Supporting information

Reduction of sulfoxides catalyzed by the commercially available manganese complex $MnBr(CO)_5$

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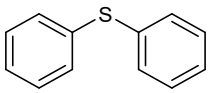
Table of contents

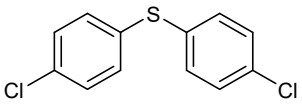
1. General information

All the reactions were carried out under air atmosphere and without using any dry solvent. Sulfoxides, catalyst, silanes and boranes were obtained from commercial suppliers and were used without further purification. ^{1}H NMR spectra were measured on a Bruker Avance II^{+} 400 MHz and 300 MHz spectrometers. Chemical shifts are reported in parts per million (ppm) downfield from an internal standard.

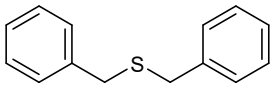
2. Characterization data of the products



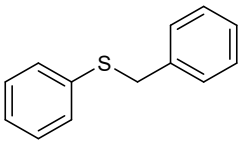
Phenyl sulfide: Light yellow liquid, 90 mg, 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.25 (m, 10 H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 135.8, 131.0, 129.2, 127.0 ppm.[1]



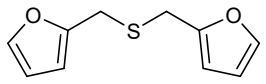
4-Chlorophenyl sulfide: White solid, 123 mg, 97%, m.p. = 91-93 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.26 (m, 4H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 133.9, 133.5, 132.3, 129.5 ppm.[1]



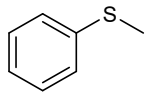
Dibenzyl sulfide: Beige solid, 102 mg, 95%, m.p. 44-47ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (brs, 10 H), 3.63 (s, 4H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 138.2, 129.1, 128.5, 127.0, 35.6 ppm.[1]



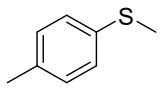
Benzyl phenyl sulfide: Light yellow poder, 94 mg, 94%, m.p. 39-42ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.21 (m, 10H), 4.15 (s, 2H, SCH_2Ph) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ137.5, 136.4, 129.8, 128.8, 128.5, 127.2, 126.4, 39.1 ppm.[2]



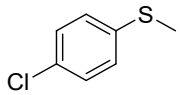
Difurfuryl sulfide: Yellow liquid, 88 mg, 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, 2H, *J* = 0.96 Hz), 6.32 (t, 2H, *J* = 2.92 Hz, *J* = 1.84 Hz), 6.20 (d, 2H, *J* = 2.96 Hz), 3.69 (s, 4H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 151.3, 142.3, 110.4, 107.8, 27.7 ppm.[3]



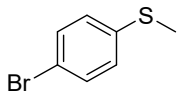
Methyl phenyl sulfide: Colorless liquid, 52 mg, 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.29 (m, 4 H), 7.19-7.15 (m, 1H), 2.52 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 138.4, 128.8, 126.6, 125.0, 15.9 ppm.[1]



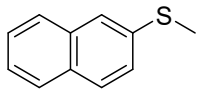
Methyl *p*-tolyl sulfide: Colorless liquid, 67 mg, 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, 2H, *J* = 6.6 Hz), 7.18 (d, 2H, *J* = 7.6 Hz), 2,53 (s, 3H), 2,39 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 135.0, 134.8, 129.7, 127.3, 21.0, 16.5 ppm.[1]



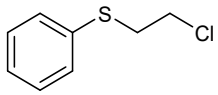
4-Chlorothioanisole: Colorless liquid, 76 mg, 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, 2H, *J* = 8.6 Hz), 7.20 (d, 2H, *J* = 8.7 Hz), 2,49 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 137.1, 130.9, 128.9, 127.9, 16.1 ppm.[4]



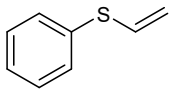
4-Bromothioanisole: Dark orange poder, 96 mg, 95%, m.p. 38-40 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, 2H, *J* = 7.9 Hz), 7.14 (d, 2H, *J* = 7.8 Hz), 2,41 (s, 3H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 137.7, 131.8, 128.1, 118.6, 15.9 ppm.[4]



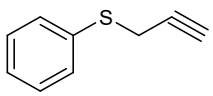
2-(Methylthio)naphthalene: Cream solid, 83 mg, 95%, m.p. 62-63°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.75 (m, 3H), 7.63 (brs, 1H), 7.51-7.39 (m, 3H), 2.61 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 136.1, 133.9, 131.3, 128.2, 127.7, 126.8, 126.6, 125.7, 125.2, 123.4 ppm.[4]



2-Chloroethyl phenyl sulfide: Light yellow liquid, 84 mg, 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, 2H, *J* = 7.5 Hz), 7.35 (t, 2H, *J* = 7.2 Hz, *J* = 7.7 Hz), 7.28 (t, 1H, *J* = 5.2 Hz, *J* = 2,2 Hz), 3.64 (t, 2H, *J* = 7.7 Hz, *J* = 8.2 Hz), 3.25 (t, 2H, *J* = 8.3 Hz, *J* = 7.6 Hz) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 134.3, 130.5, 129.2, 127.1, 42.3, 36.2 ppm.[3]

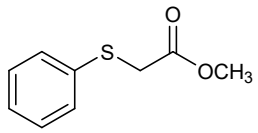


Phenyl vinyl sulfide: Light yellow liquid, 61 mg, 89%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43-7.27 (m, 5 H), 6.58 (dd, 1H, *J* = 9.5 Hz, *J* = 16.4 Hz), 5.40 (s, 1H), 5.37 (d, *J* = 9.2 Hz, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 134.3, 131.9, 130.5, 129.1, 127.1, 115.5 ppm.[1]

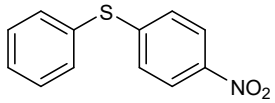


Phenyl propargyl sulfide: Yellow liquid, 68 mg, 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, 2H, *J* = 7.8 Hz), 7.36 (t, 2H, *J* = 7.3 Hz, *J* = 7.8 Hz), 7.28 (t, 1H, *J* = 7.5 Hz, *J* = 7.1

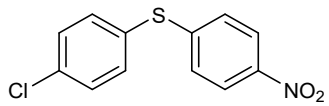
Hz), 3.64 (d, 2H, J = 2.6 Hz), 2.28 (t, 1H, J = 2.6 Hz, J = 2.4 Hz) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 135.0, 130.1, 129.0, 127.0, 79.9, 71.6, 22.6 ppm.[3]



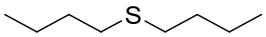
Methoxycarbonylmethyl phenyl sulfide: Colorless oil, 67 mg, 87%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, 2H, J = 7.4 Hz), 7.34-7.25 (m, 3H), 3.73 (s, 3H), 3.67 (s, 2H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 170.2, 135.0, 129.9, 129.1, 127.0, 52.6, 36.5 ppm.[1]



4-nitrophenyl phenyl sulfide: Yellow solid, 89 mg, 77%, m. p. 54-55ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, 2H, J = 8.9 Hz), 7.58-7.56 (m, 2H), 7.49-7.48 (m, 3H), 7.20 (d, 2H, J = 8.9 Hz) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 148.5, 145.4, 134.8, 130.5, 130.1, 129.7, 126.7, 124.1 ppm.[3]



4-chlorophenyl 4-nitrophenyl sulfide: Yellow solid, 105 mg, 79%, m.p. 83-84ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, 2H, J = 8.9 Hz), 7.52-7.44 (m, 4H), 7.21 (d, 2H, J = 8.9 Hz) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 147.6, 145.6, 136.1, 135.9, 130.3, 129.2, 127.0, 124.2 ppm.[3]



Dibutyl sulfide: Colorless liquid, 69 mg, 95%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.50 (t, 2 H, *J* = 7.8 Hz, *J* = 6.8 Hz), 1.60-1.53 (m, 2H), 1.45-1.36 (m, 2H), 0.91 (t, 3H, *J* = 7.2 Hz) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 31.8, 22.1, 13.7 ppm.[1]

Tetrahydrothiophene: Colorless liquid, 42 mg, 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.82 (brs, 4H), 1.92 (d, 4H, *J* = 2.2 Hz) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 31.8, 31.1 ppm.[1]

3. NMR spectra

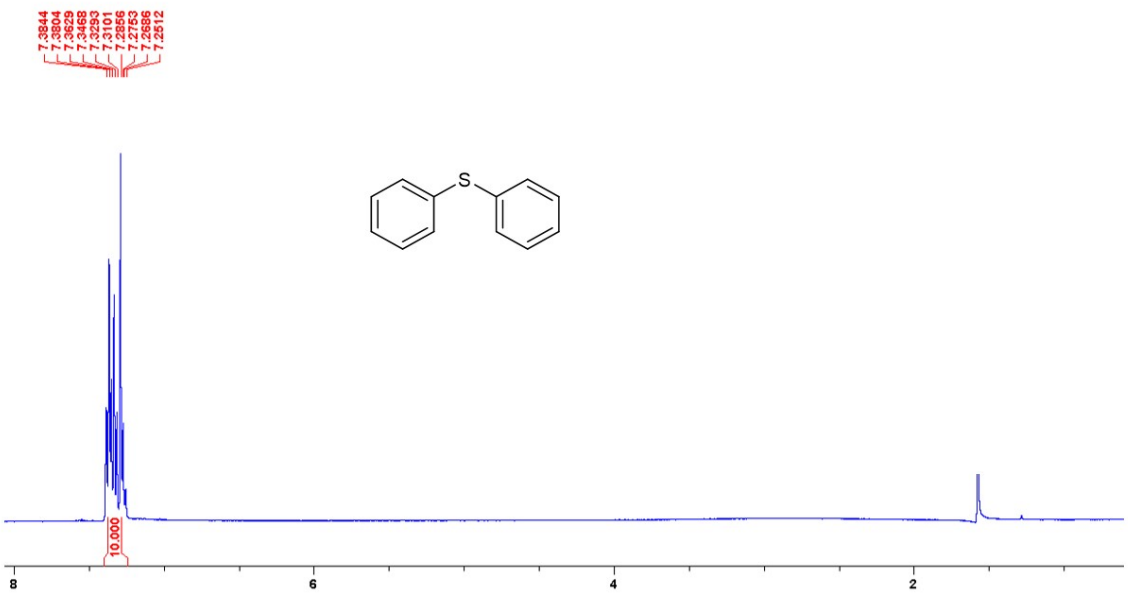


Figure S1 - ^{1}H NMR spectrum of phenyl sulfide in $CDCl_3$.

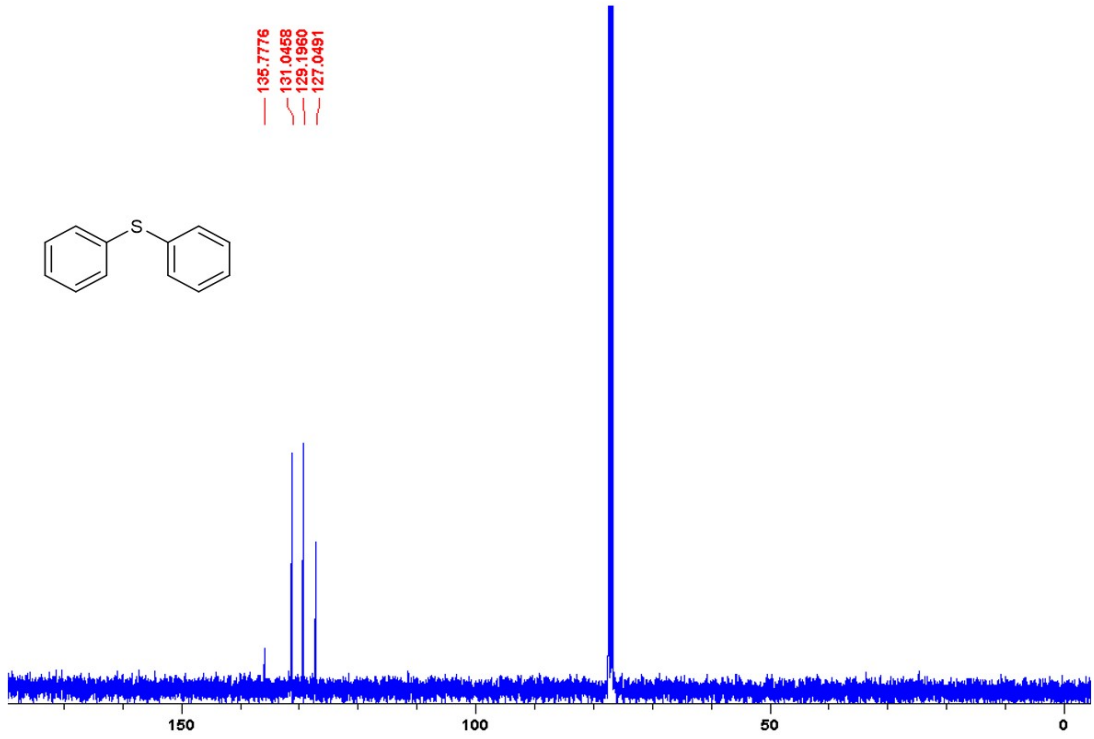


Figure S2 - ^{13}C NMR spectrum of phenyl sulfide in $CDCl_3$.

