

Supporting Information

Palladium-catalyzed bithiolation of terminal alkynes for the assembly of diverse (*Z*)-1,2-bis(arylthio)alkene derivatives

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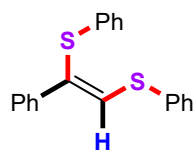
Materials and methods

Melting points were measured using a melting point instrument and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.24 and 77.0 ppm, respectively, and chloroform was used as a solvent with TMS as the internal standard. GC-MS data were obtained using electron ionization. HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). TLC was performed using commercially available 100–400 mesh silica gel plates (GF₂₅₄). Unless otherwise noted, purchased chemicals were used without further purification.

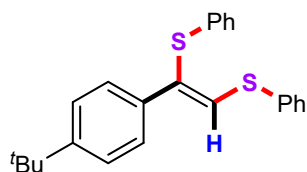
Typical procedure for the preparation of (*Z*)-1,2-bis(arylthio)alkenes

A mixture of IPr-Pd-Im-Cl₂ (0.650 mg, 0.5 mol %), ionic liquid [Bmim]PF₆ (2 mL), and H₂O₂ (2 equiv) were added to an Schlenk tube equipped with a stir-bar. A balloon filled with N₂ was connected to the Schlenk tube *via* the side tube and purged 3 times. Then, alkyes (**1**, 0.2 mmol), and arylhydrazines (**2**, 0.48 mmol), and Na₂S₂O₃ (0.4 mmol) were quickly added to the tube under N₂ atmosphere and stirred at 120 °C for 12 h. After the reaction was finished, the N₂ gas was released carefully and the reaction was quenched by water and extracted with CH₂Cl₂ three times. The combined organic layers were dried over anhydrous Na₂SO₄ and evaporated under vacuum. The residue was purified by flash column chromatography on silica gel (hexanes/ethyl acetate) to afford the desired products **3** and **4**.

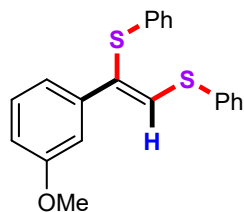
Characterization data for all products



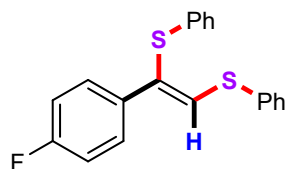
(Z)-1-(1-Phenylethene-1,2-diyl)bis(phenylsulfane) (3a).^[1] Yield: 84%; ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 8.2 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.37 (d, J = 7.0 Hz, 1H), 7.35 - 7.29 (m, 5H), 7.24 (dd, J = 10.4, 5.8 Hz, 3H), 7.14 (t, J = 7.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 138.9, 136.7, 135.4, 134.8, 130.6, 129.5, 129.3, 128.9, 128.6, 128.3, 127.8, 127.6, 126.7, 125.9 ppm; ν_{\max} (KBr)/cm⁻¹ 3048, 2932, 1560, 1477, 1432, 734; MS (EI) m/z 77, 108, 178, 211, 277, 320; HRMS-ESI (m/z): calcd for C₂₀H₁₆NaS₂, [M+Na]⁺: 343.0586, found 343.0583.



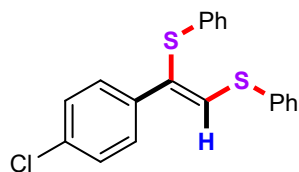
(Z)-1-(4-(*tert*-Butyl)phenyl)ethene-1,2-diylbis(phenylsulfane) (3b).^[1] Yield: 90%; ¹H NMR (400 MHz, CDCl₃) δ 7.48 (t, J = 8.4 Hz, 4H), 7.35 (t, J = 7.2 Hz, 2H), 7.28 (m, 6H), 7.21 (t, J = 7.6 Hz, 2H), 7.09 (t, J = 7.2 Hz, 1H), 1.26 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 150.9, 136.6, 136.2, 135.5, 135.2, 130.4, 129.3, 129.1, 128.9, 127.9, 127.5, 126.4, 125.8, 125.5, 34.7, 31.3 ppm; ν_{\max} (KBr)/cm⁻¹ 3054, 2933, 1572, 1530, 1443, 1258, 742; MS (EI) m/z 108, 211, 251, 319, 376; HRMS-ESI (m/z): calcd for C₂₄H₂₄NaS₂, [M+Na]⁺: 399.1212, found 399.1207.



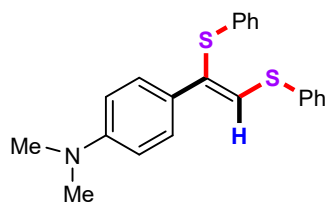
(Z)-1-(3-Methoxyphenyl)ethene-1,2-diylbis(phenylsulfane) (3c). ^[2] Yield: 92%; ¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.0 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 3H), 7.20 - 7.14 (m, 4H), 7.13 - 7.07 (m, 2H), 6.73 (d, *J* = 7.2, 1H), 3.74 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 159.7, 140.3, 136.7, 135.2, 134.7, 130.5, 129.4, 129.3, 129.0, 128.8, 128.3, 127.5, 126.2, 119.3, 113.1, 112.7, 55.2 ppm; ν_{\max} (KBr)/cm⁻¹ 3056, 2946, 1570, 1464, 1266, 753; MS (EI) *m/z* 77, 108, 226, 319, 350; HRMS-ESI (*m/z*): calcd for C₂₁H₁₈NaOS₂, [M+Na]⁺: 373.0691, found 373.0685.



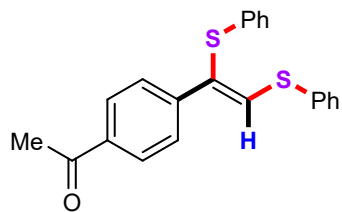
(Z)-1-(4-Fluorophenyl)ethene-1,2-diylbis(phenylsulfane) (3d). ^[1] Yield: 80%; ¹H NMR (400 MHz, CDCl₃) δ 7.58 - 7.47 (m, 4H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.18 (m, 3H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.93 (t, *J* = 8.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 162.5 (d, *J* = 247.7 Hz), 136.2 (d, *J* = 1.4 Hz), 135.1, 135.0 (d, *J* = 3.2 Hz), 134.4, 130.6, 129.4, 128.8, 128.6, 128.5, 128.2, 127.8, 126.2, 115.4 (d, *J* = 21.8 Hz) ppm; ν_{\max} (KBr)/cm⁻¹ 3055, 2933, 1564, 1512, 1439, 746; MS (EI) *m/z* 77, 109, 229, 338; HRMS-ESI (*m/z*): calcd for C₂₀H₁₅FNaS₂, [M+Na]⁺: 361.0491, found 361.0487.



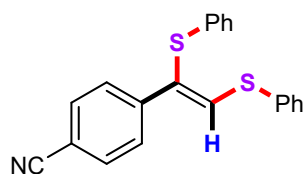
(Z)-1-(4-Chlorophenyl)ethene-1,2-diylbis(phenylsulfane) (3e).^[2] Yield: 75%; ¹H NMR (400 MHz, CDCl₃) δ 7.48 (m, 3H), 7.39 - 7.30 (m, 5H), 7.25 - 7.16 (m, 6H), 7.14 - 7.08 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 137.5, 137.2, 135.1, 134.2, 133.8, 133.6, 133.4, 130.7, 129.4, 129.1, 128.7, 128.5, 128.0, 126.2 ppm; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3046, 2933, 1562, 1516, 1438, 744; MS (EI) m/z 109, 210, 245, 354; HRMS-ESI (m/z): calcd for C₂₀H₁₅ClNaS₂, [M+Na]⁺: 377.0196, found 377.0192.



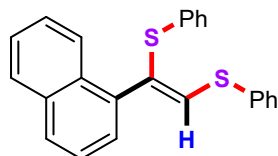
(Z)-4-(1,2-Bis(phenylthio)vinyl)-N,N-dimethylaniline (3f).^[2] Yield: 70%; ¹H NMR (400 MHz, CDCl₃) δ 7.48 (t, *J* = 7.0 Hz, 4H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 3H), 7.18 (t, *J* = 7.2 Hz, 2H), 7.11 - 7.05 (m, 2H), 6.60 (d, *J* = 8.0 Hz, 2H), 2.90 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 150.2, 136.1, 135.5, 131.7, 130.2, 130.0, 129.2, 128.8, 128.0, 127.8, 127.1, 126.8, 125.6, 112.2, 40.4 ppm; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3052, 2936, 1556, 1504, 1443, 1256, 747; MS (EI) m/z 109, 144, 210, 254, 327, 363; HRMS-ESI (m/z): calcd for C₂₂H₂₁NNaS₂, [M+Na]⁺: 386.1008, found 386.1005.



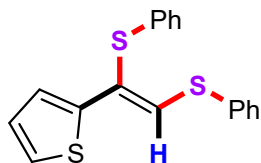
(Z)-1-(4-(1,2-Bis(phenylthio)vinyl)phenyl)ethan-1-one (3g).^[2] Yield: 82%; ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, J = 8.2 Hz, 2H), 7.68 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 7.6 Hz, 2H), 7.48 - 7.37 (m, 4H), 7.29 (d, J = 4.8 Hz, 2H), 7.21 (t, J = 7.6 Hz, 2H), 7.15 (t, J = 7.2 Hz, 1H), 2.58 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 197.5, 143.0, 140.2, 135.8, 134.6, 134.2, 130.8, 129.4, 129.1, 128.7, 128.4, 128.0, 127.9, 126.6, 126.2, 26.6 ppm; ν_{\max} (KBr)/cm⁻¹ 3044, 2932, 1690, 1566, 1472, 1416, 1264, 748; MS (EI) m/z 86, 117, 207, 321, 362; HRMS-ESI (m/z): calcd for C₂₂H₁₉OS₂, [M+H]⁺: 363.0872, found 363.0866.



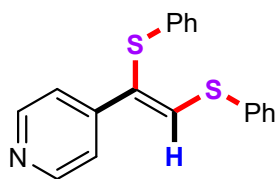
(Z)-4-(1,2-Bis(phenylthio)vinyl)benzonitrile (3h).^[2] Yield: 70%; ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, J = 8.4 Hz, 1H), 7.52 (t, J = 6.8 Hz, 4H), 7.43 - 7.35 (m, 5H), 7.25 - 7.17 (m, 2H), 7.15 (t, J = 7.2 Hz, 1H), 6.72 (t, J = 7.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 147.8, 143.2, 141.3, 132.2, 132.1, 131.4, 131.1, 129.7, 129.5, 129.1, 128.3, 127.1, 118.0, 114.3, 108.0 ppm; ν_{\max} (KBr)/cm⁻¹ 3049, 2940, 2223, 1556, 1436, 1414, 744; MS (EI) m/z 103, 133, 207, 281, 345; HRMS-ESI (m/z): calcd for C₂₁H₁₆NS₂, [M+H]⁺: 346.0719, found 346.0714.



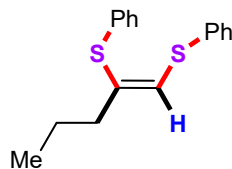
(Z)-1-(1-(Naphthalen-1-yl)ethene-1,2-diyl)bis(phenylsulfane) (3i). Yield: 86%; ^1H NMR (400 MHz, CDCl_3) δ 8.04 (s, 1H), 7.82 - 7.74 (m, 2H), 7.72 (d, $J = 10.2$ Hz, 2H), 7.53 (d, $J = 8.2$ Hz, 2H), 7.43 (m, 3H), 7.36 (d, $J = 8.2$ Hz, 3H), 7.32 (t, $J = 7.6$ Hz, 2H), 7.18 (t, $J = 7.6$ Hz, 2H), 7.06 (d, $J = 7.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.6, 136.3, 135.2, 134.7, 133.4, 132.7, 130.6, 130.0, 129.5, 129.3, 129.0, 128.4, 128.2, 127.8, 127.6, 126.4, 126.1, 126.1, 126.0, 124.6 ppm; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3048, 2934, 1622, 1566, 1472, 1429, 745; MS (EI) m/z 109, 228, 261, 325, 370; HRMS-ESI (m/z): calcd for $\text{C}_{24}\text{H}_{18}\text{NaS}_2$, $[\text{M}+\text{Na}]^+$: 393.0742, found 393.0738.



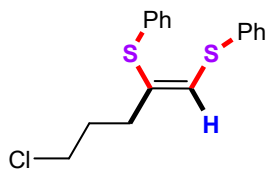
(Z)-2-(1,2-Bis(phenylthio)vinyl)thiophene (3j). Yield: 73%; ^1H NMR (400 MHz, CDCl_3) δ 7.50 (d, $J = 7.2$ Hz, 2H), 7.43 - 7.34 (m, 3H), 7.30 (t, $J = 8.2$ Hz, 4H), 7.25 - 7.18 (m, 4H), 7.12 (t, $J = 7.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.8, 136.2, 135.2, 134.8, 130.6, 129.3, 129.0, 127.8, 127.5, 126.1, 125.8, 125.6, 124.2, 122.2 ppm; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3040, 2933, 1626, 1566, 1472, 1416, 754; MS (EI) m/z 65, 109, 217, 260, 326; HRMS-ESI (m/z): calcd for $\text{C}_{18}\text{H}_{14}\text{NaS}_3$, $[\text{M}+\text{Na}]^+$: 349.0150, found 349.0144.



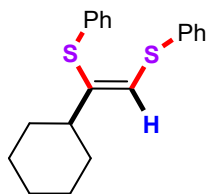
(Z)-4-(1,2-Bis(phenylthio)vinyl)pyridine (3k). Yield: 65%; ^1H NMR (400 MHz, CDCl_3) δ 8.78 (s, 1H), 8.42 (d, $J = 4.8$ Hz, 1H), 7.83 (d, $J = 8.2$ Hz, 1H), 7.52 (d, $J = 7.6$ Hz, 2H), 7.39 (t, $J = 7.2$ Hz, 2H), 7.35 (d, $J = 7.2$ Hz, 1H), 7.30 (s, 1H), 7.24 (d, $J = 7.0$ Hz, 2H), 7.20 (t, $J = 7.6$ Hz, 2H), 7.18 - 7.10 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.5, 147.7, 138.3, 134.6, 134.0, 133.6, 130.7, 129.3, 129.2, 129.1, 128.9, 127.8, 126.6, 126.2, 123.1 ppm; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3048, 2942, 1558, 1510, 1456, 1407, 748; MS (EI) m/z 96, 191, 207, 281, 321; HRMS-ESI (m/z): calcd for $\text{C}_{19}\text{H}_{16}\text{NS}_2$, $[\text{M}+\text{H}]^+$: 322.0719, found 322.0715.



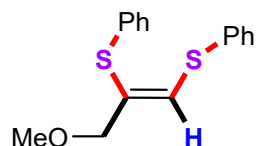
(Z)-Pent-1-ene-1,2-diylbis(phenylsulfane) (3l).^[1] Yield: 91%; ^1H NMR (400 MHz, CDCl_3) δ 7.44 (d, $J = 7.6$ Hz, 2H), 7.39 (d, $J = 8.0$ Hz, 2H), 7.35 (d, $J = 7.2$ Hz, 2H), 7.30 (t, $J = 5.8$ Hz, 2H), 7.24 - 7.18 (m, 2H), 6.58 (s, 1H), 2.24 (t, $J = 7.2$ Hz, 2H), 1.59 - 1.49 (m, 2H), 0.86 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 135.8, 134.0, 130.6, 129.7, 129.4, 129.1, 128.8, 128.7, 126.8, 126.7, 39.2, 21.8, 13.4 ppm; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3056, 2938, 1545, 1426, 1268, 1020, 744; MS (EI) m/z 65, 91, 109, 135, 167, 286; HRMS-ESI (m/z): calcd for $\text{C}_{17}\text{H}_{18}\text{NaS}_2$, $[\text{M}+\text{Na}]^+$: 309.0742, found 309.0738.



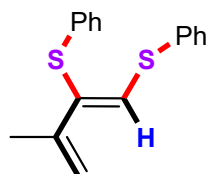
(Z)-(5-Chloropent-1-ene-1,2-diyl)bis(phenylsulfane) (3m).^[2] Yield: 93%; ¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 3H), 7.36 - 7.29 (m, 4H), 7.25 (t, J = 5.2 Hz, 1H), 6.68 (s, 1H), 3.49 (t, J = 6.8 Hz, 2H), 2.44 (t, J = 7.2 Hz, 2H), 1.96 (t, J = 6.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 135.5, 133.3, 131.6, 131.5, 130.6, 130.0, 129.3, 129.1, 127.2, 127.0, 44.1, 33.8, 31.0 ppm; ν_{\max} (KBr)/cm⁻¹ 3056, 2924, 1568, 1466, 1432, 1270, 1025, 745; MS (EI) m/z 65, 109, 167, 285, 320; HRMS-ESI (m/z): calcd for C₁₇H₁₇ClNaS₂, [M+Na]⁺: 343.0352, found 343.0348.



