Supporting Information

Copper-Catalyzed Cascade Aminoalkynylation-Oxidation of Propargylic Alcohols: Stereospecific Synthesis of (Z)-2-Amino Conjugated Enynals/Enynones

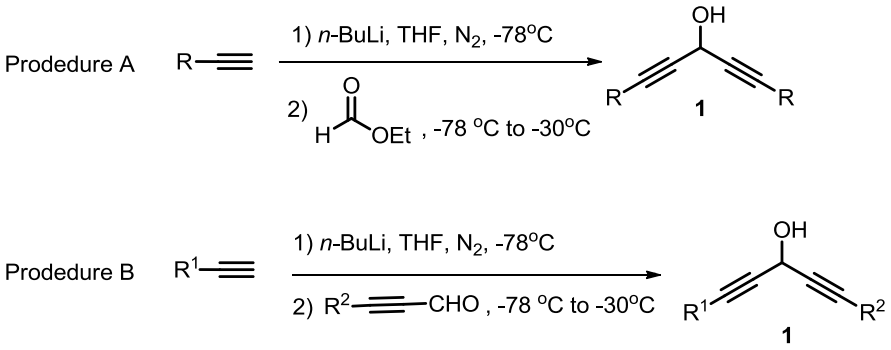
Jiaqiong Sun, Guangfan Zheng, Yongmei Fu, LiHong Wang, Yan Li,* and Qian Zhang

Table of Contents

I. General Information.

All reagents were purchased from commercial suppliers and used without further purification. The reactions were monitored with the aid of thin-layer chromatography (TLC) on 0.25 mm precoated silica gel plates. Visualization was carried out with UV light and aqueous potassium permanganate stain. Melting points were measured on Büchi B-540 apparatus. ^{1}H NMR spectra were recorded at 25 °C on a Bruker 600 or Varian 500 MHz, ^{13}C NMR spectra were recorded at 25 °C on a Bruker 150 or Varian 125 MHz. Chemical shifts (δ) are given in ppm relative to the residual solvent signals (chloroform, 7.26 ppm for ^{1}H NMR and 77.00 ppm for ^{13}C NMR). Coupling constants (*J*) are given in Hertz (Hz). Letters m, s, d, t and q stand for multiplet, singlet, doublet, triplet and quartet, respectively. High resolution mass spectra were recorded on Bruck microtof.

II. General procedure for synthesis of substrates 1.[1]



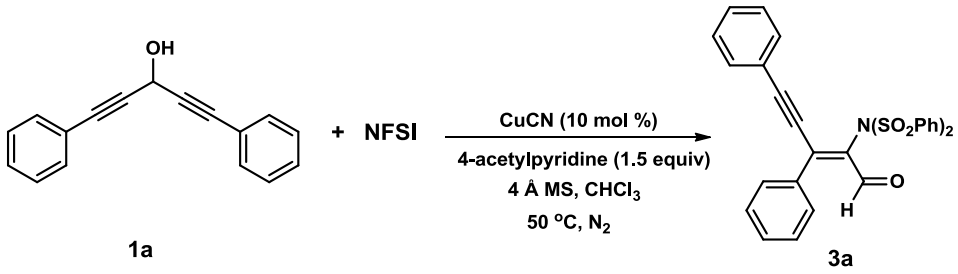
Procedure A

n-Butyllithium (2.2 mL, 2.5 M solution in hexanes) was added to a solution of the acetylene (5.5 mmol) in THF (10 mL) at -78 ℃. The solution was stirred for 1 h at this temperature. After that ethyl formate (186 mg, 2.5 mmol) was added via syringe. The reaction was stirred for 2 h, during which time it was allowed to warm to -30 ℃. The reaction was quenched at this temperature with a mixture of aqueous saturated NH_4Cl (10 mL) and 1 M HCl (2 mL), the phases were separated and the aqueous phase was extracted with Et_2O (2 × 10 mL). The combined organics were washed with brine (20 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel chromatography (10% EtOAc in petroleum ether).

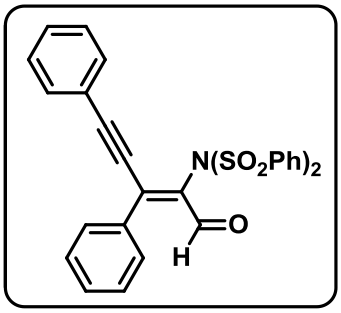
Procedure B:

n-Butyllithium (2 mL, 2.5 M solution in hexanes) was added to a solution of the acetylene (5 mmol) in THF (10 mL) at -78 ℃. The solution was stirred for 1 h at this temperature. After that propargyl aldehyde[2] (5 mmol) was added via syringe. The reaction was stirred for 2 h, during which time it was allowed to warm to -30 ℃. The reaction was quenched at this temperature with a mixture of aqueous saturated NH_4Cl (10 mL) and 1M HCl (2 mL), the phases were separated and the aqueous phase was extracted with Et_2O (2 × 10 mL). The combined organics were washed with brine (20 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel chromatography (10% EtOAc in petroleum ether).

III. Experiment Details and Analytical Data of 3 and 4

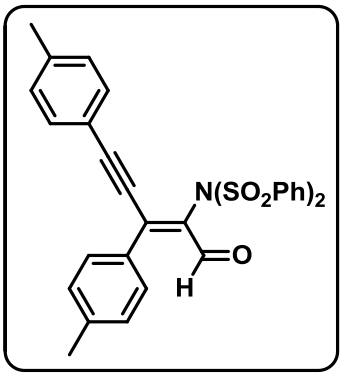


Take **3a** as an example: In a nitrogen-filled glove-box, a flame dried screw-cap reaction tube equipped with a magnetic stir bar was charged with **1a** (0.2 mmol, 46.4 mg), CuCN (0.02 mmol, 1.8 mg), anhydrous $CHCl_3$ (2 mL), 4-acetylpyridine (0.30 mmol, 33 μL), NFSI (0.4 mmol, 126.0 mg) and 4Å molecular sieve (0.2 g). The test tube was then sealed off with a screw-cap and removed from the glove-box, and the reaction mixture was stirred at 50 ℃ for 8.0 h. After the reaction finished, the reaction mixture was cooled to room temperature and quenched by water. The mixture was extracted with CH_2Cl_2 (3 × 5.0 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum. The residue was purified by column chromatography (petroleum ether/ethyl acetate 15:1 (v/v)) to give the corresponding product **3a.**



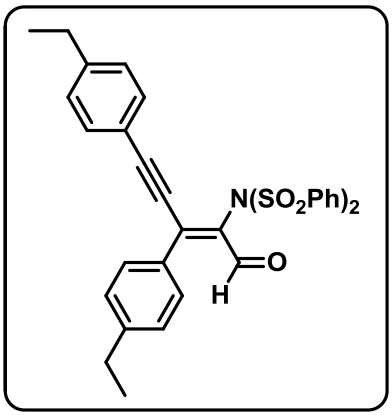
(*Z*)-*N*-(1-oxo-3,5-diphenylpent-2-en-4-yn-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide 3a

Yellow solid (80.0 mg, 76%), mp. 193 – 194 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.60 (s, 1H), 8.11 (d, *J* = 7.8 Hz, 4H), 7.61 – 7.59 (m, 2H), 7.56 – 7.54 (m, 1H), 7.52 – 7.46 (m, 4H), 7.42 – 7.37 (m, 5H), 7.33 (d, *J* = 7.2 Hz, 2H), 7.30 – 7.27 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.3, 149.2, 139.9, 135.5, 133.9, 133.8, 132.8, 131.0, 130.4, 130.2, 129.3, 128.8, 128.6, 128.1, 121.4, 110.7, 88.1. HRMS (ESI-TOF) (m/z): Calcd for $C_{29}H_{21}NNaO_5S_2$, ($[M + Na]^+$), 550.0753, found 550.0755.



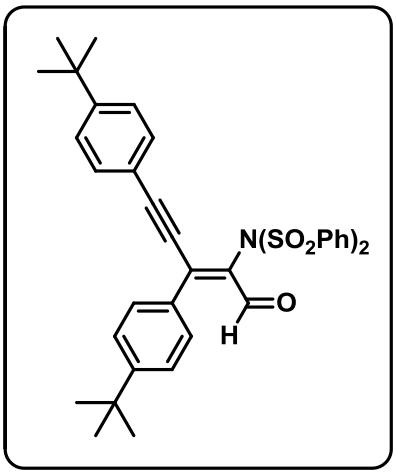
(*Z*)-*N*-(1-oxo-3,5-di-p-tolylpent-2-en-4-yn-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide 3b

Yellow solid (95.7 mg, 86%), mp. 222 – 223 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.60 (s, 1H), 8.11 (d, *J* = 7.8 Hz, 4H), 7.50 – 7.46 (m, 4H), 7.42 – 7.39 (t, *J* = 7.8 Hz, 4H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 2.44 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.5, 149.6, 141.7, 141.0, 140.0, 134.7, 133.7, 132.8, 131.2, 130.3, 129.5, 129.3, 128.9, 128.6, 118.5, 111.2, 88.0, 21.8, 21.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{31}H_{25}NNaO_5S_2$, ($[M + Na]^+$), 578.1066, found 578.1080.



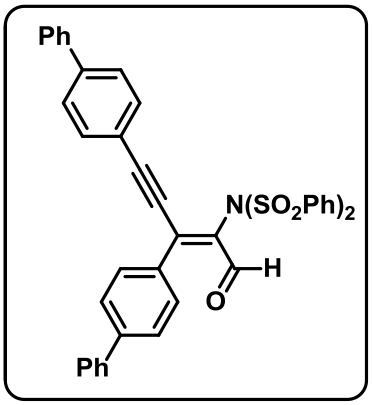
(*Z*)-*N*-(3,5-bis(4-ethylphenyl)-1-oxopent-2-en-4-yn-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide 3c

Yellow solid (90.7 mg, 78%), mp. 193 – 194 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.61 (s, 1H), 8.10 (d, *J* = 7.8 Hz, 4H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.40 (t, *J* = 7.8 Hz, 4H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 2.74 (q, *J* = 7.8 Hz, 2H), 2.66 (q, *J* = 7.8 Hz, 2H), 1.29 (t, *J* = 7.8 Hz, 3H), 1.24 (t, *J* = 7.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.5, 149.7, 147.9, 147.3, 140.0, 134.7, 133.7, 132.9, 131.4, 130.4, 129.3, 128.6, 128.3, 127.7, 118.7, 111.3, 88.0, 29.0, 28.8, 15.3, 15.2. HRMS (ESI-TOF) (m/z): Calcd for $C_{33}H_{29}NNaO_5S_2$, ($[M + Na]^+$), 606.1379, found 606.1389.



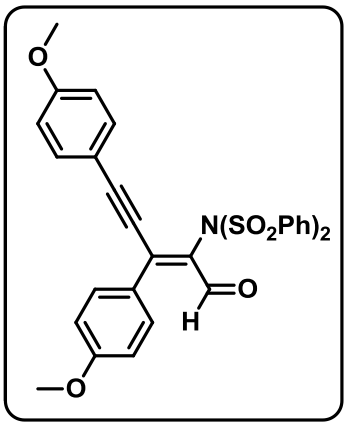
(*Z*)-*N*-(3,5-bis(4-(tert-butyl)phenyl)-1-oxopent-2-en-4-yn-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide 3d

Yellow solid (93.2 mg, 73%), mp. 110 – 111 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.61 (s, 1H), 8.10 (d, *J* = 7.8 Hz, 4H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 4H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 1.38 (s, 9H), 1.33 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.5, 154.8, 154.1, 149.7, 140.0, 134.8, 133.7, 132.7, 131.1, 130.3, 129.3, 128.6, 125.8, 125.2, 118.5, 111.3, 88.1, 35.0, 31.2, 31.1. HRMS (ESI-TOF) (m/z): Calcd for $C_{37}H_{37}NNaO_5S_2$, ($[M + Na]^+$), 662.2005, found 662.2006.



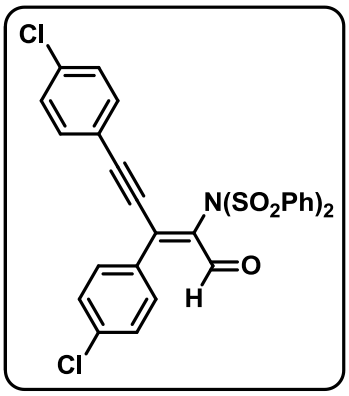
(*Z*)-*N*-(3,5-di([1,1'-biphenyl]-4-yl)-1-oxopent-2-en-4-yn-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide 3e

Yellow solid (108.1 mg, 80%), mp. 124 – 125 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.69 (s, 1H), 8.14 (d, *J* = 7.8 Hz, 4H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 7.8 Hz, 2H), 7.66 (d, *J* = 7.2 Hz, 2H), 7.62 (d, *J* = 7.3 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.51 – 7.46 (m, 6H), 7.45 – 7.41 (m, 8H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.3, 148.9, 144.1, 143.1, 140.0, 139.9, 139.6, 135.2, 133.8, 133.4, 132.7, 130.9, 129.3, 129.0, 128.9, 128.7, 128.3, 128.1, 127.5, 127.2, 127.1, 126.8, 120.3, 110.7, 88.9. HRMS (ESI-TOF) (m/z): Calcd for $C_{41}H_{29}F_2NNaO_5S_2$, ($[M + Na]^+$), 702.1379, found 702.1429.



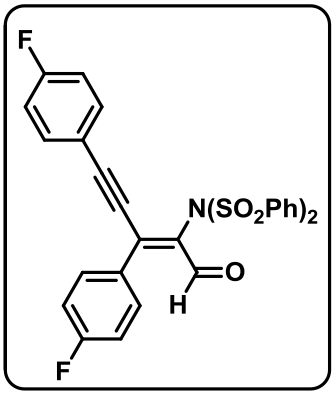
(*Z*)-*N*-(3,5-bis(4-methoxyphenyl)-1-oxopent-2-en-4-yn-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide 3f

Red solid (83.6 mg, 71%), mp. 55 – 56 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.59 (s, 1H), 8.09 (d, *J* = 7.8 Hz, 4H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.40 (t, *J* = 7.8 Hz, 4H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 3.89 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.3, 162.2, 161.4, 149.4, 140.1, 134.8, 133.6, 132.3, 129.3, 128.5, 126.5, 114.2, 113.9, 111.6, 88.1, 55.5, 55.4. HRMS (ESI-TOF) (m/z): Calcd for $C_{31}H_{25}Cl_2NNaO_7S_2$, ($[M + Na]^+$), 610.0965, found 610.0969.



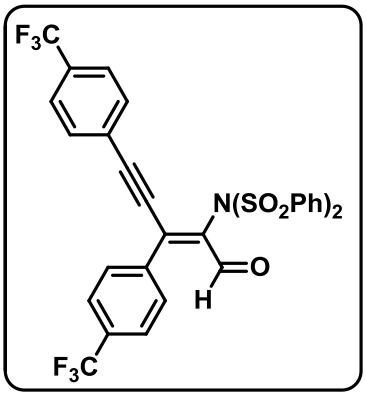
(*Z*)-*N*-(3,5-bis(4-chlorophenyl)-1-oxopent-2-en-4-yn-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide 3g

Yellow solid (94.9 mg, 80%), mp. 72 – 73 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.59 (s, 1H), 8.07 (d, *J* = 7.8 Hz, 4H), 7.54 – 7.49 (m, 6H), 7.42 (t, *J* = 7.8 Hz, 4H), 7.29 – 7.27 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.7, 147.3, 139.7, 137.6, 136.9, 135.9, 134.0, 133.9, 131.9, 131.4, 129.3, 129.2, 128.7, 128.6, 119.7, 109.2, 88.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{29}H_{19}Cl_2NNaO_5S_2$, ([M + Na]$^+$), 617.9974, found 617.9997.



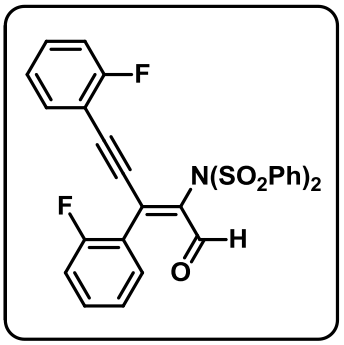
(*Z*)-*N*-(3,5-bis(4-fluorophenyl)-1-oxopent-2-en-4-yn-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide 3h

Yellow solid (76.2 mg, 68%), mp. 119 – 120 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.59 (s, 1H), 8.08 (d, *J* = 7.8 Hz, 4H), 7.61 – 7.58 (m, 2H), 7.50 (t, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 4H), 7.36 – 7.34 (m, 2H), 7.21 (t, *J* = 8.4 Hz, 2H), 7.00 (t, *J* = 8.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.9, 164.4 (*J* = 252.1 Hz), 163.9 (*J* = 252.4 Hz), 147.8, 139.8, 135.6, 135.1 (*J* = 8.8 Hz), 133.9, 132.3 (*J* = 8.8 Hz), 129.7 (*J* = 3.1 Hz), 129.3, 128.6, 117.5 (*J* = 3.4 Hz), 116.2 (*J* = 22.0 Hz), 115.7 (*J* = 22.3 Hz), 109.6, 87.9. HRMS (ESI-TOF) (m/z): Calcd for $C_{29}H_{19}F_2NNaO_5S_2$, ([M + Na]$^+$), 586.0565, found 586.0568.



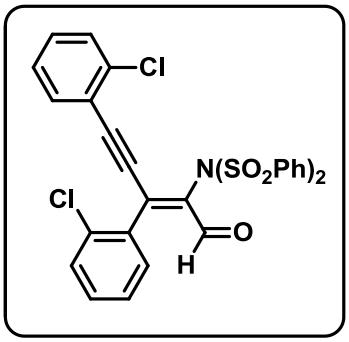
(*Z*)-*N*-(1-oxo-3,5-bis(4-(trifluoromethyl)phenyl)pent-2-en-4-yn-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide 3i

Yellow solid (68.7 mg, 52%), mp. 60 – 61 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.57 (s, 1H), 8.10 – 8.06 (m, 4H), 7.80 (d, *J* = 7.8 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 2H), 8.46 – 8.42 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.4, 146.4, 139.6, 137.2, 136.8, 134.1, 133.0, 133.0 (q, *J* = 32.9 Hz), 132.0 (q, *J* = 32.6 Hz), 130.3, 129.3, 128.8, 126.0 (q, *J* = 3.75 Hz), 125.2 (q, *J* = 3.75 Hz), 124.7, 123.6 (q, *J* = 270.8 Hz), 123.5 (q, *J* = 271.1 Hz), 108.2, 88.9. HRMS (ESI-TOF) (m/z): Calcd for $C_{31}H_{19}F_6NNaO_5S_2$, ([M + Na]$^+$), 686.0501, found 686.0502.



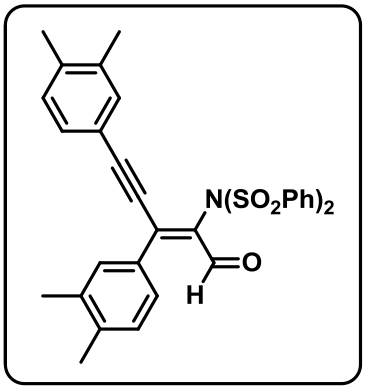
(*E*)-*N*-(3,5-bis(2-fluorophenyl)-1-oxopent-2-en-4-yn-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide 3j

Yellow solid (90.5 mg, 80%), mp. 75 – 76 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.51 (d, *J* = 3.0 Hz, 1H), 8.12 (d, *J* = 7.8 Hz, 4H), 7.57 – 7.55 (m, 1H), 7.49 (t, *J* = 7.2 Hz, 3H), 7.42 (t, *J* = 7.2 Hz, 4H), 7.37 – 7.35 (m, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.21 (t, *J* = 9.0 Hz, 1H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.99 (t, *J* = 9.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.7 (*J* = 3.0 Hz), 162.6 (*J* = 254.0 Hz), 159.1 (*J* = 249.8 Hz), 141.3, 139.7, 136.2, 134.7, 133.8, 132.7 (*J* = 8.1 Hz), 132.3 (*J* = 8.0 Hz), 131.5 (*J* = 0.9 Hz), 129.3, 128.6, 124.7 (*J* = 3.6 Hz), 123.9 (*J* = 3.8 Hz), 121.1 (*J* = 14.0 Hz), 116.3 (*J* = 21.3 Hz), 115.2, (*J* = 20.1 Hz), 110.2 (*J* = 15.1 Hz), 102.4, 91.6 (*J* = 2.9 Hz). HRMS (ESI-TOF) (m/z): Calcd for $C_{29}H_{19}F_2NNaO_5S_2$, ($[M + Na]^+$), 586.0565, found 586.0550.



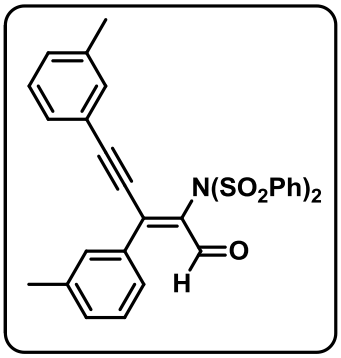
(*E*)-*N*-(3,5-bis(2-chlorophenyl)-1-oxopent-2-en-4-yn-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide 3k

Yellow solid (62.5 mg, 52%), mp. 204 – 205 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.42 (s, 1H), 8.18 – 7.15 (m, 4H), 7.56 – 7.53 (m, 2H), 7.52 – 7.47 (m, 3H), 7.45 – 7.42 (m, 1H), 7.40 – 7.35 (m, 5H), 7.31 – 7.27 (m, 2H), 7.19 – 7.16 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.8, 145.1, 140.1, 139.7, 136.9, 136.6, 134.8, 133.9, 133.8, 132.9, 132.1, 131.4, 131.3, 131.2, 130.4, 129.4, 129.3, 129.0, 128.7, 128.6, 127.1, 126.3, 121.6, 106.4, 90.9. HRMS (ESI-TOF) (m/z): Calcd for $C_{29}H_{19}Cl_2NNaO_5S_2$, ($[M + Na]^+$), 617.9974, found 617.9981.



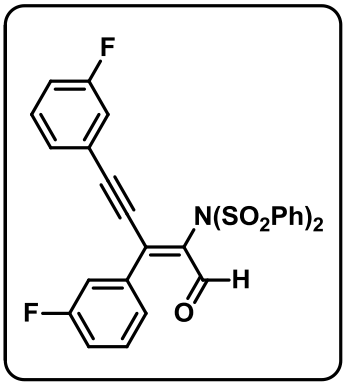
(*Z*)-*N*-(3,5-bis(3,4-dimethylphenyl)-1-oxopent-2-en-4-yn-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide 3l

Yellow solid (65.1 mg, 56%), mp. 79 – 80 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.59 (s, 1H), 8.12 (d, *J* = 7.8 Hz, 4H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 7.8 Hz, 4H), 7.35 – 7.32 (m, 2H), 7.25 – 7.24 (m, 1H), 7.07 – 7.03 (m, 3H), 2.34 (s, 6H), 2.27 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.6, 149.9, 140.4, 140.1, 139.8, 137.3, 136.5, 134.5, 133.8, 133.7, 131.7, 131.3, 130.5, 130.0, 129.5, 129.3, 128.6, 127.9, 118.8, 111.7, 87.9, 20.0, 19.8, 19.7, 19.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{33}H_{29}NNaO_5S_2$, ($[M + Na]^+$), 606.1379, found 606.1401.



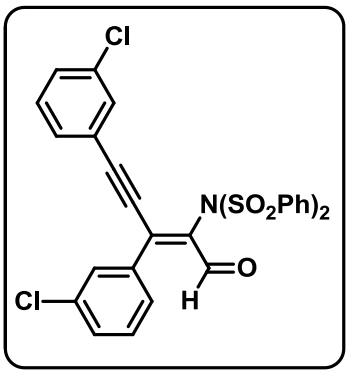
(*Z*)-*N*-(1-oxo-3,5-di-m-tolylpent-2-en-4-yn-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide 3m

Yellow solid (82.6 mg, 74%), mp. 189 – 190 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.59 (s, 1H), 8.12 (d, *J* = 7.8 Hz, 4H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.42 – 7.37 (m, 7H), 7.35 – 7.33 (m, 1H), 7.19 – 7.15 (m, 2H), 7.14 – 7.13 (m, 1H), 7.08 (s, 1H), 2.44 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.5, 149.5, 140.0, 138.8, 137.8, 135.4, 133.9, 133.7, 133.2, 131.8, 131.3, 130.6, 130.0, 129.3, 128.7, 128.6, 128.0, 127.3, 121.3, 111.1, 87.9, 21.3, 21.1. HRMS (ESI-TOF) (m/z): Calcd for $C_{31}H_{25}NNaO_5S_2$, ([M + Na]$^{+}$), 578.1066, found 578.1088.



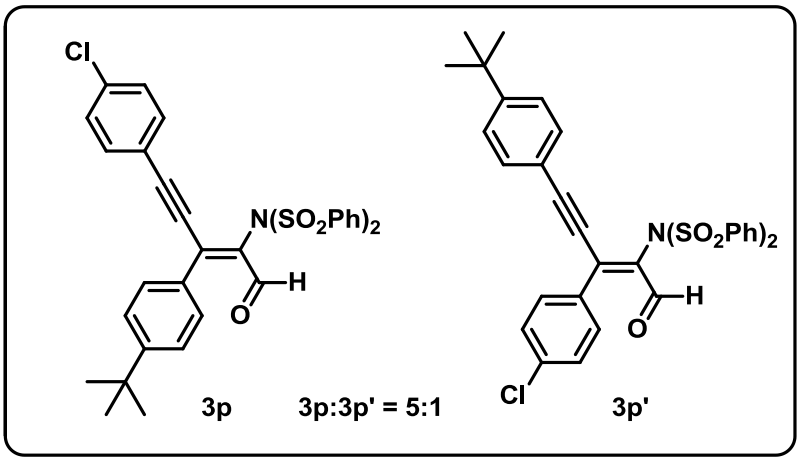
(*Z*)-*N*-(5-(3-fluorophenyl)-3-(4-fluorophenyl)-1-oxopent-2-en-4-yn-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide 3n

Yellow solid (78.7 mg, 70%), mp. 144 – 145 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.61 (s, 1H), 8.10 (d, *J* = 7.8 Hz, 4H), 7.52 – 7.47 (m, 3H), 7.44 (t, *J* = 7.8 Hz, 4H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.33 – 7.30 (m, 1H), 7.29 – 7.24 (m, 2H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.12 – 7.09 (m, 1H), 7.01 – 7.00 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.8, 162.6 (*J* = 248.1 Hz), 162.0 (*J* = 246.0 Hz), 146.8, 139.8, 136.6, 135.3 (*J* = 7.8 Hz), 134.0, 130.6 (*J* = 8.4 Hz), 129.8 (*J* = 8.4 Hz), 129.3, 128.7 (*J* = 3.15 Hz), 128.7, 126.0 (*J* = 3.0 Hz), 122.9 (*J* = 9.45 Hz), 119.4 (*J* = 23.0 Hz) 118.2 (*J* = 21.45 Hz), 117.9 (*J* = 21.0 Hz), 116.9 (*J* = 22.95 Hz), 108.6 (*J* = 3.6 Hz), 87.9. HRMS (ESI-TOF) (m/z): Calcd for $C_{29}H_{19}F_2NNaO_5S_2$, ([M + Na]$^{+}$), 586.0565, found 586.0575.



(*Z*)-*N*-(5-(3-chlorophenyl)-3-(4-chlorophenyl)-1-oxopent-2-en-4-yn-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide 3o

Yellow solid (66.5 mg, 56%), mp. 136 – 137 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.59 (s, 1H), 8.10 (d, *J* = 7.8 Hz, 4H), 7.58 – 7.57 (m, 1H), 7.54 – 7.51 (m, 3H), 7.46 – 7.43 (m, 6H), 7.38 – 7.36 (m, 1H), 7.24 – 7.22 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.7, 146.6, 139.8, 136.7, 135.2, 135.0, 134.1, 134.0, 132.4, 131.1, 130.9, 130.7, 130.2, 129.7, 129.5, 129.3, 128.7, 128.2, 122.7, 108.5, 88.2. HRMS (ESI-TOF) (m/z): Calcd for $C_{29}H_{19}Cl_2NNaO_5S_2$, ([M + Na]$^{+}$), 617.9974, found 617.9995.

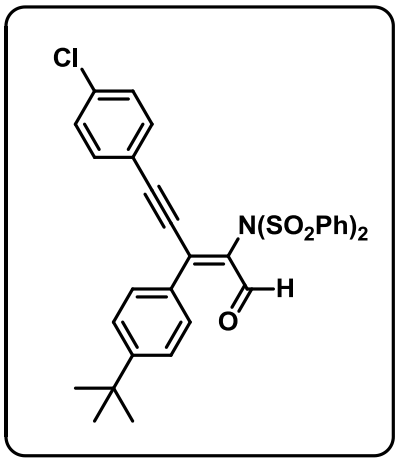


(*Z*)-*N*-(3-(4-(tert-butyl)phenyl)-5-(4-chlorophenyl)-1-oxopent-2-en-4-yn-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide 3p

(*Z*)-*N*-(5-(4-(tert-butyl)phenyl)-3-(4-chlorophenyl)-1-oxopent-2-en-4-yn-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide 3p'

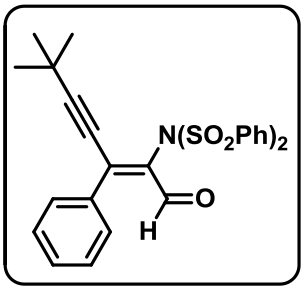
The regio-isomer **3p** and **3p'** can not be separated by column chromatography so we characterized as mixture. The major product **3p** was further purified by recrystallization from hexane and ether. Structure of **3p** was confirmed by comparison with ^{1}H NMR spectrum of **3d** and **3g**.

For **3p** and **3p'** (63.3 mg, 51%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.63 (s, 1H), 9.57 (s, 0.2H), 8.09 (d, *J* = 7.52 Hz, 5H), 7.54 – 7.52 (m, 4.8H), 7.51 – 7.47 (m, 2.5H), 7.42 – 7.39 (m, 5H), 7.29 – 7.25 (m, 4.8H), 1.37 (s, 9H), 1.32 (s, 2H).^{13}C NMR (150 MHz, $CDCl_3$) δ 186.4, 185.8, 155.0, 154.4, 148.9, 148.1, 139.9, 139.8, 137.4 136.6, 135.3, 134.0, 133.8, 132.7, 131.4, 130.7, 130.2, 129.3, 129.2, 129.1, 128.6, 128.5, 125.9, 125.2, 120.0, 118.2, 112.0, 108.4, 88.9, 87.8, 35.1, 35.0, 31.1, 31.0.