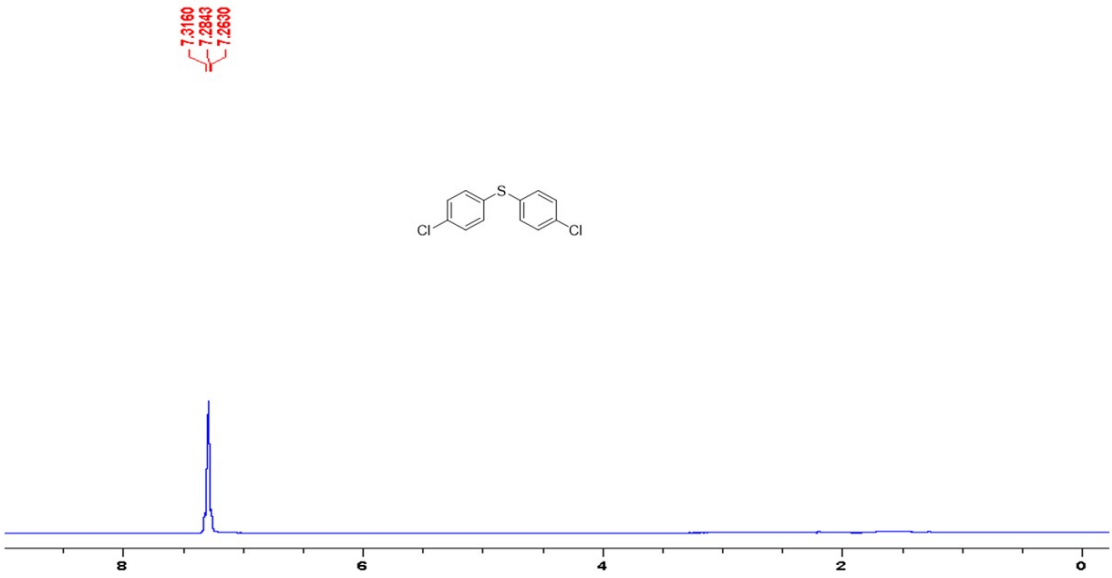


Figure S3 - ^{1}H NMR spectrum of 4-chlorophenyl sulfide in $CDCl_3$.

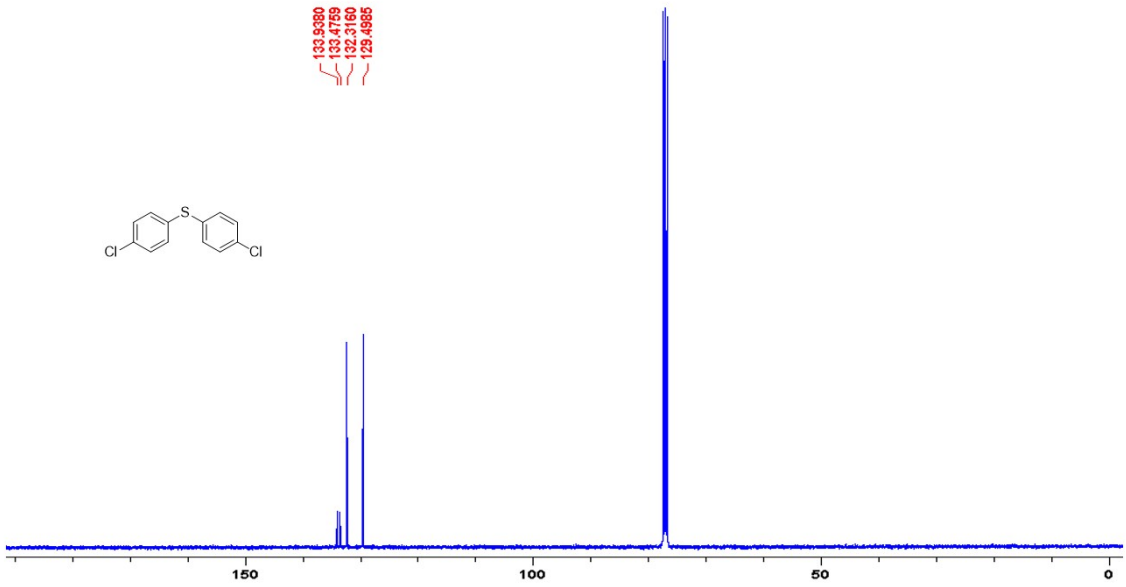


Figure S4 - ^{13}C NMR spectrum of 4-chlorophenyl sulfide in $CDCl_3$.

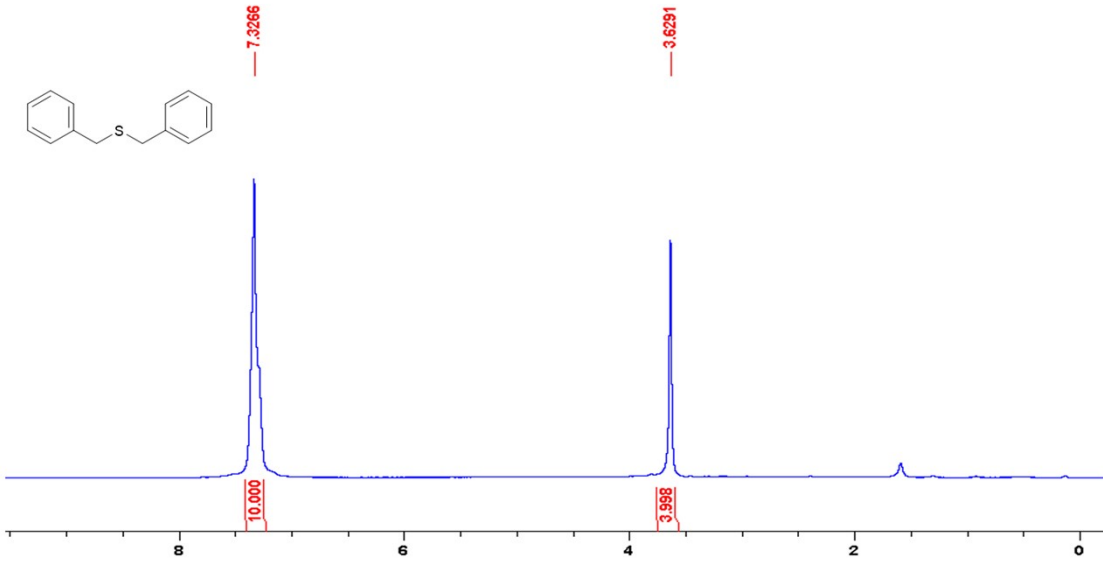


Figure S5 - ^{1}H NMR spectrum of dibenzyl sulfide in $CDCl_3$.

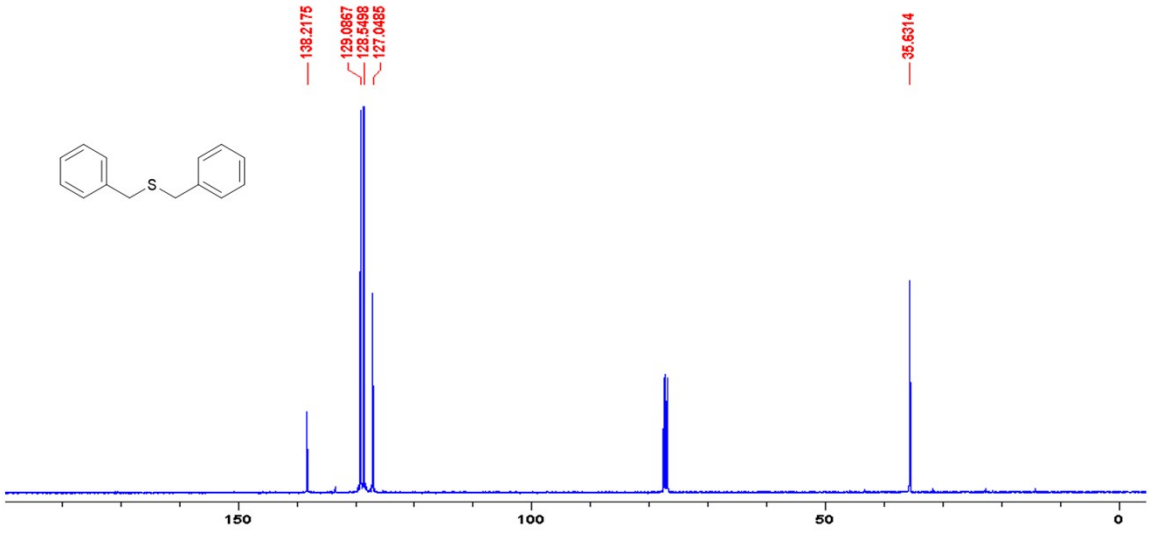


Figure S6 - ^{13}C NMR spectrum of dibenzyl sulfide in $CDCl_3$.

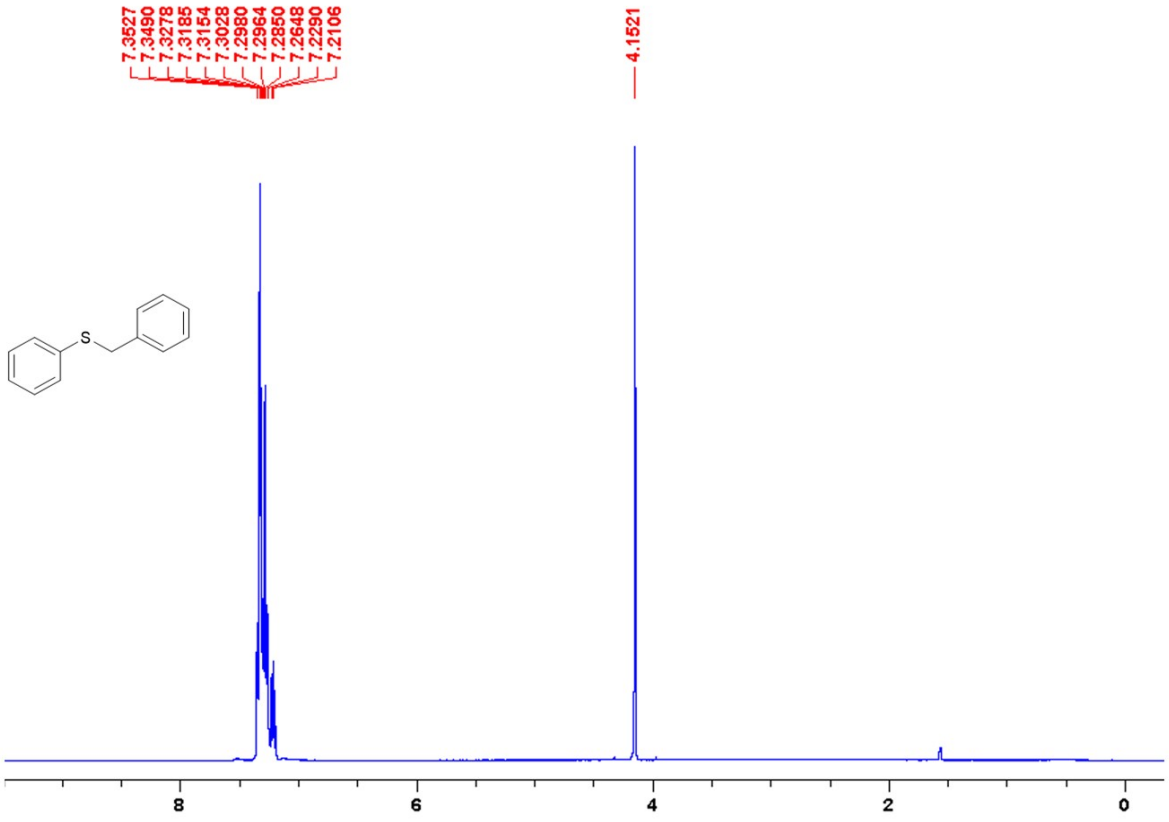


Figure S7 - ^{1}H NMR spectrum of benzyl phenyl sulfide in $CDCl_3$.

