Supporting Information

Photocatalytic Deoxygenation of Sulfoxides Using Visible Light: Mechanistic Investigations and Synthetic Applications

Aimee K. Clarke,[‡] Alison Parkin, Richard J. K. Taylor,* William P. Unsworth* and James A. Rossi-Ashton[‡]*

Department of Chemistry, University of York, Heslington, York, U.K., YO10 5DD

william.unsworth@york.ac.uk, richard.taylor@york.ac.uk, james.rossiashton@york.ac.uk

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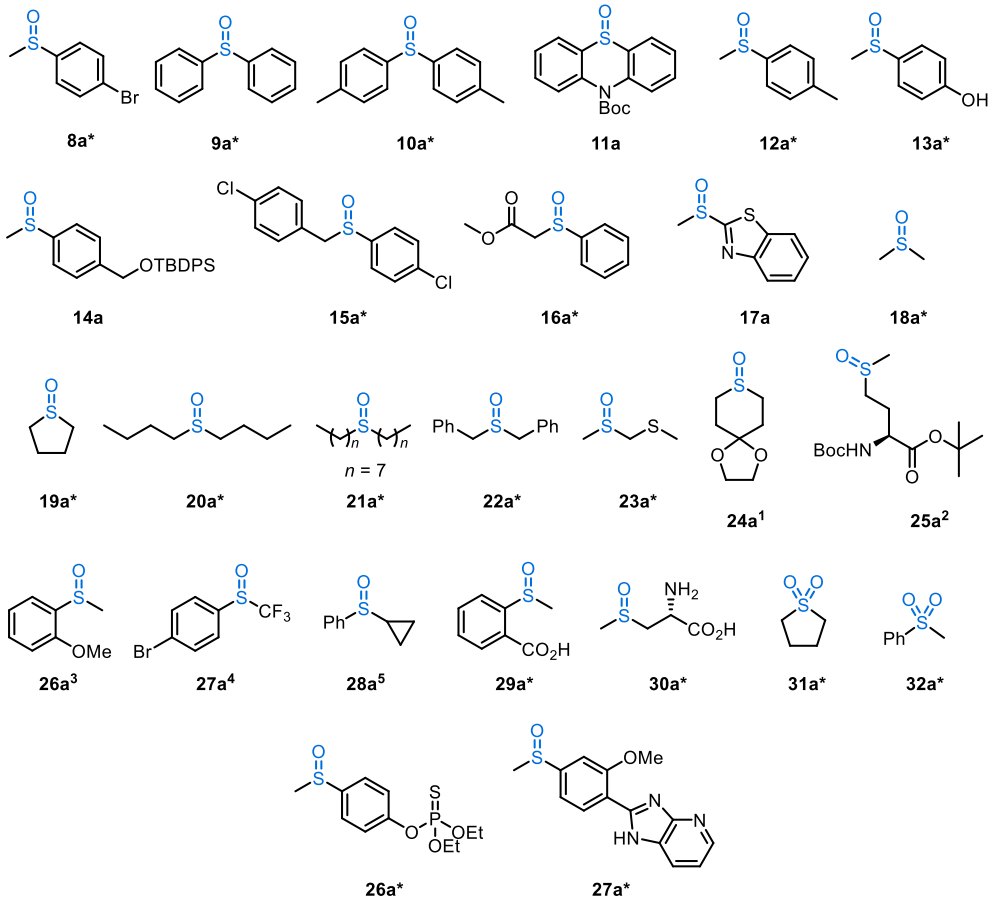
General Information

Except where stated, all reagents were purchased from commercial sources and used without further purification. Anhydrous CH_2Cl_2 and toluene were obtained from an Innovative Technology Inc. PureSolv® solvent purification system. Anhydrous THF was obtained by distillation over sodium benzophenone ketyl immediately before use. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL ECX400 or JEOL ECS400 spectrometer, operating at 400 MHz and 100 MHz. All spectral data was acquired at 295 K unless stated otherwise. Chemical shifts (δ) are quoted in parts per million (ppm). The residual solvent peaks, δ_H 7.26 and δ_c 77.16 for $CDCl_3$ were used as a reference. Coupling constants (*J*) are reported in Hertz (Hz) to the nearest 0.1 Hz. The multiplicity abbreviations used are: br s broad singlet, s singlet, d doublet, t triplet, q quartet, dt doublet of triplets, m multiplet. Signal assignment was achieved by analysis of DEPT, COSY, HMBC and HSQC experiments where required. Infrared (IR) spectra were recorded on a PerkinElmer UATR 2 spectrometer as a thin film dispersed from either CH_2Cl_2 or $CDCl_3$. Mass spectra (high-resolution) were obtained by the University of York Mass Spectrometry Service, using Electrospray Ionisation (ESI) or Atmospheric Pressure Chemical Ionisation (APCI) on a Bruker Daltonics, Micro-tof spectrometer. Melting points were determined using Gallenkamp apparatus. Thin layer chromatography was carried out on Merck silica gel $60F_{254}$ pre-coated aluminium foil sheets and were visualised using UV light (254 nm) and stained with basic aqueous potassium permanganate or vanillin. Flash column chromatography was carried out using slurry packed Fluka silica gel (SiO_2), 35–70 μm, 60 Å, under a light positive pressure, eluting with the specified solvent system.

List of starting materials

All the starting materials used in this publication are listed below. Commercially available starting materials (denoted with a *) were used as supplied, those with a reference number are known compounds prepared via the cited literature method, while for all others, preparative details and spectroscopic characterization data are provided.



8a* **9a*** **10a*** **11a** **12a*** **13a***

14a **15a*** **16a*** **17a** **18a***

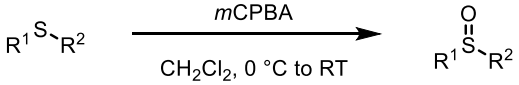
19a* **20a*** **21a*** **22a*** **23a*** **24a**[1] **25a**[2]

26a[3] **27a**[4] **28a**[5] **29a*** **30a*** **31a*** **32a***

26a* **27a***

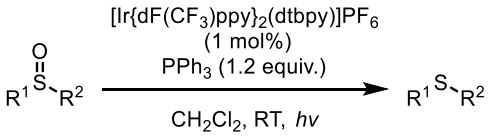
General procedures

General procedure A – Sulfoxide preparation



To a solution of sulfide (1.00 mmol) in anhydrous CH_2Cl_2 (3 mL) at 0 °C was added 3-chloroperbenzoic acid (1.20 mmol) portionwise. The reaction mixture was left to gradually warm to RT and stirred overnight. The reaction was quenched by the addition of sat. aq. $NaHCO_3$ (1 mL) and stirred for 5 min. Following this, the reaction mixture was concentrated *in vacuo* and purified by column chromatography to afford the sulfoxide product.

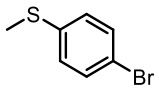
General procedure B – Sulfoxide reduction



To an 8 mL vial equipped with a PTFE septum and a magnetic stirrer bar was added $[Ir\{dF(CF_3)ppy\}_2(dtbpy)]PF_6$ (0.003 mmol, 0.01 equiv.), PPh_3 (0.36 mmol, 1.2 equiv.) and sulfoxide (if solid, 0.30 mmol, 1.0 equiv.). The reaction vessel was purged by alternating vacuum and argon three times before anhydrous and degassed CH_2Cl_2 (1.5 mL) was added. Sulfoxide (if liquid, 0.30 mmol, 1.0 equiv.) was added and the septum additionally sealed with paraffin film. The reaction was irradiated with a 60 W blue LED floodlight for 24 h, with rapid stirring and cooling from a small fan to maintain an ambient temperature. The reaction mixture was then directly poured on to silica and purified by column chromatography affording the desired sulfide product.

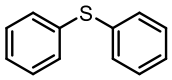
Compound characterisation data and procedures

(4-Bromophenyl)(methyl)sulfane (8b)



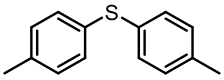
Prepared according to general procedure B using [Ir{dF(CF$_3$)ppy}$_2$(dtbpy)]PF$_6$ (3.4 mg, 0.003 mmol), PPh$_3$ (94.6 mg, 0.36 mmol) and 1-bromo-4-(methylsulfinyl)benzene **8a** (65.7 mg, 0.30 mmol) in anhydrous CH_2Cl_2 (1.5 mL). Purification by flash chromatography on silica gel (100% pentane, then 9:1 pentane:Et_2O) afforded the title compound **8b** as a white solid (57.0 mg, 94% yield); mp 34–36 °C; R_f 0.45 (9:1 pentane:Et_2O); δ_H (400 MHz, $CDCl_3$) 7.39 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 2.46 (s, 3H); δ_C (100 MHz, $CDCl_3$) 137.8, 131.9, 128.2, 118.7, 16.1. Spectroscopic data is consistent with those reported in the literature.[6]

Diphenylsulfane (9b)



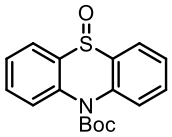
Prepared according to general procedure B using [Ir{dF(CF$_3$)ppy}$_2$(dtbpy)]PF$_6$ (3.4 mg, 0.003 mmol), PPh$_3$ (94.6 mg, 0.36 mmol) and sulfinyldibenzene **9a** (60.7 mg, 0.30 mmol) in anhydrous CH_2Cl_2 (1.5 mL). Purification by flash chromatography on silica gel (99:1 pentane:Et_2O) afforded the title compound **9b** as a clear and colourless oil (44.6 mg, 80% yield); R_f 0.53 (99:1 pentane:Et_2O); δ_H (400 MHz, $CDCl_3$) 7.39–7.28 (m, 8H), 7.28–7.23 (m, 2H); δ_C (100 MHz, $CDCl_3$) 135.9, 131.2, 129.3, 127.2; HRMS (APCI$^+$): Found: 187.057105; $C_{12}H_{11}S^+$ (MH^+) Requires 187.057598 (2.6 ppm error). Spectroscopic data is consistent with those reported in the literature.[7]

Di-*p*-tolylsulfane (10b)



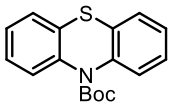
Prepared according to general procedure B using [Ir{dF(CF$_3$)ppy}$_2$(dtbpy)]PF$_6$ (3.4 mg, 0.003 mmol), PPh$_3$ (94.6 mg, 0.36 mmol) and 4,4'-sulfinylbis(methylbenzene) **10a** (69.1 mg, 0.30 mmol) in anhydrous CH_2Cl_2 (1.5 mL). Purification by flash chromatography on silica gel (100% pentane, then 99:1 pentane:Et_2O) afforded the title compound **10b** as a white solid (62.3 mg, 97% yield); mp 53–55 °C; R_f 0.22 (100% pentane); δ_H (400 MHz, $CDCl_3$) 7.24 (d, *J* = 8.0 Hz, 4H), 7.11 (d, *J* = 8.0 Hz, 4H), 2.34 (s, 6H); δ_C (100 MHz, $CDCl_3$) 137.0, 132.8, 131.2, 130.0, 21.2; HRMS (APCI$^+$): Found: 215.08827; $C_{14}H_{15}S^+$ (MH^+) Requires 215.088898 (3.1 ppm error). Spectroscopic data is consistent with those reported in the literature.[8]

***tert*-Butyl 10*H*-phenothiazine-10-carboxylate 5-oxide (11a)**



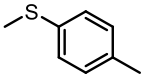
Prepared according to general procedure A using *tert*-butyl 10*H*-phenothiazine-10-carboxylate **11b*** (1.20 g, 4.00 mmol) and *m*CPBA (830 mg, 4.80 mmol) in anhydrous CH_2Cl_2 (12 mL). Purification by flash chromatography on silica gel (6:4 hexane:Et_2O with 2% AcOH added to eluent, then 6:4 Et_2O:hexane) afforded the title compound **11a** as a white solid (1.00 g, 79% yield); mp 146–148 °C; R_f 0.30 (6:4 Et_2O:hexane); ν_{max} (thin film)/cm^{-1} 2978, 1717, 1475, 1458, 1322, 1295, 1249, 1232, 1153, 1098, 1021, 843, 764, 728; δ_H (400 MHz, $CDCl_3$) 7.84 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.73 (dd, *J* = 8.0, 1.3 Hz, 2H), 7.49 (ddd, *J* = 7.6, 7.6, 1.7 Hz, 2H), 7.43 (ddd, *J* = 7.6, 7.6, 1.3 Hz, 2H), 1.53 (s, 9H); δ_C (100 MHz, $CDCl_3$) 151.5, 138.7, 133.5, 130.2, 126.9, 126.3, 124.2, 83.6, 28.3; HRMS (ESI$^+$): Found: 316.1000; $C_{17}H_{18}NO_3S^+$ (MH^+) Requires 316.1002 (0.7 ppm error). *This material is commercially available.

***tert*-Butyl 10*H*-phenothiazine-10-carboxylate (11b)**



Prepared according to general procedure B using [Ir{dF(CF$_3$)ppy}$_2$(dtbpy)]PF_6 (3.4 mg, 0.003 mmol), PPh_3 (94.6 mg, 0.36 mmol) and *tert*-butyl 10*H*-phenothiazine-10-carboxylate 5-oxide **11a** (94.6 mg, 0.30 mmol) in anhydrous CH_2Cl_2 (1.5 mL). Purification by flash chromatography on silica gel (95:5 pentane:Et_2O) afforded the title compound **11b** as a white solid (88.8 mg, 99% yield); mp 110–112 °C; R_f 0.42 (8:2 pentane:Et_2O); δ_H (400 MHz, $CDCl_3$) 7.53 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.35 (dd, *J* = 7.6, 1.4 Hz, 2H), 7.30–7.24 (m, 2H), 7.15 (ddd, *J* = 7.6, 1.4, 1.4 Hz, 2H), 1.49 (s, 9H); δ_C (100 MHz, $CDCl_3$) 152.6, 138.8, 132.3, 127.6, 127.3, 126.7, 126.2, 82.2, 28.3. Spectroscopic data is consistent with those reported in the literature.[9]

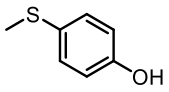
Methyl(*p*-tolyl)sulfane (12b)



Prepared according to general procedure B using [Ir{dF(CF$_3$)ppy}$_2$(dtbpy)]PF_6 (3.4 mg, 0.003 mmol), PPh_3 (94.6 mg, 0.36 mmol) and 1-methyl-4-(methylsulfinyl)benzene **12a** (46.3 mg, 0.30 mmol) in anhydrous CH_2Cl_2 (1.5 mL). Purification by flash chromatography on silica gel (100% pentane, then 9:1 pentane:Et_2O) afforded the title compound **12b** as a pale yellow oil (29.5 mg, 71% yield); R_f 0.57 (9:1 pentane:Et_2O); δ_H (400 MHz, $CDCl_3$) 7.21–7.17 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 2.47 (s, 3H), 2.32 (s, 3H); δ_C (100 MHz, $CDCl_3$) 135.2, 134.8, 129.7, 127.4,

21.1, 16.7; HRMS (APCI$^+$): Found: 139.057984; $C_8H_{11}S^+$ (MH^+) Requires 139.057598 (2.8 ppm error). Spectroscopic data is consistent with those reported in the literature.[10]

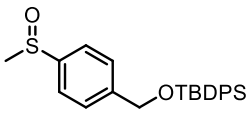
4-(Methylthio)phenol (13b)



To an 8 mL vial equipped with a PTFE septum and a magnetic stirrer bar was added $Ir[(dF(CF_3)ppy)_2(d(CF_3)bpy)]PF_6$ (3.4 mg, 0.003 mmol), PPh_3 (94.6 mg, 0.36 mmol) and 4-(methylsulfinyl)phenol **13a** (46.9 mg, 0.30 mmol). The reaction vessel was purged by alternating vacuum and argon three times before anhydrous and degassed CH_2Cl_2 (1.5 mL) was added and the septum additionally sealed with paraffin film. The reaction was irradiated with a 60 W blue LED floodlight for 4 days, with rapid stirring and cooling from a small fan to maintain an ambient temperature. The reaction mixture was then directly poured on to silica and purified by column chromatography to afford the title compound **13b** as a white solid (33 mg, 78% yield); mp 77–79 °C; R_f 0.32 (8:2 pentane:Et_2O); δ_H (400 MHz, $CDCl_3$) 7.23 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 4.70 (br s, 1H), 2.44 (s, 3H); δ_C (100 MHz, $CDCl_3$) 154.2, 130.5, 129.0, 116.2, 18.2. Spectroscopic data is consistent with those reported in the literature.[11]

Compound **13b** was also prepared according to general procedure B using $[Ir\{dF(CF_3)ppy\}_2(dtbpy)]PF_6$ (3.4 mg, 0.003 mmol), PPh_3 (94.6 mg, 0.36 mmol) and 4-(methylsulfinyl)phenol **13a** (46.9 mg, 0.30 mmol) in anhydrous CH_2Cl_2 (1.5 mL). Purification by flash chromatography on silica gel (8:2 pentane:Et_2O) afforded the title compound **13b** as a white solid (24.9 mg, 59% yield).

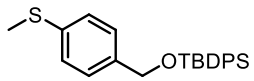
***tert*-Butyl((4-(methylsulfinyl)benzyl)oxy)diphenylsilane (14a)**



To a solution of (4-(methylsulfinyl)phenyl)methanol (511 mg, 3.00 mmol) and imidazole (245 mg, 3.60 mmol) in anhydrous CH_2Cl_2 (3 mL) at 0 °C was added *tert*-butyl(chloro)diphenylsilane (0.9 mL, 3.30 mmol) dropwise. The reaction mixture was warmed to RT and stirred overnight. The reaction mixture was then concentrated *in vacuo* and purified by flash column chromatography on silica gel (7:3 EtOAc:hexane, then 8:2 EtOAc:hexane, then 100% EtOAc) to afford the title compound **14a** as a clear and colourless oil (906 mg, 74% yield); R_f 0.30 (8:2 EtOAc:hexane); ν_{max} (thin film)/cm^{-1} 2931, 2857, 1428, 1111, 1085, 1054, 1014, 824, 702; δ_H (400 MHz, $CDCl_3$) 7.71–7.65 (m, 4H), 7.64–7.60 (m, 2H), 7.53–7.48 (m, 2H), 7.47–7.35 (m, 6H), 4.82 (s, 2H), 2.73 (s, 3H), 1.11 (s,

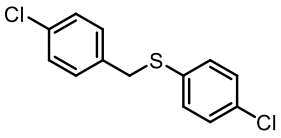
9H); δ_C (100 MHz, $CDCl_3$) 144.7, 144.1, 135.7, 133.2, 130.0, 127.9, 126.9, 123.7, 65.1, 44.1, 27.0, 19.4; HRMS (ESI^+): Found: 409.1650; $C_{24}H_{29}O_2SSi^+$ (MH^+) Requires 409.1652 (0.5 ppm error).

***tert*-Butyl((4-(methylthio)benzyl)oxy)diphenylsilane (14b)**



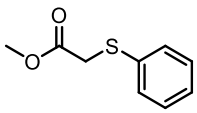
Prepared according to general procedure B using [Ir{dF(CF_3)ppy}$_2$(dtbpy)]PF_6 (3.4 mg, 0.003 mmol), PPh_3 (94.6 mg, 0.36 mmol) and *tert*-butyl((4-(methylsulfinyl)benzyl)oxy)diphenylsilane **14a** (123 mg, 0.30 mmol) in anhydrous CH_2Cl_2 (1.5 mL). Purification by flash chromatography on silica gel (9:1 hexane:CH_2Cl_2, then 8:2 hexane:CH_2Cl_2) afforded the title compound **14b** as a clear and colourless oil (106 mg, 90% yield); R_f 0.38 (8:2 hexane:CH_2Cl_2); ν_{max} (thin film)/cm^{-1} 2930, 2856, 1427, 1106, 1082, 823, 798, 740, 699, 611; δ_H (400 MHz, $CDCl_3$) 7.76–7.68 (m, 4H), 7.49–7.38 (m, 6H), 7.32–7.22 (m, 4H), 4.76 (s, 2H), 2.51 (s, 3H), 1.12 (s, 9H); δ_C (100 MHz, $CDCl_3$) 138.3, 136.7, 135.7, 133.6, 129.8, 127.9, 126.9, 126.8, 65.3, 27.0, 19.4, 16.3; HRMS (ESI^+): Found: 415.1515; $C_{24}H_{28}NaOSSi^+$ (MH^+) Requires 415.1522 (1.7 ppm error).

(4-Chlorobenzyl)(4-chlorophenyl)sulfane (15b)



Prepared according to general procedure B using [Ir{dF(CF_3)ppy}$_2$(dtbpy)]PF_6 (3.4 mg, 0.003 mmol), PPh_3 (94.6 mg, 0.36 mmol) and 1-chloro-4-((4-chlorobenzyl)sulfinyl)benzene **15a** (85.6 mg, 0.30 mmol) in anhydrous CH_2Cl_2 (1.5 mL). Purification by flash chromatography on silica gel (100% pentane) afforded the title compound **15b** as a white solid (76.6 mg, 95% yield); mp 62–64 °C; R_f 0.26 (100% pentane); δ_H (400 MHz, $CDCl_3$) 7.27–7.15 (m, 8H), 4.02 (s, 2H); δ_C (100 MHz, $CDCl_3$) 135.9, 134.1, 133.2, 133.0, 132.0, 130.2, 129.2, 128.8, 38.9. Spectroscopic data is consistent with those reported in the literature.[12]

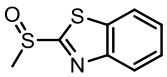
Methyl 2-(phenylthio)acetate (16b)



Prepared according to general procedure B using [Ir{dF(CF_3)ppy}$_2$(dtbpy)]PF_6 (3.4 mg, 0.003 mmol), PPh_3 (94.6 mg, 0.36 mmol) and methyl 2-(phenylsulfinyl)acetate **16a** (59.5 mg, 0.30 mmol) in anhydrous CH_2Cl_2 (1.5 mL). Purification by flash chromatography on silica gel (9:1 pentane:Et_2O) afforded the title compound **16b** as a pale

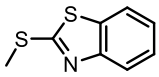
yellow oil (52.3 mg, 96% yield); R_f 0.38 (9:1 pentane:Et_2O); δ_H (400 MHz, $CDCl_3$) 7.43–7.38 (m, 2H), 7.34–7.28 (m, 2H), 7.26–7.21 (m, 1H), 3.72 (s, 3H), 3.66 (s, 2H); δ_C (100 MHz, $CDCl_3$) 170.3, 135.0, 130.1, 129.2, 127.2, 52.7, 36.6; HRMS (APCI$^+$): Found: 183.046798; $C_9H_{11}O_2S^+$ (MH^+) Requires 183.047427 (−3.4 ppm error). Spectroscopic data is consistent with those reported in the literature.[13]

2-(Methylsulfinyl)benzo[*d*]thiazole (17a)



Prepared according to general procedure A using 2-(methylthio)benzo[*d*]thiazole **17b*** (1.87 g, 10.0 mmol) and *m*CPBA (2.07 g, 12.0 mmol) in anhydrous CH_2Cl_2 (30 mL). Purification by flash chromatography on silica gel (7:3 Et_2O:hexane with 1% AcOH added to eluent) afforded the title compound **17a** as a white solid (1.37 g, 70% yield); mp 59–61 °C; R_f 0.35 (8:2 Et_2O:hexane); ν_{max} (thin film)/cm^{-1} 3062, 3004, 2915, 1474, 1426, 1313, 1235, 1085, 1060, 1001, 953, 758, 729, 678; δ_H (400 MHz, $CDCl_3$) 8.08-8.04 (m, 1H), 8.02-7.98 (m, 1H), 7.56 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.51-7.46 (m, 1H), 3.07 (s, 3H); δ_C (100 MHz, $CDCl_3$) 178.5, 153.9, 136.1, 127.1, 126.4, 124.1, 122.5, 43.3; HRMS (ESI$^+$): Found: 219.9862; $C_8H_7NNaOS_2^+$ (MNa^+) Requires 219.9861 (−0.4 ppm error). *This material is commercially available.

