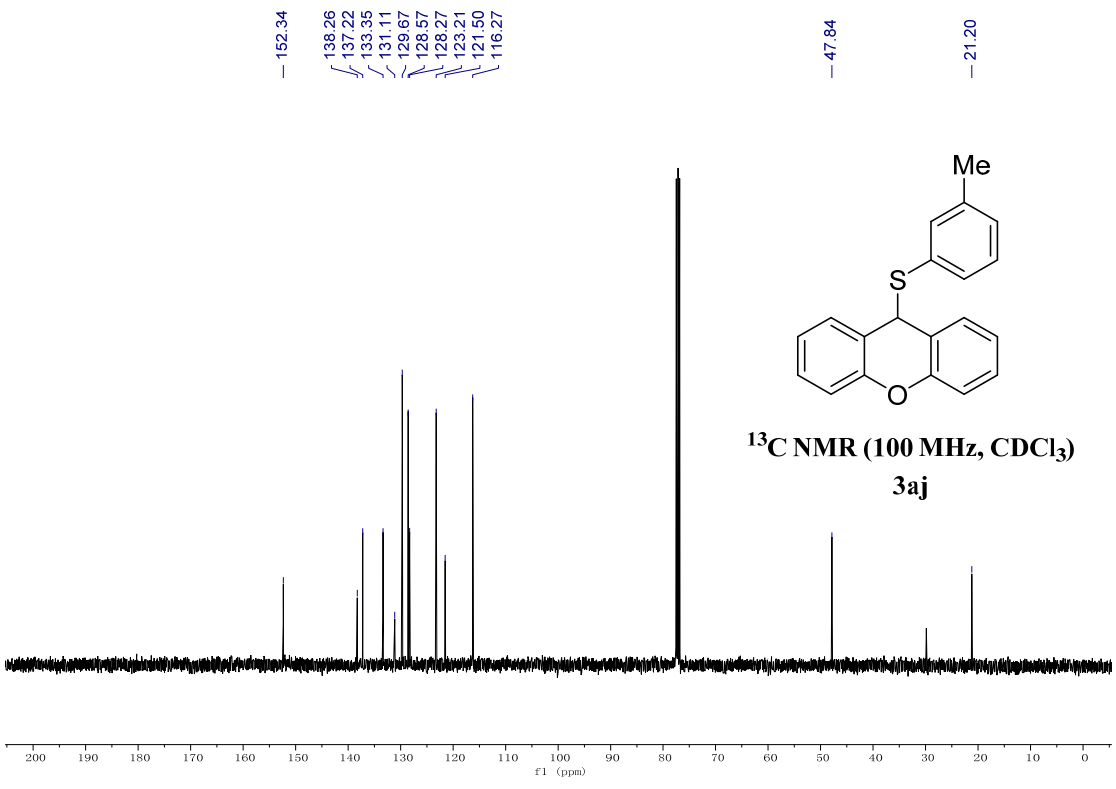
^{13}C NMR (100 MHz, $CDCl_3$)

3ah



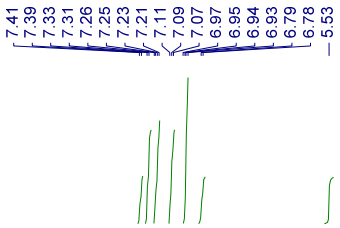
^{1}H NMR (400 MHz, $CDCl_3$)

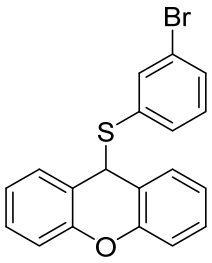
3aj



^{13}C NMR (100 MHz, $CDCl_3$)

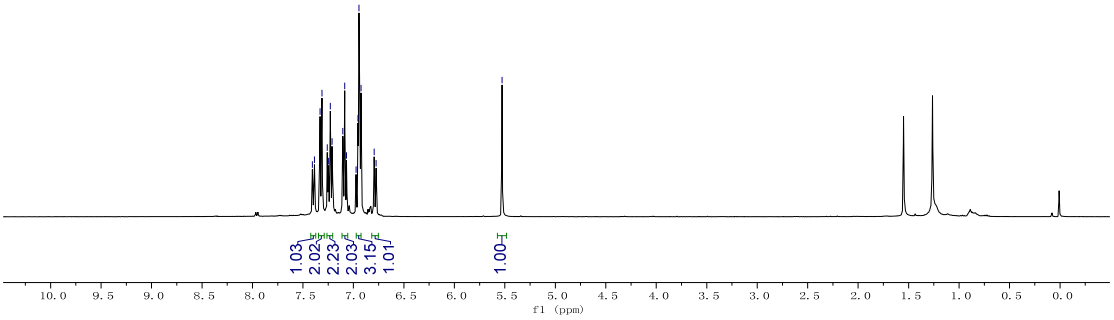
3aj

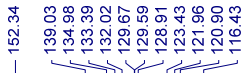


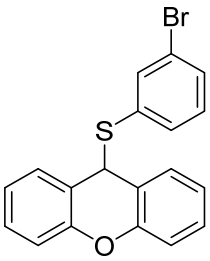


^{1}H NMR (400 MHz, $CDCl_3$)

3al

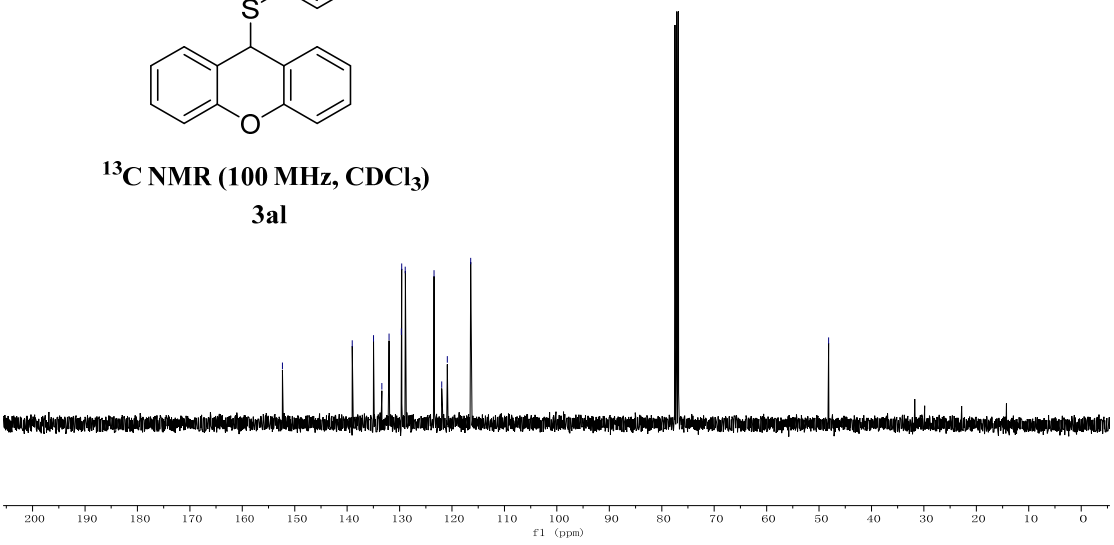


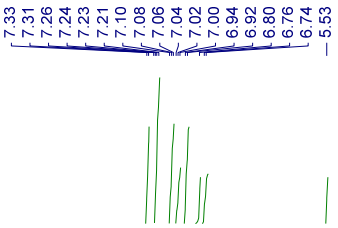


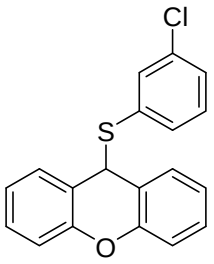


^{13}C NMR (100 MHz, $CDCl_3$)

3al

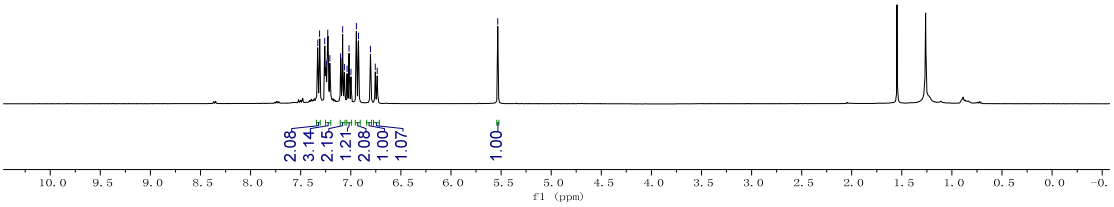


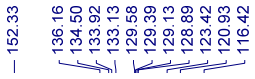


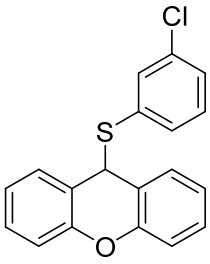


^{1}H NMR (400 MHz, $CDCl_3$)

3am

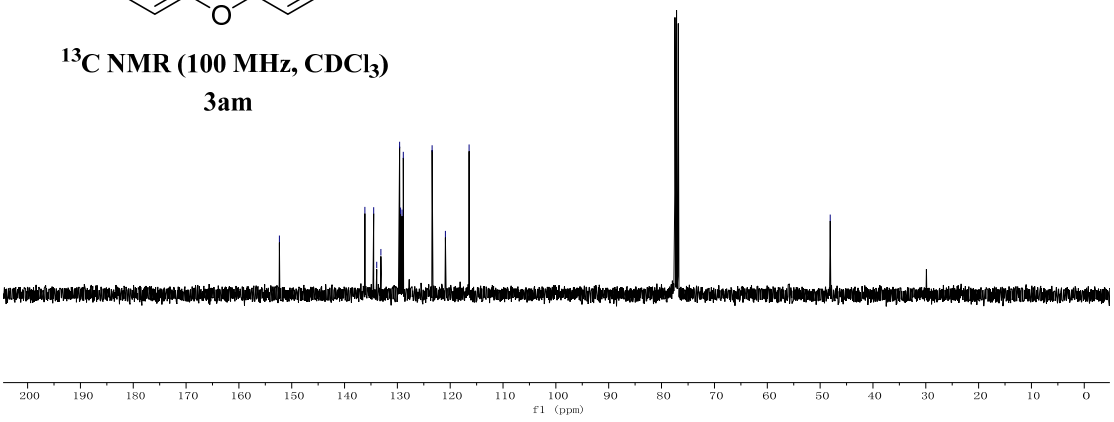


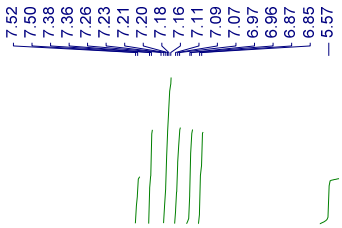


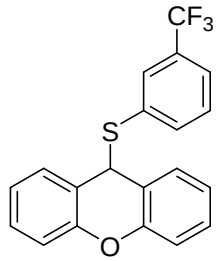


^{13}C NMR (100 MHz, $CDCl_3$)

3am

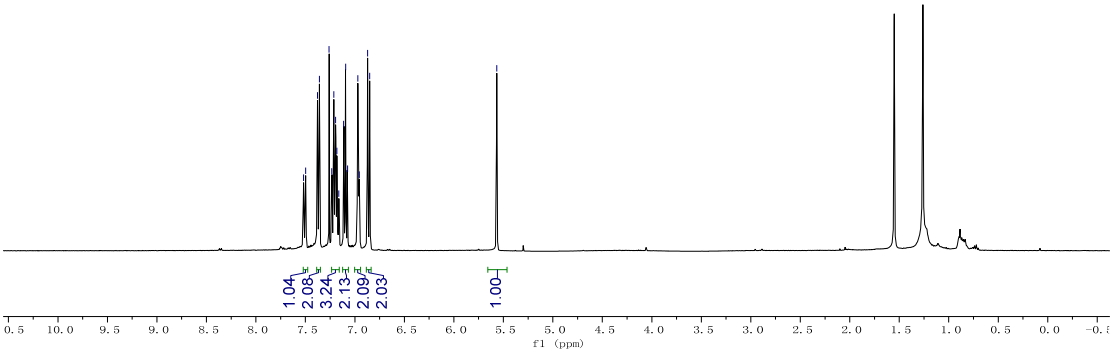


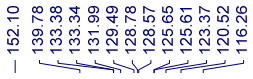


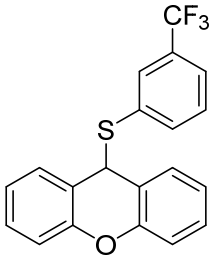


^{1}H NMR (400 MHz, $CDCl_3$)

3an

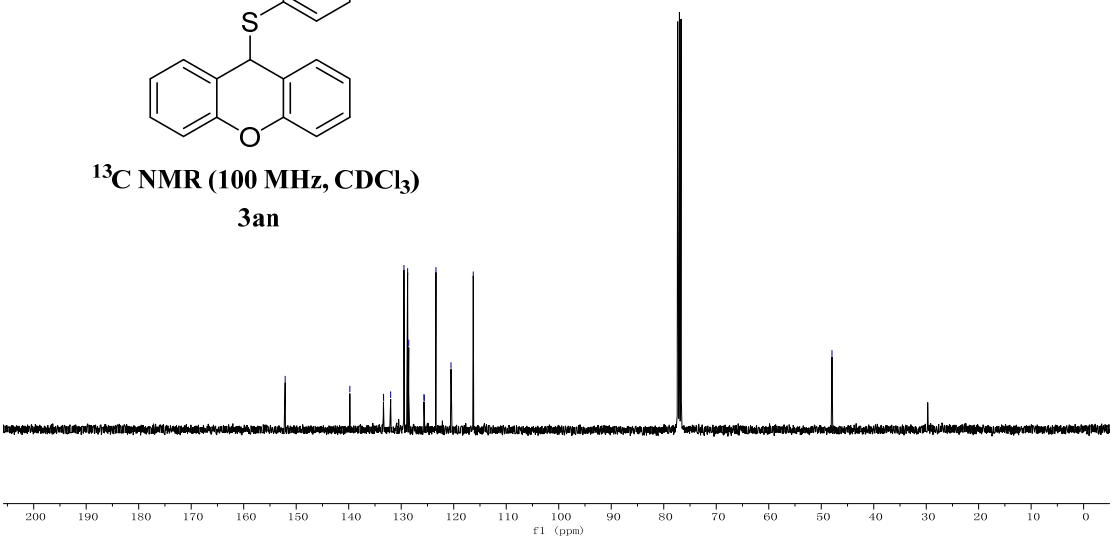


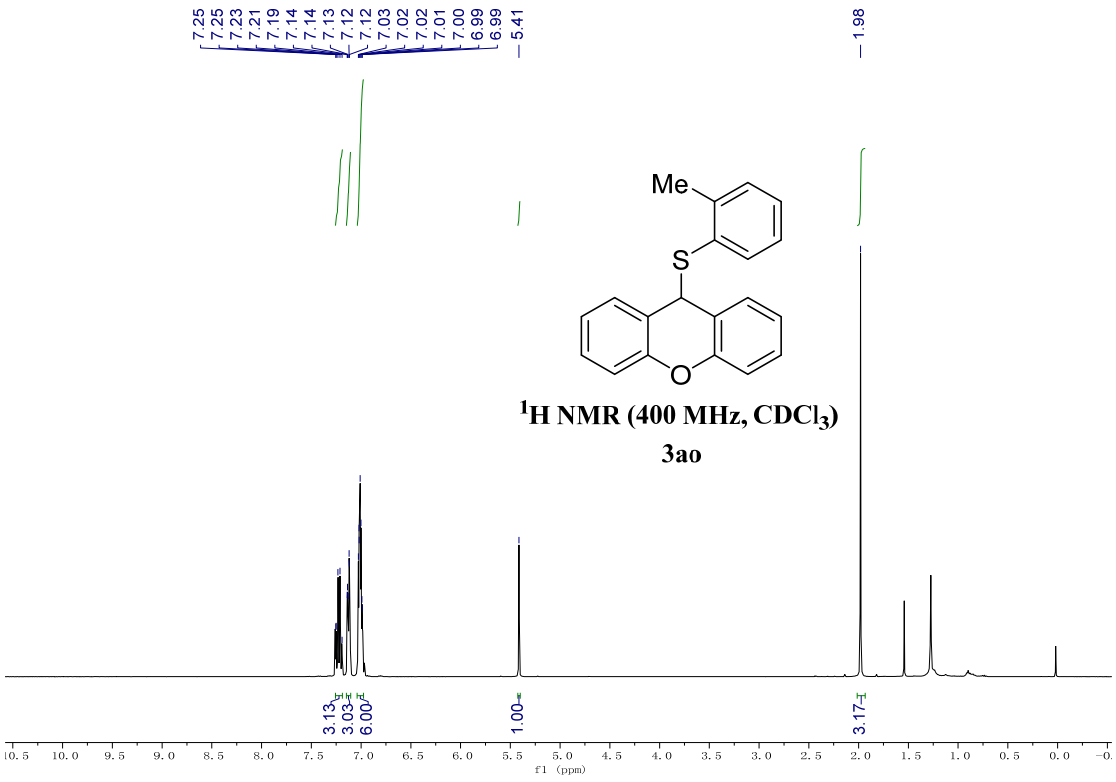




^{13}C NMR (100 MHz, $CDCl_3$)

