Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supporting Information

Iodine-mediated photoinduced tuneable disulfonylation and sulfinylsulfonylation of alkynes with sodium arylsulfinates

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1. General considerations

Chemicals were purchased and used without further purification unless otherwise stated. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on Varian VNMR spectrometers (400 and 500 MHz for ^{1}H NMR; 101 and 126 MHz for ^{13}C NMR) with TMS as an internal standard. Mass spectra were recorded on Agilent-6546-QToF spectrometer. TLC was performed on using Merck pre-coated TLC plates (Merck 60 F_{254}) and detected under UV light. Flash column chromatography (FCC) was performed using either silica gel [Davisil, 230-400 mesh (40-63 µm)] or using a Biotage Isolera® UV-VIS Flash Purification System Version 2.3.1 with Sfär Silica HC D (20 µm) prepacked silica cartridges.

Details of Light source:

Manufacturer: Kessil; Model: PR160L; Wavelength: 456 nm, Distance: 5 cm. Manufacturer gives spectral width as ~430-510 nm with radiant flux max at 456 nm of ~0.3 W/nm and 'average intensity of PR160 series' as 399mW/cm^2 (measured from 1 cm distance), max power consumption 50W.

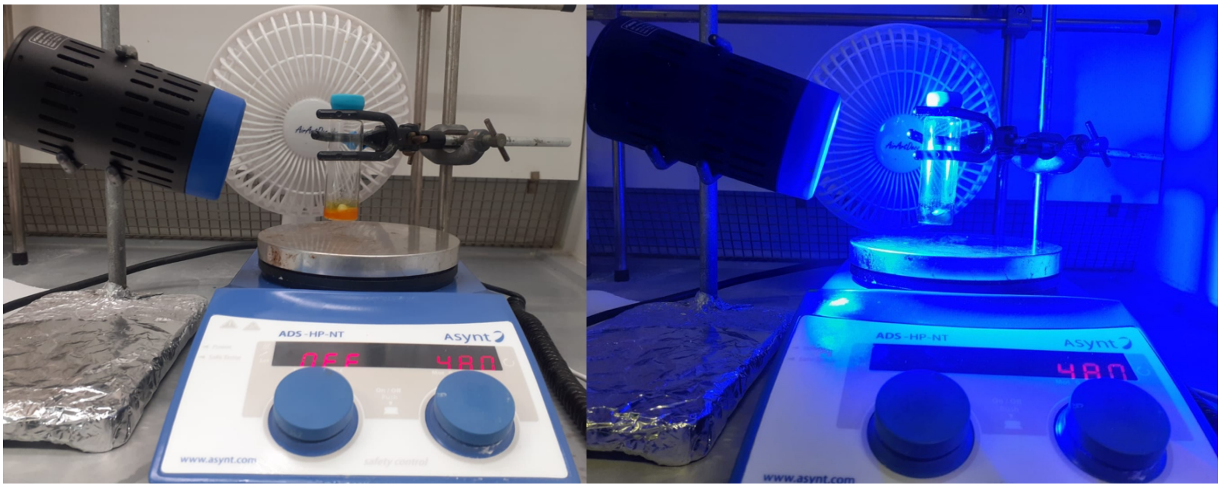


Fig. S1. Reaction setup.

2. UV-Visible spectra

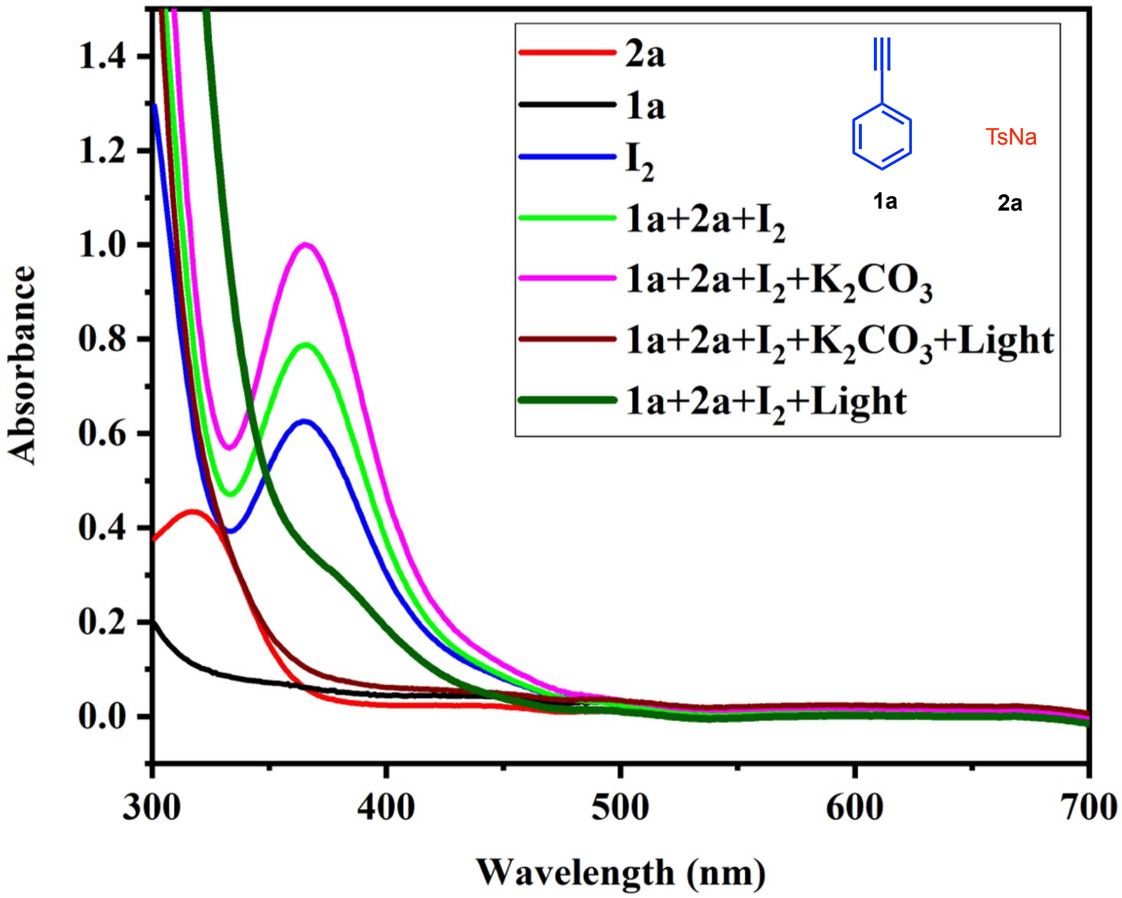
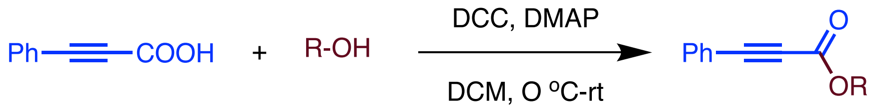


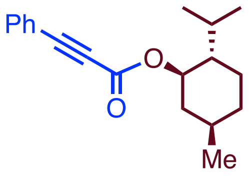
Fig. S2. UV-Visible absorption spectra of a *p*-tolunesulfinate **2a** (3 mM), phenylacetylene **1a** (5 mM), **I$_2$** (0.5 mM) with and without K$_2$CO$_3$, before and after irradiation of blue LED (10 minutes) in DMF solutions.

3. General procedures and spectral data

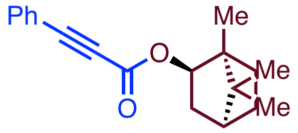
3.1 Preparation of 1bd, 1bg-1bi[1]

To a solution of 3-phenylpropiolic acid (2.0 mmol), corresponding alcohol (2.0 mmol) and DMAP (0.05 mmol) in DCM (4 mL) was added dropwise a solution of DCC (3.0 mmol) in DCM (4 mL) at 0 °C under a nitrogen atmosphere. After the addition was complete, the reaction was warmed to room temperature and stirred for another 2 h. After the completion of the reaction, the reaction mixture was filtrated. The filtrate was concentrated under reduced pressure and crude product was purified by flash column chromatography using EtOAc/pentane as an eluent to furnish the corresponding products. The NMR spectra matched literature data.[1]

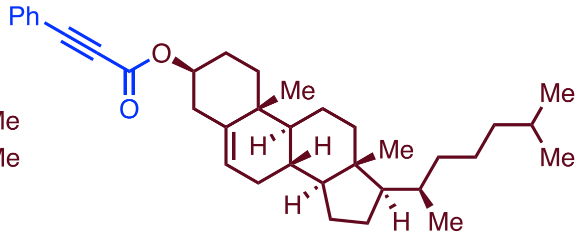




1bg, 91%



1bh, 89%



1bi, 68%

3.2 General procedure A for the synthesis of 1,2-bissulfonylethenes

The reaction tube was charged with alkyne (0.10 mmol), arylsulfinate (0.22 mmol), iodine (0.10 mmol) and K_2CO_3 (0.10 mmol) in dry DMF (1 mL). The mixture was stirred under blue LED irradiation for 2 hours (4 hours for internal alkynes). Then, the reaction mixture was diluted with ethyl acetate (10 mL) and washed with sodium thiosulfate (10 mL) and brine solution (10 mL). The organic layer was dried over Na_2SO_4 and then evaporated under reduced pressure. The crude product was purified by flash column chromatography using EtOAc/pentane as an eluent to furnish the corresponding 1,2-bissulfonylethenes.

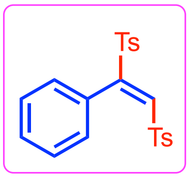
Note: Using a CFL bulb instead of the blue LED produced **3a** in 20% yield after 2 hours.

In all cases the reaction gave single geometrical isomer; in the cases of **3a-3c**, **3e-3m**, **3o** and **3p** our data matched the literature known *E*-alkene[2] and the other products are assigned as E-alkenes by analogy.

3.3 Scale-up reaction

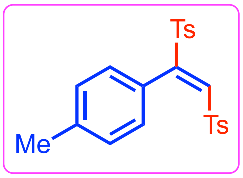
A 100 mL round bottom flask was charged with phenyl acetylene (0.510 g, 5 mmol), sodium *p*-tolunesulfinate (1.958 g, 11 mmol), iodine (1.265 g, 5 mmol) and K_2CO_3 (0.690 g, 5 mmol) in dry DMF (20 mL). The mixture was stirred under blue LED irradiation for 3.5 hours. Then, the reaction mixture was diluted with ethyl acetate (50 mL) and washed with sodium thiosulfate (100 mL) and brine solution (100 mL). The organic layer was dried over Na_2SO_4 and then evaporated under reduced pressure. The crude product was purified by flash column chromatography (EtOAc/pentane) to furnish (*E*)-4,4'-(1-phenylethene-1,2-diyldisulfonyl)bis(methylbenzene) as a light brown solid (1.457 g, 71%).

(*E*)-4,4'-(1-Phenylethene-1,2-diyldisulfonyl)bis(methylbenzene) (3a)[2]



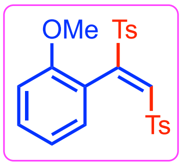
3a (35 mg) was synthesized following general procedure A; white solid; 88% yield (eluent: EtOAc/Pentane = 1:4); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (s, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.37 (app. d, *J* = 8.2 Hz, 3H), 7.22 – 7.18 (m, 6H), 6.93 (d, *J* = 7.6 Hz, 2H), 2.42 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.7, 145.7, 145.4, 137.5, 136.3, 133.9, 130.2, 130.00, 129.8, 129.7, 129.2, 128.2, 127.7, 127.0, 21.7, 21.6.

(*E*)-4,4'-(1-(*p*-Tolyl)ethene-1,2-diyldisulfonyl)bis(methylbenzene) (3b)[2]



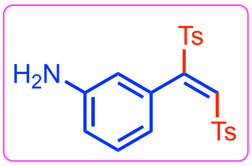
3b (37 mg) was synthesized following general procedure A; white solid; 84% yield (eluent: EtOAc/Pentane = 1:4); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (s, 1H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.21 (app. t, *J* = 8.0 Hz, 4H), 7.02 (d, *J* = 7.8 Hz, 2H), 6.87 – 6.80 (m, 2H), 2.43 (s, 3H), 2.40 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.8, 145.6, 145.3, 140.3, 137.4, 136.4, 133.3, 130.1, 129.8, 129.7, 129.2, 128.5, 128.2, 123.9, 21.7, 21.5.

(*E*)-4,4'-(1-(2-Methoxyphenyl)ethene-1,2-diyldisulfonyl)bis(methylbenzene) (3c)[2]



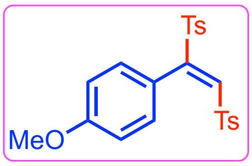
3c (33 mg) was synthesized following general procedure A; pale yellow solid; 75% yield (eluent: EtOAc/Pentane = 1:4); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.71 (s, 1H), 7.54 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.3 Hz, 2H), 7.32 (ddd, J = 8.3, 7.4, 1.8 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.20 – 7.16 (m, 2H), 6.98 (dd, J = 7.5, 1.8 Hz, 1H), 6.90 (td, J = 7.5, 1.0 Hz, 1H), 6.58 (dd, J = 8.3, 1.0 Hz, 1H), 3.26 (s, 3H), 2.43 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 156.9, 149.4, 145.2, 145.1, 137.6, 136.3, 133.8, 131.7, 131.0, 129.7, 129.5, 129.2, 128.4, 119.9, 116.1, 109.9, 54.7, 21.7.

(*E*)-3-(1,2-Ditosylvinyl)aniline (3d)



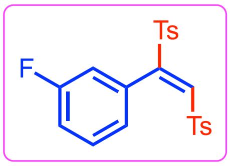
3d (29 mg) was synthesized following general procedure A; yellow solid; 68% yield (eluent: EtOAc/Pentane = 1:1); mp: 152-154 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.71 (s, 1H), 7.49 (d, J = 8.3 Hz, 2H), 7.45 – 7.39 (m, 2H), 7.21 (app dd, J = 8.3, 2.9 Hz, 4H), 6.95 (t, J = 7.8 Hz, 1H), 6.72 – 6.65 (m, 1H), 6.30 (s, 1H), 6.26 (d, J = 7.6 Hz, 1H), 2.41 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 152.7, 145.6, 145.3, 137.4, 136.2, 133.3, 129.7, 129.7, 129.2, 128.7, 128.3, 127.8, 121.2, 117.1, 116.8, 21.7, 21.6; HRMS: [M+H]$^+$ calculated for $C_{22}H_{22}NO_4S_2$: 428.0990, Found: 428.0982.

(*E*)-4,4'-(1-(4-Methoxyphenyl)ethene-1,2-diyldisulfonyl)bis(methylbenzene) (3e)[2]



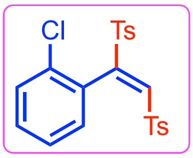
3e (34 mg) was synthesized following general procedure A; white solid; 79% yield (eluent: EtOAc/Pentane = 1:4); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.72 (s, 1H), 7.48 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.3 Hz, 2H), 7.23 – 7.19 (m, 4H), 6.92 (d, J = 8.8 Hz, 2H), 6.73 (d, J = 8.8 Hz, 2H), 3.81 (s, 3H), 2.42 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 161.1, 152.6, 145.5, 145.3, 137.4, 136.5, 133.5, 131.8, 129.8, 129.7, 129.1, 128.2, 118.8, 113.3, 55.3, 21.7.

(*E*)-4,4'-(1-(3-Fluorophenyl)ethene-1,2-diyldisulfonyl)bis(methylbenzene) (3f)[2]



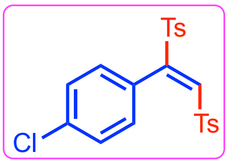
3f (33 mg) was synthesized following general procedure A; white solid; 78% yield (eluent: EtOAc/Pentane = 1:4); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (s, 1H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.21 (m, 4H), 7.20 – 7.16 (m, 1H), 7.06 (tdd, *J* = 8.5, 2.6, 1.0 Hz, 1H), 6.72 (dt, *J* = 7.6, 1.3 Hz, 1H), 6.63 (ddd, *J* = 9.1, 2.6, 1.6 Hz, 1H), 2.43 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.8 (d, *J* = 248.3 Hz), 151.1, 146.0, 145.7, 138.1, 138.1, 136.1, 132.9, 129.9 (d, *J* = 6.8 Hz), 129.4 (d, *J* = 8.3 Hz), 129.1, 128.9 (d, *J* = 8.4 Hz), 126.3 (d, *J* = 3.4 Hz), 117.2 (d, *J* = 5.2 Hz), 117.0 (d, *J* = 3.0 Hz), 21.7, 21.6.

(*E*)-4,4'-(1-(2-Chlorophenyl)ethene-1,2-diyldisulfonyl)bis(methylbenzene) (3g)[2]



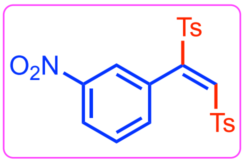
3g (34 mg) was synthesized following general procedure A; white solid; 74% yield (eluent: EtOAc/Pentane = 1:4); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (s, 1H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.33 (m, 1H), 7.32 – 7.29 (m, 2H), 7.26 – 7.20 (m, 4H), 7.09 (dd, *J* = 7.9, 1.7 Hz, 1H), 2.45 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 149.1, 146.0, 145.8, 137.7, 134.7, 132.9, 131.6, 131.3, 130.1, 129.8, 129.7, 129.2, 128.5, 126.6, 126.2, 21.8, 21.7.

(*E*)-4,4'-(1-(4-Chlorophenyl)ethene-1,2-diyldisulfonyl)bis(methylbenzene) (3h)[2]



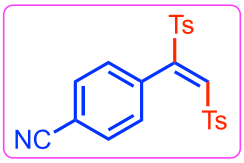
3h (39 mg) was synthesized following general procedure A; white solid; 86% yield (eluent: EtOAc/Pentane = 1:4); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (s, 1H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.26 – 7.19 (m, 6H), 6.89 (d, *J* = 8.5 Hz, 2H), 2.44 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 151.4, 145.9, 145.7, 137.9, 136.6, 136.1, 132.9, 131.5, 129.9, 129.9, 129.1, 128.2, 128.1, 125.5, 21.75, 21.73.

(*E*)-4,4'-(1-(3-Nitrophenyl)ethene-1,2-diyldisulfonyl)bis(methylbenzene) (3i) [2]



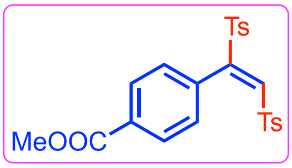
3i (37 mg) was synthesized following general procedure A; white solid; 81% yield (eluent: EtOAc/Pentane = 2:3); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.79 (s, 1H), 7.61 (t, *J* = 2.0 Hz, 1H), 7.53 – 7.45 (m, 3H), 7.41 (d, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 7.7 Hz, 1H), 7.26 (app. dd, *J* = 11.9, 8.1 Hz, 4H), 2.43 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.2, 147.4, 146.6, 146.2, 138.7, 136.2, 135.9, 132.4, 130.2, 130.1, 129.2, 129.0, 128.9, 128.1, 124.8, 124.7, 21.8, 21.7.

(*E*)-4-(1,2-Ditosylvinyl)benzonitrile (3j)[2]



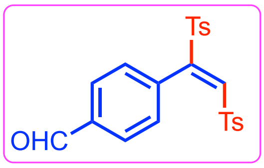
3j (37 mg) was synthesized following general procedure A; white solid; 84% yield (eluent: EtOAc/Pentane = 1:4); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (s, 1H), 7.55 – 7.52 (m, 4H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.32 – 7.29 (m, 2H), 7.26 – 7.23 (m, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 2.47 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.6, 146.4, 146.1, 138.0, 135.9, 132.7, 132.1, 131.4, 130.8, 130.2, 130.1, 129.1, 128.2, 117.9, 113.9, 21.8.

Methyl (*E*)-4-(1,2-ditosylvinyl)benzoate (3k)[2]



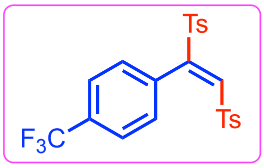
3k (42 mg) was synthesized following general procedure A; white solid; 89% yield (eluent: EtOAc/Pentane = 2:3); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 – 7.87 (m, 2H), 7.76 (s, 1H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.26 – 7.23 (m, 2H), 7.22 – 7.19 (m, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 3.94 (s, 3H), 2.43 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.3, 151.7, 146.0, 145.8, 137.8, 136.1, 132.9, 131.8, 131.4, 130.3, 130.0, 129.9, 129.1, 128.8, 128.2, 52.4, 21.7.

(*E*)-4-(1,2-Ditosylvinyl)benzaldehyde (3l)[2]



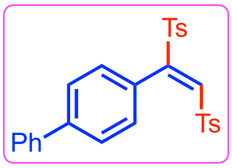
3l (39 mg) was synthesized following general procedure A; white solid; 88% yield (eluent: EtOAc/Pentane = 1:4); ^{1}H NMR (400 MHz, CDCl$_3$): δ 10.00 (s, 1H), 7.72 (app. dd, J = 5.9, 2.3 Hz, 3H), 7.50 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.3 Hz, 2H), 7.27 – 7.22 (m, 2H), 7.21 – 7.17 (m, 2H), 7.11 (d, J = 8.2 Hz, 2H), 2.42 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$): δ 191.4, 151.4, 146.2, 145.9, 137.8, 136.9, 136.0, 133.3, 132.8, 130.9, 130.1, 129.9, 129.1, 128.7, 128.2, 21.73, 21.70.

(*E*)-4,4'-(1-(4-(Trifluoromethyl)phenyl)ethene-1,2-diyldisulfonyl)bis(methylbenzene) (3m)[2]



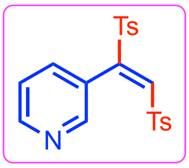
3m (42 mg) was synthesized following general procedure A; white solid; 88% yield (eluent: EtOAc/Pentane = 1:4); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.76 (s, 1H), 7.44 (d, J = 7.9 Hz, 4H), 7.37 (d, J = 7.9 Hz, 2H), 7.21 (t, J = 6.3 Hz, 4H), 7.02 (d, J = 7.9 Hz, 2H), 2.40 (s, 6H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 151.0, 146.2, 145.8, 138.4, 135.9, 132.8, 131.9 (app d, J = 33.1 Hz), 130.9, 130.6, 129.9, 129.2, 128.2, 124.6 (q, J = 3.5 Hz), 21.7, 21.6; ^{19}F NMR (376 MHz, CDCl$_3$): δ -63.00.

(*E*)-4-(1,2-Ditosylvinyl)-1,1'-biphenyl (3n)[2]



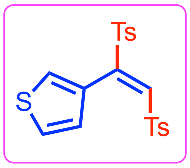
3n (42 mg) was synthesized following general procedure A; white solid; 85% yield (eluent: EtOAc/Pentane = 1:4); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.79 (s, 1H), 7.60 – 7.57 (m, 2H), 7.50 – 7.47 (m, 3H), 7.46 – 7.39 (m, 6H), 7.22 – 7.19 (m, 4H), 7.01 (d, J = 8.3 Hz, 2H), 2.40, 2.41 (2 x s, 6H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 152.5, 145.7, 145.4, 142.7, 139.8, 137.8, 136.3, 133.3, 130.7, 129.8, 129.8, 129.2, 128.9, 128.3, 128.0, 127.1, 126.3, 125.8, 21.7, 21.6.

(*E*)-3-(1,2-Ditosylvinyl)pyridine (3o)



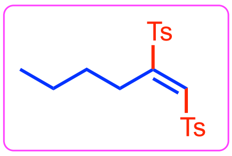
3o (31 mg) was synthesized following general procedure A; white solid; 78% yield (eluent: EtOAc/Pentane = 1:1); mp: 135-137 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.64 (br s, 1H), 8.06 (br s, 1H), 7.81 (s, 1H), 7.55 – 7.49 (m, 2H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 3H), 7.24 (d, *J* = 8.1 Hz, 2H), 2.45 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.1, 149.2, 149.0, 146.4, 146.1, 138.8, 138.1, 135.9, 132.5, 130.2, 130.2, 129.1, 128.2, 21.8; HRMS: $[M+H]^+$ calculated for $C_{21}H_{20}NO_4S_2$: 414.0833, Found: 414.0824.

(*E*)-3-(1,2-Ditosylvinyl)thiophene (3p)[2]



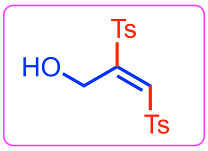
3p (34 mg) was synthesized following general procedure A; white solid; 79% yield (eluent: EtOAc/Pentane = 1:4); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (s, 1H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.28 – 7.25 (m, 1H), 7.24 – 7.17 (m, 5H), 6.86 (dd, *J* = 5.0, 1.3 Hz, 1H), 2.42 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 148.6, 145.6, 145.4, 137.8, 136.2, 133.5, 129.9, 129.8, 129.8, 129.3, 128.9, 128.1, 126.1, 125.3, 21.7.

(*E*)-4,4'-(Hex-1-ene-1,2-diyldisulfonyl)bis(methylbenzene) (3q)



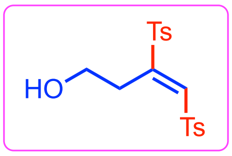
3q (21 mg) was synthesized following general procedure A; white solid; 55% yield (eluent: EtOAc/Pentane = 1:4); mp: 124-126 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.42 – 7.36 (m, 4H), 7.34 (s, 1H), 2.73 – 2.66 (m, 2H), 2.49 (s, 3H), 2.47 (s, 3H), 1.40 (tt, *J* = 8.0, 6.0 Hz, 2H), 1.34 – 1.28 (m, 2H), 0.84 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 154.7, 145.8, 145.7, 136.9, 135.2, 134.2, 130.3, 130.2, 128.8, 127.9, 31.8, 26.7, 23.0, 21.7, 13.4; HRMS: $[M+H]^+$ calculated for $C_{20}H_{25}O_4S_2$: 393.1194, Found: 393.1192.

(*E*)-2,3-Ditosylprop-2-en-1-ol (3r)



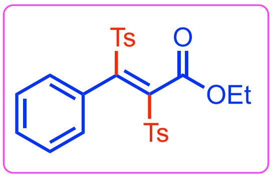
3r (19 mg) was synthesized following general procedure A; white solid; 48% yield (eluent: EtOAc/Pentane = 1:3); mp: 87-89 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.43 (s, 1H), 7.39 (m, 4H), 4.64 (d, *J* = 7.2 Hz, 2H), 3.12 (t, *J* = 7.6 Hz, 1H), 2.48 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.3, 146.5, 146.2, 137.8, 135.5, 133.8, 130.5, 130.4, 128.9, 128.2, 55.5, 21.79, 21.77; HRMS: $[M+H]^+$ calculated for $C_{17}H_{19}O_5S_2$: 367.0673, Found: 367.0668.

(*E*)-3,4-Ditosylbut-3-en-1-ol (3s)



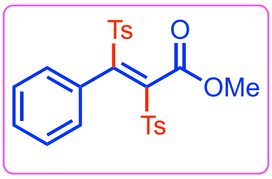
3s (22 mg) was synthesized following general procedure A; white solid; 59% yield (eluent: EtOAc/Pentane = 1:3); mp: 90-92 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.45 (s, 1H), 7.42 – 7.36 (m, 4H), 3.69 (q, *J* = 6.4 Hz, 2H), 3.05 (t, *J* = 6.4 Hz, 2H), 2.48 (s, 3H), 2.47 (s, 3H), 2.30 (t, *J* = 6.5 Hz, 1H).; ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.8, 146.1, 146.1, 137.1, 136.3, 133.7, 130.4, 130.4, 128.9, 128.0, 61.2, 29.9, 21.8; HRMS: $[M+H]^+$ calculated for $C_{18}H_{21}O_5S_2$: 381.0830, Found: 381.0824.

Ethyl (*E*)-3-phenyl-2,3-ditosylacrylate (4a)



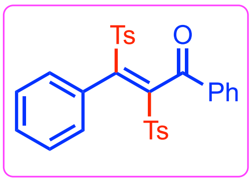
4a (35 mg) was synthesized following general procedure A; white solid; 75% yield (eluent: EtOAc/Pentane = 1:4); mp: 184-186 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.1 Hz, 2H), 7.34 – 7.29 (m, 1H), 7.29 – 7.25 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.11 (app dd, *J* = 16.6, 8.1 Hz, 4H), 6.67 (d, *J* = 7.6 Hz, 2H), 4.53 (q, *J* = 7.2 Hz, 2H), 2.402, 2.398 (2 x s, 6H), 1.49 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.6, 149.5, 145.9, 145.5, 145.1, 136.3, 133.5, 130.9, 129.8, 129.6, 129.4, 129.4, 128.6, 127.2, 126.8, 63.5, 21.76, 21.71, 13.9; HRMS: $[M+Na]^+$ calculated for $C_{25}H_{24}O_6S_2Na$: 507.0912, Found: 507.0902. A single crystal suitable for X-ray diffraction analysis was grown by slow evaporation from a $CHCl_3$ solution (see section 5 below).

Methyl (*E*)-3-phenyl-2,3-ditosylacrylate (4b)



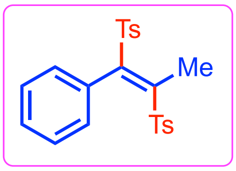
4b (34 mg) was synthesized following general procedure A; white solid; 72% yield (eluent: EtOAc/Pentane = 1:4); mp: 179-181 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.3 Hz, 2H), 7.30 (tt, *J* = 7.5, 1.3 Hz, 1H), 7.26-7.23 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.12 – 7.05 (m, 4H), 6.64 (d, *J* = 7.6 Hz, 2H), 4.06 (s, 3H), 2.39, 2.38 (2 x s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.1, 149.9, 145.9, 145.6, 144.9, 136.2, 133.3, 130.8, 129.8, 129.7, 129.4, 129.4, 128.6, 127.3, 53.9, 21.8, 21.7; HRMS: $[M+Na]^+$ calculated for $C_{24}H_{22}O_6S_2Na$: 493.0755, Found: 493.0754.