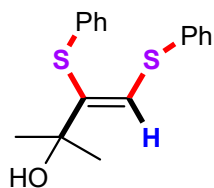
(Z)-(1-Cyclohexylethene-1,2-diyl)bis(phenylsulfane) (3n).^[2] Yield: 82%; ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, J = 7.6 Hz, 2H), 7.33 (d, J = 4.8 Hz, 3H), 7.29 (d, J = 7.6 Hz, 3H), 7.25 (d, J = 7.0 Hz, 1H), 7.19 (t, J = 6.8 Hz, 1H), 6.72 (s, 1H), 2.15 (t, J = 10.2 Hz, 1H), 1.94 (d, J = 11.2 Hz, 2H), 1.74 (d, J = 11.2 Hz, 2H), 1.30 - 1.25 (m, 3H), 1.22 - 1.14 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 137.1, 135.2, 133.8, 132.1, 130.2, 129.1, 128.8, 128.5, 127.0, 125.8, 46.2, 32.8, 26.4, 26.1 ppm; ν_{\max} (KBr)/cm⁻¹ 3058, 2927, 1565, 1466, 1415, 1268, 1058, 746; MS (EI) m/z 79, 91, 109, 167, 217, 326; HRMS-ESI (m/z): calcd for C₂₀H₂₂NaS₂, [M+Na]⁺: 349.1055, found 349.1052.



(Z)-(3-Methoxyprop-1-ene-1,2-diyl)bis(phenylsulfane) (3o).^[2] Yield: 84%; ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.39 - 7.30 (m, 5H), 7.25-7.20 (m, 1H), 7.00 (s, 1H), 3.96 (s, 2H), 3.30 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 135.2, 134.5, 133.4, 130.3, 130.1, 129.2, 129.0, 127.4, 127.2, 126.8, 74.5, 58.1 ppm; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3052, 2923, 1567, 1475, 1426, 1268, 1116, 748; MS (EI) m/z 69, 109, 177, 243, 288; HRMS-ESI (m/z): calcd for C₁₆H₁₇OS₂, [M+H]⁺: 289.0715, found 289.0712.



(Z)-(3-Methylbuta-1,3-diene-1,2-diyl)bis(phenylsulfane) (3p).^[2] Yield: 91%; ¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, J = 7.2 Hz, 2H), 7.40 - 7.29 (m, 3H), 7.25 - 7.20 (m, 4H), 7.19 - 7.12 (m, 2H), 5.51 (s, 1H), 4.98 (s, 1H), 2.00 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 140.2, 138.6, 135.6, 135.1, 130.4, 129.6, 129.2, 128.8, 127.6, 127.3, 125.5, 115.5, 20.9 ppm; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3048, 2926, 1665, 1576, 1457, 1419, 1268, 1015, 749; MS (EI) m/z 65, 91, 109, 175, 207, 251, 284; HRMS-ESI (m/z): calcd for C₁₇H₁₇S₂, [M+H]⁺: 285.0766, found 285.0763.



(Z)-2-Methyl-3,4-bis(phenylthio)but-3-en-2-ol (3q).^[1] Yield: 72%; ¹H NMR (400 MHz, CDCl₃)

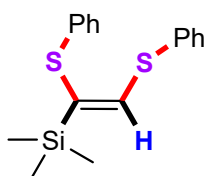
δ 7.43 (d, $J = 7.2$ Hz, 2H), 7.41 - 7.36 (m, 6H), 7.35 - 7.29 (m, 2H), 7.18 (t, $J = 7.2$ Hz, 1H), 2.17

(s, 1H), 1.46 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 137.8, 135.0, 134.8, 134.8, 130.6, 129.3,

129.2, 127.5, 127.1, 125.8, 75.1, 29.4 ppm; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3050, 2932, 1576, 1466, 1414, 1268,

1024, 750; MS (EI) m/z 59, 91, 134, 177, 207, 287, 302; HRMS-ESI (m/z): calcd for C₁₇H₁₉OS₂,

[M+H]⁺: 303.0872, found 303.0868.



(Z)-(1,2-Bis(phenylthio)vinyl)trimethylsilane (3r).^[3] Yield: 76%; ¹H NMR (400 MHz, CDCl₃)

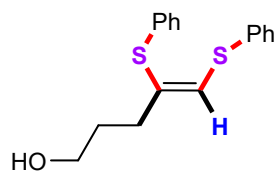
δ 7.40 (d, $J = 7.6$ Hz, 2H), 7.37 - 7.29 (m, 5H), 7.25 - 7.20 (m, 3H), 7.19 (d, $J = 7.2$ Hz, 1H), 0.01

(s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 149.8, 134.8, 134.7, 132.0, 130.4, 129.8, 129.7, 129.6,

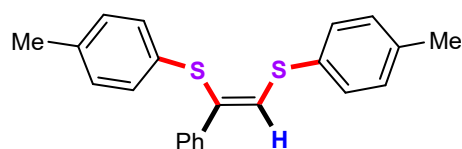
129.5, 128.6, 0.00 ppm; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3058, 2940, 1578, 1506, 1472, 1266, 747; MS (EI) m/z 91,

109, 186, 262, 316; HRMS-ESI (m/z): calcd for C₁₇H₂₀NaOS₂Si, [M+Na]⁺: 339.0668, found

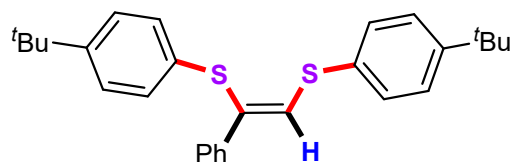
339.0664.



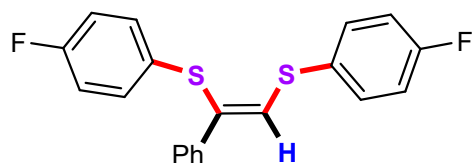
(Z)-4,5-Bis(phenylthio)pent-4-en-1-ol (3s). Yield: 83%; ^1H NMR (400 MHz, CDCl_3) δ 7.44 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.34 (d, 8.0 Hz, 4H), 7.25 - 7.20 (m, 2H), 6.63 (s, 1H), 3.60 (t, J = 6.4 Hz, 2H), 2.38 (t, J = 7.6 Hz, 2H), 1.84 - 1.73 (m, 2H), 1.41 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 135.8, 133.4, 132.8, 130.5, 130.4, 129.8, 129.2, 129.1, 127.0, 126.8, 61.7, 33.3, 31.5 ppm; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3360, 2938, 1580, 1475, 1419, 1028, 748; MS (EI) m/z 91, 109, 167, 277, 302; HRMS-ESI (m/z): calcd for $\text{C}_{17}\text{H}_{19}\text{OS}_2$, $[\text{M}+\text{H}]^+$: 303.0872, found 303.0867.



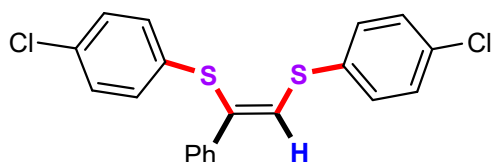
(Z)-(1-Phenylethene-1,2-diyl)bis(*p*-tolylsulfane) (4a). ^[1] Yield: 87%; ^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 7.35 - 7.29 (m, 2H), 7.24 - 7.15 (m, 6H), 7.05 (d, J = 8.0 Hz, 2H), 2.40 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.8, 137.7, 136.8, 135.7, 131.7, 131.1, 131.0, 130.0, 129.6, 129.2, 128.5, 128.4, 127.5, 126.6, 21.2, 21.0 ppm; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3058, 2929, 1538, 1466, 1418, 1268, 756; MS (EI) m/z 165, 210, 281, 348; HRMS-ESI (m/z): calcd for $\text{C}_{22}\text{H}_{20}\text{NaS}_2$, $[\text{M}+\text{Na}]^+$: 371.0899, found 371.0896.



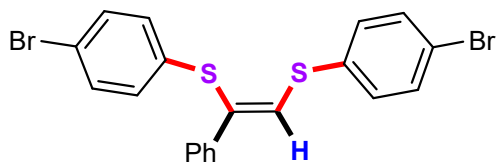
(Z)-(1-Phenylethene-1,2-diyl)bis((4-(*tert*-butyl)phenyl)sulfane) (4b). ^[2] Yield: 90%; ¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 5.6 Hz, 3H), 7.23 (d, *J* = 5.6 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 4H), 1.34 (s, 9H), 1.25 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 151.1, 149.0, 139.2, 137.7, 131.7, 131.3, 130.7, 128.4, 128.4, 127.6, 127.4, 126.6, 126.5, 126.2, 34.7, 34.5, 31.3, 31.2 ppm; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3054, 2939, 1593, 1528, 1476, 1262, 1114, 756; MS (EI) *m/z* 121, 207, 268, 387, 432; HRMS-ESI (*m/z*): calcd for C₂₈H₃₃S₂, [M+H]⁺: 433.2018, found 433.2014.



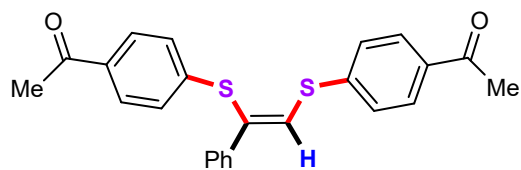
(Z)-(1-Phenylethene-1,2-diyl)bis((4-fluorophenyl)sulfane) (4c). ^[2] Yield: 81%; ¹H NMR (400 MHz, CDCl₃) δ 7.50 (t, *J* = 7.0 Hz, 4H), 7.25 - 7.18 (m, 5H), 7.14 - 7.05 (m, 3H), 6.90 (t, *J* = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 162.7 (d, *J* = 248.7 Hz), 161.8 (d, *J* = 246.3 Hz), 138.4, 135.8, 133.2 (d, *J* = 8.4 Hz), 130.8 (d, *J* = 8.1 Hz), 130.2, 130.1 (d, *J* = 3.8 Hz), 129.6 (d, *J* = 3.5 Hz), 128.5, 127.7, 126.8, 116.6 (d, *J* = 22.3 Hz), 116.4 (d, *J* = 22.2 Hz) ppm; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3045, 2932, 1578, 1486, 1413, 1226, 826; MS (EI) *m/z* 127, 165, 294, 356; HRMS-ESI (*m/z*): calcd for C₂₀H₁₅F₂S₂, [M+H]⁺: 357.0578, found 357.0573.



(Z)-(1-Phenylethene-1,2-diyl)bis((4-chlorophenyl)sulfane) (4d).^[2] Yield: 82%; ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, J = 7.6 Hz, 2H), 7.42 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 7.2 Hz, 3H), 7.19 - 7.09 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 138.2, 135.7, 133.8, 133.5, 133.1, 132.0, 131.8, 129.8, 129.6, 129.5, 129.1, 128.5, 128.0, 126.7 ppm; ν_{\max} (KBr)/cm⁻¹ 3044, 2928, 1536, 1476, 1423, 756; MS (EI) m/z 108, 165, 245, 338, 388; HRMS-ESI (m/z): calcd for C₂₀H₁₅Cl₂S₂, [M+H]⁺: 388.9987, found 388.9983.

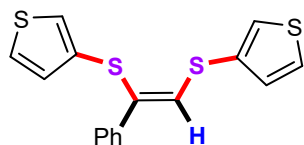


(Z)-(1-Phenylethene-1,2-diyl)bis((4-bromophenyl)sulfane) (4e).^[2] Yield: 75%; ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, J = 7.6 Hz, 2H), 7.44 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 5.2 Hz, 1H), 7.25 - 7.20 (m, 2H), 7.19 - 7.08 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 138.3, 135.7, 133.8, 133.4, 133.1, 132.0, 131.8, 129.8, 129.7, 129.5, 129.1, 128.7, 128.0, 126.7 ppm; ν_{\max} (KBr)/cm⁻¹ 3046, 2932, 1569, 1477, 1418, 754; MS (EI) m/z 96, 208, 398, 476; HRMS-ESI (m/z): calcd for C₂₀H₁₅Br₂S₂, [M+H]⁺: 476.8976, found 476.8972.



(Z)-1,1'-(((1-Phenylethene-1,2-diyl)bis(sulfanediyl))bis(4,1-phenylene))bis(ethan-1-one) (4f).

[2] Yield: 71%; ^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, $J = 8.4$ Hz, 2H), 7.78 (d, $J = 8.4$ Hz, 2H), 7.60 (d, $J = 7.2$ Hz, 2H), 7.54 (d, $J = 8.4$ Hz, 2H), 7.39 (s, 1H), 7.34 - 7.28 (m, 3H), 7.25 - 7.20 (m, 2H), 2.59 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.3, 197.2, 141.6, 141.5, 138.1, 135.6, 134.8, 134.5, 130.2, 129.2, 129.0, 128.8, 128.7, 128.4, 127.1, 126.6, 26.7, 26.5 ppm; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3047, 2926, 1668, 1576, 1486, 1415, 1263, 1089, 756; MS (EI) m/z 96, 207, 281, 380, 404; HRMS-ESI (m/z): calcd for $\text{C}_{24}\text{H}_{21}\text{O}_2\text{S}_2$, $[\text{M}+\text{H}]^+$: 405.0977, found 405.0972.

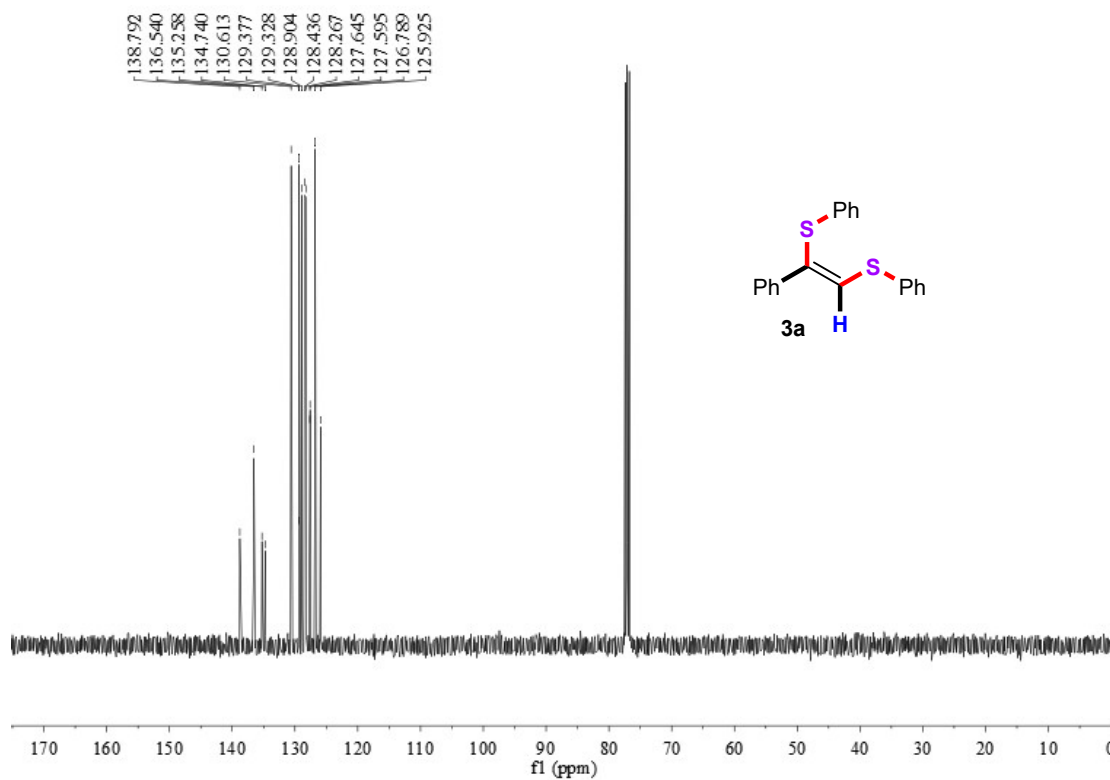
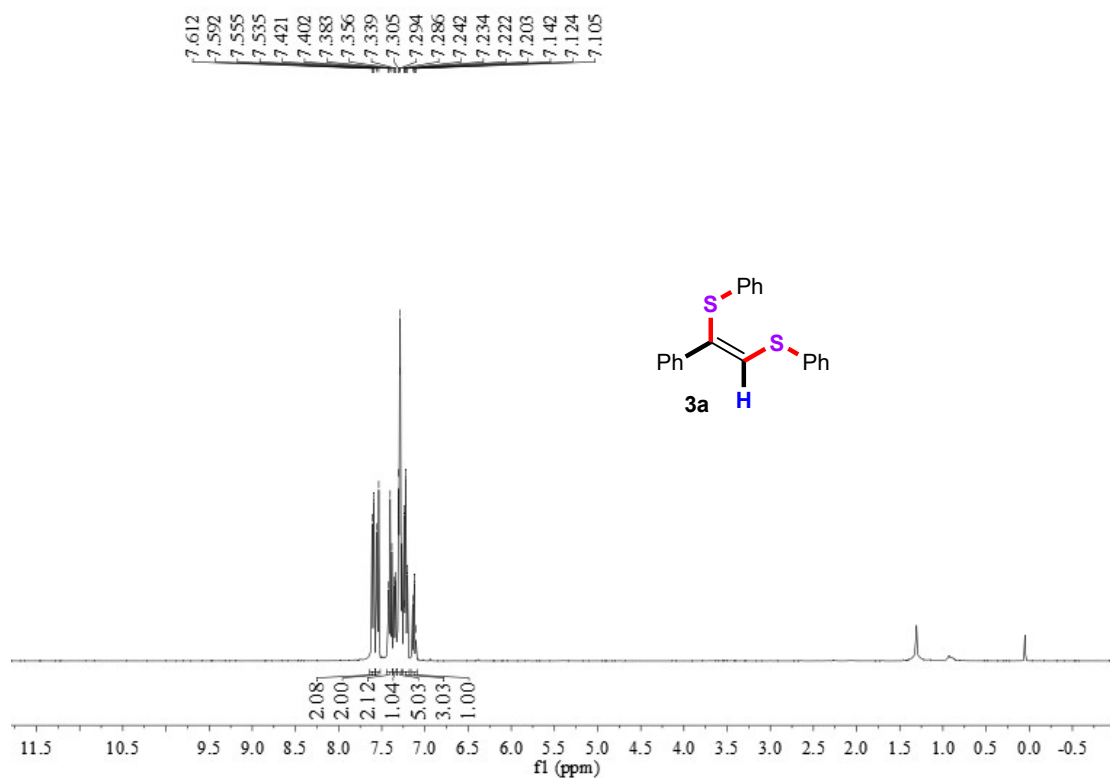