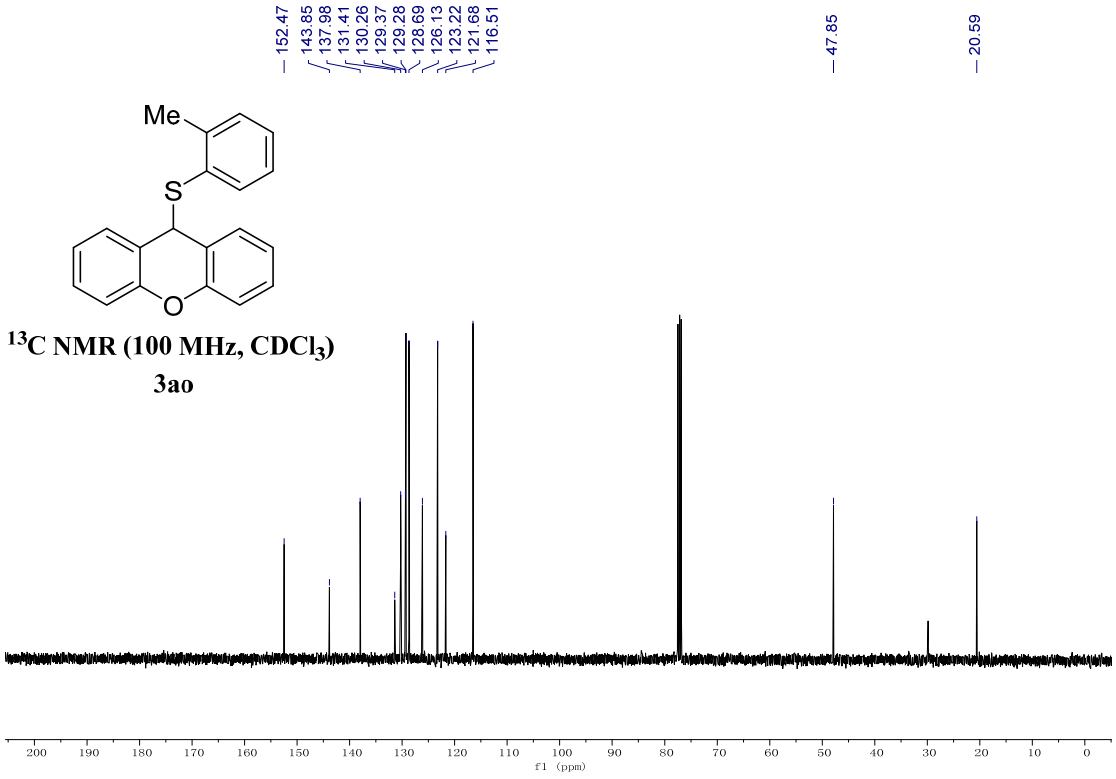
3an





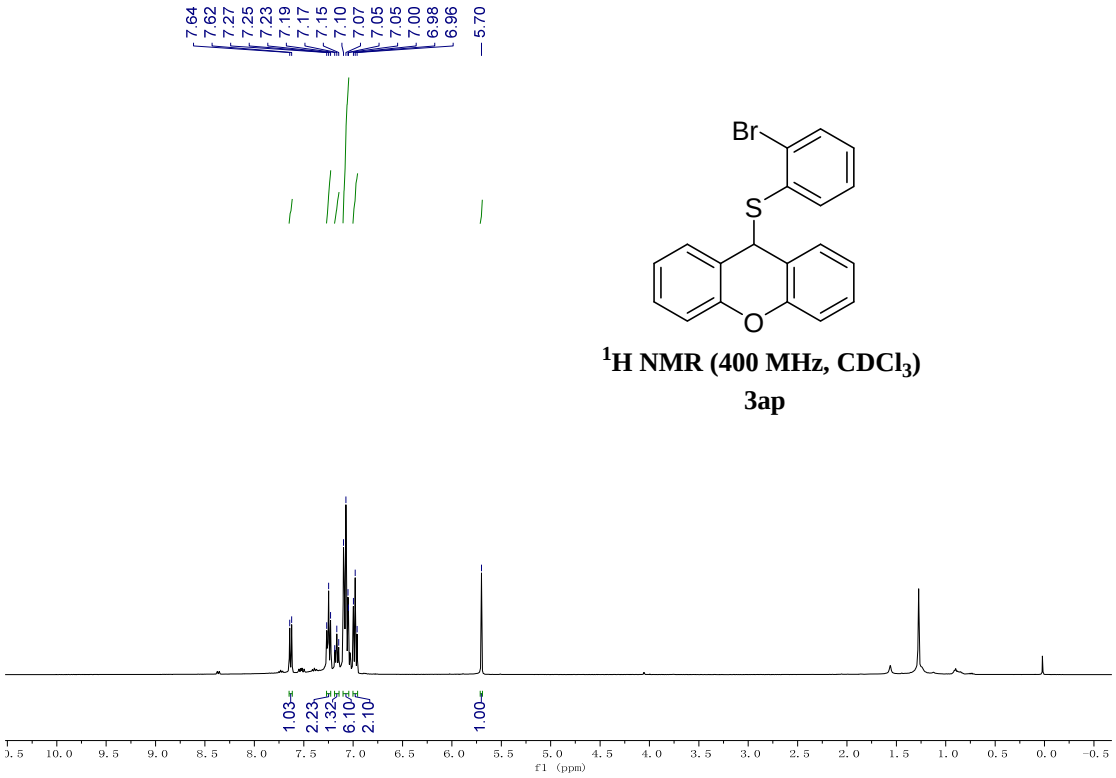
^{1}H NMR (400 MHz, $CDCl_3$)

3ao



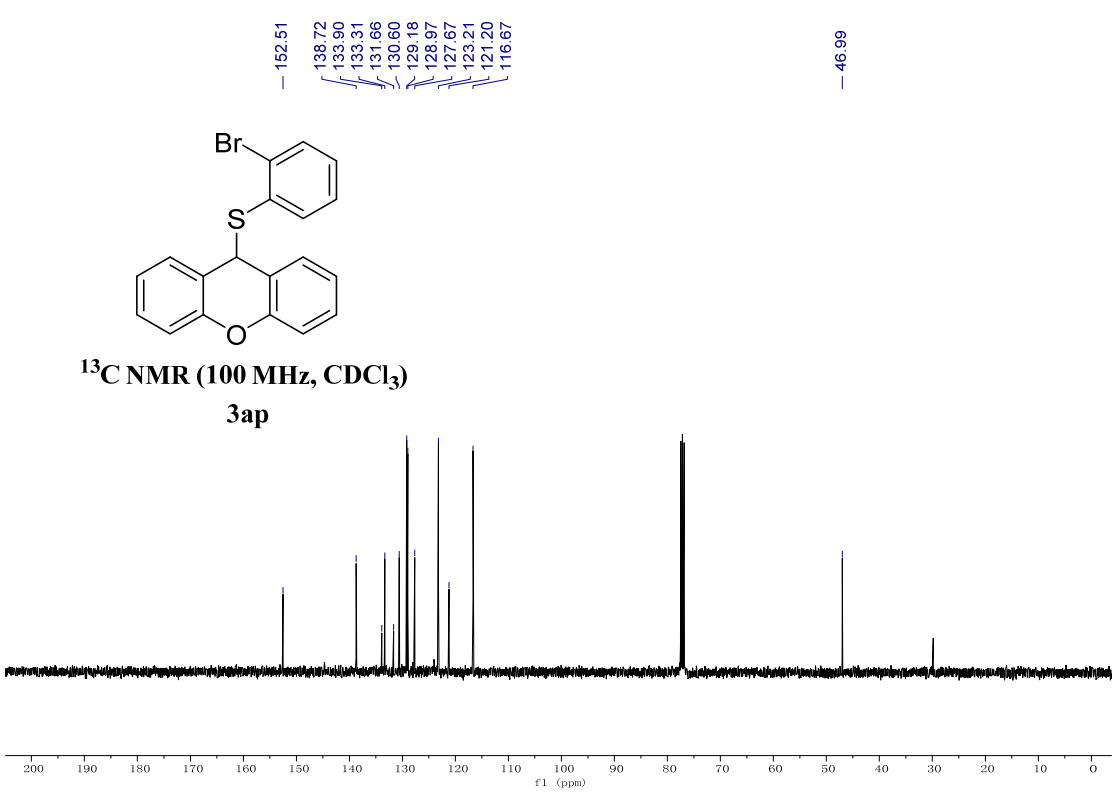
^{13}C NMR (100 MHz, $CDCl_3$)

3ao



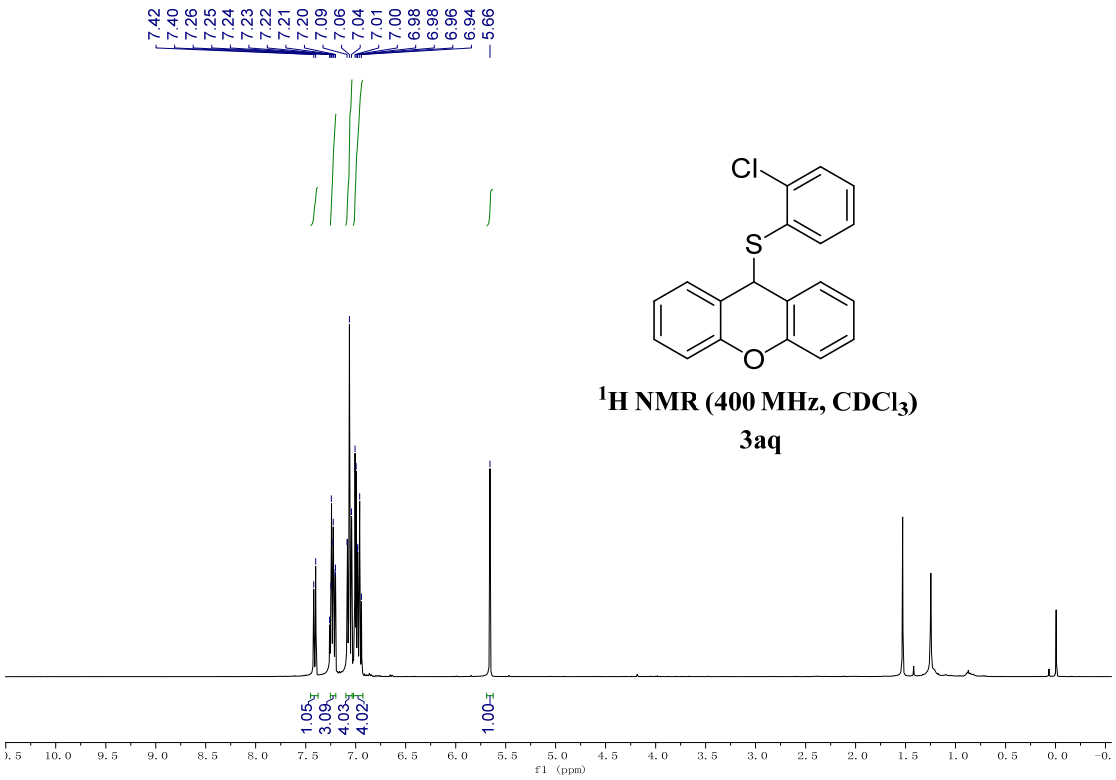
^{1}H NMR (400 MHz, $CDCl_3$)

3ap



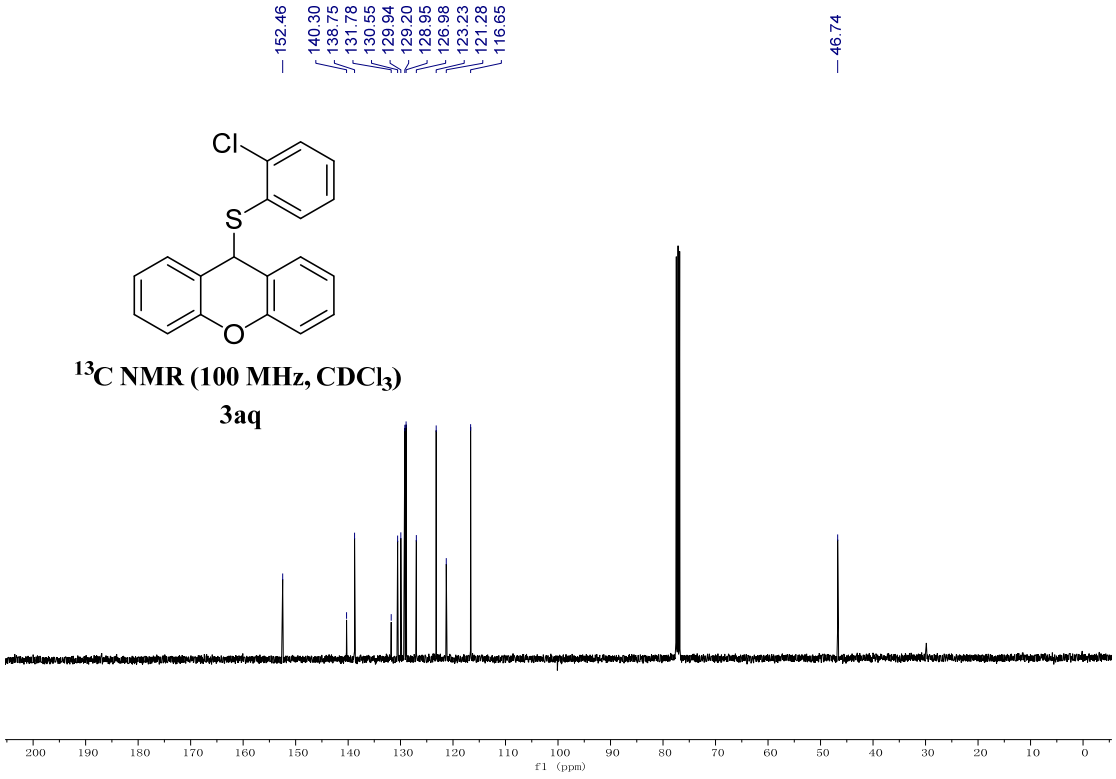
^{13}C NMR (100 MHz, $CDCl_3$)

3ap



^{1}H NMR (400 MHz, $CDCl_3$)

3aq



^{13}C NMR (100 MHz, $CDCl_3$)

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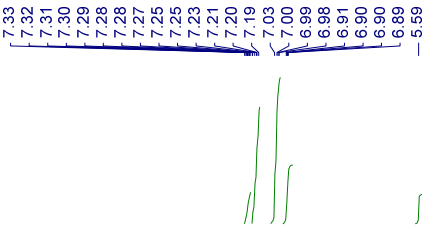
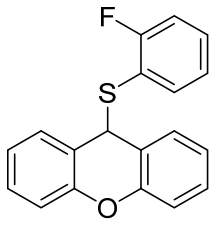
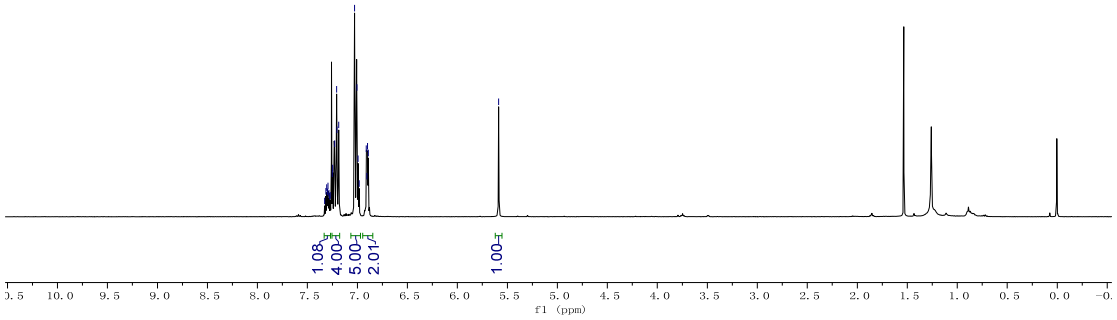
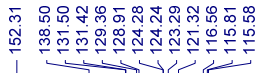