(*E*)-1,3-Diphenyl-2,3-ditosylprop-2-en-1-one (4c)



4c (28 mg) was synthesized following general procedure A; off white solid; 57% yield (eluent: EtOAc/Pentane = 2:3); mp: 208-210 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 – 8.13 (m, 2H), 7.72 – 7.66 (m, 1H), 7.60 (dd, *J* = 8.2, 7.0 Hz, 2H), 7.34 (tt, *J* = 7.4, 1.4 Hz, 1H), 7.29 (br t, *J* = 7.5 Hz, 1H), 7.23 (br d, *J* = 7.6 Hz, 1H), 7.21 – 7.16 (m, 4H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.97 (br t, *J* = 7.5 Hz, 1H), 6.33 (br d, *J* = 7.7 Hz, 1H), 2.38 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 188.5 (C=O), 150.6 (4°C), 150.1 (4°C), 145.8 (4°C), 145.4 (4°C), 137.0 (4°C), 136.5 (4°C), 134.0 (CH), 133.3 (4°C), 132.1 (CH), 129.9, 129.7, 129.5, 129.5, 129.5, 129.3, 128.8, 128.8, 127.6, 127.2 (CH), 21.7, 21.6; HRMS: $[M+H]^+$ calculated for $C_{29}H_{25}O_5S_2$: 517.1143, Found: 517.1135.

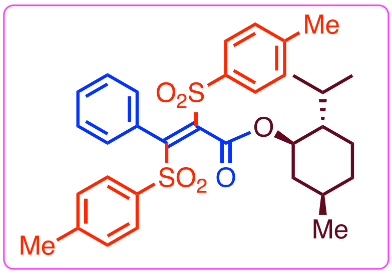
(*E*)-4,4'-(1-Phenylprop-1-ene-1,2-diyldisulfonyl)bis(methylbenzene) (4d)



4d (21 mg) was synthesized following general procedure A; white solid; 48% yield (eluent: EtOAc/Pentane = 1:4); mp: 110-112 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.1 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.24 – 7.19 (m, 1H), 7.13 (app dd, *J* = 10.5, 8.1 Hz, 4H), 7.04 (t, *J* = 7.8 Hz, 2H), 6.78 (dd, *J* = 8.1, 1.5 Hz, 2H), 2.77 (s, 3H), 2.39 (s, 3H), 2.37 (s, 3H); ^{13}C NMR

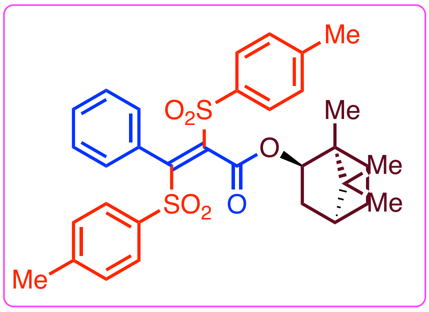
(126 MHz, $CDCl_3$): δ 148.9, 148.9, 145.1, 144.6, 136.4, 135.5, 131.4, 130.6, 129.5, 129.4, 129.0, 128.7, 127.9, 127.2, 21.6, 21.6, 15.8; HRMS: $[M+Na]^+$ calculated for $C_{23}H_{22}O_4S_2Na$: 449.0857, Found: 449.0847.

(1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl (*E*)-3-phenyl-2,3-ditosylacrylate (4f)



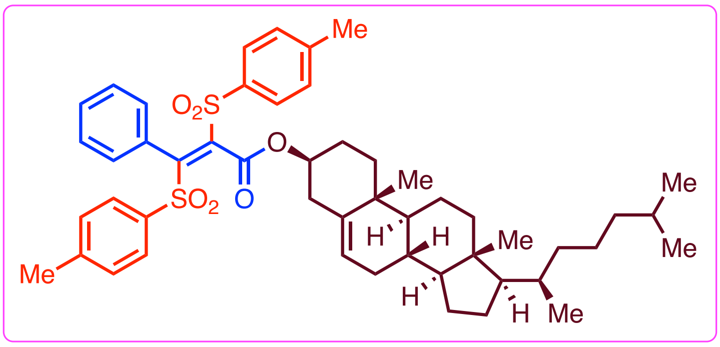
4f (41 mg) was synthesized following general procedure A; white solid; 71% yield (eluent: EtOAc/Pentane = 1:4); mp: 83-55 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 7.45 – 7.37 (m, 2H), 7.29 – 7.26 (m, 1H), 7.24 – 7.20 (m, 2H), 7.19 – 7.14 (m, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 7.04 (t, *J* = 7.7 Hz, 2H), 6.60 (br s, 2H), 5.07 (td, *J* = 10.9, 4.4 Hz, 1H), 2.53 (t, *J* = 8.8 Hz, 1H), 2.44 (qd, *J* = 7.1, 2.7 Hz, 1H), 2.39 (s, 3H), 2.38 (s, 3H), 1.77 (m, 2H), 1.67 – 1.61 (m, 2H), 1.27 – 1.15 (m, 2H), 0.98 (m, 7H), 0.89 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.2, 149.2, 145.7, 145.5, 145.2, 136.8, 133.6, 131.1, 130.8, 129.6, 129.4, 129.3, 128.4, 127.1, 126.9, 78.9, 47.3, 39.8, 34.3, 31.6, 25.3, 23.0, 22.1, 21.7, 21.7, 21.1, 15.8; HRMS: $[M+NH_4]^+$ calculated for $C_{33}H_{38}O_6S_2NH_4$: 612.2453, Found: 612.2444.

(1*S*,2*R*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl (*E*)-3-phenyl-2,3-ditosylacrylate (4g)



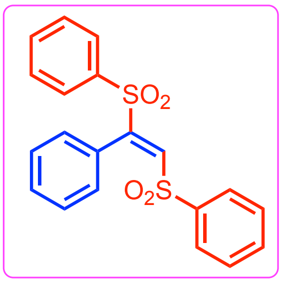
4g (42 mg) was synthesized following general procedure A; white solid; 73% yield (eluent: EtOAc/Pentane = 1:4); mp: 80-82 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.30 (m, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.19 – 7.16 (m, 2H), 7.13 – 7.10 (m, 2H), 7.09 – 7.03 (m, 2H), 6.64 (br s, 2H), 5.24 (d, *J* = 9.4 Hz, 1H), 2.54 – 2.46 (m, 1H), 2.39 (br s, 6H), 2.16 (ddd, *J* = 14.8, 10.0, 4.0 Hz, 1H), 1.84 (tt, *J* = 8.3, 3.7 Hz, 1H), 1.77 (t, *J* = 4.4 Hz, 1H), 1.50 – 1.39 (m, 3H), 1.06 (s, 3H), 0.99 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.8, 149.2, 145.8, 145.4, 136.6, 133.6, 131.1, 130.8, 129.7, 129.6, 129.4, 129.4, 128.5, 127.2, 127.2, 126.9, 84.3, 49.2, 48.0, 44.8, 27.9, 27.4, 21.7, 21.6, 19.7, 18.9, 13.5; HRMS: $[M+Na]^+$ calculated for $C_{33}H_{36}O_6S_2Na$: 615.1851, Found: 615.1839.

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl (*E*)-3-phenyl-2,3-ditosylacrylate (4h)



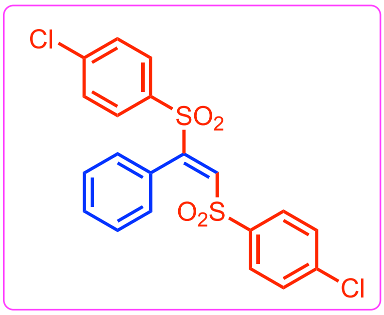
4h (23 mg) was synthesized following general procedure A; white solid; 58% yield (eluent: EtOAc/Pentane = 1:4); mp: 231-233 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.29 (m, 1H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 7.11 – 7.07 (m, 2H), 6.67 (br s, 2H), 5.47 (d, *J* = 5.0 Hz, 1H), 5.01 (tt, *J* = 11.0, 5.0 Hz, 1H), 2.58 (d, *J* = 14.2 Hz, 2H), 2.40 (br s, 6H), 2.20 (d, *J* = 12.9 Hz, 1H), 2.05 – 1.92 (m, 3H), 1.85 (ddt, *J* = 16.0, 13.7, 7.0 Hz, 2H), 1.64 – 1.56 (m, 2H), 1.50 (td, *J* = 9.0, 4.8 Hz, 2H), 1.40 – 1.31 (m, 3H), 1.28 – 1.11 (m, 8H), 1.09 (s, 4H), 1.02 (ddd, *J* = 12.1, 9.9, 5.3 Hz, 4H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.87 (dd, *J* = 6.6, 2.3 Hz, 6H), 0.70 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.9, 149.1, 145.8, 145.4, 145.3, 139.4, 136.4, 133.6, 130.9, 129.7, 129.6, 129.4, 128.7, 127.2, 126.9, 123.1, 77.7, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 37.6, 37.0, 36.6, 36.1, 35.8, 31.9, 31.8, 28.2, 28.0, 27.4, 24.3, 23.8, 22.8, 22.6, 21.8, 21.7, 21.0, 19.4, 18.7, 11.9; HRMS: $[M+Na]^+$ calculated for $C_{50}H_{64}O_6S_2Na$: 847.4042, Found: 847.4028.

(*E*)-(1-Phenylethene-1,2-diyldisulfonyl)dibenzene (5a)[3]



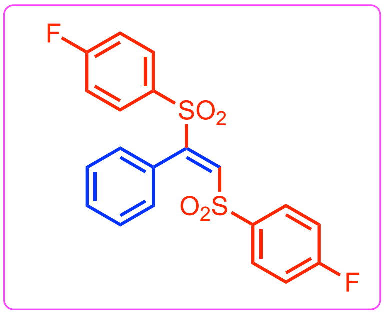
5a (32 mg) was synthesized following general procedure A; white solid; 85% yield (eluent: EtOAc/Pentane = 1:4); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (s, 1H), 7.62 – 7.56 (m, 4H), 7.53 – 7.48 (m, 2H), 7.46 – 7.41 (m, 4H), 7.38 – 7.34 (m, 1H), 7.19 (dd, *J* = 8.6, 7.1 Hz, 2H), 6.93 – 6.89 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.9, 139.2, 137.7, 136.1, 134.4, 134.2, 130.2, 130.1, 129.2, 129.2, 129.1, 128.2, 127.8, 126.8.

(*E*)-4,4'-(1-Phenylethene-1,2-diyldisulfonyl)bis(chlorobenzene) (5b)[3]



5b (36 mg) was synthesized following general procedure A; white solid; 81% yield (eluent: EtOAc/Pentane = 1:4); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (s, 1H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.44 – 7.40 (m, 3H), 7.39 – 7.35 (m, 4H), 7.24 (dd, *J* = 8.6, 7.2 Hz, 2H), 6.94 – 6.89 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.9, 141.6, 141.2, 137.9, 137.4, 134.5, 130.5, 130.5, 130.2, 129.6, 129.5, 129.5, 128.1, 126.5.

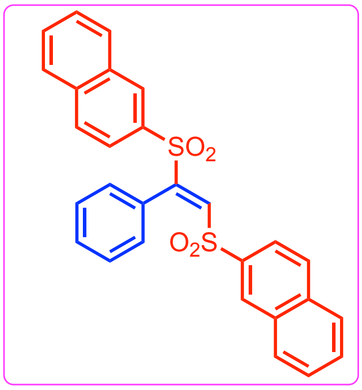
(*E*)-4,4'-(1-Phenylethene-1,2-diyldisulfonyl)bis(fluorobenzene) (5c)[3]



5c (34 mg) was synthesized following general procedure A; white solid; 82% yield (eluent: EtOAc/Pentane = 1:4); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (s, 1H), 7.57 – 7.52 (m, 2H), 7.52

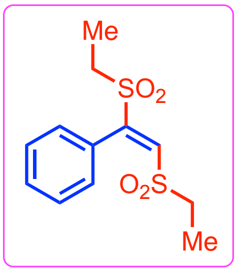
– 7.47 (m, 2H), 7.38 (m, 1H), 7.22 (dd, *J* = 8.6, 7.0 Hz, 2H), 7.06 (app dt, *J* = 8.9, 7.9 Hz, 4H), 6.93 – 6.89 (m, 2H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 166.2 (d, *J* = 259.6 Hz), 166.1 (d, *J* = 258.3 Hz), 152.9, 137.8, 135.1, 132.1, 132.0, 131.1 (d, *J* = 9.8 Hz), 130.4, 130.1, 128.0, 126.6, 116.6 (d, *J* = 4.8 Hz), 116.4 (d, *J* = 4.9 Hz).

(*E*)-2,2'-(1-Phenylethene-1,2-diyldisulfonyl)dinaphthalene (5d)[4]



5d (34 mg) was synthesized following general procedure A; white solid; 72% yield (containing ~10% unknown impurity) (eluent: EtOAc/Pentane = 1:4); ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.06 (d, *J* = 1.8 Hz, 1H), 8.00 (d, *J* = 1.9 Hz, 1H), 7.94 (s, 1H), 7.88 (app. dt, *J* = 8.1, 3.8 Hz, 3H), 7.85 – 7.81 (m, 2H), 7.79 (d, *J* = 6.8 Hz, 1H), 7.67 (app. dtd, *J* = 7.0, 3.7, 2.4 Hz, 2H), 7.62 – 7.57 (m, 3H), 7.44 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.23 – 7.20 (m, 1H), 7.04 (dd, *J* = 8.5, 7.1 Hz, 2H), 6.84 (dd, *J* = 8.2, 1.4 Hz, 2H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 153.1, 138.0, 135.8, 135.5, 135.4, 132.9, 131.9, 131.8, 131.6, 130.6, 130.2, 129.8, 129.7, 129.6, 129.58, 129.5, 129.3, 128.0, 127.9, 127.8, 127.7, 126.7, 123.1, 122.4.

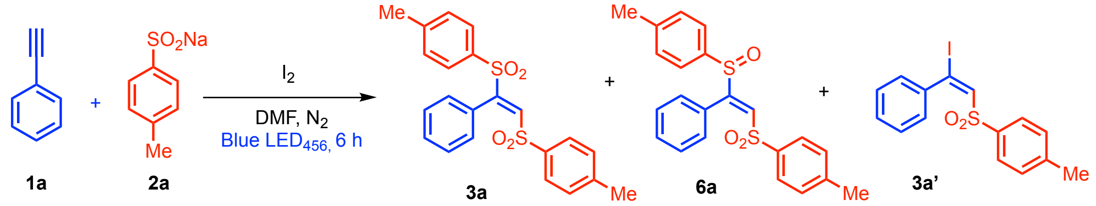
(*E*)-(1,2-bis(ethylsulfonyl)vinyl)benzene (5e)



5d (15 mg) was synthesized following general procedure A; off white solid; 52% yield (eluent: EtOAc/Pentane = 2:3); mp: 92-94 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.62 – 7.58 (m, 2H), 7.56 – 7.53 (m, 2H), 7.52 – 7.47 (m, 2H), 2.86 (app dq, *J* = 14.8, 7.4 Hz, 4H), 1.29 (app dt, *J* = 14.2, 7.5 Hz, 6H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 151.3, 136.1, 131.3, 129.9, 128.8, 127.2, 49.5, 45.9, 6.7, 6.6; HRMS: [M+Na]$^+$ calculated for $C_{12}H_{17}O_4S_2$: 289.0568; found: 289.0565.

3.4 Optimization table for β-sulfinyl alkenylsulfones

Table S1:



Entry	Additive	Time	Concentration	Yield (%)^b		
				3a	**6a**	**3a'**
1	None	2	0.1	10	30	35
1	None	6	0.1	15	41	35
2	None	6	0.05	15	55	20
3	H_2O (10 equiv.)	6	0.05	10	50	20
4	HCOOH (1 equiv.)	6	0.05	0	30	25
5	PPh_3 (1 equiv.)	6	0.05	0	35	10

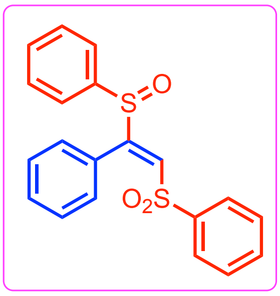
^{a}**Standard reaction conditions: 1a** (0.1 mmol), **2a** (0.22 mmol), I_2 (0.1 mmol), and K_2CO_3 (0.1 mmol) in DMF was irradiated with a blue LED (456 nm, 40W) under a N_2 atmosphere. ^{b}Isolated yields. n.r.= no reaction.

3.5 General procedure B for the synthesis of β-sulfinyl alkenylsulfones

The reaction tube was charged with alkyne (0.10 mmol), arylsulfinate (0.22 mmol) and iodine (0.10 mmol) in DMF (2 mL). The mixture was stirred under blue LED irradiation for 6 hours. Then, the reaction mixture was diluted with ethyl acetate and washed with sodium thiosulfate and brine solution. The organic layer was dried over Na_2SO_4 and then evaporated under reduced pressure. The crude material was purified by flash column chromatography using EtOAc/pentane as an eluent to furnish the corresponding β-sulfinyl alkenylsulfones.

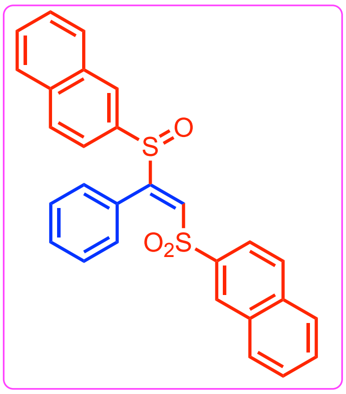
In all cases a single geometrical isomer was isolated; in the case of **6c-6g** this was established as being the *E*-alkene by comparison to the literature.[5]

(*E*)-((2-Phenyl-2-(phenylsulfinyl)vinyl)sulfonyl)benzene (6a)



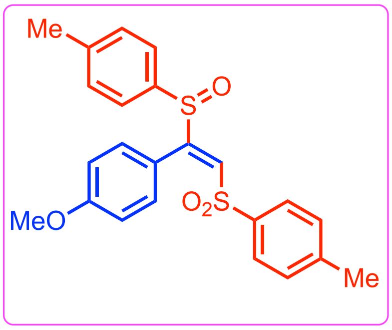
6a (18 mg) was synthesized following general procedure B; white solid; 51% yield (eluent: EtOAc/Pentane = 1:4); mp: 177-179 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.71 – 7.66 (m, 2H), 7.60 – 7.56 (m, 1H), 7.46 – 7.41 (m, 3H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.27 (d, *J* = 4.7 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.22 – 7.18 (m, 2H), 6.93 – 6.89 (m, 2H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 161.1, 140.3, 140.1, 133.8, 132.1, 130.2, 129.4, 129.2, 129.1, 129.1, 128.2, 127.9, 127.8, 125.3; HRMS: [M+H]$^+$ calculated for $C_{20}H_{17}O_3S_2$: 369.0619; found: 369.0611.

(*E*)-2-((2-(Naphthalen-2-ylsulfinyl)-2-phenylvinyl)sulfonyl)naphthalene (6b)



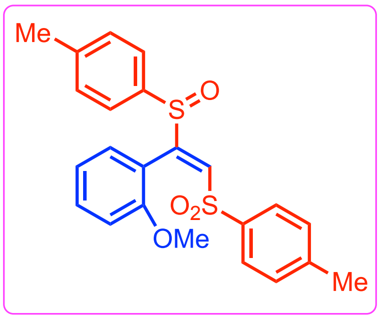
6b (15 mg) was synthesized following general procedure B; white solid; 34% yield (containing ~10% unknown impurity) (eluent: EtOAc/Pentane = 1:4); mp: 173-175 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.15 (d, *J* = 1.9 Hz, 1H), 7.89 (dd, *J* = 8.7, 3.1 Hz, 2H), 7.83 (app. dd, *J* = 8.7, 5.0 Hz, 3H), 7.70 – 7.66 (m, 4H), 7.58 (app. dt, *J* = 8.1, 6.7 Hz, 3H), 7.53 (d, *J* = 1.4 Hz, 1H), 7.51 (s, 1H), 7.29 (s, 1H), 7.15 (t, *J* = 7.8 Hz, 2H), 6.88 – 6.85 (m, 2H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 161.0, 136.9, 135.2, 134.7, 132.4, 131.9, 130.2, 129.9, 129.8, 129.6, 129.4, 129.3, 129.2, 128.5, 128.3, 128.1, 128.0, 127.9, 127.6, 127.4, 126.8, 122.47, 120.25; HRMS: [M+H]$^+$ calculated for $C_{28}H_{21}O_3S_2$: 469.0932; found: 469.0928.

(*E*)-1-Methoxy-4-(1-(*p*-tolylsulfinyl)-2-tosylvinyl)benzene (6c)[5]



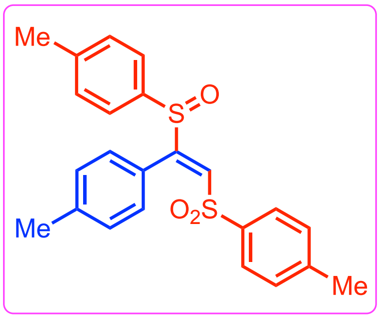
6c (25 mg) was synthesized following general procedure B; pale yellow solid; 62% yield (eluent: EtOAc/Pentane = 2:3); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.27 (s, 1H), 7.25 – 7.23 (m, 2H), 7.12 (s, 4H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H), 2.42 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 161.1, 160.4, 144.7, 142.6, 137.6, 137.3, 130.9, 129.8, 129.7, 128.7, 127.9, 125.4, 120.2, 113.6, 55.3, 21.6, 21.5.

(*E*)-1-Methoxy-2-(1-(*p*-tolylsulfinyl)-2-tosylvinyl)benzene (6d)[5]



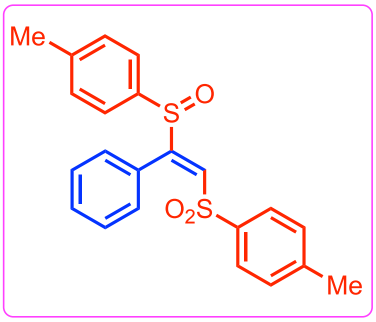
6d (23 mg) was synthesized following general procedure B; pale yellow solid; 55% yield (eluent: EtOAc/Pentane = 2:3); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.39 (s, 1H), 7.30 (ddd, *J* = 8.3, 7.5, 1.7 Hz, 1H), 7.22 – 7.18 (m, 2H), 7.13 (s, 4H), 6.80 (t, *J* = 7.5 Hz, 1H), 6.69 (d, *J* = 8.4 Hz, 1H), 6.58 (s, 1H), 3.48 (s, 3H), 2.40 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 156.4, 144.4, 142.4, 137.4, 131.6, 129.7, 129.4, 129.4, 128.1, 125.7, 119.9, 110.2, 55.0, 21.6, 21.5.

(*E*)-1-Methyl-4-((2-(*p*-tolyl)-2-(*p*-tolylsulfinyl)vinyl)sulfonyl)benzene (6e)[5]



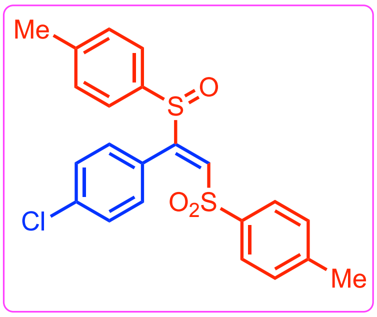
6e (25 mg) was synthesized following general procedure B; white solid; 61% yield (eluent: EtOAc/Pentane = 1:4); ^1H NMR (500 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.28 (s, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.12 (s, 4H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.85 (d, *J* = 7.9 Hz, 2H), 2.41 (s, 3H), 2.35 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.7, 144.8, 142.6, 140.4, 137.6, 137.1, 129.8, 129.7, 129.2, 128.9, 128.8, 127.9, 125.5, 125.2, 21.6, 21.5, 21.4.

(*E*)-1-Methyl-4-((2-phenyl-2-(*p*-tolylsulfinyl)vinyl)sulfonyl)benzene (6f)[5]



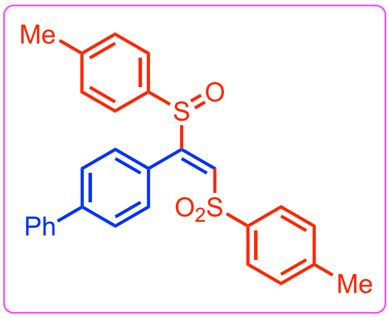
6f (21 mg) was synthesized following general procedure B; white solid; 55% yield (eluent: EtOAc/Pentane = 1:4); ^1H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.39 – 7.34 (m, 1H), 7.33 (s, 1H), 7.28 – 7.21 (m, 4H), 7.14 – 7.08 (m, 4H), 6.95 – 6.90 (m, 2H), 2.41 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.6, 144.8, 142.7, 137.5, 136.9, 130.1, 129.8, 129.7, 129.4, 129.2, 128.2, 128.0, 127.9, 125.4, 21.6, 21.4; HRMS: $[M+H]^+$ calculated for $C_{22}H_{21}O_3S_2$: 397.0932; found: 397.0926.

(*E*)-1-Chloro-4-(1-(*p*-tolylsulfinyl)-2-tosylvinyl)benzene (6g)[5]



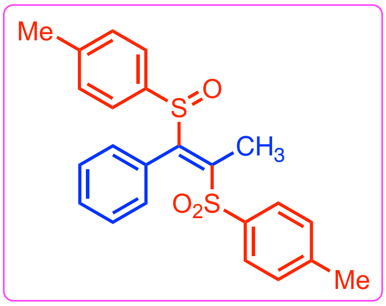
6g (16 mg) was synthesized following general procedure B; white solid; 38% yield (eluent: EtOAc/Pentane = 1:4); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.32 (s, 1H), 7.26 (app d, *J* = 7.2, 3.8 Hz, 4H), 7.17 – 7.12 (m, 4H), 6.89 – 6.84 (m, 2H), 2.43 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.3, 145.1, 143.1, 137.2, 136.6, 136.5, 130.5, 130.0, 130.0, 129.8, 128.4, 127.9, 126.6, 125.5, 21.7, 21.5.

(*E*)-4-(1-(*p*-Tolylsulfinyl)-2-tosylvinyl)-1,1'-biphenyl (6h)[5]



6h (19 mg) was synthesized following general procedure B; white solid; 40% yield (eluent: EtOAc/Pentane = 1:4); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 – 7.58 (m, 4H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.46 (s, 2H), 7.43 – 7.38 (m, 2H), 7.35 (s, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.14 (app. d, *J* = 6.1 Hz, 3H), 7.01 (d, *J* = 8.3 Hz, 2H), 2.41 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.3, 144.8, 142.8, 139.8, 137.5, 136.9, 129.9, 129.7, 129.5, 128.9, 128.9, 128.0, 127.9, 127.0, 126.9, 126.6, 125.5, 21.6, 21.5.

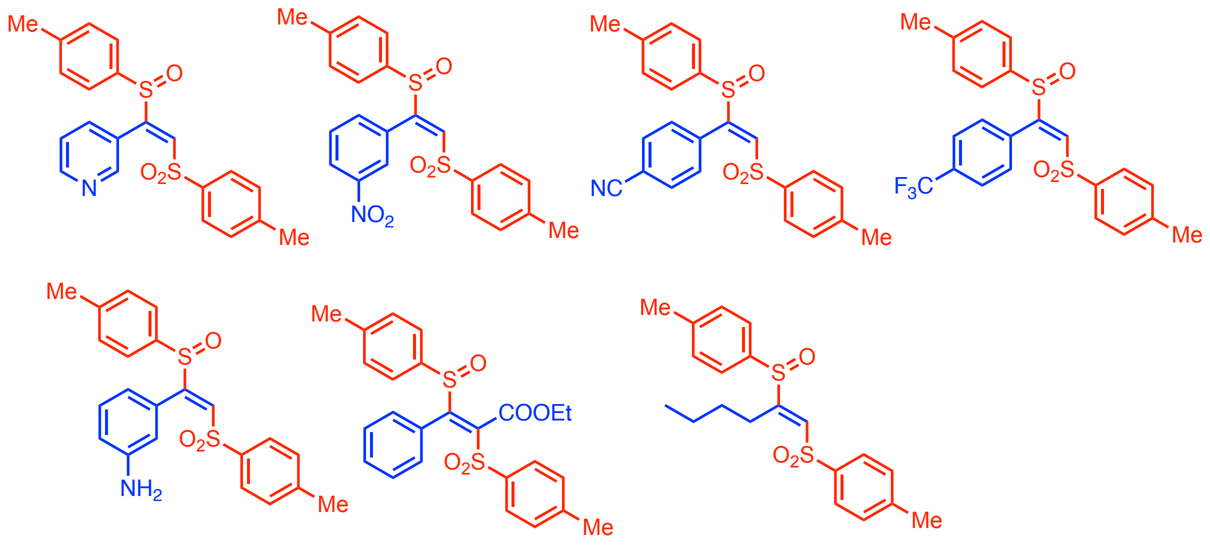
(*E*)-1-Methyl-4-((1-phenyl-1-(*p*-tolylsulfinyl)prop-1-en-2-yl)sulfonyl)benzene (6k)[5]



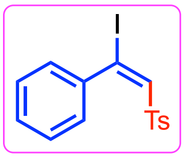
6k (14 mg) was synthesized following general procedure B; white solid; 35% yield (eluent: EtOAc/Pentane = 1:4); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.29 – 7.26 (m, 4H), 7.18 – 7.14 (m, 2H), 7.12 – 7.09 (m, 2H), 7.05 – 6.96 (m, 3H), 6.76 (br s, 1H), 6.22 (br s, 1H), 2.72 (s, 3H), 2.38 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 153.5, 144.5, 144.0, 141.9, 137.8, 136.5, 129.6, 129.4, 128.8, 128.0, 126.7, 124.3, 21.6, 21.4, 15.7.

