Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Visible-Light Mediated Allylation of Thiols with Allylic Alcohols

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General Experimental

^{1}H and ^{13}C spectra were recorded on Bruker Avance 400 and 500 spectrophotometers. The chemical shifts (δ ppm) and coupling constants (Hz) are reported in the standard fashion with reference to internal chloroform. The high-resolution mass measurements were carried out using Micromass Q-ToF ESI instrument using direct inlet mode. Analytical thin-layer chromatography (TLC) were performed on pre-coated 0.2 mm thick Merck 60 F_{245} silica plates and various combinations of ethyl acetate and Petroleum ether were used as eluent. Visualization of spots was accomplished by exposure to UV and basic $KMnO_4$ solution. All compounds were purified using silica gel (100-200 mesh) column chromatography and gave spectroscopic data consistent with being ≥95% the assigned structure. Dry DCM, ACN, DMF, acetone and 1,2-DCE were prepared by distilling over calcium hydride. All the commercial reagents were used as such without further purification. The allylic alcohols were prepared as per the pervious literature[1] and the thiols were purchased from sigma Aldrich or TCI and used directly.

Fluorescence quenching studies.

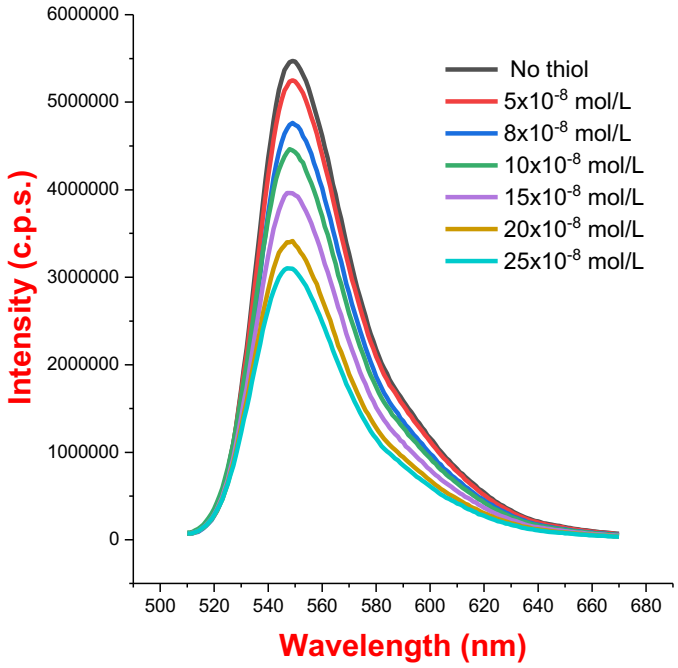


Figure 1- Fluorescence quenching of Eosin Y in presence of thiol **2b.**

The fluorescence emission intensities were recorded on a Horiba Fluormax-4 spectrofluorometer and the excitation wavelength was fixed at 500nm. The samples were prepared by mixing Eosin Y (1.0 ×10-6 mol/L) stock solution and different amount of thiophenol **2b** in MeCN in a light path quartz fluorescence cuvette. The concentration of **2b** stock solution is 1.0×10^{-8}mol/L in DMF. For each quenching experiment, 0.5 mL of **2b** stock solution was titrated to a mixed solution of Eosin Y (0.1mL of the stock solution, in a total volume = 1.0 mL). Then the emission intensity was collected and the results were presented in Figure 1.

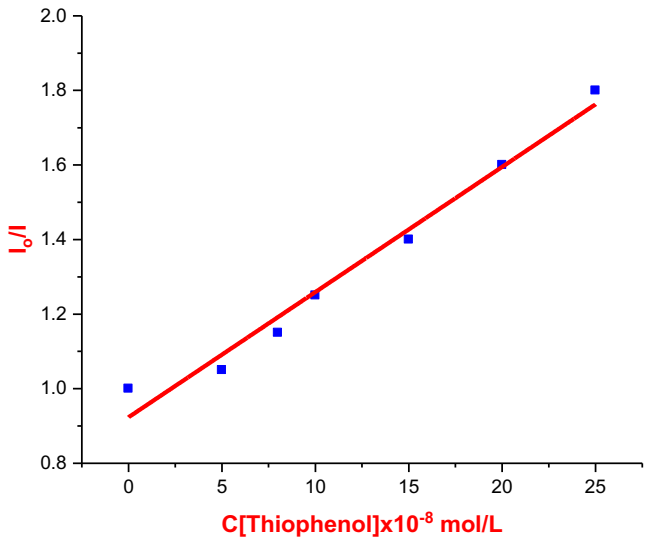


Figure 2: Stern- Volmer plots.

We indeed observed an energy/electron transfer from exited state of Eosin Y to **2b**. Fluorescence quenching phenomenon of EosinY under various concentrations of thiophenol was is evident from a curve of [I_0/I] vs C[**2a**], as shown in Figure 2 (Stern-Volmer plots).

The fluorescence emission intensities were recorded on a Horiba Fluormax-4 spectrofluorometer. The excitation wavelength was fixed at 500nm and the samples were prepared by mixing Eosin Y (1.0 ×10-6 mol/L) stock solution and different amounts of alkyne **1a** in MeCN (total volume = 0.1 mL) in a light path quartz fluorescence cuvette. The concentration of **1a** stock solution is 1.0×10^{-8}mol/L in MeCN. For each quenching experiment, 0.5 mL of **1a** stock solution was titrated to a

mixed solution of EosinY (0.1mL, in a total volume = 1.0 mL). Then the emission intensity was collected and the results were presented in Figure 3.

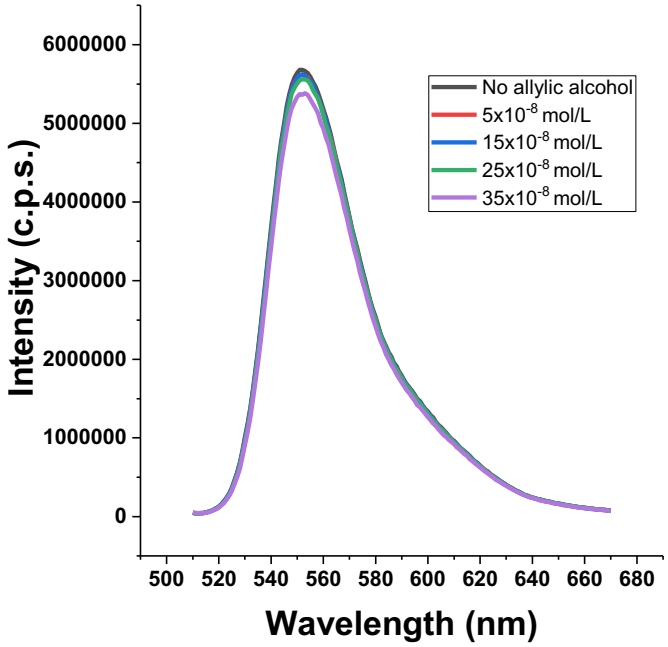


Figure 3- Fluorescence quenching of Eosin Y in presence of allylic alcohol **1a.**

No energy transfer from exited state of Eosin Y to **1a** was observed. Absence of any Fluorescence quenching of EosinY under various concentrations of alkyne **1a** is evident from a curve of [I_0/I] vs C[**1a**], as shown in Figure 4 (Stern-Volmer plots).

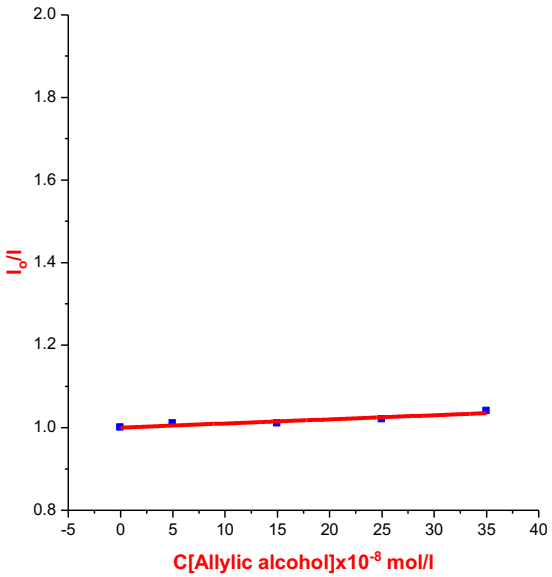
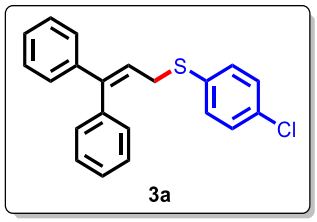


Figure 4: Stern-Volmer plots**.**

General procedure for visible light mediated synthesis of allylic sulphide derivatives employing allylic alcohols:

In a sample vial equipped with a magnetic bead was added **1a** (42 mg, 0.2 mmol) and 4-chlorobenzene thiol **2a** (43 mg, 0.3 mmol, 1.5 equiv). To this was added eosin Y catalyst (6.9 mg, 0.01 mmol, 5 mol%) followed by addition of 2 mL ACN. The reaction was allowed to stir overnight at room temperature under air and irradiation with green LED's. The contents of the vial were evaporated under reduced pressure and subjected to silica gel column chromatography with EtOAc/Petroleum ether as eluent to afford the desired product **3a** weighing 59 mg (87%) as a yellow oily liquid.



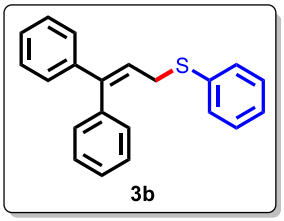
(4-chlorophenyl)(3,3-diphenylallyl)sulfane: (3a)[2]

Physical Apperance: Yellow oily liquid.

R_f: 0.6 (2:98, Ethyl acetate: Petroleum ether).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.36 (m, 3H), 7.31-7.27 (m, 3H), 7.24-7.20 (m, 6H), 7.12-7.10 (m, 2H), 6.17 (t, *J* = 7.8 Hz, 1H), 3.66 (d, *J* = 7.8 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 141.9, 138.9, 134.3, 132.5, 131.8, 130.0, 129.0, 128.4, 128.3, 127.7, 127.6, 127.6, 123.9, 34.2 ppm.



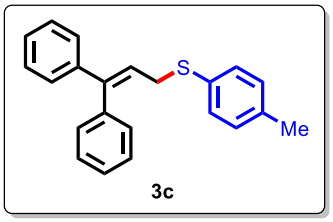
(3,3-diphenylallyl)(phenyl)sulfane: (3b) [2]

Physical Apperance: Colorless oily liquid.

R_f: 0.6 (2:98, Ethyl acetate: Petroleum ether).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50-7.35 (m, 3H), 7.32-7.25 (m, 7H), 7.22-7.19 (m, 3H), 7.12-7.11 (m, 2H), 6.19 (t, *J* = 7.8 Hz, 1H), 3.66 (d, *J* = 7.8 Hz, 2H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.5, 142.0, 139.0, 135.8, 130.4, 130.0, 128.9, 128.4, 128.3, 127.6, 127.4, 126.4, 124.3, 34.0 ppm.



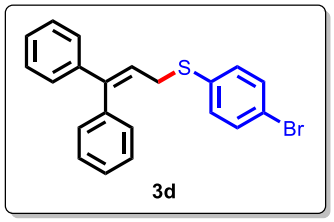
(3,3-diphenylallyl)(p-tolyl)sulfane: (3c)[2]

Physical Apperance: Colorless oily liquid.

R_f: 0.6 (2:98, Ethyl acetate: Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.4-7.34 (m, 3H), 7.29-7.24 (m, 4H), 7.23-7.20 (m, 3H), 7.10-7.08 (m, 4H), 6.20 (t, *J* = 7.8 Hz, 1H), 3.62 (d, *J* = 7.8 Hz, 2H) 2.34 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 142.1, 139.1, 136.6, 132.0, 131.2, 130.0, 129.7, 128.3, 128.2, 127.6, 127.5, 127.4, 124.6, 34.7, 21.2 ppm.



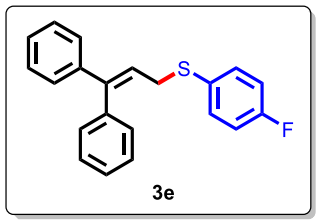
(4-bromophenyl)(3,3-diphenylallyl)sulfane: (3d)[2]

Physical Apperance: Colorless oily liquid.

R_f: 0.7 (2:98, Ethyl acetate: Petroleum ether).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.33 (m, 5H), 7.29-7.26 (m, 3H), 7.18-7.17 (m, 2H), 7.11-7.08 (m, 4H), 6.13 (t, J = 7.8 Hz, 1H), 3.63 (d, J = 7.8 Hz, 2H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 141.9, 138.9, 135.0, 132.0, 131.9, 130.0, 128.4, 128.3, 127.71, 127.67, 127.6, 123.8, 120.4, 34.1 ppm.



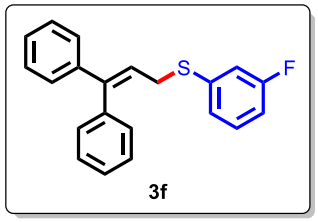
(3,3-diphenylallyl)(4-fluorophenyl)sulfane: (3e)[2]

Physical Apperance: Colorless oily liquid.

R_f: 0.5 (2:98, Ethyl acetate: Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.29 (m, 3H), 7.27-7.22 (m, 5H), 7.16-7.13 (m, 2H), 7.00-6.98 (m, 2H), 6.92 (t, J = 8.7 Hz, 2H), 6.11 (t, J = 7.8 Hz, 1H), 3.56 (d, J = 7.8 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, J^1 = 248 Hz), 144.6, 141.9, 138.9, 133.8 (J^3 = 8.3 Hz), 130.4 (J^4 = 3.4 Hz), 130.0, 128.31, 128.29, 127.62, 127.56, 127.5, 124.3, 116.0 (J^2 = 21.8 Hz), 35.2 ppm.



(3,3-diphenylallyl)(3-fluorophenyl)sulfane: (3f)

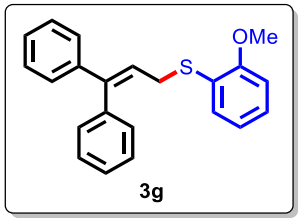
Physical Apperance: Colorless oily liquid.

R_f: 0.6 (2:98, Ethyl acetate: Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.34 (m, 3H), 7.27-7.26 (m, 3H), 7.22-7.13 (m, 5H), 7.02 (d, J = 7.9 Hz, 1H), 6.94 (dt, J = 9.6, 2.0 Hz, 1H), 6.86 (td, J = 8.6, 2.0 Hz, 1H), 6.15 (t, J = 7.6 Hz, 1H), 3.66 (d, J = 7.6 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9 (d, J^1 = 246 Hz), 145.1, 141.9, 138.9, 138.5 (J^3 = 8.3 Hz), 130.1 (d, J^3 = 8.3 Hz), 128.5, 128.3, 127.74, 127.72, 127.6, 125.2 (d, J^4 = 2.9 Hz), 123.7, 116.3 (d, J^2 = 22.8 Hz), 113.1 (d, J^2 = 22.8 Hz), 33.5 ppm.

HRMS (ESI, M+H$^+$) m/z calcd. for $C_{21}H_{18}FS$ 321.1108, found 321.1112.



(3,3-diphenylallyl)(2-methoxyphenyl)sulfane (3g)

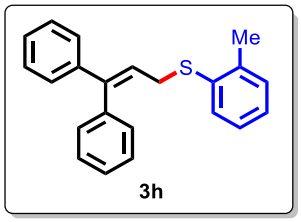
Physical Apperance: Colorless oily liquid.

R_f: 0.6 (2:98, Ethyl acetate: Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.32 (m, 3H), 7.28-7.23 (m, 4H), 7.21-7.16 (m, 3H), 7.09-7.07 (m, 2H), 6.88 (td, J = 7.5, 1.0 Hz, 1H), 6.80 (dd, J = 8.2, 0.8 Hz, 1H), 6.18 (t, J = 7.9 Hz, 1H), 3.75 (s, 3H), 3.65 (d, J = 7.8 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 144.3, 142.2, 139.1, 131.8, 130.0, 128.2, 128.0, 127.8, 127.7, 127.4,124.7, 123.4, 121.4, 120.9, 110.6, 55.6, 32.3 ppm.

HRMS (ESI, M+H$^+$) m/z calcd. for $C_{21}H_{22}OS$ 333.1308, found 347.1301.



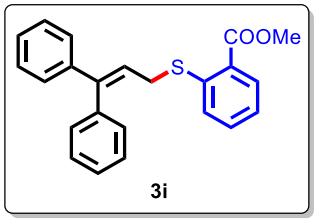
(3,3-diphenylallyl)(o-tolyl)sulfane: (3h)[2]

Physical Appearance: Colorless oily liquid.

R_f: 0.6 (2:98, Ethyl acetate: Petroleum ether).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.35 (m, 3H), 7.30-7.20 (m, 6H), 7.19-7.10 (m, 5H), 6.20 (t, *J* = 7.9 Hz, 1H), 3.63 (d, *J* = 7.9 Hz, 2H), 2.36 (s, 3H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.6, 142.0, 139.0, 138.7, 135.0, 130.2, 130.0, 128.4, 128.2, 127.59, 127.55, 127.5, 126.42, 126.39, 124.2, 33.3, 20.5 ppm.



methyl 2-((3,3-diphenylallyl)thio)benzoate: (3i)

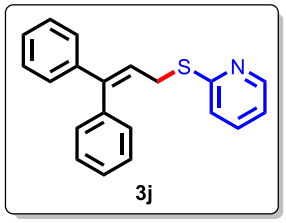
Physical Appearance: Colorless oily liquid.

R_f: 0.6 (2:98, Ethyl acetate: Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.44-7.36 (m, 3H), 7.33 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.28-7.23 (m, 5H), 7.20-7.18 (m, 2H), 7.15-7.09 (m, 2H), 6.17 (t, *J* = 7.8 Hz, 1H), 3.92 (s, 3H), 3.70 (t, *J* = 7.7 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 145.4, 142.0, 141.4, 139.1, 132.3, 131.4, 130.0, 128.5, 128.2, 127.8, 127.7, 127.6, 126.4, 124.0, 123.4, 52.2, 32.3 ppm.

HRMS (ESI, M+Na^+) m/z calcd. for $C_{23}H_{21}NaO_2S$ 383.1080, found 383.1080.



2-((3,3-diphenylallyl)thio)pyridine: (3j)

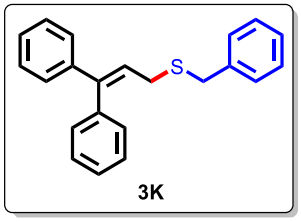
Physical Appearance: Colorless oily liquid.

R_f: 0.6 (2:98, Ethyl acetate: Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (ddd, *J* = 4.9, 1.9, 1.0 Hz, 1H), 7.45 (ddd, *J* = 9.2, 7.4, 1.9 Hz, 1H), 7.42-7.37 (m, 2H), 7.36-7.32 (m, 1H), 7.26-7.21 (m, 7H), 7.13 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.0 (ddd, *J* = 7.4, 4.9, 1.0 Hz, 1H), 6.27 (t, *J* = 7.8 Hz, 1H), 3.90 (d, *J* = 7.8 Hz, 2H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 149.6, 144.4, 142.1, 139.3, 136.0, 130.1, 128.5, 128.2, 127.7, 127.6, 127.5, 124.3, 122.3, 119.5, 30.1 ppm.

HRMS (ESI, M+H$^+$) m/z calcd. for $C_{20}H_{18}NS$ 304.1155, found 304.1154.



benzyl(3,3-diphenylallyl)sulfane: (3k)

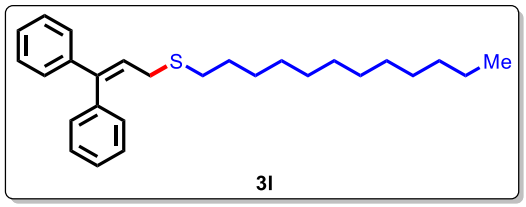
Physical Appearance: Colorless oily liquid.

R_f: 0.6 (2:98, Ethyl acetate: Petroleum ether).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.36 (m, 3H), 7.34-7.23 (m, 10H), 7.20-7.18 (m, 2H), 6.17 (t, *J* = 7.8 Hz, 1H), 3.70 (s, 2H), 3.26 (d, *J* = 7.8 Hz, 2H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 142.1, 139.1, 138.5, 130.2, 128.8, 128.4, 128.3, 128.2, 127.6, 127.4, 126.9, 125.3, 35.9, 30.9 ppm.

HRMS (ESI, M+H$^+$) m/z calcd. for $C_{22}H_{21}S$ 309.1671, found 309.1671.



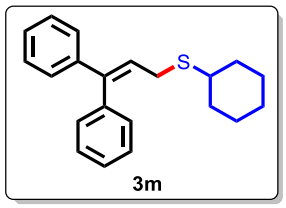
(3,3-diphenylallyl)(dodecyl)sulfane: (3l)[2]

Physical Appearance: Colorless oily liquid.

R_f: 0.6 (2:98, Ethyl acetate: Petroleum ether).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.37 (m, 3H), 7.32-7.27 (m, 5H), 7.24-7.22 (m, 2H), 6.17 (t, *J* = 7.9 Hz, 1H), 3.27 (d, *J* = 7.9 Hz, 2H), 2.46 (d, *J* = 7.4 Hz, 2H), 1.42 (quint, *J* = 6.0 Hz, 2H), 1.34-1.25 (m, 18H), 0.91 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 142.1, 139.3, 130.2, 128.4, 128.3, 127.6, 127.5, 125.7, 32.1, 31.3, 30.9, 29.81, 29.79, 29.77, 29.74, 29.66, 29.5, 29.4, 29.0, 22.8, 14.3 ppm.



cyclohexyl(3,3-diphenylallyl)sulfane: (3m)

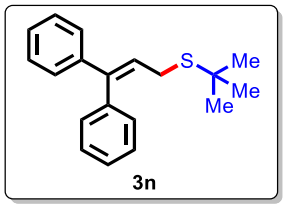
Physical Appearance: Colorless oily liquid.

R_f: 0.6 (2:98, Ethyl acetate: Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.32 (m, 2H), 7.28-7.24 (m, 6H), 7.23-7.21 (m, 2H), 6.16 (t, *J* = 7.9 Hz, 1H), 3.27 (d, *J* = 7.9 Hz, 2H), 2.60 (m, 1H), 1.81-1.77 (m, 2H), 1.70-1.69 (m, 2H), 1.31-1.16 (m, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 142.2, 139.3, 130.1, 128.34, 128.28, 127.6, 127.5, 127.4, 126.0, 42.9, 33.7, 29.5, 26.3, 25.9 ppm.

HRMS (ESI, M+H$^+$) m/z calcd. for $C_{21}H_{25}S$ 309.1671, found 309.1671.



tert-butyl(3,3-diphenylallyl)sulfane: (3n)

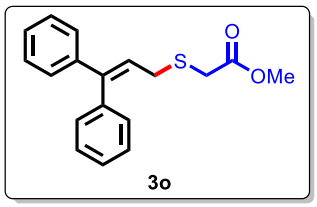
Physical Appearance: Colorless oily liquid.

R_f: 0.6 (2:98, Ethyl acetate: Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.31 (m, 3H), 7.30-7.21 (m, 7H), 6.15 (t, *J* = 7.8 Hz, 1H), 3.28 (d, *J* = 7.8 Hz, 2H), 1.28 (s, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 142.3, 139.3, 130.0, 128.3, 128.2, 127.6, 127.5, 127.4, 125.7, 42.8, 31.1, 28.7 ppm.

HRMS (ESI, M+H$^+$) m/z calcd. for $C_{19}H_{23}S$ 281.1515, found 281.1524.



methyl 2-((3,3-diphenylallyl)thio)acetate: (3o)

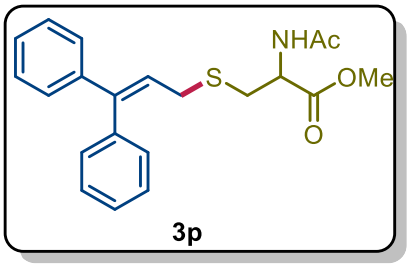
Physical Appearance: Colorless oily liquid.

R_f: 0.6 (2:98, Ethyl acetate: Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.34 (m, 3H), 7.29-7.23 (m, 5H), 7.21-7.19 (m, 2H), 6.15 (t, *J* = 8.0 Hz, 1H), 3.59 (s, 3H), 3.38 (d, *J* = 7.8 Hz, 2H), 3.20 (s, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 145.1, 141.8, 138.9, 130.1, 128.4, 128.3, 127.7, 127.6, 127.5, 123.9, 52.4, 32.9, 31.9 ppm.

HRMS (ESI, M+H$^+$) m/z calcd. for $C_{18}H_{18}NaO_2S$ 321.0920, found 321.0929.



methyl N-acetyl-S-(3,3-diphenylallyl)cysteinate (3p)

Physical Appearance: Colorless oily liquid.

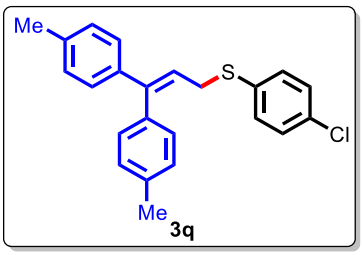
R_f: 0.4 (3:7, Ethyl acetate: Petroleum ether).

IR (neat) 3049, 2929, 1737, 1680, 1570, 1451, 1000, 819, 721 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.33 (m, 3H), 7.30-7.19 (m, 7H), 6.13-6.07 (m, 2H), 4.77-4.72 (m, 1H), 3.67 (s, 3H), 3.25 (d, *J* = 8.0 Hz, 2H), 2.98 (dd, *J* = 13.9, 4.7 Hz, 1H), 2.90 (dd, *J* = 13.9, 4.7 Hz, 1H), 1.92 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 169.8, 144.8, 141.6, 138.9, 130.0, 128.4, 128.2, 127.63, 127.61, 127.4, 124.0, 52.6, 52.1, 33.7, 32.2, 23.0, 14.3 ppm.

HRMS (ESI, M+Na^+) m/z calcd. for $C_{21}H_{23}NNaO_3S$ 392.1296, found 392.1296.



(4-chlorophenyl)(3,3-di-p-tolylallyl)sulfane: (3q)

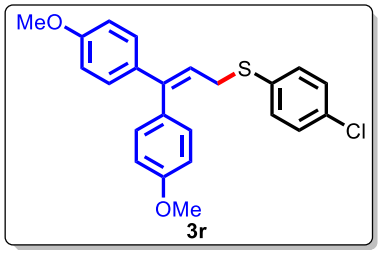
Physical Appearance: Colorless oily liquid.

R_f: 0.6 (2:98, Ethyl acetate: Petroleum ether).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20-7.16 (m, 6H), 7.07-7.06 (m, 4H), 7.0 (d, *J* = 8.0 Hz, 2H), 6.06 (t, *J* = 7.7 Hz, 1H), 3.62 (d, *J* = 7.7 Hz, 2H), 2.40 (s, 3H), 2.33 (s, 3H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.8, 139.3, 137.5, 137.3, 136.1, 134.5, 132.3, 131.6, 129.9, 129.04, 128.97, 128.9, 127.5, 122.8, 34.2, 21.4, 21.2 ppm.

HRMS (ESI, M+H^+) m/z calcd. for $C_{23}H_{22}ClS$ 365.1125, found 365.1132.



(3,3-bis(4-methoxyphenyl)allyl)(4-chlorophenyl)sulfane: (3r)

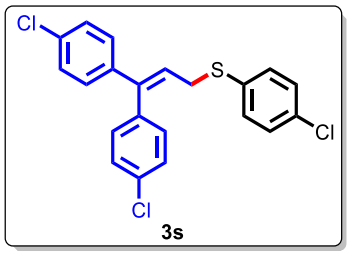
Physical Apperance: Colorless oily liquid.