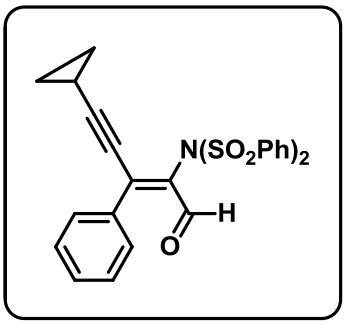
(*Z*)-*N*-(3-(4-(tert-butyl)phenyl)-5-(4-chlorophenyl)-1-oxopent-2-en-4-yn-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide 3p

Yellow solid, mp. 111 – 112 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.62 (s, 1H), 8.10 – 8.08 (m, 4H), 7.53 – 7.51 (m, 4H), 7.49 (t, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 4H), 7.27 – 7.26 (m, 4H), 1.38 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.4, 155.1, 148.9, 139.9, 136.6, 135.3, 134.0, 133.8, 130.7, 130.2, 129.3, 128.7, 128.6, 125.9, 120.0, 108.5, 88.9, 35.1, 31.2. HRMS (ESI-TOF) (m/z): Calcd for $C_{33}H_{29}ClNO_5S_2$, ([M + Na]$^{+}$), 618.1170, found 618.1153.



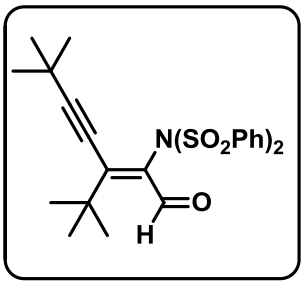
(*Z*)-*N*-(6,6-dimethyl-1-oxo-3-phenylhept-2-en-4-yn-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide 3q

Yellow solid (51.4 mg, 51%), mp. 99 – 100 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.50 (s, 1H), 8.01 (d, *J* = 8.4 Hz, 4H), 7.63 (t, *J* = 7.8 Hz, 2H), 7.55 – 7.50 (m, 7H), 7.48 – 7.46 (m, 2H), 1.12 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 186.5, 150.8, 140.0, 135.3, 134.8, 133.8, 130.9, 130.3, 129.4, 128.7, 128.6, 122.7, 78.7, 30.0, 29.1. HRMS (ESI-TOF) (m/z): Calcd for $C_{27}H_{25}NNaO_5S_2$, ($[M + Na]^+$), 530.1066, found 530.1062.



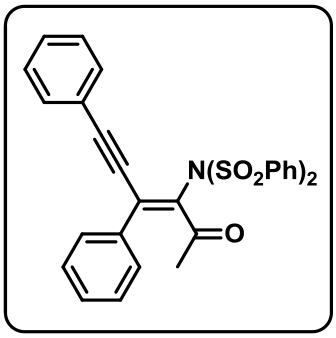
(*Z*)-*N*-(5-cyclopropyl-1-oxo-3-phenylpent-2-en-4-yn-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide 3r

Yellow solid (42.6 mg, 43%), mp. 114 – 115 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.1 (s, 1H), 8.03 (d, *J* = 7.8 Hz, 4H), 7.66 (t, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.8 Hz, 4H), 7.49 – 7.48 (m, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.41 – 7.39 (m, 2H), 1.97 – 1.93 (m, 1H), 1.18 – 1.16 (m, 2H), 0.91 – 0.87 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.0, 157.2, 139.3, 136.0, 134.1, 132.1, 130.4, 129.3, 128.8, 128.7, 120.7, 105.6, 80.5, 16.5, 11.3. HRMS (ESI-TOF) (m/z): Calcd for $C_{26}H_{21}NNaO_5S_2$, ($[M + Na]^+$), 514.0753, found 514.0761.



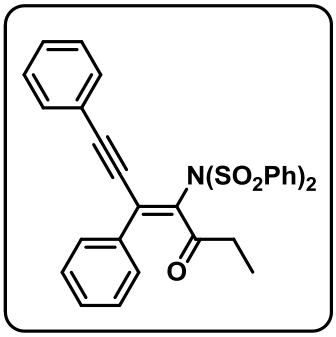
(*Z*)-*N*-(3-(tert-butyl)-6,6-dimethyl-1-oxohept-2-en-4-yn-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide 3s

Yellow solid (57.9 mg, 59%), mp. 72 – 73 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.14 (s, 1H), 7.93 – 7.92 (m, 4H), 7.61 (t, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.8 Hz, 4H), 1.48 (s, 9H), 1.11 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.5, 161.4, 140.0, 134.9, 133.6, 129.5, 128.4, 124.4, 78.7, 37.5, 32.6, 29.9, 29.1. HRMS (ESI-TOF) (m/z): Calcd for $C_{25}H_{29}NNaO_5S_2$, ($[M + Na]^+$), 510.1379, found 510.1387.



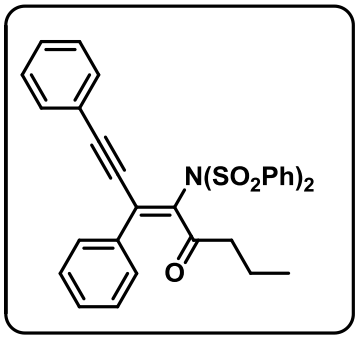
(*Z*)-*N*-(2-oxo-4,6-diphenylhex-3-en-5-yn-3-yl)-*N*-(phenylsulfonyl)benzenesulfonamide 3t

Yellow solid (73.2 mg, 68%), mp. 168 – 169 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.2 Hz, 4H), 7.50 (t, *J* = 7.2 Hz, 2H), 7.47 – 7.43 (m, 9H), 7.33 – 7.30 (m, 1H), 7.26 – 7.24 (m, 4H), 1.84 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.7, 139.9, 139.8, 136.1, 134.7, 133.8, 132.3, 130.5, 129.5, 129.4, 128.9, 128.8, 128.6, 127.9, 121.9, 104.5, 87.3, 29.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{30}H_{23}NNaO_5S_2$, ($[M + Na]^+$), 564.0910, found 564.0921.



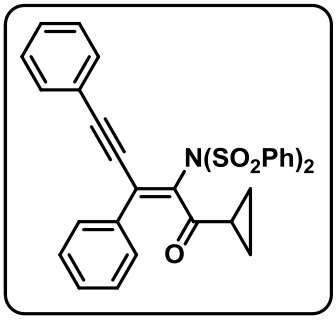
(*Z*)-*N*-(5-oxo-1,3-diphenylhept-3-en-1-yn-4-yl)-N-(phenylsulfonyl)benzenesulfonamide 3u

White solid (70.2 mg, 63%), mp. 160 – 161 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 – 8.21 (m, 4H), 7.53 – 7.48 (m, 2H), 7.48 – 7.37 (m, 9H), 7.33 – 7.29 (m, 1H), 7.27 – 7.23 (m, 4H), 2.15 (q, *J* = 7.2 Hz, 2H), 0.86 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.6, 139.8, 139.2, 136.3, 134.4, 133.8, 132.2, 130.3, 129.4, 129.4, 128.9, 128.7, 128.6, 127.9, 121.9, 103.9, 87.2, 35.3, 8.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{31}H_{25}NNaO_5S_2$, ($[M + Na]^+$), 578.1084, found 578.1066.



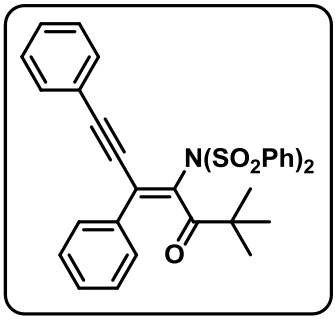
(*Z*)-*N*-(5-oxo-1,3-diphenyloct-3-en-1-yn-4-yl)-*N*-(phenylsulfonyl)benzenesulfonamide 3v

White solid (69.0 mg, 61%), mp. 165 – 166 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.8 Hz, 4H), 7.52 – 7.49 (m, 2H), 7.47 – 7.44 (m, 5H), 7.43 – 7.42 (m, 2H), 7.40 – 7.38 (m, 2H), 7.33 – 7.30 (m, 1H), 7.27 – 7.23 (m, 4H), 2.10 (t, *J* = 7.2 Hz, 2H), 1.45 – 1.39 (m, 2H), 0.64 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.6, 139.8, 139.4, 136.4, 134.5, 133.8, 132.2, 130.2, 129.5, 129.4, 128.9, 128.7, 128.6, 127.9, 122.0, 104.0, 87.3, 43.9, 17.5, 13.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{32}H_{27}NNaO_5S_2$, ($[M + Na]^+$), 592.1223, found 592.1240.



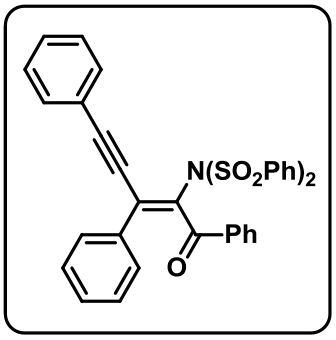
(*Z*)-*N*-(1-cyclopropyl-1-oxo-3,5-diphenylpent-2-en-4-yn-2-yl)-N-(phenylsulfonyl)benzenesulfonamide 3w

White solid (69.8 mg, 61%), mp. 190 – 191 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 – 8.21 (m, 4H), 7.51 – 7.48 (m, 4H), 7.46 – 7.40 (m, 7H), 7.34 – 7.30 (m, 1H), 7.30 – 7.24 (m, 4H), 1.54 – 1.45 (m, 1H), 1.02 – 0.93 (m, 2H), 0.59 – 0.56 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 200.8, 140.2, 139.9, 136.2, 134.6, 133.7, 132.3, 130.2, 129.5, 129.4, 128.6, 128.5, 128.0, 122.0, 104.3, 87.7, 22.9, 14.2. HRMS (ESI-TOF) (m/z): Calcd for $C_{32}H_{25}NNaO_5S_2$, ($[M + Na]^+$), 590.1066, found 590.1066.



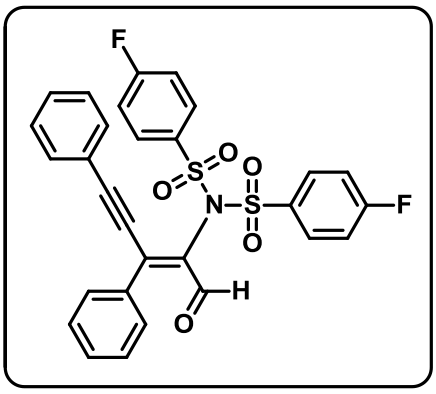
(*Z*)-*N*-(6,6-dimethyl-5-oxo-1,3-diphenylhept-3-en-1-yn-4-yl)-N-(phenylsulfonyl)benzenesulfonamide 3x

White solid (88.5 mg, 76%), mp. 122 – 123 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 (dd, *J* = 7.2, 1.2 Hz, 4H), 7.50 – 7.43 (m, 6H), 7.44 – 7.38 (m, 5H), 7.29 – 7.25 (m, 1H), 7.23 – 7.17 (m, 4H), 0.97 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 211.8, 140.1, 136.8, 136.6, 133.7, 132.0, 131.3, 130.2, 129.7, 129.0, 128.9, 128.5, 127.7, 122.1, 101.6, 87.4, 44.8, 28.9. HRMS (ESI-TOF) (m/z): Calcd for $C_{33}H_{29}NNaO_5S_2$, ($[M + Na]^+$), 606.1379, found 606.1379.



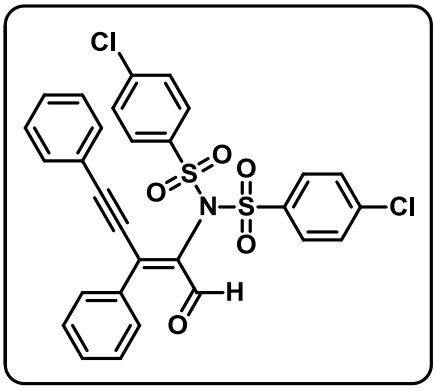
(*Z*)-*N*-(1-oxo-1,3,5-triphenylpent-2-en-4-yn-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide 3y

White solid (75.2 mg, 62%), mp. 117 – 118 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.8 Hz, 4H), 7.64 (d, *J* = 7.2 Hz, 2H), 7.50 (t, *J* = 7.2 Hz, 2H), 7.44 (t, *J* = 7.2 Hz, 4H), 7.36 – 7.33 (m, 3H), 7.31 – 7.27 (m, 4H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.11 (t, *J* = 7.8 Hz, 2H), 7.09 – 7.05 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.9, 141.1, 140.0, 136.7, 136.0, 133.8, 132.4, 132.2, 131.8, 130.0, 129.7, 129.6, 129.5, 129.4, 128.5, 128.2, 128.0, 127.7, 122.0, 104.4, 87.7. HRMS (ESI-TOF) (m/z): Calcd for $C_{35}H_{25}Cl_2NNaO_5S_2$, ($[M + Na]^+$), 626.1066, found 626.1080.



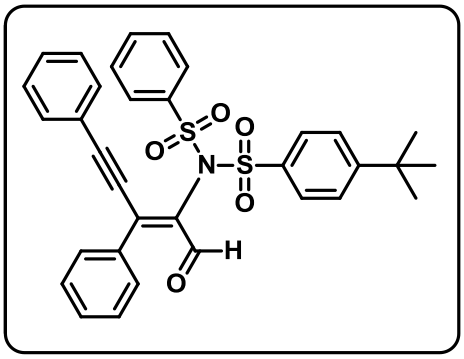
(*Z*)-4-fluoro-*N*-((4-fluorophenyl)sulfonyl)-*N*-(1-oxo-3,5-diphenylpent-2-en-4-yn-2-yl)benzenesulfonamide 4b

Yellow solid (91.7 mg, 81%), mp. 191 – 192 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.61 (s, 1H), 8.14 – 8.11 (m, 4H), 7.59 – 7.58 (m, 2H), 7.56 – 7.54 (m, 1H), 7.52 – 7.49 (m, 2H), 7.42 – 7.39 (m, 1H), 7.35 – 7.30 (m, 4H), 7.05 (t, *J* = 8.4 Hz, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.4, 165.8 (*J* = 255.5 Hz), 149.2, 135.8 (*J* = 2.85 Hz), 135.4, 133.5, 132.6, 132.3 (*J* = 9.8 Hz), 131.2, 130.6, 130.1, 128.9, 128.3, 121.1, 115.9 (*J* = 22.8 Hz), 110.7, 87.8. HRMS (ESI-TOF) (m/z): Calcd for $C_{29}H_{19}F_2NNaO_5S_2$, ($[M + Na]^+$), 586.0565, found 586.0575.



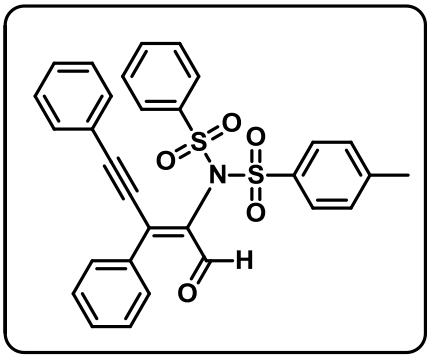
(*Z*)-4-chloro-*N*-((4-chlorophenyl)sulfonyl)-*N*-(1-oxo-3,5-diphenylpent-2-en-4-yn-2-yl)benzenesulfonamide 4c

Yellow solid (101.9 mg, 85%), mp. 225 – 226 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.61 (s, 1H), 8.04 (d, *J* = 8.4 Hz, 4H), 7.58 – 7.57 (m, 2H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 2H), 7.43 – 7.40 (m, 1H), 7.36 (d, *J* = 8.4 Hz, 4H), 7.33 – 7.32 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.3, 149.2, 140.8, 138.3, 135.3, 133.5, 132.6, 131.3, 130.7, 130.6, 130.2, 129.0, 128.9, 128.4, 121.1, 110.9, 87.8. HRMS (ESI-TOF) (m/z): Calcd for $C_{29}H_{19}Cl_2NNaO_5S_2$, ($[M + Na]^+$), 617.9974, found 617.9986.



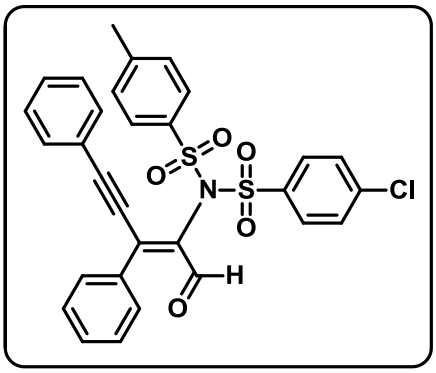
(*Z*)-4-(tert-butyl)-*N*-(1-oxo-3,5-diphenylpent-2-en-4-yn-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide 4d

Yellow solid (89.6 mg, 77%), mp. 123 – 124 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.62 (s, 1H), 8.11 – 8.10 (m, 2H), 8.05 – 8.03 (m, 2H), 7.62 – 7.59 (m, 2H), 7.56 – 7.53 (m, 1H), 7.52 – 7.48 (m, 3H), 7.44 – 7.40 (m, 4H), 7.38 – 7.34 (m, 3H), 7.28 (t, *J* = 7.2 Hz, 2H), 1.18 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.5, 157.7, 149.0, 140.1, 136.9, 135.6, 134.0, 133.7, 132.9, 131.0, 130.4, 130.2, 129.3, 129.2, 128.8, 128.6, 128.2, 125.8, 121.5, 110.5, 88.1, 35.1, 30.8. HRMS (ESI-TOF) (m/z): Calcd for $C_{33}H_{29}NNaO_5S_2$, ($[M + Na]^+$), 606.1379, found 606.1379.



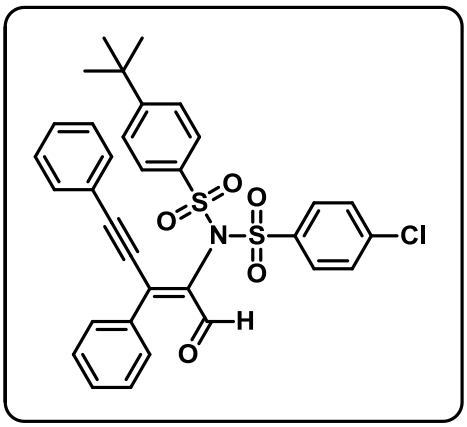
(*Z*)-4-methyl-*N*-(1-oxo-3,5-diphenylpent-2-en-4-yn-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide 4e

Yellow solid (84.8 mg, 78%), mp. 187 – 188 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.60 (s, 1H), 8.12 (d, *J* = 7.2 Hz, 2H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.60 – 7.59 (m, 2H), 7.56 – 7.53 (m, 1H), 7.51 – 7.47 (m, 3H), 7.43 – 7.41 (m, 2H), 7.39 – 7.36 (m, 1H), 7.33 – 7.31 (m, 2H), 7.30 – 7.27 (m, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 2.23 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.4, 149.0, 145.0, 140.1, 137.0, 135.7, 133.9, 133.7, 132.8, 131.0, 130.3, 130.2, 129.4, 129.3, 128.8, 128.6, 128.1, 121.5, 110.4, 88.1, 21.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{30}H_{23}NNaO_5S_2$, ($[M + Na]^+$), 564.0910, found 564.0920.



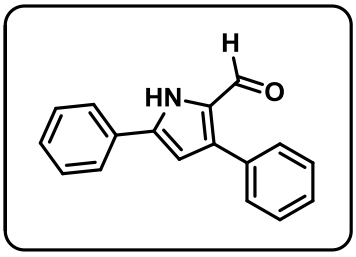
(*Z*)-4-chloro-*N*-(1-oxo-3,5-diphenylpent-2-en-4-yn-2-yl)-*N*-tosylbenzenesulfonamide 4f

Yellow solid (94.9 mg, 82%), mp. 224 – 225 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.60 (s, 1H), 8.05 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.60 – 7.58 (m, 2H), 7.56 – 7.53 (m, 1H), 7.51 – 7.49 (m, 2H), 7.40 – 7.38 (m, 1H), 7.38 – 7.35 (m, 2H), 7.33 – 7.29 (m, 4H), 7.17 (d, *J* = 7.8 Hz, 2H), 2.23 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.41, 149.0, 145.2, 140.5, 138.6, 136.8, 135.6, 133.7, 132.7, 131.1, 130.8, 130.4, 130.2, 129.4, 129.3, 128.9, 128.8, 128.2, 121.3, 110.5, 87.9, 21.5. HRMS (ESI-TOF) (m/z): Calcd for $C_{30}H_{22}ClNNaO_5S_2$, ($[M + Na]^+$), 598.0520, found 598.0539.



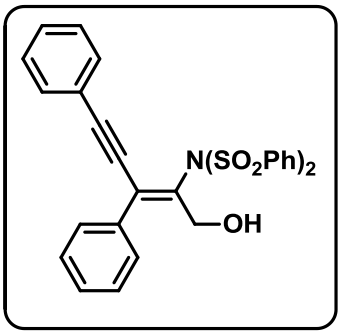
(*Z*)-4-(tert-butyl)-*N*-((4-chlorophenyl)sulfonyl)-*N*-(1-oxo-3,5-diphenylpent-2-en-4-yn-2-yl)benzenesulfonamide 4g

Yellow solid (98.3 mg, 80%), mp. 192 – 193 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.62 (s, 1H), 8.05 (d, *J* = 8.4 Hz, 2H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.61 – 7.59 (m, 2H), 7.57 – 7.54 (m, 1H), 7.52 – 7.50 (m, 2H), 7.42 – 7.39 (m, 2H), 7.38 – 7.36 (m, 4H), 7.35 – 7.34 (m, 1H), 7.31 – 7.29 (m, 2H), 1.17 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.5, 157.9, 149.1, 140.5, 138.6, 136.7, 135.5, 133.8, 132.8, 131.1, 130.8, 130.5, 130.2, 129.2, 128.9, 128.8, 128.3, 125.8, 121.3, 110.6, 87.9, 35.1, 30.8. HRMS (ESI-TOF) (m/z): Calcd for $C_{33}H_{28}ClNNaO_5S_2$, ($[M + Na]^+$), 640.0990, found 640.1007.



3,5-diphenyl-1*H*-pyrrole-2-carbaldehyde 5

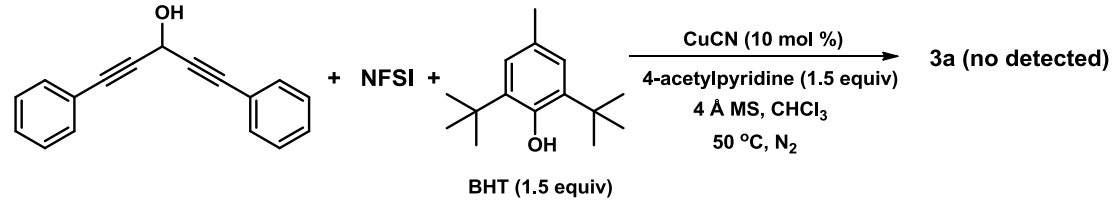
White solid (21.0 mg, 42%), mp. 154 – 155 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.67 (s, 1H), 9.64 (s, 1H), 7.67 – 7.65 (m, 2H), 7.56 – 7.55 (m, 2H), 7.48 – 7.45 (m, 4H), 7.42 – 7.37 (m, 2H), 6.73 (d, *J* = 2.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 179.3, 138.8, 138.2, 133.5, 130.4, 129.2, 129.1, 129.0, 128.8, 128.0, 125.2, 109.0. HRMS (ESI-TOF) (m/z): Calcd for $C_{17}H_{13}NNaO$, ($[M + Na]^+$), 270.0889, found 270.0896.

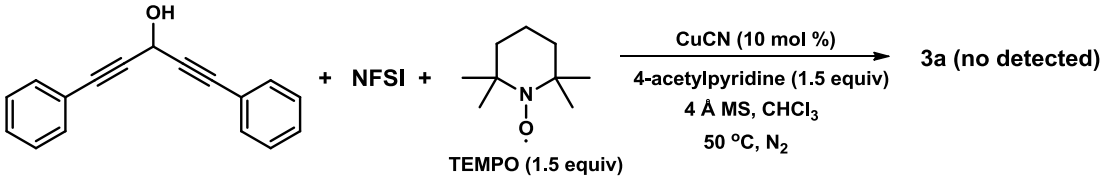


(*Z*)-*N*-(1-hydroxy-3,5-diphenylpent-2-en-4-yn-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide 6

Yellow solid (79.2 mg, 75%), mp. 111 – 112 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.8 Hz, 4H), 7.57 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.43 – 7.38 (m, 7H), 7.32 – 7.28 (m, 1H), 7.25 (t, *J* = 4.8 Hz, 4H), 4.33 (d, *J* = 2.4 Hz, 2H), 2.96 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.8, 136.7, 136.2, 136.1, 133.9, 132.2, 129.2, 129.1, 129.0, 128.8, 128.7, 128.5, 127.9, 122.4, 98.6, 87.4, 62.6. HRMS (ESI-TOF) (m/z): Calcd for $C_{29}H_{23}NNaO_5S_2$, ($[M + Na]^+$), 552.0910, found 552.0899.

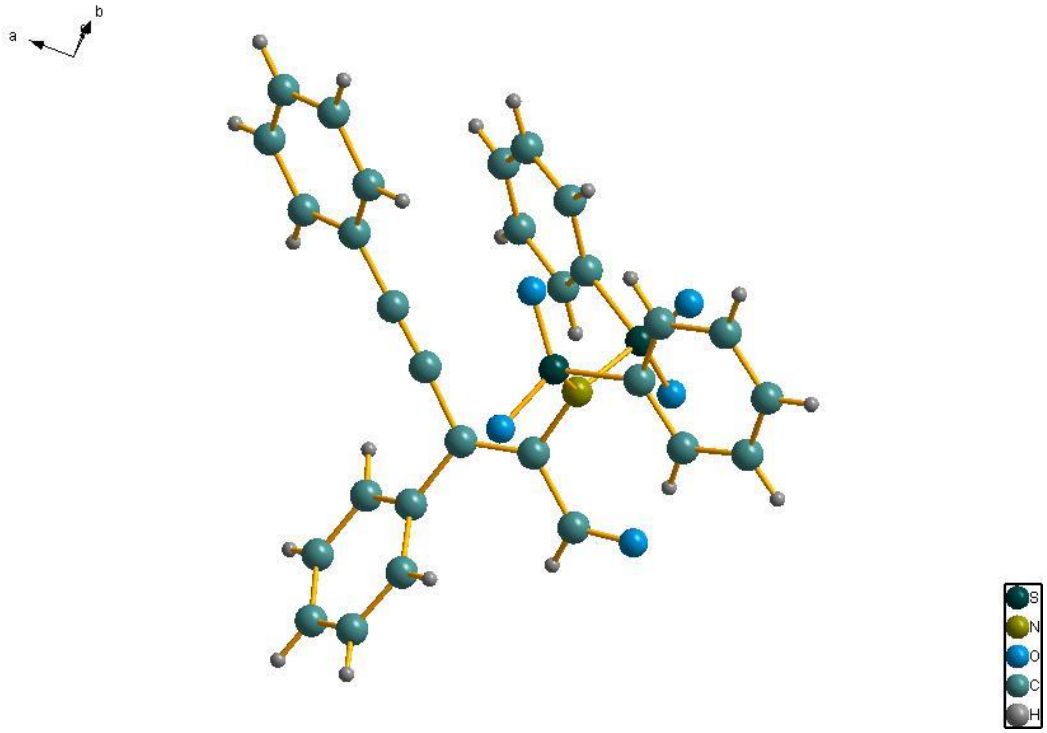
IV. The Radical Scavenger Experiments





In a nitrogen-filled glove-box, a flame dried screw-cap reaction tube equipped with a magnetic stir bar was charged with **1a** (0.2 mmol, 46.4 mg), CuCN (0.02 mmol, 1.8 mg), anhydrous $CHCl_3$ (2 mL), 4-acetylpyridine (0.30 mmol, 33 μL), NFSI (0.4 mmol, 126.0 mg), BHT (0.3mmol, 66.0mg) or 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 46.9 mg) and 4Å molecular sieve (0.2 g). The test tube was then sealed off with a screw-cap and removed from the glove-box, and the reaction mixture was stirred at 50 ℃ for 8.0 h. After the reaction finished, monitored by TLC, we found that the reaction of **1a** and NFSI was completely suppressed and no desired **3a** was observed.