2-(Methylthio)benzo[*d*]thiazole (17b)



To an 8 mL vial equipped with a PTFE septum and a magnetic stirrer bar was added *fac*-Ir(ppy)$_3$ (2.0 mg, 0.003 mmol), PPh_3 (94.6 mg, 0.36 mmol) and 2-(methylsulfinyl)benzo[*d*]thiazole **17a** (59.2 mg, 0.30 mmol). The reaction vessel was purged by alternating vacuum and argon three times before anhydrous and degassed CH_2Cl_2 (1.5 mL) was added and the septum additionally sealed with paraffin film. The reaction was irradiated with a 60 W blue LED floodlight for 48 h, with rapid stirring and cooling from a small fan to maintain an ambient temperature. The reaction mixture was then directly poured on to silica and purified by column chromatography to afford the title compound **17b** as a white solid (52.5 mg, 97% yield); mp 43–45 °C; R_f 0.41 (97:3 pentane:Et_2O); δ_H (400 MHz, $CDCl_3$) 7.87 (d, *J* = 8.11 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.45-7.39 (m, 1H), 7.32-7.26 (m, 1H), 2.80 (s, 3H); δ_C (100 MHz, $CDCl_3$) 168.2, 153.5, 135.3, 126.2, 124.2, 121.5, 121.1, 16.1; HRMS (ESI$^+$): Found: 182.0091; $C_8H_8NS_2^+$ (MH^+) Requires 182.0093 (0.9 ppm error). Spectroscopic data is consistent with those reported in the literature.[14]

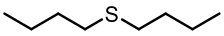
Dimethylsulfane (18b)

Prepared according to general procedure B using $[Ir\{dF(CF_3)ppy\}_2(dtbpy)]PF_6$ (3.4 mg, 0.003 mmol), PPh_3 (94.6 mg, 0.36 mmol) and (methylsulfinyl)methane **18a** (23.4 mg, 0.30 mmol) in anhydrous CH_2Cl_2 (1.5 mL). The crude reaction mixture was analysed by ^1H NMR spectroscopy using a trimethoxybenzene internal standard and a 98% yield of title compound **18b** was calculated. Due to the extremely volatile nature of this compound, purification was not performed.

Tetrahydrothiophene (19b)

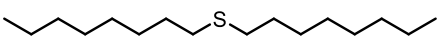
Prepared according to general procedure B using $[Ir\{dF(CF_3)ppy\}_2(dtbpy)]PF_6$ (3.4 mg, 0.003 mmol), PPh_3 (94.6 mg, 0.36 mmol) and tetrahydrothiophene 1-oxide **19a** (31.3 mg, 0.30 mmol) in anhydrous CH_2Cl_2 (1.5 mL). The crude reaction mixture was analysed by ^1H NMR spectroscopy using a trimethoxybenzene internal standard and a 99% yield of title compound **19b** was calculated. Due to the extremely volatile nature of this compound, purification was not performed.

Dibutylsulfane (20b)



Prepared according to general procedure B using $[Ir\{dF(CF_3)ppy\}_2(dtbpy)]PF_6$ (3.4 mg, 0.003 mmol), PPh_3 (94.6 mg, 0.36 mmol) and 1-(butylsulfinyl)butane **20a** (48.7 mg, 0.30 mmol) in anhydrous CH_2Cl_2 (1.5 mL). Purification by flash chromatography on silica gel (100% pentane) afforded the title compound **20b** as a pale yellow oil (33.7 mg, 78% yield); R_f 0.19 (100% pentane); δ_H (400 MHz, $CDCl_3$) 2.50 (t, J = 7.4 Hz, 4H), 1.61–1.49 (m, 4H), 1.45–1.34 (m, 4H), 0.91 (t, J = 7.3 Hz, 6H); δ_C (100 MHz, $CDCl_3$) 32.0 (2 x C), 22.2, 13.9. Spectroscopic data is consistent with those reported in the literature.[15]

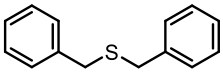
Dioctylsulfane (21b)



Prepared according to general procedure B using $[Ir\{dF(CF_3)ppy\}_2(dtbpy)]PF_6$ (3.4 mg, 0.003 mmol), PPh_3 (94.6 mg, 0.36 mmol) and 1-(octylsulfinyl)octane **21a** (82.4 mg, 0.30 mmol) in anhydrous CH_2Cl_2 (1.5 mL). Purification by flash chromatography on silica gel (100% pentane, then 99:1 pentane:Et_2O) afforded the title compound **21b** as a clear and colourless oil (73.7 mg, 95% yield); R_f 0.40 (100% pentane); δ_H (400 MHz, $CDCl_3$) 2.50 (t, J = 7.4 Hz,

4H), 1.62–1.52 (m, 4H), 1.40–1.23 (m, 20H), 0.92–0.84 (m, 6H); δ_C (100 MHz, $CDCl_3$) 32.3, 32.0, 29.9, 29.37, 29.35, 29.1, 22.8, 14.2; HRMS (APCI$^+$): Found: 259.244383; $C_{16}H_{35}S^+$ (MH^+) Requires 259.245399 (−3.9 ppm error). Spectroscopic data is consistent with those reported in the literature.[16]

Dibenzylsulfane (22b)

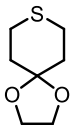


Prepared according to general procedure B using [Ir{dF(CF$_3$)ppy}$_2$(dtbpy)]PF$_6$ (3.4 mg, 0.003 mmol), PPh_3 (94.6 mg, 0.36 mmol) and (sulfinylbis(methylene))dibenzene **22a** (69.1 mg, 0.30 mmol) in anhydrous CH_2Cl_2 (1.5 mL). Purification by flash chromatography on silica gel (100% pentane, then 98:2 pentane:Et_2O) afforded the title compound **22b** as a clear and colourless oil (62.5 mg, 97% yield); R_f 0.30 (98:2 pentane:Et_2O); δ_H (400 MHz, $CDCl_3$) 7.40–7.20 (m, 10H), 3.61 (s, 4H); δ_C (100 MHz, $CDCl_3$) 138.3, 129.1, 128.6, 127.1, 35.7. Spectroscopic data is consistent with those reported in the literature.[15]

Bis(methylthio)methane (23b)

Prepared according to general procedure B using [Ir{dF(CF$_3$)ppy}$_2$(dtbpy)]PF$_6$ (3.4 mg, 0.003 mmol), PPh_3 (94.6 mg, 0.36 mmol) and methyl((methylsulfinyl)methyl)sulfane **23a** (37.3 mg, 0.30 mmol) in anhydrous CH_2Cl_2 (1.5 mL). Purification by flash chromatography on silica gel (100% pentane, then 99:1 pentane:Et_2O) afforded the title compound **23b** as a clear and colourless oil (22.7 mg, 70% yield); R_f 0.25 (95:5 hexane:Et_2O); δ_H (400 MHz, $CDCl_3$) 3.62 (s, 2H), 2.15 (s, 6H); δ_C (100 MHz, $CDCl_3$) 40.2, 14.5. Spectroscopic data is consistent with those reported in the literature.[17]

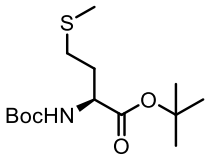
1,4-Dioxa-8-thiaspiro[4.5]decane (24b)



Prepared according to general procedure B using [Ir{dF(CF$_3$)ppy}$_2$(dtbpy)]PF$_6$ (3.4 mg, 0.003 mmol), PPh_3 (94.6 mg, 0.36 mmol) and 1,4-dioxa-8-thiaspiro[4.5]decane 8-oxide **24a** (52.9 mg, 0.30 mmol) in anhydrous CH_2Cl_2 (1.5 mL). Purification by flash chromatography on silica gel (9:1 pentane:Et_2O) afforded the title compound **24b** as a pale yellow oil (43.4 mg, 90% yield); ν_{max} (thin film)/cm^{-1} 2948, 2916, 2880, 1427, 1269, 1248, 1102, 1055, 1026, 885; R_f 0.21 (9:1 hexane:Et_2O); δ_H (400 MHz, $CDCl_3$) 3.94 (s, 4H), 2.77–2.67 (m, 4H), 1.92–1.85 (m, 4H); δ_C (100

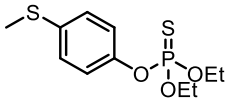
MHz, $CDCl_3$) 107.3, 64.5, 36.9, 27.1; HRMS (APCI$^+$): Found: 161.063557; $C_7H_{13}O_2S^+$ (MH^+) Requires 161.063077 (−3.0 ppm error). Spectroscopic data is consistent with those reported in the literature.[18]

***tert*-Butyl (*tert*-butoxycarbonyl)-*L*-methioninate (25b)**



Prepared according to general procedure B using [Ir{dF(CF_3)ppy}$_2$(dtbpy)]PF_6 (3.4 mg, 0.003 mmol), PPh_3 (94.6 mg, 0.36 mmol) and 1,4-dioxa-8-thiaspiro[4.5]decane 8-oxide **25a** (96.4 mg, 0.30 mmol) in anhydrous CH_2Cl_2 (1.5 mL). Purification by flash chromatography on silica gel (8:2 pentane:Et_2O) afforded the title compound **25b** as a pale yellow oil as a 7:1 mixture of rotamers (91.0 mg, 99% yield); R_f 0.34 (8:2 hexane:Et_2O); δ_H (400 MHz, $CDCl_3$) 5.10 (br s, 1H, major rotamer), 4.84 (br s, 1H, minor rotamer), 4.25 (br s, 1H, major), 4.12 (br s, 1H, minor), 2.59–2.43 (m, both, 4H), 2.16–2.01 (m, both, 8H), 1.95–1.80 (m, 2H, both), 1.45 (s, 18H, both), 1.42 (s, 18H, both); δ_C (100 MHz, $CDCl_3$) 171.5, 155.4, 82.2, 79.9, 53.5, 32.7, 30.0, 28.4, 28.1, 15.6; HRMS (ESI$^+$): Found: 328.1552; $C_{14}H_{27}NNaO_4S^+$ (MNa^+) Requires 328.1553 (0.2 ppm error). Spectroscopic data is consistent with those reported in the literature.[2]

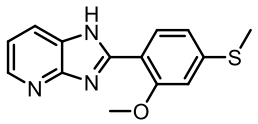
***O*,*O*-Diethyl *O*-(4-(methylthio)phenyl) phosphorothioate (26b)**



To an 8 mL vial equipped with a PTFE septum and a magnetic stirrer bar was added *fac*-Ir(ppy)$_3$ (1.96 mg, 0.003 mmol), PPh_3 (94.6 mg, 0.36 mmol) and *O*,*O*-diethyl *O*-(4-(methylsulfinyl)phenyl) phosphorothioate **33a** (92.5 mg, 0.30 mmol). The reaction vessel was purged by alternating vacuum and argon three times before anhydrous and degassed CH_2Cl_2 (1.5 mL) was added and the septum additionally sealed with paraffin film. The reaction was irradiated with a 60 W blue LED floodlight for 48 h, with rapid stirring and cooling from a small fan to maintain an ambient temperature. The reaction mixture was then directly poured on to silica and purified by column chromatography to afford the title compound **33b** as a pale yellow oil (84.4 mg, 96% yield); R_f 0.35 (6:4 $CHCl_3$:hexane); δ_H (400 MHz, $CDCl_3$) 7.23 (d, J = 8.7 Hz, 2H), 7.11 (d, J = 8.7 Hz, 2H), 4.28–4.16 (m, 4H), 2.46 (s, 3H), 1.36 (t, J = 7.1 Hz, 6H); δ_C (100 MHz, $CDCl_3$) 148.6 (d, $^2J_{C\text{-}P}$ = 7.7 Hz), 135.0, 128.2, 121.6 (d, $^3J_{C\text{-}P}$ = 4.8 Hz), 65.2 (d, $^2J_{C\text{-}P}$ = 5.6 Hz), 16.6, 16.0 (d, $^3J_{C\text{-}P}$ = 7.5 Hz); HRMS (ESI$^+$): Found: 293.0429; $C_{11}H_{18}O_3PS_2^+$ (MH^+) Requires 293.0429 (1.7 ppm error). Spectroscopic data is consistent with those reported in the literature.[19]

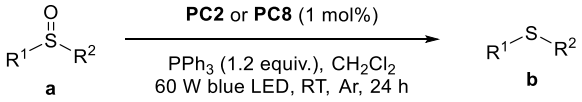
Compound **33b** was also prepared according to general procedure B using [Ir{dF(CF_3)ppy}$_2$(dtbpy)]PF_6 (3.4 mg, 0.003 mmol), PPh_3 (94.6 mg, 0.36 mmol) and *O*,*O*-diethyl *O*-(4-(methylsulfinyl)phenyl) phosphorothioate **33a** (92.5 mg, 0.30 mmol) in anhydrous CH_2Cl_2 (1.5 mL). Purification by flash chromatography on silica gel (6:4 $CHCl_3$:hexane) afforded the title compound **33b** as a pale yellow oil (49.4 mg, 56% yield).

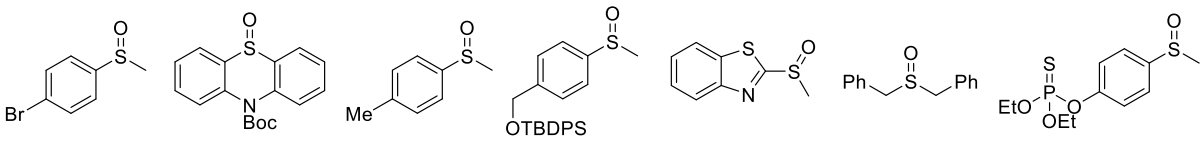
2-(2-Methoxy-4-(methylthio)phenyl)-1*H*-imidazo[4,5-*b*]pyridine (34b)



To an 8 mL vial equipped with a PTFE septum and a magnetic stirrer bar was added *fac*-Ir(ppy)$_3$ (0.85 mg, 1.3 μmol), PPh_3 (42.0 mg, 0.16 mmol) and 2-(2-Methoxy-4-(methylsulfinyl)phenyl)-1*H*-imidazo[4,5-*b*]pyridine **34a** (37.5 mg, 0.13 mmol). The reaction vessel was purged by alternating vacuum and argon three times before anhydrous and degassed CH_2Cl_2 (0.7 mL) was added and the septum additionally sealed with paraffin film. The reaction was irradiated with a 60 W blue LED floodlight for 24 h, with rapid stirring and cooling from a small fan to maintain an ambient temperature. The reaction mixture was then directly poured on to silica and purified by column chromatography to afford the title compound **34b** as a pale yellow oil (22.0 mg, 62% yield); R_f 0.36 (100% EtOAc); ν_{max} (thin film)/cm^{-1} 3238, 3060, 2926, 1599, 1560, 1529, 1462, 1405, 1278, 1241, 1115, 1072, 1027, 879, 779; δ_H (400 MHz, $CDCl_3$) 8.49 (d, *J* = 8.3 Hz, 1H), 8.42-8.29 (m, 2H), 8.01 (d, *J* = 7.9 Hz, 1H), 7.25–7.19 (m, 1H), 6.99 (dd, *J* = 8.4, 1.3 Hz, 1H), 6.92 (s, 1H), 4.06 (s, 3H), 2.55 (s, 3H); δ_C (100 MHz, CD_3OD) 159.2, 153.7, 153.4, 147.1, 144.3, 131.6, 130.8, 123.6, 119.3, 119.0, 114.2, 109.6, 56.5, 14.8; HRMS (ESI$^+$): Found: 272.0853; $C_{14}H_{14}N_3OS^+$ (MH^+) Requires 272.0852 (−0.3 ppm error).

Photocatalyst Comparative Studies[a]





8a 11a 12a 14a 17a 22a 33a

Entry	Sulfoxide	PC2 yield / %	PC8 yield / %
1	**8a**	99	99
2	**11a**	99	43
3	**12a**	96	60
4	**14a**	93	28
5	**17a**	34	>99[b]
6	**22a**	97	60
7	**26a**	56	>99[c]

[a]^{1}H NMR yields reported based on a trimethoxybenzene internal standard. [b]Reaction performed for 4 days. [c]Reaction performed for 48 h.

Cyclic Voltammetry Information

The cyclic voltammograms were performed using a 5 mL electrochemical cell vial containing a glassy carbon disk working electrode, platinum counter electrode and Ag/AgCl reference electrode, all from the IKA ElectraSyn range. The cell lid was modified in-house to permit connection to an EmStat potentiostat and the data was collected using the complementary PSTrace software.

The same procedure was followed for experiments conducted on both PPh_3 and sulfoxide, **8a**. First, 77 mg of tetrabutylammonium hexafluorophosphate (0.2 mmol Bu_4NPF_6, Acros Organics, 98%) was added to the cell vial, the lid was attached and then the vial was purged with N_2 for approximately 5 min via the access port. After this, 2 mL anhydrous CH_2Cl_2 was added then three control "background" cyclic voltammograms were recorded over a range of -2 V to +2 V at a scan rate of 100 mVs^{-1} and under an atmosphere of N_2 (achieved by attaching a N_2-filled balloon to the cell lid). A 0.2 mL aliquot of 0.1 M analyte in CH_2Cl_2 was then added to the cell (final concentration 4.8 mM) and three cyclic voltammograms were recorded under the same conditions. Voltammetric data from the second potential sweep is shown (Scheme 3, C in manuscript). In between experiments the electrode surface was cleaned by abrasion using alumina.

For experiments on the mixture of sulfoxide + PPh_3, first 0.2 mL of 0.1 M **8a** was added to the cell solution, followed by 0.3 mL of PPh_3 solution.

UV-Vis Spectroscopy Studies

UV-vis spectra were recorded using Shimadzu UV-Vis Spectrophotometer UV-2600 system. A quartz cuvette with 10mm path length (Hellma Macro, AS4C-QS/QG,) was used. Substrates were dissolved in anhydrous CH_2Cl_2 (0.005 M) unless otherwise stated.

Samples were prepared for analysis as described below:

Sulfoxide **8a** (3.3 mg, 0.015 mmol) was dissolved in CH_2Cl_2 (3 mL) and were analysed between 200–400 nm (blue line).

PPh_3 (3.9 mg, 0.015 mmol) was dissolved in CH_2Cl_2 (3 mL) and were analysed between 200–400 nm (grey line).

Equimolar quantities of sulfoxide **8a** (3.3 mg, 0.015 mmol) and PPh_3 (3.9 mg, 0.015 mmol) were dissolved in CH_2Cl_2 (3 mL) and were analysed between 200–400 nm (orange line).

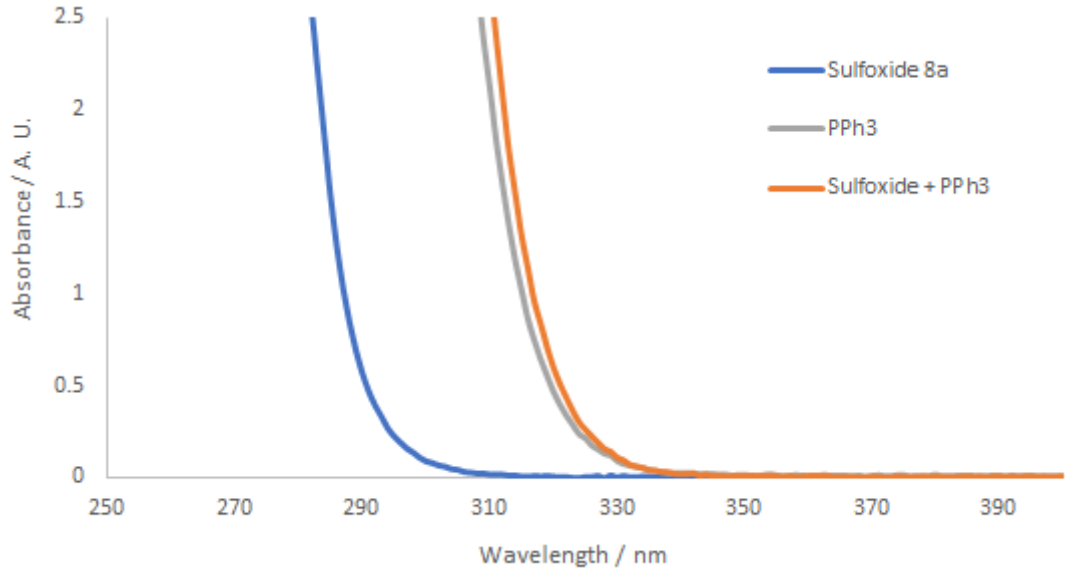
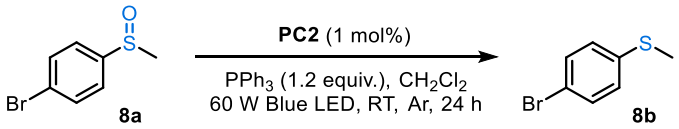


Figure S1. UV-vis spectroscopy studies of sulfoxide 8a, PPh_3 and an equimolar solution of both.

^{19}F NMR Spectra

Examination of the reaction mixture for the conversion of **8a** into **8b** using **PC2** revealed that **PC2** remained unchanged. All ^{19}F NMR signals corresponding to pure **PC2** (*bottom, red*) are observed in the ^{19}F NMR spectrum of the reaction mixture for the conversion of **8a** into **8b** (*top, blue*), suggesting that the catalyst does not degrade significantly or form aggregates during the course of the reaction.