R_f: 0.6 (2:98, Ethyl acetate: Petroleum ether).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20-7.15 (m, 4H), 7.10 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 5.98 (t, *J* = 7.8 Hz, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 3.63 (d, *J* = 7.8 Hz, 2H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 159.0, 144.1, 134.9, 134.6, 132.3, 131.6, 131.4, 131.2, 128.9, 128.8, 121.7, 113.7, 113.6, 55.39, 55.37, 34.3 ppm.

HRMS (ESI, M+H$^+$) m/z calcd. for $C_{23}H_{22}ClO_2S$ 397.1024, found 347.1015.



(3,3-bis(4-chlorophenyl)allyl)(4-chlorophenyl)sulfane: (3s)

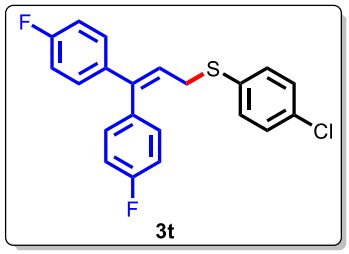
Physical Apperance: Colorless oily liquid.

R_f: 0.6 (2:98, Ethyl acetate: Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.23-7.16 (m, 6H), 7.05 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.10 (t, *J* = 7.8 Hz, 1H), 3.56 (d, *J* = 7.8 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 139.9, 136.8, 133.90, 133.86, 133.8, 133.0, 132.4, 131.3, 129.1, 128.8, 128.6, 124.9, 34.4 ppm.

HRMS (ESI, M+Na+) m/z calcd. for $C_{21}H_{15}Cl_3NaS$ 426.9852, found 426.9877.



(3,3-bis(4-fluorophenyl)allyl)(4-chlorophenyl)sulfane: (3t)

Physical Apperance: Colorless oily liquid.

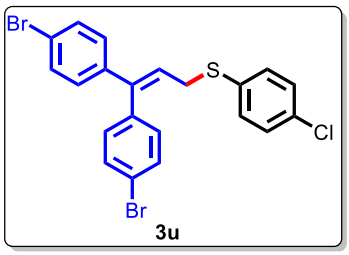
R_f: 0.6 (2:98, Ethyl acetate: Petroleum ether).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24-7.19 (m, 4H), 7.14-6.96 (m, 8H), 6.08 (t, J = 7.9 Hz, 1H), 3.60 (d, J = 7.9 Hz, 2H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.56 (d, J^1 = 247.6 Hz), 162.34 (d, J^1 = 247.6 Hz), 142.8, 137.9 (d, J^4 = 3.9 Hz), 134.6 (d, J^4 = 3.4 Hz), 134.0, 132.8, 132.1, 131.6 (d, J^3 = 8.0 Hz), 129.2 (d, J^3 = 8.0 Hz), 129.0, 124.0, 115.5 (d, J^2 = 21.4 Hz), 115.3 (d, J^2 = 21.2 Hz), 34.3 ppm.

^{19}F NMR (470 MHz, $CDCl_3$): δ -114.0, -114.4 ppm.

HRMS (ESI, M+H$^+$) m/z calcd. for $C_{21}H_{16}ClF_2S$ 373.0624, found 373.0612.



(3,3-bis(4-bromophenyl)allyl)(4-chlorophenyl)sulfane: (3u)

Physical Apperance: Colorless oily liquid.

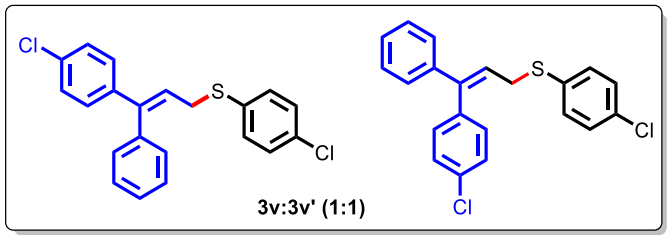
R_f: 0.6 (2:98, Ethyl acetate: Petroleum ether).

IR (neat) 3051, 1904, 1586, 1487, 1475, 1396, 1094, 1010, 820, 739 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 8.6 Hz, 2H), 7.22-7.16 (m, 4H), 7.00 (d, J = 8.6 Hz, 2H), 6.89 (d, J = 8.3 Hz, 2H), 6.12 (t, J = 7.8 Hz, 1H), 3.56 (d, J = 7.9 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 140.2, 137.1, 133.6, 132.9, 132.3, 131.6, 131.5, 131.4, 129.02, 129.01, 124.9, 122.01, 121.98, 34.3 ppm.

HRMS (ESI, M+Na+) m/z calcd. for $C_{21}H_{15}Br_2ClNaS$ 516.8821, found 516.8837.



(4-chlorophenyl)(3-(4-chlorophenyl)-3-phenylallyl)sulfane: (3v)

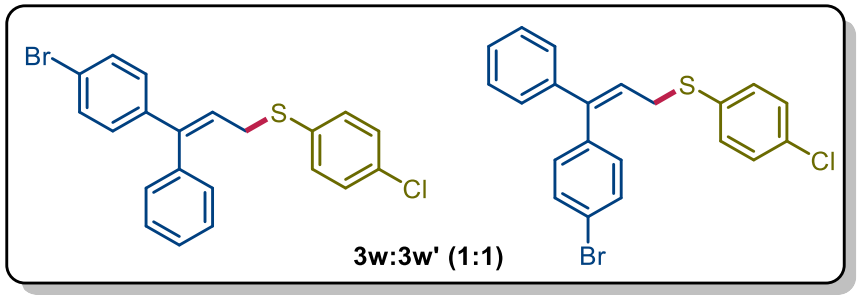
Physical Apperance: Colorless oily liquid.

R_f: 0.6 (2:98, Ethyl acetate: Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.33 (m, 5H), 7.29-7.27 (m, 3H), 7.25-7.14 (m, 12H), 7.10 (d, *J* = 8.6 Hz, 2H), 7.06-7.04 (m, 2H), 7.00 (d, *J* = 8.3 Hz, 2H), 6.17-6.09 (m, 2H), 3.62-3.58 (m, 4H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.64, 143.61, 141.4, 140.3, 138.3, 137.2, 134.0, 133.9, 133.6, 133.5, 132.7, 132.6, 132.2, 131.8, 131.2, 129.8, 129.4, 128.97, 128.95, 128.8, 128.6, 128.43, 128.38, 128.3, 127.83, 127.8, 127.5, 124.3, 34.3, 34.1 ppm.

HRMS (ESI, M+Na+) m/z calcd. for $C_{21}H_{16}Cl_2NaS$ 393.0247, found 393.0270.



(3-(4-bromophenyl)-3-phenylallyl)(4-chlorophenyl)sulfane (3w)

Physical Apperance: Colorless oily liquid.

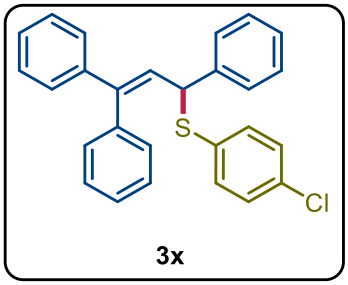
R_f: 0.6 (2:98, Ethyl acetate: Petroleum ether).

IR (neat) 3030, 2944, 1577, 1444, 1021, 811, 745 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.39-7.33 (m, 6H), 7.29-7.25 (m, 4H), 7.20-7.12 (m, 10H), 7.04-7.00 (m, 4H), 6.93-6.90 (m, 2H), 6.13 (t, *J* = 7.9 Hz, 1H), 6.10 (t, *J* = 7.9 Hz, 1H), 3.60 (d, *J* = 6.6 Hz, 2H), 3.57 (d, *J* = 6.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 143.6, 141.2, 140.7, 138.2, 137.7, 133.94, 133.86, 132.8, 132.6, 132.2, 131.9, 131.6, 131.5, 131.3, 129.8, 129.2, 129.1, 129.0, 128.9, 128.4, 128.3, 127.83, 127.79, 127.4, 124.4, 124.3, 121.7, 34.3, 34.1.

HRMS (ESI, M+Na^+) m/z calcd. for $C_{21}H_{17}BrClS$ 416.9897, found 416.9883.



(4-chlorophenyl)(1,3,3-triphenylallyl)sulfane (3x)

Physical Apperance: Colorless oily liquid.

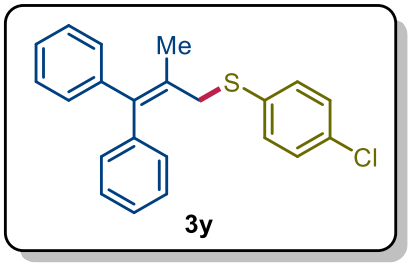
R_f: 0.6 (2:98, Ethyl acetate: Petroleum ether).

IR (neat) 3051, 2922, 1555, 1469, 1033, 831, 741 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.3 Hz, 2H), 7.40-7.35 (m, 5H), 7.32-7.28 (m, 4H), 7.21-7.17 (m, 6H), 6.96-6.94 (m, 2H), 6.43 (d, *J* = 11.0 Hz, 1H), 5.01 (d, *J* = 11.0 Hz, 1H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.1, 141.8, 140.2, 138.9, 134.9, 133.8, 133.0, 129.9, 128.94, 128.87, 128.3, 128.1, 127.9, 127.8, 127.71, 127.69, 127.66, 53.2 ppm.

HRMS (ESI, M+Na^+) m/z calcd. for $C_{27}H_{21}ClNaS$ 435.0950, found 435.0955.



(4-chlorophenyl)(2-methyl-3,3-diphenylallyl)sulfane (3y)

Physical Apperance: Colorless oily liquid.

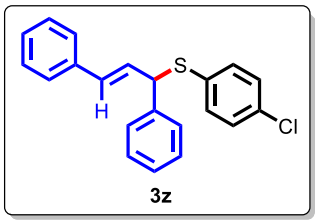
R_f: 0.6 (2:98, Ethyl acetate: Petroleum ether).

IR (neat) 3050, 2921, 1590, 1461, 1000, 839, 741 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.16 (m, 10H), 7.06-7.01 (m, 4H), 3.69 (s, 2H), 1.94 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 141.9, 141.7, 134.7, 132.4, 132.1, 129.6, 129.5, 129.4, 128.8, 128.1, 128.0, 126.8, 126.7, 40.5, 19.6 ppm.

HRMS (ESI, M+Na^+) m/z calcd. for $C_{22}H_{19}ClNaS$ 373.0794, found 373.0799.



3z

(E)-(4-chlorophenyl)(1,3-diphenylallyl)sulfane: (3z)

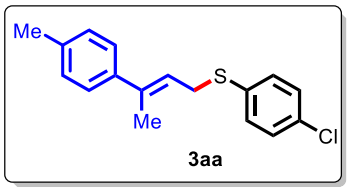
Physical Appearance: Colorless oily liquid.

R_f: 0.6 (2:98, Ethyl acetate: Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.3 Hz, 2H), 7.38-7.29 (m, 9H), 7.27-7.21 (m, 3H), 6.48 (dd, *J* = 15.5, 8.4 Hz, 1H), 6.34 (d, *J* = 15.5 Hz, 1H), 4.92 (d, *J* = 8.3 Hz, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 136.6, 134.6, 133.8, 133.4, 131.9, 129.0, 128.8, 128.7, 128.0, 127.9, 127.8, 126.6, 57.0 ppm.

HRMS (ESI, M+H^+) m/z calcd. for $C_{21}H_{18}ClS$ 337.0812, found 337.0826.



3aa

(E)-(4-chlorophenyl)(3-phenylbut-2-en-1-yl)sulfane: (3aa)

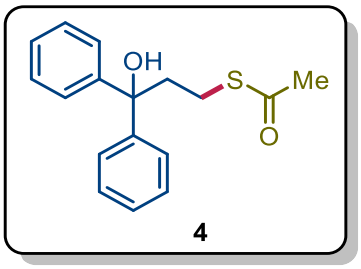
Physical Apperance: Colorless oily liquid.

R_f: 0.6 (2:98, Ethyl acetate: Petroleum ether).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.25-7.23 (m, 4H), 7.13 (d, *J* = 7.8 Hz, 2H), 5.83 (t, *J* = 8.0 Hz, 1H), 3.70 (d, *J* = 7.8 Hz, 2H), 2.34, (s, 3H), 1.93 (s, 3H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.1, 138.8, 137.2, 134.8, 132.7, 132.2, 129.1, 129.0, 125.7, 121.7, 33.5, 21.2, 15.9 ppm.

HRMS (ESI, M+H$^+$) m/z calcd. for $C_{17}H_{18}ClS$ 289.0182, found 289.0188.



4

S-(3-hydroxy-3,3-diphenylpropyl) ethanethioate (4)

Physical Apperance: Colorless oily liquid.

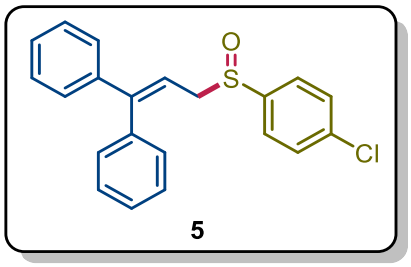
R_f: 0.5 (1:9, Ethyl acetate: Petroleum ether).

IR (neat) 3493, 3049, 2945, 1755, 1715, 1565, 1455, 1011, 861, 766 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.6 Hz, 4H), 7.32 (t, *J* = 7.4 Hz, 4H), 7.23 (t, *J* = 7.2 Hz, 2H), 2.84-2.81 (m, 2H), 2.58-2.55 (m, 2H), 2.30 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 196.6, 146.2, 128.3, 127.1, 126.0, 42.1, 30.6, 24.4.

HRMS (ESI, M+Na$^+$) m/z calcd. for $C_{17}H_{18}NaO_2S$ 309.0925, found 309.0929.



5

(3-((4-chlorophenyl)sulfinyl)prop-1-ene-1,1-diyl)dibenzene (5)

In a reaction tube equipped with a magnetic stirring bar was dissolved sulphide **3a** (67 mg, 0.2 mmol) in2 mL of DCM. To this solution was added *m*-CPBA (56 mg, 0.21 mmol, 1.05 equiv) at 0 °C and the resulting solution was stirred at room temperature for 5 h. After completion, the reaction was quenched with sat $NaHCO_3$ and extraction with DCM (4 x 10 mL). The organics were dried over Na_2SO_4, evaporated and chromatographed with ethyl acetate in petroleum ether to give sulfoxide **5** in 94 % yield (66 mg) as a colorless liquid.

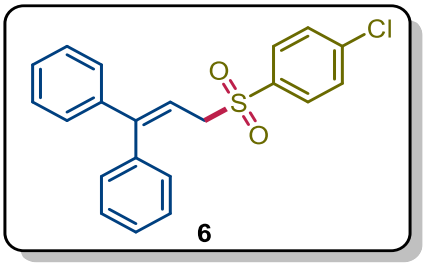
R_f: 0.4 (3:7, Ethyl acetate: Petroleum ether).

IR (neat) 3062, 2954, 1578, 1466, 1012, 821, 761 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.41 (m, 4H), 7.32-7.32 (m, 3H), 7.27-7.26 (m, 3H), 7.17-7.15 (m, 2H), 6.93-6.92 (m, 2H), 6.04 (t, *J* = 7.7 Hz, 1H), 3.75-3.71 (m, 1H), 3.64-3.60 (m, 1H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 141.1, 138.3, 137.3, 129.6, 129.3, 128.4, 128.3, 128.2, 127.8, 127.4, 125.8, 114.4, 57.4 ppm.

HRMS (ESI, M+Na^+) m/z calcd. for $C_{21}H_{17}ClNaOS$ 375.0586, found 375.0580.



(3-((4-chlorophenyl)sulfonyl)prop-1-ene-1,1-diyl)dibenzene (6)

In a reaction tube equipped with a magnetic stirring bar was dissolved sulphide **3a** (67 mg, 0.2 mmol) in 2 mL of DCM. To this solution was added *m*-CPBA (116 mg, 0.44 mmol, 2.2 equiv) at 0 °C and the resulting solution was stirred at room temperature for 6 h. After completion, the reaction was quenched with sat $NaHCO_3$ and extraction with DCM (3 x 10 mL). The organics were dried over Na_2SO_4, evaporated and chromatographed with ethyl acetate in petroleum ether to give sulfone **6** in 60 % yield (44 mg) as a colorless liquid.

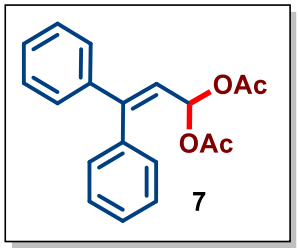
R_f: 0.4 (1:9, Ethyl acetate: Petroleum ether).

IR (neat) 3061, 2925, 2850, 1712, 1583, 1475, 1319, 1142, 1088, 761, 703, 550 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.31-7.23 (m, 6H), 7.18-7.15 (m, 2H), 6.71 (dd, *J* = 7.8, 1.5 Hz, 2H), 6.12 (t, *J* = 8.0 Hz, 1H), 3.95 (d, *J* = 8.0 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 140.8, 140.6, 137.7, 137.2, 130.0, 129.5, 129.2, 128.53, 128.50, 128.0, 127.6, 113.7, 57.5 ppm.

HRMS (ESI, M+Na^+) m/z calcd. for $C_{21}H_{17}ClO_2S$ 391.0530, found 391.0529.



3,3-diphenylprop-2-ene-1,1-diyl diacetate (7)

A solution of sulfide **3a** (67 mg, 0.2 mmol), tetrabutylammonium bromide (TBABr, 193 mg, 0.6 mmol, 3.0 equiv) and $PhI(OAc)_2$ (129 mg, 0.4 mmol, 2.0 equiv) in dichloromethane (2 mL) was stirred in reaction tube at room temperature for 6 h under nitrogen atmosphere. The reaction was then concentrated in vacuum and purified by column chromatography using petroleum ether/ethyl acetate to afford corresponding product **7** in 54% (33 mg) isolated yield.

Physical Apperance: Colorless oily liquid.

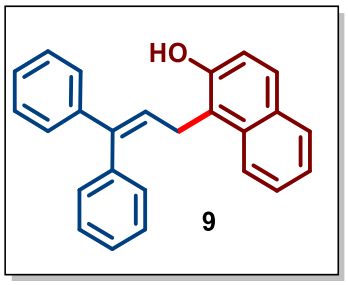
R_f: 0.4 (1:9, Ethyl acetate: Petroleum ether).

IR (neat) 3031, 2933, 1732, 1588, 1452, 1011, 833, 741 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.40 (m, 3H), 7.34-7.28 (m, 5H), 7.24 (d, J = 7.8 Hz, 2H), 7.17 (d, J = 8.1 Hz, 1H), 6.15 (d, J = 8.1 Hz, 1H), 2.10 (s, 6H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4, 148.5, 140.7, 137.9, 129.6, 128.6, 128.5, 128.4, 128.3, 127.8, 121.1, 88.3, 21.1 ppm.

HRMS (ESI, M+Na^+) m/z calcd. for $C_{19}H_{18}NaO_4$ 333.1103, found 333.1102.



1-(3,3-diphenylallyl)naphthalen-2-ol (9)

A reaction tube was charged with sulfoxide **5** (70 mg, 0.2 mmol), 2-naphthol **8** (58 mg, 0.4 mmol), and CH_2Cl_2 (2.0 mL). To the tube was added trifluoroacetic anhydride (42 μL, 0.3 mmol) in one portion, and the resulting solution was stirred at 25 °C for 1 h. After the reaction, saturated aqueous $NaHCO_3$ was added and the resulting biphasic solution was extracted with EtOAc (10 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under

reduced pressure. The residue was purified by column chromatography using petroleum ether/ethyl acetate as eluent to provide **9** (40 mg, 60 %) as a colorless oil.

Rf: 0.4 (1:9, Ethyl acetate: Petroleum ether).

IR (neat) 3498, 3030, 2944, 1588, 1478, 1021, 822, 766 cm^{-1}.

1H NMR (400 MHz, CDCl3) δ 7.81-7.78 (m, 2H), 7.66 (d, *J* = 9.0 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.47-7.42 (m, 4H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.22-7.16 (m, 5H), 7.08 (d, *J* = 8.9 Hz, 1H), 6.20 (d, *J* = 7.2 Hz, 1H), 5.04 (br. s, 1H), 3.90 (d, *J* = 7.3 Hz, 2H).

13C NMR (100 MHz, CDCl3) δ 151.2, 142.6, 142.1, 139.7, 133.2, 130.2, 129.5, 128.8, 128.7, 128.3, 128.2, 127.9, 127.4, 127.3, 127.0, 126.6, 123.25, 123.19, 118.1, 118.0, 26.0.

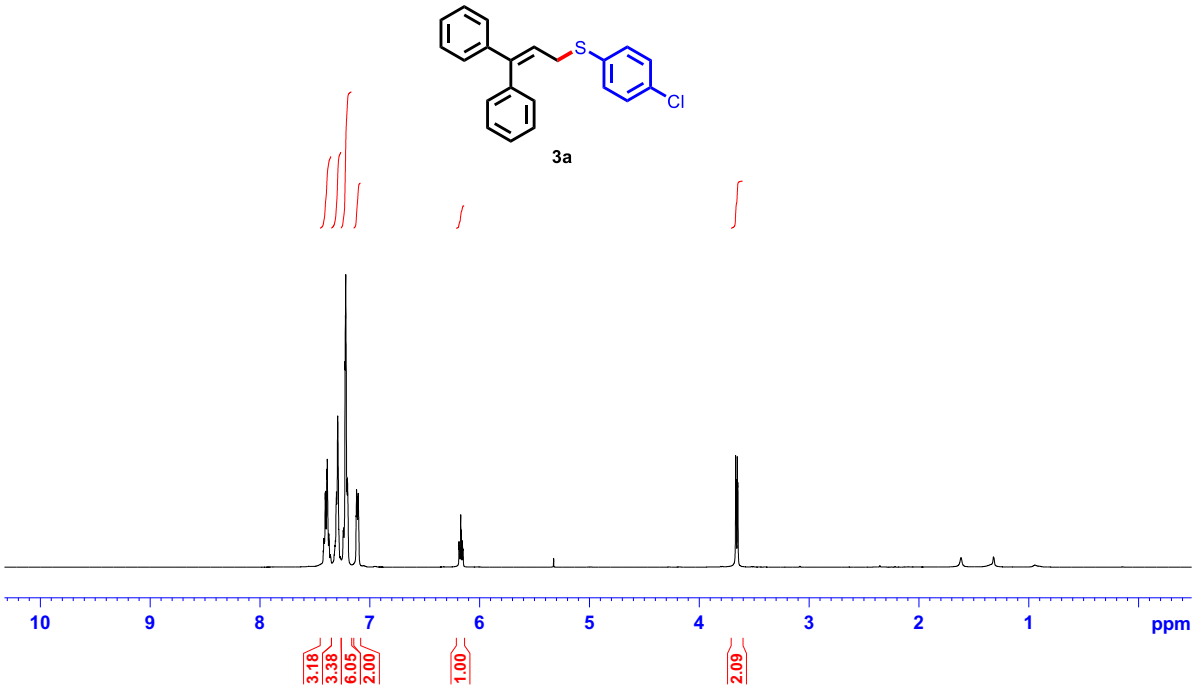
HRMS (ESI, M+Na^+) m/z calcd. for $C_{25}H_{20}NaO$ 359.1412, found 359.1419.

References

1) (a) X.-Q. Hu, Z. Hu, A. S. Trita, G. Zhang and L. J. Goossen, *Chem. Sci*., **2018**, *9*, 5289; (b) S. Sarkar, A. Banerjee, W. Yao, E. V. Patterson and M.-Y. Ngai, *ACS Catal*., **2019**, *9*, 10358; (c)

2) G. Guo, Y. Yuan, S. Wan, X. Cao, Y. Sun and C. Huo, *Org. Chem. Front.,* **2021**, *8*, 2990.

CMRV-AN-4-DA-1H



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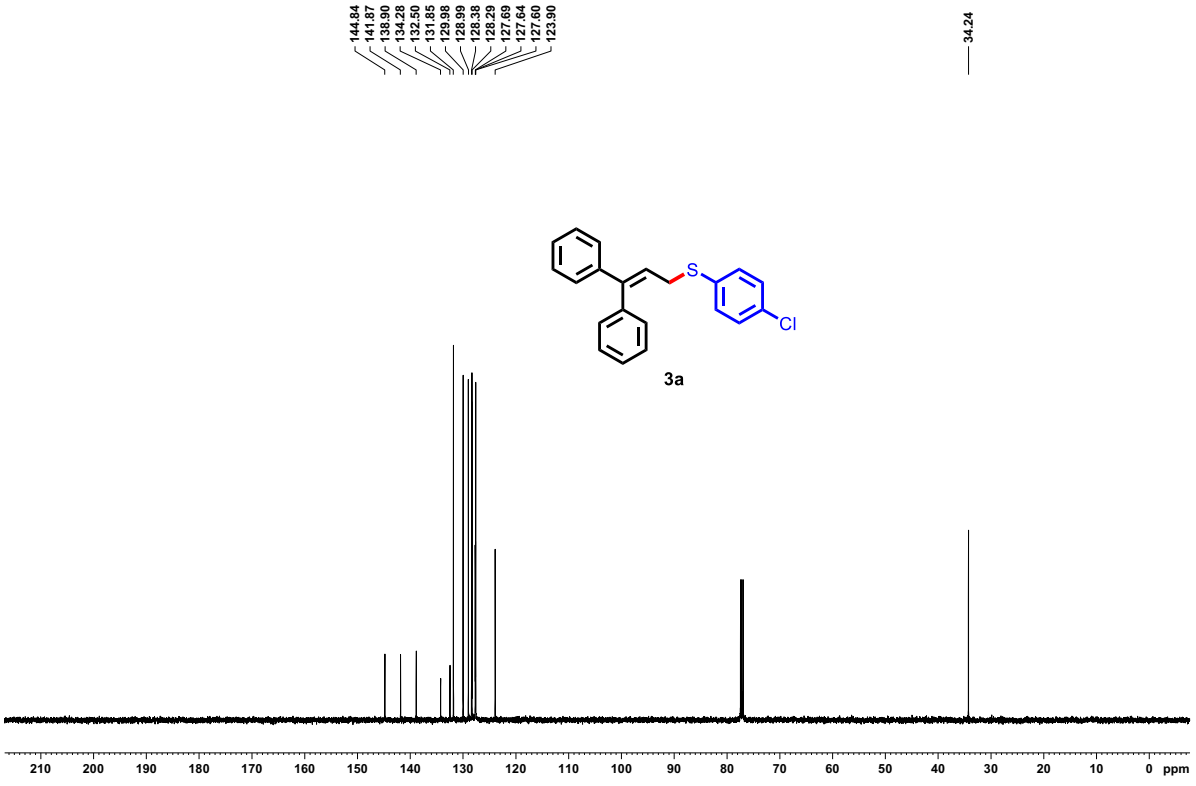

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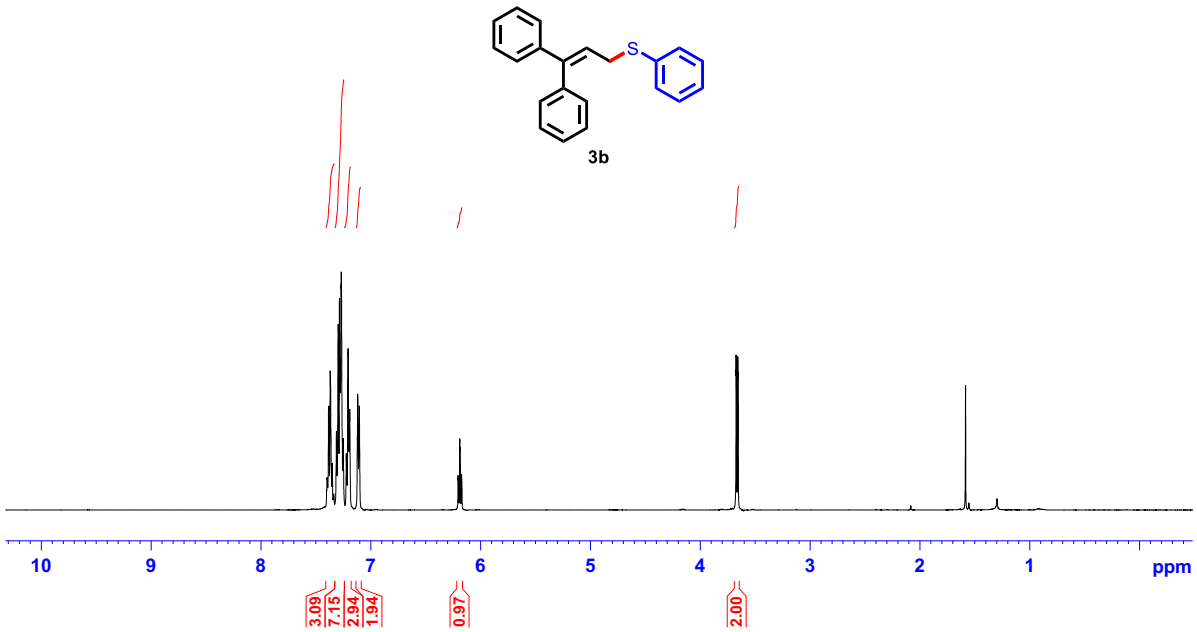

