Supplementary Information (SI) for Organic & Biomolecular Chemistry.

Supporting information

Disulfide mediated ruthenium catalyzed direct C-H thiolation in benzoxazinone systems: Selective synthesis of *ortho*-thiolated 2-arylbenzoxazinones

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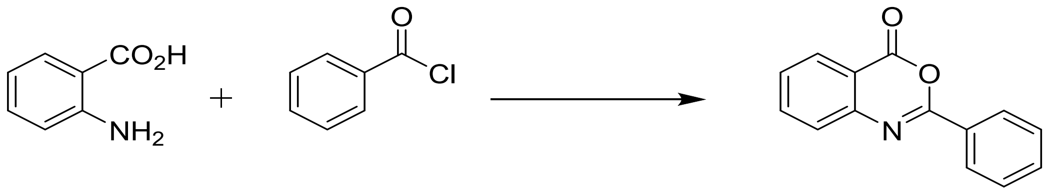
1. Representative experimental procedure of 2-arylbenzoxazinones: Experimental procedure for 2-arylbenzoxazinones:[1]



To solution of anthranilic acid (10 mmol) in pyridine (20 ml) cooled to 0 °C in an ice bath was added an acid chloride (20 mmol) drop-wise slowly and carefully with proper control. An exothermic reaction occurred. The reaction mixture was stirred by 5 min at 0 ° C. The ice bath was removed and the reaction mixture was warmed slowly to room temperature. The reaction mixture was further stirred by 0.5 h at room temperature. After completion of the reaction (TLC) the mixture was poured into ice cooled water (200 mL) and the residue was collected by filtration and washed cooled water (180 mL) and dried. The crude benoxazinones was recrystallized from ethanol.

2. General information:

General Information. All the commercial starting materials and reagents were used without further purification. Silica gel (silica gel, f24), TLC plates were purchased from Merck. In column chromatographic purification process, silica gel 100-200 mesh has been used. ^{1}H NMR spectra were recorded using Brucker Spectrometer at 300 MHz, 400 MHz. The ^{19}F spectra of synthesized fluorinated product was recorded in $CDCl_3$ on Brucker Spectrometer, 300 MHz 400 MHz. ^{13}C NMR spectra were recorded at 75 MHz, 100 MHz. In all NMR, $CDCl_3$ and TMS have been used as solvent and internal standard. respectively. The chemical shifts are reported in ppm scale considering standard signal of TMS at 0.00 ppm. The coupling constants (J values) are measured in Hz and splitting patterns of the proton are described as s (singlet), d (doublet), t (triplet), and m (multiplet). HRMS were measured in methanol solvent on waters Micromass Q-tof Micromass spectrometer. LCMS was recorded using COLUMN-X-Bridge-C18 (4.6 x 50 mm, 5 μm).

Crystallographic Data Collection and Refinement Methods: The X-ray single-crystal data for compound **3a** has been collected at room temperature in a Bruker made APEX III diffractometer. At first, single crystals of both the compounds have been isolated and then mounted on the glass fiber tip using commercial super glue. Mo−Kα radiation (λ = 0.71073 Å) from a sealed tube X-ray source has been used. The raw data have been integrated using the SAINT[2] program and by utilizing SADABS,[3] the absorption corrections were performed. The structures have been solved by SHELXL-2016/6,[4] and full-matrix least-squares refinements on F^2 for all non-hydrogen atoms were performed by SHELXL-2016/6,[4] with anisotropic displacement parameters. All the calculations and molecular graphics were done by SHELXL-

2016/6,[4] WinGX system Ver-1.80,[5] Diamond v3.2 and Mercury.[6] All the crystallographic data and structural refinement parameters for the product **3a** has been mentioned in Figure 4.

3. Standardization of the reaction condition:

In DMF solvent medium dimethylamino (-NMe_2) group of DMF is transferred to the benzoxazinone substrate resulting formation of dimethyl benzamide derivative through cleavage of the oxazinone ring (entry 4). In DMSO solvent medium disulphide undergoes oxidation to produce sulfoxide compound (entries 5, 8, 28). Persulfate oxidant was also found to oxidise disulphide to sulfoxide compound (entries 1, 2).

4. General experimental procedures for C-H activation reactions:

Representative experimental procedure for C-H thiolated product, 3a:

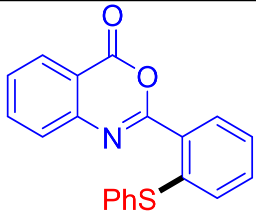
In an oven dried sealed tube (15 mL) was added 2-phenyl-4H-benzo [d] [1,3] oxazin-4-one (0.2 mmol, 45 mg), along with diphenyl disulfide (50 mg, 0.23 mmol), Ag_2CO_3 (66 mg, 0.24 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (4.6 mg, 5 mol%) XPhos (7.2 mg, 10 mol %), $AgSbF_6$ (10 mg, 20 mol%) in dry DCE solvent (2 mL) under inert atmosphere. The resulting mixture was heated at 110 ^oC for 24 h. After the reaction was completed (checked by TLC), the mixture was cooled at room temperature and was extracted with ethyl acetate (3 × 20 mL) followed by washing with brine (10 mL). The combined organic layer was dried with anhydrous Na_2SO_4 and filtered. After removal of the solvent, the residue (crude product was purified by column chromatography over silica gel (100-200 mesh) (hexane/ethyl acetate, 98:2) to afford the desired product **3a**.

Representative experimental procedure for C-H selenylated product, 4a:

In an oven dried schule tube (15 mL) was added 2-phenyl-4H-benzo [d] [1,3] oxazin-4-one (0.15 mmol, 34 mg), along with diphenyl diselenide (72 mg, 0.23 mmol), Ag_2 CO_3 (66 mg, 0.24 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol%) XPhos (10 mol %), $AgSbF_6$ (20 mol %) in dry DCE solvent (3 mL) under inert atmosphere. The resulting mixture was heated at 110 ^oC for 48 h. After the reaction was completed (checked by TLC), the mixture was cooled at room temperature and was extracted with ethyl acetate (3 × 20 mL) followed by washing with brine (10 mL). The combined organic layer was dried with anhydrous Na_2SO_4 and filtered. After removal of the solvent, the residue (crude product) was purified by column chromatography over silica gel (100-200 mesh) (hexane/ethyl acetate, 99:1) to afford the desired product **4a**.

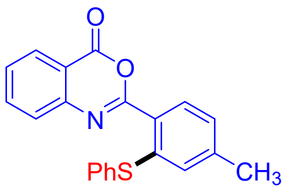
Similar procedure was followed to prepare **5a**-**5c** compounds by C-H thiolation of 2-arylpyridine compounds.

5. Characterization data of all synthesized products:



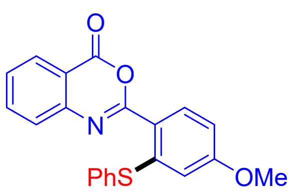
3a,

2-(2-(phenylthio)phenyl)-4H-benzo[d][1,3]oxazin-4-one (3a, Table 2): White solid; Yield: 78% (51 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (1H, dd, *J*=7.8 Hz), 8.13-8.10 (1H, m), 7.88-7.78 (2H, m), 7.58-7.52 (3H, m), 7.42-7.40 (3H, m), 7.30-7.28 (1H, m), 7.25-7.21 (1H, m), 6.99-6.96 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.48, 156.09, 146.36, 142.03, 136.61, 135.15, 133.52, 131.73, 130.13, 129.73, 128.97, 128.71, 128.60, 127.70, 127.26, 124.93, 116.86, 100.01. HRMS (ESI) m/z calcd for $C_{20}H_{14}NO_2S$ $[M + H]^+$, 332.07, found 332.00.



3b

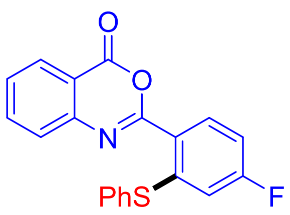
2-(4-methyl-2-(phenylthio)phenyl)-4H-benzo[d][1,3]oxazin-4-one (3b, Table 2): White solid; Yield: 70% (47 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (1H, dd, *J*=7.2 Hz), 8.01 (1H, dd, *J*=7.5 Hz), 7.85-7.80 (2H, m), 7.78-7.76 (3H, m), 7.57-7.39 (3H, m), 7.06-7.04 (1H, m), 6,79-6.78 (1H, m), 2.21 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.51, 156.12, 146.40, 142.76, 139.32, 139.57, 135.41, 131.66, 130.56, 130.08, 129.68, 128.57, 128.55, 128.27, 127.35, 127.26, 124.64, 116.87, 21.31. HRMS (ESI) m/z calcd for $C_{20}H_{15}NO_2SNa$ $[M + Na]^+$, 368.08, found 368.15.



3c

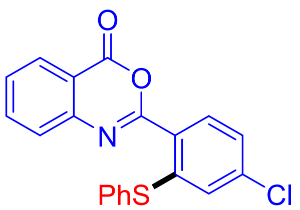
2-(4-methoxy-2-(phenylthio)phenyl)-4H-benzo[d][1,3]oxazin-4-one (3c, Table 2): White solid; Yield: 72% (52 mg); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.25-8.23 (1H, dd, *J*=7.8 Hz), 8.13 (1H, dd, *J*=7.4 Hz)

7.84-7.80 (2H, m), 7.78-7.76 (2H, m), 7.62-7.43 (4H, m), 6.75-6.72 (1H, m), 6.40-6.39 (1H, m), 3.64 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.18, 159.67, 155.87, 146.72, 144.90, 136.50, 135.67, 133.13, 131.96, 129.80, 129.29, 128.53, 128.04, 126.98, 119.69, 116.62, 113.74, 110.43, 55.18. HRMS (ESI) m/z calcd for $C_{21}H_{16}NO_3S$ [M + H] $^+$, 362.07, found 362.05.



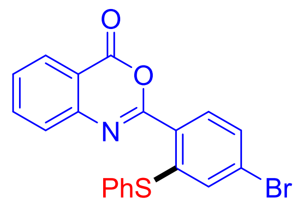
3d

2-(4-fluoro-2-(phenylthio)phenyl)-4H-benzo[d][1,3]oxazin-4-one (3d, Table 2): White solid; Yield**:** 68% (48 mg); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.28-8.25 (1H, m), 8.17 (1H, dd, *J*=7.7 Hz), 7.86-7.81 (2H, m), 7.79-7.60 (3H, m), 7.59-7.46 (3H,m), 6.94-6.87 (1H, m), 6.56 (1H, dd, J=7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.30, 162.92, 159.35, 155.15, 146.29, 146.27 (d, J_{C-F}=28 Hz), 136.72, 135.77, 132.39, 132.26, 130.11, 129.78, 128.66, 128.63, 127.16, 116.74, 114.85 (d, J_{C-F}=255 Hz), 112.12 (d, J_{C-F}=3 Hz). ^{19}F NMR (282 MHZ, $CDCl_3$) -106.06. HRMS (ESI) m/z calcd for $C_{20}H_{13}FNO_2S$ [M + H] $^+$, 350.05, found 350.04.



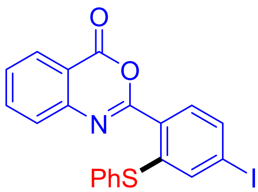
3e

2-(4-chloro-2-(phenylthio)phenyl)-4H-benzo[d][1,3]oxazin-4-one (3e, Table 2): White solid; Yield**:** 61% (45 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26-8.25 (1H, m), 8.08 (1H, d, *J*= 7.5 Hz), 7.86-7.82 (2H, m), 7.60-7.57 (3H, m), 7.47-7.46 (3H, m), 7.21-7.19 (1H, m), 6.86-6.86 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.22, 155.21, 146.21, 144.73, 138.41, 136.69, 135.49, 132.34, 131.19, 130.06, 129.65, 128.76, 128.66, 127.73, 127.25, 125.40, 125.01, 116.83. HRMS (ESI) m/z calcd for $C_{20}H_{13}ClNO_2S$ [M + H] $^+$, 366.02, found 366.04.



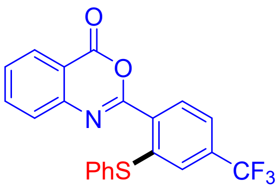
3f

2-(4-bromo-2-(phenylthio)phenyl)-4H-benzo[d][1,3]oxazin-4-one (3f, Table 2): White solid; Yield**:** 67% (56 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (1H, dd, *J*=7.9 Hz), 7.88 (1H, dd, *J*=7.3 Hz), 7.85-7.78 (2H, m), 7.59-7.56 (3H, m), 7.54-7.45 (3H, m), 7.37-7.34 (1H, m), 7.02-7.01 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.20, 155.32, 146.20, 144.74, 136.69, 135.39, 132.40, 131.25, 130.69, 130.05, 129.62, 128.78, 128.67, 127.96, 127.26, 127.00, 125.92, 116.84. HRMS (ESI) m/z calcd for $C_{20}H_{13}BrNO_2S$ [M + H] $^+$, 409.97, found 409.25.



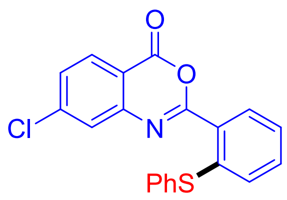
3g

2-(4-iodo-2-(phenylthio)phenyl)-4H-benzo[d][1,3]oxazin-4-one (3g, Table 2): White solid; Yield**:** 64% (58 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (1H, dd, *J*=7.2 Hz), 7.87-7.78 (3H, m), 7.58-7.54 (4H, m), 7.47-7.45 (3H, m), 7.23 (1H, d, *J*=7.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.19, 155.51, 146.19, 144.35, 136.83, 136.67, 135.20, 133.94, 132.56, 131.07, 130.00, 129.52, 128.78, 128.66, 127.28, 126.68, 116.87, 99.49. HRMS (ESI) m/z calcd for $C_{20}H_{13}INO_2S$ [M + H] $^+$, 457.96, found 457.92.



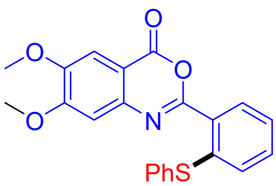
3h

2-(2-(phenylthio)-4-(trifluoromethyl)phenyl)-4H-benzo[d][1,3]oxazin-4-one (3h, Table 2): White solid; Yield**:** 63% (50 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (1H, dd, *J*=7.3 Hz), 8.23 (1H, d, *J*=7.8 Hz), 7.90-7.81 (2H, m), 7.62-7.56 (3H, m), 7.47-7.44 (4H, m), 7.17-7.16 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.99, 154.89, 145.98, 143.98, 136.78, 135.28, 133.39, 133.07, 132.16, 130.50, 130.09, 129.73, 129.15, 128.73, 127.44, 124.99 (q, $J_{C\text{-}F}$=274 Hz), 124.62, 121.24 (q, $J_{C\text{-}F}$=18 Hz), 116.97. ^{19}F NMR (376 MHZ, $CDCl_3$) -63.53. HRMS (ESI) m/z calcd for $C_{21}H_{13}F_3NO_2S$ [M + H] $^+$, 400.05, found 400.07.



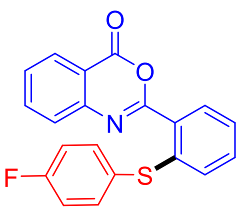
3i

7-chloro-2-(2-(phenylthio)phenyl)-4H-benzo[d][1,3]oxazin-4-one (3i, Table 2): White solid; Yield**:** 68% (50 mg); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.19-8.17 (1H, m), 8.12-8.10 (1H, m), 7.80-7.79 (1H, m), 7.57-7.48 (3H, m), 7.43-7.41 (3H, m), 7.30-7.28 (1H, m), 7.25-7.21 (1H, m), 6.98-6.96 (1H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.67, 157.19, 147.41, 143.04, 142.58, 135.19, 133.33, 132.06, 131.65, 130.25, 129.87, 129.78, 129.10, 129.07, 128.70, 127.03, 124.90, 115.21. HRMS (ESI) m/z calcd for $C_{20}H_{13}ClNO_2S$ $[M + H]^+$, 366.02, found 366.04.



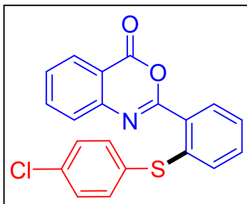
3j

6,7-dimethoxy-2-(2-(phenylthio)phenyl)-4H-benzo[d][1,3]oxazin-4-one (3j, Table 2): White solid; Yield**:** 65% (51 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10-8.08 (1H, m), 7.59-7.56 (3H, m), 7.41-7.40 (3H, m), 7.24-7.22 (2H, m), 7.20-7.18 (1H, m), 6.98-6.96 (1H, m) 4.04 (3H, s), 4.01 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.42, 156.54, 155.53, 150.01, 142.71, 141.54, 135.15, 133.56, 131.44, 129.94, 129.71, 128.94, 128.61, 127.89, 124.91, 109.47, 108.16, 107.63, 56.59, 56.47. HRMS (ESI) m/z calcd for $C_{22}H_{18}NO_4S$ $[M + H]^+$, 392.08, found 392.05.



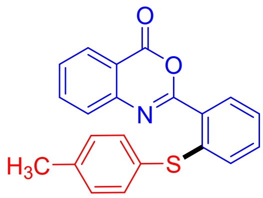
3k

2-(2-((4-fluorophenyl)thio)phenyl)-4H-benzo[d][1,3]oxazin-4-one (3k, Table 2): White solid; Yield**:** 62% (45 mg); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.25 (1H, dd, *J*=7.6 Hz), 8.14-8.11 (1H, m), 7.88-7.79 (2H, m), 7.57-7.54 (3H, m), 7.31-7.27 (1H, m), 7.25-7.22(1H, m), 7.15-7.10 (2H, m), 6.92-6.89 (1H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.62, 162.13, 159.38, 156.00, 146.31, 142.13, 137.42 (d, J_{C-F}=272 Hz), 136.61, 131.79, 130.17, 128.73(d, J_{C-F}=6 Hz), 128.63 (d, J_{C-F}=55 Hz), 128.22, 127.52, 127.21, 124.94, 117.08, 116.87. ^{19}F NMR (282 MHZ, $CDCl_3$) -111.48. HRMS (ESI) m/z calcd for $C_{20}H_{13}FNO_2S$ $[M + H]^+$, 350.05, found 350.11.



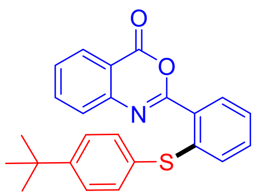
3l

2-(2-((4-chlorophenyl)thio)phenyl)-4H-benzo[d][1,3]oxazin-4-one (3l, Table 2): White solid; Yield**:** 66% (48 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28-8.25 (1H, m), 8.13-8.10 (1H, m), 7.88-7.77 (2H, m), 7.58-7.50 (3H, m), 7.48-7.37 (2H, m), 7.31-7.27 (1H, m), 7.26-7.25 (1H, m), 6.97-6.94 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.42, 155.94, 146.24, 141.36, 136.68, 136.33, 135.30, 132.21, 131.87, 130.20, 129.98, 128.72, 128.70, 128.64, 127.84, 127.22, 125.23, 116.82. HRMS (ESI) m/z calcd for $C_{20}H_{13}ClNO_2S$ $[M + H]^+$, 366.02, found 366.02.



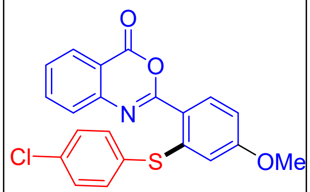
3m

2-(2-(p-tolylthio)phenyl)-4H-benzo[d][1,3]oxazin-4-one (3m, Table 2): White solid; Yield**:** 65% (45 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (1H, dd, *J*=7.5 Hz), 8.10 (1H, dd, *J*=7.8 Hz), 7.87-7.83 (2H, m), 7.81-7.79 (1H, m), 7.57-7.53 (2H, m), 7.47-7.19 (4H, m), 6.94 (1H, dd, *J*=7.4 Hz), 2.39 (3H,s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.51, 156.12, 146.40, 142.76, 139.32, 136.57, 135.41, 131.66, 130.56, 130.08, 129.68, 128.57, 128.55, 128.27, 127.35, 127.26, 124.64, 116.87, 21.31. HRMS (ESI) m/z calcd for $C_{21}H_{14}NO_2S$ $[M + H]^+$, 346.08, found 346.10.



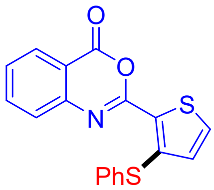
3n

2-(2-((4-(tert-butyl)phenyl)thio)phenyl)-4H-benzo[d][1,3]oxazin-4-one (3n, Table 2): White solid; Yield**:** 67% (52 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (1H, dd, *J*=7.6 Hz), 8.09 (1H, dd, *J*=7.1 Hz), 7.86-7.77 (2H, m), 7.56-7.40 (5H, m), 7.31-7.27 (1H, m), 7.24-7.01 (1H, m), 6.99-6.99 (1H, m), 1.22 (9H, S). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.70, 159.52, 156.19, 152.39, 146.40, 142.49, 136.58, 134.95, 131.68, 130.93, 130.14, 128.86, 128.56, 128.50, 127.25, 126.79, 124.73, 116.84, 34.77, 31.25, 27.74, 19.17. HRMS (ESI) m/z calcd for $C_{24}H_{22}NO_2S$ [M + H] $^+$, 388.12, found 388.15.



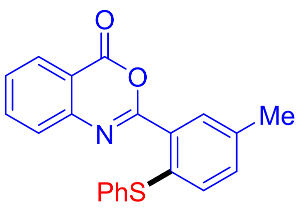
3o

2-(2-((4-chlorophenyl)thio)-4-methoxyphenyl)-4H-benzo[d][1,3]oxazin-4-one (3o, Table 2): White solid; Yield**:** 60% (48 mg); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.24 (1H, dd, *J*=7.3 Hz), 8.14 (1H, d, *J*=7.6 Hz), 7.83-7.81 (1H, m), 7.77-7.76 (1H, m), 7.54-7.51 (3H, m), 7.42-7.40 (2H, m), 6.77-6.74 (1H, m), 6.39-6.38 (1H, m), 3.69 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.24, 159.62, 155.74, 146.62, 144.07, 136.79, 136.57, 135.63, 132.08, 131.80, 130.06, 128.58, 128.15, 126.94, 119.87, 116.60, 114.10, 110.31, 55.33. HRMS (ESI) m/z calcd for $C_{21}H_{15}ClNO_3S$ [M + H] $^+$, 396.03, found 396.13.



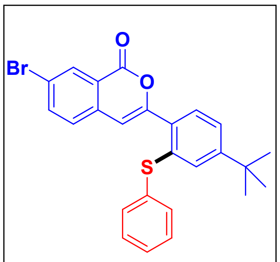
3p

2-(3-(phenylthio)thiophen-2-yl)-4H-benzo[d][1,3]oxazin-4-one (3p, Table 2): White solid; Yield**:** 54% (36 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (1H, dd, *J* = 7.9 Hz,) , 7.84-7.80 (1H, m), 7.73-7.70 (1H, dd, *J* = 8.2 Hz), 7.68 – 7.61 (2H m), 7.53 – 7.41 (4H, m) 7.36 (1H, d, *J* = 5.3 Hz), 6.41 (d, *J* = 5.3 Hz, 1H) ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.95, 153.58, 147.11, 143.60, 136.63, 134.99, 132.82, 130.09, 129.70, 129.40, 128.89, 128.74, 127.79, 126.88, 121.92, 116.23. HRMS (ESI) m/z calcd for $C_{18}H_{12}NO_2S_2$ [M + H] $^+$, 338.02, found 338.02.



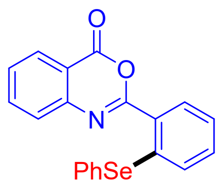
3q

2-(5-methyl-2-(phenylthio)phenyl)-4H-benzo[d][1,3]oxazin-4-one (3q, Table 2): White solid; Yield**:** 66% (44 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (1H, dd, *J*=7.3 Hz), 7.91 (1H, S), 7.86-7.76 (2H, m), 7.56-7.51 (3H, m), 7.39-7.33 (3H, m), 7.12-7.09 (1H, m), 6,92-6.90 (1H, m), 2.36 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.60, 156.29, 146.41, 138.09, 136.60, 135.15, 134.62, 134.19, 132.18, 130.55, 129.59, 129.37, 129.32, 128.61, 128.55, 128.01, 127.24, 116.79, 20.69. HRMS (ESI) m/z calcd for $C_{20}H_{15}NO_2S$ [M + H] $^+$, 346.08, found 346.09.



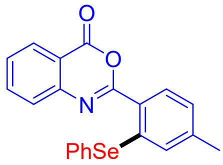
3r

7-bromo-3-(4-(tert-butyl)-2-(phenylthio)phenyl)-1H-isochromen-1-one (3r, Table 2): White solid; Yield: 58% (49 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 837 (1H, d, *J*=6.8 Hz), 8.05-8.03 (1H, m), 7.92-7.89 (1H, m), 7.67-7.65 (1H, m), 7.57-7.54 (2H, m), 7.42-7.41 (3H, m), 7.25-7.22 (1H, m), 6.98-6.97 (1H, d, *J*=6.7 Hz) 1.12 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.40, 156.41, 155.56, 145.43, 141.84, 139.66, 135.07, 133.71, 131.02, 129.99, 129.64, 128.95, 128.87, 126.22, 124.47, 122.28, 121.54, 118.13, 35.10, 30.83, 30.68, 22.71 HRMS (ESI) m/z calcd for $C_{25}H_{21}BrO_2S$ [M + H] $^+$ 466.04, found 466.03.



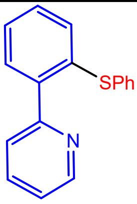
4a

2-(2-(phenylselanyl)phenyl)-4H-benzo[d][1,3]oxazin-4-one (4a, Table 2): White solid; Yield: 64% (37 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 8.29-8.24 (2H, m), 7.91 – 7.81 (2H, m), 7.77 – 7.70 (2H, m), 7.58-7.53 (1H, m), 7.47-7.42 (3H, m), 7.29-7.26 (1H, m), 7.25-7.19 (1H, m), 7.04 (1H, dd, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.33, 156.01, 146.12, 139.59, 137.27, 136.69, 131.97, 130.50, 130.03, 130.00, 129.82, 129.16, 128.73, 128.57, 127.65, 126.95, 125.22, 116.81. HRMS (ESI) m/z calcd for $C_{20}H_{14}NO_2Se$ [M + H] $^+$, 380.07, found 380.06.



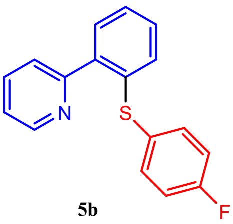
4b

2-(5-methyl-2-(phenylselanyl)phenyl)-4H-benzo[d][1,3]oxazin-4-one (4b): White solid; Yield**:** 58% (34 mg);^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (1H, dt, *J* = 7.8 Hz), 8.14 (1H, d, *J* = 8.1 Hz), 7.93 – 7.79 (2H, m), 7.77 – 7.62 (2H, m), 7.59 – 7.35 (4H, m), 7.21 – 7.01 (1H, m), 6.89 – 6.79 (1H, m), ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.30, 142.76, 139.41, 137.21, 136.93, 136.64, 130.45, 129.94, 129.75, 129.57, 129.09, 128.69, 128.32, 126.84, 126.32, 125.01, 116.72, 100.01, 21.46. HRMS (ESI) m/z calcd for $C_{21}H_{16}NO_2Se$ $[M + H]^+$, 394.02, found 394.06.



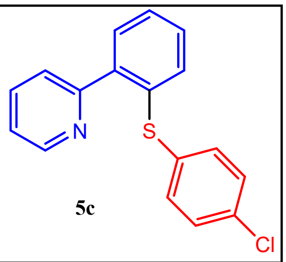
5a

2-(2-(phenylthio)phenyl)pyridine (5a)[7]: Colourless oil: 89% (70 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72-8.69 (1H, m), 7.78-7.73 (1H, m), 7.62-7.53 (2H, m), 7.35-7.22 (9H, m), ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.95, 148.68, 140.75, 136.37, 135.51, 135.41, 132.07, 131.51, 130.45, 129.22, 129.16, 127.32, 126.85, 125.51, 122.29.



5b

2-(2-((4-fluorophenyl)thio)phenyl)pyridine(5b)[8]: White solid: 78% (43.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (1H, d, *J*=4.6 Hz), 7.78-7.74 (1H, m), 7.58 (1H, d, *J*=7.6 Hz), 7.52-7.50 (1H. m), 7.34-7.23 (5H, m), 7.14-7.11 (1H, m), 7.00-6.96 (2H, m), ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.51, (d, J_{C-F}=246.2 Hz), 158.09, 148.88, 140.31, 136.27, 135.02 (d, J_{C-F}=2.2 Hz), 130.34, 130.31, 130.18, 130.14, 129.05, 129.49, 124.24, 122.27, 116.42 (d, J_{C-F}=18.6 Hz),. ^{19}F NMR (376 MHZ, $CDCl_3$) -113.63.