V. X-ray Crystal Diffraction Data for 3a

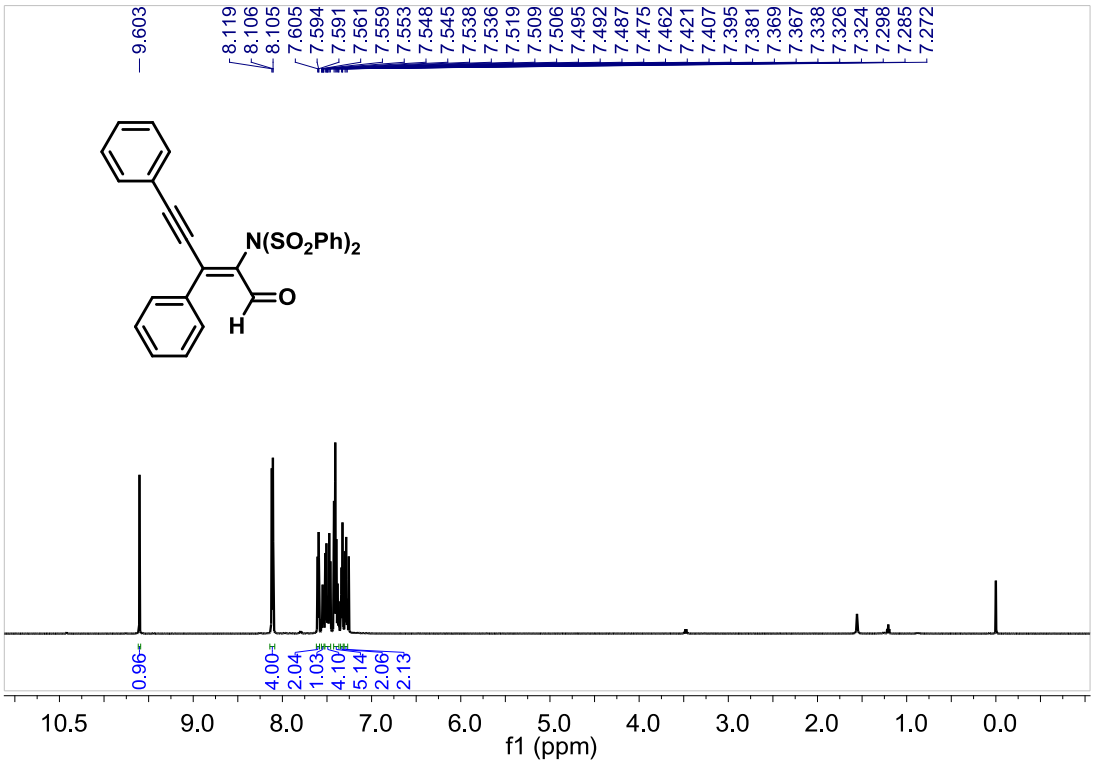


CCDC	1562685
Empirical formula, Formula weight	$C_{29}H_{21}NO_5S_2$, 527.59
Temperature, Wavelength	293(2) K, 0.71073 Å
Crystal system, space group	Monoclinic, P 1 21/n 1
Unit cell dimensions	a = 14.152 Å alpha = 90 deg. b = 11.196 Å beta = 96.74 deg. c = 16.264 Å gamma = 90 deg.
Volume	2559.2 Å ^3
Z, Calculated density	4, 1.369 Mg/m^3
Absorption coefficient	0.249 mm^-1
F(000)	1096
Theta range for data collection	3.30 to 25.00 deg.
Reflections collected / unique	9201 / 4476 [R(int) = 0.0384]
Completeness to theta = 25.00	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.75535
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4476 / 0 / 334
Goodness-of-fit on F^2	1.016
Final R indices [I>2sigma(I)]	R_1 = 0.0573, wR_2 = 0.1581
R indices (all data)	R_1 = 0.0791, wR_2 = 0.1753
Largest diff. peak and hole	0.273 and -0.336 e.Å ^-3

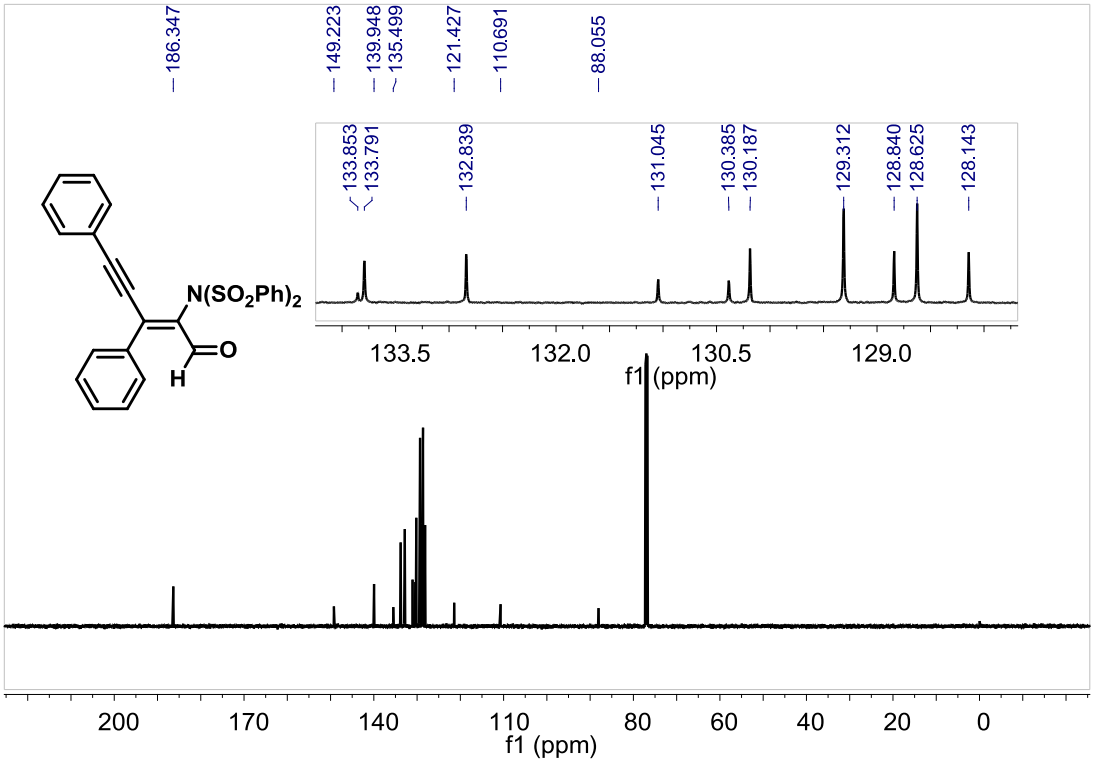
VI. References

1. Wang, T.; Shi, S.; Hansmann, M. M.; Rettenmeier, E.; Rudolph, M.; and Hashmi A. S. K. *Angew. Chem. Int. Ed.* **2014**, *53*, 3715 - 3719.
2. Frimpong, K.; Wzorek, J.; Lawlor, C.; Spencer, K.; and Mitzel T. *J. Org. Chem.* **2009**, *74*, 5861 - 5870

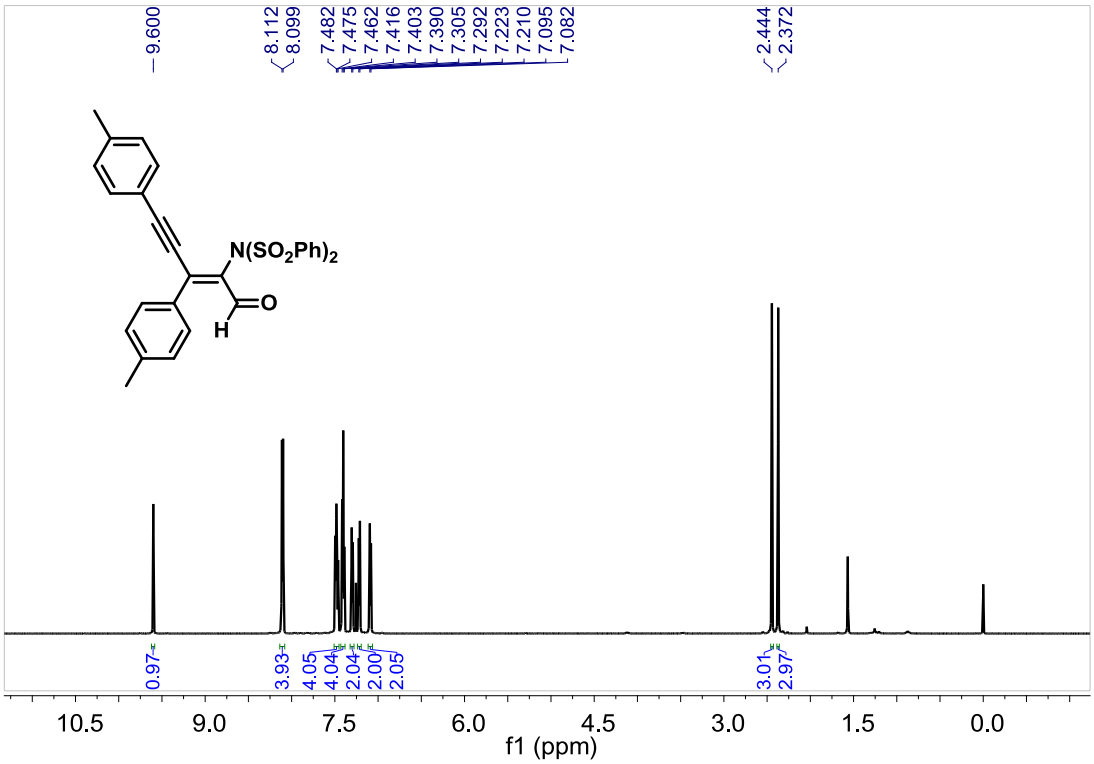
VII. ^{1}H, ^{13}C NMR Spectra of New Compounds.



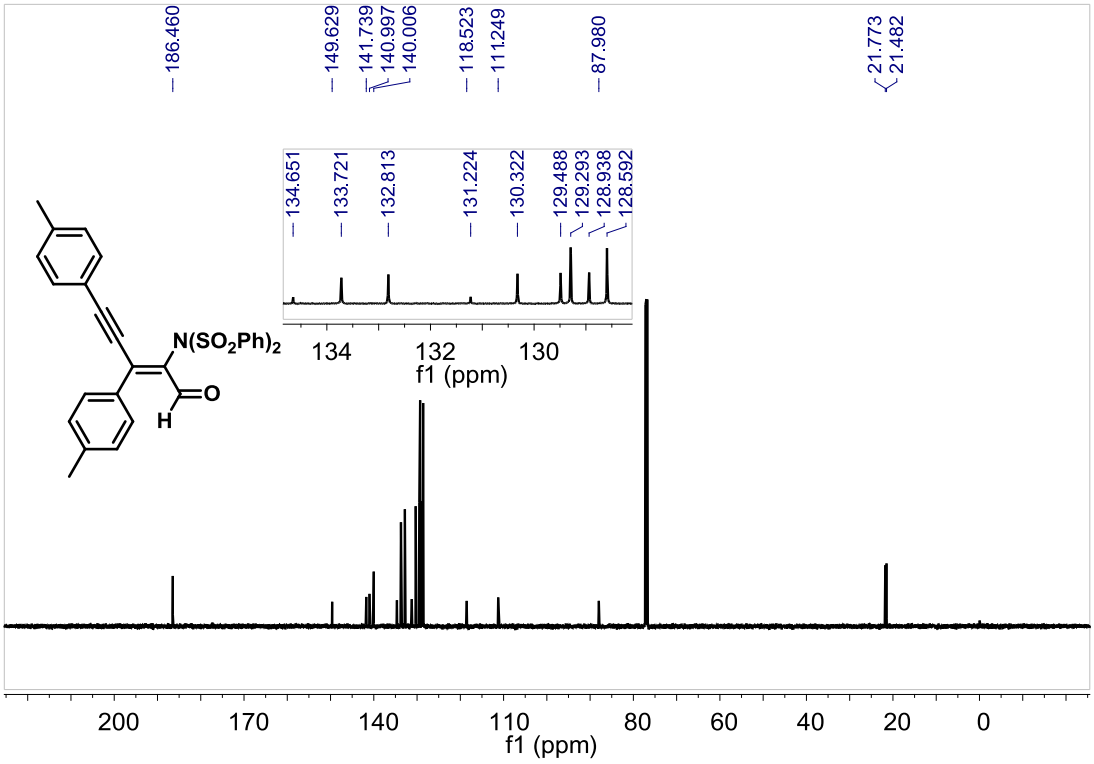
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3a.



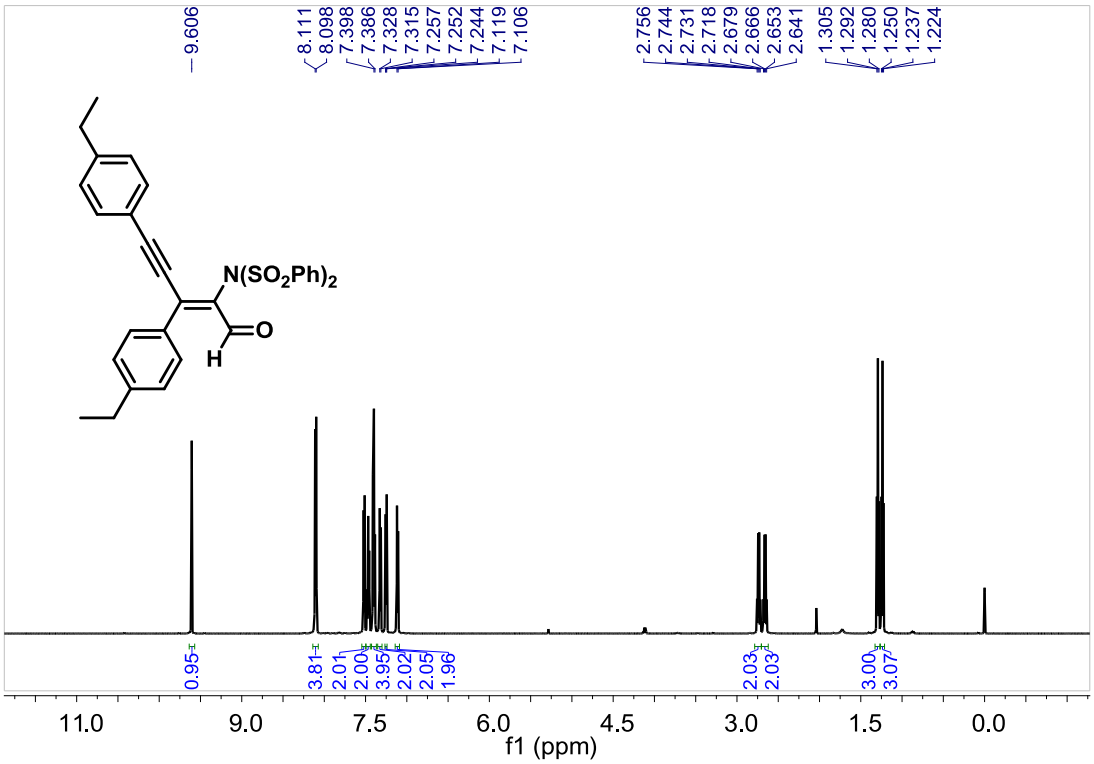
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3a.



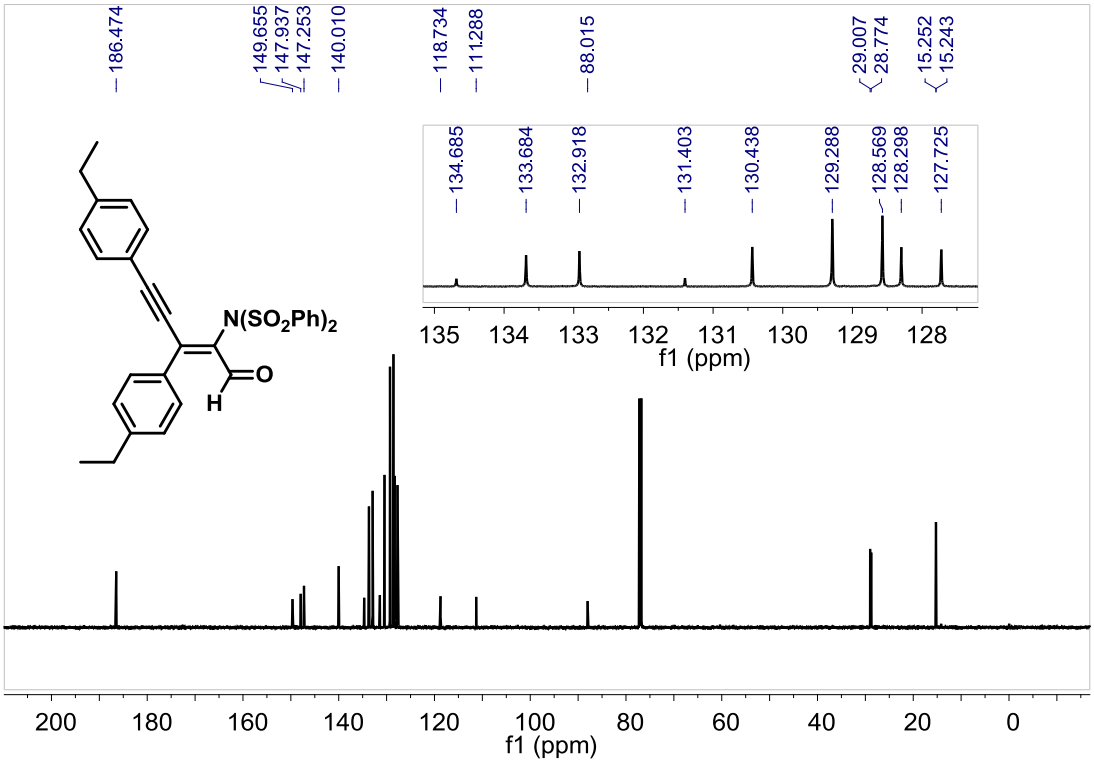
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3b.



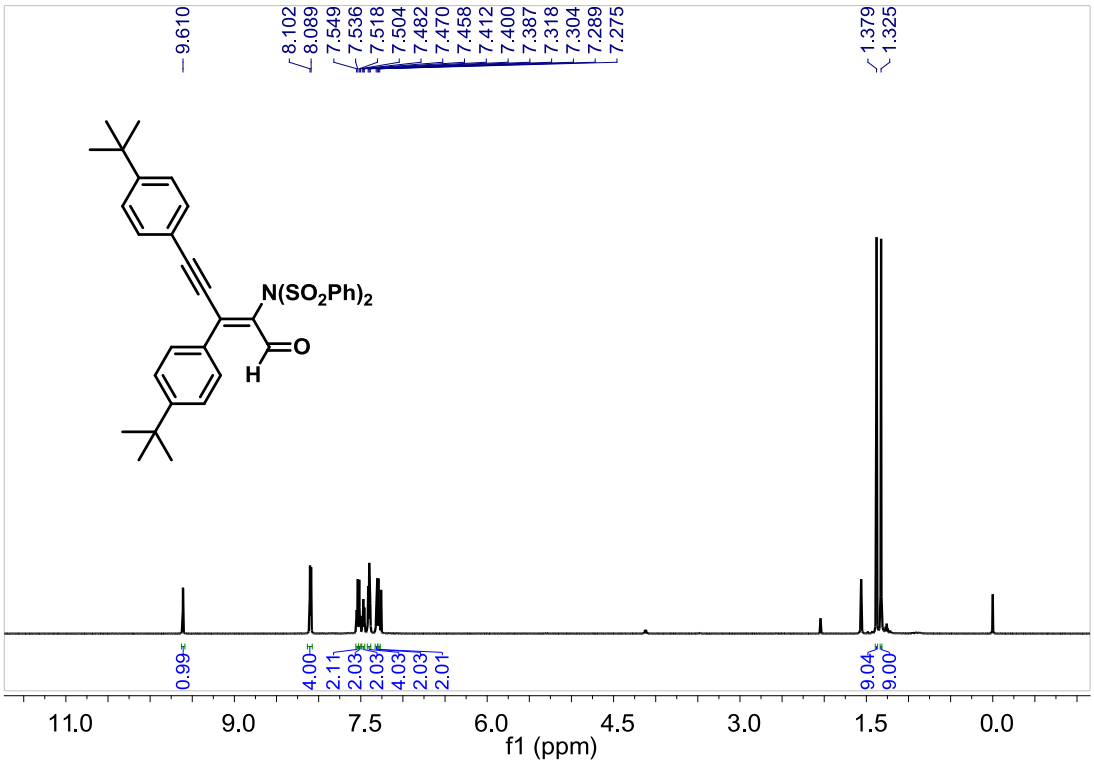
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3b.



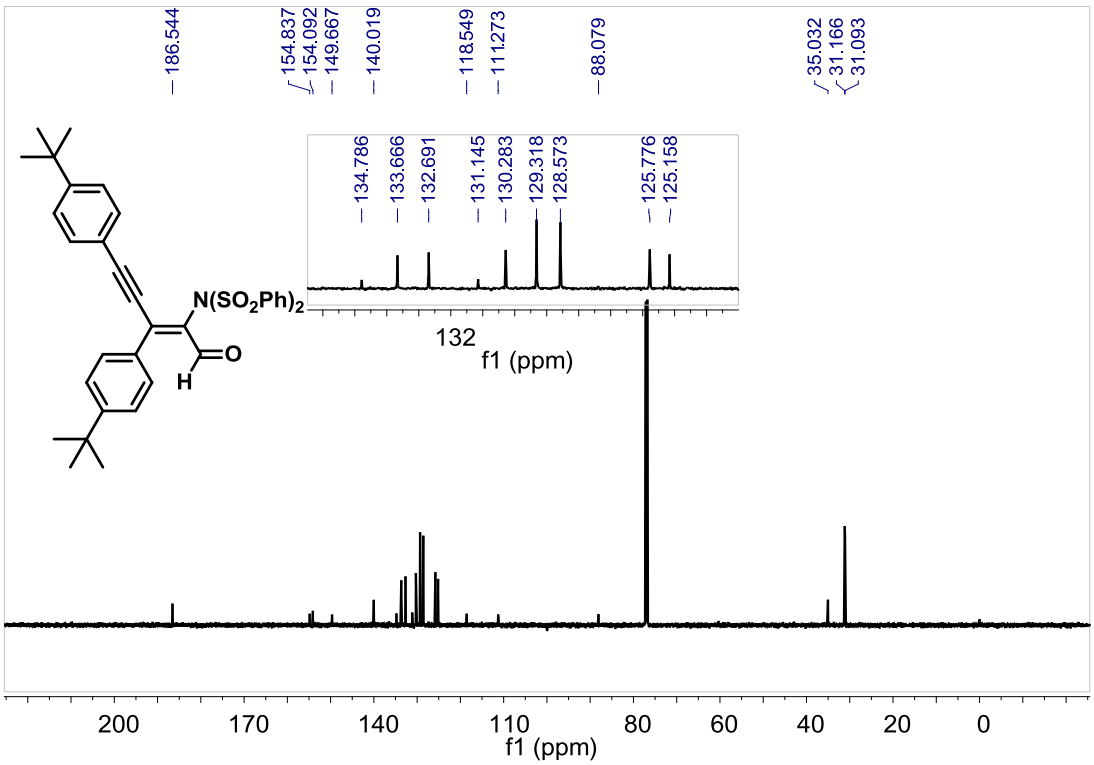
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3c.



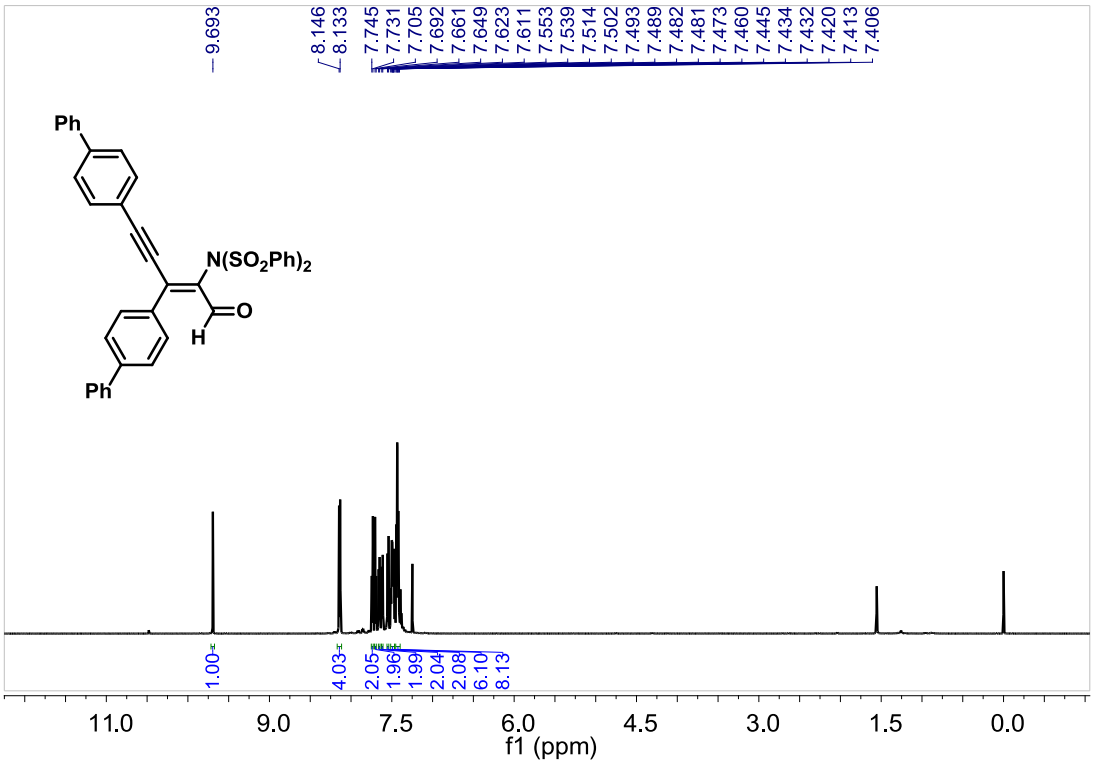
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3c.



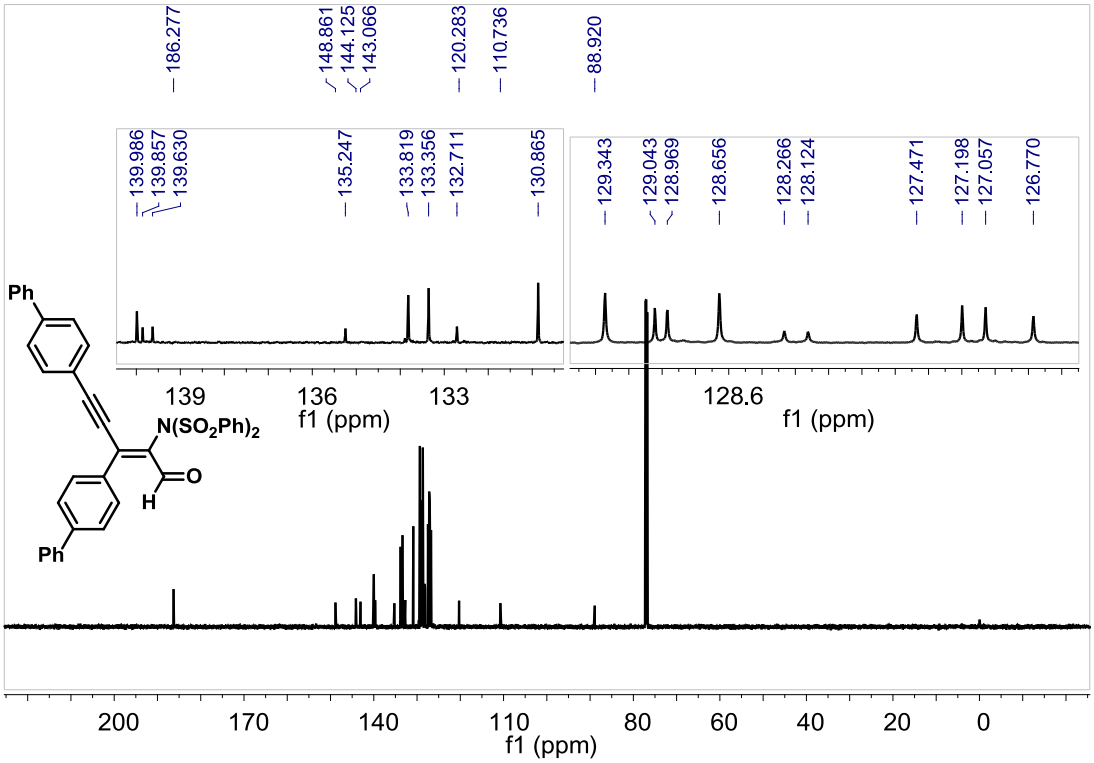
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3d.



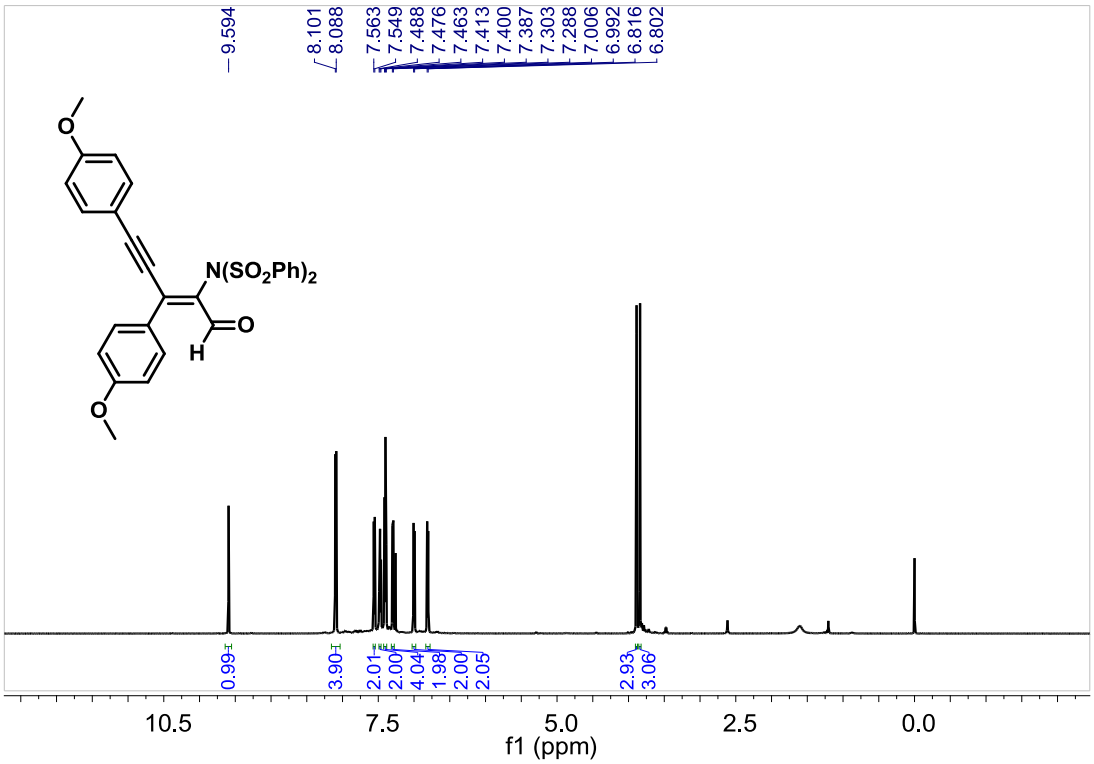
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3d.



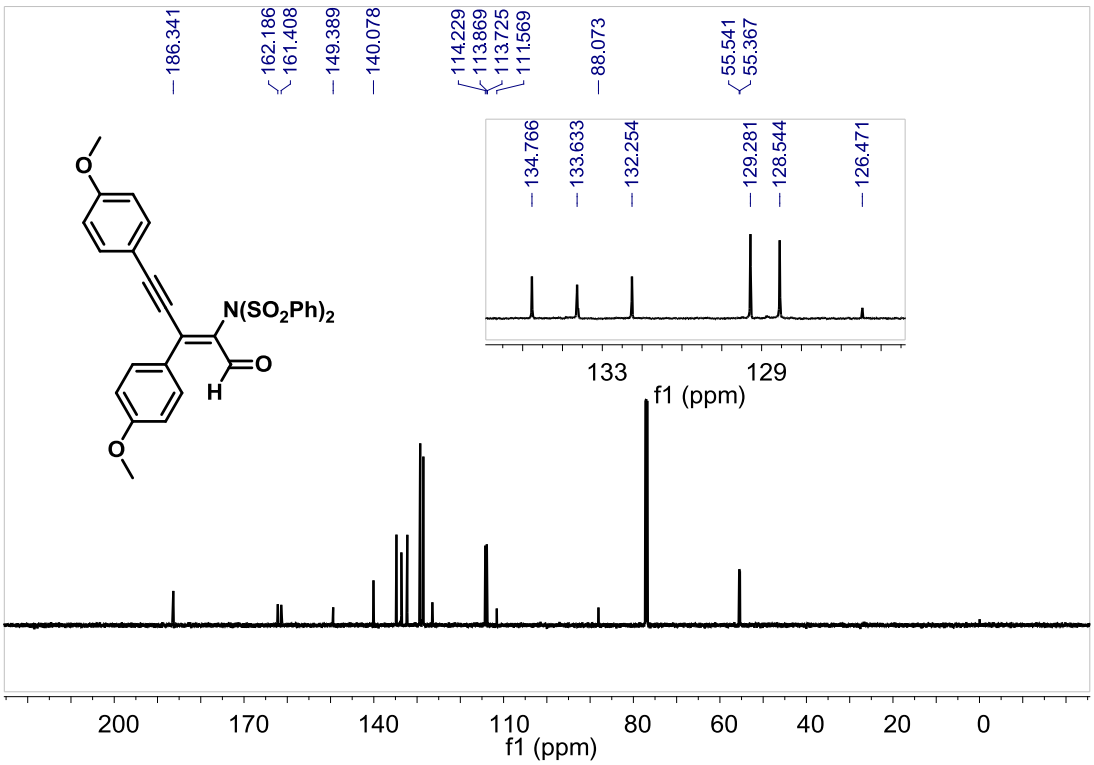
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3e.