Unsuccessful derivatives of β-sulfinyl alkenylsulfones:

The bellow β-sulfinyl alkenylsulfones are unsuccessful, corresponding alkynes gave major product of 1,2-bisulfonylethenaes and desired β-sulfinyl alkenylsulfones were observed in less than ~20% in TLC.

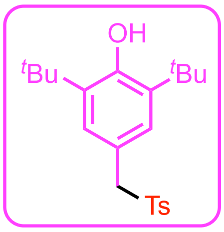


(*E*)-1-((2-Iodo-2-phenylvinyl)sulfonyl)-4-methylbenzene (3a')[6]



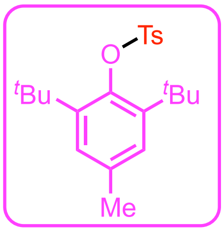
3a', (21 mg) was synthesized by following general procedure A except the reaction was quenched after 1 hour; white solid; 35% yield (eluent: EtOAc/Pentane = 1:9); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.36 (s, 1H), 7.33 – 7.27 (m, 3H), 7.24 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.21 – 7.18 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 144.6, 141.28, 141.26, 139.7, 137.3, 129.8, 129.7, 127.91, 127.88, 127.7, 114.1, 21.6.

2,6-di-*tert*-butyl-4-(tosylmethyl)phenol (7)[7]



7, (22 mg) was synthesized by following general procedure A with addition of BHT (4 equiv.); white solid; 27% yield (eluent: EtOAc/Pentane = 1:9); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 6.71 (s, 2H), 5.22 (s, 1H), 4.17 (s, 2H), 2.38 (s, 3H), 1.30 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.2, 144.3, 135.9, 134.9, 129.3, 128.9, 127.6, 118.9, 63.2, 34.1, 30.0, 21.5; HRMS: $[M+Na]^+$ calculated for $C_{22}H_{30}O_3SNa$: 397.1813; found: 397.1808.

2,6-Di-*tert*-butyl-4-methylphenyl 4-methylbenzenesulfonate (8)[7]

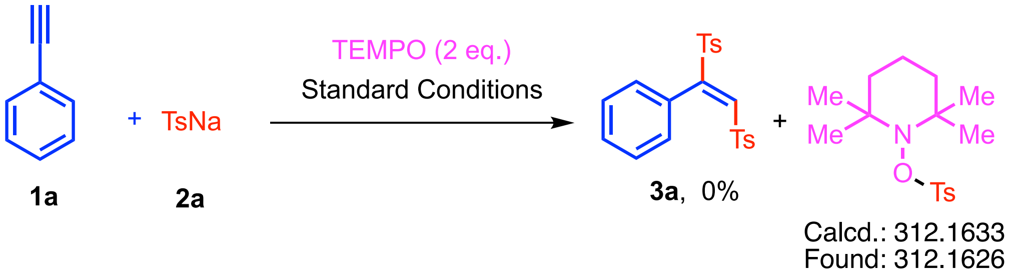


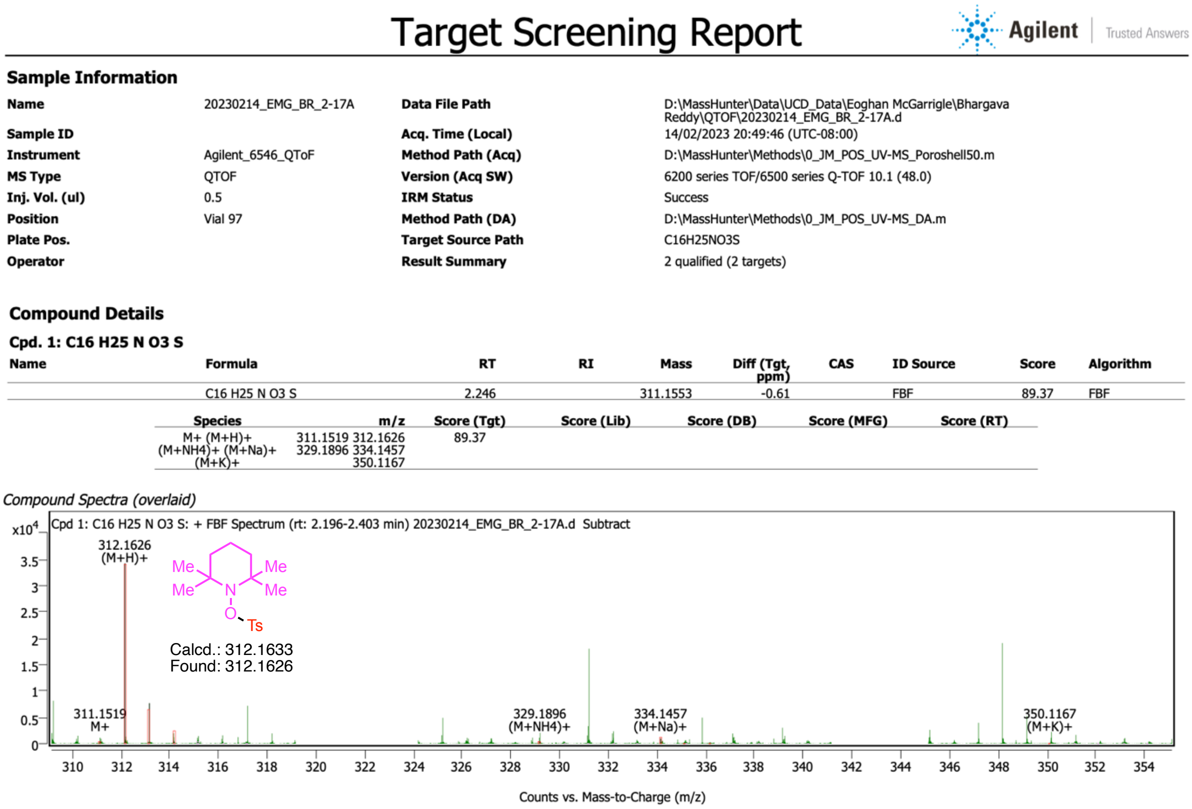
7, (15 mg) was synthesized by following general procedure A with addition of BHT (4 equiv.); white solid; 19% yield (eluent: EtOAc/Pentane = 5:95); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 7.7 Hz, 2H), 6.62 (s, 2H), 2.34 (s, 3H), 1.79 (s, 3H), 1.08 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 183.7, 151.2, 145.3, 135.7, 130.6, 130.2, 128.8, 65.8, 35.2, 28.9, 21.6, 18.5.

4. Intermediate trapping experiment

4.a HRMS analysis of reaction mixture

General Procedure A was followed except that TEMPO (2 eq.) was added. **3a** was not formed. After completion of the reaction, the reaction mixture was directly analysed by HRMS.





Target Screening Report

Sample Information

Name	20230214_EMG_BR_2-17A	**Data File Path**	D:\MassHunter\Data\UCD_Data\Eoghan McGarrigle\Bhargava Reddy\QTOF\20230214_EMG_BR_2-17A.d
Sample ID		**Acq. Time (Local)**	14/02/2023 20:49:46 (UTC-08:00)
Instrument	Agilent_6546_QToF	**Method Path (Acq)**	D:\MassHunter\Methods\0_JM_POS_UV-MS_Poroshell50.m
MS Type	QTOF	**Version (Acq SW)**	6200 series TOF/6500 series Q-TOF 10.1 (48.0)
Inj. Vol. (ul)	0.5	**IRM Status**	Success
Position	Vial 97	**Method Path (DA)**	D:\MassHunter\Methods\0_JM_POS_UV-MS_DA.m
Plate Pos.		**Target Source Path**	C16H25NO3S
Operator		**Result Summary**	2 qualified (2 targets)

Compound Details

Cpd. 1: C16 H25 N O3 S

Name	Formula	RT	RI	Mass	Diff (Tgt, ppm)	CAS	ID Source	Score	Algorithm
	C16 H25 N O3 S	2.246		311.1553	-0.61		FBF	89.37	FBF

Species	m/z	Score (Tgt)	Score (Lib)	Score (DB)	Score (MFG)	Score (RT)
M+ (M+H)+ (M+NH4)+ (M+Na)+ (M+K)+	311.1519 312.1626 329.1896 334.1457 350.1167	89.37				

Compound Spectra (overlaid)

Cpd 1: C16 H25 N O3 S: + FBF Spectrum (rt: 2.196-2.403 min) 20230214_EMG_BR_2-17A.d Subtract

Fig. S3. HRMS spectrum.

5. X-ray crystallographic studies of compound 4a (CCDC 2245556)

A single crystals of compound **4a** for X-ray diffraction analysis were grown using $CHCl_3$ solvent under slow evaporation method.

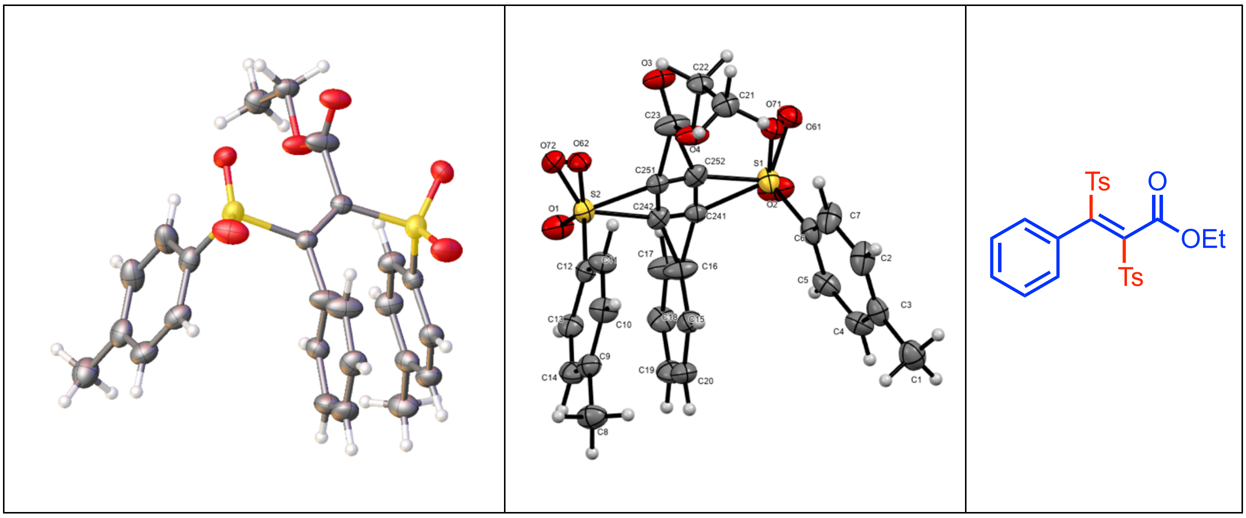


Fig. S4. Asymmetric unit, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Experimental:

A translucent light colourless, block shaped crystal of **4a** was mounted.

Data were obtained at a temperature of 92(6) K in a SuperNova, Dual, Cu at home/near four-circle diffractometer with a microfocus sealed X-ray tube, using a mirror as a monochromator and an Atlas detector and with Cu Kα radiation (λ = 1.54184 Å).

All data were integrated with CrysAlisPro and a gaussian absorption correction using SCALE3 ABSPACK was applied. All structures was solved by dual methods using SHELXT and refined by full-matrix least-squares methods against F^2 by SHELXL using OLEX2 as an interface. Hydrogen atoms were placed in calculated positions and refined using a riding model with their displacement parameters equal to 1.2 Uiso of the non-hydrogen atom to which they are attached.

All non-hydrogen atoms were refined with anisotropic displacement parameters while All C-bonded hydrogen atoms were refined at the calculated positions. The atoms C241-C242 as well as O61, O62, O71 and O72 presented a positional disorder which was refined.

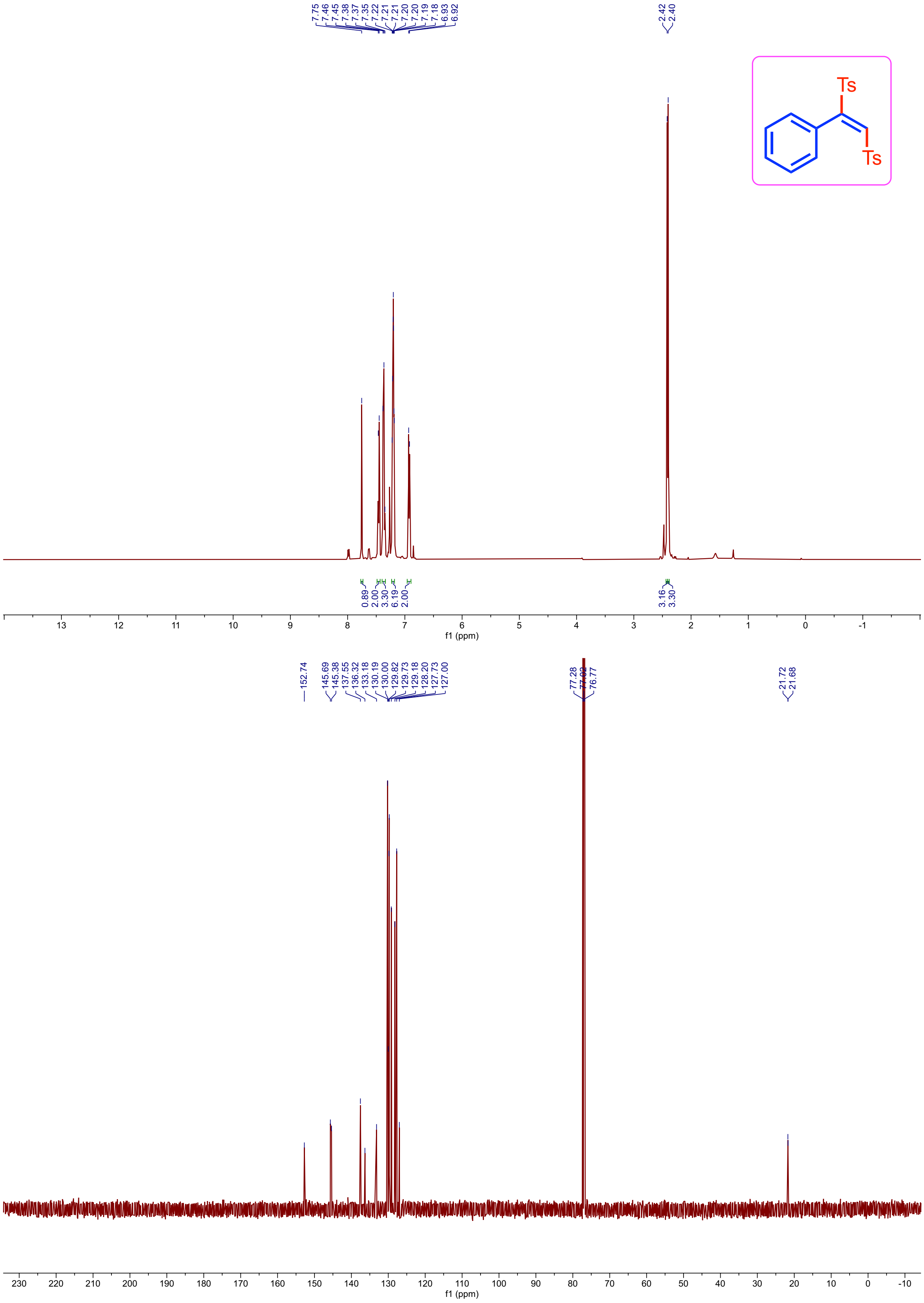
Table S2. Crystal data and structure refinement for compound **4a**.

Empirical formula	$C_{25}H_{24}O_{6.03}S_2$
Formula weight	485.04
Temperature [K]	92(6)
Crystal system	monoclinic
Space group (number)	$P2_1/c$ (14)
***a* [Å]**	7.48110(10)
***b* [Å]**	14.9608(2)
***c* [Å]**	20.8358(2)
α [°]	90
β [°]	93.7760(10)
γ [°]	90
Volume [Å^3]	2326.95(5)
Z	4
ρ_{calc} [gcm^{-3}]	1.385
μ [mm^{-1}]	2.413
***F*(000)**	1017
Crystal size [mm^3]	0.29×0.24×0.15
Crystal colour	translucent light colourless
Crystal shape	block
Radiation	Cu K_α (λ=1.54184 Å)
2θ range [°]	7.28 to 145.18 (0.81 Å)
Index ranges	$-9 \leq h \leq 9$ $-15 \leq k \leq 18$ $-25 \leq l \leq 25$
Reflections collected	30525
Independent reflections	4575 $R_{int} = 0.0439$ $R_{sigma} = 0.0204$
Completeness to θ = 67.684°	100.0 %
Data / Restraints / Parameters	4575/0/341
Goodness-of-fit on F^2	1.023
Final *R* indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0349$ $wR_2 = 0.0892$
Final *R* indexes [all data]	$R_1 = 0.0394$ $wR_2 = 0.0930$
Largest peak/hole [eÅ^{-3}]	0.35/-0.37

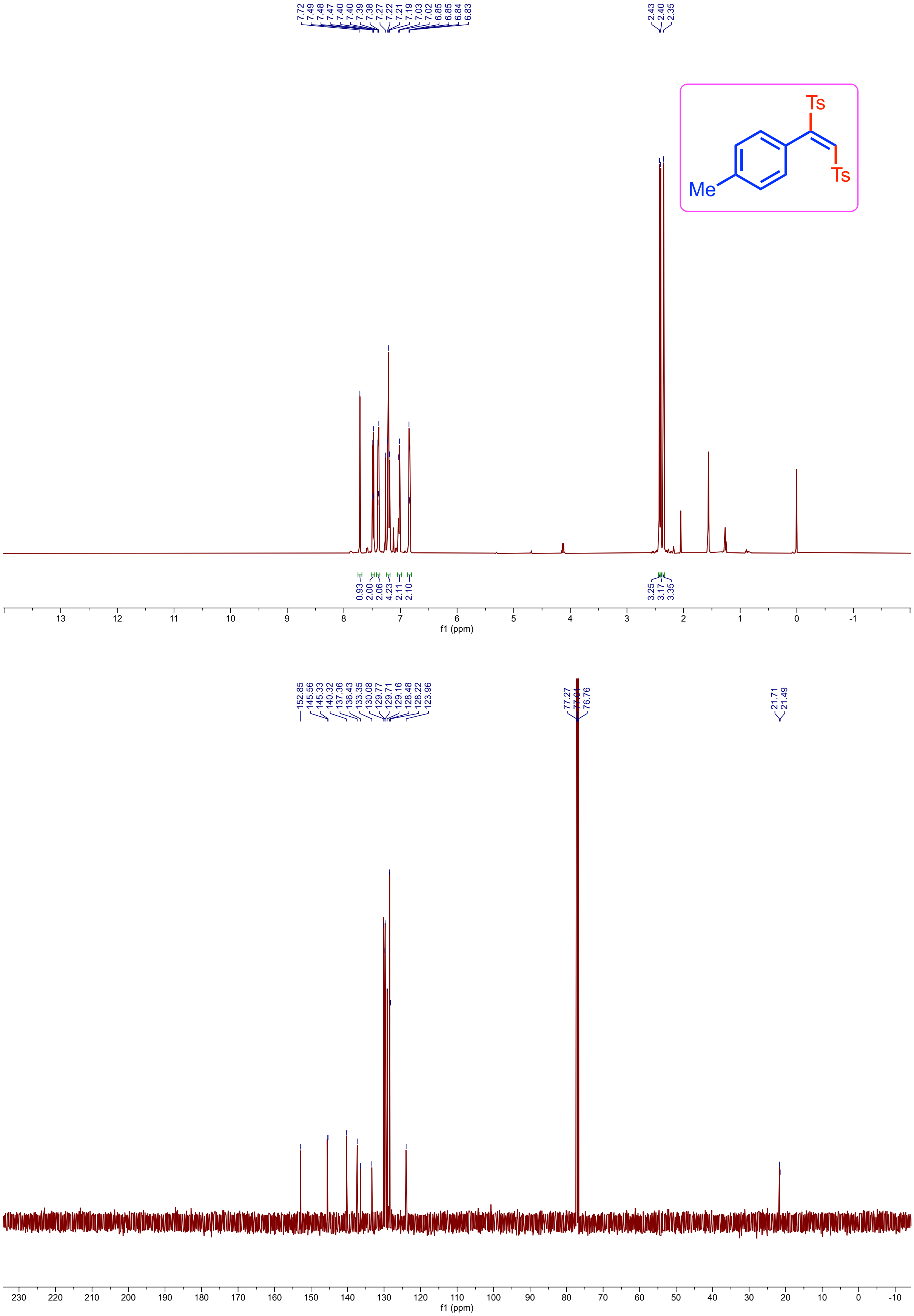
References:

1. R. Shen, K. Chen, Q. Deng, J. Yang, and L. Zhang, *Org. Lett.,* 2014, **16**, 1208–1211.
2. Y. Wang, K. Tang, Z. Liu and Y. Ning, *Chem. Commun.*, 2020, **56**, 13141–13144.
3. H. Fu, J.-Q. Shang, T. Yang, Y. Shen, C.-Z. Gao and Y.-M. Li, *Org. Lett.*, 2018, **20**, 489-492.
4. Z. Liu, L. Yang, K. Zhang, W. Chen, T. Yu, L. Wang, W. Gao and B. Tang, *Org. Lett.*, 2020, **22**, 2081-2086.
5. Z. Wang, Z. Zhang, W. Zhao, P. Sivaguru, G. Zanoni, Y. Wang, E. A. Anderson and X. Bi, *Nat. Commun.*, 2021, **12**, 5244-5255.
6. Y. Sun, A. Abdukader, D. Lu, H. Zhang and C. Liu, *Green Chem.*, 2017, **19**, 1255–1258.
7. L.-J. Wang, J.-M. Chen, W. Dong, C.-Y. Hou, M. Pang, W.-B. Jin, F.-G. Dong, Z.-D. Xu and W. Li, *J. Org. Chem.*, 2019, **84**, 2330–2338.

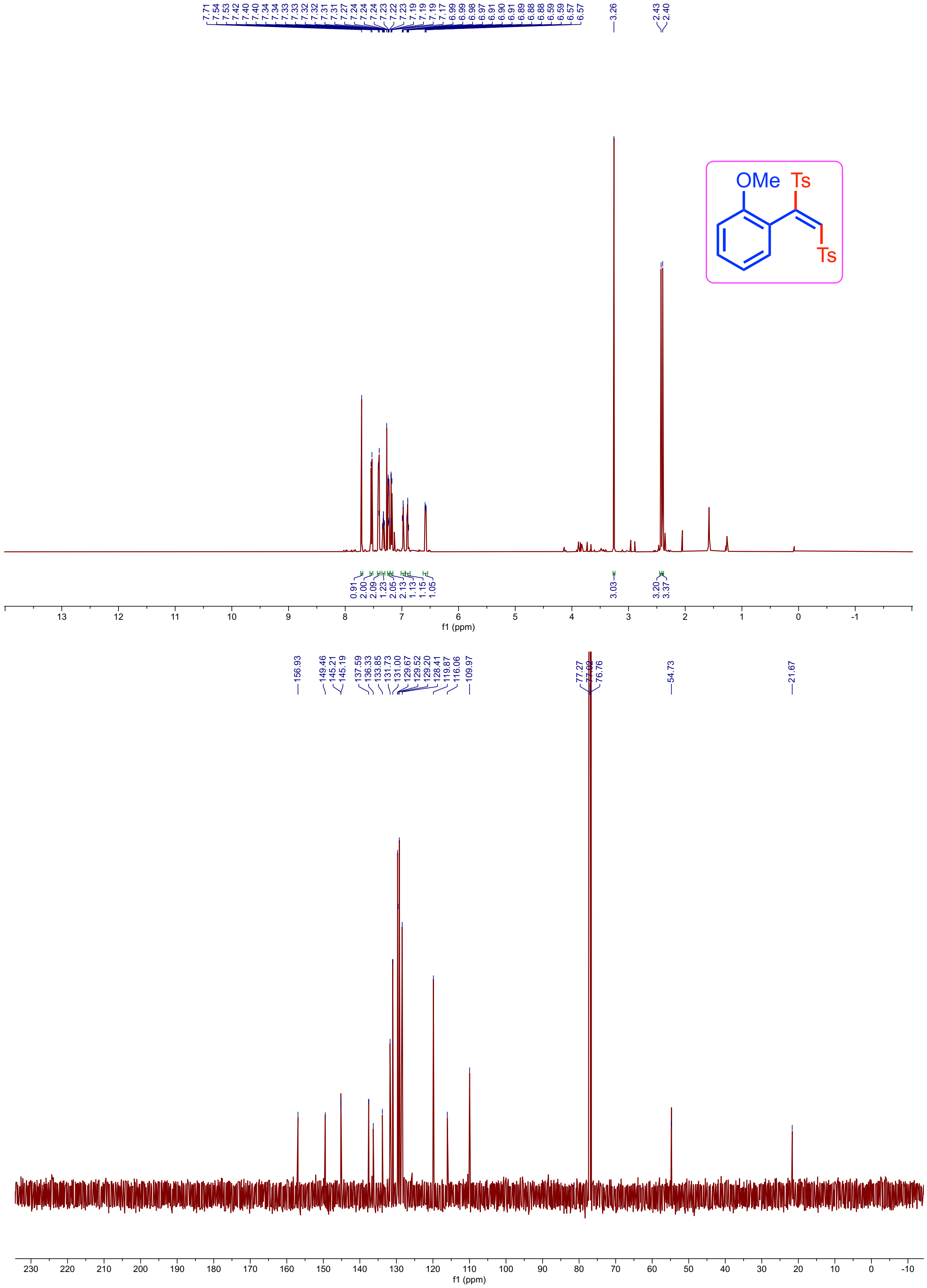
8. Copies of 1H and 13C NMR spectra:



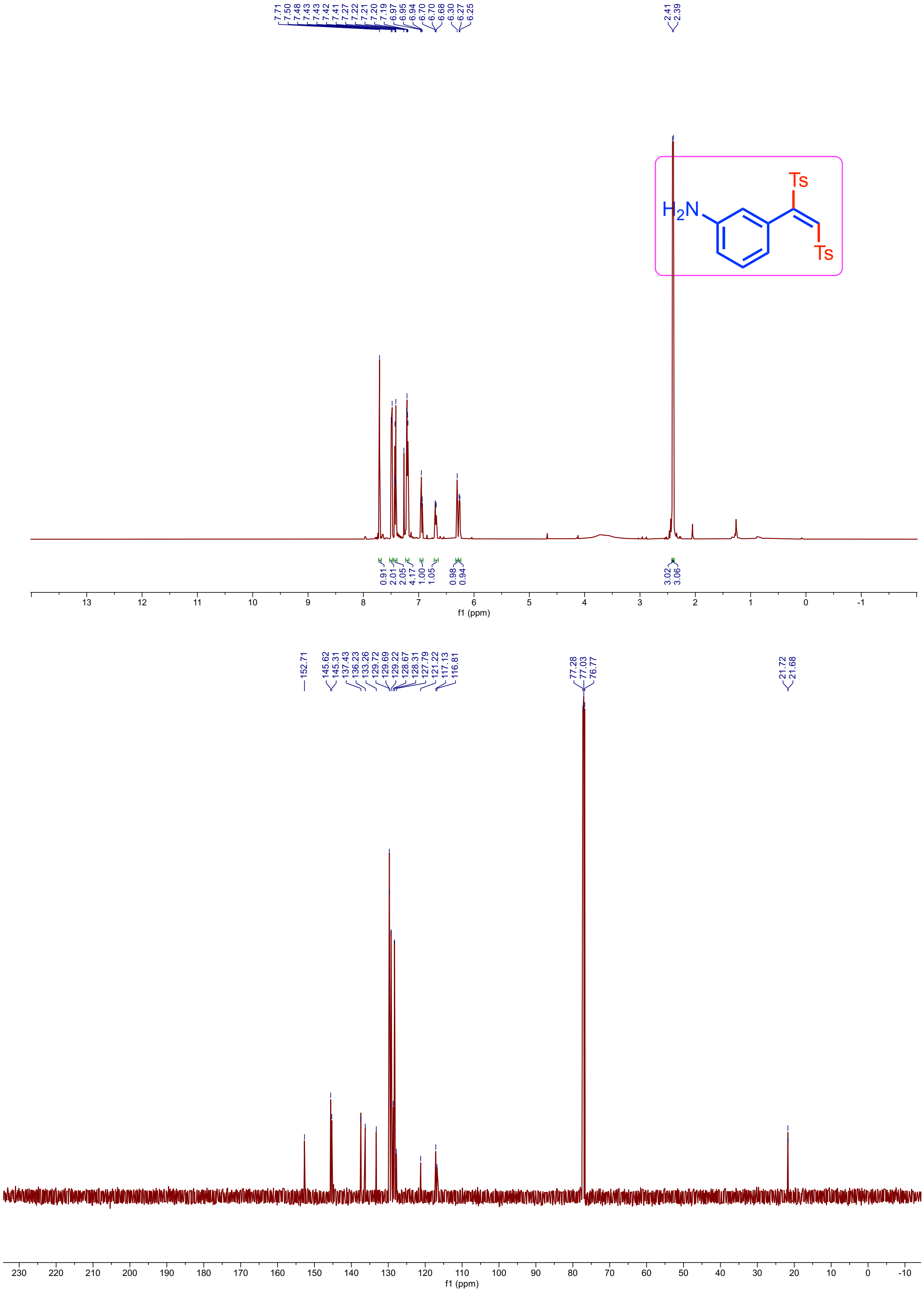
^{1}H (500 MHz) and ^{13}C (126 MHz) spectra of compound 3a in CDCl$_3$