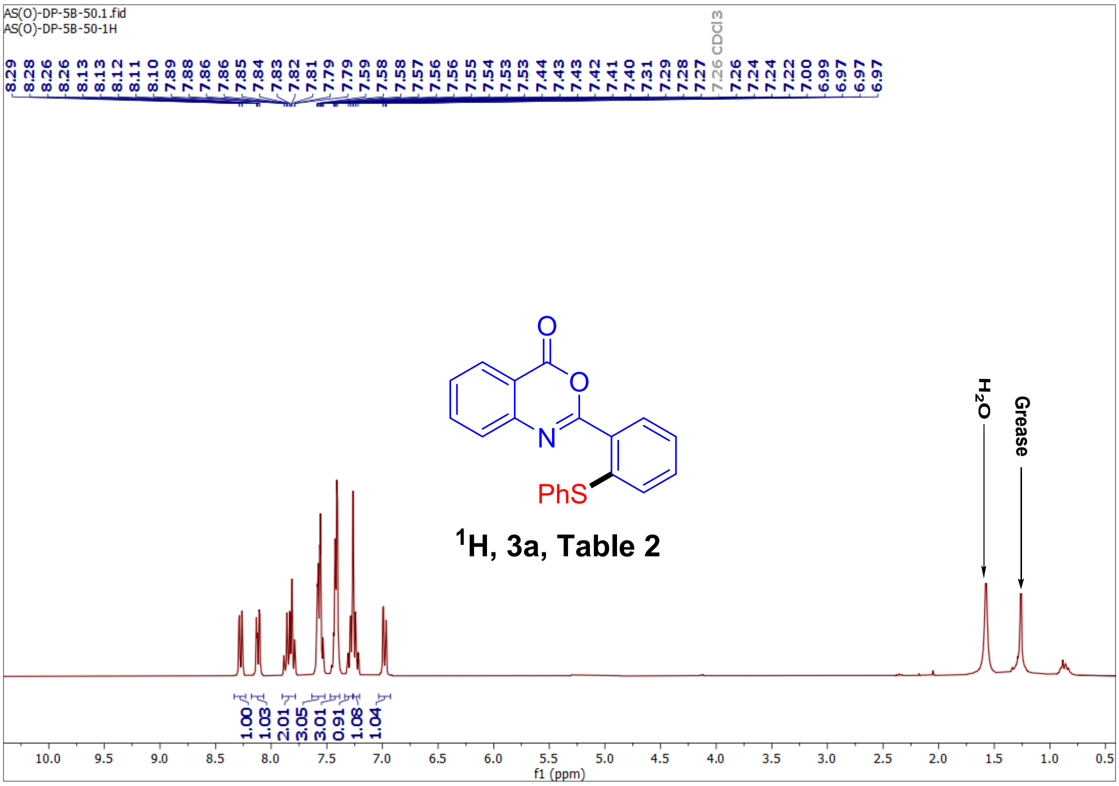


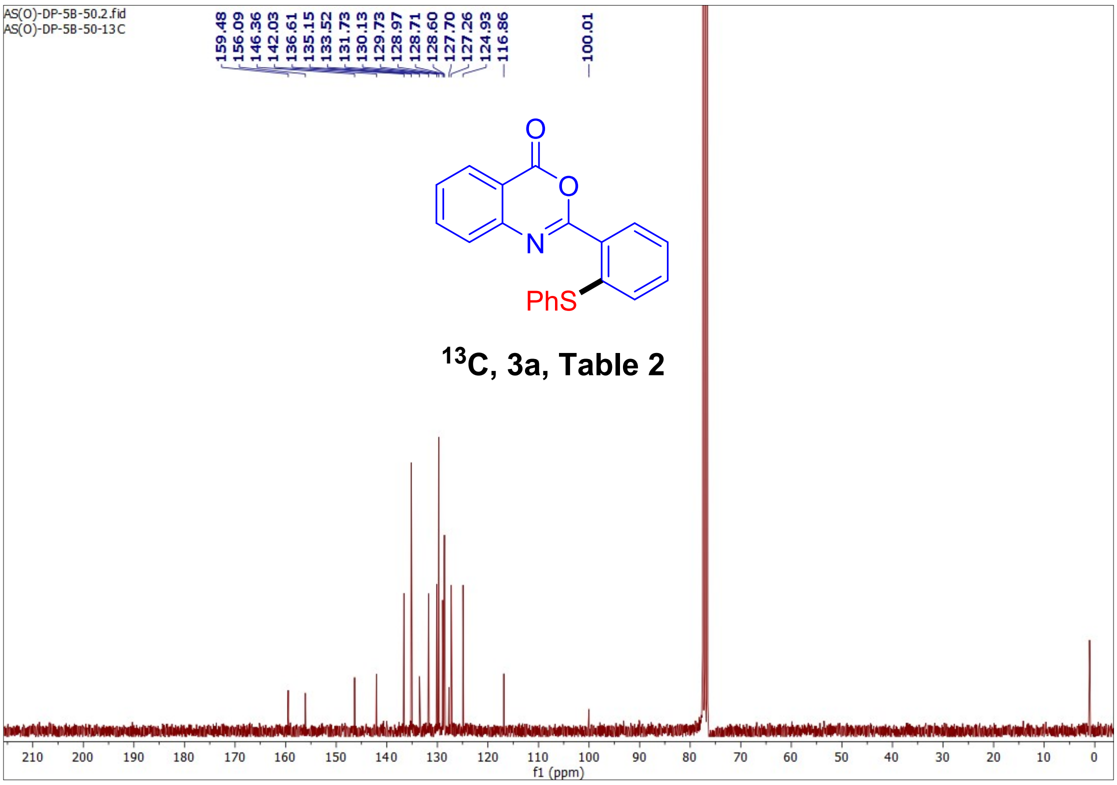
5c

2-(2-((4-chlorophenyl)thio)phenyl)pyridine(5c)[8]: Colourless oil: 68% (40 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (1H, d, J=4.8 Hz), 7.82—7.78 (1H, m), 7.61-7.56 (2H, m), 7.36-7.30 (2H, m), 7.27-7.25 (3H, m), 7.22-7.19 (3H, m), ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.88, 134.82, 134.22, 133.38, 133.06, 131.84, 130.69, 129.49, 129.44, 129.39, 129.32, 127.37, 127.33, 124.66, 122.56.

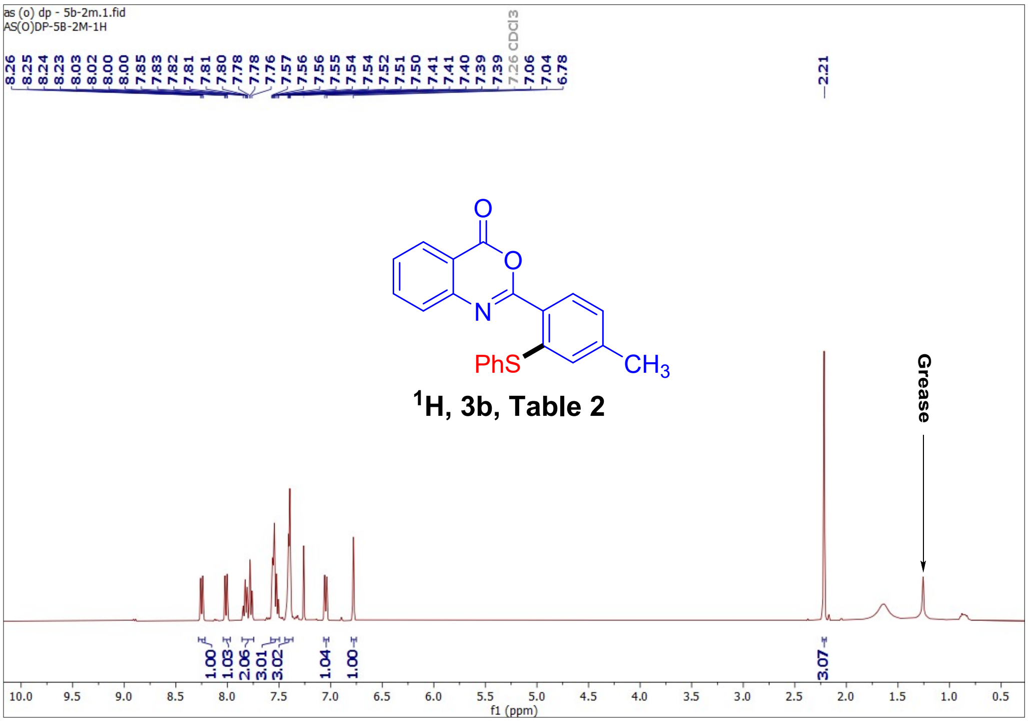
6. Characterization data of all synthesized products:

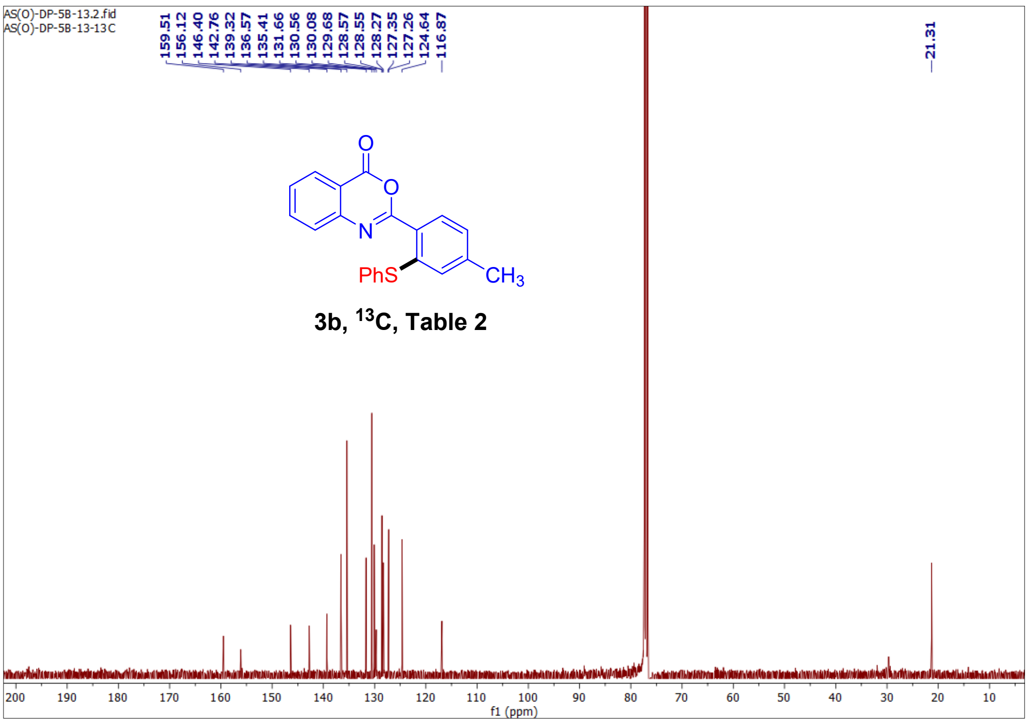
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3a



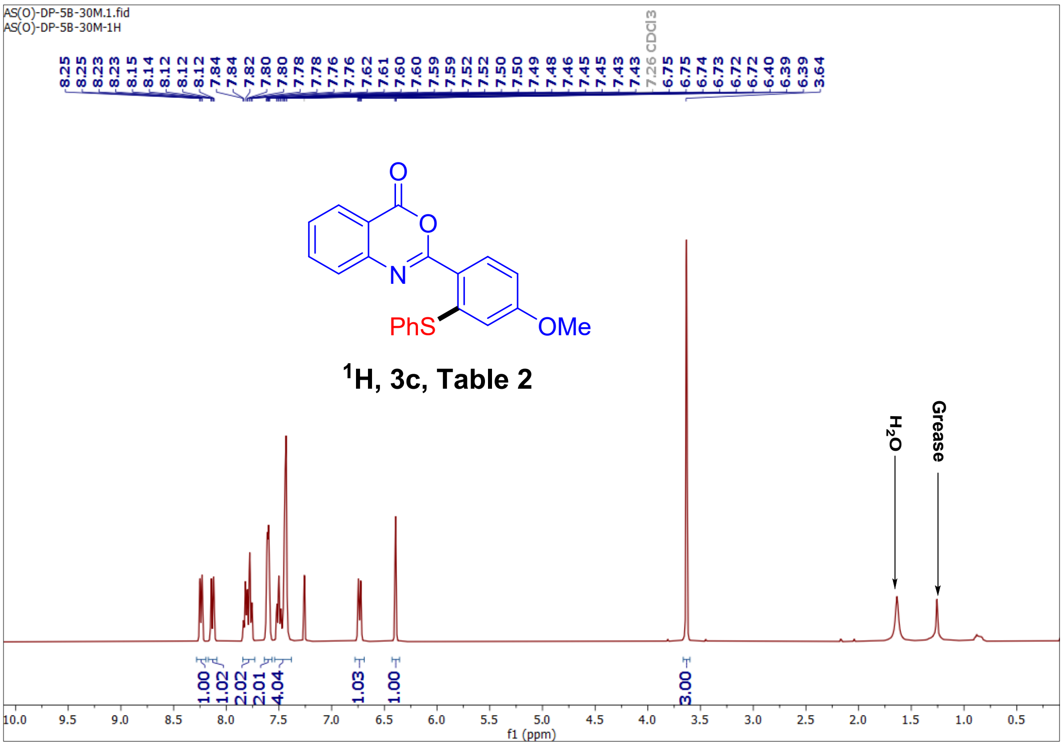


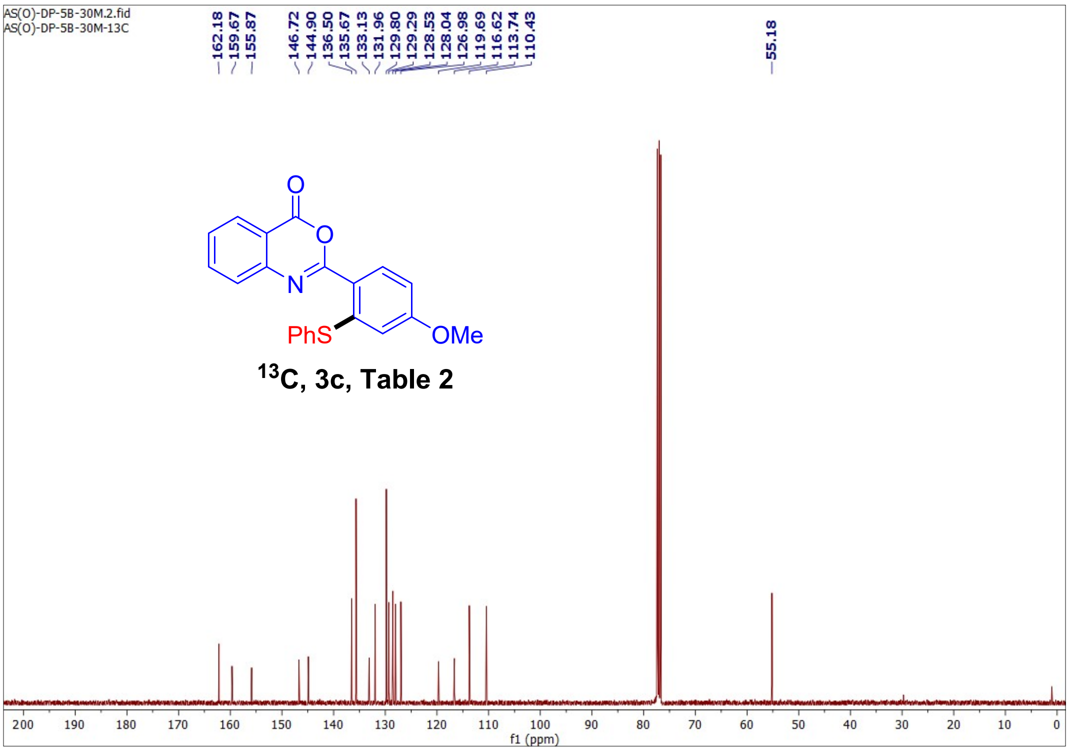
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3b



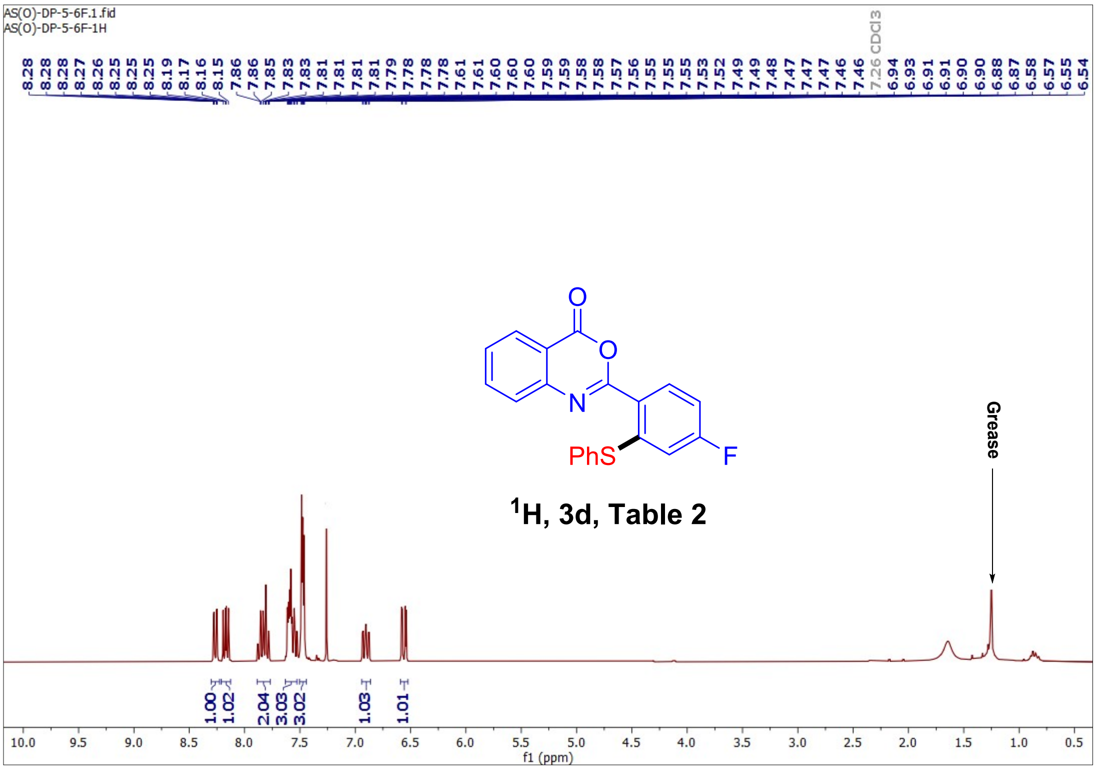


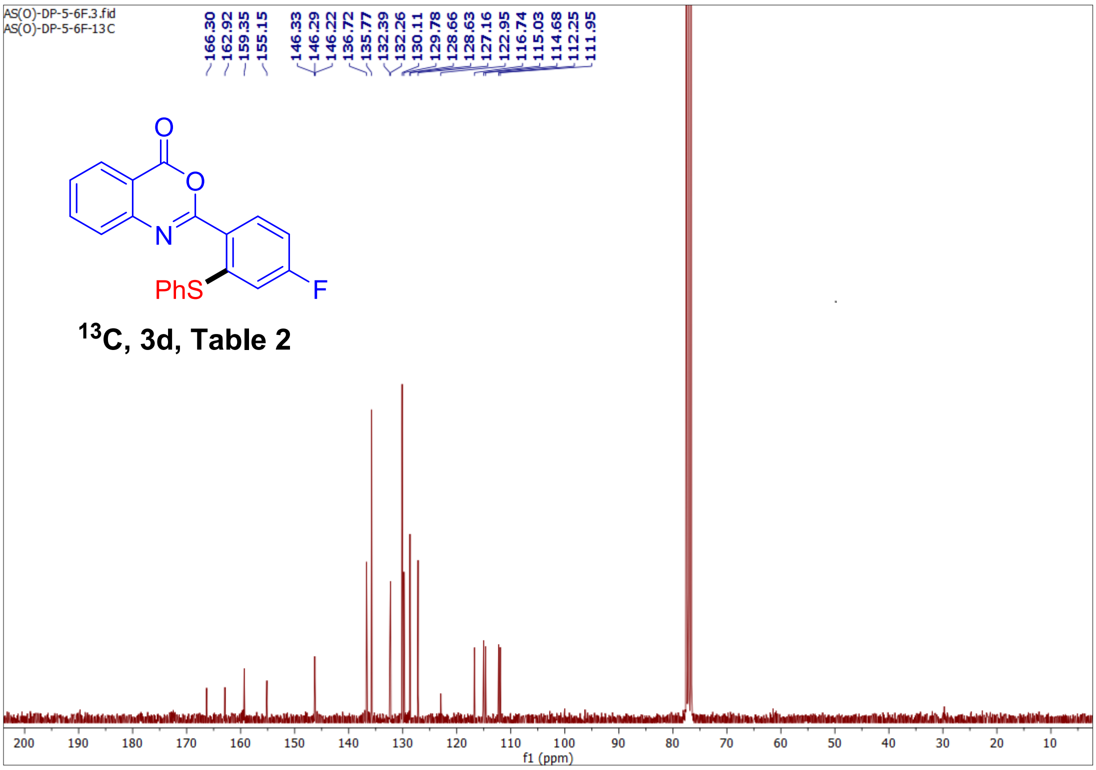
^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of 3c