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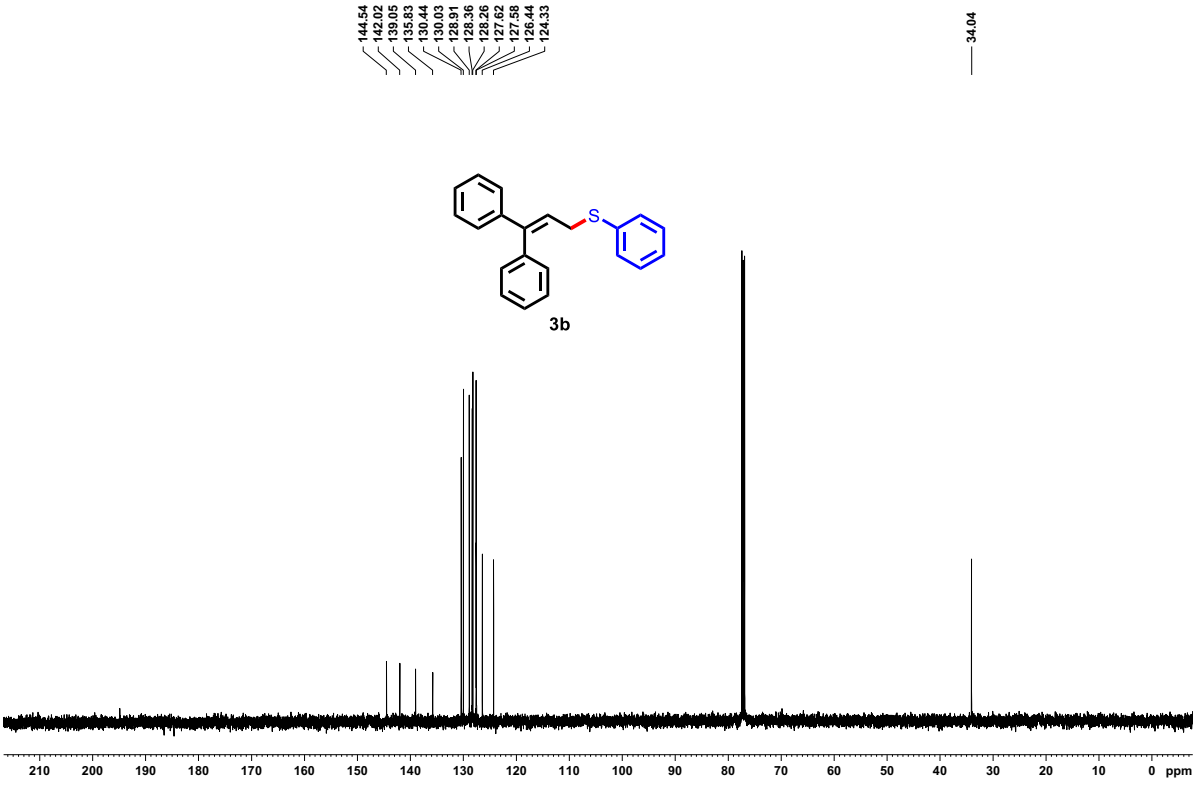

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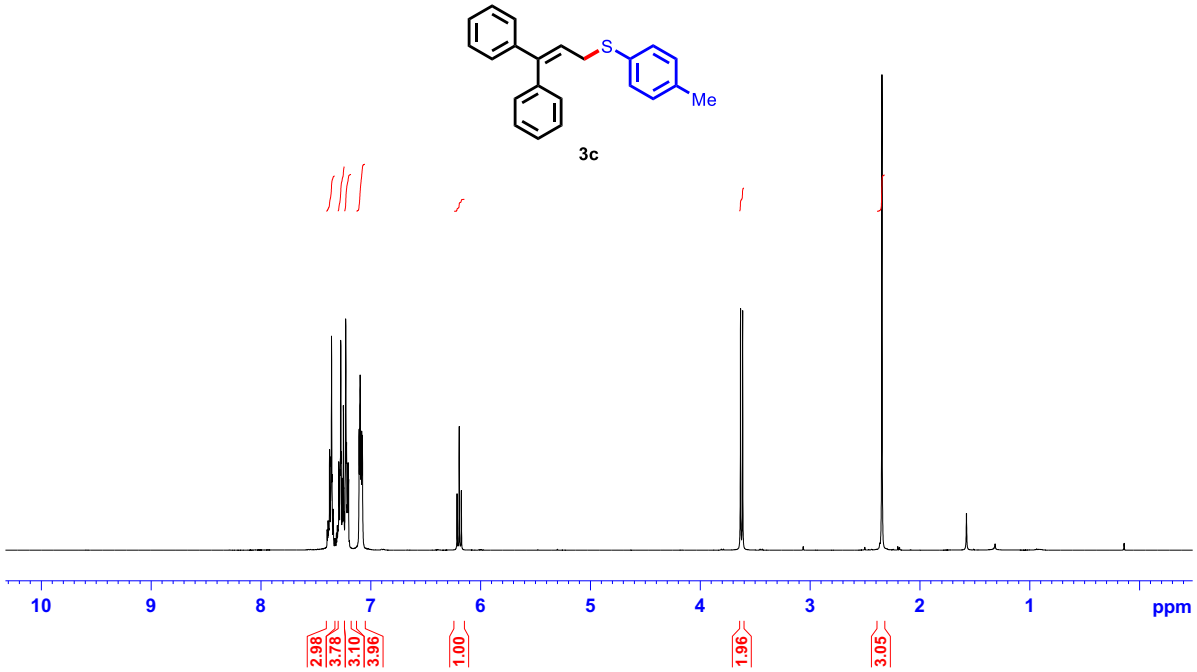

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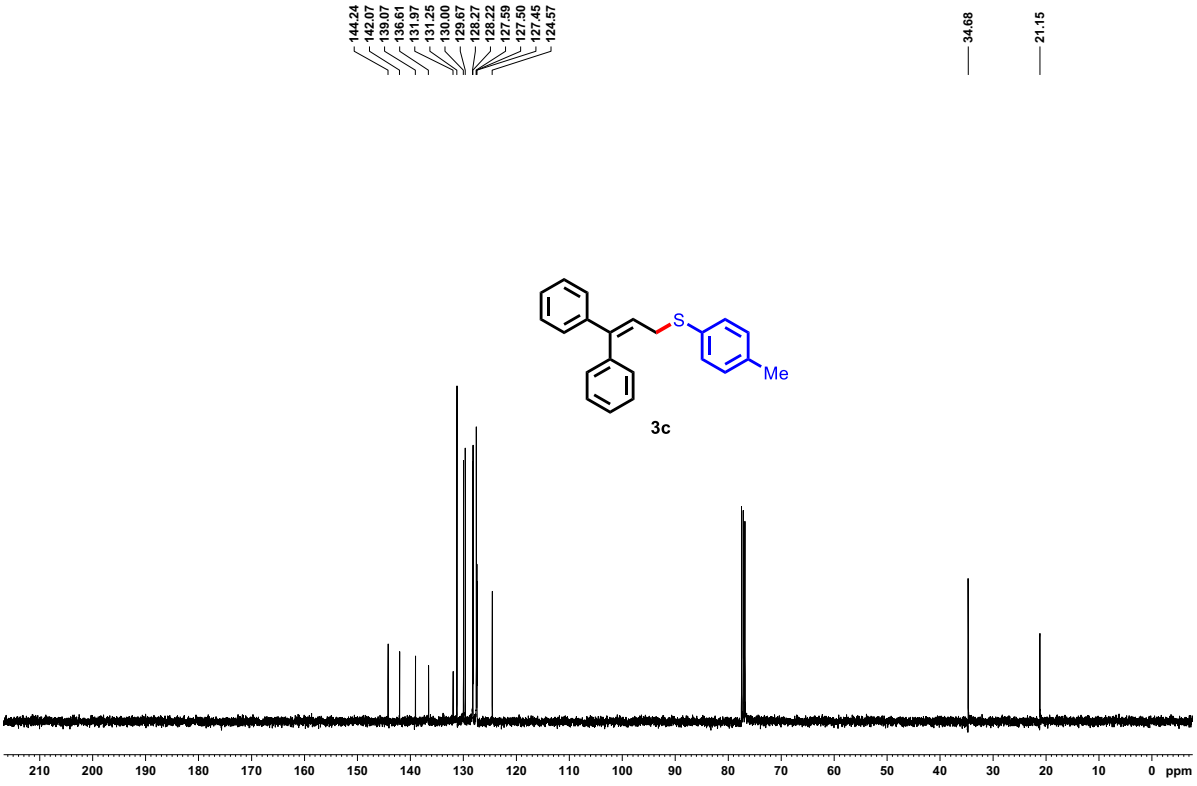

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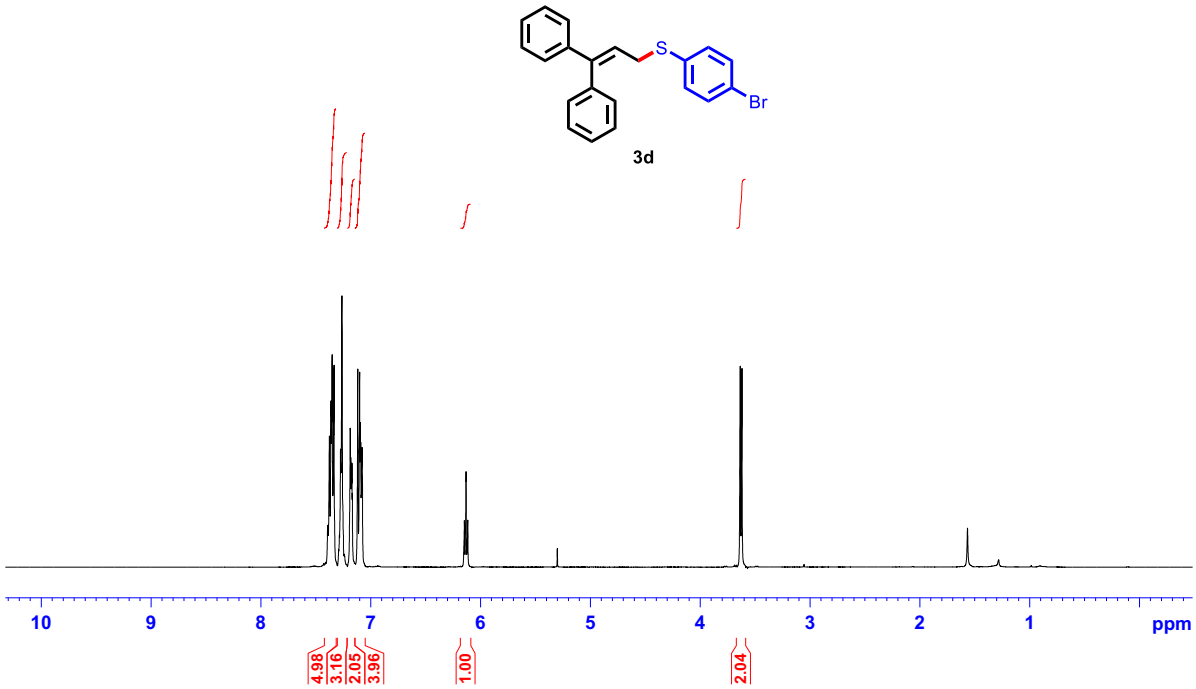

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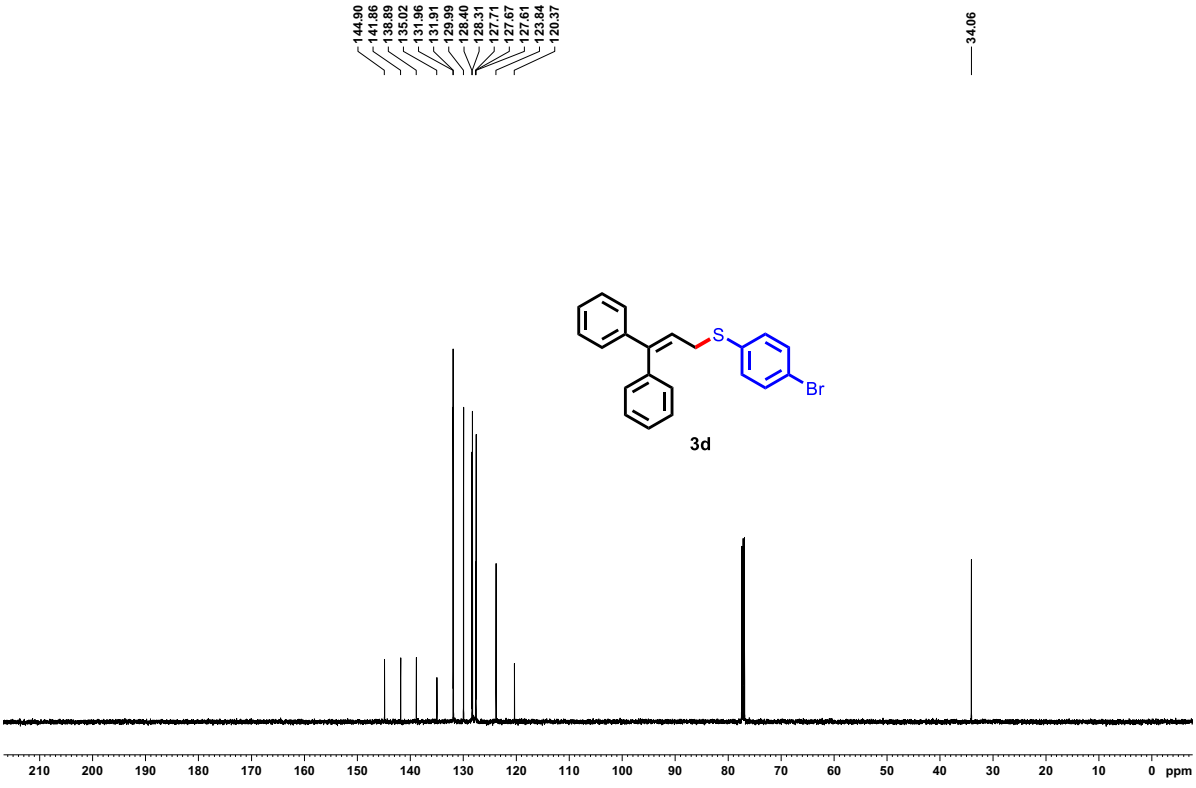

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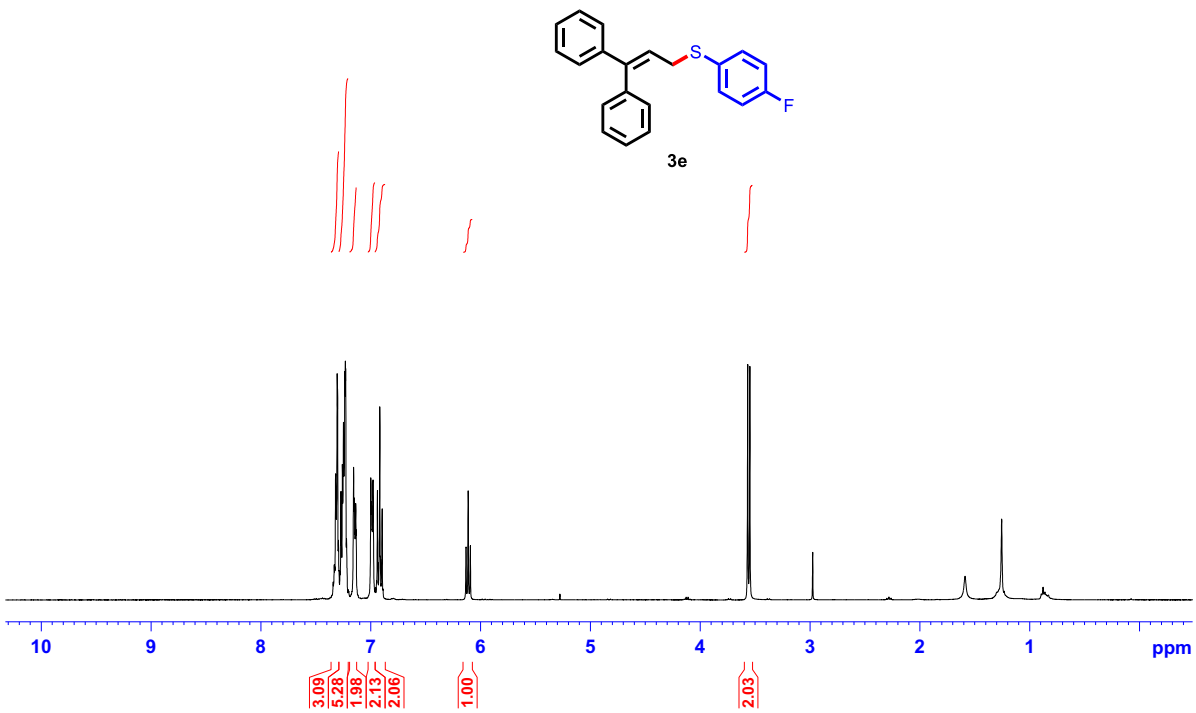

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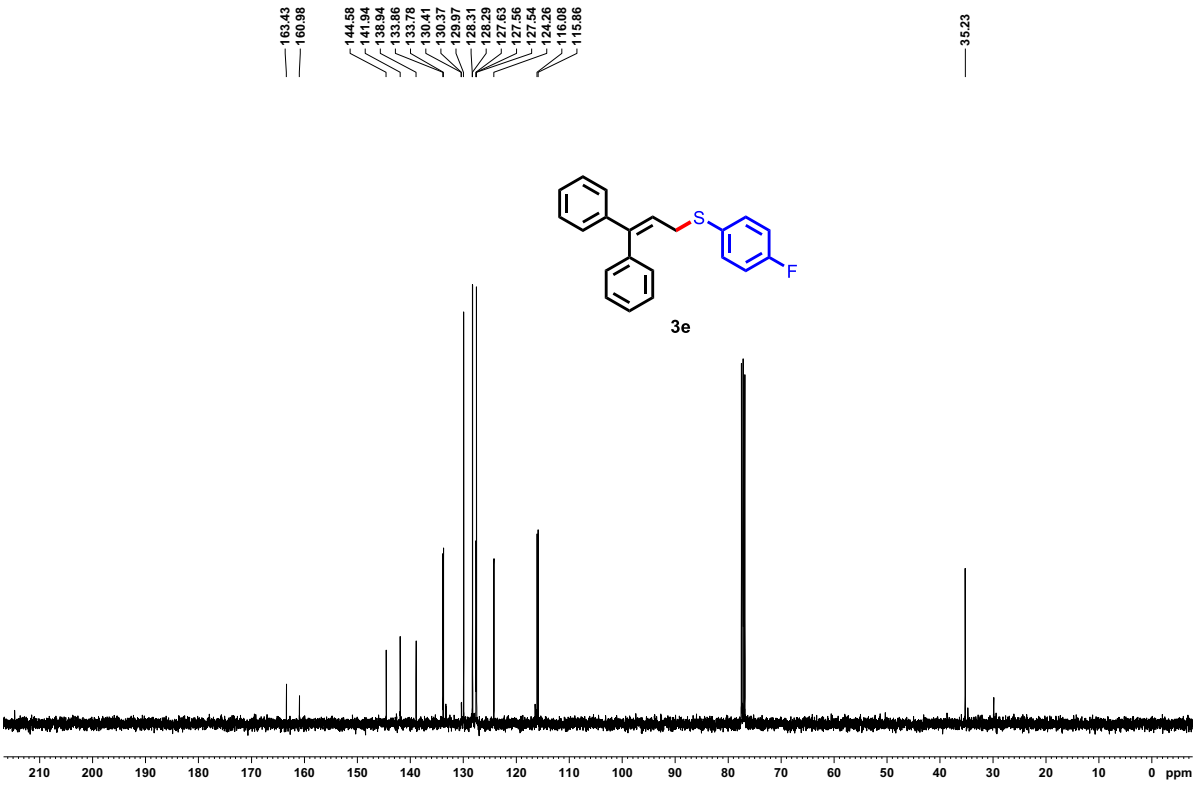

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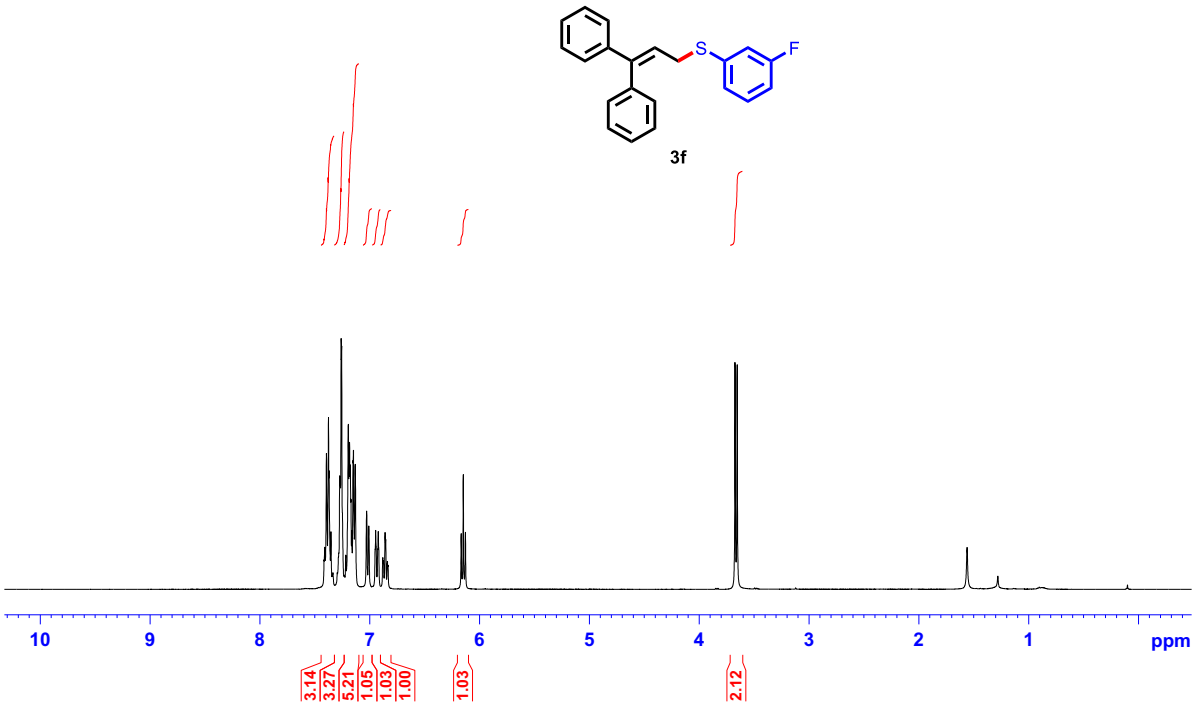

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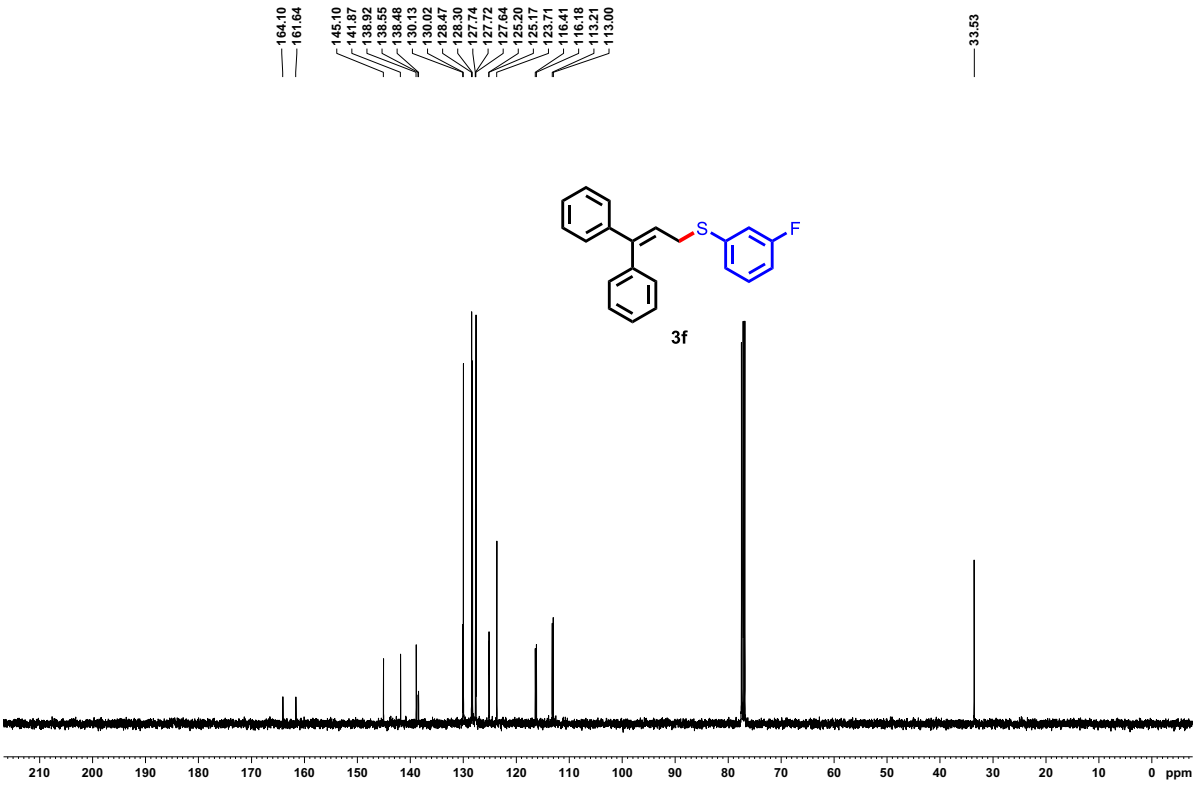