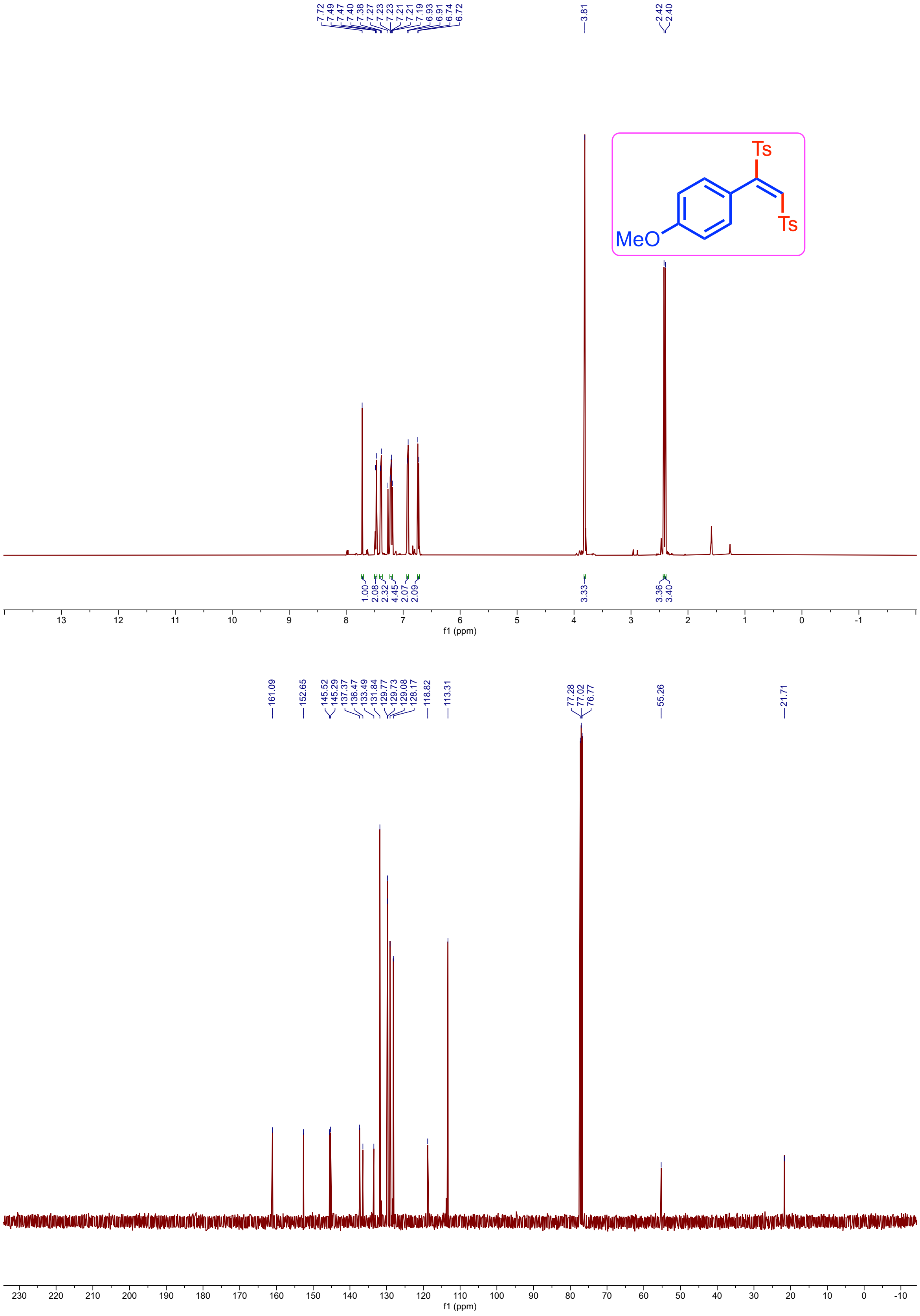
^{1}H (500 MHz) and ^{13}C (126 MHz) spectra of compound 3b in CDCl$_3$



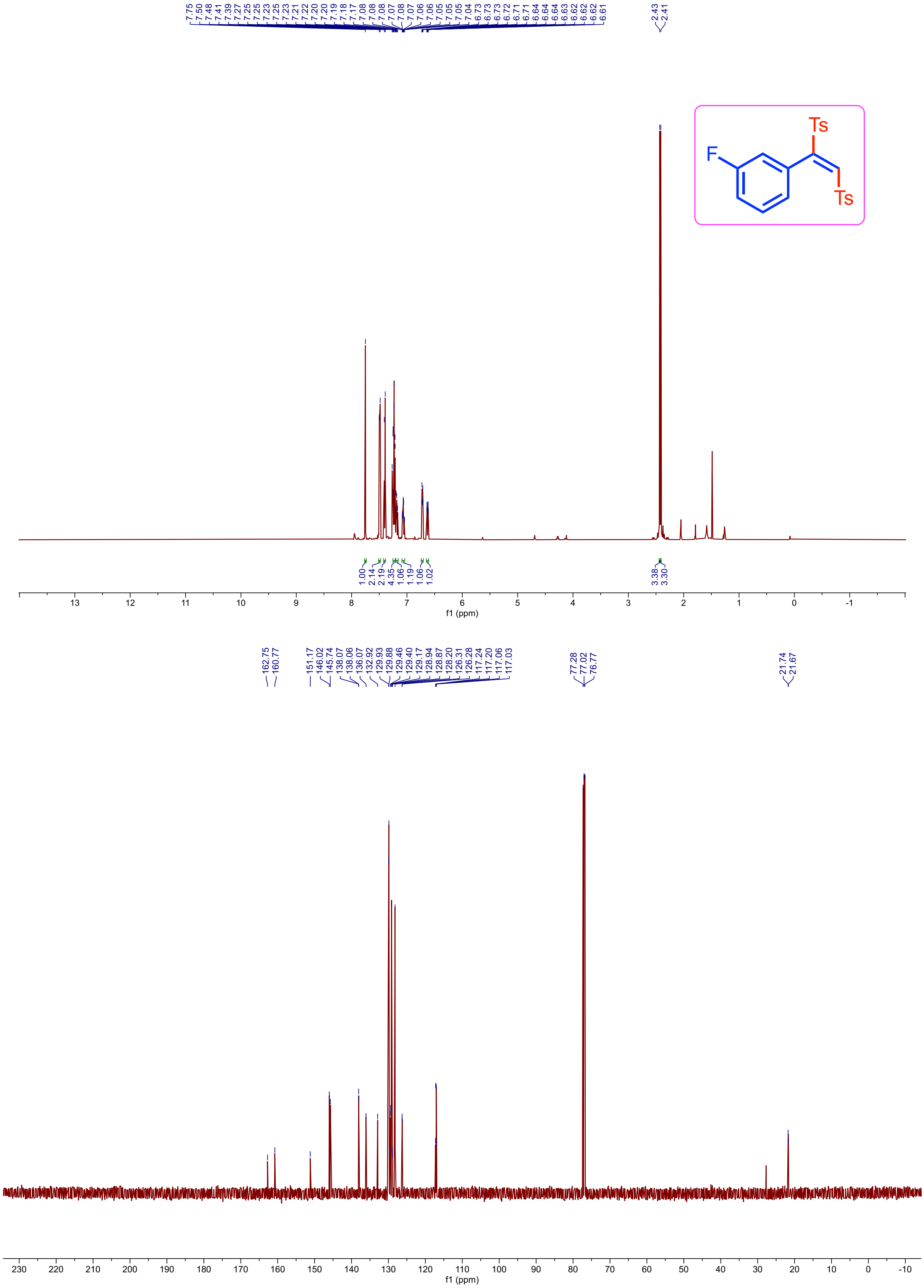
^{1}H (500 MHz) and ^{13}C (126 MHz) spectra of compound 3c in $CDCl_3$



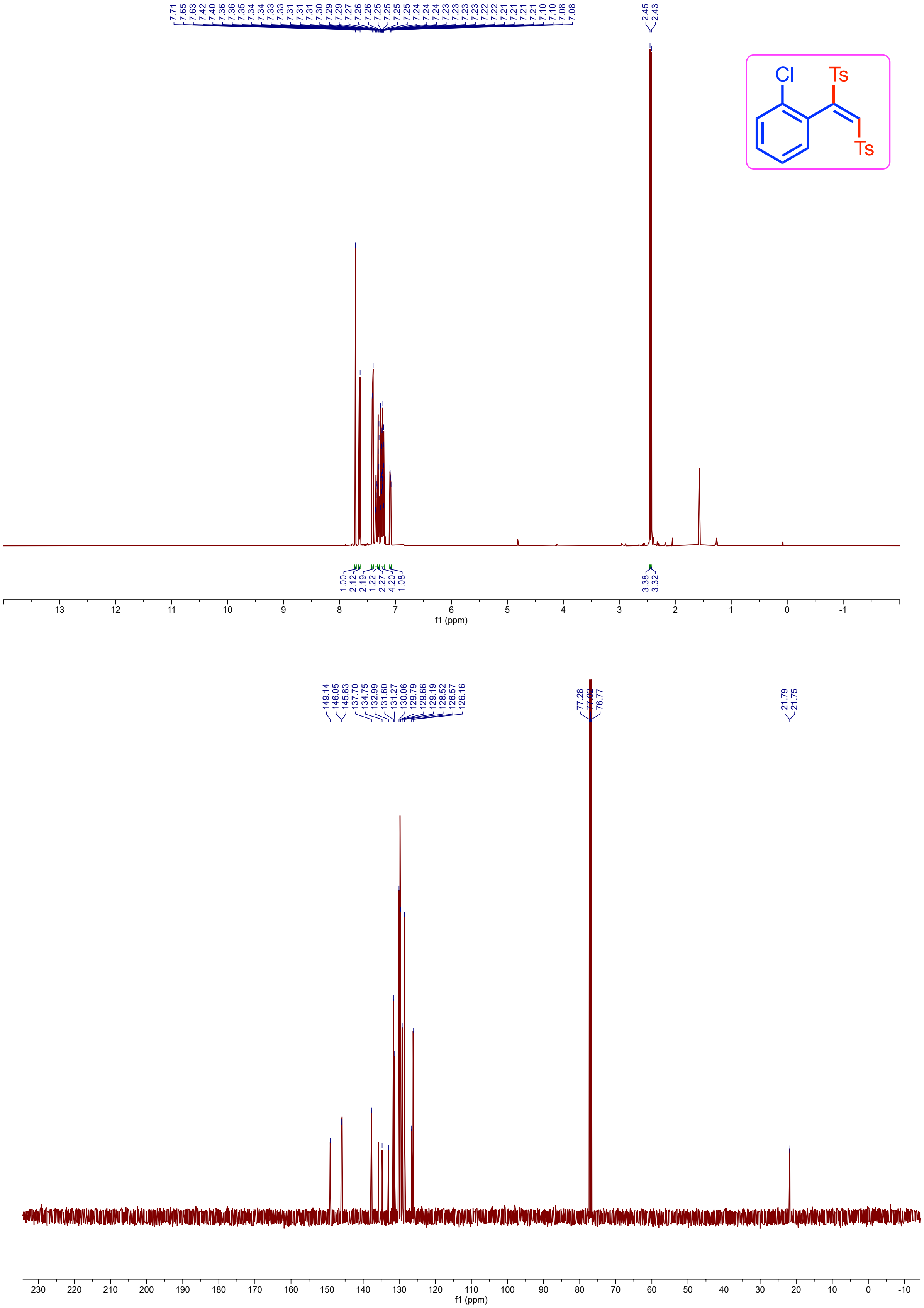
^{1}H (500 MHz) and ^{13}C (126 MHz) spectra of compound 3d in $CDCl_3$



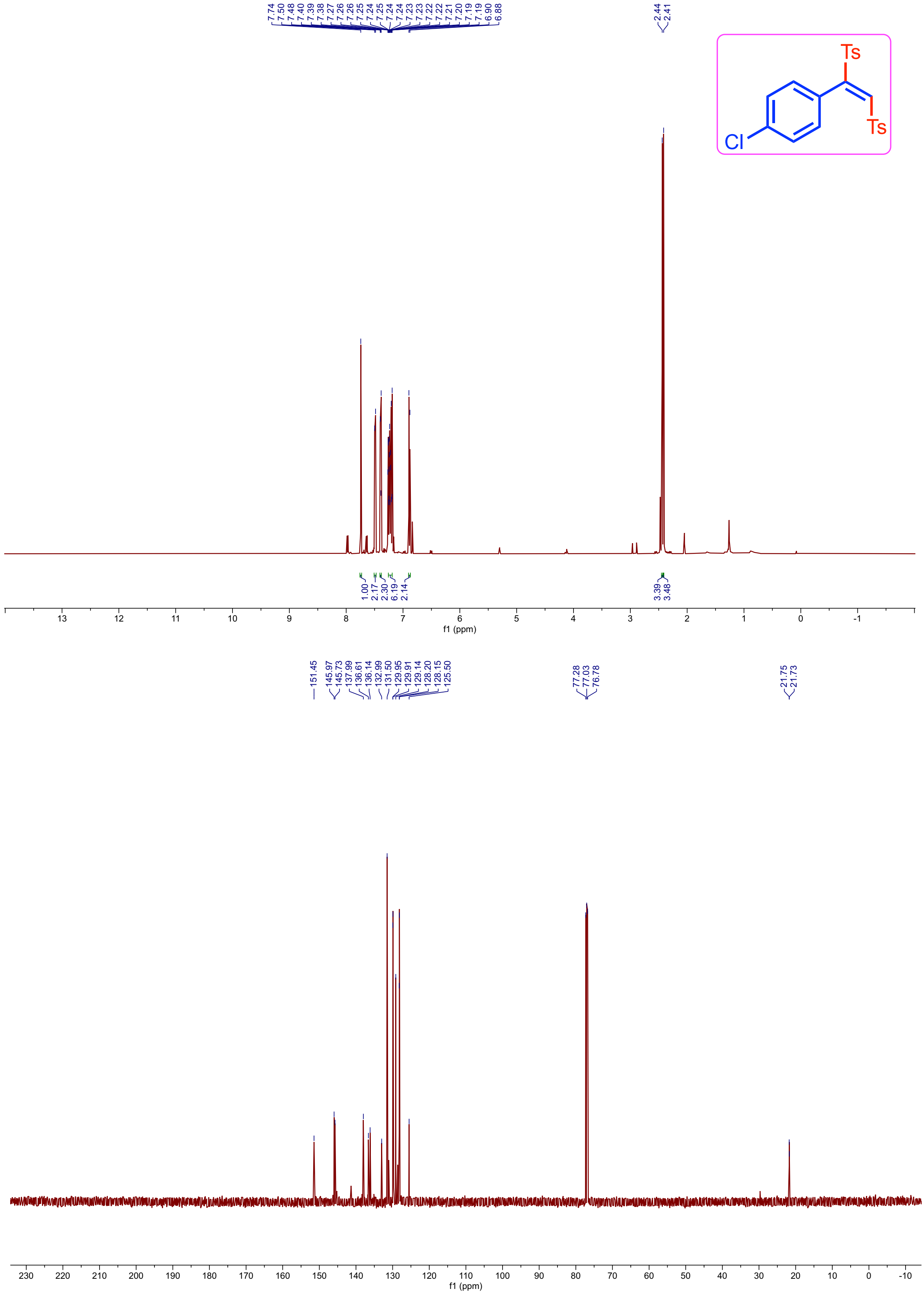
^{1}H (500 MHz) and ^{13}C (126 MHz) spectra of compound 3e in CDCl$_3$



^{1}H (500 MHz) and ^{13}C (126 MHz) spectra of compound 3f in CDCl$_3$



^{1}H (500 MHz) and ^{13}C (126 MHz) spectra of compound 3g in $CDCl_3$



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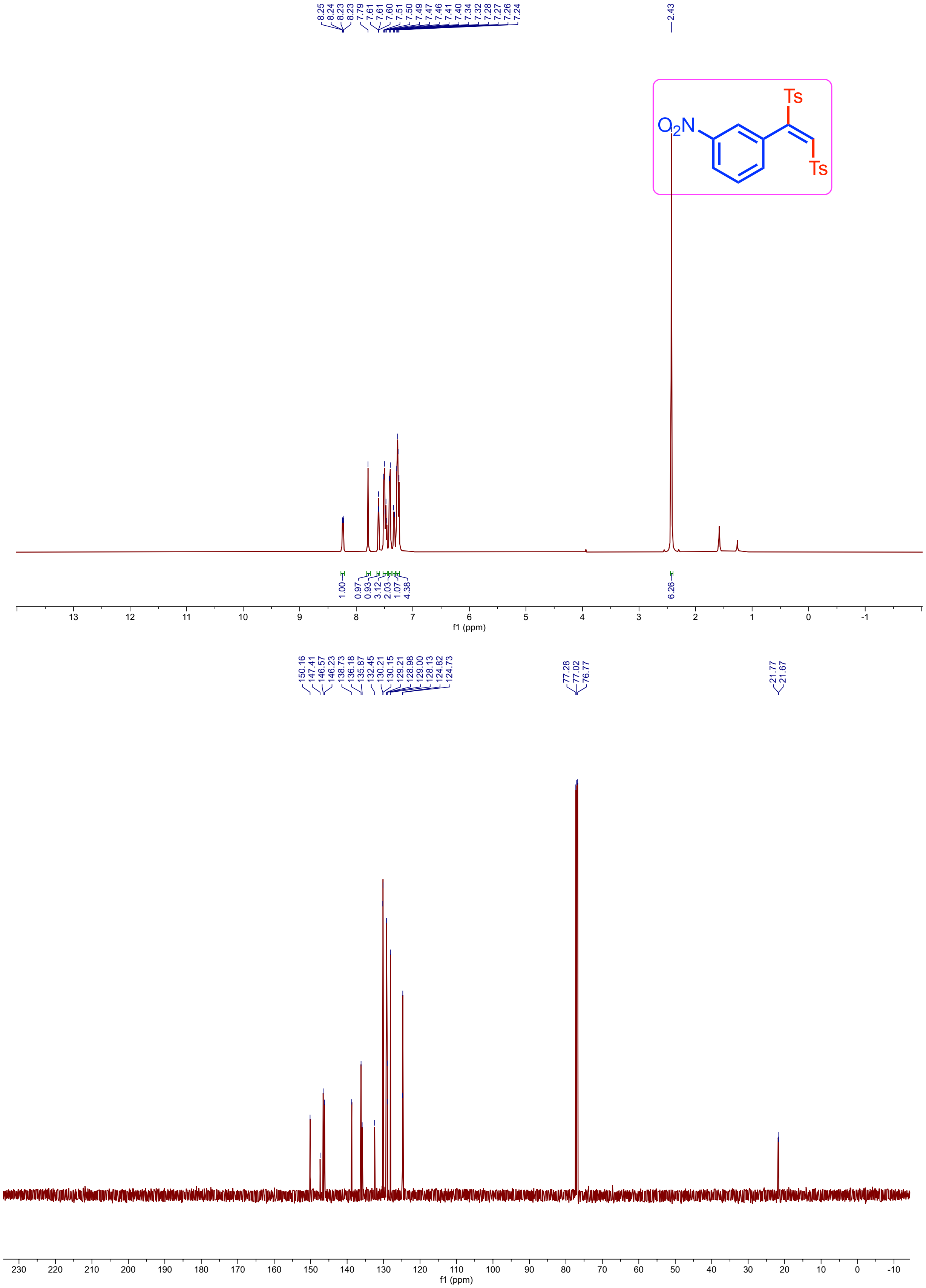

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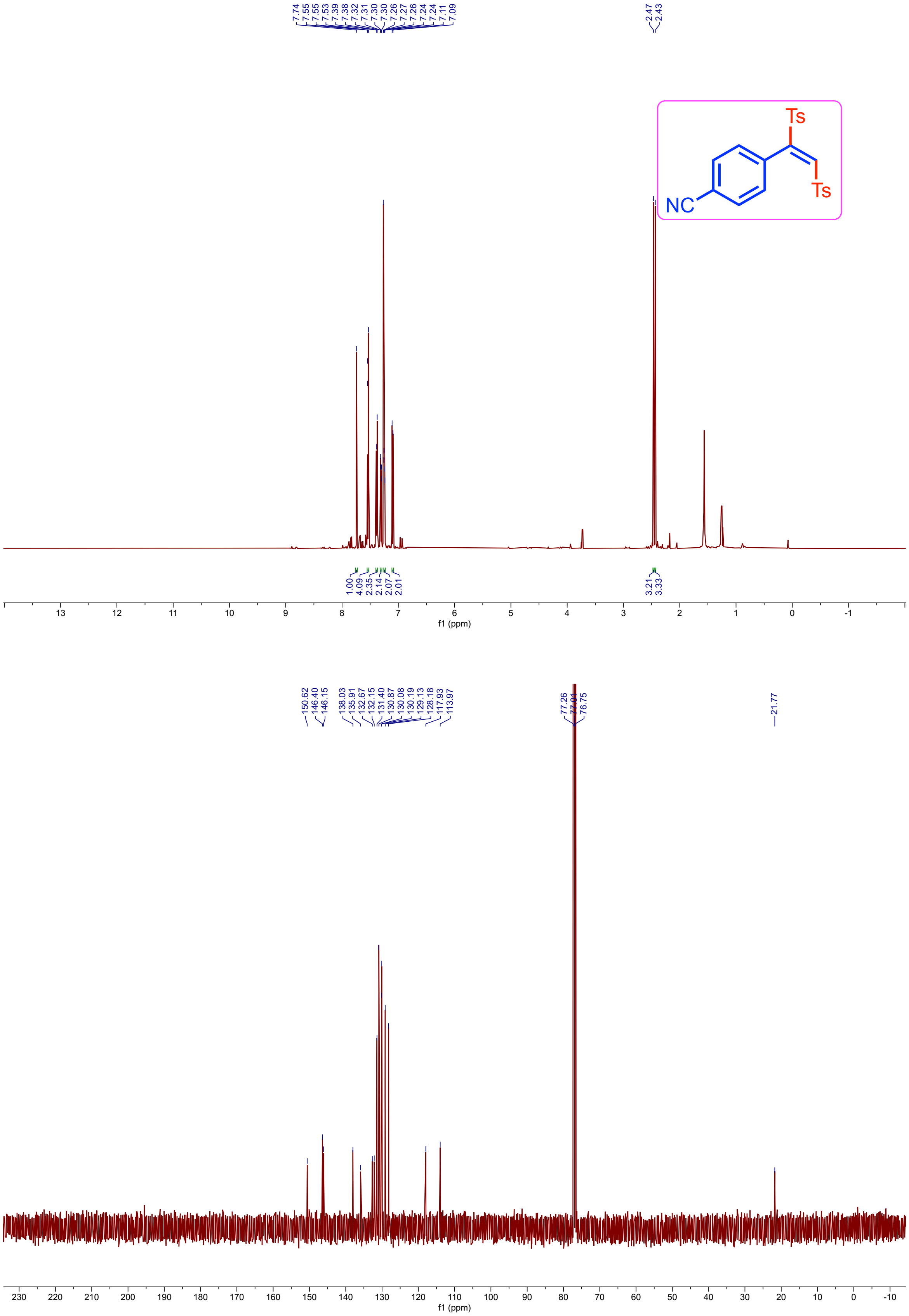

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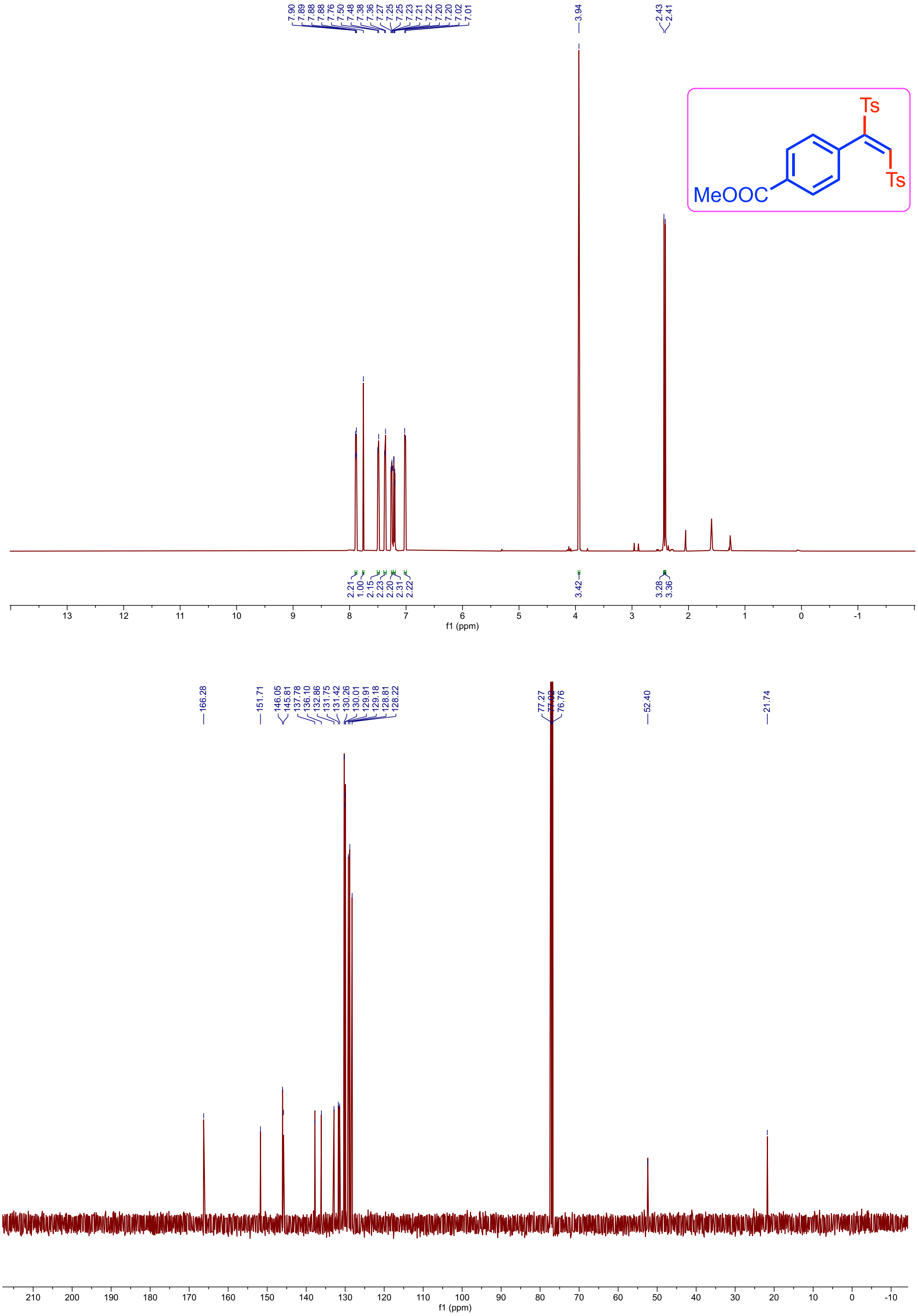
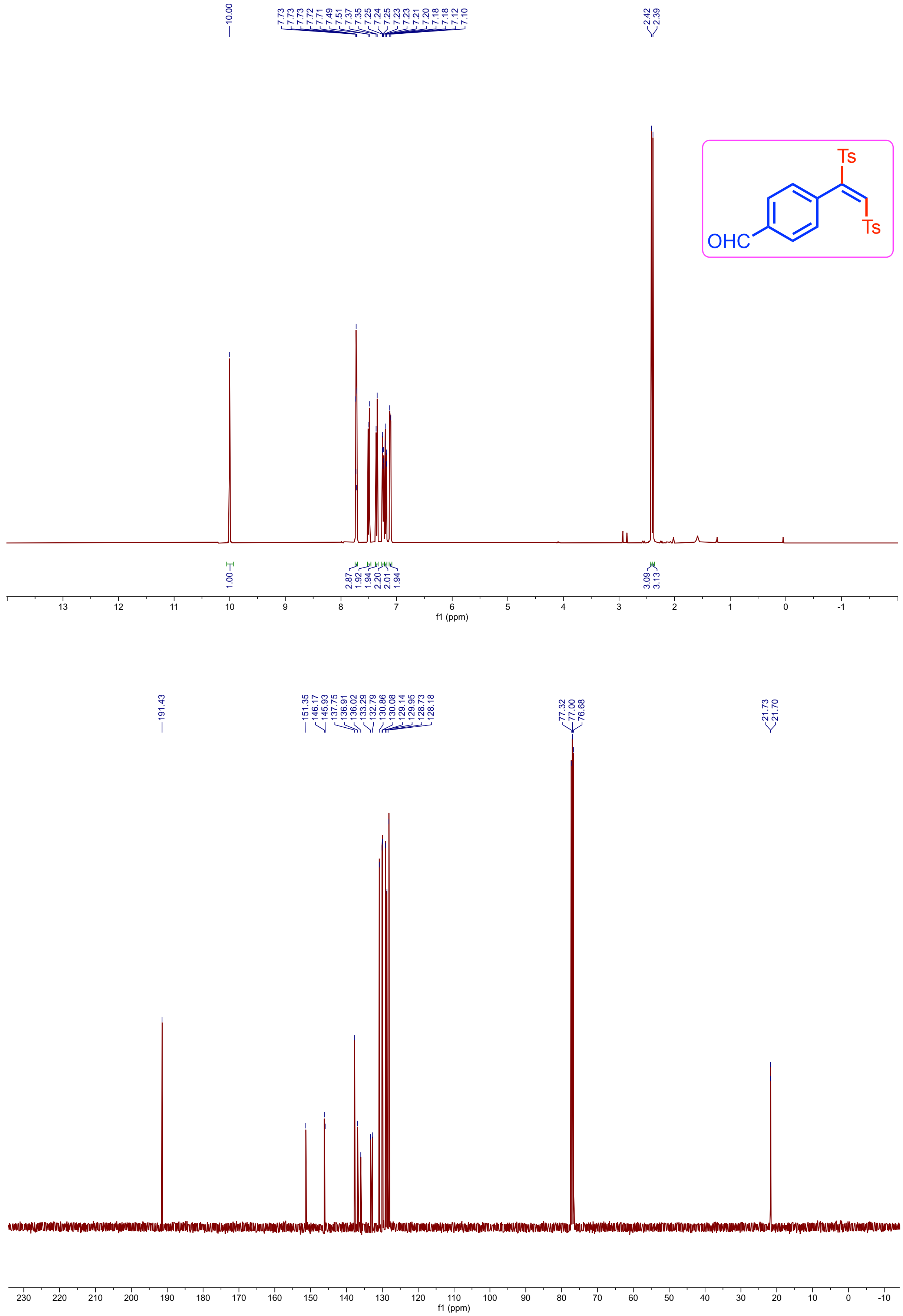
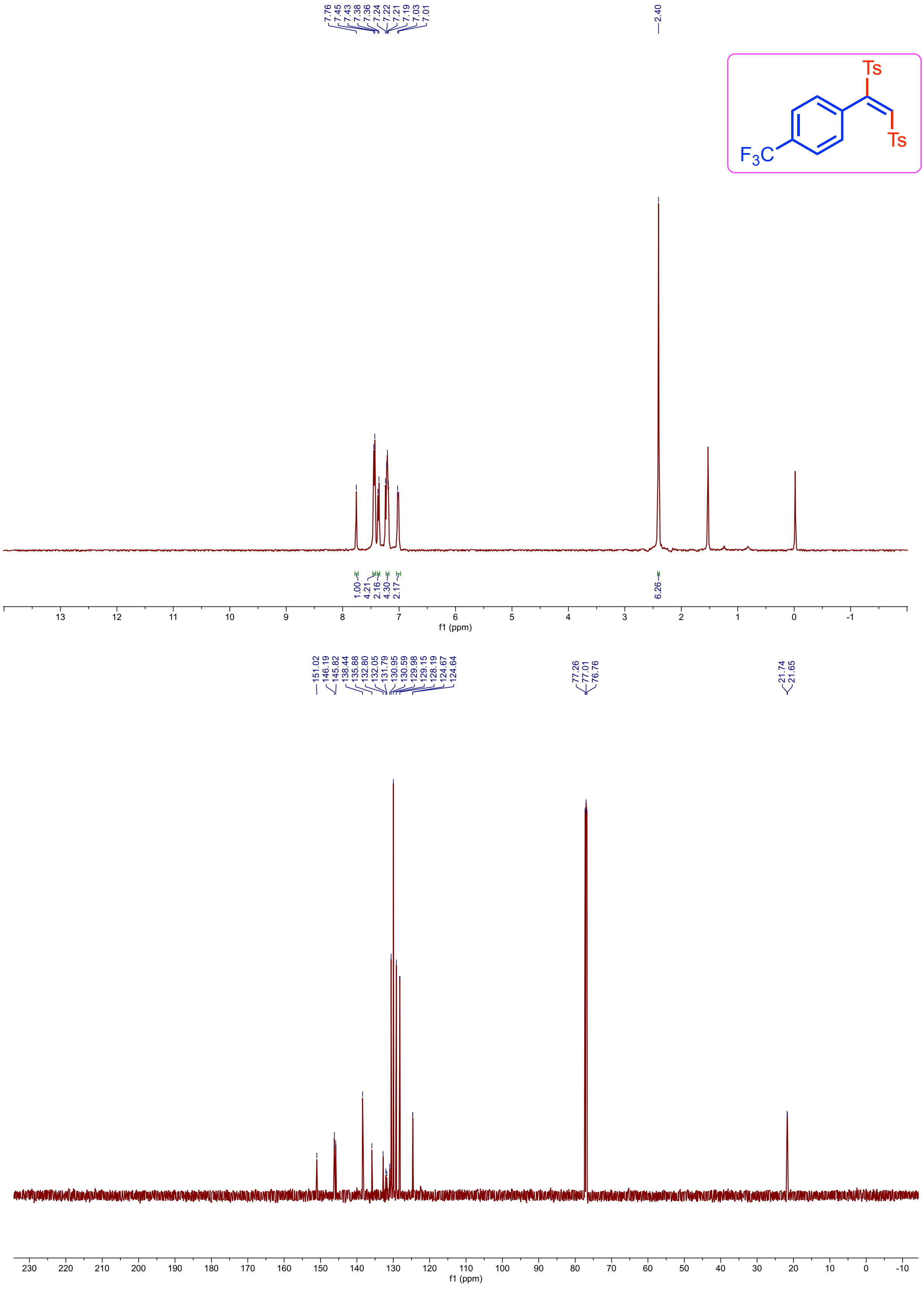