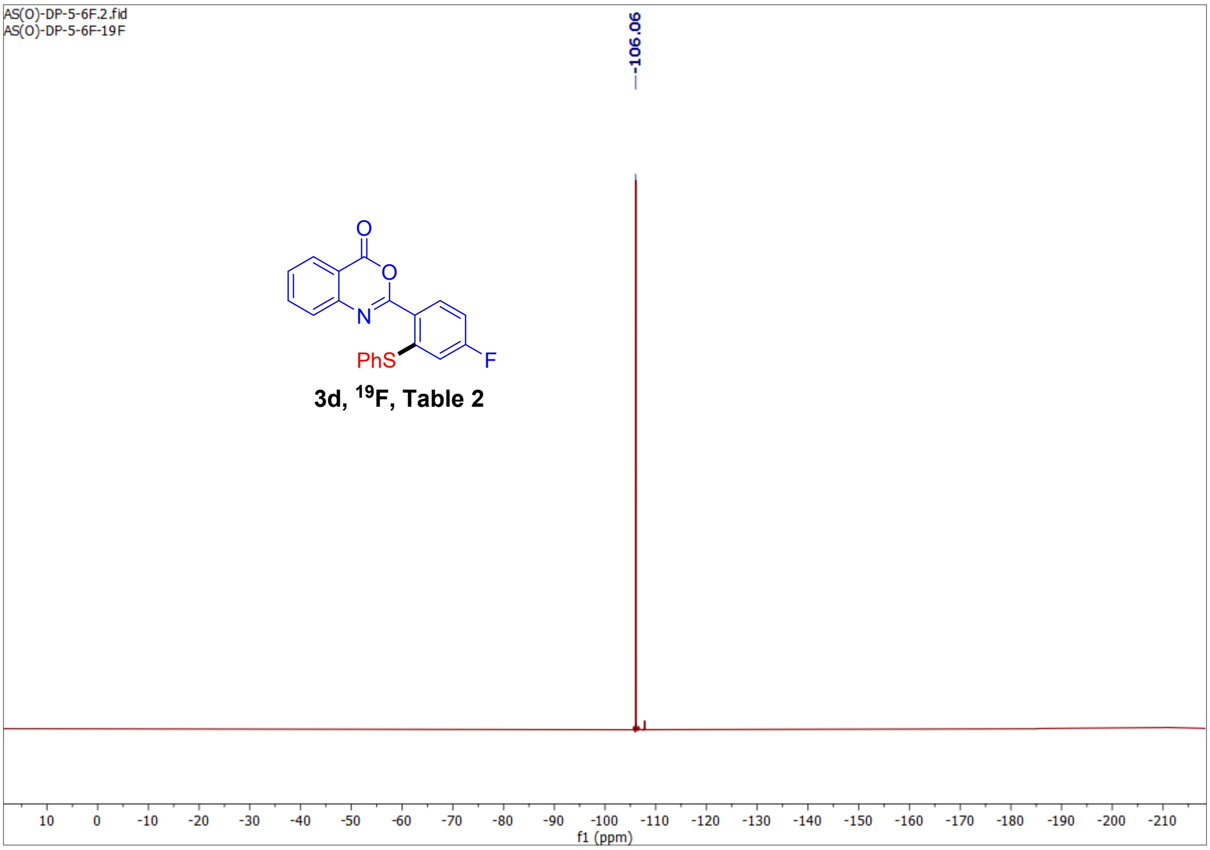


^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of 3d

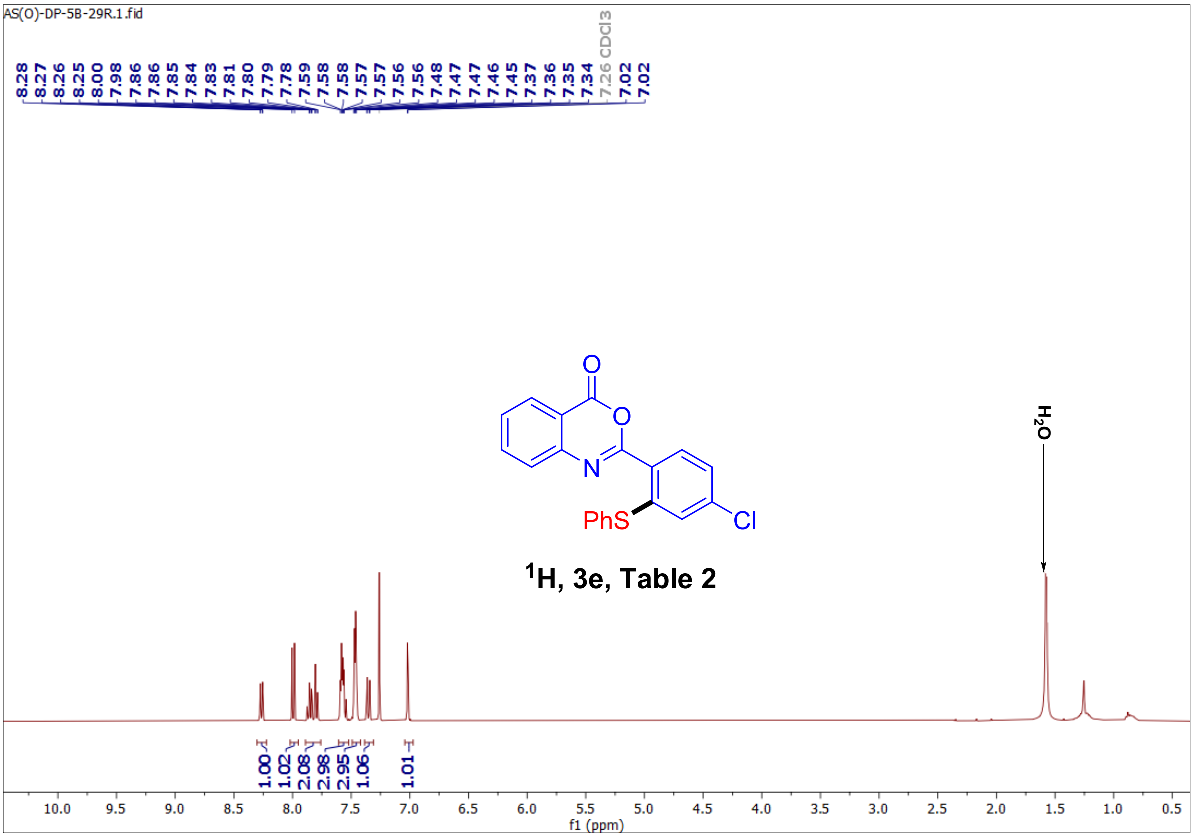


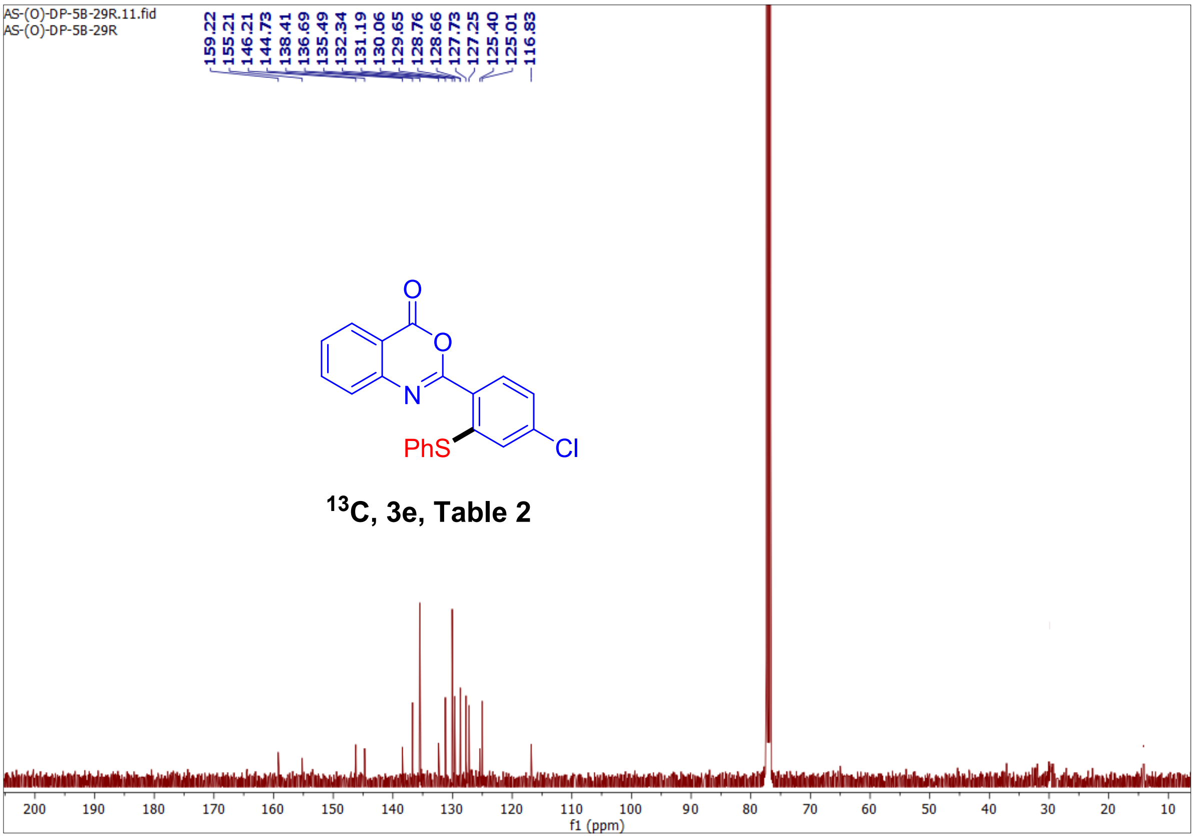


[19] F NMR (282 MHz, $CDCl_3$) spectrum of 3d

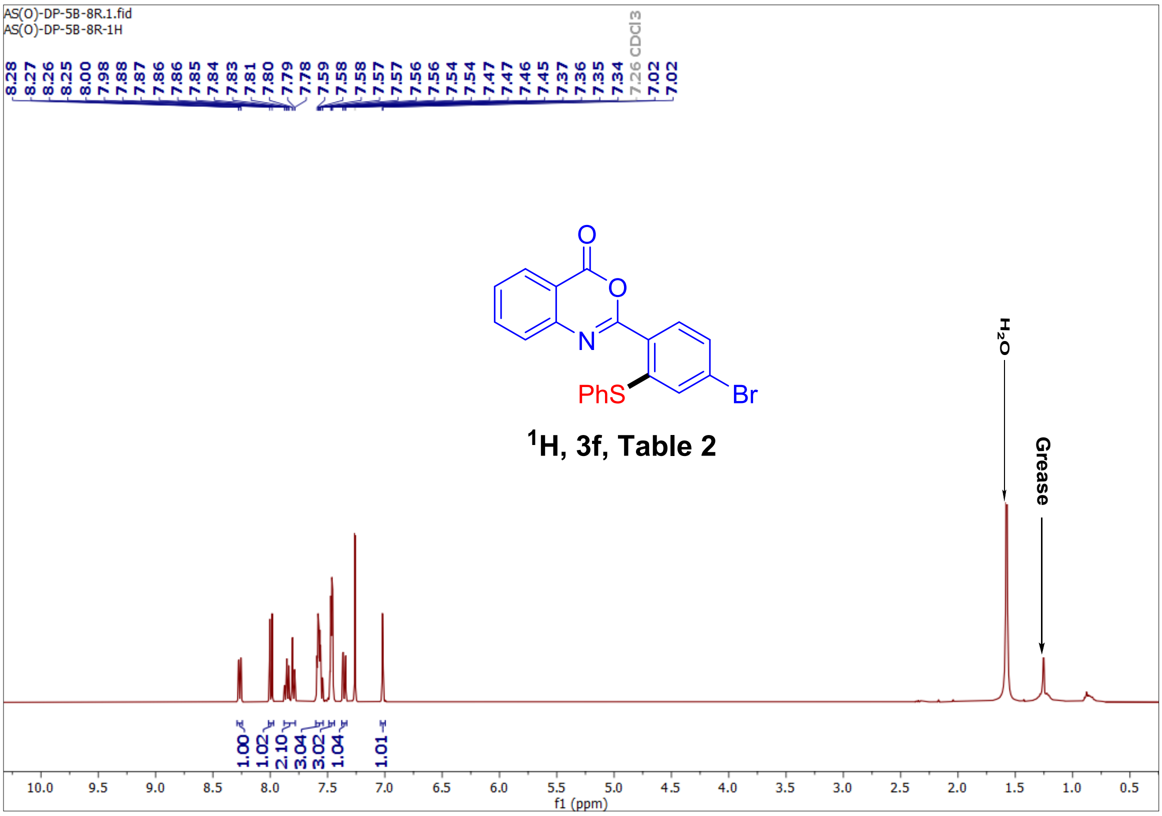


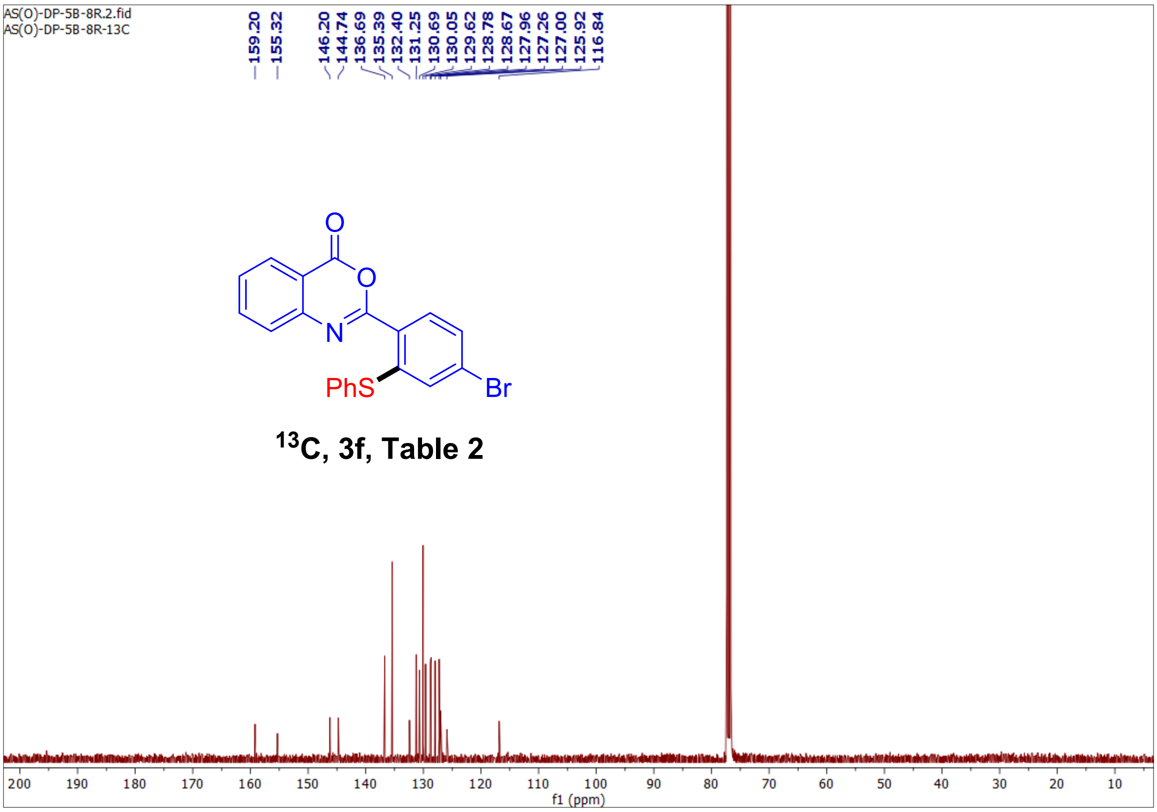
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3e



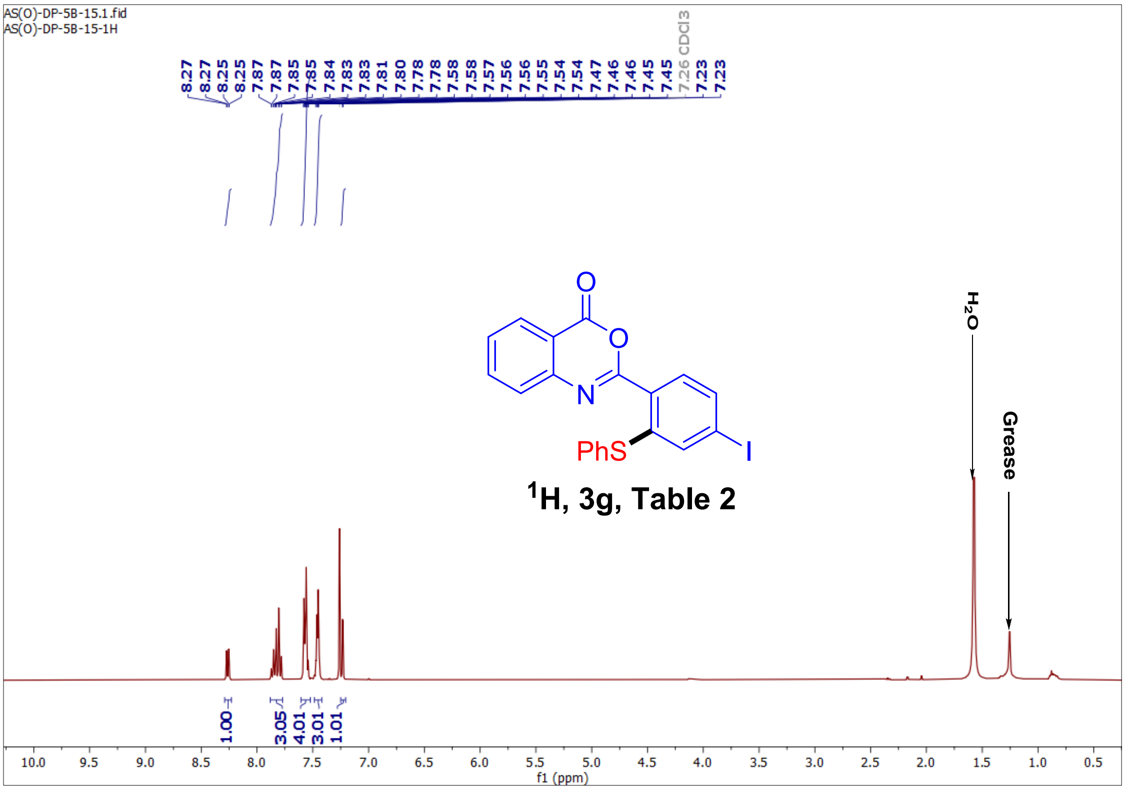


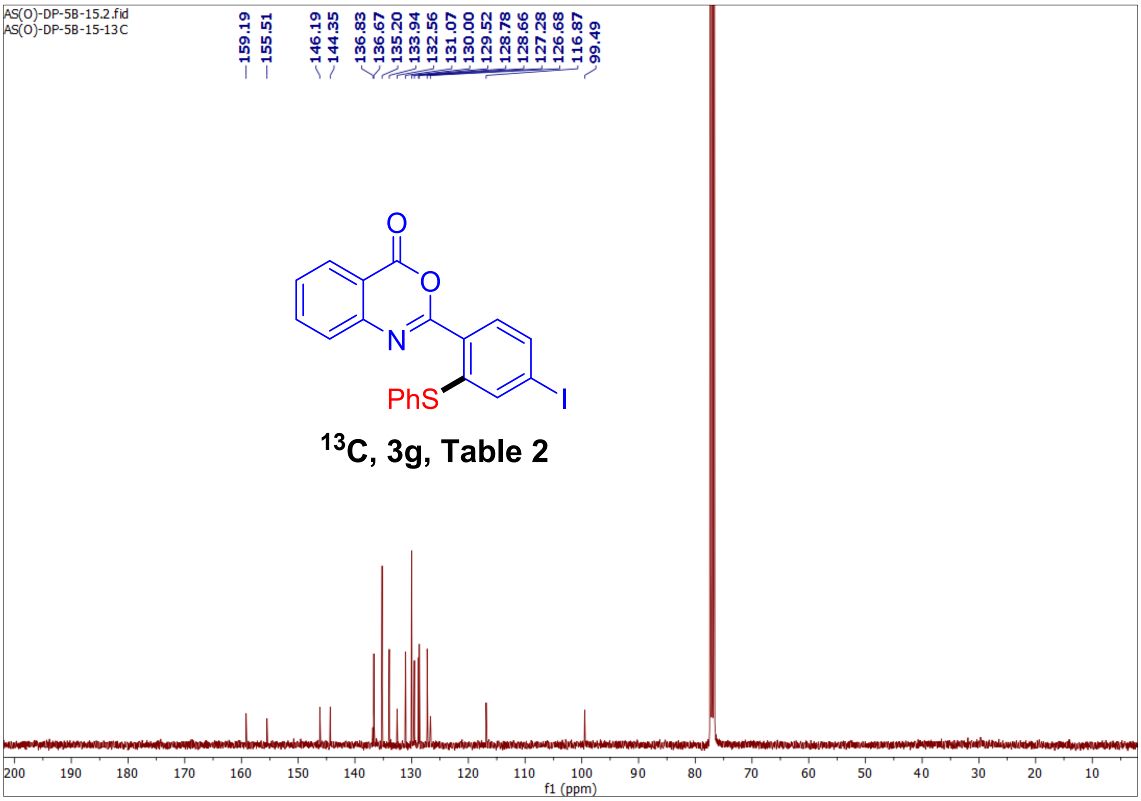
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3f



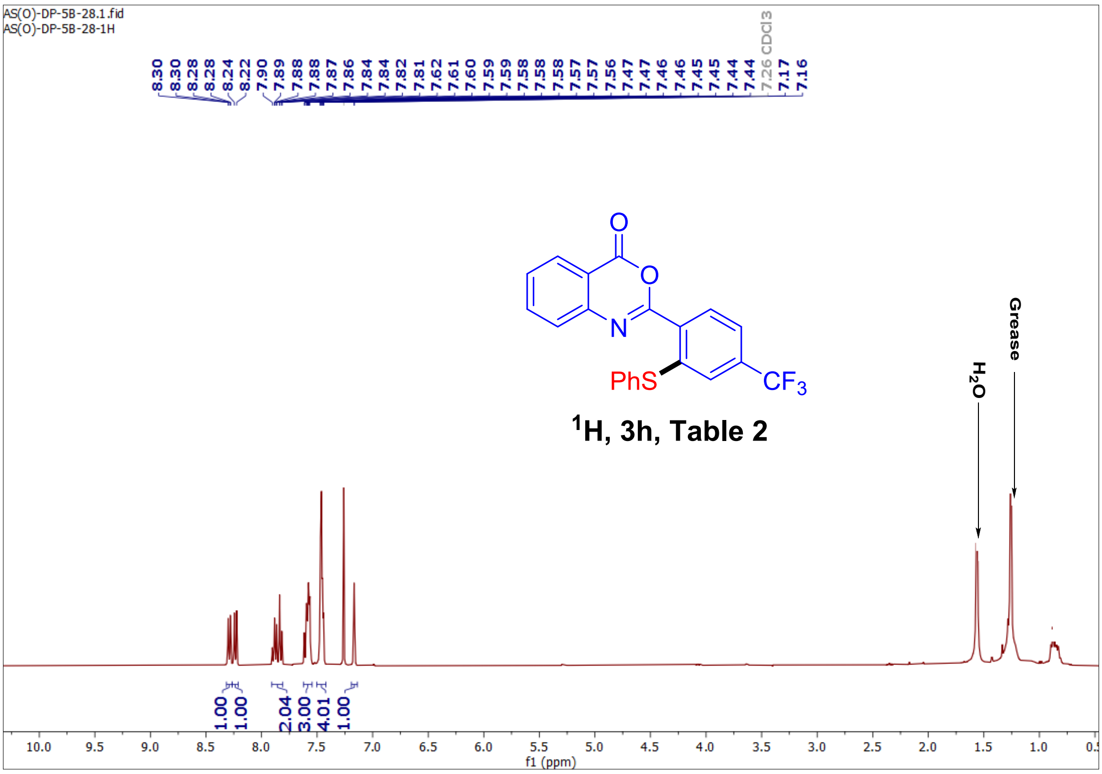


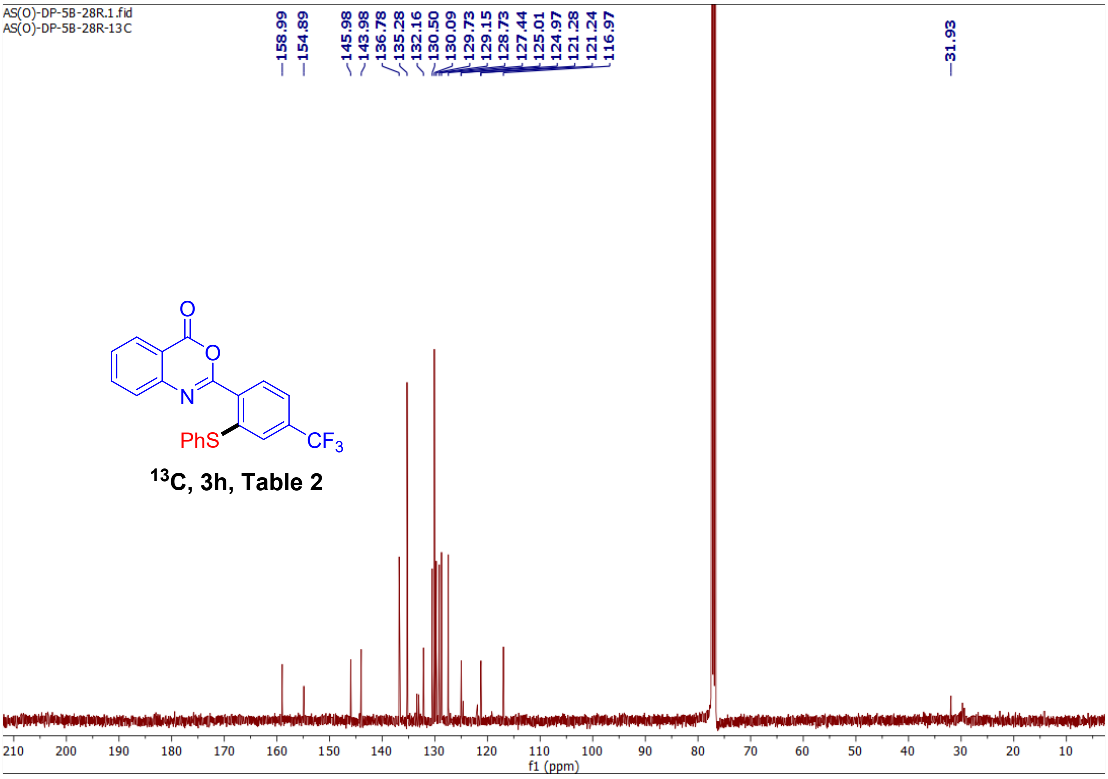
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3g



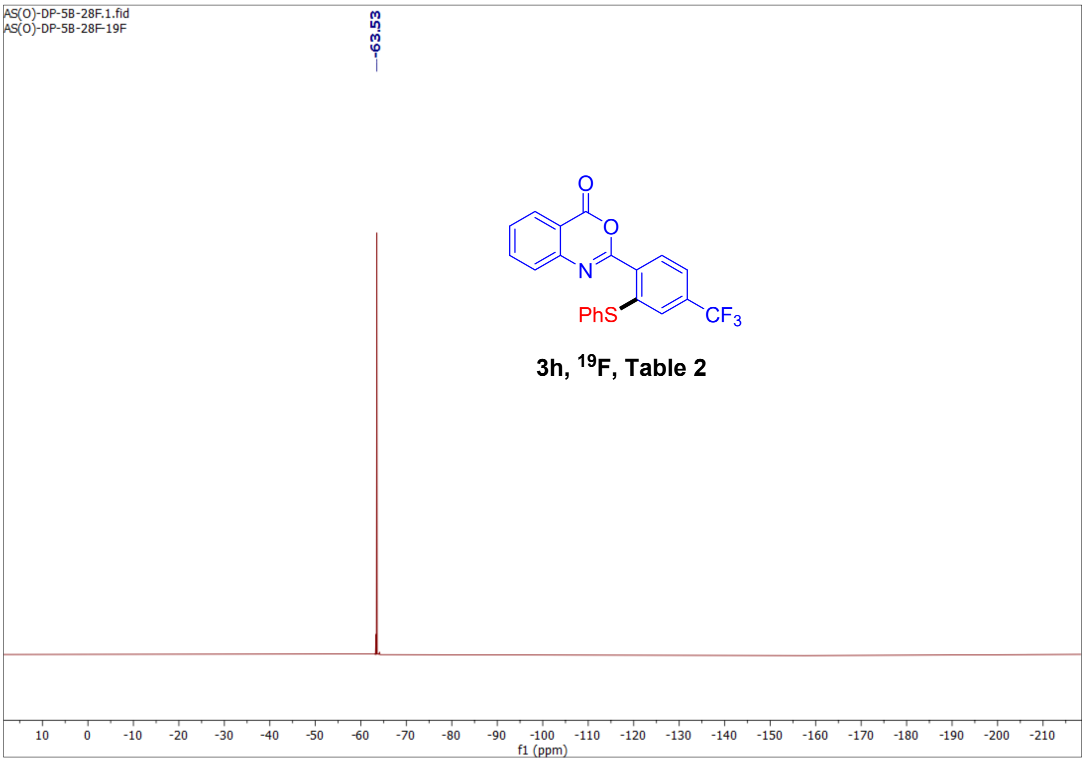


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3h

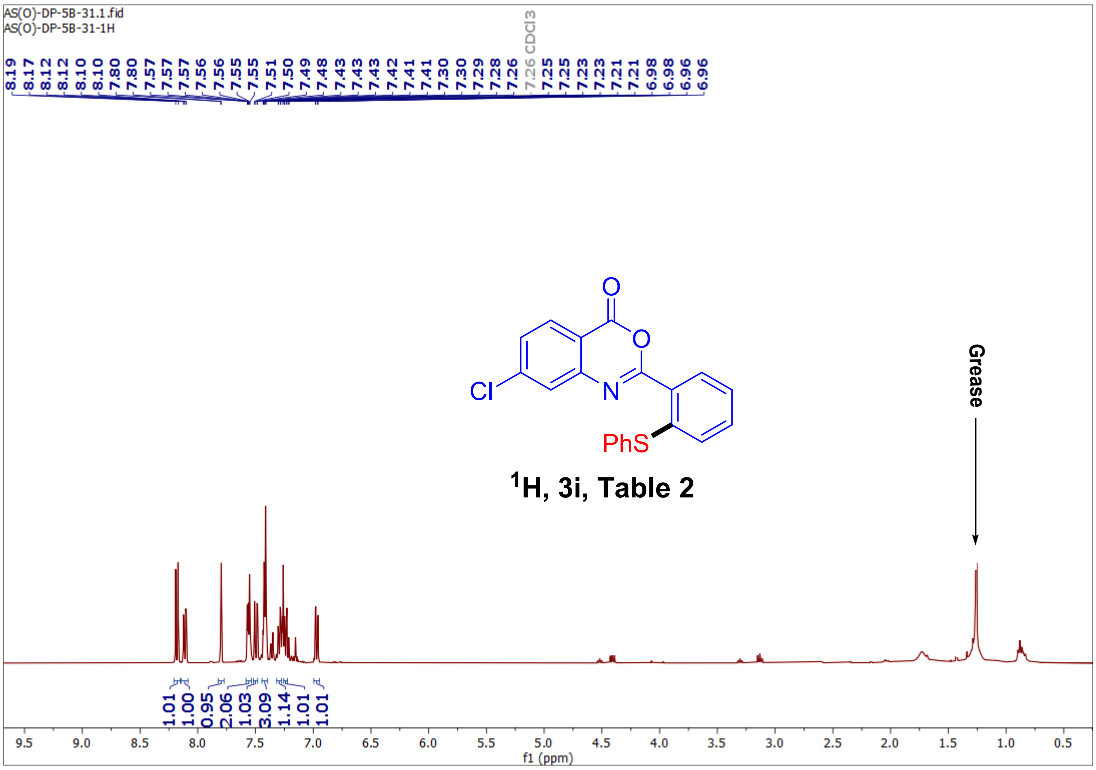


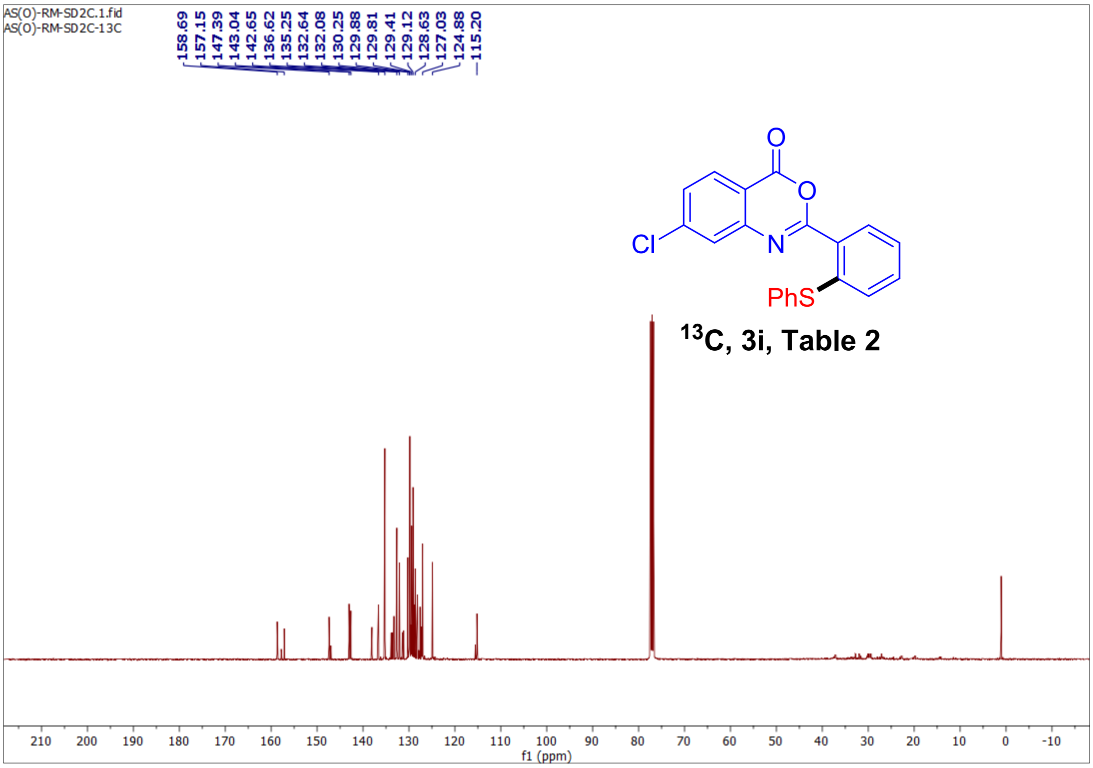


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3h

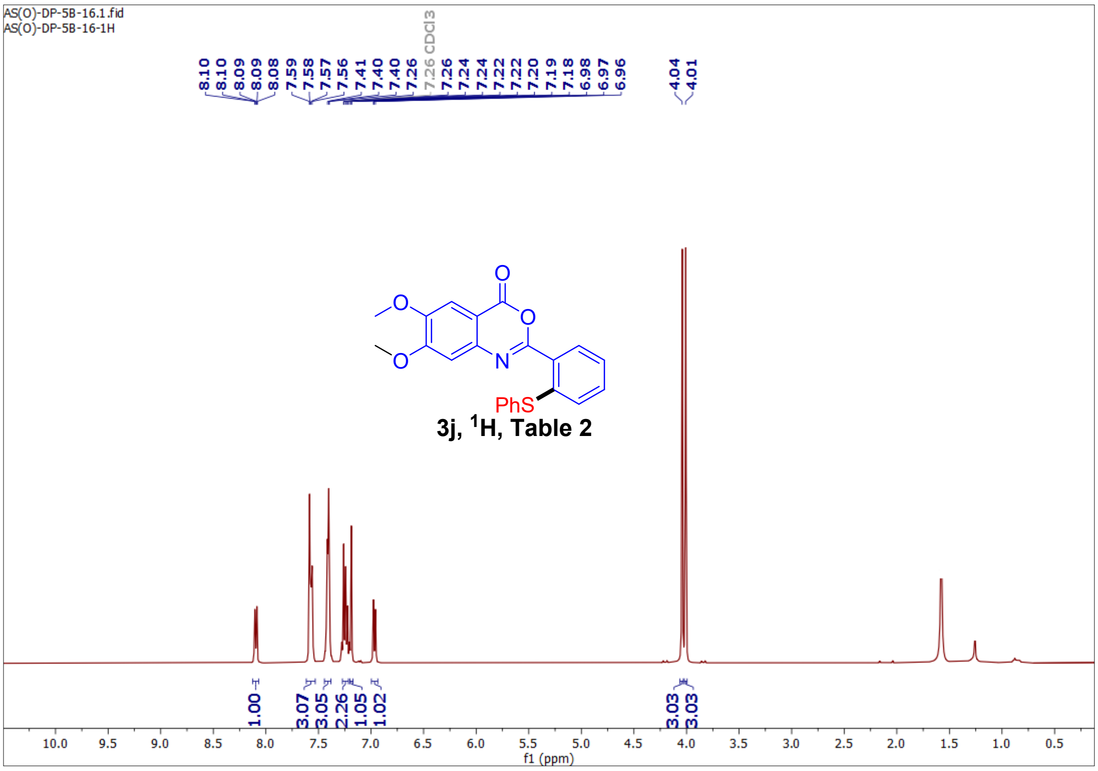


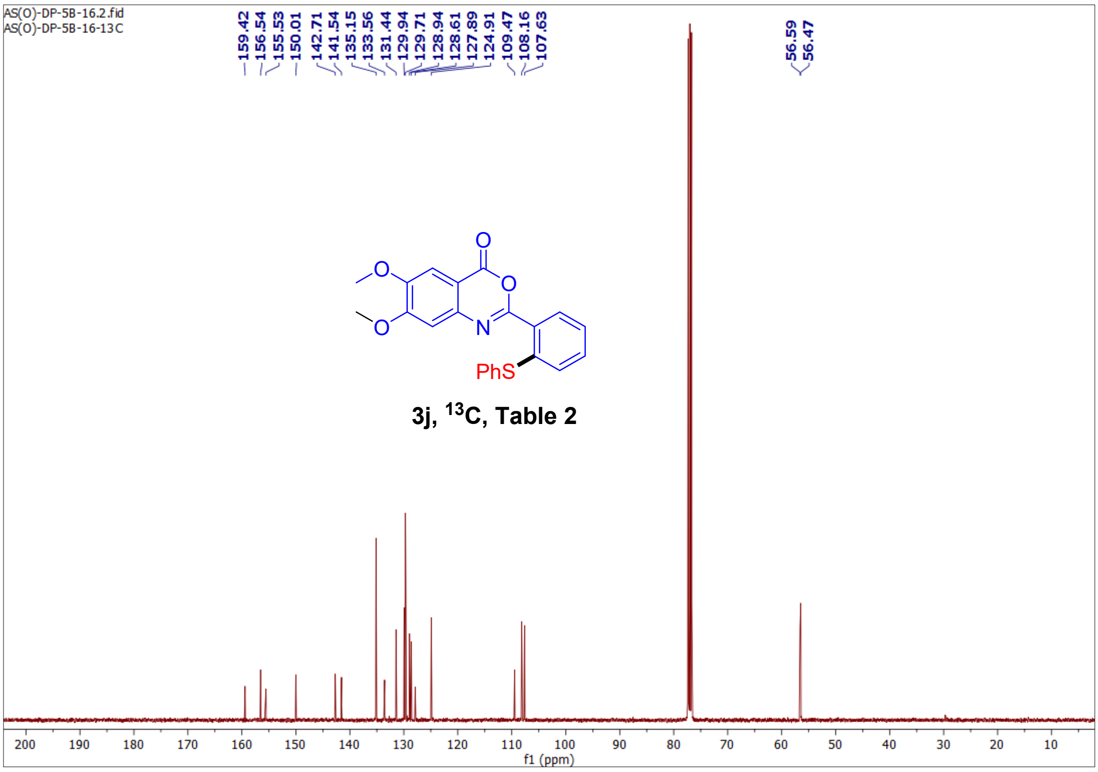
^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of 3i