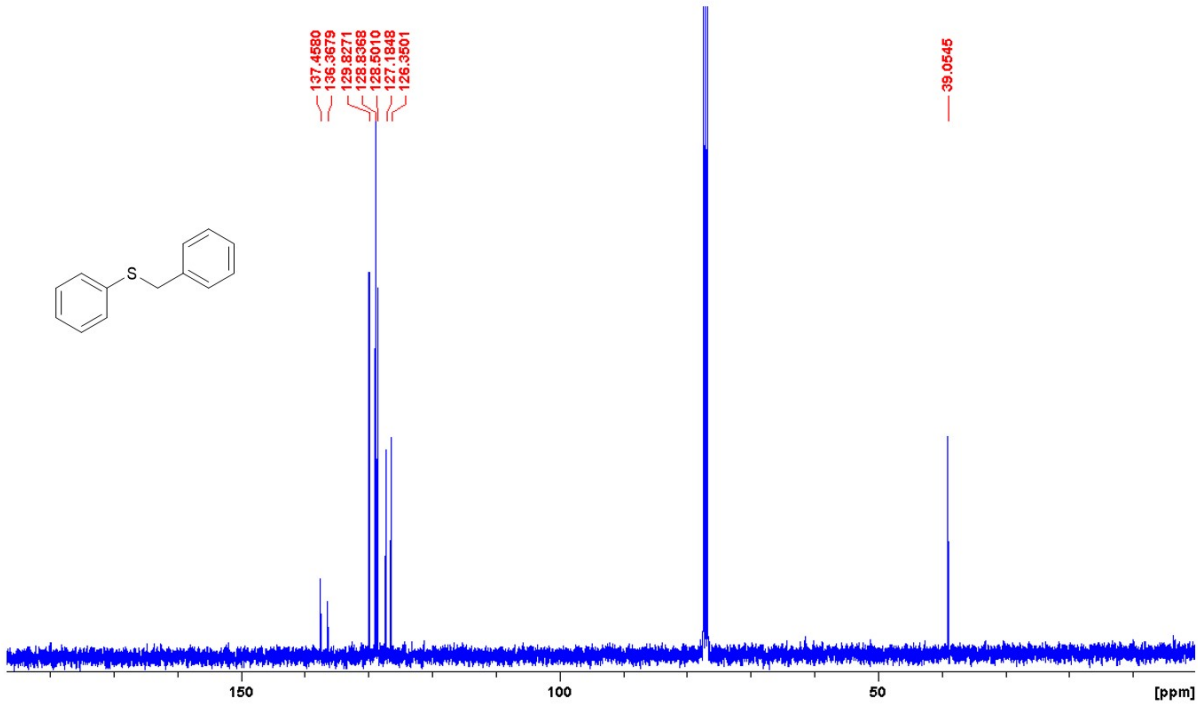


Figure S8 - ^{13}C NMR spectrum of benzyl phenyl sulfide in $CDCl_3$.

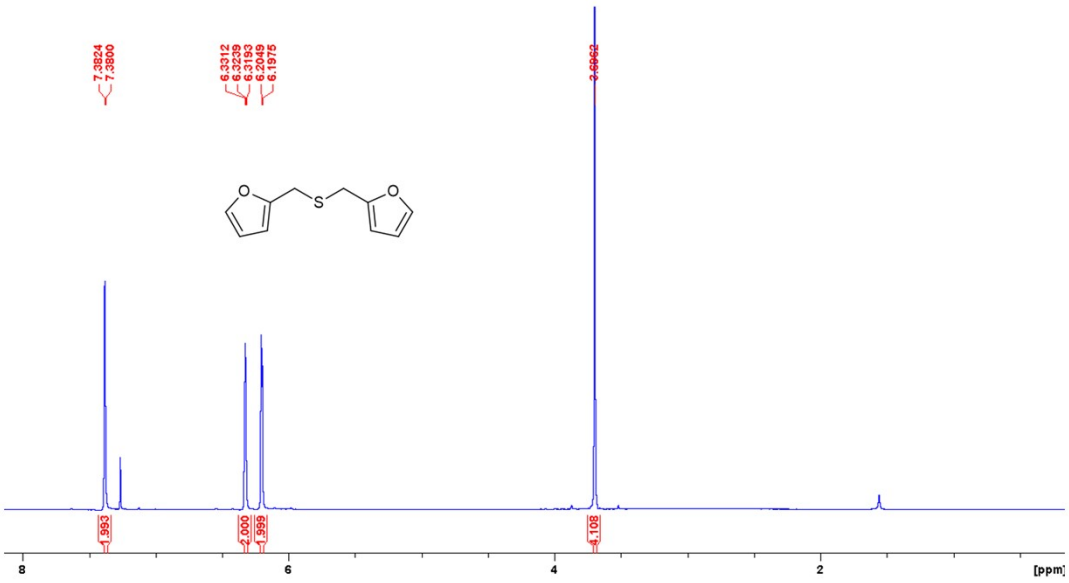


Figure S9 - ^{1}H NMR spectrum of difurfuryl sulfide in $CDCl_3$.

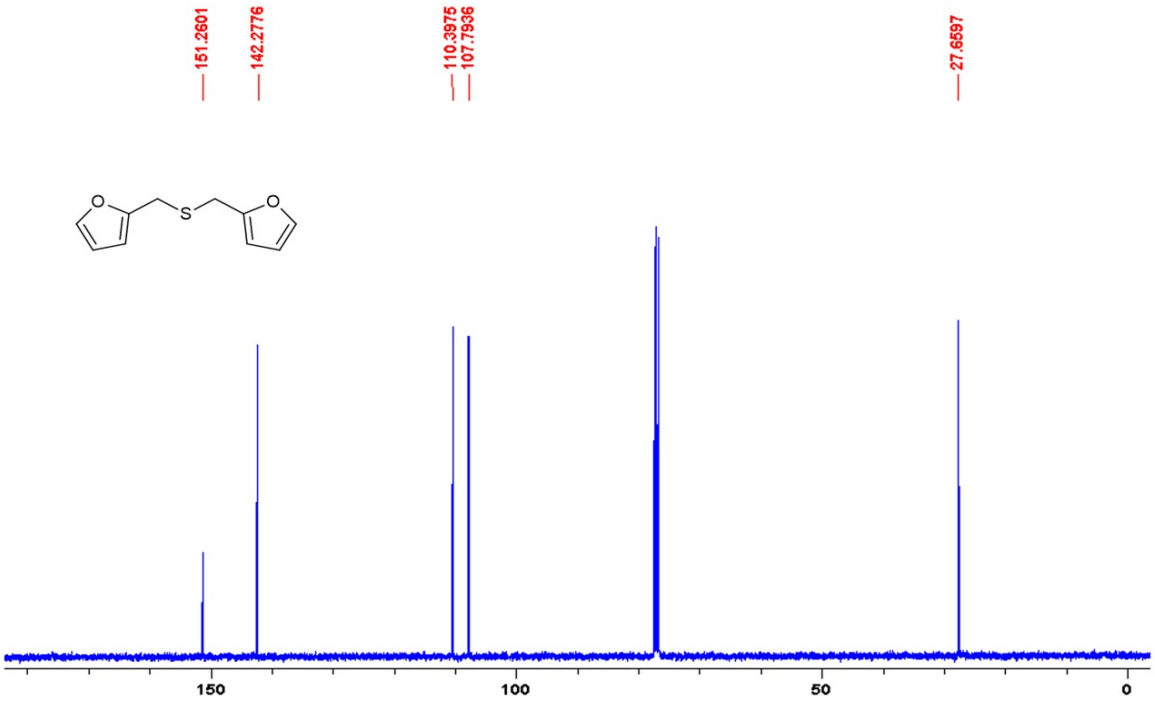


Figure S10 - ^{13}C NMR spectrum of difurfuryl sulfide in $CDCl_3$.

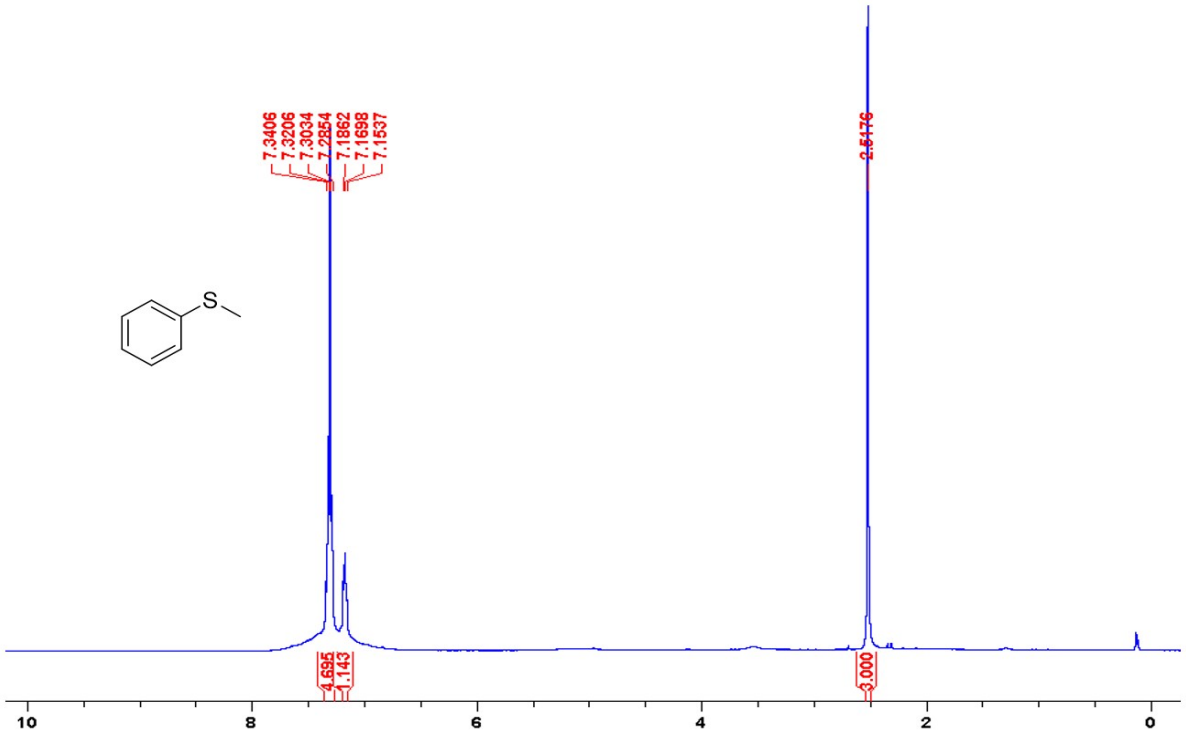


Figure S11 - ^{1}H NMR spectrum of methyl phenyl sulfide in $CDCl_3$.

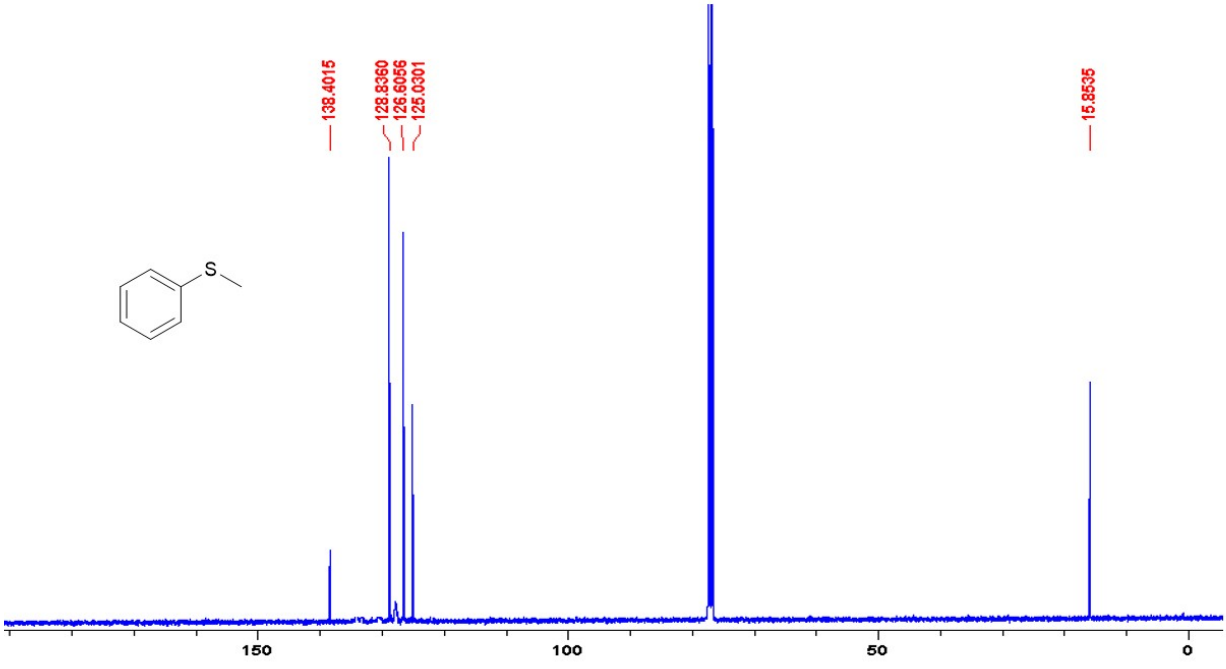


Figure S12 - ^{13}C NMR spectrum of methyl phenyl sulfide in $CDCl_3$.