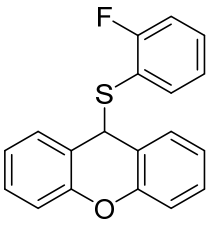


^{1}H NMR (400 MHz, $CDCl_3$)

3ar

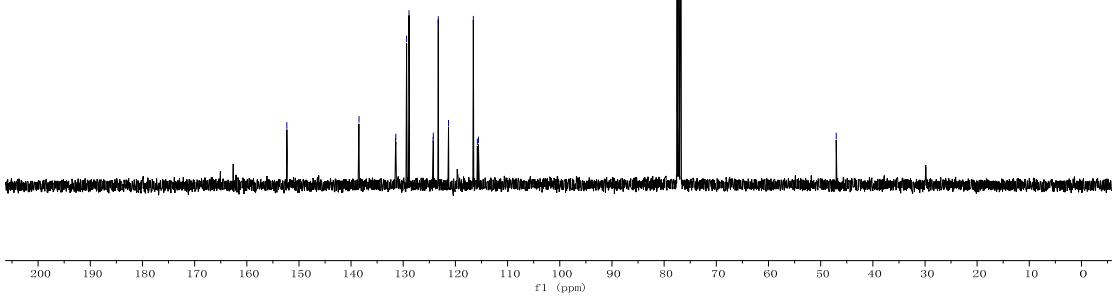


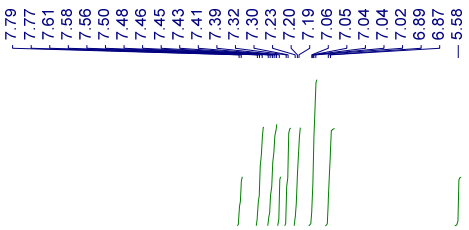


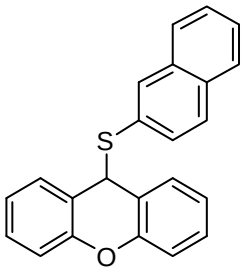


^{13}C NMR (100 MHz, $CDCl_3$)

3ar

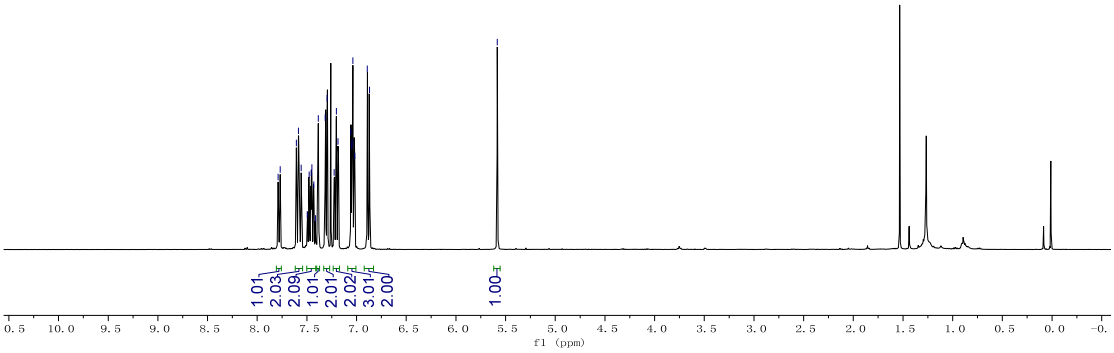


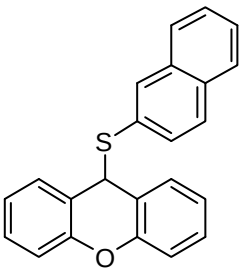




^{1}H NMR (400 MHz, $CDCl_3$)

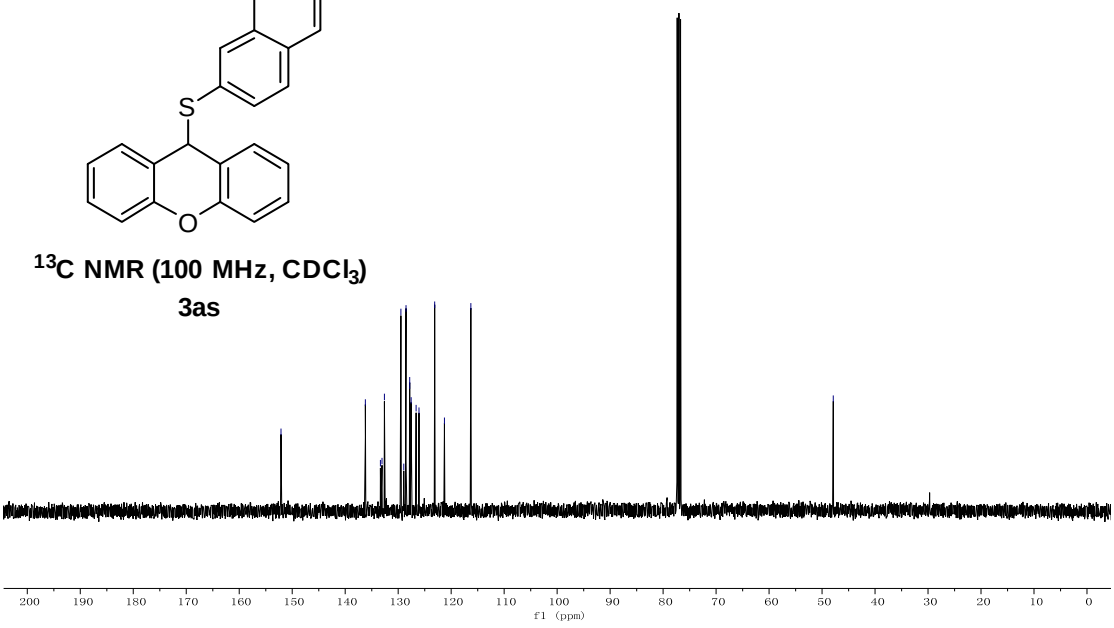
3as

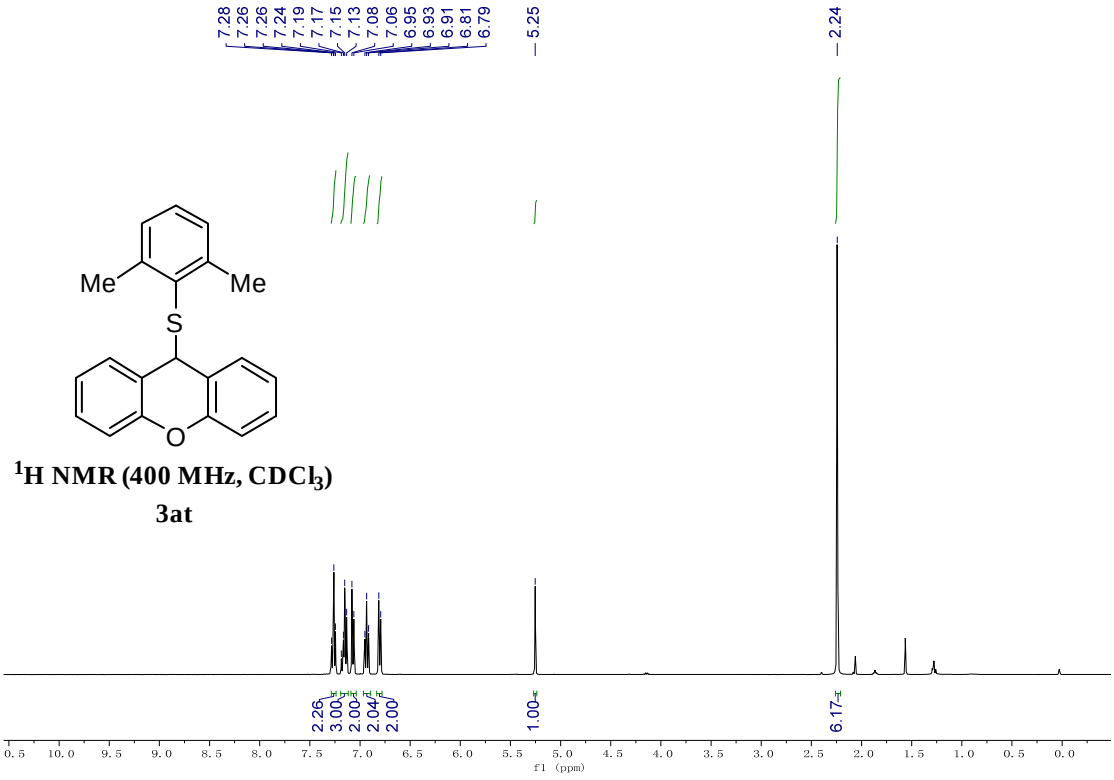




^{13}C NMR (100 MHz, $CDCl_3$)

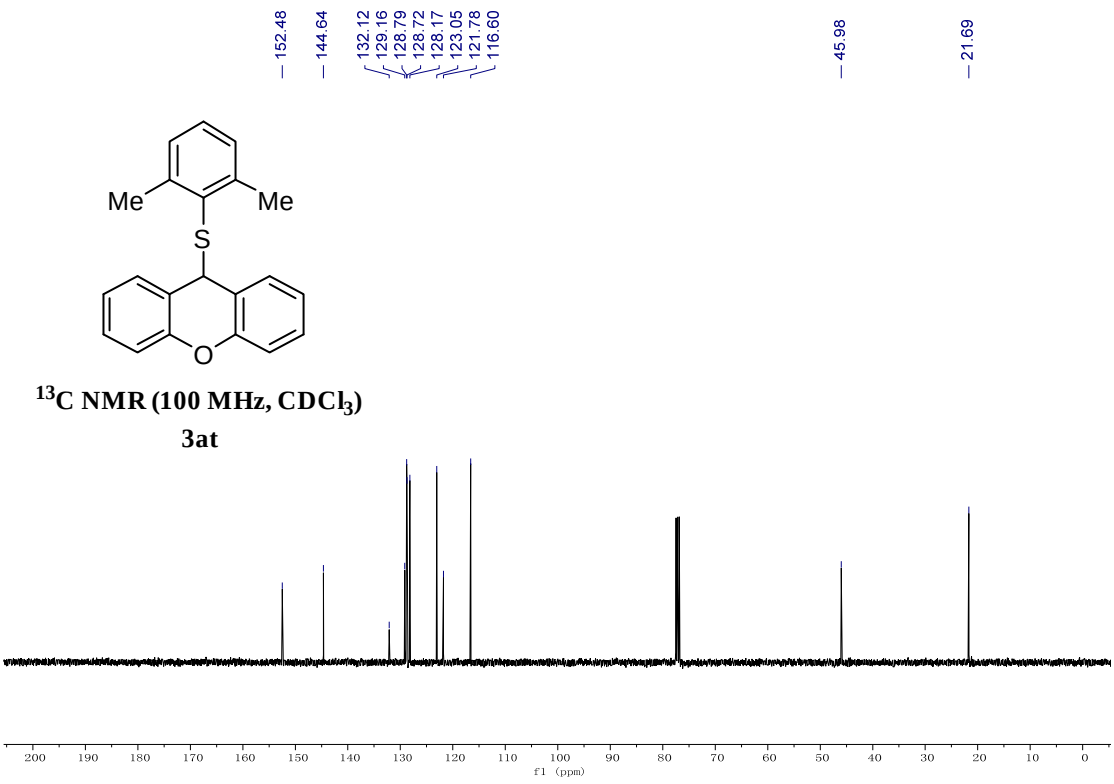
3as





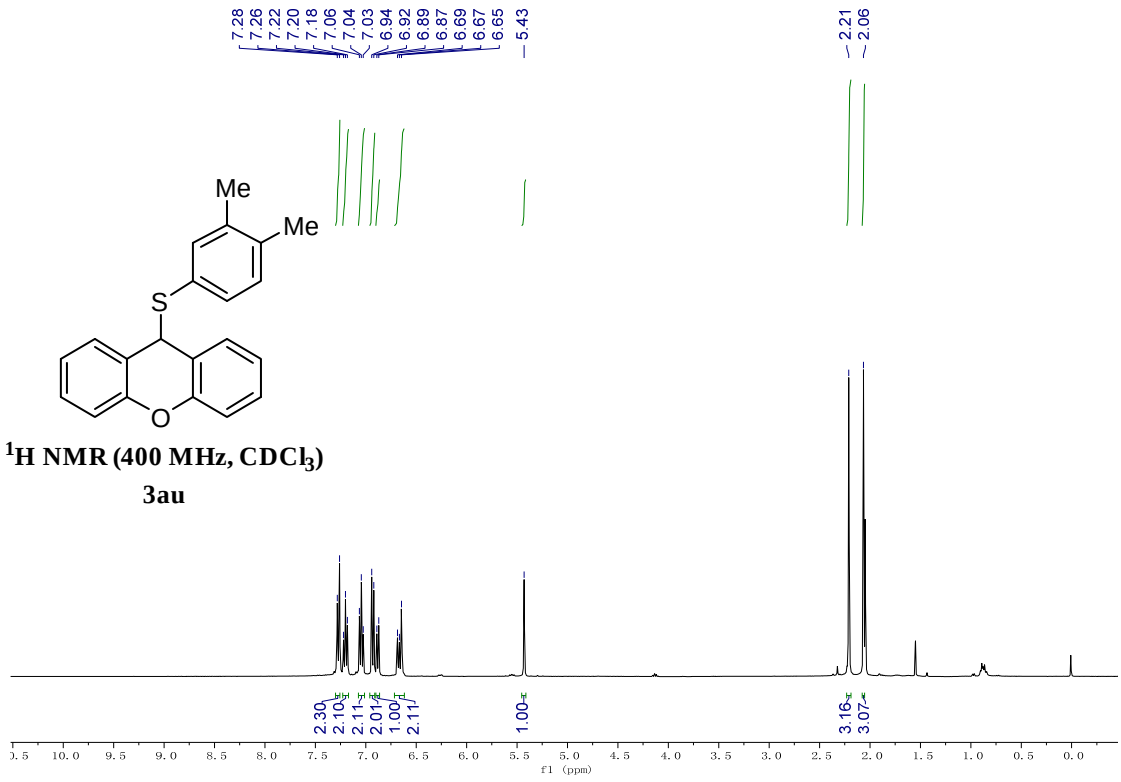
^{1}H NMR (400 MHz, $CDCl_3$)

3at



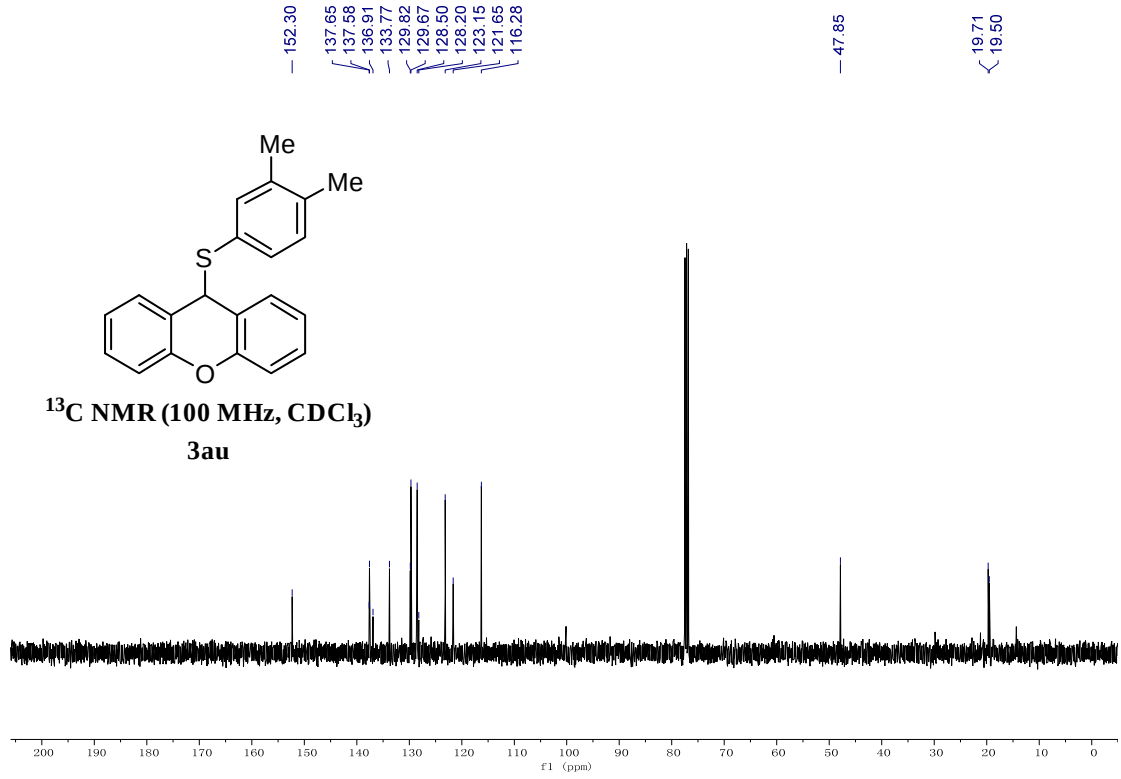
^{13}C NMR (100 MHz, $CDCl_3$)