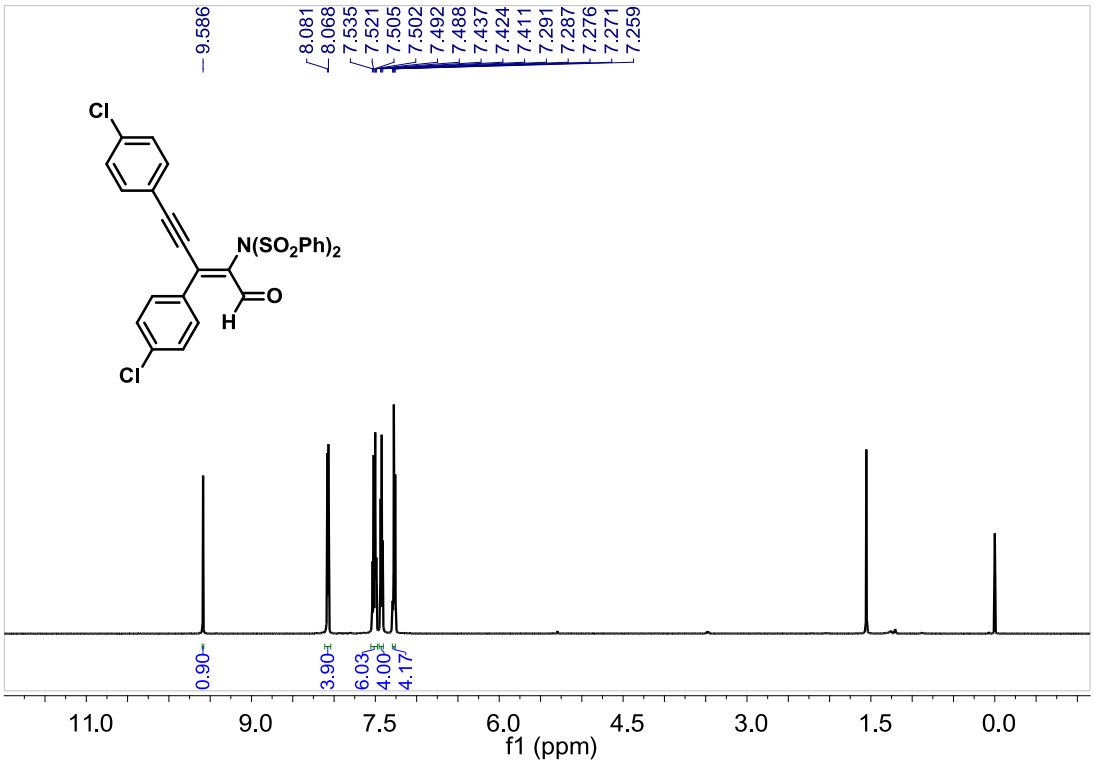
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3e.



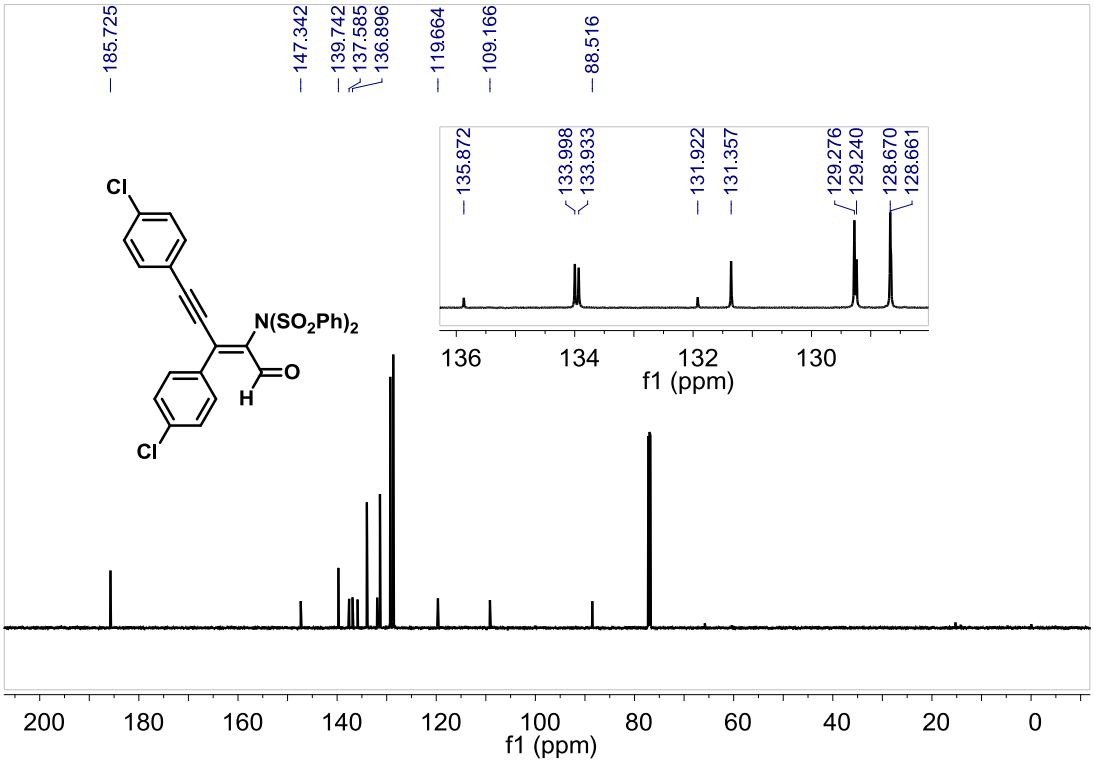
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3f.



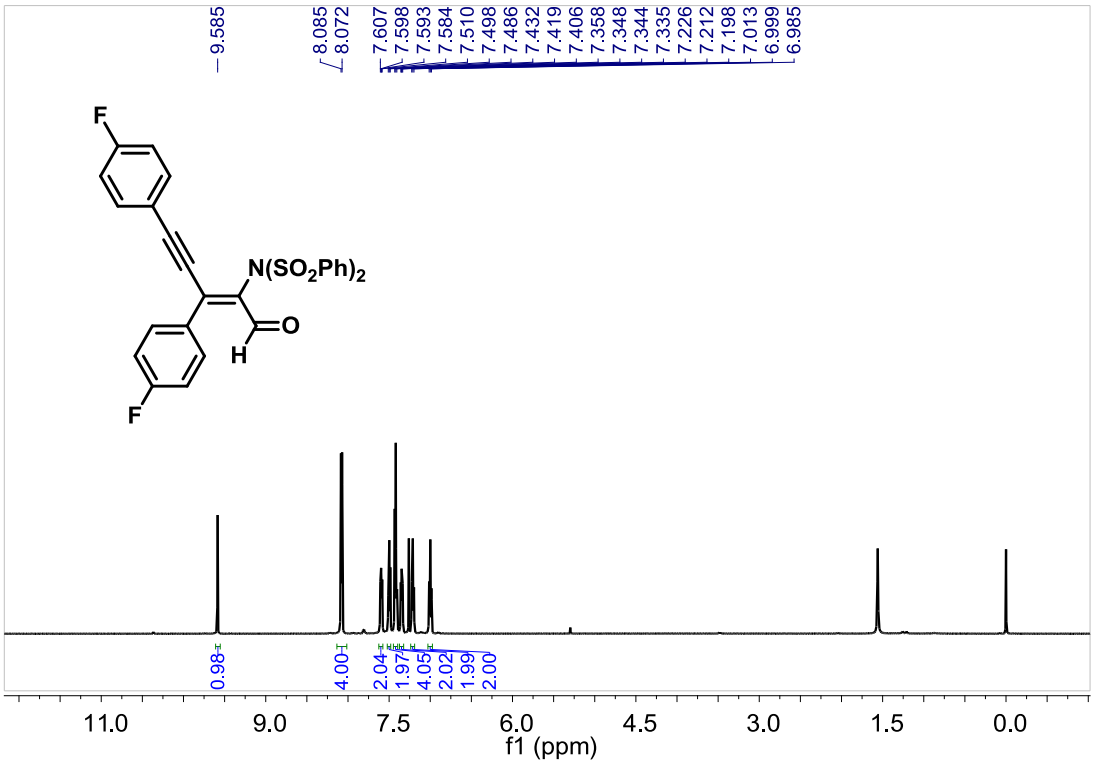
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3f.



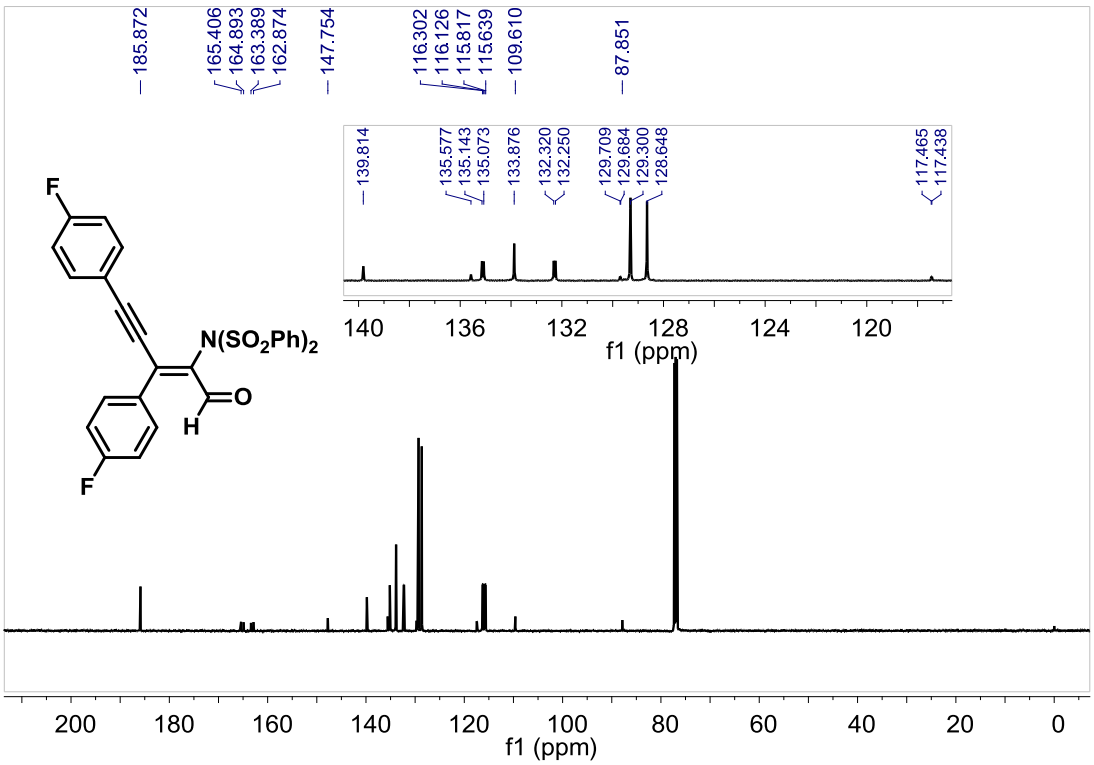
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3g.



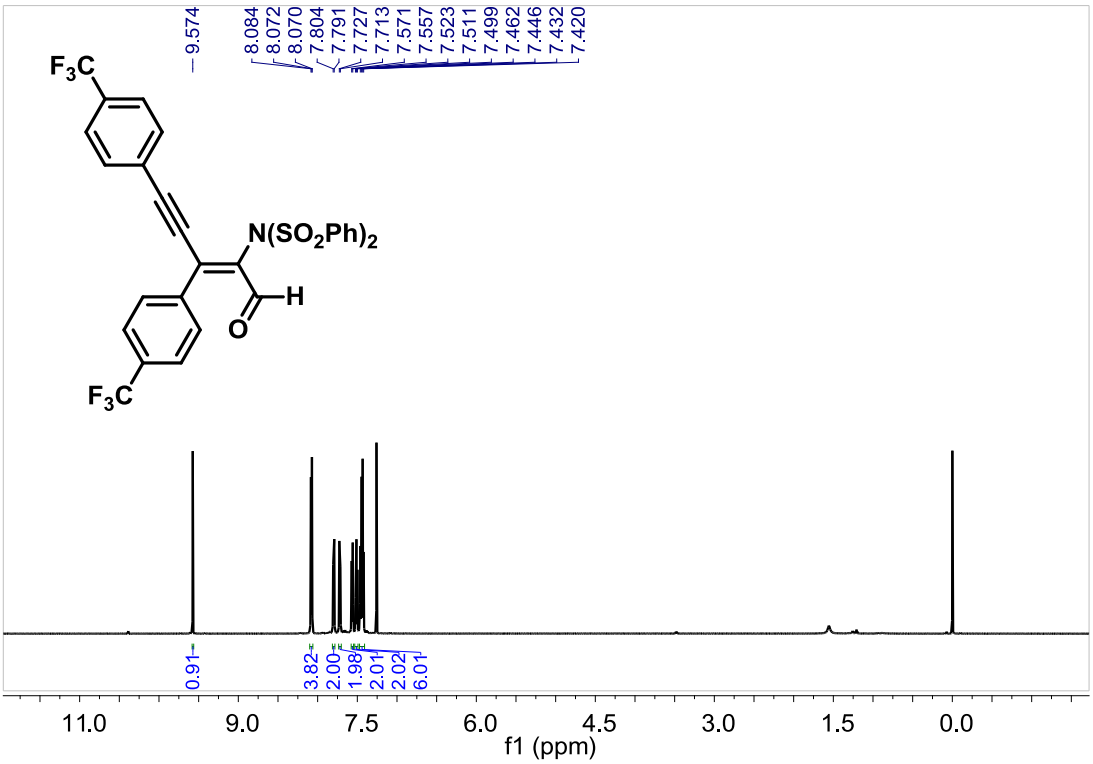
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3g.



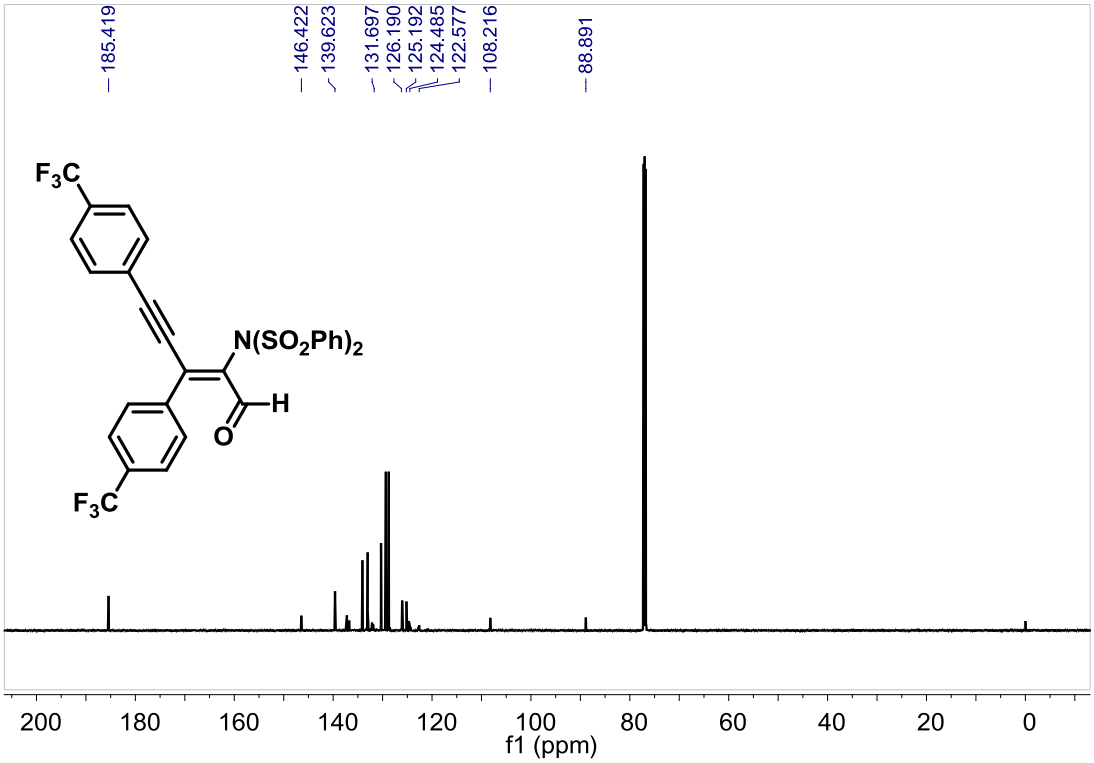
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3h.



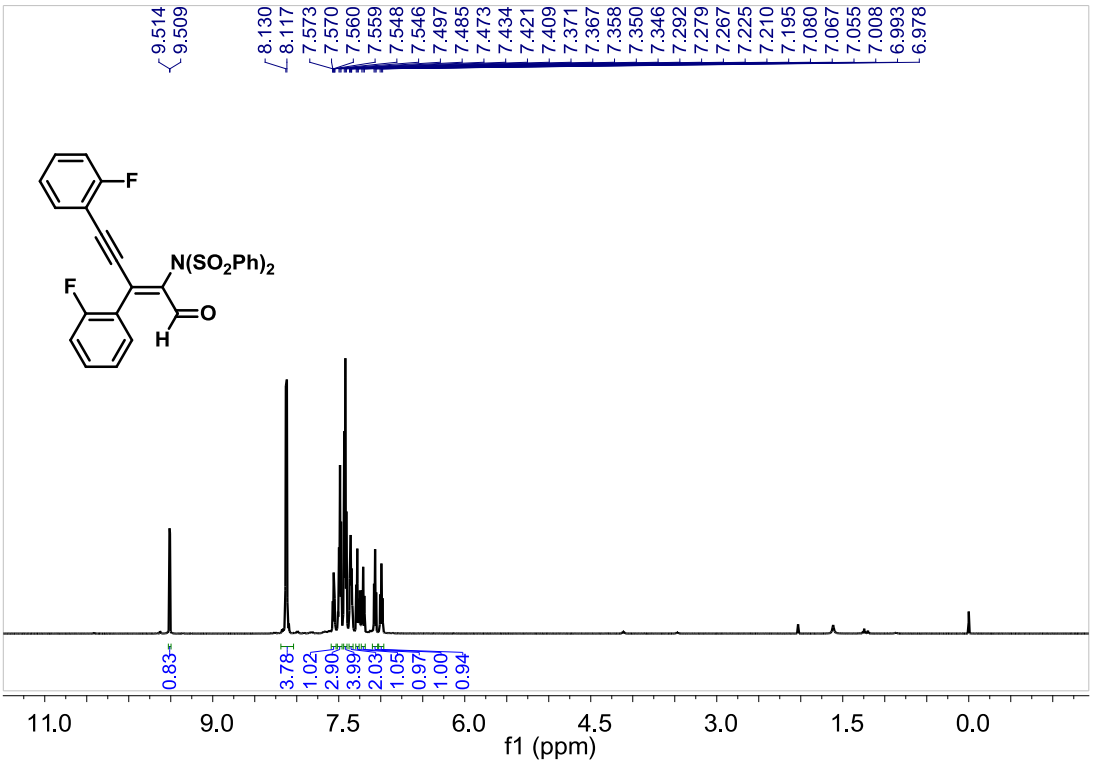
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3h.



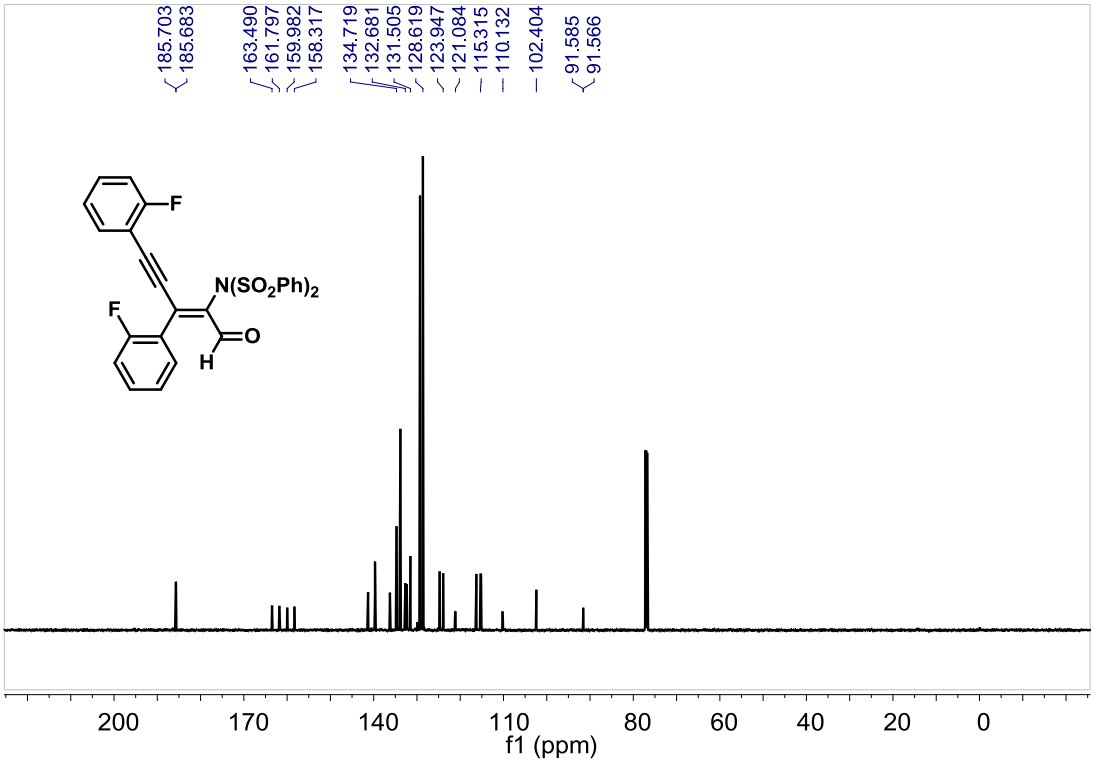
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3i.



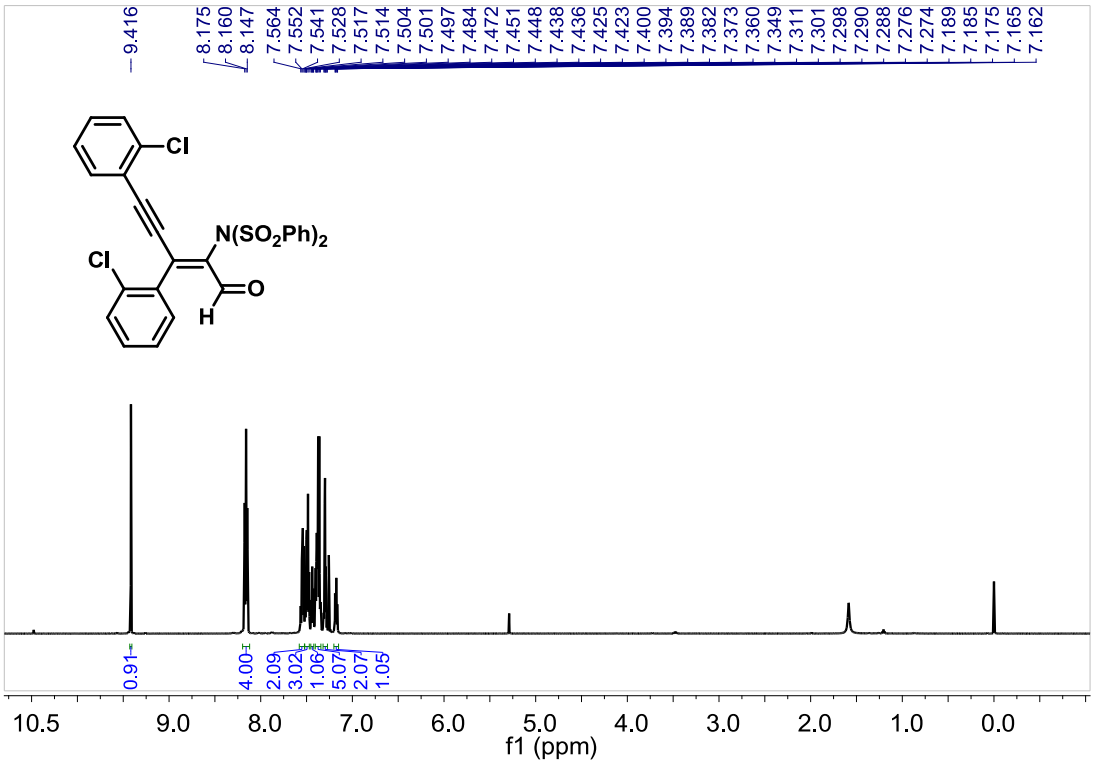
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3i.



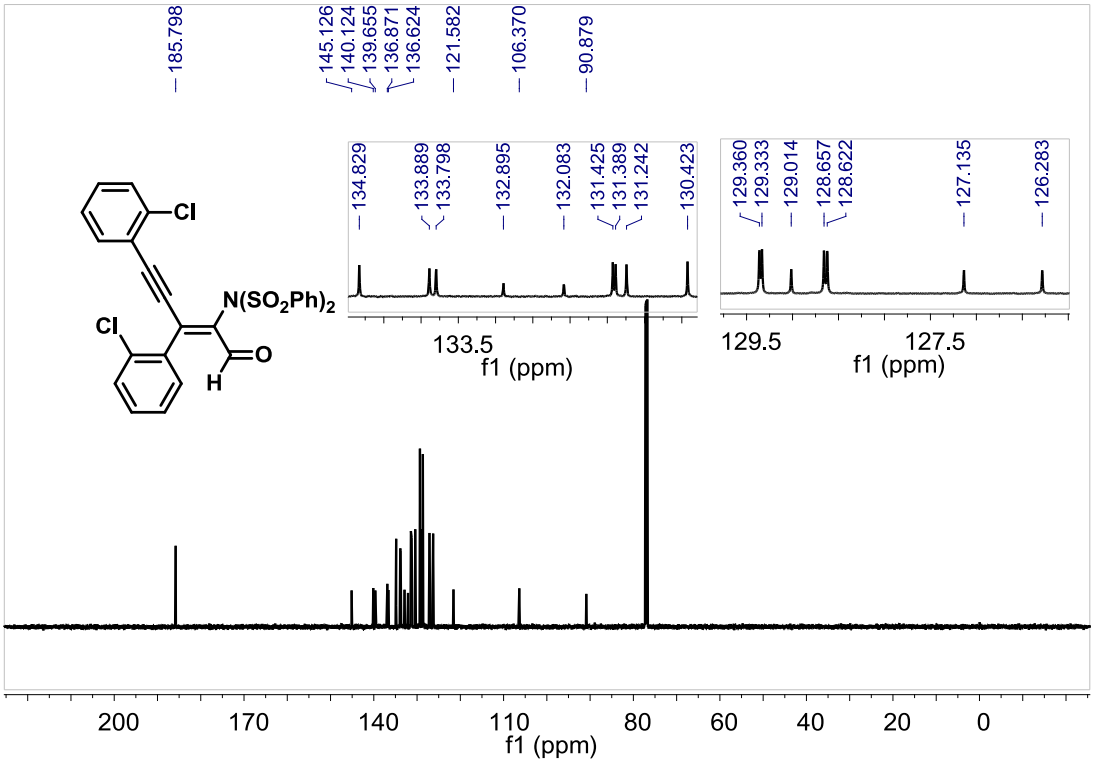
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3j.



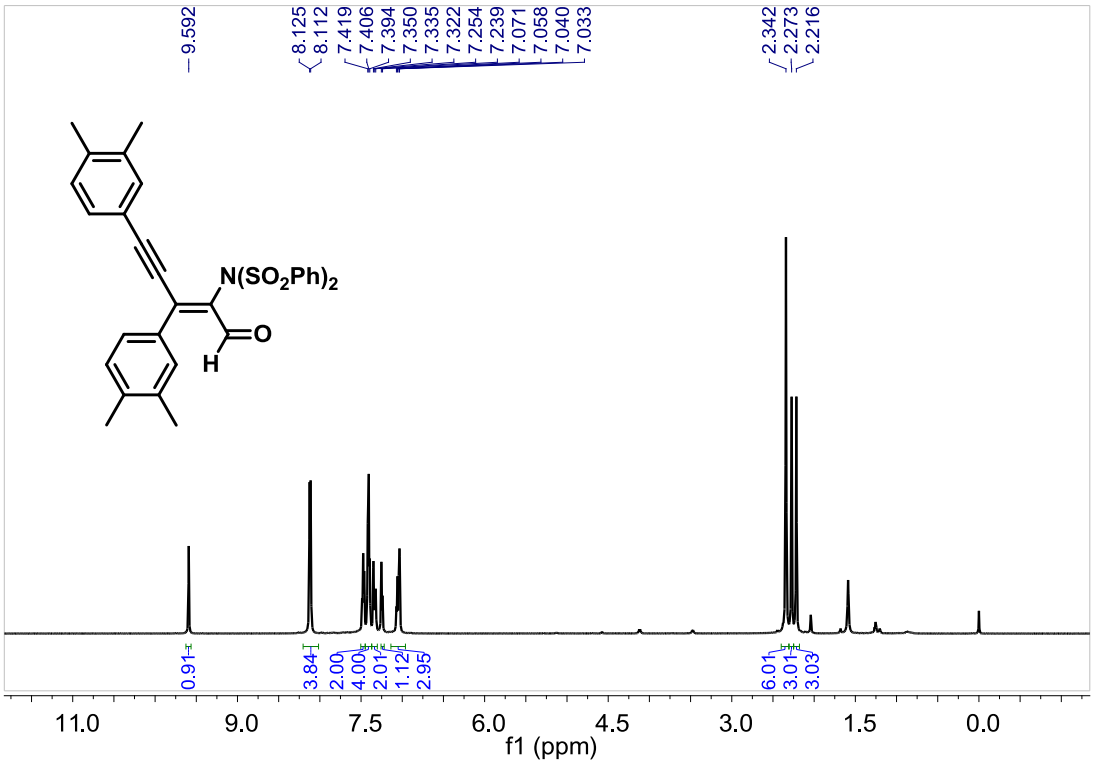
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3j.