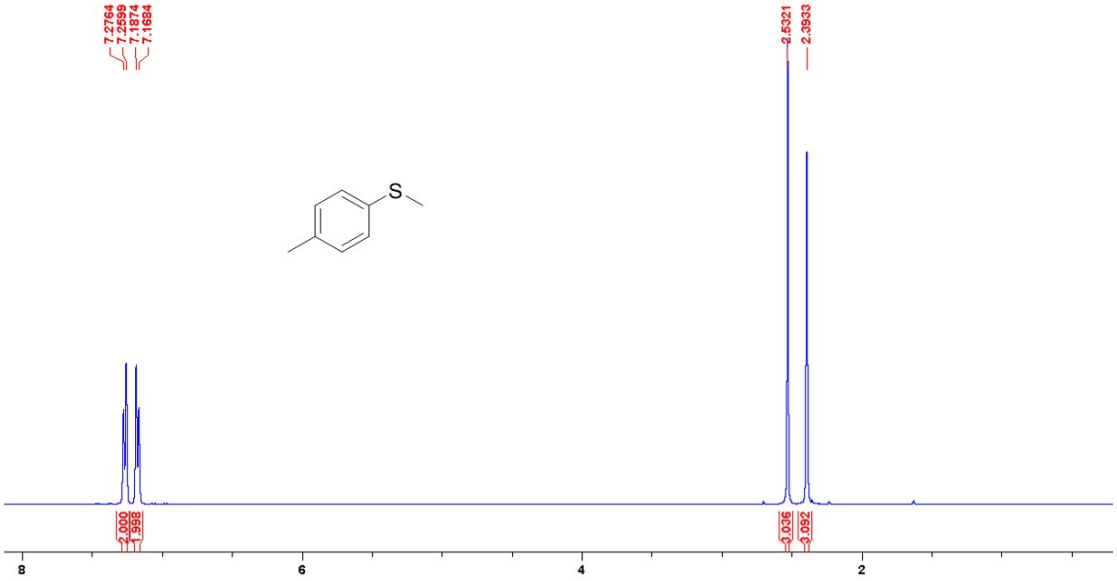


Figure S13 - ^{1}H NMR spectrum of methyl *p*-tolyl sulfide in $CDCl_3$.

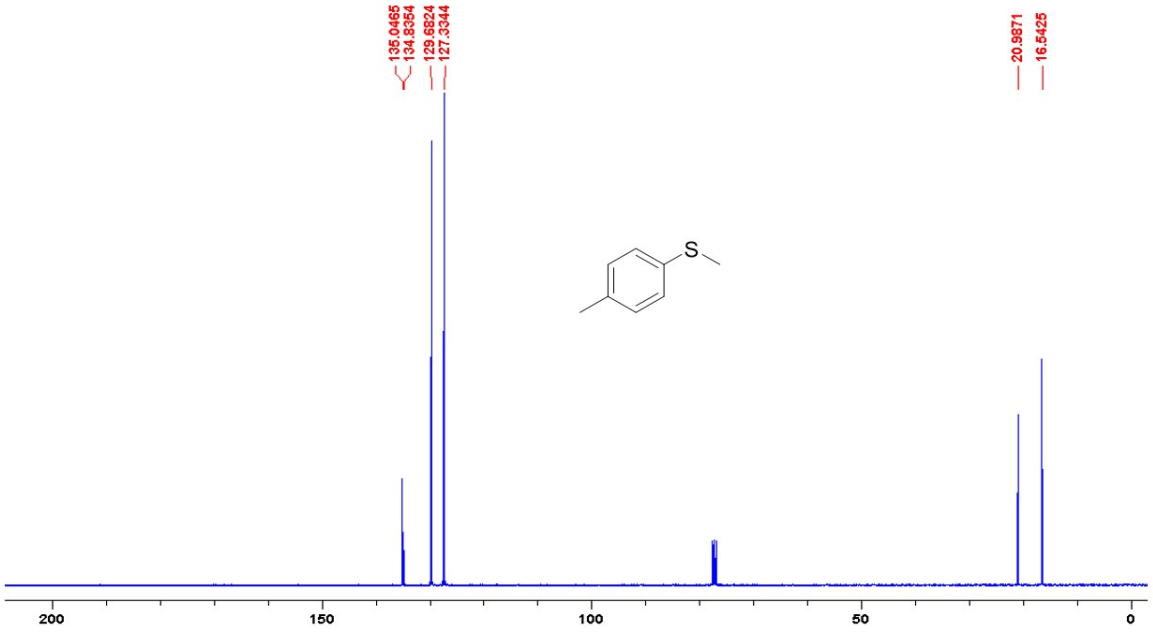


Figure S14 - ^{13}C NMR spectrum of methyl *p*-tolyl sulfide in $CDCl_3$.

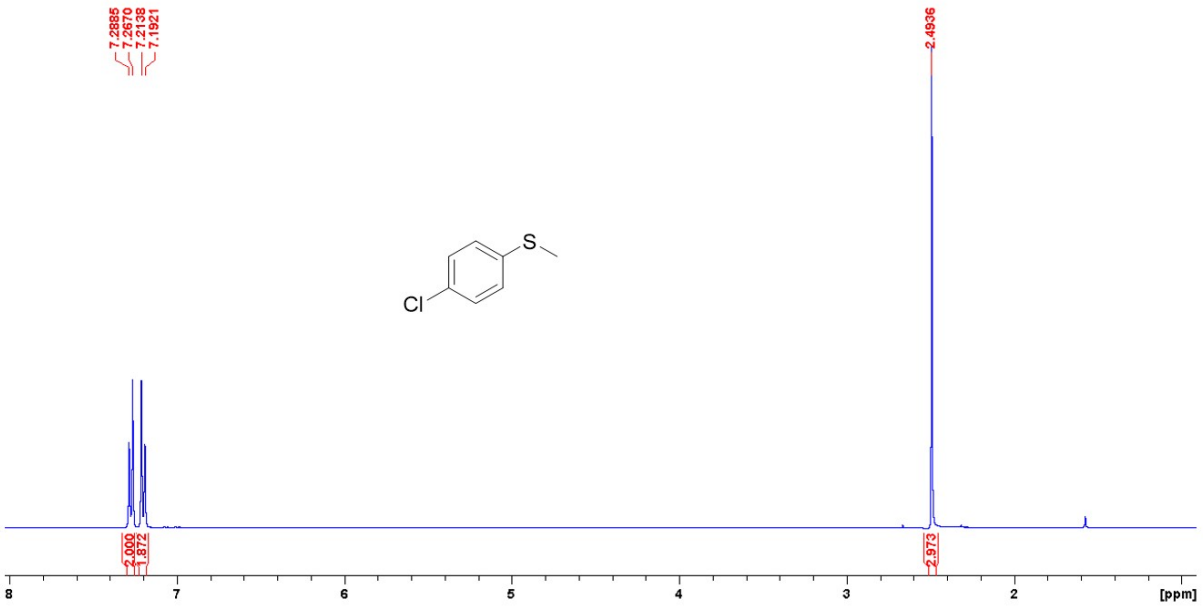


Figure S15 - ^{1}H NMR spectrum of 4-clorothioanisole in $CDCl_3$.

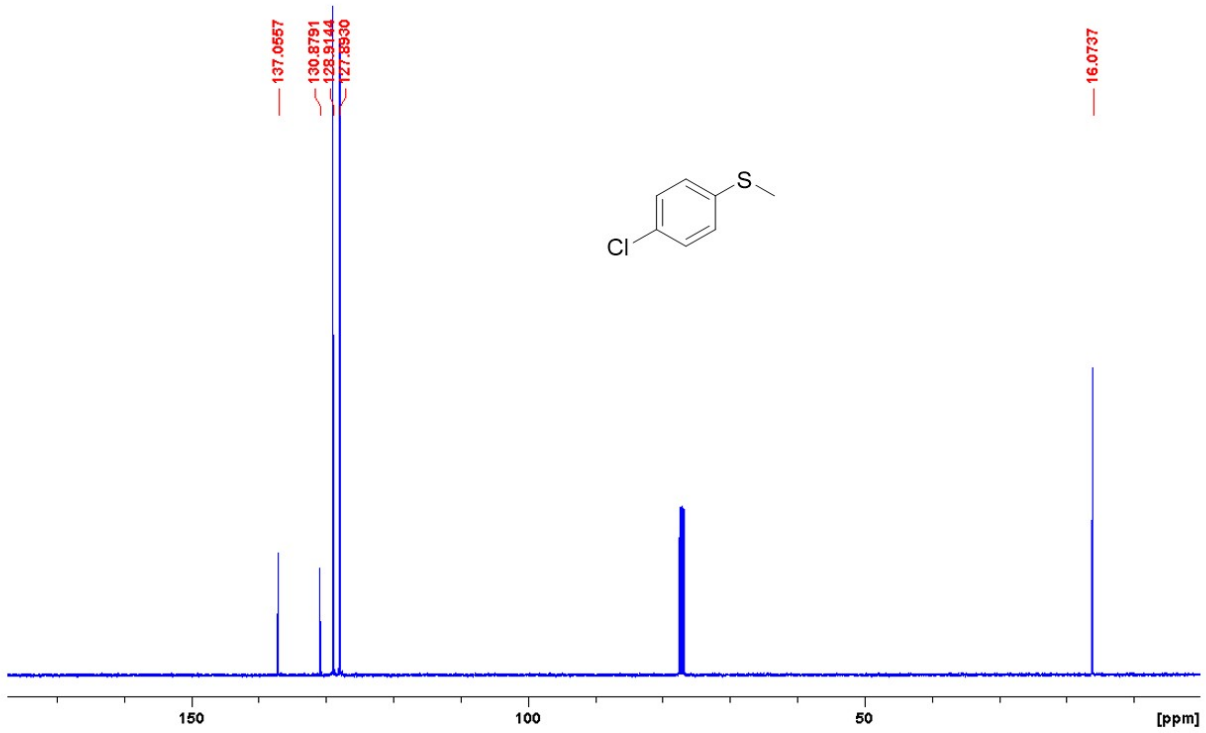


Figure S16 - ^{13}C NMR spectrum of 4-clorothioanisole in $CDCl_3$.

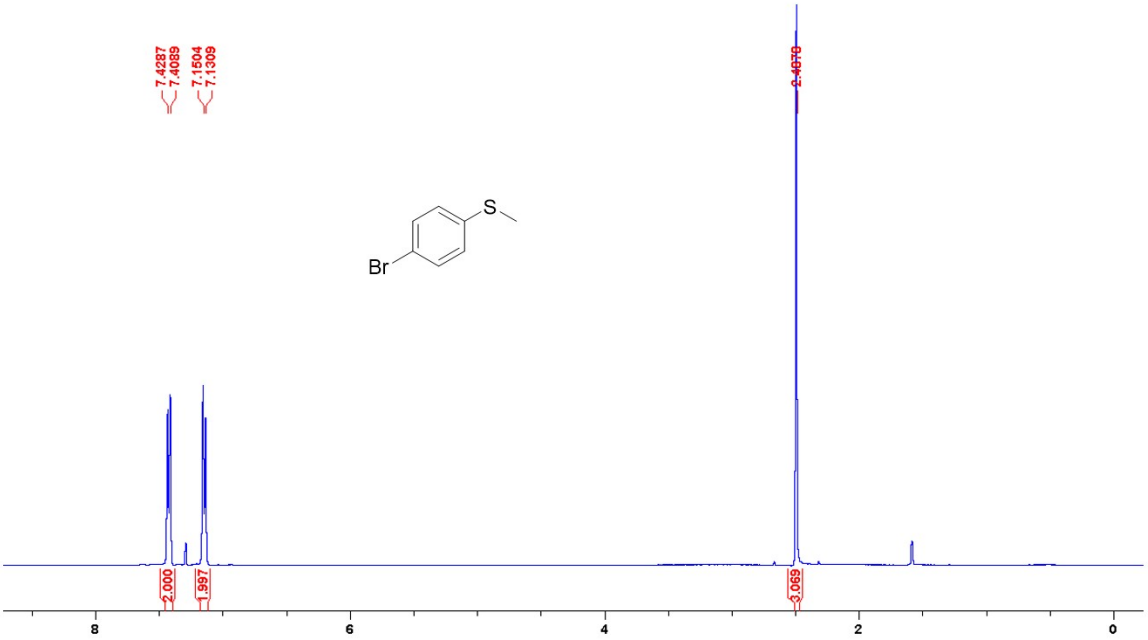


Figure S17 - ^{1}H NMR spectrum of 4-bromothioanisole in $CDCl_3$.