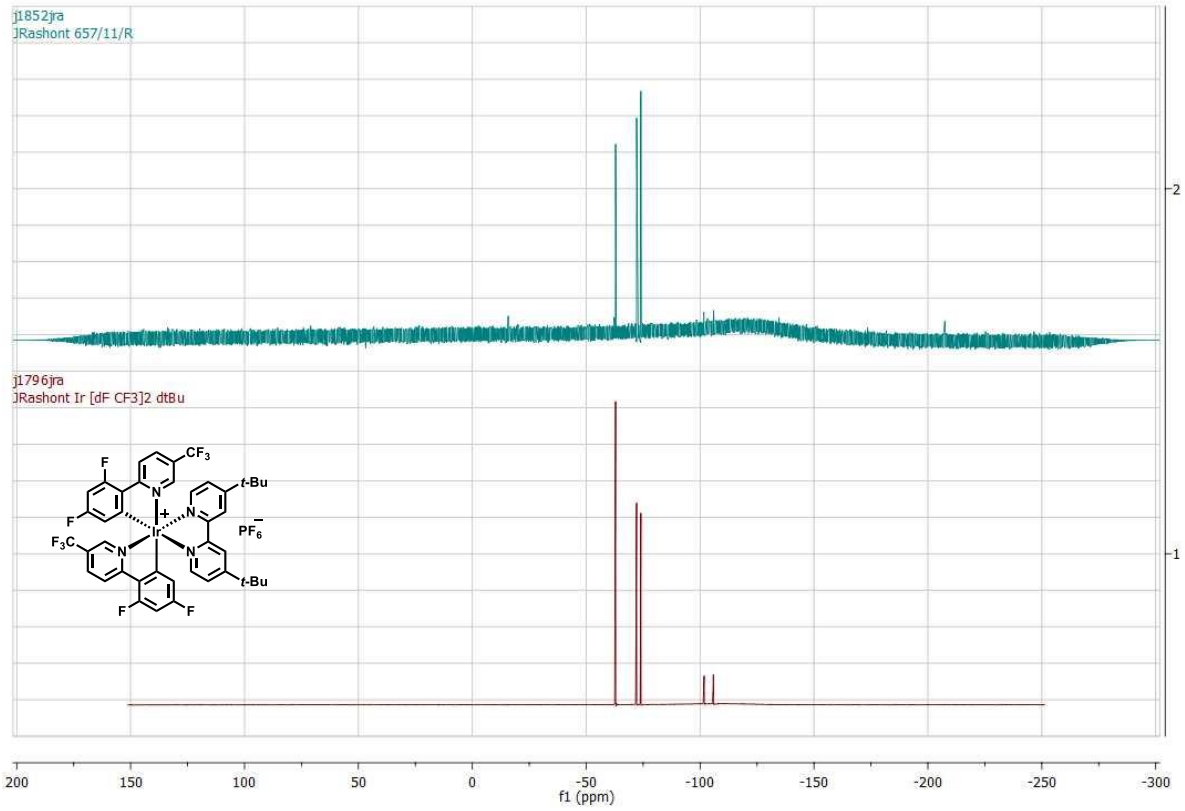
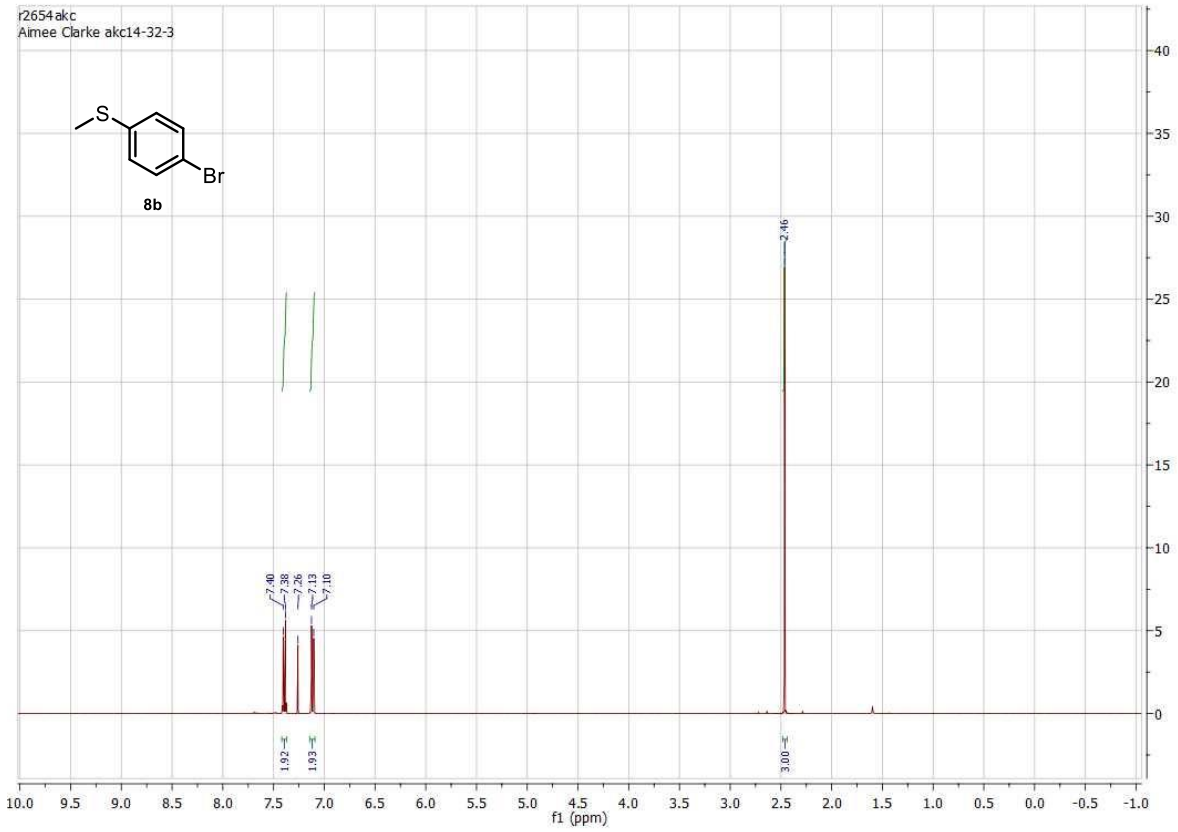
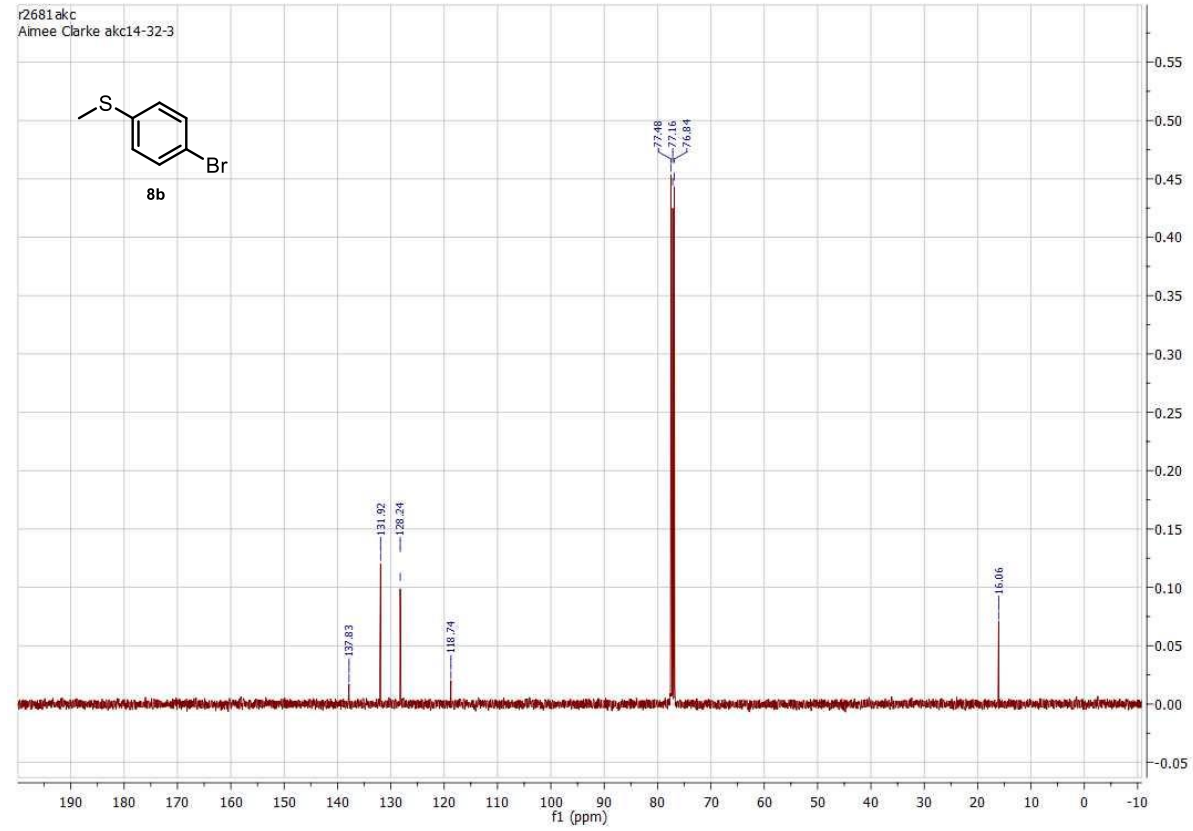


Figure S2. Overlaid ^{19}F NMR spectra of the reaction mixture for the conversion of 8a into 8b using PC2 (top, blue) and pure PC2 (bottom, red).


r2654akc
Aimee Clarke akc14-32-3
S
Br
8b
7.40
7.38
7.26
7.13
7.10
2.46
1.92
1.93
3.00
f1 (ppm)


r2681akc
Aimee Clarke akc14-32-3
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131.92
128.24
137.83
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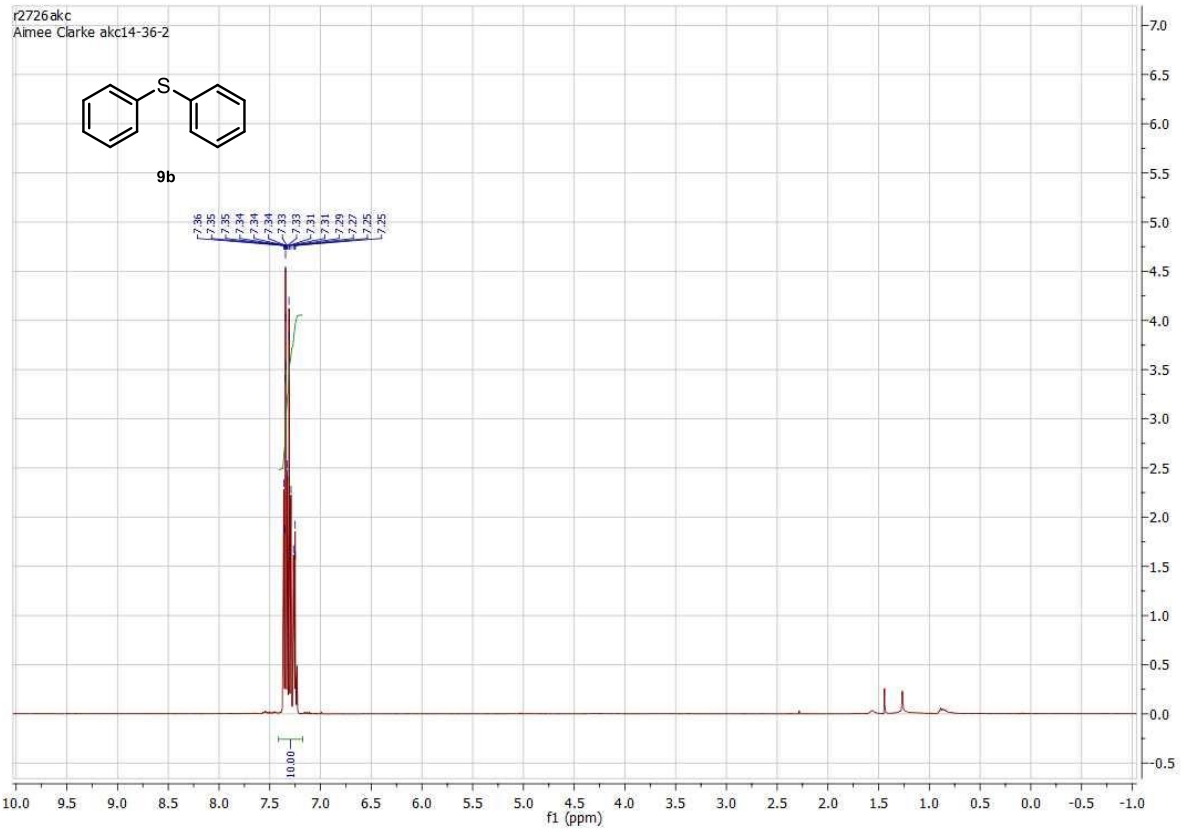
16.06
f1 (ppm)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Aimee Clarke akc14-36-2
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7.35
7.34
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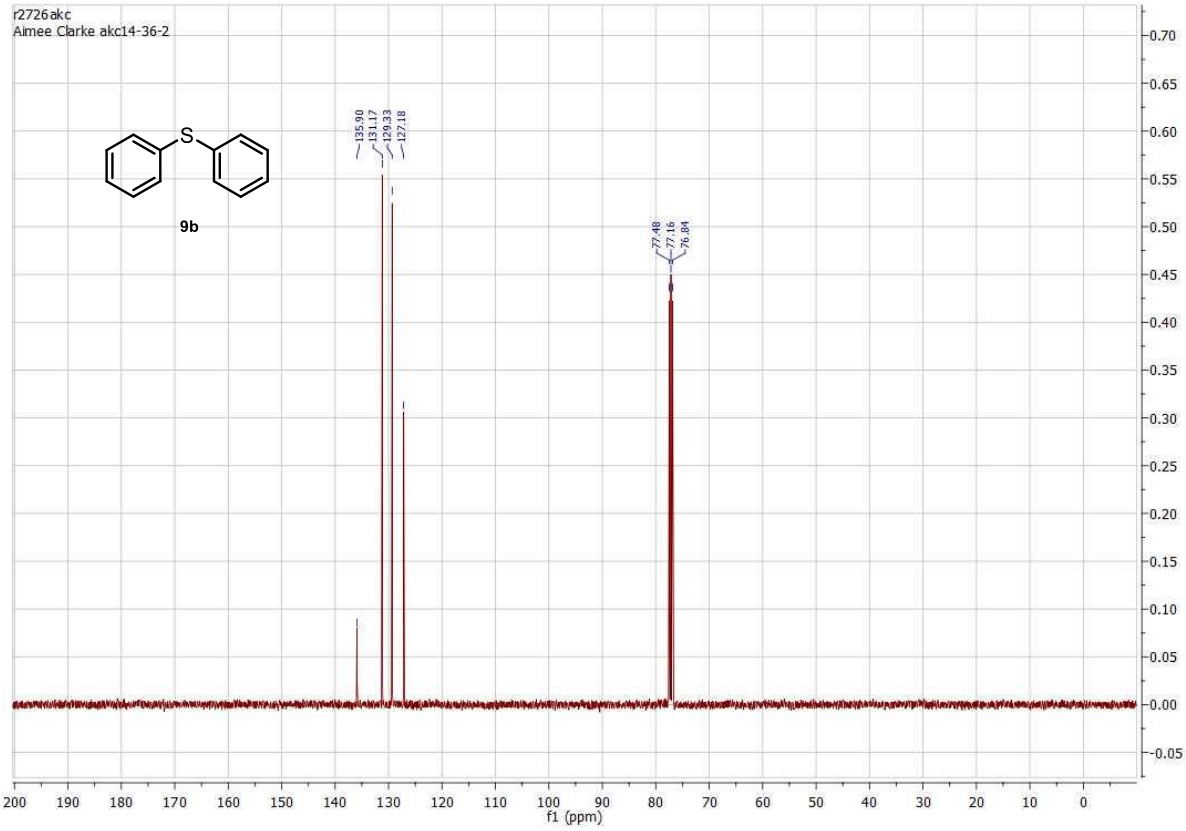
7.27
7.25
7.25
10.00
f1 (ppm)


r2726akc
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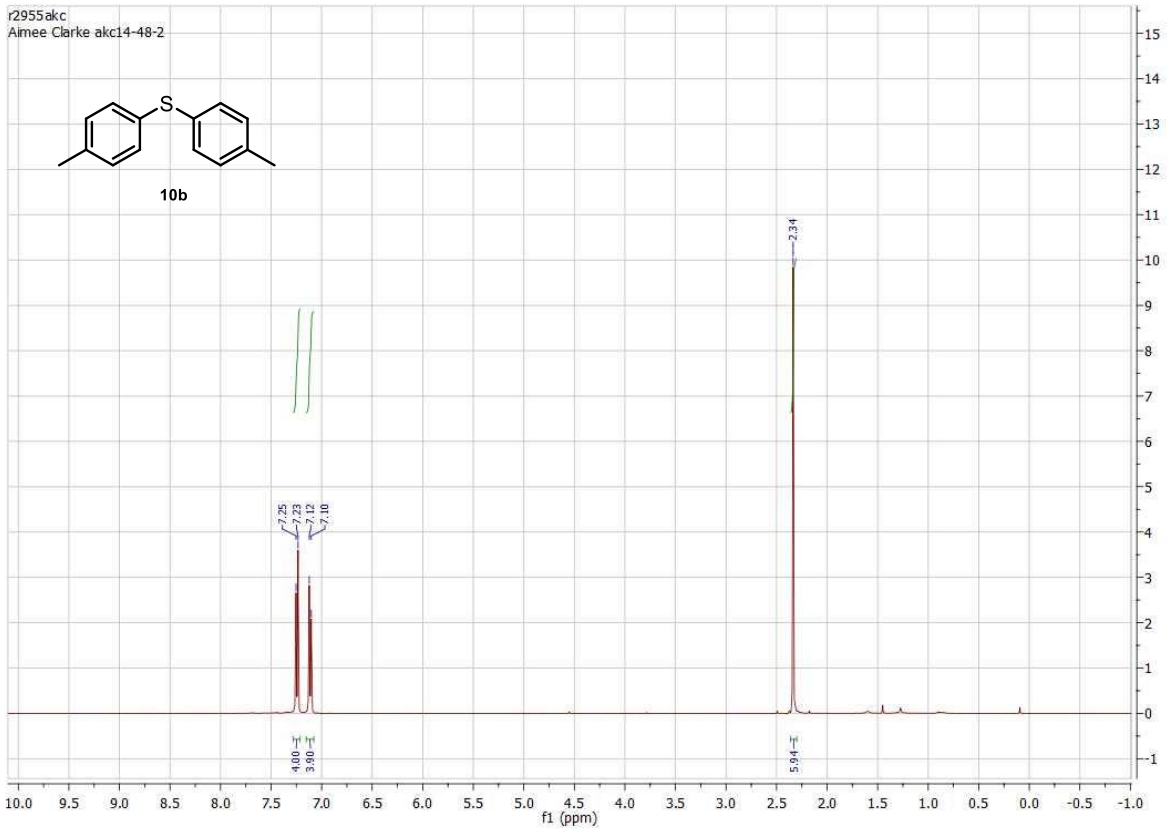
77.48
77.16
76.84
f1 (ppm)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Aimee Clarke akc14-48-2
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7.23
7.12
7.10
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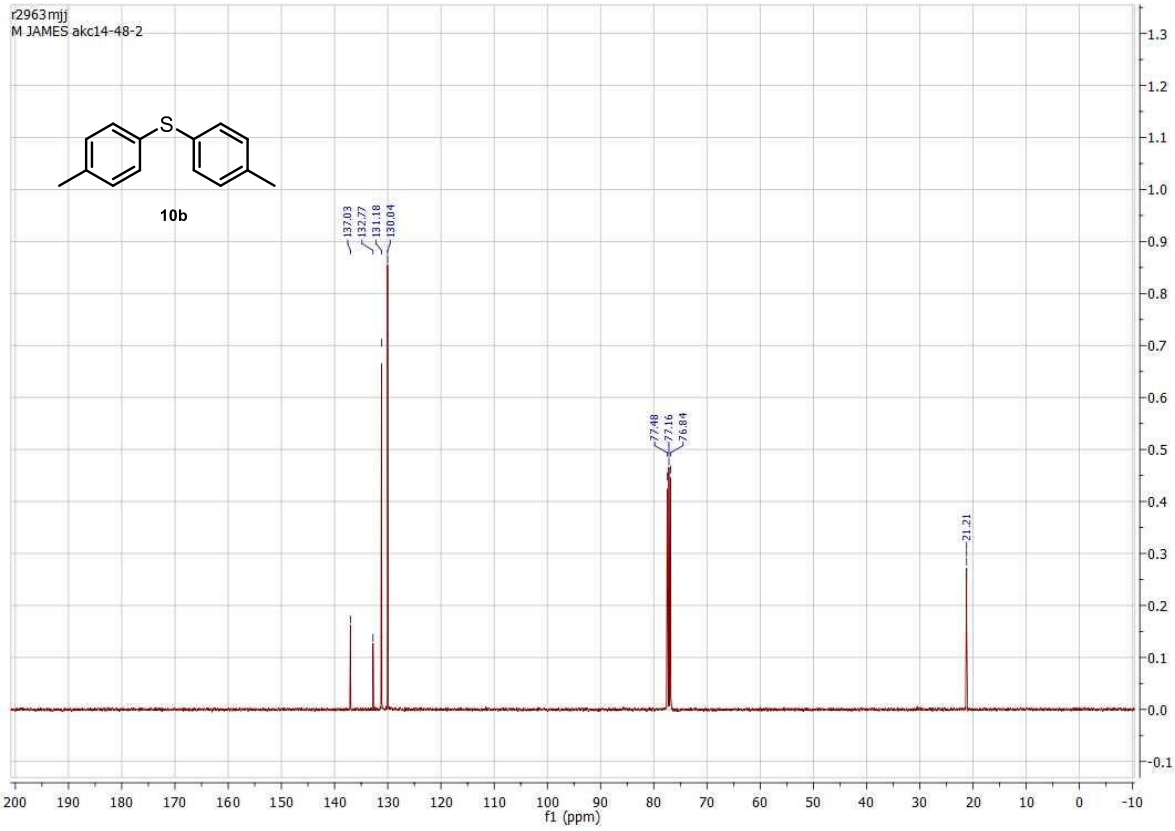
4.00
3.90
5.94
f1 (ppm)


r2963mjj
M JAMES akc14-48-2
10b
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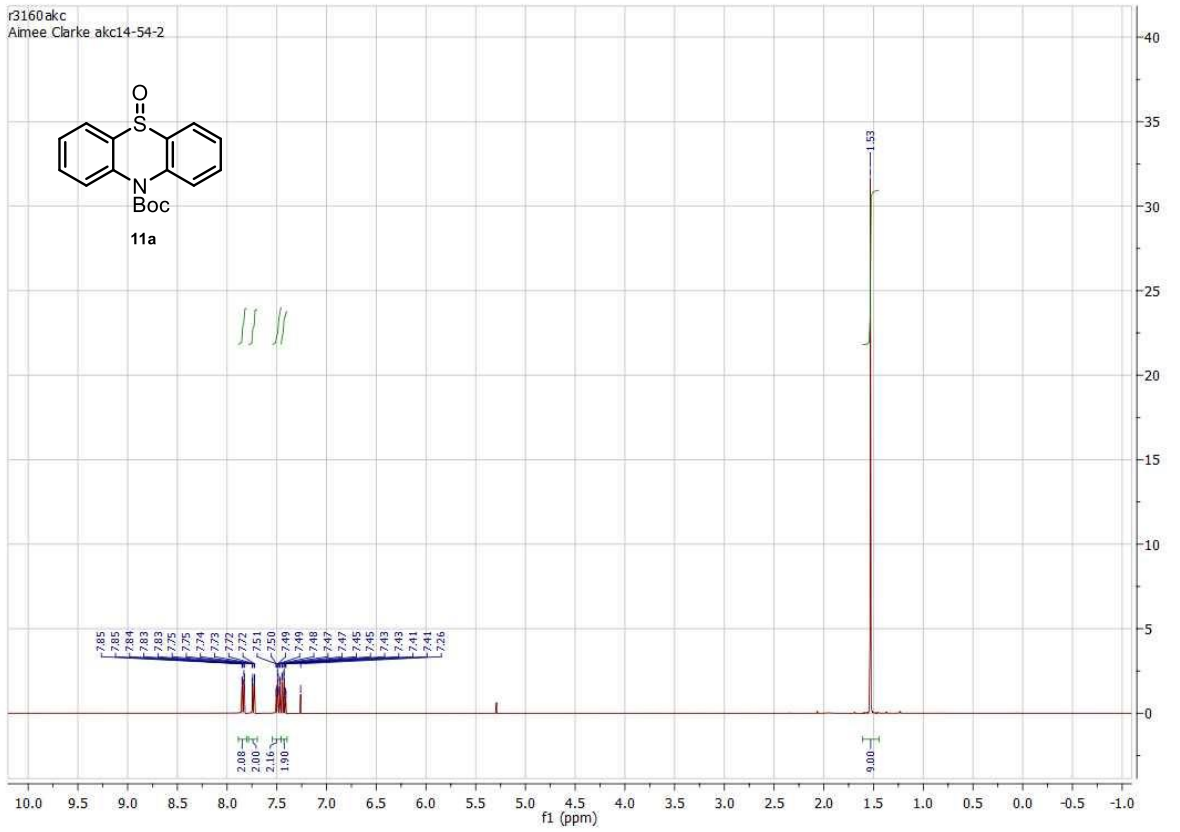
132.77
131.18
130.04
77.48
77.16
76.84
21.21
f1 (ppm)


