Supporting Information For

Copper and triphenylphosphine-promoted sulfenylation of quinones with arylsulfonyl chlorides

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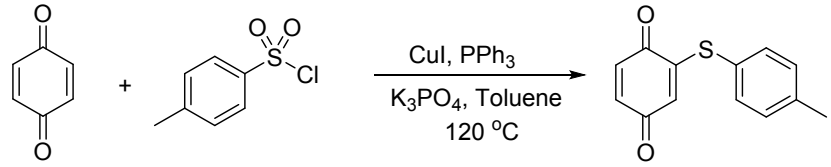
1. General Information

Copper iodide, triphenylphosphine phosphine and other chemicals were obtained from commercial resource and used without further purification. All solvents were dried and purified by known procedures and freshly distilled under nitrogen from appropriate drying agents prior to use. The products were isolated by column chromatography on silica gel (200-300 mesh or 100-200 mesh) by using petroleum ether (60-90 °C) and ethyl acetate as eluents. Silica gel for column chromatography was purchased from Qingdao Haiyang Chemical Co., Lt. All yields described herein are the isolated yields after column chromatography. Reaction progress and product mixtures were routinely monitored by TLC using TLC SiO_2 sheets, and compounds were visualized under ultraviolet light. ^{1}H-NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer. ^{1}H-NMR chemical shifts are referenced to tetramethylsilane (TMS) (0 ppm). Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m). HRMS were recorded on Thermo Scientific LTQ Orbitrap XL spectrometer equipped with an ESI source.

2. Details of experimental procedures

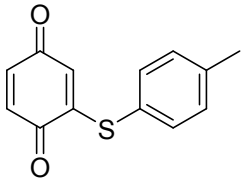
2.1. Typical procedure for the synthesis of quinones and arylsulfonyl chlorides:



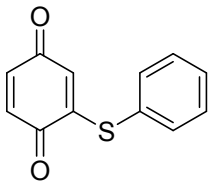
1a **2a** **4a**

The mixture of quinone (**1a**) (1.0 mmol), benzenesulfonyl chloride (**2a**) (2.5 mmol), CuI (10 mol%), PPh_3 (2.5 mmol) and K_3PO_4 (1.5 mmol) in toluene (5 mL) was stirred at 120 °C under air for 10 h. Upon completion, the reaction mixture was removed the solvents to give the residue. The residue was then purified by column chromatography on silica gel (petroleum ether / ethyl acetate = 15:1) to provide the corresponding product as yellow solid **4a**.

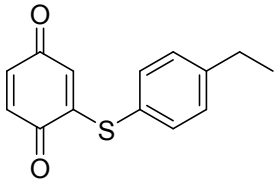
2.2. ^{1}H and ^{13}CNMR spectra of compounds



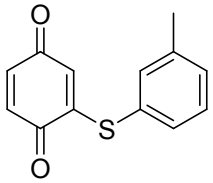
2-(*p*-tolylthio)cyclohexa-2,5-diene-1,4-dione (4a). (Known compound, ref: S. H. Kim, E. A. Theodorakis, *Sci of Synt.* 2006, **28**, 53-69), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.9 Hz, 2 H), 7.29 (d, *J* = 7.9 Hz, 2 H), 6.82 (d, *J* = 10.0 Hz, 1 H), 6.68 (dd, *J* = 10.0, 2.4 Hz, 1 H), 5.89 (d, *J* = 2.4 Hz, 1 H), 2.42 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.5, 184.0, 154.9, 141.1, 137.4, 135.9, 135.5, 131.2, 125.8, 123.2, 21.3.



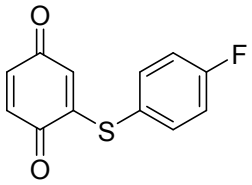
2-(phenylthio)cyclohexa-2,5-diene-1,4-dione (4b). (Known compound, ref: V. K. Tandon, H. K. Maurya, *Tetrahedron Lett.* 2009, **50**, 5896-5902.), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 5 H), 6.85 (d, *J* = 10.0, 0.8 Hz, 1 H), 6.71 (ddd, *J* = 10.0, 2.4, 0.8 Hz, 1 H), 5.91 (dd, *J* = 2.4, 0.8 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.4 183.9, 154.5, 137.5, 135.9, 135.6, 130.6, 130.4, 126.0, 125.9.



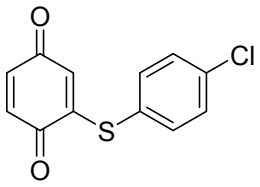
2-((4-ethylphenyl)thio)cyclohexa-2,5-diene-1,4-dione (4c). (Known compound, ref: D. Wang, X. Yu, W. Yao, W.. Hu, C. Ge, and X. Shi, *Chem. Eur. J.* 2016, **22**, 8863-8868) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.0 Hz, 2 H), 7.32 (t, *J* = 7.2 Hz, 2 H), 6.82 (dd, *J* = 10.0, 0.8 Hz, 1 H), 6.67 (ddd, *J* = 10.0, 2.4, 0.8 Hz, 1 H), 5.90 (dd, *J* = 2.4, 0.9 Hz, 1 H), 2.71 (q, *J* = 7.6 Hz, 2 H), 1.31 – 1.24 (t, *J* = 7.6 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.5, 184.0, 154.9, 147.2, 137.4, 135.9, 135.5, 130.0, 125.8, 123.4, 28.7, 15.2.



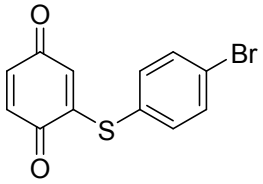
2-(m-tolylthio)cyclohexa-2,5-diene-1,4-dione (4d). (Known compound, ref: D. Wang, X. Yu, W. Yao, W.. Hu, C. Ge, and X. Shi, *Chem. Eur. J.* 2016, **22**, 8863-8868) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 1 H), 7.33 – 7.30 (m, 3 H), 6.86 (d, *J* = 10.0 Hz, 1 H), 6.69 (dd, *J* = 10.0, 2.4 Hz, 1 H), 5.92 (d, *J* = 2.5 Hz, 1 H), 2.41 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.5, 184.0, 154.7, 140.5, 137.5, 136.0, 135.9 132.6, 131.4, 130.2, 126.5, 125.9, 21.3.



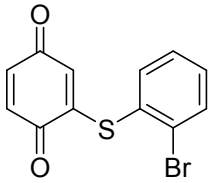
2-((4-fluorophenyl)thio)cyclohexa-2,5-diene-1,4-dione (4e). (Known compound, ref: D. Wang, X. Yu, W. Yao, W.. Hu, C. Ge, and X. Shi, *Chem. Eur. J.* 2016, **22**, 8863-8868) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 2 H), 7.25 – 7.18 (t, *J* = 8.6 Hz, 2 H), 6.85 (d, *J* = 10.1 Hz, 1 H), 6.71 (dd, *J* = 10.0, 2.4 Hz, 1 H), 5.87 (d, *J* = 2.4 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.3, 183.8, 165.4, 162.9, 154.3, 137.79 (d, *J* = 8.8 Hz), 137.5, 135.9, 125.9, 124.5, 124.0, 122.15 (d, *J* = 3.6 Hz), 119.1, 117.89 (d, *J* = 22.2 Hz).



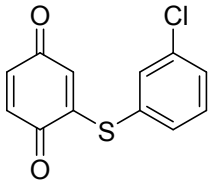
2-((4-chlorophenyl)thio)cyclohexa-2,5-diene-1,4-dione (4f). (Known compound, ref: Uemura, Akio and Shirai, Masashi.; *Jpn. Kokai Tokkyo Koho*, 2011, 2011116749, 16 Jun.), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.42 (m, 4 H), 6.83 (d, *J* = 10.1 Hz, 1 H), 6.70 (dd, *J* = 10.1, 2.4 Hz, 1 H), 5.87 (d, *J* = 2.4 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.3, 183.7, 153.9, 137.5, 137.3, 136.9, 135.8, 130.7, 126.0, 125.4.



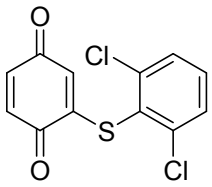
2-((4-bromophenyl)thio)cyclohexa-2,5-diene-1,4-dione (4g). (Known compound, ref: D.. Wang, X. Yu, W. Yao, W.. Hu, C. Ge, and X. Shi, *Chem. Eur. J.* 2016, **22**, 8863-8868) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71(m, *J* = 6.9, 1.6 Hz, 2 H), 7.37 (dd, *J* = 7.0, 1.4 Hz, 2 H), 6.87 – 6.78 (m, 1 H), 6.69 (ddd, *J* = 10.1, 2.4, 1.2 Hz, 1 H), 5.87 (dd, *J* = 2.4, 1.2 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.2, 183.7, 153.7, 137.5, 137.1, 135.8, 133.7, 126.0, 125.6.



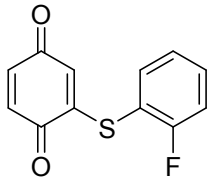
2-((2-bromophenyl)thio)cyclohexa-2,5-diene-1,4-dione (4h). (Known compound, ref: Uemura, Akio and Shirai, Masashi, *Jpn. Kokai Tokkyo Koho*, 2011, 2011116749, 16 Jun.)，^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.8, 1.5 Hz, 1 H), 7.64 (dd, *J* = 7.5, 1.8 Hz, 1 H), 7.46 (td, *J* = 7.6, 1.6 Hz, 1 H), 7.41 (td, *J* = 7.6, 1.6 Hz, 1 H), 6.89 (d, *J* = 10.0 Hz, 1 H), 6.72 (dd, *J* = 10.0, 2.4 Hz, 1 H), 5.79 (d, *J* = 2.4 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.3, 183.8, 151.7, 137.8, 137.5, 135.9, 134.6, 132.3, 130.7, 129.1, 128.4, 126.0.



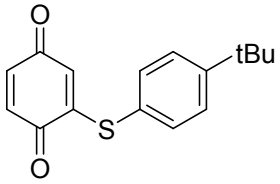
2-((3-chlorophenyl)thio)cyclohexa-2,5-diene-1,4-dione (4i). (Known compound, ref: D. Wang, X. Yu, W. Yao, W.. Hu, C. Ge, and X. Shi, *Chem. Eur. J.* 2016, **22**, 8863-8868) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 2 H), 7.47 (d, *J* = 7.6 Hz, 1 H), 7.43 – 7.39 (m, 1 H), 6.86 (d, *J* = 10.0 Hz, 1 H), 6.75 – 6.69 (dd, *J* = 10.0, 2.4 Hz, 1 H), 5.92 (d, *J* = 2.4 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.3, 183.6 153.7, 137.5, 136.0, 135.8, 135.3, 133.8, 131.4, 130.9, 128.8, 126.1.



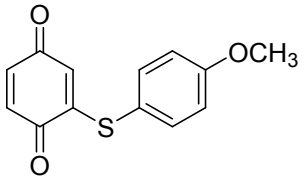
2-((2,6-dichlorophenyl)thio)cyclohexa-2,5-diene-1,4-dione (4j). (Known compound, ref: D. Wang, X. Yu, W. Yao, W.. Hu, C. Ge, and X. Shi, *Chem. Eur. J.* 2016, **22**, 8863-8868) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.8 Hz, 2 H), 7.41 (dd, *J* = 8.8, 7.3 Hz, 1 H), 6.87 (d, *J* = 10.1 Hz, 1 H), 6.72 (dd, *J* = 10.1, 2.4 Hz, 1 H), 5.72 (d, *J* = 2.4 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.2, 183.6, 149.6, 141.7, 137.6, 136.0, 132.50 (s), 129.5, 126.0, 125.4.



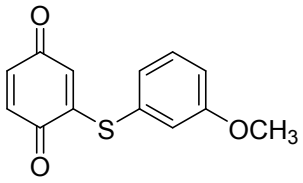
2-((2-fluorophenyl)thio)cyclohexa-2,5-diene-1,4-dione (4k). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.51 (m, 2 H), 7.30 (dd, *J* = 7.6, 1.2 Hz, 1 H), 7.27 (dd, *J* = 5.5, 5.0 Hz, 1 H), 6.86 (d, *J* = 10.1 Hz, 1 H), 6.72 (dd, *J* = 10.1, 2.4 Hz, 1 H), 5.91 (dd, *J* = 2.4, 1.2 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.3, 183.8, 164.0, 161.5, 151.8, 137.4 (d, *J* = 12.0 Hz), 135.9, 133.4 (d, *J* = 8.1 Hz), 126.1, 125.81 (d, *J* = 4.0 Hz), 117.2 (d, *J* = 22.3 Hz), 114.2 (d, *J* = 18.5 Hz). HRMS Calculated for $C_{12}H_8FO_2S$ $[M+H]^+$ 235.0229, found 235.0226.