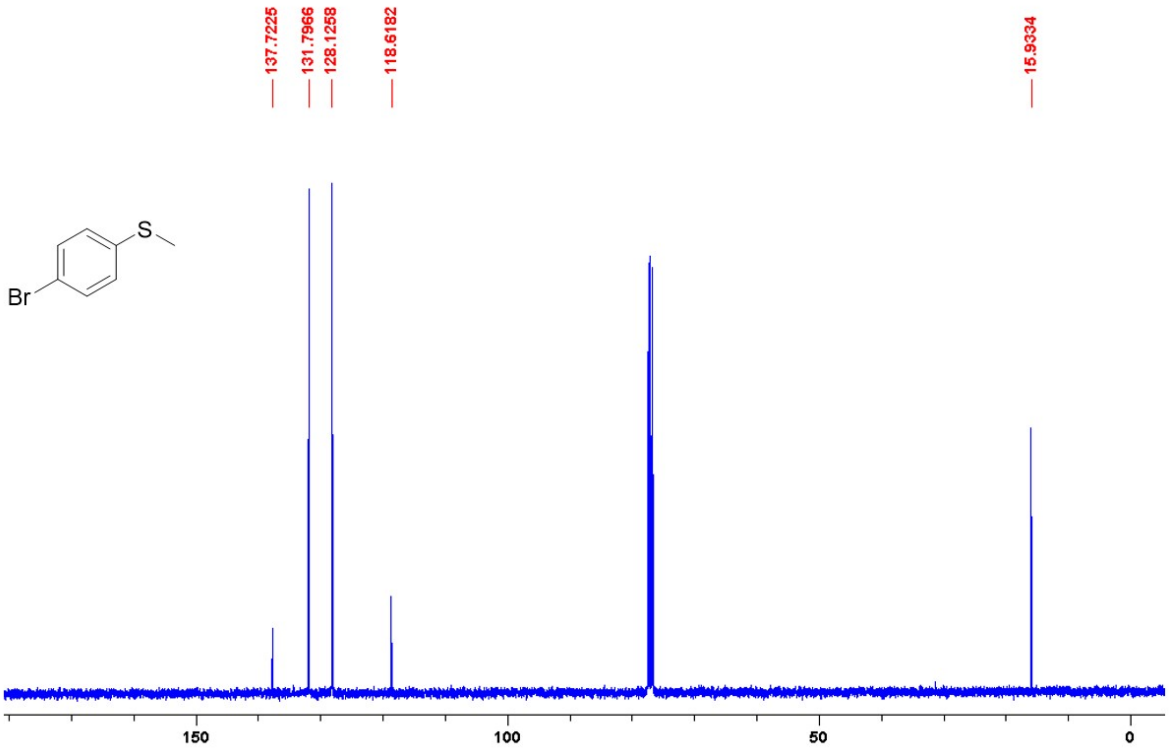


Figure S18 - ^{13}C NMR spectrum of 4-bromothioanisole in $CDCl_3$.

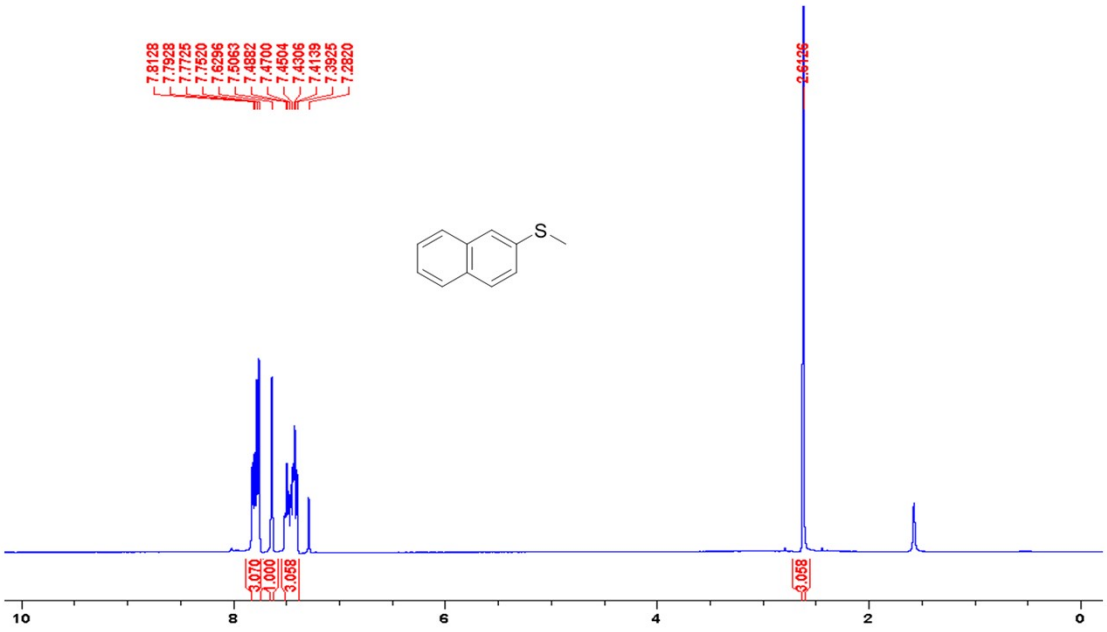


Figure S19 - ^{1}H NMR spectrum of 2-(methylthio)naphthalene in $CDCl_3$.

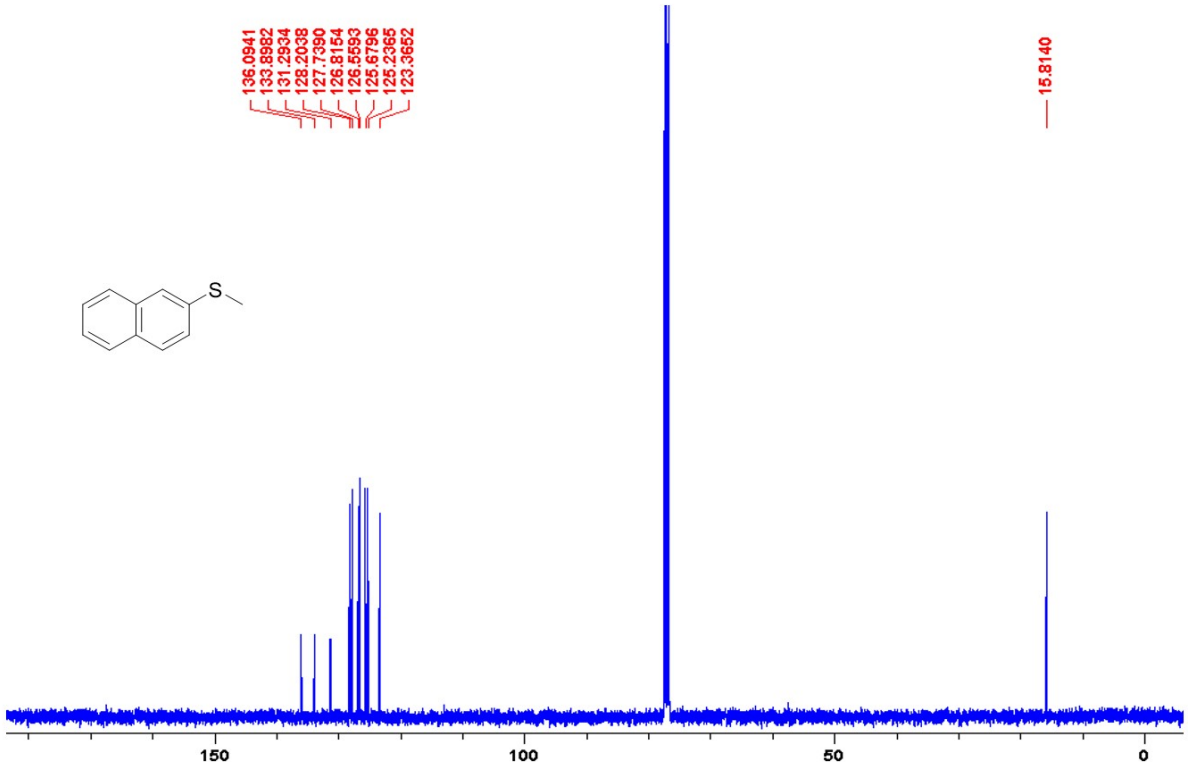


Figure S20 - ^{13}C NMR spectrum of 2-(methylthio)naphthalene in $CDCl_3$.

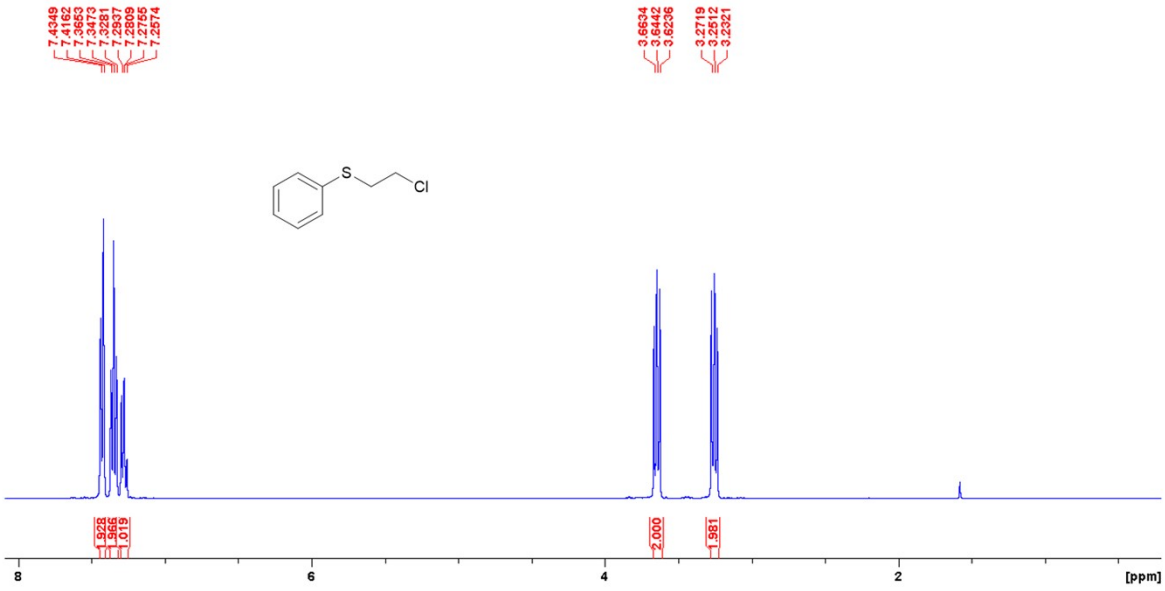


Figure S21 - ^{1}H NMR spectrum of 2-chloroethyl phenyl sulfide in $CDCl_3$.