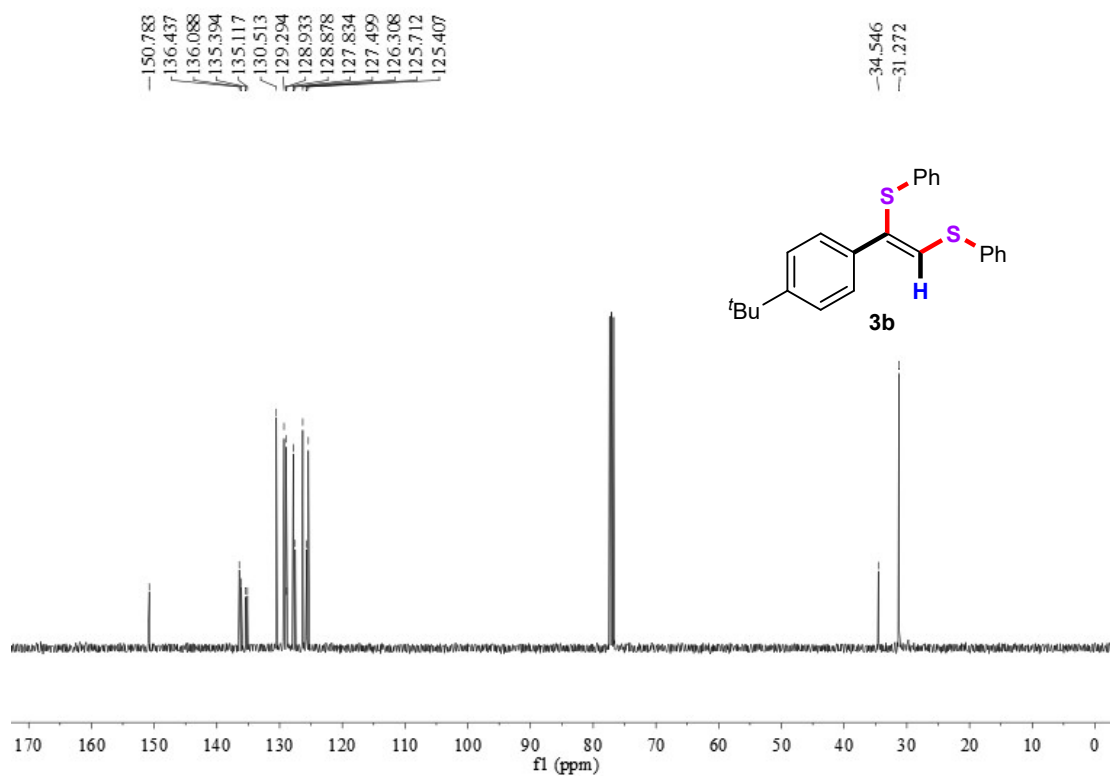
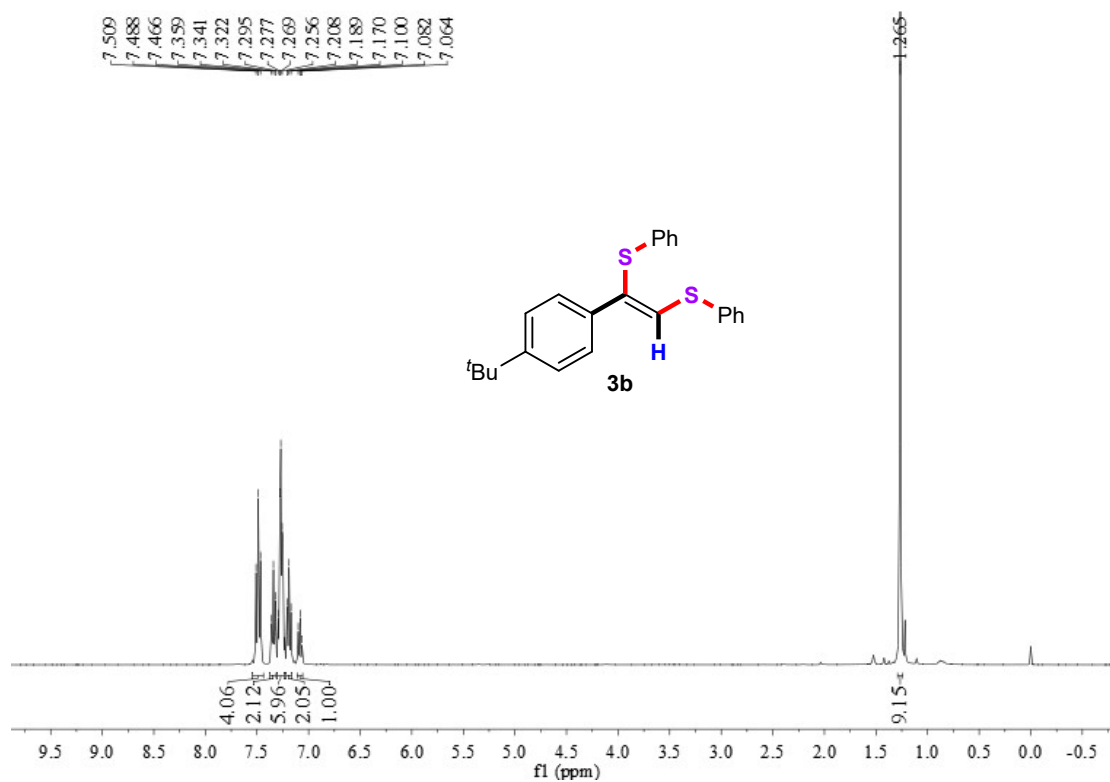
(Z)-3,3'-(((1-Phenylethene-1,2-diyl)bis(sulfanediyl))dithiophene) (4g). Yield: 66%; ^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, $J = 7.6$ Hz, 2H), 7.39 (d, $J = 5.2$ Hz, 1H), 7.24 (d, $J = 5.6$ Hz, 4H), 7.19 (d, $J = 5.6$ Hz, 1H), 7.08 (d, $J = 3.6$ Hz, 1H), 7.02 (dd, $J = 5.4, 3.8$ Hz, 1H), 6.82 (dd, $J = 5.4, 3.8$ Hz, 1H), 6.79 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.1, 135.8, 133.6, 133.0, 132.7, 131.7, 131.5, 130.0, 129.1, 128.2, 127.8, 127.7, 127.3, 127.2 ppm; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3046, 2928, 1548, 1456, 1417, 757; MS (EI) m/z 71, 115, 217, 277, 332; HRMS-ESI (m/z): calcd for $\text{C}_{16}\text{H}_{12}\text{NaS}_4$, $[\text{M}+\text{Na}]^+$: 354.9714, found 354.9710.

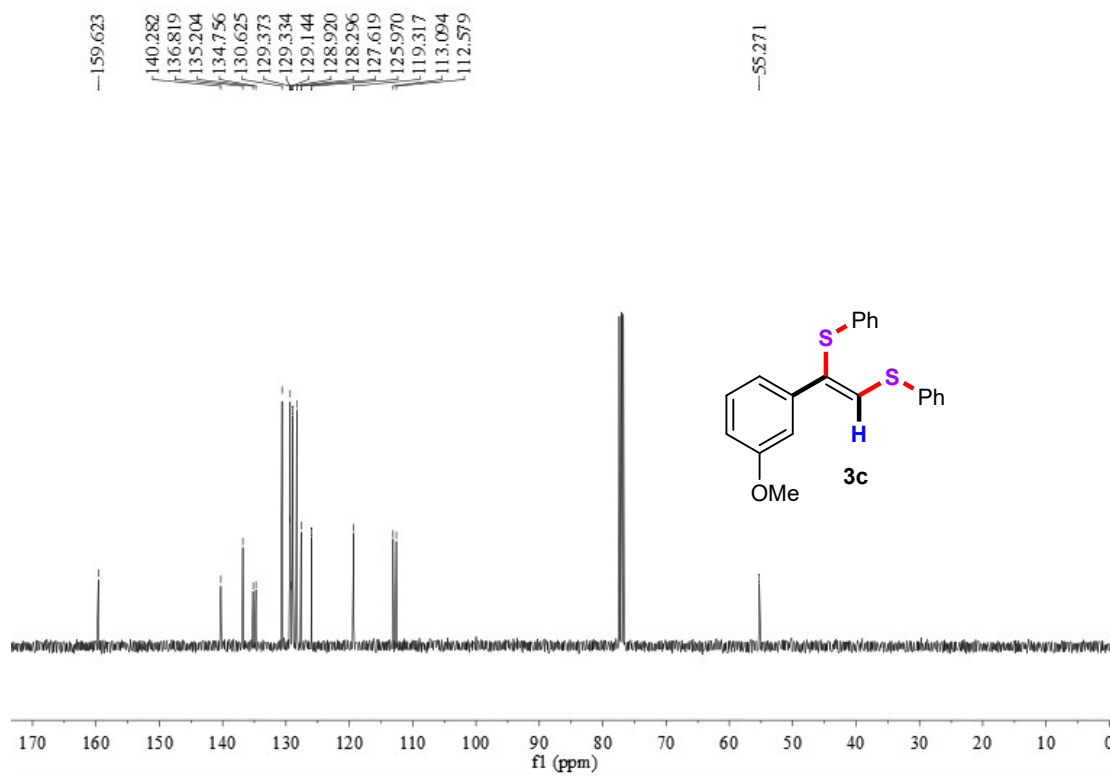
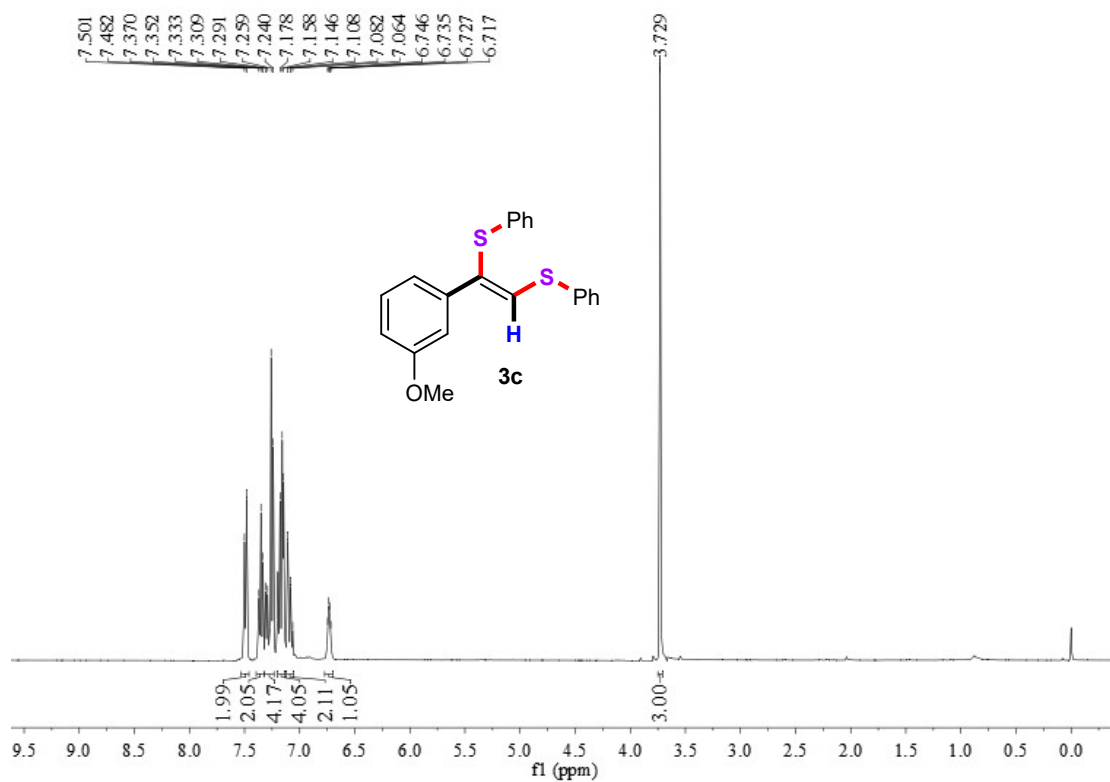
References

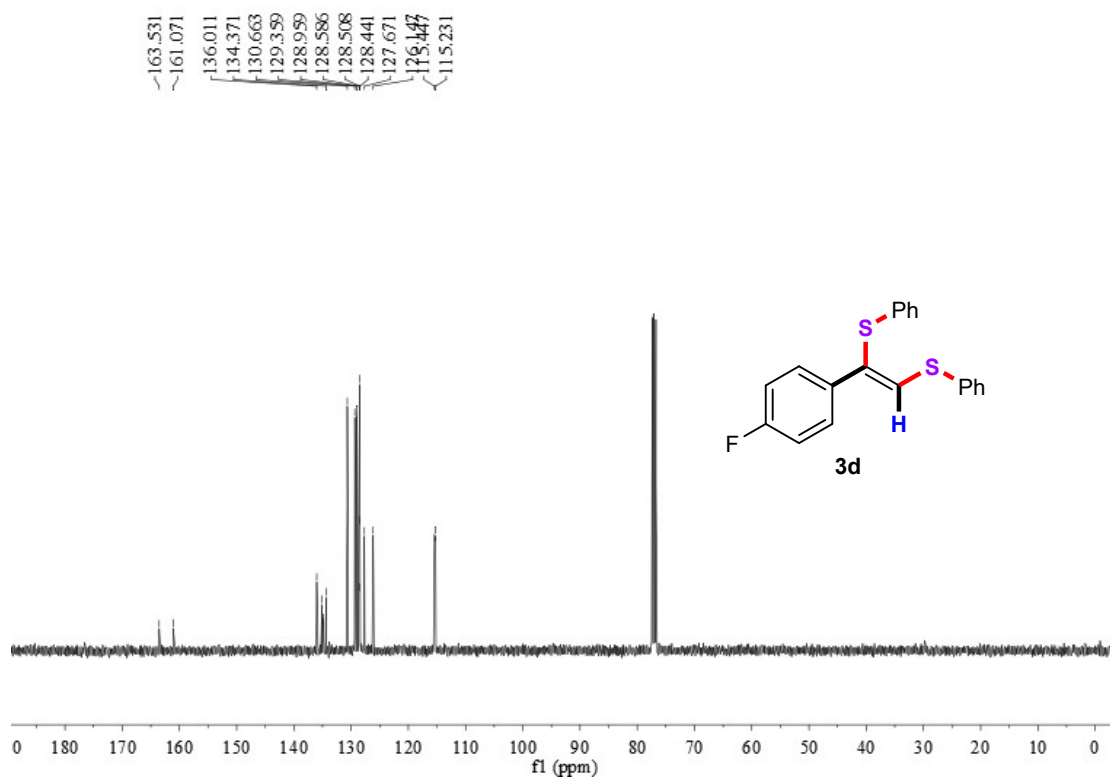
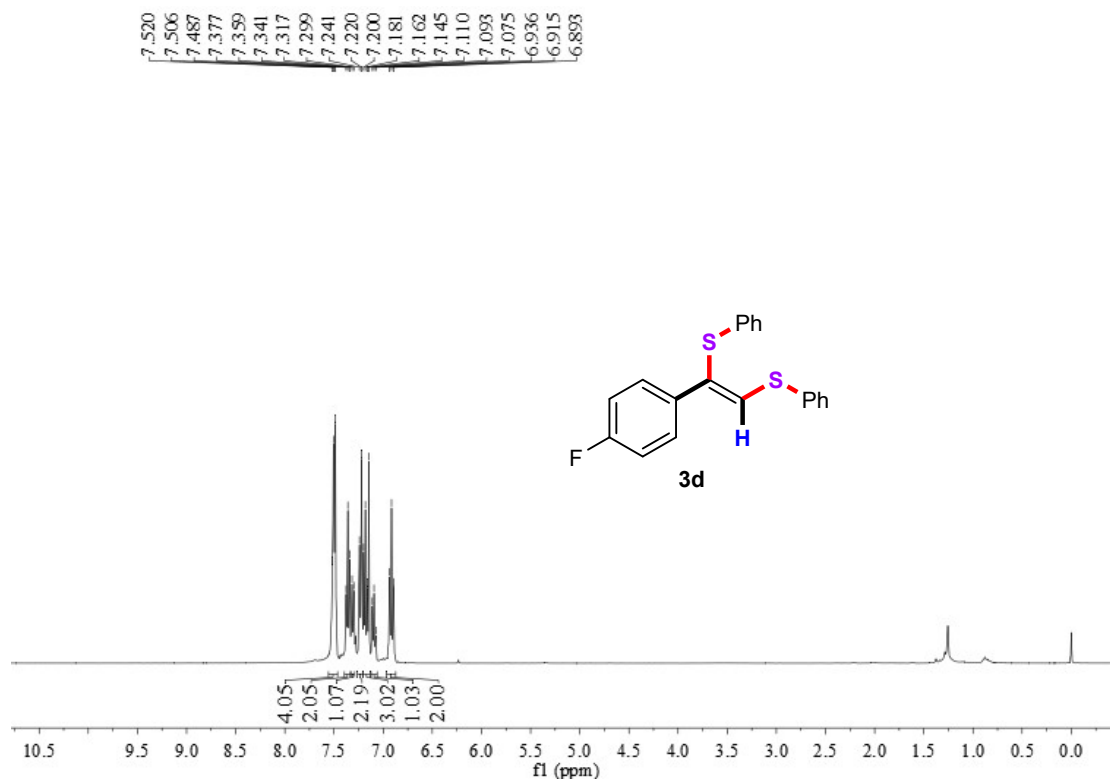
1. J. Chen, S. Chen, X. Xu, Z. Tang, C.-T. Au and R. Qiu, *J. Org. Chem.*, 2016, **81**, 3246-3255.
2. J. Li, C. Li, L. Ouyang, C. Li, S. Yang, W. Wu and H. Jiang, *Adv. Synth. Catal.*, 2018, **360**, 1138-1150.
3. K. B. Zou, X. H. Yin, W. Q. Liu, R. H. Qiu, R. X. Li, L. L. Shao, Y. H. Li, X. Hua Xu, and R. H. Yang, *Synthetic Commun.*, 2009, **39**, 2464-2471.