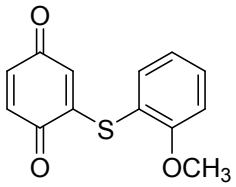
2-((4-(*tert*-butyl)phenyl)thio)cyclohexa-2,5-diene-1,4-dione (4l). (Known compound, ref: D. Wang, X. Yu, W. Yao, W.. Hu, C. Ge, and X. Shi, *Chem. Eur. J.* 2016, **22**, 8863-8868) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 2 H), 7.46 – 7.40 (m, 2 H), 6.84 (d, *J* = 10.0 Hz, 1 H), 6.70 (dd, *J* = 10.0, 2.5 Hz, 1 H), 5.96 (d, *J* = 2.5 Hz, 1 H), 1.36 (s, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.6, 184.1, 154.8, 154.1, 137.5, 135.9, 135.3, 127.5, 125.8, 123.2, 34.94, 31.2.



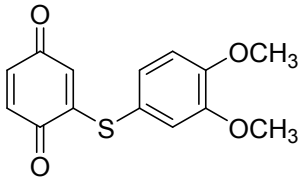
2-((4-methoxyphenyl)thio)cyclohexa-2,5-diene-1,4-dione (4m). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2 H), 7.05 – 6.98 (m, 2 H), 6.83 (d, *J* = 10.0 Hz, 1 H), 6.69 (dd, *J* = 10.0, 2.5 Hz, 1 H), 5.88 (d, *J* = 2.5 Hz, 1 H), 3.88 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.5, 184.2, 161.5, 155.3, 137.5, 137.1, 135.9, 125.8, 117.0, 116.0, 55.5. HRMS Calculated for $C_{13}H_{11}O_3S$ $[M+H]^+$ 247.0429, found 247.0428.



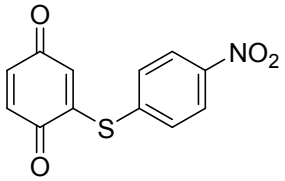
2-((3-methoxyphenyl)thio)cyclohexa-2,5-diene-1,4-dione (4n). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 1 H), 7.13 – 7.02 (m, 3 H), 6.84 (d, *J* = 10.0 Hz, 1 H), 6.70 (dd, *J* = 10.0, 2.5 Hz, 1 H), 5.96 (d, *J* = 2.5 Hz, 1 H), 3.84 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.5, 184.0, 160.8, 154.4, 137.5, 135.9, 131.2, 127.7, 127.6, 126.0, 120.6, 116.5, 55.5. HRMS Calculated for $C_{13}H_{11}O_3S$ $[M+H]^+$ 247.0429, found 247.0429.



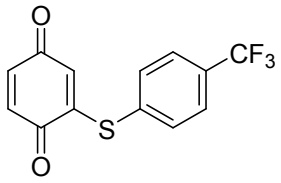
2-((2-methoxyphenyl)thio)cyclohexa-2,5-diene-1,4-dione (4o). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dtd, *J* = 9.0, 7.4, 1.7 Hz, 2 H), 7.09 – 7.00 (m, 2 H), 6.83 (d, *J* = 10.0 Hz, 1 H), 6.69 (dd, *J* = 10.0, 2.5 Hz, 1 H), 5.84 (d, *J* = 2.5 Hz, 1 H), 3.87 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.6, 184.3, 159.9, 152.5, 137.4, 137.3, 136.0, 132.9, 125.6, 122.0, 114.2, 112.0, 56.0. HRMS Calculated for $C_{13}H_{11}O_3S$ $[M+H]^+$ 247.0429, found 247.0426.



2-((3,4-dimethoxyphenyl)thio)cyclohexa-2,5-diene-1,4-dione (4p). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (dd, *J* = 8.3, 2.1 Hz, 1 H), 7.00 – 6.93 (m, 2 H), 6.84 (d, *J* = 10.0 Hz, 1 H), 6.70 (dd, *J* = 10.0, 2.5 Hz, 1 H), 5.92 (d, *J* = 2.5 Hz, 1 H), 3.95 (s, 3 H), 3.89 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.5, 184.1, 155.2, 151.2, 150.2, 137.5, 135.9, 128.9, 125.9, 117.6, 117.1, 112.4, 56.1, 56.0. HRMS Calculated for $C_{14}H_{13}O_4S$ $[M+H]^+$ 277.0535, found 277.0538.

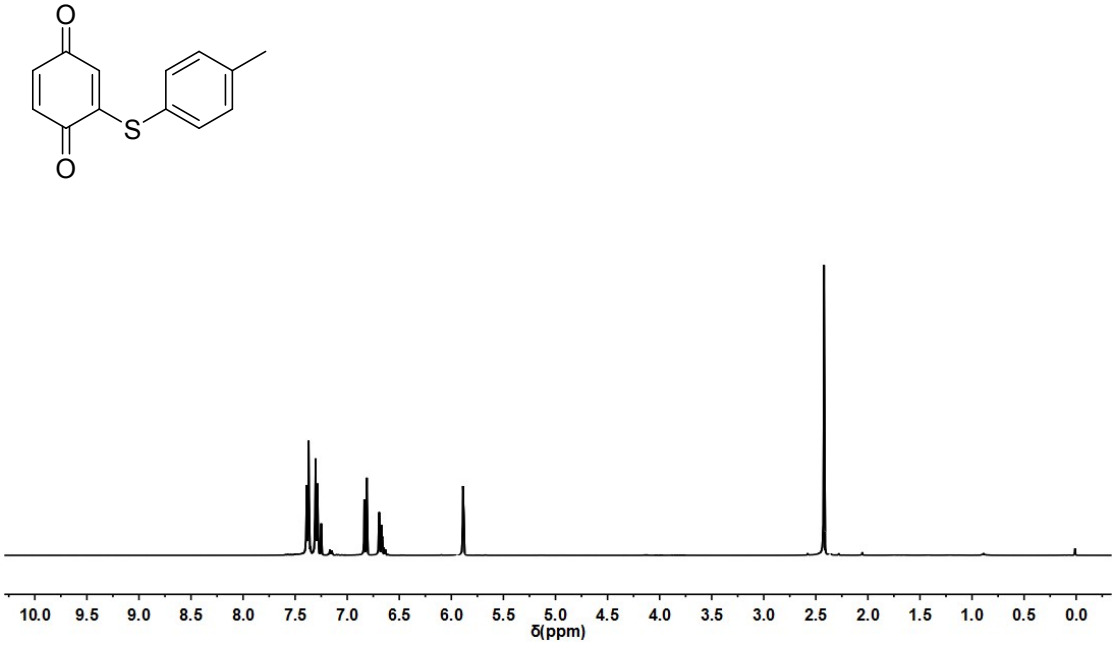


2-((4-nitrophenyl)thio)cyclohexa-2,5-diene-1,4-dione (4q). (Known compound, ref: M. C. Carreño , J. L. G. Ruano, A. Urbano, C. Z. Remor and Y. Arroyo, *J. Org. Chem.*, 2000, **65** (2), 453–458.) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 – 8.28 (m, 2 H), 7.77 – 7.71 (m, 2 H), 6.90 (d, *J* = 10.1 Hz, 1 H), 6.76 (dd, *J* = 10.1, 2.4 Hz, 1 H), 5.97 (d, *J* = 2.4 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.0, 183.2, 152.3, 149.0, 137.5, 136.3, 135.9, 135.7, 126.7, 125.1. HRMS Calculated for $C_{12}H_8NO_4S$ $[M+H]^+$ 262.0174, found 262.0178.

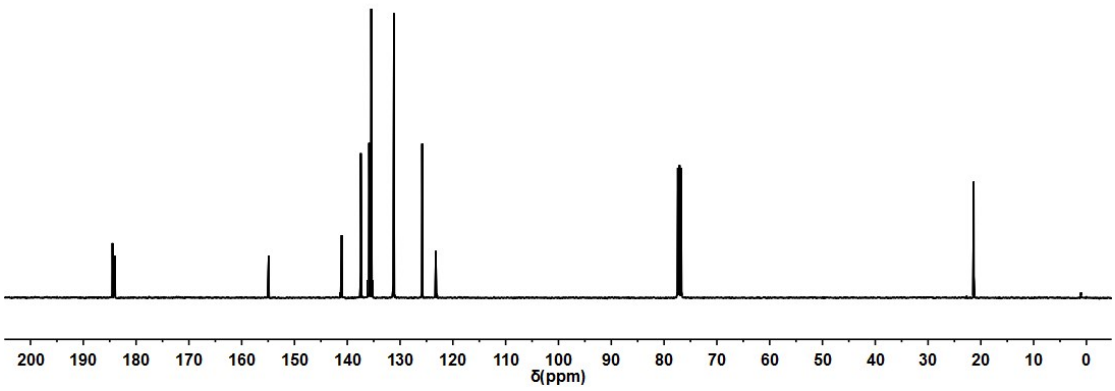


2-((4-(trifluoromethyl)phenyl)thio)cyclohexa-2,5-diene-1,4-dione (4r). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2 H), 7.68 (d, *J* = 8.1 Hz, 2 H), 6.88 (d, *J* = 10.1 Hz, 1 H), 6.73 (dd, *J* = 10.1, 2.4 Hz, 1 H), 5.91 (d, *J* = 2.4 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.2, 183.5, 153.2, 137.5, 136.0, 135.9, 127.2(m), 126.2. HRMS Calculated for $C_{13}H_8F_3O_2S$ $[M+H]^+$ 285.0197, found 285.0194.