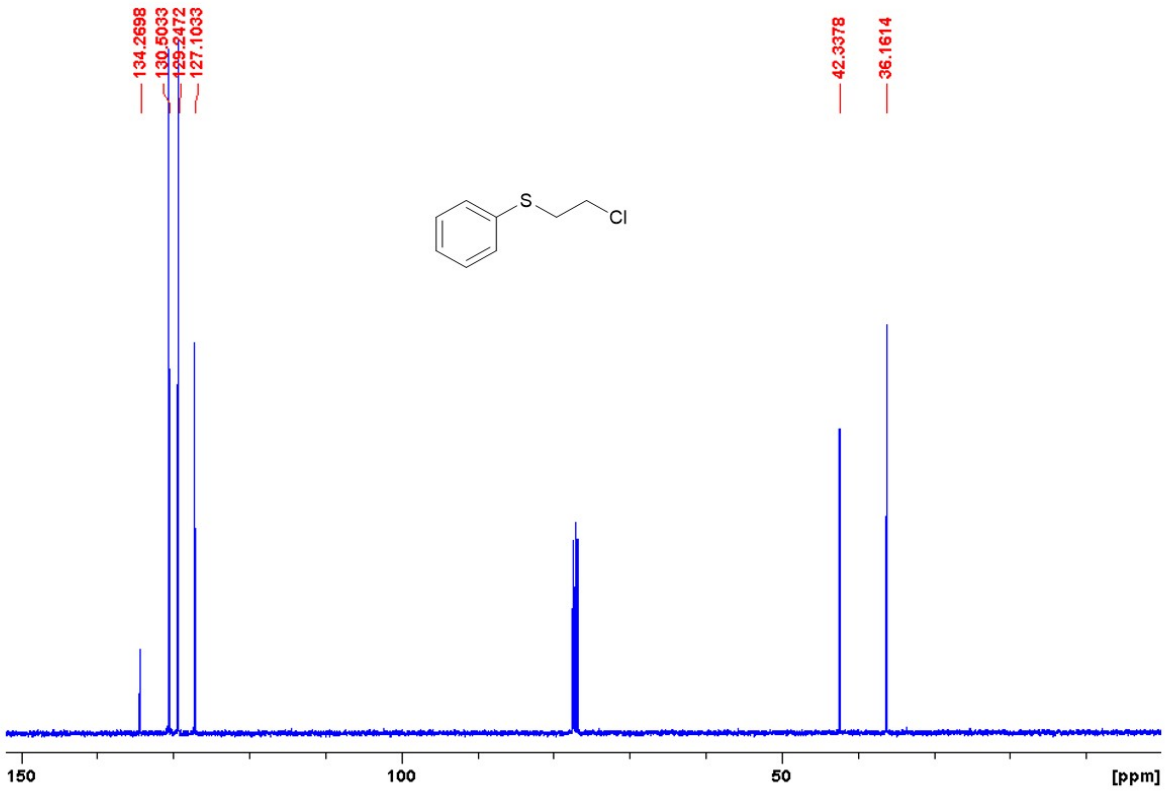


Figure S22 - ^{13}C NMR spectrum of 2-chloroethyl phenyl sulfide in $CDCl_3$.

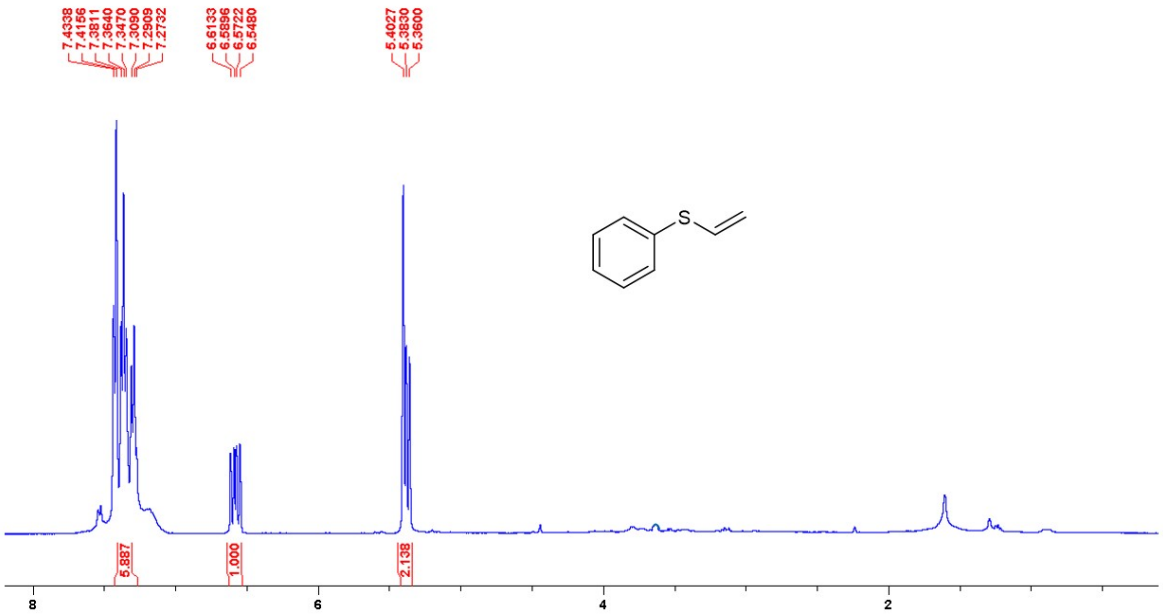


Figure S23 - ^{1}H NMR spectrum of phenyl vinyl sulfide in $CDCl_3$.

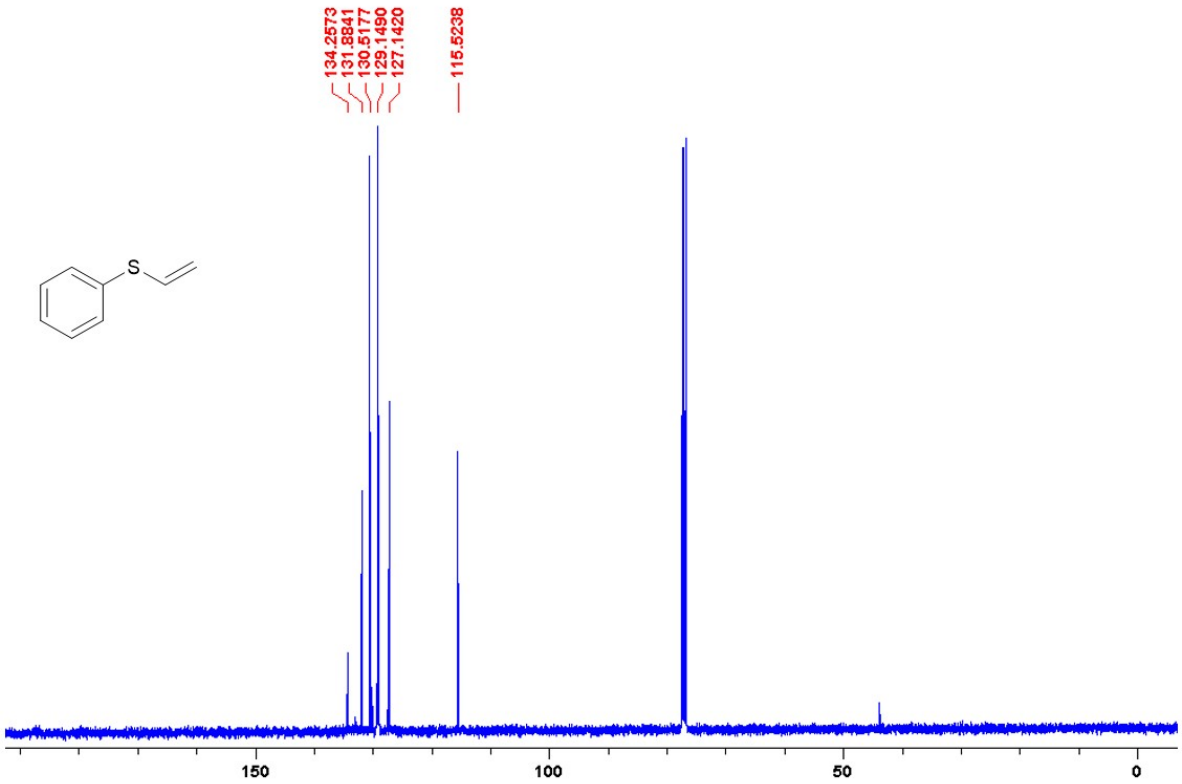


Figure S24 - ^{13}C NMR spectrum of phenyl vinyl sulfide in $CDCl_3$.

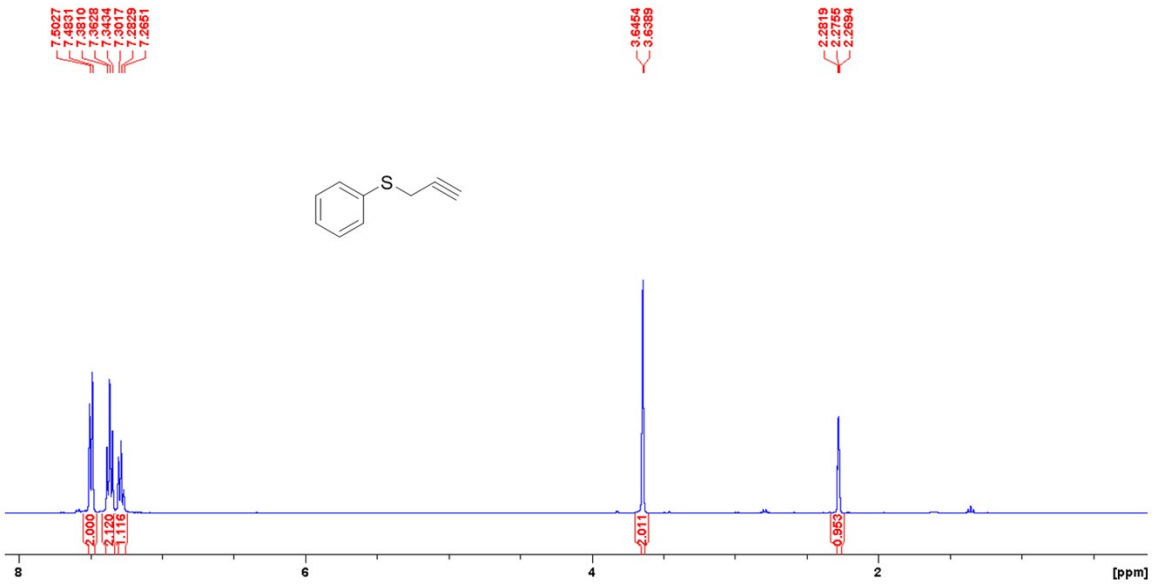


Figure S25 - ^{1}H NMR spectrum of phenyl propargyl sulfide in $CDCl_3$.

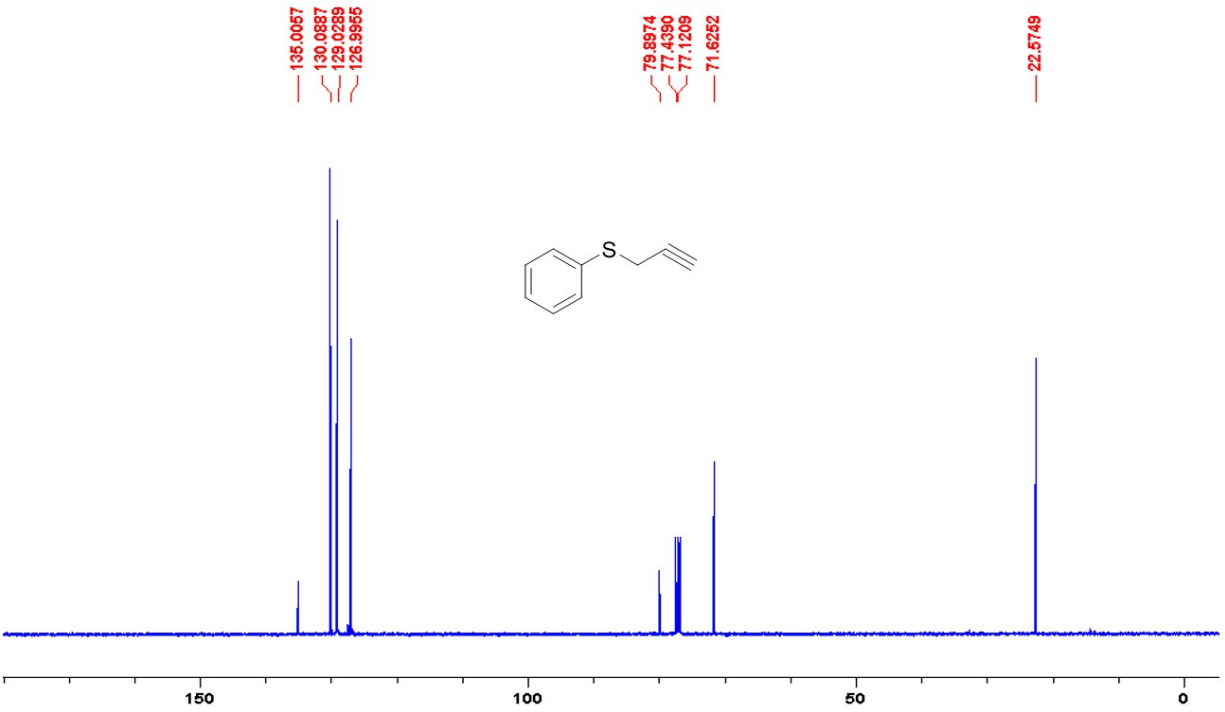


Figure S26 - ^{13}C NMR spectrum of phenyl propargyl sulfide in $CDCl_3$.