^{1}H (500 MHz) and ^{13}C (126 MHz) spectra of compound 3k in CDCl$_3$



^{1}H (400 MHz) and ^{13}C (101 MHz) spectra of compound 3l in $CDCl_3$



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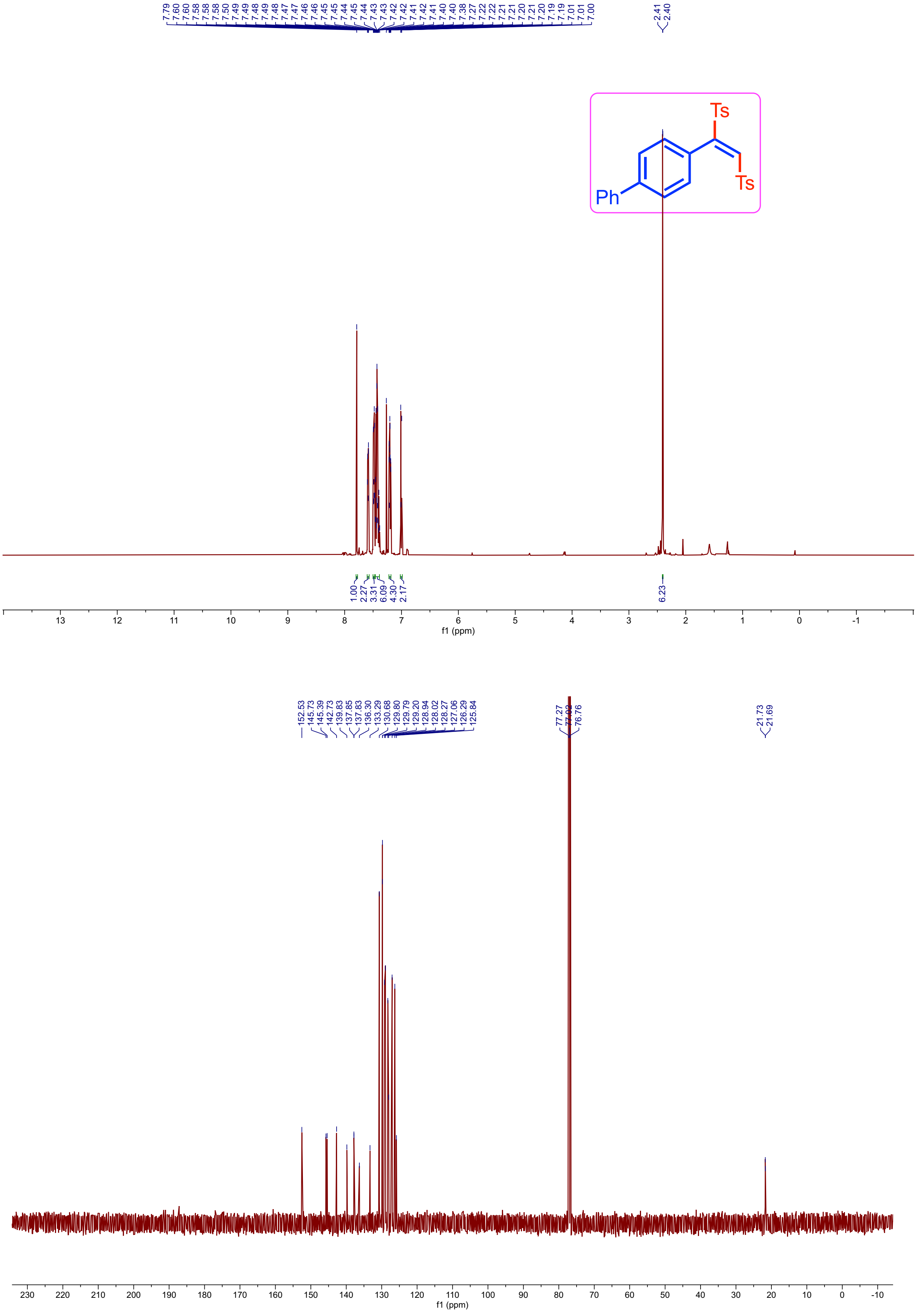

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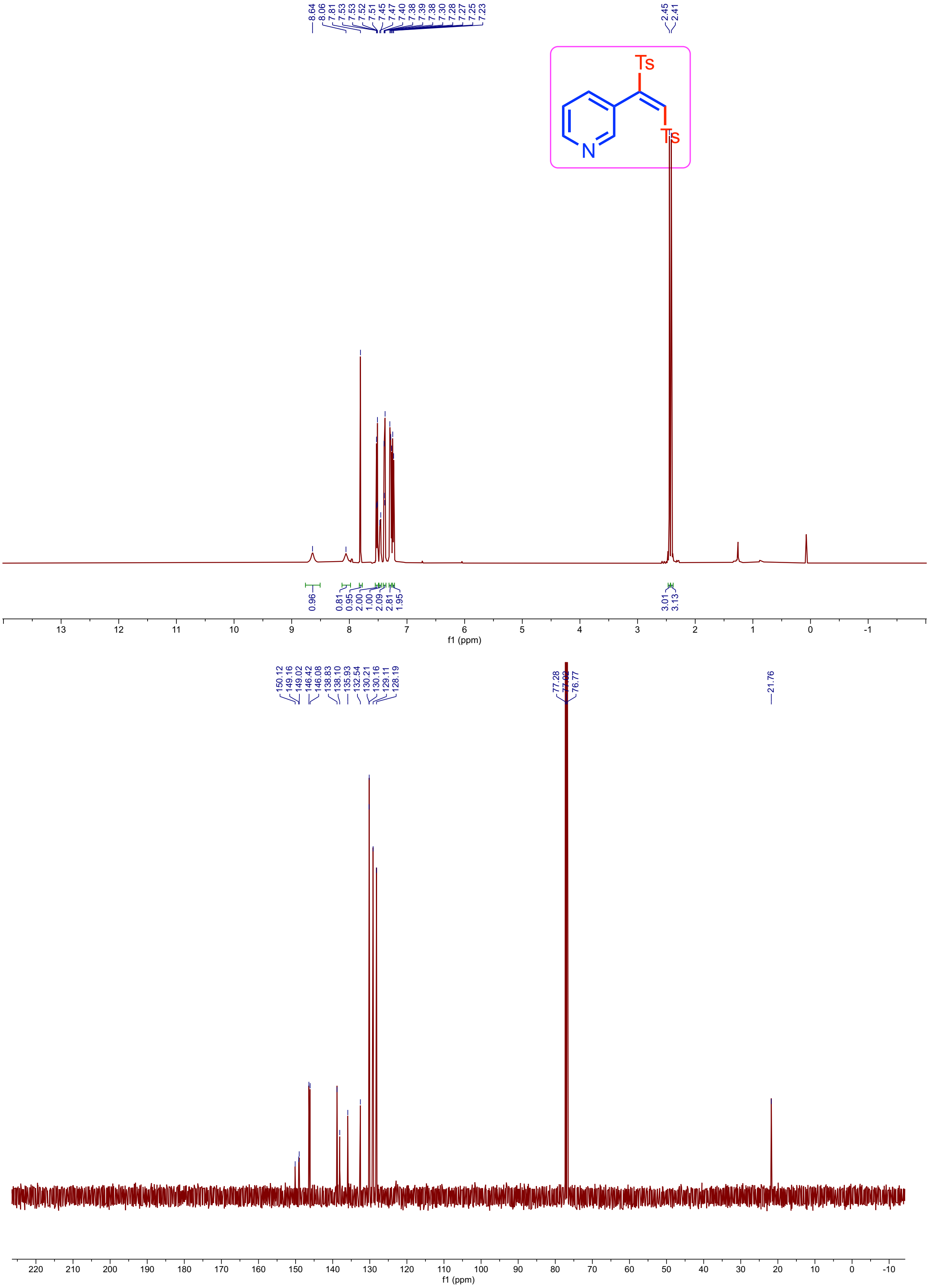
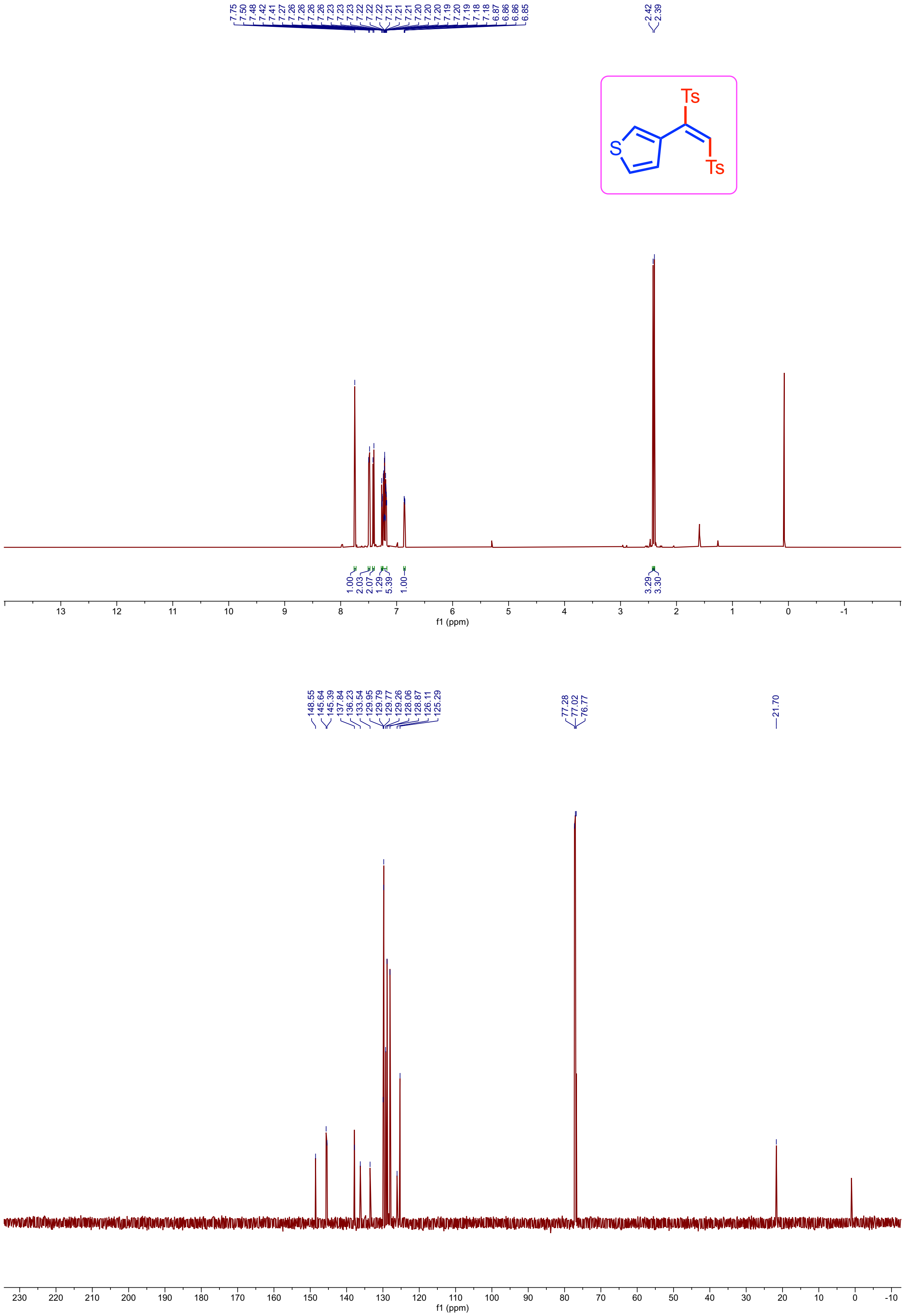


^{1}H (500 MHz) and ^{13}C (126 MHz) spectra of compound 3o in $CDCl_3$



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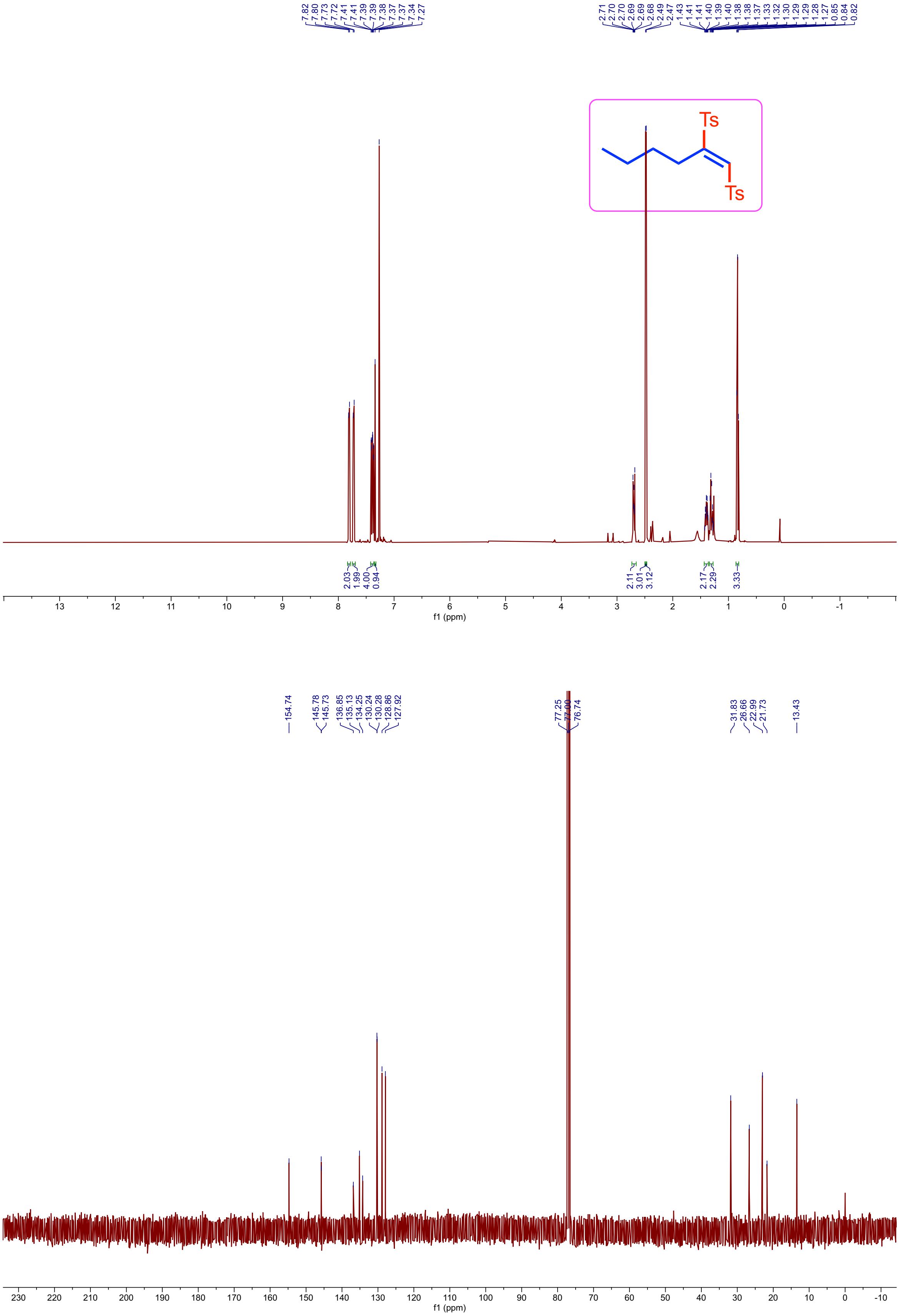
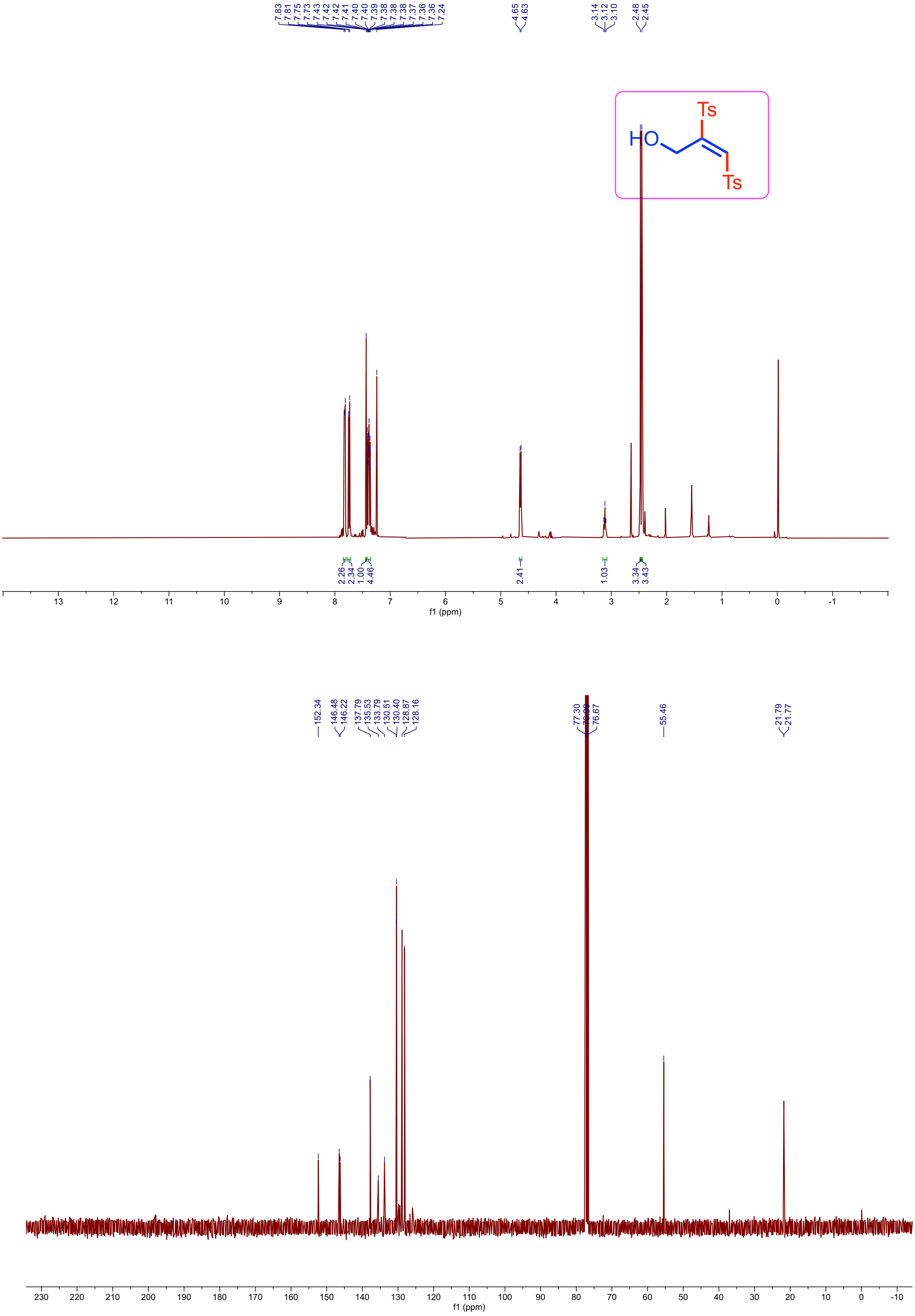
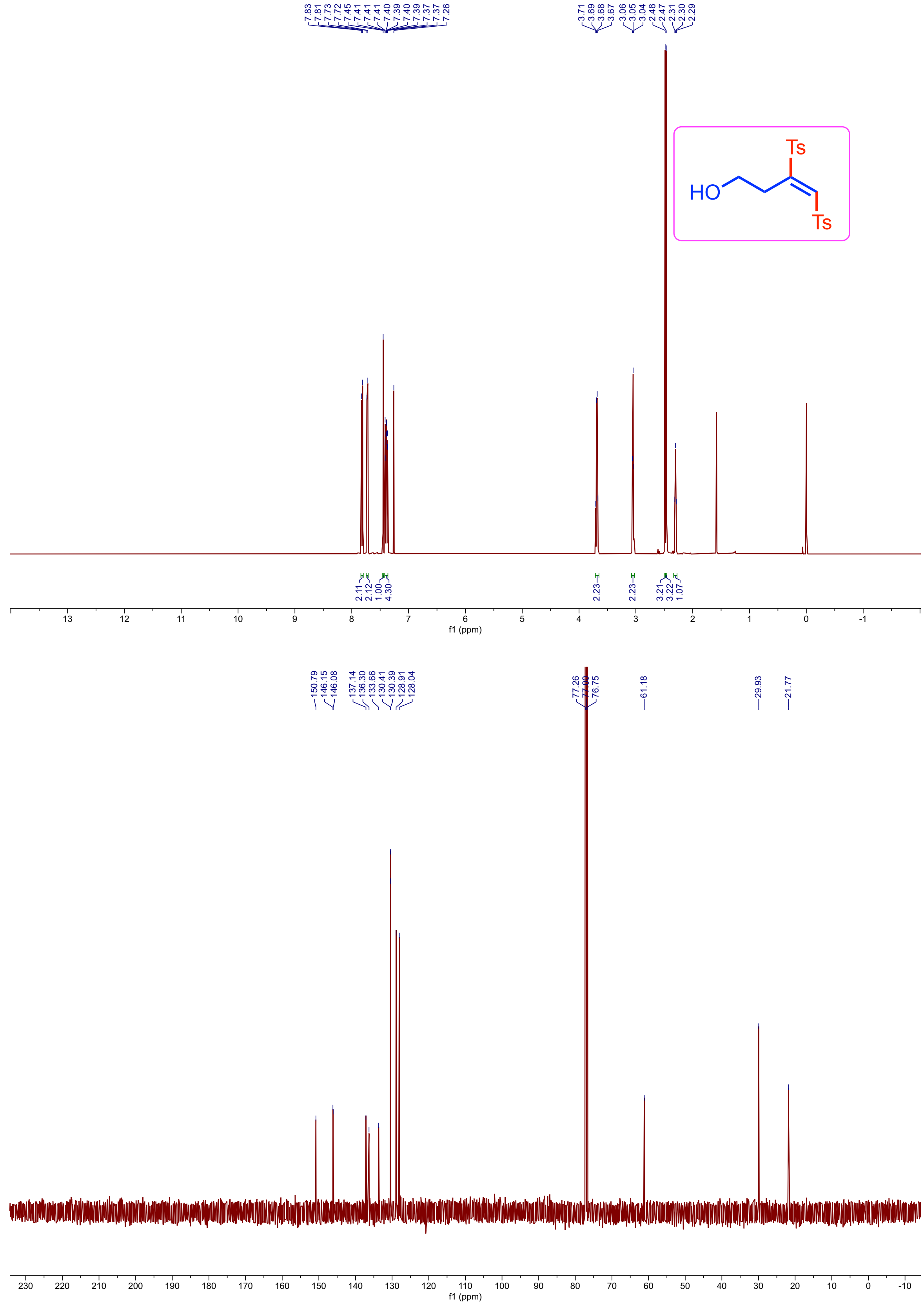