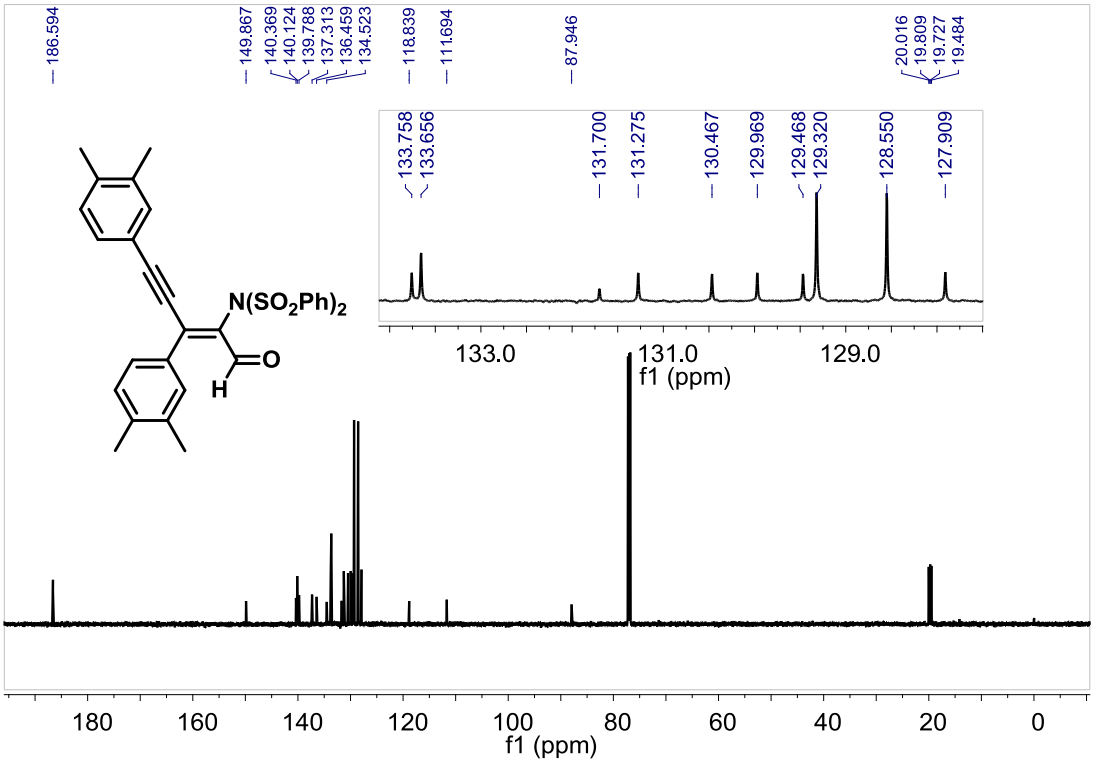
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3k.



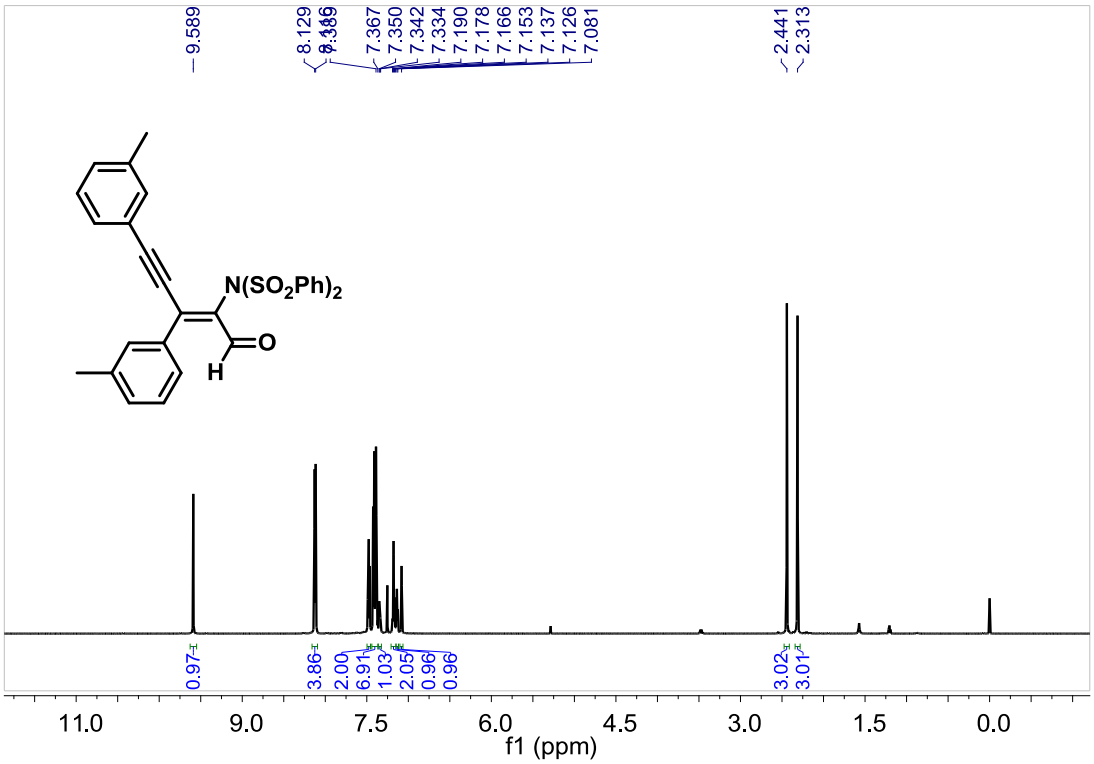
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3k.



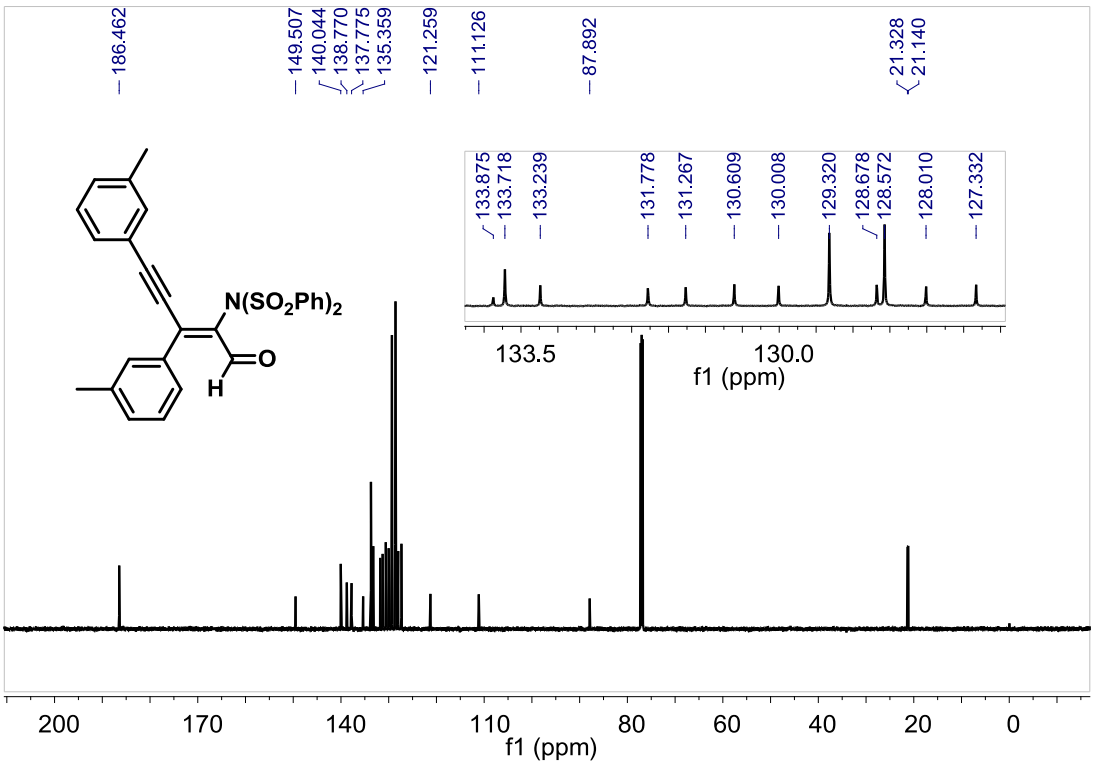
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3l.



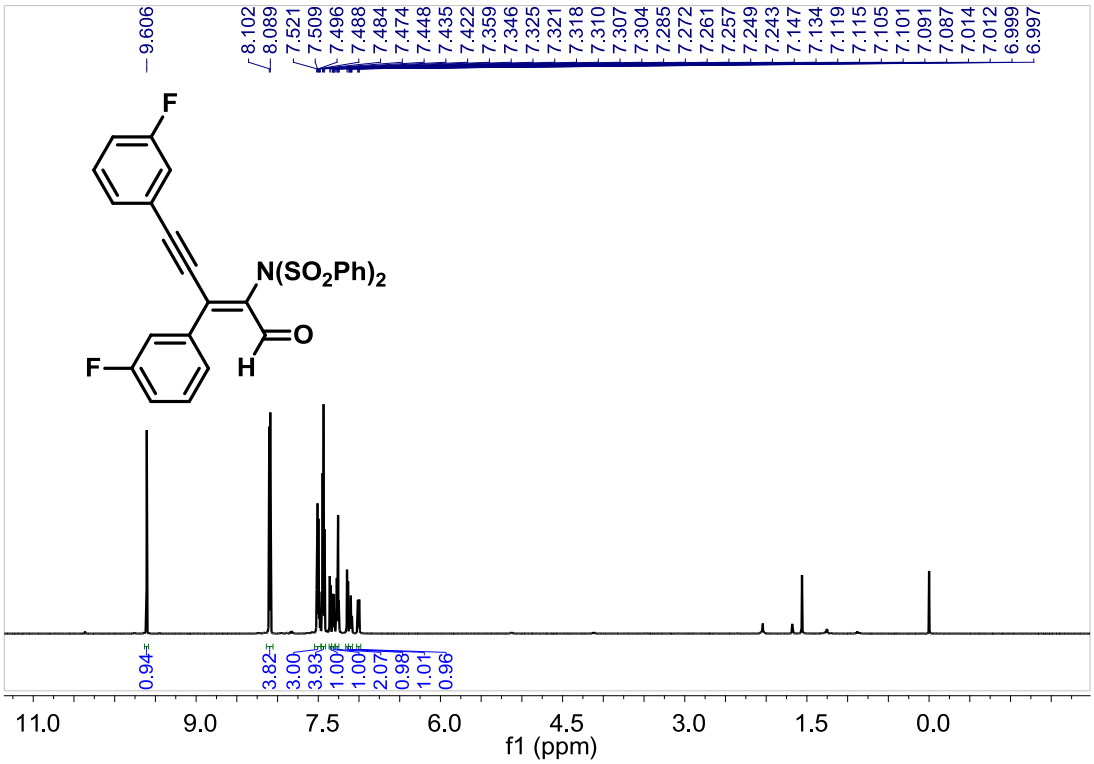
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3l.



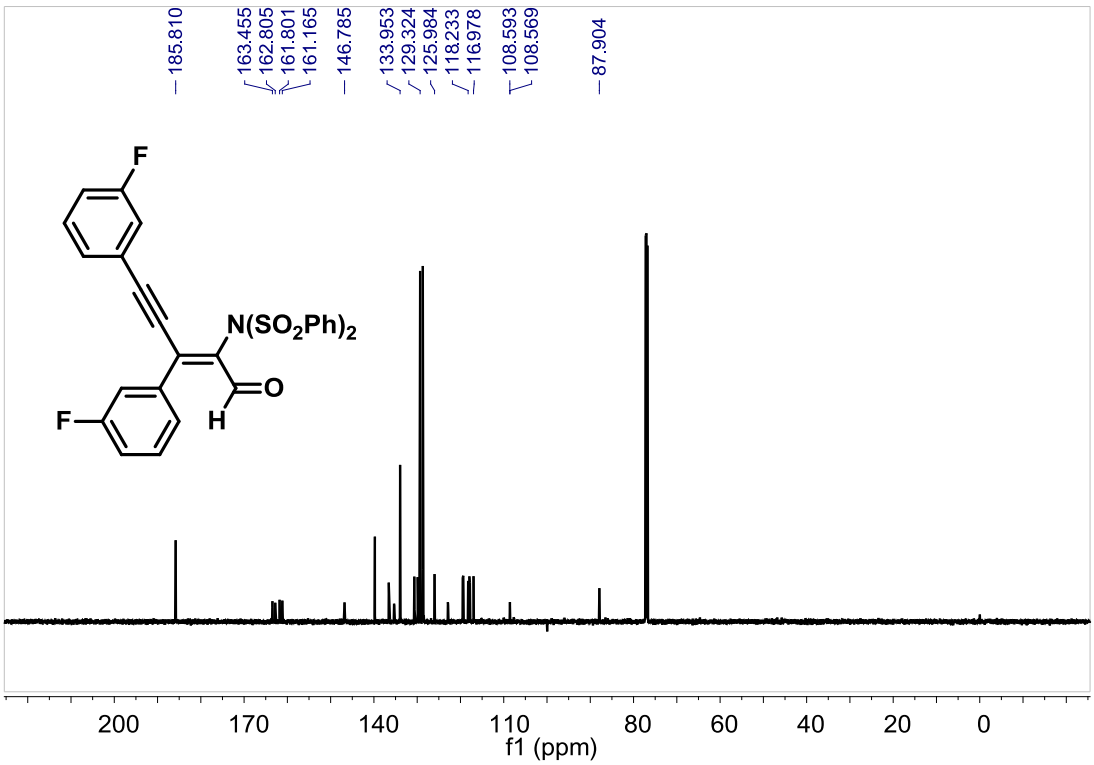
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3m.



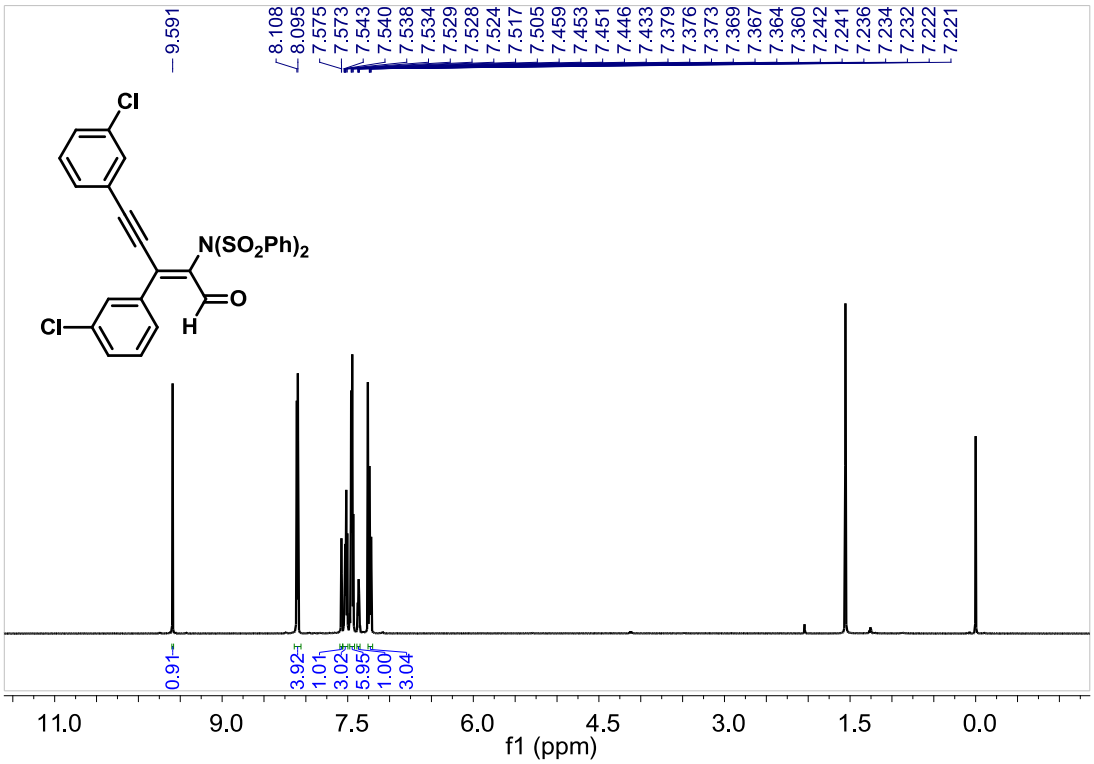
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3m.



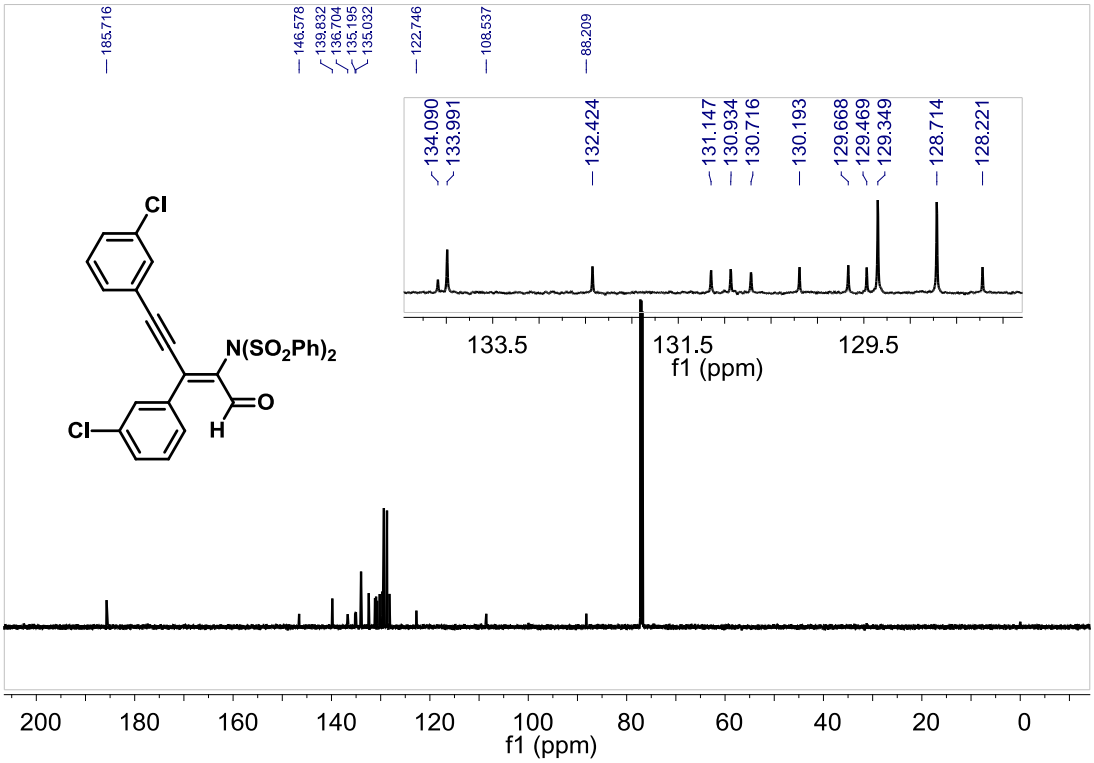
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3n.



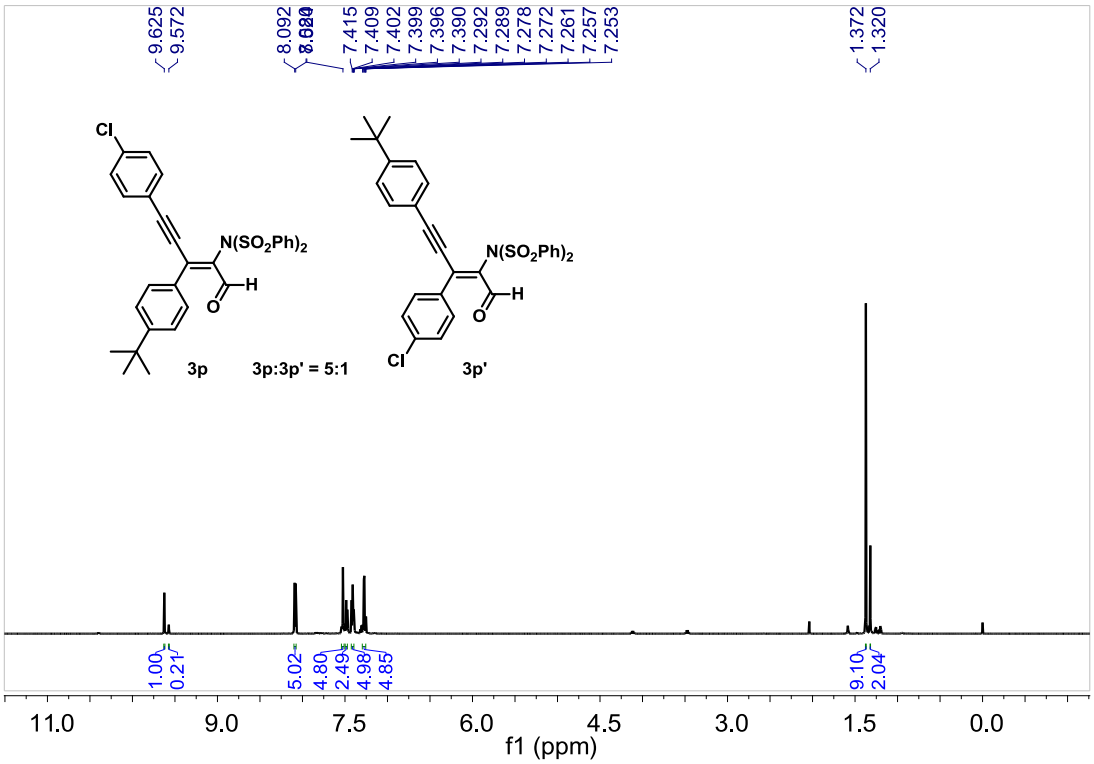
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3n.



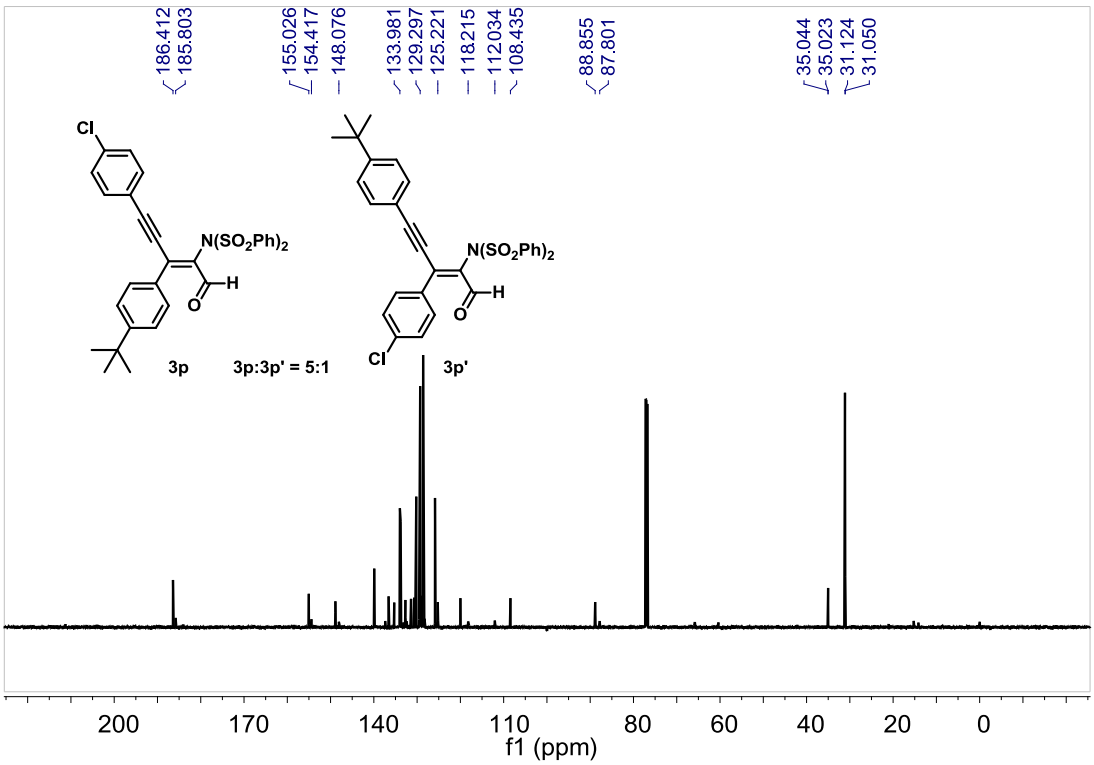
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3o.



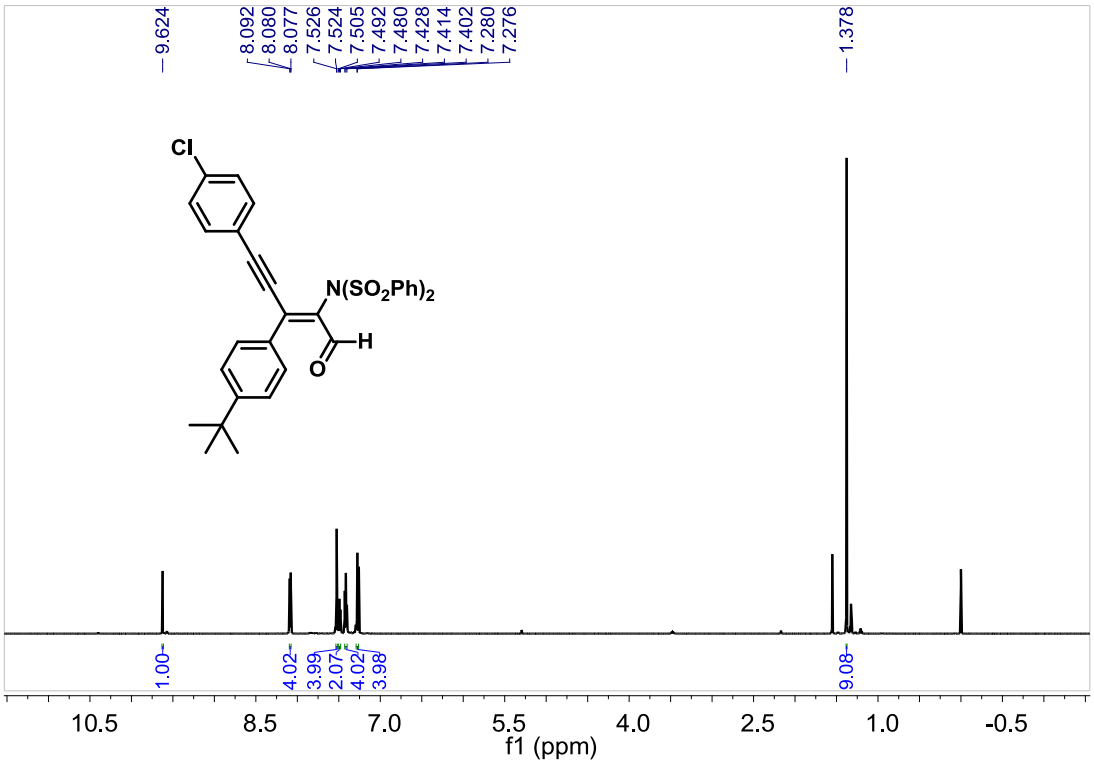
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3o.



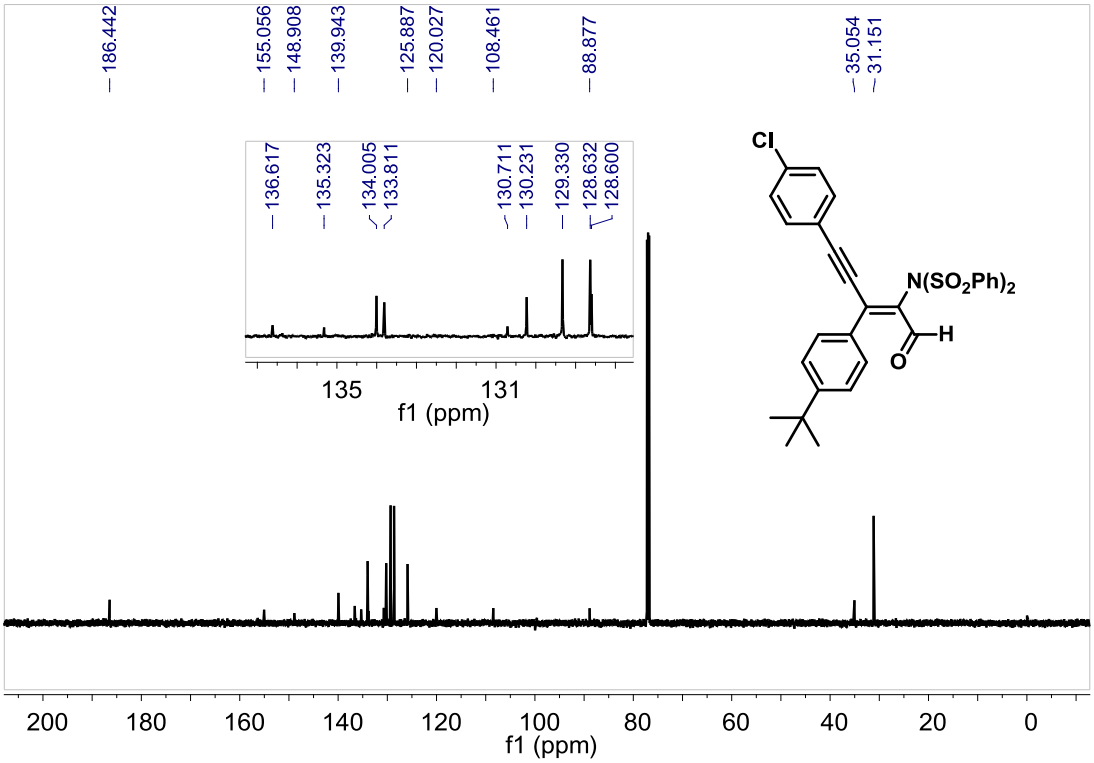
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3p + 3p'.