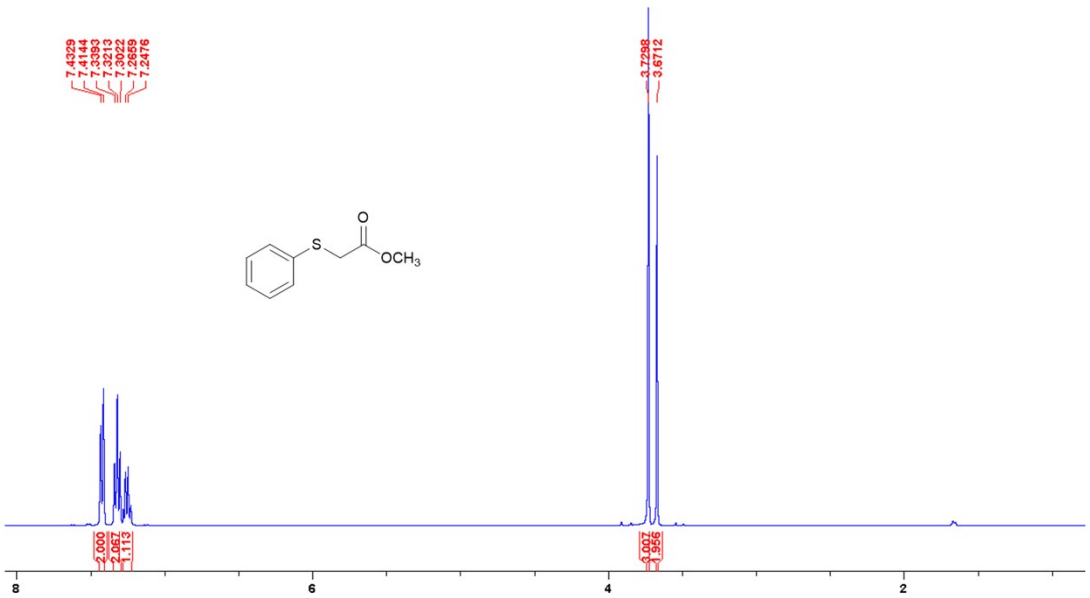


Figure S27 - ^{1}H NMR spectrum of methyl (phenylthio) acetate in $CDCl_3$.

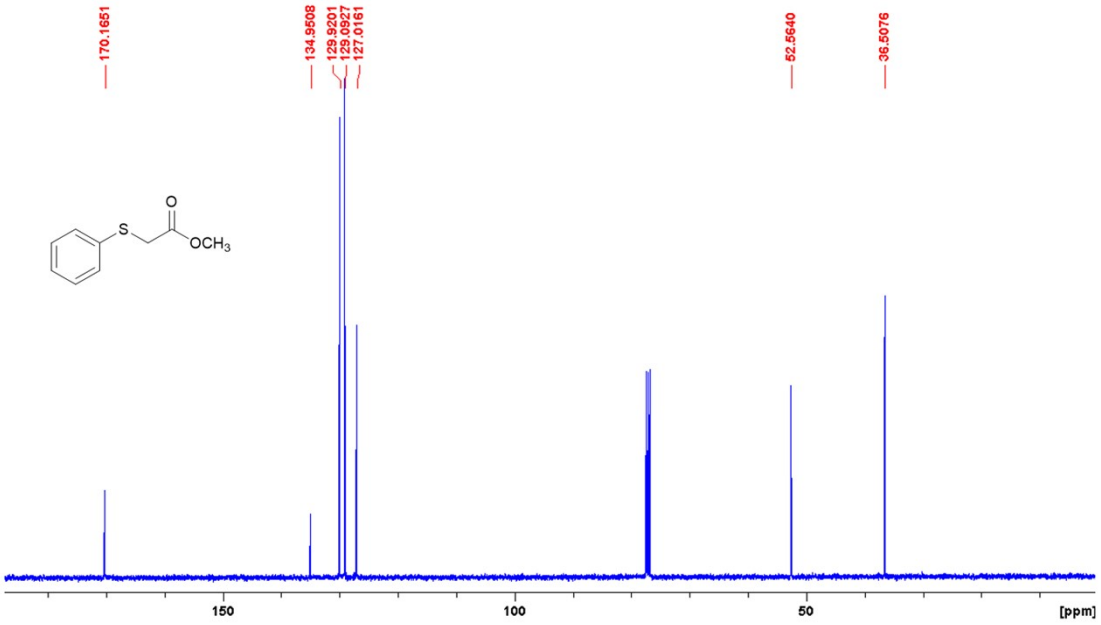


Figure S28 - ^{13}C NMR spectrum of methyl (phenylthio) acetate in $CDCl_3$.

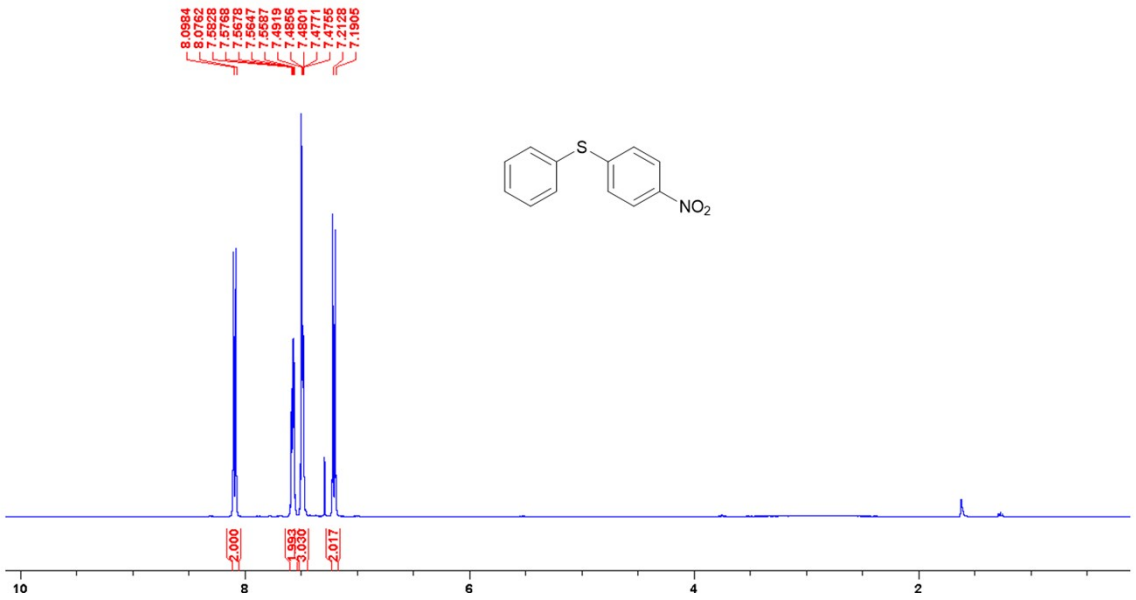


Figure S29 - ^{1}H NMR spectrum of 4-nitrophenyl phenyl sulfide in $CDCl_3$.

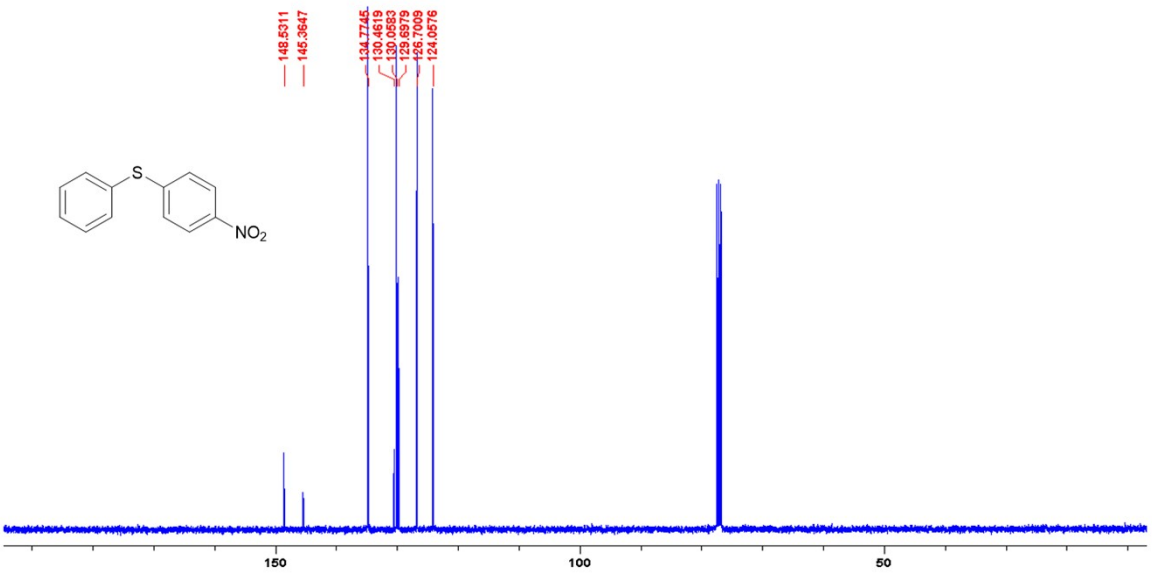


Figure S30 - ^{13}C NMR spectrum of 4-nitrophenyl phenyl sulfide in $CDCl_3$.

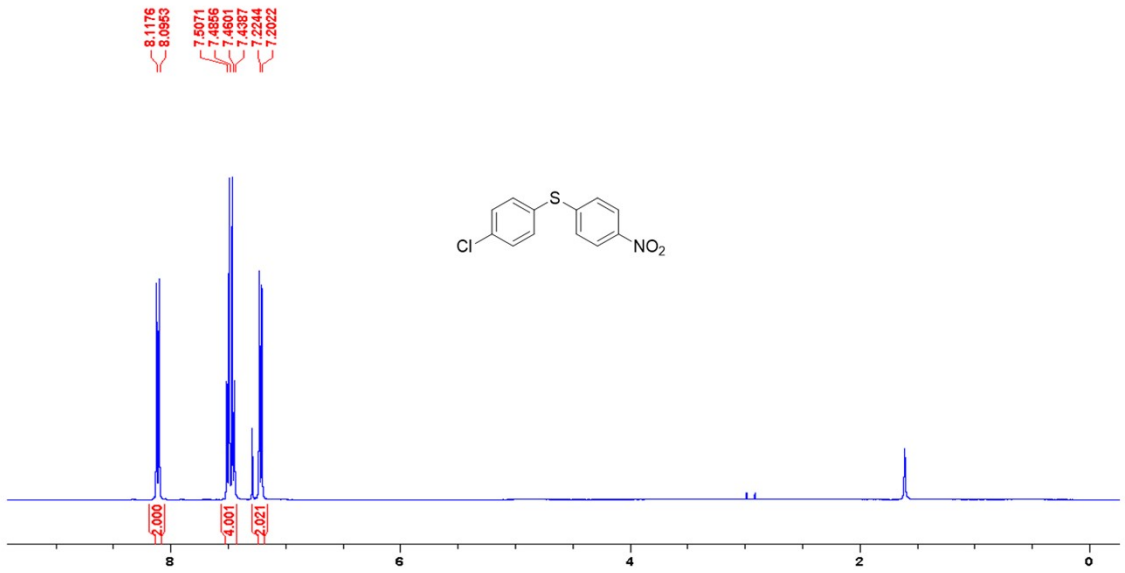


Figure S31 - ^{1}H NMR spectrum of 4-chloro-4-nitrodiphenyl sulfide in $CDCl_3$.