3at



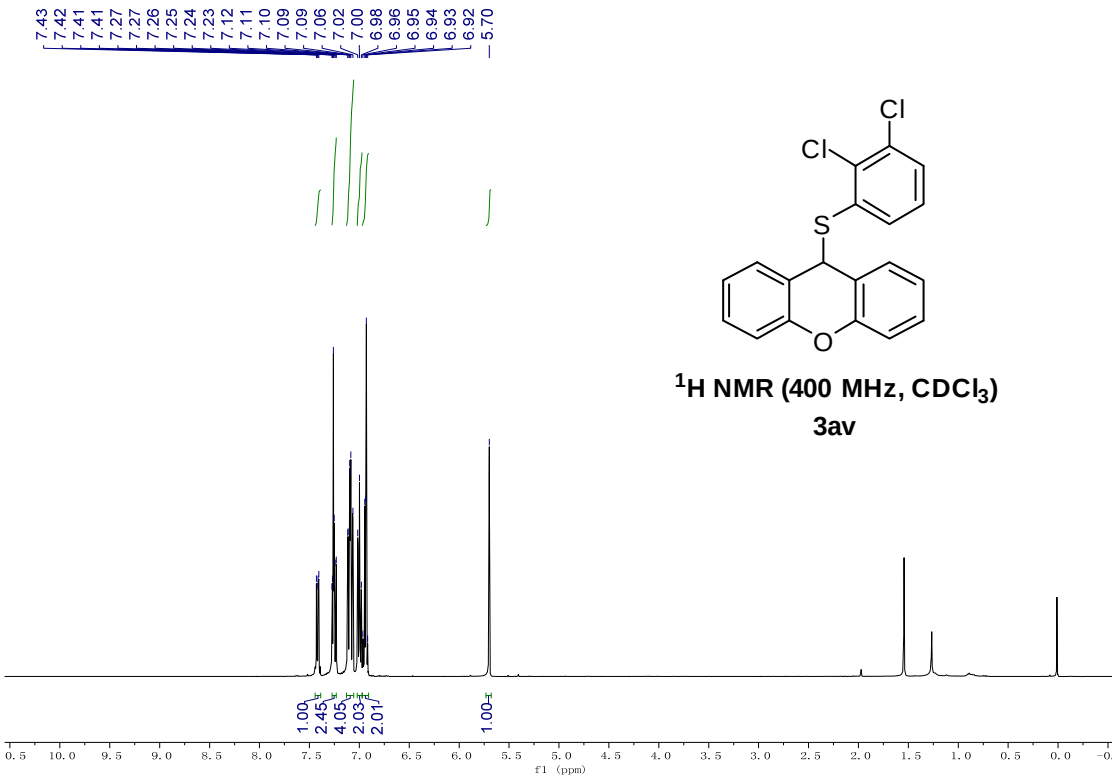
^{1}H NMR (400 MHz, $CDCl_3$)

3au



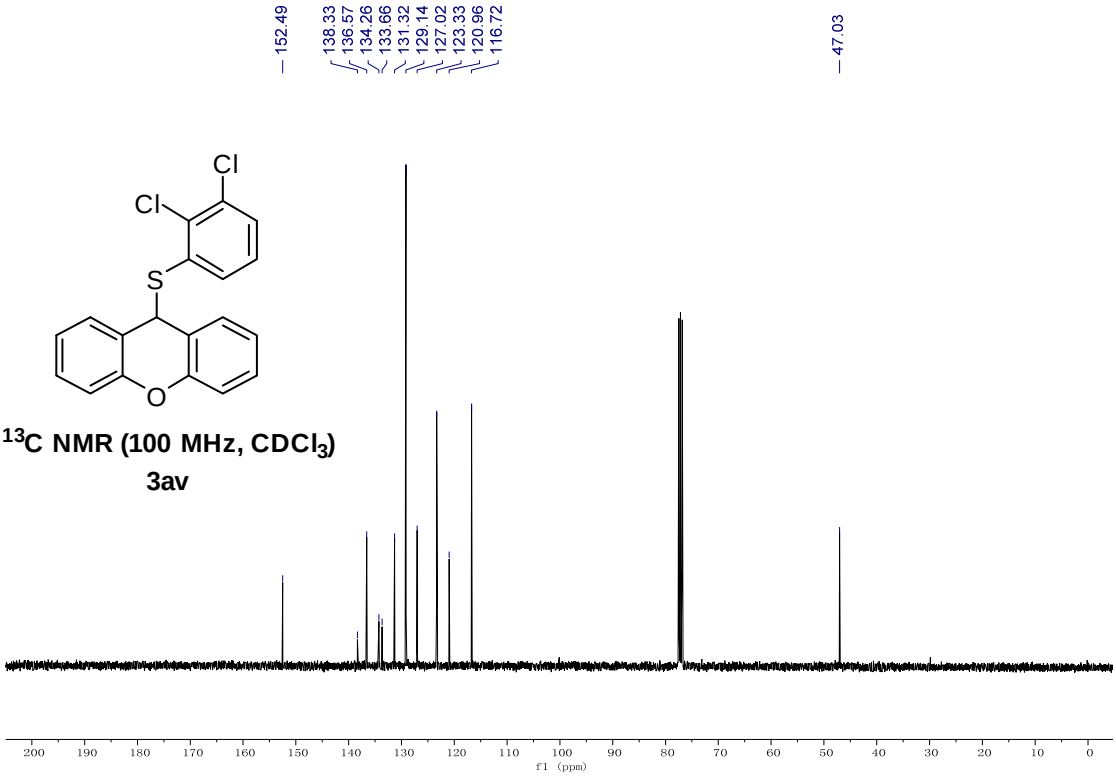
^{13}C NMR (100 MHz, $CDCl_3$)

3au



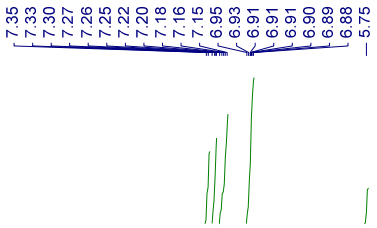
^{1}H NMR (400 MHz, $CDCl_3$)

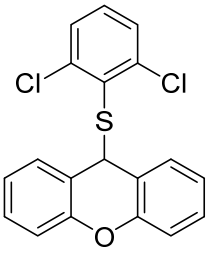
3av



^{13}C NMR (100 MHz, $CDCl_3$)

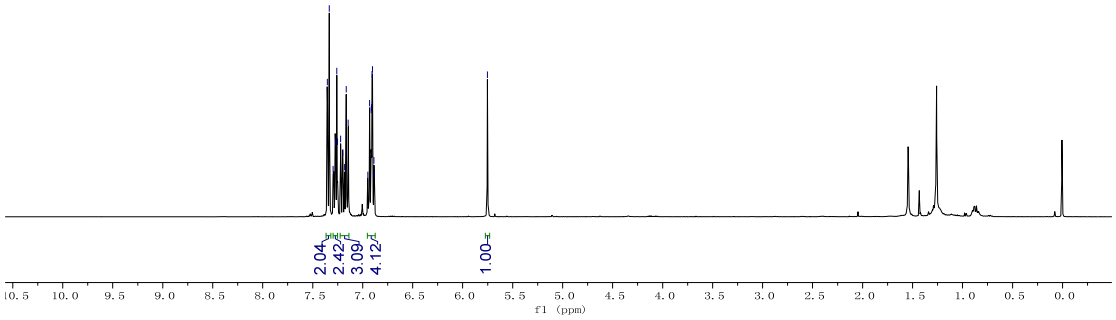
3av

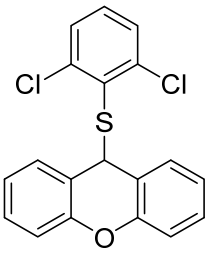




^{1}H NMR (400 MHz, $CDCl_3$)

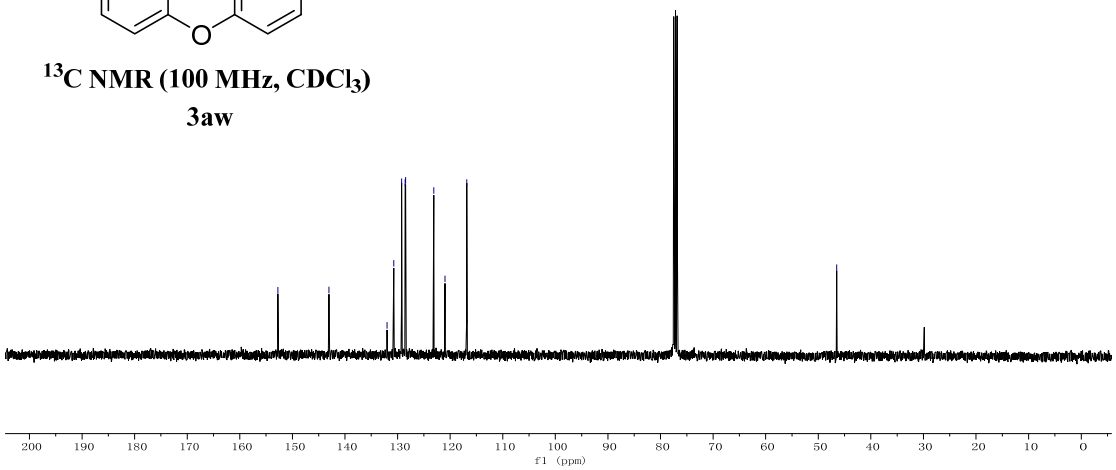
3aw

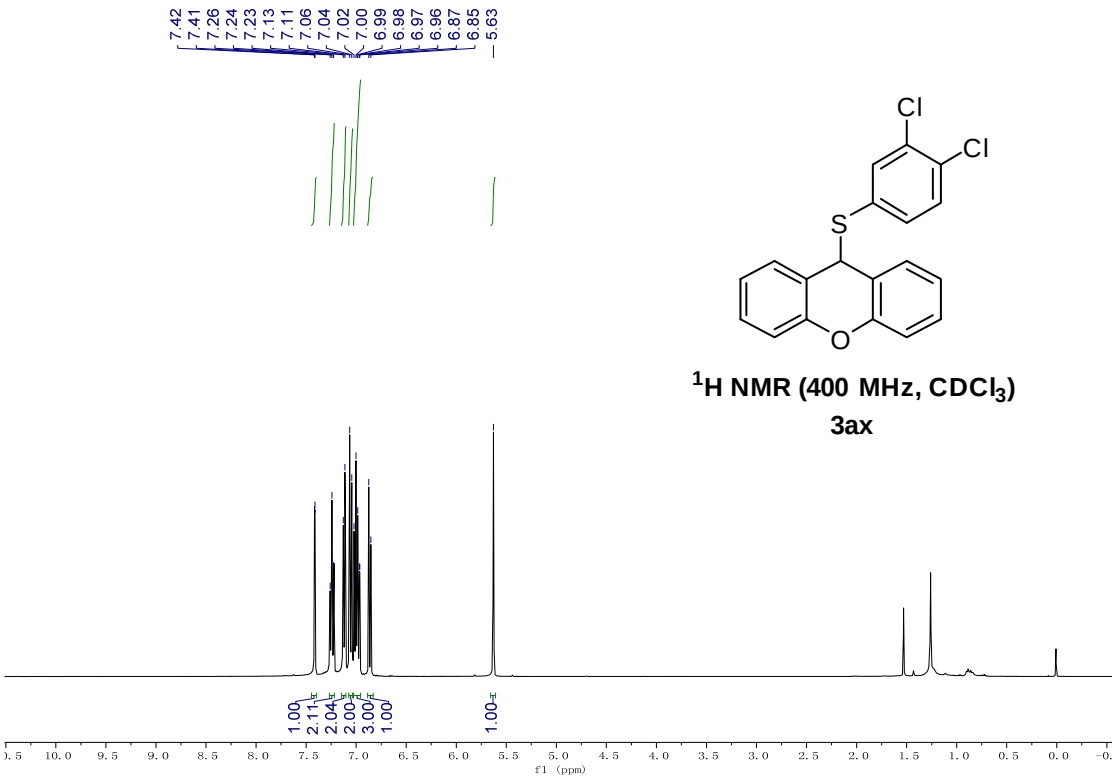




^{13}C NMR (100 MHz, $CDCl_3$)

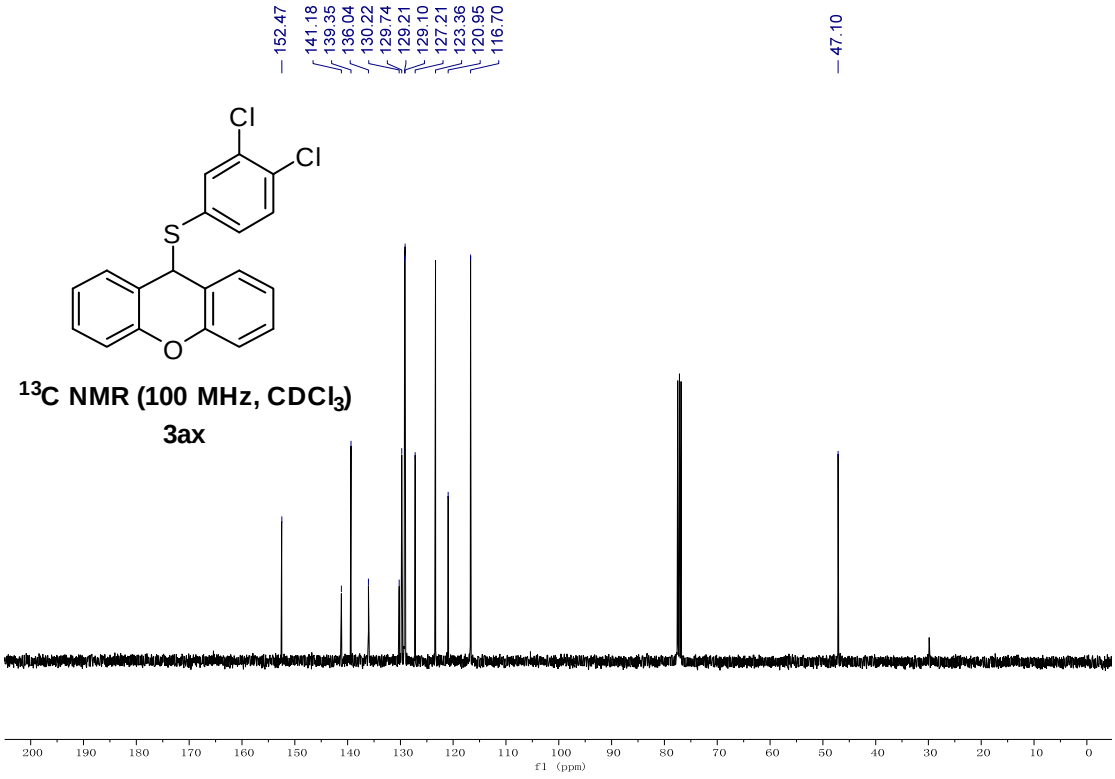
3aw





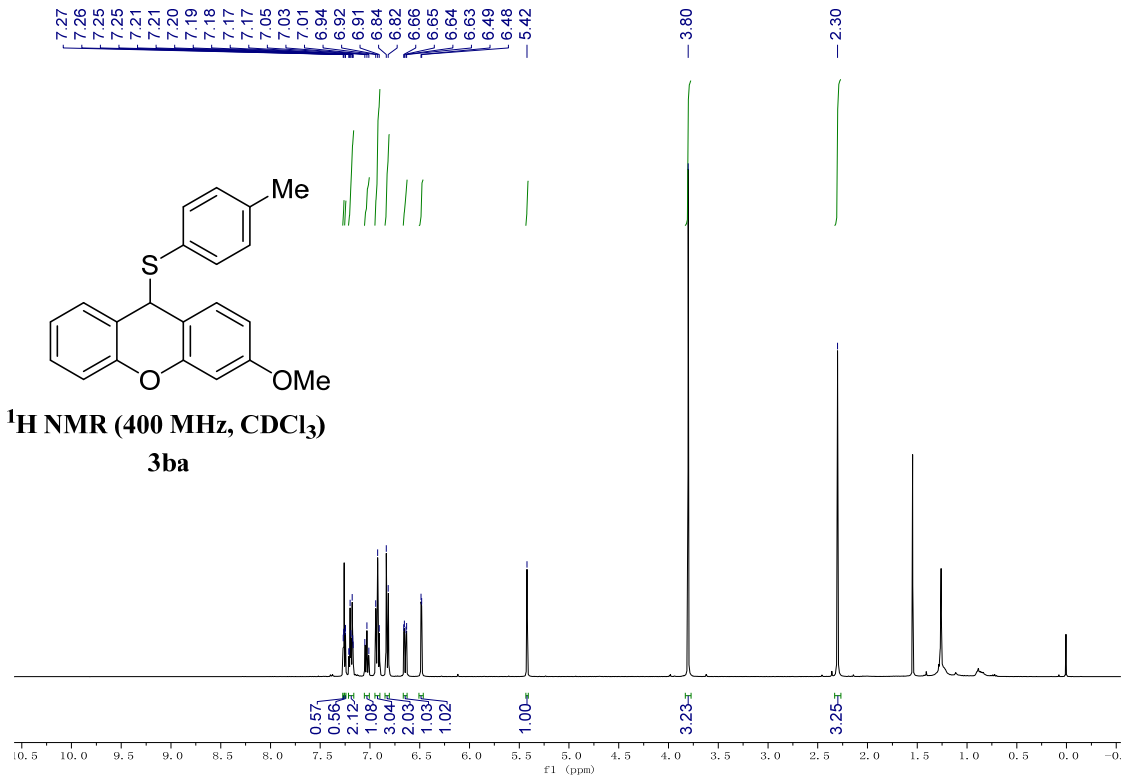
^{1}H NMR (400 MHz, $CDCl_3$)