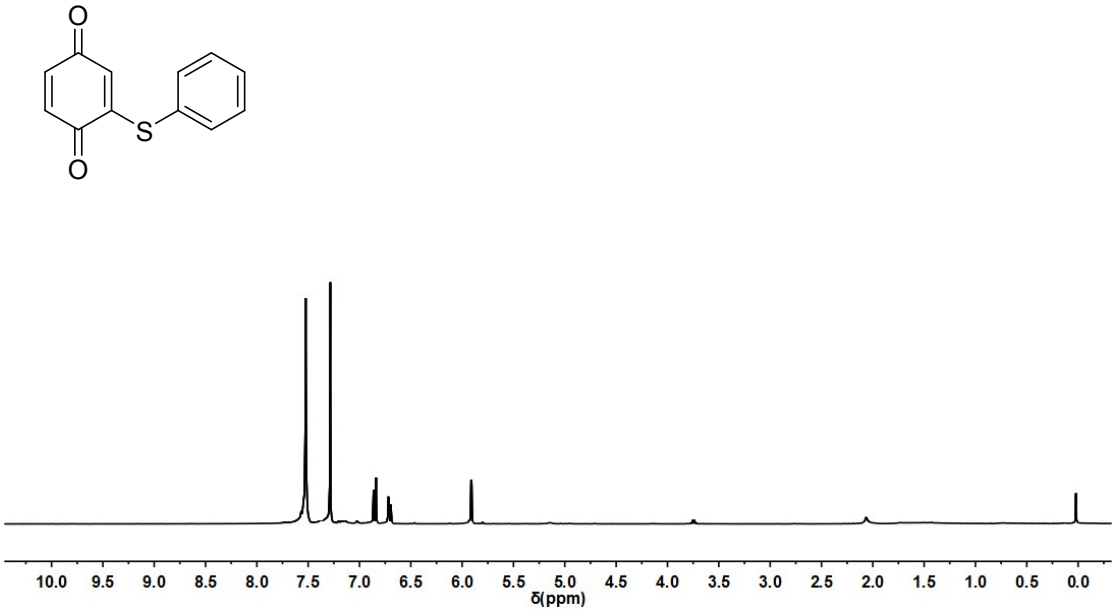
3. Copies of NMR spectra



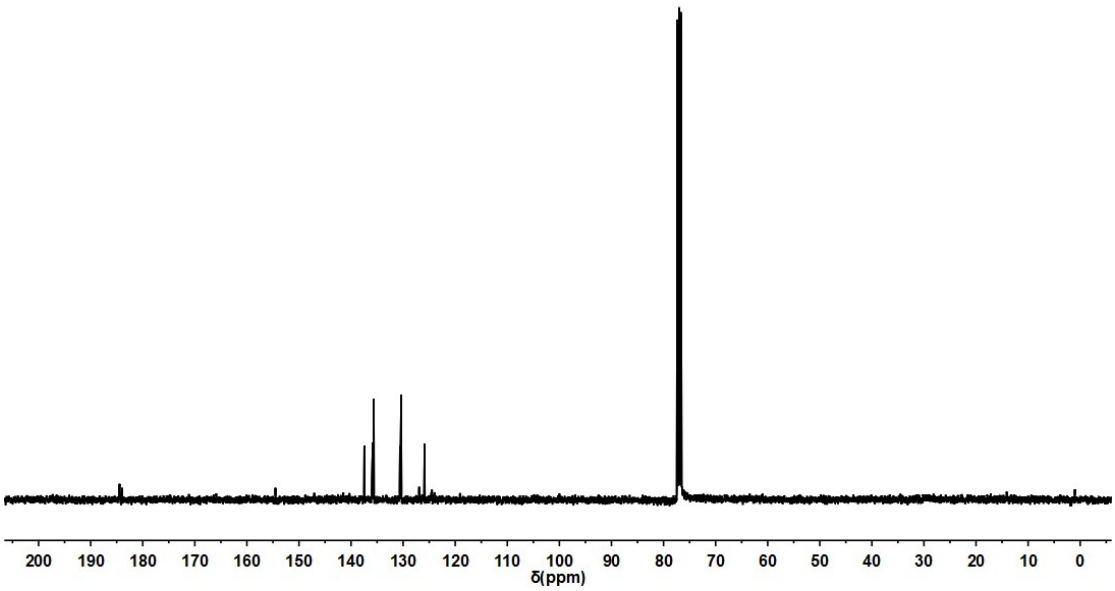
^{1}H-NMR spectrum of 4a



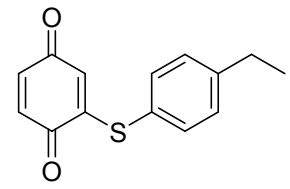
^{13}C-NMR spectrum of 4a

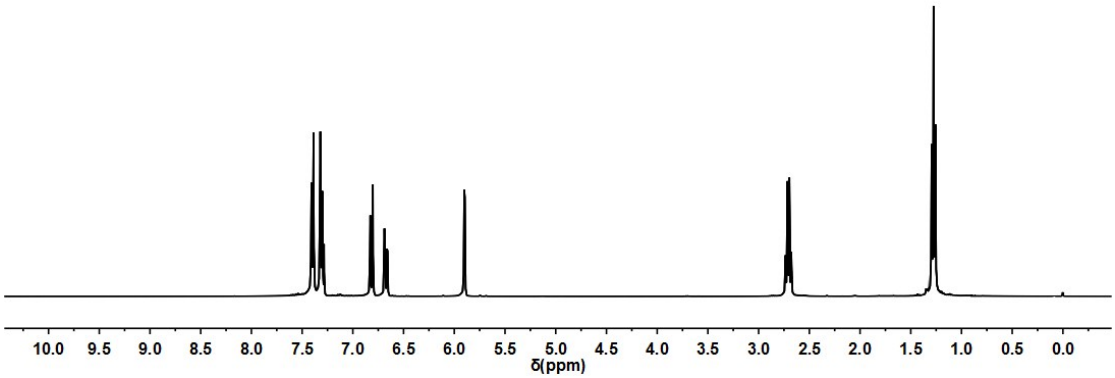


^{1}H-NMR spectrum of 4b

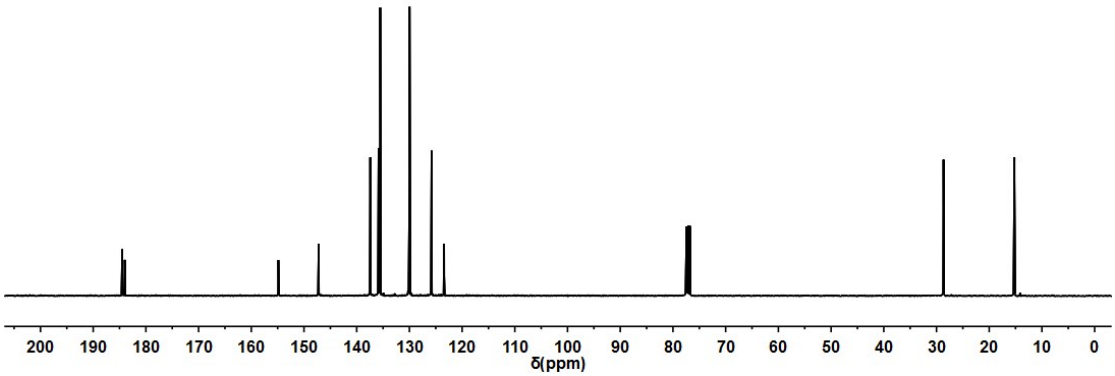


^{13}C-NMR spectrum of 4b

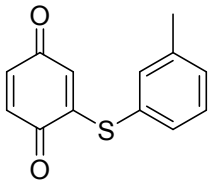


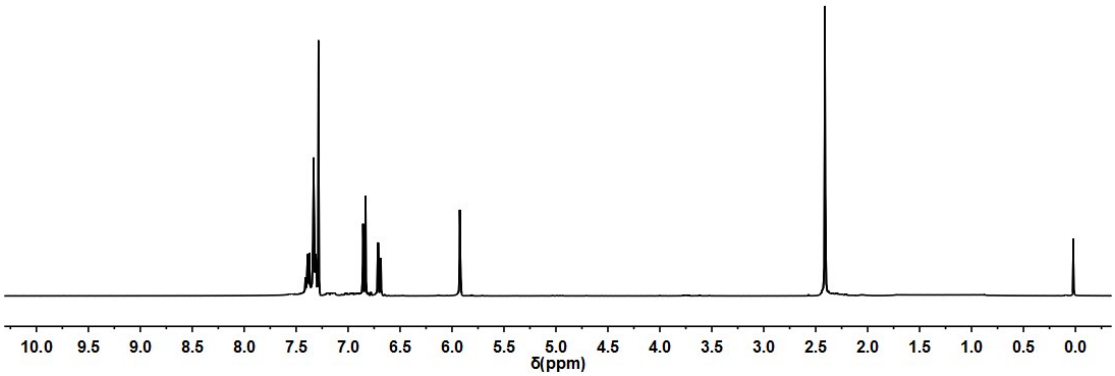


^{1}H-NMR spectrum of 4c

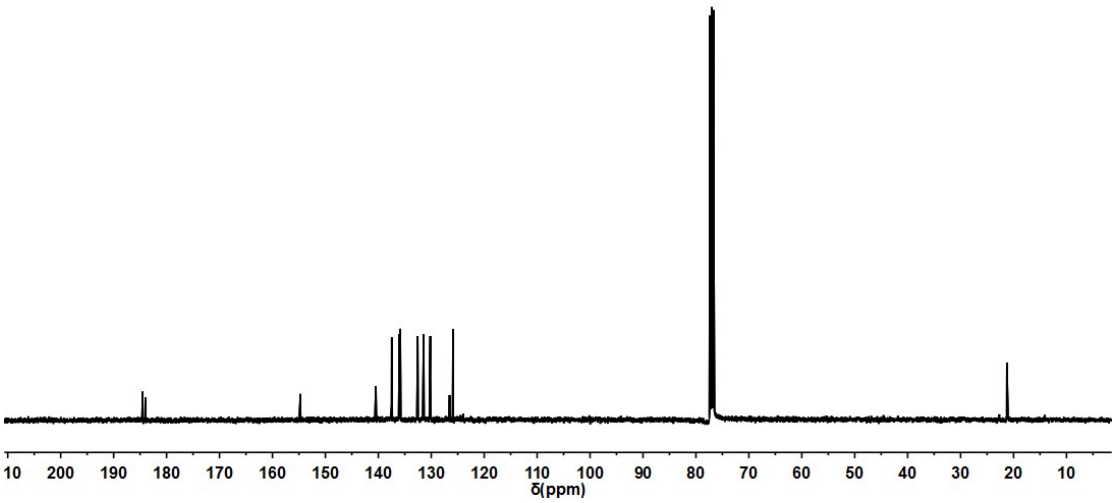


^{13}C-NMR spectrum of 4c

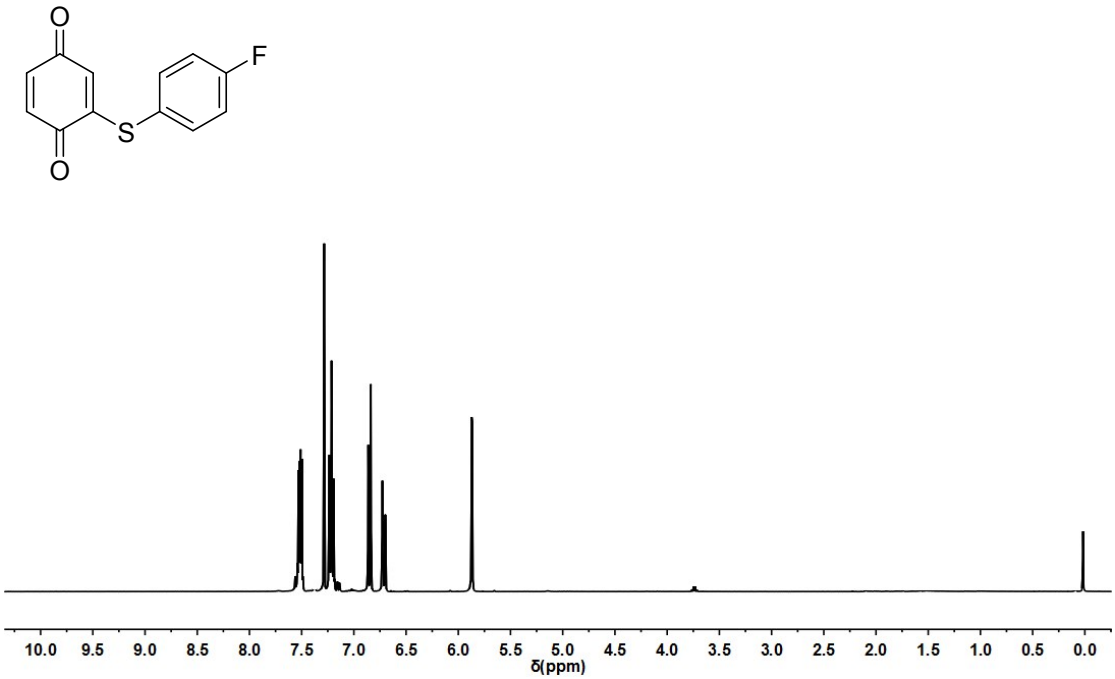