r3160akc
Aimee Clarke akc14-54-2
O
S
N
Boc
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7.83
7.75
7.75
7.74
7.73
7.72
7.72
7.51
7.50
7.49
7.49
7.48
7.47
7.47
7.45
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9.00
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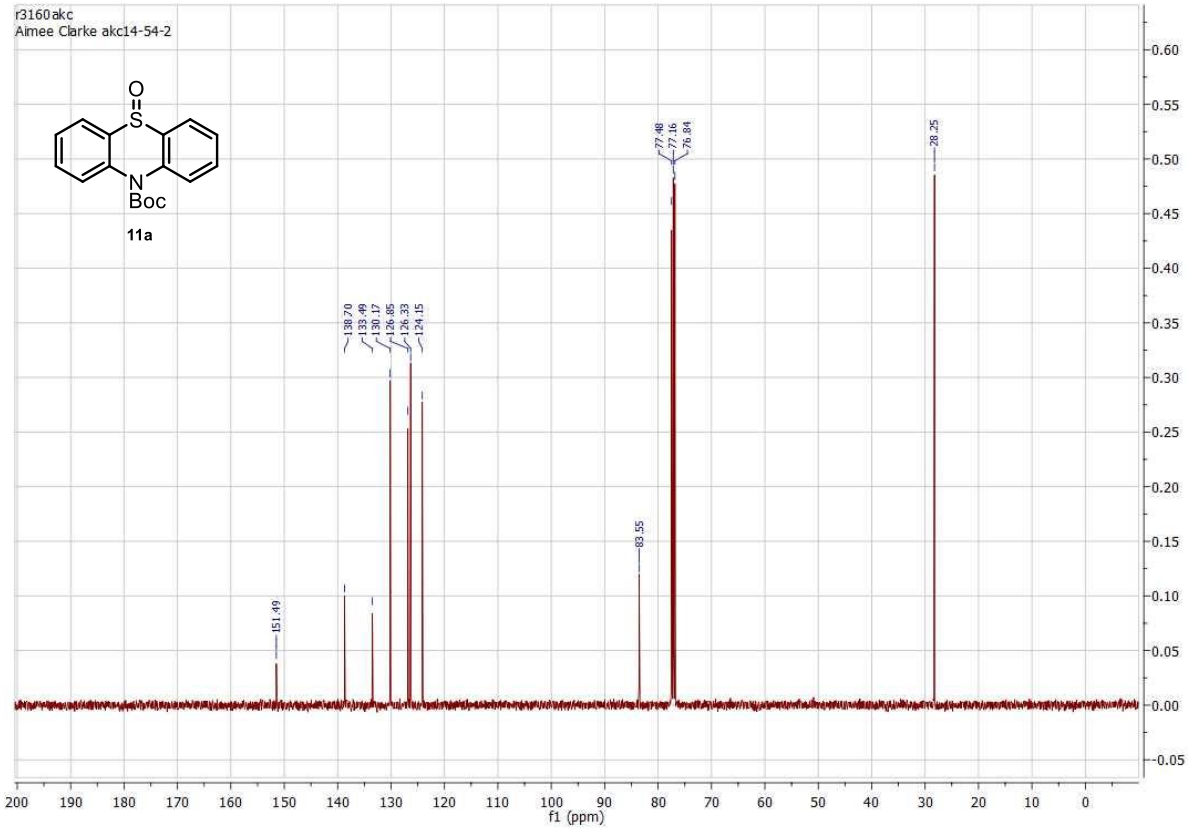
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S
N
Boc
11a
77.48
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130.17
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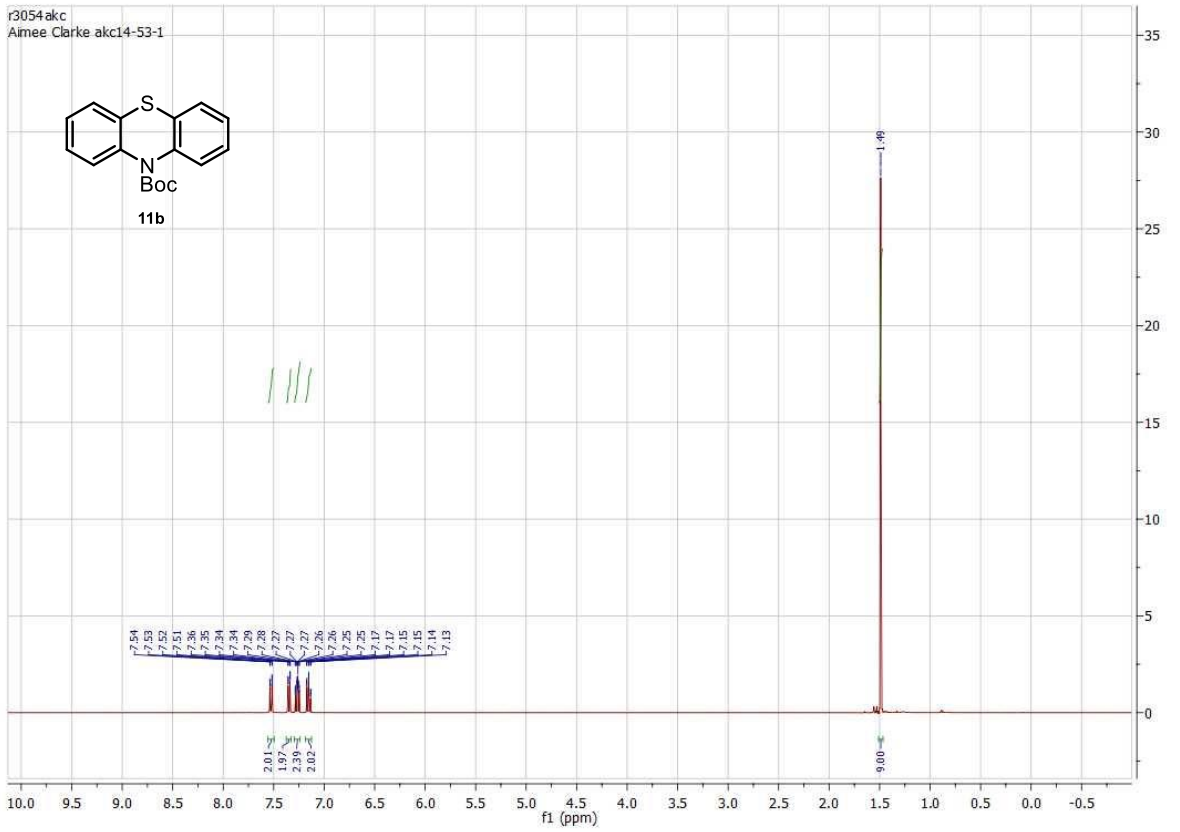
124.15
83.55
151.49
f1 (ppm)


r3054akc
Aimee Clarke akc14-53-1
S
N
Boc
11b
1.49
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7.53
7.52
7.51
7.36
7.35
7.34
7.34
7.29
7.28
7.27
7.27
7.27
7.26
7.26
7.25
7.25
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7.17
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7.15
7.14
7.13
2.01
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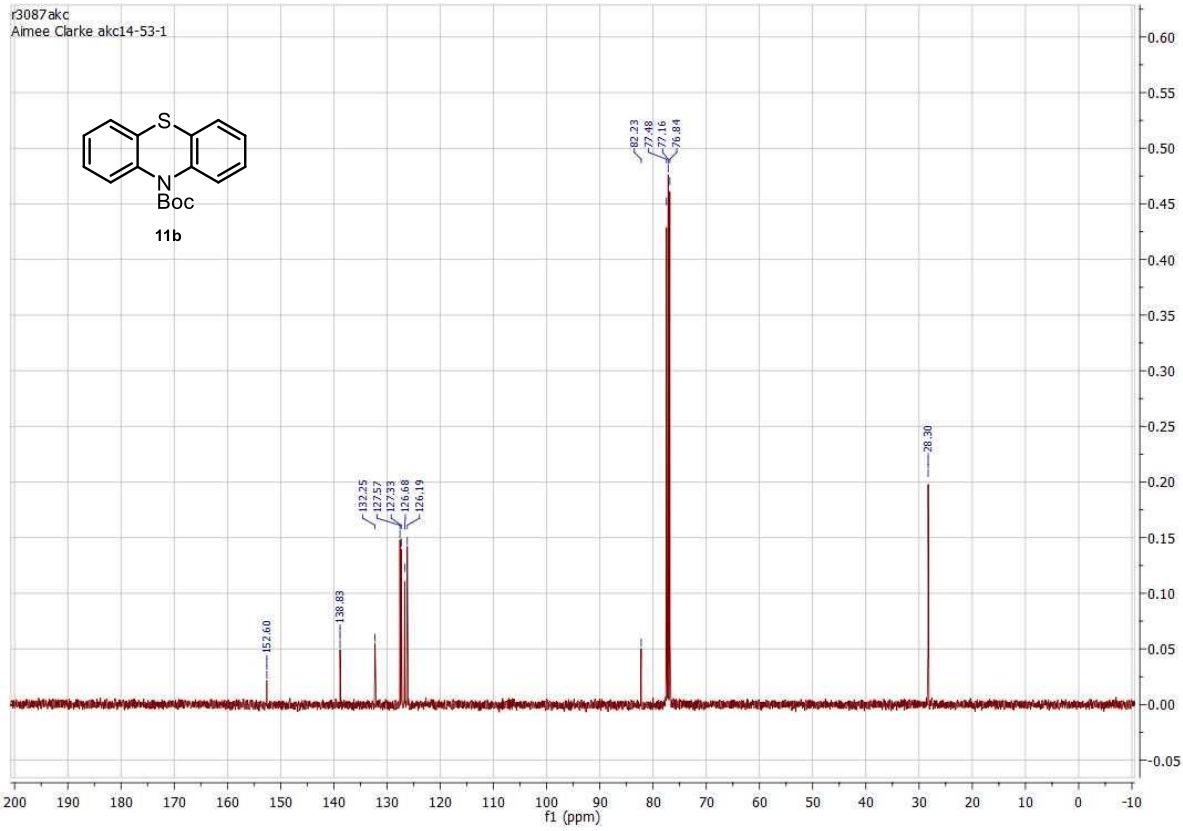
2.39
2.02
9.00
f1 (ppm)


r3087akc
Aimee Clarke akc14-53-1
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N
Boc
11b
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76.84
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127.33
126.68
126.19
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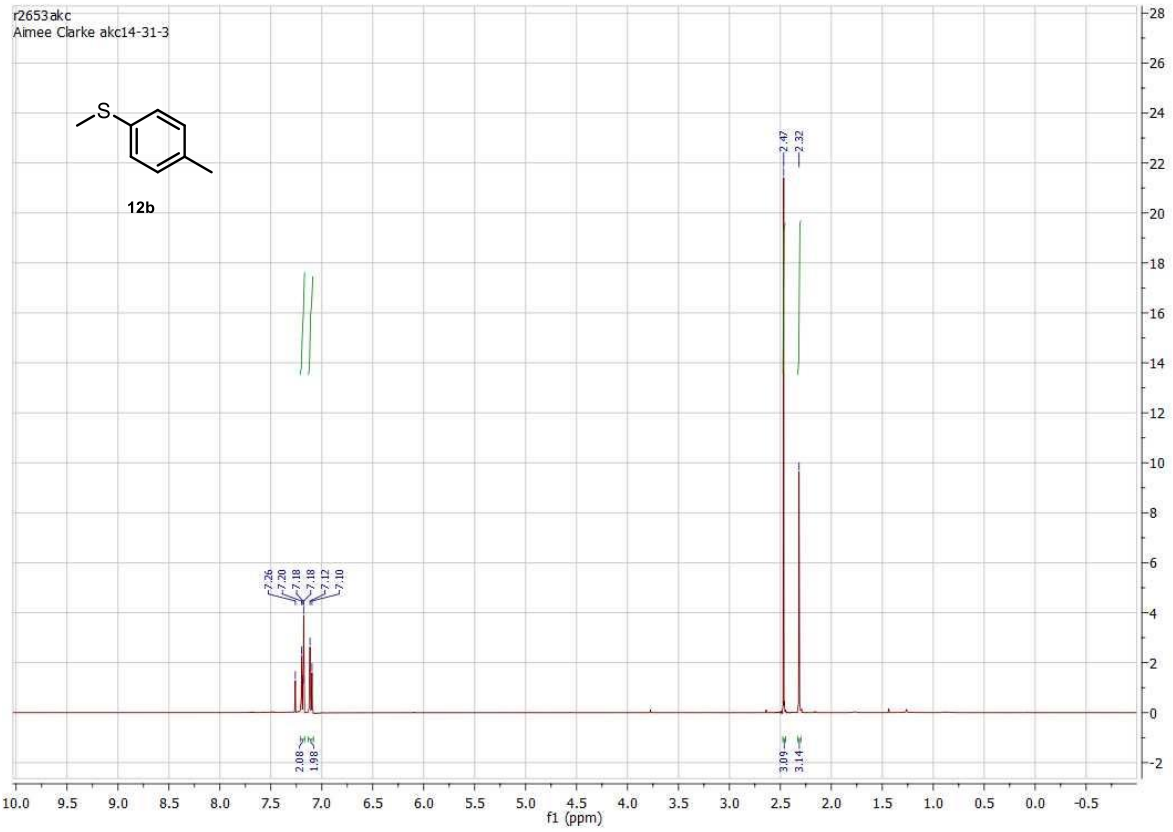
152.60
28.30
f1 (ppm)


r2653akc
Aimee Clarke akc14-31-3
12b
2.47
2.32
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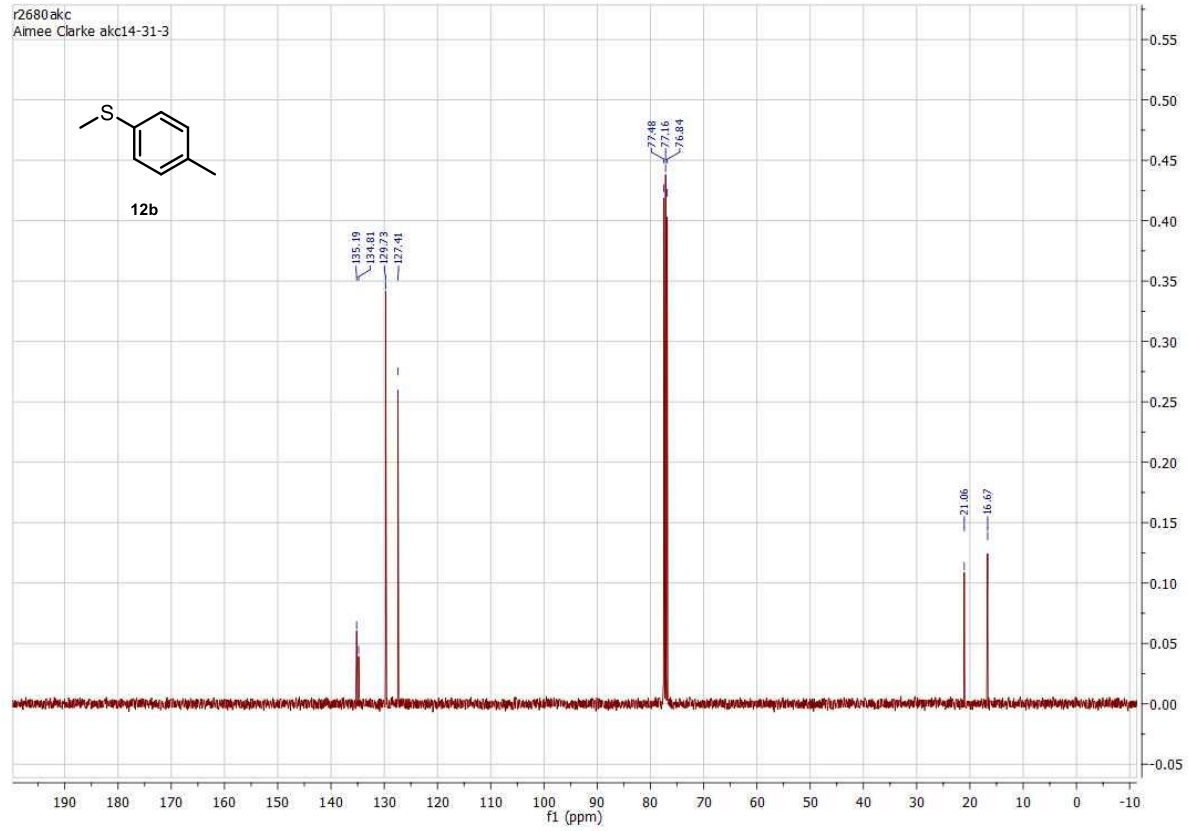
7.20
7.18
7.18
7.12
7.10
2.08
1.98
3.09
3.14
f1 (ppm)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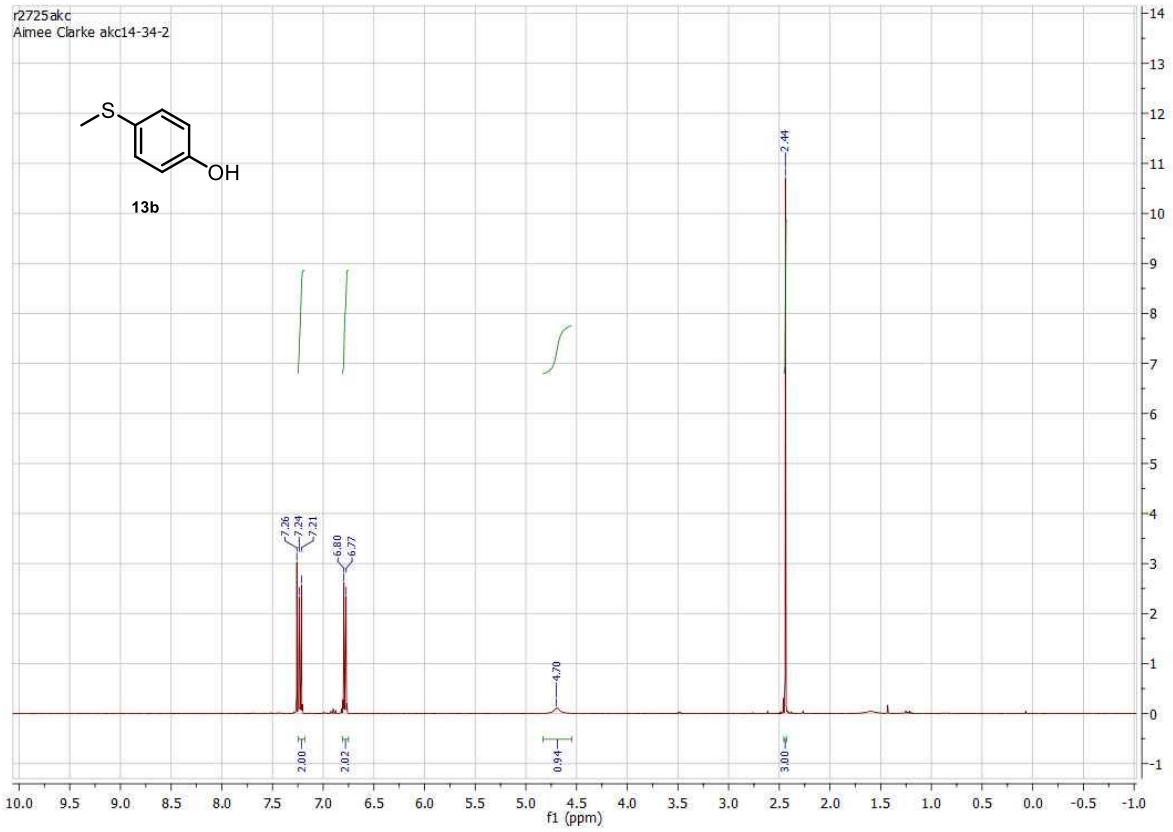
f1 (ppm)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Aimee Clarke akc14-34-2
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OH
13b
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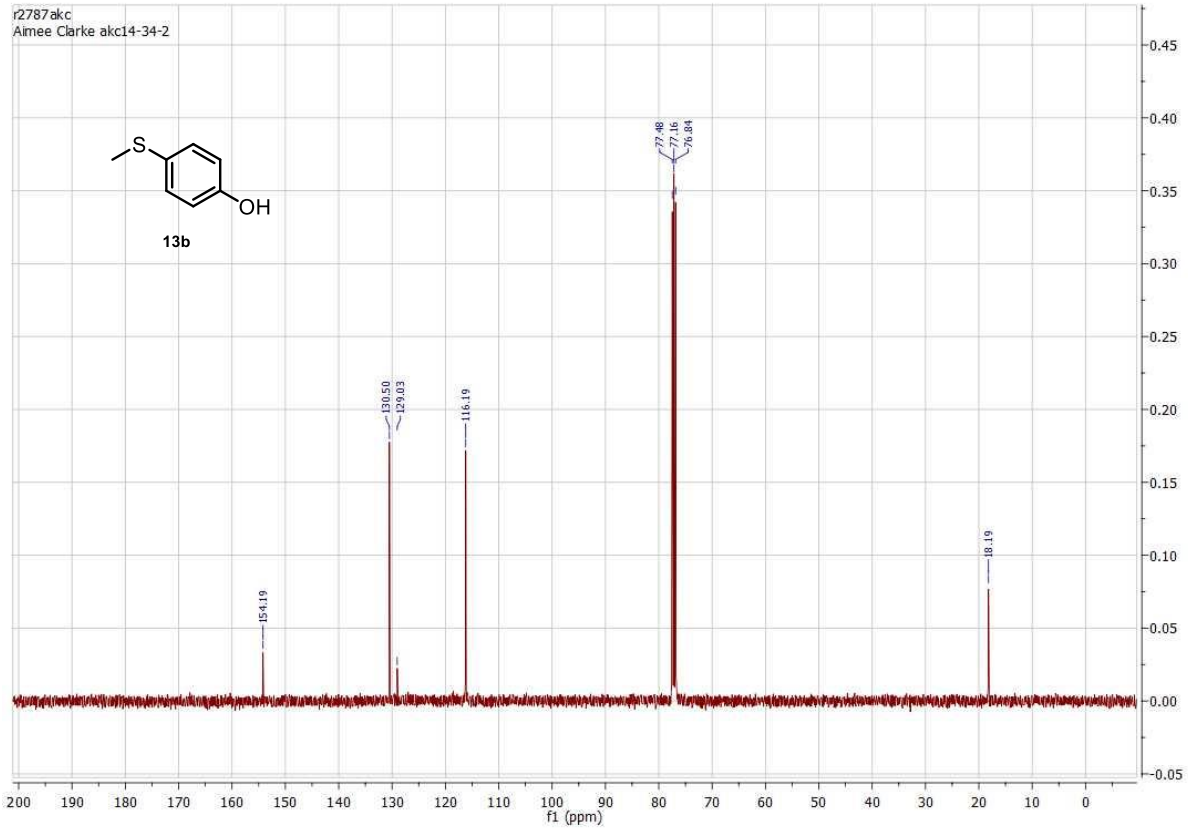
2.02
0.94
3.00
f1 (ppm)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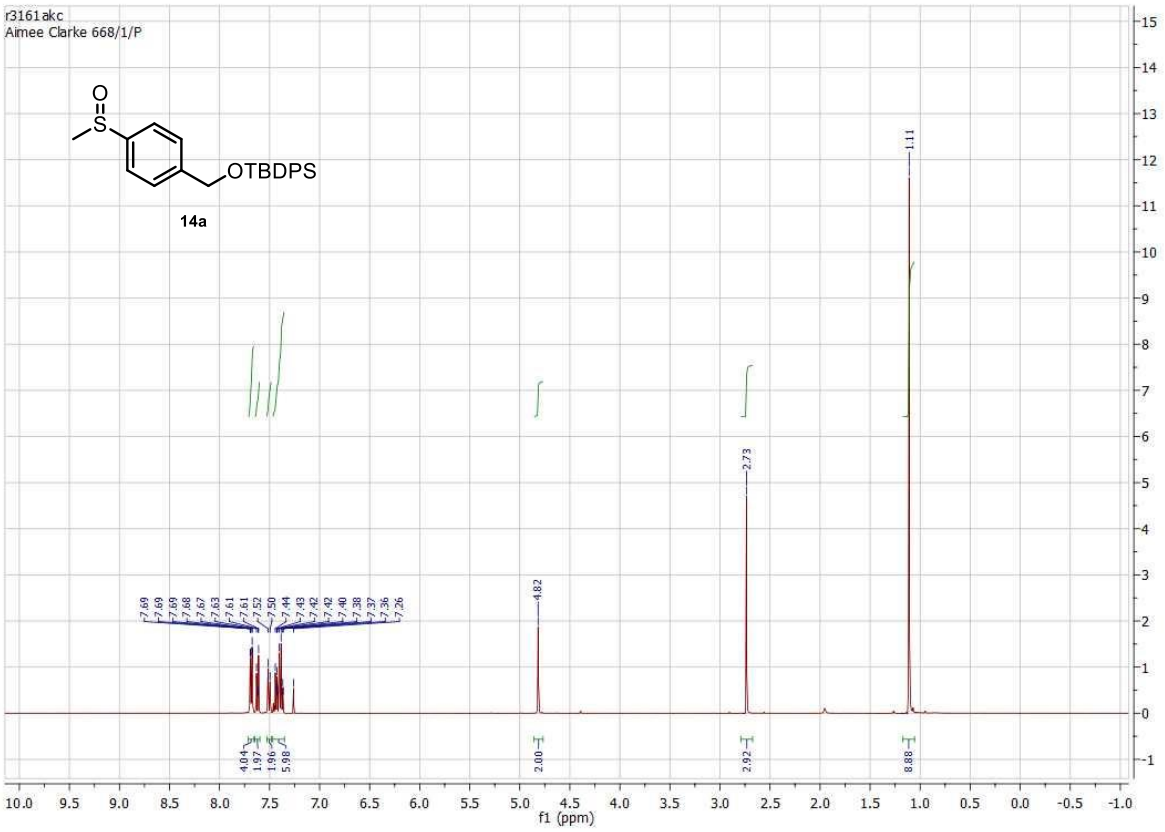
18.19
f1 (ppm)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Aimee Clarke 668/1/P
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OTBDPS
14a
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7.68
7.67
7.63
7.61
7.61
7.52
7.50
7.44
7.43
7.42
7.42
7.40
7.38
7.37
7.36
7.26
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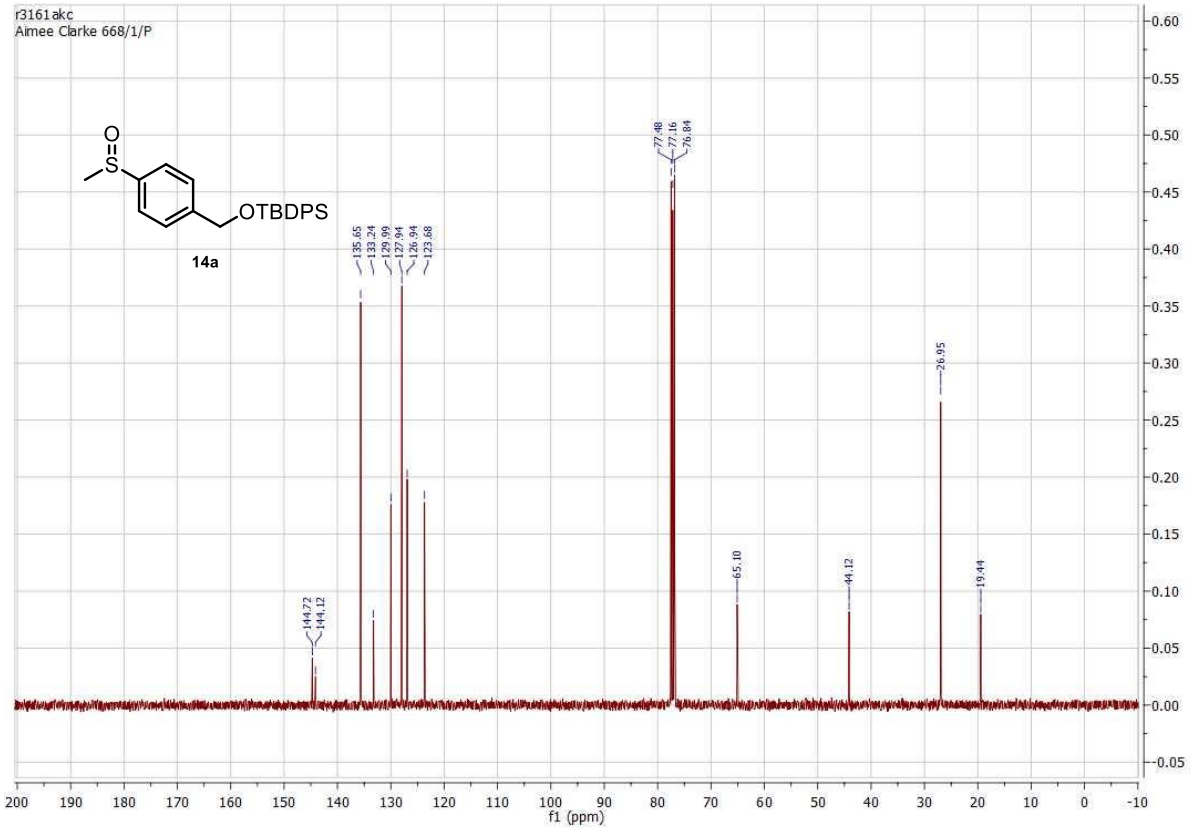
1.11
4.04
1.97
1.96
5.98
2.00
2.92
8.88
f1 (ppm)