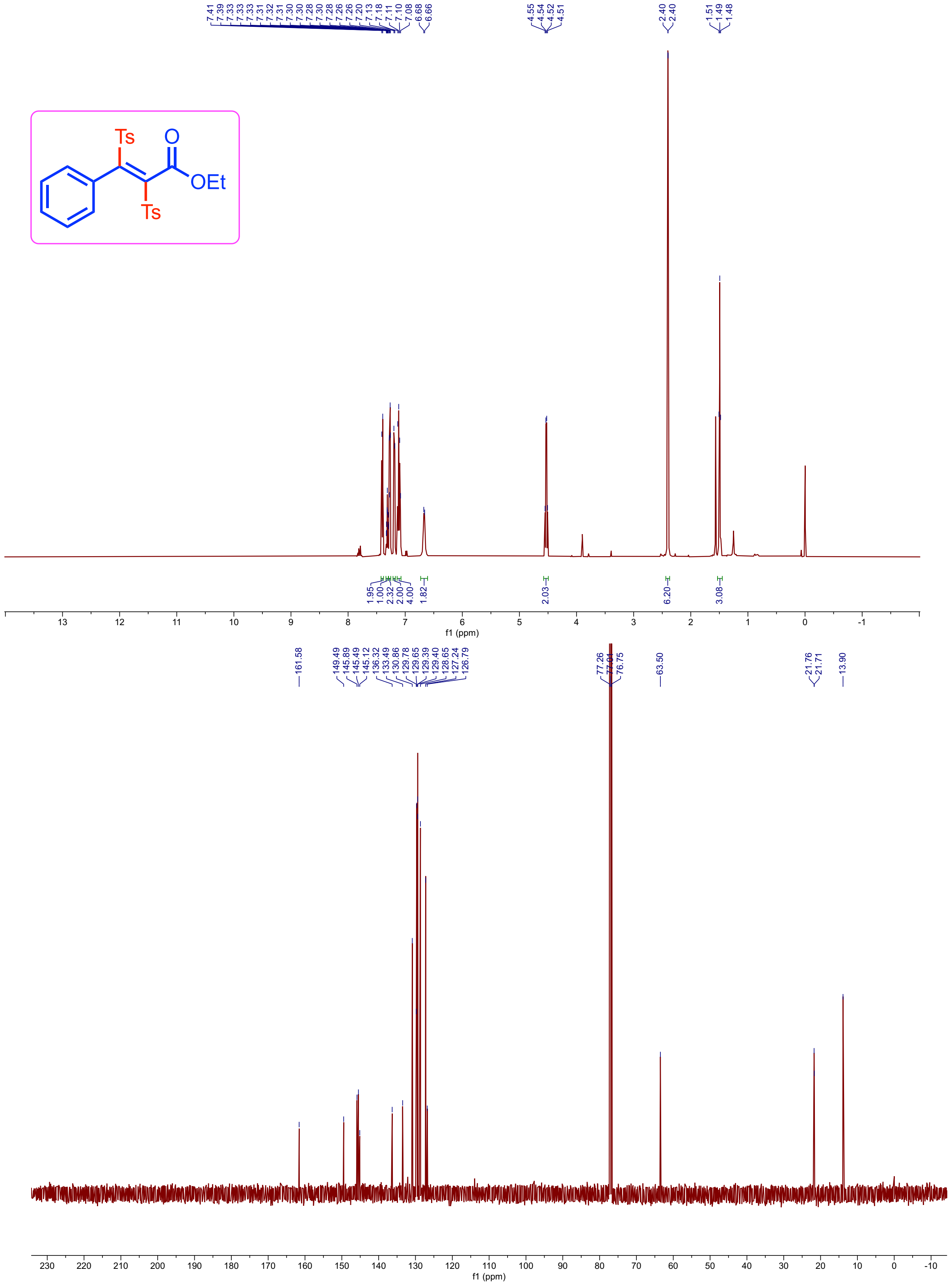
^{1}H (500 MHz) and ^{13}C (126 MHz) spectra of compound 3q in CDCl$_3$



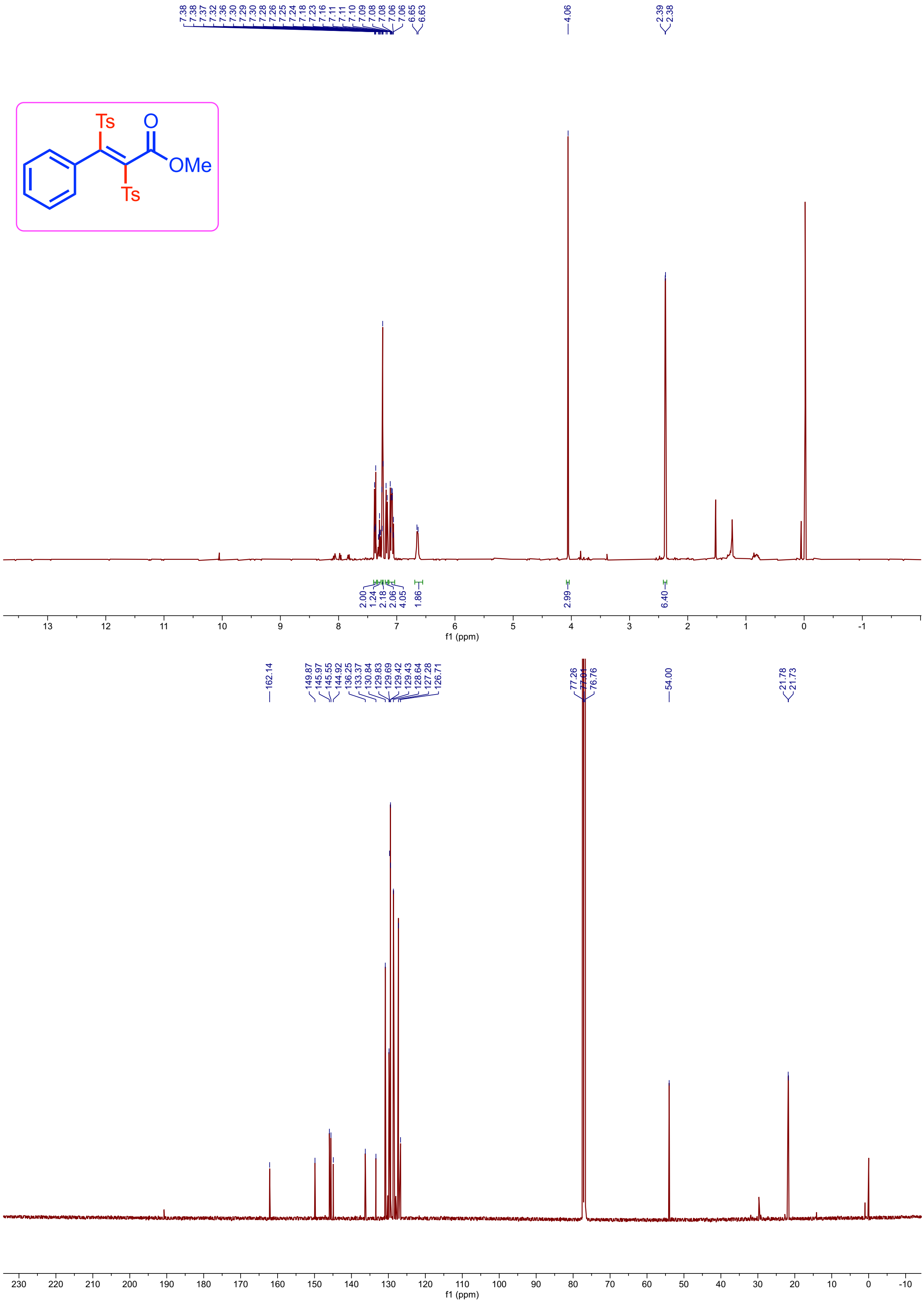
^{1}H (400 MHz) and ^{13}C (101 MHz) spectra of compound 3r in $CDCl_3$



^{1}H (500 MHz) and ^{13}C (126 MHz) spectra of compound 3s in $CDCl_3$



^{1}H (500 MHz) and ^{13}C (126 MHz) spectra of compound 4a in CDCl$_3$



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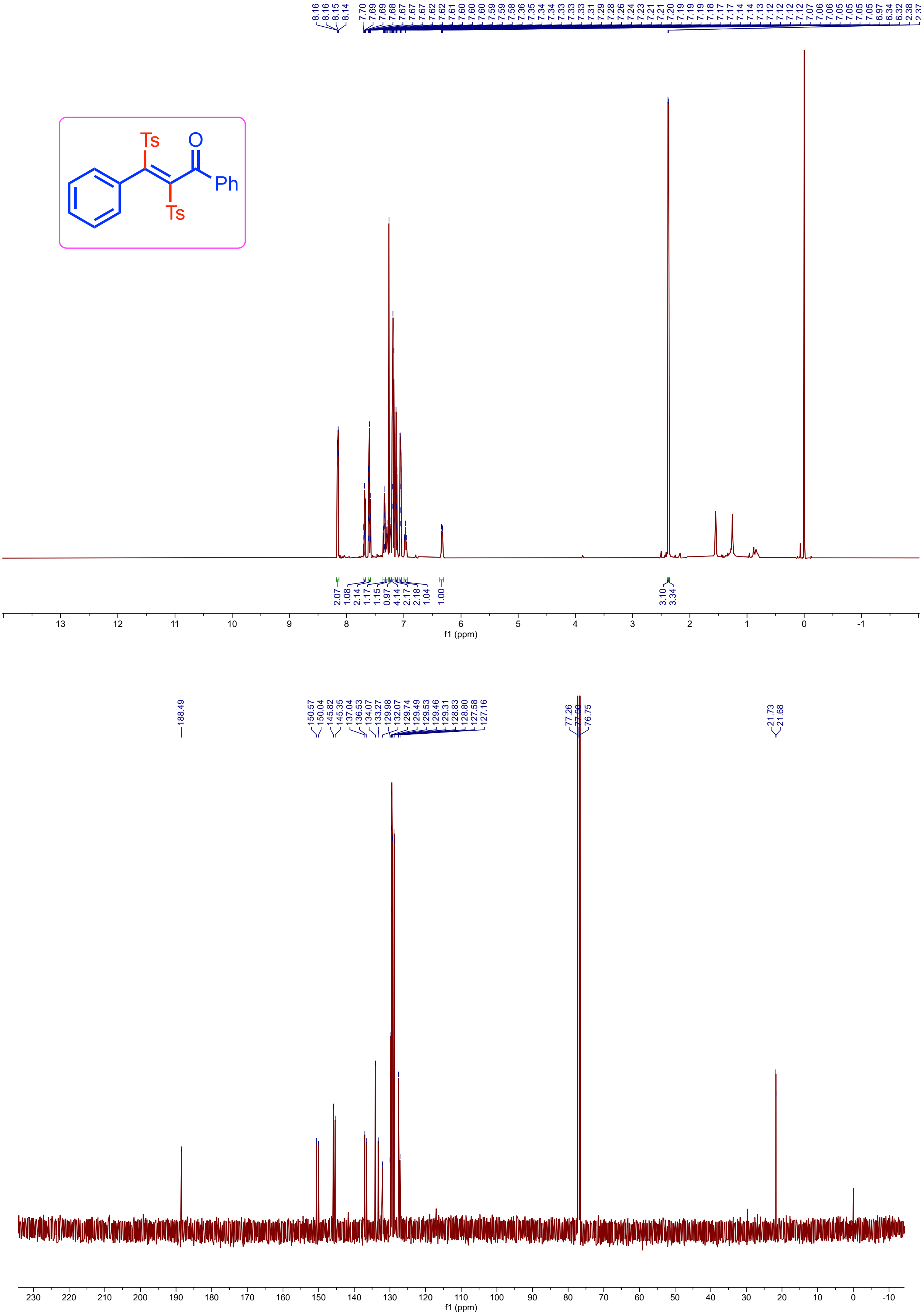

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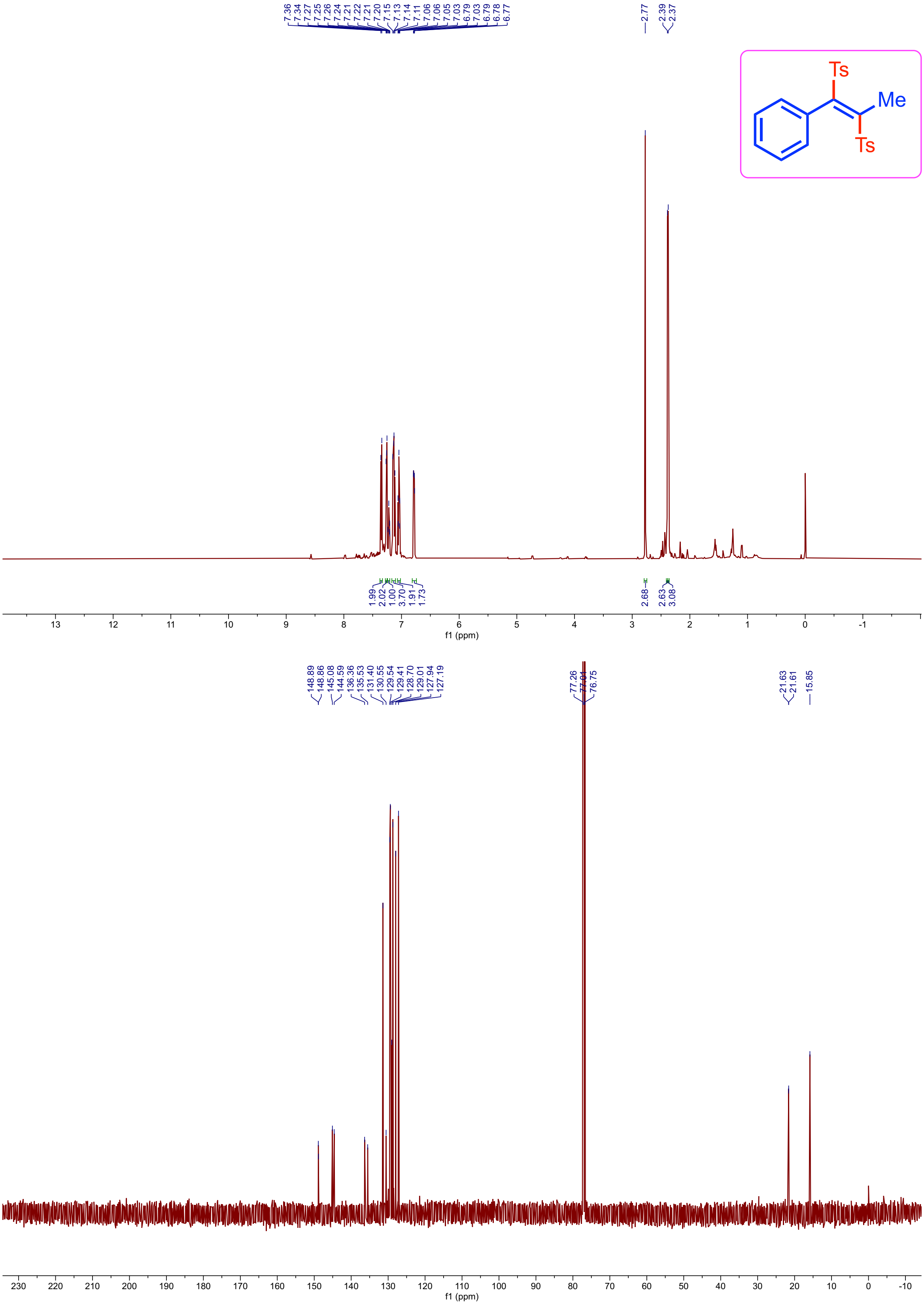

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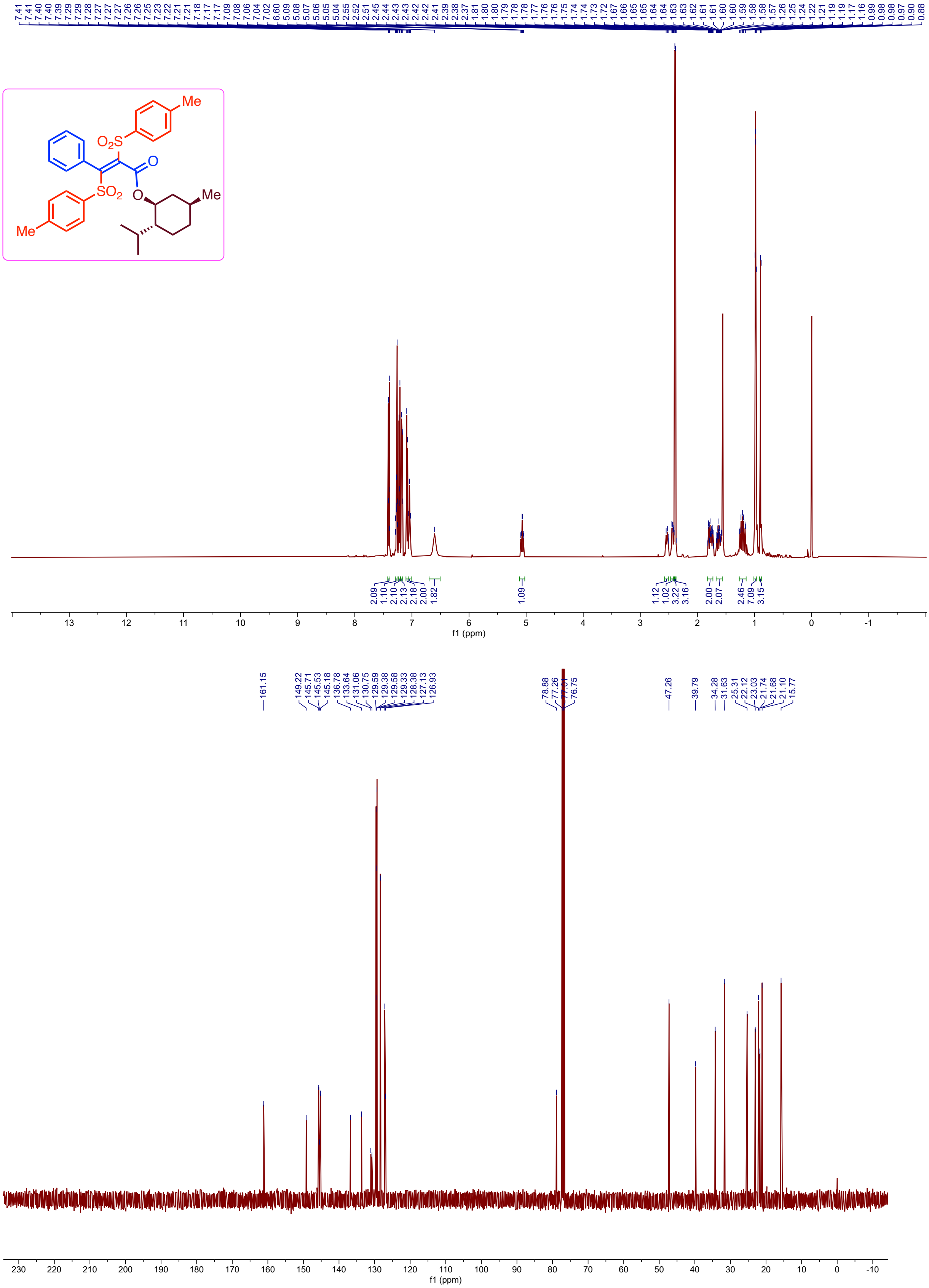
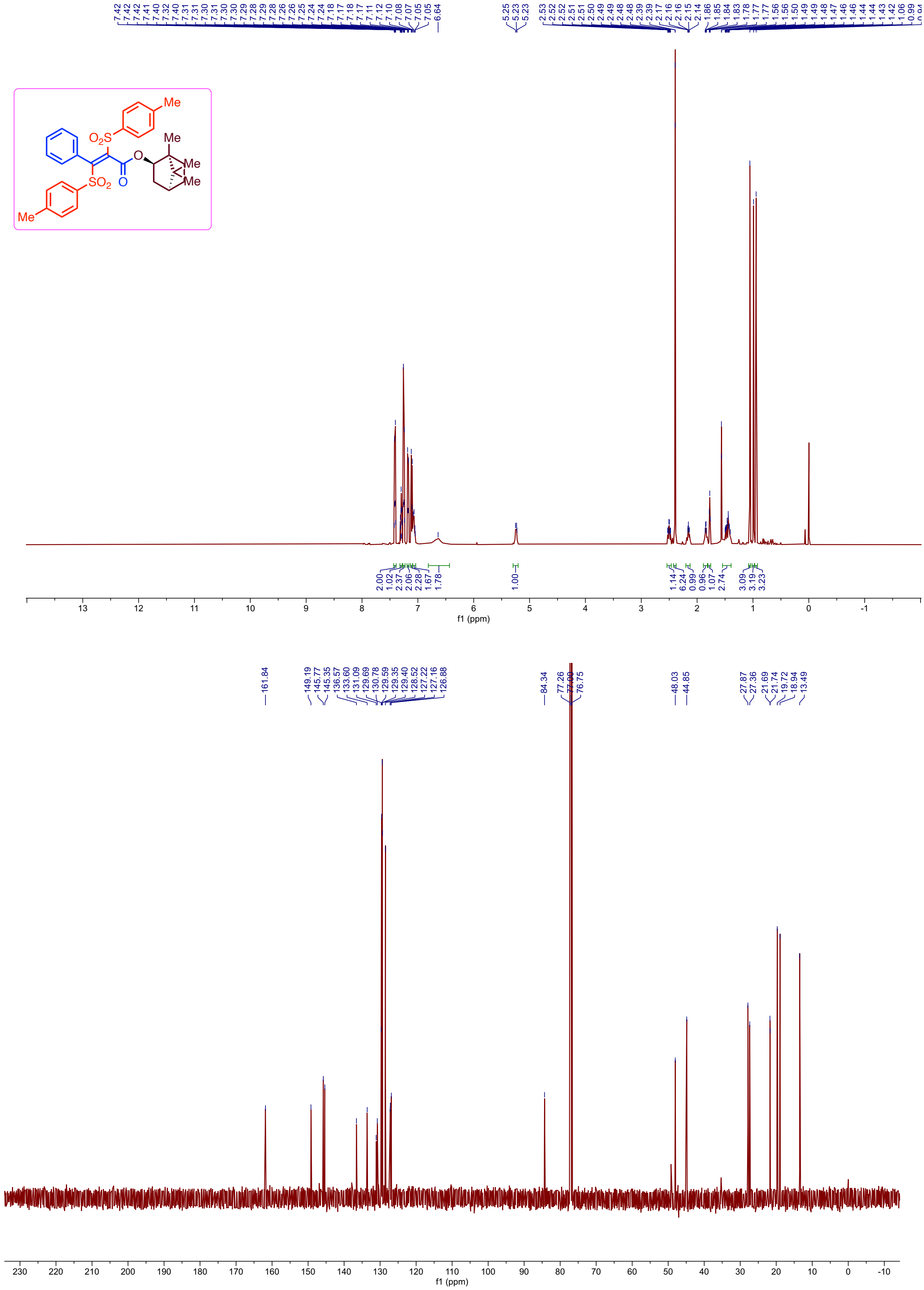
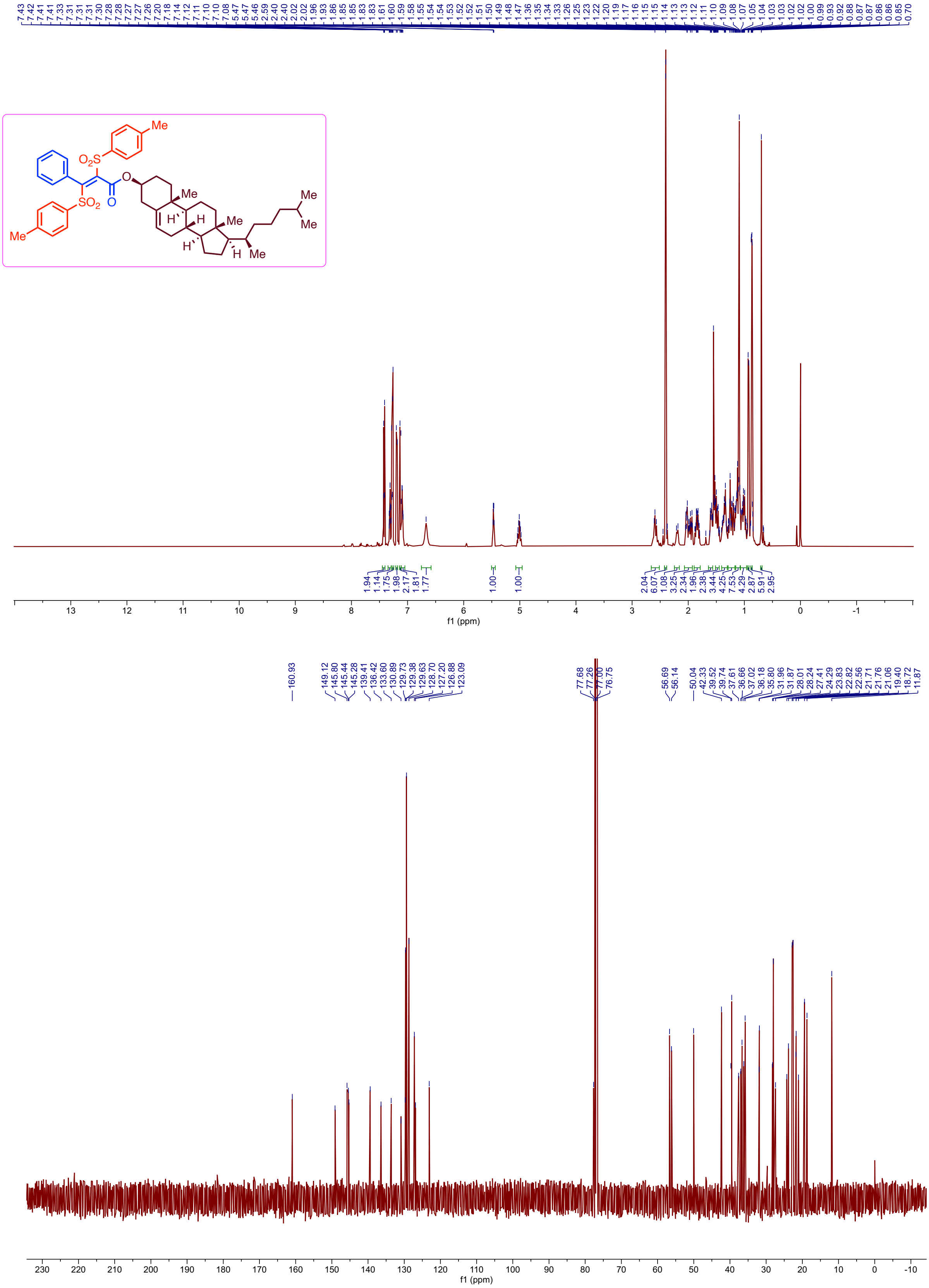


^{1}H (500 MHz) and ^{13}C (126 MHz) spectra of compound 4f in $CDCl_3$



^{1}H (500 MHz) and ^{13}C (126 MHz) spectra of compound 4g in $CDCl_3$



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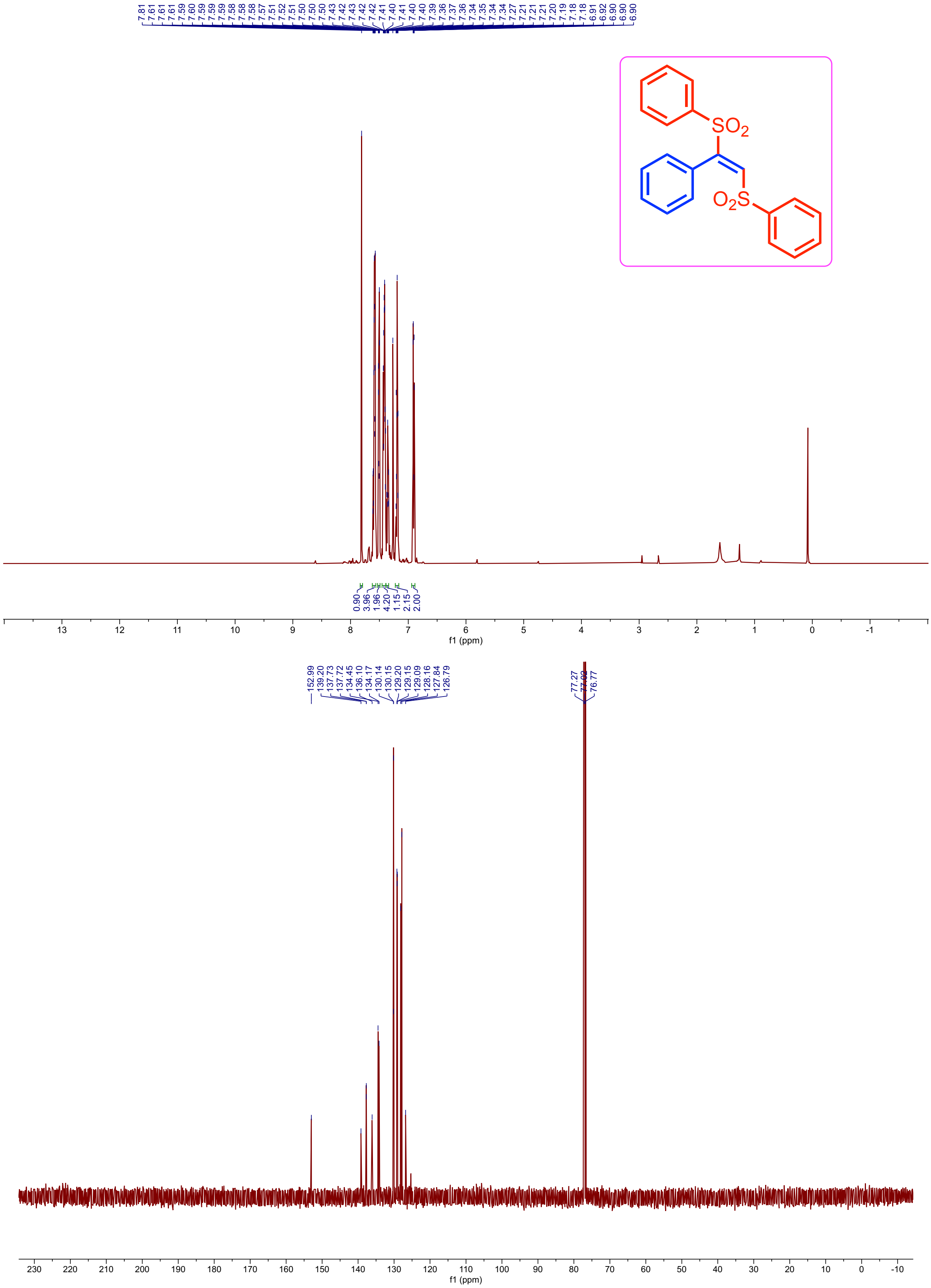