3ax



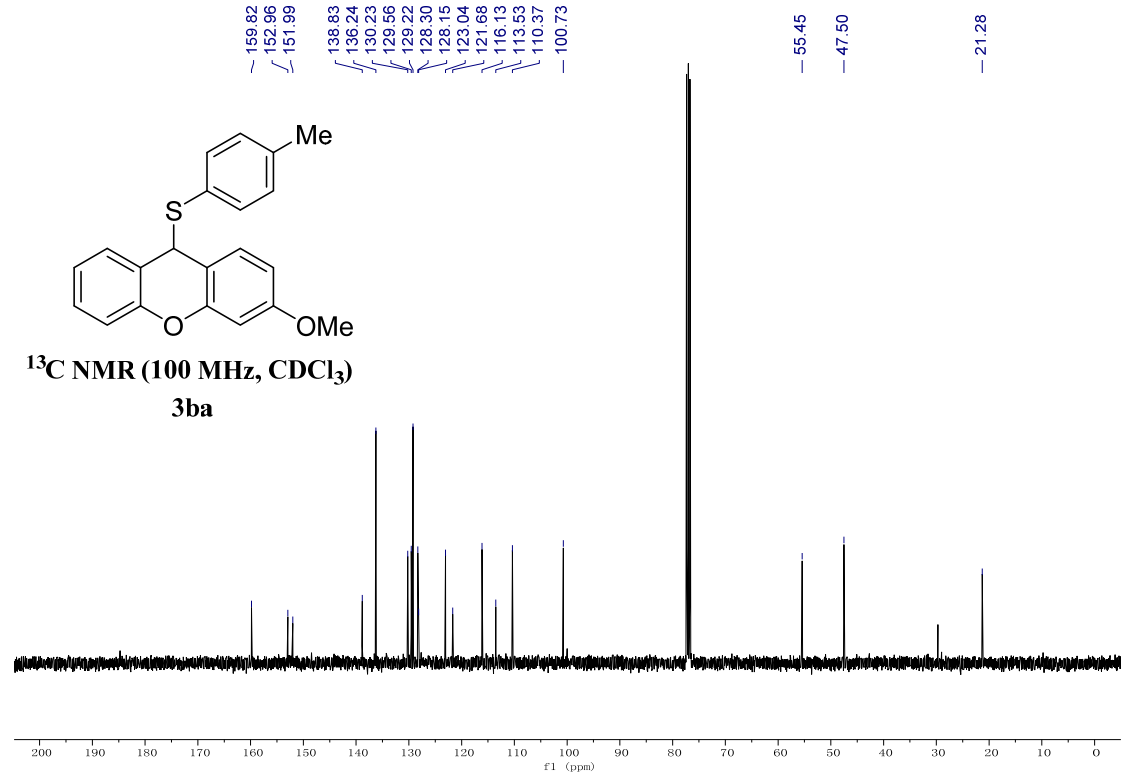
^{13}C NMR (100 MHz, $CDCl_3$)

3ax



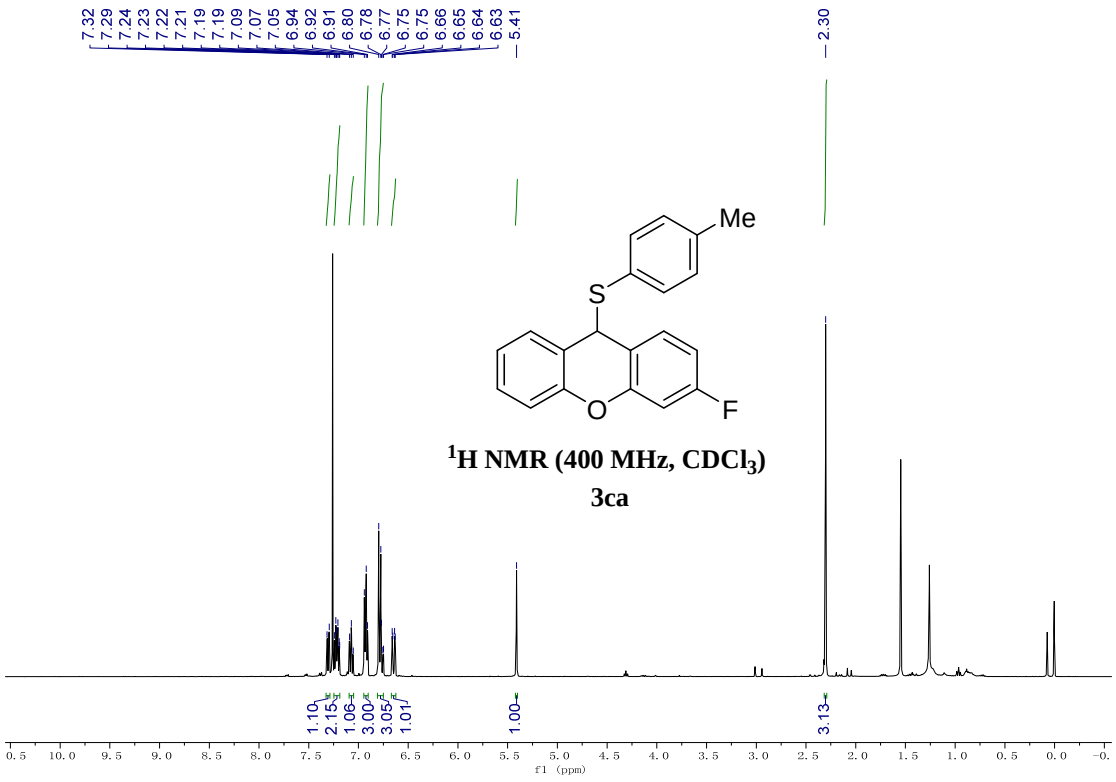
^{1}H NMR (400 MHz, $CDCl_3$)

3ba



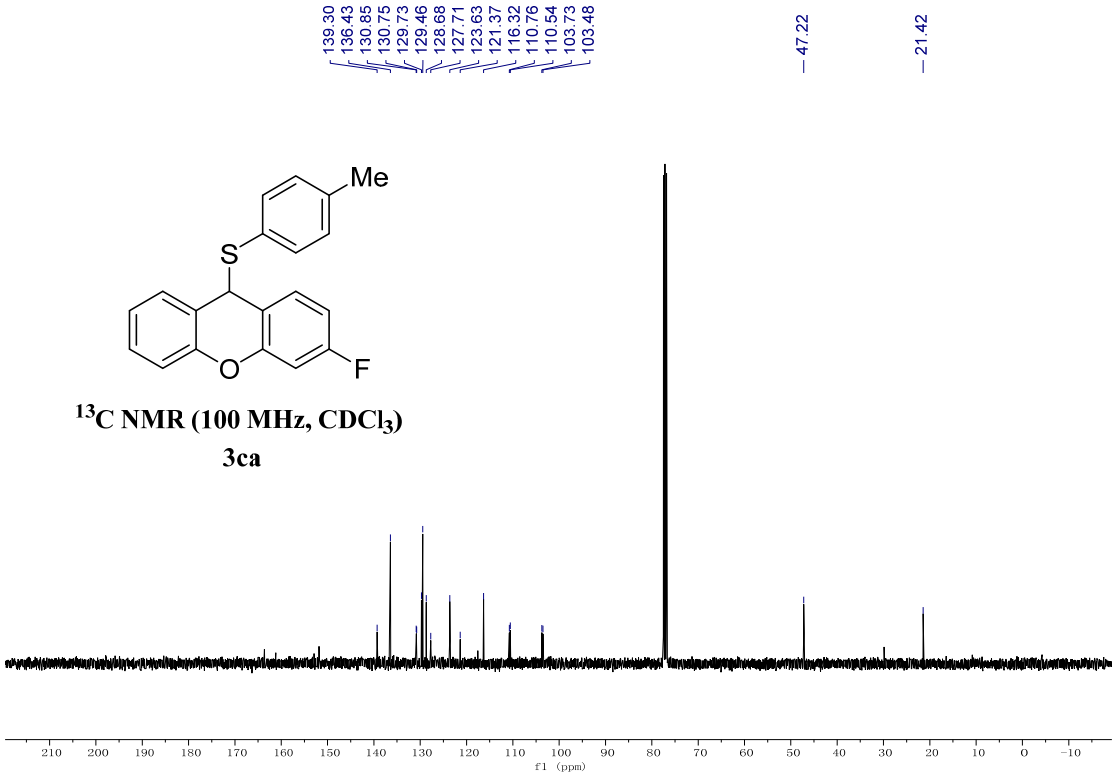
^{13}C NMR (100 MHz, $CDCl_3$)

3ba



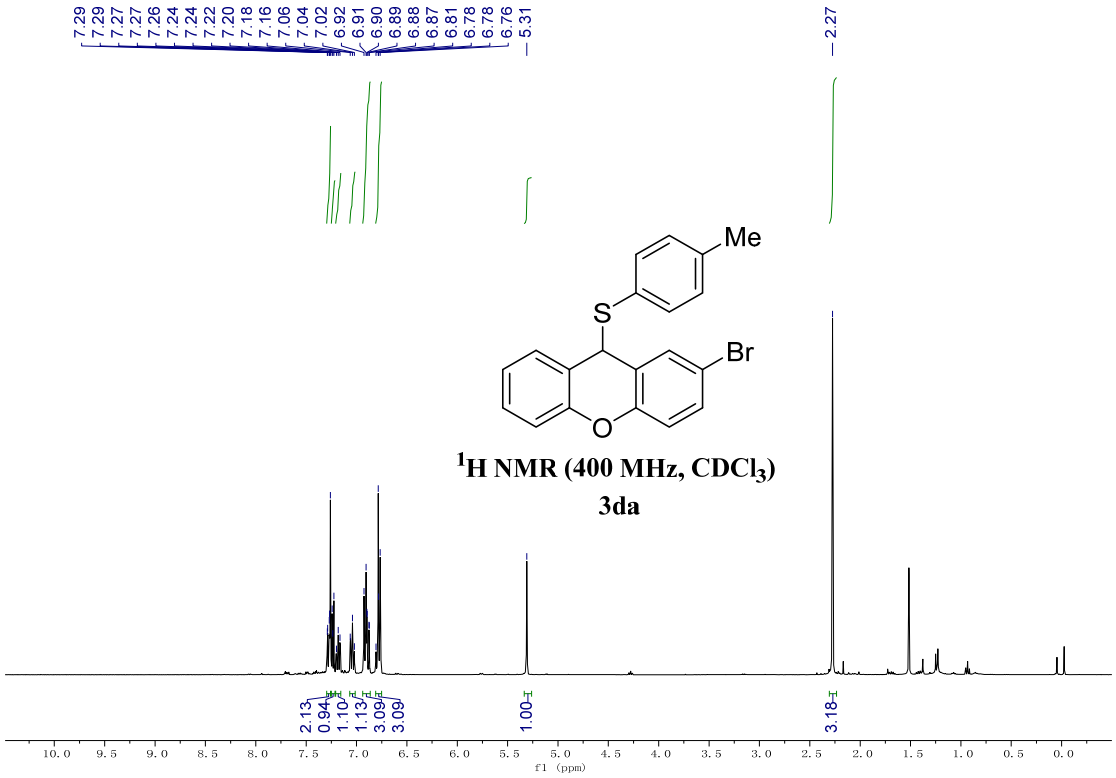
^{1}H NMR (400 MHz, $CDCl_3$)

3ca



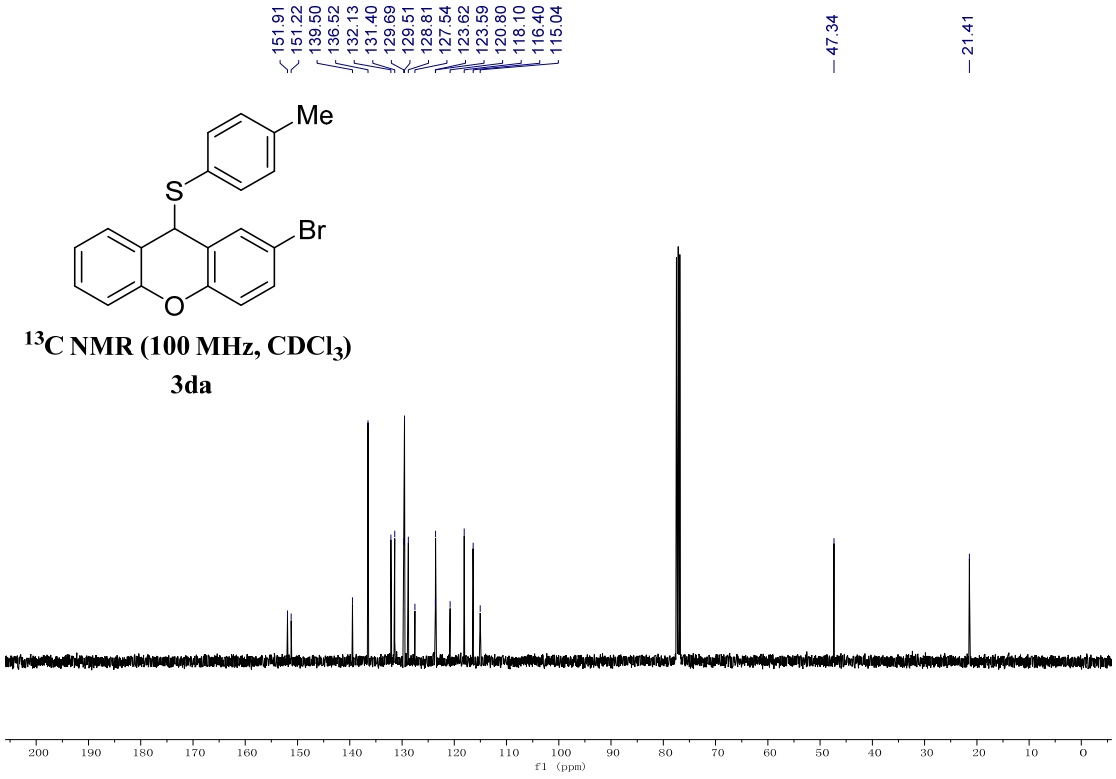
^{13}C NMR (100 MHz, $CDCl_3$)