r3161akc
Aimee Clarke 668/1/P
O
S
OTBDPS
14a
135.65
133.24
129.99
127.94
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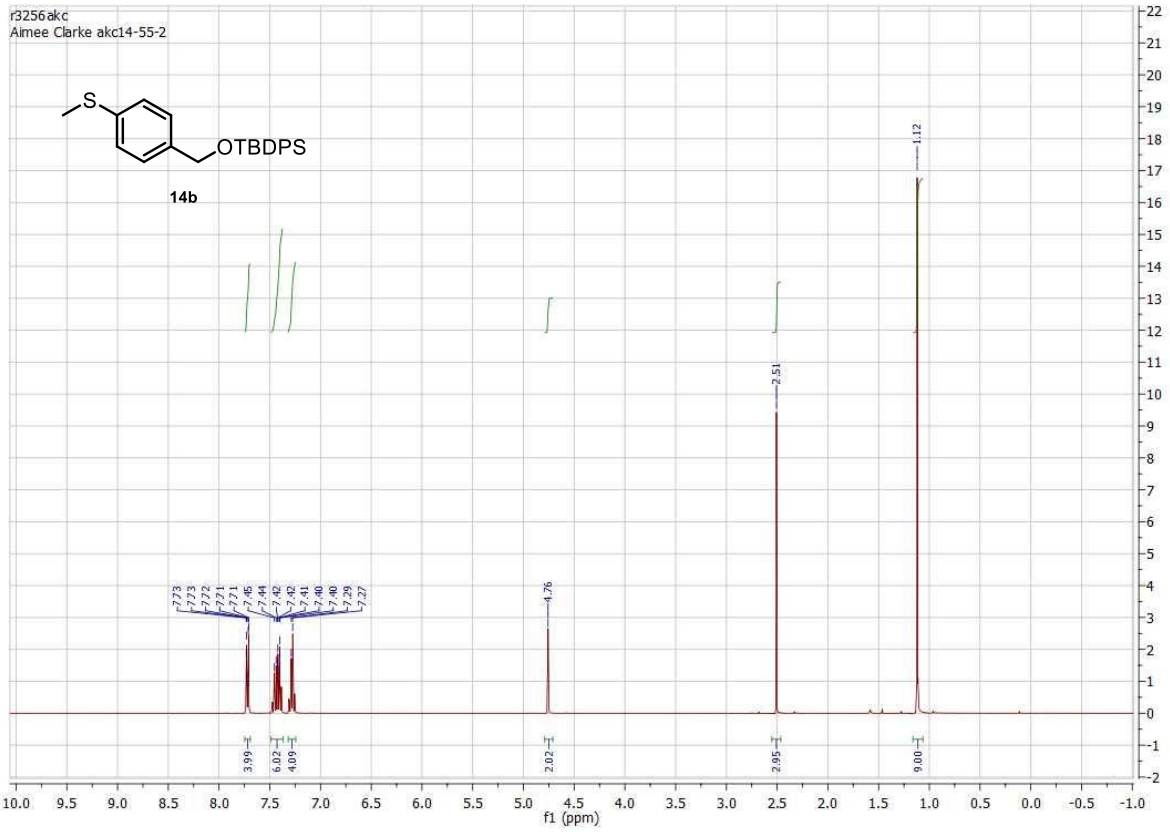
65.10
44.12
26.95
19.44
f1 (ppm)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Aimee Clarke akc14-55-2
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OTBDPS
14b
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7.73
7.72
7.71
7.71
7.45
7.44
7.42
7.42
7.41
7.40
7.40
7.29
7.27
4.76
2.51
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3.99
6.02
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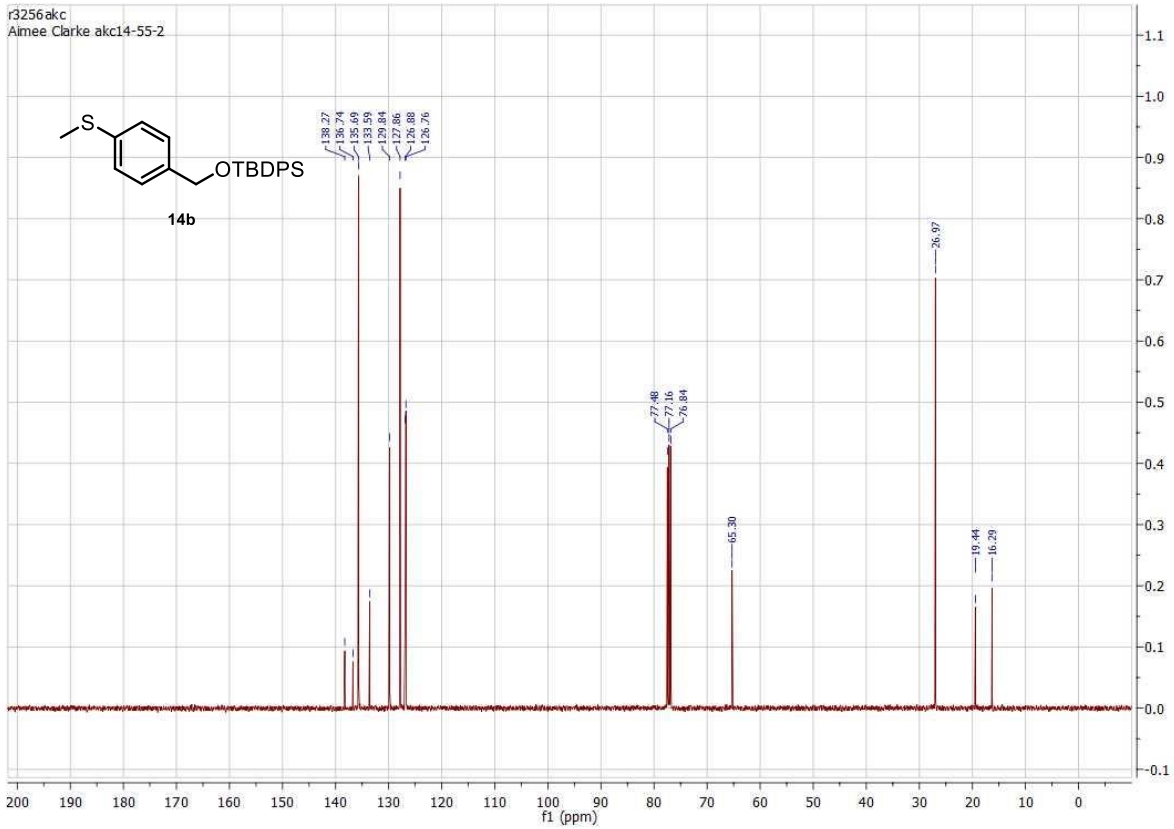
2.02
2.95
9.00
f1 (ppm)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Aimee Clarke akc14-55-2
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OTBDPS
14b
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136.74
135.69
133.59
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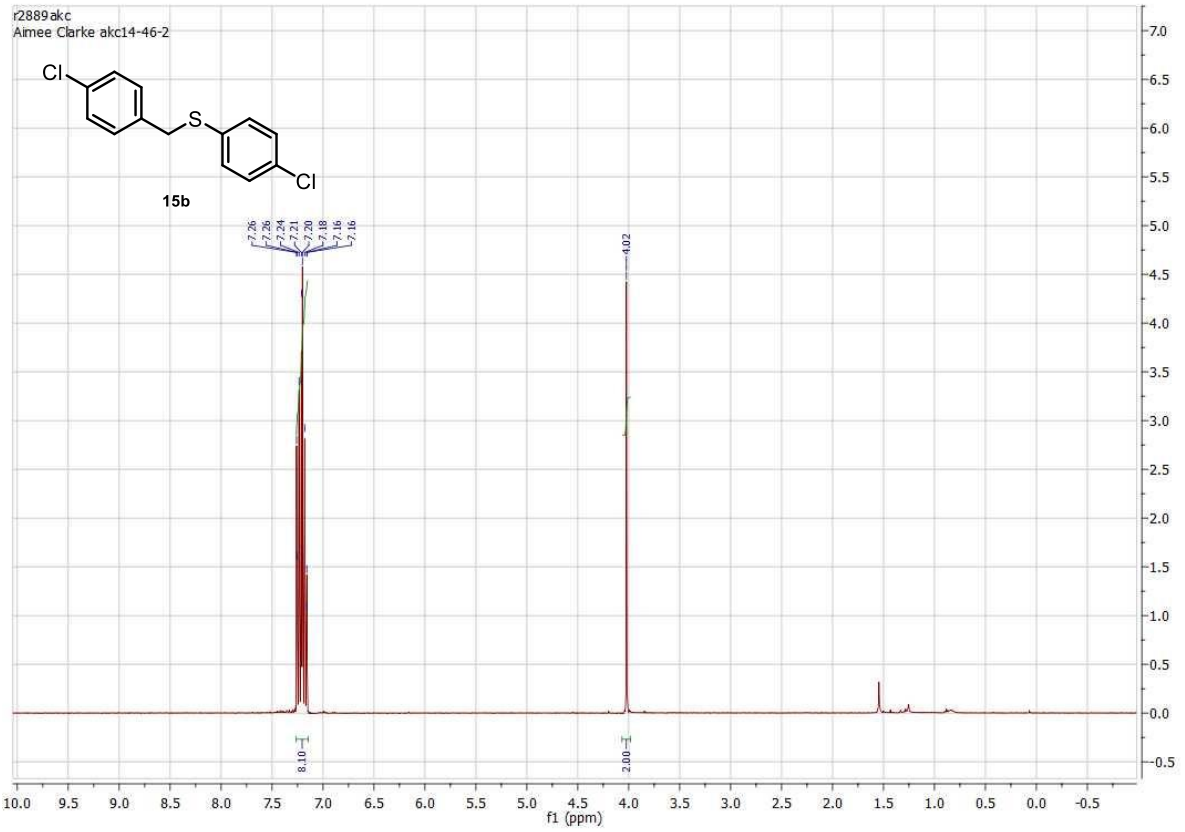
127.86
126.88
126.76
77.48
77.16
76.84
65.30
26.97
19.44
16.29
f1 (ppm)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Aimee Clarke akc14-46-2
Cl
S
Cl
15b
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7.24
7.21
7.20
7.18
7.16
7.16
4.02
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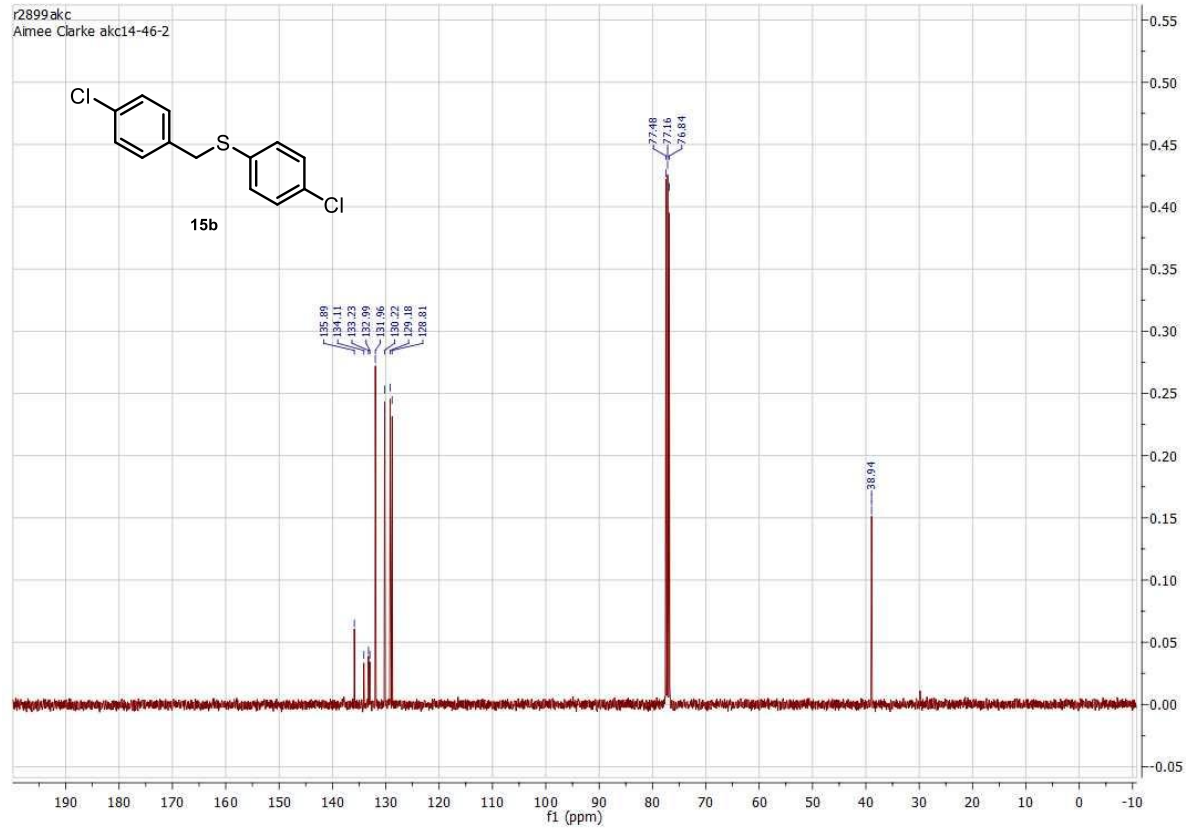
2.00
f1 (ppm)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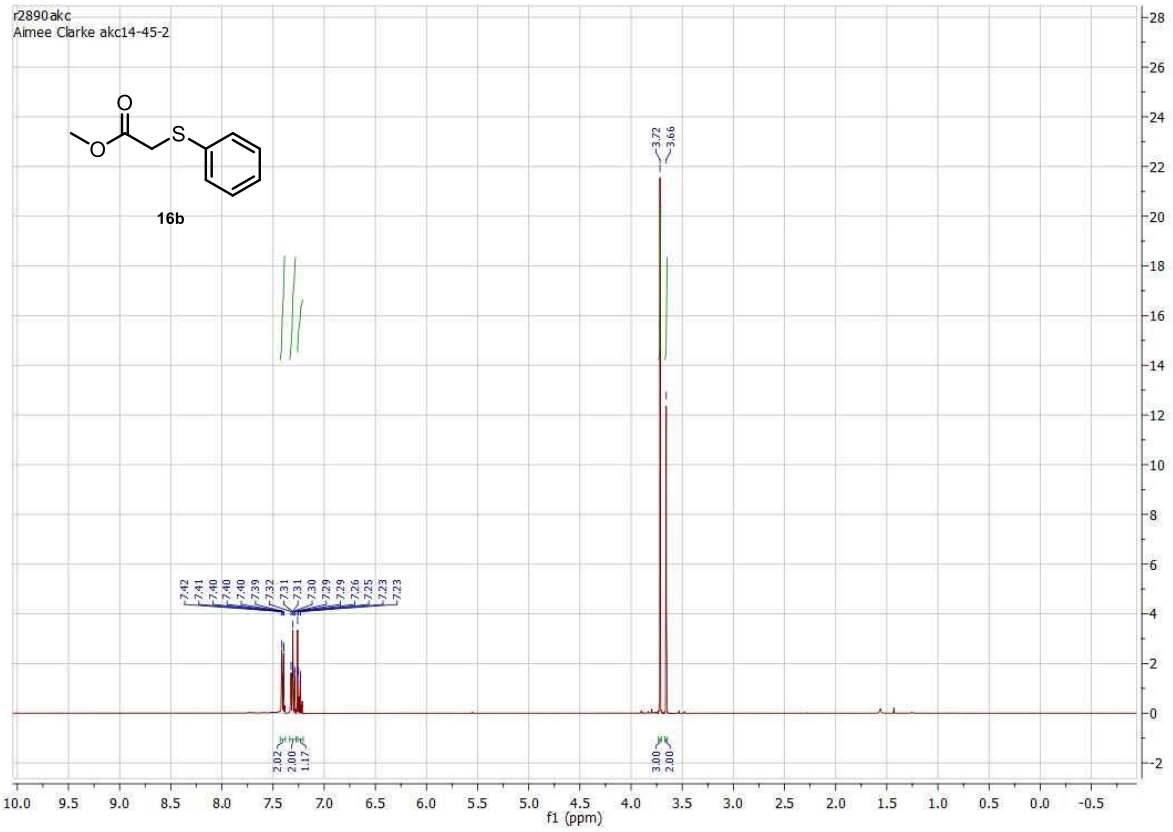
Aimee Clarke akc14-46-2
Cl
S
Cl
15b
135.89
134.11
133.23
132.99
131.96
130.22
129.18
128.81
77.48
77.16
76.84
38.94
f1 (ppm)