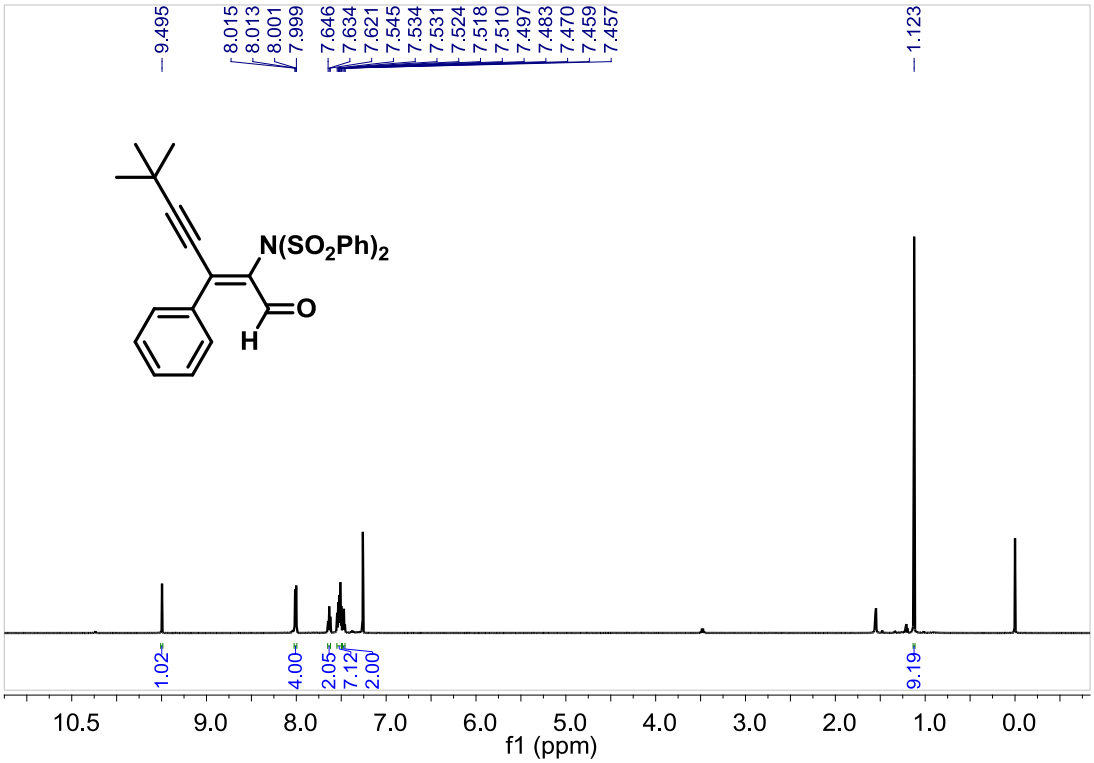
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3p + 3p'.



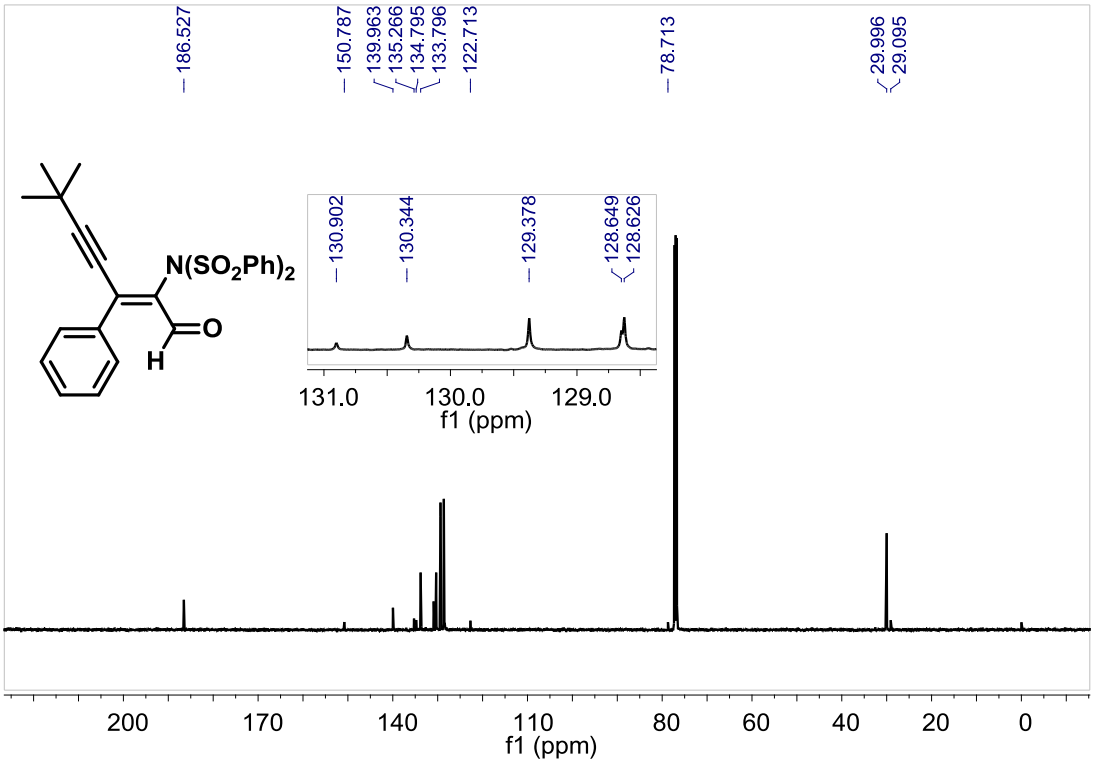
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3p.



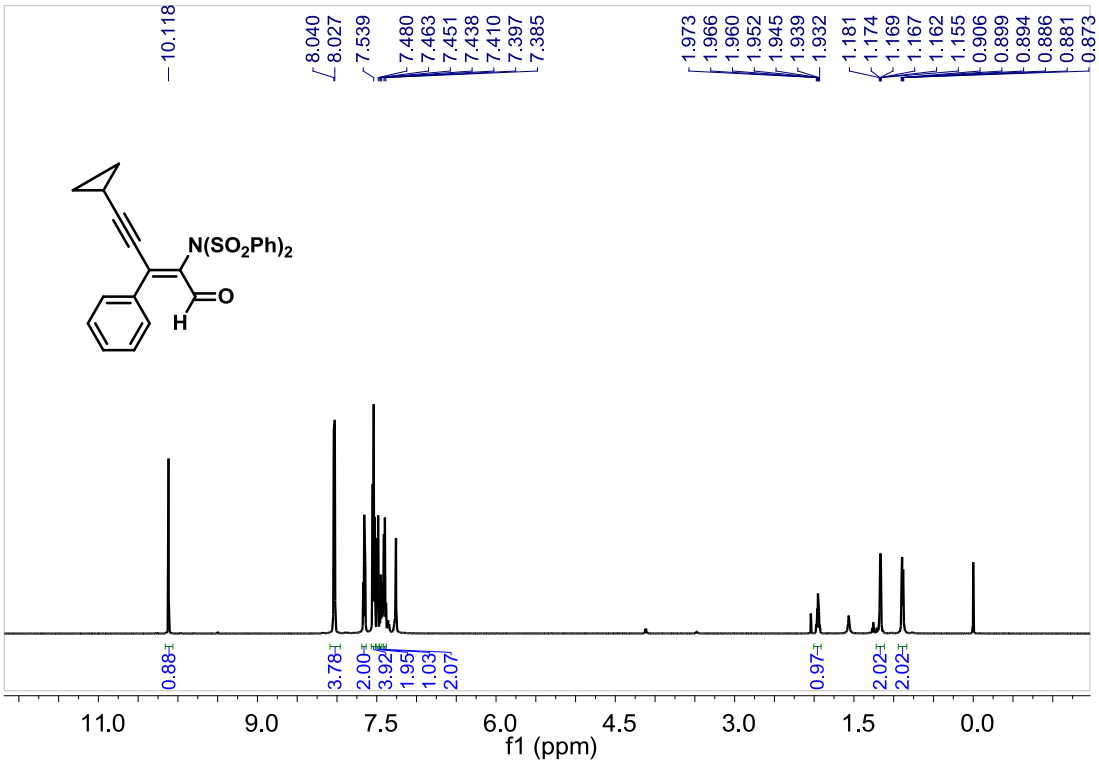
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3p.



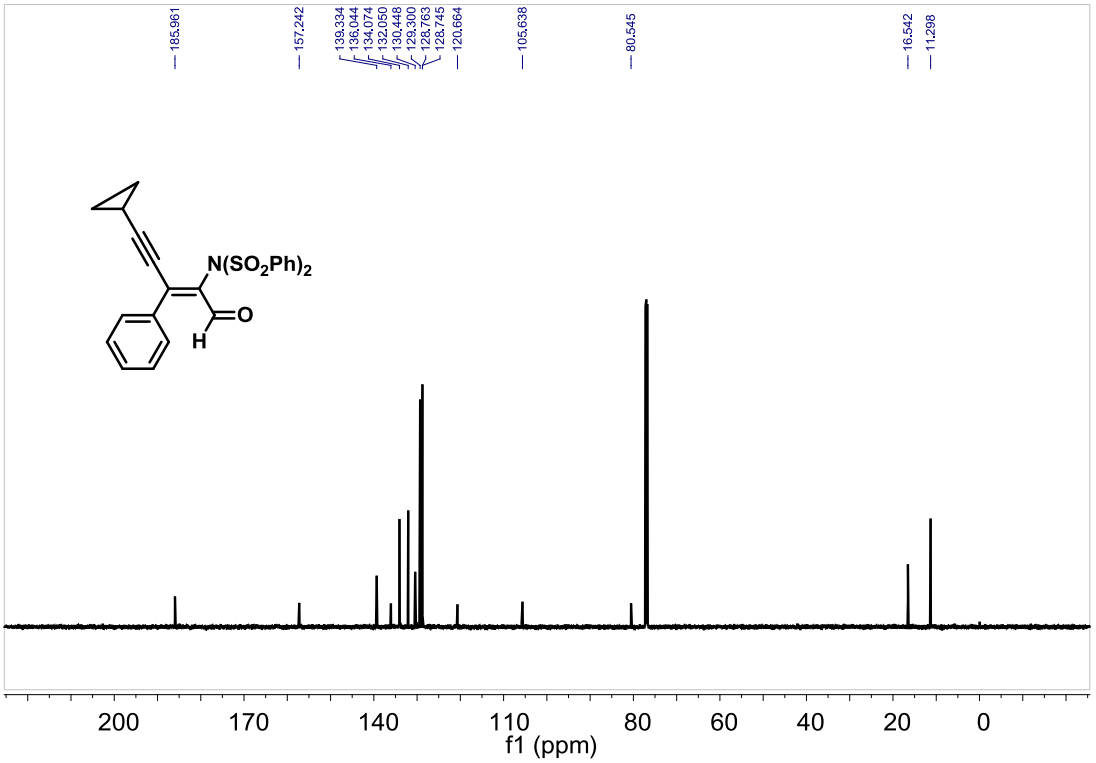
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3q.



^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3q.

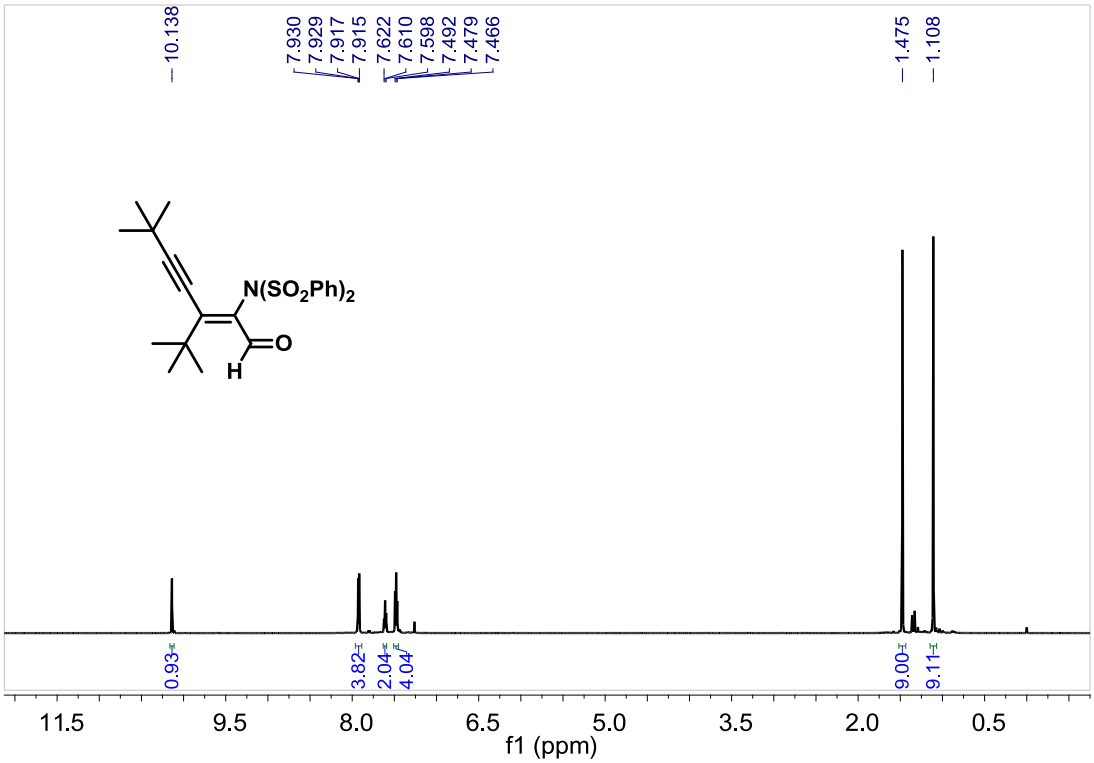


^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3r.

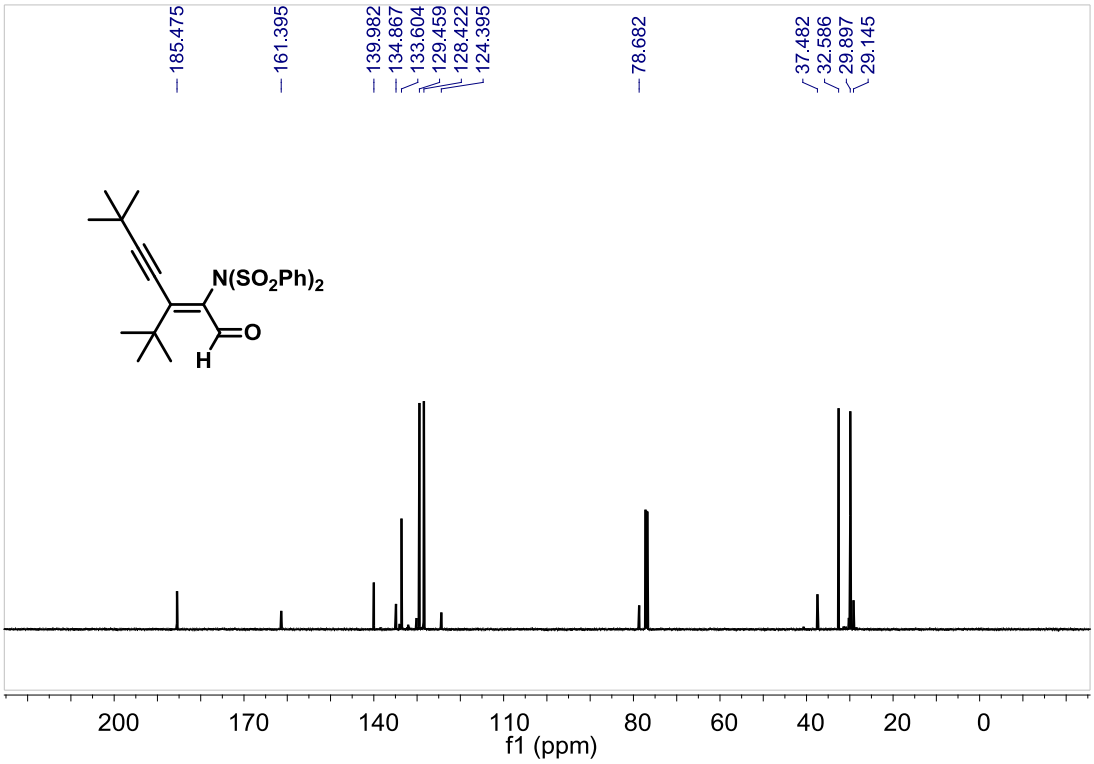


^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3r.

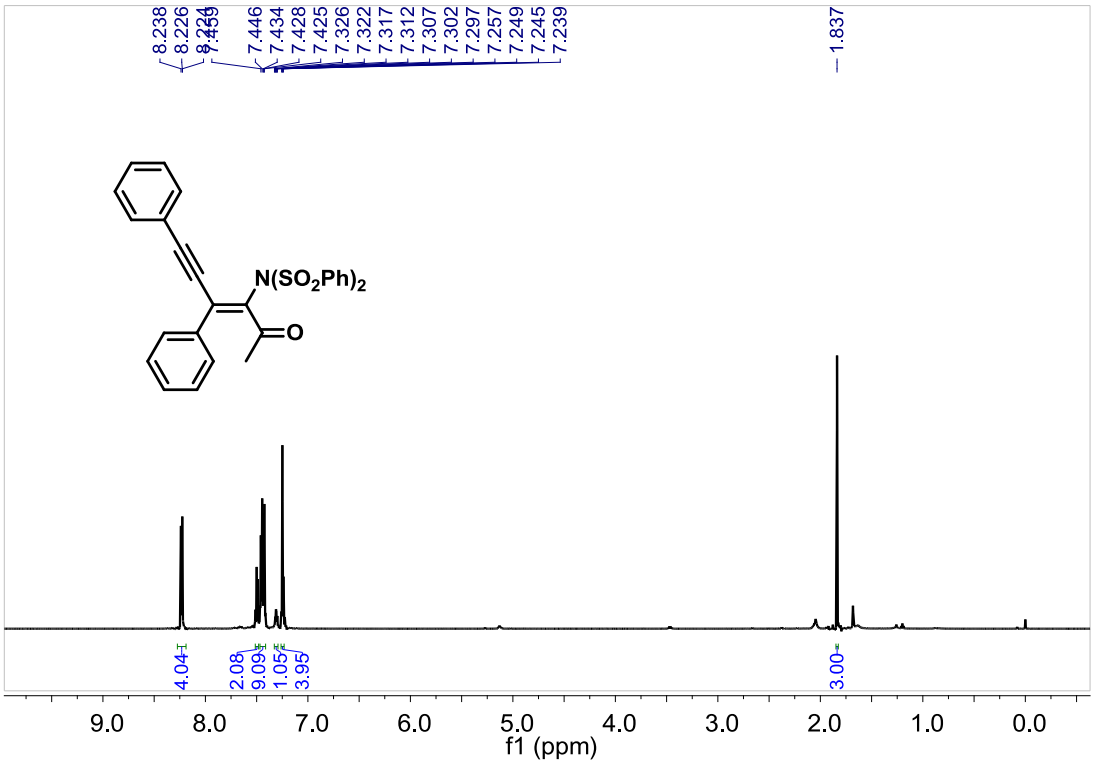
.



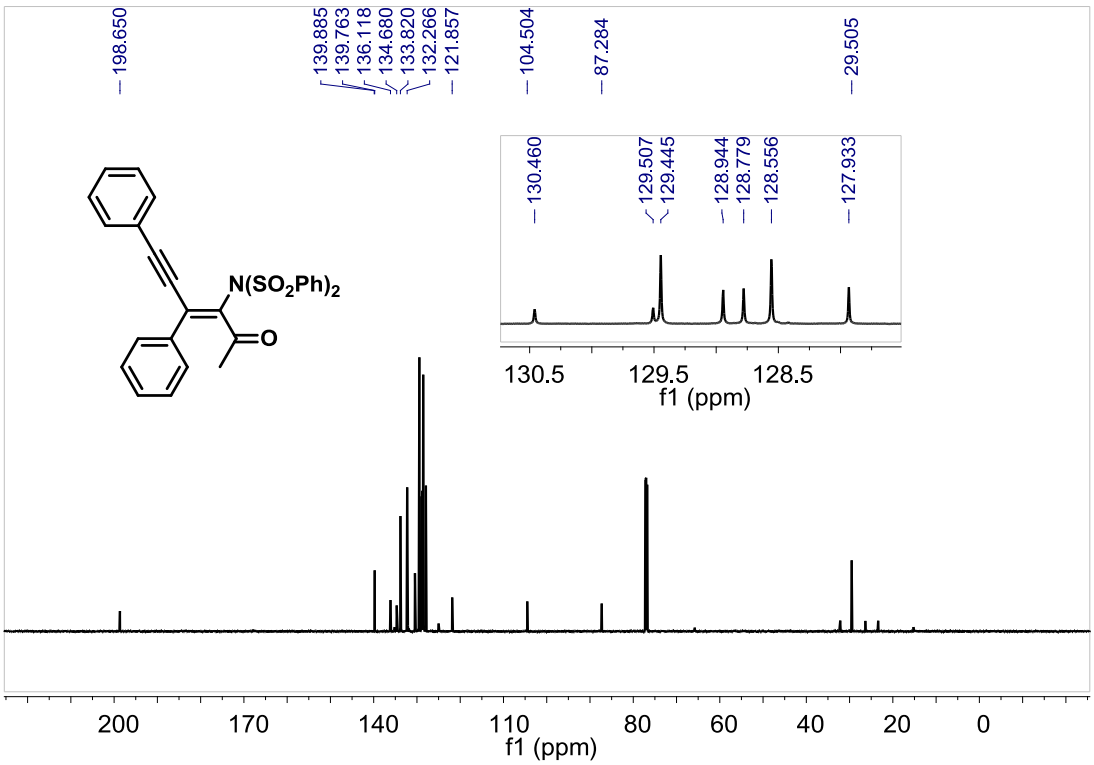
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3s.



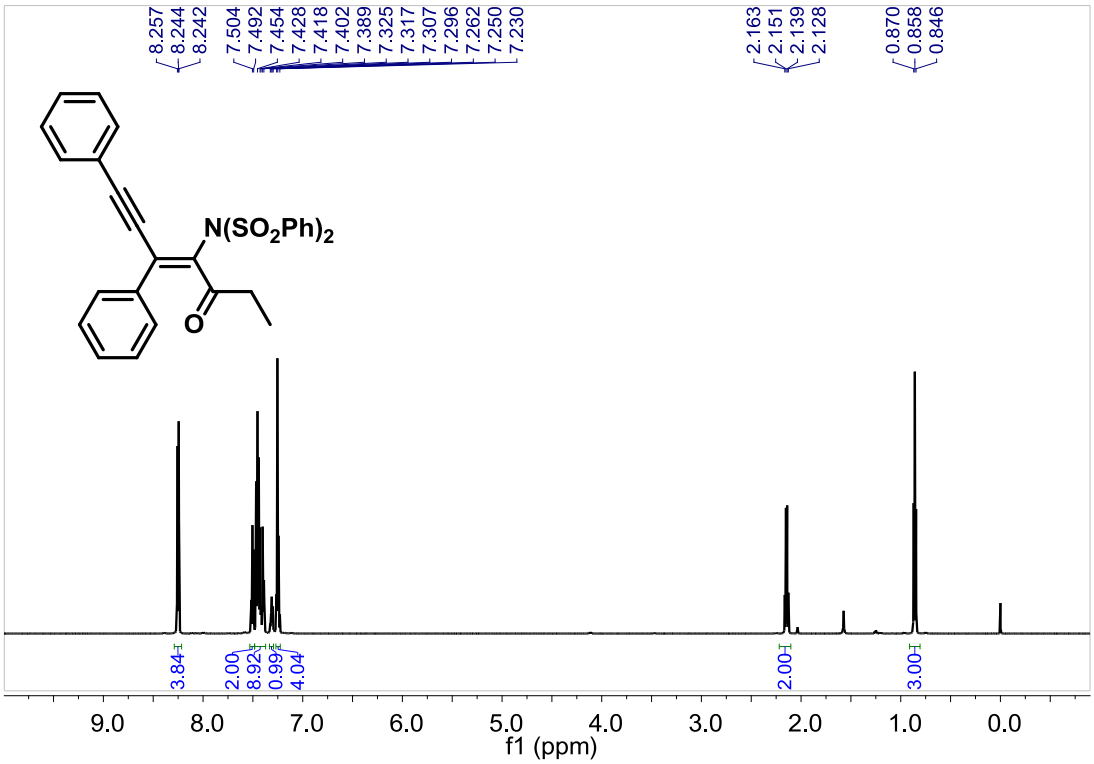
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3s.



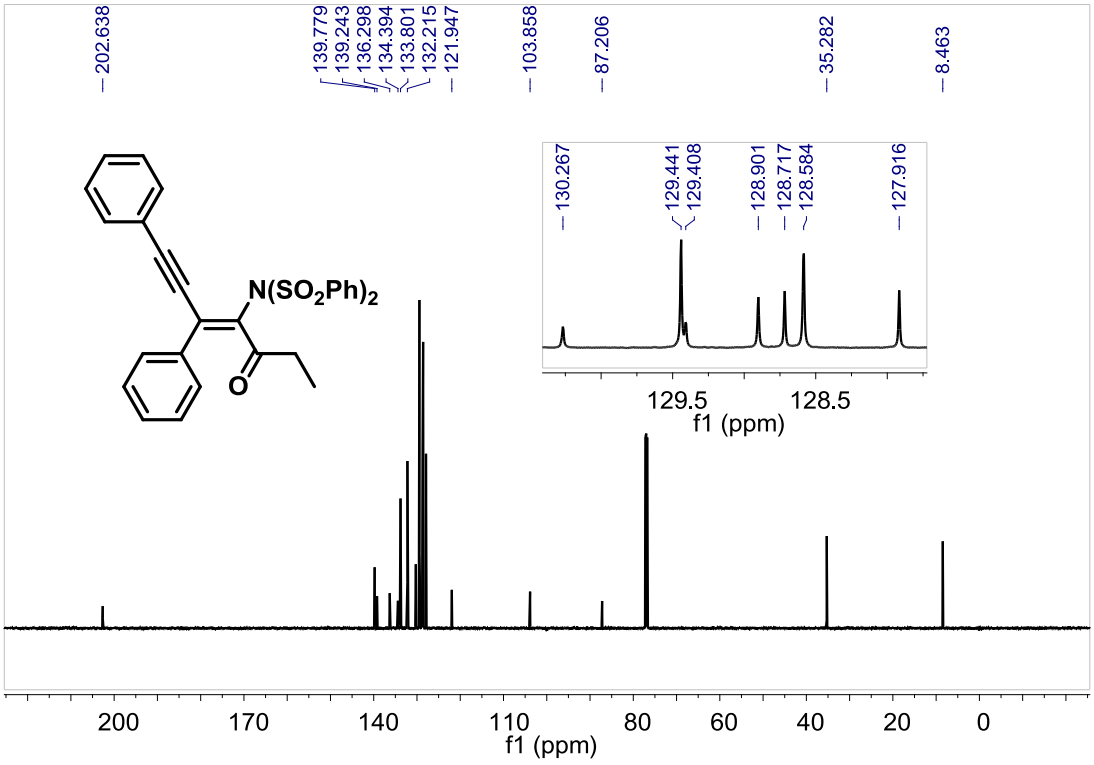
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3t.



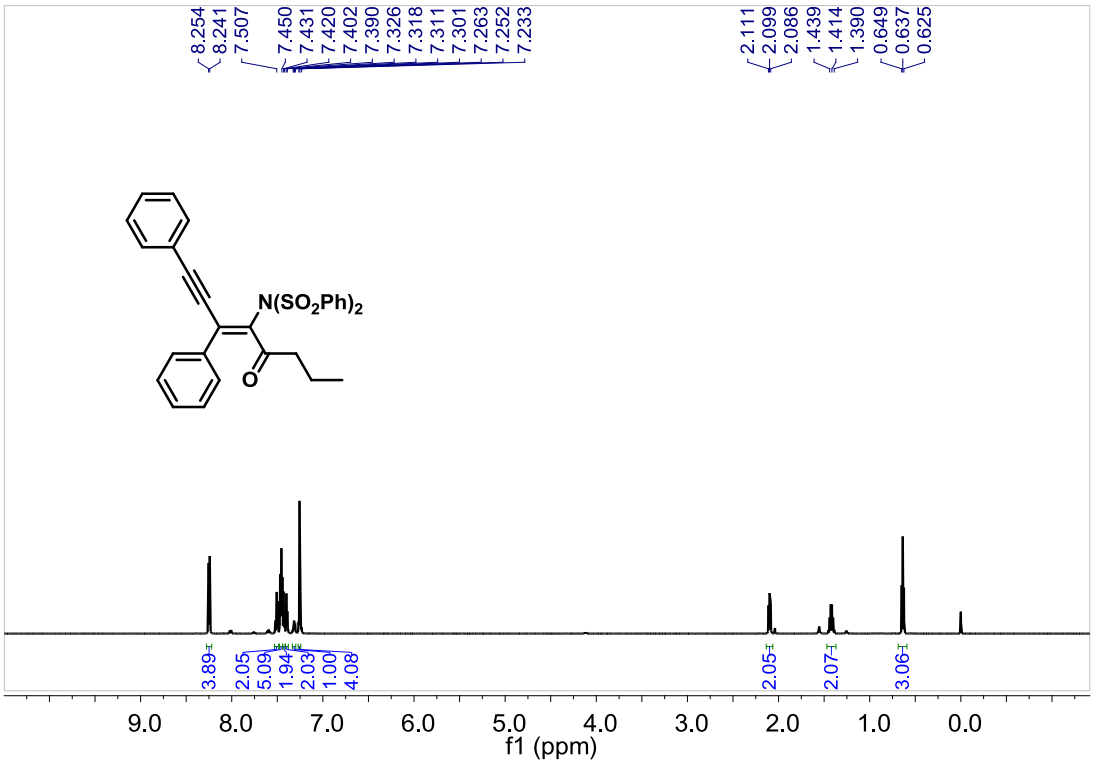
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3t.



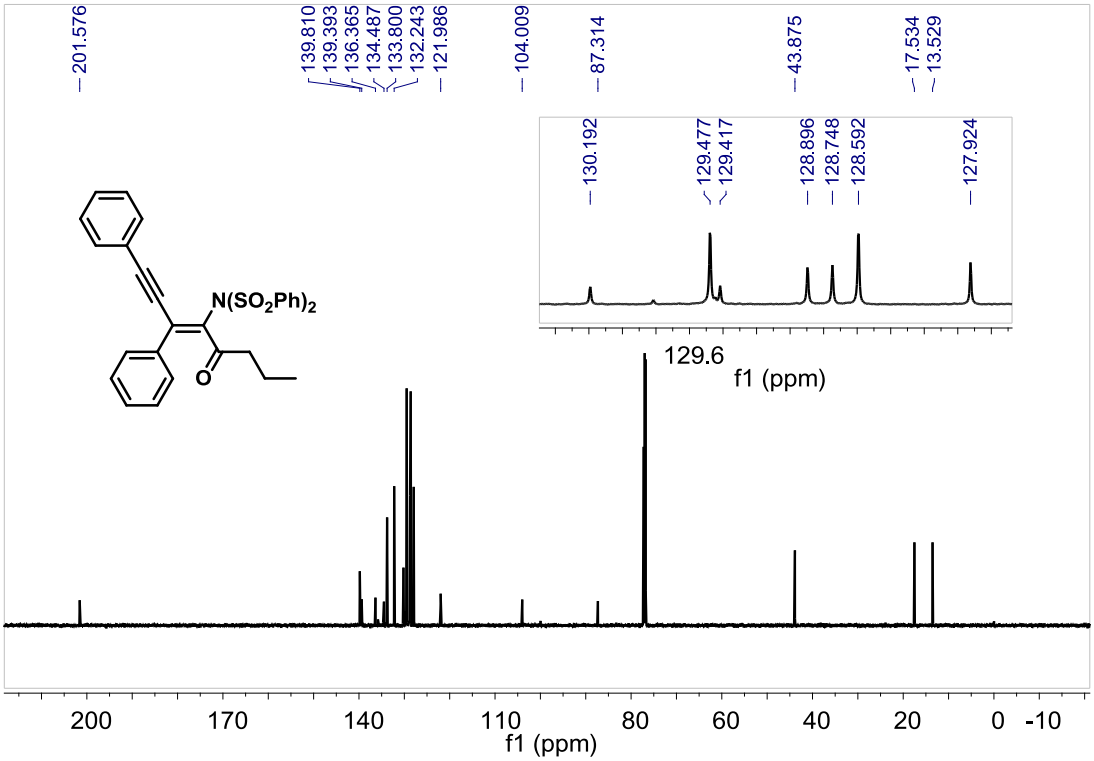
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3u.