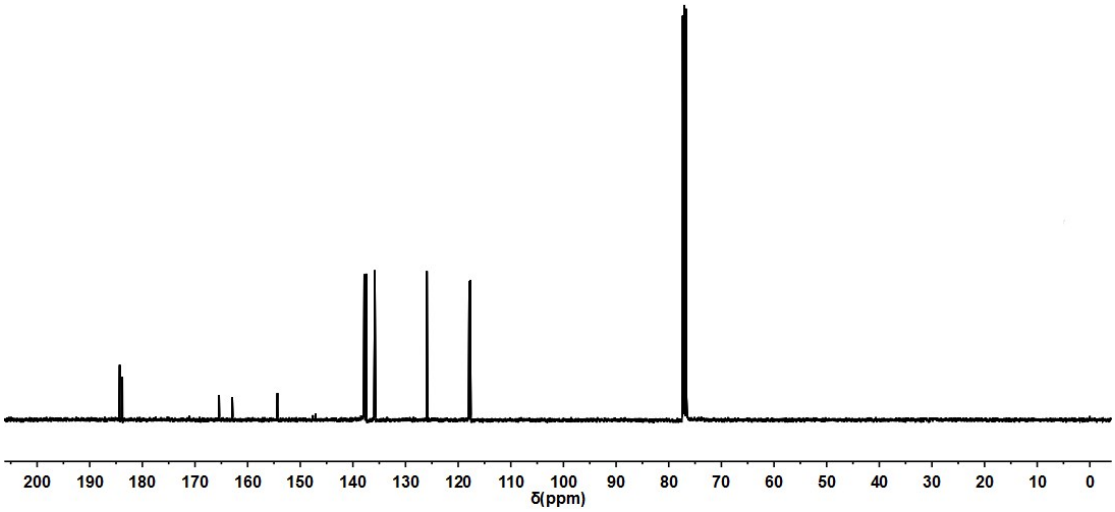
^{1}H-NMR spectrum of 4d



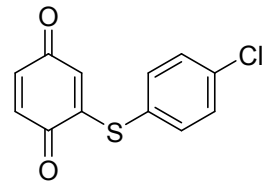
^{13}C-NMR spectrum of 4d

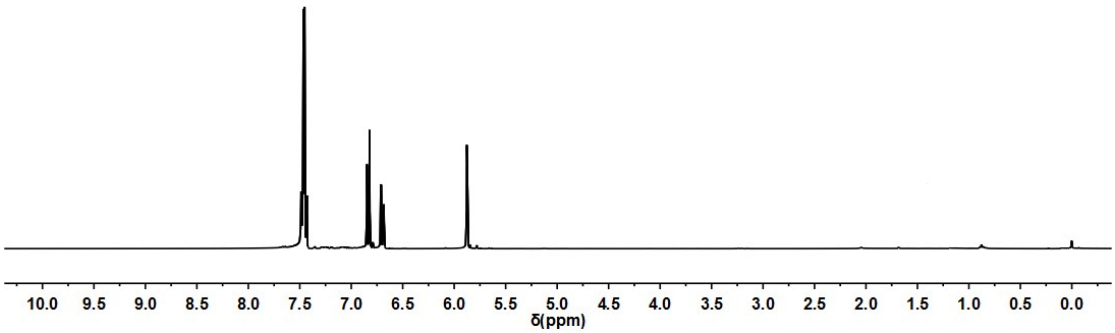


^{1}H-NMR spectrum of 4e

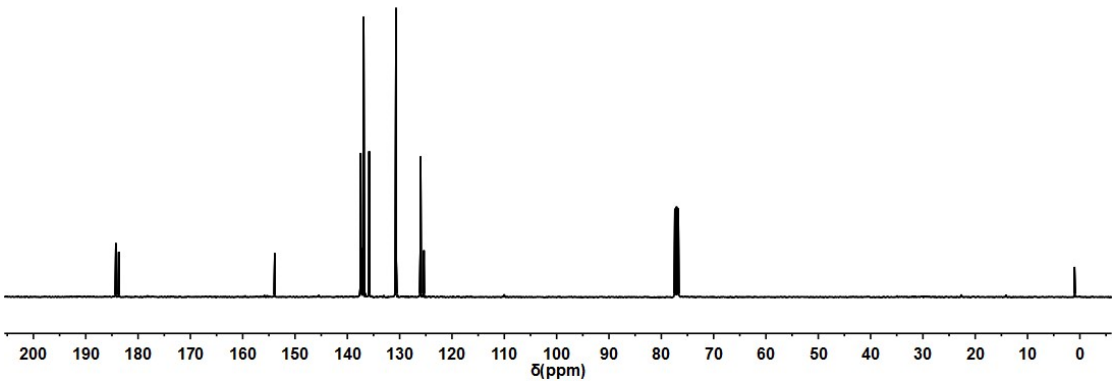


^{13}C-NMR spectrum of 4e

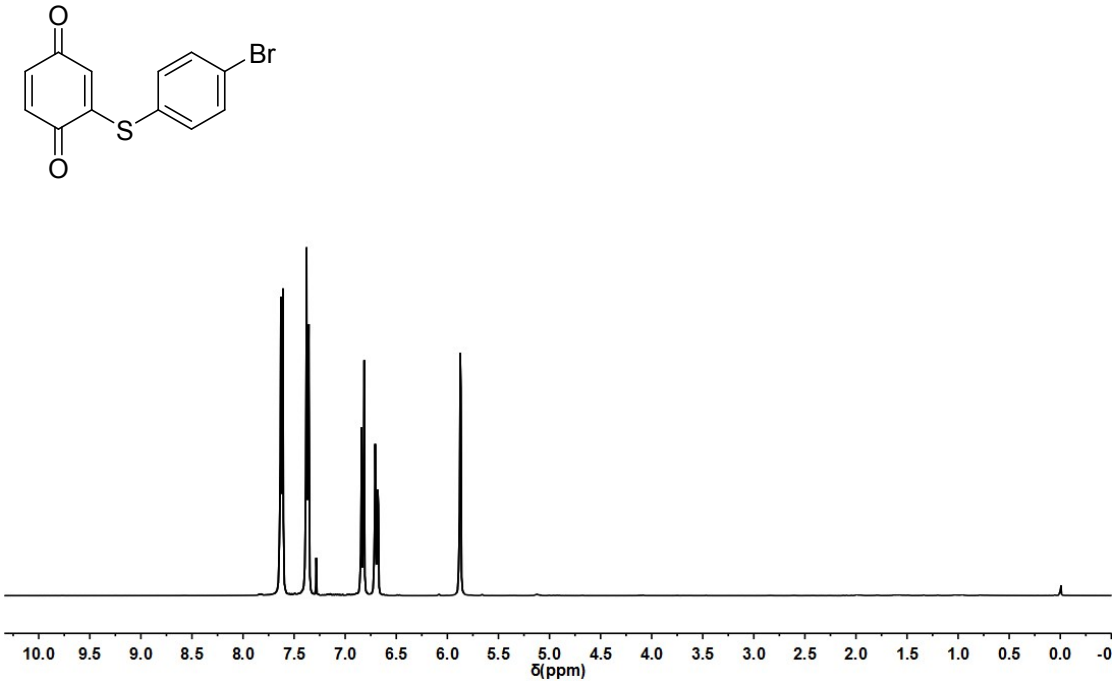




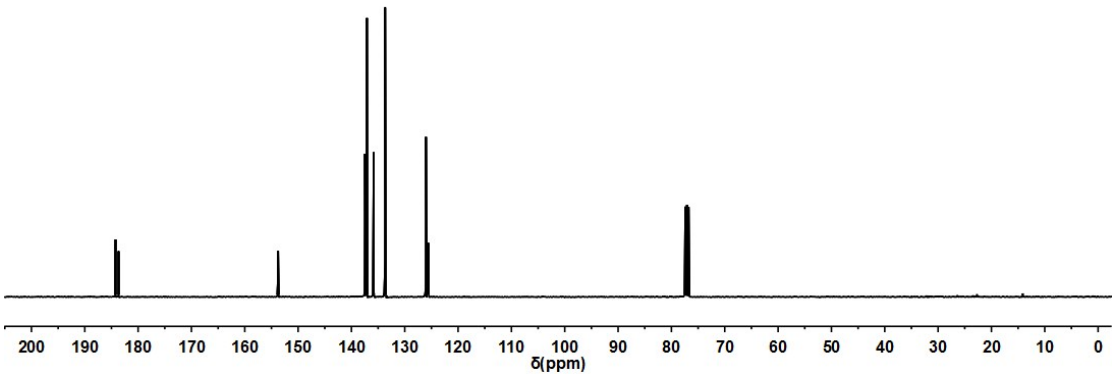
^{1}H-NMR spectrum of 4f



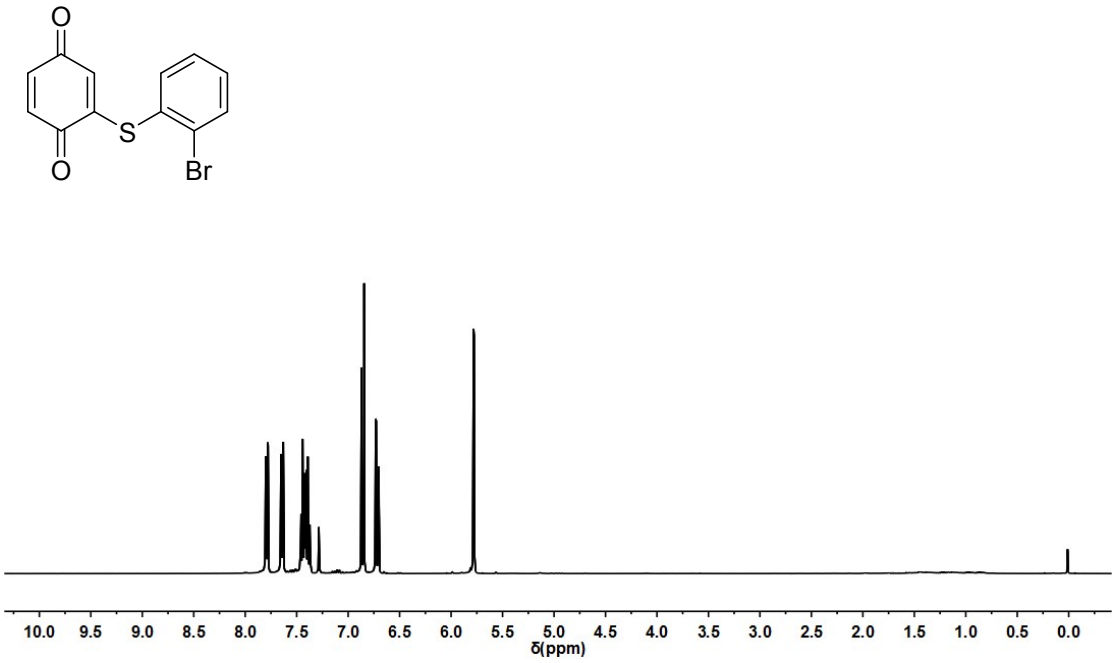
^{13}C-NMR spectrum of 4f



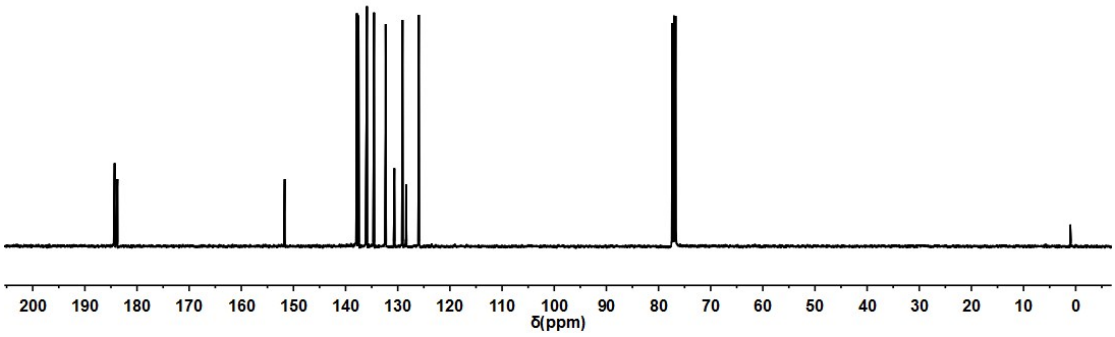
^{1}H-NMR spectrum of 4g



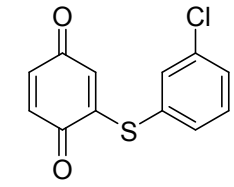