3ca



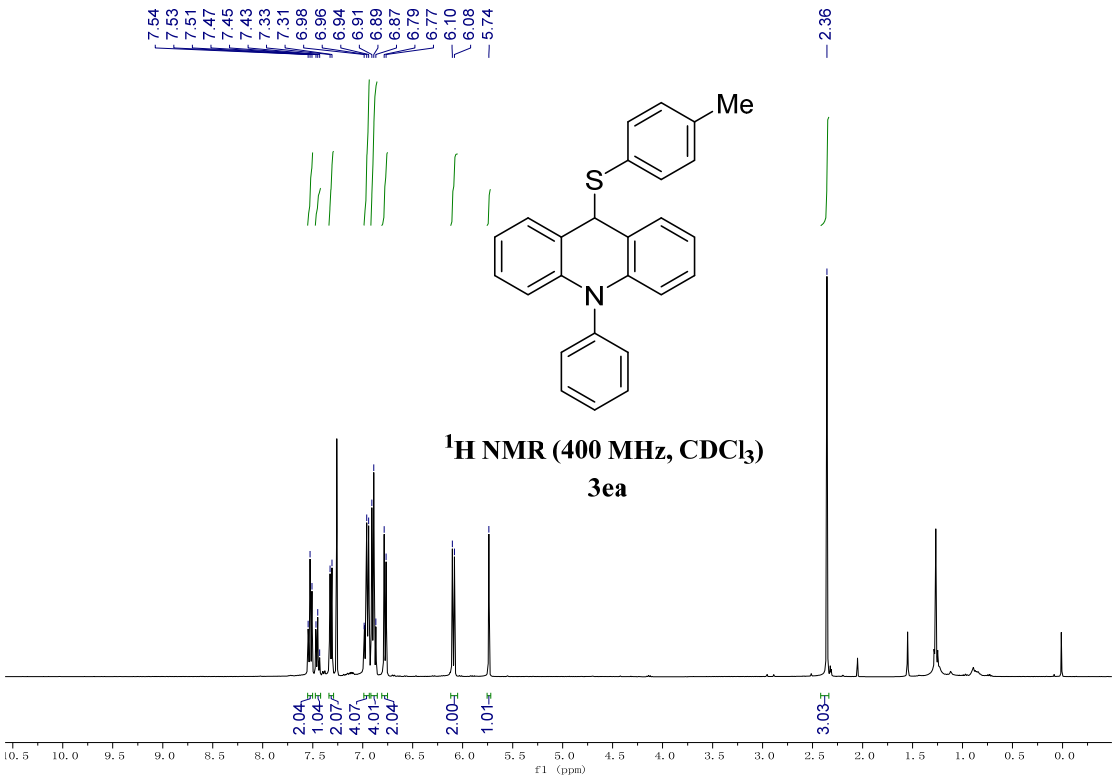
^{1}H NMR (400 MHz, $CDCl_3$)

3da



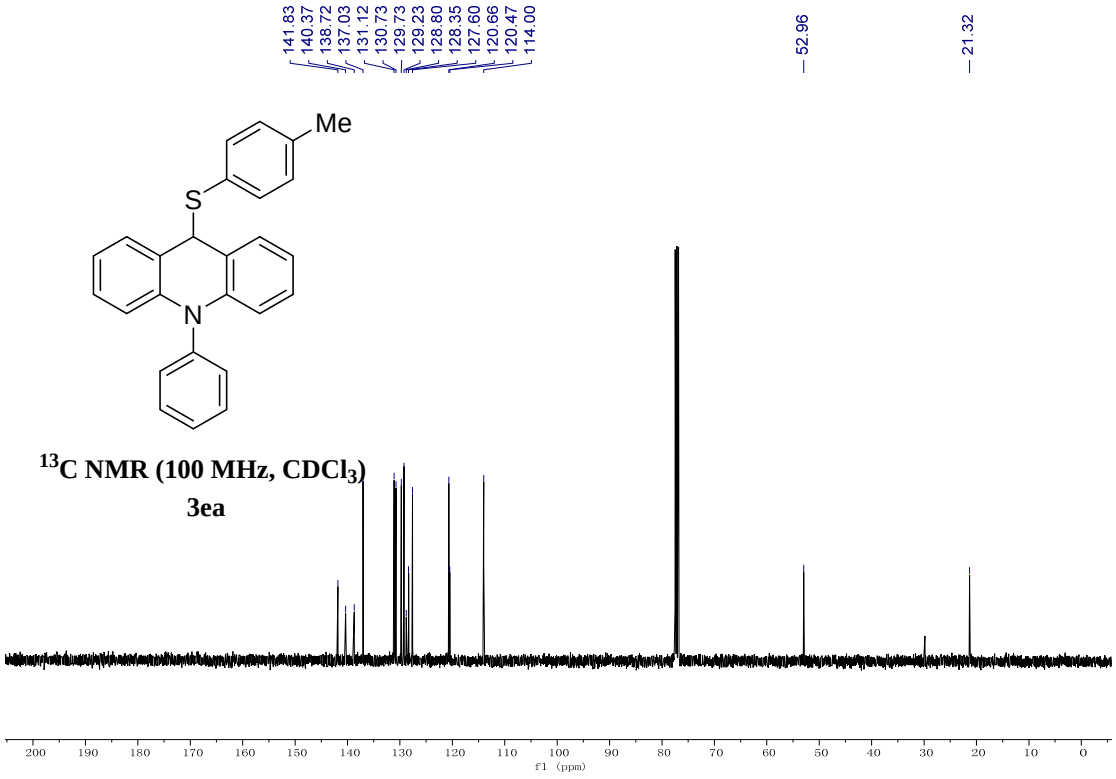
^{13}C NMR (100 MHz, $CDCl_3$)

3da



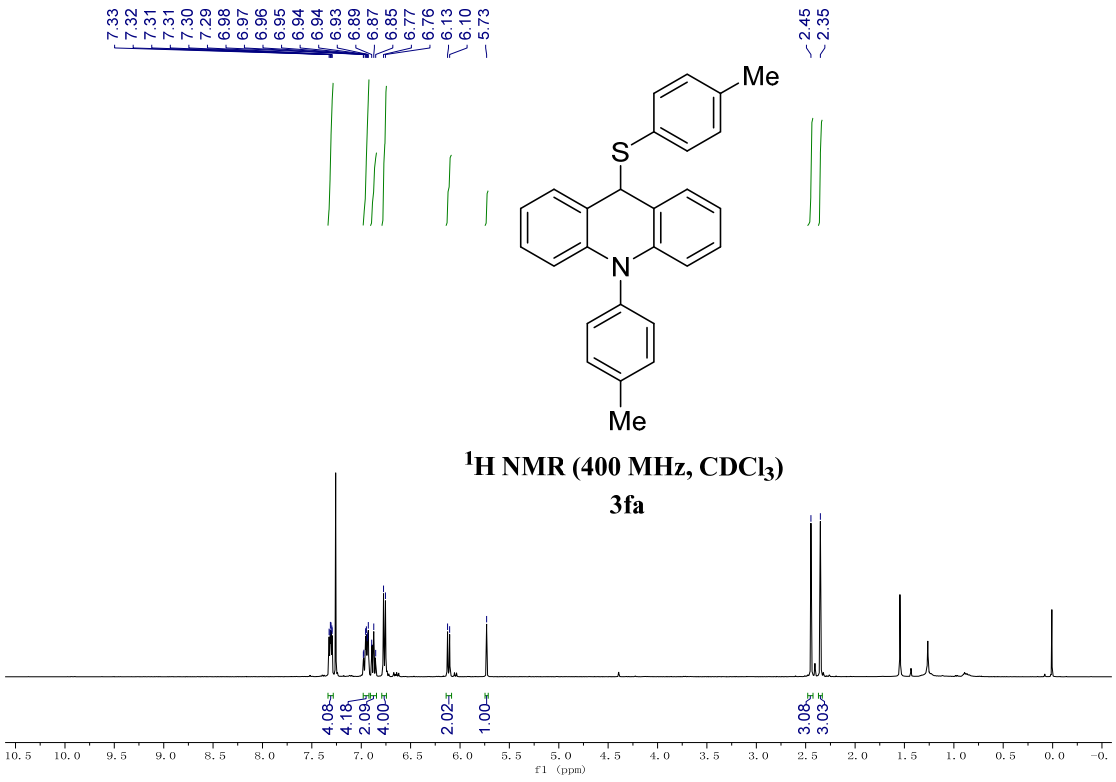
^{1}H NMR (400 MHz, $CDCl_3$)

3ea



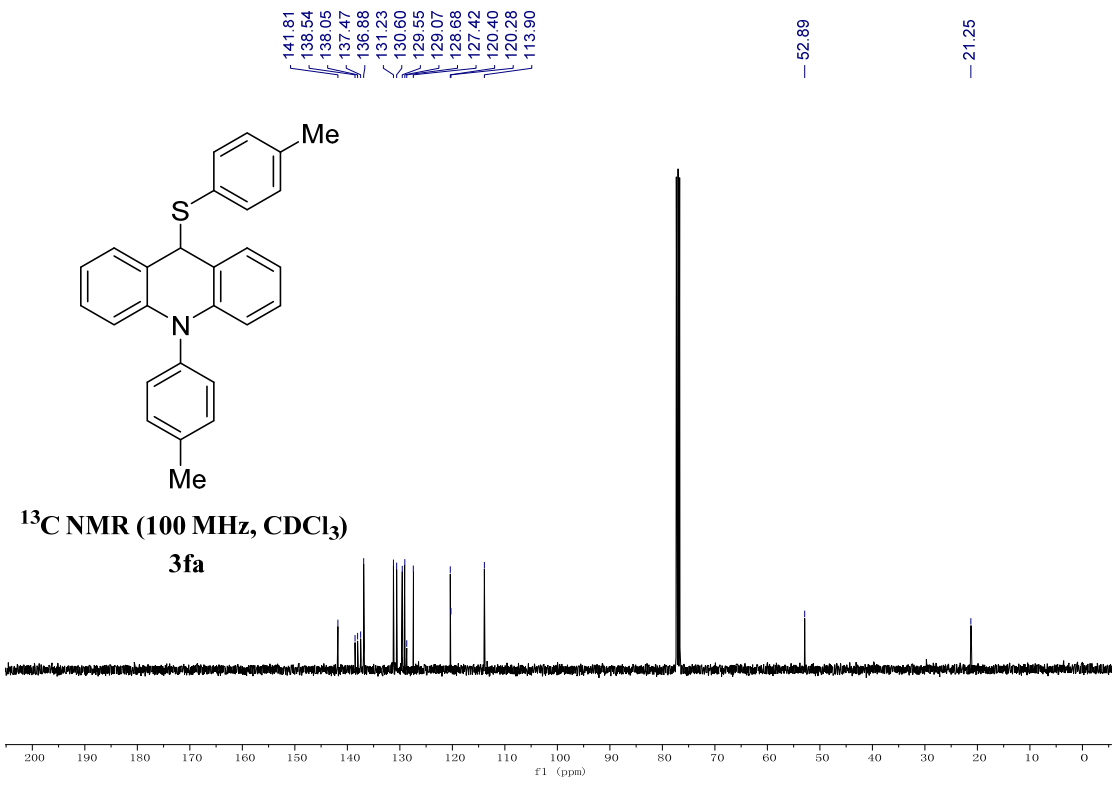
^{13}C NMR (100 MHz, $CDCl_3$)

3ea



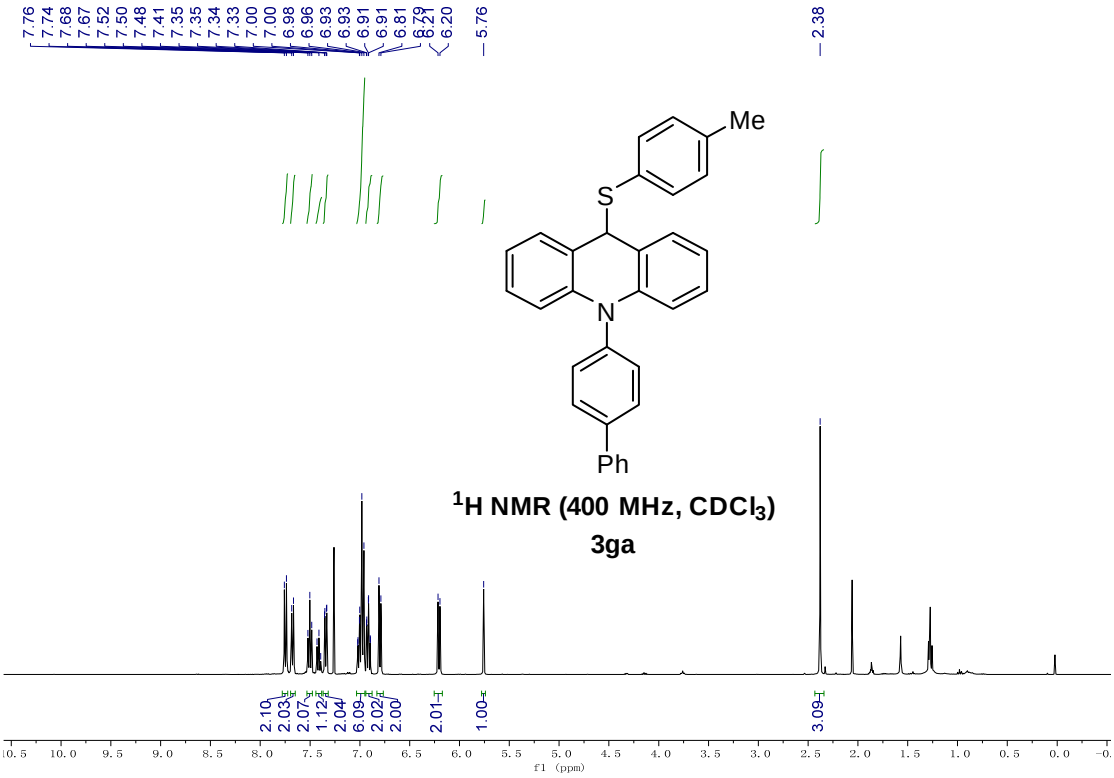
^{1}H NMR (400 MHz, $CDCl_3$)

3fa



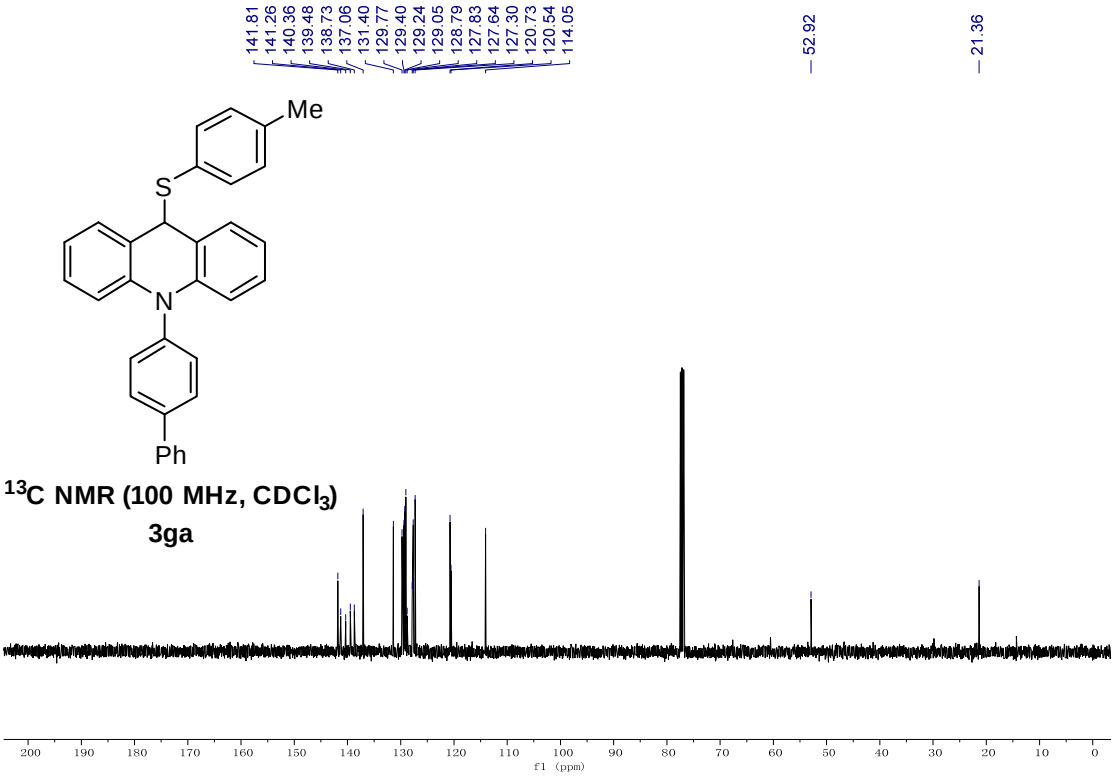
^{13}C NMR (100 MHz, $CDCl_3$)