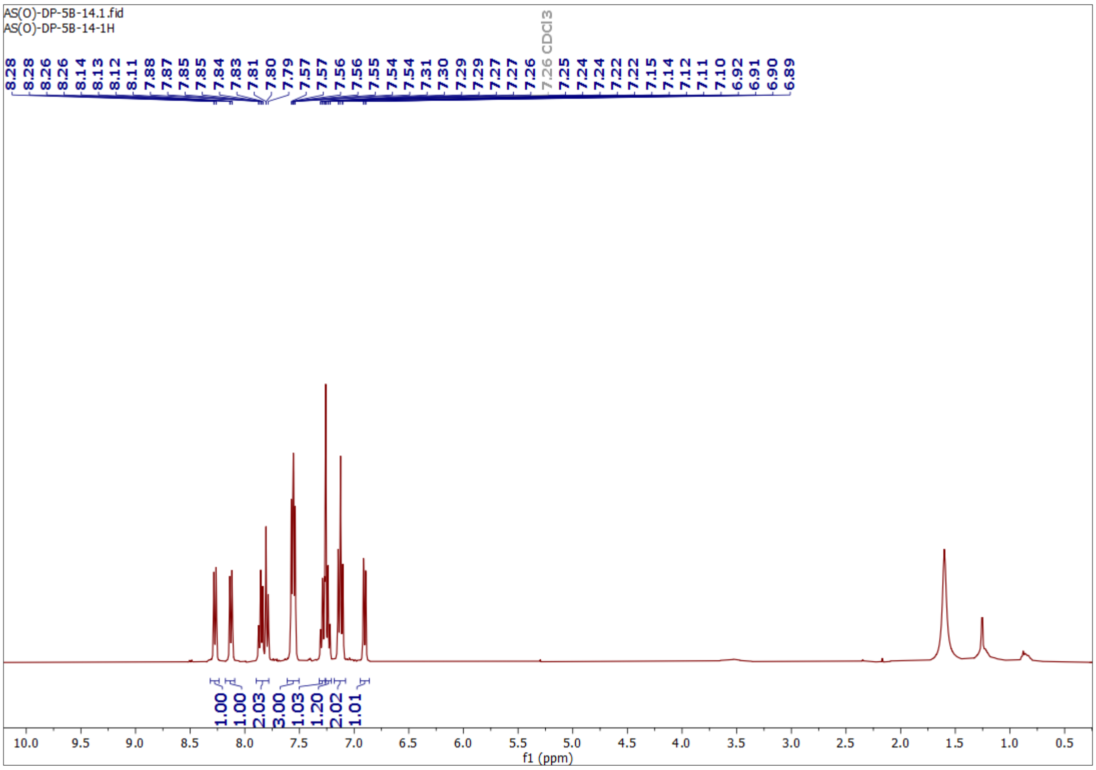


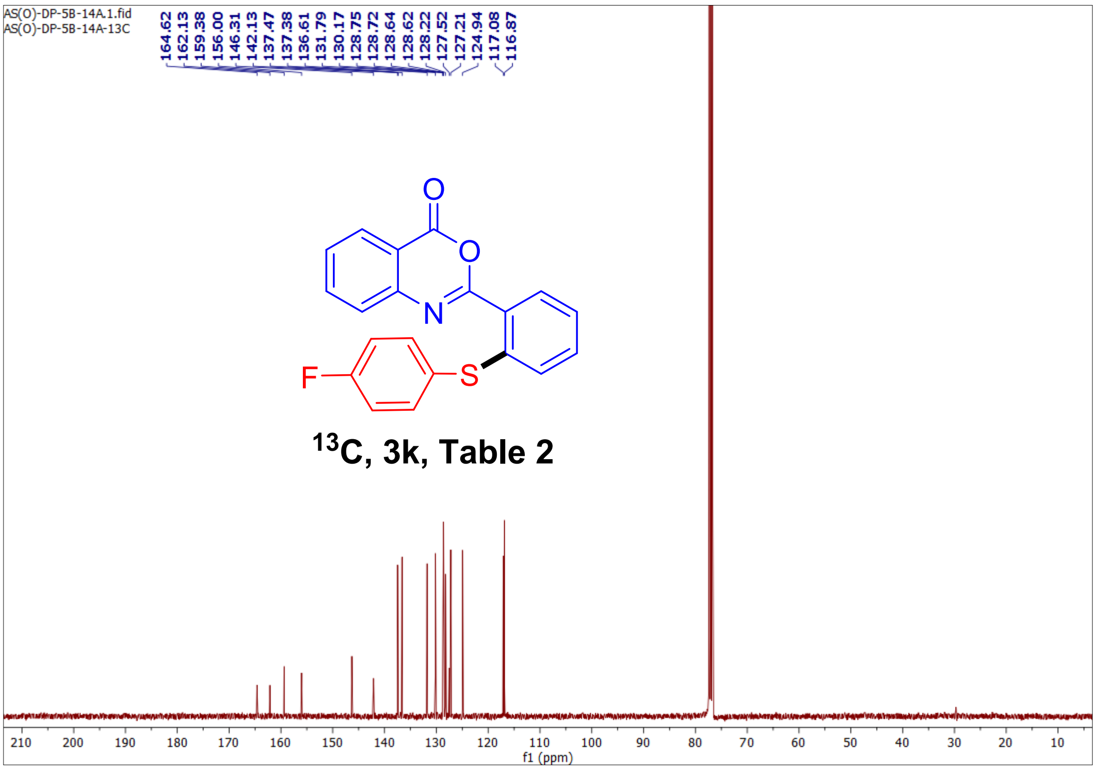
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3j



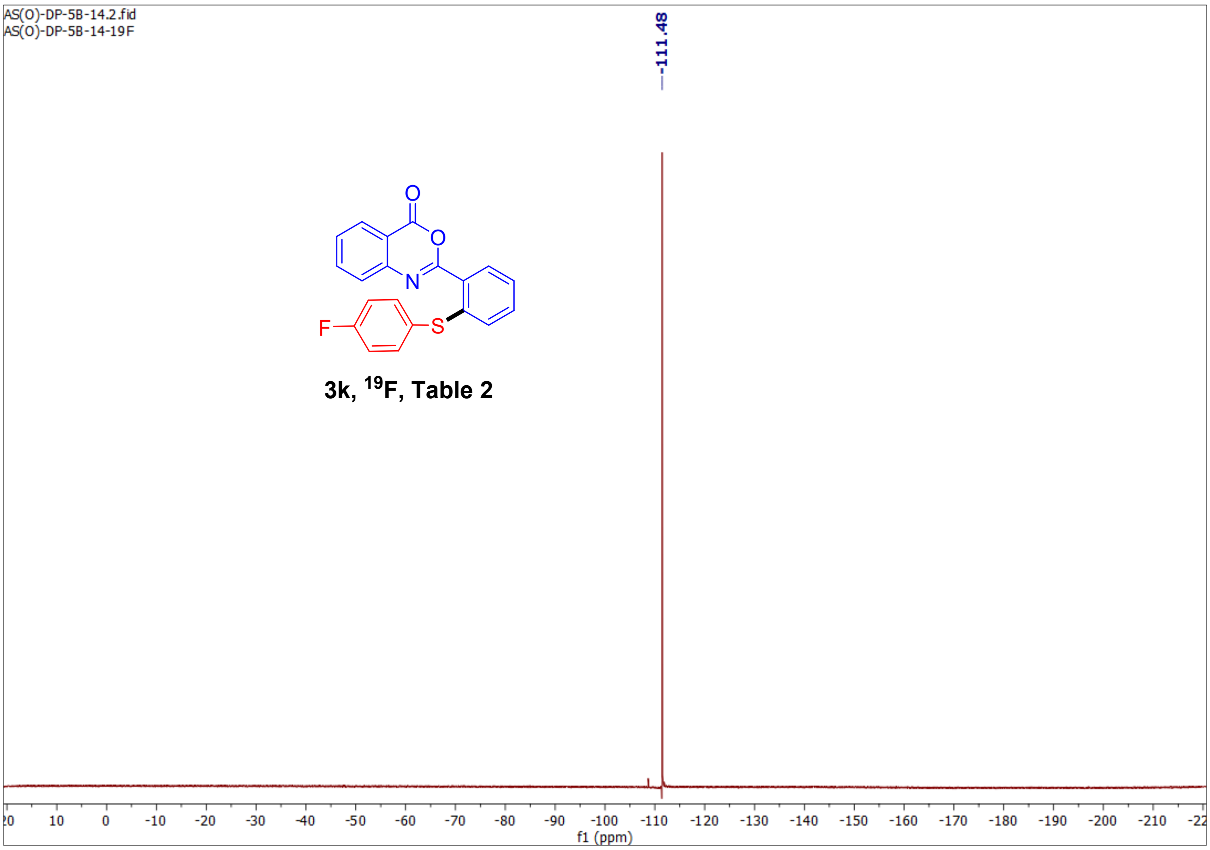


^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of 3k

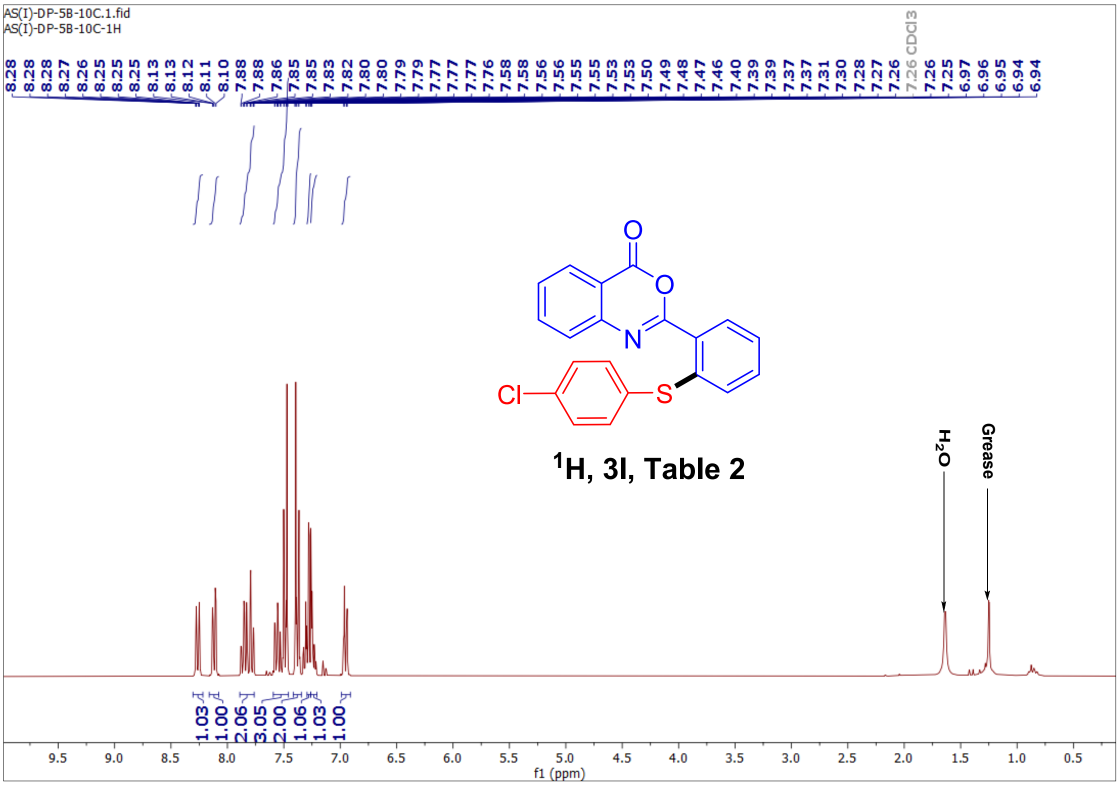


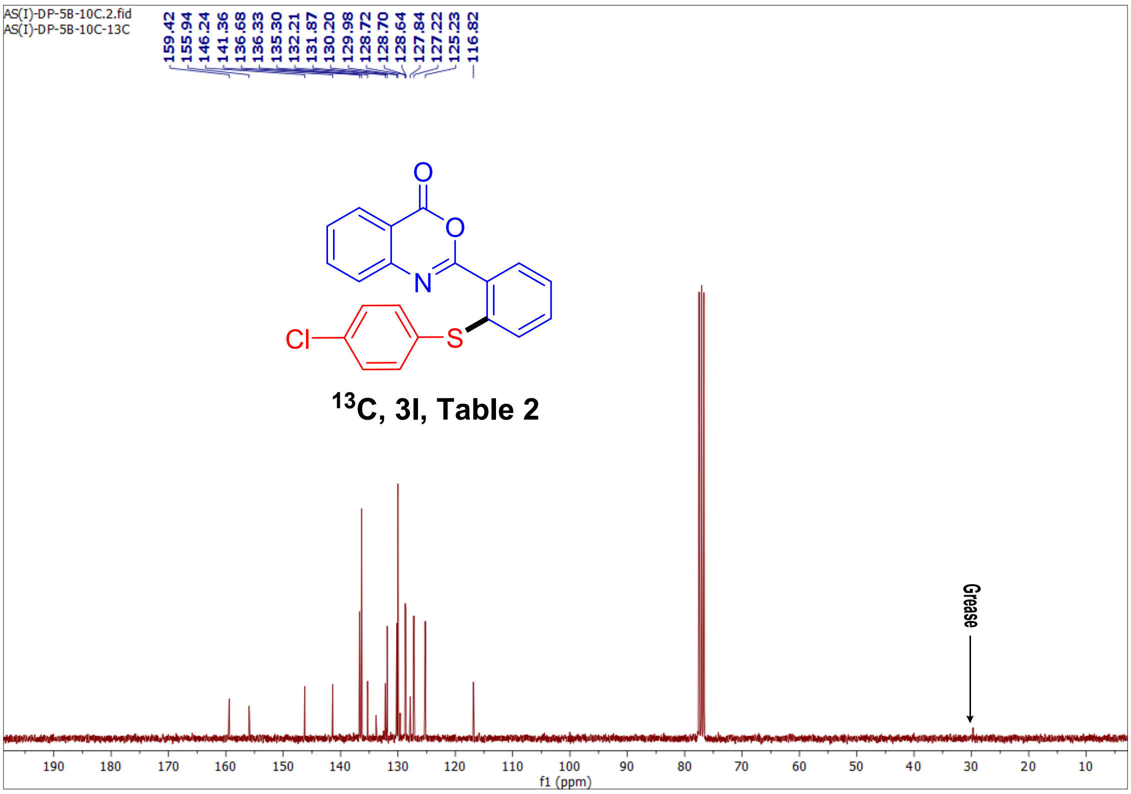


^{19}F NMR (282 MHz, $CDCl_3$) spectrum of 3k

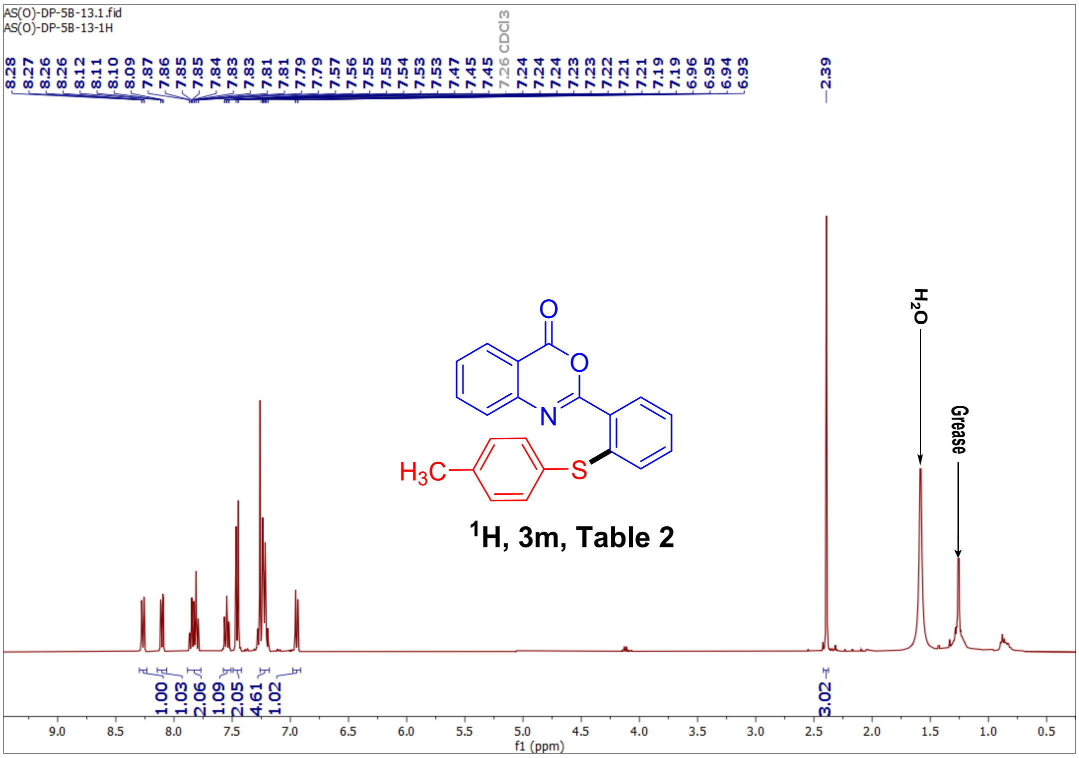


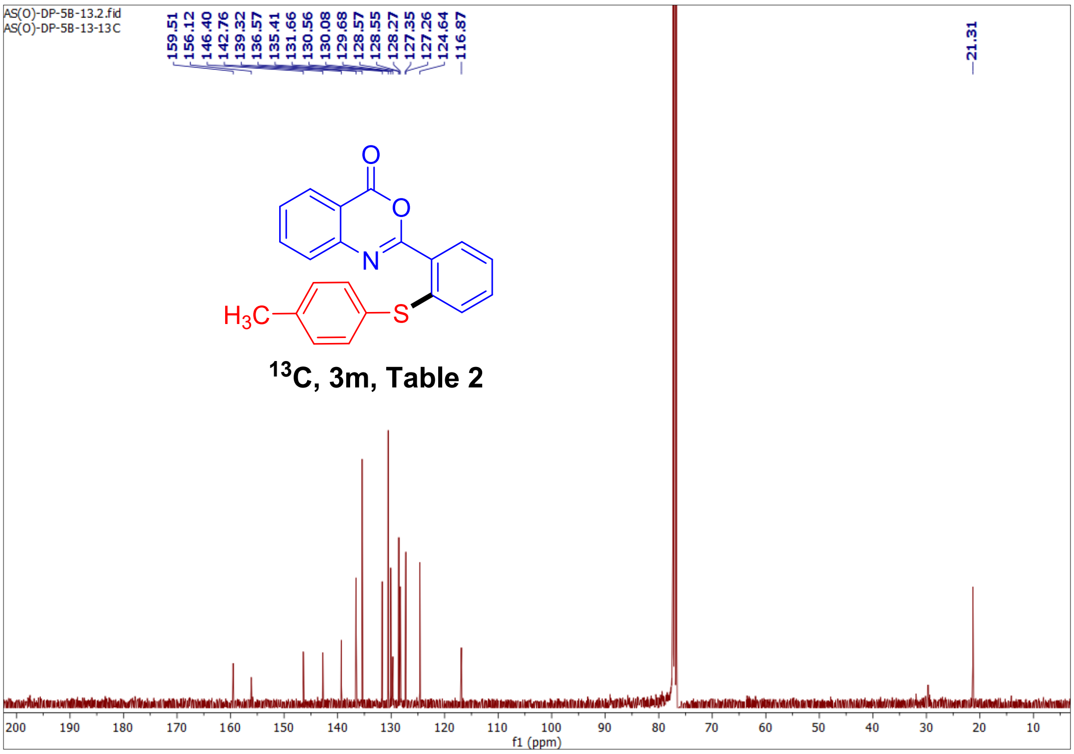
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3l



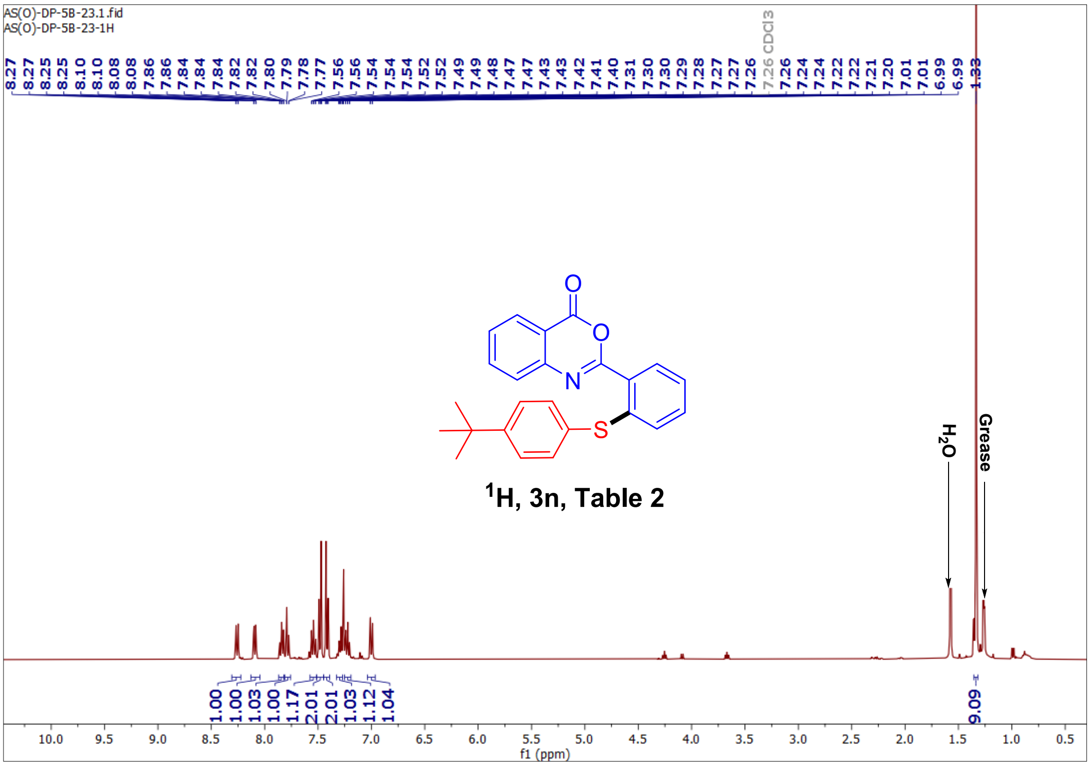


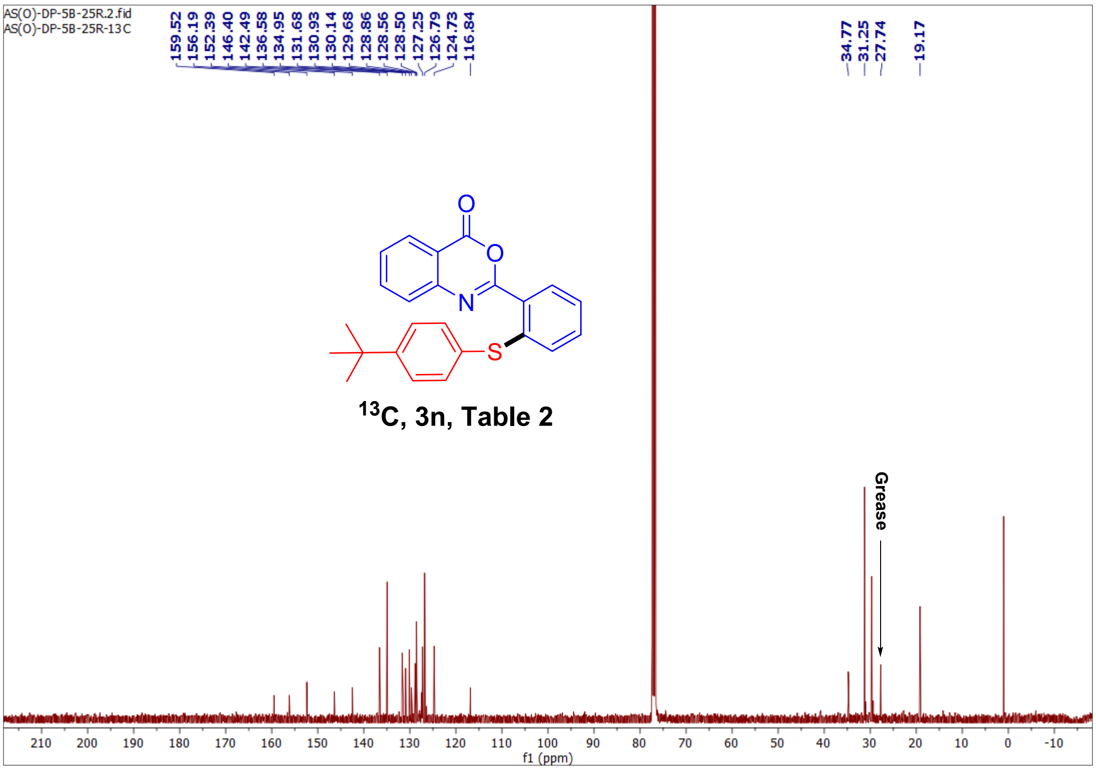
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3m



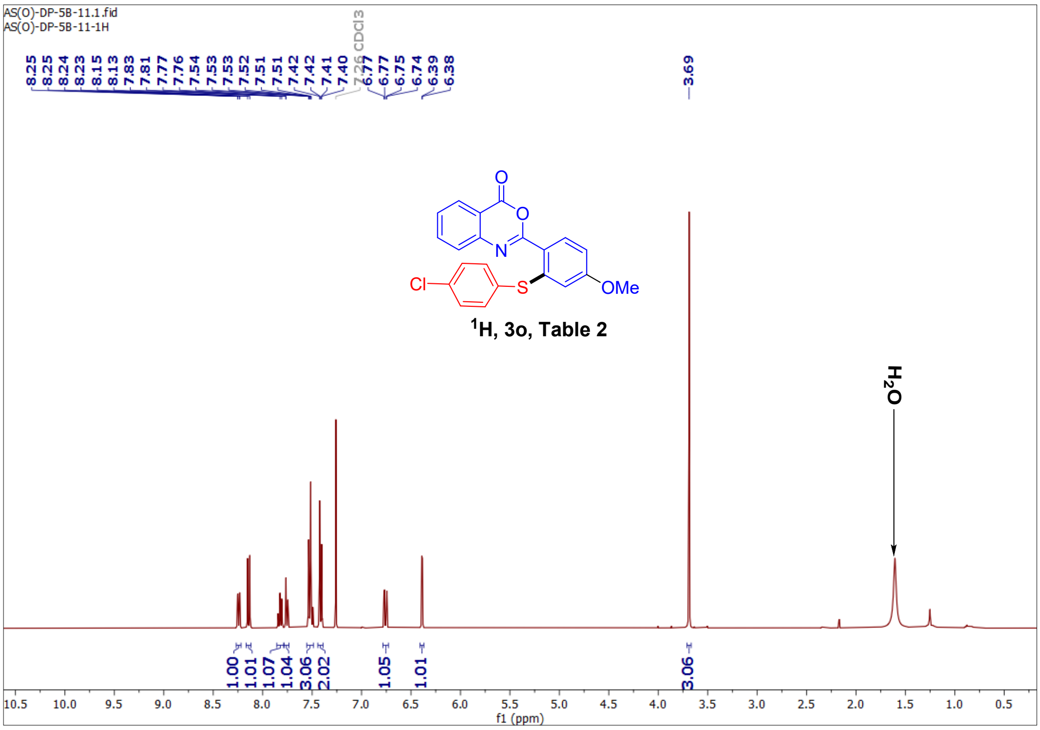


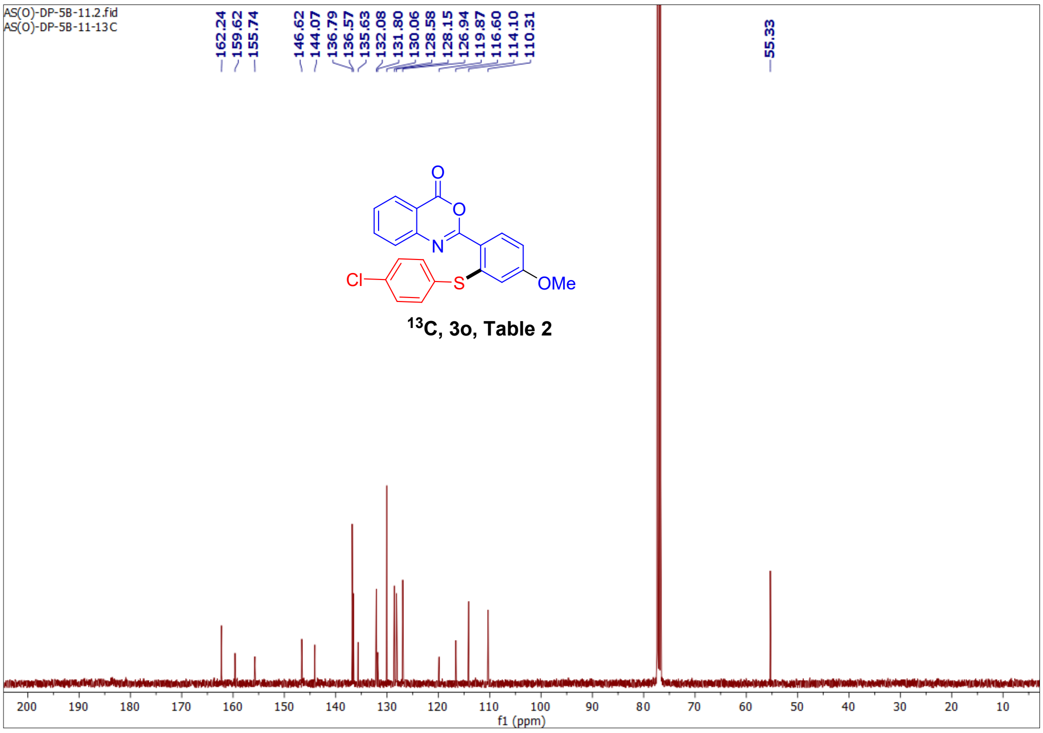
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3n