^{13}C-NMR spectrum of 4g

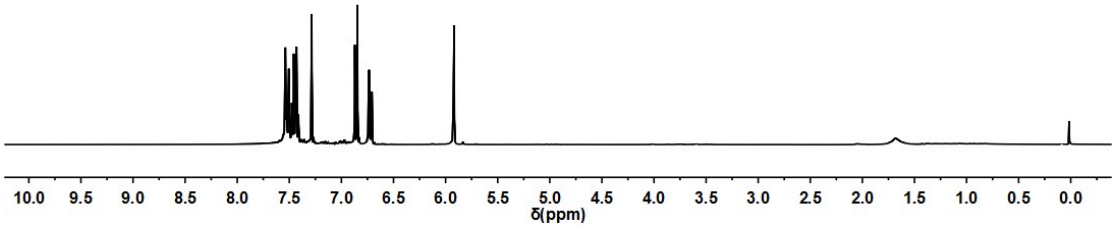


^{1}H-NMR spectrum of 4h

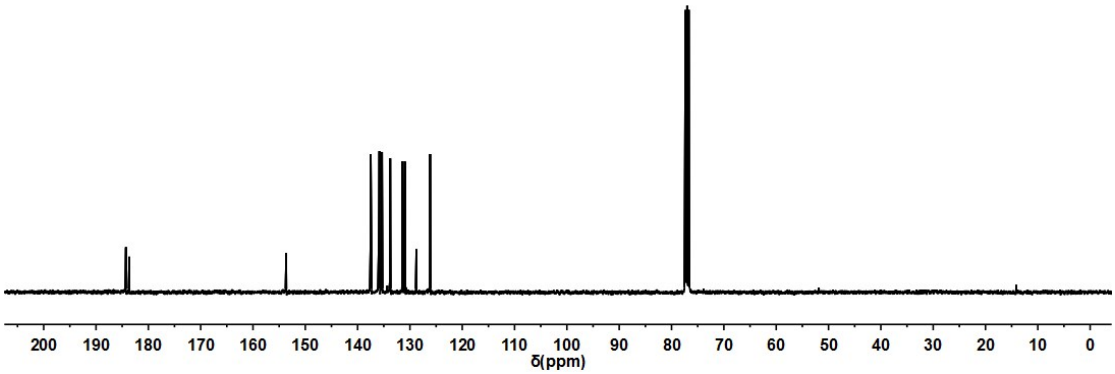


^{13}C-NMR spectrum of 4h

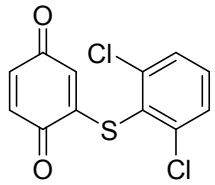


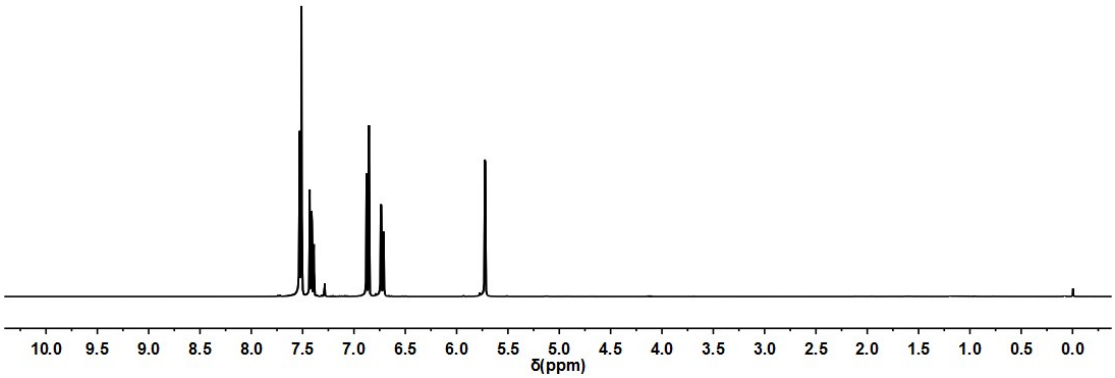


^{1}H-NMR spectrum of 4i

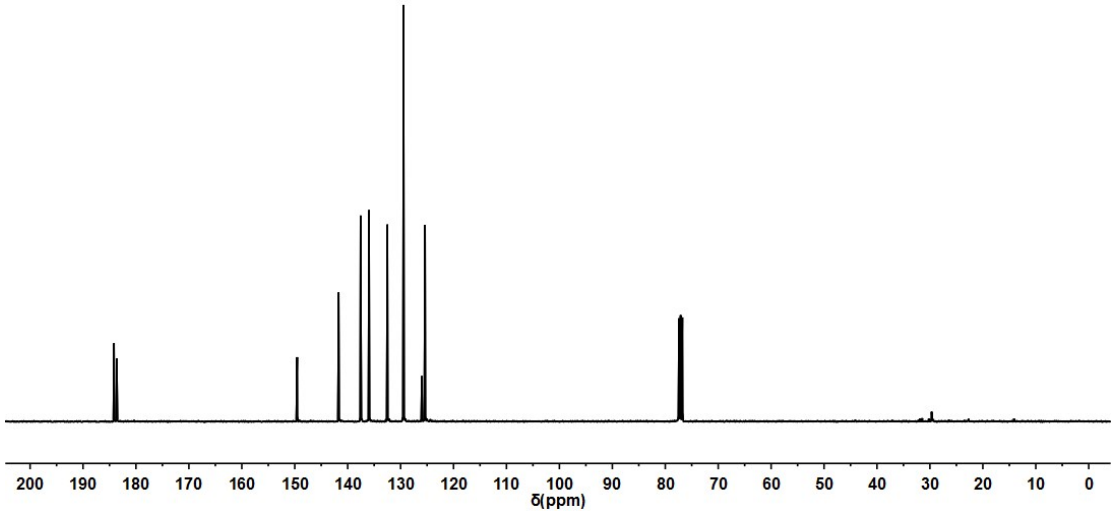


^{13}C-NMR spectrum of 4i

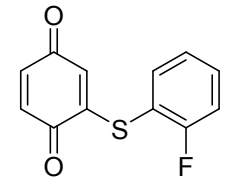


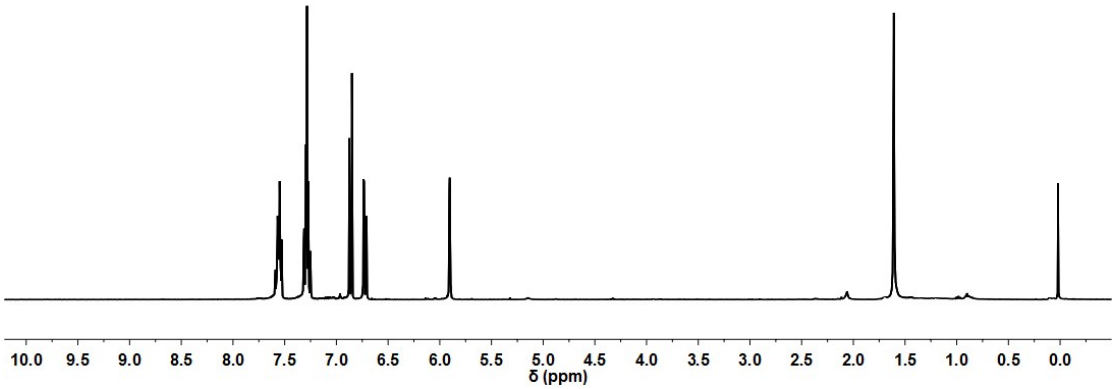


^{1}H-NMR spectrum of 4j

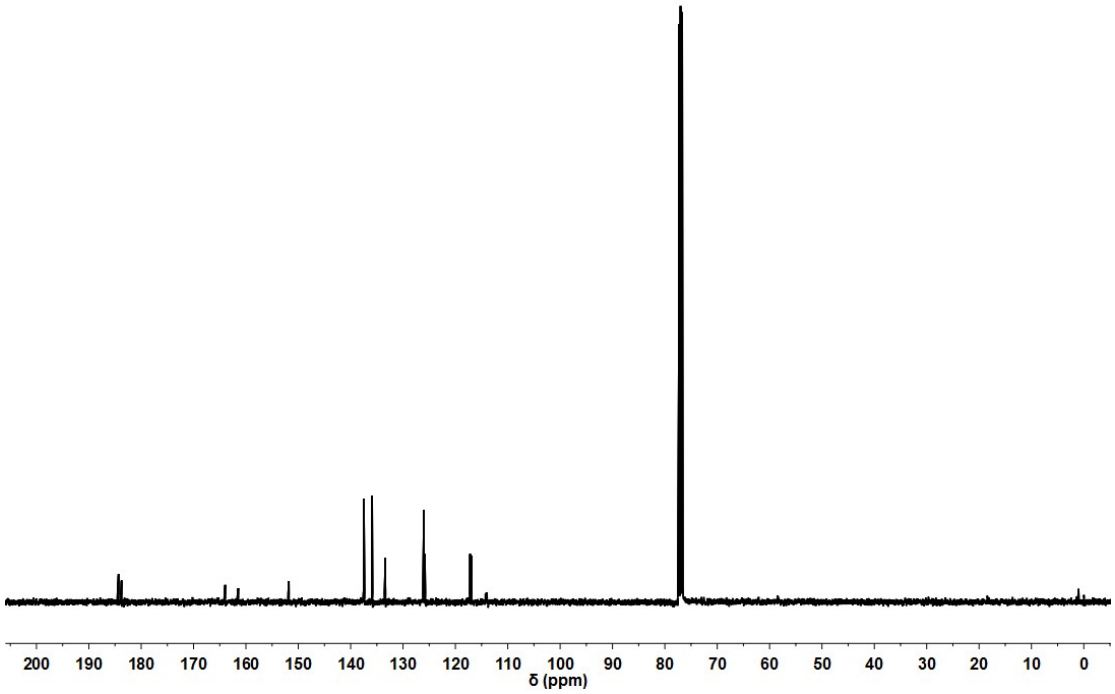


^{13}C-NMR spectrum of 4j

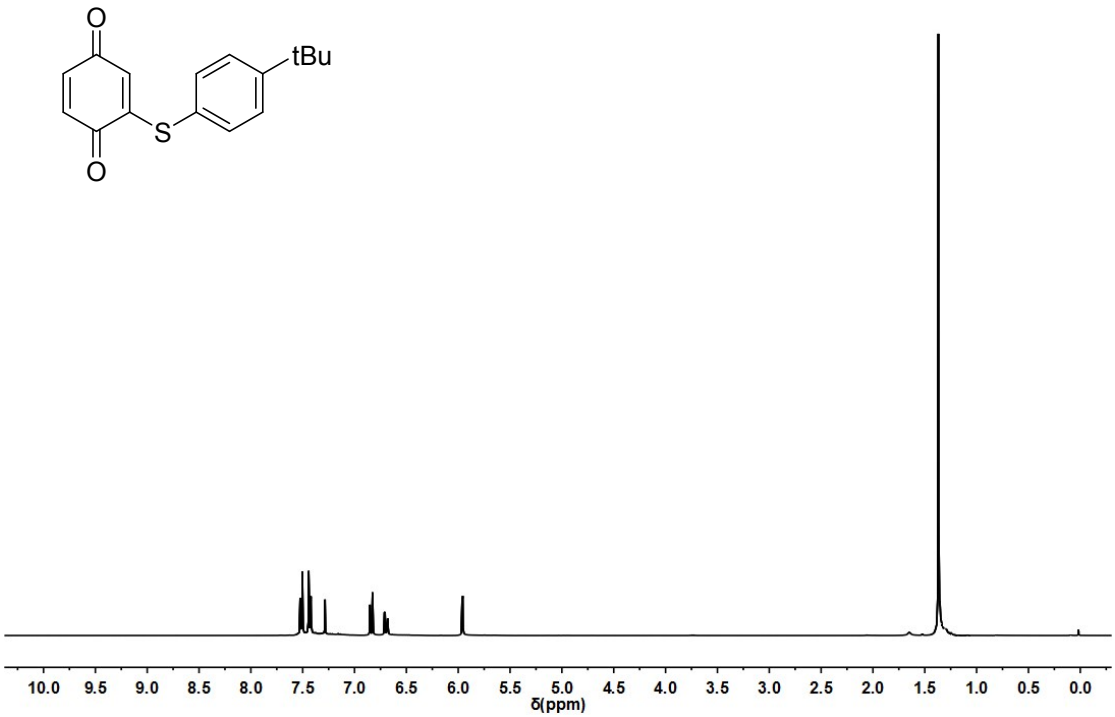