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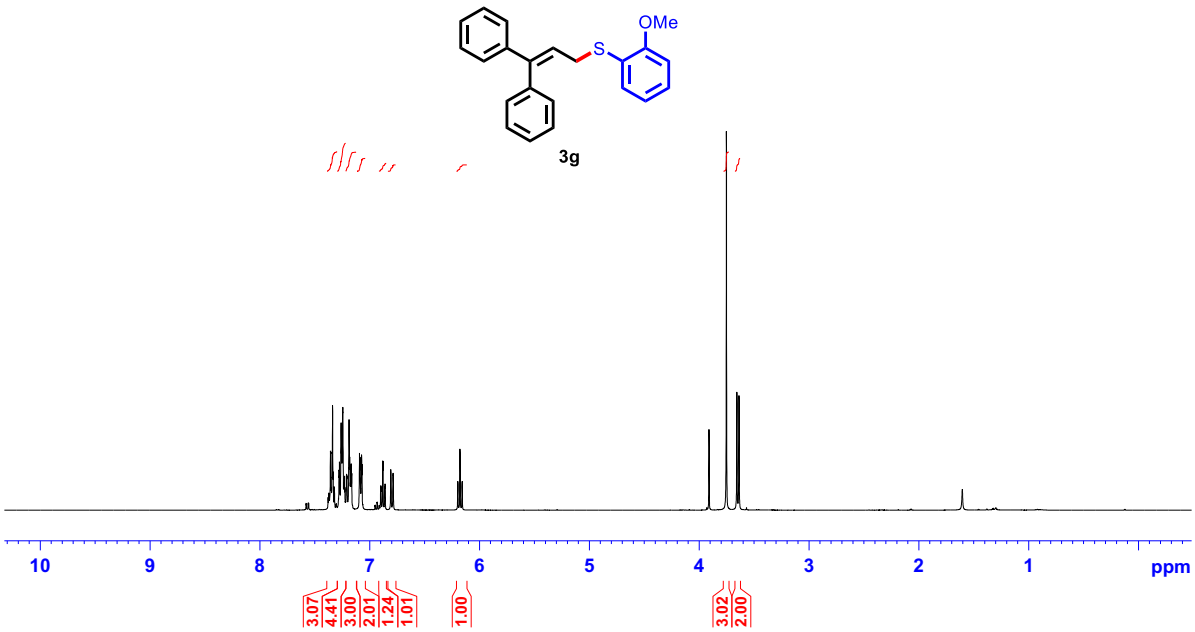

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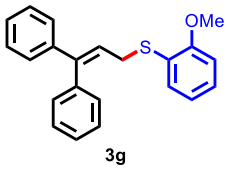

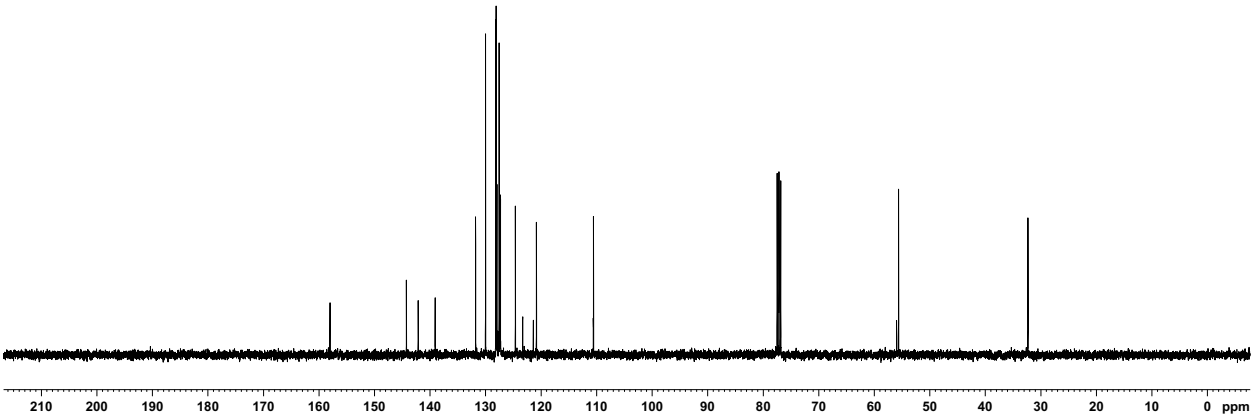

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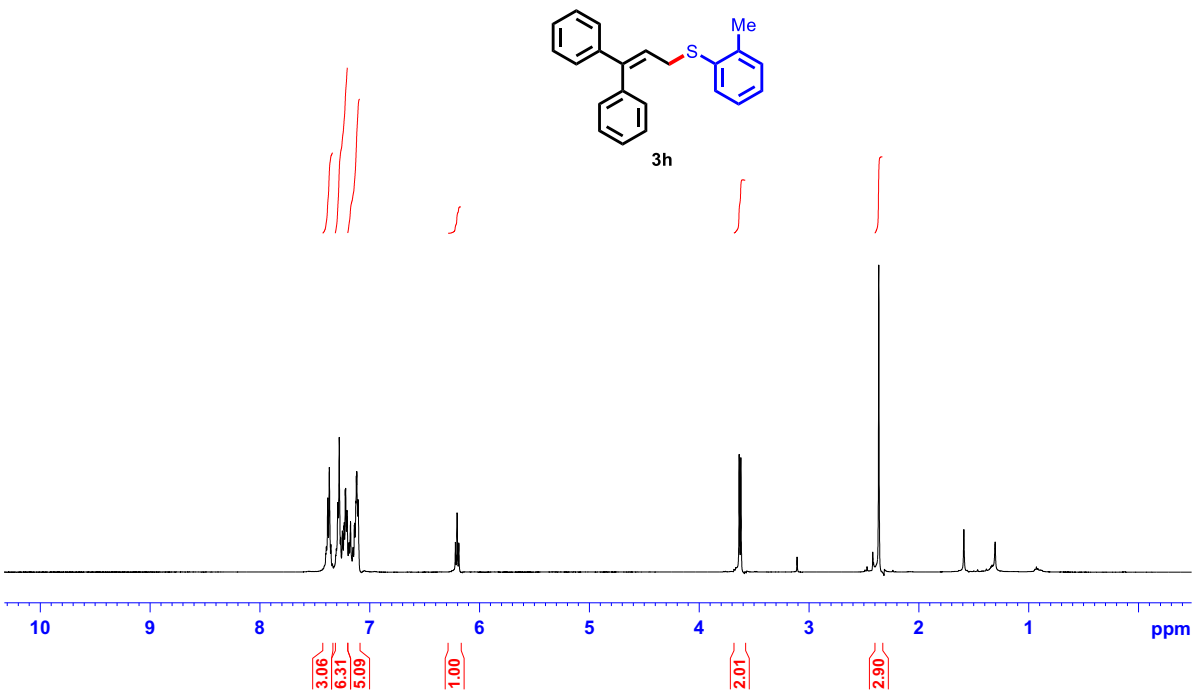

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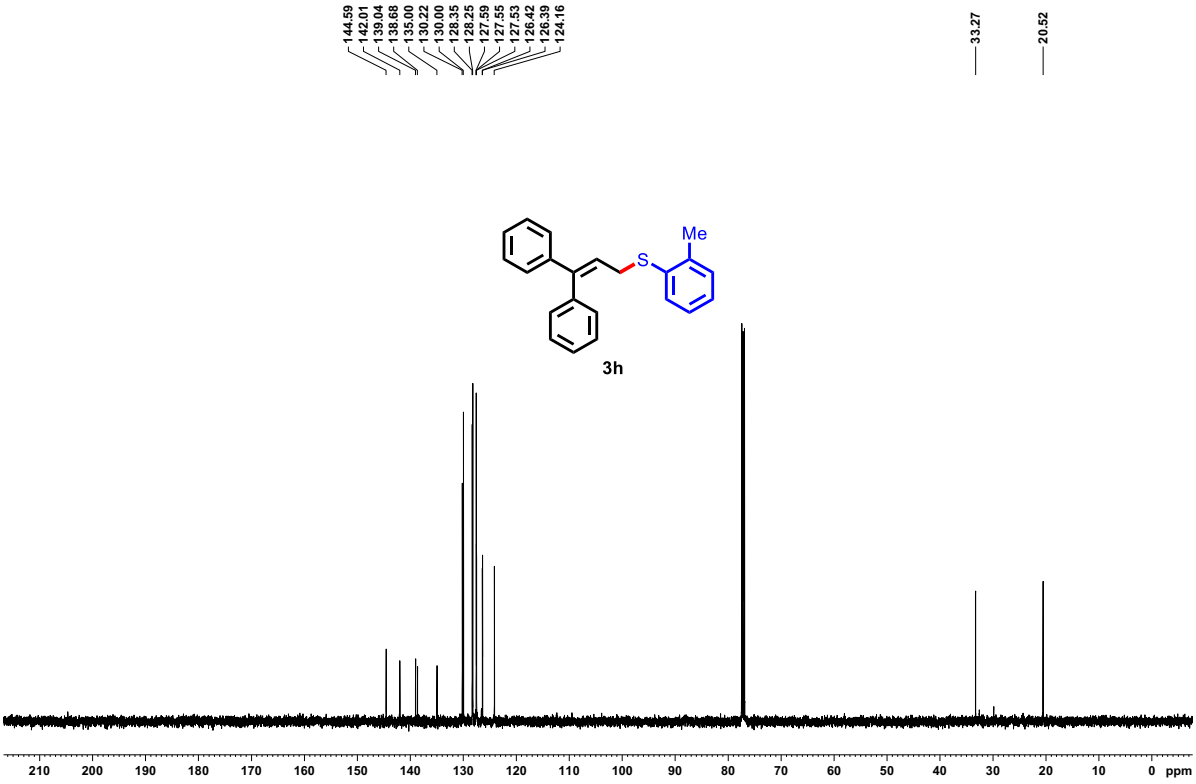

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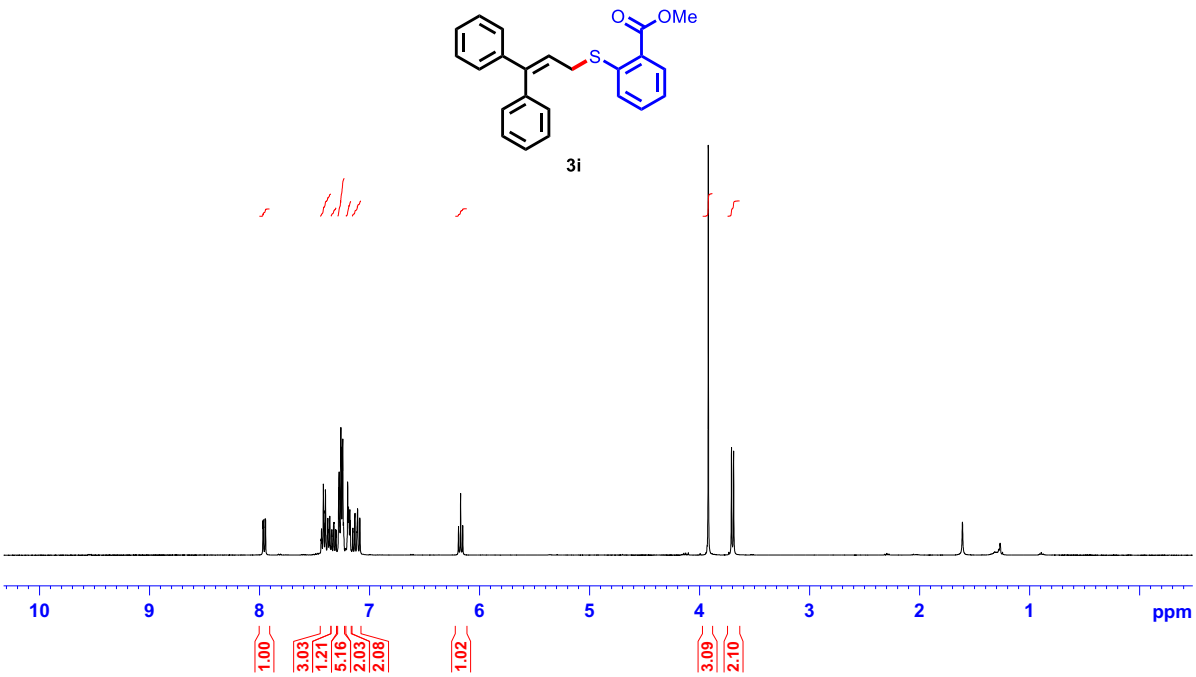

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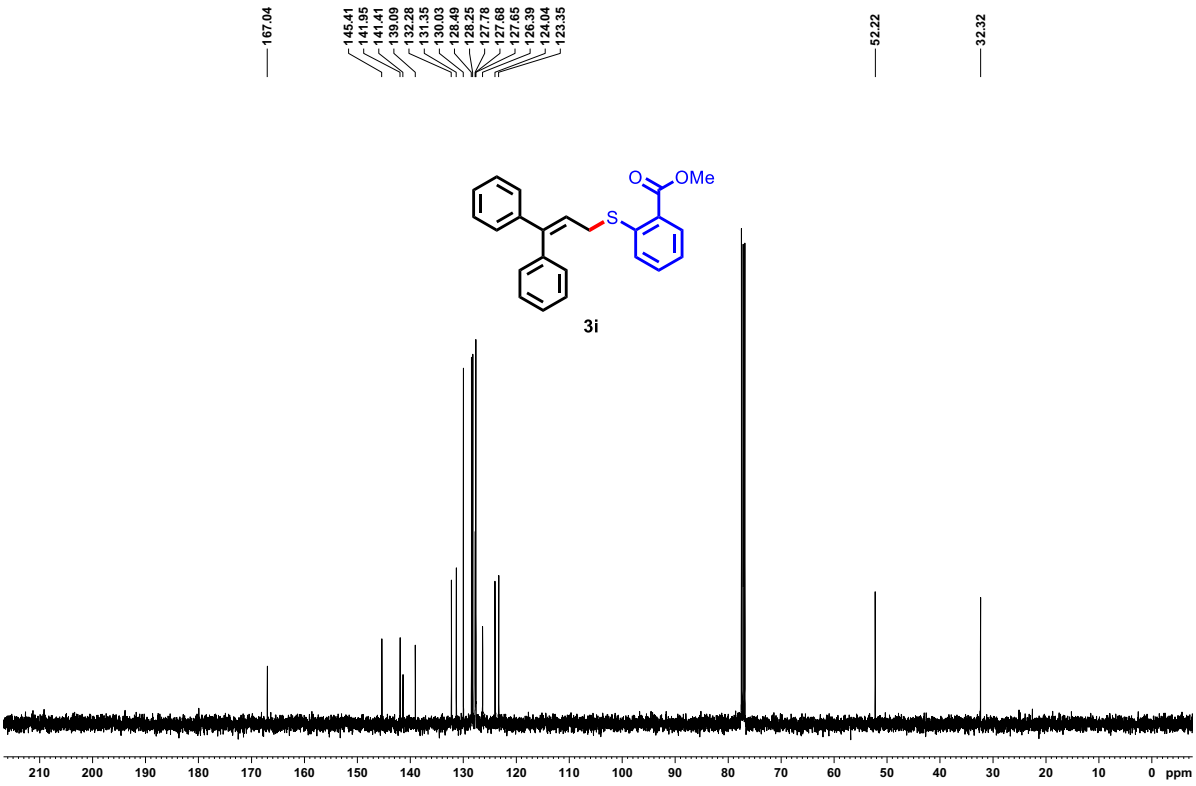

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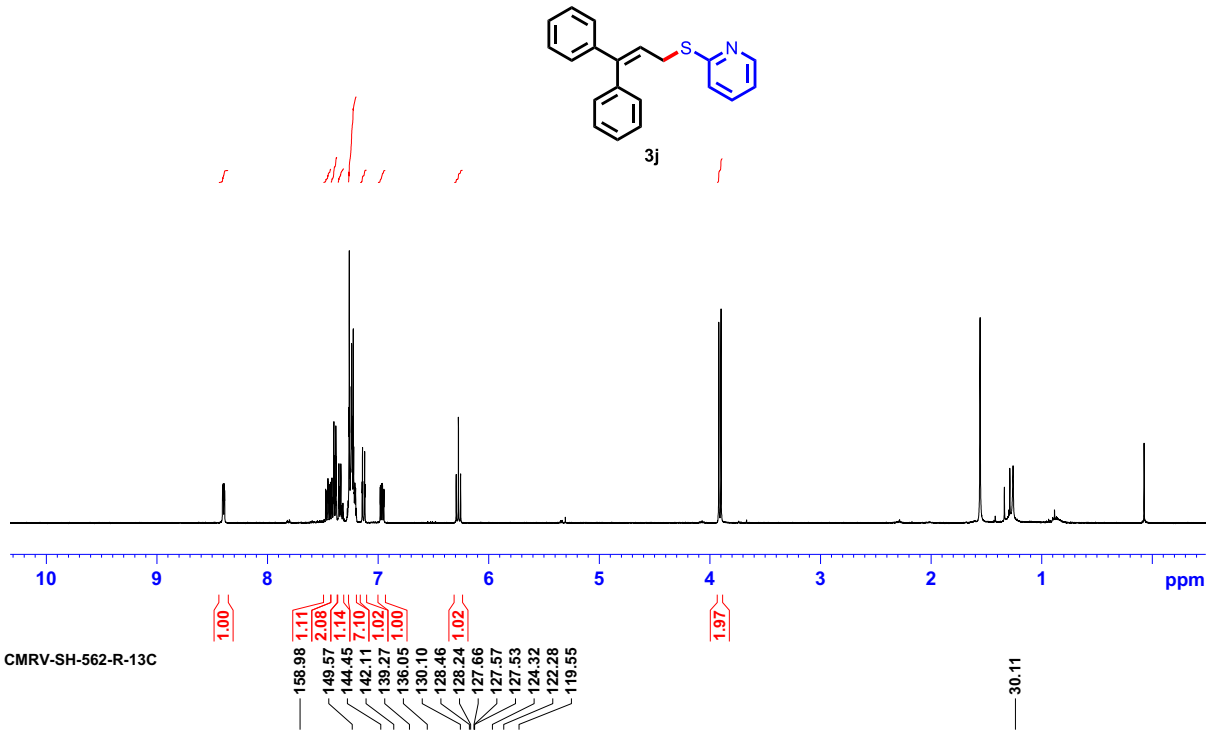

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127.53
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119.55
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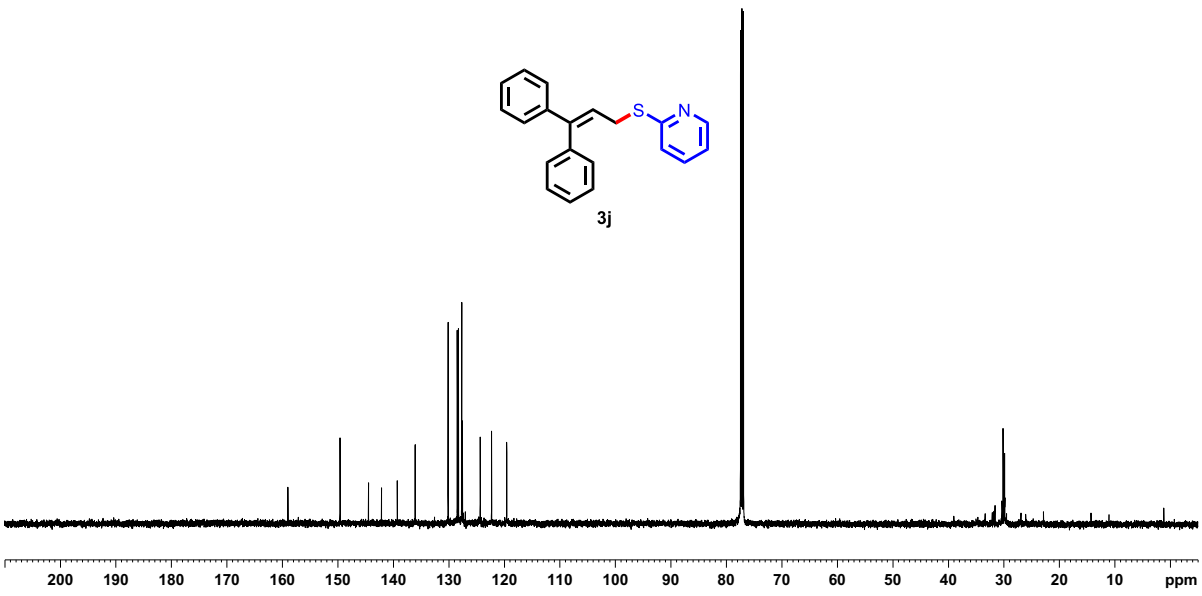

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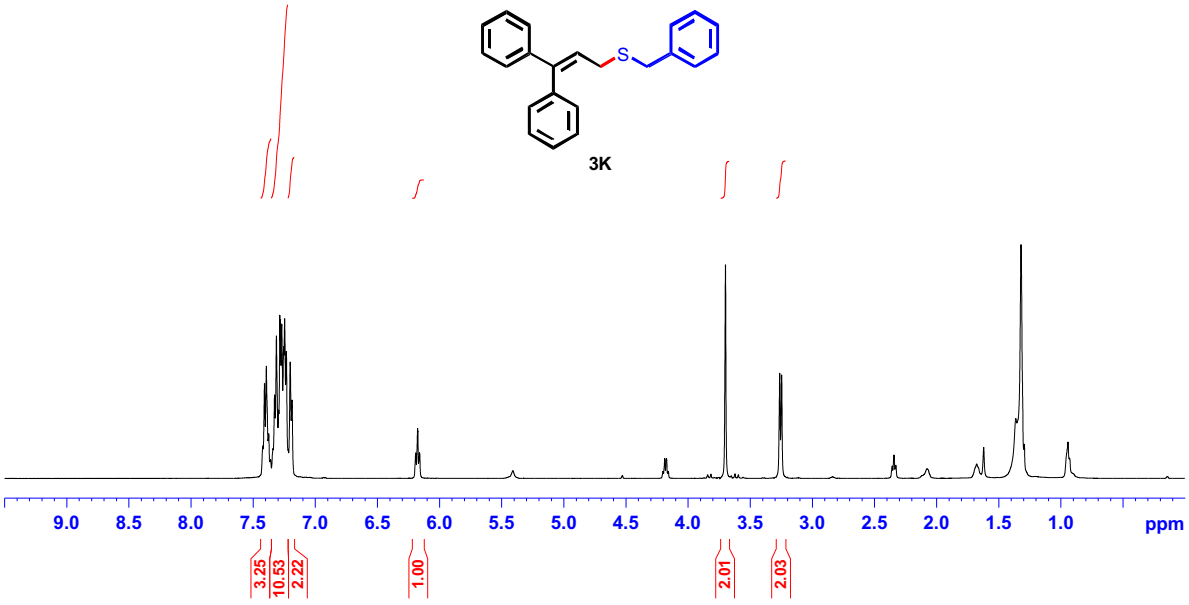

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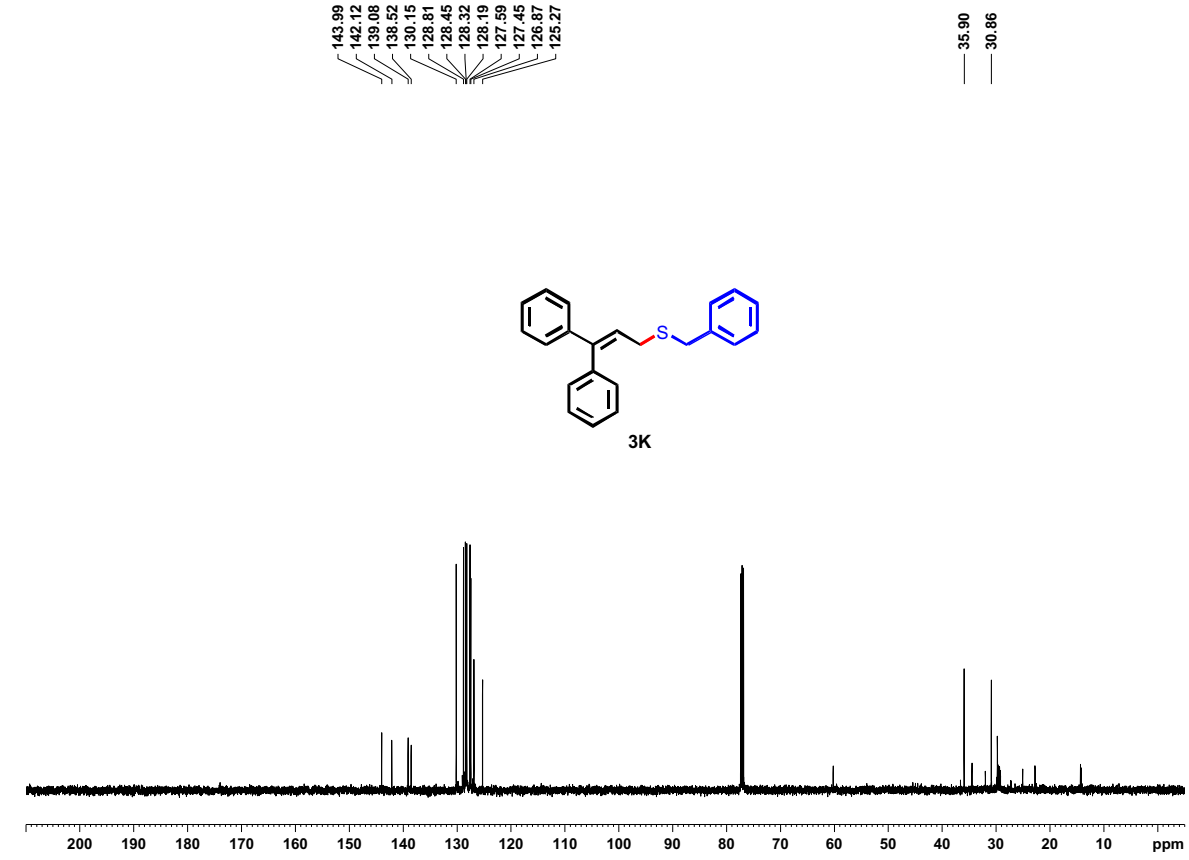

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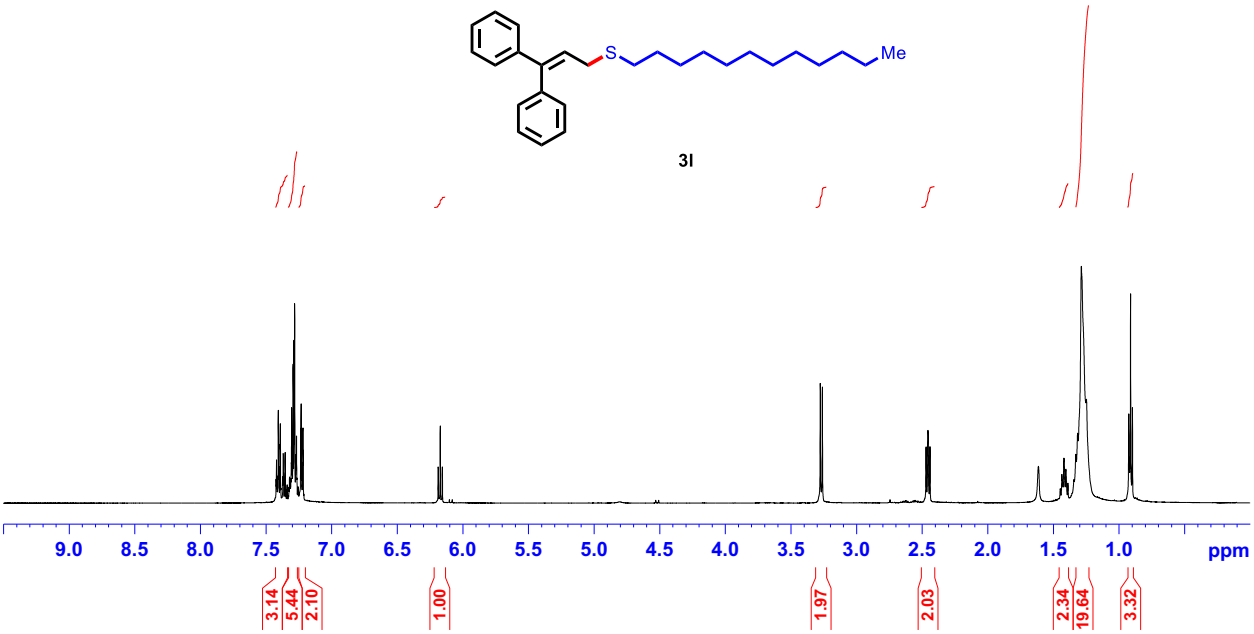