r2890akc
Aimee Clarke akc14-45-2
16b
3.72
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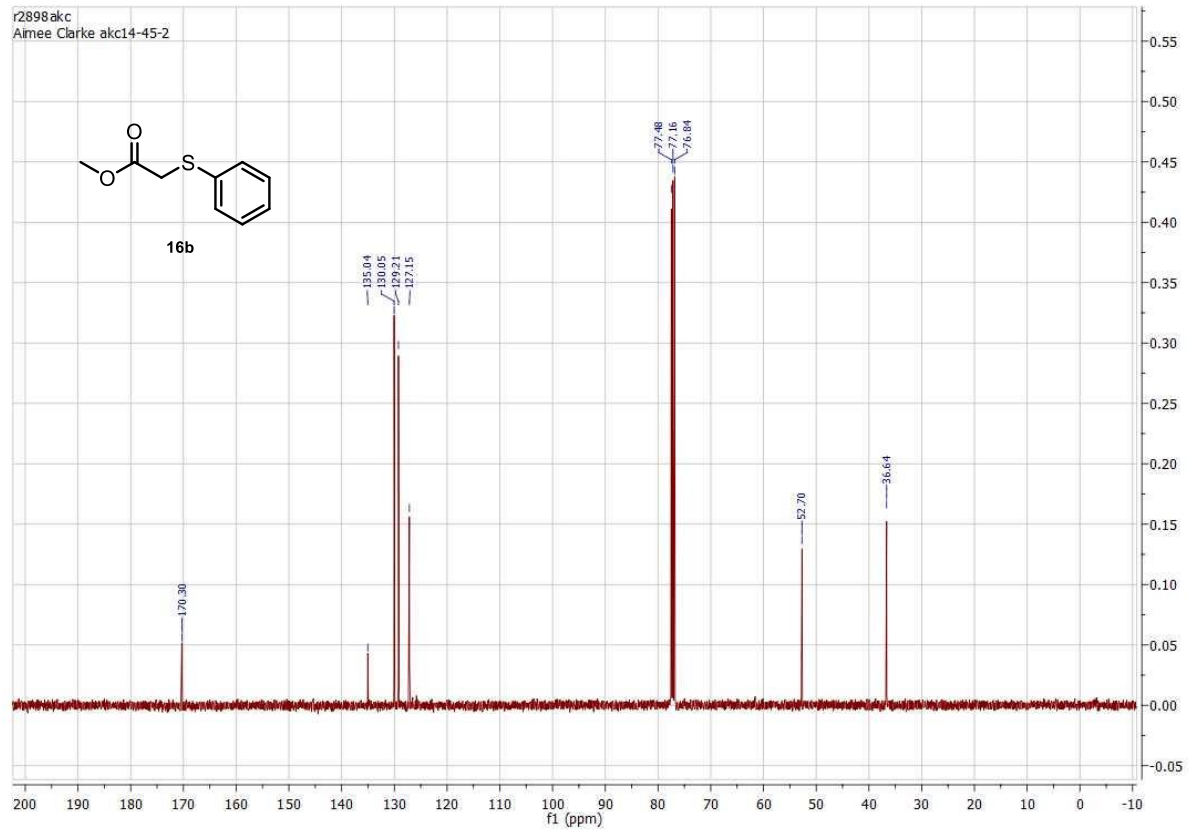
7.42
7.41
7.40
7.40
7.40
7.39
7.32
7.31
7.31
7.30
7.29
7.29
7.26
7.25
7.23
7.23
2.02
2.00
1.17
3.00
2.00
f1 (ppm)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Aimee Clarke akc14-45-2
16b
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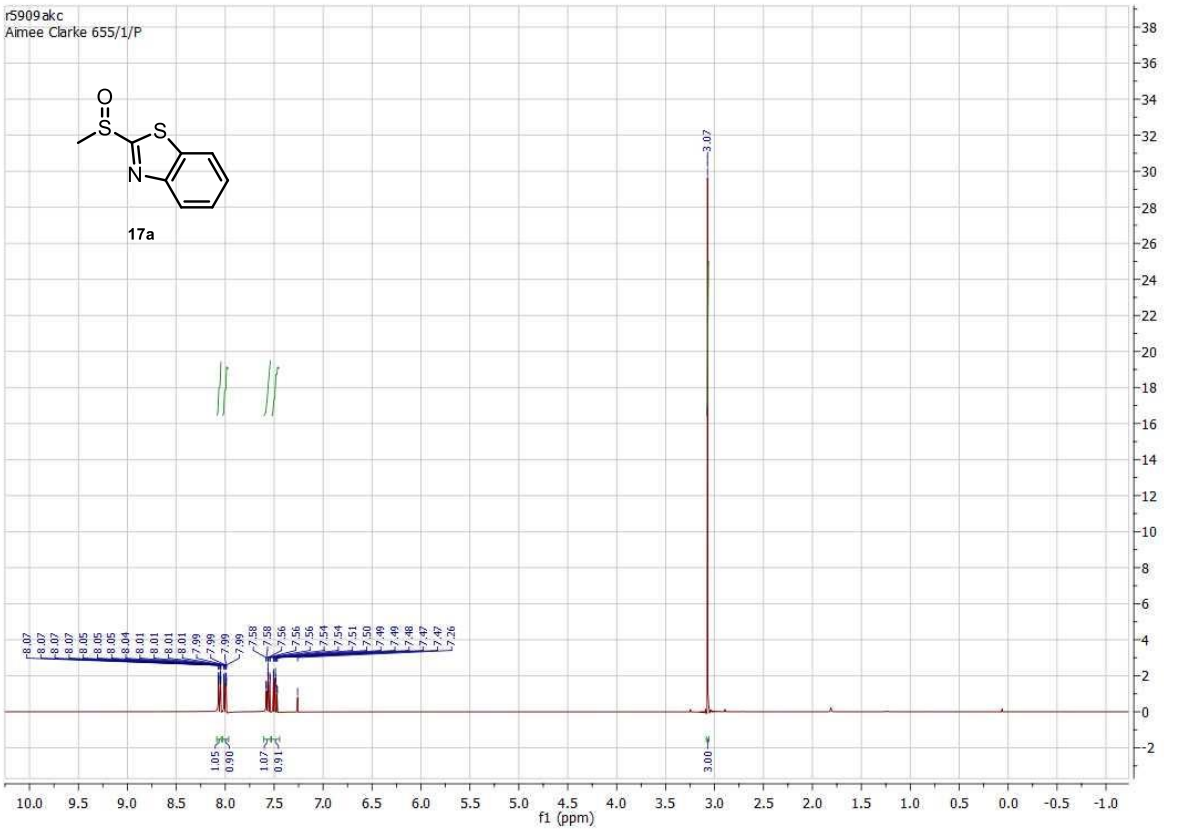
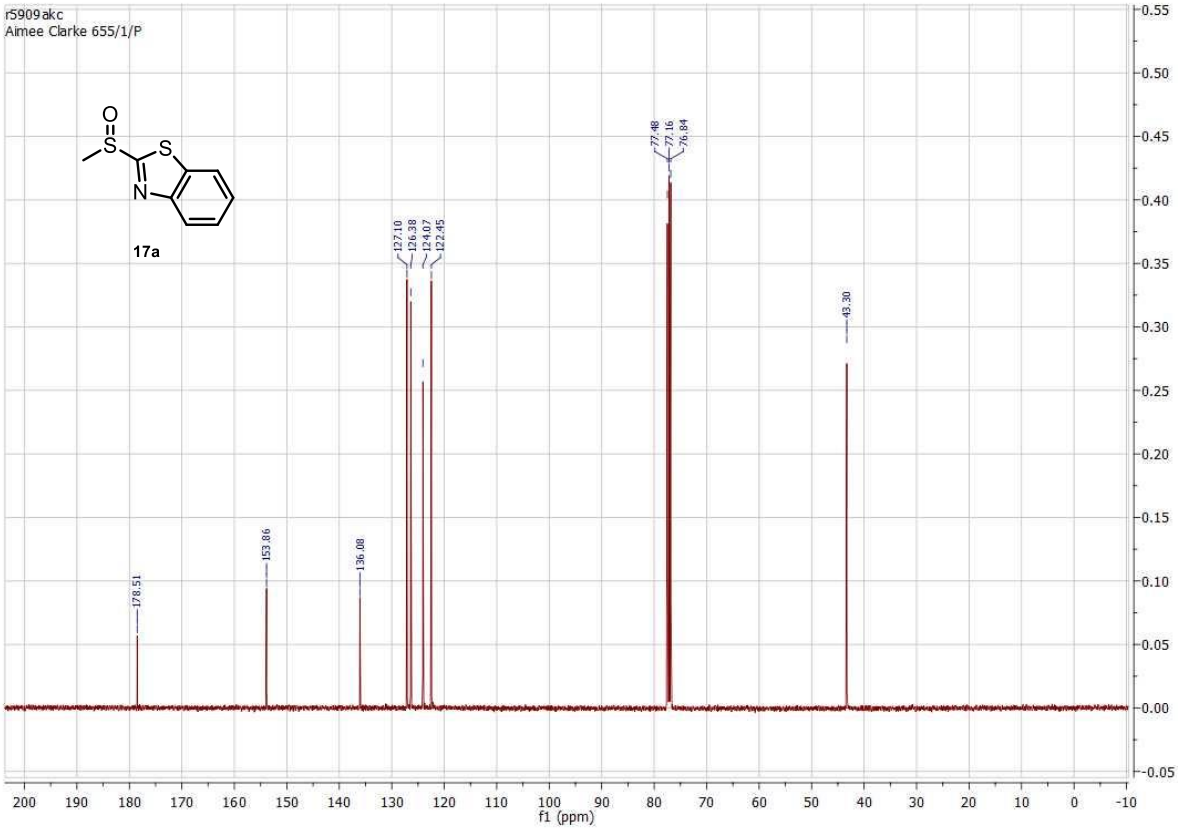
127.15
77.48
77.16
76.84
170.30
52.70
36.64
f1 (ppm)


r5909akc
Aimee Clarke 655/1/P
17a
f1 (ppm)


r5909akc
Aimee Clarke 655/1/P
17a
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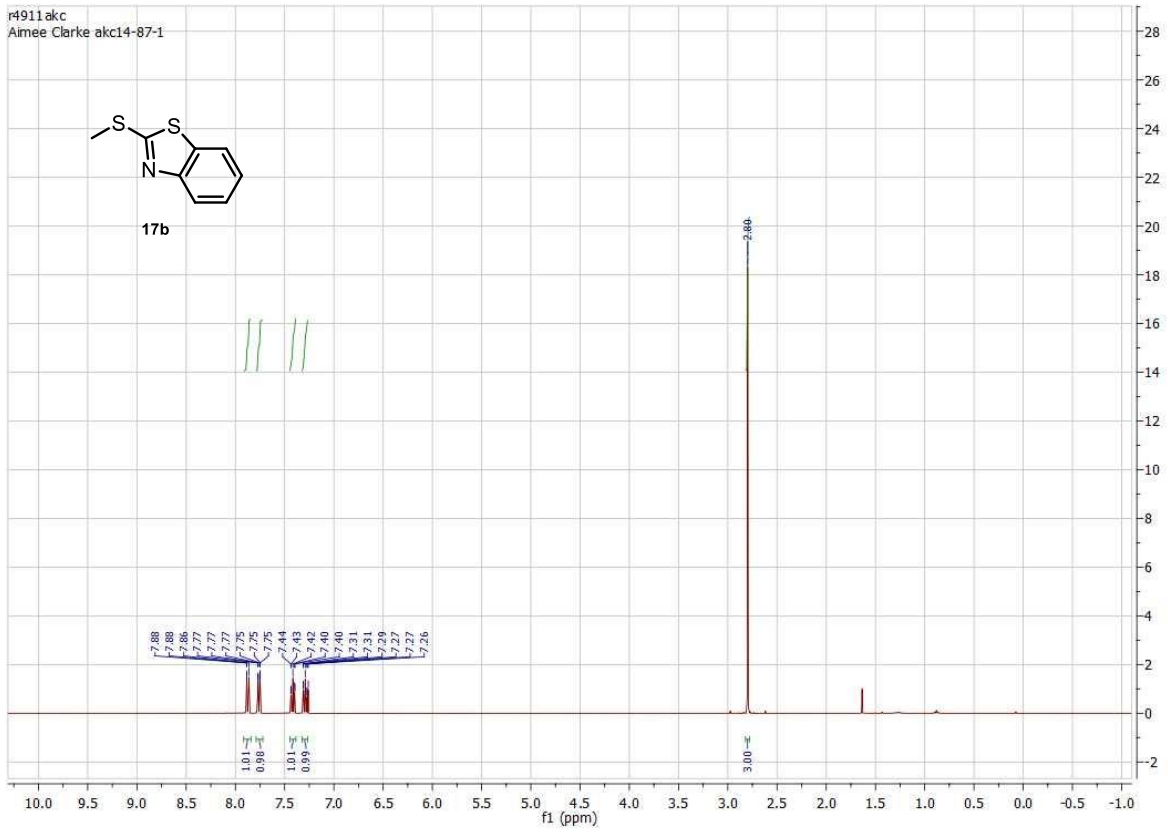
127.10
126.38
124.07
122.45
77.48
77.16
76.84
43.30
f1 (ppm)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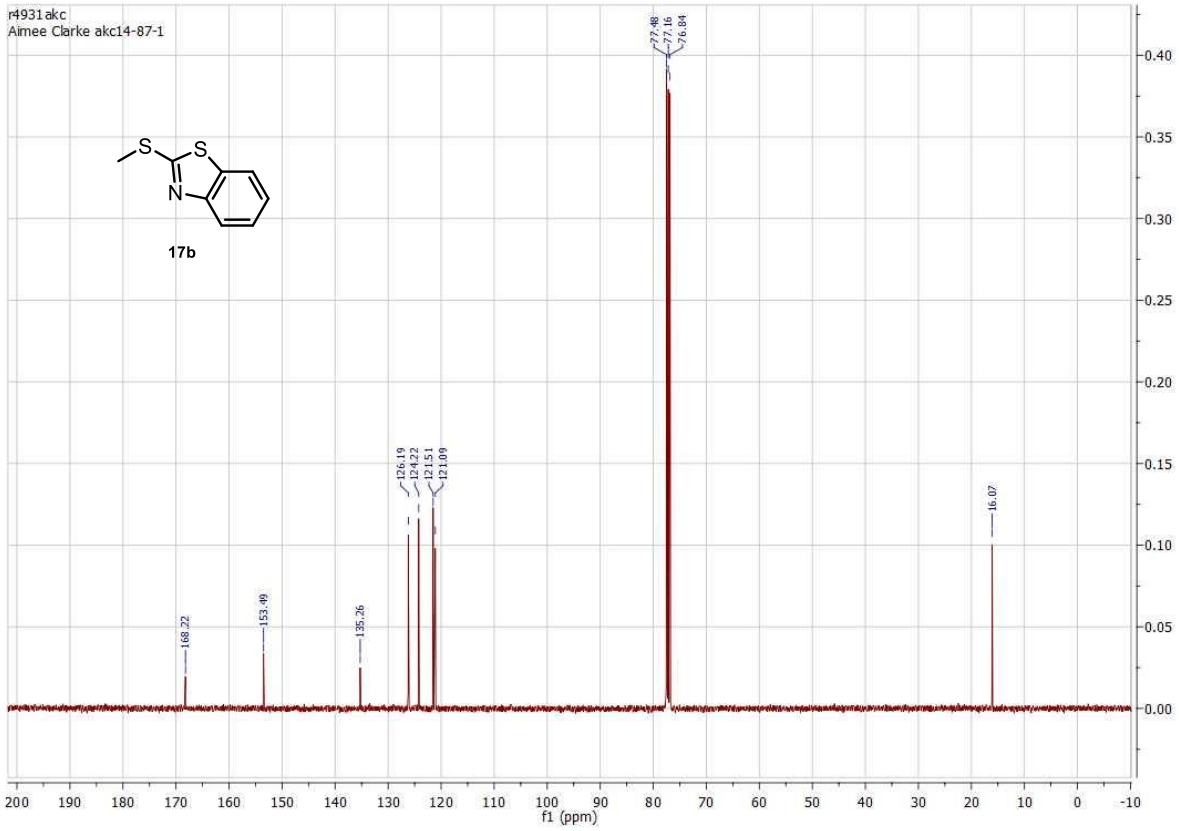
Aimee Clarke akc14-87-1
17b
f1 (ppm)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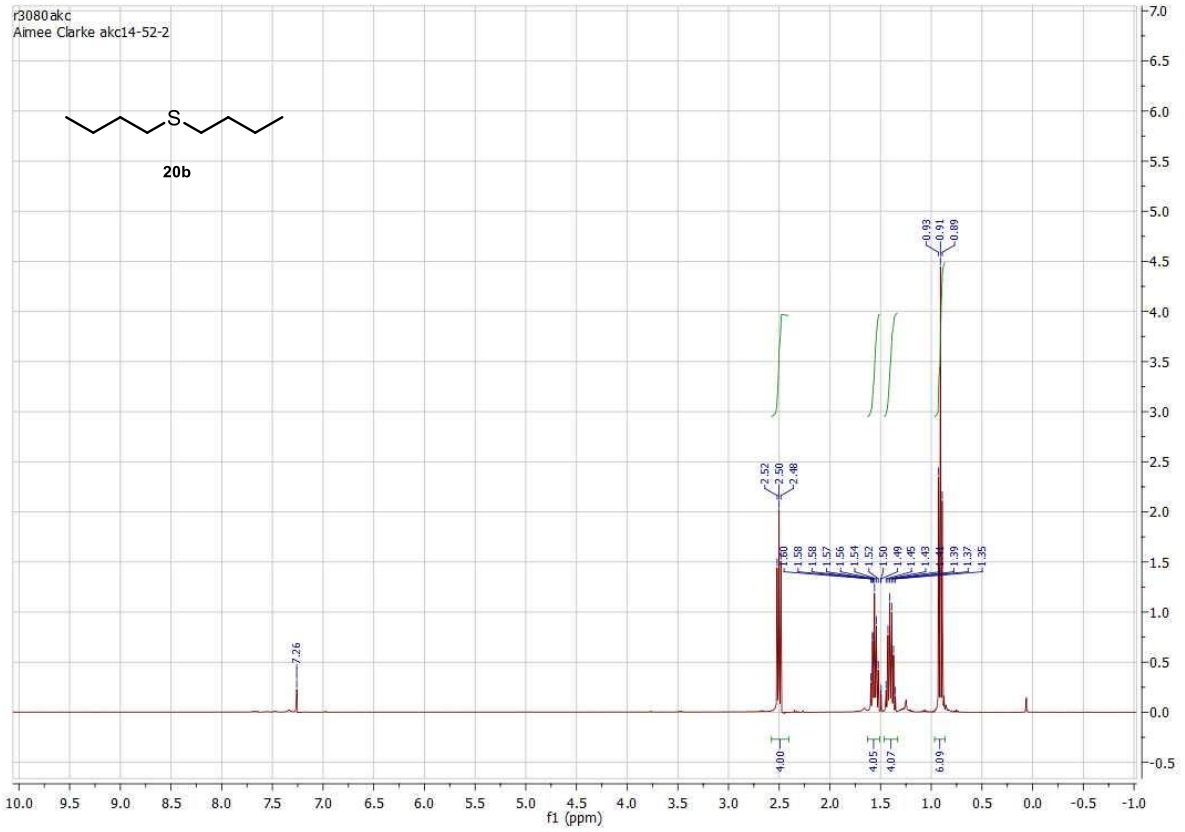
Aimee Clarke akc14-87-1
17b
f1 (ppm)