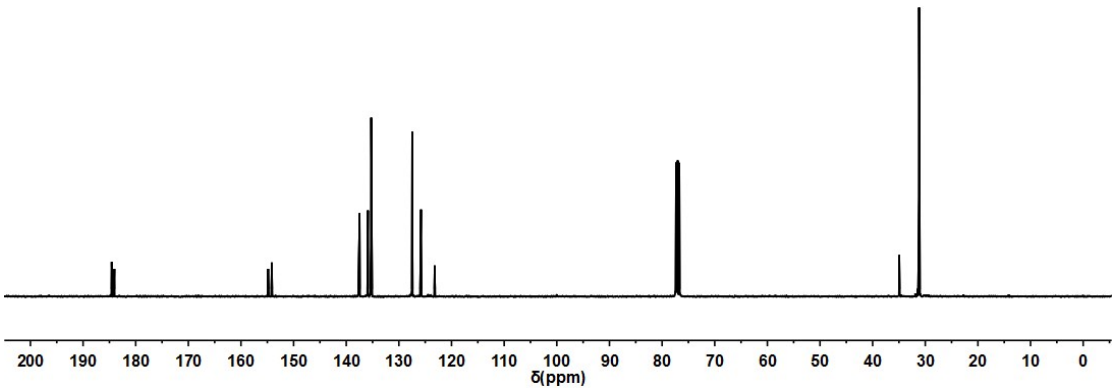
^{1}H-NMR spectrum of 4k



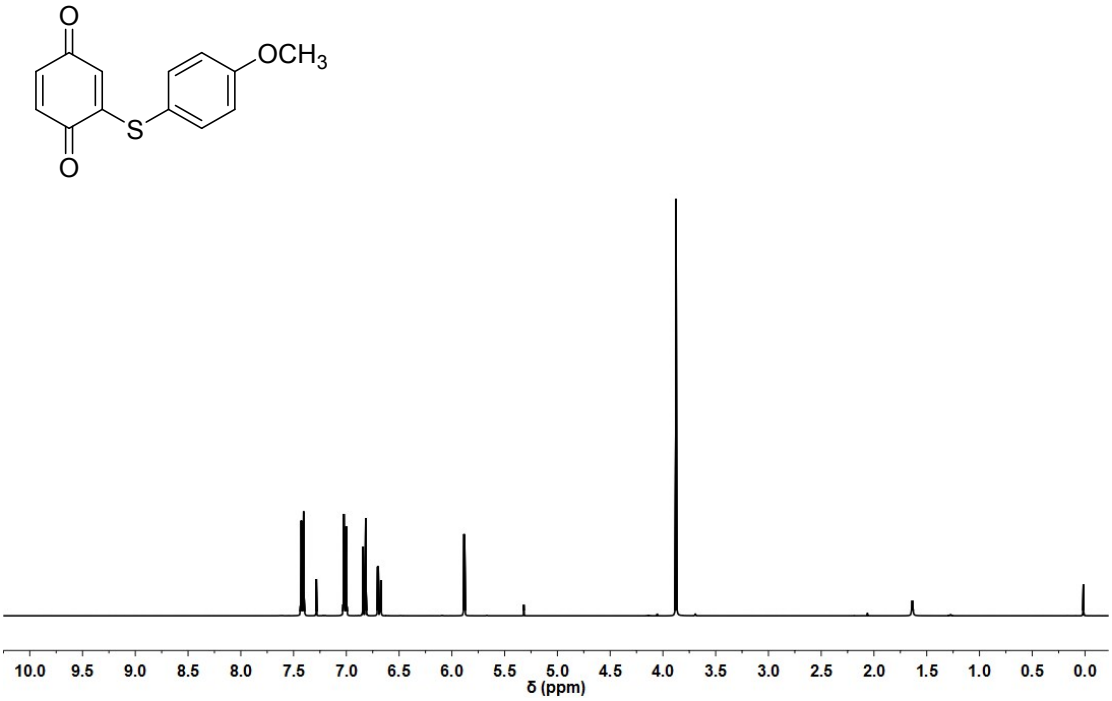
^{13}C-NMR spectrum of 4k



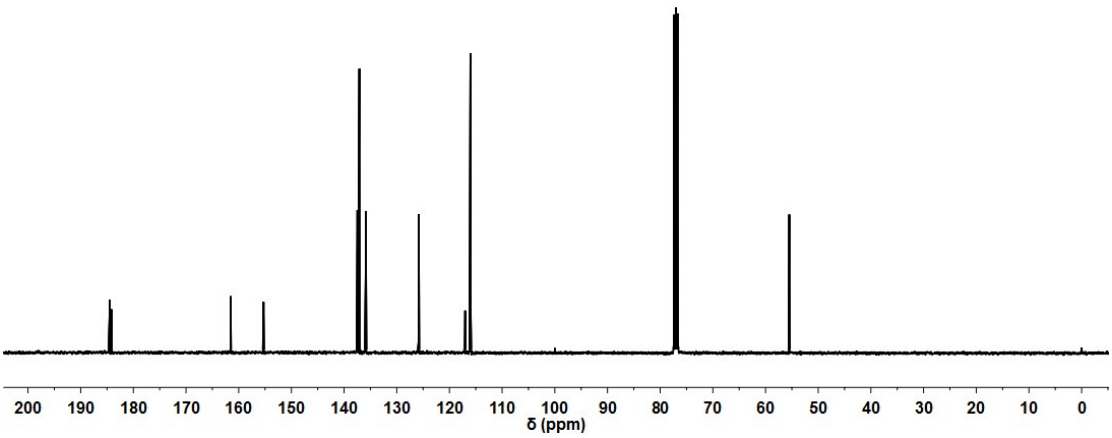
^{1}H-NMR spectrum of 4l



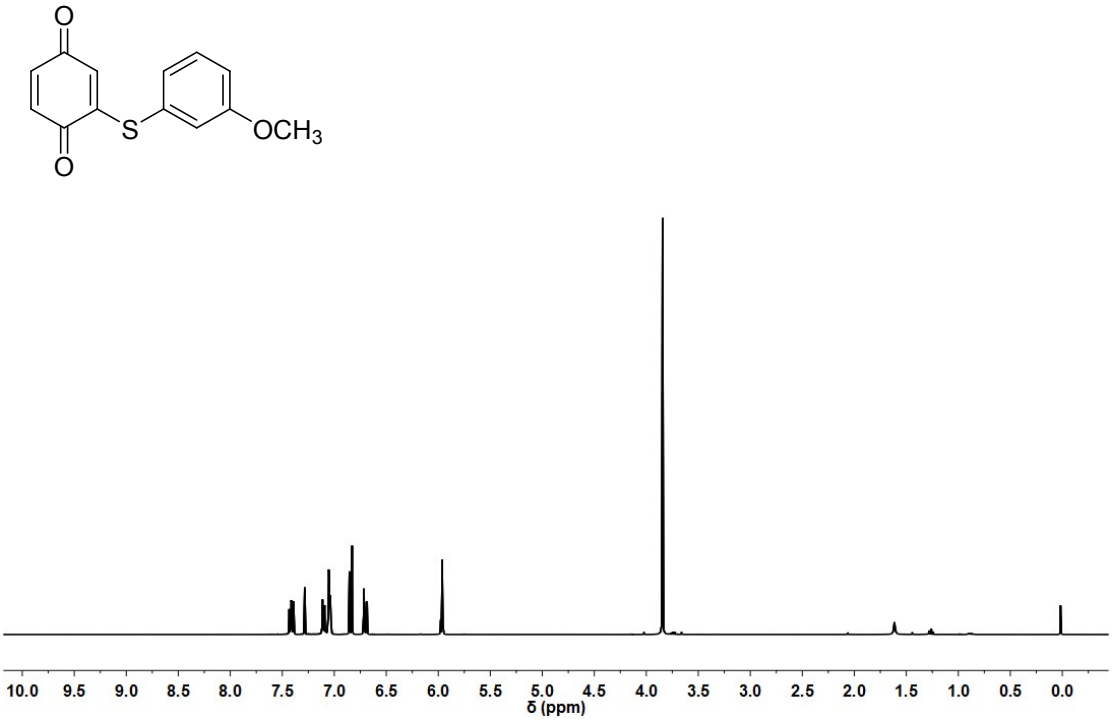
^{13}C-NMR spectrum of 4l



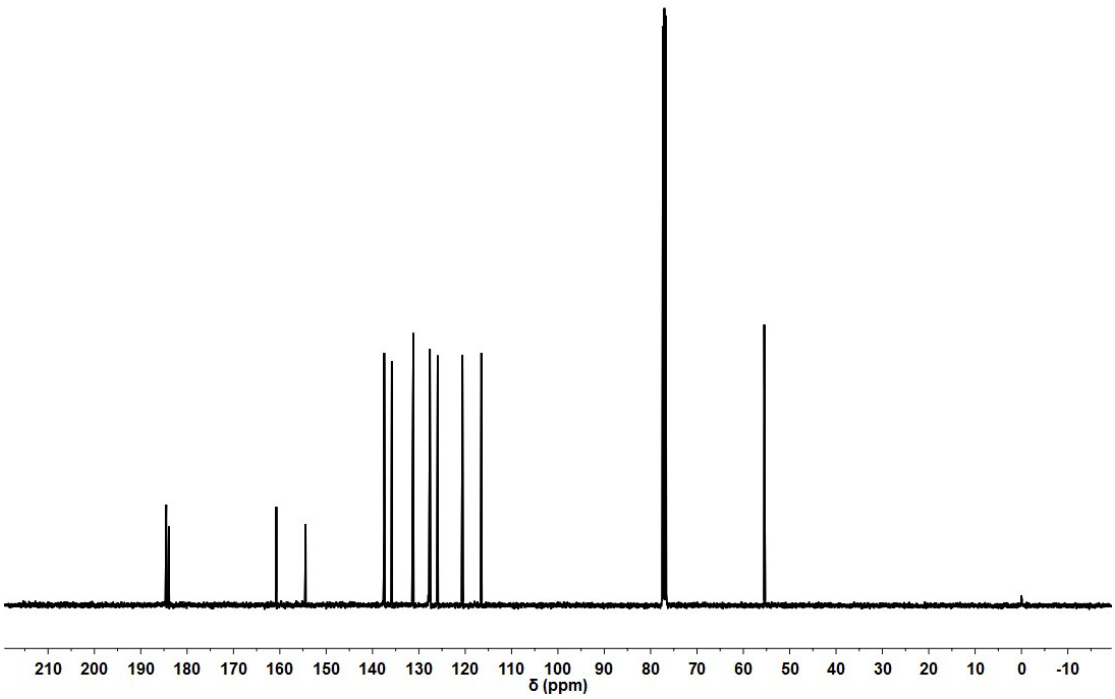
^{1}H-NMR spectrum of 4m



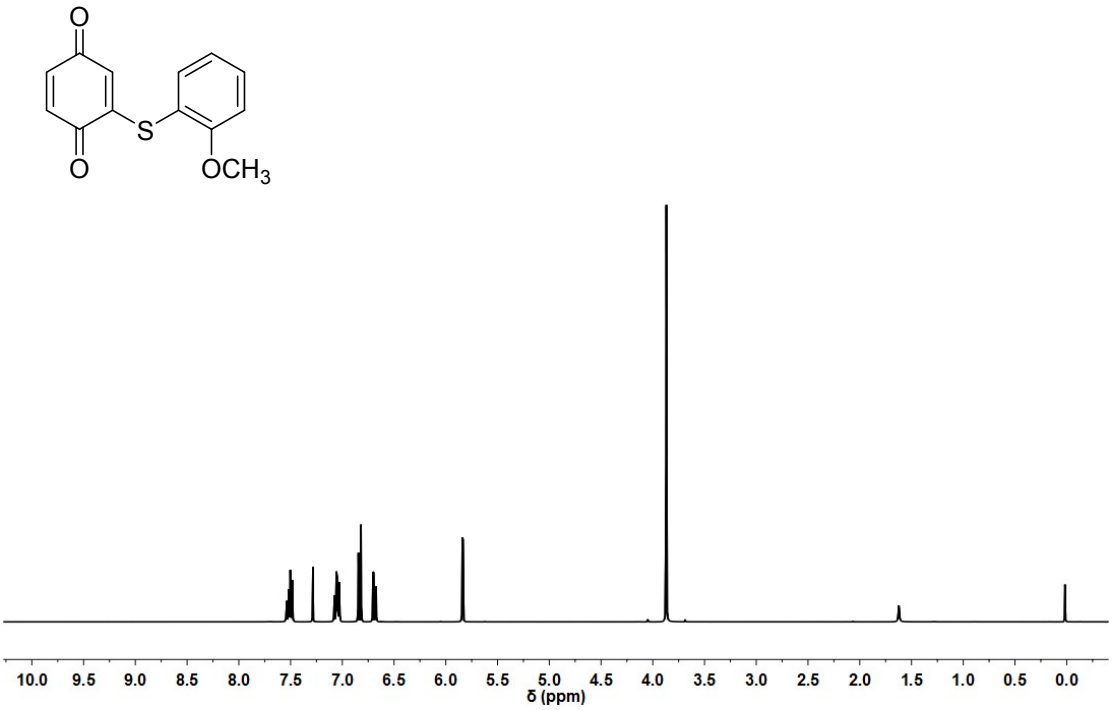
^{13}C-NMR spectrum of 4m



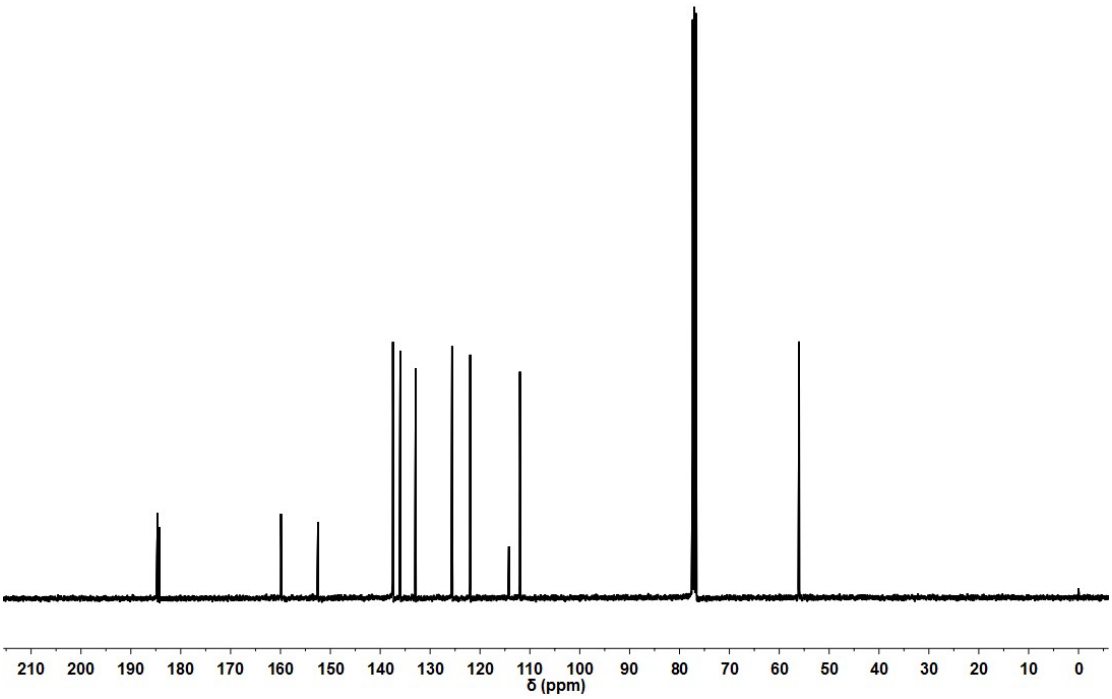
^{1}H-NMR spectrum of 4n



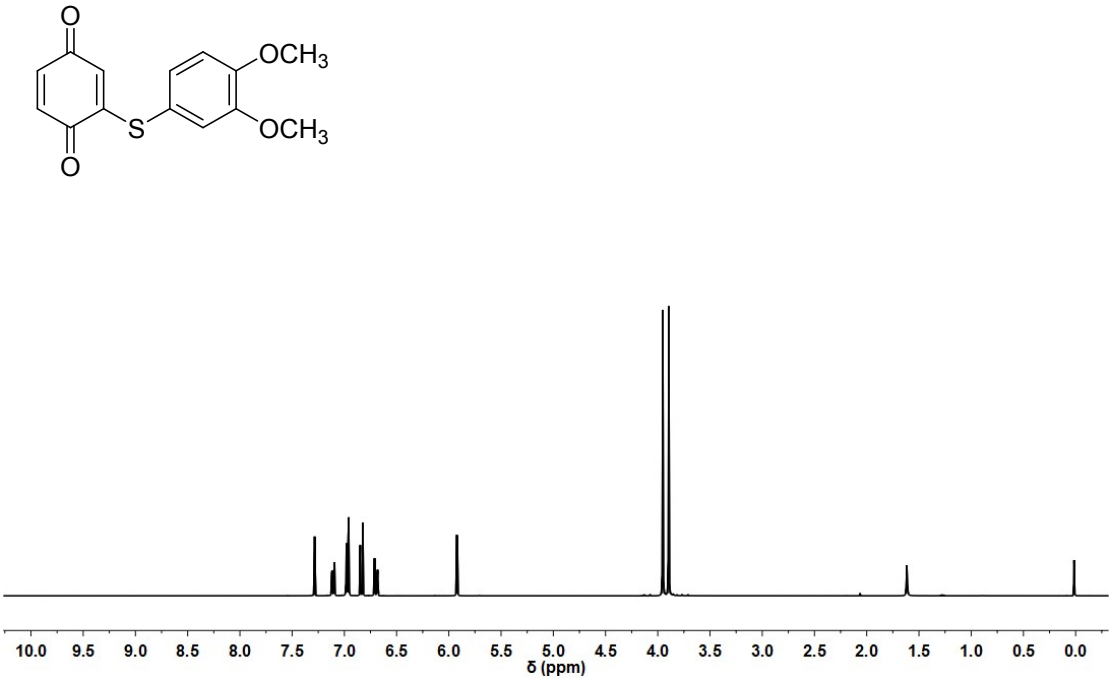
^{13}C-NMR spectrum of 4n