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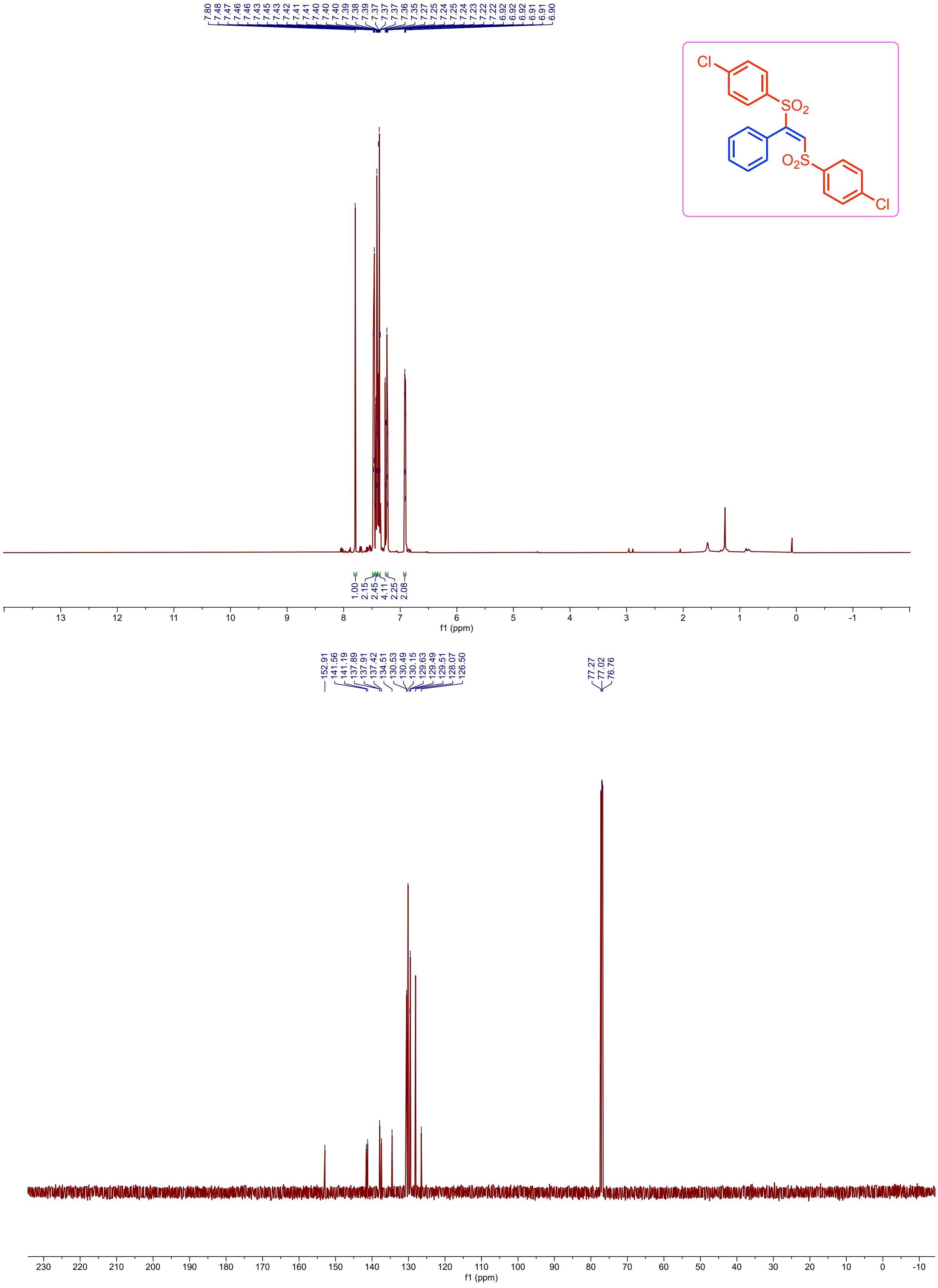

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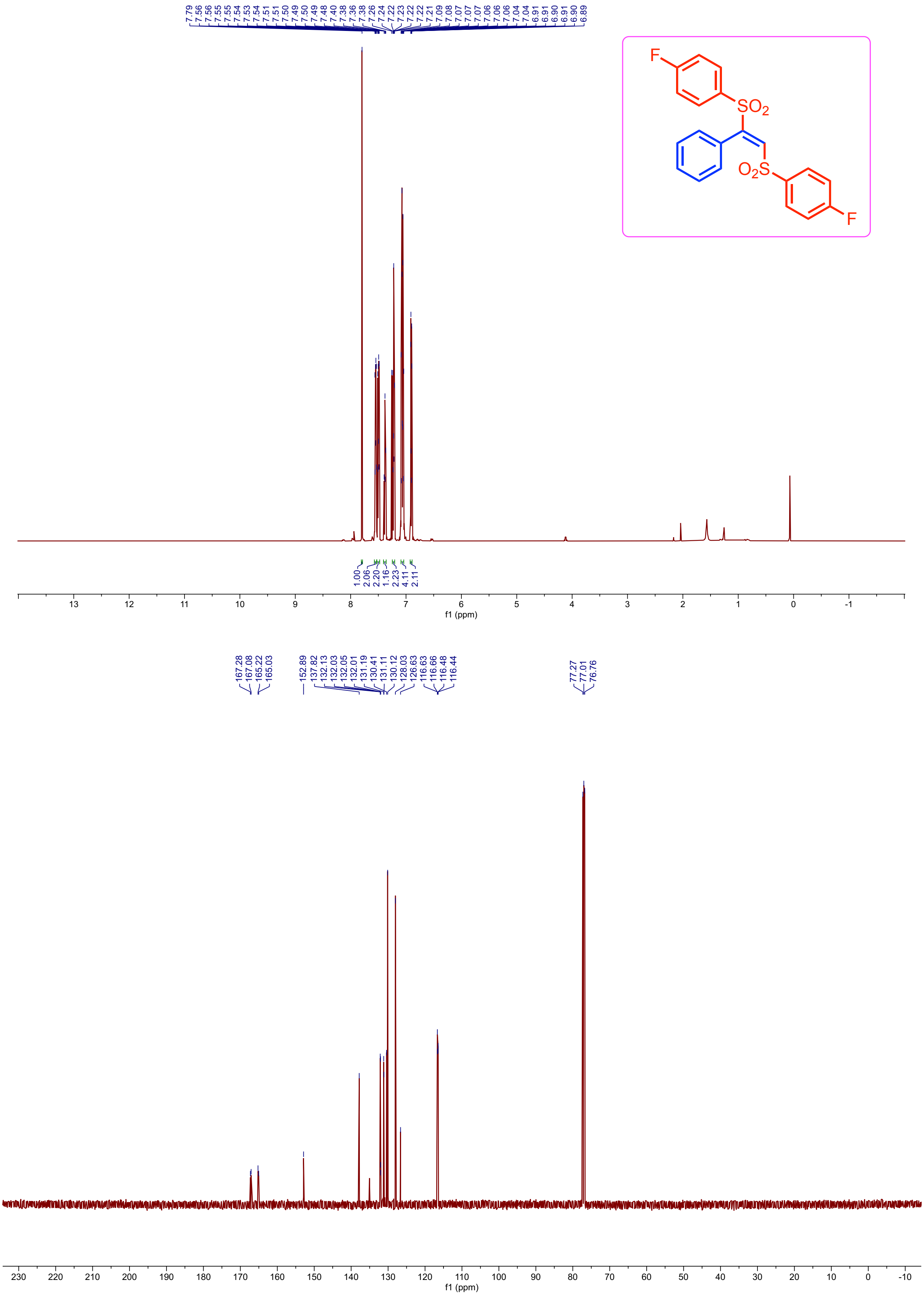

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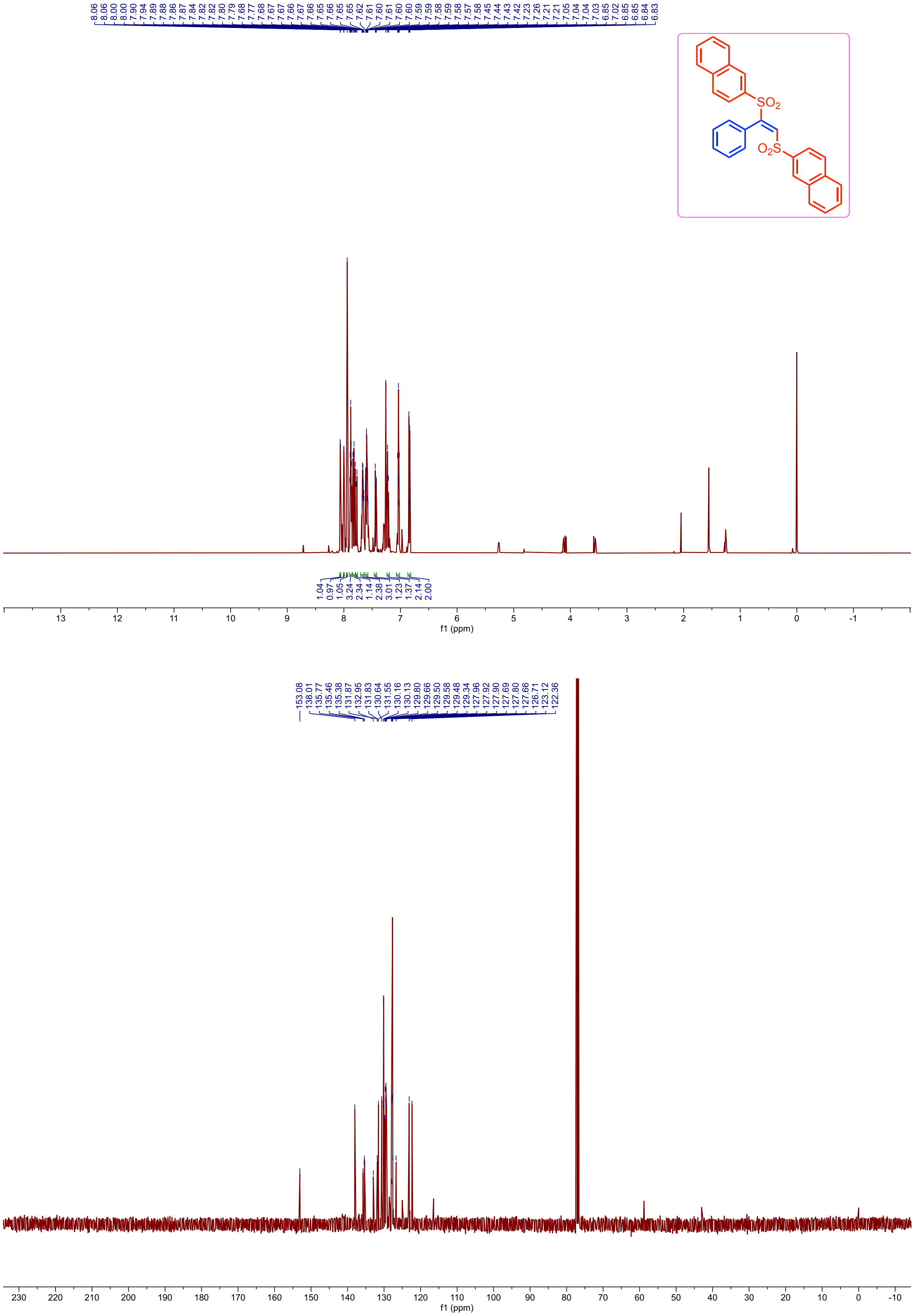

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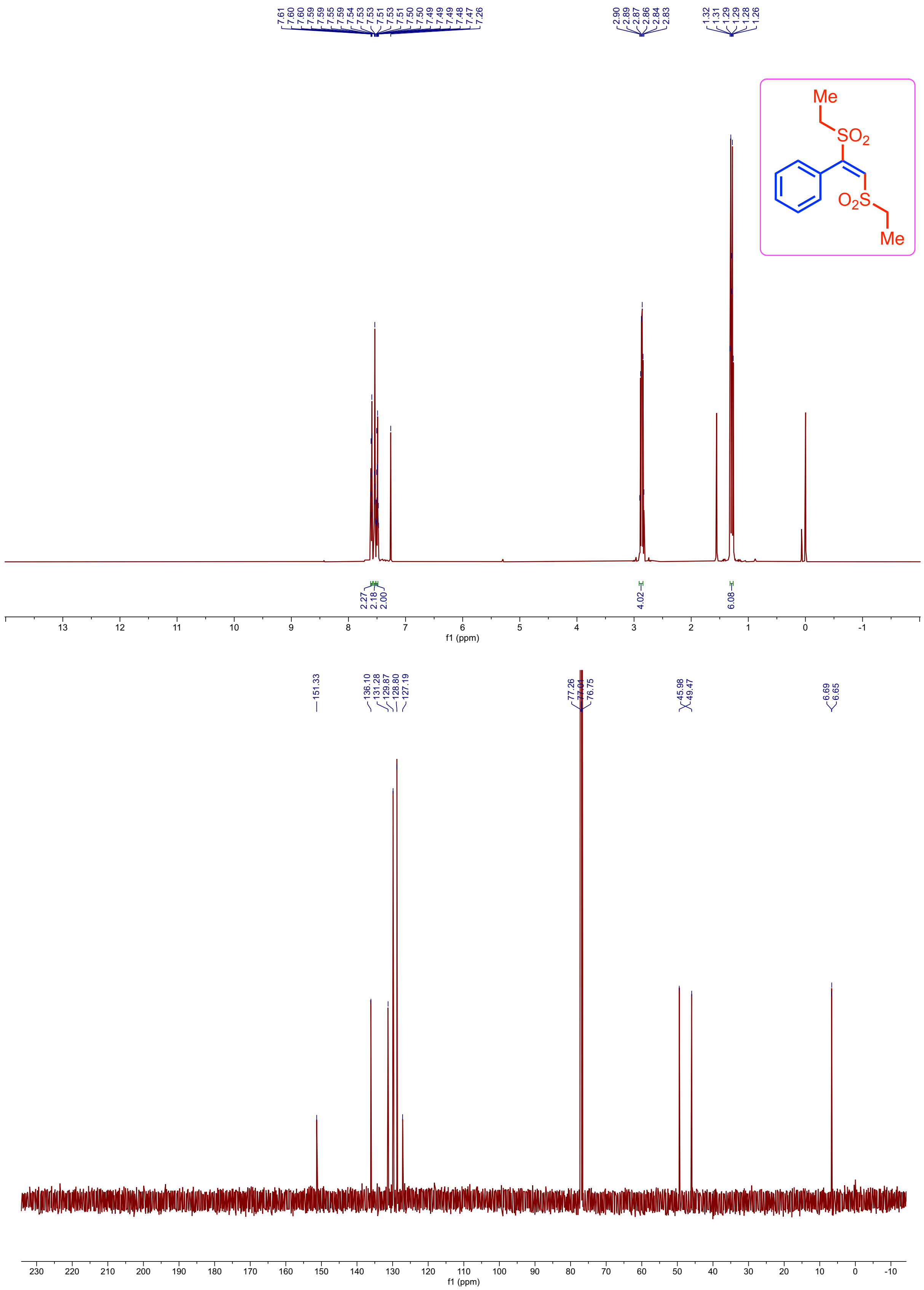

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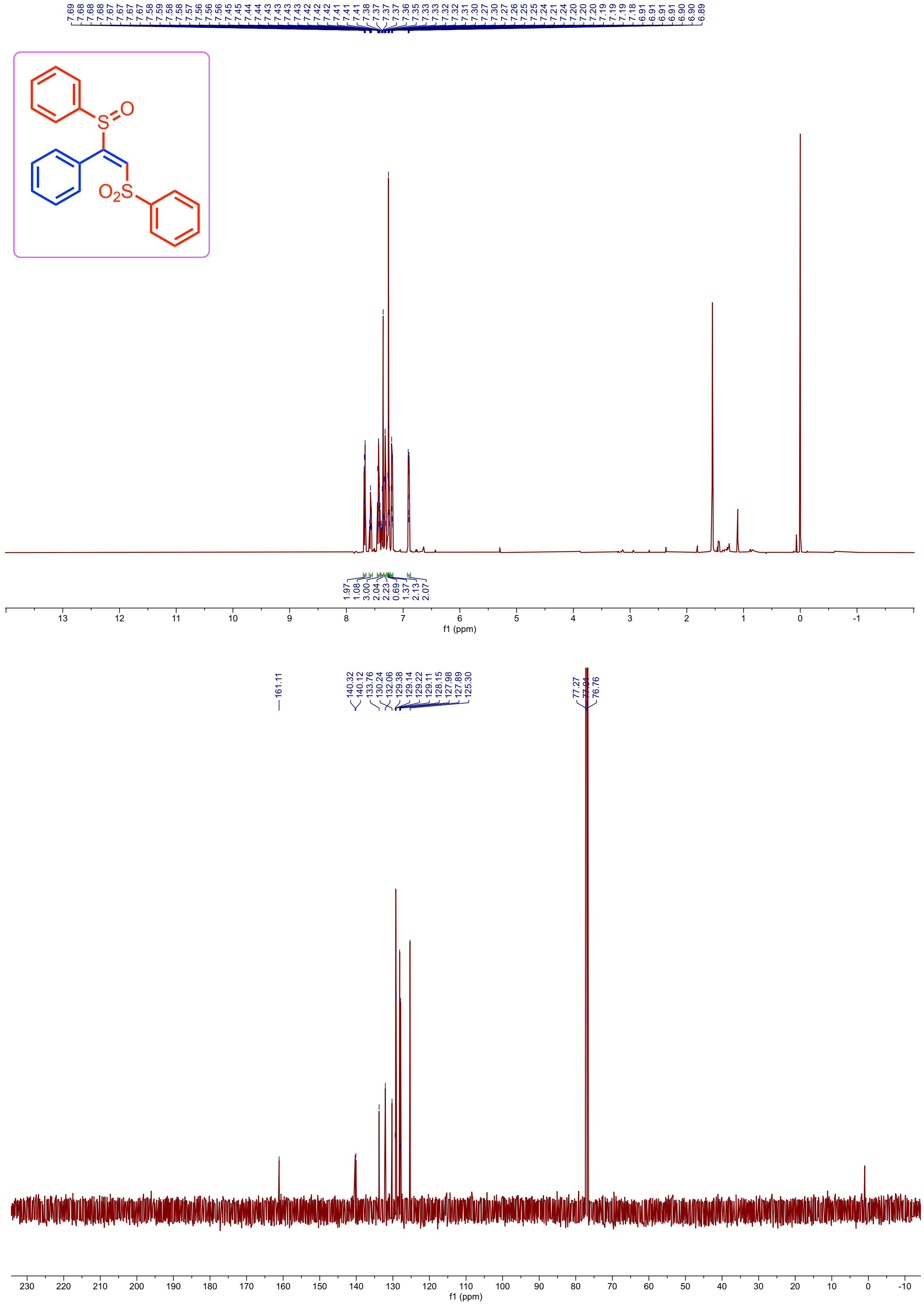

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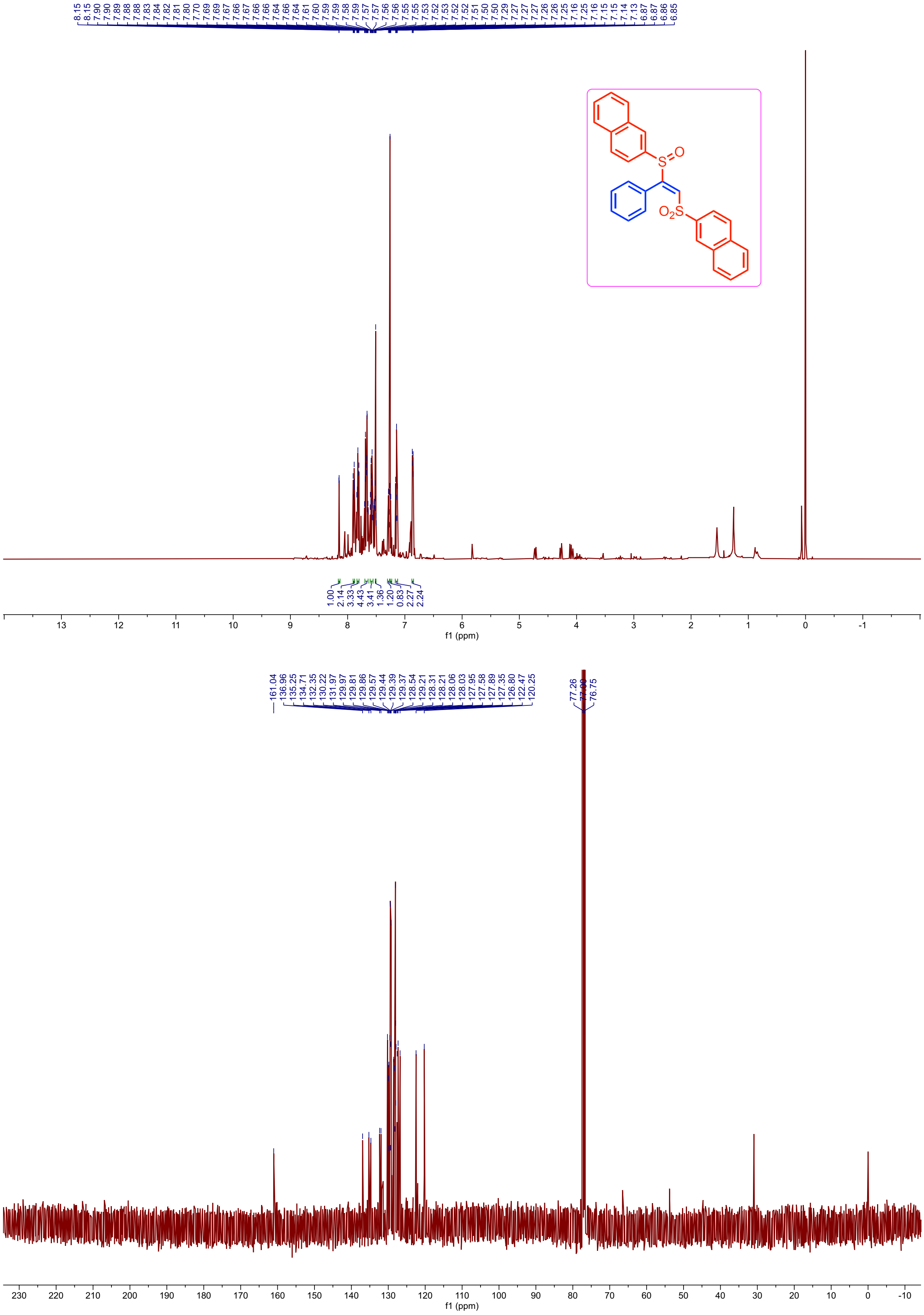

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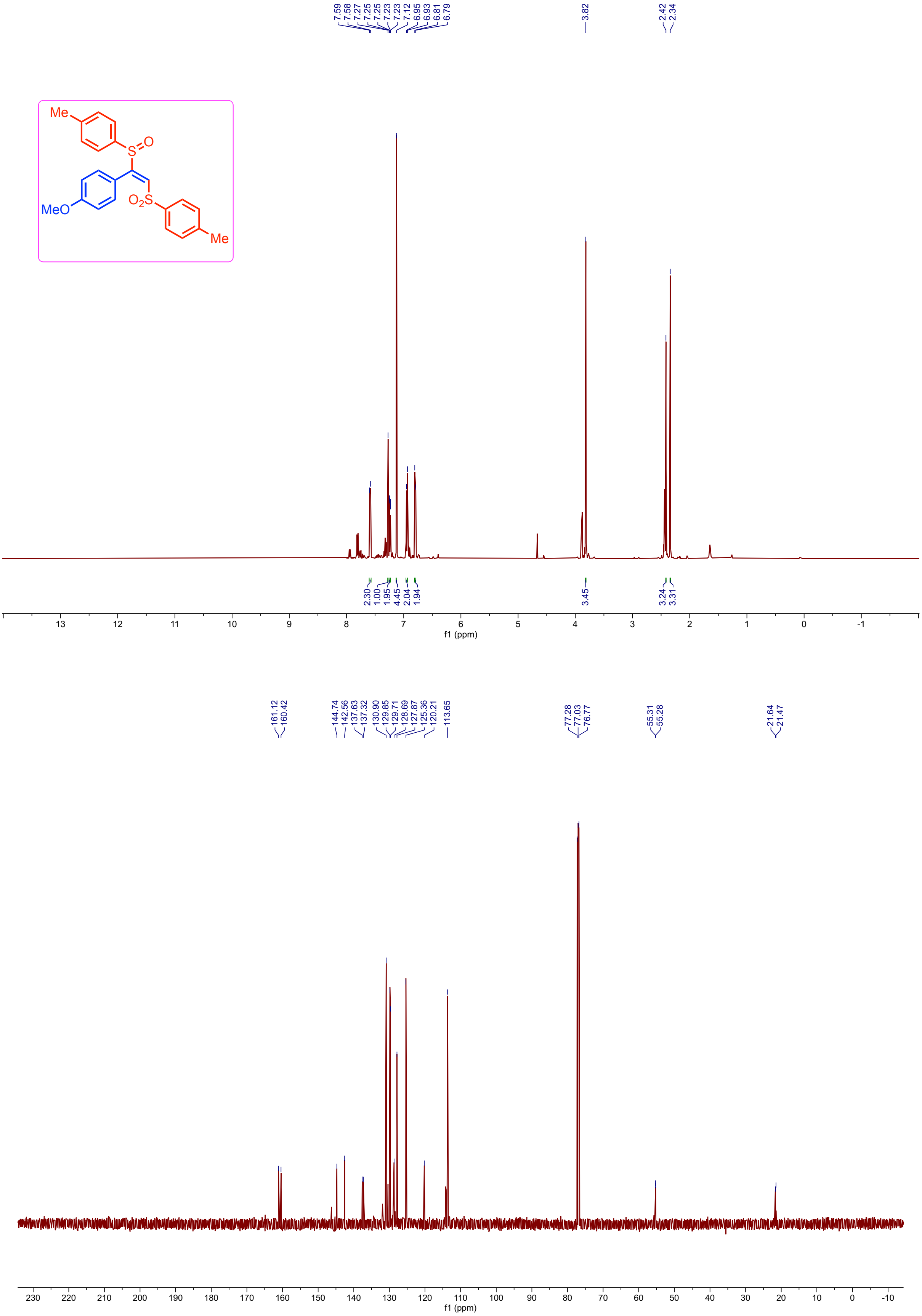

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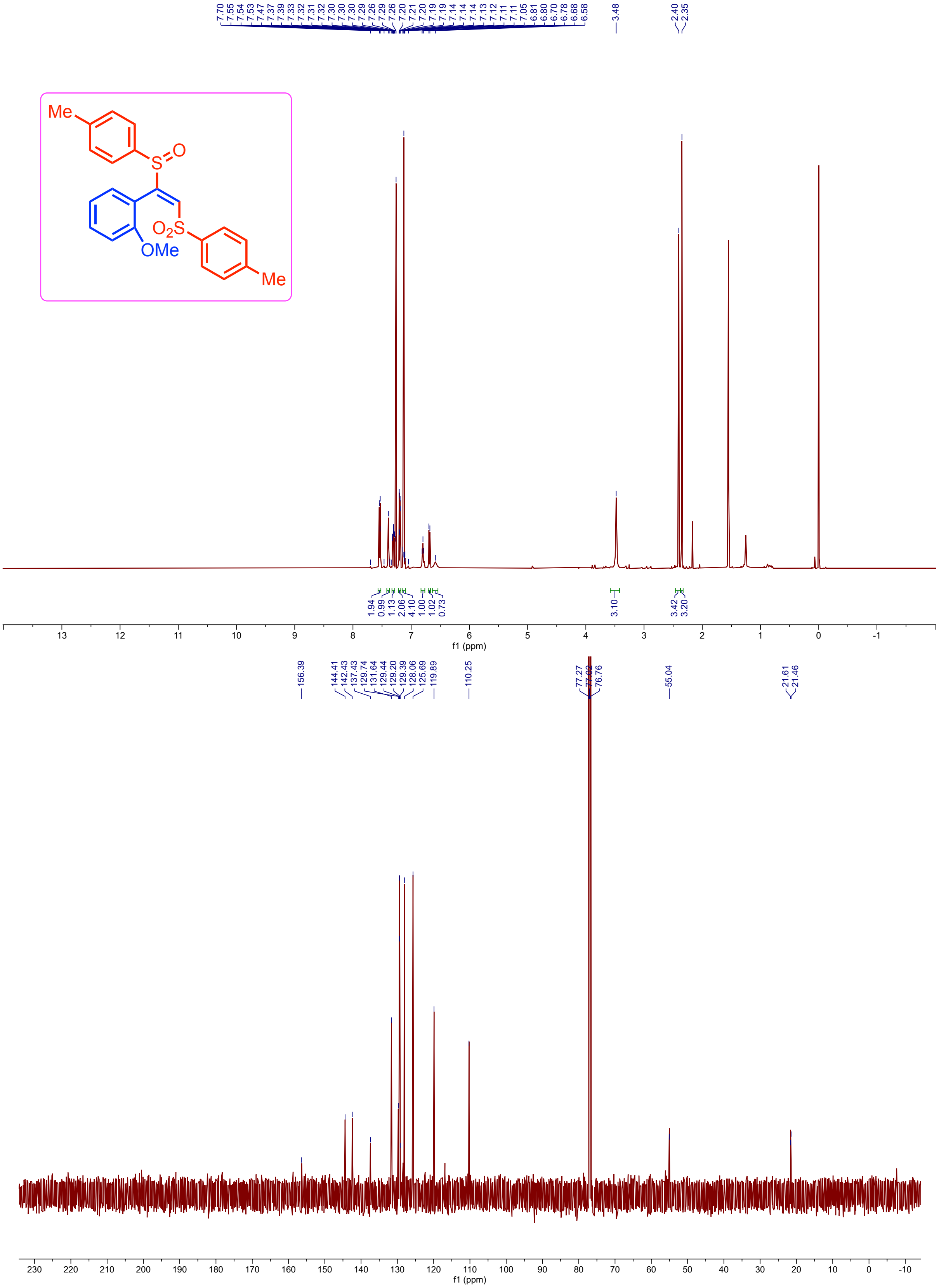