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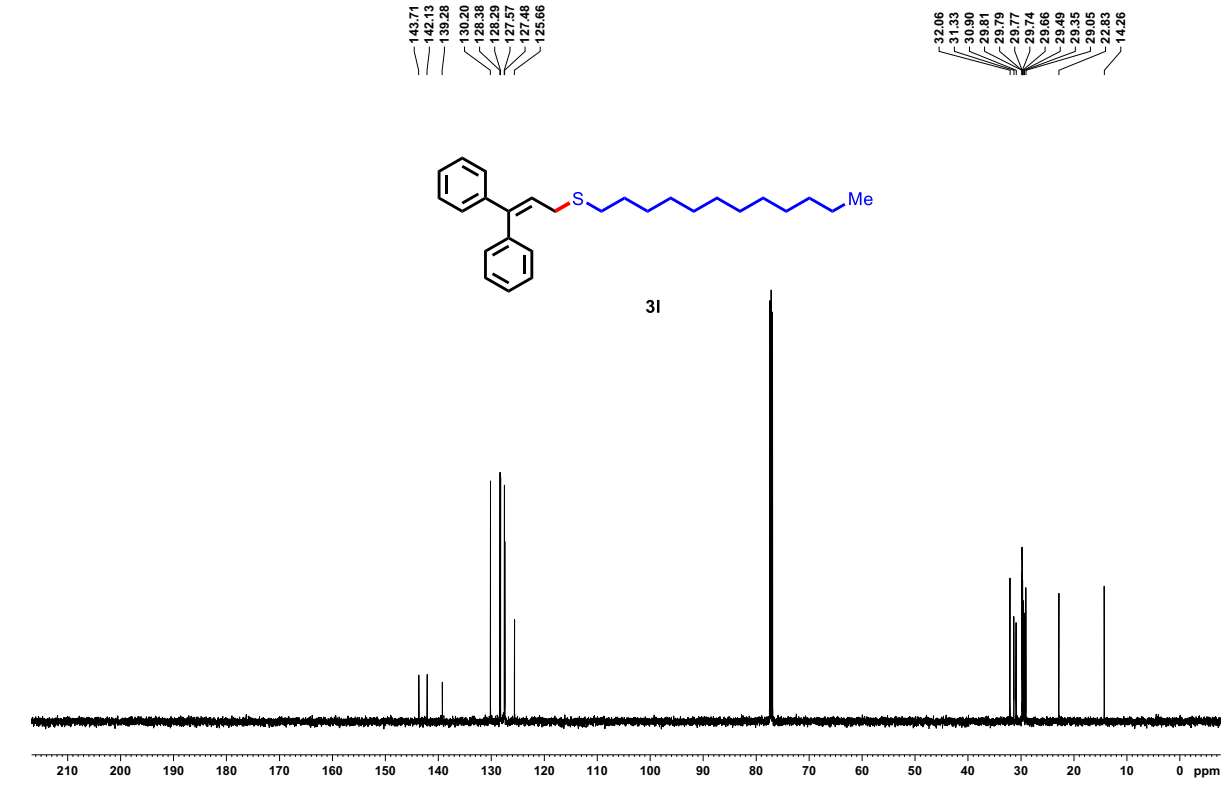

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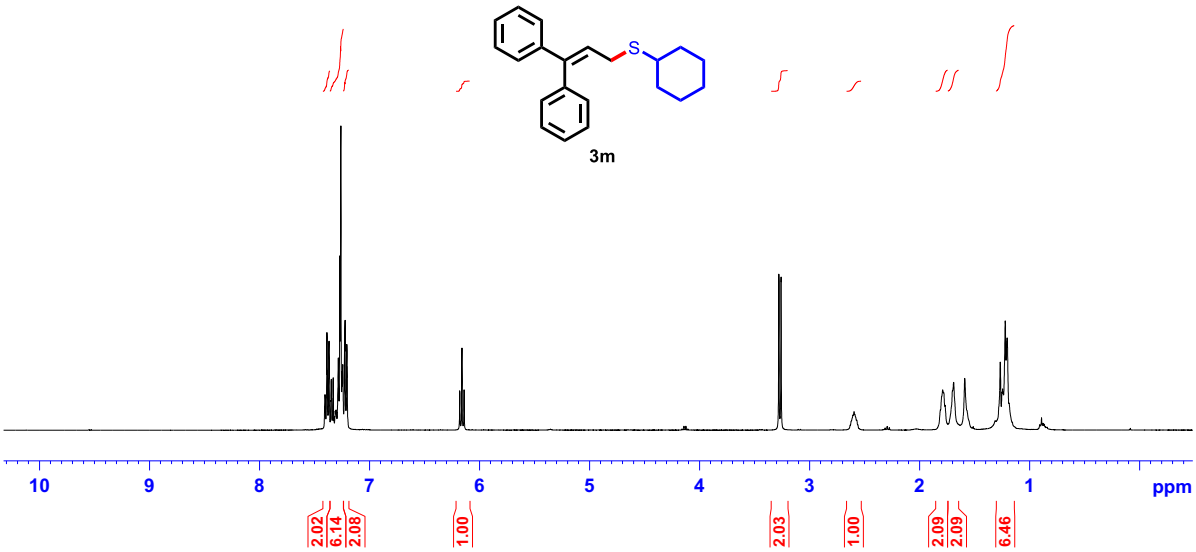

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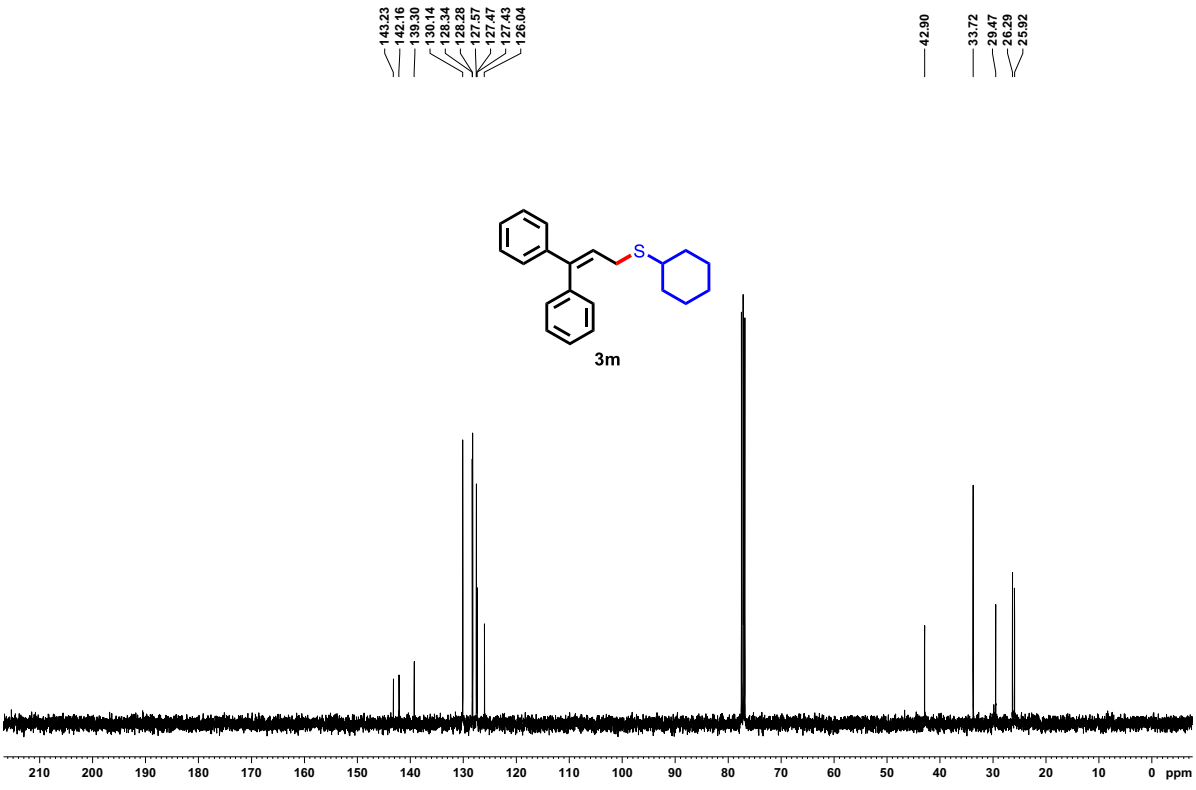

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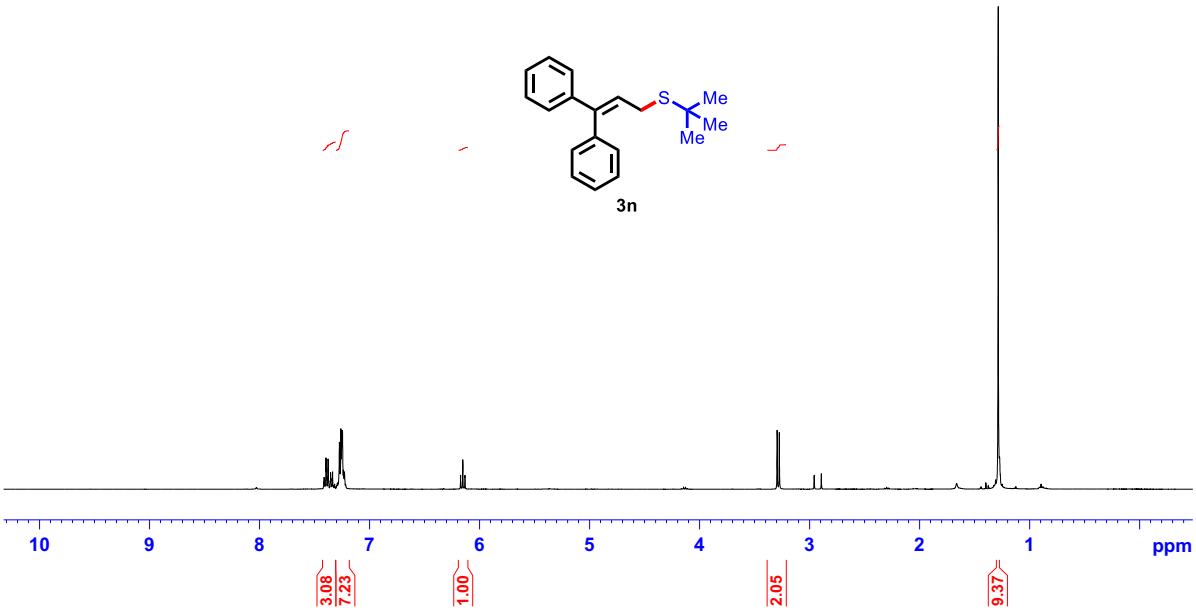

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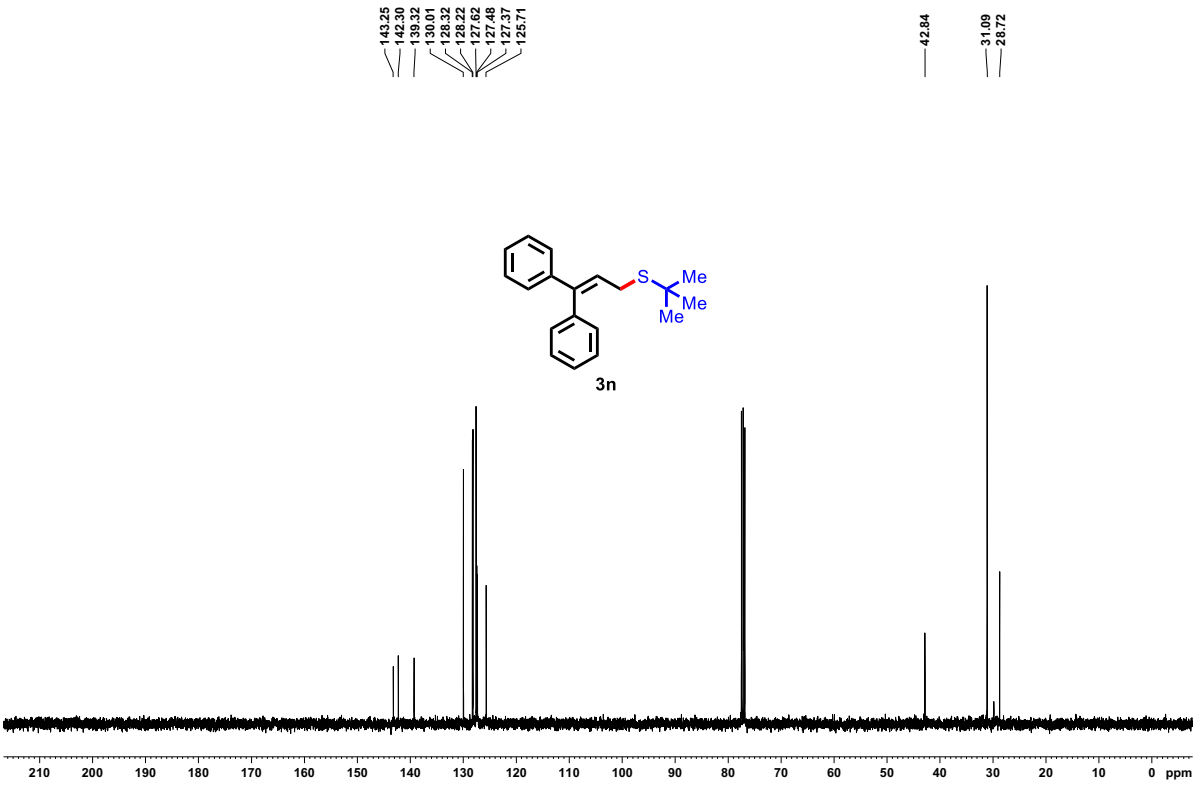

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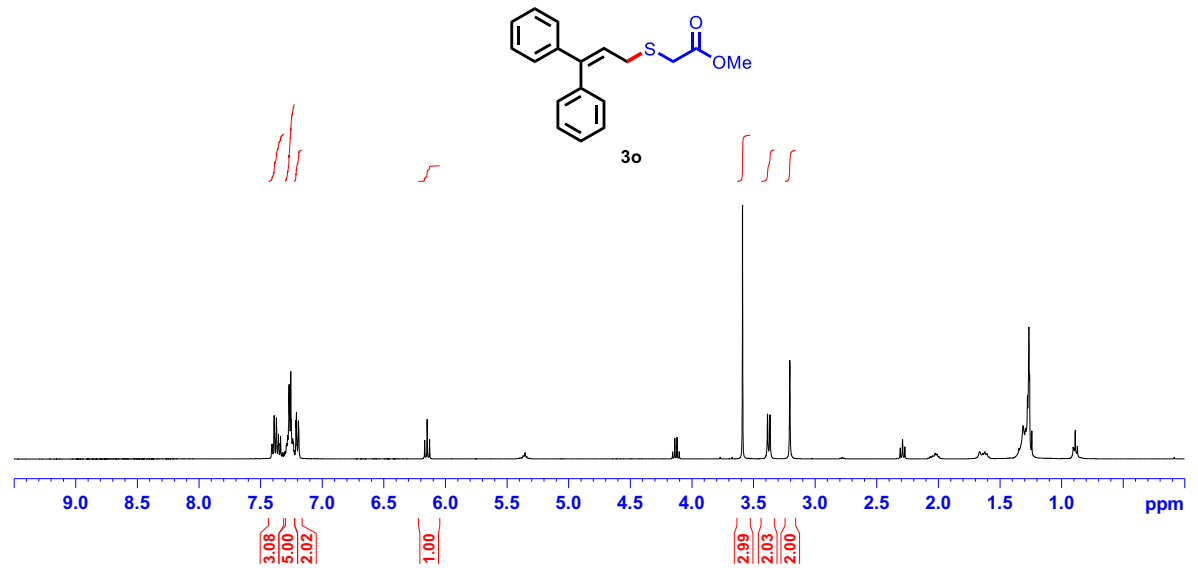

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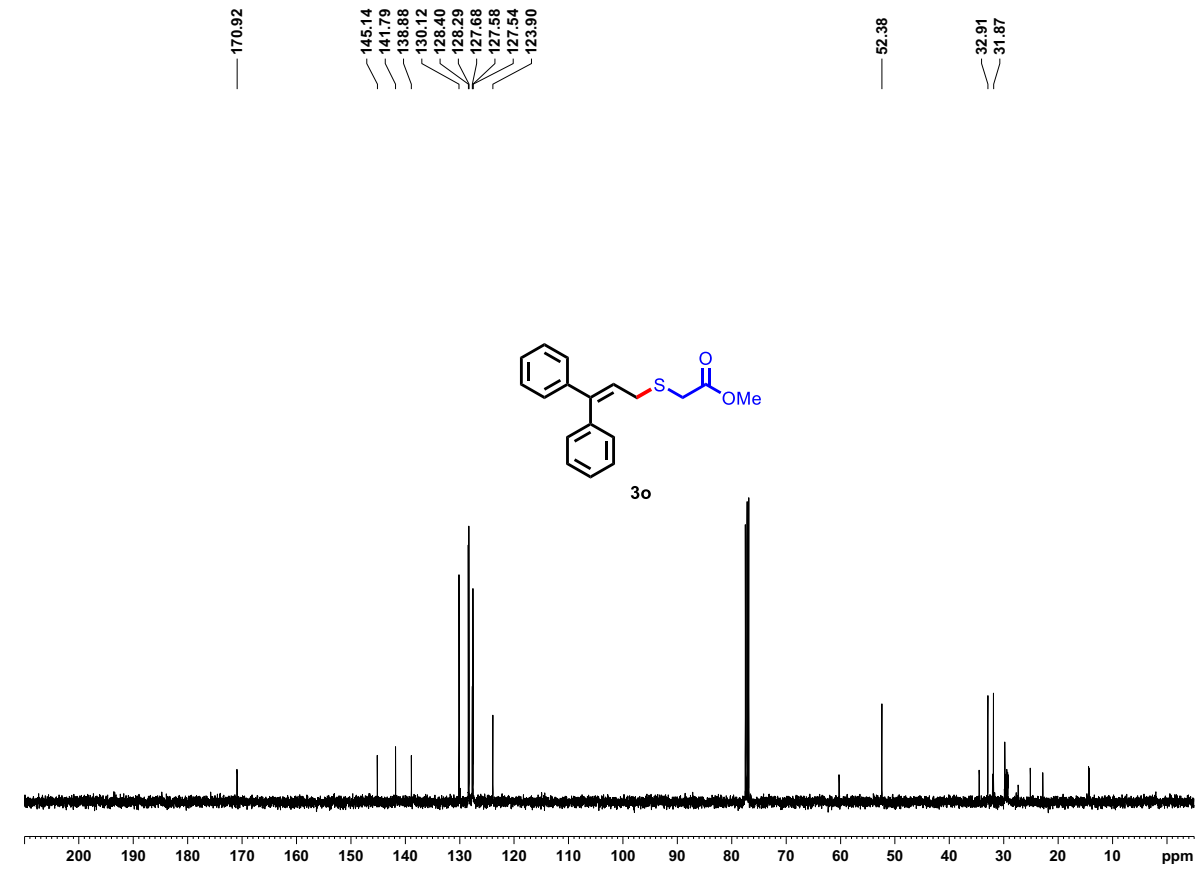

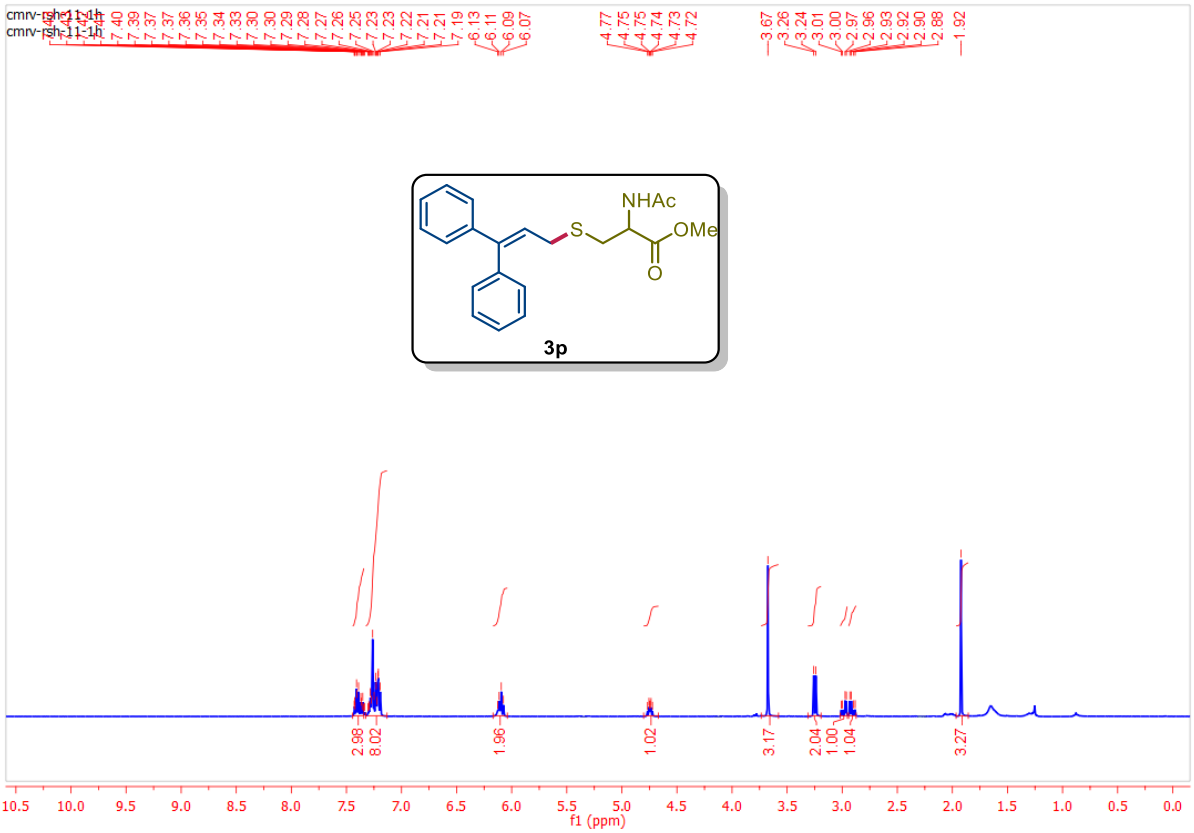
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S
OMe
O
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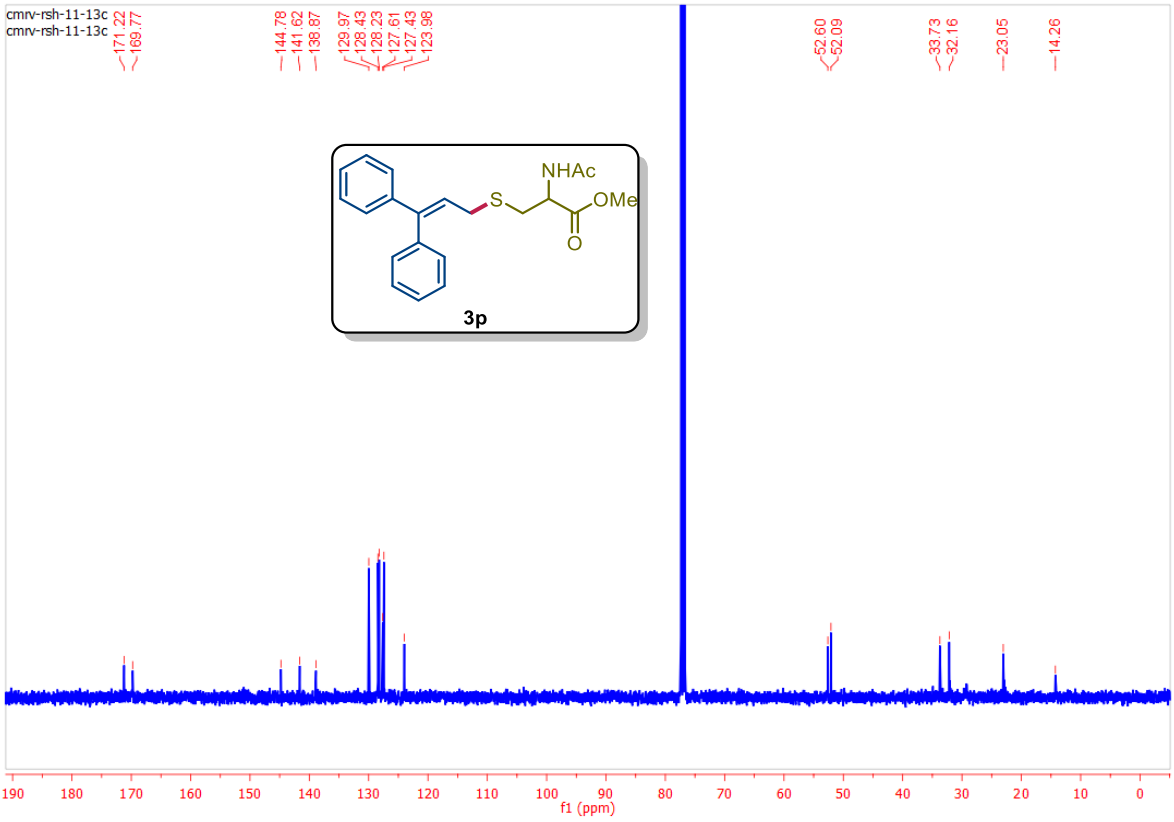
1.00
1.04
3.27
f1 (ppm)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S
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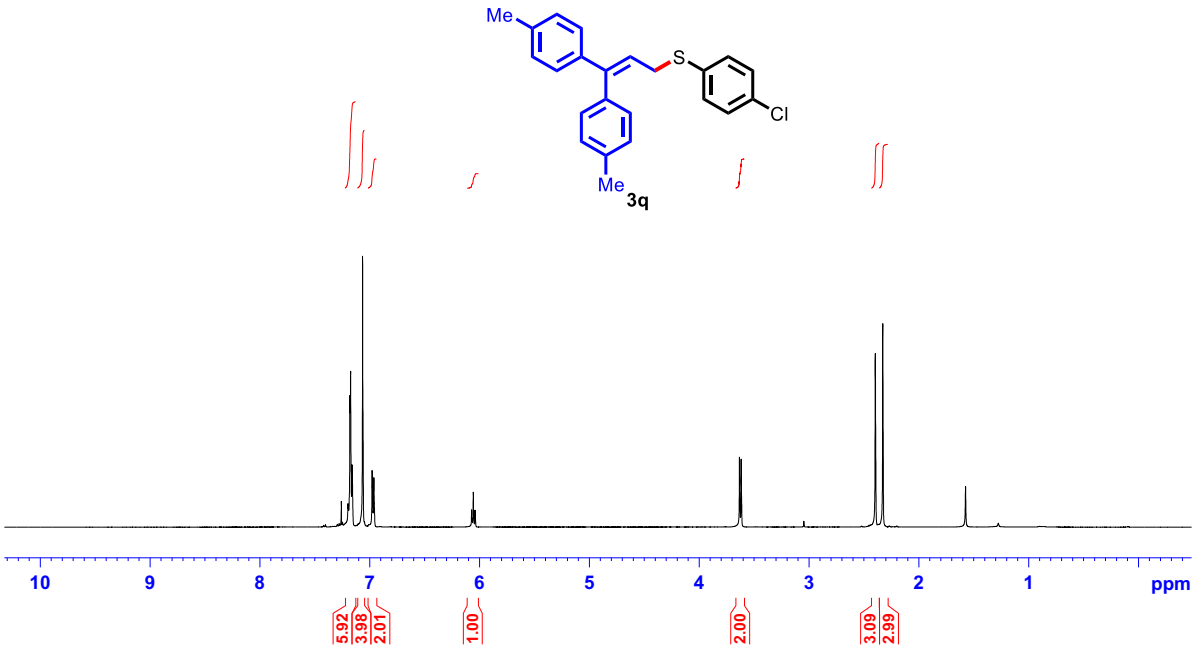
O
3p
f1 (ppm)