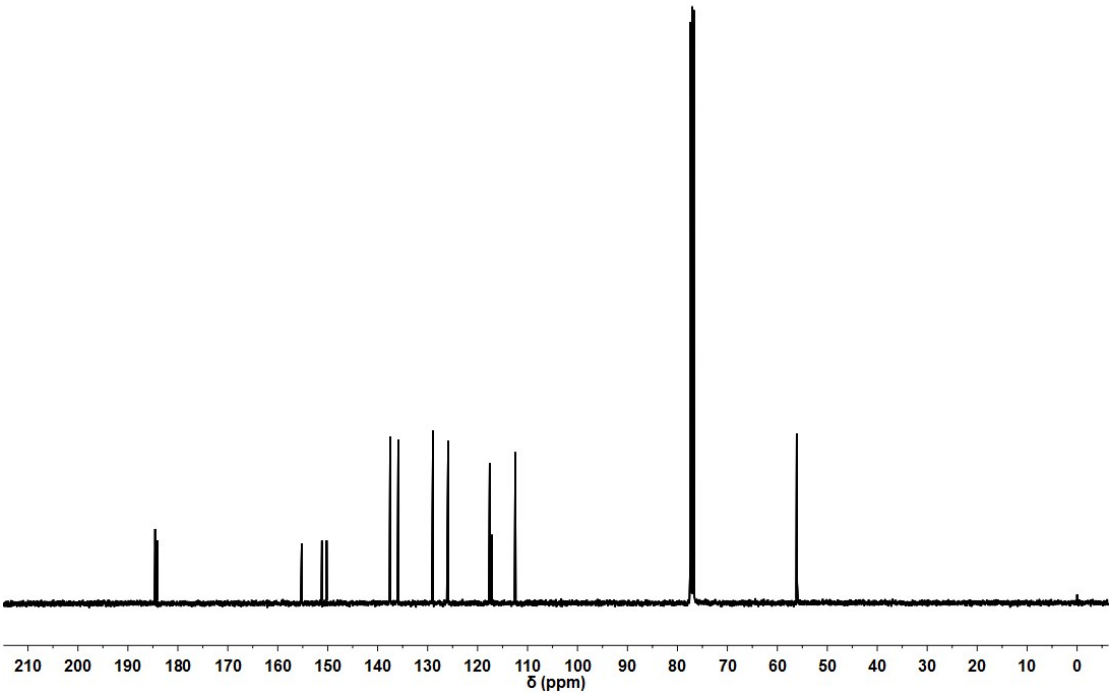
^{1}H-NMR spectrum of 4o



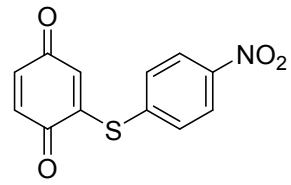
^{13}C-NMR spectrum of 4o

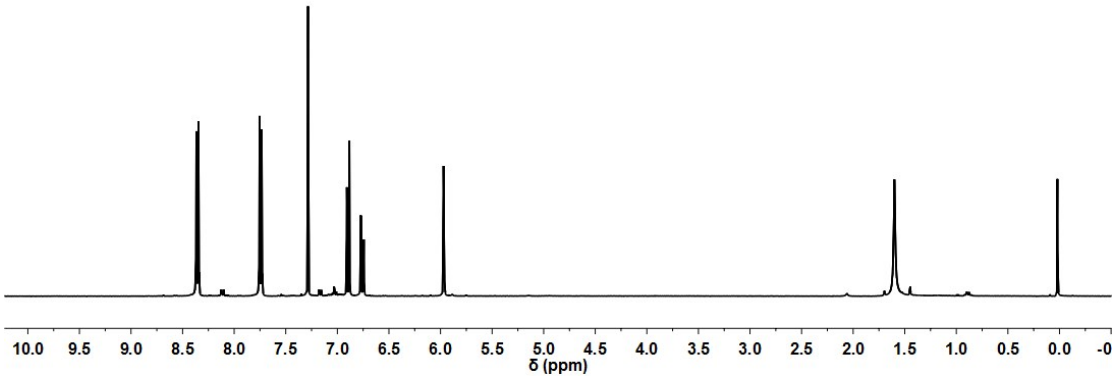


^{1}H-NMR spectrum of 4p

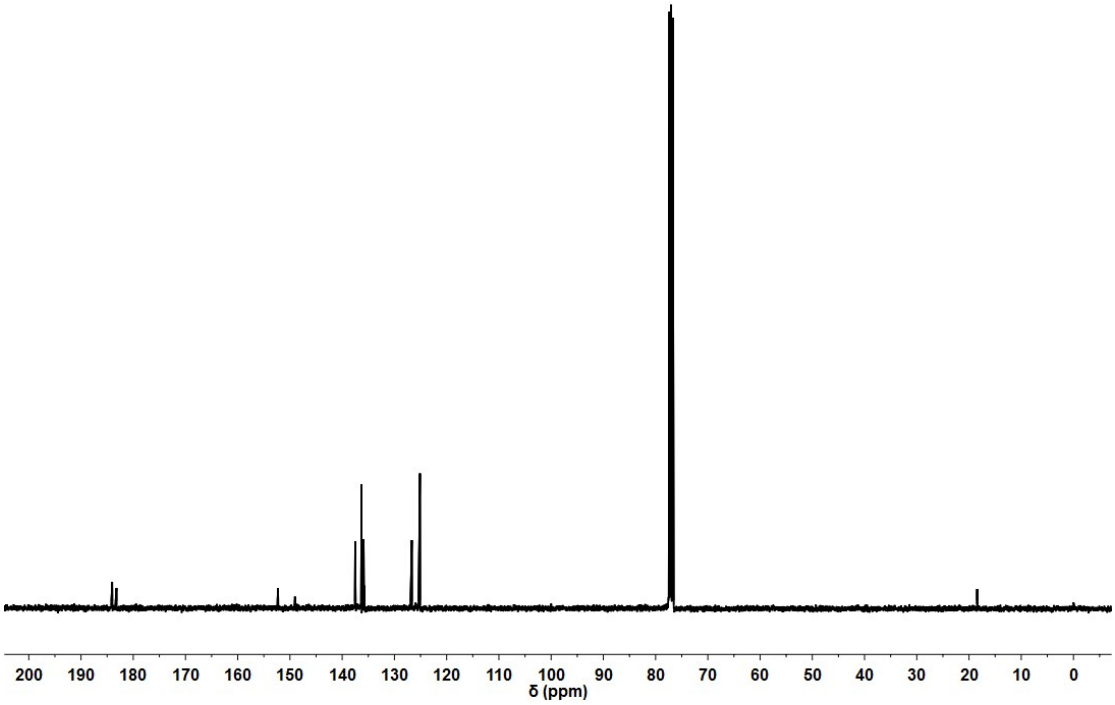


^{13}C-NMR spectrum of 4p

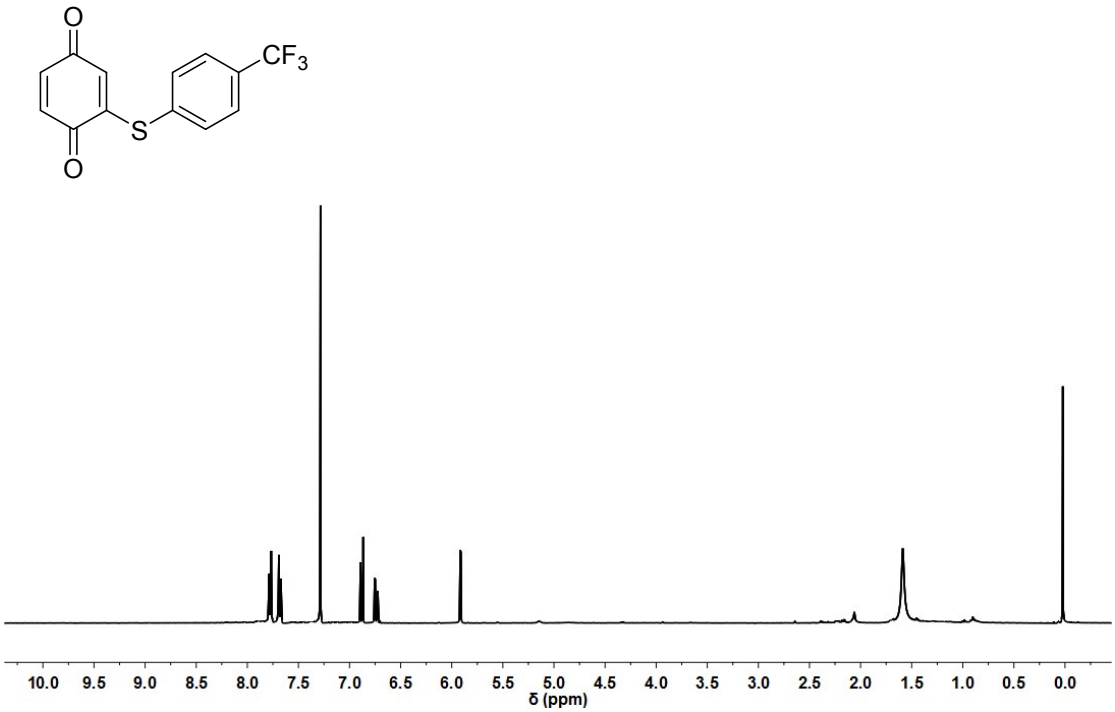




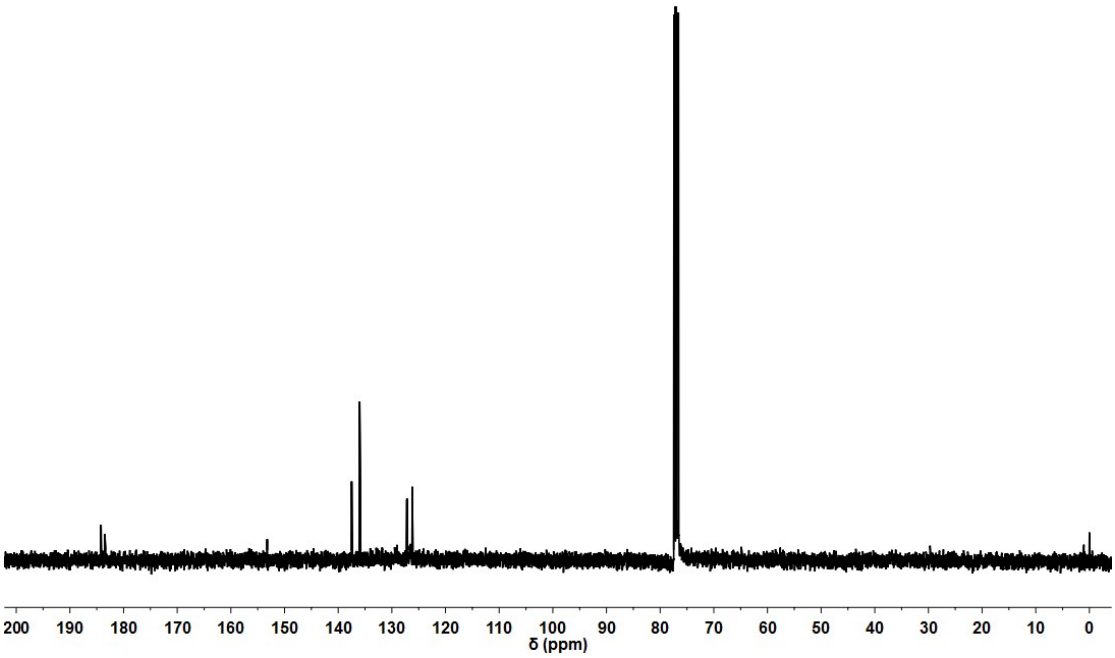
^{1}H-NMR spectrum of 4q



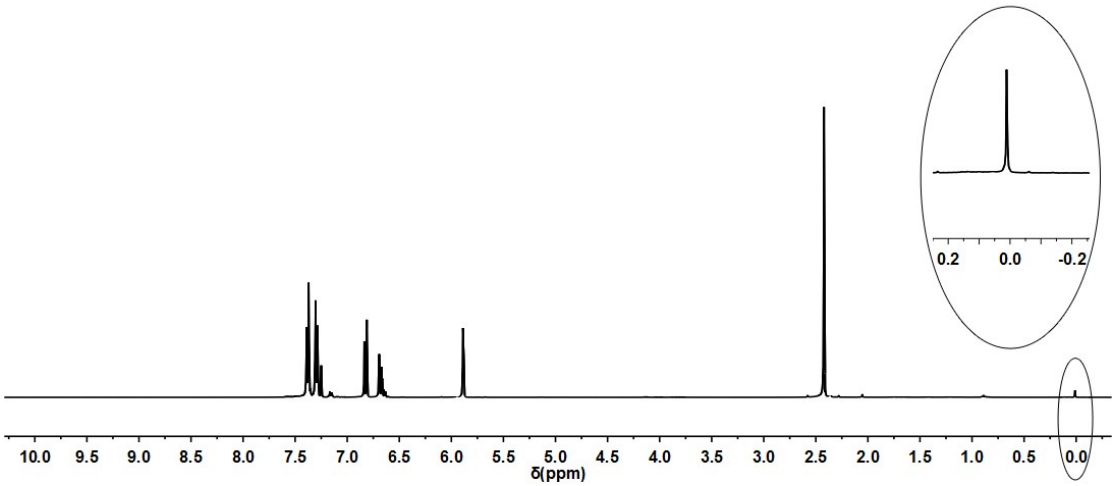
^{13}C-NMR spectrum of 4q



^{1}H-NMR spectrum of 4r

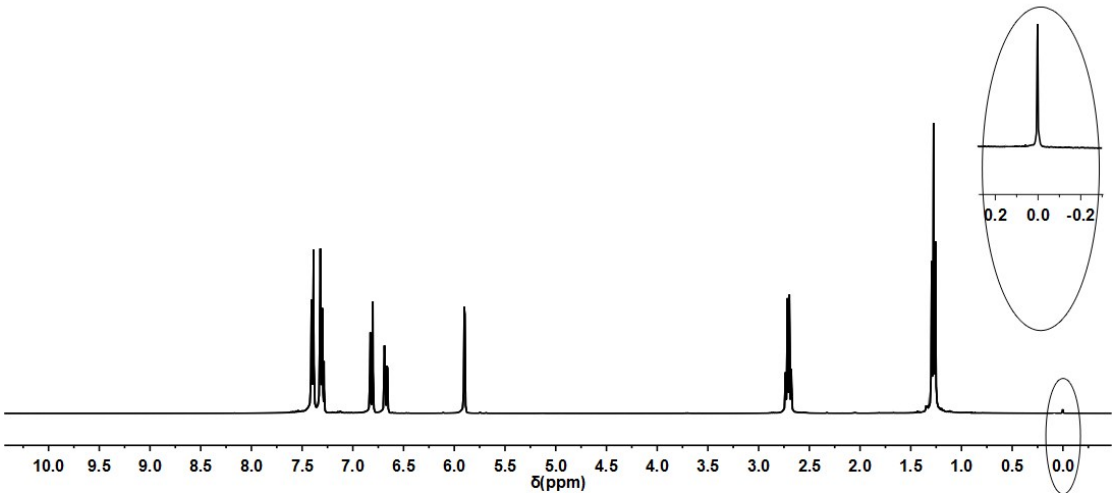


^{13}C-NMR spectrum of 4r



^{1}H-NMR spectrum of 4a