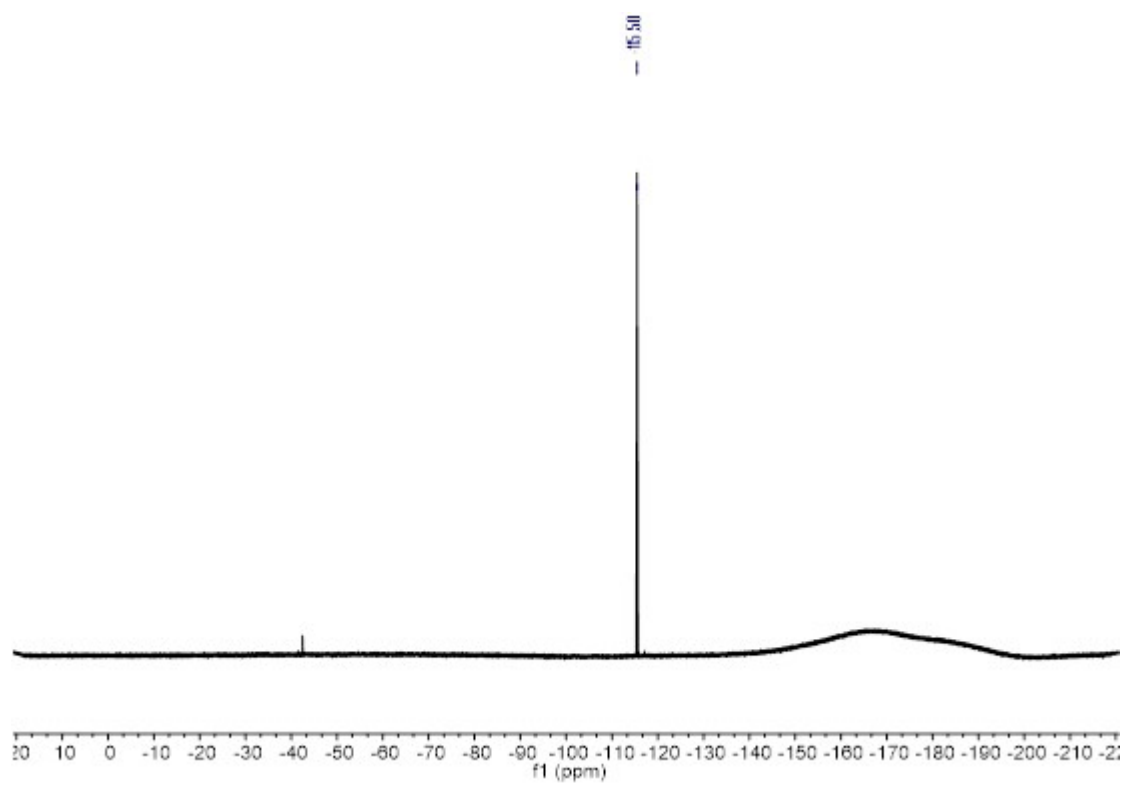
^1H and ^{13}C NMR spectra of compounds 3



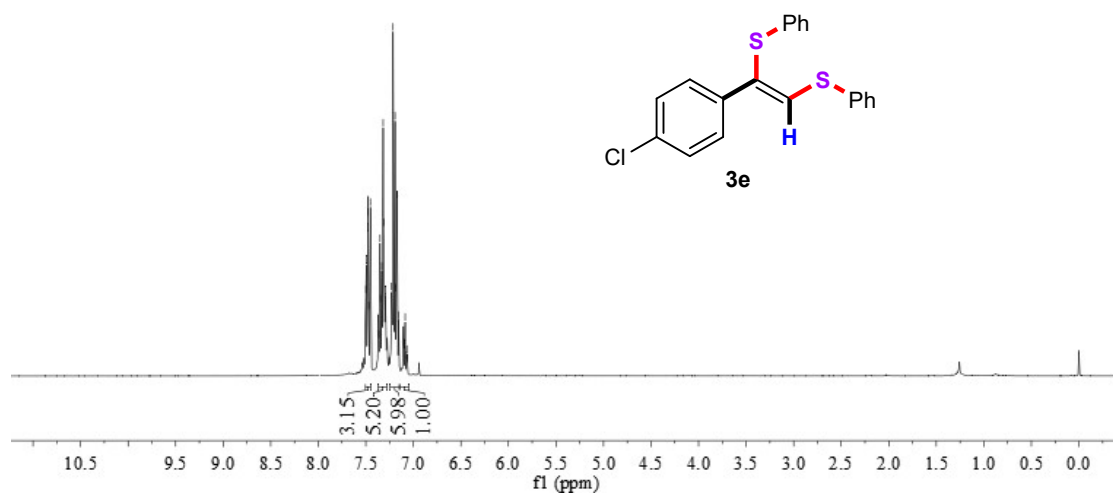


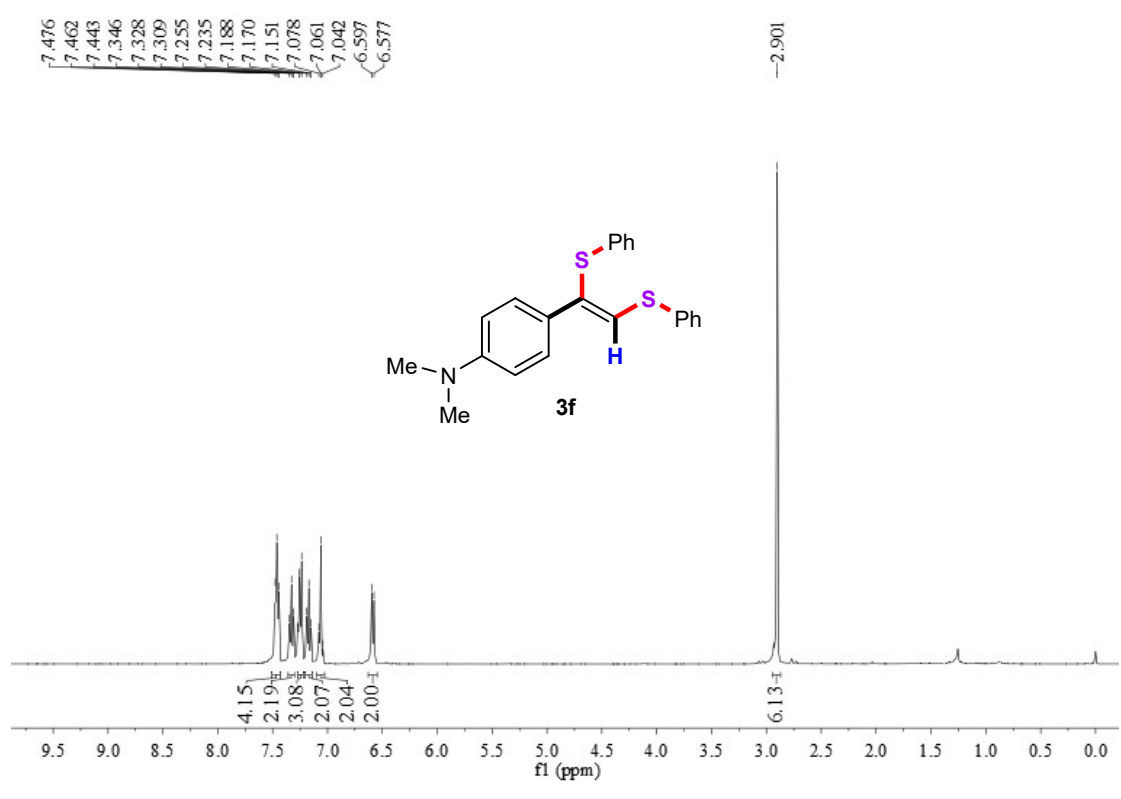
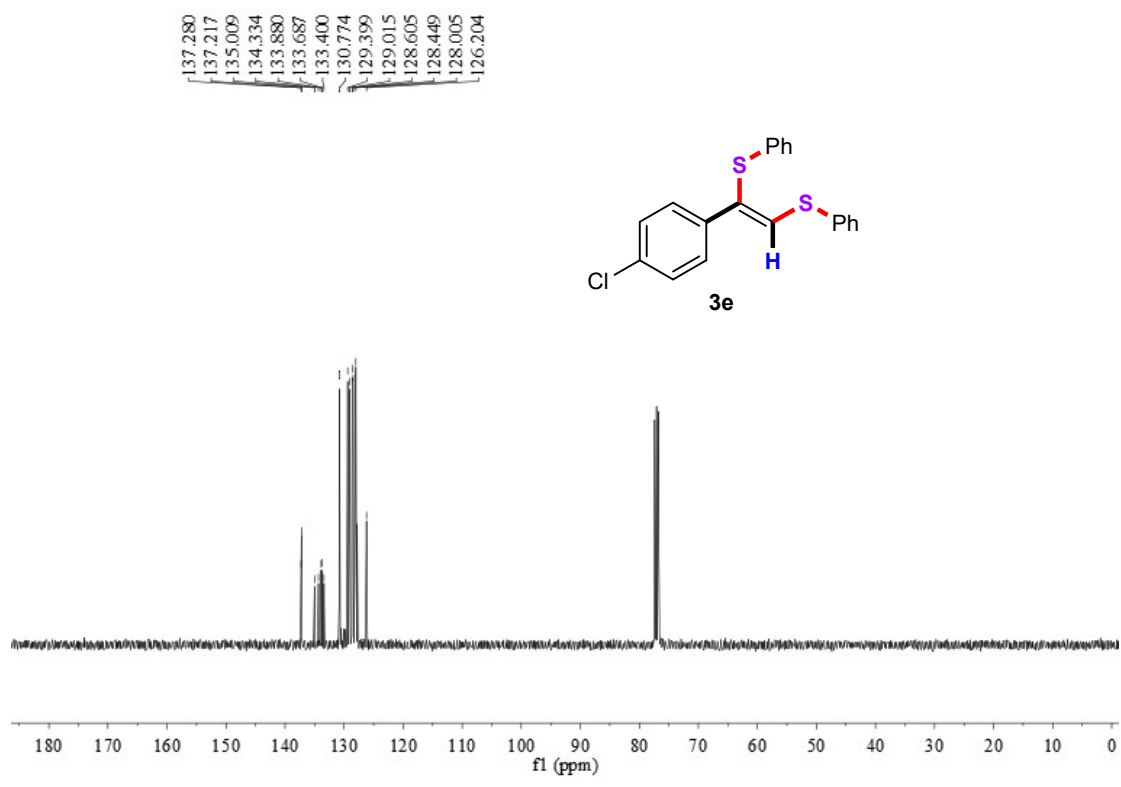


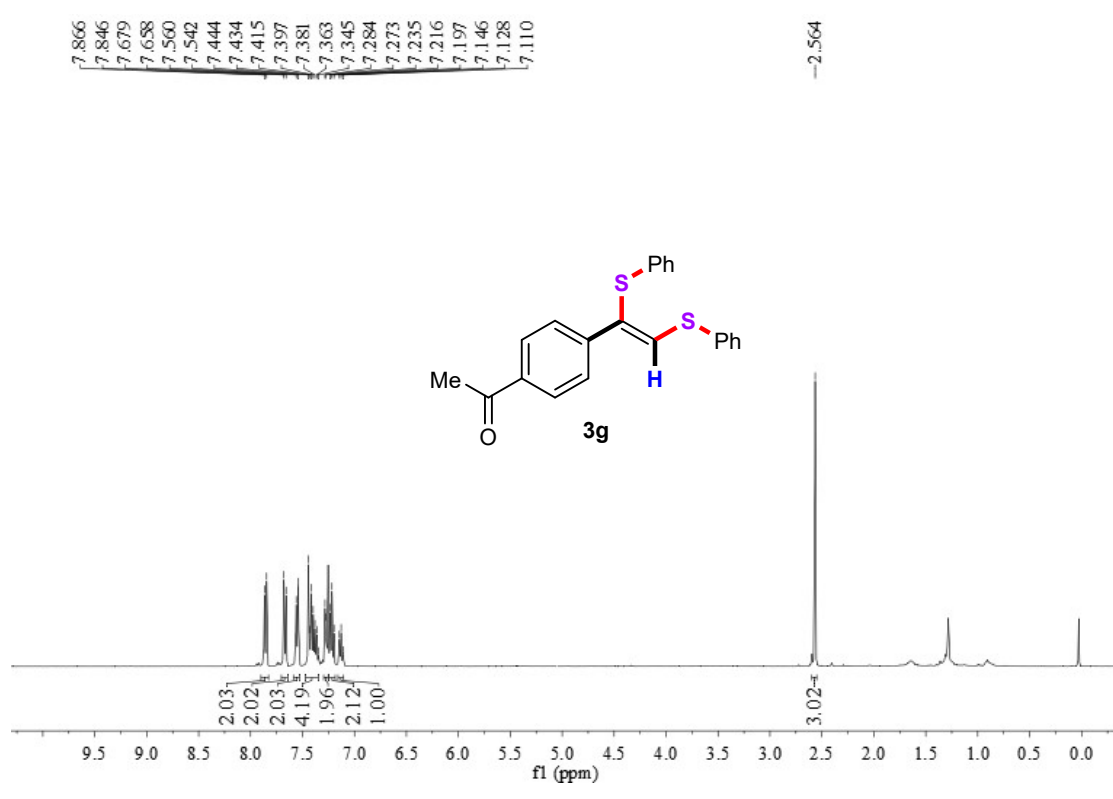
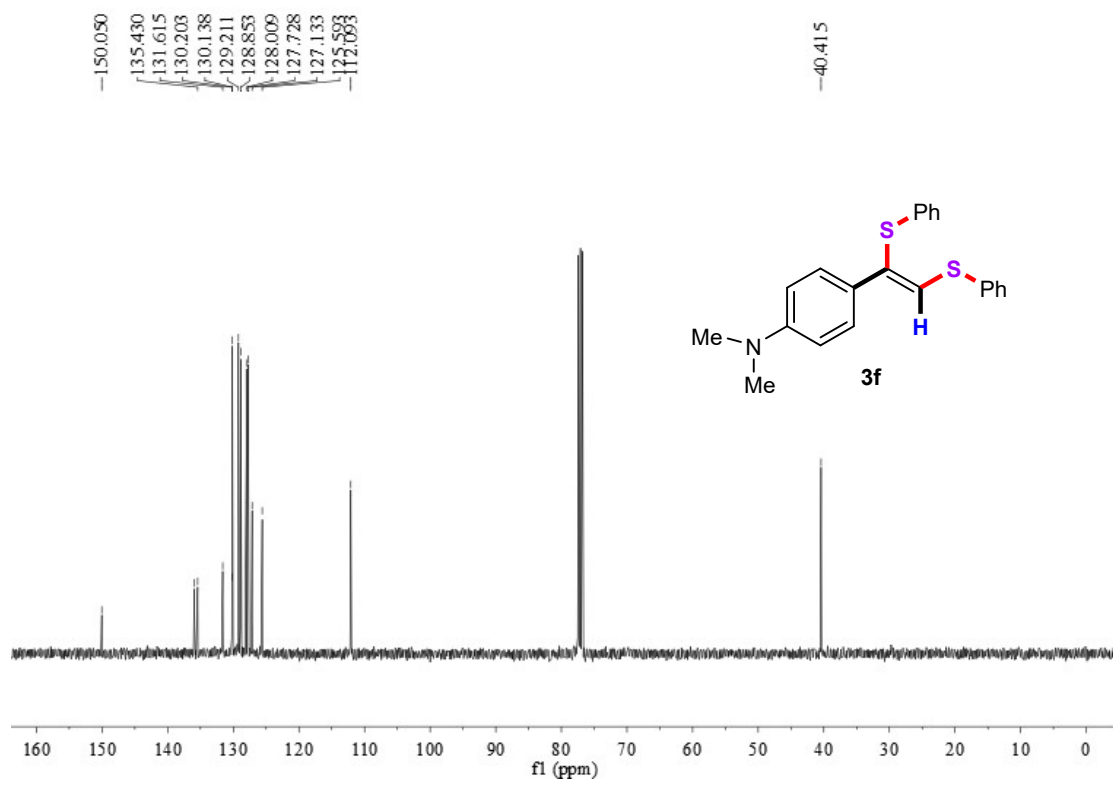