CMRV-SK-803-1H



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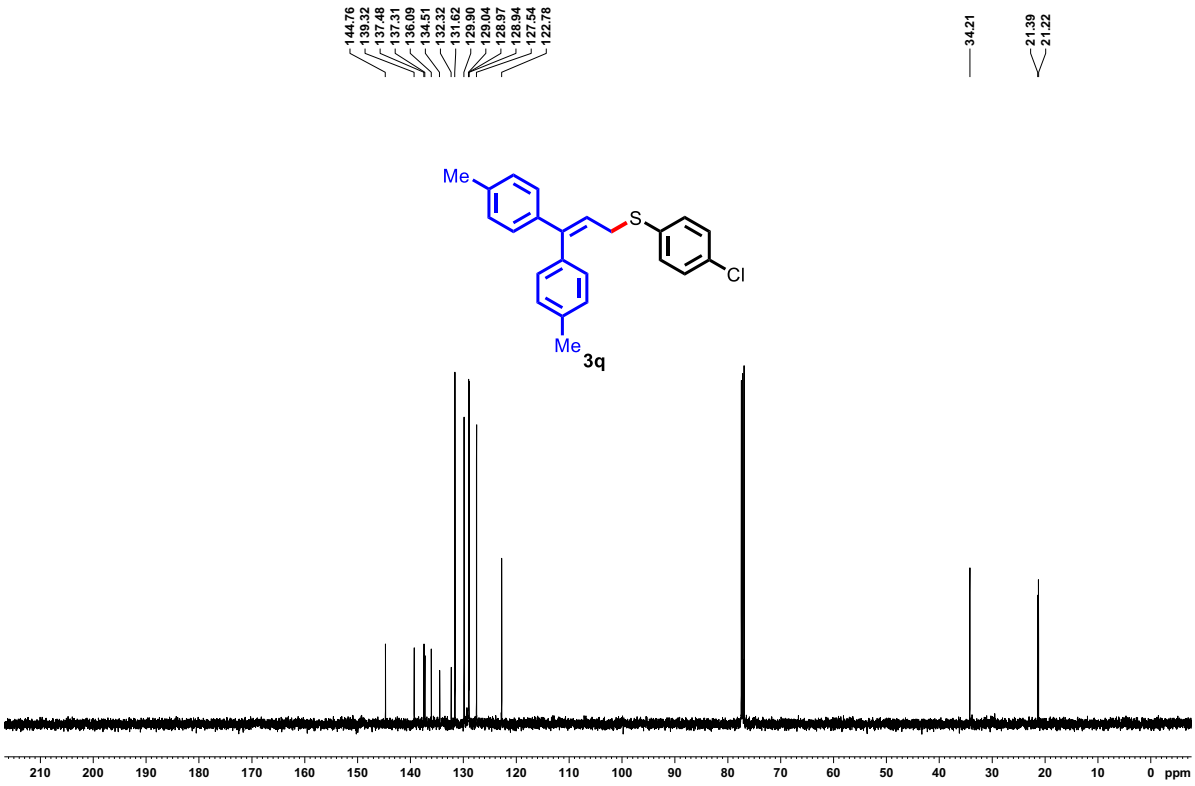

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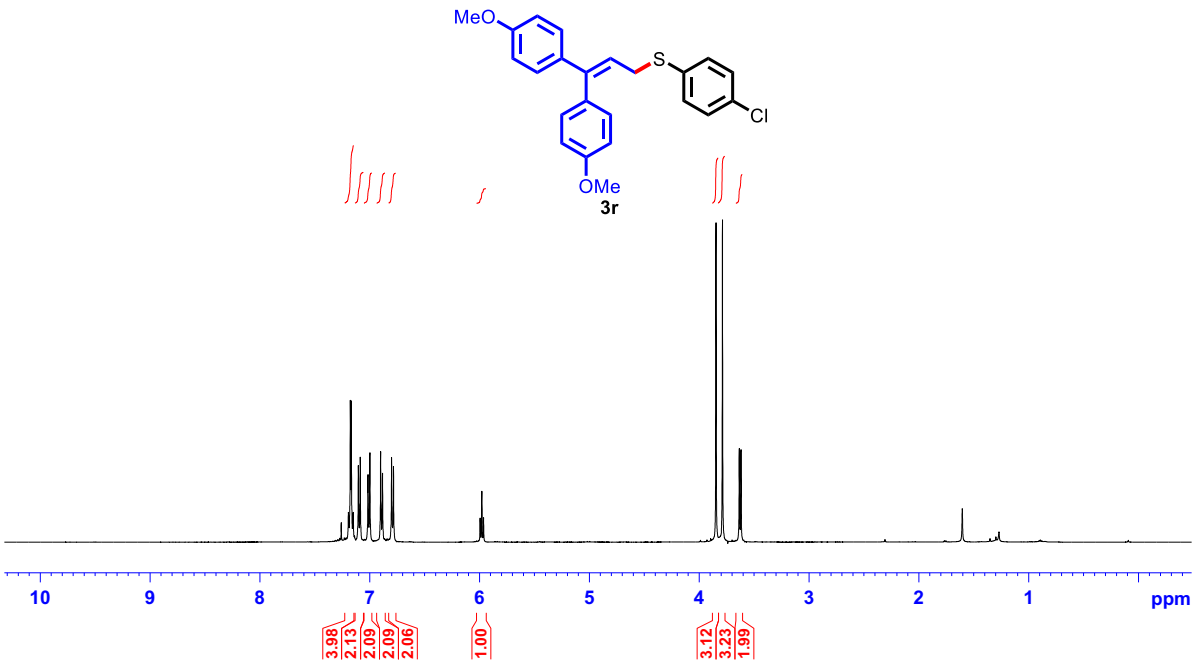

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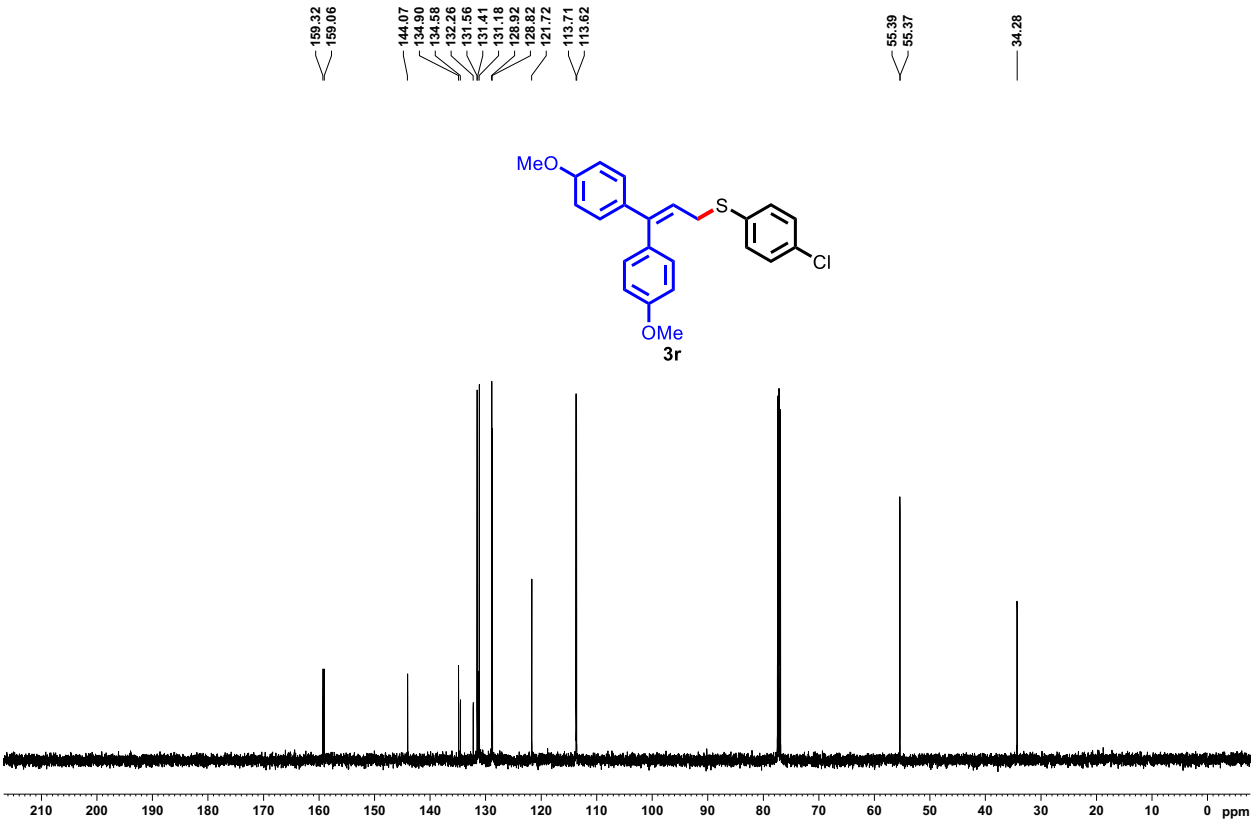

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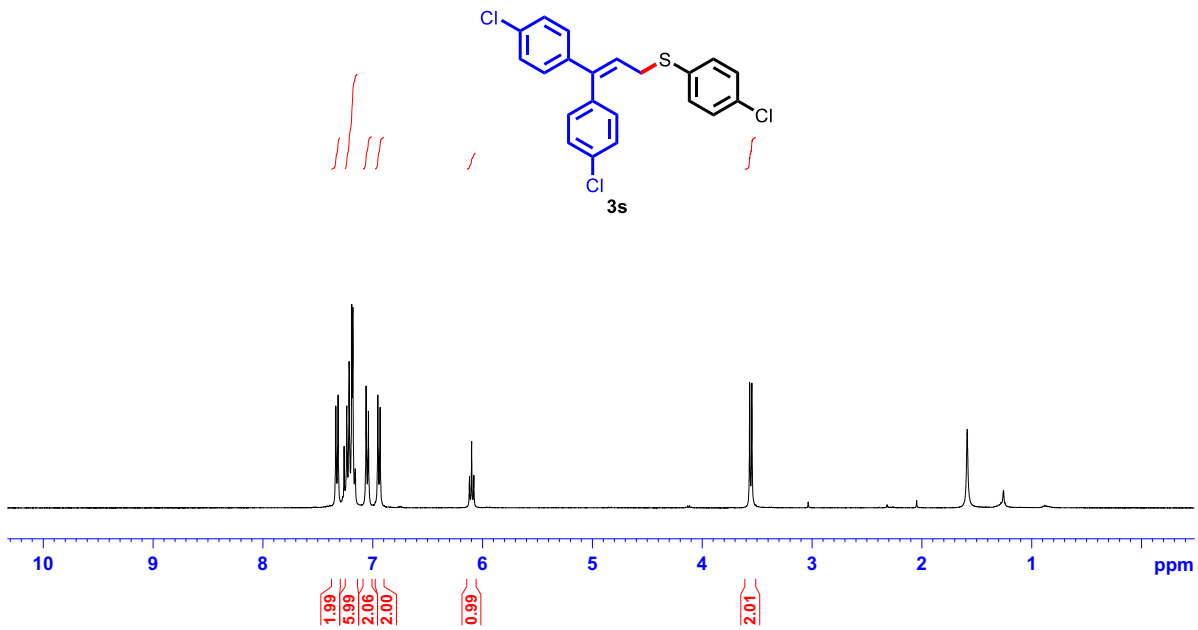

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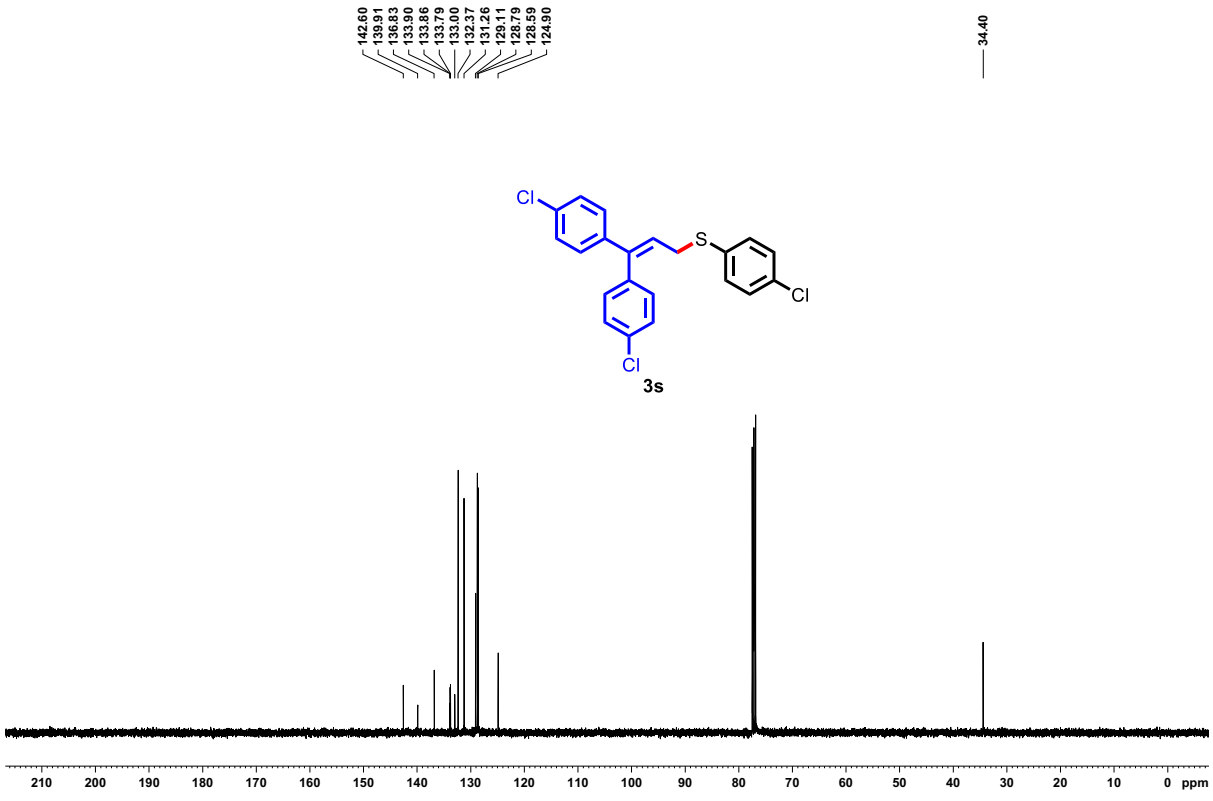

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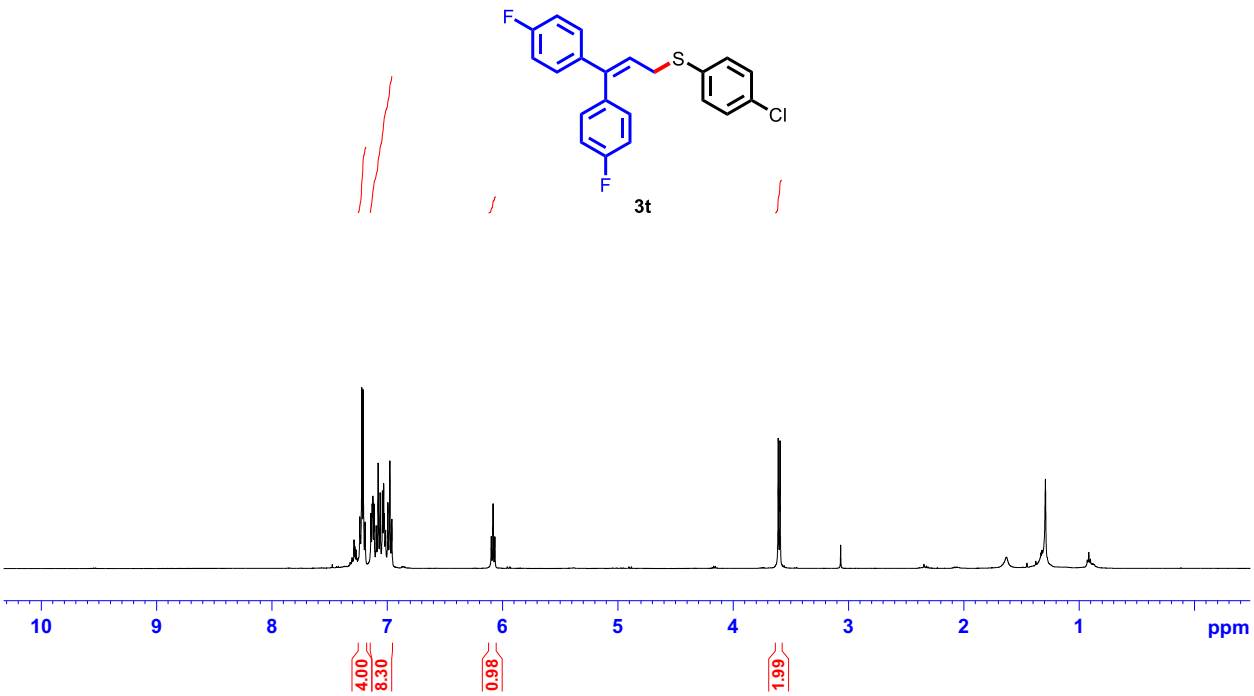

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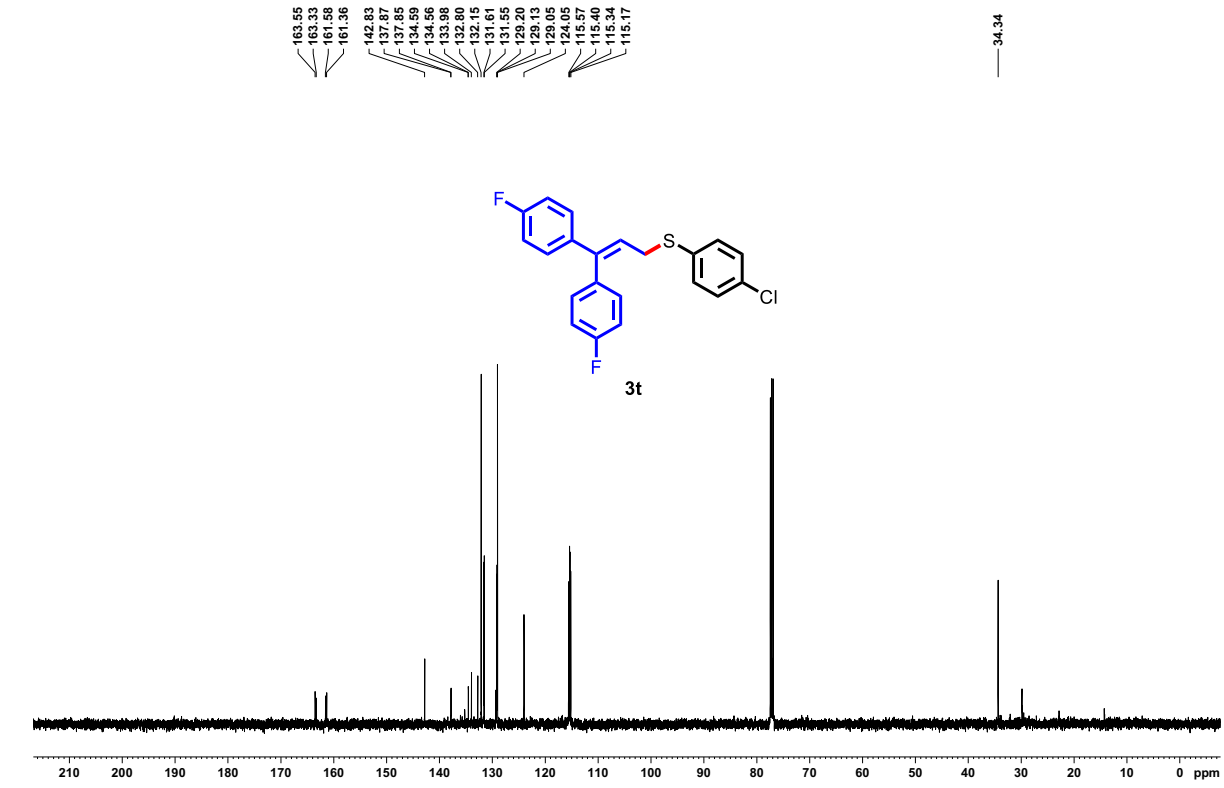

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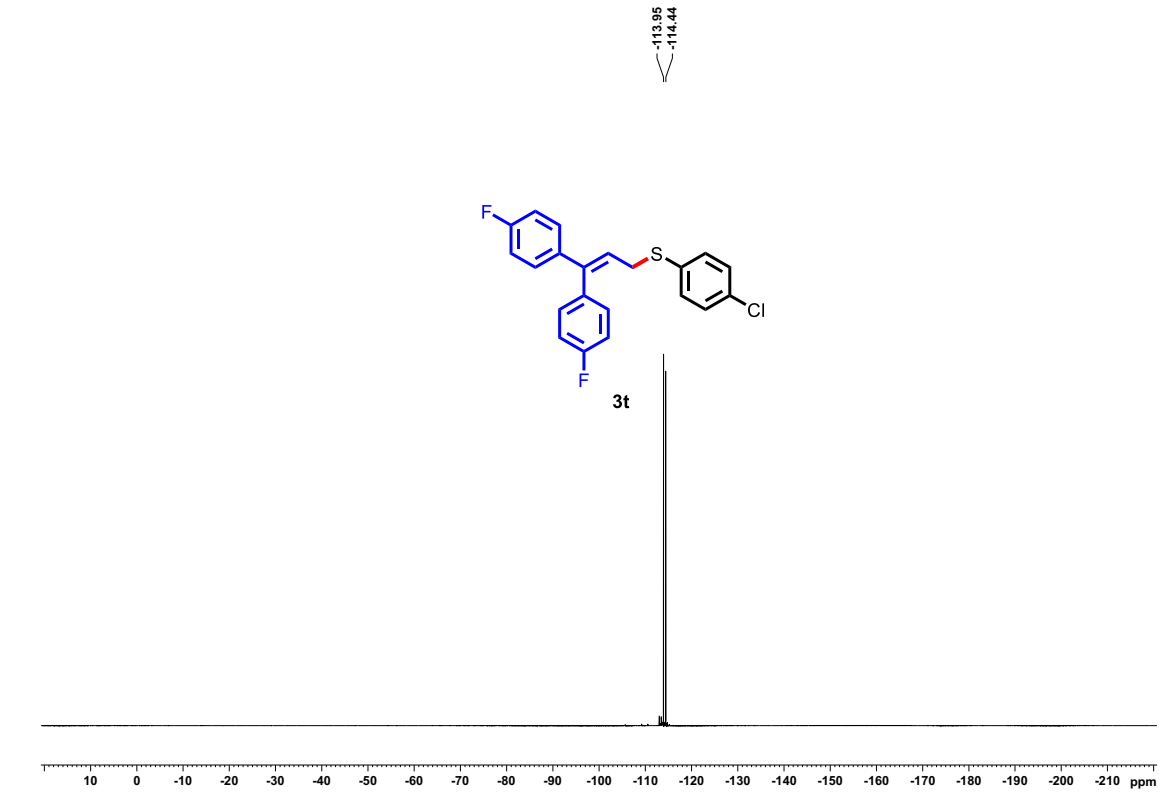

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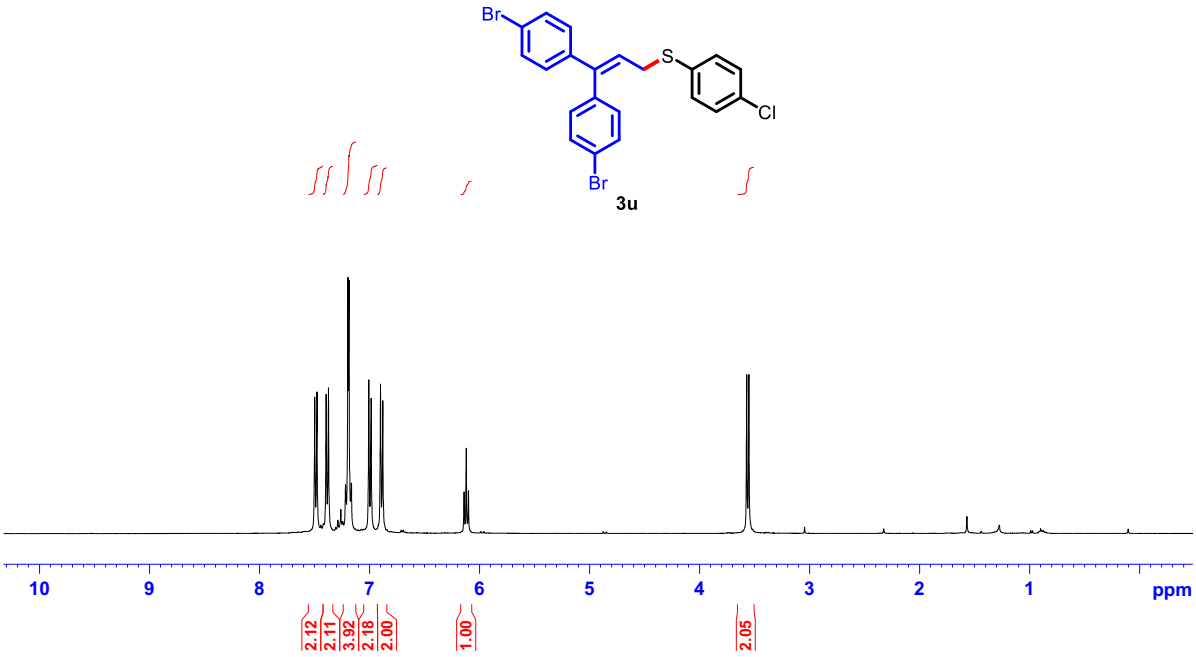

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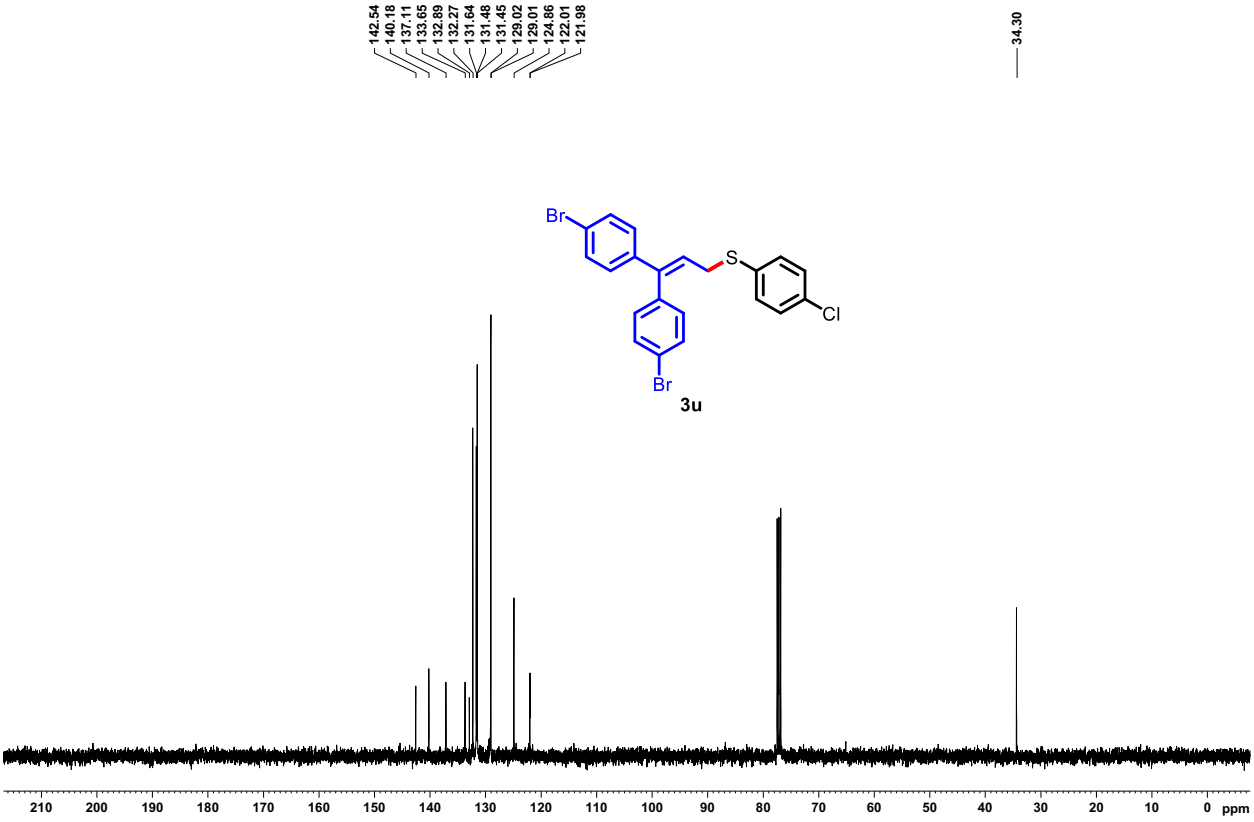