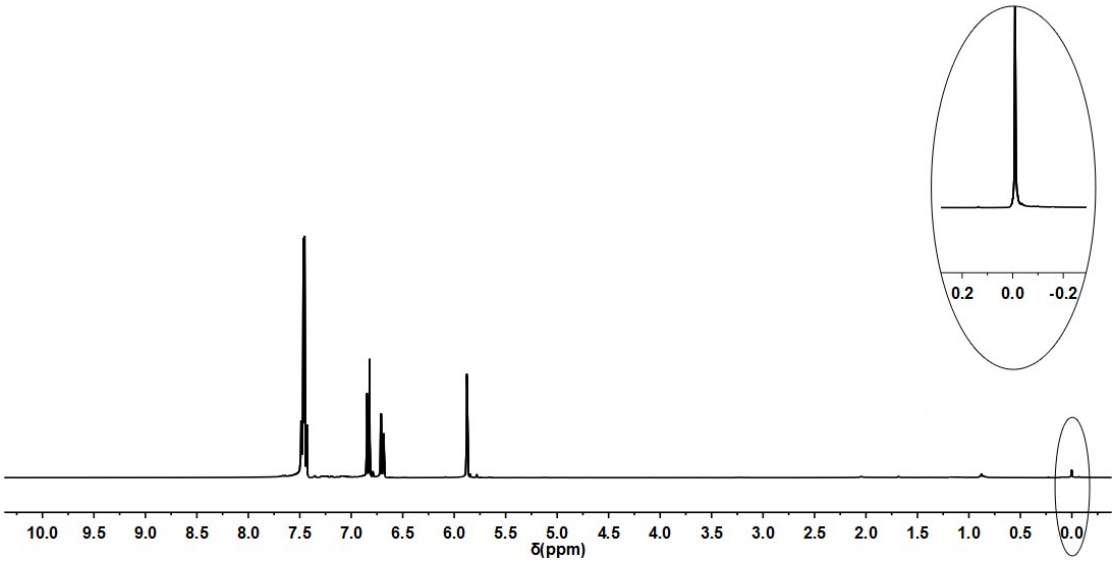
^{1}H-NMR spectrum of 4b



^{1}H-NMR spectrum of 4c

^{1}H-NMR spectrum of 4d

^{1}H-NMR spectrum of 4e

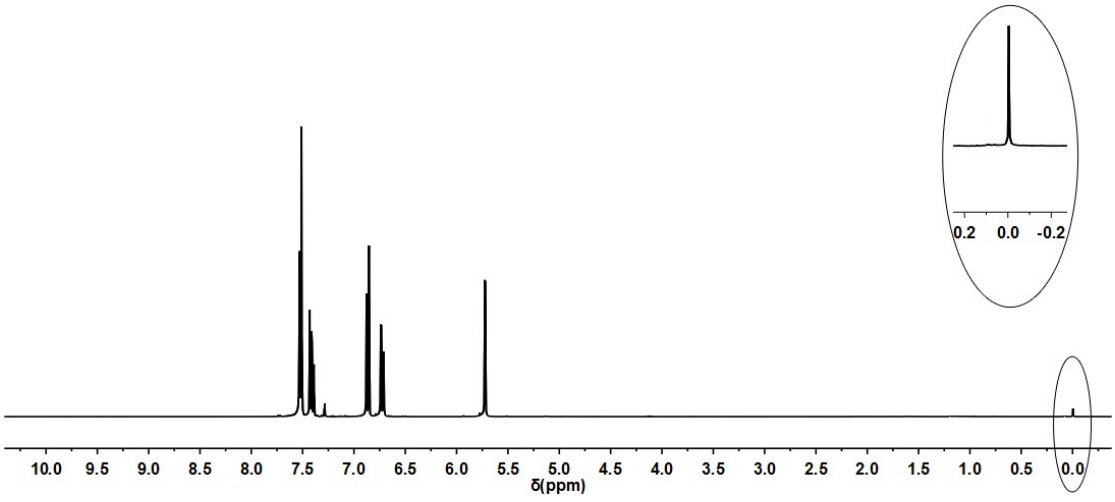


^{1}H-NMR spectrum of 4f

^{1}H-NMR spectrum of 4g

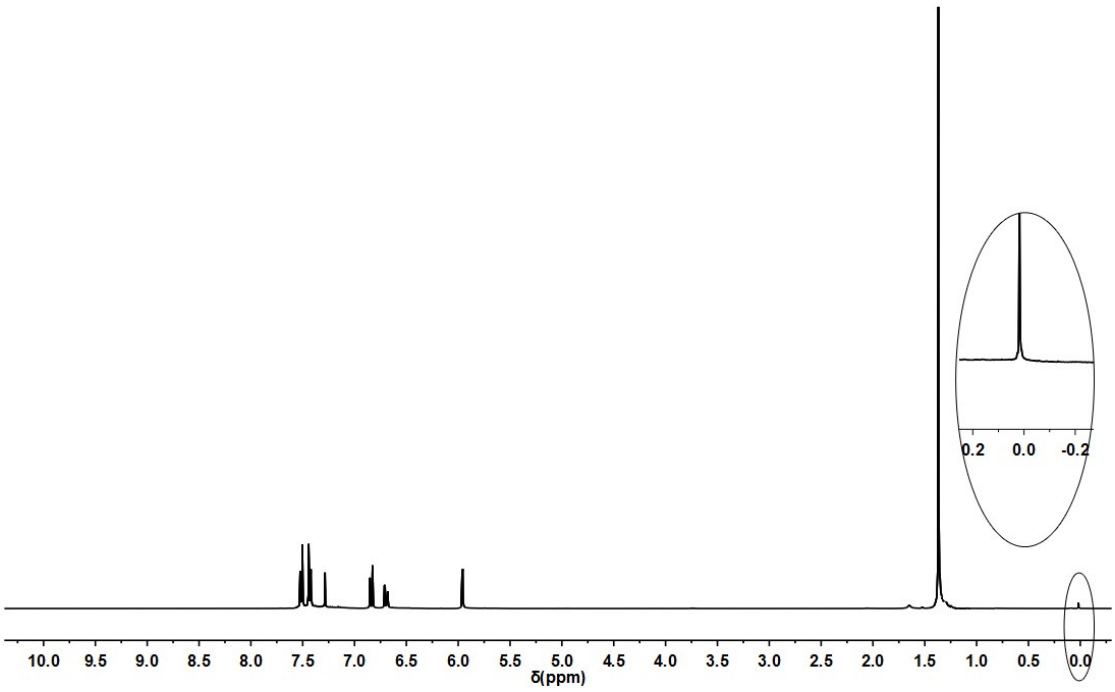
^{1}H-NMR spectrum of 4h

^{1}H-NMR spectrum of 4i



^{1}H-NMR spectrum of 4j

^{1}H-NMR spectrum of 4k



^{1}H-NMR spectrum of 4l

^{1}H-NMR spectrum of 4m

^{1}H-NMR spectrum of 4n

^{1}H-NMR spectrum of 4o

^{1}H-NMR spectrum of 4p

^{1}H-NMR spectrum of 4q

^{1}H-NMR spectrum of 4r