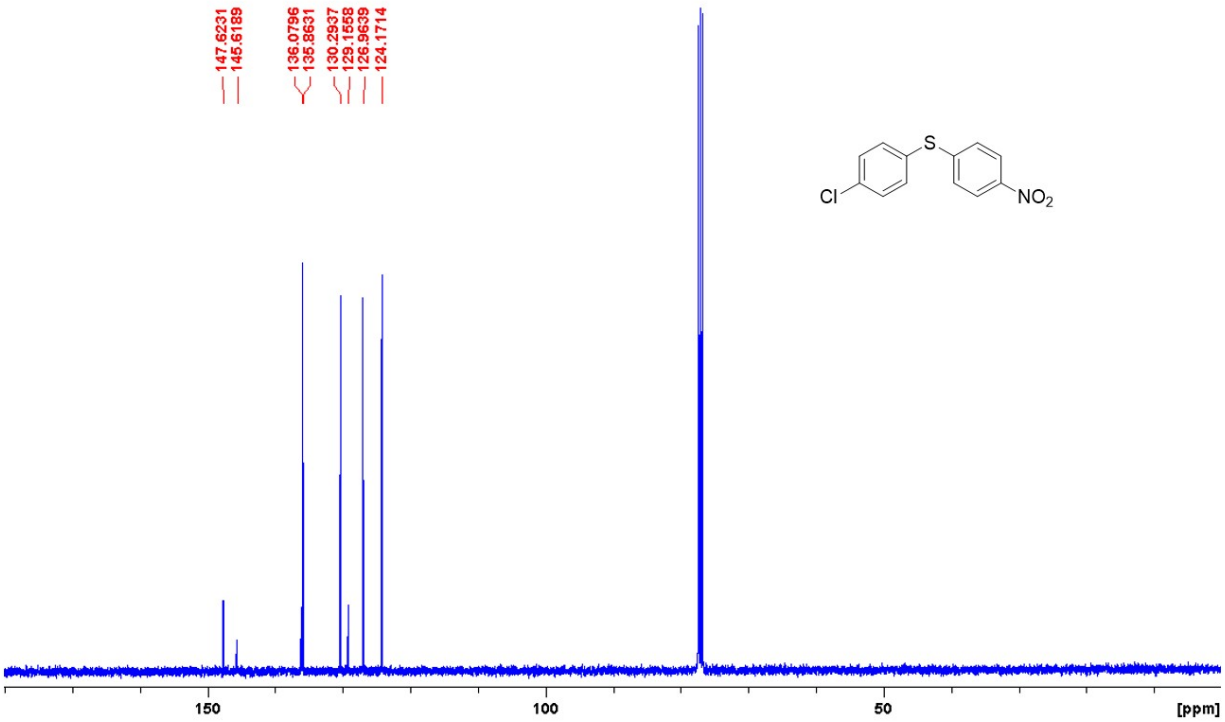


Figure S32 - ^{13}C NMR spectrum of 4-chloro-4-nitrodiphenyl sulfide in $CDCl_3$.

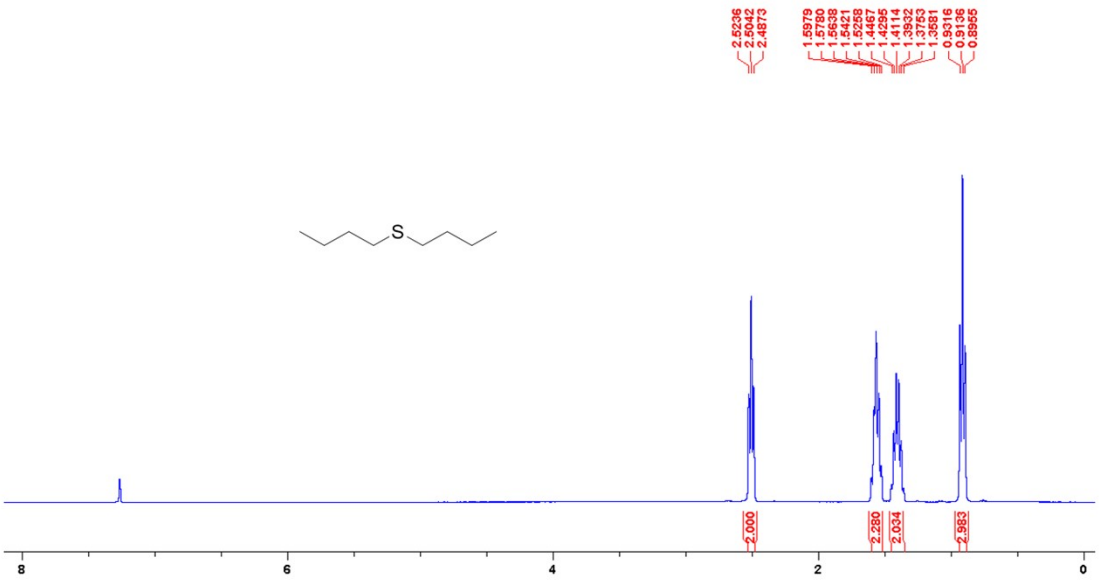


Figure S33 - ^{1}H NMR spectrum of dibutyl sulfide in $CDCl_3$.

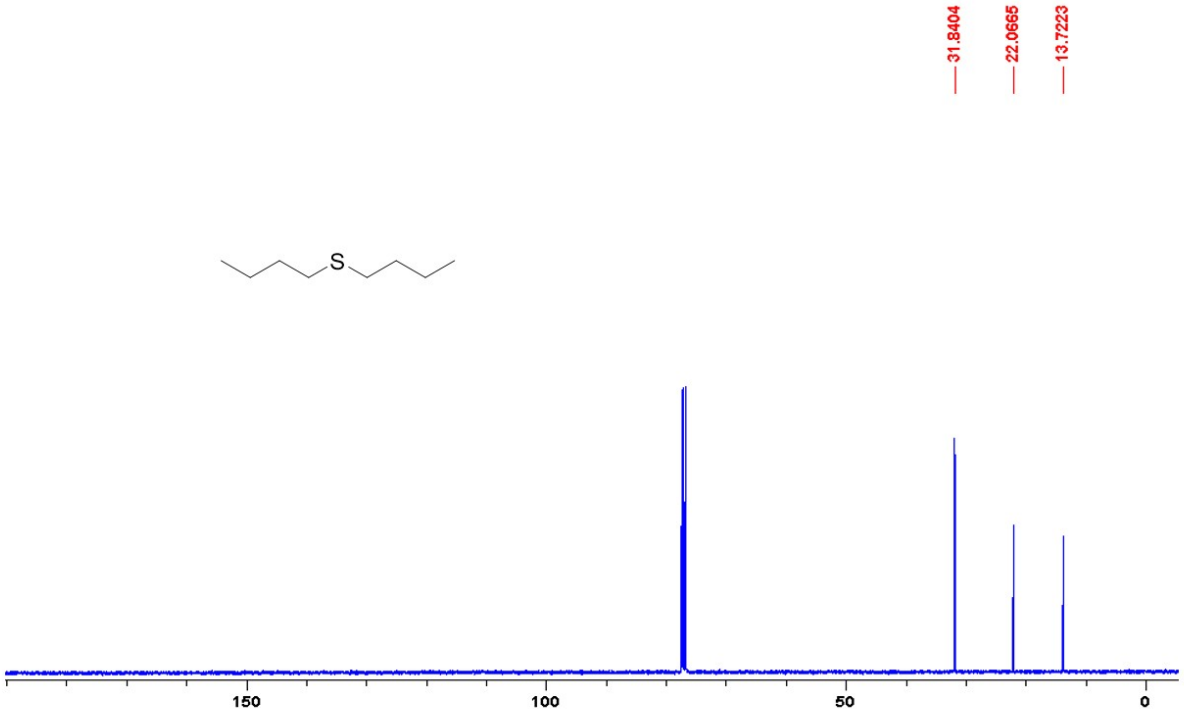


Figure S34 - ^{13}C NMR spectrum of dibutyl sulfide in $CDCl_3$.

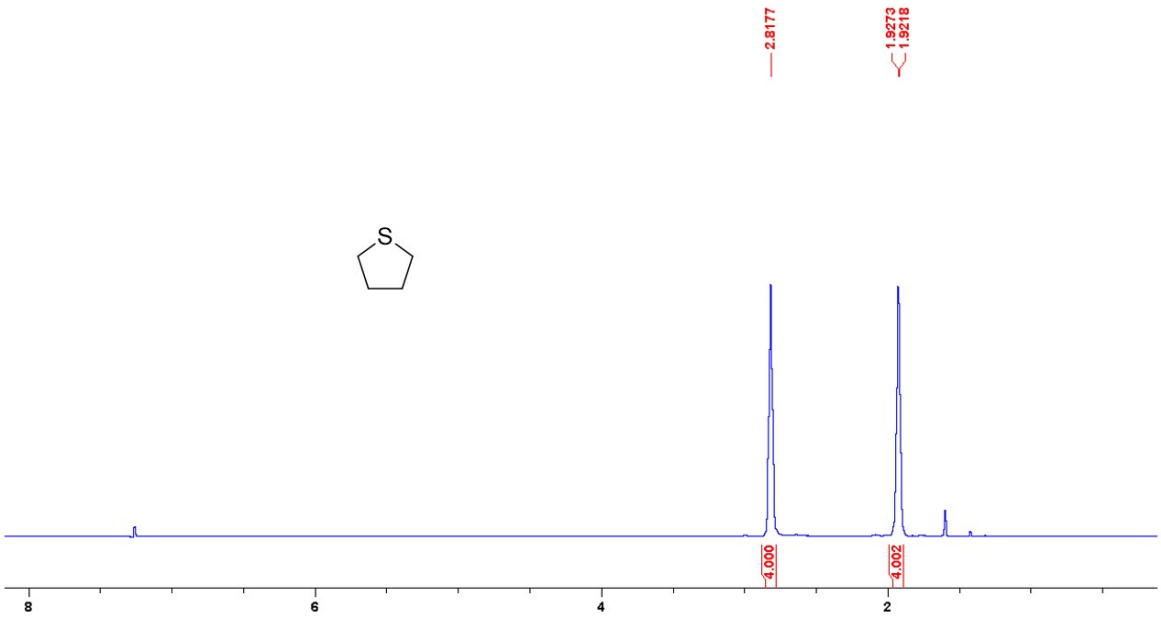


Figure S35 - ^{13}C NMR spectrum of tetrahydrothiophene in $CDCl_3$.

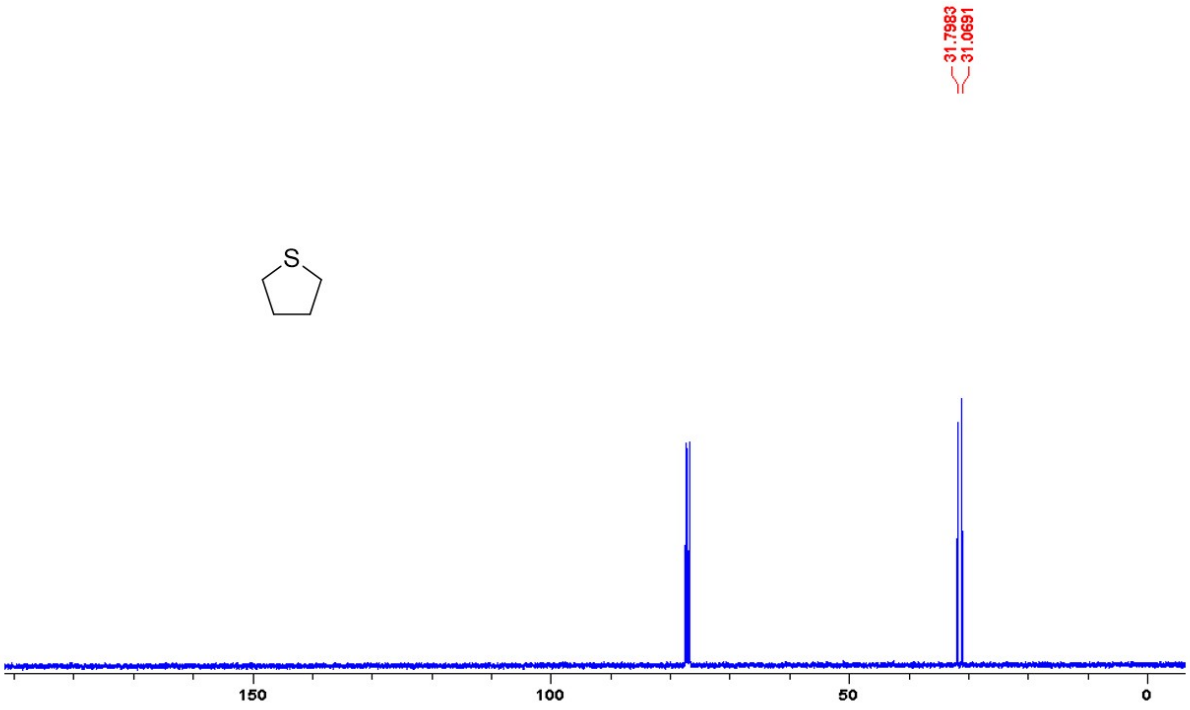


Figure S36 - ^{13}C NMR spectrum of tetrahydrothiophene in $CDCl_3$.

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