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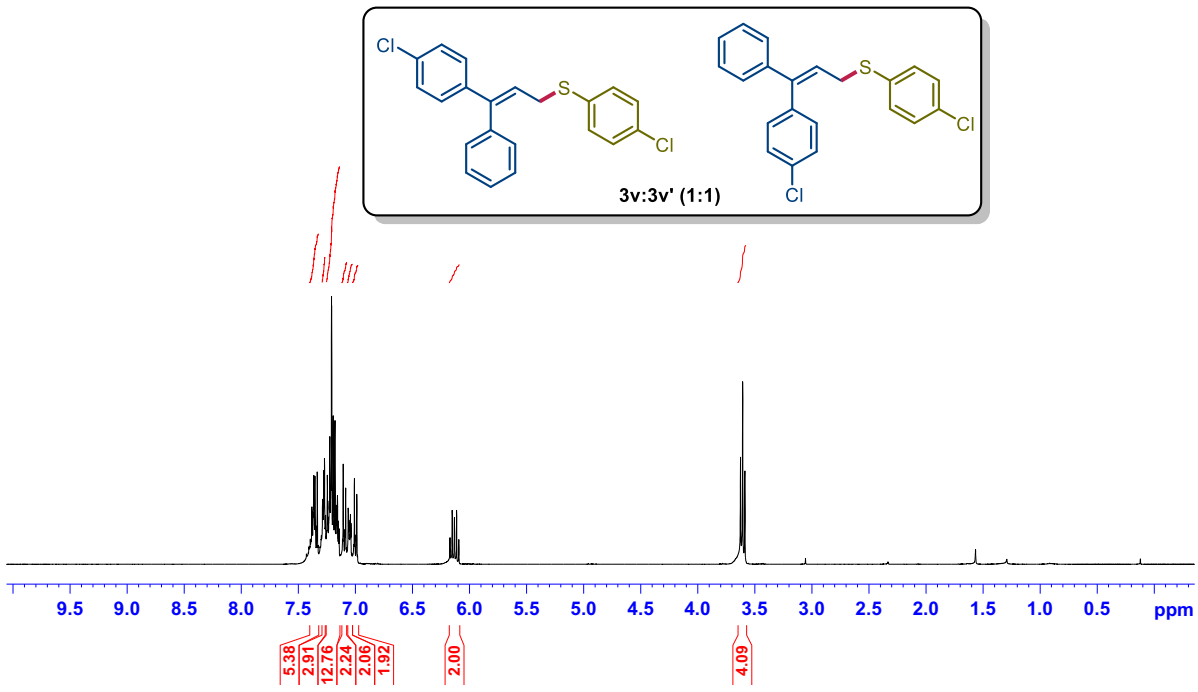

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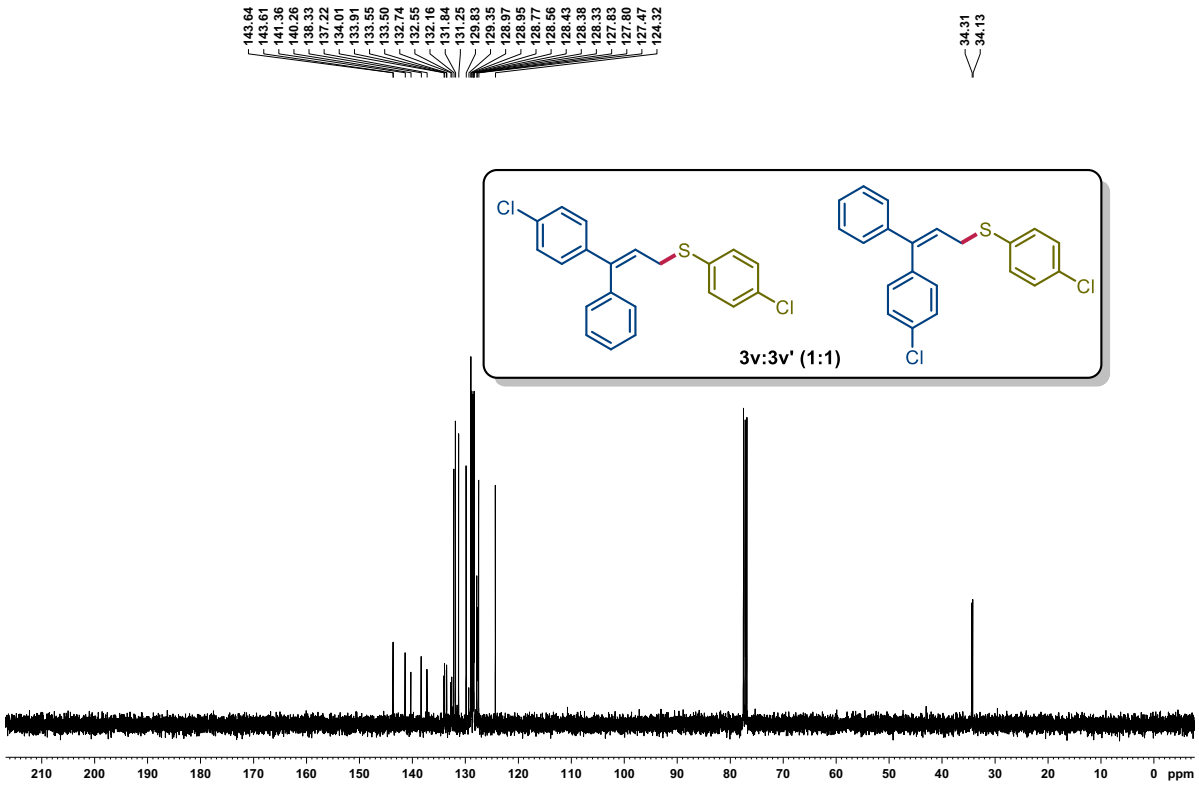

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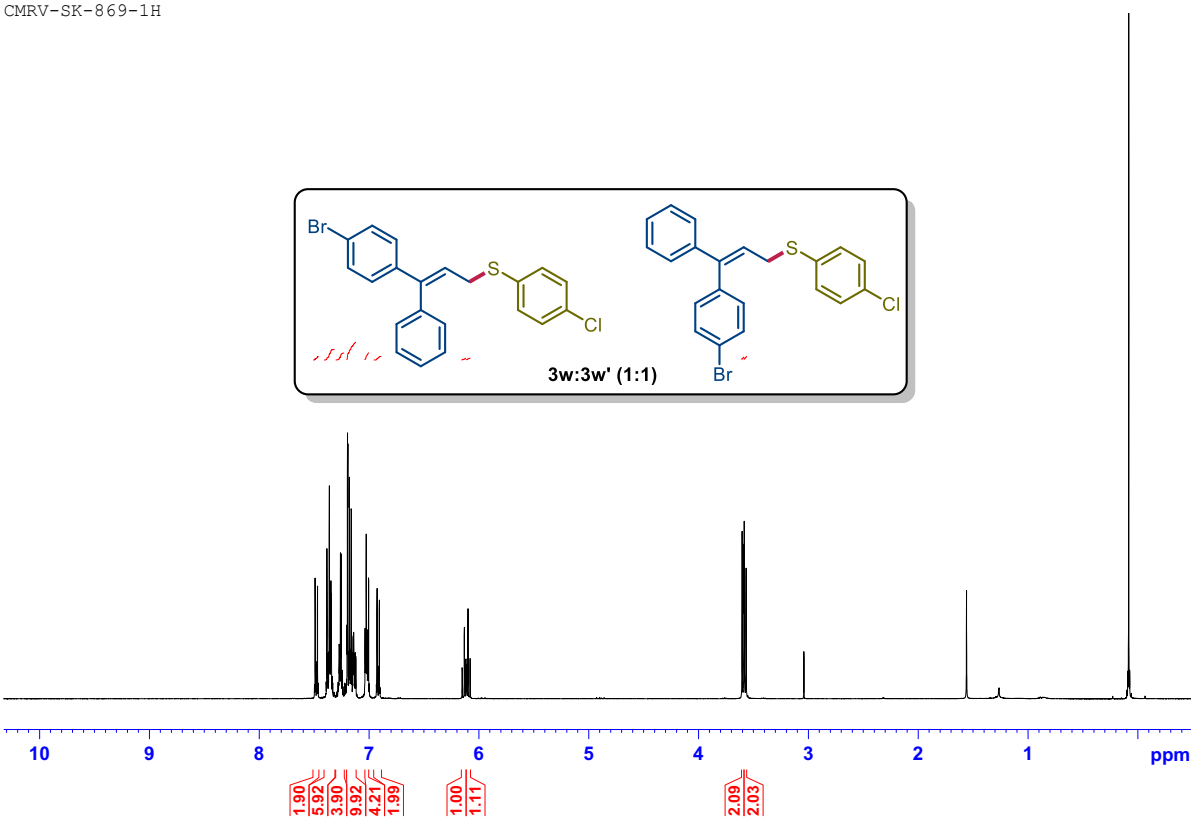

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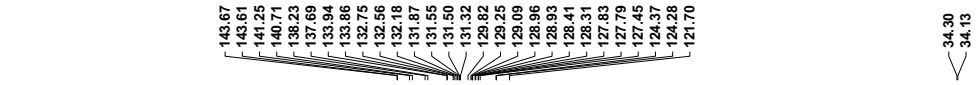

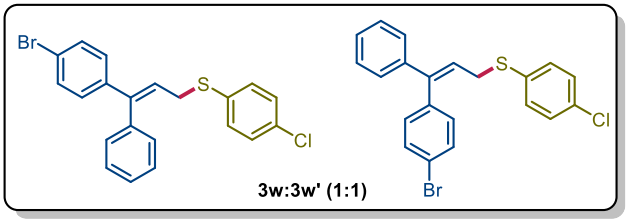

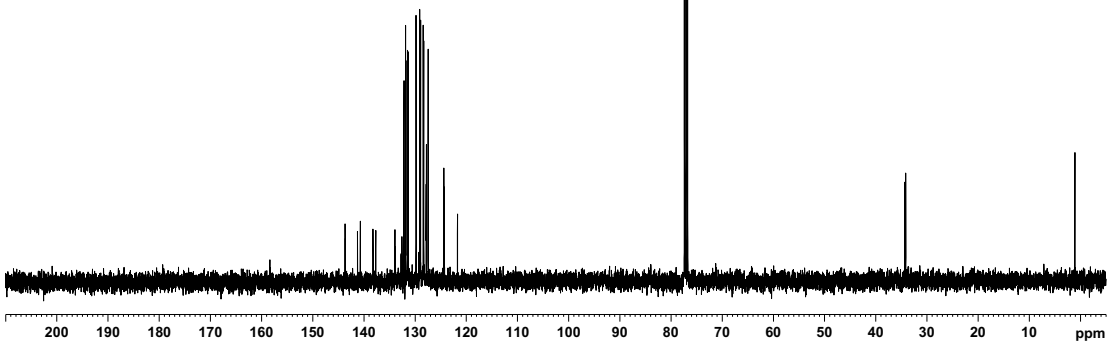

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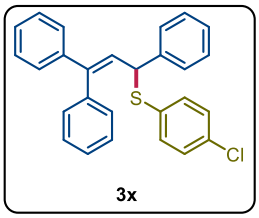

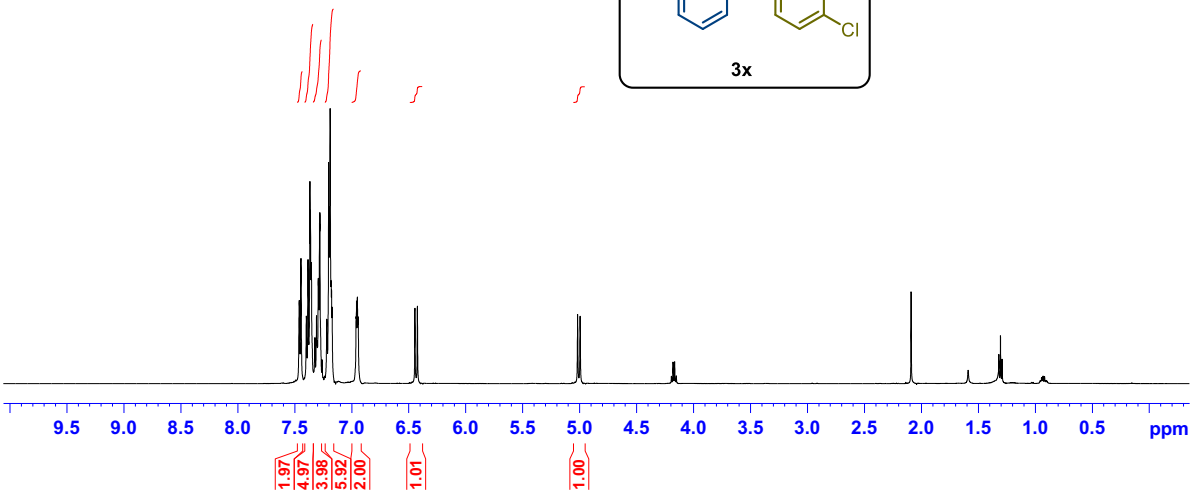

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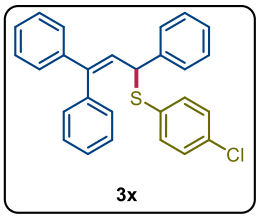

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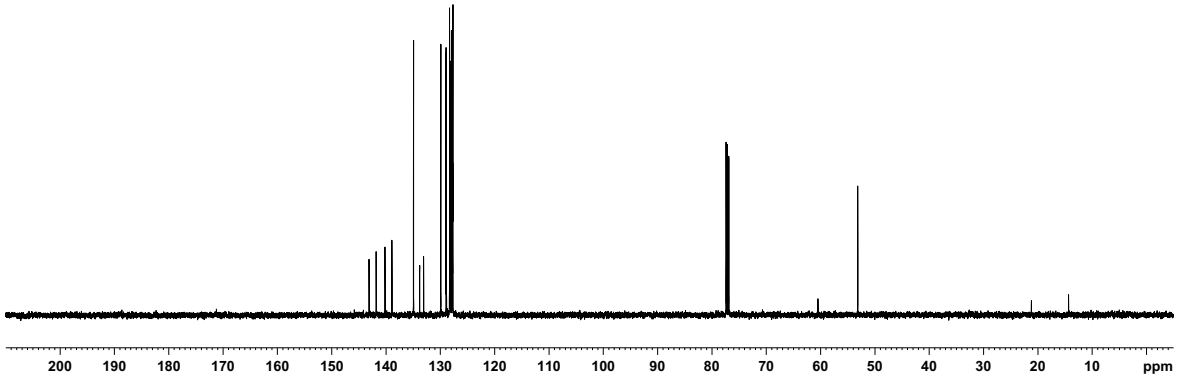

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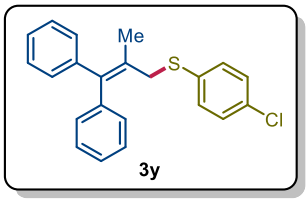

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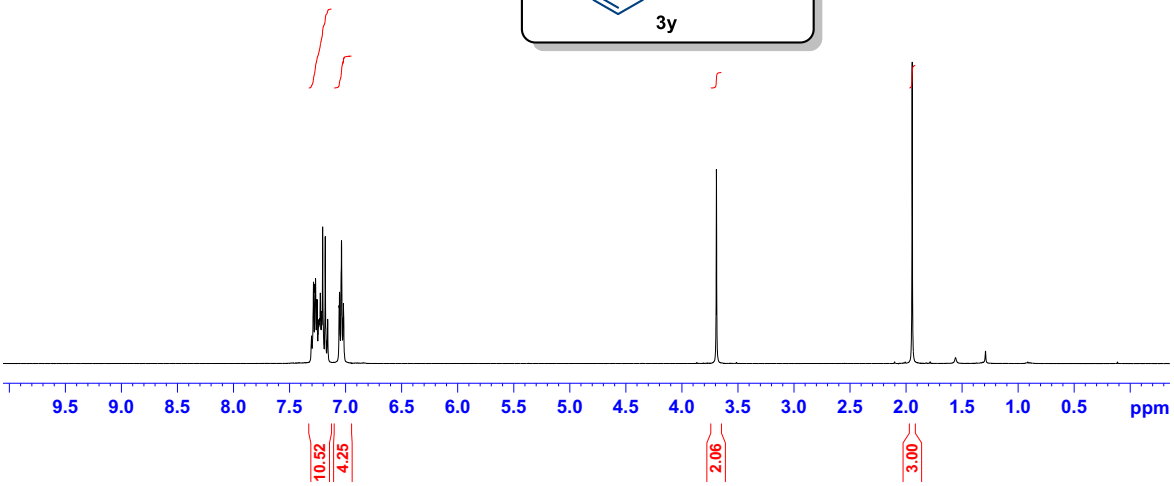

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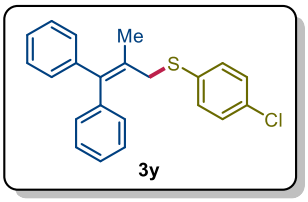

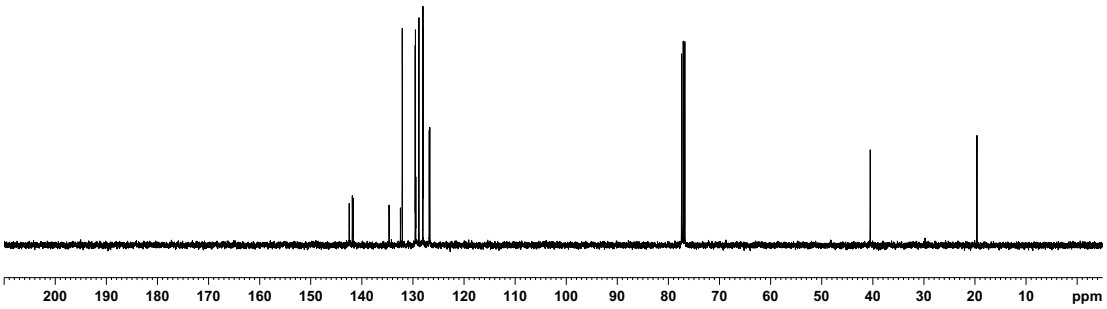

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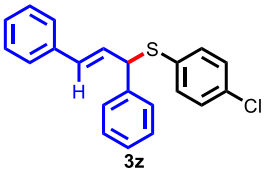

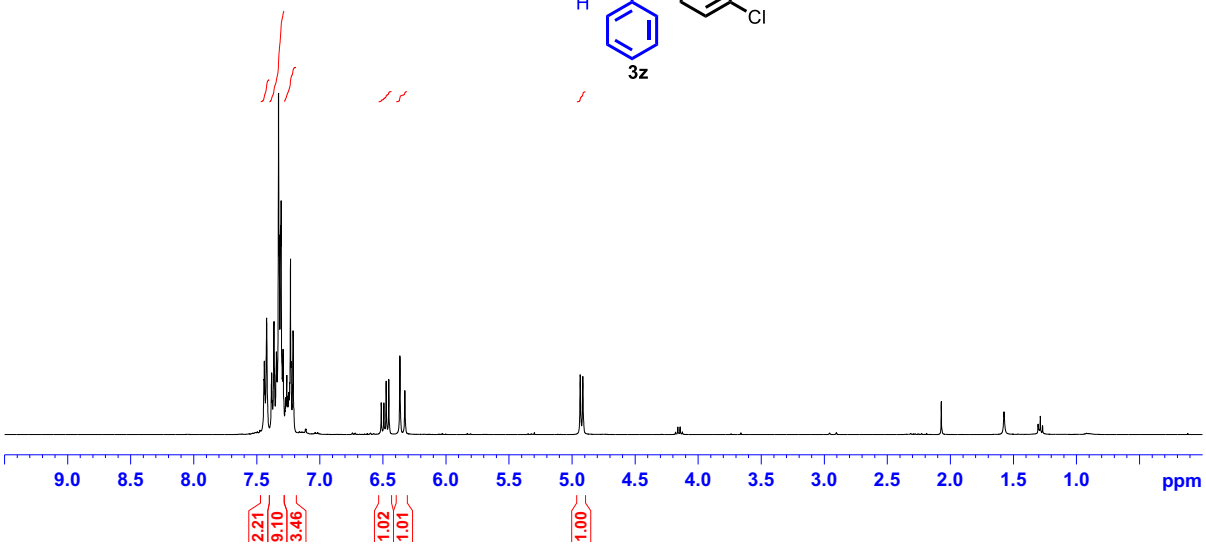

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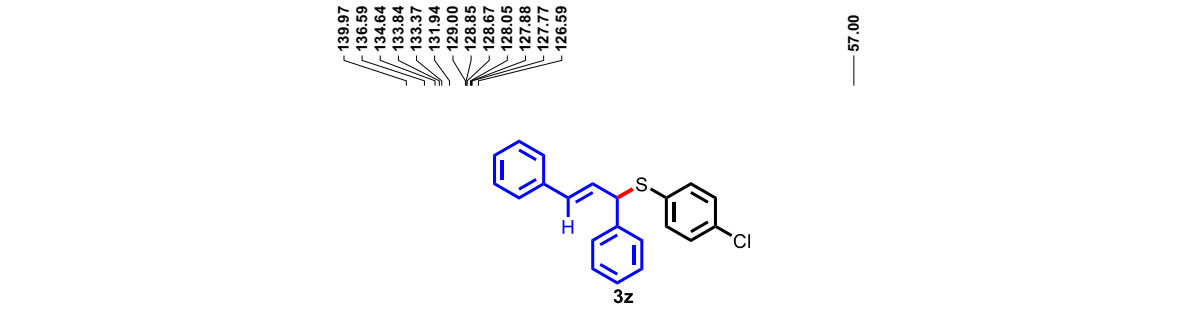

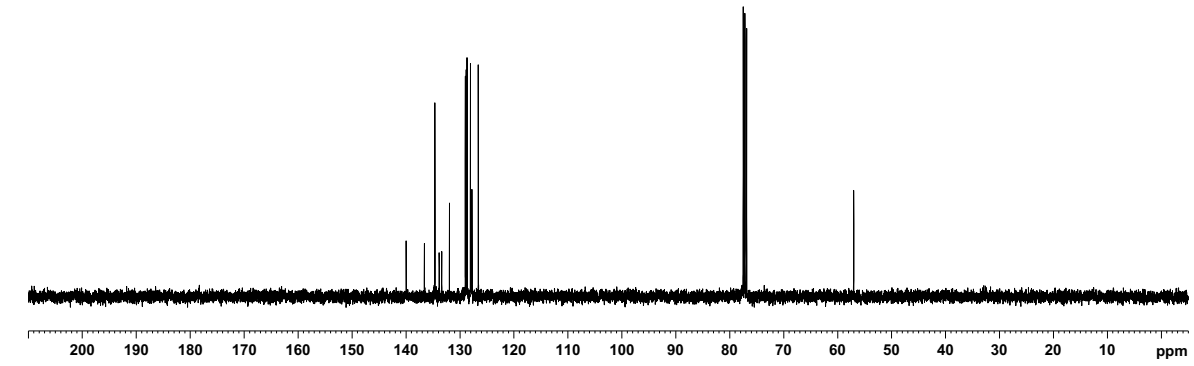

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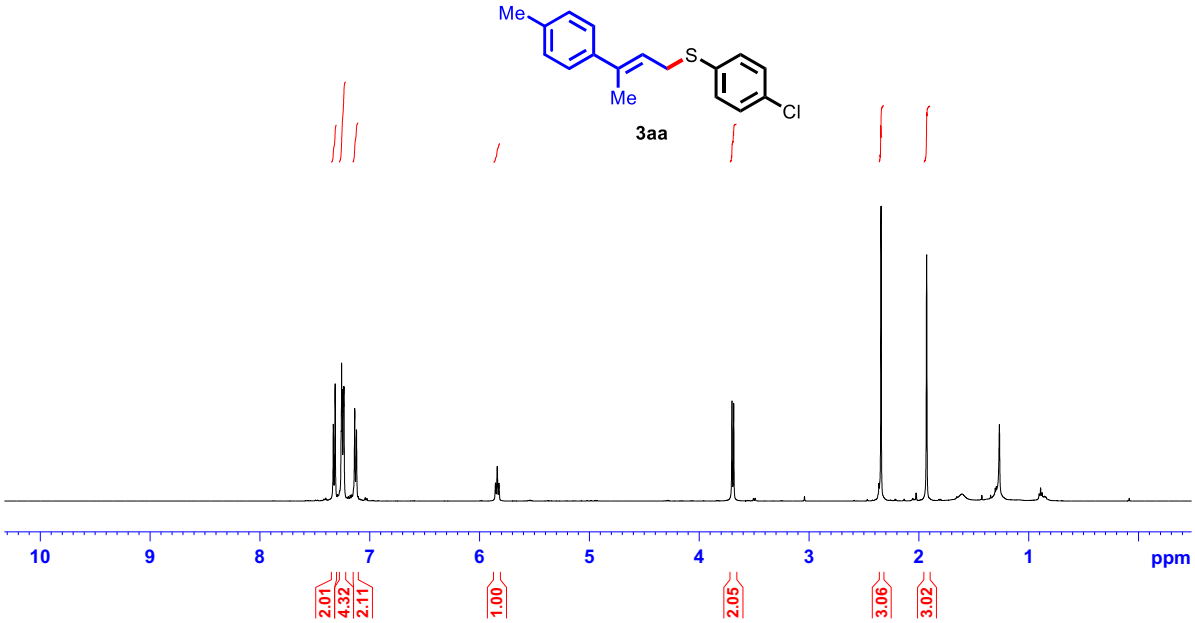

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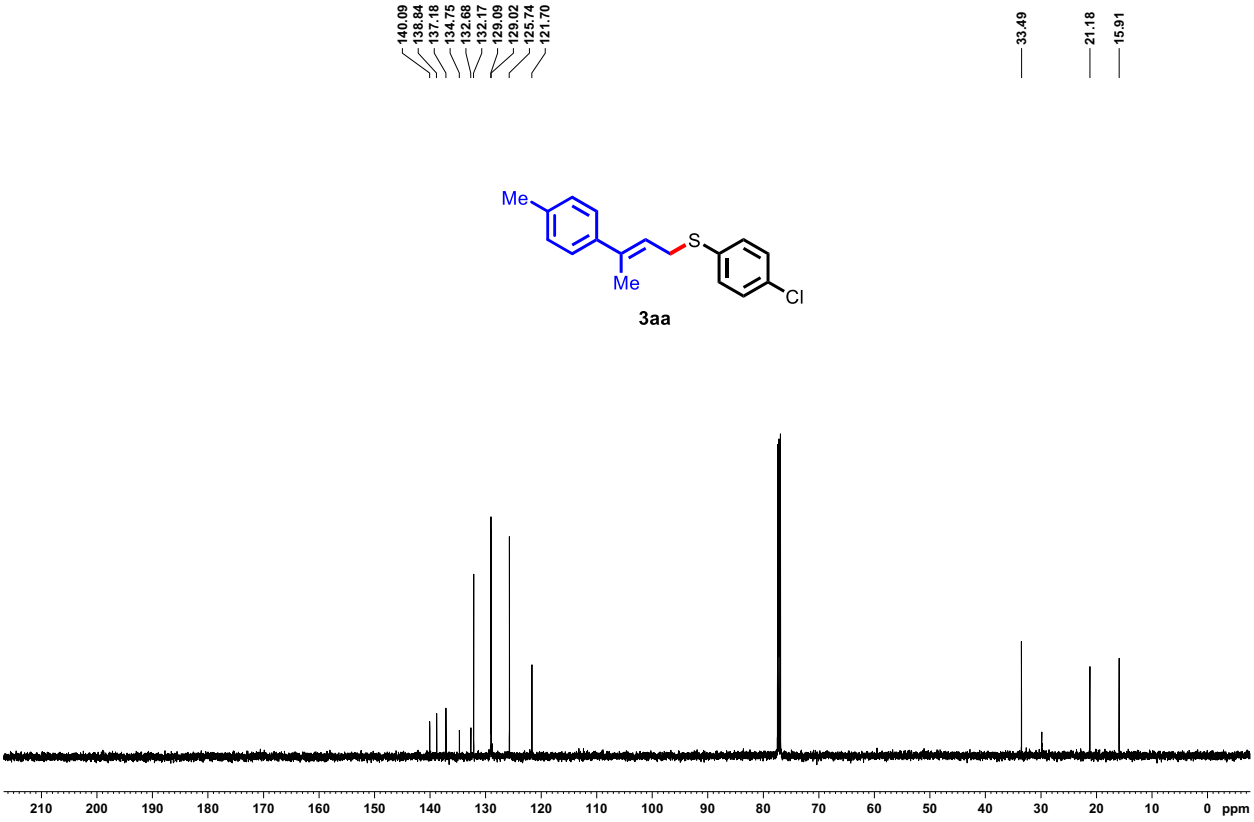