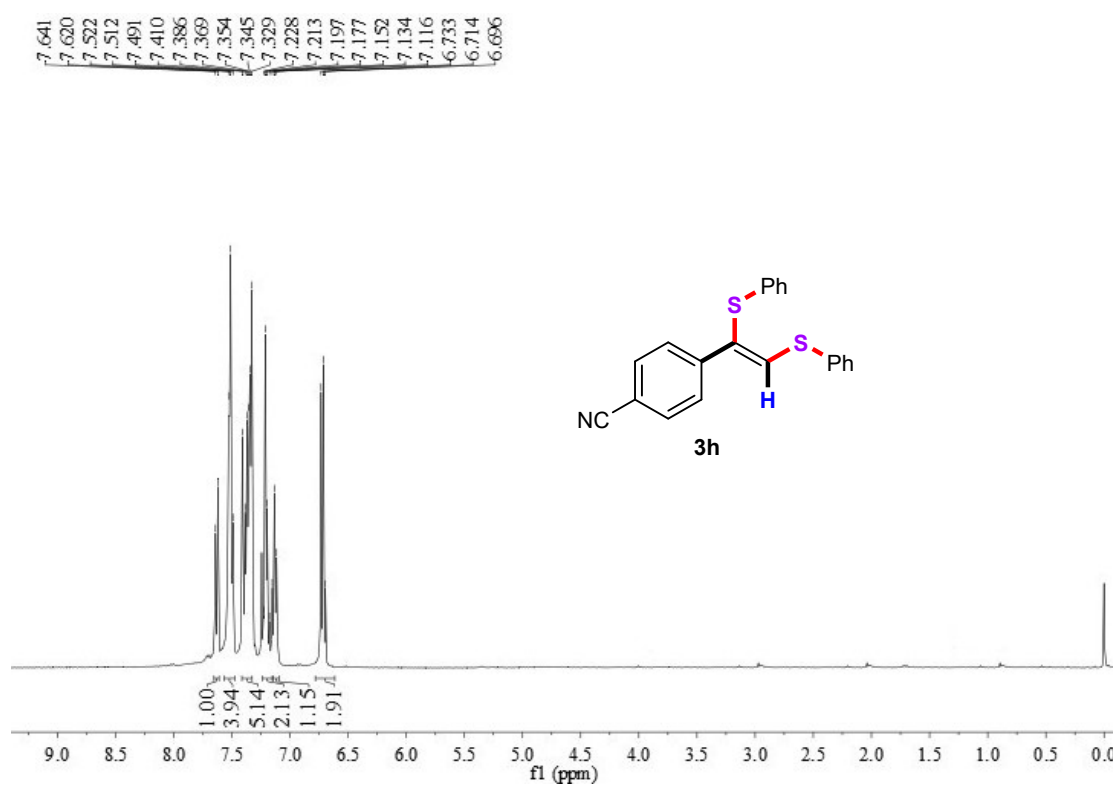
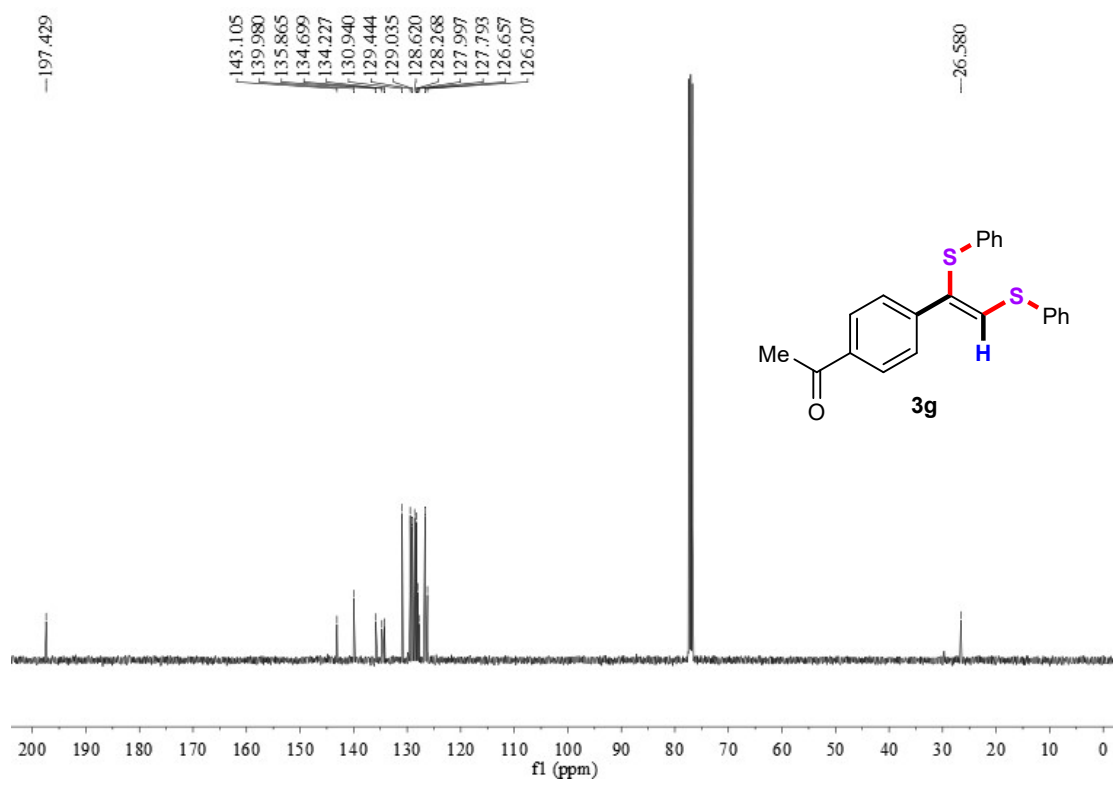


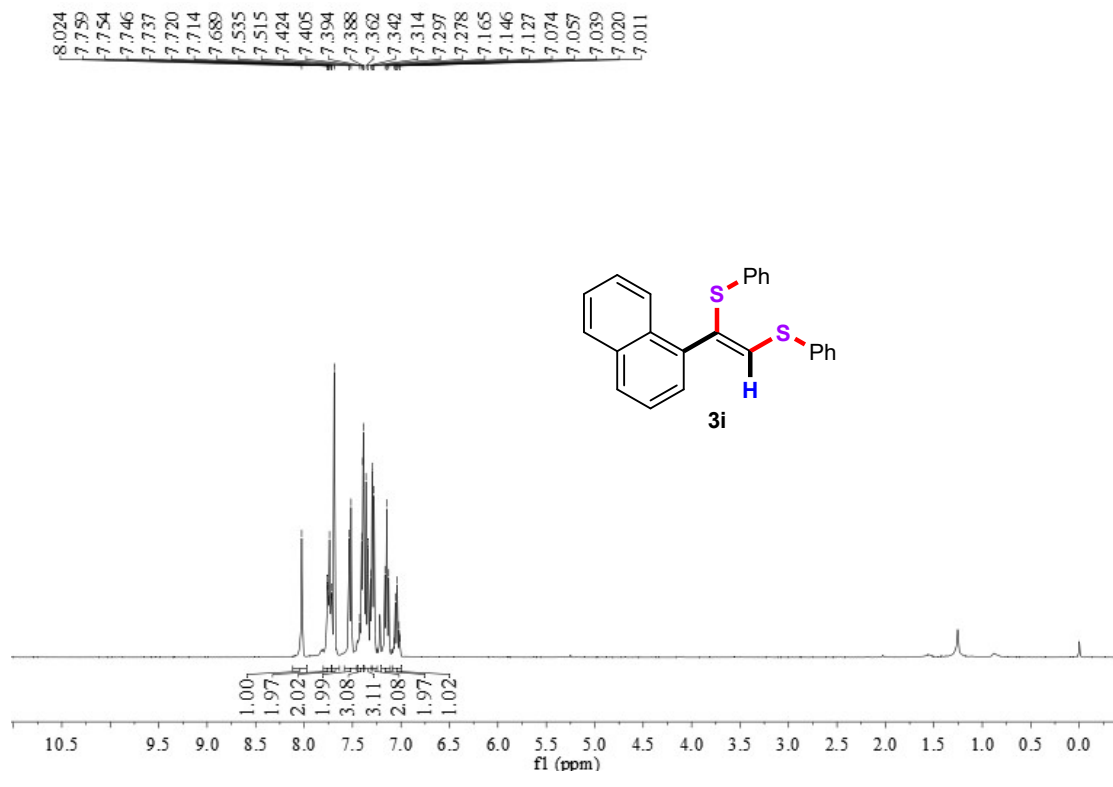
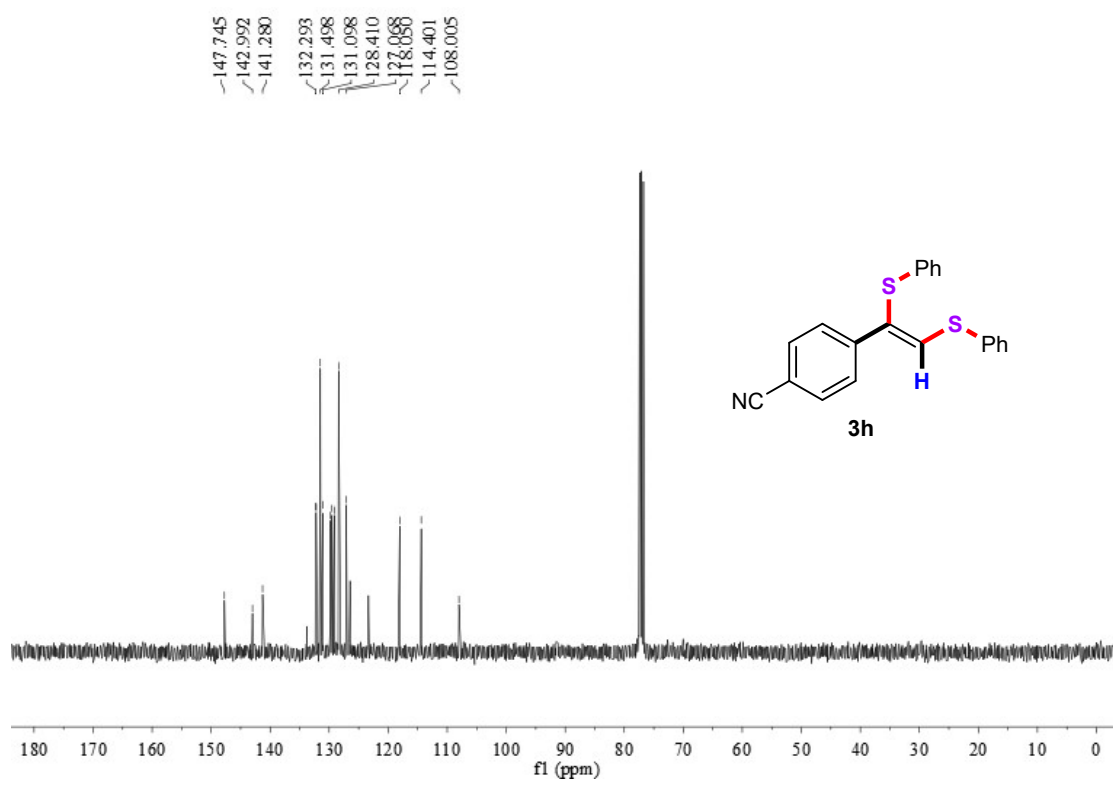
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7.065

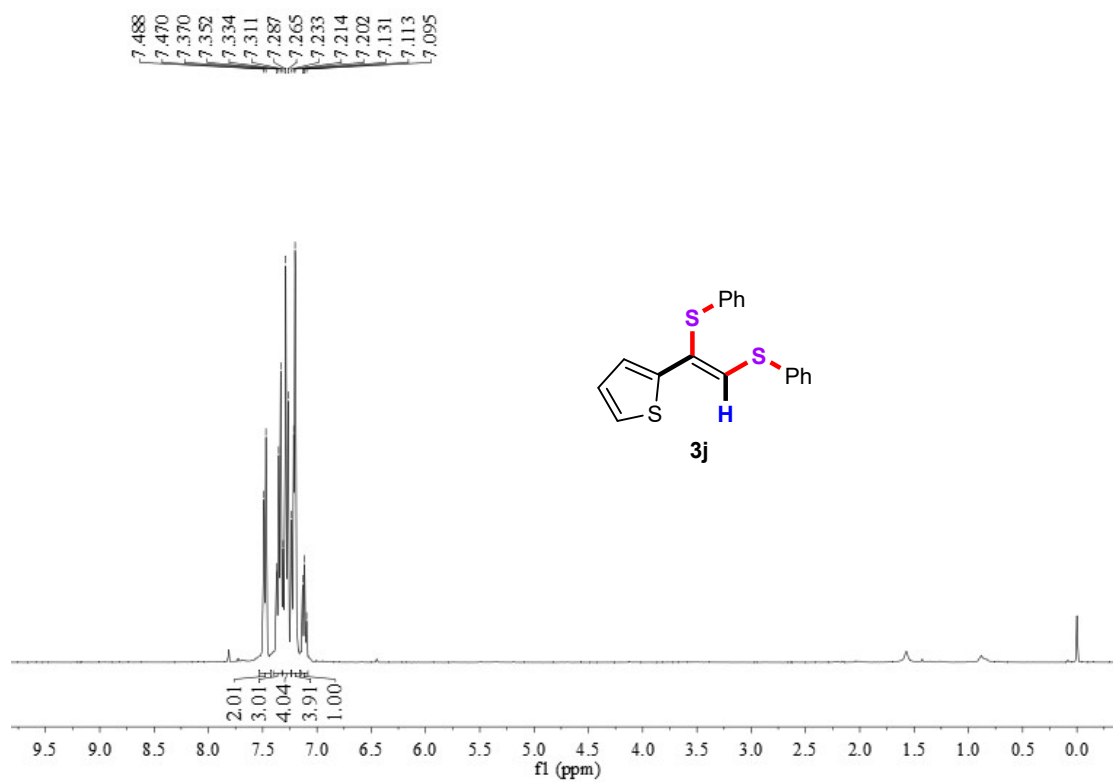
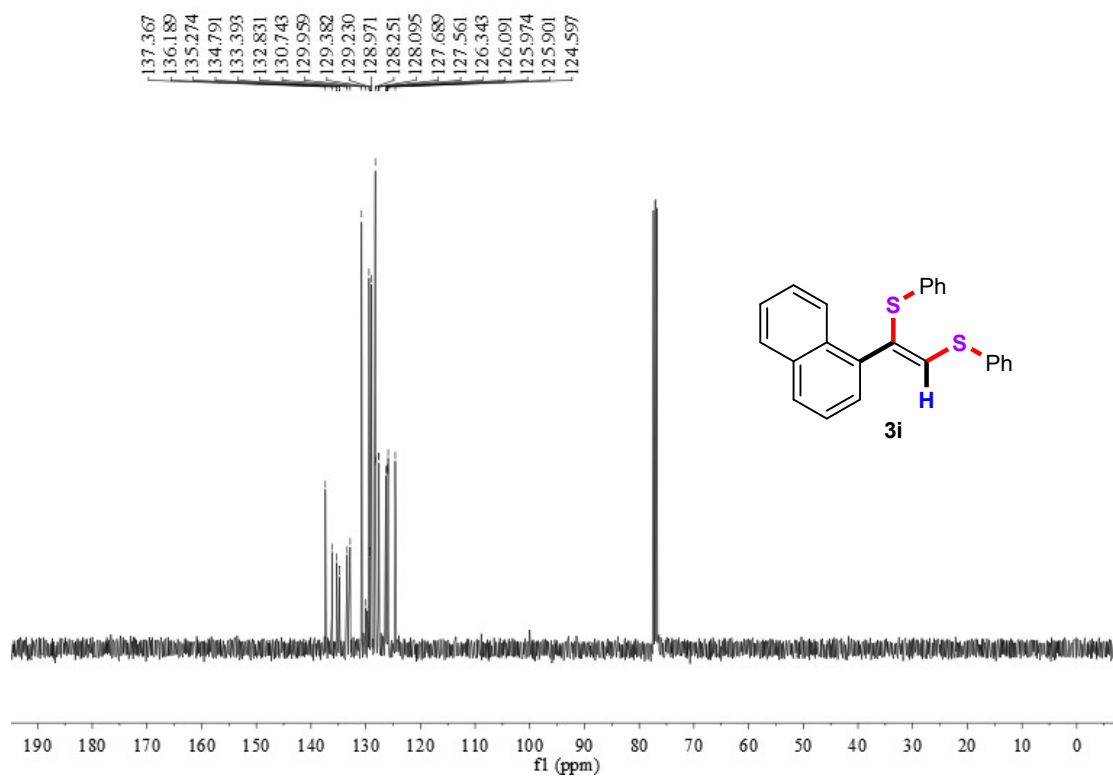