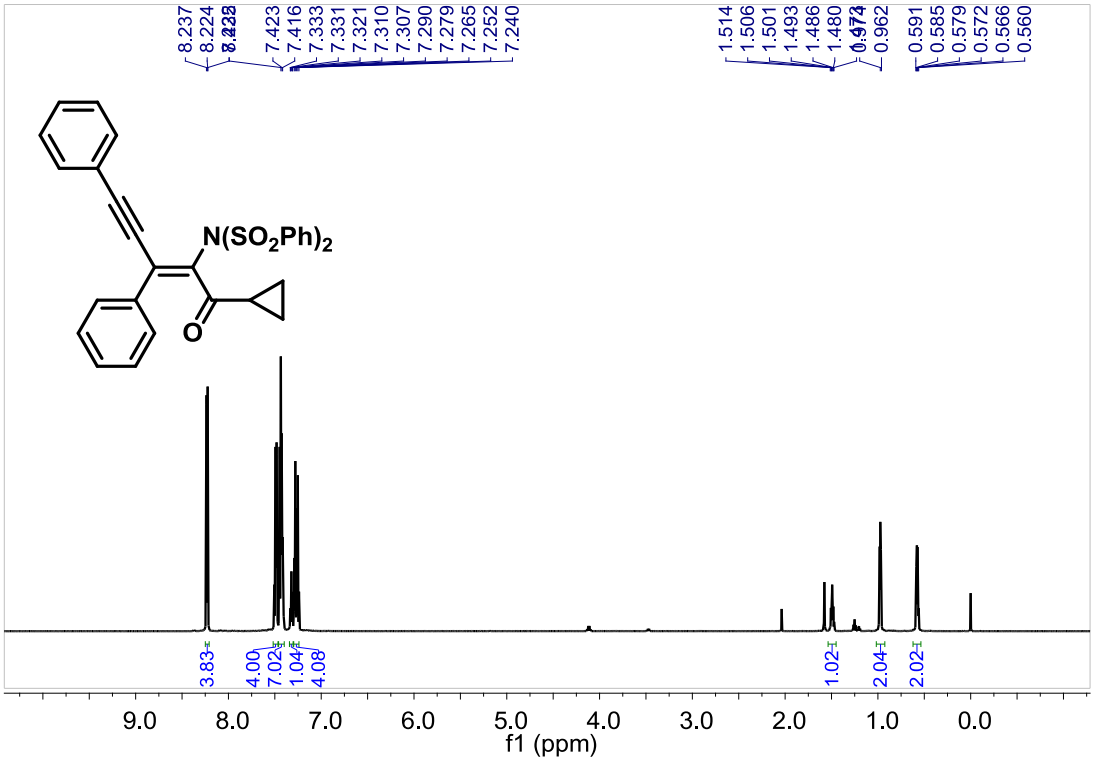
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3u.



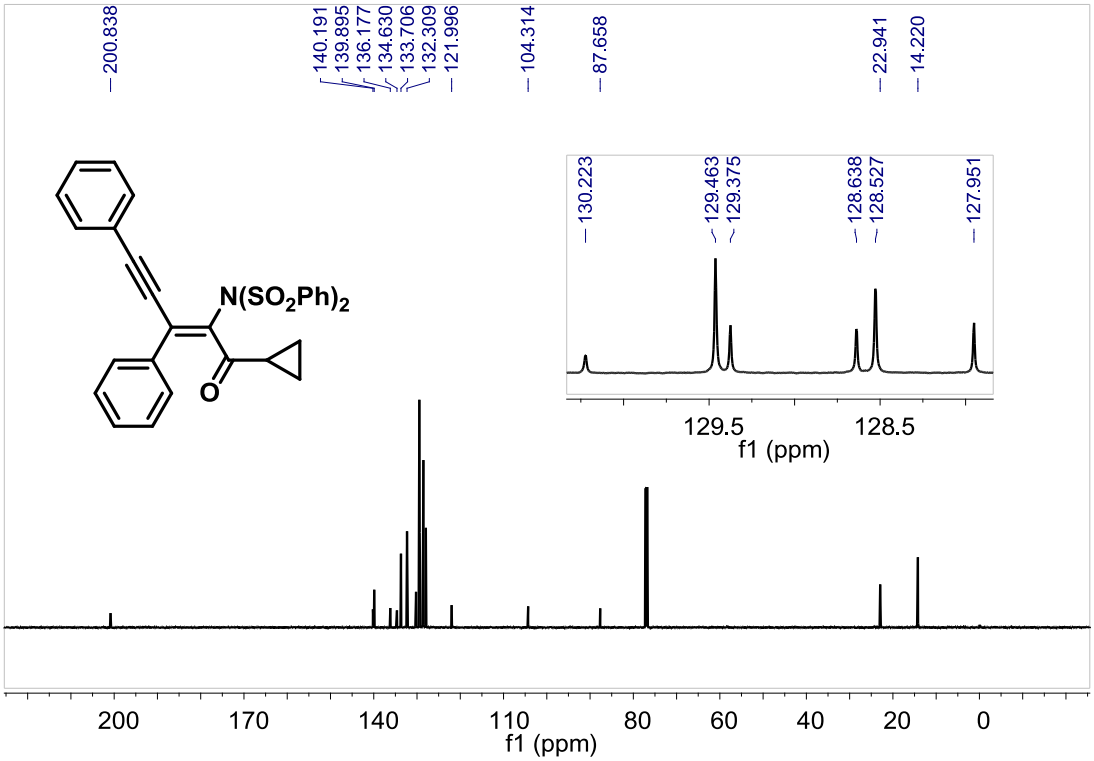
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3v.



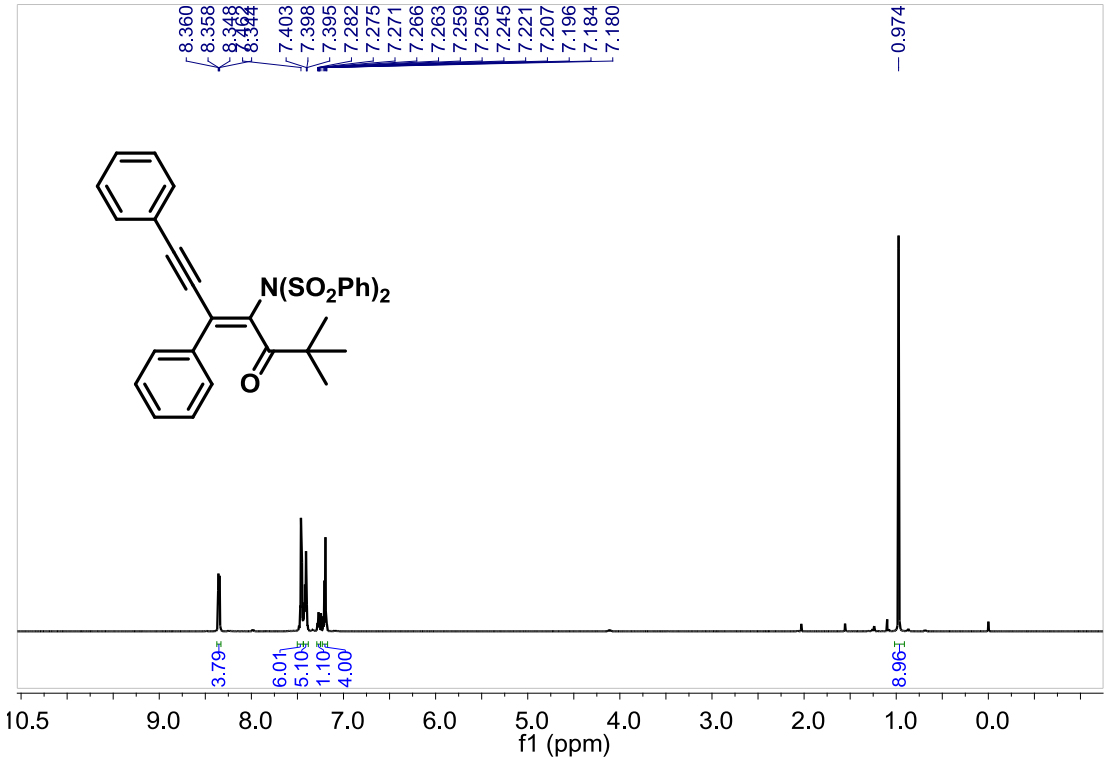
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3v.



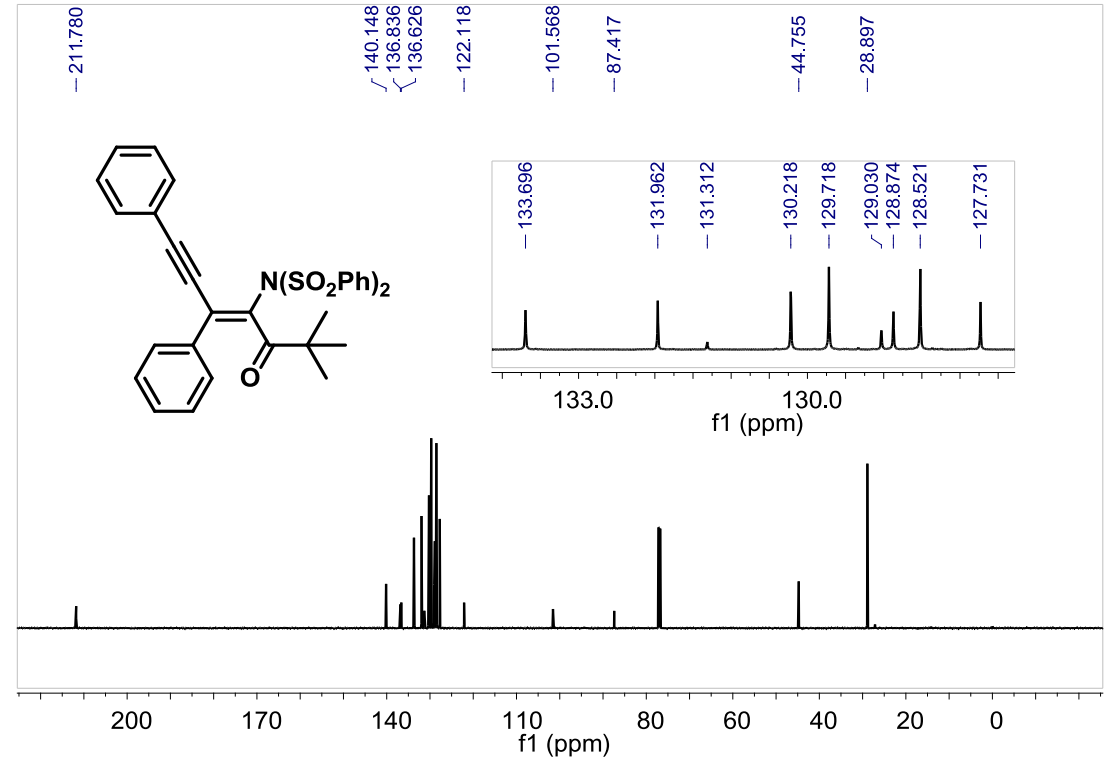
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3w.



^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3w.

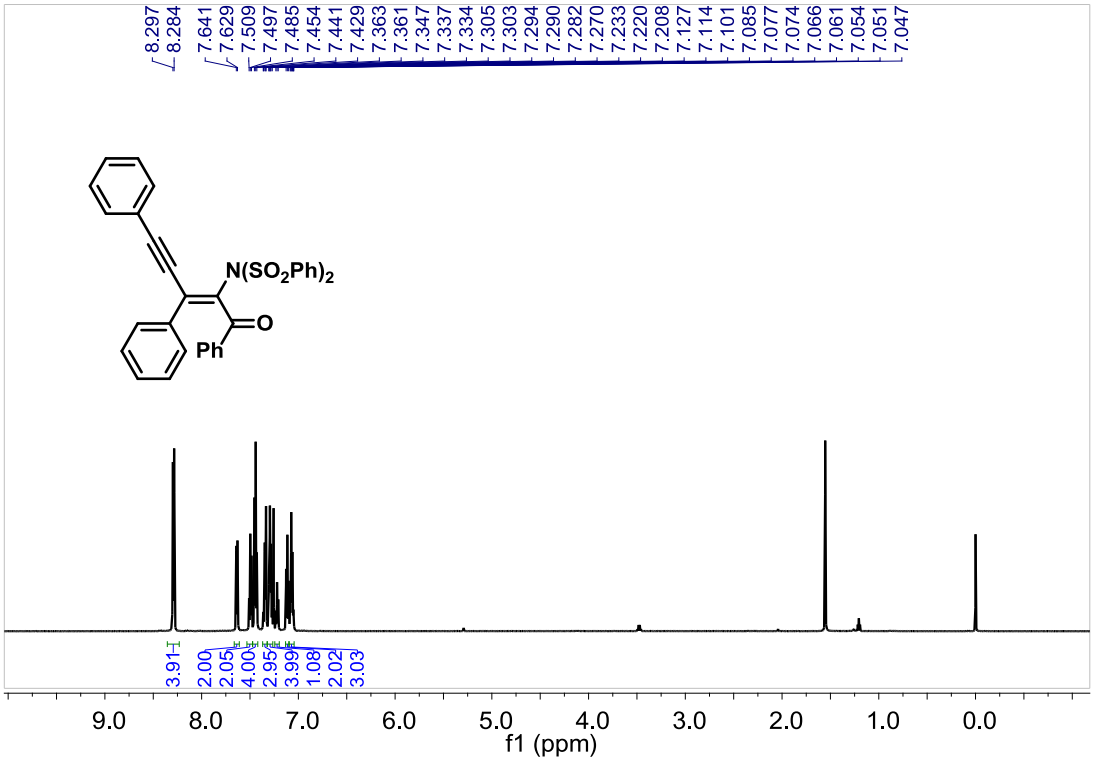


^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3x.

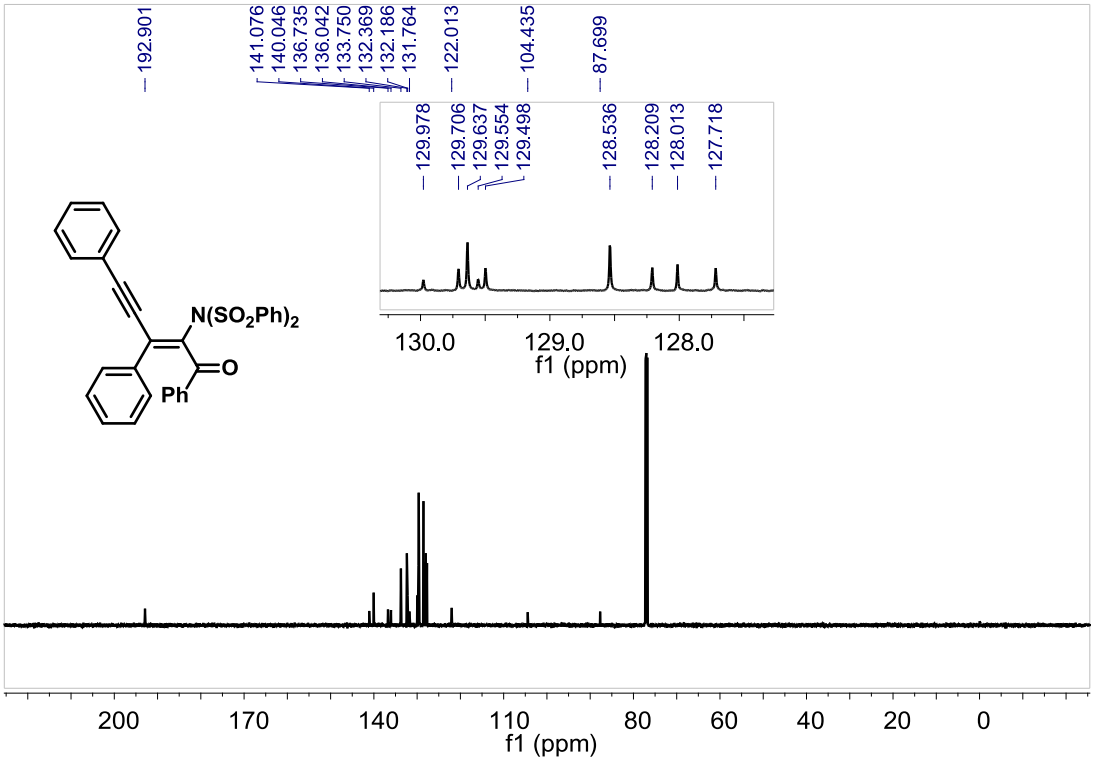


^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3x

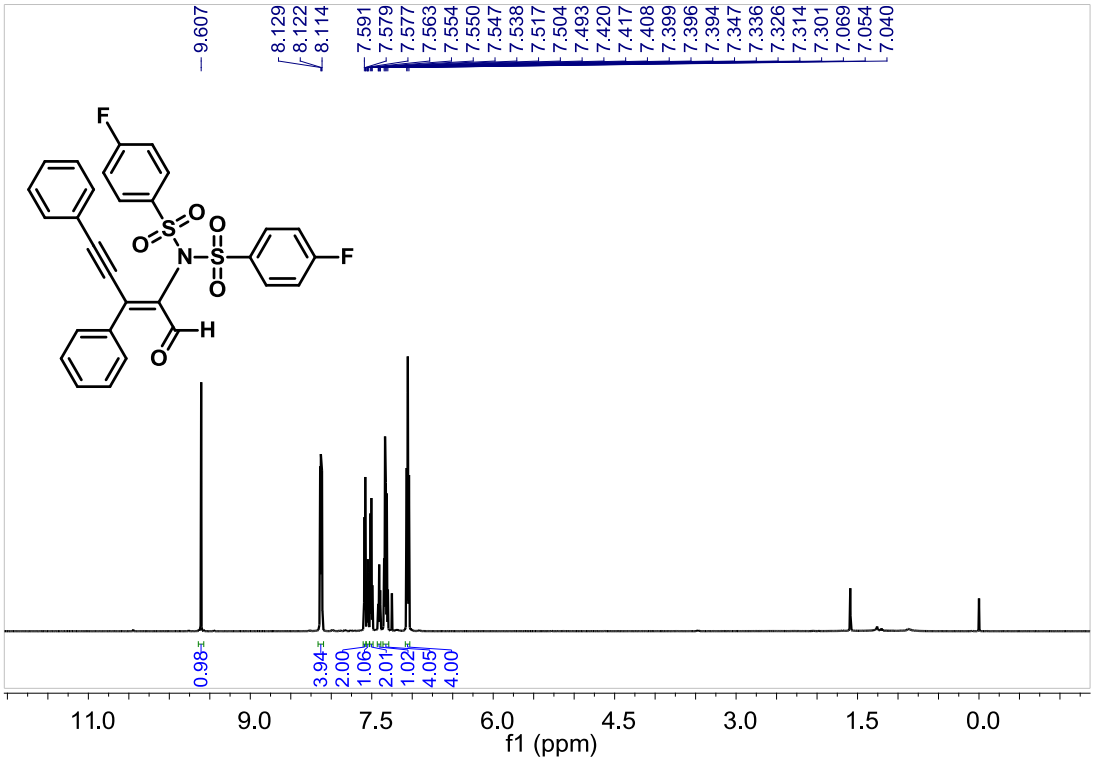
.



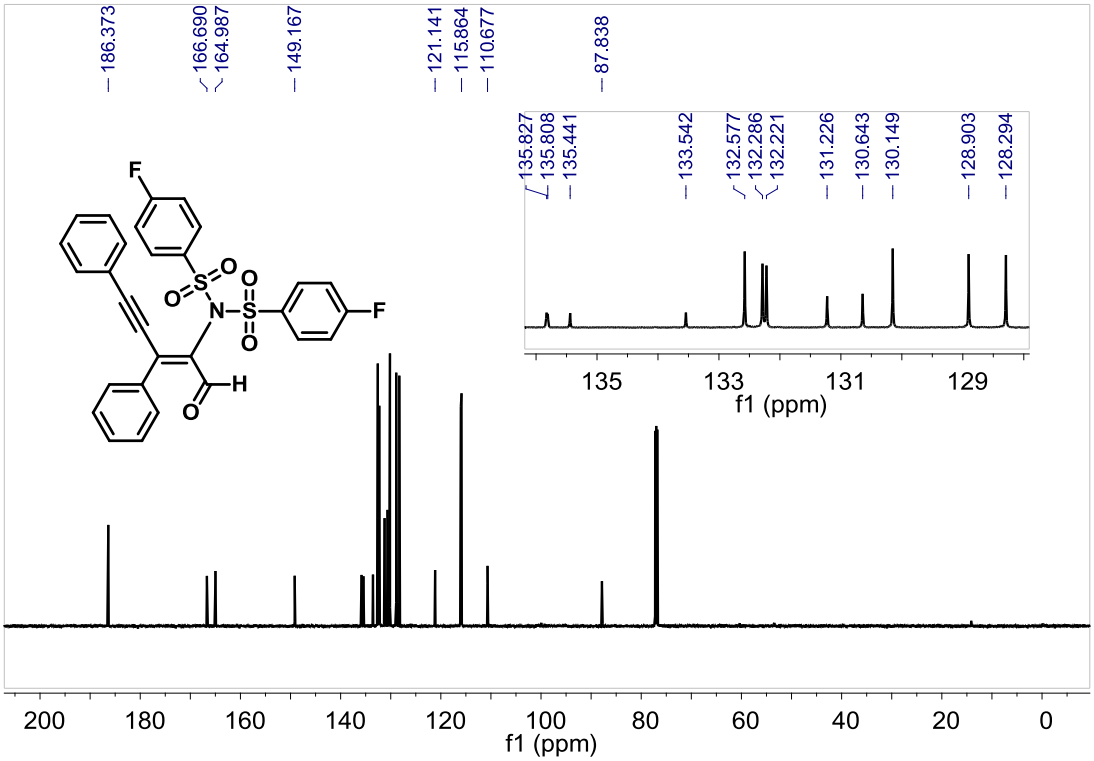
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 3y.



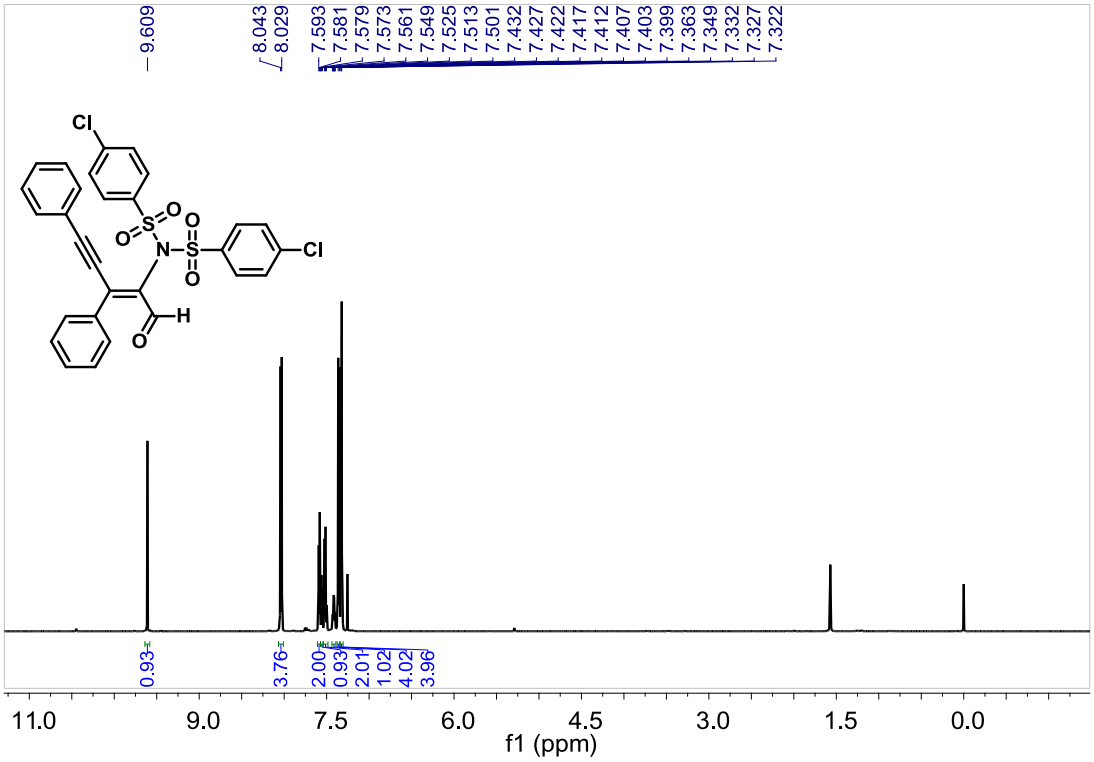
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 3y.



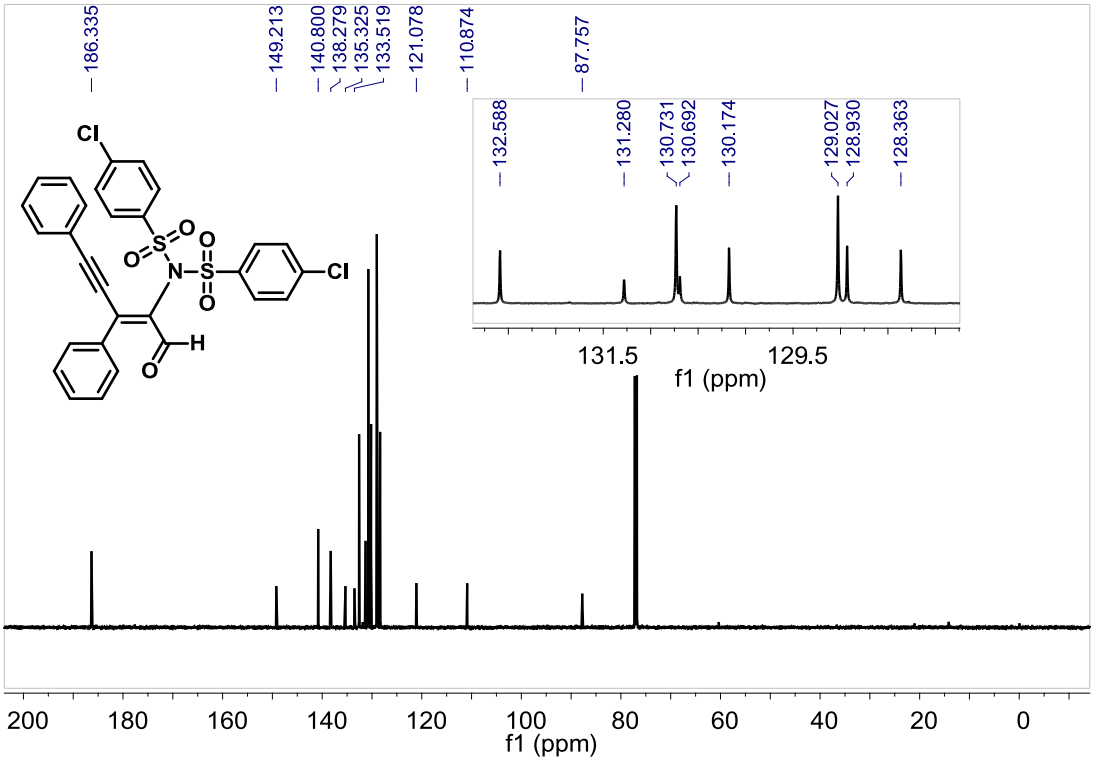
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 4b.



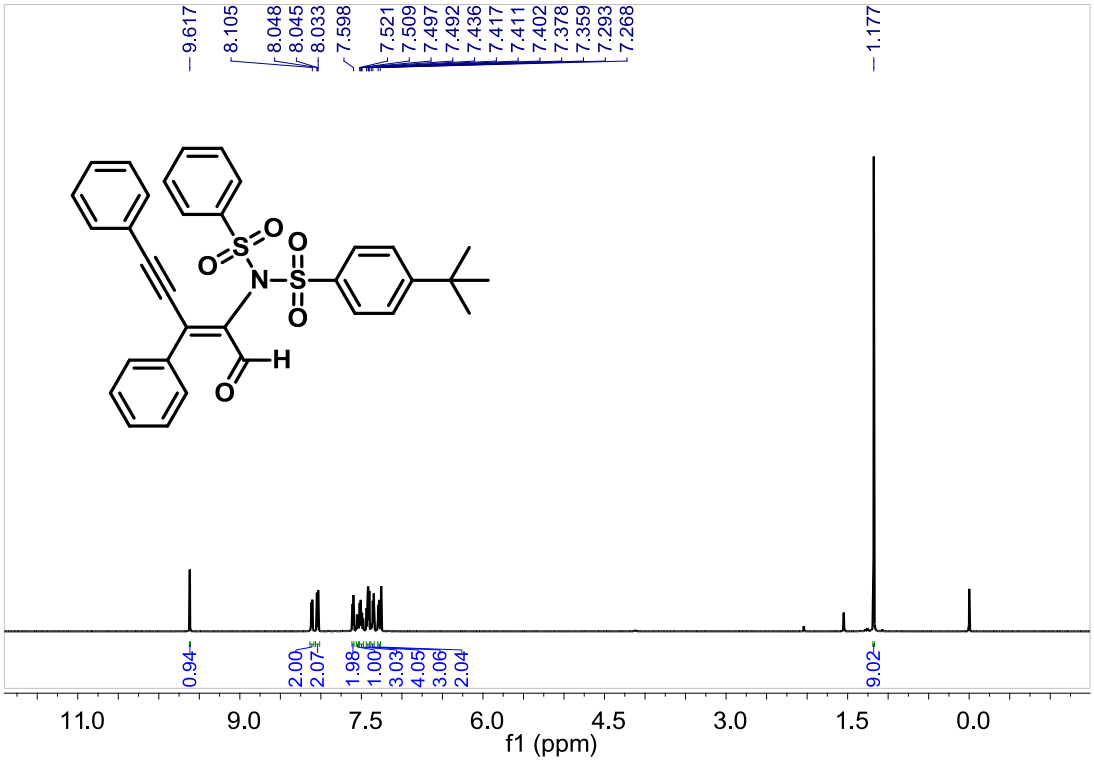
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 4b.