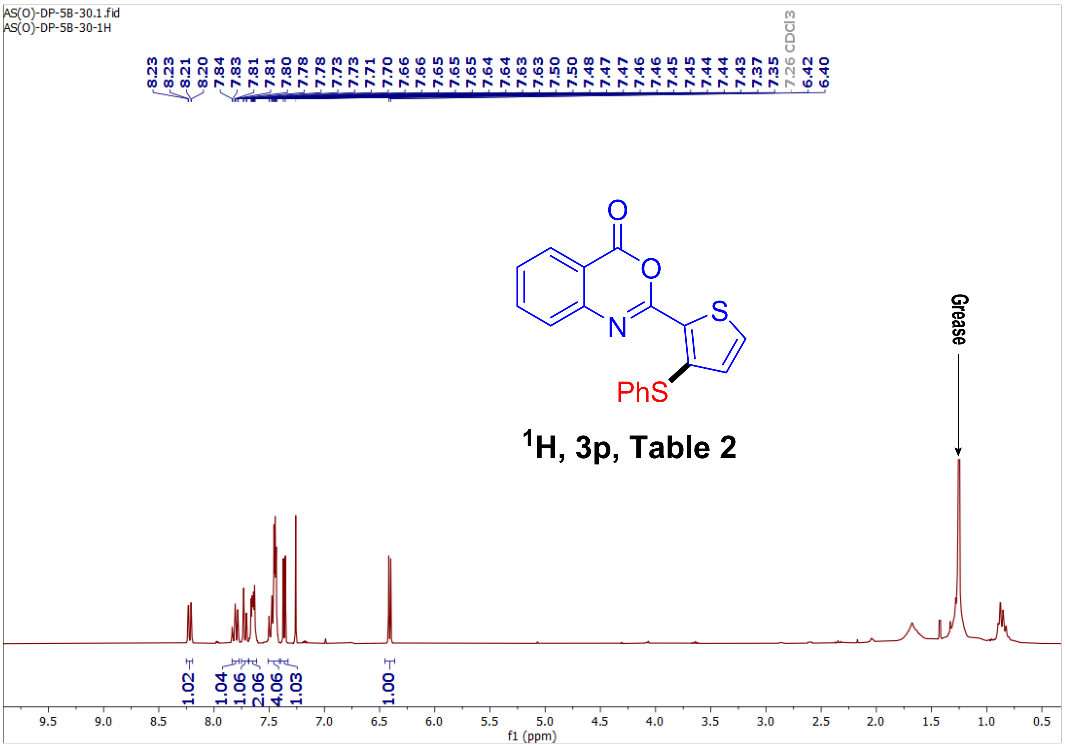


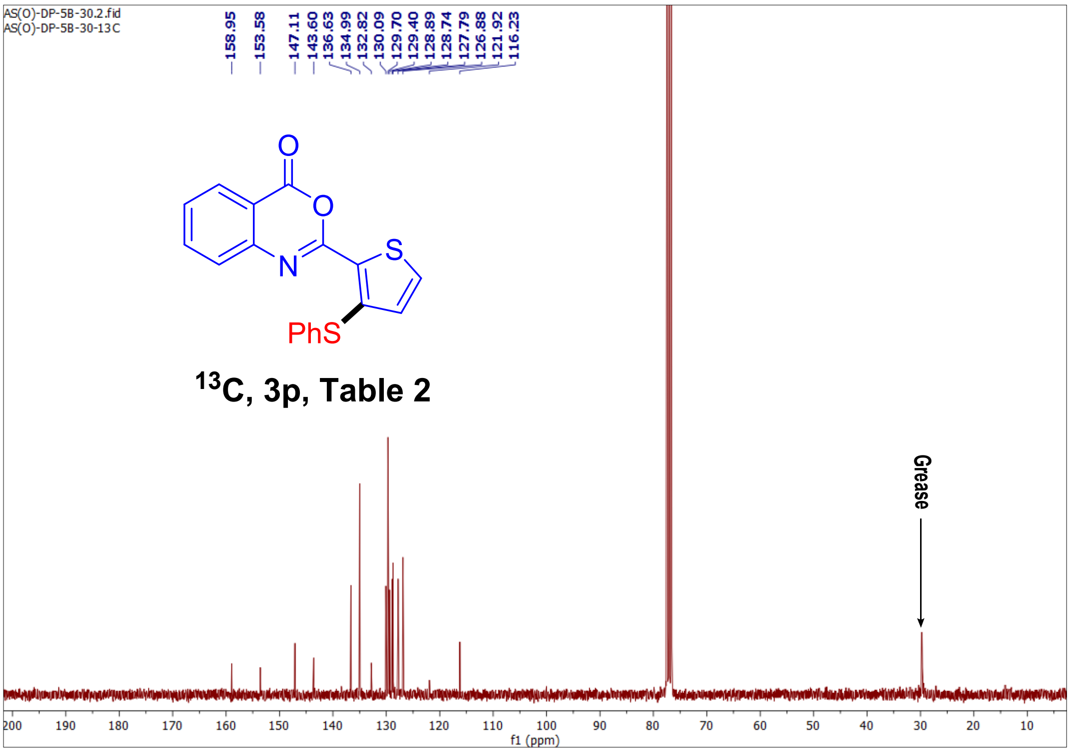
[1]H NMR (300 MHz, $CDCl_3$) and [13]C NMR (75 MHz, $CDCl_3$) spectrum of 3o



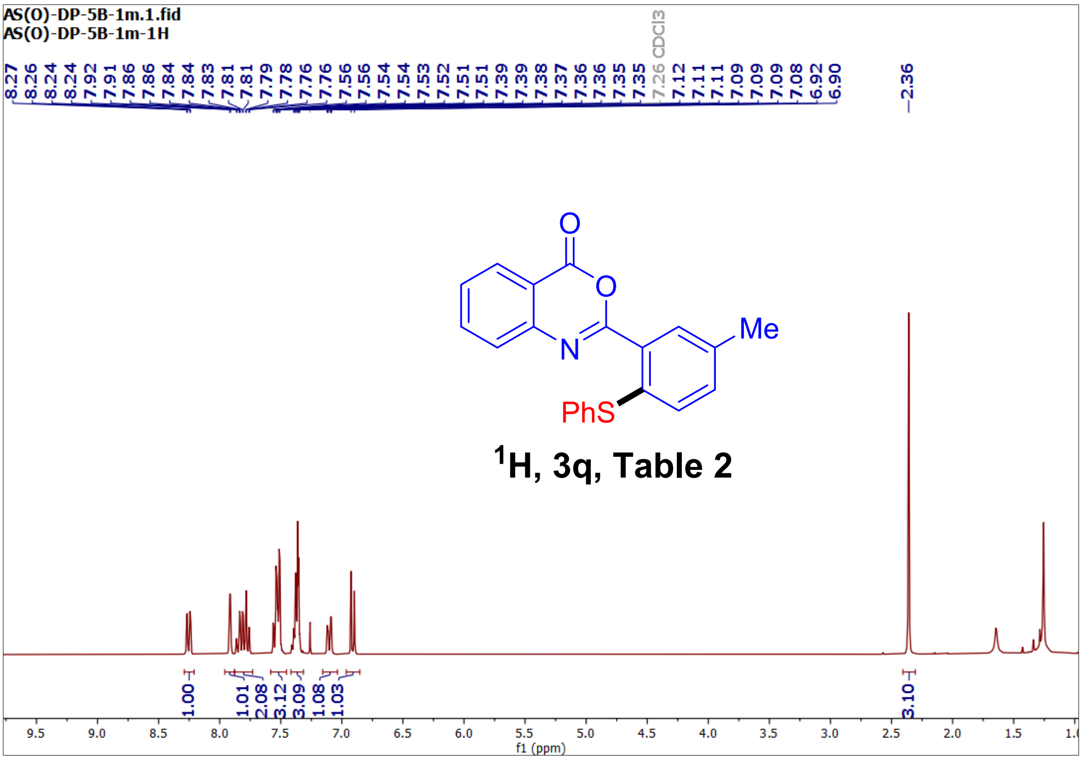


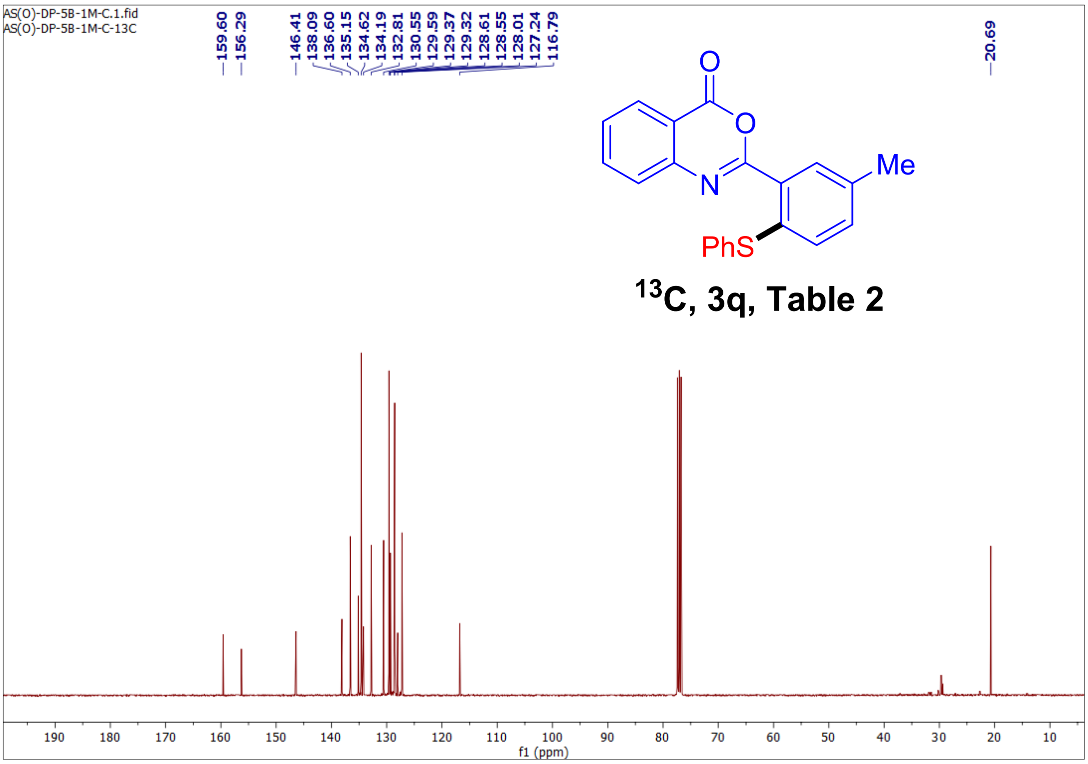
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3p



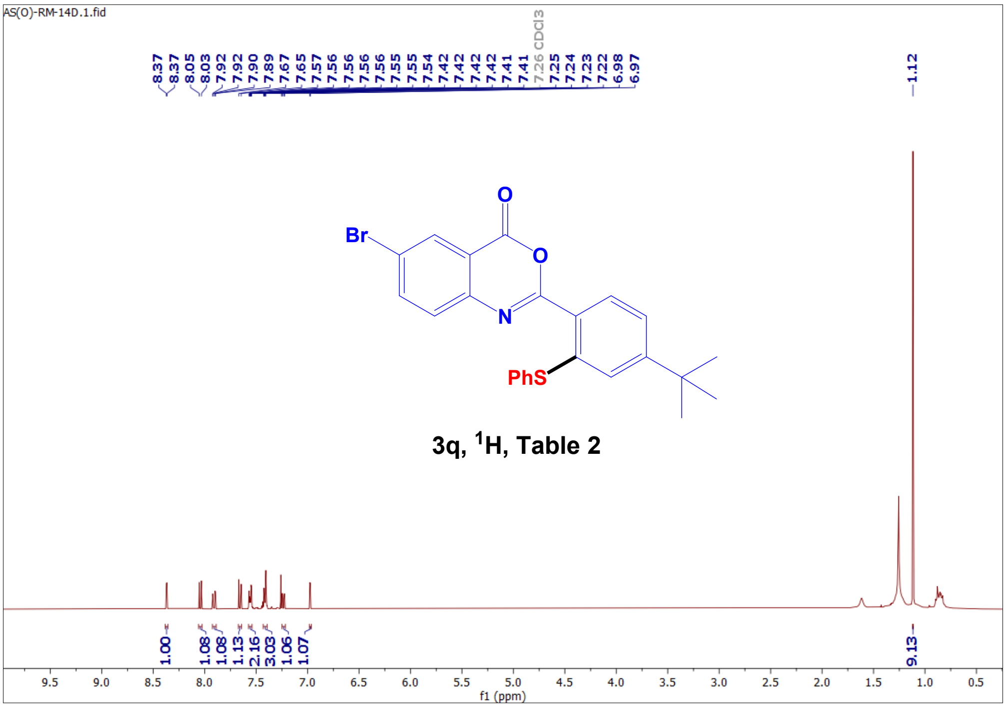


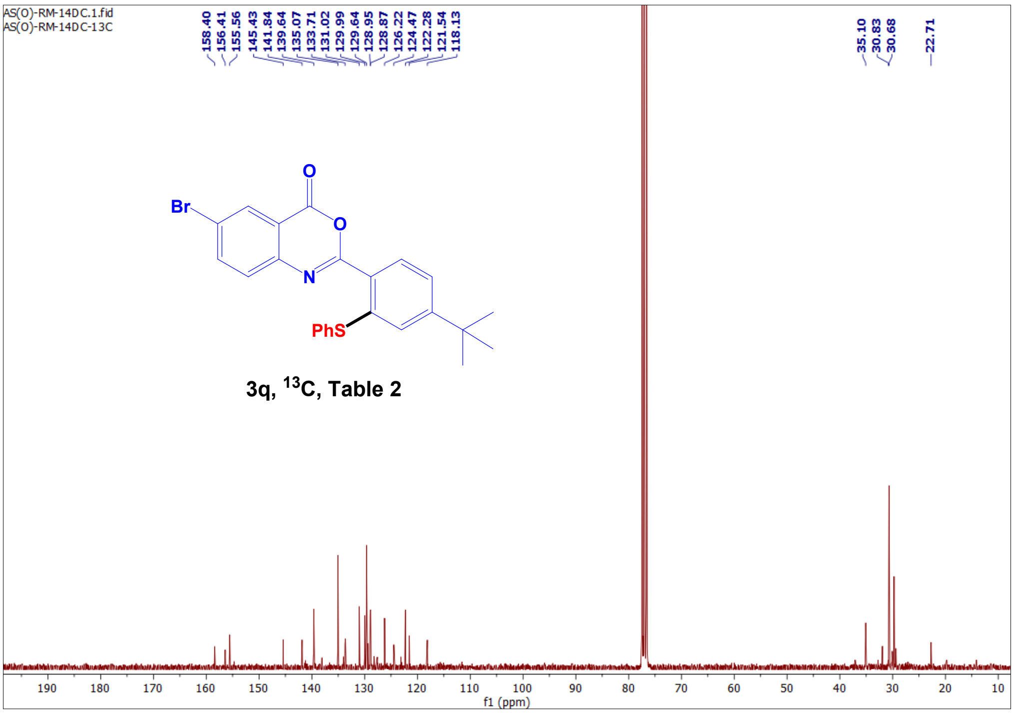
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3q



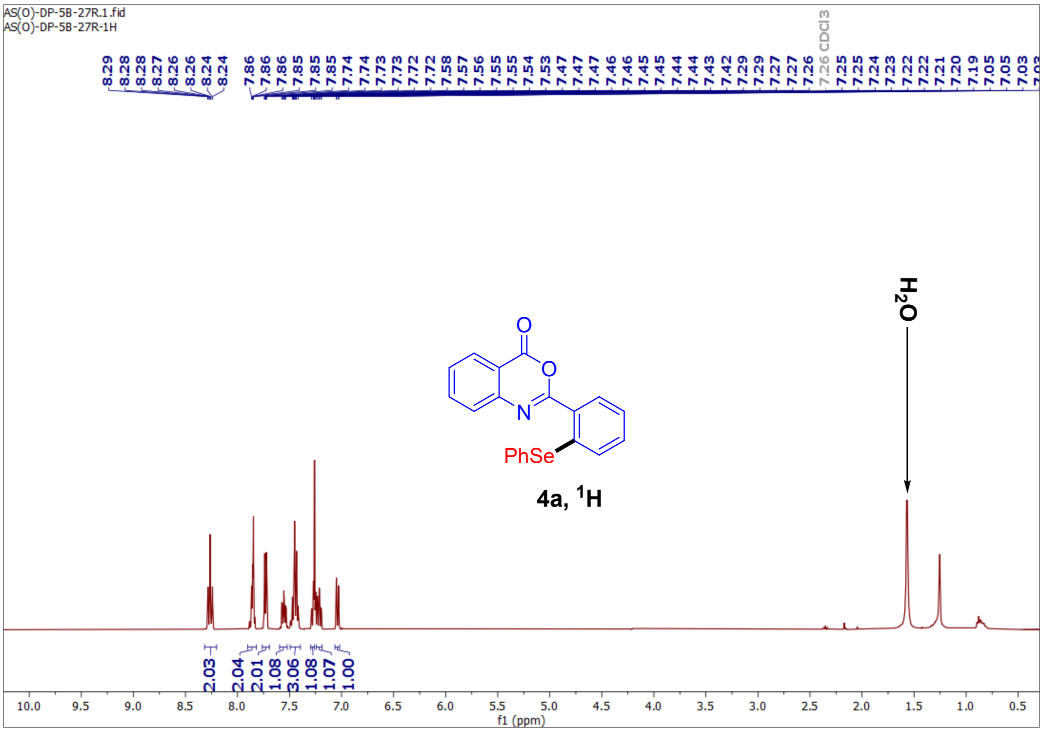


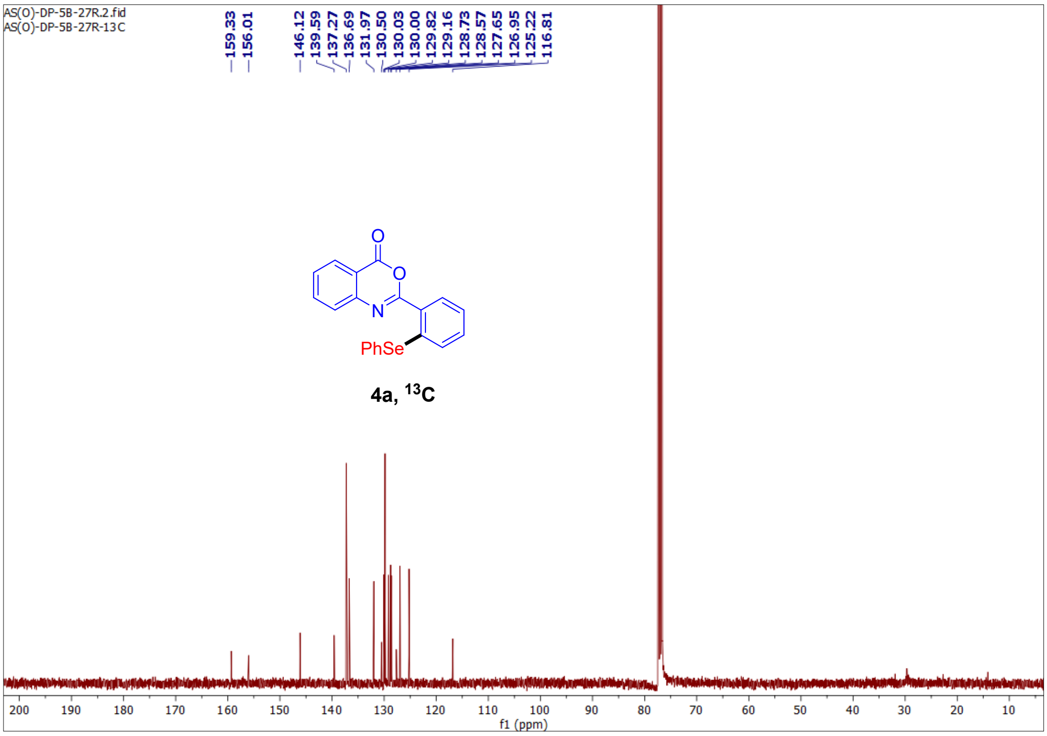
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3r



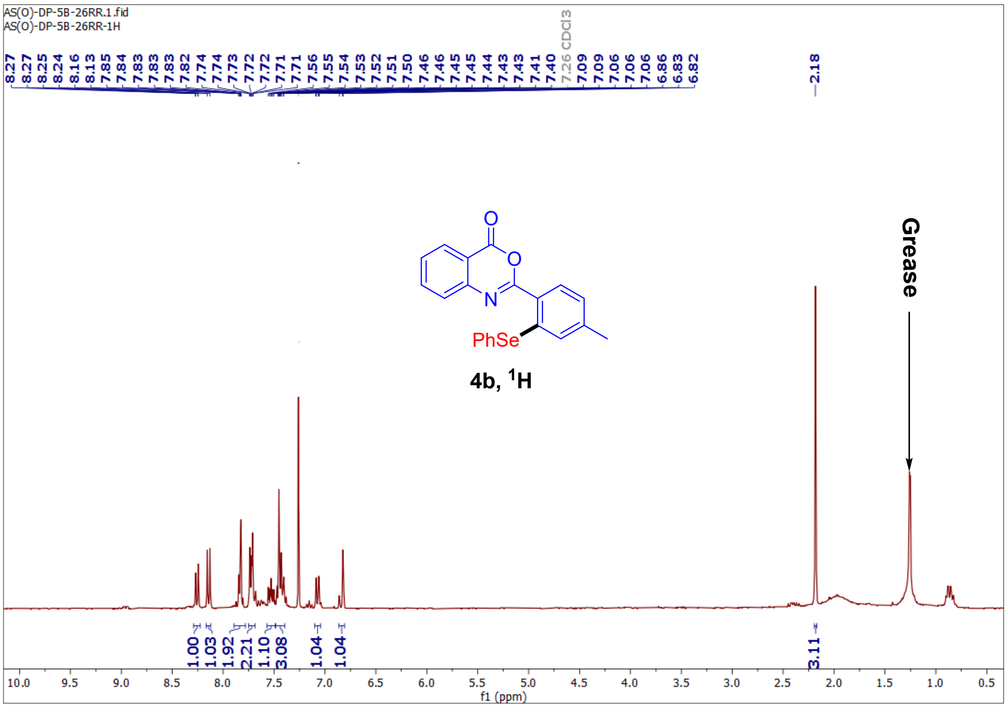


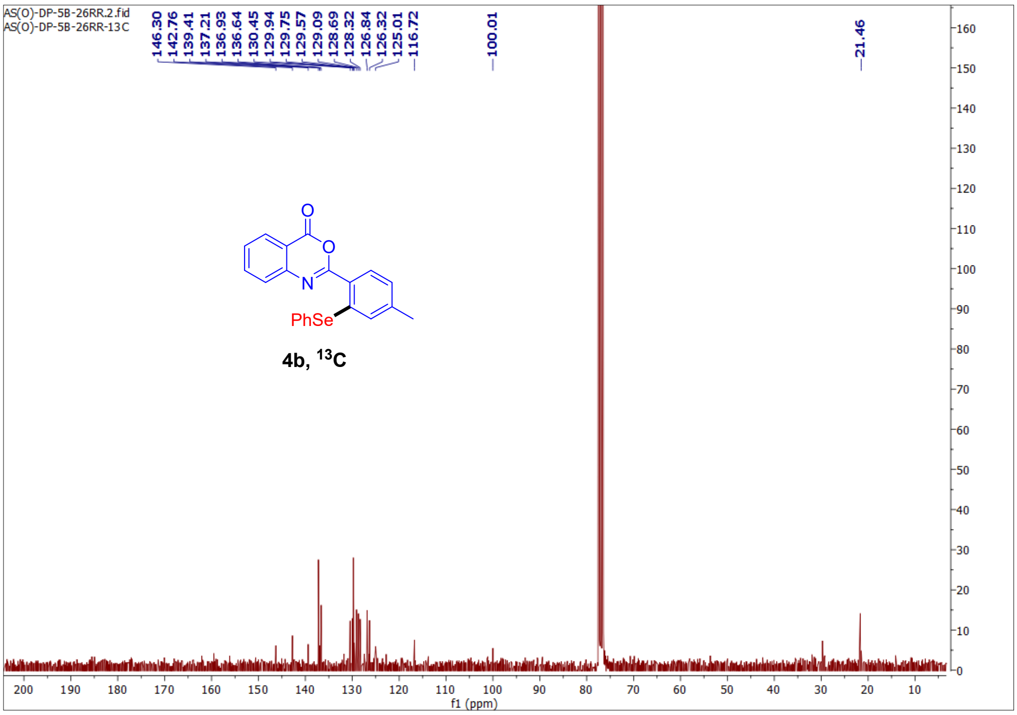
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4a



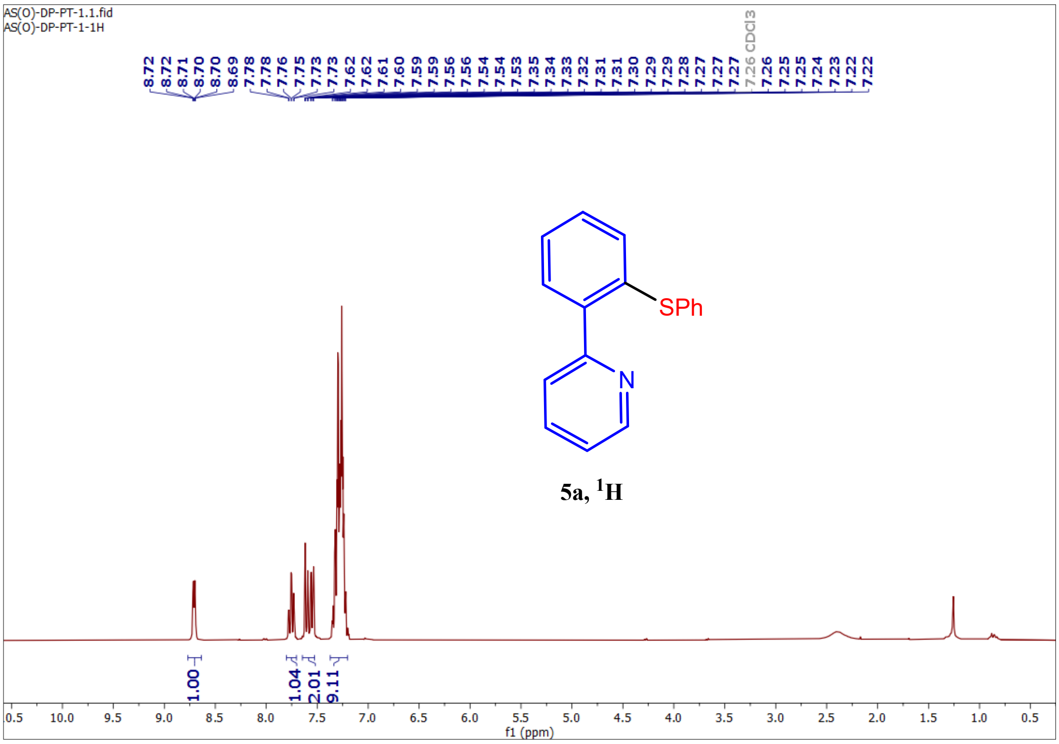


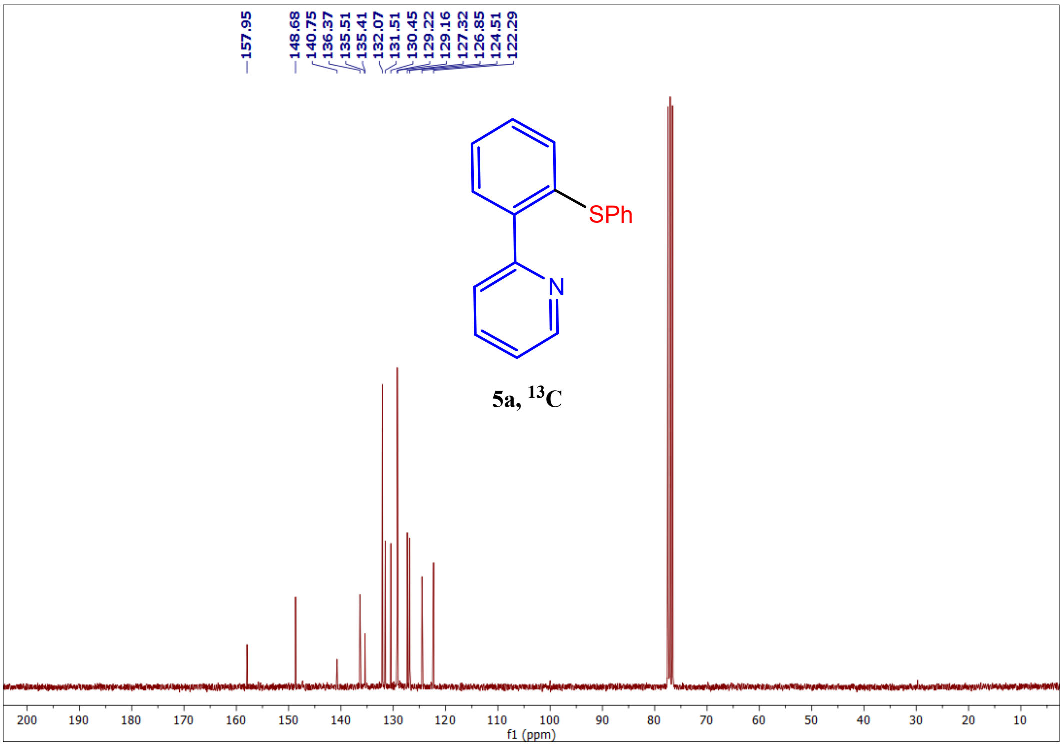
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4b