3fa



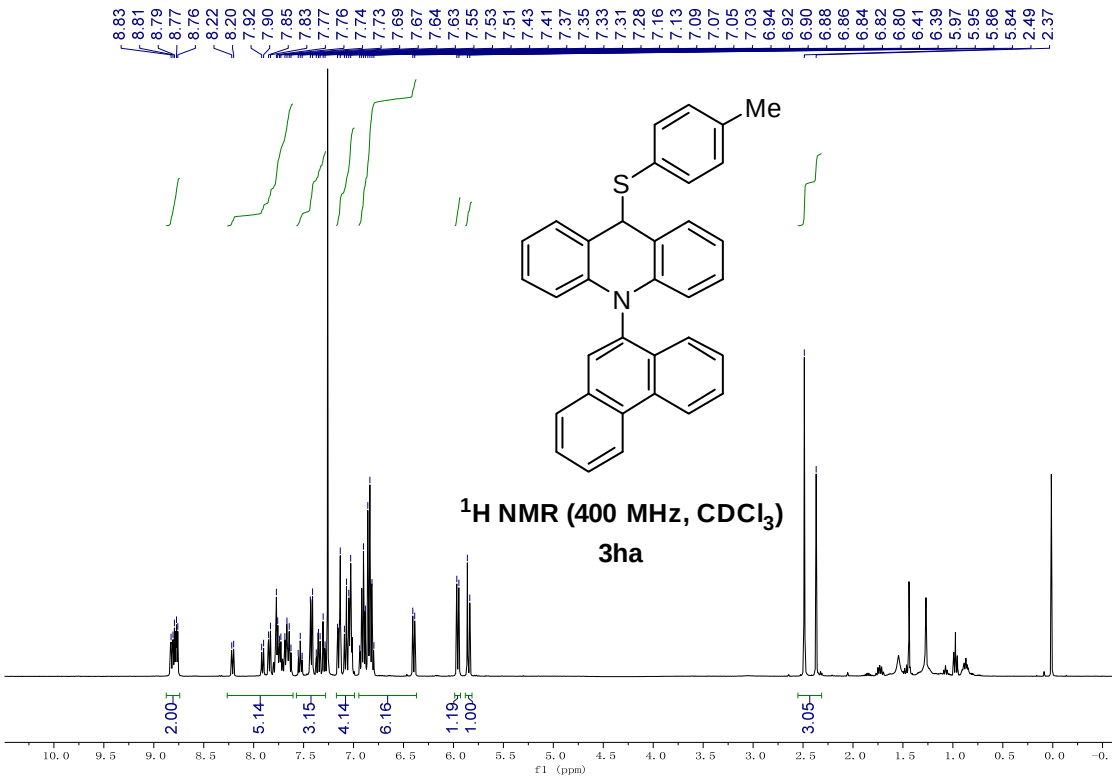
^{1}H NMR (400 MHz, $CDCl_3$)

3ga



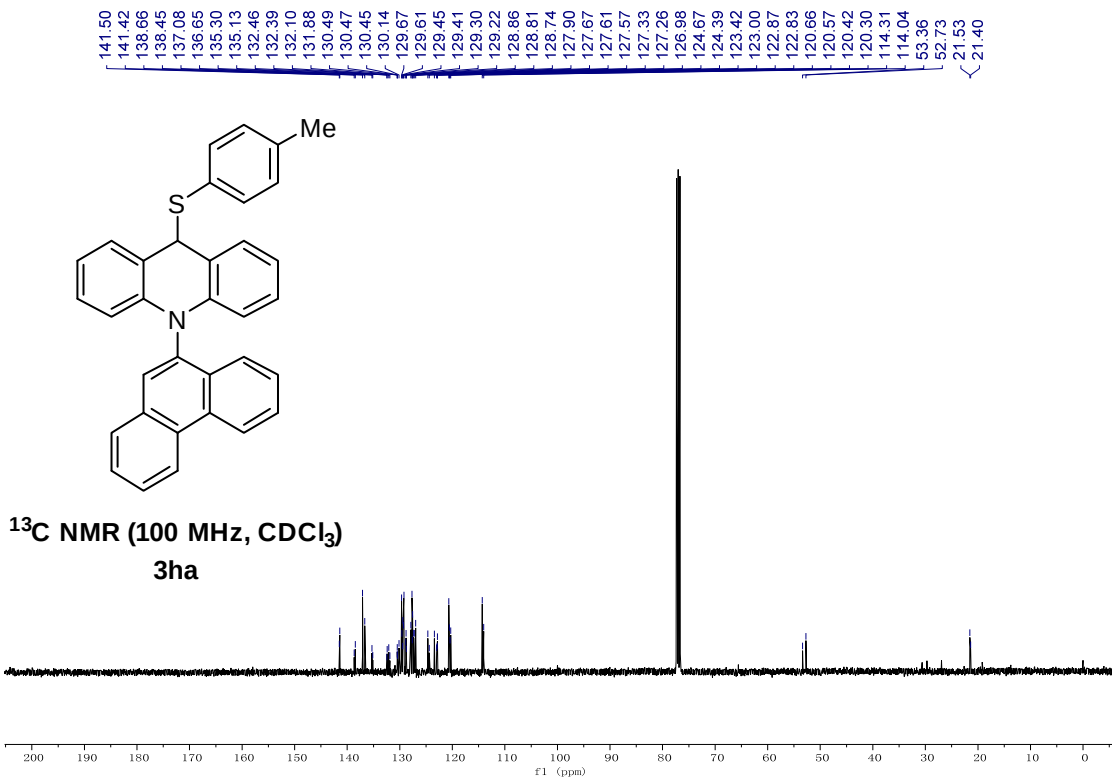
^{13}C NMR (100 MHz, $CDCl_3$)

3ga



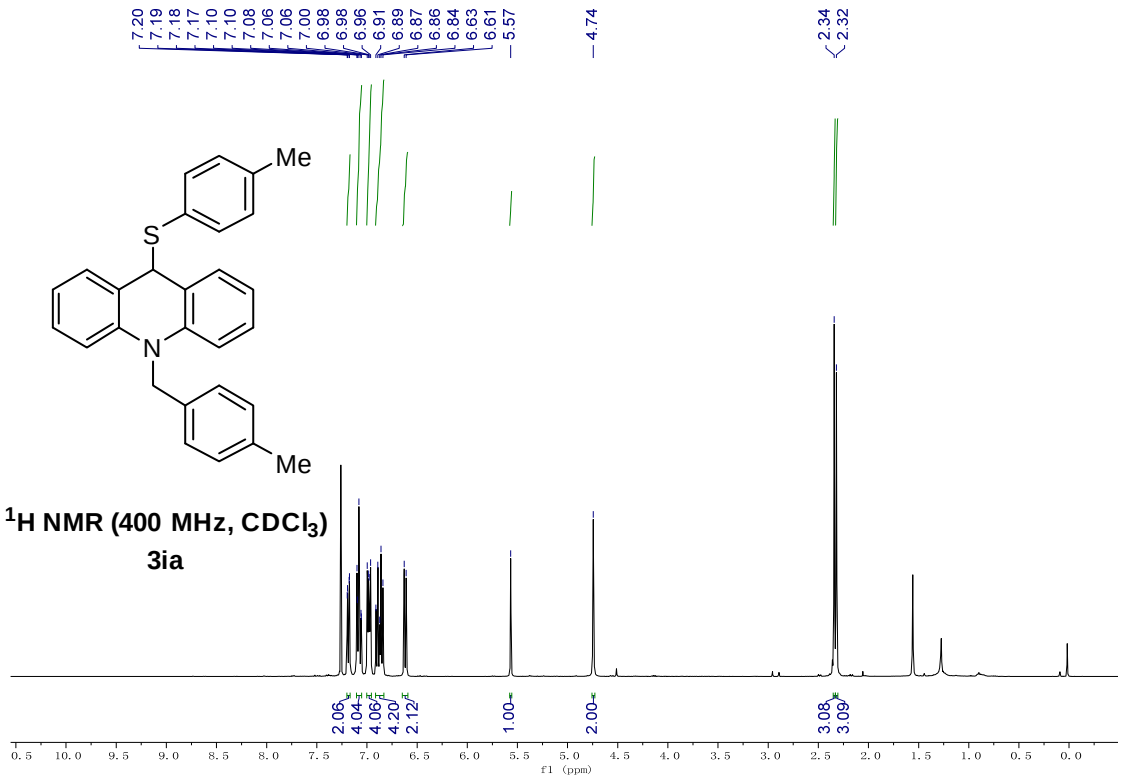
^{1}H NMR (400 MHz, $CDCl_3$)

3ha



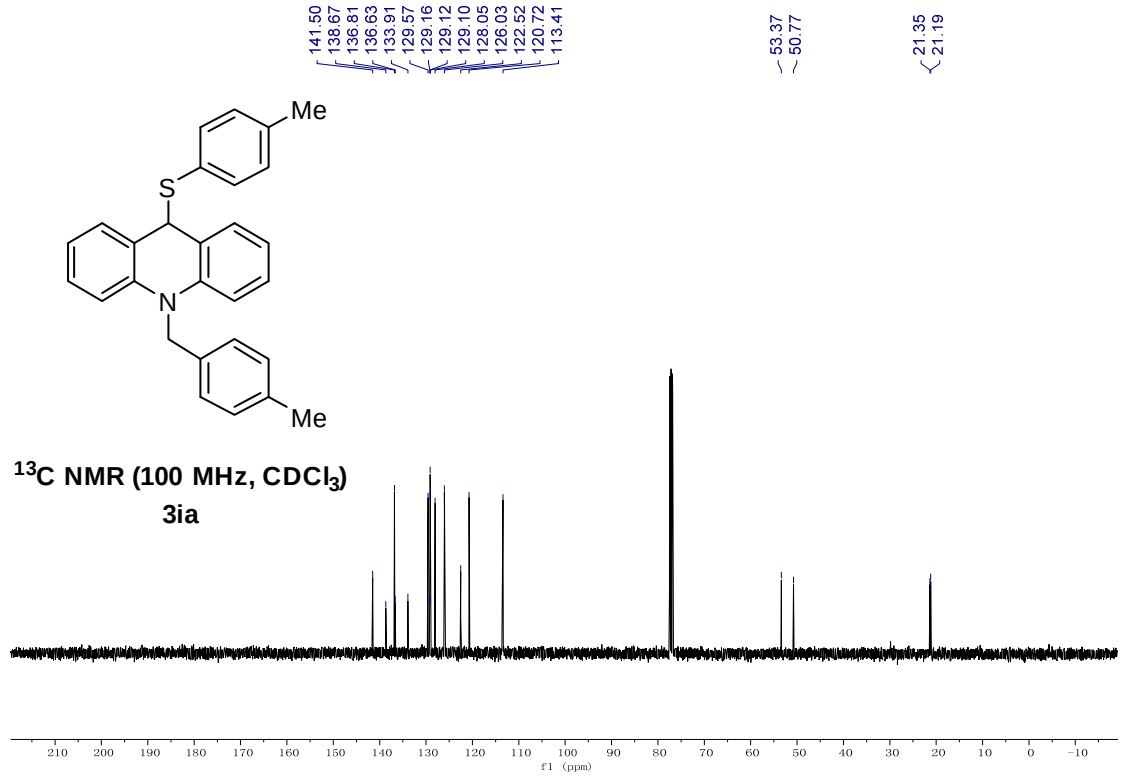
^{13}C NMR (100 MHz, $CDCl_3$)

3ha



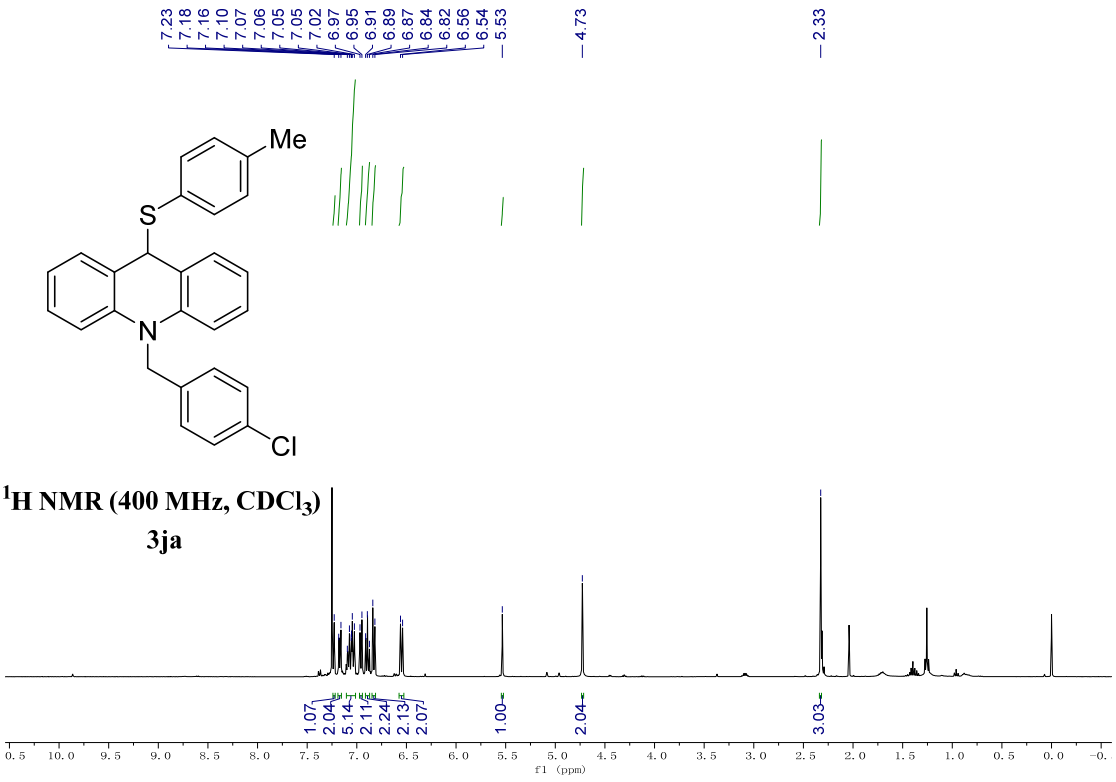
^{1}H NMR (400 MHz, $CDCl_3$)

3ia



^{13}C NMR (100 MHz, $CDCl_3$)

3ia



^{1}H NMR (400 MHz, $CDCl_3$)

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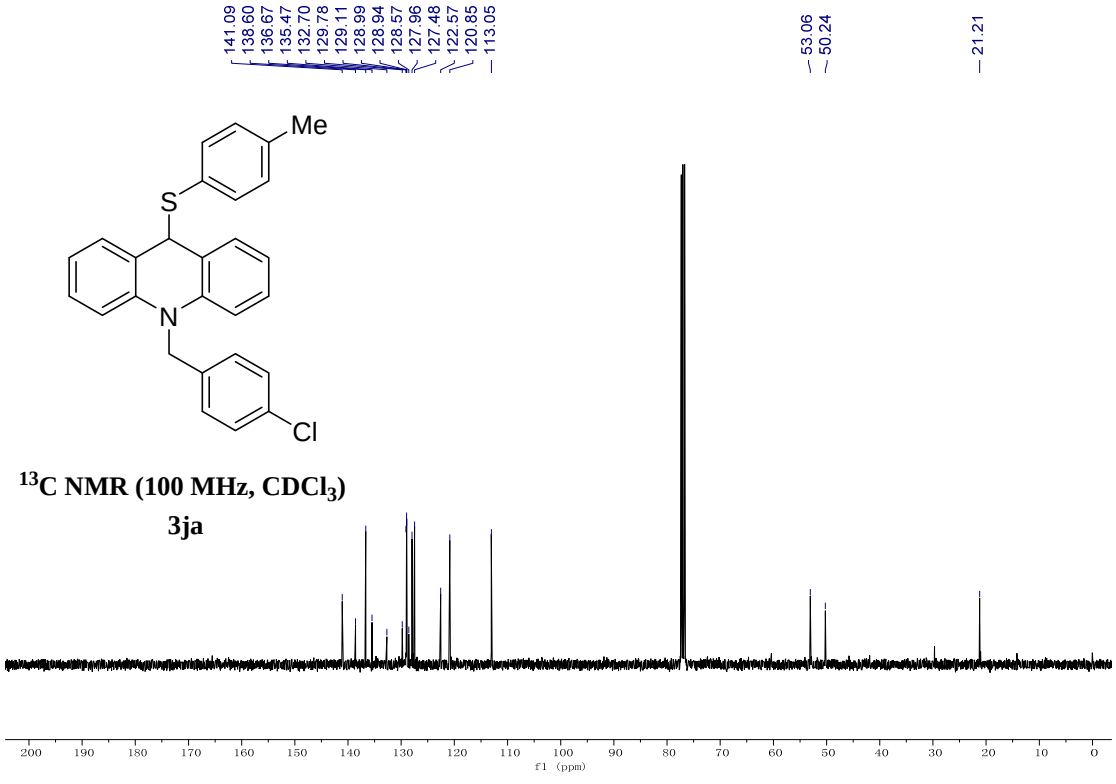

^{13}C NMR (100 MHz, $CDCl_3$)