r3080akc
Aimee Clarke akc14-52-2
S
20b
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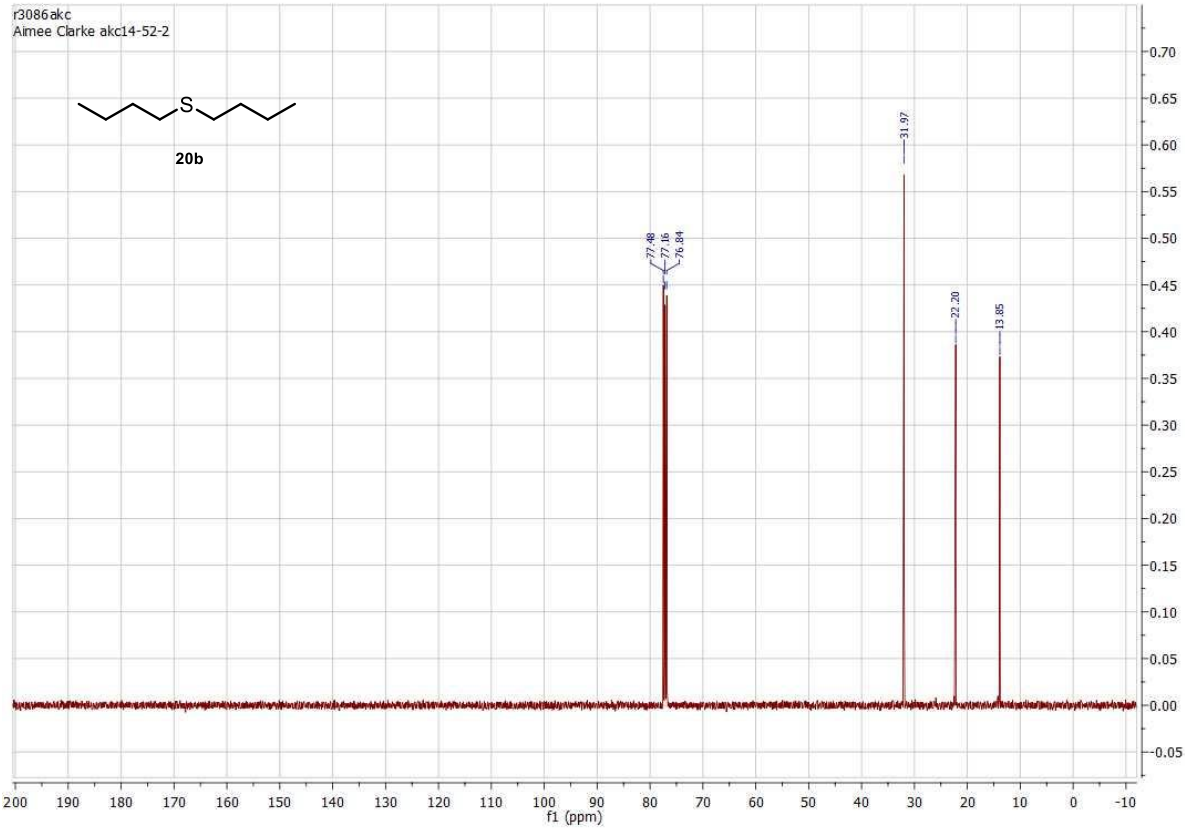
2.52
2.50
2.48
1.60
1.58
1.58
1.57
1.56
1.54
1.52
1.50
1.49
1.45
1.43
1.39
1.37
1.35
0.93
0.91
0.89
4.00
4.05
4.07
6.09
f1 (ppm)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Aimee Clarke akc14-52-2
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20b
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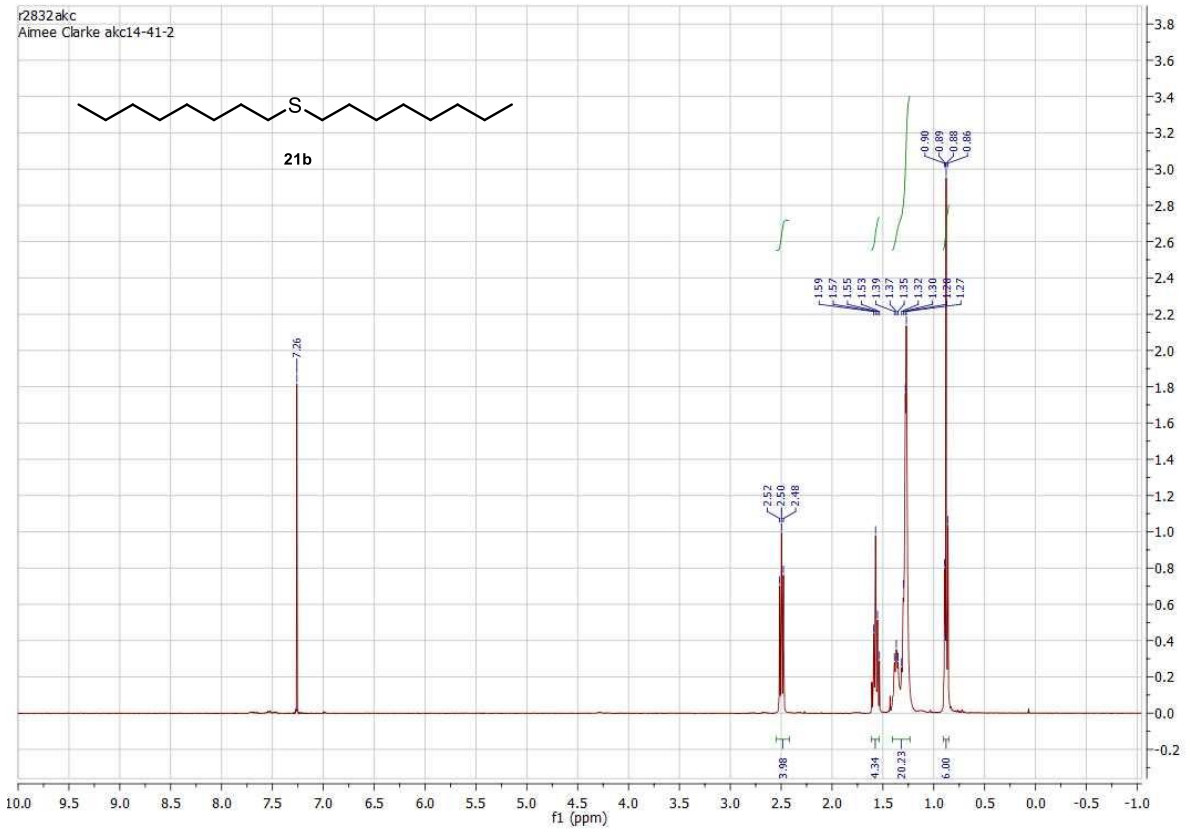
76.84
31.97
22.20
13.85
f1 (ppm)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Aimee Clarke akc14-41-2
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21b
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2.52
2.50
2.48
1.59
1.57
1.55
1.53
1.39
1.37
1.35
1.32
1.30
1.27
0.90
0.89
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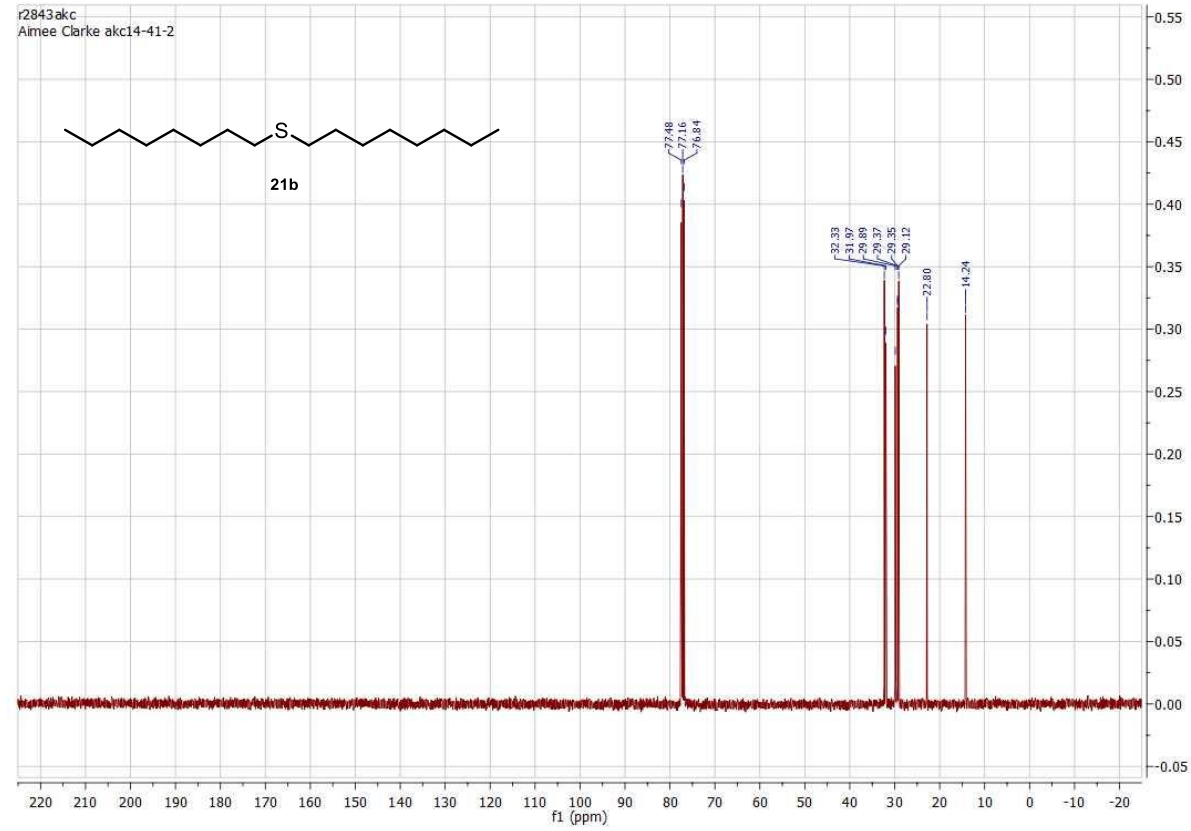
0.86
3.98
4.34
20.23
6.00
f1 (ppm)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21b
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76.84
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29.12
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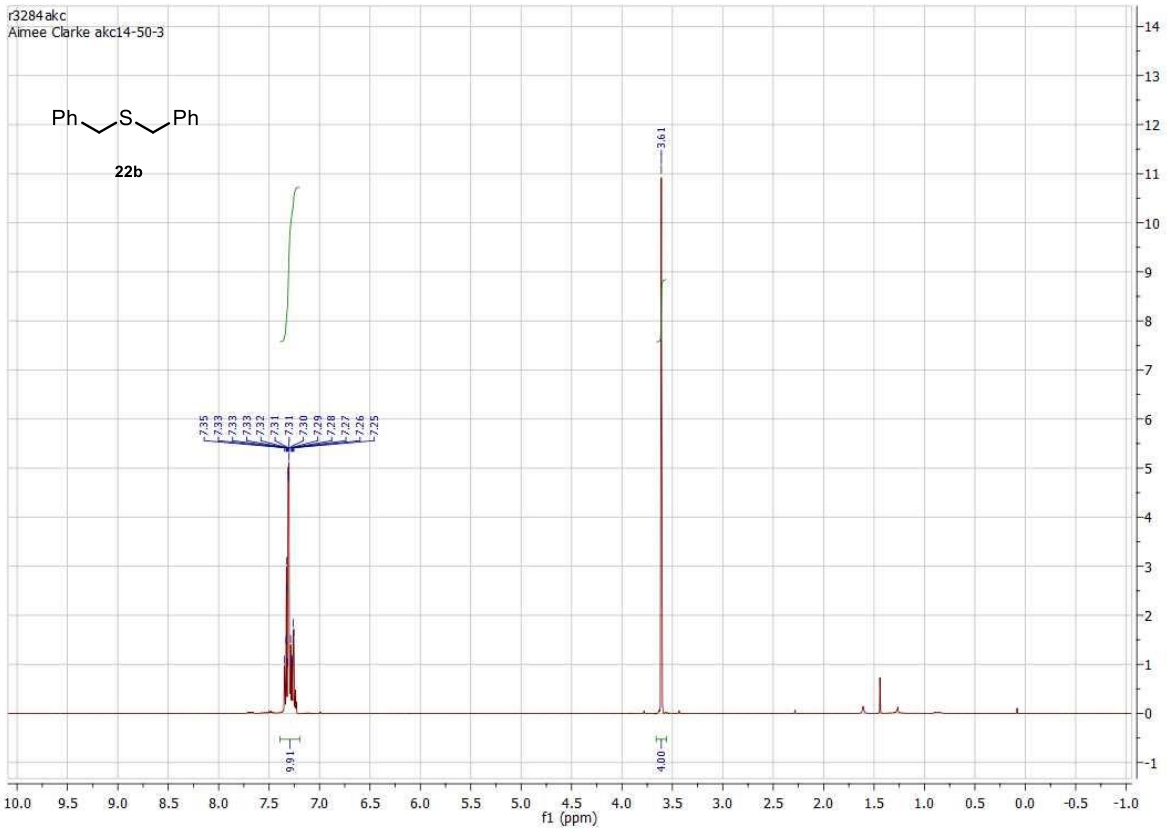
f1 (ppm)


r3284akc
Aimee Clarke akc14-50-3
Ph S Ph
22b
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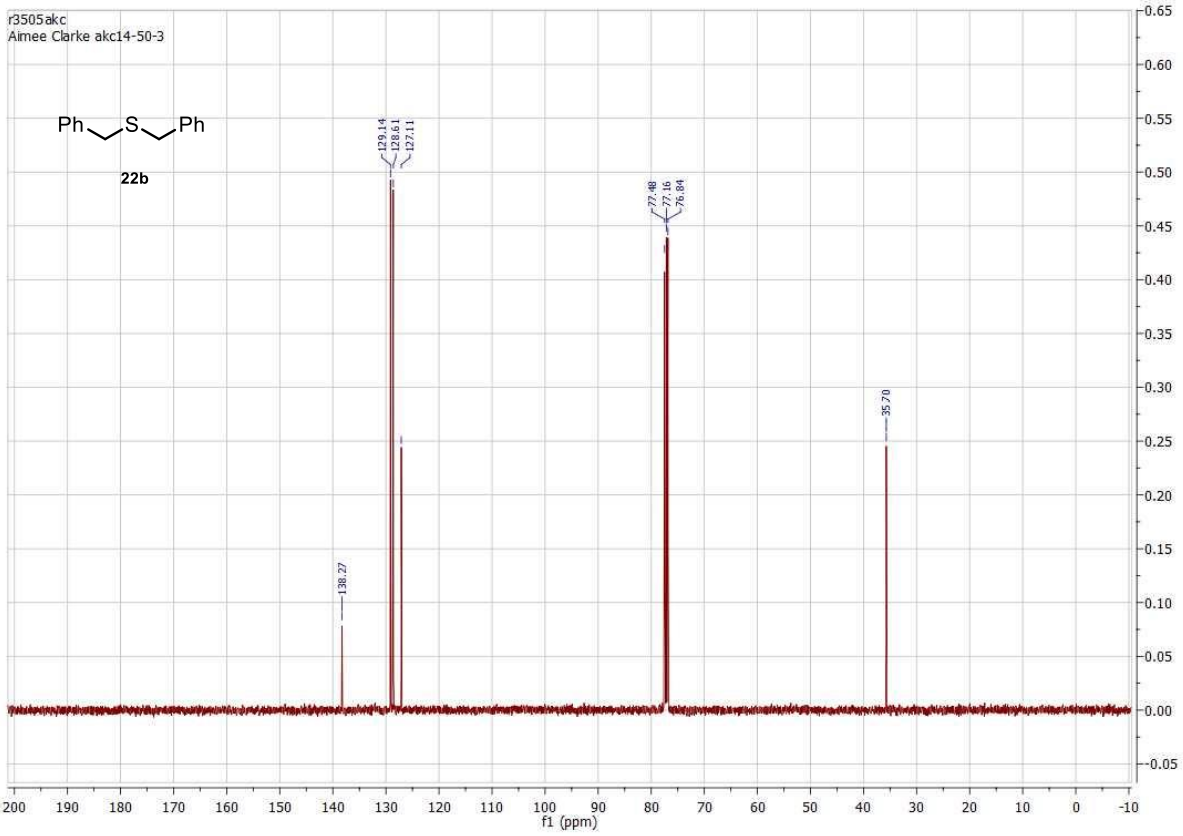
7.35
7.33
7.33
7.33
7.32
7.31
7.31
7.30
7.29
7.28
7.27
7.26
7.25
9.91
4.00
f1 (ppm)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Aimee Clarke akc14-50-3
Ph S Ph
22b
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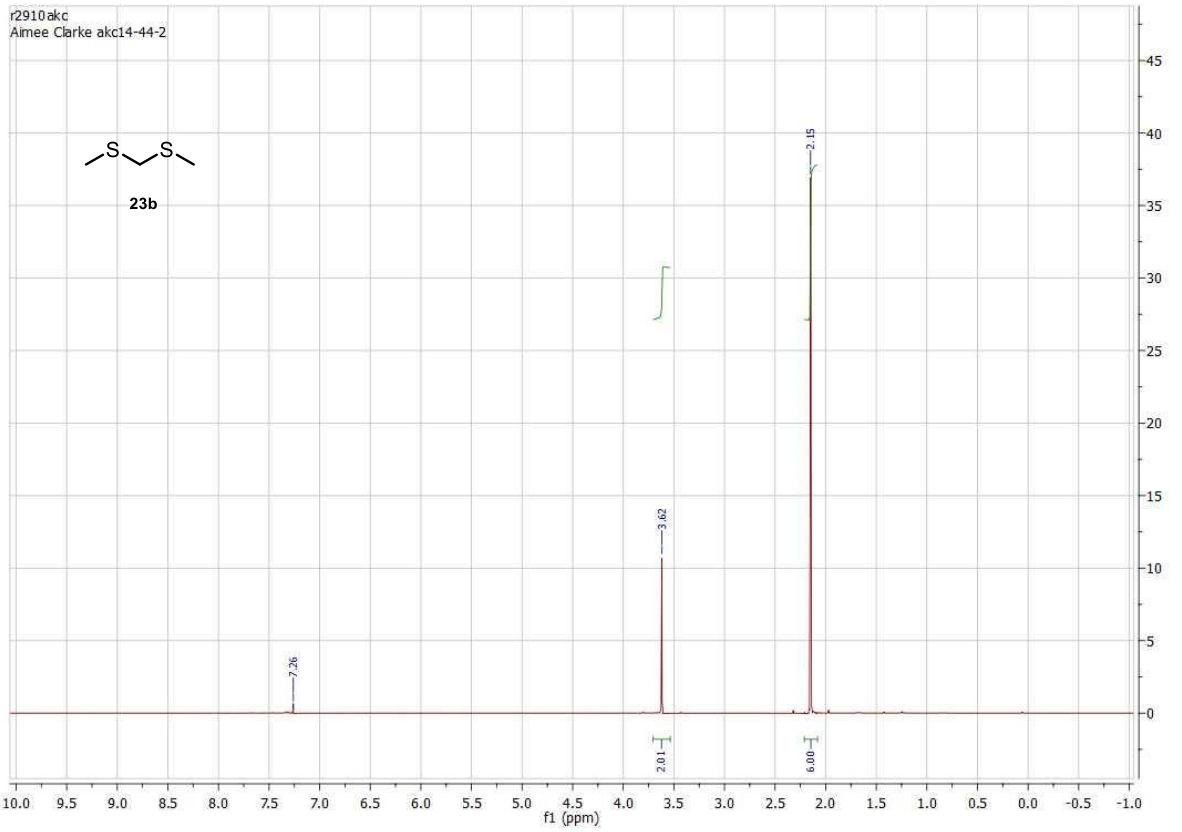
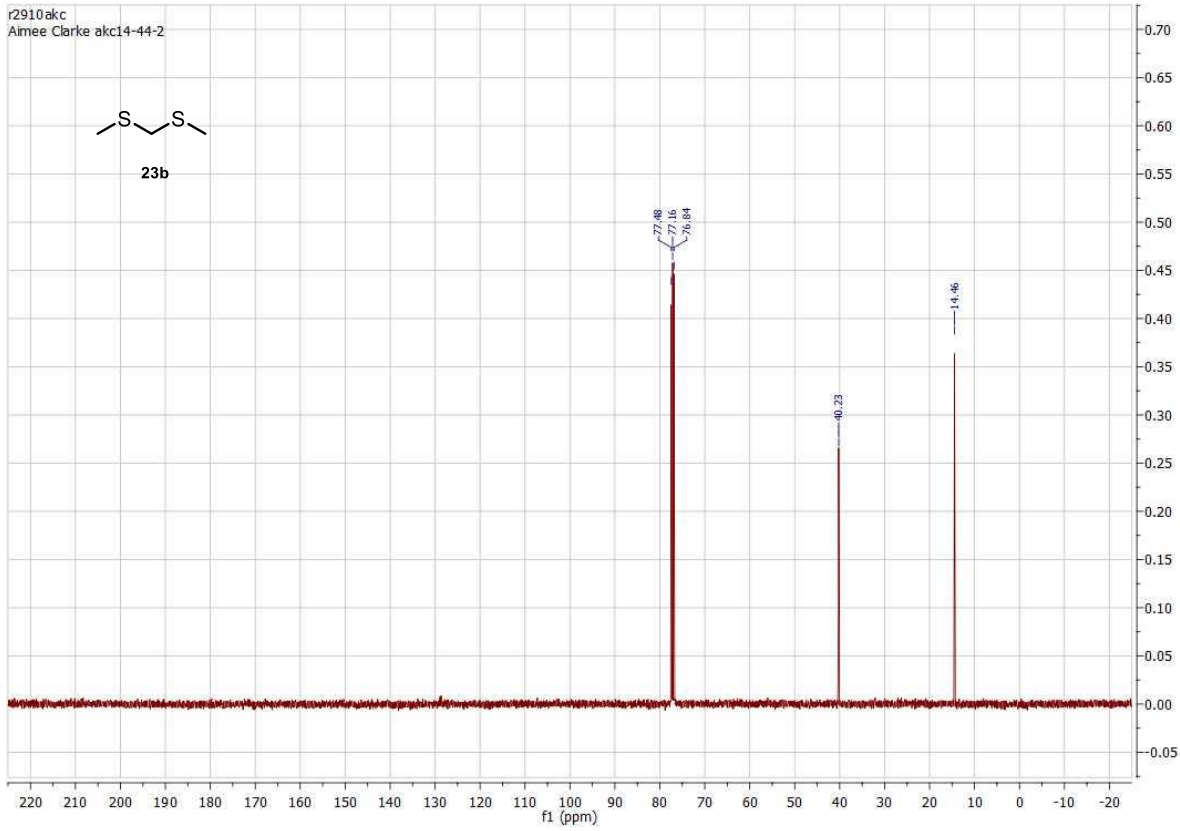
128.61
127.11
77.48
77.16
76.84
138.27
35.70
f1 (ppm)