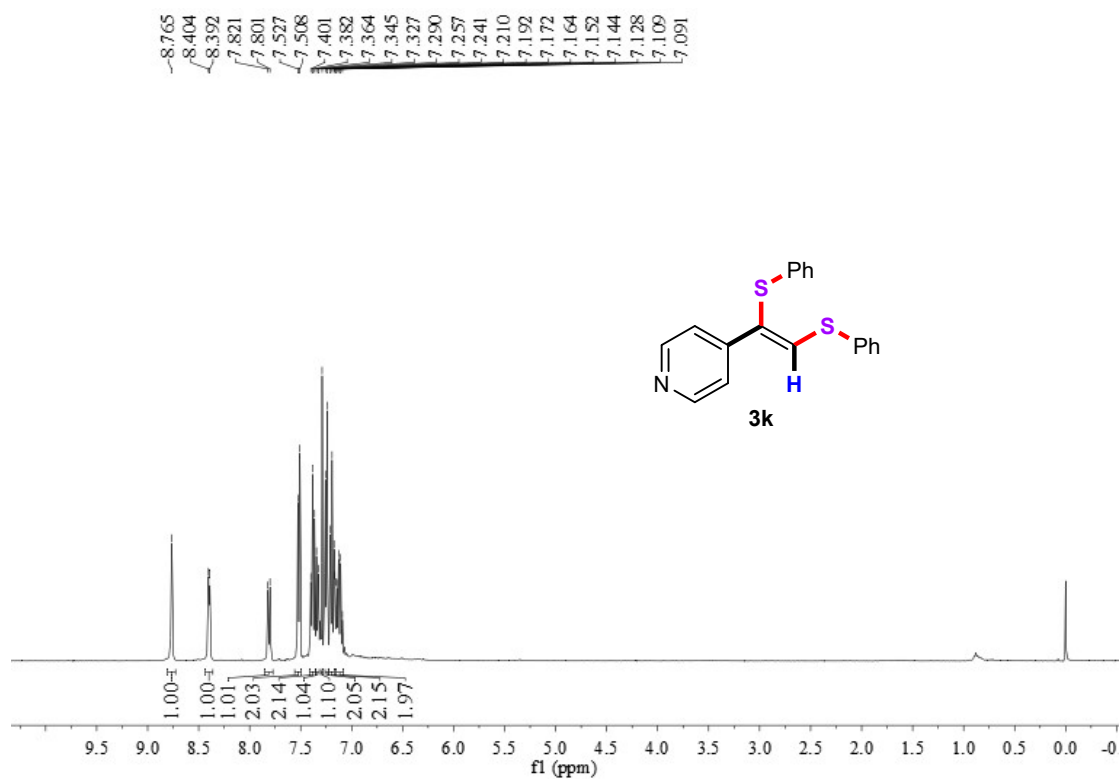
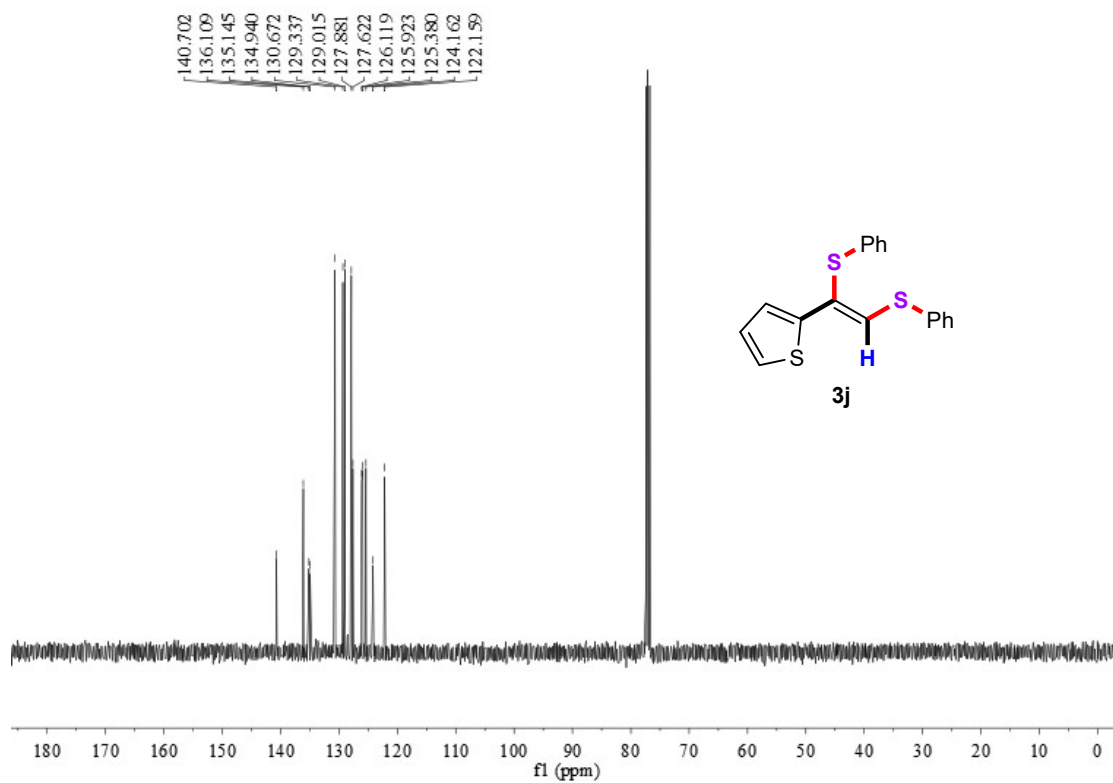


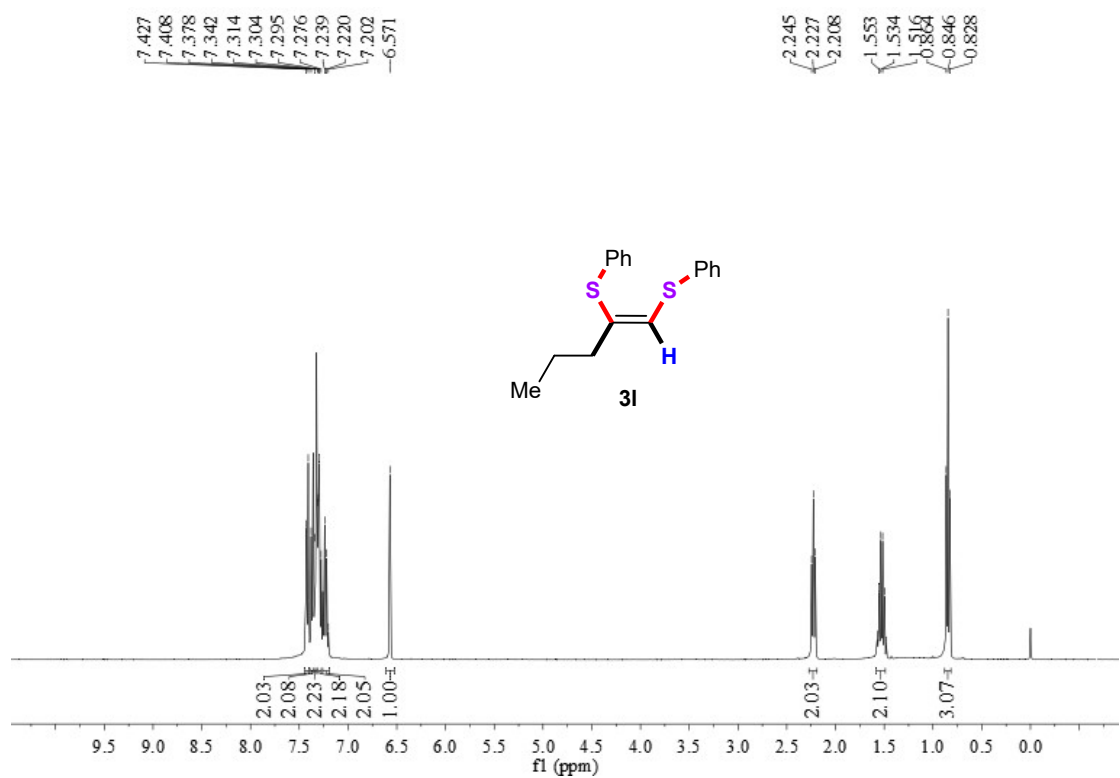
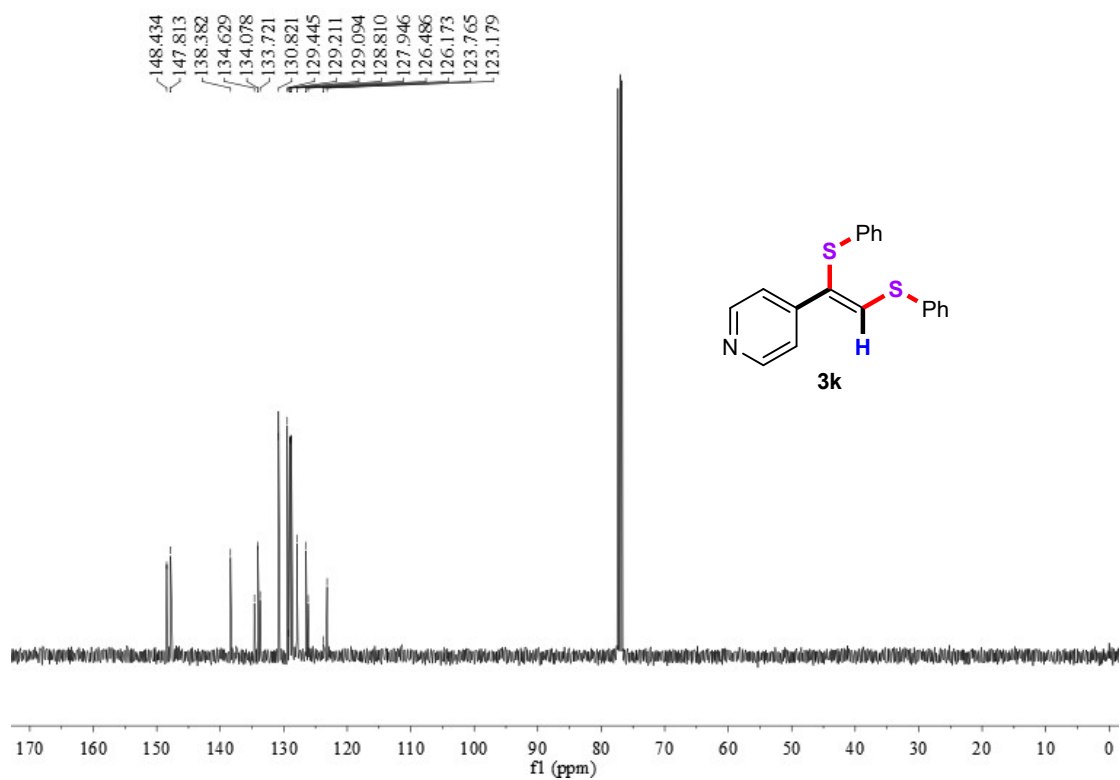


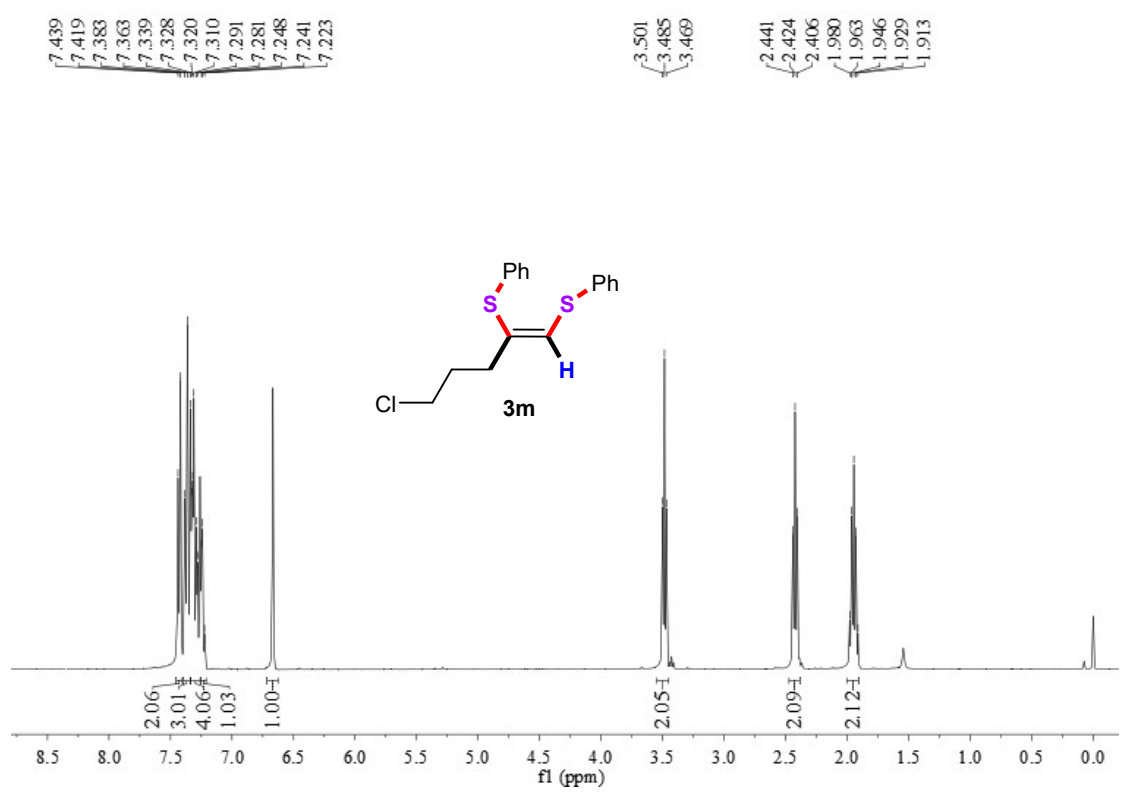
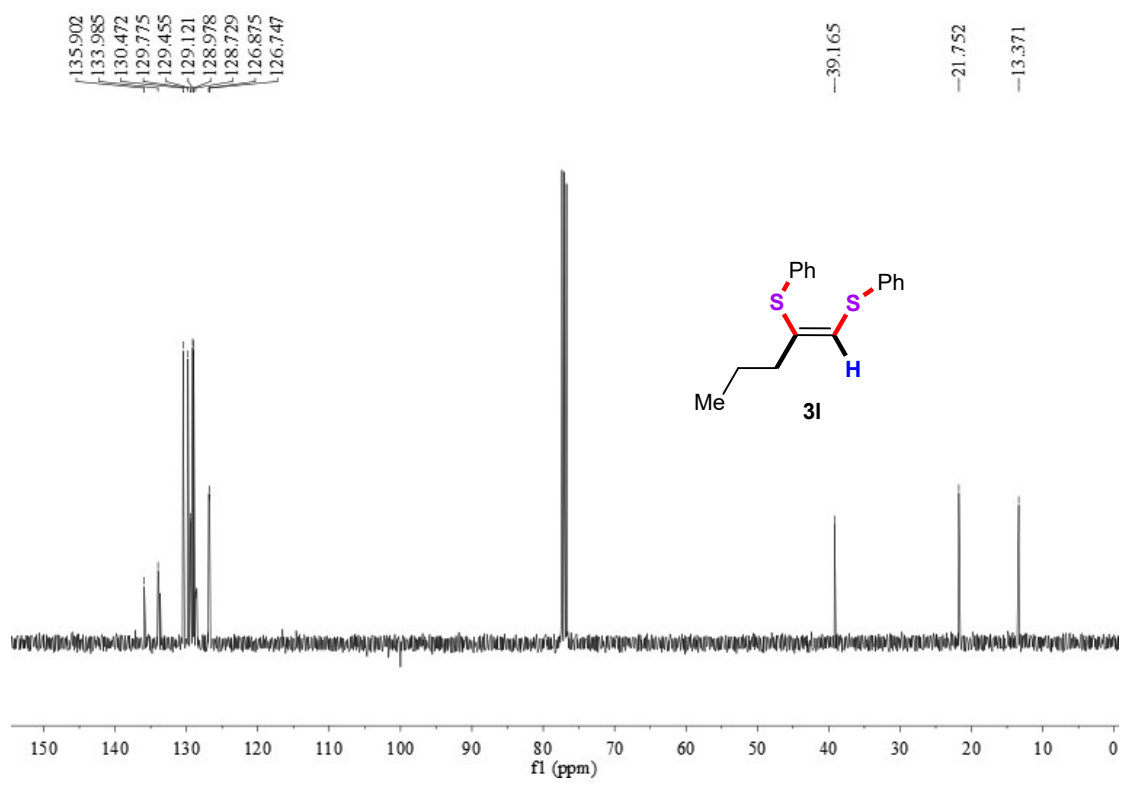