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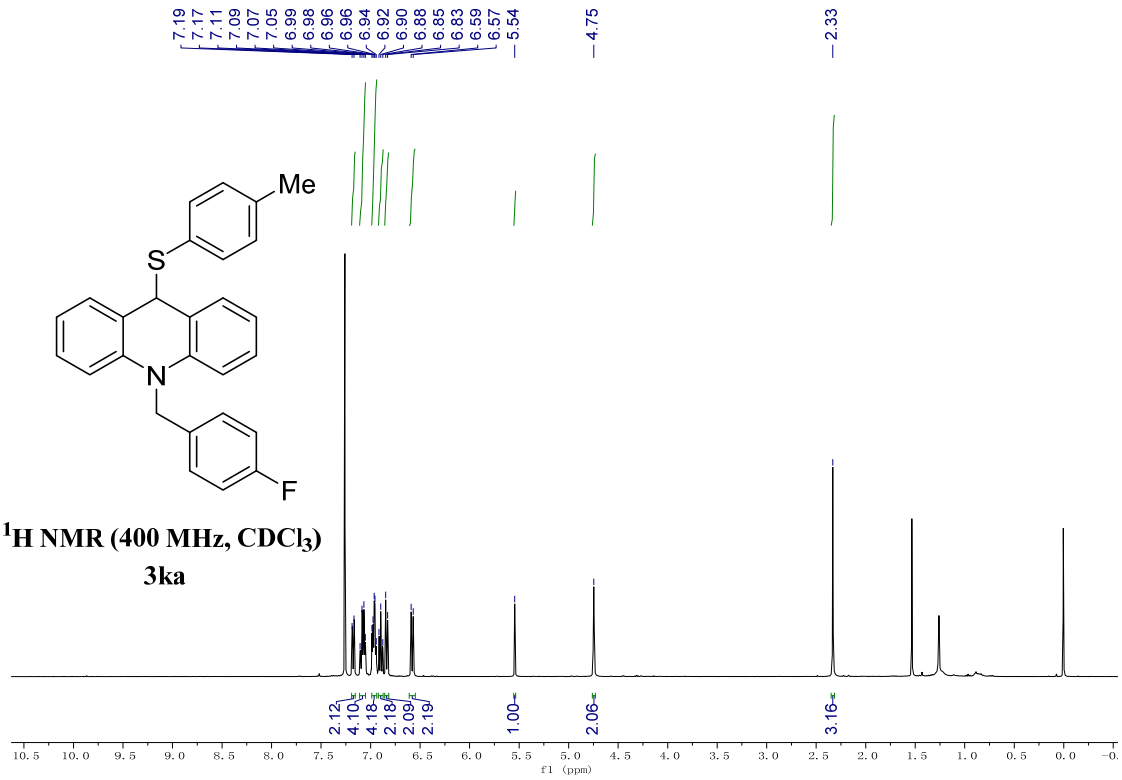
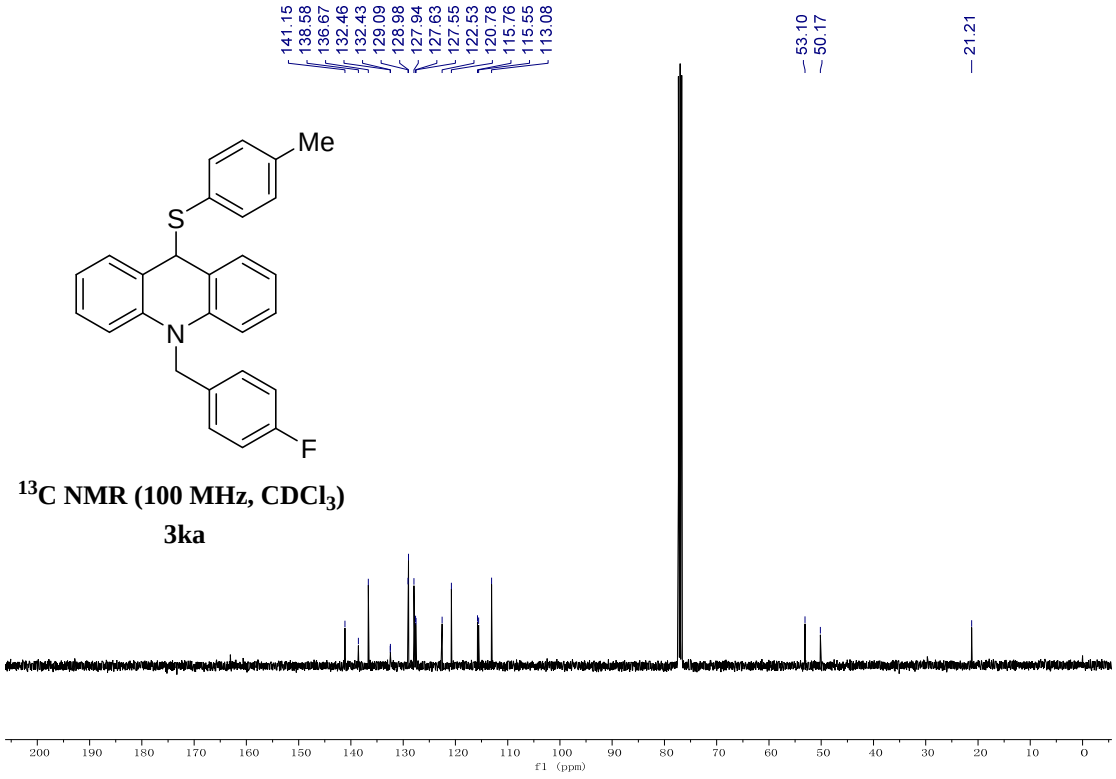


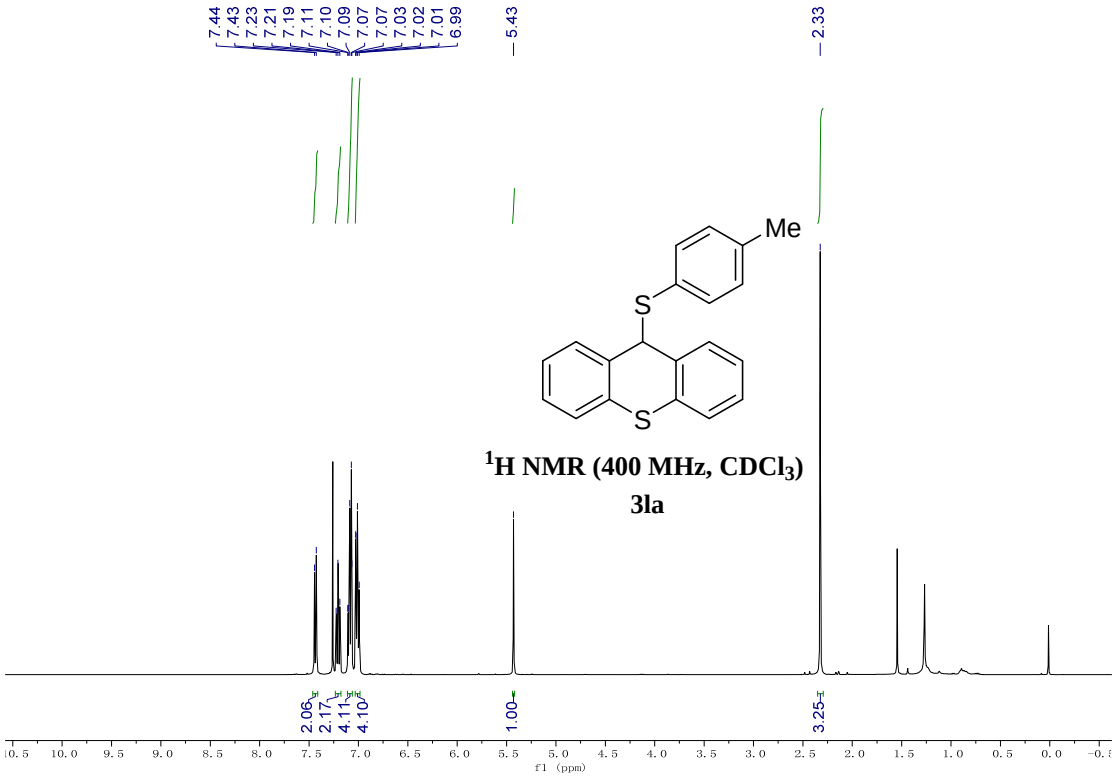
^{1}H NMR (400 MHz, $CDCl_3$)

3ka



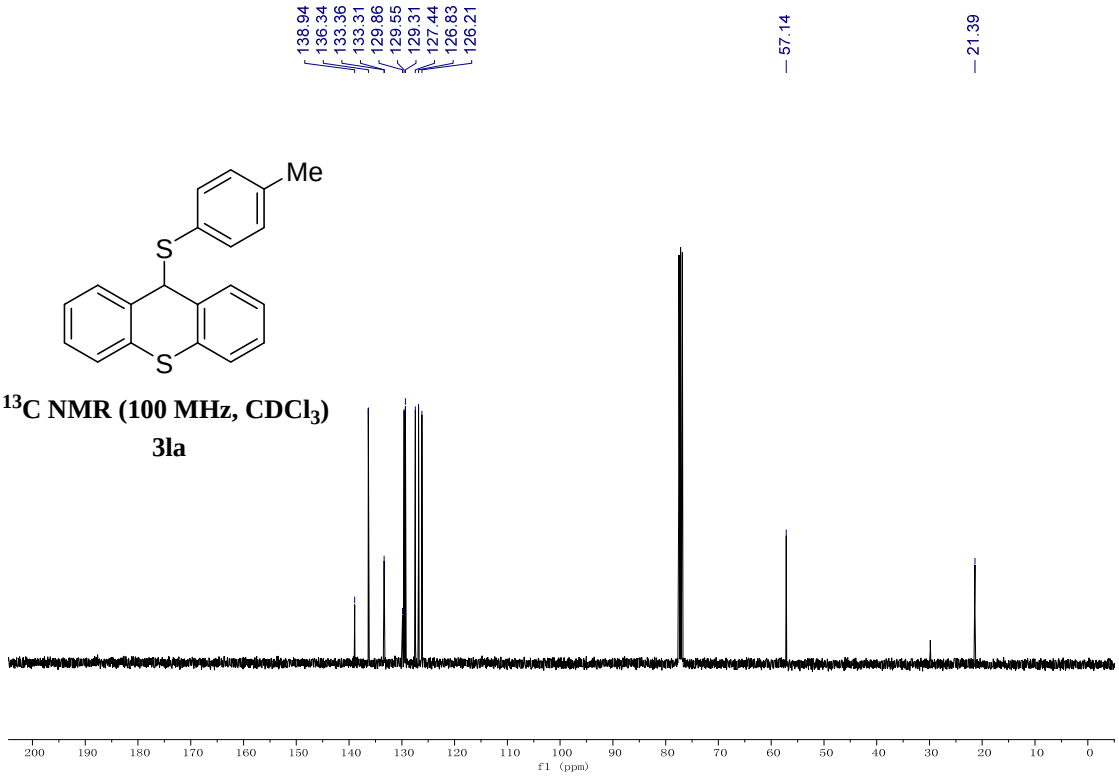
^{13}C NMR (100 MHz, $CDCl_3$)

3ka



^{1}H NMR (400 MHz, $CDCl_3$)

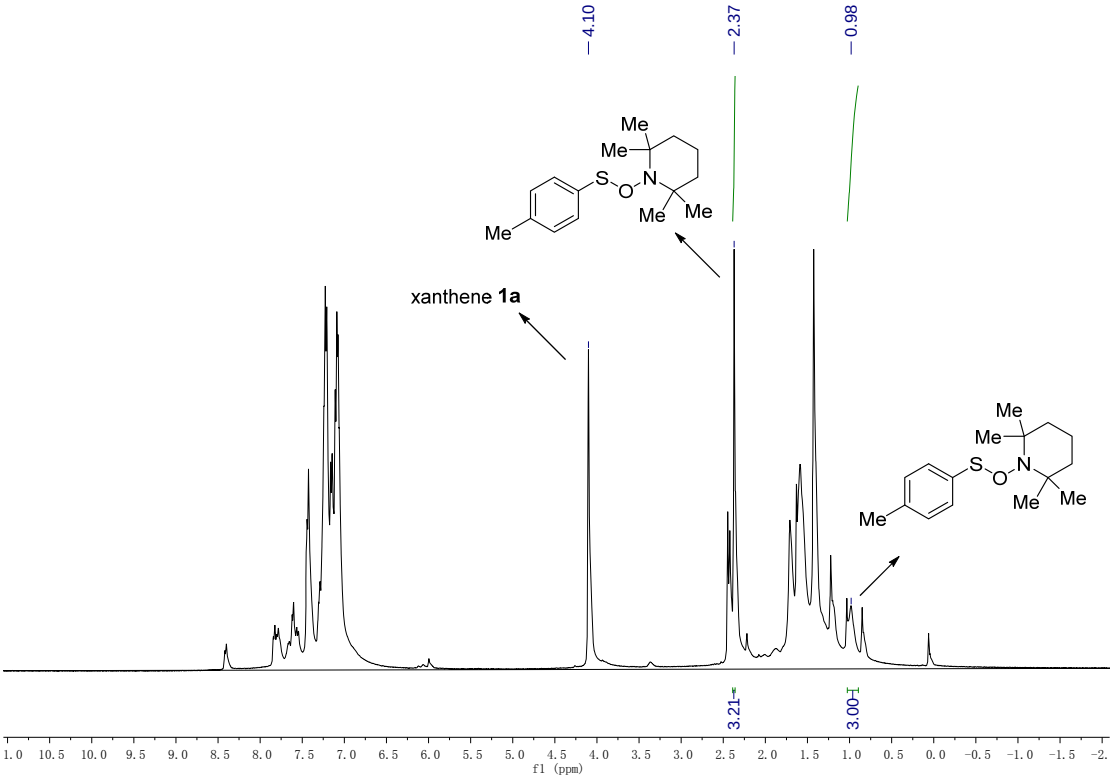
3la

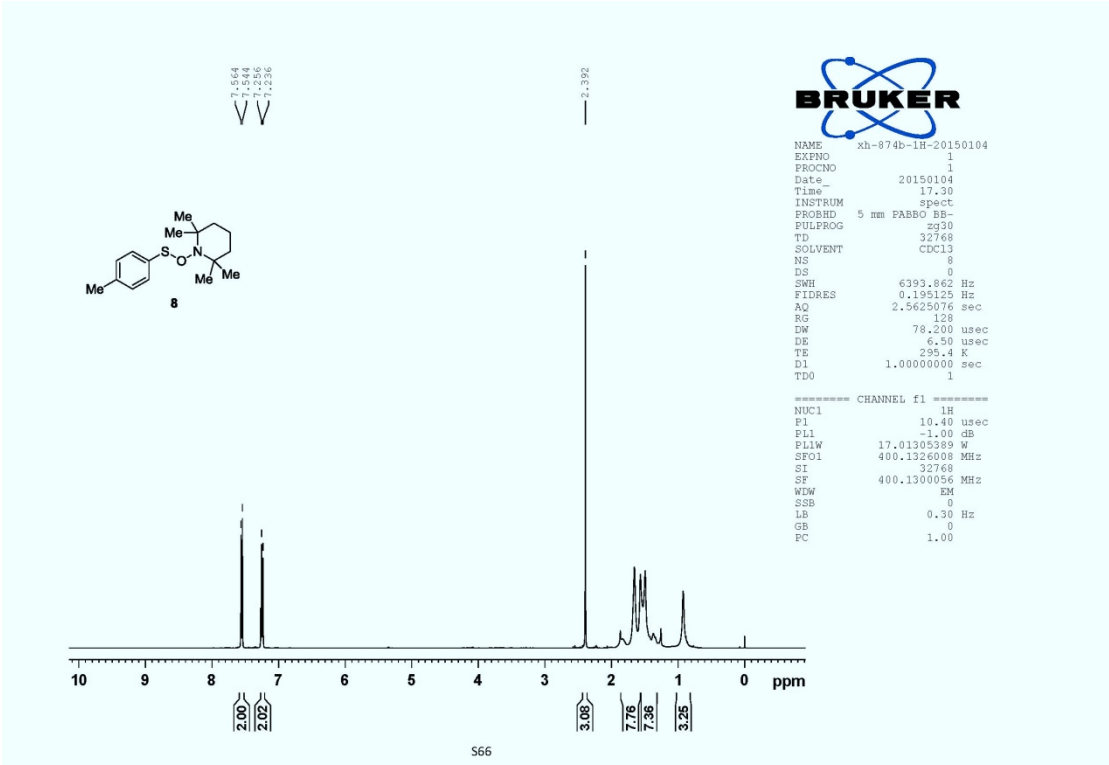


^{13}C NMR (100 MHz, $CDCl_3$)

3la

6. Copy of ^{1}H NMR spectra for crude products of TEMPO-trapping reaction





^{1}H NMR of TEMPO-STol adduct

Reference: H. Xi, B. Deng, Z. Zong, S. Lu and Z. Li, *Org. Lett.*, 2015, **17**, 1180.