r2910akc
Aimee Clarke akc14-44-2
23b
7.26
3.62
2.15
2.01
6.00
f1 (ppm)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Aimee Clarke akc14-44-2
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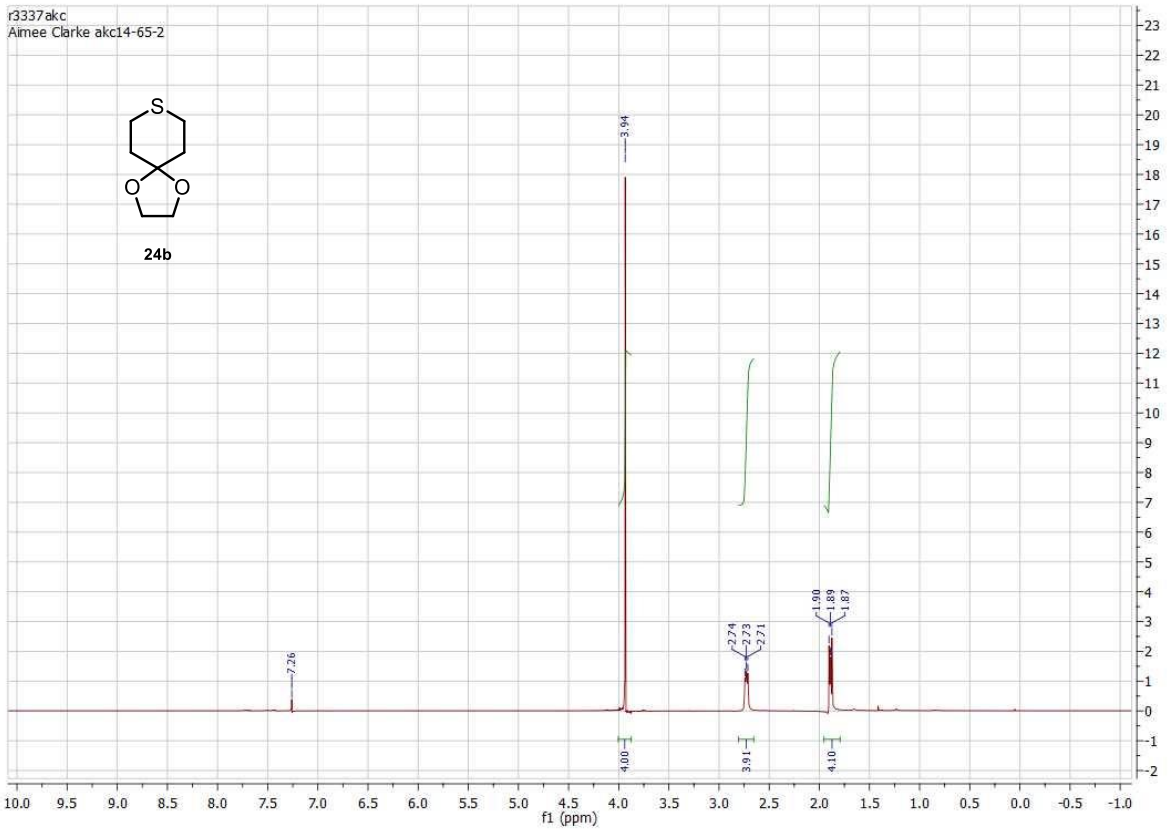
77.16
76.84
40.23
14.46
f1 (ppm)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24b
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2.71
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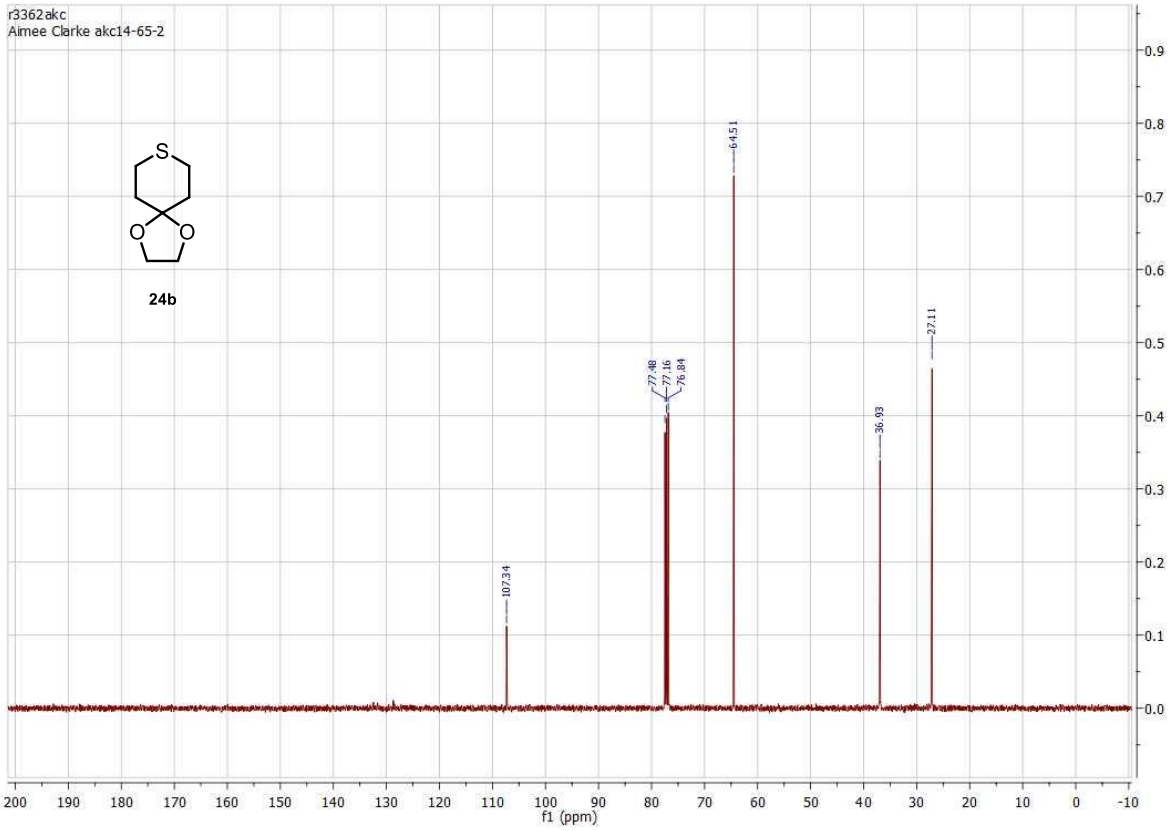
1.89
1.87
4.00
3.91
4.10
f1 (ppm)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Aimee Clarke akc14-65-2
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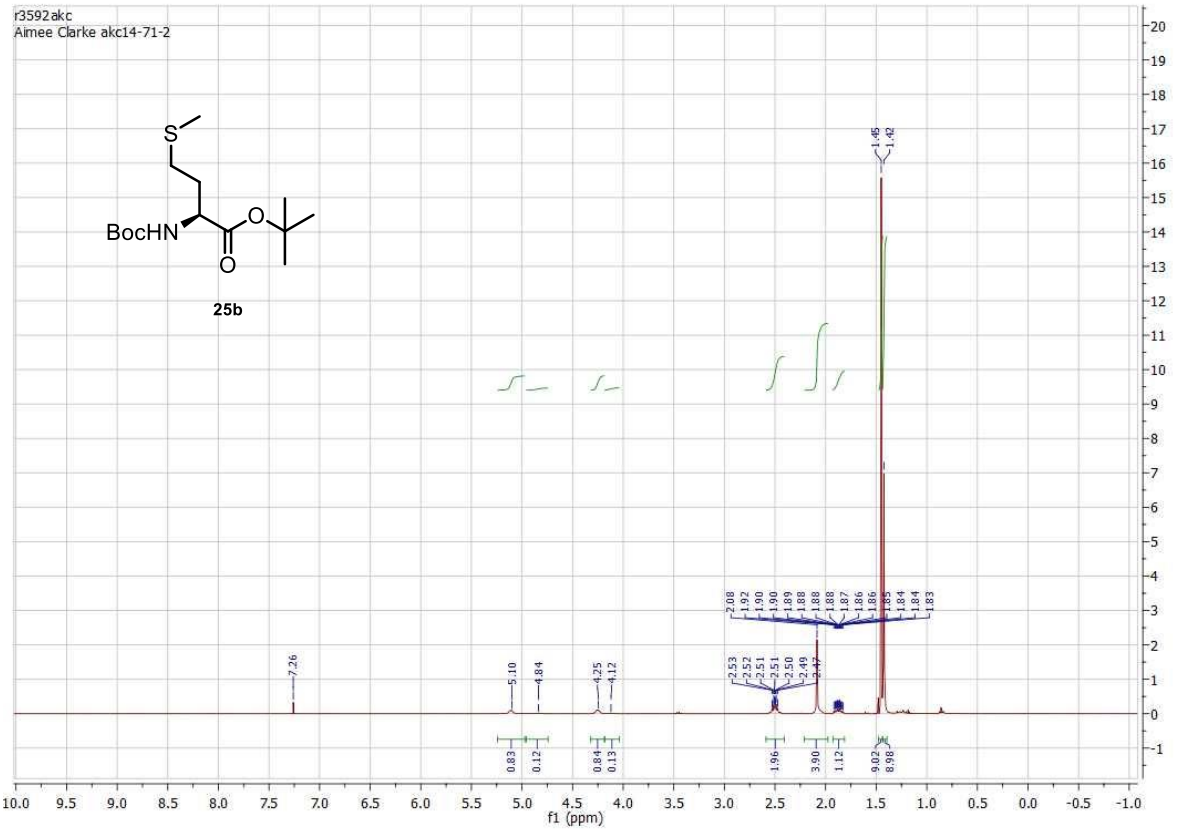
77.16
76.84
36.93
27.11
107.34
f1 (ppm)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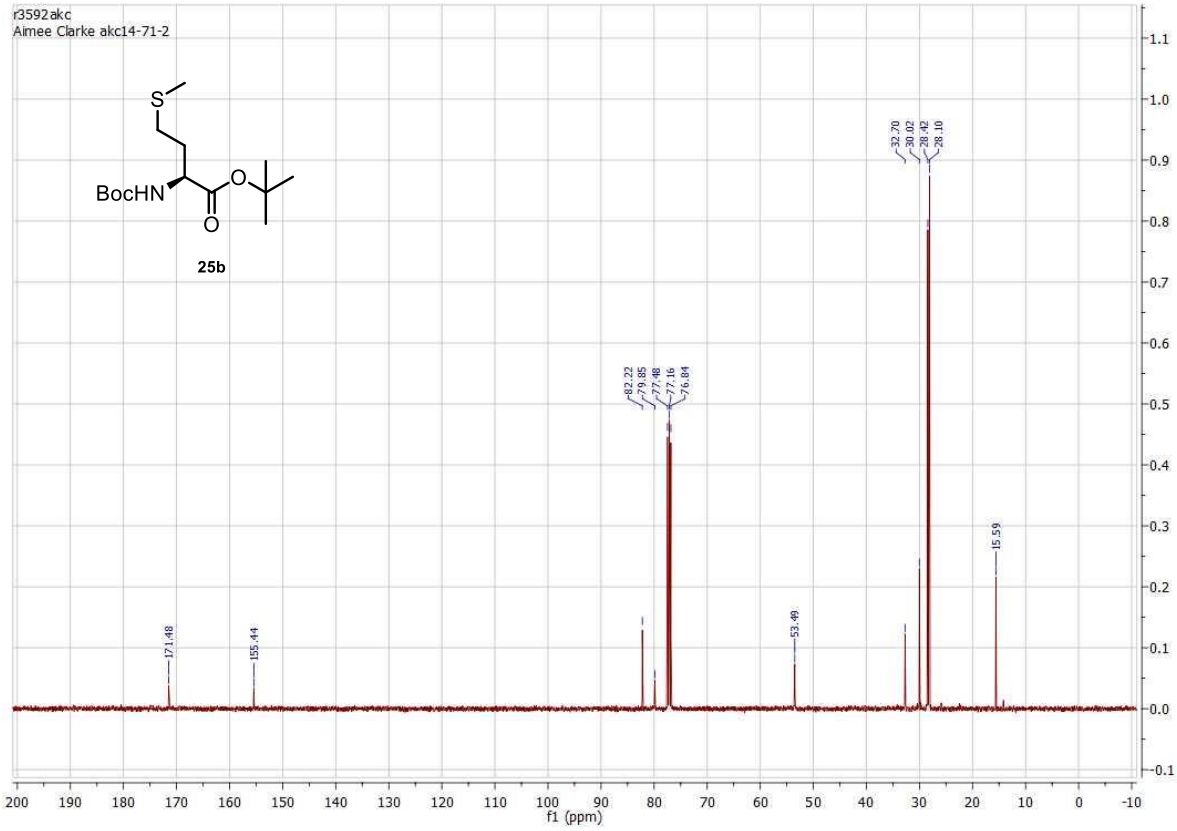
Aimee Clarke akc14-71-2
BocHN
25b
f1 (ppm)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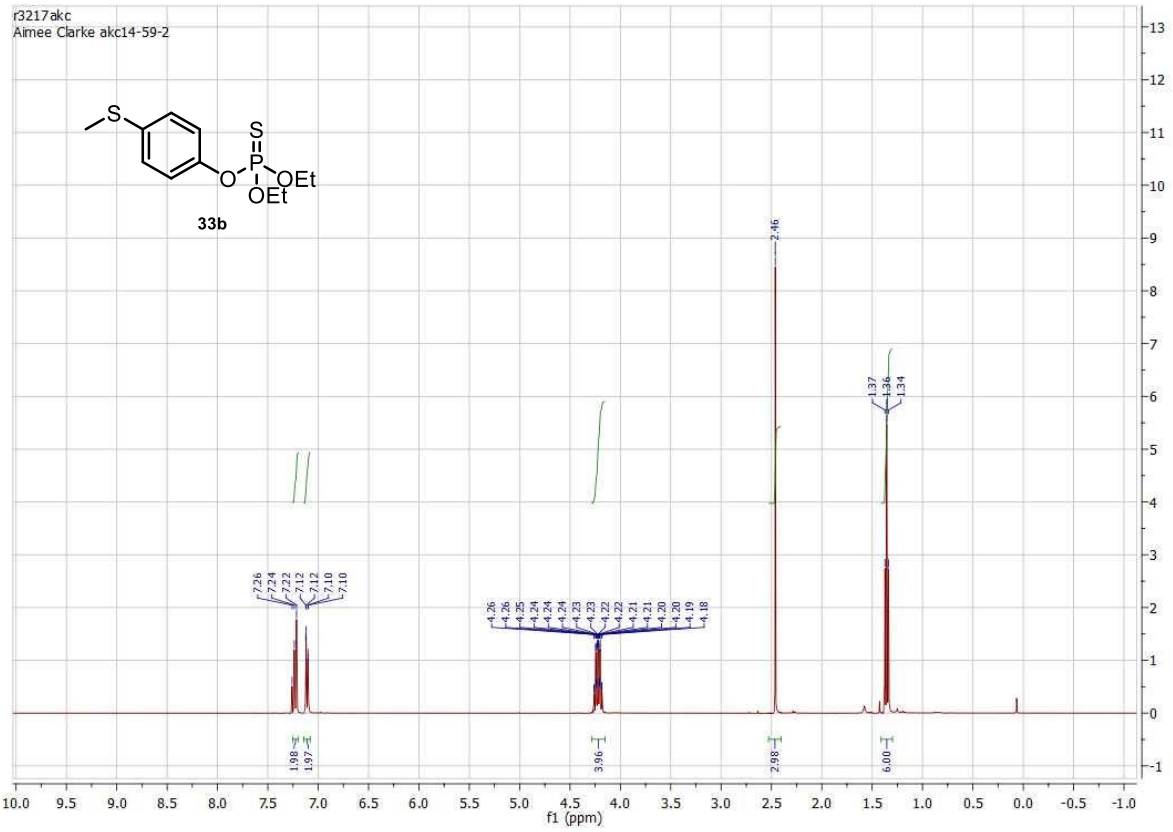
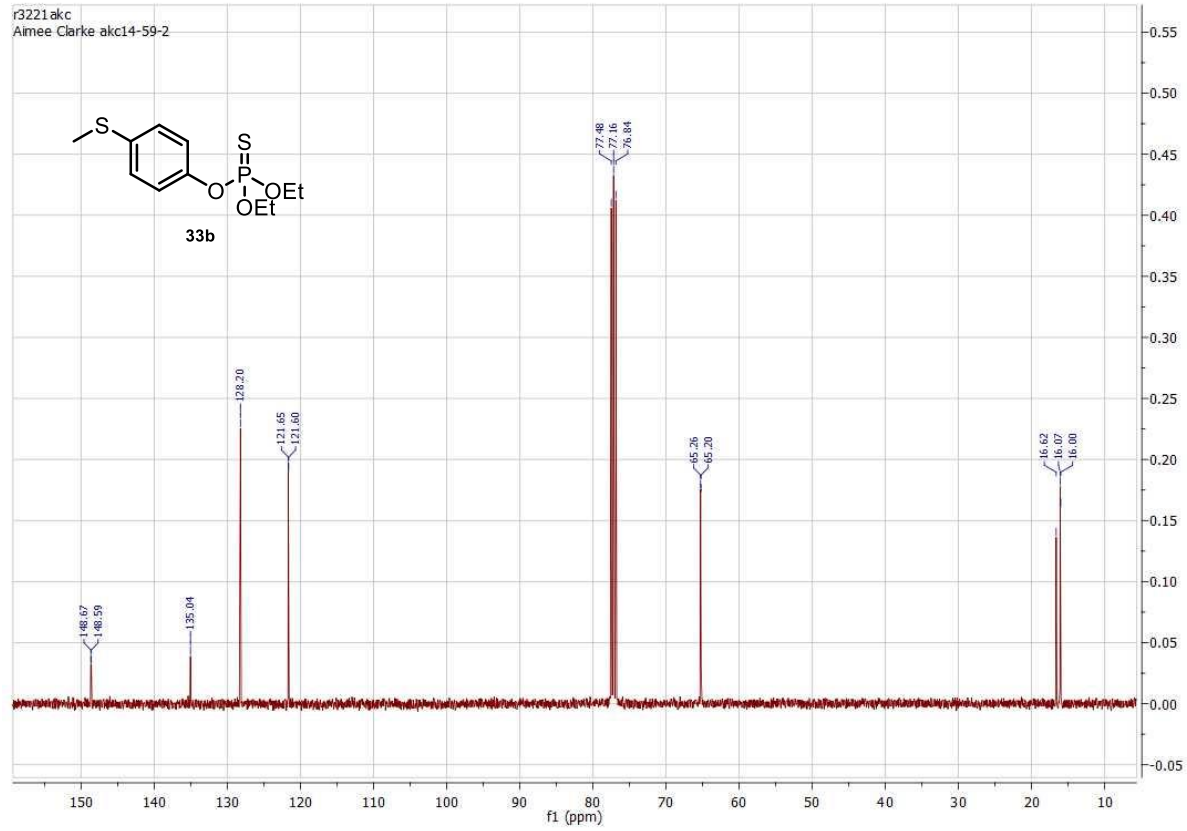
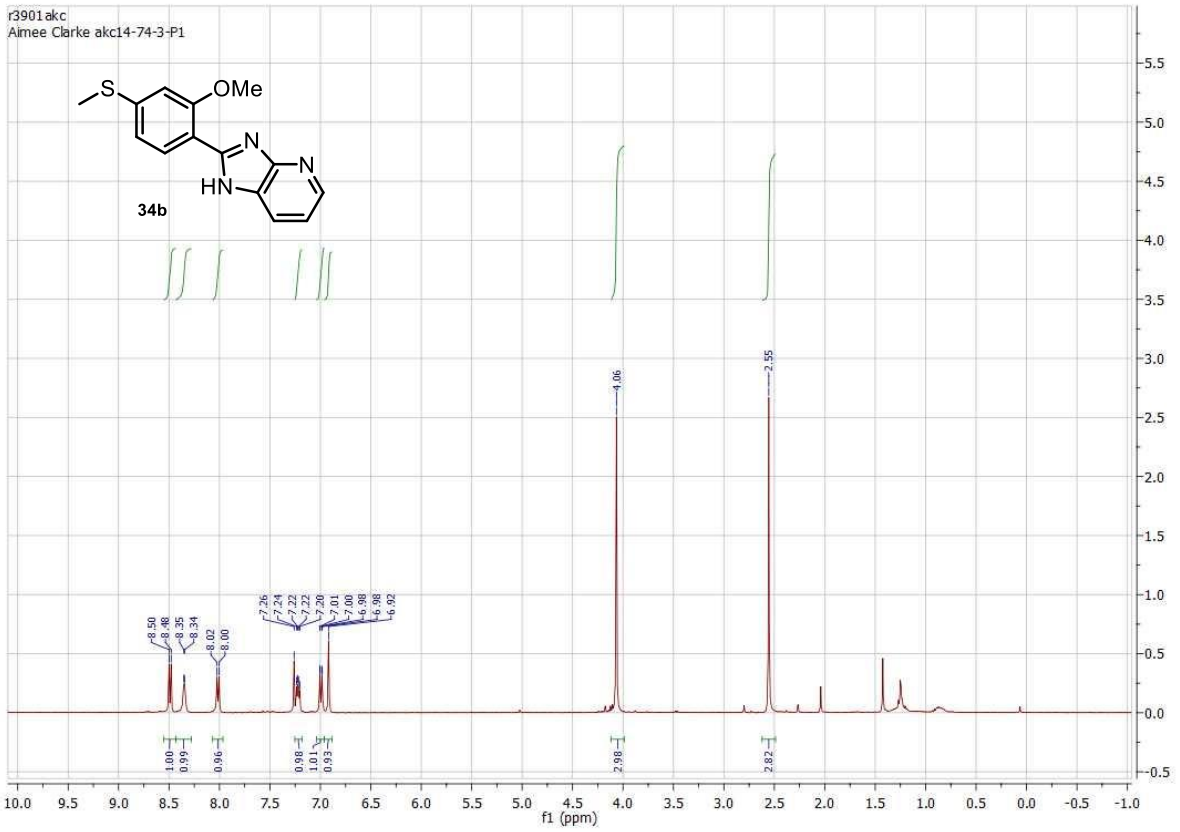
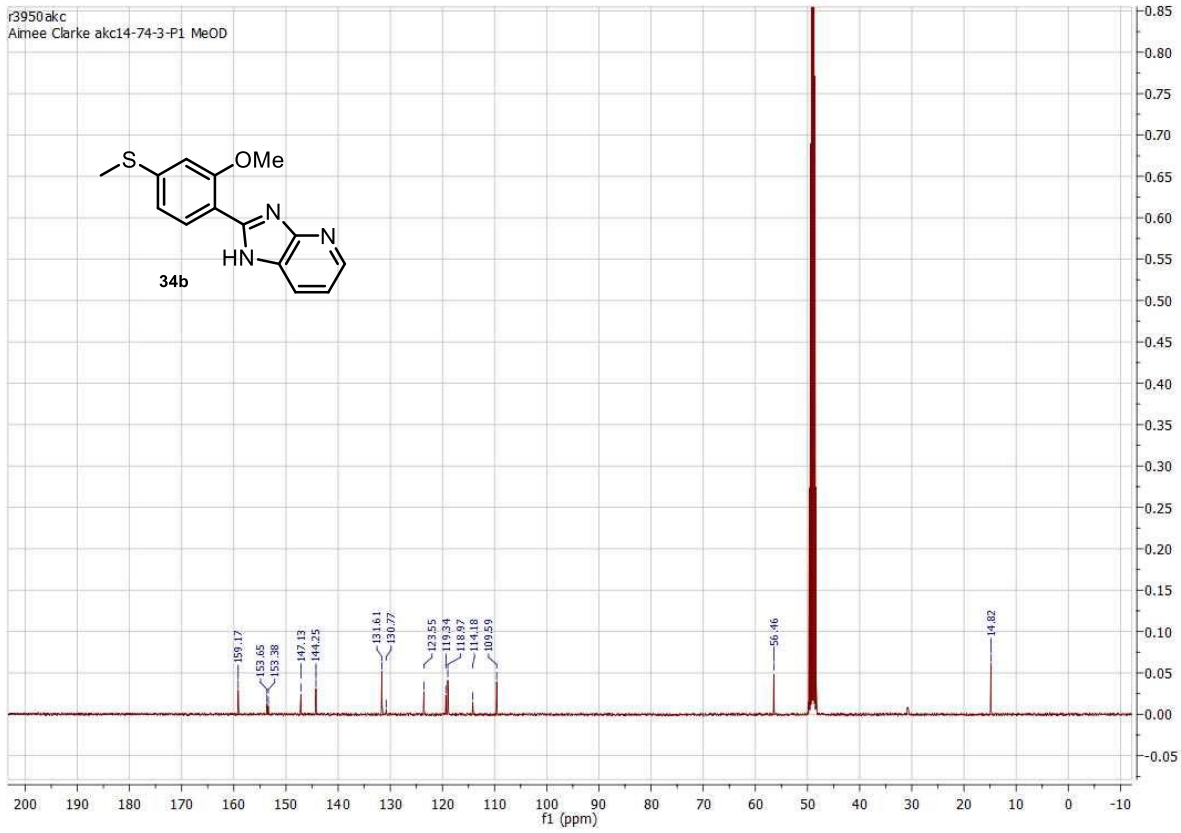
Aimee Clarke akc14-71-2
BocHN
25b
f1 (ppm)


r3217akc
Aimee Clarke akc14-59-2
33b
f1 (ppm)


r3221akc
Aimee Clarke akc14-59-2
33b
f1 (ppm)


r3901akc
Aimee Clarke akc14-74-3-P1
S
OMe
N
N
HN
34b
8.50
8.48
8.35
8.34
8.02
8.00
7.36
7.24
7.22
7.22
7.20
7.01
7.00
6.98
6.98
6.92
4.06
2.55
1.00
0.99
0.96
0.98
1.01
0.93
2.98
2.82
f1 (ppm)


r3950akc
Aimee Clarke akc14-74-3-P1 MeOD
S
OMe
N
N
HN
34b
159.17
153.65
153.38
147.13
144.25
131.61
130.77
123.55
119.34
118.97
114.18
109.59
56.46
14.82
f1 (ppm)

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1. Rehaud, P. Reactions of sulfinylated radicals. Stereoselectivity in six-membered rings. *Helv. Chim. Acta* **1991**, *74*, 1305–1313

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