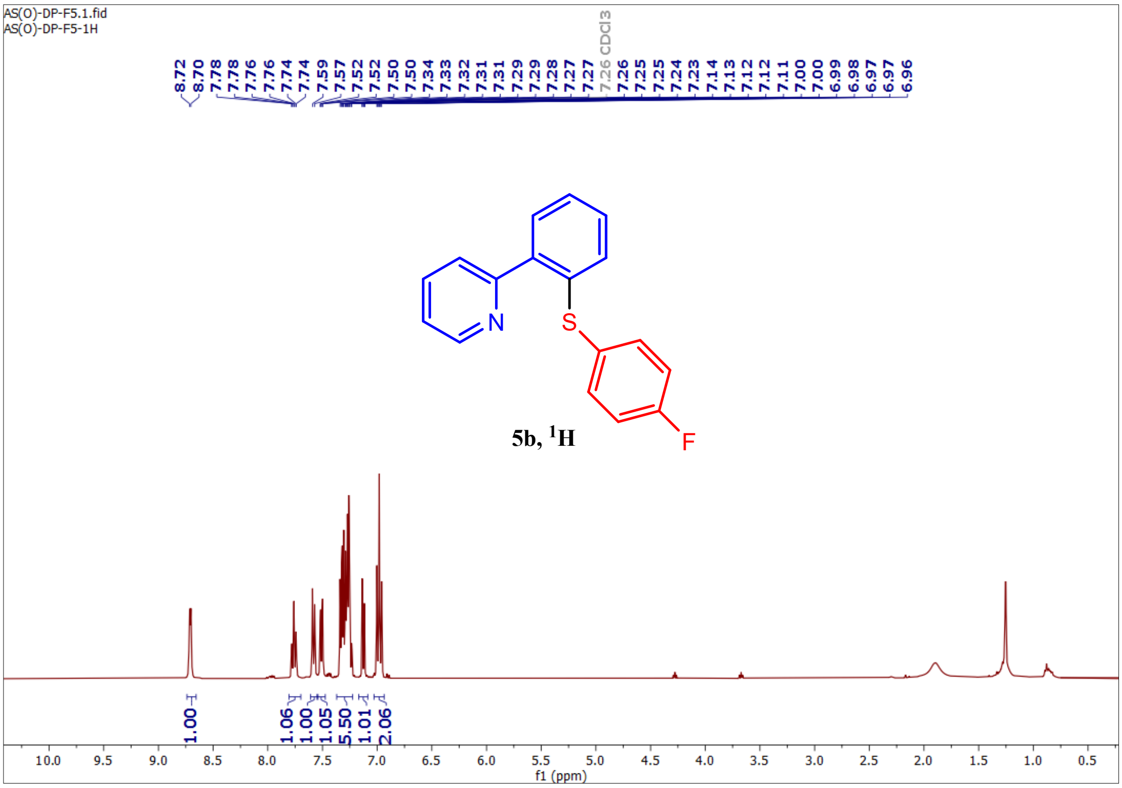


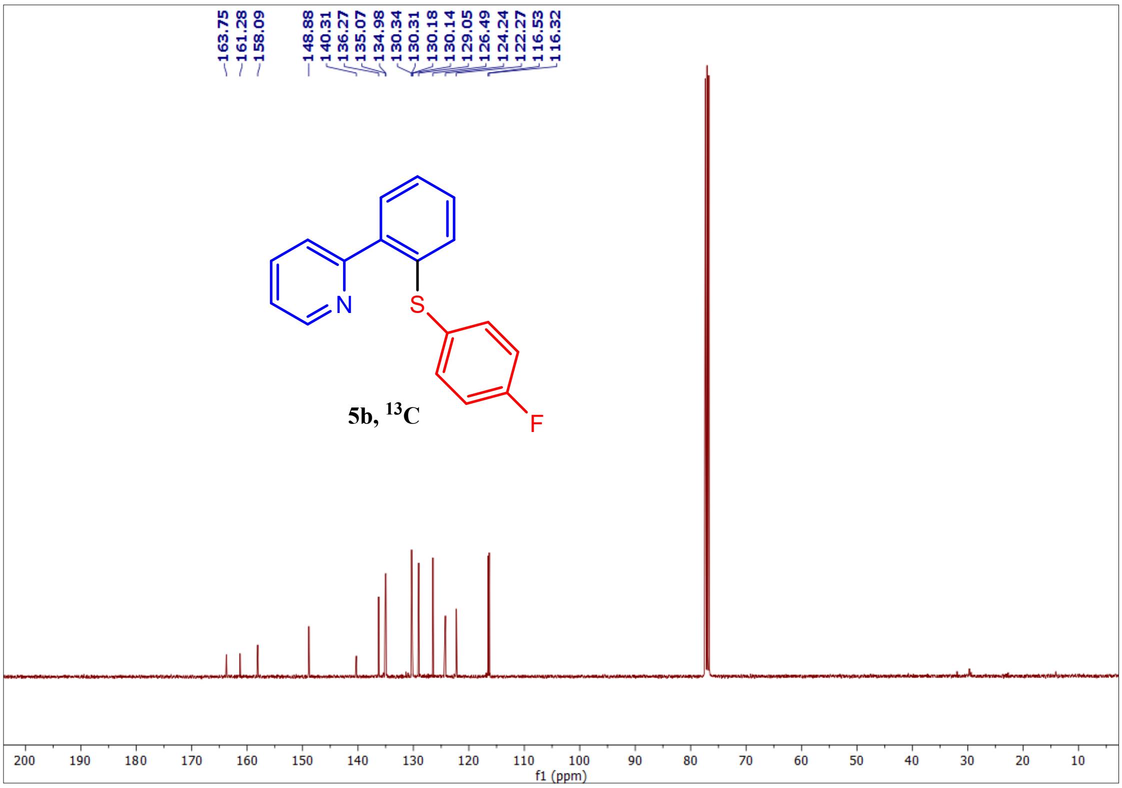
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 5a



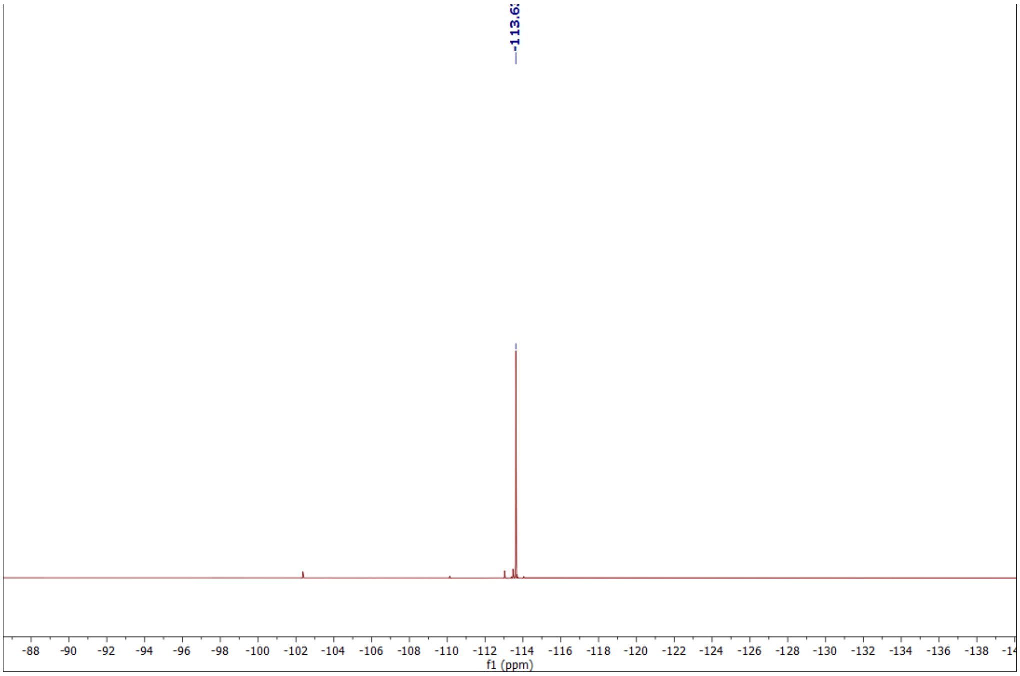


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 5b

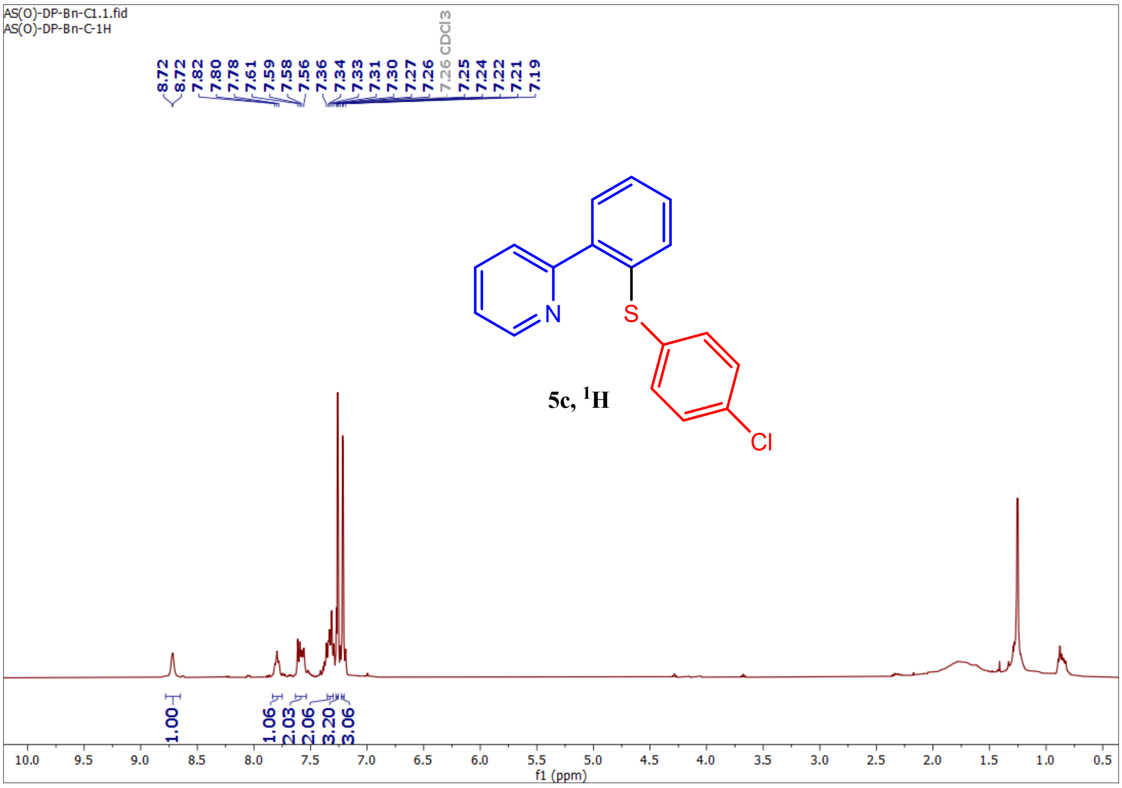


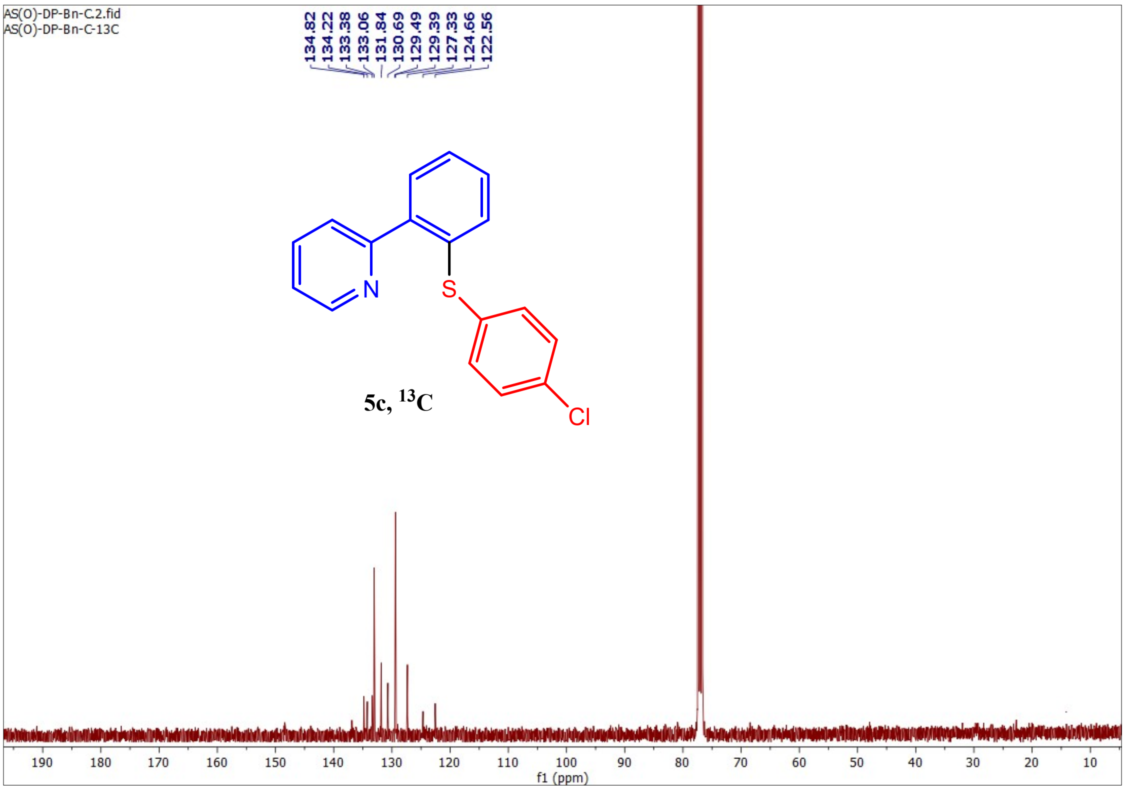


^{19} F NMR (376 MHz, $CDCl_3$) spectrum of 5b

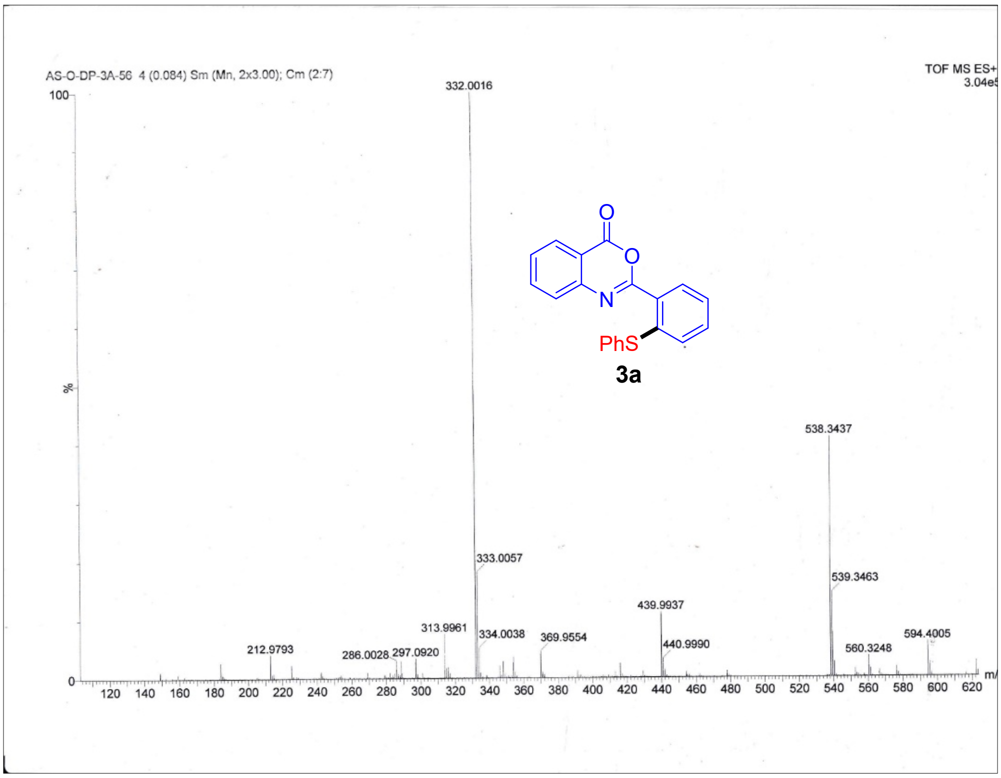


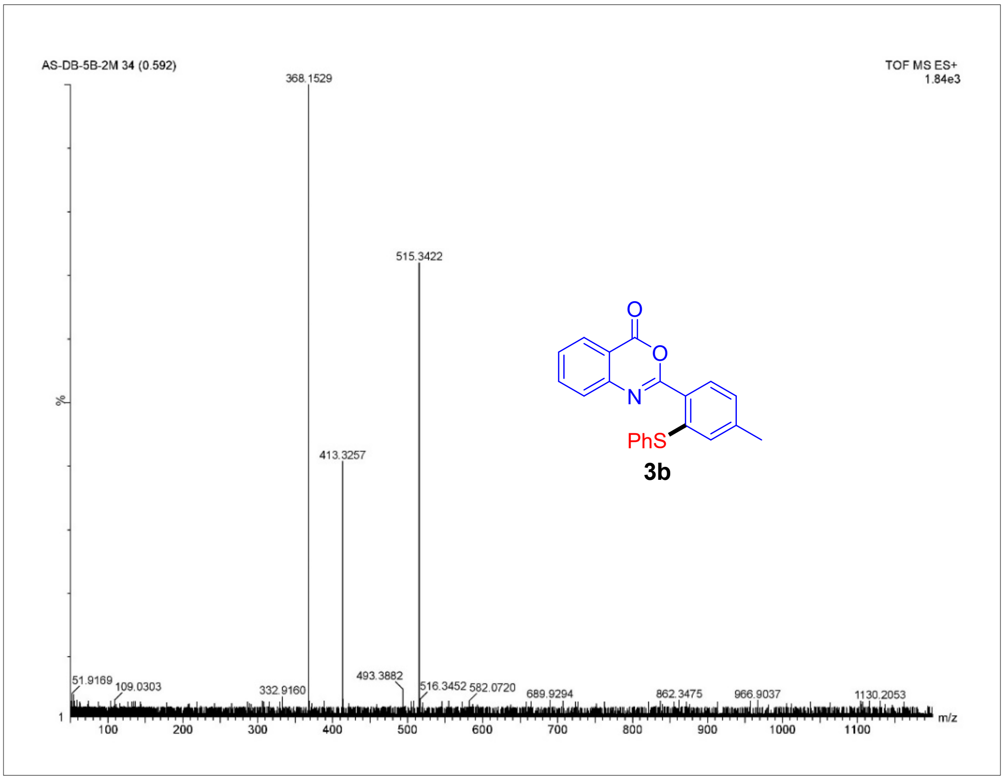
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 5c

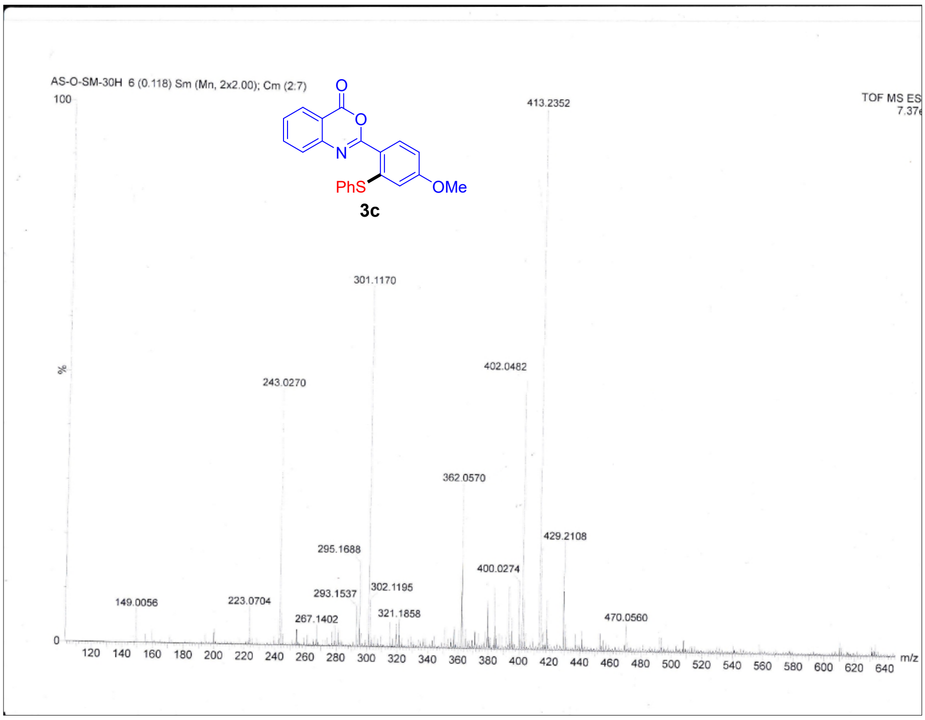


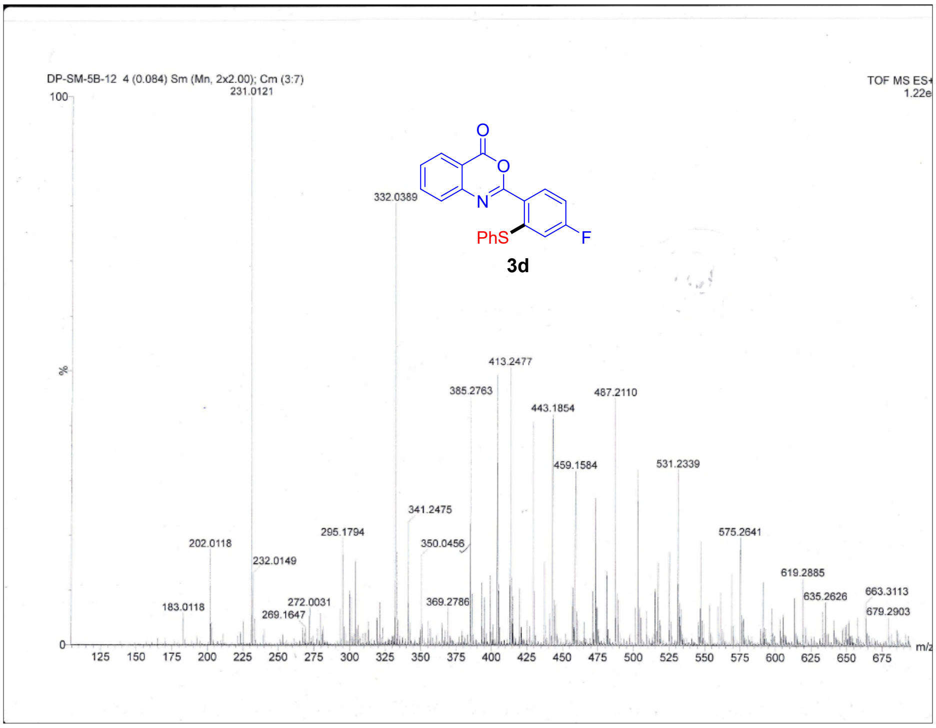


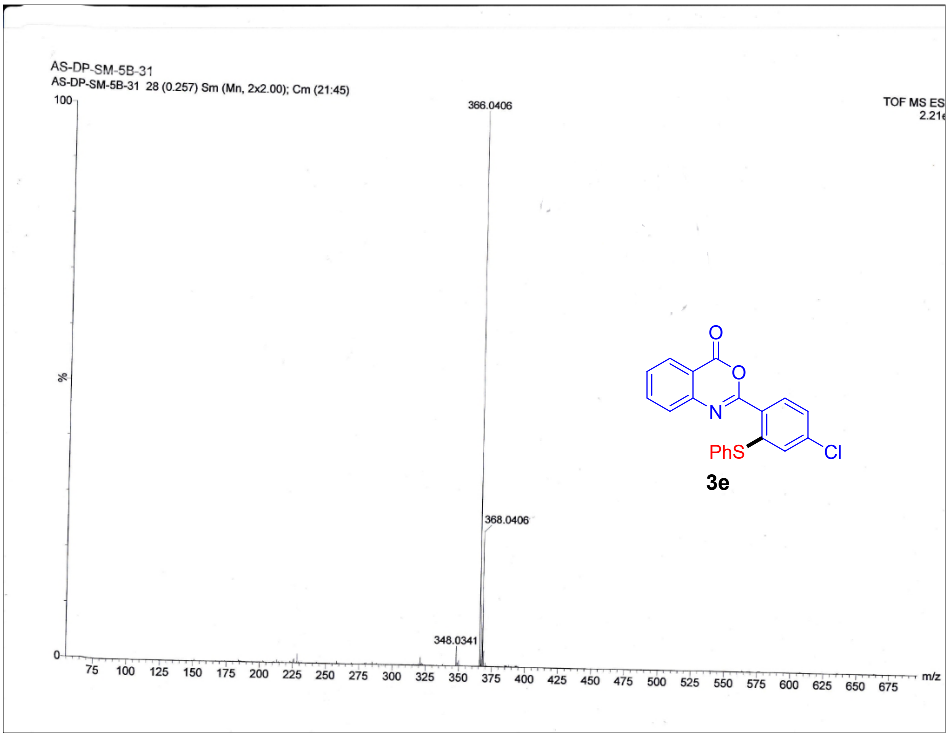
7. Mass spectra of all products:

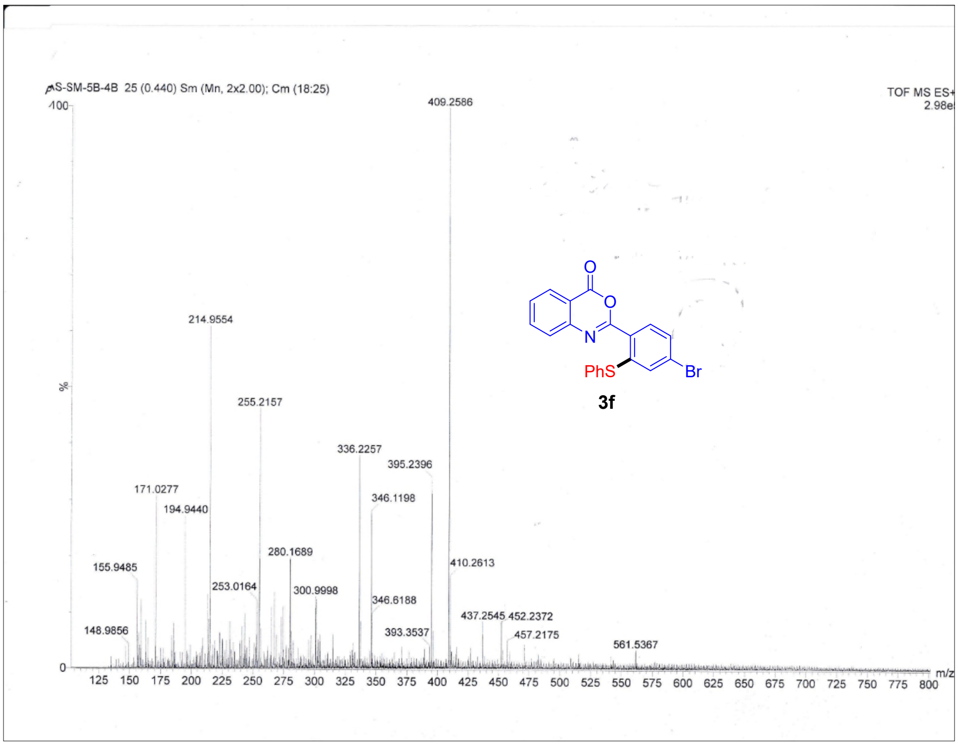


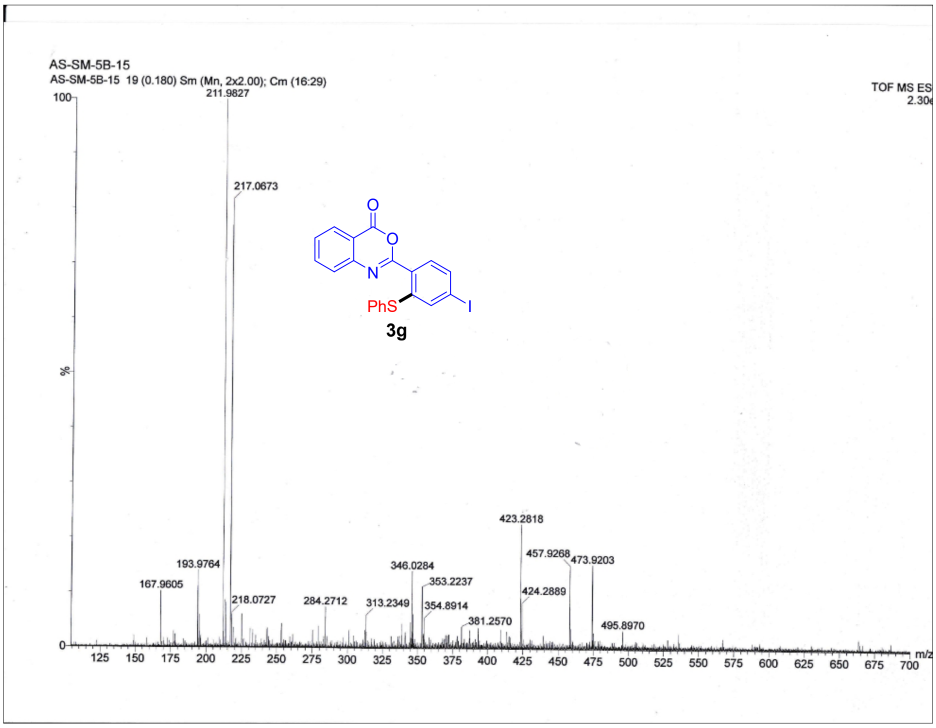


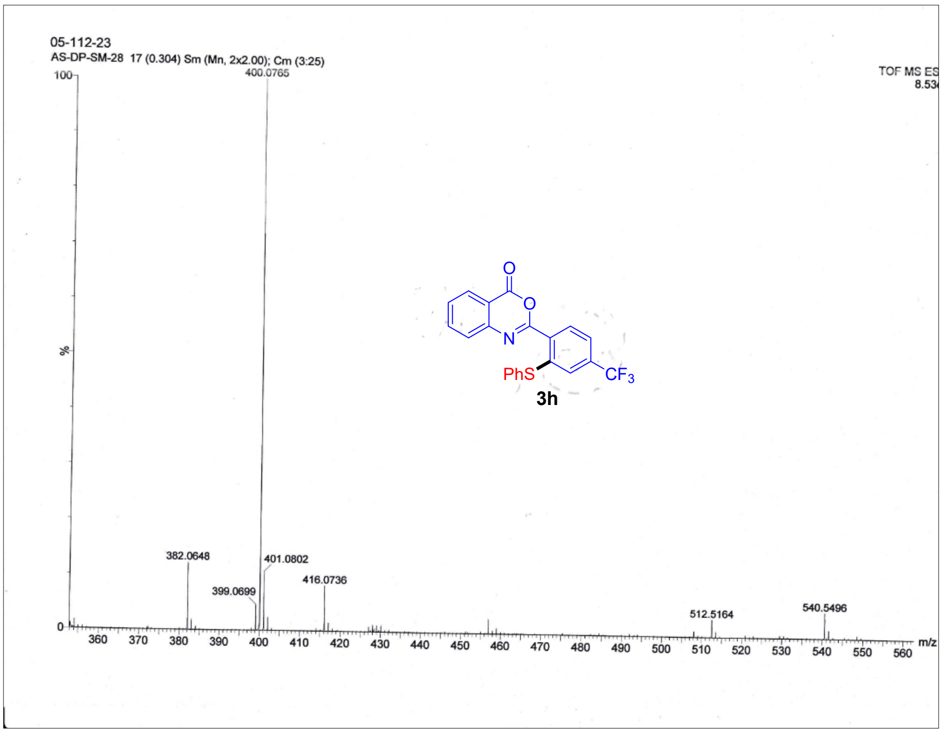

AS-O-SM-30H 6 (0.118) Sm (Mn, 2x2.00); Cm (2:7)
TOF MS ES
3c
PhS
OMe
413.2352
301.1170
402.0482
243.0270
362.0570
429.2108
295.1688
400.0274
149.0056
223.0704
293.1537
302.1195
267.1402
321.1858
470.0560
m/z