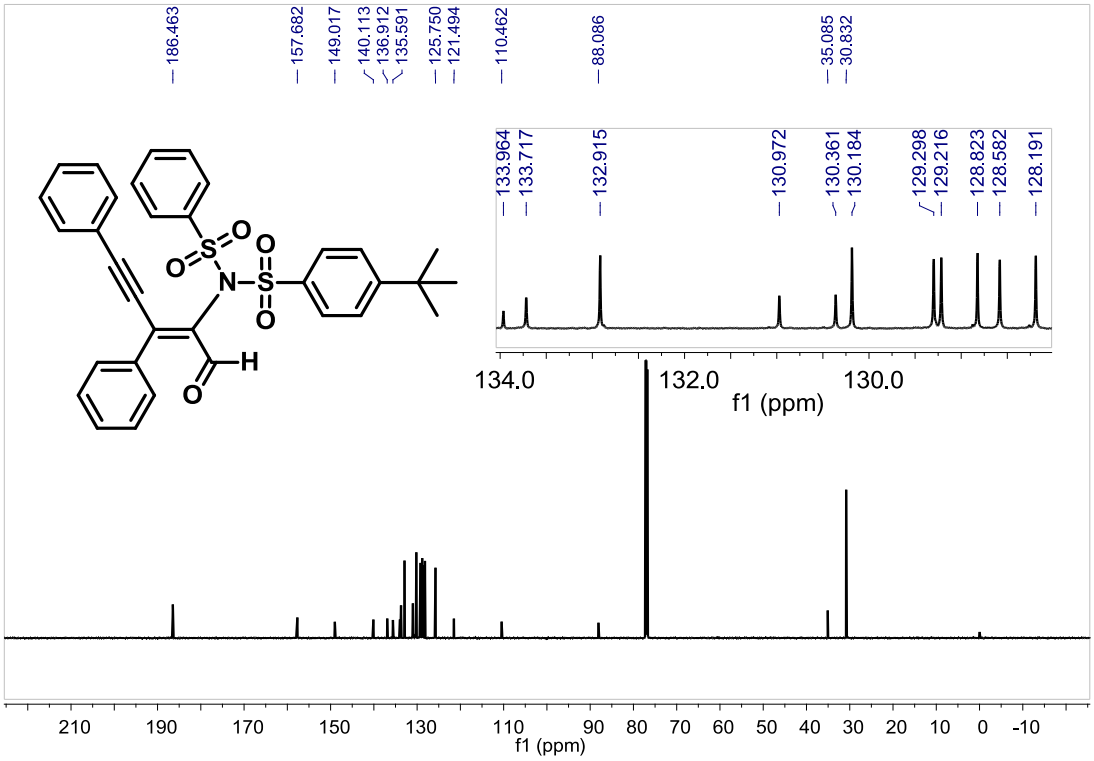
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 4c.



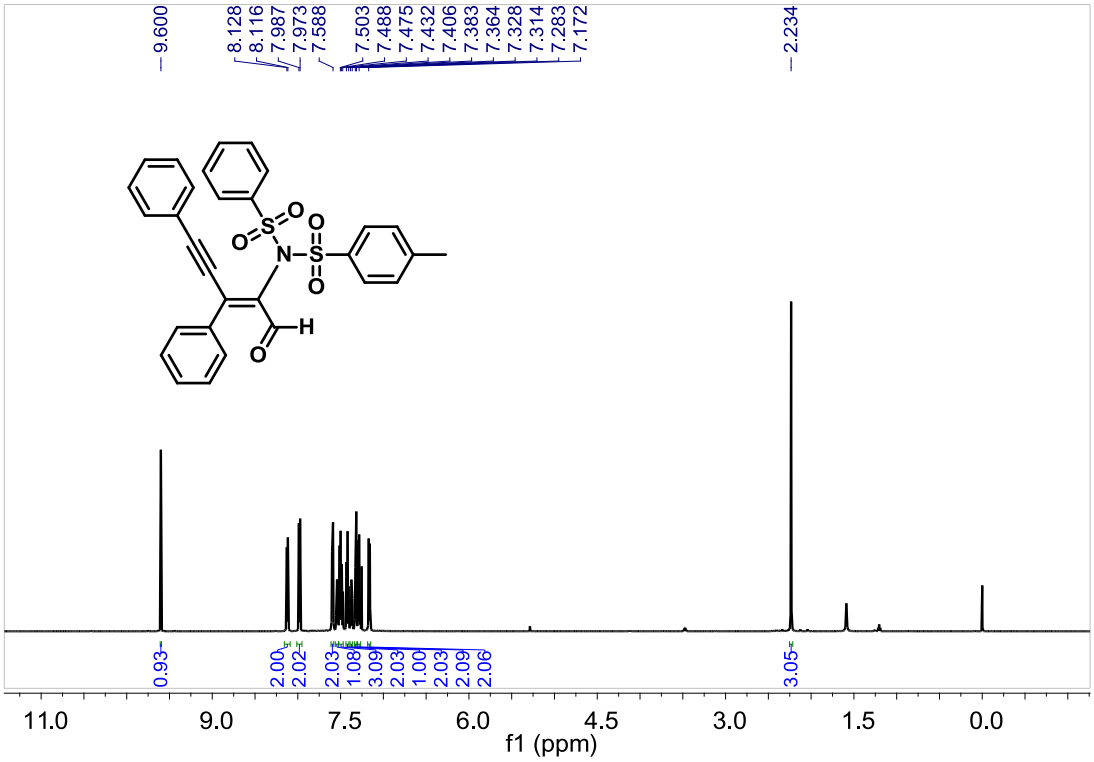
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 4c.



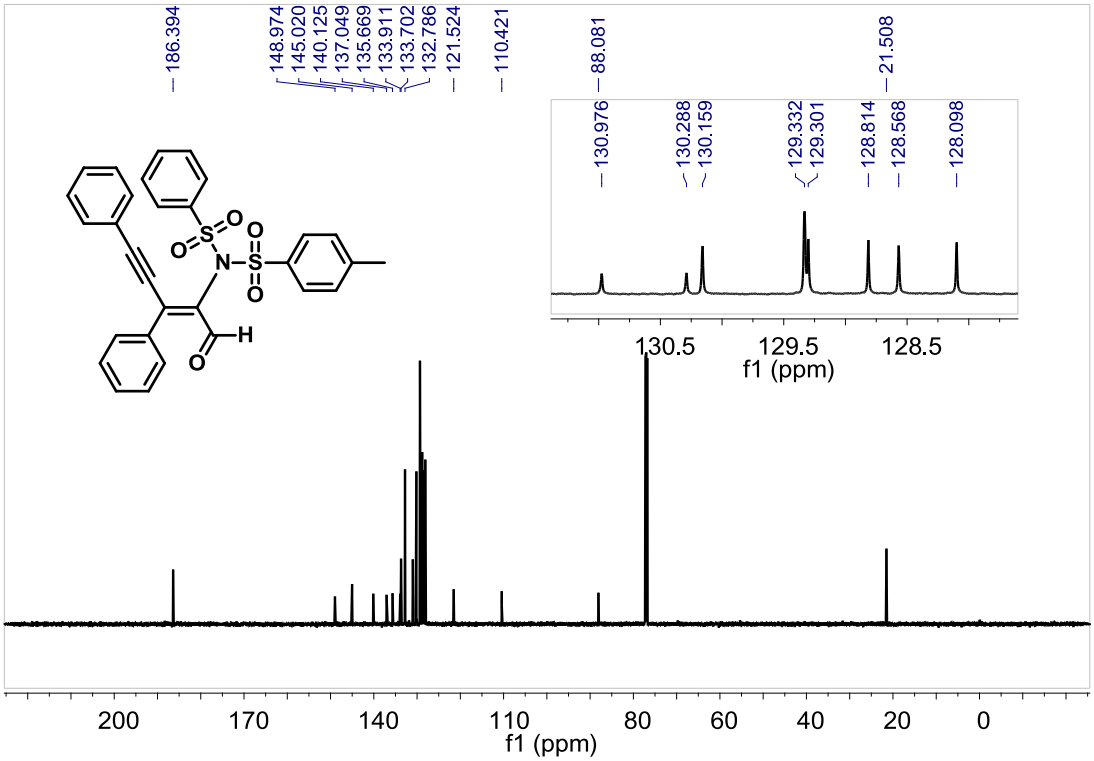
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 4d.



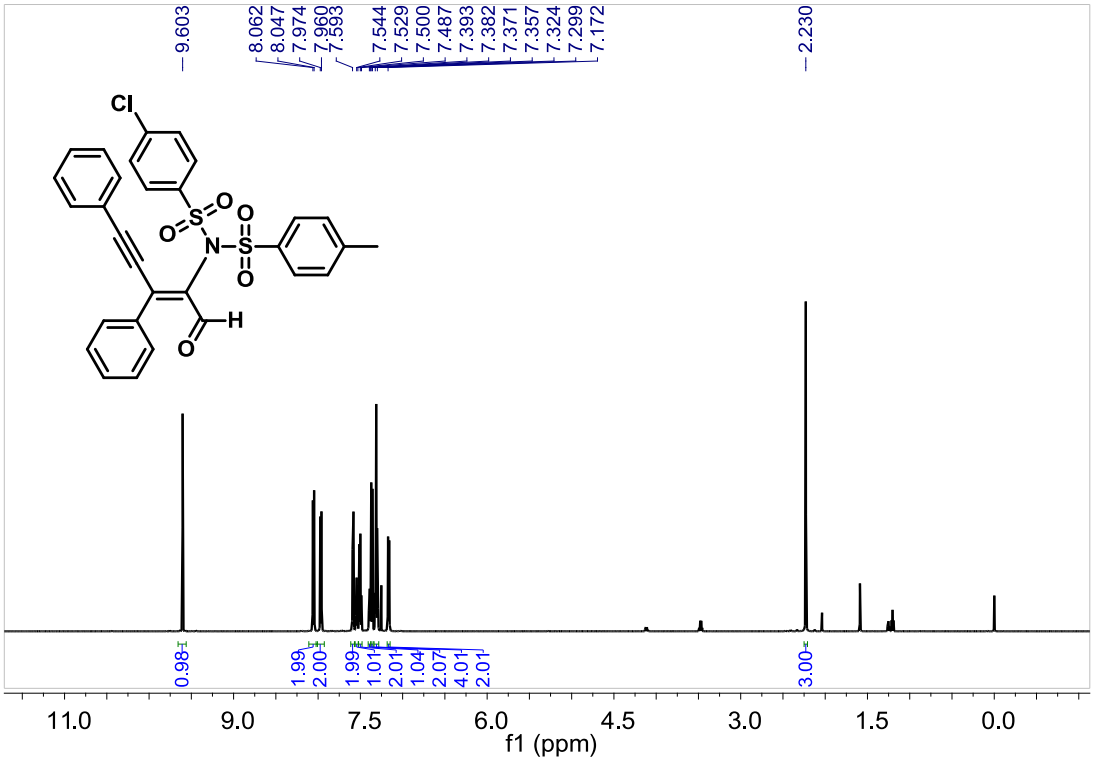
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 4d.



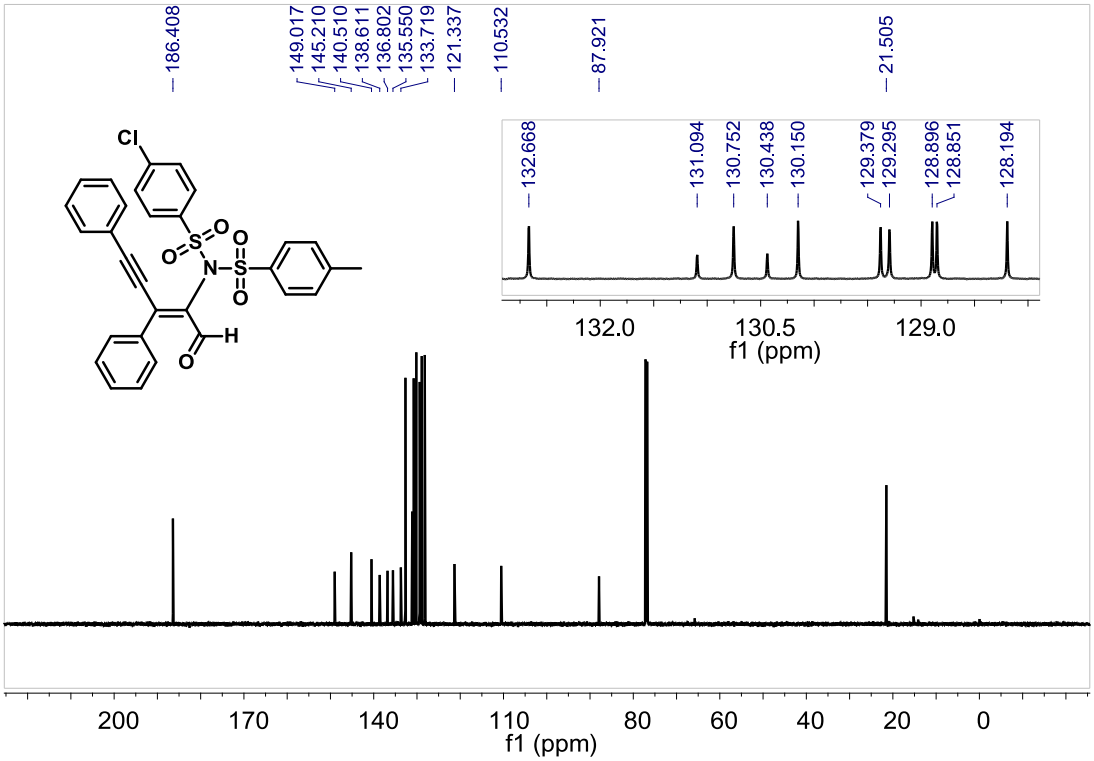
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 4e.



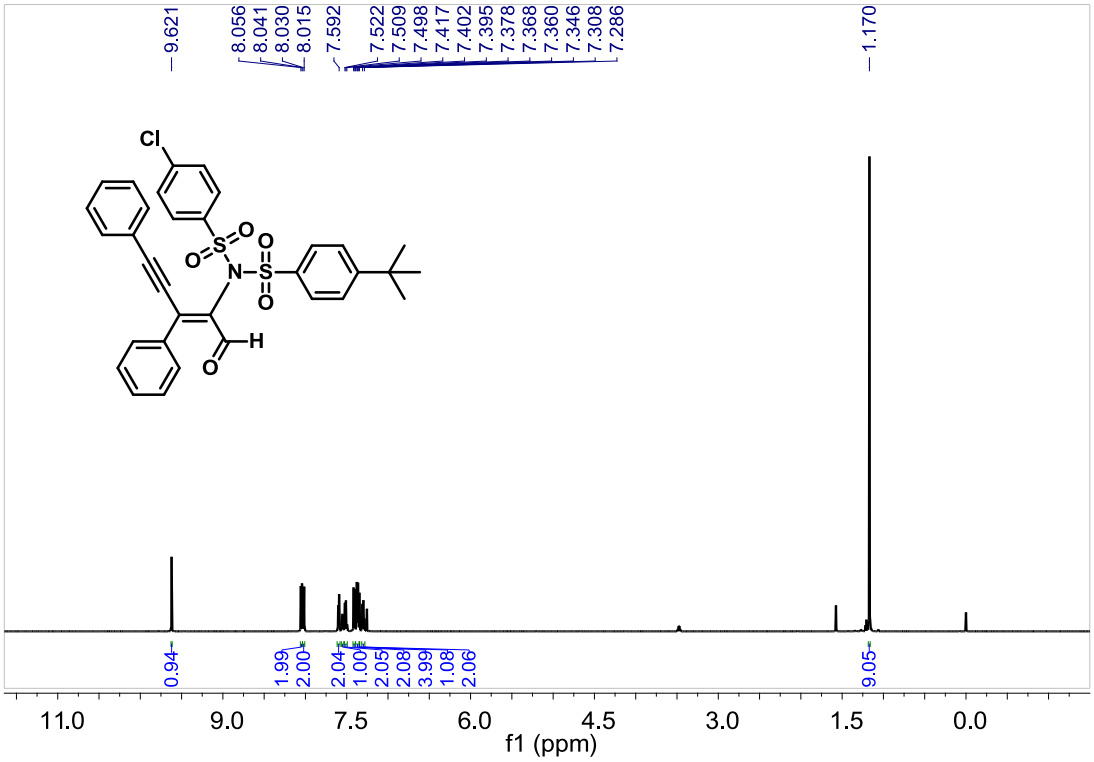
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 4e.



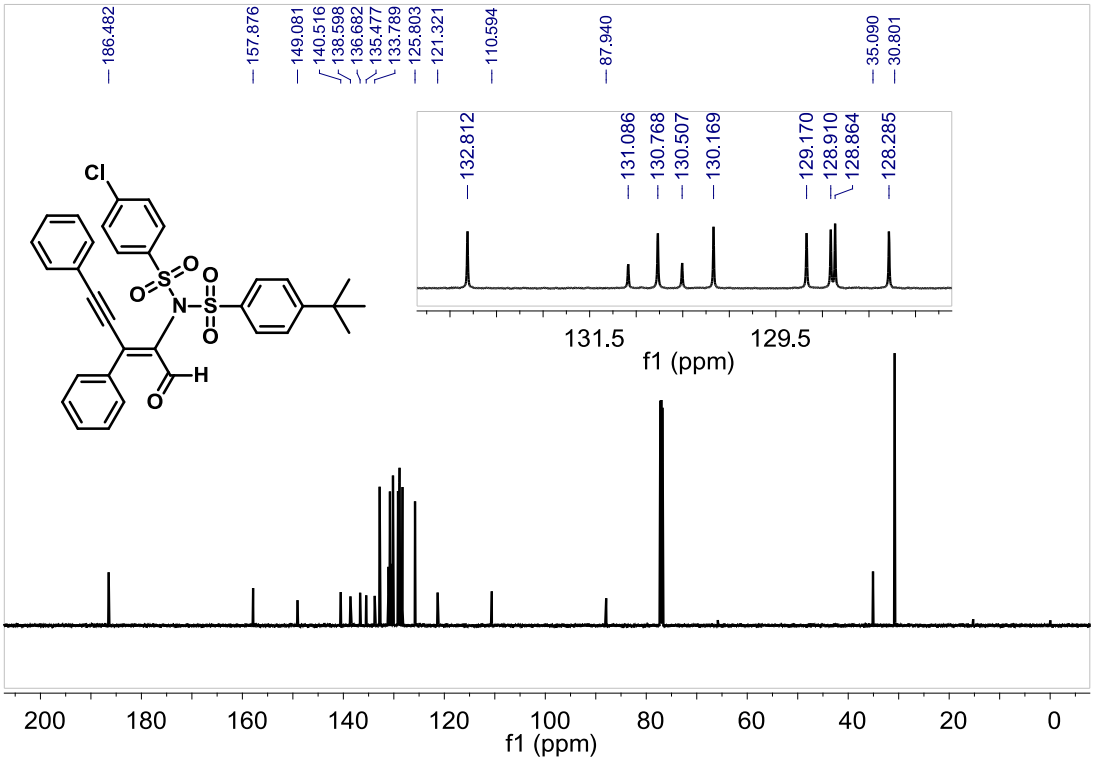
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 4f.



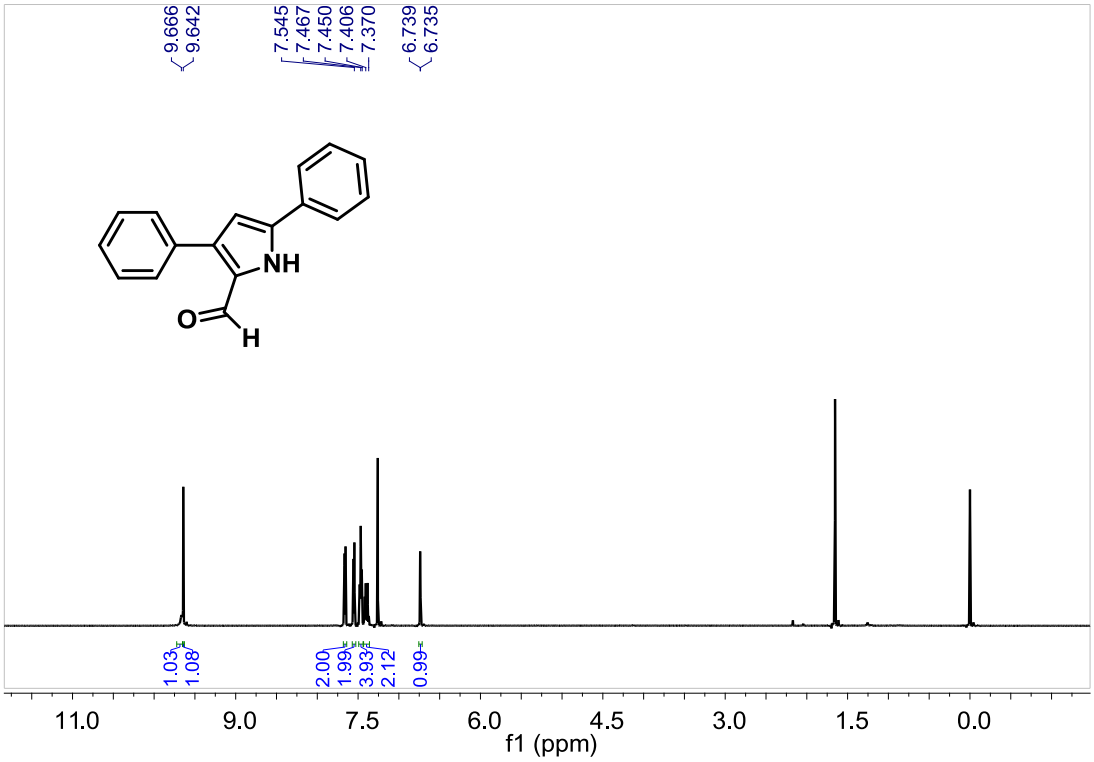
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 4f.



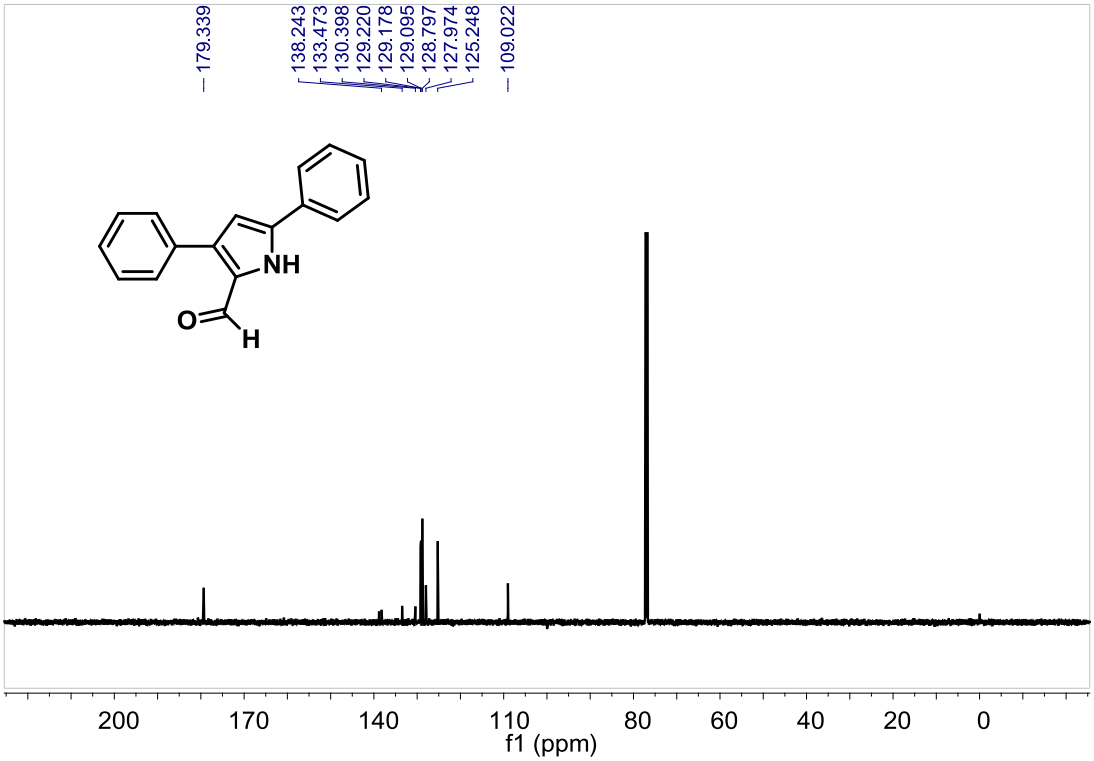
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 4g.



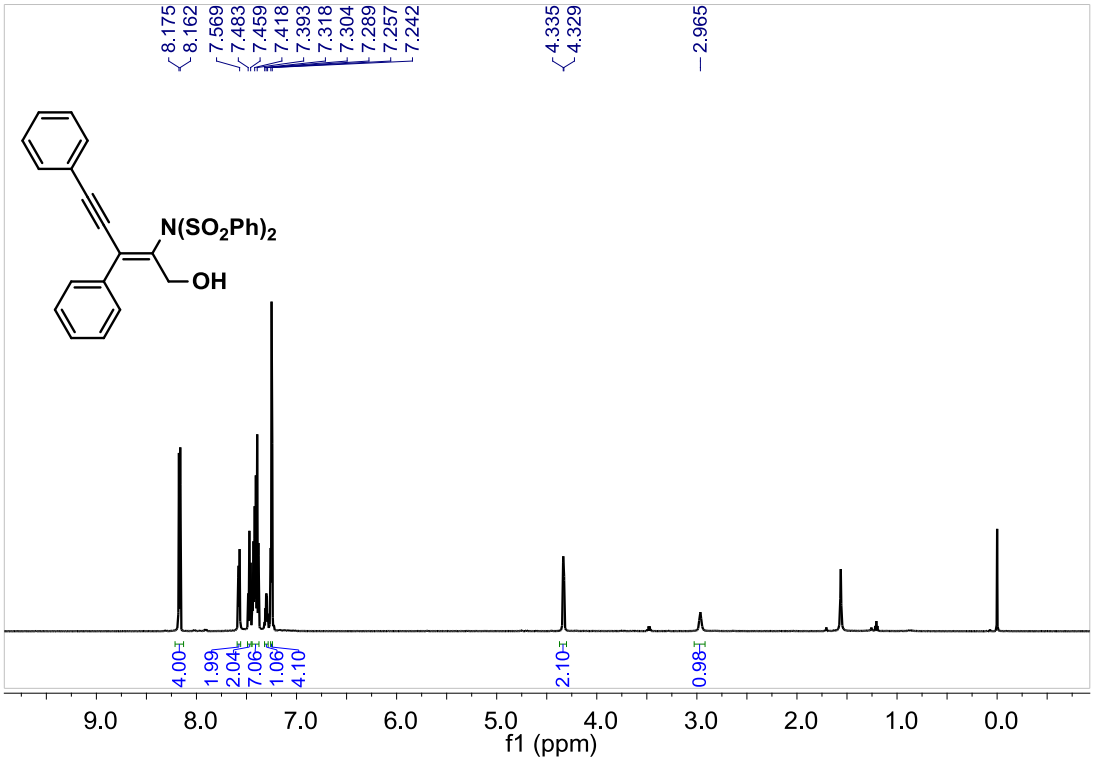
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 4g.



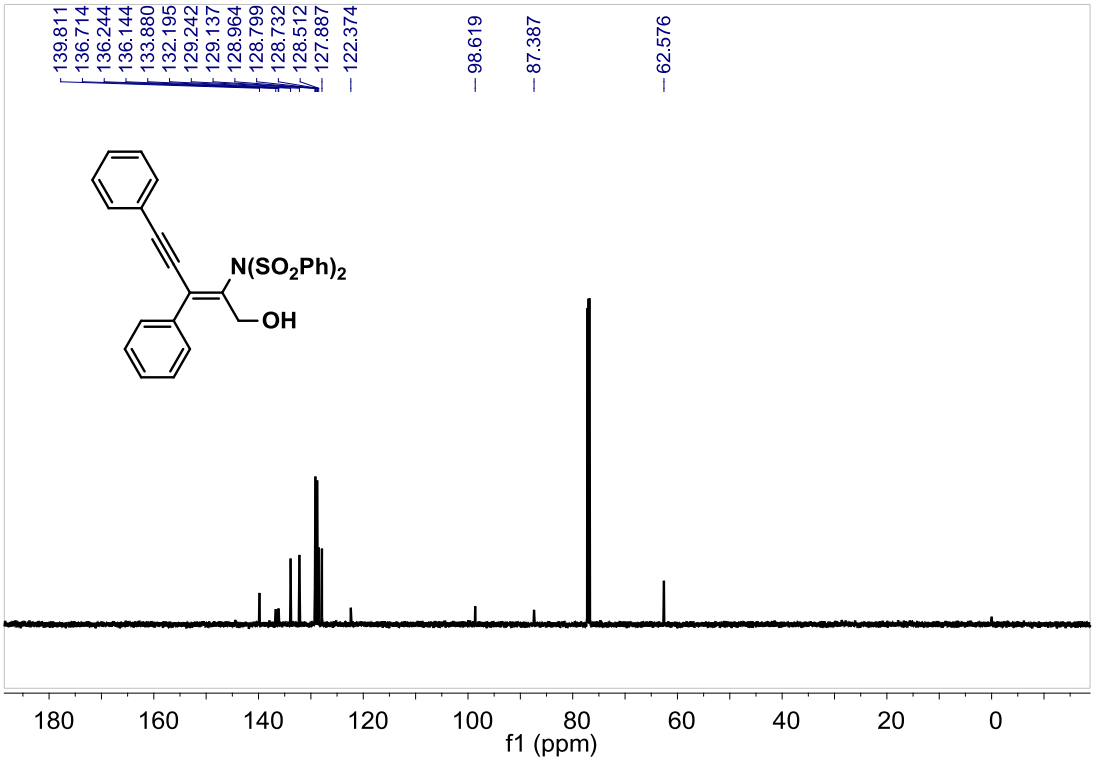
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 5.



^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 5.



^{1}H NMR (600 MHz, $CDCl_3$) spectrum for 6.



^{13}C NMR (150 MHz, $CDCl_3$) spectrum for 6.