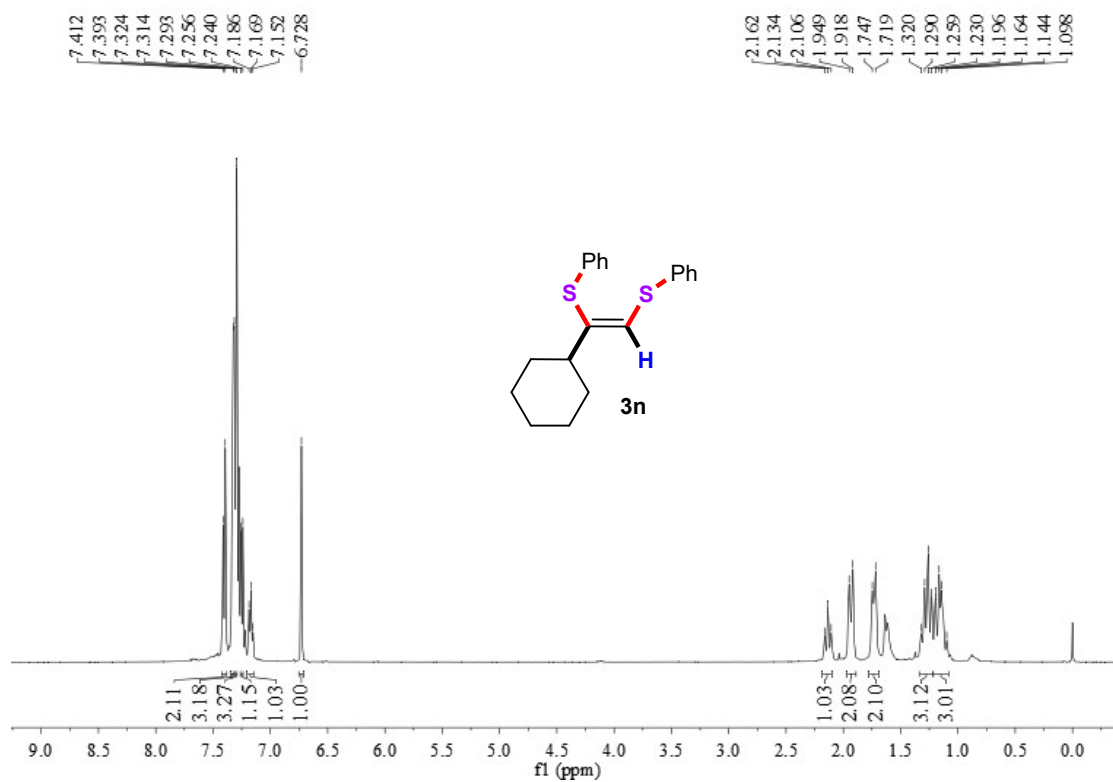
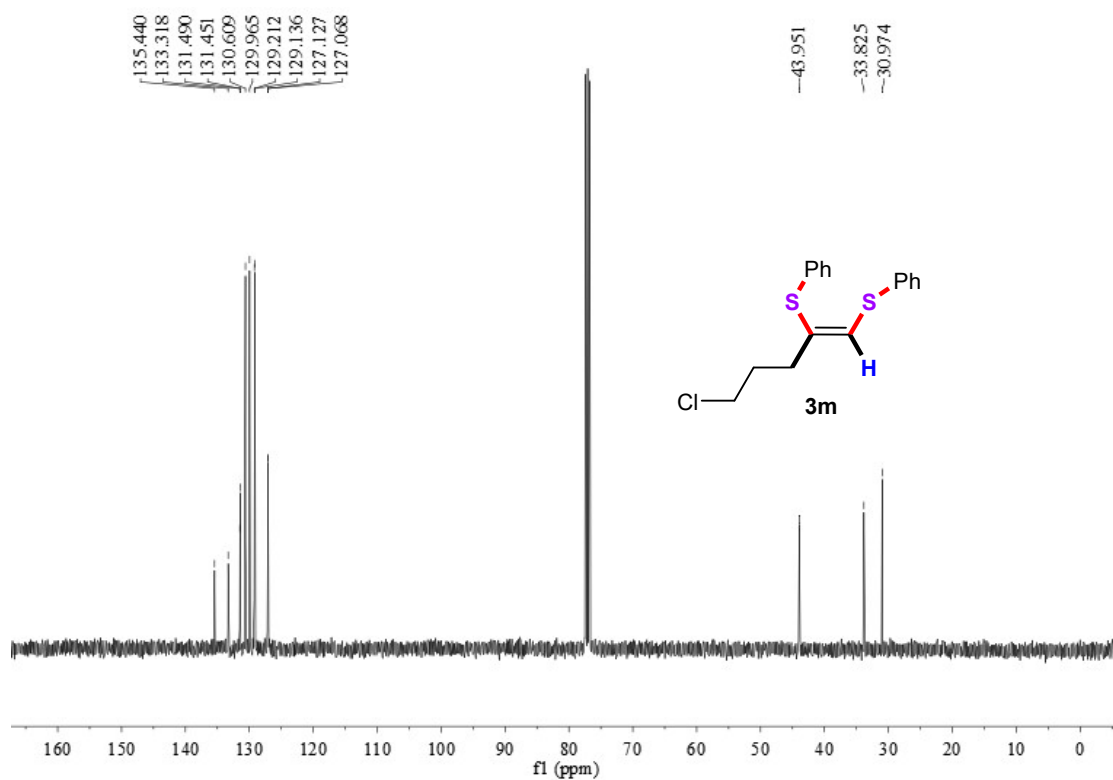


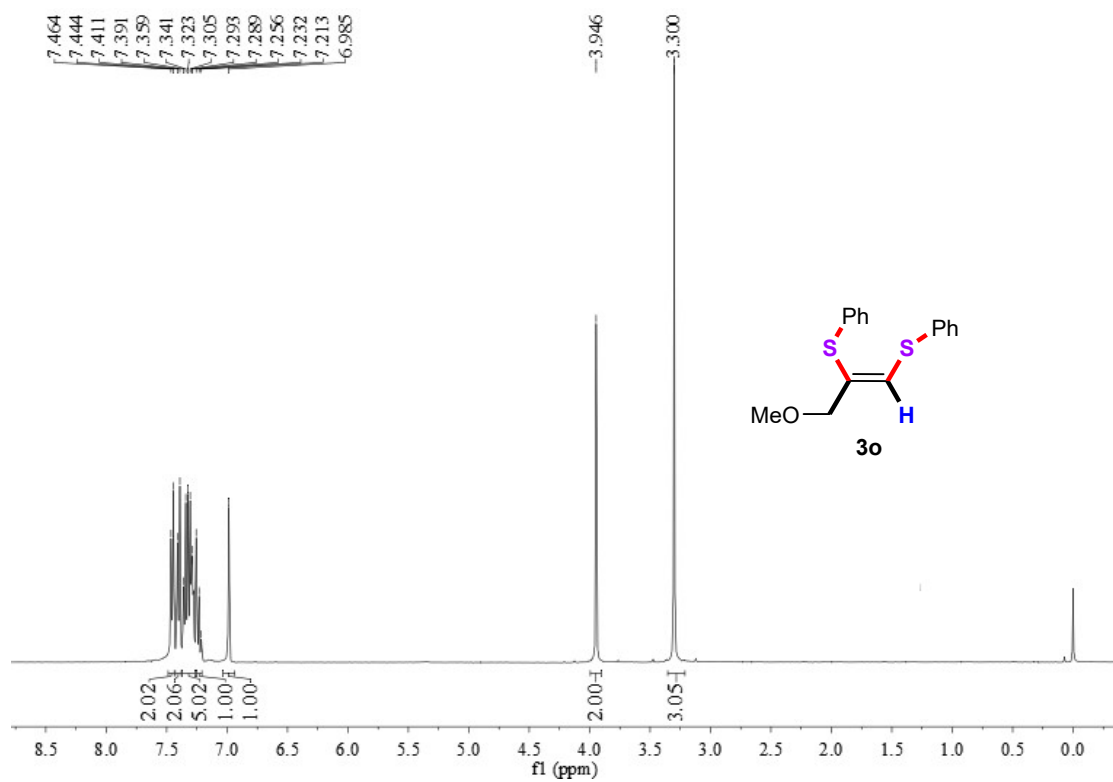
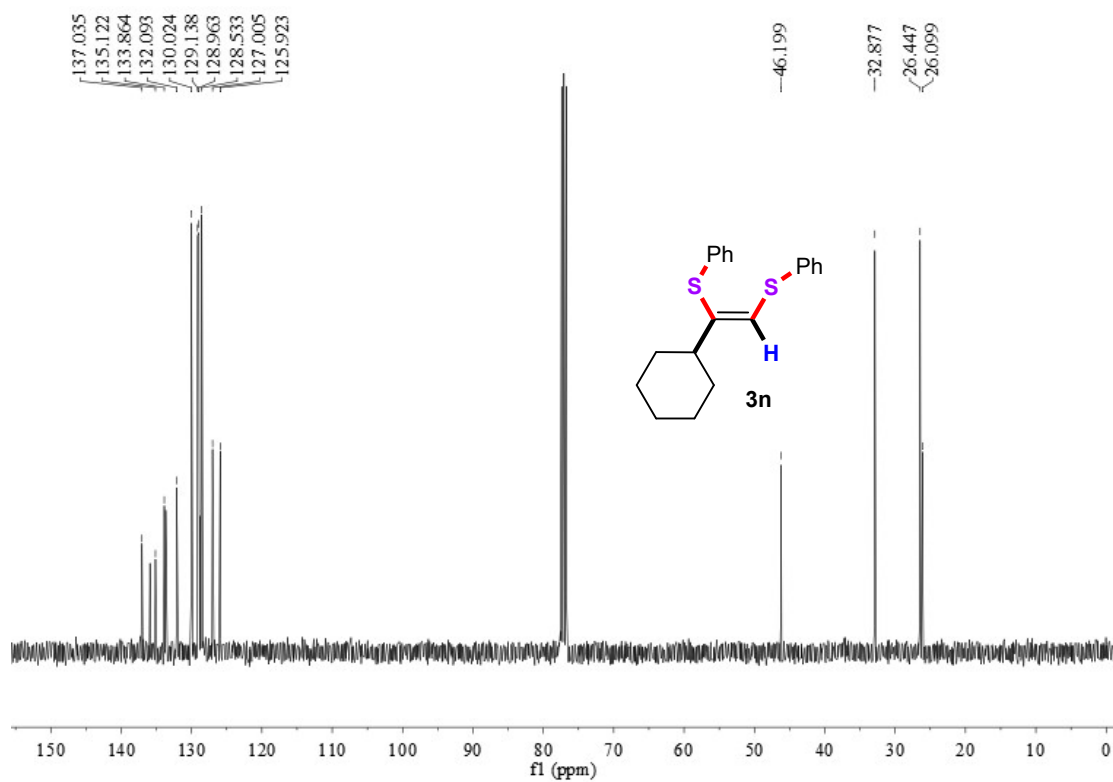


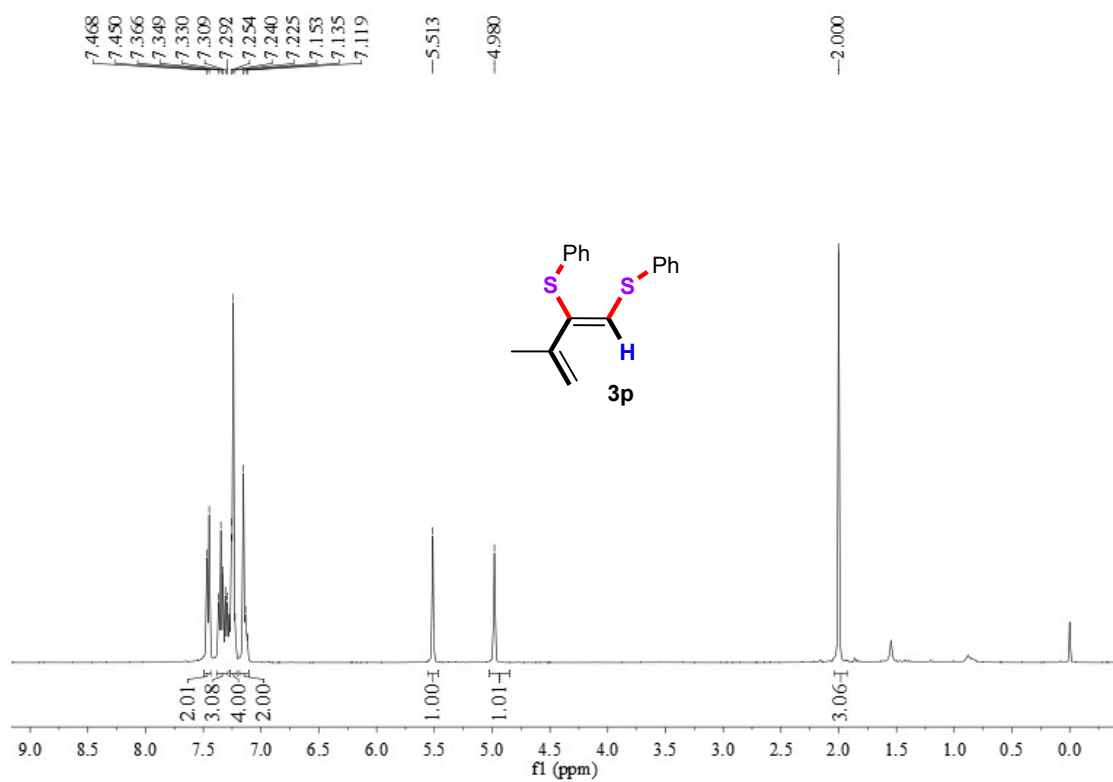
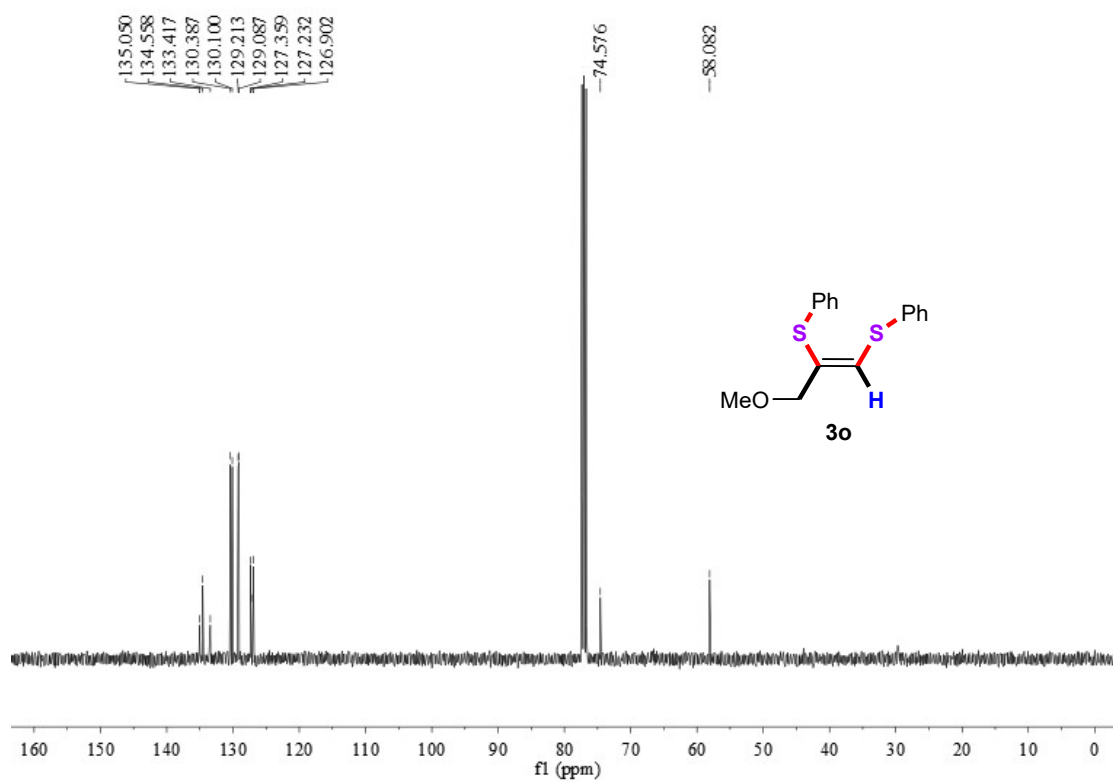