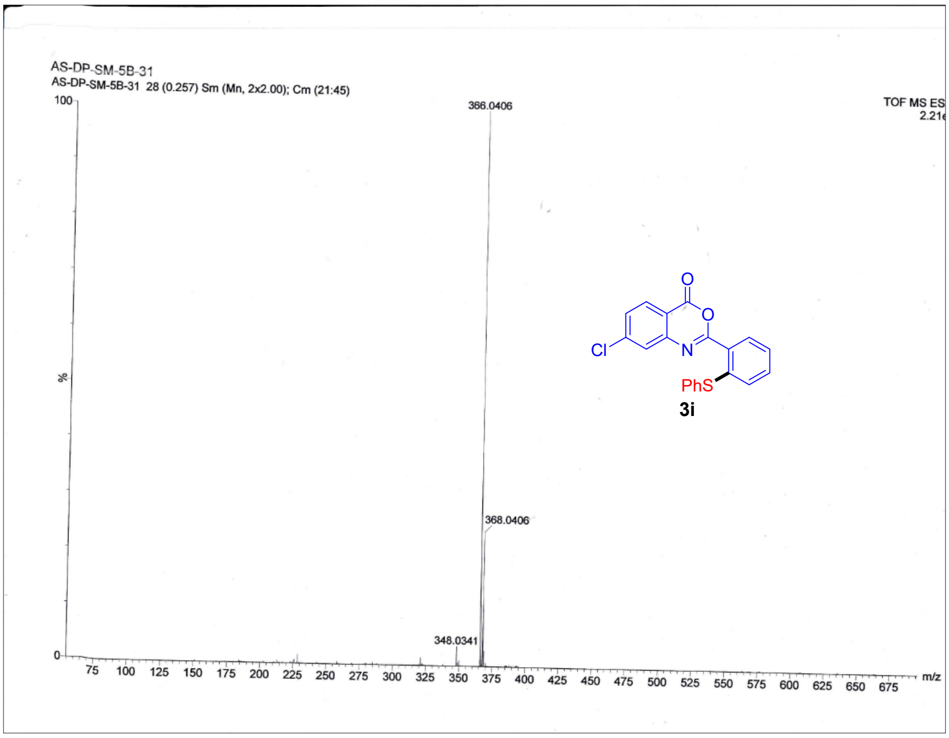

DP-SM-5B-12 4 (0.084) Sm (Mn, 2x2.00); Cm (3:7)
TOF MS ES+
231.0121
332.0389
3d
PhS
F
413.2477
385.2763
487.2110
443.1854
459.1584
531.2339
341.2475
575.2641
295.1794
202.0118
350.0456
232.0149
619.2885
663.3113
635.2626
183.0118
272.0031
369.2786
679.2903
269.1647
m/z


AS-DP-SM-5B-31
AS-DP-SM-5B-31 28 (0.257) Sm (Mn, 2x2.00); Cm (21:45)
TOF MS ES
366.0406
368.0406
348.0341
%
m/z
PhS
Cl
3e

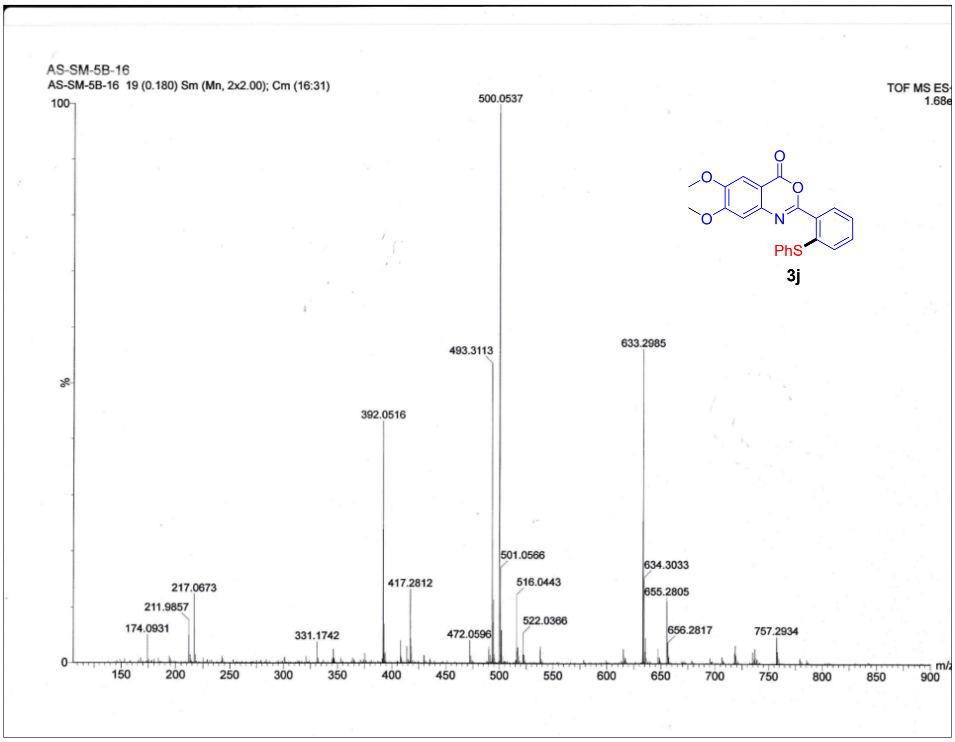

AS-SM-5B-4B 25 (0.440) Sm (Mn, 2x2.00); Cm (18:25)
TOF MS ES+
409.2586
214.9554
255.2157
336.2257
395.2396
171.0277
194.9440
346.1198
280.1689
155.9485
410.2613
253.0164
300.9998
346.6188
437.2545
452.2372
148.9856
393.3537
457.2175
561.5367
%
m/z
PhS
Br
3f


AS-SM-5B-15
AS-SM-5B-15 19 (0.180) Sm (Mn, 2x2.00); Cm (16:29)
TOF MS ES
211.9827
217.0673
423.2818
457.9268
473.9203
193.9764
346.0284
353.2237
167.9605
218.0727
284.2712
313.2349
354.8914
424.2889
381.2570
495.8970
PhS
I
3g
m/z
%

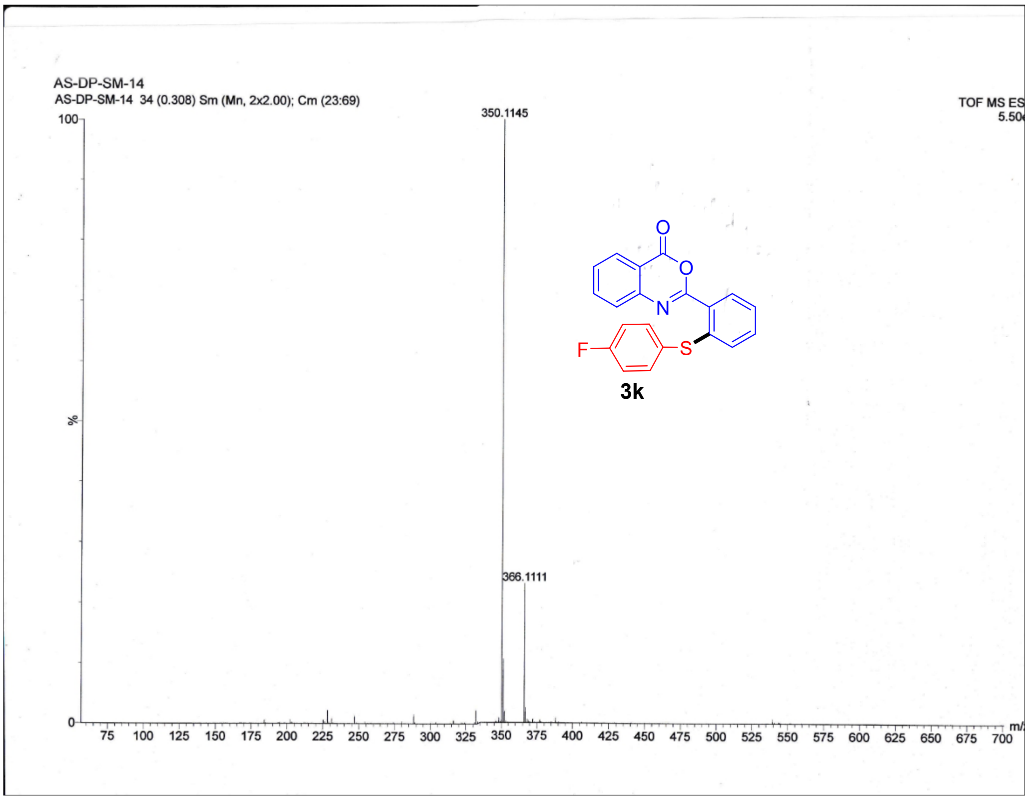

05-112-23
AS-DP-SM-28 17 (0.304) Sm (Mn, 2x2.00); Cm (3:25)
TOF MS ES
400.0765
382.0648
401.0802
399.0699
416.0736
512.5164
540.5496
PhS
CF3
3h
m/z
%

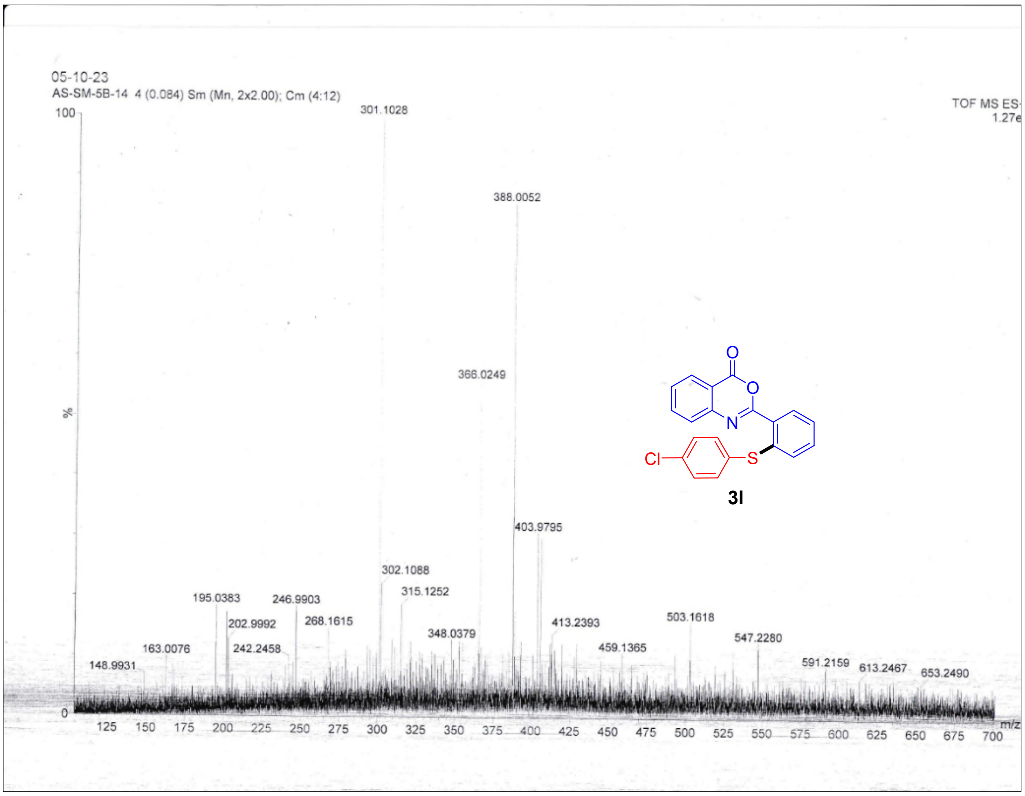

AS-DP-SM-5B-31
AS-DP-SM-5B-31 28 (0.257) Sm (Mn, 2x2.00); Cm (21:45)
TOF MS ES
100
366.0406
%
368.0406
348.0341
0
m/z
Cl
O
O
N
PhS

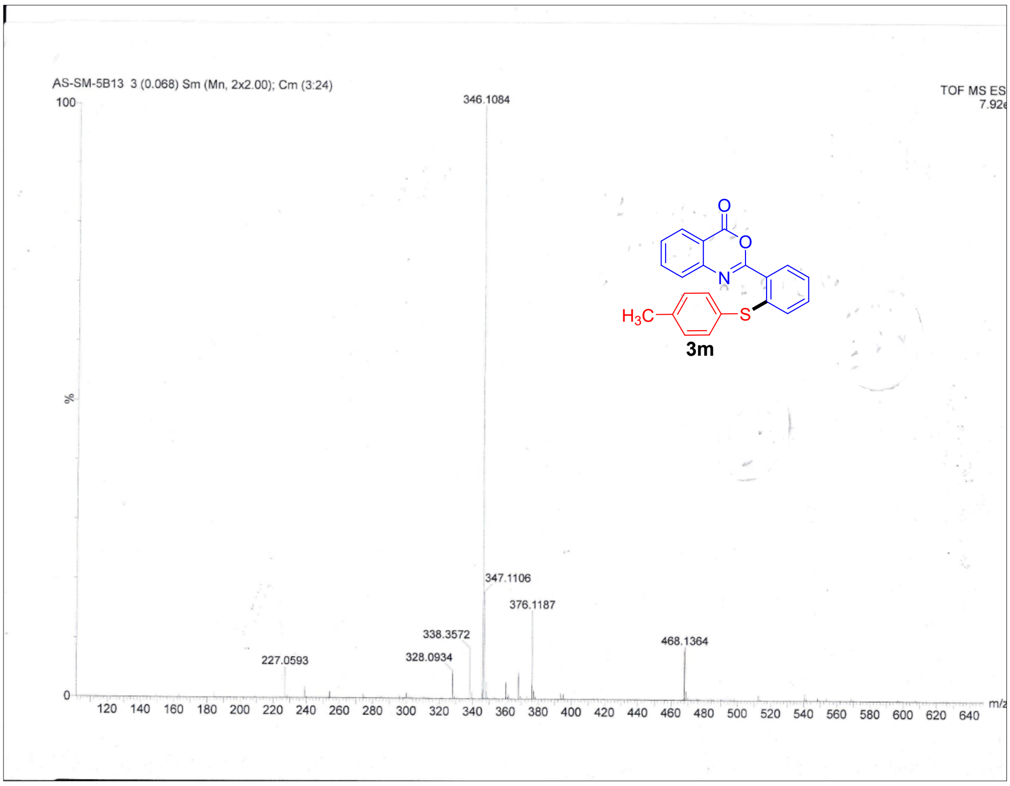
3i

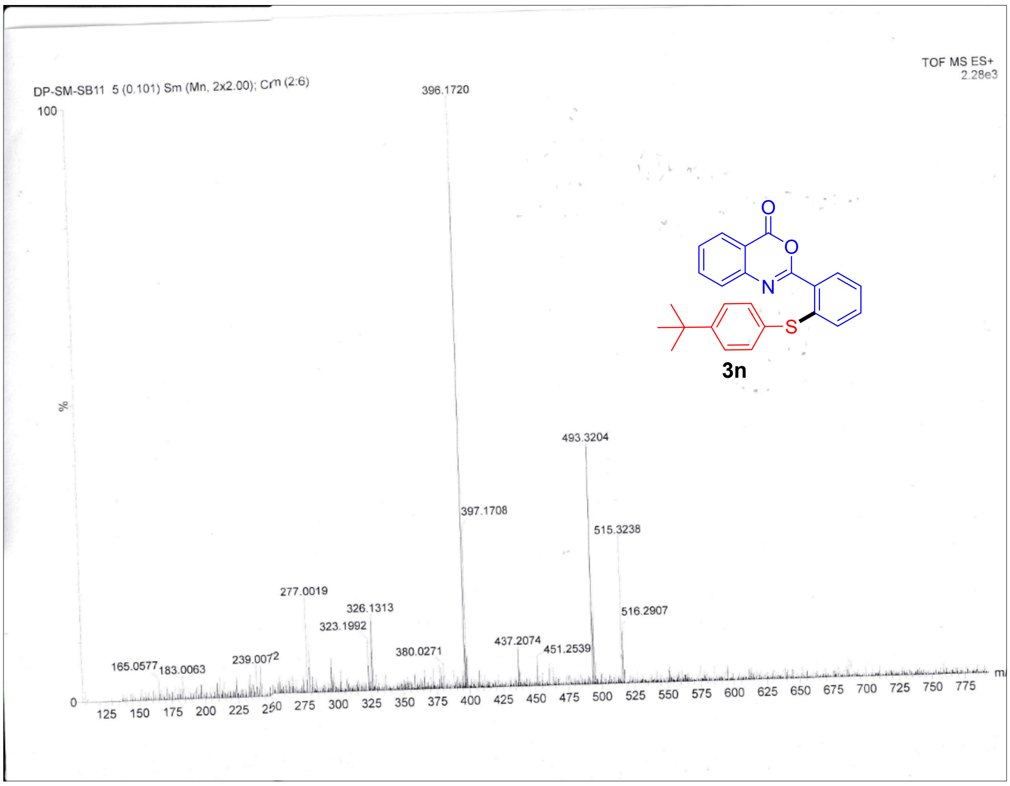

AS-SM-5B-16
AS-SM-5B-16 19 (0.180) Sm (Mn, 2x2.00); Cm (16:31)
TOF MS ES
100
500.0537
493.3113
633.2985
392.0516
501.0566
634.3033
217.0673
417.2812
516.0443
655.2805
211.9857
174.0931
522.0366
331.1742
472.0596
656.2817
757.2934
%
0
O
O
N
PhS

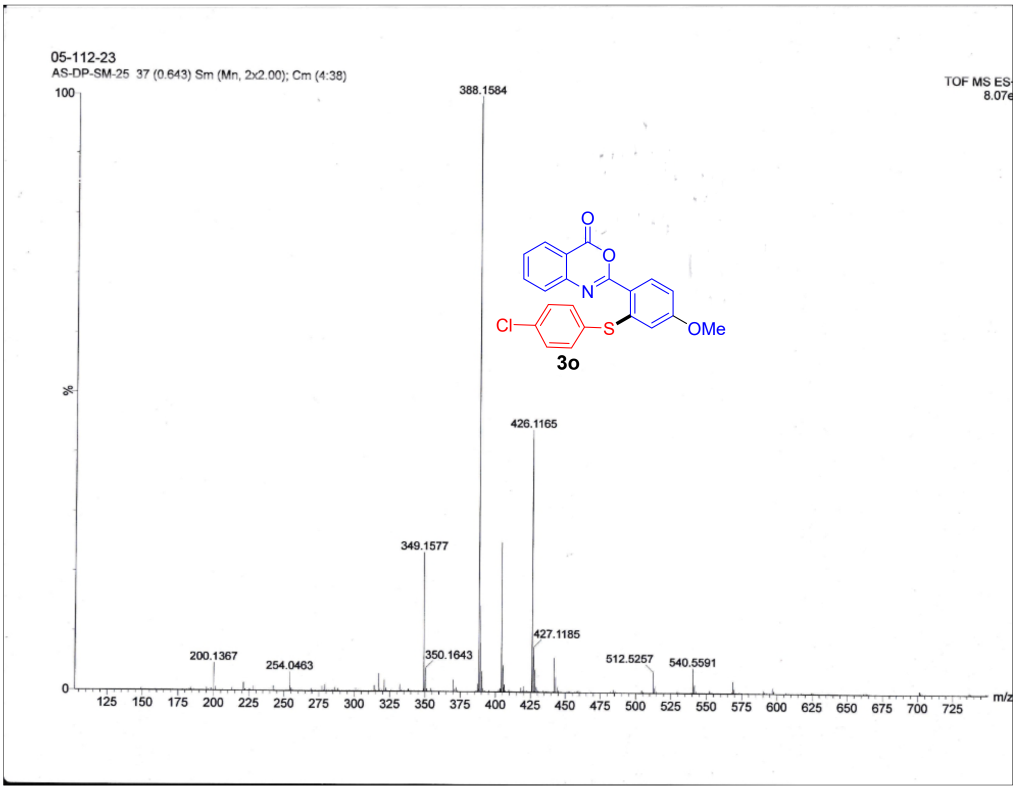
3j

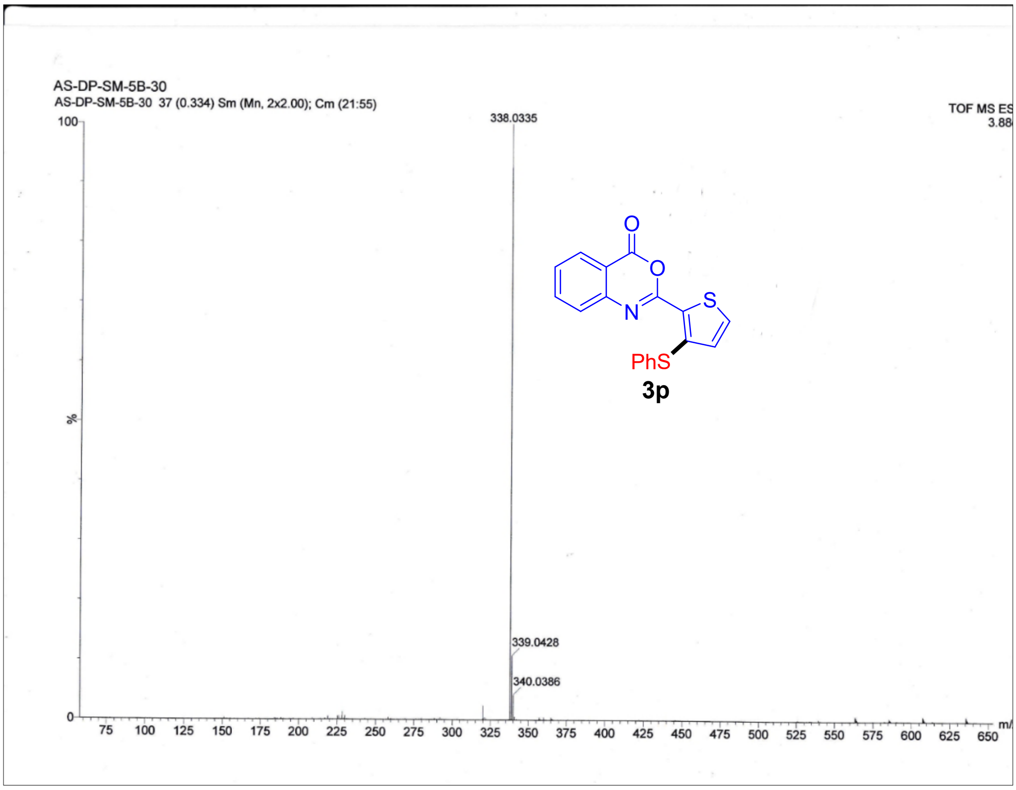

AS-DP-SM-14
AS-DP-SM-14 34 (0.308) Sm (Mn, 2x2.00); Cm (23:69)
TOF MS ES
5.50
100
%
0
350.1145
366.1111
3k
m/z

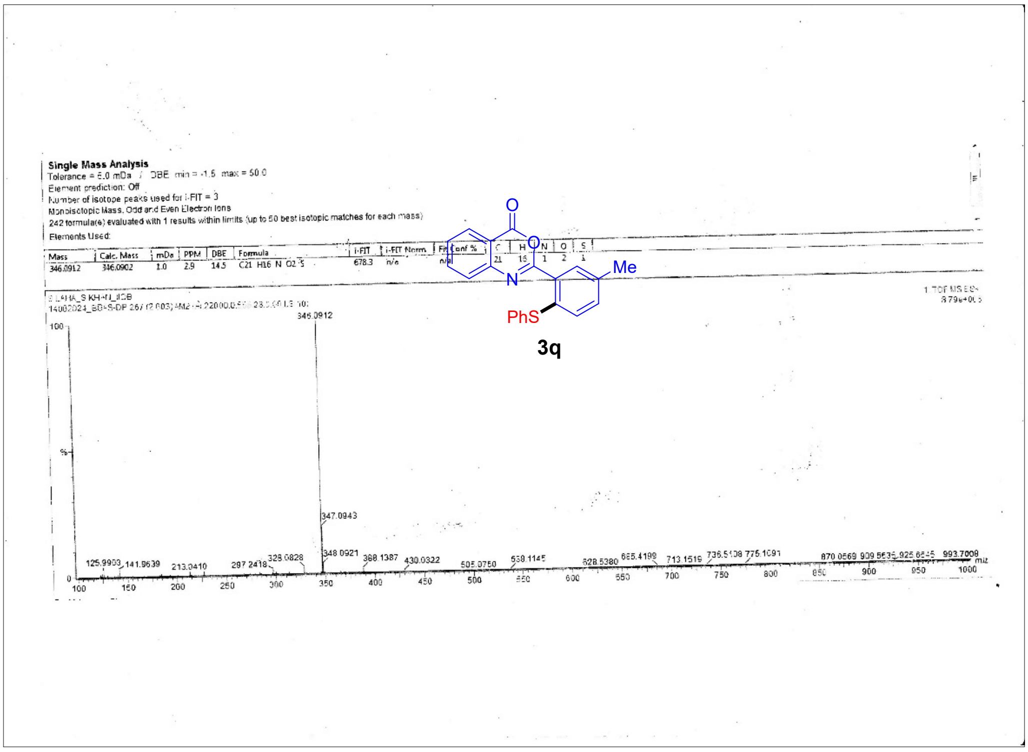

05-10-23
AS-SM-5B-14 4 (0.084) Sm (Mn, 2x2.00); Cm (4:12)
TOF MS ES
1.27e
301.1028
388.0052
366.0249
403.9795
302.1088
315.1252
195.0383
246.9903
202.9992
268.1615
163.0076
242.2458
148.9931
348.0379
413.2393
459.1365
503.1618
547.2280
591.2159
613.2467
653.2490
3l
m/z


AS-SM-5B13 3 (0.068) Sm (Mn, 2x2.00); Cm (3:24)
TOF MS ES
7.92e
100
%
0
346.1084
347.1106
376.1187
338.3572
328.0934
227.0593
468.1364
H3C
S
N
O
O
3m
120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560 580 600 620 640
m/z

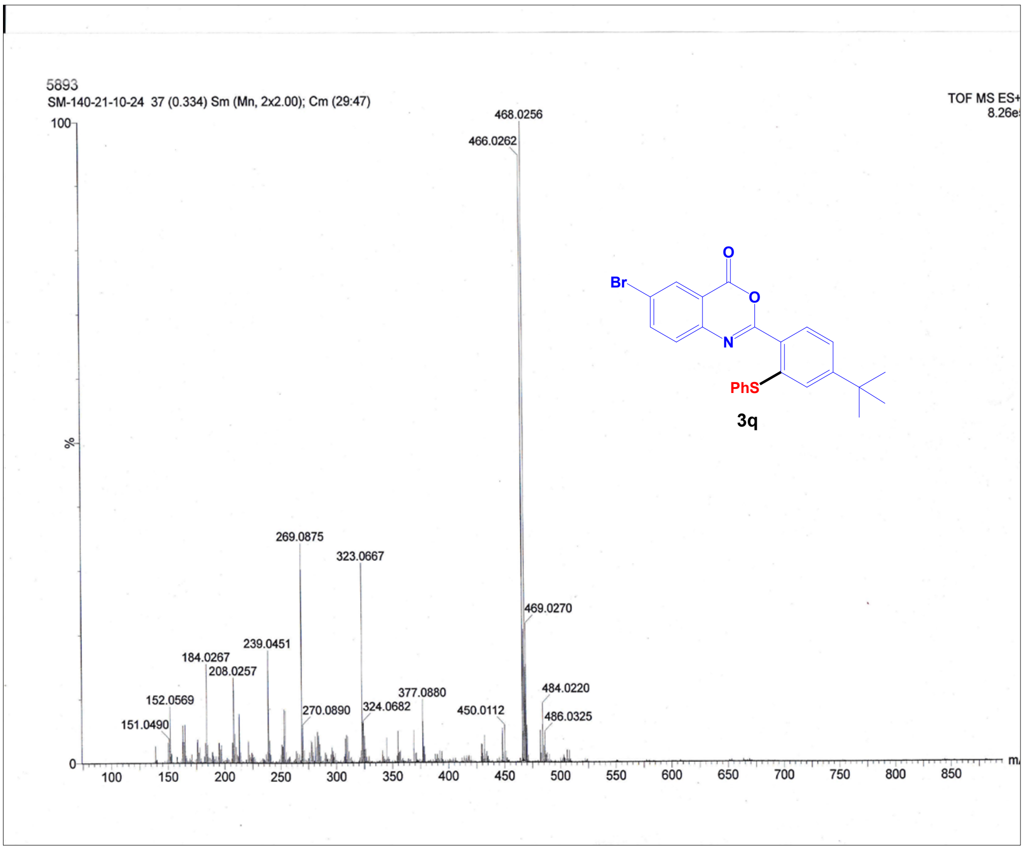

DP-SM-SB11 5 (0.101) Sm (Mn, 2x2.00); Cm (2:6)
TOF MS ES+
2.28e3
100
%
0
396.1720
397.1708
493.3204
515.3238
516.2907
277.0019
326.1313
323.1992
380.0271
437.2074
451.2539
165.0577
183.0063
239.0072
S
N
O
O
3n
125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 625 650 675 700 725 750 775


05-112-23
AS-DP-SM-25 37 (0.643) Sm (Mn, 2x2.00); Cm (4:38)
TOF MS ES
8.07e
388.1584
426.1165
349.1577
427.1185
350.1643
200.1367
254.0463
512.5257
540.5591
Cl
S
OMe
O
O
N
3o
m/z