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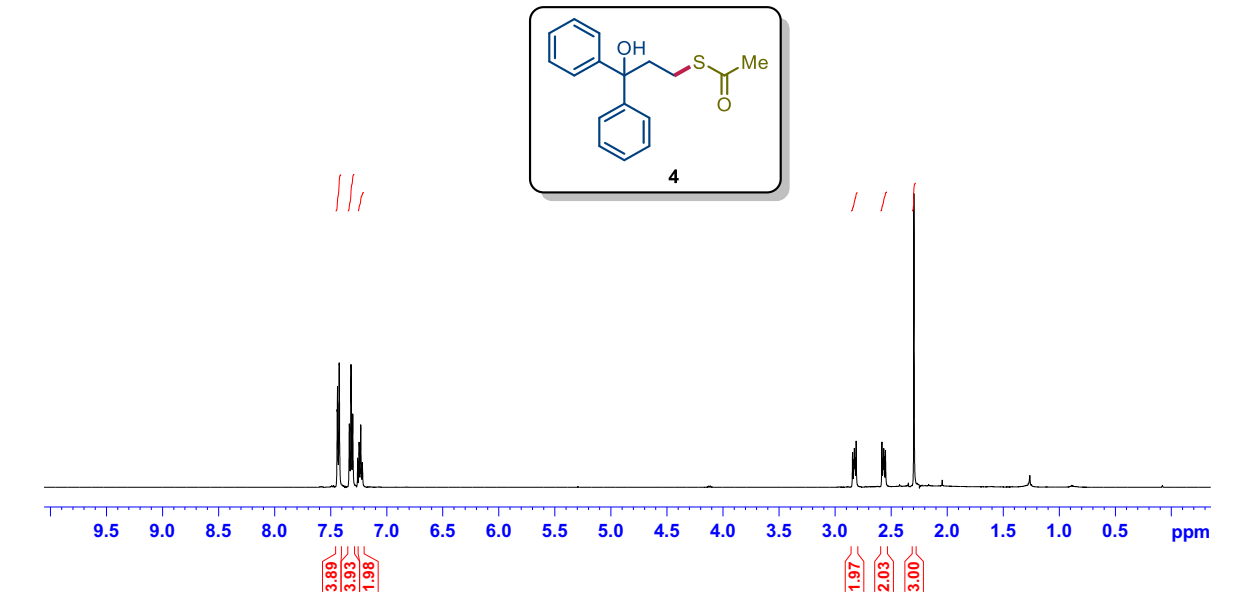

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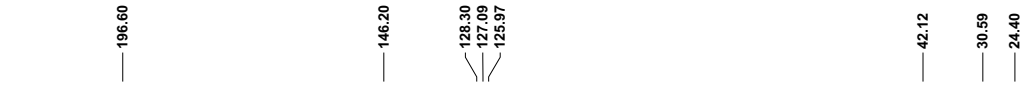

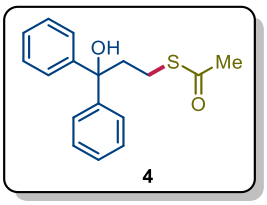

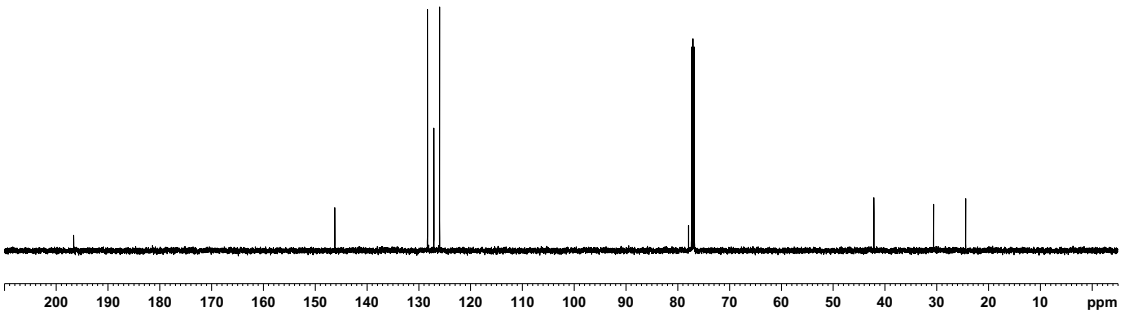

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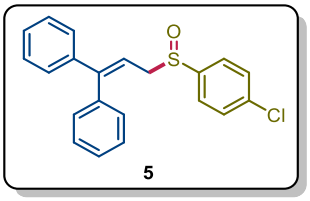

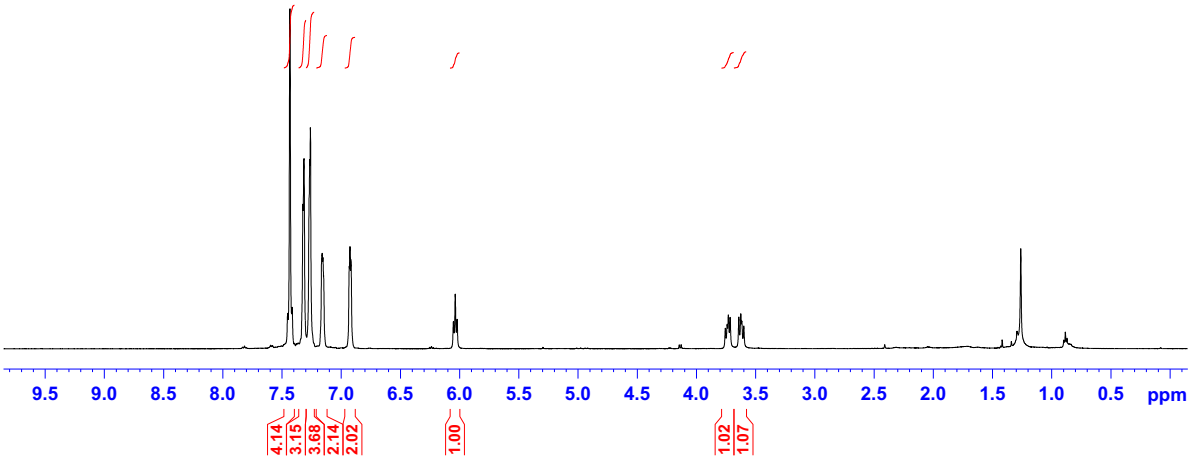

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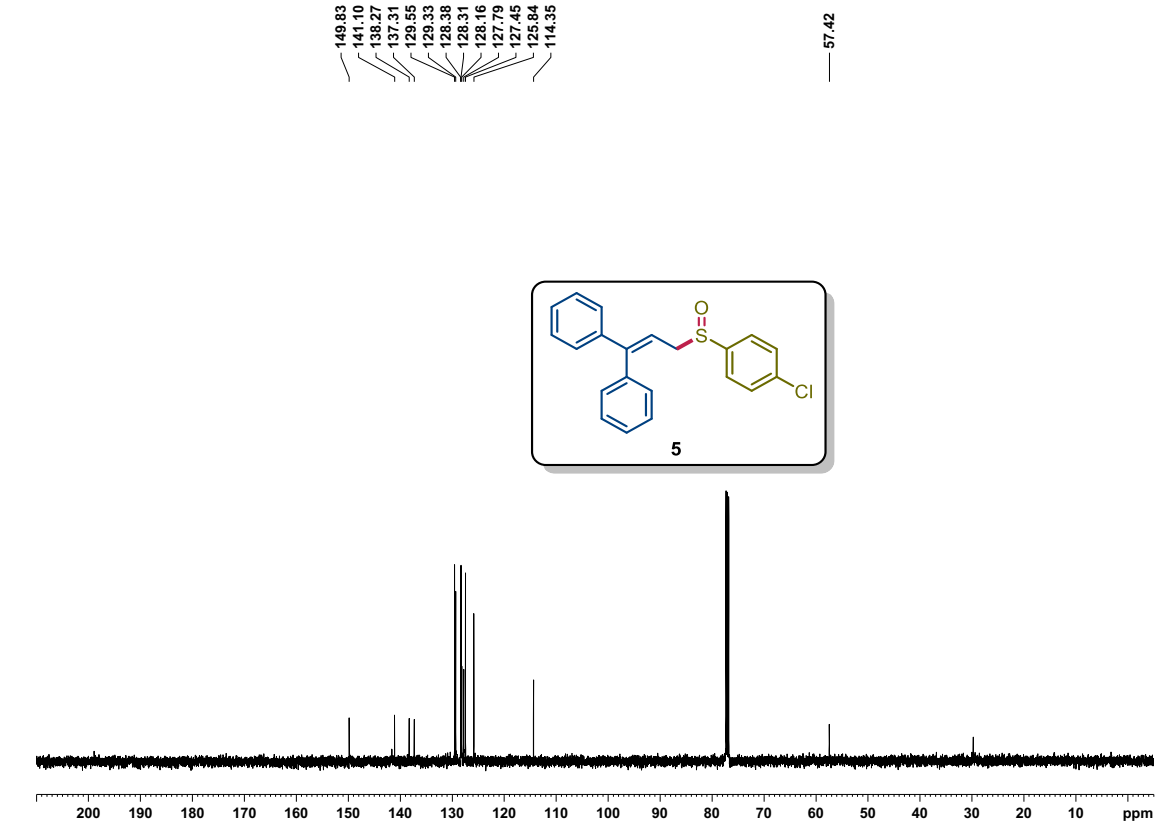

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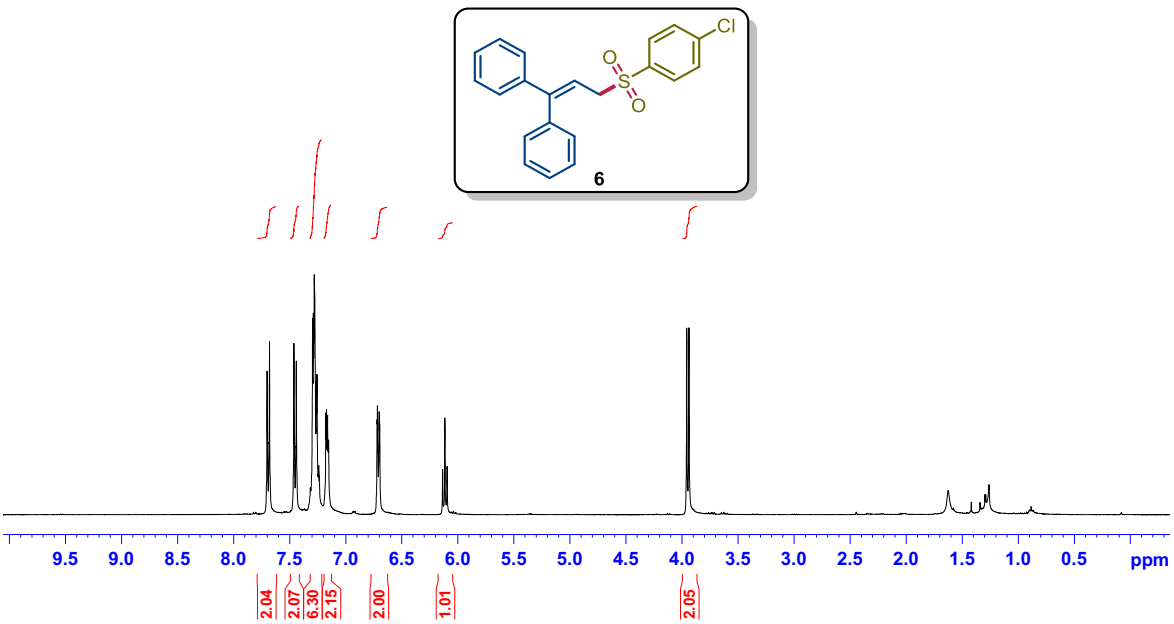

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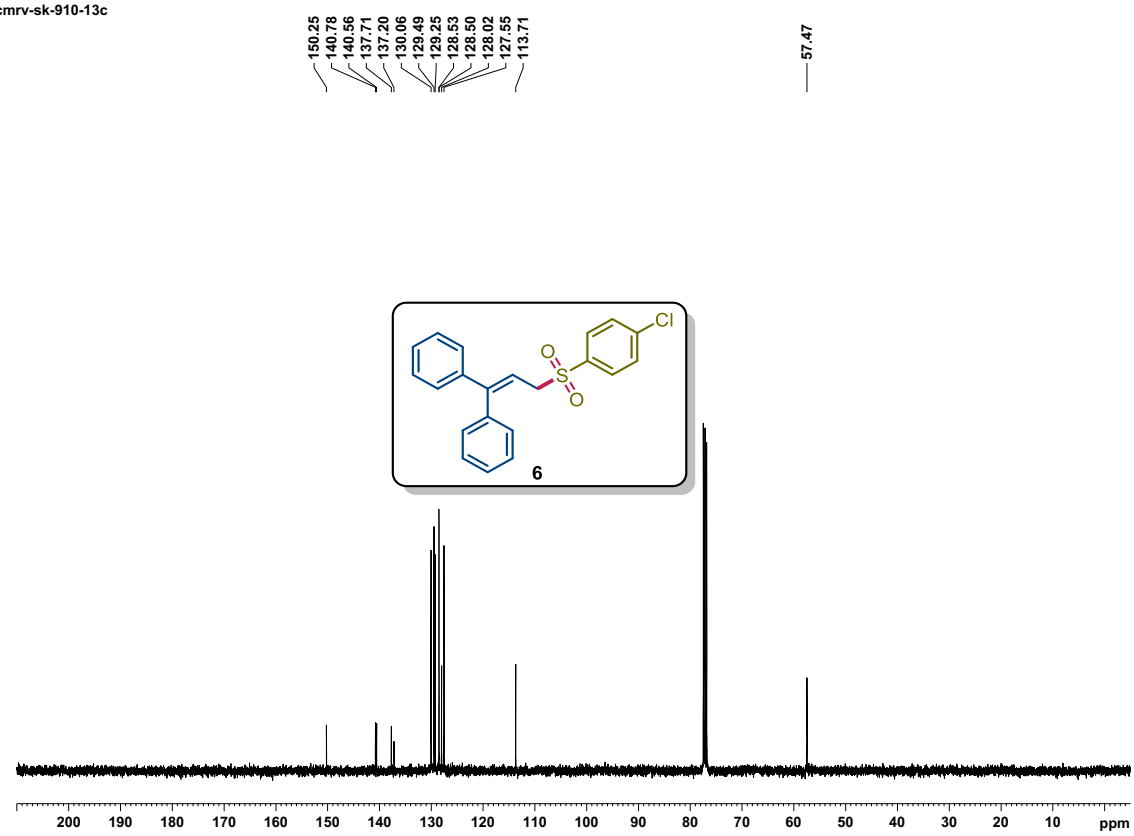

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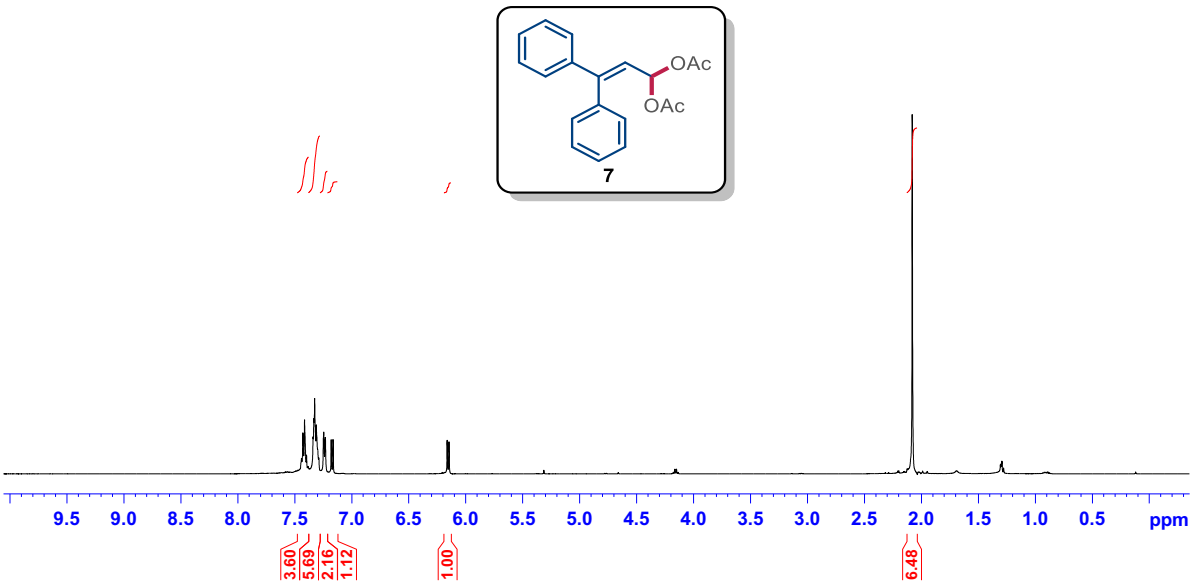

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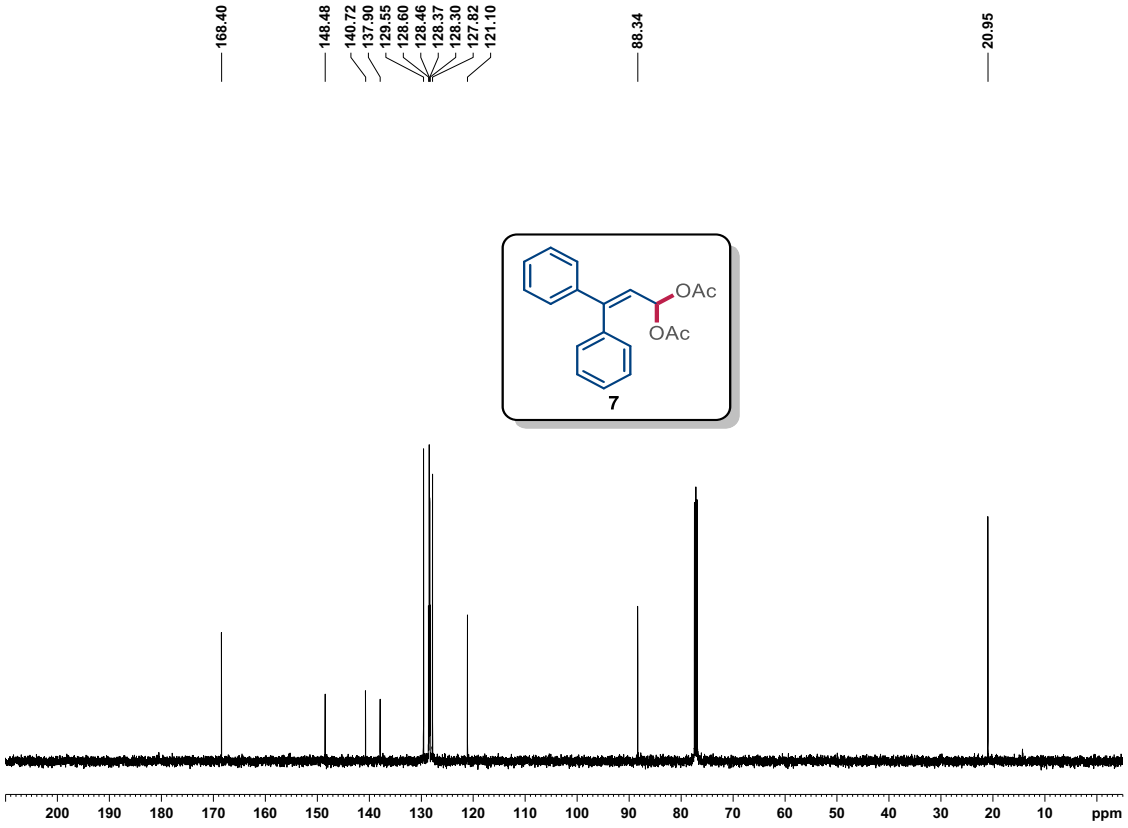

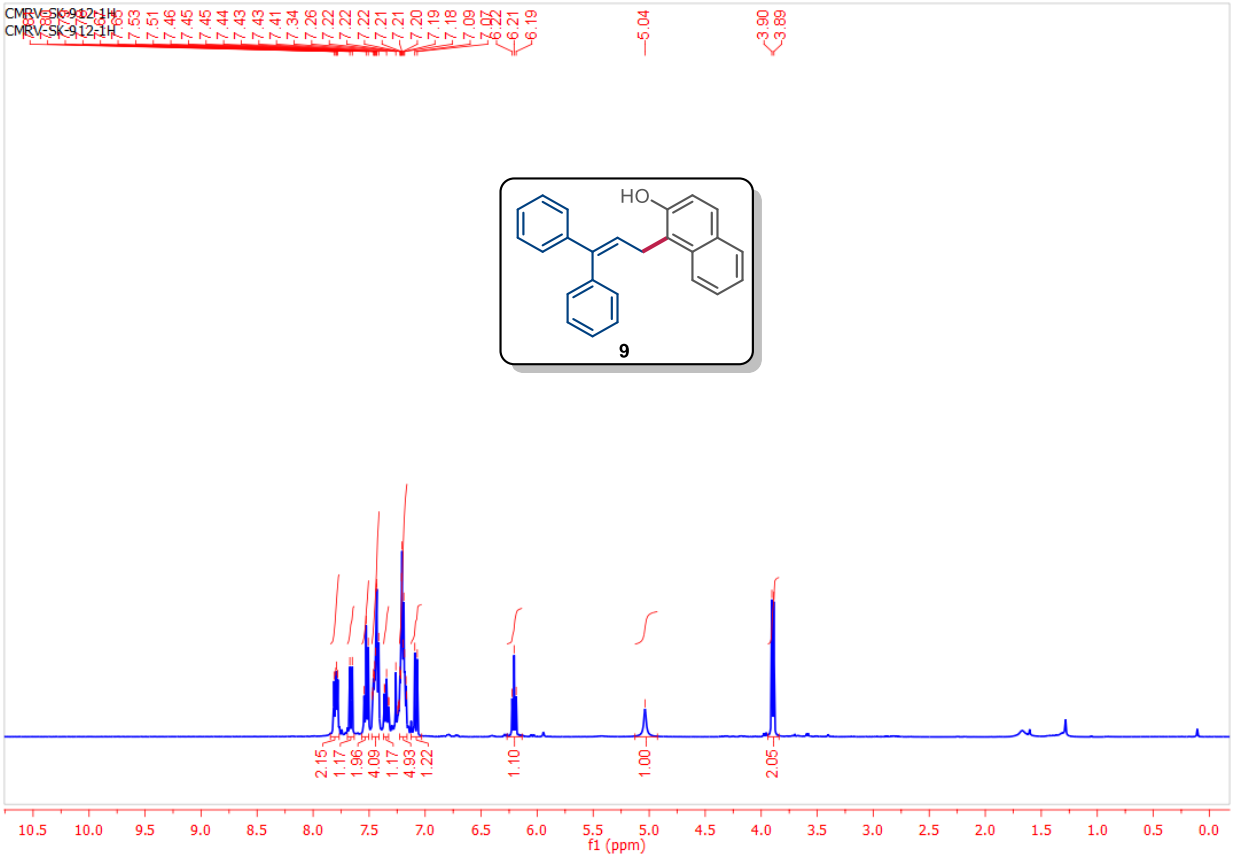

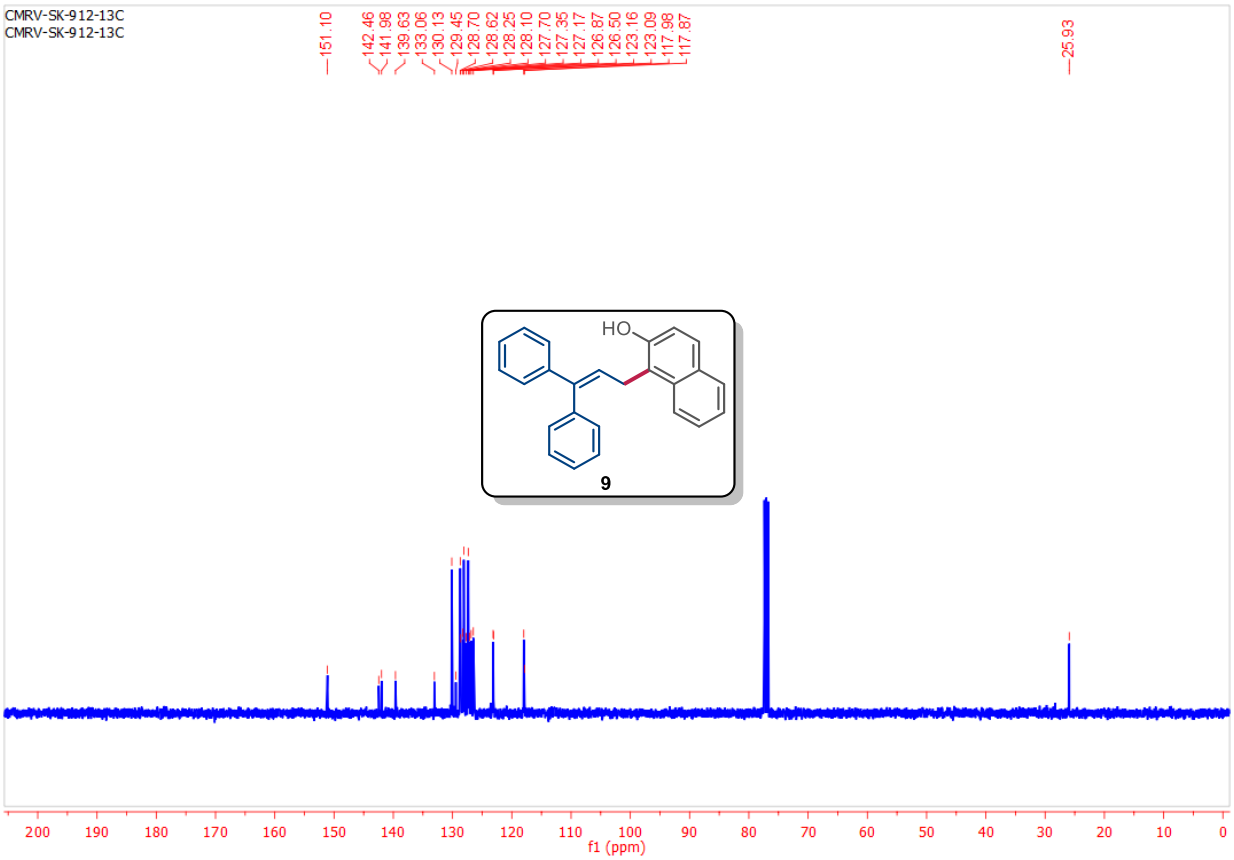
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