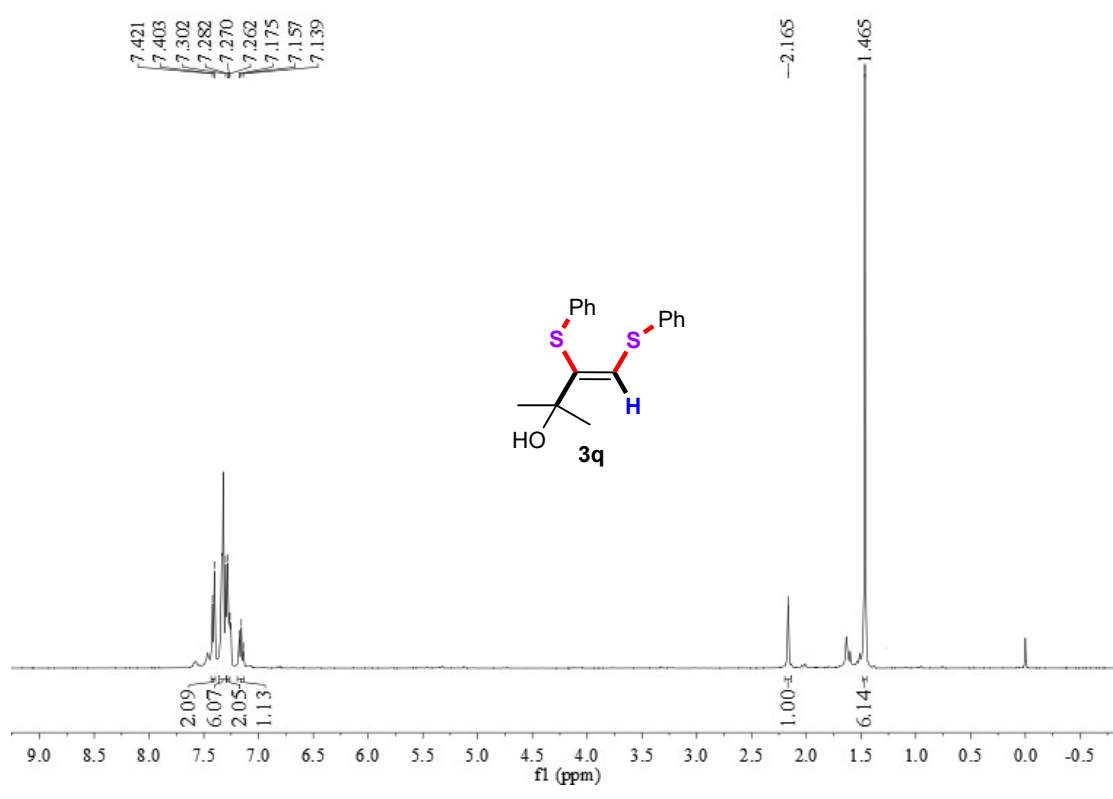
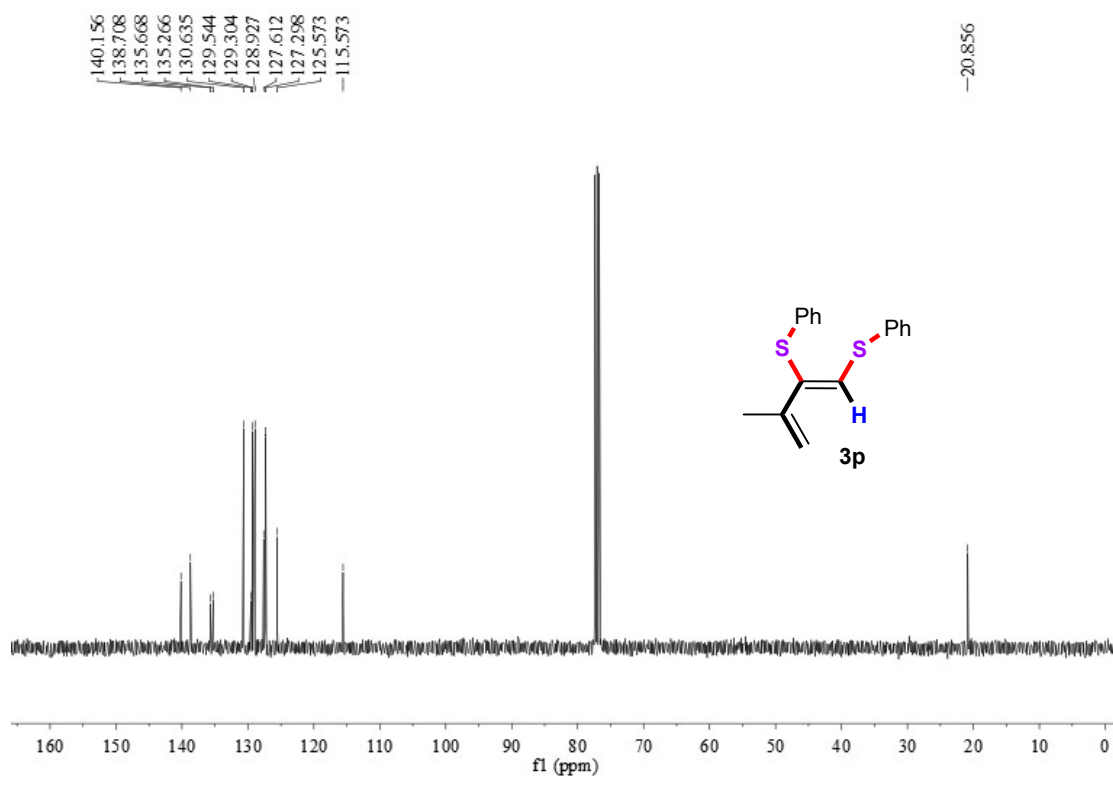


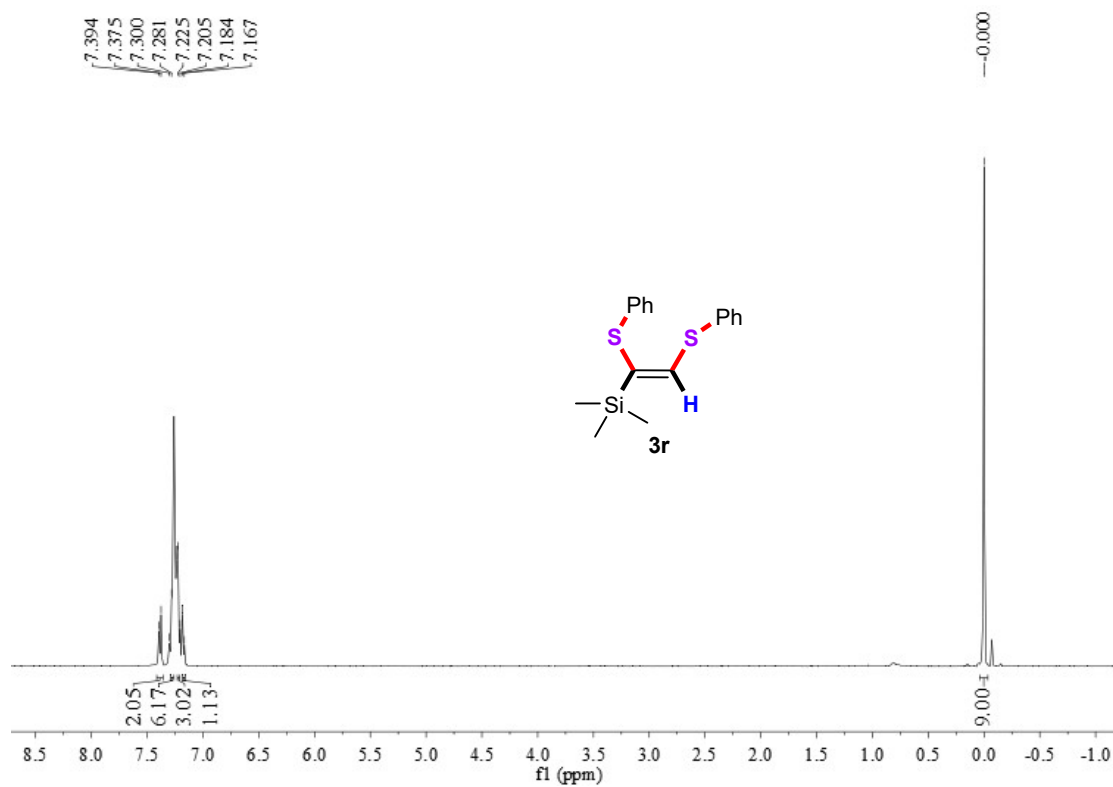
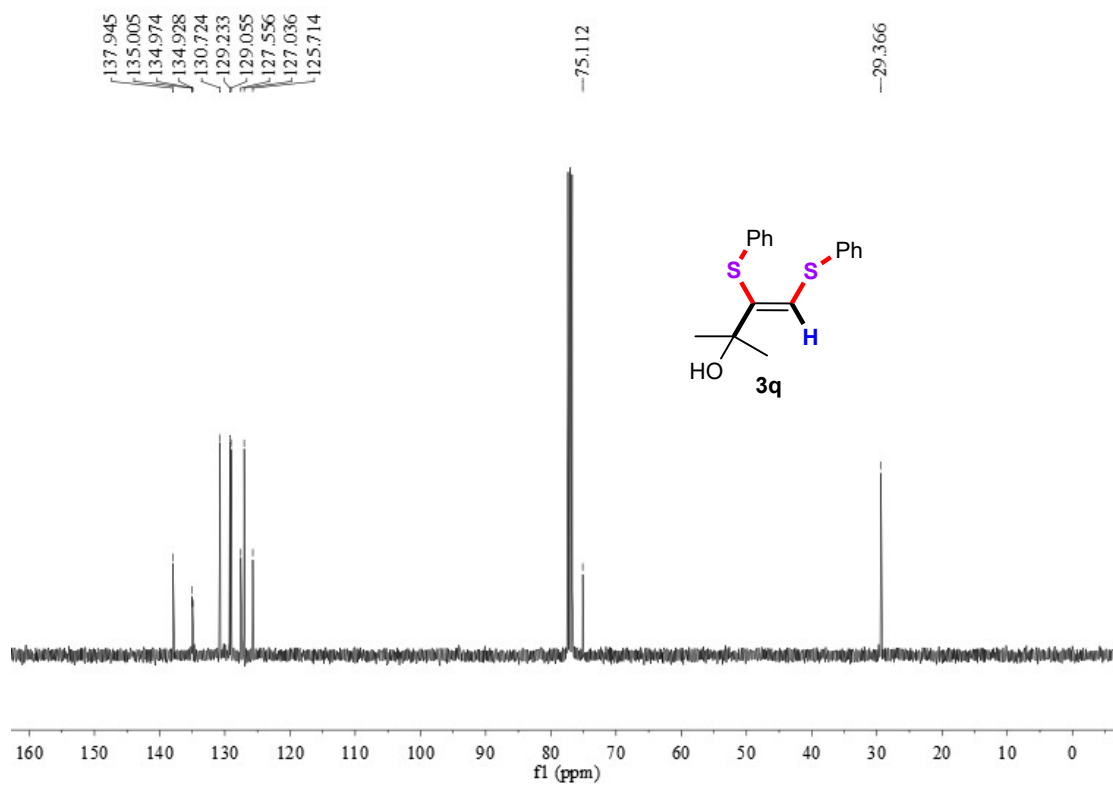


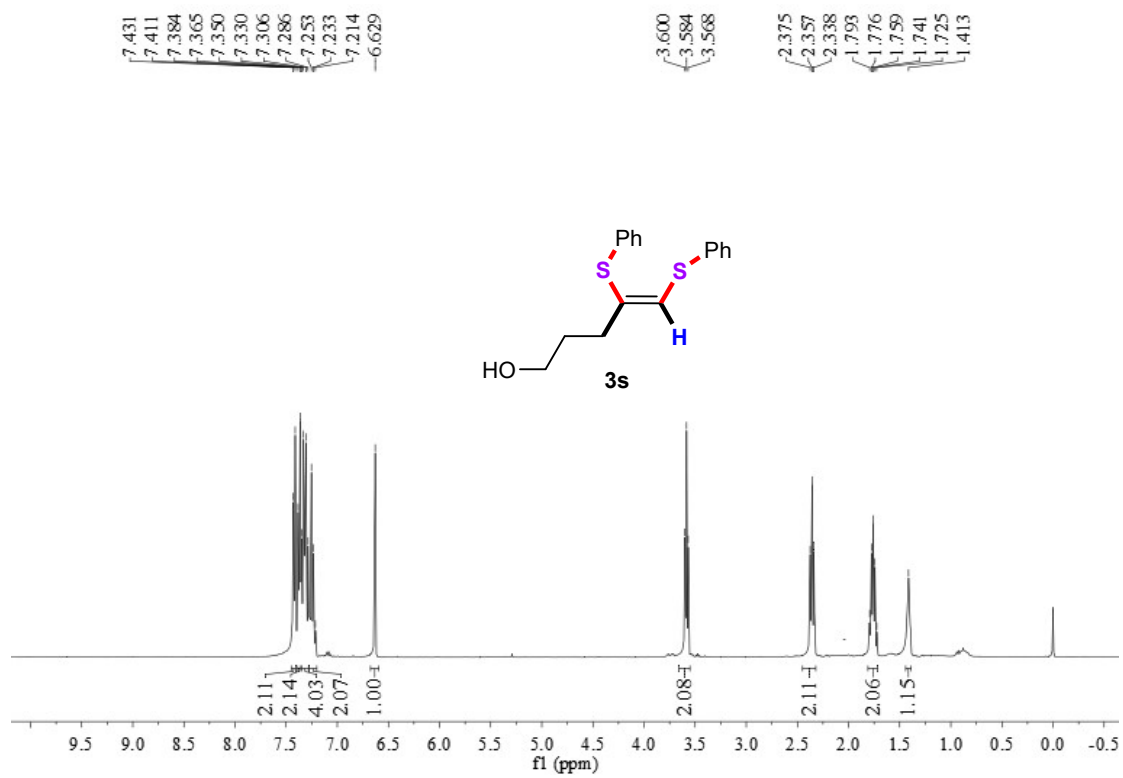
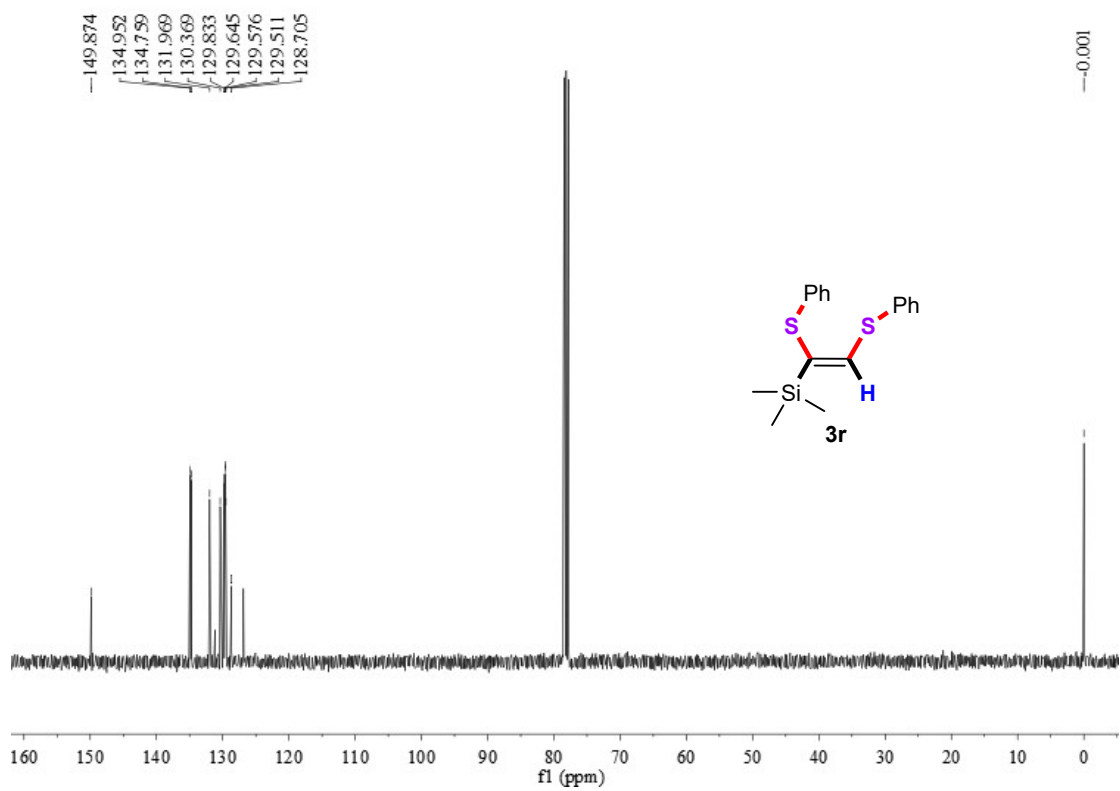


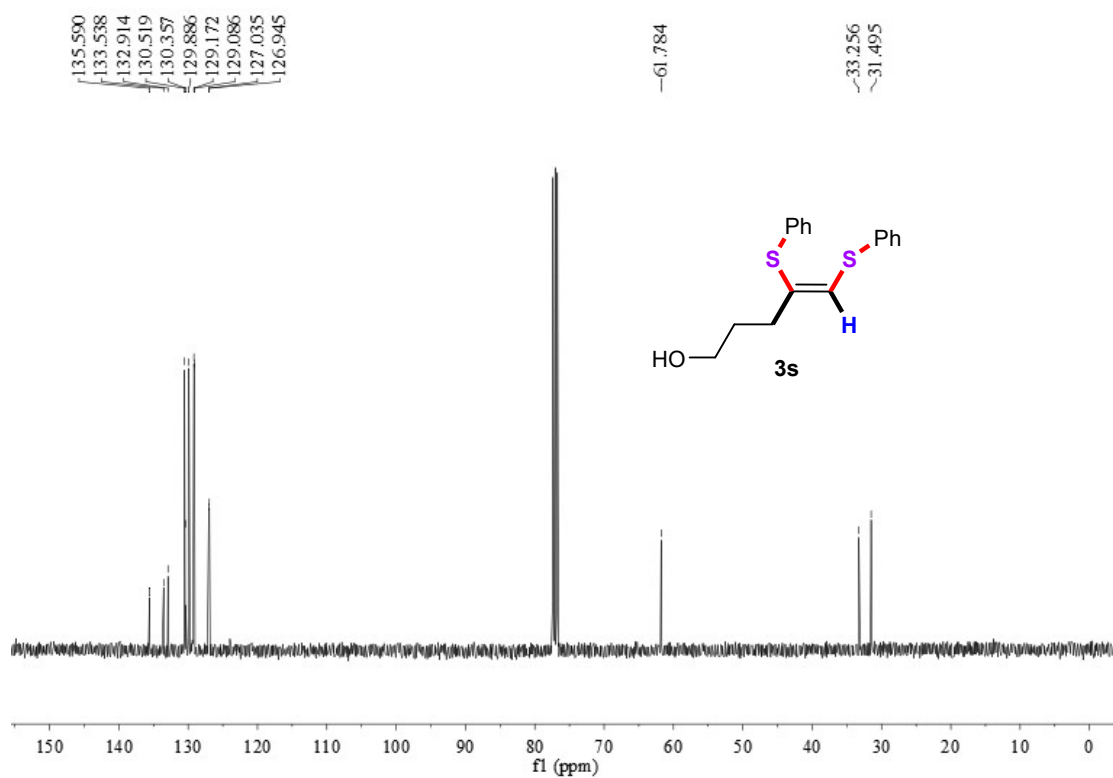












¹H and ¹³C NMR spectra of compounds 4