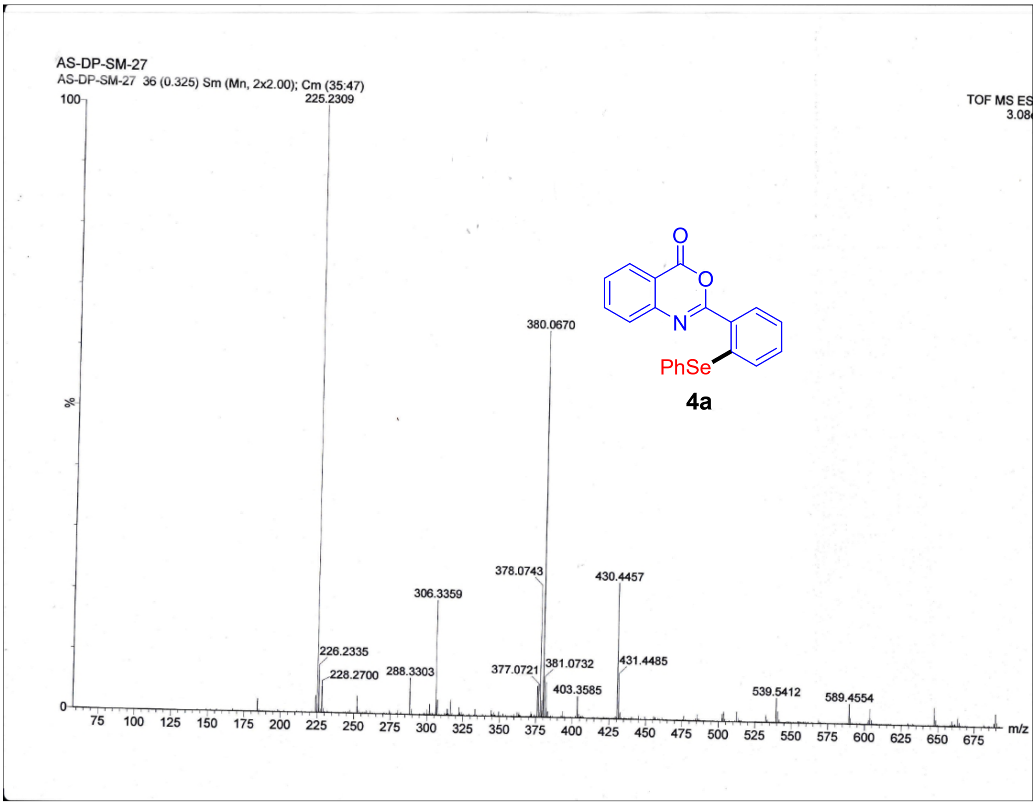

AS-DP-SM-5B-30
AS-DP-SM-5B-30 37 (0.334) Sm (Mn, 2x2.00); Cm (21:55)
TOF MS ES
3.88
338.0335
339.0428
340.0386
O
O
N
S
PhS
3p


Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Odd and Even Electron Ions
242 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
Mass | Calc. Mass | mDa | PPM | DBE | Formula | i-FIT | i-FIT Norm | Fit Conf % | C | H | N | O | S
346.0912 | 346.0902 | 1.0 | 2.9 | 14.5 | C21 H16 N O2 S | 678.3 | n/a | n/a | 21 | 16 | 1 | 2 | 1
346.0912
347.0943
348.0921
m/z
O
N
Me
PhS

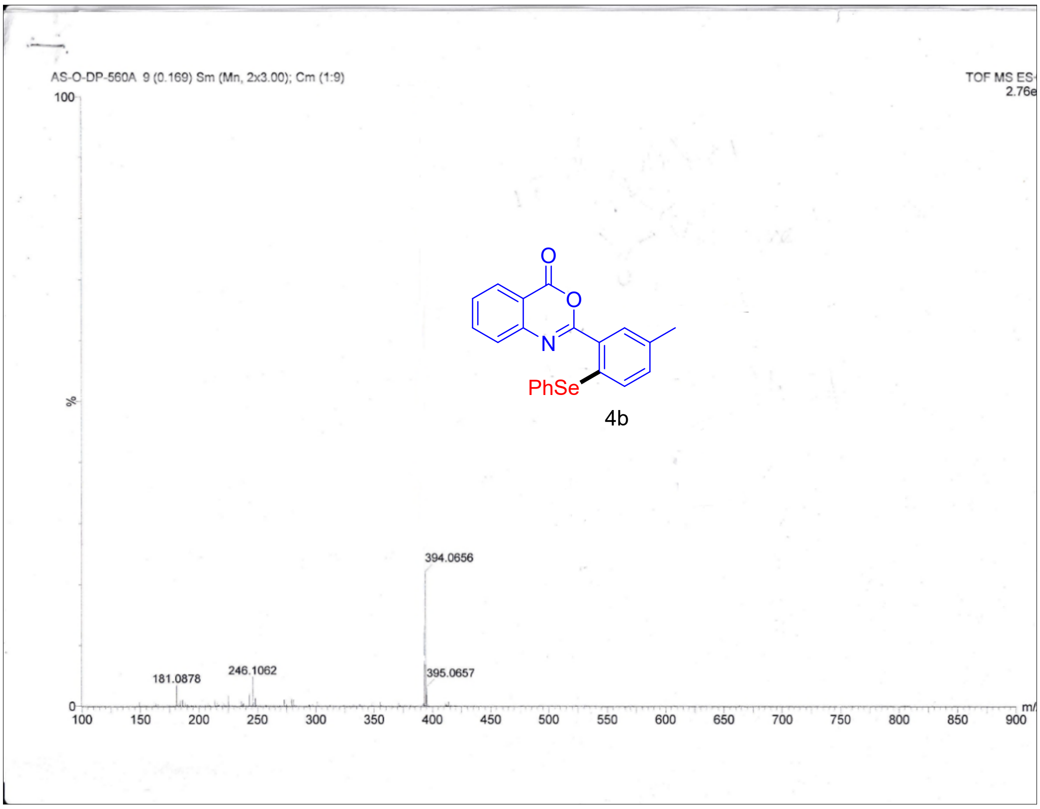
3q


5893
SM-140-21-10-24 37 (0.334) Sm (Mn, 2x2.00); Cm (29:47)
TOF MS ES+
8.26e
100
%
0
468.0256
466.0262
269.0875
323.0667
469.0270
239.0451
184.0267
208.0257
377.0880
484.0220
152.0569
270.0890
324.0682
450.0112
486.0325
151.0490
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
m/
Br
O
O
N
PhS

3q


AS-DP-SM-27
AS-DP-SM-27 36 (0.325) Sm (Mn, 2x2.00); Cm (35:47)
TOF MS ES
3.08
100
%
0
225.2309
380.0670
378.0743
430.4457
306.3359
226.2335
228.2700
288.3303
377.0721
381.0732
431.4485
403.3585
539.5412
589.4554
75
100
125
150
175
200
225
250
275
300
325
350
375
400
425
450
475
500
525
550
575
600
625
650
675
m/z
O
O
N
PhSe

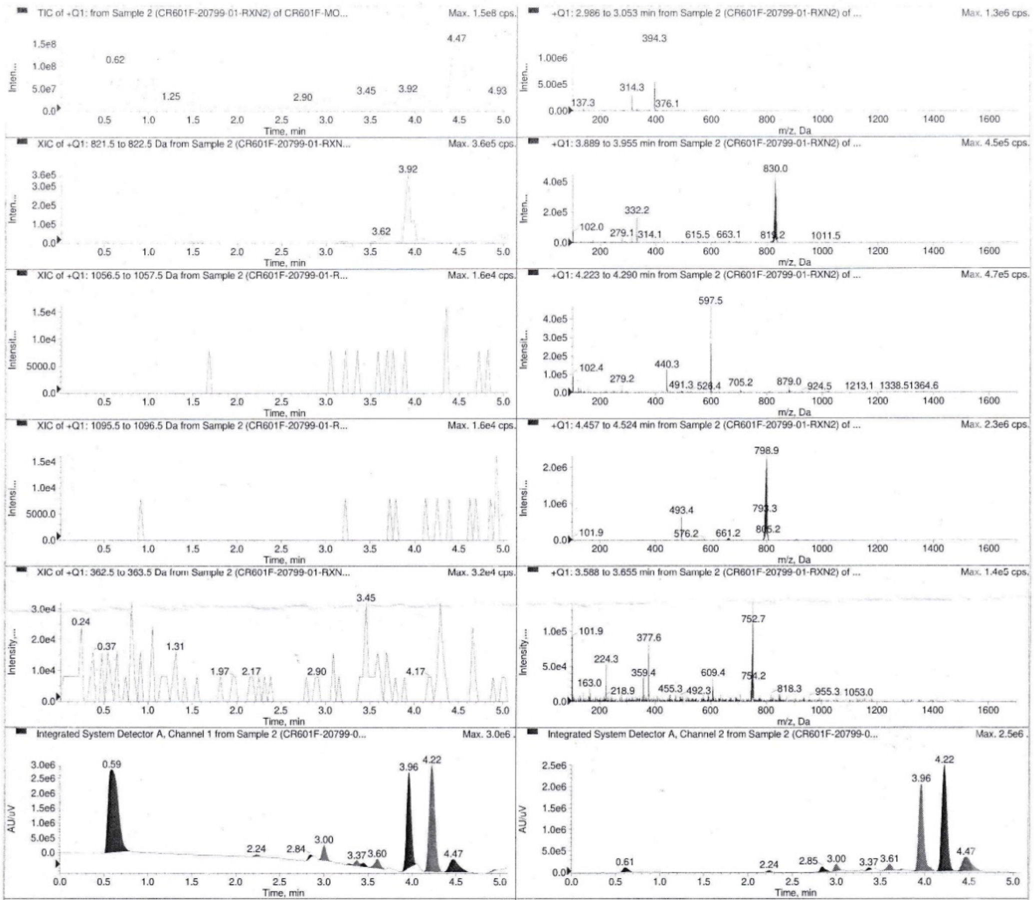
4a



8. LCMS and ESI-MS spectra:

TCG Lifesciences Private Limited Kolkata India

Sample Name: CR601F-20799-01-RXN2 | Acq. Time: 16:48 | Acq. Date: Wednesday, January 17, 2024



Peak List for "Integrated System Detector A, Channel 1 from Sample 2 (CR601F-20799-01-RXN2) of CR601F-...

	Time (min)	Area (counts)	%Area	Height	%Height	Width (min)	Baseline Type
1	0.5853	2.2550e7	38.1385	2.7868e6	24.4751	0.2967	Base to Base
2	2.2376	2.3482e5	0.3972	7.8705e4	0.6912	0.0967	Base to Base
3	2.8446	2.8722e5	0.4858	1.1348e5	0.9967	0.0783	Base to Base
4	2.9991	1.6628e6	2.8123	5.1203e5	4.4970	0.1300	Base to Base
5	3.2886	1.0091e5	0.1707	3.9515e4	0.3470	0.0650	Valley
6	3.3728	5.9517e5	1.0066	1.7074e5	1.4995	0.0967	Valley
7	3.4461	4.0651e5	0.6875	1.1706e5	1.0281	0.1000	Valley
8	3.6048	1.3009e6	2.2002	3.0731e5	2.6990	0.1750	Valley
9	3.9594	1.2069e7	20.4119	3.2266e6	28.3385	0.1583	Base to Base
10	4.2206	1.6585e7	28.0495	3.5852e6	31.4879	0.2150	Base to Base
11	4.4675	3.2046e6	5.4200	4.2627e5	3.7438	0.2733	Base to Base
12	4.9542	1.3001e5	0.2199	2.2331e4	0.1961	0.1083	Base to Base

Peak List for "Integrated System Detector A, Channel 2 from Sample 2 (CR601F-20799-01-RXN2) of CR601F-...

	Time (min)	Area (counts)	%Area	Height	%Height	Width (min)	Baseline Type
1	0.6115	4.5311e5	1.9470	1.0941e5	1.9912	0.1367	Base to Base
2	2.2407	1.2682e5	0.5450	4.2343e4	0.7707	0.0917	Base to Base
3	2.8454	4.9530e5	2.1283	1.2812e5	2.3319	0.1517	Base to Base
4	3.0029	5.2344e5	2.2492	1.5672e5	2.8523	0.1200	Base to Base
5	3.3710	1.4317e5	0.6152	5.3973e4	0.9823	0.0833	Base to Base
6	3.6061	5.4269e5	2.3319	1.4549e5	2.6480	0.1467	Base to Base
7	3.7441	1.8704e4	0.0804	8125.8009	0.1479	0.0517	Base to Base
8	3.9609	8.0099e6	34.4185	2.0398e6	37.1248	0.2383	Base to Base
9	4.2222	1.0538e7	45.2805	2.4822e6	45.1767	0.2067	Base to Base
10	4.4668	2.4212e6	10.4040	3.2824e5	5.9741	0.2700	Base to Base

LCMS MONITORING SAMPLE IN 5 MIN RUN | COLUMN- X-Bridge-C18 (4.6X50mm , 5μm) ACN:NH4OAc | TCGLS/ARD/LCMS18/K72

Channel 1 at wavelength 220 nm
Channel 2 at wavelength 260 nm

Analysed By : Prince Kr.Singh

Checked By

Figure 1. LCMS spectra of the crude reaction mixture (Scheme 4c of manuscript)

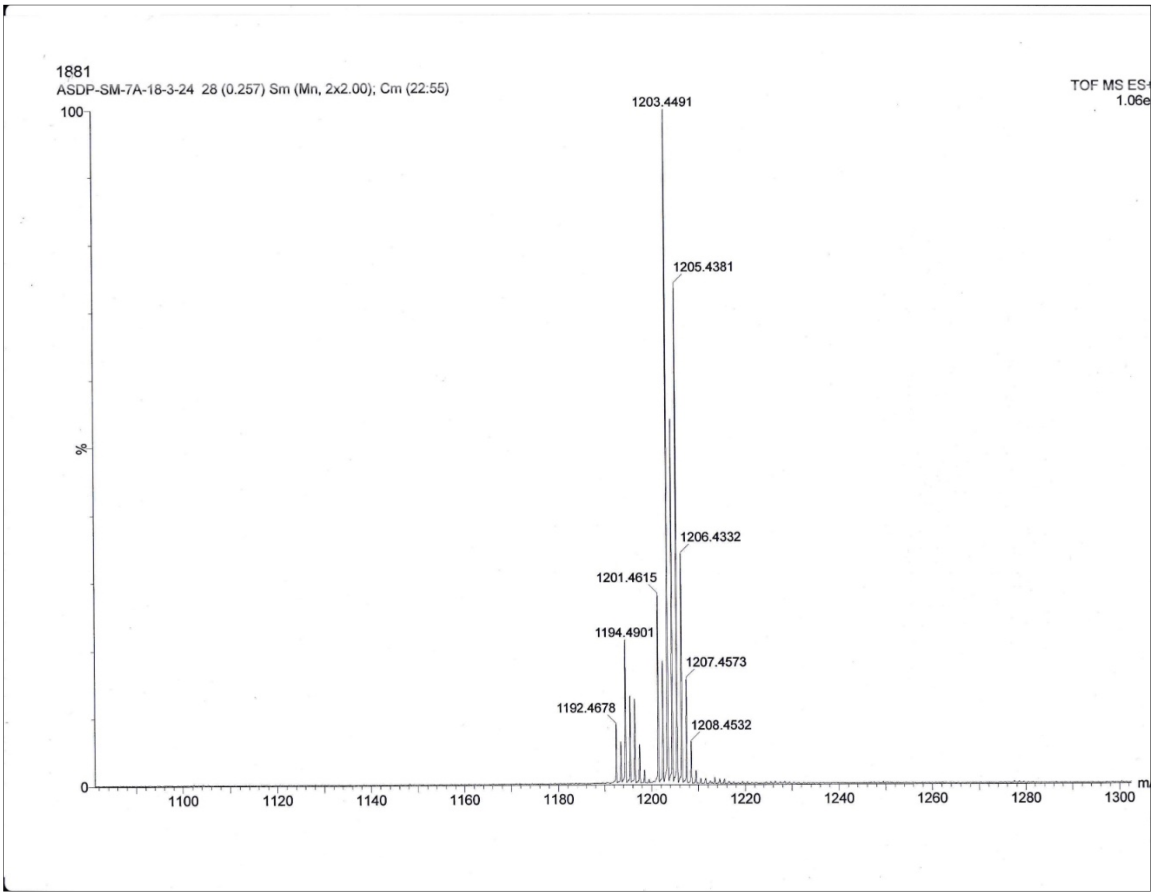


Figure 2. ESI-MS spectra of the crude reaction mixture (Scheme 4c of manuscript)

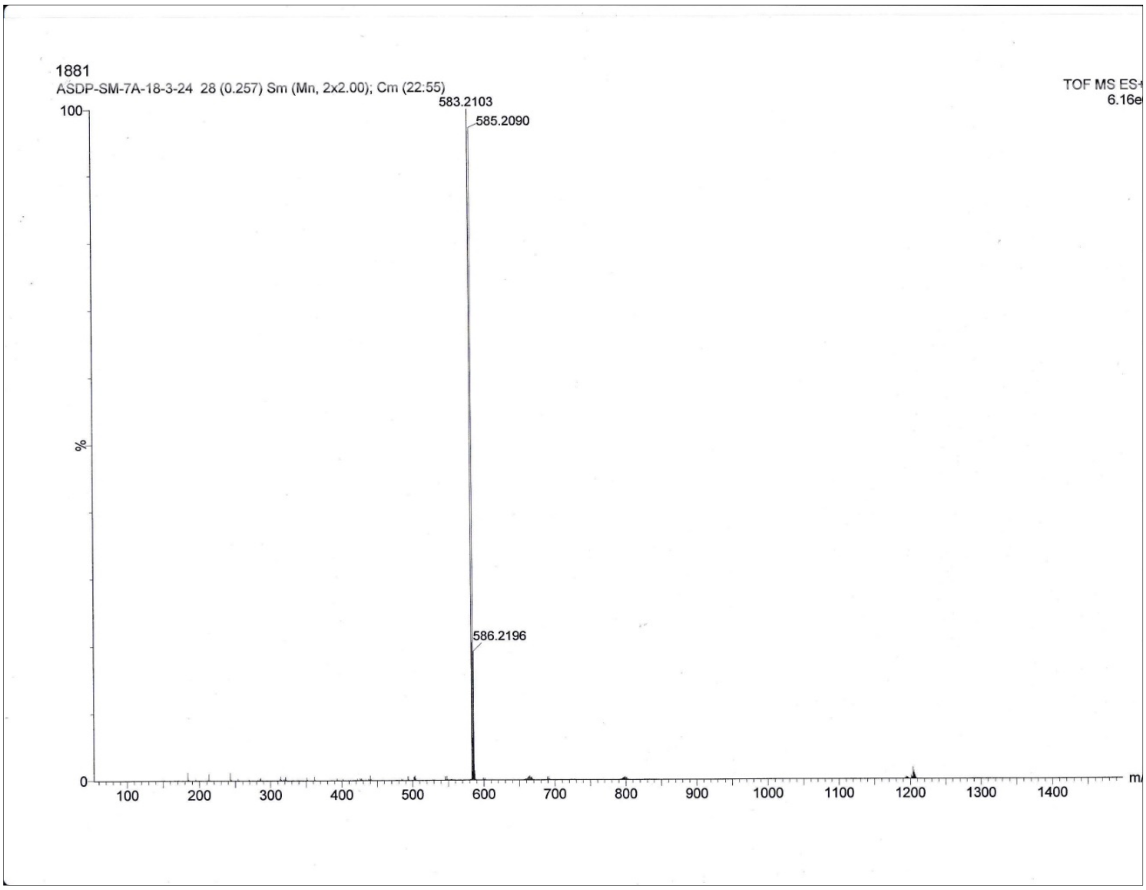
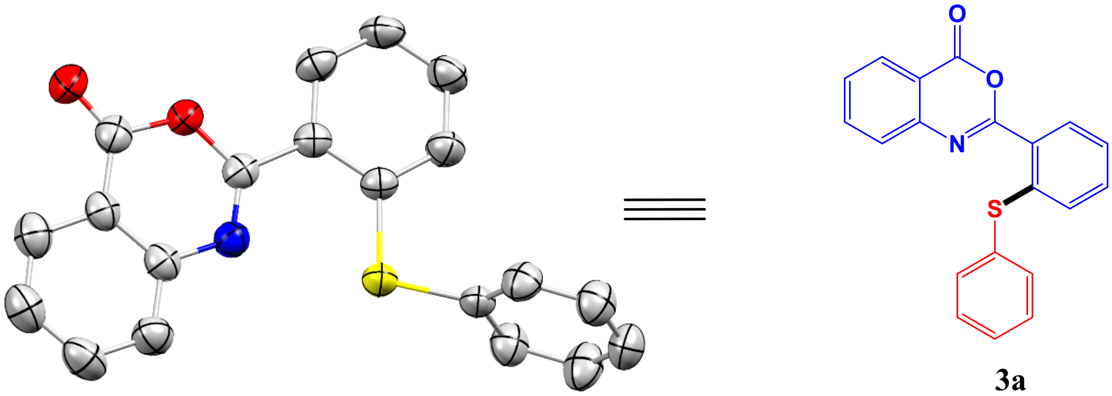


Figure 3. ESI-MS spectra of the crude reaction mixture (Scheme 4c of manuscript)

9. X-ray Crystallography Data:



3a

Figure 4. ORTEP diagram of the crystal structure of **3a** at 50% probability level

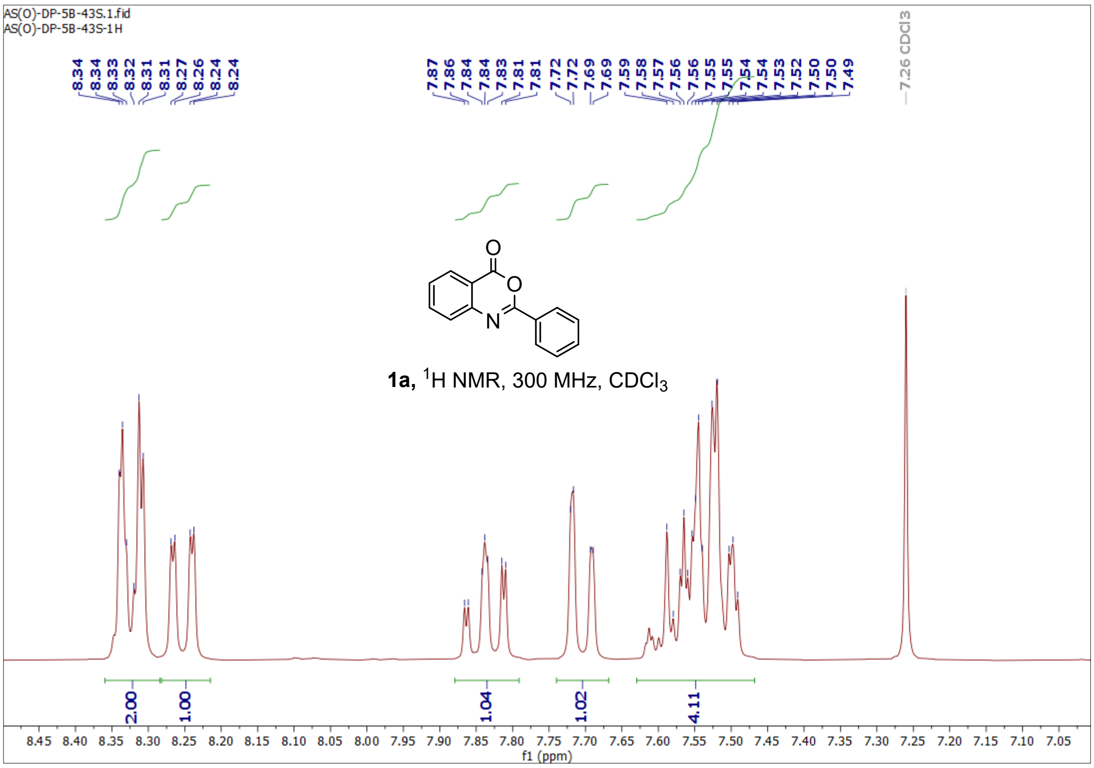
Details of the crystal structure investigation can be obtained from the Cambridge crystallographic data centre, 12 Union Road, Cambridge, CB2 1EZ, UK. (**3a: CCDC deposition no 2302174**).

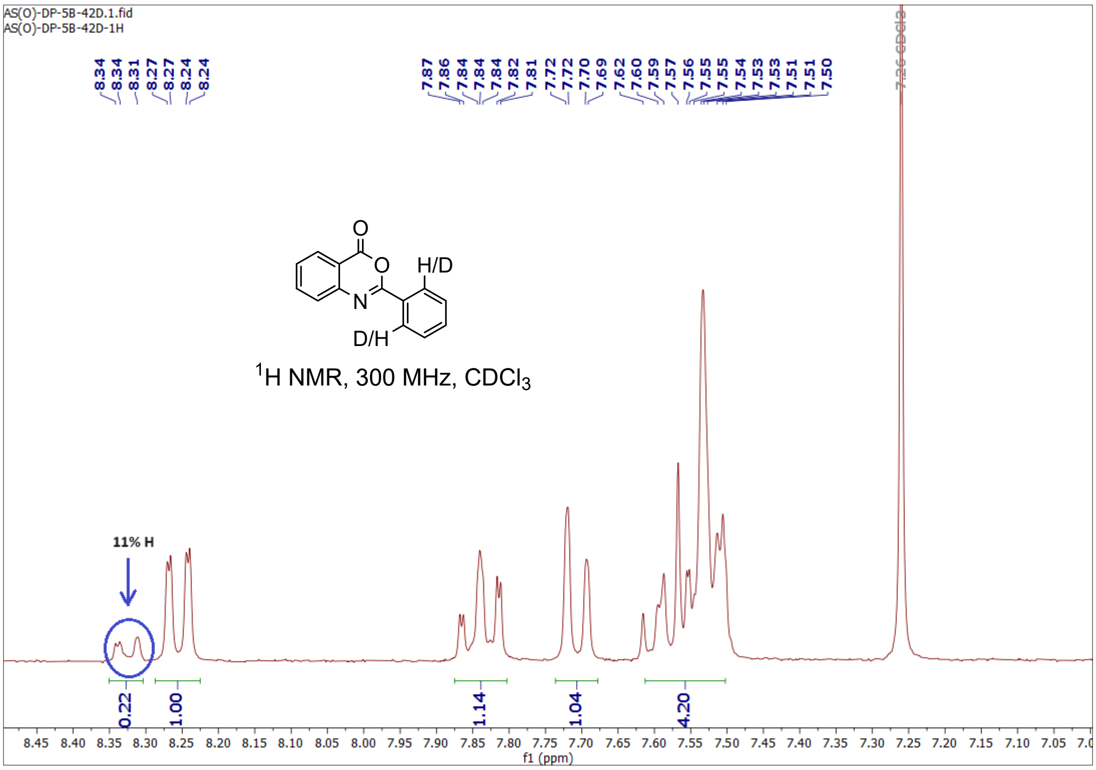
Crystallographic data and structural refinement parameters for 3a

	3a
Formula	$C_{20}H_{13}NO_2S$
Formula weight	331.31
Crystal system	triclinic
Space group	P-1
a/ Å	7.8169(5)
b/Å	8.3525(6)
c/ Å	12.4587(8)
α/°	81.958(2)
β/°	82.535(2)
γ/°	78.805(2)
V/ Å^3	785.68(9)
Z	2
D_c/ g cm^{-3}	1.401
μ /mm^{-1}	0.218
F_{000}	344
θ range/°	2.5, 27.5
reflections collected	24491
unique reflections	3566
reflections $I > 2\sigma(I)$	2731
R_{int}	0.088
goodness-of-fit (F^2)	1.14
R_1 ($I > 2\sigma$(I)) [a]	0.0666
wR_2($I > 2\sigma$(I)) [a]	0.1812
$\Delta\rho$ min / max /e Å^3	-0.27, 0.25

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{½}$

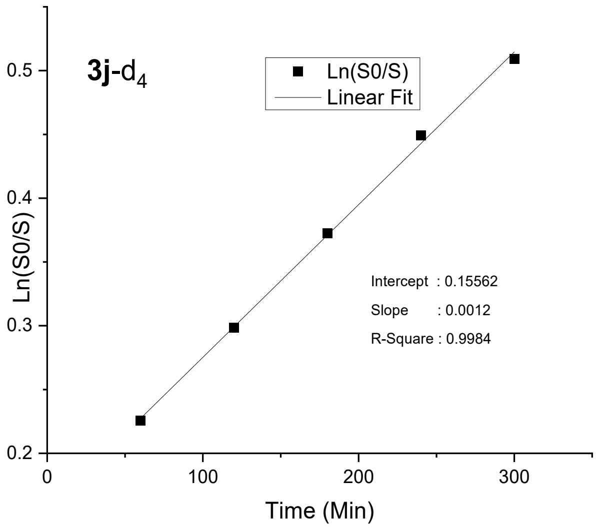
10. ^{1}H NMR spectra of deuterium labelling experiment.



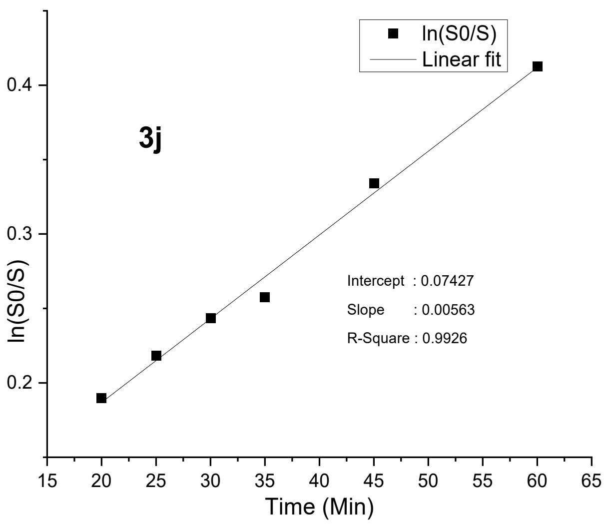


11. KIE Experiments

2-C_6D_5-benzoxazinone substrate



2-C_6H_5-benzoxazinone substrate



K_H/K_D = 0.00563/0.0012 = 4.69

$$\frac{K_H}{K_D} = \frac{0.00563}{0.0012} = 4.69$$

HPLC method has been used to determine the yields of the compounds at different time intervals.

12/9/2024 5:19 PM Chromatogram C:\USERS\KM\DESKTOP\NEW FOLDER\INSTRUMENT 1 - 12_6_2024 5_41_44 PM.PRM Page 1 of 1

DEPARTMENT OF CHEMISTRY

JADAVPUR UNIVRSITY

KOLKATA

Column	: Venusil XPB C18(4.8x250mm), 100Ans.	Detection	: 254 nm
Mobile Phase	: ACN: WATER85:15	Temperature	: RT
Flow Rate	: 2.0 mL/min	Pressure	:
Note	: AS 70		
Autostop	: 5.00 min	External Start	: Start - Restart, Down
Detector 1	: Channel 1	Range 1	: Bipolar, 10000 mV, 10 Samp. per Sec.
Subtraction Chromatogram	: (None)	Matching	: No Change

Base	: Not Used	Calibration File	: None	Calculation	: Uncal
Scale Factor	: Not Used	Units After Scaling	: Not Used	Uncal. Response	: 0
Unretained Time	: 0.00 min	Column Length	: 50.00 mm	Column Calc.	: From Width at 50% of Height
Result Table Reports	: All Peaks	Hide ISTD Peak	: Enabled		

12. References

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