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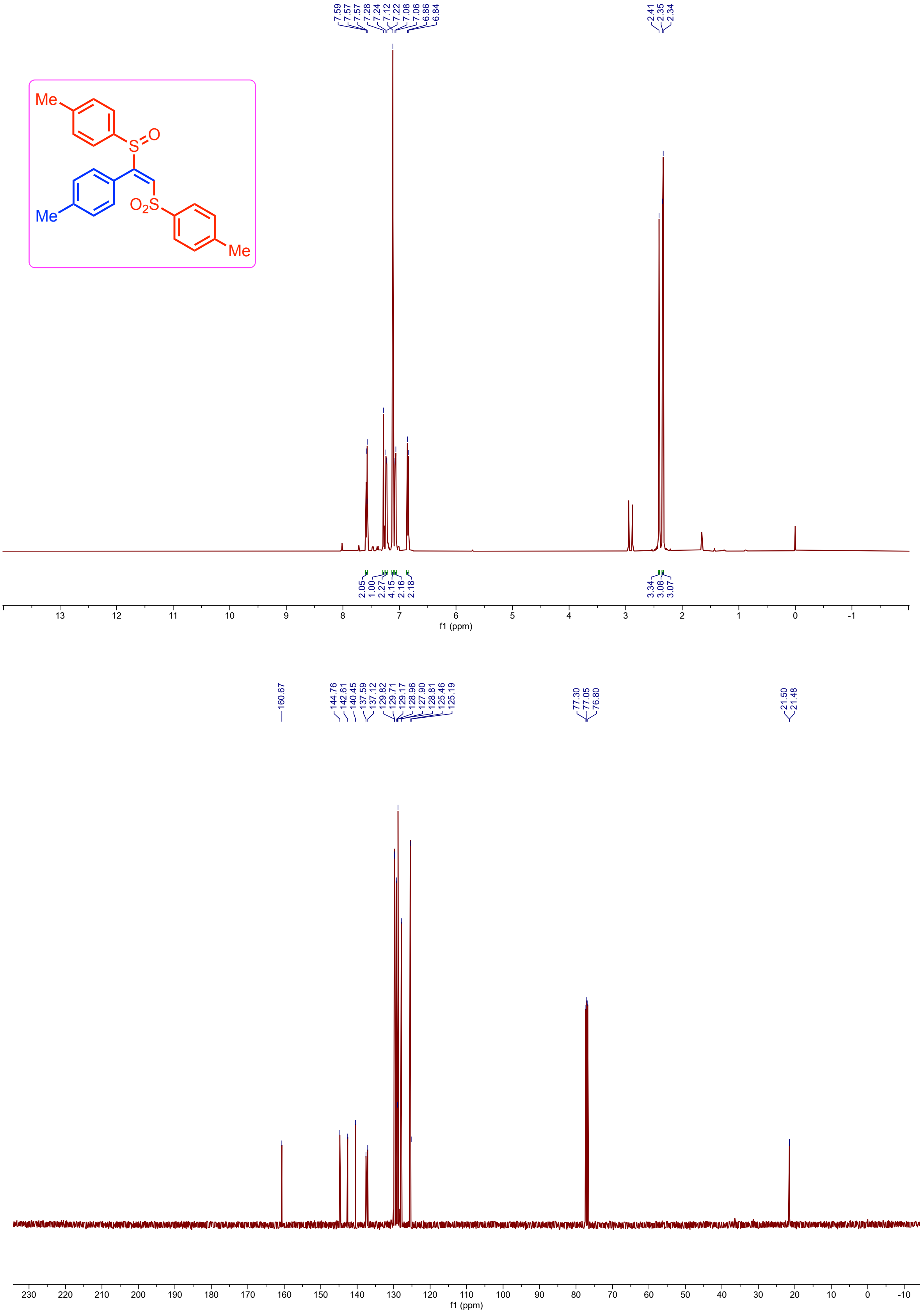

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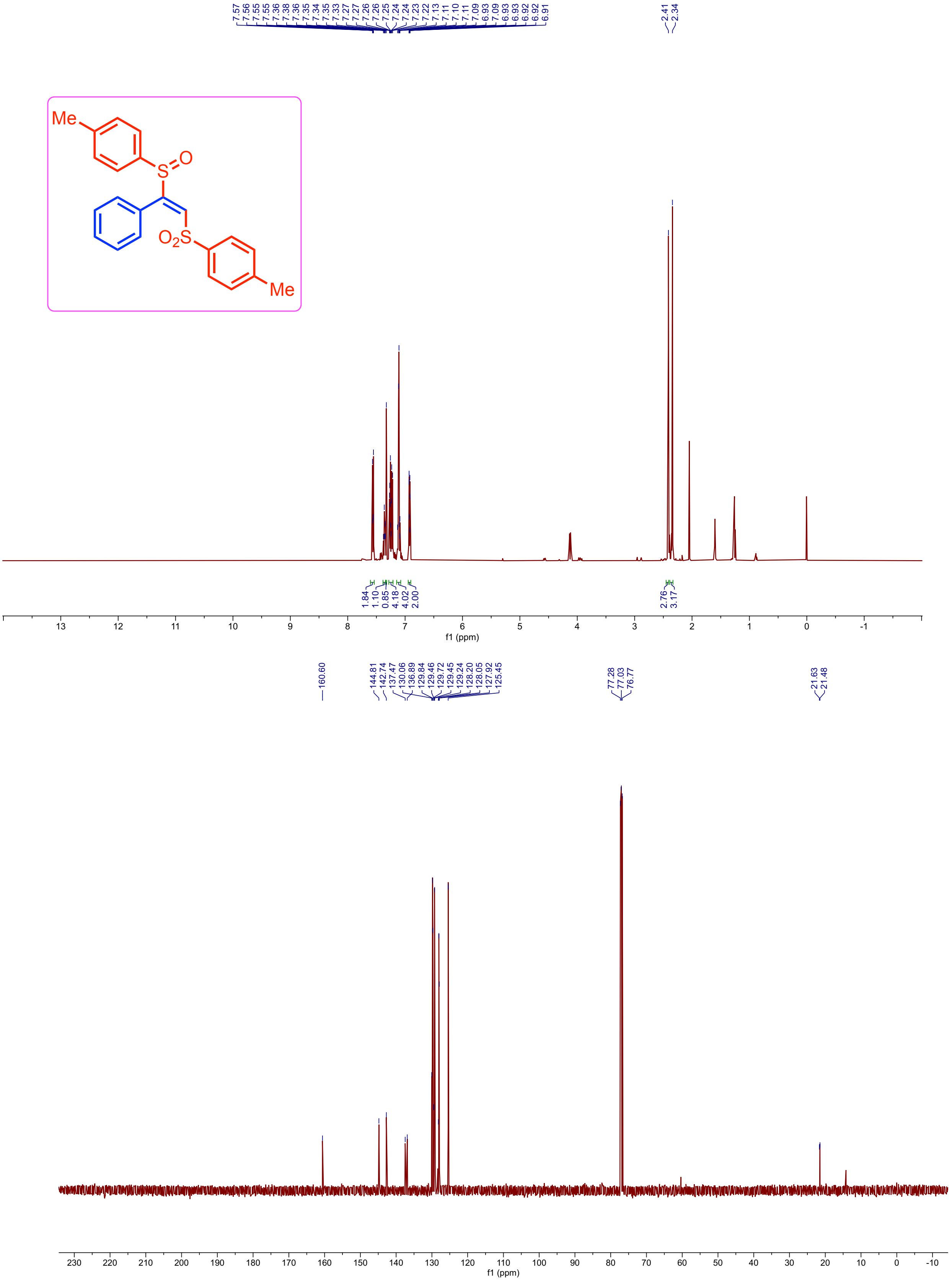

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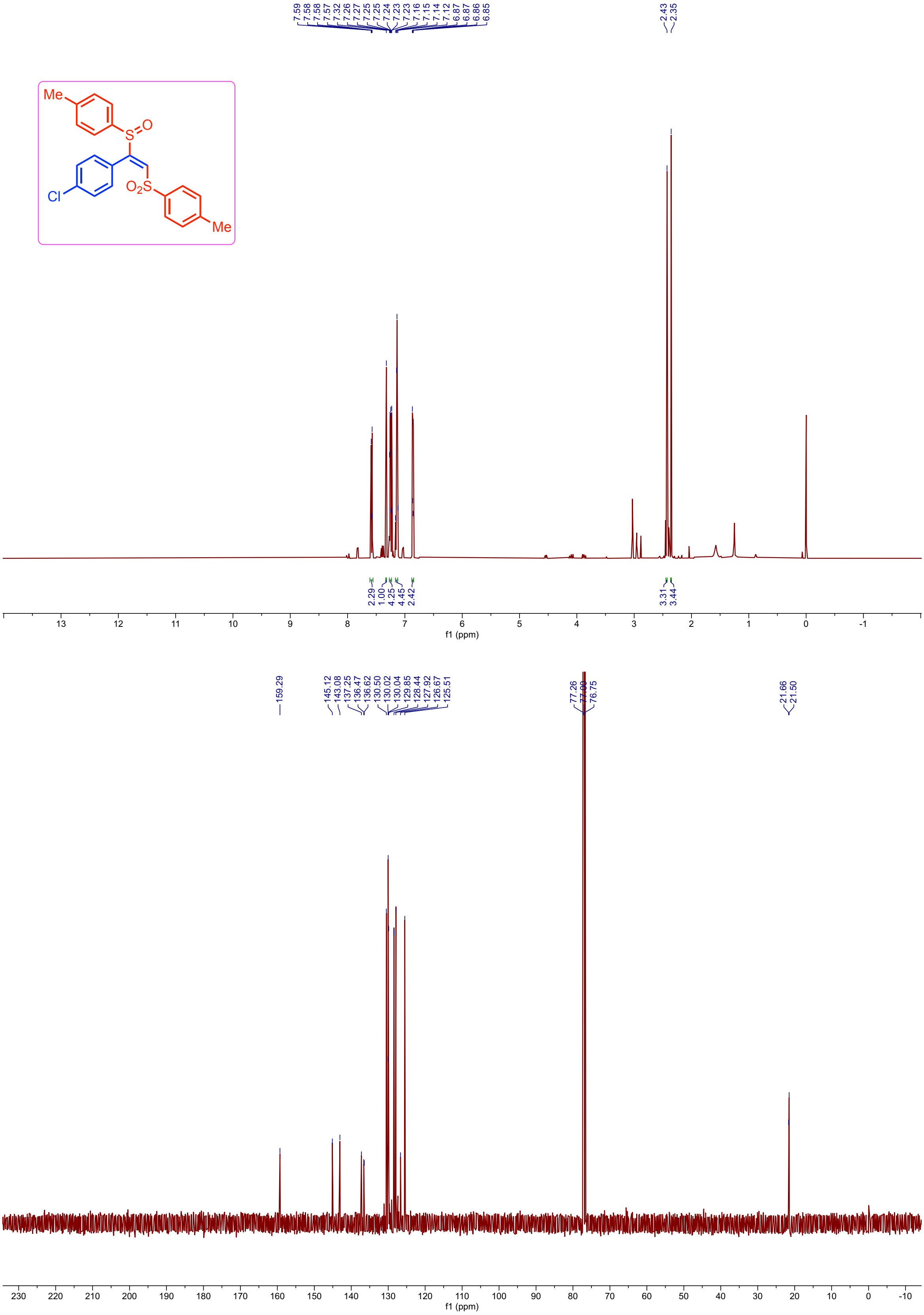

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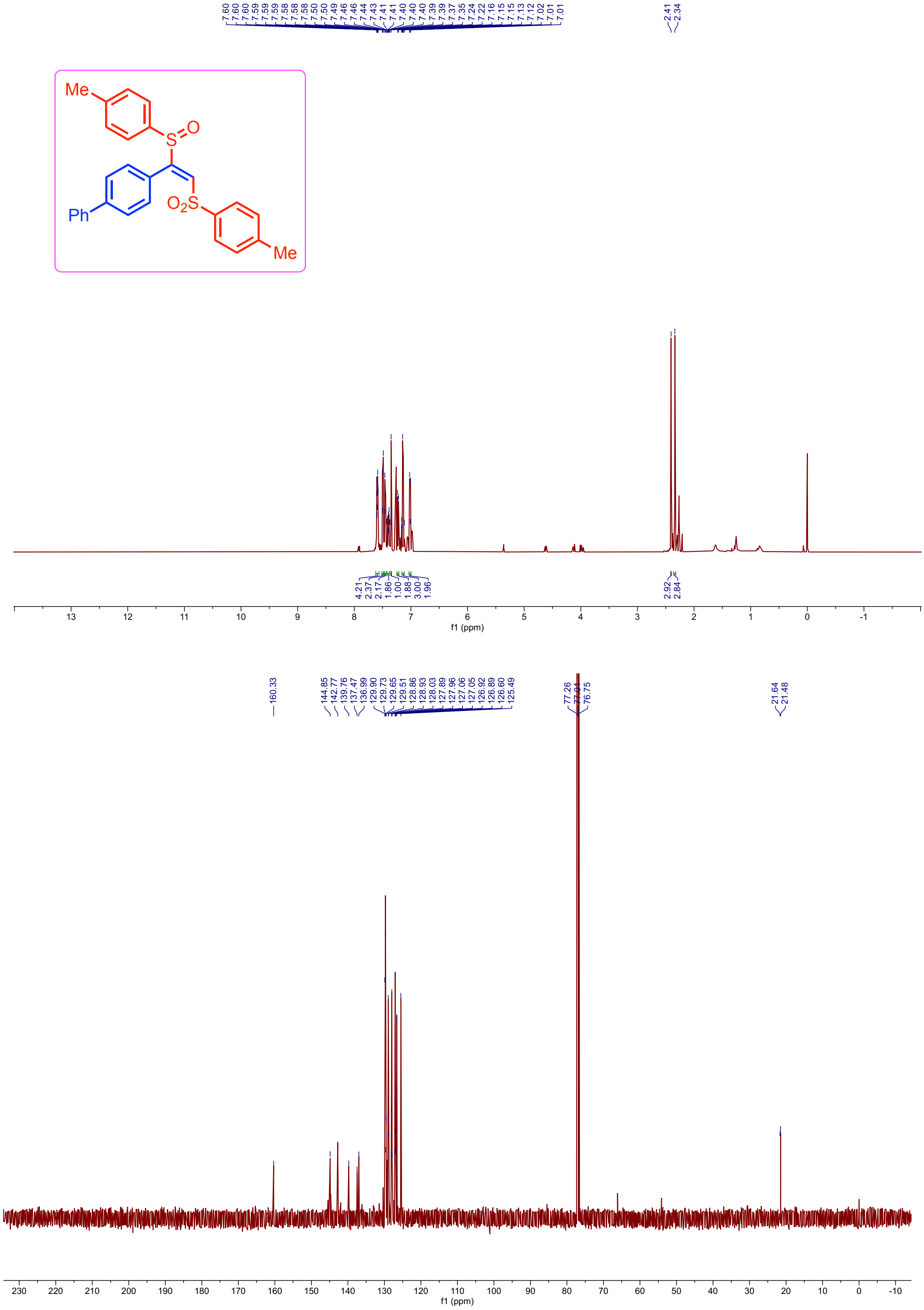

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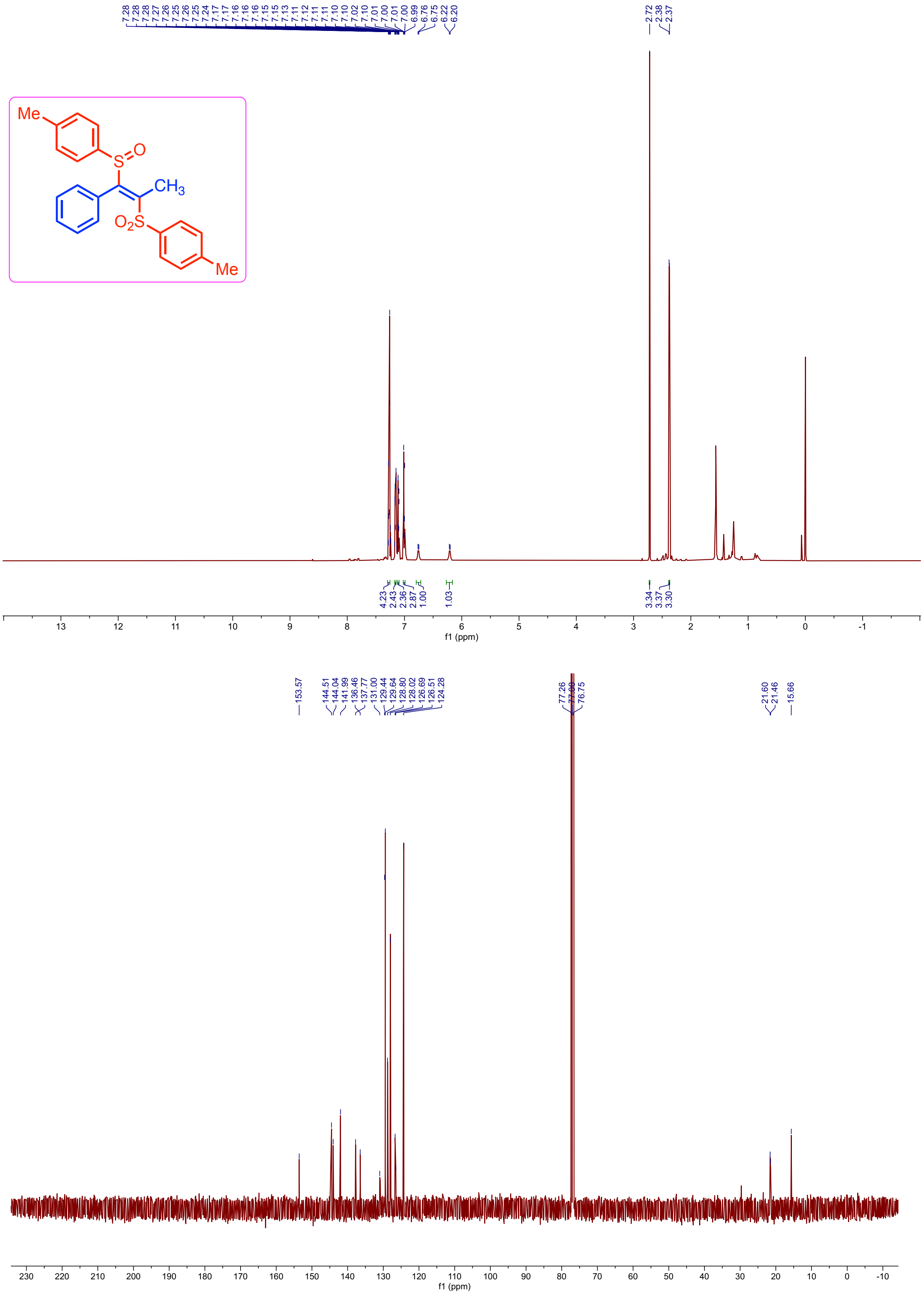

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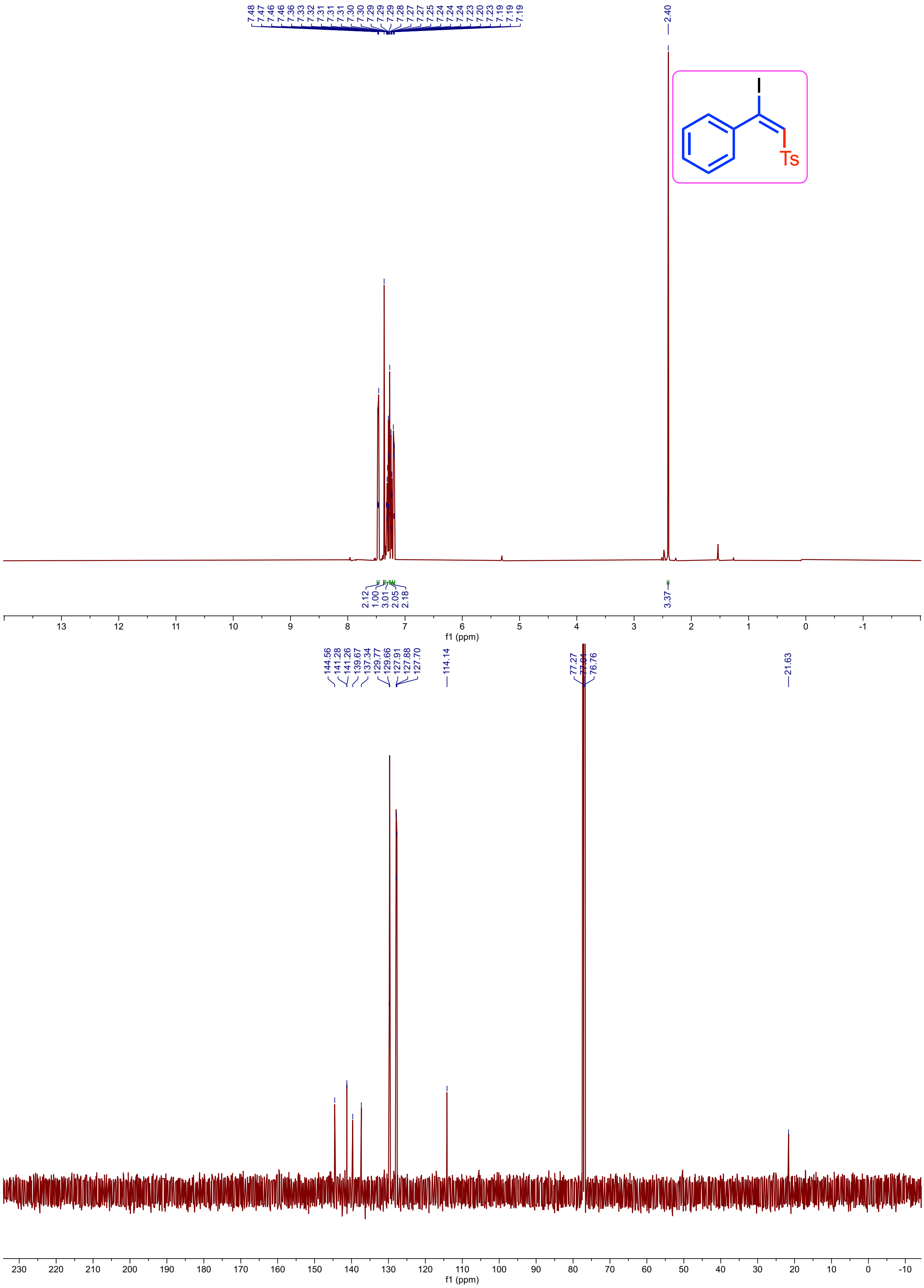

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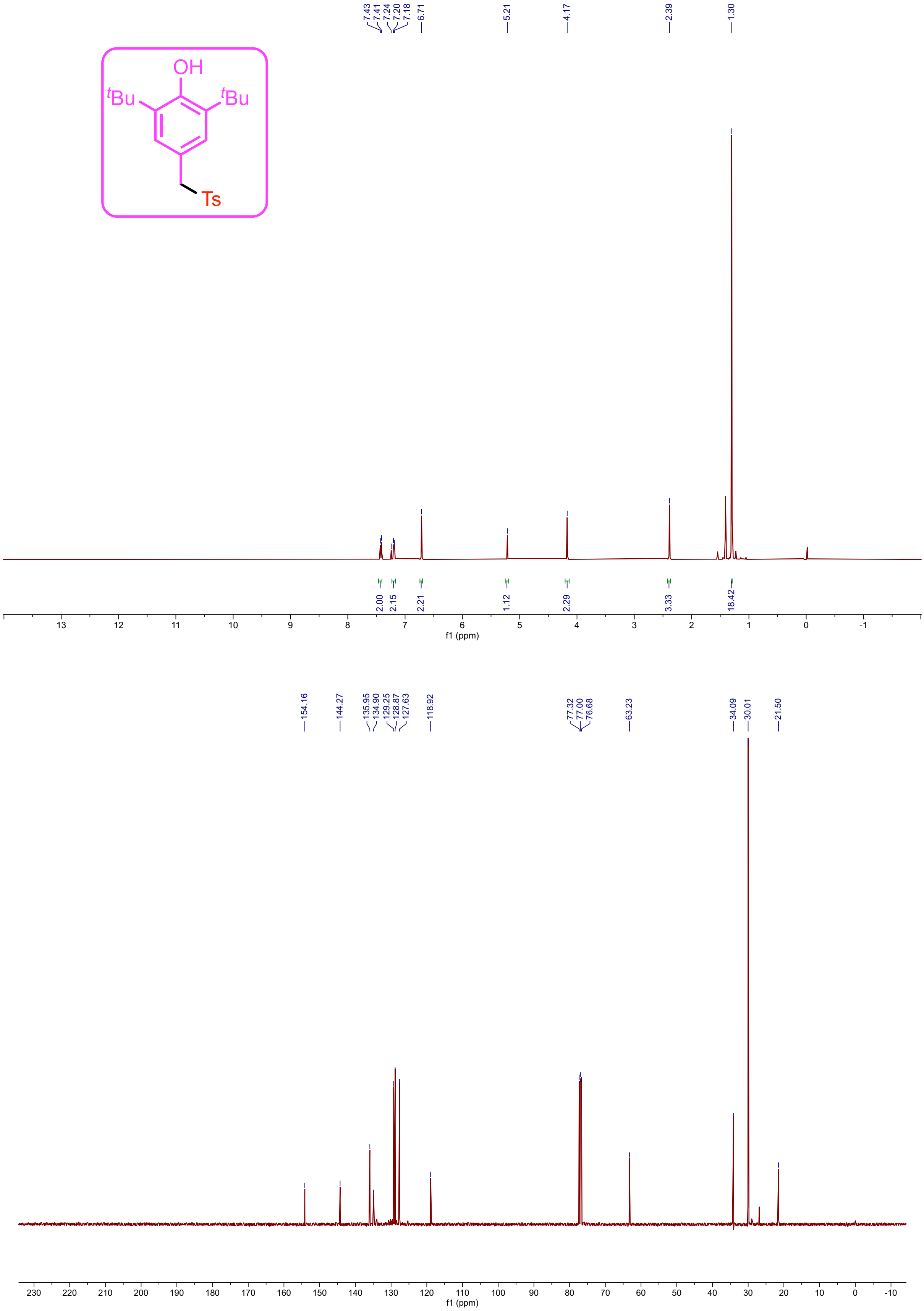

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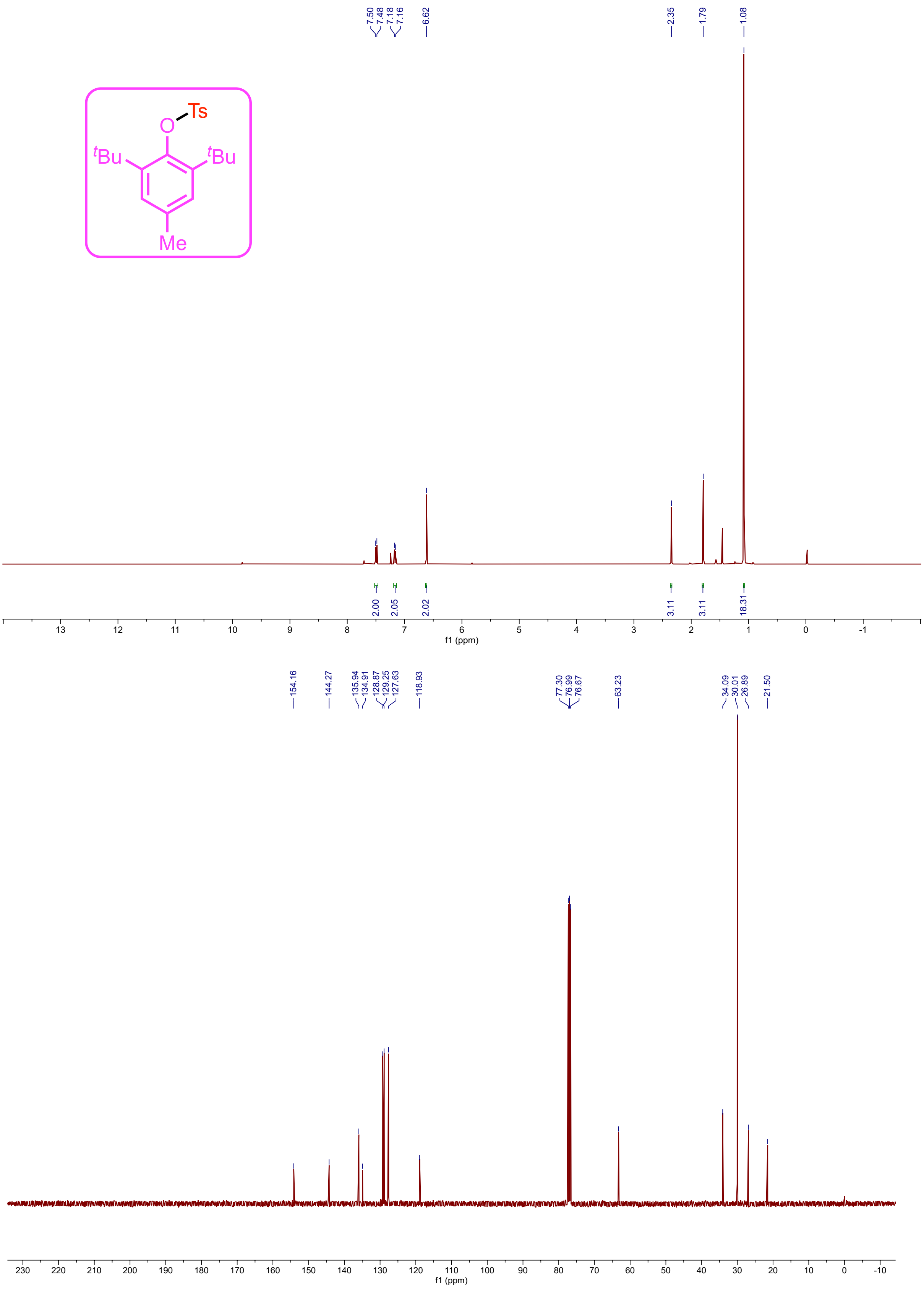

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